

Regioselective Arylation and Alkynylation of 2,3-Dibromo-1*H*-inden-1-one by Suzuki–Miyaura and Sonogashira Cross-Coupling Reactions

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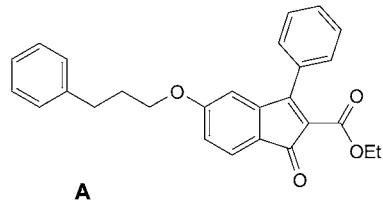
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Suzuki–Miyaura reactions of 2,3-dibromo-1*H*-inden-1-one afforded a wide range of arylated 1*H*-inden-1-ones. *Sonogashira* cross-coupling reactions gave alkynylated indenones. The reactions proceeded with very good regioselectivity in the less sterically hindered and more electron-deficient position 3.

Introduction. – Functionalized indenones exhibit a wide spectrum of pharmacological applications [1]. Indenone-containing compounds constitute a novel and interesting chemical class for the treatment of diabetes type 2. For example, compound **A** has been reported to have a very good agonistic activity with an EC_{50} value of 50 nm and shows a new binding mode in the co-crystal structure. Furthermore, nitrated indenoisoquinolines have been revealed as potent topoisomerase I (Top1) inhibitors [1][2].



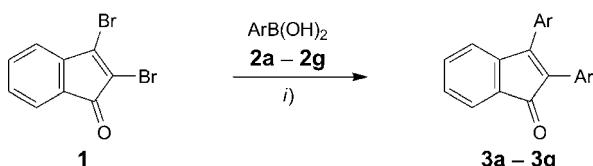
Indenones have been synthetically available for many decades by intramolecular Friedel–Crafts acylations and by various other established procedures [3]. Recently, novel syntheses of indenones based on Pd-catalyzed cyclizations have been developed [4]. An alternative approach involves regioselective functionalization reactions of polybrominated indenones. For example, the reaction of 2,3-dibromo-1*H*-inden-1-one with amines and C-nucleophiles was reported already many years ago [5]. Regioselective Pd-catalyzed cross-coupling reactions have increasingly gained importance in the last decade¹⁾. The selectivity of these reactions is generally influenced by electronic and steric factors. Recently, we have reported the synthesis of 2,3-diaryl-1*H*-inden-1-ones by regioselective *Suzuki–Miyaura* reactions of 2,3-dibromo-1*H*-inden-1-one [7]. Here, we report full details of these studies. With regard to our preliminary

¹⁾ For reviews of cross-coupling reactions of polyhalogenated heterocycles, see [6].

communication, we have considerably extended the scope, and report, for the first time, *Sonogashira* reactions which also proceed with excellent regioselectivity.

Results and Discussion. – The *Suzuki–Miyaura* reaction of 2,3-dibromo-1*H*-inden-1-one (**1**) with arylboronic acids **2a**–**2g** (2.2 equiv.) afforded the 2,3-diaryl-1*H*-inden-1-ones **3a**–**3g**, respectively, in 86–98% yield (*Scheme 1* and *Table 1*). The reactions were carried out by with $\text{Pd}(\text{PPh}_3)_4$ (5 mol-%) as the catalyst and K_2CO_3 (2M aq. soln.) as the base. 1,4-Dioxane was used as the solvent, and the reactions were performed at 70° for 6 h. The reactions could be successfully carried out with both electron-rich and electron-poor arylboronic acids. The yields were all excellent (>95%). The presence of a substituent in the *ortho*-position of the arylboronic acid resulted in a minor decrease of the yield (e.g., **3d**).

Scheme 1. *Synthesis of 3a*–*3g*



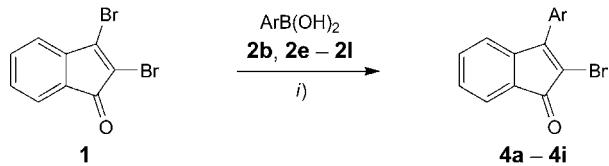
i) **2** (2.2 equiv.), $\text{Pd}(\text{PPh}_3)_4$ (5 mol-%), 2M aq. K_2CO_3 , dioxane, 70°, 6 h.

Table 1. *Synthesis of 3a*–*3g*

2,3	Ar	Yield [%] of the isolated product 3
a	Ph	97
b	4-Me-C ₆ H ₄	98
c	4-F-C ₆ H ₄	95
d	2-MeO-C ₆ H ₄	86
e	3-MeO-C ₆ H ₄	98
f	4-MeO-C ₆ H ₄	97
g	3-F-C ₆ H ₄	96

The *Suzuki–Miyaura* reaction of **1** with 1 equiv. of arylboronic acids **2b** and **2e**–**2l** afforded the 3-aryl-2-bromo-1*H*-inden-1-ones **4a**–**4l**, respectively, in excellent yields and with very good regioselectivity (*Scheme 2* and *Table 2*). The first attack occurred at C(3) of **1**. The temperature played an important role during the optimization, as a good selectivity was achieved only at 45°. At higher temperatures, the formation of a mixture of starting material, and mono- and disubstituted products was observed. The reactions of the highly reactive (electron rich) MeO-substituted arylboronic acids had to be carried out at 40° instead of 45°.

The structure of compound **4i** was established by means of 1D- and 2D-NMR (HMQC, NOESY, and HMBC) data (*Fig. 1*). The H-atoms of the 4-MeO-C₆H₄ moiety, H–C(2',6') ($\delta(\text{H})$ 7.60) showed a clear HMBC correlation with C(3) ($\delta(\text{C})$ 155.5) of the indenone part, but no correlation appeared with C(2) ($\delta(\text{C})$ 115.6), indicating the connectivity of C(3) with C(1'). A key NOESY correlation of H–C((2',6') ($\delta(\text{H})$ 7.60) with H–C(4) ($\delta(\text{H})$ 7.11) further established the position of

Scheme 2. Synthesis of **4a–4i**

i) **2b, 2e – 2l** (1.0 equiv.), Pd(PPh₃)₄ (3 mol-%), 2M aq. K₂CO₃, dioxane, 45°, 4 h.

Table 2. Synthesis of 3-Aryl-2-bromo-1H-inden-1-ones **4a–4i**

4	2	Ar	Yield [%] of the isolated product 4
a	b	4-Me-C ₆ H ₄	98
b	h	4-Et-C ₆ H ₄	93
c	i	4-Bu-C ₆ H ₄	89
d	g	3-F-C ₆ H ₄	83
e	j	4-CF ₃ -C ₆ H ₄	88
f	k	2,6-(MeO) ₂ C ₆ H ₃	83 ^a)
g	l	3,5-Me ₂ C ₆ H ₃	88
h	e	3-MeO-C ₆ H ₄	95 ^a)
i	f	4-MeO-C ₆ H ₄	93 ^a)

^a) Reaction temperature: 40°.

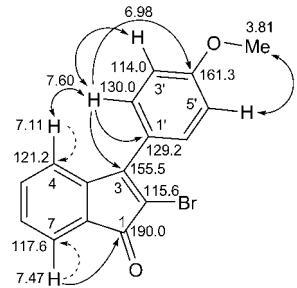


Fig. 1. HMQC (H → C), NOESY (H ↔ H), and HMBC (H → C) correlations of **4i**

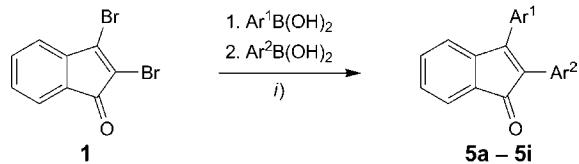
the 4-MeO-C₆H₄ moiety at C(3). The structure of **4f** was confirmed by an X-ray crystal-structure analysis [7].

The one-pot reaction of **1** with two different arylboronic acids afforded the unsymmetrically substituted 2,3-diaryl-1H-inden-1-ones **5a–5i** (*Scheme 3* and *Table 3*). The boronic acids were added in a sequential manner. The first step was carried out at 45° (or at 40° in case of **2k**, **2n**, and **2o**), and the second step was performed out at 70°. All reactions proceeded in excellent yields.

The structures of **5d** and **5i** were independently confirmed by X-ray crystal-structure analyses (*Figs. 2* and *3*)²⁾.

The *Sonogashira* reaction of **1** with alkynes **6a–6d** (2.2 equiv.) gave the 2,3-bis(alkynyl-alkynyl)-1H-inden-1-ones **7a–d** in 89–94% yield (*Scheme 4* and *Table 4*).

²⁾ CCDC-869743 and -869744 contain all crystallographic details for **5d** and **5i**, respectively, which are available free of charge via www.ccdc.cam.ac.uk/data_request/cif.

