

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

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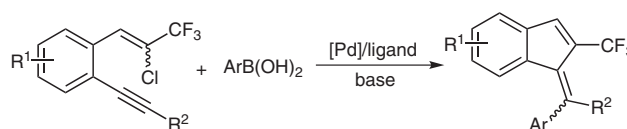
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Abstract: A palladium-catalyzed tandem carbocyclization–Suzuki coupling is described leading to the synthesis of trifluoromethyl-containing indenes in moderate to good yields. The reactions take place in the presence of palladium(II) acetate, a phosphorus-containing ligand [dicyclohexyl(2',4',6'-triisopropylbiphenyl-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,¹ pharmaceutical molecules² and functional materials,³ as well as in metallocene complexes utilized in alkene polymerization.⁴ As a consequence, a number of synthetic approaches have been developed for the construction of this carbocycle,⁵ in particular, 1-methyleneindene.⁶ 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.⁷ Larock and co-workers reported the palladium- or copper-catalyzed carboannulations of alkynylmalonates leading to indenes.⁸ Trifluoromethylated compounds have wide applicability in pharmaceuticals, agrochemicals and organic materials,⁹ however, examples of the selective synthesis of trifluoromethylated indenes are scarce.¹⁰ 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),¹¹ or the direct trifluoromethylation of arenes, albeit with poor regioselectivity.¹² Alternatively, the transformation of synthons containing a trifluoromethyl group at the appropriate position is an effective method to target trifluoromethylated compounds.¹³ In continuation of our interest in the synthesis of trifluoromethylated compounds,¹⁴ we wanted to prepare trifluoromethyl-containing indene derivatives starting

from our previously reported building blocks.^{14d} 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

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**) (*Z/E* = 97:3)¹⁵ 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). Finally, 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).

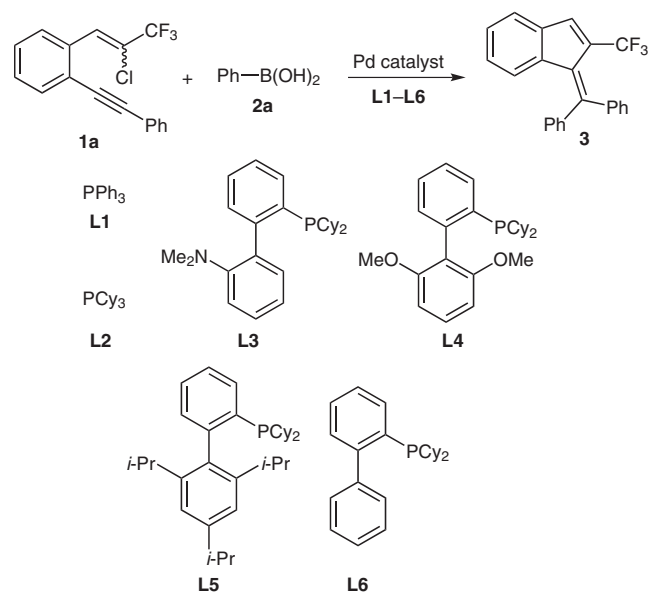
With optimized reaction conditions established, the substrate scope of trifluoromethyl-containing building blocks and arylboronic acids was next examined (Table 2). We initially investigated the reaction of 1-(2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2-(phenylethynyl)benzene (**1a**) with arylboronic acids **2b–I** (Table 2, entries 1–11). The results demonstrated that a wide range of arylboronic acids containing both electron-withdrawing and electron-

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Table 1 Optimization of the Reaction Conditions^a

