Electronic Supplementary Information

Deoxygenative dual CO_2 conversions: methylenation and switchable *N*-formylation/*N*-methylation of tryptamines

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1. General information

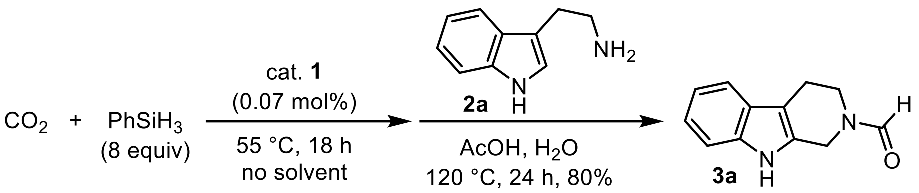
Instrumentation. Melting points were measured on a Yanaco melting point apparatus (uncorrected). Optical rotations were measured on a Horiba SEPA-300. IR spectra were recorded on a Shimadzu IRAffinity-1. NMR spectra were recorded on a JEOL JNM-ECS400 or a JNM-ECZ600R/S3. Data are reported as follows: chemical shifts in ppm using the residual solvent peak as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broadened), and coupling constants (Hz). High-resolution mass spectra were performed on a JEOL JMS-700N (FAB and EI) or a Bruker ultrafleXtreme (ESI-TOF). TLC analyses were carried out on glass sheets coated with silica gel 60 F_{254} (AS ONE, 0.25 mm), and visualization was accomplished with UV light. Column chromatography was performed on silica gel (Fuji Silysia BW-127 ZH, 100−270 mesh). Preparative HPLC (GPC) was performed on a LC-5060 HPLC system (Japan Analytical Industry) using a JAIGEL-2HH (ø 20 mm × 600 mm) (Japan Analytical Industry). Chiral HPLC analysis was performed on a LC-20AT/SPD-20A (Shimadzu) using a CHIRALPAK IA or a CHIRALPAK IC (Daicel).

Materials. Most reagents were purchased and used without further purification unless otherwise specified. Hydrosilanes were dried over molecular sieves 3Å. $^{13}CO_2$ (99%) was purchased from Taiyo Nippon Sanso Corporation. $LiAlD_4$ (98%) was purchased from Strem Chemicals to prepare $PhSiD_3$.[S1] Substrates **2f**,[S2] **2g**,[S3] **2h**,[S4] **2i**,[S4] and **2j**[S5] were synthesized according to the literature.

DFT calculations. The calculations were performed using Gaussian16, revision C01 at the B3LYP/6-31+G(d,p) level with the self-consistent reaction filed (SCRF) method (H_2O). M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

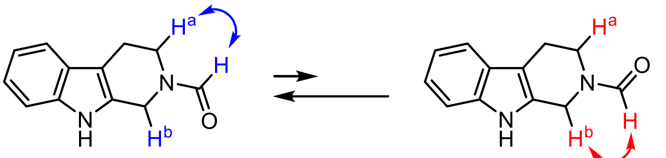
2. Synthesis and characterization of 3a and 4a

Procedure for the synthesis of formyltryptoline 3a from CO_2 and tryptamine (2a) (Table 1, entry 4)



Catalyst **1** (3.0 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The NMR yield was determined by using styrene as an internal standard (83%). The residue was purified by column chromatography (SiO_2, EtOAc/$CHCl_3$ = 1/1) to afford **3a** (39.8 mg, 199 μmol, 80%) as a colorless powder. ^{1}H NMR and ^{1}H-^{1}H NOESY spectra in $CDCl_3$ at 25 °C revealed that **3a** was present as an equilibrium mixture of the *Z*-form (80%) and the *E*-form (20%) (Fig. S1).

Mp 172–175 °C; **IR** (KBr) 3267, 2961, 2931, 2874, 1728, 1659, 1441, 1394, 1261, 1213, 1047, 1026, 802, 744 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.31 (s, 0.2H), 8.27 (s, 0.8H), 8.06 (br s, 0.8H), 7.93 (br s, 0.2H), 7.49 (d, *J* = 8.0 Hz, 0.2H), 7.47 (d, *J* = 7.9 Hz, 0.8H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.22−7.09 (m, 2H), 4.76 (s, 1.6H), 4.61 (s, 0.4H), 3.93 (t, *J* = 5.9 Hz, 0.4H), 3.76 (t, *J* = 5.8 Hz, 1.6H), 2.92−2.82 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 161.8, 136.4, 136.3, 128.8, 128.7, 126.9, 126.8, 122.3, 122.1, 119.9, 119.7, 118.3, 118.0, 111.2, 111.1, 109.4, 108.0, 44.3, 43.9, 38.7, 38.6, 22.3, 20.9; **HR MS** (ESI$^-$) Calcd for $C_{12}H_{11}N_2O$: 199.0877 [M − H]$^-$. Found: 199.0865.



(*Z*)-**3a** (*E*)-**3a**

[(*Z*)-**3a**] : [(*E*)-**3a**] = 80 : 20

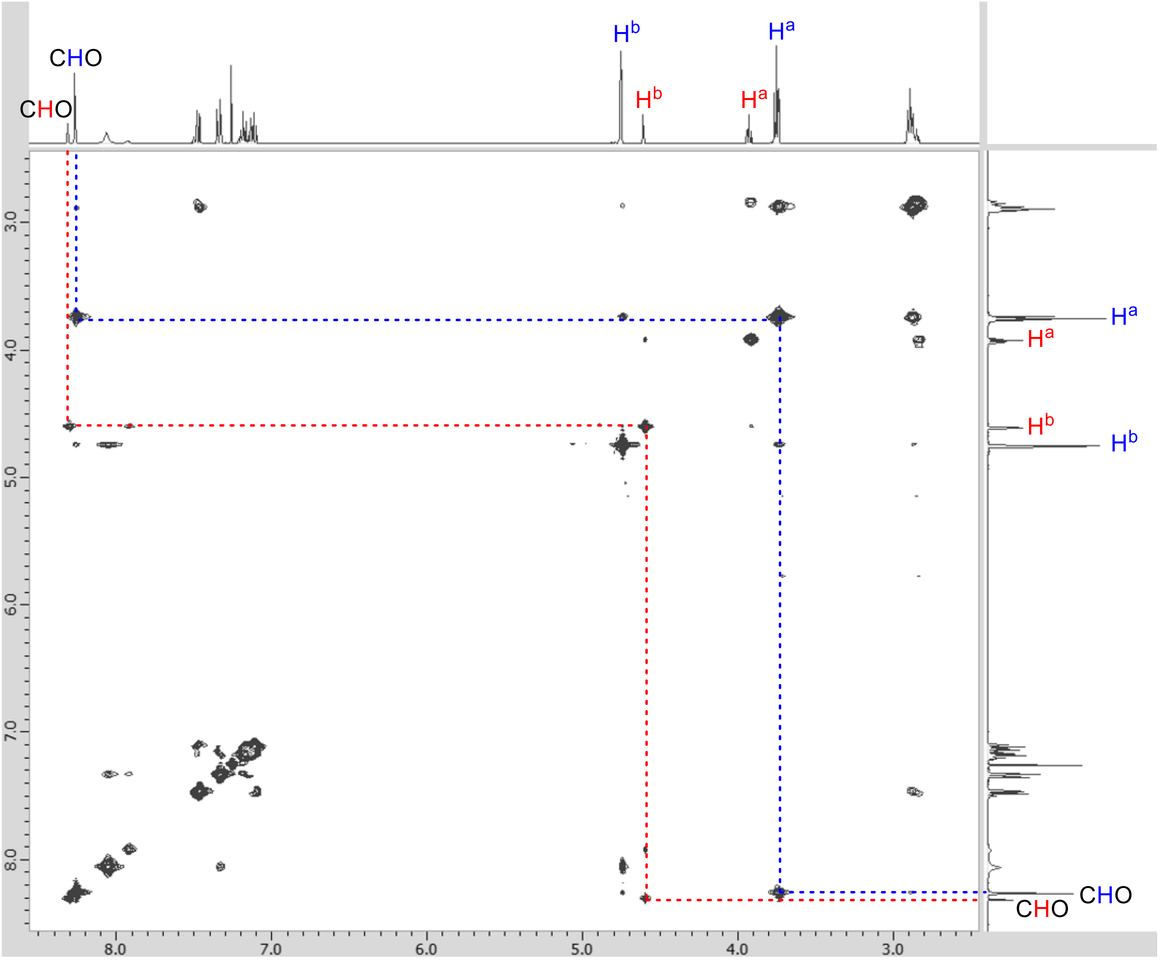
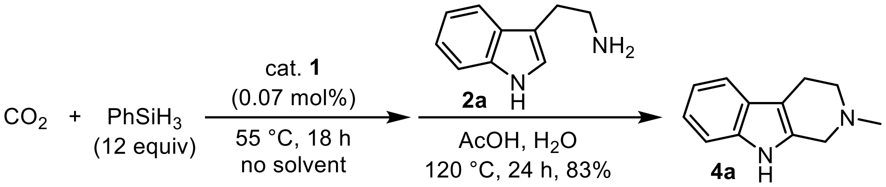


Fig. S1 ^{1}H-^{1}H NOESY spectrum of **3a** (400 MHz, $CDCl_3$, 25 °C).

Procedure for the synthesis of methyltryptoline 4a from CO_2 and tryptamine (2a) (Table 1, entry 10)



Catalyst **1** (4.6 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The NMR yield was determined by using styrene as an internal standard (82%). The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH = 9/1 then 4/1) to afford **4a** (38.5 mg, 207 μmol, 83%) as a colorless powder. **4a** was characterized according to the literature.[S6]

Mp 201–203 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (br s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.13 (td, *J* = 1.4, 7.4 Hz, 1H), 7.09 (td, *J* = 1.2, 7.4 Hz, 1H), 3.64 (s, 2H), 2.89−2.78 (m, 4H), 2.54 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.2, 131.8, 127.3, 121.4, 119.4, 118.1, 110.9, 108.1, 53.1, 52.3, 45.7, 21.6.

3. X-ray crystal structures and conformational analysis

Needle shaped colorless single crystals of **3a** were obtained by vapor diffusion of a THF/hexane solution. The data were collected by a Rigaku Varimax with Saturn diffractometer using multi-layer mirror monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 200 K. A total of 21034 reflections (2943 independent reflections (R_{int} = 0.0768)) were measured. The structure was solved by the direct method (SHELXT) and refined by full-matrix least-squares on F^2 (SHELXL-2018/3). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{12}H_{12}N_2O$; FW = 200.24, crystal size 0.15 mm × 0.04 mm × 0.03 mm, orthorhombic, $P2_12_12_1$, a = 6.0306(3) Å, b = 10.3023(6) Å, c = 16.1959(10) Å, α = 90°, β = 90°, γ = 90°, V = 1006.24(10) Å^3, Z = 4, D_{c} = 1.322 g cm^{-3}. The refinement converged to R_1 = 0.1013, wR_2 = 0.1205 (all data), GOF = 1.023. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2413450.

Prism shaped colorless single crystals of **4a** were obtained by vapor diffusion of a THF/hexane solution. The data were collected by a Rigaku Varimax with Saturn diffractometer using multi-layer mirror monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. A total of 18579 reflections (2840 independent reflections (R_{int} = 0.1092)) were measured. The structure was solved by the direct method (SHELXT) and refined by full-matrix least-squares on F^2 (SHELXL-2018/3). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{12}H_{14}N_2O$; FW = 186.25, crystal size 0.15 mm × 0.04 mm × 0.02 mm, monoclinic, $P2_1$/n, a = 12.4491(7) Å, b = 6.2533(2) Å, c = 13.2178(7) Å, α = 90°, β = 108.117(6)°, γ = 90°, V = 977.97(9) Å^3, Z = 4, D_{c} = 1.265 g cm^{-3}. The refinement converged to R_1 = 0.0822, wR_2 = 0.1525 (all data), GOF = 1.023. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2413452.

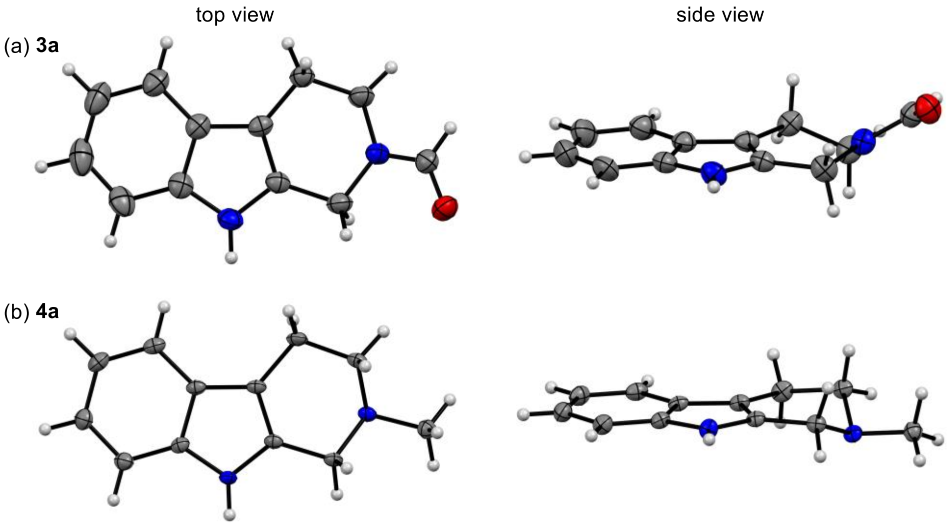
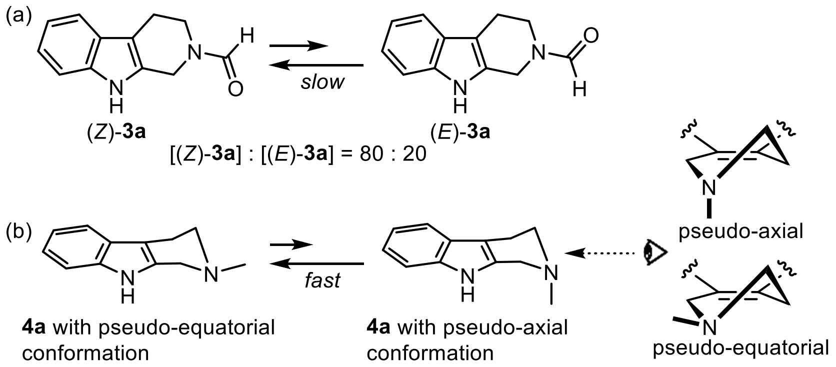


Fig. S2 ORTEP drawing of X-ray crystal structures of (a) **3a** and (b) **4a**. The thermal ellipsoids are scaled to the 50% probability level.

The geometry of the formamide moiety of the X-ray structure of **3a** was the *Z*-form. In contrast, ^{1}H NMR spectum in $CDCl_3$ at 24 °C revealed that **3a** was present as an equilibrium mixture of the *Z*-form (80%) and the *E*-form (20%) (Scheme S1). On the basis of the Boltzmann distribution, the *Z*/*E* ratio corresponds to an energy difference of 0.8 kcal mol^{-1}. DFT calculations at the B3LYP/6-31+G(d,p) level also support the preference of the *Z*-form; (*Z*)-**3a** was found to be more stable than (*E*)-**3a** by 0.7 kcal mol^{-1} (Fig. S3a). The geometry of the X-ray structure of **4a**, which includes a tetrahydropyridine ring with a half-chair conformation, adopted a pseudo-equatorial conformation rather than a pseudo-axial conformation. Although the ^{1}H NMR spectrum of **4a** suggested an averaged structure due to the rapid interconversion between the two conformers on the NMR time scale, the DFT calculations suggested that the pseudo-equatorial conformer was more stable than the pseudo-axial conformer by 2.2 kcal mol^{-1} (Fig. S3b), indicating that the pseudo-equatorial conformer was dominant even in solution.



Scheme S1 (a) An equilibrium between (*Z*)-**3a** and (*E*)-**3a** in $CDCl_3$ at 24 °C. (b) An equilibrium between the pseudo-equatorial and pseudo-axial conformers of **4a**.

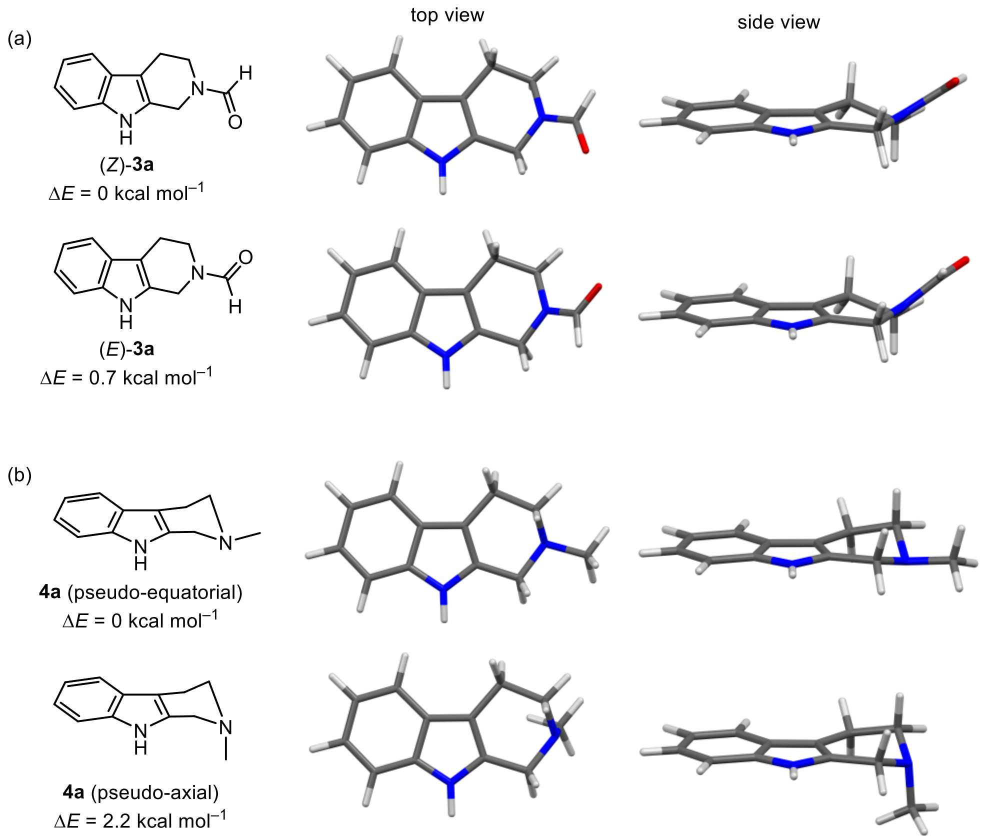
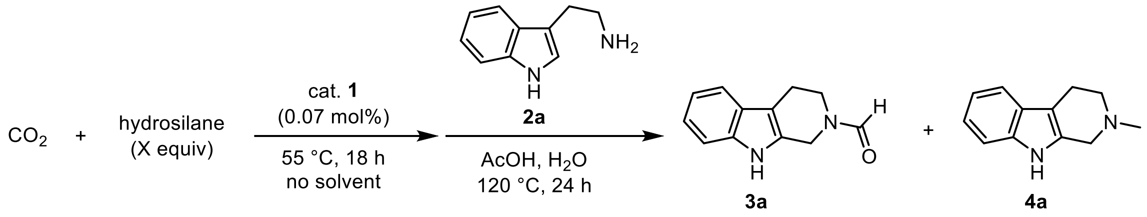


Fig. S3 DFT-optimized strucures of (a) **3a** and (b) **4a** at the B3LYP/6-31+G(d,p) level.

4. Optimization of reaction conditions

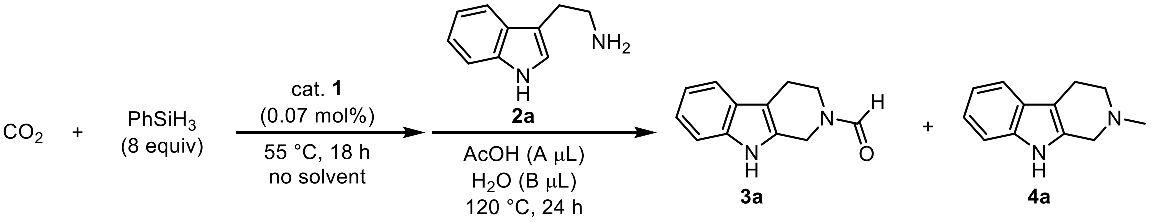
Table S1 Optimization of hydrosilanes[a]



Entry	Hydrosilane	X (equiv)	Yield (%)[b] 3a	Yield (%)[b] 4a
1[c]	$PhSiH_3$	8	83	6
2	$MePhSiH_2$	12	65	16
3	Me_2PhSiH	24	0	0
4	PMHS	24	0	0
5	none	–	0	0

[a] Conditions: CO_2 (1 atm, balloon), hydrosilane (8–24 equiv), cat. **1** (3.0 mg, 1.4 μmol), **2a** (0.25 mmol), AcOH (200 μL), H_2O (100 μL). [b] Determined by ^1H NMR using styrene as an internal standard. PMHS: polymethylhydrosiloxane. [c] Conditions of entry 4 in Table 1.

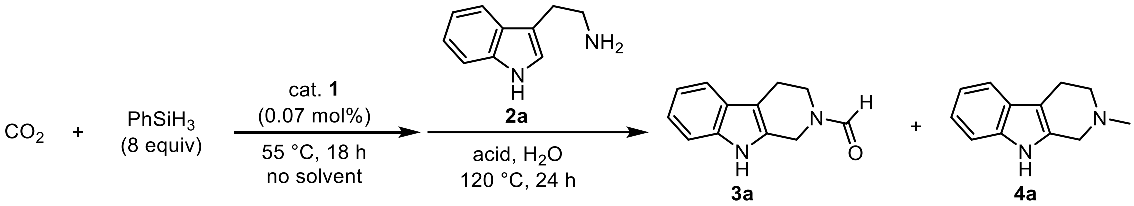
Table S2 Optimization of volumes of additives[a]



Entry	A (μL)	B (μL)	Yield (%)[b] 3a	Yield (%)[b] 4a
1[c]	200	100	83	6
2	100	100	67	12
3	100	50	75	0
4	300	100	72	11
5	300	150	74	14

[a] Conditions: CO_2 (1 atm, balloon), $PhSiH_3$ (8 equiv), cat. **1** (3.0 mg, 1.4 μmol), **2a** (0.25 mmol).
[b] Determined by ^1H NMR using styrene as an internal standard. [c] Conditions of entry 4 in Table 1.

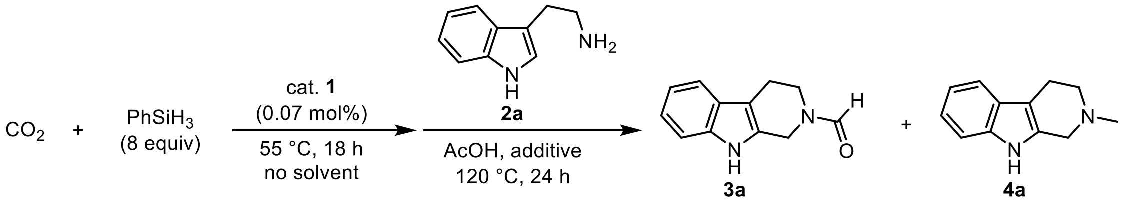
Table S3 Optimization of acids[a]



Entry	Acid	Yield (%)[b]	
		3a	**4a**
1[c]	AcOH	83	6
2	PhOH	70	4
3	propionic acid	62	22
4	CF_3CO_2H	0	0
5	conc. HCl aq.	0	0

[a] Conditions: CO_2 (1 atm, balloon), $PhSiH_3$ (8 equiv), cat. **1** (3.0 mg, 1.4 μmol), **2a** (0.25 mmol), acid (200 μL), H_2O (100 μL). [b] Determined by ^{1}H NMR using styrene as an internal standard. [c] Conditions of entry 4 in Table 1.

Table S4 Optimization of additives[a]

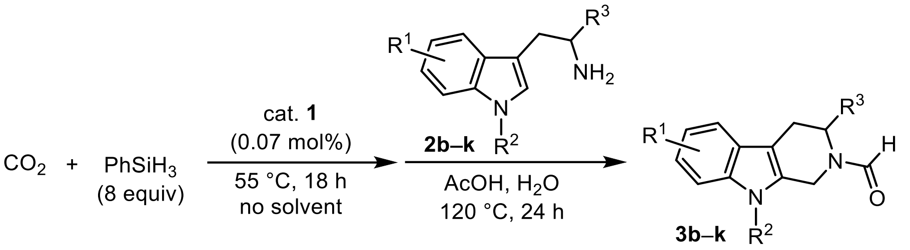


Entry	Additive	Yield (%)[b]	
		3a	**4a**
1[c]	H_2O	83	6
2	MeOH	36	17
3	DMSO	27	38
4	MeCN	54	17
5	benzene	68	7

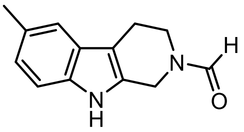
[a] Conditions: CO_2 (1 atm, balloon), $PhSiH_3$ (8 equiv), cat. **1** (3.0 mg, 1.4 μmol), **2a** (0.25 mmol), AcOH (200 μL), additive (100 μL). [b] Determined by ^{1}H NMR using styrene as an internal standard. [c] Conditions of entry 4 in Table 1.

5. Synthesis and characterization of 3b–l, 4b–l, 7, and 8

General procedure for the synthesis of formyltryptolines 3b−k



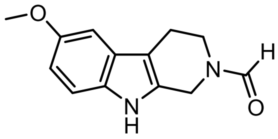
Catalyst **1** (3.0 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm, ca. 3.7 L) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and tryptamine **2b−k** (250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. After the NMR yields were determined using styrene as an internal standard, the main products were purified according to the procedures shown below.



3b

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 3/1) to afford **3b** (40.7 mg, 190 μmol, 76%) as a yellow powder.

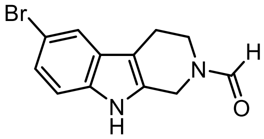
Mp 158–161 °C; **IR** (KBr) 3202, 2910, 2735, 1655, 1487, 1437, 1393, 1234, 1194, 1171, 1042, 1030, 908, 872, 791, 756, 679, 629 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.28 (s, 0.2H), 8.26–8.18 (m, 1.6H), 8.11 (br s, 0.2H), 7.28 (s, 0.2H), 7.26 (s, 0.8H), 7.22 (d, J = 8.2 Hz, 0.8H), 7.21 (d, J = 8.1 Hz, 0.2H), 7.04–6.98 (m, 1H), 4.71 (s, 1.6H), 4.56 (s, 0.4H), 3.91 (t, J = 5.7 Hz, 0.2H), 3.72 (t, J = 5.6 Hz, 0.8H), 2.92–2.78 (m, 2H), 2.48 (s, 0.6H), 2.46 (s, 2.4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 161.8, 134.72, 134.66, 129.2, 129.0, 128.9, 128.8, 127.2, 127.1, 123.8, 123.6, 118.1, 117.8, 110.8, 110.7, 108.9, 107.5, 44.3, 43.9, 38.7, 38.6, 25.3, 22.3, 21.6, 20.9; **HR MS** (FAB$^+$; NBA) Calcd for $C_{13}H_{14}N_2O$: 214.1101 $[M]^+$. Found: 214.1105.



3c

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 3/1) to afford **3c** (44.9 mg, 195 μmol, 78%) as a yellow powder.

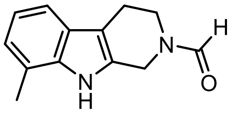
Mp 75–78 °C; **IR** (KBr) 3296, 2927, 2883, 1662, 1485, 1436, 1398, 1265, 1215, 1177, 1159, 1130, 1111, 1028, 804, 748 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.40 (br s, 1H), 8.24 (s, 0.2H), 8.23 (s, 0.8H), 7.21 (d, *J* = 8.7 Hz, 0.8H), 7.20 (d, *J* = 8.7 Hz, 0.2H), 6.92 (d, *J* = 2.4 Hz, 0.2H), 6.91 (d, *J* = 2.4 Hz, 0.8H), 6.85–6.80 (m, 1H), 4.70 (s, 1.6H), 4.51 (s, 0.4H), 3.89 (t, *J* = 5.8 Hz, 0.4H), 3.85 (s, 3H), 3.71 (t, *J* = 5.8 Hz, 1.6H), 2.83 (t, *J* = 5.7 Hz, 1.6H), 2.79 (t, *J* = 5.8 Hz, 0.4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 161.8, 154.3, 154.2, 131.5, 131.4, 129.7, 127.2, 112.1, 111.9, 111.8, 111.7, 109.0, 107.7, 100.42, 100.36, 56.04, 56.00, 44.3, 43.9, 38.8, 38.6, 22.3, 20.9; **HR MS** (ESI$^+$) Calcd for $C_{13}H_{14}N_2O_2Na$: 253.0947 [M + Na]$^+$. Found: 253.0947.



3d

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 3/1) to afford **3d** (35.6 mg, 128 μmol, 51%) as a pale yellow powder.

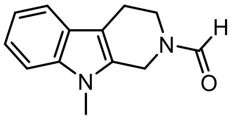
Mp 220–223 °C; **IR** (KBr) 3221, 2941, 2864, 1667, 1487, 1437, 1396, 1315, 1236, 1207, 1155, 1043, 997, 974, 907, 873, 810, 750, 658 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.30 (s, 0.8H), 8.25 (s, 0.2H), 8.16 (br s, 0.8H), 7.97 (br s, 0.2H), 7.61 (d, *J* = 1.7 Hz, 0.2H), 7.59 (d, *J* = 1.8 Hz, 0.8H), 7.24–7.28 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 0.8H), 7.20 (d, *J* = 8.6 Hz, 0.2H), 4.75 (s, 1.6H), 4.61 (s, 0.4H), 3.91 (t, *J* = 5.9 Hz, 0.4H), 3.75 (t, *J* = 5.7 Hz, 1.6H), 2.84 (tt, *J* = 1.6, 5.8 Hz, 1.6H), 2.80 (tt, *J* = 1.5, 5.9 Hz, 0.4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.1, 161.6, 135.2, 135.1, 130.3, 130.0, 128.9, 128.8, 125.3, 125.1, 121.2, 120.9, 113.4, 113.2, 112.53, 112.45, 109.7, 108.1, 44.1, 43.8, 38.6, 38.5, 22.3, 20.8; **HR MS** (FAB$^+$; NBA) Calcd for $C_{12}H_{11}{}^{79}BrN_2O$: 278.0049 [M]$^+$. Found: 278.0048.



3e

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 3/1) to afford **3e** (33.2 mg, 155 μmol, 62%) as a colorless oil.

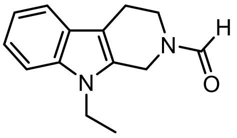
IR (neat) 3302, 3053, 2922, 2857, 1668, 1591, 1443, 1398, 1373, 1328, 1306, 1215, 1163, 1045, 920, 777, 750, 667 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.62 (br s, 0.8H), 8.32 (br s, 0.2H), 8.29 (s, 0.2H), 8.25 (s, 0.8H), 7.34 (d, *J* = 7.1 Hz, 0.2H), 7.33 (d, *J* = 7.6 Hz, 0.8H), 7.06 (t, *J* = 7.4 Hz, 0.2H), 7.05 (t, *J* = 7.5 Hz, 0.8H), 7.02–6.97 (m, 1H), 4.77 (s, 1.6H), 4.58 (s, 0.4H), 3.91 (t, *J* = 5.9 Hz, 0.2H), 3.73 (t, *J* = 5.8 Hz, 0.8H), 2.88 (t, *J* = 5.7 Hz, 0.8H), 2.83 (t, *J* = 5.8 Hz, 0.2H), 2.50 (s, 2.4H), 2.49 (s, 0.6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 161.8, 136.0, 135.9, 128.6, 128.5, 126.5, 126.4, 122.9, 122.7, 120.5, 120.3, 120.1, 119.9, 116.0, 115.6, 109.7, 108.3, 44.3, 44.0, 38.8, 38.6, 22.4, 21.0, 16.8; **HR MS** (EI$^+$) Calcd for $C_{13}H_{14}N_2O$: 214.1101 [M]$^+$. Found: 214.1108.



3f

The second step was carried out at 110 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 3/1) to afford **3f** (32.3 mg, 151 μmol, 60%) as a yellow oil.

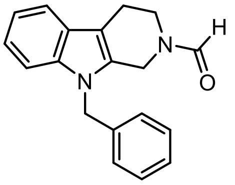
IR (neat) 3051, 2922, 2849, 1668, 1472, 1435, 1398, 1383, 1346, 1306, 1246, 1213, 1186, 1171, 1148, 1047, 991, 831, 743 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.34 (s, 0.2H), 8.27 (s, 0.8H), 7.51–7.48 (m, 0.2H), 7.48 (d, *J* = 7.9 Hz, 0.8H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.25–7.20 (m, 1H), 7.13 (ddd, *J* = 1.0, 7.0, 7.9 Hz, 0.2H), 7.12 (ddd, *J* = 0.9, 7.1, 7.8 Hz, 0.8H), 4.74 (s, 1.6H), 4.58 (s, 0.4H), 3.90 (t, *J* = 5.8 Hz, 0.4H), 3.73 (t, *J* = 5.7 Hz, 1.6H), 3.65 (s, 0.6H), 3.64 (s, 2.4H), 2.89 (t, *J* = 5.7 Hz, 1.6H), 2.85 (t, *J* = 5.8 Hz, 0.4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 161.7, 137.26, 137.22, 130.3, 130.1, 126.4, 126.3, 121.8, 121.6, 119.5, 119.4, 118.3, 118.0, 109.0, 108.9, 108.3, 106.9, 44.2, 43.2, 38.5, 38.0, 29.6, 22.3, 20.9; **HR MS** (EI$^+$) Calcd for $C_{13}H_{14}N_2O$: 214.1101 [M]$^+$. Found: 214.1105.



3g

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$) to afford **3g** (41.7 mg, 183 μmol, 73%) as a pale yellow oil.

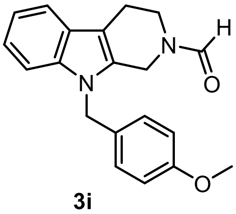
IR (neat) 3051, 2976, 2930, 2849, 1668, 1456, 1398, 1379, 1348, 1306, 1236, 1211, 1186, 1084, 1049, 1015, 991, 743, 669 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.35 (s, 0.2H), 8.28 (s, 0.8H), 7.51–7.46 (m, 0.2H), 7.48 (d, *J* = 7.9 Hz, 0.8H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.24–7.20 (m, 0.2H), 7.21 (ddd, *J* = 1.1, 7.1, 8.2 Hz, 0.8H), 7.12 (ddd, *J* = 0.9, 7.0, 8.0 Hz, 0.2H) , 7.11 (ddd, *J* = 0.9, 7.0, 7.8 Hz, 0.8H), 4.75 (s, 1.6H), 4.61 (s, 0.4H), 4.10 (q, *J* = 7.2 Hz, 1.6H), 4.09 (q, *J* = 7.3 Hz, 0.4H), 3.92 (t, *J* = 5.8 Hz, 0.4H), 3.75 (t, *J* = 5.8 Hz, 1.6H), 2.91 (tt, *J* = 1.6, 5.8 Hz, 1.6H), 2.86 (tt, *J* = 1.6, 5.9 Hz, 0.4H), 1.38 (t, *J* = 7.3 Hz, 2.4H), 1.37 (t, *J* = 7.3 Hz, 0.6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 161.6, 136.1, 129.5, 129.3, 126.7, 126.5, 121.7, 121.5, 119.4, 119.3, 118.4, 118.1, 109.1, 108.3, 107.0, 44.2, 43.1, 38.5, 38.2, 37.9, 22.3, 20.9, 15.6, 15.5; **HR MS** (FAB$^+$; NBA) Calcd for $C_{14}H_{16}N_2O$: 228.1257 [M]$^+$. Found: 228.1262.



3h

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 5/1) to afford **3h** (61.3 mg, 211 μmol, 84%) as a yellow oil.

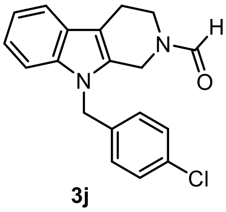
IR (neat) 3055, 3030, 2924, 2851, 1651, 1494, 1456, 1350, 1306, 1207, 1167, 1148, 991, 831, 804, 743, 702 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.24 (s, 0.8H), 8.21 (s, 0.2H), 7.55 (d, *J* = 7.9 Hz, 0.2H), 7.53 (d, *J* = 7.7 Hz, 0.8H), 7.31–7.22 (m, 4H), 7.22–7.13 (m, 2H), 7.05–6.95 (m, 2H), 5.26 (s, 2H), 4.64 (s, 1.6H), 4.43 (s, 0.4H), 3.90 (t, *J* = 5.8 Hz, 0.4H), 3.72 (t, *J* = 5.7 Hz, 1.6H), 2.95–2.91 (m, 1.6H), 2.91–2.87 (m, 0.4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.2, 161.7, 137.18, 137.16, 130.2, 130.1, 129.1, 129.0, 127.8, 127.7, 126.64, 126.55, 126.3, 126.1, 122.2, 122.0, 119.8, 119.7, 118.5, 118.2, 109.5, 109.4, 109.2, 107.8, 46.9, 46.7, 44.2, 43.2, 38.5, 38.0, 22.3, 20.9; **HR MS** (FAB$^+$; NBA) Calcd for $C_{19}H_{18}N_2O$: 290.1414 [M]$^+$. Found: 290.1418.



3i

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$) and GPC ($CHCl_3$) to afford **3i** (36.1 mg, 113 μmol, 45%) as a yellow oil.

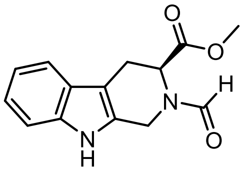
IR (neat) 3051, 3003, 2930, 2839, 1668, 1614, 1514, 1456, 1381, 1306, 1246, 1177, 1034, 991, 831, 745 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.23 (s, 0.8H), 8.21 (s, 0.2H), 7.56–7.48 (m, 1H), 7.35 (s, 0.2H), 7.29 (s, 0.8H), 7.23–7.10 (m, 2H), 7.00–6.92 (m, 2H), 6.84–6.78 (m, 2H), 5.19 (s, 2H), 4.64 (s, 1.6H), 4.43 (s, 0.4H), 3.89 (t, J = 6.8 Hz, 0.4H), 3.77 (s, 0.6H), 3.76 (s, 2.4H), 3.72 (t, J = 5.7 Hz, 1.6H), 2.92 (t, J = 4.9 Hz, 1.6H), 2.88 (t, J = 5.9 Hz, 0.4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 161.7, 159.2, 159.1, 137.1, 130.2, 130.1, 129.2, 129.1, 127.6, 127.5, 126.6, 126.5, 122.1, 121.9, 119.7, 119.6, 118.5, 118.1, 114.5, 114.4, 109.5, 109.4, 109.1, 107.7, 55.4, 46.4, 44.2, 43.3, 38.5, 38.1, 22.4, 20.9; **HR MS** (FAB^{+}; NBA) Calcd for $C_{20}H_{20}N_2O_2$: 320.1519 [M]$^{+}$. Found: 320.1525.



3j

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$) to afford **3j** (45.8 mg, 141 μmol, 56%) as a yellow oil.

IR (neat) 3051, 2924, 2851, 1668, 1617, 1493, 1381, 1306, 1244, 1207, 1169, 1094, 1047, 1015, 989, 831, 743 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.25 (s, 0.8H), 8.23 (s, 0.2H), 7.57–7.51 (m, 1H), 7.30–7.13 (m, 5H), 6.95 (d, J = 8.4 Hz, 1.6H), 6.94 (d, J = 8.4 Hz, 0.4H), 5.21 (s, 2H), 4.63 (s, 1.6H), 4.43 (s, 0.4H), 3.91 (t, J = 5.9 Hz, 0.4H), 3.73 (t, J = 5.8 Hz, 1.6H), 2.94 (t, J = 5.7 Hz, 1.6H), 2.89 (t, J = 5.8 Hz, 0.4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 161.6, 137.0, 135.7, 133.6, 133.5, 130.0, 129.9, 129.2, 129.1, 127.6, 127.5, 126.7, 126.6, 122.3, 122.1, 119.9, 119.8, 118.6, 118.3, 109.4, 109.3, 109.2, 108.0, 46.2, 44.1, 43.1, 38.4, 37.9, 22.3, 20.9; **HR MS** (EI^{+}) Calcd for $C_{19}H_{17}ClN_2O$: 324.1024 [M]$^{+}$. Found: 324.1028.



(*S*)-**3k**

The second step was carried out at 130 or 90 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 3/1) to afford (*S*)-**3k** (16.5 mg, 63.9 μmol, 26%, 78% ee at 130 °C and 11.0 mg, 42.6 μmol, 17%, 97% ee at 90 °C) as a colorless powder. The ee values were determined by HPLC analysis (Fig. S4).

(*S*)-**3k** (98% ee): **mp** 164–167 °C; **[α]**$_D^{23}$ = +60 ($CHCl_3$, *c* 0.16); **IR** (KBr) 3404, 3061, 2953, 2859, 1740, 1676, 1626, 1449, 1429, 1408, 1211, 1175, 1024, 1015, 1007, 988, 949, 806, 746, 733 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (3:2 (0.6:0.4)) δ 8.39 (s, 0.4H), 8.29 (s, 0.6H), 7.96 (br s, 0.6H), 7.88 (br s, 0.4H), 7.51 (d, *J* = 6.5 Hz, 0.4H), 7.49 (d, *J* = 7.0 Hz, 0.6H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.22–7.10 (m, 2H), 5.71 (dd, *J* = 1.1, 7.0 Hz, 0.4H), 5.21 (dd, *J* = 1.5, 16.9 Hz, 0.6H), 4.92 (dt, *J* = 2.0, 15.5 Hz, 0.4H), 4.74 (dd, *J* = 1.2, 6.4 Hz, 0.6H), 4.65 (dd, *J* = 1.5, 15.5 Hz, 0.4H), 4.47 (d, *J* = 16.7 Hz, 0.6H), 3.67 (s, 1.8H), 3.66 (s, 1.2H), 3.54 (d, *J* = 15.6 Hz, 0.6H), 3.46 (dd, *J* = 16.0 Hz, 0.4H), 3.22–3.06 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 171.0, 163.1, 162.7, 136.8, 136.7, 128.3, 127.9, 126.9, 126.8, 122.5, 122.3, 120.0, 119.9, 118.4, 118.1, 111.2, 111.1, 107.1, 105.8, 56.2, 52.9, 52.7, 49.6, 41.8, 37.9, 24.3, 23.1; **HR MS** (ESI$^+$) Calcd for $C_{14}H_{14}N_2O_3Na$: 281.0897 [M + Na]$^+$. Found: 281.0901.

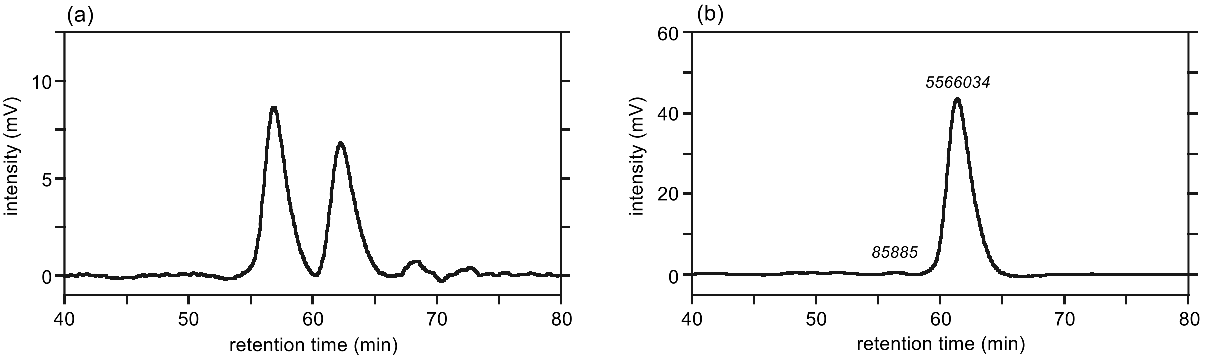
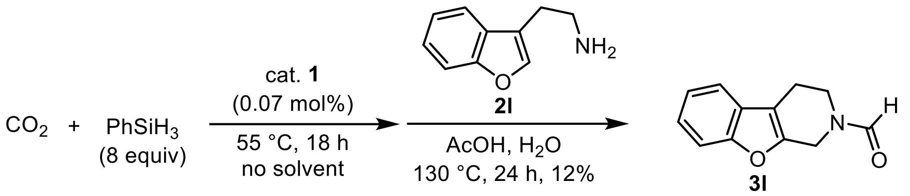


Fig. S4 HPLC chromatograms of the (a) racemic and (b) optically active (97% ee) samples of **3k**. Conditions: CHIRALPAK IA, $CHCl_3$/hexane/Et_3N = 60/40/0.5, 0.8 mL/min, UV detection at 280 nm.

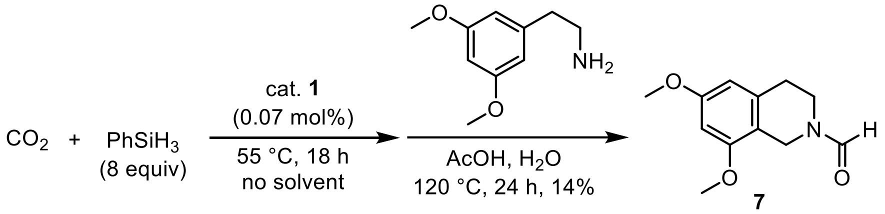
Procedure for the synthesis of 3l



Catalyst **1** (3.1 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and 3-benzofuranethylamine **2l** (40.4 mg, 250 μmol) were added, and the reaction mixture was stirred at 130 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The NMR yield was determined by using styrene as an internal standard (13%). The residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 5/1) and GPC ($CHCl_3$) to afford **3l** (6.04 mg, 30.0 μmol, 12%) as a light brown powder.

Mp 84–87 °C; **IR** (KBr) 3046, 2924, 2853, 1674, 1452, 1435, 1368, 1302, 1279, 1179, 1123, 1043, 993, 891, 858, 818, 762, 646 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$, an equilibrium mixture of two conformers (5:2 (0.7:0.3)) δ 8.31 (s, 0.3H), 8.26 (s, 0.7H), 7.48–7.41 (m, 2H), 7.28–7.21 (m, 2H), 4.72 (s, 1.4H), 4.58 (s, 0.6H), 3.92 (d, *J* = 5.9 Hz, 0.6H), 3.75 (t, *J* = 5.7 Hz, 1.4H), 2.83 (t, *J* = 5.7 Hz, 1.4H), 2.79 (t, *J* = 5.7 Hz, 0.3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.1, 161.9, 155.03, 154.98, 148.3, 147.9, 127.6, 127.5, 124.4, 124.2, 123.1, 122.9, 119.1, 118.8, 112.9, 111.6, 111.5, 111.4, 44.0, 43.6, 38.9, 38.0, 22.0, 20.6; **HR MS** (FAB^+; NBA) Calcd for $C_{12}H_{11}NO_2$: 201.0784 $[M]^+$. Found: 201.0789.

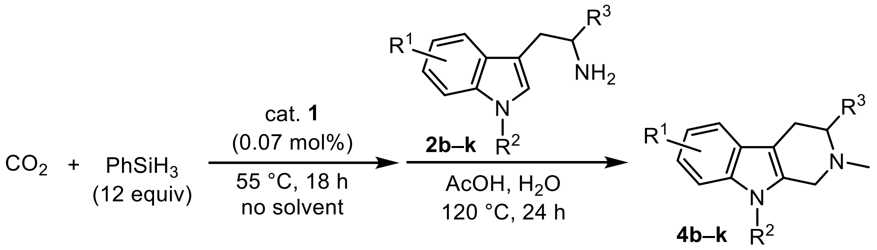
Procedure for the synthesis of 7



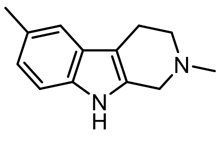
Catalyst **1** (3.1 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and 3,5-dimethoxybenzeneethanamine (45.4 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed with brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The NMR yield was determined by using styrene as an internal standard (21%). The residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 5/1) and GPC ($CHCl_3$) to afford **7** (7.50 mg, 33.9 μmol, 14%) as a colorless powder.

Mp 105–108 °C; **IR** (KBr) 2999, 2959, 2839, 1659, 1495, 1454, 1420, 1373, 1281, 1211, 1196, 1146, 1096, 932, 824 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (1:1 (0.5:0.5)) δ 8.27 (s, 0.5H), 8.18 (s, 0.5H), 6.33 (d, J = 1.8 Hz, 1H), 6.26 (d, J = 2.3 Hz, 0.5H), 6.24 (d, J = 2.3 Hz, 0.5H), 4.52 (s, 1H), 4.40 (s, 1H), 3.81 (s, 1.5H), 3.80 (s, 1.5H), 3.789 (s, 1.5H), 3.788 (s, 1.5H), 3.76 (t, J = 5.9 Hz, 1H), 3.60 (t, J = 6.0 Hz, 1H), 2.84 (t, J = 5.9 Hz, 1H), 2.81 (t, J = 6.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 161.5, 159.6, 159.3, 157.4, 156.9, 136.3, 135.3, 113.7, 113.4, 104.5, 104.2, 96.6, 96.5, 55.54, 55.51, 55.45, 55.41, 43.32, 43.27, 38.5, 37.7, 30.3, 28.6; **HR MS** (EI^{+}) Calcd for $C_{12}H_{15}NO_3$: 221.1046 [M]$^{+}$. Found: 221.1051.

General procedure for the synthesis of methyltryptolines 4b−k



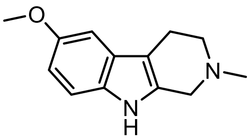
Catalyst **1** (4.6 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and tryptamine **2b−k** (250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. After the NMR yields were determined using styrene as an internal standard, the main products were purified according to the procedures shown below. **4b**,[S7] **4c**,[S8] **4f**,[S9] **4h**,[S10] and **4k**[S11] were characterized according to the literature.



4b

The product was purified by column chromatography (SiO_2, $CHCl_3$/MeOH = 10/1) and GPC ($CHCl_3$) to afford **4b** (27.5 mg, 137 μmol, 55%) as a yellow powder.

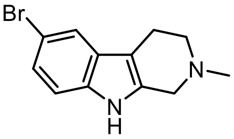
Mp 203–207 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (br s, 1H), 7.25 (s, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.95 (d, J = 7.3 Hz, 1H), 3.58 (s, 2H), 2.81 (s, 4H), 2.50 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.5, 131.9, 128.6, 127.5, 122.9, 117.9, 110.6, 107.5, 53.2, 52.4, 45.7, 21.62, 21.57.



4c

The second step was carried out at 130 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3/MeOH/Et_3N$ = 9/1/0.5 and $CHCl_3/MeOH$ = 5/1) to afford **4c** (27.6 mg, 128 μmol, 51%) as a yellow powder.

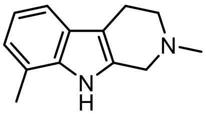
Mp 202–205 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (br s, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 2.4, 8.7 Hz, 1H), 3.85 (s, 3H), 3.53 (s, 2H), 2.81 (s, 4H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.1, 132.6, 131.3, 127.7, 111.5, 111.1, 107.9, 100.5, 56.1, 53.1, 52.4, 45.7, 21.6; **HR MS** (ESI$^+$) Calcd for $C_{13}H_{17}N_2O$: 217.1335 $[M + H]^+$. Found: 217.1332.



4d

The product was purified by column chromatography (SiO_2, $CHCl_3/MeOH/Et_3N$ = 10/1/0.2 and $CHCl_3/MeOH$ = 30/1) to afford **4d** (30.5 mg, 115 μmol, 46%) as a yellow powder.

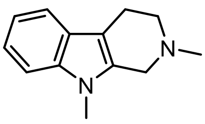
Mp 241–243 °C; **IR** (KBr) 3130, 3026, 2841, 1446, 1315, 1296, 1246, 1163, 1096, 1043, 997, 970, 907, 854, 783, 633 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (br s, 1H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.21 (dd, *J* = 1.9, 8.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 3.63 (s, 2H), 2.83–2.78 (m, 4H), 2.53 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 134.9, 133.1, 129.2, 123.3, 120.9, 112.9, 112.2, 108.1, 53.0, 52.4, 45.6, 21.4; **HR MS** (FAB$^+$; NBA) Calcd for $C_{12}H_{13}{}^{79}BrN_2$: 264.0257 $[M]^+$. Found: 264.0257.



