Supporting Information

Ligand-free Guerbet-Type Reactions in Air Catalyzed by *In-Situ* Formed Complexes of Base Metal Salt Cobaltous Chloride

Pran Gobinda Nandi,[a] Pradhuman Kumar[a] and Akshai Kumar*[a,b,c]

[a]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati – 781039, Assam, India

[b]Center for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati – 781039, Assam, India

[c]School of Health Sciences, Indian Institute of Technology Guwahati, Guwahati – 781039, Assam, India.

Email: akshaikumar@iitg.ac.in

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1. Experimental Section

General Procedure and Materials. All manipulations were carried out in air. The Co metal salts, NaO^{t}Bu, KO^{t}Bu, NaOH, KOH, Na_2CO_3, K_2CO_3, $CDCl_3$, benzyl alcohol, 1-phenyl ethanol and their derivatives were purchased either from MERCK or Sigma−Aldrich and used as such. To prepare the stock solution, $CoCl_2$ was dissolved either in benzyl alcohol or 1-phenyl ethanol. All catalytic reactions were carried out in air using oven-dried glassware. The 1-phenyl ethanol derivatives which were commercially not available were prepared according to literature procedure.[1a]

Physical Measurements. ^1H, $^{13}C\{H\}$ and ^{19}F NMR were recorded on a Bruker ASCEND 600 operating at 600 MHz for ^1H, 150 MHz for $^{13}C\{H\}$ or on a Bruker AVANCE 400 operating at 400 MHz for ^1H, 100 MHz for $^{13}C\{H\}$ or on a Bruker AVANCE 500 operating at 500 MHz for ^1H, 125 MHz for $^{13}C\{H\}$. Chemical shifts (δ) are reported in ppm. HRMS measurements were done using an Agilent Accurate-Mass Q-TOF ESI–MS 6520. The X-band EPR spectra were recorded on a JES-FA200 ESR spectrometer. The field-emission scanning electon microscopy (FESEM) were performed using JSM-7610F instrument. Transmission electron microscopy (TEM) analysis were carried out using a JEOL JEM-2100F FETEM instrument.

General procedure for $CoCl_2$ catalyzed *β*-alkylation of alcohols. In a 10 mL pear-shaped flask, 1-phenyl ethanol or benzyl alcohol were taken in air. This was followed by addition of 2.5 mol % of NaO^{t}Bu and 0.01 mol % of $CoCl_2$ (from a stock solution either in 1-phenyl ethanol or benzyl alcohol). After the addition, the reaction mixture contained 0.61 mL (5.00 mmol) of 1-phenyl ethanol, 0.52 mL (5.00 mmol) of benzyl alcohol, 24 mg (0.25 mmol) of NaO^{t}Bu and 0.13 mg (1 μmol) of $CoCl_2$. The mixture was heated at 140 °C for 24 h in air. The reaction mixture was then cooled to room temperature. An aliquot (Typically 10 mg) was withdrawn from reaction mixture and the NMR yield was determined by ^1H NMR using $CDCl_3$ as solvent and toluene (Typically 10 μL) as an internal standard. The yield was determined by ^1H NMR spectroscopy.[1b]

Preparation of FESEM sample. An aliquot (approximately 10 mg) was withdrawn from reaction mixture and dropcasted on a glass slide. The dropcasted sample was submitted for FESEM analysis. A JSM-7610F instrument was used for the field-emission scanning electron microscopy (FESEM) analysis.

Preparation of TEM sample. An aliquot (approximately 10 mg) was withdrawn from reaction mixture and dropcasted on a TEM grid. The dropcasted sample was submitted for TEM analysis. Transmission electron microscopy (TEM) analysis were carried out using a JEOL JEM-2100F FETEM instrument.

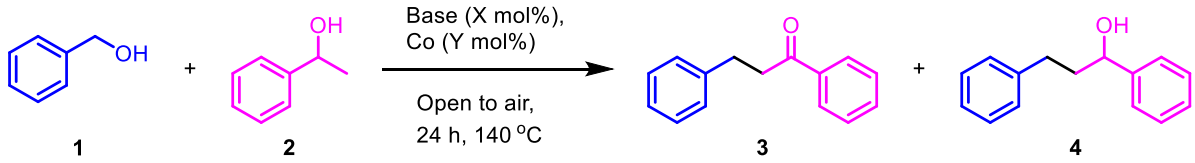
General procedure for $CoCl_2$ catalyzed *β*-alkylation of alcohols-kinetic study. In a 10 mL pear-shaped flask, 1-phenyl ethanol or benzyl alcohol were taken in air. This was followed by addition of 2.5 mol % of NaO^{t}Bu and 0.01 mol % of $CoCl_2$ (from a stock solution either in 1-phenyl ethanol or benzyl alcohol). After the addition, the reaction mixture contained 0.61 mL (5.00 mmol) of 1-phenyl ethanol, 0.52 mL (5.00 mmol) of benzyl alcohol, 24 mg (0.25 mmol) of NaO^{t}Bu and 0.13 mg (1 μmol) of $CoCl_2$. The mixture was heated at 140 °C and aliquots were withdrawn at periodic intervals of 0.5h, 1h, 2h, 3h, 5h, 6h, 9h, 12h, 15h, 18h, 21h and 24 h. Yield of the desried product was determined by ^1H NMR using $CDCl_3$ as solvent and toluene as standard.

Procedure for $CoCl_2$ catalyzed *β*-alkylation of alcohols with hot filtration. In a 10 mL pear-shaped flask, 1-phenyl ethanol or benzyl alcohol were taken in air. This was followed by addition of 5 mol % of NaO^{t}Bu and 0.02 mol % of $CoCl_2$ (from a stock solution either in 1-phenyl ethanol or benzyl alcohol). After the addition, the reaction mixture contained 0.61 mL (5.00 mmol) of 1-phenyl ethanol, 0.52 mL (5.00 mmol) of benzyl alcohol, 24 mg (0.25 mmol) of NaO^{t}Bu and 0.13 mg (1 μmol) of $CoCl_2$. The mixture was heated at 140 °C and an aliquot was withdrawn after 1h and the yield of the desried product was determined by ^{1}H NMR using $CDCl_3$ as solvent and toluene as standard. The hot reaction mixture was subsequently filtered using 0.2 μm Nylon Membrane Filter. The filterate was then heated at 140 °C and aliquots were withdrawn at periodic intervals of 0.5h, 1h, 2h, 3h, 5h, 6h, 9h, 12h, 15h, 18h, 21h and 24 h. Yield of the desried product was determined by ^{1}H NMR using $CDCl_3$ as solvent and toluene as standard.

Procedure for $CoCl_2$ catalyzed *β*-alkylation of alcohols with 3h interval after 3h of reaction. In a 10 mL pear-shaped flask, 1-phenyl ethanol or benzyl alcohol were taken in air. This was followed by addition of 5 mol % of NaO^{t}Bu and 0.02 mol % of $CoCl_2$ (from a stock solution either in 1-phenyl ethanol or benzyl alcohol). After the addition, the reaction mixture contained 0.61 mL (5.00 mmol) of 1-phenyl ethanol, 0.52 mL (5.00 mmol) of benzyl alcohol, 24 mg (0.25 mmol) of NaO^{t}Bu and 0.13 mg (1 μmol) of $CoCl_2$. The mixture was heated at 140 °C and aliquots were withdrawn after 1h, 2h and 3h. The reaction mixture was then allowed to stand for 3h. After this 3h break, heating was then resumed and aliquots were withdrawn at periodic intervals of 5h, 6h, 9h, 12h, 15h, 18h, 21h and 24 h of reaction at 140 °C. Yield of the desried product was determined by ^{1}H NMR using $CDCl_3$ as solvent and toluene as standard.

2. Optimization table and Substrate Scope

Table S1. Solvent-Free *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol under Varying Conditions[a]

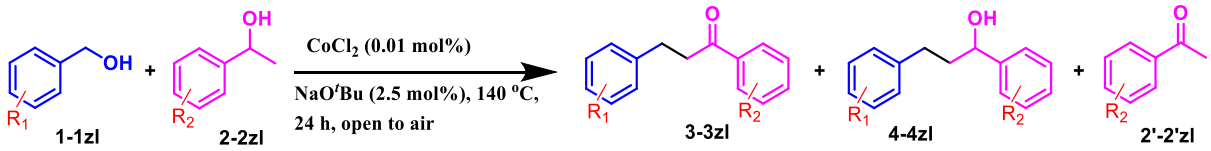


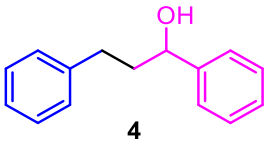
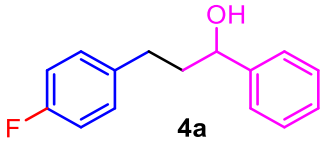
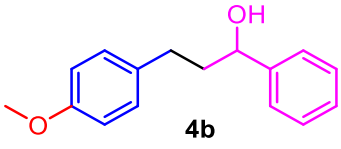
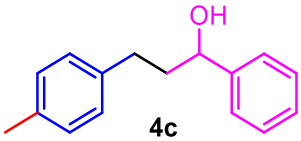
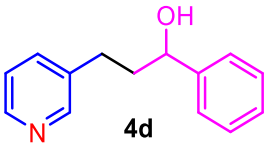
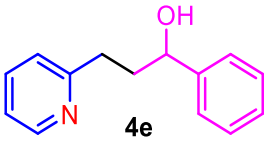
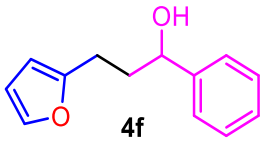
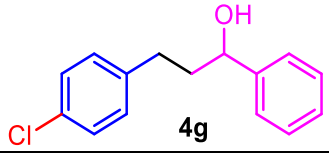
1 2 3 4

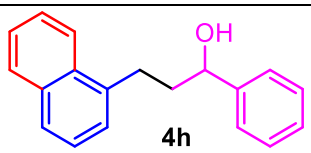
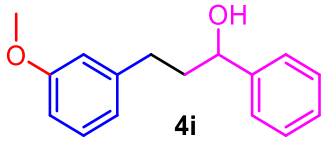
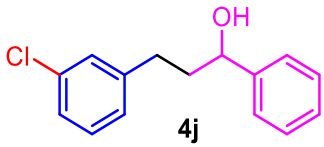
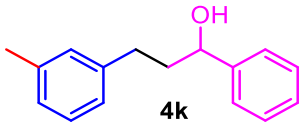
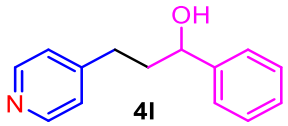
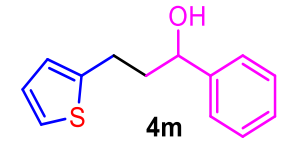
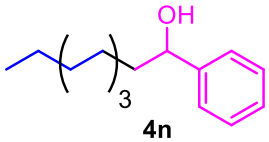
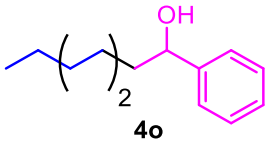
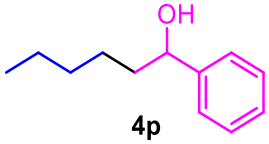
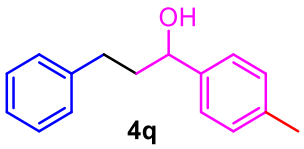
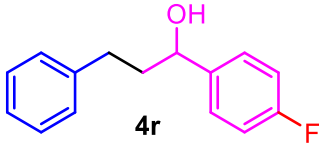
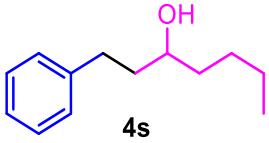
Entry	Catalyst (Y mol %)[b]	Base (X mol%)[b]	Yield[c] of Products, %		Selectivity of **4** ((Yield of **4**/ Total yield (**3** + **4**)) *100)
			3	**4**	
1	$CoCl_2$ (1.0)	NaO^{t}Bu (2.5)	4(4)[e]	25(8)[e]	86
2[d]	$CoCl_2$ (1.0)	NaO^{t}Bu (2.5)	7	44	86
3	$CoCl_2$ (0.5)	NaO^{t}Bu (2.5)	4	49	92
4	$CoCl_2$ (0.1)	NaO^{t}Bu (2.5)	4	74	95
5	$CoCl_2$ (0.05)	NaO^{t}Bu (2.5)	4	81	95
6	$CoCl_2$ (0.01)	NaO^{t}Bu (2.5)	9((9)[e]	87(88)[e]	91
7[d]	$CoCl_2$ (0.01)	NaO^{t}Bu (2.5)	2	88	98
8	$CoCl_2$ (0.005)	NaO^{t}Bu (2.5)	4	78	95
9	$CoCl_2$ (0.01)	NaO^{t}Bu (1.25)	4	58	94
10	$CoCl_2.6H_2O$ (0.01)	NaO^{t}Bu (2.5)	3	63	95
11	$CoCl_2$ (0.01)	KO^{t}Bu (2.5)	4	41	91
12	$CoCl_2$ (0.01)	Na_2CO_3 (2.5)	0	0	0
13	$CoCl_2$ (0.01)	K_2CO_3 (2.5)	0	0	0
14	$CoCl_2$ (0.01)	KOH (2.5)	3	40	93
15	$CoCl_2$ (0.01)	NaOH (2.5)	6	82	93
16	$Co(OAc)_2$ (0.01)	NaO^{t}Bu (2.5)	4	84	95
17	$Co(acac)_2$ (0.01)	NaO^{t}Bu (2.5)	4	68	94
18	-	NaO^{t}Bu (2.5)	2	8	80
19	$CoCl_2$ (0.01)	NaO^{t}Bu (1)	6	19	76
20	$CoCl_2$ (0.01)	NaO^{t}Bu (5)	10	88	90
21	$CoCl_2$ (0.01)	NaO^{t}Bu (10)	8	86	91

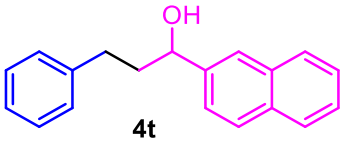
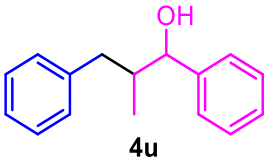
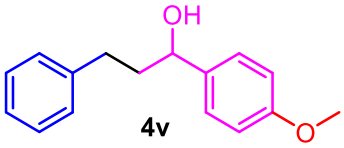
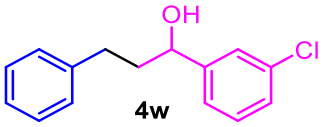
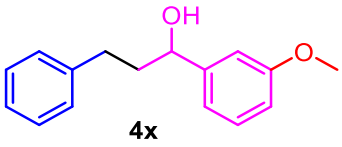
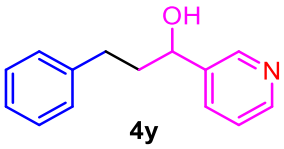
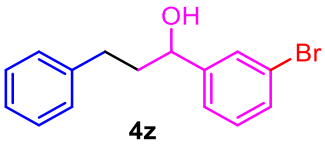
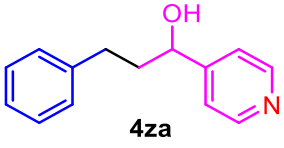
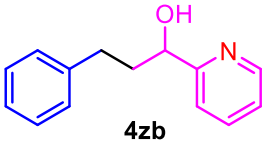
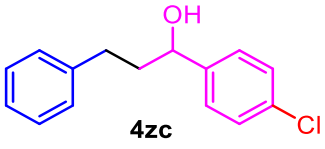
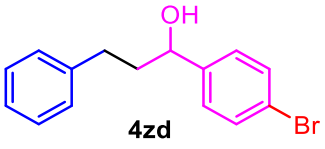
[a]Reaction conditions: 5 mmol of **1**, 5 mmol of **2**, X mol% of base and Y mol% of Co catalyst at 140 °C. [b]mol % of base and catalyst is with respect to total alcohol content (**1**+**2**). [c]Yield is determined from ^{1}H NMR using toluene as external standard. [d]Performed under argon atmosphere. [e]Performed in the presence of excess Hg.

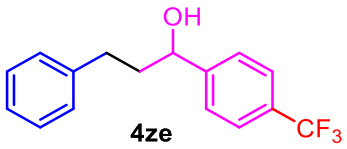
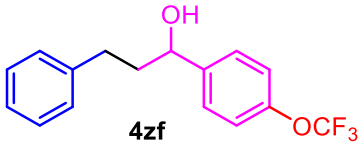
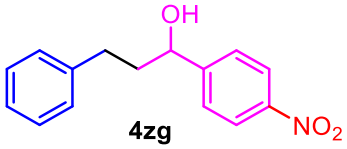
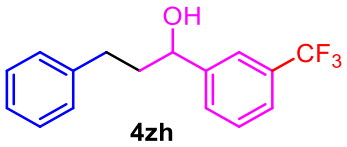
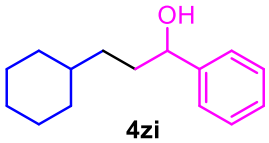
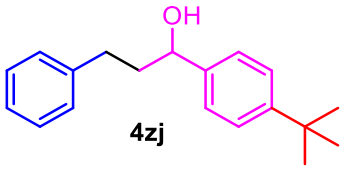
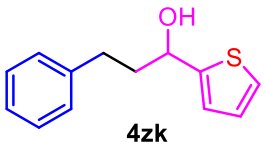
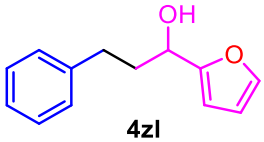
Table S2. The $CoCl_2$ Catalyzed Solvent-Free *β*-alkylation of Various Primary and Secondary Alcohols[a]



Entry	Product	**4 -4zl** Yield (%)	**3-3zl** Yield (%)	**2'-2'zl** Yield (%)	Total yield[b] [TON]	**4-4zl** Selectivity[c]
1	 **4**	87	9	trace	96 [9600]	91
2	 **4a**	56	4	2	62 [6200]	93
3	 **4b**	84	4	0	88 [8800]	95
4	 **4c**	82	16	0	98 [9800]	84
5	 **4d**	43	1	1	45 [4500]	98
		34[d]	2	trace	36 [3600]	94
6	 **4e**	14	4	0	18 [1800]	78
7	 **4f**	2	2	1	5 [500]	50
		19[e]	2	2	23 [230]	90
		3[d]	1	1	5 [500]	75
8	 **4g**	55	4	1	60 [6000]	93

9	 4h	41	4	2	47 [4700]	91
		63[d]	16	2	81 [8100]	80
10	 4i	71	3	2	76 [7600]	96
11	 4j	81	8	trace	89 [8900]	91
12	 4k	56	7	0	63 [6300]	89
13	 4l	10	5	trace	15 [1500]	67
14	 4m	80	3	trace	83 [8300]	96
		80[f]	4	1	85 [8500]	95
15	 4n	6	nd	4	10 [1000]	100
16	 4o	5	trace	2	7 [700]	100
		18[d]	trace	3	21 [2100]	100
17	 4p	4	trace	3	7 [700]	100
		3[e]	0	1	4 [40]	100
		7[d]	0	5	12 [1200]	100
18	 4q	84	12	trace	96 [9600]	88
19	 4r	4	2	1	7 [700]	67
		8[e]	4	1	13 [130]	67
		5[d]	2	1	8 [800]	71
20	 4s	7	2	0	9 [900]	78
		12[d]	2	0	14 [1400]	86

21	 4t	84	7	trace	91 [9100]	92
22	 4u	3 (two diastereomer)	trace	5	8 [800]	100
23	 4v	36	2	3	41 [4100]	95
		81[d]	14	1	96 [9600]	85
24	 4w	74	3	trace	77 [7700]	96
25	 4x	83	5	trace	88 [8800]	94
26	 4y	0	2	0	2 [200]	0
27	 4z	89	9	trace	98 [9800]	91
28	 4za	0	0	22	22 [2200]	0
29	 4zb	21	2	3	26 [2600]	91
30	 4zc	88	8	trace	96 [9600]	92
31	 4zd	81	4	1	86 [8600]	95

32	 4ze	81	5	trace	86 [8600]	94
33	 4zf	53	4	1	58 [5800]	93
34	 4zg	0	0	1	1 [100]	0
35	 4zh	66	3	1	70 [7000]	96
36	 4zi	5	trace	3	8 [800]	100
37	 4zj	34	4	3	41 [4100]	89
		86[d]	5	1	92 [9200]	95
38	 4zk	80	16	1	97 [9700]	83
39	 4zl	4	1	0	5 [500]	80
		3[d]	1	1	5 [500]	75

[a]Reaction conditions: 5 mmol of **1**, 5 mmol of **2**, 2.5 mol% of base and 0.01 mol% of $CoCl_2$ (mol % of base and catalyst is with respect to total alcohol content (**1**+**2**)) at 140 °C, yield is determined from ^{1}H NMR using toluene as external standard. [b]Total yield are calculated as yield of (**3**+**4**+**2'**).[c]Selectivity = yield of **4**/yield of (**3**+**4**). [d]Performed under argon atmosphere. [e]Reaction performed with 0.1 mol% $CoCl_2$ (with respect to both the substrates). [f]Reaction was repeated under same conditions.

3. NMR Spectra

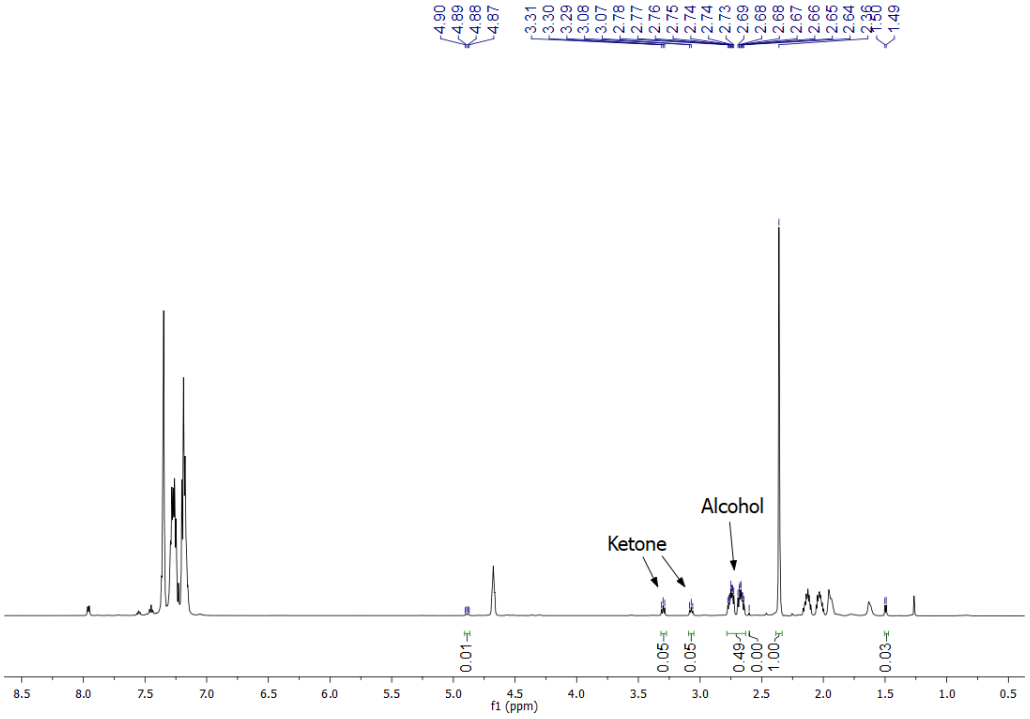


Figure S1: ^{1}H NMR spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 1)[2-4]

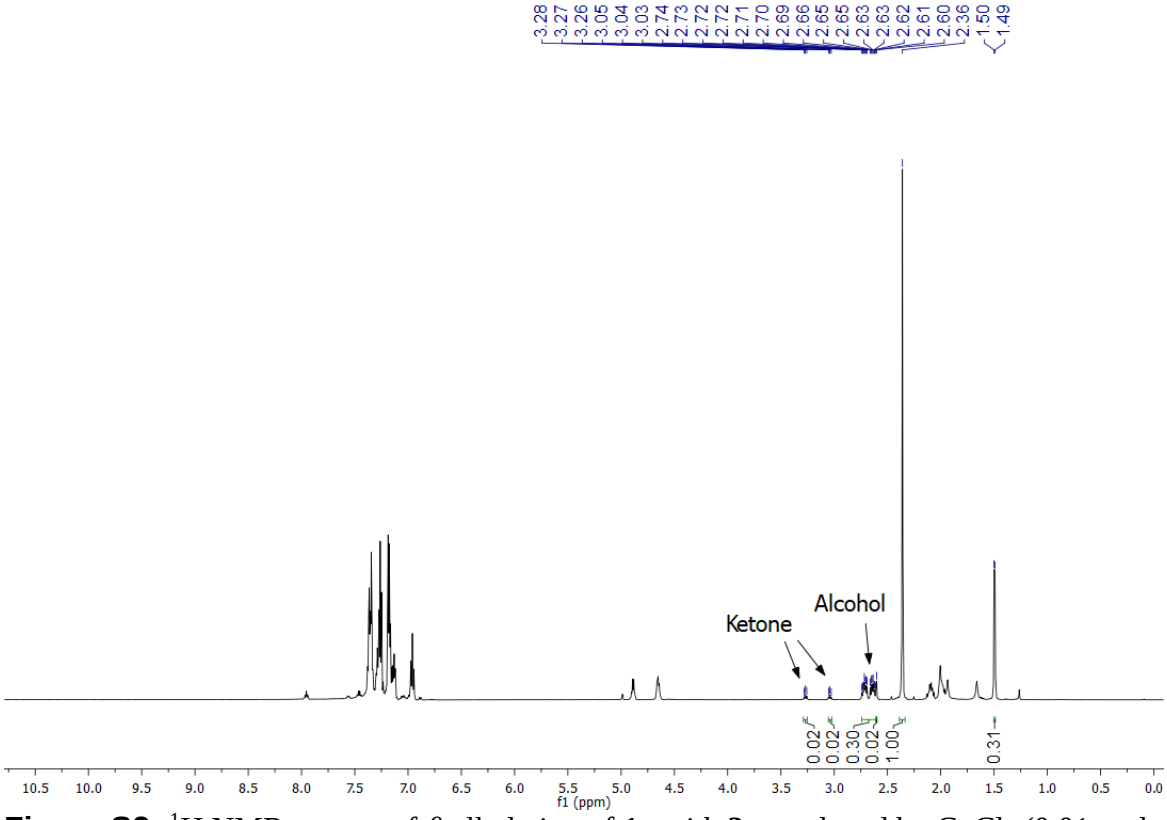


Figure S2: ^{1}H NMR spectra of *β*-alkylation of **1a** with **2a** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 2)[4]

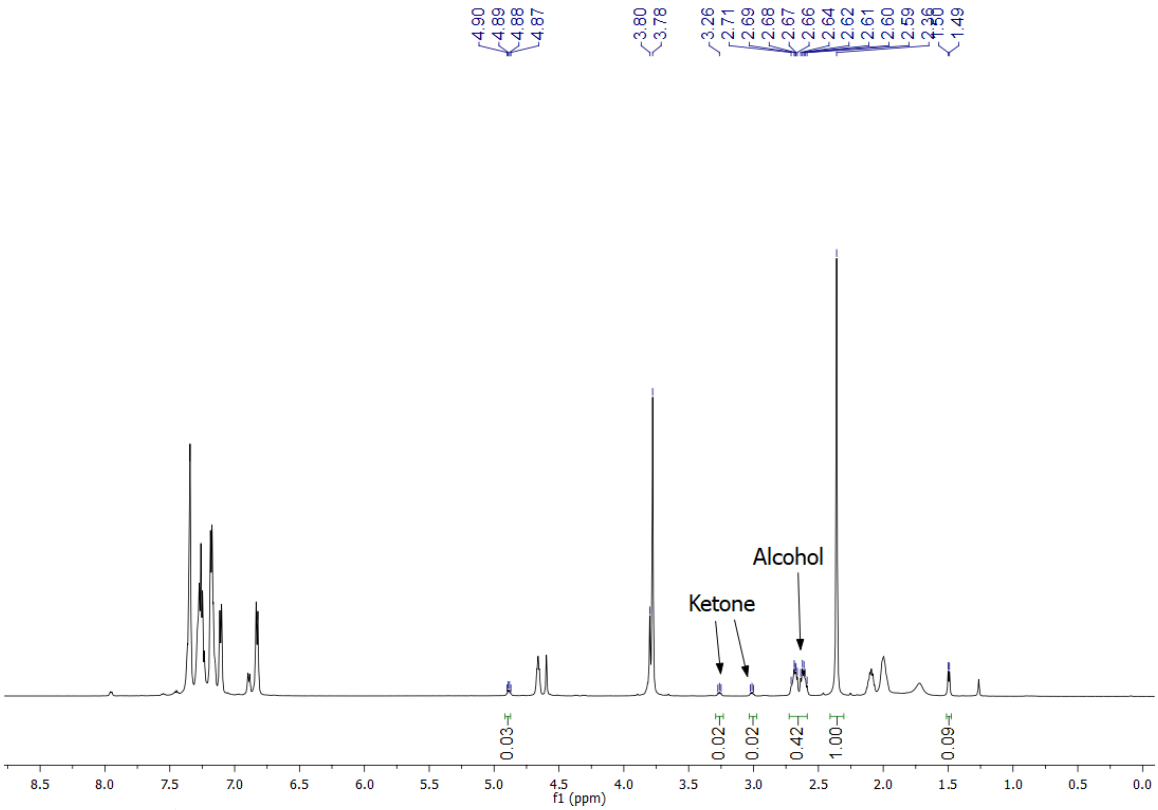


Figure S3: ^{1}H NMR spectra of *β*-alkylation of **1b** with **2b** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 3)[2, 4-5]

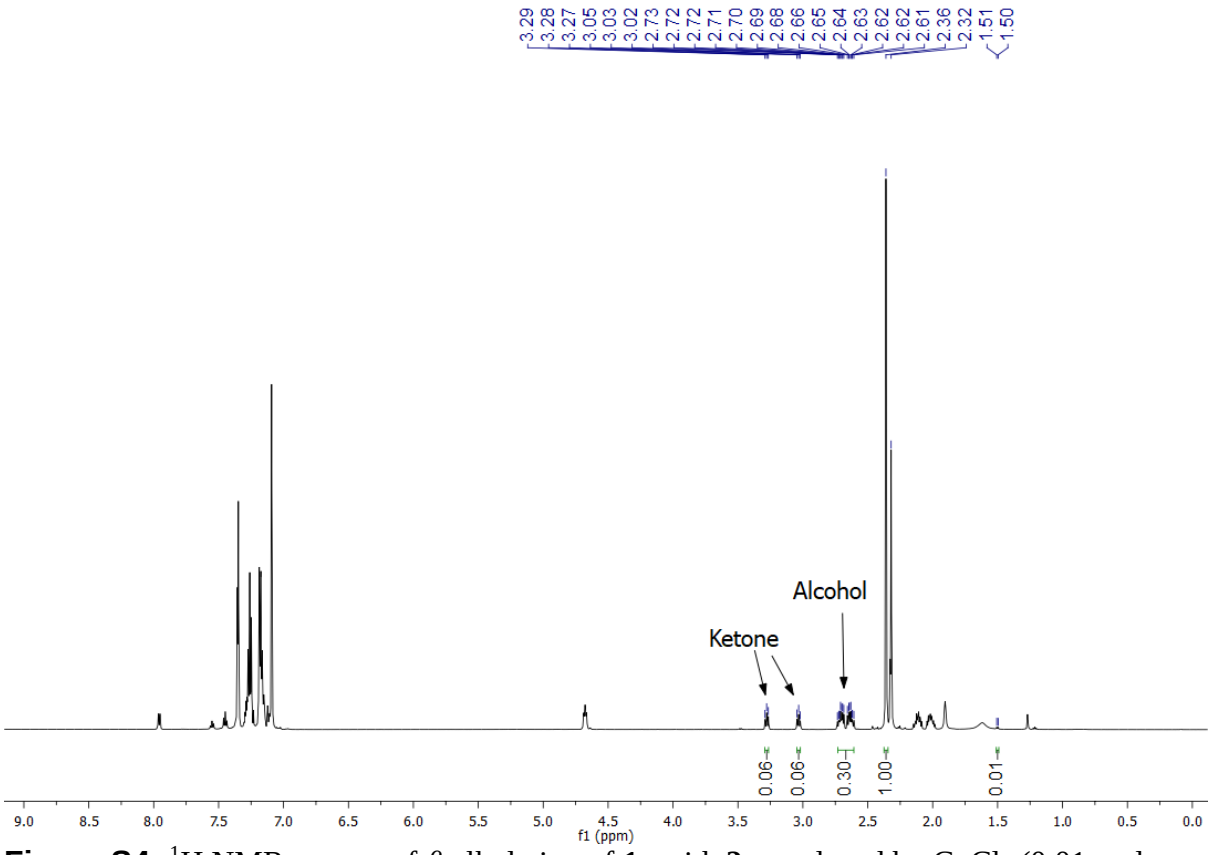


Figure S4: ^{1}H NMR spectra of *β*-alkylation of **1c** with **2c** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 4)[2-4]

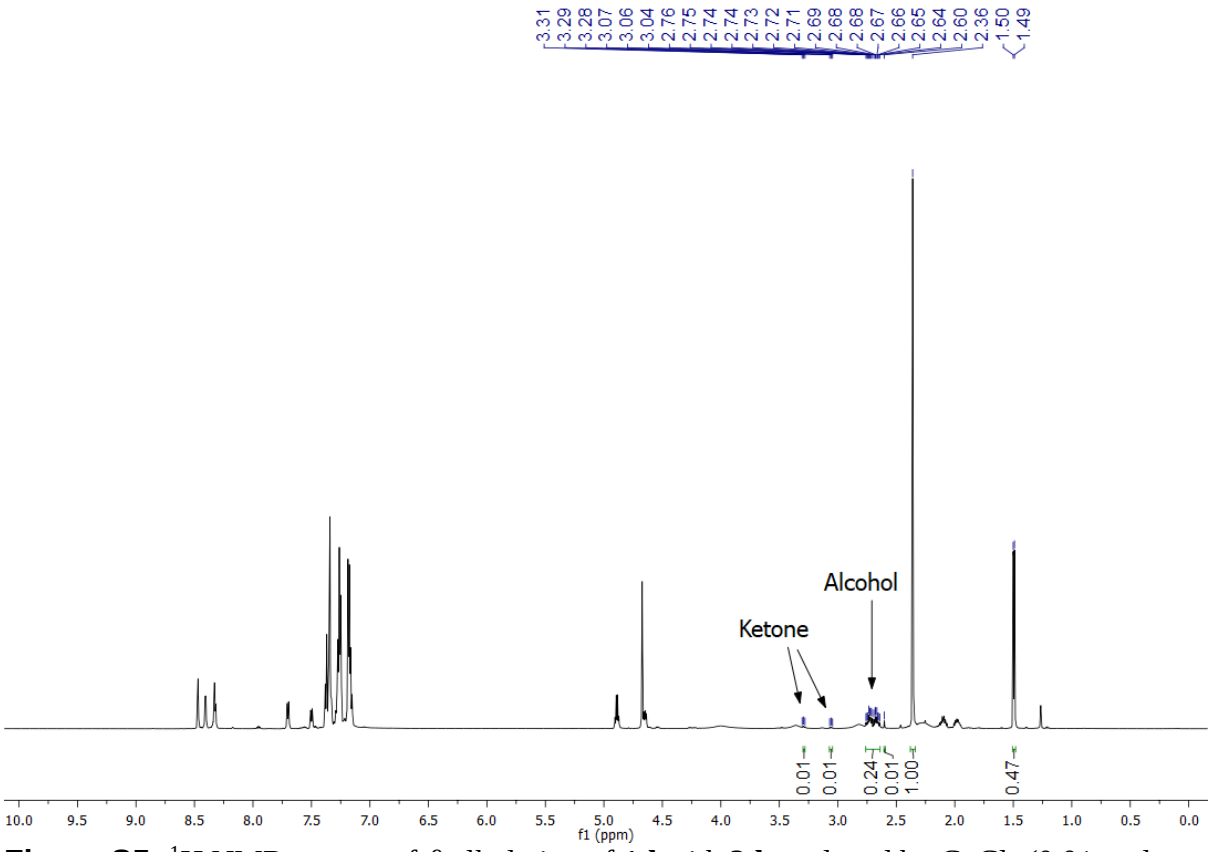


Figure S5: ^{1}H NMR spectra of *β*-alkylation of **1d** with **2d** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 5)[13]

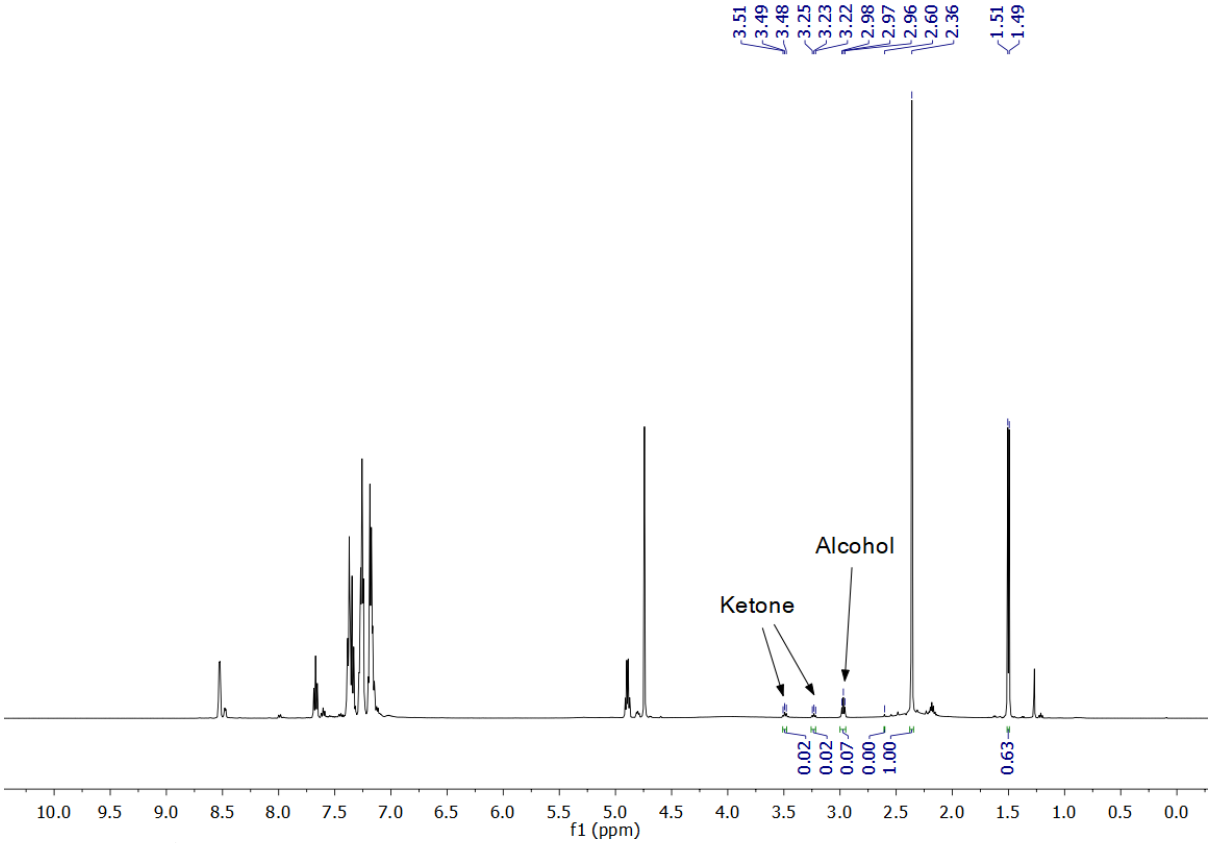


Figure S6: ^{1}H NMR spectra of *β*-alkylation of **1e** with **2e** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 6)[6]

