# **Supporting Information**

# Iron-catalyzed regioselective C–H alkylation of indoles: an additive-free approach in renewable solvent

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#### **1.** General Experimental

All the manipulations were conducted under an argon atmosphere either in a glove box or using standard Schlenk techniques in pre-dried glassware. The catalytic reactions were performed in flame-dried reaction vessels with Teflon screw cap. Solvents were dried over Na/benzophenone or CaH<sub>2</sub> and distilled prior to use. Liquid reagents were flushed with argon prior to use. The alkenes 9-allyl-9H-carbazole, 1-allyl-1H-indole, 1-allyl-4-methoxy-1H-1-allyl-6-fluoro-1*H*-indole, 1-(but-3-en-1-yl)-1*H*-indole,<sup>S1</sup> and iron complex indole, Fe(PMe<sub>3</sub>)<sub>4</sub> were synthesized according to the previously described procedures and stored under argon at -30 °C.<sup>S2</sup> All other chemicals were obtained from commercial sources and were used without further purification. High resolution mass spectrometry (HRMS) mass spectra were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. EPR spectra were recorded on Bruker EMX Plus EPR Spectrometer with X band (Standard Frequency (X band) 9.0-9.8 GHz) at 100 K. NMR: (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) spectra were recorded at 400 or 500 MHz (1H), 100 or 125 MHz {13C, DEPT (distortionless enhancement by polarization transfer)}, 377 MHz (<sup>19</sup>F), respectively in CDCl<sub>3</sub> solutions, if not otherwise specified; chemical shifts ( $\delta$ ) are given in ppm. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra are referenced to residual solvent signals (CDCl<sub>3</sub>:  $\delta$  H = 7.26 ppm,  $\delta$  C = 77.2 ppm). The abbreviations are as follows: s = singlet, br s = broad singlet, d = doublet, t = triplet, dd = double doublet, vt =virtual triplet, dt = double triplet, td = triple doublet, tt = triple triplet.

GC Method. Gas Chromatography analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s auto sampler and a Restek RTX-5 capillary column (30 m x 0.25 mm x 0.25 $\mu$ m). The instrument was set to an injection volume of 1  $\mu$ L, an inlet split ratio of 10:1, and inlet and detector temperatures of 250 and 320 °C, respectively. UHP-grade nitrogen (N<sub>2</sub>) was used as carrier gas with a flow rate of 30 mL/min. The temperature program used for all the analyses is as follows: 80 °C, 1 min; 30 °C/min to 200 °C, 2 min; 30 °C/min to 260 °C, 3 min; 30 °C/min to 300 °C, 3 min. Response factors for all the necessary compounds with respect to standard *n*-dodecane were calculated from the average of three independent GC runs.

#### 2. Synthesis and Characterization of Starting Compounds



Synthesis of 1-Phenyl-1*H*-indole: To a stirred solution of indole (1.0 g, 8.54 mmol), CuI (0.163 g, 0.854 mmol, 10 mol%), *L*-Proline (0.197 g, 1.71 mmol, 20 mol%) and K<sub>2</sub>CO<sub>3</sub> (2.360 g, 17.1 mmol, 2 equiv) in DMSO, iodo benzene (2.61 g, 12.81 mmol) was added at room temperature and allowed the reaction mixture to stir at 80 °C for 22 h. The progress of the reaction was monitored by TLC. The product was extracted with ethyl acetate (20 mL x 3) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic phase was concentrated in vacuum to obtain the crude mixture, which was further purified by column chromatography on silica gel (petroleum ether/EtOAc : 100/1) to yield 1-phenyl-1*H*-indole (1.50 g, 91%) as a yellow liquid.

#### General Procedure for Preparation of N-Alkylated Indoles (Procedure B)



Synthesis of 1-(3-Methylbut-3-en-1-yl)-1*H*-indole: To a stirred solution of indole (1.0 g, 8.54 mmol) in THF (15 mL) at 0 °C was added sodium hydride (60% in mineral oil, 0.410 g, 17.1 mmol). The reaction was warmed to room temperature and allowed to stir for 30 min. The reaction flask was cooled again to 0 °C and 4-bromo-2-methylbut-1-ene (1.53 g, 10.27 mmol) was added. The reaction mixture was warmed to room temperature and allowed to stir until the reaction completion (monitored by TLC) and then cooled to 0 °C and quenched with saturated aqueous NH<sub>4</sub>Cl. The product was extracted with ethyl acetate (3 x 20 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic phase was concentrated in vacuum to obtain the crude mixture which was further purified by column chromatography on silica gel (petroleum ether/EtOAc : 70/1) to yield 1-(3-methylbut-3-en-1-yl)-1*H*-indole (1.34 g, 85%) as a yellow liquid.

**General Procedure for Preparation of C-3 Carbonyl Indoles (Procedure C)** 



Synthesis of 2-Methyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1b): To a solution of 1-phenyl-1*H*-indole (1.0 g, 5.17 mmol) in 20 mL of anhydrous toluene at 0 °C was added isobutyryl chloride (1.10 g, 10.36 mmol). After stirring for 15 min at 0 °C, a solution of SnCl<sub>4</sub> (2.70 g, 10.35 mmol) in 20 mL of anhydrous toluene was added. The resultant solution was stirred at 0 °C for 2 h and 75 mL of 8% NaHCO<sub>3</sub> was added dropwise. The resultant slurry was extracted with 100 mL of EtOAc and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic phase was concentrated in vacuum to obtain the crude mixture, which was further purified by column chromatography on silica gel (petroleum ether/EtOAc : 20/1) to yield **1b** (1.1 g, 81%) as a white solid.



**2-Methyl-1-(1-phenyl-1***H***-indol-3-yl)propan-1-one (1b): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): \delta = 8.52 (d, J = 8.0 Hz, 1H, Ar–H), 7.98 (s, 1H, Ar–H), 7.60-7.45 (m, 6H, Ar–H), 7.36 (td, J = 7.7, 1.1 Hz, 1H, Ar–H ), 7.30 (td, J = 7.0, 1.1 Hz, 1H, Ar–H), 3.39 (sept, J = 6.7 Hz, 1H, CH), 1.30 (d, J = 6.9 Hz, 6H, 2CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>): \delta = 200.7 (CO), 138.6 (C<sub>q</sub>), 137.2 (C<sub>q</sub>), 134.1 (CH), 130.1 (2C, CH), 127.1 (C<sub>q</sub>), 128.1 (CH), 125.1 (2C, CH), 124.1 (CH), 123.2 (CH), 123.1 (CH), 117.2 (C<sub>q</sub>), 110.9 (CH), 37.5 (CH), 19.9 (2C, CH<sub>3</sub>). HRMS (ESI)** *m/z***: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>NO<sup>+</sup> 264.1383; Found 264.1375.** 



**Cyclopentyl(1-phenyl-1***H***-indol-3-yl)methanone (1d):** The representative procedure **C** was followed, using 1-phenyl-1*H*-indole (1.0 g, 5.17 mmol) and cyclopentanecarbonyl chloride (1.37 g, 10.33 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) yielded **1d** (1.35 g, 90%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.53 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.97 (s, 1H, Ar–H), 7.60-7.52 (m, 4H, Ar–H), 7.60-7.52 (m, 2H, Ar–H), 7.35 (dt, *J* = 6.0, 1.0 Hz, 1H, Ar–H), 7.30 (dt, *J* = 7.2, 1.4 Hz, 1H, Ar–H), 3.59 (qt, *J* = 8.2 Hz, 1H, CH), 2.09-1.91 (m, 4H, 2CH<sub>2</sub>), 1.86-1.76 (m, 2H, CH<sub>2</sub>), 1.72-1.64 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 199.1 (CO), 138.6 (C<sub>q</sub>), 137.2 (C<sub>q</sub>), 134.3 (CH), 130.0 (2C, CH), 128.1 (CH), 127.1 (C<sub>q</sub>), 125.1 (2C, CH), 124.0 (CH), 123.2 (CH), 123.1 (CH), 118.2 (C<sub>q</sub>), 110.9 (CH), 48.2 (CH), 30.7 (2C, CH<sub>2</sub>), 26.6 (2C, CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>20</sub>NO<sup>+</sup> 290.1539; Found 290.1530.



**1-(1-(4-Isopropylphenyl)-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one (1h): The representative procedure C was followed, using 1-(4-isopropylphenyl)-1***H***-indole (1.0 g, 4.25 mmol) and pivaloyl chloride (1.03 g, 8.54 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded <b>1h** (1.22 g, 90%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.58 (d, *J* = 7.7 Hz, 1H, Ar–H), 7.99 (s, 1H, Ar–H), 7.45-7.39 (m, 5H, Ar–H), 7.33-7.22 (m, 2H, Ar–H), 3.02 (sept, *J* = 6.9 Hz, 1H, CH), 1.44 (s, 9H, 3CH<sub>3</sub>), 1.33 (d, *J* = 6.9 Hz, 6H, 2CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 202.5 (CO), 149.1 (C<sub>q</sub>), 136.4 (C<sub>q</sub>), 136.3 (C<sub>q</sub>), 133.5 (CH), 128.6 (C<sub>q</sub>), 128.0 (2C, CH), 125.2 (2C, CH), 123.8 (CH), 123.6 (CH), 123.1 (CH), 114.4 (C<sub>q</sub>), 110.7 (CH), 44.4 (C<sub>q</sub>), 34.1 (CH), 29.1 (3C, CH<sub>3</sub>),

24.2 (2C, CH<sub>3</sub>). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>26</sub>NO<sup>+</sup> 320.2009; Found 320.2000.



**1-(1-(4-(***tert***-Butyl)phenyl)-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one (1i): The representative procedure C was followed, using 1-(4-(***tert***-butyl)phenyl)-1***H***-indole (1.1 g, 4.41 mmol) and pivaloyl chloride (1.07 g, 8.87 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded <b>1i** (1.40 g, 95%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.58$  (d, J = 7.7 Hz, 1H, Ar–H), 8.00 (s, 1H, Ar–H), 7.57 (d, J = 7.5 Hz, 2H, Ar–H), 7.44 (vt, J = 8.3 Hz, 3H, Ar–H), 7.33-7.24 (m, 2H, Ar–H), 1.44 (s, 9H, 3CH<sub>3</sub>), 1.40 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 202.5$  (CO), 151.4 (C<sub>q</sub>), 136.4 (C<sub>q</sub>), 136.1 (C<sub>q</sub>), 133.5 (CH), 128.6 (C<sub>q</sub>), 126.9 (2C, CH), 124.8 (2C, CH), 123.8 (CH), 123.6 (CH), 123.1 (CH), 114.4 (C<sub>q</sub>), 110.7 (CH), 44.4 (C<sub>q</sub>), 34.9 (C<sub>q</sub>), 31.5 (3C, CH<sub>3</sub>), 29.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>28</sub>NO<sup>+</sup> 334.2165; Found 334.2166.



**2,2-Dimethyl-1-(1-(4-(methylthio)phenyl)-1***H***-indol-3-yl)propan-1-one** (11): The representative procedure C was followed, using 1-(4-(methylthio)phenyl)-1*H***-indole** (0.85 g, 3.55 mmol) and pivaloyl chloride (0.86 g, 7.13 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **11** (0.83 g, 72%) as a pink solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.58 (d, *J* = 7.7 Hz, 1H, Ar–H), 8.00 (s, 1H, Ar–H), 7.41 (d, *J* = 7.5 Hz, 2H, Ar–H), 7.34-7.25 (m, 5H, Ar–H), 2.55 (s, 3H, CH<sub>3</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 202.5 (CO), 139.0 (C<sub>q</sub>), 136.3 (C<sub>q</sub>), 135.6 S7

(C<sub>q</sub>), 133.2 (CH), 128.6 (C<sub>q</sub>), 127.7 (2C, CH), 125.7 (2C, CH), 124.0 (CH), 123.7 (CH), 123.1 (CH), 114.6 (C<sub>q</sub>), 110.5 (CH), 44.4 (C<sub>q</sub>), 29.0 (3C, CH<sub>3</sub>), 16.0 (CH<sub>3</sub>). HRMS (ESI) *m/z*:  $[M + H]^+$  Calcd for C<sub>20</sub>H<sub>22</sub>SNO<sup>+</sup> 324.1417; Found 324.1414.



**1-(1-(2-Methoxyphenyl)-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one** (1m): The representative procedure C was followed, using 1-(2-methoxyphenyl)-1*H*-indole (1.0 g, 4.48 mmol) and pivaloyl chloride (1.10 g, 9.12 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded 1m (1.12 g, 81%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.56 (d, *J* = 8.0 Hz, 1H, Ar–H), 8.01 (s, 1H, Ar–H), 7.44 (vt, *J* = 8.5 Hz, 2H, Ar–H), 7.29 (vt, *J* = 7.3 Hz, 1H, Ar–H), 7.24-7.17 (m, 2H, Ar–H) 7.10 (vt, *J* = 7.4 Hz, 2H, Ar–H), 3.77 (s, 3H, CH<sub>3</sub>), 1.44(s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 202.5 (CO), 154.5 (C<sub>q</sub>), 136.9 (C<sub>q</sub>), 135.3 (CH), 129.8 (CH), 128.2 (CH), 128.0 (C<sub>q</sub>), 127.0 (C<sub>q</sub>), 123.5 (CH), 123.3 (CH), 122.7 (CH), 121.1 (CH), 113.9 (C<sub>q</sub>), 112.7 (CH), 110.8 (CH), 55.9 (CH<sub>3</sub>), 44.4 (C<sub>q</sub>), 29.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub><sup>+</sup> 308.1645; Found 308.1636.



**2,2-Dimethyl-1-(1-(3-methylbut-3***en***-1-yl)-1***H***-indol-3-yl)propan-1-one** (1u): The representative procedure C was followed, using 1-(3-methylbut-3-en-1-yl)-1*H*-indole (0.50 g, 2.70 mmol) and pivaloyl chloride (0.66 g, 5.47 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **1u** (0.48 g, 66%) as a brown liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.52$  (d, J = 6.9 Hz, 1H, Ar–H), 7.80 (s, 1H, Ar–H), 7.34-7.25 (m, 3H, Ar–H), 4.84 (s, 1H, CH<sub>2</sub>), 4.67 (s, 1H, CH<sub>2</sub>), 4.27 (t, J = 7.3 Hz, 2H, CH<sub>2</sub>), 2.56 (t, J = 7.1 Hz, 2H, CH<sub>2</sub>), 1.77 (s, 3H, CH<sub>3</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 202.2$  (CO), 141.6 (Cq), 135.7 (Cq), 133.7 (CH), 128.6 (Cq), 123.6 (CH), 123.2 (CH), 122.5 (CH), 113.5 (CH<sub>2</sub>), 112.8 (Cq), 109.4 (CH), 45.6 (CH<sub>2</sub>), 44.2

(C<sub>q</sub>), 37.9 (CH<sub>2</sub>), 29.1 (3C, CH<sub>3</sub>), 22.6 (CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for  $C_{18}H_{24}NO^+$  270.1852; Found 270.1845.

