Electronic Supplementary Information (ESI) for

Photocatalytic aerobic α-oxygenation of amides to imides using a highly durable decatungstate tetraphenylphosphonium salt

Chen Gu, Takafumi Yatabe, Kazuya Yamaguchi and Kosuke Suzuki*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

Contents

1. Experimental

Reagents

Tetraphenylphosphonium bromide (TPPBr), *N*-methylphthalimide, benzophenone, xanthone, anthraquinone, 2-chloroanthraquinone, acetonitrile-d_3 (CD_3CN), 2-pyrrolidone, 1-ethyl-2-pyrrolidone, 1-phenyl-2-pyrrolidone, 2-piperidone, *N*-methylacetamide, *N*-methylbenzamide, and *N*-benzylacetamide were obtained from Tokyo Chemical Industry. Acetonitrile and acetone were obtained from Kanto Chemical. Eosin Y, 1-methyl-2-piperidone, and water-^{18}O (97 atom% ^{18}O) were obtained from Sigma-Aldrich. 1-Methyl-2-pyrrolidone was obtained from FUJIFILM Wako Pure Chemical. TiO_2 (P25) was obtained from Ishihara Sangyo. $^{18}O_2$ (98 atom% ^{18}O) was obtained from Taiyo Nippon Sanso. These reagents were used as received. $TBA_4[W_{10}O_{32}]$ (TBA**W10**),[S1] $TBA_3[\alpha\text{-}PW_{12}O_{40}]$,[S2] and $TBA_4H[\gamma\text{-}PV_2W_{10}O_{40}]$[S3] were synthesized according to the reported procedures, and characterized by ESI-MS, IR, and/or NMR spectra.

Instruments

Positive-ion electrospray ionization mass spectrometry (ESI-MS) spectra were measured on JEOL JMS-T100CS spectrometer. IR spectra were measured on JASCO FT/IR-4100 using KBr disks. UV-vis spectra were measured on JASCO V-770 using a quartz cell of 1 cm path length. Gas chromatography (GC) analyses were conducted by Shimadzu GC-2025 equipped with a flame ionization detector (FID) with an InertCap5 capillary column using N_2 as carrier gas. GC mass spectrometry (GC-MS) spectra were measured on Shimadzu GCMS-QP2020 with an InertCap5 capillary column at an ionization voltage of 70 eV. ^1H and ^{31}P NMR spectra were measured on JEOL ECA-500 spectrometer (^1H, 500.16 MHz; ^{31}P, 202.47 MHz) using 5 mm tubes. Chemical shifts (δ) were reported in ppm from tetramethylsilane for ^1H NMR spectra and from H_3PO_4 (solvent, D_2O) for ^{31}P NMR spectra.

Synthesis of $TPP_4[W_{10}O_{32}]$ (TPPW10)

Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$, 16 g) and water (100 mL) were added into a 300 mL-round flask, and the resultant solution was heated to approximately 100 °C with stirring. Hot 3M HCl aqueous solution (33.5 mL) was quickly added to the solution. After stirring the solution for a few minutes, hot tetraphenylphosphonium bromide (TPPBr) aqueous solution (10.4 g of TPPBr in 30 mL of hot water) was added to the reaction solution. The solution was vigorously stirred and filtrated to collect the precipitate. The white solid was successively washed with hot water (90 °C, 100 mL), water (100 mL), ethanol (50 mL), and diethyl ether (50 mL). The solid was dried in vacuo for 3 h, then freeze dried over night to obtain TPP**W10** (16 g, 89% yield based on W). Single crystals suitable for the X-ray diffraction analysis were obtained by recrystallization of the product in a mixed solvent of acetonitrile and diethyl ether ESI-MS: *m/z* 2193.4 ($[TPP_6W_{10}O_{32}]^{2+}$), 4047.0 ($[TPP_5W_{10}O_{32}]^{+}$). IR (KBr): 1167, 1632, 1586, 1484, 1438, 1338, 1320, 1190, 1109, 997, 958, 900, 802, 753, 724, 689, 528, 436, 402, 335 cm^{-1}. UV-vis (CH_3CN): 324 nm. ^1H NMR (CD_3CN): 7.93 (m, 4H), 7.76 (m, 8H), 7.69 (m, 8H) ppm. ^{31}P NMR (CD_3CN): 23.3 ppm.

Single-crystal X-ray diffraction analysis

Diffraction measurements for the single crystals of TPP**W10** were performed on a Rigaku XtaLab Synergy-R diffractometer with rotating-anode Mo Kα radiation (λ = 0.71073 Å, 50 kV, 24 mA) at –180 °C. The data were collected and processed using CrysAlisPro.[S4] In the reduction of data, Lorentz and polarization corrections were made. Structural analyses were performed using Olex2.[S5] All structures were solved by SHELXS and refined by SHELXL-2018/3.[S6] All non-hydrogen atoms were refined anisotropically. CCDC-2336024 contains the crystallographic data for TPP**W10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical procedure for photocatalytic aerobic α-oxygenation of amides to imides

Into a glass test tube, substrate (amide, 0.6 mmol), TPP**W10** (0.7 mol%), acetonitrile (3 mL) and a Teflon-coated magnetic stir bar were added, then heated at 50 °C for a few minutes to dissolve the substrate and TPP**W10**. The test tube was placed in a water bath and photo-irradiated using a xenon lamp (λ > 350 nm, Excelitas Technologies PE300BFA) or LED (λ = 365 nm and 405 nm, Asahi Spectra Co., Ltd.) for 4 h under open air (Fig. S7). Detailed reaction conditions are described in the footnotes of tables and figures. After the photocatalytic reaction, *N*-methylphthalimide was added to the reaction solution as internal standard. The reaction solution was diluted with acetone for GC and GC-MS measurements. The conversion of substrate and yields of products were determined with GC by using internal standard technique. The products were identified by the retention time of GC, GC-MS spectra, and ^{1}H NMR spectra. Several products were isolated by silica gel column chromatography.

Recovery of TPPW10 after the photocatalytic reaction

After the photocatalytic oxidation of **1a** for 4 h using TPP**W10** as photocatalyst in acetonitrile (3 mL), the reaction solution was diluted with acetonitrile (1 mL) then added into ethyl acetate (15 mL). The solution was allowed to stand for 5 min and the precipitated TPP**W10** was collected by filtration. Recovered TPP**W10** was vacuum dried and characterized by IR, ESI-MS, and NMR spectra.

2. Characterization of TPPW10

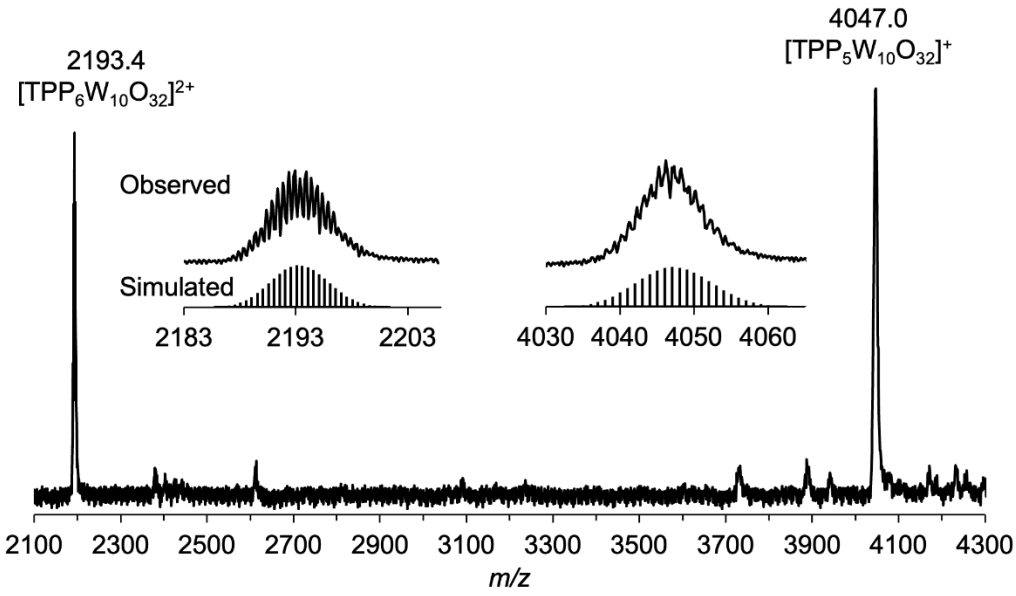


Fig. S1 Positive-ion ESI-MS spectrum of TPP**W10** in CH_3CN.

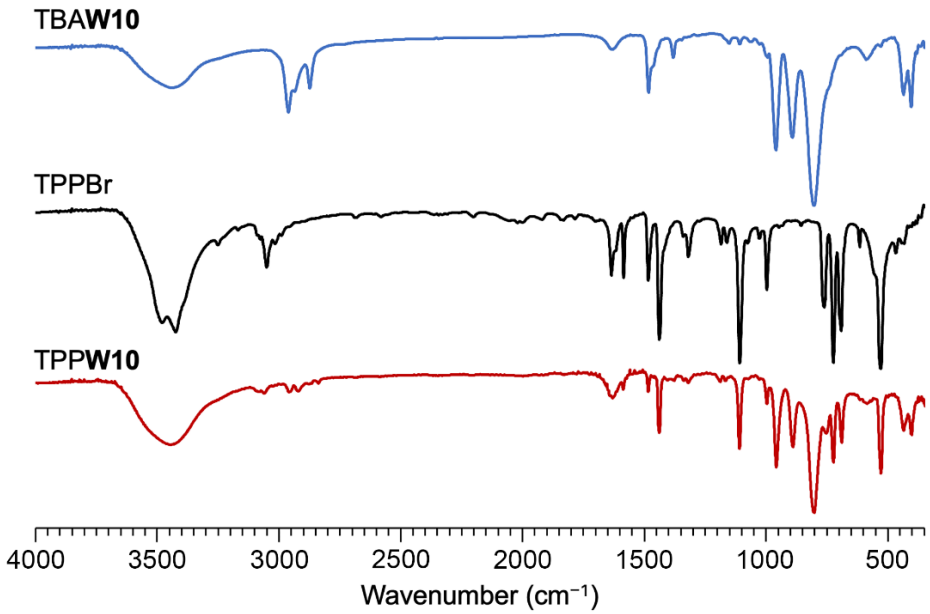


Fig. S2 IR spectra of TBA**W10**, TPPBr, and TPP**W10** (KBr disc).