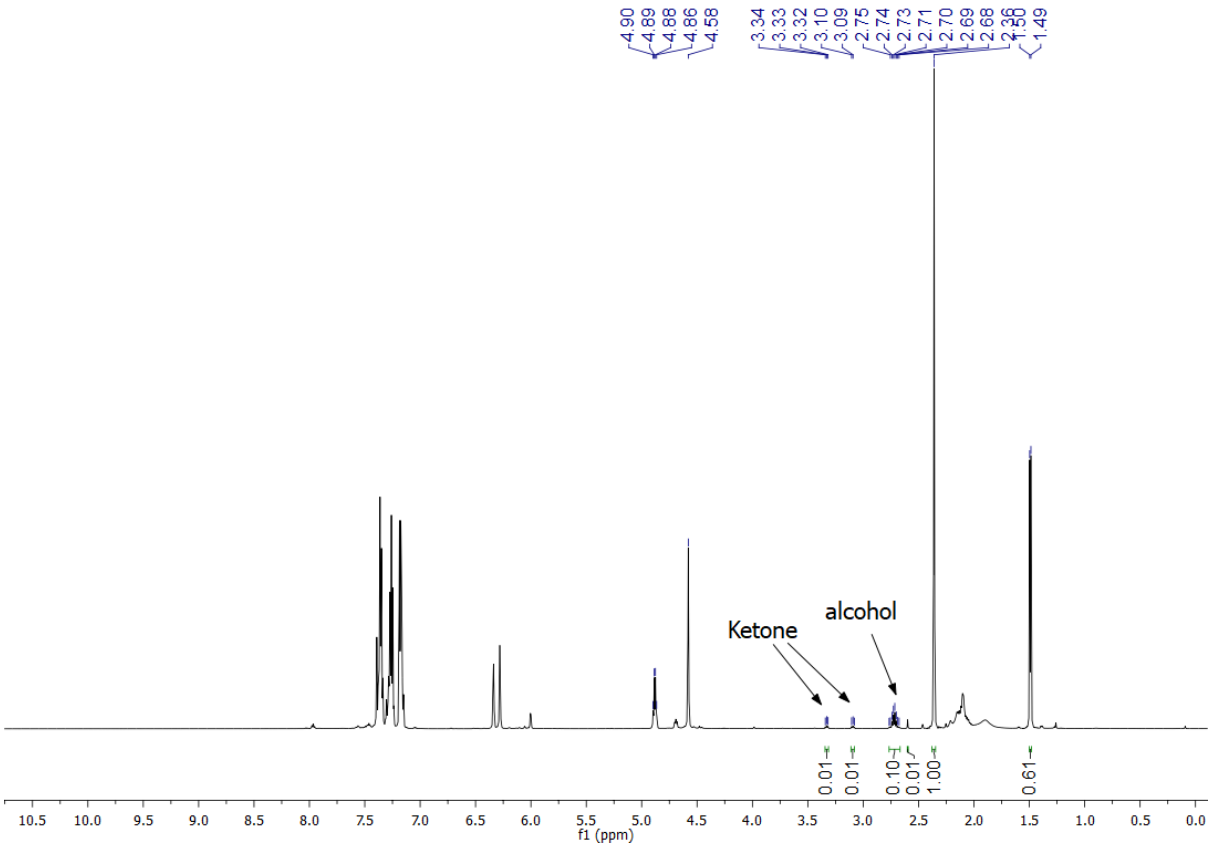


Figure S7: ^{1}H NMR spectra of *β*-alkylation of **1f** with **2f** catalyzed by $CoCl_2$ (0.1 mol %) at 140 °C (Table S2, entry 7)[2, 7, 8]

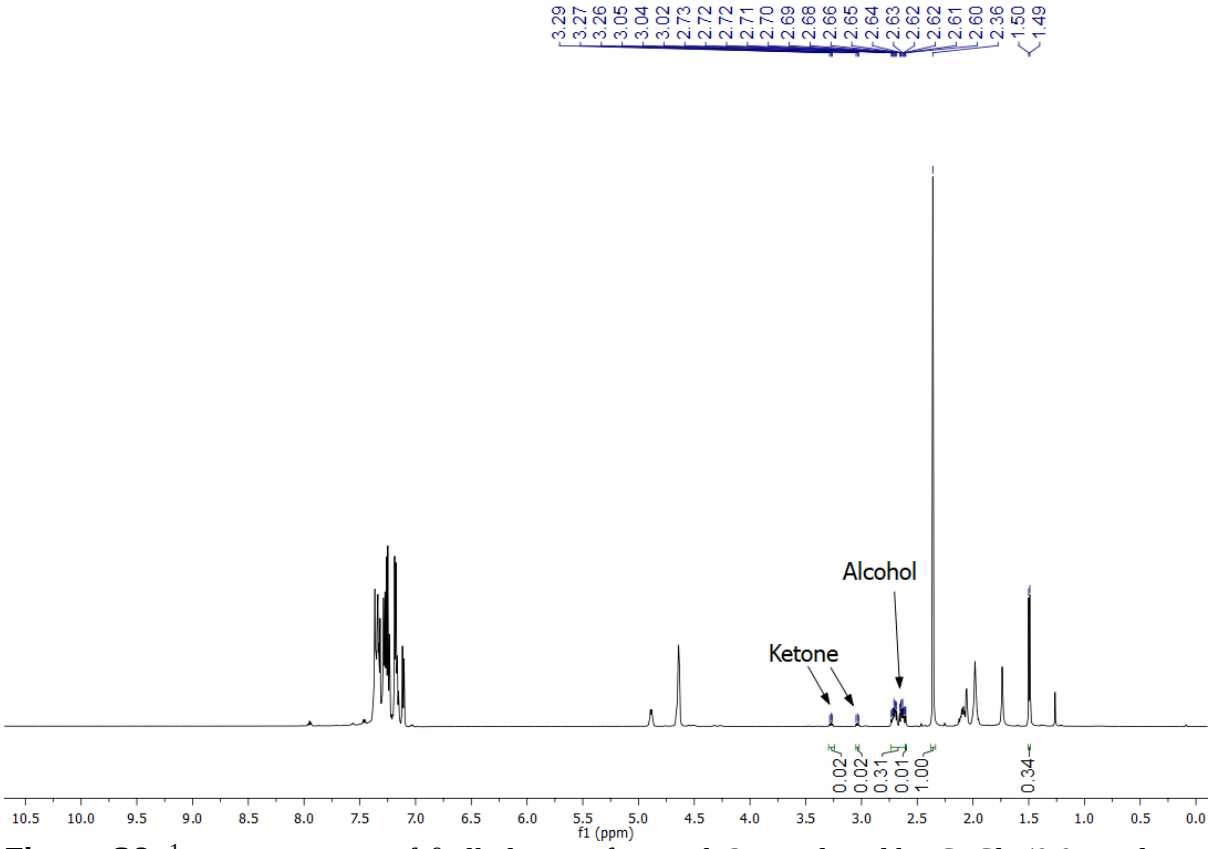


Figure S8: ^{1}H NMR spectra of *β*-alkylation of **1g** with **2g** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 8)[2, 4, 5]

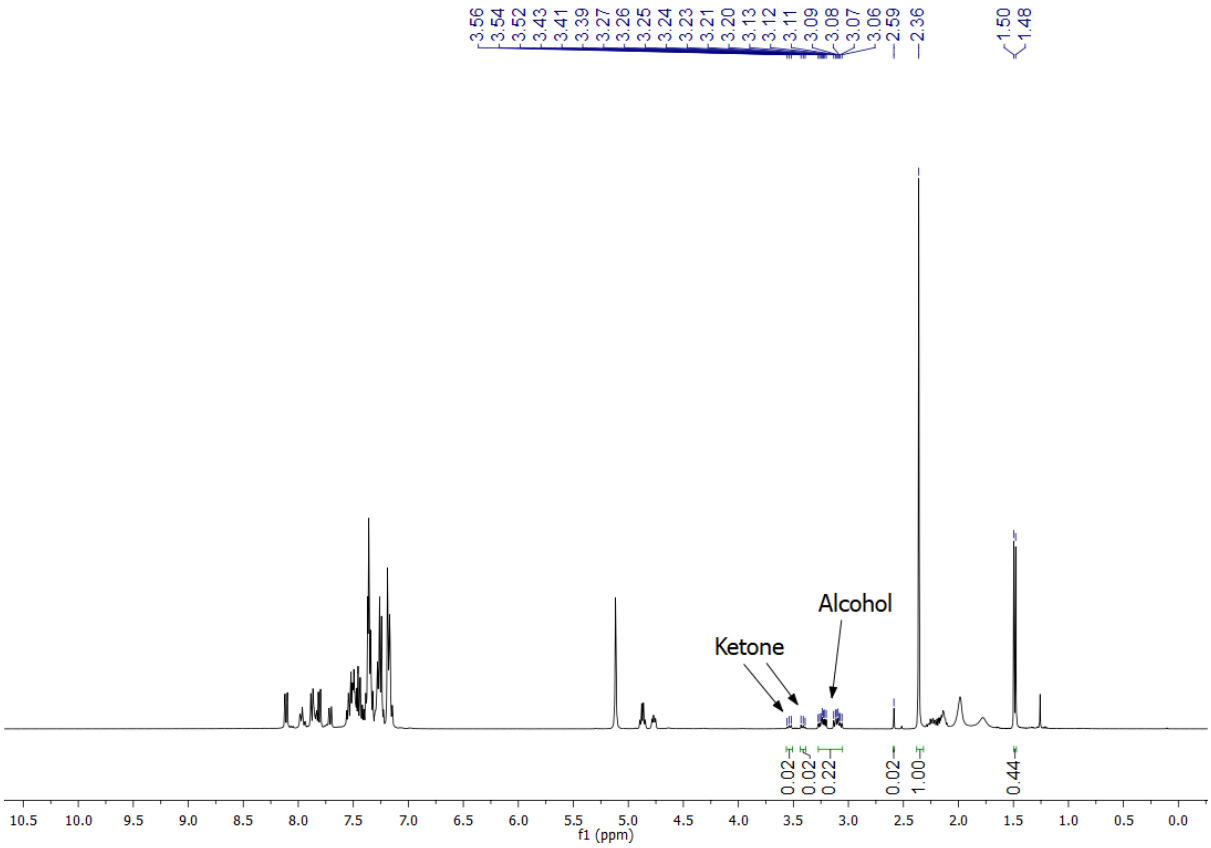


Figure S9: ^{1}H NMR spectra of *β*-alkylation of **1h** with **2h** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 9)[4, 6]

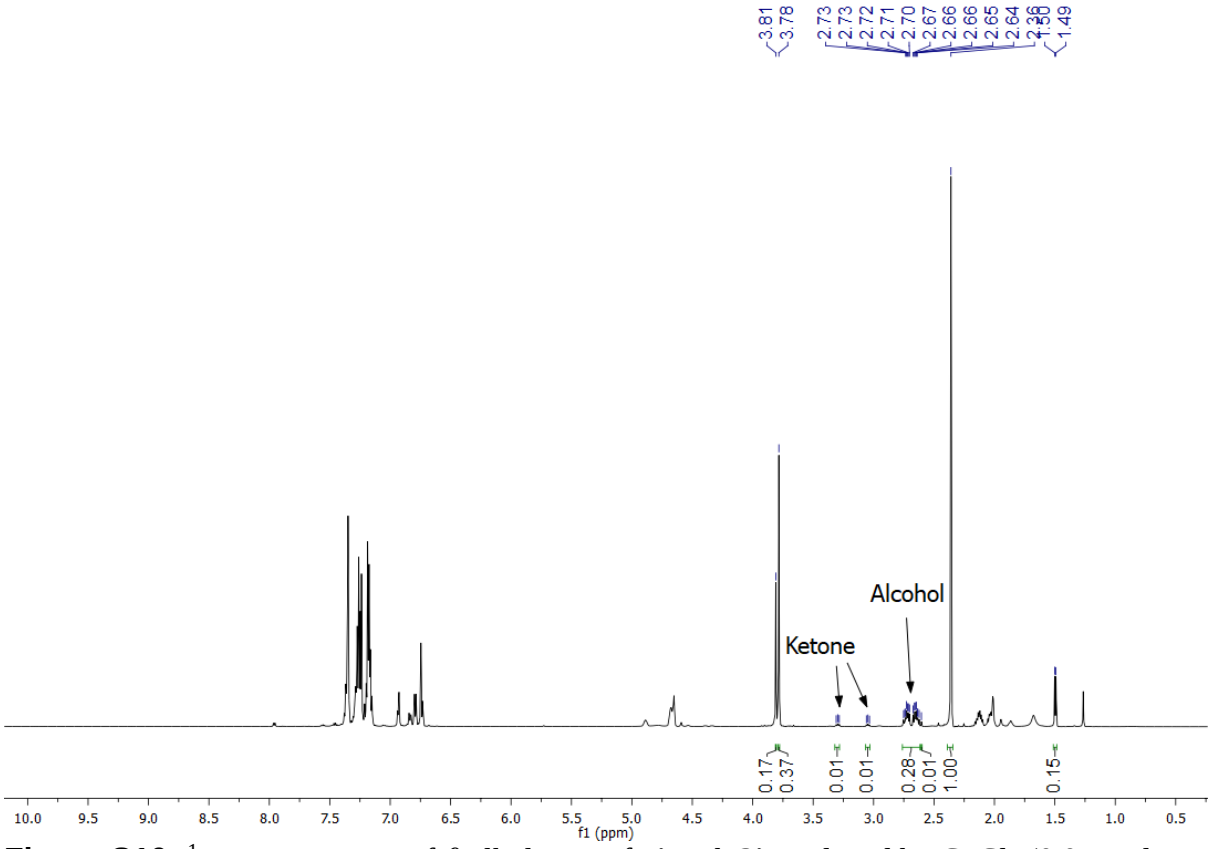


Figure S10: ^{1}H NMR spectra of *β*-alkylation of **1i** with **2i** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 10)[6]

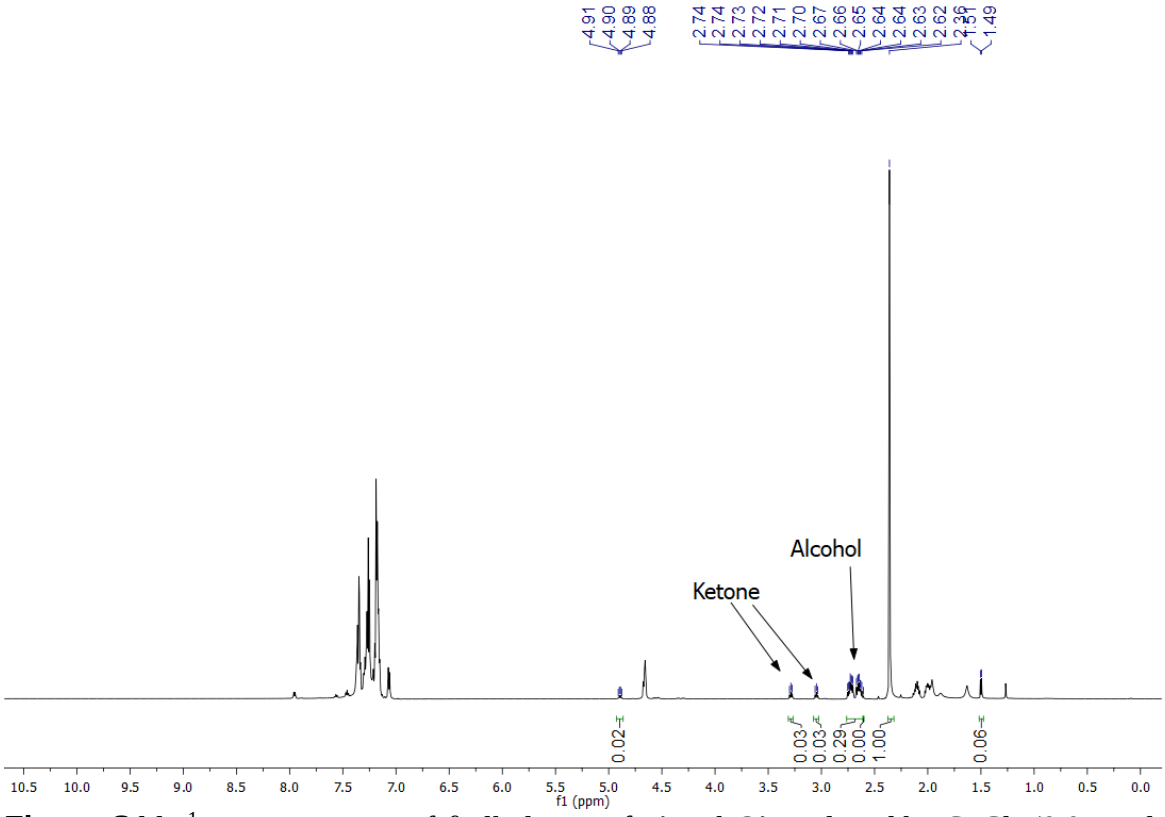


Figure S11: ^{1}H NMR spectra of *β*-alkylation of **1j** with **2j** catalyzed by $CoCl_2$ (0.01 mol %) at 140 ^{o}C (Table S2, entry 11)[4, 6]

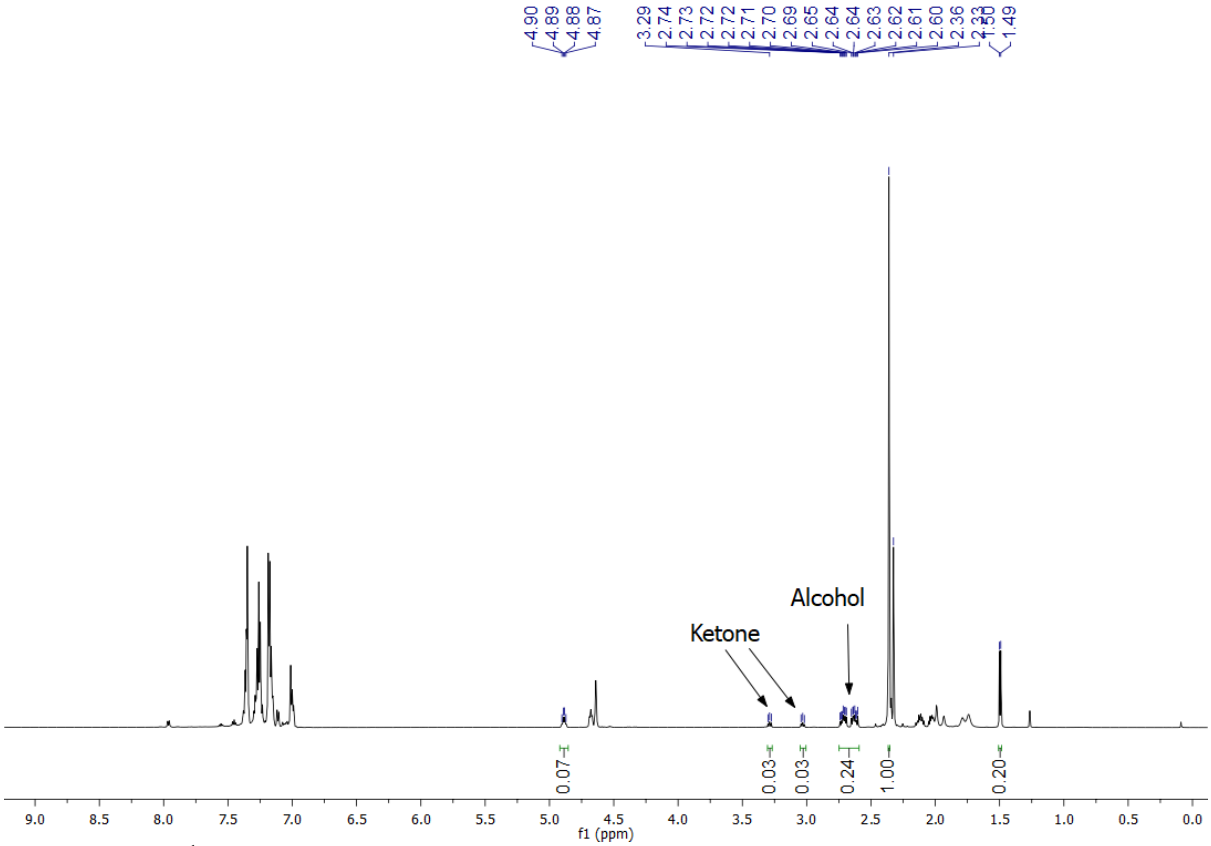


Figure S12: ^{1}H NMR spectra of *β*-alkylation of **1k** with **2k** catalyzed by $CoCl_2$ (0.01 mol %) at 140 ^{o}C (Table S2, entry 12)[6]

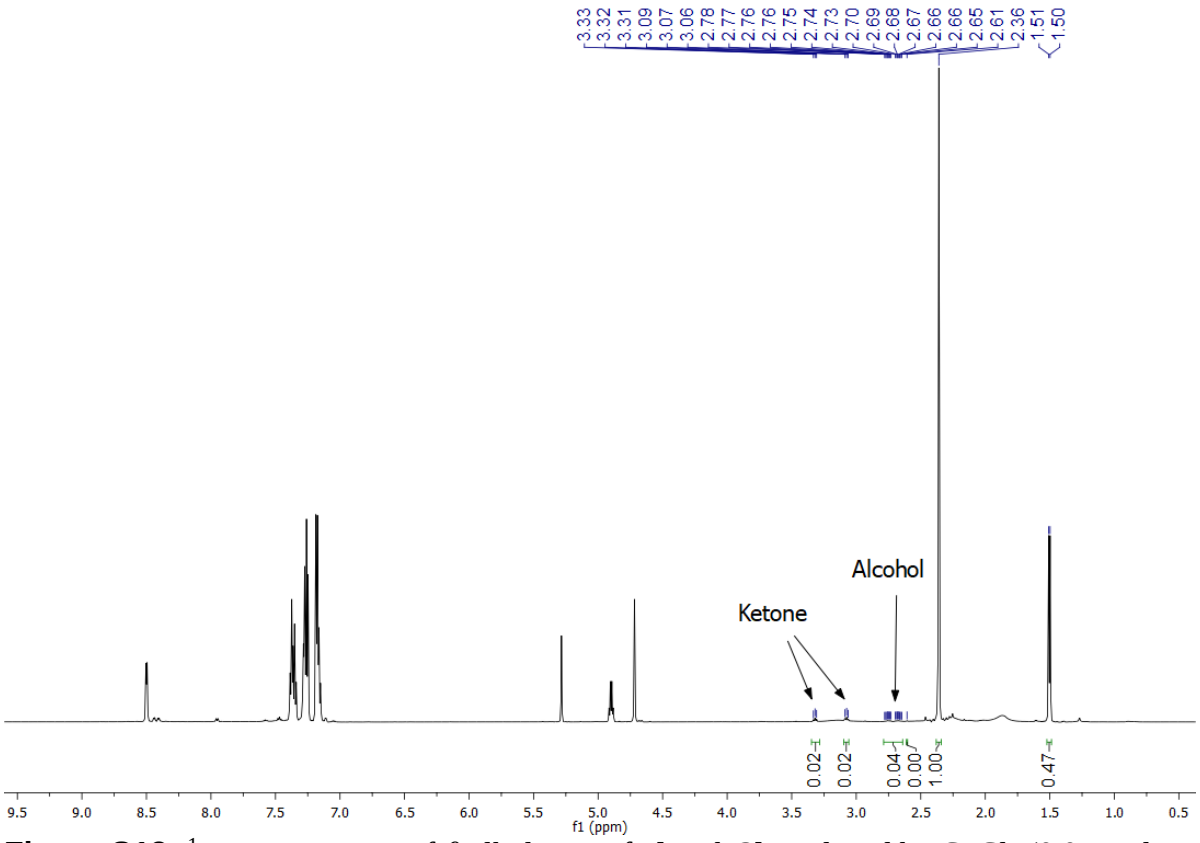


Figure S13: ^{1}H NMR spectra of *β*-alkylation of **1l** with **2l** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 13)[6]

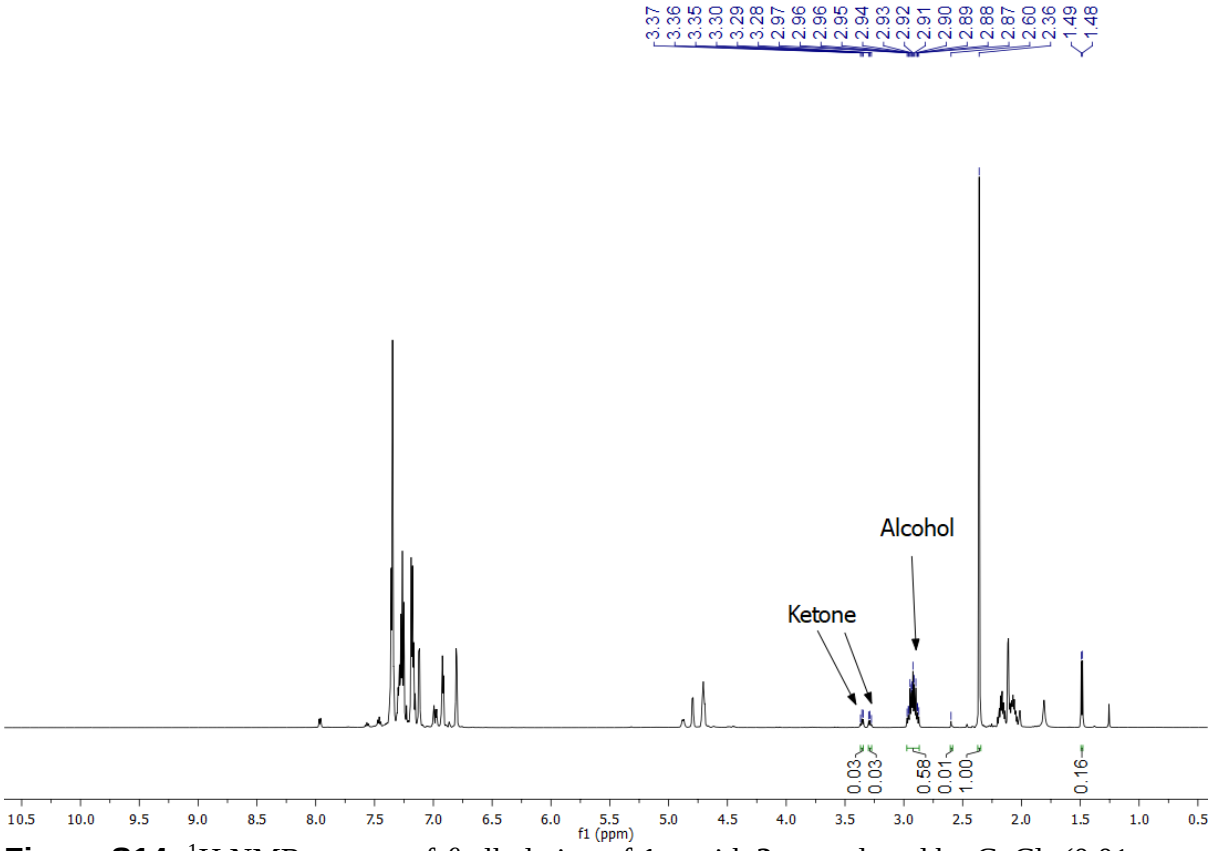


Figure S14: ^{1}H NMR spectra of *β*-alkylation of **1m** with **2m** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 14)[4, 7]

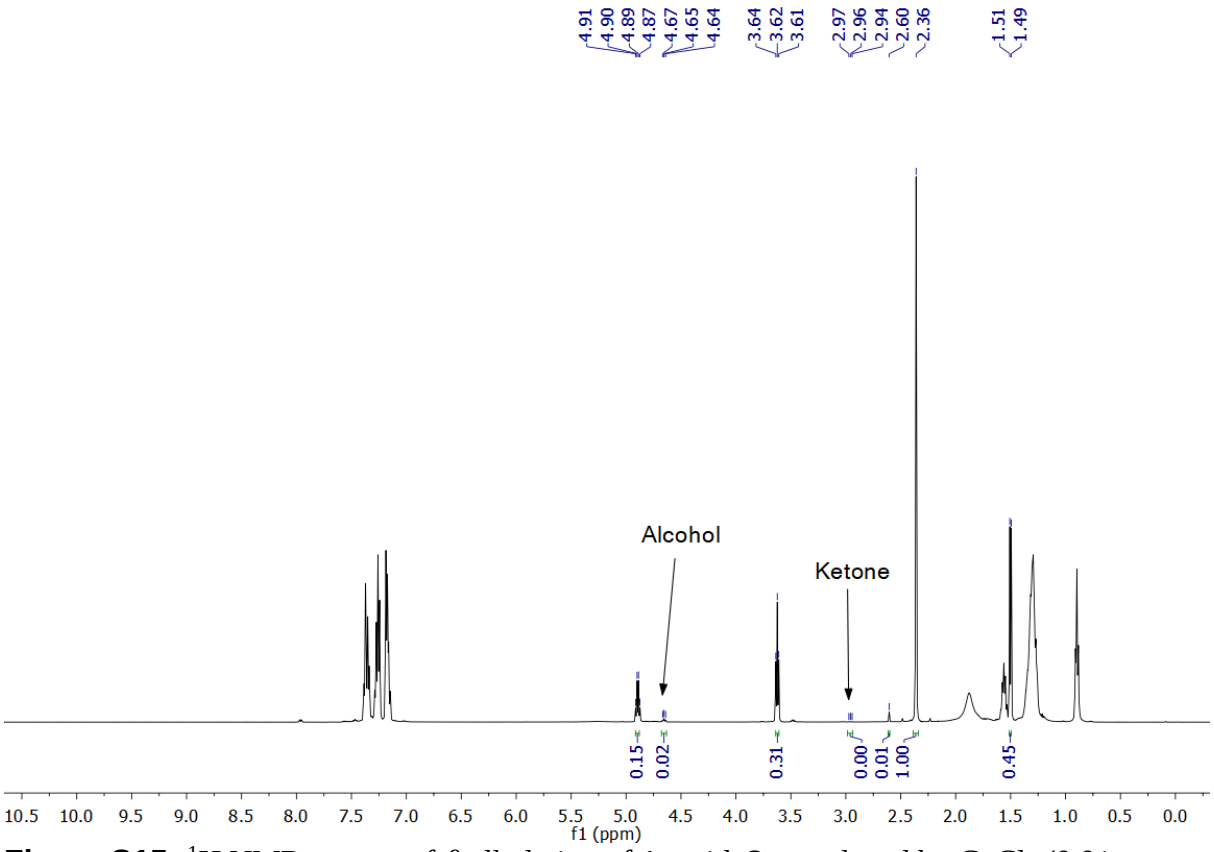


Figure S15: ^{1}H NMR spectra of *β*-alkylation of **1n** with **2n** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 15)[3, 4]

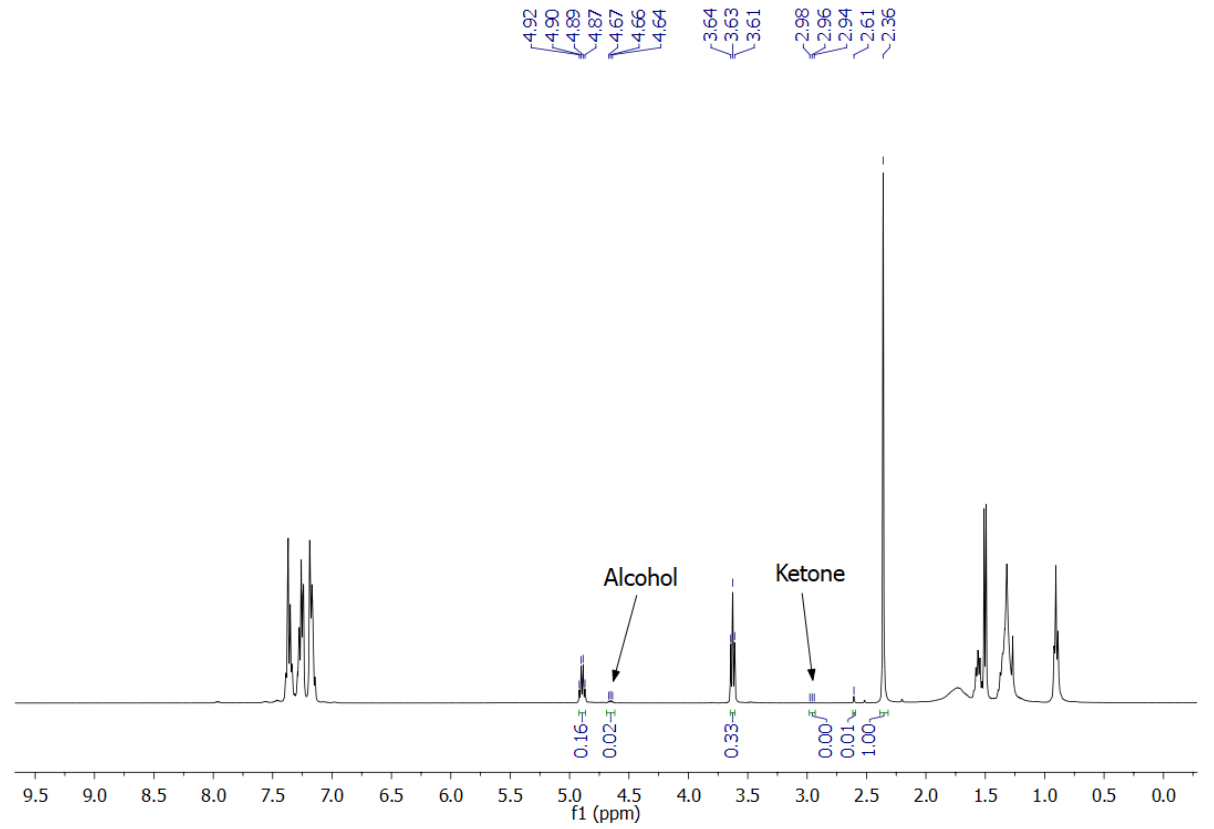


Figure S16: ^{1}H NMR spectra of *β*-alkylation of **1o** with **2o** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 16)[4, 5]

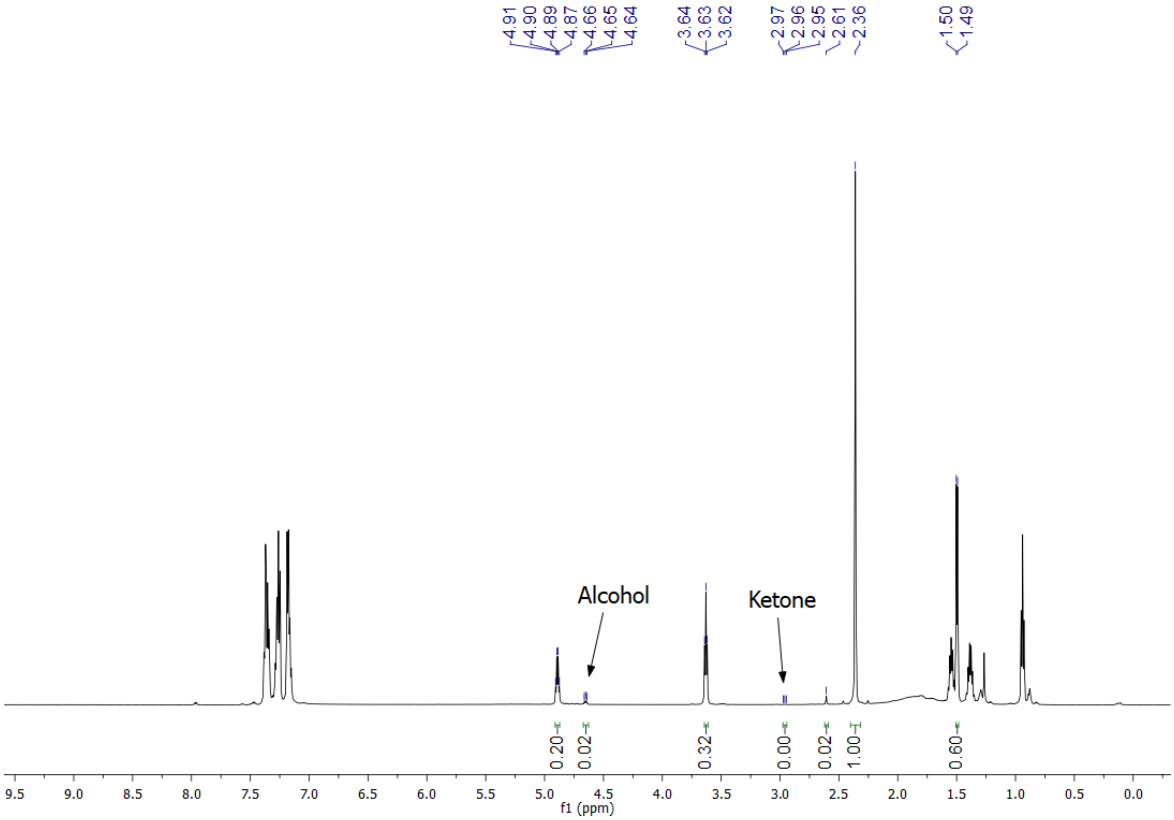


Figure S17: ^{1}H NMR spectra of *β*-alkylation of **1p** with **2p** catalyzed by $CoCl_2$ (0.01 mol %) at 140 ^{o}C (Table S2, entry 17)[4]

