Supplementary Information

Co-N_2P_2 Single-Atom Catalysts Enable Efficient α–Alkylation of Aromatic Ketones.

Natarajan Anbuselvan.[a] Selvam Sivaprakash,[a] Duraiarasan Sneha,[a] Biplab Ghosh,[b,c] Devarajan Suresh,*[a] and Arlin Jose Amali.*[a]

[a]Department of Chemistry, School of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur, Tamil Nadu, 613 401, India.

[b]Beamline Development &Application Section, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India.

[c]High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India

Experimental Methods

Materials and reagents

All the chemicals, reagents, and solvents were purchased from commercial suppliers (Sigma Aldrich, Merck, Hi-Media) and used without further purification.

Characterization

The phase composition was investigated using a Powder X-ray diffractometer (XRD, Rigaku, Japan) instrument with K_β filter for Cu-K_α radiation at 2θ = 10 °- 80 ° and a scan speed of 5 min. High-resolution transmission electron microscope (HR-TEM) characterization was carried out with a Tecnai G^2 Spirit microscope operating at 200 kV. Inductively Coupled Plasma Atomic Emission Spectroscope (ICP-AES) analysis was carried out by using SPECTRO (GmbH, Germany) Analytical Instruments at IIT Bombay. The surface analysis was determined by model K-alpha XPS (X-ray Photoelectron Spectrometer) manufactured by Thermo scientific (USA). Co XANES and XAFS spectra were carried out on Co-N_2P_2 sample in fluorescence mode at BL-09 of Indus-2, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore. The Co K-edge energy range were calibrated using Co foil at 7709 eV. For the analysis of the XAFS data, the energy-dependent absorption coefficient μ(E) has been converted to the energy-dependent absorption function χ(E) and then to the wave number-dependent absorption coefficient χ(k). Finally, k3 weighted χ(k) spectra were Fourier transformed in R space to generate the χ(R) versus R spectra regarding the accurate distance from the center of the absorbing atoms. The XANES and XAFS data were analyzed using the FEFF 6.0 code 1 with the help of the Demeter software program. The interatomic distances and number of atoms were calculated by normalizing the backscattering amplitude and phase functions from FEFF to fit the EXAFS data. EXAFS data best fit were obtained to minimize Rfactor in the above process.

Preparation of porous carbon from rice husk

The rice husk was activation carried out by previously reported literature. The first step, Rice husk (5.0 g) and H_3PO_4 (10.0 g) was taken in a beaker and stirred at 12h at room temperature. Then it dried at 100 °C for 24 h. Resultant material subjected to pyrolysis at 550 °C (5 °C/min) for 1 h under N_2 atmosphere. After that, the sample was washed with deionized water until reach the neutral pH, and the H_3PO_4-activated carbon samples were labeled as AC. In second step, AC (1.0 g) and $K_2C_2O_4$ (3.0 g) at 1:3 mass ratio grounded into fine powder. Then it was pyrolyzed at 800 °C for 1 hour under N_2 atmosphere. The temperature was cooled down to room temperature and washed with water to afford porous carbon (PC).

Synthesis of Covalent Triazine Polymer (CTP)

In a typical method, cyanuric chloride (6.0 mmol, 1.25 g) and melamine (6.0 mmol, 0.76 g) were dissolved in 70 mL of acetonitrile, and stirred at room temperature for 6 h under N_2 atmosphere. Then the solution was transferred into the teflon-lined stainless steel autoclave heated at 200 °C for 24 h and cooled down to room temperature. The dark red colour precipitate was separated by centrifugation, washed with excess acetonitrile, ethanol, and DI water three times, respectively, and then dried overnight in a vacuum oven at 100 °C.

Synthesis of $Co(PPh_3)_2Cl_2$ complex

In a round-bottom flask, $CoCl_2.6H_2O$ (1.0 mmol) was dissolved in isopropanol (5 mL), and a solution of triphenylphosphine (2.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise under stirring. The reaction mixture was refluxed for 4 h. The solid product was collected by filtration, washed with 10% ethyl acetate in hexane, and dried under vacuum to afford the $Co(PPh_3)_2Cl_2$ complex.

Synthesis of Co single atom catalyst trapped on hierarchically porous carbon doped with P and N (Co-N_2P_2)

In a 100 mL round bottom flask, porous carbon (0.5 g) and N-CTP (0.5 g) were mixed in acetone (50 mL) to obtain a uniform dispersion. Subsequently, $CHCl_3$ (5 mL) containing $Co(PPh_3)_2Cl_2$ (r) added. The reaction mixture was stirred at room temperature for 24 h. The resulting precipitate was filtered and washed with acetone and EtOH to remove unbound metal ions. Finally, the obtained solid was subjected to pyrolysis at 800 °C (5 °C min^{-1}) under N_2 flow for 4 h to afford the Co-N_2P_2.