=0

-SiMe<sub>3</sub>

#### **Detailed Optimization Studies** 3.

Table S1 Optimization of Reaction Parameters in Details <sup>a</sup>



Entry	[M]/mol%	Ligand	Additives	Solvent	<b>Yield (%)</b> <sup>b</sup>
1	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			toluene	73
2	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			1,4-dioxane	19
3	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			cyclohexane	81
4	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			THF	84
5	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			<sup>t</sup> Bu-benzene	99 (95)
6	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			<i>n</i> -hexane	99 (96)
7	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			2-MeTHF	99 (96)
8 <sup>c</sup>	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			2-MeTHF	99 (96)
9 <sup>d</sup>	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15				97 (91)
10	Fe(PMe <sub>3</sub> ) <sub>4</sub> /10			2-MeTHF	86
11	Fe(PMe <sub>3</sub> ) <sub>4</sub> /10			<sup>t</sup> Bu-benzene	84
12	Fe(PMe <sub>3</sub> ) <sub>4</sub> /10			<i>n</i> -hexane	86
13 <sup>e</sup>	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			2-MeTHF	85
14 <sup>f</sup>	Fe(PMe <sub>3</sub> ) <sub>4</sub> /15			2-MeTHF	87
15	FeCl <sub>2</sub> /15	PMe <sub>3</sub>		2-MeTHF	NR
16	FeCl <sub>2</sub> /15	PMe <sub>3</sub>	Zn	2-MeTHF	NR
17	FeCl <sub>2</sub> /15	PMe <sub>3</sub>	Mg	2-MeTHF	trace
18 <sup>g</sup>	FeCl <sub>2</sub> /15	PMe <sub>3</sub>	Mg	2-MeTHF	27
19	FeCl <sub>2</sub> /15	PMe <sub>3</sub>	LiAlH <sub>4</sub>	2-MeTHF	NR
20	FeCl <sub>2</sub> /15	PMe <sub>3</sub>	NaH	2-MeTHF	NR
21	FeCl <sub>2</sub> /15	PMe <sub>3</sub>	LiBHEt <sub>3</sub>	2-MeTHF	NR
22 <sup>g</sup>	FeCl <sub>2</sub> /15	PCy <sub>3</sub>	Mg	2-MeTHF	21

23 <sup>g</sup>	FeCl <sub>2</sub> /15	PPh <sub>3</sub>	Mg	2-MeTHF	NR
24 <sup>g</sup>	FeCl <sub>2</sub> /15	dcype	Mg	2-MeTHF	NR
25 <sup>g</sup>	FeCl <sub>2</sub> /15	dppe	Mg	2-MeTHF	NR
26 <sup>g</sup>	FeCl <sub>2</sub> /15	dppbz	Mg	2-MeTHF	NR
27 <sup>g</sup>	FeCl <sub>2</sub> /15	xantphos	Mg	2-MeTHF	NR
28 <sup>g</sup>	FeCl <sub>2</sub> /15	bpy	Mg	2-MeTHF	NR
29	$Pd_2(dba)_3/15$	PMe <sub>3</sub>		2-MeTHF	NR
30	$Pd(OAc)_2/15$	PMe <sub>3</sub>		2-MeTHF	NR
31	Ni(COD) <sub>2</sub> /15	PMe <sub>3</sub>		2-MeTHF	trace
32	NiCl <sub>2</sub> (DME)/15	PMe <sub>3</sub>		2-MeTHF	NR
33	CoCl <sub>2</sub> /15	PMe <sub>3</sub>		2-MeTHF	NR
34	$MnCl_2/15$	PMe <sub>3</sub>		2-MeTHF	NR
35		PMe <sub>3</sub>		2-MeTHF	NR

<sup>*a*</sup> Conditions: **1a** (0.056 g, 0.202 mmol), trimethyl(vinyl)silane (**2a**; 0.040 g, 0.40 mmol), Fe(PMe<sub>3</sub>)<sub>4</sub> (0.011 g, 0.03 mmol), solvent (0.5 mL), 40 °C, 16 h. For entries 15-21 and 29-35: PMe<sub>3</sub> (0.12 mmol, 60 mol%) was used. PCy<sub>3</sub> (0.12 mmol, 60 mol%), PPh<sub>3</sub> (0.12 mmol, 60 mol%), dcype (0.06 mmol, 30 mol%), dppe (0.06 mmol, 30 mol%), dppe (0.06 mmol, 30 mol%), dppe (0.06 mmol, 30 mol%), bpy (0.12 mmol, 60 mol%). Additive 0.20 mmol was used in specified entries. <sup>*b*</sup> GC yield using *n*-dodecane as internal standard, isolated yield is given in parentheses. <sup>*c*</sup> Reaction performed using 0.1 mL of 2-MeTHF. <sup>*d*</sup> Reaction performed without solvent at 60 °C. <sup>*e*</sup> Reaction performed for 12 h. <sup>*f*</sup> Reaction performed at room temperature. For entries 17-18 and 22-28: Mg (0.15 mmol, 75 mol%). <sup>*g*</sup> Few glass pieces were added in the reaction mixture.

# 4. Representative Procedure for Alkylation (Procedure D)

Synthesis of 2,2-Dimethyl-1-(1-phenyl-2-(2-(trimethylsilyl)ethyl)-1*H*-indol-3yl)propan-1-one (3aa). To a flame-dried screw-cap tube equipped with magnetic stir bar were introduced 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), trimethyl(vinyl)silane (0.040 g, 0.40 mmol), Fe(PMe<sub>3</sub>)<sub>4</sub> (0.011 g, 0.0305 mmol, 15.0 mol%) inside the glove box. To the above mixture in the tube was added 2-MeTHF (0.1 mL). The resultant reaction mixture in the tube was immersed in a preheated oil bath at 40 °C and stirred for 16 h. At ambient temperature, the reaction mixture was quenched with distilled H<sub>2</sub>O (10.0 mL) and the crude product was extracted with EtOAc (15 mL x 3). The combined S10 organic extract was dried over  $Na_2SO_4$  and the volatiles were evaporated *in vacuo*. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) to yield **3aa** (0.073 g, 96%) as a light-yellow liquid.

# 5. Evaluation of Green Chemistry Metrics

Table S2 Evaluation of green chemistry metrics for the synthesis of alkylated indole C.

	OMe N N Me (A) (B) (C) (A) (B) (C) (C) (C) (C) (C) (C) (C) (C	<sup>i)3</sup> CI→→ H <sup>+</sup> → ( l equiv) °C		NH2 DMe
0.2 mmol       0.3 mmol       93% yield (0.186 mmol)         Chemical formula: $C_{17}H_{16}N_2O$ $C_8H_8$ $C_{18}H_{17}NO$ $C_7H_9NO$				
Reactant 1 (A)	(E)-N-(4-methoxyphenyl)-1-(1-	0.053 g	0.0002 mol	FW: 264.1263
	methyl-1H-indol-3-			
	yl)methanimine			
Reactant 2 (B)	styrene	0.0312 g	0.0003 mol	FW: 104.0626
Solvent	Diethyl ether	0.278 g		FW: 74.0732
Auxiliary 1	CyMgCl	0.0284 g	0.0002 mol	FW: 142.0400
Auxiliary 2	Tetramethylethylenediamine	0.0464 g	0.0004 mol	FW: 116.1313
Auxiliary 3	HCl	0.0072 g	0.0002 mol	FW: 35.9767
Product	С	0.0489 g	0.000186 mol	FW: 263.1310
byproduct (D)	4-methoxyaniline	0.0229 g	0.000186 mol	FW: 123.0684

**Product yield = 93%** 

 $\mathbf{E}\text{-factor} = [\{(0.053 + 0.0312 + 0.278 + 0.0284 + 0.0464 + 0072) - (0.0489)\}/0.0489] = \mathbf{8.1} \text{ kg} \\ \text{waste/ 1 kg product} \\ \textbf{Atom economy} = (263.1310/794.5228) \times 100 = \mathbf{33\%} \\ \textbf{Atom efficiency} = 93 \times (63/100) = \mathbf{31\%} \\ \textbf{Carbon efficiency} = (18/29) \times 100 = \mathbf{62\%} \\ \textbf{Reaction mass efficiency} = \{0.0489/(0.053 + 0.0312)\} \times 100 = \mathbf{58\%} \\ \end{array}$ 

#### 6. Characterization Data of Alkylated Compounds



**2,2-Dimethyl-1-(1-phenyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)propan-1-one (3aa): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.70 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.59-7.49 (m, 3H, Ar–H), 7.37 (d, *J* = 7.3 Hz, 2H, Ar–H), 7.18 (vt, *J* = 7.5 Hz, 1H, Ar–H), 7.11 (vt, *J* = 7.6 Hz, 1H, Ar–H), 7.00 (d, *J* = 8.1 Hz, 1H, Ar–H), 2.71-2.67 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 0.67-0.62 (m, 2H, CH<sub>2</sub>), -0.16 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.1 (CO), 146.8 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 137.2 (C<sub>q</sub>), 129.8 (2C, CH), 128.8 (CH), 128.7 (2C, CH), 125.5 (C<sub>q</sub>), 121.8 (CH), 121.1 (CH), 121.0 (CH), 115.2 (C<sub>q</sub>), 110.7 (CH), 44.7 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.8 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>32</sub>NOSi<sup>+</sup> 378.2248; Found 378.2252.



**2-Methyl-1-(1-phenyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)propan-1-one (**3ba**): The representative procedure D was followed, using 2-methyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1b**; 0.053 g, 0.201 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ba** (0.065 g, 89%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.90 (d, *J* = 8.2 Hz, 1H, Ar–H), 7.55-7.47 (m, 3H, Ar–H), 7.29-7.27 (m, 2H, Ar–H), 7.24-7.20 (m, 1H, Ar–H), 7.11-7.07 (m, 1H, Ar–H), 6.91 (d, *J* = 8.1 Hz, 1H, Ar–H), 3.55 (sept, *J* = 6.7 Hz, 1H, CH), 2.90-2.86 (m, 2H, CH<sub>2</sub>), 1.26 (d, *J* = 6.9 Hz, 6H, 2CH<sub>3</sub>), 0.73-0.68 (m, 2H, CH<sub>2</sub>), -0.21 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 201.8 (CO), 135.1 (C<sub>q</sub>), 138.2 (C<sub>q</sub>), 136.4 (C<sub>q</sub>), 129.9 (2C, CH), 129.3 (CH), 128.9 (2C, CH), 125.7 (C<sub>q</sub>), 122.3 (CH), 122.2 (CH), 120.7 (CH), 112.3 (C<sub>q</sub>), 111.2 (CH), 39.1 (CH), 21.1 (CH<sub>2</sub>), 19.2 (2C, CH<sub>3</sub>), 16.8 (CH<sub>2</sub>), -2.0 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>30</sub>NOSi<sup>+</sup> 364.2091; Found 364.2079.



**1-(1-Phenyl-2-(2-(trimethylsilyl)ethyl)-1***H***-indol-3-yl)ethan-1-one (3ca): The representative procedure D was followed, using 1-(1-phenyl-1***H***-indol-3-yl)ethan-1-one (1c; 0.047 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded <b>3ca** (0.052 g, 77%) as a light-yellow liquid. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.02$  (d, J = 8.1 Hz, 1H, Ar–H), 7.61-7.53 (m, 3H, Ar–H), 7.35-7.33 (m, 2H, Ar–H), 7.29 (vt, J = 7.1 Hz, 1H, Ar–H), 7.16 (vt, J = 8.0 Hz, 1H, Ar–H), 6.97 (d, J = 8.1 Hz, 1H, Ar–H), 2.96-2.91 (m, 2H, CH<sub>2</sub>), 2.75 (s, 3H, CH<sub>3</sub>), 0.78-0.74 (m, 2H, CH<sub>2</sub>), -0.12 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 194.6$  (CO), 152.9 (C<sub>q</sub>), 138.2 (C<sub>q</sub>), 136.4 (C<sub>q</sub>), 130.0 (2C, CH), 129.3 (CH), 128.8 (2C, CH), 126.5 (C<sub>q</sub>), 122.5 (CH), 122.2 (CH), 120.8 (CH), 113.5 (C<sub>q</sub>), 111.2 (CH), 31.8 (CH<sub>3</sub>), 21.1 (CH<sub>2</sub>), 16.8 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd C<sub>21</sub>H<sub>26</sub>NOSi<sup>+</sup> 336.1778; Found 336.1778.



**Cyclopentyl(1-phenyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)methanone (3da): The representative procedure D was followed, using cyclopentyl(1-phenyl-1*H*-indol-3-yl)methanone (1d; 0.058 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3da (0.073 g, 94%) as a yellow solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.99 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.59-7.50 (m, 3H, Ar–H), 7.34-7.32 (m, 2H, Ar–H), 7.25 (t, *J* = 8.1 Hz, 1H, Ar–H), 7.13 (t, *J* = 7.6 Hz, 1H, Ar–H), 6.95 (d, *J* = 8.1 Hz, 1H, Ar–H), 3.80 (quintet, *J* = 7.7 Hz, 1H, CH), 2.96-2.92 (m, 2H, CH<sub>2</sub>), 2.10-1.97 (m, 4H, 2CH<sub>2</sub>), 1.87-1.77 (m, 2H, CH<sub>2</sub>), 1.74-1.65 (m, 2H, CH<sub>2</sub>), 0.78-0.73 (m, 2H, CH<sub>2</sub>), -0.15 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 200.3 (CO), 152.6 (C<sub>q</sub>), 138.2 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 129.8 (2C, CH), 129.2 (CH), 128.8 (2C, CH), 126.0 (C<sub>q</sub>), 122.3 (CH), 122.2 (CH), 120.7 (CH), 113.2 (C<sub>q</sub>), 111.1 S13

(CH), 50.3 (CH), 30.0 (2C, CH<sub>2</sub>), 26.4 (2C, CH<sub>2</sub>), 21.1 (CH<sub>2</sub>), 16.9 (CH<sub>2</sub>), −2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>32</sub>NOSi<sup>+</sup> 390.2248; Found 390.2248.



Cyclohexyl(1-phenyl-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)methanone (3ea): The representative procedure D was followed, using cyclohexyl(1-phenyl-1H-indol-3yl)methanone (1e; 0.061 g, 0.201 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ea** (0.077 g, 95%) as a yellow solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.94$  (d, J = 8.1 Hz, 1H, Ar-H), 7.61-7.53 (m, 3H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.31-7.26 (m, 1H, Ar-H), 7.18-7.14 (m, 1H, Ar–H), 6.98 (d, *J* = 8.1 Hz, 1H, Ar–H), 3.31 (tt, *J* = 11.4, 3.1 Hz, 1H, CH), 2.97-2.93 (m, 2H, CH<sub>2</sub>), 2.07 (d, *J* = 12.2 Hz, 2H, CH<sub>2</sub>), 1.93 (dt, *J* = 12.2, 3.1 Hz, 2H, CH<sub>2</sub>), 1.82-1.79 (m, 1H, CH<sub>2</sub>), 1.69-1.59 (m, 2H, CH<sub>2</sub>), 1.54-1.43 (m, 2H, CH<sub>2</sub>), 1.40-1.33 (m, 1H, CH<sub>2</sub>), 0.80-0.76 (m, 2H, CH<sub>2</sub>), -0.13 (s, 9H, 3CH<sub>3</sub>).  ${}^{13}C{}^{1}H$ -NMR (100 MHz, CDCl<sub>3</sub>):  $\delta =$ 201.1 (CO), 152.9 (C<sub>a</sub>), 138.2 (C<sub>a</sub>), 136.5 (C<sub>a</sub>), 129.8 (2C, CH), 129.2 (CH), 128.6 (2C, CH), 125.9 (C<sub>a</sub>), 122.4 (CH), 122.2 (CH), 120.6 (CH), 112.6 (C<sub>a</sub>), 111.1 (CH), 49.6 (CH), 29.3 (2C, CH<sub>2</sub>), 26.4 (2C, CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 21.1 (CH<sub>2</sub>), 16.9 (CH<sub>2</sub>), -2.0 (3C, CH<sub>3</sub>). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>34</sub>NOSi<sup>+</sup> 404.2404; Found 404.2397.



