

Electronic supplementary information (ESI)

Photocatalytic dehydrative etherification of alcohols with a nanoporous gold catalyst

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1. General information

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE NEO 400 spectrometer. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl_3 at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), and coupling constants (Hz). ^{13}C NMR spectra are recorded with complete proton decoupling, and chemical shifts are reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra with electrospray ionization were obtained on a Bruker Daltonics micrOTOF II spectrometer. GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (20 m x 0.18 mm capillary column, HP-5MS). Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μm , KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F₂₅₄ (Merck). Scanning electron microscope (FE-SEM) observations were carried out using Hitachi Co. Ltd. S-5000 instruments operated at accelerating voltages of 15 kV. EDX analysis was carried out using JEOL JSM-6010LA. The XPS measurements were carried out employing monochromatic Mg K X-ray radiation (AXIS-ULTRA, Kratos). The system was operated at 15 kV and 150 W. The base pressure of the analysis chamber was less than 2×10^{-8} Torr. Inductively coupled plasma optical emission spectrometer (ICP OES) measurements were performed by Perkin Elmer Avio 200. Au (99.99%) and Ag (99.99%) are purchased from Tanaka Holdings Co., Ltd. Solvents were purchased and used without further purification. Compounds **2a**,¹ **2b**,² **2c**,³ **4a**,⁴ **4b**,⁵ **4c**,⁶ **4d**,⁷ **4e**,⁴ **4f**,⁴

4g,⁸ **4h**,⁹ **5a**,¹⁰ **5b**,¹¹ **5c**,¹² **5d**,¹¹ **5e**,¹³ **5f**,¹⁴ **5g**,¹⁵ **7a**,¹⁶ **7b**¹⁷ were reported before and their NMR data are consistent with ours.

2. Fabrication of AuNPore catalyst

Au (99.99%) and Ag (99.99%) grains were melted with electric arc-melting furnace under Ar atmosphere to form Au-Ag alloy (30:70, in at%), which was rolled down to thickness of 40 μm . The resulting ribbon was annealed 850 $^{\circ}\text{C}$ for 24 h, and it was cut into small pieces (2 x 5 mm). Treatment of the resulting several chips (50.0 mg) with 70 wt% nitric acid for 1 hours at room temperature resulted in the formation of the nanoporous structure by selective leaching of silver. The material was washed with saturated aqueous NaHCO_3 , pure water, and acetone, successively. Drying of the material under reduced pressure gave AuNPore (23.0 mg), and its composition was found to be $\text{Au}_{95}\text{Ag}_5$ by EDX analysis.

3. UV–Vis extinction spectrum of AuNPore catalyst

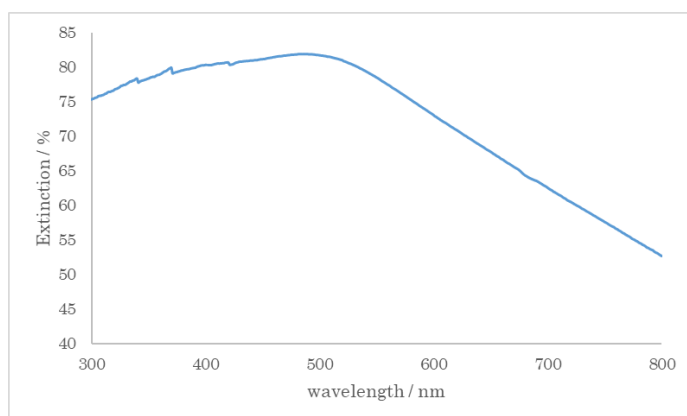


Fig. S1 UV–Vis extinction spectrum of AuNPore catalyst.

4. General procedure for the catalytic reactions

The preparation of **2a** is representative. To a mixture of (CH₂Cl)₂ (0.067 mL) and CCl₄ (0.033 mL) containing AuNPore (0.98 mg, 0.005 mmol) in a V-shaped glass tube was added 1-phenylethanol **1a** (0.2 mmol) under N₂, and the resulting mixture was irradiated with two blue LEDs (HLV3-22BL-2, 2.7 W, 465 nm, CCS inc.) from either side at room temperature for 1 h. The catalyst was separated, and the reaction mixture was concentrated under reduced pressure to give a crude product. The ¹H NMR yield of **2a** was found to be 91% by use of *p*-xylene as an internal standard. The separated catalyst was washed with acetone followed by a mixture of H₂O₂ (30% solution in water, 2 mL) and NaOH (0.1 M solution in water, 0.05 mL) at 50 °C for 15 min. After washing with pure water and acetone successively, the catalyst was dried under vacuum and reused.