General Procedure for α-Alkylation of the ketones with benzyl alcohol

In a screw capped tube, aromatic ketone (0.5 mmol), benzyl alcohol (0.6 mmol), Co-N_2P_2 (10 mg, 4.04717×10^{-7} mmol), KO^tBu (0.5 mmol), and toluene (1.0 mL) were added and the tube was sealed and heated at 100 °C for 12 h. After that, the tube was cooled down to room temperature, catalyst was separated by centrifugation and the solvent was evaporated under reduced pressure. The crude product was extracted with ethyl acetate twice. The organic layer dried over anhydrous sodium sulphate (Na_2SO_4), then the solvent was evaporated under reduced pressure. Finally, the product was purified by column chromatography using hexane/ethyl acetate as the eluent.

Acid leaching test

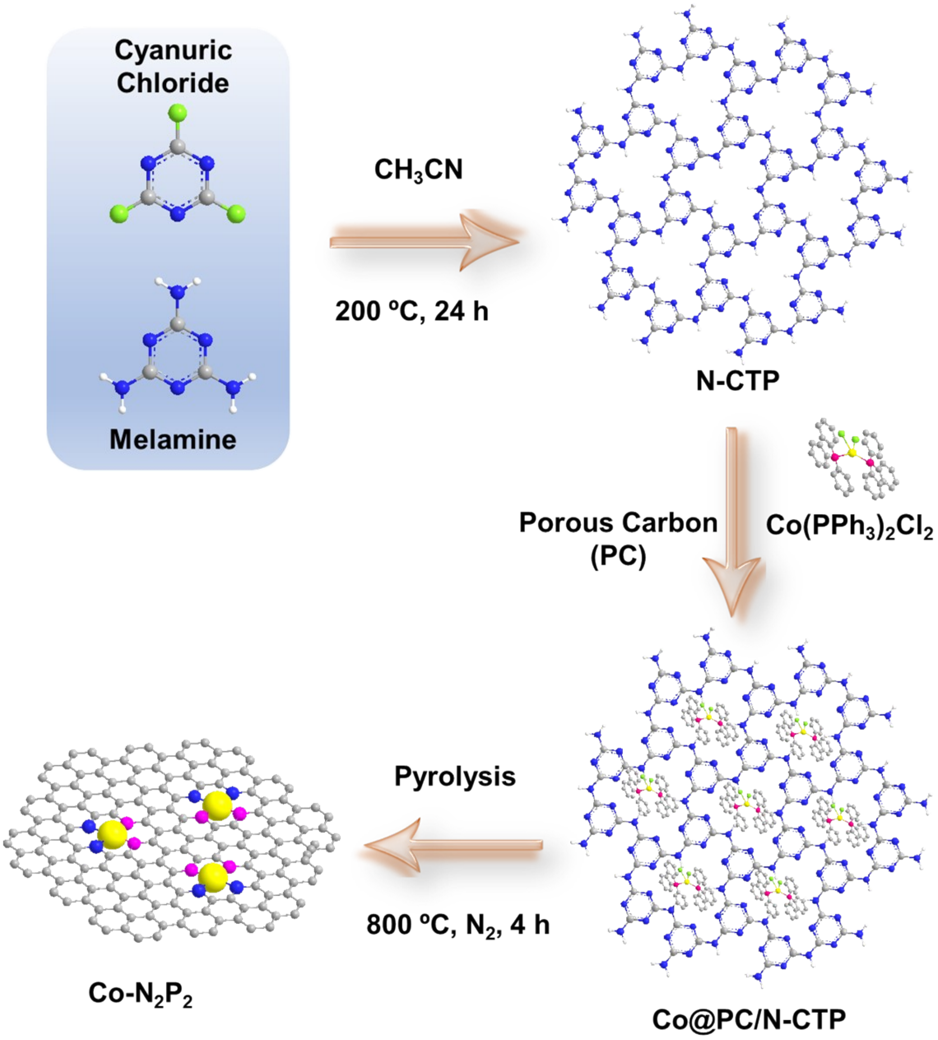
For acid treatment, the fresh catalyst (50 mg) was dispersed in 5 M HCl (25 mL) and stirred at room temperature for 12 h. The solid was washed with deionized water until the filtrate reached neutral pH (~7) and dried at 60 °C overnight. The acid-treated catalyst was subsequently employed for α-alkylation of the ketones with benzyl alcohols under the standard reaction conditions.

KSCN Poisoning test

Co-N_2P_2 (50 mg), KSCN (5.0 mmol) and water (5.0 mL) were added (5 mL) in a round-bottom flask and stirred at room temperature for 12 h. The resulting solid was filtered, washed thoroughly with deionized water, and dried in an oven at 60 °C overnight. The obtained material was subsequently employed for α-alkylation of the ketones with benzyl alcohols under the standard reaction conditions.

Gram scale synthesis of 1,3-diphenylpropan-1-one catalyzed by Co-N_2P_2

In a screw capped tube, acetophenone (1.0 g, 8.3 mmol), benzyl alcohol (0.89 g, 8.3 mmol), Co-N_2P_2 catalyst (0.1 g, 4.04717×10^{-6} mol), KO^{t}Bu (0.93 g, 8.3 mmol), and toluene (15 mL) were added and heated at 100 °C 12 h. After that, the tube was cooled down to room temperature, catalyst was separated by centrifugation and the solvent was evaporated under reduced pressure. The crude product was extracted with ethyl acetate twice. The organic layer dried over anhydrous sodium sulphate (Na_2SO_4), then the solvent was evaporated under reduced pressure. Finally, the product was purified by column chromatography using hexane/ethyl acetate as the eluent. Green chemistry metrics was determined (Table S5).



