Palladium complexes grafted onto mesoporous silica catalysed the double carbonylation of aryl iodides with amines to give α-ketoamides

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Supplementary Information

1. General information

Low-angle X-ray powder diffraction (XRD) data were acquired on a Bruker D5005 diffractometer using Cu Kα monochromatic radiation (λ = 1.054184 Å). Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micromeritics ASAP 2020M physisorption analyzer. The samples were evacuated at 110°C for 24 h before the measurements. Specific surface areas were calculated following the BET procedure. Pore size distribution was obtained by using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherm. A Netzsch thermoanalyser STA 409PC was used for simultaneous thermal analysis combining thermogravimetric (TGA) and differential thermoanalysis (DTA) at a heating rate of 10°C min^{-1} in air from 25–900°C. Solid state NMR MAS and CP-MAS experiments were performed on a Bruker DSX 400 spectrometer at spectral frequencies of 161.99, 79.49 and 100.63 MHz for respectively ^{31}P, ^{29}Si and ^{13}C nuclei. Chemical shifts were referenced to 85% aqueous H_3PO_4 for ^{31}P NMR and to TMS for ^{29}Si and ^{13}C. A 4 mm triple resonance Bruker MAS probe was used for CP-MAS on ^{29}Si and ^{13}C. The spinning rate nucleus for both was 10 kHz and samples were spun at the magic angle using ZrO_2 rotors. The experimental details for the ^{29}Si and ^{13}C CP-MAS NMR experiments were as follows: contact time: 5 ms and 3 ms respectively, 90° ^{1}H transmitter pulse length: 3μs, number of scans: 15000 to 50000 and repetition time: 4s. ^{31}P CP MAS experiments were performed with a 2.5 mm double resonance Brucker MAS probe at a spinning rate of 20 kHz. Contact time was set to 2 ms, repetition time to 10 ms and the number of scans was fixed at 20000 with a 90° ^{1}H transmitter pulse of 2.85 μs. Metal determinations were performed by ICP-AES (Activa Jobin Yvon) spectroscopy from a solution obtained by treatment of the solid catalyst with a mixture of HF, HNO_3 and H_2SO_4 in a Teflon reactor at 150°C.Characterization of palladium hybrid mesoporous silica materials

2. Characterization data for palladium hybrid mesoporous silica materials

The synthesized hybrid materials were characterized by a variety of spectroscopic (^{13}C, ^{31}P and ^{29}Si MAS and CP-MAS, X-ray diffraction) and quantitative (TGA/DTA, elemental analysis) techniques (Figure S-1-Figure S-14). The physicochemical data of the hybrid materials derived from the powder XRD and adsorption analyses are summarized in Table S-1. The quantitative determination of organic and metal contents was performed using thermogravimetric and elemental analyses and is reported in Table S-2.

$PdCl_2(PPh_2)_2$@SBA-15: ^{13}C CP-MAS NMR (100.63 MHz) δ (ppm) 7.9, 17.4, 20.9, 59.1, 129,1; ^{29}Si CP-MAS NMR (79.49 MHz) δ (ppm) -44.7, -51.7, -99.6, -105.5; ^{31}P MAS NMR (161.99 MHz) δ (ppm) 22.9 (*trans*-isomer, 85%), 34.4 (*cis*-isomer, 15%).

$PdCl_2(PCy_2)_2$@SBA-15: ^{13}C CP-MAS NMR (100.63 MHz) δ (ppm) 11.8, 17.5, 20.6, 27.2, 59.7; ^{29}Si CP-MAS NMR (79.49 MHz) δ (ppm) -36.4, -41.1, -94.6, -98.5, -104.8; ^{31}P MAS NMR (161.99 MHz) δ (ppm) 23.8.

$PdCl_2$(PNP)@SBA-15: ^{13}C CP-MAS NMR (100.63 MHz) δ (ppm) 8.7, 17.1, 30.4, 58.8, 129.3; ^{29}Si CP-MAS NMR (79.49 MHz) δ (ppm) -38,8, -41.2, -86.5, -99.1, -105.0; - ^{31}P MAS NMR (161.99 MHz) δ (ppm) 11.7.

Table S-1 Physical and textural properties of palladium hybrid mesoporous silica materials

Catalyst	d_{100} [a] (Å)	a_0 [b] (Å)	Wall thickness [c] (Å)	V_p [d] ($cm^3.g^{-1}$)	D_p [e] (Å)	S_{BET} ($m^2.g^{-1}$)	C_{BET}
$PdCl_2(PPh_2)_2$@SBA-15	96	111	57	0.66	54	601	181
$PdCl_2(PCy_2)_2$@SBA-15	100	115	52	0.80	63	553	114
$PdCl_2$(PNP)@SBA-15	105	121	63	0.53	58	367	110

[a] d(100) spacing. [b] $a_0 = 2d(100)/\sqrt{3}$, hexagonal lattice parameter calculated from XRD. [c] Calculated by a_0 – pore size. [d] Total pore volume at $P/P_0 = 0.976$. [e] Pore size from desorption branch applying the BJH pore analysis.

Table S-2 Elemental analyses of palladium hybrid mesoporous silica materials

Catalysts	Weight %				Molar ratio (Expected)		
	Pd	P	Cl	N	P/Pd	Cl/Pd	N/Pd
$PdCl_2(PPh_2)_2$@SBA-15	3.1	1.9	2.1	-	2.1 (2)	2.1 (2)	-
$PdCl_2(PCy_2)_2$@SBA-15	1.2	0.9	0.8	-	2.4 (2)	2.0 (2)	-
$PdCl_2$(PNP)@SBA-15	3.8	2.3	2.7	0.9	2.1 (2)	2.1 (2)	1.8 (1)

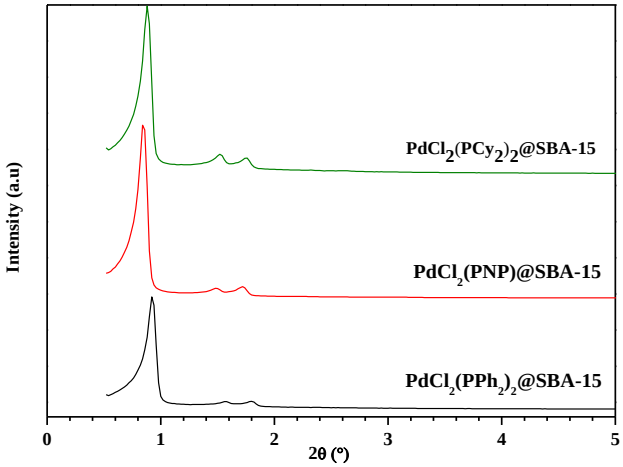


Figure S-1: X-ray power diffractions patterns of palladium hybrid mesoporous silica materials.

