ELECTRONIC SUPPLEMENTARY INFORMATION

Protic onium salts-catalyzed synthesis of 5-aryl-2-oxazolidinones from aziridines and CO_2 under mild conditions

Zhen-Zhen Yang, Yu-Nong Li, Yang-Yang Wei and Liang-Nian He*

,State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, People's Republic of China

** Corresponding author: Tel: +86-22-23501493; Fax: +86-22-23501493; E-mail: heln@nankai.edu.cn*

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1. General experimental methods

Caution

Experiments using compressed gases CO_2 are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

Materials

Aziridines and ionic liquids were synthesized according to the published procedures.[1, 2] CO_2 with a purity of 99.99% was commercially available. The other organic and inorganic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

Experimental methods

^1H NMR spectra was recorded at Bruck 300 or 400 spectrometer in $CDCl_3$ and $CDCl_3$ (7.26 ppm) was used as internal reference, ^{13}C NMR was recorded at 75 or 100.6 MHz in $CDCl_3$ and $CDCl_3$ (77.0 ppm) was used as internal reference. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-5, 30 m × 0.25 μm) using a flame ionization detector. Melting points were measured on an X4 apparatus and uncorrected.

2. General procedures for the preparation of protic onium salts

Protic onium salts

To a 50 mL three-neched flask was added the base (10 mmol). A solution of the corresponding acid (10 mmol) was then added dropwise at the temperature of < 5 ^oC cooled by ice bath. After addition, the ice bath was removed and the reaction mixture was stirred for a further 10 h and then the solvent was evaporated. The remaining solid was dried under vacuum at 60 ^oC for 24 h after washing by ethyl ether for three times to afford the protic onium salts.

C_4DABCOCl

A solution of freshly sublimed DABCO (0.5609 g, 5 mmol) in MeCN (5 mL) was prepared at r.t. under Ar in a flame dried round-bottomed flask equipped with a reflux condenser. The resulting clear, colorless solution was treated with 1-chlorobutane (2.5 mmol), added dropwise via syringe, and the reaction mixture was heated to 80 °C (oil bath temperature) and stirred for 22 h. After being cooled to r.t., the reaction mixture was transferred via cannula into 20 mL of Et_2O, yielding a white slurry which eventually separated into two layers. The whole was transferred to a separatory funnel, and the bottom layer was collected, washed repeatedly with Et_2O and dried under high vacuum at 60 ^oC for 16 h to yield 1-butyl-4-aza-1-azaniabicyclo[2.2.2]octane chloride as a white solid.

3. General procedure for the preparation of aziridines

Typical procedure was described as below. The bromine (32.0 g, 0.2 mol) in dry CH_2Cl_2 (40 mL) was added dropwise over 30 min to ice-cooled 40 mL CH_2Cl_2 solution of dimethyl sulfide (12.4 g, 0.2 mol). During the addition, light orange crystals of bromodimethyl sulfonium bromide began to separate. After addition of bromine, the orange crystals **S1** were collected by filtration and then washed with dry diethyl ether and dried under vacuum. Yield: 80%, Mp 80 ^oC (dec).

Olefin (160 mmol) was added dropwise to the 160 mL CH_3CN solution of **S1** (35.56 g, 160 mmol) in ice-water bath. During the addition, the white solid began to separate. The solution was further stirred for 10 min. The crystals **S2** was collected by filtration, dried under vacuum. Yield: 32-38.6 %.

A solution of amine (20-50 mmol) in water was added dropwise to a stirred solution of compound **S2** (10 mmol) in 20 mL of H_2O at r.t., and the resulting mixture was stirred overnight. The mixture was added into 20 mL of saturated brine, extracted with diethyl ether (3×20 mL), dried with anhydrous $MgSO_4$ overnight and evaporated under reduced pressure. Aziridine was obtained by distillation under reduced pressure. Yield: 85-100 %.

4. General Procedure for Carboxylation of Aziridine with CO_2

In a typical reaction, the carboxylation of aziridines with CO_2 was carried out in a 25 mL stainless steel

autoclave. Aziridine (1 mmol) and the catalyst were charged into the reactor at room temperature. CO_2 was introduced into the autoclave and then the mixture was stirred at predetermined temperature for 5 min to reach the equilibration. The pressure was then adjusted to the desired pressure and the mixture was stirred continuously. When the reaction finished, the reactor was cooled in ice-water and CO_2 was ejected slowly. An aliquot of sample was taken from the resultant mixture and dissolved in dry CH_2Cl_2 for GC analysis using a flame ionization detector. The residue was purified by column chromatography on silica gel (eluting with 8:1 to 1:1 petroleum ether/ethyl acetate) to afford the product. The products were further identified by ^{1}H NMR, ^{13}C NMR and MS which are consistent with those reported in the literature[1] and in good agreement with the assigned structures. For the catalyst recycling process, firstly, a very small part of the resultant mixture was taken and analyzed by GC and then, substrate (**1a**, 1 mmol) for the next run was added to the residual reaction mixture. Finally, the reaction was carried out under identical reaction conditions.

5. Characterization of protic onium salts

HPyI

Light yellow solid; Mp 172-173 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 8.78 (d, ^3J = 6 Hz, 2 H), 8.63 (t, ^3J = 8 Hz, 1 H), 8.08 (t, ^3J = 6.8 Hz, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 147.1, 141.1, 127.4; Elemental analysis calcd. (%) for C_5H_6NI: C 29.01, H 2.92, N 6.77, I 61.30, found: C 29.02, H 3.01, N 6.45.

HPyBr

Light yellow solid; Mp 146-149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, ^3J = 4 Hz, 2 H), 8.55 (t, ^3J = 7.6 Hz, 1 H), 8.08 (t, ^3J = 6.8 Hz, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 146.2, 140.9, 127.3; ESI-MS (4.8 kV): m/z (%) = 80.13 (100) $[M-Br]^+$.