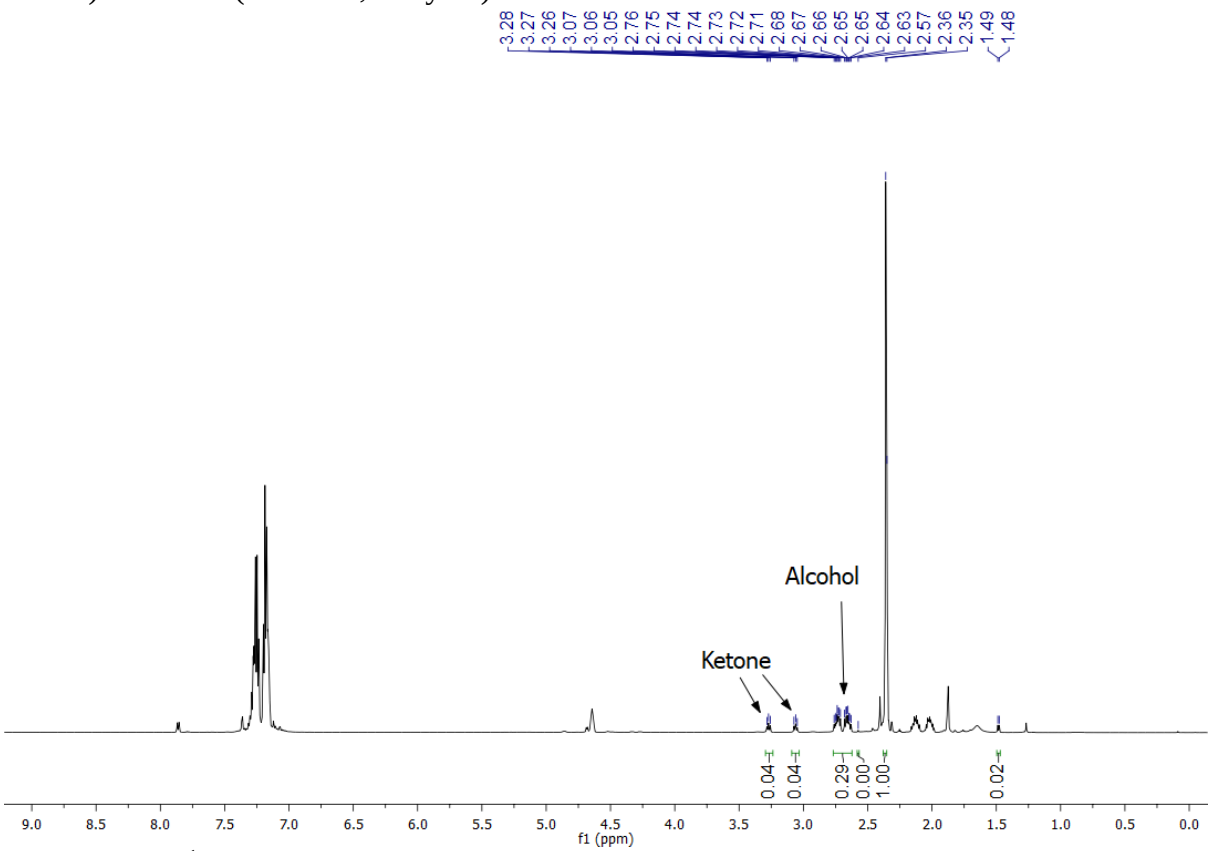


Figure S18: ^{1}H NMR spectra of *β*-alkylation of **1q** with **2q** catalyzed by $CoCl_2$ (0.01 mol %) at 140 ^{o}C (Table S2, entry 18)[4]

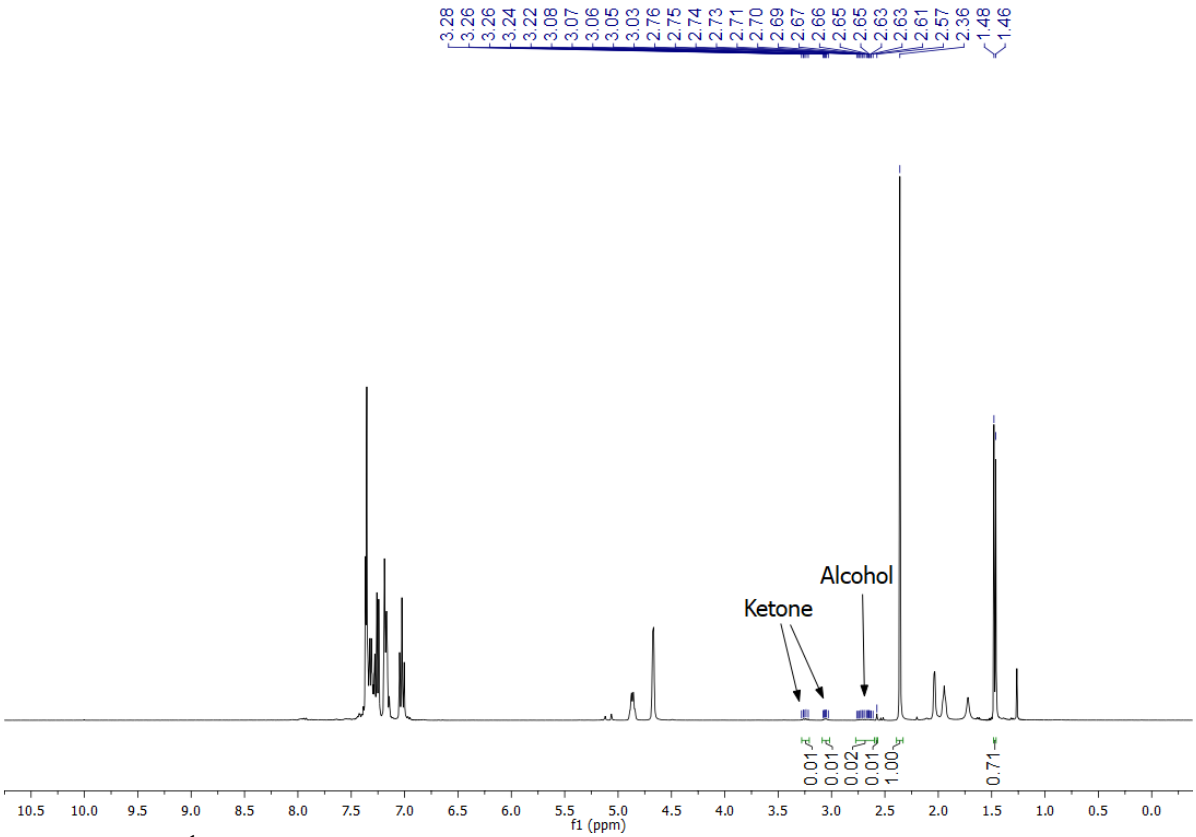


Figure S19: ^{1}H NMR spectra of *β*-alkylation of **1r** with **2r** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 19)[3, 4]

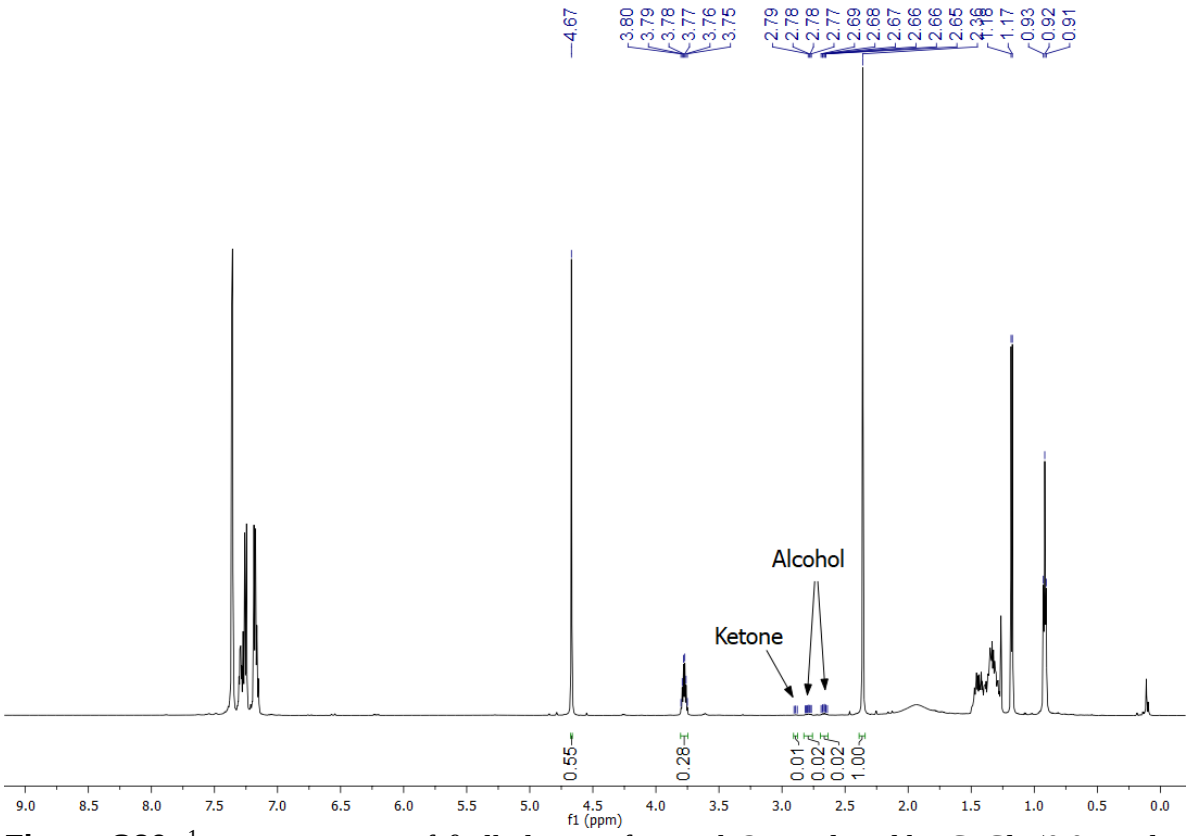


Figure S20: ^{1}H NMR spectra of *β*-alkylation of **1s** with **2s** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 20)[2]

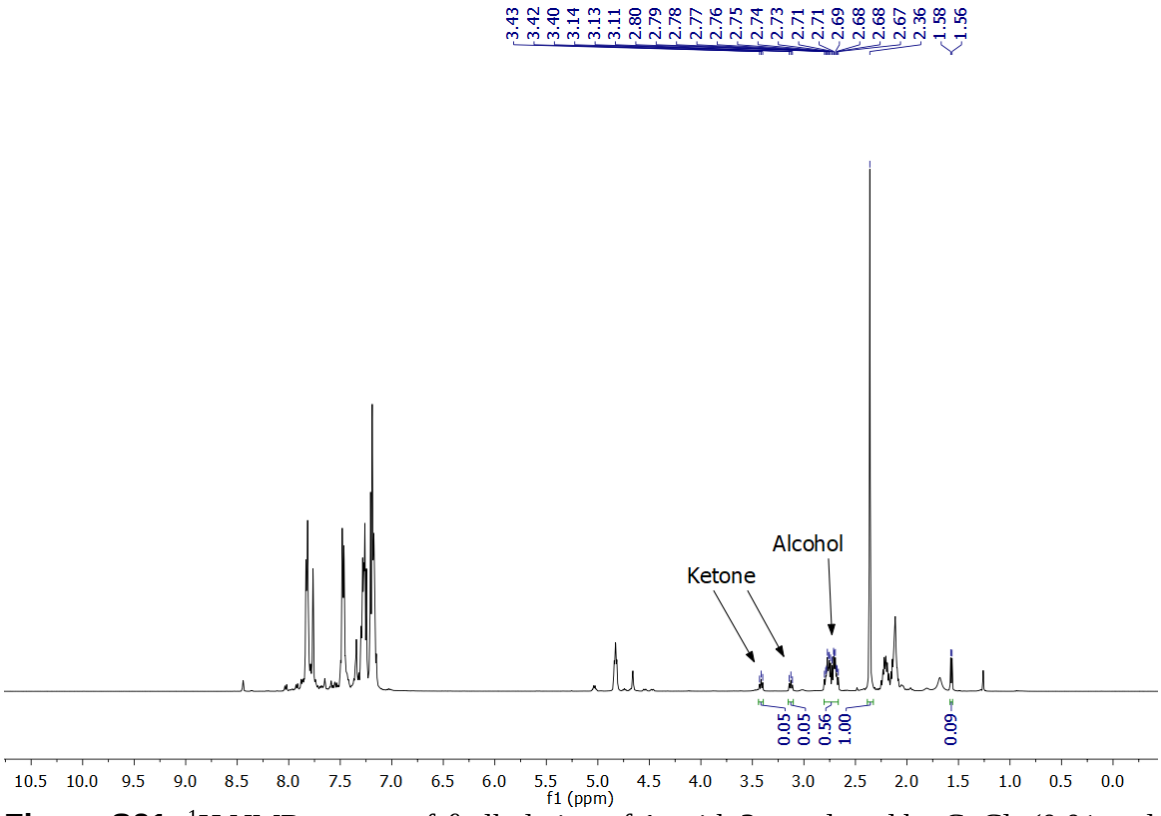


Figure S21: ^{1}H NMR spectra of *β*-alkylation of **1t** with **2t** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 21)[4]

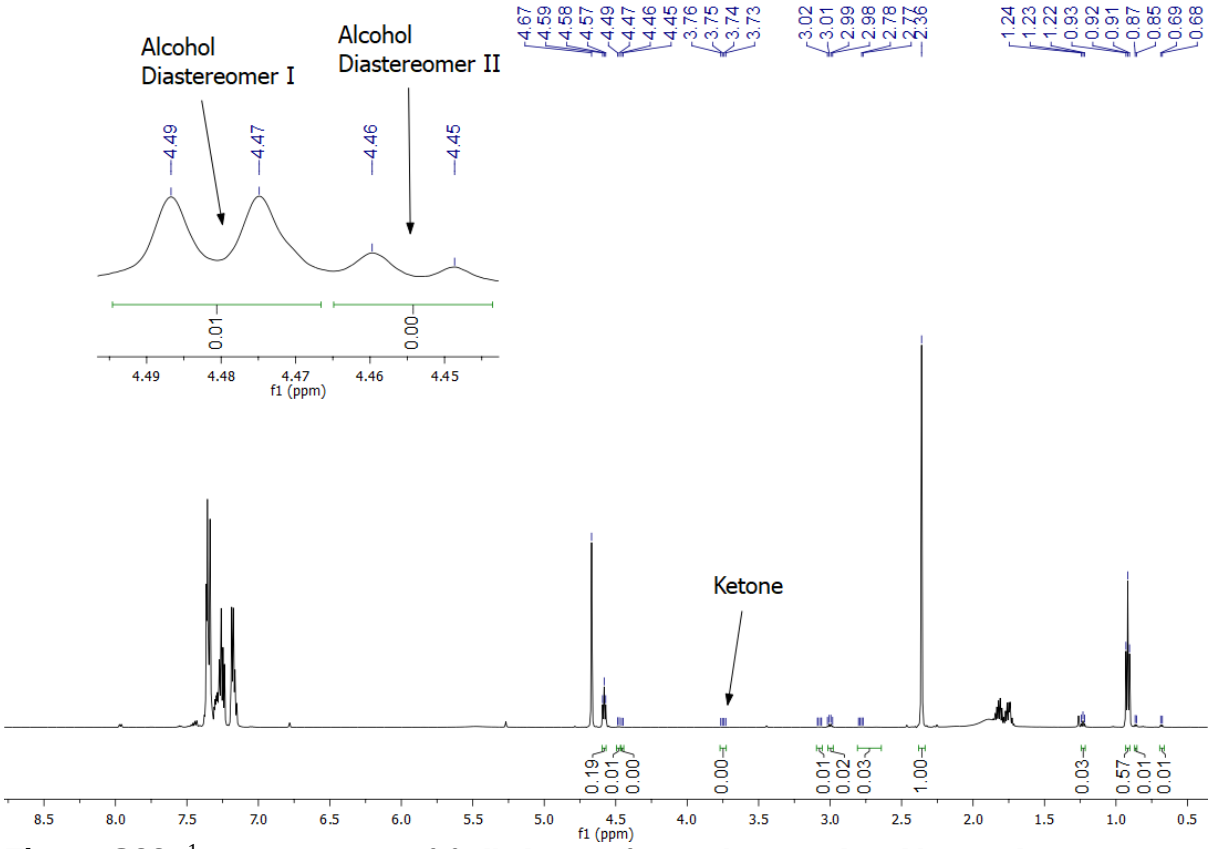


Figure S22: ^{1}H NMR spectra of *β*-alkylation of **1u** with **2u** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 22)[9]

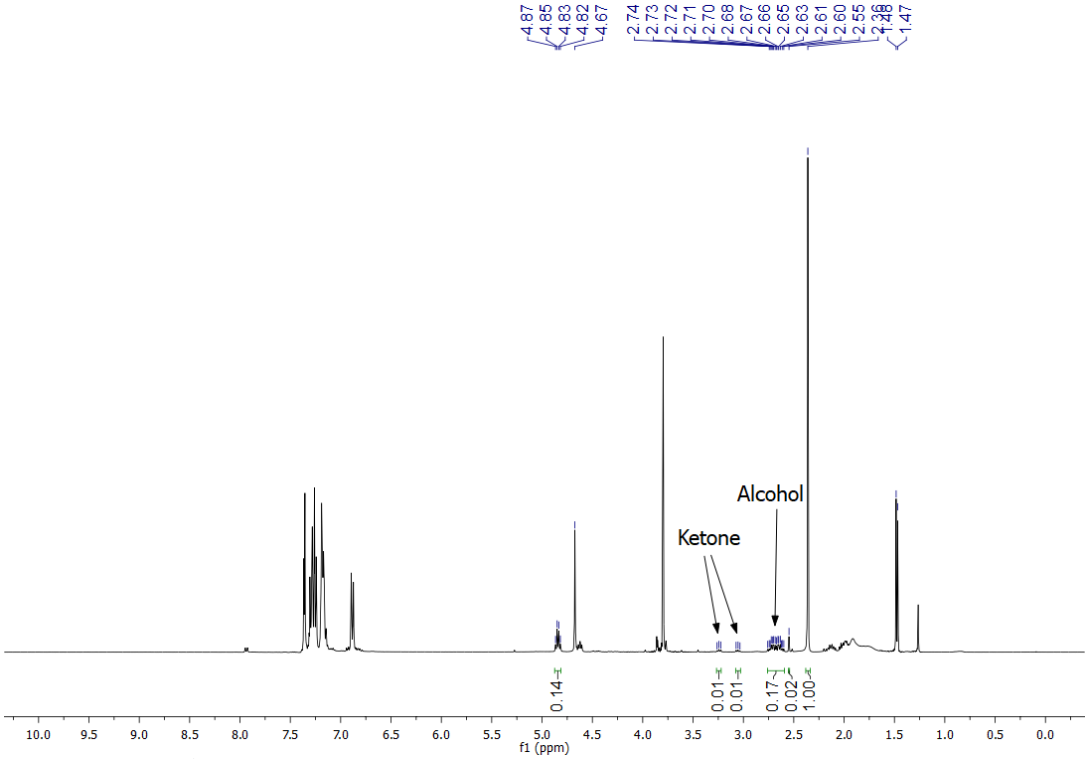


Figure S23: ^{1}H NMR spectra of *β*-alkylation of **1v** with **2v** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 23)[4]

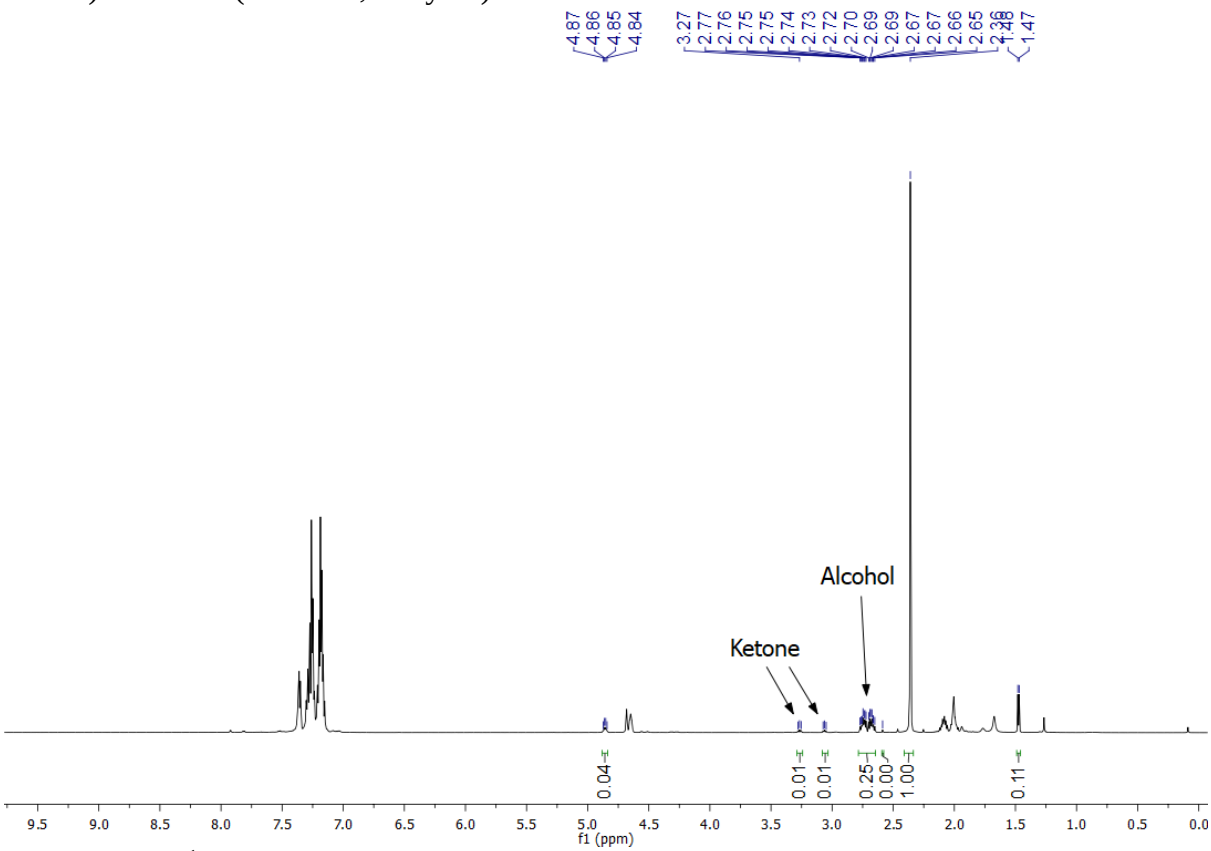


Figure S24: ^{1}H NMR spectra of *β*-alkylation of **1w** with **2w** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 24)[6]

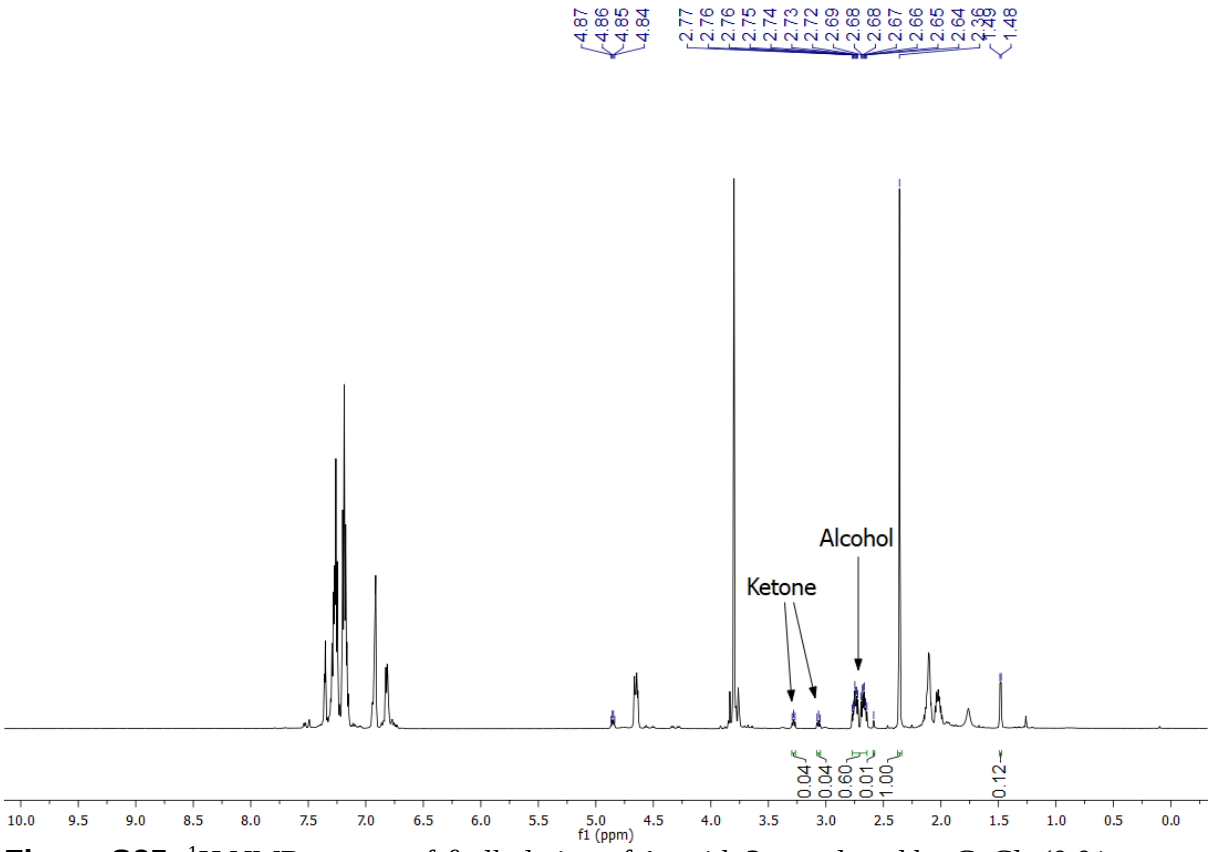


Figure S25: ^{1}H NMR spectra of *β*-alkylation of **1x** with **2x** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 25)[4]

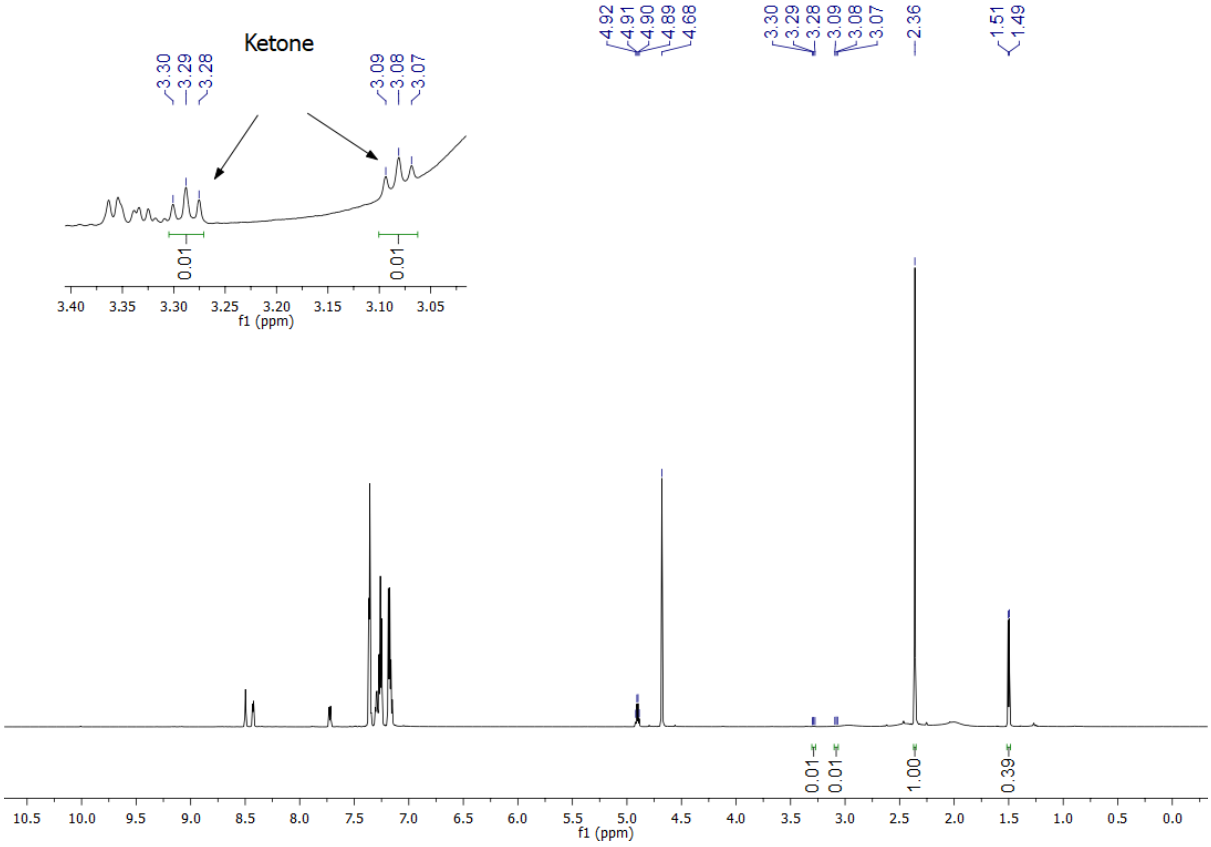


Figure S26: ^{1}H NMR spectra of *β*-alkylation of **1y** with **2y** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 26)[4]

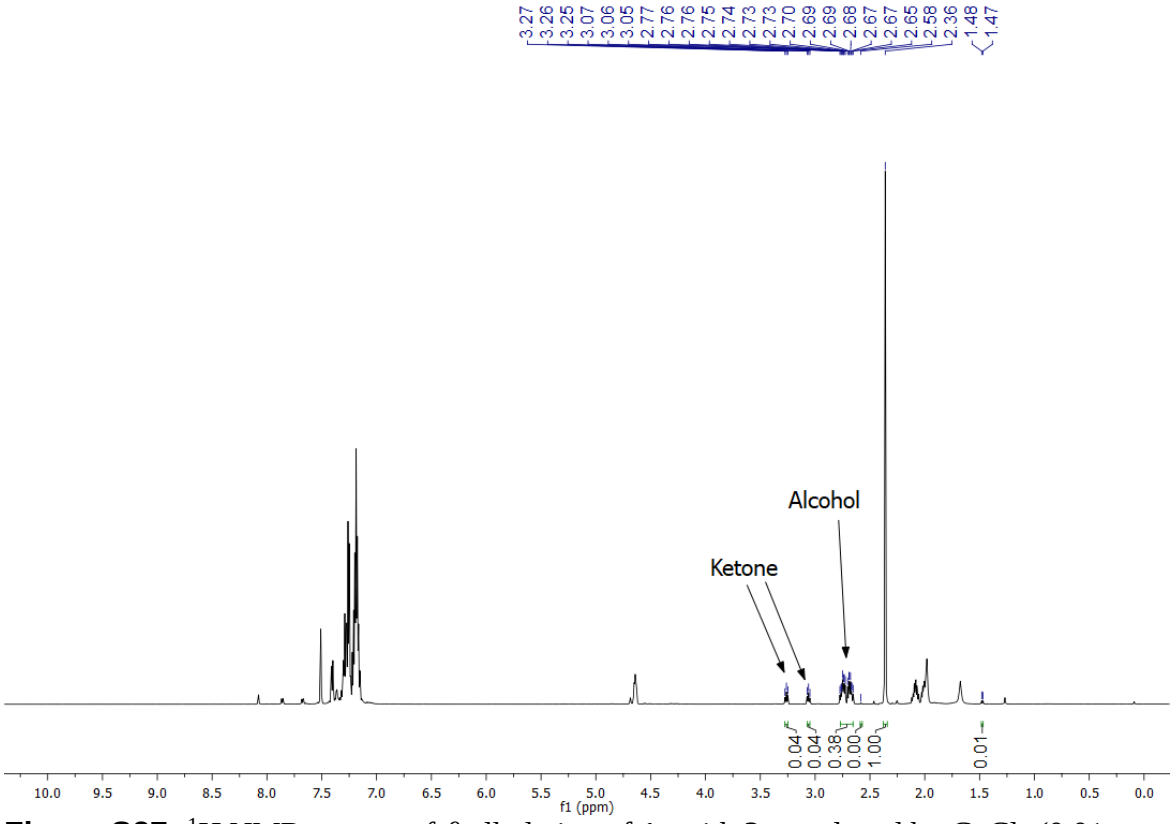


Figure S27: ^{1}H NMR spectra of *β*-alkylation of **1z** with **2z** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 27)[6]

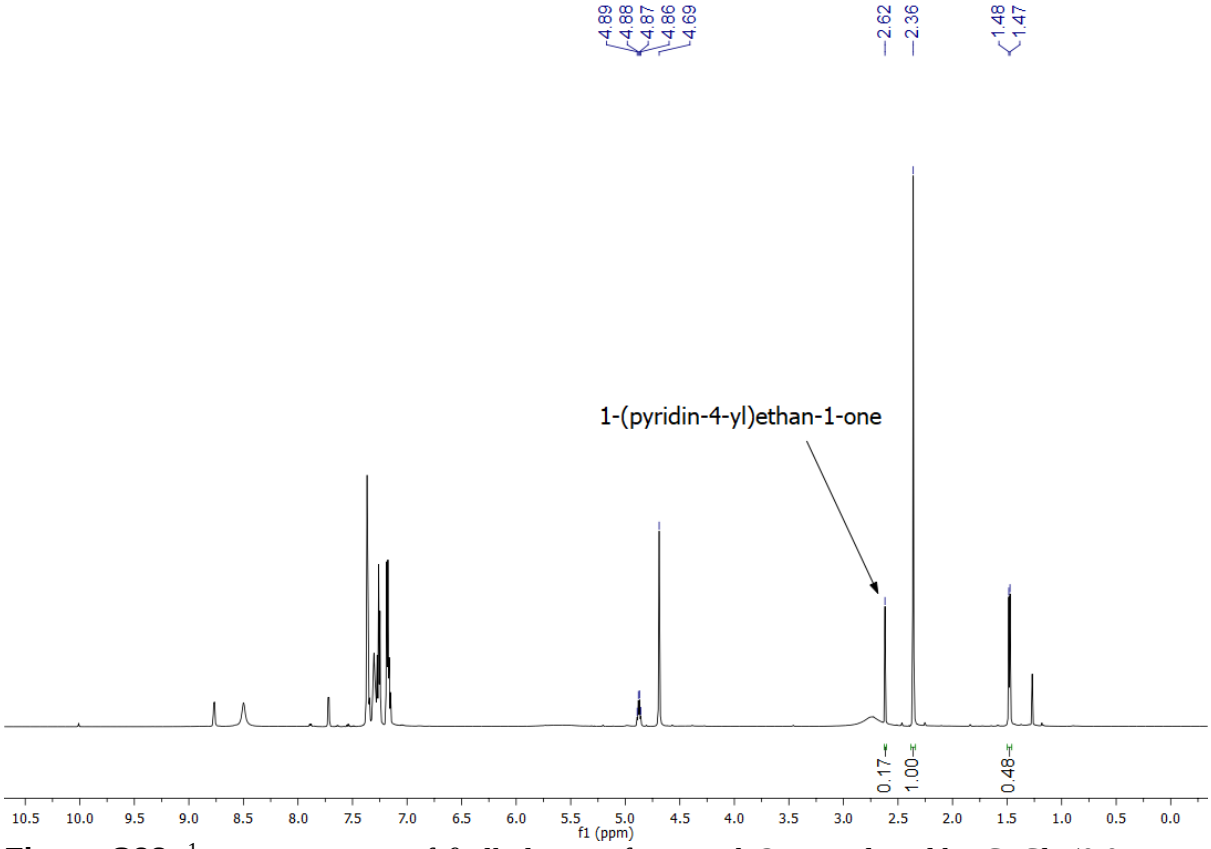


Figure S28: ^{1}H NMR spectra of *β*-alkylation of **1za** with **2za** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 28)[10]

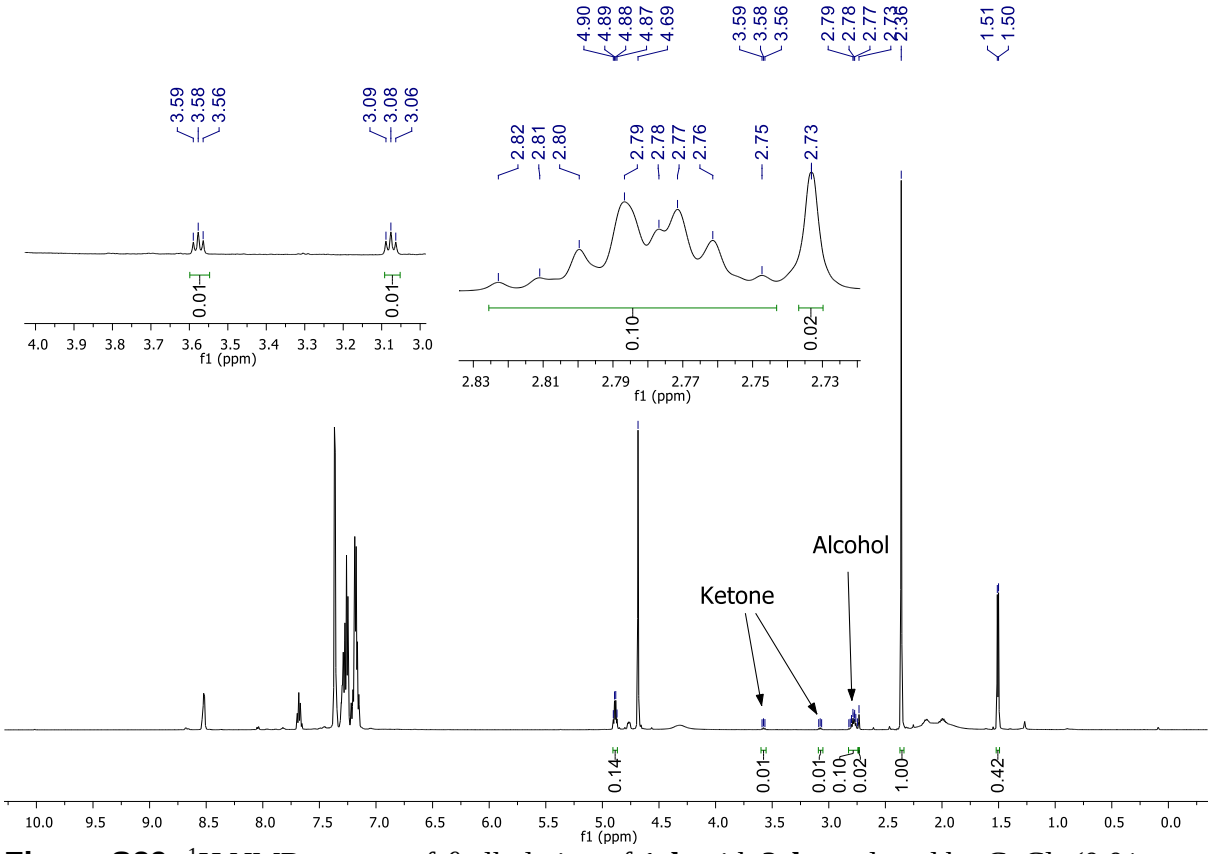


Figure S29: ^{1}H NMR spectra of *β*-alkylation of **1zb** with **2zb** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 29)[2]