(1-Benzyl-2-(2-(trimethylsilyl)ethyl)-1*H*-indol-3-yl)(*p*-tolyl)methanone (3fa): The representative procedure was D followed, using (1-benzyl-1*H*-indol-3-yl)(*p*-tolyl)methanone (1f; 0.066 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3fa (0.069 g, 80%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.69$  (d, J = 7.9 Hz, 2H,

Ar–H), 7.32-7.21 (m, 7H, Ar–H), 7.12 (t, J = 8.3 Hz, 1H, Ar–H), 7.07-7.03 (m, 3H, Ar–H), 5.39 (s, 2H, CH<sub>2</sub>), 2.96-2.92 (m, 2H, CH<sub>2</sub>), 2.44 (s, 3H, CH<sub>3</sub>), 0.85-0.80 (m, 2H, CH<sub>2</sub>), -0.03 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 192.9$  (CO), 151.6 (C<sub>q</sub>), 142.1 (C<sub>q</sub>), 139.0 (C<sub>q</sub>), 136.8 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 129.4 (2C, CH), 129.1 (2C, CH), 129.0 (2C, CH), 127.9 (CH), 127.5 (C<sub>q</sub>), 126.2 (2C, CH), 122.2 (CH), 121.5 (CH), 121.4 (CH), 113.1 (C<sub>q</sub>), 110.0 (CH), 46.7 (CH<sub>2</sub>), 21.8 (CH<sub>3</sub>), 20.4 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -1.9 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>32</sub>NOSi<sup>+</sup> 426.2248; Found 426.2239.



**2,2-Dimethyl-1-(1-(***p***-tolyl)-2-(2-(trimethylsilyl)ethyl)-1***H***-indol-3-yl)propan-1-one (<b>3ga**): The representative procedure D was followed, using 2,2-dimethyl-1-(1-(*p*-tolyl)-1*H*-indol-3yl)propan-1-one (**1g**; 0.059 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ga** (0.072 g, 91%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.69 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.34 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.23 (dt, *J* = 8.2, 1.9 Hz, 2H, Ar–H), 7.17 (td, *J* = 7.0, 1.0 Hz, 1H, Ar–H), 7.10 (td, *J* = 7.0, 1.0 Hz, 1H, Ar–H), 6.99 (d, *J* = 8.1 Hz, 1H, Ar–H), 2.70-2.66 (m, 2H, CH<sub>2</sub>), 2.48 (s, 3H, CH<sub>3</sub>), 1.43 (s, 9H, 3CH<sub>3</sub>), 0.68-0.64 (m, 2H, CH<sub>2</sub>), -0.15 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.0 (CO), 147.2 (C<sub>q</sub>), 138.7 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 134.4 (C<sub>q</sub>), 130.3 (2C, CH), 128.4 (2C, CH), 125.4 (C<sub>q</sub>), 121.7 (CH), 121.1 (CH), 120.9 (CH), 114.9 (C<sub>q</sub>), 110.7 (CH), 44.6 (C<sub>q</sub>), 27.8 (3C, CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.8 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>34</sub>NOSi<sup>+</sup> 392.2404; Found 392.2412.



1-(1-(4-Isopropylphenyl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)-2,2-dimethylpropan-1-one (3ha): The representative procedure D was followed, using 1-(1-(4-isopropylphenyl)-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1h; 0.064 0.20 mmol) g, and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ha** (0.078 g, 93%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.72 (d, J = 8.0 Hz, 1H, Ar–H), 7.41 (d, J = 8.2 Hz, 2H, Ar–H), 7.28 (d, J = 8.3 Hz, 2H, Ar–H), 7.18 (td, J = 6.9, 1.0 Hz, 1H, Ar–H), 7.11 (td, J = 7.0, 1.0 Hz, 1H, Ar-H), 7.03 (d, J = 8.1 Hz, 1H, Ar-H), 3.10-2.99 (sept, J = 6.9 Hz, 1H, CH), 2.71-2.66 (m, 2H, CH<sub>2</sub>), 1.45 (s, 9H, 3CH<sub>3</sub>), 1.34 (d, *J* = 7.0 Hz, 6H, 2CH<sub>3</sub>), 0.68-0.63 (m, 2H, CH<sub>2</sub>), -0.18 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 209.8$  (CO), 149.7 (C<sub>a</sub>), 147.4 (C<sub>a</sub>), 137.8 (C<sub>q</sub>), 134.6 (C<sub>q</sub>), 128.5 (2C, CH), 127.7 (2C, CH), 125.4 (C<sub>q</sub>), 121.7 (CH), 121.2 (CH), 120.9 (CH), 114.8 (C<sub>a</sub>), 110.8 (CH), 44.5 (C<sub>a</sub>), 34.1 (CH), 27.7 (3C, CH<sub>3</sub>), 24.2 (2C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.6 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>38</sub>NOSi<sup>+</sup> 420.2717; Found 420.2719.



# 1-(1-(4-(tert-Butyl)phenyl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)-2,2-

**dimethylpropan-1-one (3ia):** The representative procedure D was followed, using 1-(1-(4-(*tert*-butyl)phenyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (**1i**; 0.067 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ia** (0.076 g, 87%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.72 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.57 (d, *J* = 8.2 Hz, 2H, Ar–H), 7.28 (d, J = 8.4 Hz, 2H, Ar–H), 7.18 (t, J = 8.0 Hz, 1H, Ar–H), 7.11 (t, J = 7.5 Hz, 1H, Ar–H), 7.04 (d, J = 8.1 Hz, 1H, Ar–H), 2.70-2.66 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 1.42 (s, 9H, 3CH<sub>3</sub>), 0.67-0.62 (m, 2H, CH<sub>2</sub>), -0.19 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 209.8$  (CO), 152.0 (C<sub>q</sub>), 147.5 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 134.3 (C<sub>q</sub>), 128.2 (2C, CH), 126.6 (2C, CH), 125.4 (C<sub>q</sub>), 121.7 (CH), 121.2 (CH), 120.9 (CH), 114.8 (C<sub>q</sub>), 110.8 (CH), 44.5 (C<sub>q</sub>), 35.0 (C<sub>q</sub>), 31.5 (3C, CH<sub>3</sub>), 27.7 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.6 (CH<sub>2</sub>), -2.6 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>40</sub>NOSi<sup>+</sup> 434.2874; Found 434.2876.



**1-(1-(4-Fluorophenyl)-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)-2,2-dimethylpropan-1one (3ja): The representative procedure D was followed, using 1-(1-(4-fluorophenyl)-1*H*indol-3-yl)-2,2-dimethylpropan-1-one (1j; 0.060 g, 0.203 mmol) and trimethyl(vinyl)silane ( 0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ja (0.045 g, 56%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.67$  (d, J = 8.0 Hz, 1H, Ar–H), 7.36-7.32 (m, 2H, Ar–H), 7.82-7.23 (m, 2H, Ar–H), 7.19-7.16 (m, 1H, Ar–H), 7.13-7.09 (m, 1H, Ar–H), 6.94 (d, J = 8.1 Hz, 1H, Ar–H), 2.66-2.61 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.63-0.59 (m, 2H, CH<sub>2</sub>), -0.16 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 210.2$  (CO), 162.5 (d, <sup>1</sup> $J_{C-F} = 248.7$  Hz, C<sub>q</sub>), 146.6 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 133.2 (d, <sup>4</sup> $J_{C-F} = 3.0$  Hz, C<sub>q</sub>), 130.5 (d, <sup>3</sup> $J_{C-F} = 9.2$  Hz, 2C, CH), 125.5 (C<sub>q</sub>), 122.0 (CH), 121.2 (CH), 121.1 (CH), 116.8 (d, <sup>2</sup> $J_{C-F} = 23.0$  Hz, 2C, CH), 116.7 (CH), 115.4 (C<sub>q</sub>), 110.5 (CH), 44.7 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.9 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). <sup>19</sup>F-NMR (377 MHz, CDCl<sub>3</sub>):  $\delta = -112.2$  (s). HRMS (ESI) *m*/*z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>FNOSi<sup>+</sup> 396.2153; Found 396.2470.



### 2,2-Dimethyl-1-(1-(4-(trifluoromethyl)phenyl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-

**yl)propan-1-one (3ka):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-(4-(trifluoromethyl)phenyl)-1*H*-indol-3-yl)propan-1-one (**1k**; 0.070 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ka** (0.037 g, 41%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.85 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.65 (d, *J* = 7.9 Hz, 2H, Ar–H), 7.52 (d, *J* = 8.3 Hz, 2H, Ar–H), 7.19 (vt, *J* = 8.0 Hz, 1H, Ar–H), 7.13 (td, *J* = 7.1, 1.1 Hz, 1H, Ar–H), 6.99 (d, *J* = 8.1 Hz, 1H, Ar–H), 2.68-2.64 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.60-0.55 (m, 2H, CH<sub>2</sub>), -0.18 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.5 (CO), 145.5 (C<sub>q</sub>), 140.7 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 130.9 (q, <sup>2</sup>*J*<sub>C–F</sub> = 33.6 Hz, C<sub>q</sub>), 129.1 (2C, CH), 127.0 (q, <sup>3</sup>*J*<sub>C–F</sub> = 3.8 Hz, 2C, CH), 125.8 (C<sub>q</sub>), 123.9 (q, <sup>1</sup>*J*<sub>C–F</sub> = 272.4 Hz, CF<sub>3</sub>), 122.3 (CH), 121.5 (CH), 121.3 (CH), 116.2 (C<sub>q</sub>), 110.3 (CH), 44.6 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). <sup>19</sup>F-NMR (377 MHz, CDCl<sub>3</sub>):  $\delta$  = -62.6 (s). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>31</sub>F<sub>3</sub>NOSi<sup>+</sup> 446.2122; Found 446.2122.



# 2,2-Dimethyl-1-(1-(4-(methylthio)phenyl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-

yl)propan-1-one (3la): The representative procedure D was followed, using 2,2-dimethyl-1-(1-(4-(methylthio)phenyl)-1*H*-indol-3-yl)propan-1-one (1l; 0.065 g, 0.201 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3la** (0.050 g, 59%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.66 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.42-7.40 (m, 2H, Ar–H), 7.28-7.25 (m, 2H, Ar–H), 7.16 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H, Ar–H), 7.10 (ddd, *J* = 8.3, 7.1, 1.0 Hz, 1H, Ar–H), 6.98 (d, J = 8.0 Hz, 1H, Ar–H), 2.68-2.63 (m, 2H, CH<sub>2</sub>), 2.57 (s, 3H, CH<sub>3</sub>), 1.40 (s, 9H, 3CH<sub>3</sub>), 0.65-0.60 (m, 2H, CH<sub>2</sub>), -0.16 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 210.2$  (CO), 146.6 (C<sub>q</sub>), 139.8 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 129.0 (2C, CH), 127.4 (2C, CH), 125.6 (C<sub>q</sub>), 121.9 (CH), 121.2 (CH), 121.1 (CH), 115.3 (C<sub>q</sub>), 110.6 (CH), 44.7 (C<sub>q</sub>), 27.8 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.9 (CH<sub>2</sub>), 16.0 (CH<sub>3</sub>), -2.0 (3C, CH<sub>3</sub>). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>34</sub>NOSSi<sup>+</sup> 424.2125; Found 424.2115.



# 1-(1-(2-Methoxyphenyl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)-2,2-dimethylpropan-

1-one (3ma): The representative procedure D was followed, using 1-(1-(2-methoxyphenyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (1m; 0.062 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ma** (0.073 g, 89%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.73 (d, J = 8.0 Hz, 1H, Ar–H), 7.49 (td, J = 7.9, 1.6 Hz, 1H, Ar–H), 7.30 (dd, J = 7.6, 1.5 Hz, 1H, Ar–H), 7.19-7.07 (m, 4H, Ar–H), 6.89 (d, J = 8.0 Hz, 1H, Ar-H), 3.70 (s, 3H, CH<sub>3</sub>), 2.74-2.50 (m, 2H, CH<sub>2</sub>), 1.45 (s, 9H, 3CH<sub>3</sub>), 0.77-0.60 (m, 2H, CH<sub>2</sub>), -0.17 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 209.5$  (CO), 156.1 (C<sub>a</sub>), 148.2 (C<sub>a</sub>), 137.5 (C<sub>a</sub>), 130.7 (CH), 130.5 (CH), 125.6 (C<sub>a</sub>), 125.4 (C<sub>a</sub>), 121.5 (CH), 121.1 (2C, CH), 120.7 (CH), 114.5 (C<sub>a</sub>), 112.5 (CH), 110.5 (CH), 55.7 (CH<sub>3</sub>), 44.5 (C<sub>a</sub>), 27.7 (3C, CH<sub>3</sub>), 20.8 (CH<sub>2</sub>), 17.2 (CH<sub>2</sub>), -2.2 (3C, CH<sub>3</sub>). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>34</sub>NO<sub>2</sub>Si<sup>+</sup> 408.2353; Found 408.2353.



1-(1-(3,5-Dimethylphenyl)-2-(2-(trimethylsilyl)ethyl)-1*H*-indol-3-yl)-2,2dimethylpropan-1-one (3na): The representative procedure D was followed, using 1-(1(3,5-dimethylphenyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (**1n**; 0.062 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3na** (0.078 g, 95%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.71 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.20-7.09 (m, 3H, Ar–H), 7.04 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.99 (s, 2H, Ar–H), 2.74-2.69 (m, 2H, CH<sub>2</sub>), 2.42 (s, 6H, 2CH<sub>3</sub>), 1.45 (s, 9H, 3CH<sub>3</sub>), 0.73-0.68 (m, 2H, CH<sub>2</sub>), -0.13 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.9 (CO), 147.2 (C<sub>q</sub>), 139.5 (CH), 137.6 (C<sub>q</sub>), 136.9 (C<sub>q</sub>), 130.3 (2C, C<sub>q</sub>), 126.2 (2C, CH), 125.4 (C<sub>q</sub>), 121.6 (CH), 121.1 (CH), 120.9 (CH), 114.9 (C<sub>q</sub>), 110.8 (CH), 44.6 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 21.3 (2C, CH<sub>3</sub>), 20.7 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>36</sub>NOSi<sup>+</sup> 406.2561; Found 406.2561.