HPyCl

White solid; Mp 118-120 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 8.78 (d, ^3J = 5.6 Hz, 2 H), 8.62 (t, ^3J = 7.6 Hz, 1 H), 8.07 (t, ^3J = 6.8 Hz, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 147.2, 141.0, 127.4; ESI-MS (4.8 kV): m/z (%) = 80.11 (100) $[M-Cl]^+$.

HPyNO$_3$

White solid; Mp 110-113 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 8.80 (d, ^3J = 5.6 Hz, 2 H), 8.64 (t, ^3J = 8 Hz, 1 H), 8.10 (t, ^3J = 7.2 Hz, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 147.1, 141.1, 127.4.

HPyHSO$_4$:

White solid; Mp 93-95 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 8.79 (d, ^3J = 5.6 Hz, 2 H), 8.64 (t, ^3J = 8 Hz, 1 H), 8.09 (t, ^3J = 6.8 Hz, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 147.2, 141.1, 127.4.

HPyH$_2$PO$_4$

White solid; Mp 93-95 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 8.79 (d, ^3J = 5.2 Hz, 2 H), 8.64 (t, ^3J = 8 Hz, 1 H), 8.09 (t, ^3J = 6.4 Hz, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 147.2, 141.1, 127.4.

HMImCl

White solid; Mp 78-79 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 8.70 (s, 1 H), 7.47 (s, 2 H), 3.95 (s, 3 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 135.0, 123.0, 119.5, 35.5; ESI-MS (4.8 kV): m/z (%) = 83.16 (100) $[M-Cl]^+$.

HDABCOCl

White solid; Mp 207-208 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ 3.22 (s, 12 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 43.9; ESI-MS (4.8 kV): m/z (%) = 113.20 (100) $[M-Cl]^+$.

C$_4$DABCOCl

White solid; Mp 36-37 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (t, ^3J = 7.2 Hz, 6 H), 3.54 (t, ^3J = 8.4 Hz, 2 H), 3.25 (t, ^3J =,7.2 Hz, 6 H), 1.69-1.77 (m, 2 H), 1.36-1.45 (m, 2 H), 0.97 (t, ^3J =7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 64.3, 52.4, 45.4, 23.9, 19.7, 13.7; ESI-MS calcd for $C_{10}H_{21}N_2Cl$ 204.74, found 169.44 $[M-Cl]^+$.

HDBUCl

White solid; Mp 65-66 °C; ^{1}H NMR (400 MHz, D_2O) δ 3.57-3.60 (m, 2 H), 3.54 (t, ^{3}J = 6 Hz, 2 H), 3.33 (t, ^{3}J = 5.6 Hz, 2 H); 2.63-2.65 (m, 2 H); 2.02 (quintet, ^{3}J = 5.6 Hz, 2 H)1.69-1.74 (m, 6 H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 165.9, 54.2, 48.5, 37.7, 31.9, 28.7, 26.5, 23.7, 19.2; HR-MS (ESI): m/z = 135.1386, calcd. for $C_9H_{17}N_2$ (M-Cl^+): 153.1383.

HTBDCl

White solid; Mp 179-180 °C; ^{1}H NMR (400 MHz, D_2O) δ 3.36 (t, ^{3}J = 6 Hz, 4 H), 3.28 (t, ^{3}J = 5.6 Hz, 4 H); 2.02 (quintet, ^{3}J = 6 Hz, 4 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 151.0, 46.5, 37.8, 20.2; HR-MS (ESI): m/z = 140.1182, calcd. for $C_7H_{14}N_3$ (M-Cl^+): 140.1177.

HHMTACl

White solid; Mp 139-141 °C; ^{1}H NMR (400 MHz, D_2O) δ 4.75 (s, 6 H), 4.74 (s, 6 H); ^{13}C {^{1}H} NMR (100.6 MHz, D_2O) δ 71.7; HR-MS (ESI): m/z = 141.1135, calcd. for $C_7H_{14}N_3$ (M-Cl^+): 141.1131, 317.1963, calcd. for $C_{12}H_{26}N_8Cl$ (2 M-Cl^+):317.1971.

6. Characterization of aziridines

1-Ethyl-2-phenylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, ^{3}J = 9.6 Hz, 3H), 1.65 (d, ^{2}J = 8.8 Hz, 1H), 1.89 (d, ^{2}J = 4.4 Hz, 1H), 2.30 (dd, ^{3}J = 4.4 Hz, ^{3}J = 4.8 Hz, 1H), 2.44 (q, ^{3}J = 9.6 Hz, 2H), 7.18-7.31 (m, 5H); ESI-MS calcd for $C_{10}H_{13}N$ 147.10, found 148.31 $[M + H]^+$.

2-(4-Chlorophenyl)-1-ethylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, ^{3}J = 6.9 Hz, 3H), 1.65 (d, ^{2}J = 6.6 Hz, 1H), 1.83 (d, ^{2}J = 3.3 Hz, 1H), 2.25-2.46 (m, 3H), 7.15-7.23 (m, 4H); ESI-MS calcd for $C_{10}H_{12}NCl$ 181.66, found 182.13 $[M + H]^+$.

1-Ethyl-2-p-tolylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, ^{3}J = 7.2 Hz, 3H), 1.62 (d, ^{2}J = 6.4 Hz, 1H), 1.86 (d, ^{2}J = 3.2 Hz, 1H), 2.26 (dd, ^{3}J = 3.6 Hz, ^{3}J = 3.2 Hz, 1H), 2.31 (s, 3H), 2.37-2.48 (m, 2H), 7.09-7.15 (m, 4H); ESI-MS calcd for $C_{11}H_{15}N$ 161.24, found 162.20 $[M + H]^+$.

