

Supporting Information

The effect of *N*-vacancy on the photocatalytic activity of graphitic carbon nitride in oxidative Mannich reaction

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Materials

Urea ($\text{CH}_4\text{N}_2\text{O}$) (Merck) (99%), Tetrahydroisoquinoline ($\text{C}_9\text{H}_{11}\text{N}$) (THIQ) (Sigma-Aldrich) (95%), Copper(I) iodide (CuI) (98%), tripotassium phosphate (K_3PO_4) (Sigma-Aldrich) (98%), Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), Iodobenzene ($\text{C}_6\text{H}_5\text{I}$) (Alfa Aesar) (98%), 4'-Iodoacetophenone ($\text{C}_8\text{H}_7\text{IO}$) (Alfa Aesar) (98%), Potassium iodide (KI) (Merck), Hydrogen Peroxide (H_2O_2) (ISOLAB) (35%), were purchased from various companies. All chemicals and solvents were used as received without further purification

Catalyst characterization

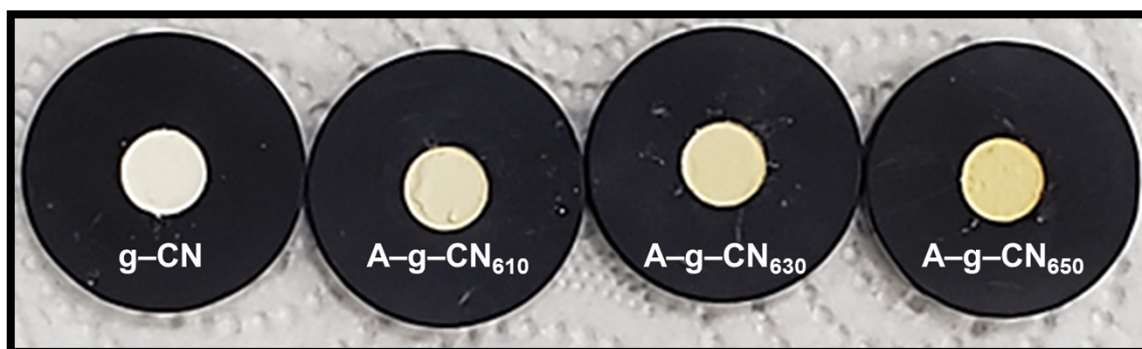


Figure S1. Images of g-CN, A-g-CN₆₁₀, A-g-CN₆₃₀ and A-g-CN₆₅₀ in sample holders.

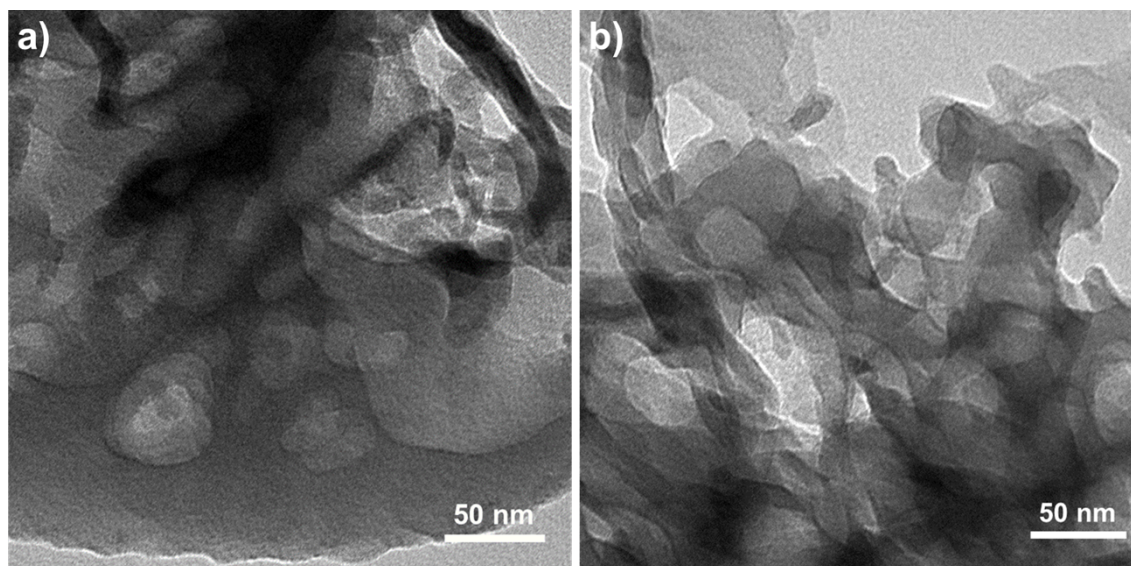


Figure S2. TEM images of A-g-CN₆₁₀ and A-g-CN₆₃₀.