Scheme S1. Schematic representation of synthesis of Co single atom catalyst trapped on hierarchically porous carbon doped with P and N ($Co-N_2P_2$).

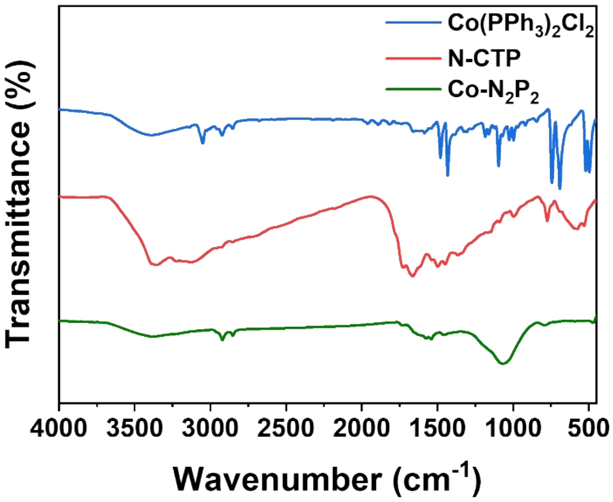


Fig. S1. FT-IR spectra of Co(PPh$_3$)$_2$Cl$_2$, N-CTP and Co-N$_2$P$_2$

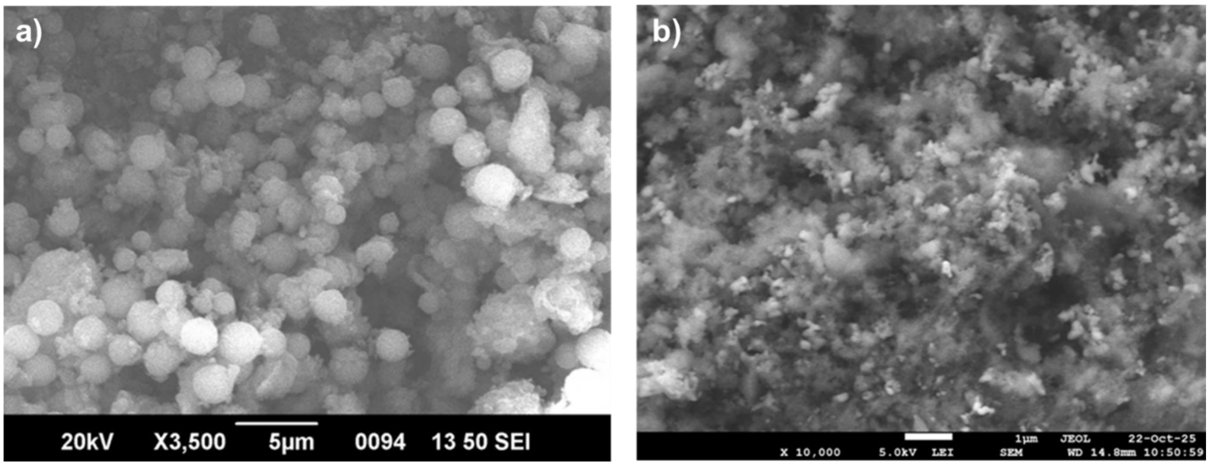


Fig. S2. SEM images of N-CTP (a) and Co-N$_2$P$_2$ (b).

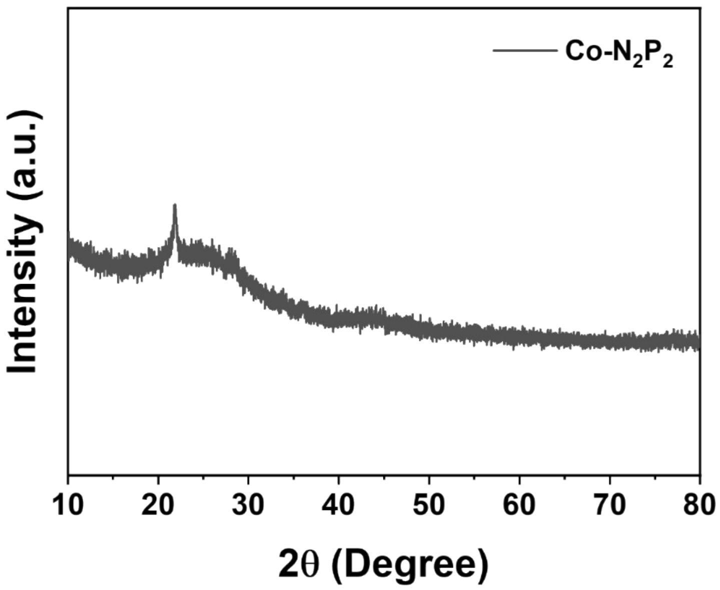


Fig. S3. PXRD pattern of Co-N$_2$P$_2$.