1-Propyl-2-phenylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, ^{3}J = 10.0 Hz, 3H), 1.60-1.67 (m, 3H), 1.89 (d, ^{2}J = 4.0 Hz, 1H), 2.24-2.33 (m, 2H), 2.43-2.51 (m, 1H), 7.18-7.31 (m, 5H); ESI-MS calcd for $C_{11}H_{15}N$ 161.12, found 162.28 $[M + H]^+$.

1-Isopropyl-2-phenylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (d, ^{3}J = 0.9 Hz, 3H), 1.19 (d, ^{3}J = 0.9 Hz, 3H), 1.57-1.66 (m, 2H), 1.89 (d, ^{2}J = 3.3 Hz, 1H), 2.34 (dd, ^{3}J = 3.3 Hz, ^{3}J = 3.3 Hz, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for $C_{11}H_{15}N$ 161.12, found 162.32 $[M + H]^+$.

1-Butyl-2-phenylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, ^{3}J = 7.2 Hz, 3H), 1.33-1.45 (m, 2H), 1.55-1.67 (m, 3H), 1.88 (d, ^{2}J =3.3 Hz, 1H), 2.27-2.36 (m, 2H), 2.45-2.54 (m, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for $C_{12}H_{17}N$ 175.14, found 176.38 $[M + H]^+$.

1-Isobutyl-2-phenylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, ^{3}J = 6.6 Hz, 3H), 0.98 (d, ^{3}J = 6.6 Hz, 3H), 1.65 (d, ^{2}J = 6.3 Hz, 1H), 1.85-1.94 (m, 2H), 2.08 (dd, ^{3}J = 6.3 Hz, ^{3}J = 6.6 Hz, 1H), 2.28 (q, ^{3}J = 3.3 Hz, 1H), 2.44 (dd, ^{3}J = 7.2 Hz, ^{2}J = 11.4 Hz, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for $C_{12}H_{17}N$ 175.14, found 176.36 $[M + H]^+$.

1-Benzyl-2-phenylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84 (d, ^{2}J = 6.3 Hz, 1H), 1.98 (d, ^{2}J = 3.3 Hz, 1H), 2.50 (q, ^{3}J = 3.3 Hz, 1H), 3.65 (ABq, $^{3}J_{AB}$ = 13.8 Hz, $\Delta\nu_{AB}$ = 18.8 Hz, 2H), 7.18-7.38 (m, 10H); ESI-MS calcd for $C_{15}H_{15}N$ 209.29, found 210.13 $[M + H]^+$.

1-Cyclohexyl-2-phenylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.87 (m, 13H), 2.34 (dd, ^{3}J =3.3 Hz, ^{3}J =3.0 Hz, 1H), 7.17-7.27 (m, 5H);

ESI-MS calcd for $C_{14}H_{19}N$ 201.15, found 202.37 $[M + H]^+$.

1-Cyclohexyl-2-p-tolylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.85 (m, 13 H), 2.29-2.32 (m, 4 H), 7.07-7.16 (m, 4 H).

2-(4-Chlorophenyl)-1-cyclohexylaziridine

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16-1.82 (m, 13 H), 2.31 (dd, ^3J = 3.3 Hz, ^3J = 3.0 Hz, 1 H), 7.17-7.26 (m, 4 H).

7. Characterization of oxazolidinones and piperazines

3-Ethyl-5-phenyloxazolidin-2-one

Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, ^3J = 7.2 Hz, 3H), 3.29-3.45 (m, 3H), 3.92 (t, ^3J = 8.7 Hz, 1H), 5.48 (t, ^3J = 7.8 Hz, 1H), 7.34-7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 38.8, 51.5, 74.2, 125.4, 128.6, 128.8, 138.8, 157.5; ESI-MS calcd for $C_{11}H_{13}NO_2$ 191.09, found 192.29 $(M + H)^+$, 214.38 $(M + Na)^+$, 405.01 $(2 M + Na)^+$.

3-Ethyl-4-phenyloxazolidin-2-one

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, ^3J = 7.2 Hz, 3H), 2.79-2.88 (m, 1H), 3.48-3.57 (m, 1H), 4.10 (t, ^3J = 8.0 Hz, 1H), 4.62 (t, ^3J = 8.8 Hz, 1H), 4.81 (t, ^3J = 7.2 Hz, 1H), 7.30 7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 36.8, 59.3, 69.7, 126.9, 129.0, 129.2, 137.8, 158.1; ESI-MS calcd for $C_{11}H_{13}NO_2$ 191.09, found 192.29 $(M + H)^+$, 214.38 $(M + Na)^+$, 405.01 $(2M + Na)^+$.

1, 4-Diethyl-2, 5-diphenylpiperazine

White crystals; Mp 116-119 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, ^3J=7.2 Hz, 6H), 1.99-2.05 (m, 2H), 2.30 (t, ^3J=10.8 Hz, 2H), 2.54-2.62 (m, 2H), 3.08 (dd, ^2J=11.6 Hz, ^3J=2.4 Hz, 2H), 3.45 (dd, ^3J=2.0 Hz, ^2J=12.0 Hz, 2H), 7.29-7.43 (m, 10H). LC-MS, calcd for $C_{20}H_{26}N_2$ 294.21, found 295.35 $(M + H)^+$.

1, 4-Diethyl-2, 3-diphenyl-piperazine

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, ^3J=7.2 Hz, 6H), 2.17-2.26 (m, 2H), 2.33-2.26 (m, 2H), 2.65-2.69 (m, 2H), 2.95-2.99 (q, ^3J=6.0 Hz, 2H), 3.73 (s, 2H), 7.27-7.38 (m, 6H), 7.69-7.71 (d, ^3J=7.2 Hz, 4H). LC-MS, calcd for $C_{20}H_{26}N_2$ 294.21, found 295.31$(M+H)^+$.

