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Supplementary Material

Ru-gC3N4 Catalyzed Hydrodebenzylation of Benzyl Protected Alcohol and Acid Groups Using Sodium Hypophosphite as a Hydrogen Source

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Abstract: A straightforward process for hydrodebenzylation of benzyl protected acid and alcohol derivatives to the corresponding acids and alcohols using sodium hypophosphite in the presence of Ru-GCN catalyst is reported. The developed Ru-GCN catalyst is cost effective compared to other noble metal-based catalysts and has been explored to exhibit excellent activity for catalytic hydrodebenzylation reactions under moderate reaction conditions. The non-corrosive sodium hypophosphite has been found as a better hydrogen donor compared to alkali metal formats in presence of Ru-GCN catalyst. The stated catalyst was characterized using several spectrometric and material characterization methods such as PXRD, IR, SEM, TEM, XPS, and TGA. The Ru-GCN catalyst corroborated good reusability and stability for multiple cycles. The catalyst preparation is facile and the developed process is simple and safe as it avoids use of high hydrogen pressure. The developed protocol can also be replicated on industrial scale on account of excellent recyclability and retained activity after multiple cycles and makes the process sustainable. Gram scale reaction was performed to verify the industrial potential of reported catalyst.

Keywords: heterogeneous catalyst; hydrogen transfer reaction; graphitic carbon nitride

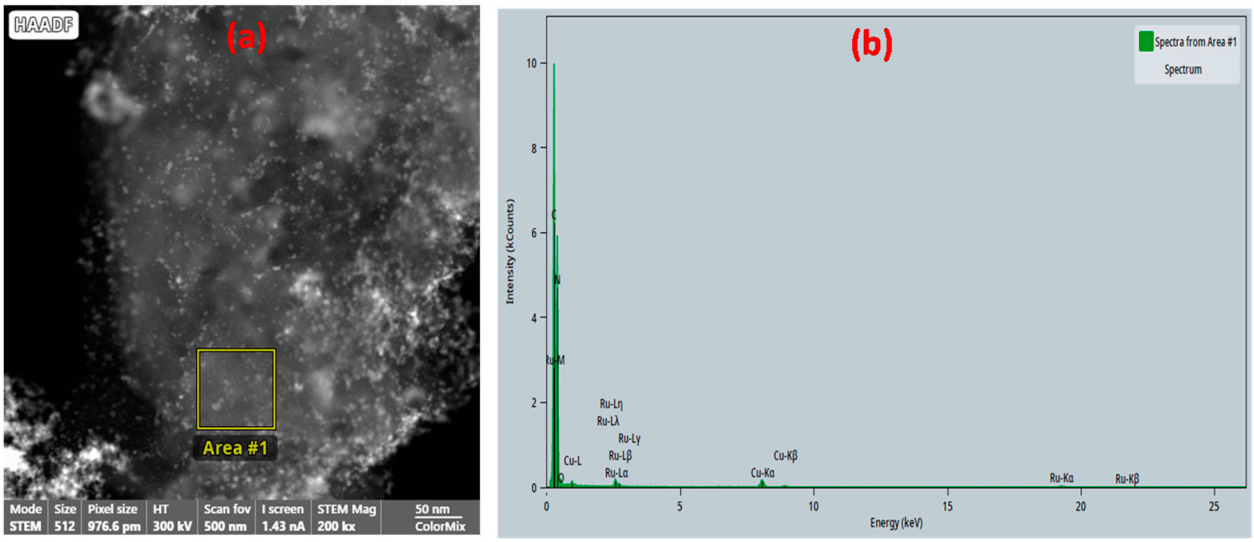


Figure S1. TEM image (**a**) and EDAX (**b**) of Ru-GCN.

Table S1. Elemental composition of Ru-GCN material.

Element	Weight %	Atomic %	Uncert. %	Detector Correction	K Factor
C	59.58	65.24	2.47	1.00	1.00
N	36.26	34.05	4.16	1.00	0.79
O	0.24	0.20	23.92	1.00	0.69
Ru	3.92	0.51	1.67	1.00	6.52