Table S1. ICP-AES result of Co-N$_2$P$_2$

Sample	Co (ppm)
Co-N$_2$P$_2$	**2.385**

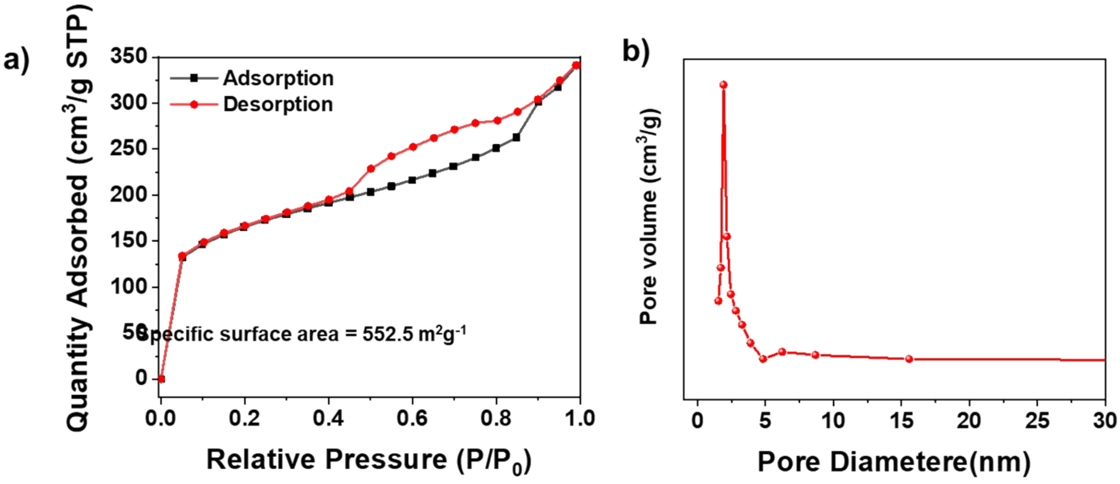


Fig. S4. N_2 adsorption-desorption isotherm (a) and the corresponding pore size distribution plot (b) of Co-N_2P_2.

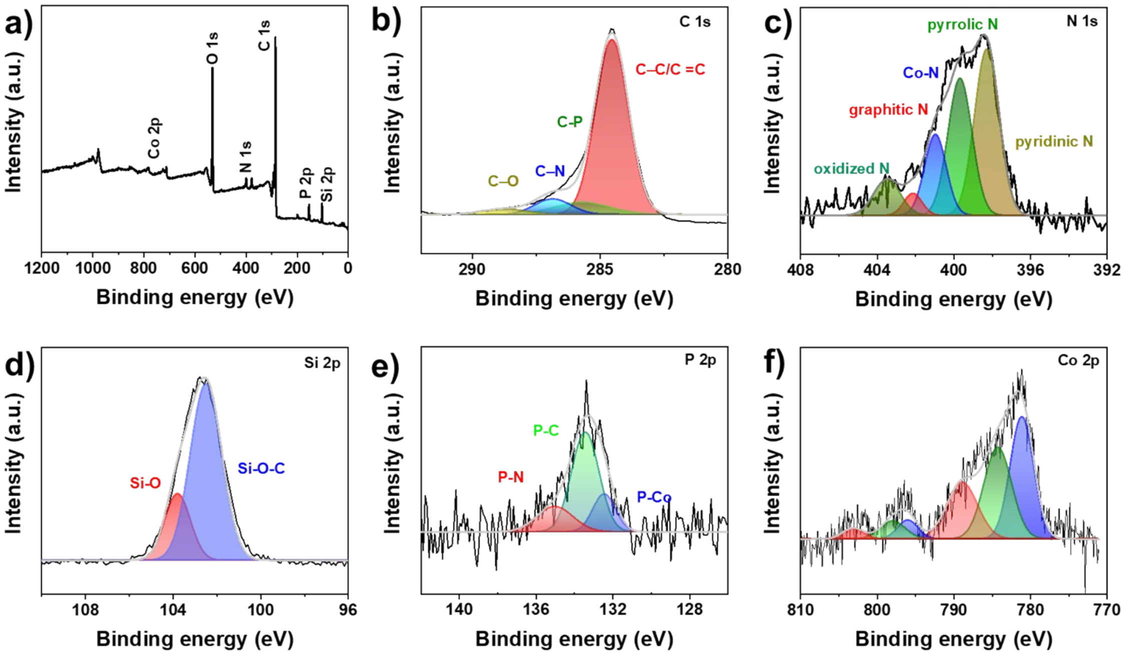


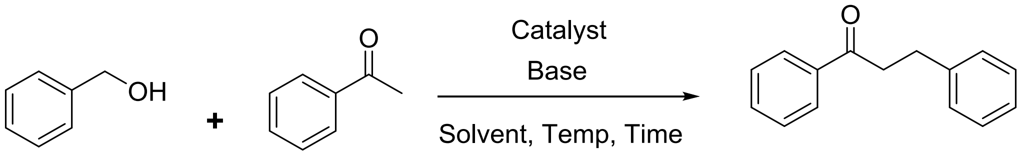
Fig. S5. XPS Spectra of Co-N_2P_2 Survey spectrum (a) C 1s spectra (b) N 1s spectra (c) Si 2p spectra (d) P 2p spectra (e) and Co 2p spectra of Co-N_2P_2

