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Electronic supplementary information (ESI) for

# A Heterogeneous Cobalt Catalyst for Sustainable Synthesis of C–C Bonds through Borrowing-Hydrogen Strategy

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#### 1. Chemicals

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Kanto Chemical), Pd(NO<sub>3</sub>)<sub>2</sub> (Wako Pure Chemical Industries), Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, and Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (Sigma-Aldrich, 1.5 wt% Ru) were used as metal precursors for the catalyst preparation. Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Kanto Chemical), Sr(NO<sub>3</sub>)<sub>2</sub> (Kanto Chemical), Ba(NO<sub>3</sub>)<sub>2</sub> (Kanto Chemical), LiNO<sub>3</sub> (Kanto Chemical), NaNO<sub>3</sub> (Wako Pure Chemical Industries), NaOH (Kanto Chemical), and Cs<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich) were used as a source for the co-deposited basic site in the catalyst. TiO<sub>2</sub> (Isihara Sangyo Kaisha, ST-01, 300 m<sup>2</sup>/g), MgO (Ube Material Industries, 500A, 28-38 m<sup>2</sup>/g),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Japan Reference Catalyst, JRC-ALO-6, 180 m<sup>2</sup>/g), SiO<sub>2</sub> (CARiACT Q10, 302 m<sup>2</sup>/g, Fuji Silysia Chemicals), CeO<sub>2</sub> (Japan Reference Catalyst, JRC-CEO-5, 92.0 m<sup>2</sup>/g) and ZrO<sub>2</sub> (Japan Reference Catalyst, JRC-ZRO-6, 279.3 m<sup>2</sup>/g) were used as catalyst supports.

The following solvents were used for catalytic reactions and characterizations during the research. Acetophenone, tetrahydrofuran (THF), furfuryl alcohol, 4-methoxybenzyl alcohol, 4-methoxyacetophenone were supplied by Tokyo Chemical Industries. Toluene, methanol, cyclohexane, acetonitrile, dichloromethane, hexane, ethyl acetate, benzyl alcohol, 2-methoxybenzyl alcohol were supplied by Kanto Chemical. *N*,*N*-dimethylformamide (DMF), and acetone were supplied by Wako Pure Chemical Industries. 4-Methylbenzyl alcohol, 4-methoxybenzyl alcohol, 4-fluorobenzyl alcohol, 1-pentanol, 4-methylacetophenone, 2-methoxyacetophenone, 4-nitroacetophenone, 2-pentanone were supplied by Sigma-Aldrich.

# 2. Instruments

X-ray diffraction of all catalysts was recorded using Ultima IV, Rigaku with Cu Ka radiation  $\lambda = 1.5405$  Å (40 kV, 40 mA) in the 20 range of 10–90°. In determining the crystalline structures, the obtained patterns were then referred to the Joint Committee for Powder Diffraction (JSPDS). The Brunauer-Emmett-Teller (BET) specific surface areas were measured with a surface area analyzer (Quantachrome Nova-4200e) at -196 °C and the relative pressure (P/P<sub>0</sub>) range of 0.05-0.30. The samples were degassed in situ under vacuum at 150 °C for 1 h before measurement. H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was performed using a chemisorption analyzer (BELCAT-A, BEL Japan) with a thermal conductivity detector (TCD). The thermal profiles were measured from 50 °C to 800 °C under 5%  $H_2/Ar$  flow (50 mL min<sup>-1</sup>). X-ray photoelectron spectroscopy analyses were performed with Shimadzu ESCA-3200 spectrometer using Mg Karadiation (1486.6 eV). Samples were fixed on double-sided carbon tape. The binding energies were calibrated using C (1s peak at 284.6 eV). The inductively coupled plasma atomic emission spectroscopy (ICP-AES) to measure the amounts of leaching metals was performed with a Shimadzu ICPS-8100 spectrometer. The liquid from the reaction mixture was separated by filtration followed by evaporation. It was then added by HNO<sub>3</sub> and transferred into the 25 mL volumetric flask and diluted with distilled water. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were recorded using a field emission transmission electron microscope (JEM-2100F, JEOL) at an acceleration voltage of 200 kV