5. Photocatalytic dehydrative etherification of alcohols.

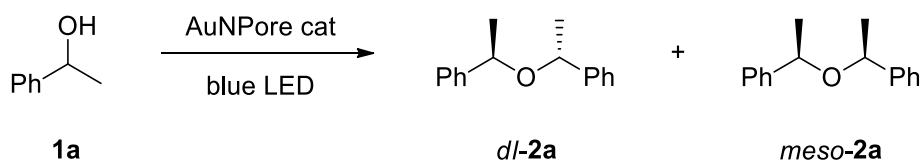


Table S1^a

entry	solvent ^b	Time (h)	yield (%) ^c	ratio (<i>dl</i> : <i>meso</i>) ^c	recovery of 1 (%) ^c
1 ^d	(CH ₂ Cl) ₂ - CCl ₄	1	0	-	99
2 ^e	(CH ₂ Cl) ₂ - CCl ₄	1	0	-	99
3 ^f	(CH ₂ Cl) ₂ - CCl ₄	1	0	-	98
4 ^g	(CH ₂ Cl) ₂ - CCl ₄	1	10	50:50	88
5 ^h	(CH ₂ Cl) ₂ - CCl ₄	1	71	61:39	28
6 ⁱ	(CH ₂ Cl) ₂ - CCl ₄	1	0	-	99
7	(CH ₂ Cl) ₂	1	0	-	99
8	CCl ₄	3	33	50:50	67

^a 1-Phenylethanol (**1a**) (0.2 mmol), AuNPore cat (0.005 mmol), solvent (0.1 mL), blue LED under N₂ atmosphere at rt. ^b Volume ratio of (CH₂Cl)₂ and CCl₄ is 2:1. ^c Determined by ¹H NMR. ^d Reaction was conducted in the absence of the catalyst. ^e Reaction was conducted without LED lamp. ^{f-h} Reactions were conducted at 40 °C,^f 75 °C,^g and 100 °C,^h in the dark. ⁱ Reaction was conducted at 100 °C in the dark in the absence of the catalyst.

6. Influence of the amount of CCl₄ on the reaction

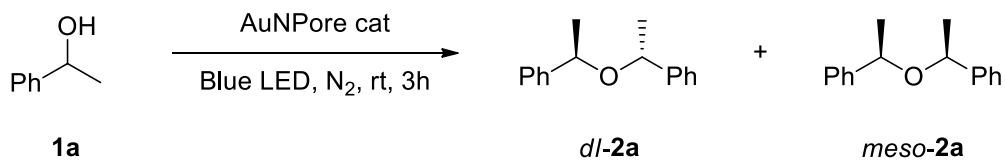


Table S2^a

entry	volume ratio		amount of CCl ₄ (mmol)	yield (%) ^b	ratio (dl:meso) ^b	recovery of 1a (%) ^b
	PhCF ₃	CCl ₄				
1	0	1	1.03	33	50:50	67
2	2	1	0.34	94	60:40	4
3	5	1	0.17	87	60:40	4
4	100	1	0.01	2	-	93
5	1	0	0	2	-	90

^a 1-Phenylethanol (**1a**) (0.2 mmol), AuNPore (0.005 mmol), solvent (0.1 mL), 3 h, N₂ atmosphere. ^b Determined by ¹H NMR.

7. SEM image of used AuNPore catalyst

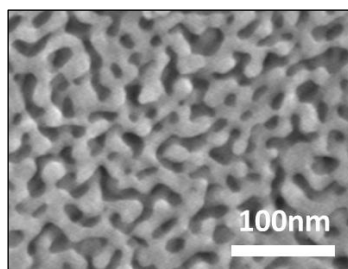


Fig. S2 SEM image of AuNPore catalyst after five time uses.

8. Light on/off experiments

The reaction of 1-phenylethanol (**1a**) (0.2 mmol) was conducted with AuNPore catalyst (0.005 mmol) under alternating periods of irradiation and darkness, and the progress of the reaction was monitored by GC as shown in Figure S3. The results clearly indicate that the catalyst shows a distinct response to light and product formation was observed only during light irradiation periods.