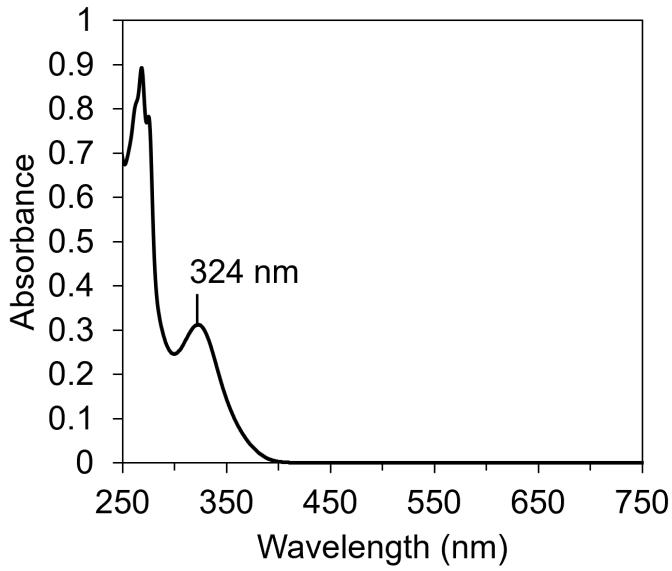


Fig. S3 UV-vis spectrum of TPP**W10** in CH_3CN (0.03 mM).

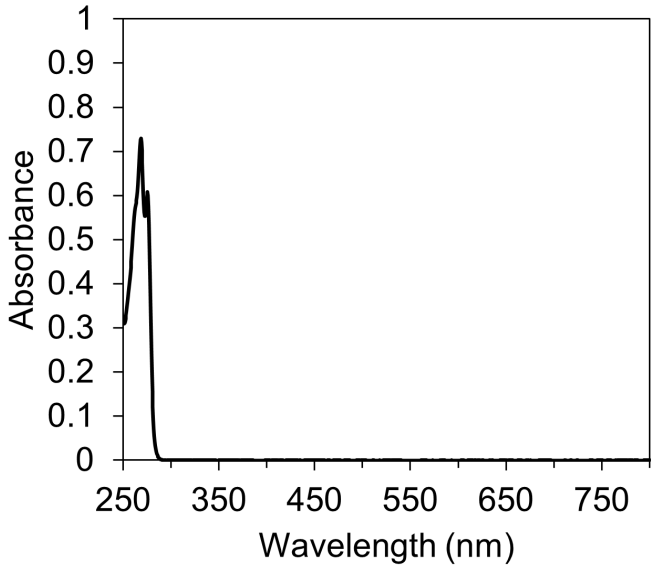


Fig. S4 UV-vis spectrum of TPPBr in CH_3CN (1.0 M).

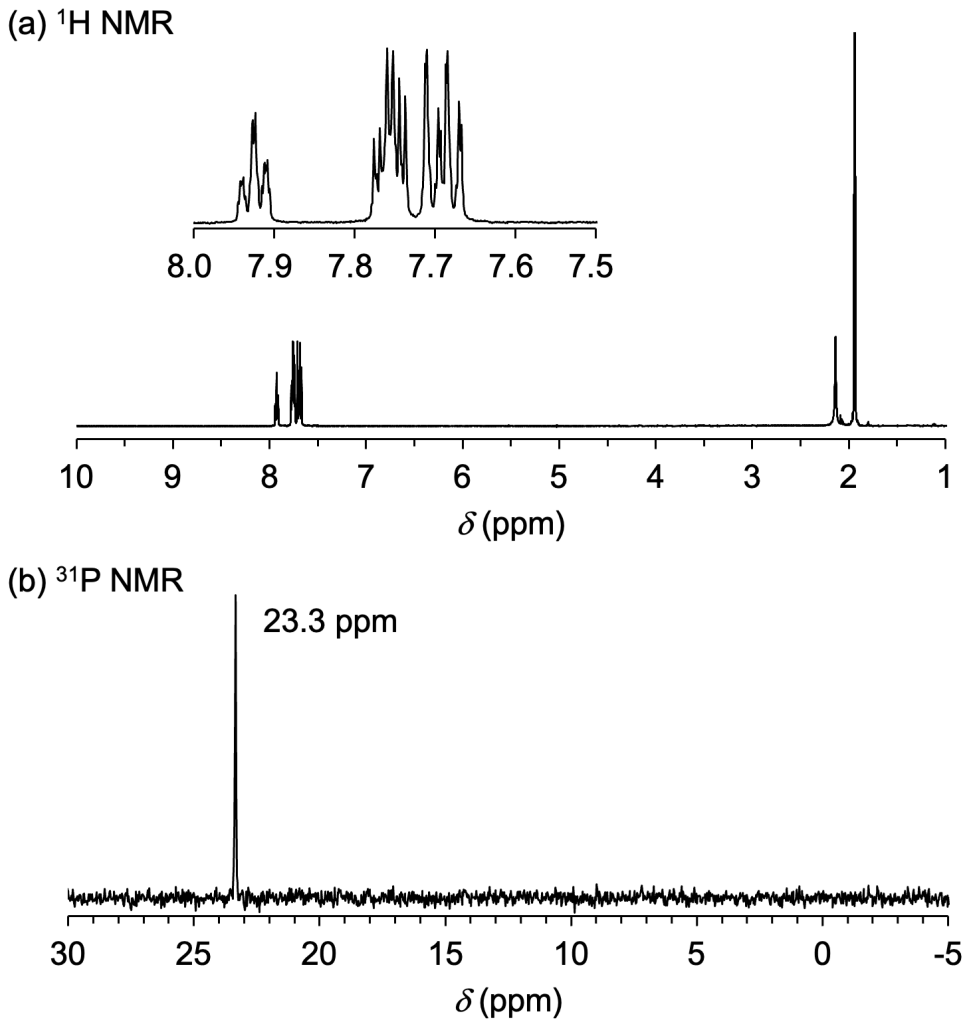


Fig. S5 (a) ^{1}H and (b) ^{31}P NMR spectra of TPP**W10** in CD_3CN.

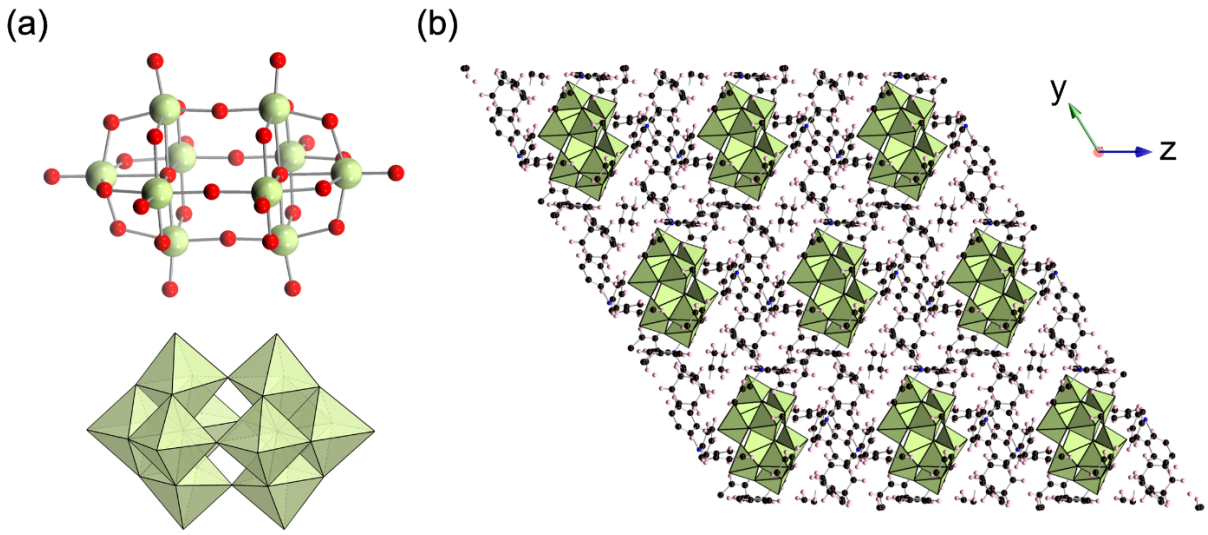


Fig. S6 Crystal structure of TPP**W10**: (a) anion structures and (b) packing structures (color code: W, green; O, red; C, black; P, blue; H, pink; {WO_6}, green octahedra).

