Electronic Supplementary Information

Synthesis of silyl formates, formamides, and aldehydes via solvent-free organocatalytic hydrosilylation of CO_2

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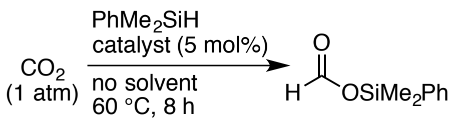
[A] General methods.

NMR spectra were measured on a Varian 400-MR spectrometer or a JEOL JNM-ECS400 spectrometer, and chemical shifts are reported as the delta scale in ppm using an internal reference (δ = 7.26 ppm ($CDCl_3$) for ^1H NMR and δ = 77.16 ppm ($CDCl_3$) for ^{13}C NMR). GC was measured on a Shimadzu GC-8A with a packed column, Shincarbon-ST 50/80 (ø 3 mm × 6 m) (Shinwa Chemical Industries Ltd.). Melting points were measured on a Yanaco melting point apparatus (uncorrected). Column chromatography was carried out using Fuji Silysia BW-127 ZH (100–270 mesh), and thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}. $^{13}CO_2$ (99%) purchased from Taiyo Nippon Sanso Corporation was used for the isotope labeling experiment.

[B] Solvent-free hydrosilylation of CO_2.

General procedure. A catalyst (0.10 mmol, 5 mol%) was put in a 30 mL Schlenk flask fitted with a rubber septum. After the flask was quickly evacuated and filled with CO_2 (balloon), hydrosilane (2.0 mmol) was added. The mixture was stirred at constant temperature for reaction time. After addition of $CDCl_3$ (ca. 1 mL) and mesitylene (internal standard) and stirring, a small portion of the mixture was added to $CDCl_3$ in an NMR tube, and the yield was determined by ^1H NMR using mesitylene as the internal standard.

Table S1. Screening of catalysts for the solvent-free hydrosilylation of CO_2.[a]



entry	catalyst	yield (%)[b]
1	TBAF·3H_2O	52
2	TBAC	0
3	TBAB	0
4	TBAI	0
5	TBAA	76
6	TBD	0
7	CsF	0
8	KF·2H_2O	0
9	K_2CO_3	0
10	Cs_2CO_3	0

[a] Reaction conditions: CO_2 (1 atm, balloon), $PhMe_2SiH$ (2.0 mmol), catalyst (5 mol%), 60 °C, 8 h.
[b] Total yield of silyl formate and formic acid. Determined by ^1H NMR using mesitylene as an internal standard.

Generation of H_2 as a side reaction.

Although $PhSiH_3$ appeared to function as a highly reactive reductant in the TBAA-catalyzed hydrosilylation of CO_2, a side reaction generating H_2 also occurred. We consider that an active species reacted with water (impurity) contained in $PhSiH_3$ or TBAA to generate H_2. Probably because of this side reaction, the yields of silyl formates were modest especially when $PhSiH_3$ was used at high temperature.

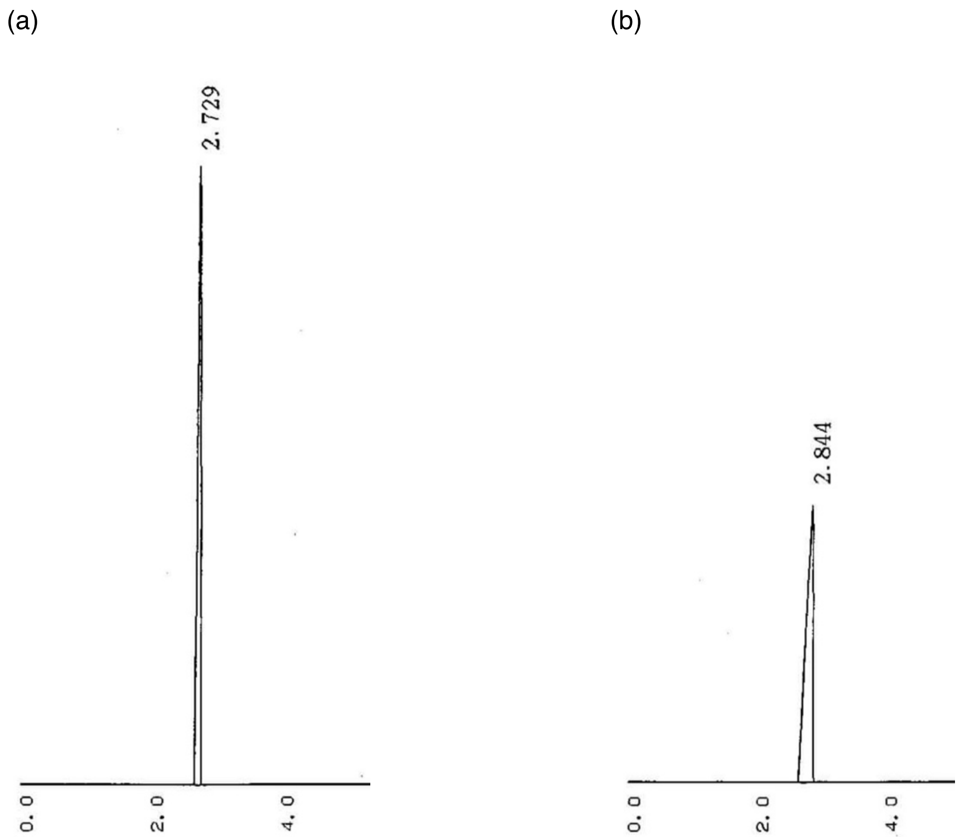


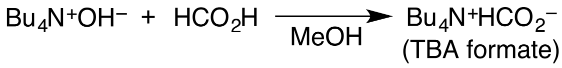
Fig. S1 GC charts: Inj. 200 °C, Col. 50 °C, Det. (TCD) 200 °C, Ar.
(a) The gas above the reaction mixture. (b) Authentic sample of H_2.

TBAA (30.1 mg, 0.10 mmol, 5 mol%) was put in a 30 mL Schlenk flask fitted with a rubber septum. After the flask was evacuated and filled with CO_2 (balloon), the flask was closed, and the CO_2 balloon was removed. $PhSiH_3$ (250 µL, 2.0 mmol, stored over molecular sieves 3A) was added via a syringe. The mixture was stirred at 60 °C for 1 h. The gas (0.4 mL) above the reaction mixture was taken by a syringe and analyzed by GC. As a result, H_2 was detected (Fig. S1).

The generation of H_2 was also confirmed by ^1H NMR spectroscopy. When the gas (5 mL) above the reaction mixture was taken by a syringe and bubbled into $CDCl_3$ in an NMR tube, a singlet signal assigned as H_2 appeared at 4.62 ppm.

Supporting data for the proposed reaction mechanism.

(a) Preparation of an authentic sample of TBA formate.



To a solution of TBA hydroxide ($Bu_4N^+OH^-$) in MeOH (37%, 1.40 g, 2.0 mmol) was added dropwise formic acid (88% in water, 164 mg, 3.1 mmol). The reaction mixture was stirred at room temperature for 2 h and then evacuated at 60 °C under reduced pressure to give TBA formate ($Bu_4N^+HCO_2^-$) as a white powder (570 mg, 1.98 mmol, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.02 (t, J = 7.4 Hz, 12H), 1.41–1.50 (m, 8H), 1.63–1.71 (m, 8H), 3.29–3.34 (m, 8H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 19.8, 24.0, 58.9, 166.9.

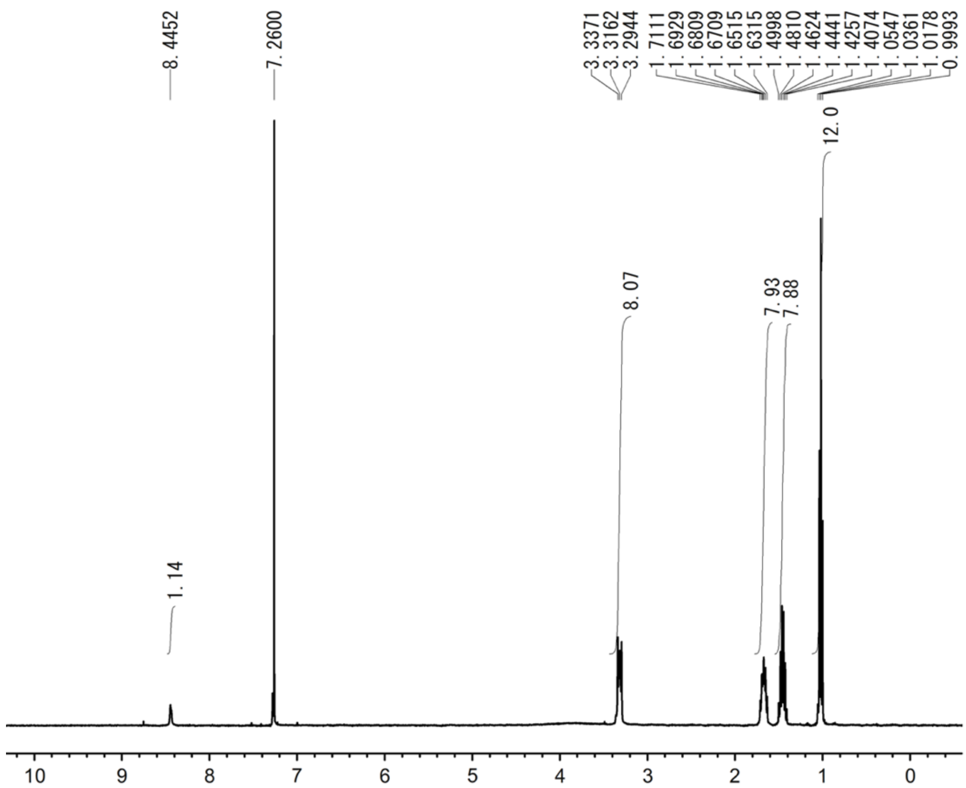
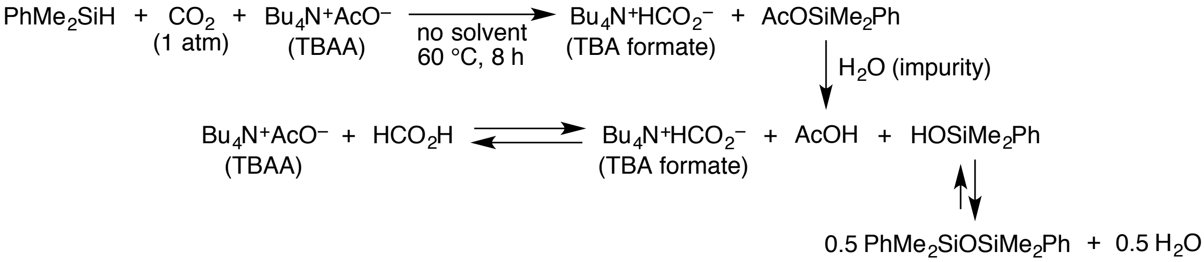


Fig. S2 ^{1}H NMR spectrum of TBA formate in $CDCl_3$.

(b) Generation of TBA formate from $PhMe_2SiH$ and TBAA under CO_2 atmosphere.



In a glovebox (purge type) under N_2 atmosphere, TBAA (603 mg, 2.0 mmol, 100 mol%) was put in a 30 mL Schlenk flask fitted with a rubber septum, and the flask was taken out from the glovebox. After the flask was evacuated and filled with CO_2 (balloon), the flask was heated at 60 °C, and $PhMe_2SiH$ (310 µL, 2.0 mmol) was added via a syringe. The reaction mixture was stirred at 60 °C for 8 h. After cooling, $CDCl_3$ (2 mL) was added, and mesitylene (70 µL, 0.50 mmol) was added as an internal standard. ^1H NMR spectrum indicated the formation of TBA formate in 47% yield (Fig. S3). The generation of TBA formate from $PhMe_2SiH$ and TBAA under CO_2 atmosphere supports the initial step of the reaction mechanism shown in Scheme 2.

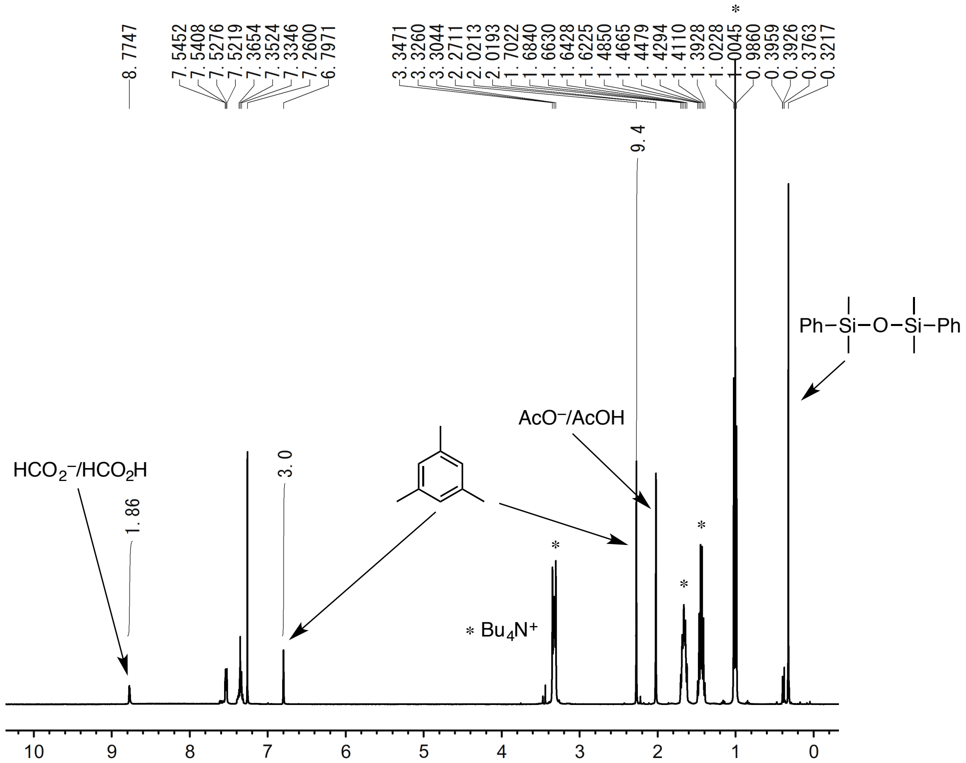
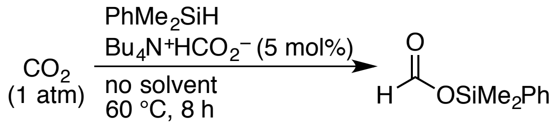


Fig. S3 ^1H NMR spectrum of the reaction mixture containing TBA formate in $CDCl_3$.

The signal for the formyl group of TBA formate can be seen at 8.77 ppm, which appeared downfield as compared with that of pure TBA formate (8.45 ppm, Fig. S2). The signal at 8.77 ppm was upfield shifted upon addition of TBA formate (authentic sample) with an increase of the integral. We suppose that the HCO_2^- ion was hydrogen-bonded in the reaction mixture. The signal for the acetyl group of TBAA/acetic acid can be seen at 2.02 ppm. We suppose that $AcOSiMe_2Ph$ was hydrolyzed with water (impurity) contained in TBAA.

(c) Solvent-free synthesis of HCO_2SiMe_2Ph using TBA formate as a catalyst.



TBA formate (28.7 mg, 0.10 mmol, 5 mol%) was put in a 30 mL Schlenk flask fitted with a rubber septum. After the flask was evacuated and filled with CO_2 (balloon), the flask was heated at 60 °C, and $PhMe_2SiH$ (310 µL, 2.0 mmol) was added via a syringe. The reaction mixture was stirred at 60 °C for 8 h. After cooling, mesitylene (70 µL, 0.50 mmol) was added as an internal standard. ^1H NMR spectrum indicated the formation of HCO_2SiMe_2Ph in 72% yield (Fig. S4).
The solvent-free synthesis of HCO_2SiMe_2Ph using TBA formate as a catalyst supports the catalytic cycle shown in Scheme 2.

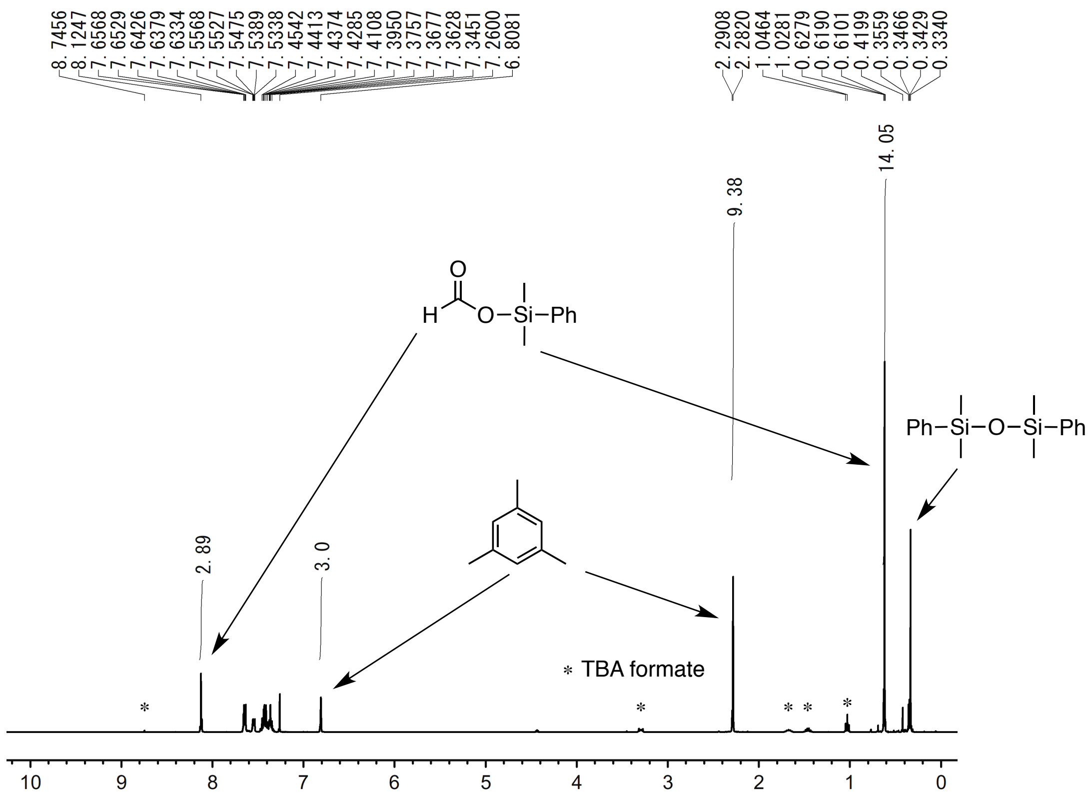
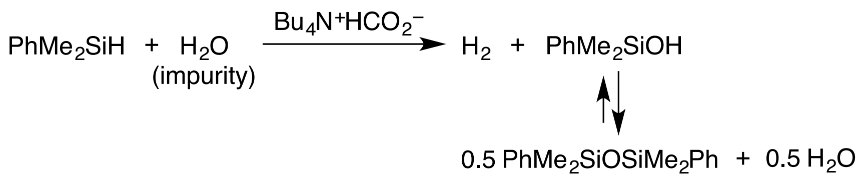
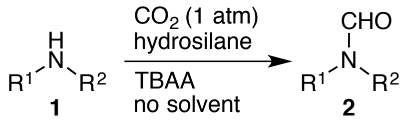


Fig. S4 ^1H NMR spectrum of the reaction mixture in $CDCl_3$.

We consider that $PhMe_2SiOSiMe_2Ph$ was formed by a side reaction shown below.

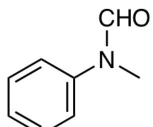


[C] Solvent-free *N*-formylation of amines with CO_2 and hydrosilane.



General procedure. TBAA (30.1 mg, 0.10 mmol, 5 mol% based on silane) was put in a 30 mL Schlenk flask fitted with a rubber septum. After the flask was evacuated and filled with CO_2 (balloon), amine **1** (0.50 mmol) and hydrosilane (2.0 mmol) were added in this order via syringes. The mixture was stirred at constant temperature for reaction time. Purification by silica gel column chromatography gave formamide **2**.

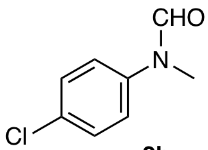
***N*-Methyl-*N*-phenylformamide (2a).**



2a

51.7 mg (0.383 mmol, 76% yield); Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.32 (s, 3H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 8.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.1, 122.4, 126.5, 129.7, 142.2, 162.5.

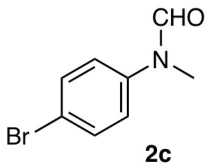
***N*-(4-Chlorophenyl)-*N*-methylformamide (2b).**



2b

54.3 mg (0.321 mmol, 64% yield); Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.29 (s, 3H), 7.10 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 8.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.2, 123.7, 129.9, 132.2, 140.9, 162.2.

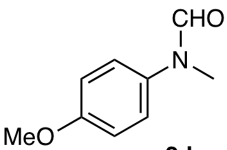
***N*-(4-Bromophenyl)-*N*-methylformamide (2c).**



2c

69.0 mg (0.322 mmol, 64% yield); White solid; mp 69.0−69.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.30 (s, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 2H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.1, 119.9, 123.9, 132.9, 141.4, 162.1.

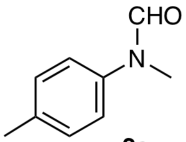
***N*-(4-Methoxyphenyl)-*N*-methylformamide (2d).**



2d

53.2 mg (0.322 mmol, 64% yield); Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.24 (s, 3H), 3.79 (s, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.7, 55.6, 114.8, 124.7, 135.3, 158.3, 162.5.

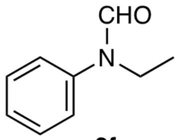
N-Methyl-N-(4-methylphenyl)formamide (2e).



2e

68.0 mg (0.456 mmol, 91% yield); Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 3.29 (s, 3H), 7.06 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.0, 32.4, 122.7, 130.3, 136.5, 139.8, 162.5.

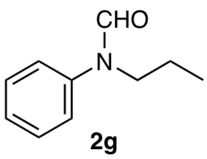
N-Ethyl-N-phenylformamide (2f).



2f

72.0 mg (0.483 mmol, 97% yield); Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (t, J = 7.1 Hz, 3H), 3.87 (q, J = 7.1 Hz, 2H), 7.17 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.2, 40.2, 124.4, 127.0, 129.8, 141.0, 162.2.

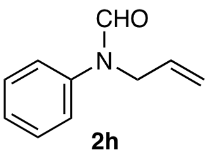
N-Phenyl-N-propylformamide (2g).



2g

60.7 mg (0.372 mmol, 74% yield); Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, J = 7.4 Hz, 3H), 1.54–1.59 (m, 2H), 3.78 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.4 Hz, 2H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.3, 21.0, 46.7, 124.4, 127.0, 129.8, 141.2, 162.6; IR (neat) 3035, 2965, 2874, 1694, 1597, 1497, 1132, 1086; HRMS (EI) calcd for $C_{10}H_{13}NO$ 163.0997, found 163.0997 (M^+).

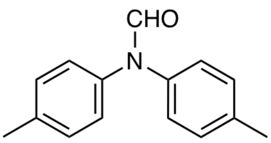
N-Allyl-N-phenylformamide (2h).



2h

46.5 mg (0.289 mmol, 58% yield); Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.42 (dt, J = 1.4, 5.5 Hz, 2H), 5.16–5.22 (m, 2H), 5.80–5.89 (m, 1H), 7.19 (dd, J = 1.0, 8.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.41 (d, J = 7.5 Hz, 2H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.9, 117.7, 123.5, 126.7, 129.6, 132.5, 141.2, 162.0.

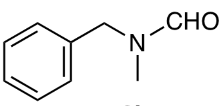
N,N-Di(4-tolyl)formamide (2i).



2i

3.9 mg (0.017 mmol, 3% yield); Yellow solid; mp 122.4–124.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.35 (s, 3H), 2.37 (s, 3H), 7.05 (d, J = 8.3 Hz, 2H), 7.15–7.20 (m, 6H), 8.62 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 21.2, 125.1, 126.0, 130.0, 130.3, 136.8, 137.0, 137.3, 139.5, 161.9.

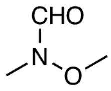
N-Benzyl-N-methylformamide (2j).



2j

51.7 mg (0.347 mmol, 69% yield); Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) (major rotamer) δ 2.78 (s, 3H), 4.39 (s, 2H), 7.19–7.39 (m, 5H), 8.28 (s, 1H); (minor rotamer) δ 2.84 (s, 3H), 4.52 (s, 2H), 7.19–7.39 (m, 5H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.5, 34.1, 47.8, 53.5, 127.5, 127.7, 128.2, 128.3, 128.8, 129.0, 135.8, 136.1, 162.7, 162.9.

***N*-Methoxy-*N*-methylformamide (2k).**



2k

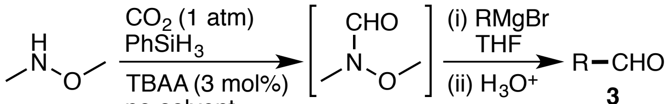
Prepared as described in section D and purified by column chromatography. 141 mg (1.58 mmol, 79% yield); Light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) (major rotamer) δ 3.16 (s, 3H), 3.74 (s, 3H), 8.42 (s, 1H); (minor rotamer) δ 3.16 (s, 3H), 3.74 (s, 3H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.5, 63.1, 162.5.

[D] One-pot aldehyde synthesis with CO_2.