Entry	Catalyst	Ligand	Base	Solvent	Yield (%) ^b
1	Pd(OAc) ₂	L1	Cs ₂ CO ₃	toluene	71
2	PdCl ₂	L1	Cs ₂ CO ₃	toluene	68
3	Pd ₂ (dba) ₃	L1	Cs ₂ CO ₃	toluene	46
4	Pd(PPh ₃) ₂ Cl ₂	L1	Cs ₂ CO ₃	toluene	70
5	Pd(PPh ₃) ₄	L1	Cs ₂ CO ₃	toluene	65
6	Pd(OAc) ₂	L2	Cs ₂ CO ₃	toluene	5
7	Pd(OAc) ₂	L3	Cs ₂ CO ₃	toluene	55
8	Pd(OAc) ₂	L4	Cs ₂ CO ₃	toluene	11
9	Pd(OAc) ₂	L5	Cs ₂ CO ₃	toluene	80
10	Pd(OAc) ₂	L6	Cs ₂ CO ₃	toluene	65
11	Pd(OAc) ₂	L5	NaOt-Bu	toluene	32
12	Pd(OAc) ₂	L5	K ₃ PO ₄	toluene	69
13	Pd(OAc) ₂	L5	K ₂ CO ₃	toluene	90
14	Pd(OAc) ₂	L5	K ₂ CO ₃	MeCN	35
15	Pd(OAc) ₂	L5	K ₂ CO ₃	NMP	<5
16	Pd(OAc) ₂	L5	K ₂ CO ₃	DMSO	<5
17	Pd(OAc) ₂	L5	K ₂ CO ₃	DMF	10
18 ^c	Pd(OAc) ₂	L5	K ₂ CO ₃	toluene	81

^a 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.

^b Yield of isolated product.

^c Reaction at 60 °C.

donating groups were suitable substrates for the tandem reactions, which gave the corresponding indene products in moderate to excellent yields, and with high stereoselec-

tivity. 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, cyano or nitro (Table 2, entries 7–10). As expected, naphthalen-1-ylboronic acid (**2i**) 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 alkenylpalladium 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 alkenylpalladium complex **B**. Next, transmetalation 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.

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

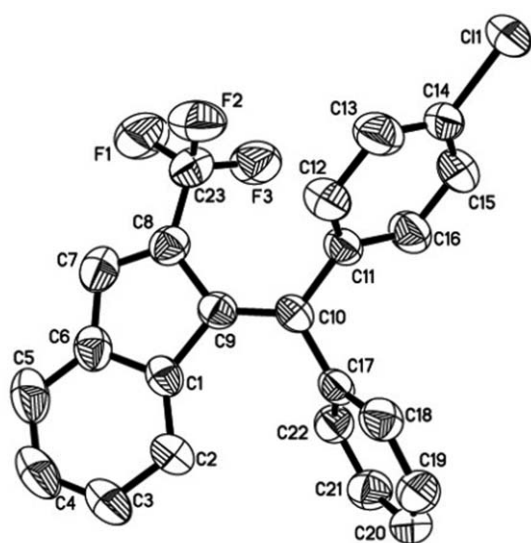
Entry	Alkyne	Boronic acid	Product	Yield (%) ^b
1			4	84 (13:87)
2	1a		5	77 (7:93)
3	1a		6	92 (13:87)
4	1a		7	89 (27:73)
5	1a		8	51 (0:100)
6	1a		9	75 (0:100)
7 ^c	1a		10	50 (0:100)
8	1a		11	57 (0:100)
9 ^c	1a		12	38 (23:77)

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

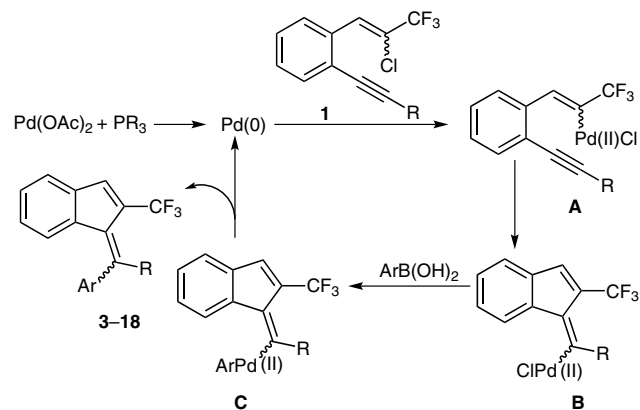
Entry	Alkyne	Boronic acid	Product	Yield (%) ^b
10 ^c			13	58 (29:71)
11			14	42 (0:100)
12			15	85
13			16	98
14			17	60
15			7	87 (97:3)
16			8	67 (100:0)
17			10	72 (100:0)

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

Entry	Alkyne	Boronic acid	Product	Yield (%) ^b
18			12	86 (67:33)
19			18	82 (60:40)