# 1-(1-(3,5-bis(trifluoromethyl)phenyl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)-2,2-

**dimethylpropan-1-one (30a):** The representative procedure D was followed, using 1-(1-(3,5-bis(trifluoromethyl)phenyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (**10**; 0.083 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **30a** (0.073 g, 71%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.05 (s, 1H, Ar–H), 7.91 (s, 2H, Ar–H), 7.65 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.25-7.16 (m, 2H, Ar–H), 6.98 (d, *J* = 7.9 Hz, 1H, Ar–H), 2.76-2.63 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.60-0.56 (m, 2H, CH<sub>2</sub>), -0.16 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.6 (CO), 144.6 (Cq), 139.3 (Cq), 137.2 (Cq), 133.7 (q, <sup>2</sup>*J*<sub>C-F</sub> = 33.6 Hz, 2C, Cq), 129.0 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.1 Hz, 2C, CH), 126.0 (Cq), 122.9 (q, <sup>1</sup>*J*<sub>C-F</sub> = 272. 4 Hz, 2 CF<sub>3</sub>), 122.8 (CH), 122.4 (sept, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz, CH), 121.9 (CH), 121.4 (CH), 117.0 (Cq), 109.8 (CH), 44.9 (Cq), 27.7 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 18.2 (CH<sub>2</sub>), -2.3 (3C, CH<sub>3</sub>). <sup>19</sup>F-NMR (377 MHz, CDCl<sub>3</sub>):  $\delta$  = -62.9 (s). HRMS (ESI) *m*/*z*: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>30</sub>F<sub>6</sub>NOSi<sup>+</sup> 514.1995; Found 514.2070.



**1-(1-Benzyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)-2,2-dimethylpropan-1-one (**3**pa): The representative procedure D was followed, using 1-(1-benzyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (**1**p; 0.059 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3pa** (0.064 g, 81%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.72 (d, *J* = 7.7 Hz, 1H, Ar–H), 7.34-7.28 (m, 3H, Ar–H), 7.24-7.14 (m, 3H, Ar–H), 7.01 (d, *J* = 6.7 Hz, 2H, Ar–H), 5.37 (s, 2H, CH<sub>2</sub>), 2.77-2.72 (m, 2H, CH<sub>2</sub>), 1.43 (s, 9H, 3CH<sub>3</sub>), 0.85-0.80 (m, 2H, CH<sub>2</sub>), 0.05 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.0 (CO), 146.7 (Cq), 137.2 (Cq), 136.3 (Cq), 129.1 (2C, CH), 127.7 (CH), 126.1 (2C, CH), 125.7 (Cq), 121.7 (CH), 121.5 (CH), 120.8 (CH), 115.0 (Cq), 110.1 (CH), 46.7 (CH<sub>2</sub>), 44.5 (Cq), 27.8 (3C, CH<sub>3</sub>), 20.4 (CH<sub>2</sub>), 18.3 (CH<sub>2</sub>), -1.8 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>34</sub>NOSi<sup>+</sup> 392.2404; Found 392.2404.



**2,2-Dimethyl-1-(1-methyl-2-(2-(trimethylsilyl)ethyl)-1***H***-indol-3-yl)propan-1-one (3qa): The representative procedure D was followed, using 2,2-dimethyl-1-(1-methyl-1***H***-indol-3-yl)propan-1-one (1q; 0.043 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3qa (0.048 g, 76%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): \delta = 7.67 (d,** *J* **= 7.6 Hz, 1H, Ar–H), 7.29 (d,** *J* **= 7.6 Hz, 1H, Ar–H), 7.22-9.14 (m, 2H, Ar–H), 3.69 (s, 3H, CH<sub>3</sub>), 2.81-2.77 (m, 2H, CH<sub>2</sub>), 1.38 (s, 9H, 3CH<sub>3</sub>), 0.88-0.84 (m, 2H, CH<sub>2</sub>), 0.10 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>): \delta = 209.6 (CO), 147.1 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 125.4 (C<sub>q</sub>), 121.5 (CH), 121.4 (CH), 120.6 (CH), 114.3 (C<sub>q</sub>), 109.4 (CH), 44.4 (C<sub>q</sub>), 29.6 (CH<sub>3</sub>), 27.8 (3C, CH<sub>3</sub>), 20.3 (CH<sub>2</sub>), 17.8 (CH<sub>2</sub>), -1.6 (3C, CH<sub>3</sub>). HRMS (ESI)** *m/z***: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>30</sub>NOSi<sup>+</sup> 316.2091; Found 316.2092.** 



1-(1-Ethyl-2-(2-(trimethylsilyl)ethyl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (3ra): The representative procedure D was followed, using 1-(1-ethyl-1*H*-indol-3-yl)-2,2dimethylpropan-1-one (1r; 0.046 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ra (0.051 g, 77%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.67 (d, J = 7.2 Hz, 1H, Ar–H), 7.31 (d, J = 7.4 Hz, 1H, Ar–H), 7.13-7.21 (m, 2H, Ar–H), 4.15 (q, J = 7.3 Hz, 2H, CH<sub>2</sub>), 2.80-2.76 (m, 2H, CH<sub>2</sub>), 1.41 (t, J = 7.3 Hz, 3H, CH<sub>3</sub>), 1.40 (s, 9H, 3CH<sub>3</sub>), 0.91-0.87 (m, 2H, CH<sub>2</sub>), 0.10 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.6 (CO), 146.7 (C<sub>q</sub>), 135.3 (C<sub>q</sub>), 125.7 (C<sub>q</sub>), 121.6 (CH), 121.3 (CH), 120.5 (CH), 114.4 (C<sub>q</sub>), 109.6 (CH), 44.4 (C<sub>q</sub>), 38.0 (CH<sub>2</sub>), 27.8 (3C, CH<sub>3</sub>), 20.2 (CH<sub>2</sub>), 18.3 (CH<sub>2</sub>), 15.4 (CH<sub>3</sub>), -1.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>32</sub>NOSi<sup>+</sup> 330.2248; Found 330.2249.



**1-(1-Isobutyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)-2,2-dimethylpropan-1-one (**3sa**): The representative procedure D was followed, using 1-(1-isobutyl-1*H*-indol-3-yl)-2,2dimethylpropan-1-one (**1s**; 0.052 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3sa** (0.059 g, 82%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.66 (d, J = 7.0 Hz, 1H, Ar–H), 7.29 (d, J = 7.0 Hz, 1H, Ar–H), 7.19-7.12 (m, 2H, Ar–H), 3.90 (d, J = 7.5 Hz, 2H, CH<sub>2</sub>), 2.82-2.78 (m, 2H, CH<sub>2</sub>), 2.26 (sept, J = 6.9 Hz, 1H, CH), 1.39 (s, 9H, 3CH<sub>3</sub>), 0.95 (d, J = 6.6 Hz, 6H, 2CH<sub>3</sub>), 0.89-0.84 (m, 2H, CH<sub>2</sub>), 0.11 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.8 (CO), 147.0 (C<sub>q</sub>), 136.1 (C<sub>q</sub>), 125.6 (C<sub>q</sub>), 121.4 (CH), 121.1 (CH), 120.4 (CH), 114.3 (C<sub>q</sub>), 110.3 (CH), 50.7 (CH<sub>2</sub>), 44.4 (C<sub>q</sub>), 29.5 (CH), 27.8 (3C, CH<sub>3</sub>), 20.5 (2C, CH<sub>3</sub>), 20.3 (CH<sub>2</sub>), 18.2 (CH<sub>2</sub>), -1.8 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>36</sub>NOSi<sup>+</sup> 358.6125; Found 358.6115.



**1-(1-Cycloheptyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)-2,2-dimethylpropan-1-one (**3ta**): The representative procedure D was followed, using 1-(1-cycloheptyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (**1t**; 0.060 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ta** (0.054 g, 67%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62-7.60 (m, 1H, Ar–H), 7.46 (d, *J* = 8.6 Hz, 1H, Ar–H), 7.14-7.08 (m, 2H, Ar–H), 4.30 (t, *J* = 8.0 Hz, 1H, CH), 2.76-2.72 (m, 2H, CH<sub>2</sub>), 2.50-2.45 (m, 2H, CH<sub>2</sub>), 2.00-1.89 (m, 4H, 2CH<sub>2</sub>), 1.72-1.57 (m, 6H, 3CH<sub>2</sub>), 1.36 (s, 9H, 3CH<sub>3</sub>), 0.88-0.83 (m, 2H, CH<sub>2</sub>), 0.12 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.9 (CO), 145.0 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 126.3 (C<sub>q</sub>), 121.5 (CH), 120.6 (CH), 119.8 (CH), 114.2 (C<sub>q</sub>), 112.4 (CH), 57.6 (CH), 44.5 (C<sub>q</sub>), 27.9 (3C, CH<sub>2</sub>), 27.8 (3C, CH<sub>3</sub>), 26.8 (3C, CH<sub>2</sub>), 20.6 (CH<sub>2</sub>), 18.5 (CH<sub>2</sub>), -1.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>40</sub>NOSi<sup>+</sup> 398.2874; Found 398.2874.



2,2-Dimethyl-1-(1-(3-methylbut-3-en-1-yl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-

**yl)propan-1-one (3ua):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-(3-methylbut-3-en-1-yl)-1*H*-indol-3-yl)propan-1-one (**1u**; 0.054 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ua** (0.052 g, 70%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.69 (d, *J* = 7.4 Hz, 1H, Ar–H), 7.32 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.22-7.15 (m, 2H, Ar–H), 4.89 (s, 1H, CH<sub>2</sub>), 4.80 (s, 1H, CH<sub>2</sub>), 4.21-4.17 (m, 2H, CH<sub>2</sub>), 2.80-2.76 (m, 2H, CH<sub>2</sub>), 2.48 (t, *J* = 7.9 Hz, 2H, CH<sub>2</sub>), 1.83 (s, 3H, CH<sub>3</sub>), 1.39 (s, 9H, 3CH<sub>3</sub>), 0.92-0.88 (m, 2H, CH<sub>2</sub>), 0.11 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.6 (CO), 146.7 (C<sub>q</sub>), 142.2 (C<sub>q</sub>), 135.4 (C<sub>q</sub>), 125.7 (C<sub>q</sub>), 121.6 (CH), 121.4 (CH), 120.5 (CH), 114.4 (C<sub>q</sub>), 112.8 (CH<sub>2</sub>), 109.6 (CH), 44.4 (C<sub>q</sub>), 42.4 (CH<sub>2</sub>), 38.0 (CH<sub>2</sub>), 27.8 (3C, CH<sub>3</sub>), 22.9 (CH<sub>3</sub>), 20.3 (CH<sub>2</sub>), 18.4 (CH<sub>2</sub>), -1.8 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>36</sub>NOSi<sup>+</sup> 370.2561; Found 370.2562.



1-(1-(Cyclohex-2-en-1-yl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)-2,2-dimethylpropan-1-one (3va): The representative D procedure was followed, using 1-(1-(cyclohex-2-en-1-yl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (1v;0.057 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3va** (0.051 g, 66%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62-7.58 (m, 1H, Ar–H), 7.52-7.47 (m, 1H, Ar–H), 7.12-7.06 (m, 2H, Ar–H), 6.05-6.01 (m, 1H, CH), 5.80 (d, J = 9.9 Hz, 1H, CH), 5.00 (br s, 1H, CH), 2.83-2.67 (m, 2H, CH<sub>2</sub>), 2.34-2.25 (m, 3H, CH<sub>2</sub>), 2.04-2.01 (m, 2H, CH<sub>2</sub>), 1.86-1.79 (m, 1H, CH<sub>2</sub>), 1.36 (s, 9H, 3CH<sub>3</sub>), 0.91-0.81 (m, 2H, CH<sub>2</sub>), 0.08 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 209.8$  (CO), 145.7 (C<sub>a</sub>), 134.7 (C<sub>a</sub>), 130.6 (CH), 128.9 (CH), 126.3 (2C, C<sub>a</sub>), 121.3 (CH), 120.7 (CH), 120.1 (CH), 112.5 (CH), 52.6 (CH), 44.6 (C<sub>a</sub>), 28.6 (CH<sub>2</sub>), 27.9 (3C, 3CH<sub>3</sub>), 24.8 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>), 20.4 (CH<sub>2</sub>), 18.6 (CH<sub>2</sub>), -1.8 (3C, 3CH<sub>3</sub>). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>36</sub>NOSi<sup>+</sup> 382.2561; Found 382.2569.



#### 2,2-Dimethyl-1-(1-(pyridin-2-yl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)propan-1-one

(3wa): The representative procedure D was followed, using 2,2-dimethyl-1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (1w; 0.056 g, 0.201 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3wa** (0.072 g, 95%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.67 (d, *J* = 3.5 Hz, 1H, Ar–H), 7.90 (td, *J* = 7.6, 1.6 Hz, 1H, Ar–H), 7.59 (d, *J* = 7.4 Hz, 1H, Ar–H), 7.44 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.37 (dd, *J* = 7.1, 5.1 Hz, 1H, Ar–H), 7.22-7.11 (m, S24 3H, Ar–H), 2.86-2.82 (m, 2H, CH<sub>2</sub>), 1.39 (s, 9H, 3CH<sub>3</sub>), 0.59-0.54 (m, 2H, CH<sub>2</sub>), –0.14 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 211.1 (CO), 150.9 (C<sub>q</sub>), 149.6 (CH), 144.6 (C<sub>q</sub>), 138.7 (CH), 136.5 (C<sub>q</sub>), 126.1 (C<sub>q</sub>), 123.0 (CH), 121.3 (CH), 121.9 (CH), 121.3 (CH), 120.9 (CH), 116.6 (C<sub>q</sub>), 110.4 (CH), 44.9 (C<sub>q</sub>), 27.6 (3C, CH<sub>3</sub>), 20.7 (CH<sub>2</sub>), 17.6 (CH<sub>2</sub>), –2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>31</sub>N<sub>2</sub>OSi<sup>+</sup> 379.2200; Found 379.2199.



### 2,2-Dimethyl-1-(1-(6-methylpyridin-2-yl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-

**yl)propan-1-one (3xa):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-(6-methylpyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (**1x**; 0.059 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **3xa** (0.068 g, 86%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81-7.79 (m, 1H, Ar–H), 7.61 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.26-7.13 (m, 5H, Ar–H), 2.88-2.85 (m, 2H, CH<sub>2</sub>), 2.64 (s, 3H, CH<sub>3</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.63-0.59 (m, 2H, CH<sub>2</sub>), -0.12 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 211.0 (CO), 159.3 (C<sub>q</sub>), 150.2 (C<sub>q</sub>), 145.0 (C<sub>q</sub>), 138.8 (CH), 136.6 (C<sub>q</sub>), 126.1 (C<sub>q</sub>), 122.5 (CH), 122.1 (CH), 121.2 (CH), 120.9 (CH), 118.8 (CH), 116.4 (C<sub>q</sub>), 110.5 (CH), 44.9 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.6 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>33</sub>N<sub>2</sub>OSi<sup>+</sup> 393.2357; Found 393.2379.