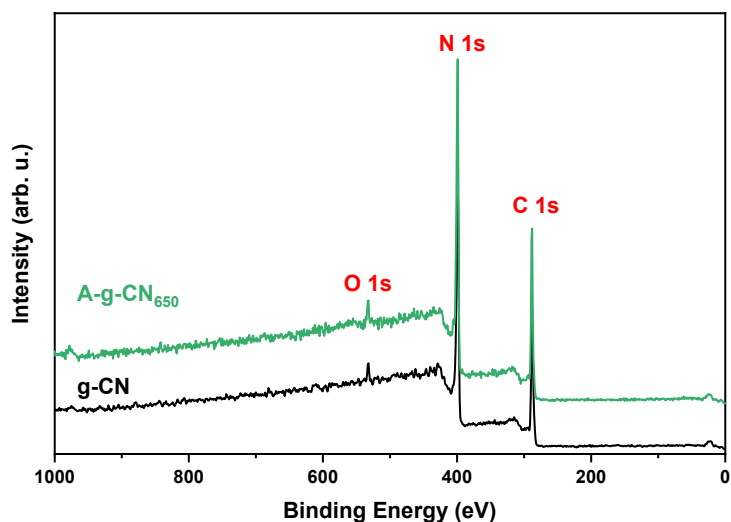


Figure S3. XPS survey spectra of g-CN and A-g-CN₆₅₀.

KI-starch test

KI-starch test was used to detect peroxides formed during the reaction^{1,2}. The KI-starch stock solution was prepared by dissolving 1 g of commercial starch and 500 mg of KI in 30 mL of distilled water. A control experiment was performed by adding 0.25 mmol of H₂O₂ (35%) to the KI-starch stock solution. The oxidative Mannich-type reaction was conducted using 0.25 mmol of *N*-phenyl tetrahydroisoquinoline (**1b**), 10 equivalents of Acetone (**2a**), 0.2 equivalents of L-proline, O₂ balloon and 5 mg of catalyst in 1 mL of DMSO. The reaction mixture was then irradiated with white light (150 W) for 2 h at 25 °C. An oxidative Mannich-type reaction was tested under three different conditions: i) without the KI-starch stock solution ii) with the addition of the KI-starch stock solution before light irradiation, and iii) with the addition of the KI-starch stock solution after 2 h of light irradiation.

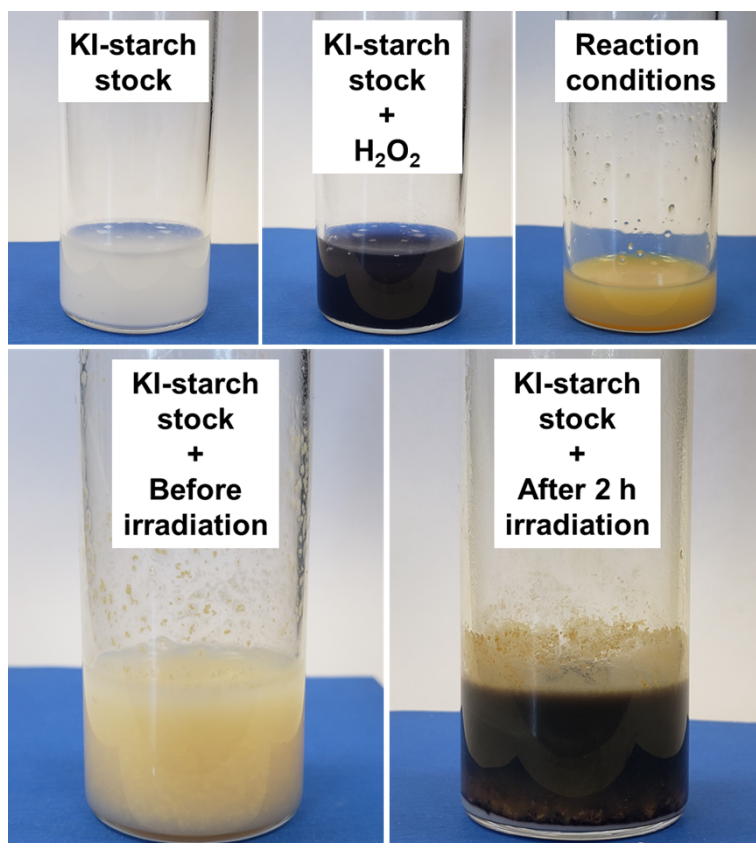


Figure S4. KI-starch test summary. From top-left, KI-starch stock, KI-starch control with H₂O₂, oxidative Mannich-type reaction conditions, oxidative Mannich-type reaction with KI-starch stock solution before light irradiation, oxidative Mannich-type reaction with KI-starch stock solution after 2 h light irradiation.