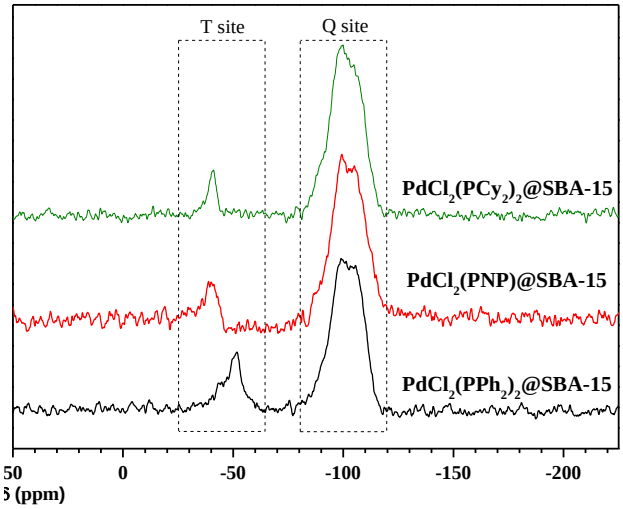


Figure S-2: CP-MAS 29Si NMR of palladium hybrid mesoporous silica materials.

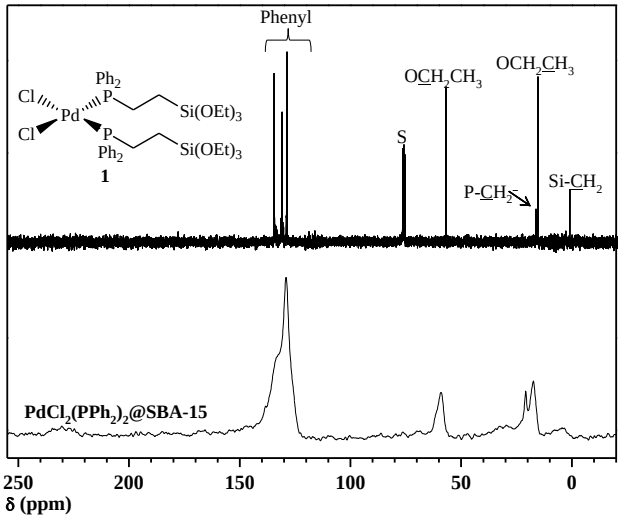


Figure S-3: ^{13}C of palladium complex **1** and CP-MAS ^{13}C NMR of **$PdCl_2(PPh_2)_2$@SBA15**. S denotes for solvents ($CDCl_3$).

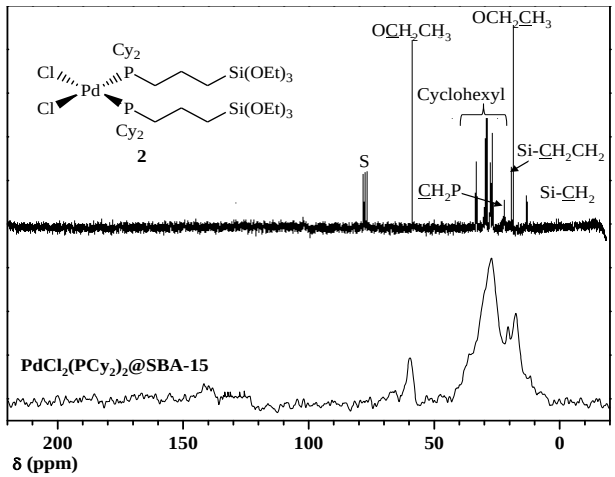


Figure S-4: ^{13}C of palladium complex **2** and CP-MAS ^{13}C NMR of **$PdCl_2(PCy_2)_2$@SBA15**. S denotes for solvents ($CDCl_3$).

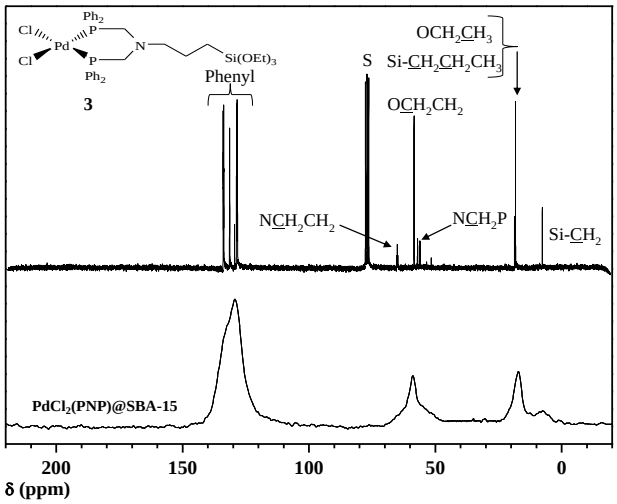


Figure S-5: ^{13}C of palladium complex **3** and CP-MAS ^{13}C NMR of **$PdCl_2(PNP)$@SBA15**. S denotes for solvents ($CDCl_3$).

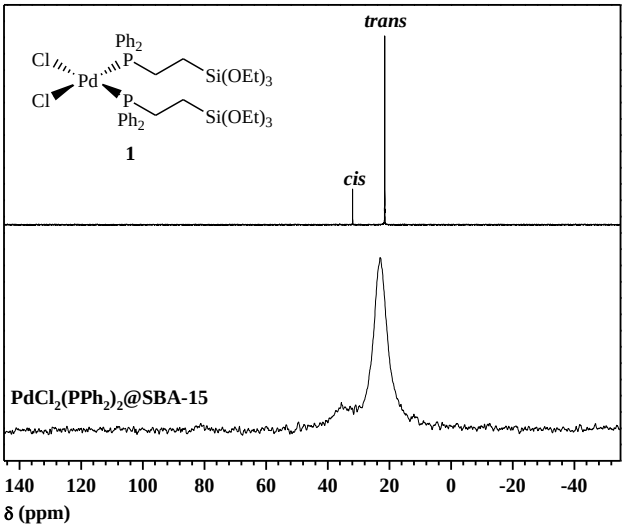


Figure S-6: ^{31}P of palladium complex **1** and CP-MAS ^{31}P NMR of **$PdCl_2(PPh_2)_2$@SBA15**.

