Supporting Information

Rh(I)-Catalyzed Carbonylative Cyclization Reactions of Alkynes with 2-Bromophenylboronic Acids Leading to Indenones

Yasuyuki Harada, Jun Nakanishi, Hirokazu Fujihara, Mamoru Tobisu, Yoshiya Fukumoto
and Naoto Chatani*

*Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Suita, Osaka 565-0871, Japan*

General Information ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-EX270 and JEOL JNM-GSX 400 spectrometers in CDCl_3 using tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer. Mass spectra were obtained on a Shimadzu GCMS-QP 5000 and Shimadzu GCMS-QP 2010 instruments with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303 instrument. Analytical GC was carried out on a Shimadzu GC-14A gas chromatograph, equipped with a flame ionization detector. Melting points were determined on a Yamato melting point apparatus and are uncorrected. Column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh)).

Materials Unless otherwise noted, all reagents were obtained from commercial suppliers and were used as received. 1,4-Dioxane was distilled over Na. $[\text{RhCl}(\text{cod})]_2$, 4-octyne, 2-hexyne, 1-phenyl-1-propyne, 1-(trimethylsilyl)-1-propyne, methyl 3-phenylpropionate, ethyl 3-(trimethylsilyl)propionate and 2,5-dichlorophenylboronic acid were purchased from Wako Pure Chemical Industries, Ltd. 2-Bromophenylboronic acid, 1-phenyl-2-(trimethylsilyl)acetylene, (dimethylphenylsilyl)acetylene, 2-chlorophenylboronic acid, *p*-tolylboronic acid, *o*-tolylboronic acid, 2,6-dimethylphenylboronic acid, 3-nitrophenylboronic acid, 4-chlorophenylboronic acid, 4-formylphenylboronic acid, 4-trifluoromethylphenylboronic acid and 2-naphthylboronic acid were purchased from Aldrich Chemical Co. Diphenylacetylene, 1-phenyl-1-hexyne, bis(trimethylsilyl)-acetylene, 3,3-dimethyl-1-butyne, methylchloroformate and 3-methoxyphenylboronic acid were purchased from Tokyo Kasei Kogyo Co., Ltd. Sodium carbonate was purchased from Nacalai Tesque, Inc. 2-Chloro-5-(trifluoromethyl)-phenylboronic acid was purchased from Lancaster Synthesis, Inc. 1-Hex-1-ynyl-4-methoxybenzene, 1-hex-1-ynyl-4-nitrobenzene and 2-hex-1-ynyl-1,3-dimethylbenzene were prepared by the Sonogashira reaction. 4,4-Dimethyl-oct-6-yn-2-one was prepared by the procedure of Johnson.¹ Cyclododecyne was prepared by the method of Brandsma with minor modifications.² 2-Bromo-5-methoxyphenylboronic acid was prepared by the method of Kuivila.³ 1-Bromo-4-methoxy-2-(trimethylsilylethynyl)benzene was prepared by the method of Flynn⁴ and a Sonogashira reaction.

Typical Procedure for the Rh-Catalyzed Formation of Indenones A 10-mL two-necked flask was charged with sodium carbonate (212.0 mg, 2.0 mmol), 2-bromophenylboronic acid (301.2

mg, 1.5 mmol), [RhCl(cod)]₂ (12.3 mg, 0.025 mmol), 4-octyne (110.2 mg, 1.0 mmol) and 1,4-dioxane/H₂O (2 mL/0.02 mL), and a three-way stopcock, connected to a vacuum line and a balloon filled with carbon monoxide, was attached to the flask. The system was carefully evacuated and refilled with carbon monoxide and then filled with carbon monoxide (1 atm). It was then immersed in an oil bath at 80 °C. After 20 hours, it was removed from the oil bath, and cooled to room temperature. The contents were transferred to a round-bottom flask and volatiles were removed *in vacuo*. The residue was subjected to column chromatography on silica-gel (eluent; hexane/EtOAc = 50/1) to give 2,3-dipropylinden-1-one (**2**) (195.0 mg, 91 % yield) as a yellow oil.

Typical Procedure for the Rh-Catalyzed Formation of Naphthalenes An oven-dried, N₂-purged 10-mL two-necked flask was charged with sodium carbonate (106.0 mg, 1.0 mmol), 2-bromophenylboronic acid (150.6 mg, 0.75 mmol), [RhCl(cod)]₂ (12.3 mg, 0.025 mmol), 4-octyne (110.2 mg, 1.0 mmol) and 1,4-dioxane/H₂O (1 mL/0.01 mL). The system was immersed in an oil bath at 50 °C. After 20 hours, it was removed from the oil bath, and cooled to room temperature. The contents were transferred to a round-bottom flask and volatiles were removed *in vacuo*. The residue was subjected to column chromatography on silica-gel (eluent; hexane only) to give 1,2,3,4-tetrapropynaphthalene (**3**) (112.8 mg, 76 % yield) as a colorless oil.

Products Compound **2**,⁵ **3**,⁶ **6**,⁷ **7**,⁸ **13**,⁵ **18**,⁹ **35**,¹⁰ **64**,¹¹ **70**,¹² are known and their spectral data were compared with those of authentic specimens. The analytical data of other products are as follows.

3-Butyl-2-(4-methoxyphenyl)inden-1-one (8) orange solid. mp 47 °C. *R_f* 0.14 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.95 (t, *J* = 7.3 Hz, 3H), 1.46 (tq, *J* = 7.3 Hz, 7.3 Hz, 2H), 1.68 (tt, *J* = 7.3 Hz, 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 3.85 (s, 3H), 6.98 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.15-7.49 (c, 4H, Ar). ¹³C NMR (CDCl₃) δ: 13.8, 23.1, 26.5, 30.2, 55.2, 113.8, 119.6, 122.2, 123.6, 128.4, 130.5, 130.7, 132.8, 133.5, 145.4, 157.7, 159.1, 197.2. IR (KBr): 2956 m, 2931 m, 2862 w, 1707 s, 1608 s, 1589 m, 1510 s, 1462 m, 1369 w, 1340 w, 1290 m, 1250 s, 1176 s, 1113 w, 1063 w, 1032 m, 862 w, 829 m, 798 w, 766 m, 733 w, 714 w, 580 w, 530 w. MS, *m/z* (relative intensity, %): 293 (M⁺+1, 21), 292 (M⁺, 93), 250 (33), 249 (100), 234 (22), 221 (12), 218 (17), 217 (30), 206 (13), 189 (26), 178 (38), 177 (11), 176 (14), 165 (10), 163 (10), 152 (13), 151 (10), 118 (10), 76 (13). Exact Mass Calcd for C₂₀H₂₀O₂: 292.1463. Found: 292.1467.

2-Butyl-3-(4-methoxyphenyl)inden-1-one (8') ¹H NMR (CDCl₃) δ: 0.86 (t, *J* = 7.3 Hz, 3H), 1.31 (tq, *J* = 7.2 Hz, 7.3 Hz, 2H), 1.48 (tt, *J* = 7.2 Hz, 7.6 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 7.04 (d, *J* = 8.6 Hz, 2H), 7.19-7.47 (c, 6H, Ar).

3-Butyl-2-phenylinden-1-one (9) and **2-Butyl-3-phenylinden-1-one (9')** orange oil. *R_f* 0.27 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: [0.83 (t, *J* = 7.2 Hz, 3H, **9'**), 0.92 (t, *J* = 7.3 Hz, 3H, **9**), [1.27-1.50 (c, 4H, **9'**), 1.43 (tq, *J* = 7.3 Hz, 7.4 Hz, 2H, **9**), 1.65 (tt, *J* = 7.4 Hz, 8.1 Hz, 2H, **9**), [2.33 (t, *J* = 7.6 Hz, 2H, **9'**), 2.69 (t, *J* = 8.1 Hz, 2H, **9**), [6.97 (d, 1H, **9'**), 7.15-7.49 (c, 9H, **9** and c, 8H, **9'**)]. ¹³C NMR (CDCl₃) δ: 13.7, 22.7 (**9'**), 23.0, 26.4, 30.2, 31.3 (**9'**), 119.8, 120.4 (**9'**), 122.2, 122.3 (**9'**), 127.6, 127.7 (**9'**), 128.1 (**9'**), 128.2, 128.6, 129.0 (**9'**), 129.3, 130.6, 130.9 (**9'**), 131.2, 132.7 (**9'**), 133.1 (**9'**), 133.2, 133.5, 135.4 (**9'**), 145.1, 145.8 (**9'**), 154.9 (**9'**), 158.8, 196.7, 198.3 (**9'**). IR (neat): 3057 w,

2956 m, 2929 m, 2862 w, 1705 s, 1601 w, 1493 w, 1458 m, 1367 w, 1342 w, 1178 w, 1086 w, 1065 w, 854 w, 756 s, 721 m, 698 s, 513 w. MS, m/z (relative intensity, %): 263 ($M^+ + 1$, 16), 262 (M^+ , 76), 221 (18), 220 (100), 219 (71), 218 (15), 215 (27), 203 (11), 202 (17), 192 (20), 191 (41), 190 (20), 189 (52), 176 (13), 165 (23), 110 (15), 101 (14), 95 (21), 88 (11), 82 (12). Exact Mass Calcd for $C_{19}H_{18}O$: 262.1358. Found: 262.1359.

