Chichibabin PyridiniumSynthesis via the Oxidative Decarboxylation of Photoexcited α–Enamine Acids

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvent were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ¹H NMR spectra were recorded on Bruker 300 / 400 / 600 (300 / 400 / 600 MHz) spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard (CDCl₃: 7.27 ppm, DMSO-d6: 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), coupling constants (Hz) and integration. ¹³C NMR spectra were recorded on Bruker 300 / 400 / 600 (75 / 100 / 150 MHz) with complete proton decoupling spectrophotometers (CDCl₃: 77.0 ppm, DMSO: 40.0 ppm). ESIMS and HRESIMS were taken on Agilent 6540 Q-TOF spectrometer. UV-Vis measurements were carried out on a HITACHI U-4100 spectrophotometer. Cyclic voltammetry studies was carried out on a CHI 760E electrochemical workstation (Shanghai CH Instruments Co., China). All amino acids were used from commercial suppliers or prepared using standard literature procedures. All aldehydes were used from commercial suppliers or prepared using standard literature procedures.

2. General Procedures



A glass tube equipped with a stirring bar and a rubber septum was charged with proline derivatives (0.125 mmol), NaI (0.125 mmol), and 1.0 mL CHCl₃, followed by aldehyde derivatives (0.5 mmol). The reaction mixture was placed at approximately 5 cm away from two parallel household full spectrum 23 W compact fluoresecent light bulbs (Philips-YPZ220V23W50Hz/S-RR·E, 23 W CFL, 56.0 mW/cm²), and then irradiated at 25 °C for 16 hours. The mixture was directly loaded onto silica gel column and eluted with methanol/dichloromethane to give the target pyridiniums **3**.

3. Photochemical Reaction Setup

A glass tube equipped with a stirring bar, two parallel household full spectrum 23 W compact fluorescent light bulbs (Philips-YPZ220V23W50Hz/S-RR·E, 23 W CFL) are placed perpendicular to the sidewall of the glass tube, so that the glass tube can be equally exposed to the LEDs (at approximately 5 cm away from the light source, 56.0 mW/cm^2).



Figure S1. Details for the photochemical reaction setup.



Figure S2. Emission spectra of the 23 W CFL used in our experiments. The emission spectra was recorded on a Fluorescence Spectrophotometer F-7000.

4. Mechanistic Experiments

4.1 Optical Absorption Spectra



Figure S3. Optical absorption spectra recorded in dry DMSO in 1 cm path quartz cuvettes under argon using a Shimadzu 2550 UV-visible spectrophotometer.

Synthesis of the enamine I



A glass tube equipped with a stirring bar and freshly activated 4 Å molecular sieves (in powder). 7.5 mg (0.065 mmol) of proline **1a**, 700 µL of dry DMSO-*d6*, 7.7 µL (0.065 mmol) of freshly distilled phenylacetaldehyde **2a**, and were then filled with argon. The reaction mixture was stirred under an argon atmosphere until full conversion of the starting material (about 1 h). The reaction mixture was then filtered over Celite[®], and was directly applied for spectroscopic studies. Analytical data: ¹H NMR (600 MHz, DMSO): δ 7.14-7.09 (m, 5H), 6.89-6.86 (m, 1H), 5.01 (d, *J* = 14.4 Hz, 1H), 4.08-4.06 (m, 1H), 3.31-3.28 (m, 1H), 3.22-3.18 (m, 1H), 2.18-2.15 (m, 1H), 1.99-1.95 (m, 1H), 1.92-1.88 (m, 2H); ¹³C NMR (150 MHz, DMSO): δ 175.1, 140.2, 136.0, 128.8, 123.5, 123.1, 98.4, 62.3, 48.5, 30.2, 23.8.

Characterization of synthetic enamine I



Figure S4. ¹H-NMR spectrum of the enamine I in DMSO- d_6 .



Figure S5. ¹³C-NMR spectrum of the enamine I in DMSO- d_6 .



Figure S6. COSY-NMR spectrum of the enamine I in DMSO-d₆.



Figure S7. HSQC-NMR spectrum of the enamine I in DMSO- d_6 .



Figure S8. HMBC-NMR spectrum of the enamine I in DMSO-*d*₆.



Figure S9. ROESY-NMR spectrum of the enamine I in DMSO-*d*₆.

4.2 Emission spectrum of the synthetic enamine I

The emission spectra were recorded in a Fluorescence Spectrophotometer F-7000. A 0.005 M solution (dry DMSO) of the enamine I were placed in a 1.0 cm quartz cuvette under an argon atmosphere. The excitation wavelength was fixed at 390 nm, while the emission light was acquired from 410 nm to 700 nm (emission light slit regulated to 5.0 mm). A solvent blank was subtracted from the measurement.



Figure S10. Emission spectrum of the enamine I (excitation wavelength 390 nm).

4.3 Stern-Volmer Quenching Studies

Fluorescence quenching experiments were performed on a Fluorescence Spectrophotometer F-7000. In a typical experiment, a 0.005 M solution of synthetic enamine I in dry DMSO was added in an 1.0 cm quartz cuvette. The samples were vigorously bubbled measurement. This research proves that oxygen is a quencher for the excited state of synthetic enamine I.



Figure S11. Quenching of the synthetic enamine I emission (0.005 M in DMSO) in the presence of oxygen.