Preparation of Grignard reagents. Grignard reagents (RMgBr, 1 M) for the synthesis of **3a**–**e** and **3i** were freshly prepared by the dropwise addition of the corresponding aryl bromide or alkyl bromide (RBr) to Mg turnings (1.2 equiv) in dry THF at ambient temperature, and those for the synthesis of **3f**–**h** were freshly prepared by the dropwise addition of the corresponding heterocycle or terminal alkyne (RH) to a suspension of EtMgBr (1 M, 1.1 equiv) in dry THF in an ice bath followed by heating at 50–60 °C for 2–3 h.

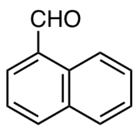
Preparation of *N*,*O*-dimethylhydroxylamine (1k). KOH (7.70 g, 137 mmol) was added portionwise to a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (5.40 g, 55.4 mmol) in water (7 mL) in an ice bath, and distillation at 60 °C (bath temperature) gave *N*,*O*-dimethylhydroxylamine (**1k**) (2.70 g, 44.2 mmol), which was stored over molecular sieves 3A (dried at 150 °C for 2 h in vacuo and cooled to room temperature in advance).

General procedure for one-pot synthesis of aldehydes with CO_2 via Weinreb formamide (2k).



In a glovebox (purge type) under N_2 atmosphere, TBAA (18.0 mg, 0.060 mmol, 3 mol%) was put in a 30 mL Schlenk flask fitted with a rubber septum, and the flask was taken out from the glovebox. After the flask was evacuated and filled with CO_2 (balloon), the flask was cooled in an ice bath. Amine **1k** (155 µL, 2.0 mmol) and $PhSiH_3$ (250 µL, 2.0 mmol, stored over molecular sieves 3A) were added in this order via syringes. The mixture was stirred in an ice bath for 1 h and then at 20 °C for 5 h. This reaction mixture containing Weinreb formamide **2k** was used in the following reaction without purification. The CO_2 balloon was replaced by a N_2 balloon, and the reaction mixture was cooled in an ice bath, and a suspension of a Grignard reagent (RMgBr, 1 M) in dry THF (4 mL) was added. The mixture was stirred at 0 °C for 2 h, and the reaction was quenched with saturated aqueous NH_4Cl (2 mL). The product was extracted with Et_2O (10 mL × 3), and the organic layers were combined and dried over Na_2SO_4. Purification by silica gel column chromatography gave aldehyde **3**.

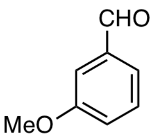
1-Naphthaldehyde (3a).



3a

222 mg (1.42 mmol, 71% yield); Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58–7.72 (m, 3H), 7.93 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 7.0 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 9.26 (d, J = 8.6 Hz, 1H), 10.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 125.0, 127.1, 128.6, 129.2, 130.7, 131.6, 133.9, 135.4, 136.8, 193.6.

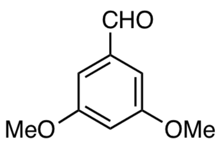
3-Methoxybenzaldehyde (3b).



3b

228 mg (1.67 mmol, 84% yield); Light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 3H), 7.18–7.20 (m, 1H), 7.40 (d, J = 2.1 Hz, 1H), 7.45–7.46 (m, 2H), 9.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 112.2, 121.7, 123.7, 130.2, 138.0, 160.3, 192.3.

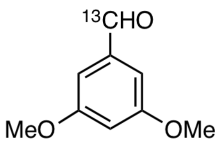
3,5-Dimethoxybenzaldehyde (3c).



3c

286 mg (1.72 mmol, 86% yield); White solid; mp 39.4–39.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (s, 6H), 6.71 (t, J = 2.3 Hz, 1H), 7.02 (d, J = 2.3 Hz, 2H), 9.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.8, 107.4, 107.5, 138.8, 161.6, 191.8; HRMS (EI) calcd for $C_9H_{10}O_3$ 166.0630, found 166.0629 (M^+).

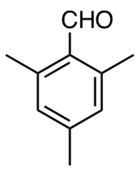
3,5-Dimethoxybenzaldehyde labeled with the ^{13}C atom (3c').



3c'

3c' was obtained with $^{13}CO_2$. 185 mg (1.11 mmol, 55% yield); White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (s, 6H), 6.71 (t, J = 2.3 Hz, 1H), 7.02 (dd, J = 2.3, 5.5 Hz, 2H), 9.91 (d, J = 176 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.8, 107.3, 107.3 (d, J = 6.9 Hz), 138.5 (d, J = 52.5 Hz), 161.4 (d, J = 6.2 Hz), 192.1; HRMS (EI) calcd for $^{12}C_8{}^{13}CH_{10}O_3$ 167.0663, found 167.0661 (M^+).

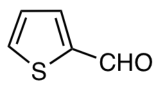
2,4,6-Trimethylbenzaldehyde (3d).



3d

225 mg (1.52 mmol, 76% yield); Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.58 (s, 6H), 6.90 (s, 2H), 10.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.6, 21.6, 130.1, 130.7, 141.6, 144.0, 193.1.

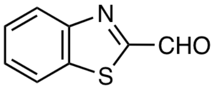
2-Formylthiophene (3e).



3e

128 mg (1.14 mmol, 57% yield); Dark yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21–7.24 (m, 1H), 7.76–7.80 (m, 2H), 9.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 128.4, 135.3, 136.4, 144.2, 183.1.

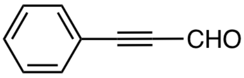
Benzothiazole-2-carboxaldehyde (3f).



3f

202 mg (1.24 mmol, 62% yield); Yellow solid; mp 60.5–62.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57–7.65 (m, 2H), 8.01–8.03 (m, 1H), 8.25–8.27 (m, 1H), 10.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.8, 125.9, 127.5, 128.6, 136.5, 153.7, 165.5, 185.6.

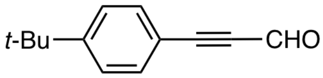
3-Phenyl-2-propynal (3g).



3g

153 mg (1.18 mmol, 59% yield); Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39–7.43 (m, 2H), 7.48–7.50 (m, 1H), 7.60–7.62 (m, 2H), 9.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 88.6, 95.1, 119.5, 128.8, 131.4, 133.3, 176.9.

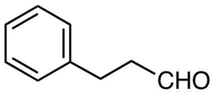
3-(4-*tert*-Butylphenyl)-2-propynal (3h).



3h

239 mg (1.28 mmol, 64% yield); Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (s, 9H), 7.43 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 9.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.1, 35.2, 88.5, 95.9, 116.4, 125.9, 133.3, 155.2, 176.9.

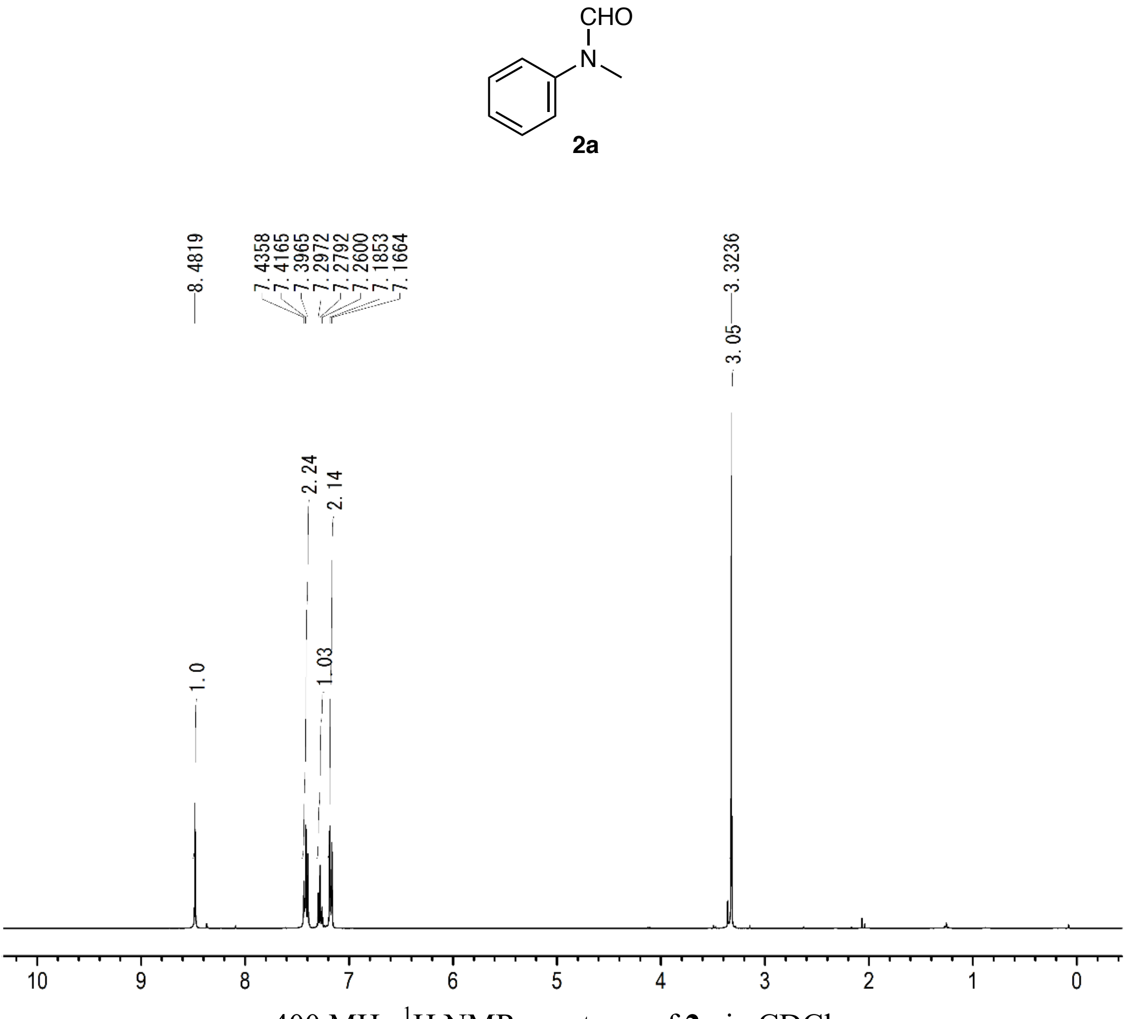
3-Phenylpropanal (3i).



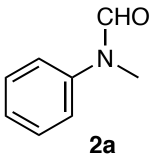
3i

150 mg (1.12 mmol, 56% yield); Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.77–2.81 (m, 2H), 2.97 (t, J = 7.6 Hz, 2H), 7.19–7.23 (m, 3H), 7.27–7.32 (m, 2H), 9.83 (t, J = 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.2, 45.4, 126.4, 128.4, 128.7, 140.5, 201.7.

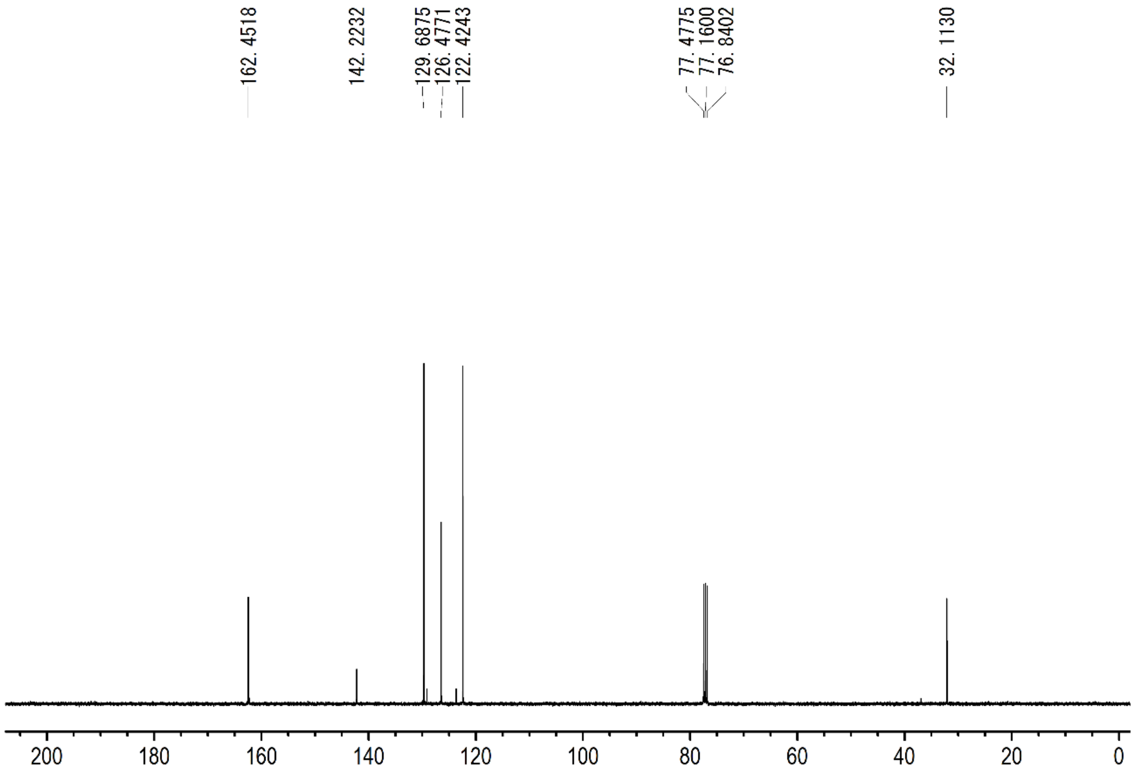
[E] NMR spectra.



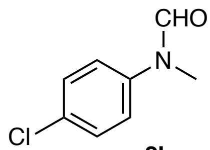
400 MHz ^{1}H NMR spectrum of **2a** in $CDCl_3$.



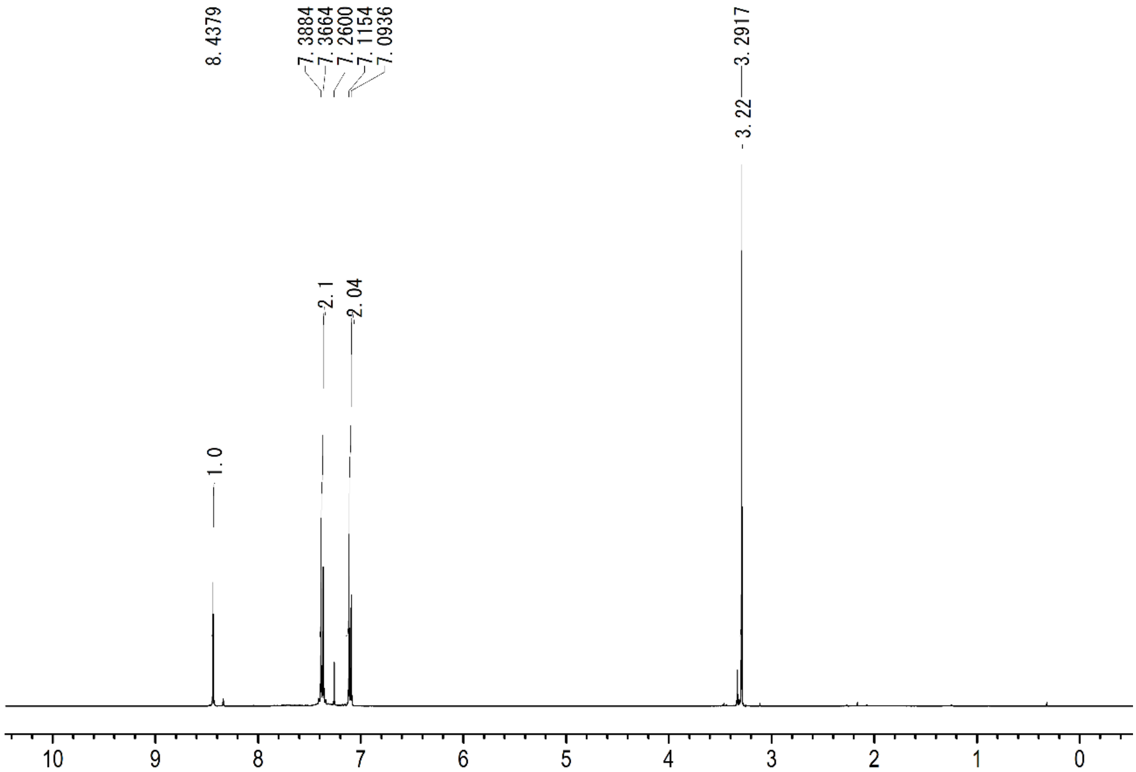
2a



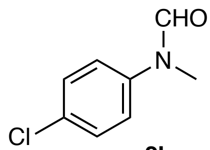
100 MHz ^{13}C NMR spectrum of **2a** in $CDCl_3$.



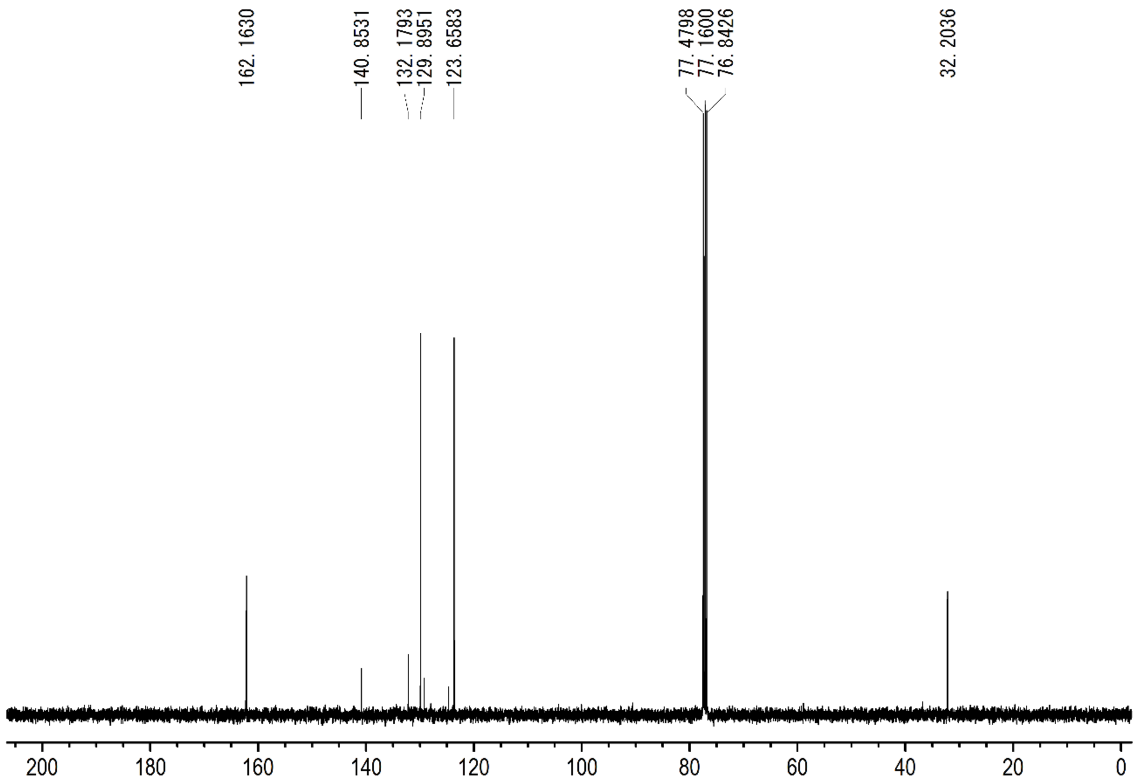
2b



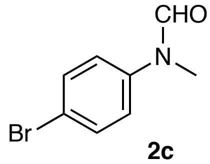
400 MHz ^{1}H NMR spectrum of **2b** in $CDCl_3$.



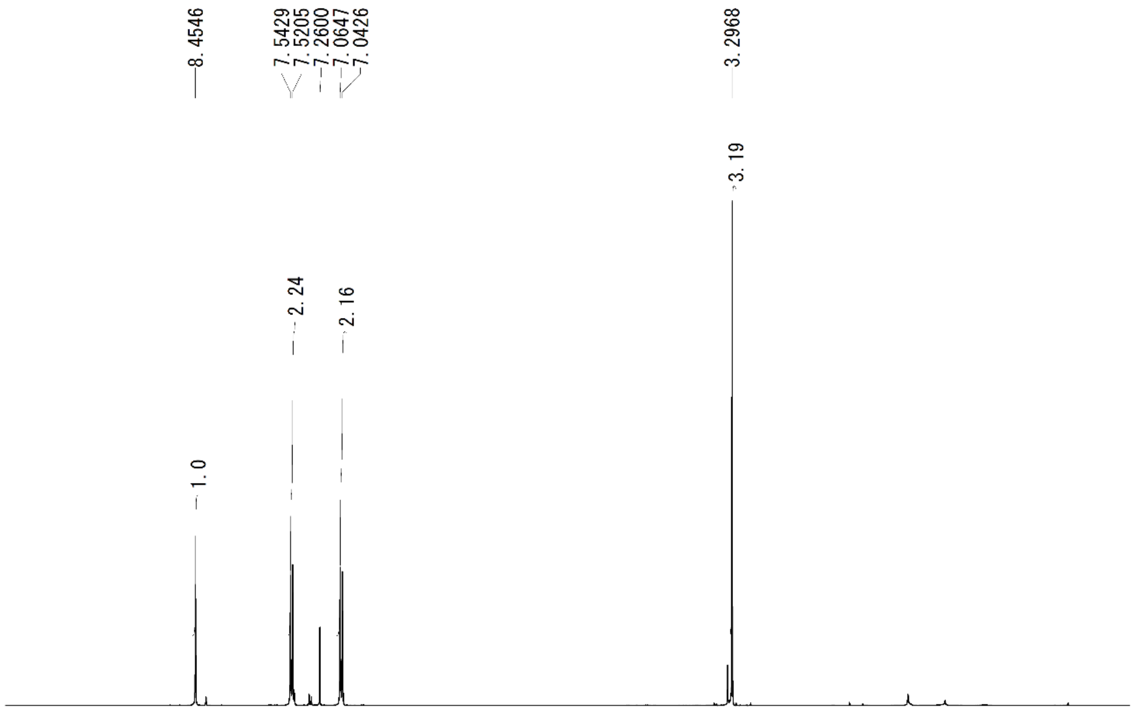
2b



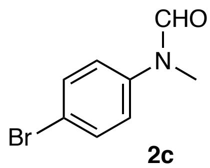
100 MHz ^{13}C NMR spectrum of **2b** in $CDCl_3$.



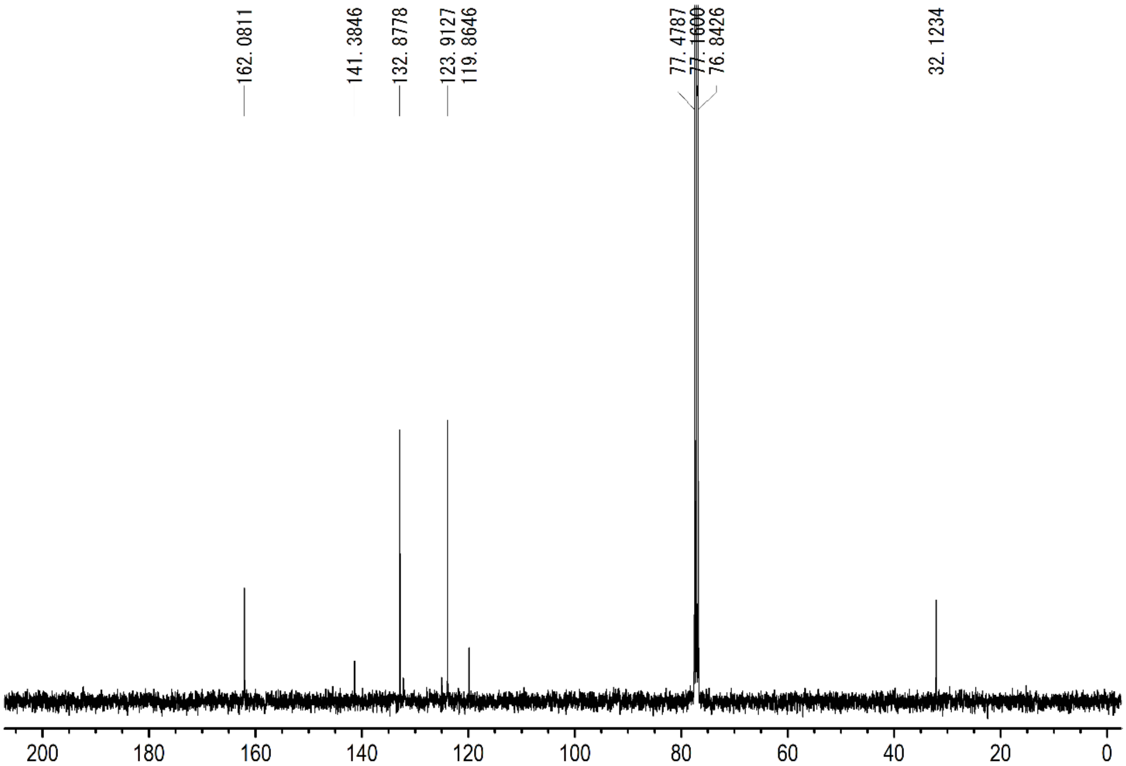
2c



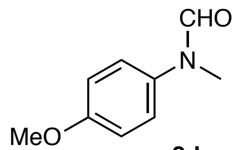
400 MHz ^{1}H NMR spectrum of **2c** in $CDCl_3$.