3-Butyl-2-(4-nitrophenyl)inden-1-one (10) yellow solid. mp 96 °C.

R_f 0.11 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.93 (t, J = 7.3 Hz, 3H), 1.44 (tq, J = 7.3 Hz, 7.3 Hz, 2H), 1.69 (tt, J = 7.3 Hz, 7.8 Hz, 2H), 2.73 (t, J = 7.8 Hz, 2H), 7.24-7.56 (c, 6H), 8.28 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 13.7, 23.0, 26.6, 30.3, 120.5, 122.7, 123.5, 129.6, 130.1, 130.4,

131.0, 133.9, 138.3, 144.4, 146.9, 161.4, 195.5. IR (KBr): 2952 w, 2925 w, 2862 w, 1707 s, 1597 s, 1516 s, 1454 w, 1346 s, 1176 w, 1107 w, 858 w, 841 m, 766 m, 752 m, 721 w, 696 m, 507 w. MS, m/z (relative intensity, %): 307 (M^+ , 16), 266 (17), 265 (100), 231 (10), 219 (11), 218 (25), 203 (12), 202 (18), 190 (14), 189 (36), 101 (13), 94 (17). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.16; H, 5.52; N, 4.57.

2-Butyl-3-(4-nitrophenyl)inden-1-one (10') 1H NMR ($CDCl_3$) δ : 0.84 (t, J = 7.3 Hz, 3H), 1.28 (tq, J = 7.3 Hz, 7.3 Hz, 2H), 1.47 (tt, J = 7.3 Hz, 7.7 Hz, 2H), 2.33 (t, J = 7.7 Hz, 2H), 6.92 (d, J = 6.8 Hz, 1H), 7.21-7.64 (c, 5H), 8.39 (d, J = 8.4 Hz, 2H).

3-Butyl-2-(2,6-dimethylphenyl)inden-1-one (11) yellow oil. R_f 0.17

(hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.96 (t, J = 7.3 Hz, 3H), 1.44 (tq, J = 7.3 Hz, 7.3 Hz, 2H), 1.67 (tt, J = 7.3 Hz, 7.7 Hz, 2H), 2.30 (s, 6H), 2.52 (t, J = 7.7 Hz, 2H), 7.19-7.39 (c, 5H, Ar), 7.52 (dd, J = 6.8 Hz, 7.3 Hz, 1H), 7.61 (d, J = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 13.6, 23.3, 22.9, 26.9, 29.1, 119.7, 122.1, 127.2,

127.8, 128.5, 130.7, 131.0, 133.3, 134.4, 137.1, 145.0, 160.4, 196.6. IR (neat): 3064 w, 3018 w, 2956 s, 2929 s, 2870 m, 1707 s, 1604 m, 1587 m, 1460 s, 1375 m, 1335 w, 1309 w, 1173 m, 1101 w, 1084 w, 1053 w, 1028 w, 858 m, 768 s, 729 s, 673 w, 534 w. MS, m/z (relative intensity, %): 290 (M^+ , 35), 234 (44), 233 (100), 219 (11), 218 (14), 215 (11), 203 (15), 202 (21), 189 (14), 107 (13), 101 (19). Exact Mass Calcd for $C_{21}H_{22}O$: 290.1671. Found: 290.1674.

3-Methyl-2-trimethylsilylinden-1-one (12) 1H NMR ($CDCl_3$) δ : 0.29 (s, 9H), 2.30 (s, 3H), 7.12 (d, J = 7.3 Hz, 1H), 7.24 (dd, J = 6.8 Hz, 7.0 Hz, 1H), 7.37 (dd, J = 6.8 Hz, 7.3 Hz, 1H), 7.40 (d, J = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 0.0, 14.7, 118.7, 121.3, 128.8, 132.3, 132.8, 147.1, 168.7, 201.7. Although the compound **11** was known⁸, the identification of the regiochemistry was wrong¹³. We confirmed the regiochemistry of **11** on the basis of the long-range C-H COSY.

2,3-Bistrimethylsilylinden-1-one (14) yellow solid. mp 84 °C. R_f 0.29

(hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.32 (s, 9H), 0.43 (s, 9H), 7.18 (dd, J = 6.8 Hz, 7.3 Hz, 1H), 7.26-7.35 (c, 2H), 7.41 (d, J = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 1.4, 1.5, 122.4, 122.9, 128.1, 131.0, 133.3, 149.6, 150.4, 172.7, 203.1. IR (KBr): 3068 w, 2954 m, 2898 m, 1697 s, 1604 m, 1589 m, 1485 m, 1456 m,

1410 w, 1282 m, 1250 s, 1209 m, 1082 m, 1011 w, 918 s, 870 s, 841 s, 769 s, 712 s, 694 m, 627 m, 543 w. MS, m/z (relative intensity, %): 274 (M^+ , 7), 259 (13), 243 (12), 231 (11), 143 (13), 135 (23), 73 (100). Anal. Calcd for $C_{15}H_{22}OSi_2$: C, 65.63; H, 8.08. Found: C, 65.45; H, 7.94.

2-Methoxycarbonyl-3-phenylinden-1-one (15) yellow solid. mp 103 °C. R_f 0.17 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 3.76 (s, 3H), 7.21 (m, 1H), 7.41-7.64 (c, 8H). ^{13}C NMR ($CDCl_3$) δ : 51.9, 123.5, 123.9, 128.1, 128.5, 130.4, 130.6, 131.2, 131.3, 133.6, 143.0, 163.5, 165.8, 192.0. IR (KBr): 2948 w, 1714 s, 1606 w, 1560 m, 1491 w, 1456 w, 1433 w, 1363 w, 1340 w, 1225 m, 1184 w, 1126 m, 1080 w, 781 w, 758 w, 744 w, 698 m. MS, m/z (relative intensity, %): 264 (M^+ , 49), 234 (29), 233 (100), 206 (12), 177 (17), 176 (40), 151 (14), 88 (15). Exact Mass Calcd for $C_{17}H_{12}O_3$: 264.0786. Found: 264.0790.

3-Methoxycarbonyl-2-phenylinden-1-one (15') 1H NMR ($CDCl_3$) δ : 3.83 (s, 3H), 7.30-7.59 (c, 9H).

3-Ethoxycarbonyl-2-trimethylsilanylinden-1-one (16) yellow oil. R_f 0.40 (hexane/EtOAc = 5/1). 1H NMR ($CDCl_3$) δ : 0.29 (s, 9H), 1.44 (t, J = 7.2 Hz, 3H), 4.42 (q, J = 7.2 Hz, 2H), 7.26-7.49 (c, 4H). ^{13}C NMR ($CDCl_3$) δ : -0.6, 14.3, 61.6, 121.8, 123.0, 129.2, 131.4, 133.6, 141.5, 143.4, 157.6, 165.3, 200.5. IR (neat): 3070 w, 2981 m, 2956 w, 2900 w, 1711 s, 1601 w, 1543 w, 1458 m, 1371 w, 1298 s, 1245 s, 1194 s, 1099 s, 1026 w, 974 w, 850 s, 762 s, 702 m, 642 w, 619 w. MS, m/z (relative intensity, %): 274 (M^+ , 0), 259 (64), 232 (22), 231 (100), 215 (21), 213 (16), 204 (19), 203 (80), 159 (30), 155 (35), 143 (43), 131 (17), 129 (23), 117 (21), 115 (32), 105 (15), 77 (20), 75 (58), 53 (17). Exact Mass Calcd for $C_{15}H_{18}O_3Si$: 274.1025. Found: 274.1026.