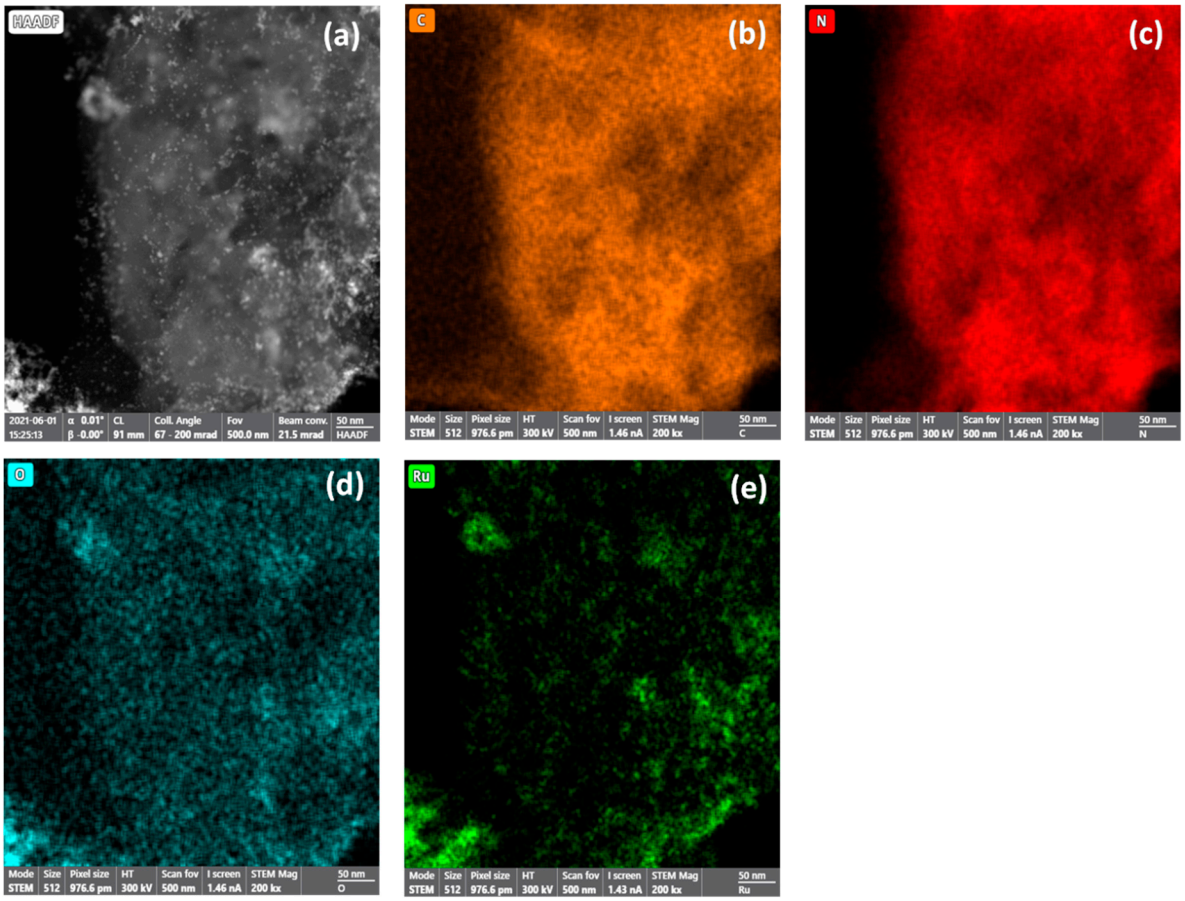


Figure S2. Elemental mapping of Ru-GCN material; (b) carbon, (c) nitrogen, (d) oxygen and (e) ruthenium.

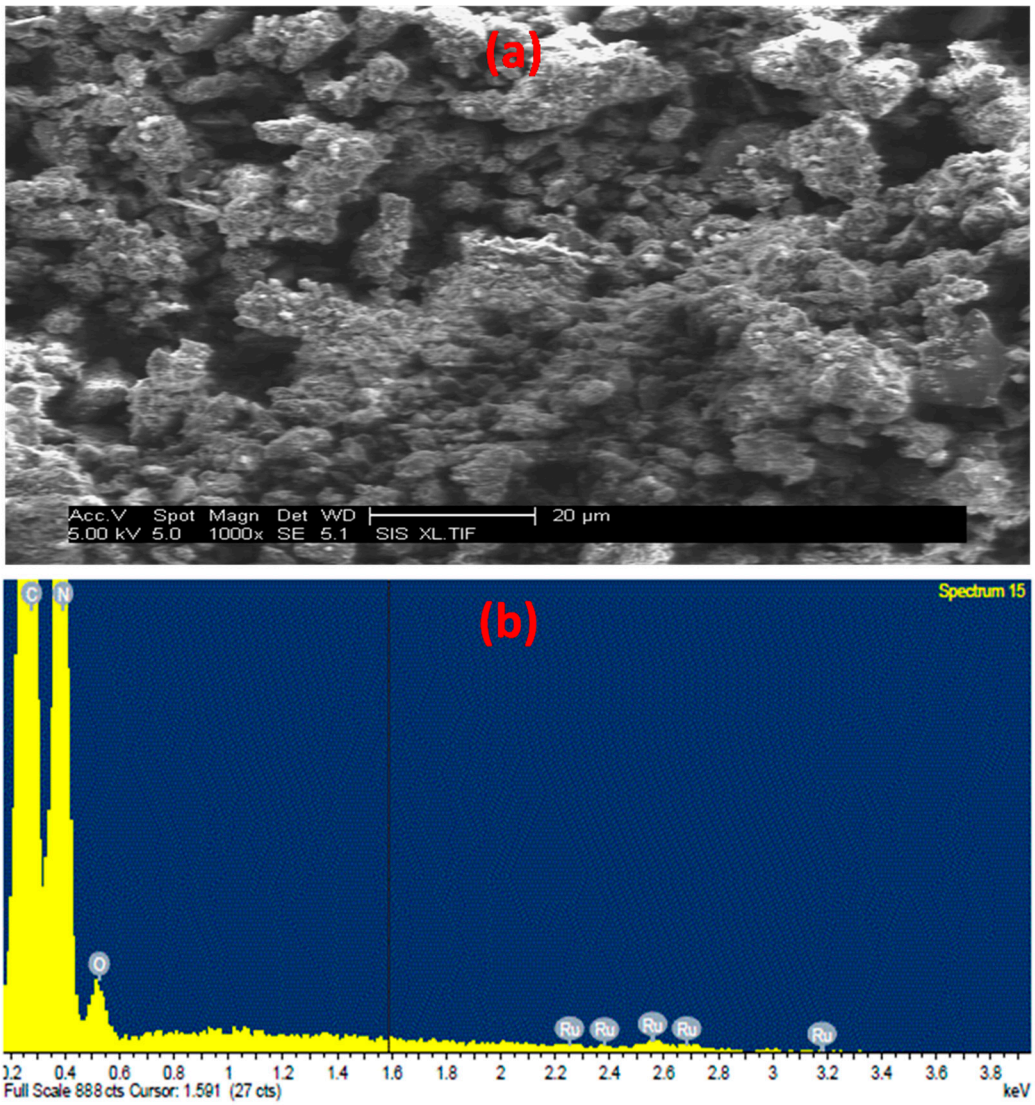


Figure S3. SEM image (**a**) elemental quantification (**b**) of Ru-GCN material.

Table S2. Elemental composition of Ru-GCN material.

Element	APP Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
C K	26.98	2.1379	32.82	0.83	36.17
N K	16.01	0.6628	61.06	1.17	59.35
O K	2.48	1.4538	2.27	0.42	3.68
Ru L	1.38	0.5864	3.85	1.38	0.80

Table S3. XPS Elemental composition/Quantification of Ru-GCN.