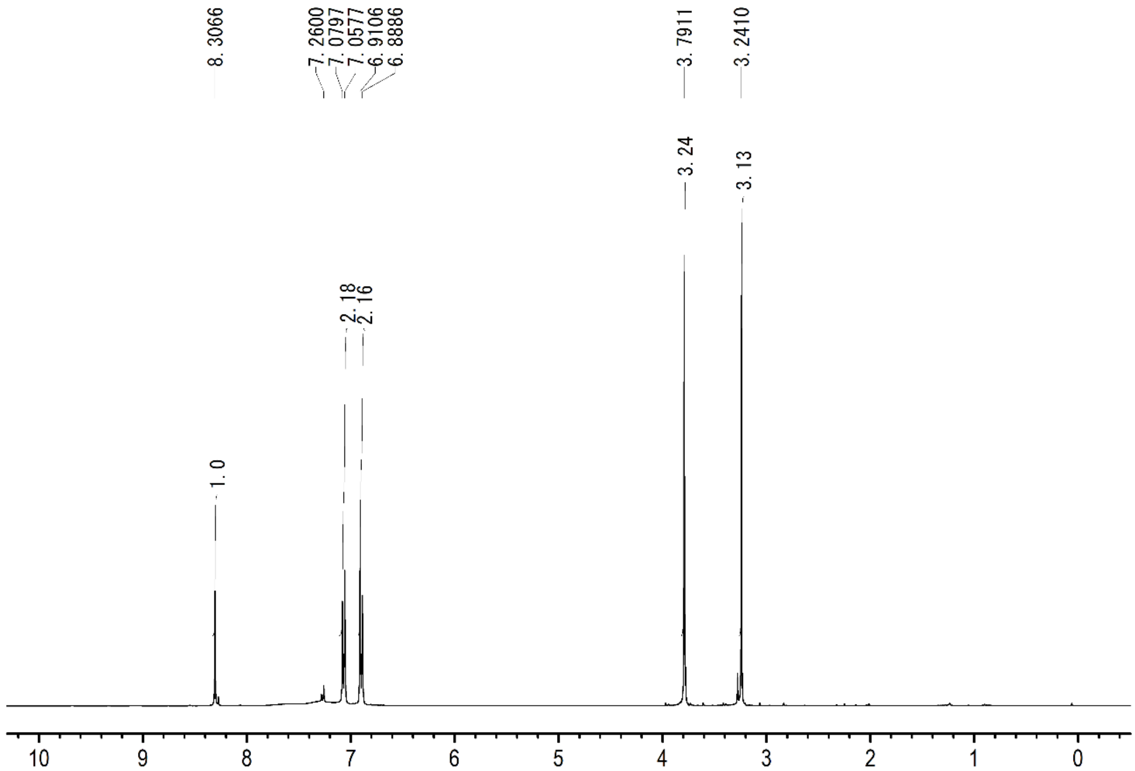
2c



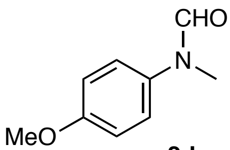
100 MHz ^{13}C NMR spectrum of **2c** in $CDCl_3$.



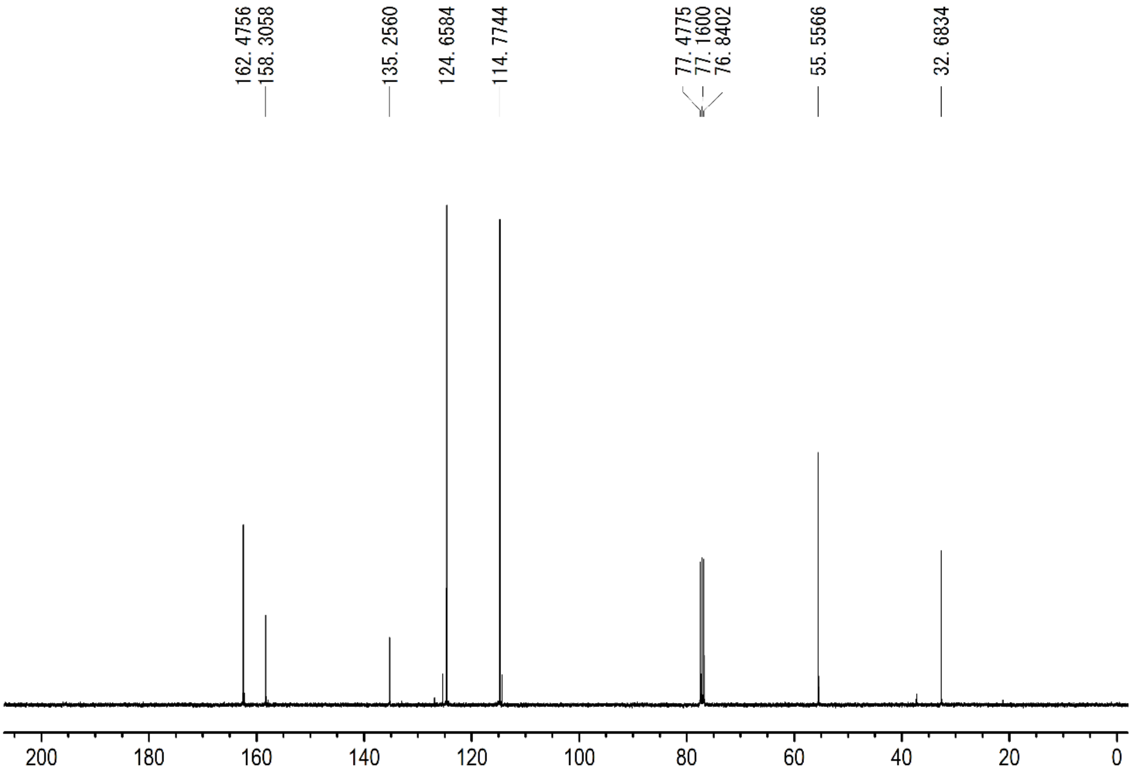
2d



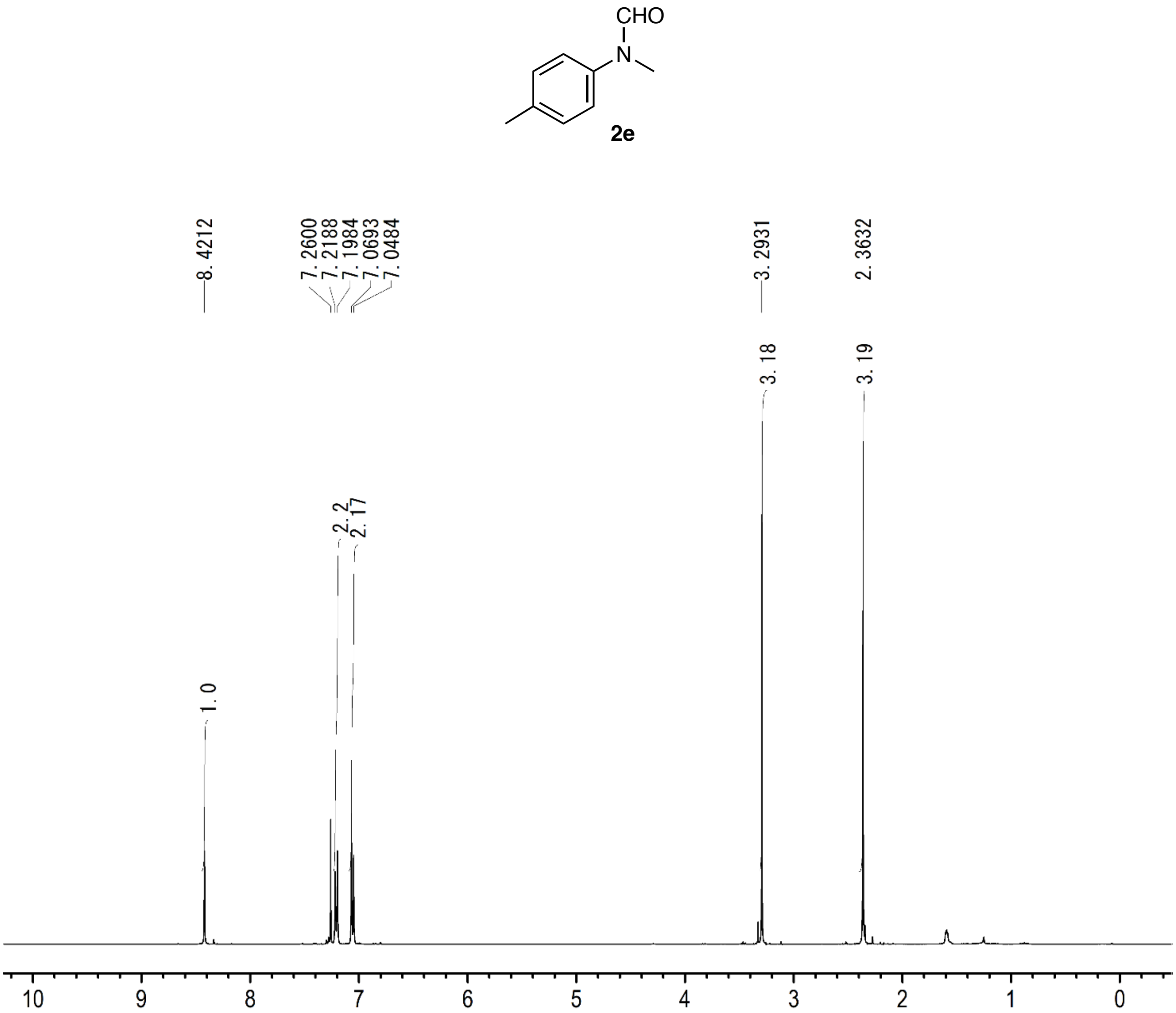
400 MHz ^{1}H NMR spectrum of **2d** in $CDCl_3$.



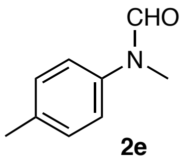
2d

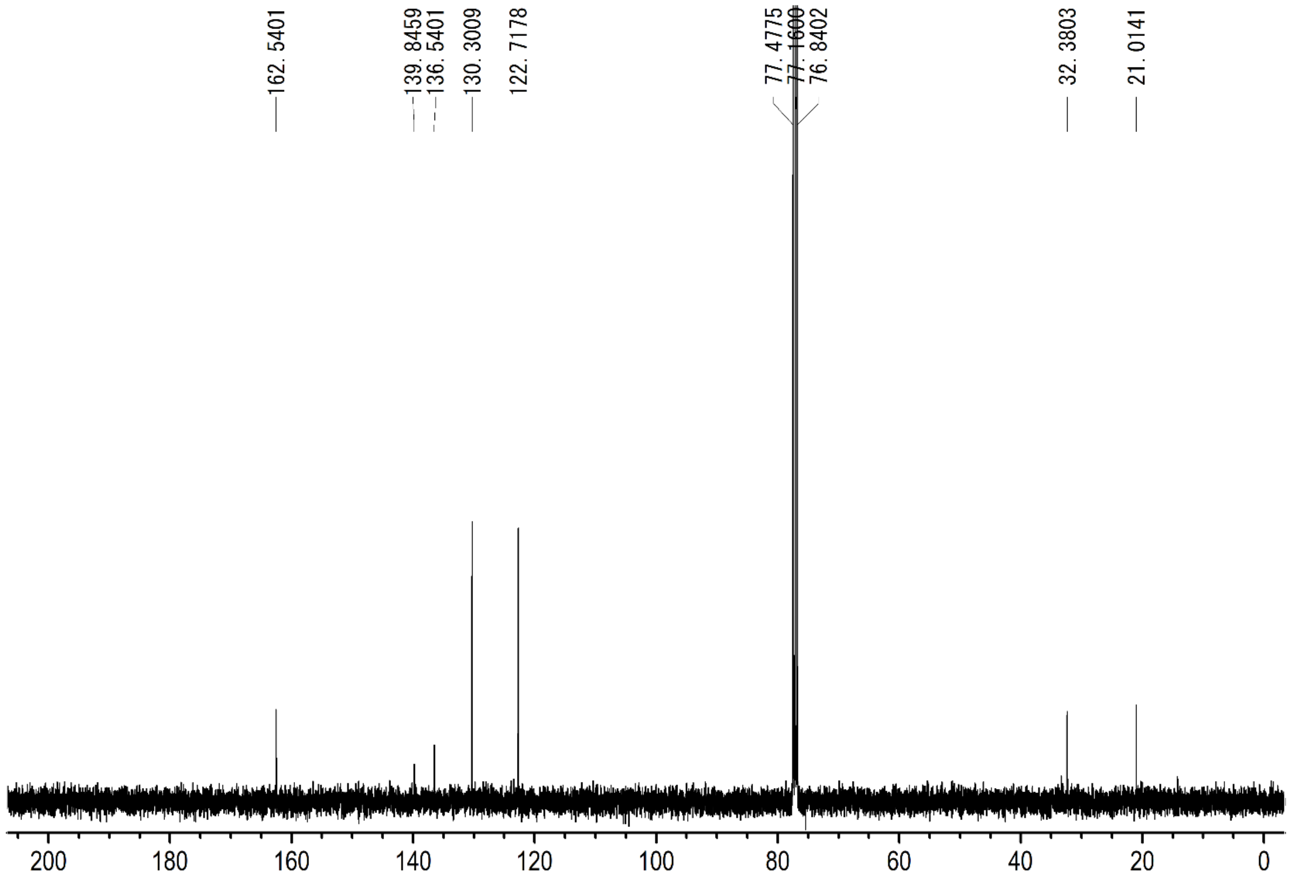


100 MHz ^{13}C NMR spectrum of **2d** in $CDCl_3$.

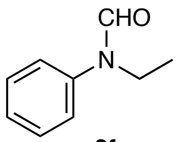


400 MHz ^{1}H NMR spectrum of **2e** in $CDCl_3$.

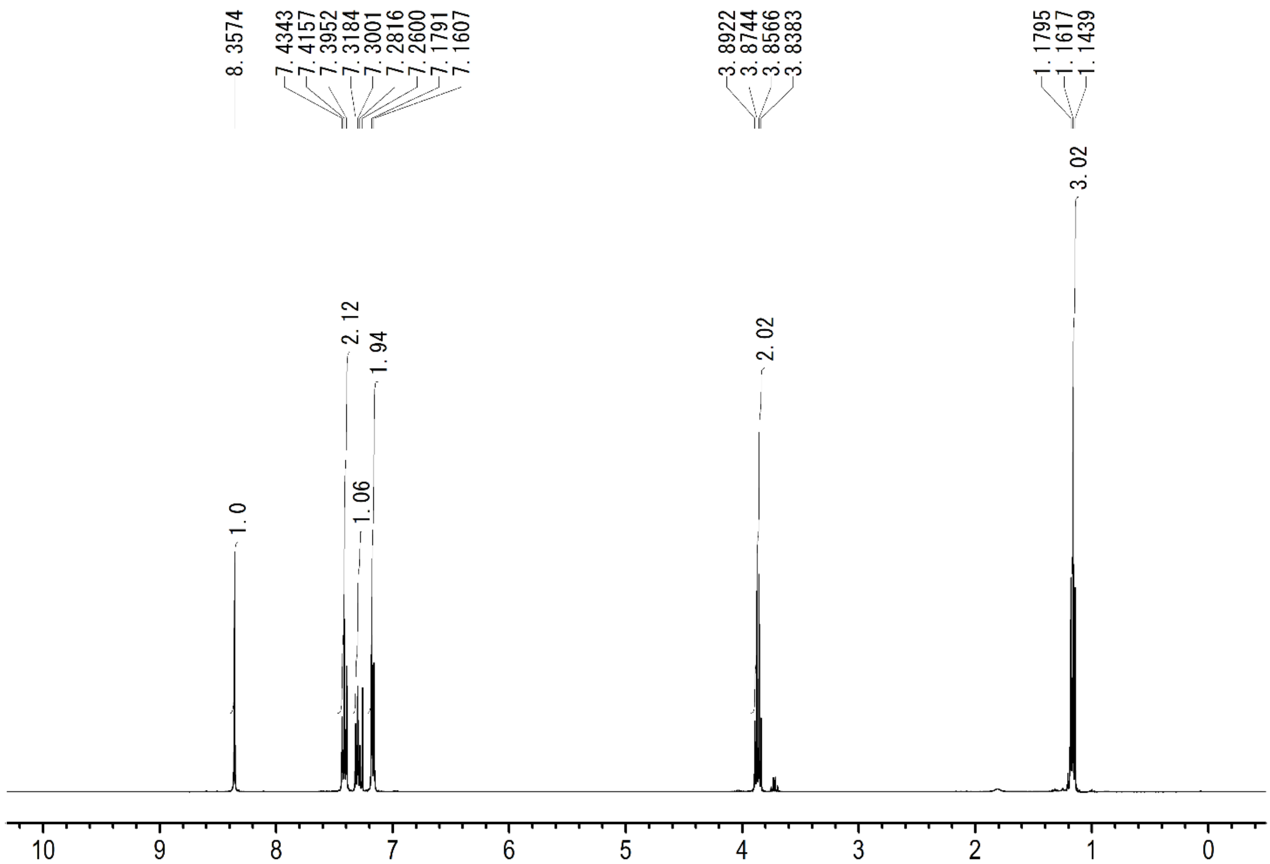




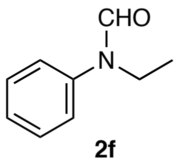
100 MHz ^{13}C NMR spectrum of **2e** in $CDCl_3$.

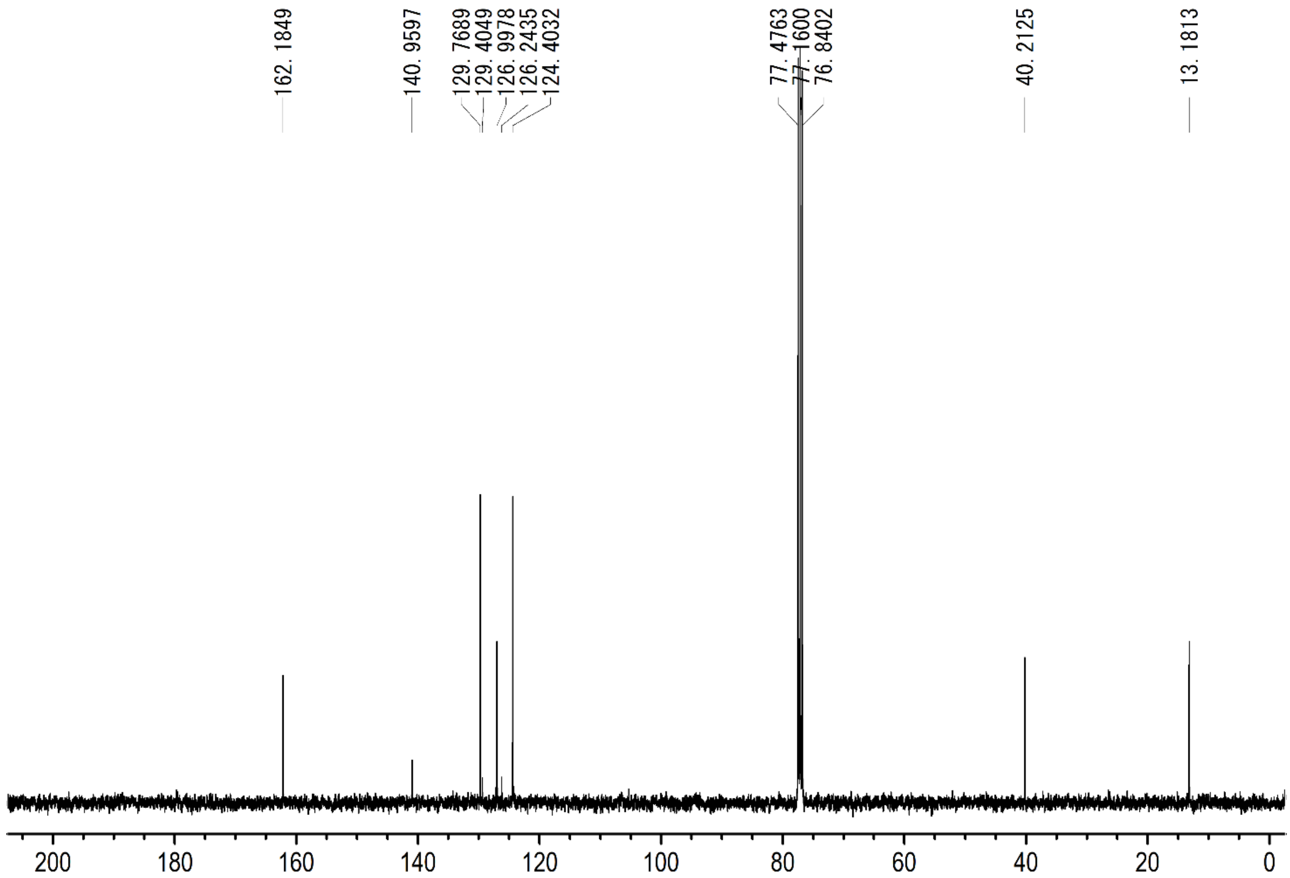


2f

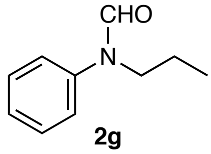


400 MHz ^{1}H NMR spectrum of **2f** in $CDCl_3$.

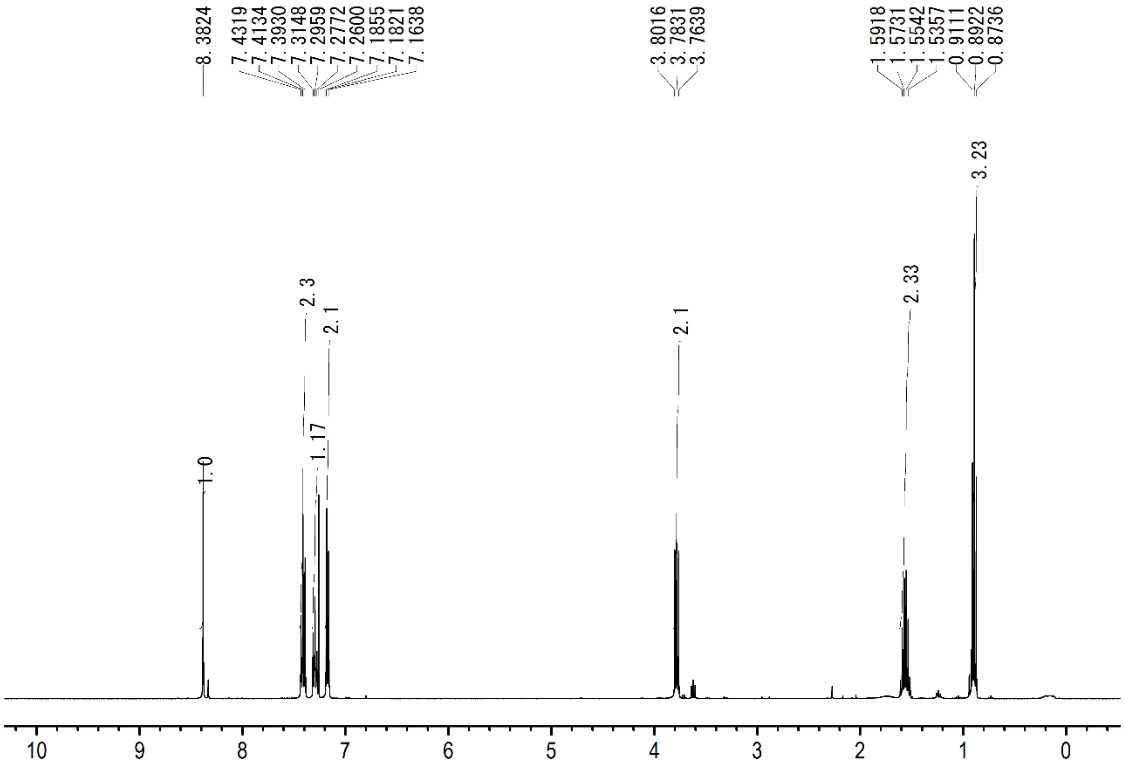




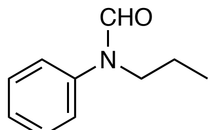
100 MHz ^{13}C NMR spectrum of **2f** in $CDCl_3$.