3. Photocatalytic reaction setup

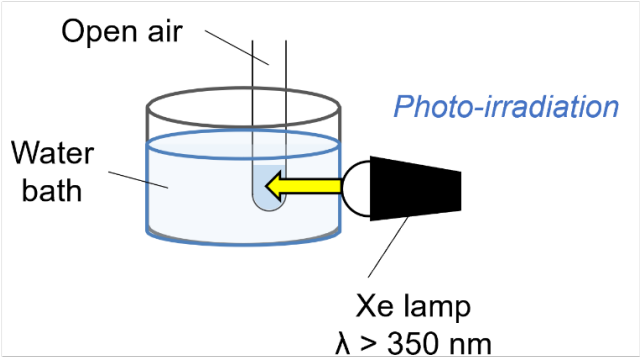


Fig. S7 A reaction set up for the photocatalytic reaction.

4. Recovery of TPPW10 after the photocatalytic reaction

Fig. S8 A photograph of the recovered TPP**W10** after the photocatalytic aerobic α-oxygenation of **1a**.

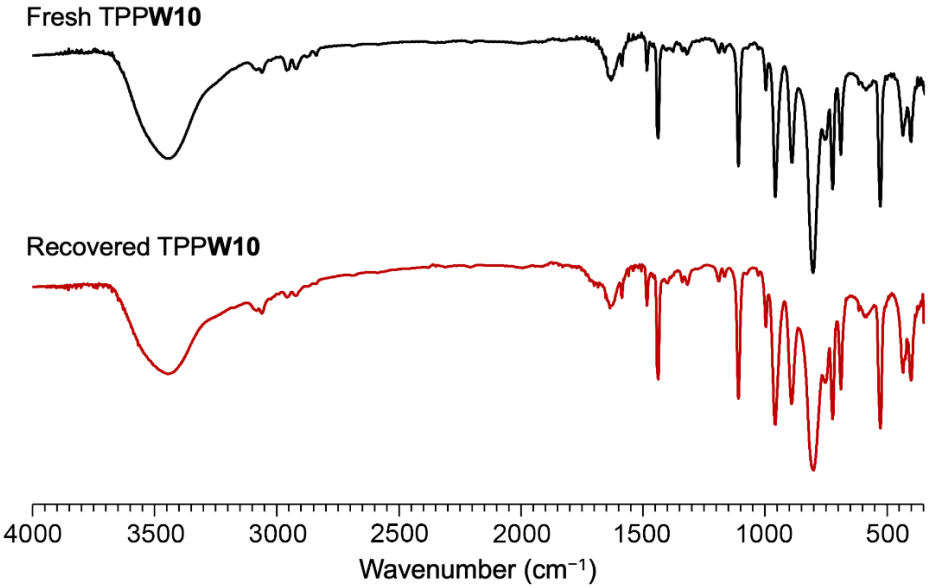


Fig. S9 IR spectra of the fresh and recovered TPP**W10** after the photocatalytic aerobic α-oxygenation of **1a** (KBr disc).

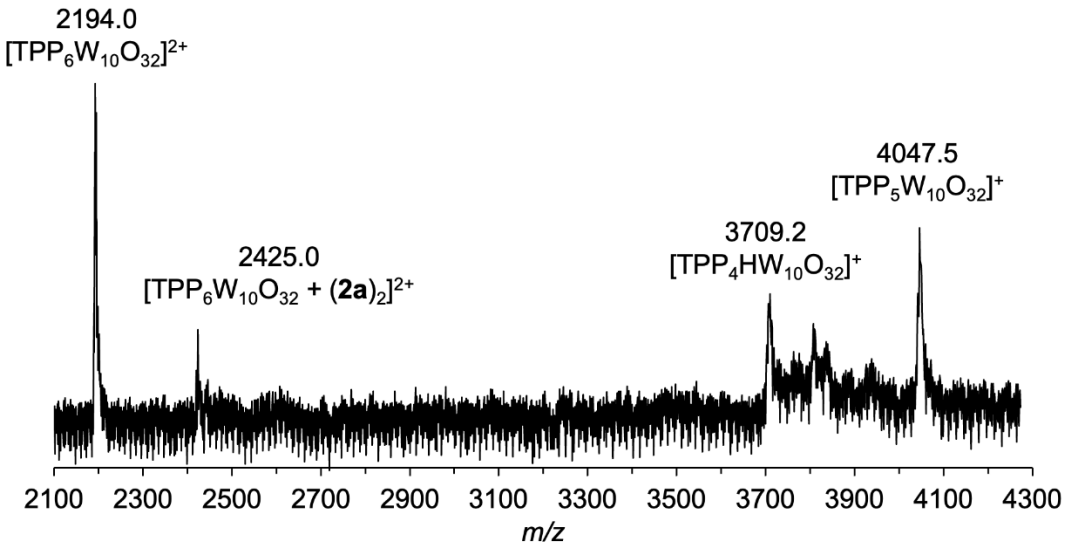


Fig. S10 ESI-MS spectrum of the recovered TPP**W10** in CH_3CN after the photocatalytic aerobic α-oxygenation of **1a**.

5. Degradation of TBAW10 after the photocatalytic reaction

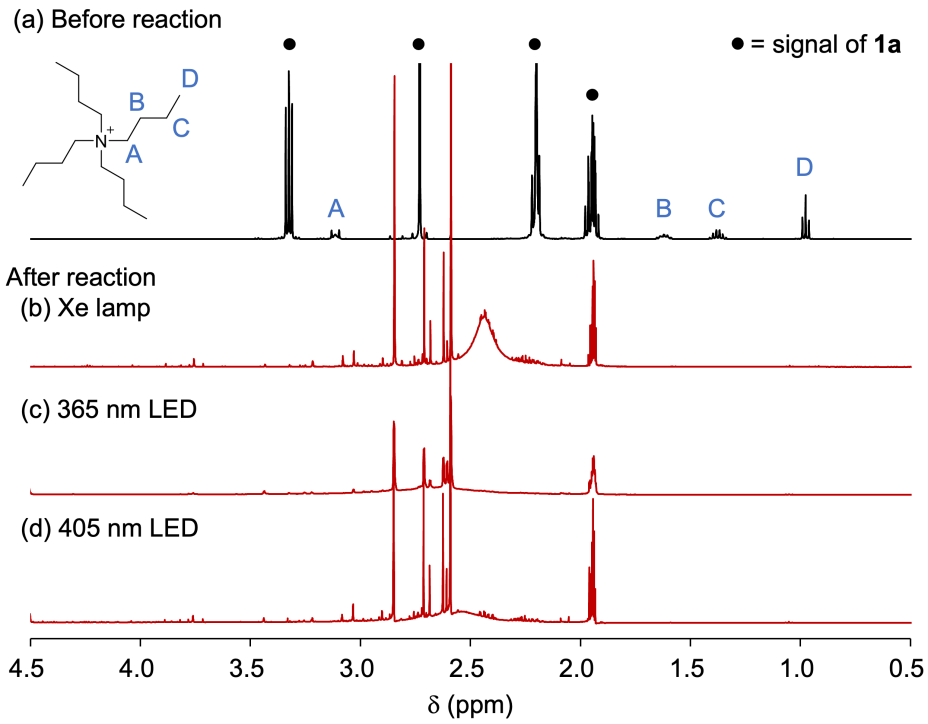


Fig. S11 ^{1}H NMR spectra of TBA**W10** in CD_3CN before and after the photocatalytic aerobic α-oxygenation of **1a**. (a) Before the reaction, (b) after the reaction using Xe lamp, (c) after the reaction using 365 nm LED, and (c) after the reaction using 405 nm LED. The degradation of TBA was observed after the photocatalytic reaction using both Xe lamp and LED.

6. ^{18}O isotope labelling experiments

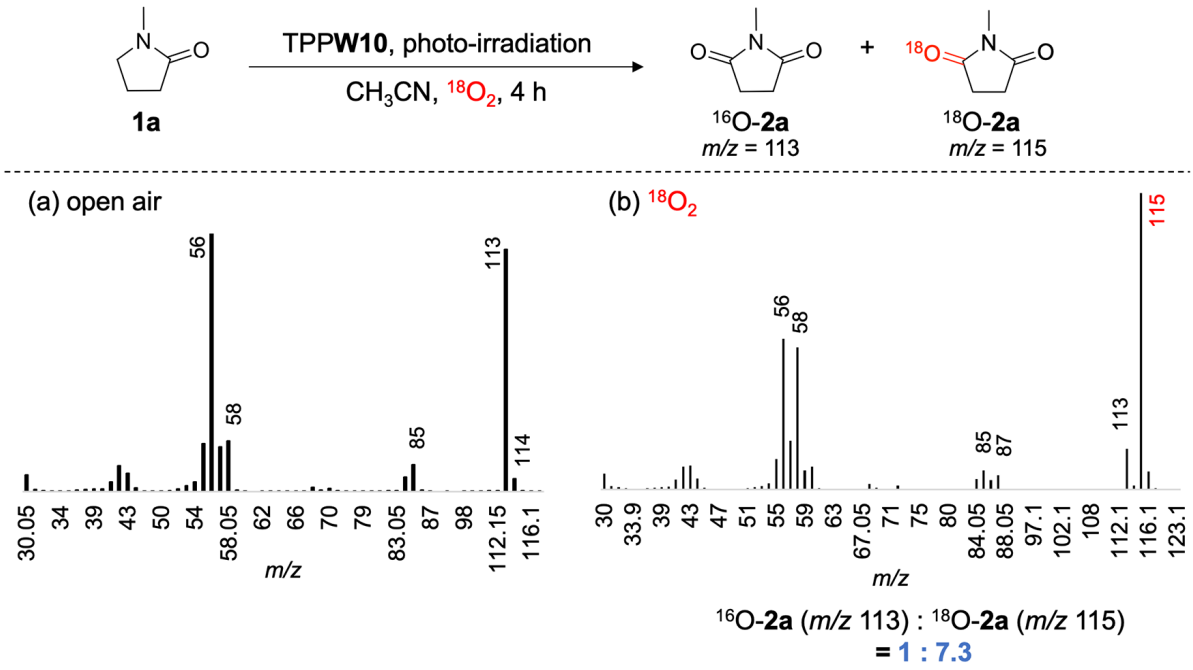


Fig. S12 GC-MS spectra of the product **2a** when the α-oxygenation of **1a** using TPP**W10** (0.7 mol%) was performed under (a) open air and (b) $^{18}O_2$ atmosphere.

