

## General Methods

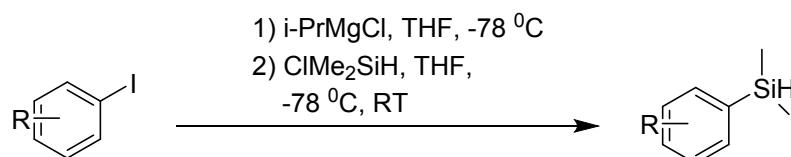
NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for  $\text{CDCl}_3$  were 7.26 ppm ( $^1\text{H}$ -NMR) and 77.0 ppm ( $^{13}\text{C}$ -NMR).  $^{13}\text{CNMR}$  spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25  $\mu\text{m}$  film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

All reactions were carried out under air atmosphere. All the reagents were purchased from Sigma-Aldrich, TCI, abcr or Alfa-Aesar chemical company.

## Typical reaction procedure for the carbonylative synthesis of indenones:

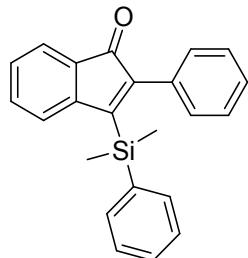
General procedure: Under Ar, a 4 mL screw-cap vial was charged with  $[\text{Cp}^*\text{RhCl}_2]_2$  (4 mol%),  $t\text{-Bubpy}$  (15 mol%), alkyne (0.2 mmol), silane (0.3 mmol), TEMPO (0.8 mmol),  $\text{AgSF}_6$  (20 mol%), *p*-xylene (2 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. Then the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL). At room temperature, the autoclave is flushed with carbon monoxide for three times and 20 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 120 °C for 24 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 80:1).

## Preparation of Various Functionalized silanes<sup>[1]</sup>



$i\text{PrMgCl}$  (4.26 mL of 2 M solution in THF, 8.52 mmol, 1.3 equiv.) was slowly added to a cooled solution of aryl iodide (6.55 mmol) in THF (15 mL). After 30 min, the solution was slowly added a cooled solution of chlorodimethylsilane (1.09 mL, 9.82 mmol, 1.5 equiv.) in THF (15 mL). The reaction mixture was allowed to warm to RT over 4 h. The crude mixture was quenched with  $\text{NH}_4\text{Cl}$  aq. at 0 °C and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was dried over  $\text{MgSO}_4$  and concentrated under reduced pressure to give silanes as yellow oil.

### **3-(Dimethyl(phenyl)silyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.45-7.31 (m, 2H), 7.23 (ddd, *J* = 7.0, 1.3, 0.6 Hz, 1H), 7.20-7.12 (m, 6H), 7.09-7.00 (m, 4H), 6.85-6.76 (m, 1H), 0.07 (s, 6H).

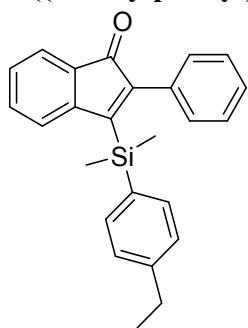
<sup>13</sup>C NMR (75 MHz, DMSO) δ 195.04, 152.39, 146.58, 146.07, 134.88, 132.77, 131.88, 130.93, 127.81, 127.75, 127.25, 126.48, 126.46, 126.34, 125.85, 121.88, 120.96, -3.29.

<sup>29</sup>Si NMR (60 MHz, DMSO) δ -11.36.

GC-MS(EI-70eV): m/z(%)=340(79), 263(18), 247(27), 205(30), 176(58), 135(100), 105(44).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>23</sub>H<sub>20</sub>OSi:340.1283, found[M]<sup>+</sup>: 340.1278.

### **3-((4-Ethylphenyl)dimethylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.62-7.57 (m, 2H), 7.32-7.30 (m, 1H), 7.29-7.26 (m, 1H), 7.19-7.08 (m, 5H), 6.97-6.90 (m, 2H), 6.89-6.81 (m, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.44 (s, 6H).

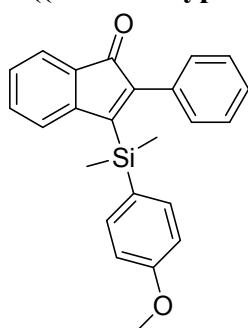
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 191.60, 150.30, 144.48, 140.97, 133.86, 133.36, 132.32, 129.31, 129.15, 128.53, 127.38, 126.66, 126.42, 126.08, 125.65, 125.39, 124.66, 27.50, 13.96, -0.85.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.59.