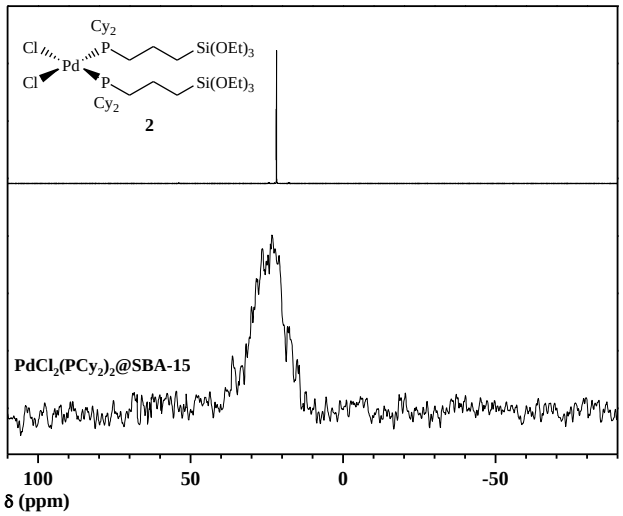


Figure S-7: ^{31}P of palladium complex **2** and CP-MAS ^{31}P NMR of **$PdCl_2(PCy_2)_2$@SBA15**.

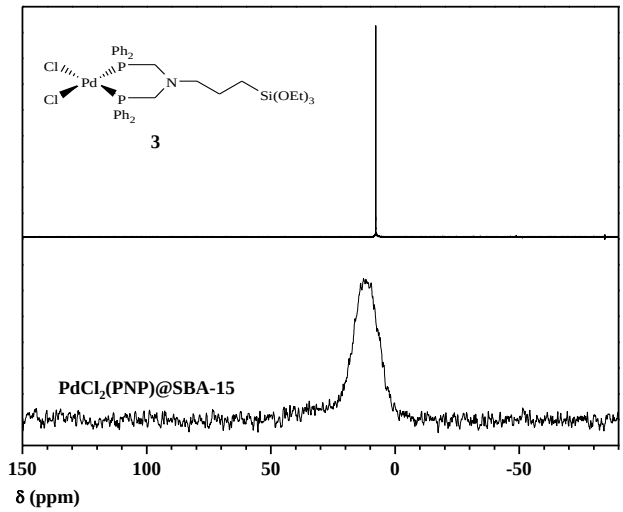


Figure S-8: ^{31}P of palladium complex **3** and CP-MAS ^{31}P NMR of **$PdCl_2(PNP)$@SBA15**.

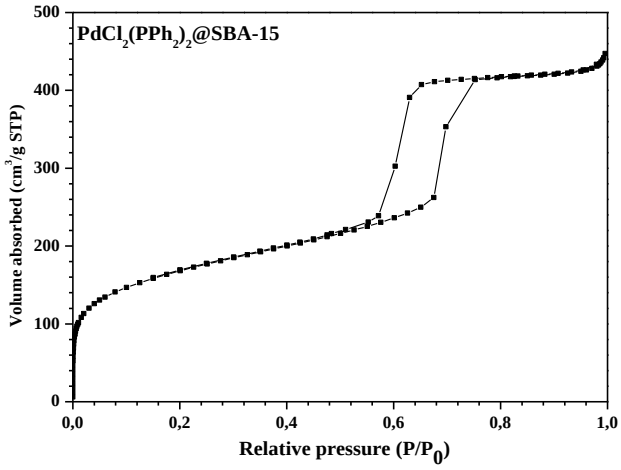


Figure S-9: Nitrogen adsorption/desorption isotherms of **$PdCl_2(PPh_2)_2$@SBA15**.

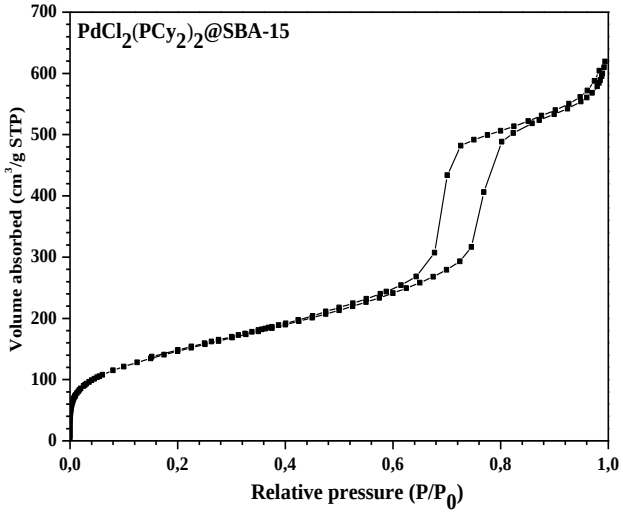


Figure S-10: Nitrogen adsorption/desorption isotherms of **$PdCl_2(PCy_2)_2$@SBA15**.

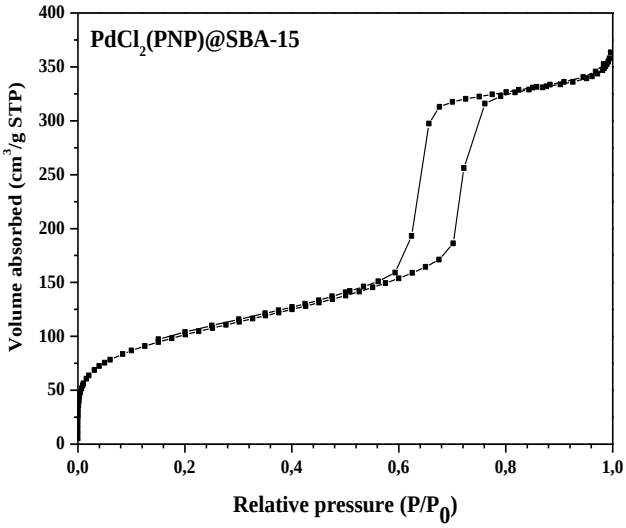


Figure S-11: Nitrogen adsorption/desorption isotherms of **$PdCl_2(PNP)$@SBA15**.

