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Site-Selective Synthesis of Arylated Indenones by Suzuki–Miyaura Cross-Coupling Reactions of 2,3,5-Tribromoinden-1-one

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The first transition-metal-catalyzed cross-coupling reactions of 2,3,5-tribromo-1*H*-inden-1-one are reported. The Suzuki-Miyaura reaction of 2,3,5-tribromo-1*H*-inden-1-one with three equivalents of arylboronic acid gave 2,3,5-triaryl-1*H*-inden-1-ones. The reaction with one and two equivalents of arylboronic acid gave 2,5-dibromo-3-aryl-1*H*-inden-1-ones and 5-bromo-2,3-diaryl-1*H*-inden-1-ones, respectively, with

Arylated indenones represent a pharmacologically important molecular entity.^[1] For example, 2,3-diarylindenones have been studied as ligands for the estrogen receptor,^[1a] and 3-arylindenone-2-carboxylic acid derivatives have been studied as selective inhibitors of fibroblast growth factor receptor-1 tyrosine kinase.^[1d] Indenones also occur in several biologically relevant natural products, such as euplectin, which contains both a benzofuran and an inden-1-one substructure.^[2] Other examples include neo-lignans isolated from the fruits of Virola sebifera.[3] Pauciflorol F is a 2,3-diarylindanone that has been prepared by palladium-catalyzed Larock cyclization, hydrogenation, and subsequent epimerization.^[4] 2,3-Diarylindenones are available by classical methods that include, for example, intramolecular Friedel–Crafts acylations,^[5a] reactions of phthalides or 1H-indene-1,3(2H)-diones with Grignard reagents.^[5b,5c] and synthetic transformations of dibenzovlmethane,^[5d] benzophenone derivatives,^[5e] or diphenyl acetylene.[5f] Transition-metal-catalyzed syntheses of 2,3-diarylinden-1-ones include the Larock cyclization^[4] and related processes.[6]

Reactions of functionalized indenones, such as hydrogenations, reactions of the carbonyl group, and conjugate additions, have been widely studied. We were interested in palladium-catalyzed cross-coupling reactions of halogenated inden-1-ones. Whereas reactions of 2,3-dibromo-1*H*-inden-1-one with amines, Grignard reagents, and CH-acidic compounds were reported nearly a century ago,^[7] transitionmetal-catalyzed reactions of this molecule were unknown until our recent report^[8] in this field. Site-selective palladium-catalyzed reactions of dibromofuranones, which are very good site-selectivity. The one-pot reaction of 2,3,5-tribromo-1*H*-inden-1-one with one equivalent of two different arylboronic acids afforded 5-bromo-2,3-diaryl-1*H*-inden-1ones containing two different terminal aryl groups. Other one-pot reactions allowed the synthesis of 2,3,5-triaryl-1*H*inden-1-ones containing different aryl groups.

closely related to 2,3-dibromoindenones, have been previously reported by Bellina and co-workers.^[9] In general, site-selective palladium(0)-catalyzed cross-coupling reactions of polyhalogenated heterocycles are of considerable current interest in organic chemistry because they allow facile assembly of complex heterocycles in only one step.^[10–12] Recently, we have reported site-selective Suzuki–Miyaura (SM)^[13] reactions of 2,3-dibromoinden-1-one.^[8] Herein, we report, to the best of our knowledge, the first site-selective SM reactions of 2,3,5-tribromoinden-1-one. These reactions provide a convenient approach to various arylated inden-1ones. Interestingly, our starting material, 2,3,5-tribromoinden-1-one, represents a new compound that has, to the best of our knowledge, not been synthesized or studied before.

Results and Discussion

2,3,5-Tribromoinden-1-one (2) was prepared in 62% yield by reaction of commercially available 5-bromoindan-1-one with *N*-bromosuccinimide (NBS) in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) (Scheme 1). Unfortunately, use of toxic benzene is required in this reaction. Toluene cannot be used, due to competing benzylic bromination. Whereas 2,3-dibromoinden-1-one is known,^[14] the synthesis of **2** has, to the best of our knowledge, not been previously reported.



Scheme 1. Synthesis of **2**. *Reagents and conditions:* (i) **1** (1.0 equiv.), NBS (3.5 equiv.), AIBN (10 mol-%), benzene, reflux, 7 h.

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The SM reaction of 2,3,5-tribromoinden-1-one (2) with three equivalents of arylboronic acids 3a-g afforded the 2,3,5-triaryl-1*H*-inden-1-ones 4a-g in 76–88% yields (Scheme 2, Table 1). The best yields were obtained using 3.3 equiv. of arylboronic acid, [Pd(PPh_3)₄] (5 mol-%) as the catalyst, and K₂CO₃ (2 M aqueous solution) as the base (1,4-dioxane, 70 °C, 6 h). Compounds 4 could be prepared in equally good yields using [Pd(PPh_3)₂Cl₂] as the catalyst. Similar conditions were used for the SM reactions of 2,3dibromoinden-1-one.^[8] The reactions were successful for both electron-rich and electron-poor arylboronic acids.



Scheme 2. Synthesis of **4a**–g. *Reagents and conditions:* (i) ArB-(OH)₂ **3a–e** (3.3 equiv.), $[Pd(PPh_3)_4]$ (5 mol-%), K_2CO_3 (2 M, 1 mL), dioxane, 70 °C, 6 h.

Table 1. Synthesis of 2,3,5-triaryl-indenone 4a-g.

3,4	Ar	Yield 4 [%] ^[a]	
a	Ph	83	
b	$4-\text{EtC}_6\text{H}_4$	88	
c	$4-t\mathrm{Bu}\mathrm{C}_{6}\mathrm{H}_{4}$	85	
d	$3-(MeO)C_6H_4$	76	
e	$3-C1C_6H_4$	79	
f	$4-FC_6H_4$	81	
g	$3-(CF_3)C_6H_4$	78	

[a] Isolated product.

The SM reaction of 2 with arylboronic acids 3a, 3c, 3e, and 3g–j (1.0 equiv.) afforded the 3-aryl-2,5-dibromo-1*H*inden-1-ones 5a–g in 78–92% yields with very good siteselectivity (Scheme 3, Table 2). The first aryl substitution occurred at the 3-position. The yields dropped when more than exactly 1.0 equiv. of the boronic acid was used. The reactions were carried out using [Pd(PPh_3)_4] (3 mol-%) as the catalyst, except in case of 5c, for which [Pd(PPh_3)_2Cl_2] was employed. It proved to be important to carry out the reactions at 45 °C instead of 70 °C. Significant amounts of side-products, derived from multifold coupling, were formed when the temperature was too high. The reactions could be successfully carried out with both electron-rich and electron-poor arylboronic acids.



Scheme 3. Synthesis of **5a–g**. *Reagents and conditions:* (i) ArB-(OH)₂ **3a**, **3c**, **3e**, or **3g–j** (1.0 equiv.), $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_2Cl_2]$ (3 mol-%), K₃PO₄ (1.5 equiv.), dioxane, 45 °C, 9 h.

The structure of all products were confirmed by spectroscopic methods. The structure of **5d** was independently confirmed by X-ray crystal structure analysis (Figure 1),^[15]



Table 2. Synthesis of 3-aryl-2,5-dibromoindenones 5a-g.

	-		-
3	5	Ar	Yield of 5 [%] ^[a]
a	a	C ₆ H ₅	83
с	b	$4-tBuC_6H_4$	86
е	с	$3-ClC_6H_4$	82 ^[b]
g	d	$3-(CF_3)C_6H_4$	80
h	e	$4-(CF_3O)C_6H_4$	78
i	f	$4-MeC_6H_4$	86
i	g	$4-(MeO)C_6H_4$	92

[[]a] Isolated product. [b] [Pd(PPh₃)₂Cl₂] was used.

which showed that the aryl group and the indenone moiety are twisted out of plane.



Figure 1. Molecular structure of 5d.

The SM reaction of 2 with arylboronic acids 3b–d, 3f, 3g, 3j, and 3k (2.0 equiv.) afforded the 2,3-diaryl-5-bromo-1*H*-inden-1-ones 6a-g in 75–88% yields with very good site-selectivity (Scheme 4, Table 3). The reactions were again successful for both electron-rich and electron-poor arylboronic acids. The first arylation occurred at positions 2 and 3, while the 5-position remained unaffected. The reactions were best carried out at 60 °C using exactly 2.0 equiv. of boronic acid and 5 mol-% catalyst.



Scheme 4. Synthesis of **6a–g**. *Reagents and conditions:* (i) ArB-(OH)₂ **3b–d**, **3f**, **3g**, **3j**, and **3k** (2.0 equiv.), $[Pd(PPh_3)_4]$ (5 mol-%), K₃PO₄ (3.0 equiv.), dioxane, 60 °C, 6 h.

Table 3. Synthesis of 5-bromo-2,3-diaryl-indenone 6a-g.

3	6	Ar	Yield 6 [%] ^[a]
b	a	4-EtC ₆ H ₄	88
c	b	$4-tBuC_6H_4$	83
d	с	$3-(MeO)C_6H_4$	75
f	d	$4 - FC_6H_4$	78
g	e	$3-(CF_3)C_6H_4$	77
ĭ	f	$4-(MeO)C_6H_4$	85
k	g	$4-ClC_6H_4$	87

[a] Isolated product.

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The structure of **6g** was independently confirmed by X-ray crystal structure analysis (Figure 2),^[15] which showed that both aryl groups and the indenone moiety are twisted out of plane.

Figure 2. Molecular structure of **6**g.

The one-pot reaction of **2** with two different arylboronic acids, which were sequentially added, afforded the unsymmetrical 2,3-diaryl-5-bromo-1*H*-inden-1-ones **7a–c**, containing two different aryl groups (Scheme 5, Table 4). To achieve good site-selectivity in favor of position 3 of the substrate, it proved to be important that the first step was carried out at 45 °C (9 h) and the second step at 60 °C (6 h).



Scheme 5. One-pot synthesis of **7a–c**. *Reagents and conditions:* (i) (1) $Ar^{1}B(OH)_{2}$ (1.0 equiv.), $[Pd(PPh_{3})_{4}]$ (5 mol-%), $K_{3}PO_{4}$ (4.5 equiv.), dioxane, 45 °C, 9 h; (2) $Ar^{2}B(OH)_{2}$ (1.0 equiv.), 60 °C, 6 h.