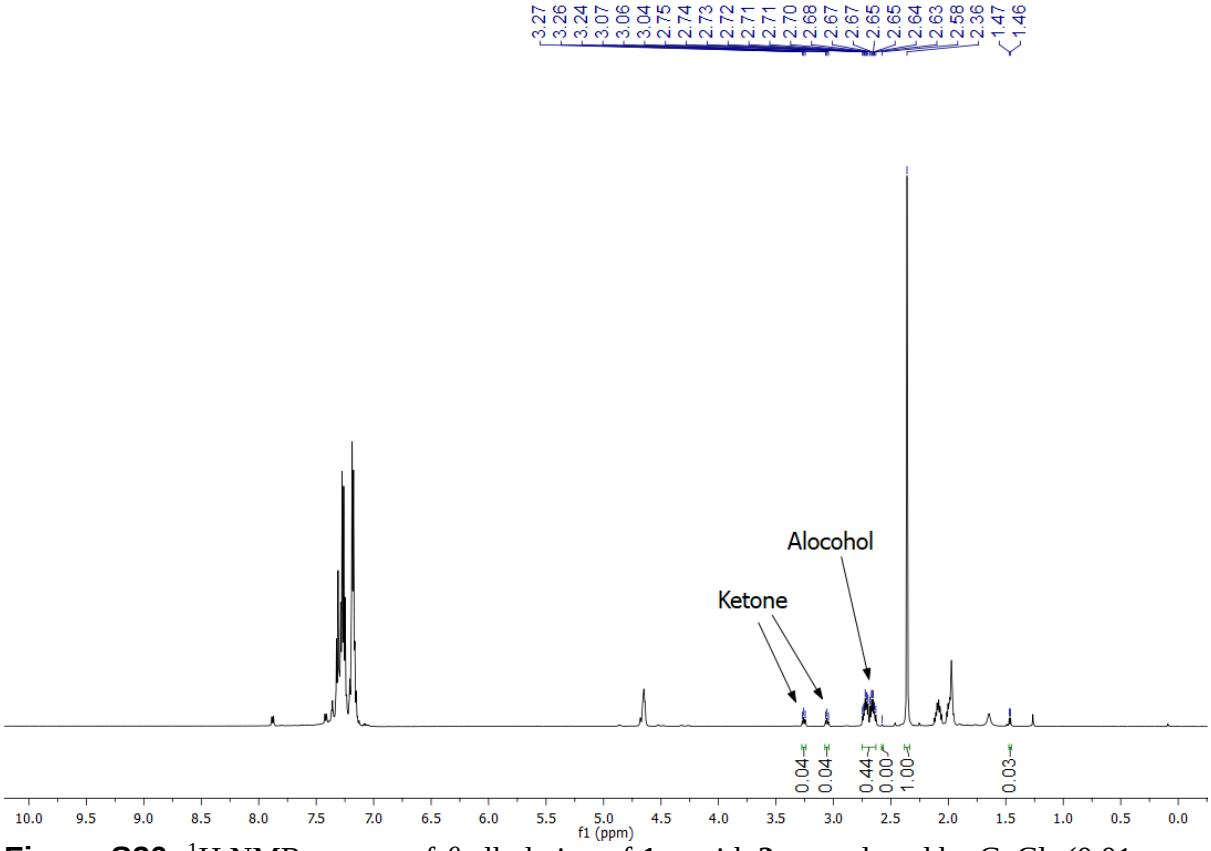


Figure S30: ^{1}H NMR spectra of *β*-alkylation of **1zc** with **2zc** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 30)[4, 6]

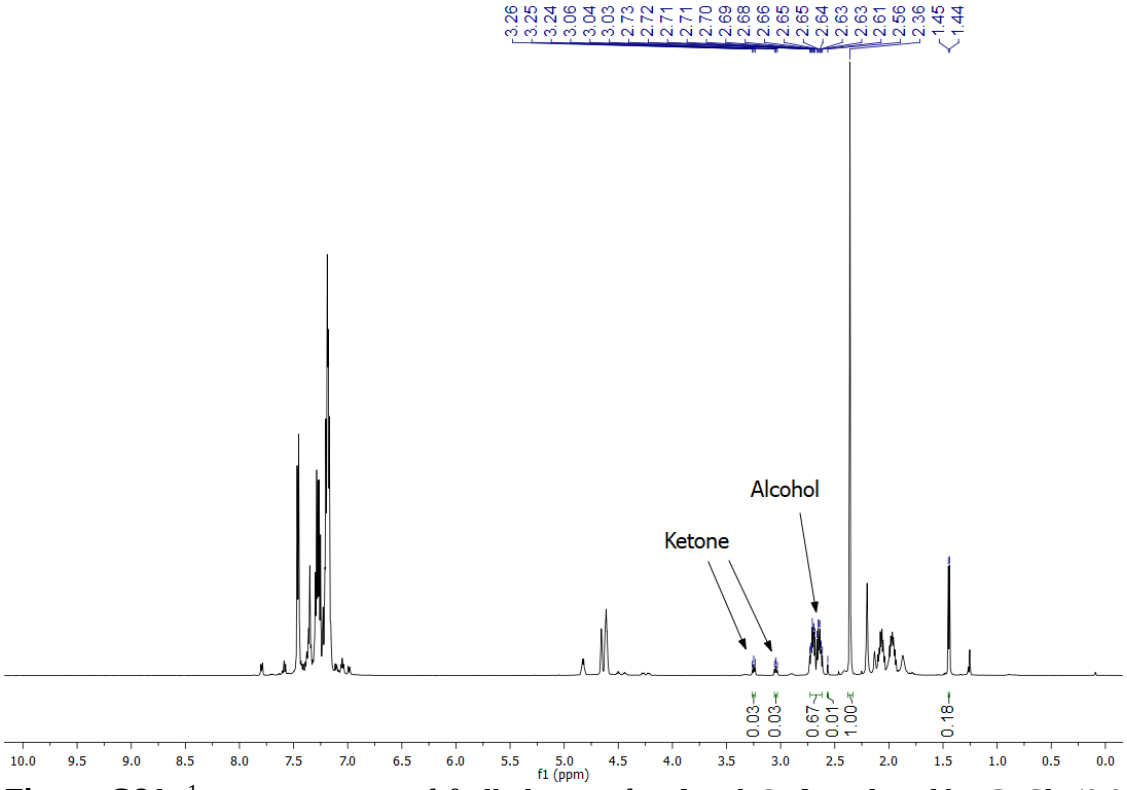


Figure S31: ^{1}H NMR spectra of *β*-alkylation of **1zd** with **2zd** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 31)[6]

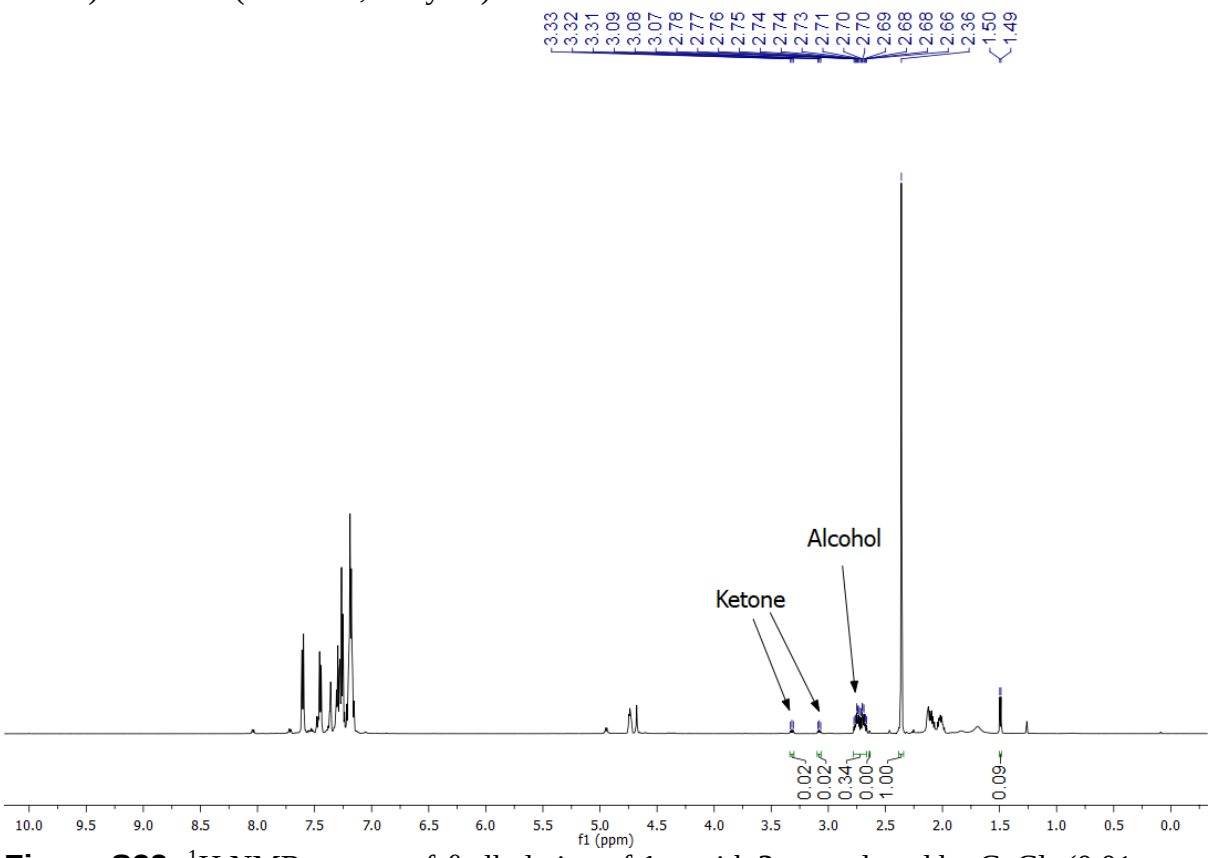


Figure S32: ^{1}H NMR spectra of *β*-alkylation of **1ze** with **2ze** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 32)[2, 6]

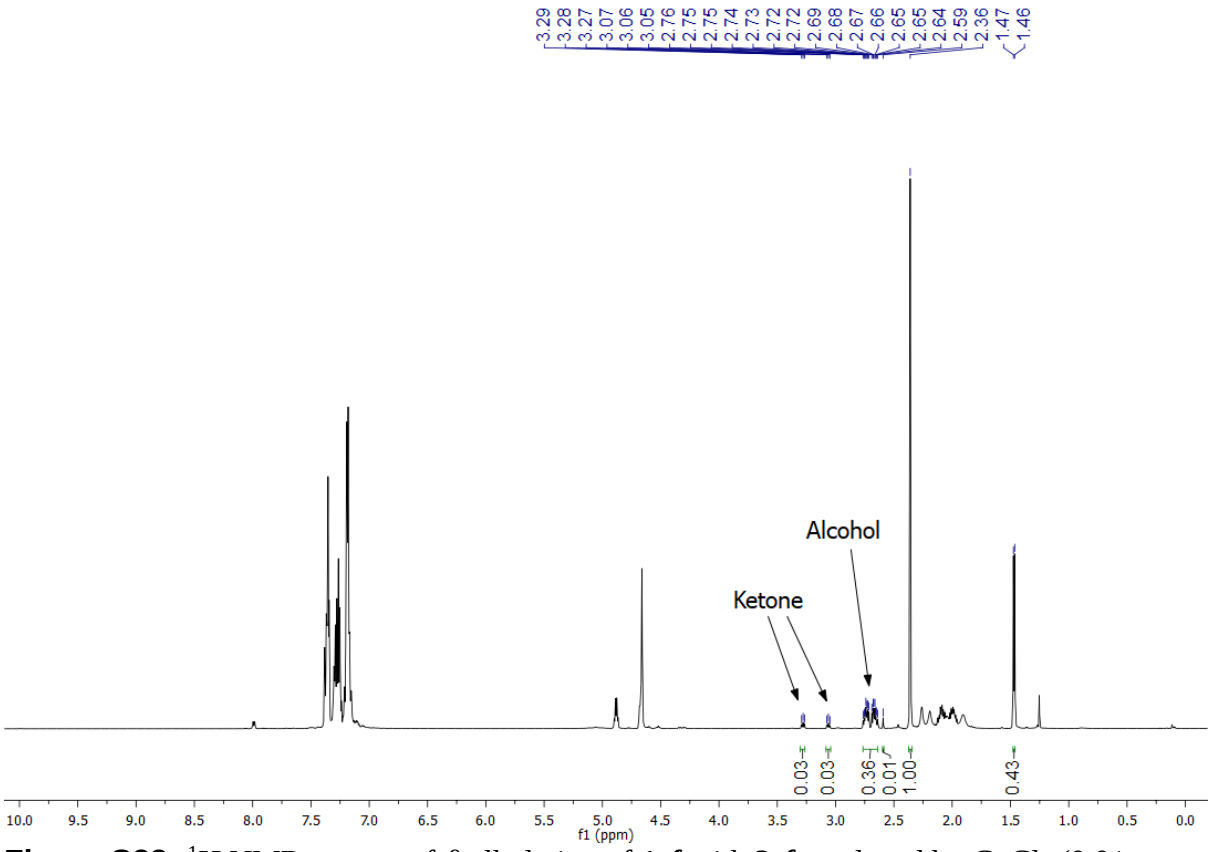


Figure S33: ^{1}H NMR spectra of *β*-alkylation of **1zf** with **2zf** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 33)[13]

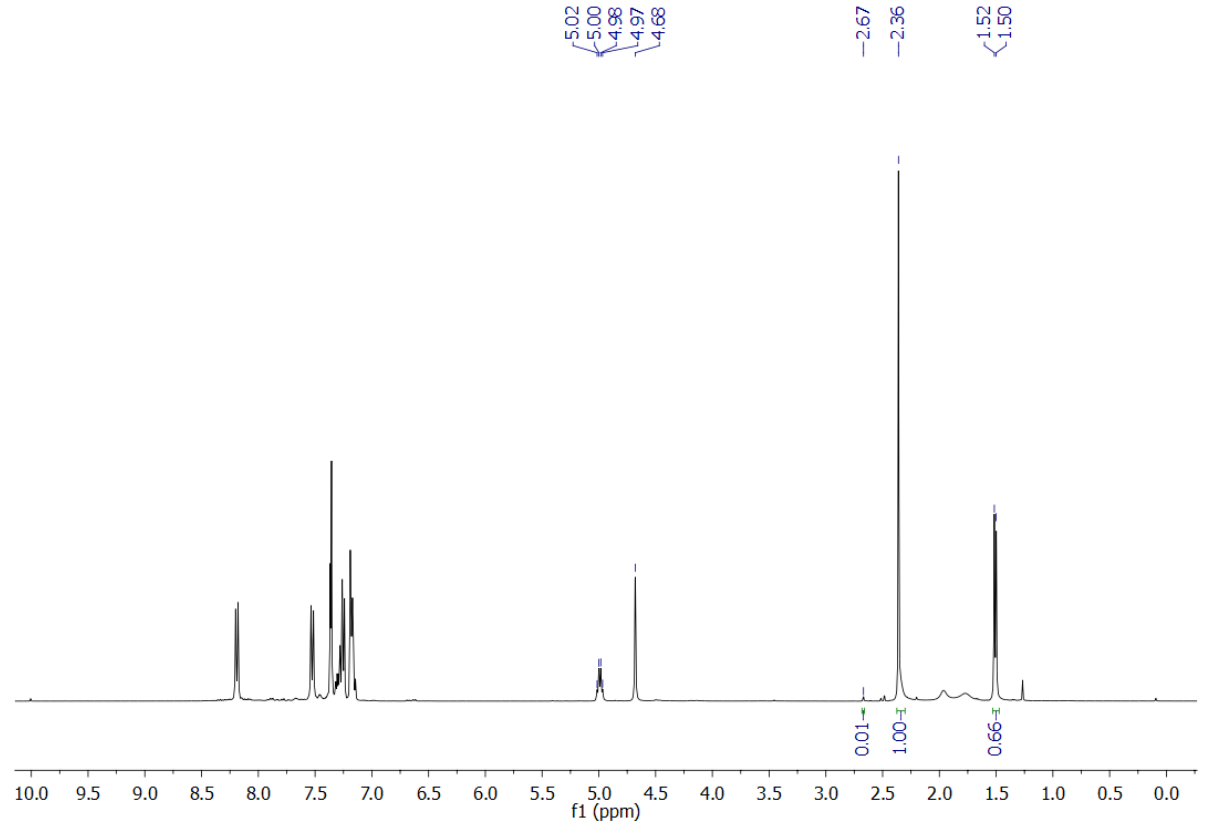


Figure S34: ^{1}H NMR spectra of *β*-alkylation of **1zg** with **2zg** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 34)[11]

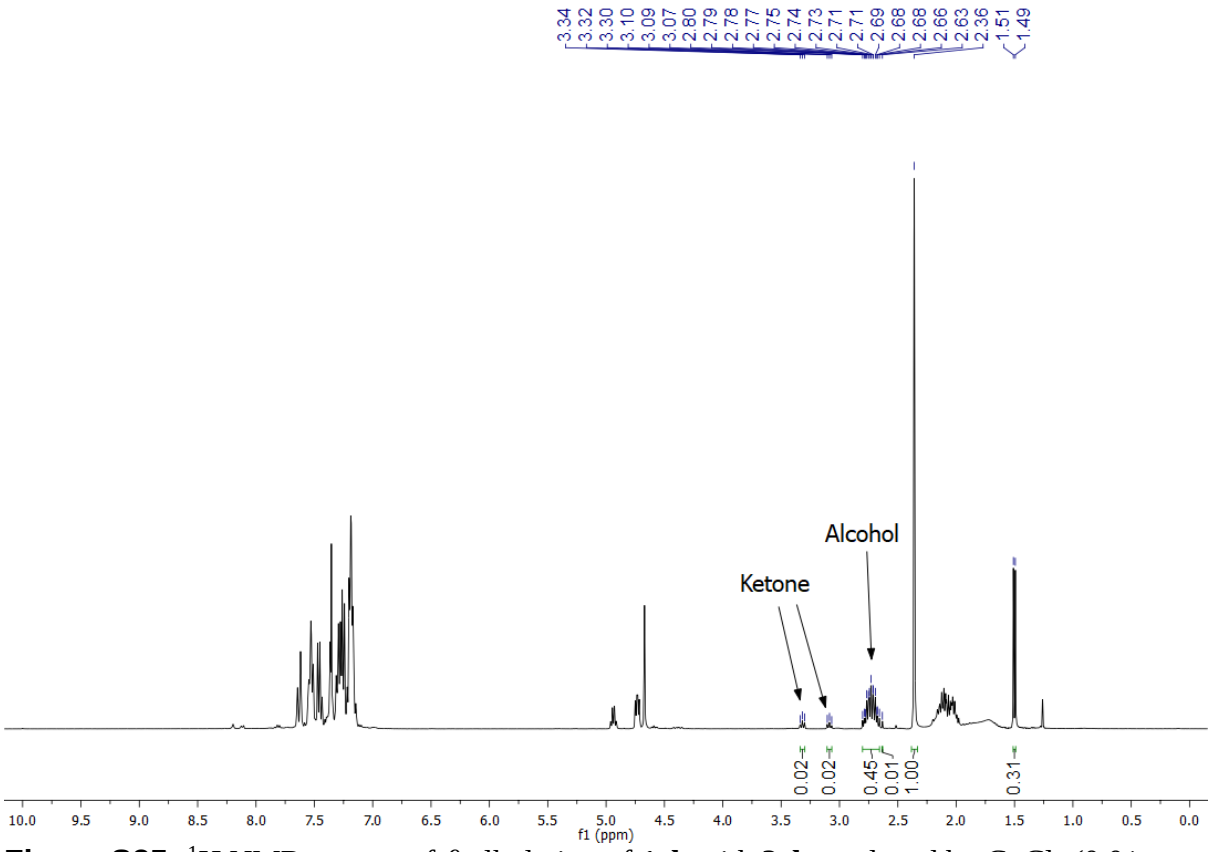


Figure S35: ^{1}H NMR spectra of *β*-alkylation of **1zh** with **2zh** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 35)[6]

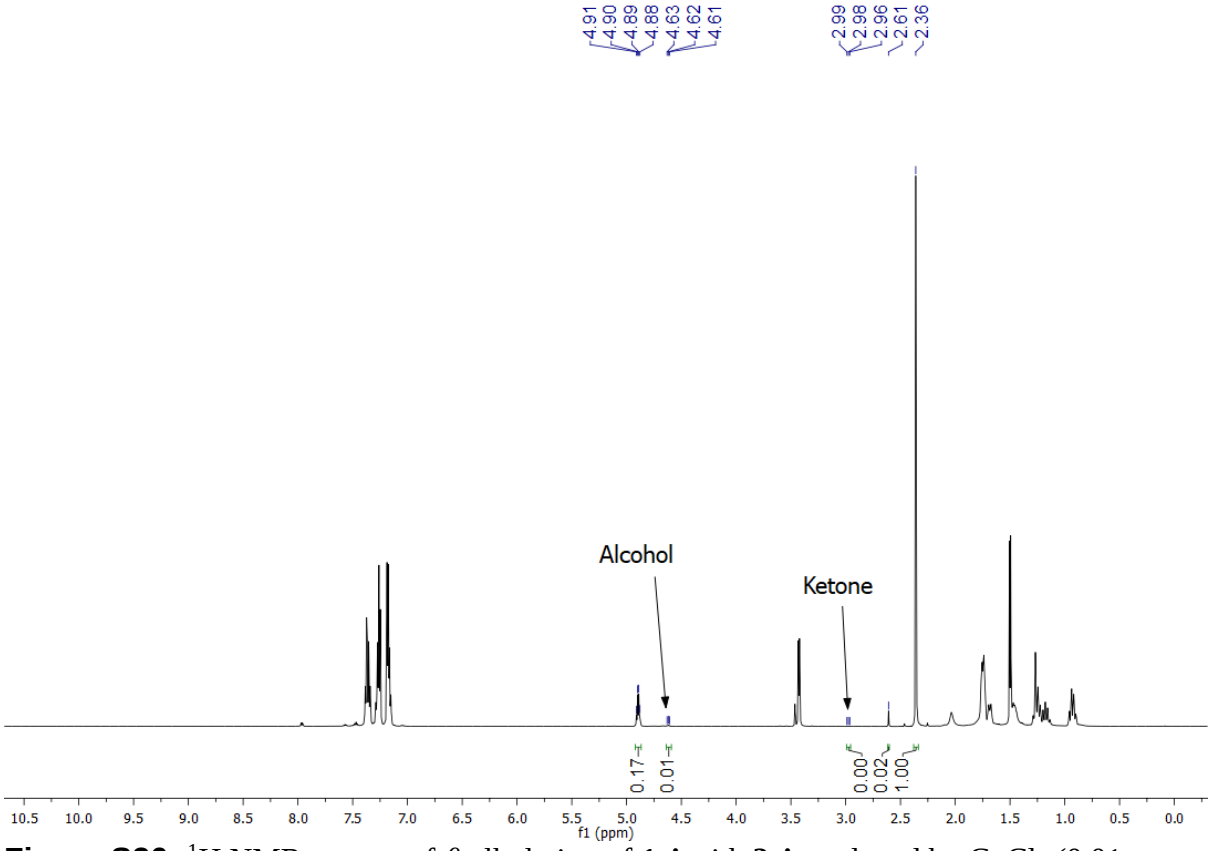


Figure S36: ^{1}H NMR spectra of *β*-alkylation of **1zi** with **2zi** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 36)[4]

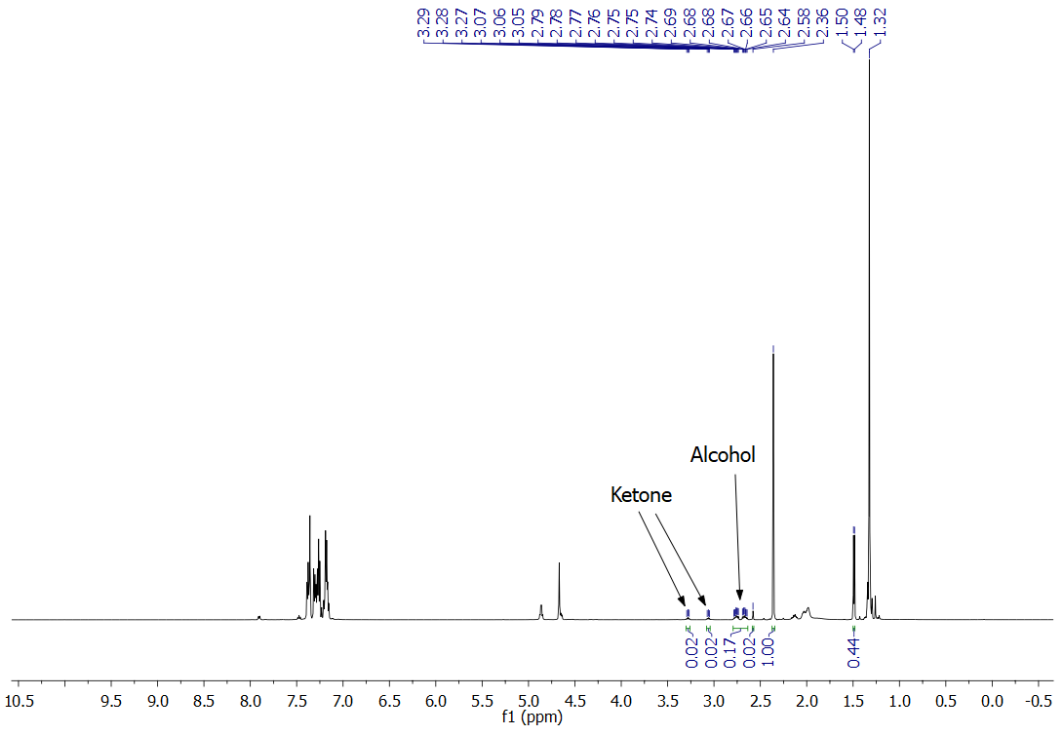


Figure S37: ^{1}H NMR spectra of *β*-alkylation of **1zj** with **2zj** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 37)[12]

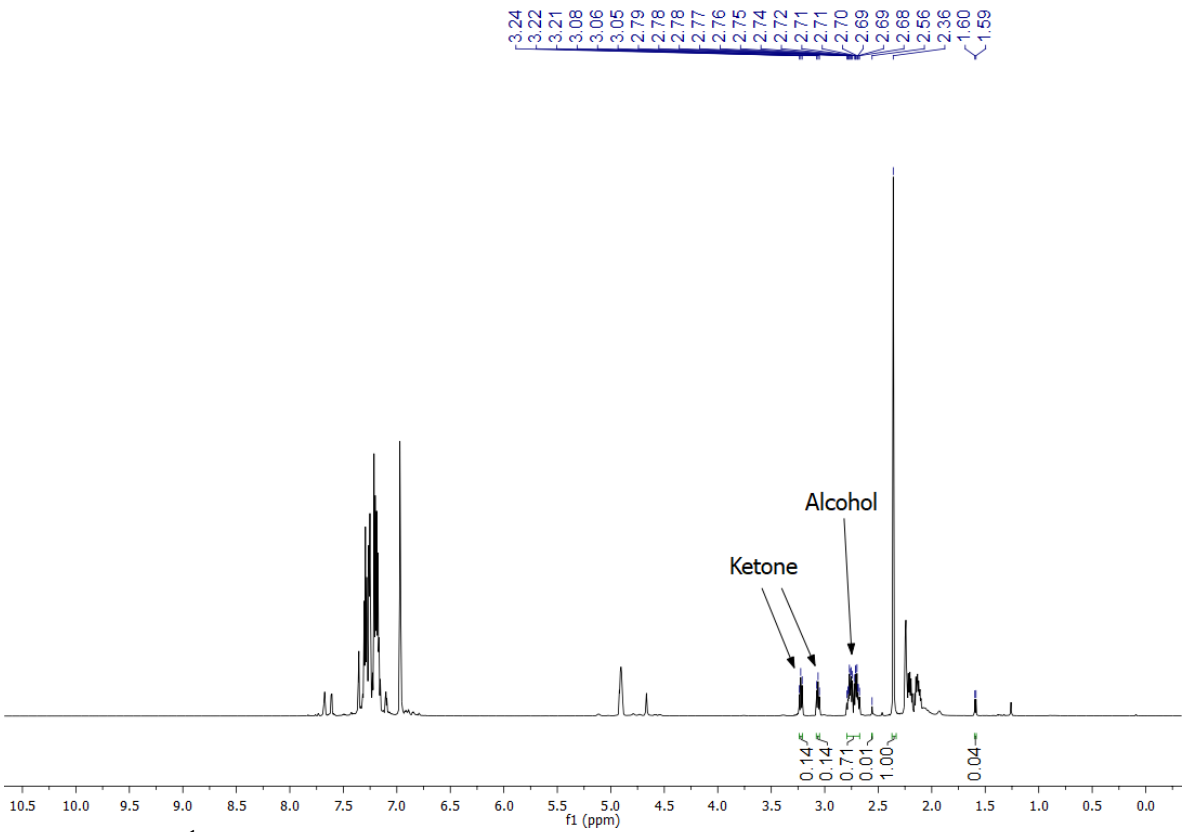


Figure S38: ^{1}H NMR spectra of *β*-alkylation of **1zk** with **2zk** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 38)[8]

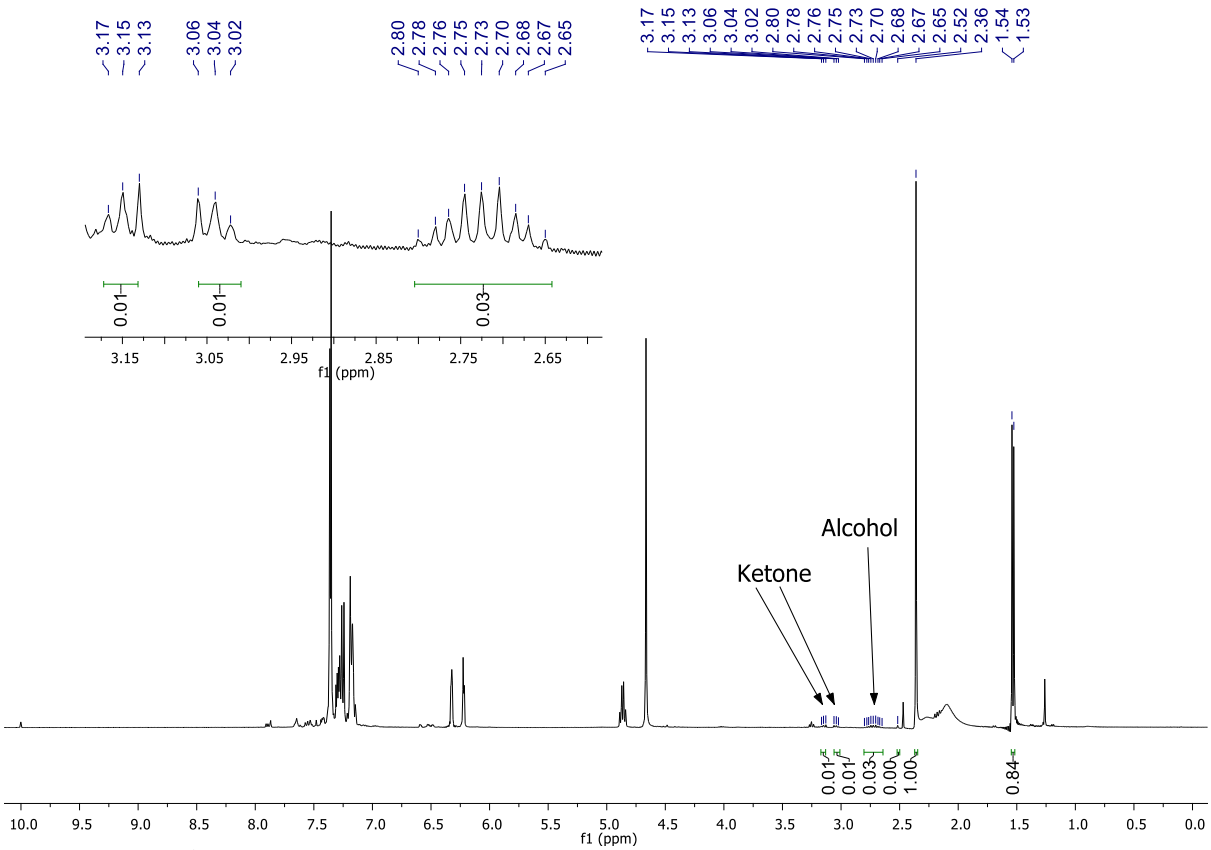


Figure S39: ^{1}H NMR spectra of *β*-alkylation of **1zl** with **2zl** catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C (Table S2, entry 39)[2]

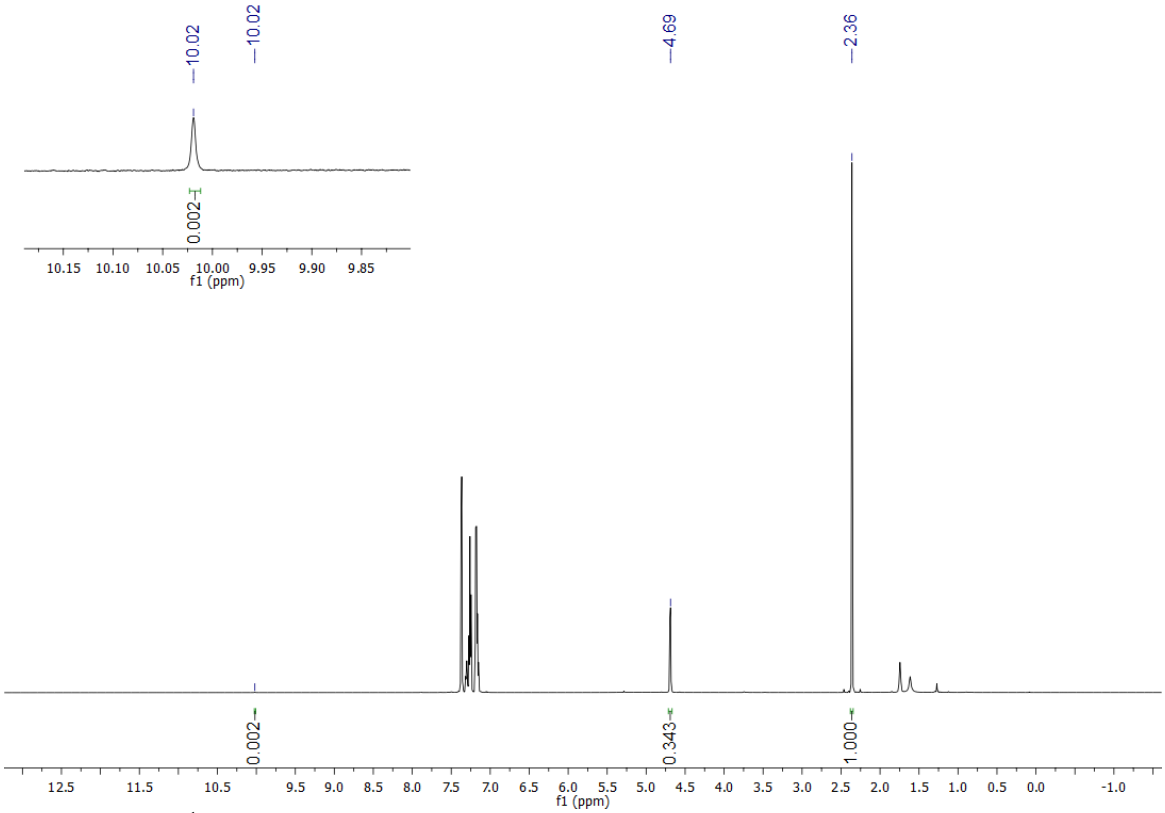


Figure S40: ^{1}H NMR spectra of benzyl alcohol in presence $CoCl_2$ (0.01 mol %) and NaO^{t}Bu (2.5 mol %) at 140 °C

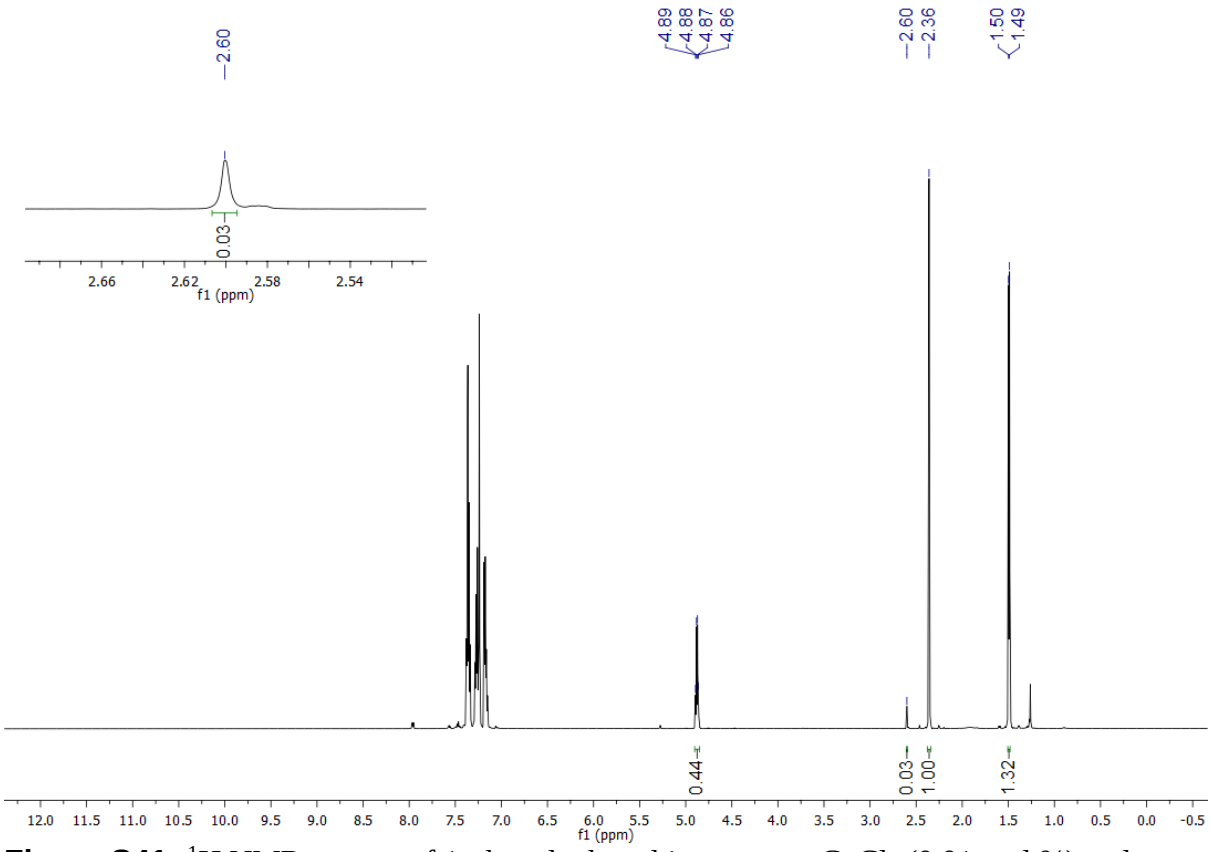


Figure S41: ^{1}H NMR spectra of 1-phenyl ethanol in presence $CoCl_2$ (0.01 mol %) and NaO^{t}Bu (2.5 mol %) at 140 ^{o}C

4. HRMS Analysis

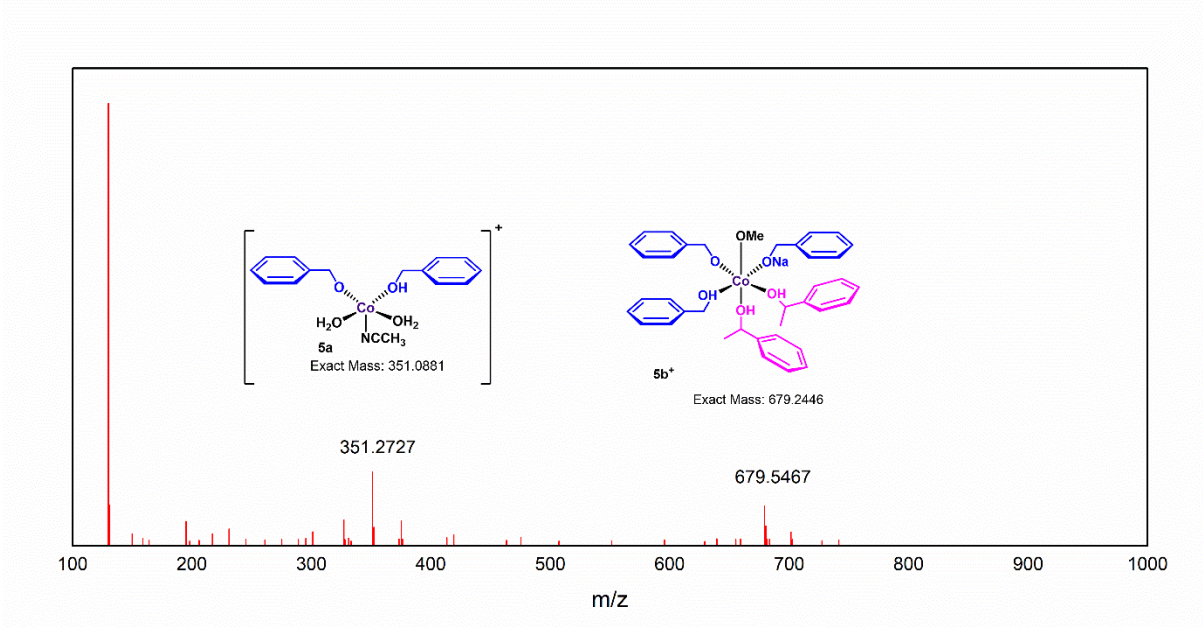


Figure S42: HRMS(ESI) spectra of spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) and NaO^{t}Bu (2.5 mol %) at t = 0 h at 140 ^{o}C.