equipped with the Electron Dispersive X-ray Spectroscopy (EDS) detector. The samples were dispersed on a carbon sheet with ethanol followed by drying before the measurement. Thermogravimetry-Differential thermal analysis (TG-DTA) was performed with Rigaku TG-DTA8122 equipped with Rigaku smart loader auto sampler. Approximately 10 mg sample was pressed in the Platina sample holder. The thermal profiles were measured from room temperature to 800 °C. Gas chromatography (GC) analyses were conducted using a gas chromatography (GC-17A, Shimadzu) equipped with an InertCap 17 capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector (FID). Mass spectrometry (MS) measurements were recorded on a spectrometer (GCMS-QP2010 SE, Shimadzu) equipped with an InertCap 17MS capillary column (internal diameter = 0.25 mm, length = 30 m) at an ionization voltage of 70 eV. The isolation of the product was performed with a single channel automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance III-400 spectrometers (1H, 400 MHz; <sup>13</sup>C, 100 MHz). All <sup>1</sup>H NMR chemical shifts were recorded in ppm ( $\delta$ ) relative to tetramethyl silane or referenced to the chemical shifts of residual solvent resonances (CHCl<sub>3</sub> was used as internal standard,  $\delta$  7.26). All <sup>13</sup>C NMR chemical shifts were recorded in ppm ( $\delta$ ) relative to carbon resonances in CDCl<sub>3</sub> at  $\delta$  77.16.

#### GC-FID measurement conditions and temperature program



Internal standard	: chlorobenzene
Carrier Gases	: $N_2$ (50 mL/min)
Injection temperature	: 250 °C
Detector temperature	: 250 °C

#### TPD of NH<sub>3</sub> and CO<sub>2</sub> measurement conditions and temperature program

Surface concentrations of acidic and basic sites were determined by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) and carbon dioxide (CO<sub>2</sub>-TPD), respectively. Before TPD experiments, the catalysts were pre-treated, at atmospheric pressure, by flowing Ar/H<sub>2</sub> (50 mL/min) from room temperature to 600 °C at a heating rate of 10 °C/min. Then, the samples were maintained under Ar/H<sub>2</sub> flow at 600 °C for 60 min. After cleaning with helium, the samples were saturated for 15 min in flow of a gas mixture containing NH<sub>3</sub>/He at 110°C or CO<sub>2</sub> at 110 °C (the total flow rate was 50 ml/min in both cases). Then, the samples were purged in helium flow until a constant baseline level was attained. TPD measurements were performed in the temperature range 50–800 °C at a rate of 2 °C/min using helium (30 ml/min) as carrier flow. The evolved ammonia or carbon dioxide were detected by an on-line thermal-conductivity detector, calibrated by the peak area of known pulses of NH<sub>3</sub> or CO<sub>2</sub>.

### 3. Preparation of Co-MgO/TiO<sub>2</sub>

In a typical preparation of 5Co-20MgO/TiO<sub>2</sub>, 0.25 g (0.86 mmol) Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1.27 g (4.95 mmol) Mg(NO)<sub>2</sub>·6H<sub>2</sub>O were dissolved with H<sub>2</sub>O (100 mL) in the plastic flask. To the solution, 0.75 g of TiO<sub>2</sub> was added and the resulting suspension was stirred at room temperature (r.t.) for 1 h. Then, the pH was adjusted with aqueous ammonia followed by additional stirring at r.t. for 2h. The solid obtained was separated by filtration and washed with H<sub>2</sub>O (100 mL). The solid was dried at 90 °C overnight followed by reduction by H<sub>2</sub> gas (flow rate= 30 mL/min) at 600 °C for 2 hours before it was finally transferred to Ar glove box without exposure to air to give 5Co-20MgO/TiO<sub>2</sub>.