^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.**Figure 1** Single crystal X-ray structure (ORTEP diagram) of the *Z*-isomer of compound **8**

In summary, we have developed an efficient method for the synthesis of trifluoromethyl-containing indenenes. 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 indenenes in moderate to excellent yields. The present process represents a new synthetic application for trifluoromethyl-containing building blocks, as

**Scheme 2** A possible reaction mechanism

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 Colid 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-

trometer using CDCl_3 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. ^{19}F NMR data are reported relative to CFCl_3 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**¹⁵ (0.2 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 5 mol%), dicyclohexyl(2',4',6'-triisopropylbiphenyl-2-yl)phosphine (**L5**) (9.5 mg, 10 mol%), K_2CO_3 (55.2 mg, 0.4 mmol) and arylboronic acid **2** (0.24 mmol) in toluene (2 mL) was stirred at 80 °C under an N_2 atm for 3 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): 1713, 1357, 1117, 891, 756 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.48 (s, 1 H), 7.46–7.42 (m, 1 H), 7.41–7.36 (m, 4 H), 7.33–7.29 (m, 4 H), 7.24–7.22 (m, 2 H), 7.18–7.15 (m, 1 H), 6.94–6.91 (m, 1 H), 6.39 (d, J = 8.0 Hz, 1 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 152.3, 142.9, 142.2, 138.8, 138.3, 137.4 (q, $J_{\text{C-F}}$ = 6.0 Hz), 133.3, 131.1, 130.4, 130.1 (q, $J_{\text{C-F}}$ = 33.5 Hz), 129.2, 128.8, 128.7, 127.4, 127.2, 126.9, 124.3, 122.8 (q, $J_{\text{C-F}}$ = 268.0 Hz), 122.5.

^{19}F NMR (470 MHz, CDCl_3): δ = –54.3 (3 F).

MS (EI, 70 eV): m/z (%) = 348 (100) $[\text{M}]^+$, 279 (87), 250 (12), 202 (12), 138 (25).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{16}\text{F}_3$: 349.1199; found: 349.1212.

1-[Phenyl(*p*-tolyl)methylene]-2-(trifluoromethyl)-1H-indene (4) (Table 2, Entry 1)

Yield: 60.6 mg (84%, Z/E = 13:87); yellow oil.

IR (neat): 2922, 1381, 1285, 1120, 744 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.47 (s, 1 H), 7.39–7.35 (m, 2 H), 7.34–7.30 (m, 2 H), 7.22–7.19 (m, 6 H), 7.18–7.11 (m, 1 H), 6.97–6.93 (m, 1 H), 6.52 (d, J = 8.0 Hz, 1 H), 2.43 (s, 2.6 H), 2.35 (s, 0.4 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 152.7, 142.5, 140.0, 139.5, 138.8, 138.5, 137.0 (q, $J_{\text{C-F}}$ = 5.9 Hz), 133.0, 131.3, 130.7, 130.0 (q, $J_{\text{C-F}}$ = 33.5 Hz), 129.4, 128.8, 127.4, 127.0, 126.8, 124.2, 122.9 (q, $J_{\text{C-F}}$ = 268.0 Hz), 122.4, 21.5.

^{19}F NMR (470 MHz, CDCl_3): δ = –54.1 (2.6 F), –54.2 (0.4 F).

MS (EI, 70 eV): m/z (%) = 362 (100) $[\text{M}]^+$, 347 (11), 293 (48), 277 (35), 138 (18).

HRMS (EI): m/z $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{17}\text{F}_3$: 362.1277; found: 362.1279.

1-[Phenyl(*m*-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, CDCl_3): δ = 7.47 (s, 1 H), 7.38–7.28 (m, 6 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).

^{13}C NMR (125 MHz, CDCl_3): δ = 152.6, 142.8, 142.3, 138.8, 138.4, 137.3 (q, $J_{\text{C-F}}$ = 6.0 Hz), 133.2, 131.6 (q, $J_{\text{C-F}}$ = 3.4 Hz), 131.0,

130.8, 129.9, 129.1 (q, $J_{\text{C-F}}$ = 40.6 Hz), 128.8, 128.6, 127.5, 127.4 (q, $J_{\text{C-F}}$ = 2.4 Hz), 127.1, 126.9, 124.4, 122.9 (q, $J_{\text{C-F}}$ = 268.0 Hz), 122.4, 21.3.