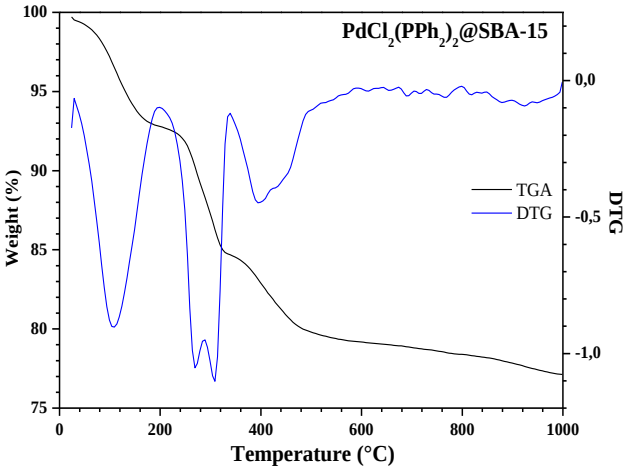


Figure S-12: Thermogravimetric weight loss curve and derivative plots for **$PdCl_2(PPh_2)_2$@SBA15**.

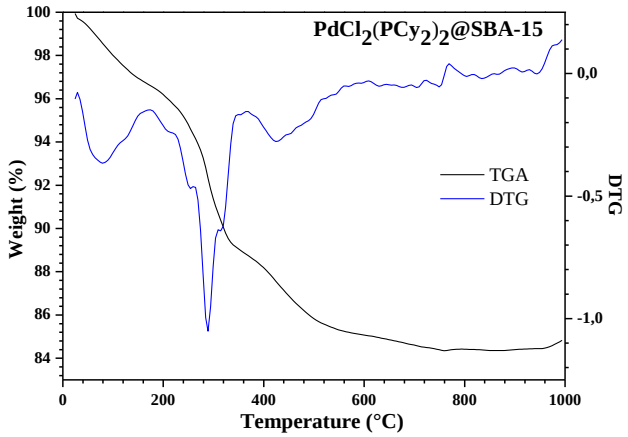


Figure S-13: Thermogravimetric weight loss curve and derivative plots for **$PdCl_2(PCy_2)_2$@SBA15**.

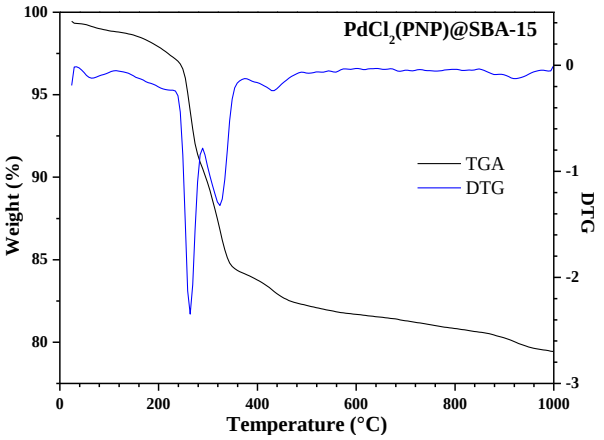


Figure S-14: Thermogravimetric weight loss curve and derivative plots for **$PdCl_2$(PNP)@SBA15**.

3. Comparison between homogenous $Cl_2Pd[PPh_2CH_2CH_2Si(OEt)_3]_2$ and heterogeneous $PdCl_2(PPh_2)_2$@SBA-15 catalysts

To carried out this study, the homogeneous catalyst chosen is the precursor used to synthesis the heterogeneous catalyst **$PdCl_2(PPh_2)_2$@SBA-15** i.e. **$Cl_2Pd[PPh_2CH_2CH_2Si(OEt)_3]_2$**. It was used in loading of 0.3 mol% and 1 mol%. In another set we used **$PdCl_2(PPh_2)_2$@SBA-15** in the same palladium loading.

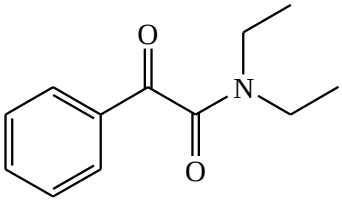
Table S-3 Comparison between homogenous and heterogeneous catalysts on double carbonylation reaction of iodobenzene with diethylamine.

Catalyst	Pd loading mol%	Time (h)	Conv. PhI (%)[b]	Sel. **4/5** (%)[b]
$Cl_2Pd[PPh_2CH_2CH_2Si(OEt)_3]_2$	0.3	6	15	93
		24	60	92
	1	6	52	93
		24	98	92
$PdCl_2(PPh_2)_2$@SBA-15	0.3	6	2	100
		24	45	95
	1	6	6	100
		24	91	85

[a] Iodobenzene (1 mmol), diethylamine (2 mmol), K_2CO_3 (2 mmol), MEK (10 ml). [b] Determined by GC.

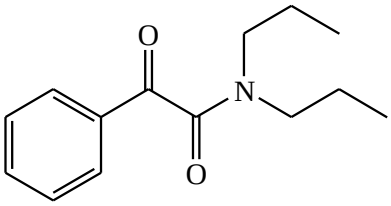
The results reported in the Table S-3 show that as expected the homogeneous catalyst is more active than the corresponding heterogeneous one. However, after 24 hours run to achieve almost quantitative conversion, the differences stay in the error limit of the analytical method minimising thus the apparent benefit in using a soluble catalyst. The real benefit in using the heterogeneous one stays in the recycling possibility since no decrease of its activity was observed.

4. Characterization of reaction products obtained by double carbonylation aryl iodide derivatives



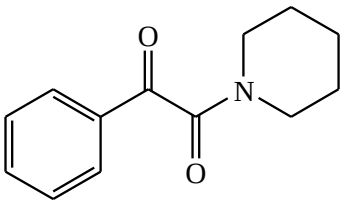
_N,N_-diethyl-2-oxo-2-phenylacetamide[1] (CAS Register Number: 34906-86-0)

Isolated by flash chromatography on silica gel using EP/AcOEt (70/30) as eluent. Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.16 (3H, t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 3H, CH_3), 1.29 (3H, t, $^{3}J_{H\text{-}H}$= 7.2 Hz, 3H, CH_3), 3.24 (2H, q, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2H, C*H*$_2$CH$_3$), 3.57 (2H, q, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, C*H*$_2$CH$_3$), 7.45 – 7.55 (2H, m, ArH), 7.58 – 7.69 (1H, m, ArH), 7.90 – 7.99 (2H, m, ArH); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm) 12.9 (CH_3), 14.2 (CH_3), 38,9 (CH_2), 42.2 (CH_2), 129.1 (CHAr), 129,7 (CHAr), 133.3 (CAr), 134.7 (CHAr), 166.8 (CON), 191.7 (*C*OCAr); EI/MS: m/z 205 (M^+, 2%), 105 (50), 100 (100), 77 (36), 72 (83).