2-Ethoxycarbonyl-3-trimethylsilanylinden-1-one (16') yellow oil. R_f 0.33 (hexane/EtOAc = 5/1). 1H NMR ($CDCl_3$) δ : 0.39 (s, 9H), 1.37 (t, J = 7.2 Hz, 3H), 4.32 (q, J = 7.2 Hz, 2H), 7.26-7.50 (c, 4H). ^{13}C NMR ($CDCl_3$) δ : -0.4, 14.2, 61.4, 123.4, 124.6, 129.3, 129.6, 134.0, 138.7, 146.6, 164.9, 165.3, 193.4. IR (neat): 2981 w, 2900 w, 1734 s, 1714 s, 1606 w, 1591 w, 1558 w, 1541 w, 1458 w, 1367 w, 1304 s, 1257 s, 1207 m, 1115 m, 1024 w, 926 m, 845 s, 771 w, 633 w. MS, m/z (relative intensity, %): 274 (M^+ , 5), 259 (32), 232 (17), 229 (11), 203 (11), 187 (10), 171 (11), 145 (11), 143 (29), 129 (10), 128 (13), 115 (21), 77 (15), 75 (31), 73 (15). Exact Mass Calcd for $C_{15}H_{18}O_3Si$: 274.1025. Found: 274.1022.

5,6,7,8,9,10,11,12,13,14-Decahydrocycloclododeca[a]inden-15-one (17) yellow oil. R_f 0.24 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 1.28-1.80 (m, 16H), 2.29 (t, J = 7.2 Hz, 2H), 2.57 (t, J = 7.3 Hz, 2H), 7.05 (d, J = 7.3 Hz, 7.3 Hz, 1H), 7.14 (dd, J = 7.2 Hz, 7.3 Hz, 1H), 7.28 (dd, J = 7.2 Hz, 7.3 Hz, 1H), 7.36 (d, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 20.5, 22.0, 22.2, 23.5, 24.2, 24.5, 24.9, 25.2, 25.6, 26.4, 119.5, 121.5, 127.8, 131.2, 133.1, 135.0, 145.7, 157.9, 198.8. IR (neat): 3064 w, 2933 s, 2854 s, 1767 s, 1606 m, 1591 m, 1468 s, 1369 w, 1354 w, 1173 w, 1136 w, 1080 w, 937 w, 762 m, 723 s, 617 w, 571 w. MS, m/z (relative intensity, %): 269 (M^+ , 13), 268 (M^+ , 63), 211 (21), 199 (17), 197 (25), 185 (40), 184 (15), 183 (23), 171 (15), 169 (15), 159 (20), 158 (66),

157 (95), 156 (47), 146 (17), 145 (42), 144 (100), 143 (17), 141 (33), 132 (28), 129 (39), 128 (76), 127 (24), 115 (47), 77 (18), 55 (44). Anal. Calcd for C₁₉H₂₄O: C, 85.03; H, 9.01. Found: C, 84.83; H, 8.86.

2-(2,2-Dimethyl-4-oxo-pentyl)-3-methyl-inden-1-one (19) and 3-(2,2-Dimethyl-4-oxo-pentyl)-2-methyl-inden-1-one (19') yellow oil. *R_f* 0.03

(hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: [1.01 (s, 6H, **19**), 1.08 (s, 6H, **19'**)], [1.80 (s, 3H, **19'**), 2.13 (s, 3H, **19**)], [2.34 (s, 2H, **19**), 2.36 (s, 3H, **19**), 2.48 (s, 3H, **19'**), 2.65 (s, 3H, **19'**)], [7.04 (d, *J* = 7.3 Hz, 1H, **19**), 7.05-7.37 (c, 3H, **19** and c, 4H, **19'**)]. ¹³C NMR (CDCl₃) δ: 9.2 (**19'**), 12.6, 27.4, 28.2 (**19'**), 32.3, 34.6, 35.8, 36.5 (**19'**), 36.9 (**19'**), 54.1, 54.7 (**19'**), 118.7, 120.0 (**19'**), 121.6, 121.7 (**19'**), 127.7 (**19'**), 128.3, 130.5, 132.5, 133.2, 133.3 (**19'**), 146.0, 156.6, 198.4, 208.7. IR (neat): 3072 w, 2958 m, 2873 w, 1707 s, 1610 w, 1593 w, 1456 m, 1433 w, 1385 m, 1362 m, 1155 w, 1084 w, 1005 w, 933 w, 908 w, 758 m, 721 w, 696 w, 640 w. MS, *m/z* (relative intensity, %): 256 (M⁺, 3), 199 (21), 198 (90), 183 (18), 159 (13), 158 (100), 157 (27), 130 (16), 129 (25), 128 (38), 127 (16), 115 (14), 77 (11), 51 (10). Exact Mass Calcd for C₁₇H₂₀O₂: 256.1463. Found: 256.1456.

5-Methoxy-2,3-dipropylinden-1-one (23) yellow oil. *R_f* 0.17

(hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.93 (t, *J* = 7.3 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H), 1.48 (tq, *J* = 7.3 Hz, 7.7 Hz, 2H), 1.63 (tq, *J* = 7.3 Hz, 7.6 Hz, 2H), 2.23 (t, *J* = 7.7 Hz, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 6.53 (dd, *J* = 1.6 Hz, 8.1 Hz, 1H), 6.60 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H). ¹³C NMR (CDCl₃) δ: 14.1, 14.3, 21.4, 22.4, 25.0, 28.0, 55.5, 108.4, 108.5, 123.3, 123.8, 136.3, 148.2, 155.1, 164.2, 197.1. IR (neat): 2960 s, 2933 s, 2871 m, 2841 w, 1703 s, 1597 s, 1477 s, 1431 m, 1369 s, 1288 m, 1234 s, 1213 s, 1173 s, 1109 w, 1084 m, 1030 m, 1005 w, 949 w, 914 w, 870 w, 820 w, 783 m, 665 w, 607 w. MS, *m/z* (relative intensity, %): 245 (M⁺+1, 10), 244 (M⁺, 56), 216 (21), 215 (100), 202 (29), 201 (35), 187 (33), 174 (24), 173 (46), 172 (12), 145 (12), 129 (10), 128 (17), 114 (27), 63 (11). Exact Mass Calcd for C₁₆H₂₀O₂: 244.1463. Found: 244.1458.

5-Methoxy-3-methyl-2-trimethylsilylinden-1-one (24) yellow solid.

R_f 0.23 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.28 (s, 9H), 2.25 (s, 3H), 3.85 (s, 3H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 1H). ¹³C NMR (CDCl₃) δ: 0.0, 14.5, 55.7, 107.5, 110.3, 122.9, 125.1, 134.4, 149.7, 163.9, 166.2, 200.3. IR (KBr): 2989 m, 2898 m, 2833 m, 1695 s, 1597 s, 1560 s, 1475 m, 1433 m, 1408 m, 1375 s, 1338 m, 1296 s, 1250 s, 1228 s, 1190 m, 1172 s, 1126 m, 1084 s, 1041 s, 1030 s, 864 s, 841 s, 826 s, 760 m, 748 m, 711 m, 688 m, 631 s. MS, *m/z* (relative intensity, %): 246 (M⁺, 27), 232 (19), 231 (100), 188 (13), 115 (20), 75 (10). Anal. Calcd for C₁₄H₁₈O₂Si: C, 68.25; H, 7.36; O, 12.99. Found: C, 68.19; H, 7.26.

5-Methoxy-3-phenyl-2-trimethylsilylinden-1-one (25) yellow solid.

R_f 0.26 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.04 (s, 9H), 3.79 (s, 3H), 6.43 (d, *J* = 1.6 Hz, 1H), 6.66 (dd, *J* = 2.0 Hz, 8.2 Hz, 1H), 7.33-7.35 (c, 2H), 7.44-7.47 (c, 4H). ¹³C NMR (CDCl₃) δ: -0.2, 55.7, 109.4, 110.8, 124.0,

125.1, 127.7, 128.3, 129.0, 134.8, 136.6, 149.9, 164.1, 168.5, 200.4. IR (KBr): 2956 m, 1691 s, 1608 s, 1599 s, 1543 s, 1489 m, 1471 m, 1431 m, 1362 s, 1302 m, 1286 s, 1246 s, 1221 s, 1176 m, 1095 s, 1024 s, 870 s, 847 s, 829 s, 810 m, 779 m, 754 m, 719 s, 702 m, 625 m. MS, m/z (relative intensity, %): 309 ($M^+ + 1$, 11), 308 (M^+ , 43), 294 (23), 293 (100), 277 (18), 250 (10), 235 (11), 147 (17), 139 (20). Exact Mass Calcd for $C_{19}H_{20}O_2Si$: 308.1233. Found: 308.1231.