4.4 Electrochemical analysis of the enamine I

Enamine I (0.1 mmol) and tetrabutylammonium hexafluorophosphate (378 mg, 1.0 mmol) were added to dry DMSO (10 mL), and the solution was vigorously bubbled with argon for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate. A completely irreversible reduction wave was observed with $E_p = 0.60$ V vs. SCE in DMSO.



Figure S12. The cyclic voltammogram of enamine I vs SCE in DMSO at 0.1 V/s.

The redox potential of the excited enamine **I** was calculated with the following equation¹:

$$E(\mathbf{II}/\mathbf{I}^*) = E(\mathbf{II}/\mathbf{I}) - E_{0-0}(\mathbf{I}^*/\mathbf{I})$$

The electrochemical oxidation of the enamine I ($E_p = 0.60$ V) was totally irreversible, therefore the irreversible peak potential EPA was used for E(II/I). And the excited state energy of the enamine I, $E_{0-0}(I^*/I)$, was estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum recorded in DMSO, the solvent used for the electrochemical analysis, according to Meclchiorre's reports.¹ This corresponds to 450 nm, which translates into an $E_{0-0}(I^*/I)$ of 2.71 eV for the enamine I.

$$E(II/I^*) = 0.60 - 2.71 = -2.11 V (vs SCE)$$

4.5 Role Analysis of Salt Additives (MX)



A series of parallel reactions have been conducted in the same time and the same condition. Proline **1a** (0.5 mmol), additive (0.55 mmol), phenylacetaldehyde **2a** (2.0 mmol), and 4.0 mL CHCl₃ were added in a reaction tube, and were stirring in dark at 25 °C for corresponding time. The mixture was directly loaded onto silica gel column and eluted with ethyl acetate/petroleum ether = 1 : 20 to give the aldol condensation product **S1**. The obtained weight of product **S1** was recorded in the following table. This analysis result proves that NaI is an efficient inhibitor for the aldol condensation of phenylacetaldehyde **2a**.

Table S1. The yield of the aldol condensation product S1.

Time (h)	none	NaI	NaOTf	NaBF ₄
1.5	27.5%	14.9%	15.3%	19.8%
3.0	41.0%	20.7%	22.5%	32.0%
6.0	57.2%	26.1%	27.0%	43.2%
9.0	67.1%	28.8%	34.7%	47.3%
12.0	73.0%	33.3%	37.8%	53.6%
16.0	80.2%	40.5%	46.4%	58.6%



Figure S13. The role analysis of additives.

4.6 Gibbs energy profile of the decarboxylation reaction

DFT calculations were performed with the Gaussian 09 software package, E.01 version.² (Unrestricted) Becke's three parameter hybrid functional^{3a} was used along with split-valence basis sets^{3b} 6-31+G(d,p), with diffuse functions^{3c} and polarization functions^{3d} added. The D3 version of Grimme's dispersion with Becke-Johnson damping were also applied.⁴ Geometry optimization of gas (namely CO₂) was carried out in gas-phase, while optimizations for all other species were carried out in solution-phase with chloroform as the solvent using the SMD solvation model.⁵ Vibrational frequency were also calculated at the same level to confirm that each stationary points found were either minima or transition states and to evaluate thermal corrections at standard states, including zero-point energy corrections. Quasi harmonic corrections were applied during the entropy calculations by setting all of the non-negative frequencies less than 100 cm⁻¹ to 100 cm^{-1.6} These were added to the electronic energies to get the final Gibbs free energy values.

Table S2. Computational Data of All Species

	E (a.u.)	TCG (a.u.)	QuasiCorr (kcal/mol)
Intermediate III	-709.113635	0.203079	1.698231
Ts1	-709.1002592	0.19732	2.347587
Intermediate IV	-520.5055864	0.189707	1.337261
CO ₂	-188.5920342	-0.009149	0

E: Electronic energy; TCG: Thermal correction to Gibbs Free Energy; QuasiCorr: Quasiharmonic Correction to Entropy

Charge, spin multiplicity and Cartesian coordinates of all species

Intermediate III

0 2			
С	4.19967500	-1.21263300	0.31758800
С	2.81333800	-1.19864300	0.26110200
С	2.12043500	-0.02695500	-0.14426000
С	2.88460600	1.11843600	-0.48914500
		5	14

С	4.27189100	1.09609900	-0.42909100
С	4.93659600	-0.06894500	-0.02578000
С	0.69387200	0.06863700	-0.23051700
С	-0.20253300	-0.94378800	0.11721700
Ν	-1.51594000	-0.84795800	-0.01089600
С	-2.43868200	-1.92486400	0.39068100
С	-2.24067500	0.32577600	-0.50397500
С	-3.64958300	-1.67207300	-0.50386100
С	-3.71555400	-0.13703300	-0.55340400
С	-2.07264500	1.60930000	0.41138800
0	-2.53675100	2.64109600	-0.12841100
0	-1.54534300	1.45041600	1.53433400
Н	4.71623300	-2.11532500	0.62886500
Н	2.26426300	-2.09521100	0.52758000
Н	2.36436800	2.02093800	-0.79626200
Н	4.83893500	1.98316900	-0.69343300
Н	6.02101800	-0.08819500	0.02183900
Н	0.29686400	1.01337100	-0.58267800
Н	0.15081800	-1.88826900	0.51684300
Н	-2.68671000	-1.78329100	1.45036100
Н	-1.95550000	-2.89515000	0.26216900
Н	-1.85318800	0.57513300	-1.49556200
Н	-4.55812400	-2.12438700	-0.09973500
Н	-3.46750400	-2.08742500	-1.50104600
Н	-4.24731900	0.24380900	0.32421000
Н	-4.22027300	0.24455700	-1.44190700