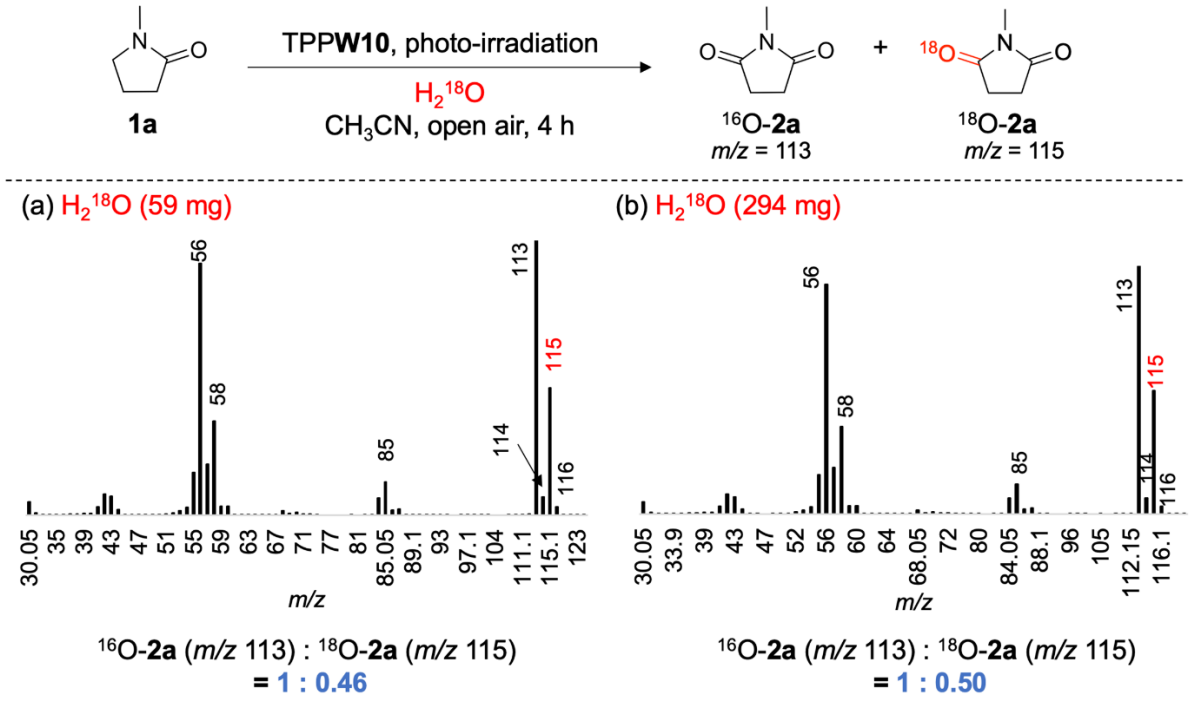
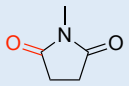
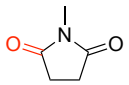
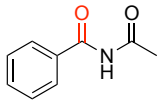
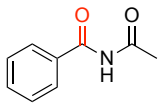
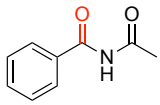
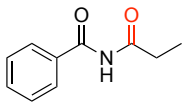
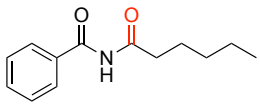
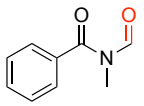
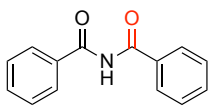


Fig. S13 GC-MS spectra of the product **2a** when the α-oxygenation of **1a** using TPP**W10** (0.7 mol%) was performed in the presence of $H_2{}^{18}O$ (a, 59 mg; b, 294 mg).

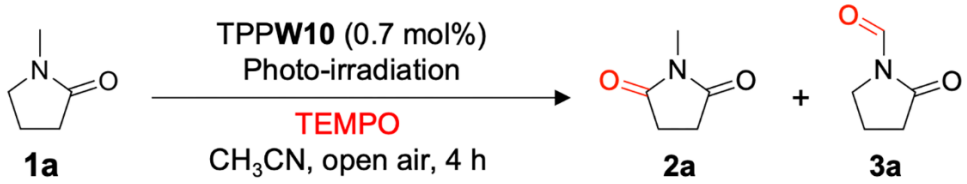
7. Comparison with previously reported photocatalytic systems

Table S1. Reported photocatalytic systems for direct imides synthesis via α-oxygenation of amides.

Photocatalyst	Additive	Oxidant, O source	Time (h)	Scope	Product and yield	Ref.
TPP**W10** (0.7 mol%)	–	O_2	4	Lactams, aliphatic amides, benzamides, benzylamides	 83%	**This work**
Benzophenone (25 mol%)	–	O_2	Not described	Lactams	 60%	S7
TiO_2 (0.5 mol%)	–	O_2	48	Lactams		S8
I_2 (1 mol%)	–	O_2	48	Benzylamides	 71%	S9
48% HBr aq (5 mol%)	$Ca(OH)_2$ (2.5 mol%)	O_2	10	Benzylamides	 96%	S10
2-Chloroanthraquinone (10 mol%)	–	O_2	10	Benzylamides	 95%	S11
KBr (30 mol%)	–	Oxone (2 mol%)	7	*N*-alkylbenzamides, lactams, aliphatic amides, benzylamides	 85%	S12
N-bromosuccinimide (NBS) (200 mol%)	–	H_2O	1	*N*-alkylbenzamides, benzylamides	 91%	S13
$CuCl_2$ (5 mol%)	NH_4Cl (20 mol%)	O_2, H_2O	72	Benzamides, etc.	 83%	S14
$Fe(NO_3)_3$•$9H_2O$ (8 mol%)	$NaBrO_3$ (200 mol%)	O_2, H_2O, •OH	12	Benzylamides, benzamide, aliphatic amides	 94%	S15

8. Radical scavenger test

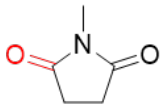
Table S2. Effect of radical scavenger for the photocatalytic α-oxygenation of **1a** using TPP**W10**. [a]



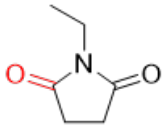
Entry	Radical scavenger	Conv. (%) of **1a**	Yield (%)	
			2a	**3a**
1	–	>99	83	1
2	TEMPO	64	3	<1

[a] Reaction conditions: **1a** (0.6 mmol), photocatalyst (0.7 mol%), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 2 equivalents with respect to **1a**), acetonitrile (3 mL), open air, 4 h, photo-irradiation by Xe lamp (λ > 350 nm). Conversions and yields were determined by GC using *N*-methylphthalimide as an internal standard.

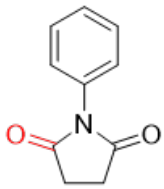
9. Product data



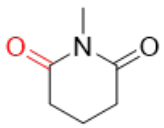
2a (CAS No. 1121-07-9): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 5.33 min. MS (EI) *m/z* (%): 114 (5), 113 (94) [M^+], 85 (11), 84 (6), 58 (20), 57 (17), 56 (100), 55(19), 43 (7), 42 (10), 30(6).[S16] ^{1}H NMR (500 MHz, CD_3CN, TMS) δ: 2.85 (s, 3H, -CH_3), 2.59 (s, 4H, -CH_2-) ppm. ^{13}C NMR (125 MHz, CD_3CN, TMS): δ 178.9, 28.9, 24.9 ppm. Isolated as white solid (Isolated yield: 34%; silica gel column chromatography; ethyl acetate/*n*-hexane = 1/0.5, R_f = 0.32).



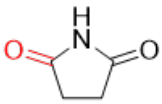
2b (CAS No. 2314-78-5): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 5.97 min. MS (EI) *m/z* (%): 128(7), 127 (93) [M^+], 112(15), 100(5), 99 (23), 84 (60), 71(7), 70 (11), 57 (18), 56 (100), 55 (38), 44 (15), 42 (16), 41 (16), 30(10).[S17]



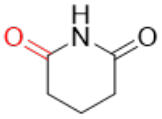
2c (CAS No. 83-25-0): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 12.2 min. MS (EI) *m/z* (%): 176 (12), 175 (100) [M^+], 147 (12), 146 (9), 130(7), 120 (31), 119 (65), 118 (13), 104(9), 93 (37), 92 (20), 91 (20), 77 (26), 64 (16), 63(8), 56(22), 55 (30), 51 (10), 39(6). [S16]



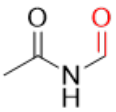
2d (CAS No. 25077-25-2): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 6.76 min. MS (EI) *m/z* (%): 127 (62) [M^+], 99(9), 98 (20), 71 (12), 70 (22), 58 (9), 55 (15), 43 (12), 41 (100), 41 (12), 39(11).[S18]



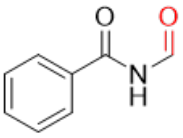
2e (CAS No. 123-56-8): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 5.84 min. MS (EI) *m/z* (%): 100 (5), 99 (100) [M^+], 70 (6), 56 (84), 55 (8), 42 (6.6). [S18] ^{1}H NMR (500 MHz, CD_3CN, TMS) δ: 9.02 (s, 1H, -NH-), 2.62 (s, 4H, -CH_2-) ppm. ^{13}C NMR (125 MHz, CD_3CN, TMS): δ 179.8, 30.4 ppm. Isolated as white solid (Isolated yield: 69%, silica gel column chromatography; ethyl acetate/*n*-hexane = 1/0.2, R_f = 0.29).