Table 4. Synthesis of 7a-c.

7	Ar ¹	Ar ²	Yield 8 [%] ^[a]
a	$\begin{array}{l} \text{4-Et-}C_6H_4\\ \text{4-}Cl\text{-}C_6H_4\\ \text{4-}Cl\text{-}C_6H_4 \end{array}$	4-(MeO)C ₆ H ₄	80
b		4-Et-C ₆ H ₄	79
c		4-(MeO)C ₆ H ₄	82

[a] Isolated product.

The reaction of 5g with 2.2 equiv. of 4-(*tert*-butyl)phenylboronic acid afforded the 2,3,5-triarylinden-1-one **8a** in 78% yield (Scheme 6, Table 5). The one-pot reaction of **2** with one equivalent of 4-chlorophenylboronic acid and with 2.2 equiv. of a different arylboronic acid (sequential addition) afforded the 2,3,5-triarylinden-1-ones **8b** and **8c**, respectively, in good yields (Scheme 6, Table 5). During the optimization of the one-pot reaction, the temperature and stoichiometry were again found to play an important role.



Scheme 6. Synthesis of **8a–c**. *Reagents and conditions:* (i) (1) $Ar^{1-}B(OH)_{2}$ (2.0 equiv.), $[Pd(PPh_{3})_{4}]$ (5 mol-%), $K_{3}PO_{4}$ (4.5 equiv.), dioxane, 45 °C, 9 h; (2) $Ar^{2}B(OH)_{2}$ (2.2 equiv.), 70 °C, 6 h; (ii) $Ar^{2-}B(OH)_{2}$ (2.2 equiv.), $[Pd(PPh_{3})_{4}]$ (3 mol-%), $K_{2}CO_{3}$ (2 M, 1 mL), dioxane, 70 °C, 6 h.

Table 5. Synthesis of **8a–c**.

8	Ar ¹	Ar ²	Yield 8 [%] ^[a]
a b c	$\begin{array}{l} \text{4-(MeO)C}_6\text{H}_4\\ \text{4-ClC}_6\text{H}_4\\ \text{4-ClC}_6\text{H}_4 \end{array}$	$\begin{array}{l} \text{4-}t\text{BuC}_6\text{H}_4\\ \text{4-}\text{EtC}_6\text{H}_4\\ \text{4-}(\text{MeO})\text{C}_6\text{H}_4 \end{array}$	78 ^[b] 81 ^[c] 84 ^[c]

[a] Isolated product. [b] Prepared from 5g. [c] Prepared from 2.

The reaction of **6d** with 1.1 equiv. of 3-methoxyphenylboronic acid afforded the 2,3,5-triarylinden-1-one **9a** in 88% yield (Scheme 7, Table 6). The one-pot reaction of **2** with 2.2 equiv. of 4-(trifluoromethyl)phenylboronic acid and with 1.1 equiv. of 4-methoxyphenylboronic acid (sequential addition) afforded 2,3,5-triarylinden-1-one **9b** in 86% yield. During the optimization of the one-pot reaction, the temperature (60 °C for the first step and 70 °C for the second step) and the stoichiometry (2.0 equiv. for the first step and 1.1 equiv. for the second step) proved to be important. The structure of **9b** was independently confirmed by X-ray crystal structure analysis (Figure 3).^[15]



Scheme 7. Synthesis of **9a** and **9b**. *Reagents and conditions:* (i) (1) $Ar^{1}B(OH)_{2}$ (2.0 equiv.), $[Pd(PPh_{3})_{4}]$ (5 mol-%), $K_{3}PO_{4}$ (4.5 equiv.), dioxane, 60 °C, 6 h; (2) $Ar^{2}B(OH)_{2}$ (1.1 equiv.), 70 °C, 6 h; (ii) **6d** (1.0 equiv.), $Ar^{2}B(OH)_{2}$ (1.1 equiv.), $[Pd(PPh_{3})_{4}]$ (3 mol-%), $K_{2}CO_{3}$ (2 M, 1 mL), dioxane, 70 °C, 6 h.

Table 6. Synthesis of 9a and 9b.

9	Ar ¹	Ar ²	Yield 9 [%] ^[a]
a	4-F-C ₆ H ₄	3-(MeO)C ₆ H ₄	88 ^[b]
b	4-CF ₃ -C ₆ H ₄	4-(MeO)C ₆ H ₄	86 ^[c]

[a] Isolated product. [b] Prepared from 6d. [c] Prepared from 2.

The development of a site-selective, one-pot process that can be used to sequentially introduce three different aryl groups in one step, failed. However, the synthesis of such



Figure 3. Molecular structure of 9b.

molecules can be realized by reaction of 2,3-diaryl-5-bromoinden-1-ones 7a-c with arylboronic acids.

The order of reactivity of the three different positions of 2,3,5-tribromoinden-1-one is C-3 > C-2 > C-5 (Figure 4). The site-selectivity can be explained by the fact that position 3 is considerably more electron-deficient than positions 2 and 5. The second aryl substitution occurs at position C-2, which is sterically more hindered than position 5, and electronically less deficient. This result is surprising because it does not follow the rule suggested by Handy and Zhang for the prediction of the site-selectivity of palladium-catalyzed reactions of polyhalogenated substrates.^[11] To predict the selectivity, the ¹H NMR spectra of the non-halogenated parent compounds were studied, which reflects the electronic situation of the different positions. According to the rule of the authors, the first arylation should occur at the position that has the higher chemical shift value of the respective proton. In case of the ¹H NMR spectrum of inden-1-one, which is the parent molecule of 2,3,5-tribromoinden-1-one (2), the chemical shift of the 5-H proton is significantly shifted downfield with regard to the 2-H proton, which is the most upfield-resonating proton of the molecule. In contrast, proton 3-H resonates most downfield of all the protons of inden-1-one. Therefore, the rule of Handy and Zhang correctly predicts the selectivity in favor of position 3, but not the selectivity favoring position 2 (with respect to position 5). The selectivity in favor of position 2 versus position 5 might be explained by chelation of the catalyst to the carbonyl oxygen atom, which may enhance the rate of the oxidative addition of palladium, favoring arylation at C-2.



Figure 4. Possible explanation for the site-selectivity.

In conclusion, we have reported the site-selective Suzuki– Miyaura reactions of 2,3,5-tribromo-1*H*-inden-1-one, which is a novel brominated indenone derivative, that pro-



vides a convenient and site-selective approach to various arylated inden-1-ones in good yields. The order of the selectivity is C-3 > C-2 > C-5. Position C-3 is the most electron-deficient, and the first aryl substitution takes place there. The selectivity in favor of position C-2 can be explained by chelation of the catalyst to the neighboring carbonyl group.

Experimental Section

2,3,5-Tribromo-1H-inden-1-one (2): A round-bottomed flask was equipped with a condenser, and a suspension of 5-bromo-indanone 1 (1.50 g, 7.14 mmol), N-bromosuccinamide (4.43 g, 24.89 mmol), and AIBN (0.12 g, 10-mol-%) in benzene (35 mL) was heated to reflux under argon for 7 h and then cooled to 20 °C. The reaction mixture was quenched with triethylamine (1 mL) and benzene was evaporated in vacuo. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic layers were dried (Na2SO4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptanes). Compound 2 was isolated as a light-yellow crystalline solid (1.62 g, 62%); m.p. 160-161 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.26 (d, J = 7.7 Hz, 1 H, ArH), 7.28 (d, J = 1.5 Hz, 1 H, ArH), 7.41 (dd, J = 1.6, 7.7 Hz, 1 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 123.8 (C), 124.0, 124.7 (CH), 127.6, 129.4 (C), 132.6 (CH), 144.1, 144.6 (C), 185.4 (CO) ppm. IR (KBr): $\tilde{v} = 3416$, 3084, 3015, 2922, 2850, 2674 (w), 1722, 1594, 1584, 1540, 1438, 1401, 1337 (m), 1260, 1218 (w), 1200 (s), 1094, 1085, 1054, 1041, 933, 876 (m), 831 (s), 811, 764, 691, 680, 618, 593, 577 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 370 (13) [M, ⁸¹Br, ⁸¹Br, ⁸¹Br]⁺, 368 (41) [M, ⁷⁹Br, ⁸¹Br, ⁸¹Br]⁺, 366 (42) [M, ⁷⁹Br, ⁷⁹Br, ⁸¹Br]⁺, 287 (100), 259 (23), 178 (17). HRMS (EI, 70 eV): calcd. for C₉H₃Br₃O [M, ⁸¹Br, ⁸¹Br, ⁸¹Br]⁺: 369.76671; found 369.76599; calcd. for C₉H₃Br₃O [M, ⁷⁹Br, ⁸¹Br, ⁸¹Br]⁺: 367.76876; found 367.76801; calcd. for C₉H₃Br₃O [M, ⁷⁹Br, ⁷⁹Br, ⁸¹Br]⁺: 365.77081; found 365.77001, calcd. for C₉H₃Br₃O [M, ⁷⁹Br, ⁷⁹Br, ⁷⁹Br]⁺: 363.77285; found 363.77181.

Suzuki Cross-Coupling Reactions; General Procedure A: The reaction was carried out in a pressure tube. To a suspension of the brominated indenone, $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_2Cl_2]$ (3–5 mol-%), and arylboronic acid (1.0–1.1 per cross coupling) in dioxane (3–5 mL), was added either K₃PO₄ (1.5 equiv. per cross coupling) or an aqueous solution of K₂CO₃ (2 m, 1 mL). The mixture was heated at the indicated temperature (45–70 °C) under an argon atmosphere for the indicated period of time (5–9 h). The reaction mixture was diluted with water and extracted with CH₂Cl₂ (3×25 mL). The combined organic layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel; EtOAc/heptanes).