^{19}F NMR (470 MHz, CDCl_3): δ = –54.3 (2.8 F), –56.6 (0.2 F).

MS (EI, 70 eV): m/z (%) = 362 (100) $[\text{M}]^+$, 307 (9), 293 (65), 278 (38), 138 (19).

HRMS (EI): m/z $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{17}\text{F}_3$: 362.1277; found: 362.1281.

1-[(2-Methoxyphenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (6) (Table 2, Entry 3)

Yield: 69.3 mg (92%, Z/E = 13:87); yellow solid; mp 113.2–115.1 °C.

IR (neat): 1597, 1356, 1113, 1025, 891, 750, 697 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.45 (s, 2 H), 7.41–7.38 (m, 1 H), 7.35 (d, J = 7.5 Hz, 2 H), 7.30–7.29 (m, 2 H), 7.25–7.20 (m, 2 H), 7.17–7.14 (m, 1 H), 7.03–7.00 (m, 1 H), 6.96–6.92 (m, 2 H), 6.30 (d, J = 8.0 Hz, 1 H), 3.80 (s, 0.4 H), 3.58 (s, 2.6 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 156.4, 148.7, 141.5, 138.6, 138.2, 137.6 (q, $J_{\text{C-F}}$ = 6.3 Hz), 133.8, 132.1, 131.0, 130.2 (q, $J_{\text{C-F}}$ = 1.6 Hz), 129.6 (q, $J_{\text{C-F}}$ = 33.8 Hz), 129.0, 128.0, 127.3, 127.2, 127.0, 123.9, 122.4, 121.3, 121.1 (q, $J_{\text{C-F}}$ = 267.6 Hz), 112.2, 55.7.

^{19}F NMR (470 MHz, CDCl_3): δ = –54.7 (2.6 F), –57.1 (0.4 F).

MS (EI, 70 eV): m/z (%) = 378 (100) $[\text{M}]^+$, 278 (14), 265 (12), 181 (35), 138 (10).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{O}$: 379.1304; found: 379.1317.

1-[(4-Methoxyphenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (7) (Table 2, Entry 4)

Yield: 67.1 mg (89%, Z/E = 27:73); yellow oil.

IR (neat): 1716, 1346, 1235, 888, 685 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.47 (s, 1 H), 7.40–7.37 (m, 2 H), 7.34–7.31 (m, 2 H), 7.23–7.21 (m, 4 H), 7.18 (m, 1 H), 6.99–6.96 (m, 1 H), 6.92–6.90 (m, 2 H), 6.61 (d, J = 8.0 Hz, 1 H), 3.88 (s, 2.2 H), 3.84 (s, 0.8 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 160.8, 152.5, 142.5, 138.7, 138.5, 136.5 (q, $J_{\text{C-F}}$ = 6.0 Hz), 135.1, 133.2, 132.8, 131.7, 130.0 (q, $J_{\text{C-F}}$ = 33.4 Hz), 129.0, 127.3, 126.8, 126.7, 124.0, 123.0 (q, $J_{\text{C-F}}$ = 279.6 Hz), 122.4, 114.0, 55.3.

^{19}F NMR (470 MHz, CDCl_3): δ = –53.9 (0.8 F), –54.1 (2.2 F).

MS (EI, 70 eV): m/z (%) = 378 (100) $[\text{M}]^+$, 309 (36), 294 (16), 265 (21), 138 (9).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{O}$: 379.1304; found: 379.1312.

(*E*)-1-[(4-Chlorophenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (8) (Table 2, Entry 5)

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, CDCl_3): δ = 7.49 (s, 1 H), 7.40–7.37 (m, 4 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).

^{13}C NMR (125 MHz, CDCl_3): δ = 150.6, 141.9, 141.2, 138.9, 138.0, 137.7 (q, $J_{\text{C-F}}$ = 6.0 Hz), 135.5, 133.6, 132.0, 131.2, 130.2 (q, $J_{\text{C-F}}$ = 43.5 Hz), 129.1, 129.0, 127.5, 127.4, 127.1, 124.2, 122.7 (q, $J_{\text{C-F}}$ = 268.0 Hz), 122.6.