#### 4. Preparation of supported Co catalyst

In the round bottom flask, 0.25 g (0.86 mmol)  $Co(NO_3)_2 \cdot 6H_2O$  (5 wt% of Co) was dissolved in H<sub>2</sub>O (100 mL). TiO<sub>2</sub> (95 wt%) was dispersed into the solution. The mixture was then stirred at r.t. for 1 hour followed by evaporation (60 °C, 90 MPa) leaving a solid. The obtained solid was dried at 90 °C overnight and reduced by H<sub>2</sub> gas (flow rate = 30 mL/min) at 600 °C for 2 hours before it was finally transferred to Ar glove box without exposure to air to give Co/TiO<sub>2</sub>.

#### 5. Procedure for α-alkylation of ketones with primary alcohols

All experiments were performed in the sealed glass tube under an argon atmosphere under anhydrous conditions unless otherwise stated. The  $\alpha$ -alkylation of ketones with primary alcohols was carried out in a 15 mL glass tube equipped with a magnetic stirrer. Into the reactor, 0.5 mmol of ketones and 0.5 mmol of alcohols, 5 mL of toluene, and 100 mg of catalyst were loaded. The glass tube was then heated in the oil bath at 110 °C under 100 rpm stirring speed.

#### 6. Procedure for reuse experiments

The catalytic reaction was carried out according to the general procedure under

100 rpm stirring speed. In the catalyst reactivation, the catalyst was filtered by filtration and washed with MeOH (10 mL). The resulting solid was then dried at 90 °C overnight followed by reduction by  $H_2$  gas (flow rate = 30 mL/min) at 600 °C for 2 hours before it was finally transferred to Ar glove box without exposure to air.

# 7. Catalytic system optimization

Table S1 Catalysts screening<sup>a</sup>

o C	+ HO	catalyst toluene I0 °C. 20 h			
1a	2a		3aa		4aa
Entry	Catalvat	Con	version (%)	Yield	(%)
Entry	Catalyst	<b>1</b> a	2a	<b>3</b> aa	4aa
1	5Ru-20MgO/TiO <sub>2</sub>	56	71	3	0
2	5Pd-20MgO/TiO <sub>2</sub>	88	95	29	10
3	5Pt-20MgO/TiO <sub>2</sub>	93	97	33	2
4	5Co-20MgO/TiO <sub>2</sub>	>99	>99	95	1
5	5Co-20MgO/SiO <sub>2</sub>	67	72	2	14
6	5Co-20MgO/CeO <sub>2</sub>	50	86	4	2
7	5Co-20MgO/γ-Al <sub>2</sub> C	<b>9</b> <sub>3</sub> <b>9</b> 1	91	55	1
8	5Co-20SrO/TiO <sub>2</sub>	81	72	16	9
9	5Co-20CaO/TiO <sub>2</sub>	98	82	45	1
10	5Co-20BaO/TiO <sub>2</sub>	68	64	2	9
11	5Co-20Li <sub>2</sub> O/TiO <sub>2</sub>	54	65	7	4
12	5Co-20Na <sub>2</sub> O/TiO <sub>2</sub>	92	90	59	5
13	5Co-20Cs <sub>2</sub> O/TiO <sub>2</sub>	89	95	38	1
14	5Co/MgO	96	94	40	1
15	5Co/TiO <sub>2</sub>	70	75	2	18
16	5Co/SiO <sub>2</sub>	58	80	0	0
17	5Co/CeO <sub>2</sub>	53	73	5	0
18	5Co/y-Al <sub>2</sub> O <sub>3</sub>	68	79	20	2
19	5Co/ZrO <sub>2</sub>	57	69	2	2

<sup>a</sup>Reaction conditions: catalyst (0.1 g), 1a (0.5 mmol), 2a (0.5 mmol), toluene (5 mL), 110

°C, 20 h, Ar (1 atm). Conversion and yield were determined by GC analysis.