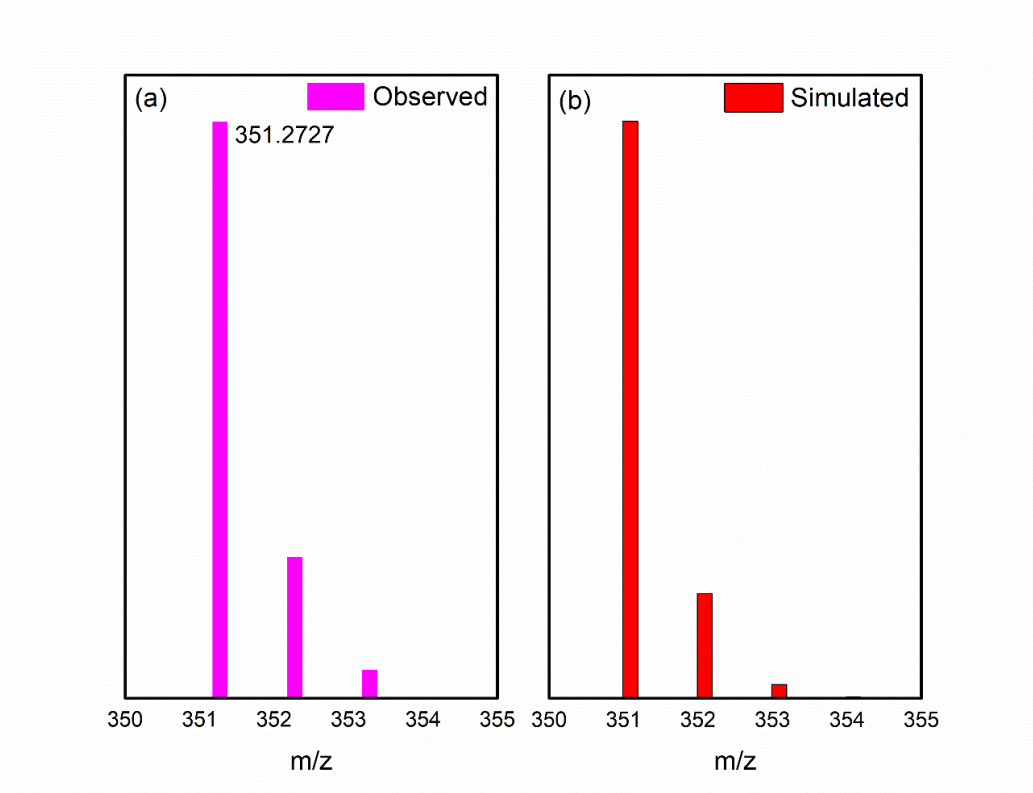


Figure S43: HRMS(ESI) expanded spectra of m/z 351.2727 (a) Observed (b) Simulated.

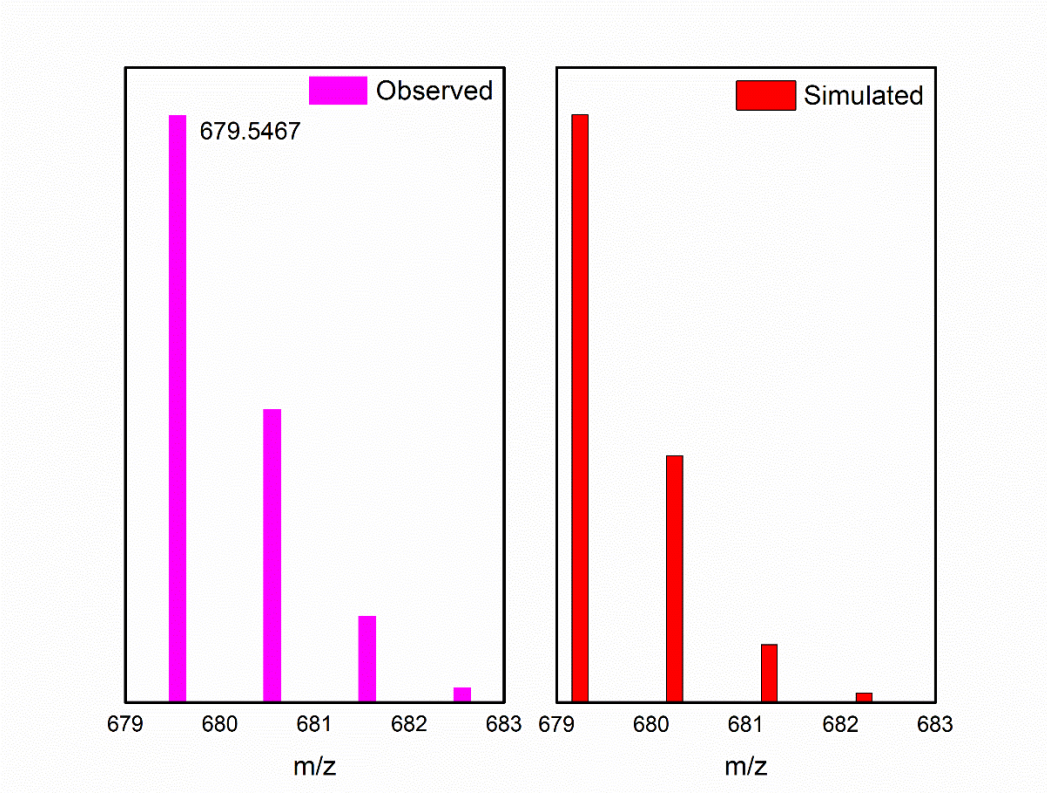


Figure S44: HRMS(ESI) expanded spectra of m/z 679.5467 (a) Observed (b) Simulated.

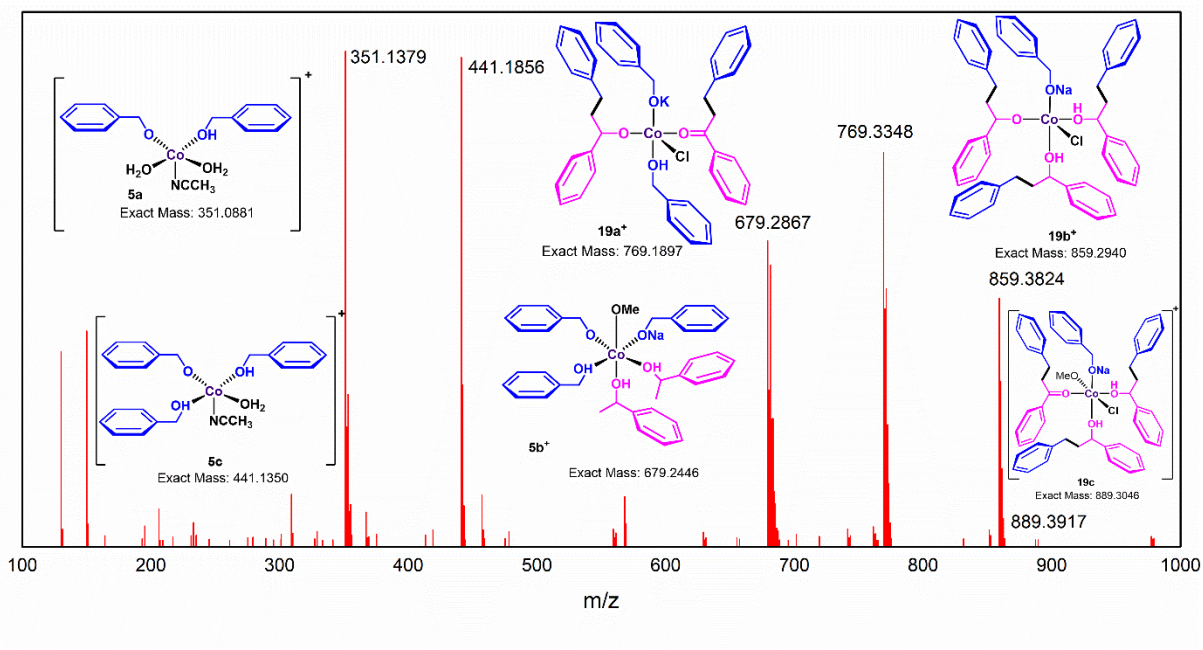


Figure S45: HRMS(ESI) spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) and NaO^tBu(2.5 mol %) at t = 1 h at 140 ^oC.

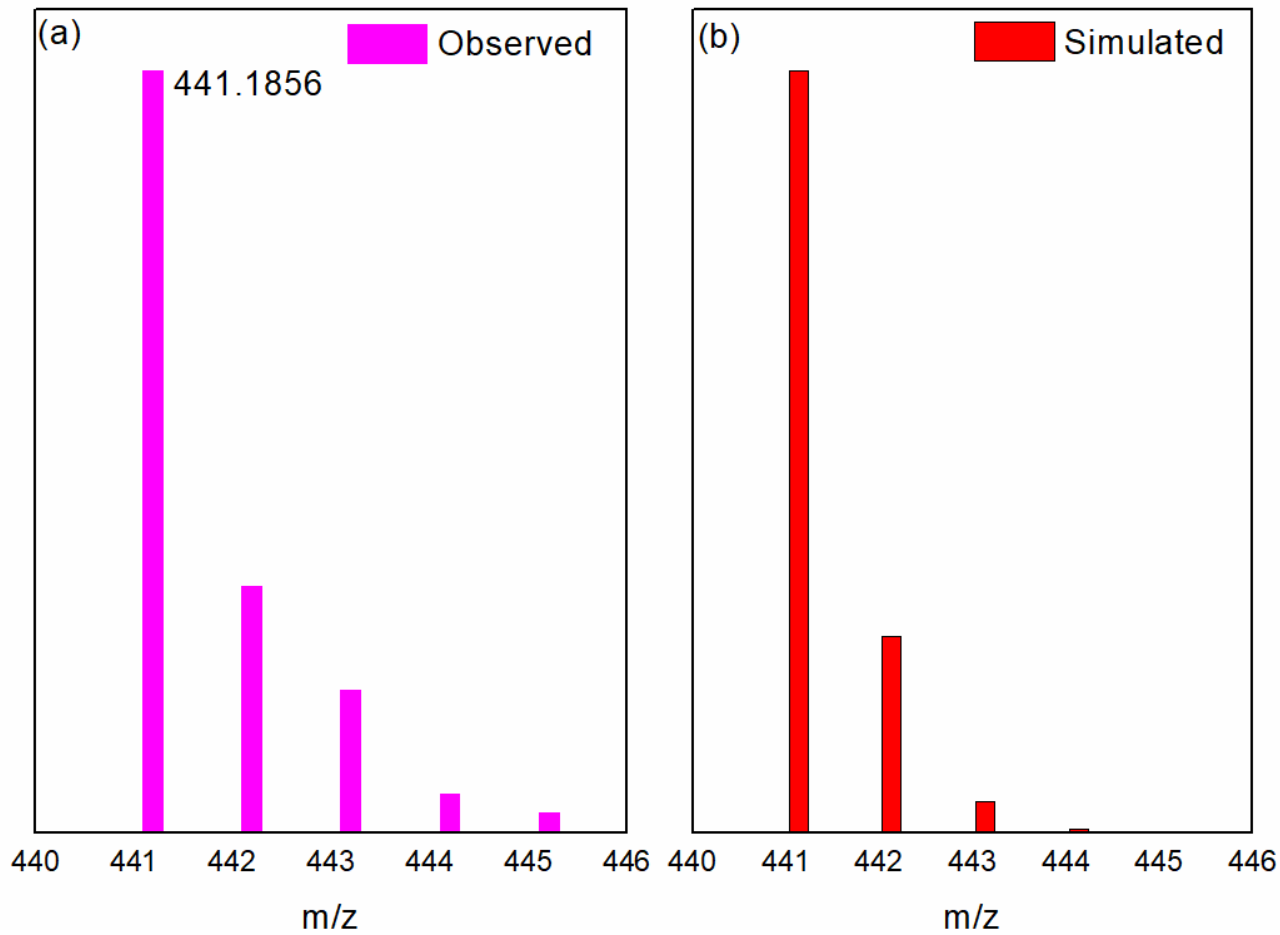


Figure S46: HRMS(ESI) expanded spectra of m/z 441.1856 (a) Observed (b) Simulated.

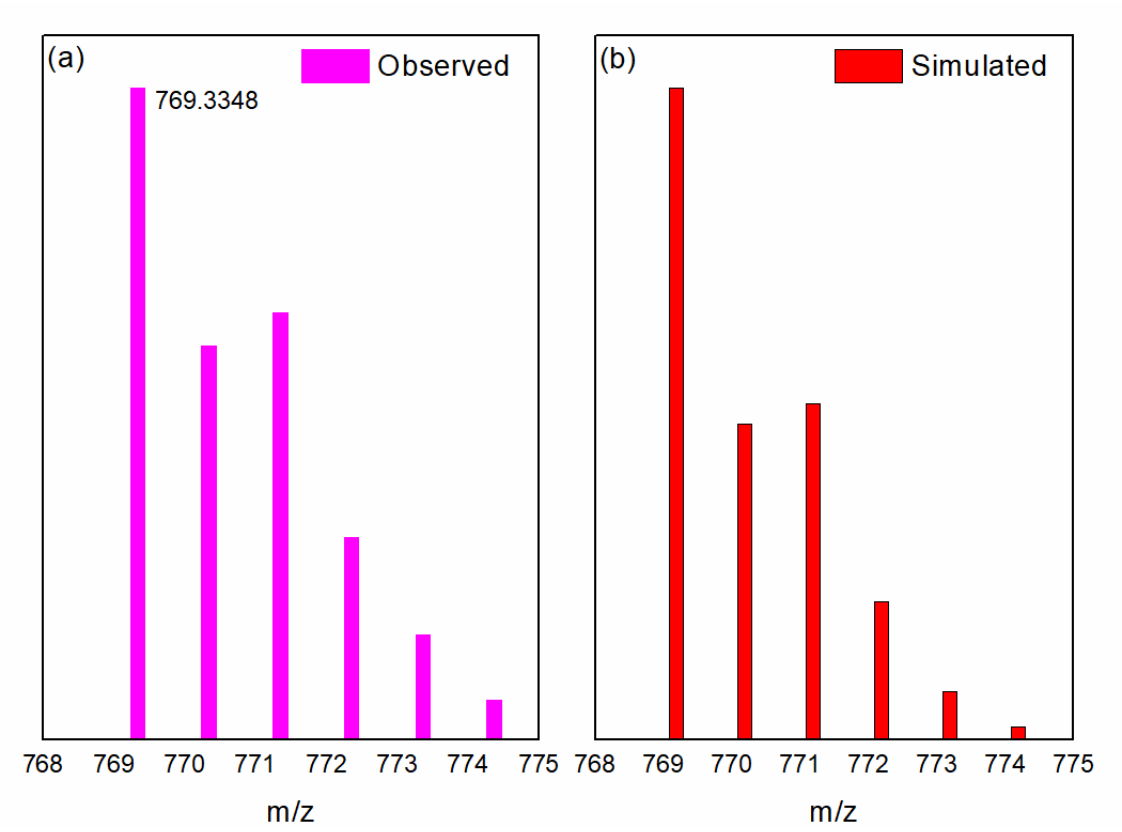


Figure S47: HRMS(ESI) expanded spectra of m/z 769.3348 (a) Observed (b) Simulated.

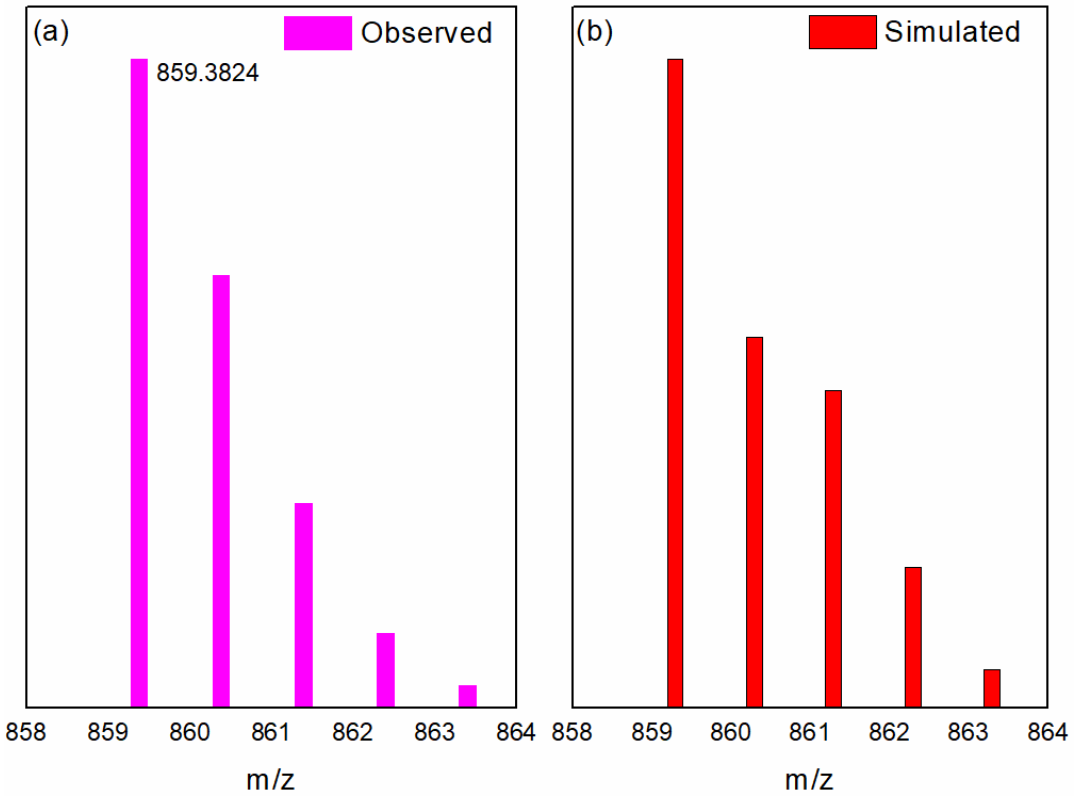


Figure S48: HRMS(ESI) expanded spectra of m/z 859.3824 (a) Observed (b) Simulated.

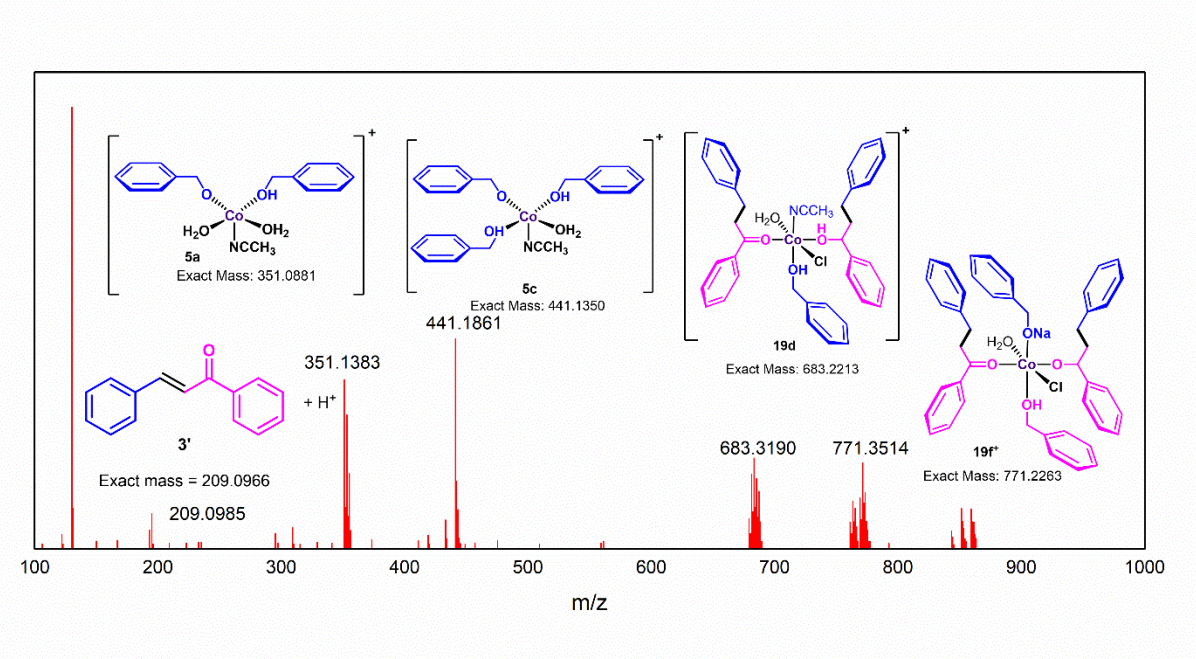


Figure S49: HRMS(ESI) spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) and NaO^tBu(2.5 mol %) at t = 5 h at 140 °C

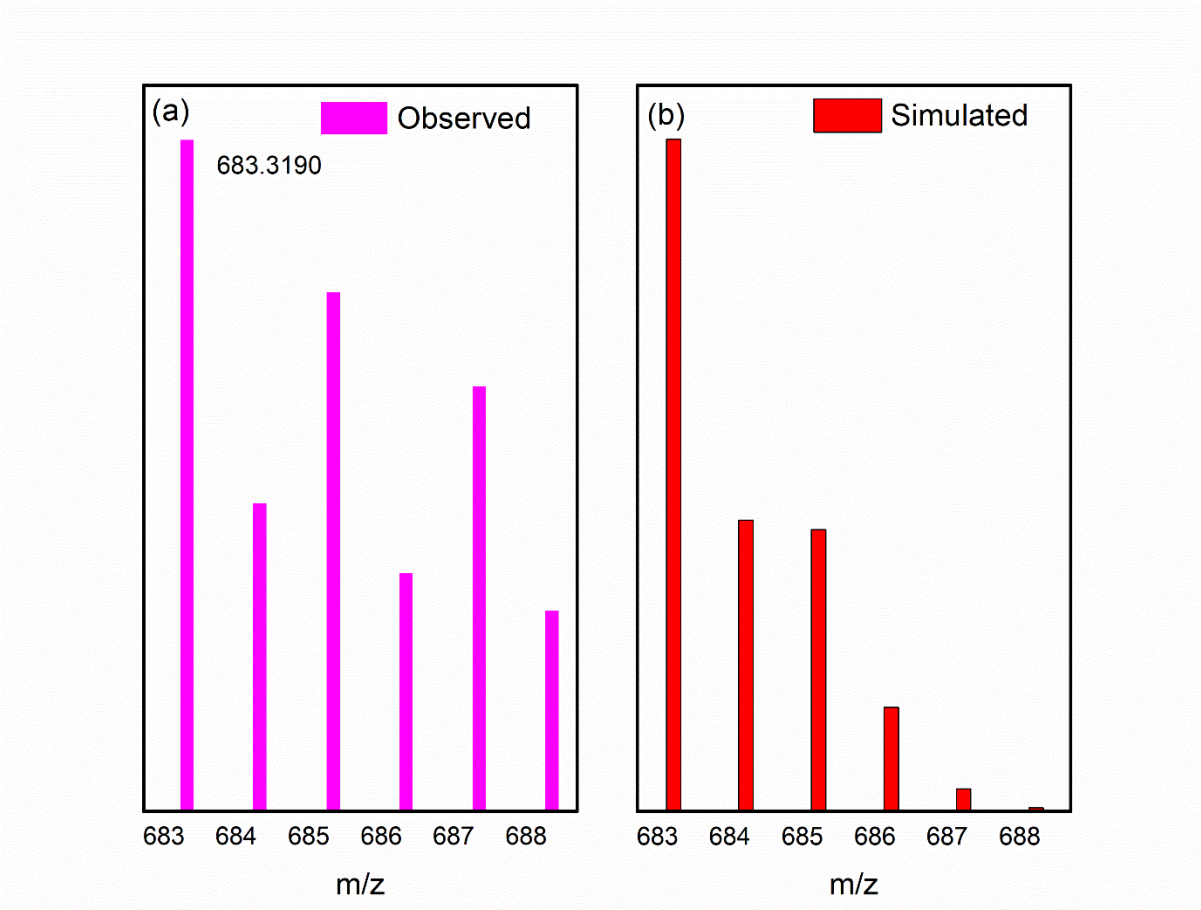


Figure S50: HRMS(ESI) expanded spectra of m/z 683.3190 (a) Observed (b) Simulated.

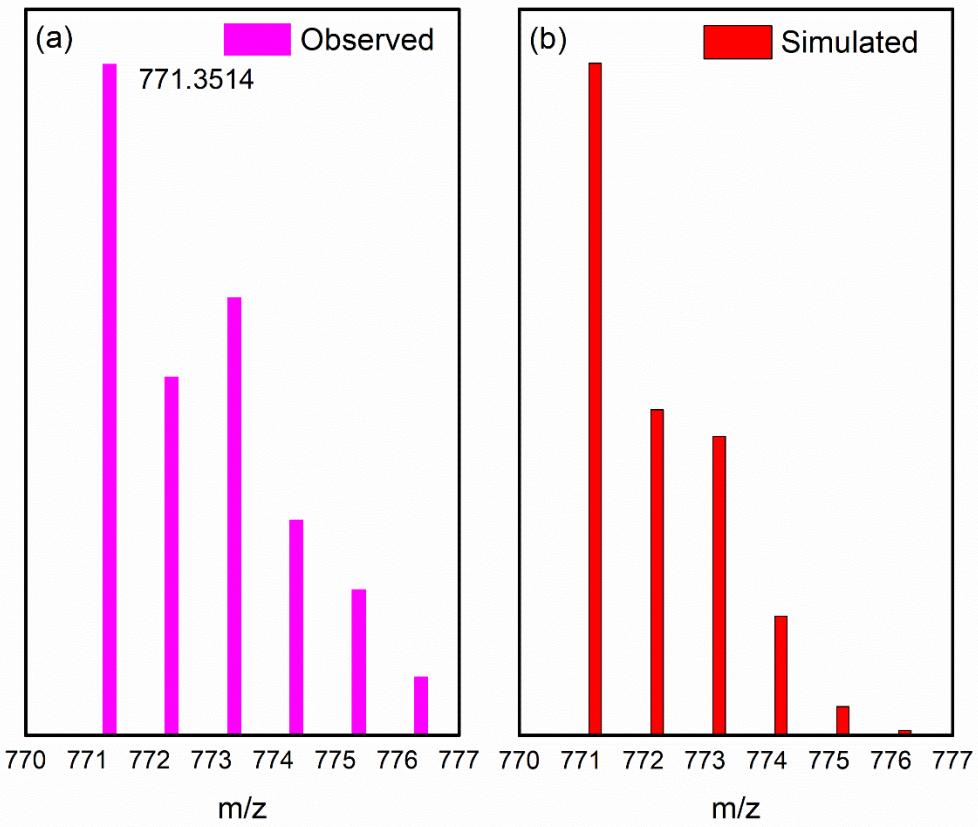


Figure S51: HRMS(ESI) expanded spectra of m/z 771.3514 (a) Observed (b) Simulated.

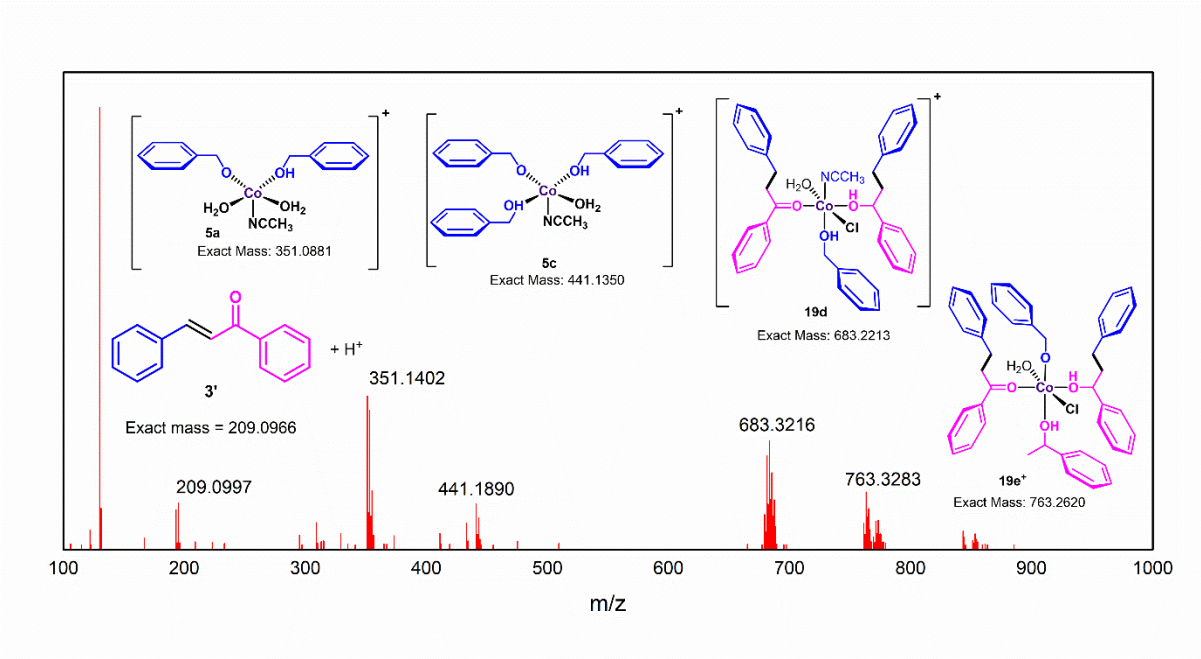


Figure S52: HRMS(ESI) spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) and NaO^tBu(2.5 mol %) at t = 10 h at 140 ^oC.

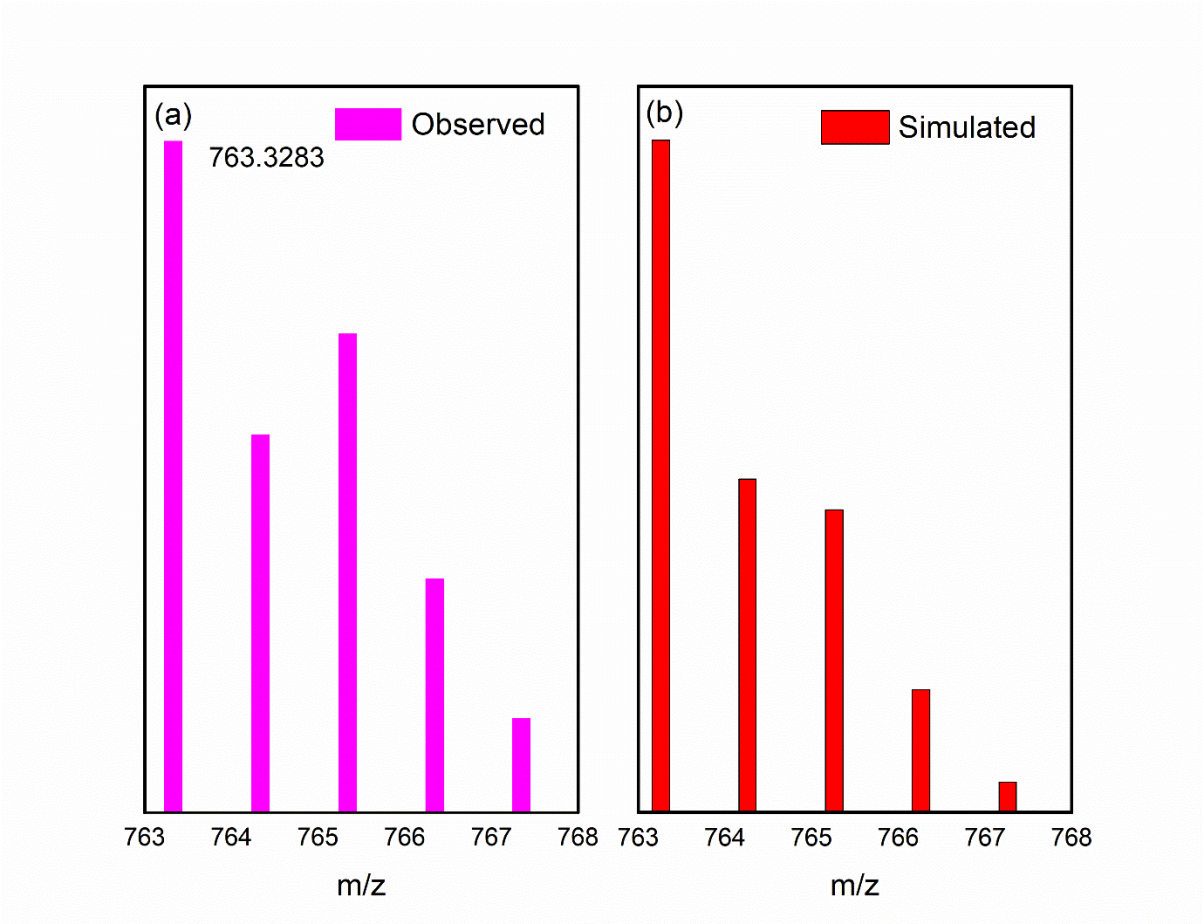


Figure S53: HRMS(ESI) expanded spectra of m/z 763.3283 (a) Observed (b) Simulated.

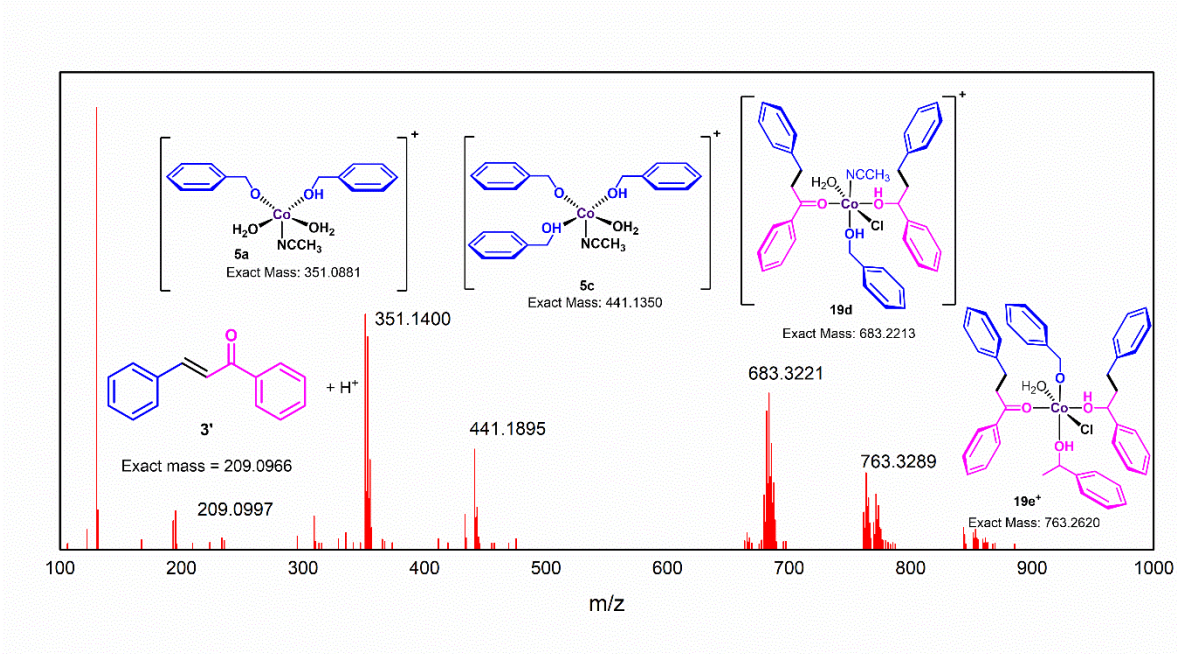


Figure S54: HRMS(ESI) spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) and NaO^tBu (2.5 mol %) at t = 24 h at 140 ^oC.