Ts1

02

C 4.23217300 -1.23060800 0.34564800

С	2.84594300	-1.23398200	0.20885000
С	2.15293700	-0.06967800	-0.19043000
С	2.91631500	1.08621000	-0.46020600
С	4.30422400	1.08655900	-0.32644200
С	4.97282400	-0.07196600	0.08046600
С	0.70302400	-0.00075800	-0.33972200
С	-0.17773100	-0.96342000	0.04227400
Ν	-1.54023900	-0.90468800	-0.15217600
С	-2.45640100	-1.80773700	0.57498200
С	-2.23270300	0.06940500	-0.81616300
С	-3.75336600	-1.69650800	-0.23216900
С	-3.70779400	-0.25893700	-0.80539000
С	-2.07938100	1.95213700	0.57827900
0	-2.15208600	2.83444400	-0.21792800
0	-2.00125600	1.44523800	1.65100400
Н	4.74067600	-2.14003400	0.65378000
Н	2.30009400	-2.15160400	0.40455700
Н	2.40433900	1.99270100	-0.77251700
Н	4.86399600	1.99300500	-0.53939200
Н	6.05365200	-0.07578200	0.18474700
Н	0.32284500	0.92013100	-0.77339400
Н	0.14397400	-1.86727300	0.54748000
Н	-2.57568100	-1.44547900	1.60314400
Н	-2.03333300	-2.81442700	0.60223800
Н	-1.73676800	0.58515300	-1.63007100
Н	-4.63703800	-1.88233400	0.38205400
Н	-3.74216000	-2.42439800	-1.04972200
Н	-4.27115800	0.43268600	-0.16576700
н	-4.14543200	-0.19129000	-1.80638300

Intermediate IV

02

С	-3.60742900	1.31867700	-0.01774200
С	-2.23299300	1.09367100	-0.01488700
С	-1.70428400	-0.22022300	-0.00461100
С	-2.63377600	-1.28704500	-0.00275300
С	-4.00859100	-1.05857600	-0.00707200
С	-4.51063800	0.24769200	-0.01376600
С	-0.28182800	-0.52153800	0.00411200
С	0.72352300	0.40723700	0.03463500
Ν	2.06461000	0.12936500	0.01980900
С	3.06506200	1.20943900	0.17533800
С	2.68186400	-1.09153700	-0.04134000
С	4.37527700	0.54756200	-0.26548100
С	4.16387200	-0.94055500	0.09397200
Н	-3.97900500	2.34012100	-0.02538300
Н	-1.56274500	1.94772400	-0.02230200
Н	-2.25950400	-2.30794600	0.00351900
Н	-4.69157000	-1.90405400	-0.00503900
Н	-5.58125800	0.42881400	-0.01720400
Н	-0.02496400	-1.57710100	-0.01326200
Н	0.50935300	1.46973500	0.06465600
Н	3.09886100	1.51366400	1.22906100
Н	2.77980800	2.07299200	-0.43001500
Н	2.10777500	-2.00500500	-0.00688600
Н	5.24414400	0.99144000	0.22602600
Н	4.49836700	0.65331900	-1.34821100
Н	4.50338000	-1.14139400	1.12447000
Н	4.72473800	-1.61667500	-0.56052200

CO ₂			
01			
С	0.00000000	0.00000000	0.00000000
0	0.00000000	0.00000000	1.16932800
0	0.00000000	0.00000000	-1.16932800

4.7 Alternative method for generation of radical cation II by oxidation with CAN



A light-proof two-neck round bottom with a stirring bar was charged with Lproline (0.125 mmol, 14.4 mg, 1.0 equiv.), phenylacetaldehyde (2.0 mmol, 60.0 mg, 4.0 equiv.) and 1.0 mL of CHCl₃, followed by CAN (0.19 mmol, 88.0 mg, 1.5 equiv.). The reaction mixture was stirred under dark and air atmosphere at 25°C for 12 hours. After the reaction mixture was filtered, the organic layer was concentrated. The residue was purified by silica gel chromatography (DCM/MeOH = 10:1) to give 12.0 mg of pyridinium in 29% yield.

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6. Characterizations of Synthetic Products