GC-MS(EI-70eV): m/z(%)=368(50), 339(100), 247(29), 205(28), 163(53), 151(21), 133(17).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>25</sub>H<sub>24</sub>OSi:368.1596, found[M+H]<sup>+</sup>: 369.1665.

### **3-((4-Methoxyphenyl)dimethylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.38-7.32 (m, 3H), 7.23-7.19 (m, 3H), 7.15-7.08 (m, 4H), 6.83 (dt, *J* = 7.3, 0.8 Hz, 1H), 6.80-6.76 (m, 2H), 3.70 (s, 3H), 0.17 (s, 6H).

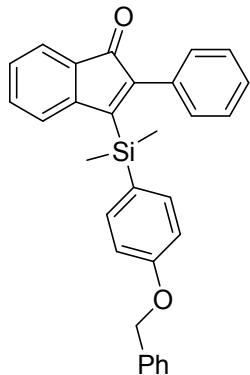
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.60, 161.65, 155.81, 149.84, 149.55, 136.26, 134.96, 133.91, 130.78, 130.66, 130.22, 129.19, 128.81, 128.68, 124.66, 123.94, 114.86, 55.95, 0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.79.

GC-MS(EI-70eV): m/z(%)=370(100), 339(30), 247(38), 205(16), 176(52), 165(56).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>Si:370.1389, found[M+Na]<sup>+</sup>: 393.1283.

**3-((4-(BenzylOxy)phenyl)dimethylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.51-7.32 (m, 6H), 7.17-7.12 (m, 3H), 7.07 (dd, *J* = 8.0, 2.8 Hz, 3H), 6.97-6.91 (m, 2H), 6.84 (dd, *J* = 7.9, 1.6 Hz, 2H), 5.13 (s, 2H), 0.44 (s, 6H).

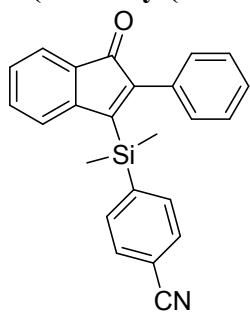
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 192.34, 165.63, 159.46, 151.03, 141.72, 136.22, 134.85, 134.63, 134.54, 129.45, 129.29, 128.57, 128.04, 127.45, 127.17, 126.92, 126.85, 126.42, 126.16, 125.43, 69.26, -0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.69.

GC-MS(EI-70eV): m/z(%)=446(82), 357(24), 207(15), 135(33), 91(100), 77(16).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>28</sub>O<sub>2</sub>Si:446.1702, found[M+Na]<sup>+</sup>: 469.1748.

**4-(Dimethyl(1-oxo-2-phenyl-1*H*-inden-3-yl)silyl)benzonitrile**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.43-7.33 (m, 2H), 7.28-7.15 (m, 7H), 6.95 (ddd, *J* = 19.4, 8.1, 1.7 Hz, 4H), -0.00 (s, 6H).

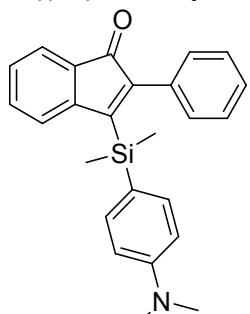
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.16, 164.36, 154.14, 146.05, 141.06, 138.09, 136.30, 134.65, 132.92, 132.04, 131.83, 130.47, 130.10, 130.00, 129.92, 129.40, 129.05, 114.70, -0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.47.

GC-MS(EI-70eV): m/z(%)=365(90), 350(60), 332(15), 263(22), 247(22), 176(100), 160(80), 151(50), 130(38), 91(23).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>24</sub>H<sub>19</sub>NOSi:365.1236, found[M+H]<sup>+</sup>: 366.1225.

**3-((4-(Dimethylamino)phenyl)dimethylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.31 (ddd, *J* = 6.9, 1.4, 0.6 Hz, 1H), 7.28-7.24 (m, 2H), 7.19-7.16 (m, 3H), 7.11-7.07 (m, 3H), 7.02-6.97 (m, 1H), 6.90-6.80 (m, 1H), 6.57 (d, *J* = 8.7 Hz, 2H), 2.81 (s, 6H), 0.10 (s, 6H).