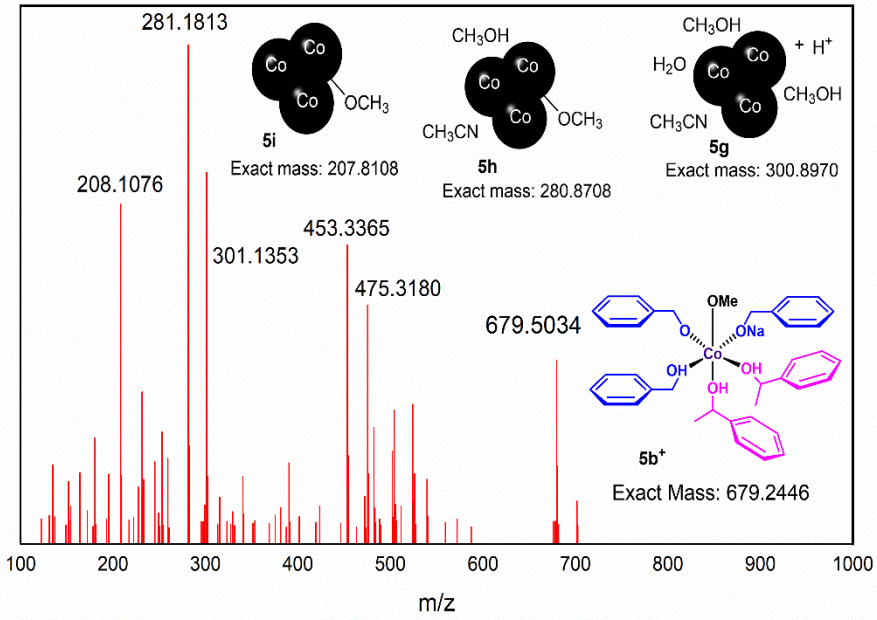


Figure S55: HRMS(ESI) spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (1 mol %) and NaO^tBu (2.5 mol %) at t = 0 h at 140 °C.

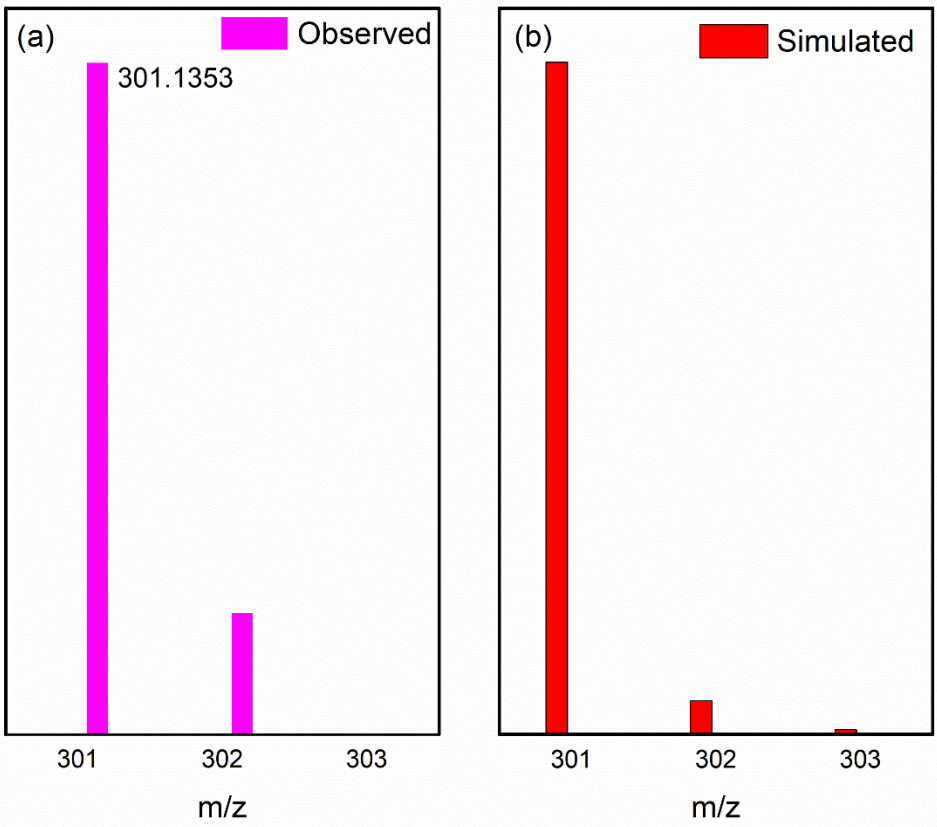


Figure S56: HRMS(ESI) expanded spectra of m/z 301.1353 (a) Observed (b) Simulated

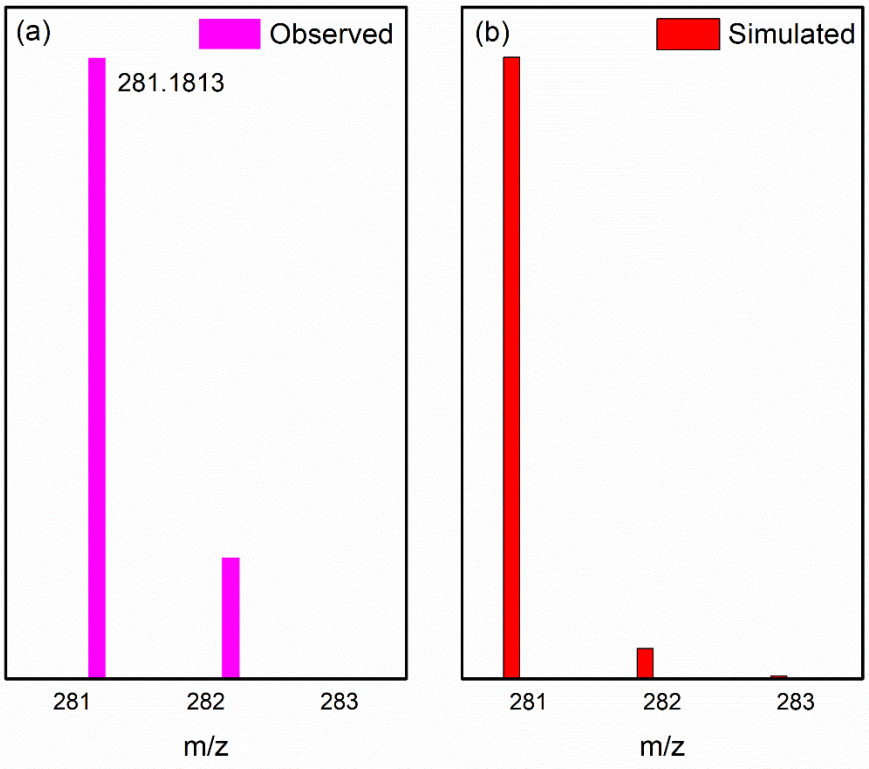


Figure S57: HRMS(ESI) expanded spectra of m/z 281.1813 (a) Observed (b) Simulated

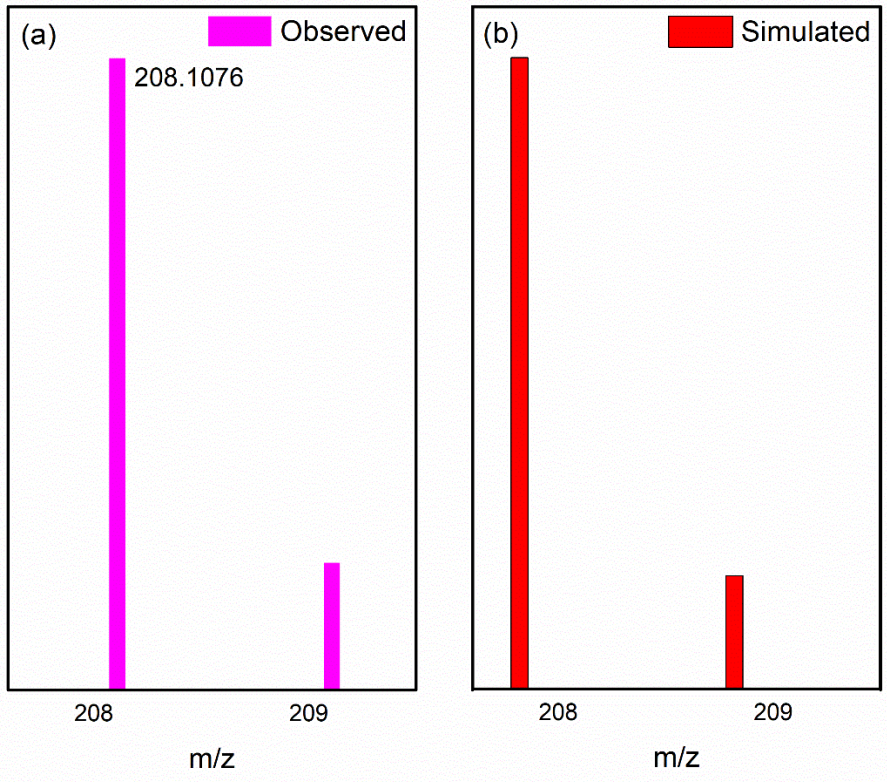


Figure S58: HRMS(ESI) expanded spectra of m/z 208.1076 (a) Observed (b) Simulated

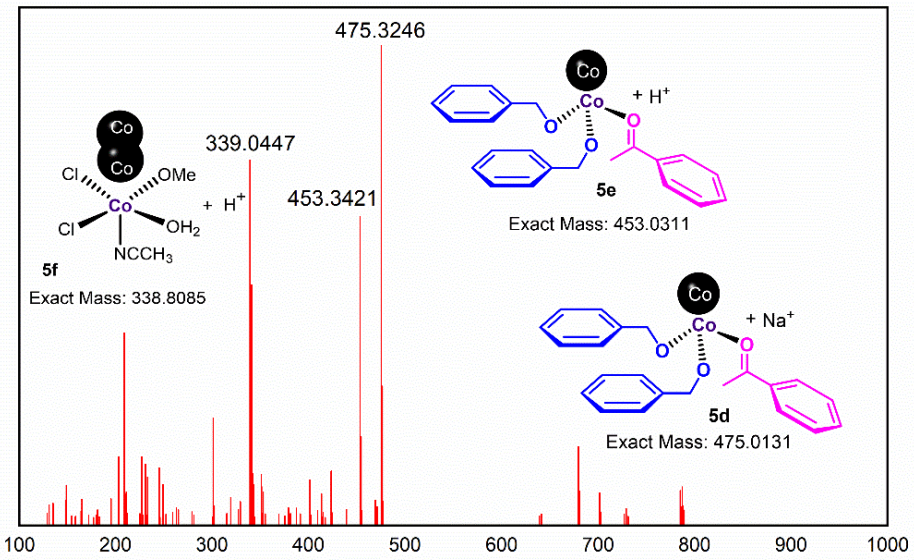


Figure S59: HRMS(ESI) spectra of *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (1 mol %) and NaO^tBu (2.5 mol %) at t = 1 h at 140 °C.

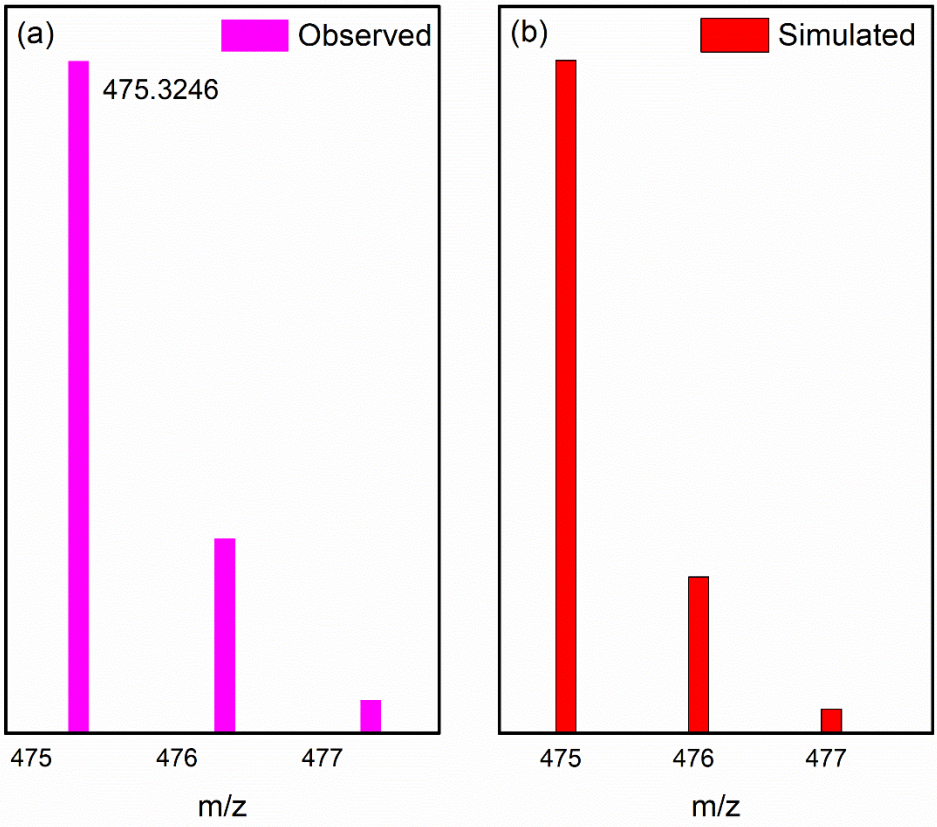


Figure S60: HRMS(ESI) expanded spectra of m/z 475.3246 (a) Observed (b) Simulated

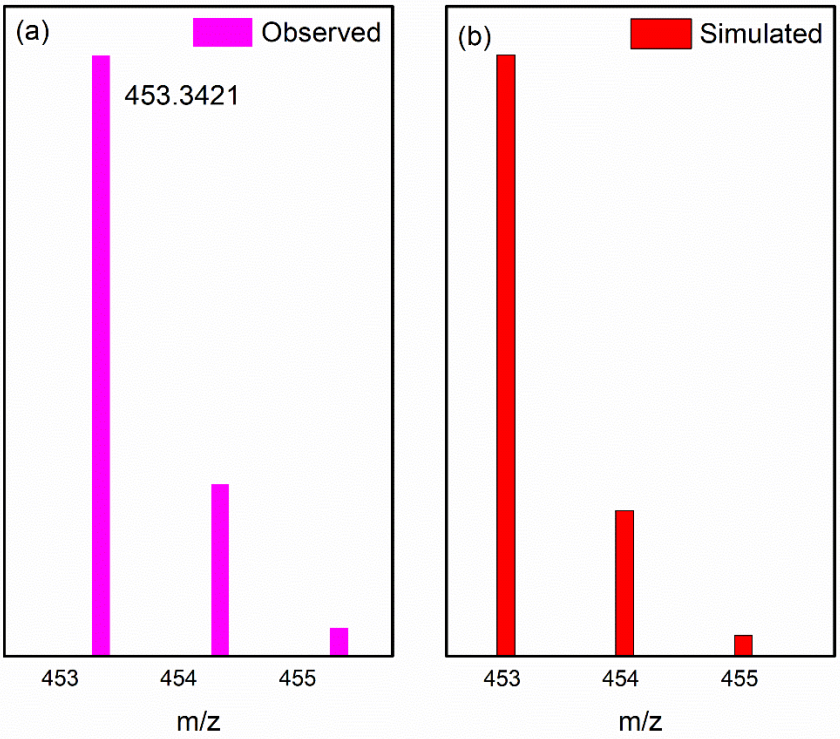


Figure S61: HRMS(ESI) expanded spectra of m/z 453.3421 (a) Observed (b) Simulated

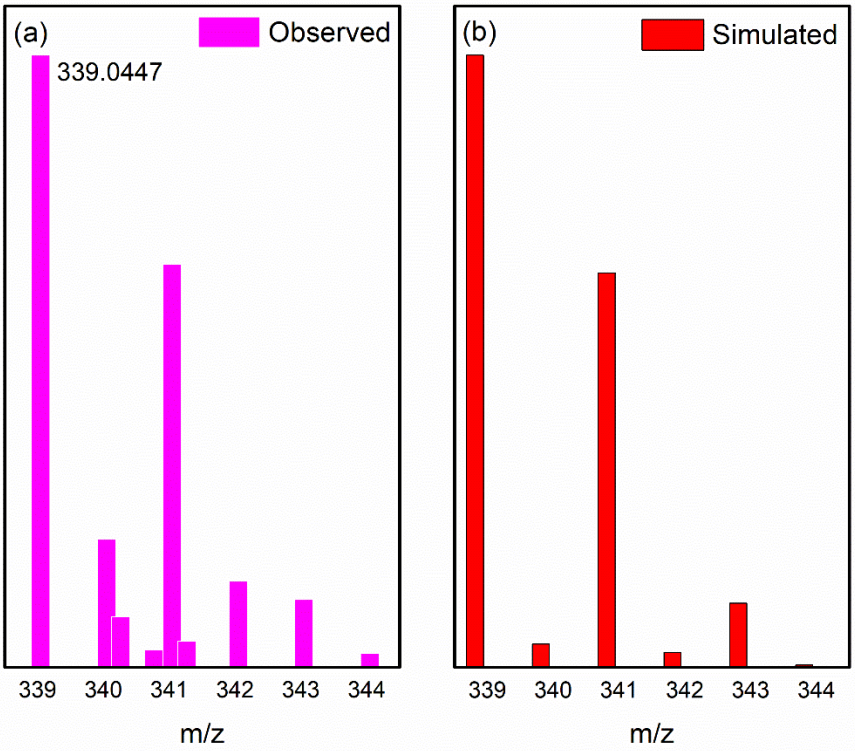


Figure S62: HRMS(ESI) expanded spectra of m/z 339.0447 (a) Observed (b) Simulated

5. EPR Analysis

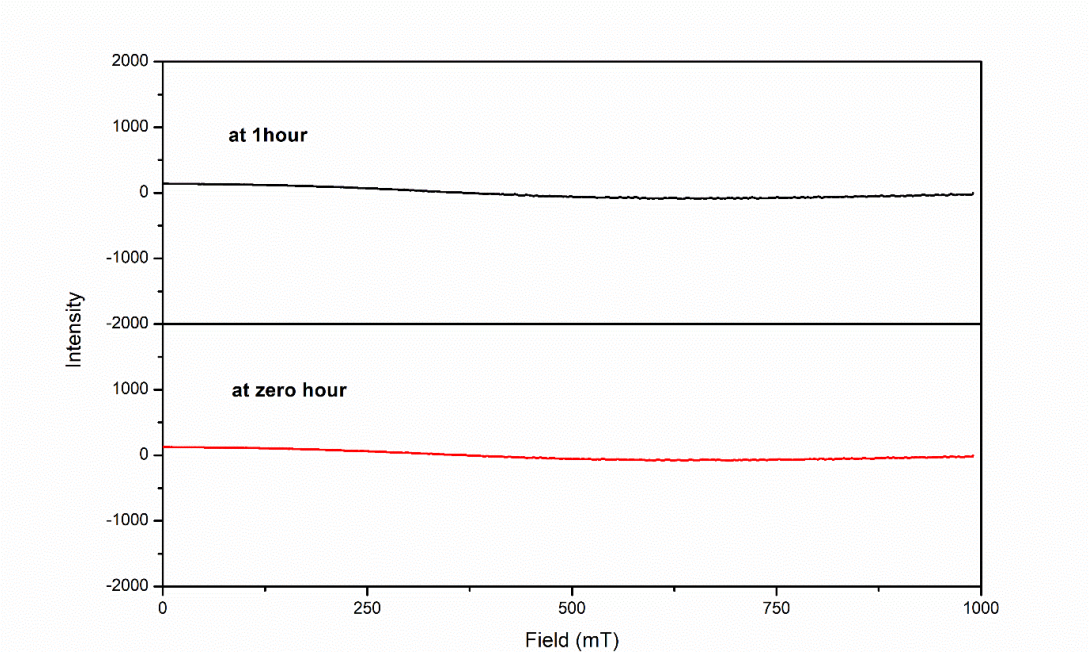


Figure S63: X band EPR spectrum at 77K of the aliquot withdrawn from the *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) after 0 h and 1 h

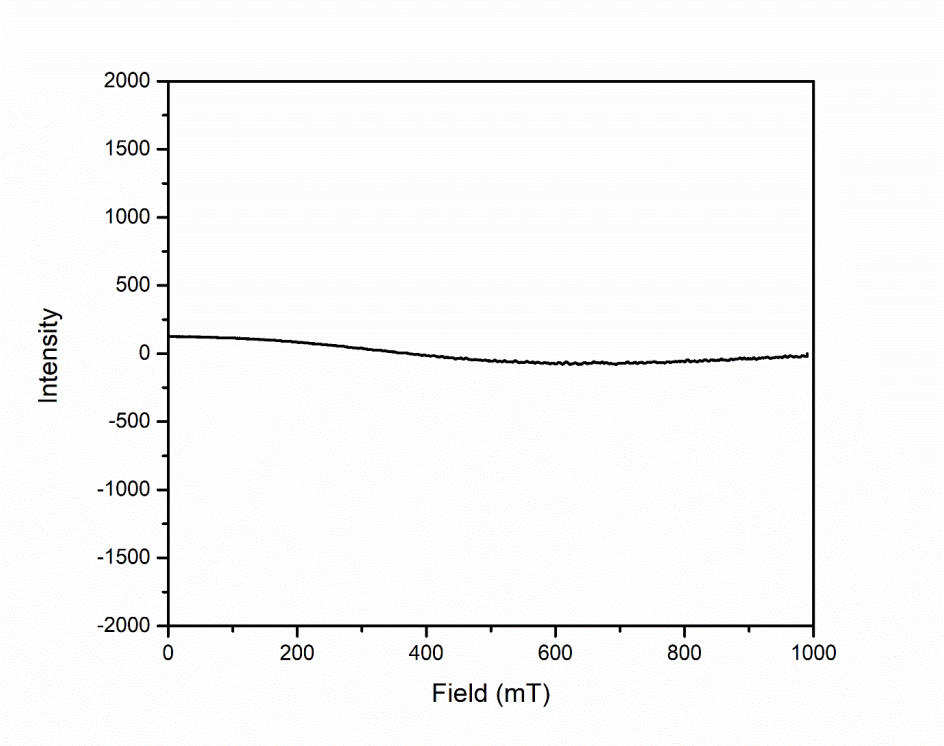


Figure S64: X band EPR spectrum at 77K of the aliquot withdrawn from the *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) after 0 h

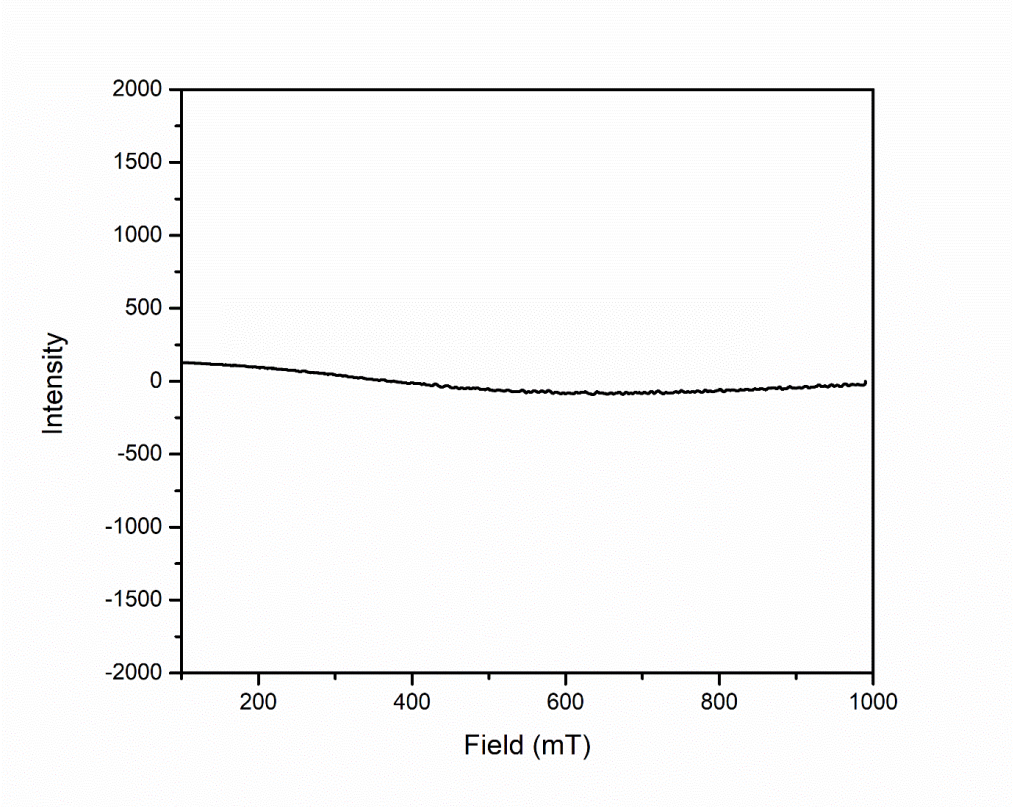


Figure S65: X band EPR spectrum at 77K of the aliquot withdrawn from the *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) after 1h

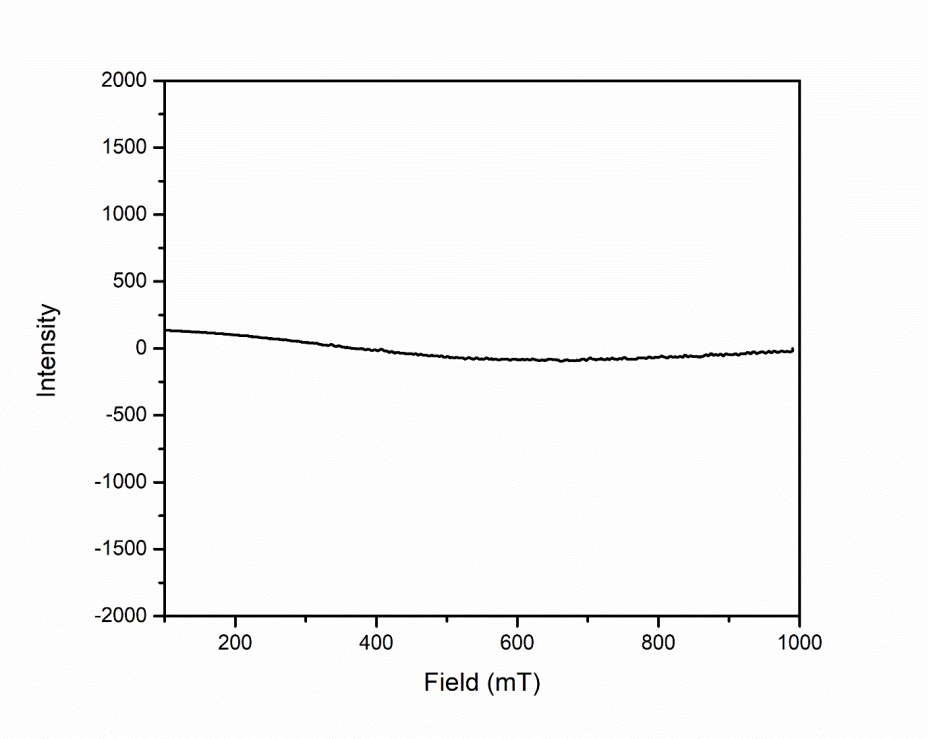


Figure S66: X band EPR spectrum at 77K of the aliquot withdrawn from the *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) after 5h

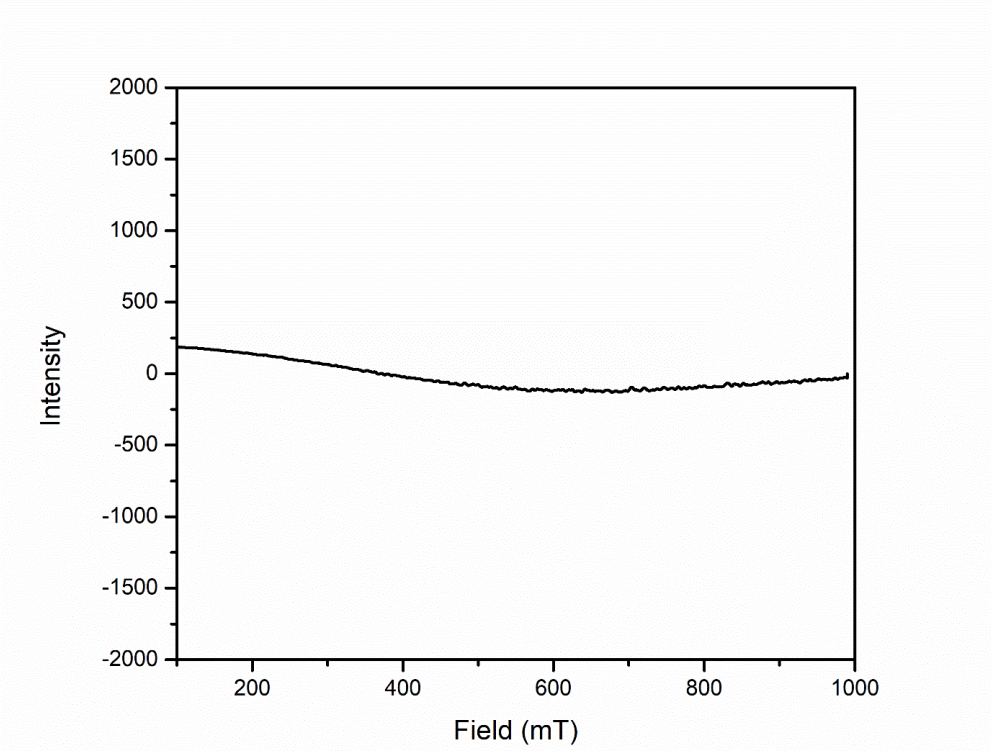


Figure S67: X band EPR spectrum at 77K of the aliquot withdrawn from the *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) after 10h

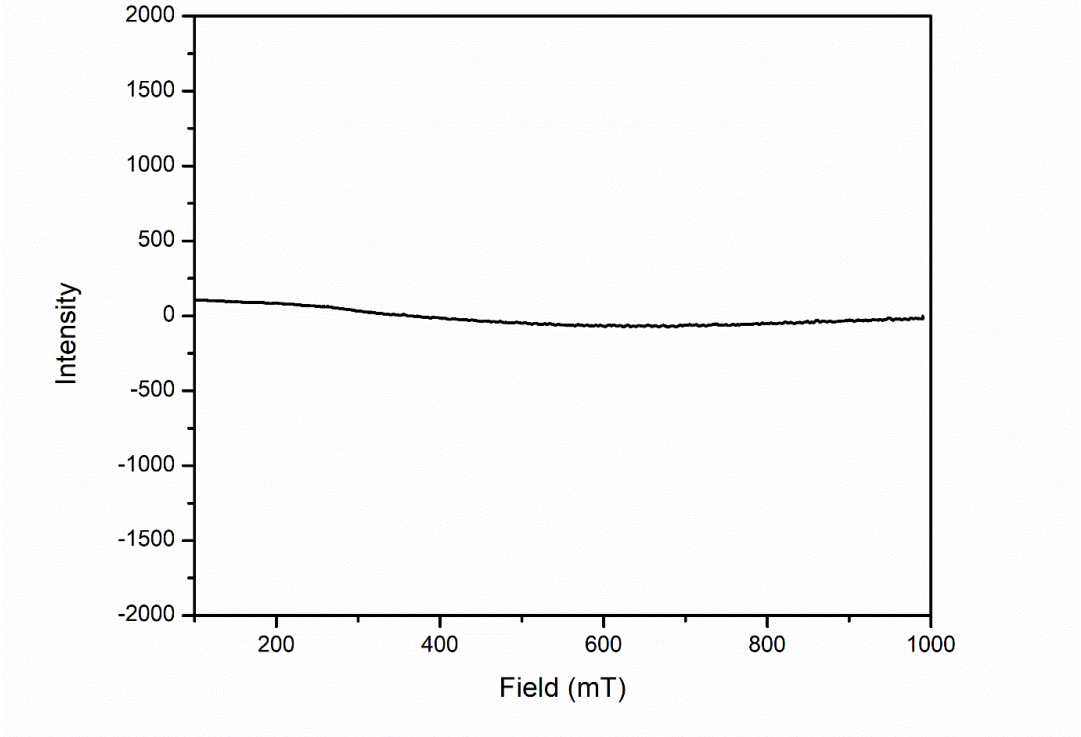


Figure S68: X band EPR spectrum at 77K of the aliquot withdrawn from the *β*-alkylation of **1** with **2** catalyzed by $CoCl_2$ (0.1 mol %) after 24 h

6. Gas Chromatography Analysis

GC analysis (TCD detection) was performed on a Agilent 7820-GC instrument fitted with Agilent Front SSZ Inlet N_2 HP-PLOT Q column (30 m length x 530 µm x 40 µm) using the following method:

Agilent 7820-GC back detector TCD
Oven temperature: 50 °C
Inlet temperature: 100 °C
Detector temperature (TCD): 250 °C
Detector temperature (FID): 300 °C
Time at starting temp: 0 min
Hold time = 10 min
Flow rate (carrier): 25 mL/min (N_2)
Split flow: 50 mL/min
Split ratio: 10

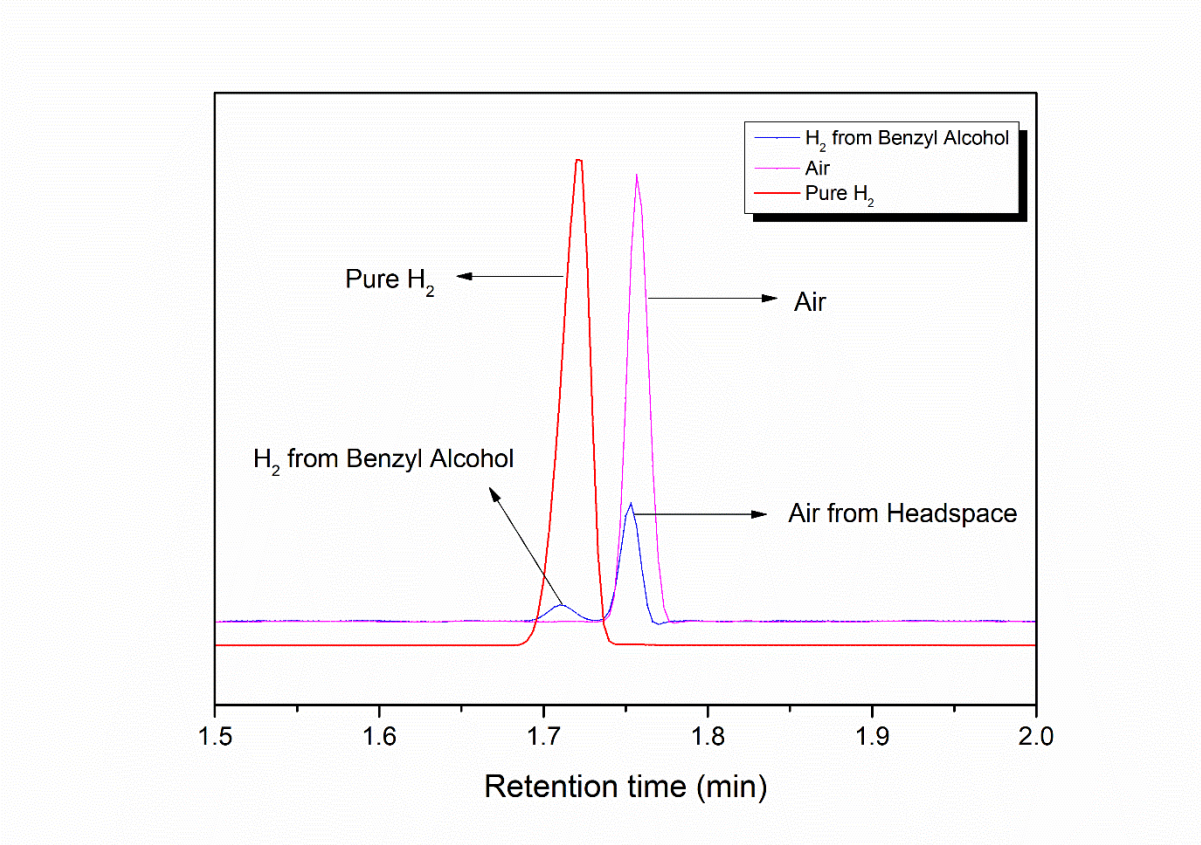


Figure S69a: Evidence for H_2 evolution in the dehydrogenation of benzyl alcohol (**1**) catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C via GC analysis.

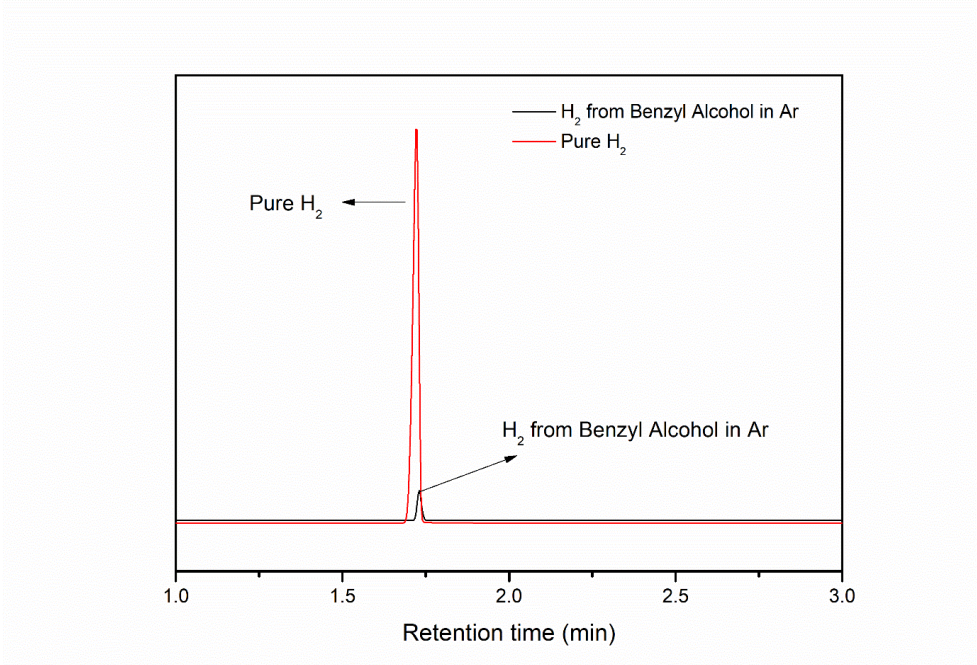


Figure S69b: Evidence for H_2 evolution in the dehydrogenation of benzyl alcohol (**1**) in presence of argon catalyzed by $CoCl_2$ (0.01 mol %) at 140 °C via GC analysis.