Reusability experiments

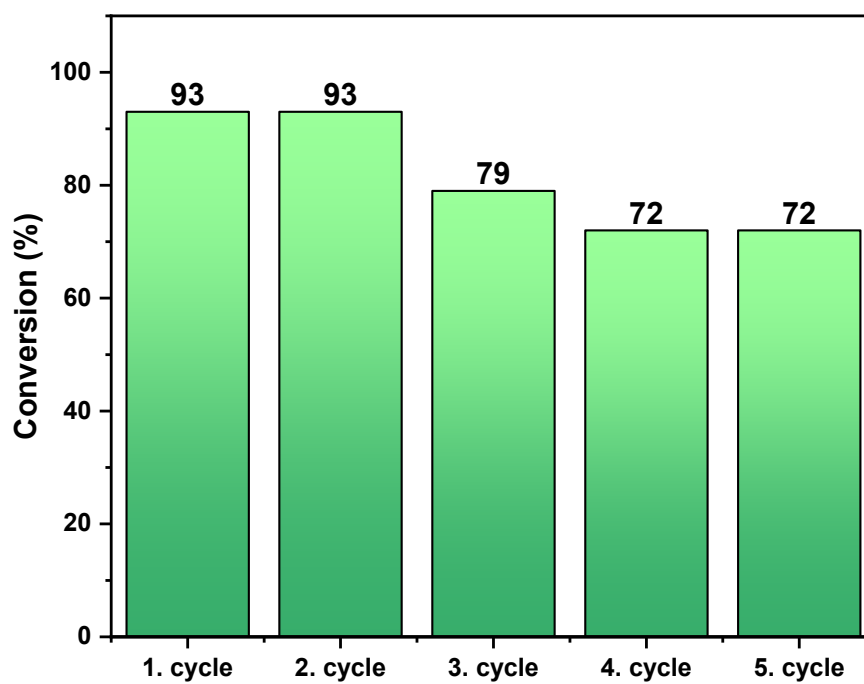


Figure S5. Reusability of A-g-CN₆₅₀ on photoredox oxidative Mannich reaction.