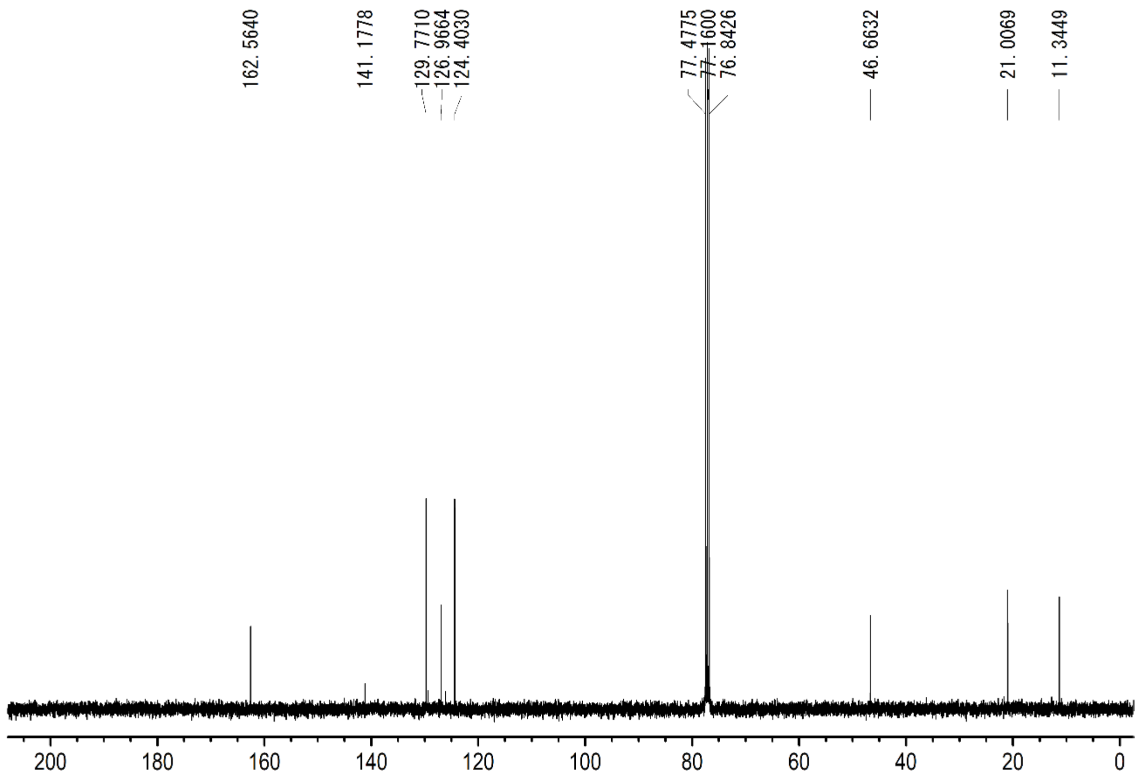
2g



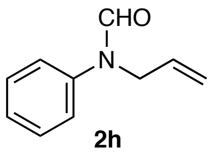
400 MHz ^{1}H NMR spectrum of **2g** in $CDCl_3$.



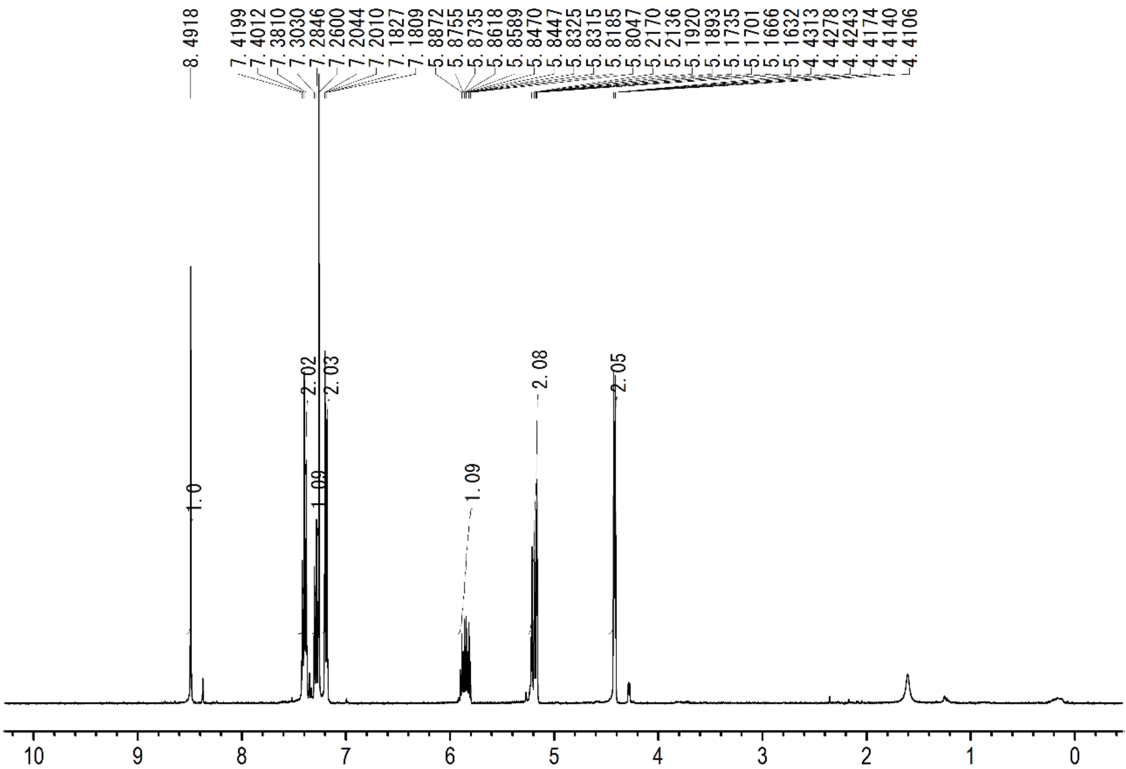
2g



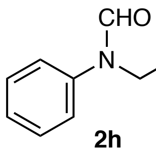
100 MHz ^{13}C NMR spectrum of **2g** in $CDCl_3$.



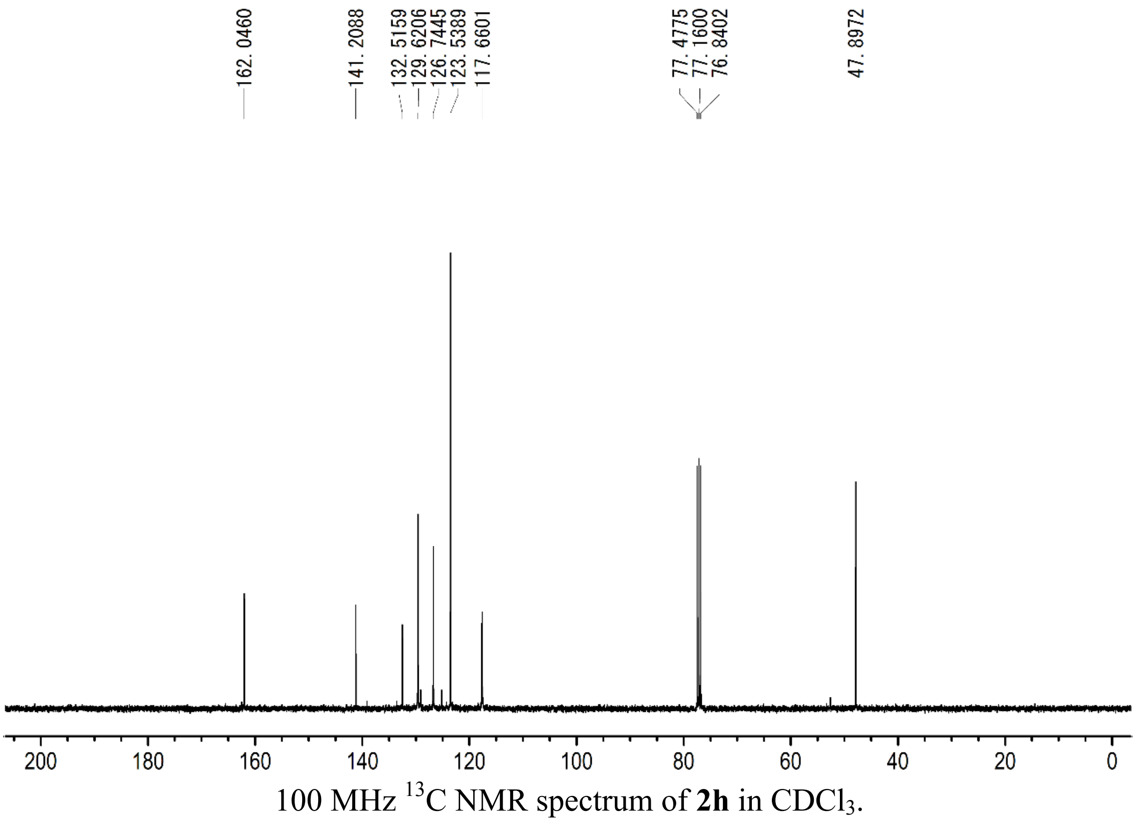
2h



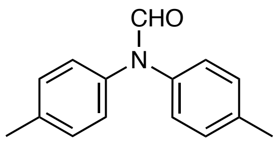
400 MHz ^{1}H NMR spectrum of **2h** in $CDCl_3$.



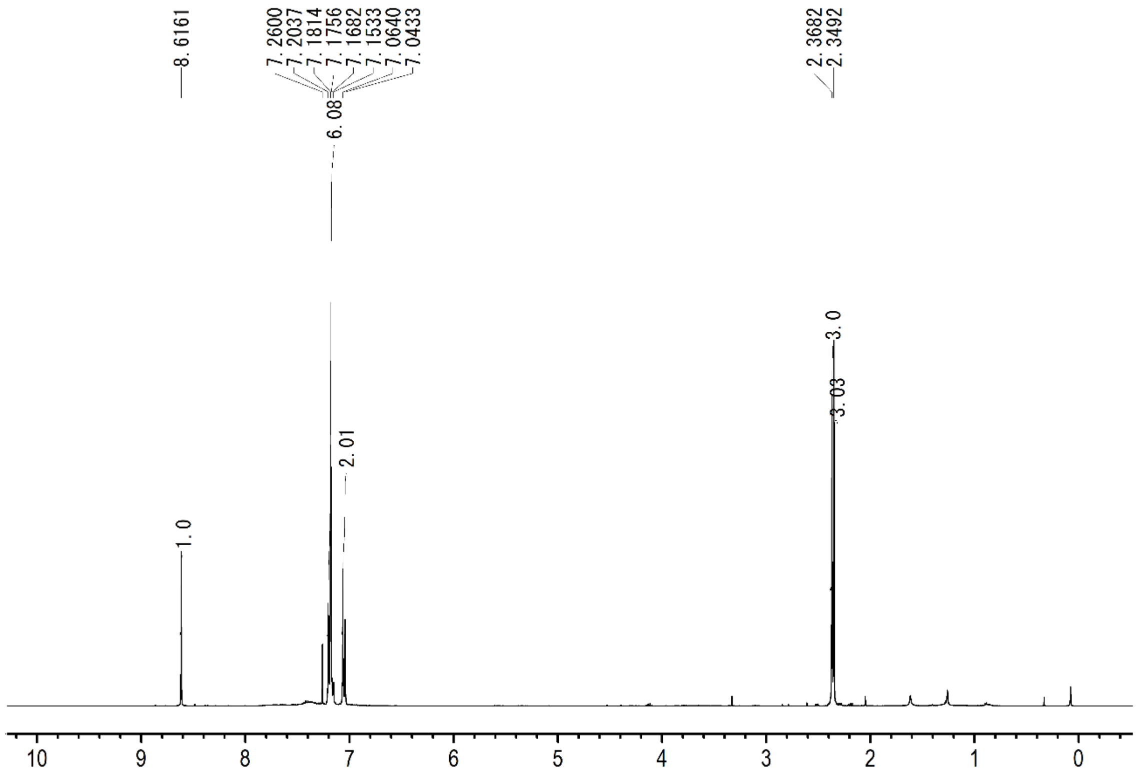
2h



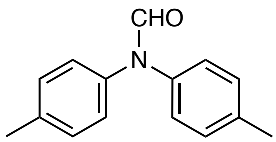
100 MHz ^{13}C NMR spectrum of **2h** in $CDCl_3$.



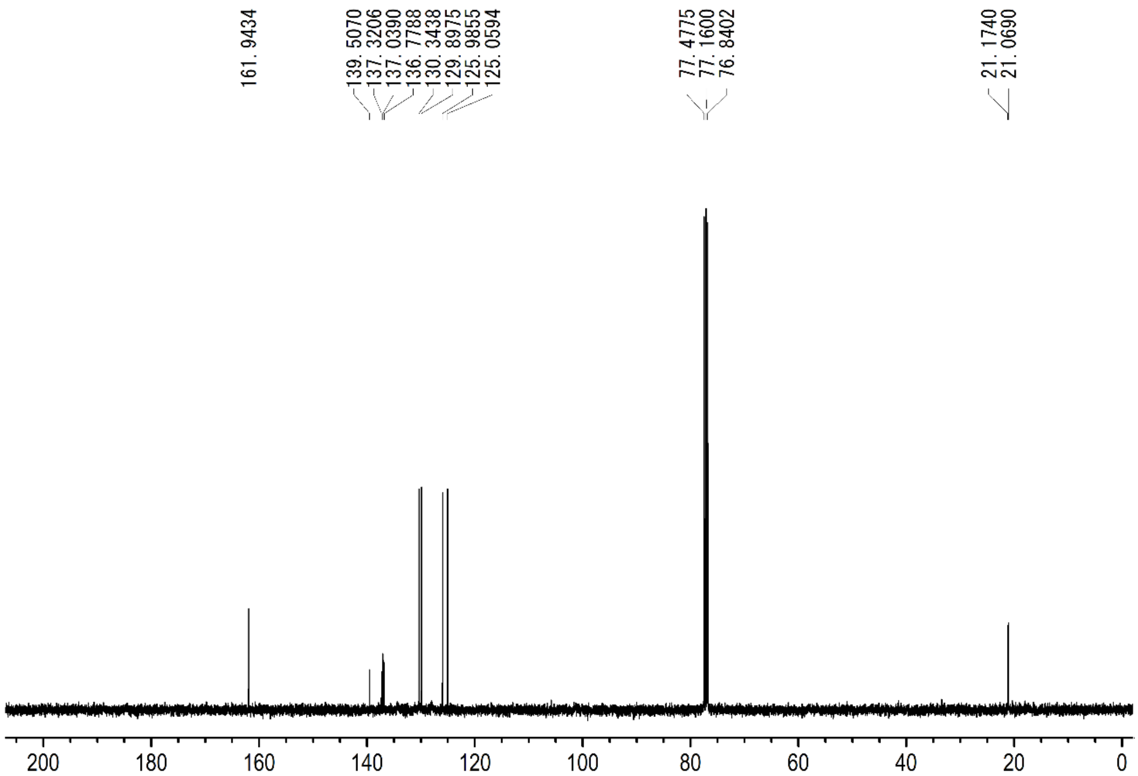
2i



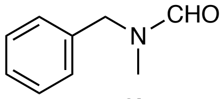
400 MHz ^{1}H NMR spectrum of **2i** in $CDCl_3$.



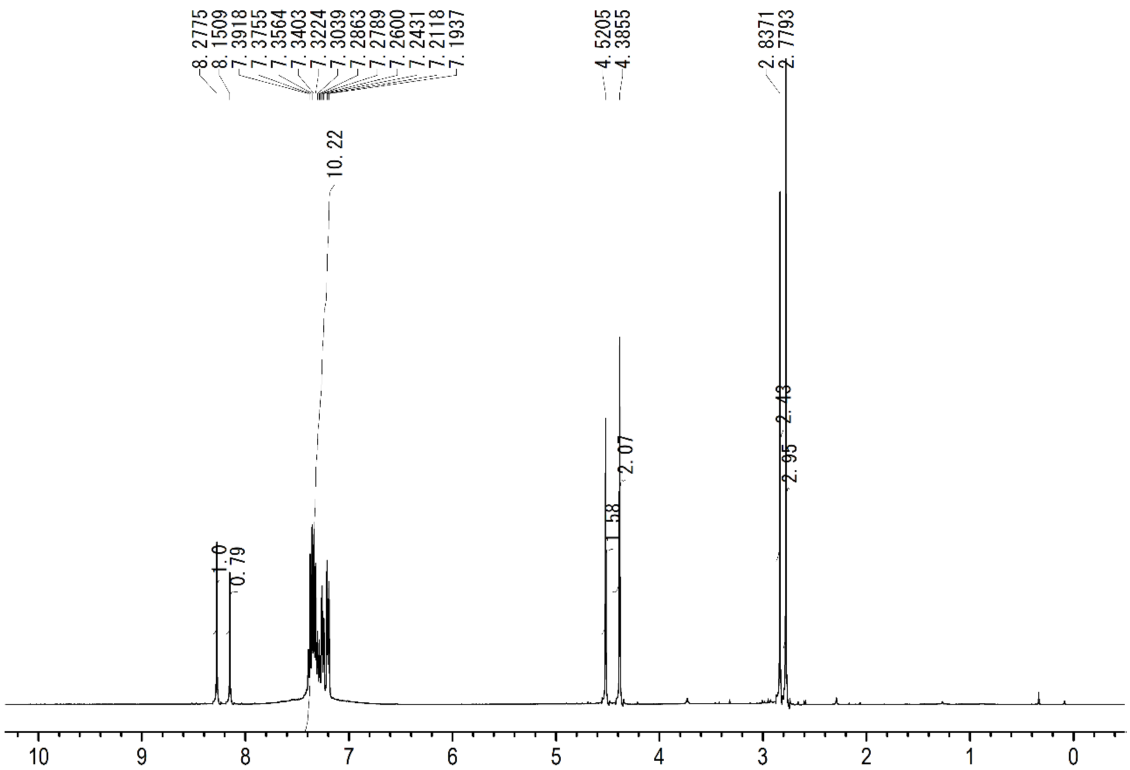
2i



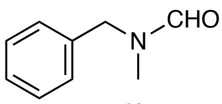
100 MHz ^{13}C NMR spectrum of **2i** in $CDCl_3$.



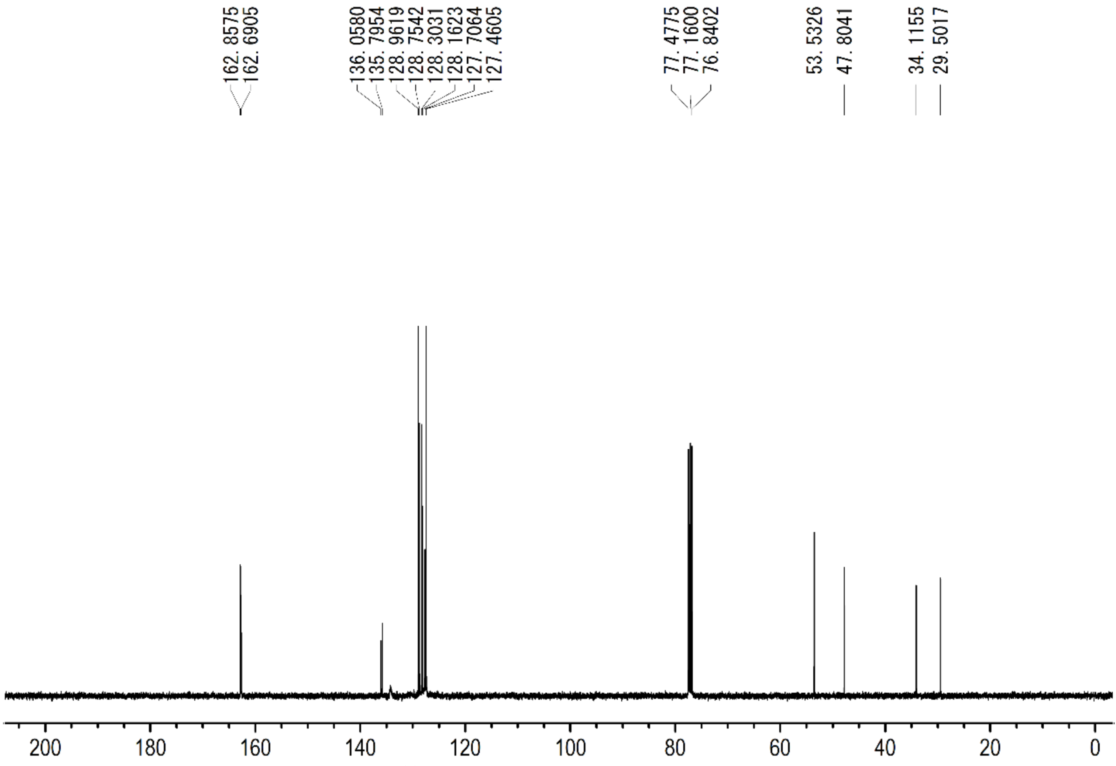
2j



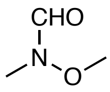
400 MHz ^{1}H NMR spectrum of **2j** in $CDCl_3$.



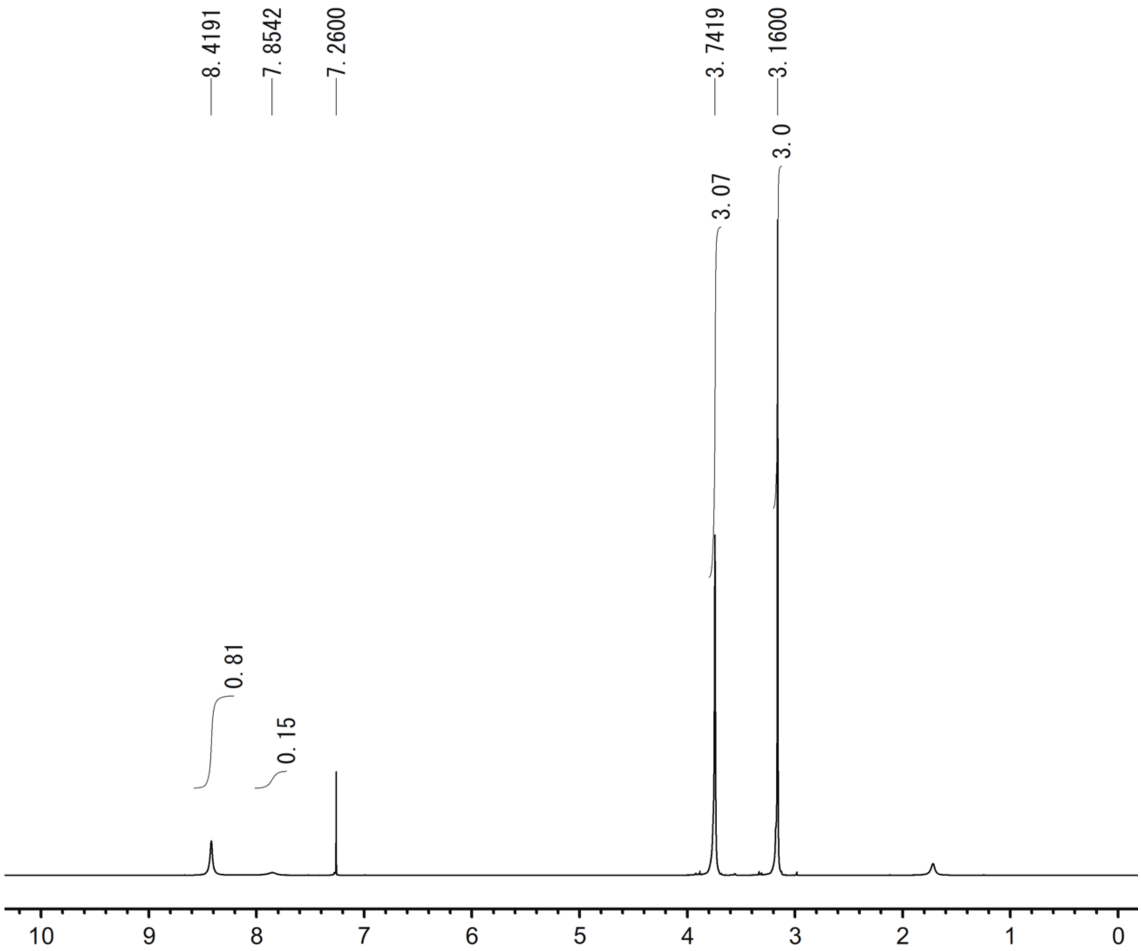
2j



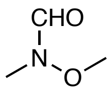
100 MHz ^{13}C NMR spectrum of **2j** in $CDCl_3$.



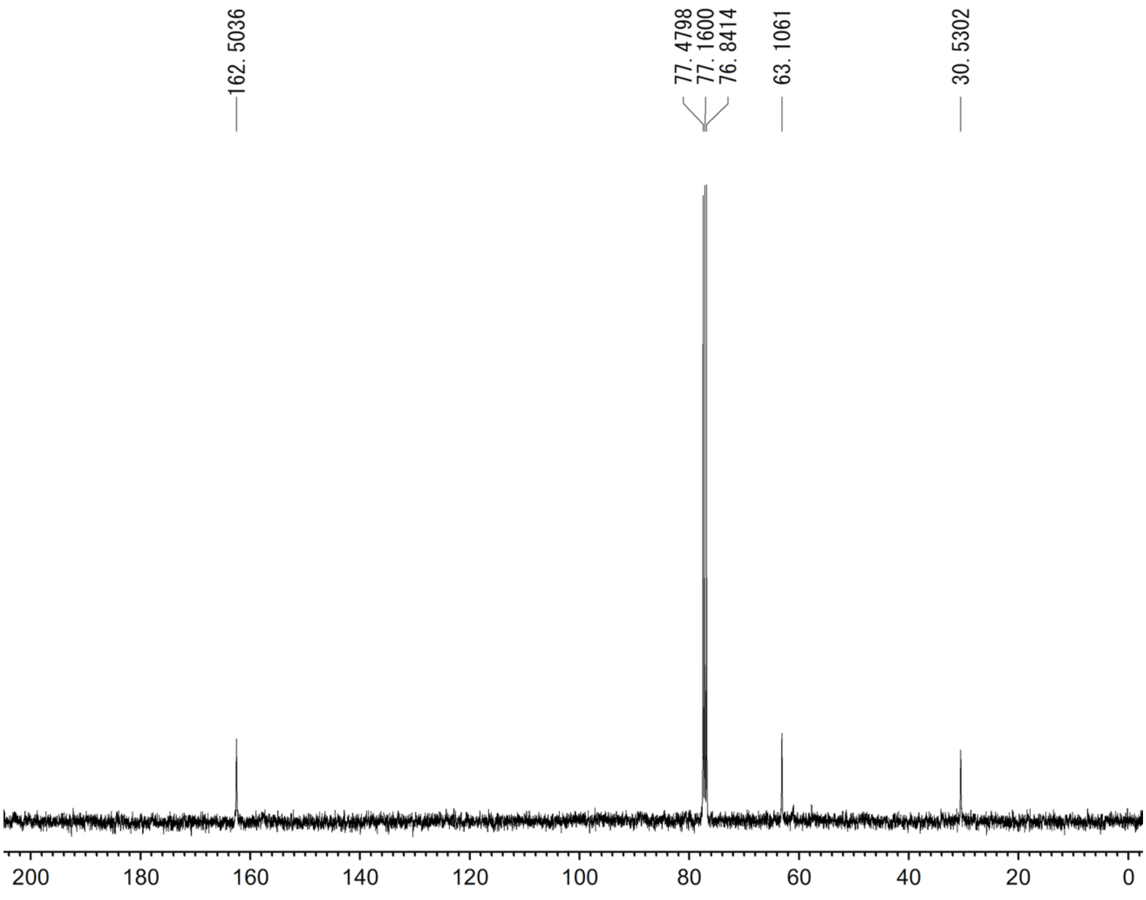
2k



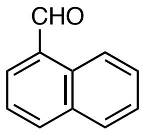
400 MHz ^{1}H NMR spectrum of **2k** in $CDCl_3$.