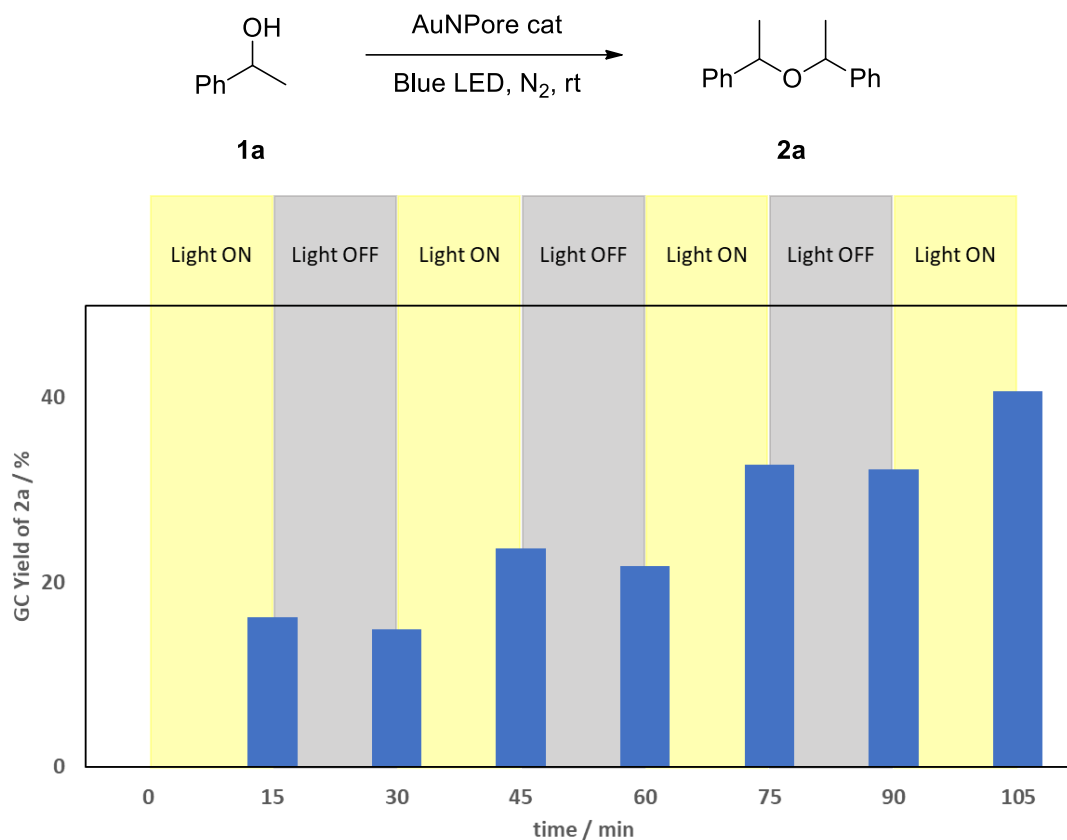


Fig. S3 Light on/off experiments in the AuNPore-catalyzed photoetherification of 1-phenylethanol **1a**.

9. Leaching test

The reaction of 1-phenylethanol (**1a**) (0.15 mmol) was performed with AuNPore catalyst (0.01 mmol), which was hung with a thin copper wire through a small hole in the catalyst (Figure S4a). After 15 min, the catalyst was removed from the reaction mixture by pulling up with a copper wire (Figure S4b). The product **2a** was produced in 21% yield at 15 min, but the chemical yield was not increased at 30 min. The yield of **2a** was determined by ^1H NMR using *p*-xylene as an internal standard.

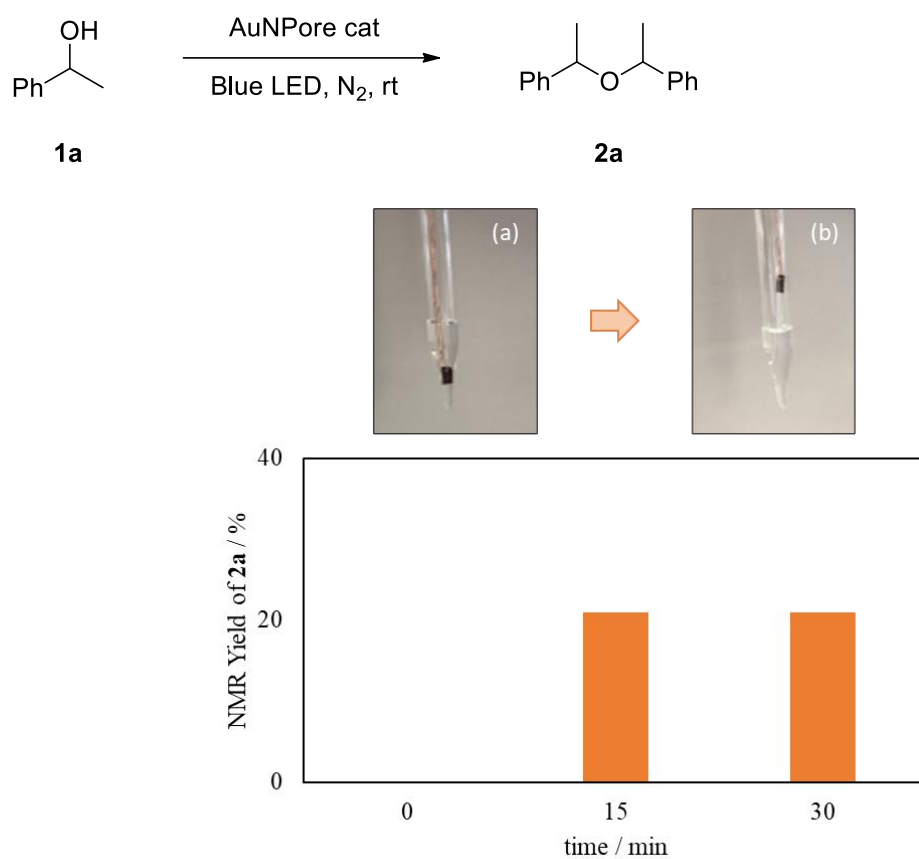


Fig. S4 Leaching test in the reaction of 1-phenylethanol **1a**. The catalyst was (a) in the reaction mixture from the beginning to 15 min and (b) out from the mixture from 15 min.