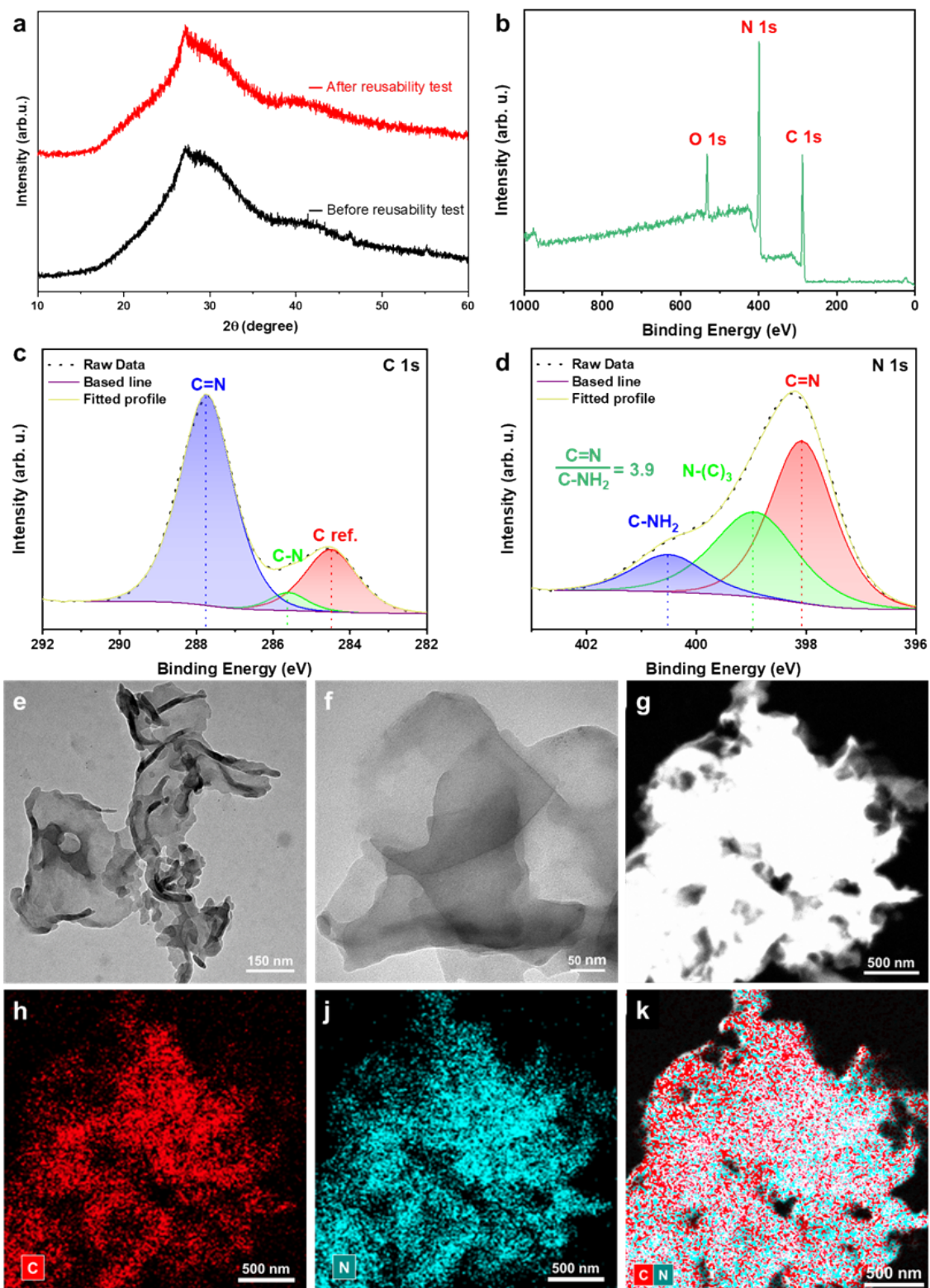


Figure S6. a) XRD patterns before and after reusability of A-g-CN₆₅₀. b) XPS survey spectra, and high-resolution spectra of c) C1s, d) N1s regions of A-g-CN₆₅₀ after reusability test. e-f) TEM images of A-g-CN₆₅₀ after reusability test at different magnifications. g) HAADF-STEM image and h-k) elementals mappings of the A-g-CN₆₅₀ after reusability test.

Conversion calculations from the ^1H NMR for the substrate scope of the C–C bond formation

The reaction conversions were calculated using relative areas of peak from ^1H NMR of products after drying. As a reference, hydrogen atoms highlighted in red (**Figure S 5**) were calibrated to value of two and the quartet peak at δ 5.4 was attributed to the hydrogen atom in the product highlighted in the blue. The conversion was calculated by taking percent ratio of product peak to the sum of (**H**) reactant peak divided by two and (**H**) product peak. The sample calculation example is given below.