2f (CAS No. 1121-89-7): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 6.64 min. MS (EI) *m/z* (%): 114(3), 113 (48) [M^+], 70 (33), 55 (2), 44 (2), 43 (5), 42 (100), 41 (10), 39 (9).[S19] ^{1}H NMR (500 MHz, CD_3CN, TMS) δ: 8.74 (brs, 1H, -NH-), 2.48 (t, J = 6.5 Hz, 4H), 1.94-1.89 (m, 2H). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ 174.4, 32.1, 18.5 ppm. Isolated as white solid (Isolated yield: 46%, Silica gel column chromatography; ethyl acetate/*n*-hexane = 1/0.5, R_f = 0.21).

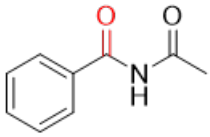


2g (CAS No. 21163-79-1): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 3.16 min. MS (EI) *m/z* (%): 87 (8) [M^+], 59 (100), 44 (47), 43 (86), 42 (23), 41 (5).[S20]

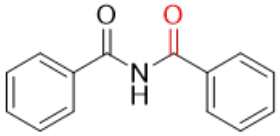


2h (CAS No. 4252-31-7): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C;

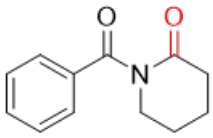
retention time, 10.2 min. MS (EI) *m/z* (%): 149 (9) [M^+], 121 (50), 106 (8), 105 (100), 104 (7), 103 (7), 78 (8), 77 (81), 51 (32), 50 (13). ^{1}H NMR (500 MHz, CD_3CN, TMS) δ: 9.69 (brs, 1H, -NH-), 9.27 (d, J = 9.5 Hz, 1H, -CHO-), 7.94-7.92 (m, 2H, Ar-H), 7.67 (t, J = 7.5 Hz, 1H, Ar-H), 7.54 (t, J = 8.0 Hz, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, CD_3CN, TMS): δ 168.2, 164.4, 134.5, 132.8, 129.8, 129.1 ppm. Isolated as white solid (Isolated yield: 31%, silica gel column chromatography; ethyl acetate/*n*-hexane = 1/0.7, R_f = 0.42).



2i (CAS No. 1575-95-7): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 10.5min. MS (EI) *m/z* (%): 163(22) [M^+], 162(24), 70 (33), 106 (9), 105 (100), 77 (51), 51 (18), 50 (6), 43 (23).[S22] ^{1}H NMR (500 MHz, CD_3CN, TMS) δ: 9.30 (brs, 1H, -NH-), 7.87 (d, J = 7.5 Hz, 2H, Ar-H), 7.61 (t, J = 7.5 Hz, 1H, Ar-H), 7.50 (t, J = 8.0 Hz, 2H, Ar-H), 2.41 (s, 3H, -CH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN, TMS): δ 173.3, 167.2, 134.3, 133.8, 129.6, 129.0, 25.8 ppm. Isolated as white solid (Isolated yield: 45%, silica gel column chromatography; ethyl acetate/*n*-hexane = 1/3, R_f = 0.21).

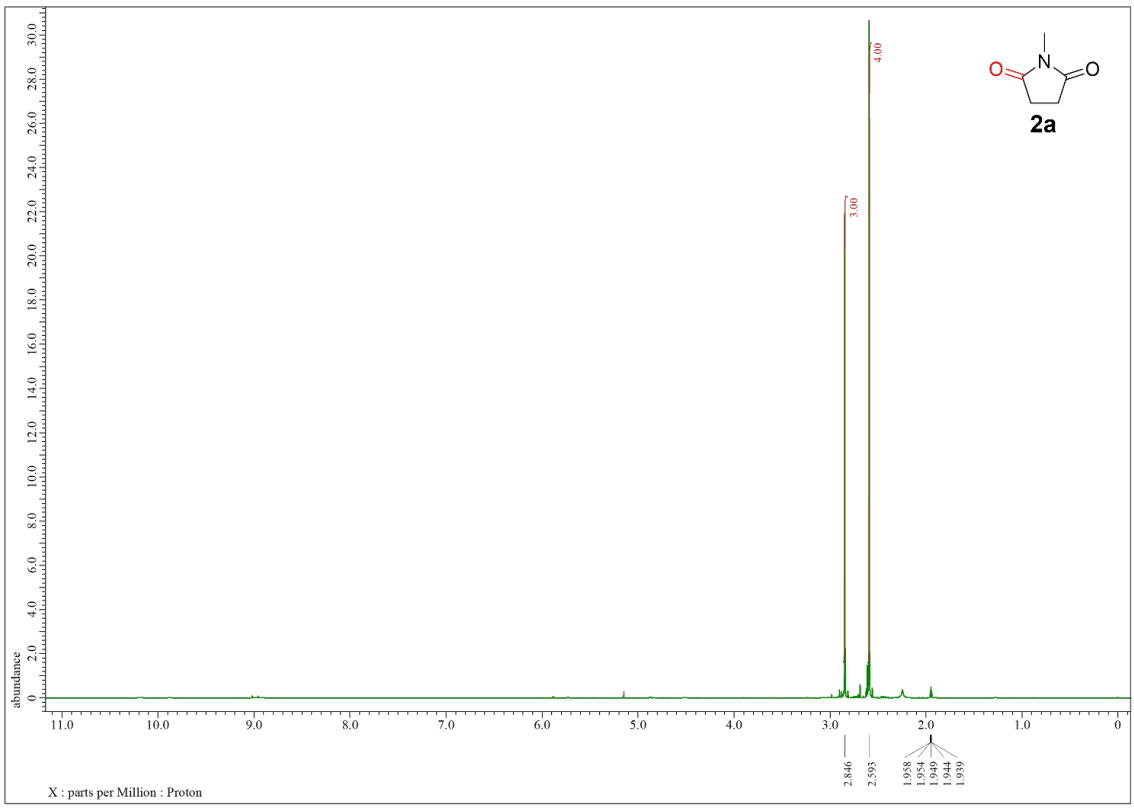


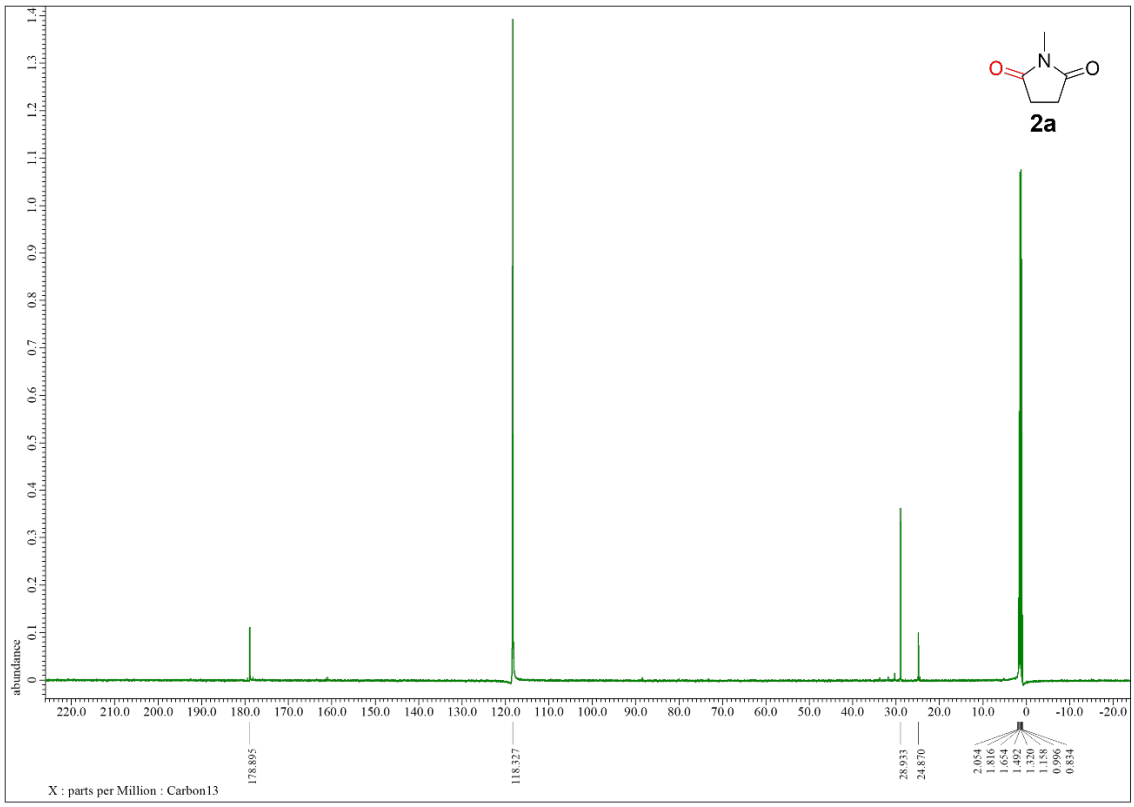
2j (CAS No. 614-28-8): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 50 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 14.9 min. MS (EI) *m/z* (%): 225 (18) [M^+], 207 (16), 197 (10), 122 (19), 105 (100), 103 (55), 77 (61), 76 (24), 51 (24), 50 (15).[S22,S23]