4e

The product was purified by column chromatography (SiO_2, $CHCl_3/MeOH$ = 10/1) to afford **4e** (29.2 mg, 146 μmol, 58%) as a colorless powder.

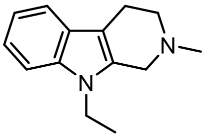
Mp 154–156 °C; **IR** (KBr) 3265, 2914, 2853, 2783, 1625, 1447, 1411, 1381, 1334, 1310, 1246, 1167, 1059, 1042, 970, 920, 847, 792, 745 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (br s, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 3.67 (s, 2H), 2.88–2.78 (m, 4H), 2.55 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.6, 131.5, 126.9, 122.1, 119.9, 119.6, 115.8, 108.7, 53.1, 52.5, 45.8, 21.6, 16.8; **HR MS** (EI$^+$) Calcd for $C_{13}H_{16}N_2$: 200.1308 $[M]^+$. Found: 200.1312.



4f

The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 1/1) to afford **4f** (25.3 mg, 126 μmol, 50%) as a yellow powder.

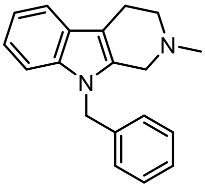
Mp 95–97 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H), 6.78 (ddd, *J* = 0.9, 7.0, 7.9 Hz, 1H), 3.66 (s, 2H), 3.61 (s, 3H), 2.92–2.85 (m, 2H), 2.84–2.78 (m, 2H), 2.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.2, 133.5, 126.8, 120.8, 118.9, 118.1, 108.7, 107.0, 53.1, 51.7, 46.1, 29.3, 21.7.



4g

The product was purified by column chromatography (SiO_2, $CHCl_3$/MeOH = 30/1) to afford **4g** (39.6 mg, 185 μmol, 74%) as a brown oil.

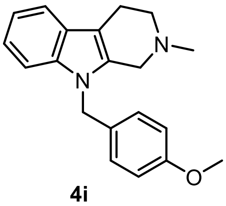
IR (neat) 3051, 2974, 2938, 2841, 2781, 1674, 1456, 1385, 1310, 1285, 1252, 1182, 1134, 1059, 1050, 972, 795, 739 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.70 (s, 2H), 2.92–2.80 (m, 4H), 2.59 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.1, 131.8, 126.9, 121.0, 118.9, 118.2, 108.9, 106.9, 52.5, 51.1, 45.2, 37.9, 21.1, 15.6; **HR MS** (FAB$^+$; NBA) Calcd for $C_{14}H_{18}N_2$: 214.1465 [M]$^+$. Found: 214.1470.



4h

The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 1/1) to afford **4h** (55.4 mg, 200 μmol, 80%) as a yellow oil.

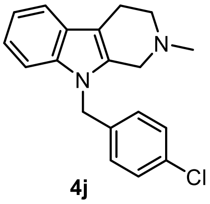
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 2.4, 6.5 Hz, 1H), 7.29–7.19 (m, 4H), 7.15–7.07 (m, 2H), 7.00 (dd, *J* = 1.3, 8.0 Hz, 2H), 5.22, (s, 2H), 3.56 (s, 2H), 2.90 (t, *J* = 5.4 Hz, 2H), 2.80 (t, *J* = 5.7 Hz, 2H), 2.51 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 136.9, 133.3, 128.8, 127.4, 127.0, 126.1, 121.1, 119.2, 118.1, 109.2, 107.7, 53.0, 51.6, 46.5, 46.0, 21.8.



4i

The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 1/1) to afford **4i** (42.1 mg, 137 μmol, 55%) as a brown oil.

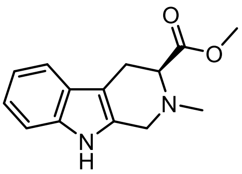
IR (neat) 3049, 2936, 2839, 2781, 1645, 1612, 1514, 1464, 1385, 1323, 1246, 1177, 1034, 970, 824, 741 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.15–7.05 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 5.16 (s, 2H), 3.76 (s, 3H), 3.56 (s, 2H), 2.90 (t, *J* = 5.4 Hz, 2H), 2.80 (t, *J* = 5.6 Hz, 2H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 136.9, 133.3, 129.8, 127.4, 127.1, 121.1, 119.1, 118.1, 114.2, 109.3, 107.7, 55.4, 53.0, 51.7, 46.1, 46.0, 21.8; **HR MS** (FAB$^+$; NBA) Calcd for $C_{20}H_{22}N_2O$: 306.1727 [M]$^+$. Found: 306.1732.



4j

The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 1/1) to afford **4j** (69.2 mg, 223 μmol, 89%) as a yellow oil.

IR (neat) 3051, 2939, 2843, 2783, 1616, 1464, 1408, 1385, 1323, 1250, 1179, 1096, 1015, 970, 820, 799, 739 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 2.5, 6.2 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.20–7.08 (m, 3H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.18 (s, 2H), 3.54 (s, 3H), 2.90 (t, *J* = 5.7 Hz, 2H), 2.81 (t, *J* = 5.6 Hz, 2H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 136.3, 133.2, 133.1, 129.0, 127.5, 127.1, 121.3, 119.4, 118.3, 109.1, 108.1, 52.9, 51.6, 46.0, 45.9, 21.7; **HR MS** (EI$^+$) Calcd for $C_{19}H_{19}ClN_2$: 310.1231 [M]$^+$. Found: 310.1235.



(*S*)-**4k**

The second step was carried out at 80 °C for 3 h or 45 °C under otherwise the same conditions. The product was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 1/1) to afford (*S*)-**4k** (23.2 mg, 95.0 μmol, 38%, 74% ee at 80 °C and 11.1 mg, 45.4 μmol, 18%, 98% ee at 45 °C) as a colorless powder. The ee values were determined by HPLC analysis (Fig. S5).

(*S*)-**4k** (98% ee): **mp** 173–176 °C; **[α]$_D$^{23}** = +23 ($CHCl_3$, *c* 0.17); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.14 (td, *J* = 1.4, 7.3 Hz, 1H), 7.10 (td, *J* = 1.2, 7.4 Hz, 1H), 4.10 (d, *J* = 15.2 Hz, 1H), 3.83 (d, *J* = 15.2 Hz, 1H), 3.74 (t, *J* = 5.5 Hz, 1H), 3.72 (s, 3H), 3.21–3.09 (m, 2H), 2.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 136.3, 131.2, 127.0, 121.5, 119.4, 118.0, 111.0, 105.7, 61.6, 51.8, 49.1, 42.1, 23.9.

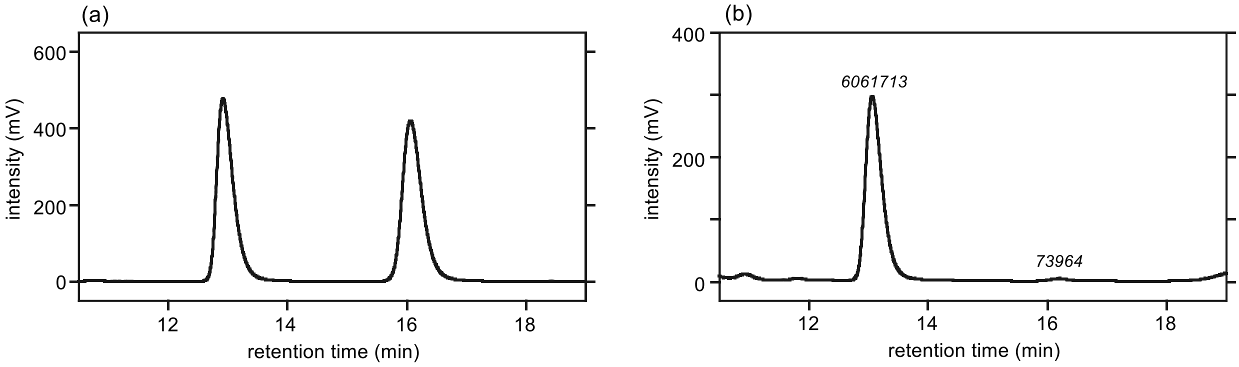
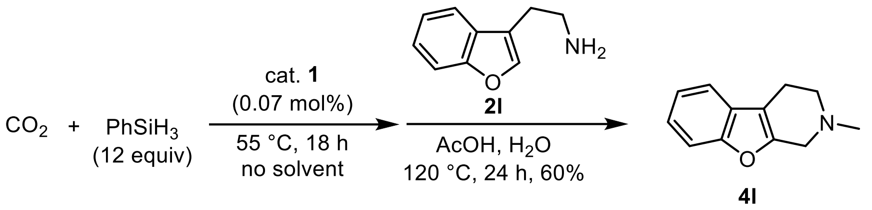


Fig. S5 HPLC chromatograms of the (a) racemic and (b) optically active (98% ee) samples of **4k**. Conditions: CHIRALPAK IC, $CHCl_3$/hexane/Et_3N = 75/25/0.1, 0.5 mL/min, UV detection at 280 nm.

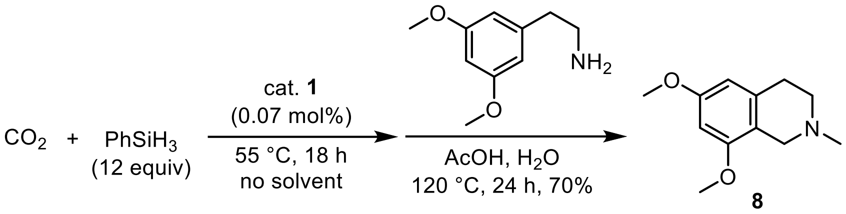
Procedure for the synthesis of 4l



Catalyst **1** (4.6 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and 3-benzofuranethylamine **2l** (40.4 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The NMR yield was determined by using styrene as an internal standard (64%). The residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOAc = 5/1) to afford **4l** (28.3 mg, 151 μmol, 60%) as a light brown powder.

Mp 182–186 °C; **IR** (KBr) 3057, 2928, 2766, 1670, 1450, 1377, 1304, 1271, 1234, 1188, 1157, 1092, 1042, 970, 895, 843, 746, 719 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.26–7.16 (m, 2H), 3.66 (s, 2H), 2.85–2.65 (m, 4H), 2.57 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 151.1, 128.1, 123.5, 122.5, 118.7, 111.2, 111.1, 52.4, 52.2, 45.5, 21.0; **HR MS** (FAB$^+$; NBA) Calcd for $C_{12}H_{13}NO$: 187.0992 $[M]^+$. Found: 187.0997.

Procedure for the synthesis of 8



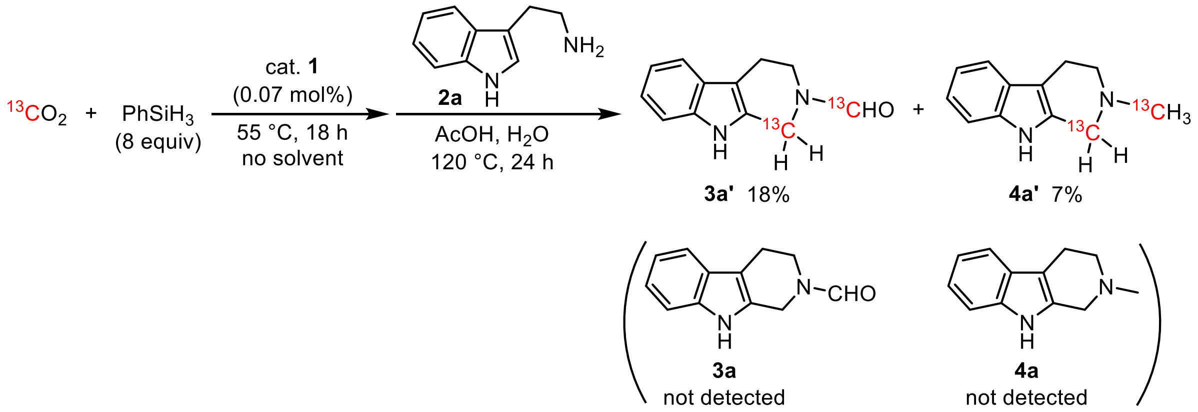
Catalyst **1** (4.6 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and 3,5-dimethoxybenzeneethanamine (46.0 mg, 254 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (four times). The organic layer was washed with brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The NMR yield was determined by using styrene as an internal standard (67%). The residue was purified by column chromatography (SiO_2, $CHCl_3$ and $CHCl_3$/MeOH = 5/1) to afford **8** (37.1 mg, 179 μmol, 70%) as a yellow oil.

IR (neat) 2997, 2940, 2837, 2779, 1668, 1494, 1427, 1342, 1281, 1211, 1150, 1090, 1042, 964, 934, 820, 779 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.27 (d, *J* = 2.2 Hz, 1H), 6.24 (d, *J* = 2.3 Hz, 1H), 3.784 (s, 3H), 3.778 (s, 3H), 3.48 (s, 2H), 2.89 (t, *J* = 5.9 Hz, 1H), 2.67 (t, *J* = 5.9 Hz, 1H), 2.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 156.9, 135.8, 116.2, 104.0, 96.0, 55.4, 55.3, 52.6, 52.5, 46.3, 29.9; **HR MS** (FAB^+; NBA) Calcd for $C_{12}H_{17}NO_2$: 207.1254 $[M]^+$. Found: 207.1257.

6. Isotope-labeling and control experiments

Procedures for the control isotope-labeling experiments in Scheme 3

Scheme 3a



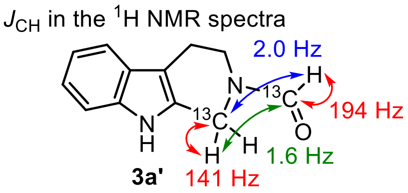
Catalyst **1** (3.0 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A $^{13}CO_2$ balloon (1 atm, 0.3 L) was attached to the flask, and the flask was quickly evacuated and filled with $^{13}CO_2$. PhSiH$_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H$_2$O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH$_3$ aq., and the product was extracted with CHCl$_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na$_2$SO$_4$, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO$_2$, EtOAc/CHCl$_3$ = 1/3 then MeOH/ CHCl$_3$ = 1/10) and GPC (CHCl$_3$/Et$_3$N = 19/1) to afford **3a'** (9.1 mg, 45 μmol, 18%) as a coloreless powder and **4a'** (3.3 mg, 18 μmol, 7%) as a coloreless powder.

3a': **mp** 178–180 °C; **IR** (KBr) 3271, 2970, 2931, 2876, 1620, 1429, 1394, 1207, 1161, 1045, 988, 813, 745, 682 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.31 (dd, *J* = 2.0, 193.0 Hz, 0.2H), 8.26 (dd, *J* = 4.1, 194.0 Hz, 0.8H), 8.13 (br s, 0.8H), 7.98 (br s, 0.2H), 7.49 (d, *J* = 8.4 Hz, 0.2H), 7.47 (d, *J* = 8.0 Hz, 0.8H), 7.36–7.32 (m, 1H), 7.22–7.08 (m, 2H), 4.80–4.76 (m, 0.2H), 4.75 (d, *J* = 140.7 Hz, 1.6H), 4.45–4.41 (m, 0.2H), 3.96–3.90 (m, 0.4H), 3.78–3.72 (m, 1.6H), 2.89 (t, *J* = 5.4 Hz, 1.6H), 2.85 (*J* = 5.9 Hz, 0.4H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 162.2, 161.7 (d, *J* = 4.7 Hz), 136.4 (d, *J* = 2.9 Hz), 136.3 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 53.3 Hz), 128.7 (d, *J* = 54.4 Hz), 126.9, 126.8, 122.3, 122.1, 119.9, 119.7, 118.3, 118.0, 111.2, 111.1, 109.4, 108.0, 44.3 (d, *J* = 4.2 Hz), 43.9 (d, *J* = 4.9 Hz), 38.7, 22.3, 20.9; **HR MS** (EI$^+$) Calcd for $^{12}C_{12}{}^{13}C_2H_{12}N_2O$: 202.1011 [M]$^+$. Found: 202.1016.

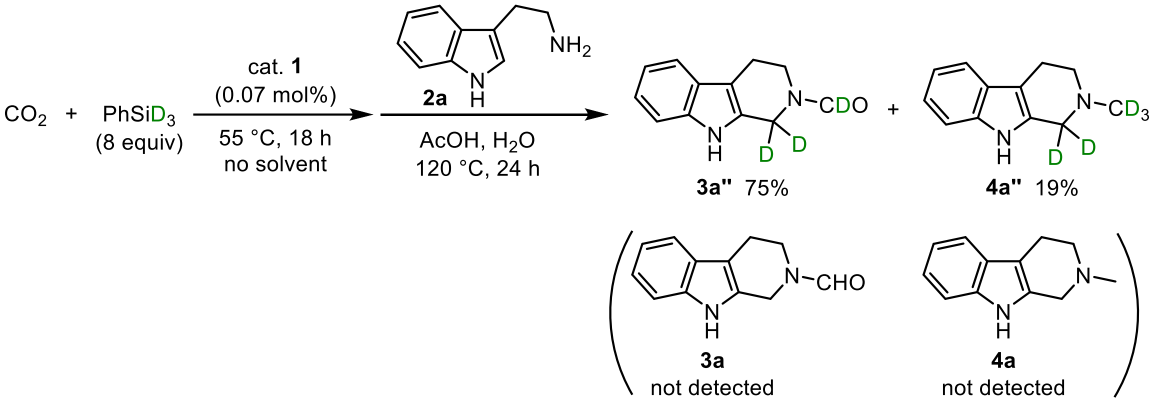
4a': **mp** 206–209 °C; **IR** (KBr) 3055, 2932, 2841, 2783, 1722, 1624, 1454, 1372, 1247, 1163, 1053, 962, 791, 733 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.77 (br s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.14 (td, *J* = 1.3, 7.5 Hz, 1H), 7.09 (td, *J* = 1.2, 7.3 Hz, 1H), 3.65 (d, *J* = 134.1 Hz, 2H), 2.90–2.80 (m, 4H), 2.54 (dd, *J* = 5.7, 133.6 Hz, 3H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 136.2 (d, *J* = 2.3 Hz), 131.6 (dd, *J* =

4.4, 51.9 Hz), 127.3 (d, J = 1.8 Hz), 121.5, 119.4, 118.1, 110.9, 118.1, 53.1, 52.4, 45.7, 21.5 (d, J = 4.1 Hz); **HR MS** (EI$^+$) Calcd for $^{12}C_{12}{}^{13}C_2H_{14}N_2$: 188.1219 [M]$^+$. Found: 188.1223.

^{13}C-labeled **3a'** and **4a'** were confirmed by NMR and MS analyses; for example, in the ^{13}C NMR spectra, extremely strong signals were detected at 162.2 and 38.7 ppm (161.7 and 43.9 ppm for the minor conformer) for **3a'** and at 52.4 and 45.7 ppm for **4a'**, and reasonable ^{13}C–H coupling constants (J_{CH}) were observed in the ^{1}H NMR spectra.



Scheme 3b



Catalyst **1** (3.0 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO$_2$ balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO$_2$. PhSiD$_3$ (253 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H$_2$O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH$_3$ aq., and the product was extracted with CHCl$_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na$_2$SO$_4$, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO$_2$, EtOAc/CHCl$_3$ = 1/3 then MeOH/ CHCl$_3$ = 1/10) and GPC (CHCl$_3$) to afford **3a''** (38.1 mg, 187 μmol, 75%) as a coloreless powder and **4a''** (9.1 mg, 47.6 μmol, 19%) as a coloreless powder.

3a'': **mp** 176–178 °C; **IR** (KBr) 3383, 3057, 2931, 2887, 1705, 1653, 1450, 1420, 1252, 1198, 1049, 1013, 968, 893, 854, 756 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$, an equilibrium mixture of two conformers (4:1 (0.8:0.2)) δ 8.01 (br s, 0.8H), 7.89 (s, br s, 0.2H), 7.50 (d, J = 7.8 Hz, 0.2H), 7.48 (d, J = 7.8 Hz, 0.8H), 7.34 (d, J = 8.0 Hz, 1H), 7.22−7.09 (m, 2H), 3.92 (t, J = 5.9 Hz, 0.4H), 3.75 (t, J = 5.8 Hz, 1.6H), 2.90 (t, J

= 5.8 Hz, 1.6H), 2.85 (t, *J* = 5.9 Hz, 0.4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.0 (t, *J* = 30.4 Hz), 161.5 (t, *J* = 30.8 Hz), 136.43, 136.35, 128.72, 128.69, 126.9, 126.8, 122.2, 122.0, 119.8, 119.7, 118.3, 118.0, 111.2, 111.1, 109.3, 107.9, 44.2, 44.0−42.8 (m), 38.5, 38.1 (quin, *J* = 21.3 Hz), 22.3, 20.8; **HR MS** (EI$^+$) Calcd for $C_{12}H_9D_3N_2O$: 203.1132 [M]$^+$. Found: 203.1137.

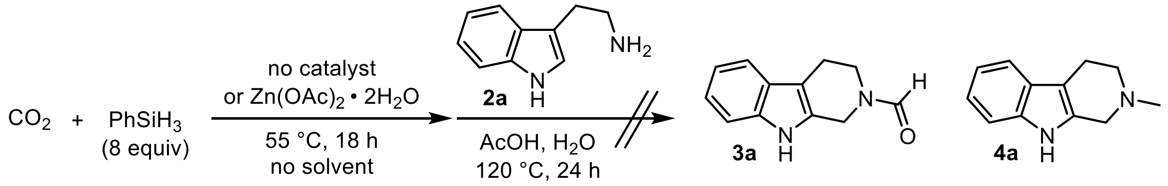
4a'': **mp** 194–197 °C; **IR** (KBr) 3057, 2922, 2851, 2793, 2176, 2048, 1719, 1622, 1452, 1362, 1298, 1265, 1184, 1155, 1070, 937, 733 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 2.89−2.78 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.2, 131.8, 127.3, 121.4, 119.4, 118.1, 110.9, 108.2, 53.0, 51.5 (quin, *J* = 20.0 Hz), 44.8 (septet, *J* = 20.3 Hz), 21.6; **HR MS** (EI$^+$) Calcd for $C_{12}H_9D_5N_2$: 191.1465 [M]$^+$. Found: 191.1470.

D-labeled **3a''** and **4a''** were confirmed by NMR and MS analyses. For the characterization by the ^{1}H NMR spectra, the signals at 8.3 and 4.7 ppm in the spectrum of **3a''** and the signals at 3.6 and 2.5 ppm in the spectrum of **4a''** were not observed. In addition, the reasonable ^{13}C–D couplings ($^1J_{CD}$ = 20–31 Hz) were detected in the ^{13}C NMR spectra.

J_{CD} in the ^{13}C NMR spectra

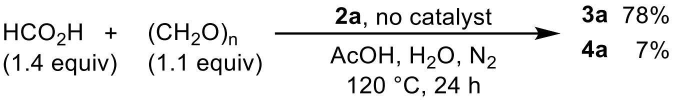
3a'' **4a''**

Scheme 3c



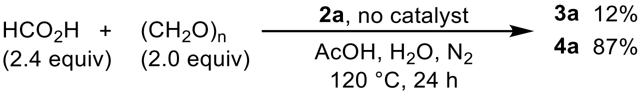
$Zn(OAc)_2{\cdot}2H_2O$ (0 or 1.5 mg (6.8 μmol, 0.35 mol%)) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The ^{1}H NMR spectra were measured, and neither **3a** nor **4a** was detected.

Scheme 3d



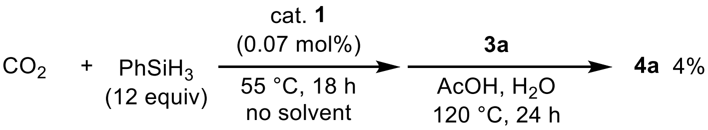
Paraformaldehyde (8.26 mg, 275 μmol) and **2a** (40.1 mg, 250 μmol) were put in a dry Schlenk flask (30 mL). Formic acid (13.3 μL, 350 μmol), H_2O (100 μL), and AcOH (200 μL) were added via syringes, and the reaction mixture was stirred at 120 °C for 24 h under N_2 atmosphere. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The yields of **3a** (78%) and **4a** (7%) were determined by ^1H NMR spectroscopy using styrene as an internal standard.

Scheme 3e



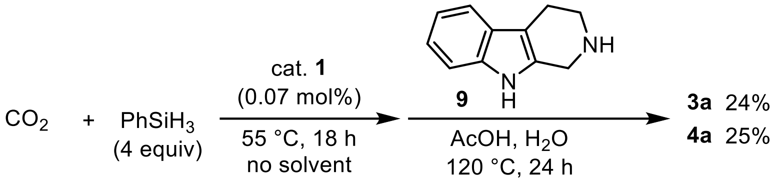
Paraformaldehyde (15.1 mg, 500 μmol) and **2a** (40.1 mg, 250 μmol) were put in a dry Schlenk flask (30 mL). Formic acid (22.8 μL, 600 μmol), H_2O (100 μL), and AcOH (200 μL) were added via syringes, and the reaction mixture was stirred at 120 °C for 24 h under N_2 atmosphere. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed with brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The yields of **3a** (12%) and **4a** (87%) were determined by ^1H NMR spectroscopy using styrene as an internal standard.

Scheme 3f



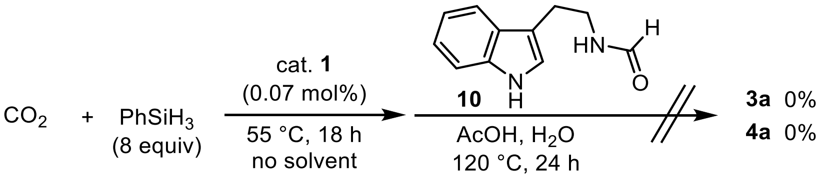
Catalyst **1** (4.63 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (396 μL, 3.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **3a** (50.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The yield of **4a** (4%) was determined by ^1H NMR spectroscopy using styrene as an internal standard after passing through a column (SiO_2, $CHCl_3$/MeOH = 10/1).

Scheme 3g



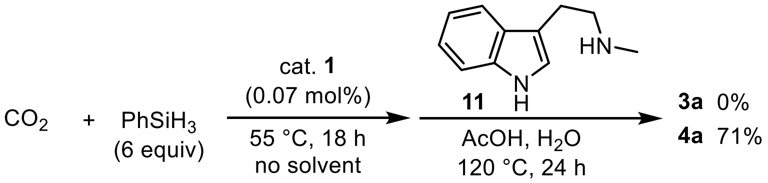
Catalyst **1** (1.54 mg, 0.70 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (123 μL, 1.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **9** (43.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The yields of **3a** (24%) and **4a** (25%) were determined by ^1H NMR spectroscopy using styrene as an internal standard.

Scheme 3h



Catalyst **1** (3.1 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **10** (47.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The ^1H NMR spectrum was measured, and neither **3a** nor **4a** was detected.

Scheme 3i



Catalyst **1** (2.35 mg, 1.07 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (185 μL, 1.50 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **11** (43.6 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The yields of **3a** (0%) and **4a** (71%) were determined by ^1H NMR spectroscopy using styrene as an internal standard.

7. CO_2 reduction with $PhSiH_3$

Procedure for the CO_2 reduction (Fig. S6)

Catalyst **1** (0.07 mol% based on $PhSiH_3$) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (2.00 or 3.00 mmol) was added via a syringe at 55 °C, and the mixture was stirred for 18 h. After addition of mesitylene (35 μL, 0.25 mmol) as an internal standard, the proton-coupled ^{13}C NMR spectra (151 MHz, benzene-d_6) of soluble substances of the mixtures were measured, and silyl formates, bis(silyl)acetals, and methoxysilanes were detected.

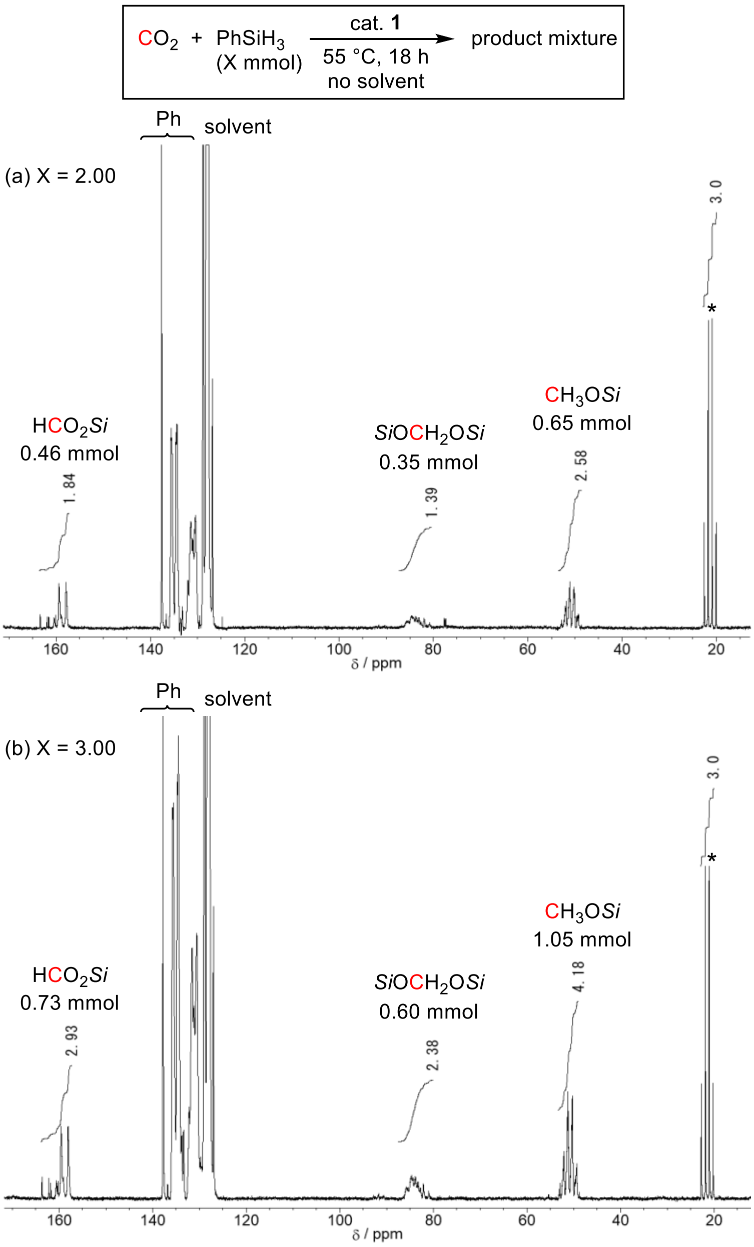
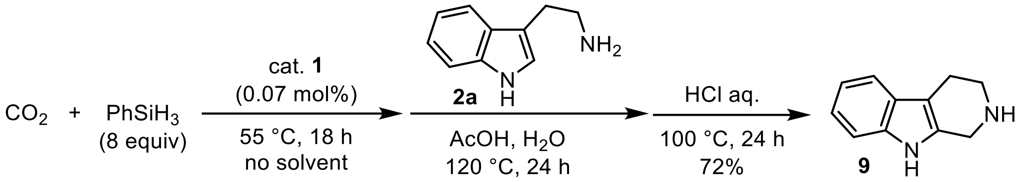


Fig. S6 Proton-coupled ^{13}C NMR spectra (151 MHz, benzene-d_6) of product mixtures of the reduction of CO_2. *Mesitylene (internal standard).

8. One-pot three-step synthesis

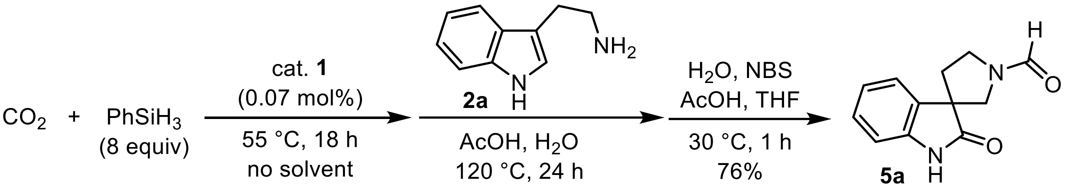
Procedure for the synthesis of tryptoline (9)



Catalyst **1** (3.1 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe, and the mixture was stirred at 55 °C for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2a** (40.2 mg, 251 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, 1 M HCl aq. (5.0 mL) was added, and the mixture was stirred at 100 °C for 24 h. After cooling to rt, the reaction was quenched with 28 wt% NH_3 aq., and the product was extracted with $CHCl_3$ (four times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH/Et_3N = 10/1/1) to afford **9** as a pale yellow powder (31.1 mg, 181 μmol, 72%). **9** was characterized according to the data of an authentic sample.

Mp 204–207 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.15 (td, *J* = 1.3, 7.4 Hz, 1H), 7.10 (td, *J* = 1.2, 7.4 Hz, 1H), 4.02 (t, *J* = 1.5 Hz, 2H), 3.20 (t, *J* = 5.7 Hz, 2H), 2.76 (tt, *J* = 1.6, 5.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.7, 133.0, 127.7, 121.6, 119.5, 118.0, 110.8, 108.8, 44.0, 43.4, 22.7.

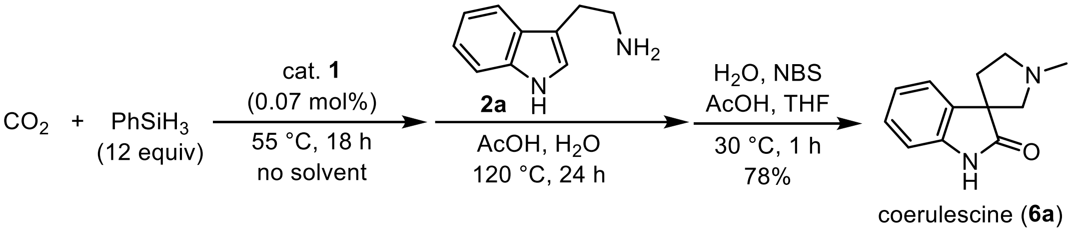
Procedure for the synthesis of 5a



Catalyst **1** (3.1 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe, and the mixture was stirred at 55 °C for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, H_2O (1.0 mL), THF (2.0 mL), NBS (53.4 mg, 300 μmol), and AcOH (1.0 mL) were added, and the mixture was stirred at 30 °C for 1 h. The reaction was quenched with 10 wt% NaOH aq., and the product was extracted with EtOAc (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, EtOAc/$CHCl_3$ = 1/1) to afford **5a** as a colorless oil (40.9 mg, 189 μmol, 76%).

IR (neat) 3217, 2953, 2889, 1714, 1651, 1487, 1472, 1387, 1341, 1231, 1188, 1107, 1042, 1018, 754, 673 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (3:2 (0.6:0.4)) δ 9.06 (br s, 0.6H), 8.94 (br s, 0.4H), 8.38 (s, 0.4H), 8.31 (s, 0.6H), 7.29–7.22 (m, 1H), 7.17 (d, *J* = 7.1 Hz, 0.4H), 7.10 (d, *J* = 6.3 Hz, 0.6H), 7.08–7.02 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 0.6H), 6.96 (d, *J* = 8.4 Hz, 0.4H), 4.07 (dt, *J* = 7.3, 10.3 Hz, 0.4H), 3.88–3.80 (m 3H), 3.72 (d, *J* = 12.4 Hz, 0.6H), 3.70 (d, *J* = 10.6 Hz, 0.4H), 2.57–2.40 (m, 1H), 2.24–2.12 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.6, 179.1, 161.2, 161.1, 140.6, 140.3, 132.1, 131.7, 128.9, 123.25, 123.17, 122.8, 122.7, 110.5, 110.4, 54.6, 52.3, 51.9, 51.6, 45.4, 43.0, 36.0, 35.1; **HR MS** (ESI^+) Calcd for $C_{12}H_{12}N_2ONa$: 239.0791 $[M + Na]^+$. Found: 239.0791.

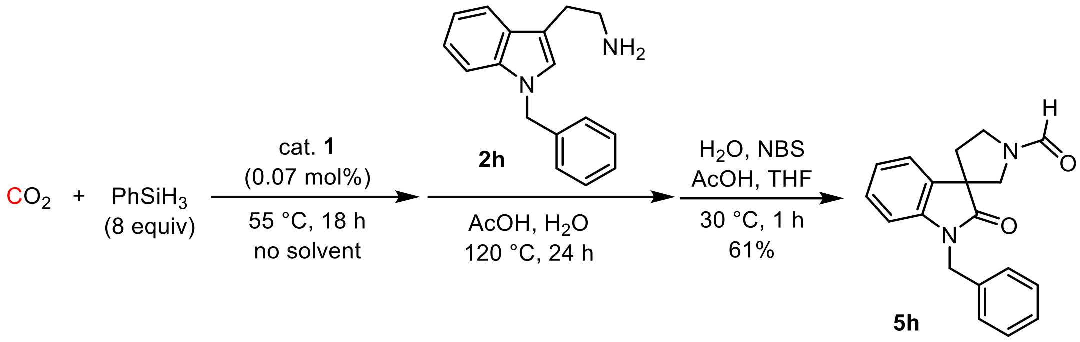
Procedure for the synthesis of coerulescine (6a)



Catalyst **1** (4.6 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe, and the mixture was stirred at 55 °C for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2a** (40.1 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, H_2O (1.0 mL), THF (2.0 mL), NBS (89.0 mg, 500 μmol), and AcOH (1.0 mL) were added, and the mixture was stirred at 30 °C for 1 h. The reaction was quenched with 10 wt% NaOH aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, EtOAc/hexane/Et_3N = 6/7/1) to afford coerulescine (**6a**) as a yellow oil (39.7 mg, 196 μmol, 78%). **6a** was characterized according to the literature.[S12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.04–2.97 (m, 1H), 2.86 (AB q, Δν = 6.4 Hz, *J* = 9.6 Hz, 2H), 2.77 (q, *J* = 8.1 Hz, 1H), 2.45 (s, 3H), 2.42 (ddd, *J* = 2.4, 7.9, 12.8 Hz, 1H), 2.09 (dt, *J* = 7.4, 12.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.6, 140.5, 136.2, 127.8, 123.3, 122.8, 109.8, 66.3, 56.8, 53.8, 41.9, 38.0.

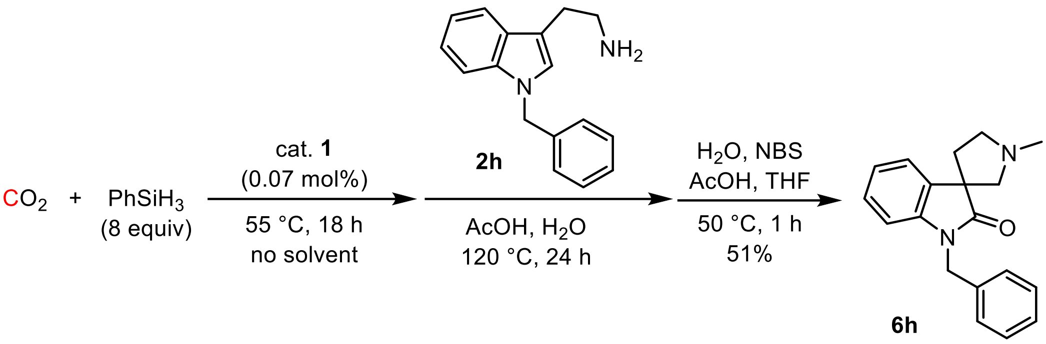
Procedure for the synthesis of 5h



Catalyst **1** (3.1 mg, 1.4 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (246 μL, 2.00 mmol) was added via a syringe, and the mixture was stirred at 55 °C for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2h** (62.6 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, H_2O (1.0 mL), THF (2.0 mL), NBS (89.2 mg, 500 μmol), and AcOH (1.0 mL) were added, and the mixture was stirred at 30 °C for 1 h. The reaction was quenched with 10 wt% NaOH aq., and the product was extracted with EtOAc (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, EtOAc/$CHCl_3$ = 1/3) and GPC ($CHCl_3$) to afford **5h** as a yellow oil (46.9 mg, 153 μmol, 61%).

IR (neat) 3061, 3030, 3007, 2949, 2878, 1715, 1668, 1489, 1468, 1423, 1379, 1217, 1174, 1107, 1078, 1030, 968, 752, 698 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, an equilibrium mixture of two conformers (6:5 (0.55:0.45)) δ 8.39 (s, 0.45H), 8.31 (s, 0.55H), 7.36–7.16 (m, 6.45H), 7.11 (d, *J* = 6.5 Hz, 0.55H), 7.05 (t, *J* = 7.4 Hz, 0.45H), 7.04 (t, *J* = 7.5 Hz, 0.55H), 6.80 (d, *J* = 7.8 Hz, 0.55H), 6.77 (d, *J* = 7.5 Hz, 0.45H), 4.94 (AB q, Δν = 18.2 Hz, *J* = 14.0 Hz, 1.1H), 4.92 (AB q, Δν = 19.2 Hz, *J* = 12.7 Hz, 0.9H), 4.12 (dt, *J* = 7.4, 10.0 Hz, 0.45 H), 3.97–3.83 (m, 2.55H), 3.76 (d, *J* = 12.4 Hz, 0.45H), 3.71 (d, *J* = 10.5 Hz, 0.55H), 2.59 (dt, *J* = 8.9, 12.9 Hz, 0.55 H), 2.47 (ddd, *J* = 5.6, 7.5, 12.9 Hz, 0.45 H), 2.28–2.12 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.2, 176.7, 161.0, 160.9, 142.3, 142.0, 135.6, 135.5, 131.8, 131.2, 128.9, 128.8, 128.7, 127.9, 127.8, 127.3, 127.2, 123.3, 123.2, 122.5, 122.4, 109.6, 109.5, 54.7, 51.9, 51.8, 51.4, 45.3, 44.1, 43.9, 42.9, 36.0, 35.3; **HR MS** (EI$^+$) Calcd for $C_{19}H_{18}N_2O_2$: 306.1363 [M]$^+$. Found: 306.1367.

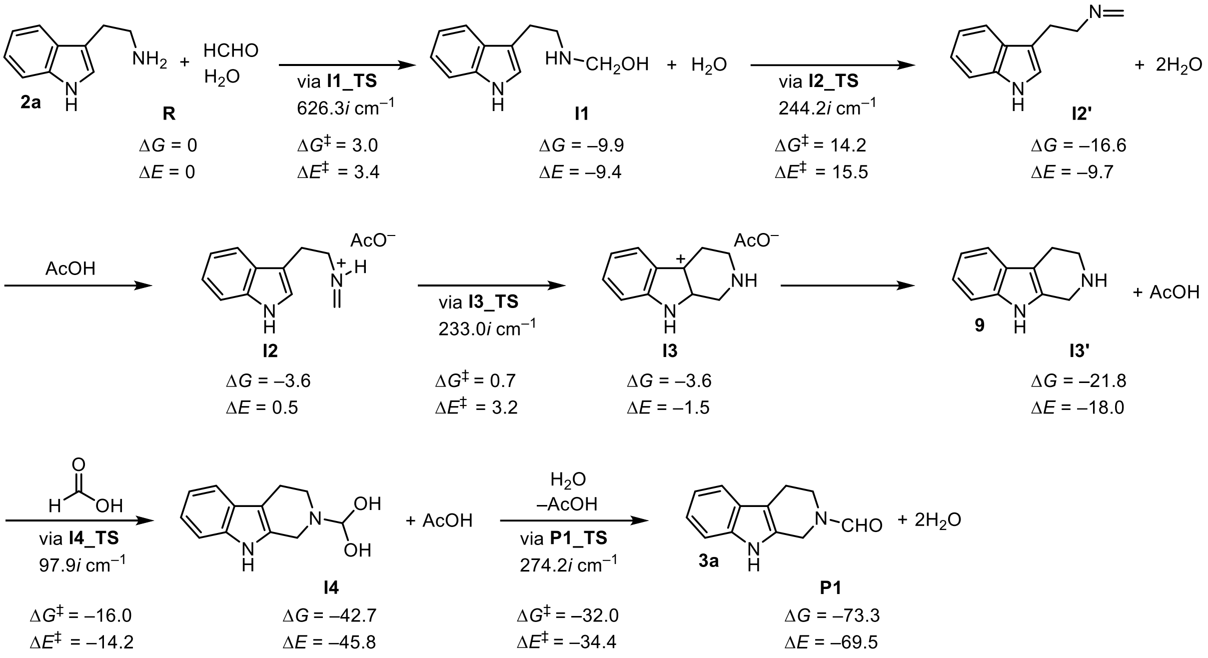
Procedure for the synthesis of 6h



Catalyst **1** (4.6 mg, 2.1 μmol) was put in a dry Schlenk flask (30 mL). A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. $PhSiH_3$ (369 μL, 3.00 mmol) was added via a syringe, and the mixture was stirred at 55 °C for 18 h. Then, H_2O (100 μL), AcOH (200 μL), and **2h** (62.6 mg, 250 μmol) were added, and the reaction mixture was stirred at 120 °C for 24 h. After cooling to rt, H_2O (1.0 mL), THF (2.0 mL), NBS (89.0 mg, 500 μmol), and AcOH (1.0 mL) were added, and the mixture was stirred at 50 °C for 1 h. The reaction was quenched with 10 wt% NaOH aq., and the product was extracted with $CHCl_3$ (three times). The organic layer was washed successively with water and brine. After dried over Na_2SO_4, the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, EtOAc/$CHCl_3$ = 1/1 then $CHCl_3$/Et_3N = 1/1) to afford **6h** as a colorless oil (37.3 mg, 128 μmol, 51%). **6h** was characterized according to the literature.[S13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 0.9, 7.4 Hz, 1H), 7.32–7.23 (m, 5H), 7.14 (td, *J* = 1.0, 7.7 Hz, 1H), 7.03 (td, *J* = 1.0, 7.6 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.91 (s, 2H), 3.13–3.09 (m, 1H), 2.95 (d, *J* = 9.3 Hz, 1H), 2.89 (d, *J* = 9.3 Hz, 1H), 2.80 (q, *J* = 8.1 Hz, 1H). 2.49 (s, 3H), 2.43 (ddd, *J* = 4.2, 8.0, 12.5 Hz, 1H), 2.15 (dt, *J* = 7.7, 12.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.4, 142.0, 136.0, 135.8, 128.8, 127.7, 127.6, 127.3, 123.2, 123.0, 108.8, 66.5, 56.9, 53.4, 43.9, 42.0, 38.2.

9. DFT calculations



Scheme S2 Reaction pathway for the synthesis of **3a**. Δ*G* and Δ*E* values are shown in kcal mol^{-1}.

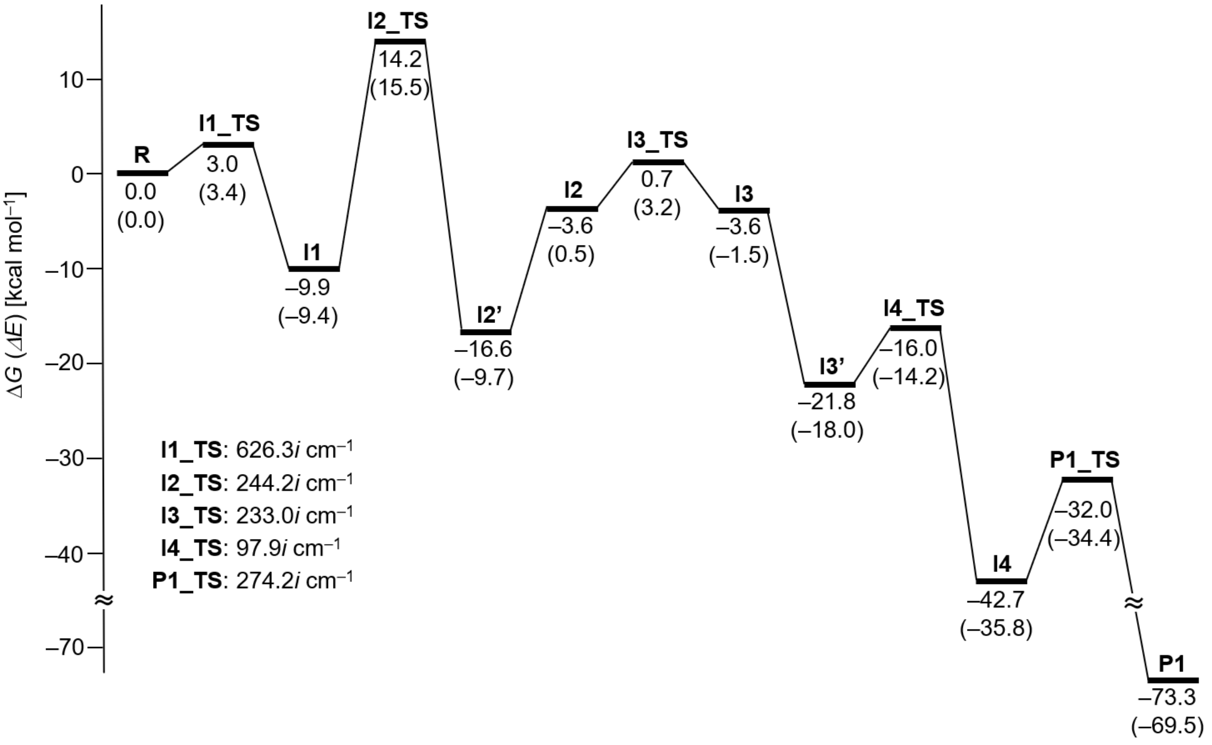


Fig. S7 Theoretical energy profile (Δ*G* at 393.15 K) for the formation of **3a**. Δ*E* values are given in parentheses.

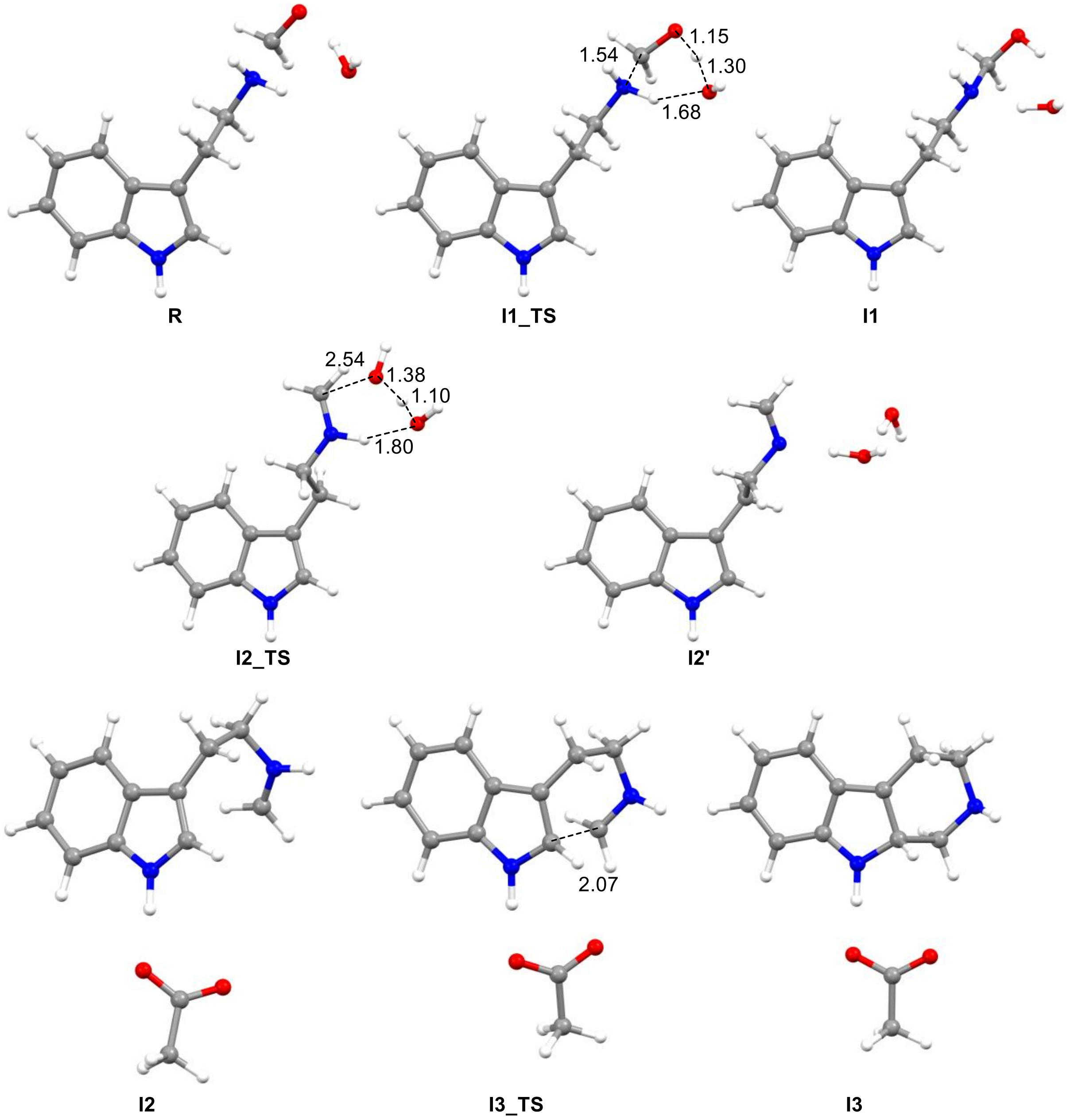


Fig. S8 Optimized transition state, reactant, and product structures in the formation of **3a**. Distances are shown in Å.