Table S2. K-edge fitting parameters

S.No.	Sample	Path	N	R (Å)	Error (Å)	$\sigma^2 \times 10^2$ (Å^2)	$\triangle E_0$ (eV)	R-factor
1	Co Foil	Co-Co	12.0	2.489	+/- 0.0028	0.006	6.352	0.002
2	CoO	Co-O	6.0	2.094	+/- 0.034	0.011	-4.066	0.009
		Co-Co	12.0	3.003	+/- 0.013	0.009	-4.066	0.009
3	CoPc	Co-N	4.0	1.905	+/- 0.009	0. 003	3.02	0.015
		Co-C	4.0	2.909	+/- 0.013	0. 001	3.02	0.015
4	**Co-N_2P_2**	Co-N	2	1.892	+/- 0.0262	0.0012	-7.633	0.018
		Co-P	2	2.298	+/- 0.0267	0.0009	-7.633	0.018

N - coordination number, R - the internal atomic distance, σ^2 - Debye-Waller factor and $\triangle E_0$ - edge-energy shift.

Table S3. Optimization for the α-alkylation reaction catalyzed by Co-N_2P_2

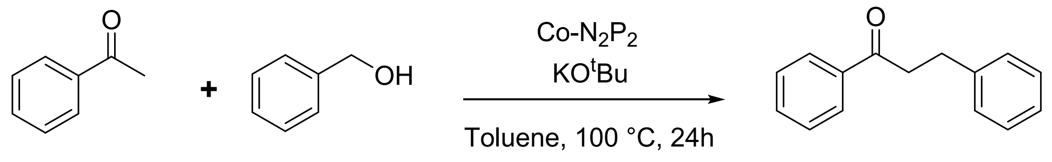


S. No	Catalyst	Solvent	Base	Temp (°C)	Time (h)	Yield (%)
1	-	Toluene	-	100	12	NR
2	-	Toluene	KO^tBu	100	12	NR
3	PC	Toluene	KO^tBu	100	12	NR
4	$Co(PPh_3)_2Cl_2$	Toluene	KO^tBu	100	12	trace
5	Co-N_2P_2	Toluene	-	100	12	NR
6	**Co-N_2P_2**	**Toluene**	**KO^tBu**	**100**	**12**	**90**
7	Co-N_2P_2	Xylene	KO^tBu	100	12	80
8	Co-N_2P_2	H_2O	KO^tBu	100	12	50
9	Co-N_2P_2	Dioxane	KO^tBu	100	12	85
10	Co-N_2P_2	Toluene	KOH	100	12	70
11	Co-N_2P_2	Toluene	NaOH	100	12	64
12	Co-N_2P_2	Toluene	K_2CO_3	100	12	trace
13	Co-N_2P_2	Toluene	Na_2CO_3	100	12	trace
14	Co-N_2P_2	Toluene	KO^tBu	80	12	54
15	Co-N_2P_2	Toluene	KO^tBu	120	12	92
16	Co-N_2P_2	Toluene	KO^tBu	100	18	90
17	Co-N_2P_2	Toluene	KO^tBu	100	24	92

Table S4. Comparison of catalytic activity of Co-N_2P_2 with previously reported catalysts for α-alkylation reactions

S.No.	Catalyst	Mol (%)	Base	Temp (ºC)	Solvent	Yield (%)	No. of runs	Ref
1	Pd/C	1	K_3PO_4	80	toluene	100	4	1
2	Ni/SiO_2-Al_2O_3	20	K_3PO_4	175	---	86	5	2
3	CuO_X-250	71	K_3PO_4	170	n-hexane	90	5	3
4	LCN@Zn-SAC	1.5	KOH	110	toluene	92	8	4
5	Nano-Fe_2O_3	30	KO^tBu	135	toluene	97	5	5
6	MnO_2@PDCS	1.5	NaOH	120	toluene	89	6	6
7	Mn-MgO/Al_2O_3	9.1	-	160	toluene	95	4	7
8	Mn@CeO_2	10	NaOH	130	toluene	98	6	8
9	**Co-N_2P_2**	**0.8**	**KO^tBu**	**100**	**toluene**	**92**	**5**	**This work**

Table S5. Evaluation of Green Chemistry Metrics.