3a, 41.5 mg, 83% yield. Analytical data: ¹H NMR (400 MHz, DMSO): δ 9.49 (s, 1H), 8.81 (s, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 6.8 Hz, 2H), 7.64-7.58 (m, 6H), 4.98 (t, J = 7.6 Hz, 2H), 3.56 (t, J = 7.2 Hz, 2H), 2.45-2.41 (m, 2H); ¹³C NMR (100 MHz, DMSO): δ 155.6, 142.1, 138.5, 138.1, 137.9, 135.0, 133.8, 130.4, 130.0, 129.9, 129.5, 129.3, 127.9, 60.2, 32.7, 22.1. HRMS (ESI) calcd for C₂₀H₁₈N⁺: 272.1434, found 272.1431; HRMS (EI) calcd for I⁻: 126.9045, found 126.9049. The product was purified as a pale yellow powder by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3ab, 28 mg, 53% yield. Analytical data: ¹H NMR (400 MHz, DMSO): δ 9.46 (s, 1H), 8.80 (s, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 7.2 Hz, 2H), 7.64-7.57 (m, 6H), 4.97 (t, J = 7.6 Hz, 2H), 3.55 (t, J = 7.2 Hz, 2H), 2.47-2.42 (m, 2H); ¹³C NMR (100 MHz, DMSO): δ 153.5, 140.0, 136.4, 136.1, 135.8, 132.9, 131.7, 128.3, 127.9, 127.8, 127.4, 127.2, 125.8, 123.9-114.3 (q, J = 320.3 Hz, 1C), 58.1, 30.5, 20.0. HRMS (ESI) calcd for C₂₀H₁₈N⁺: 272.1439, found 272.1438; HRMS (ESI) calcd for CF₃O₃S⁻: 148.9520, found 148.9522. The product was purified as a yellow powder by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3ac, 21 mg, 47% yield. Analytical data: ¹H NMR (400 MHz, DMSO): δ 9.46 (s, 1H), 8.81 (s, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 7.2 Hz, 2H), 7.65-7.56 (m, 6H), 4.97 (t, J = 7.6 Hz, 2H), 3.56 (t, J = 7.6 Hz, 2H), 2.51-2.42 (m, 2H); ¹³C NMR (100 MHz, DMSO): δ 155.6, 142.1, 138.5, 138.1, 137.9, 135.0, 133.8, 130.4, 130.0, 129.9, 129.5, 129.3, 127.9, 60.2, 32.6, 22.0; ¹⁹F NMR (565 MHz, DMSO): δ -148.3; HRMS (ESI) calcd for C₂₀H₁₈N⁺: 272.1439, found 272.1441; HRMS (EI) calcd for BF₄⁻: 87.0029, found 87.0031. The product was purified as a yellow foam by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3b, 55.5 mg, 80% yield. Analytical data:¹H NMR (400 MHz, CDCl₃): δ 9.74 (s, 1H), 8.28 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 5.37 (t, *J* = 7.6 Hz, 2H), 3.60 (t, *J* = 7.6 Hz, 2H), 2.62-2.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 154.9, 141.7, 138.5, 138.0, 133.0, 132.8 131.7, 130.1, 129.3, 125.3, 124.9, 61.0, 32.7, 22.1. HRMS (ESI) calcd for C₂₀H₁₆Br₂N⁺: 427.9644, found 427.9647; HRMS (EI) calcd for I⁻: 126.9045, found 126.9048. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3c, 53 mg, 76% yield. Analytical data: ¹H NMR (300 MHz, CDCl₃): δ 9.67 (s, 1H), 8.28 (s, 1H), 7.94-7.92 (m, 2H), 7.69-7.68 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.47-7.38 (m, 2H), 5.40 (t, *J* = 7.5 Hz, 2H), 3.63 (t, *J* = 7.5 Hz, 2H), 2.66-2.56 (m, 2H); ¹³C

NMR (100 MHz, CDCl₃): δ 155.5, 142.2, 139.0, 138.2, 137.6, 136.0, 134.9, 133.4, 133.2, 131.4, 131.3, 131.1, 130.3, 127.4, 126.8, 123.6, 123.4, 61.2, 32.8, 22.0. HRMS (ESI) calcd for C₂₀H₁₆Br₂N⁺: 427.9644, found 427.9641; HRMS (EI) calcd for I⁻: 126.9045, found 126.9050. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3d, 44.5 mg, 82% yield. Analytical data: ¹H NMR (400 M Hz, CDCl₃): δ 9.55 (s, 1H), 8.42 (s, 1H), 8.09-8.05 (m, 1H), 7.63-7.47 (m, 3H), 7.38-7.35 (m, 2H), 7.30-7.24 (m, 1H), 7.22-7.19 (m, 1H), 5.46 (t, *J* = 7.6 Hz, 2H), 3.55 (t, *J* = 7.6 Hz, 2H), 2.69-2.61 (m, 2H); ¹³C NMR (100 M Hz, CDCl₃): δ 160.6 (d, *J* = 54.6 Hz, 1C), 158.1 (d, *J* = 53.9 Hz, 1C), 156.1, 145.7 (d, *J* = 5.9, 1C), 140.1, 134.3, 133.1, 132.5 (d, *J* = 5.5 Hz, 1C), 132.4 (d, *J* = 5.7 Hz, 1C), 131.3, 125.8 (d, *J* = 3.7, 1C), 125.5 (d, *J* = 3.7, 1C), 121.6 (d, *J* = 14.6 Hz, 1C), 120.9 (d, *J* = 11.7 Hz, 1C), 116.6 (d, *J* = 3.0 Hz, 1C), 116.3 (d, *J* = 2.6 Hz, 1C), 61.4, 32.5 (d, *J* = 3.7 Hz, 1C), 21.8. HRMS (ESI) calcd for C₂₀H₁₆F₂N⁺: 308.1245, found 308.1245; HRMS (EI) calcd for I⁻: 126.9045, found 126.9046. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3e, 51 mg, 79% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.88 (s, 1H), 8.37 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 5.42 (t, J = 7.2 Hz, 2H), 3.97 (s, 3H), 3.92 (s, 3H), 3.64 (t, J = 7.2 Hz, 2H), 2.62-2.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 155.7,