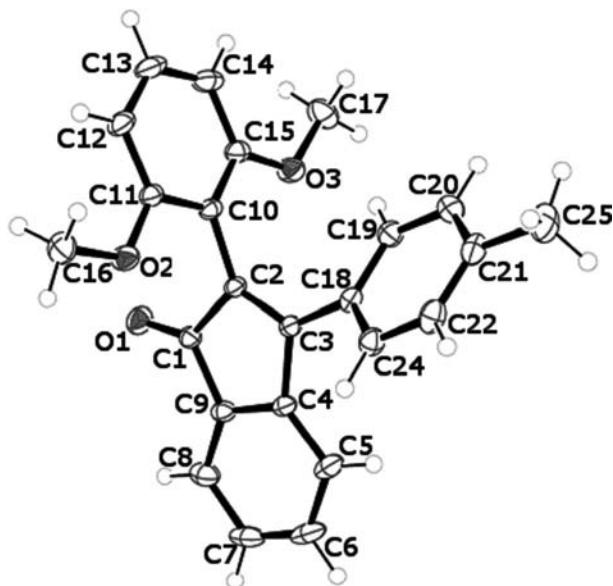
Scheme 3. *Synthesis of 5a–5i*

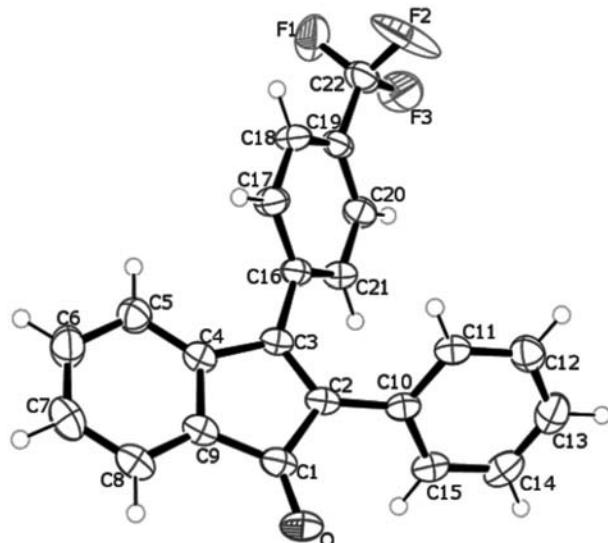
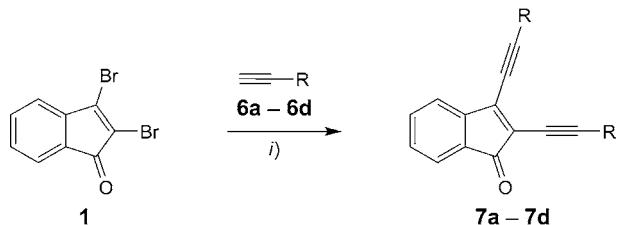
i) 1) $\text{Ar}^1\text{B}(\text{OH})_2$ (1.0 equiv.), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 2M aq. K_2CO_3 , dioxane, 45° , 4 h. 2) $\text{Ar}^2\text{B}(\text{OH})_2$ (1.1 equiv.), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 70° , 6 h.

Table 3. *Synthesis of 5a–5i*

5	2	Ar ¹	Ar ²	Yield [%] of the isolated product 5
a	b,f	4-Me-C ₆ H ₄	4-MeO-C ₆ H ₄	93
b	b,m	4-Me-C ₆ H ₄	3-Cl-C ₆ H ₄	89
c	k,c	2,6-(MeO) ₂ C ₆ H ₃	4-F-C ₆ H ₄	86 ^a)
d	b,k	4-Me-C ₆ H ₄	2,6-(MeO) ₂ C ₆ H ₃	90
e	d,b	2-MeO-C ₆ H ₄	4-Me-C ₆ H ₄	85 ^a)
f	h,n	4-Et-C ₆ H ₄	4-Cl-C ₆ H ₄	83
g	m,b	3-Cl-C ₆ H ₄	4-MeC ₆ H ₄	79
h	h,f	4-Et-C ₆ H ₄	4-MeO-C ₆ H ₄	93
i	j,a	4-CF ₃ -C ₆ H ₄	Ph	87

^a) Reaction temperature: 40° .

Fig. 2. *Crystal structure of 5d* (50% probability level)

Fig. 3. Crystal structure of **5i** (50% probability level)Scheme 4. Synthesis of **7a–7d**

i) **6a–6d** (2.2 equiv.), (i-Pr)₂NH (1.5 equiv.), CuI (20 mol-%), [Pd(PPh₃)₂Cl₂] (6 mol-%), DMF, 20°, 30 min.

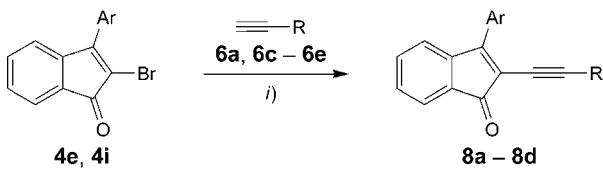
Table 4. Synthesis of **7a–7d**

7	6	R	Yield [%] of the isolated product 7
a	a	Ph	89
b	b	4-Me-C ₆ H ₄	93
c	c	4-Bu-C ₆ H ₄	94
d	d	Me(CH ₂) ₇	92

The reaction was carried out by using catalytic amounts of CuI (10 mol-%) and [Pd(PPh₃)₂Cl₂] (3 mol-%), and proceeded smoothly at room temperature, needing only 30 min to completion. In the reaction, (i-Pr)₂NH (1.5 equiv.) was used as the base. The Sonogashira reaction of **1** with 1 equiv. of alkynes proved to be unsuccessful as regioisomeric mixtures were formed.

The reaction of **4e** and **4i** with 1 equiv. aliphatic or aromatic alkynes, **6a**, **6c**–**6e**, afforded the 2-(alkynyl)-3-aryl-1*H*-inden-1-ones **8a**–**8d** in 78–94% yield (*Scheme 5* and *Table 5*).

Scheme 5. Synthesis of 8a–8d

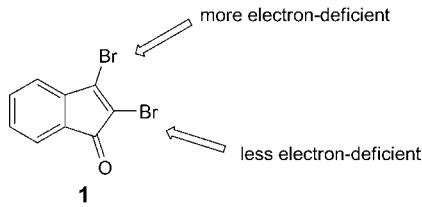


i) **6a**, **6c**–**6e** (1.0 equiv.), (i-Pr)₂NH (1.5 equiv.), CuI (10 mol-%), [Pd(PPh₃)₂Cl₂] (3 mol-%), 20°, 2 h.

Table 5. Synthesis of 8a–8d

8	4	Ar	R	Yield [%] of the isolated product 8
a	e	4-CF ₃ -C ₆ H ₄	Ph	93
b	i	4-MeO-C ₆ H ₄	4-Bu-C ₆ H ₄	94
c	e	4-CF ₃ -C ₆ H ₄	Me(CH ₂) ₇	92
d	i	4-MeO-C ₆ H ₄	6-Methoxynaphthalen-2-yl	78

Conclusions.— We have reported an efficient method for the synthesis of substituted indenones by regioselective *Suzuki–Miyaura* reactions of 2,3-dibromo-1*H*-inden-1-one (**1**). The regioselective formation of **4a**–**4i** and **5a**–**5i** can be explained by the finding that the first attack in the Pd⁰-catalyzed cross-coupling reactions generally occurs at the more electron-deficient and sterically less hindered position (*Fig. 4*).



*Fig. 4. Possible explanation for the site-selectivity of cross-coupling reactions of **1***

Financial support from the State of Pakistan (*HEC* scholarships for *R. A. K.* and *M. H.*), from the *DAAD* (scholarships for *R. A. K.* and *N. T. H.*), from the State of Mecklenburg-Vorpommern (scholarships for *M. H.*), from the *Friedrich-Irmgard-Harms-Stiftung* (scholarships for *R. A. K.*), and from State of Vietnam (*MOET* scholarship for *N. T. H.*) is gratefully acknowledged.

Experimental Part

General. See [8].

General Procedure for the Synthesis of 3a–3e and 4a–4e (GPA). The reaction was carried out in a pressure tube. To a suspension of **1** (144 mg, 0.5 mmol), Pd(PPh₃)₄ (2.5–3.0 mol-% per cross-coupling), and boronic acid **2** (0.5–0.55 mmol per cross-coupling) in dioxane (5 ml), a 2M aq. K₂CO₃ soln. (1 ml)

was added. The mixture was heated at the indicated temp. ($40\text{--}70^\circ$) under Ar for 4–6 h. The mixture was diluted with H_2O and extracted with CH_2Cl_2 ($3 \times 25 \text{ ml}$). The combined org. layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography (CC; silica gel, AcOEt/heptanes).

2,3-Diphenyl-1H-inden-1-one (3a). From **1** (144 mg, 0.50 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K_2CO_3 soln. (1 ml), and PhB(OH)_2 (**2a**; 134 mg, 1.1 mmol), according to *GPA*; reaction temp./time: $70^\circ/6 \text{ h}$. Yield: 137 mg (97%). Brownish yellow solid. M.p. $154\text{--}155^\circ$. IR (KBr): 1700, 1604, 1455, 1444, 1348, 1178, 1157, 1149, 999, 929, 858, 840, 807w, 780, 760, 751, 723, 699, 675, 637, 612, 587, 549s, 537m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.04–7.07 (*m*, 1 arom. H); 7.16–7.22 (*m*, 6 arom. H); 7.30–7.34 (*m*, 6 arom. H); 7.45–7.51 (*m*, 1 arom. H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 121.3, 123.0, 127.7, 128.1, 128.5, 128.8, 129.0, 129.3, 130.0 (CH); 130.8, 132.4, 132.7 (C); 133.4 (CH); 141.3, 145.2, 155.3 (C); 196.0 (C=O). GC/EI-MS (70 eV): 282 (100, M^+), 281 (82), 265 (16), 253 (39), 252 (47), 250 (18), 126 (12). HR-EI-MS (70 eV): 282.103409 (M^+ , $\text{C}_{21}\text{H}_{14}\text{O}^+$; calc. 282.10392).