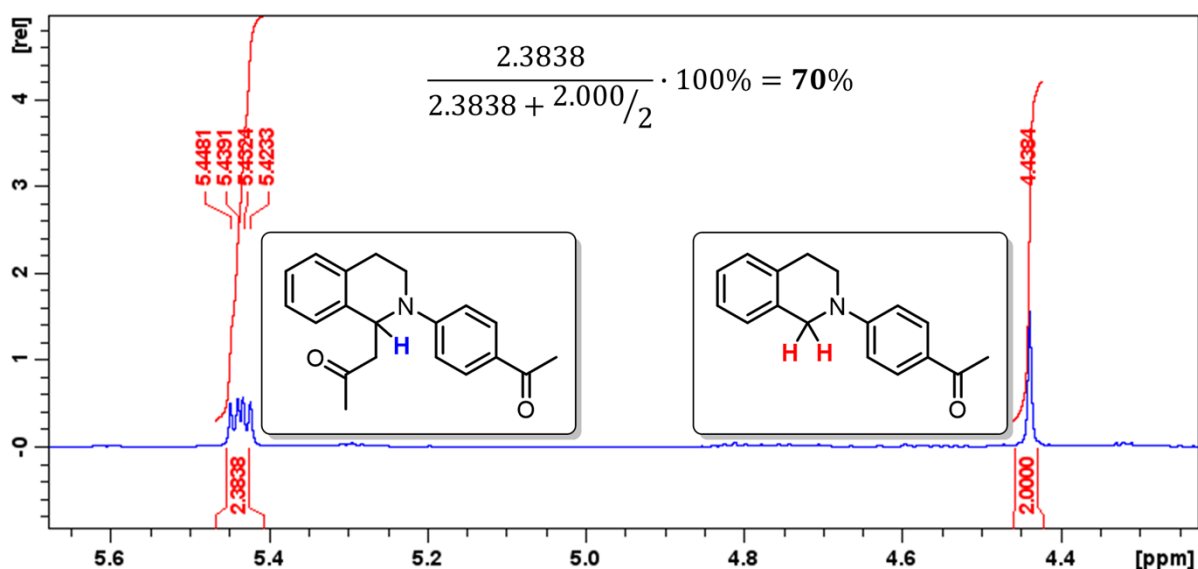
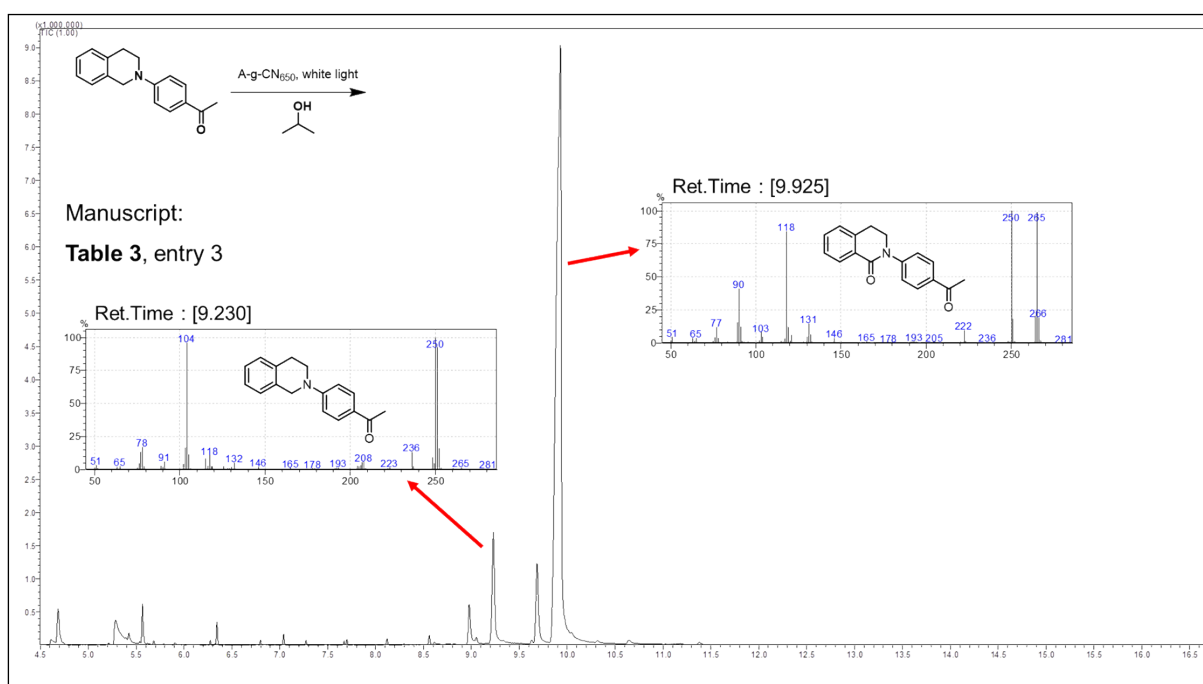