#### 2,2-Dimethyl-1-(5-methyl-1-phenyl-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)propan-1-

one (3ya): The representative procedure D was followed, using 2,2-dimethyl-1-(5-methyl-1-phenyl-1*H*-indol-3-yl)propan-1-one (1y; 0.059 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum

ether/EtOAc: 30/1) yielded **3ya** (0.068 g, 86%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.58-7.47 (m, 4H, Ar–H), 7.36 (d, J = 7.6 Hz, 2H, Ar–H), 6.96-6.89 (m, 2H, Ar–H), 2.71-2.66 (m, 2H, CH<sub>2</sub>), 2.48 (s, CH<sub>3</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 0.66-0.62 (m, 2H, CH<sub>2</sub>), -0.16 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.2 (CO), 146.6 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 136.1 (C<sub>q</sub>), 130.3 (C<sub>q</sub>), 129.7 (2C, CH), 128.6 (3C, CH), 125.8 (C<sub>q</sub>), 123.3 (CH), 120.9 (CH), 114.9 (C<sub>q</sub>), 110.3 (CH), 44.6 (C<sub>q</sub>), 27.8 (3C, CH<sub>3</sub>), 21.8 (CH<sub>3</sub>), 20.7 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>34</sub>NOSi<sup>+</sup> 392.2332; Found 392.2324.



**1-(5-Chloro-1-phenyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)-2,2-dimethylpropan-1one (**3za**): The representative procedure D was followed, using 1-(5-chloro-1-phenyl-1*H*indol-3-yl)-2,2-dimethylpropan-1-one (**1z**; 0.063 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3za** (0.067 g, 80%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62 (s, 1H, Ar–H), 7.58-7.50 (m, 3H, Ar–H), 7.33 (d, *J* = 7.5 Hz, 2H, Ar–H), 7.05 (d, *J* = 8.6 Hz, 1H, Ar–H), 6.90 (d, *J* = 8.8 Hz, 1H, Ar–H), 2.68-2.64 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.64-0.60 (m, 2H, CH<sub>2</sub>), -0.17 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.7 (CO), 147.7 (C<sub>q</sub>), 136.8 (C<sub>q</sub>), 136.1 (C<sub>q</sub>), 129.9 (2C, CH), 129.1 (CH), 128.5 (2C, CH), 126.8 (C<sub>q</sub>), 126.5 (C<sub>q</sub>), 122.1 (CH), 120.4 (CH), 114.7 (C<sub>q</sub>), 111.6 (CH), 44.7 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.7 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>CINOSi<sup>+</sup> 412.1858; Found 412.1873.



**1-(6-Fluoro-1-phenyl-2-(2-(trimethylsilyl)ethyl)-1***H***-indol-3-yl)-2,2-dimethylpropan-1one (3Aa):** The representative procedure D was followed, using 1-(6-fluoro-1-phenyl-1*H*- indol-3-yl)-2,2-dimethylpropan-1-one (**1A**; 0.059 g, 0.20 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3Aa** (0.066 g, 83%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.58-7.51 (m, 4H, Ar–H), 7.35 (d, *J* = 7.6 Hz, 2H, Ar–H), 6.92 (vt, *J* = 9.0 Hz, 1H, Ar–H), 6.68 (d, *J* = 9.5 Hz, 1H, Ar–H), 2.68-2.64 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.65-0.60 (m, 2H, CH<sub>2</sub>), -0.17 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.0 (CO), 159.7 (d, <sup>1</sup>*J*<sub>C-F</sub> = 238.8 Hz, C<sub>q</sub>), 146.7 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.1 Hz, C<sub>q</sub>), 137.9 (d, <sup>3</sup>*J*<sub>C-F</sub> = 12.2 Hz, C<sub>q</sub>), 136.8 (C<sub>q</sub>), 129.9 (2C, CH), 129.0 (CH), 128.5 (2C, CH), 122.0 (C<sub>q</sub>), 121.7 (d, <sup>3</sup>*J*<sub>C-F</sub> = 9.2 Hz, CH), 115.1 (C<sub>q</sub>), 109.4 (d, <sup>2</sup>*J*<sub>C-F</sub> = 23.6 Hz, CH), 97.0 (d, <sup>2</sup>*J*<sub>C-F</sub> = 25.9 Hz, CH), 44.7 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.7 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -2.2 (3C, CH<sub>3</sub>). <sup>19</sup>F-NMR (377 MHz, CDCl<sub>3</sub>):  $\delta$  = -120.8 HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>FNOSi<sup>+</sup> 396.2153; Found 396.2470.



**1-(6-Chloro-1-phenyl-2-(2-(trimethylsilyl)ethyl)-1***H*-indol-3-yl)-2,2-dimethylpropan-1one (**3Ba**): The representative procedure D was followed, using 1-(6-chloro-1-phenyl-1*H*indol-3-yl)-2,2-dimethylpropan-1-one (**1B**; 0.063 g, 0.202 mmol) and trimethyl(vinyl)silane (0.040 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3Ba** (0.070 g, 84%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57-7.52 (m, 4H, Ar–H), 7.34 (d, *J* = 7.4 Hz, 2H, Ar–H), 7.13 (d, *J* = 8.5 Hz, 1H, Ar–H), 6.97 (s, 1H, Ar–H), 2.66-2.62 (m, 2H, CH<sub>2</sub>), 1.39 (s, 9H, 3CH<sub>3</sub>), 0.63-0.59 (m, 2H, CH<sub>2</sub>), -0.18 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.9 (CO), 147.1 (C<sub>q</sub>), 138.1 (C<sub>q</sub>), 136.6 (C<sub>q</sub>), 129.9 (2C, CH), 129.1 (CH), 128.6 (2C, CH), 127.8 (C<sub>q</sub>), 124.1 (C<sub>q</sub>), 121.8 (CH), 121.6 (CH), 115.1 (C<sub>q</sub>), 110.6 (CH), 44.7 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>ClNOSi<sup>+</sup> 412.1858; Found 412.1910.



**2,2-Dimethyl-1-(1-phenyl-2-(2-(triethylsilyl)ethyl)-1***H***-indol-3-yl)propan-1-one (3ab): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1***H***-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol) and triethyl(vinyl)silane (2b; 0.057 g, 0.402 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ab (0.075 g, 88%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): \delta = 7.69 (d,** *J* **= 7.9 Hz, 1H, Ar–H), 7.59-7.49 (m, 3H, Ar–H), 7.40 (d,** *J* **= 6.9 Hz, 2H, Ar–H), 7.18 (td,** *J* **= 7.0, 1.1 Hz, 1H, Ar–H), 7.11 (td,** *J* **= 7.0, 1.2 Hz, 1H, Ar–H), 7.00 (d,** *J* **= 8.0 Hz, 1H, Ar–H), 2.72-2.68 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 0.79 (t,** *J* **= 7.9 Hz, 9H, 3CH<sub>3</sub>), 0.70-0.65 (m, 2H, CH<sub>2</sub>), 0.38 (q, 6H, 3CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>): \delta = 210.3 (CO), 146.8 (Cq), 137.7 (Cq), 137.2 (Cq), 129.8 (2C, CH), 128.8 (CH), 128.7 (2C, CH), 125.5 (Cq), 121.8 (CH), 121.1 (CH), 121.0 (CH), 115.2 (Cq), 110.6 (CH), 44.6 (Cq), 27.7 (3C, CH<sub>3</sub>), 20.5 (CH<sub>2</sub>), 12.9 (CH<sub>2</sub>), 7.3 (3C, CH<sub>3</sub>), 3.0 (3C, CH<sub>2</sub>). HRMS (ESI)** *m/z***: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>38</sub>NOSi<sup>+</sup> 420.2717; Found 420.2719** 



**1-(2-(2-(Dimethyl(phenyl)silyl)ethyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one** (**3ac):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and dimethyl(phenyl)(vinyl)silane (**2c**; 0.065 g, 0.402 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ac** (0.081 g, 91%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.72 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.59-7.54 (m, 3H, Ar–H), 7.37-7.30 (m, 7H, Ar–H), 7.23-7.19 (m, 1H, Ar–H), 7.16-7.12 (m, 1H, Ar–H), 7.02 (d, *J* = 8.1 Hz, 1H, Ar–H), 2.74-2.69 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 0.98-0.93 (m, 2H, CH<sub>2</sub>), 0.16 (s, 6H, 2CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.2 (CO), 146.3 (C<sub>q</sub>), 138.4 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 137.1 (C<sub>q</sub>), 133.6 (2C, CH), 129.8 (2C, CH), 129.0 (CH), 128.8 (CH), 128.7 (2C, CH), 128.0 (2C, S28) CH), 125.5 (C<sub>q</sub>), 121.9 (CH), 121.1 (CH), 121.0 (CH), 115.3 (C<sub>q</sub>), 110.6 (CH), 44.6 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 20.8 (CH<sub>2</sub>), 16.6 (CH<sub>2</sub>), -3.3 (2C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>34</sub>NOSi<sup>+</sup> 440.2404; Found 440.2401.



**2,2-Dimethyl-1-(1-phenyl-2-(2-(triethoxysilyl)ethyl)-1***H*-indol-3-yl)propan-1-one (**3ad**): The representative procedure was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and triethoxy(vinyl)silane (**2d**; 0.082 g, 0.401 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ad** (0.065 g, 69%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.67 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.57-7.47 (m, 3H, Ar–H), 7.37 (d, *J* = 7.3 Hz, 2H, Ar–H), 7.17 (t, *J* = 7.4 Hz, 1H, Ar–H), 7.10 (t, *J* = 7.5 Hz, 1H, Ar–H), 6.97 (d, *J* = 8.0 Hz, 1H, Ar–H), 3.64 (q, *J* = 7.0 Hz, 6H, 2CH<sub>2</sub>), 2.81-2.76 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 1.12 (t, *J* = 7.0 Hz, 9H, 3CH<sub>3</sub>), 0.81-0.77 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.3 (CO), 145.6 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 137.2 (C<sub>q</sub>), 129.9 (2C, CH), 128.8 (2C, CH), 128.7 (CH), 125.5 (C<sub>q</sub>), 121.9 (CH), 121.8 (CH), 121.0 (CH), 115.5 (C<sub>q</sub>), 110.7 (CH), 58.4 (3C, CH<sub>2</sub>), 44.7 (C<sub>q</sub>), 27.7 (3C, CH<sub>3</sub>), 19.8 (CH<sub>2</sub>), 18.4 (3C, CH<sub>3</sub>), 11.5 (CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>38</sub>NO<sub>4</sub>Si<sup>+</sup> 468.2565; Found 468.2630.



# 1-(2-(2-(1,1,1,5,5,5-Hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)ethyl)-1-phenyl-

1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (3ae): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), and 1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)-3-vinyltrisiloxane (2e; 0.129 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ae (0.108 g, 89%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta =$  S29

7.63 (d, J = 7.9 Hz, 1H, Ar–H), 7.58-7.48 (m, 3H, Ar–H), 7.38-7.36 (m, 2H, Ar–H), 7.16 (td, J = 6.0, 1.1 Hz, 1H, Ar–H), 7.09 (td, J = 7.0, 1.1 Hz, 1H, Ar–H), 6.97 (d, J = 8.1 Hz, 1H, Ar–H), 2.73-2.68 (m, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>), 0.60-0.55 (m, 2H, CH<sub>2</sub>), 0.02 (s, 27H, 9CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 210.7$  (CO), 145.3 (C<sub>q</sub>), 137.6 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 129.9 (2C, CH), 128.6 (CH), 128.7 (2C, CH), 125.7 (C<sub>q</sub>), 121.8 (CH), 120.9 (CH), 120.8 (CH), 115.5 (C<sub>q</sub>), 110.6 (CH), 44.8 (C<sub>q</sub>), 27.8 (3C, CH<sub>3</sub>), 20.3 (CH<sub>2</sub>), 16.0 (CH<sub>2</sub>), 1.8 (9C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>50</sub>NO<sub>4</sub>Si<sub>4</sub><sup>+</sup> 600.2811; Found 600.2795.



**2,2-Dimethyl-1-(1-phenyl-2-(3-(trimethylsilyl)propyl)-1***H***-indol-3-yl)propan-1-one (3af):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and allyltrimethylsilane (**2f**; 0.046 g, 0.402 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3af** (0.048 g, 61%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.69 (d, *J* = 7.7 Hz, 1H, Ar–H), 7.58-7.49 (m, 3H, Ar–H), 7.36-7.33 (m, 2H, Ar–H), 7.17 (td, *J* = 5.9, 1.1 Hz, 1H, Ar–H), 7.10 (td, *J* = 5.9, 1.2 Hz, 1H, Ar–H), 6.97 (d, *J* = 7.9 Hz, 1H, Ar–H), 2.75 (t, *J* = 7.9 Hz, 2H, CH<sub>2</sub>), 1.42 (s, 9H, 3CH<sub>3</sub>), 1.38-1.31 (m, 2H, CH<sub>2</sub>) 0.35-0.31 (m, 2H, CH<sub>2</sub>), -0.17 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.3 (CO), 144.3 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 137.3 (C<sub>q</sub>), 129.8 (2C, CH), 128.8 (CH), 128.7 (2C, CH), 125.4 (C<sub>q</sub>), 121.9 (CH), 121.2 (CH), 121.1 (CH), 116.3 (C<sub>q</sub>), 110.8 (CH), 44.7 (C<sub>q</sub>), 29.9 (CH<sub>2</sub>), 27.8 (3C, CH<sub>3</sub>), 24.5 (CH<sub>2</sub>), 17.0 (CH<sub>2</sub>), -1.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>34</sub>NOSi<sup>+</sup> 392.2404; Found 392.2404.



**2,2-Dimethyl-1-(2-phenethyl-1-phenyl-1H-indol-3-yl)propan-1-one** (3ag): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1H-indol-3-S30

yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and styrene (**2g**; 0.042 g, 0.403 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ag** (0.052 g, 67%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.61-7.52 (m, 3H, Ar–H), 7.31 (dd, *J* = 8.0, 2.0 Hz, 2H, Ar–H), 7.25-7.13 (m, 5H, Ar–H), 7.02 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.92 (d, *J* = 8.0 Hz, 2H, Ar–H), 3.09-3.05 (m, 2H, CH<sub>2</sub>), 2.76-2.72 (m, 2H, CH<sub>2</sub>), 1.47 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 209.5 (CO), 144.0 (C<sub>q</sub>), 141.3 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 137.0 (C<sub>q</sub>), 129.9 (2C, CH), 129.0 (CH), 128.7 (2C, CH), 128.5 (2C, CH), 128.4 (2C, CH), 126.2 (CH), 125.2 (C<sub>q</sub>), 122.1 (CH), 121.5 (CH), 121.2 (CH), 116.3 (C<sub>q</sub>), 110.9 (CH), 44.6 (C<sub>q</sub>), 36.4 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 27.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>28</sub>NO<sup>+</sup> 382.2165; Found 382.2168.