2,3-Bis(4-methylphenyl)-1H-inden-1-one (3b). From **1** (144 mg, 0.50 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K_2CO_3 soln. (1 ml), and (4-Me-C₆H₄)B(OH)₂ (**2b**; 150 mg, 1.1 mmol), according to *GPA*; reaction temp./time: $70^\circ/6 \text{ h}$. Yield: 152 mg (98%). Brownish yellow solid. M.p. $147\text{--}148^\circ$. IR (KBr): 3032, 2921w, 1706s, 1595, 1502, 1454, 1386, 1342, 1283, 1175, 1150, 973, 922, 851m, 806, 794s, 783m, 763, 727, 708s, 689, 644, 638, 623, 573, 540m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 2.23 (*s*, Me); 2.32 (*s*, Me); 6.98–7.29 (*m*, 11 arom. H); 7.46–7.49 (*m*, 1 arom. H). $^{13}\text{C-NMR}$ (75.5 MHz, CDCl_3): 21.3, 21.5 (Me); 121.1, 122.8 (CH); 128.0 (C); 128.5, 128.7, 128.9, 129.5, 129.9 (CH); 130.0, 131.0, 132.1 (C); 133.3 (CH); 137.5, 139.4, 145.5, 154.8 (C); 196.8 (C=O). GC/EI-MS (70 eV): 310 (100, M^+), 309 (21), 296 (15), 295 (61), 293 (9), 266 (11), 265 (20), 263 (10), 252 (18). HR-EI-MS (70 eV): 310.135147 (M^+ , $\text{C}_{23}\text{H}_{18}\text{O}^+$; calc. 310.13522).

2,3-Bis(4-fluorophenyl)-1H-inden-1-one (3c). From **1** (144 mg, 0.50 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K_2CO_3 soln. (1 ml), and (4-F-C₆H₄)B(OH)₂ (**2c**; 154 mg, 1.1 mmol), according to *GPA*; reaction temp./time: $70^\circ/6 \text{ h}$. Yield: 151 mg (95%). Brownish yellow solid. M.p. $134\text{--}135^\circ$. IR (KBr): 1705, 1592, 1575, 1512m, 1498s, 1455, 1409, 1344, 1303m, 1220s, 1159, 1149, 1071, 924, 860, 838m, 824, 794, 768, 733, 708s, 680, 658, 630, 572m, 541s. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 6.85–6.94 (*m*, 2 arom. H); 7.01–7.08 (*m*, 3 arom. H); 7.13–7.34 (*m*, 6 arom. H); 7.49–7.52 (*m*, 1 arom. H). $^{13}\text{C-NMR}$ (75.5 MHz, CDCl_3): 115.3 (*d*, $J(\text{C},\text{F})=21.5$, CH); 116.2 (*d*, $J(\text{C},\text{F})=21.5$, CH); 121.1, 123.2 (CH); 126.6 (*d*, $J(\text{C},\text{F})=3.4$, C); 128.5 (*d*, $J(\text{C},\text{F})=3.6$, C); 129.2 (CH); 130.5 (*d*, $J(\text{C},\text{F})=8.3$, CH); 131.5 (C); 131.8 (*d*, $J(\text{C},\text{F})=8.3$, CH); 133.6 (CH); 144.9, 154.1 (C); 162.4 (*d*, $J(\text{C},\text{F})=48.4$, CF); 163.2 (*d*, $J(\text{C},\text{F})=250.3$, CF); 196.2 (C=O). $^{19}\text{F-NMR}$ (282.4 MHz, CDCl_3): –113.0, –158.4 (ArF). GC/EI-MS (70 eV): 318 (100, M^+), 317 (53), 301 (14), 289 (19), 288 (36), 270 (6), 268 (9). HR-EI-MS (70 eV): 318.085333 (M^+ , $\text{C}_{21}\text{H}_{12}\text{F}_2\text{O}^+$; calc. 318.08507).

2,3-Bis(2-methoxyphenyl)-1H-inden-1-one (3d). From **1** (144 mg, 0.50 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K_2CO_3 soln. (1 ml), and (4-MeO-C₆H₄)B(OH)₂ (**2d**; 167 mg, 1.1 mmol), according to *GPA*; reaction temp./time: $70^\circ/6 \text{ h}$. Yield: 149 mg (86%). Brownish yellow solid. M.p. $121\text{--}122^\circ$. IR (KBr): 3078, 3012, 2938, 2843, 1707s, 1606m, 1571s, 1475m, 1429s, 1333m, 1280, 1231s, 1177m, 1127, 1045s, 953, 877, 790m, 768, 726, 707, 695, 683s, 598, 560m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 3.42 (*s*, MeO); 3.54 (*s*, MeO); 6.72–6.91 (*m*, 5 arom. H); 7.01–7.28 (*m*, 6 arom. H); 7.44–7.48 (*m*, 1 arom. H). $^{13}\text{C-NMR}$ (75.5 MHz, CDCl_3): 55.1, 55.2 (MeO); 111.0, 111.1, 120.3, 120.5 (CH); 120.2 (C); 121.5, 122.5 (CH); 123.0 (C); 128.3, 129.1, 129.2, 130.3 (CH); 131.0 (C); 131.1 (CH); 132.5 (C); 133.1 (CH); 145.6, 154.8, 156.8, 157.4 (C); 196.2 (C=O). GC/EI-MS (70 eV): 342 (100, M^+), 312 (18), 311 (12), 281 (9), 255 (16), 252 (9), 239 (15), 234 (16), 226 (58), 207 (58). HR-EI-MS (70 eV): 342.125581 (M^+ , $\text{C}_{23}\text{H}_{18}\text{O}_3^+$; calc. 342.12559).

2,3-Bis(3-methoxyphenyl)-1H-inden-1-one (3e). From **1** (144 mg, 0.50 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K_2CO_3 soln. (1 ml), and (3-MeO-C₆H₄)B(OH)₂ (**2e**; 167 mg, 1.1 mmol), according to *GPA*; reaction temp./time: $70^\circ/6 \text{ h}$. Yield: 167 mg, (98%). Brownish yellow solid. M.p. $141\text{--}142^\circ$. IR (KBr): 3079, 3012, 2960, 2939, 2916, 2843, 2831w, 1708s, 1606, 1595m, 1572s, 1476, 1454, 1446m, 1429s, 1333, 1290m, 1280, 1231s, 1194, 1178, 1162m, 1128s, 995, 969, 954, 903, 887, 878, 872, 846, 791m, 769s, 726, 708, 695, 683, 675s, 626, 639, 599, 560, 542m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 3.57 (*s*, MeO); 3.63 (*s*, MeO); 6.69–6.90 (*m*, 7 arom. H); 7.05–7.30 (*m*, 4 arom. H); 7.46–7.50 (*m*, 1 arom. H).

¹³C-NMR (75.5 MHz, CDCl₃): 55.1, 55.3 (MeO); 113.7, 114.1, 115.0, 115.1, 120.8, 121.4, 122.5, 123.0, 129.0, 1291, 130.0 (CH); 130.7, 132.0, 132.3 (C); 133.5 (CH); 134.0, 145.2, 155.4, 159.2, 159.8 (C); 196.3 (C=O). GC/EI-MS (70 eV): 342 (100, M⁺), 327 (11), 311 (20), 284 (10), 268 (12), 239 (16), 226 (14), 207 (10). HR-EI-MS (70 eV): 342.124291 (M⁺, C₂₃H₁₈O₃⁺; calc. 342.12505).

2,3-Bis(4-methoxyphenyl)-1H-inden-1-one (3f). From **1** (144 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K₂CO₃ soln. (1 ml), and (4-MeO-C₆H₄)B(OH)₂ (**2f**; 167 mg, 1.1 mmol), according to *GPA*; reaction temp./time: 70°/6 h. Yield: 166 mg (97%). Brownish yellow solid. M.p. 94–95°. IR (KBr): 3000, 2955, 2835w, 1697, 1603, 1500s, 1454, 1342, 1291m, 1243, 1172s, 1071m, 1026s, 907, 854, 818, 797, 765m, 732s, 682, 647, 581, 531m. ¹H-NMR (300 MHz, CDCl₃): 3.69 (s, MeO); 3.75 (s, MeO); 6.72 (d, J=8.9, 2 arom. H); 6.84 (d, J=8.9, 2 arom. H); 7.06 (d, J=7.2, 1 arom. H); 7.12–7.18 (m, 3 arom. H); 7.22–7.28 (m, 3 arom. H); 7.42–7.46 (m, 1 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 55.2, 55.3 (MeO); 113.7, 114.2, 121.0, 122.7 (CH); 123.4, 125.1 (C); 128.6, 130.2 (CH); 131.0, 131.2 (C); 131.3, 133.3 (CH); 145.5, 153.8, 159.1, 160.3 (C); 196.9 (C=O). GC/EI-MS (70 eV): 342 (100, M⁺), 327 (14), 239 (9), 226 (10). HR-EI-MS (70 eV): 342.125095 (M⁺, C₂₃H₁₈O₃⁺; calc. 342.12559).