Entry	Catalyst	Reduction	Conver	rsion (%)	Yield (%)	
	Catalyst	Temp. (°C)	1a	2a	3aa	4aa
1	5Co-20MgO/TiO <sub>2</sub>	600	>99	>99	95	1
2	10Co-15MgO/TiO <sub>2</sub>	600	92	>99	65	1
3	15Co-10MgO/TiO <sub>2</sub>	600	90	>99	56	7
4	10Co-10MgO/TiO <sub>2</sub>	600	84	80	36	6
5	5Co-20MgO/TiO <sub>2</sub>	500	77	77	7	19
6	5Co-20MgO/TiO <sub>2</sub>	700	73	90	41	2

Table S2 Screening on composition ratio and reduction temperature <sup>a</sup>

<sup>a</sup> Reaction conditions: catalyst (0.1 g), **1a** (0.5 mmol), **2a** (0.5 mmol), toluene (5 mL),

110 °C, 20 h, Ar (1 atm). Conversion and yield were determined by GC analysis.

Table S3 Solvent screening<sup>a</sup>

	+ HO catalyst toluene 90 °C, 20 h			+	
Id	20	Conversion	<b>v</b> (%)	Vield (	%)
Entry	Solvent	<u>1a</u>	<u>2a</u>	<u> </u>	4aa
1	Toluene	94	99	77	3
2	Methanol	35	52	0	0
3	Cyclohexane	53	67	3	5
4	Acetonitrile	44	56	0	0
5	Dichloromethane	50	65	1	2
6	DMF	40	54	0	0
7	THF	47	63	2	1

<sup>*a*</sup> Reaction conditions: catalyst (0.1 g), **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (5 mL), 90

°C, 20 h, Ar (1 atm). Conversion and yield were determined by GC analysis.

Table S4 Optimization of catalytic system<sup>a</sup>

	+ HO	Co-MgO/TiO <sub>2</sub> toluene 20 h			+	
1a	2a		:	Baa	4	aa
Entry	Catalyst	Reaction	Conver	sion (%)	Yield	d (%)
Entry	loading (mg)	Temp. (°C)	<b>1</b> a	2a	3aa	4aa
1	50	110	78	93	55	4
2	100	110	>99	>99	95	1
3	200	110	94	>99	91	-
4	100	90	94	>99	77	3
5	100	130	94	>99	83	2
6 <sup>b</sup>	100	110	78	86	54	4
7°	100	110	87	>99	73	5
8 <sup>d</sup>	100	110	92	>99	82	4
9e	100	110	98	>99	63	-
10 <sup>f</sup>	100	110	69	79	42	2

<sup>a</sup> Reaction conditions: 5Co-20MgO/TiO<sub>2</sub>, 1a (0.5 mmol), 2a (0.5 mmol), toluene (5 mL),
20 h, Ar (1 atm), <sup>b</sup> 2a (0.6 mmol), <sup>c</sup> 1a (0.6 mmol), <sup>d</sup> 1a (0.55 mmol), <sup>e</sup> Toluene (1 mL), <sup>f</sup>
1a (5 mmol), 2a (5 mmol), no solvent. Conversion and yield were determined by GC analysis

**Table S5** Selected previous work on the alkylation of acetophenone with benzyl alcohol

Catalyst	Catalyst loading	Base	Solvent	T (°C)	time (h)	Yield (%)	Ref
Co-MgO/TiO <sub>2</sub>	17 mol%	-	Toluene	110	20	95	This work
Co(II) complex	2 mol%	KOtBu	Toluene	120	24	93	<b>S</b> 1
Fe complex	2 mol%	$Cs_2CO_3$	Toluene	140	24	80	S2
Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	20 mol%	$K_3PO_4$	-	175	14.5	86	S3
MnO <sub>2</sub> @PDCS	1 mol%	NaOH	Toluene	120	12	89	S4
LCN@Zn-SAC	1.5 mol%	KOH	Toluene	110	6	92	S5
Pd/C	5 mol%	KOH	Dioxane	100	40	75	<b>S</b> 6
Pd/AlO(OH)	0.2 mol%	$K_3PO_4$	Toluene	110	3	85	<b>S</b> 7

	OH — Toluer	Catalyst ne (5 mL), 110 °C, 20 h	
	2a	2a'	
Entry	Catalyst	Conversion 2a (%)	Yield 2a' (%)
1	Co-MgO/TiO <sub>2</sub>	58	7
2	Co/TiO <sub>2</sub>	62	11

Table S6 Control experiment: dehydrogenation step

<sup>*a*</sup> Reaction conditions: catalyst (0.1 g), **2a** (0.5 mmol), toluene (5 mL), 110 °C, 20 h, Ar (1 atm). Conversion and yield were determined by GC analysis.