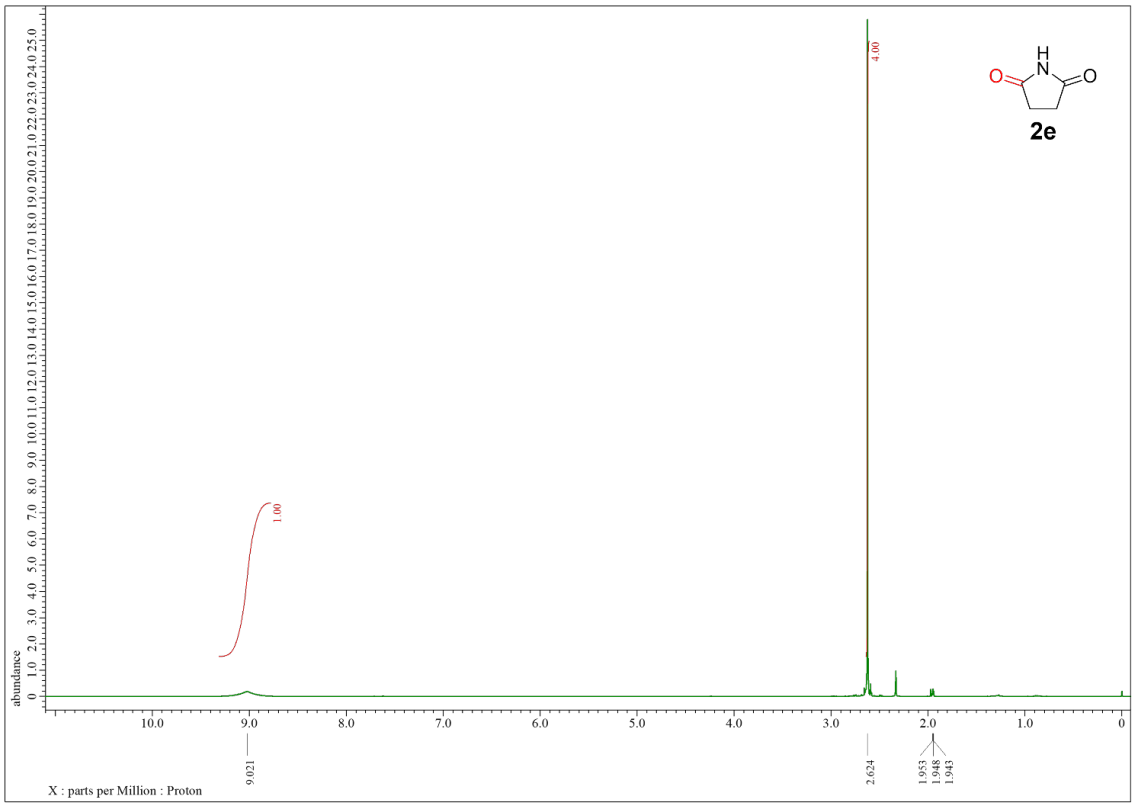


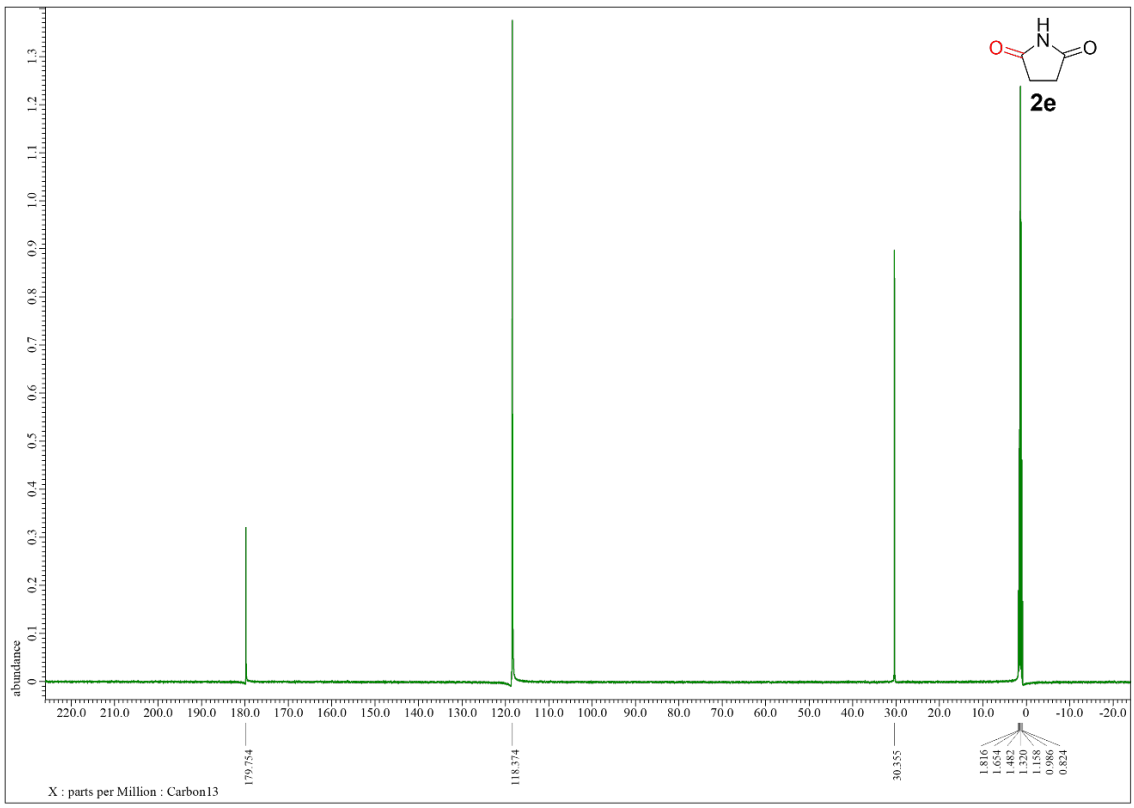
2k (CAS No. 4252-56-6): GC conditions and analysis: InertCap5 capillary column (df = 0.25 μm, I.D. = 0.25 mm, 30 m, GL Science Inc.); carrier gas (N_2) flow rate, 1.6 mL/min; initial column temp., 50 °C; final column temp., 280 °C; progress rate, 10 °C min^{-1} (10 min), 20 °C min^{-1} (6.5 min); injection temp., 250 °C; detection temp., 280 °C; retention time, 13.4 min. MS (EI) *m/z* (%): 203 (10) [M^+], 202 (9), 175 (12), 146 (3), 105 (100), 77 (49), 51 (12).[S23]

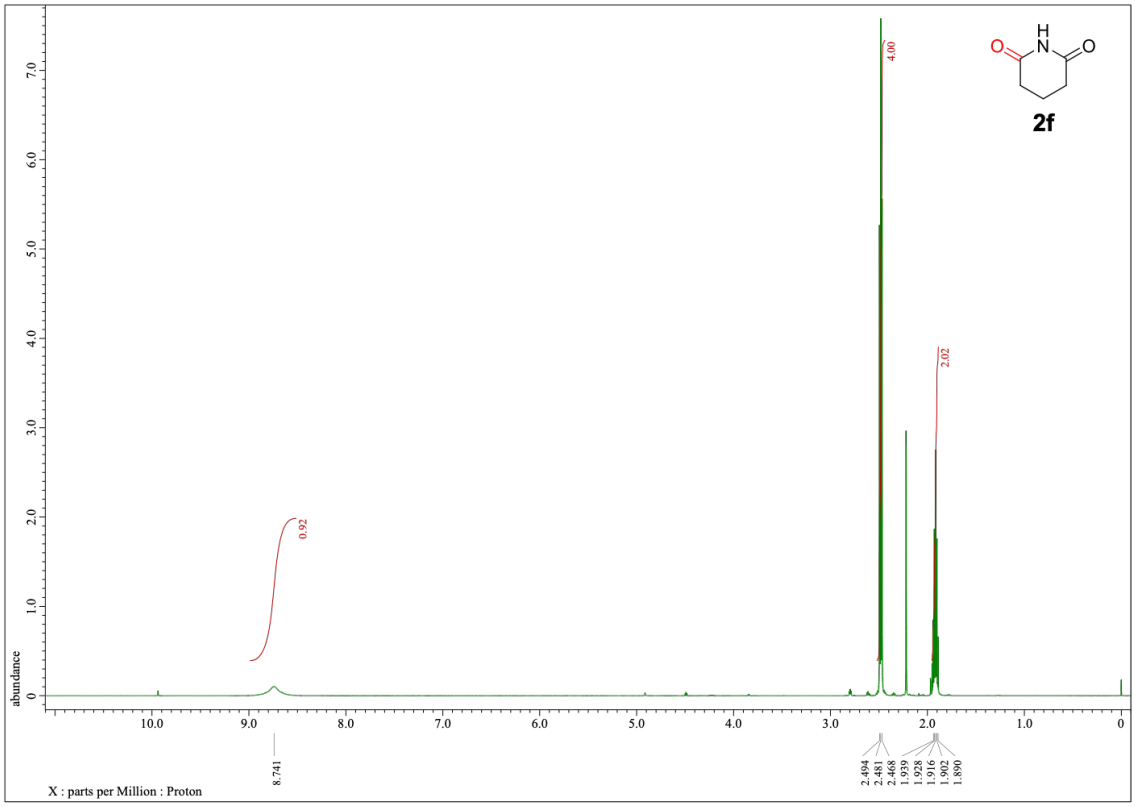
^{1}H and ^{13}C NMR spectra of products