^{19}F NMR (470 MHz, CDCl_3): δ = –54.4 (3 F).

MS (EI, 70 eV): m/z (%) = 384 (35) $^{[37\text{C}]}[\text{M}]^+$, 382 (100) $^{[35\text{C}]}[\text{M}]^+$, 307 (19), 278 (79), 138 (36).

HRMS (EI): m/z [M]⁺ calcd for C₂₃H₁₄F₃Cl: 382.0731; found: 382.0727.

(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).

¹³C NMR (125 MHz, CDCl₃): δ = 163.5 (d, J_{C-F} = 248.9 Hz), 151.0, 142.1, 138.9, 138.8 (d, J_{C-F} = 3.4 Hz), 138.2, 137.5 (q, J_{C-F} = 6.0 Hz), 133.5, 132.7 (d, J_{C-F} = 8.3 Hz), 131.3, 130.0 (q, J_{C-F} = 33.6 Hz), 129.1, 127.5, 127.3, 127.0, 124.1, 122.8 (q, J_{C-F} = 268.0 Hz), 122.6, 115.9 (d, J_{C-F} = 21.5 Hz).

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

MS (EI, 70 eV): m/z (%) = 366 (100) [M]⁺, 297 (80), 296 (24), 276 (14), 138 (15).

HRMS (EI): m/z [M]⁺ calcd for C₂₃H₁₄F₄: 366.1026; found: 366.1024.

(E)-1-(4-{Phenyl[2-(trifluoromethyl)-1H-inden-1-ylidene]methyl}phenyl)ethanone (10) (Table 2, Entry 7)

Yield: 39.3 mg (50%); yellow solid; mp 99.7–101.5 °C.

IR (neat): 2532, 2160, 1686, 1266, 1068, 697 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 7.99 (d, J = 8.0 Hz, 2 H), 7.50 (s, 1 H), 7.43 (d, J = 8.0 Hz, 2 H), 7.40–7.36 (m, 2 H), 7.35–7.32 (m, 2 H), 7.22–7.18 (m, 3 H), 6.95–6.92 (m, 1 H), 6.40 (d, J = 8.0 Hz, 1 H), 2.66 (s, 3 H).

¹³C NMR (125 MHz, CDCl₃): δ = 197.7, 150.3, 147.4, 141.5, 138.9, 138.2 (q, J_{C-F} = 6.1 Hz), 137.7, 137.1, 134.0, 131.4, 130.9, 130.6, 129.9 (q, J_{C-F} = 33.8 Hz), 129.0, 128.7, 127.6 (q, J_{C-F} = 3.9 Hz), 127.2, 124.3, 122.7, 122.6 (q, J_{C-F} = 268.0 Hz), 26.7.

¹⁹F NMR (470 MHz, CDCl₃): δ = -54.6 (3 F).

MS (EI, 70 eV): m/z (%) = 390 (100) [M]⁺, 347 (43), 307 (29), 278 (54), 132 (17).

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₅H₁₈F₃O: 391.1304; found: 391.1314.

(E)-1-{Phenyl[4-(trifluoromethyl)phenyl]methylene}-2-(trifluoromethyl)-1H-indene (11) (Table 2, Entry 8)

Yield: 47.8 mg (57%); yellow solid; mp 66.4–68.2 °C.

IR (neat): 1693, 1322, 1064, 832, 753 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 7.66 (d, J = 8.0 Hz, 2 H), 7.50 (s, 1 H), 7.45 (d, J = 8.0 Hz, 2 H), 7.40–7.37 (m, 2 H), 7.35–7.32 (m, 2 H), 7.22–7.19 (m, 3 H), 6.98–6.95 (m, 1 H), 6.35 (d, J = 8.0 Hz, 1 H).

¹³C NMR (125 MHz, CDCl₃): δ = 149.9, 146.3, 141.5, 139.0, 138.3 (q, J_{C-F} = 6.1 Hz), 137.7, 134.1, 131.3 (q, J_{C-F} = 41.3 Hz), 130.9, 130.7, 130.1 (q, J_{C-F} = 35.6 Hz), 129.1, 128.5 (q, J_{C-F} = 1.6 Hz), 127.7 (q, J_{C-F} = 7.7 Hz), 127.3, 125.8 (q, J_{C-F} = 3.7 Hz), 124.2, 124.0 (q, J_{C-F} = 270.6 Hz), 122.8, 122.6 (q, J_{C-F} = 268.0 Hz).