2,3-Bis(3-fluorophenyl)-1H-inden-1-one (3g). From **1** (144 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 5 mol-%), dioxane (5 ml), 2M aq. K₂CO₃ soln. (1 ml), and (3-F-C₆H₄)B(OH)₂ (**2g**; 154 mg, 1.1 mmol), according to *GPA*; reaction temp./time: 70°/6 h. Yield: 152 mg (96%). Brownish yellow solid. M.p. 124–125°. IR (KBr): 3065, 2961w, 1702, 1610m, 1580, 1475, 1455, 1437, 1339, 1266, 1243, 1220, 1184, 1170, 1157, 1125, 973, 930, 890, 859, 797m, 776, 763, 725, 706, 690s, 682, 639, 596, 583, 559m. ¹H-NMR (300 MHz, CDCl₃): 6.83–7.08 (m, 7 arom. H), 7.58–7.36 (m, 4 arom. H), 7.49–7.52 (m, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 114.1 (d, J(C,F)=21.3, CH); 114.4 (d, J(C,F)=22.3, CH); 115.5 (d, J(C,F)=21.1, CH); 115.8 (d, J(C,F)=22.2, CH); 120.4, 122.4 (CH); 123.2 (d, J(C,F)=3.3, CH); 124.7 (d, J(C,F)=3.0, CH); 128.5 (CH); 129.3 (C); 128.7 (d, J(C,F)=8.4, CH); 130.6 (d, J(C,F)=2.2, C); 129.8 (d, J(C,F)=8.4, CH); 131.4 (d, J(C,F)=8.3, C); 132.8 (CH); 133.4 (d, J(C,F)=8.0, C); 143.5 (C); 153.6 (d, J(C,F)=1.9, C); 161.6 (d, J(C,F)=245.2, C–F); 161.9 (d, J(C,F)=247.5, C–F); 194.5 (C=O). ¹⁹F-NMR (282.4 MHz, CDCl₃): -112.8, -111.3. GC/EI-MS (70 eV): 318 (100, M⁺), 317 (49), 301 (14), 289 (30), 288 (36), 270 (11), 268 (12). HR-EI-MS (70 eV): 318.085575 (M⁺, C₂₁H₁₂F₂O⁺; calc. 318.08507).

2-Bromo-3-(4-methylphenyl)-1H-inden-1-one (4a). From **1** (144 mg, 0.5 mmol), Pd(PPh₃)₄ (18 mg, 3 mol-%), and **2b** (68 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 146 mg (98%). White yellow solid. M.p. 119–120°. IR (KBr): 3022, 2919, 2855w, 1711s, 1599, 1504, 1450, 1362, 1284, 1182, 1099, 1020, 918, 832, 797m, 755, 701s, 669, 629, 569. ¹H-NMR (300 MHz, CDCl₃): 2.37 (s, Me); 7.08 (dt, J=7.2, 1.0, 1 arom. H); 7.18 (td, J=7.9, 1.1, 1 arom. H); 7.24–7.29 (m, 3 arom. H); 7.45–7.51 (m, 3 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 21.6 (Me); 117.4 (C); 121.3, 123.6 (CH); 128.2 (C); 128.3, 128.9, 129.5 (CH); 130.1 (C); 133.7 (CH); 140.8, 144.6, 157.0 (C); 189.9 (C=O). GC/EI-MS (70 eV): 298 (100, M⁺), 219 (36), 191 (21), 190 (18), 189 (50), 176 (13), 165 (9). HR-EI-MS (70 eV): 297.998324 (M⁺, C₁₆H₁₁BrO⁺; calc. 297.99878).

2-Bromo-3-(4-ethylphenyl)-1H-inden-1-one (4b). From **1** (144 mg, 0.5 mmol), Pd(PPh₃)₄ (18 mg, 3 mol-%), and (4-Et-C₆H₄)B(OH)₂ (**2b**; 75 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 145 mg (93%). Colorless crystalline solid. IR (KBr): 3066w, 2962m, 2928, 2871w, 1712s, 1606, 1596, 1503, 1455, 1284, 1183, 1101, 1018, 918, 843, 759m, 704s, 627, 545m. ¹H-NMR (300 MHz, CDCl₃): 0.72 (t, J=7.8, Me); 2.16 (q, J=7.5, CH₂); 6.57–6.55 (m, 1 arom. H); 6.63–6.68 (m, 2 arom. H); 6.78 (d, J=7.9, 2 arom. H); 6.95–6.97 (m, 1 arom. H); 7.01 (d, J=7.9, 2 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 15.2 (Me); 28.9 (CH₂); 117.4 (C); 121.3, 123.5, 128.2, 128.3, 128.4 (CH); 128.8, 130.1 (C); 133.6 (CH); 144.6, 147.0, 156.9 (C); 189.9 (C=O). GC/EI-MS (70 eV): 314 (100, [M(⁸¹Br)]⁺), 312 (99, [M(⁷⁹Br)]⁺), 299 (58), 297 (56), 202 (14), 190 (16), 189 (43), 176 (10), 109 (12), 95 (10). HR-EI-MS (70 eV): 312.013869 ([M(⁸¹Br)]⁺, C₁₇H₁₃BrO⁺; calc. 312.01443).

2-Bromo-3-[4-(tert-butyl)phenyl]-1H-inden-1-one (4c). From **1** (144 mg, 0.5 mmol), Pd(PPh₃)₄ (18 mg, 3 mol-%), and (4-Bu-C₆H₄)B(OH)₂ (**2i**; 89 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 151 mg (89%). Colorless crystalline solid. IR (KBr): 3066w, 2959m, 2902, 2865w, 1713s, 1606, 1556, 1407, 1362, 1267, 1099, 1015, 919, 800, 764m, 704s, 626, 533m. ¹H-NMR (300 MHz, CDCl₃): 1.31 (s, 3 Me); 7.10–7.13 (m, 1 arom. H); 7.15–7.20 (m, 1 arom. H); 7.24–7.30 (m, 2 arom. H); 7.47 (d, J=8.5, 2 arom. H); 7.55 (d, J=8.5, 2 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 31.2 (Me); 35.0, 117.4 (C); 121.4, 123.5, 125.6, 128.1 (CH); 128.2 (C); 128.8 (CH); 130.1 (C); 133.6 (CH); 144.5, 153.8, 156.8 (C); 189.9

(C=O). GC/EI-MS (70 eV): 340 (51, M^+), 327 (96), 325 (100), 299 (16), 297 (15), 231 (12), 202 (23), 189 (12), 176 (14), 109 (29), 95 (16). HR-EI-MS (70 eV): 340.045511 (M^+ , $C_{19}H_{17}BrO^+$; calc. 340.04573).

2-Bromo-3-(3-fluorophenyl)-1H-inden-1-one (4d). From **1** (144 mg, 0.5 mmol), Pd(PPh_3)₄ (18 mg, 3 mol-%), and **2g** (70 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 125 mg (83%). White-yellow solid. M.p. 116–117°. IR (KBr): 1714s, 1596, 1579, 1564, 1484, 1427, 1418, 1354, 1298, 1284, 1209, 1178, 1134, 965, 893, 824, 787m, 758, 700, 670s, 657, 614, 599, 555m. ¹H-NMR (300 MHz, CDCl₃): 7.04–7.07 (m, 1 arom. H); 7.11–7.23 (m, 2 arom. H); 7.27–7.38 (m, 3 arom. H); 7.42–7.51 (m, 2 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 115.3 (d, $J(C,F) = 22.8$, CH); 117.3 (d, $J(C,F) = 21.8$, CH); 118.8 (C); 121.1, 123.9 (CH); 124.1 (d, $J(C,F) = 3.1$, CH); 129.1 (CH); 129.7 (C); 130.6 (d, $J(C,F) = 8.3$, CH); 133.1 (d, $J(C,F) = 8.2$, C); 134.0 (CH); 144.2 (C); 155.5 (d, $J(C,F) = 2.5$, C); 163.1 (d, $J(C,F) = 247.5$, C=F); 189.5 (C=O). ¹⁹F-NMR (282.4 MHz, CDCl₃): –111.3. GC/EI-MS (70 eV): 302 (100, M^+), 224 (10), 223 (64), 195 (28), 194 (63), 175 (24), 169 (13), 168 (16), 112 (11), 97 (14). HR-EI-MS (70 eV): 302.982201 ([$M + H$]⁺, $C_{15}H_8BrFO^+$; calc. 301.98153).

2-Bromo-3-[4-(trifluoromethyl)phenyl]-1H-inden-1-one (4e). From **1** (144 mg, 0.5 mmol), Pd(PPh_3)₄ (18 mg, 3 mol-%), and (4-CF₃-C₆H₄)B(OH)₂ (**2j**; 95 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 155 mg (88%). Colorless crystalline solid. IR (KBr): 3080, 2929w, 1718s, 1598, 1407m, 1318s, 1156m, 1109, 1099, 1064s, 1014, 850, 761m, 704s, 622m. ¹H-NMR (300 MHz, CDCl₃): 6.24 (d, $J = 7.2$, 1 arom. H); 6.41–6.47 (m, 1 arom. H); 6.51–6.56 (m, 1 arom. H); 6.74 (d, $J = 7.0$, 1 arom. H); 6.91–6.93 (m, 2 arom. H); 6.96–6.99 (m, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 120.2, 118.8, 119.5 (CH); 120.2 (q, $J = 275.0$, CF₃); 122.4 (C); 126.7 (q, $J = 1.0$, C); 128.9 (CH); 132.6 (q, $J = 8.0$, CH); 135.2 (C); 138.1 (CH); 152.5 (q, $J = 36.1$, C); 157.8, 165.7 (C); 196.7 (C=O). ¹⁹F-NMR (282 MHz, CDCl₃): –63.4. GC/EI-MS (70 eV): 354 (100, [$M^{81}Br$]⁺), 352 (99, [$M^{79}Br$]⁺), 274 (11), 274 (61), 245 (28), 225 (27), 176 (34), 112 (10). HR-EI-MS (70 eV): 351.970583 ([$M^{79}Br$]⁺, $C_{16}H_8BrO^+$; calc. 351.97051).