**1-(2-(4-Methoxyphenethyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one (3ah):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and 1-methoxy-4-vinylbenzene (**2h**; 0.054 g, 0.402 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3ah** (0.060 g, 72%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.61-7.53 (m, 3H, Ar–H), 7.33-7.30 (m, 2H, Ar–H), 7.23 (td, *J* = 7.0, 1.0 Hz, 1H, Ar–H), 7.15 (td, *J* = 7.0, 1.0 Hz, 1H, Ar–H), 7.02 (d, *J* = 8.2 Hz, 1H, Ar–H), 6.83 (d, *J* = 8.5 Hz, 2H, Ar–H), 6.74 (d, *J* = 8.6 Hz, 2H, Ar–H), 3.76 (s, 3H, CH<sub>3</sub>), 3.05-3.01 (m, 2H, CH<sub>2</sub>), 2.70-2.66 (m, 2H, CH<sub>2</sub>), 1.47 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.5 (CO), 158.1 (Cq), 144.1 (Cq), 137.7 (Cq), 137.0 (Cq), 133.4 (Cq), 129.8 (2C, CH), 129.4 (2C, CH), 128.9 (CH), 128.7 (2C, CH), 125.2 (Cq), 122.1 (CH), 121.4 (CH), 121.2 (CH), 116.2 (Cq), 113.9 (2C, CH), 110.9 (CH), 55.4 (CH<sub>3</sub>), 44.6 (Cq), 35.5 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 27.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>30</sub>NO<sub>2</sub><sup>+</sup> 412.2271; Found 412.262.



#### 1-(2-(4-(tert-Butoxy)phenethyl)-1-phenyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one

(3ai): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), and 1-(*tert*-butoxy)-4-vinylbenzene (2i; 0.071 g, 0.401 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ai (0.065 g, 71%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.75$  (d, J = 8.0 Hz, 1H, Ar–H), 7.59-7.51 (m, 3H, Ar–H), 7.30-7.28 (m, 2H, Ar–H), 7.20 (td, J = 5.9, 1.1 Hz, 1H, Ar–H), 7.12 (td, J = 6.0, 1.1 Hz, 1H, Ar–H), 6.99 (d, J = 8.0 Hz, 1H, Ar–H), 6.77 (d, J = 3.6 Hz, 4H, Ar–H), 3.03-2.99 (m, 2H, CH<sub>2</sub>), 2.67-2.63 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 1.29 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 209.6$  (CO), 153.7 (Cq), 114.2 (Cq), 137.8 (Cq), 137.1 (Cq), 136.2 (Cq), 130.0 (2C, CH), 129.0 (CH), 128.8 (2C, CH), 128.7 (2C, CH), 125.3 (Cq), 124.3 (2C, CH), 122.1 (CH), 121.5 (CH), 121.2 (CH), 116.2 (Cq), 110.9 (CH), 78.3 (Cq), 44.6 (Cq), 35.7 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 29.0 (3C, CH<sub>3</sub>), 27.8 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>36</sub>NO<sub>2</sub><sup>+</sup> 454.2741; Found 454.2733.



**1-(2-(4-(Benzyloxy)phenethyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one (3aj):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), 1-(benzyloxy)-4-vinylbenzene (**2j**; 0.084 g, 0.40 mmol), and 0.2 mL of 2-MeTHF. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **3aj** (0.060 g, 61%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.73 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.53-7.45 (m, 3H, Ar–H), 7.37-7.30 (m, 4H, Ar–H), 7.28-7.22 (m, 3H, Ar–H), 7.17 (vt, *J* = 7.4 Hz, 1H, Ar–H), 7.08 (vt, *J* = 7.5 Hz, 1H, Ar–H), 6.95 (d, *J* = 8.1 Hz, 1H, Ar–H), 6.76 (vt, *J* = 9.4 Hz, 4H, Ar–H), 4.95 (s, 2H, CH<sub>2</sub>), 2.97 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 2.62 (t, *J* = 8.0 Hz, 2H, CH<sub>2</sub>), 1.41 (s, 9H, 3CH<sub>3</sub>). S32 <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 209.5$  (CO), 157.3 (C<sub>q</sub>), 144.1 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 137.3 (C<sub>q</sub>), 137.0 (C<sub>q</sub>), 133.7 (C<sub>q</sub>), 129.8 (2C, CH), 129.4 (2C, CH), 128.9 (CH), 128.7 (2C, CH), 128.6 (2C, CH), 128.0 (CH), 127.5 (2C, CH), 125.2 (C<sub>q</sub>), 122.1 (CH), 121.4 (CH), 121.2 (CH), 116.2 (C<sub>q</sub>), 114.9 (2C, CH), 110.9 (CH), 70.1 (CH<sub>2</sub>), 44.5 (C<sub>q</sub>), 35.4 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 27.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>34</sub>NO<sub>2</sub><sup>+</sup> 488.2584; Found 488.2646.



**1-(2-(2-(9***H***-Carbazol-9-yl)ethyl)-1-phenyl-1***H***-indol-3-yl)ethan-1-one (3ck): The representative procedure D was followed, using 1-(1-phenyl-1***H***-indol-3-yl)ethan-1-one (1c; 0.047 g, 0.20 mmol), and 9-vinyl-9***H***-carbazole (2k; 0.078 g, 0.403 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ck (0.056 g, 74%) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDC1<sub>3</sub>): \delta = 8.03 (d, J = 7.5 Hz, 3H, Ar–H), 7.57-7.49 (m, 3H, Ar–H), 7.38-7.31 (m, 3H, Ar–H), 7.24-7.11 (m, 7H, Ar–H), 6.99 (d, J = 8.1 Hz, 1H, Ar–H), 4.50 (t, J = 7.7 Hz, 2H, CH<sub>2</sub>), 3.54 (t, J = 7.7 Hz, 2H, CH<sub>2</sub>), 2.93 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDC1<sub>3</sub>): \delta = 195.2 (CO), 145.5 (2C, Cq), 140.2 (2C, Cq), 138.4 (2C, Cq), 135.7 (2C, Cq), 130.2 (2C, CH), 129.4 (CH), 128.7 (2C, CH), 125.8 (2C, CH), 122.9 (CH), 122.7 (CH), 120.5 (CH), 120.2 (2C, CH), 119.0 (2C, CH), 115.5 (Cq), 111.5 (CH), 108.7 (2C, CH), 41.7 (CH<sub>2</sub>), 32.1 (CH<sub>3</sub>), 26.3 (CH<sub>2</sub>).** 



1-(2-(3-(9*H*-Carbazol-9-yl)propyl)-1-phenyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (3al): The representative procedure was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), 9-allyl-9*H*-carbazole (2l; 0.083 g, 0.402

mmol), and 0.2 mL of 2-MeTHF. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3al** (0.077 g, 79%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.01 (d, J = 7.7 Hz, 2H, Ar–H), 7.74 (d, J = 8.1 Hz, 1H, Ar–H), 7.35 (vt, J = 7.4 Hz, 2H, Ar–H), 7.21-7.04 (m, 9H, Ar–H), 6.99 (d, J = 7.7 Hz, 2H, Ar–H), 6.88 (d, J = 8.3 Hz, 1H, Ar–H), 4.17 (t, J = 6.9 Hz, 2H, CH<sub>2</sub>), 2.82-2.78 (m, 2H, CH<sub>2</sub>), 2.00-1.93 (m, 2H, CH<sub>2</sub>), 1.42 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 208.9 (CO), 144.3 (C<sub>q</sub>), 140.3 (2C, C<sub>q</sub>), 137.7 (C<sub>q</sub>), 136.2 (C<sub>q</sub>), 129.5 (2C, CH), 128.7 (CH), 127.9 (2C, CH), 125.7 (2C, CH), 125.0 (C<sub>q</sub>), 121.0 (CH), 108.6 (2C, CH), 44.5 (C<sub>q</sub>), 42.6 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 27.6 (3C, CH<sub>3</sub>), 24.4 (CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>33</sub>N<sub>2</sub>O<sup>+</sup> 485.2587; Found 485.2605.



1-(2-(2-(1H-Indol-1-yl)ethyl)-1-phenyl-1H-indol-3-yl)ethan-1-one (3cm): The representative procedure D was followed, using 1-(1-phenyl-1*H*-indol-3-yl)ethan-1-one (1c; 0.047 g, 0.20 mmol), and 1-vinyl-1H-indole (2m; 0.057 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3cm (0.046 g, 61%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.02$  (d, J = 8.1 Hz, 1H, Ar-H), 7.58 (d, J = 7.0 Hz, 1H, Ar-H), 7.48 (t, J = 7.5 Hz, 1H, Ar-H), 7.39-7.33 (m, 3H, Ar–H), 7.20 (t, J = 7.6 Hz, 1H, Ar–H), 7.07-7.01 (m, 2H, Ar–H), 6.96-6.89 (m, 4H, Ar–H), 6.86 (d, J = 3.0 Hz, 1H, Ar–H), 6.37 (d, J = 3.1 Hz, 1H, Ar–H), 4.44 (t, J = 7.2 Hz, 2H, CH<sub>2</sub>), 3.45 (t, J = 7.2 Hz, 2H, CH<sub>2</sub>), 2.88 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta =$ 194.9 (CO), 146.0 (C<sub>a</sub>), 138.4 (C<sub>a</sub>), 135.9 (C<sub>a</sub>), 135.5 (C<sub>a</sub>), 129.8 (2C, CH), 129.4 (CH), 128.7 (C<sub>a</sub>), 128.5 (2C, CH), 128.0 (CH), 125.9 (C<sub>a</sub>), 122.9 (CH), 122.7 (CH), 121.6 (CH), 120.9 (CH), 120.5 (CH), 119.4 (CH), 115.1 (C<sub>a</sub>), 111.7 (CH), 109.2 (CH), 101.4 (CH), 36.4 (CH<sub>2</sub>), 45.3 (CH<sub>2</sub>), 32.1 (CH<sub>3</sub>), 28.2 (CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O<sup>+</sup> 379.1805; Found 379.1809.



**1-(2-(3-(1***H***-Indol-1-yl)propyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one (<b>3an**): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and 1-allyl-1*H*-indole (**2n**; 0.063 g, 0.402 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3an** (0.057 g, 65%) as a light-yellow liquid. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.74 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.57 (dt, *J* = 7.6, 1.0 Hz, 1H, Ar–H), 7.40-7.36 (m, 3H, Ar–H), 7.22-7.16 (m, 4H, Ar–H), 7.13-7.06 (m, 3H, Ar–H), 6.95 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.85 (d, *J* = 3.1 Hz, 1H, Ar–H), 6.35 (d, *J* = 3.1 Hz, 1H, Ar–H), 4.01 (t, *J* = 6.9 Hz, 2H, CH<sub>2</sub>), 2.76-2.72 (m, 2H, CH<sub>2</sub>), 1.99-1.91 (m, 2H, CH<sub>2</sub>), 1.42 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.2 (CO), 143.9 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 135.9 (C<sub>q</sub>), 129.8 (2C, CH), 128.9 (CH), 128.7 (C<sub>q</sub>), 128.3 (2C, CH), 127.6 (CH), 125.1 (C<sub>q</sub>), 122.2 (CH), 121.5 (CH), 121.4 (CH), 121.3 (CH), 121.0 (CH), 119.3 (CH), 116.2 (C<sub>q</sub>), 110.9 (CH), 109.4 (CH), 101.1 (CH), 46.1 (CH<sub>2</sub>), 44.6 (C<sub>q</sub>), 30.1 (CH<sub>2</sub>), 27.6 (3C, CH<sub>3</sub>), 24.1 (CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>31</sub>N<sub>2</sub>O<sup>+</sup> 435.2431; Found 435.2442.



**1-(2-(4-(1***H***-indol-1-yl)butyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-1-one (3ao): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1***H***-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), and 1-(but-3-en-1-yl)-1***H***-indole (2o; 0.069 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded 3ao (0.039 g, 43%) as a red liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): \delta = 7.74 (d,** *J* **= 8.1 Hz, 1H, Ar–H), 7.63 (vt,** *J* **= 7.6 Hz, 1H, Ar–H), 7.44-7.39 (m, 3H, Ar–H), 7.22-7.08 (m, 7H, Ar–H), 6.95-6.93 (m, 2H, Ar–H), 6.43 (d,** *J* **= 3.1 Hz, 1H, Ar–H), 3.97 (t,** *J* **= 6.9 Hz, 2H, CH<sub>2</sub>), 2.75 (t,** *J* **= 7.7Hz, 2H, CH<sub>2</sub>), 1.75-1.68 (m, 2H, CH<sub>2</sub>), 1.43-1.39 (m, 11H, 1CH<sub>2</sub>, S35**  3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 209.6$  (CO), 144.3 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 136.8 (C<sub>q</sub>), 136.0 (C<sub>q</sub>), 129.8 (2C, CH), 128.9 (CH), 128.8 (C<sub>q</sub>), 128.6 (2C, CH), 127.9 (CH), 125.1 (C<sub>q</sub>), 122.1 (CH), 121.4 (2C, CH), 121.2 (CH), 121.0 (CH), 119.3 (CH), 116.2 (C<sub>q</sub>), 110.6 (CH), 109.5 (CH), 101.0 (CH), 45.9 (CH<sub>2</sub>), 44.6 (C<sub>q</sub>), 29.9 (CH<sub>2</sub>), 27.7 (3C, CH<sub>3</sub>), 27.2 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>33</sub>N<sub>2</sub>O<sup>+</sup> 449.2587; Found 449.2810.



**1-(2-(2-(5-Methoxy-1***H***-indol-1-yl)ethyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-1one (3ap): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1***H***-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), and 5-methoxy-1-vinyl-1***H***-indole (2p; 0.070 g, 0.404 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded <b>3ap** (0.058 g, 64%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.85 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.53-7.46 (m, 3H, Ar–H), 7.24-7.11 (m, 4H, Ar–H), 7.02-6.95 (m, 2H, Ar–H), 6.78 (d, *J* = 3.1 Hz, 1H, Ar–H), 6.66 (dd, *J* = 6.5, 8.9 Hz, 1H, Ar–H), 6.57 (d, *J* = 8.9 Hz, 1H, Ar–H), 6.26 (d, *J* = 3.0 Hz, 1H, Ar–H), 4.24 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.82 (s, CH<sub>3</sub>), 3.18 (t, *J* = 7.7 Hz, 2H, CH<sub>2</sub>), 1.48 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 208.5 (CO), 154.1 (C<sub>q</sub>), 142.2 (C<sub>q</sub>), 138.0 (C<sub>q</sub>), 136.4 (C<sub>q</sub>), 131.2 (C<sub>q</sub>), 130.0 (2C, CH), 129.2 (CH), 129.0 (C<sub>q</sub>), 128.8 (2C, CH), 128.5 (CH), 124.8 (C<sub>q</sub>), 122.5 (CH), 121.9 (CH), 121.6 (CH), 116.8 (C<sub>q</sub>), 111.9 (CH), 112.2 (CH), 111.0 (CH), 102.6 (CH), 101.0 (CH), 56.1 (CH<sub>3</sub>), 46.5 (C<sub>q</sub>), 44.5 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 27.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 451.2380; Found 451.2387.