7. Kinetic Studies

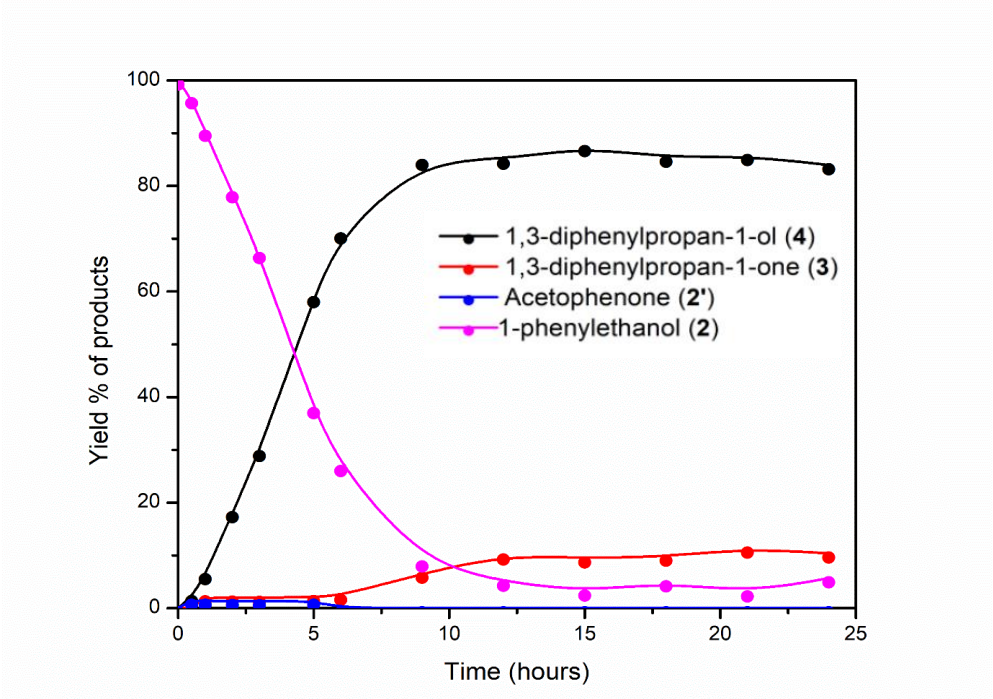


Figure S70: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

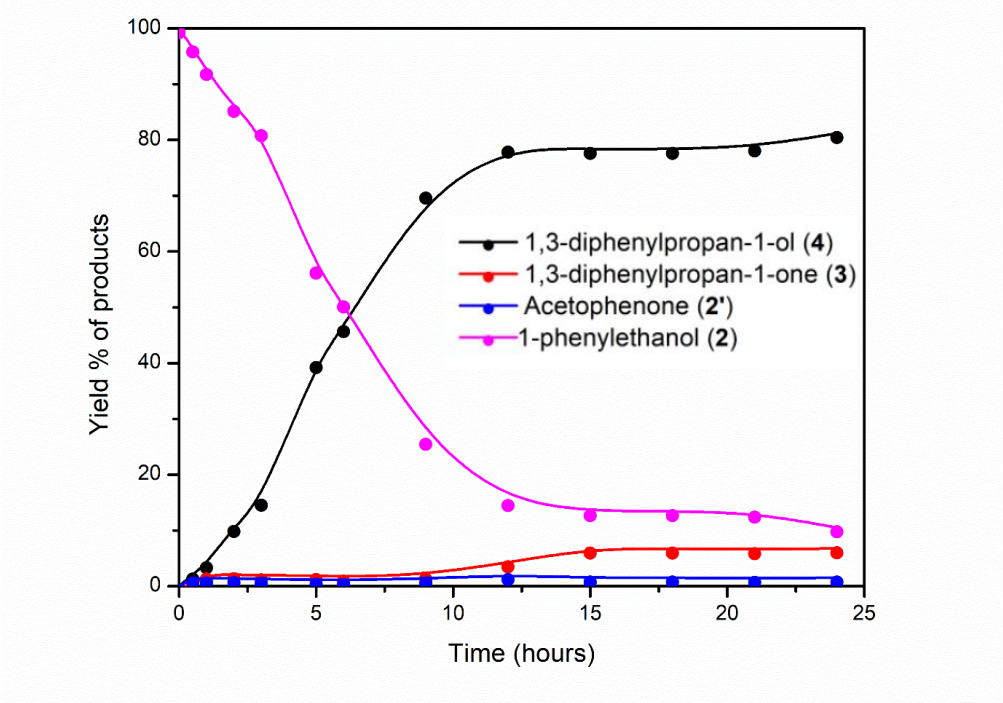


Figure S71: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.005 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

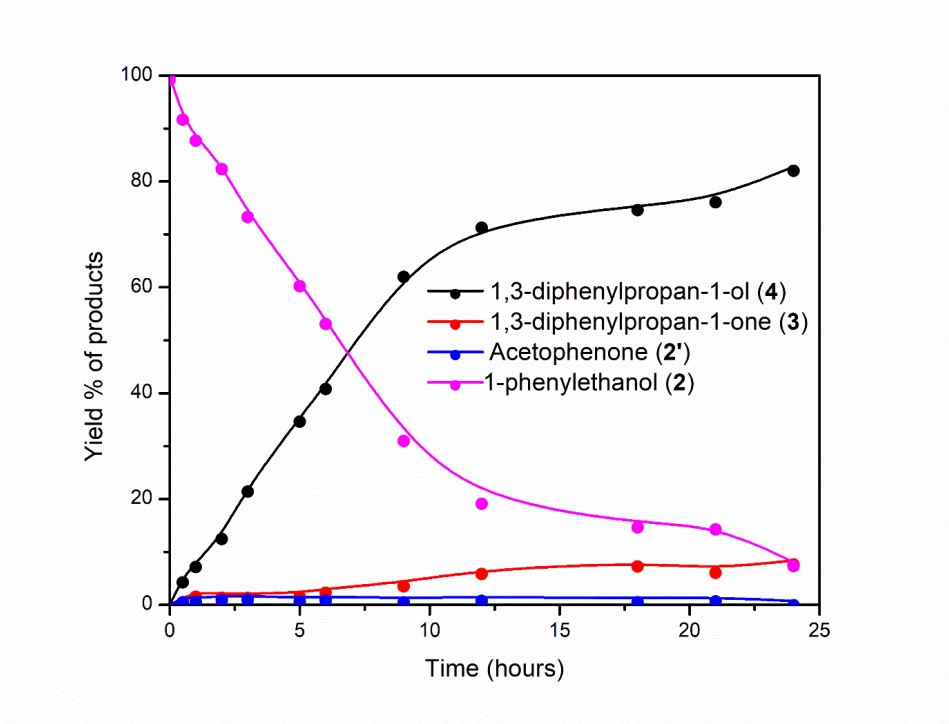


Figure S72: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.025 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

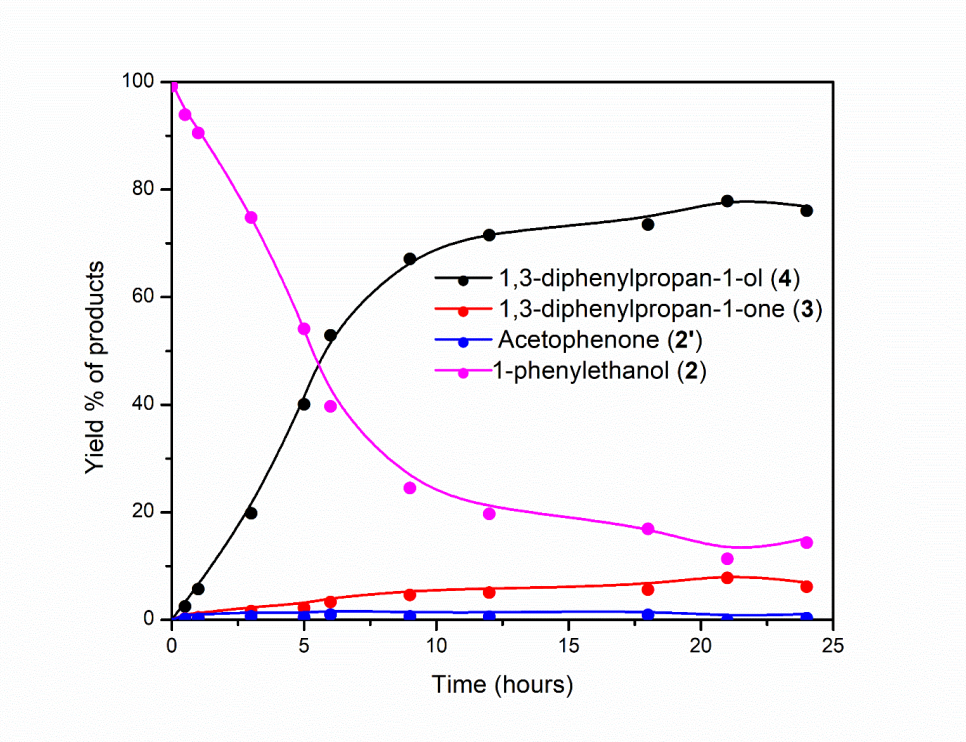


Figure S73: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.05 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

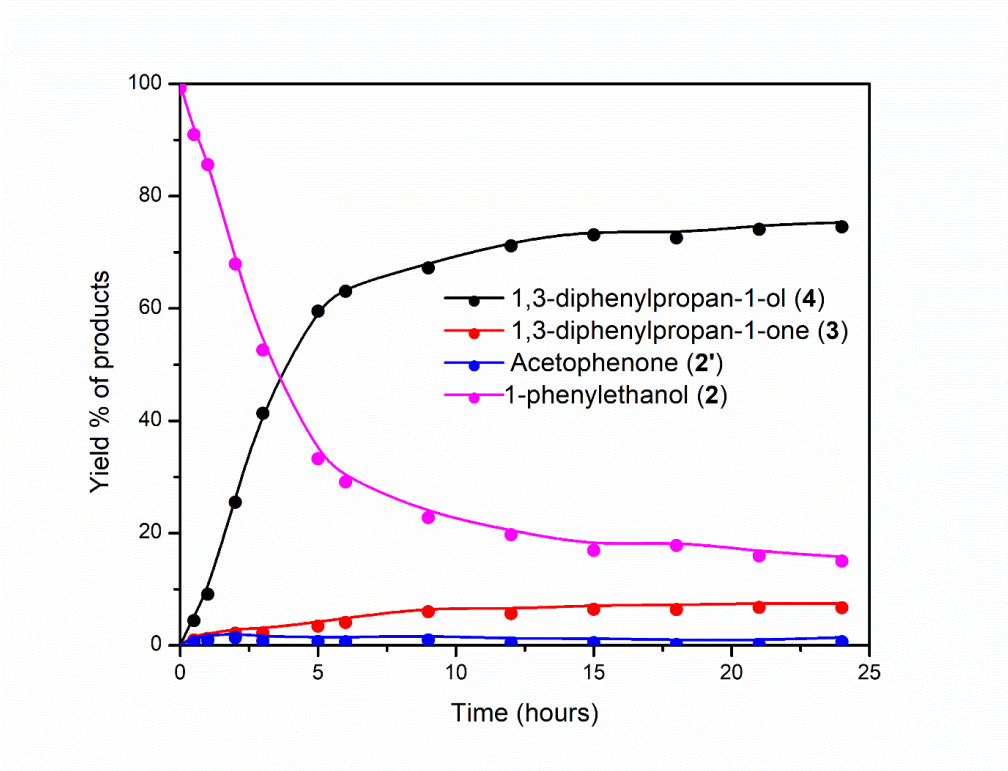


Figure S74: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.075 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

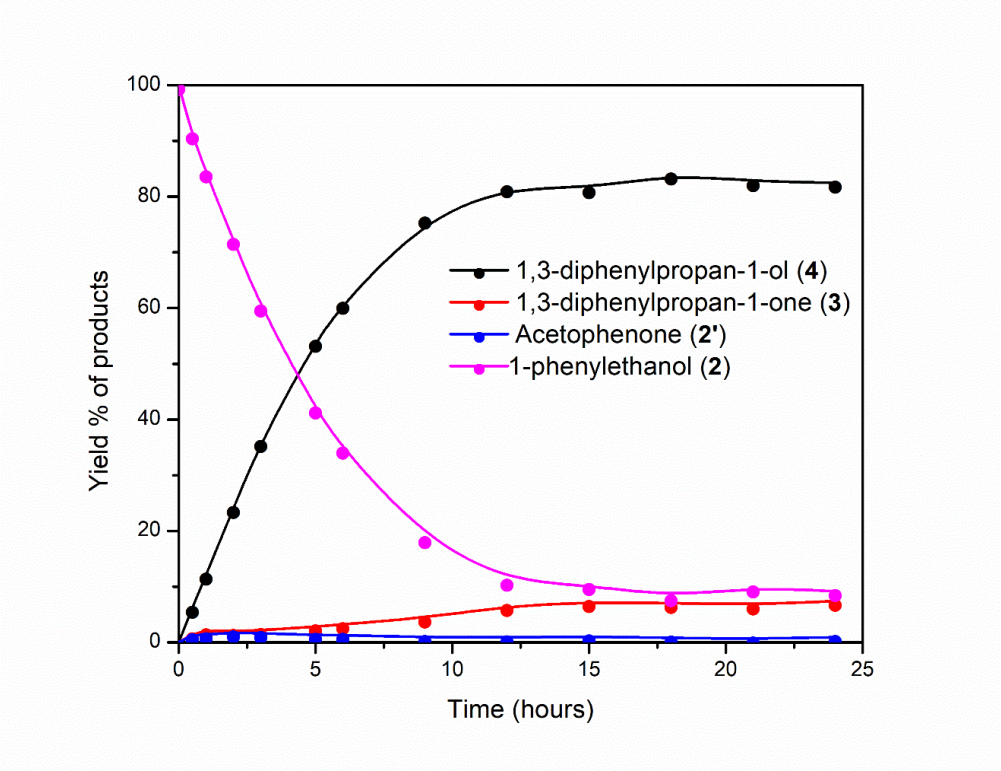


Figure S75: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.1 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

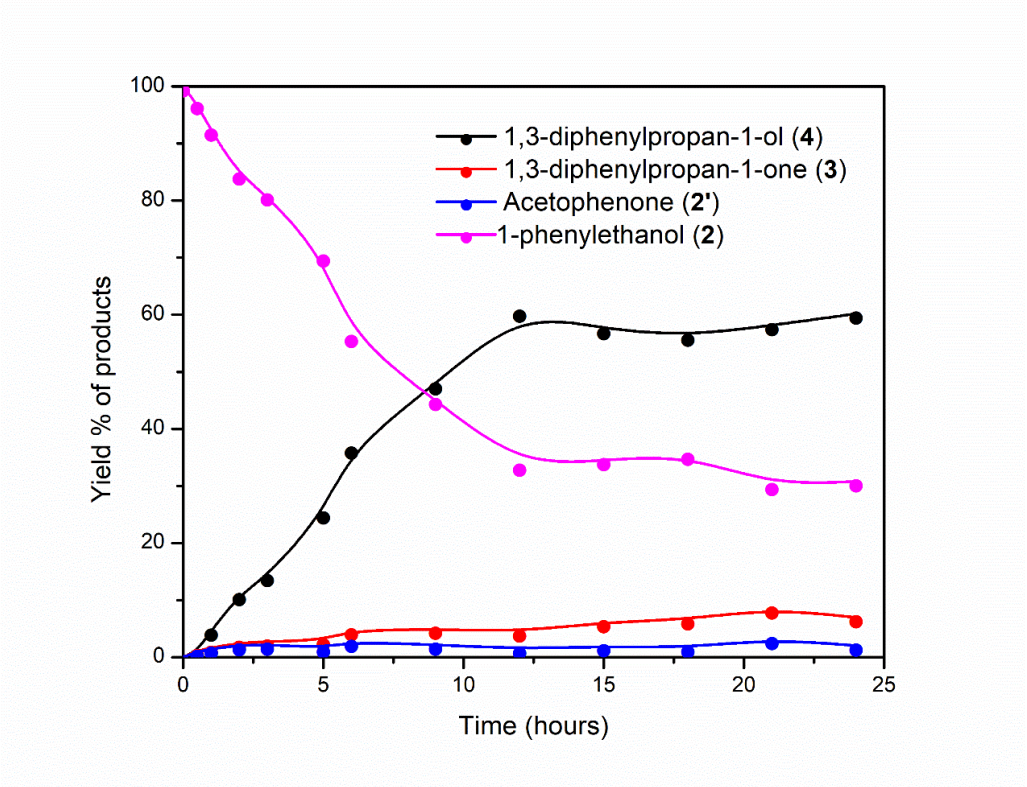


Figure S75a: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.0025 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

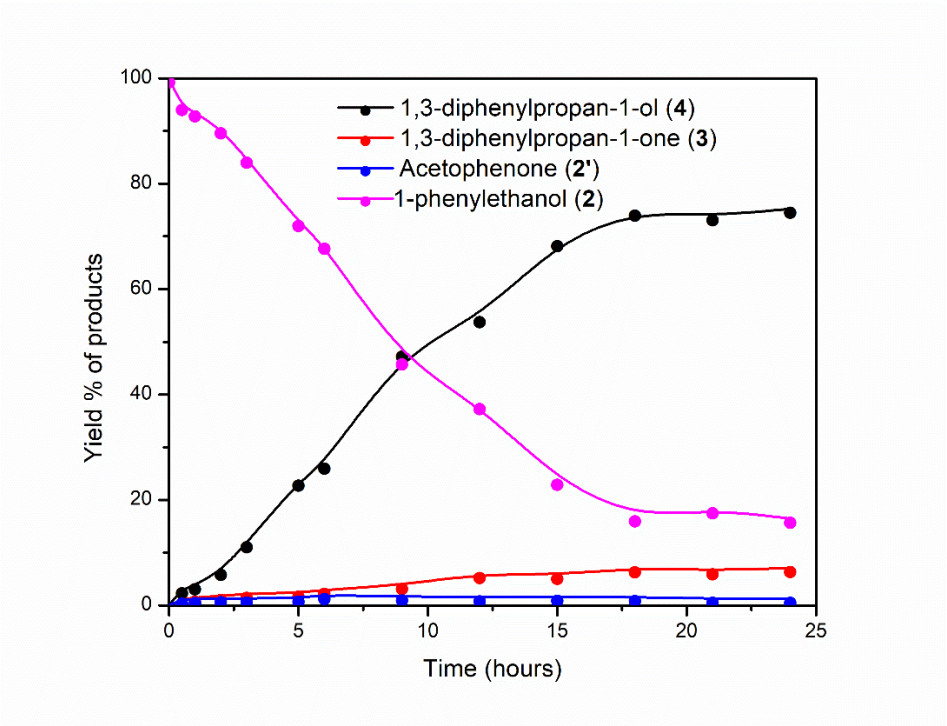


Figure S75b: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01375 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

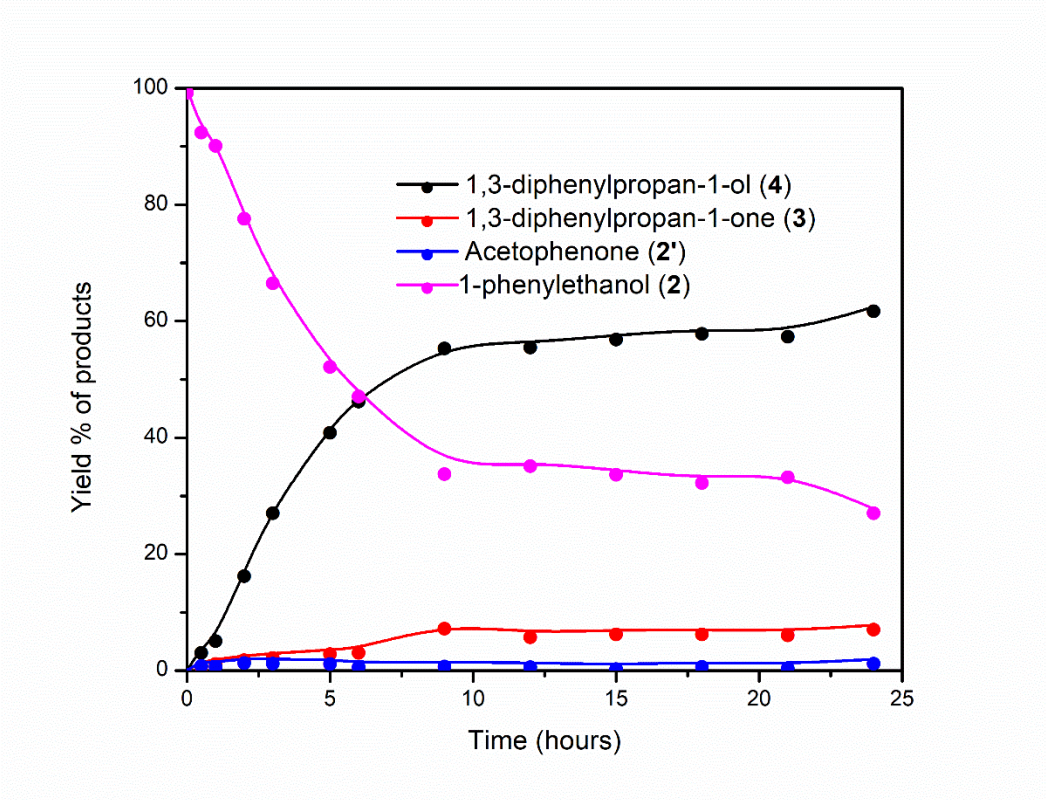


Figure S75c: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.0175 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

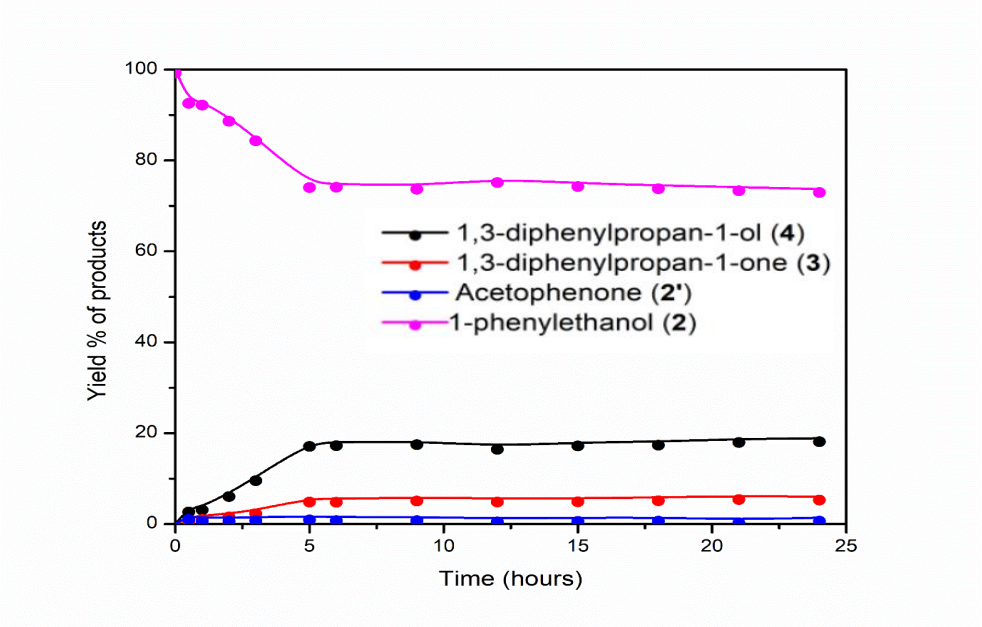


Figure S76: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 1 mol% NaO^tBu at 140 °C

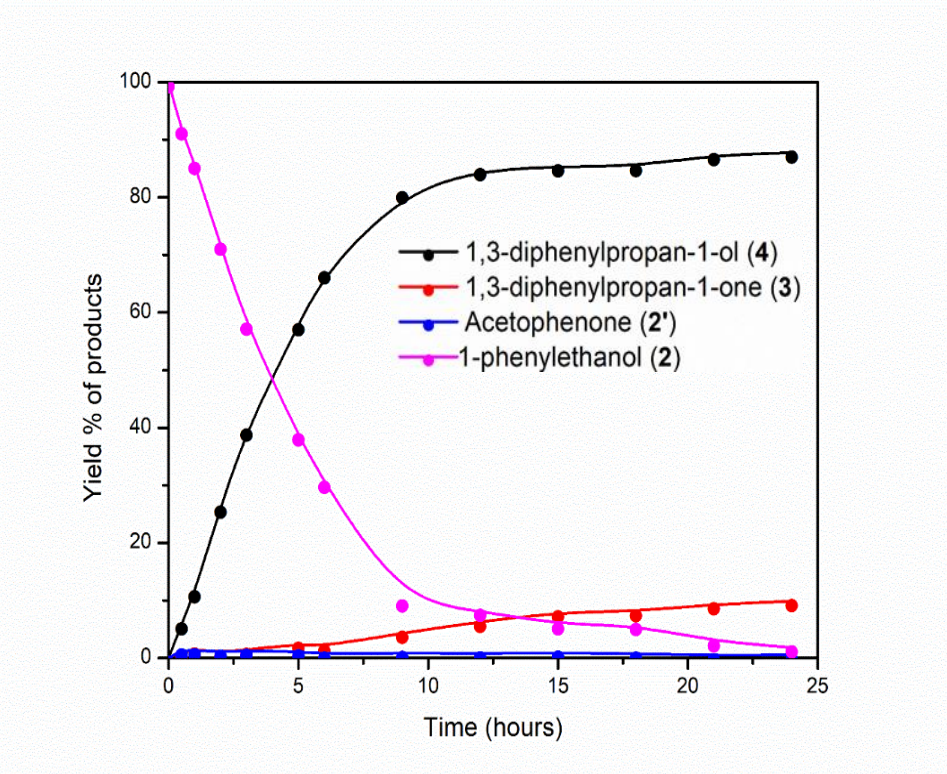


Figure S77: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 5 mol% NaO^tBu at 140 °C

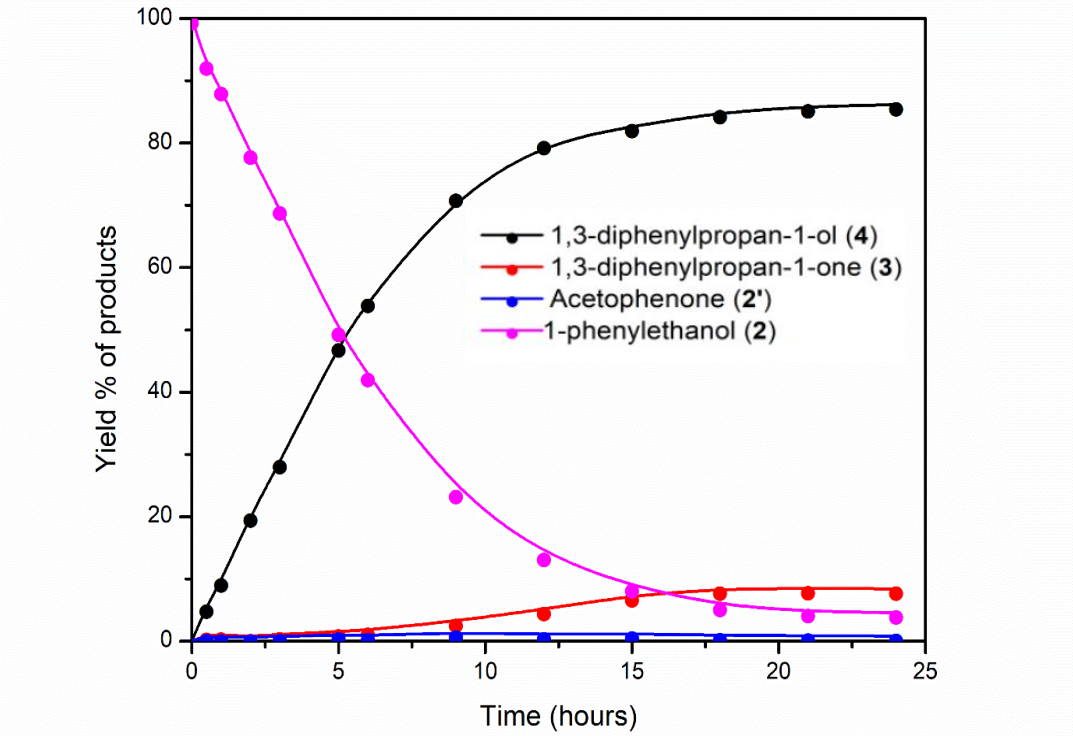


Figure S78: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 10 mol% NaO^tBu at 140 °C

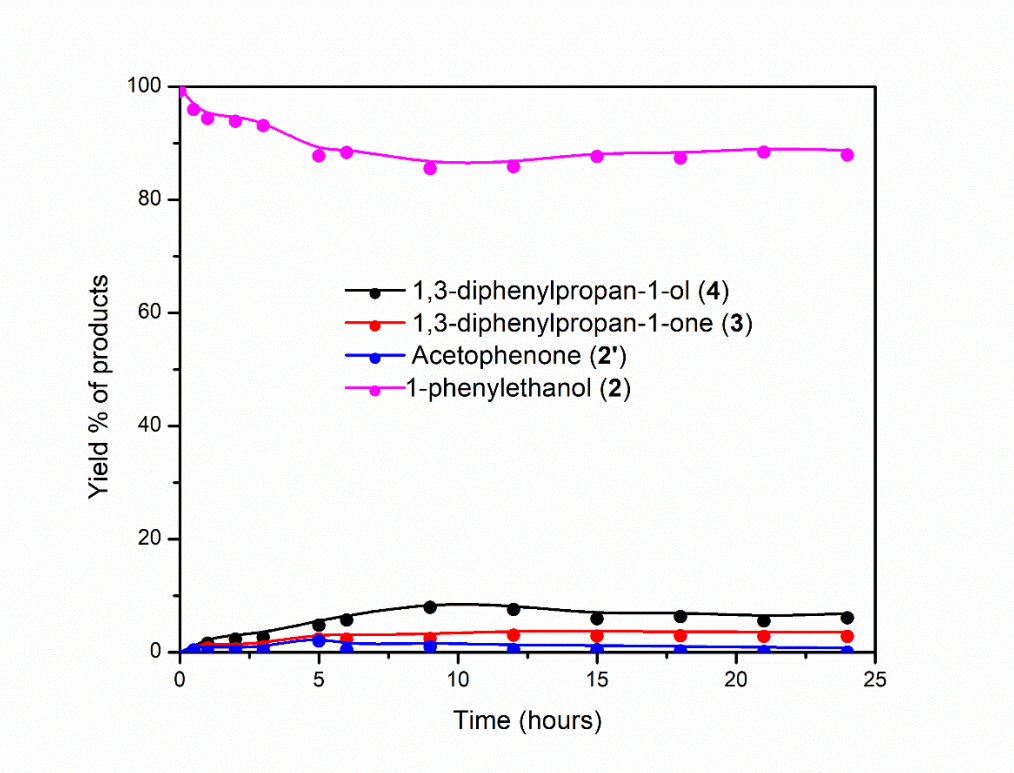


Figure S78a: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 0.5 mol% NaO^tBu at 140 °C

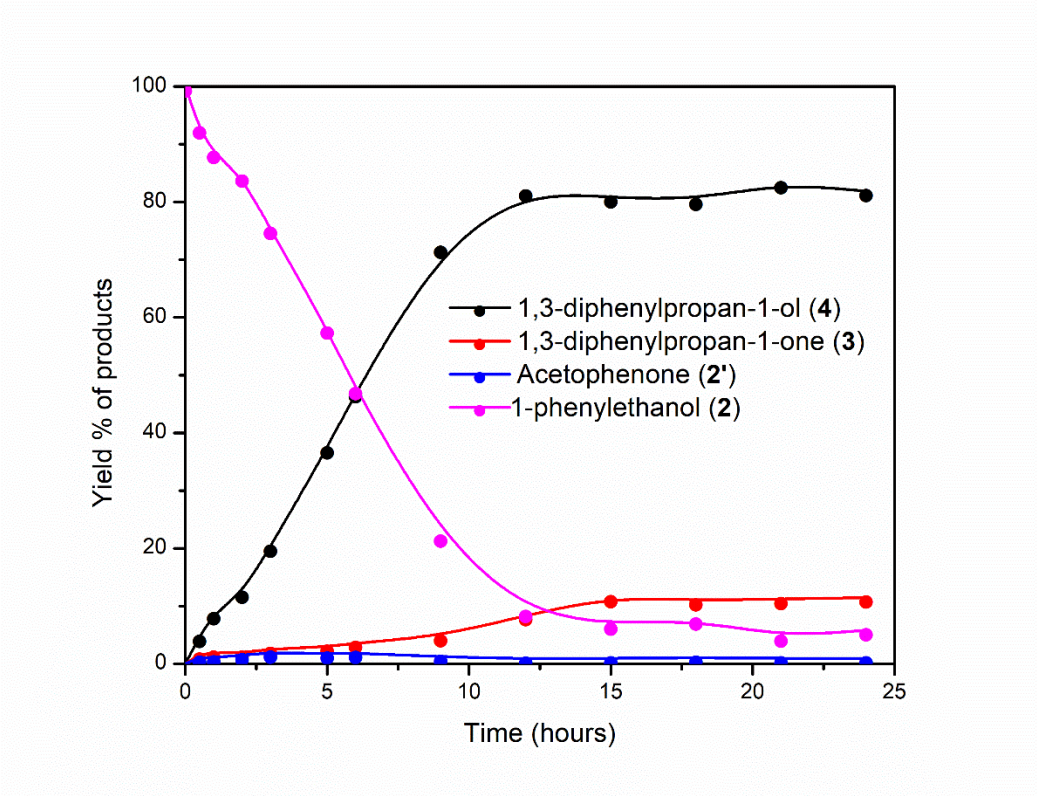


Figure S78b: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 3.75 mol% NaO^tBu at 140 °C

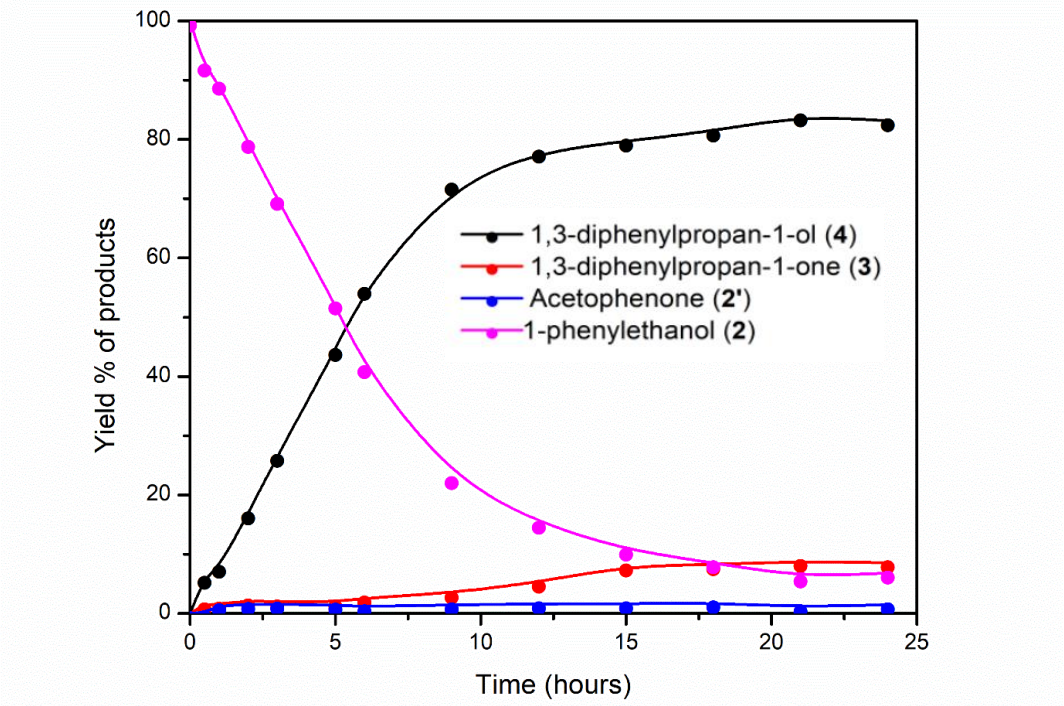


Figure S79: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 3.75 mmol of **1**, 5 mmol of **2**, 129 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

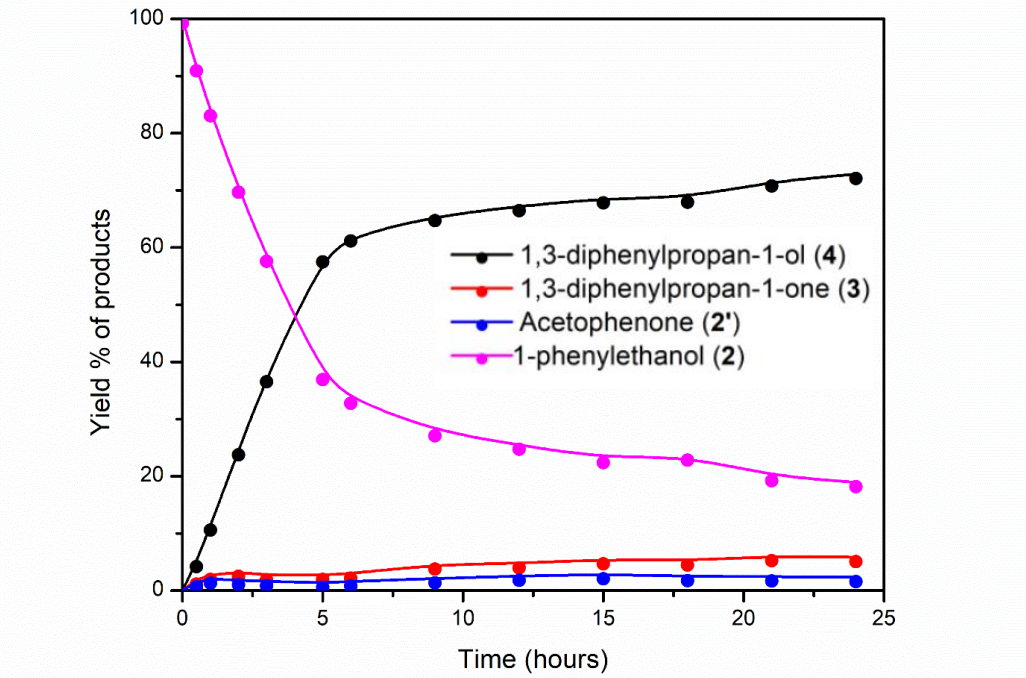


Figure S80: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 2.5 mmol of **1**, 5 mmol of **2**, 257 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

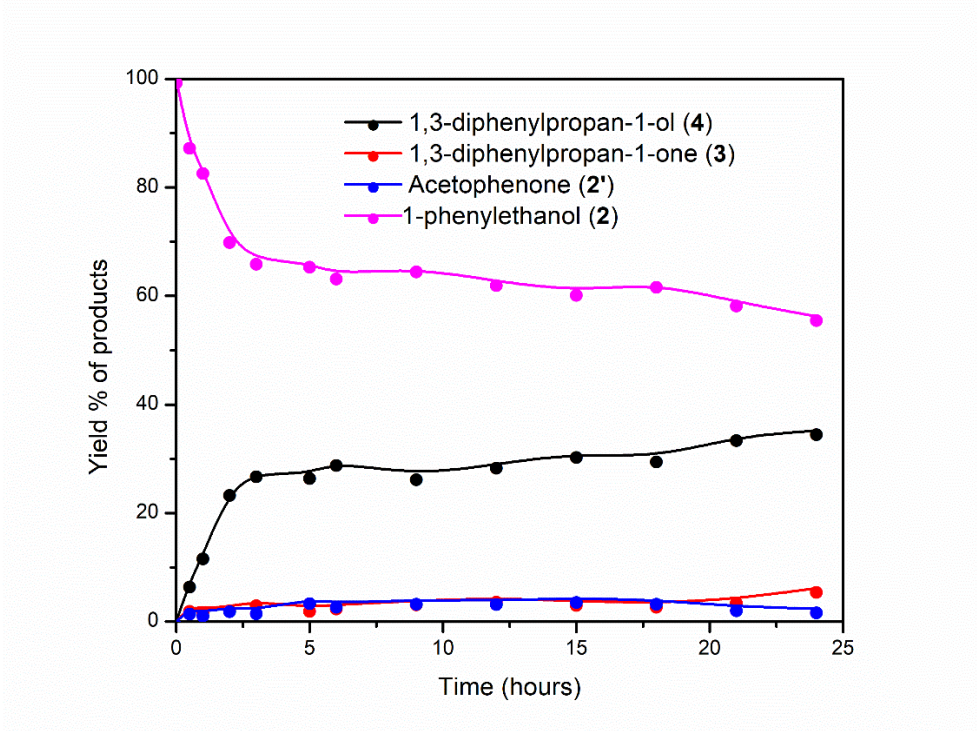


Figure S80a: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 0.625 mmol of **1**, 5 mmol of **2**, 450.6 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