142.1, 139.2, 138.3, 138.2, 138.0, 136.9, 131.6, 131.6, 130.7, 130.5, 128.8, 127.8, 61.1, 52.5, 52.4, 32.9, 22.1. HRMS (ESI) calcd for $C_{24}H_{22}NO_4^+$: 388.1549, found 388.1546; HRMS (EI) calcd for I⁻: 126.9045, found 126.9043. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3f, 42 mg, 65% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.82 (s, 1H), 8.28 (s, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.12-7.10 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 5.39 (t, J = 7.6 Hz, 2H), 4.03 (s, 3H), 3.97 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H), 3.62 (t, J = 7.5 Hz, 2H), 2.58-2.50 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 153.6, 150.8, 150.4, 150.0, 149.6, 141.0, 139.0, 138.6, 137.4, 126.8, 125.6, 121.4, 120.4, 111.7, 111.6, 110.7, 60.7, 57.6, 56.7, 56.1, 56.1, 32.8, 22.2. HRMS (ESI) calcd for C₂₄H₂₆NO₄⁺: 392.1856, found 392.1848; HRMS (EI) calcd for I[:] 126.9045, found 126.9047. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3g, 37 mg, 57% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.78 (s, 1H), 8.32 (s, 1H), 7.02 (d, J = 2.0 Hz, 2H), 6.61-6.58 (m, 4H), 5.45 (t, J = 7.6 Hz, 2H), 3.92 (s, 6H), 3.86 (s, 6H), 3.60 (t, J = 7.6 Hz, 2H), 2.64-2.56 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 161.7, 161.4, 154.8, 142.0, 139.2, 138.7, 136.1, 135.0, 106.7, 105.7, 102.5, 101.5, 60.9, 56.4, 55.9, 32.7, 22.1. HRMS (ESI) calcd for C₂₄H₂₆NO₄⁺:

392.1856, found 392.1844; HRMS (EI) calcd for I⁻: 126.9045, found 126.9052. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3h, 52 mg, 75% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 8.34 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.66-7.63 (m, 4H), 7.55 (d, J = 7.2 Hz, 2H), 7.51-7.48 (m, 2H), 7.44-7.35 (m, 4H), 5.43 (t, J = 7.6 Hz, 2H), 3.67 (t, J = 7.6 Hz, 2H), 2.62-2.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 154.5, 142.9, 141.5, 139.6, 139.5, 139.0, 138.5, 138.1, 133.0, 131.6, 129.1, 129.0, 128.2, 128.2, 128.1, 128.1, 127.2, 127.0, 61.0, 32.8, 22.0. HRMS (ESI) calcd for C₃₂H₂₆N⁺: 424.2060, found 424.2044; HRMS (EI) calcd for I⁻: 126.9045, found 126.9041. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3i, 48 mg, 77% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.79 (s, 1H), 8.45 (s, 1H), 8.36 (d, J = 0.8 Hz, 1H), 8.10 (s, 1H), 8.03-7.90 (m, 4H), 7.85-7.78 (m, 2H), 7.70-7.66 (m, 1H), 7.64-7.63 (m, 1H), 7.62-7.57 (m, 2H), 7.56-7.34 (m, 1H), 7.42-7.35 (m, 1H), 5.31 (t, J = 7.6 Hz, 2H), 3.57 (t, J = 7.6 Hz, 2H), 2.49-2.41 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 154.5, 141.8, 139.0, 138.7, 138.1, 133.5, 133.4, 133.2, 133.1, 131.5, 129.8, 129.5, 129.3, 128.9, 128.7, 128.6, 127.8, 127.7, 127.6, 127.5, 127.3, 126.9, 125.3, 124.2, 60.8, 32.8, 22.0. HRMS (ESI) calcd for $C_{28}H_{22}N^+$: 372.1747, found 372.1733; HRMS (EI) calcd for I: 126.9045, found 126.9049. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3g, 47.5 mg, 66% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.66 (s, 1H), 8.34 (d, J = 1.2 Hz, 1H), 8.04 (s, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 6.8 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.48-7.35 (m, 3H), 7.33-7.28 (m, 2H), 5.35 (t, J = 7.6 Hz, 2H), 3.99 (s, 2H), 3.86 (s, 2H), 3.59 (t, J = 7.6 Hz, 2H), 2.55-2.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 154.0, 144.6, 144.4, 143.9, 143.7, 143.6, 143.5, 141.4, 140.4, 140.3, 139.5, 139.0, 137.6, 132.3, 131.0, 127.9, 127.7, 127.4, 127.1, 127.0, 126.6, 125.3, 125.2, 124.3, 120.8, 120.6, 120.5, 119.9, 60.9, 37.1, 37.0, 32.8, 29.7, 22.1. HRMS (ESI) calcd for C₃₄H₂₆N⁺: 448.2060, found 448.2049; HRMS (EI) calcd for I⁻: 126.9045, found 126.9051. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3k, 38 mg, 45% yield. Analytical data: ¹H NMR (600 MHz, CDCl₃): δ 9.70 (s, 1H), 8.65 (s, 1H), 8.47 (s, 1H), 8.33-8.29 (m, 2H), 7.98 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.39-7.35

(m, 2H), 5.49 (t, J = 7.8 Hz, 2H), 3.63 (t, J = 7.2 Hz, 2H), 2.69-2.64 (m, 2H), 1.73 (s, 18H); ¹³C NMR (150 MHz, CDCl₃): δ 154.2, 149.1, 142.3, 138.4, 136.1, 135.5, 133.7, 131.9, 127.7, 127.1, 126.9, 126.1, 125.8, 125.6, 124.0, 124.0, 118.9, 118.7, 116.0, 114.3, 113.8, 85.4, 85.3, 61.2, 32.7, 28.3, 28.2, 21.8. HRMS (ESI) calcd for C₃₄H₃₆N₃O₄⁺: 550.2700, found 550.2692; HRMS (EI) calcd for I⁻: 126.9045, found 126.9050. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 25.