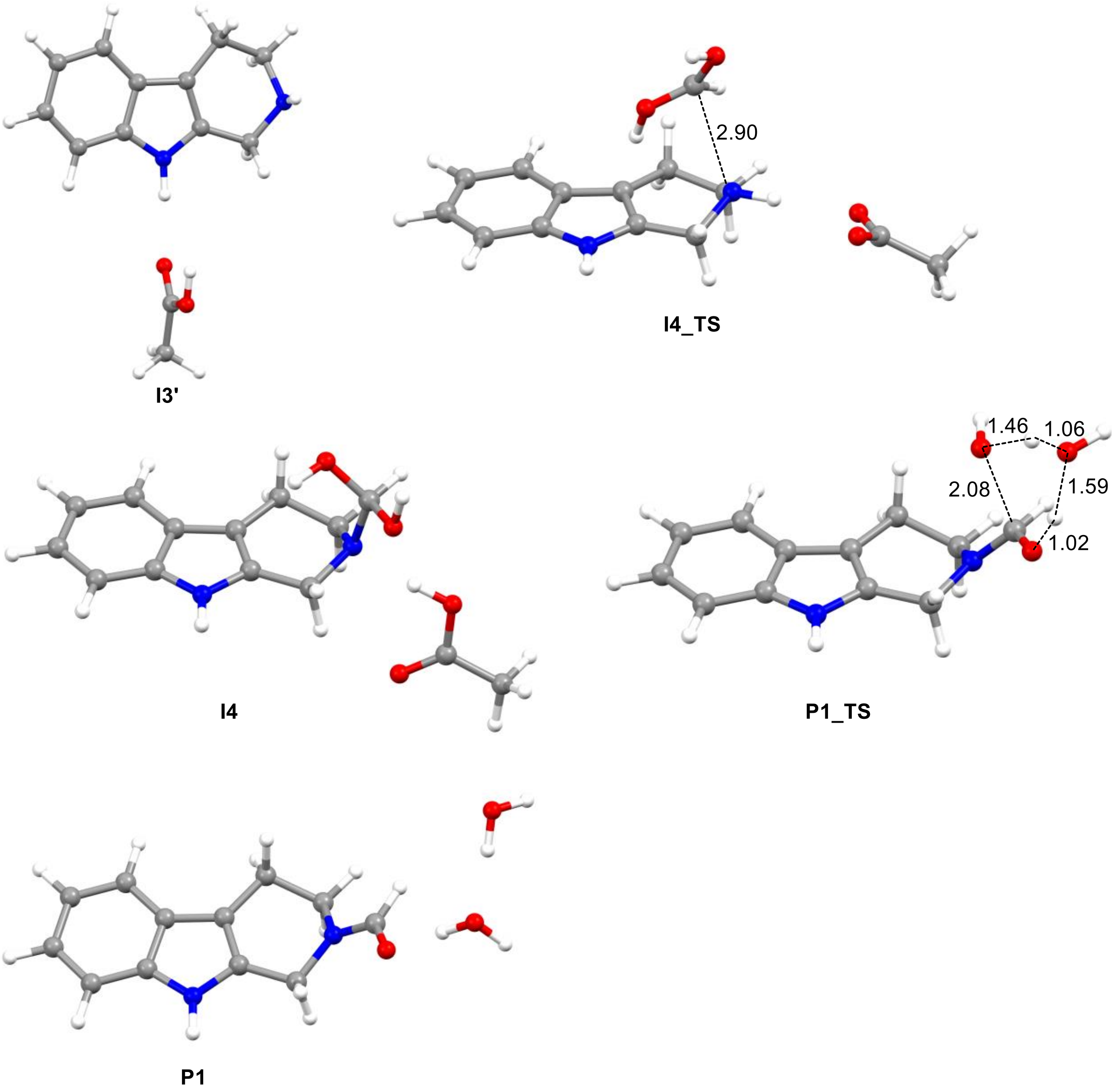
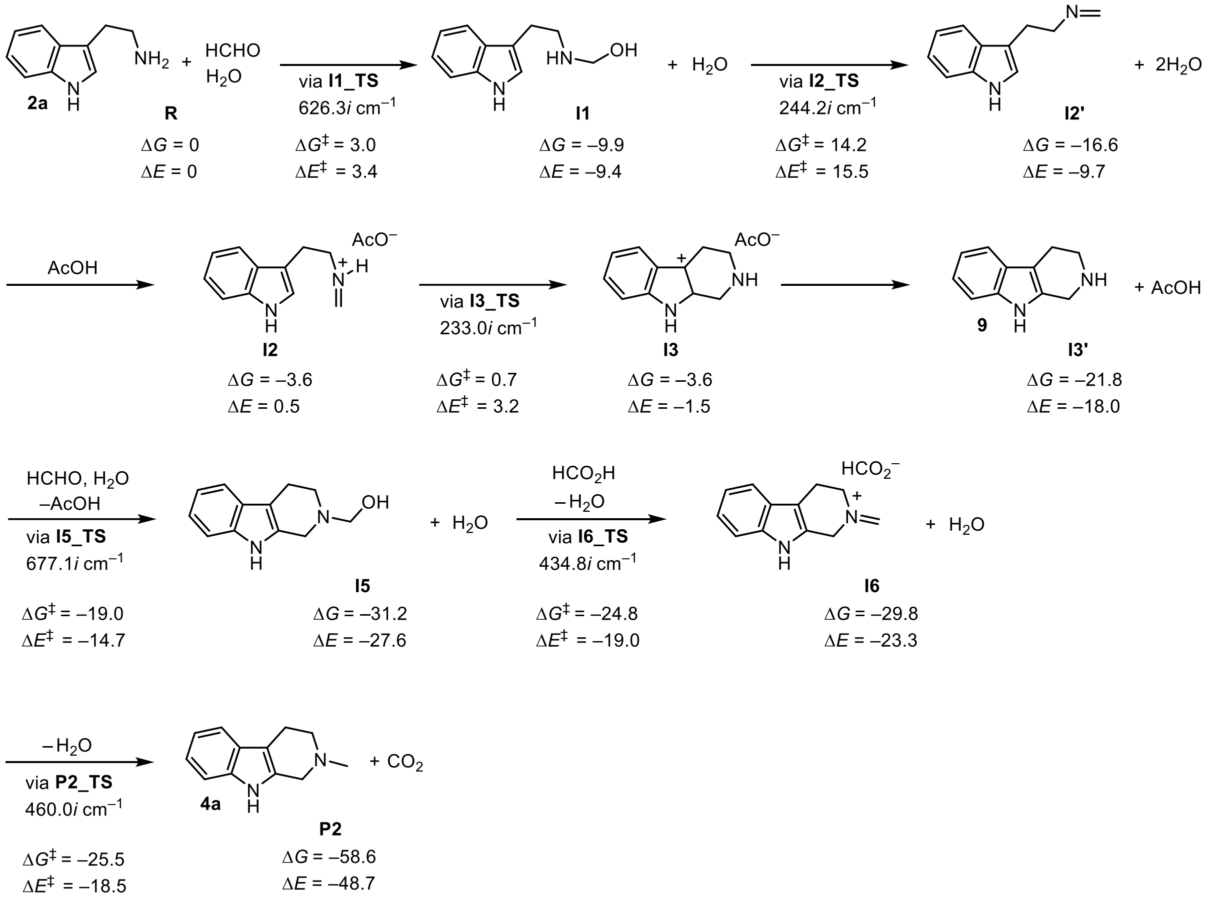


Fig. S8 Continued.

Cyclization then methylation



Scheme S3 Reaction pathway (cyclization then methylation) for the synthesis of **4a**. Δ*G* and Δ*E* values are shown in kcal mol^{-1}.

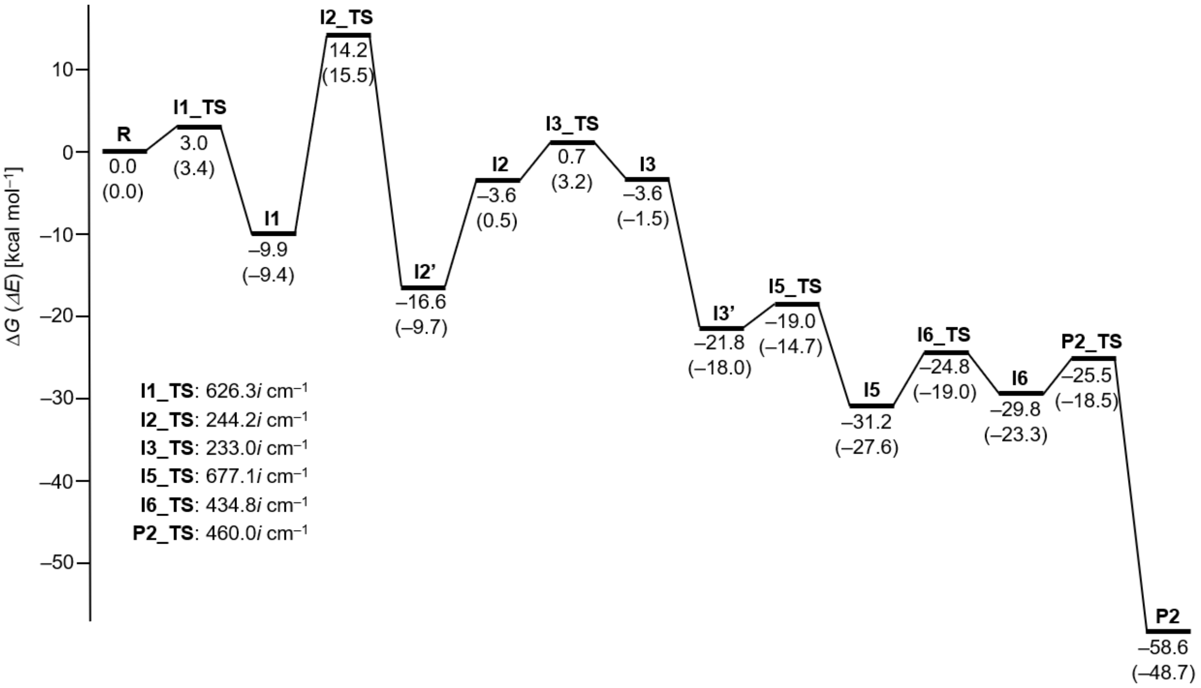


Fig. S9 Theoretical energy profile (Δ*G* at 393.15 K) for the formation of **4a** (cyclization then methylation). Δ*E* values are given in parentheses.

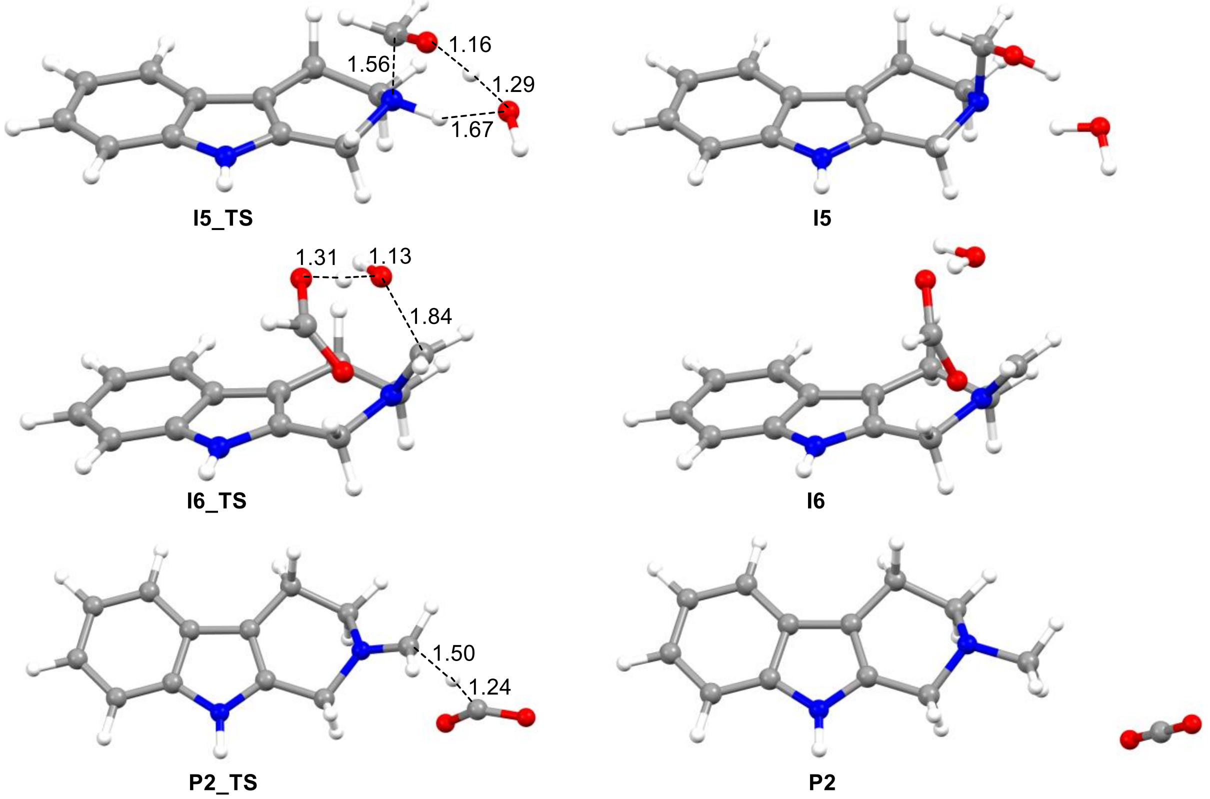
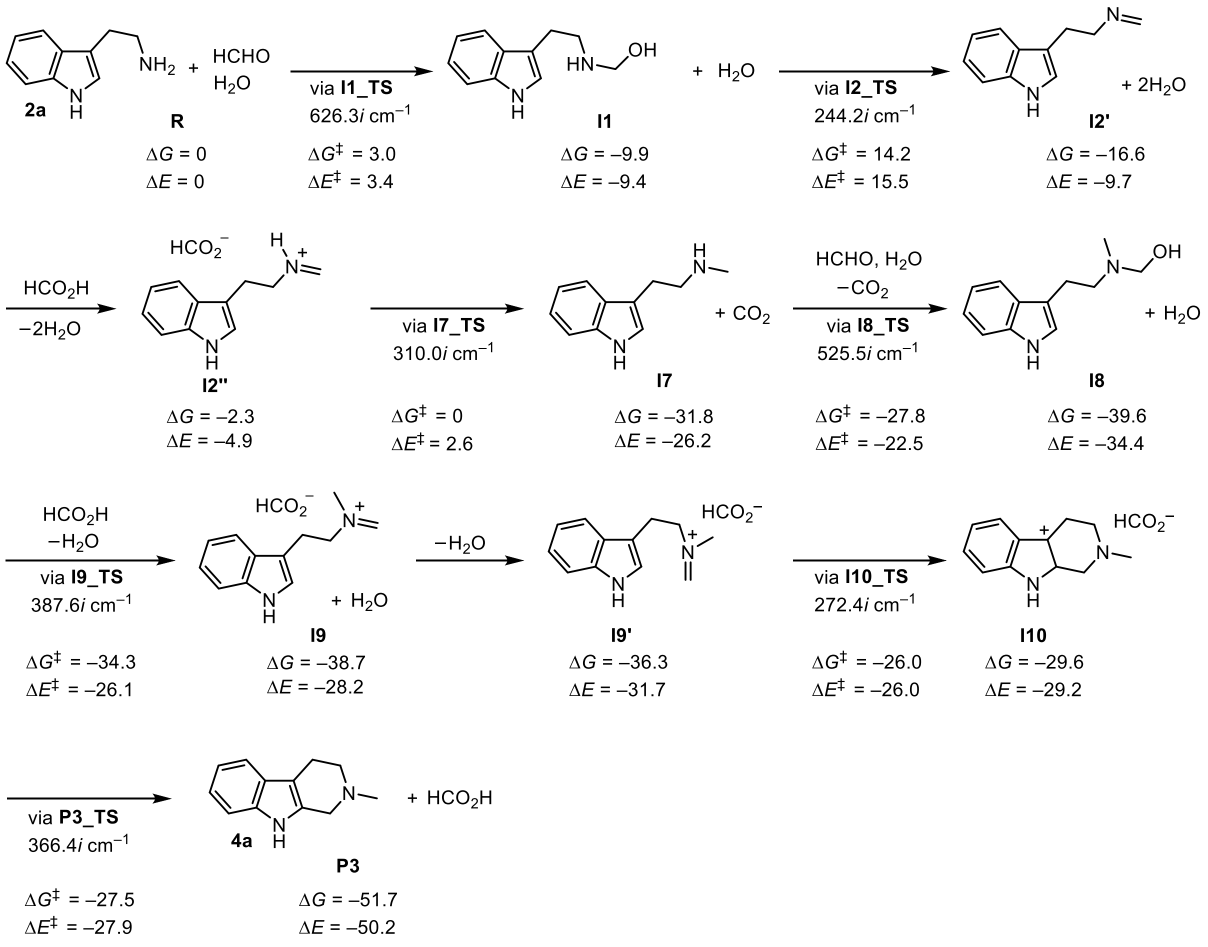


Fig. S10 Optimized transition state, reactant, and product structures in the formation of **4a** (cyclization then methylation). Distances are shown in Å.

Methylation then cyclization



Scheme S4 Reaction pathway (methylation then cyclization) for the synthesis of **4a**. ΔG and ΔE values are shown in kcal mol^{-1}.

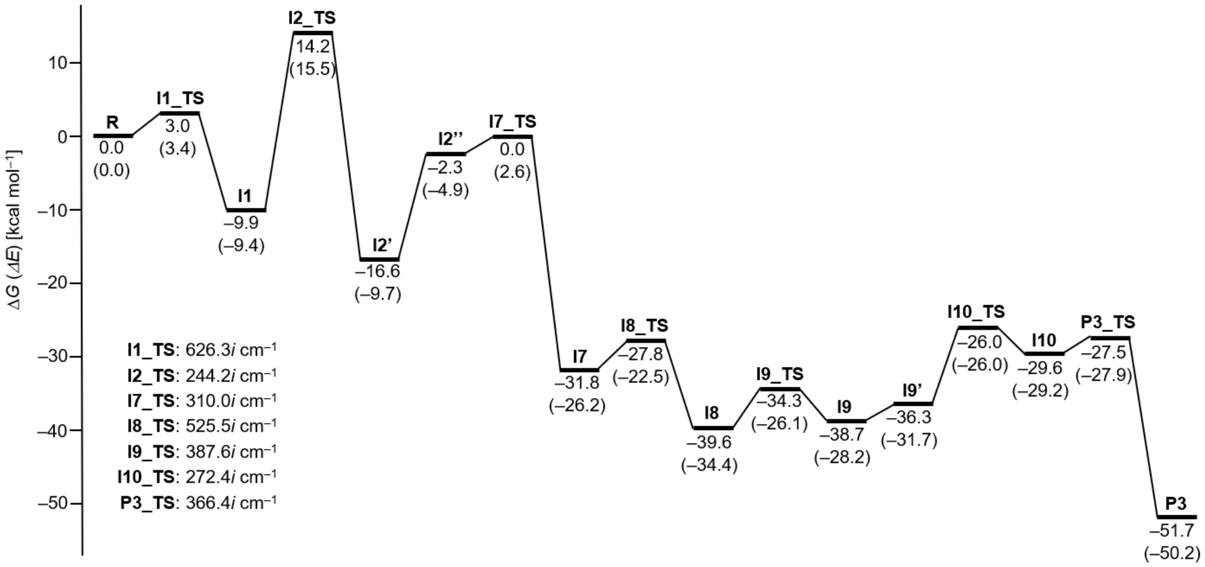


Fig. S11 Theoretical energy profile (ΔG at 393.15 K) for the formation of **4a** (methylation then cyclization). ΔE values are given in parentheses.

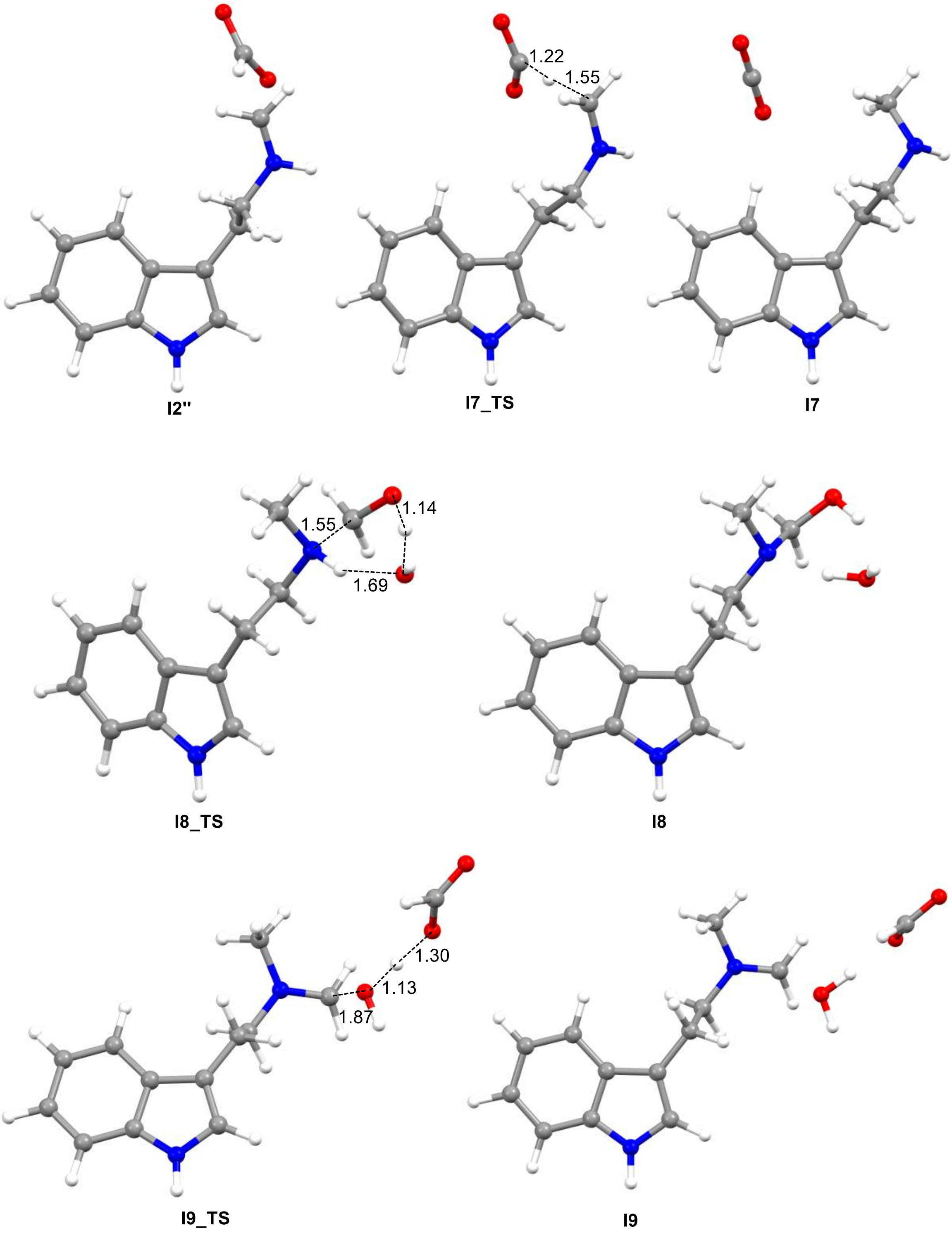
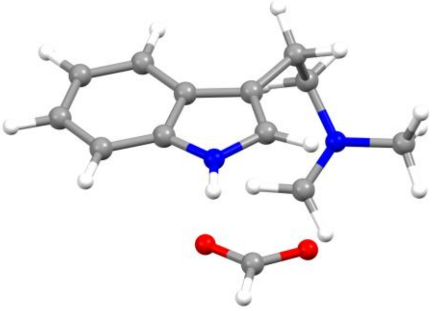
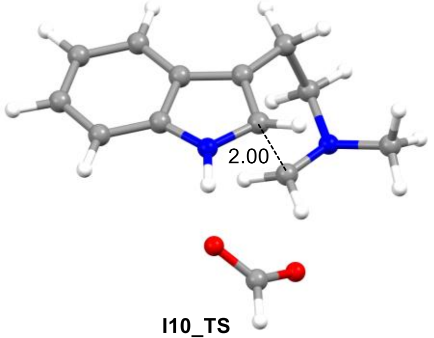


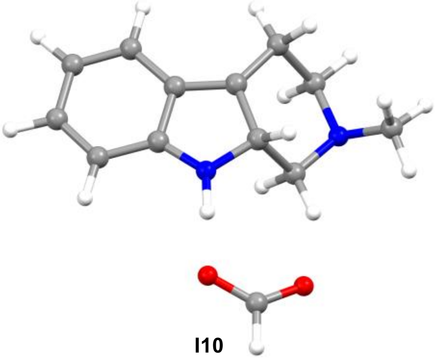
Fig. S12 Optimized transition state, reactant, and product structures in the formation of **4a** (methylation then cyclization). Distances are shown in Å.



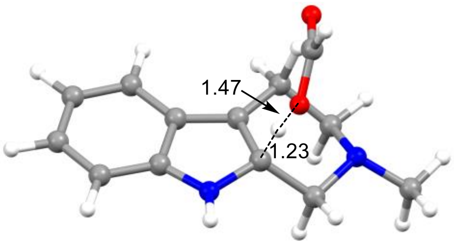
I9'



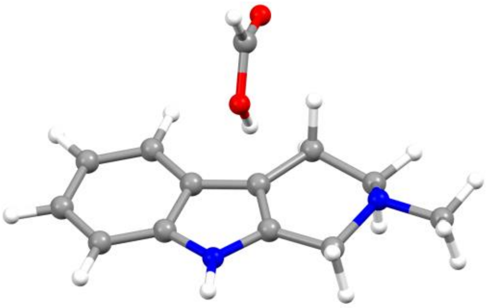
I10_TS



I10



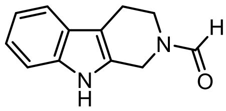
P3_TS



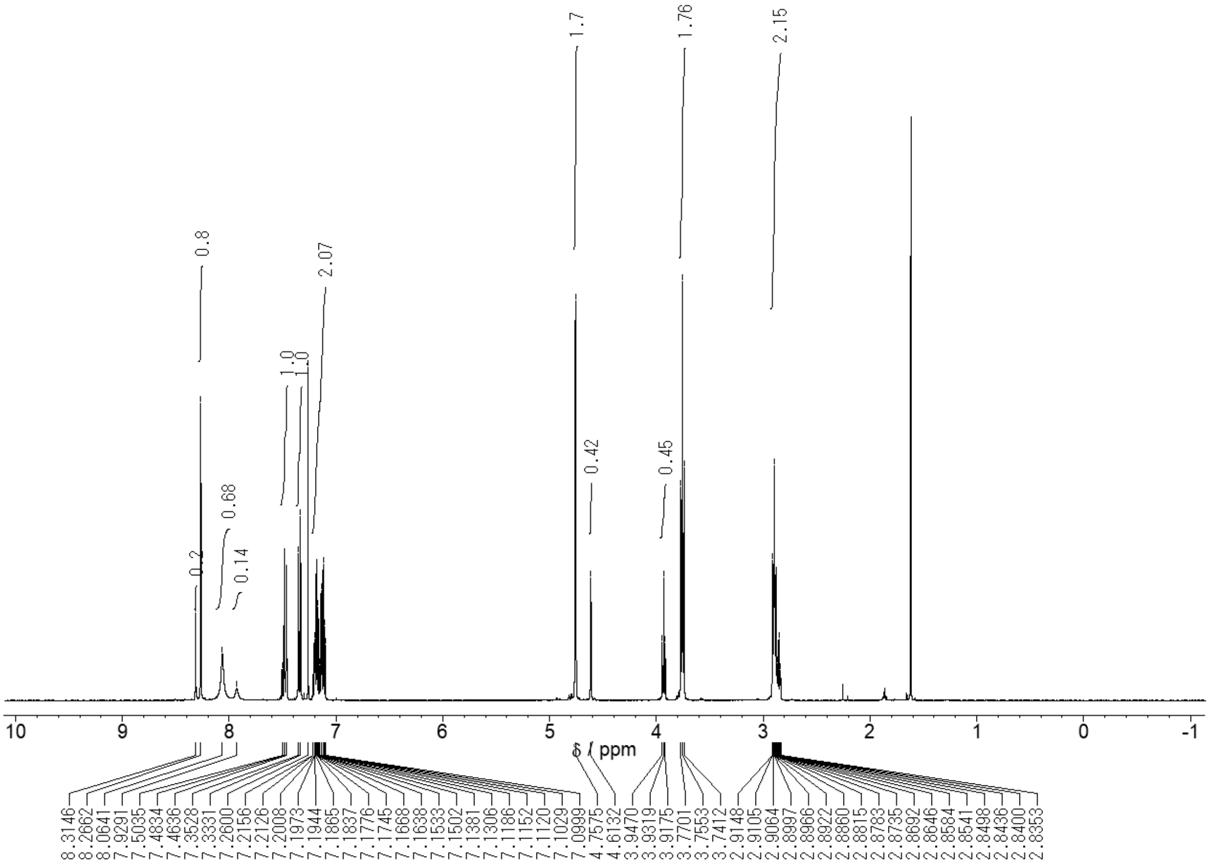
P3

Fig. S12 Continued.

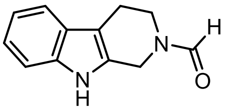
10. ^{1}H and ^{13}C NMR spectra



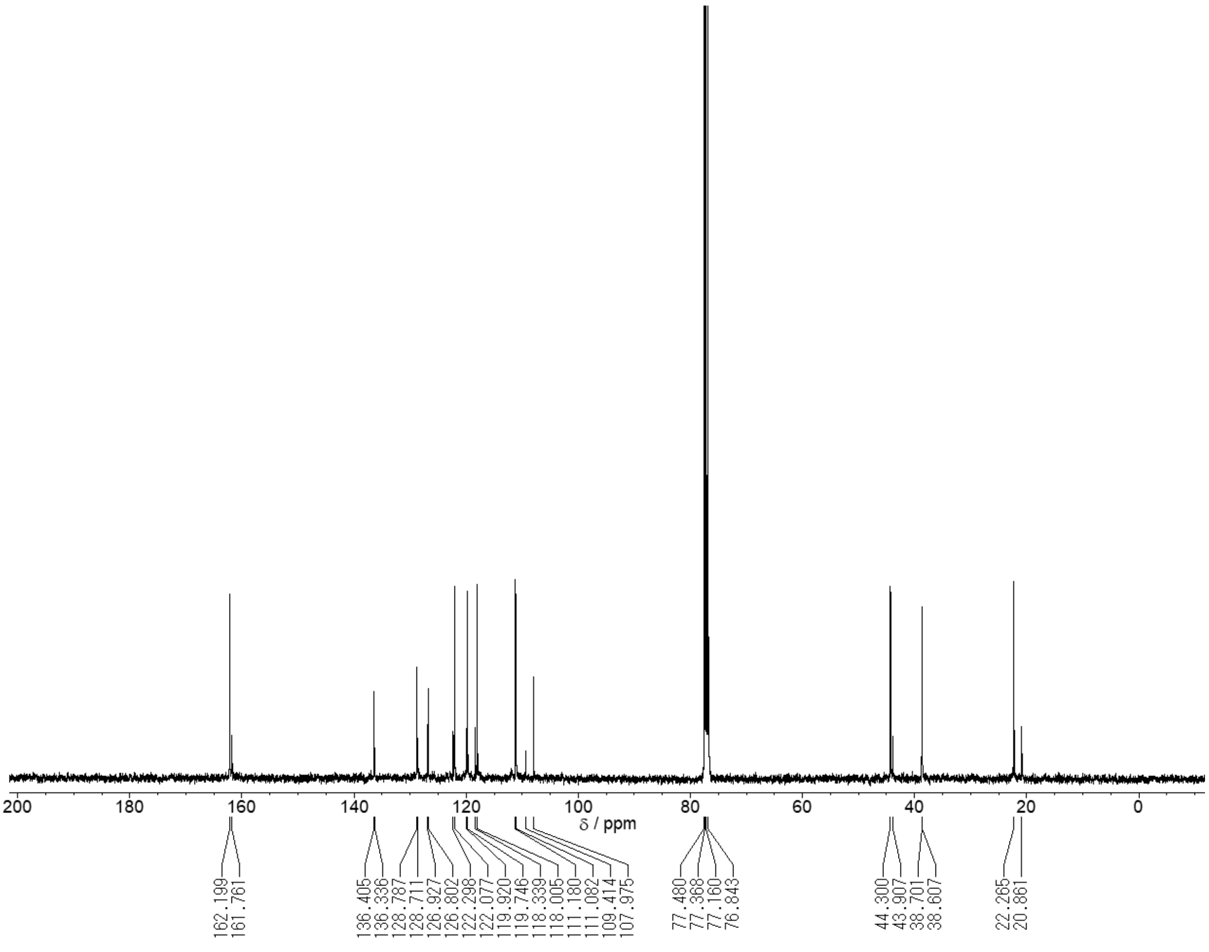
3a



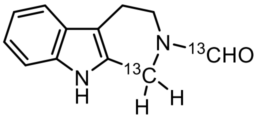
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



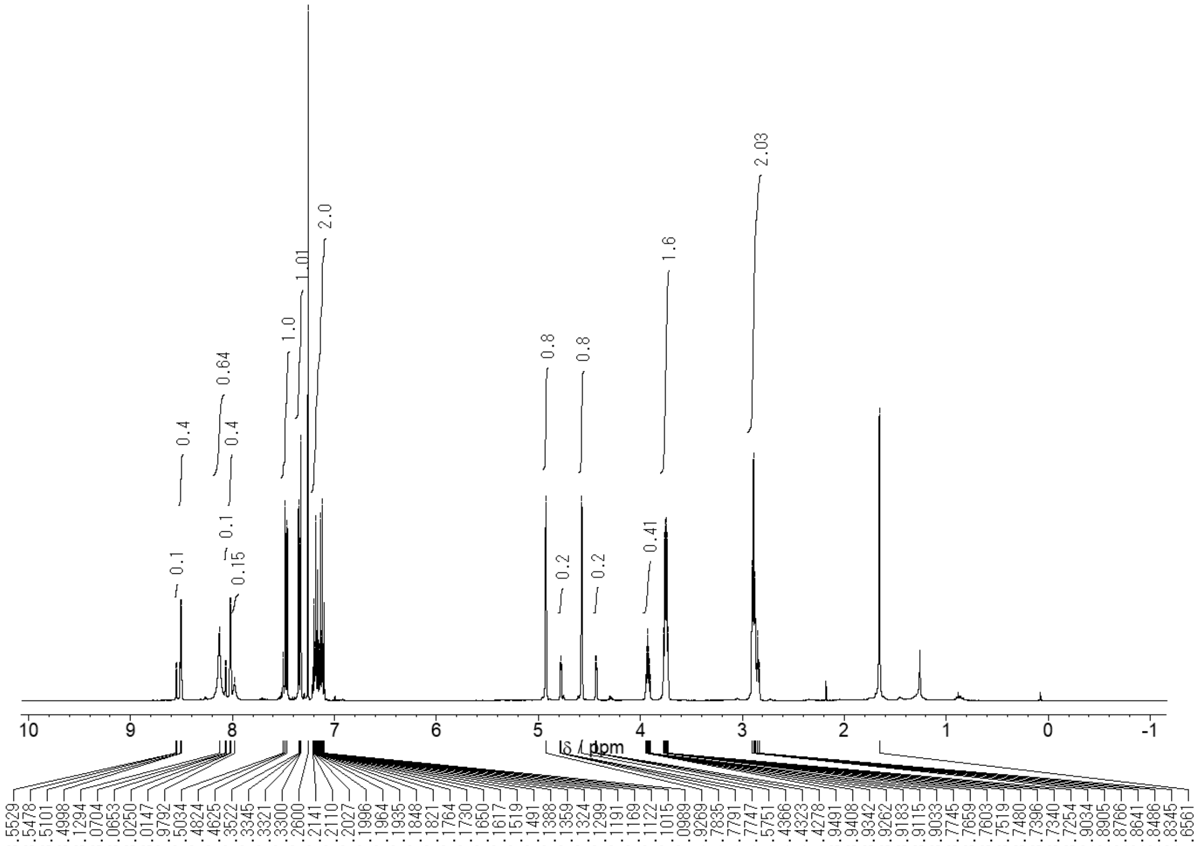
3a



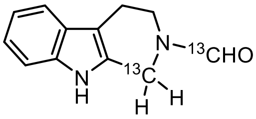
^{13}C NMR spectrum of **3a** (101 MHz, CDCl$_3$)



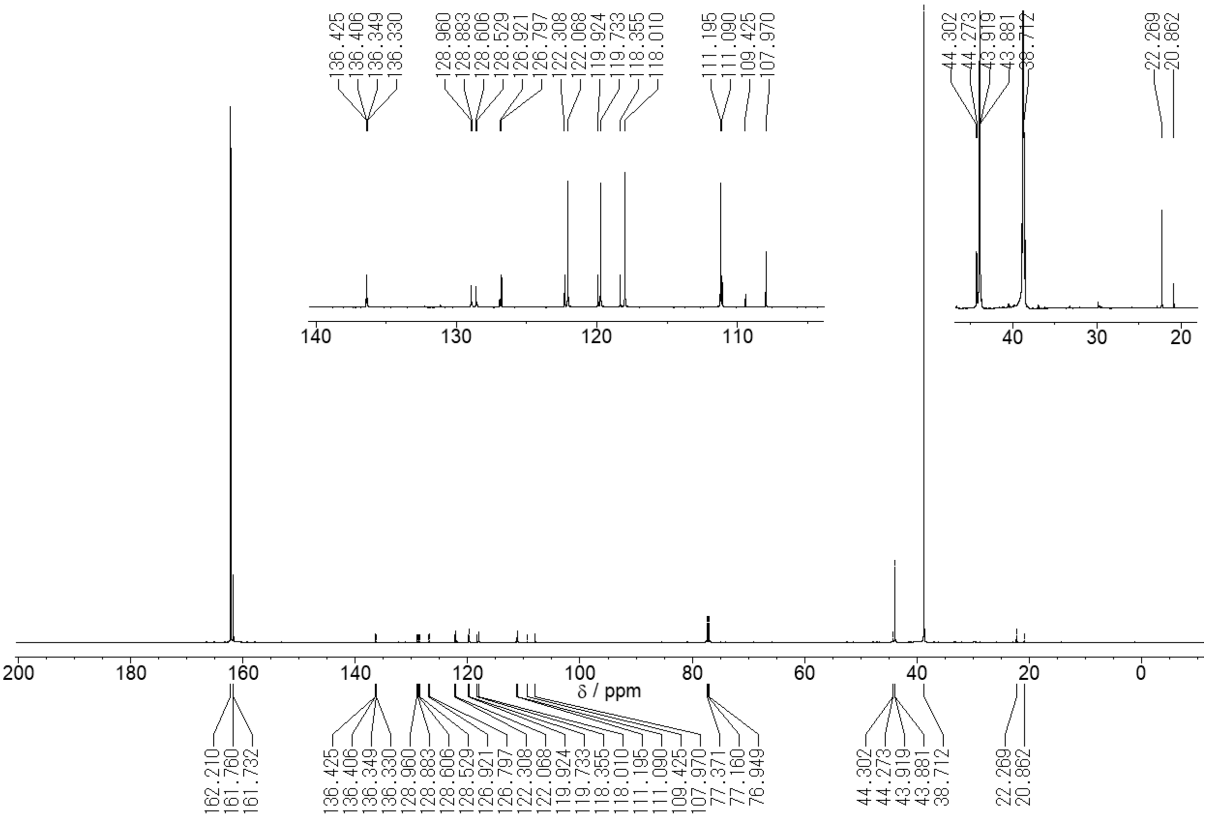
3a'



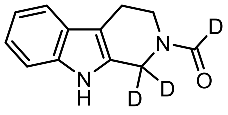
^{1}H NMR spectrum of **3a'** (400 MHz, CDCl$_3$)



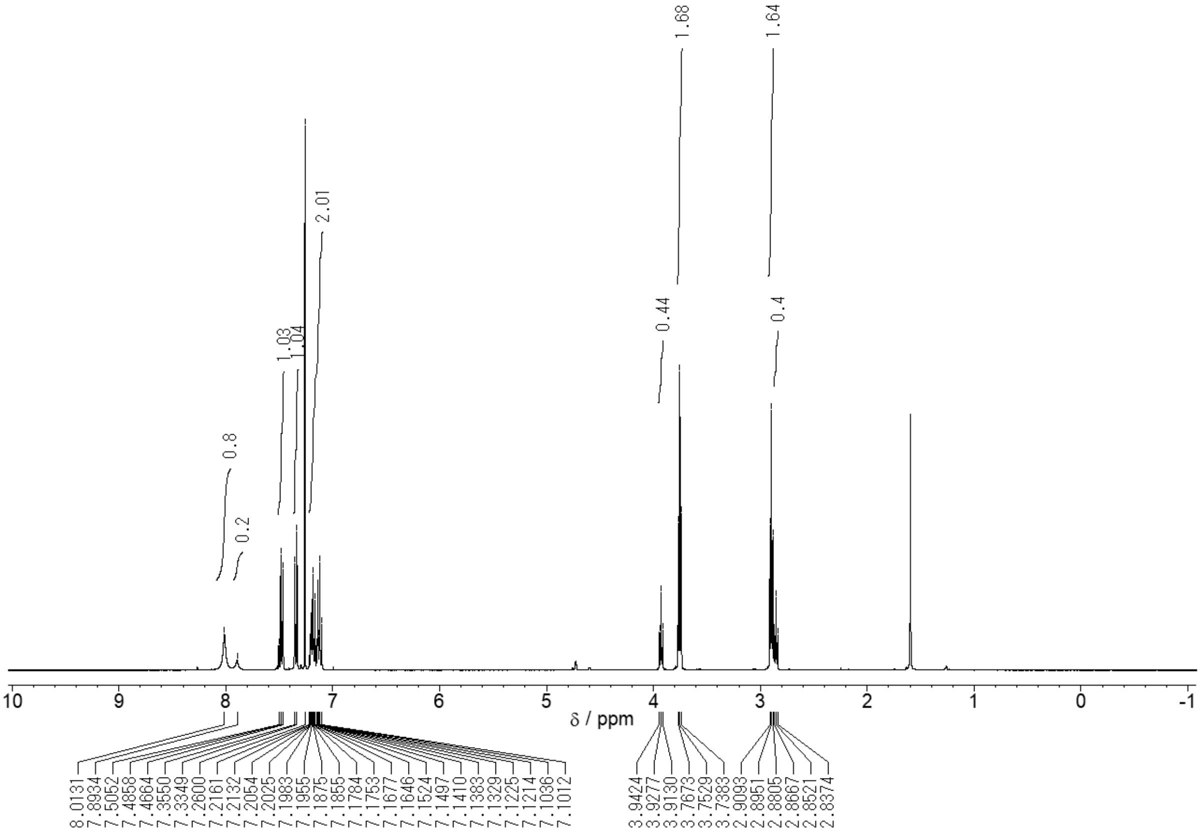
3a'



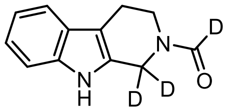
^{13}C NMR spectrum of **3a'** (151 MHz, CDCl$_3$)



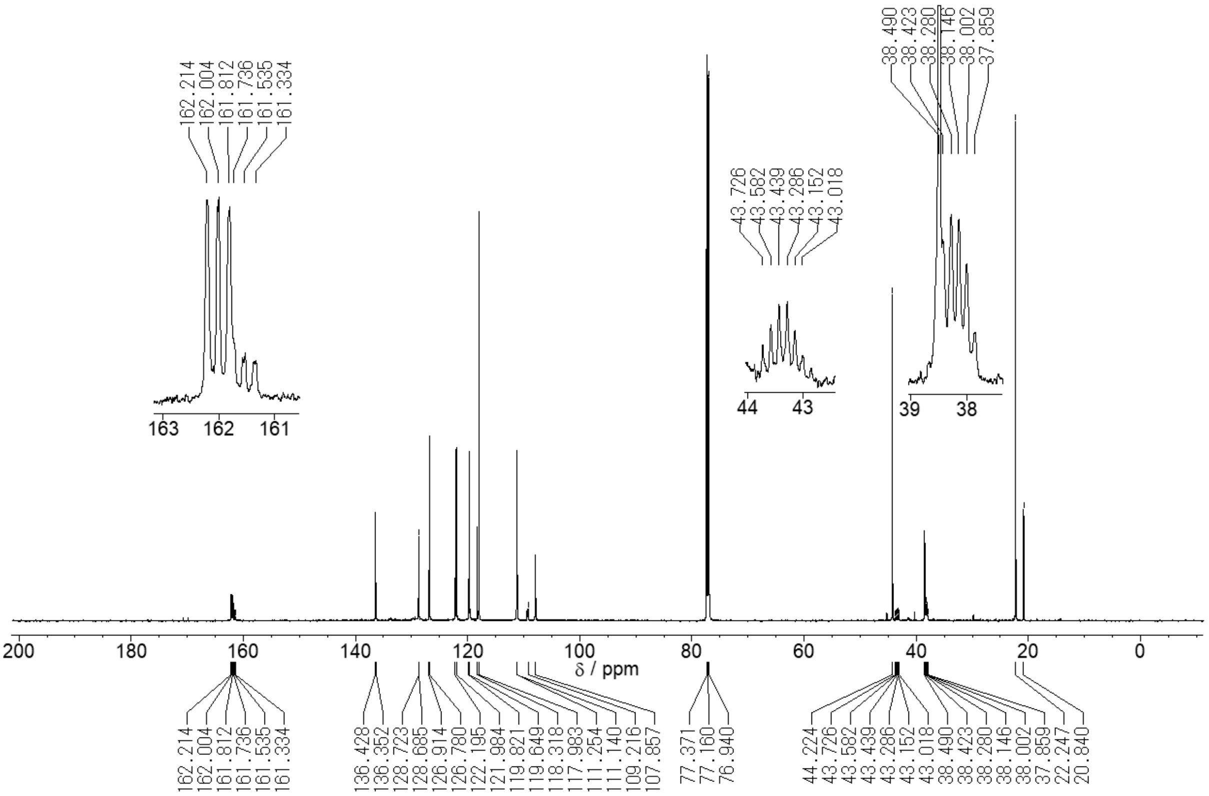
3a''



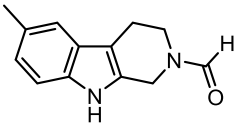
^{1}H NMR spectrum of **3a''** (400 MHz, $CDCl_3$)



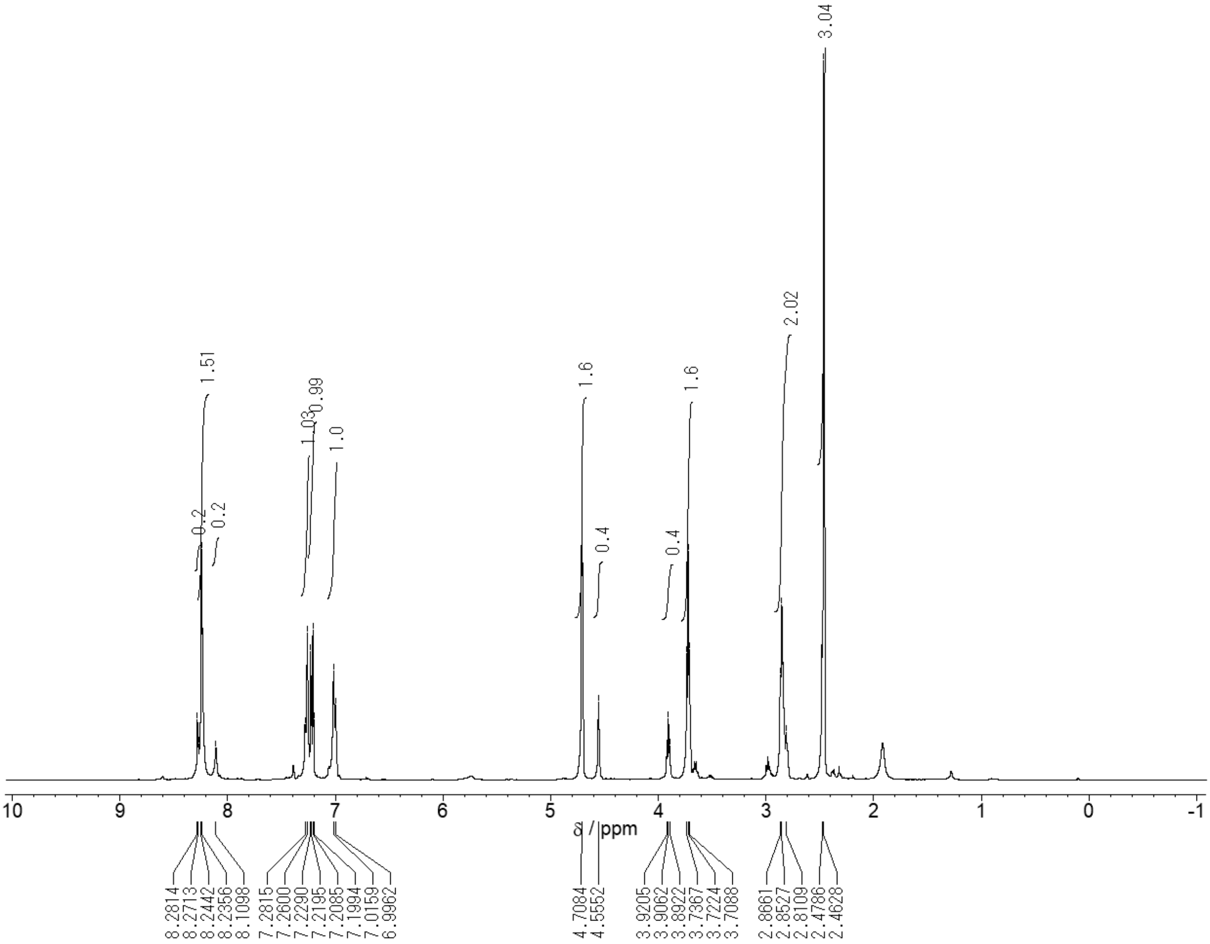
3a''



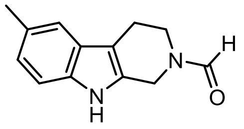
^{13}C NMR spectrum of **3a''** (151 MHz, CDCl$_3$)