2,3,5-Triphenyl-1*H***-inden-1-one (4a):** Starting with **2** (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₂CO₃ (2 m, 1 mL), and phenylboronic acid (81 mg, 0.66 mmol), **4a** was isolated as a brownish-yellow solid (60 mg, 83%). Reaction temperature: 70 °C for 6 h; m.p. 182–183 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.17–7.21 (m, 4 H, ArH), 7.26–7.42 (m, 11 H, ArH), 7.46–7.49 (m, 2 H, ArH), 7.57 (d, *J* = 7.4 Hz, 1 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 120.5, 123.4, 127.2, 127.5, 127.8, 128.1, 128.3, 128.5, 128.9, 129.3 (CH), 129.5 (C), 130.0 (CH), 130.8, 132.7, 132.2, 140.4, 146.1, 146.8, 154.8 (C), 196.8 (CO) ppm. IR (KBr): \tilde{v} = 3054, 3030, 2955, 2921, 2849 (w), 1704, 1597 (s), 1573, 1467, 1442, 1355, 1340, 1331, 1279, 1263, 1184, 1177, 1097, 1079, 1063, 1029, 1012, 939, 917, 894, 850, 837 (w), 793, 778, 758,

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727 (m), 690 (s), 672, 657, 596 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 358 (100) [M]⁺, 341 (11). 326 (11), 252 (15). HRMS (EI, 70 eV): calcd. for C₂₇H₁₈O [M]⁺ 358.13522; found 358.135167.

2,3,5-Tris(4-ethylphenyl)-1H-inden-1-one (4b): Starting with 2 (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 4-ethylphenylboronic acid (99 mg, 0.66 mmol), 4b was isolated as a brownish-yellow solid (78 mg, 88%). Reaction temperature: 70 °C for 6 h; m.p. 133-134 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.16–1.23 (m, 9 H, 3× CH₃), 2.54 $(q, J = 7.5 \text{ Hz}, 2 \text{ H}, \text{ CH}_2), 2.56-2.66 \text{ (m, 4 H, } 2 \times \text{ CH}_2), 7.02 \text{ (d,})$ *J* = 8.1 Hz, 2 H, ArH), 7.13–7.27 (m, 9 H, ArH), 7.36 (dd, *J* = 1.4, 7.5 Hz, 1 H, ArH), 7.40 (d, J = 8.3 Hz, 2 H, ArH), 2.53 (d, J =7.5 Hz, 1 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 14.1, 14.2, 14.5 (CH₃), 27.5, 27.6, 27.8 (CH₂), 119.3, 122.2, 126.0, 126.1, 126.6 (CH), 127.2 (C), 127.2, 127.3, 127.6 (CH), 128.4 (C), 128.9 (CH), 129.1, 131.7, 136.8, 142.7, 143.5, 144.5, 145.3, 145.6, 153.2 (C), 195.4 (CO) ppm. IR (KBr): $\tilde{v} = 2962$, 2928, 2873 (w), 1698, 1595 (s), 1500, 1455, 1351, 1336, 1259, 1181, 1142, 1116, 1095, 1071, 1048, 1017, 1012, 936, 821 (m), 786 (m), 740, 729, 703, 674, 660, 638, 623 (w), 568 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 442 (100) [M]⁺, 413 (26), 207 (26). HRMS (EI, 70 eV): calcd. for C₃₃H₃₀O [M]⁺ 442.22912; found 442.228900.

2,3,5-Tris(4-tert-butylphenyl)-1H-inden-1-one (4c): Starting with 2 (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 4-tert-butylphenylboronic acid (118 mg, 0.66 mmol), 4c was isolated as a brownish-yellow solid (89 mg, 85%). Reaction temperature: 70 °C for 6 h; m.p. 98-100 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.23$ (s, 9 H, 3 × CH₃), 1.27 (s, 9 H, $3 \times CH_3$, 1.29 (s, 9 H, $3 \times CH_3$), 7.16–7.23 (m, 4 H, ArH), 7.28– 7.46 (m, 10 H, ArH), 7.53 (d, J = 7.4 Hz, 1 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 31.2 (6× CH₃), 31.3 (3× CH₃), 34.6, 34.7, 34.9 (C), 120.5, 123.2, 125.0, 125.7, 125.8, 126.9, 127.0 (CH), 128.0 (C), 128.3 (CH), 129.5 (C), 129.6 (CH), 129.9, 132.6, 146.4, 146.5, 150.6, 151.4, 152.4, 154.2 (C), 196.6 (CO) ppm. IR (KBr): $\tilde{v} = 2958, 2927, 2903, 2866$ (w), 1704 (s), 1598, 1462, 1362, 1351, 1268, 1187, 1112, 1093, 1069, 1015, 938 (m), 821, 785, 766, 756, 726, 708, 693, 648, 637, 579 (w), 558 (s), 538, 528 (s) cm^{-1} . GC-MS (EI, 70 eV): m/z (%) = 526 (100) [M]⁺, 511 (60). 248 (26). HRMS (EI, 70 eV): calcd. for C₃₉H₄₂O [M]⁺ 526.32302; found 526.323938.

2,3,5-Tris(3-methoxyphenyl)-1H-inden-1-one (4d): Starting with 2 (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 3-methoxyphenylboronic acid (101 mg, 0.66 mmol), 4d was isolated as a brownish-yellow solid (68 mg, 76%). Reaction temperature: 70 °C for 6 h; m.p. 163-165 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.60 (s, 3 H, OCH₃), 3.65 (s, 3 H, OCH₃), 3.78 (s, 3 H, OCH₃), 6.71-6.90 (m, 6 H, ArH), 6.93 (dt, J = 1.1, 7.5 Hz, 1 H, ArH), 7.00 (t, J = 1.8 Hz, 1 H, ArH), 7.05–7.14 (m, 2 H, ArH), 7.26–7.31 (m, 3 H, ArH), 7.40 (dd, J = 1.4, 7.5 Hz, 1 H, ArH), 7.56 (d, J = 7.5 Hz, 1 H, ArH) ppm. ¹³C NMR $(75.5 \text{ MHz}, \text{ CDCl}_3): \delta = 54.5, 54.7, 54.8 (\text{OCH}_3), 112.6, 112.7,$ 113.1, 113.6, 114.3, 114.6, 119.1, 120.0, 120.2, 121.9, 122.7, 127.1, 128.5 (CH), 129.0 (C), 129.3, 129.5 (CH), 131.4, 132.5, 133.4, 141.3, 145.4, 146.1, 154.3, 158.5, 159.2, 159.4 (C), 195.3 (CO) ppm. IR (KBr): $\tilde{v} = 2921$, 2852, 2830 (w), 1698, 1600, 1581 (s), 1461, 1465, 1453, 1440, 1432, 1317, 1351, 1329, 1319, 1301, 1290, 1281, 1262, 1236, 1218, 1182, 1165, 1136, 1101, 1079, 1056, 1046, 1032, 962, 879, 845, 795, 784, 767, 729, 699, 685, 675 (m), 641, 621, 603, 590, 554 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 448 (100) [M]⁺, 417 (11). HRMS (EI, 70 eV): calcd. for $C_{30}H_{24}O_4$ [M]⁺ 448.16691; found 448.165998.

2,3,5-Tris(3-chlorophenyl)-1*H***-inden-1-one (4e):** Starting with **2** (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL),

K₂CO₃ (2 M, 1 mL), and 3-chlorophenylboronic acid (103 mg, 0.66 mmol), 4e was isolated as a brownish-yellow solid (73 mg, 79%). Reaction temperature: 70 °C for 6 h; m.p. 135–137 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.01 (dt, J = 0.9, 7.5 Hz, 1 H, ArH), 7.09–7.30 (m, 5 H, ArH), 7.28–7.44 (m, 8 H, ArH), 7.58 (d, J = 7.4 Hz, 1 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 120.3, 123.8, 125.4, 126.6, 127.3, 128.0, 128.1, 128.2, 128.3, 128.4, 129.5 (CH), 129.6 (C), 129.8, 129.9, 130.2, 130.6 (CH), 131.9, 132.5, 134.0, 134.2, 134.9, 135.2, 141.9, 145.5, 145.6, 154.0 (C), 194.9 (CO) ppm. IR (KBr): $\tilde{v} = 2955$, 2921, 2851 (w), 1699 (s), 1596, 1579, 1561 (m), 1461, 1437, 1423 (w), 1344, 1328, 1297, 1259, 1249, 1186, 1078, 1063, 957, 892, 875, 851, 799, 779, 769, 743, 713, 682, 667 (m), 602, 592 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 466 (05) [M, ³⁷Cl₃]⁺, 464 (37) [M, ³⁷Cl₂, ³⁵Cl]⁺, 462 (98) [M, ³⁷Cl, ³⁵Cl₂]⁺, 460 (100) [M, ³⁵Cl₃]⁺, 425 (42). 362 (21), 326 (31). HRMS (EI, 70 eV): calcd. for C₂₇H₁₅Cl₃O [M, ³⁵Cl₃]⁺ 460.01830; found 460.017500.

2,3,5-Tris(4-fluorophenyl)-1*H*-inden-1-one (4f): Starting with 2 (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 4-fluorophenylboronic acid (93 mg, 0.66 mmol), 4f was isolated as a brownish-yellow solid (67 mg, 81%). Reaction temperature: 70 °C for 6 h; m.p. 236-237 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.91 (t, J = 8.8 Hz, 2 H, ArH), 7.03– 7.10 (m, 4 H, ArH), 7.15-7.20 (m, 3 H, ArH), 7.30-7.34 (m, 2 H, ArH), 6.91 (dd, J = 1.4, 7.5 Hz, 1 H, ArH), 7.42–7.47 (m, 2 H, ArH), 6.91 (d, J = 7.4 Hz, 1 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): $\delta = -113.6, -112.8, -110.3 \text{ ppm}.$ ¹³C NMR (75.5 MHz, CDCl₃): δ = 115.4 (d, $J_{\rm F,C1}$ = 21.5 Hz, CH), 115.9 (d, $J_{\rm F,C}$ = 21.6 Hz, CH), 115.9 (d, $J_{\rm F,C}$ = 21.8 Hz, CH), 120.1, 123.6 (CH), 125.4 (d, $J_{F,C}$ = 3.4 Hz, C), 126.5 (CH), 127.3 (d, $J_{F,C}$ = 4.3 Hz, C), 128.9 (d, *J*_{F,C} = 8.2 Hz, CH), 128.2 (C), 130.5 (d, *J*_{F,C} = 8.2 Hz, CH), 131.8 (d, $J_{F,C}$ = 8.0 Hz, CH), 131.4 (C), 135.3 (d, $J_{F,C}$ = 3.4 Hz, C), 144.8, 144.9, 152.5 (C), 161.5 (d, $J_{\rm F,C}$ = 248.8 Hz, C-F), 161.7 (d, $J_{F,C}$ = 249.3 Hz, C-F), 162.0 (d, $J_{F,C}$ = 250.8 Hz, C-F), 194.6 (CO) ppm. IR (KBr): $\tilde{v} = 2956$, 2922, 2851 (w), 1697, 1592 (s), 1515, 1496, 1463, 1350 (m), 1220 (s), 1185, 1158, 1143, 1094, 1070, 1012, 935, 906, 871, 857 (m), 827, 812, 799 (s), 787, 748, 740 (m), 722, 712, 700, 661 (w), 620, 569, 557, 538 (m) $\rm cm^{-1}.$ GC-MS (EI, 70 eV): m/z (%) = 412 (100) [M]⁺, 395 (11), 288 (13). HRMS (EI, 70 eV): calcd. for C₂₇H₁₅OF₃ [M]⁺ 412.10695; found 412.107062.