¹⁹F NMR (470 MHz, CDCl₃): δ = -54.7 (3 F), -62.5 (3 F).

MS (EI, 70 eV): m/z (%) = 416 (100) [M]⁺, 347 (88), 278 (26), 251 (10), 138 (18).

HRMS (EI): m/z [M]⁺ calcd for C₂₄H₁₄F₆: 416.0994; found: 416.0999.

4-{Phenyl[2-(trifluoromethyl)-1H-inden-1-ylidene]methyl}benzotrile (12) (Table 2, Entry 9)

Yield: 28.6 mg (38%, Z/E = 23:77); yellow solid; mp 112.3–114.2 °C.

IR (neat): 1547, 1356, 1118, 829, 733, 697 cm⁻¹.

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 H), 6.34 (d, J = 7.5 Hz, 0.77 H).

¹³C NMR (125 MHz, CDCl₃): δ = 149.1, 147.3, 141.7, 139.1, 138.7 (q, J_{C-F} = 6.0 Hz), 137.4, 134.5, 132.5, 131.3, 131.1, 130.0, 129.2, 129.0 (q, J_{C-F} = 32.8 Hz), 127.7, 127.3, 124.2, 122.9, 122.5 (q, J_{C-F} = 268.0 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).

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₄H₁₅F₃N: 374.1151; found: 374.1158.

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 H), 6.30 (d, J = 8.0 Hz, 0.71 H).

¹³C NMR (125 MHz, CDCl₃): δ = 148.6, 148.1, 143.4, 141.6, 139.1, 138.6 (q, J_{C-F} = 6.1 Hz), 136.5, 134.8, 131.5, 131.1, 130.1, 129.2, 128.7 (q, J_{C-F} = 29.5 Hz), 128.5, 127.9, 127.5, 125.6, 124.5, 123.9, 122.8, 122.3 (q, J_{C-F} = 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).

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₃H₁₅F₃NO₂: 394.1050; found: 394.1043.

(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, 1 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_{C-F} = 6.1 Hz), 137.7, 134.9, 133.9, 131.0, 130.4, 130.0, 129.5 (q, J_{C-F} = 33.8 Hz), 129.0, 128.6, 128.3, 127.4 (q, J_{C-F} = 11.5 Hz), 127.3, 127.2, 126.9, 126.3, 125.8, 125.5, 124.3, 122.9 (q, J_{C-F} = 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).

HRMS (EI): m/z [M]⁺ calcd for C₂₇H₁₇F₃: 398.1277; found: 398.1279.

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_{C-F} = 6.1 Hz), 136.8, 136.4, 133.4, 131.0, 130.4, 129.1 (q,

J_{C-F} = 33.4 Hz), 129.0, 128.7, 128.6, 128.0, 127.4, 125.3, 122.9 (q, J_{C-F} = 267.8 Hz), 122.1, 21.8.

^{19}F NMR (470 MHz, CDCl_3): δ = -54.3 (3 F).

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

HRMS (EI): m/z $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{17}\text{F}_3$: 362.1277; found: 362.1283.

1-(Diphenylmethylene)-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, CDCl_3): δ = 7.41–7.38 (m, 2 H), 7.38–7.35 (m, 2 H), 7.35–7.31 (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).

^{13}C NMR (125 MHz, CDCl_3): δ = 159.2, 150.3, 142.9, 142.2, 140.3, 137.0 (q, J_{C-F} = 6.2 Hz), 133.3, 132.8, 131.4, 131.0, 130.9 (q, J_{C-F} = 42.5 Hz), 130.4, 128.9, 128.6 (q, J_{C-F} = 3.8 Hz), 127.4, 125.3, 122.7 (q, J_{C-F} = 268.0 Hz), 113.0, 107.4, 55.4.

^{19}F NMR (470 MHz, CDCl_3): δ = -54.4 (3 F).

MS (EI, 70 eV): m/z (%) = 378 (100) $[\text{M}]^+$, 363 (11), 309 (37), 265 (26), 165 (15).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{O}$: 379.1304; found: 379.1320.