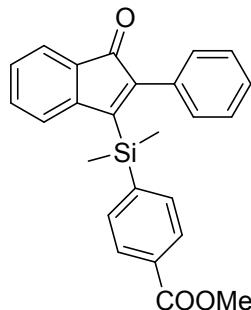
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.71, 156.52, 149.67, 149.43, 135.83, 134.86, 134.01, 130.75, 130.64, 129.02, 128.59, 128.57, 124.72, 123.72, 112.96, 40.97, -0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -12.26.

GC-MS(EI-70eV): m/z(%)=383(M<sup>+</sup>, 100), 368(13), 339(17), 247(30), 205(21), 178(49), 151(28), 134(24), 77(14).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>25</sub>H<sub>25</sub>NOSi:383.1705, found[M+H]<sup>+</sup>: 384.1780.

### Methyl 4-(dimethyl(1-oxo-2-phenyl-1*H*-inden-3-yl)silyl)benzoate



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 8.05-7.95 (m, 2H), 7.70-7.61 (m, 2H), 7.13-6.99 (m, 5H), 6.87 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.81-6.72 (m, 2H), 3.89 (s, 3H), 0.41 (s, 6H).

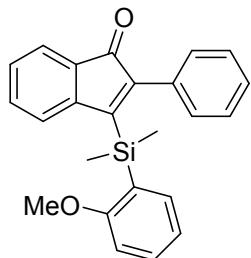
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 191.30, 165.85, 162.94, 150.42, 143.39, 140.78, 134.05, 132.98, 132.39, 129.73, 128.63, 128.22, 127.85, 126.73, 126.44, 126.05, 125.69, 125.07, 51.04, -0.99.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.84.

GC-MS(EI-70eV): m/z(%)=398(67), 383(46), 339(100), 263(25), 205(31), 193(74), 176(73), 151(16), 134(24), 119(42), 105(29).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>25</sub>H<sub>22</sub>O<sub>3</sub>Si:398.1338, found[M+H]<sup>+</sup>: 399.1416.

### 3-((2-Methoxyphenyl)dimethylsilyl)-2-phenyl-1*H*-inden-1-one



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.39-7.30 (m, 3H), 7.25- 7.17 (m, 3H), 7.14-7.00 (m, 4H), 7.017-7.04 (m, 1H), 6.77-6.84 (m, 3H), 3.70 (s, 3H), 0.17 (s, 6H).

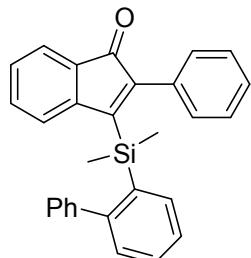
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 193.16, 167.61, 163.37, 150.81, 142.40, 134.65, 131.73, 129.91, 129.75, 127.44, 127.30, 126.82, 125.84, 123.50, 121.12, 109.99, 55.01, 0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -13.01.

GC-MS(EI-70eV): m/z(%)=370(100), 355(18), 339(28), 247(35), 205(16), 176(52), 165(56), 151(21), 135(22).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>Si:370.1389, found[M+H]<sup>+</sup>: 371.1456.

### 3-([1,1'-Biphenyl]-2-yldimethylsilyl)-2-phenyl-1*H*-inden-1-one



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.58 (ddd, *J* = 6.5, 2.1, 0.6 Hz, 1H), 7.36-7.20 (m, 3H), 7.20-6.78 (m, 13H), 6.47- 6.37 (m, 1H), 0.00 (d, *J* = 0.6 Hz, 6H).

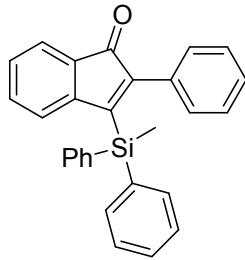
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.98, 155.09, 148.86, 148.16, 146.81, 142.92, 135.75, 134.17, 133.21, 132.26, 129.42, 129.31, 128.87, 128.77, 127.57, 127.18, 127.09, 127.02, 126.72, 126.29, 122.66, 122.18, -0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.62.

GC-MS(EI-70eV): m/z(%)=416(M<sup>+</sup>, 46), 339(11), 195(100), 176(49), 165(30), 152(25), 75(28).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>29</sub>H<sub>24</sub>O<sub>2</sub>Si:416.1596, found[M+H]<sup>+</sup>: 417.1668.