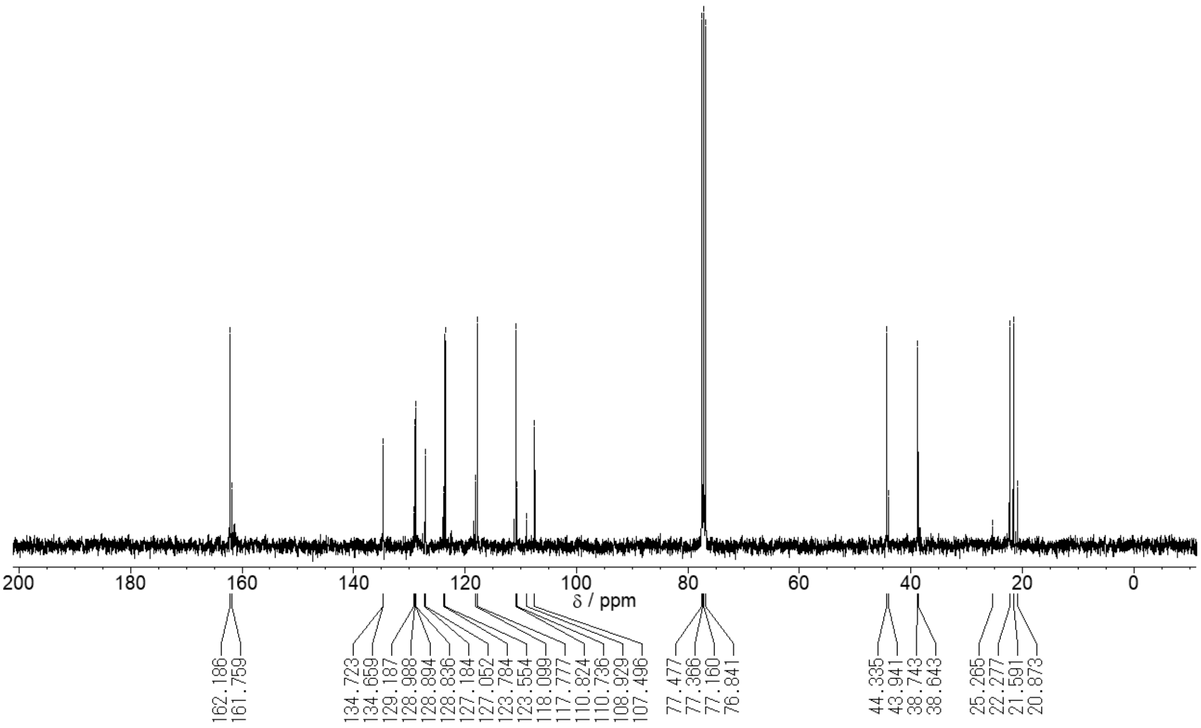
3b



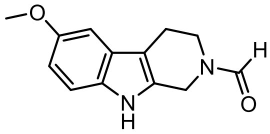
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



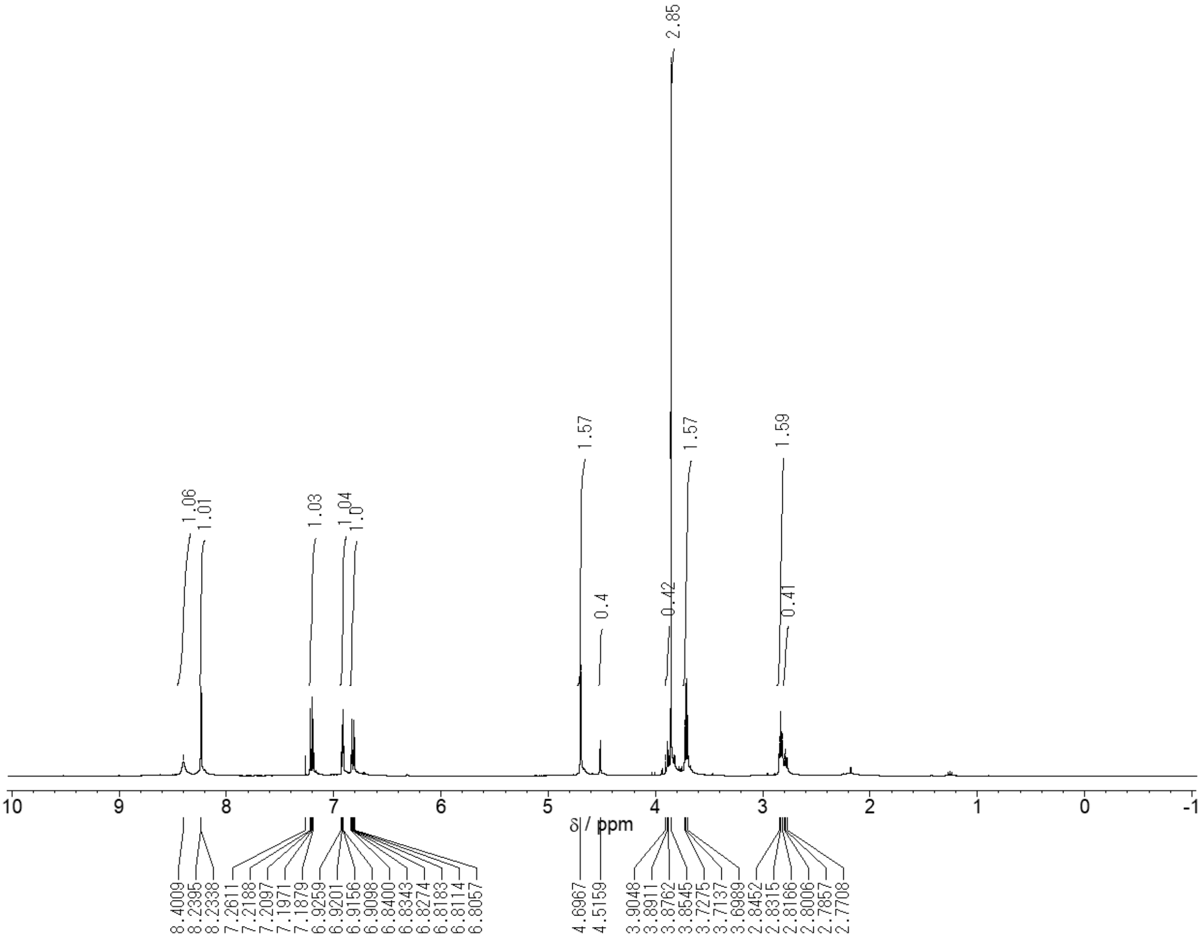
3b



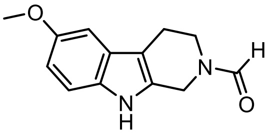
^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$)



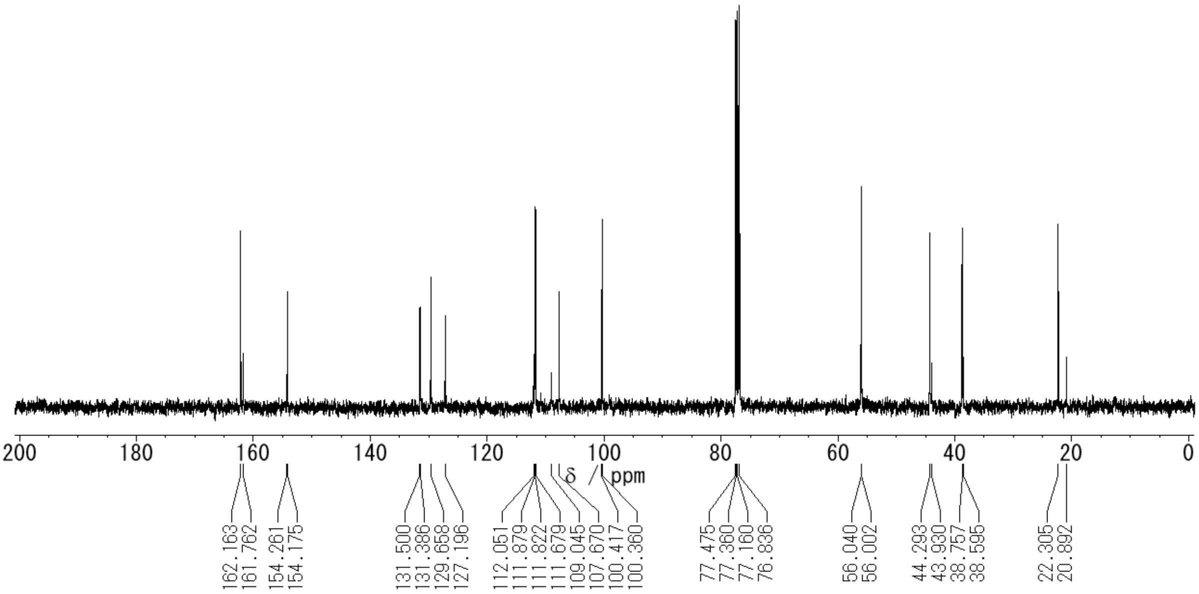
3c



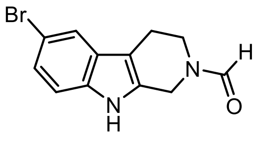
^{1}H NMR spectrum of **3c** (400 MHz, CDCl$_3$)



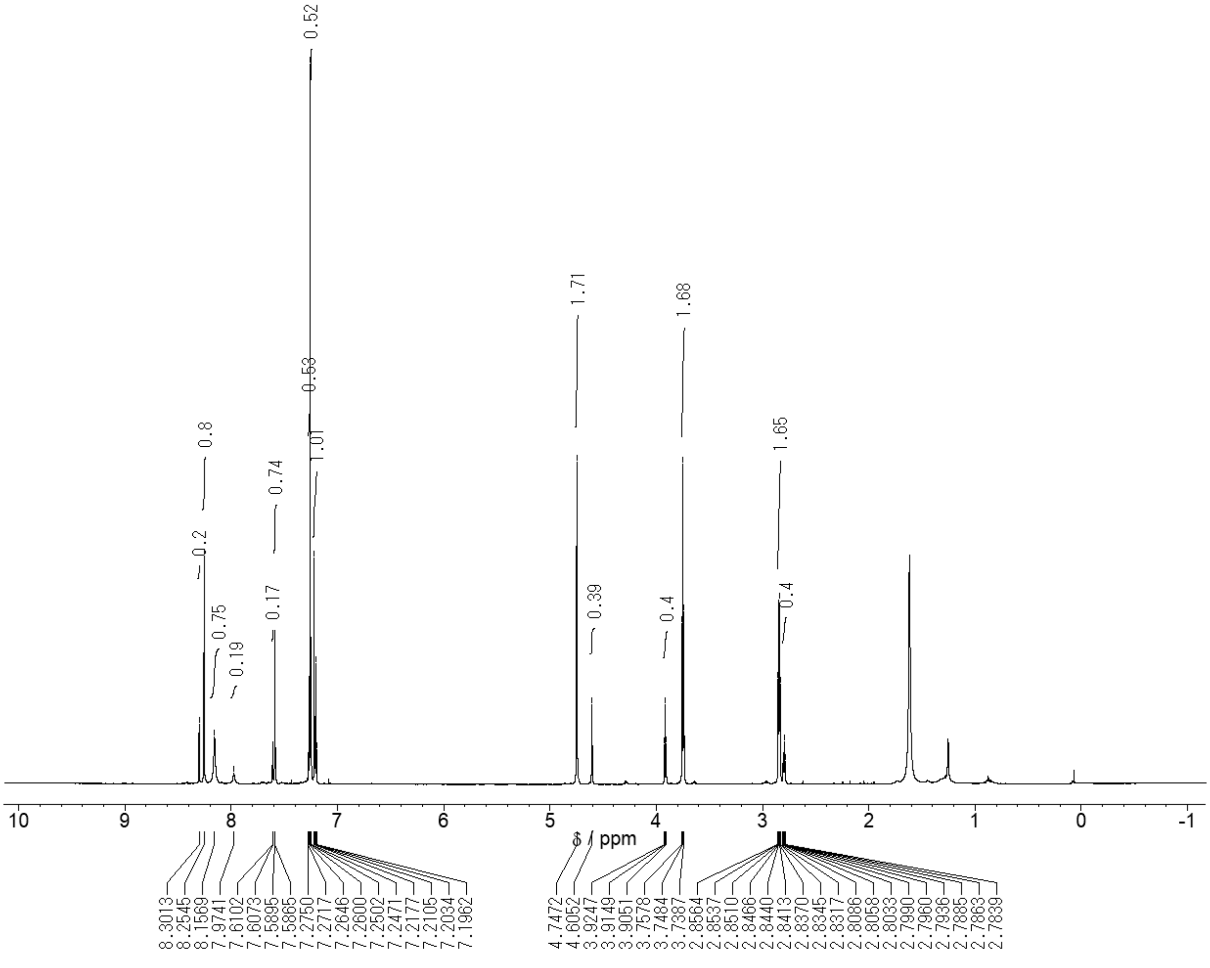
3c



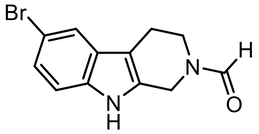
^{13}C NMR spectrum of **3c** (101 MHz, $CDCl_3$)



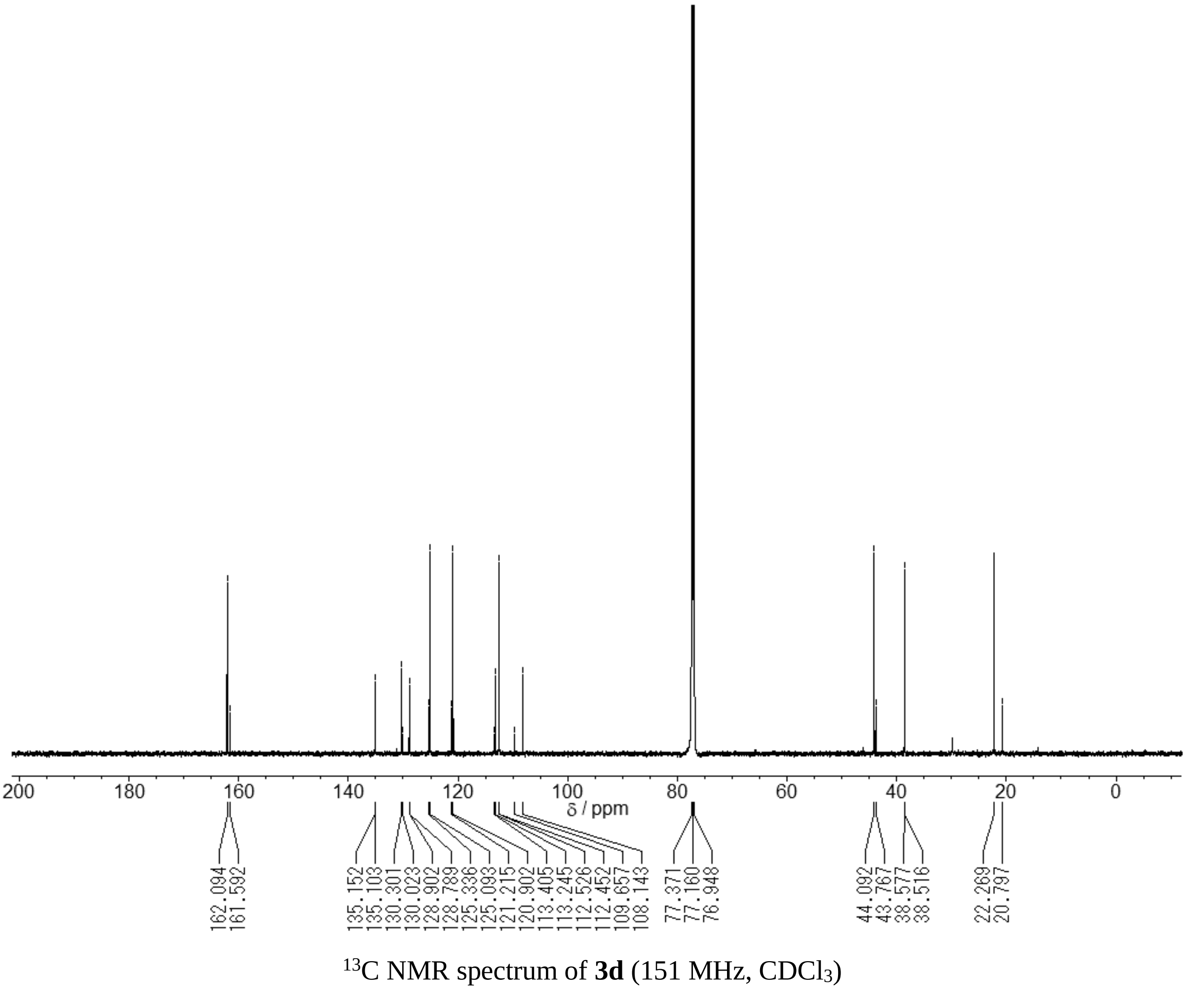
3d



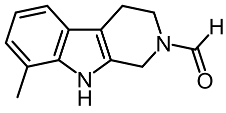
^{1}H NMR spectrum of **3d** (600 MHz, CDCl$_3$)



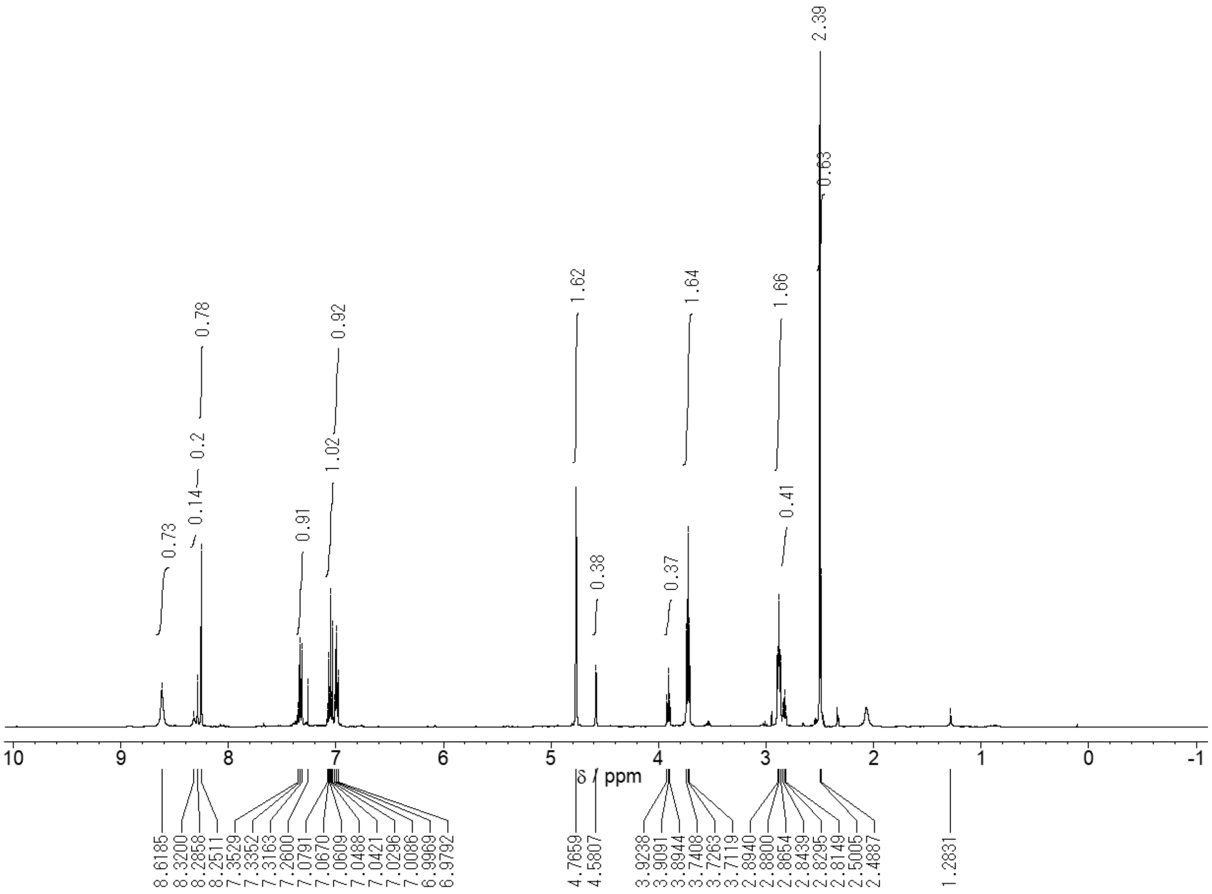
3d



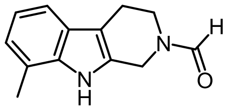
^{13}C NMR spectrum of **3d** (151 MHz, $CDCl_3$)



3e



^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



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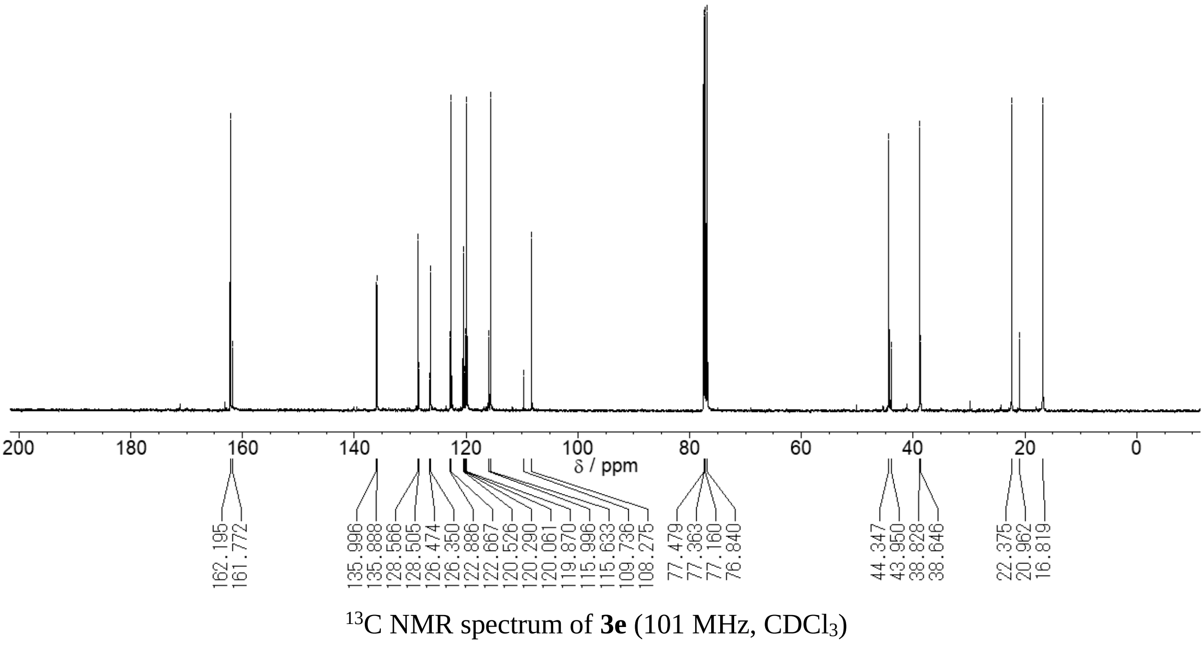
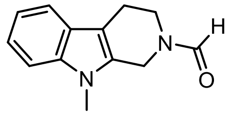
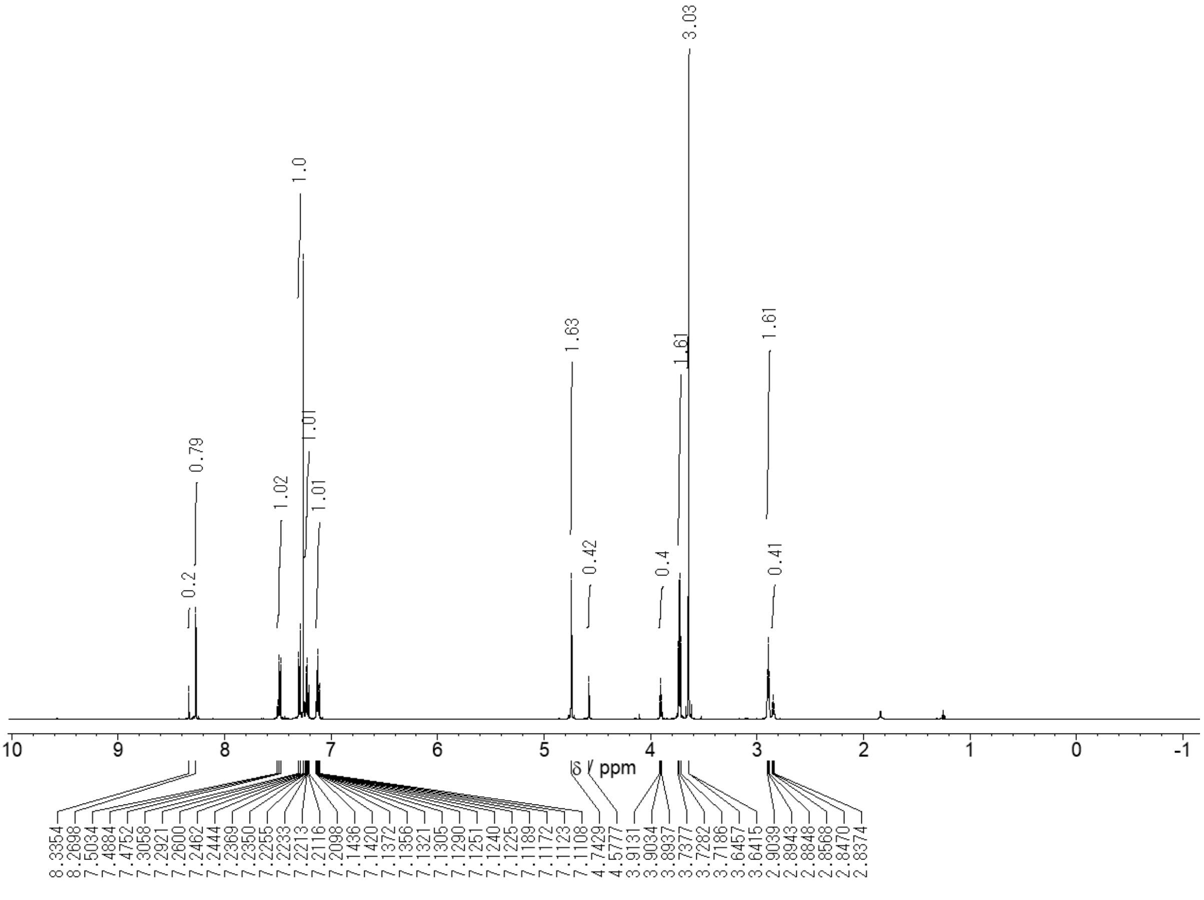


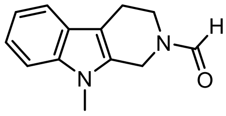
^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$)



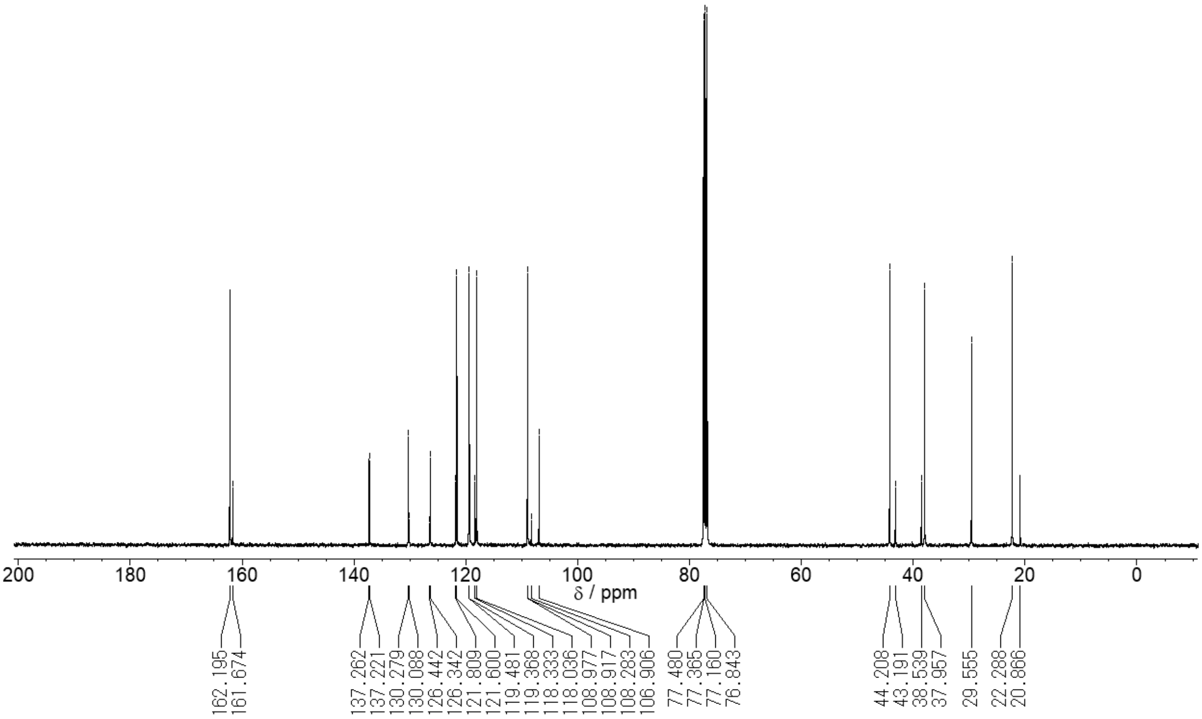
3f



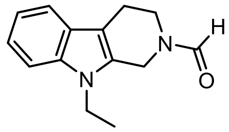
^{1}H NMR spectrum of **3f** (600 MHz, CDCl$_3$)



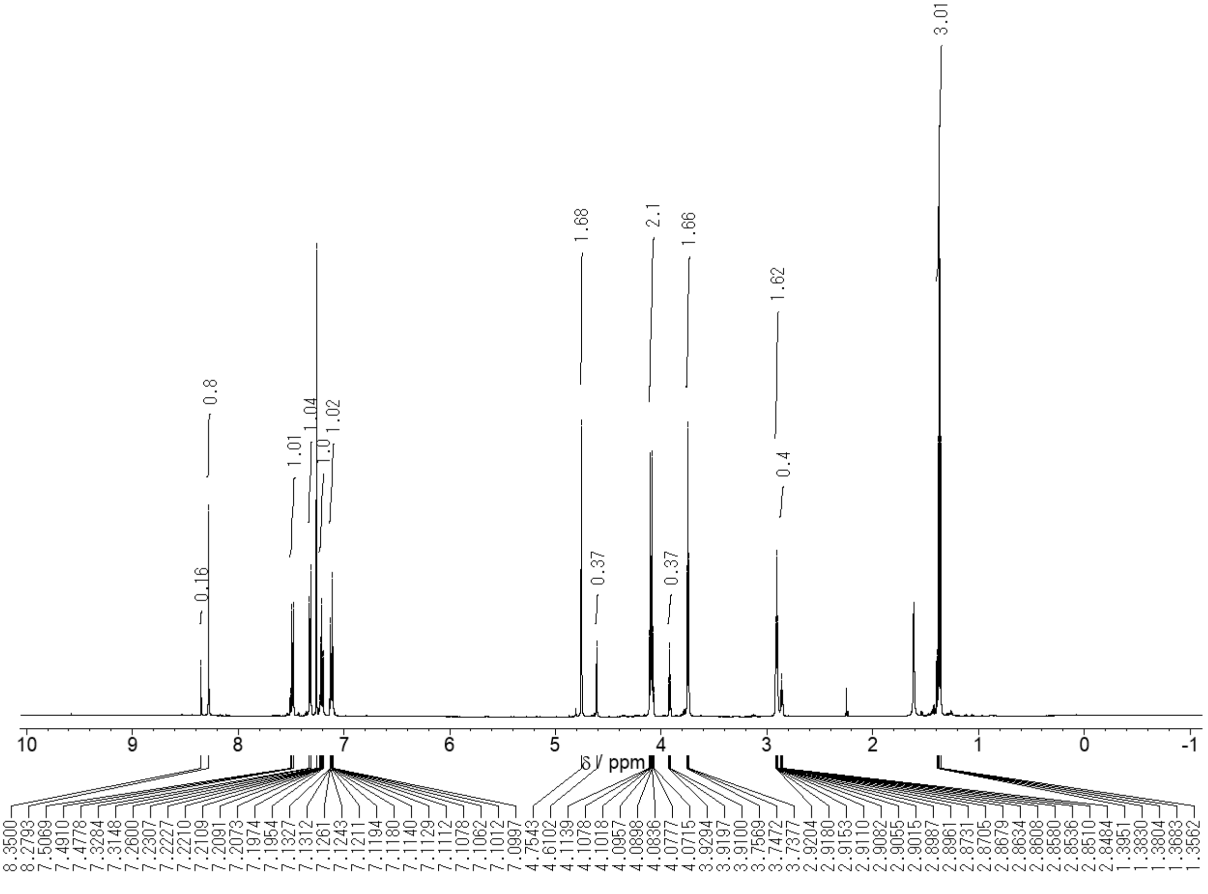
3f



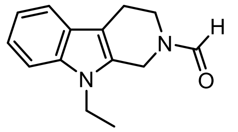
^{13}C NMR spectrum of **3f** (101 MHz, CDCl$_3$)



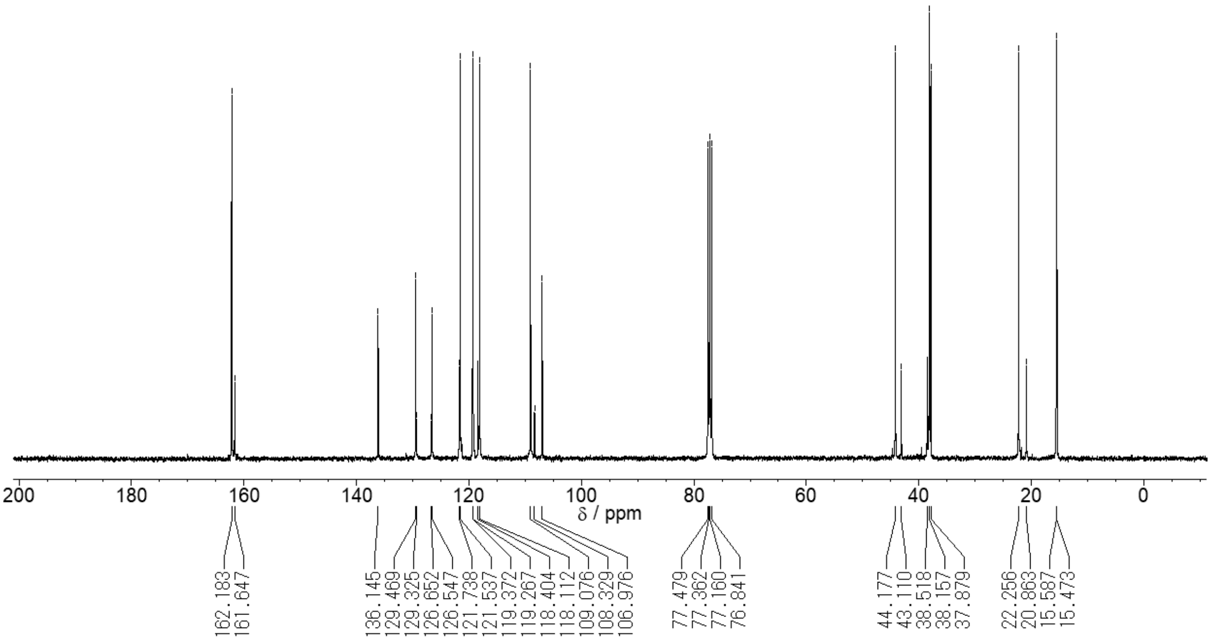
3g



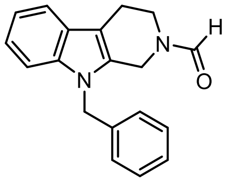
^{1}H NMR spectrum of **3g** (600 MHz, CDCl$_3$)



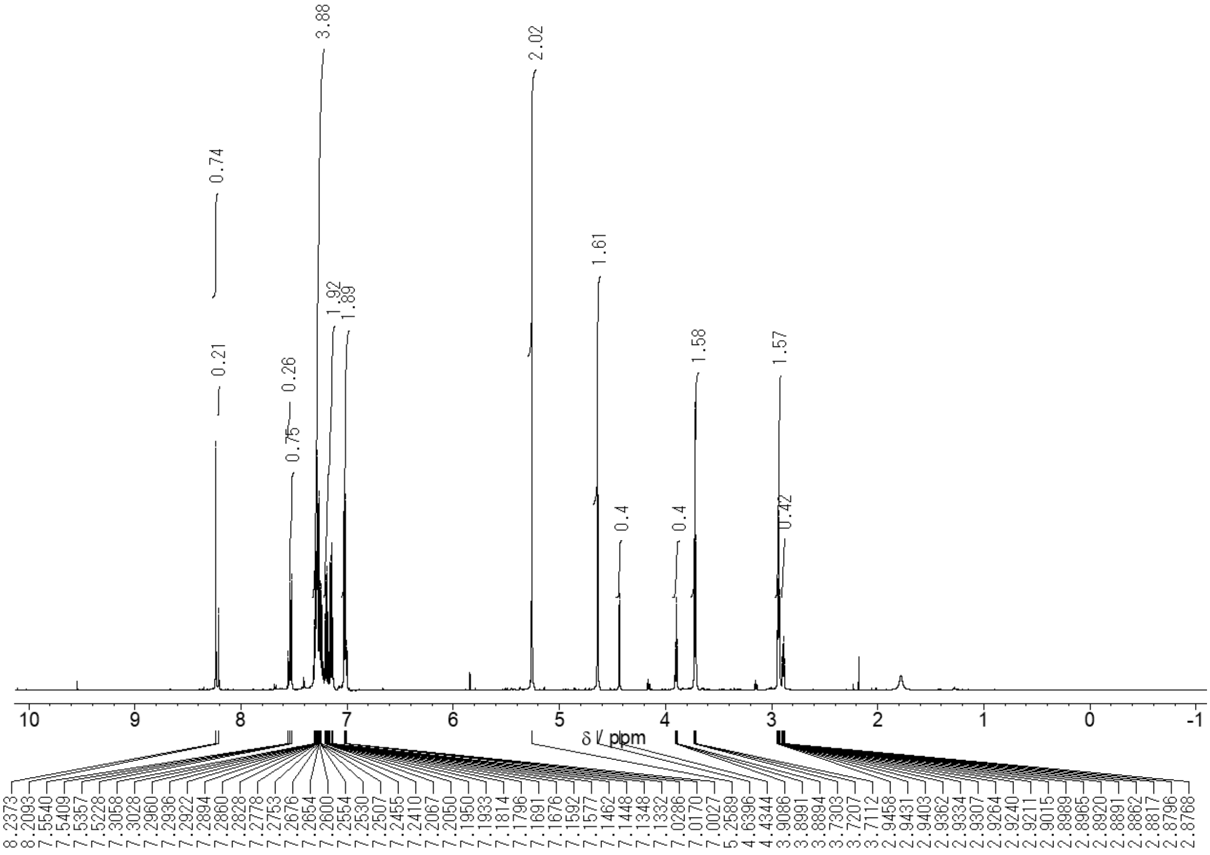
3g



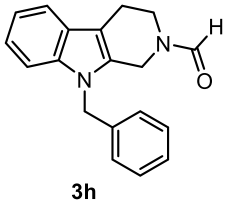
^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$)



3h



^{1}H NMR spectrum of **3h** (600 MHz, $CDCl_3$)



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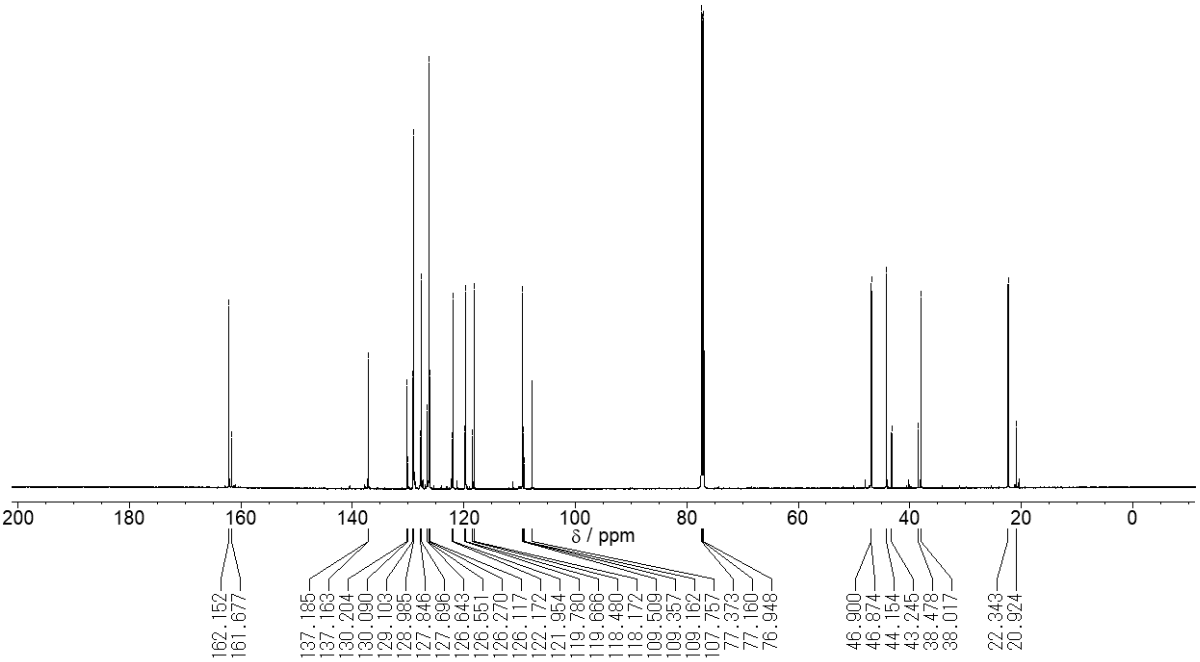
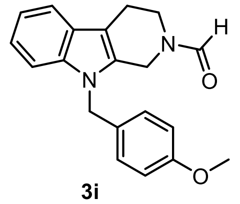
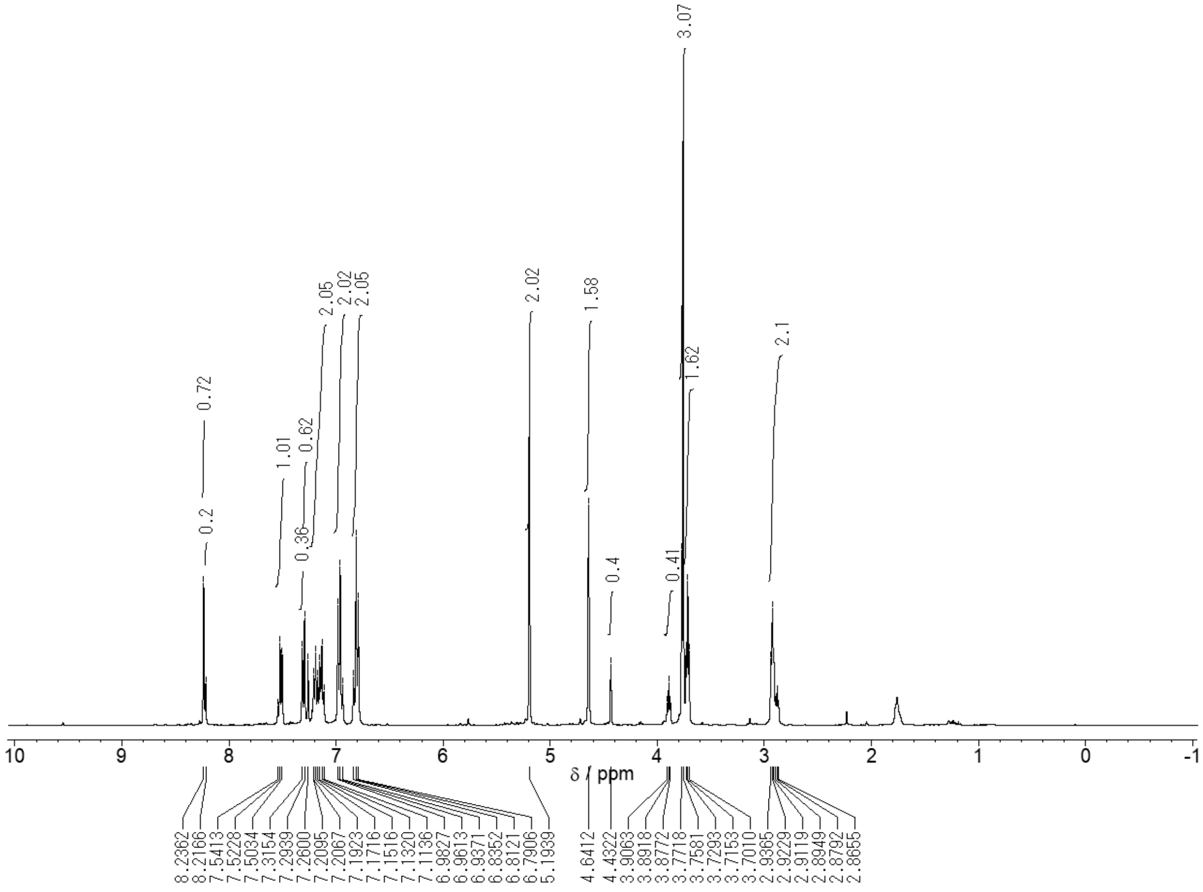


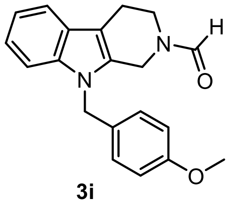
^{13}C NMR spectrum of **3h** (151 MHz, $CDCl_3$)



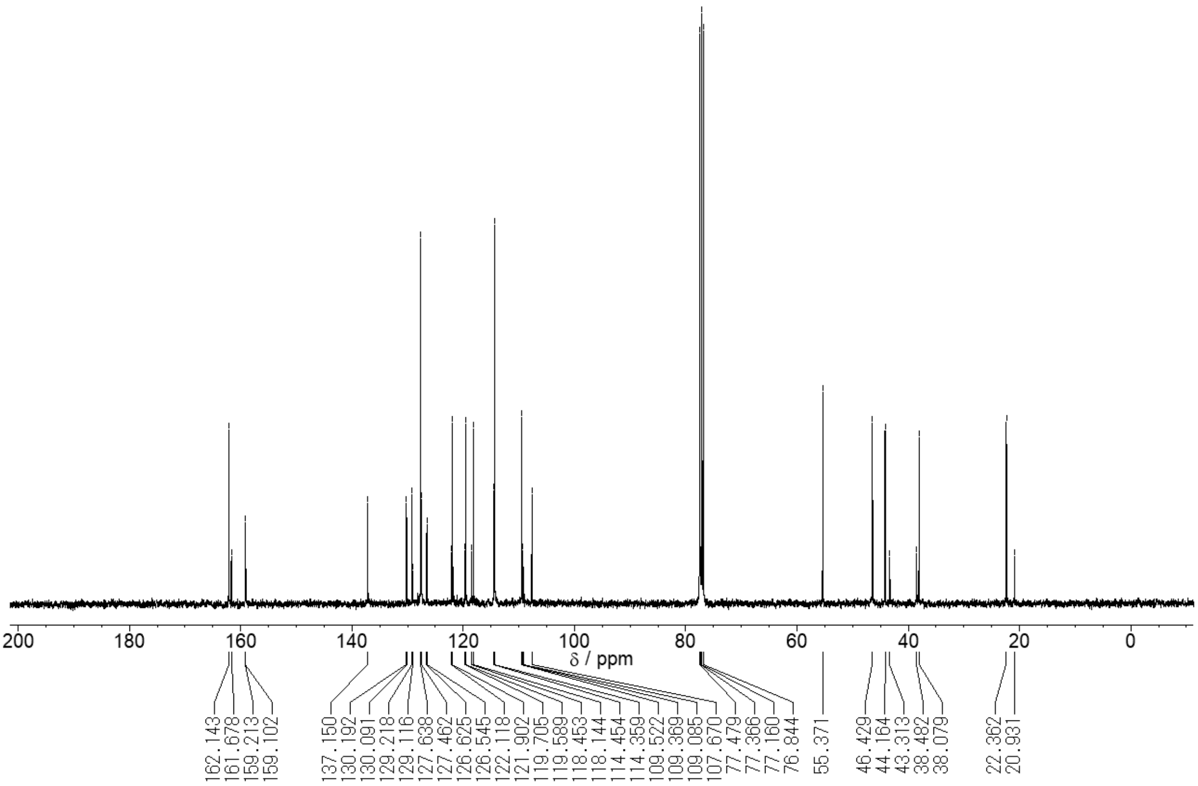
3i



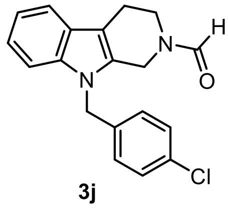
^{1}H NMR spectrum of **3i** (400 MHz, CDCl$_3$)



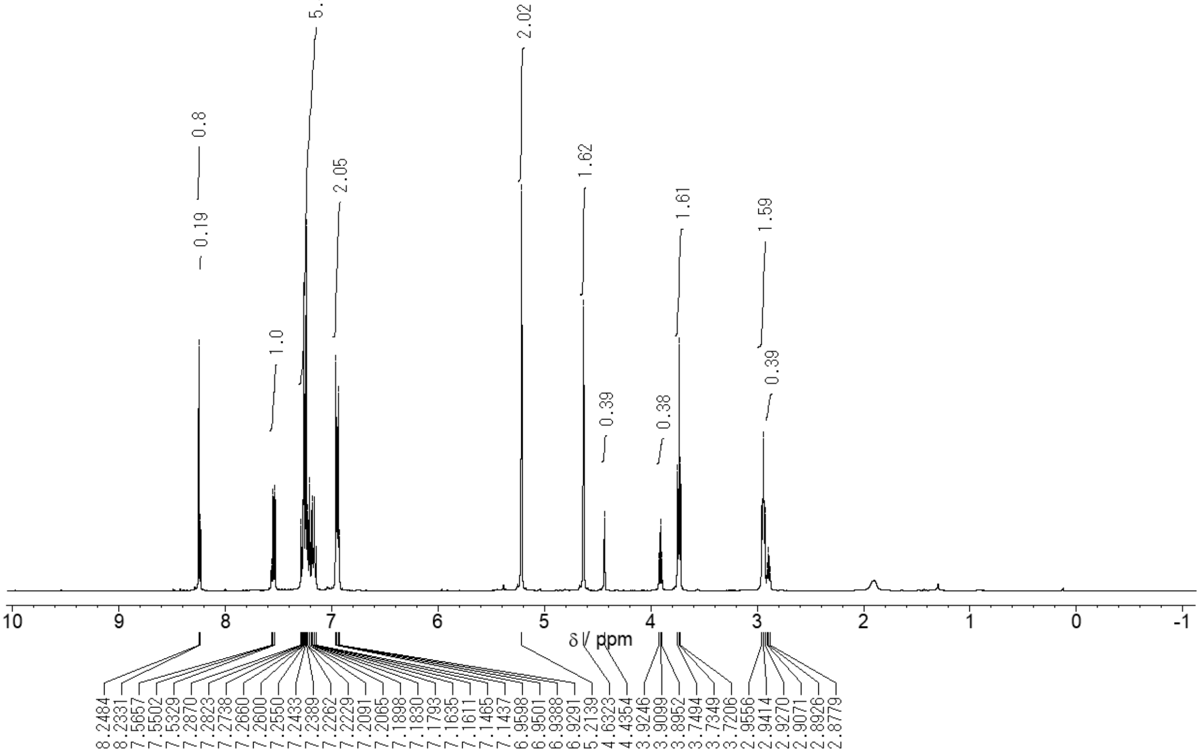
3i



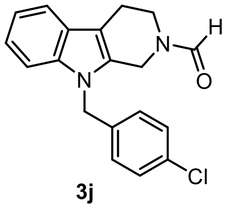
^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$)