3-Ethyl-5-(4-chlorophenyl)oxazolidin-2-one

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, ^3J=7.3 Hz, 3H), 3.30-3.43 (m, 2H), 3.69-3.76 (m, 1H), 3.92 (t, ^3J=8.7 Hz, 1H), 5.44 (t, ^3J=8.0 Hz, 1H), 7.27-7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 38.9, 51.5, 73.6, 126.9, 129.1, 134.7, 137.4, 157.4; ESI-MS calcd for $C_{11}H_{12}ClNO_2$ 225.67, found 451.64 $(2M + H)^+$.

3-Ethyl-5-p-tolyloxazolidin-2-one

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, ^3J=7.3 Hz, 3H), 1.62 (d, ^3J=6.4 Hz, 1H),1.87 (d, ^3J=3.2 Hz, 1H), 2.27 (dd, ^3J=6.6 Hz, ^2J=3.2 Hz, 1H), 2.31 (s, 3H), 2.36-2.48 (m, 2H), 7.09- 7.15 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 21.2, 38.9, 51.6, 74.3, 125.6, 129.5, 135.8, 138.7, 157.7; ESI-MS calcd for $C_{12}H_{15}NO_2$ 205.25, found 206.45 $(M + H)^+$, 411.15 $(2M + H)^+$.

3-Propyl-5-phenyloxazolidin-2-one

Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, ^3J=7.2 Hz, 3H), 1.52-1.61 (m, 2H), 3.18-3.31 (m, 2H) 3.40 (t, ^3J=8.0 Hz, 1H), 3.90 (t, ^3J=8.8 Hz, 1H), 5.46 (t, ^3J=8.0 Hz, 1H), 7.31-7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.7, 20.3, 45.5, 51.8, 74.0, 125.2, 128.4, 128.5, 138.7, 157.6; ESI-MS calcd for $C_{12}H_{15}NO_2$ 205.11, found 206.30 $(M + H)^+$, 228.30 $(M + Na)^+$, 433.04 $(2M + Na)^+$.

3-Isopropyl-5-phenyloxazolidin-2-one

Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, ^3J=6.8 Hz, 3H), 1.22 (d, ^3J=6.8 Hz, 3H), 3.37 (t, ^3J=8.0 Hz, 1H), 3.87 (t, ^3J=8.8 Hz, 1H), 4.13-4.23 (m, 1H), 5.48 (t, ^3J=8.0 Hz, 1H), 7.34-7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 19.6, 44.5, 47.0, 74.2, 125.1, 128.3, 128.5, 138.7, 156.7; ESI-MS calcd for $C_{12}H_{15}NO_2$ 205.11, found 206.29 $(M + H)^+$, 433.08 $(2M + Na)^+$.

3-Butyl-5-phenyloxazolidin-2-one

Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, ^3J=7.2 Hz, 3H), 1.31-140 (m, 2H), 1.51-1.58 (m, 2H), 3.23-3.38 (m, 2H) 3.43 (t, ^3J=8.0 Hz, 1H), 3.92 (t, ^3J=8.8 Hz, 1H), 5.49 (t, ^3J=8.0 Hz, 1H), 7.28-7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 19.5, 29.1, 43.6, 51.8, 74.1, 125.2, 128.4, 128.5, 138.7, 157.7; ESI-MS calcd for $C_{13}H_{17}NO_2$ 219.13, found 220.34 $(M + H)^+$, 259.48 $(M + K)^+$, 461.05 $(2M + Na)^+$.

3-Isobutyl-5-phenyloxazolidin-2-one

White crystals; Mp 38-42 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, ^{3}J=4.8 Hz, 3H), 0.93 (d, ^{3}J=4.8 Hz, 3H), 1.81-1.95 (m, 1H), 3.02-3.16 (m, 2H), 3.42 (dd, ^{2}J=8.7 Hz , ^{3}J=7.5 Hz, 1H), 3.91 (t, ^{3}J=8.7 Hz, 1H), 5.48 (t, ^{3}J=8.4 Hz, 1H), 7.32-7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7, 19.8, 26.7, 51.6, 52.6, 74.1, 125.3, 128.5, 128.7, 138.8, 158.0; ESI-MS calcd for $C_{13}H_{17}NO_2$ 219.13, found 461.22 $(2M + Na)^+$, 679.70 $(3M + Na)^+$.

3-Benzyl-5-phenyloxazolidin-2-one

White crystals; Mp 60-64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (t, ^{3}J=8.4 Hz, 1H), 3.75 (t, ^{3}J=8.7 Hz, 1H), 4.45 (ABq, J_{AB}=15.0 Hz, $\Delta\nu_{AB}$ =36.0 Hz, 2H), 5.43 (t, ^{3}J=8.1 Hz, 1H), 7.27-7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.1, 51.3, 74.3, 125.3, 127.8, 127.9, 128.6, 128.7, 135.5, 138.5, 157.8; ESI-MS calcd for $C_{16}H_{15}NO_2$ 253.11, found 276.44$(M + Na)^+$, 781.66 $(3M + Na)^+$.

3-Cyclohexyl-5-phenyloxazolidin-2-one

White crystals; Mp 92-93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0-1.8 (m, 10H), 3.38 (t, ^{3}J=8.4 Hz, 1H), 3.70-3.73 (m, 1H), 3.88 (t, ^{3}J=8.7 Hz, 1H), 5.45 (t, ^{3}J=8.4 Hz, 1H), 7.35-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 25.2, 29.9, 30.3, 48.1, 52.4, 74.4, 125.3, 128.5, 128.7, 138.9, 157.0; ESI-MS calcd for $C_{15}H_{19}NO_2$ 245.14, found 246.27 $(M + H)^+$, 757.70 $(3M + Na)^+$.