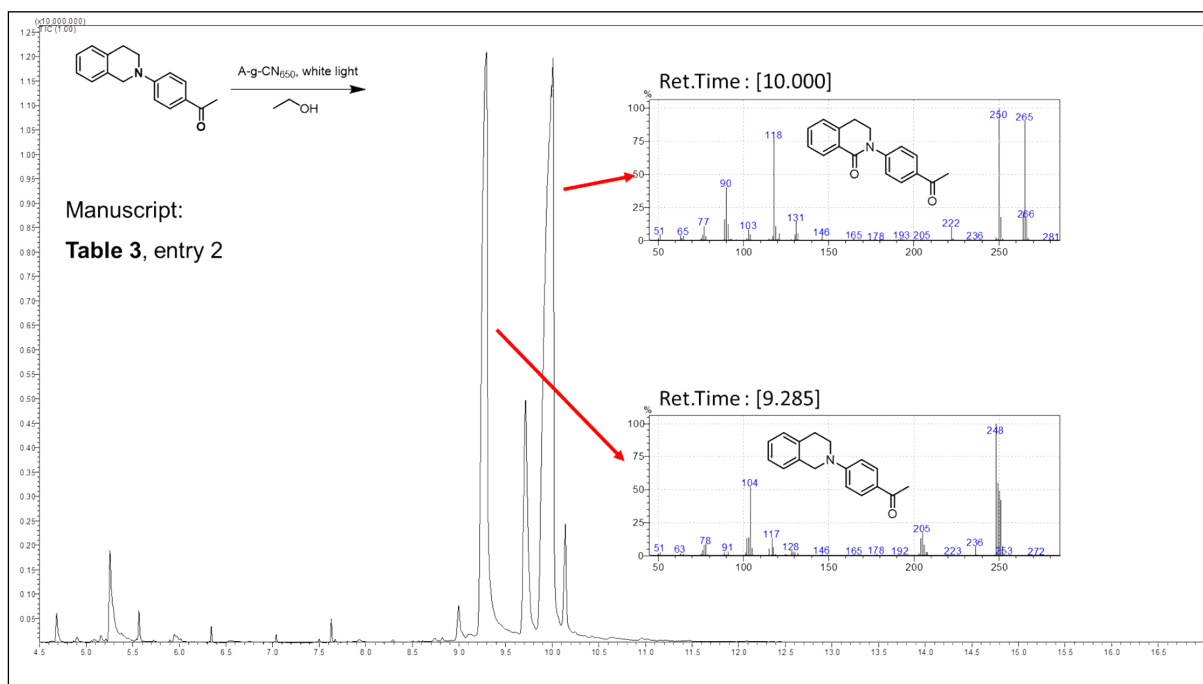
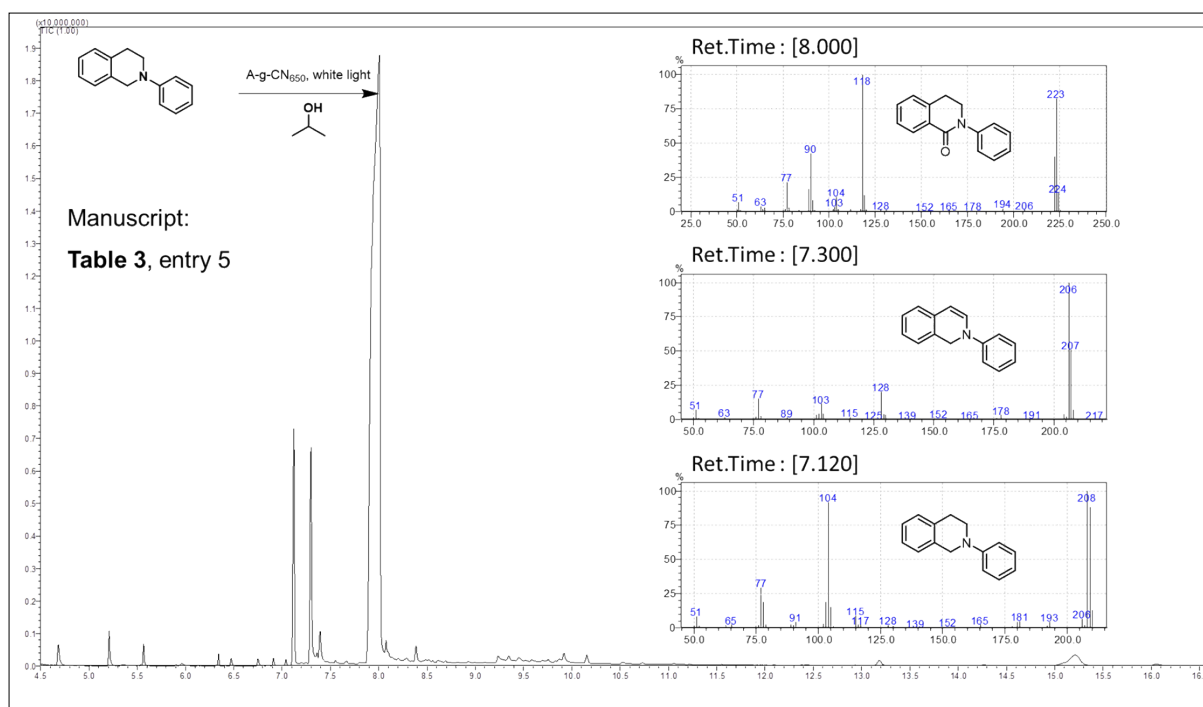