Element	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]
C 1s	36.89	0.28	25.77	0.22
N 1s	52.37	0.30	42.66	0.26
O 1s	6.38	0.32	5.94	0.29
Ru 3d	4.36	0.05	25.64	0.22

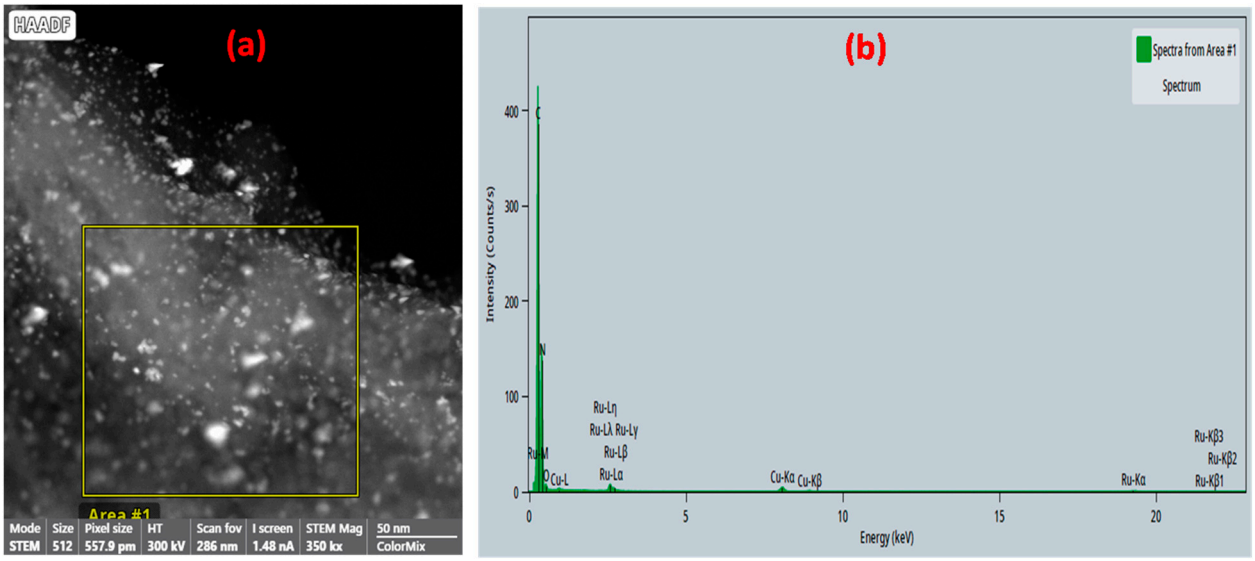


Figure S4. TEM image (a) and EDAX (b) of recycled Ru-GCN catalyst.

Table S4. Elemental composition of recycled Ru-GCN catalyst.

	Weight %	Atomic %	Uncert. %	Detector correction	K factor
C	74.16	79.14	2.05	1.00	1.00
N	21.56	19.73	1.80	1.00	0.79
O	0.87	0.70	1.69	1.00	0.69
Ru	3.41	0.43	0.75	1.00	6.52

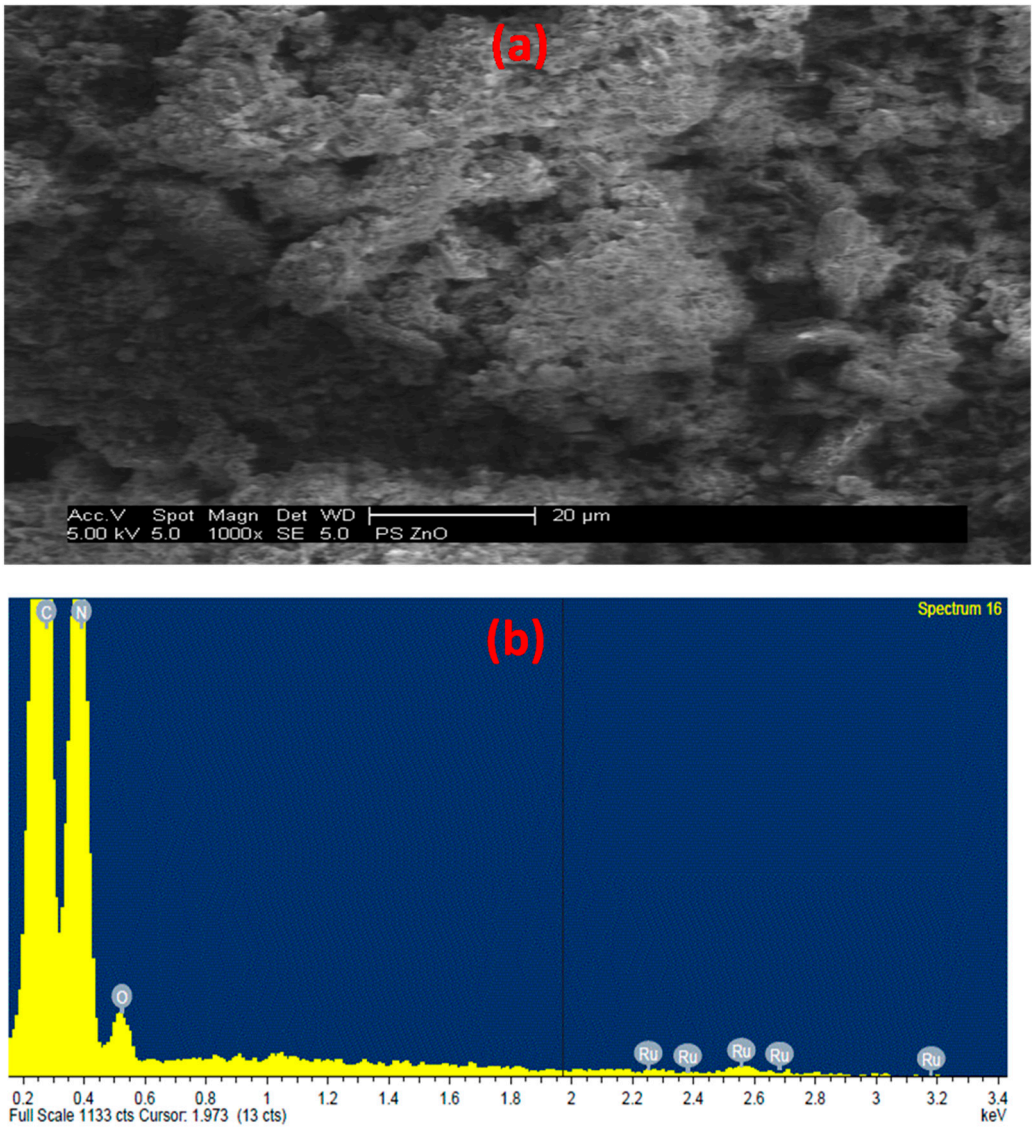


Figure S5. SEM image (a) elemental quantification (b) of recycled Ru-GCN catalyst.

Table S5. Elemental composition of recycled Ru-GCN catalyst.