1-(Diphenylmethylene)-6-fluoro-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, 1463, 1266, 1111, 878, 751, 697 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): δ = 162.4 (d, J_{C-F} = 242.4 Hz), 153.6, 142.2, 141.9, 140.2 (q, J_{C-F} = 8.4 Hz), 136.6 (q, J_{C-F} = 5.7 Hz), 134.8 (q, J_{C-F} = 2.1 Hz), 132.7, 131.0, 130.3, 129.9 (q, J_{C-F} = 33.8 Hz), 129.6, 129.1, 128.9, 127.5, 123.2 (d, J_{C-F} = 9.2 Hz), 122.6 (q, J_{C-F} = 268.0 Hz), 114.2 (d, J_{C-F} = 23.5 Hz), 111.8 (d, J_{C-F} = 26.1 Hz).

^{19}F NMR (470 MHz, CDCl_3): δ = -54.4 (3 F), -113.6 (1 F).

MS (EI, 70 eV): m/z (%) = 366 (100) $[\text{M}]^+$, 325 (10), 297 (68), 165 (15), 138 (19).

HRMS (EI): m/z $[\text{M}]^+$ calcd for $\text{C}_{23}\text{H}_{14}\text{F}_4$: 366.1026; found: 366.1021.

1-[(4-Methoxyphenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (7) (Table 2, Entry 15)

Yield: 65.6 mg (87%, Z/E = 97:3); yellow solid; mp 130.4–131.8 °C.

IR (neat): 1603, 1355, 1115, 830, 755 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.48 (s, 1 H), 7.46–7.44 (m, 1 H), 7.41–7.38 (m, 3 H), 7.31–7.28 (m, 2 H), 7.17–7.13 (m, 3 H), 6.93–6.90 (m, 1 H), 6.86 (d, J = 9.0 Hz, 2 H), 6.38 (d, J = 8.0 Hz, 1 H), 3.87 (s, 0.1 H), 3.84 (s, 2.9 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 160.5, 152.5, 143.0, 138.7, 138.5, 136.6 (q, J_{C-F} = 6.0 Hz), 135.0, 133.2, 132.6, 131.0, 130.1 (q, J_{C-F} = 44.1 Hz), 129.4, 128.6, 126.8, 126.7, 124.1, 122.4, 120.9 (q, J_{C-F} = 268.3 Hz), 112.9, 55.2.

^{19}F NMR (470 MHz, CDCl_3): δ = -53.9 (2.9 F), -54.1 (0.1 F).

MS (EI, 70 eV): m/z (%) = 378 (100) $[\text{M}]^+$, 309 (33), 265 (17), 138 (5), 132 (7).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{O}$: 379.1304; found: 379.1316.

(Z)-1-[(4-Chlorophenyl)(phenyl)methylene]-2-(trifluoromethyl)-1H-indene (8) (Table 2, Entry 16)

Yield: 51.4 mg (67%); yellow solid; mp 117.8–119.5 °C.

IR (neat): 1723, 1254, 1089, 826, 761 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.49 (s, 1 H), 7.42–7.37 (m, 4 H), 7.31–7.27 (m, 4 H), 7.19–7.15 (m, 3 H), 6.95–6.91 (m, 1 H), 6.38 (d, J = 8.0 Hz, 1 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 150.6, 142.4, 140.6, 138.8, 138.1, 137.8 (q, J_{C-F} = 6.1 Hz), 135.1, 133.7, 132.4, 130.5, 129.7 (q, J_{C-F} = 33.6 Hz), 129.4, 128.8, 127.8, 127.4, 127.1, 124.3, 122.8 (q, J_{C-F} = 268.0 Hz), 122.6.

^{19}F NMR (470 MHz, CDCl_3): δ = -54.2 (3 F).

MS (EI, 70 eV): m/z (%) = 382 (97) $[\text{M}]^+$, 313 (36), 278 (100), 154 (16), 138 (56).

HRMS (EI): m/z $[\text{M}]^+$ calcd for $\text{C}_{23}\text{H}_{14}\text{F}_3\text{Cl}$: 382.0731; found: 382.0729.