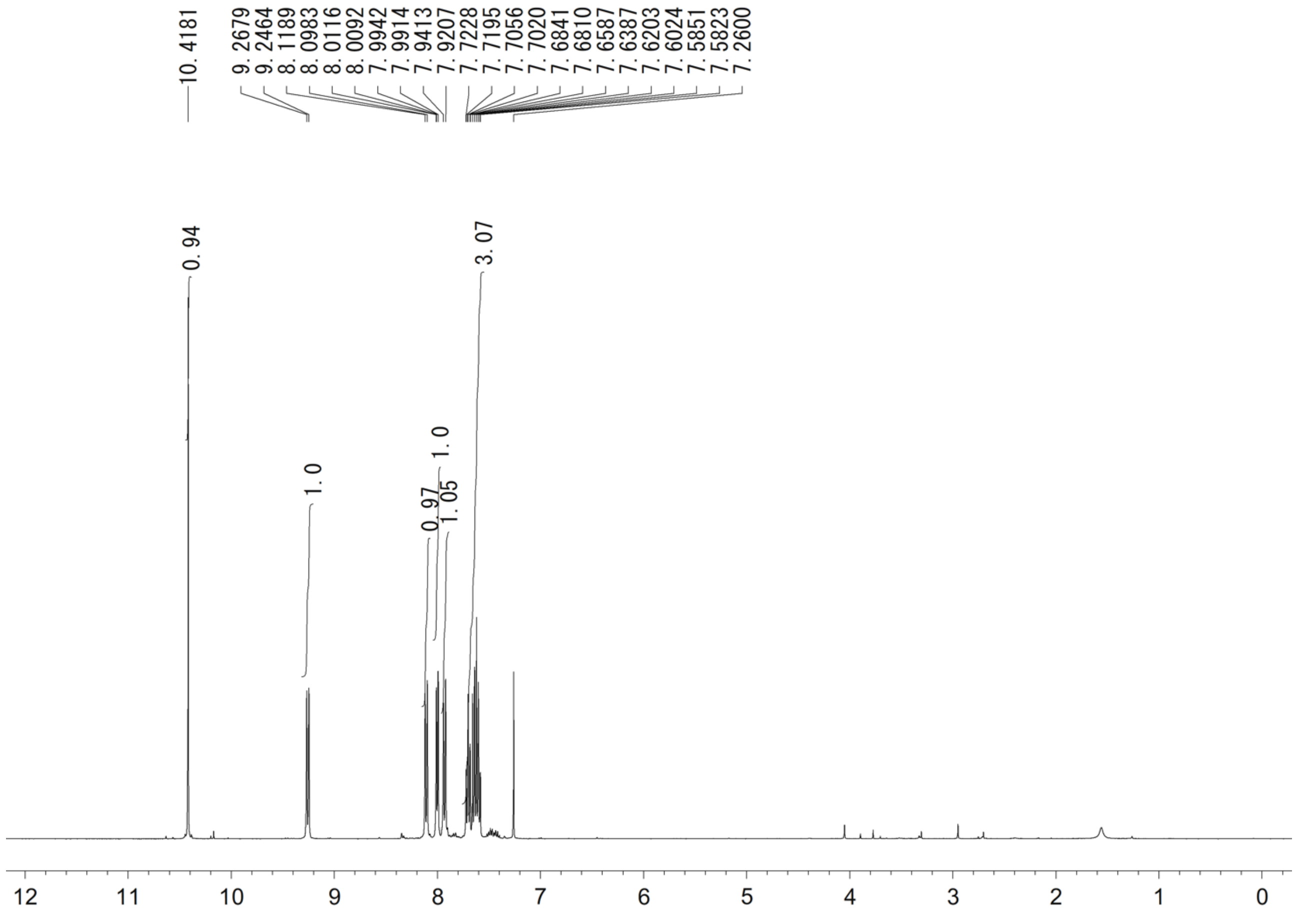
2k



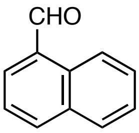
100 MHz ^{13}C NMR spectrum of **2k** in $CDCl_3$.



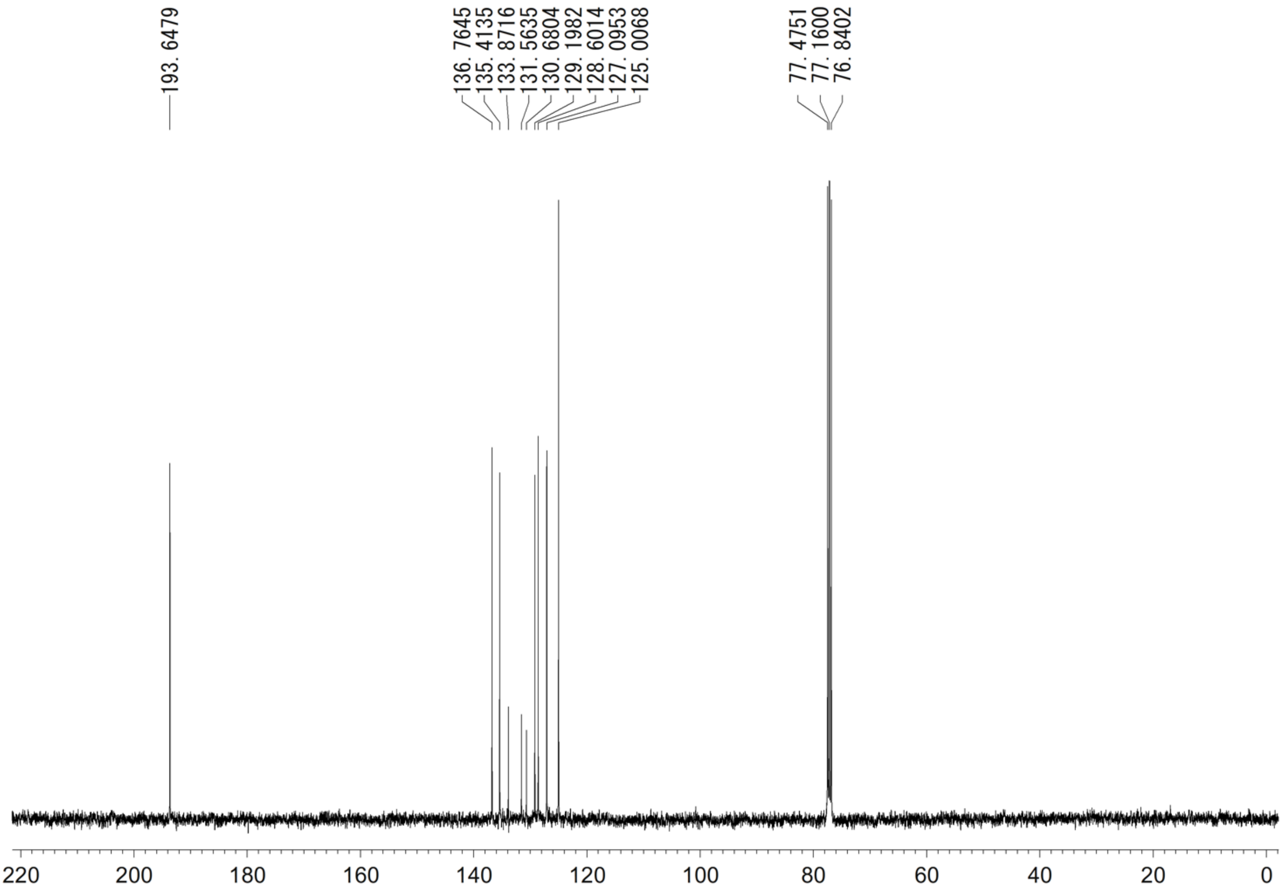
3a



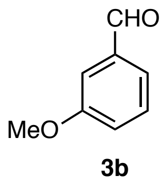
400 MHz ^{1}H NMR spectrum of **3a** in $CDCl_3$.



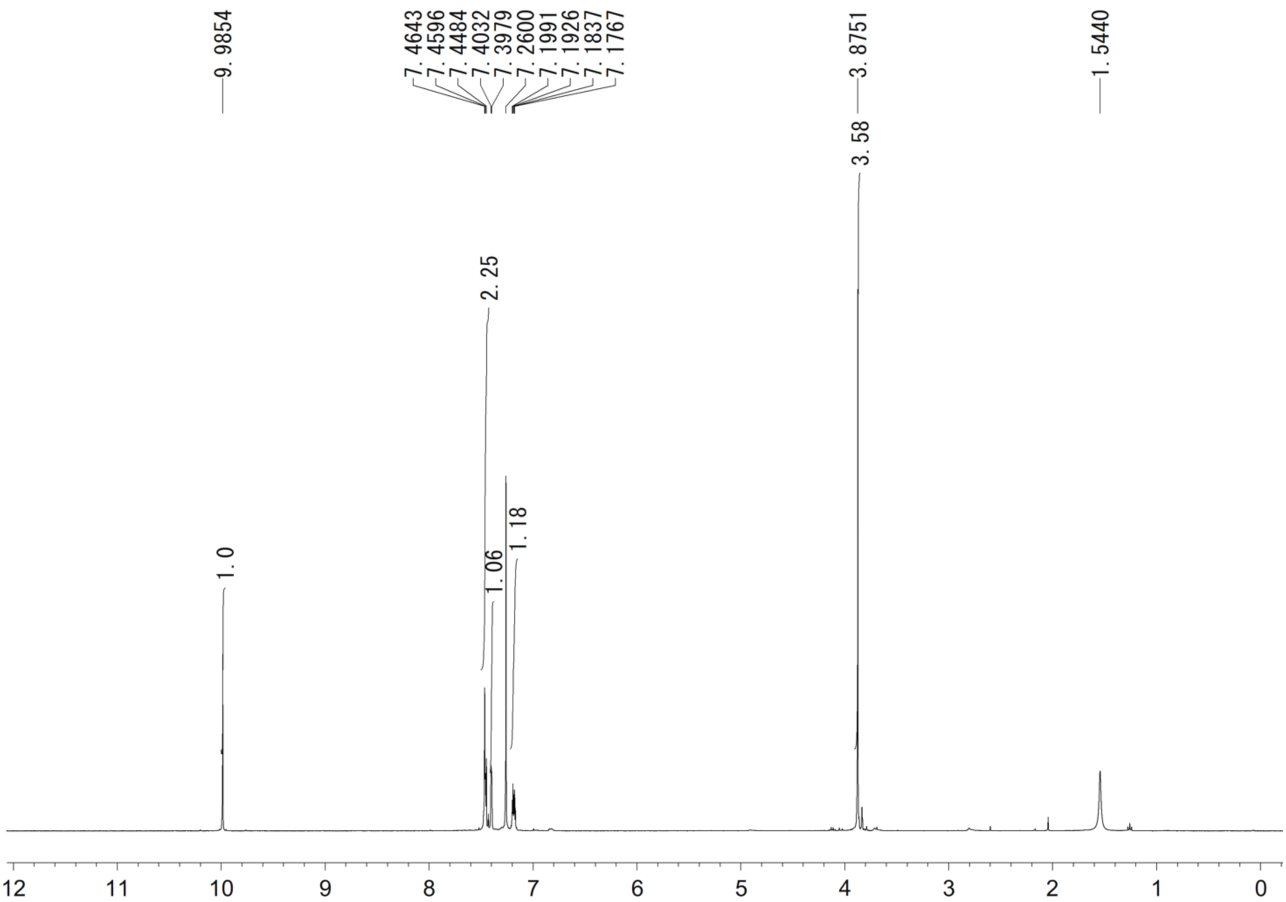
3a



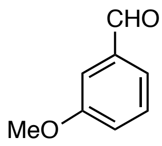
100 MHz ^{13}C NMR spectrum of **3a** in $CDCl_3$.



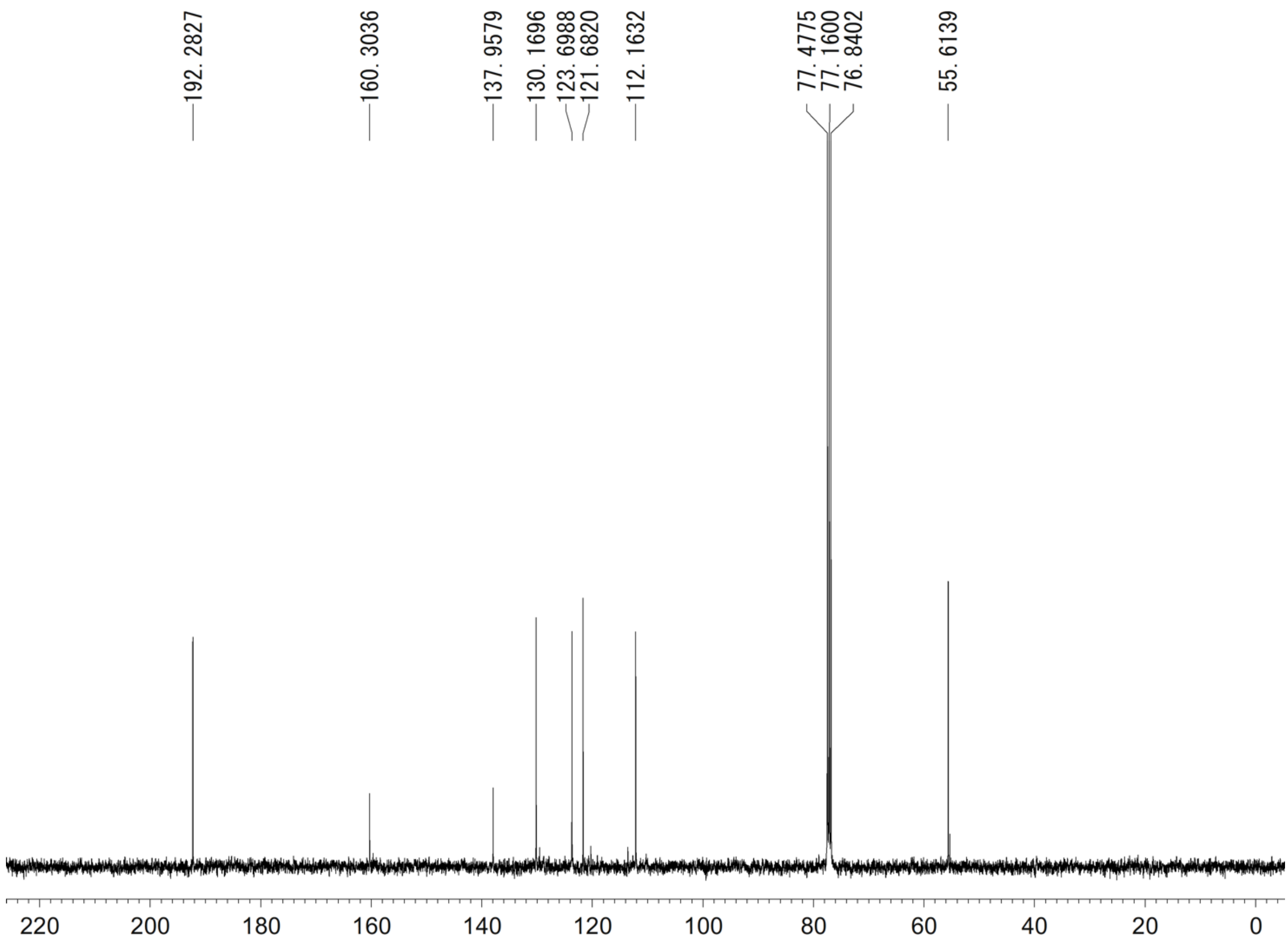
3b



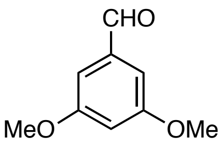
400 MHz ^{1}H NMR spectrum of **3b** in $CDCl_3$.



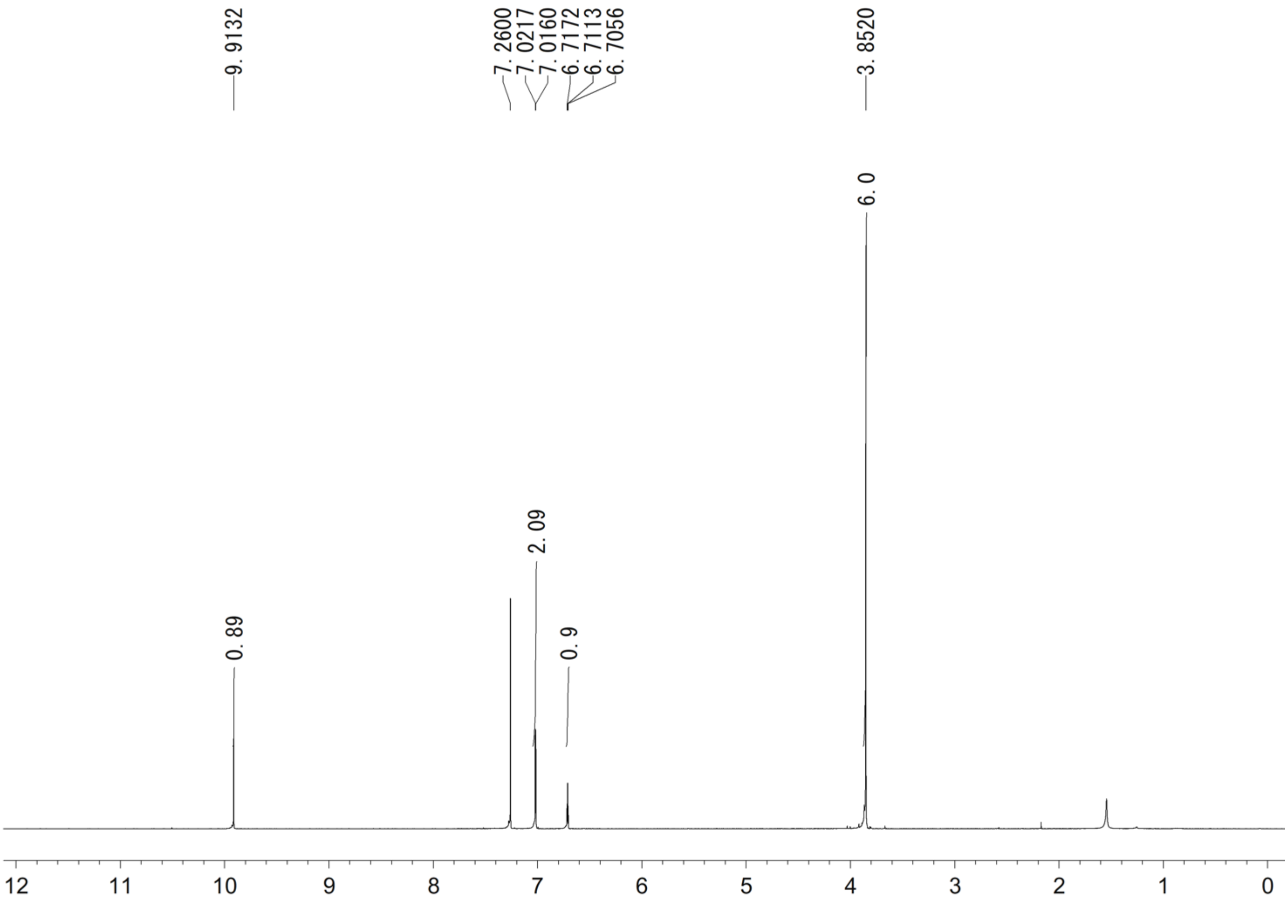
3b



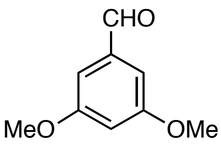
100 MHz ^{13}C NMR spectrum of **3b** in $CDCl_3$.



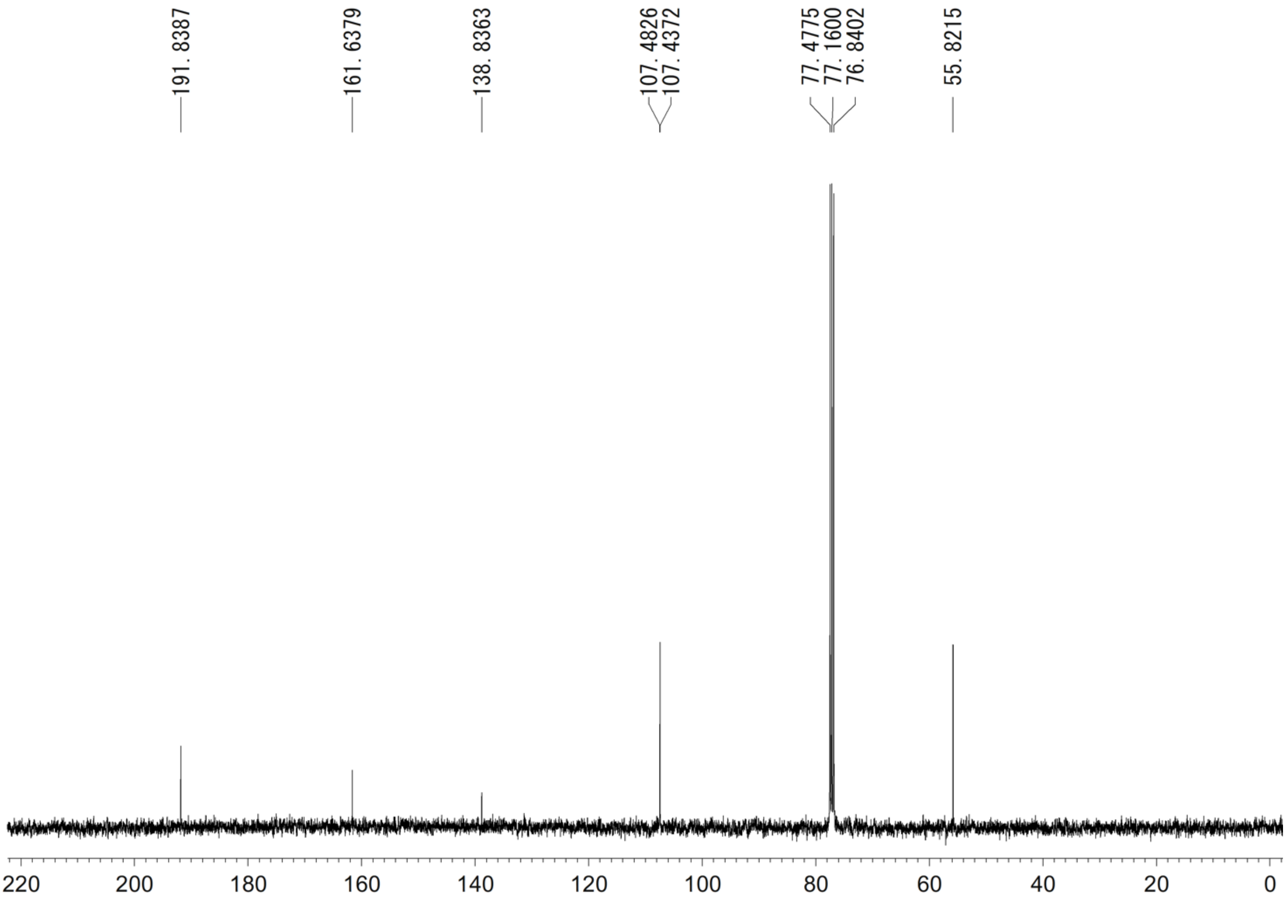
3c



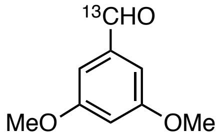
400 MHz ^{1}H NMR spectrum of **3c** in $CDCl_3$.