### **3-(Methyldiphenylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.42 (tt, *J* = 6.5, 1.6 Hz, 5H), 7.35-7.21 (m, 6H), 7.18-6.97 (m, 7H), 6.56-6.50 (m, 1H), 0.31 (s, 3H).

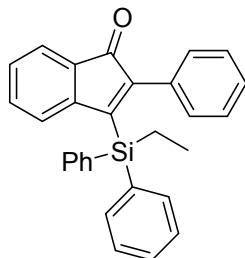
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.96, 153.07, 150.44, 149.18, 135.67, 135.33, 134.53, 132.90, 132.83, 130.23, 130.18, 128.77, 128.64, 128.33, 128.09, 124.79, 123.48, -1.84.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.57.

GC-MS(EI-70eV): m/z(%)=402(60), 387(35), 324(50), 309(25), 205(57), 197(70), 176(100), 151(63), 105(22), 78(30).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>28</sub>H<sub>22</sub>OSi:402.1440, found[M]<sup>+</sup>: 402.1434.

### **3-(Ethyldiphenylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.50-7.38 (m, 5H), 7.36-7.19 (m, 6H), 7.19-7.05 (m, 5H), 7.05-6.96 (m, 2H), 6.61-6.50 (m, 1H), 0.81-0.75 (m, 2H), 0.68 (t, *J* = 7.4 Hz, 3H).

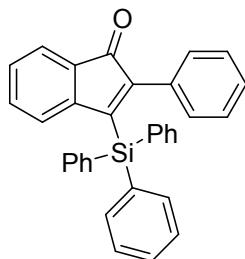
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.51, 152.21, 150.18, 148.79, 135.29, 134.20, 134.02, 132.55, 129.94, 129.76, 129.05, 128.45, 128.14, 127.89, 127.64, 124.63, 122.98, 7.46, 5.80.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -14.07.

GC-MS(EI-70eV): m/z(%)=416(M<sup>+</sup>, 72), 387(79), 338(21), 309(74), 278(13), 265(40), 205(33), 181(100), 151(28), 105(45), 78(27).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>29</sub>H<sub>24</sub>OSi:416.1596, found[M+H]<sup>+</sup>: 417.1668.

### **2-Phenyl-3-(triphenylsilyl)-1*H*-inden-1-one**



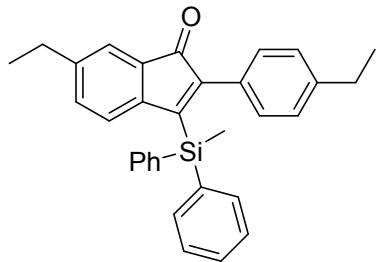
<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.56 (dd, *J* = 8.0, 1.5 Hz, 6H), 7.41-7.26 (m, 9H), 7.24-7.10 (m, 3H), 7.01-6.82 (m, 5H), 6.48 (d, *J* = 7.5 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, DMSO) δ 197.28, 150.98, 149.84, 148.91, 135.93, 134.80, 132.83, 131.53, 130.53, 130.32, 129.90, 129.42, 128.59, 128.16, 127.30, 124.81, 123.28.

GC-MS(EI-70eV): m/z(%)=464(M<sup>+</sup>, 29), 386(45), 309(23), 281(17), 259(100), 205(22), 176(80), 155(19), 105(16), 78(18).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>33</sub>H<sub>24</sub>OSi:464.1596, found[M+H]<sup>+</sup>: 465.1672.

**6-Ethyl-2-(4-ethylphenyl)-3-(methyldiphenylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.47-7.37 (m, 4H), 7.31-7.19 (m, 7H), 6.99-6.77 (m, 5H), 6.41 (d, *J* = 7.5 Hz, 1H), 2.49 (qd, *J* = 7.6, 2.2 Hz, 4H), 1.11 (t, *J* = 7.6 Hz, 6H), 0.34 (s, 3H).

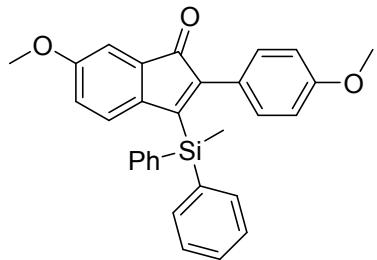
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.62, 152.65, 150.13, 146.85, 144.84, 136.00, 135.46, 133.52, 130.77, 130.40, 130.20, 128.66, 127.67, 124.60, 123.46, 29.25, 29.09, 15.98, 15.79, -1.76.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.60.