10. Quantification of the XPS data

Quantification of the Ag 3d peaks relative to the Au 4f peaks of the pristine and the refreshed sample in XPS survey spectra was conducted and the atomic percent of Au and Ag are shown in Table S3.

Table S3

Sample	At%	
	Au	Ag
Pristine sample	75.79	24.21
Refreshed sample	77.99	22.01

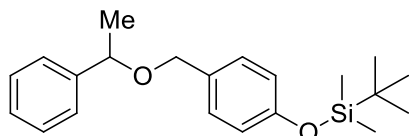
The atomic ratio of the pristine sample was found to be 95:5 by EDX. The average depth of analysis for an XPS measurement is approximately 5 nm, while EDX measures 300 nm to 5,000 nm below the surface. Therefore, the observed ratio by XPS would provide the actual composition of the catalyst at the surface.

11. Analysis of catalyst leaching

The samples were prepared based on the method of Reed et al.¹⁸ Evaporation of solvents of the reaction mixture and the washed solution of the catalyst with H₂O₂/NaOH, followed by treatment of the resulting residues with HNO₃ for Ag and aqua regia for Au, respectively. The digestions were performed in glass beakers on a hot plate at 200 °C until reduction of the volume to ~5 mL. This solution was then diluted in a volumetric flask with HNO₃ for analysis by ICPOES.

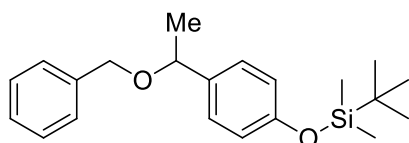
12. Spectroscopic data of the products

*tert-butyl*dimethyl(4-((1-phenylethoxy)methyl)phenoxy)silane (8a)



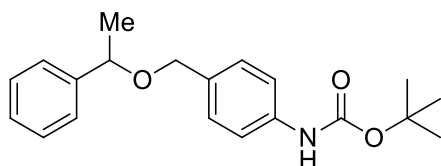
Colorless liquid. Rf = 0.64 (Hexane:EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.35 (m, 4H), 7.35 – 7.27 (m, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.50 (q, J = 6.5 Hz, 1H), 4.39 (d, J = 11.4 Hz, 1H), 4.24 (d, J = 11.4 Hz, 1H), 1.49 (d, J = 6.5 Hz, 3H), 1.01 (d, J = 5.9 Hz, 9H), 0.21 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.25 (C), 143.97 (C), 131.44 (C), 129.30 (CH), 128.60 (CH), 127.58 (CH), 126.49 (CH), 120.06 (CH), 70.20 (CH_2), 25.83 (3x CH_3), 24.36 (CH_3), 18.34 (C), -4.29 (2x CH_3); IR (Film): 2953, 2860, 1610, 1508, 1249, 1083 cm^{-1} ; HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{33}\text{O}_2\text{Si}$ [M^+]: 342.2010; found: 342.2030.

4-((1-(benzyloxy)ethyl)phenoxy)(tert-butyl)dimethylsilane (8b)



Colorless liquid. Rf = 0.64 (Hexane:EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.30 (m, 5H), 7.27 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 4.58 – 4.41 (m, 2H), 4.33 (d, J = 11.9 Hz, 1H), 1.52 (d, J = 6.5 Hz, 3H), 1.06 (s, 9H), 0.39 – 0.14 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.15 (C), 138.91 (C), 136.38 (C), 128.45 (CH), 127.85 (CH), 127.64 (CH), 127.54 (CH), 120.05 (CH), 76.84 (CH), 70.18 (CH_2), 25.82 (3x CH_3), 24.19 (CH_3), 18.32 (C), -4.26 (2x CH_3); IR (Film): 2951, 2854, 1606, 1512, 1253, 1083 cm^{-1} ; HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{33}\text{O}_2\text{Si}$ [M^+]: 342.2010; found: 342.2020.