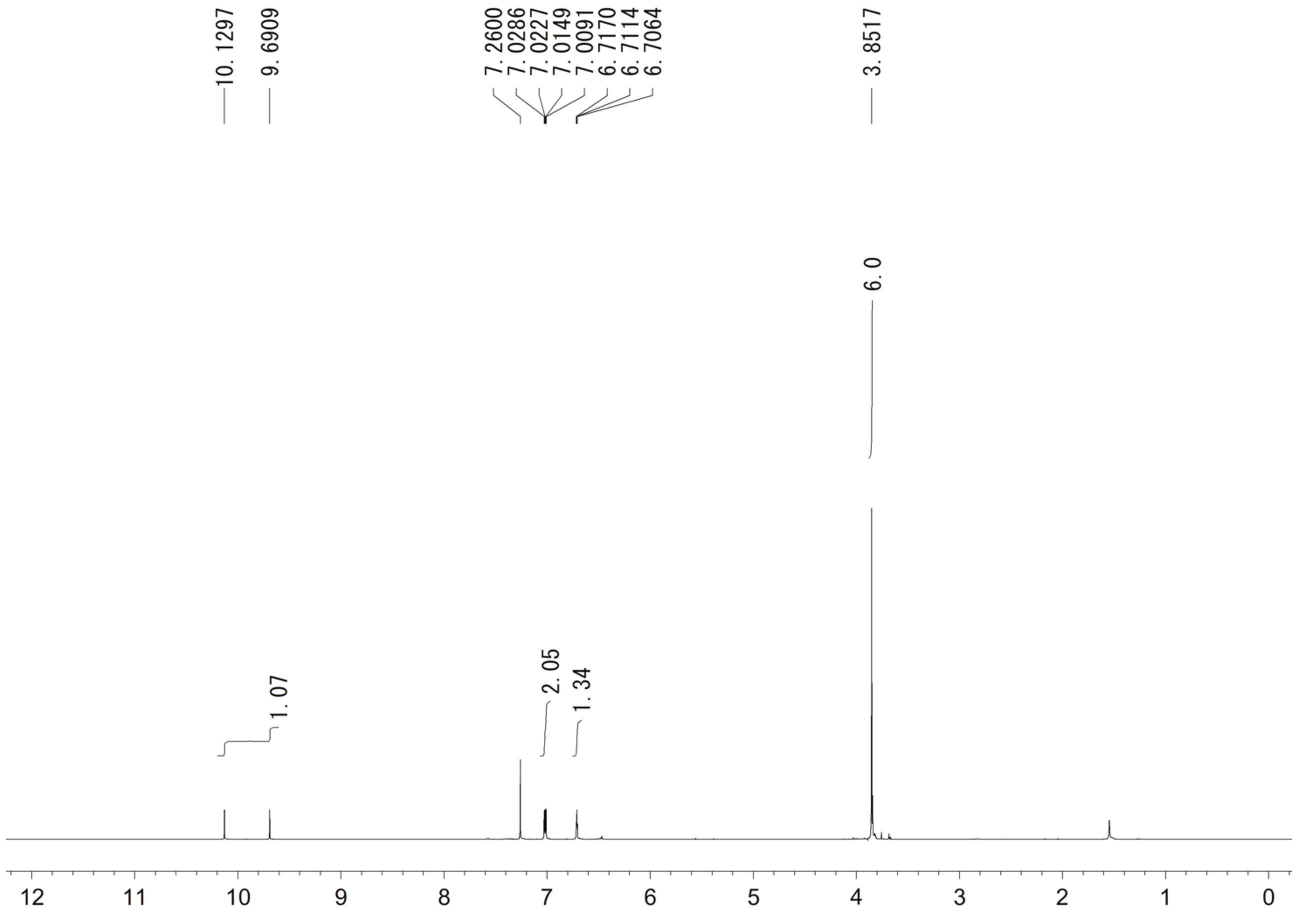
3c



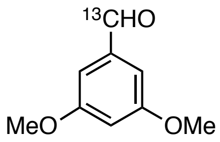
100 MHz ^{13}C NMR spectrum of **3c** in $CDCl_3$.



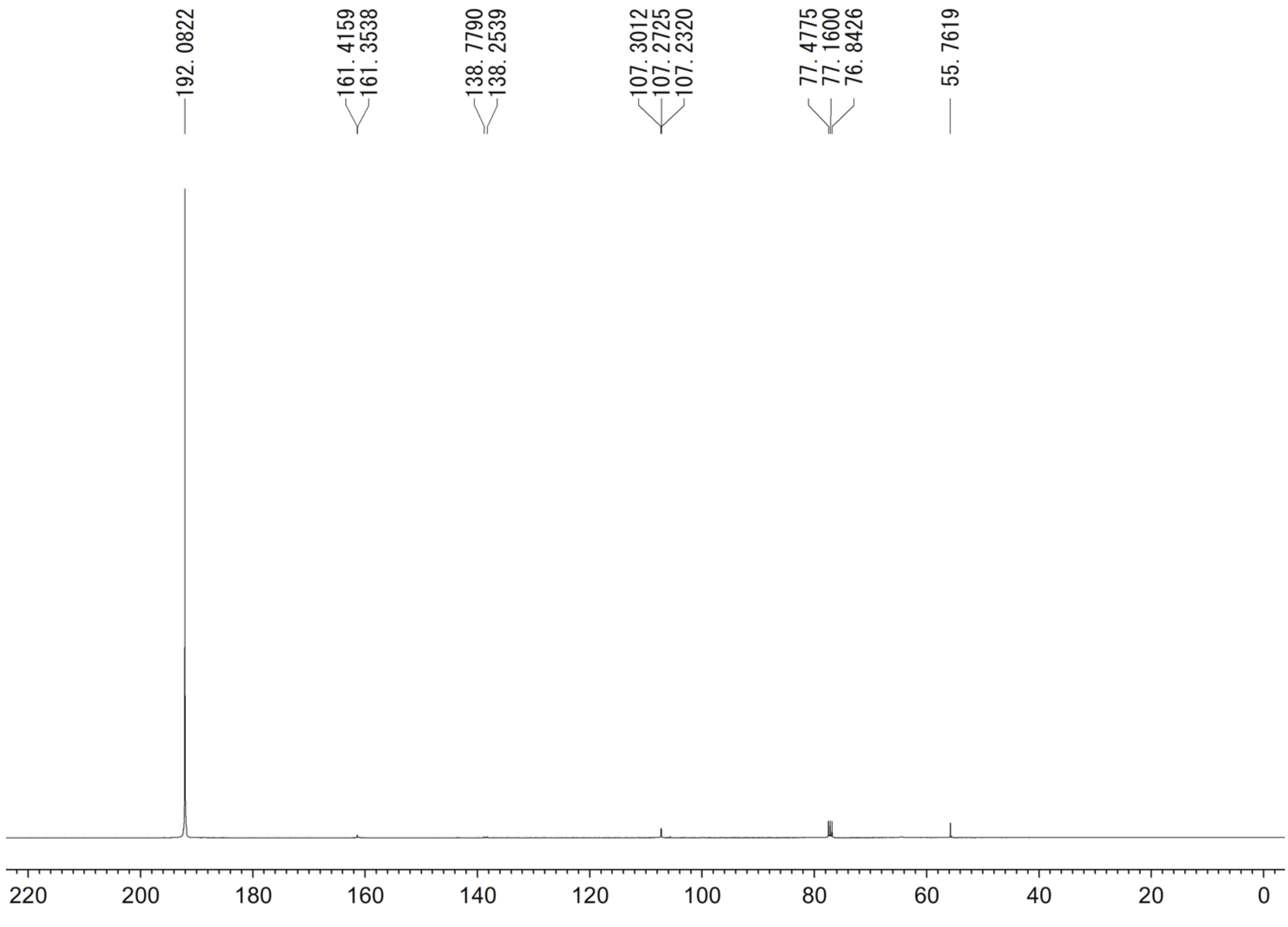
3c'



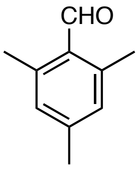
400 MHz ^{1}H NMR spectrum of **3c'** in $CDCl_3$.



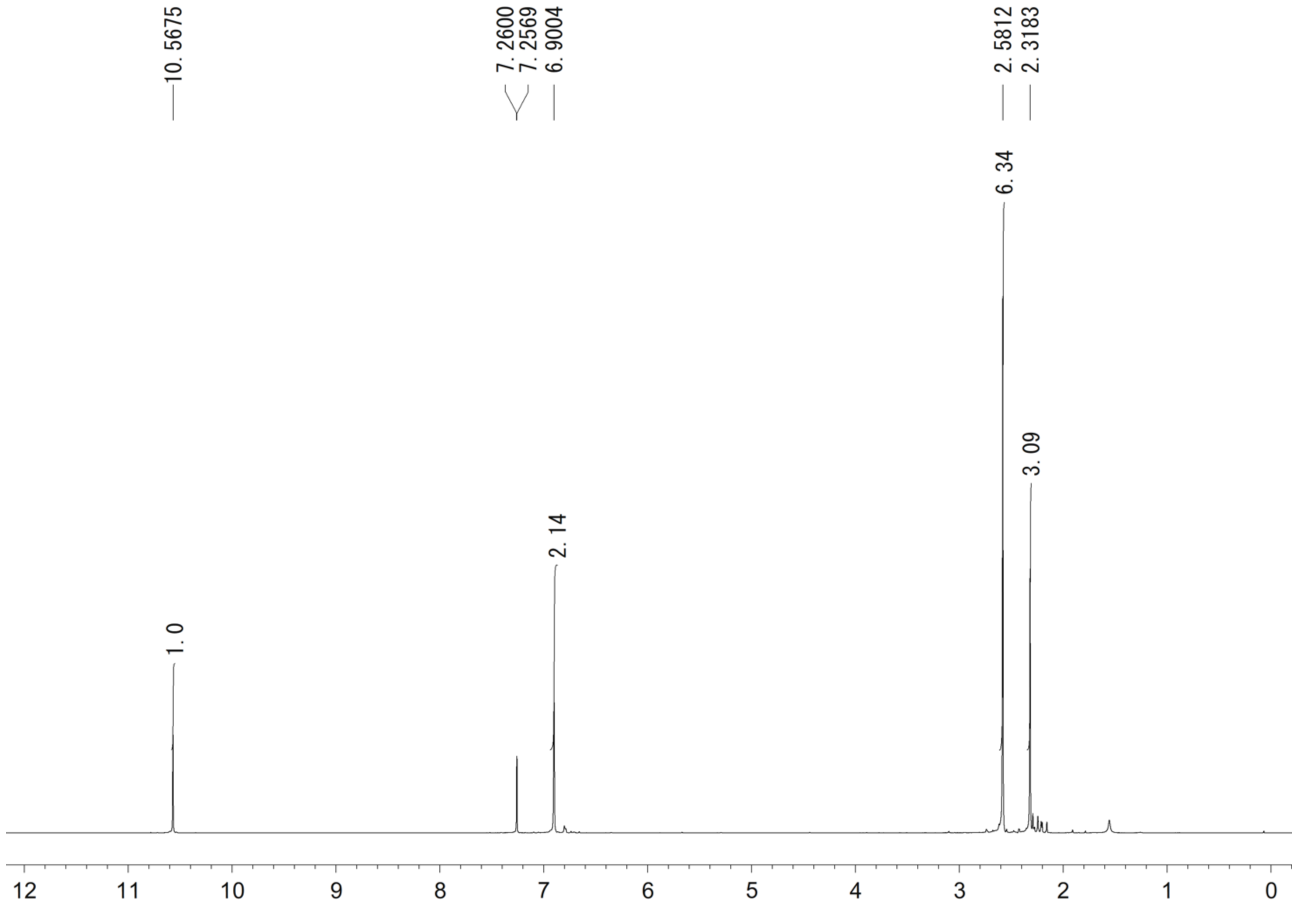
3c'



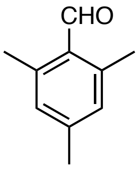
100 MHz ^{13}C NMR spectrum of **3c'** in $CDCl_3$.



3d



400 MHz [1]H NMR spectrum of **3d** in $CDCl_3$.



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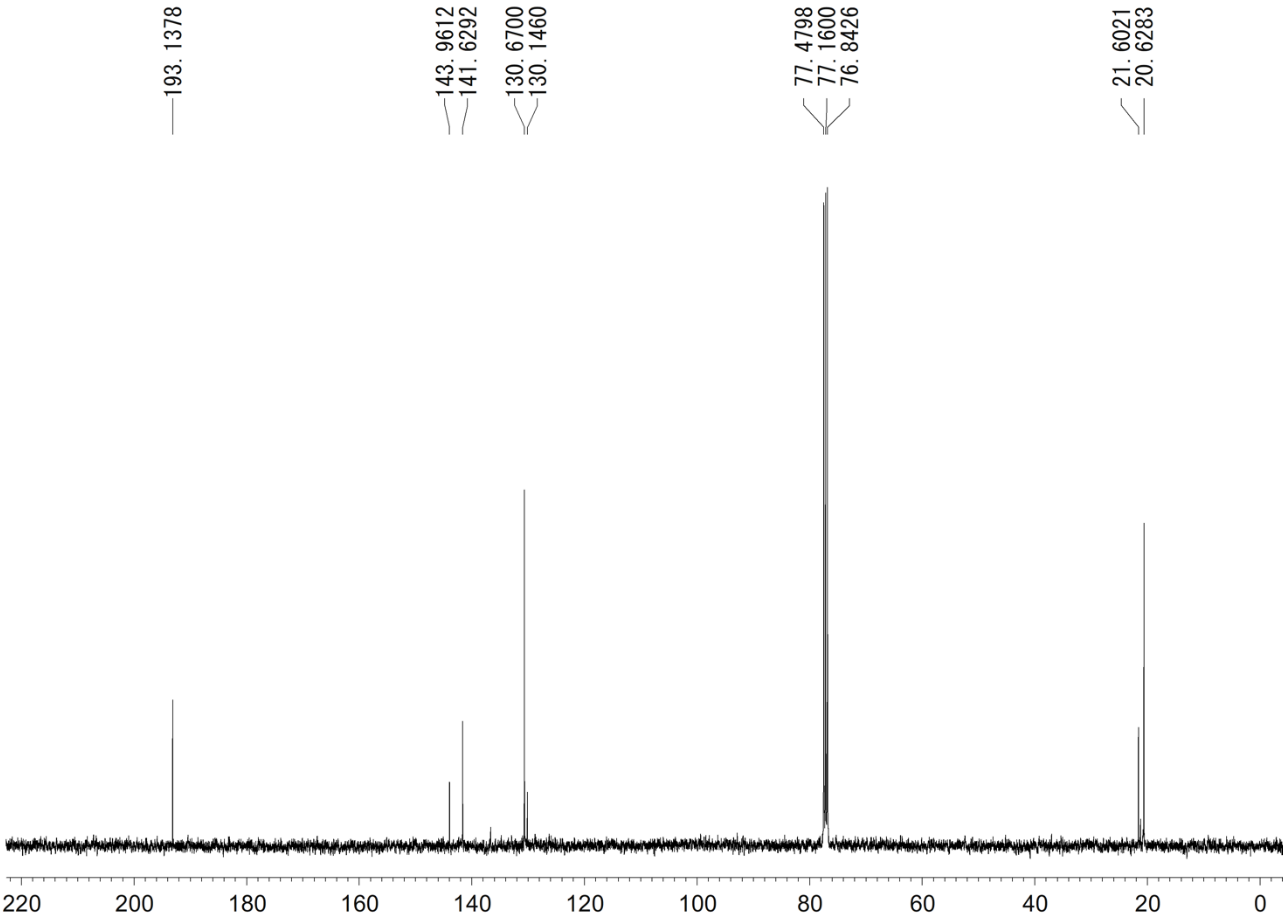
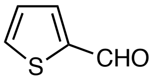


100 MHz ^{13}C NMR spectrum of **3d** in $CDCl_3$.



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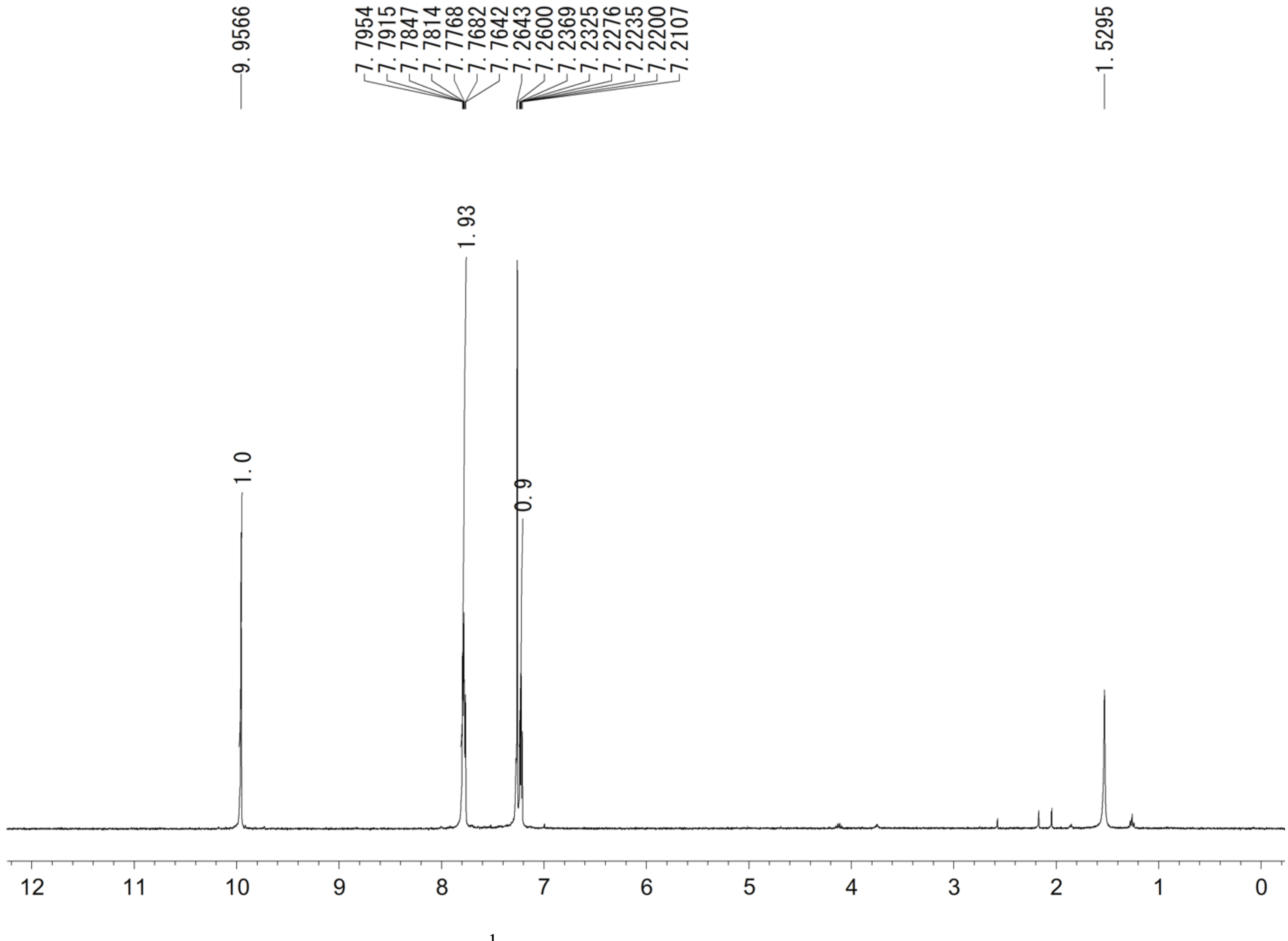

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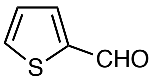

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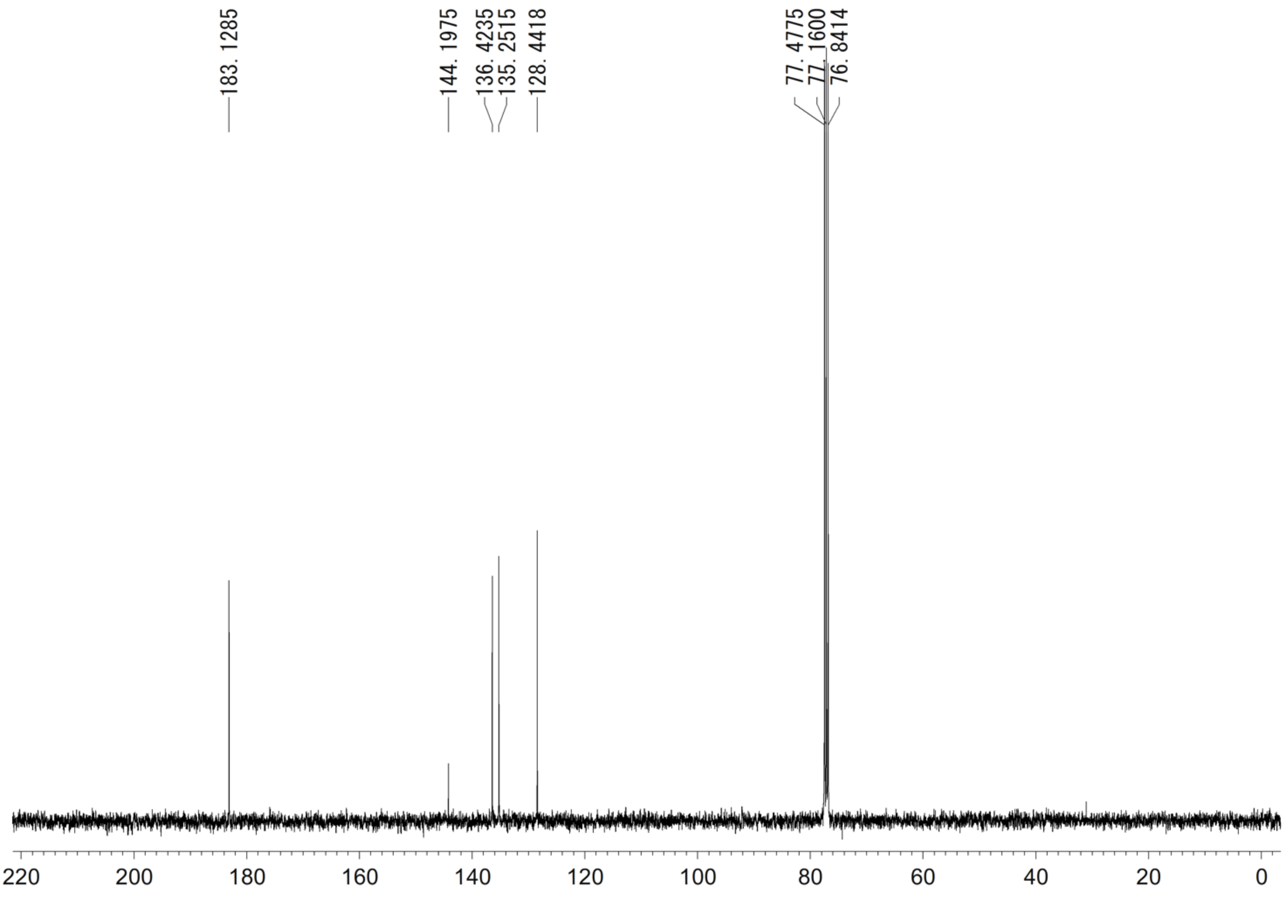
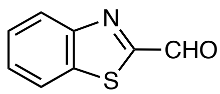


100 MHz ^{13}C NMR spectrum of **3e** in $CDCl_3$.



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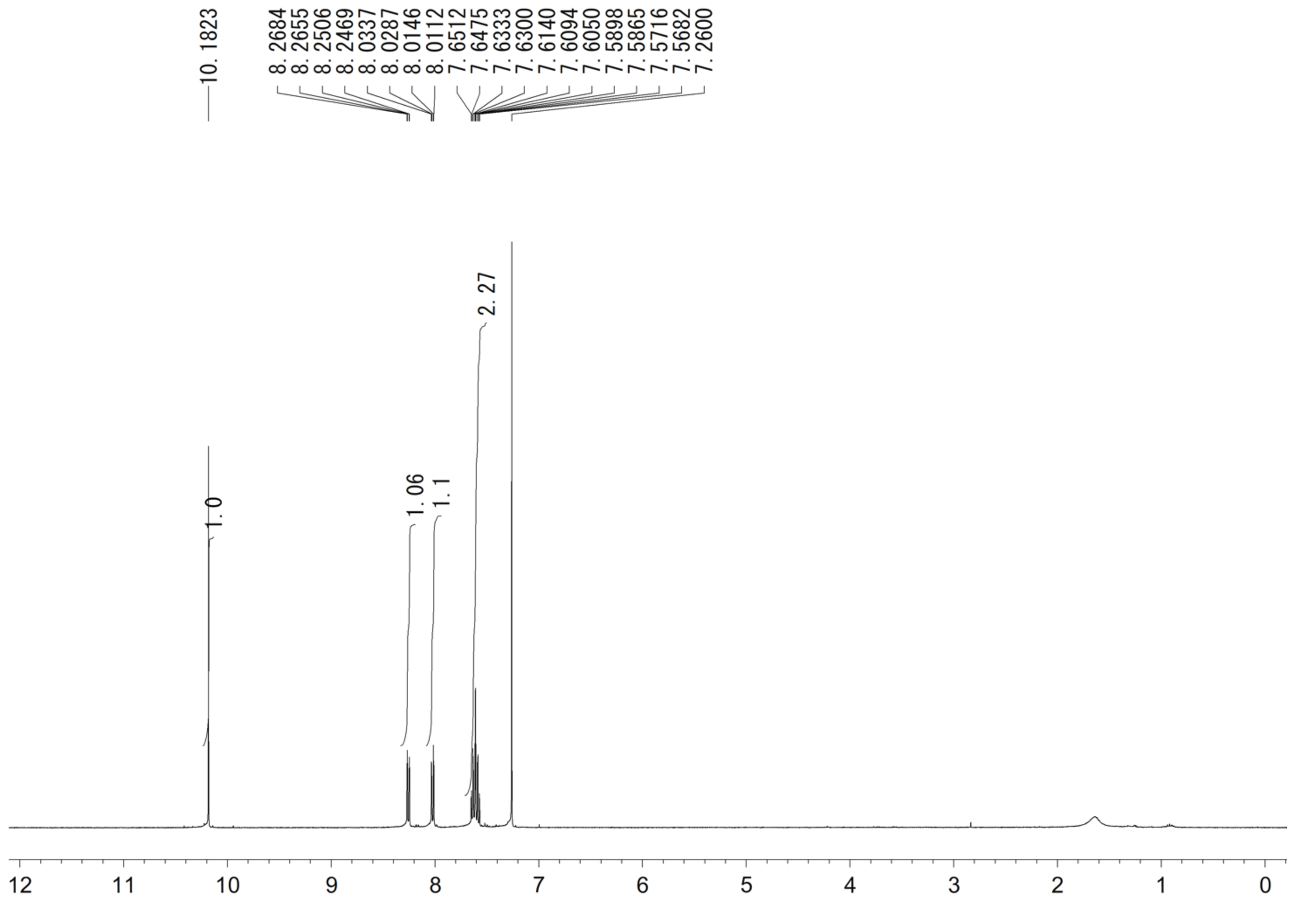
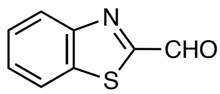