GC-MS(EI-70eV): m/z(%)=458(M<sup>+</sup>, 72), 429(71), 365(19), 261(24), 197(100), 165(23), 105(28), 77(11).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>30</sub>OSi:458.2066, found[M+H]<sup>+</sup>: 459.2130.

**6-Methoxy-2-(4-methoxyphenyl)-3-(methyldiphenylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.35-7.25 (m, 4H), 7.23-7.07 (m, 6H), 6.90-6.79 (m, 3H), 6.54-6.42 (m, 2H), 6.36- 6.18 (m, 2H), 3.51 (s, 6H), 0.20 (s, 3H).

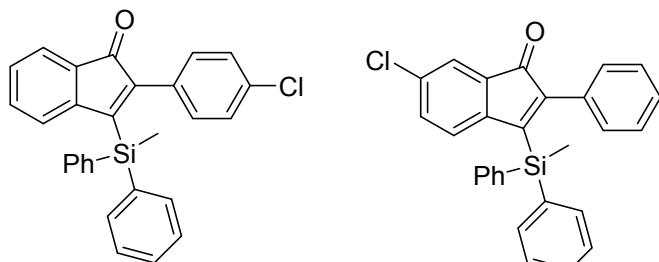
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.02, 162.12, 161.92, 154.69, 150.76, 143.07, 137.75, 137.18, 134.76, 134.04, 133.27, 131.99, 130.45, 127.15, 119.34, 115.46, 112.75, 57.95, 57.49, -0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.57.

GC-MS(EI-70eV): m/z(%)=462(M<sup>+</sup>, 85), 431(24), 265(17), 197(100), 185(16), 151(13), 105(28).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>26</sub>O<sub>3</sub>Si:462.1651, found[M+H]<sup>+</sup>: 463.1724.

**2-(4-chlorophenyl)-3-(methyldiphenylsilyl)-1*H*-inden-1-one and 6-chloro-3-(methyldiphenylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.52 – 7.13 (m, 17H), 7.06 (d, *J* = 2.2 Hz, 2H), 6.74 – 6.64 (m, 1H), 0.56 (s, 3H).

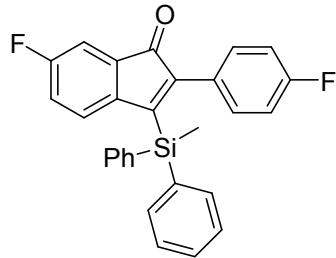
<sup>13</sup>C NMR (75 MHz, DMSO) δ 198.69, 150.37, 150.21, 136.83, 136.51, 135.24, 133.51, 133.00, 132.00, 131.27, 130.70, 130.43, 130.33, 129.57, 126.27, 125.19, 123.46, -0.50, -2.01.

<sup>29</sup>Si NMR (60 MHz, DMSO) δ -16.21.

GC-MS(EI-70eV): m/z(%)=436(38), 401(29), 358(33), 197(100), 176(50), 105(40), 78(25).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>28</sub>H<sub>21</sub>ClOSi:436.1050, found[M+H]<sup>+</sup>: 436.1054.

**6-Fluoro-2-(4-fluorophenyl)-3-(methyldiphenylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 7.9, 1.5 Hz, 4H), 7.34-7.29 (m, 2H), 7.29-7.21 (m, 4H), 7.11 (dd, *J* = 7.1, 2.7 Hz, 1H), 6.97 (dd, *J* = 8.9, 5.5 Hz, 2H), 6.80-6.62 (m, 3H), 6.47 (dd, *J* = 8.2, 4.3 Hz, 1H), 0.39 (s, 3H).

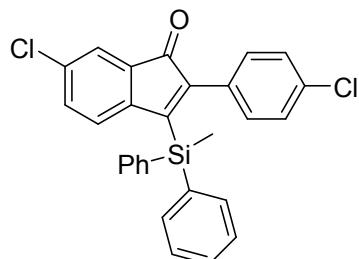
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.37, 161.20(d, *J* = 247.6 Hz), 151.53, 147.36(d, *J* = 4.5 Hz), 142.28 (d, *J* = 3.3 Hz), 133.17, 132.97, 130.25(d, *J* = 7.4 Hz), 129.79(d, *J* = 8.4 Hz), 128.34, 126.67, 123.67, 123.58, 117.72(d, *J* = 21.4 Hz), 113.57(d, *J* = 21.7 Hz), 110.02, 109.69, -4.09.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.61.