3-Cyclohexyl-5-p-tolyloxazolidin-2-one

White crystals; Mp 89-91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03-1.86 (m, 10 H), 2.36 (s, 3 H), 3.38 (t, ^{3}J = 8.0 Hz, 1 H), 3.71-3.75 (m, 1 H), 3.85 (t, ^{3}J = 8.7 Hz, 1 H), 5.43 (t, ^{3}J = 8.0 Hz, 1 H), 7.17-7.26 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 25.2, 25.3, 25.4, 30.1, 30.5, 48.3, 52.5, 74.5, 125.5, 129.5, 136.0, 138.6, 157.3; ESI-MS calcd for $C_{16}H_{21}NO_2$ 259.16, found 260.02 $(M + H)^+$, 799.55 $(3M + Na)^+$; HRMS: calcd for $C_{16}H_{21}NO_2$ $(M + H)^+$ 260.1645, found 260.1652.

5-(4-Chlorophenyl)-3-cyclohexyloxazolidin-2-one

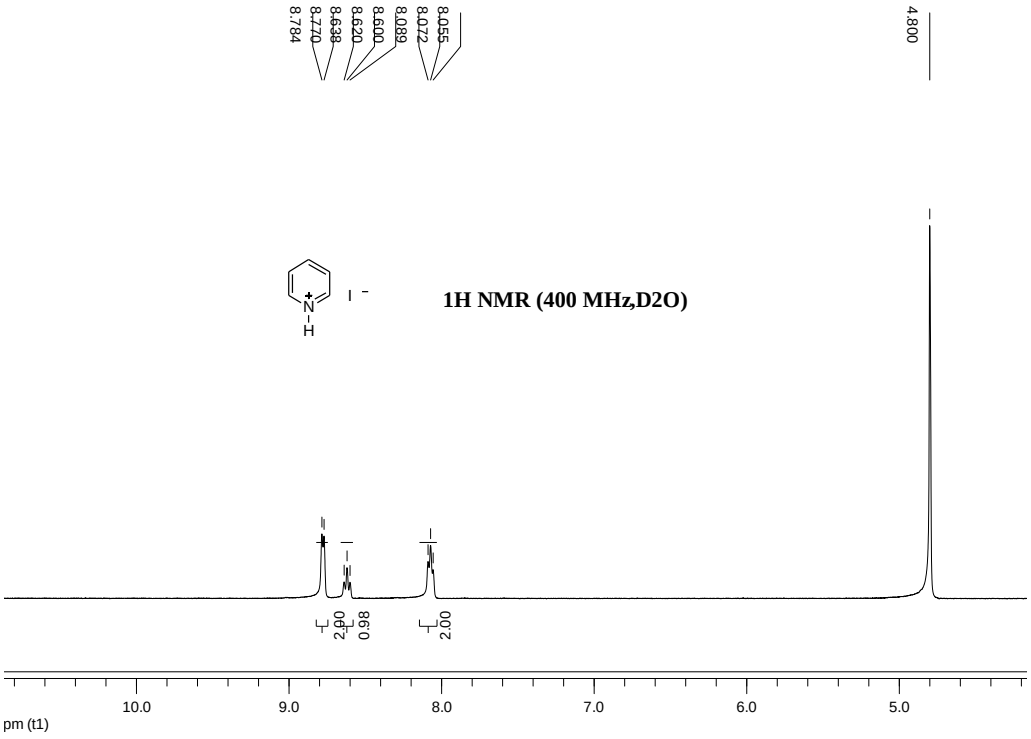
White crystals; Mp 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 - 1.83 (m, 10 H), 3.34 (t, ^{3}J = 8.0 Hz, 1 H), 3.69-3.76 (m, 1 H), 3.89 (t, ^{3}J = 8.7 Hz, 1 H), 5.44 (t, ^{3}J = 8.0 Hz, 1 H), 7.27-7.38 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 25.3, 30.0, 30.4, 48.2, 52.6, 73.8, 126.8, 129.0, 134.5, 137.6, 156.8; APCI-MS calcd for $C_{15}H_{18}ClNO_2$ 279.10, found 839.62 $(3M+H)^+$, 859.60 $(3M+Na)^+$; HRMS: calcd for $C_{15}H_{18}ClNO_2$ $(M + H)^+$ 280.1099, found 280.1101.

8. References :

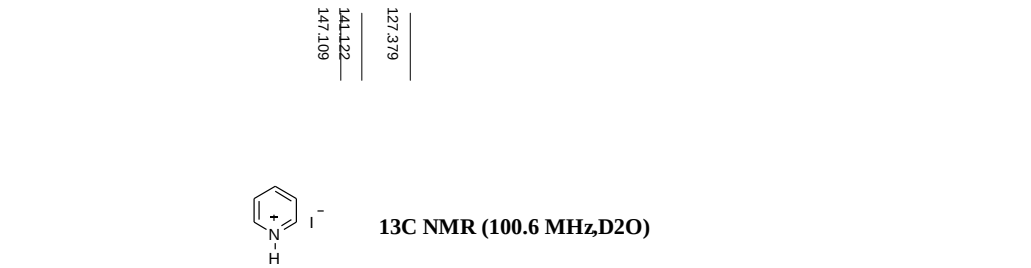
1 (a) Y. Du, Y. Wu, A.-H. Liu and L.-N. He, *J. Org. Chem.*, 2008, **73**, 4709-4712; (b) Y. Wu, L.-N. He, et. al., *Tetrahedron*, 2009, **65,** 6204-6210.
2 Z.-Z. Yang, L.-N. He, C.-X. Miao and S. Chanfreau, *Adv. Synth. Catal.*, 2010, **352**, 2233-2240.