400 MHz ^{1}H NMR spectrum of **3f** in $CDCl_3$.



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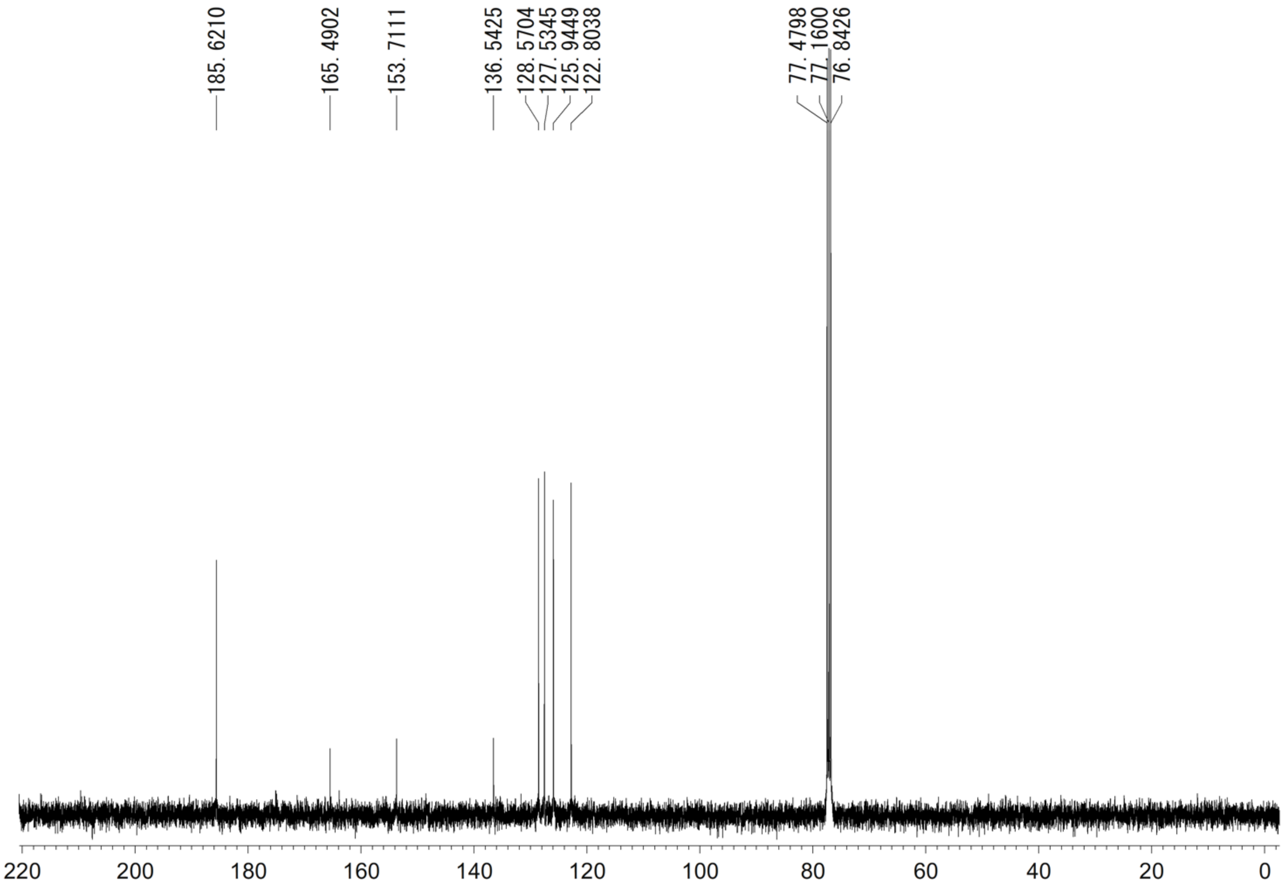
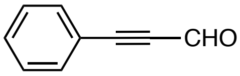


100 MHz ^{13}C NMR spectrum of **3f** in $CDCl_3$.



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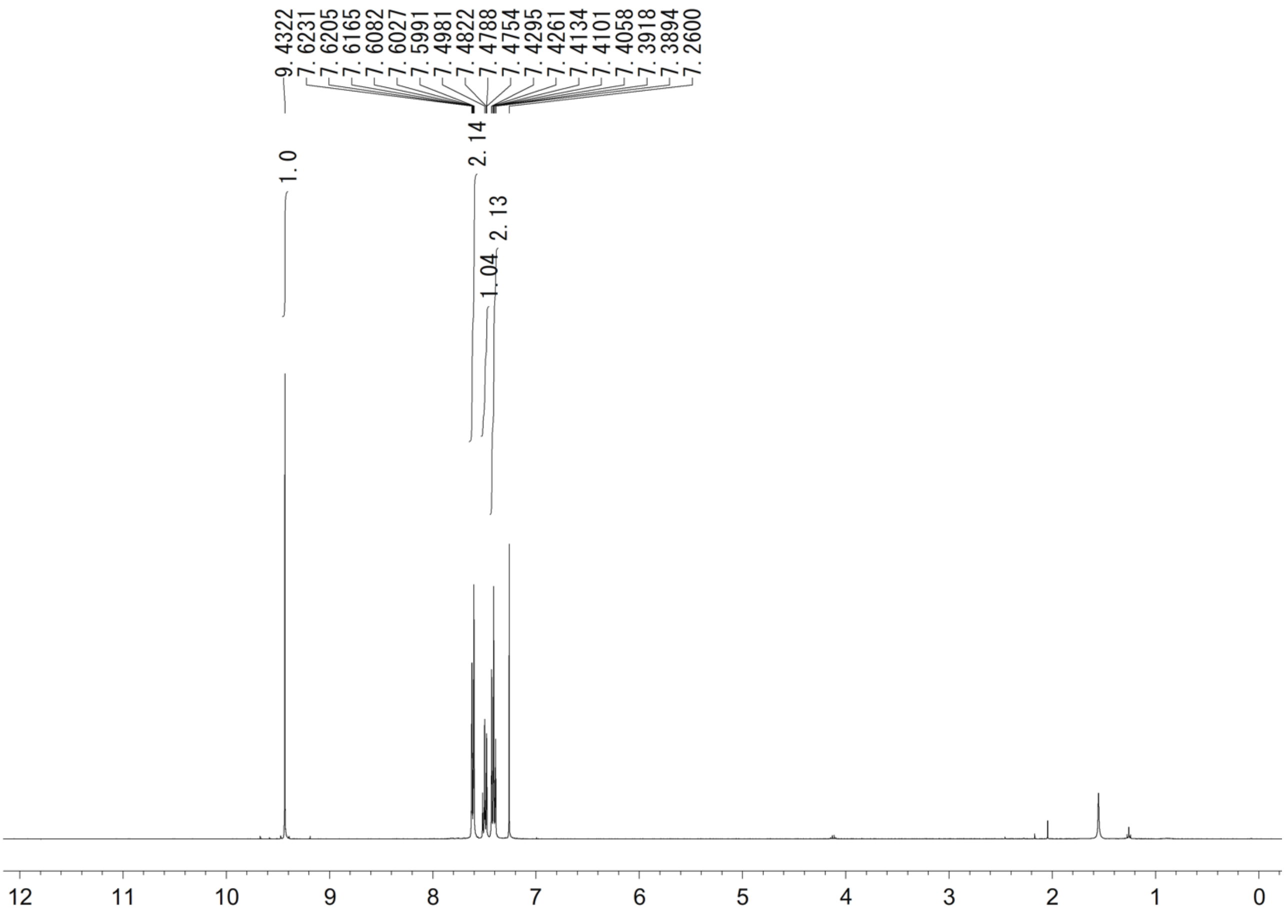
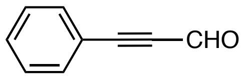


400 MHz ^{1}H NMR spectrum of **3g** in $CDCl_3$.



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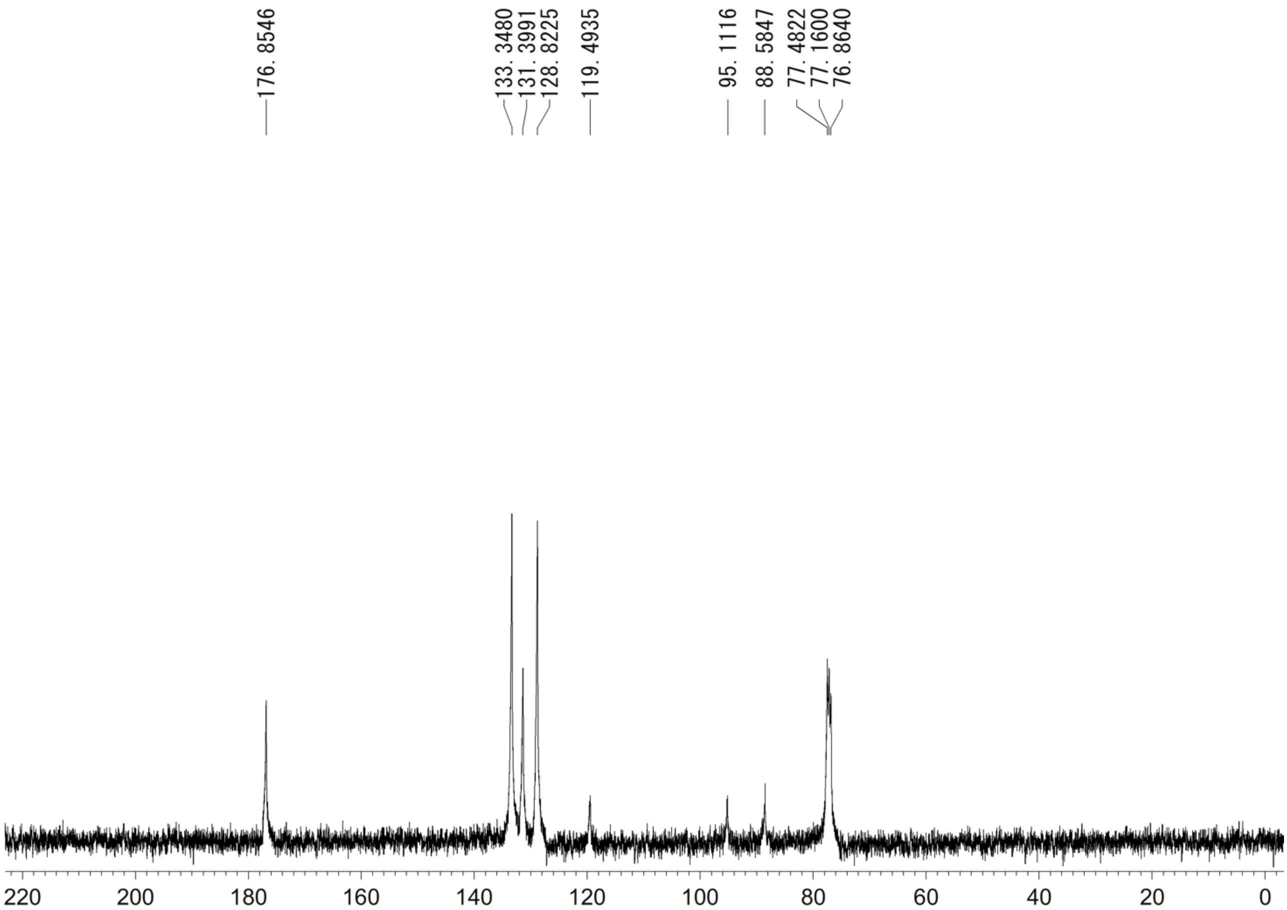
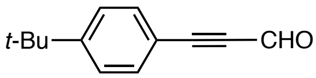


100 MHz ^{13}C NMR spectrum of **3g** in $CDCl_3$.



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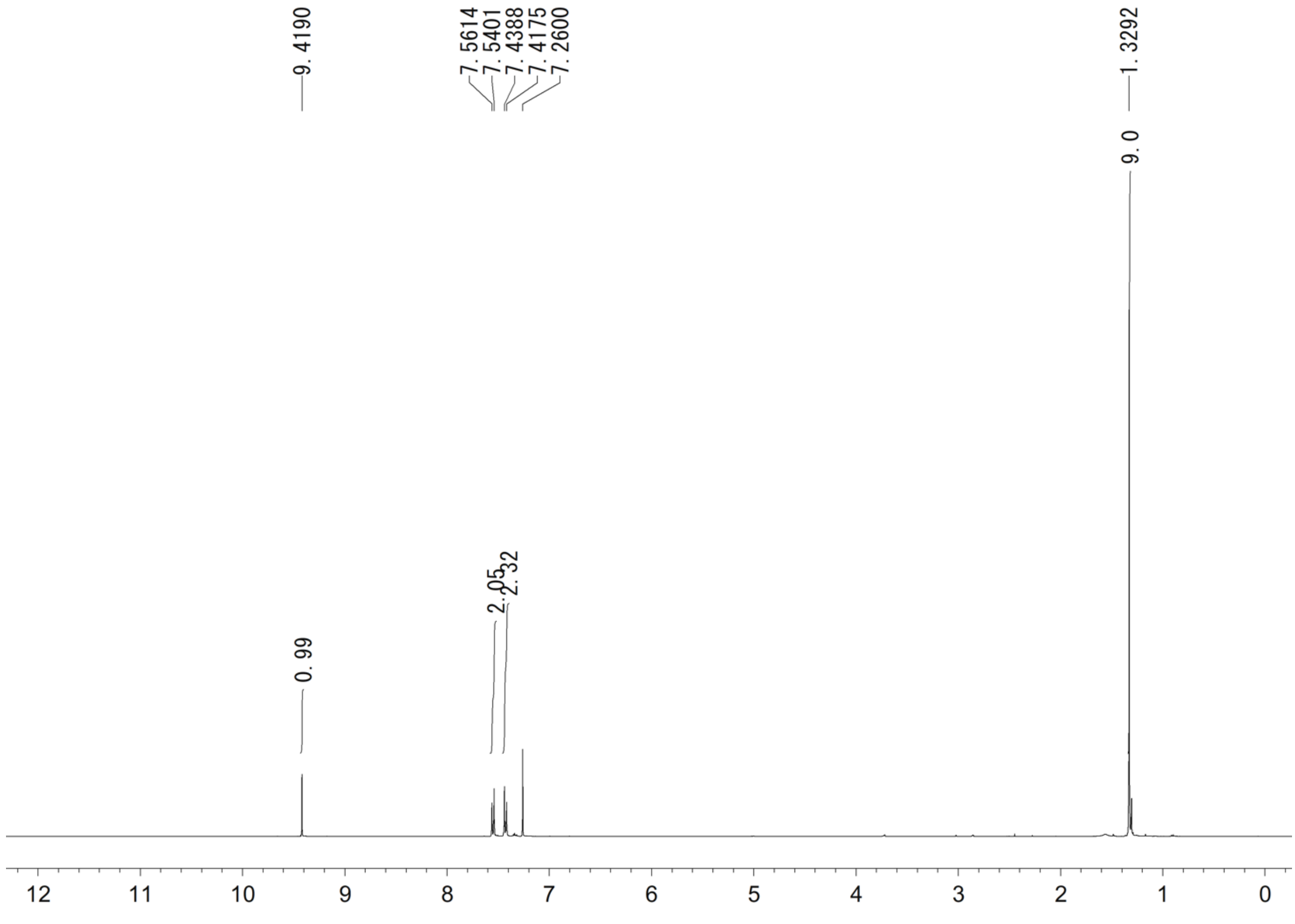
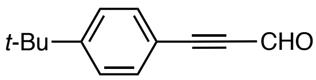


400 MHz ^{1}H NMR spectrum of **3h** in $CDCl_3$.



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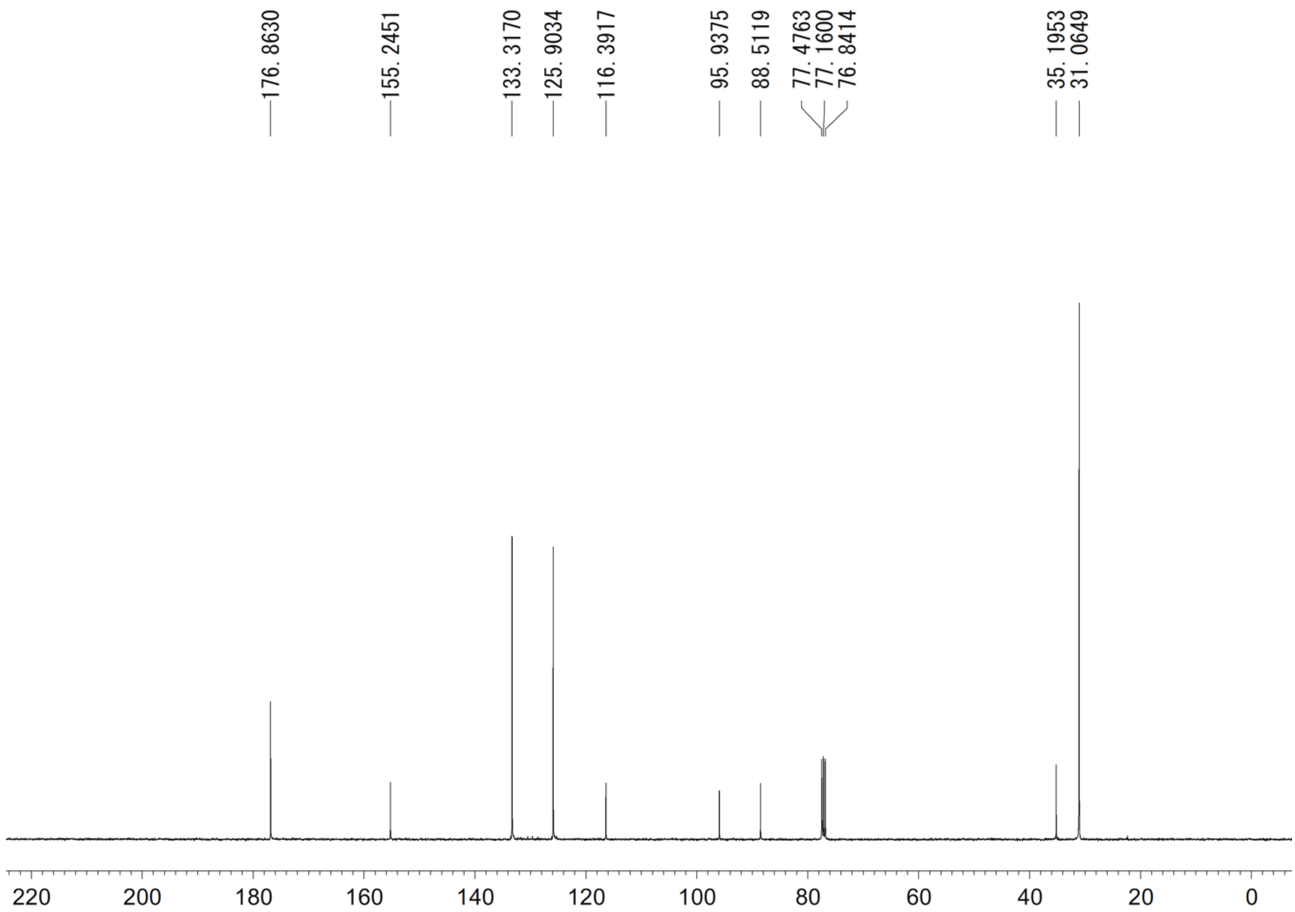
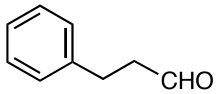
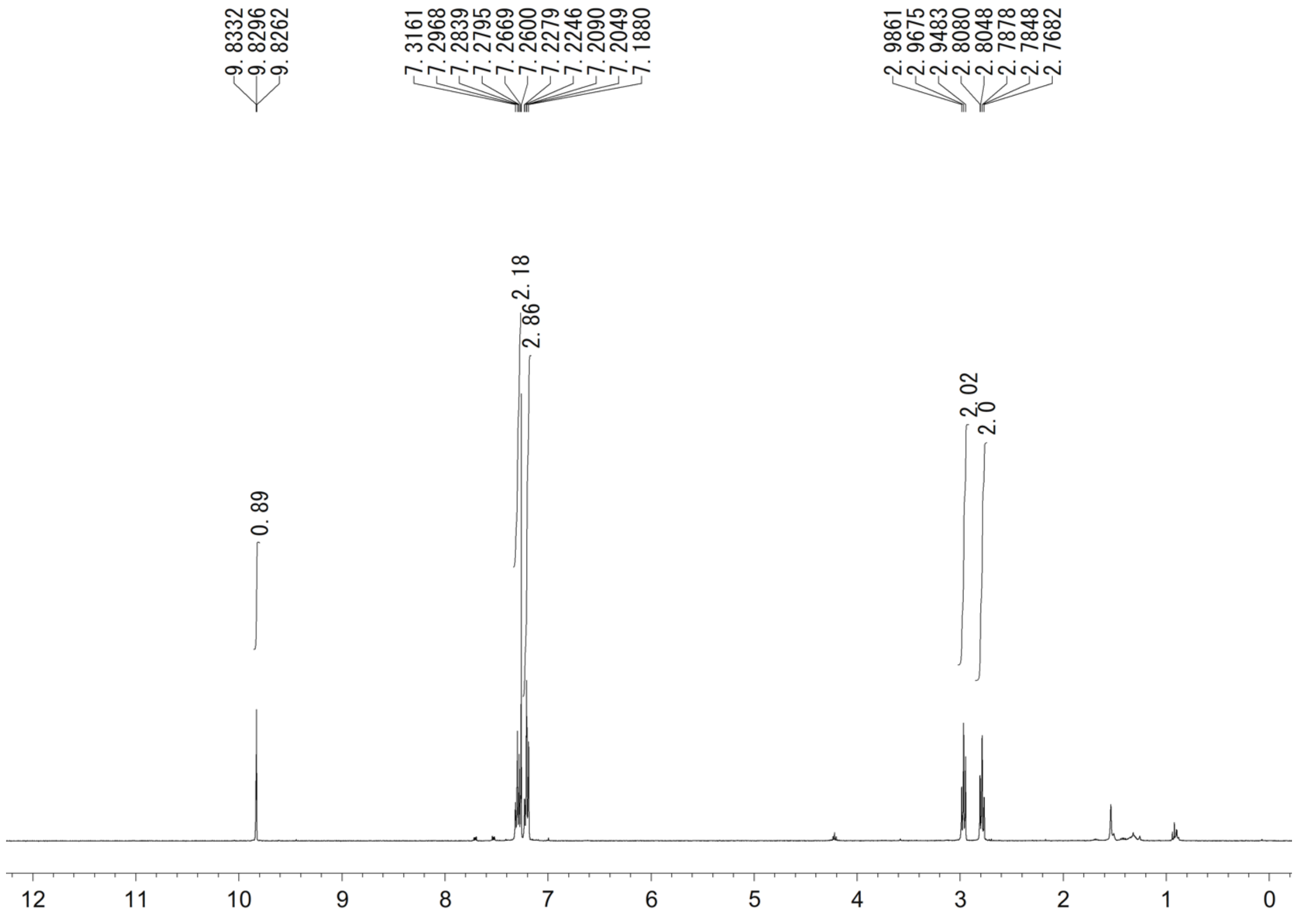


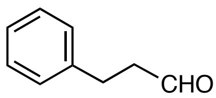
100 MHz ^{13}C NMR spectrum of **3h** in $CDCl_3$.