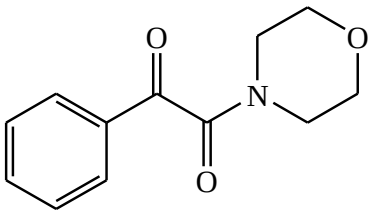
2-oxo-2-phenyl-_N,N_-dipropylacetamide[1a, 1b] (CAS Register Number: 84017-26-5)

Isolated by flash chromatography on silica gel using EP/AcOEt (70/30) as eluent. Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 0.79 (3H, t, $^{3}J_{H\text{-}H}$ = 7.31 Hz, CH_3), 1.00 (3H, t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, CH_3), 1.42-1.82 (3H, m, NCH_2), 3.13 (2H, q, $^{3}J_{H\text{-}H}$ = 7.55, NCH_2), 3.47 (2H, 2H, q, $^{3}J_{H\text{-}H}$ = 7.53, C*H*$_2$CH$_2$), 7.44-7.56 (2H, m, ArH), 7.57-7.69 (1H, m, ArH), 7.89-8.00 (2H, m, ArH); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm) 11.1 (CH_3), 11.5 (CH_3), 20.7 (*C*H$_2$CH$_3$), 21.9 (*C*H$_2$CH$_3$), 45.9 (NCH_2), 49.4 (NCH_2), 129.0 (CHAr), 129.7 (CHAr), 133.4 (CAr), 134.6 (CHAr), 167.3 (CON), 191.7 (*C*OCAr); EI/MS: m/z 233 (M^+, 2%), 128 (60), 105 (45), 77 (31).



1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione[1a, 1c] (CAS Registe Number: 14377-63-0

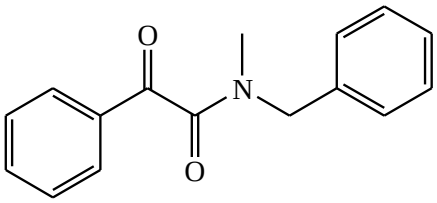
Isolated by flash chromatography on silica gel using EP/AcOEt (70/30) as eluent. White solid; m.p. 106.3-107.4; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.49-1.61 (2H, m, CH_2), 1.65-1.74 (4H, m, C*H*$_2$CH$_2$N), 3.26-3.33 (2H, m, CH_2N), 3.67-3.75 (2H, m, CH_2N), 7.46-7.56 (2H, m, ArH), 7.60-7.69 (1H, m, ArH), 7.91-7.99 (2H, m, ArH); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm) 24.5 (CH_2), 25.6 (CH_2), 26.3 (CH_2), 42.3 (CH_2N), 47.2 (CH_2N), 129.1 (CHAr), 129.7 (CHAr), 133.4 (CAr), 134.8 (CHAr), 165.6 (CON), 192.1 (*C*OCAr); MS : EI/MS: m/z 217 (M^+, 2%), 112 (100), 105 (52), 84 (23), 77 (39), 69 (68).



1-morpholino-2-phenylethane-1,2-dione[1b, 1c] (CAS Register Number: 40991-78-4)

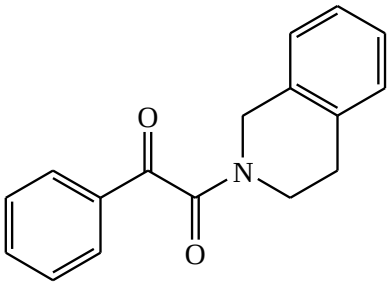
Isolated by flash chromatography on silica gel using EP/AcOEt (50/50) as eluent. Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 3.34-3.38 (2H, m, CH_2N), 3.62-3.69 (2H, m, CH_2N), 3.75-3.83 (4H, m, CH_2O), 7.47-7.57 (2H, m, ArH), 7.62-7.70 (1H, m,

ArH), 7.92-8.00 (2H, m, ArH); ^{13}C (63 MHz, $CDCl_3$) δ (ppm) 41.8 (CH_2N), 46.4 (CH_2N), 66.8 (CH_2O), 66.9 (CH_2O), 129.2 (CHAr), 129.8 (CHAr), 133.2 (CAr), 135.1 (CHAr), 165.6 (CON), 191.3 (COAr); EI/MS: m/z 219 (M^+, 4%), 114 (20), 105 (100), 86 (5), 77 (29), 70 (29).



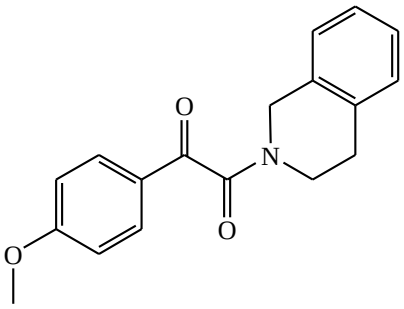
_N_-benzyl-_N_-methyl-2-oxo-2-phenylacetamide[1a] (CAS Register Number: 95725-09-0)

Isolated by flash chromatography on silica gel using EP/AcOEt (70/30) as eluent. Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm); 2.73 and 2.88 (3H, s, CH_3), 4.28 and 4.63 (2H, s, CH_2), 7.10-7.32 (6H, m, ArH + $CHCl_3$ solvent), 7.36-7.45 (2H, m, ArH), 7.49-7.58 (1H, m, ArH), 7.82-7.92 (2H, m, ArH); ^{13}C (63 MHz, $CDCl_3$) δ (ppm) 31.5 and 34.6 (CH_3), 53.6 and 49.9 (CH_2), 128.0 and 128.1 (CHAr), 128.4 and 128.5 (CHArH), 129.0 (two close signals, CHAr), 129.1 and 129.2 (CHAr), 129.8 and 129.9 (CHAr), 133.2 and 133.4 (CAr), 134,9 (two close signals, CHAr), 135.0 and 135.9 (CAr), 167.3 and 167.5 (CON), 191.6 and 191.7 (COAr); EI/MS: m/z 253 (M^+, 2%), 148 (8), 120 (50), 105 (85), 91 (100), 77 (38), 65 (11).