Toluene was detected when the dehydrogenation was performed using cyclohexane as a solvent.

	0 + 0 1a	toluen 110 °C, 2 2a'	st ne 20 h	O 4aa	
Entry	Catalyst	Catalyst loading	Convers	sion (%)	Yield
y	Cuturyst	(mg)	1a	2a'	(%)
1	Co-MgO/TiO <sub>2</sub>	100	87	92	71
2	Ru-MgO/TiO <sub>2</sub>	100	>99	82	9
3	TiO <sub>2</sub>	100	92	93	28
4	MgO	20	52	55	13
5	$Co_3O_4$	(5 mg Co)	45	49	1
6	Co nanoparticle	5	45	54	0
7	$RuO_2$	(5 mg Ru)	46	49	0
8	Ru/TiO <sub>2</sub>	100	60	90	18
9	Ru/MgO	100	51	51	10
10	Co/TiO <sub>2</sub>	100	86	90	69
11	Co/MgO	100	80	92	60
12 <sup>b</sup>	Co/TiO <sub>2</sub>	100	88	93	73
13 <sup>b</sup>	Co/MgO	100	76	86	49

Table S7. Control experiment: condensation of 2a' with 1a

<sup>*a*</sup> Reaction conditions: catalyst (0.1 g), **1a** (0.5 mmol), **2a'** (0.5 mmol), toluene (5 mL), 110 °C, 20 h, Ar (1 atm); <sup>*b*</sup> run for 6 h. Conversion and yield were determined by GC analysis.

	Specific	Crysta	Crystallite diameter (nm)				
	surface area (m <sup>2</sup> /g)	Со	MgO	TiO <sub>2</sub>			
Co-MgO/TiO <sub>2</sub>	56		6.3	20.3			
Co/TiO <sub>2</sub>	30	5.6	-	24.7			
Co/MgO	139	16.3	38.3	-			
MgO/TiO <sub>2</sub>		-	9.6	22.2			

Table S8. Physical properties of the catalyst

Table S9 Recycling experiment (activity in the first reuse)<sup>a</sup>



 $\overline{a}$  Reaction conditions: catalyst 5Co-20MgO/TiO<sub>2</sub> 1a (0.5 mmol), 2a (0.5 mmol), toluene

(5 mL), 20 h, Ar (1 atm); Conversion and yield were determined by GC analysis

0 I	+ HO catalyst toluene 110 °C. 20 h	0 C		+		
1a	2a	3aa		4aa	l	
	Due	Conversio	on (%)	Yield (%)		
Entry	Kull	<b>1</b> a	2a	3aa	4aa	
1	1	>99	>99	95	1	
2	$2(1^{st} reuse)$	>99	>99	93	3	
3	$3 (2^{nd} reuse)$	>99	>99	88	5	
4	4 (3 <sup>rd</sup> reuse)	83	92	71	7	
			( <b>0</b> -	1 1 /		

Table S10 Recycling experiment (activity results for 4 runs)<sup>a</sup>

<sup>*a*</sup> Reaction conditions: catalyst (0.1 g), **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (5 mL), 90 °C, 20 h, Ar (1 atm). Conversion and yield were determined by GC analysis.

Table S11 Product distribution for selected reactions <sup>a</sup>

1a	2 + H0 2a	)-	cata tolue 110 °C	lyst ene , 20 h		3a				4aa	
					(	GC are	ea rati	0(%)			
Entry	Catalyst	1a	2a	3aa	<b>4</b> aa	1a'	2a'	5aa	6aa	<b>7</b> aa	others
1	Ru-										
1	MgO/TiO <sub>2</sub>	41	34	4	0	10	4	4	0	0	3
2	Pt-MgO/TiO <sub>2</sub>	9	7	42	3	3	1	0	1	5	1
3	Pd-MgO/TiO <sub>2</sub>	15	6	41	14	6	1	0	<1	2	1
4	Co/MgO	3	1	25	1	4	0	0	<1	9	2
5	Co/TiO <sub>2</sub>	34	27	3	22	20	2	0	1	0	2
	4		10.4		( a =	45		-	-		-

<sup>a</sup> Reaction conditions: catalyst (0.1 g), **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (5 mL), 90

°C, 20 h, Ar (1 atm). Conversion and yield were determined by GC analysis.