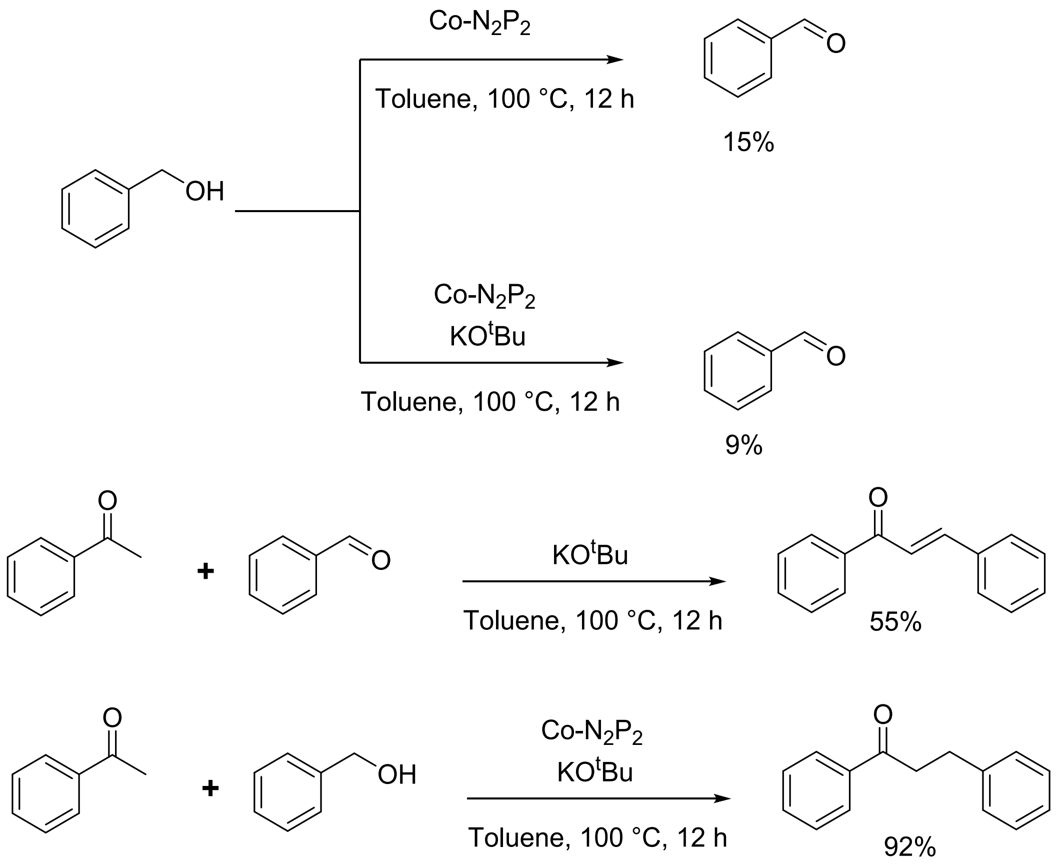


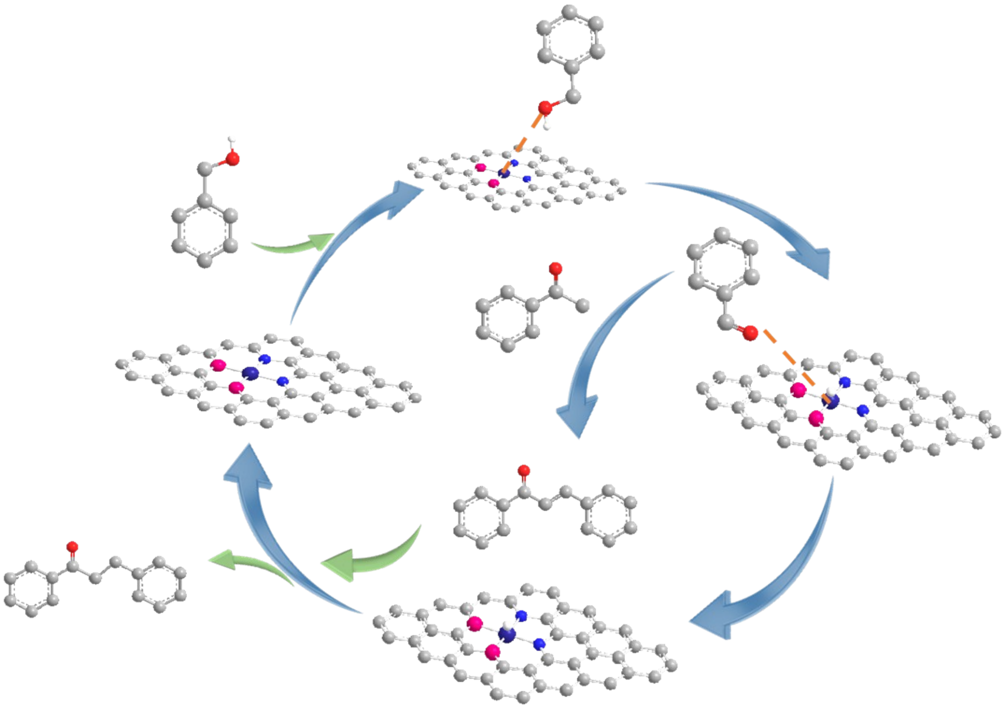
	Chemical	**Weight (g)**	**Mol. Weight**
Reactant 1	Acetophenone	1.000	120.15
Reactant 2	Benzyl alcohol	0.897	108.14
Base	KO^{t}Bu	0.931	112.21
Solvent	toluene	13.00 (15 mL)	092.06
Recycled solvent	toluene	12.18	
Product	1,3-diphenylpropan-1-one	1.46	210.28
By product	H_2O	0.125	018.01