5-Methoxy-2-methoxycarbonyl-3-phenylinden-1-one (26) yellow

solid. R_f 0.50 (hexane/EtOAc = 1/1). 1H NMR ($CDCl_3$) δ : 3.74 (s, 3H), 3.84 (s, 3H), 6.73-6.81 (c, 2H), 7.51-7.59 (c, 6H). ^{13}C NMR ($CDCl_3$) δ : 52.1, 56.0, 112.5, 112.7, 123.1, 125.4, 125.5, 128.1, 128.5, 130.4, 131.3, 145.7, 163.4, 163.5, 164.3, 190.6. IR (KBr): 2949 w, 2844 w, 2362 w, 1736 s, 1703 m, 1593 m, 1477 m, 1452 w, 1433 m, 1360 s, 1344 m, 1284 m, 1228 s, 1188 w, 1140 w, 1117 m, 1093 m, 1026 w, 978 m, 883 w, 812 w, 777 w, 731 w, 704 w, 661 w. MS, m/z (relative intensity, %): 295 ($M^+ + 1$, 13), 294 (M^+ , 64), 264 (35), 263 (100), 236 (14), 235 (12), 164 (12), 163 (17). Exact Mass Calcd for $C_{18}H_{18}O_4$: 294.0892. Found: 294.0899.

5,6-Difluoro-2,3-dipropylinden-1-one (27) yellow oil. R_f 0.36

(hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.91 (t, J = 7.4 Hz, 3H), 1.01 (t, J = 7.3 Hz, 3H), 1.46 (tq, J = 7.4 Hz, 7.8 Hz, 2H), 1.60 (tq, J = 7.3 Hz, 7.6 Hz, 2H), 2.23 (t, J = 7.8 Hz, 2H), 2.46 (t, J = 7.6 Hz, 2H), 6.83 (dd, J = 6.5 Hz, 9.5 Hz, 1H), 7.18 (dd, J = 7.7 Hz, 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 14.1, 14.2, 21.0, 22.4, 25.0, 28.2, 109.3 (d, J = 20.6 Hz), 112.2 (d, J = 20.0 Hz), 127.1 (dd, J = 4.5 Hz, 4.5 Hz), 136.1 (d, J = 5.0 Hz), 142.5 (dd, J = 3.8 Hz, 7.2 Hz), 149.7 (dd, J = 13.9 Hz, 217.5 Hz), 153.4 (dd, J = 13.9 Hz, 220.9 Hz), 155.7 (dd, J = 1.9 Hz, 2.4 Hz), 195.6. IR (neat): 2964 m, 2935 w, 2873 w, 1714 s, 1633 w, 1606 m, 1485 s, 1435 w, 1387 m, 1255 m, 1192 w, 1113 w, 1084 w, 891 w, 789 w, 771 w. MS, m/z (relative intensity, %): 250 (M^+ , 37), 222 (13), 221 (76), 208 (16), 207 (25), 193 (38), 180 (31), 179 (100), 178 (19), 177 (16), 165 (20), 164 (34), 151 (53), 145 (13), 55 (12). Exact Mass Calcd for $C_{15}H_{16}F_2O$: 250.1169. Found: 250.1161.

5,6-Difluoro-3-methyl-2-trimethylsilylinden-1-one (28) yellow solid. R_f

0.43 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.28 (s, 9H), 2.26 (s, 3H), 6.93 (dd, J = 6.4 Hz, 8.8 Hz, 1H), 7.22 (t, J = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : -0.3, 14.6, 109.0 (d, J = 19.7 Hz), 111.7 (d, J = 19.7 Hz), 128.7 (dd, J = 3.3 Hz, 5.0 Hz), 134.6 (d, J = 4.1 Hz), 143.9 (dd, J = 3.3 Hz, 7.0 Hz), 150.8 (dd, J = 14.7 Hz, 231.6 Hz), 153.3 (dd, J = 14.7 Hz, 234.1 Hz), 166.7, 198.9. IR (KBr): 3043 m, 2956 m, 1695 s, 1608 m, 1572 s, 1556 s, 1483 s, 1431 s, 1389 s, 1367 m, 1286 m, 1246 s, 1188 m, 1120 m, 974 s, 924 w, 874 s, 841 s, 785 s, 769 m, 752 m, 708 m, 625 m. MS, m/z (relative intensity, %): 252 (M^+ , 27), 238 (18), 237 (100), 151 (11), 145 (10), 75 (16), 63 (10). Exact Mass Calcd for $C_{13}H_{14}F_2OSi$: 252.0782. Found: 252.0770.

5,6-Difluoro-3-phenyl-2-(trimethylsilyl)inden-1-one (29) yellow solid.

R_f 0.34 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.19 (s, 9H), 6.84 (dd, J = 6.5 Hz, 9.3 Hz, 1H), 7.41-7.48 (c, 3H), 7.61-7.64 (c, 3H). ^{13}C NMR ($CDCl_3$) δ : -0.3, 110.8 (d, J = 21.3 Hz), 112.4 (d, J = 19.6 Hz), 127.5, 128.5, 129.6, 134.1,

136.2 (d, $J = 5.0$ Hz), 143.9 (dd, $J = 3.7$ Hz, 7.0 Hz), 150.7 (dd, $J = 14.4$ Hz, 208.3 Hz), 153.2 (dd, $J = 14.3$ Hz, 210.8 Hz), 168.6, 198.9. IR (KBr): 2956 m, 1697 s, 1626 m, 1603 s, 1552 s, 1481 s, 1442 s, 1431 s, 1369 s, 1298 s, 1279 s, 1246 s, 1190 s, 1142 s, 1103 s, 1057 s, 1026 m, 876 s, 843 s, 787 s, 750 s, 715 s, 702 s, 625 m, 565 m. MS, m/z (relative intensity, %): 315 ($M^+ + 1$, 10), 314 (M^+ , 40), 300 (25), 299 (100), 284 (10), 283 (37), 240 (11), 238 (14), 149 (18), 142 (13), 77 (13), 75 (13). Exact Mass Calcd for $C_{18}H_{16}F_2OSi$: 314.0938. Found: 314.0942.

4-Fluoro-2,3-dipropylinden-1-one (30) yellow oil. R_f 0.29 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.94 (t, $J = 7.4$ Hz, 3H), 1.04 (t, $J = 7.4$ Hz, 3H), 1.47 (tq, $J = 7.4$ Hz, 7.6 Hz, 2H), 1.66 (tq, $J = 7.4$ Hz, 7.7 Hz, 2H), 2.23 (t, $J = 7.6$ Hz, 2H), 2.60 (t, $J = 7.7$ Hz, 2H), 7.01 (m, 1H), 7.12-7.21 (c, 2H). ^{13}C NMR ($CDCl_3$) δ : 14.2, 14.3, 21.4 (d, $J = 2.8$ Hz), 22.6, 24.7, 30.2 (d, $J = 2.1$ Hz), 117.8 (d, $J = 2.8$ Hz), 122.3 (d, $J = 23.3$ Hz), 129.4 (d, $J = 12.8$ Hz), 130.1 (d, $J = 6.7$ Hz), 133.9 (d, $J = 3.8$ Hz), 134.9 (d, $J = 2.8$ Hz), 155.2 (d, $J = 250.4$ Hz), 156.7 (d, $J = 3.8$ Hz), 197.0 (d, $J = 1.7$ Hz). IR (neat): 2962 m, 2933 w, 2873 w, 1711 s, 1618 m, 1468 m, 1373 w, 1356 w, 1236 w, 1088 w, 1018 w, 806 w, 762 m. MS, m/z (relative intensity, %): 232 (M^+ , 52), 204 (15), 203 (85), 190 (19), 189 (34), 175 (26), 162 (26), 161 (100), 159 (10), 147 (16), 146 (27), 132 (42). Exact Mass Calcd for $C_{15}H_{17}FO$: 232.1263. Found: 232.1274.