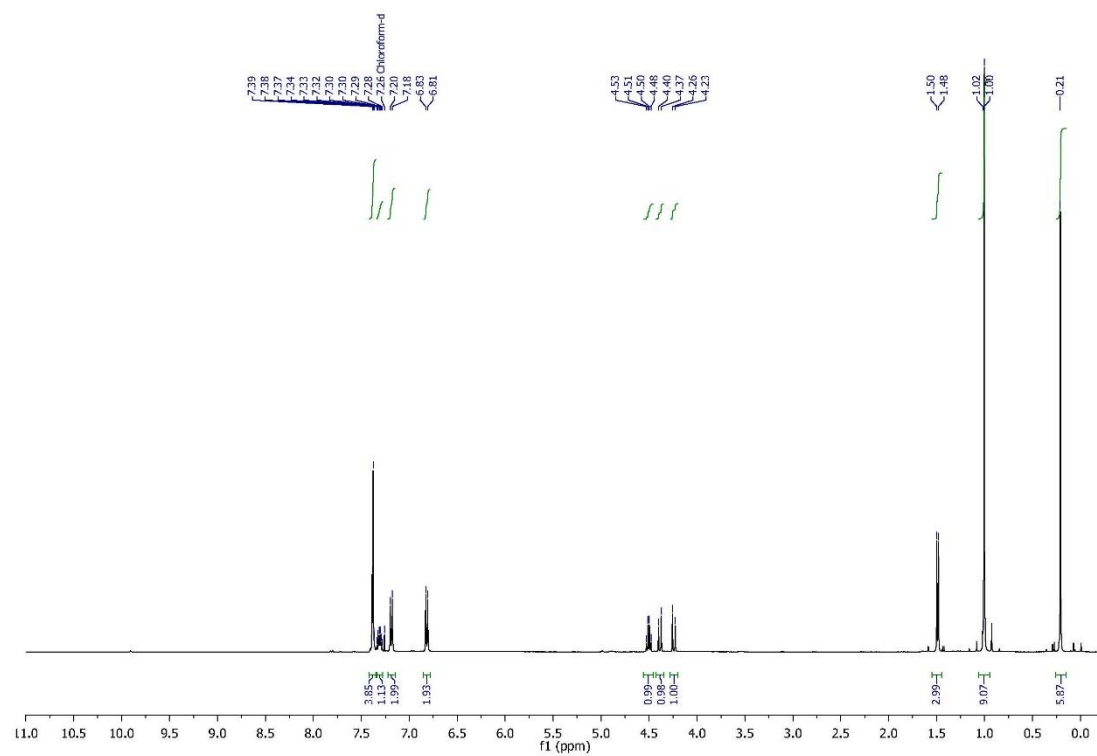
tert-butyl (4-((1-phenylethoxy)methyl)phenyl)carbamate (8c)



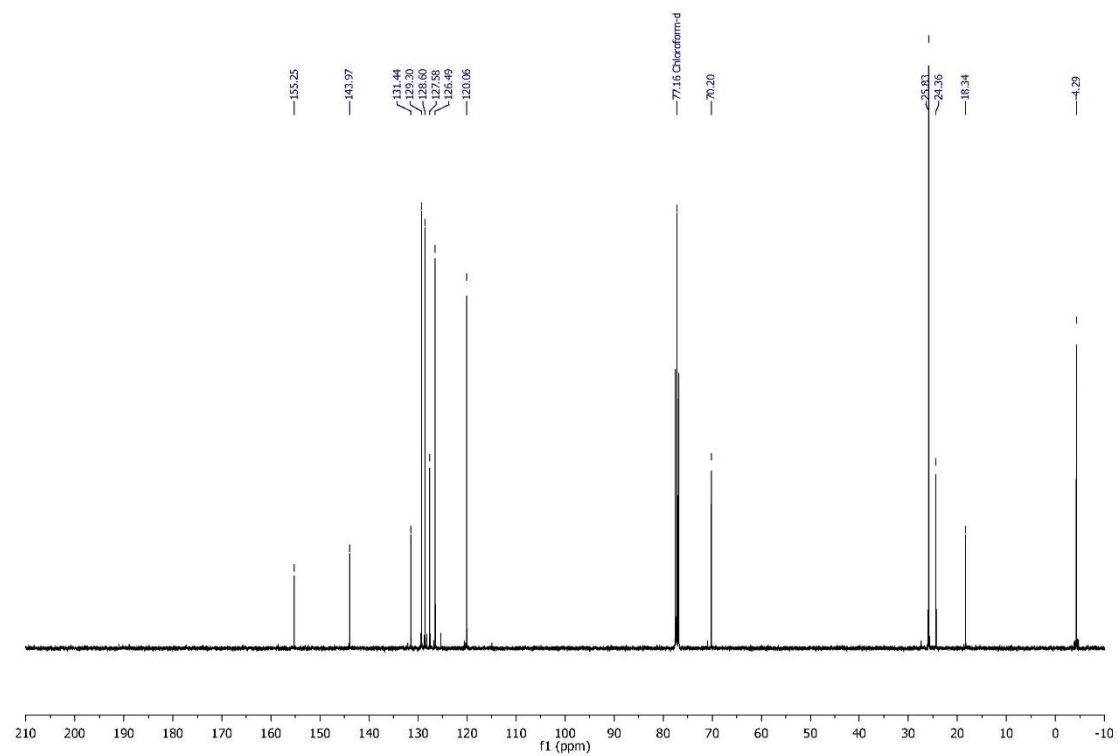
Colorless liquid. Rf = 0.40 (Hexane:EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.29 (m, 7H), 7.24 (d, J = 8.5 Hz, 2H), 6.58 (bs, 1H), 4.48 (q, J = 6.5 Hz, 1H), 4.41 (d, J = 11.7 Hz, 1H), 4.24 (d, J = 11.7 Hz, 1H), 1.53 (s, 9H), 1.47 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.88 (C=O), 143.82 (C), 137.83 (C), 133.26 (C), 128.72

(CH), 128.59 (CH), 127.59 (CH), 126.46 (CH), 118.58 (CH), 80.57 (C), 76.96 (CH), 69.94 (CH₂), 28.46 (3xCH₃), 24.29 (CH₃); IR (Film): 2970, 2862, 2245, 1718, 1695, 1595, 1153 cm⁻¹; HRMS (ESI): Calcd for C₂₀H₂₅NO₃ [M⁺+Na]: 350.1727; found: 350.1715.