Element	APP Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
C K	30.62	2.1298	32.19	0.75	35.45
N K	18.97	0.6687	61.8	1.05	59.98
O K	3.03	1.4498	2.67	0.39	3.86
Ru L	1.41	0.5846	3.34	1.20	0.70

Table S6. XPS Elemental composition/Quantification of recycled Ru-GCN catalyst.

Element	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]
C 1s	38,51	0,35	27,95	0,29
N 1s	49,38	0,35	41,79	0,31
O 1s	8,50	0,34	8,22	0,33
Ru 3d	3,61	0,05	22,04	0,26

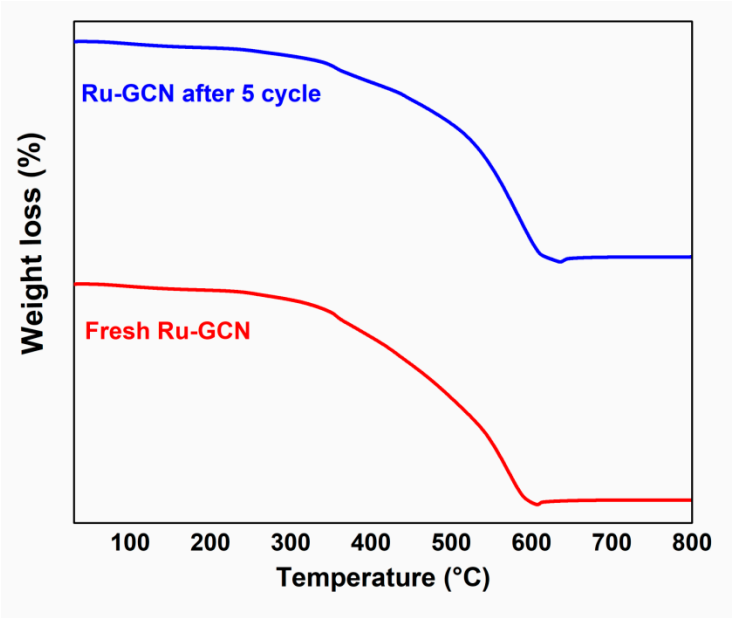


Figure S6. Comparison of TGA of fresh and recycled Ru-GCN catalyst.

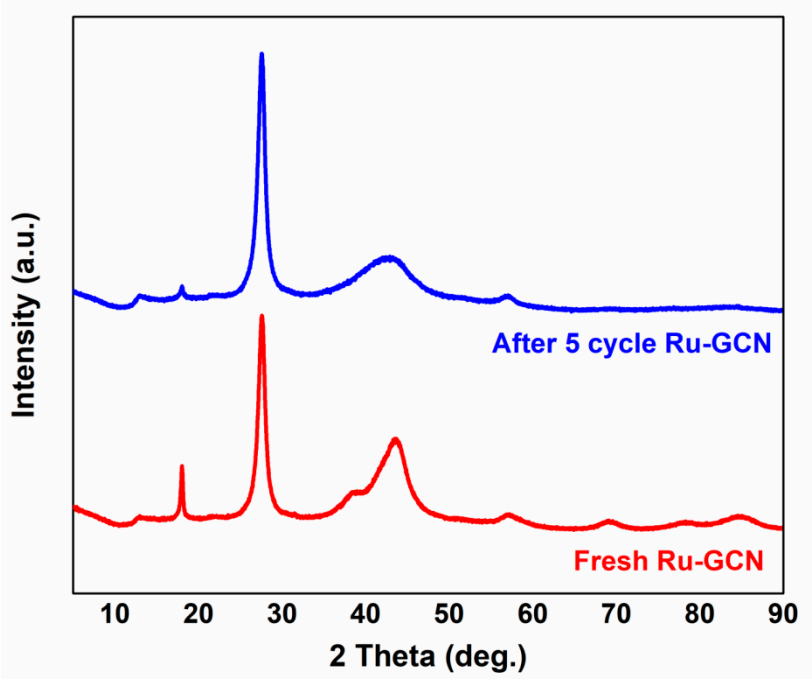
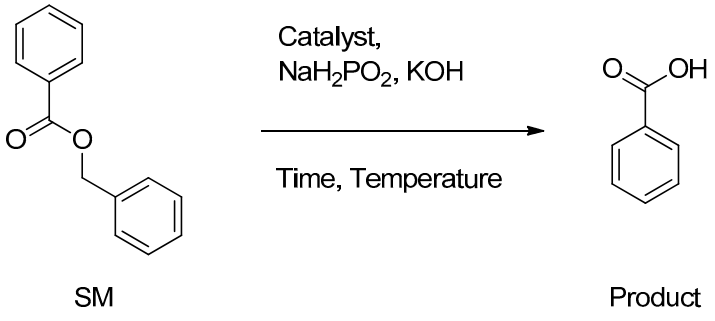