2-Bromo-3-(2,6-dimethoxyphenyl)-1H-inden-1-one (4f). From **1** (144 mg, 0.5 mmol), Pd(PPh_3)₄ (18 mg, 3 mol-%), and (2,6-(MeO)₂C₆H₃)B(OH)₂ (**2k**; 91 mg, 0.5 mmol), according to *GPA*; reaction temp.: 40°. Yield: 143 mg (83%). Brown crystalline solid. M.p. 189–190°. IR (KBr): 3009, 2965, 2933, 2836w, 1729, 1594, 1583, 1470, 1423s, 1358, 1300w, 1290m, 1249s, 1169w, 1101s, 1027m, 952, 942, 903, 873, 845w, 817, 771m, 756, 703s, 650, 633, 595, 577m. ¹H-NMR (250 MHz, CDCl₃): 3.71 (s, 2 MeO); 6.58–6.68 (m, 3 arom. H); 7.05–7.18 (m, 2 arom. H); 7.22–7.34 (m, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 54.8 (MeO); 104.0 (CH); 107.8 (C); 120.1 (CH); 120.6 (C); 121.8, 127.1 (CH); 128.3 (C); 129.8, 132.7 (CH); 144.3, 153.3, 156.7 (C); 189.1 (C=O). GC/EI-MS (70 eV): 344 (M^+ , 44), 265 (13), 251 (18), 250 (100), 237 (16), 235 (17), 234 (16), 221 (9), 207 (14), 165 (14), 163 (12), 151 (10). HR-EI-MS (70 eV): 345.0121 ([$M + H$]⁺, $C_{17}H_{14}BrO_3^+$; calc. 345.0127).

2-Bromo-3-(3,5-dimethylphenyl)-1H-inden-1-one (4g). From **1** (144 mg, 0.5 mmol), (PPh₃)₄Pd (18 mg, 3 mol-%), and (3,5-Me₂C₆H₃)B(OH)₂ (**2l**; 75 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 138 mg (88%). White-yellow solid. M.p. 136–137°. IR (KBr): 3072, 2959, 2913, 2856w, 1713s, 1600, 1553, 1455, 1374, 1309, 1227, 1103, 1080, 949, 859, 819, 801, 756, 731m, 705s, 668, 621, 547m. ¹H-NMR (300 MHz, CDCl₃): 2.32 (s, 2 Me); 7.03–7.29 (m, 5 arom. H); 7.43–7.46 (m, 1 arom. H). ¹³C-NMR (75.4 MHz, CDCl₃): 21.4 (2 Me); 117.6 (C); 121.4, 123.5, 125.8, 128.9 (CH); 130.0, 131.0 (C); 132.1, 133.7 (CH); 138.4, 144.7, 157.3 (C); 190.0 (C=O). GC/EI-MS (70 eV): 312 (100, M^+), 233 (36), 203 (14), 202 (19), 190 (14), 189 (43). HR-EI-MS (70 eV): 312.014774 (M^+ , $C_{17}H_{13}BrO^+$; calc. 312.01443).

2-Bromo-3-(3-methoxyphenyl)-1H-inden-1-one (4h). From **1** (144 mg, 0.5 mmol), Pd(PPh_3)₄ (18 mg, 3 mol-%), and **2e** (76 mg, 0.5 mmol), according to *GPA*; reaction temp.: 45°. Yield: 133 mg (85%). White-yellow solid. M.p. 218–219°. IR (KBr): 3069, 3005, 2839w, 1714s, 1593, 1563, 1483, 1453, 1365, 1304, 1287m, 1234s, 1172, 957, 837, 822m, 793, 758, 707, 673s, 659, 614, 548m. ¹H-NMR (300 MHz, CDCl₃): 3.80 (s, MeO); 6.96–7.00 (m, 1 arom. H); 7.07–7.21 (m, 4 arom. H); 7.25–7.30 (m, 1 arom. H); 7.38 (t, $J = 7.9$, 1 arom. H); 7.46–7.49 (m, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 55.4 (MeO); 113.7, 116.0 (CH); 118.1 (C); 120.5, 121.3, 123.7, 128.9, 129.9 (CH); 132.4 (C); 133.8 (CH); 144.5, 156.8, 159.7 (C); 189.8 (C=O). GC/EI-MS (70 eV): 314 (100, M^+), 235 (30), 192 (10), 176 (12), 164 (27), 163 (38), 117 (10). HR-EI-MS (70 eV): 313.993841 (M^+ , $C_{16}H_{11}BrO_2^+$; calc. 313.99369).

2-Bromo-3-(4-methoxyphenyl)-1H-inden-1-one (4i). From **1** (144 mg, 0.5 mmol), Pd(PPh_3)₄ (18 mg, 3 mol-%), and **2f** (76 mg, 0.5 mmol), according to *GPA*; reaction temp.: 40°. Yield: 139 mg (88%). White-yellow solid. M.p. 80–81°. IR (KBr): 3412, 3080, 3043, 3016, 2968, 2917, 2841, 1747w, 1715, 1607s,

1577*m*, 1505*s*, 1468, 1445, 1417, 1367, 1352, 1301*m*, 1258, 1178*s*, 1113, 918, 830, 858, 791*m*, 769*s*, 724*m*, 704*s*, 667, 652, 624, 576, 546*m*. ¹H-NMR (300 MHz, CDCl₃): 3.81 (*s*, MeO); 6.97 (*d*, *J*=8.8, 2 arom. H); 7.09–7.19 (*m*, 2 arom. H); 6.26 (*td*, *J*=7.7, 1.3, 1 arom. H); 7.44–7.47 (*m*, 1 arom. H); 7.59 (*d*, *J*=8.9, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 54.4 (MeO); 113.1 (CH); 115.6 (C); 120.3 (CH); 122.3 (C); 122.4, 127.8, 129.1 (CH); 129.2 (C); 132.5 (CH); 143.4, 155.5, 160.2 (C); 188.9 (C=O). GC/EI-MS (70 eV): 314 (100, M⁺), 235 (15), 164 (24), 163 (38), 118 (58). HR-EI-MS (70 eV): 313.99354 (M⁺, C₁₆H₁₁BrO₂⁺; calc. 313.99369).

General Procedure for the One-Pot Synthesis of 5a–5j (GP B) The reaction was carried out in a pressure tube. To a suspension of **1** (1.0 mmol), Pd(PPh₃)₄ (35 mg, 3 mol-%), and Ar¹B(OH)₂ (1.0 mmol) in dioxane (5 ml) was added a 2M aq. K₂CO₃ soln. (1 ml). The mixture was heated at 40–45° under Ar for 6 h. The mixture was cooled to 20°, and Ar²B(OH)₂ (1.1 mmol) and an additional amount of Pd(PPh₃)₄ (35 mg, 3 mol-%) were added. The mixture was heated under Ar for 6 h at 70°. After cooling to 20°, the mixture was diluted with H₂O and extracted with CH₂Cl₂ (3×25 ml). The combined org. layers were dried (Na₂SO₄) and concentrated *in vacuo*. The residue was purified by CC (AcOEt/heptanes).

2-(4-Methoxyphenyl)-3-(4-methylphenyl)-1*H*-inden-1-one (5a**).** From **1** (288 mg, 1.0 mmol), **2b** (136 mg, 1.0 mmol), and **2f** (167 mg, 1.1 mmol), resp., according to GP B; reaction temp.: 45 and 70°, resp. Yield: 303 mg (93%). Brown crystalline solid. M.p. 154–155°. IR (KBr): 3387, 3042, 2999, 2937, 2843, 2548, 2368, 2335*w*, 1704, 1699*s*, 1596, 1515, 1501, 1453, 1417, 1380, 1340, 1295*m*, 1251, 1176*s*, 1151, 1114, 922, 850*m*, 831, 806, 798*s*, 775*m*, 764, 733*s*, 713, 631, 575*m*, 555, 533*s*. ¹H-NMR (250 MHz, CDCl₃): 2.41 (*s*, Me); 3.80 (*s*, MeO); 6.81 (*d*, *J*=8.52, 2 arom. H); 7.12–7.21 (*m*, 1 arom. H); 7.14–7.28 (*m*, 8 arom. H); 7.52–7.57 (*m*, 1 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 21.5 (Me); 55.2 (MeO); 113.6, 121.0, 127.7 (CH); 123.3 (C); 128.5, 128.6, 129.5 (CH); 130.0, 130.9 (C); 131.3 (CH); 131.6 (C) 133.3 (CH); 139.3, 145.6, 154.0, 159.1 (C); 197.0 (C=O). GC/EI-MS (70 eV): 326 (100, M⁺), 311 (20), 268 (11), 239 (19). HR-EI-MS (70 eV): 326.130187 (M⁺, C₂₃H₁₈O₂⁺; calc. 326.13013).