# Indexes

1a	: acetophenone
2a	: benzyl alcohol
1a'	: 1-phenylethanol
2a'	: benzaldehyde
3aa	: 1,3-diphenylpropan-1-one
4aa	: chalcone
5aa	: benzene
6aa	: 1,3-diphenylpropane

7aa : 1,3-diphenylpropan-1-ol

# 8. Figures



Fig. S1 XPS Co 2p spectrum



Fig. S2 (a) XRD patterns and (b) XPS Co 2p spectra of fresh and recovered Co-MgO/TiO $_2$ 



Fig. S3 Bright-field TEM image of fresh and recovered Co-MgO/TiO<sub>2</sub>.



Fig. S4 EDX profiles of (a) fresh catalyst and (b) used catalyst.



Fig. S5 Adsorption/desorption isotherm of Co-MgO/TiO $_2$ .



Fig. S6 XRD patterns of 5Co-20MgO/TiO<sub>2</sub> (a) before and after reduction at (b) 500 °C, (c) 600 °C, (d) 700 °C.



Fig. S7 A gradual decrease of MgO detected on the XRD patterns of catalysts for reuse experiments ●: MgO, ■: MgTiO<sub>3</sub>.



Fig. S8 (a)  $CO_2$ -TPD and (b)  $NH_3$ -TPD profiles of  $Co-MgO/TiO_2$  and  $Ru-MgO/TiO_2$ .



Fig. S9 Classical GC chromatograms of key reactions.

# 9. Spectral data NMR Spectra

After the reaction was finished, the reaction mixture was filtered, and the collected filtrate was concentrated by rotary evaporator. Otherwise mentioned, the obtained residue was purified by a silica gel column using ethyl acetate/hexane (30:70, v/v) as an eluent.

#### 1,3-diphenylpropan-1-one (3aa)<sup>8</sup>



Colorless liquid. Yield: 94 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94–7.92 (m, 2H), 7.54–7.50 (m, 1H), 7.44–7.40 (m, 2H), 7.30–7.19 (m, 5H), 3.34–325 (m, 2H), 3.05 (t, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.2, 141.3, 136.9, 133.1, 128.6, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2 ppm.

# 1-phenyl-3-(p-tolyl)propan-1-one (3ab)9



Light yellow liquid. Yield: 82 % <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (dd, *J*=1.4, 7.08, 2H), 7.53–7.51 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.10 (q, *J* = 8.3 Hz, 4H), 3.28–3.24 (m, 2H), 3.03–3.02 (m, 2H), 2.31 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.4, 138.3, 136.9, 135.7, 133.1, 129.3, 128.7, 128.4, 128.1, 40.7, 29.8, 21.1 ppm.

#### 3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ac)<sup>10</sup>



Colorless liquid. Yield: 90 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (dd, J = 1.4, 7.1 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 3.25 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.5, 158.0, 136.9, 133.3, 133.1, 129.4, 128.6, 128.1, 114.0, 55.3, 40.7, 29.3 ppm.

# 3-(2-methoxyphenyl)-1-phenylpropan-1-one (3ad)<sup>11</sup>



Colorless liquid. Yield: 78%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (dd, J = 1.4, 7.1 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.4 Hz, 2H), 7.22–7.18 (m, 2H), 6.91–6.84 (m, 2H), 3.82 (s, 3H), 3.25 (t, J = 7.2 Hz, 2H), 3.04 (t, J = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.0, 157.6, 137.0, 132.9, 130.2, 129.6, 128.6, 128.2, 127.6, 120.6, 110.3, 55.2, 39.0, 25.8 ppm