Figure S6. Sample conversion calculation example of oxidative Mannich type reaction.

GC-MS spectra of the tetrahydroisoquinoline derivatives with alcohols.

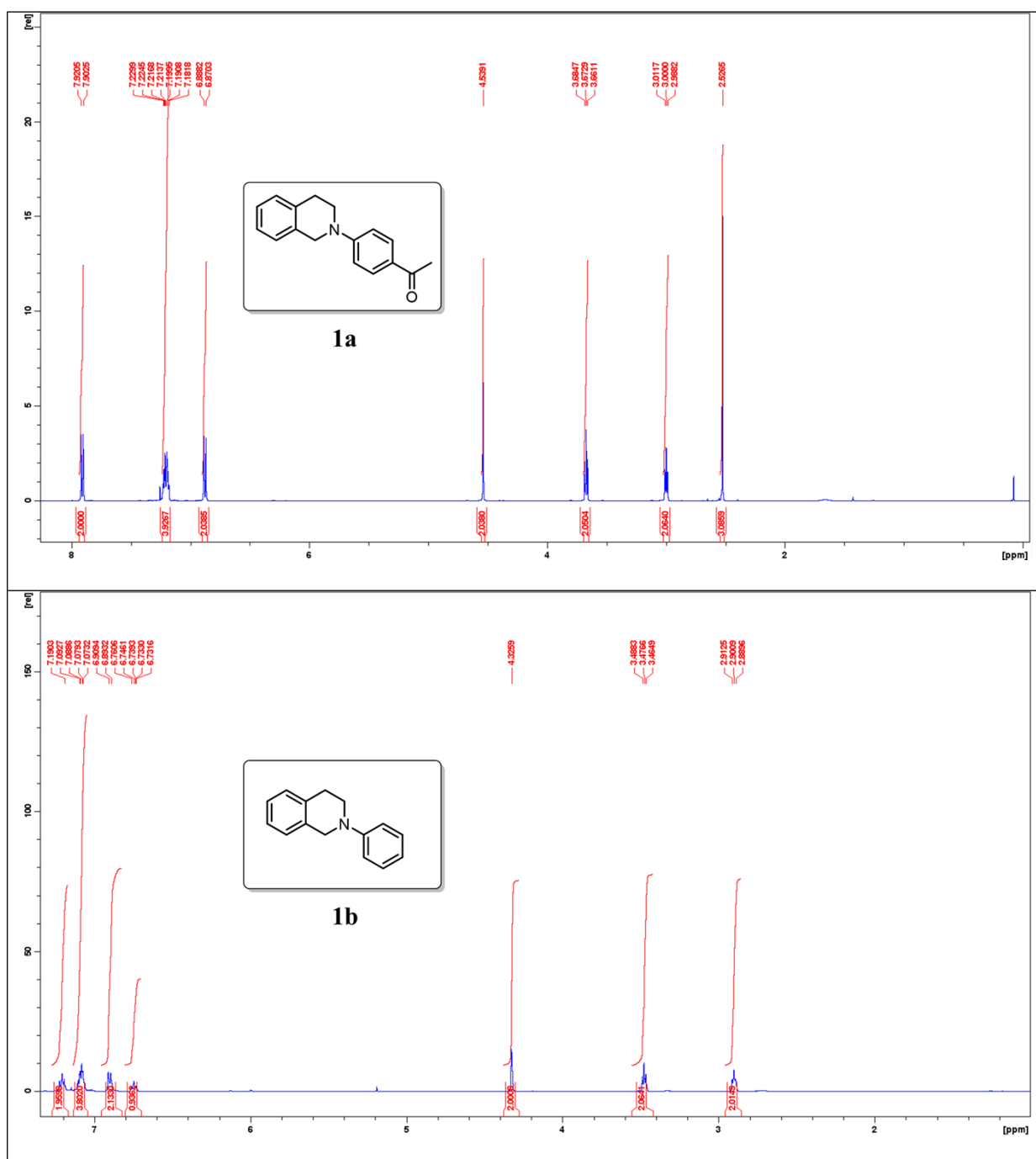


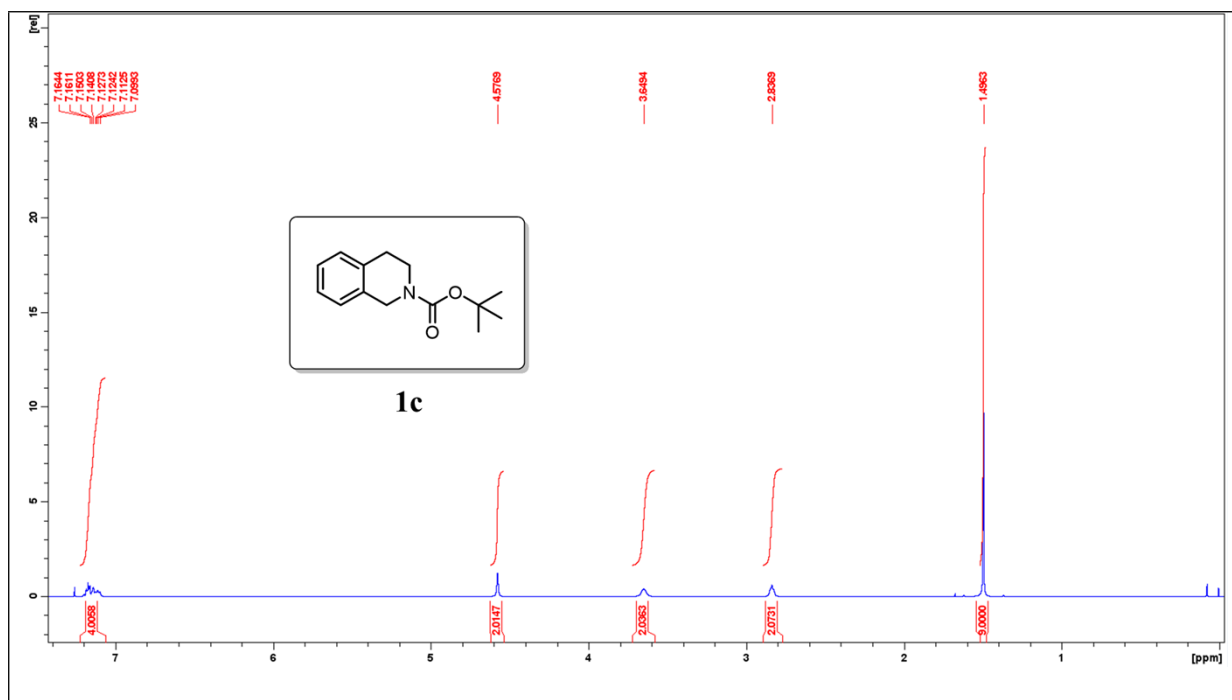


¹H NMR spectra of the tetrahydroisoquinoline derivatives.

	<p><i>N</i>-(4-acetylphenyl)tetrahydroisoquinoline (1a)³</p> <p>isolation by column chromatography (hexane/EtOAc: 90/5)</p> <p>¹H NMR (500 MHz, CDCl₃): δ 8.22 – 8.20 (d, <i>J</i> = 8.4 Hz, 2H), 7.52 – 7.50 (m, 2H), 7.41 – 7.40 (m, 1H), 6.33 – 6.31 (m, 1H), 6.28 – 6.26 (m, 1H), 1.43 (s, 9H).</p>
	<p><i>N</i>-phenyl tetrahydroisoquinoline (1b)³</p> <p>isolation by column chromatography (hexane/EtOAc: 90/5)</p> <p>¹H NMR (500 MHz, CDCl₃): δ 7.19 (m, 2H), 7.09 – 7.07 (m, 4H), 6.90 – 6.89 (m, 2H), 6.76 – 6.73 (m, 1H), 4.32 (s, 2H), 3.49 – 3.46 (m, 2H), 2.91 – 2.89 (m, 2H).</p>
	<p><i>N</i>-<i>tert</i>-butoxycarbonyl tetrahydroisoquinoline (1c)⁴</p> <p>isolation by column chromatography (hexane/EtOAc: 90/5)</p> <p>¹H NMR (500 MHz, CDCl₃): δ 7.36 – 7.27 (m, 5H), 6.24 – 6.22 (m, 1H), 6.19 (dd, <i>J</i> = 3.2, 1.8 Hz, 1H), 1.34 (s, 9H).</p>

¹H NMR spectral data of the tetrahydroisoquinoline derivatives.





References

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- 2 E. Tatumashvili, B. Chan, P. E. Nashar and C. S. P. McErlean, *Org Biomol Chem*, 2020, **18**, 1812–1819.
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