3j



^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



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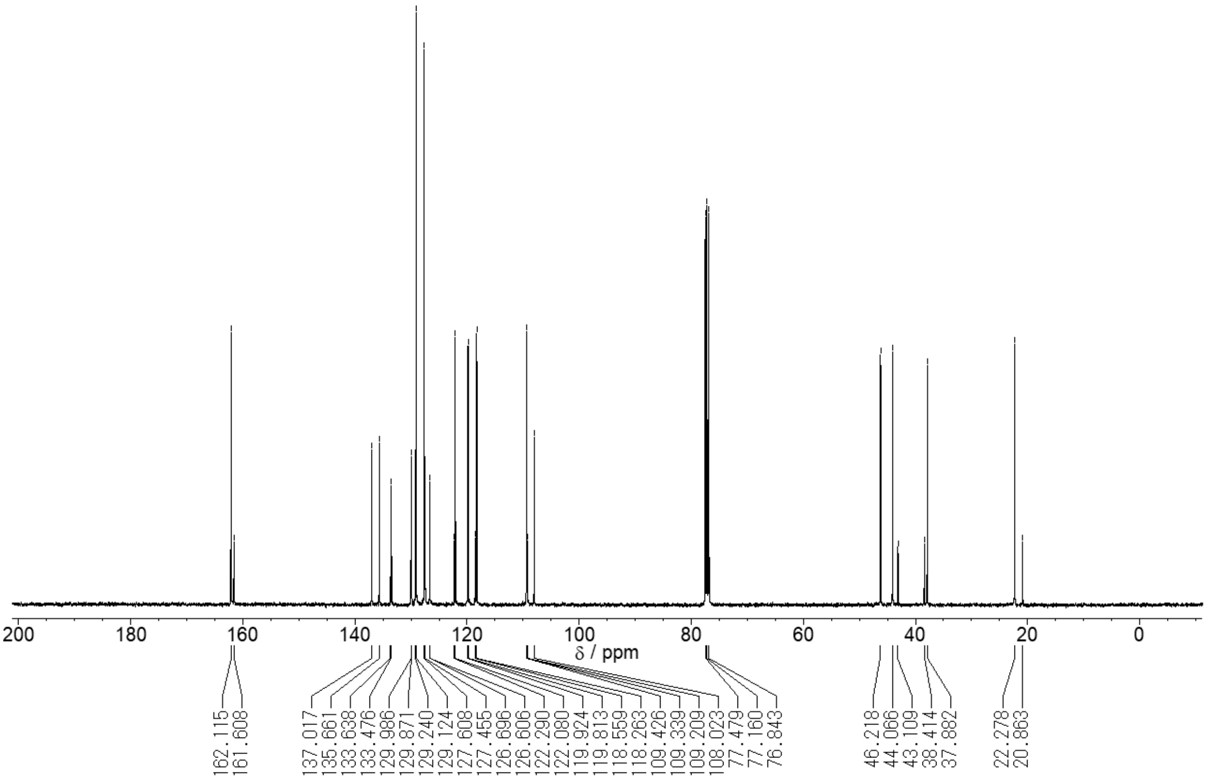
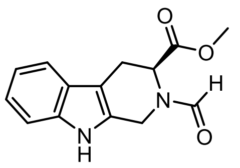
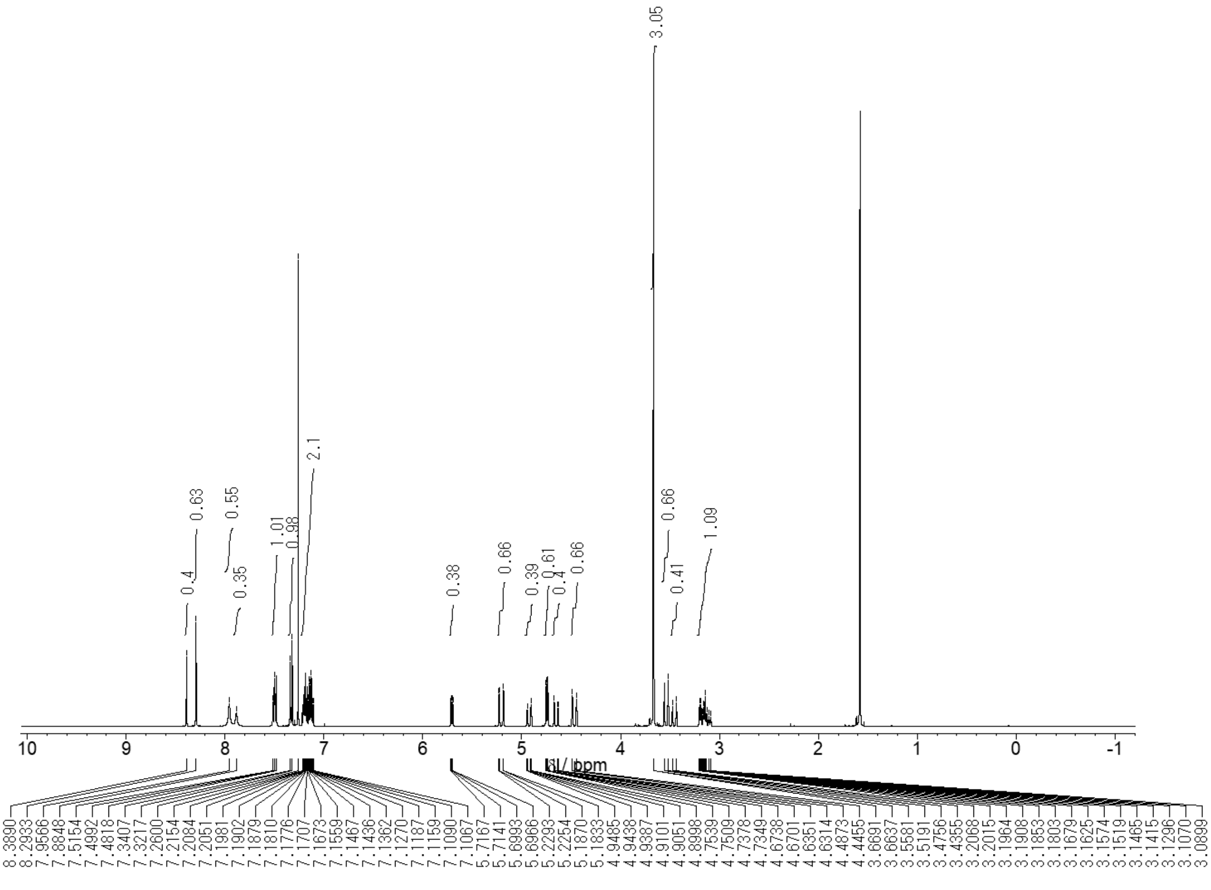


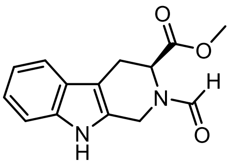
^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$)



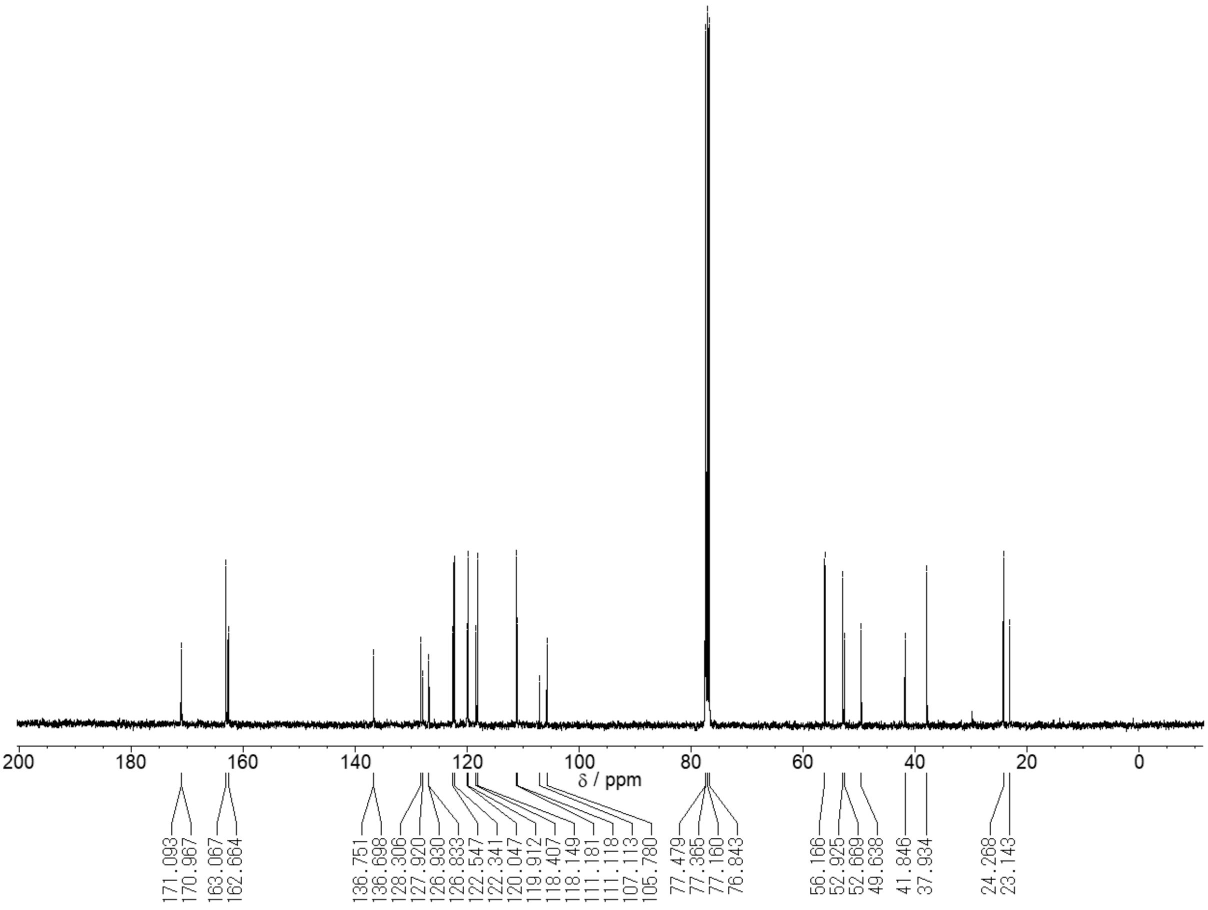
(*S*)-**3k**



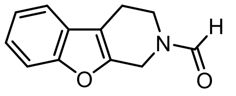
^{1}H NMR spectrum of (*S*)-**3k** (400 MHz, $CDCl_3$)



(*S*)-**3k**



^{13}C NMR spectrum of (*S*)-**3k** (101 MHz, $CDCl_3$)



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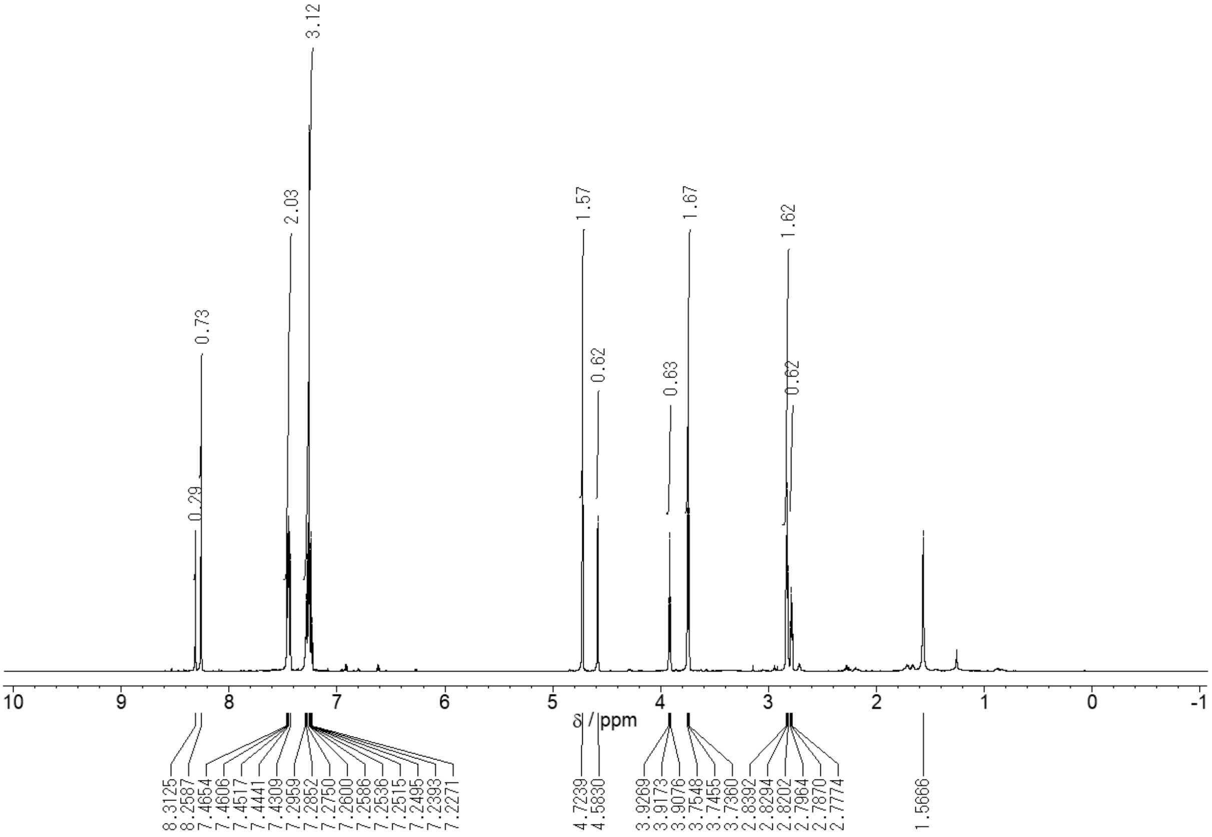
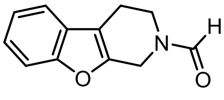
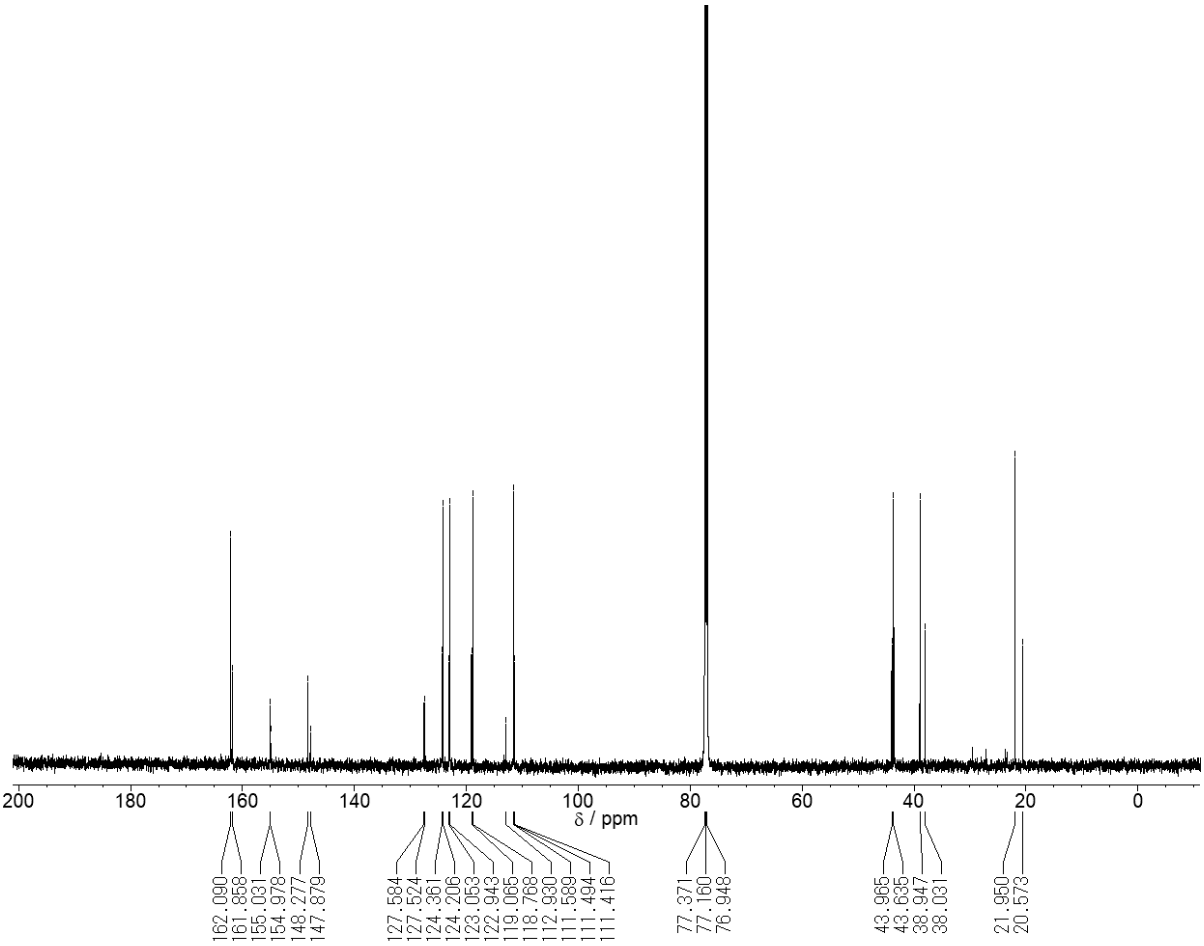


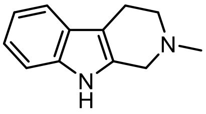
^{1}H NMR spectrum of **3l** (600 MHz, $CDCl_3$)



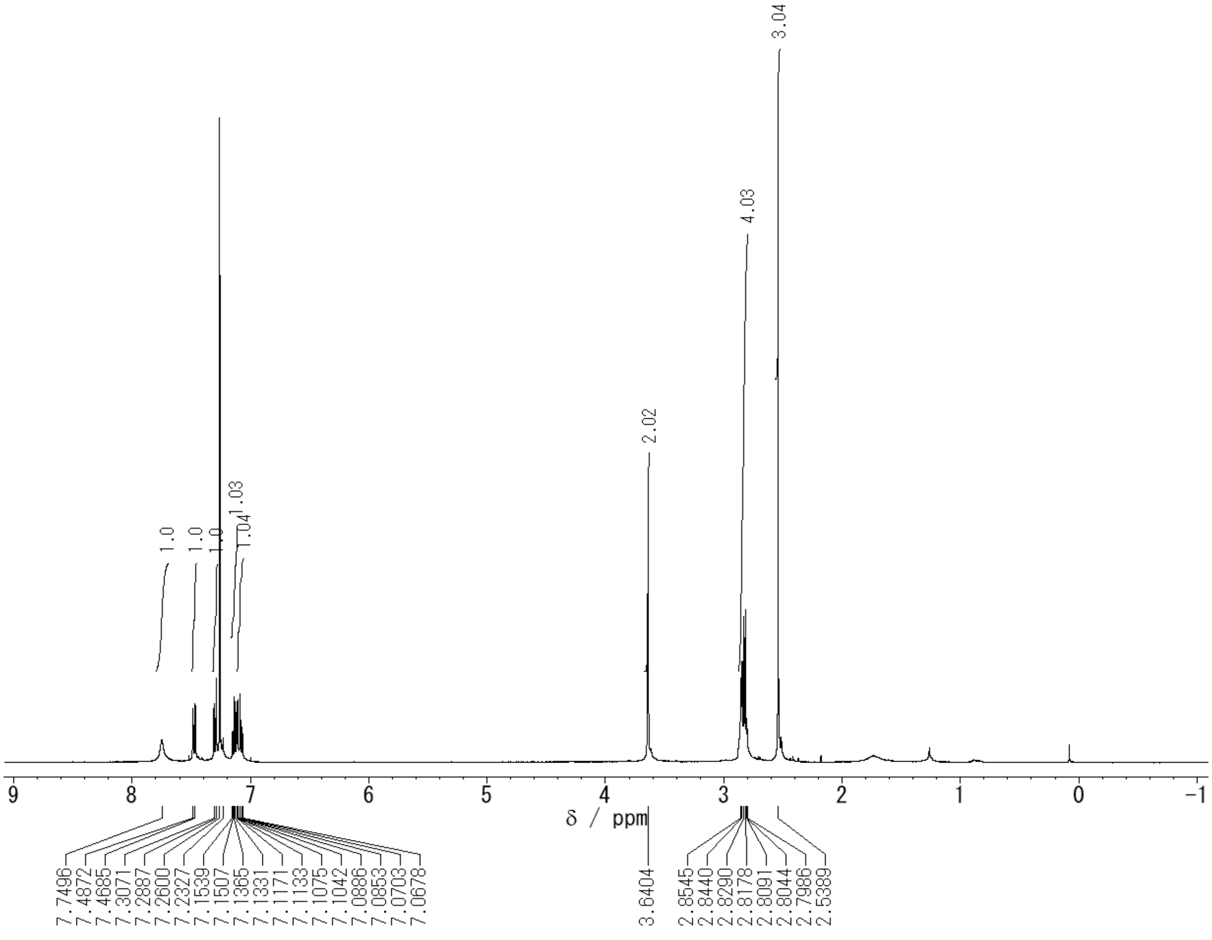
3l



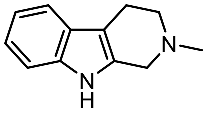
^{13}C NMR spectrum of **3l** (151 MHz, CDCl$_3$)



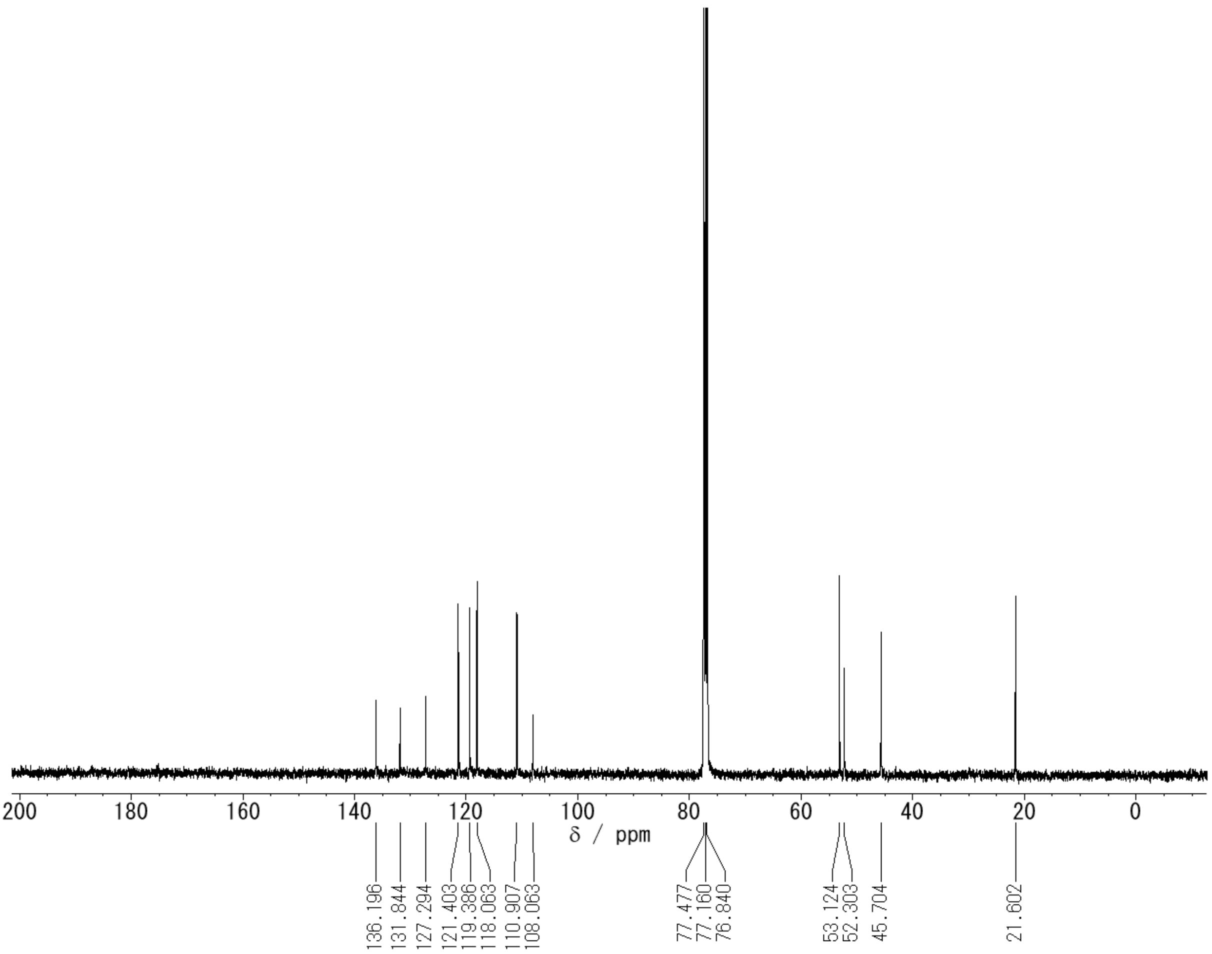
4a



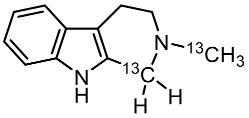
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



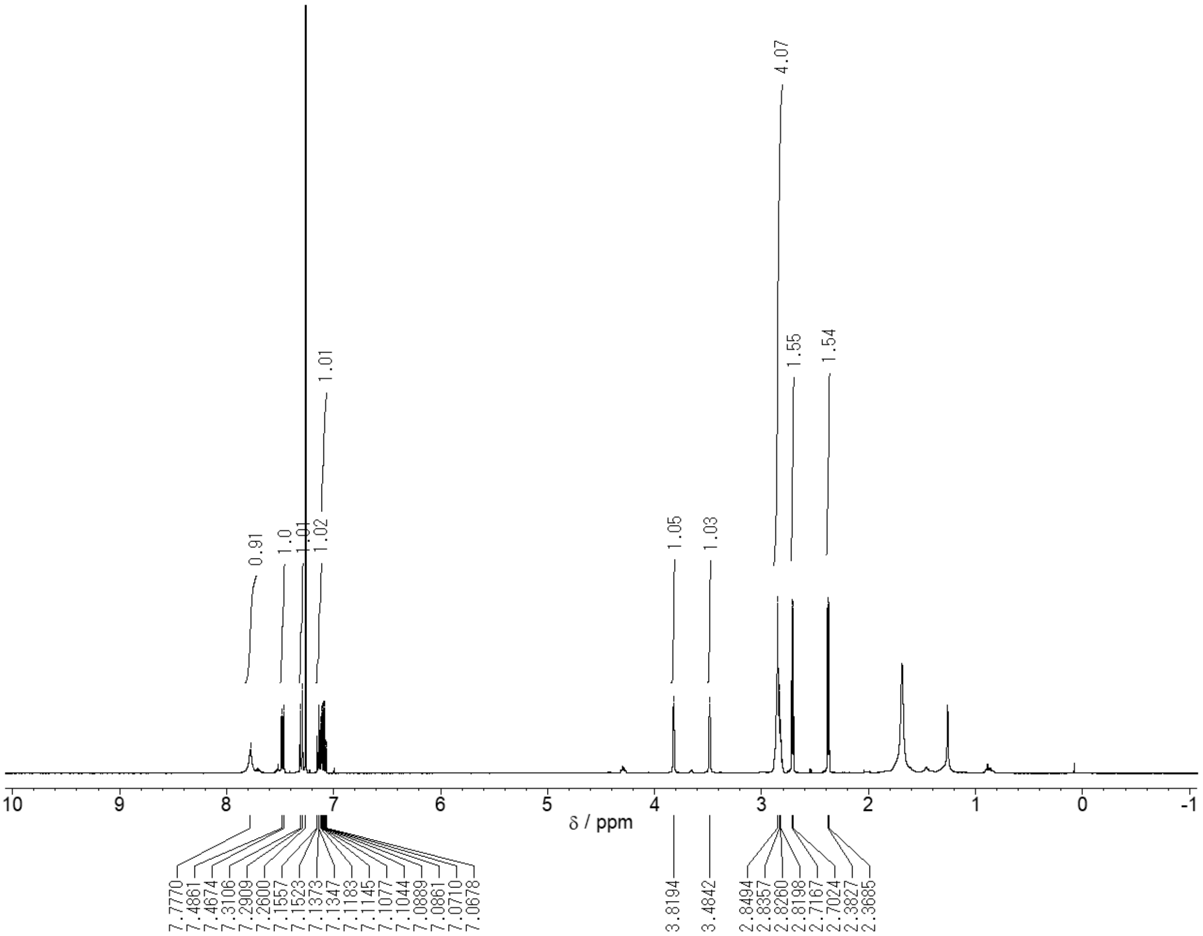
4a



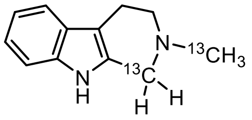
^{13}C NMR spectrum of **4a** (101 MHz, $CDCl_3$)



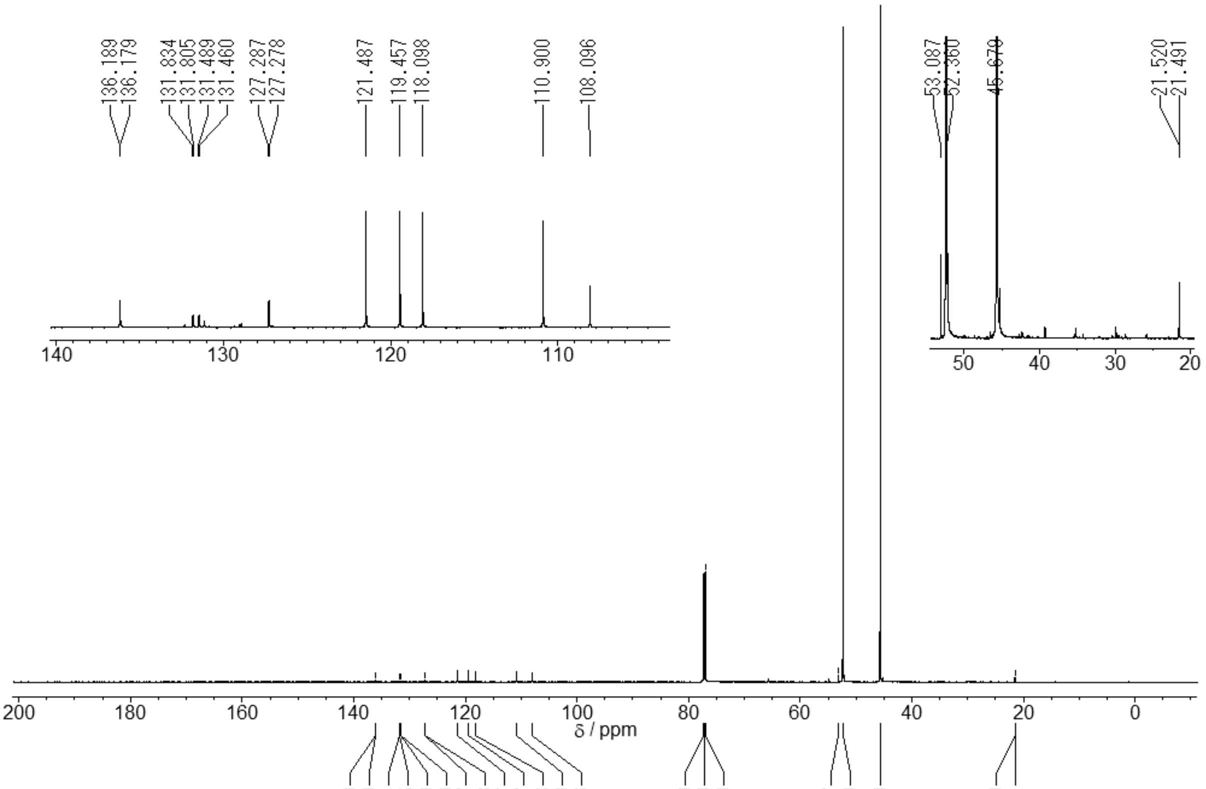
4a'



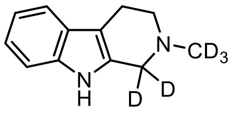
^{1}H NMR spectrum of **4a'** (400 MHz, CDCl$_3$)



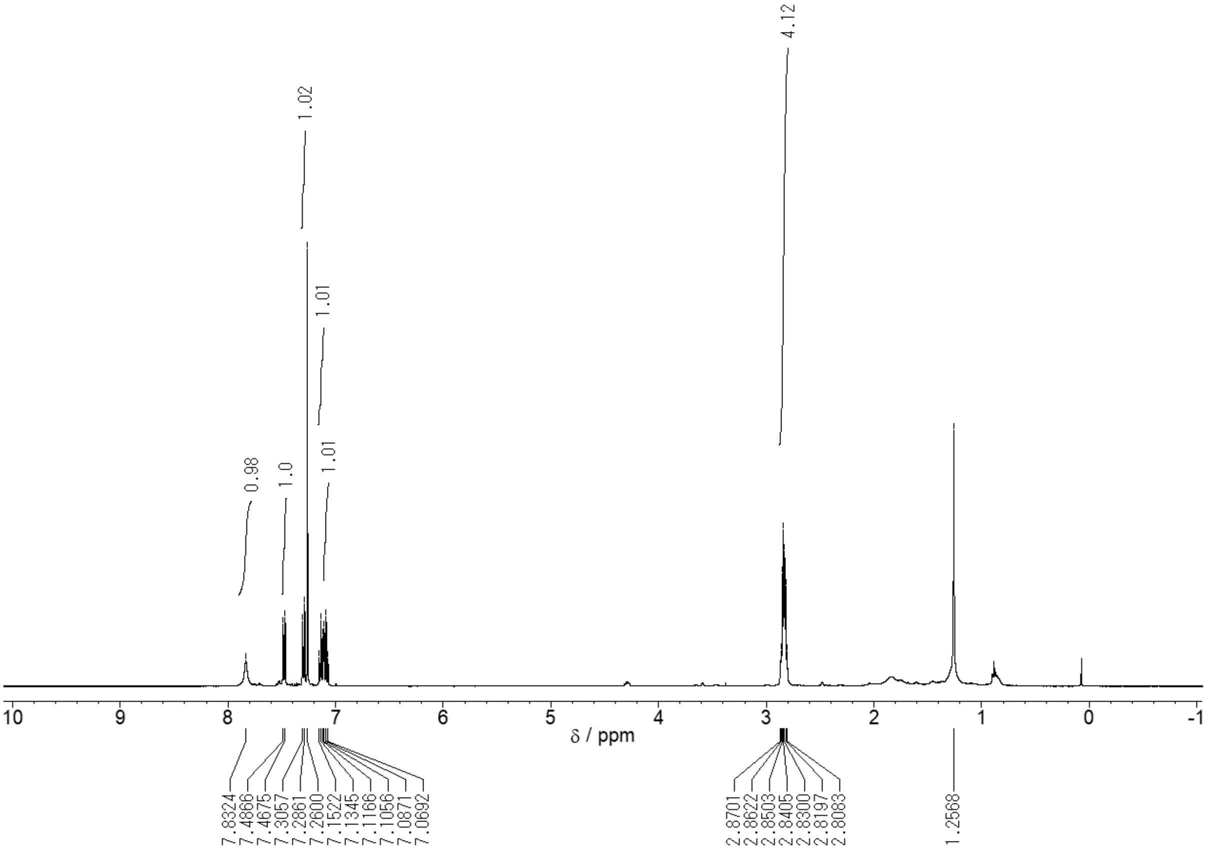
4a'



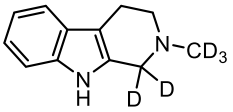
^{13}C NMR spectrum of **4a'** (151 MHz, CDCl$_3$)



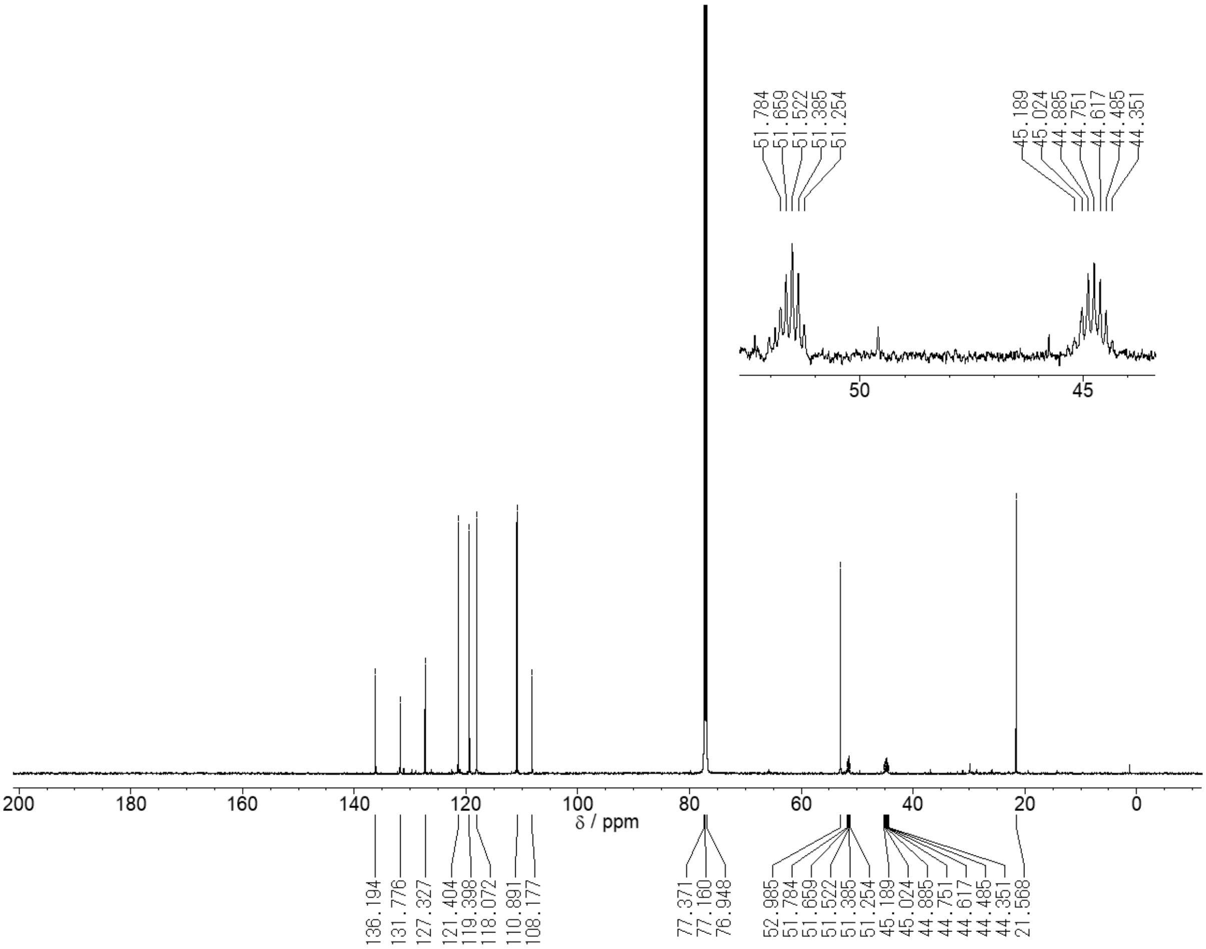
4a''



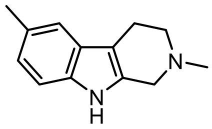
^{1}H NMR spectrum of **4a''** (400 MHz, $CDCl_3$)



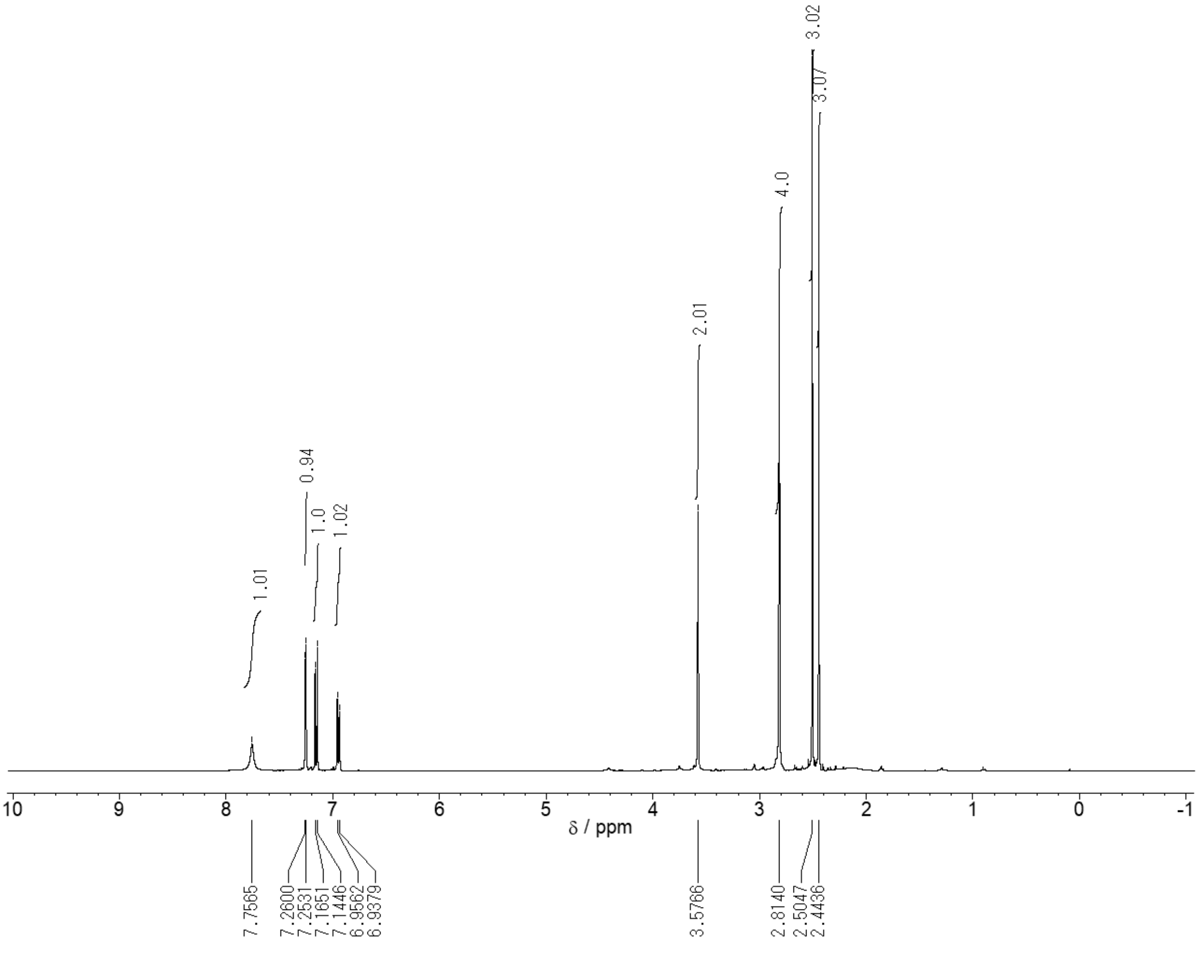
4a''



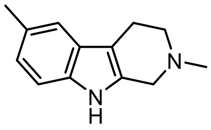
^{13}C NMR spectrum of **4a''** (151 MHz, CDCl$_3$)



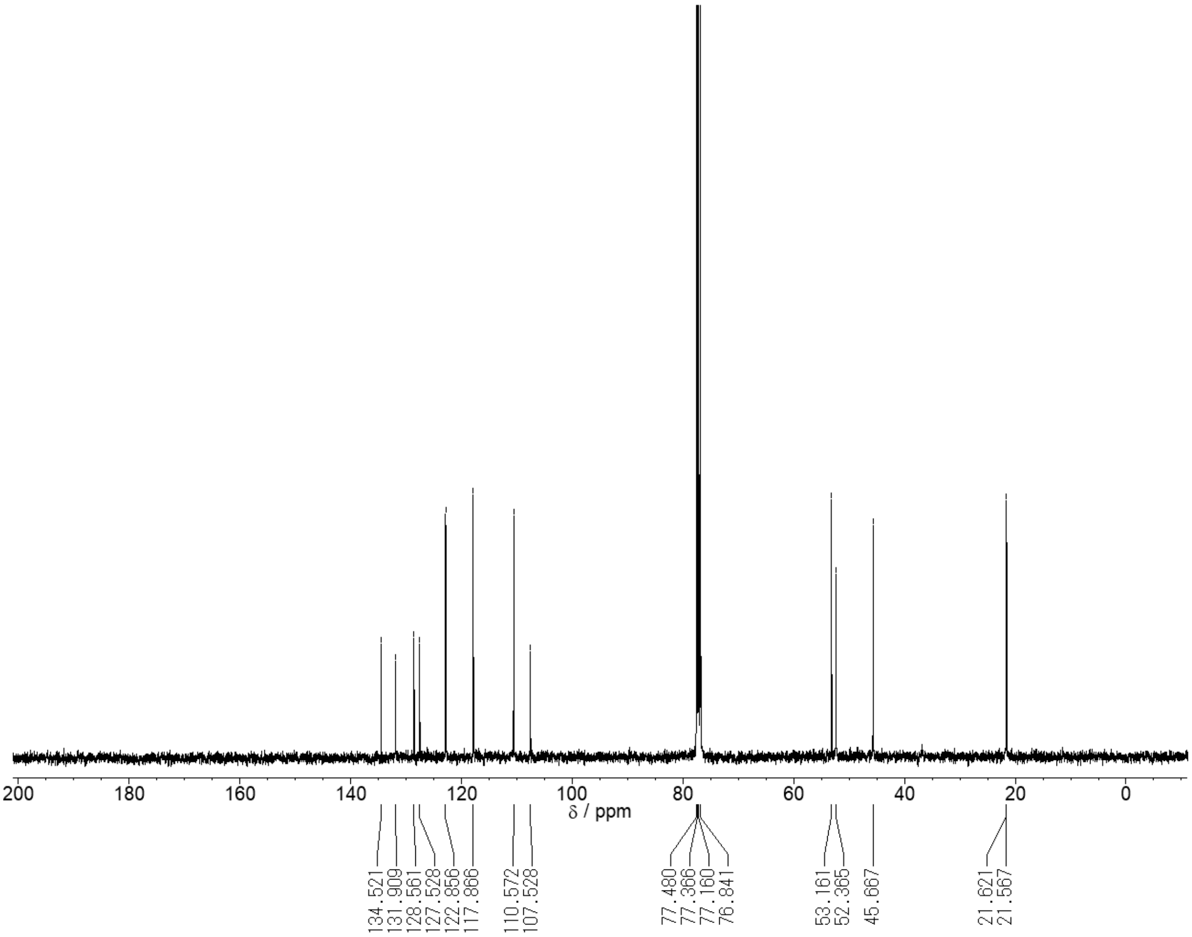
4b



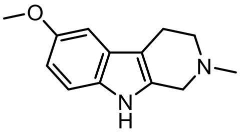
^{1}H NMR spectrum of **4b** (400 MHz, CDCl$_3$)



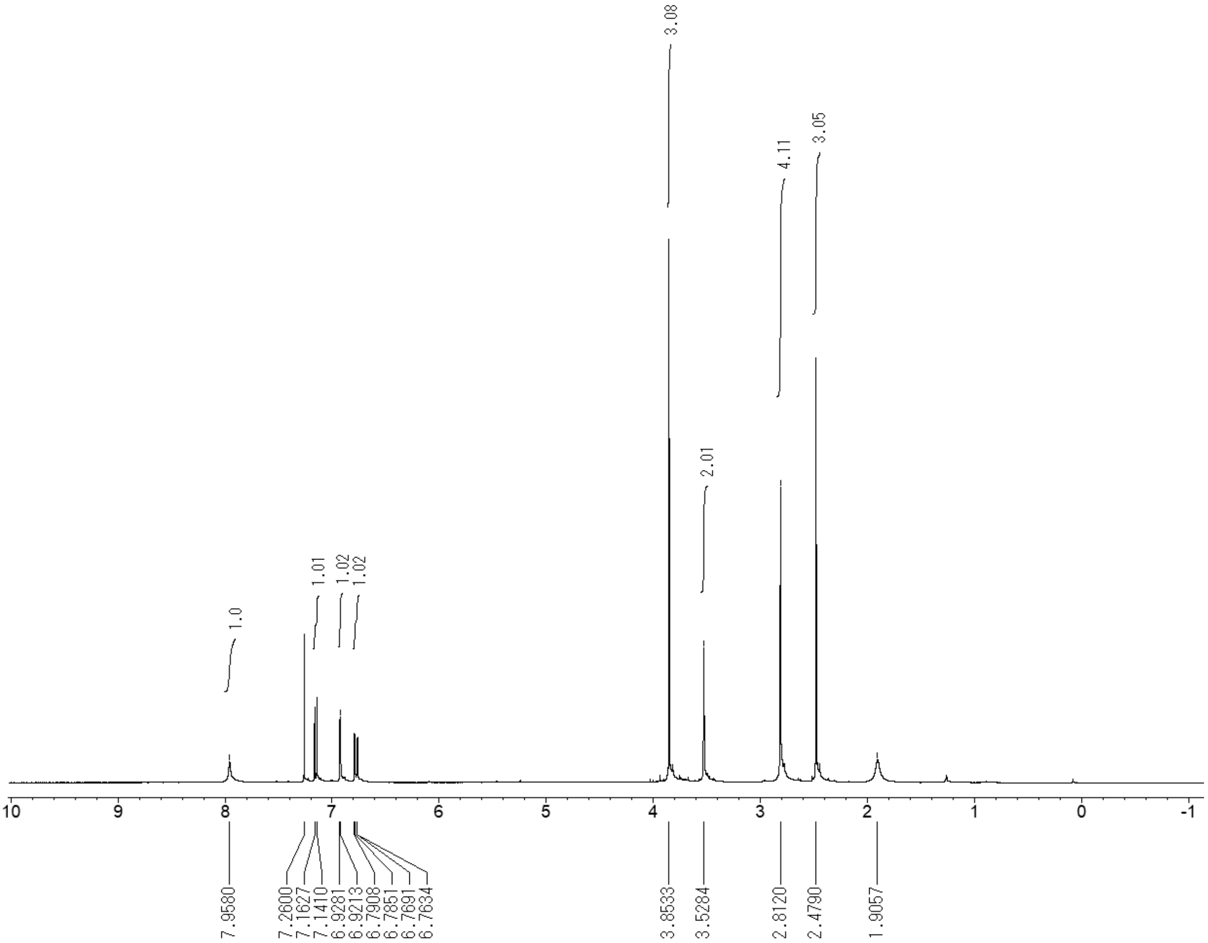
4b



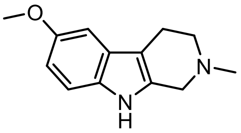
^{13}C NMR spectrum of **4b** (101 MHz, $CDCl_3$)



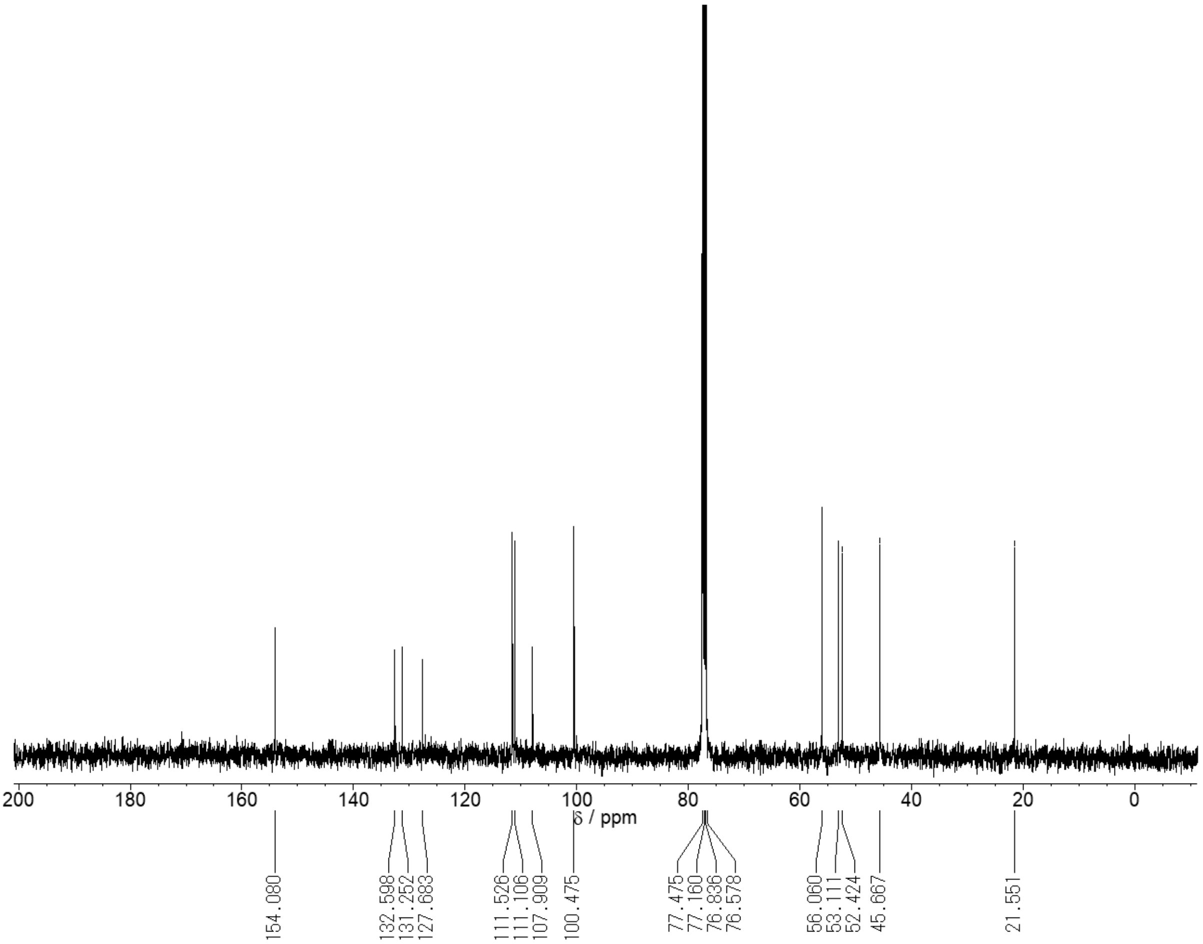
4c



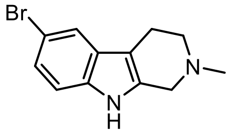
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