31, 33.5 mg, 63% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.00 (s, 1H), 7.75 (s, 1H), 7.36-7.32 (m, 5H), 7.31-7.29 (m, 1H), 7.27-7.24 (m, 2H), 7.12-7.10 (m, 2H), 5.09 (t, J = 7.6 Hz, 2H), 4.15 (s, 2H), 4.09 (s, 2H), 3.38 (t, J = 8.0 Hz, 2H), 2.58-2.50 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 155.3, 145.2, 140.7, 139.0, 138.1, 136.9, 135.5, 129.3, 129.0, 127.6, 127.5, 60.1, 38.3, 38.1, 31.4, 21.1. HRMS (ESI) calcd for C₂₂H₂₂N⁺: 300.1747, found 300.1751; HRMS (EI) calcd for I⁻: 126.9045, found 126.9048. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3m, 14.5 mg, 35% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.07 (s, 1H), 7.88 (s, 1H), 5.22 (t, *J* = 7.6 Hz, 2H), 3.52 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.66-2.58 (m, 2H), 1.81-1.67 (m, 4H), 1.04-0.98 (m, 6H); ¹³C NMR (100 M Hz, CDCl₃): δ 154.4, 144.4, 141.3, 139.0, 138.5, 60.2, 34.3, 34.0, 31.1, 23.7, 22.4, 21.4, 13.8, 13.7. HRMS (ESI) calcd for C₁₄H₂₂N⁺: 204.1747, found 204.1745; HRMS (EI) calcd for I⁻: 126.9045, found 126.9053. The product was purified

as pale yellow powder by silica gel column chromatography with methanol/dichloromethane = 1 : 30.

√+ N
I[−]

3n, 20 mg, 48% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.15 (s, 1H), 7.96 (s, 1H), 5.25 (t, *J* = 7.6 Hz, 2H), 3.54 (t, *J* = 8.0 Hz, 2H), 3.24-3.10 (m, 2H), 2.67-2.59 (m, 2H), 1.40 (d, *J* = 7.2 Hz, 6H), 1.35 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 153.7, 147.7, 145.0, 139.7, 137.6, 60.3, 32.0, 30.9, 30.6, 23.3, 22.4, 21.5. HRMS (ESI) calcd for C₁₄H₂₂N⁺: 204.1747, found 204.1748; HRMS (EI) calcd for I⁻: 126.9045, found 126.9051. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



30, 19 mg, 43% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.31 (s, 1H), 8.20 (d, *J* = 1.6 Hz, 1H), 5.29 (t, *J* = 7.6 Hz, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.63-2.56 (m, 2H), 1.48 (s, 9H), 1.47 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 153.5, 149.8, 146.8, 139.3, 137.5, 60.0, 35.7, 34.9, 34.0, 30.8, 29.8, 22.2. HRMS (ESI) calcd for C₁₆H₂₆N⁺: 232.2060, found 232.2062; HRMS (EI) calcd for I⁻: 126.9045, found 126.9049. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.

+ N I⁻ **3p**, 24 mg, 50% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.15 (s, 1H), 7.92 (s, 1H), 5.26 (t, *J* = 7.6 Hz, 2H), 3.50 (t, *J* = 7.6 Hz, 2H), 3.24-3.09 (m, 2H), 2.64-2.56 (m, 2H), 2.27-2.14 (m, 4H), 1.91-1.85 (m, 4H), 1.83-1.75 (m, 8H); ¹³C NMR (100 M Hz, CDCl₃): δ 153.7, 145.8, 143.0, 140.4, 137.8, 60.3, 43.0, 41.8, 34.3, 33.5, 31.2, 25.5, 25.3, 21.4. HRMS (ESI) calcd for C₁₈H₂₆N⁺: 256.2060, found 256.2058; HRMS (EI) calcd for I⁻: 126.9045, found 126.9042. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3q, 31 mg, 61% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.07 (s, 1H), 7.90 (s, 1H), 5.27 (t, *J* = 7.6 Hz, 2H), 3.52 (t, *J* = 7.6 Hz, 2H), 2.80-2.73 (m, 2H), 2.70-2.57 (m, 2H), 2.00-1.76 (m, 10H), 1.58-1.37 (m, 10H); ¹³C NMR (100 M Hz, CDCl₃): δ 153.7, 146.8, 143.9, 140.3, 137.6, 60.4, 41.8, 40.7, 33.7, 32.9, 30.9, 26.3, 26.2, 25.6, 25.4, 21.5. HRMS (ESI) calcd for C₂₀H₃₀N⁺: 284.2373, found 284.2367; HRMS (EI) calcd for I⁻: 126.9045, found 126.9046. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3r, 30 mg, 50% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.39 (s, 1H), 8.43 (d, J = 1.2 Hz, 1H), 7.88 (dd, J = 2.0, 8.0 Hz, 2H), 7.62-7.59 (m, 2H), 7.58-7.52 (m, 6H), 7.38 (d, J = 4.4 Hz, 3H), 7.34-7.26 (m, 2H), 5.79 (dd, J = 8.4, 13.2 Hz, 1H), 5.27 (dd, J = 9.2, 12.8 Hz, 1H), 4.35-4.26 (m, 1H), 4.00 (dd, J = 8.0, 18.0 Hz, 1H), 3.83 (dd, J = 9.2, 18.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 153.7, 142.9, 140.3,