GC-MS(EI-70eV): m/z(%)=438(56), 360(31), 241(18), 197(100), 105(24), 78(13).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>28</sub>H<sub>20</sub>F<sub>2</sub>OSi:438.1252, found[M+H]<sup>+</sup>: 439.1332.

**3,4-Bis(4-chlorophenyl)-1-methyl-1-phenylbenzo[*b*]silin-2(*1H*)-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40-7.33 (m, 6H), 7.29-7.20 (m, 6H), 7.03-6.97 (m, 3H), 6.94-6.89 (m, 2H), 6.51-6.42 (m, 1H), 0.41 (s, 3H).

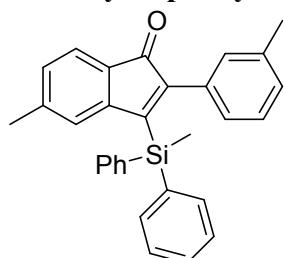
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.35, 155.84, 151.10, 149.01, 137.25, 137.05, 136.87, 136.65, 136.43, 135.79, 133.39, 132.46, 130.80, 130.32, 130.16, 127.65, 126.11, -0.00.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.62.

GC-MS(EI-70eV): m/z(%)=470(26), 435(72), 392(16), 273(32), 210(35), 197(100), 165(21), 119(20), 105(43), 77(18).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>28</sub>H<sub>20</sub>Cl<sub>2</sub>OSi:470.0660, found[M+Na]<sup>+</sup>: 493.0550.

**5-Methyl-1-phenyl-3,4-di-*m*-tolylbenzo[*b*]silin-2(*1H*)-one**



<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.32-7.27 (m, 4H), 7.24-7.15 (m, 5H), 7.15-7.10 (m, 2H), 6.95-6.64 (m, 4H), 6.59 (qd, *J* = 1.5, 0.7 Hz, 1H), 6.09 (dt, *J* = 1.3, 0.6 Hz, 1H), 1.90 (s, 3H), 1.81 (s, 3H), 0.20 (s, 3H).

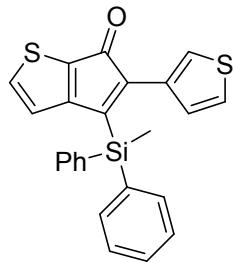
<sup>13</sup>C NMR (75 MHz, DMSO) δ 196.74, 152.06, 150.22, 149.15, 145.24, 136.91, 135.43, 134.97, 132.59, 130.63, 130.27, 129.29, 128.65, 128.57, 127.86, 127.22, 127.01, 125.67, 123.26, 22.05, 21.26, -2.48.

<sup>29</sup>Si NMR (60 MHz, DMSO) δ -16.03.

GC-MS(EI-70eV): m/z(%)=430(M<sup>+</sup>, 98), 415(61), 352(22), 337(37), 309(21), 233(26), 197(100), 189(60), 181(23), 105(47), 77(12).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>26</sub>OSi:430.1753, found[M+H]<sup>+</sup>: 431.1824.

**4-(Methyldiphenylsilyl)-5-(thiophen-3-yl)-6H-cyclopenta[b]thiophen-6-one**



<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 7.87 (dd, *J* = 4.6, 0.5 Hz, 1H), 7.59-7.33 (m, 11H), 7.24 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.85 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.89 (d, *J* = 4.6 Hz, 1H), 0.56 (s, 3H).

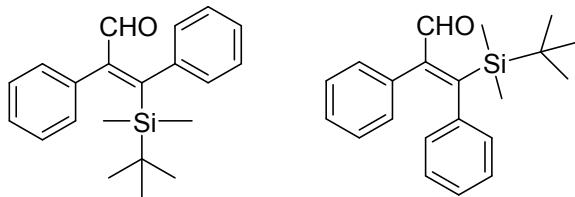
<sup>13</sup>C NMR (75 MHz, DMSO) δ 188.81, 163.61, 145.29, 142.70, 139.88, 135.07, 135.04, 132.91, 130.49, 129.12, 128.77, 126.90, 125.78, 123.55, -3.36.

<sup>29</sup>Si NMR (60 MHz, DMSO) δ -15.80.

GC-MS(EI-70eV): m/z(%)=414(M<sup>+</sup>, 62), 371(12), 321(17), 278(17), 217(21), 197(100), 145(90), 119(27), 105(57), 93(17), 77(21).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>24</sub>H<sub>18</sub>OS<sub>2</sub>Si:414.0568, found[M+H]<sup>+</sup>: 415.0639.