(Z)-1-(4-{Phenyl[2-(trifluoromethyl)-1H-inden-1-ylidene]methyl}phenyl)ethanone (10) (Table 2, Entry 17)

Yield: 56.3 mg (72%); yellow solid; mp 134.0–135.8 °C.

IR (neat): 1730, 1356, 1119, 826, 746 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 7.92 (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).

^{13}C NMR (125 MHz, CDCl_3): δ = 197.7, 150.3, 146.7, 142.1, 138.8, 138.3 (q, J_{C-F} = 6.0 Hz), 138.0, 136.8, 134.0, 131.1, 130.2, 129.6 (q, J_{C-F} = 33.6 Hz), 129.4, 128.9, 127.6, 127.5, 127.3, 124.5, 122.7 (q, J_{C-F} = 268.0 Hz), 122.6, 26.7.

^{19}F NMR (470 MHz, CDCl_3): δ = -54.2 (3 F).

MS (EI, 70 eV): m/z (%) = 390 (100) $[\text{M}]^+$, 347 (35), 307 (24), 278 (53), 138 (30).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{18}\text{F}_3\text{O}$: 391.1304; found: 391.1317.

(Z)-4-{Phenyl[2-(trifluoromethyl)-1H-inden-1-ylidene]methyl}benzotrile (12) (Table 2, Entry 18)

Yield: 64.1 mg (86%, 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, CDCl_3): 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, 0.67 H), 6.34 (d, J = 8.0 Hz, 0.33 H).

^{13}C NMR (125 MHz, CDCl_3): δ (E/Z mixture) = 149.1, 148.9, 147.3, 146.4, 141.7, 141.0, 139.1, 138.9 (q, J_{C-F} = 6.0 Hz), 138.8, 138.7 (q, J_{C-F} = 6.0 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_{C-F} = 45.4 Hz), 129.5, 129.2, 129.1, 129.0 (q, J_{C-F} = 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_{C-F} = 267.9 Hz), 122.5 (q, J_{C-F} = 268.0 Hz), 118.6, 118.4, 112.7, 112.3.

^{19}F NMR (470 MHz, CDCl_3): δ = -54.4 (2 F), -54.8 (1 F).

MS (EI, 70 eV): m/z (%) = 373 (79) $[\text{M}]^+$, 304 (100), 276 (11), 138 (18).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{15}\text{F}_3\text{N}$: 374.1151; found: 374.1156.

(Z)-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, 762, 694 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 8.27–8.25 (m, 1 H), 8.18 (d, J = 8.5 Hz, 1 H), 7.52–7.51 (m, 2 H), 7.47–7.33 (m, 5 H), 7.30–7.28 (m, 1 H), 7.25–7.20 (m, 2 H), 6.97–6.92 (m, 1 H), 6.39 (d, J = 7.5 Hz, 0.6 H), 6.36 (d, J = 8.0 Hz, 0.4 H).

^{13}C NMR (125 MHz, CDCl_3): δ (*E/Z* mixture) = 149.2, 148.5, 148.3, 148.2, 148.0, 147.8, 141.6, 141.0, 139.1 (q, $J_{\text{C-F}}$ = 4.0 Hz), 138.8 (q, $J_{\text{C-F}}$ = 4.0 Hz), 137.8, 137.4, 136.0, 134.8, 132.4, 132.2, 131.6, 131.3, 130.8, 130.0, 129.8, 129.5 (q, $J_{\text{C-F}}$ = 40.0 Hz), 129.1, 128.8, 128.7 (q, $J_{\text{C-F}}$ = 43.0 Hz), 128.0 (q, $J_{\text{C-F}}$ = 5.6 Hz), 127.8, 127.5, 127.4, 124.6, 124.2, 124.0, 123.8, 123.0, 122.9, 122.8, 122.6 (q, $J_{\text{C-F}}$ = 267.9 Hz), 122.5 (q, $J_{\text{C-F}}$ = 268.0 Hz).

^{19}F NMR (470 MHz, CDCl_3): δ = –54.3 (1.8 F), –54.8 (1.2 F).

MS (EI, 70 eV): m/z (%) = 393 (100) $[\text{M}]^+$, 324 (59), 294 (41), 276 (81), 138 (79).

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{15}\text{F}_3\text{NO}_2$: 394.1050; found: 394.1046.

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