139.1, 138.1, 137.5, 134.0, 133.0 130.5, 130.2, 129.9, 129.5, 129.4, 128.6, 128.3, 127.8, 127.3, 66.2, 41.9, 40.3. HRMS (ESI) calcd for $C_{26}H_{22}N^+$: 348.1747, found 348.1742; HRMS (EI) calcd for I⁻: 126.9045, found 126.9040. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3s, 22 mg, 43% yield. Analytical data: ¹H NMR (400 MHz, DMSO): δ 9.52 (s, 1H), 8.88 (d, *J* = 1.6 Hz, 1H), 8.00 (t, *J* = 1.6 Hz, 2H), 7.78 (t, *J* = 1.6 Hz, 2H), 7.66-7.56 (m, 6H), 5.77 (t, *J* = 4.0 Hz, 1H), 5.05 (dd, *J* = 4.4, 14.0 Hz, 1H), 4.83 (dd, *J* = 5.6, 10.4 Hz, 2H), 4.00 (dd, *J* = 5.2, 18.0 Hz 1H), 3.22 (d, *J* = 18.0 Hz, 1H); ¹³C NMR (100 M Hz, DMSO): δ 153.8, 142.5, 139.2, 138.4, 138.3, 134.7, 133.8, 130.5, 130.2, 130.0, 129.6, 129.4, 128.0, 67.9, 67.2, 42.3. HRMS (ESI) calcd for C₂₀H₁₈NO⁺: 288.1383, found 288.1384; HRMS (EI) calcd for I⁻: 126.9045, found 126.9049. The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 10.



3t, 43 mg, 76% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.49 (d, J = 1.6 Hz, 1H), 8.36 (d, J = 1.6 Hz, 1H), 7.92-7.89 (m, 2H), 7.58-7.52 (m, 8H), 5.90 (dd, J = 6.4, 13.2 Hz, 1H), 3.63 (dd, J = 6.8, 17.2 Hz, 1H), 3.27 (dd, J = 7.2, 17.6 Hz, 1H), 3.12-3.04 (m, 1H), 2.49-2.43 (m, 1H), 2.21-2.13 (m, 1H), 1.86-1.80 (m, 2H), 1.64-1.56 (m, 2H), 1.49-1.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 153.8, 142.0, 139.9, 139.6, 137.2, 134.2, 133.2, 130.3, 130.1, 129.8, 129.5, 128.6, 127.8, 70.5, 36.2, 36.1, 28.0, 26.0, 21.5, 21.1. HRMS (ESI) calcd for C₂₄H₂₄N⁺: 326.1903, found 326.1898; HRMS

(EI) calcd for I⁻: 126.9045, found 126.9039. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.

3u, 37 mg, 72% yield. Analytical data: ¹H NMR (300 MHz, CDCl₃): δ 9.55 (s, 1H), 8.32 (d, *J* = 1.5 Hz, 1H), 7.90 (dd, *J* = 1.8, 8.1 Hz, 2H), 7.68-7.45 (m, 8H), 5.67 (d, *J* = 14.7 Hz, 1H), 5.46 (dd, *J* = 6.3, 14.7 Hz, 1H), 2.94-2.88 (m, 1H), 2.67-2.59 (m, 1H), 1.73-1.66 (m, 1H), 1.36-1.32 (m, 1H); ¹³C NMR (100 M Hz, CDCl₃): δ 155.5, 142.1, 139.2, 138.8, 137.9, 134.1, 133.1, 130.2, 130.1, 129.7, 129.6, 128.5, 127.7, 62.7, 24.0, 17.2, 16.9. HRMS (ESI) calcd for C₂₁H₁₈N⁺: 284.1434, found 284.1434; HRMS (EI) calcd for I⁻: 126.9045, found 126.9046. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.

3v, 42 mg, 81% yield. Analytical data: ¹H NMR (300 MHz, DMSO): δ 9.37 (d, *J* = 1.8 Hz, 1H), 8.69 (d, *J* = 1.8Hz, 1H), 8.00 (dd, *J* = 1.8, 8.4 Hz, 2H), 7.64-7.56 (m, 8H), 4.76 (t, *J* = 6.0 Hz, 2H), 3.07 (t, *J* = 6.6 Hz, 2H), 2.12 (t, *J* = 7.8 Hz, 2H), 1.92-1.83 (m, 2H); ¹³C NMR (100 MHz, DMSO): δ 153.7, 142.3, 141.2, 136.4, 135.5, 133.6, 130.4, 129.9, 129.9, 129.7, 129.4, 127.9, 56.7, 26.9, 20.7, 17.8. HRMS (ESI) calcd for C₂₁H₂₀N⁺: 286.1590, found 286.1595; HRMS (EI) calcd for I⁻: 126.9045, found 126.9049. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3w, 43 mg, 75% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.97 (d, *J* = 1.6 Hz, 1H), 8.32 (d, *J* = 1.6 Hz, 1H), 7.87 (dd, *J* = 2.0, 8.4 Hz, 2H), 7.65-7.59 (m, 5H), 7.50-7.44 (m, 4H), 7.33 (dd, *J* = 3.2, 5.6 Hz, 2H), 7.19 (dd, *J* = 4.1, 5.4 Hz, 1H), 6.42 (s, 2H), 4.59 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 142.5, 141.4, 141.3, 138.4, 134.7, 132.5, 130.7, 130.4, 130.0, 129.7, 129.5, 129.4, 129.3, 128.1, 127.7, 126.8, 61.4, 35.1. HRMS (ESI) calcd for C₂₅H₂₀N⁺: 334.1590, found 334.1588; HRMS (EI) calcd for I⁻: 126.9045, found 126.9042. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 30.