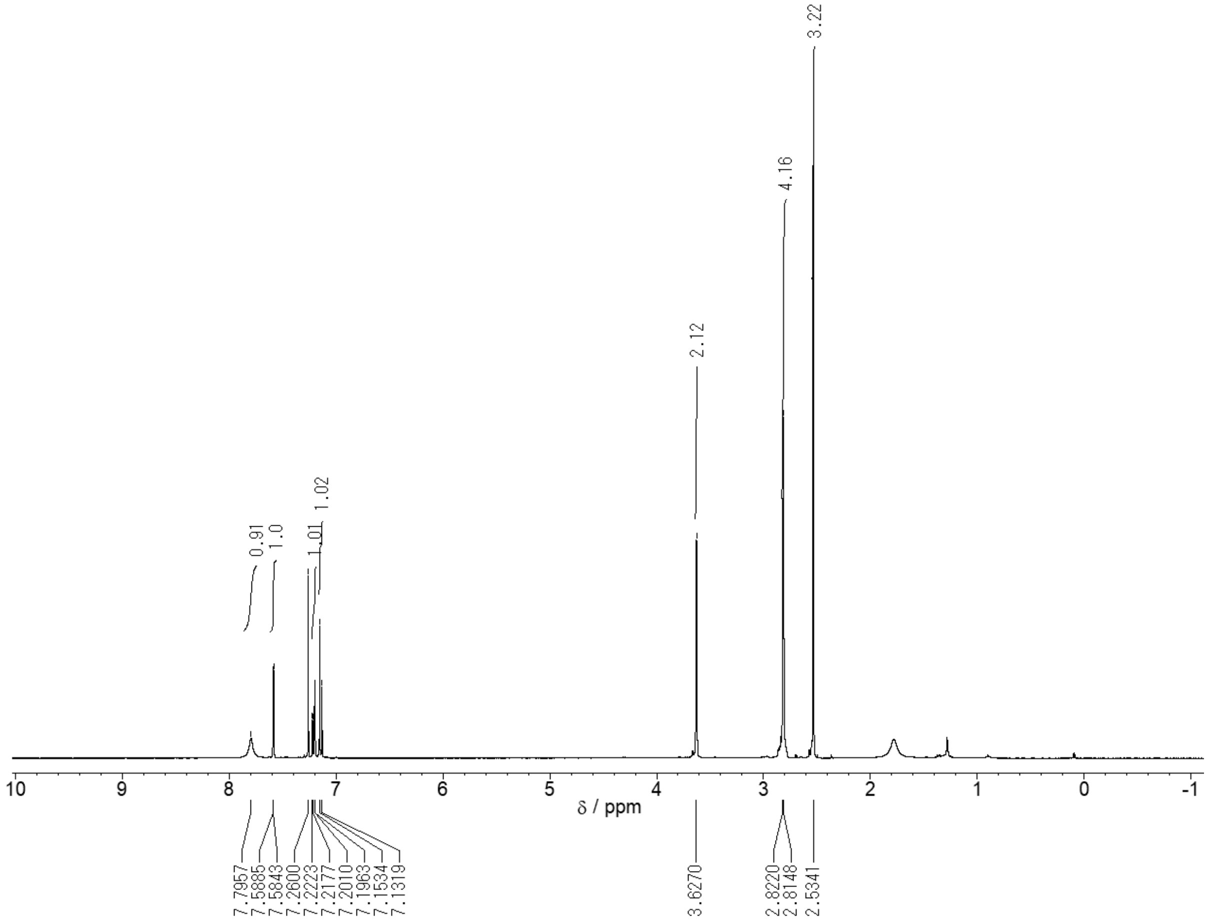
4c



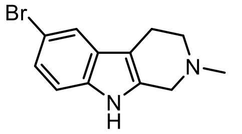
^{13}C NMR spectrum of **4c** (101 MHz, CDCl$_3$)



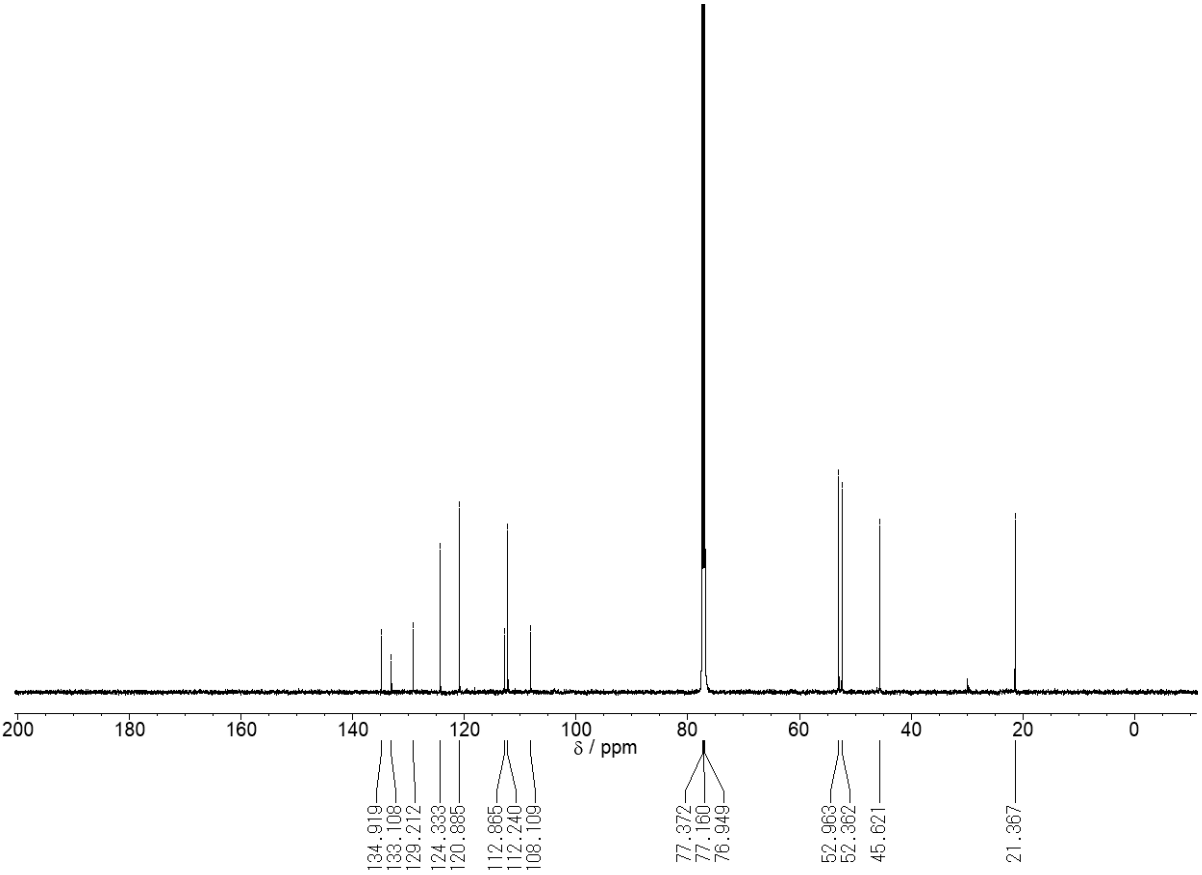
4d



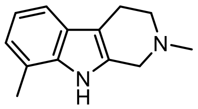
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



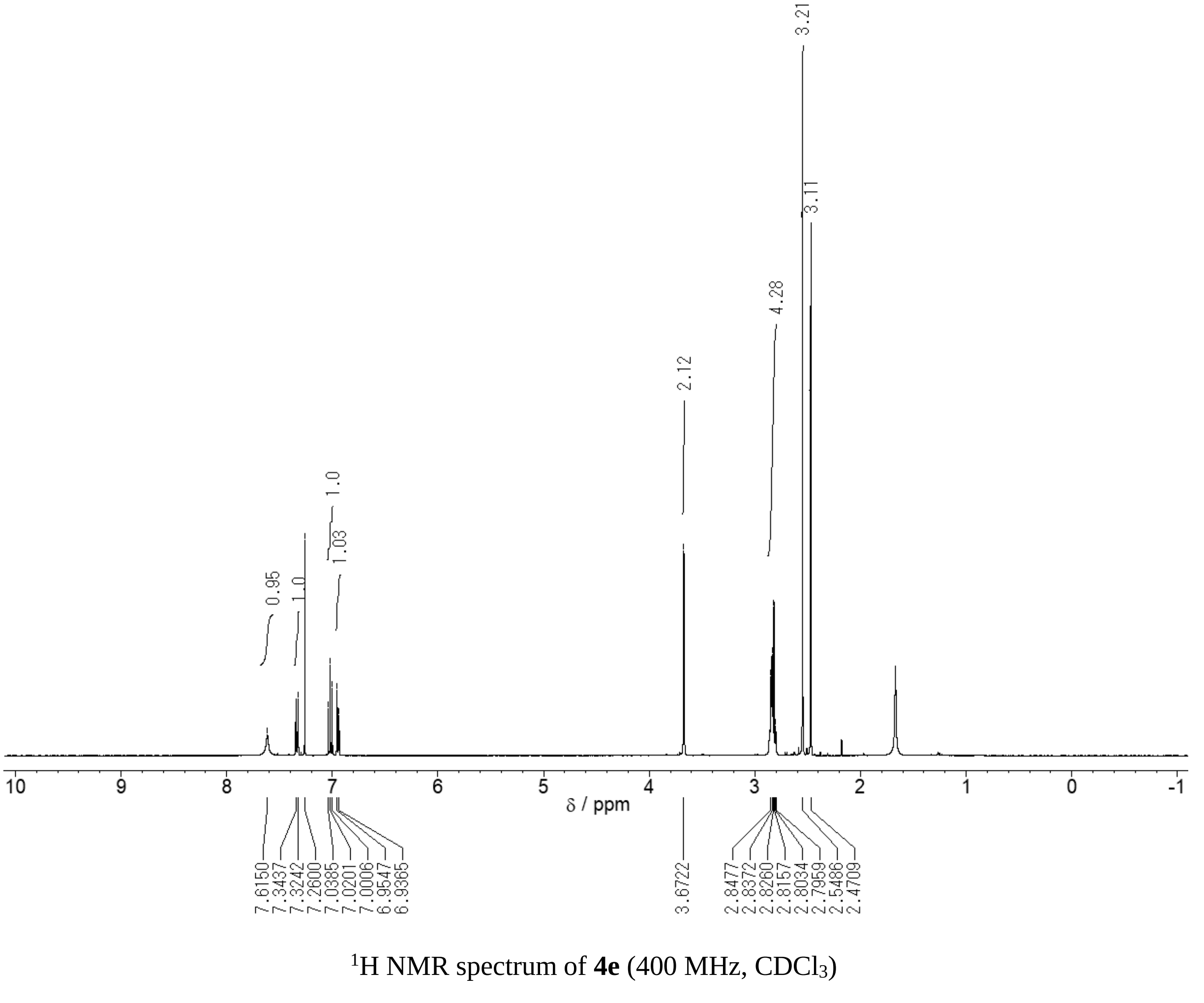
4d



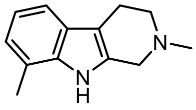
^{13}C NMR spectrum of **4d** (151 MHz, $CDCl_3$)



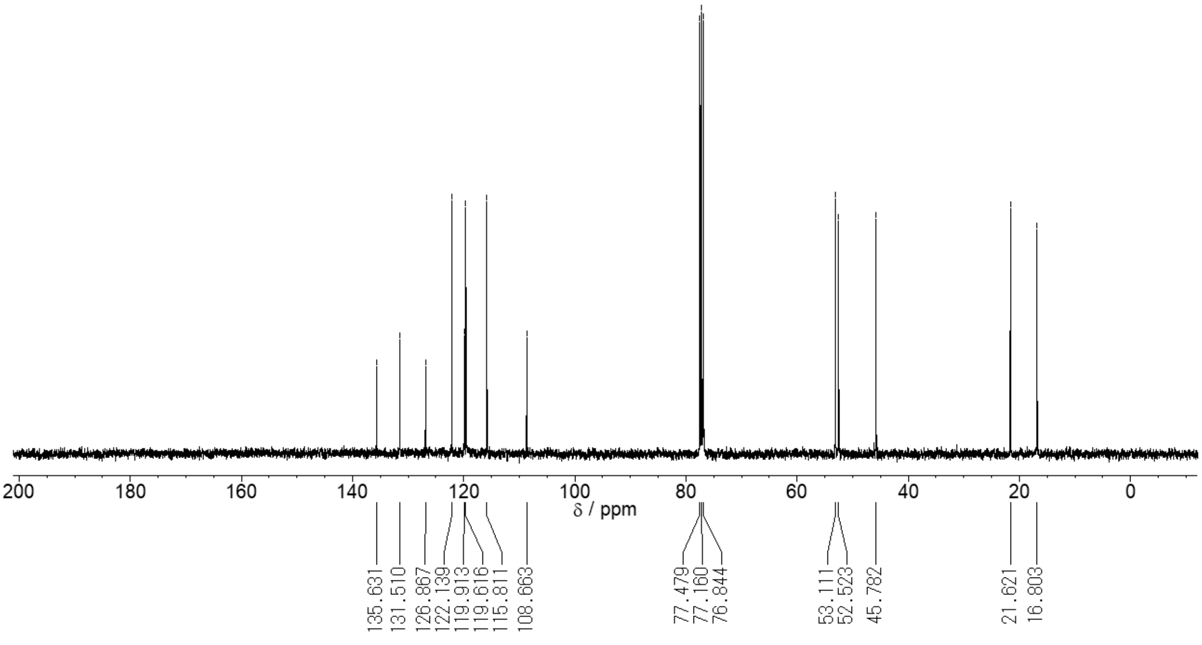
4e



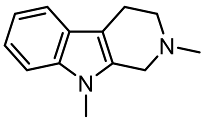
^{1}H NMR spectrum of **4e** (400 MHz, CDCl$_3$)



4e



^{13}C NMR spectrum of **4e** (101 MHz, CDCl$_3$)



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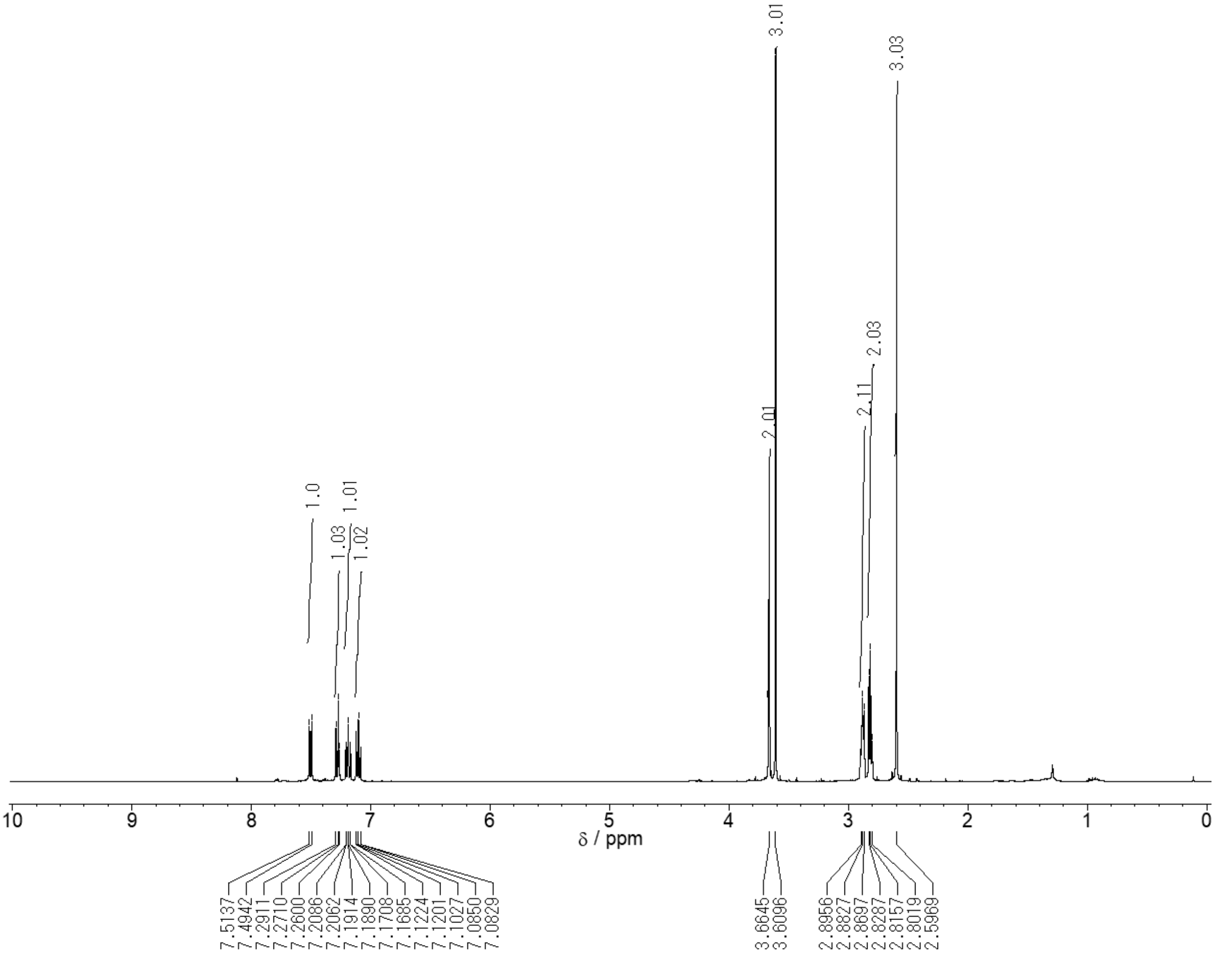
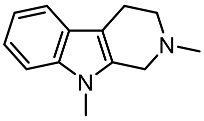
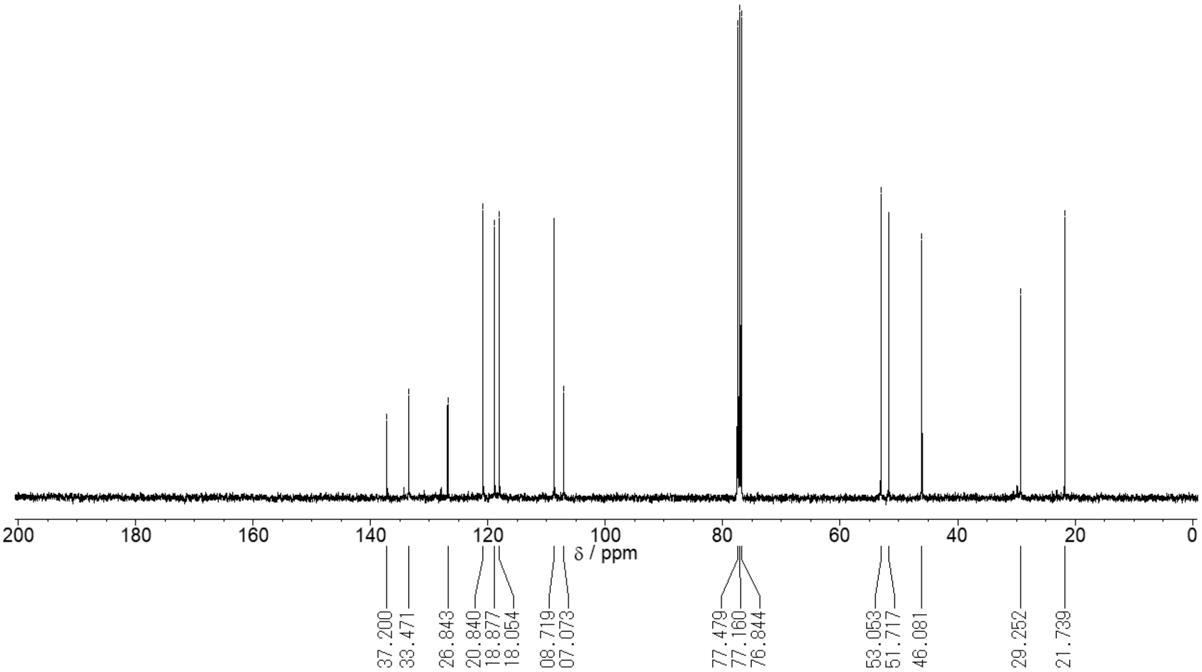


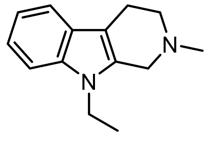
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



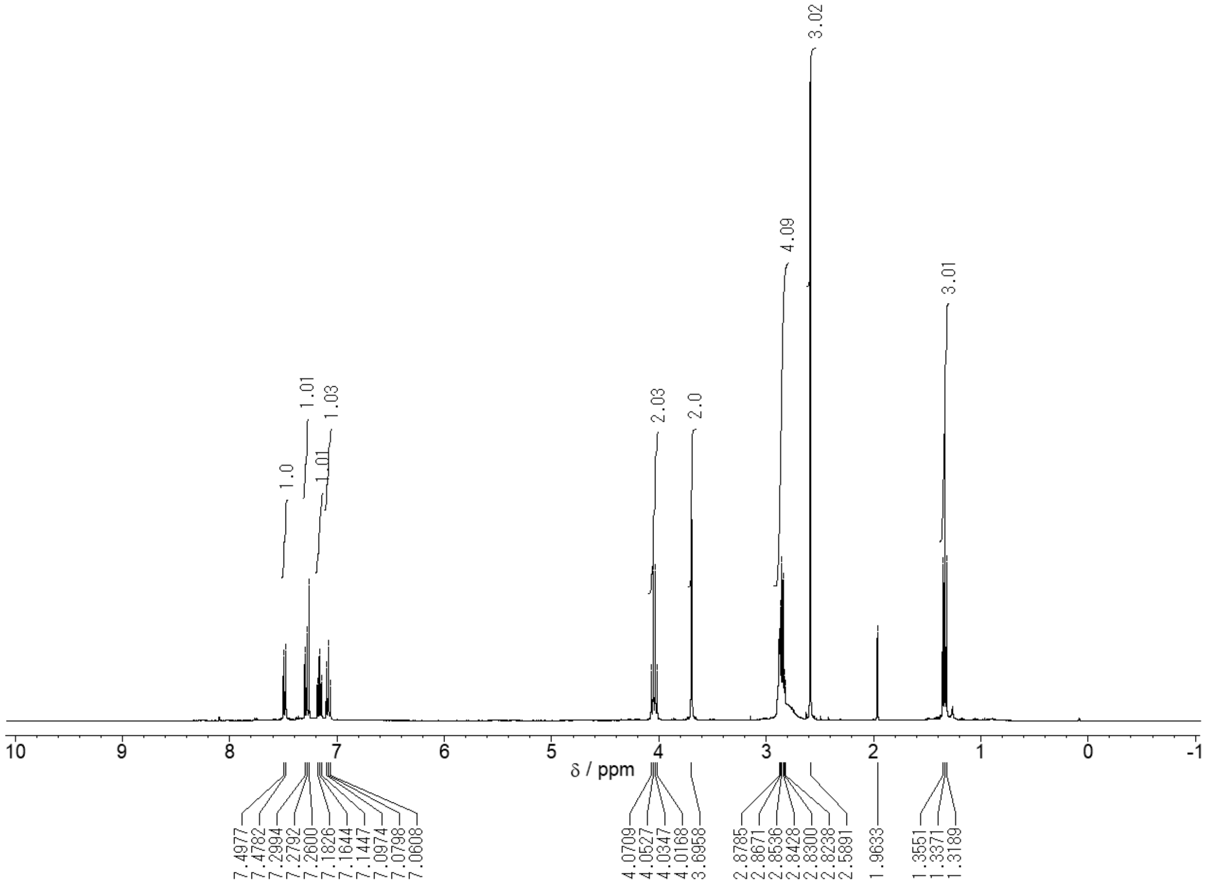
4f



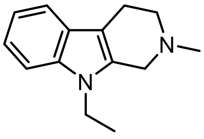
^{13}C NMR spectrum of **4f** (101 MHz, CDCl$_3$)



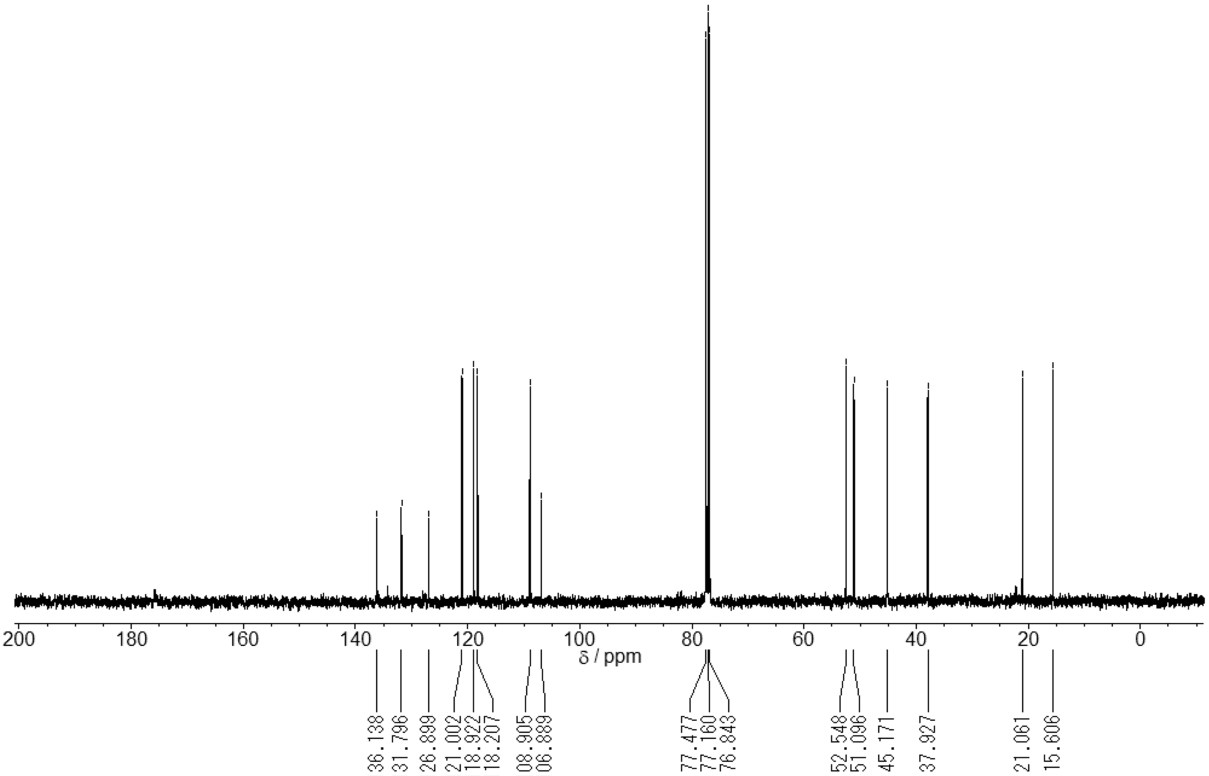
4g



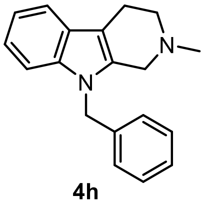
^{1}H NMR spectrum of **4g** (400 MHz, CDCl$_3$)



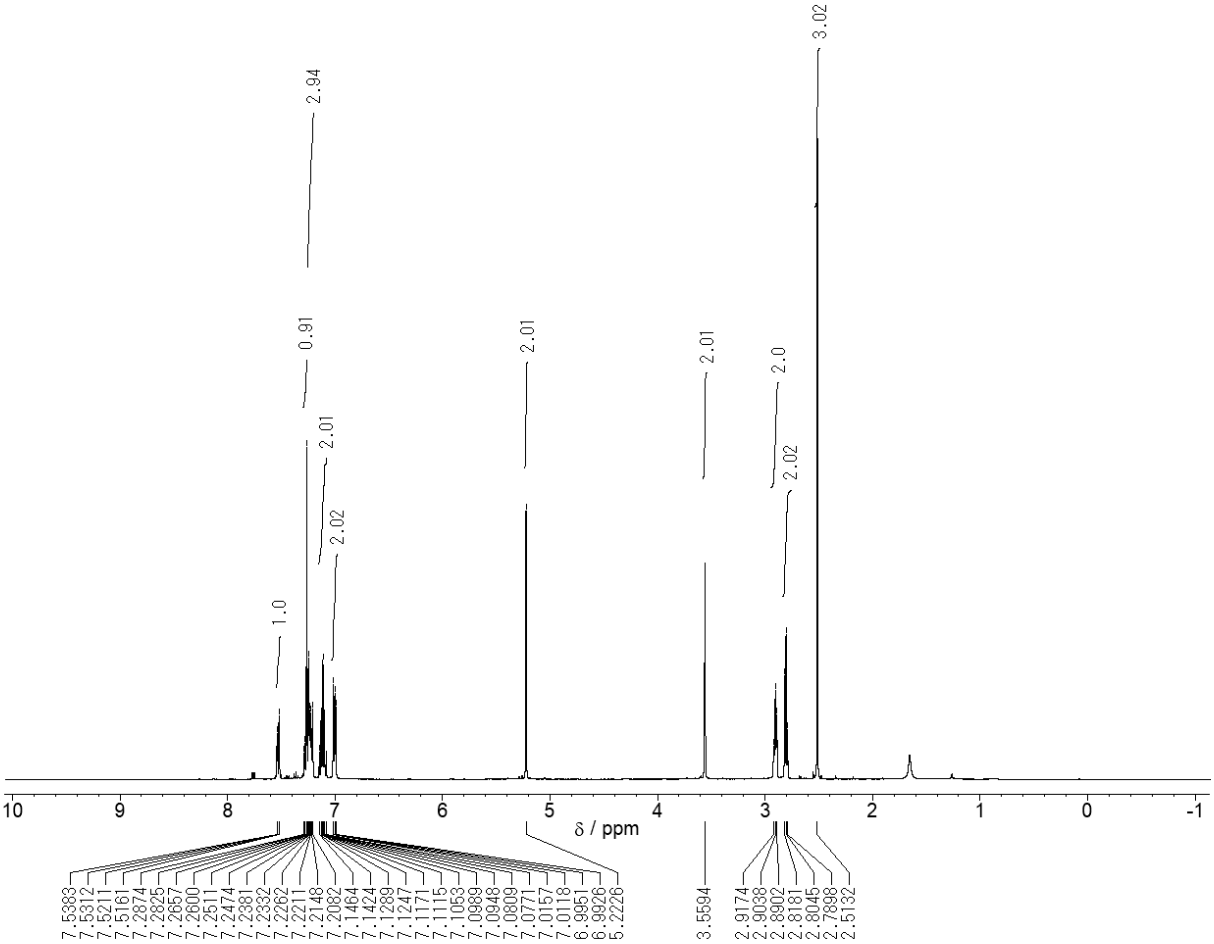
4g



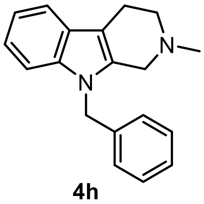
^{13}C NMR spectrum of **4g** (101 MHz, CDCl$_3$)



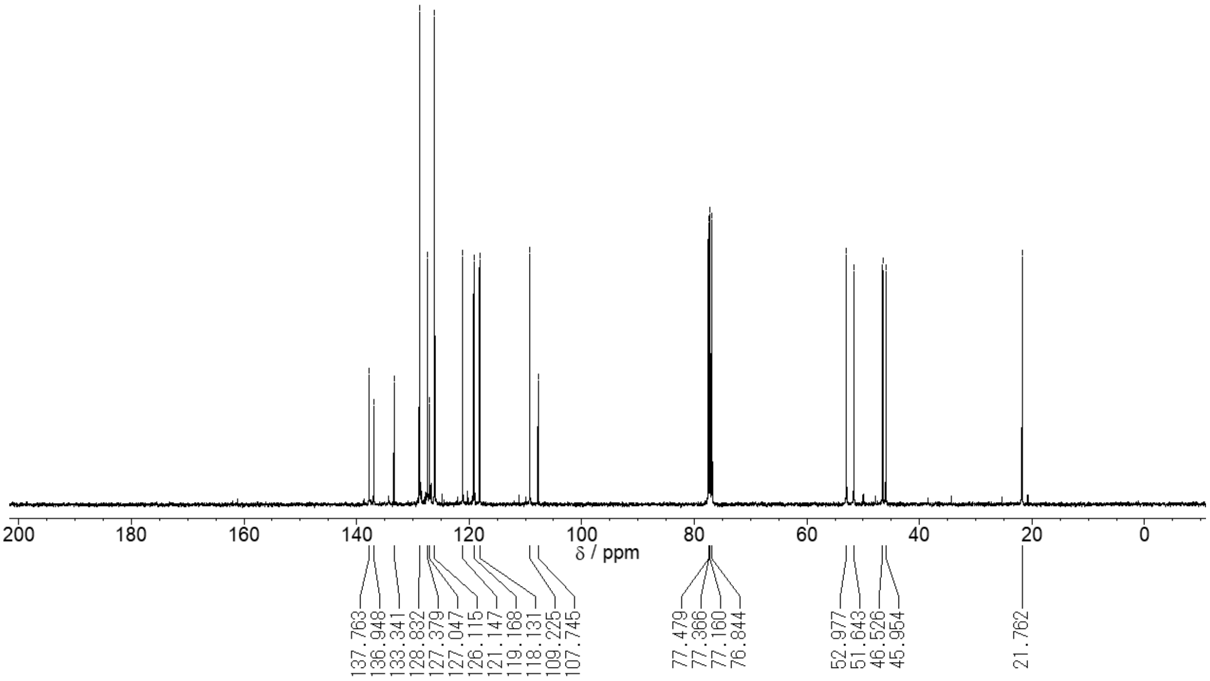
4h



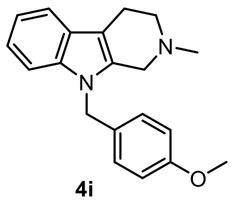
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



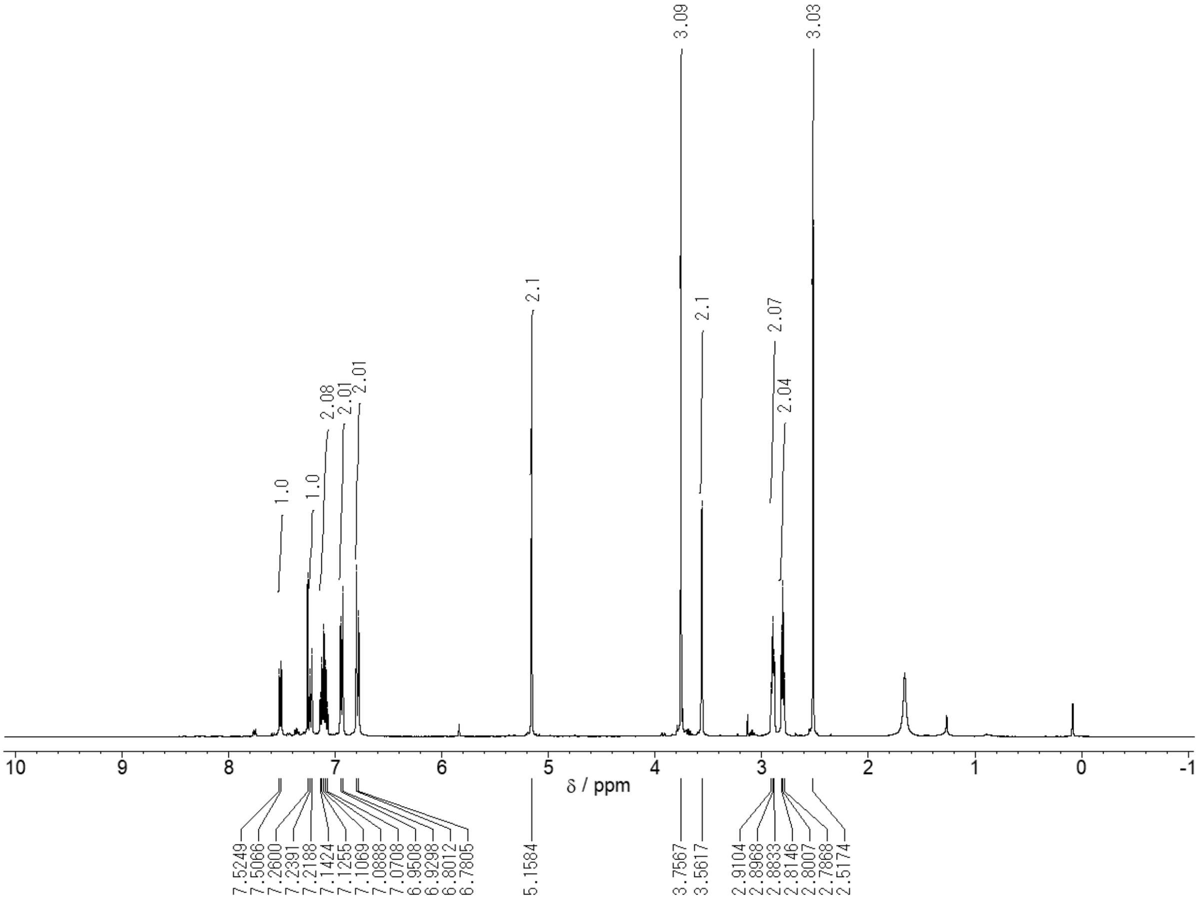
4h



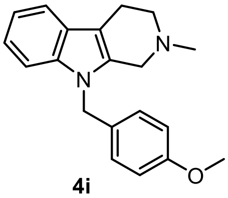
^{13}C NMR spectrum of **4h** (101 MHz, $CDCl_3$)



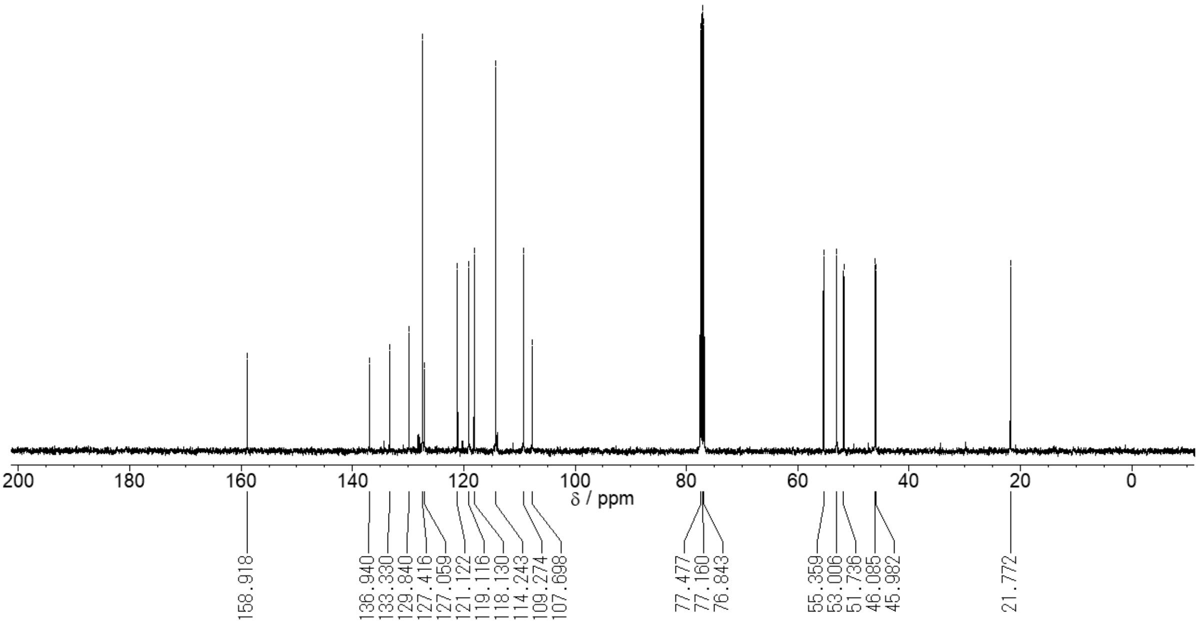
4i



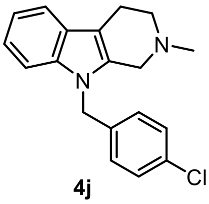
^{1}H NMR spectrum of **4i** (400 MHz, CDCl$_3$)



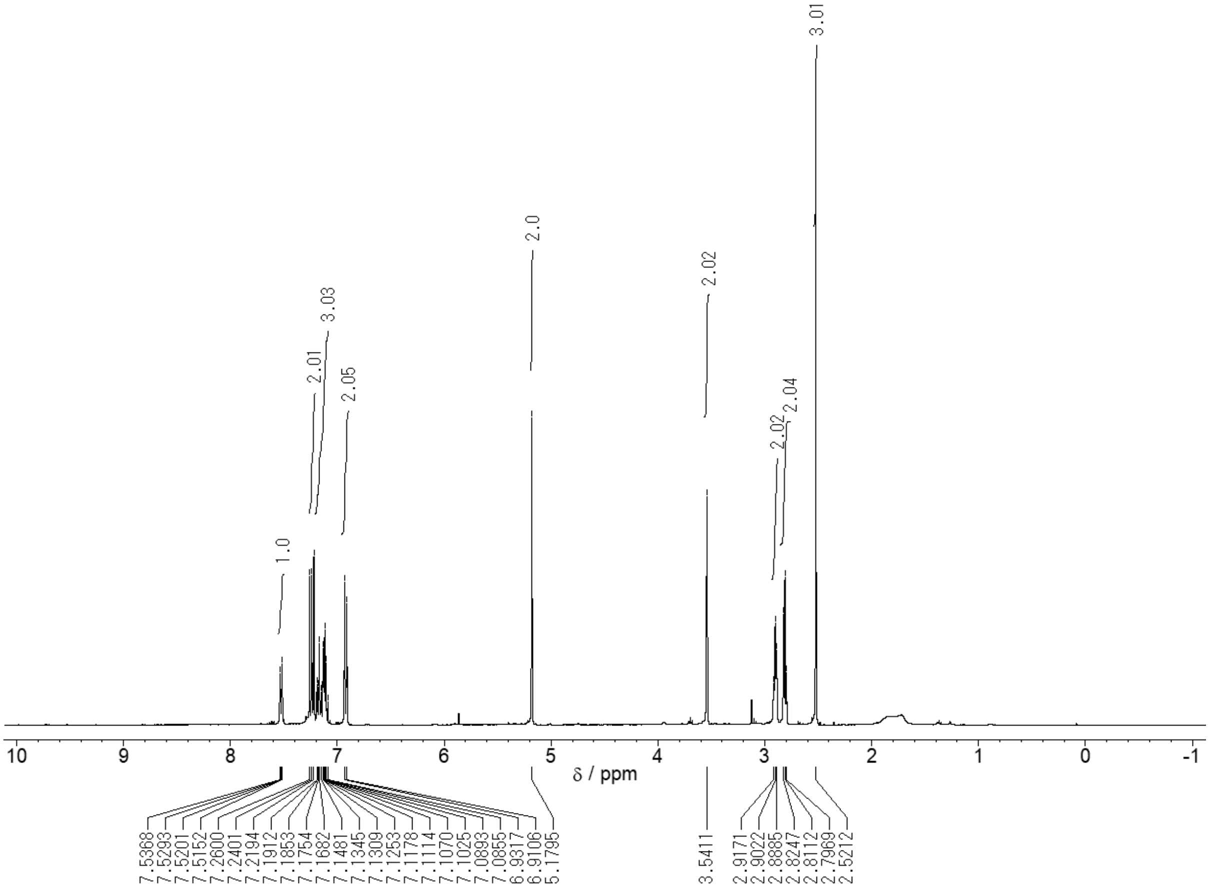
4i



^{13}C NMR spectrum of **4i** (101 MHz, $CDCl_3$)



4j



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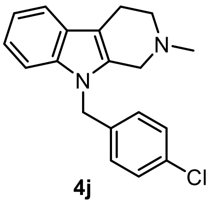
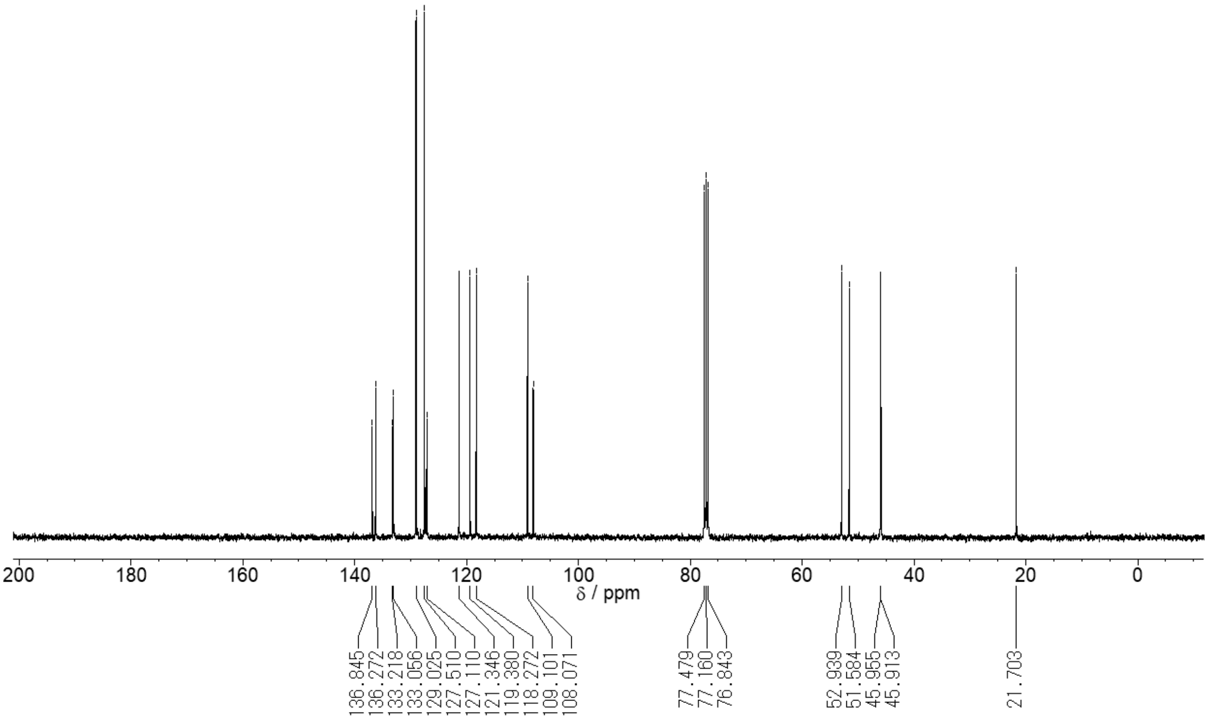
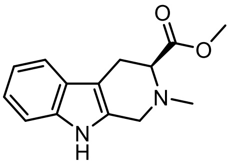


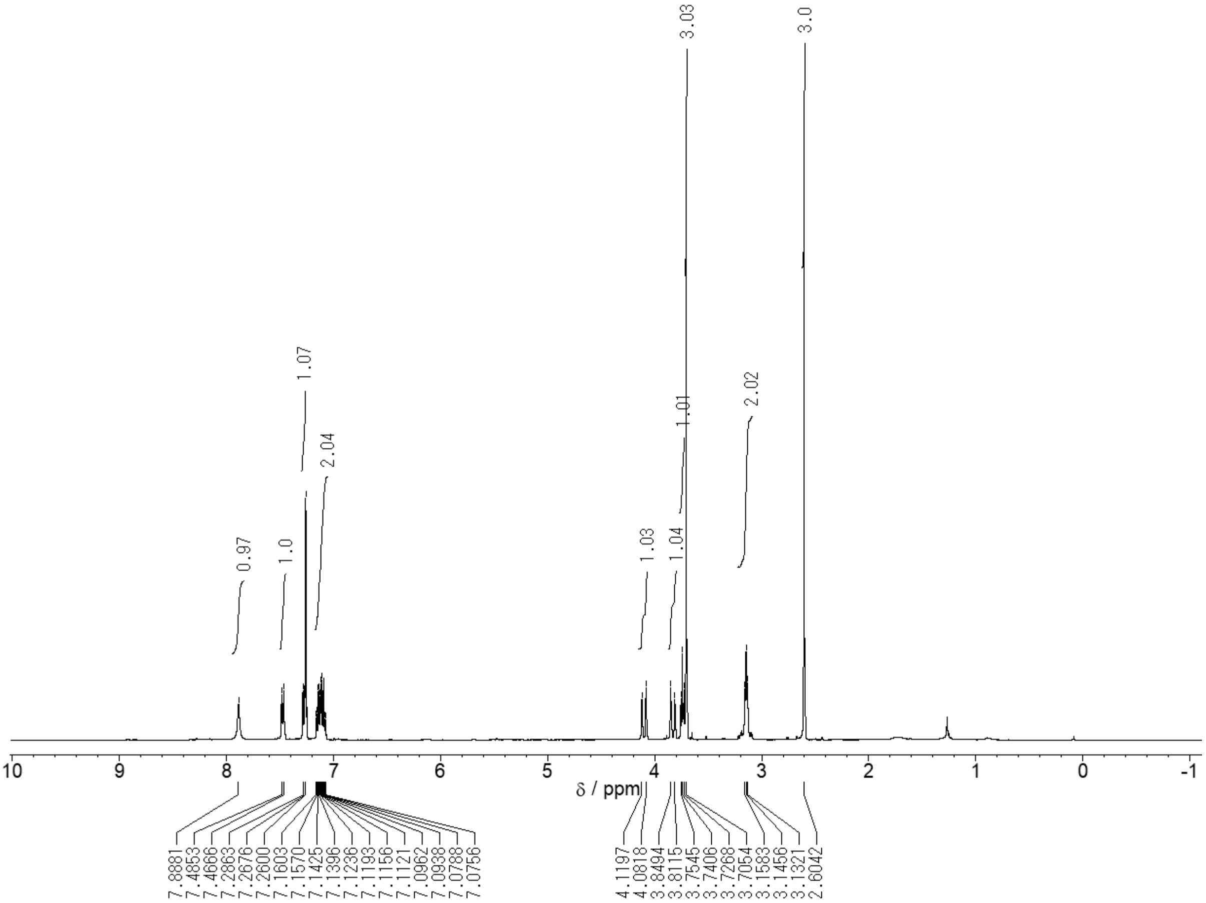
4j



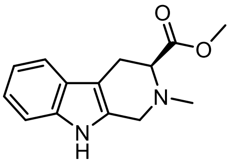
^{13}C NMR spectrum of **4j** (101 MHz, $CDCl_3$)