9. The ^{1}H NMR and ^{13}C NMR Charts for protic onium salts

HPyI: pyridin-1-ium iodide

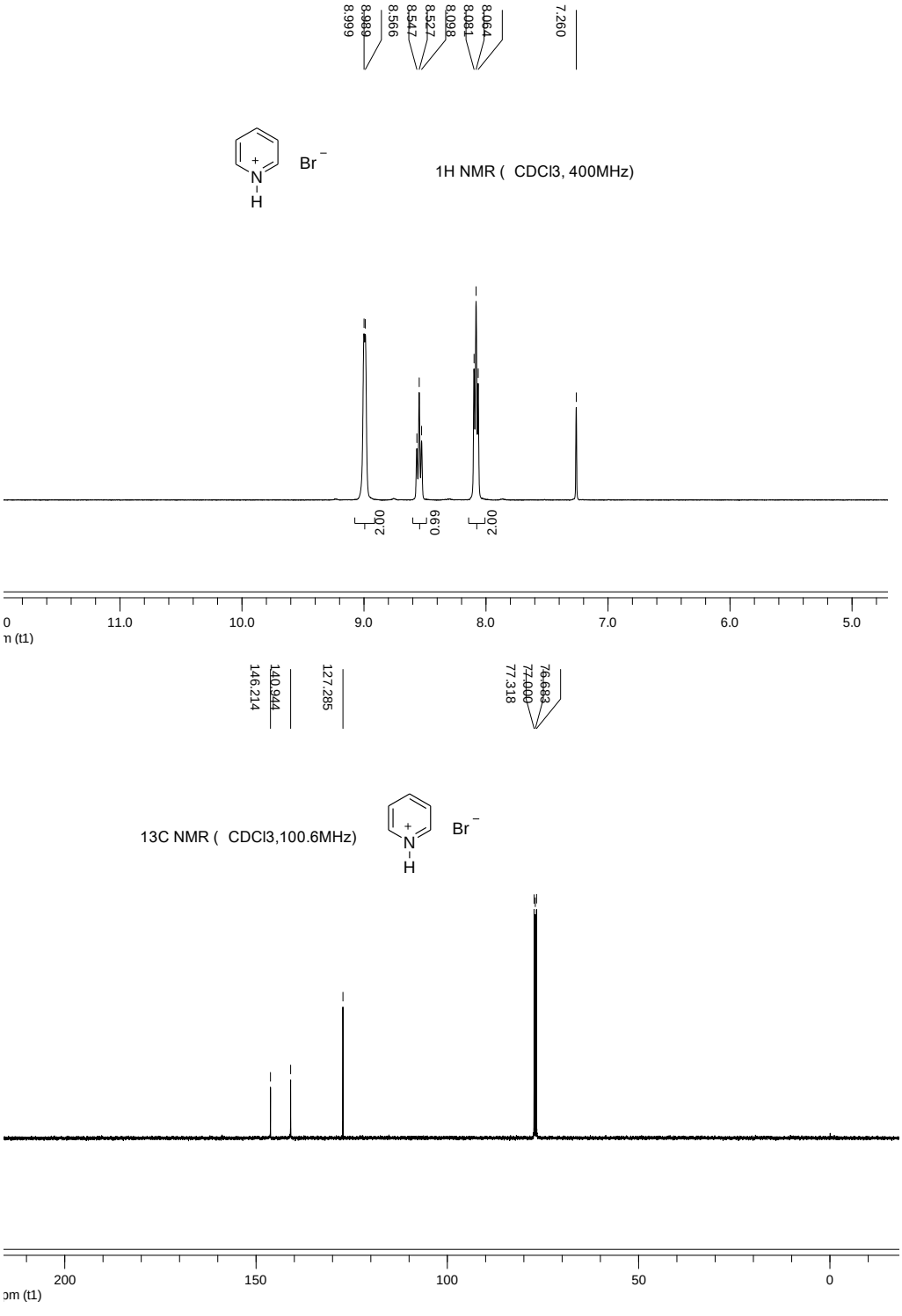


1H NMR (400 MHz,D2O)