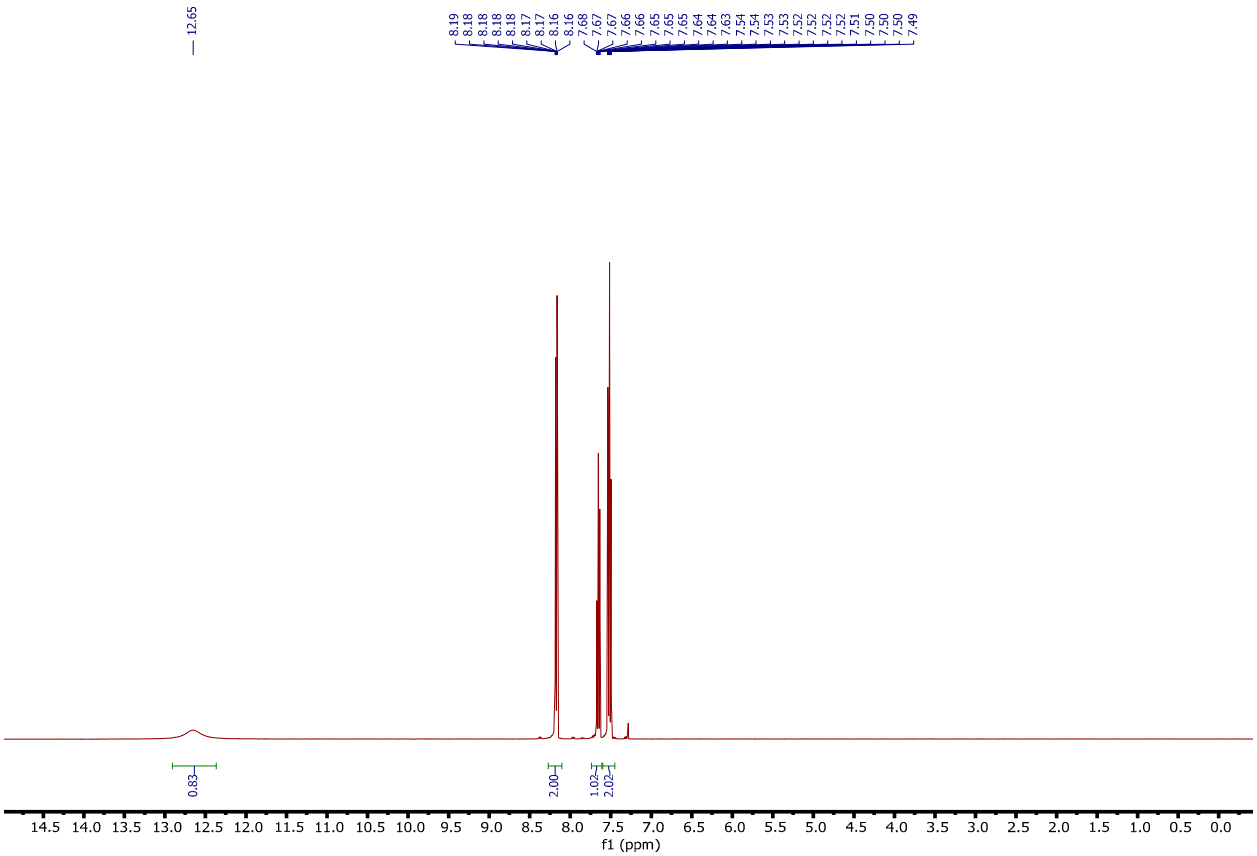
Figure S7. Comparison of XRD of fresh and recycled Ru-GCN catalyst.

Experimental Data:

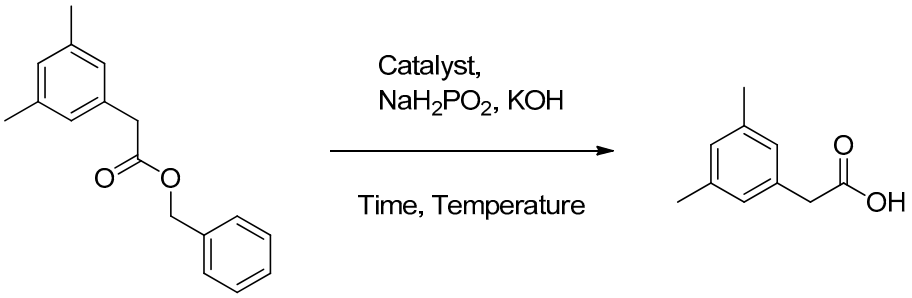
1. Hydrodebenzylation of Benzylbenzoate:



After following the procedure described in the experimental section the isolated product was analyzed by 1H NMR. 1H NMR (400 MHz, Chloroform-d) δ/ppm: 12.65 (s, 1H), 8.19 – 8.16 (m, 2H), 7.68 – 7.63 (m, 1H), 7.54 – 7.49 (m, 2H).