2-(3-Chlorophenyl)-3-(4-methylphenyl)-1*H*-inden-1-one (5b**).** From **1** (288 mg, 1.0 mmol), **2b** (136 mg, 1.0 mmol), and (3-Cl-C₆H₄)B(OH)₂ (**2m**; 172 mg, 1.1 mmol), resp., according to GP B; reaction temp.: 45 and 70°, resp. Yield: 294 mg (89%). White-yellow solid. M.p. 147–148°. IR (KBr): 3382, 3057, 3043, 2917, 2854, 2354, 2138, 2001, 1938*w*, 1702*s*, 1606, 1595, 1575, 1563, 1509, 1454, 1403, 1340, 1300, 1284, 1184, 1148, 1115, 998, 959, 921, 885, 854, 824, 788*m*, 776, 767, 731, 726*s*, 716*m*, 693, 678*s*, 662, 601, 567, 558*m*. ¹H-NMR (300 MHz, CDCl₃): 2.32 (*s*, Me); 7.00–7.32 (*m*, 11 arom. H); 7.50 (*dd*, *J*=7.1, 0.6, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 21.6 (Me); 121.6, 123.0, 127.7, 128.1, 128.4, 129.2 (CH); 129.2 (C); 129.3, 129.6, 129.9 (CH); 130.6, 130.8, 132.9 (C); 133.5 (CH); 133.9, 139.9, 144.9, 156.6 (C); 195.9 (C=O). GC/EI-MS (70 eV): 330 (100, M⁺), 315 (19), 295 (33), 280 (12), 265 (18), 263 (13). HR-ESI-MS (pos.): 331.0883 ([M+H]⁺, C₂₂H₁₆ClO⁺; calc. 331.0884).

3-(2,6-Dimethoxyphenyl)-2-(4-fluorophenyl)-1*H*-inden-1-one (5c**).** From **1** (288 mg, 1.0 mmol), **2k** (182 mg, 1.0 mmol), and **2c** (154 mg, 1.1 mmol), resp., according to GP B; reaction temp.: 40 and 70°, resp. Yield: 309 mg, (86%). Brownish yellow solid. M.p. 206–207°. IR (KBr): 3046, 2963, 2838*w*, 1696, 1591, 1574, 1504, 1462, 1432*m*, 1359, 1296*w*, 1255, 1222, 1156*m*, 974, 941, 903*w*, 853, 825, 794, 781*m*, 761, 721, 709*s*, 684, 643, 626*w*, 585, 542*m*, 528*s*. ¹H-NMR (300 MHz, CDCl₃): 3.51 (*s*, 2 MeO); 6.53 (*d*, *J*=8.4, 2 arom. H); 6.68 (*dt*, *J*=7.1, 0.8, 1 arom. H); 6.70–6.87 (*m*, 3 arom. H); 7.58–7.31 (*m*, 5 arom. H); 7.43–7.46 (*m*, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 55.7 (2 MeO); 108.3 (CH); 114.7 (*d*, *J*(C,F)=21.4, CH); 121.2, 121.3, 128.3 (CH); 128.5 (*d*, *J*(C,F)=3.3, C); 1130.3 (*d*, *J*(C,F)=8.0, CH); 130.4 (C); 130.9, 133.5 (CH); 145.8, 150.6, 157.8, 158.5 (C); 162.1 (*d*, *J*(C,F)=247.4, CF); 196.8 (C=O). ¹⁹F-NMR (282.4 MHz, CDCl₃): -114.2. GC/EI-MS (70 eV): 360 (100, M⁺), 273 (10), 257 (9), 172 (8). HR-EI-MS (70 eV): 360.11556 (M⁺, C₂₃H₁₇FO₃⁺; calc. 360.11562).

2-(2,6-Dimethoxyphenyl)-3-(4-methylphenyl)-1*H*-inden-1-one (5d**).** From **1** (288 mg, 1.0 mmol), **2b** (136 mg, 1.0 mmol), and **2k** (200 mg, 1.1 mmol), resp., according to GP B; reaction temp.: 45 and 70°, resp. Yield: 320 mg (90%). White-yellow solid. M.p. 207–208°. IR (KBr): 3077, 2996, 2971, 2941, 2918, 2837*w*, 1704*s*, 1470, 1455, 1445, 1430, 1360, 1332*m*, 1250*s*, 1180*m*, 1105*s*, 1061, 1030, 924, 855, 817*m*, 765, 724*s*, 677, 645, 604, 545*m*. ¹H-NMR (300 MHz, CDCl₃): 2.26 (*s*, Me); 3.49 (*s*, 2 MeO); 6.44 (*d*, *J*=8.3, 2 arom. H); 7.05 (*d*, *J*=7.9, 2 arom. H); 7.12–7.29 (*m*, 6 arom. H); 7.45–7.48 (*m*, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 21.1 (Me); 55.8 (2 MeO); 104.3 (CH); 109.8 (C); 120.9, 122.6, 127.4, 128.4 (CH);

128.6 (C); 128.9, 129.7 (CH); 130.9, 132.0 (C); 132.8 (CH); 139.0, 145.5, 157.4, 158.8 (C); 196.0 (C=O). GC/EI-MS (70 eV): 356 (100, M^+), 326 (27), 311 (17), 252 (10), 239 (12), 233 (34), 226 (9), 119 (9). HR-EI-MS (70 eV): 356.139956 (M^+ , $C_{24}H_{20}O_3^+$; calc. 356.14070).

3-(2-Methoxyphenyl)-2-(4-methylphenyl)-1H-inden-1-one (5e). From **1** (288 mg, 1.0 mmol), **2d** (152 mg, 1.0 mmol), and **2b** (150 mg, 1.1 mmol), resp., according to *GP B*; reaction temp.: 40 and 70°, resp. Yield: 277 mg (85%) White-yellow solid.. M.p. 157–158°. IR (KBr): 3042, 2998, 2937, 2843w, 1698, 1596, 1514, 1453, 1416, 1340, 1295m, 1250, 1176s, 1068m, 1029s, 922, 850, 830m, 798s, 764m, 733s, 680, 665, 555m. ¹H-NMR (300 MHz, CDCl₃): 2.21 (s, Me); 3.52 (s, MeO); 6.80 (dt, J =7.2, 0.8, 1 arom. H); 6.87–6.97 (m, 4 arom. H); 7.09–7.34 (m, 6 arom. H); 7.44–7.47 (m, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 21.3 (Me); 55.3 (MeO); 111.6, 120.9, 121.3 (CH); 122.4 (C); 128.4, 128.7, 129.1 (CH); 129.8 (C); 130.5 (CH); 130.6, 133.2 (C); 133.4 (CH); 137.4, 145.8, 152.8, 157.0 (C); 196.9 (C=O). GC/EI-MS (70 eV): 326 (100, M^+), 311 (19), 268 (10), 239 (18). HR-EI-MS (70 eV): 326.130186 (M^+ , $C_{23}H_{18}O_2^+$; calc. 326.13013).

2-(4-Chlorophenyl)-3-(4-ethylphenyl)-1H-inden-1-one (5f). From **1** (288 mg, 1.0 mmol), **2b** (150 mg, 1.0 mmol), and (4-Cl-C₆H₄)B(OH)₂ (**2n**; 171 mg, 1.1 mmol), resp., according to *GP B*; reaction temp.: 45 and 70°, resp. Yield: 285 mg (83%). Brown solid. M.p. 94–95°. IR (KBr): 3393, 3026, 2963, 2930, 2872, 2676, 1704s, 1607, 1579m, 1487, 1455, 1340, 1181s, 1068, 1013m, 814, 794, 764, 727, 708s, 679, 628, 574m. ¹H-NMR (300 MHz, CDCl₃): 1.21 (t, J =7.6, Me); 2.64 (q, J =7.8, CH₂); 7.12–7.33 (m, 11 arom. H); 7.48–7.51 (m, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 15.2 (Me); 28.8 (CH₂); 121.5, 123.0, 128.3, 128.4, 128.5, 129.1 (CH); 129.5, 129.6, 130.8 (C); 131.3, 133.5 (CH); 133.6, 136.3, 145.1, 146.0, 156.0 (C) 196.3 (C=O). GC/EI-MS (70 eV): 344 (100, M^+), 317 (12), 315 (33), 309 (11), 280 (15), 265 (19), 263 (13), 252 (16), 131 (9). HR-ESI-MS (70 eV): 344.095128 (M^+ , $C_{23}H_{17}ClO_2^+$; calc. 344.09624).

3-(3-Chlorophenyl)-2-(4-methylphenyl)-1H-inden-1-one (5g). From **1** (288 mg, 1.0 mmol), (3-Cl-C₆H₄)B(OH)₂ (**2m**; 156 mg, 1.1 mmol), and **2b** (150 mg, 1.1 mmol), resp., according to *GP B*; reaction temp.: 45 and 70°, resp. Yield: 260 mg (79%). Brown solid. M.p. 147–148°. IR (KBr): 3057, 3028, 2916w, 1701s, 1595, 1558, 1453, 1403, 1340, 1299, 1263, 1183, 1148, 1115, 998, 921, 885m, 766, 731, 692, 677s, 600, 556m. ¹H-NMR (300 MHz, CDCl₃): 2.22 (s, Me); 6.96–7.00 (m, 3 arom. H); 7.05–7.32 (m, 8 arom. H); 7.46–7.49 (m, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 21.4 (Me); 120.9, 123.2, 126.9 (CH); 127.3 (C); 128.3, 129.0, 129.3, 129.8, 130.3 (CH); 130.5, 133.0 (C); 133.6 (CH); 134.7, 134.8, 137.7, 145.1, 152.8 (C); 196.4 (C=O). GC/EI-MS (70 eV): 330 (100, M^+), 329 (13), 317 (10), 315 (31), 295 (42), 280 (14), 265 (19), 263 (13), 252 (27), 250 (12), 131 (10). HR-ESI-MS (pos.): 330.080183 (M^+ , $C_{22}H_{15}ClO_2^+$; calc. 330.08004).