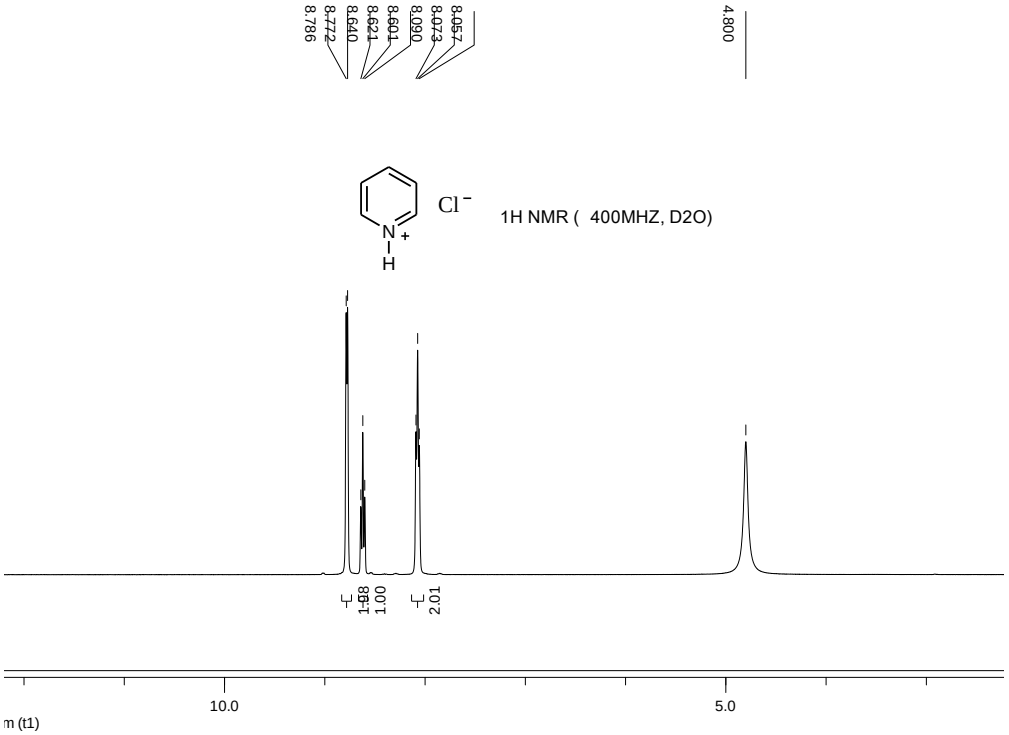


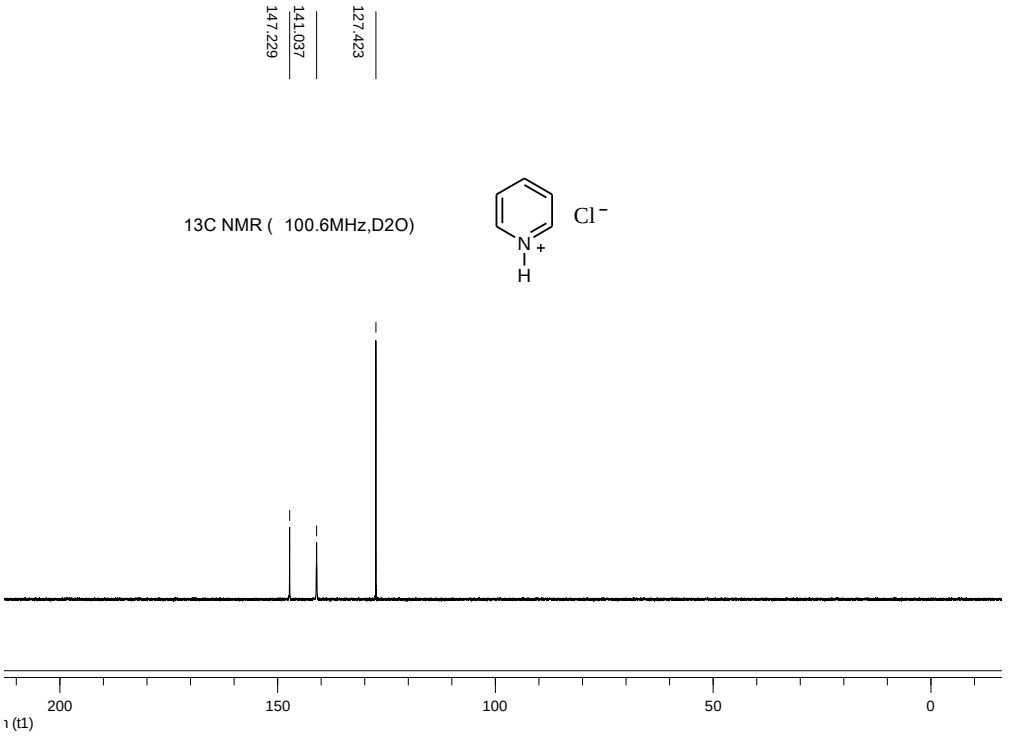
13C NMR (100.6 MHz,D2O)