4-Fluoro-3-methyl-2-trimethylsilylinden-1-one (31) yellow solid. R_f 0.49 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.29 (s, 9H), 2.46 (s, 3H), 7.01-7.06 (m, 1H), 7.21-7.23 (c, 2H). ^{13}C NMR ($CDCl_3$) δ : -0.1, 17.9 (d, $J = 3.3$ Hz), 117.7 (d, $J = 1.5$ Hz), 121.9 (d, $J = 22.9$ Hz), 131.2 (d, $J = 12.2$ Hz), 131.4 (d, $J = 6.6$ Hz), 133.3 (d, $J = 2.5$ Hz), 135.8 (d, $J = 3.2$ Hz), 156.1 (d, $J = 254.6$ Hz), 168.0 (d, $J = 4.1$ Hz), 200.63 (d, $J = 1.7$ Hz). IR (KBr): 2954 w, 2897 w, 2362 w, 1695 s, 1604 m, 1558 m, 1468 m, 1383 w, 1346 w, 1286 m, 1259 m, 1238 s, 1151 w, 1130 w, 1041 w, 958 w, 854 s, 843 s, 812 m, 771 s, 690 w, 638 w, 573 w, 476 w. MS, m/z (relative intensity, %): 234 (M^+ , 21), 220 (19), 219 (100), 129 (16), 128 (11), 75 (11), 63 (31). Exact Mass Calcd for $C_{13}H_{25}FOSi$: 234.0876. Found: 234.0877.

4-Fluoro-3-phenyl-2-trimethylsilylinden-1-one (32) yellow solid R_f 0.23 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.01 (s, 9H), 6.98 (t, $J = 8.9$ Hz, 1H), 7.21-7.43 (c, 7H). ^{13}C NMR ($CDCl_3$) δ : -0.2, 118.6 (d, $J = 2.8$ Hz), 122.7 (d, $J = 22.9$ Hz), 127.4 (d, $J = 1.7$ Hz), 128.1, 129.1, 131.2 (d, $J = 11.1$ Hz), 131.8 (d, $J = 6.7$ Hz), 135.5 (d, $J = 2.2$ Hz), 136.3, 136.5, 155.9 (d, $J = 257.0$ Hz), 169.0 (d, $J = 2.8$ Hz), 200.5. IR (KBr): 3033 w, 2954 w, 1699 s, 1604 m, 1543 w, 1487 w, 1468 m, 1442 w, 1365 w, 1230 m, 1244 s, 1149 w, 1107 m, 1026 w, 970 w, 839 s, 756 s, 698 m, 625 w, 523 w. MS, m/z (relative intensity, %): 296 (M^+ , 29), 282 (22), 281 (100), 265 (38), 202 (18), 189 (11), 77 (23). Exact Mass Calcd for $C_{18}H_{17}FOSi$: 296.1033. Found: 296.1040.

5-Chloro-2,3-dipropylinden-1-one (33) yellow oil. R_f 0.29 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.92 (t, $J = 7.3$ Hz, 3H), 1.03 (t, $J = 7.3$ Hz, 3H), 1.48 (tq, $J = 7.3$ Hz, 7.7 Hz, 2H), 1.62 (tq, $J = 7.3$ Hz, 7.6 Hz, 2H), 2.23 (t, $J = 7.7$ Hz, 2H), 2.49 (t, $J = 7.6$ Hz, 2H), 6.98 (s, 1H), 7.11 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 14.1, 14.3, 21.1, 22.4, 24.9,

28.1, 119.8, 122.5, 127.3, 129.2, 136.2, 139.2, 147.6, 156.4, 197.0. IR (neat): 2962 m, 2933 m, 2871 m, 1711 s, 1604 m, 1585 m, 1464 m, 1410 w, 1360 m, 1261 w, 1227 w, 1159 w, 1113 w, 1066 m, 1009 w, 947 w, 910 w, 874 w, 829 m, 783 w, 744 w, 596 w. MS, m/z (relative intensity, %): 250 ($M^+ + 2$, 17), 248 (M^+ , 46), 221 (33), 220 (22), 219 (100), 206 (24), 205 (32), 191 (39), 179 (29), 178 (35), 177 (67), 165 (21), 149 (37), 141 (29), 139 (25), 128 (52), 127 (53), 126 (23), 115 (31), 77 (25), 75 (29), 63 (33), 55 (21), 51 (24). Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89; Cl, 14.25. Found: C, 72.20; H, 6.74; Cl, 14.51.

2,3-Dipropyl-5-trifluoromethylinden-1-one (34) yellow oil. R_f 0.32 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.94 (t, J = 7.4 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H), 1.50 (tq, J = 7.4 Hz, 7.6 Hz, 2H), 1.65 (tq, J = 7.4 Hz, 7.7 Hz, 2H), 2.27 (t, J = 7.6 Hz, 2H), 2.56 (t, J = 7.7 Hz, 2H), 7.21 (s, 1H), 7.42-7.48 (c, 2H). ^{13}C NMR ($CDCl_3$) δ : 14.1, 14.3, 21.1, 22.4, 24.9, 28.2, 115.5 (q, J = 3.4 Hz), 121.4, 123.7 (q, J = 271.1 Hz), 125.6 (q, J = 4.3 Hz), 133.8 (q, J = 1.0 Hz), 134.7 (q, J = 31.7 Hz), 136.4, 146.4, 157.3, 197.0. IR (neat): 2964 m, 2935 w, 2873 w, 1714 s, 1618 w, 1464 w, 1429 m, 1379 m, 1317 s, 1269 w, 1171 m, 1130 s, 1057 m, 912 w, 893 w, 849 w, 793 w, 729 w, 685 w. MS, m/z (relative intensity, %): 283 ($M^+ + 1$, 13), 282 (M^+ , 47), 254 (22), 253 (100), 240 (29), 239 (27), 225 (51), 212 (30), 211 (94), 183 (42), 182 (15), 177 (46), 151 (15), 146 (16), 141 (20), 133 (23), 128 (32), 115 (21), 55 (31), 51 (20). Exact Mass Calcd for $C_{16}H_{17}F_3O$: 282.1231. Found: 282.1239.

1-Bromo-2-(dimethylphenylsilyl)ethynylbenzene (44) colorless oil. R_f 0.37 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.53 (s, 6H), 7.18 (dt, J = 1.9 Hz, 7.8 Hz, 1H), 7.26 (dt, J = 1.4 Hz, 7.6 Hz, 1H), 7.34-7.44 (c, 3H), 7.54 (dd, J = 1.9 Hz, 7.6 Hz, 1H), 7.58 (dd, J = 1.4 Hz, 8.1 Hz, 1H), 7.73-7.76 (c, 2H). ^{13}C NMR ($CDCl_3$) δ : -0.6, 97.5, 104.7, 125.1, 125.9, 127.0, 128.0, 129.6, 129.8, 132.5, 133.8, 133.9, 136.7. IR (neat): 3068 w, 2962 w, 2164 m, 1466 m, 1429 m, 1252 m, 1221 w, 1117 m, 1047 w, 1028 w, 850 s, 810 m, 783 m, 756 s, 733 m, 702 m, 675 w, 656 w, 607 w, 550 w. MS, m/z (relative intensity, %): 316 ($M^+ + 1$, 6), 315 (M^+ , 6), 314 ($M^+ - 1$, 7), 302 (23), 301 (99), 300 (22), 299 (100), 235 (19), 234 (60), 233 (27), 220 (15), 219 (73), 218 (13), 217 (42), 207 (13), 205 (13), 204 (13), 201 (33), 199 (33), 193 (16), 192 (66), 191 (37), 189 (10), 178 (11), 165 (12), 129 (18), 128 (10), 117 (12), 115 (20), 109 (18), 107 (16), 105 (25), 103 (12), 91 (18), 78 (11), 77 (18), 53 (21), 51 (11). Exact Mass Calcd for $C_{16}H_{15}BrSi$: 314.0126. Found: 314.0121.

3-Phenyl-2-dimethylphenylsilylinden-1-one (45) yellow oil. R_f 0.14 (hexane/EtOAc = 20/1). 1H NMR ($CDCl_3$) δ : 0.29 (s, 6H), 6.91 (d, J = 6.2 Hz, 1H), 7.26-7.30 (c, 7H), 7.35-7.37 (c, 3H), 7.49-7.52 (c, 3H). ^{13}C NMR ($CDCl_3$) δ : -1.8, 121.0, 122.4, 127.6, 127.7, 128.2, 128.9, 129.1, 129.3, 132.3, 132.9, 133.0, 133.9, 134.5, 138.3, 147.0, 171.6, 201.6. IR (neat): 1699 s, 1547 w, 1489 w, 1456 w, 1427 w, 1298 w, 1252 w, 1182 w, 1095 w, 1030 w, 833 m, 773 w, 719 m, 702 m, 654 w. MS, m/z (relative intensity, %): 341 ($M^+ + 1$, 30), 340 (M^+ , 100), 339 ($M^+ - 1$, 38), 326 (13), 325 (41), 265 (11), 263 (23), 248 (18), 247 (75), 217 (10), 202 (19). Exact Mass Calcd for $C_{23}H_{20}OSi$: 340.1283. Found: 340.1289.