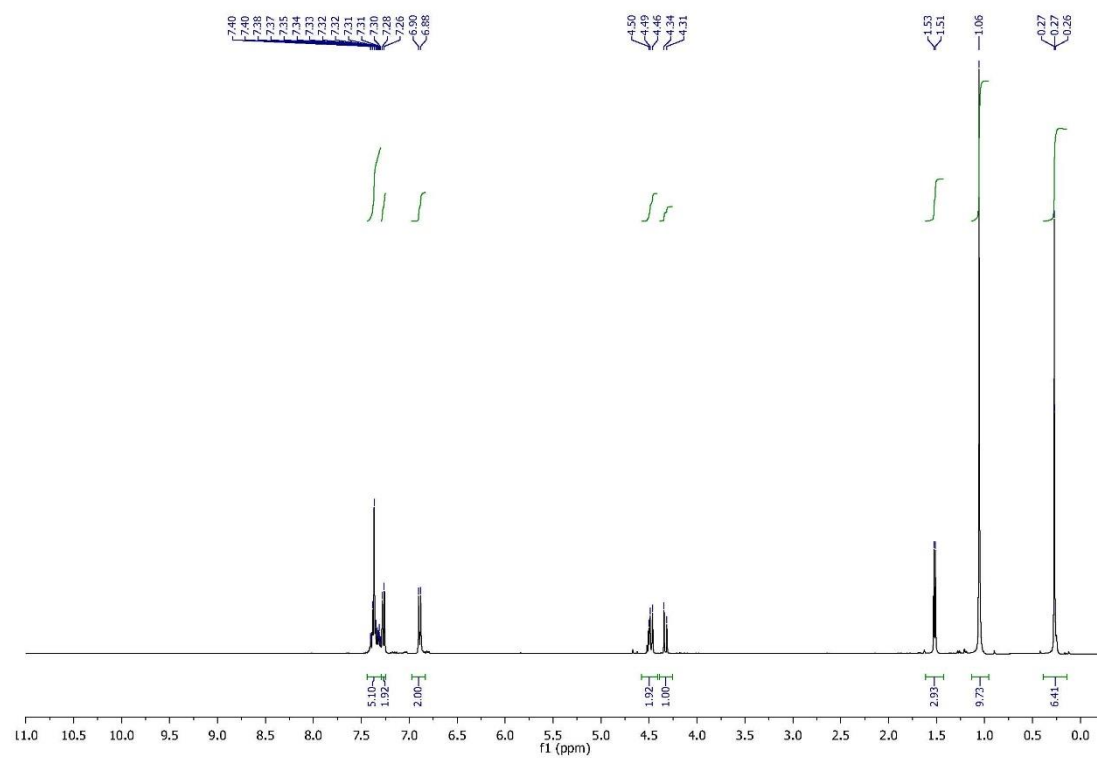
^1H NMR spectrum of **8a**



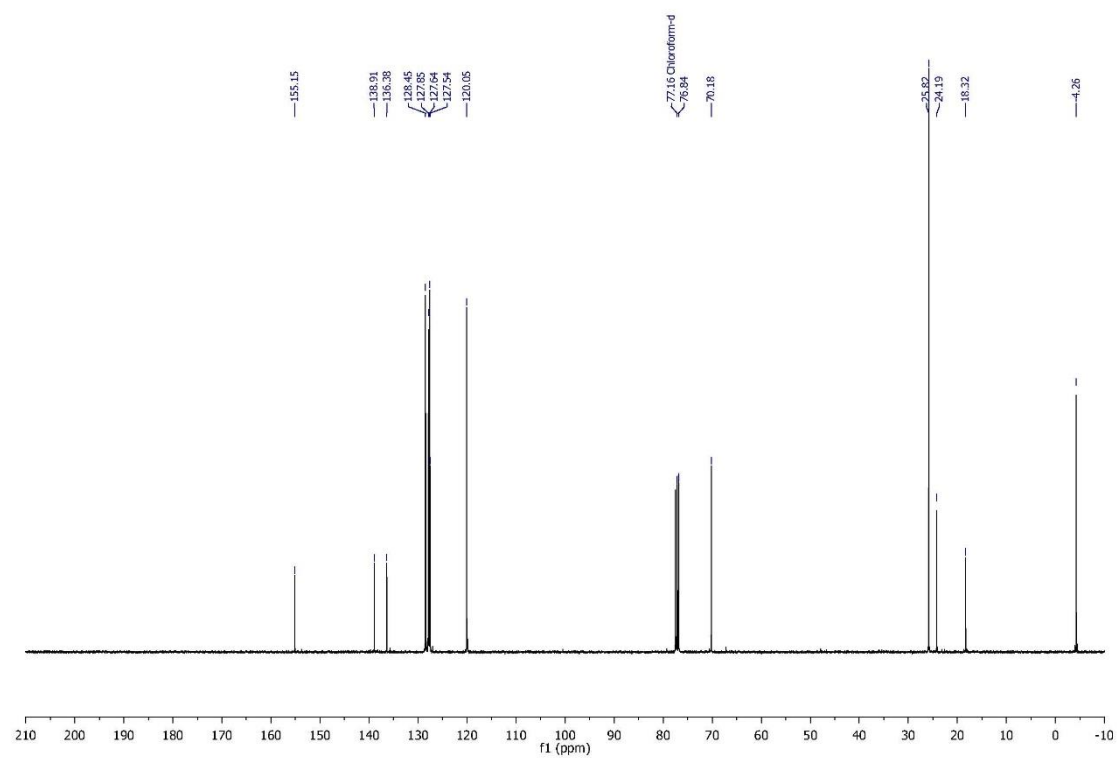
^{13}C NMR spectrum of **8a**



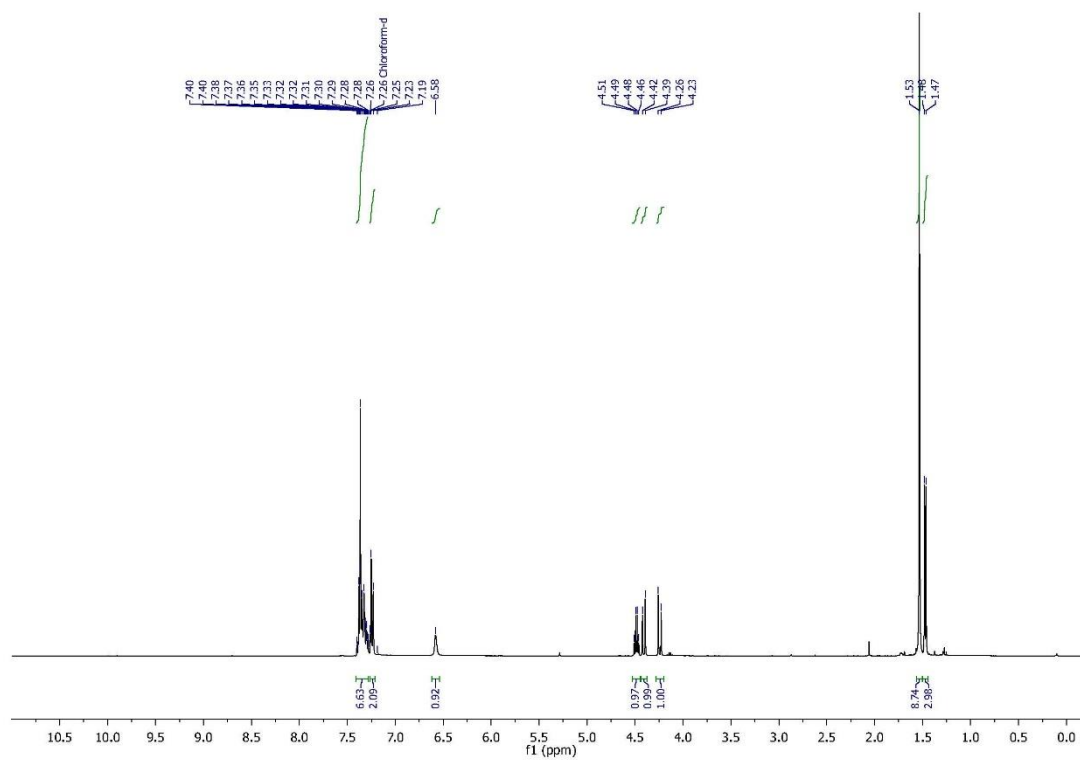
¹H NMR spectrum of **8b**



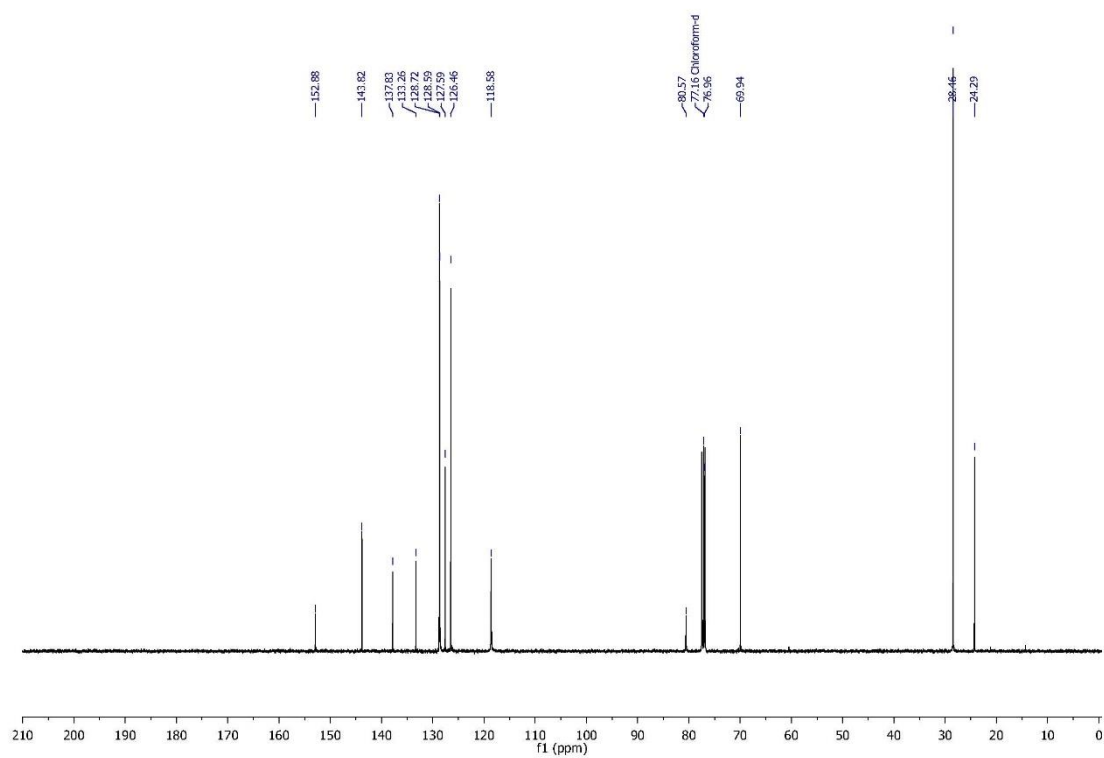
¹³C NMR spectrum of **8b**



¹H NMR spectrum of **8c**



¹³C NMR spectrum of **8c**



13. References

1. R. Sanz, D. Miguel, A. Martinez, J. M. Alvarez-Gutierrez and F. Rodriguez, *Org. Lett.* **2007**, *9*, 2027-2030.
2. M. Noji, Y. Konno and K. Ishii, *J. Org. Chem.* **2007**, *72*, 5161-5167.
3. A. Petronilho, A. Vivancos and M. Albrecht, *Catal. Sci. Technol.* **2017**, *7*, 5766-5774.
4. T. Shintou and T. Mukaiyama, *J. Am. Chem. Soc.* **2004**, *126*, 7359-7367.
5. G. A. Molander and B. Canturk, *Org. Lett.* **2008**, *10*, 2135-2138.