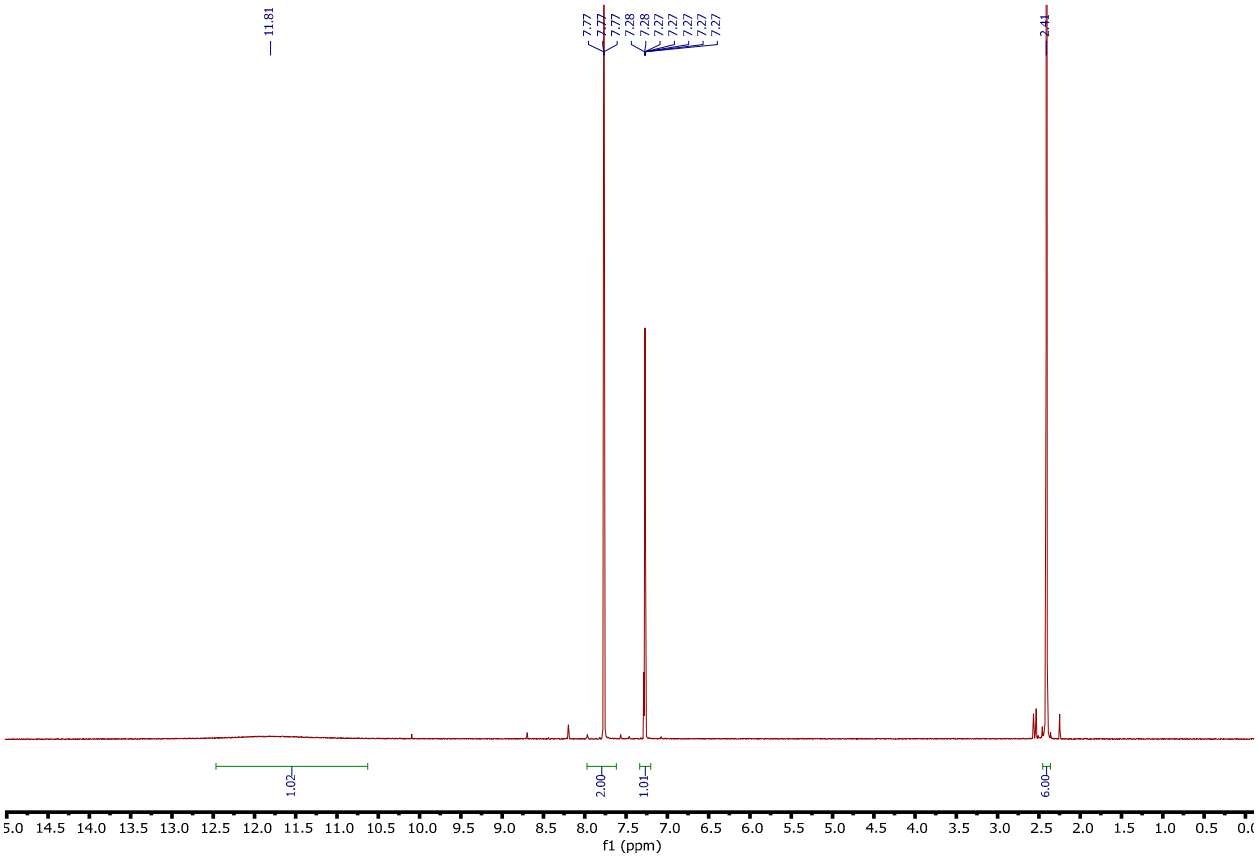


2. Hydrodebenzylation of benzyl 2-(3,5-dimethylphenyl)acetate:

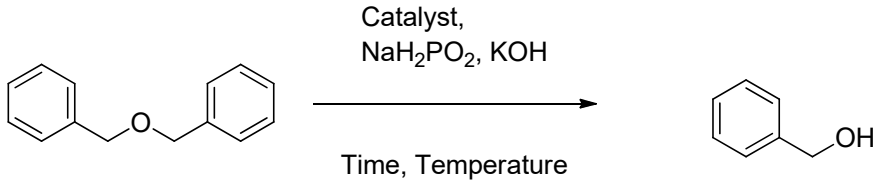


SM Product

After following the procedure described in the experimental section the isolated product was analyzed by 1H NMR. 1H NMR (400 MHz, Chloroform-d) δ/ppm: 11.81 (s, 1H), 7.77 – 7.77 (m, 2H), 7.28 – 7.27 (m, 1H), 2.41 (s, 6H).

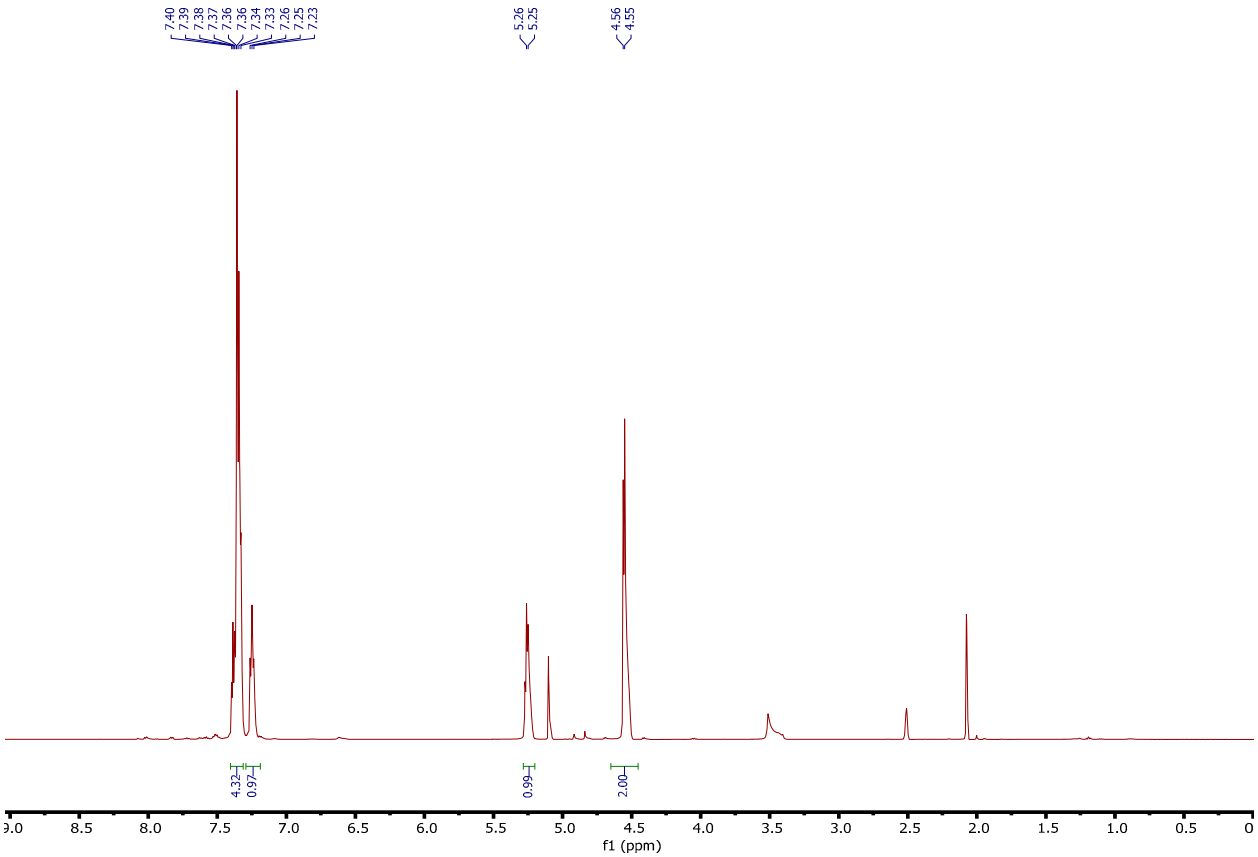


3. Hydrodebenzylation of (oxybis(methylene))dibenzene:

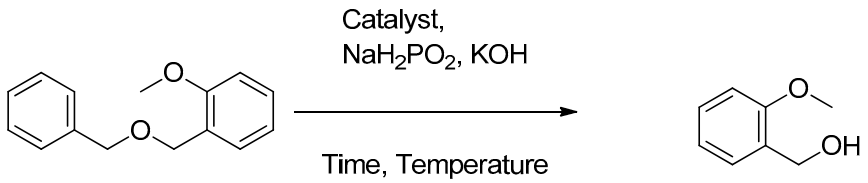


SM Product

After following the procedure described in the experimental section the isolated product was analyzed by 1H NMR. 1H NMR (500 MHz, DMSO-d6) δ/ppm: 7.40 – 7.33 (m, 4H), 7.26 – 7.23 (m, 1H), 5.26 (d, *J = 5.5 Hz*, 1H), 4.56 (d, *J = 5.5 Hz*, 2H).