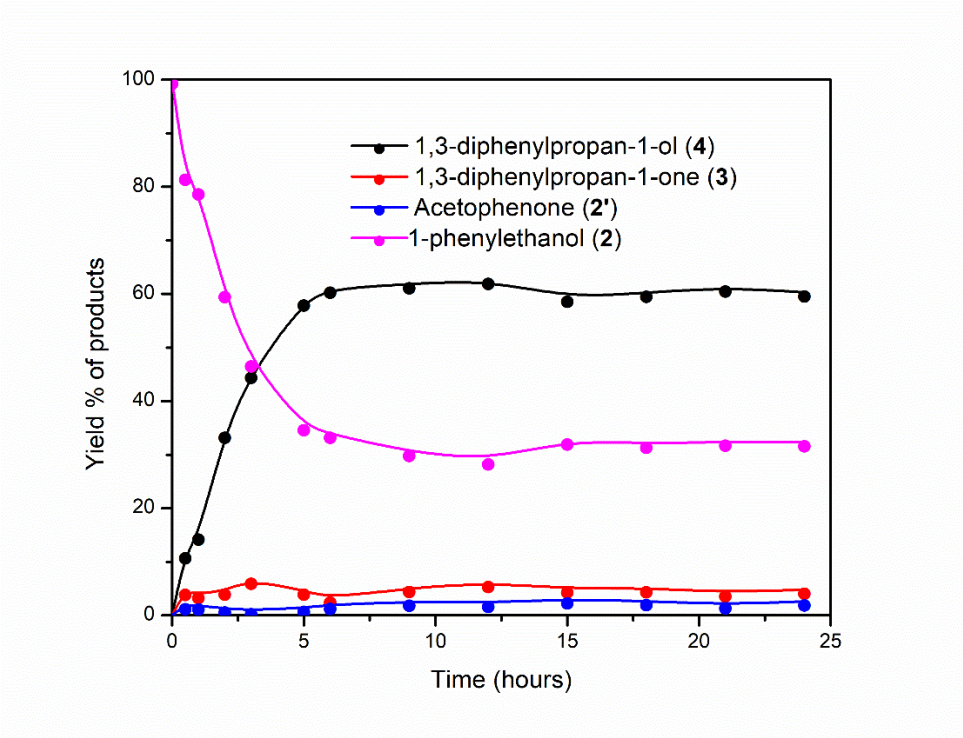


Figure S80b: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 1.25 mmol of **1**, 5 mmol of **2**, 386 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

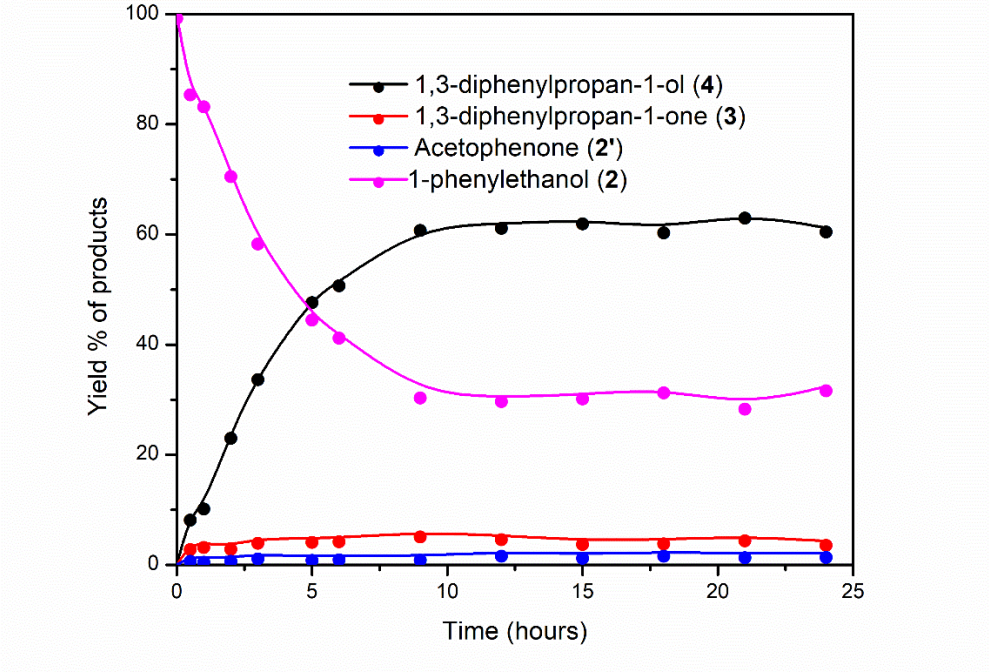


Figure S80c: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 1.875 mmol of **1**, 5 mmol of **2**, 322 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

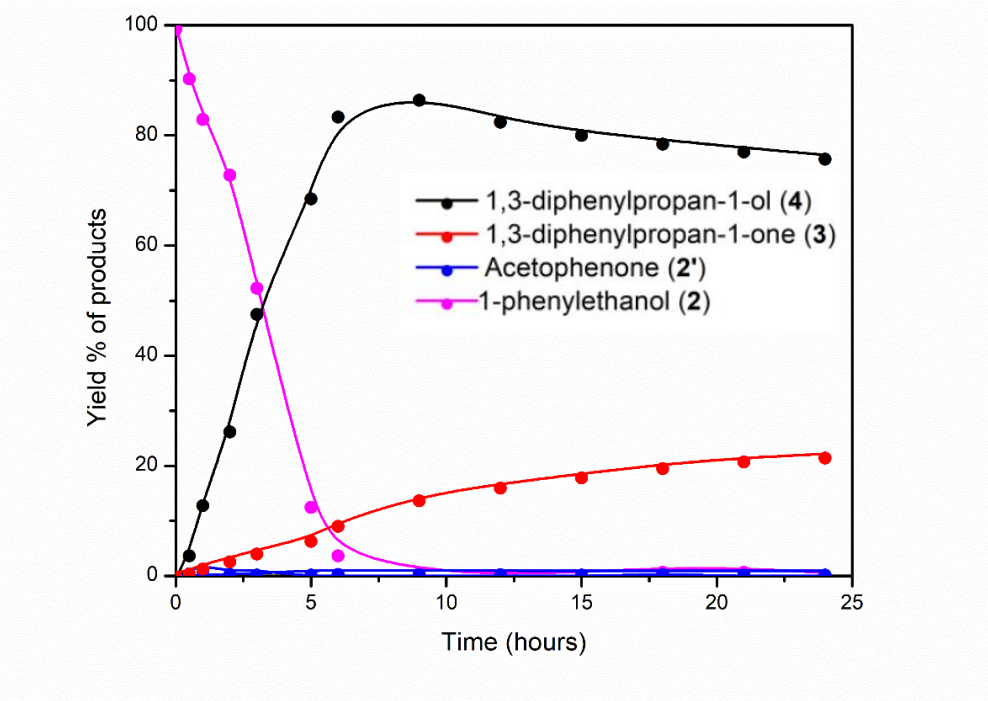


Figure S81: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 2.5 mmol of **2**, 302 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

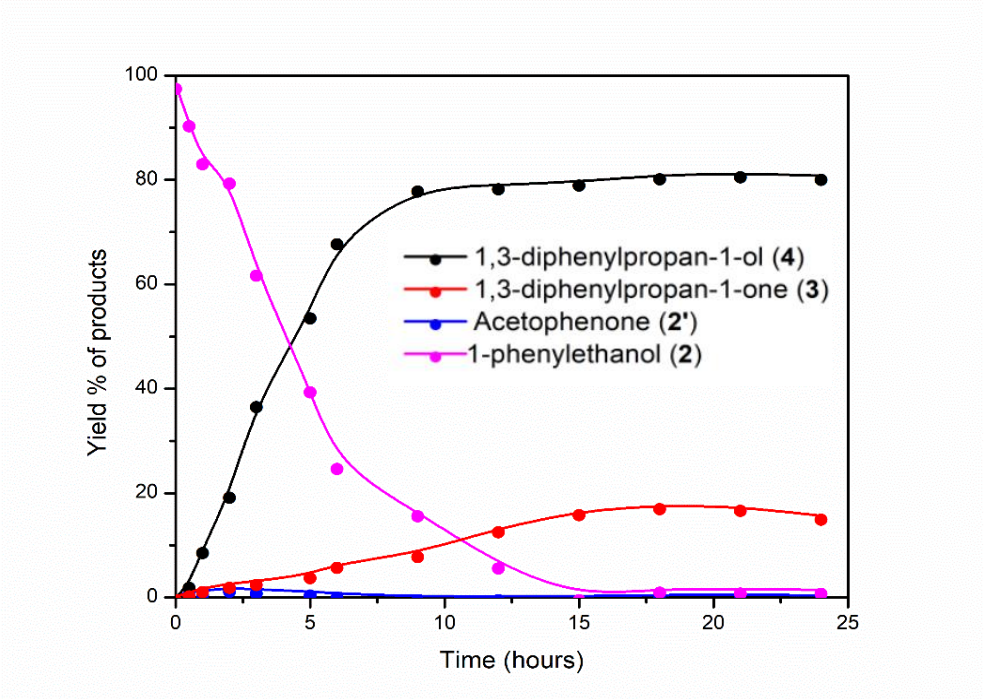


Figure S82: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 3.75 mmol of **2**, 151 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

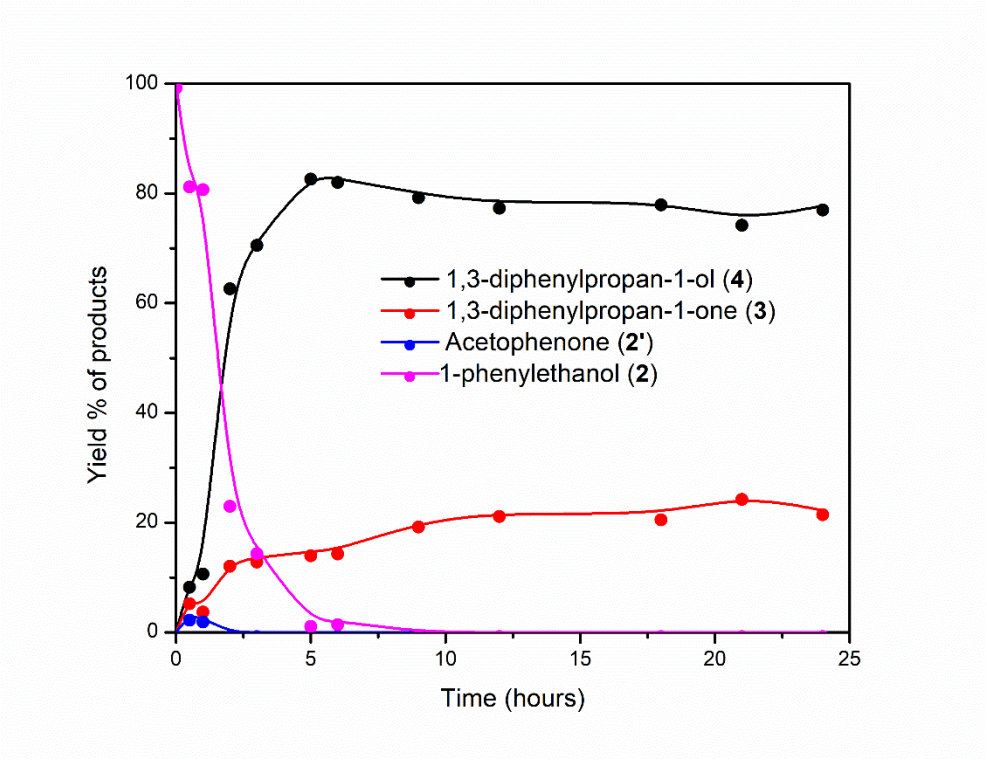


Figure S82a: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 0.625 mmol of **2**, 529 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

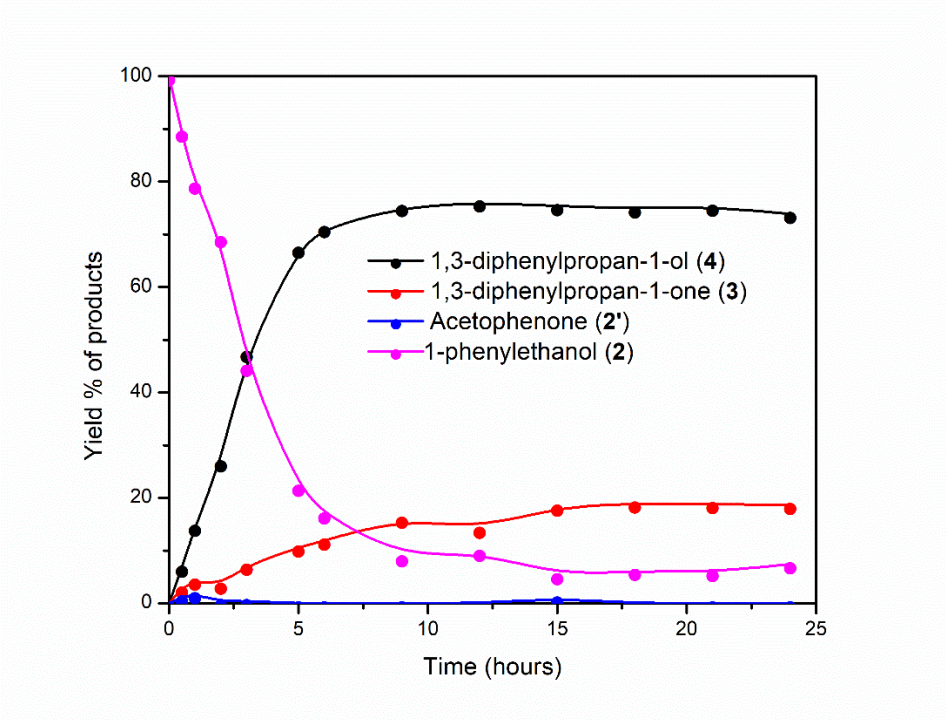


Figure S82b: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 1.25 mmol of **2**, 453 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

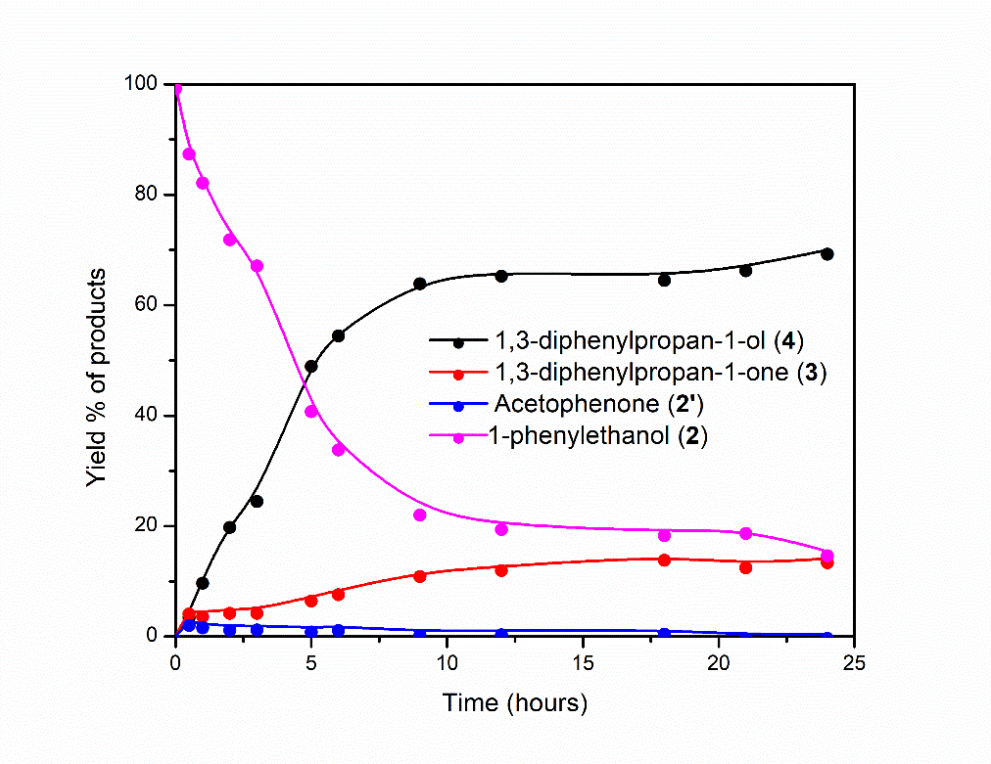


Figure S82c: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 5 mmol of **1**, 1.875 mmol of **2**, 377 μL mesitylene, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

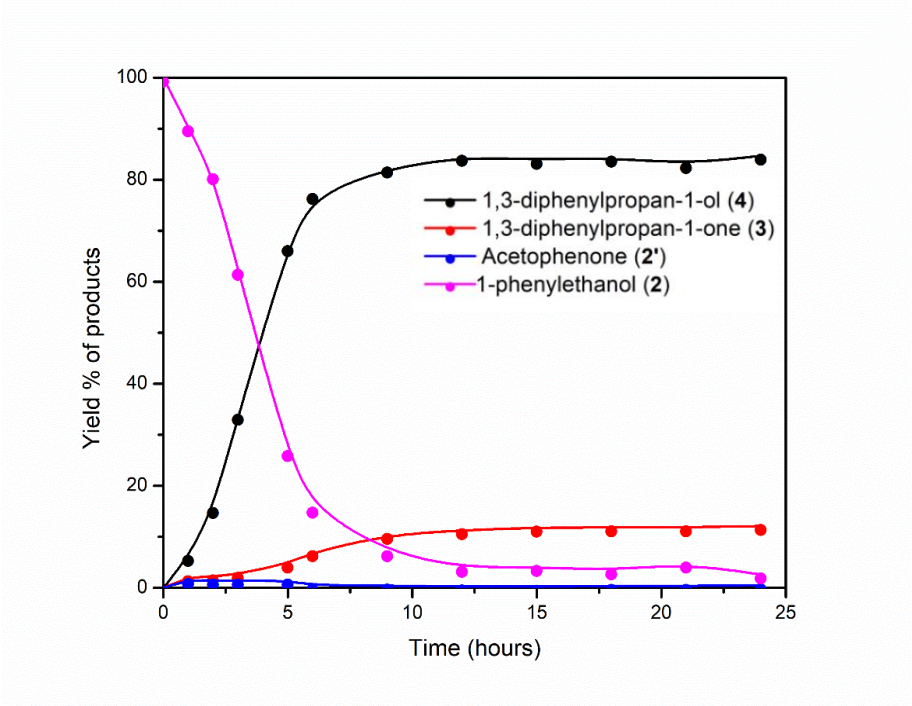


Figure S83: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: after hot filtration with 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

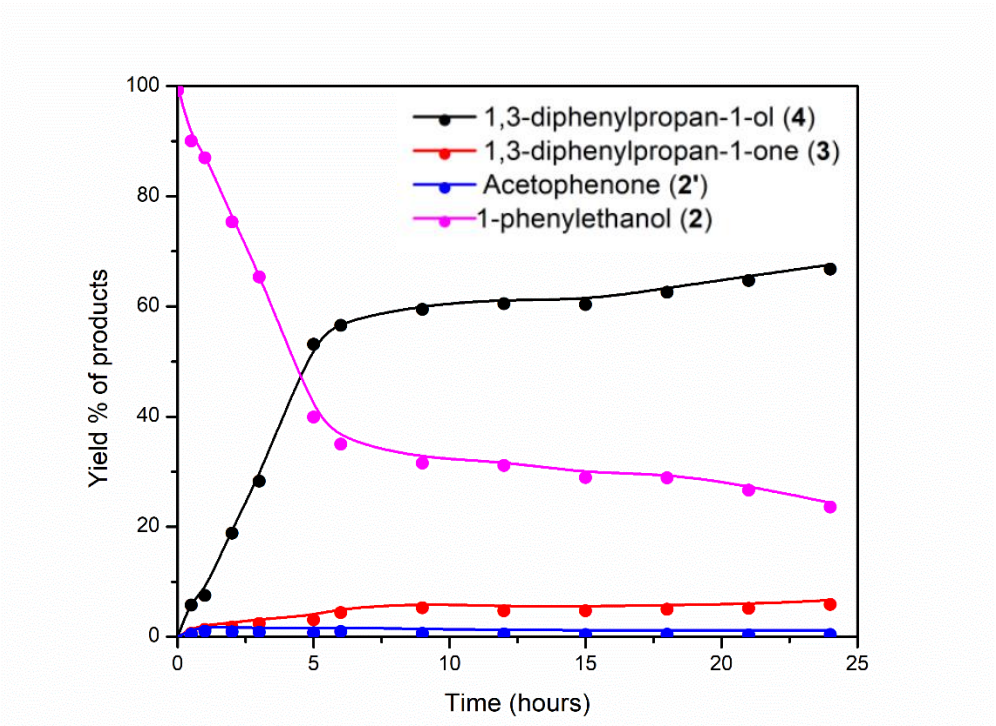


Figure S84: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: 3 hours interval after 3 hours with 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

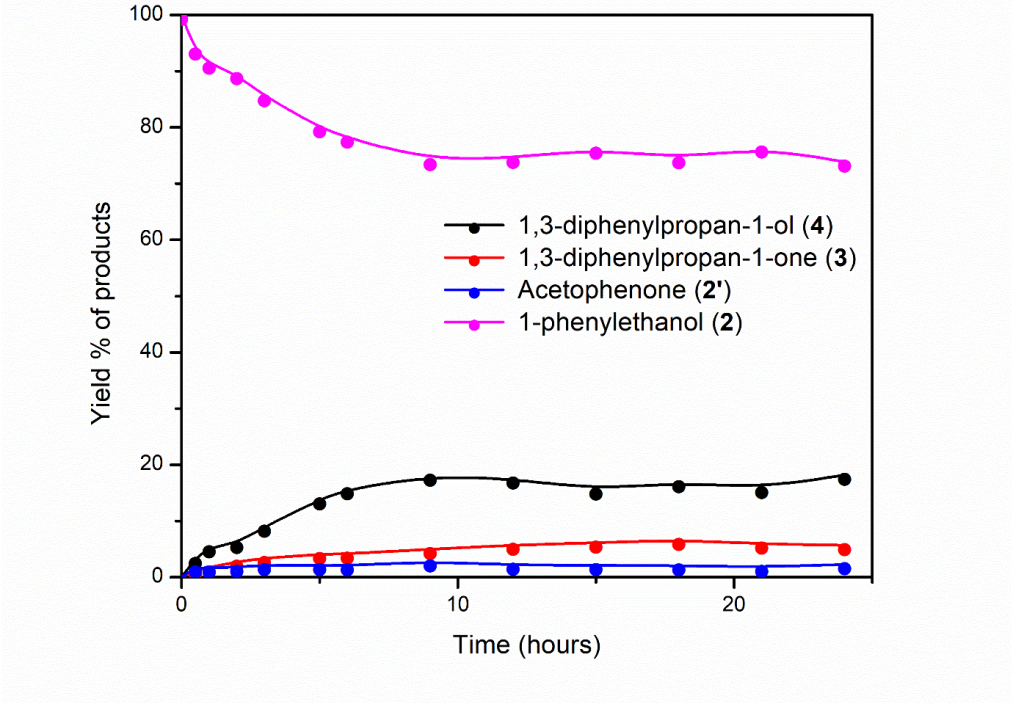


Figure S85: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol (average plot). Reaction condition: 5 mmol of **1**, 5 mmol of **2**, 1 mol% $CoCl_2$, 2.5 mol% NaO^{t}Bu at 140 °C

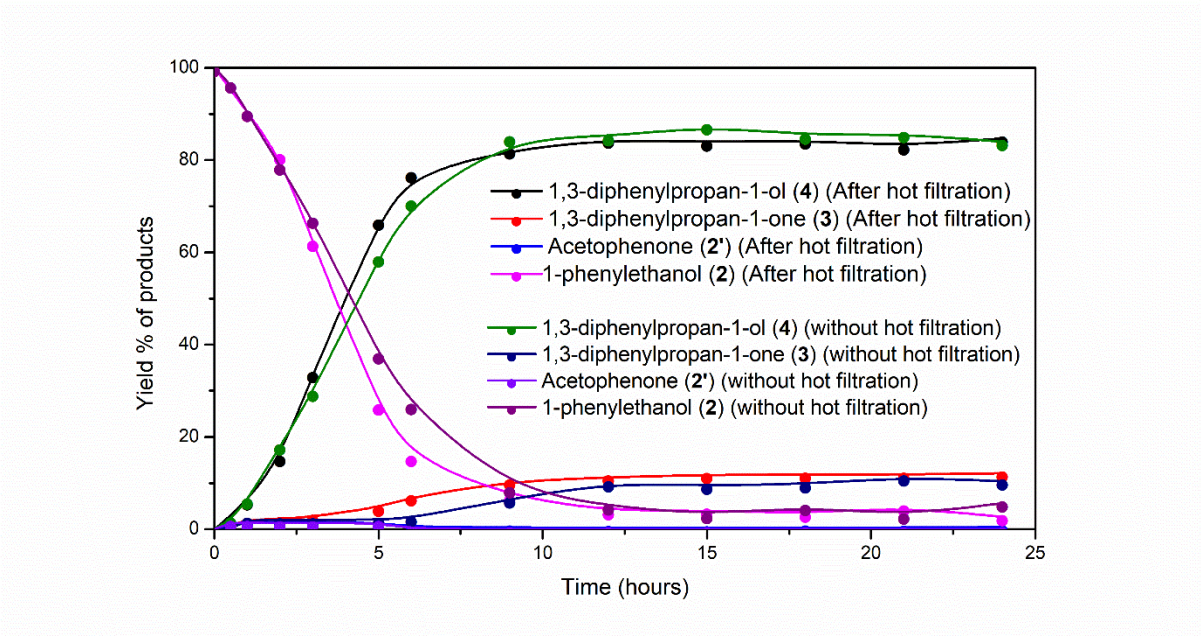


Figure S86: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: after and before hot filtration with 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

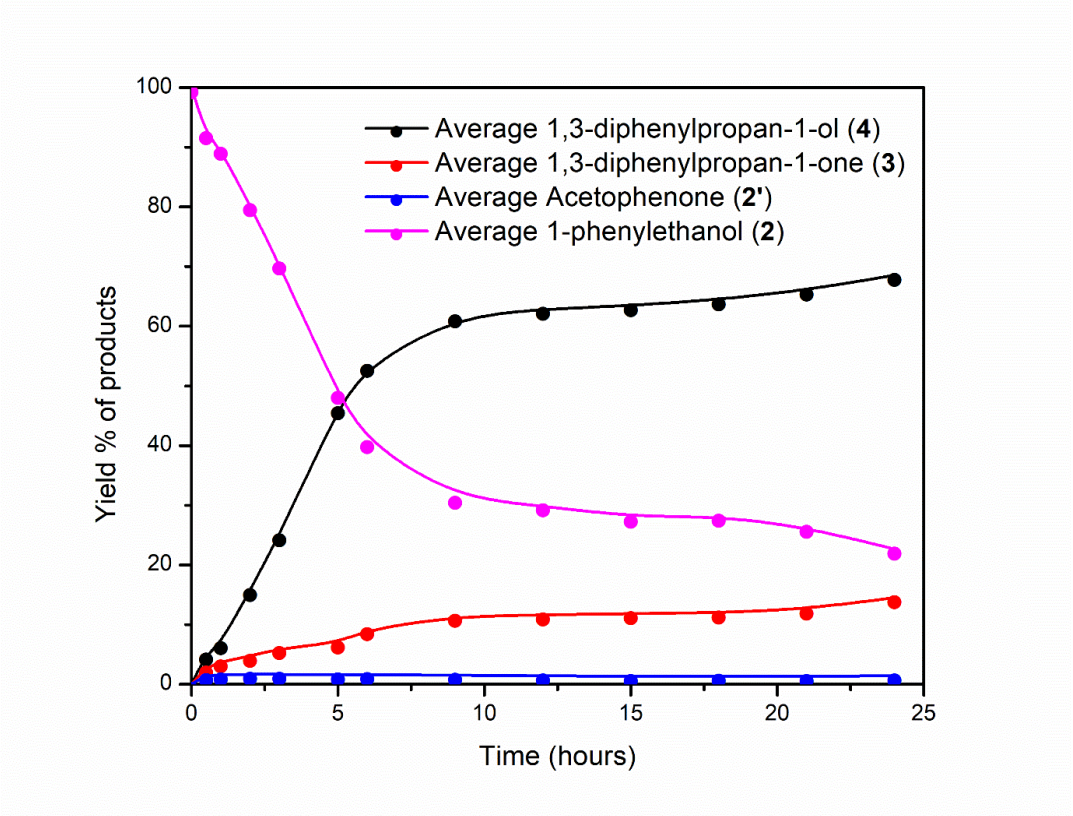


Figure S87: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: average plot of 3h interval after 3h with 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

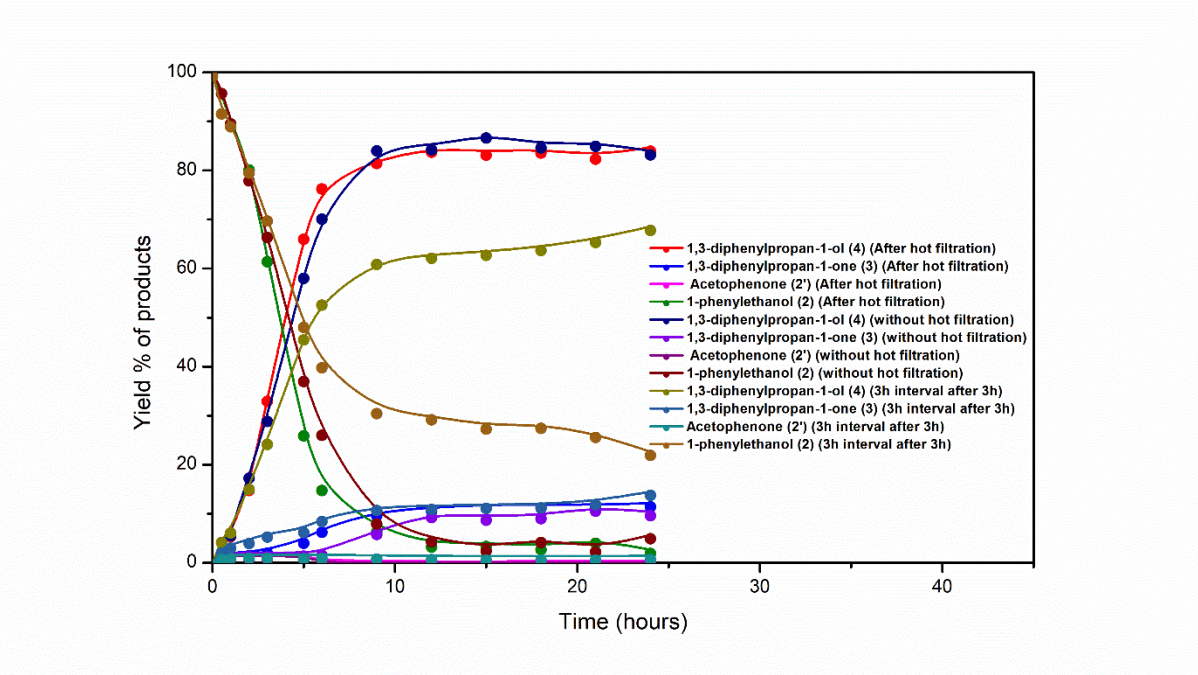


Figure S88: Time-profile of the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol. Reaction condition: effect of hot filtration with 5 mmol of **1**, 5 mmol of **2**, 0.01 mol% $CoCl_2$, 2.5 mol% NaO^tBu at 140 °C

8. FESEM Analysis

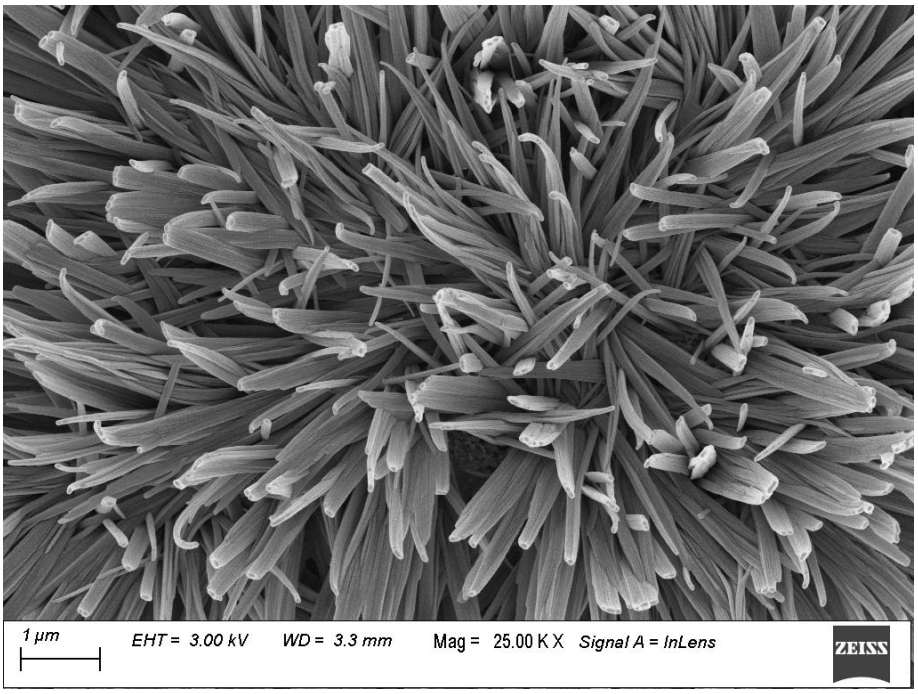


Figure S89: FESEM image of the black particles formed in the *β*-alkylation reaction (entry 7, Table 1).

9. TEM Analysis

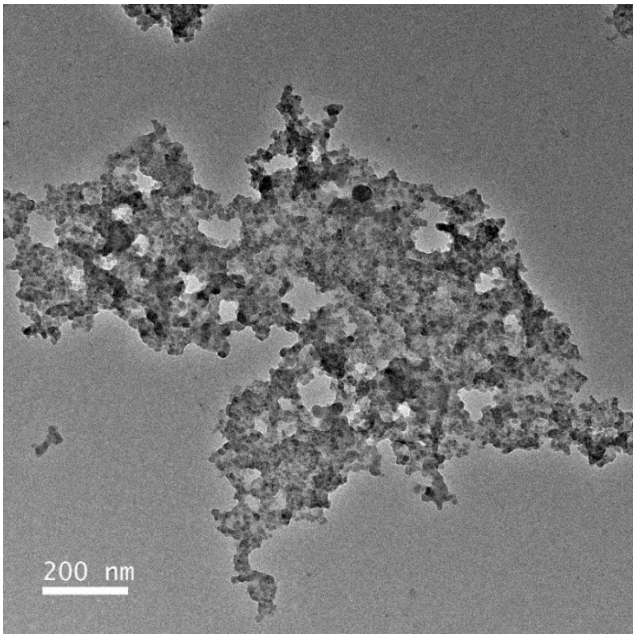


Figure S90: TEM image of the black particles formed in the *β*-alkylation reaction (entry 7, Table 1).

10. Evidence for the formation of Black particles

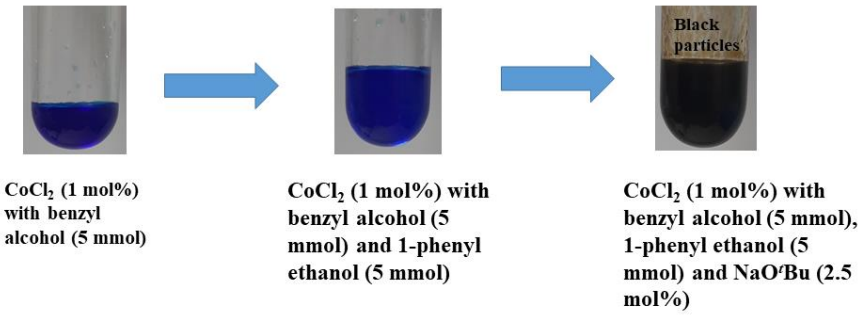


Figure S91: Visual appearance of the reaction mixture in the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol in the presence of 1 mol% $CoCl_2$ and 2.5 mol% of NaO^tBu within 5 minutes (Entry 1, Table 1)

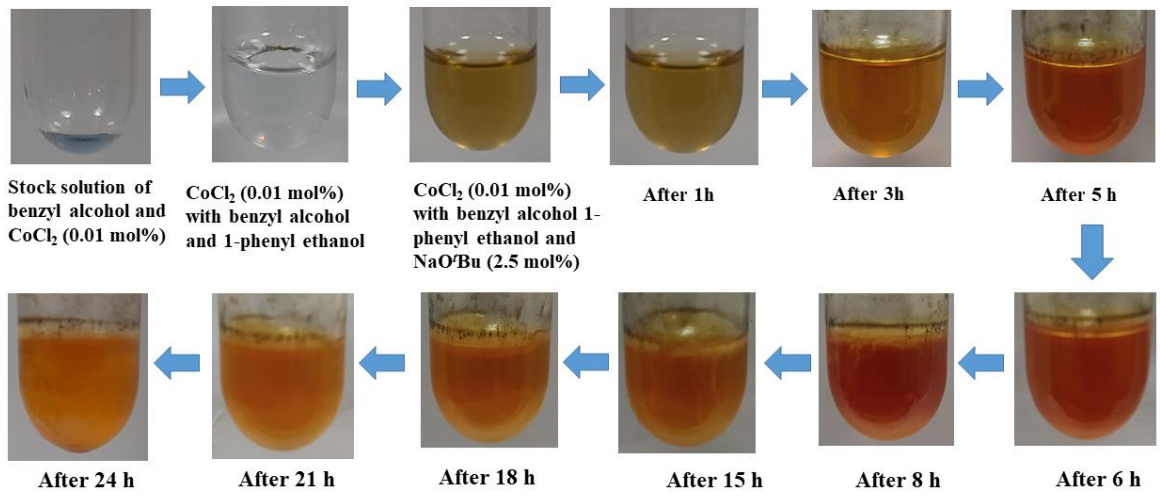


Figure S92: Visual appearance of the reaction mixture in the *β*-alkylation of Benzyl Alcohol with 1-Phenyl Ethanol in the presence of 0.01 mol% $CoCl_2$ and 2.5 mol% of NaO^tBu at 140 °C (Entry 7, Table 1)

11. References

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