2,3,5-Tris[3-(trifluoromethyl)phenyl]-1H-inden-1-one (4g): Starting with 2 (80 mg, 0.20 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 3-(trifluoromethyl)phenylboronic acid (125 mg, 0.66 mmol), 4g was isolated as a brownish-yellow solid (88 mg, 78%). Reaction temperature: 70 °C for 6 h; m.p. 155-156 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.21 (d, J = 1.1 Hz, 1 H, ArH), 7.31-7.66 (m, 13 H, ArH), 7.71 (s, 1 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ = -63.1, -63.0, -62.7 ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 120.4 (CH), 123.5 (q, J_{F,C} = 272.7 Hz, CF₃), 123.7 (q, $J_{F,C}$ = 272.0 Hz, CF₃), 123.8 (q, $J_{F,C}$ = 271.3 Hz, CF₃), 123.9 (q, $J_{\rm F,C}$ = 3.8 Hz, CH), 124.1 (CH), 124.9 (q, $J_{F,C}$ = 3.6 Hz, CH), 125.2 (q, $J_{F,C}$ = 3.5 Hz, CH), 125.3 (q, $J_{F,C}$ = 3.8 Hz, CH), 126.5 (q, $J_{\rm F,C}$ = 3.8 Hz, CH), 126.7 (q, $J_{\rm F,C}$ = 3.9 Hz, CH), 128.6, 128.8, 129.6, 129.9, 130.5 (CH), 130.7 (C), 130.6 (q, $J_{F,C}$ = 22.6 Hz, C-CF₃), 130.7 (q, $J_{F,C}$ = 22.4 Hz, C-CF₃), 130.6 (q, $J_{F,C} = 24.8$ Hz, C-CF₃), 131.6 (CH), 132.7, 132.9 (C), 133.1 (CH), 140.8, 145.4, 145.7, 154.1 (C), 194.7 (CO) ppm. IR (KBr): $\tilde{v} = 1706$, 1600, 1438, 1429, 1361, 1327, 1314, 1303, 1283, 1241, 1182, 1162 (m), 1112, 1098, 1067 (s), 1031, 999, 955, 917, 907, 895, 849, 817 (w), 798, 782, 769, 738, 698, 689, 677, 654 (m), 636, 621, 601, 533 (w) cm⁻¹. EI (70 eV): m/z (%) = 562 (100) [M]⁺,



493 (16). HRMS (EI, 70 eV): calcd. for $C_{30}H_{15}F_9O$ [M]⁺ 562.09737; found 562.097569.

2,5-Dibromo-3-phenyl-1H-inden-1-one (5a): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (8 mg, 3 mol-%), dioxane (3 mL), K₃PO₄ (86 mg, 0.41 mmol), and phenylboronic acid (33 mg, 0.27 mmol), 5a was isolated as a brownish-yellow solid (60 mg, 83%). Reaction temperature: 45 °C for 8 h; m.p. 108-110 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.19–7.20 (m, 1 H, ArH), 7.32–7.38 (m, 2 H, ArH), 7.45–7.57 (m, 5 H, ArH) ppm. ¹³C NMR $(62.9 \text{ MHz}, \text{CDCl}_3): \delta = 119.1 \text{ (C)}, 124.7, 128.1 \text{ (CH)}, 128.4, 128.8$ (C), 128.9 (CH), 130.5 (C), 130.6, 131.6 (CH), 146.3, 155.8 (C), 188.6 (CO) ppm. IR (KBr): $\tilde{v} = 3087, 3062, 2921, 2850$ (w), 1728 (s), 1599, 1557, 1486, 1442, 1397, 1342 (m), 1299, 1282 (w), 1266, 1176, 1149, 1098, 1052, 1028 (m), 1000 (w), 931, 917, 875, 833, 814, 769, 755, 714 (w), 688 (s), 663, 634, 611, 586 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 366 (51) [M, ⁸¹Br, ⁸¹Br]⁺, 364 (100) [M, ⁷⁹Br, ⁸¹Br]⁺, 362 (51) [M, ⁷⁹Br, ⁷⁹Br]⁺, 285 (27), 176 (51). HRMS (EI, 70 eV): calcd. for C₁₅H₈Br₂O [M, ⁸¹Br, ⁸¹Br]⁺: 365.88955; found 365.889828, calcd. for C₁₅H₈Br₂O [M, ⁷⁹Br, ⁸¹Br]⁺: 363.89160; found 363.891541, calcd. for $C_{15}H_8Br_2O$ [M, ⁷⁹Br, ⁷⁹Br]⁺: 361.89364; found 361.893675.

2,5-Dibromo-3-(4-tert-butylphenyl)-1H-inden-1-one (5b): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (8 mg, 3 mol-%), dioxane (3 mL), K₃PO₄ (86 mg, 0.41 mmol), and 4-tert-butylphenylboronic acid (48 mg, 0.27 mmol), 5b was isolated as a brownish-yellow solid (72 mg, 86%). Reaction temperature: 45 °C for 8 h; m.p. 133-135 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.32$ (s, 9 H, 3 × CH₃), 7.26–7.38 (m, 3 H, ArH), 7.48–7.55 (m, 4 H, ArH) ppm. ¹³C NMR $(62.9 \text{ MHz}, \text{ CDCl}_3): \delta = 31.6 (3 \times \text{ CH}_3), 35.1, 118.5 (C), 124.6,$ 124.8, 125.9 (CH), 127.6 (C), 128.0 (CH), 128.6, 128.7 (C), 131.5 (CH), 146.3, 154.2, 155.8 (C), 188.7 (CO) ppm. IR (KBr): $\tilde{v} = 3088$, 2960, 2903, 2866 (w), 1720 (s), 1600, 1592, 1565, 1495, 1463, 1448 (m), 1401, 1362, 1339, 1289, 1272, 1191, 1177 (w), 1155, 1106, 1092, 1047, 1017, 930, 878, 834 (m), 812 (s), 770, 717, 686, 632 (m), 588 (w), 550 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 422 (25) [M, ⁸¹Br, ⁸¹Br]⁺, 420 (49) [M, ⁷⁹Br, ⁸¹Br]⁺, 418 (24) [M, ⁷⁹Br, ⁷⁹Br]⁺, 405 (100), 202 (11). HRMS (EI, 70 eV): calcd. for C₁₉H₁₆Br₂O [M, ⁷⁹Br, ⁸¹Br]+: 419.95420; found 419.954735, calcd. for C₁₉H₁₆Br₂O [M, ⁷⁹Br, ⁷⁹Br]⁺: 417.95624; found 417.957228.

2,5-Dibromo-3-(3-chlorophenyl)-1H-inden-1-one (5c): Starting with 2 (100 mg, 0.27 mmol), $[Pd(PPh_3)_4]$ (8 mg, 3 mol-%), dioxane (3 mL), K₃PO₄ (86 mg, 0.41 mmol), and 3-chlorophenylboronic acid (42 mg, 0.27 mmol), 5a was isolated as a brownish-yellow solid (63 mg, 80%). Reaction temperature: 45 °C for 8 h; m.p. 120-122 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.15 (d, J = 1.1 Hz, 1 H, ArH), 7.35–7.45 (m, 5 H, ArH), 7.52–7.53 (m, 1 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 120.8 (C), 124.5, 125.0, 126.2, 128.0 (CH), 128.5, 129.0 (C), 130.4, 130.6, 131.8 (CH), 132.3, 135.1, 145.9, 154.3 (C), 188.2 (CO) ppm. IR (KBr): v = 3065, 2918, 2849, 2156, 2137 (w), 1721 (s), 1598, 1585, 1553 (m), 1470, 1446, 1420, 1397 (m), 1337, 1272, 1180, 1167, 1153 (w), 1097, 1091, 1081, 1050, 951, 884, 835, 817, 786, 767, 712, 705, 682 (m), 650, 638, 600, 588 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 400 (63) [M, ⁸¹Br, ⁸¹Br]⁺, 398 (100) [M, ⁷⁹Br, ⁸¹Br]⁺, 396 (43) [M, ⁷⁹Br, ⁷⁹Br]⁺, 319 (33), 210 (20). HRMS (EI, 70 eV): calcd. for $C_{15}H_7Br_2O$ [M, ⁸¹Br, ⁸¹Br]⁺: 399.85058; found 399.850749, calcd. for C₁₅H₇Br₂ClO [M, ⁷⁹Br, ⁸¹Br]⁺: 397.85262; found 397.852713, calcd. for C₁₅H₇Br₂ClO [M, ⁷⁹Br, ⁷⁹Br]⁺: 395.85467; found 395.855006.