# 3-(4-fluorophenyl)-1-phenylpropan-1-one (3ae)<sup>12</sup>



Colorless liquid. Yield: 92 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, J = 7.24 Hz, 2H), 7.53 (t, J = 7.36 Hz, 1H), 7.43 (t, J = 7.44 Hz, 2H), 7.23 (dd, J = 8.32, 5.72 Hz, 2H), 6.95 (t, J=8.68 Hz, 2H), 3.26 (t, J = 7.8 Hz, 2H), 3.02 (t, J = 7.48 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.0, 162.7, 160.2, 137.0, 133.2, 129.9 (d, J=7.65 Hz), 128.7, 128.0, 115.3 (d, J = 21.1 Hz), 40.4, 29.3 ppm.





Colorless liquid. Yield: 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.96–7.94 (m, 2H), 7.55–7.51 (m, 1H), 7.46–7.42 (m, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 1.76–1.69 (m, 2H), 1.39–1.29 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  200.6, 137.2, 132.9, 128.6, 128.1, 38.7, 31.7, 29.1, 24.4, 22.6, 14.1 ppm.

# 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3ba)<sup>14</sup>

S21



Yellowish solid. Yield: 91% <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.31–7.28 (m, 2H), 7.25–7.20 (m, 3H), 3.33–3.29 (m, 2H), 3.06 (t, J = 7.4 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.3, 141.0, 139.6, 134.4 (q, J = 32.6 Hz), 128.7, 128.5, 128.4, 126.4, 125.8 (q, J = 3.8 Hz), 123.7 (q, J = 271 Hz) 40.8, 30.0 ppm.

# 3-phenyl-1-(p-tolyl)propan-1-one (3ca)<sup>15</sup>



Yellowish solid. Yield: 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 8.2 Hz, 2H), 7.28–7.21 (m, 7H), 3.24 (t, J = 8.2 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H) ppm; 13C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.0, 143.9, 141.5, 134.5, 129.3, 128.6, 128.5, 128.2, 126.2, 40.5, 30.3, 21.7 ppm.

#### 1-(4-methoxyphenyl)-3-phenylpropan-1-one (3da)<sup>16</sup>



Yellowish solid. Yield: 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, J = 9.0 Hz, 2H), 7.28–25 (m, 5H), 6.91 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 3.25–3.21 (m, 2H), 3.05 (t, J = 8.2 Hz, 2H); 13C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.8, 163.5, 141.5, 130.4, 130.0, 128.6, 128.5, 126.2, 113.8, 55.5, 40.2, 30.4 ppm.

# 1-(2-methoxyphenyl)-3-phenylpropan-1-one (3ea)<sup>17</sup>



Light yellow liquid. Yield: 82%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70–7.67 (m, 1H), 7.47–7.43 (m, 1H), 7.30–7.19 (m, 5H), 7.02–6.94 (m, 2H), 3.88 (s, 3H), 3.32–3.28 (m, 2H), 3.04–3.02 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.8, 158.6, 141.8, 133.5, 130.5, 128.5, 128.5, 128.4, 126.0, 120.7, 111.6, 55.6, 45.5, 30.5 ppm.

# 1-phenylhexan-3-one (3fa)<sup>18</sup>



Colorless liquid. Yield: 68%. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ 7.27–7.26 (m, 2H), 7.20–7.17 (m, 3H), 2.91–2.87 (m, 2H), 2.74–2.70 (m, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.62–2.70 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 210.3, 141.2, 128.5, 128.3, 126.1, 45.0, 44.3, 29.8, 17.3, 13.8 ppm.

#### 1-phenylnonan-3-one (3ga)<sup>19</sup>



Colorless liquid. Yield: 81%. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  7.32–7.28 (m, 2H), 7.23–7.20 (m, 3H), 2.91 (t, *J* = 7.9 Hz, 2H), 2.77–2.74 (m, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.55 (t, *J* = 7.4 Hz, 2H), 1.29–1.23 (m, 6H), 0.89–0.85 (m, 3 H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>)  $\delta$  210.5, 141.3, 128.6, 128.4, 126.2, 44.3, 43.2, 31.7, 29.9, 29.0, 23.9, 22.6, 14.1 ppm.