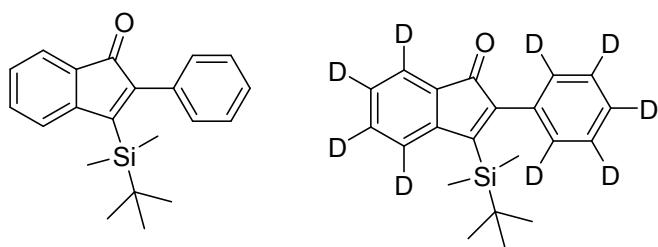
**(Z and E)-3-(tert-Butyldimethylsilyl)-2,3-diphenylacrylaldehyde**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.81 (ddt, *J* = 7.7, 1.3, 0.6 Hz, 1H), 7.64 (ddd, *J* = 7.8, 7.2, 1.3 Hz, 1H), 7.50 (dq, *J* = 7.8, 0.9 Hz, 1H), 7.41 – 7.19 (m, 5H), 7.19 – 7.10 (m, 2H), 3.93 (s, 1H), 3.08 (s, 1H), 0.91 (s, 9H), 0.14 (s, 3H), -0.00 (s, 3H).

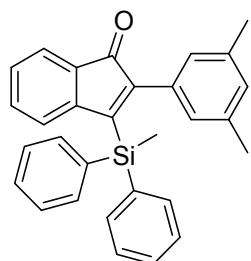
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 206.11, 158.88, 140.36, 134.94, 134.59, 128.89, 127.13, 127.00, 126.31, 126.00, 125.18, 57.56, 37.91, 27.26, 17.89, -5.49, -7.49.

**3-(tert-Butyldimethylsilyl)-2-phenyl-1*H*-inden-1-one and 3-(tert-butyldimethylsilyl)-2-(phenyl-d<sub>5</sub>)-1*H*-inden-1-one-4,5,6,7-d<sub>4</sub>**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.56-7.30 (m, 4H), 7.28-7.20 (m, 2H), 1.06 (s, 9H), 0.00 (s, 6H).

### **2-(3,5-Dimethylphenyl)-3-(methyldiphenylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.47-7.37 (m, 5H), 7.32-7.22 (m, 6H), 7.05-6.99 (m, 2H), 6.76 (tt, *J* = 1.5, 0.7 Hz, 1H), 6.62 (dp, *J* = 1.6, 0.6 Hz, 2H), 6.54-6.45 (m, 1H), 2.08 (s, 6H), 0.32 (s, 3H).

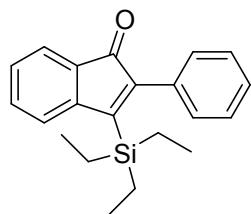
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.78, 153.52, 151.48, 149.95, 138.14, 136.65, 135.95, 135.12, 133.33, 131.18, 131.01, 130.82, 129.22, 128.86, 128.67, 125.30, 124.07, 111.44, 22.26, -1.38.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.79.

GC-MS(EI-70eV): m/z(%)=430(95), 137(50), 197(100), 105(38).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>26</sub>OSi:430.1753, found[M+H]<sup>+</sup>: 431.1824.

### **2-(3, 5-Dimethylphenyl)-3-(triethylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.08-6.93 (m, 5H), 6.85-6.74 (m, 2H), 6.73-6.63 (m, 2H), 0.97-0.84 (m, 9H), 0.75- 0.60 (m, 6H).

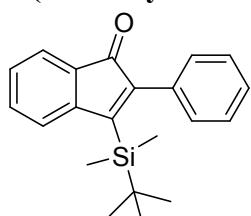
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 192.85, 166.86, 152.81, 142.45, 135.33, 129.88, 129.67, 127.62, 127.42, 126.91, 126.52, 125.78, 7.58, 5.90.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -2.34.

GC-MS(EI-70eV): m/z(%)=320(10), 263(60), 245(100), 215(15).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>21</sub>H<sub>24</sub>OSi:368.1596, found[M]<sup>+</sup>: 320.1599.

### **3-(*tert*-Butyldimethylsilyl)-2-phenyl-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-d) δ 7.52 (ddd, *J* = 7.1, 1.3, 0.6 Hz, 1H), 7.47-7.18 (m, 8H), 1.06 (s, 9H), -0.00 (s, 6H).