Product yield: (Isolated yield / theoretical yield) x 100 = 84%

- ✓ Product yield: 84%
- ✓ E factor = [{(1 + 0.897 + 0.931 +14 + 0.125) - (1.46 + 12.18)}/1.46] = 2.269 kg waste/ 1 kg product
- ✓ Atom economy = (210.28/228.29) x 100 = 92.11%
- ✓ Atom efficiency = 84 x (92.11 /100) = 77.34%
- ✓ Carbon efficiency = (15/15) x 100 = 100%
- ✓ Reaction mass efficiency = (1.46/1.897) x 100 = 83.90%

Scheme S2. Mechanistic studies





Scheme S3. Proposed reaction mechanism for α- alkylation of acetophenone catalyzed by Co-N_2P_2

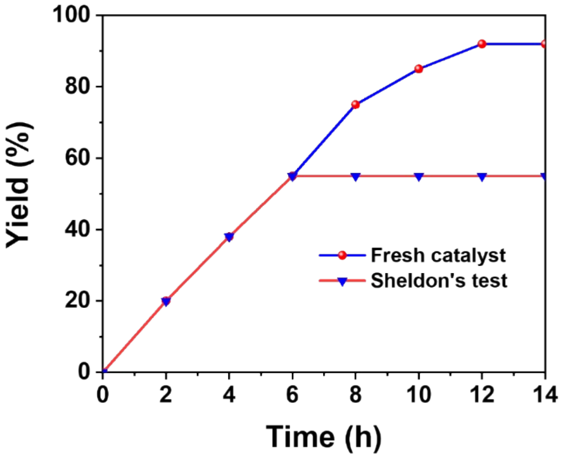


Fig. S5. Sheldon's test for Co-N_2P_2 catalyzed α- alkylation of acetophenone.

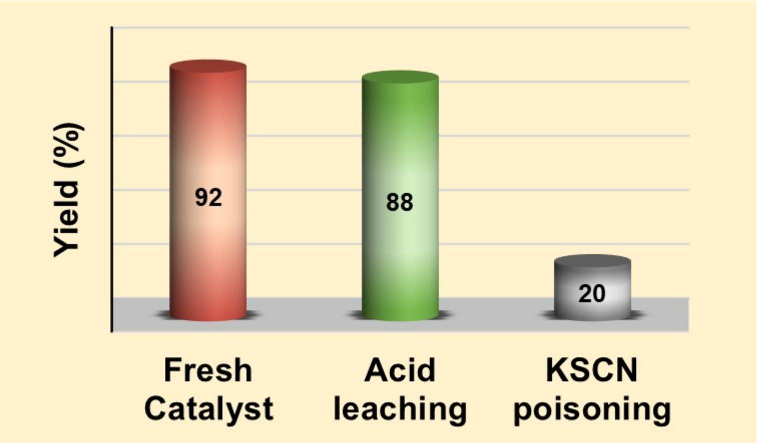


Fig. S6. Acid leaching and KSCN poisoning experiment

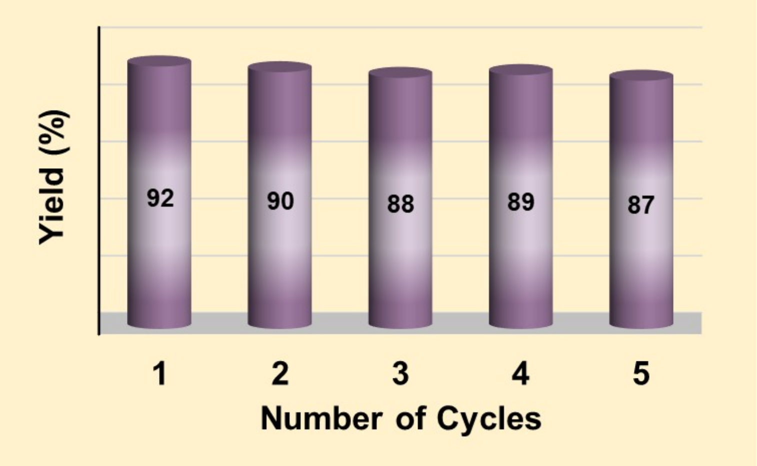


Fig. S7. Reusability of Co-N_2P_2 catalyzed α- alkylation of acetophenone.