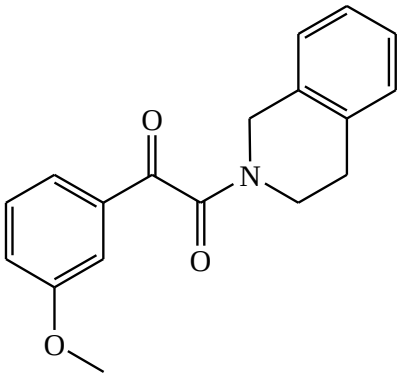
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-phenylethane-1,2-dione (CAS Register Number: 1267191-68-3)

Isolated by flash chromatography on silica gel using EP/AcOEt (70/30) as eluent. Pale yellow solid; m. p.: 68.2-69.8; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.87 and 3.01 (2H, 2 t, $^3J_{H-H}$ = 5.8 and $^3J_{H-H}$ = 6.0 Hz, CH_2CAr), 3.57-3.67 and 3.96-4.04 (2H, m; CH_2N), 4.54 and 4.92 (2H, s, $CArCH_2N$), 6.90-7.25 (4H, m, ArH), 7.44-7.58 (2H, m, ArH), 7.59-7.71 (1H, m, ArH) 7.90-8.04 (2H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 28.4 and 29.3 (CH_2CAr), 39.5, 43.6 (two close signals) and 47.5 (CH_2N), 126.2, 126.7, 126.8, 127.0 (two close signals), 127.3, 128.9, 129.0, 129.1, 129.2 (2 close signals), 129.3, 129.7 and 129.8 (CHAr), 131.6 and 131.9 ($CArCH_2N$), 133.1 and 133.2 ($CArCO$), 133.5 and 134.3 ($CArCH_2$), 134.9 and 135.0 (CHAr), 165.9 and 166.2 (CON), 191.1 and 191.6 ($COCAr$); HSMR (ESI-MS) m/z calculated for $C_{17}H_{15}NO_2$ 265.1103, found: 266.1177 $[M+H]^+$; Elemental analysis required for $C_{17}H_{15}NO_2$: C, 77.0; H, 5,7; N, 5.3; found: C, 76,9; H, 5,6; N, 5,2.



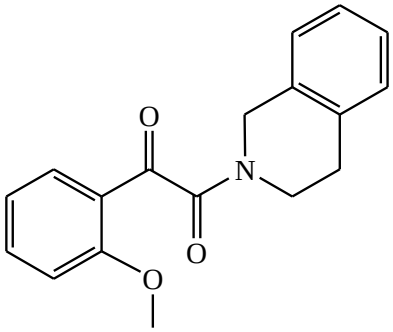
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-(4-methoxyphenyl)ethane-1,2-dione (CAS Register Number: 1282706-31-3)

Isolated by flash chromatography on silica gel using EP/AcOEt (50/50) as eluent. White solid; m. p.: 124.8-125.6; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.85 and 3.00 (2H, 2 t, $^3J_{H-H}$ = 5.8 and $^3J_{H-H}$ = 6.0 Hz, CH_2CAr), 3.57-3.66 and 3.94-4.02 (2H, m; CH_2N), 3.87 and 3.89 (3H, s, CH_3), 4.54 and 4.90 (2H, s, $CArCH_2N$), 6.90-7.25 (6H, m, ArH), 7.86-8.00 (2H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 28.4 and 29.4 (CH_2CAr), 39.4, 43.5, 43.7 and 47.5 (CH_2N), 55,8 (Two close signals, CH_3), 114,5 ($CHArCOCH_3$), 126.2 (CHAr) , 126.4 ($CArCO$), 126.7, 126.8, 126.9, 127.0, 127.3, 129.0 and 129.1 (CHAr), 131.9 and 132.1 ($CArCH_2N$), 132.3 and 132.4 (CHAr), 133.6 and 134.4 ($CArCH_2$), 165.1 (Two close signals, $COCH3$), 166.3 and 166.6 (CON), 190.2 and 190.4 ($COCAr$); HSMR (ESI-MS) m/z calculated for $C_{18}H_{17}NO_3$ 295.1208, found: 296.1276 $[M+H]^+$; Elemental analysis required for $C_{17}H_{15}NO_2$: C, 73.2; H, 5,8; N, 4.7; found: C, 73.3; H, 5,8; N, 4.8.



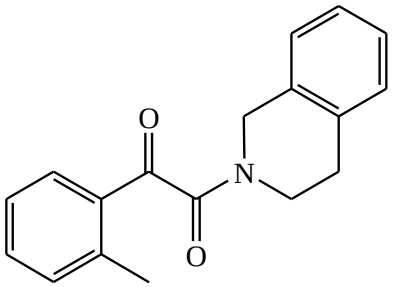
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-(3-methoxyphenyl) ethane-1,2-dione (CAS Register Number: 128917-24-7)

Isolated by flash chromatography on silica gel using EP/AcOEt (70/30) as eluent. White solid; m. p.: 112.6-113.2; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.86 and 3.01 (2H, 2 t, $^{3}J_{H\text{-}H}$ = 5.8 and $^{3}J_{H\text{-}H}$ = 6.0 Hz, CH_2CAr), 3.55-3.66 and 3.94-4.03 (2H, m; CH_2N), 3.82 and 3.86 (3H, s, CH_3), 4.53 and 4.91 (2H, s, $CArCH_2N$), 6.90-7.25 (5H, m, ArH), 7.33-7.55 (3H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 28.4 and 29.3 (*C*H_2CAr), 39.5, 43.6, 43.7 and 47.5 (CH_2N), 55.6 and 55.7 (CH_3), 112.8 (*C*HArCOCH_3), 122.0 (two close signals), 123.0, 123.1, 126.2, 126.8 (Two close signals), 127.0 (Two close signals), 127.4, 128.9, 129.1 and 130.3 (CHAr), 131.7 and 131.9 (*C*ArCH_2N), 133.5 and 134.5 (*C*ArCH_2), 134.3 and 134.5 (*C*ArCO), 160.2 and 160.3 (*C*OCH3), 165.9 and 166.2 (CON), 191.4 and 191.6 (*C*OCAr); HSMR (ESI-MS) m/z calculated for $C_{18}H_{17}NO_3$ 295.1208, found: 296.1283 $[M+H]^+$; Elemental analysis required for $C_{18}H_{17}NO_3$: C, 73.2; H, 5,8; N, 4.7; found: C, 73.1; H, 5,8; N, 4.85