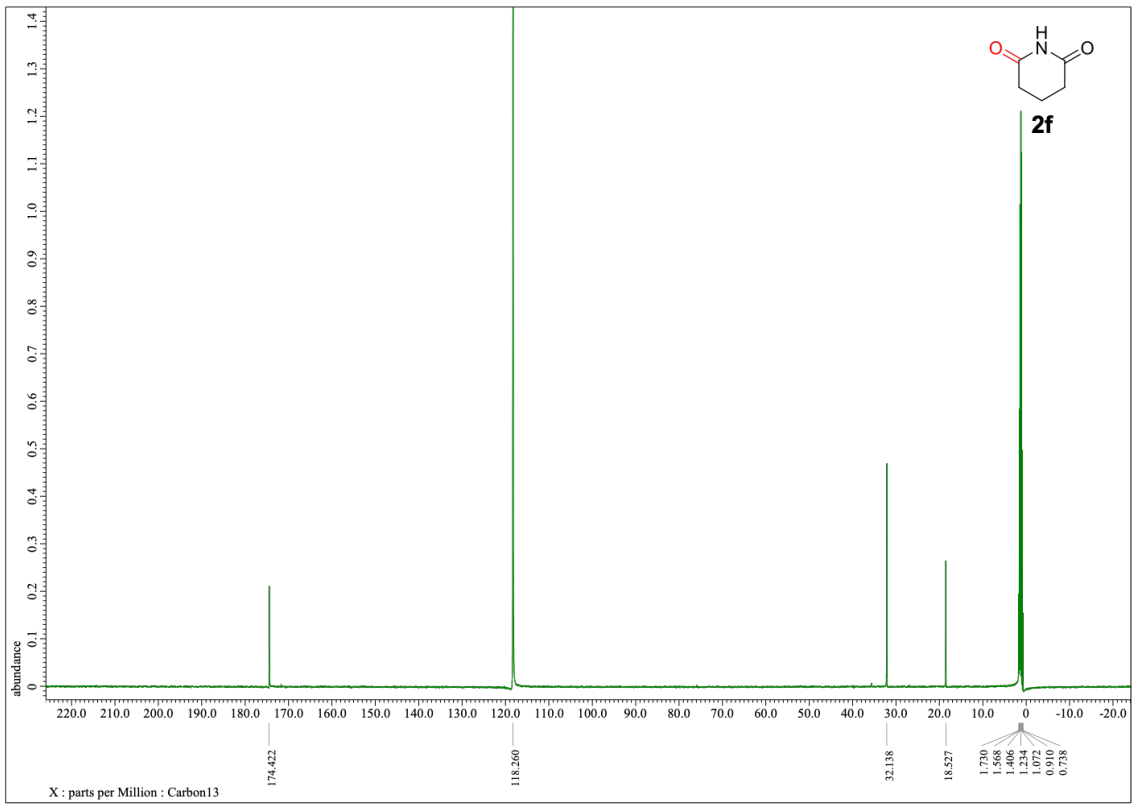


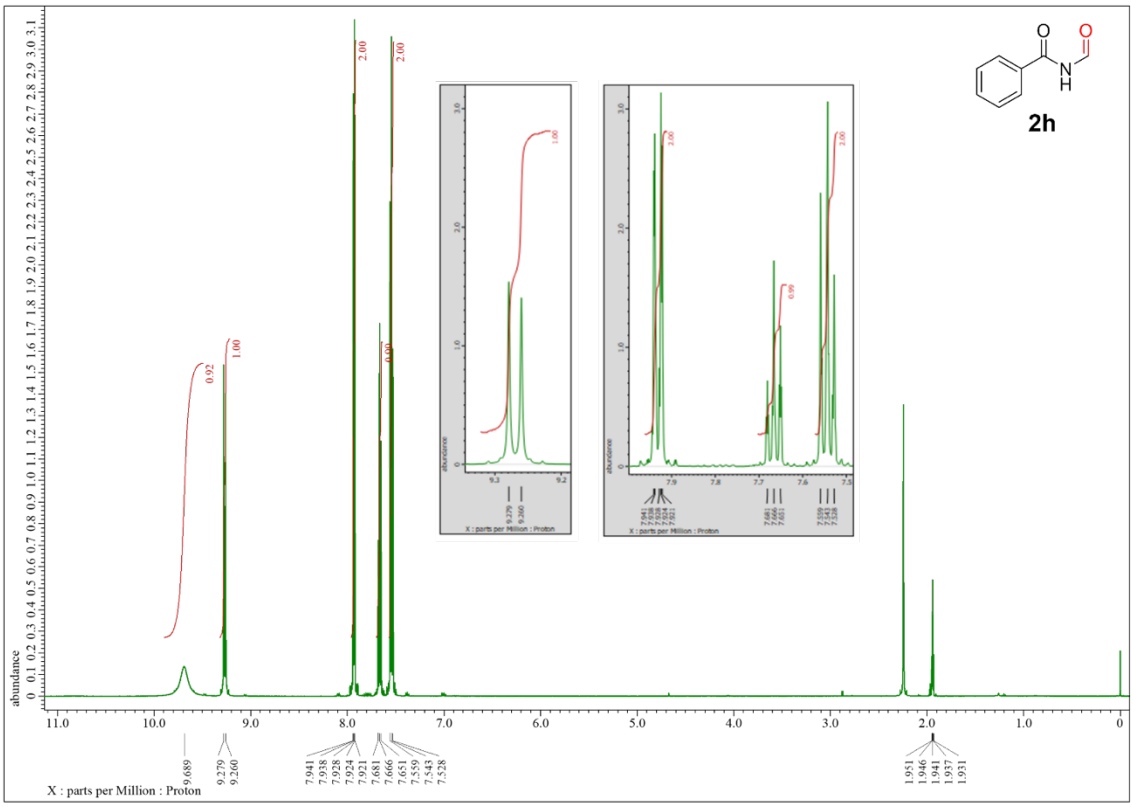


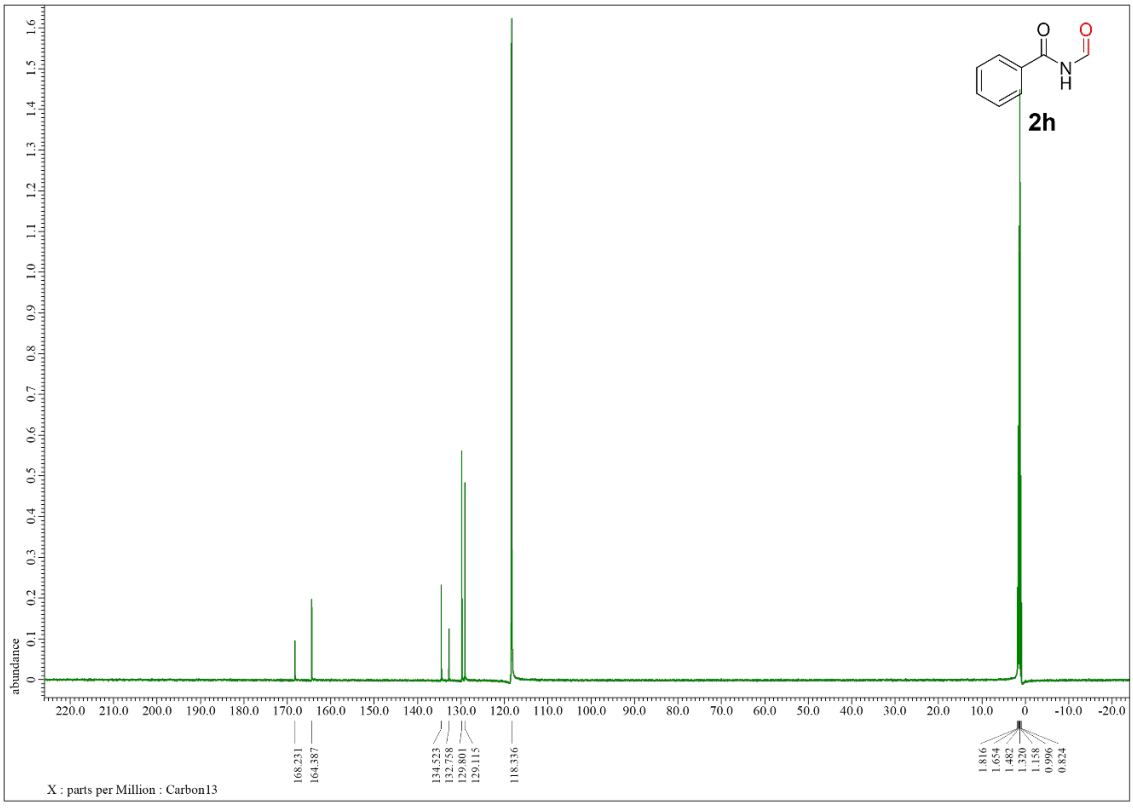

2e
4.00
1.00
abundance
9.021
2.624
1.953
1.948
1.943
X : parts per Million : Proton