3i



400 MHz [1]H NMR spectrum of **3i** in $CDCl_3$.



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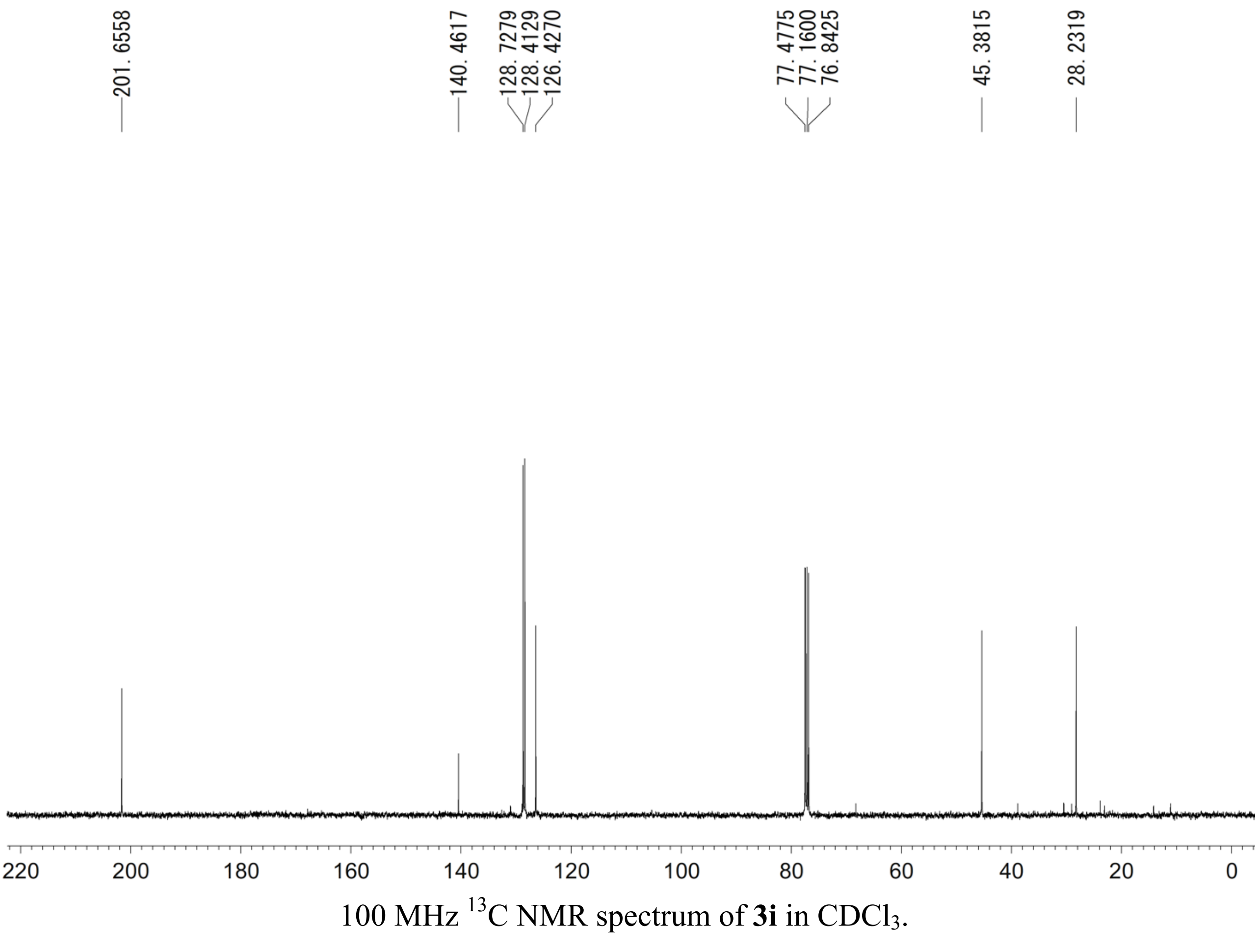

100 MHz ^{13}C NMR spectrum of **3i** in $CDCl_3$.

[F] Computational details.

All the computations were performed with Gaussian 16 (Rev.A.03) program.[S1] Density functional theory (DFT) calculations were performed at the ωb97xd/6-31G(d) level of theory[S2], except for the hydride of $PhSiH_3$ employing the 6-31++G(d,p) basis set. The self-consistent reaction field (SCRF) method with the polarizable continuum model (PCM)[S3] was adopted to take into account the solvation effect, and the dielectric constant of toluene was used (Eps = 2.3741). Relative potential energies and Gibbs free energies calculated at 303 K in solution are reported. Natural population analysis (NPA)[S4] was done to calculate the natural atomic charges with Gaussian NBO Version 3.1. Harmonic frequency and normal mode were calculated to verify the transition-state structures.

(S1) *Gaussian 16, Revision A.03*, 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, 2016.

(S2) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.

(S3) (*a*) S. Miertuš, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117–129; (*b*) B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151–5158; (*c*) R. Cammi, B. Mennucci and J. Tomasi, *J. Phys. Chem. A*, 2000, **104**, 5631–5637.

(S4) (*a*) A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066–4073; (*b*) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.

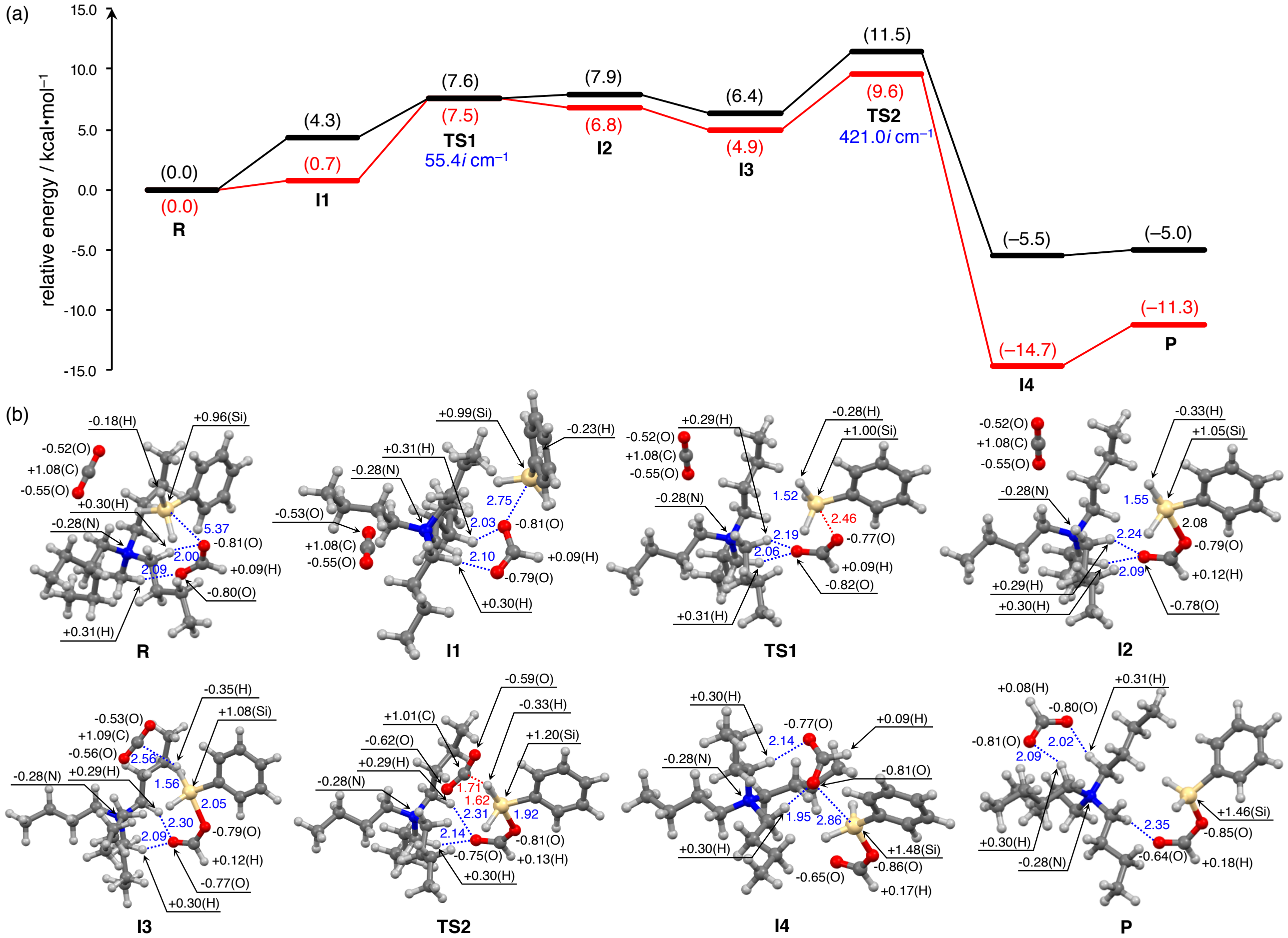

Fig. S5 (a) Energy profile for the hydrosilylation of CO_2 with $PhSiH_3$ and TBA formate. Potential energies and free energies (303 K) are shown in red and black, respectively. (b) Optimized intermediate and transition-state structures. Distances (Å) are given in blue or red, and NBO charges are shown in black.

[G] Cartesian coordinates.

R

N	-1.3750	-0.2030	-0.0780
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H	-2.2230	-0.7120	-1.9050
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H	-4.1080	0.6300	0.1510
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H	-4.5300	-0.2120	-2.7570
C	-6.0660	0.9400	-1.7650
H	-5.7570	1.9100	-2.1710
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H	-0.5120	0.6740	-1.7550
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O -0.7680 -1.5540 1.5550
H -2.0070 -2.7060 2.6520
Si -3.0780 0.1530 -0.3990
H -2.9540 1.2120 -1.4870
H -2.4670 -1.0070 -1.0970
H -2.2600 0.7800 0.6680
C -4.9570 0.1580 -0.1800
C -5.7010 1.0510 -0.9690
C -5.6670 -0.6600 0.7150
C -7.0890 1.1290 -0.8750
H -5.1860 1.6990 -1.6740
C -7.0540 -0.5860 0.8110
H -5.1130 -1.3560 1.3340
C -7.7710 0.3080 0.0180
H -7.6360 1.8310 -1.5000
H -7.5800 -1.2310 1.5110

H	-8.8530	0.3640	0.0960
C	3.0560	4.1950	-0.0130
O	2.6390	4.9810	-0.7620
O	3.4730	3.4000	0.7330

I2

N	1.7750	-0.2930	-0.0170
C	2.1870	-1.2730	1.0640
H	1.2490	-1.6200	1.5070
H	2.6550	-2.1160	0.5570
C	3.1380	-0.7370	2.1270
H	2.6790	0.0790	2.6940
H	4.0590	-0.3450	1.6780
C	3.5040	-1.8640	3.0980
H	3.9730	-2.6860	2.5420
H	2.5880	-2.2700	3.5420
C	4.4470	-1.3900	4.2020
H	3.9880	-0.5900	4.7940
H	4.6970	-2.2090	4.8830
H	5.3830	-1.0020	3.7830
C	1.0120	0.8440	0.6510
H	1.7240	1.3470	1.3080
H	0.2410	0.3530	1.2520
C	0.3660	1.8620	-0.2800
H	-0.4210	1.3960	-0.8810
H	1.0910	2.3000	-0.9770
C	-0.2660	2.9860	0.5480
H	-0.9590	2.5460	1.2730
H	0.5120	3.5010	1.1300
C	-1.0160	3.9840	-0.3300
H	-1.8210	3.4770	-0.8740
H	-1.4630	4.7790	0.2740
H	-0.3460	4.4500	-1.0620
C	2.9680	0.2910	-0.7310
H	2.5690	0.9550	-1.5000
H	3.4880	0.9160	-0.0010
C	3.9430	-0.6860	-1.3720
H	4.2940	-1.4300	-0.6480

H 3.4580 -1.2280 -2.1900
C 5.1520 0.0750 -1.9260
H 4.8090 0.8390 -2.6350
H 5.6510 0.6090 -1.1070
C 6.1490 -0.8540 -2.6170
H 7.0060 -0.2930 -3.0010
H 6.5270 -1.6120 -1.9220
H 5.6820 -1.3740 -3.4600
C 0.8160 -0.9760 -0.9890
H -0.1660 -0.8950 -0.5250
H 0.8400 -0.3790 -1.9040
C 1.0420 -2.4530 -1.2930
H 2.0770 -2.6800 -1.5710
H 0.7960 -3.0430 -0.4050
C 0.1110 -2.8730 -2.4350
H 0.3650 -2.3070 -3.3410
H -0.9200 -2.6020 -2.1750
C 0.1950 -4.3700 -2.7220
H -0.4700 -4.6500 -3.5450
H 1.2140 -4.6650 -2.9980
H -0.0970 -4.9540 -1.8420
O -3.0750 -1.4760 1.2610
C -2.0140 -1.9640 1.7520
O -0.8390 -1.6870 1.4620
H -2.1920 -2.7320 2.5350
Si -3.0170 0.0020 -0.2080
H -2.8660 1.0910 -1.3020
H -2.3820 -1.0830 -1.0220
H -2.2050 0.7340 0.8130
C -4.9180 0.1010 -0.1160
C -5.5740 1.0040 -0.9680
C -5.7240 -0.6600 0.7470
C -6.9600 1.1470 -0.9640
H -4.9850 1.6120 -1.6510
C -7.1100 -0.5220 0.7580
H -5.2500 -1.3670 1.4160
C -7.7350 0.3820 -0.0980
H -7.4340 1.8570 -1.6380

H	-7.7060	-1.1250	1.4390
H	-8.8170	0.4890	-0.0890
C	2.9880	4.2280	-0.0230
O	2.5460	5.0180	-0.7530
O	3.4300	3.4290	0.7040

I3

N	2.2020	0.0660	-0.3530
C	2.8140	1.3880	0.0680
H	1.9640	2.0340	0.3020
H	3.3610	1.1980	0.9910
C	3.7490	2.0450	-0.9400
H	3.2300	2.2710	-1.8770
H	4.5950	1.3900	-1.1830
C	4.2930	3.3530	-0.3540
H	4.8200	3.1400	0.5850
H	3.4530	4.0110	-0.1000
C	5.2350	4.0690	-1.3200
H	4.7210	4.3220	-2.2550
H	5.6140	4.9980	-0.8830
H	6.0960	3.4390	-1.5710
C	1.3200	0.3230	-1.5700
H	1.9880	0.6390	-2.3740
H	0.6760	1.1580	-1.2810
C	0.4640	-0.8480	-2.0340
H	-0.2690	-1.1110	-1.2660
H	1.0650	-1.7420	-2.2360
C	-0.2910	-0.4670	-3.3110
H	-0.7970	0.4930	-3.1570
H	0.4230	-0.3250	-4.1340
C	-1.3270	-1.5250	-3.6850
H	-2.0750	-1.6190	-2.8890
H	-1.8470	-1.2590	-4.6100
H	-0.8570	-2.5050	-3.8320
C	3.2520	-0.9470	-0.7340
H	2.7150	-1.8530	-1.0170
H	3.7390	-0.5620	-1.6340
C	4.2940	-1.2910	0.3200

H	4.7850	-0.3900	0.7050
H	3.8220	-1.7950	1.1700
C	5.3580	-2.2180	-0.2780
H	4.8730	-3.1130	-0.6890
H	5.8480	-1.7130	-1.1200
C	6.4050	-2.6320	0.7540
H	7.1580	-3.2890	0.3080
H	6.9230	-1.7560	1.1620
H	5.9430	-3.1680	1.5900
C	1.2960	-0.4540	0.7600
H	0.3410	0.0510	0.6130
H	1.1680	-1.5210	0.5710
C	1.7160	-0.1970	2.2030
H	2.7600	-0.4630	2.4000
H	1.5940	0.8670	2.4280
C	0.8060	-1.0070	3.1330
H	0.9470	-2.0780	2.9380
H	-0.2400	-0.7820	2.8950
C	1.0790	-0.7080	4.6050
H	0.4260	-1.3010	5.2530
H	2.1170	-0.9380	4.8710
H	0.9010	0.3500	4.8280
O	-2.3340	2.2830	0.7240
C	-1.1880	2.8180	0.8380
O	-0.0810	2.3090	0.6070
H	-1.2190	3.8710	1.1930
Si	-2.5310	0.3490	0.0730
H	-2.5690	-1.1230	-0.4280
H	-1.8030	0.0140	1.3390
H	-1.7850	0.8420	-1.1260
C	-4.4240	0.5450	0.1320
C	-5.2160	-0.5780	-0.1540
C	-5.0960	1.7400	0.4380
C	-6.6080	-0.5200	-0.1340
H	-4.7310	-1.5210	-0.3970
C	-6.4880	1.8080	0.4560
H	-4.5130	2.6240	0.6680
C	-7.2500	0.6770	0.1710

H	-7.1910	-1.4100	-0.3580
H	-6.9790	2.7470	0.6950
H	-8.3360	0.7290	0.1860
C	-1.7660	-3.5320	-0.1220
O	-2.7800	-3.9070	-0.5540
O	-0.7300	-3.2160	0.3120

TS2

N	2.2470	0.0330	-0.3660
C	2.8550	1.3340	0.1180
H	2.0040	1.9710	0.3710
H	3.3930	1.1050	1.0370
C	3.7980	2.0390	-0.8500
H	3.2800	2.3270	-1.7700
H	4.6340	1.3890	-1.1350
C	4.3600	3.3020	-0.1890
H	4.8940	3.0250	0.7300
H	3.5300	3.9510	0.1150
C	5.3010	4.0680	-1.1170
H	4.7810	4.3850	-2.0280
H	5.6930	4.9630	-0.6250
H	6.1530	3.4470	-1.4150
C	1.3840	0.3430	-1.5830
H	2.0620	0.7010	-2.3610
H	0.7330	1.1620	-1.2670
C	0.5400	-0.8070	-2.1160
H	-0.1570	-1.1520	-1.3480
H	1.1560	-1.6650	-2.4080
C	-0.2610	-0.3380	-3.3350
H	-0.7500	0.6150	-3.1020
H	0.4210	-0.1480	-4.1740
C	-1.3220	-1.3600	-3.7360
H	-2.0460	-1.5000	-2.9250
H	-1.8700	-1.0320	-4.6240
H	-0.8710	-2.3350	-3.9570
C	3.2990	-0.9670	-0.7760
H	2.7590	-1.8580	-1.1000
H	3.7960	-0.5500	-1.6560

C	4.3280	-1.3600	0.2740
H	4.8280	-0.4780	0.6900
H	3.8420	-1.8840	1.1030
C	5.3820	-2.2830	-0.3460
H	4.8860	-3.1590	-0.7840
H	5.8830	-1.7610	-1.1720
C	6.4190	-2.7400	0.6780
H	7.1640	-3.3950	0.2160
H	6.9460	-1.8840	1.1130
H	5.9450	-3.2950	1.4960
C	1.3290	-0.5350	0.7150
H	0.3700	-0.0380	0.5720
H	1.2070	-1.5940	0.4850
C	1.7320	-0.3310	2.1710
H	2.7790	-0.5880	2.3650
H	1.5960	0.7220	2.4420
C	0.8340	-1.1940	3.0640
H	0.9980	-2.2530	2.8280
H	-0.2160	-0.9860	2.8270
C	1.0920	-0.9450	4.5470
H	0.4510	-1.5780	5.1680
H	2.1350	-1.1610	4.8110
H	0.8890	0.1000	4.8110
O	-2.3590	2.2120	0.6750
C	-1.2140	2.7790	0.7710
O	-0.1080	2.2710	0.5780
H	-1.2810	3.8450	1.0620
Si	-2.5240	0.3570	0.2080
H	-2.5530	-1.2210	-0.1720
H	-1.7810	0.0080	1.4570
H	-1.7930	0.6350	-1.0650
C	-4.4180	0.4660	0.2050
C	-5.1650	-0.6070	-0.3060
C	-5.1310	1.5740	0.6920
C	-6.5580	-0.5760	-0.3380
H	-4.6500	-1.4860	-0.6850
C	-6.5230	1.6060	0.6730
H	-4.5840	2.4220	1.0870

C	-7.2420	0.5310	0.1550
H	-7.1080	-1.4210	-0.7450
H	-7.0480	2.4750	1.0620
H	-8.3290	0.5570	0.1370
C	-2.0440	-2.8490	-0.1800
O	-2.9280	-3.3700	-0.7720
O	-1.0080	-2.8030	0.3980

I4

N	-2.4060	-0.3300	0.0460
C	-3.6810	-0.4230	0.8470
H	-3.5250	-1.2370	1.5610
H	-3.7570	0.5040	1.4160
C	-4.9780	-0.6390	0.0760
H	-4.9670	-1.5900	-0.4680
H	-5.1280	0.1580	-0.6610
C	-6.1630	-0.6430	1.0480
H	-6.1980	0.3150	1.5830
H	-6.0090	-1.4200	1.8080
C	-7.4920	-0.8810	0.3330
H	-7.4960	-1.8490	-0.1790
H	-8.3260	-0.8720	1.0430
H	-7.6800	-0.1040	-0.4170
C	-2.2270	-1.6150	-0.7500
H	-3.0820	-1.6850	-1.4250
H	-2.2970	-2.4310	-0.0210
C	-0.9300	-1.7040	-1.5460
H	-0.0750	-1.4380	-0.9230
H	-0.9340	-0.9900	-2.3730
C	-0.7040	-3.1120	-2.1020
H	-0.3970	-3.7840	-1.2900
H	-1.6380	-3.5160	-2.5160
C	0.3670	-3.0760	-3.1930
H	1.2330	-2.4900	-2.8590
H	0.7150	-4.0830	-3.4500
H	-0.0150	-2.6000	-4.1030
C	-2.4350	0.8160	-0.9490
H	-1.5240	0.7490	-1.5520

H -3.2940 0.6290 -1.5990
C -2.4760 2.2250 -0.3860
H -3.3280 2.3920 0.2890
H -1.5510 2.4170 0.1680
C -2.5280 3.2140 -1.5540
H -1.6840 2.9930 -2.2190
H -3.4450 3.0530 -2.1370
C -2.4660 4.6660 -1.0850
H -2.4990 5.3570 -1.9340
H -3.3060 4.9060 -0.4210
H -1.5370 4.8560 -0.5340
C -1.2120 -0.2050 0.9910
H -0.9220 -1.2280 1.2510
H -0.4190 0.2390 0.3830
C -1.4050 0.5900 2.2800
H -1.8580 1.5690 2.0970
H -2.0660 0.0590 2.9770
C -0.0470 0.7970 2.9610
H 0.6460 1.2970 2.2700
H 0.3980 -0.1810 3.1880
C -0.1770 1.6080 4.2520
H 0.7980 1.7410 4.7310
H -0.5890 2.6030 4.0480
H -0.8390 1.1090 4.9680
O 3.4160 -2.2760 1.1310
C 2.6230 -3.2780 1.4680
O 1.4210 -3.3060 1.2960
H 3.1810 -4.1020 1.9380
Si 2.6730 -0.9010 0.3380
H 2.1430 1.1060 -2.3140
H 1.6860 -0.3980 1.2950
H 2.1210 -1.5110 -0.8900
C 4.1530 0.2100 0.0840
C 3.9910 1.5910 -0.1200
C 5.4550 -0.3100 0.1160
C 5.0970 2.4190 -0.2880
H 2.9850 2.0000 -0.1510
C 6.5620 0.5170 -0.0590

H 5.6080 -1.3730 0.2840
C 6.3840 1.8840 -0.2600
H 4.9550 3.4860 -0.4400
H 7.5620 0.0930 -0.0370
H 7.2470 2.5320 -0.3890
C 1.0850 1.1070 -1.9380
O 0.1800 1.0840 -2.7960
O 0.9500 1.1360 -0.6810

P

N -1.5300 0.2990 -0.0400
C -2.2780 0.6660 1.2220
H -1.5250 1.0560 1.9140
H -2.9430 1.4890 0.9620
C -3.0710 -0.4780 1.8460
H -2.4060 -1.1290 2.4220
H -3.5210 -1.1130 1.0720
C -4.1730 0.0610 2.7610
H -4.8550 0.6910 2.1730
H -3.7420 0.7080 3.5380
C -4.9630 -1.0760 3.4070
H -4.3150 -1.6930 4.0390
H -5.7780 -0.6920 4.0290
H -5.3930 -1.7270 2.6380
C -0.6560 -0.9040 0.2840
H -1.3320 -1.7320 0.5340
H -0.0730 -0.6190 1.1660
C 0.2630 -1.3860 -0.8300
H 1.0260 -0.6420 -1.0920
H -0.3130 -1.5930 -1.7390
C 0.9550 -2.6790 -0.3860
H 1.4740 -2.5030 0.5670
H 0.1840 -3.4310 -0.1900
C 1.9550 -3.1840 -1.4240
H 2.7480 -2.4480 -1.6070
H 2.4320 -4.1110 -1.0910
H 1.4580 -3.3880 -2.3790
C -2.4760 -0.0900 -1.1680

H -1.9100 0.0550 -2.0930
H -2.7040 -1.1530 -1.0360
C -3.8160 0.6310 -1.2430
H -4.4180 0.3850 -0.3620
H -3.7140 1.7210 -1.2820
C -4.5730 0.1360 -2.4800
H -3.9860 0.3550 -3.3830
H -4.6670 -0.9530 -2.4070
C -5.9560 0.7720 -2.5990
H -6.4820 0.4050 -3.4860
H -6.5700 0.5340 -1.7240
H -5.8870 1.8640 -2.6760
C -0.6280 1.4440 -0.4300
H 0.0670 1.5770 0.4040
H -0.0580 1.1020 -1.2950
C -1.2760 2.7790 -0.7710
H -1.8850 2.6910 -1.6770
H -1.9320 3.1250 0.0350
C -0.1800 3.8260 -1.0020
H 0.4930 3.4780 -1.7960
H 0.4270 3.9140 -0.0930
C -0.7560 5.1890 -1.3790
H 0.0410 5.9220 -1.5380
H -1.3450 5.1280 -2.3010
H -1.4110 5.5720 -0.5880
O 3.6120 1.9070 1.6710
C 2.6650 2.6420 2.2400
O 1.4810 2.5400 2.0090
H 3.0830 3.3600 2.9560
Si 3.1370 0.7160 0.5170
H -3.8350 -4.5890 -0.1750
H 2.5140 1.4430 -0.6130
H 2.1880 -0.2100 1.1660
C 4.6600 -0.2080 0.0110
C 5.6780 0.3980 -0.7410
C 4.7910 -1.5630 0.3480
C 6.7970 -0.3270 -1.1370
H 5.6000 1.4450 -1.0230

C	5.9070	-2.2930	-0.0530
H	4.0130	-2.0580	0.9240
C	6.9100	-1.6740	-0.7930
H	7.5790	0.1540	-1.7160
H	5.9920	-3.3420	0.2120
H	7.7810	-2.2410	-1.1070
C	-3.3750	-3.5690	-0.0730
O	-2.2250	-3.5370	0.4210
O	-4.0870	-2.6120	-0.4650