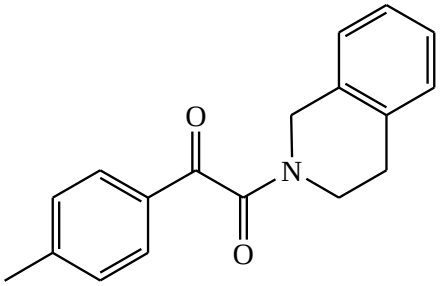
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-(2-methoxyphenyl) ethane-1,2-dione (CAS Register Number: 1283280-96.5)

Isolated by flash chromatography on silica gel using EP/AcOEt (50/50) as eluent. White solid; m. p.: 153.8-155.1; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.90 and 2.99 (2H, 2 t, $^{3}J_{H\text{-}H}$ = 5.9 and $^{3}J_{H\text{-}H}$ = 6.0 Hz, CH_2CAr), 3.42 and 3.69 (3H, s, CH_3), 3.60-3.68 and 3.88-3.98 (2H, m; CH_2N), 4.56 and 4.84 (2H, s, $CArCH_2N$), 6.78-7.24 (6H, m, ArH), 7.47-7.63 (1H, m, ArH), 7.88-8.02 (1H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 28.0 and 28.7 (*C*H_2CAr), 39.3, 43.2, 43.4 and 47.4 (CH_2N), 55.3 and 56.0 (CH_3), 112.2 and 112.8 (*C*HArCOCH_3), 123.6 and 123.7 (*C*ArCO), 126.3, 126.6, 126.8 (two close signals), 126.9, 127.1, 128.8, 129.1, 131.2 and 131.3 (CHAr), 132.5 and 132.6 (*C*ArCH_2N), 134.0 and 134.4 (*C*ArCH_2), 136.1 and 136.3 (CHAr), 160.0 and 160.3 (*C*OCH3), 167,7 and 167.9 (CON), 190.4 and 190.9 (*C*OCAr); HSMR (ESI-MS) m/z calculated for $C_{18}H_{17}NO_3$ 295.1208, found: 296.1277 $[M+H]^+$; Elemental analysis required for $C_{18}H_{17}NO_3$: C, 73.2; H, 5,8; N, 4.7; found: C, 73.3; H, 5,85; N, 4.85



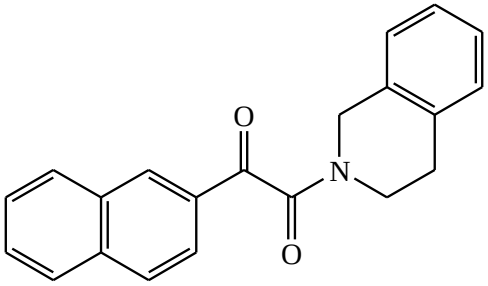
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-o-tolylethane-1,2-dione (CAS Register Number: not listed)

Isolated by flash chromatography on silica gel using EP/AcOEt (80/20) as eluent. White solid; m. p.: 108.5-109.4; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.68 and 2.70 (3H, s, CH_3), 2.88 and 3.01 (2H, 2 t, $^{3}J_{H\text{-}H}$ = 5.8 and $^{3}J_{H\text{-}H}$ = 6.0 Hz, CH_2CAr), 3.57-3.69 and 3.93-4.04 (2H, m; CH_2N), 4.57 and 4.90 (2H, s, $CArCH_2N$), 6.91-7.37 (6H, m, ArH), 7.42-7.55 (1H, m, ArH), 7.61-7.79 (1H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 21.9 and 22.0 (CH_3), 28.3 and 29.3 (*C*H_2CAr), 39.5, 43.6 (two close signals) and 47.5 (CH_2N), 126.2, 126.3, 126.7, 126.8, 126.9, 127.0, 127.3, 128.9, and 129.1 (CHAr), 131.6 (*C*ArCO), 131.7 and 132.0 (*C*ArCH_2N), 132.7, 132.8 (two close signals), and 133.0 (CHAr), 133.6 and 134.4 (*C*ArCH_2), 133.9 (Two close signals, CHAr), 141.7 and 141.7 (*C*ArCH_3), 166.7 and 166.9 (CON), 193.4 and 193.6 (*C*OCAr); HSMR (ESI-MS) m/z calculated for $C_{18}H_{17}NO_2$ 279.1259, found: 280.1329 $[M+H]^+$; Elemental analysis required for $C_{17}H_{15}NO_2$: C, 77.4; H, 6.1; N, 5.0; found: C, 77.5; H, 6.2; N, 5.1



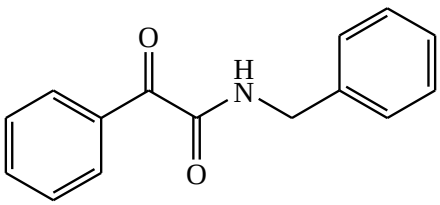
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-p-tolylethane-1,2-dione (CAS Register Number: 1282916-13-5)

Isolated by flash chromatography on silica gel using EP/AcOEt (80/20) as eluent. White solid; m. p.: 126.2-126.8; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.42 and 2.44 (3H, s, CH_3), 2.85 and 3.00 (2H, 2 t, $^{3}J_{H\text{-}H}$ = 5.8 and $^{3}J_{H\text{-}H}$ = 6.0 Hz, CH_2CAr), 3.53-3.70 and 3.90-4.06 (2H, m; CH_2N), 4.53 and 4.91 (2H, s, $CArCH_2N$), 6.88-7.39 (6H, m, ArH), 7.79-7.96 (2H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 22.1 (CH_3), 28.4 and 29.4 (CH_2CAr), 39.4, 43.5, 43.6, and 47.5 (CH_2N), 126.2, 126.7, 126.8, 126.9, 127.0, 127.3, 128.9, 129.1, 129.9 (Two close signals) and 130.0 (CHAr), 130.7 and 130.8 (*C*ArCO), 131.7 and 132.0 ($CArCH_2N$), 133.6 and 134.3 ($CArCH_2$), 146.3 (Two close signals, $CArCH_3$), 166.1 and 166.4 (CON), 193.3 and 193.4 (*C*OCAr); HSMR (ESI-MS) m/z calculated for $C_{18}H_{17}NO_2$ 279.1259, found: 280.1326 $[M+H]^+$; Elemental analysis required for $C_{17}H_{15}NO_2$: C, 77.4; H, 6.1; N, 5.0; found: C, 77.5; H, 6.25; N, 5.1