1-Chloro-2-(dimethylphenylsilylethynyl)benzene (46) colorless oil. *R_f* 0.57 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.28 (s, 9H), 7.16-7.24 (c, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (CDCl₃) δ: 0.2, 100.3, 101.4, 123.1, 126.3, 129.2, 129.5, 133.6, 136.2. IR (neat): 3068 w, 2960 m, 2900 w, 2164 m, 1952 w, 1923 w, 1890 w, 1589 w, 1562 w, 1470 s, 1433 m, 1252 s, 1223 m, 1130 w, 1059 m, 1034 m, 945 w, 868 s, 845 s, 756 s, 696 m, 642 m, 555 w. MS, *m/z* (relative intensity, %): 208 (*M*⁺, 20), 195 (35), 194 (16), 193 (100), 131 (10), 129 (10), 115 (30), 97 (14), 65 (11), 63 (23). Exact Mass Calcd for C₁₁H₁₃ClSi: 208.0475. Found: 208.0465.

3-(4-Methylphenyl)-2-trimethylsilanylinden-1-one (47) yellow oil. *R_f* 0.34 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.06 (s, 9H), 2.44 (s, 3H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.23-7.29 (c, 6H), 7.48 (d, *J* = 6.8 Hz, 1H). ¹³C NMR (CDCl₃) δ: 0.1, 21.6, 121.0, 122.3, 127.8, 129.1, 129.2, 132.1, 132.7, 133.0, 134.5, 139.3, 147.4, 171.1, 202.0. IR (neat): 2954 w, 2360 m, 1697 s, 1610 w, 1550 w, 1502 w, 1454 w, 1410 w, 1298 m, 1248 m, 1182 w, 1093 m, 866 m, 845 m, 798 w, 760 w, 719 w, 692 w, 615 w. MS, *m/z* (relative intensity, %): 292 (*M*⁺, 35), 278 (26), 277 (100), 261 (25), 218 (11), 203 (16), 202 (18), 189 (11), 139 (15), 131 (19), 75 (11). Exact Mass Calcd for C₁₉H₂₀OSi: 292.1283. Found: 292.1285.

3-(2-Methylphenyl)-2-trimethylsilanylinden-1-one (48) yellow solid. *R_f* 0.31 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: -0.05 (s, 9H), 2.19 (s, 3H), 6.59 (dd, *J* = 2.5 Hz, 5.4 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.19-7.29 (c, 5H), 7.44-7.47 (m, 1H). ¹³C NMR (CDCl₃) δ: -0.5, 20.0, 120.8, 122.3, 125.8, 127.7, 128.7, 129.2, 130.2, 132.1, 133.3, 134.9, 135.0, 135.3, 147.4, 171.3, 201.9. IR (KBr): 2951 w, 1693 s, 1595 m, 1552 m, 1479 w, 1454 m, 1350 w, 1296 m, 1284 m, 1246 m, 1173 w, 1084 m, 1041 w, 1007 w, 862 m, 845 s, 804 w, 760 s, 721 m, 696 w, 632 w, 607 w. MS, *m/z* (relative intensity, %): 293 (*M*⁺+1, 13), 292 (*M*⁺, 55), 291 (*M*⁺-1, 23), 278 (26), 277 (100), 263 (18), 261 (17), 218 (16), 217 (14), 215 (16), 204 (15), 203 (83), 202 (69), 201 (14), 191 (10), 189 (25), 165 (11), 75 (50), 73 (54), 59 (67). Exact Mass Calcd for C₁₉H₂₀OSi: 292.1283. Found: 292.1281.

3-(3-Methoxyphenyl)-2-trimethylsilanylinden-1-one (50) yellow oil. *R_f* 0.09 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.07 (s, 9H), 3.86 (s, 3H), 6.89-7.00 (c, 4H), 7.26-7.33 (c, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 6.2 Hz, 1H). ¹³C NMR (CDCl₃) δ: 0.1, 13.2, 55.5, 114.6, 120.1, 120.9, 122.3, 129.1, 129.6, 132.3, 133.3, 134.7, 136.3, 147.1, 159.5, 170.5, 201.6. IR (neat): 2954 m, 2898 w, 2835 w, 1699 s, 1599 m, 1549 m, 1483 m, 1458 m, 1427 m, 1352 w, 1300 m, 1244 s, 1174 w, 1142 w, 1092 m, 1045 m, 962 w, 868 s, 847 s, 791 m, 760 m, 717 m, 700 w, 631 w. MS, *m/z* (relative intensity, %): 309 (*M*⁺+1, 12), 308 (*M*⁺, 46), 294 (26), 293 (100), 278 (11), 277 (40), 247 (10). Exact Mass Calcd for C₁₉H₂₀O₂Si: 308.1233. Found: 308.1239.

3-(3-Nitrophenyl)-2-trimethylsilanylinden-1-one (51) yellow oil. *R_f* 0.14 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.07 (s, 9H), 6.82 (dd, *J* = 2.0 Hz, 5.8 Hz, 1H), 7.27-7.37 (c, 2H), 7.54 (dd, *J* = 2.2 Hz, 5.9 Hz, 1H), 7.70 (dd, *J* = 1.4 Hz, 4.1 Hz, 2H), 8.26 (d, *J* = 1.4 Hz, 1H), 8.32-8.36 (m, 1H). ¹³C NMR (CDCl₃) δ: -0.0, 120.6, 123.01, 123.03, 124.1, 129.8, 129.9, 132.0, 133.5, 133.9, 136.9, 137.0, 146.6, 148.3, 167.3, 201.0. IR (neat): 3076 w, 2956 w, 1703 s, 1601 w, 1529 s, 1456 w, 1348 s, 1292 m, 1250 m, 1184 w, 1101 m, 1082 m, 955 w, 910 w, 843 s, 800 m, 764 m, 739 w, 700 m, 631 w, 606 w. MS, *m/z* (relative intensity, %): 324 (M⁺+1, 15), 323 (M⁺, 70), 309 (23), 308 (91), 263 (23), 262 (55), 261 (29), 249 (10), 248 (24), 247 (100), 219 (14), 218 (15), 217 (22), 204 (10), 203 (19), 202 (43), 201 (20), 189 (20), 176 (11), 123 (20), 109 (11), 75 (18), 73 (12). Exact Mass Calcd for C₁₈H₁₇NO₃Si: 323.0978. Found: 323.0974.

3-(4-Chlorophenyl)-2-trimethylsilanylinden-1-one (52) yellow solid. *R_f* 0.31 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.06 (s, 9H), 6.85 (d, *J* = 6.4 Hz, 1H), 7.25-7.33 (c, 4H), 7.46-7.51 (c, 3H). ¹³C NMR (CDCl₃) δ: 0.0, 120.8, 122.6, 128.9, 129.3, 129.4, 132.4, 133.2, 133.6, 135.3, 135.5, 147.1, 169.3, 201.6. IR (KBr): 2958 w, 1693 s, 1595 w, 1541 w, 1481 w, 1454 w, 1398 w, 1363 w, 1298 w, 1244 w, 1174 w, 1092 m, 1012 w, 862 m, 845 m, 795 w, 756 w, 719 w, 638 w, 611 w. MS, *m/z* (relative intensity, %): 314 (M⁺+1, 10), 312 (M⁺-1, 26), 299 (37), 298 (24), 297 (100), 281 (18), 277 (17), 203 (16), 202 (20), 189 (14), 176 (11), 131 (12), 75 (10), 73 (10), 62 (18). Anal. Calcd for C₁₈H₁₇ClOSi: C, 69.10; H, 5.48; Cl, 11.33; O, 5.11. Found: C, 68.92; H, 5.36; Cl, 11.68.