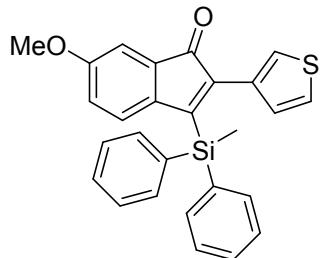
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.08, 163.13, 155.39, 149.80, 149.13, 133.92, 133.71, 129.88, 129.76, 128.08, 127.95, 127.68, 124.65, 123.46, 122.97, 27.85, 17.87, -3.41.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -1.96.

GC-MS(EI-70eV): m/z(%)=320(31), 291(31), 273(29), 245(100), 205(35), 176(41), 59(30).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>21</sub>H<sub>24</sub>OSi:368.1596, found[M]<sup>+</sup>: 320.1599.

### **6-Methoxy-3-(methyldiphenylsilyl)-2-(thiophen-3-yl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.50 – 7.41 (m, 4H), 7.36 – 7.24 (m, 7H), 7.05 – 6.95 (m, 2H), 6.68 – 6.58 (m, 2H), 5.88 (d, *J* = 4.6 Hz, 1H), 3.69 (s, 3H), 0.36 (s, 3H).

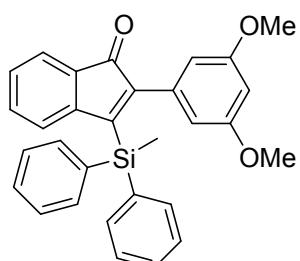
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 189.72, 163.34, 159.83, 150.36, 141.97, 137.10, 135.34, 134.95, 134.89, 131.09, 129.83, 129.16, 128.27, 128.20, 125.01, 123.33, 113.19, 55.23, -3.13.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.52.

GC-MS(EI-70eV): m/z(%)=438(100), 345(43), 302(46), 197(97), 165(35), 137(50), 105(83).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>27</sub>H<sub>22</sub>O<sub>2</sub>SSi: 438.1110, found[M]<sup>+</sup>: 438.1094.

### **2-(3,5-dimethoxyphenyl)-3-(methyldiphenylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 8.53-8.46 (m, 1H), 8.43- 8.38 (m, 3H), 8.30-8.22 (m, 7H), 8.06-7.91 (m, 2H), 7.45-7.37 (m, 1H), 7.21 (d, *J* = 2.3 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 2H), 4.43 (s, 6H), 1.32 (s, 3H).

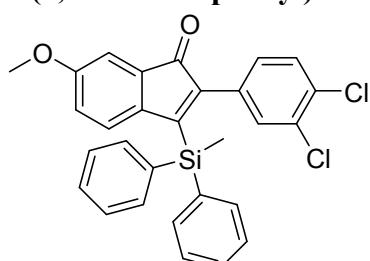
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.14, 160.09, 153.11, 150.16, 148.59, 135.50, 134.90, 134.38, 134.11, 133.96, 129.90, 129.79, 128.21, 127.93, 124.34, 123.06, 107.62, 101.40, 55.06, -1.22.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.37.

GC-MS(EI-70eV): m/z(%)=462 (45), 369(55), 341(49), 197(100), 105(43).

HRMS (ESI), m/z: [M]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>26</sub>O<sub>3</sub>Si:462.1651, found[M+H]<sup>+</sup>: 463.1724

### **2-(3,4-Dichlorophenyl)-6-methoxy-3-(methyldiphenylsilyl)-1*H*-inden-1-one**



<sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.43-7.41 (m, 4H), 7.37-7.26 (m, 6H), 7.18 (s, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.69-6.59 (m, 2H), 6.42 (s, 1H), 3.69 (s, 3H), 0.36 (s, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.51, 160.19, 150.42, 148.20, 137.50, 134.83, 134.75, 131.56, 131.23, 131.11, 130.10, 129.97, 129.37, 128.42, 128.35, 126.03, 124.59, 123.99, 113.35, 55.25, -2.66.

<sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -15.39.

GC-MS(EI-70eV): m/z(%)=500(27), 197(100), 165(13), 119(11), 105(29).

HRMS (EI), m/z: [M]<sup>+</sup>, calculated for C<sub>29</sub>H<sub>22</sub>O<sub>2</sub>Cl<sub>2</sub>Si:500.0766, found [M]<sup>+</sup>: 500.0751.