3x, 29.5 mg, 55% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.65 (d, J = 2.0 Hz, 1H), 8.28 (d, J = 2.0, 1H), 7.94-7.92 (m, 2H), 7.56-7.45 (m, 8H), 5.13 (t, J = 8.0 Hz, 2H), 2.85 (s, 3H), 2.06-1.98 (m, 2H), 1.68-1.56 (m, 2H), 1.02 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 M Hz, CDCl₃): δ 150.8, 143.3, 142.7, 138.5, 135.6, 132.5, 130.4, 129.7, 129.7, 129.3, 129.1, 127.8, 60.0, 32.9, 19.7, 18.5, 13.7. HRMS (ESI) calcd for C₂₂H₂₄N⁺: 302.1909, found 302.1912; HRMS (EI) calcd for I⁻: 126.9045, found 126.9051. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



3y, 37 mg, 63% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.89 (s, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 8.04-8.01 (m, 2H), 7.58-7.51 (m, 6H), 7.40-7.38 (m, 2H), 5.21 (t, *J* = 8.0 Hz, 2H), 3.06 (d, *J* = 7.2 Hz, 2H), 2.10-2.00 (m, 2H), 1.99-1.90 (m, 1H), 1.67-1.58 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 153.1, 143.9, 143.5, 143.0, 138.6, 136.2, 132.2, 130.6, 129.8, 129.6, 129.3, 129.2, 127.9, 58.9, 37.8, 34.5, 29.9, 22.6, 19.8, 13.7. HRMS (ESI) calcd for C₂₅H₃₀N⁺: 344.2378, found 344.2375; HRMS (EI) calcd for I: 126.9045, found 126.9046. The product was purified as yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.



A glass tube equipped with a stirring bar and a rubber septum was charged with proline **1a** (0.125 mmol), NaI (0.125 mmol), and 1.0 mL CHCl₃, followed by *p*-anisylacetaldehyde **2b** (0.5 mmol). The reaction mixture was placed at approximately 5 cm away from two parallel household full spectrum 23 W compact fluoresecent light bulbs (Philips-YPZ220V23W50Hz/S-RR·E, 23 W CFL, 56.0 mW/cm²), and then irradiated at room temperature for 16 hours. The mixture was directly loaded onto silica gel column and eluted with methanol/dichloromethane to give ficuseptine (**4**).

4, 29 mg, 51% yield. Analytical data: ¹H NMR (400 MHz, CDCl₃): δ 9.60 (d, J = 1.2 Hz, 1H), 8.23 (d, J = 1.6 Hz, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 5.37 (t, J = 7.2 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 3.60 (t, J = 7.6 Hz, 2H), 2.60-2.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 161.3, 160.9, 153.3, 140.8, 139.1, 138.5, 137.1, 130.0, 129.1, 126.5, 125.2, 115.1, 114.9, 60.8, 55.6, 55.5, 32.7, 22.2. HRMS (ESI) calcd for C₂₂H₂₂NO₂⁺: 332.1645, found 332.1640; HRMS (EI) calcd for I⁻: 126.9045, found 126.9044. The product was purified

as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20.

Sunlight-driven reaction: The reaction was set-up under the usual conditions and the glass tube was exposed to natural sunlight irradiation on the roof-top of the Chemical Experiment Building, Yunnan University, Kunming (China), on a partially cloudy day (3-June-2020). Stirring was continued about 9 hours (from 10:00 to 19:00). The product was purified as pale yellow oil by silica gel column chromatography with methanol/dichloromethane = 1 : 20 and afforded the title compound (21 mg, 37% yield).



Figure S14. The sunlight-driven reaction

7. Copies of ¹H NMR and ¹³C NMR Spectra





Copies of NMR spectra of 3ab



Copies of NMR spectra of 3ac





Copies of NMR spectra of **3b**





Copies of NMR spectra of 3d



Copies of NMR spectra of 3e





Copies of NMR spectra of **3g**



S44

Copies of NMR spectra of **3h**





Copies of NMR spectra of 3j



S47



Copies of NMR spectra of 31



Copies of NMR spectra of **3m**



Copies of NMR spectra of **3n**



Copies of NMR spectra of **30**



Copies of NMR spectra of **3p**



Copies of NMR spectra of 3q



Copies of NMR spectra of **3r**



Copies of NMR spectra of 3s



Copies of NMR spectra of **3t**



Copies of NMR spectra of **3u**



Copies of NMR spectra of 3v



S59

Copies of NMR spectra of 3w



Copies of NMR spectra of **3x**



S61

Copies of NMR spectra of **3y**