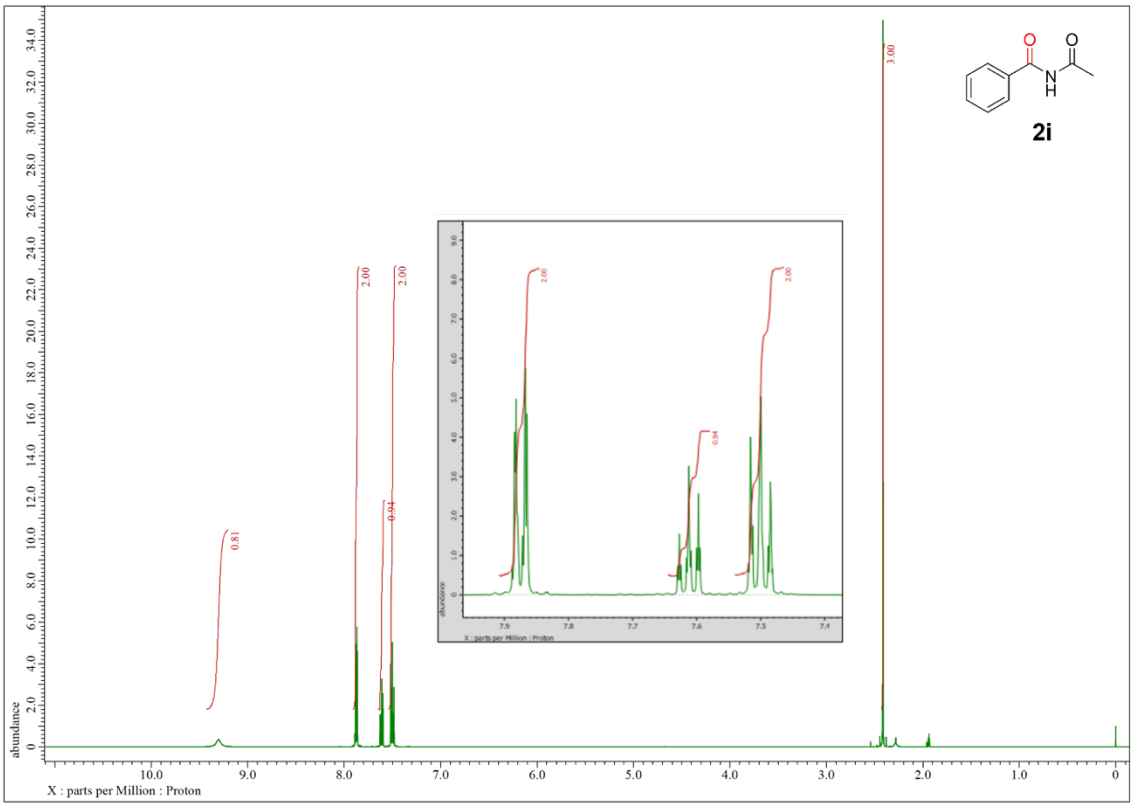

2e
abundance
179.754
118.374
30.355
1.816
1.654
1.482
1.320
1.158
0.986
0.824
X : parts per Million : Carbon13

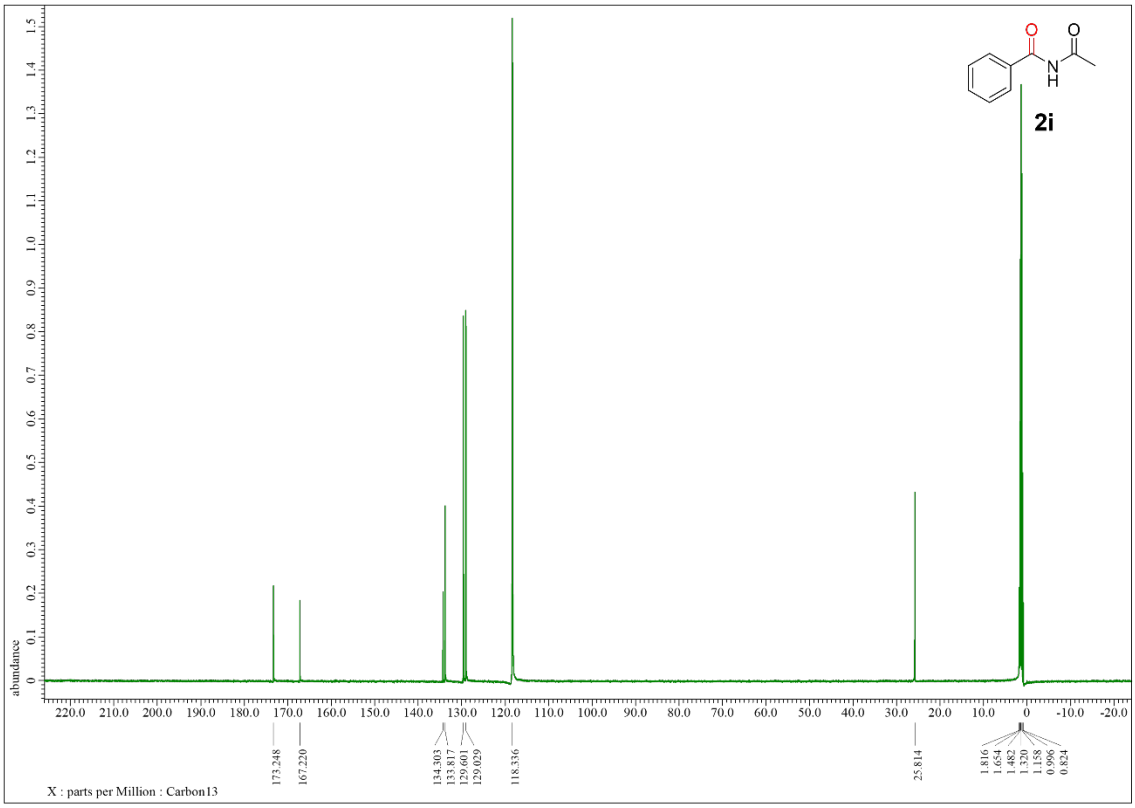

2f
4.00
2.02
0.92
abundance
X : parts per Million : Proton
8.741
2.494
2.481
2.468
1.939
1.928
1.916
1.902
1.890


2f
abundance
X : parts per Million : Carbon13
174.422
118.260
32.138
18.527
1.730
1.568
1.406
1.234
1.072
0.910
0.738


2h
abundance
X : parts per Million : Proton


2h
abundance
X : parts per Million : Carbon13


2i
abundance
X : parts per Million : Proton
0.81
2.00
0.94
2.00
3.00


2i
abundance
X : parts per Million : Carbon13
173.248
167.220
134.303
133.817
129.601
129.029
118.336
25.814
1.816
1.654
1.482
1.320
1.158
0.996
0.824

10. References

S1 M. Fournier. *Inorg. Synth.*, 1990, **27**, 81.

S2 E. Takahashi, K. Kamata, Y. Kikukawa, S. Sato, K. Suzuki, K. Yamaguchi and N. Mizuno, *Catal. Sci. Technol.*, 2015, **5**, 4778.

S3 (a) P. J. Domaille, *Inorg. Synth.*, 1990, **27**, 101; (b) P. J. Domaille, *Inorg. Synth.*, 1990, **27**, 102; (c) K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara and N. Mizuno, *Nat. Chem.*, 2010, **2**, 478.

S4 Rigaku OD. CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, England (2018).

S5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

S6 (a) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112; (b) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

S7 J. C. Gramain, R. Remuson and Y. Troin, *J. Chem. Soc., Chem. Commun*., 1976, 194.

S8 J. W. Pavlik and S. Tantayanon, *J. Am. Chem. Soc*., 1981, **103**, 6755.

S9 H. Nakayama and A. Itoh, *Synlett*, 2008, **5**, 675.

S10 N. Tada, K. Ban, M. Yoshida, S. Hirashima, T. Miura and A. Itoh, *Tetrahedron Lett*., 2010, **51**, 6098.

S11 I. Itoh, Y. Matsusaki, A. Fujiya, T. Miura and A. Itoh, *Tetrahedron Lett.,* 2014, **55**, 3160.

S12 C. Mei, Y. Hu and W. Lu, *Synthesis*, 2018, **50**, 2999.

S13 H. Chang, X. He, Z. Zhang, C. Zhou and G. Cai, *Asian J. Org. Chem*., 2022, **11**, e202200500.

S14 P. Lian, R. Li, L. Wang, X. Wan, Z. Xiang and X. Wan, *Org. Chem. Front*., 2022, **9**, 4924.

S15 S. Liu, Z. Dong, Z. Zang, C. Zhou and G. Cai, *Org. Biomol. Chem*., 2024, **22**, 1205.

S16 T. Hirata, A. Takarada, M. E. F. Hegazy, Y. Sato, A. Matsushima, Y. Kondo, A. Matsuki and H. Hamada, *J. Mol. Catal. B: Enzym*., 2005, **32**, 131.

S17 M. Wang and W. Chen, *React. Kinet. Catal. Lett*., 2006, **89**, 377.

S18 A. Maquestiau and P. Lejeune, *Bull. Soc. Chim. Belges*, 1969, **78**, 309.

S19 E. Benjamin and Y. Hijji, *Molecules*, 2008, **13**, 157.

S20 Y. L. Chow and J. N. Tam, *J. Chem. Soc. C*, 1970, 1138.

S21 F. Bai, N. Wang. Y. Bai, X. Ma, C. Gu, B. Dai and J. Chen, *J. Org. Chem*., 2023, **88**, 2985.

S22 F. Martinelli, A. Palmieri and M. Petrini, *Eur. J. Org. Chem*., 2010, **26**, 5058.

S23 K. Kataoka, K. Wachi, X. Jin, K. Suzuki, Y. Iwabuchi, J. Hasegawa, N. Mizuno, K. Yamaguchi, *Chem. Sci.*, 2018, **9**, 4756.