# 1-phenyltridecan-3-one (3ha)<sup>20</sup>



Colorless liquid. Yield: 84%. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  7.28-7.24 (m, 2H), 7.19–7.16 (m, 3H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 1.58– 1.52 (m, 2H), 1.29-1.25 (m, 14H), 0.89–0.86 (m, 3H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>)  $\delta$  210.4, 141.2, 128.5, 128.3, 126.1, 44.3, 43.1, 31.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2 23.8, 22.7, 14.1 ppm.



<sup>1</sup>H NMR of 1,3-diphenylpropan-1-one (3aa)



<sup>13</sup>C NMR of 1,3-diphenylpropan-1-one (3aa)



<sup>1</sup>H NMR of 1-phenyl-3-(p-tolyl)propan-1-one (3ab)



<sup>13</sup>C NMR of 1-phenyl-3-(p-tolyl)propan-1-one (3ab)



<sup>1</sup>H NMR of 3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ac)



<sup>13</sup>C NMR of 3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ac)



<sup>1</sup>H NMR of 3-(2-methoxyphenyl)-1-phenylpropan-1-one (3ad)



<sup>13</sup>C NMR of 3-(2-methoxyphenyl)-1-phenylpropan-1-one (3ad)



<sup>1</sup>H NMR of 3-(4-fluorophenyl)-1-phenylpropan-1-one (3ae)



<sup>13</sup>C NMR of 3-(4-fluorophenyl)-1-phenylpropan-1-one (3ae)



<sup>1</sup>H NMR of 1-phenylheptan-1-one (3af)

0 Ph 200 3af -200.64 180 160 140 \_ 120 100 8 77.44 77.12 76.80 60 40 38.68 - 31.74 - 29.11 - 24.40 - 22.60 20 -14.11 0 ppm WDW GB PC SFO2 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13 Time INSTROG PROBHD PDLPROG TD VENT US SOLVENT DS SOLVENT DS FIDRES RG RG RG DW DE TE TE TE DU DU DU DU Current | NAME EXPNO PROCNO SFO1 NUC1 P1 PLW1 ST ST F2 - Acquisition Parameters Date\_\_\_\_\_\_20210601 mime\_\_\_\_\_\_\_17.15 ī Processing parameters 32768 100.6127652 MHz = CHANNEL fl ------100.6228303 MHz 13C 13C 15.00 usec 8.89999962 W Data Parameters ES 2G 110 20 C G spect mm PABBO BB-24038.461 Hz 0.366798 Hz 1.3631488 sec 2050 usec 6.50 usec 298.5 K 2.0000000 sec 0.03000000 sec 1 sec zgpg30 65536 CDCL3 EM 0 1.00 Hz 1.40 ת rere

# <sup>13</sup>C NMR of 1-phenylheptan-1-one (3af)



<sup>1</sup>H NMR of 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3ba)



<sup>13</sup>C NMR of 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3ba)



<sup>1</sup>H NMR of 3-phenyl-1-(p-tolyl)propan-1-one (3ca)



<sup>13</sup>C NMR of 3-phenyl-1-(p-tolyl)propan-1-one (3ca)



<sup>1</sup>H NMR of 1-(4-methoxyphenyl)-3-phenylpropan-1-one (3da)



<sup>13</sup>C NMR of 1-(4-methoxyphenyl)-3-phenylpropan-1-one (3da)



<sup>1</sup>H NMR of 1-(2-methoxyphenyl)-3-phenylpropan-1-one (3ea)



<sup>13</sup>C NMR of 1-(2-methoxyphenyl)-3-phenylpropan-1-one (ea)



<sup>1</sup>H NMR of 1-phenylhexan-3-one (3fa)



<sup>13</sup>C NMR of 1-phenylhexan-3-one (3fa)



<sup>1</sup>H NMR of 1-phenylnonan-3-one (3ga)



<sup>13</sup>C NMR of 1-phenylnonan-3-one (3ga)



<sup>1</sup>H NMR of 1-phenyltridecan-3-one (3ha)



<sup>13</sup>C NMR of 1-phenyltridecan-3-one (3ha)

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