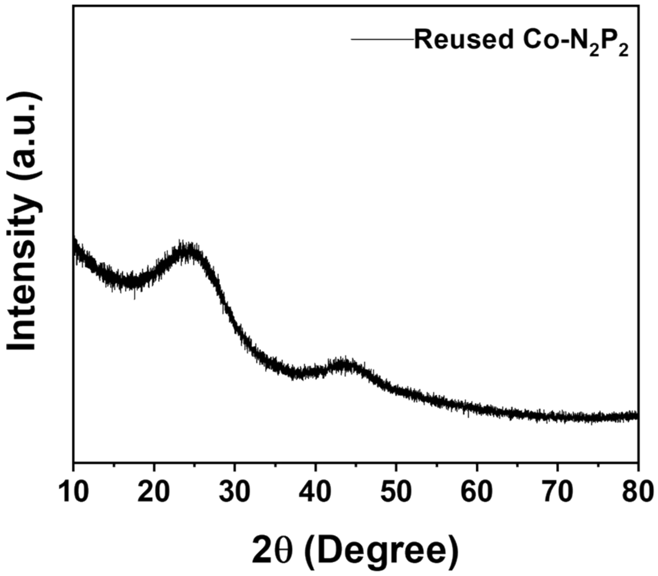


Fig. S8. PXRD patter of reused Co-N$_2$P$_2$ catalyst.

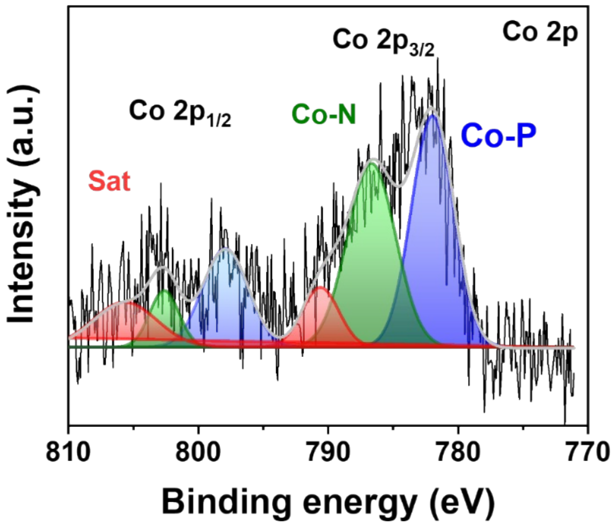
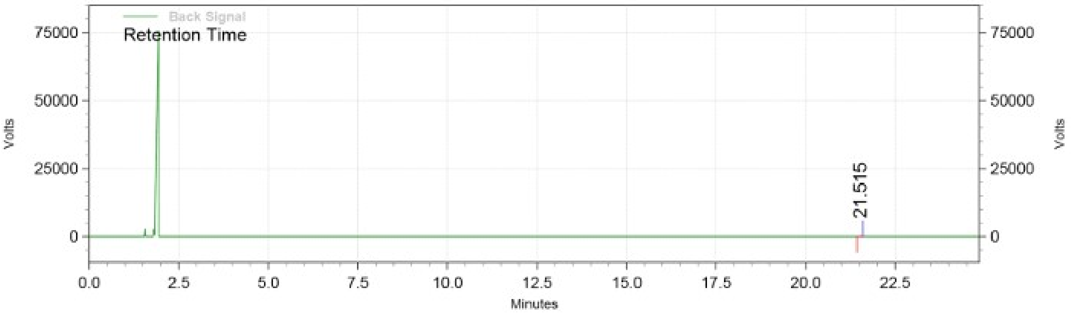


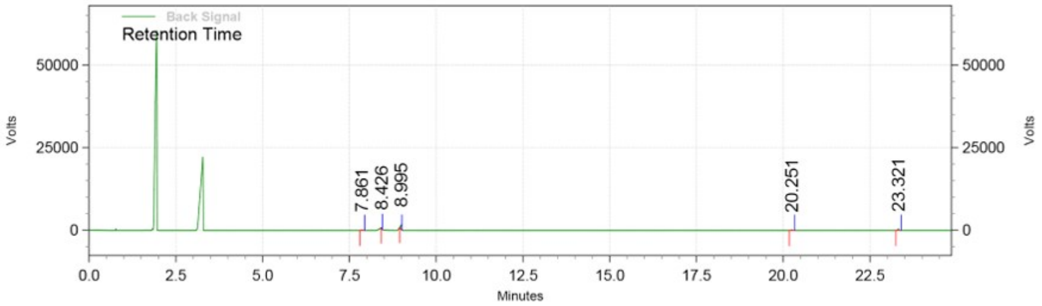
Fig. S9. Co 2p XPS spectrum of reused Co-N$_2$P$_2$ catalyst.



Back Signal
Results

Retention Time	Area	Area %	Height	Height %
21.515	3425871	100.00	1258979	100.00
Totals	3425871	100.00	1258979	100.00

Fig. S10. GC chromatogram for Co-N_2P_2 catalyzed α- alkylation of acetophenone



Back Signal
Results

Retention Time	Area	Area %	Height	Height %
7.861	2511521	6.72	1092671	6.05
8.426	2515887	6.73	2084109	11.54
8.995	21801192	58.34	10762652	59.58
20.251	3075429	8.23	1120413	6.20
23.321	7464566	19.98	3005194	16.64
Totals	37368595	100.00	18065039	100.00

Fig. S10. GC chromatogram for $Co(PPh_3)_2Cl_2$ catalyzed α- alkylation of acetophenone

References

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