3-(4-Formylphenyl)-2-trimethylsilanylinden-1-one (53) yellow solid. *R_f* 0.14 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.05 (s, 9H), 6.81 (d, *J* = 6.4 Hz, 1H), 7.26-7.32 (c, 2H), 7.52-7.55 (c, 3H), 8.01 (d, *J* = 8.0 Hz, 2H), 10.10 (s, 1H). ¹³C NMR (CDCl₃) δ: -0.2, 120.8, 122.9, 128.7, 129.6, 123.0, 132.2, 133.5, 136.3, 136.9, 141.6, 147.0, 168.9, 191.9, 201.5. IR (KBr): 2949 w, 2831 w, 2736 w, 1699 s, 1611 m, 1549 m, 1495 w, 1456 w, 1365 w, 1298 m, 1284 w, 1250 m, 1205 m, 1184 m, 1092 m, 1011 w, 870 s, 847 s, 796 m, 754 m, 714 m, 611 w. MS, *m/z* (relative intensity, %): 307 (M⁺+1, 11), 306 (M⁺, 49), 292 (25), 291 (100), 278 (10), 277 (19), 263 (25), 248 (10), 247 (39), 218 (11), 217 (35), 204 (12), 203 (27), 202 (31), 201 (14), 189 (19), 176 (11), 145 (46), 123 (21), 75 (11), 73 (13), 59 (10), 53 (11). Anal. Calcd for C₁₉H₁₈O₂Si: C, 74.47; H, 5.92. Found: C, 74.25; H, 5.81.

3-(4-Trifluoromethylphenyl)-2-trimethylsilanylinden-1-one (54) yellow oil. *R_f* 0.20 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.05 (s, 9H), 6.79-6.82 (m, 1H), 7.25-7.35 (c, 2H), 7.47-7.53 (c, 3H), 7.76 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (CDCl₃) δ: -0.1, 120.7, 122.8, 124.1 (q, *J* = 271.6 Hz), 125.6 (q, *J* = 3.4 Hz), 128.3, 129.5, 131.3 (q, *J* = 33.0 Hz), 132.1, 133.4, 136.2, 139.0, 147.0, 168.8, 201.4. IR (neat): 1702 s, 1556 m, 1456 w, 1410 m, 1327 s, 1250 m, 1173 s, 1132 s, 1066 m, 1018 m, 930 w, 868 m, 845 m, 800 w, 756 m, 717 w, 694 w, 613 w, 505 w. MS, *m/z* (relative intensity, %): 347 (M⁺+1, 8), 346 (M⁺, 31), 332 (23), 331 (100), 315

(19), 202 (8). Exact Mass Calcd for C₁₉H₁₇F₃OSi: 346.1001. Found: 346.1003.

3-(2-Naphthyl)-2-trimethylsilylinden-1-one (55) yellow solid. *R_f* 0.37 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.07 (s, 9H), 6.93 (d, *J* = 6.8 Hz, 1H), 7.24-7.33 (c, 2H), 7.46-7.58 (c, 4H), 7.85-7.97 (c, 4H). ¹³C NMR (CDCl₃) δ: 0.1, 121.1, 122.5, 125.6, 126.8, 127.0, 127.2, 128.1, 128.3, 128.4, 129.3, 132.6, 132.7, 133.0, 133.2, 133.6, 135.2, 147.4, 170.8, 202.0. IR (KBr): 2360 w, 1697 s, 1661 w, 1547 m, 1502 w, 1456 w, 1362 w, 1294 m, 1246 m, 1196 w, 1178 w, 1122 w, 1090 m, 968 w, 868 m, 845 m, 802 w, 756 m, 717 w, 694 w, 625 w. MS, *m/z* (relative intensity, %): 329 (M⁺+1, 14), 328 (M⁺, 46), 314 (28), 313 (100), 298 (10), 297 (30), 269 (10), 254 (22), 253 (19), 252 (21), 239 (15), 207 (14), 75 (11), 73 (11). Exact Mass Calcd for C₂₂H₂₀OSi: 328.1283. Found: 328.1288.

1-Bromo-4-methoxy-2-(trimethylsilyl)ethynylbenzene (56) colorless oil. *R_f* 0.37 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.28 (s, 9H), 3.78 (s, 3H), 6.75 (dd, *J* = 3.0 Hz, 8.9 Hz, 1H), 7.01 (d, *J* = 3.0 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 0.1, 55.6, 99.4, 103.1, 116.5, 116.8, 118.0, 125.7, 133.0, 158.3. IR (neat): 2962 w, 2873 w, 1335 m, 1173 w, 1134 m, 1084 w, 827 w, 521 m. MS, *m/z* (relative intensity, %): 284 (M⁺+1, 36), 282 (M⁺-1, 36), 270 (16), 269 (96), 268 (16), 267 (100), 145 (13), 135 (14), 134 (15), 128 (12), 115 (10). Exact Mass Calcd for C₁₂H₁₅BrOSi: 282.0076. Found: 282.0078.

1-Bromo-5-chloro-2-(trimethylsilyl)ethynylbenzene (57) colorless oil. *R_f* 0.54 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.27 (s, 9H), 7.21-7.26 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H). ¹³C NMR (CDCl₃) δ: 0.1, 100.9, 102.1, 123.9, 126.2, 127.4, 132.2, 134.1, 134.7. IR (neat): 3087 w, 2960 m, 2898 w, 2164 s, 1579 m, 1543 w, 1466 s, 1431 w, 1410 w, 1375 m, 1327 w, 1254 s, 1221 m, 1097 s, 1043 m, 876 s, 762 s, 727 s, 702 m, 661 w, 625 w, 561 w, 467 w. MS, *m/z* (relative intensity, %): 288 (M⁺+1, 21), 286 (M⁺-1, 16), 275 (28), 274 (15), 273 (100), 272 (13), 271 (78), 137 (10), 129 (10), 128 (27), 127 (18), 114 (13), 113 (12), 109 (10), 107 (10), 78 (13), 77 (10), 65 (10), 63 (27). Exact Mass Calcd for C₁₁H₁₂BrClSi: 285.9580. Found: 285.9593.

6-Chloro-3-phenyl-2-trimethylsilylinden-1-one (58) yellow oil. *R_f* 0.31 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.05 (s, 9H), 6.82 (d, *J* = 7.6 Hz, 1H), 7.25-7.28 (m, 1H), 7.32-7.35 (c, 2H), 7.44-7.49 (c, 4H). ¹³C NMR (CDCl₃) δ: 0.0, 121.7, 122.9, 127.6, 128.6, 129.4, 132.3, 134.1, 134.5, 135.2, 135.4, 145.3, 170.3, 200.1. IR (neat): 2954 w, 2897 w, 1702 s, 1599 w, 1547 m, 1485 w, 1458 w, 1415 m, 1333 w, 1294 m, 1250 m, 1176 m, 1103 m, 1057 w, 1030 w, 918 w, 868 s, 847 s, 787 w, 769 m, 754 m, 702 m, 511 w, 490 w, 434 w. MS, *m/z* (relative intensity, %): 312 (M⁺, 22), 299 (37), 298 (24), 297 (100), 283 (15), 281 (36), 278 (14), 277 (57), 202 (17), 189 (10). Exact Mass Calcd for C₁₈H₁₇ClOSi: 312.0737. Found: 312.0710.

1-Bromo-5-trifluoromethyl-2-(trimethylsilylethynyl)benzene (59)

colorless oil. *R_f* 0.60 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.29 (s, 9H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.83 (s, 1H). ¹³C NMR (CDCl₃) δ: 0.2, 101.8, 103.0, 123.0 (q, *J* = 271.9 Hz), 123.8 (q, *J* = 3.7 Hz), 125.0, 126.0, 129.0 (d, *J* = 1.1 Hz), 129.4 (q, *J* = 3.9 Hz), 131.2 (q, *J* = 33.1 Hz), 133.7. IR (neat): 2964 w, 2902 w, 2166 w, 1608 w, 1487 w, 1390 m, 1323 s, 1257 m, 1176 m, 1138 s, 1080 m, 1049 w, 872 m, 845 s, 764 w, 696 w, 654 w, 604 w, 561 w, 469 w. MS, *m/z* (relative intensity, %): 322 (*M*⁺+1, 11), 320 (*M*⁺-1, 11), 308 (16), 307 (93), 306 (17), 305 (100), 240 (15), 164 (16), 125 (10), 113 (10), 99 (10). Exact Mass Calcd for C₁₂H₁₂BrF₃Si: 319.9844. Found: 319.9865.