3-(4-Ethylphenyl)-2-(4-methoxyphenyl)-1H-inden-1-one (5h). From **1** (288 mg, 1.0 mmol), **2b** (150 mg, 1.0 mmol), and **2f** (167 mg, 1.1 mmol), resp., according to *GP B*; reaction temp.: 45 and 70°, resp. Yield: 316 mg (93%). Brown solid. M.p. 143–144°. IR (KBr): 3000, 2956, 2927, 2840w, 1695s, 1605, 1497, 1456, 1339, 1289, 1240, 1171s, 1032, 952, 922, 854, 802, 734, 680, 581m. ¹H-NMR (300 MHz, CDCl₃): 1.14 (t, J =7.8, Me); 2.54 (q, J =7.8, CH₂); 3.77 (s, MeO); 6.86 (d, J =7.9, 2 arom. H); 7.03 (d, J =8.2, 2 arom. H); 7.10 (d, J =8.3, 2 arom. H); 7.13–7.23 (m, 3 arom. H); 7.28 (d, J =8.4, 2 arom. H); 7.47–7.50 (m, 1 arom. H). ¹³C-NMR (75.5 MHz, CDCl₃): 15.2 (Me); 28.6 (CH₂); 55.3 (MeO); 114.1, 121.0, 122.7 (CH); 125.0 (C); 127.6 (CH); 128.3 (C); 128.7, 129.9, 130.2 (CH); 131.0, 131.7 (C); 133.2 (CH); 143.7, 145.4, 154.5, 160.3 (C); 196.7 (C=O). GC/EI-MS (70 eV): 340 (100, M^+), 325 (26), 311 (23), 252 (12), 239 (12). HR-EI-MS (70 eV): 340.145705 (M^+ , $C_{24}H_{20}O_2^+$; calc. 340.14578).

2-Phenyl-3-[4-(trifluoromethyl)phenyl]-1H-inden-1-one (5i). From **1** (288 mg, 1.0 mmol), **2j** (150 mg, 1.0 mmol), and **2a** (134 mg, 1.10 mmol), resp., according to *GP B*; reaction temp.: 45 and 70°, resp. Yield: 304 mg (87%). Brown solid. M.p. 153–154°. IR (KBr): 3070, 2961, 2855w, 1707s, 1596, 1455, 1408m, 1318s, 1165m, 1108, 1063, 1013s, 858, 801m, 752, 699s, 656, 599m. ¹H-NMR (300 MHz, CDCl₃): 7.01–7.21 (m, 6 arom. H); 7.28–7.33 (m, 2 arom. H); 7.42 (d, J =8.0, 2 arom. H); 7.51–7.54 (m, 1 arom. H); 7.59 (d, J =7.4, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 120.9 (CH); 122.7 (q, J (C,F)=274.5, C); 123.3, 125.8 (q, J (C,F)=3.8, CH); 128.1, 128.2, 128.9 (CH); 129.2 (C); 129.9 (q, J (C,F)=8, CH); 130.1 (q, J (C,F)=33.5, C); 132.4, 132.6, 135.5 (C); 133.6 (CH); 143.7, 152.3 (C); 194.9 (C=O). ¹⁹F-NMR (282 MHz, CDCl₃): -62.7. GC/EI-MS (70 eV): 350 (100, M^+), 333 (10), 281 (38), 252 (39), 126 (13). HR-EI-MS (70 eV): 350.091245 (M^+ , $C_{22}H_{13}F_3O_2^+$; calc. 350.09130).

*General Procedure for Syntheses of Alkynylindenones **7a**–**7d** and **8a**–**8d** (GP C).* In a pressure tube, a suspension of $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (5–15 mol-%), **1** or **4** (0.5 mmol), alkyne (0.50–1.10 mmol), CuI (10–20 mol-%), and $(\text{i-Pr})_2\text{NH}$ (1.5 equiv.) in DMF (5 ml) was purged with Ar and stirred at 20° for 10 min. The mixture was stirred at r.t. for 6–8 h and then poured into a 1:1 mixture $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (25 ml each). After shaking, the aq. layer was separated and extracted with CH_2Cl_2 (3×25 ml). The combined org. layers were washed with H_2O (3×20 ml), dried (Na_2SO_4), concentrated *in vacuo*, and the residue was purified by flash CC (silica gel, heptanes/AcOEt) to give **7a**–**7d** and **8a**–**8e**.

2,3-Bis(phenylethynyl)-1H-inden-1-one (7a). From **1** (144 mg, 0.50 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (52 mg, 15 mol-%), dry CuI (19 mg, 20 mol-%), $(\text{i-Pr})_2\text{NH}$ (1 ml/0.10 mmol of **1**), and *ethynylbenzene* (**6a**; 0.06 ml, 1.10 mmol), according to GP C. Yield: (147 mg, 89%). Colorless oil. IR (KBr): 3050, 2921, 2853w, 1708s, 1596, 1489, 1442, 1358, 1219, 1157, 1069, 915, 868m, 754, 688s, 528m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.26–7.32 (*m*, 5 arom. H); 7.35–7.39 (*m*, 3 arom. H); 7.41–7.45 (*m*, 2 arom. H); 7.53–7.60 (*m*, 4 arom. H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 81.9, 83.1, 103.5, 111.3 ($\text{C}\equiv$); 121.1 (CH); 121.9, 122.7 (C); 123.0, 128.3, 128.6, 129.0 (CH); 129.3, 129.5 (C); 129.9, 130.1, 132.0, 132.3, 134.3 (CH); 142.9, 143.1 (C); 192.8 (C=O). GC/EI-MS (70 eV): 330 (100, M^+), 329 (17), 300 (45), 165 (15), 150 (21), 140 (12). HR-EI-MS (70 eV): 330.109432 (M^+ , $\text{C}_{25}\text{H}_{14}\text{O}^+$; calc. 330.10392).

2,3-Bis[(4-methylphenyl)ethynyl]-1H-inden-1-one (7b). From **1** (144 mg, 0.50 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (52 mg, 15 mol-%), dry CuI (19 mg, 20 mol-%), $(\text{i-Pr})_2\text{NH}$ (1 ml/0.1 mmol of **1**), and *1-ethynyl-4-methylbenzene* (**6b**; 0.07 ml, 1.10 mmol) at r.t., according to GP C. Yield: 166 mg (93%). Colorless oil. IR (KBr): 3083, 2930w, 1714s, 1597, 1406m, 1314s, 1152m, 1106, 1093, 1060s, 1014, 850, 761m, 702s, 599m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 2.26 (*s*, Me); 2.28 (*s*, Me); 7.06 (*d*, $J=8.4$, 2 arom. H); 7.10 (*d*, $J=8.2$, 2 arom. H); 7.22 (*d*, $J=8.0$, 2 arom. H); 7.30–7.39 (*m*, 4 arom. H); 7.42 (*d*, $J=8.0$, 2 arom. H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 20.5, 20.7 (Me); 80.6, 82.0, 102.7, 110.9 ($\text{C}\equiv$); 117.9, 118.8 (C); 120.0, 121.7 (CH); 122.5 (C); 128.1 (CH); 128.3 (C); 128.4, 128.7, 130.8, 131.3, 133.2 (CH); 138.2, 139.7, 141.7, 142.1 (C); 191.1 (C=O). GC/EI-MS (70 eV): 358 (100, M^+), 313 (12), 97 (10), 83 (11), 69 (26), 43 (15). HR-EI-MS (70 eV): 358.134682 (M^+ , $\text{C}_{27}\text{H}_{18}\text{O}^+$; calc. 358.13522).

2,3-Bis[(4-tert-butyl)phenyl]ethynyl]-1H-inden-1-one (7c). From **1** (144 mg, 0.50 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (52 mg, 15 mol-%), dry CuI (19 mg, 20 mol-%), $(\text{i-Pr})_2\text{NH}$ (1 ml/0.1 mmol of **1**), and *1-(tert-butyl)-4-ethynylbenzene* (**6c**; 0.1 ml, 0.55 mmol), according to GP C. Yield: 207 mg (94%). Colorless oil. IR (KBr): 3082, 2931w, 1720s, 1590, 1405m, 1312s, 1156m, 1109, 1096, 1063s, 1010, 850, 761m, 703s, 621m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.26 (*s*, 3 Me); 1.27 (*s*, 3 Me); 7.24–7.27 (*m*, 2 arom. H); 7.31 (*d*, $J=8.6$, 2 arom. H); 7.37 (*d*, $J=8.6$, 2 arom. H); 7.37–7.42 (*m*, 2 arom. H); 7.47 (*d*, $J=8.6$, 2 arom. H); 7.52 (*d*, $J=8.6$, 2 arom. H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 31.1, 31.2 (3 Me); 34.9, 35.0 (2 CMe_3); 81.5, 83.0, 103.8, 111.9 ($\text{C}\equiv$); 121.7 (CH); 121.9, 122.7 (C); 123.0, 128.3, 128.6, 129.0 (CH); 129.3 (C); 129.9, 130.1, 132.0 (CH); 133.2, 142.9, 143.2, 152.4, 153.8 (C); 193.0 (C=O). GC/EI-MS (70 eV): 442 (32, M^+), 427 (28), 355 (10), 281 (10), 253 (10), 207 (13), 178 (12), 161 (23), 149 (15), 135 (10), 111 (12), 97 (20), 91 (17), 83 (24), 78 (65), 71 (32), 60 (16), 57 (74), 44 (90). HR-EI-MS (70 eV): 442.227998 (M^+ , $\text{C}_{33}\text{H}_{30}\text{O}^+$; calc. 442.22912).