2,5-Dibromo-3-[3-(trifluoromethyl)phenyl]-1*H***-inden-1-one** (5d): Starting with 2 (100 mg, 0.27 mmol), $[Pd(PPh_3)_4]$ (8 mg, 3 mol-%), dioxane (3 mL), K_3PO_4 (86 mg, 0.41 mmol), and 3-(trifluoromethyl)phenylboronic acid (51 mg, 0.27 mmol), 5d was isolated as

a brownish yellow solid (93 mg, 80%). Reaction temperature: 45 °C for 8 h; m.p. 111–113 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.12$ (d, J = 1.0 Hz, 2 H, ArH), 7.35-7.42 (m, 2 H, ArH), 7.61-7.74 (m, 2 H, ArH), 7.61-32, ArH), 7.81 (br. s, 1 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): $\delta = -62.8$ ppm. ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 123.6$ $(q, J_{F,C} = 272.9 \text{ Hz}, CF_3), 124.4 (CH), 125.0 (q, J_{F,C} = 3.9 \text{ Hz}, CH),$ 125.1 (CH), 127.2 (q, $J_{\rm EC}$ = 3.7 Hz, CH), 128.1, 129.1 (C), 129.7, 131.3 (CH), 131.5 (C), 131.6 (q, $J_{\rm EC}$ = 32.8 Hz, C-CF₃), 132.0 (CH), 145.8, 154.2 (C), 188.1 (CO) ppm. IR (KBr): $\tilde{v} = 3074, 2959,$ 2929 (w), 1716, 1595, 1586 (m), 1556, 1491, 1449, 1428, 1404 (w), 1326 (m), 1250, 1165, 1122, 1094, 1073, 1054 (s), 934, 926, 880, 861, 833, 818 (w), 800, 697 (m), 677, 651, 622, 600, 585 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 434 (48) [M, ⁸¹Br, ⁸¹Br]⁺, 432 (100) $[M, {}^{79}Br, {}^{81}Br]^+$, 430 (51) $[M, {}^{79}Br, {}^{79}Br]^+$, 351 (35), 244 (36). HRMS (EI, 70 eV): calcd. for C₁₆H₇Br₂OF₃ [M, ⁸¹Br, ⁸¹Br]⁺: 433.8769; found 433.877014, calcd. for C₁₆H₇Br₂OF₃[M, ⁷⁹Br, ⁸¹Br]⁺: 431.87693; found 431.878784, calcd. for C₁₆H₇Br₂OF₃ [M, ⁷⁹Br, ⁷⁹Br]⁺: 429.88103; found 429.880630.

2,5-Dibromo-3-[4-(trifluoromethoxy)phenyl]-1*H*-inden-1-one (5e): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (8 mg, 3 mol-%), dioxane (3 mL), K₃PO₄ (86 mg, 0.41 mmol), and 4-(trifluoromethoxy)phenylboronic acid (56 mg, 0.27 mmol), 5d was isolated as a brownish-yellow solid (69 mg, 78%). Reaction temperature: 45 °C for 8 h; m.p. 102–104 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.24– 7.43 (m, 5 H, ArH), 7.62 (d, J = 8.8 Hz, 2 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): $\delta = -57.6$ ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 118.8 (C), 119.5 (q, $J_{\rm EC}$ = 258.5 Hz, OCF₃), 121.2, 124.1, 125.0 (CH), 127.2, 127.9, 128.0 (C), 130.0, 131.9 (CH), 144.9, 149.5, 153.3 (C), 188.2 (CO) ppm. IR (KBr): v = 3087, 2922, 2851 (w), 1729, 1609, 1597, 1590, 1504 (m), 1446 (w), 1303, 1277, 1247, 1205 (m), 1150 (s), 1095, 1053, 1018, 928 (m), 887 (w), 832, 817, 804, 766, 717, 689 (m), 666, 620, 588 (m), 538 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 450 (50) [M, ⁸¹Br, ⁸¹Br]⁺, 448 (100) [M, ⁷⁹Br, ⁸¹Br]⁺, 446 (51) [M, ⁷⁹Br, ⁷⁹Br]⁺, 367 (29), 260 (19). HRMS (EI, 70 eV): calcd. for C₁₆H₇Br₂O₂F₃ [M, ⁸¹Br, ⁸¹Br]⁺: 449.87185; found 449.871344, calcd. for C₁₆H₇Br₂O₂F₃[M, ⁷⁹Br, ⁸¹Br]⁺: 447.87389; found 447.873233, calcd. for C₁₆H₇Br₂O₂F₃ [M, ⁷⁹Br, ⁷⁹Br]⁺: 445. 87594; found 445.875324.

2,5-Dibromo-3-p-tolyl-1H-inden-1-one (5f): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (8 mg, 3 mol-%), dioxane (3 mL), K₃PO₄ (86 mg, 0.41 mmol), and p-tolylboronic acid (37 mg, 0.27 mmol), **5f** was isolated as a brownish-yellow solid (87 mg, 86%). Reaction temperature: 45 °C for 8 h; m.p. 129–131 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.38 (s, 3 H, CH₃), 7.21–7.22 (m, 1 H, ArH), 7.29 (d, J = 8.0 Hz, 2 H, ArH), 7.33–7.37 (m, 2 H, ArH), 7.26 (d, J =8.1 Hz, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 21.7 (CH₃), 118.5 (C), 124.6, 124.7 (CH), 127.66 (C), 128.1 (CH), 128.6, 128.7 (C), 129.6, 131.5 (CH), 141.2, 146.3, 155.9 (C), 188.7 (CO) ppm. IR (KBr): $\tilde{v} = 3089$, 3027, 2915, 2850 (w), 1729 (s), 1599, 1590, 1564, 1556, 1444 (m), 1398 (w), 1343, 1289, 1270, 1184, 1150, 1097, 1053 (m), 1019 (w), 928, 880, 835, 810, 765, 720, 715, 687, 631, 588 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 380 (50) [M, ⁸¹Br, ⁸¹Br]⁺, 378 (100) [M, ⁷⁹Br, ⁸¹Br]⁺, 376 (52) [M, ⁷⁹Br, ⁷⁹Br]⁺, 297 (25), 189 (50). HRMS (EI, 70 eV): calcd. for C₁₆H₁₀Br₂O [M, ⁸¹Br, ⁸¹Br]⁺: 379.90520; found 379.905770, calcd. for C₁₆H₁₀Br₂O [M, ⁷⁹Br, ⁸¹Br]+: 377.90725; found 377.907387, calcd. for C₁₆H₁₀Br₂O [M, ⁷⁹Br, ⁷⁹Br]⁺: 375.90929; found 375.909178.

2,5-Dibromo-3-(4-methoxyphenyl)-1*H***-inden-1-one (5g):** Starting with **2** (100 mg, 0.27 mmol), $[Pd(PPh_3)_4]$ (8 mg, 3 mol-%), dioxane (3 mL), K₃PO₄ (86 mg, 0.41 mmol), and 4-methoxyphenylboronic acid (41 mg, 0.27 mmol), **5g** was isolated as a brownish-yellow solid (98 mg, 92%). Reaction temperature: 45 °C for 8 h; m.p. 194–

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195 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.84 (s, 3 H, OCH₃), 6.70 (d, J = 8.8 Hz, 2 H, ArH), 7.26 (d, J = 1.0 Hz, 1 H, ArH),7.32-7.7.39 (m, 2 H, ArH), 7.60 (d, J = 8.9 Hz, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 55.5 (OCH₃), 114.4 (CH), 117.8, 122.8 (C), 124.5, 124.7 (CH), 128.5, 128.8 (C), 130.0, 131.5 (CH), 146.3, 155.5, 161.5 (C), 188.7 (CO) ppm. IR (KBr): \tilde{v} = 3409, 3070, 3025, 2985, 2955, 2921, 2850, 2282, 2035 (w), 1715, 1597, 1503 (s), 1444, 1419, 1401, 1341, 1307, 1275 (m), 1257, 1173 (s), 1152, 1118, 1102, 1091, 1052 (m), 1017 (s), 954 (w), 927 (m), 873 (w), 822, 813 (s), 782, 766, 732, 712, 690, 632, 621, 576 (m), 528 (s) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 396 (25) [M, ⁸¹Br, ⁸¹Br]⁺, 394 (100) [M, ⁷⁹Br, ⁸¹Br]⁺, 392 (51) [M, ⁷⁹Br, ⁷⁹Br]⁺, 313 (10), 191 (09), 163 (34). HRMS (EI, 70 eV): calcd. for C₁₆H₁₀Br₂O₂ [M, ⁸¹Br, ⁸¹Br]+: 395.90011; found 395.89959, calcd. for C₁₆H₁₀Br₂O₂ [M, ⁷⁹Br, ⁸¹Br]+: 393.90216; found 393.90172, calcd. for C₁₆H₁₀Br₂O₂ [M, ⁷⁹Br, ⁷⁹Br]⁺: 391.90421; found 391.90320.

5-Bromo-2,3-bis(4-ethylphenyl)-1H-inden-1-one (6a): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), and 4-ethylphenylboronic acid (81 mg, 0.54 mmol), 6a was isolated as a brownish-yellow solid (98 mg, 88%). Reaction temperature: 60 °C for 6 h; m.p. 102-104 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.15 (t, J = 7.6 Hz, 3 H, CH₃), 1.23 (t, J = 7.6 Hz, 3 H, CH₃), 2.55 (q, J = 7.6 Hz, 2 H, CH₂), 2.64 (q, J = 7.6 Hz, 2 H, CH₂), 7.03 (d, J = 8.4 Hz, 2 H, ArH), 7.14 (d, J = 8.3 Hz, 2 H, ArH), 7.17–7.24 (m, 5 H, ArH), 7.33–7.38 (m, 2 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 14.1, 14.2 (CH₃), 28.7, 28.8 (CH₂), 123.9, 124.6, 127.7 (CH), 128.1 (C), 128.4, 128.5 (CH), 129.5, 129.6 (C), 129.9, 131.4 (CH), 132.9, 144.1, 145.9, 147.5, 153.6 (C), 195.0 (CO) ppm. IR (KBr): $\tilde{v} = 2961$, 2923, 2851 (w), 1702 (s), 1590, 1576, 1501, 1454, 1411, 1350 (m), 1328 (w), 1259, 1174, 1116, 1095, 1068, 1047, 1017 (m), 961 (w), 930, 883, 862, 837, 819, 801 (m), 743 (w), 699, 661, 648, 638, 582, 564, 536 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 418 (98) [M, ⁸¹Br]⁺, 416 (100) [M, ⁷⁹Br]⁺, 387 (36), 263 (23). HRMS (EI, 70 eV): calcd. for C₂₅H₂₁BrO [M, ⁷⁹Br]⁺ 416.07703; found 416.077060.