**1-(2-(3-(4-Methoxy-1***H***-indol-1-yl)propyl)-1-phenyl-1***H***-indol-3-yl)-2,2-dimethylpropan-<b>1-one (3aq):** The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), and 1-allyl-4-methoxy-1*H*-indole (**2q**; 0.075 g, 0.402 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **3aq** (0.052 g, 55%) as a light-yellow liquid. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.75 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.39 (d, *J* = 4.8 Hz, 3H, Ar–H), 7.22-7.04 (m, 5H, Ar–H), 6.95 (d, *J* = 8.1 Hz, 1H, Ar–H), 6.72 (d, *J* = 8.2 Hz, 2H, Ar–H), 6.50 (d, *J* = 7.6 Hz, 1H, Ar–H), 6.46 (s, 1H, Ar–H), 4.00-3.97 (m, 5H, CH<sub>2</sub>, CH<sub>3</sub>), 2.74 (t, *J* = 7.7 Hz, 2H, CH<sub>2</sub>), 1.95 (t, *J* = 7.7 Hz, 2H, CH<sub>2</sub>), 1.43 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ = 209.2 (CO), 153.6 (C<sub>q</sub>), 143.9 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 137.5 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 129.8 (2C, CH), 128.9 (CH), 128.3 (2C, CH), 126.1 (CH), 125.1 (C<sub>q</sub>), 122.3 (CH), 122.2 (CH), 121.5 (CH), 121.3 (CH), 119.2 (C<sub>q</sub>), 116.2 (C<sub>q</sub>), 110.9 (CH), 103.0 (CH), 99.3 (CH), 98.5 (CH), 55.5 (CH<sub>3</sub>), 46.2 (CH<sub>2</sub>), 44.6 (C<sub>q</sub>), 30.1 (CH<sub>2</sub>), 27.6 (3C, CH<sub>3</sub>), 24.1 (CH<sub>2</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> 465.2537; Found 465.2540.



1-(2-(3-(6-Fluoro-1*H*-indol-1-yl)propyl)-1-phenyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1one (3ar): The representative procedure D was followed, using 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a; 0.056 g, 0.202 mmol), and 1-allyl-6-fluoro-1*H*-indole (2r; 0.070 g, 0.40 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded 3ar (0.039 g, 43%) as a light-yellow liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.76 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.46 (vt, *J* = 6.7 Hz, 1H, Ar–H), 7.40 (br s, 3H, Ar–H), 7.22-7.10 (m, 4H, Ar–H), 6.95 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.85-6.82 (m, 2H, Ar–H), 6.71 (d, J = 9.9 Hz, 1H, Ar–H), 6.33 (s, 1H, Ar–H), 3.95 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>), 2.73 (t, J = 7.7 Hz, 2H, CH<sub>2</sub>), 1.94-1.88 (m, 2H, CH<sub>2</sub>), 1.43 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 209.1$  (CO), 161.0 (d, <sup>1</sup> $J_{C-F} = 236.5$  Hz, C<sub>q</sub>), 143.8 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 135.8 (d, <sup>3</sup> $J_{C-F} = 12.2$  Hz, C<sub>q</sub>), 129.8 (2C, CH), 129.0 (CH), 128.3 (CH), 128.2 (2C, CH), 125.2 (C<sub>q</sub>), 125.0 (C<sub>q</sub>), 122.3 (CH), 121.7 (CH), 121.6 (CH), 121.3 (CH), 116.2 (C<sub>q</sub>), 110.9 (CH), 108.2 (d, <sup>2</sup> $J_{C-F} = 25.8$  Hz, CH), 101.3 (CH), 95.8 (d, <sup>2</sup> $J_{C-F} = 25.9$  Hz, CH), 46.3 (CH<sub>2</sub>), 44.6 (C<sub>q</sub>), 29.7 (CH<sub>2</sub>), 27.6 (3C, CH<sub>3</sub>), 24.1 (CH<sub>2</sub>). <sup>19</sup>F-NMR (377 MHz, CDCl<sub>3</sub>):  $\delta = -121.5$ . HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>30</sub>FN<sub>2</sub>O<sup>+</sup> 453.2337; Found 453.2349.

## 7. Derivatization of Alkylated Indoles

Reduction of Carbonyl: Synthesis of 3-neopentyl-1-phenyl-2-(2-(trimethylsilyl)ethyl)-1*H*-indole (4)



**Procedure:** To a solution of **3aa** (0.060 g, 0.159 mmol) in trifluoroacetic acid (0.5 mL) was added Et<sub>3</sub>SiH (0.197 mL, 0.795 mmol) under argon at room temperature. The reaction mixture was stirred at 50 °C for 3 h. At ambient temperature, the resultant mixture was quenched with aqueous sodium bicarbonate solution and saturated brine solution. The crude product was extracted with EtOAc (10 mL x 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The remaining residue was purified by column chromatography on silica (petroleum ether/EtOAc: 70/1) to yield **4** (0.053 g, 92%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): *δ* = 7.68 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.58 (vt, *J* = 7.4 Hz, 2H, Ar–H), 7.51-7.44 (m, 3H, Ar–H), 7.19 -7.15 (m, 3H, Ar–H), 2.82-2.79 (m, 4H, 2CH<sub>2</sub>), 1.14 (s, 9H, 3CH<sub>3</sub>), 0.58-0.54 (m, 2H, CH<sub>2</sub>), -0.07 (m, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>): *δ* = 141.4 (C<sub>q</sub>), 138.8 (C<sub>q</sub>), 138.0 (C<sub>q</sub>), 129.7 (C<sub>q</sub>), 129.5 (2C, CH), 128.5 (2C, CH), 127.7 (CH), 120.9 (CH), 119.7 (CH), 119.4 (CH), 110.0 (C<sub>q</sub>), 109.7 (CH), 38.4 (CH<sub>2</sub>), 33.8 (C<sub>q</sub>), 30.5 (3C, CH<sub>3</sub>), 19.6 (CH<sub>2</sub>), 16.7 (CH<sub>2</sub>), -2.0 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + K]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>33</sub>NKSi<sup>+</sup> 402.2014; Found 402.2215.

ThionationofCarbonyl:Synthesisof2,2-dimethyl-1-(1-phenyl-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)propane-1-thione (5)



**Procedure:** To a solution of **3aa** (0.050 g, 0.132 mmol) in toluene (5 mL) was added Lawesson's reagent (0.107 g, 0.264 mmol) under argon at room temperature. The reaction mixture was stirred at 100 °C for 12 h. The resultant reaction mixture was quenched with aqueous sodium bicarbonate solution and saturated brine solution. The crude product was extracted with EtOAc (10 mL x 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The remaining residue was purified by column chromatography on silica (only petroleum ether) to yield **5** (0.032 g, 62%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.56-7.42 (m, 6H, Ar–H), 7.12-7.03 (m, 3H, Ar–H), 2.64-2.62 (m, 2H, CH<sub>2</sub>), 1.56 (s, 9H, 3CH<sub>3</sub>), 0.55-0.52 (m, 2H, CH<sub>2</sub>), -0.20 (m, 9H, 3CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.8 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 137.3 (C<sub>q</sub>), 129.7 (2C, CH), 128.5 (2C, CH), 128.4 (CH), 126.6 (C<sub>q</sub>), 125.8 (C<sub>q</sub>), 121.9 (CH), 120.8 (CH), 120.4 (CH), 110.2 (CH), 53.6 (C<sub>q</sub>), 31.9 (3C, CH<sub>3</sub>), 20.2 (CH<sub>2</sub>), 17.6 (CH<sub>2</sub>), -2.1 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>32</sub>NSSi<sup>+</sup> 394.2019; Found 394.2030.

## 8. Removal of Directing/Protecting Groups

Removal of Pivaloyl Directing Group: Synthesis of 1-phenyl-2-(2-(trimethylsilyl)ethyl)-1*H*-indole (6)



**Procedure:** In an oven dried Schlenk flask, compound **3aa** (0.20 g, 0.53 mmol) was introduced and dry toluene (10 mL) was added into it. Ethylene glycol (0.164 g, 2.65 mmol) and *p*-toluenesulphonic acid (0.091 g, 0.53 mmol) was added and the resultant reaction mixture was stirred at 100 °C for 24 h. At ambient temperature, the reaction mixture was quenched with water (20 mL x 2) and extracted with EtOAc (15 mL). The combined organic

extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and the volatiles were evaporated under vacuo. The remaining residue was purified by column chromatography on silica (petroleum ether) to yield **6** (0.122 g, 78%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.60 (d, *J* = 6.9 Hz, 1H, Ar–H), 7.55 (vt, *J* = 6.4 Hz, 2H, Ar–H), 7.47 (vt, *J* = 7.7 Hz, 2H, Ar–H), 7.37 (d, *J* = 7.6 Hz, 2H, Ar–H), 7.11 (s, 2H, Ar–H), 6.45 (s, 1H, Ar–H), 2.67-2.63 (m, 2H, CH<sub>2</sub>), 0.84-0.80 (m, 2H, CH<sub>2</sub>), -0.07 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.4 (C<sub>q</sub>), 138.6 (C<sub>q</sub>), 138.2 (C<sub>q</sub>), 129.6 (2C, CH), 128.3 (2C, CH), 128.2 (C<sub>q</sub>), 127.9 (CH), 121.2 (CH), 120.1 (CH), 119.9 (CH), 110.1 (CH), 100.0 (CH), 21.7 (CH<sub>2</sub>), 16.0 (CH<sub>2</sub>), -1.7 (3C, CH<sub>3</sub>). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>24</sub>NSi<sup>+</sup> 294.1673; Found 294.1682.

# Removal of 2-pyridinyl from 3wa: Synthesis of 2,2-dimethyl-1-(2-(2-(trimethylsilyl)ethyl)-1*H*-indol-3-yl)propan-1-one (7)



Procedure: In an oven dried round bottom flask, 2,2-dimethyl-1-(1-(pyridin-2-yl)-2-(2-(trimethylsilyl)ethyl)-1H-indol-3-yl)propan-1-one (3wa; 0.050 g, 0.132 mmol) was introduced and CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added into it. Methyl trifluoromethanesulfonate (MeOTf; 0.024 g, 0.145 mmol) was added drop wise via a syringe to the reaction mixture at 0 °C and the resultant reaction mixture was stirred at room temperature for 12 h. Then the volatiles were removed under vacuum and the residue was redissolved in MeOH (2 mL). To the resultant mixture, NaOH (2 mL, 2M aqueous) solution was added and the reaction mixture was stirred at 60 °C for 10 h. At ambient temperature, the volatiles were evaporated under reduced pressure, and the resulting residue was extracted with EtOAc (15 mL x 3). The combined organic extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) to yield 7 (0.027 g, 68%) as a light yellow liquid. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.94 (s, 1H, *NH*), 7.73 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.25 (d, *J* = 7.3 Hz, 1H, Ar–H), 7.20-7.12 (m, 2H, Ar–H), 2.91-2.87 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, 3CH<sub>3</sub>), 0.96-0.92 (m, 2H, CH<sub>2</sub>), 0.04 (s, 9H, 3CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 209.3 (CO), 146.6 (C<sub>a</sub>), 134.8 (C<sub>a</sub>), 126.1 (C<sub>a</sub>), 121.7 (CH), 121.4 (CH), 120.7 (CH), 114.0 (C<sub>a</sub>), 111.1 (CH), 44.4 (C<sub>q</sub>), 27.5 (3C, CH<sub>3</sub>), 22.2 (CH<sub>2</sub>), 16.5 (CH<sub>2</sub>), -1.8 (3C, CH<sub>3</sub>). HRMS (ESI) *m*/*z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>28</sub>NOSi<sup>+</sup> 302.1935; Found 302.2025.

#### 9. External Additive Experiments

**Procedure for TEMPO/galvinoxyl/BHT Added Experiment:** To a flame dried screw-capped tube equipped with magnetic stir bar was introduced 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), trimethyl(vinyl)silane (0.040 g, 0.40 mmol), Fe(PMe<sub>3</sub>)<sub>4</sub> (0.011 g, 0.03 mmol, 15 mol%) and TEMPO (0.094 g, 0.60 mmol) [or galvinoxyl (0.253 g, 0.60 mmol) or BHT (0.132 g, 0.60 mmol). To the reaction mixture 2-MeTHF (0.5 mL) was added and stirred at 40 °C in a pre-heated oil bath for 16 h. At ambient temperature, the reaction mixture was quenched with distilled H<sub>2</sub>O (10 mL) and *n*-dodecane (0.02 mL, 0.088 mmol; internal standard) was added. An aliquot of the sample was subjected to the GC analysis. The formation of coupled product (**3aa**) was not observed in the presence of TEMPO or whereas 13% of coupled product **3aa** was formed in the presence of BHT.

## 10. Procedure for EPR Analysis

To a flame-dried screw-cap tube equipped with magnetic stir bar were introduced 2,2dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.056 g, 0.202 mmol), trimethyl(vinyl)silane (0.040 g, 0.40 mmol), Fe(PMe<sub>3</sub>)<sub>4</sub> (0.011 g, 0.0305 mmol, 15.0 mol%) inside the glove box. To the above mixture, 2-MeTHF (1.0 mL) was added and the resultant reaction mixture was stirred at 40 °C in a preheated oil bath for 30 min. At ambient temperature, the reaction tube was introduced to the glove box, and the reaction mixture was transferred to an EPR tube and frozen at 100 K, which was then subjected to the EPR measurement (Figure 1B). The EPR spectrum of Fe(PMe<sub>3</sub>)<sub>4</sub> is shown in Figure 1A.

## 11. Reaction Rate Determination and KIE Experiments

To a Teflon-screw capped tube equipped with magnetic stir bar was introduced  $Fe(PMe_3)_4$  (0.011 g, 0.03 mmol, 0.03 M), indole **1a** (0.056 g, 0.202 mmol, 0.202 M), trimethyl(vinyl)silane (0.040 g, 0.40 mmol, 0.40 M), and *n*-dodecane (0.021 mL, 0.092 mmol, 0.092 M, internal standard), and 2-MeTHF (0.97 mL) was added to make the total volume to 1.0 mL (*Note : All reaction kinetics were performed using more amount of solvent 2-MeTHF* (~ 1.0 mL) for the convenience of withdrawing sample for GC analysis). The reaction mixture was then stirred at 40 °C in a pre-heated oil bath. At regular intervals (10, 20, 30, 45, 60 min), the reaction vessel was cooled to ambient temperature and an aliquot of sample was withdrawn to the GC vial. The sample was diluted with ethyl acetate and subjected to GC analysis. The concentration of the product **3aa** obtained in each sample was

determined with respect to the internal standard *n*-dodecane. The final data was obtained by averaging the results of three independent experiments (Table S3). The data of the concentration of the product *vs* time (min) plot for the early reaction time was drawn (Figure 2). For the calculation of rate, the plot was fitted linear with Origin Pro 8.5, and the reaction rate was determined by the initial rate method. The slope of the linear fitting represents the reaction rate. Rate =  $6.35 \times 10^{-4}$  Mmin<sup>-1</sup>

Similarly, the reaction rate was determined for **1a**-[2-D], employing 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one-2-*d* (**1a**-[**2-D**]; 0.056 g, 0.202 mmol), trimethyl(vinyl)silane (0.040 g, 0.40 mmol) and Fe(PMe<sub>3</sub>)<sub>4</sub> (0.011 g, 0.03 mmol). The data's were collected till 60 min for **1a**-[2-D]. The final data was obtained by averaging the results of two independent experiments. The initial rate obtained for the coupling of 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one-2-*d* (**1a**-[2-D]) with trimethyl(vinyl)silane is found to be 5.59 x 10<sup>-4</sup> Mmin<sup>-1</sup> (Figure 2).