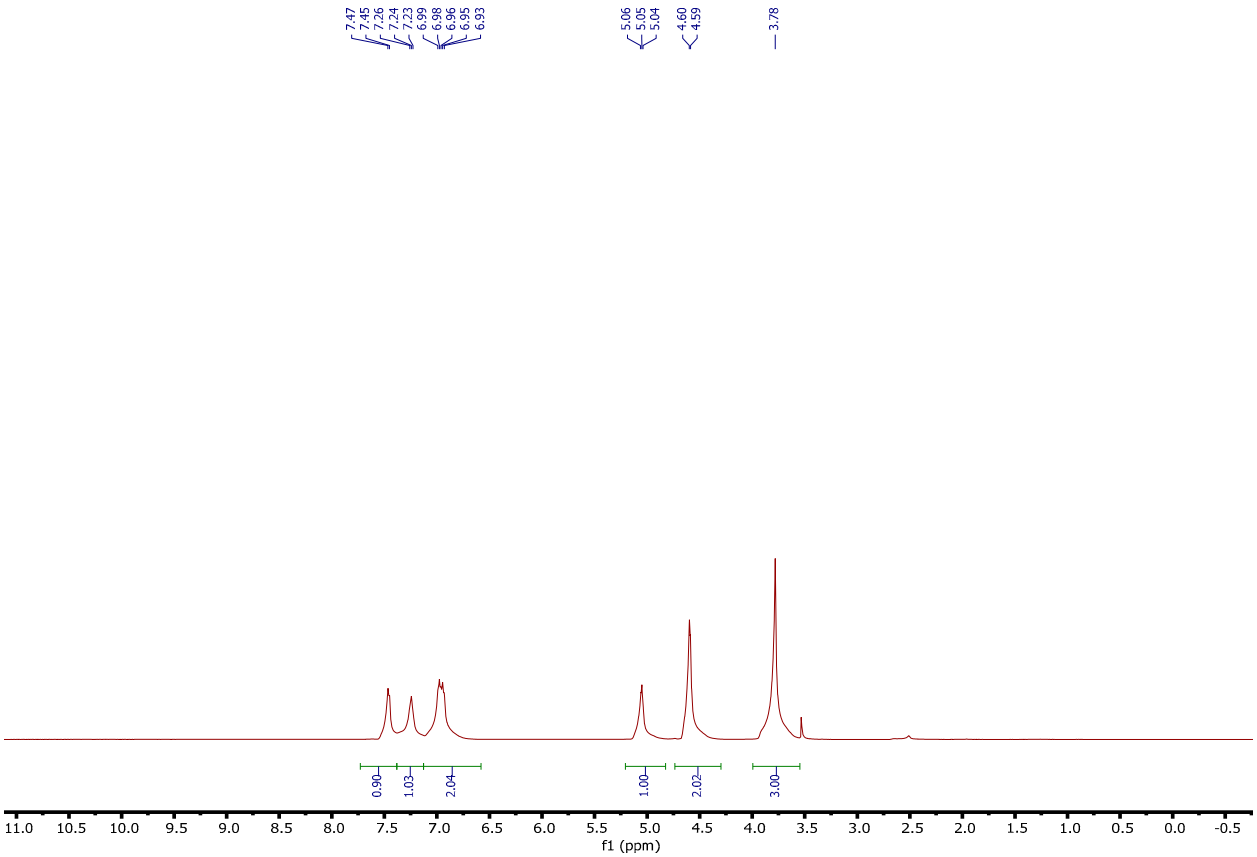


4. Hydrodebenzylation of 1-((benzyloxy)methyl-2-methoxybenzene:

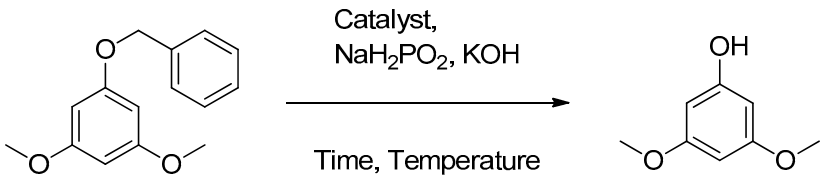


SM Product

After following the procedure described in the experimental section the isolated product was analyzed by 1H NMR. 1H NMR (500 MHz, DMSO-d6) δ/ppm: 7.46 (d, *J = 7.7 Hz*, 1H), 7.26 – 7.23 (m, 1H), 6.99 – 6.93 (m, 2H), 5.06 – 5.04 (m, 1H), 4.59 (d, *J = 6.8 Hz*, 2H), 3.78 (s, 3H).