6-Trifluoromethyl-3-phenyl-2-trimethylsilylinden-1-one (60)

yellow oil. *R_f* 0.34 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.07 (s, 9H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.33-7.37 (c, 2H), 7.49-7.51 (c, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H). ¹³C NMR (CDCl₃) δ: -0.2, 119.2 (q, *J* = 3.6 Hz), 120.9, 124.0 (q, *J* = 271.80 Hz), 127.7, 128.8, 129.7, 130.4 (q, *J* = 3.9 Hz), 131.4 (q, *J* = 32.6 Hz), 133.0, 134.4, 137.6, 150.4, 169.8, 199.9. IR (neat): 2958 w, 1705 s, 1624 m, 1599 w, 1549 m, 1489 w, 1390 w, 1323 s, 1300 m, 1257 m, 1173 s, 1130 s, 1113 m, 1080 w, 1049 w, 918 w, 870 m, 849 m, 785 w, 758 w, 735 w, 702 w. MS, *m/z* (relative intensity, %): 346 (*M*⁺, 29), 332 (23), 331 (100), 316 (10), 315 (43), 202 (15), 75 (10). Exact Mass Calcd for C₁₉H₁₇F₃OSi: 346.1001. Found: 346.1079.

3,3-Dimethyl-1-(2-bromophenyl)-1-phenyl-1-butene (62)

colorless oil. *R_f* 0.57 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: [0.97 (s, 9H, A), 1.01 (s, 9H, B)], [6.11 (s, 1H, A), 6.17 (s, 1H, B)], 7.16-7.36 (c, 8H, A), 7.57 (d, *J* = 7.8 Hz, 1H, Ar). ¹³C NMR (CDCl₃) δ: [30.7 (A), 31.7 (B)], 34.5 (A), 124.9, 126.24, 126.65, 126.69, 126.77, 127.4, 128.1, 128.7, 128.8, 128.9, 131.0, 132.1, 132.4, 132.8, 137.1, 140.7, 141.5, 142.0. IR (neat): 3057 m, 3022 w, 2958 s, 2902 m, 2866 m, 1597 w, 1560 w, 1466 m, 1363 m, 1252 w, 1192 w, 1159 w, 1117 w, 1076 w, 1028 m, 957 w, 895 w, 752 s, 696 m, 658 w, 638 w, 580 w, 503 w. MS, *m/z* (relative intensity, %): 316 (*M*⁺+1, 23), 314 (*M*⁺-1, 23), 301 (46), 299 (47), 221 (21), 220 (100), 205 (48), 143 (21), 105 (21), 101 (25), 91 (30). Exact Mass Calcd for C₁₈H₁₉Br: 314.0670. Found: 314.0675.

1-Bromo-2-(dimethylphenylsilylethynyl)benzene (63)

white solid. *R_f* 0.20 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 3.86 (s, 3H), 7.29-7.35 (m, 2H), 7.58-7.64 (m, 2H). ¹³C NMR (CDCl₃) δ: 53.1, 84.1, 84.3, 122.1, 126.5, 127.3, 131.8, 132.8, 134.9, 154.2. IR (KBr): 2227 m, 1709 s, 1579 w, 1468 m, 1429 m, 1302 s, 1275 w, 1252 m, 1203 s, 1176 m, 1117 w, 1051 w, 1026 w, 995 w, 881 w, 764 m, 742 m, 712 w, 663 w, 602 w, 565 w. MS, *m/z* (relative intensity, %): 240 (*M*⁺+1, 37), 238 (*M*⁺-1, 33), 209 (95), 207 (100), 182 (43), 180 (47), 128 (41), 101 (23), 100 (54), 99 (27), 98 (18), 75 (16), 74 (80), 50 (18). Exact Mass Calcd for C₁₀H₁₇BrO₂: 237.9629. Found: 237.9620.

1-Bromo-5-methyl-2-(trimethylsilylethynyl)benzene (65)

colorless oil. *R_f* 0.49 (hexane/EtOAc = 20/1). ¹H NMR (CDCl₃) δ: 0.27 (s, 9H), 2.32

(s, 3H), 7.03 (dd, $J = 0.7$ Hz, 8.0 Hz, 1H), 7.35-7.39 (m, 2H). ^{13}C NMR (CDCl_3) δ : 0.2, 21.3, 98.6, 103.3, 122.2, 125.5, 127.8, 132.8, 133.2, 140.1. IR (neat): 3060 w, 3032 w, 2960 s, 2898 m, 2164 s, 1601 m, 1483 s, 1446 m, 1392 m, 1252 s, 1228 s, 1043 s, 951 m, 879 s, 854 s, 820 s, 760 s, 702 m, 675 w, 633 m, 561 m, 540 w, 467 w, 417 w. MS, m/z (relative intensity, %): 268 ($\text{M}^+ + 1$, 26), 266 ($\text{M}^+ - 1$, 26), 254 (16), 253 (100), 252 (17), 251 (100), 129 (21), 128 (24), 86 (30), 72 (16). Exact Mass Calcd for $\text{C}_{12}\text{H}_{15}\text{BrSi}$: 266.0126. Found: 266.0186.

3-(2-Bromo-4-methylphenyl)-2-trimethylsilylinden-1-one (67) yellow oil. R_f 0.23 (hexane/EtOAc = 20/1). ^1H NMR (CDCl_3) δ : 0.02 (s, 9H), 2.42 (s, 3H), 6.68 (dd, $J = 1.9$ Hz, 6.2 Hz, 1H), 7.10 (d, $J = 8.1$ Hz, 1H), 7.19-7.31 (c, 3H), 7.48-7.51 (c, 2H). ^{13}C NMR (CDCl_3) δ : -0.6, 21.2, 120.9, 121.5, 122.3, 128.2, 129.0, 129.1, 131.8, 133.2, 133.3, 133.5, 136.1, 140.5, 146.8, 169.5, 201.5. IR (neat): 2954 m, 2898 w, 1701 s, 1604 m, 1558 m, 1481 m, 1454 w, 1383 w, 1352 w, 1298 m, 1248 m, 1178 m, 1097 m, 1039 w, 1009 w, 864 s, 845 s, 796 m, 756 m, 719 m, 696 w, 644 w, 615 w, 486 w, 440 w. MS, m/z (relative intensity, %): 372 ($\text{M}^+ + 1$, 16), 370 ($\text{M}^+ - 1$, 16), 358 (23), 357 (96), 356 (24), 355 (100), 291 (15), 277 (12), 276 (48), 275 (24), 262 (15), 261 (61), 247 (16), 233 (10), 232 (12), 231 (11), 217 (25), 216 (14), 215 (20), 202 (23), 189 (19), 139 (13), 137 (14), 73 (10). Exact Mass Calcd for $\text{C}_{19}\text{H}_{19}\text{BrOSi}$: 370.0389. Found: 370.0347.

2-(1-Phenyl-pentylidene)-indan-1,3-dione (71) yellow solid. R_f 0.14 (hexane/EtOAc = 20/1). ^1H NMR (CDCl_3) δ : 0.92 (q, $J = 6.8$ Hz, 3H), 1.42-1.48 (c, 4H), 3.31 (t, $J = 7.4$ Hz, 2H), 7.25-7.31 (c, 2H), 7.42-7.46 (c, 3H), 7.73-7.83 (c, 3H), 7.94-7.97 (m, 1H). ^{13}C NMR (CDCl_3) δ : 13.9, 23.0, 30.8, 35.7, 122.6, 122.8, 126.6, 127.3, 127.6, 129.0, 134.7, 134.8, 139.1, 140.5, 141.1, 171.4, 188.4, 191.2. IR (KBr): 2956 w, 2927 w, 1720 m, 1687 s, 1614 m, 1591 m, 1489 w, 1460 w, 1437 w, 1350 w, 1327 w, 1240 m, 1227 m, 1161 w, 1068 w, 1030 w, 985 w, 924 w, 768 w, 735 m, 696 w, 584 w, 550 w, 420 w. MS, m/z (relative intensity, %): 291 ($\text{M}^+ + 1$, 20), 290 (M^+ , 98), 262 (21), 261 (100), 257 (10), 248 (23), 247 (52), 246 (18), 235 (10), 233 (34), 220 (17), 219 (10), 218 (11), 215 (25), 203 (10), 202 (21), 189 (16), 133 (23), 129 (23), 128 (16), 127 (11), 115 (61), 105 (36), 104 (16), 101 (16), 91 (29), 89 (10), 77 (32), 76 (28), 75 (11), 51 (11). Exact Mass Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2$: 290.1307. Found: 290.1314.

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