5-Bromo-2,3-bis(4-tert-butylphenyl)-1H-inden-1-one (6b): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), and 4-tert-butylphenylboronic acid (97 mg, 0.54 mmol), 6b was isolated as a brownish-yellow solid (78 mg, 83%). Reaction temperature: 60 °C for 6 h; m.p. 188–190 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.22 (s, 9 H, 3× CH₃), 1.29 (s, 9 H, 3 × CH₃), 7.13–7.26 (m, 7 H, ArH), 7.34–7.39 (m, 4 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 31.1 (6× CH₃), 34.7, 34.9 (C), 123.9, 124.7, 125.1, 125.9 (CH), 127.4 (C), 128.2 (CH), 129.3, 129.5 (C), 129.6, 131.3 (CH), 132.8, 147.7, 151.0, 152.8, 153.5 (C), 195.7 (CO) ppm. IR (KBr): v = 2960, 2928, 2903, 2865 (m), 1708 (s), 1602, 1589, 1577, 1459, 1396, 1362, 1349, 1262 (m), 1199, 1181, 1113, 1104, 1092 (w), 1069, 1050, 1014 (m), 975, 958, 933 (w), 865, 857, 850, 841, 829, 818, 779, 739, 730, 654, 635, 625, 566, 559 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 474 (75) [M, ⁸¹Br]⁺, 472 (73) [M, ⁷⁹Br]⁺, 459 (100), 194 (16). HRMS (EI, 70 eV): calcd. for C₂₉H₂₉BrO [M, ⁸¹Br]⁺: 474.13758; found 474.138018; calcd. for C₂₉H₂₉BrO [M, ⁷⁹Br]⁺: 472.13963; found 472.139209

5-Bromo-2,3-bis(3-methoxyphenyl)-1*H***-inden-1-one (6c):** Starting with **2** (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), and 3-methoxyphenylboronic acid (82 mg, 0.54 mmol), **6c** was isolated as a brownish-yellow solid (63 mg, 75%). Reaction temperature: 60 °C for 6 h; m.p. 126–128 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.59 (s, 3 H, OCH₃), 3.65 (s, 3 H, OCH₃), 6.72–6.89 (m, 6 H, ArH), 7.10 (t, *J* = 7.7 Hz, 1 H, ArH), 7.18–7.20 (m, 1 H, ArH), 7.31 (t, *J* = 8.0 Hz, 1 H, ArH),

7.33–7.39 (m, 2 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 55.1, 55.3 (OCH₃), 113.7, 114.1, 115.0, 115.3, 120.6, 122.5, 124.1, 124.8 (CH), 128.4 (C), 129.2 (CH), 129.2 (C), 130.2 (CH), 131.5 (C), 131.7 (CH), 133.3, 133.5, 147.2, 154.2, 159.2, 159.9 (C), 195.1 (CO) ppm. IR (KBr): \tilde{v} = 2954, 2919, 2849, 2833 (w), 1709, 1590, 1575 (s), 1479, 1436, 1426, 1348, 1329, 1286, 1263, 1228, 1171, 1132, 1093 (m), 1042 (s), 960, 929, 919, 887, 979 (w), 786, 772, 721, 688 (m), 646, 647, 593, 566, 556 (w) cm⁻¹. GC-MS (EI, 70 eV): *mlz* (%) = 422 (71) [M, ⁸¹Br]⁺, 420 (100) [M, ⁷⁹Br]⁺, 389 (12), 298 (11), 226 (19). HRMS (EI, 70 eV): calcd. for C₂₃H₁₇BrO₃ [M, ⁸¹Br]⁺: 420.03556; found 420.034466.

5-Bromo-2,3-bis(4-fluorophenyl)-1H-inden-1-one (6d): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), and 4-fluorophenylboronic acid (77 mg, 0.54 mmol), 6d was isolated as a brownish-yellow solid (84 mg, 78%). Reaction temperature: 60 °C for 6 h; m.p. 184-185 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.90 (t, J = 8.9 Hz, 2 H, ArH), 7.07 (t, J = 8.8 Hz, 2 H, ArH), 7.13–7.18 (m, 3 H, ArH), 7.24–7.29 (m, 2 H, ArH), 7.34–7.41 (m, 2 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): $\delta = -1\delta = 12.3$, -109.8 ppm. ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 11\delta = 5.4$ (d, $J_{F,C} = 21.6$ Hz, CH), 116.4 (d, $J_{\rm EC}$ = 21.9 Hz, CH), 124.3, 124.6 (CH), 126.1 (d, $J_{\rm EC}$ = 3.6 Hz, C), 128.0 (d, $J_{F,C}$ = 3.5 Hz, C), 128.5, 129.1 (C), 130.4 (d, $J_{F,C}$ = 8.4 Hz, CH), 131.8 (d, $J_{F,C}$ = 7.6 Hz, CH), 131.9 (CH), 132.5, 146.9, 152.9 (C), 162.9 (d, $J_{F,C}$ = 249.3 Hz, CF), 163.2 (d, $J_{F,C}$ = 251.2 Hz, CF), 194.9 (CO) ppm. IR (KBr): \tilde{v} = 3076, 3047, 2922, 2852, 2158, 1895 (w), 1709 (s), 1596, 1584, 1575, 1511, 1499, 1456, 1404, 1351, 1330, 1224, 1178, 1159 (m), 1093, 1065 (w), 1050 (m), 1015, 941 (m), 927, 880, 864, 856, 845 (w), 825, 818 (s), 800, 776, 744, 732, 694, 662, 631, 619, 592, 567, 547, 532 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 398 (98) [M, ⁸¹Br]⁺, 398 (100) [M, ⁷⁹Br]⁺, 317 (52), 288 (79). HRMS (EI, 70 eV): calcd. for C₂₁H₁₁BrOF₂ [M, ⁸¹Br]+: 397.99354; found 397.993349, calcd. for C₂₁H₁₁BrOF₂ [M, ⁷⁹Br]⁺: 395.99559; found 395.995342.

5-Bromo-2,3-bis[3-(trifluoromethyl)phenyl]-1H-inden-1-one (6e): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), and 3-(trifluoromethyl)phenylboronic acid (103 mg, 0.54 mmol), 6e was isolated as a brownish-yellow solid (76 mg, 77%). Reaction temperature: 60 °C for 6 h; m.p. 150–152 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.15 (d, J = 1.0 Hz, 1 H, ArH), 7.32–7.57 (m, 9 H, ArH), 7.15 (br. d, J = 7.7 Hz, 1 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ = -63.02, -63.07 ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 123.3 (q, J_{F,C} = 272.8 Hz, CF₃), 123.4 (q, J_{F,C} = 272.6 Hz, CF₃), 124.7, 124.8 (CH), 125.1 (q, $J_{F,C}$ = 3.6 Hz, CH), 125.2 (q, $J_{F,C}$ = 3.6 Hz, CH), 126.6 (q, $J_{F,C}$ = 3.7 Hz, CH), 126.7 (q, $J_{F,C}$ = 3.7 Hz, CH), 128.8 (C), 128.9, 130.0 (CH), 130.4 (C), 130.9 (q, $J_{EC} = 32.5$ Hz, C-CF₃), 131.5 (CH), 132.0 (q, $J_{\rm EC}$ = 32.9 Hz, C-CF₃), 132.5 (CH), 132.5, 132.8, 133.1 (C), 146.2, 153.5 (C), 194.0 (CO) ppm. IR (KBr): \tilde{v} = 3070, 2923, 2851, 2143 (w), 1704 (s), 1600, 1583, 1442, 1354 (w), 1324 (s), 1313, 1295, 1276, 1261, 1163 (m), 1120 (s), 1097 (m), 1068 (s), 1051, 951, 911 (m), 881, 861, 840 (w), 806 (m), 781, 770, 740 (w), 721, 698 (m), 659, 650, 642, 631, 595 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 498 (98) [M, ⁸¹Br]⁺, 496 (100) [M, ⁷⁹Br]⁺, 417 (20), 397 (22), 320 (30). HRMS (EI, 70 eV): calcd. for C₂₃H₁₁BrOF₆ [M, ⁸¹Br]⁺: 497.98715; found 497.986267, calcd. for C₂₃H₁₁BrOF₆ [M, ⁷⁹Br]⁺: 495.98920; found 495.988980.

5-Bromo-2,3-bis(4-methoxyphenyl)-1*H***-inden-1-one (6f):** Starting with **2** (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K_3PO_4 (172 mg, 0.81 mmol), and 4-methoxyphenylboronic acid (82 mg, 0.54 mmol), **6f** was isolated as a brownish-yellow solid

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(96 mg, 85%). Reaction temperature: 60 °C for 6 h; m.p. 126-128 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.72 (s, 3 H, OCH₃), 3.79 (s, 3 H, OCH₃), 6.75 (d, J = 8.9 Hz, 2 H, ArH), 6.88 (d, J =8.9 Hz, 2 H, ArH), 7.16 (d, J = 8.9 Hz, 2 H, ArH), 7.21 (br. s, 1 H, ArH), 7.26 (d, J = 8.9 Hz, 2 H, ArH), 7.33–7.34 (m, 2 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 55.2, 55.34 (OCH₃), 113.1, 113.8 (CH), 122.9 (C), 123.2, 123.8 (CH), 124.6, 128.1, 129.6 (C), 129.4, 130.6, 130.7 (CH), 132.2, 147.6, 152.6, 159.4, 160.5 (C), 195.7 (CO) ppm. IR (KBr): \tilde{v} = 3409, 3071, 3026, 2987, 2956, 2920, 2850, 1898 (w), 1715, 1597, 1555, 1503, 1444 (s), 1420, 1401, 1342, 1307, 1275 (m), 1257, 1173 (s), 1152, 1118, 1103, 1091, 1052 (m), 1017 (s), 954 (w), 927 (m), 872 (w), 821 (s), 782, 766, 732, 712, 690, 632, 621, 588, 576 (m), 528 (s) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 422 (98) $[M, {}^{81}Br]^+$, 420 (100) $[M, {}^{79}Br]^+$, 405 (12), 255 (13), 226 (26). HRMS (EI, 70 eV): calcd. for C₂₃H₁₇BrO₃ [M, ⁸¹Br]⁺: 422.003351; found 422.03360, calcd. for C₂₃H₁₇BrO₃ [M, ⁷⁹Br]+: 420.03556; found 420.03547.