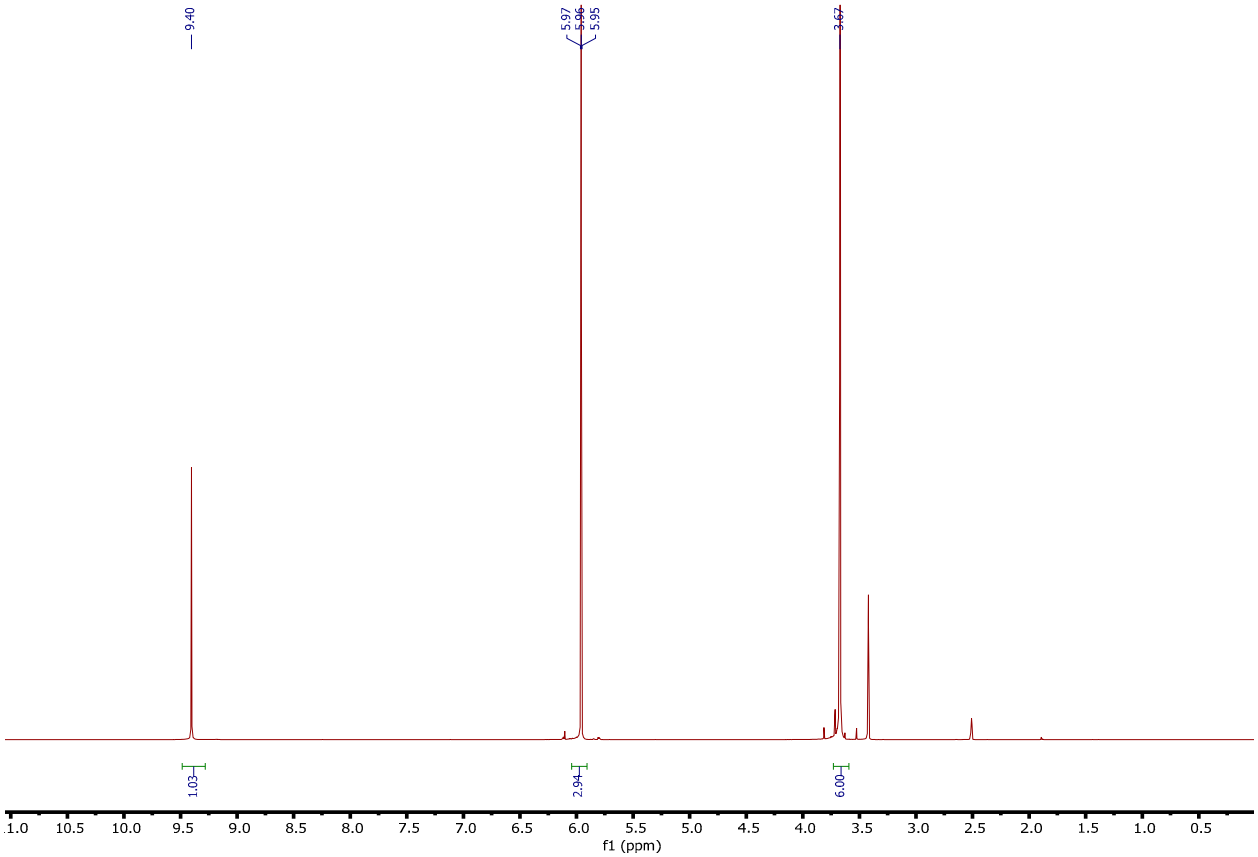


5. Hydrodebenzylation of 1-(benzyloxy)-3,5-dimethoxybenzene:

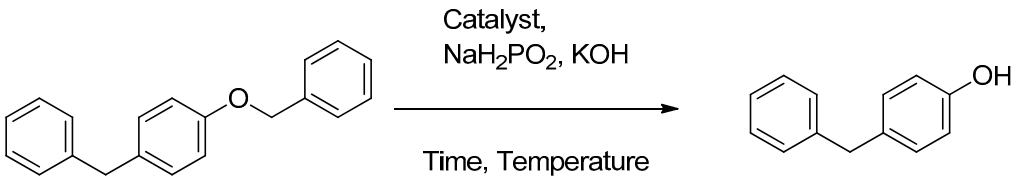


SM Product

After following the procedure described in the experimental section the isolated product was analyzed by 1H NMR. 1H NMR (500 MHz, DMSO-d6) δ/ppm: 9.40 (s, 1H), 5.97 – 5.95(m, 3H), 3.67 (s, 6H).

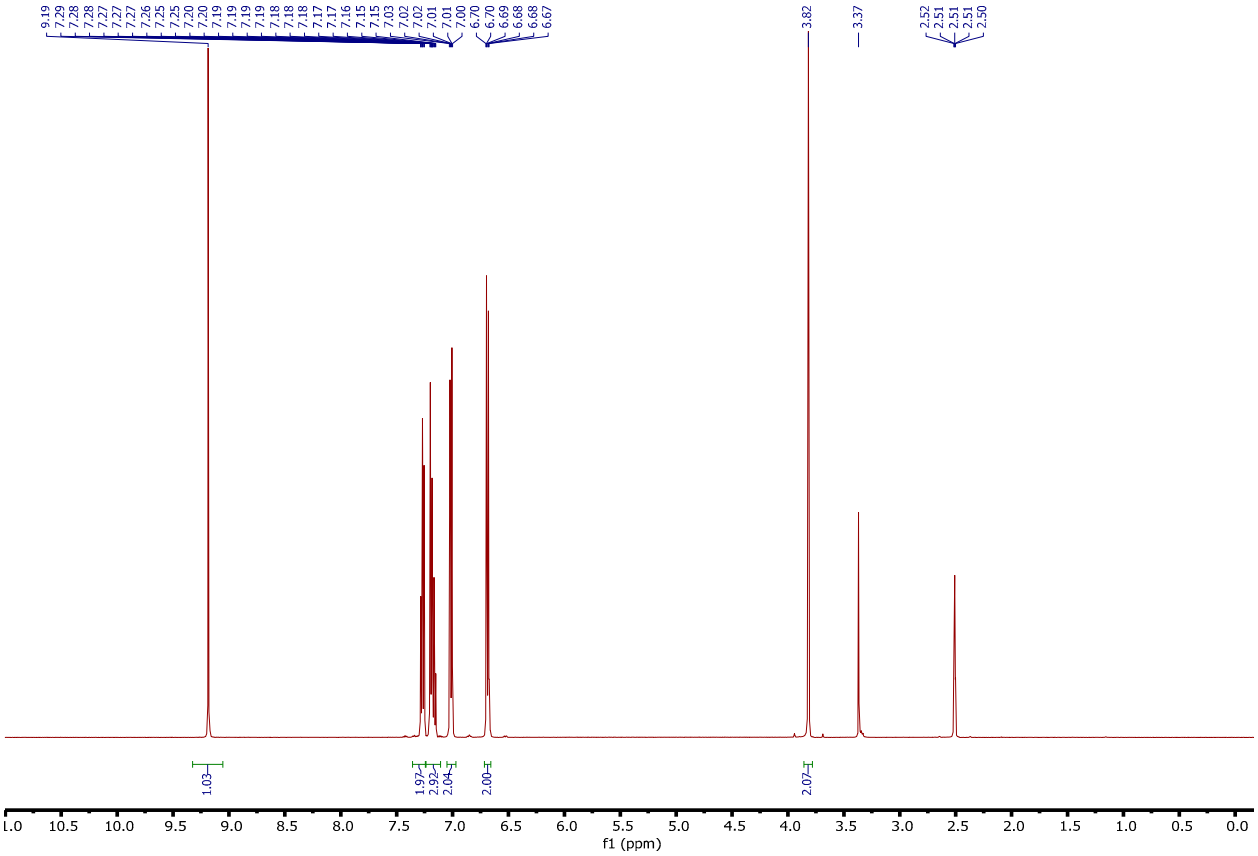


6. Hydrodebenzylation of 1-benzyl-4-(benzyloxy)benzene:



SM Product

After following the procedure described in the experimental section the isolated product was analyzed by 1H NMR. 1H NMR (500 MHz, DMSO-d6) δ/ppm: 9.19 (s, 1H), 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 7.03 – 7.0 (m, 2H), 6.70 – 6.67 (m, 2H), 3.82 (s, 2H).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