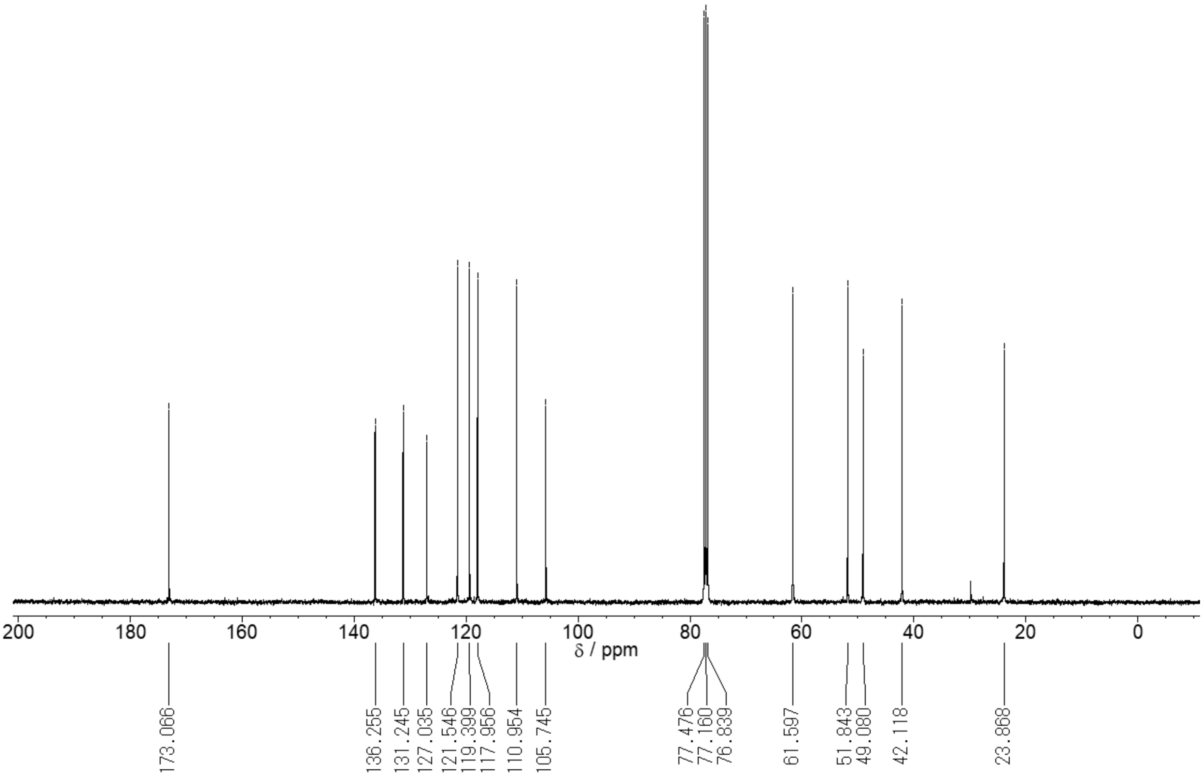
(*S*)-**4k**



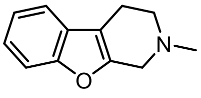
^{1}H NMR spectrum of (*S*)-**4k** (400 MHz, CDCl$_3$)



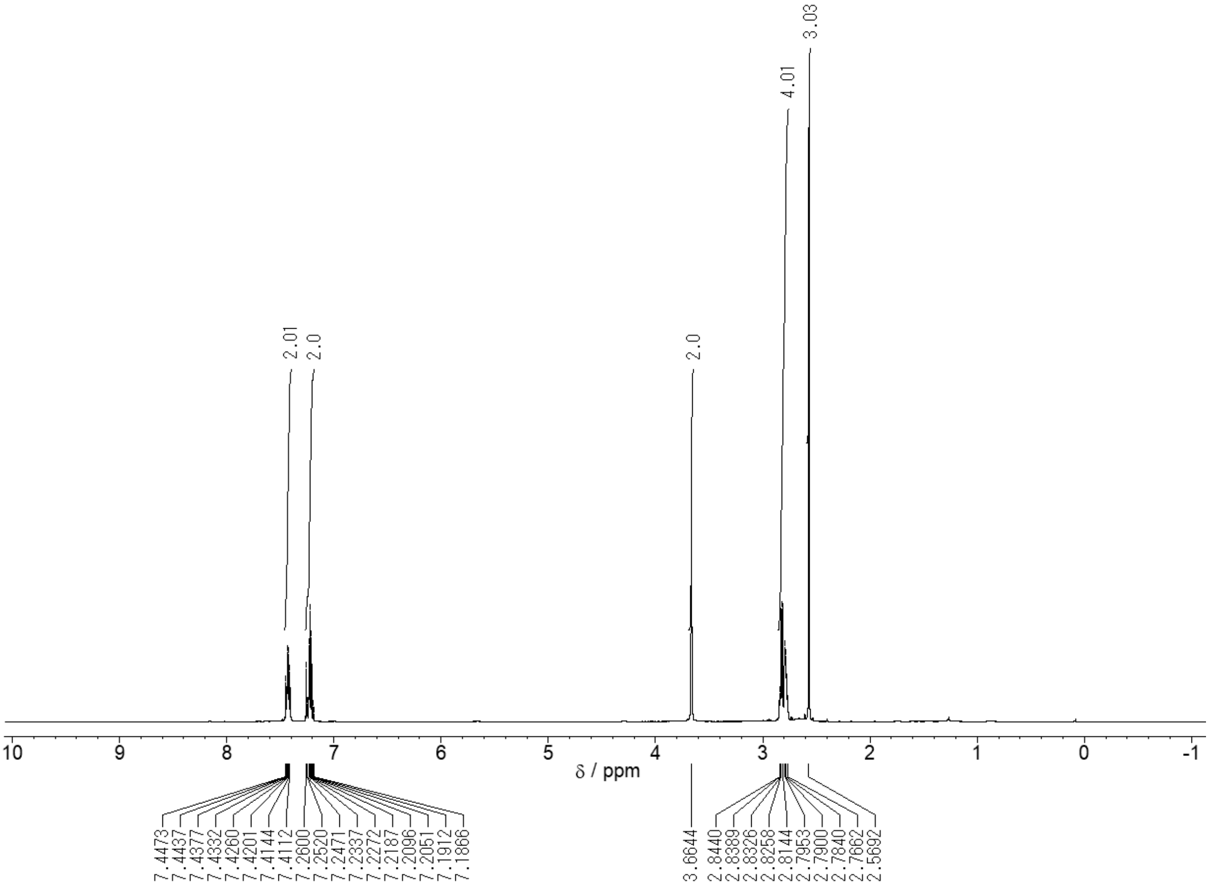
(*S*)-**4k**



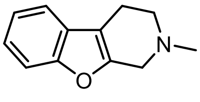
^{13}C NMR spectrum of (*S*)-**4k** (101 MHz, $CDCl_3$)



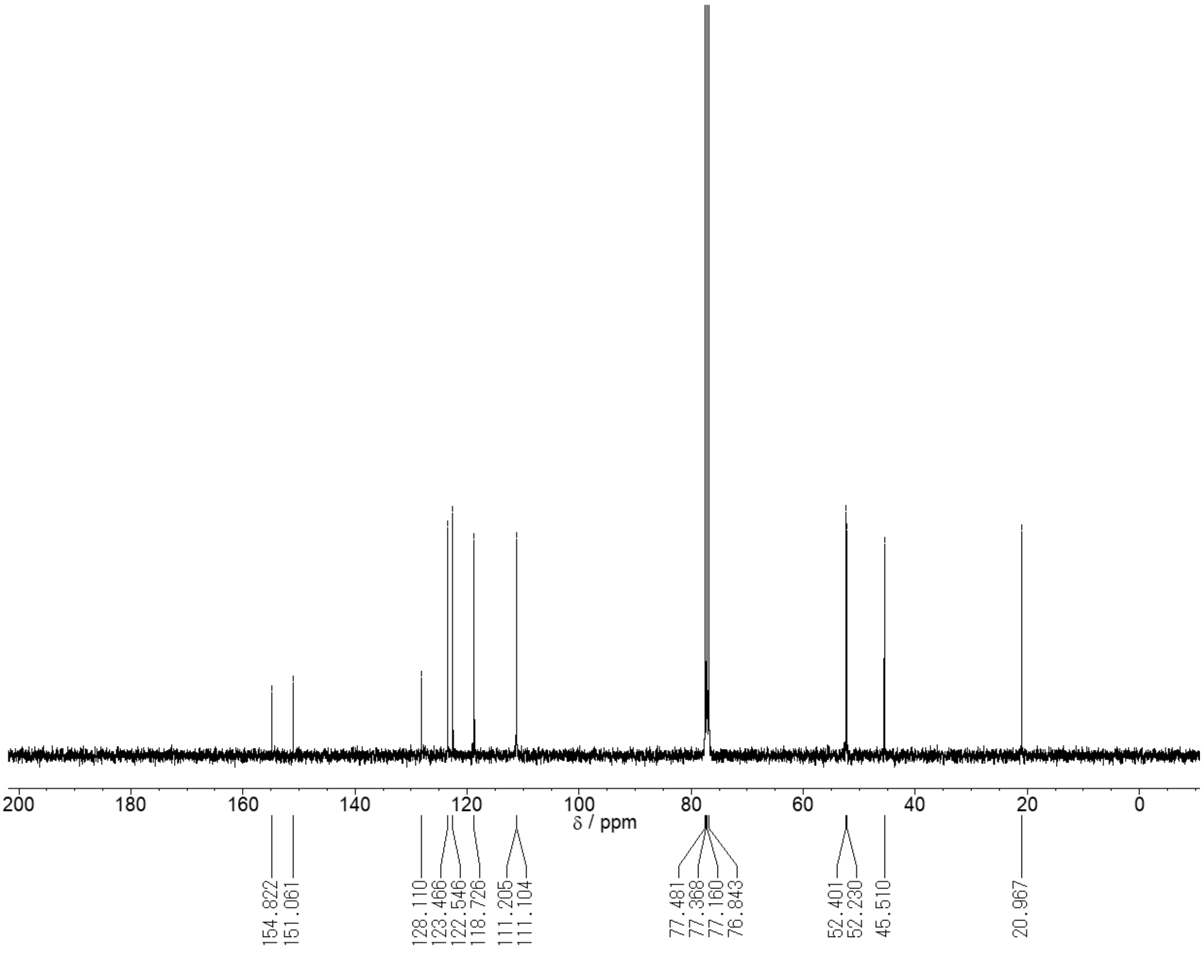
4l



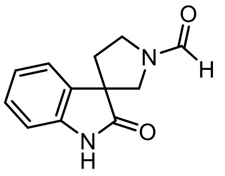
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



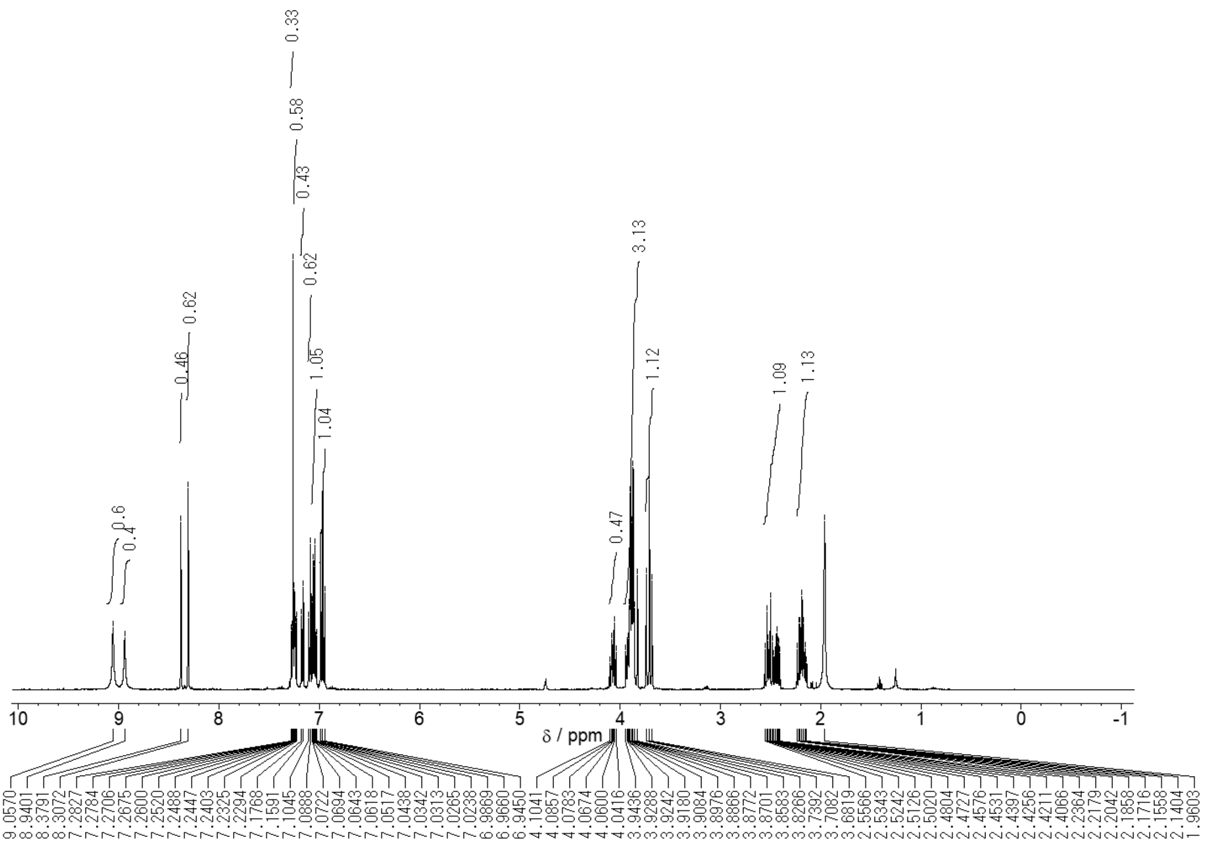
4l



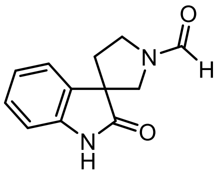
^{13}C NMR spectrum of **4l** (101 MHz, CDCl$_3$)



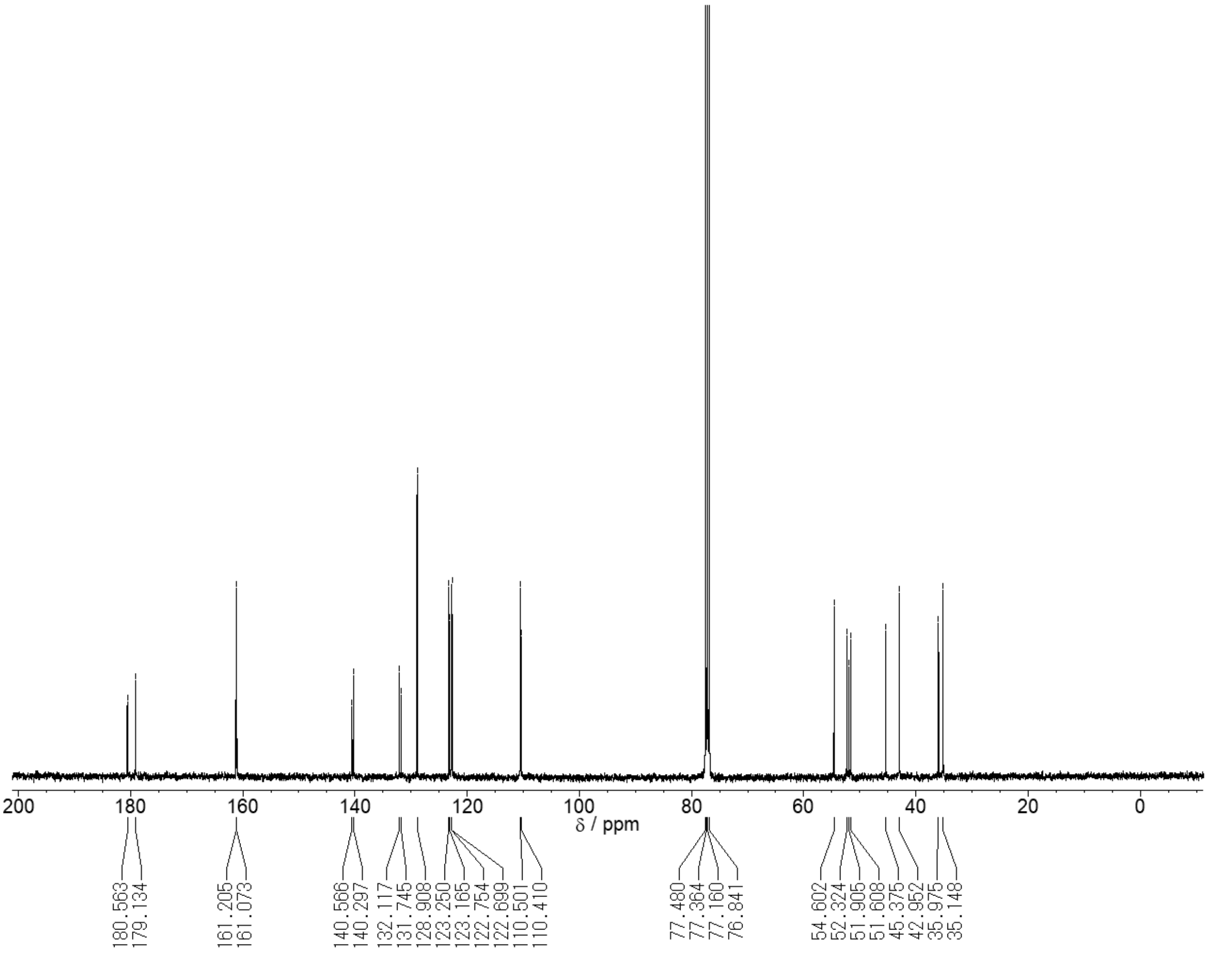
5a



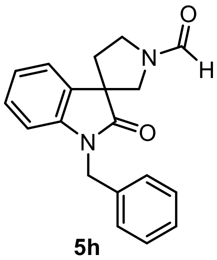
^{1}H NMR spectrum of **5a** (400 MHz, CDCl$_3$)



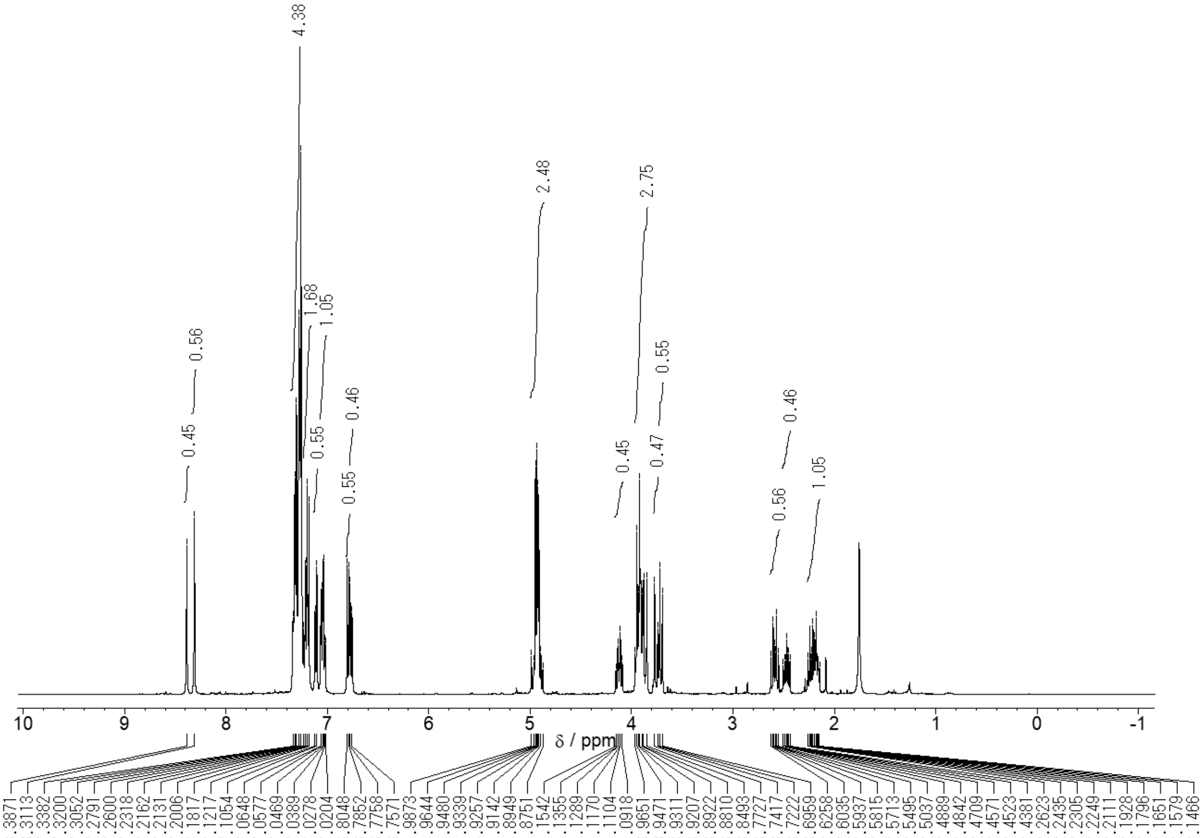
5a



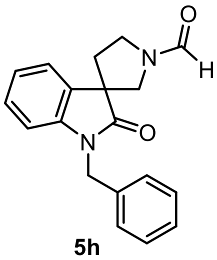
^{13}C NMR spectrum of **5a** (101 MHz, CDCl$_3$)



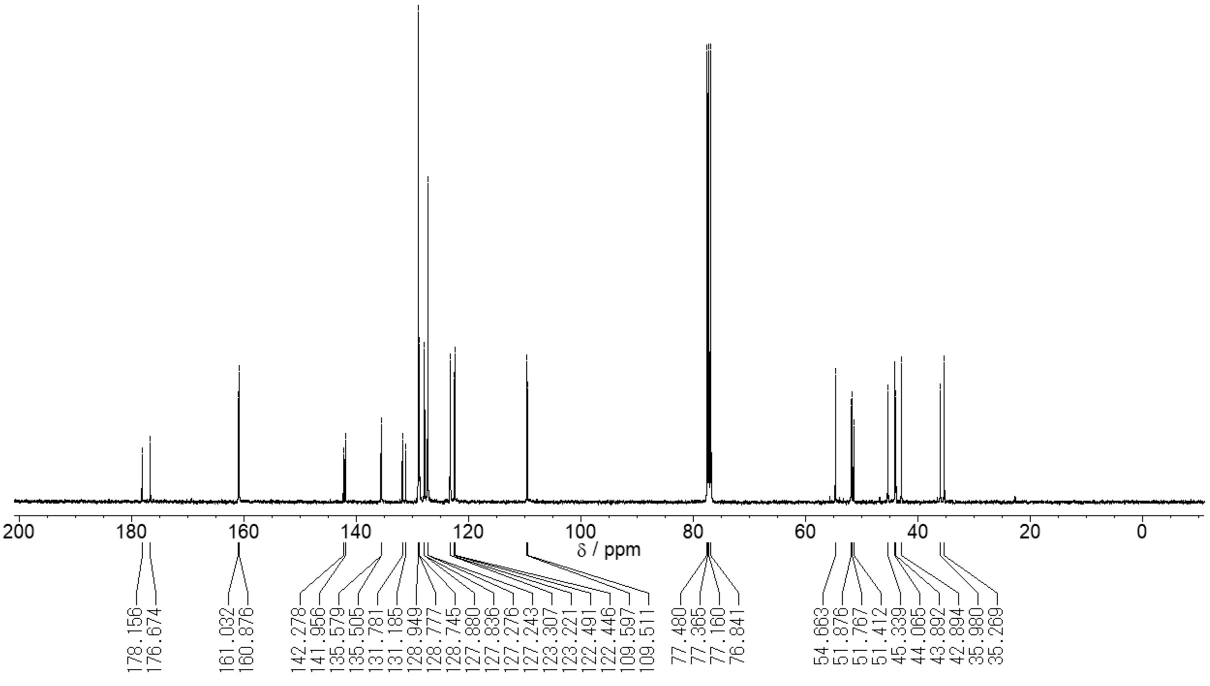
5h



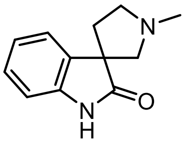
^{1}H NMR spectrum of **5h** (400 MHz, CDCl$_3$)



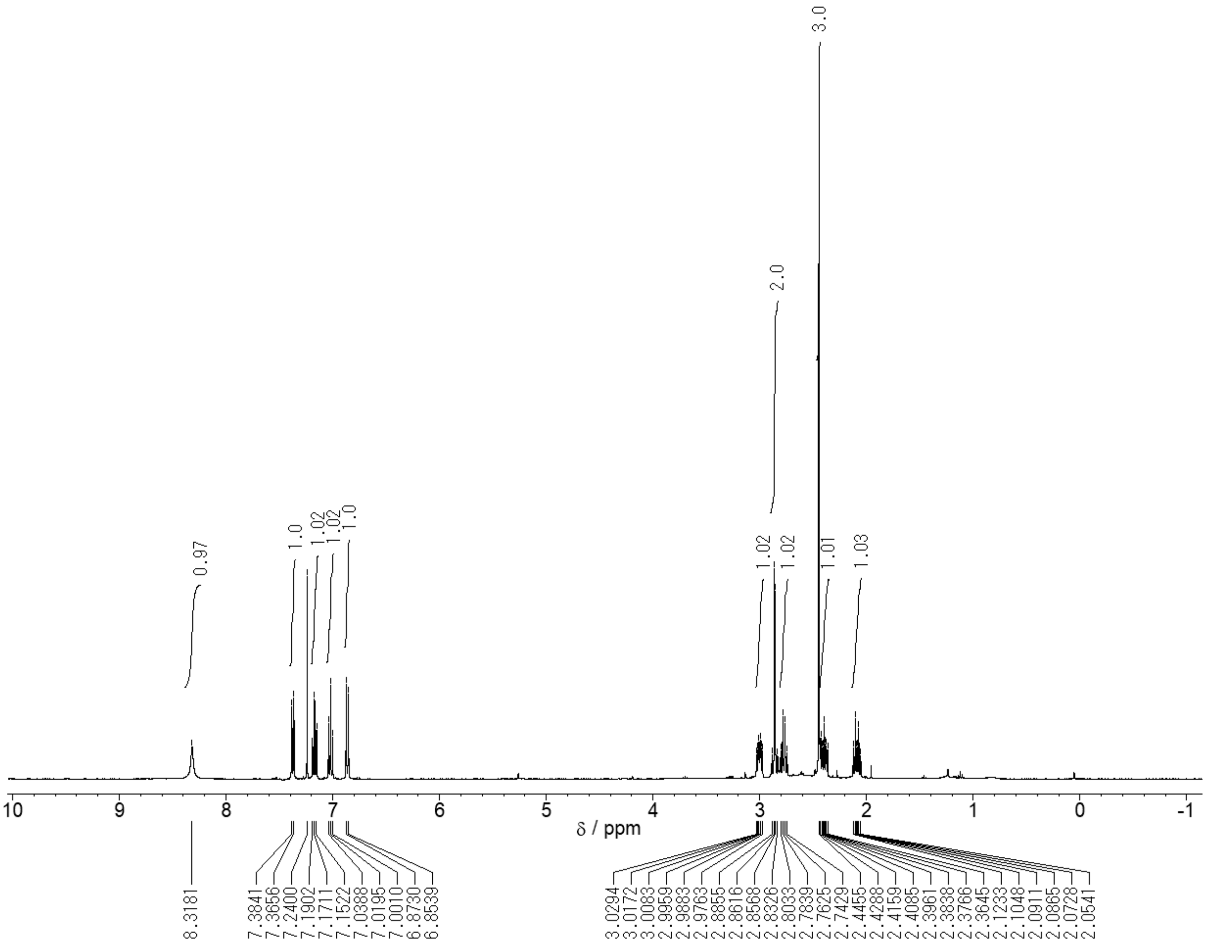
5h



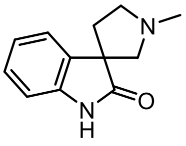
^{13}C NMR spectrum of **5h** (101 MHz, CDCl$_3$)



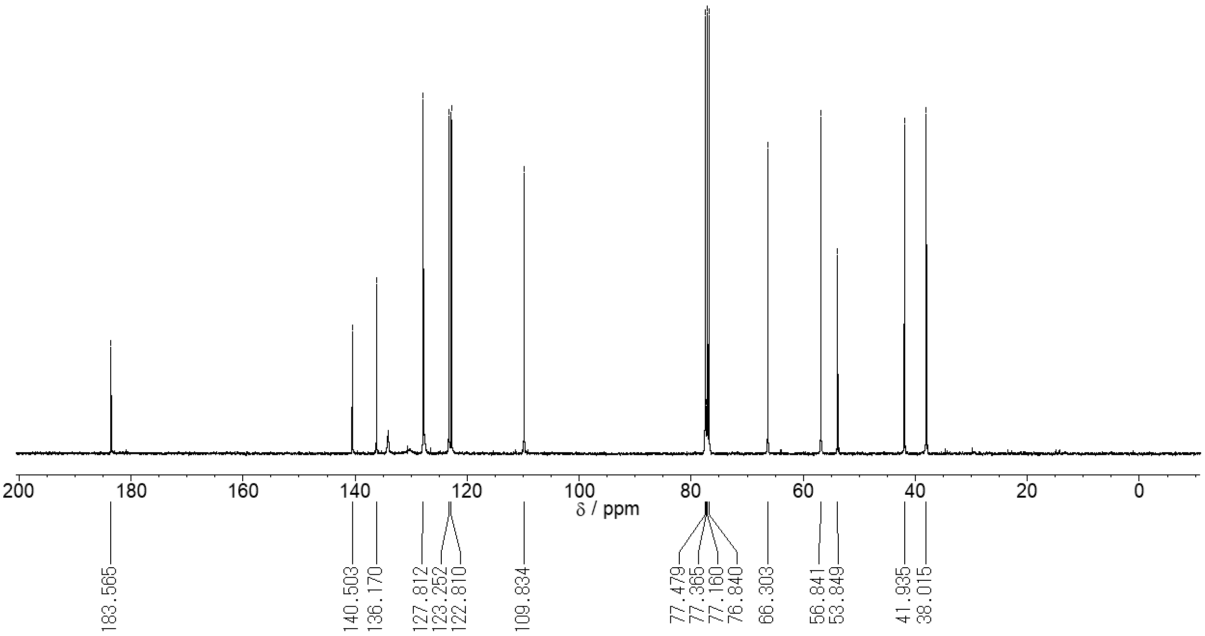
6a



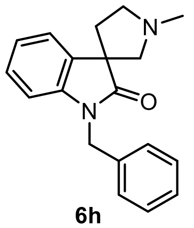
^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)



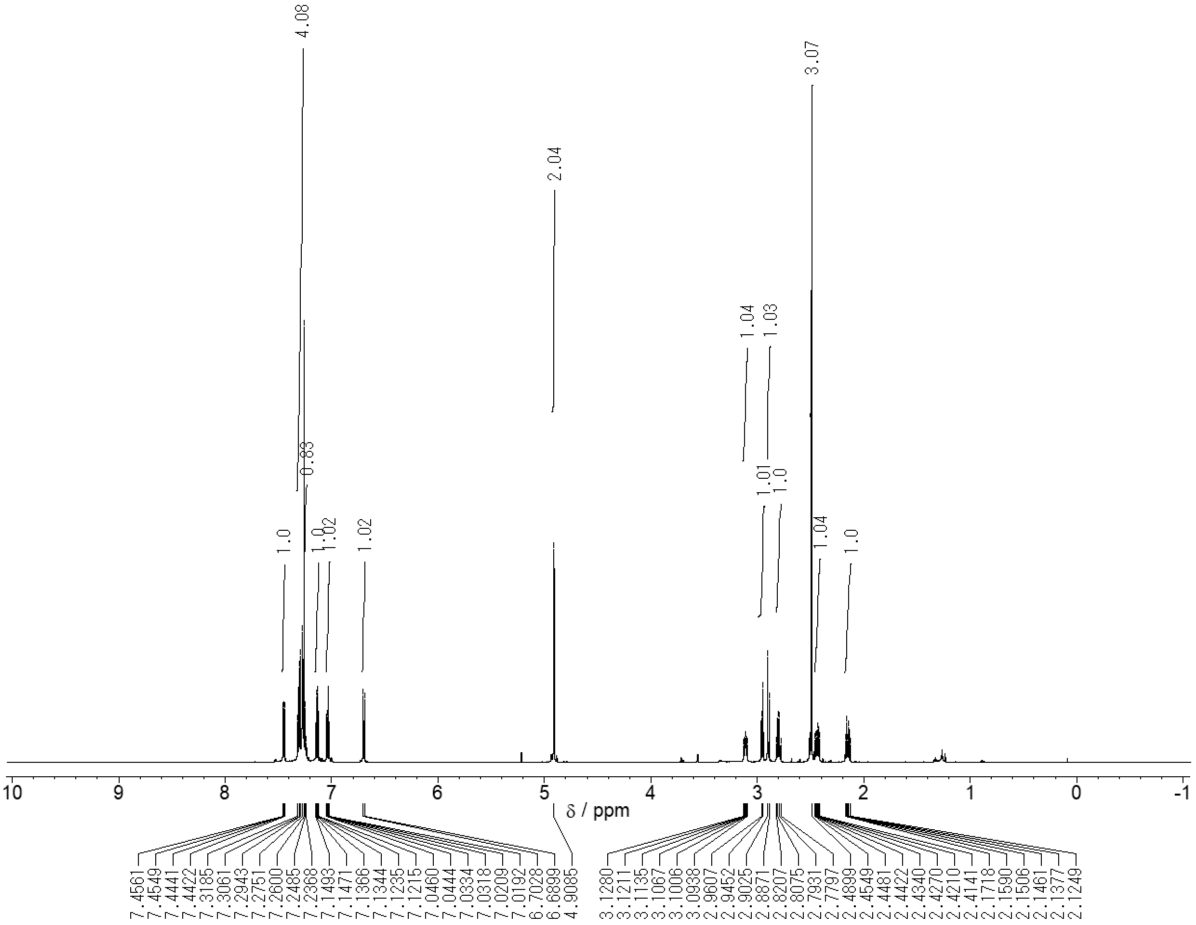
6a



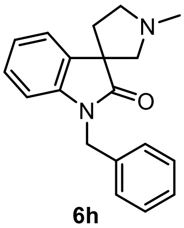
^{13}C NMR spectrum of **6a** (101 MHz, $CDCl_3$)



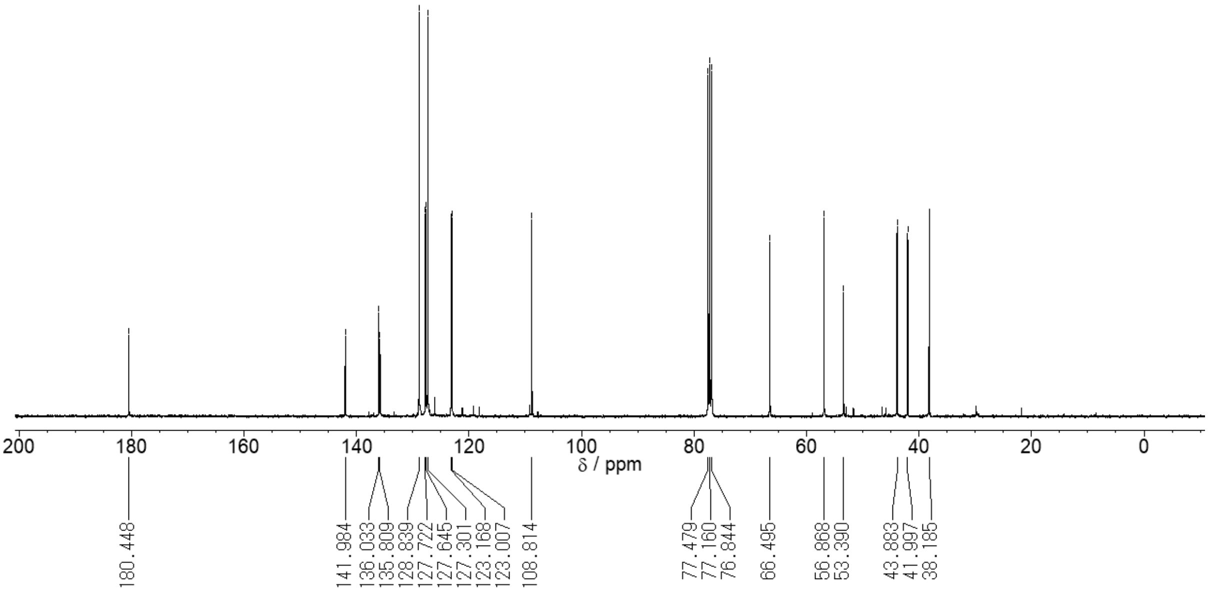
6h



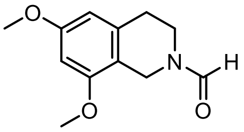
^{1}H NMR spectrum of **6h** (600 MHz, $CDCl_3$)



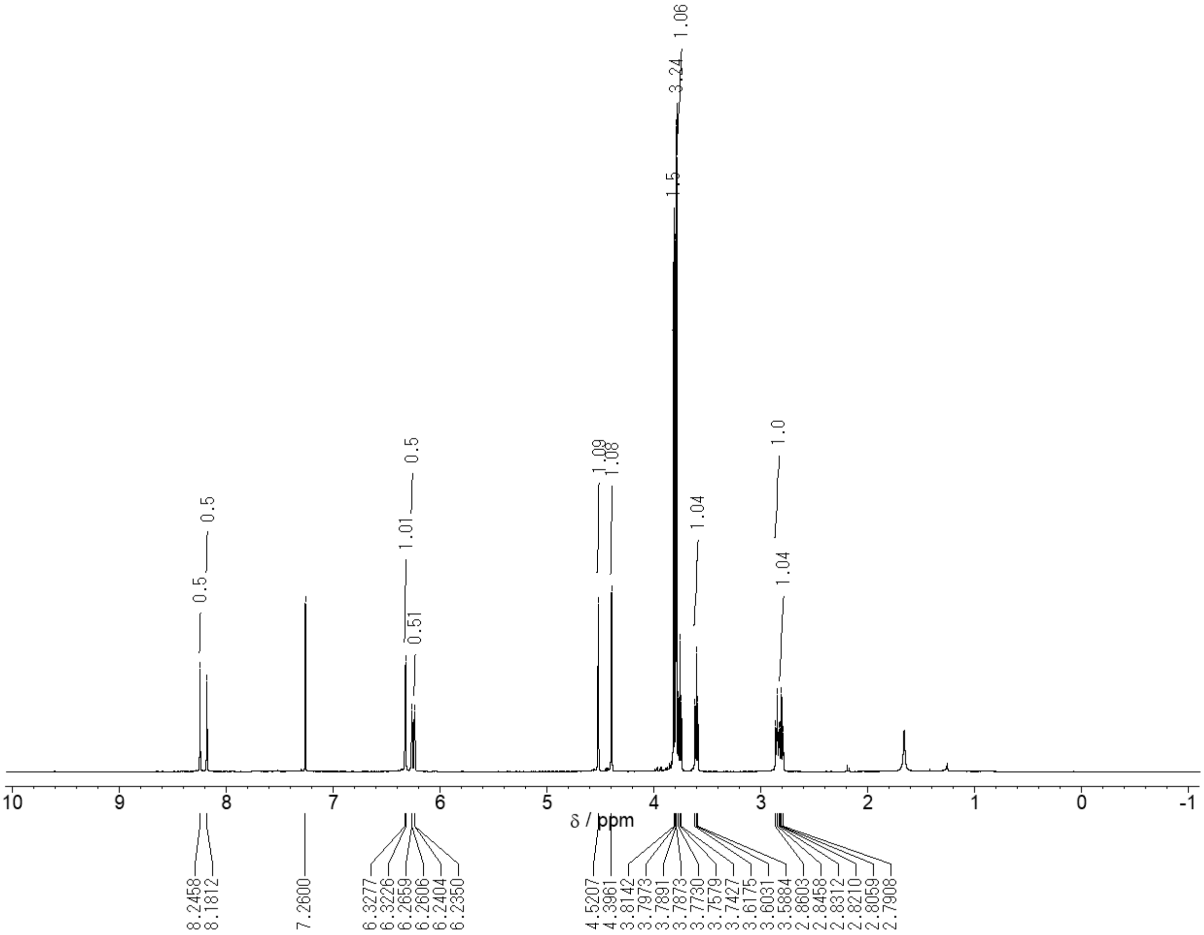
6h



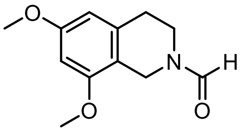
^{13}C NMR spectrum of **6h** (101 MHz, CDCl$_3$)



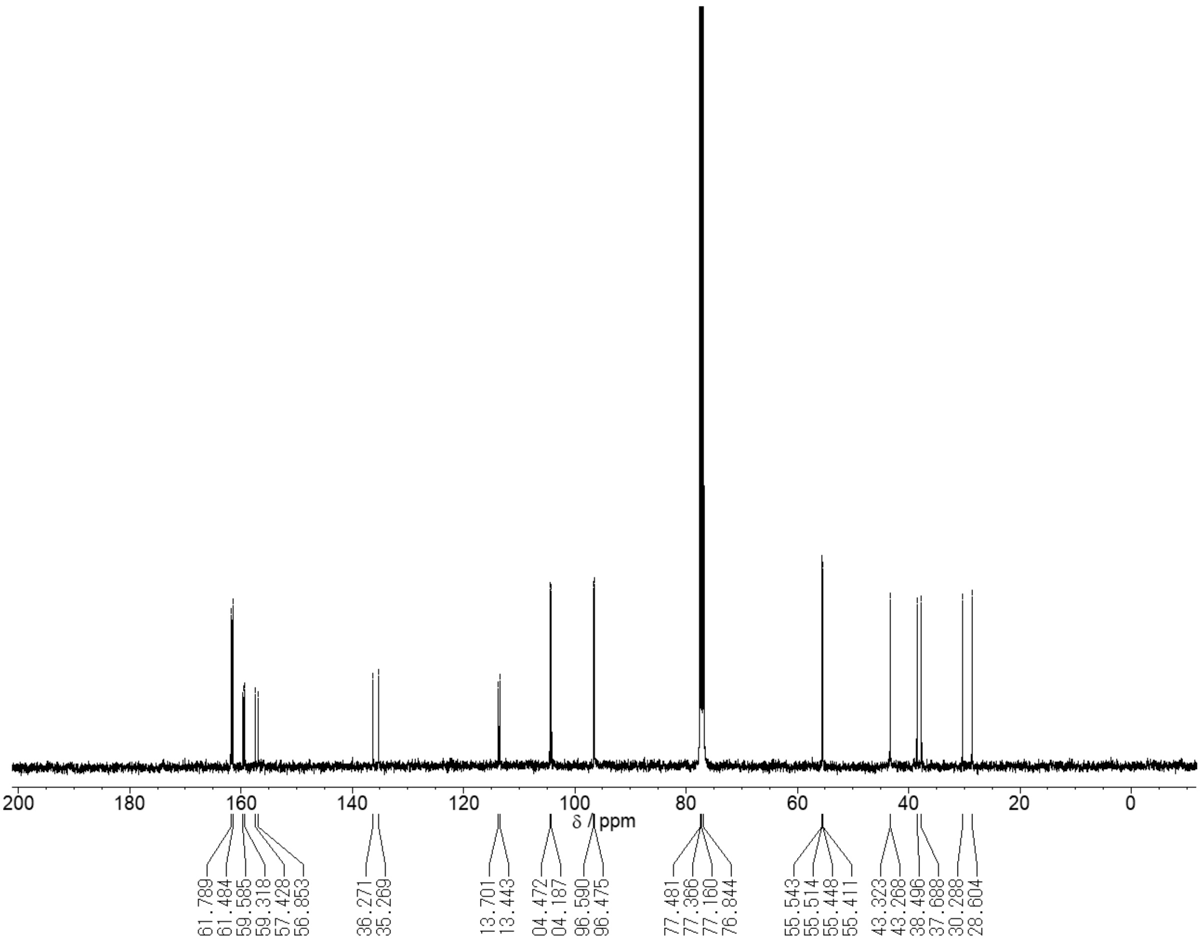
7



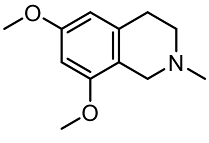
^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



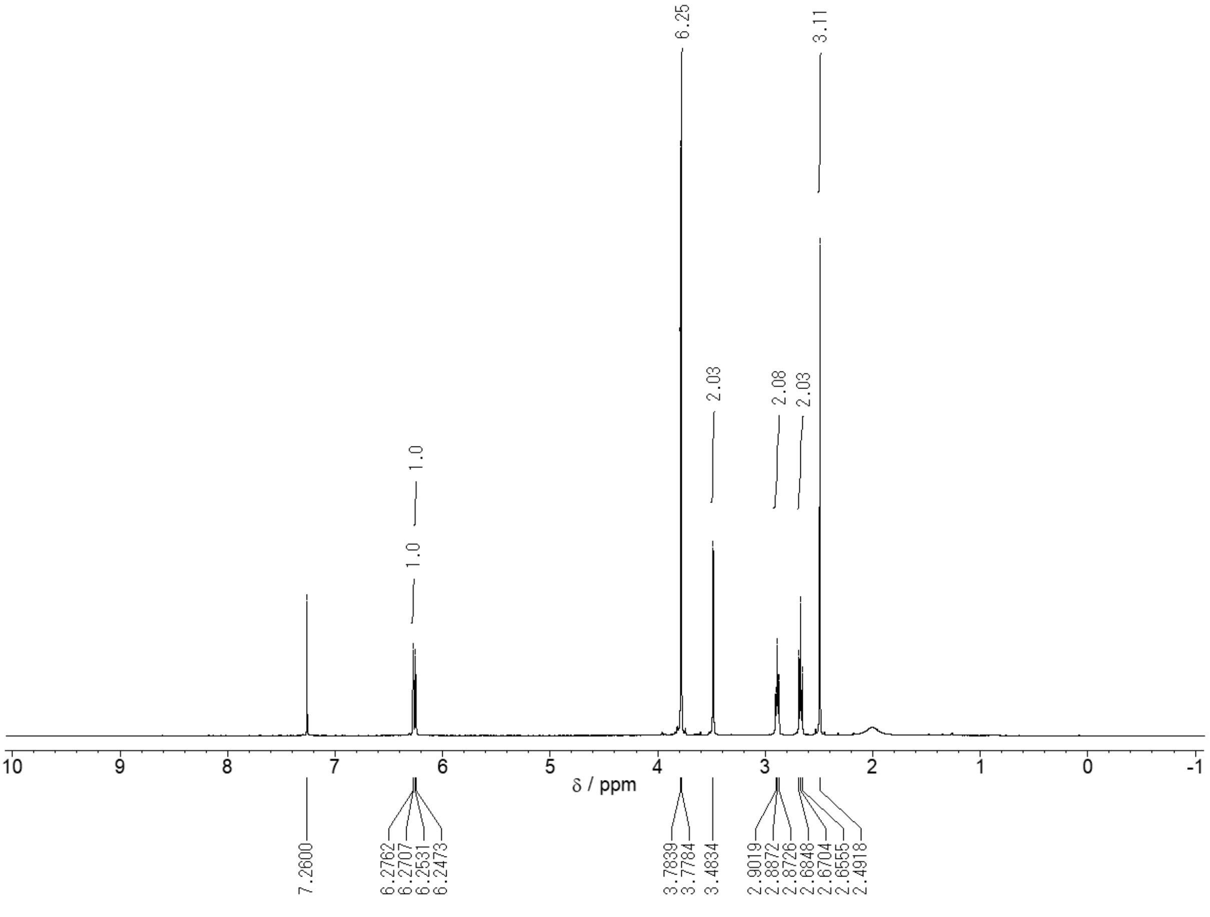
7



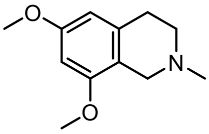
^{13}C NMR spectrum of **7** (101 MHz, $CDCl_3$)



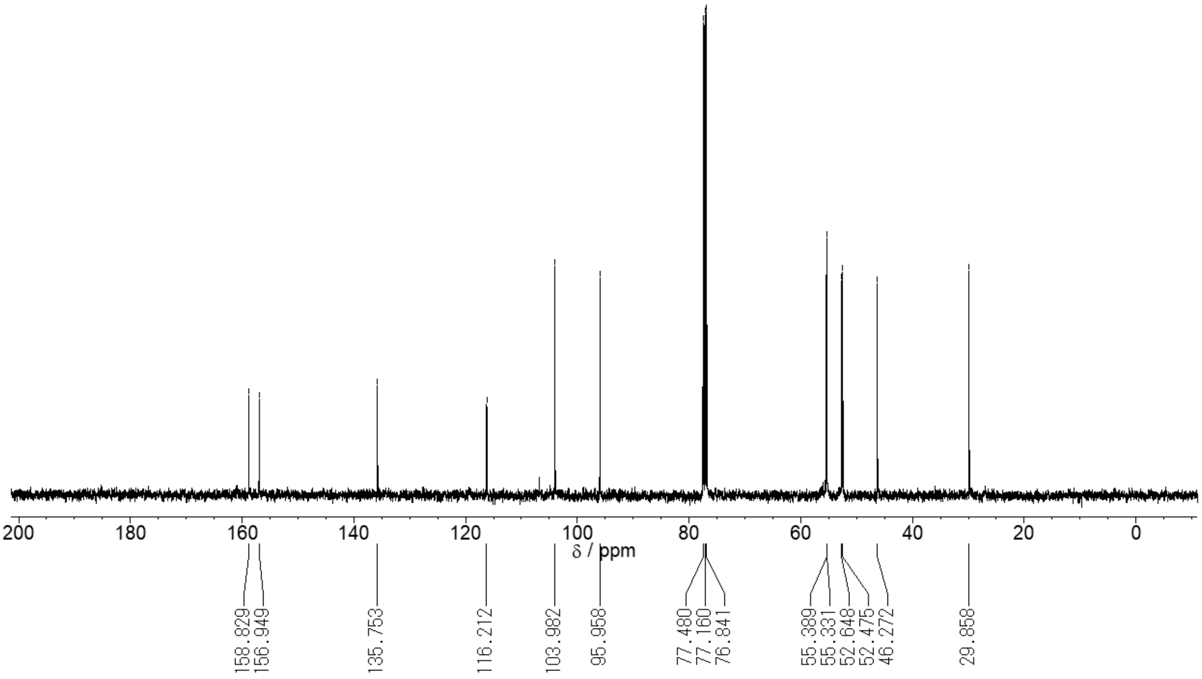
8



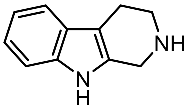
^{1}H NMR spectrum of **8** (400 MHz, CDCl$_3$)



8



^{13}C NMR spectrum of **8** (101 MHz, CDCl$_3$)