5-Bromo-2,3-bis(4-chlorophenyl)-1H-inden-1-one (6g): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), and 4-chlorophenylboronic acid (84 mg, 0.54 mmol), 6g was isolated as a brownish-yellow solid (100 mg, 87%). Reaction temperature: 60 °C for 6 h; m.p. 126– 128 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.10 (d, J = 8.8 Hz, 2 H, ArH), 7.14–7.23 (m, 5 H, ArH), 7.33–7.40 (m, 4 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 124.4, 124.6 (CH), 128.3, 128.6 (C), 128.7 (CH), 129.1 (C), 129.6, 129.7 (CH), 130.3 (C), 131.2, 132.0 (CH), 132.5, 134.5, 135.9, 146.6, 153.1 (C), 194.5 (CO) ppm. IR (KBr): $\tilde{v} = 3075$, 2919, 2850 (w), 1715 (s), 1601, 1586, 1574, 1557, 1484, 1454, 1395, 1348 (m), 1330, 1305, 1282, 1265 (w), 1174, 1150, 1174, 1150, 1087, 1063, 1045, 1013, 1063, 1046, 1013, 955, 946, 929, 877, 858, 832, 821, 812 (m), 776, 740, 726, 715, 707, 688, 647, 630, 626, 618, 589 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 434 (07) [M, ⁸¹Br, ³⁷Cl, ³⁷Cl]⁺, 432 (46) [M, ⁷⁹Br, ³⁷Cl, ³⁷Cl]⁺, 430 (100) [M, ⁷⁹Br, ³⁵Cl, ³⁷Cl]⁺, 428 (100) [M, ⁷⁹Br, ³⁵Cl, ³⁵Cl]⁺, 395 (20), 314 (30), 286 (30), 250 (53). HRMS (EI, 70 eV): calcd. for C₂₁H₁₁BrOCl₂ [M, ⁷⁹Br, ³⁵Cl, ³⁵Cl]⁺ 427.93648; found 427.93635.

Suzuki Cross-Coupling Reactions; General Procedure B: The reaction was carried out in a pressure tube. To a suspension of the brominated indenone, $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_2Cl_2]$ (5 mol-%) and $Ar^1B(OH)_2$ (1.0 equiv. per cross-coupling) in dioxane (3–5 mL), was added either K₃PO₄ (1.5 equiv. per cross coupling) or an aqueous solution of K₂CO₃ (2 M, 1 mL). The mixture was heated at the indicated temperature (45–60 °C) under an argon atmosphere for the indicated period of time (9 h) and cooled to room temperature. $Ar^2B(OH)_2$ (1.0–1.1 equiv. per cross-coupling) was added and the reaction mixture was heated further (6 h). The reaction mixture was cooled to room temperature, diluted with water and extracted with CH₂Cl₂ (3×25 mL). The combined organic layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel; EtOAc/heptanes).

5-Bromo-3-(4-ethylphenyl)-2-(4-methoxyphenyl)-1*H***-inden-1-one** (7a): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), 4-eth-ylphenylboronic acid (41 mg, 0.27 mmol), and 4-methoxyphenylboronic acid (41 mg, 0.27 mmol) following general procedure B, 7a was isolated as a brownish-yellow solid (90 mg, 80%). Reaction temperature: 45 °C for 9 h then at 60 °C for 6 h; m.p. 120–122 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.21 (t, *J* = 7.6 Hz, 3 H, CH₃), 2.63 (q, *J* = 7.6 Hz, 2 H, CH₂), 3.71 (s, 3 H, OCH₃), 6.73 (d, *J* = 8.9 Hz, 2 H, ArH), 7.13–7.23 (m, 7 H, ArH), 7.30–7.35 (m, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 15.2 (CH₃), 28.8

(CH₂), 55.2 (OCH₃), 113.7 (CH), 122.8 (C), 123.8, 124.4 (CH), 128.2 (C), 128.4, 128.5 (CH), 129.5, 129.6 (C), 131.2, 131.3 (CH), 132.5, 145.8, 147.6, 152.8, 159.4 (C), 195.5 (CO) ppm. IR (KBr): \tilde{v} = 2962, 2925, 2852, 2836 (w), 1709 (s), 1600, 1589, 1577, 1514, 1500, 1453, 1444 (m), 1400, 1349, 1329, 1293 (w), 1248, 1183, 1065, 1049, 1029, 1017, 930, 880, 852, 838, 820, 774 (m), 733, 717, 699, 681, 660, 649, 632 (w), 582, 561, 540, 526 (m) cm⁻¹. GC-MS (EI, 70 eV): *m*/*z* (%) = 420 (100) [M, ⁸¹Br]⁺, 418 (96) [M, ⁷⁹Br]⁺, 239 (19). HRMS (EI, 70 eV): calcd. for C₂₄H₁₉BrO₂ [M, ⁷⁹Br]⁺: 420.05425; found 420.054679; calcd. for C₂₄H₁₉BrO₂ [M, ⁷⁹Br]⁺: 418.05629; found 418.056241.

5-Bromo-3-(4-chlorophenyl)-2-(4-ethylphenyl)-1*H*-inden-1-one (7b): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), 4-chlorophenylboronic acid (42 mg, 0.27 mmol), and 4-ethylphenylboronic acid (41 mg, 0.27 mmol) following general procedure B, 7b was isolated as a brownish-yellow solid (90 mg, 79%). Reaction temperature: 45 °C for 9 h then at 60 °C for 6 h; m.p. 133–134 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.14 (t, J = 7.6 Hz, 3 H, CH₃), 2.55 (q, J = 7.6 Hz, 2 H, CH₂), 7.02–7.13 (m, 6 H, ArH), 7.23 (d, J = 8.6 Hz, 2 H, ArH), 7.33–7.38 (m, 3 H, ArH) ppm. ¹³C NMR (75.5 MHz, $CDCl_3$): $\delta = 14.1 (CH_3), 28.7 (CH_2), 24.2, 124.3 (CH), 127.2 (C),$ 127.9 (CH), 128.4, 129.2 (C), 129.4, 129.8, 129.9 (CH), 130.8 (C), 131.6 (CH), 133.8, 135.4, 144.6, 147.1, 152.0 (C), 195.1 (CO) ppm. IR (KBr): $\tilde{v} = 2964$, 2917, 2871, 2849 (w), 1705 (s), 1597, 1582, 1574, 1804, 1450, 1396, 1349, 1328, 1171, 1148 (m), 1120, 1108 (w), 1088, 1068, 1047, 1012, 969 (m), 951, 930 (w), 875, 860, 853, 827, 819, 779, 742, 733, 716, 692, 654, 637, 620, 589, 69, 534 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 426 (26) [M, ³⁷Cl, ⁸¹Br]⁺, 424 (100) [(M, ³⁵Cl, ⁸¹Br)⁺ or (M, ³⁷Cl, ⁷⁹Br)⁺], 4222 (76) [M, ³⁵Cl, ⁷⁹Br]⁺, 409 (33), 263 (28). HRMS (EI, 70 eV): calcd. for C₂₃H₁₆BrOCl [M, ³⁷Cl, ⁷⁹Br]⁺ 424.00381; found 424.004201.

5-Bromo-3-(4-chlorophenyl)-2-(4-methoxyphenyl)-1H-inden-1-one (7c): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), 4-chlorophenylboronic acid (42 mg, 0.27 mmol), and 4-methoxyphenylboronic acid (41 mg, 0.27 mmol) following general procedure B, 7c was isolated as a brownish-yellow solid (90 mg, 82%). Reaction temperature: 45 °C for 9 h then at 60 °C for 6 h; m.p. 201-203 °C. ¹H NMR (250 MHz, CDCl₃): δ = 3.71 (s, 3 H, OCH₃), 6.74 (d, J = 8.8 Hz, 2 H, ArH), 7.11–7.18 (m, 3 H, ArH), 7.23 (d, J = 8.6 Hz, 2 H, ArH), 7.31-7.36 (m, 4 H, ArH) ppm. ¹³C NMR (62.9 MHz, $CDCl_3$): $\delta = 54.2$ (OCH₃), 112.8 (CH), 121.2 (C), 123.1 (CH), 127.4, 128.1 (C), 128.4, 128.8 (CH), 129.9 (C), 130.3, 130.4 (CH), 132.2, 134.3, 146.2, 150.0, 158.6 (C), 194.3 (CO) ppm. IR (KBr): v = 2958, 2930, 2838 (w), 1709 (s), 1600, 1576, 1510, 1485, 1455 (m), 1445, 1416, 1407, 1396, 1352, 1329, 1295 (w), 1251, 1174, 1152, 1090, 1065, 1047, 1024, 1013 (m), 974, 957 (w), 946, 879, 846, 828, 812, 779, 742, 734, 717 (m), 691, 654, 643, 632, 618, 590 (w), 566, 536 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 426 (100) [M, ³⁷Cl]⁺, 424 (77) [M, ³⁵Cl]⁺, 267 (16), 239 (37). HRMS (EI, 70 eV): calcd. for C₂₂H₁₄BrClO₂ [M, ³⁷Cl]⁺: 425.98397; found 425.983498; calcd. for C₂₂H₁₄BrClO₂ [M, ³⁵Cl]⁺: 423.98602; found 423.985298.

2,5-Bis(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)-1*H*-inden-1-one (8a): Starting with 5g (78 mg, 0.20 mmol), [Pd(PPh₃)₄] (9 mg, 3 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 4-*tert*-butylphenylboronic acid (79 mg, 0.44 mmol), following the general procedure A, 8a was isolated as a brownish-yellow solid (78 mg, 78%). Reaction temperature: 70 °C for 6 h. M. p. 188–190 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.22 (s, 9 H, 3× CH₃), 1.27 (s, 9 H, 3× CH₃), 3.77 (s, 3 H, OCH₃), 6.85 (d, *J* = 8.8 Hz, 2 H, ArH), 7.15–7.23 (m, 4 H, ArH), 7.29–7.44 (m, 8 H, ArH), 7.52 (d, *J* =

7.3 Hz, 1 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 30.2, 30.3 (3× CH₃), 33.5, 33.6 (C), 55.3 (OCH₃), 114.3, 120.3, 123.2 (CH), 123.3 (C), 125.1, 125.8, 126.9, 127.0 (CH), 128.1 (C), 129.6, 130.2 (CH), 132.2, 137.6, 146.3, 146.3, 150.5, 150.7, 154.0, 160.3 (C), 195.4 (CO) ppm. IR (KBr): \tilde{v} = 2958, 2923, 2855 (w), 1700 (s), 1597, 1499, 1463, 1352, 1248, 1175, 1111, 1092, 1070, 1023 (m), 821 (s), 808, 784, 740, 729, 573, 543, 534 (m) cm⁻¹. GC-MS (EI, 70 eV): *m/z* (%) = 500 (100) [M]⁺, 485 (70), 235 (21). HRMS (EI, 70 eV): calcd. for C₃₆H₃₆O₂ [M]⁺ 500.27098; found 500.271551.