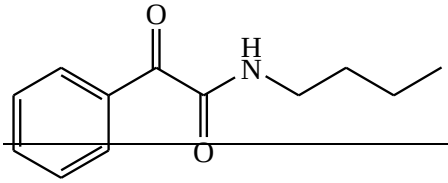
1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-(naphthalen-2-yl)ethane-1,2-dione (CAS Register Number: not listed)

Isolated by flash chromatography on silica gel using EP/AcOEt (80/20) as eluent. White solid; m. p.: 144.8-145.6; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.87 and 3.05 (2H, 2 t, $^{3}J_{H\text{-}H}$ = 5.8 and $^{3}J_{H\text{-}H}$ = 6.0 Hz, CH_2CAr), 3.62-3.73 and 3.98-4.08 (2H, m; CH_2N), 4.62 and 4.96 (2H, s, $CArCH_2N$), 6.86-7.25 (4H, m, ArH), 7.43-7.78 (3H, m, ArH), 7.88-8.18 (3H, m, ArH), 9.28-9.30 and 9.32-9.33 (1H,2 d, $^{3}J_{H\text{-}H}$ = 3.4 Hz and $^{3}J_{H\text{-}H}$ = 3.8 Hz, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm) 28.4 and 29.3 (CH_2CAr), 39.6, 43.8 (Two close signals) and 47.6 (CH_2N), 124.7 (Two close signals), 126.0, 126.2, 126.7, 126.8, 127.0 (Two close signals), 127.2 and 127.3 (CHAr), 128.5 (Two close signals, CAr), 128.9 (Two close signals), 129.1 and 129.5 (Two close signals, CHAr), 131.1 (Two close signals, *C*ArCO), 131.8 and 132.1 ($CArCH_2N$), 133.6 and 134.4 ($CArCH_2$), 142.2 (Two close signals, CAr), 134.7, 134,8, 136.1 and 136.2 (CHAr), 166.16 and 166.8 (CON), 193.8 and 194.1 (*C*OCAr); HSMR (ESI-MS) m/z calculated for $C_{21}H_{17}NO_2$ 315.1259, found: 316.1328 $[M+H]^+$; Elemental analysis required for $C_{21}H_{17}NO_2$: C, 80.0; H, 5.4; N, 4.4; found: C, 80.1; H, 5.4; N, 4.5



***N*-benzyl-2-oxo-2-phenylacetamide[2] (CAS Register Number:28193-70-6)**

Isolated by flash chromatography on silica gel using EP/AcOEt (80/20) as eluent. White solid; m.p.: 96.3-97.3; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 4.58 (2H, d, $^{2}J_{H\text{-}H}$ = 6.0, CH_2), 7.27-7.54 (8H, m; ArH and NH), 7.58-7.69 (1H, m, ArH), 8.30-8.42 (2H, m, ArH); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm); 39.3 (CH_2), 128.0, 128.1, 128.7, 129.0 and 131.4 (CHAr), 133.4 (*C*Ar*CO*), 134.6 (CHAr), 137.2 ($CArCH_2$), 161,7 (CON), 187.7 (*C*OCAr); MS : EI/MS: m/z 239 (M^+, 0.7%), 211 (0.1), 106 (55), 105 (100), 91 (39), 77 (39), 65 (8).



***N*-butyl-2-oxo-2-phenylacetamide[3] (CAS Register Number: 5070-32-6)**

Isolated by flash chromatography on silica gel using EP/AcOEt (80/20) as eluent. Colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 0.95 (3H, t, $^{3}J_{H\text{-}H}$ = 7.3, CH_3), 1.31-1.49 (2H, m; C*H*$_2$CH$_3$), 1.50-1.66 (2H, m, C*H*$_2$CH$_2$N), 3.31-3.46 (2H, m, CH_2N), 7.10 (H, s, NH), 7.39-7.53 (2H, m, CHAr), 7.54-7.67 (1H, m, CHAr), 8.24-8.38 (2H, m, CHAr); ^{13}C (63 MHZ, $CDCl_3$) δ (ppm); 13.8 (CH_3), 20.2 (*C*H$_2$CH$_3$), 31.5 (*C*H$_2$CH$_2$N), 39.3 (CH_2N), 128.6 and 131.3 (CHAr), 133.5 (CAr), 134.5 (CHAr), 161.9 (CON), 188.1 (*C*OCAr); MS : EI/MS: m/z 205 (M^+, 11%), 163 (1), 106 (10), 105 (100), 100 (6), 78 (3), 77 (32).

1. (*a*) F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto and A. Yamamoto, *J. Am. Chem. Soc.*, 1985, **107**, 3235-3245; (*b*) J. Liu, S. Zheng, W. Sun and C. Xia, *Chin. J. Chem.*, 2009, **27**, 623-627; (*c*) J. Liu, R. Zhang, S. Wang, W. Sun and C. Xia, *Org. Lett.*, 2009, **11**, 1321-1324.

2. (*a*) T. Kolasa and M. J. Miller, *J. Org. Chem.*, 1987, **52**, 4978-4984; (*b*) C.-T. Chen, S. Bettigeri, S.-S. Weng, V. D. Pawar, Y.-H. Lin, C.-Y. Liu and W.-Z. Lee, *J. Org. Chem.*, 2007, **72**, 8175-8185; (*c*) M. Bouma, G. Masson and J. Zhu, *J. Org. Chem.*, 2010, **75**, 2748-2751; (*d*) S. B. Salunke, N. S. Babu and C.-T. Chen, *Adv. Synth. Catal.*, 2011, **353**, 1234-1240.

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