Therefore, the rate(H)/rate(D) =  $6.35 \times 10^{-4} \text{ Mmin}^{-1} / 5.59 \times 10^{-4} \text{ Mmin}^{-1} = 1.14$ 

Time (min)	Conc of <b>3a</b>	<b>a</b> [M]	
	Expt 1	Expt 2	Average
10	0.012	0.016	0.014
20	0.021	0.027	0.024
30	0.025	0.030	0.0275
45	0.035	0.040	0.0375
60	0.043	0.051	0.047

Table S3. Concentration of 3aa Formed in Early Time using Fe(PMe<sub>3</sub>)<sub>4</sub>.

### 12. Procedure for Rate Order Determination

The rate order of the alkylation reaction with various reaction components was determined by the initial rate method. The data of the concentration of the product *vs* time (min) plot was fitted linear with Origin Pro 8. The slope of the linear fitting represents the reaction rate. The order of the reaction was then determined by plotting log(rate) *vs* log(conc) for a particular component.

Rate Order Determination on Fe(PMe<sub>3</sub>)<sub>4</sub> (Table S4 and Figure S1): Representative Procedure: To determine the order of the alkylation reaction on catalyst concentration Fe(PMe<sub>3</sub>)<sub>4</sub>, initial rates at different initial concentrations of catalyst were determined. The final data was obtained by averaging the results of two independent experiments for the same initial concentration. In standard experiment, a Teflon-screw cap tube equipped with magnetic stir bar was introduced specific amount of Fe(PMe<sub>3</sub>)<sub>4</sub> (as shown in the Table S4), trimethyl(vinyl)silane (0.040 g, 0.40 mmol, 0.40 M), 2,2-dimethyl-1-(1-phenyl-1H-indol-3yl)propan-1-one (1a; 0.056 g, 0.202 mmol, 0.202 M), n-dodecane (0.021 mL, 0.092 mmol, 0.092 M, internal standard), and 2-MeTHF (appropriate amount) was added to make the total volume to 1.0 mL. The reaction mixture was then heated at 40 °C in a pre-heated oil bath. At regular intervals (10, 20, 30, 45 min), the reaction vessel was cooled to ambient temperature and an aliquot of sample was withdrawn to the GC vial. The sample was diluted with ethyl acetate and subjected to GC analysis. The concentration of the product **3aa** obtained in each sample was determined with respect to the internal standard *n*-dodecane. The initial rates at different initial concentrations of catalyst, Fe(PMe<sub>3</sub>)<sub>4</sub>, are shown in Figure S1(A). The Figure S1(B) shows the log(rate) versus log(conc Fe(PMe<sub>3</sub>)<sub>4</sub>), wherein the slope represents the rate order on catalyst.

Experiment	Amount of Fe(PMe <sub>3</sub> ) <sub>4</sub>	Initial Conc. of	Initial Rate [Mmin <sup>-1</sup> ]	R <sup>2</sup>
No	(g)	$Fe(PMe_3)_4$ [M]	x 10 <sup>-4</sup>	
1	0.054	0.015	2.652	0.99463
2	0.072	0.020	4.794	0.88747
3	0.011	0.030	6.411	0.96084

Table S4. Rate of Alkylation Reaction at Different Initial Concentrations of Fe(PMe<sub>3</sub>)<sub>4</sub>.



**Figure S1.** (A) Time-dependent formation of **3aa** at different initial concentration of Fe(PMe<sub>3</sub>)<sub>4</sub>, (B) Plot of log(rate) *vs* log([Fe(PMe<sub>3</sub>)<sub>4</sub>]).

Rate Order Determination on Indole 1a (*Table S5 and Figure S2*). To determine the order of the alkylation reaction on indole 1a, the initial rates at different initial concentrations of 1a were recorded. The final data was obtained by averaging the results of two independent experiments for the same initial concentration.

Representative procedure of rate order determination was followed, employing specific amount of 2,2-dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**) (as shown in Table S5), Fe(PMe<sub>3</sub>)<sub>4</sub> (0.03 M), trimethyl(vinyl)silane (0.40 M), *n*-dodecane (0.021 mL, 0.092 mmol, 0.092 M, internal standard), and 2-MeTHF (appropriate amount) was added to make the total volume to 1.0 mL. The initial rates at different initial concentrations of **1a** are shown in Figure S2(A). The Figure S2(B) shows the log(rate) versus log(conc **1a**), wherein the slope represents the rate order on **1a**.

Experiment	Amount of <b>1a</b> (g)	Initial Conc. of	Initial Rate [Mmin <sup>-1</sup> ]	R <sup>2</sup>	
		1a [M]	x 10 <sup>-4</sup>		
1	0.056	0.20	$6.35\pm0.039$	0.9863	
2	0.083	0.30	$10.30\pm0.124$	0.9445	
3	0.110	0.40	$13.00\pm0.129$	0.9610	
4	0.166	0.60	$17.80\pm0.224$	0.9394	

 Table S5. Rate of Alkylation Reaction at Different Initial Concentrations of 2,2 

 dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a).



Figure S2. (A) Time-dependent formation of **3aa** at different initial concentration of 2,2dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (1a), (B) Plot of log(rate) vs log(conc 1a).

**Rate Order Determination on trimethyl(vinyl)silane** (*Table S6 and Figure S3*). To determine the order of the alkylation reaction on trimethyl(vinyl)silane, the initial rates at different initial concentrations of trimethyl(vinyl)silane were recorded. The final data was obtained by averaging the results of two independent experiments for the same initial concentration.

Representative procedure of rate order determination was followed, employing 2,2dimethyl-1-(1-phenyl-1*H*-indol-3-yl)propan-1-one (**1a**; 0.20 M), Fe(PMe<sub>3</sub>)<sub>4</sub> (0.03 M), specific amount of trimethyl(vinyl)silane (as shown in Table S6), *n*-dodecane (0.021 mL, 0.092 mmol, 0.092 M, internal standard), and 2-MeTHF (appropriate amount) was added to make the total volume to 1.0 mL. The initial rates at different initial concentrations of trimethyl(vinyl)silane are shown in Figure S3(A). The Figure S3(B) shows the log(rate) versus log(conc trimethyl(vinyl)silane), wherein the slope represents the rate order on trimethyl(vinyl)silane.

• •	• /			
Experiment	Amount of	Initial Conc. of	Initial Rate [Mmin-	R <sup>2</sup>
	trimethyl(vinyl)silane	trimethyl(vinyl)silane	<sup>1</sup> ] x 10 <sup>-4</sup>	
	(g)	[M]	-	
1	0.020	0.20	$4.04\pm0.027$	0.9823
2	0.030	0.30	$4.88\pm0.077$	0.9989
3	0.040	0.40	$6.35\pm0.039$	0.9846

Table S6. Rate of Alkylation Reaction at Different Initial Concentrations of trimethyl(vinyl)silane.



**Figure S3.** (A) Time-dependent formation of **3aa** at different initial concentration of trimethyl(vinyl)silane (**2a**), (B) Plot of log(rate) vs log(conc trimethyl(vinyl)silane)).

## 13. NMR Spectra of Deuterium Labeling and Controlled Studies



Figure S4. <sup>1</sup>H NMR spectrum of deuterated product 3aa-[D].



Figure S5. <sup>2</sup>H NMR spectrum of deuterated product 3aa-[D].



Figure S6. <sup>1</sup>H NMR spectrum of deuterated product 3aj-[D].



Figure S7. <sup>1</sup>H NMR spectrum of recovered deuterated compound 1a-[H/D].



Figure S8. <sup>2</sup>H NMR spectrum of recovered deuterated compound 1a-[H/D].



**Figure S9.** <sup>1</sup>H NMR spectrum of 1-(benzyloxy)-4-vinylbenzene recovered from deuteriumlabeled experiment.



**Figure S10.** <sup>2</sup>H NMR spectrum of 1-(benzyloxy)-4-vinylbenzene recovered from deuteriumlabeled experiment.



Figure S11. <sup>1</sup>H NMR spectrum of compound **3wa** isolated from deuterium scrambling experiment.



Figure S12. <sup>1</sup>H NMR spectrum of compound 1w recovered from deuterium scrambling experiment.

# 14. MALDI-TOF Spectrum of Incomplete Reaction Mixture



Figure S13. MALDI-TOF spectrum of crude reaction mixture.

## **15. DFT Energy Calculations**

All molecular structures were generated and optimized using Density Functional Theory (DFT) based methodology as implemented in the Gaussian 09 package.<sup>S3</sup> All calculations were carried out explicitly in the presence of ligand. The structures were optimized using TPSS<sup>S4</sup> level of theory with a def2-SVP using def2-TZVP basis set.<sup>S5</sup> Additionally, Grimme's DFT empirical dispersion correction with the Becke-Jonson (D3BJ) damping function are also included.<sup>S6,S7</sup> Optimized minima for geometries and transition states (TSs) were verified by performing harmonic vibrational analysis to confirm no and one imaginary frequency, respectively. Solvent effects were included in the calculations as implemented in SMD model<sup>S8</sup> for THF (as the polarities of THF and 2-MeTHF are similar and the reaction yield in both the solvents is very good, calculations are carried out using THF as solvent). The energies reported in the free energy profile are  $\Delta G$  values incorporated with zero-point energy corrections for the optimized minima at 298.15 K.



Figure S14. Transition States (TS1 – TS4) in the Ball and Stick Model. The color Scheme is as follows: iron, light blue; phosphorous, orange; nitrogen, blue; oxygen, red; light green, silicon.













**Figure S15.** Free-energy profile for the insertion of alkene to Fe–C bond. The free-energy values are given in kcal/mol.



Figure S16. Transition States (TS5–TS7) in the Ball and Stick Model. The color Scheme is as follows: iron, light blue; phosphorous, orange; nitrogen, blue; oxygen, red; light green, silicon.

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## 17. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Starting Compounds



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 1b



<sup>1</sup>H-NMR spectrum of compound **1d** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 1d



<sup>1</sup>H-NMR spectrum of compound **1h** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 1h



<sup>1</sup>H-NMR spectrum of compound **1i** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 1i



<sup>1</sup>H-NMR spectrum of compound **1**I



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 11



<sup>1</sup>H-NMR spectrum of compound 1m



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 1m



<sup>1</sup>H-NMR spectrum of compound 1u



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 1u

# 18. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Spectra of Alkylated Indoles



<sup>1</sup>H-NMR spectrum of compound **3aa** 



 $^{13}C{^{1}H}$ -NMR spectrum of compound **3aa** 



<sup>1</sup>H-NMR spectrum of compound **3ba** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3ba** 



<sup>1</sup>H-NMR spectrum of compound **3ca** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\mathbf{3ca}$ 



<sup>1</sup>H-NMR spectrum of compound **3da** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3da



<sup>1</sup>H-NMR spectrum of compound **3ea** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3ea** 



<sup>1</sup>H-NMR spectrum of compound **3fa** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3fa** 



<sup>1</sup>H-NMR spectrum of compound **3ga** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3ga** 



<sup>1</sup>H-NMR spectrum of compound **3ha** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3ha** 



<sup>1</sup>H-NMR spectrum of compound **3ia** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 3ia


<sup>1</sup>H-NMR spectrum of compound **3ja** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\mathbf{3ja}$ 



<sup>19</sup>F-NMR spectrum of compound **3ja** 



<sup>1</sup>H-NMR spectrum of compound **3ka** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 3ka



<sup>19</sup>F-NMR spectrum of compound **3ka** 



<sup>1</sup>H-NMR spectrum of compound **3la** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3la



<sup>1</sup>H-NMR spectrum of compound **3ma** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound **3ma** 



<sup>1</sup>H-NMR spectrum of compound **3na** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound **3na** 



<sup>1</sup>H-NMR spectrum of compound **30a** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **30a** 



<sup>19</sup>F-NMR spectrum of compound **30a** 



<sup>1</sup>H-NMR spectrum of compound **3pa** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3pa** 



<sup>1</sup>H-NMR spectrum of compound **3qa** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3qa** 



<sup>1</sup>H-NMR spectrum of compound **3ra** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3ra



<sup>1</sup>H-NMR spectrum of compound **3sa** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\mathbf{3sa}$ 



<sup>1</sup>H-NMR spectrum of compound **3ta** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3ta



<sup>1</sup>H-NMR spectrum of compound **3ua** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\boldsymbol{3ua}$ 



<sup>1</sup>H-NMR spectrum of compound **3va** 



<sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of compound **3va** 



<sup>1</sup>H-NMR spectrum of compound **3wa** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3wa** 



<sup>1</sup>H-NMR spectrum of compound **3xa** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3xa** 



<sup>1</sup>H-NMR spectrum of compound **3ya** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3ya** 



<sup>1</sup>H-NMR spectrum of compound **3za** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3za** 



<sup>1</sup>H-NMR spectrum of compound **3Aa** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3Aa** 



<sup>19</sup>F-NMR spectrum of compound **3Aa** 



<sup>1</sup>H-NMR spectrum of compound **3Ba** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 3Ba



<sup>1</sup>H-NMR spectrum of compound **3ab** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3ab



<sup>1</sup>H-NMR spectrum of compound **3ac** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3ac** 



<sup>1</sup>H-NMR spectrum of compound **3ad** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3ad



<sup>1</sup>H-NMR spectrum of compound **3ae** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound **3ae** 



<sup>1</sup>H-NMR spectrum of compound **3af** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\boldsymbol{3af}$ 



<sup>1</sup>H-NMR spectrum of compound 3ag



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\boldsymbol{3ag}$ 



<sup>1</sup>H-NMR spectrum of compound **3ah** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound 3ah



<sup>1</sup>H-NMR spectrum of compound **3ai** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3ai** 



<sup>1</sup>H-NMR spectrum of compound **3aj** 



 $^{13}C\{^{1}H\}$ -NMR spectrum of compound **3aj** 



 $^1\text{H-NMR}$  spectrum of compound  $\mathbf{3ck}$ 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound  $\boldsymbol{3ck}$ 



<sup>1</sup>H-NMR spectrum of compound **3al** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound **3al** 



 $^1\mathrm{H}\text{-}\mathrm{NMR}$  spectrum of compound  $\mathbf{3cm}$ 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 3cm



<sup>1</sup>H-NMR spectrum of compound **3an** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound **3an**


<sup>1</sup>H-NMR spectrum of compound **3ao** 



<sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of compound **3ao** 



<sup>1</sup>H-NMR spectrum of compound **3ap** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound 3ap



<sup>1</sup>H-NMR spectrum of compound **3aq** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\text{-}\mathrm{NMR}$  spectrum of compound  $\boldsymbol{3aq}$ 



<sup>1</sup>H-NMR spectrum of compound **3ar** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound **3ar** 



<sup>19</sup>F-NMR spectrum of compound **3ar** 





<sup>1</sup>H-NMR spectrum of compound **4** 



 $^{13}C{^{1}H}$ -NMR spectrum of compound 4



<sup>1</sup>H-NMR spectrum of compound **5** 



<sup>13</sup>C-NMR spectrum of compound **5** 



<sup>1</sup>H-NMR spectrum of compound **6** 



 $^{13}C\{^{1}H\}\text{-}NMR$  spectrum of compound  $\boldsymbol{6}$ 



<sup>1</sup>H-NMR spectrum of compound 7



 $^{13}C{^{1}H}$ -NMR spectrum of compound 7