3-(4-Chlorophenyl)-2,5-bis(4-ethylphenyl)-1*H*-inden-1-one (8b): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), 4-chlorophenylboronic acid (42 mg, 0.27 mmol), and 4-ethylphenylboronic acid (90 mg, 0.60 mmol), following general procedure B, 8b was isolated as a brownish-yellow solid (98 mg, 81%). Reaction temperature: 45 °C for 9 h then at 70 °C for 6 h; m.p. 133-134 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.15 (t, J = 7.6 Hz, 3 H, CH₃), 1.19 (t, J = 7.6 Hz, 3 H, CH₃), 2.55 (q, J = 7.5 Hz, 2 H, CH₂), 2.61 (q, J = 7.5 Hz, 2 H, CH₂), 7.04 (d, J = 8.2 Hz, 2 H, ArH), 7.12 (d, J =8.2 Hz, 2 H, ArH), 7.17-7.21 (m, 3 H, ArH), 7.26-7.34 (m, 3 H, ArH), 7.37–7.41 (m, 3 H, ArH), 7.54 (d, J = 7.3 Hz, 2 H, ArH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 14.2, 14.5 (CH₃), 27.5, 27.6 (CH₂), 119.0, 122.5, 126.1, 126.2 (CH), 126.6 (C), 126.7, 127.4 (CH), 128.1 (C), 128.2, 128.8, 129.0 (CH), 130.4, 132.5, 134.0, 136.6, 143.2, 143.7, 144.9, 145.8, 151.6 (C), 195.0 (CO) ppm. IR (KBr): \tilde{v} = 3391, 3024, 2961, 2926, 2870, 1907, 1789 (w), 1706, 1595 (s), 1515 (w), 1485, 1462, 1455 (m), 1410, 1373 (w), 1351 (m), 1260 (w), 1181 (m), 1142 (m), 1087 (s), 1069, 1049 (m), 1012 (s), 963, 948, 935, 894, 862, 850 (w), 819 (s), 784, 741, 717 (m), 700, 670, 654, 638, 621, 571 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 448 (100) [M]⁺, 433 (18). HRMS (EI, 70 eV): calcd. for C₃₁H₂₅ClO [M]⁺ 448.15884; found 448.15899.

3-(4-Chlorophenyl)-2,5-bis(4-methoxyphenyl)-1*H*-inden-1-one (8c): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), K₃PO₄ (172 mg, 0.81 mmol), 4-chlorophenylboronic acid (42 mg, 0.27 mmol), and 4-ethylphenylboronic acid (89 mg, 0.60 mmol), following general procedure B, 8c was isolated as a brownish-yellow solid (102 mg, 84%). Reaction temperature: 45 °C for 9 h then at 70 °C for 6 h; m.p. 133-134 °C. ¹H NMR $(250 \text{ MHz}, \text{CDCl}_3): \delta = 3.81 \text{ (s, 3 H, OCH}_3), 3.85 \text{ (s, 3 H, OCH}_3),$ 6.74 (d, J = 8.8 Hz, 2 H, ArH), 6.88 (d, J = 8.7 Hz, 2 H, ArH), 7.13–7.18 (m, 3 H, ArH), 7.26–7.36 (m, 5 H, ArH), 7.42 (d, J =8.7 Hz, 2 H, ArH), 7.52 (d, J = 7.5 Hz, 1 H, ArH) ppm. ¹³C NMR $(62.9 \text{ MHz}, \text{CDCl}_3): \delta = 55.2 (\text{OCH}_3), 55.4 (\text{OCH}_3), 113.8, 114.3,$ 119.5 (CH), 122.8 (C), 123.5, 126.6, 128.3 (CH), 128.7 (C), 129.3, 130.0, 131.3 (CH), 131.5, 132.7, 133.0, 135.0, 146.1, 146.4, 151.7, 159.4, 160.0 (C), 196.2 (CO) ppm. IR (KBr): v = 2951, 2925, 2835 (w), 1697, 1591 (s), 1516, 1462, 1455, 1442 (m), 1348, 1331, 1286 (w), 1246, 1173, 1141, 1087, 1071, 1039, 1013 (m), 936, 893, 850 (w), 836, 822, 811, 797, 786, 744, 738, 727, 718, 699, 655, 621, 571, 562 (m) cm⁻¹. EI (70 eV): m/z (%) = 454 (40) [M, ³⁷Cl]⁺, 452 (100) $[M, {}^{35}Cl]^+$, 226 (12). HRMS (EI, 70 eV): calcd. for $C_{29}H_{21}O_3Cl$ [M, ³⁵Cl]⁺ 452.11737; found 452.118040.

2,3-Bis(4-fluorophenyl)-5-(3-methoxyphenyl)-1*H***-inden-1-one (9a):** Starting with **6d** (79 mg, 0.20 mmol), [Pd(PPh₃)₄] (9 mg, 3 mol-%), dioxane (3 mL), K₂CO₃ (2 M, 1 mL), and 3-methoxyphenylboronic acid (33 mg, 0.22 mmol), following general procedure A, **9a** was isolated as a yellow solid (75 mg, 88%). Reaction temperature: 70 °C for 6 h; m.p. 175–177 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3 H, OCH₃), 6.84–6.94 (m, 3 H, ArH), 6.99–7.10 (m, 4 H, ArH), 7.14–7.21 (m, 3 H, ArH), 7.26–7.35 (m, 3 H, ArH), 7.41 (dd, J = 1.4, 7.5 Hz, 1 H, ArH), 7.56 (d, J = 7.5 Hz, 1 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): $\delta = -112.9, -110.4$ ppm. ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 55.4$ (OCH₃), 113.2, 113.3, 115.3 (d, $J_{F,C} = 21.5$ Hz, CH), 116.3 (d, $J_{F,C} = 21.7$ Hz, CH), 119.7, 120.4, 123.5 (CH), 126.5 (d, $J_{F,C} = 3.5$ Hz, C), 127.8 (CH), 128.5 (d, $J_{F,C} = 3.5$ Hz, C), 129.4 (C), 130.0 (CH), 130.3 (d, $J_{F,C} = 8.3$ Hz, CH), 127.9 (d, $J_{F,C} = 8.1$ Hz, CH), 132.3, 141.7, 145.7, 146.8, 153.6, 160.0 (C), 162.4 (d, $J_{F,C} = 248.6$ Hz, C), 163.2 (d, $J_{F,C} = 250.3$ Hz, C), 195.7 (CO) ppm. IR (KBr): $\tilde{v} = 2919, 2850$ (w), 1704, 1596 (s), 1575, 1510, 1495, 1463, 1351 (m), 1279, 1223, 1211, 1186, 1171, 1160, 1101, 1080, 1071, 1049, 1023, 965, 951, 944, 877, 849, 838, 816, 800, 772, 747, 736, 712, 696, 676, 666, 629, 608, 581, 568, 548, 536 cm⁻¹. EI (70 eV): m/z (%) = 424 (100) [M]⁺. HRMS (EI, 70 eV): calcd. for $C_{28}H_{18}O_2F_2$ [M]⁺ 424.12694; found 424.126918.

5-(4-Methoxyphenyl)-2,3-bis[4-(trifluoromethyl)phenyl]-1H-inden-1one (9b): Starting with 2 (100 mg, 0.27 mmol), [Pd(PPh₃)₄] (14 mg, 5 mol-%), dioxane (3 mL), 2 м K₂CO₃ (1 mL), 4-(trifluoromethyl)phenylboronic acid (102 mg, 0.54 mmol), and 4-methoyphenylboronic acid (41 mg, 0.60 mmol), following the general procedure B, 9b was isolated as a yellow solid (122 mg, 86%). Reaction temperature: 60 °C for 9 h then at 70 °C for 6 h; m.p. 200–201 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.76 (s, 3 H, OCH₃), 6.89 (d, J = 8.8 Hz, 2 H, ArH), 7.18 (m, 1 H, ArH), 7.28 (d, J = 8.1 Hz, 2 H, ArH), 7.41–7.48 (m, 7 H, ArH), 7.59 (d, J = 7.5 Hz, 1 H, ArH), 7.65 (d, J = 8.1 Hz, 2 H, ArH) ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): $\delta = -62.8$, -62.7 ppm. ¹³C NMR (62.9 MHz, CDCl₃): $\delta =$ 55.4 (OCH₃), 114.4, 120.2 (CH), 123.6 (q, $J_{\rm F,C} = 272.6$ Hz, CF₃), 123.8 (q, $J_{\rm F,C}$ = 270.3 Hz, CF₃), 124.1 (CH), 125.2 (q, $J_{\rm F,C}$ = 3.7 Hz, CH), 126.2 (q, $J_{\rm F,C}$ = 3.8 Hz, CH), 127.4 (CH), 128.2 (C), 128.3, 128.9 (CH), 130.0 (q, $J_{F,C}$ = 31.5 Hz, C-CF₃), 130.2 (CH), 131.5 (q, J_{FC} = 33.0 Hz, C-CF₃), 132.3, 132.7, 133.9, 136.0, 145.2, 146.9, 154.4, 160.2 (C), 194.8 (CO) ppm. IR (KBr): v = 2962, 2918, 2849, 2837 (w), 1699, 1593, 1520, 1471, 1416, 1410 (m), 1318 (s), 1280, 1264, 1244 (m), 1160, 1120, 1112, 1068, 1058, 1033, 1016 (s), 937, 836, 819, 730, 719, 709, 698, 618, 601, 554 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 524 (100) [M]⁺. HRMS (EI, 70 eV): calcd. for $C_{30}H_{18}O_2F_6$ [M]⁺ 524.12055; found 524.120787.

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