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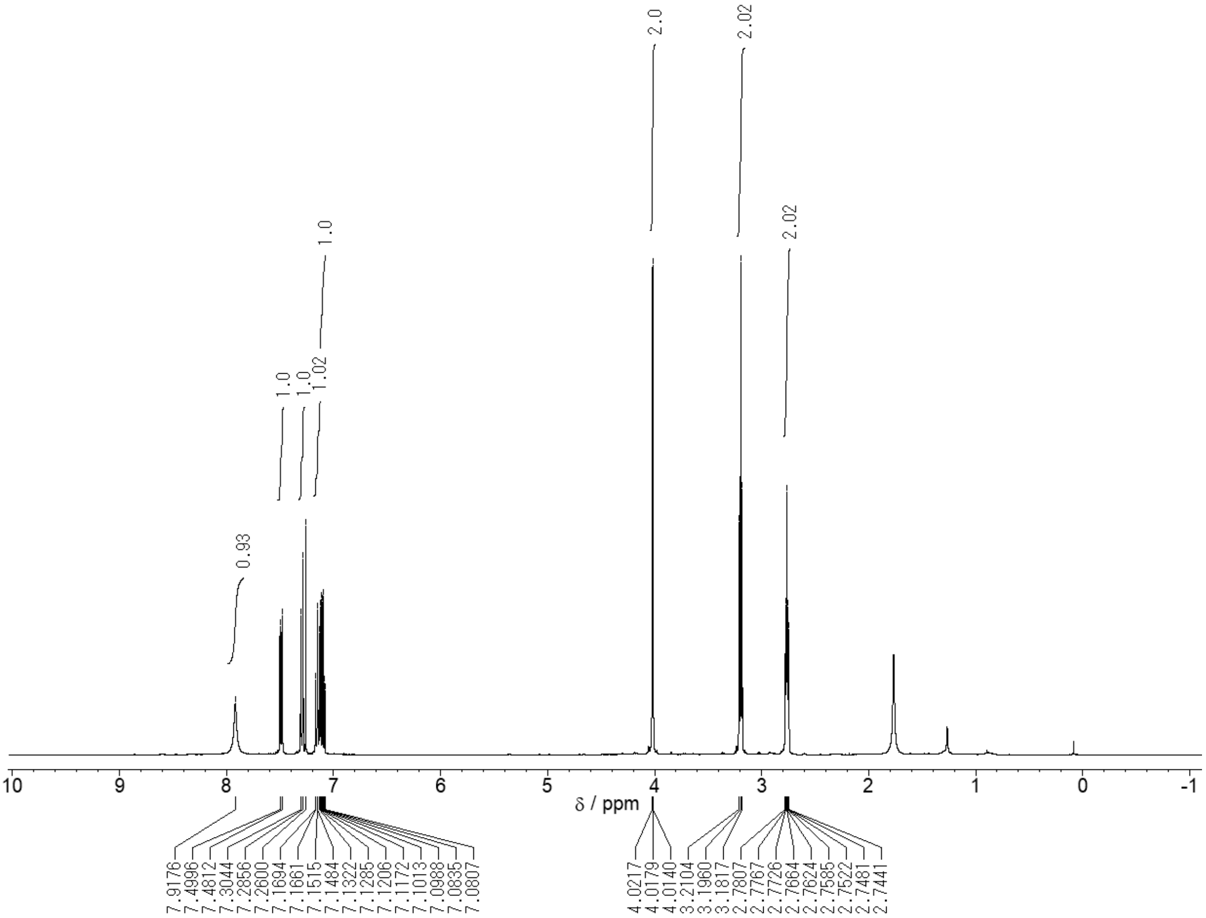
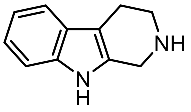
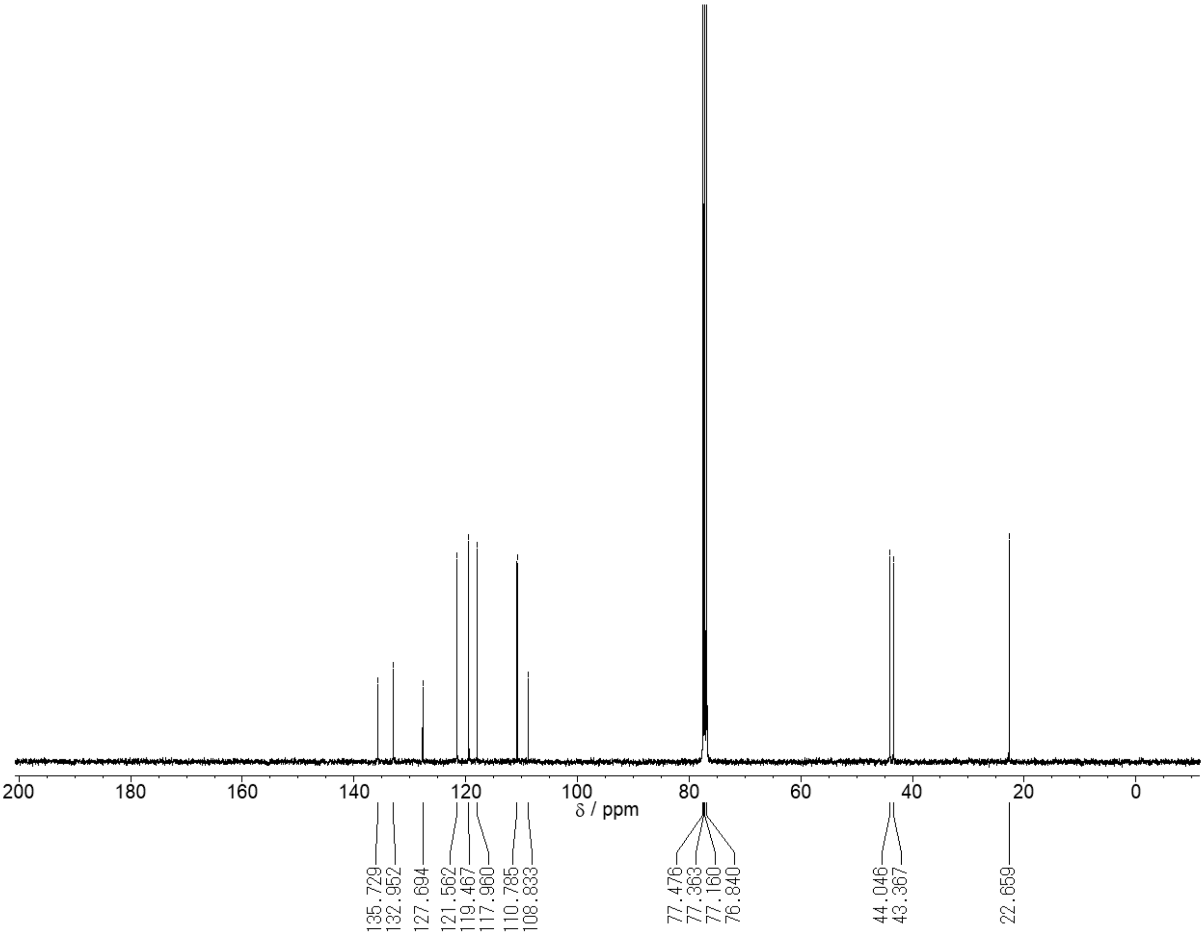


^{1}H NMR spectrum of **9** (400 MHz, CDCl$_3$)



9



^{13}C NMR spectrum of **9** (101 MHz, $CDCl_3$)

11. Coordinates of optimized structures

Coordinates of **R** (0 imaginary frequencies, –688.81980 hartree)

C	3.281913	-2.030317	0.344252
C	4.384955	-1.303839	-0.160187
C	4.279620	0.052474	-0.458988
C	3.039436	0.668375	-0.243264
C	1.911737	-0.043418	0.260368
C	2.051516	-1.414395	0.555906
N	2.645004	1.975626	-0.436545
C	1.320320	2.110127	-0.072440
C	0.823429	0.901200	0.360658
C	-0.580231	0.626259	0.824050
C	-1.417921	-0.082805	-0.252799
N	-2.807346	-0.366320	0.207647
H	3.399808	-3.086446	0.569168
H	5.332126	-1.812006	-0.316093
H	5.126908	0.612595	-0.843635
H	1.213660	-1.986216	0.945604
H	3.231764	2.723154	-0.775731
H	0.827049	3.069600	-0.145806
H	-0.562273	0.005199	1.729334
H	-1.068320	1.569292	1.094582
H	-1.496180	0.536121	-1.149318
H	-0.969440	-1.038821	-0.534162
H	-2.801889	-0.891339	1.085369
H	-3.336707	0.499823	0.392045
C	-3.739845	-1.200036	-0.817657
O	-4.979189	-1.254187	-0.357736
H	-3.581848	-0.632101	-1.755760
H	-3.201246	-2.162647	-0.886656
O	-5.272500	1.251833	0.241578
H	-5.750528	1.381310	1.070682
H	-5.342559	0.264417	0.012530

Coordinates of **I1_TS** (1 imaginary frequency, –688.81439 hartree)

C	3.277397	-2.026163	0.320707

C	4.369987	-1.279406	-0.176834
C	4.245488	0.078065	-0.462595
C	2.996848	0.674357	-0.240806
C	1.879485	-0.058071	0.256044
C	2.038479	-1.429736	0.538331
N	2.584089	1.977832	-0.421003
C	1.257980	2.090415	-0.054955
C	0.778328	0.870271	0.366099
C	-0.620655	0.570847	0.828228
C	-1.454096	-0.120157	-0.262332
N	-2.838363	-0.416107	0.211762
H	3.410280	-3.082598	0.535574
H	5.324215	-1.772618	-0.337611
H	5.084670	0.653695	-0.842007
H	1.208824	-2.016945	0.922668
H	3.160539	2.736824	-0.752376
H	0.751453	3.043653	-0.118591
H	-0.591572	-0.070967	1.718622
H	-1.118330	1.501541	1.122324
H	-1.546698	0.522552	-1.140550
H	-0.996769	-1.063491	-0.571745
H	-2.812365	-0.951892	1.082862
H	-3.412974	0.464572	0.406768
C	-3.739052	-1.171333	-0.788686
O	-5.035823	-1.085989	-0.363088
H	-3.544064	-0.674155	-1.751470
H	-3.376180	-2.203926	-0.830677
O	-4.896825	1.245448	0.247767
H	-5.320959	1.491903	1.080053
H	-5.160098	0.019560	-0.075786

Coordinates of **I1** (0 imaginary frequencies, –688.83481 hartree)

C	3.272333	-2.008223	0.395557
C	4.371982	-1.264564	-0.091309
C	4.244101	0.084423	-0.414304
C	2.985271	0.675636	-0.240524
C	1.860421	-0.053858	0.244739

C	2.023354	-1.416765	0.564820
N	2.566756	1.970062	-0.463652
C	1.228671	2.078277	-0.134056
C	0.746880	0.865092	0.303843
C	-0.659746	0.562072	0.739948
C	-1.480665	-0.176827	-0.330476
N	-2.837820	-0.474257	0.161562
H	3.407697	-3.058023	0.639834
H	5.334177	-1.753282	-0.214411
H	5.088800	0.657391	-0.785591
H	1.187173	-2.000858	0.939685
H	3.145153	2.725832	-0.798618
H	0.716806	3.025679	-0.233639
H	-0.639939	-0.048627	1.653399
H	-1.176839	1.493419	0.997076
H	-1.575595	0.457094	-1.219297
H	-0.951876	-1.092098	-0.639136
H	-2.772752	-1.040604	1.007682
H	-3.939730	0.966074	0.485009
C	-3.668574	-1.191998	-0.812010
O	-5.005714	-1.288874	-0.354005
H	-3.607800	-0.643532	-1.761671
H	-3.331841	-2.223191	-0.980585
O	-4.771848	1.507814	0.417554
H	-4.997888	1.775474	1.318187
H	-5.311784	-0.382503	-0.159059

Coordinates of **I2_TS** (1 imaginary frequency, –688.79103 hartree)

C	3.035433	-2.107534	-0.159664
C	4.227179	-1.351634	-0.074566
C	4.196825	0.040081	-0.027558
C	2.941387	0.661669	-0.065015
C	1.725816	-0.078428	-0.146540
C	1.790463	-1.485531	-0.195630
N	2.605307	1.999051	-0.042757
C	1.232431	2.124635	-0.109605
C	0.645461	0.880458	-0.173717

C	-0.827090	0.589917	-0.240455
C	-1.391906	0.145253	1.125749
N	-2.838265	-0.093090	1.062665
C	-3.410062	-1.243603	1.071563
O	-4.239458	-1.153520	-1.326683
H	3.095700	-3.191432	-0.197584
H	5.183869	-1.865135	-0.047240
H	5.111673	0.622215	0.034462
H	0.883840	-2.080684	-0.263913
H	3.256759	2.768454	-0.000847
H	0.771596	3.102849	-0.111905
H	-1.365681	1.483799	-0.572741
H	-1.030993	-0.197980	-0.974880
H	-0.911575	-0.771351	1.475287
H	-1.225008	0.926734	1.872119
H	-3.466111	0.690382	0.777152
H	-2.820259	-2.144088	1.211831
H	-4.486226	-1.297467	1.027127
H	-5.019189	-1.681259	-1.548145
O	-4.658248	1.131245	-0.501866
H	-4.576402	0.119006	-0.927513
H	-5.585253	1.300718	-0.291535

Coordinates of **I2** (0 imaginary frequencies, –688.83116 hartree)

C	3.538616	1.672227	0.781347
C	4.575280	0.769779	0.449544
C	4.294043	-0.519349	0.002869
C	2.945999	-0.887031	-0.107028
C	1.882987	0.006177	0.217298
C	2.200998	1.302876	0.668790
N	2.372671	-2.075968	-0.505326
C	0.997082	-1.962151	-0.439082
C	0.644396	-0.704461	-0.003395
C	-0.751215	-0.179414	0.185602
C	-1.212545	0.734346	-0.969974
N	-2.590205	1.176944	-0.756756
C	-2.827573	2.422291	-0.654227

O	-5.967731	-0.867082	1.782414
H	3.793639	2.669353	1.128847
H	5.609735	1.086601	0.546085
H	5.089940	-1.214261	-0.249090
H	1.414774	2.006963	0.927606
H	2.872897	-2.906425	-0.784754
H	0.366579	-2.799024	-0.706633
H	-1.453691	-1.015713	0.271232
H	-0.818401	0.387144	1.123261
H	-0.530915	1.589754	-1.080309
H	-1.191629	0.160811	-1.903804
H	-3.919294	-0.012895	-0.699070
H	-2.043623	3.185424	-0.726654
H	-3.850327	2.760568	-0.489283
H	-5.844030	-1.774844	2.087495
O	-4.653827	-0.686791	-0.646791
H	-5.499022	-0.811910	0.918398
H	-5.229834	-0.519144	-1.404207

Coordinates of **I2'** (0 imaginary frequencies, –765.037770 hartree)

N	0.646265	-0.292345	0.489855
N	-2.332433	2.857778	-0.735387
C	-0.211243	-1.311375	0.132138
C	0.070190	-2.593000	-0.364109
C	-1.007418	-3.431217	-0.639426
C	-2.339569	-3.008714	-0.423618
C	-2.618675	-1.736938	0.069299
C	-1.548428	-0.864447	0.353116
C	-1.455614	0.481694	0.865061
C	-2.581418	1.391269	1.236937
C	-3.288971	2.031532	0.003719
C	-1.443105	2.387014	-1.534770
C	-0.098560	0.774107	0.916963
H	1.693675	-0.313717	0.434827
H	-2.274466	3.841786	-0.477614
H	1.092976	-2.919563	-0.526635
H	-0.821488	-4.429559	-1.025050

H	-3.155788	-3.690121	-0.645908
H	-3.647820	-1.429307	0.235141
H	-2.233789	2.192453	1.896674
H	-3.365897	0.850316	1.778121
H	-3.663588	1.259724	-0.670160
H	-4.114471	2.672560	0.312988
H	-0.686643	3.049840	-1.939433
H	-1.487921	1.345912	-1.831433
H	0.386210	1.678718	1.260265
C	5.630692	0.201926	-0.000604
C	4.121204	0.470990	-0.031048
O	3.376548	-0.465092	0.419252
O	3.710713	1.568470	-0.495078
H	5.868258	-0.622765	-0.682445
H	5.938323	-0.111580	1.002425
H	6.203007	1.083207	-0.298383

Coordinates of **I3_TS** (1 imaginary frequency, –765.033511 hartree)

N	0.363740	-0.580035	0.625861
N	-0.405053	2.988358	-0.696653
C	-0.737099	-1.286115	0.236095
C	-0.842023	-2.622964	-0.199151
C	-2.102364	-3.088512	-0.537925
C	-3.255448	-2.259549	-0.463809
C	-3.160292	-0.944147	-0.046196
C	-1.888937	-0.436498	0.316216
C	-1.435995	0.832002	0.774592
C	-2.162891	2.122688	0.813388
C	-1.837815	2.943621	-0.502853
C	0.253860	1.825519	-0.841055
C	-0.020138	0.724959	0.890458
H	1.377447	-0.881525	0.581929
H	0.086821	3.732469	-0.213095
H	0.032556	-3.262414	-0.259492
H	-2.216006	-4.116790	-0.868615
H	-4.220995	-2.672138	-0.739194
H	-4.043616	-0.315086	0.012300

H	-1.862760	2.730592	1.671366
H	-3.245628	1.978282	0.856437
H	-2.303005	2.444837	-1.356917
H	-2.231616	3.957219	-0.424136
H	1.340265	1.833671	-0.784552
H	-0.195136	1.088925	-1.501556
H	0.630771	1.351156	1.486749
C	5.179345	-0.679935	-0.235484
C	3.711732	-0.318040	0.010088
O	2.974134	-1.248324	0.487328
O	3.314774	0.842962	-0.279716
H	5.243157	-1.358687	-1.094214
H	5.592702	-1.210729	0.627602
H	5.781362	0.206676	-0.446143

Coordinates of **I3** (0 imaginary frequencies, –765.041017 hartree)

N	0.354759	-0.481107	0.240343
N	-0.345324	3.140913	-0.570651
C	-0.729224	-1.239878	0.076093
C	-0.815827	-2.622101	-0.249108
C	-2.072965	-3.165477	-0.366829
C	-3.274418	-2.397613	-0.183008
C	-3.218746	-1.064488	0.127655
C	-1.934335	-0.451366	0.270960
C	-1.530109	0.839176	0.570520
C	-2.286524	2.103947	0.670833
C	-1.789556	3.051825	-0.493007
C	0.331749	1.879113	-0.696497
C	-0.046999	0.876940	0.504810
H	1.378011	-0.798283	0.175270
H	0.043524	3.713892	0.172666
H	0.079115	-3.216759	-0.393845
H	-2.170301	-4.219744	-0.608788
H	-4.232228	-2.894939	-0.293036
H	-4.122556	-0.481646	0.272061
H	-2.073969	2.608258	1.620227
H	-3.366090	1.949958	0.594164

H	-2.173597	2.662400	-1.441873
H	-2.209238	4.048162	-0.338693
H	1.415250	2.002947	-0.677788
H	0.037658	1.385193	-1.627815
H	0.440641	1.270426	1.402063
C	5.199782	-0.803111	-0.083668
C	3.742295	-0.370183	0.088769
O	2.870593	-1.310756	0.065844
O	3.475116	0.849955	0.236923
H	5.325991	-1.297647	-1.053110
H	5.465471	-1.534248	0.687331
H	5.879875	0.049096	-0.023949

Coordinates of **I3'** (0 imaginary frequencies, –765.067232 hartree)

N	-0.153408	-0.075248	0.168027
N	1.440222	3.320433	-0.270623
C	0.572849	-1.248892	0.098851
C	0.144863	-2.581895	0.134927
C	1.116937	-3.578722	0.043236
C	2.486341	-3.254805	-0.081503
C	2.910306	-1.927186	-0.118149
C	1.952780	-0.898333	-0.028973
C	2.015275	0.540095	-0.029465
C	3.182747	1.482964	-0.121443
C	2.733395	2.900560	0.299204
C	0.327935	2.442790	0.134275
C	0.720640	0.992928	0.083821
H	-1.164808	-0.009599	0.250789
H	1.510698	3.308619	-1.286650
H	-0.907726	-2.832712	0.231946
H	0.814537	-4.621826	0.069258
H	3.218013	-4.055169	-0.149580
H	3.966868	-1.690657	-0.214347
H	3.586063	1.510789	-1.145208
H	4.010058	1.157060	0.523375
H	2.636289	2.942290	1.391632
H	3.488707	3.638991	0.011603

H	-0.529755	2.645835	-0.517304
H	0.017097	2.716397	1.153444
H	-3.362460	0.078043	-1.729234
C	-5.549592	0.130030	0.624517
C	-4.194245	0.102734	-0.020087
O	-3.127969	0.088835	0.577398
O	-4.265246	0.095090	-1.365076
H	-6.095247	1.020518	0.298479
H	-5.444934	0.133889	1.708435
H	-6.126759	-0.743764	0.307688

Coordinates of **I4_TS** (1 imaginary frequency, –954.788823 hartree)

C	5.263552	-0.160915	0.520060
C	5.346366	-0.634154	-0.811391
C	4.199299	-0.965666	-1.533325
C	2.962507	-0.811418	-0.886668
C	2.859869	-0.322597	0.444889
C	4.034683	-0.006721	1.151500
N	1.682777	-1.069100	-1.342837
C	0.777785	-0.747845	-0.354587
C	1.448754	-0.283614	0.767524
C	-0.711732	-0.885116	-0.442962
N	-1.286967	-0.080965	0.645698
C	-0.732858	-0.479596	1.955501
C	0.738692	-0.039840	2.079890
H	6.178839	0.076433	1.054735
H	6.318817	-0.745263	-1.276861
H	4.259924	-1.332971	-2.551427
H	3.985048	0.358952	2.176338
H	1.439171	-1.346043	-2.280364
H	-1.087921	-0.515506	-1.403626
H	-0.991612	-1.952738	-0.373189
H	-2.308355	-0.189642	0.641547
H	-1.335196	-0.013847	2.740027
H	-0.792815	-1.572310	2.095050
H	0.804873	1.015634	2.383459
H	1.224957	-0.607596	2.877864

C	-0.576049	2.653243	-0.009244
O	-1.289081	3.556977	-0.568763
O	0.435648	2.177590	-0.609055
H	-0.873020	2.349613	0.986038
H	-0.992310	3.768786	-1.476059
H	0.825113	1.354096	-0.150660
C	-6.511128	-1.364094	0.060430
C	-5.203150	-0.645042	-0.324921
O	-5.033130	-0.332772	-1.543861
O	-4.400142	-0.382424	0.623125
H	-6.295867	-2.192996	0.795403
H	-7.040858	-1.780006	-0.837998
H	-7.175356	-0.618852	0.567951

Coordinates of **I4** (0 imaginary frequencies, –954.845368 hartree)

C	5.102964	-0.497576	0.902864
C	5.286740	-0.932766	-0.428455
C	4.214971	-1.010539	-1.317720
C	2.950991	-0.641610	-0.842729
C	2.741472	-0.197419	0.497644
C	3.843080	-0.130321	1.371835
N	1.726489	-0.617289	-1.484413
C	0.763728	-0.170690	-0.596506
C	1.335377	0.088928	0.625620
C	-0.696332	-0.046118	-0.918430
N	-1.418944	0.716262	0.133276
C	-0.974928	0.356380	1.505392
C	0.525194	0.575086	1.791738
H	5.959600	-0.449568	1.569194
H	6.280259	-1.212746	-0.766606
H	4.356361	-1.346125	-2.341113
H	3.713776	0.203039	2.398041
H	1.565703	-0.867393	-2.449030
H	-0.865645	0.444837	-1.880705
H	-1.162021	-1.038256	-0.981217
H	-3.042592	0.126285	0.095310
H	-1.590909	0.918531	2.213390

H	-1.215676	-0.704571	1.630772
H	0.724195	1.634687	1.993744
H	0.781174	0.026826	2.707383
C	-1.538291	2.149629	-0.094557
O	-2.239058	2.297893	-1.309490
O	-0.337258	2.897856	-0.118838
H	-2.098836	2.570734	0.746321
H	-2.277902	3.244036	-1.512175
H	0.252654	2.545170	-0.803784
C	-5.599860	-1.917432	0.157880
C	-4.158411	-1.478553	0.097154
O	-3.206307	-2.248297	0.022787
O	-4.021487	-0.151334	0.131543
H	-6.063115	-1.544290	1.076424
H	-5.663734	-3.004784	0.127580
H	-6.153408	-1.490151	-0.683949

Coordinates of **P1_TS** (1 imaginary frequency, –802.15138 hartree)

C	-4.485795	0.848127	0.835136
C	-4.768237	-0.532875	0.741992
C	-3.800167	-1.441529	0.315496
C	-2.538221	-0.934611	-0.015881
C	-2.229738	0.455801	0.071339
C	-3.228244	1.348821	0.504469
N	-1.402809	-1.585517	-0.463003
C	-0.400388	-0.653548	-0.652671
C	-0.859146	0.604100	-0.346383
C	0.975548	-0.993490	-1.139539
N	1.821370	0.207079	-1.047178
C	1.199030	1.496264	-1.395569
C	0.008728	1.822070	-0.478277
C	3.023265	0.167677	-0.485451
O	3.632651	-1.001154	-0.396413
O	2.890867	0.513918	1.563214
H	-5.263663	1.528031	1.170759
H	-5.757611	-0.894611	1.006590
H	-4.017993	-2.503110	0.242486

H	-3.022370	2.413058	0.580485
H	-1.316199	-2.581227	-0.604423
H	1.432468	-1.784037	-0.540698
H	0.954260	-1.341894	-2.181910
H	1.966633	2.270548	-1.343794
H	0.859666	1.427290	-2.435163
H	0.373019	2.160288	0.500750
H	-0.545399	2.660803	-0.916200
H	3.614336	1.074933	-0.538038
H	2.795900	1.467295	1.701682
O	5.115211	-0.572596	1.650137
H	4.392916	-0.922767	0.274438
H	4.242033	0.006469	1.789159
H	5.872437	0.025813	1.601670

Coordinates of **P1** (0 imaginary frequencies, –802.20718 hartree)

C	4.872326	1.119893	-0.795492
C	5.181205	-0.243634	-0.998572
C	4.239611	-1.242480	-0.752546
C	2.977281	-0.843997	-0.298034
C	2.641927	0.527114	-0.087128
C	3.614198	1.512599	-0.343427
N	1.863873	-1.598830	0.022319
C	0.849695	-0.750055	0.422032
C	1.278556	0.554347	0.377372
C	-0.511054	-1.211673	0.844118
N	-1.375126	-0.034244	0.999164
C	-0.781619	1.165007	1.612293
C	0.389647	1.699562	0.771935
C	-2.657543	-0.071836	0.611327
O	-3.220261	-1.062246	0.107962
O	-6.752830	1.356233	-1.740987
H	5.629975	1.871922	-0.996586
H	6.169990	-0.520246	-1.352654
H	4.477383	-2.290737	-0.908949
H	3.387790	2.564571	-0.191758
H	1.799815	-2.604354	-0.038610

H	-0.969376	-1.869720	0.101443
H	-0.469830	-1.766139	1.793262
H	-1.567273	1.915347	1.722709
H	-0.429098	0.894841	2.614975
H	0.002768	2.226220	-0.111244
H	0.935727	2.441546	1.366538
H	-3.197864	0.870771	0.777651
H	-7.393468	1.776822	-1.153443
O	-5.860056	-0.992166	-0.563503
H	-4.901136	-1.013910	-0.321277
H	-6.457006	0.541207	-1.276238
H	-6.339833	-1.310270	0.212751

Coordinates of **I5_TS** (1 imaginary frequency, –726.917214 hartree)

C	-4.285632	0.844556	0.368132
C	-4.533889	-0.541115	0.247002
C	-3.500531	-1.441697	-0.006416
C	-2.207037	-0.921879	-0.134891
C	-1.933064	0.473076	-0.017650
C	-2.997493	1.358282	0.238429
N	-1.007217	-1.563997	-0.379923
C	0.000575	-0.620916	-0.422671
C	-0.515359	0.634281	-0.212218
C	1.438076	-0.942132	-0.673077
N	2.281033	0.237752	-0.285876
C	1.724098	1.539066	-0.794256
C	0.351565	1.859406	-0.188590
H	-5.115115	1.517445	0.565535
H	-5.548972	-0.912567	0.352902
H	-3.691754	-2.506567	-0.100118
H	-2.818151	2.425695	0.332783
H	-0.888003	-2.559144	-0.500542
H	1.790666	-1.793594	-0.084841
H	1.633773	-1.159608	-1.728994
H	2.459218	2.313229	-0.566606
H	1.653309	1.441021	-1.880602

H	0.463665	2.246886	0.832792
H	-0.088959	2.673636	-0.775344
H	3.256598	0.077329	-0.694198
C	2.619131	0.243141	1.232657
O	3.507319	-0.761172	1.492244
H	3.017930	1.254534	1.404726
H	1.676587	0.119353	1.776046
O	4.854038	-0.357099	-0.465624
H	5.141182	-1.142369	-0.949720
H	4.287813	-0.669824	0.645103

Coordinates of **I5** (0 imaginary frequencies, –726.937622 hartree)

C	-4.311709	0.877365	0.297468
C	-4.573250	-0.504359	0.163566
C	-3.542097	-1.415826	-0.063943
C	-2.239399	-0.911926	-0.153938
C	-1.950800	0.480145	-0.021438
C	-3.013156	1.375461	0.207266
N	-1.040083	-1.565306	-0.369504
C	-0.015988	-0.635350	-0.375333
C	-0.525695	0.625197	-0.173443
C	1.435336	-0.951749	-0.593639
N	2.289112	0.186963	-0.185523
C	1.755685	1.477836	-0.679907
C	0.357150	1.839943	-0.132169
H	-5.138260	1.559989	0.473690
H	-5.595275	-0.864506	0.238547
H	-3.743369	-2.478196	-0.167691
H	-2.824333	2.440579	0.311605
H	-0.928549	-2.561604	-0.486718
H	1.748581	-1.834517	-0.027528
H	1.629118	-1.169119	-1.652783
H	2.480191	2.260507	-0.435030
H	1.710039	1.402768	-1.772059
H	0.437805	2.233096	0.891528
H	-0.056943	2.656216	-0.737699
H	4.012692	-0.041119	-0.816708

C	2.574159	0.194202	1.257071
O	3.464365	-0.851149	1.610235
H	3.000293	1.176739	1.495471
H	1.677653	0.036584	1.870184
O	4.996582	-0.177632	-0.776607
H	5.200456	-0.881640	-1.406623
H	4.257712	-0.762757	1.048627

Coordinates of **I6_TS** (1 imaginary frequency, –840.265507 hartree)

C	-4.441105	-0.111801	0.983153
C	-4.452044	-1.312685	0.239369
C	-3.358021	-1.691176	-0.538227
C	-2.248969	-0.837477	-0.553924
C	-2.214312	0.379088	0.190896
C	-3.334559	0.734840	0.965906
N	-1.043497	-0.950376	-1.222812
C	-0.259734	0.145146	-0.917611
C	-0.933531	0.986745	-0.065234
C	1.113948	0.382172	-1.469131
N	1.736152	1.490164	-0.722697
C	0.867186	2.651043	-0.455827
C	-0.338453	2.275887	0.425905
C	2.915195	1.332914	-0.125261
O	2.852604	0.547078	1.532674
H	-5.310874	0.152829	1.577687
H	-5.328444	-1.953384	0.272514
H	-3.366845	-2.613744	-1.111207
H	-3.337338	1.655754	1.542654
H	-0.770976	-1.722043	-1.813850
H	1.753519	-0.500092	-1.374191
H	1.068225	0.651977	-2.533953
H	1.473309	3.432554	0.006243
H	0.513398	3.021851	-1.424267
H	-0.027892	2.198788	1.477592
H	-1.067752	3.093839	0.382583
H	3.390680	2.236196	0.237636
H	3.555371	0.550692	-0.517662

H	2.063024	0.849814	2.006996
C	3.287273	-2.443415	0.379659
O	3.613304	-1.862961	-0.670764
O	2.877593	-1.890650	1.468041
H	3.337005	-3.548529	0.425525
H	2.841771	-0.580438	1.466612

Coordinates of **I6** (0 imaginary frequencies, –840.272449 hartree)

C	-4.552237	-0.254128	1.047151
C	-4.527168	-1.473144	0.333364
C	-3.430332	-1.831098	-0.448835
C	-2.354223	-0.937256	-0.499785
C	-2.357050	0.298041	0.212888
C	-3.479243	0.632292	0.994557
N	-1.153269	-1.024273	-1.180981
C	-0.412573	0.109025	-0.916969
C	-1.104108	0.946603	-0.076759
C	0.946334	0.369457	-1.487993
N	1.531775	1.524475	-0.760831
C	0.621814	2.674733	-0.528184
C	-0.545337	2.262036	0.382520
C	2.741032	1.486841	-0.327178
O	2.996765	0.522480	2.024313
H	-5.423931	-0.007385	1.646299
H	-5.378475	-2.144738	0.394474
H	-3.411313	-2.767848	-0.997752
H	-3.509105	1.566702	1.548037
H	-0.863884	-1.794479	-1.765946
H	1.629675	-0.476772	-1.373007
H	0.899194	0.637314	-2.551240
H	1.209801	3.485920	-0.099064
H	0.252218	2.983567	-1.510165
H	-0.200795	2.211159	1.423527
H	-1.298901	3.056420	0.338817
H	3.145921	2.355376	0.176519
H	3.343297	0.599568	-0.523324
H	2.142579	0.436660	2.467793

C	3.943570	-2.188803	0.108634
O	3.743165	-1.415673	-0.863822
O	3.799170	-1.929702	1.341967
H	4.286396	-3.220646	-0.129344
H	3.272112	-0.406661	1.766928

Coordinates of **P2_TS** (1 imaginary frequency, –763.804523 hartree)

N	-1.371331	-1.574956	0.214631
C	-2.594265	-0.952318	0.041794
C	-3.881093	-1.496333	-0.043387
C	-4.943826	-0.611352	-0.220212
C	-4.729673	0.782149	-0.310563
C	-3.447339	1.319742	-0.224795
C	-2.354025	0.451126	-0.045414
C	-0.931190	0.637336	0.080972
C	-0.088882	1.879441	0.052840
C	1.370872	1.496911	-0.238581
C	1.073816	-0.912089	0.408577
C	-0.383002	-0.611423	0.240019
C	2.895887	0.403557	1.337816
N	1.793170	0.359619	0.603794
H	-1.227899	-2.569310	0.311921
H	-4.045718	-2.567538	0.025832
H	-5.954972	-1.001658	-0.289841
H	-5.580950	1.442478	-0.448918
H	-3.294564	2.393189	-0.294967
H	-0.146250	2.425055	1.004134
H	-0.423065	2.571602	-0.728664
H	1.481585	1.197184	-1.286646
H	2.049089	2.329105	-0.045624
H	1.255966	-1.546148	1.281587
H	1.486916	-1.426321	-0.470735
H	3.305781	1.382348	1.569096
H	3.053951	-0.391977	2.060752
C	4.781330	-0.362249	-0.450494
O	4.086169	-0.501520	-1.457862
O	5.963735	-0.483586	-0.128680

H	4.076355	0.003209	0.503982

Coordinates of **P2** (0 imaginary frequencies, –763.852754 hartree)

N	1.812023	-1.610085	-0.160291
C	2.959573	-0.918564	0.182061
C	4.229058	-1.389587	0.535934
C	5.209609	-0.443228	0.835039
C	4.930360	0.940403	0.782299
C	3.665022	1.405853	0.428179
C	2.653799	0.475549	0.120606
C	1.271447	0.579882	-0.270067
C	0.380474	1.766028	-0.498821
C	-1.086245	1.304921	-0.529719
C	-0.592104	-1.061978	-0.823437
C	0.805800	-0.700915	-0.432762
C	-2.674261	-0.163502	-1.632631
N	-1.262993	0.119780	-1.384415
H	1.727214	-2.614394	-0.212633
H	4.443940	-2.453732	0.576515
H	6.204952	-0.777468	1.113404
H	5.716723	1.650788	1.021689
H	3.462715	2.473010	0.390645
H	0.628986	2.267025	-1.445318
H	0.502993	2.516399	0.292624
H	-1.430194	1.096744	0.502999
H	-1.720093	2.103400	-0.927197
H	-0.598076	-1.860009	-1.576406
H	-1.140389	-1.453811	0.059108
H	-3.142603	0.694470	-2.123610
H	-2.765615	-1.030255	-2.295024
C	-6.500288	-0.116754	1.088965
O	-6.009954	0.012879	2.142361
O	-6.991470	-0.246297	0.035949
H	-3.235837	-0.381353	-0.704210

Coordinates of **I2''** (0 imaginary frequencies, –725.701988 hartree)

C	-2.357658	2.355417	0.780836

C	-3.729771	2.111375	0.543298
C	-4.163920	0.907450	-0.006086
C	-3.189896	-0.052467	-0.311671
C	-1.801737	0.168500	-0.077441
C	-1.393675	1.398446	0.476512
N	-3.316802	-1.311006	-0.862483
C	-2.068472	-1.883621	-0.984786
C	-1.104658	-1.017941	-0.516757
C	0.374688	-1.272367	-0.460214
C	0.814542	-1.702858	0.955701
N	2.271342	-1.924994	1.019603
C	3.113741	-1.229450	1.687077
H	-2.053703	3.306994	1.207323
H	-4.458545	2.877330	0.791830
H	-5.217291	0.719797	-0.192322
H	-0.342712	1.602855	0.662270
H	-4.182312	-1.743144	-1.149621
H	-1.958579	-2.873749	-1.405191
H	0.646106	-2.055944	-1.175405
H	0.930545	-0.370713	-0.740973
H	0.566743	-0.947805	1.702627
H	0.340318	-2.647203	1.234191
H	4.165399	-1.490113	1.651929
H	2.763727	-0.409098	2.305306
C	4.491360	1.181053	-0.571959
O	5.202608	2.175699	-0.274980
O	4.243622	0.691929	-1.704516
H	4.007683	0.656351	0.299888
H	2.633733	-2.695786	0.457227

Coordinates of **I7_TS** (1 imaginary frequency, –725.698874 hartree)

C	-2.291632	2.357696	0.552857
C	-3.663967	2.032497	0.453456
C	-4.077813	0.753723	0.087901
C	-3.083153	-0.197945	-0.175314
C	-1.693508	0.104662	-0.078240
C	-1.307221	1.408723	0.291314

N	-3.187746	-1.518422	-0.559289
C	-1.922613	-2.050759	-0.708945
C	-0.970407	-1.097279	-0.424950
C	0.520715	-1.280969	-0.454876
C	1.108706	-1.487222	0.958101
N	2.567162	-1.633616	0.939444
C	3.424979	-0.730991	1.377786
H	-2.004067	3.365730	0.837654
H	-4.409265	2.793962	0.664206
H	-5.131865	0.503947	0.008495
H	-0.256501	1.674548	0.369578
H	-4.049148	-2.017218	-0.724444
H	-1.795235	-3.079811	-1.015753
H	0.773177	-2.151011	-1.071538
H	1.009762	-0.414058	-0.913162
H	0.872093	-0.642599	1.608990
H	0.688182	-2.391234	1.409138
H	4.470041	-1.017453	1.438251
H	3.057861	0.030598	2.059812
C	3.948270	1.095848	-0.627318
O	4.615976	2.070993	-0.267910
O	3.447108	0.687198	-1.678941
H	3.721627	0.330111	0.293744
H	2.938617	-2.434685	0.438120

Coordinates of **I7** (0 imaginary frequencies, –725.744776 hartree)

C	-1.670741	-2.153378	-1.408501
C	-3.019419	-2.347473	-1.030508
C	-3.654963	-1.473404	-0.151456
C	-2.908940	-0.394423	0.342621
C	-1.548770	-0.175319	-0.026142
C	-0.934206	-1.079327	-0.915935
N	-3.260949	0.610569	1.217477
C	-2.174288	1.444831	1.411910
C	-1.098707	1.008153	0.671065
C	0.256102	1.653325	0.580264
C	0.437865	2.505506	-0.702446

N	1.736486	3.165162	-0.867203
C	2.872584	2.262147	-1.071743
H	-1.205292	-2.855099	-2.094855
H	-3.569703	-3.193714	-1.431691
H	-4.690212	-1.623120	0.141319
H	0.101246	-0.942086	-1.215684
H	-4.160227	0.715573	1.662688
H	-2.251715	2.294028	2.077087
H	0.412892	2.301571	1.451885
H	1.033846	0.880826	0.619195
H	0.269471	1.877262	-1.586120
H	-0.337432	3.281216	-0.713749
H	3.780936	2.854531	-1.216850
H	2.705836	1.675635	-1.982074
C	4.284580	-2.113910	0.724818
O	4.817947	-2.299944	-0.298913
O	3.752158	-1.930134	1.749406
H	3.056627	1.557793	-0.245068
H	1.917547	3.765715	-0.065629

Coordinates of **I8_TS** (1 imaginary frequency, –728.122795 hartree)

C	3.494005	-2.004003	0.078165
C	4.577075	-1.196950	-0.339767
C	4.436693	0.181387	-0.482281
C	3.181807	0.737131	-0.198727
C	2.074160	-0.055745	0.221289
C	2.249160	-1.447555	0.358597
N	2.753661	2.047232	-0.242452
C	1.426977	2.105776	0.135125
C	0.962727	0.843212	0.428944
C	-0.430298	0.479251	0.864963
C	-1.252968	-0.096829	-0.299873
N	-2.679648	-0.380999	0.059097
H	3.639027	-3.075589	0.180859
H	5.536441	-1.659750	-0.552121
H	5.268767	0.802906	-0.799882
H	1.426823	-2.080996	0.680130

H	3.320056	2.843168	-0.495161
H	0.909919	3.054769	0.171755
H	-0.378532	-0.245570	1.684579
H	-0.937901	1.369100	1.254297
H	-1.275738	0.624071	-1.120297
H	-0.814069	-1.026574	-0.674213
H	-3.174477	0.513133	0.370179
C	-3.532906	-0.752423	-1.184933
O	-4.856897	-0.576522	-0.894402
H	-3.156570	-0.086487	-1.975288
H	-3.293018	-1.792702	-1.433802
O	-4.525356	1.526094	0.250970
H	-5.023670	1.646560	1.069809
H	-4.889999	0.439272	-0.381074
C	-2.844056	-1.401420	1.133326
H	-2.289826	-2.301740	0.860833
H	-2.475271	-1.007529	2.079531
H	-3.906283	-1.627244	1.221849

Coordinates of **I8** (0 imaginary frequencies, –728.141628 hartree)

C	-3.488607	-1.987175	-0.214362
C	-4.576473	-1.194917	0.219586
C	-4.429997	0.172724	0.439648
C	-3.164693	0.733016	0.216926
C	-2.051373	-0.045310	-0.216593
C	-2.233191	-1.426242	-0.432656
N	-2.728894	2.034889	0.340635
C	-1.390881	2.100750	-0.001053
C	-0.926582	0.852101	-0.349040
C	0.474843	0.498307	-0.766345
C	1.284899	-0.144821	0.376032
N	2.683986	-0.438398	0.006913
H	-3.638296	-3.050554	-0.378324
H	-5.544078	-1.660557	0.383102
H	-5.265452	0.782865	0.770567
H	-1.406157	-2.047590	-0.765454
H	-3.296283	2.821302	0.619092

H	-0.867029	3.046472	0.025320
H	0.435567	-0.180903	-1.625751
H	0.999637	1.400787	-1.100023
H	1.304075	0.554704	1.218096
H	0.775133	-1.059357	0.724542
H	3.607234	1.054268	-0.592322
C	3.498353	-0.715292	1.201327
O	4.884012	-0.675517	0.911510
H	3.232951	0.030339	1.960597
H	3.305131	-1.719984	1.606257
O	4.332658	1.734689	-0.613591
H	4.633774	1.783245	-1.530657
H	5.072613	0.196381	0.515036
C	2.794002	-1.535010	-0.969116
H	2.302920	-2.452934	-0.605220
H	2.338458	-1.246850	-1.918254
H	3.849007	-1.749225	-1.148923

Coordinates of **I9_TS** (1 imaginary frequency, –841.469690 hartree)

C	4.507365	1.748644	-0.685254
C	5.563447	0.825405	-0.507968
C	5.310325	-0.513818	-0.220540
C	3.970633	-0.910762	-0.111186
C	2.888684	0.001809	-0.281908
C	3.178158	1.349744	-0.574785
N	3.423108	-2.148445	0.152528
C	2.045547	-2.046385	0.150905
C	1.665905	-0.748563	-0.109753
C	0.259400	-0.222612	-0.179838
C	-0.141320	0.529379	1.108968
N	-1.500072	1.095141	1.075230
C	-2.523049	0.436723	1.598864
O	-3.236399	-0.793796	0.380770
C	-1.729593	2.244775	0.194455
H	4.740468	2.785334	-0.910866
H	6.590792	1.165972	-0.599155
H	6.121086	-1.224130	-0.087229

H	2.377209	2.070651	-0.714876
H	3.941052	-3.000315	0.308000
H	1.432920	-2.918950	0.331708
H	0.157635	0.450087	-1.039861
H	-0.441400	-1.048379	-0.338160
H	-0.085330	-0.149900	1.963414
H	0.552478	1.355208	1.295168
H	-2.293986	-0.292809	2.366306
H	-3.455749	0.978715	1.696617
H	-3.070622	-1.694361	0.698865
H	-0.940681	2.983079	0.356351
H	-1.727165	1.946726	-0.858697
H	-2.694144	2.696210	0.430886
O	-5.626774	-0.440714	0.119564
C	-6.051578	-0.382926	-1.096727
O	-7.225336	-0.193716	-1.447493
H	-4.347548	-0.654174	0.250269
H	-5.273739	-0.518518	-1.877170

Coordinates of **I9** (0 imaginary frequencies, –841.474312 hartree)

C	4.743397	1.557315	-0.837529
C	5.741678	0.591747	-0.573163
C	5.408216	-0.698805	-0.169274
C	4.046996	-1.002478	-0.032508
C	3.022631	-0.045399	-0.289292
C	3.392428	1.251197	-0.699609
N	3.425727	-2.177423	0.336586
C	2.058406	-1.995541	0.318477
C	1.758487	-0.705000	-0.058082
C	0.385140	-0.107868	-0.183214
C	0.019829	0.723255	1.065269
N	-1.335310	1.322247	0.972214
C	-2.334510	0.814246	1.600413
O	-3.404387	-0.872957	0.131956
C	-1.495454	2.476991	0.070629
H	5.038840	2.553634	-1.153601
H	6.787625	0.860451	-0.688954

H	6.173938	-1.442705	0.030563
H	2.637071	2.003648	-0.909353
H	3.892063	-3.041829	0.567981
H	1.394245	-2.810130	0.572632
H	0.334767	0.524132	-1.076689
H	-0.360604	-0.899544	-0.305233
H	0.038335	0.093494	1.955589
H	0.722525	1.547098	1.209978
H	-2.177114	-0.016953	2.274794
H	-3.309810	1.275728	1.527737
H	-3.257436	-1.777633	0.438870
H	-0.784879	3.251169	0.365381
H	-1.289853	2.166320	-0.955066
H	-2.513199	2.856484	0.141278
O	-5.996514	-0.442508	0.133767
C	-6.642767	-0.553966	-0.957395
O	-7.866632	-0.358213	-1.135260
H	-4.404132	-0.741607	0.116288
H	-6.041904	-0.860262	-1.845820

Coordinates of **I9'** (0 imaginary frequencies, –765.028481 hartree)

N	1.338520	-0.019525	-0.233319
N	-2.893553	-1.485549	0.678498
C	0.981995	1.295732	-0.023454
C	1.742826	2.370122	0.460800
C	1.118063	3.610644	0.563872
C	-0.235129	3.783479	0.191491
C	-0.989772	2.716708	-0.289162
C	-0.385589	1.448069	-0.401735
C	-0.837857	0.153384	-0.852026
C	-2.201818	-0.210799	-1.346561
C	-3.259720	-0.370704	-0.217805
C	-2.036832	-1.312594	1.619826
C	0.250693	-0.695473	-0.721653
H	2.276249	-0.438756	-0.053614
H	2.783056	2.238875	0.743525
H	1.681138	4.462104	0.935254

H	-0.689823	4.765859	0.281879
H	-2.027244	2.867187	-0.576110
H	-2.165697	-1.133006	-1.935301
H	-2.599311	0.566987	-2.008844
H	-3.325007	0.537342	0.382405
H	-4.242509	-0.590822	-0.635504
H	-1.704293	-2.159939	2.208966
H	-1.676249	-0.314770	1.838269
H	0.325712	-1.746076	-0.969562
C	4.174545	-2.224951	0.064470
O	3.875631	-1.011680	0.290690
O	3.428796	-3.127721	-0.388049
C	-3.437044	-2.814310	0.346748
H	-2.995301	-3.564812	0.999189
H	-4.520135	-2.786930	0.479256
H	-3.204392	-3.038928	-0.695775
H	5.227453	-2.509432	0.299731

Coordinates of **I10_TS** (1 imaginary frequency, –765.019470 hartree)

N	0.097741	1.117523	0.553717
N	-1.759108	-2.029865	-0.674313
C	1.397838	0.905899	0.208438
C	2.378816	1.826257	-0.216647
C	3.637411	1.328573	-0.509119
C	3.944884	-0.056852	-0.400604
C	2.988262	-0.967486	0.006544
C	1.690672	-0.493990	0.324758
C	0.499541	-1.131224	0.759062
C	0.170673	-2.573025	0.795584
C	-0.648361	-2.946113	-0.513317
C	-1.421253	-0.730708	-0.843255
C	-0.501033	-0.111407	0.818309
H	-0.444230	2.015735	0.492631
H	2.153706	2.884023	-0.304225
H	4.416114	2.013992	-0.830613
H	4.947674	-0.395071	-0.641863
H	3.226697	-2.023398	0.091570

H	-0.443650	-2.828675	1.664165
H	1.067133	-3.197571	0.815422
H	0.017717	-2.866218	-1.375846
H	-1.016678	-3.970187	-0.442543
H	-2.220459	0.008093	-0.838955
H	-0.600851	-0.537026	-1.529634
H	-1.382006	-0.123982	1.449711
C	-2.586400	3.170969	-0.081567
O	-1.417483	3.385411	0.370370
O	-3.095135	2.065072	-0.389444
C	-3.012107	-2.370129	0.007783
H	-3.763361	-1.613345	-0.218509
H	-3.363570	-3.339149	-0.351759
H	-2.876328	-2.426561	1.095653
H	-3.221060	4.077285	-0.214258

Coordinates of **I10** (0 imaginary frequencies, –765.024442 hartree)

N	-0.066197	1.034846	-0.295998
N	1.911008	-2.039670	0.643518
C	-1.379737	0.856530	-0.118511
C	-2.384538	1.816472	0.174893
C	-3.674691	1.358322	0.315006
C	-4.025029	-0.027472	0.183919
C	-3.071398	-0.972898	-0.095256
C	-1.717648	-0.546955	-0.258780
C	-0.536957	-1.224220	-0.534868
C	-0.217980	-2.663029	-0.563797
C	0.789160	-2.954035	0.630233
C	1.513656	-0.667818	0.745073
C	0.566704	-0.238114	-0.504475
H	0.462155	1.952814	-0.250785
H	-2.137759	2.867034	0.279769
H	-4.465351	2.070001	0.533628
H	-5.063131	-0.317160	0.307718
H	-3.332093	-2.020985	-0.200665
H	0.288271	-2.933992	-1.497282
H	-1.105530	-3.291468	-0.457833

H	0.236277	-2.859289	1.570084
H	1.147473	-3.981827	0.543089
H	2.368376	0.010517	0.736906
H	0.922037	-0.505860	1.650537
H	1.211155	-0.231888	-1.389379
C	2.514627	3.291238	0.012974
O	1.258227	3.383568	-0.173000
O	3.195147	2.241607	0.092225
C	2.972157	-2.324361	-0.323423
H	3.813107	-1.650565	-0.144222
H	3.317455	-3.352118	-0.187909
H	2.654348	-2.206313	-1.372647
H	3.052581	4.261504	0.114619

Coordinates of **P3_TS** (1 imaginary frequency, –765.008688 hartree)

N	0.745810	-0.037623	-1.645034
C	1.876043	-0.112382	-0.908742
C	3.225393	0.036593	-1.302388
C	4.188650	-0.127829	-0.326494
C	3.862410	-0.422885	1.032804
C	2.551752	-0.548639	1.433790
C	1.525923	-0.383909	0.461732
C	0.127279	-0.434397	0.521690
C	-0.814135	-0.766633	1.622703
C	-1.971931	-1.624069	1.067571
C	-1.623328	-0.911718	-1.234538
C	-0.398770	-0.103378	-0.779821
H	0.710606	0.294785	-2.599512
H	3.489926	0.258218	-2.330853
H	5.235419	-0.031607	-0.599148
H	4.666682	-0.541982	1.751193
H	2.298896	-0.763929	2.466954
H	-1.220096	0.177653	2.013364
H	-0.307825	-1.284981	2.441872
H	-1.603005	-2.644202	0.846799
H	-2.748864	-1.717063	1.831446
H	-2.116447	-0.414922	-2.075565

H	-1.286624	-1.907672	-1.580218
H	-0.803744	1.056806	-0.663263
C	-1.557790	3.062880	0.261637
O	-1.529358	2.616902	1.422907
O	-1.285828	2.437999	-0.826679
H	-1.848040	4.124545	0.106028
C	-3.793941	-1.690222	-0.532460
H	-4.513955	-1.679934	0.290627
H	-4.238866	-1.168181	-1.384738
H	-3.616805	-2.741633	-0.824925
N	-2.568824	-1.004603	-0.121366

Coordinates of **P3** (0 imaginary frequencies, –765.046152 hartree)

N	0.574985	-1.392234	-1.297066
C	1.730921	-0.994846	-0.647773
C	3.071200	-1.114889	-1.033162
C	4.039213	-0.621987	-0.158876
C	3.680316	-0.022166	1.068660
C	2.344678	0.101808	1.445472
C	1.344322	-0.385000	0.582937
C	-0.097810	-0.429721	0.633460
C	-1.075757	-0.029667	1.703247
C	-2.433056	-0.700267	1.430404
C	-1.940727	-1.352859	-0.862051
C	-0.516067	-1.046426	-0.524892
H	0.534644	-1.818499	-2.211368
H	3.347396	-1.577662	-1.976174
H	5.088633	-0.702404	-0.426996
H	4.460817	0.348840	1.726763
H	2.079736	0.567516	2.390703
H	-1.199744	1.060940	1.738870
H	-0.716615	-0.336164	2.693644
H	-2.387034	-1.766309	1.728226
H	-3.210218	-0.227297	2.037881
H	-2.164892	-1.097350	-1.905046
H	-2.121170	-2.442672	-0.754132
H	-0.344910	1.390276	-0.767806

C	-0.406153	3.305573	-0.835135
O	-0.510756	3.484293	0.361890
O	-0.315302	2.115533	-1.434548
H	-0.373568	4.112367	-1.578537
C	-4.219422	-0.948369	-0.197823
H	-4.869927	-0.306567	0.403100
H	-4.480281	-0.811132	-1.251957
H	-4.424657	-2.001404	0.072274
N	-2.823515	-0.573220	0.016354

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