6. Z. L. Shen, M. Chen, T. T. Fang, M. C. Li, W. M. Mo, B. X. Hu, N. Sun and X. Q. Hu, *Tetrahedron Lett.* **2015**, *56*, 2768-2772.
7. M. Hashimoto, M. Matsumoto and S. Terashima, *Tetrahedron* **2003**, *59*, 3019.
8. H. Fujita, H. Terasaki, S. Kakuyama, K. Hioki and M. Kunishima, *Org. Lett.* **2019**, *21*, 3093-3097.
9. K. A. H. Chehade, K. Kiegiel, R. J. Isaacs, J. S. Pickett, K. E. Bowers, C. A. Fierke, D. A. Andres and H. P. Spielmann, *J. Am. Chem. Soc.* **2002**, *124*, 8206-8219.
10. F. Michalek, D. Madge, J. Ruhe and W. Bannwarth, *J. Organomet. Chem.* **2006**, *691*, 5172-5180.
11. C. F. Zhao, C. A. Soj dak, W. Myint and D. Seidel, *J. Am. Chem. Soc.* **2017**, *139*, 10224-10227.
12. F. Ke, Z. K. Li, H. F. Xiang and X. G. Zhou, *Tetrahedron Lett.* **2011**, *52*, 318-320.
13. A. B. Cuenca, G. Mancha, G. Asensio and M. Medio-Simon, *Chem. Eur. J.* **2008**, *14*, 1518-1523.
14. F. Seyfert, M. Mitha and H. A. Wagenknecht, *Eur. J. Org. Chem.* **2021**, *2021*, 773-776.
15. G. Bartoli, M. Bosco, M. Locatelli, E. Marcantoni, P. Melchiorre and L. Sambri, *Org. Lett.* **2005**, *7*, 427-430.
16. L. M. Zhang, X. J. Si, Y. Y. Yang, M. Zimmer, S. Witzel, K. Sekine, M. Rudolph and A. S. K. Hashmi, *Angew. Chem., Int. Ed.* **2019**, *58*, 1823-1827.
17. H. Im, D. Kang, S. Choi, S. Shin and S. Hong, *Org. Lett.* **2018**, *20*, 7437-7441.

18. R. B. Reed, J. J. Faust, Y. Yang, K. Doudrick, D. G. Capco, K. Hristovski and P. Westerhoff, *ACS Sustainable Chem. Eng.* **2014**, 2, 1616-1624.