2,3-Di(*dec-1-yn-1-yl*)-1H-inden-1-one (7d). From **1** (144 mg, 0.50 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (52 mg, 15 mol-%), dry CuI (19 mg, 20 mol-%), $(\text{i-Pr})_2\text{NH}$ (1 ml/0.1 mmol of **1**), and *dec-1-yne* (**6d**; 0.09 ml, 1.10 mmol), according to GP C. Yield: 185 mg (92%). Colorless oil. IR (KBr): 2961, 2932, 2872w, 1708s, 1600, 1462, 1359, 1219, 1089, 763, 528m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.79–0.83 (*m*, 2 Me); 1.19–1.27 (*m*, 10 CH_2); 1.36–1.46 (*m*, 2 CH_2); 1.53–1.64 (*m*, 2 CH_2); 7.11–7.16 (*m*, 1 arom. H); 7.18–7.21 (*m*, 1 arom. H); 7.30–7.35 (*m*, 2 arom. H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 14.0 (2 Me); 20.3, 20.4, 20.5, 20.6, 22.6, 28.4, 28.5, 28.8, 29.0, 29.1, 29.2, 31.8, 31.9(CH_2); 72.6, 74.7, 104.7, 113.4 ($\text{C}\equiv$); 120.7, 122.5 (CH); 124.1, 129.1 (C); 129.4, 134.0 (CH); 143.4, 143.6 (C); 192.8 (C=O). GC/EI-MS (70 eV): 402 (100, M^+), 265 (12), 137 (13), 128 (26), 114 (19), 29 (15). HR-EI-MS (70 eV): 402.298533 (M^+ , $\text{C}_{29}\text{H}_{38}\text{O}^+$; calc. 402.29838).

2-(Phenylethynyl)-3-[4-(trifluoromethyl)phenyl]-1H-inden-1-one (8a). From **4e** (176 mg, 0.50 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (18 mg, 5 mol-%), dry CuI (10 mg, 10 mol-%), $(\text{i-Pr})_2\text{NH}$ (1 ml/0.1 mmol of **4e**), and **6a** (0.06 ml, 0.55 mmol), according to GP C. Yield: 164 mg (88%). Colorless oil. IR (KBr): 3062, 2961w, 1715s, 1595, 1488, 1455, 1409m, 1320s, 1165m, 1122, 1064, 1014s, 925, 855, 795m, 750, 716m, 686s, 591m. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.17–7.22 (*m*, 2 arom. H); 7.24–7.29 (*m*, 4 arom. H); 7.32–7.35

(*m*, 1 arom. H); 7.37–7.41 (*m*, 1 arom. H); 7.50–7.53 (*m*, 1 arom. H); 7.73 (*d*, *J*=8.3, 2 arom. H); 7.90 (*d*, *J*=8.3, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 80.4, 99.8 (C≡); 120.7 (CH); 121.4 (C); 122.6 (*q*, *J*(C,F)=273, C); 122.8 (C); 124.5 (*q*, *J*(C,F)=3.9, CH); 127.3, 127.6, 128.0, 128.4, 128.8 (CH); 129.3 (C); 129.9 (*d*, *J*(C,F)=32.9, C); 130.9, 132.8 (CH); 134.6, 142.7, 156.9 (C); 191.7 (C=O). ¹⁹F-NMR (282 MHz, CDCl₃): –62.7. GC/EI-MS (70 eV): 374 (100, *M*⁺), 305 (10), 276 (29). HR-EI-MS (70 eV): 374.090996 (*M*⁺, C₂₄H₁₃F₃O⁺; calc. 374.09130).

2-[(4-tert-Butyl)phenyl]ethynyl]-3-(4-methoxyphenyl)-1H-inden-1-one (8b**).** From **4i** (157 mg, 0.50 mmol), [Pd(PPh₃)₂Cl₂] (18 mg, 5 mol-%), dry CuI (10 mg, 10 mol-%), (i-Pr)₂NH (1 ml/0.1 mmol of **4i**), and **6e** (0.01 ml, 0.55 mmol), according to GP C. Yield: 157 mg (80%). Colorless oil. IR (KBr): 3080, 2929w, 1718s, 1598, 1407m, 1318s, 1156m, 1109, 1099, 1064s, 1014, 850, 761m, 704s, 622m. ¹H-NMR (300 MHz, CDCl₃): 31.1 (Me); 55.4 (MeO) 6.98 (*d*, *J*=9.0, 2 arom. H); 7.20–7.32 (*m*, 4 arom. H); 7.36 (*d*, *J*=7.9, 2 arom. H); 7.47 (*d*, *J*=9.0, 2 arom. H); 7.85 (*d*, *J*=8.6, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 31.4 (Me); 34.8 (C); 55.4 (MeO); 81.9, 99.7 (C≡); 114.0, 116.5, 120.0 (C); 122.0, 123.2, 124.8, 125.3, 129.4, 130.3 (CH); 131.1 (C); 131.5, 133.4 (CH); 144.2, 151.9, 159.5, 161.4 (C); 193.5 (C=O). GC/EI-MS (70 eV): 392 (100, *M*⁺), 377 (77), 207 (26), 144 (13), 32 (18). HR-EI-MS (70 eV): 392.177463 (*M*⁺, C₂₈H₂₄O₂⁺; calc. 392.17708).

2-(Dec-1-yn-1-yl)-3-[4-(trifluoromethyl)phenyl]-1H-inden-1-one (8c**).** From **4e** (176 mg, 0.50 mmol), [Pd(PPh₃)₂Cl₂] (18 mg, 5 mol-%), dry CuI (10 mg, 10 mol-%), (i-Pr)₂NH (1 ml/0.1 mmol of **4e**), and **6d** (0.01 ml, 0.55 mmol), according to GP C. Yield: 182 mg (89%). Colorless oil. IR (KBr): 2954, 2925, 2855w, 1710s, 1596, 1461, 1410m, 1319s, 1161m, 1125, 1066s, 1016, 926, 827, 761, 717, 681, 601m. ¹H-NMR (300 MHz, CDCl₃): 0.80 (*t*, *J*=6.9, Me); 1.12–1.16 (*m*, 5 CH₂); 1.44–1.51 (*m*, CH₂); 2.38 (*t*, *J*=7.4, CH₂); 7.14–7.34 (*m*, 3 arom. H); 7.46–7.50 (*m*, 1 arom. H); 7.69 (*d*, *J*=7.9, 2 arom. H); 7.82 (*d*, *J*=7.6, 2 arom. H). ¹³C-NMR (62.9 MHz, CDCl₃): 14.0 (Me); 20.1, 22.5, 28.3, 28.8, 29.0, 29.1, 31.8 (CH₂); 72.3, 103.3 (C≡); 121.4 (CH); 122.2 (*q*, *J*(C,F)=273.1, C); 123.7 (CH); 125.4 (*q*, *J*(C,F)=3.8, CH); 128.5, 129.5 (CH); 133.7 (*q*, *J*(C,F)=8.1, CH); 135.7 (*q*, *J*(C,F)=36.3, C); 136.5, 143.8, 157.2 (C); 193.3 (C=O). ¹⁹F-NMR (282 MHz, CDCl₃): –62.8. GC/EI-MS (70 eV): 410 (58, *M*⁺), 381 (18), 367 (41), 353 (100), 339 (54), 325 (47), 311 (69), 287 (83), 262 (34), 243 (39), 231 (26), 226 (32), 213 (63), 183 (11). HR-EI-MS (70 eV): 410.185602 (*M*⁺, C₂₆H₂₅F₃O⁺; calc. 410.18520).

2-[(6-Methoxynaphthalen-2-yl)ethynyl]-3-(4-methoxyphenyl)-1H-inden-1-one (8d**).** From **4i** (157 mg, 0.50 mmol), [Pd(PPh₃)₂Cl₂] (18 mg, 5 mol-%), dry CuI (10 mol-%), (i-Pr)₂NH (1 ml/0.1 mmol of **4i**), and 2-ethynyl-6-methoxynaphthalene (**6e**; 100 mg, 0.55 mmol), according to GP C. Yield: 162 mg (78%). Colorless oil. IR (KBr): 3014, 2932, 2849w, 1704, 1599s, 1512, 1453, 1388, 1303, 1255s, 1162m, 1025s, 947, 894m, 850s, 811, 728, 710, 661, 585m. ¹H-NMR (300 MHz, CDCl₃): 3.83 (*s*, 2 MeO); 6.98–7.63 (*m*, 7 arom. H); 7.83–7.96 (*m*, 3 arom. H). ¹³C-NMR (62.8 MHz, CDCl₃): 55.3, 55.4 (MeO); 82.3, 100.2 (C≡); 105.8, 114.0 (CH); 116.5, 117.9 (C); 119.4, 119.6, 122.0, 123.2 (CH); 124.8 (C); 126.7 (CH); 126.9, 128.4 (C); 129.0, 129.4, 130.3 (CH); 131.2 (C); 131.7, 133.4 (CH); 144.2, 158.4, 159.4, 161.4, 193.5 (C=O). GC/EI-MS (70 eV): 416 (100, *M*⁺), 330 (6), 97 (5), 69 (12), 43 (10). HR-ESI-MS (pos.): 417.1484 ([*M*+H]⁺, C₂₉H₂₁O₃⁺; calc. 417.1485).

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