HPyBr: pyridin-1-ium bromide

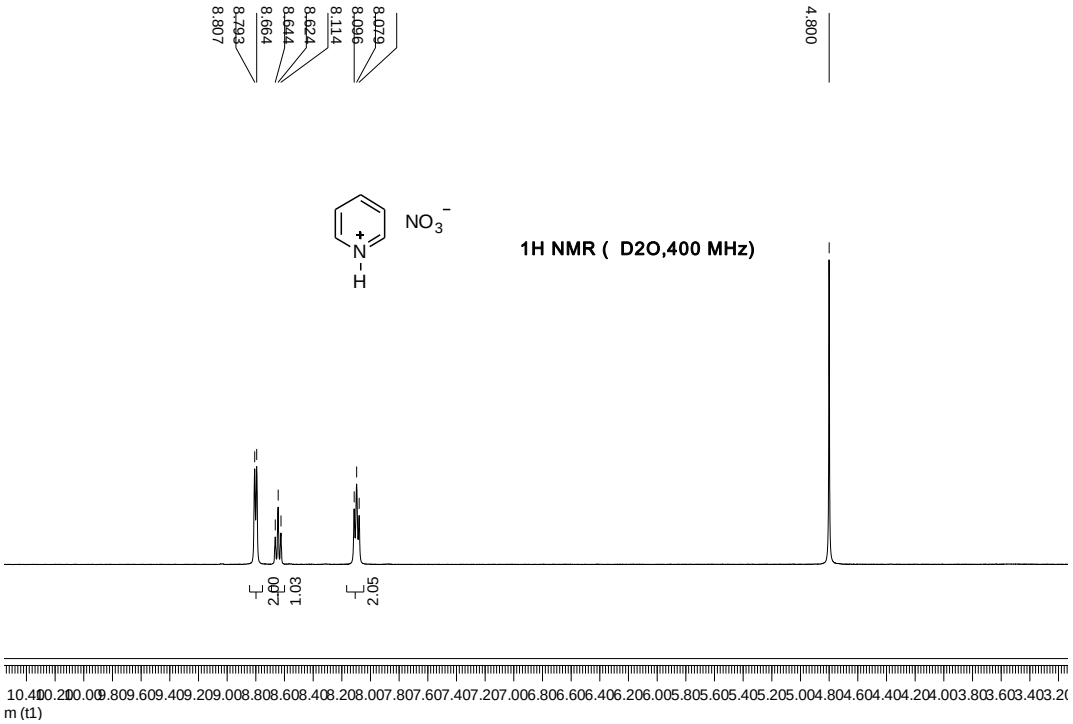


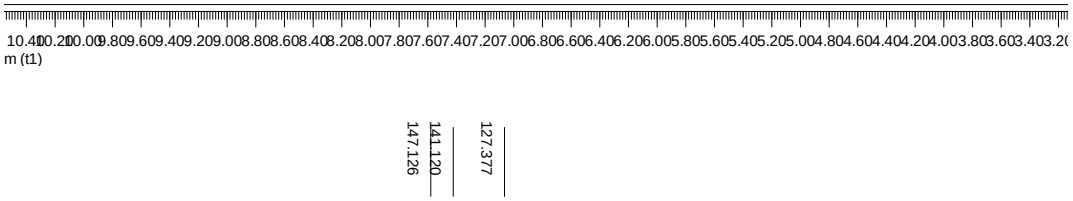
HPyCl: pyridin-1-ium chloride

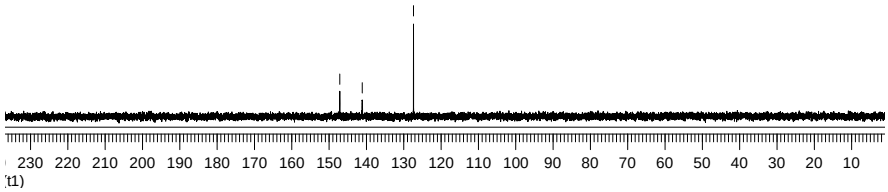




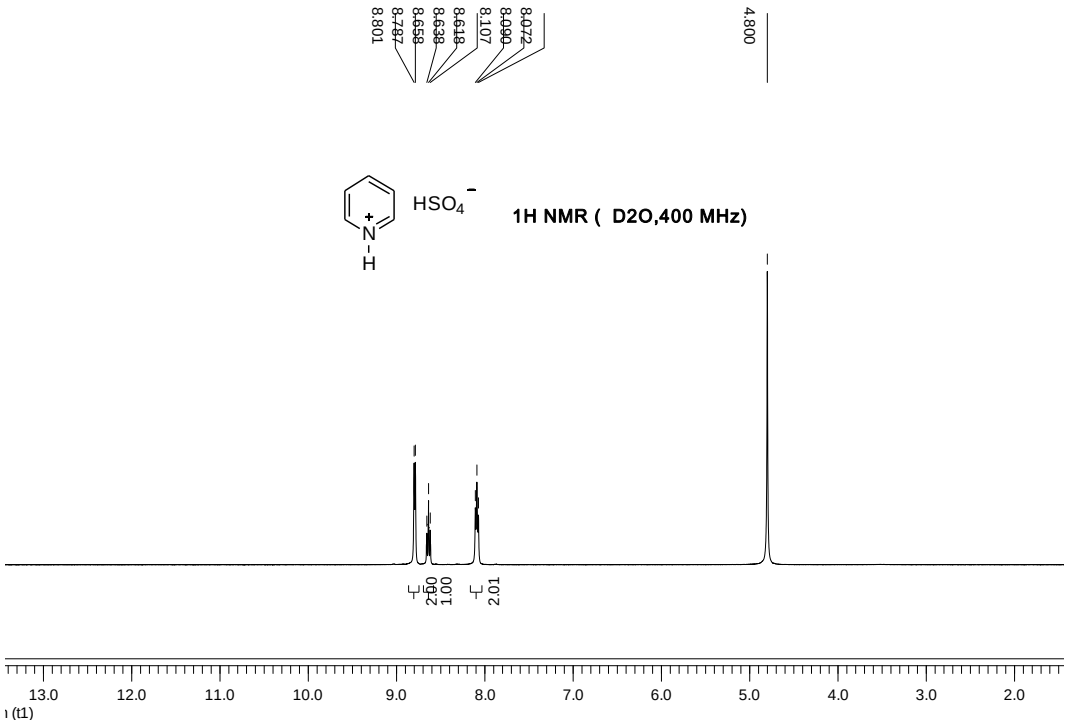
$HPyNO_3$: pyridin-1-ium nitrate

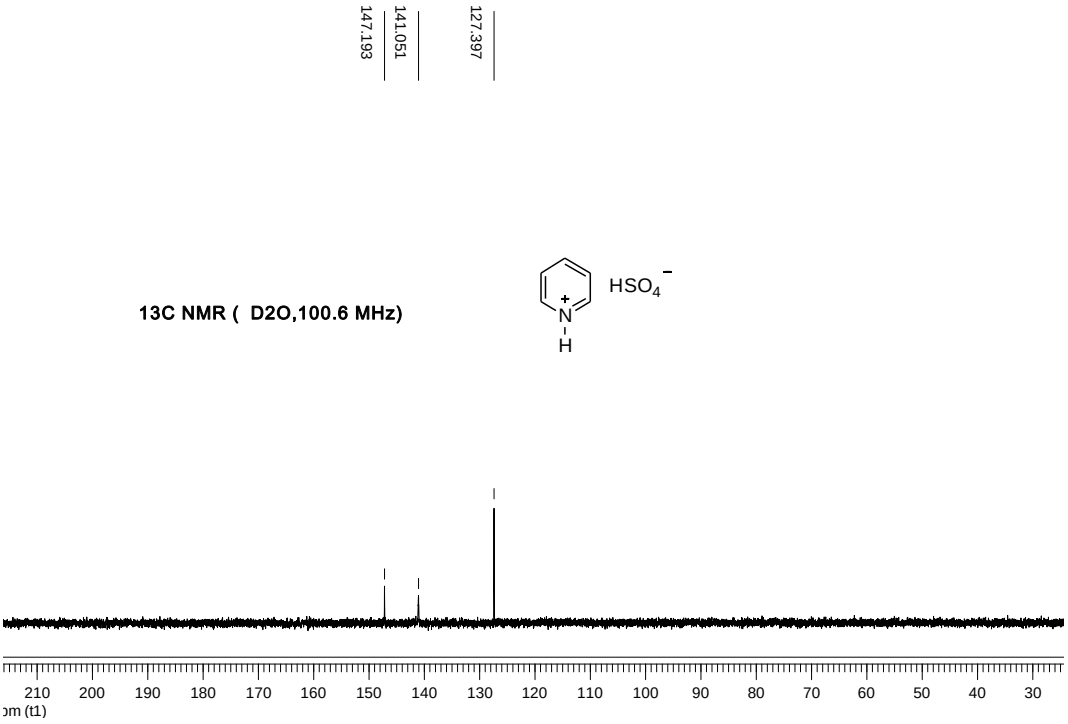




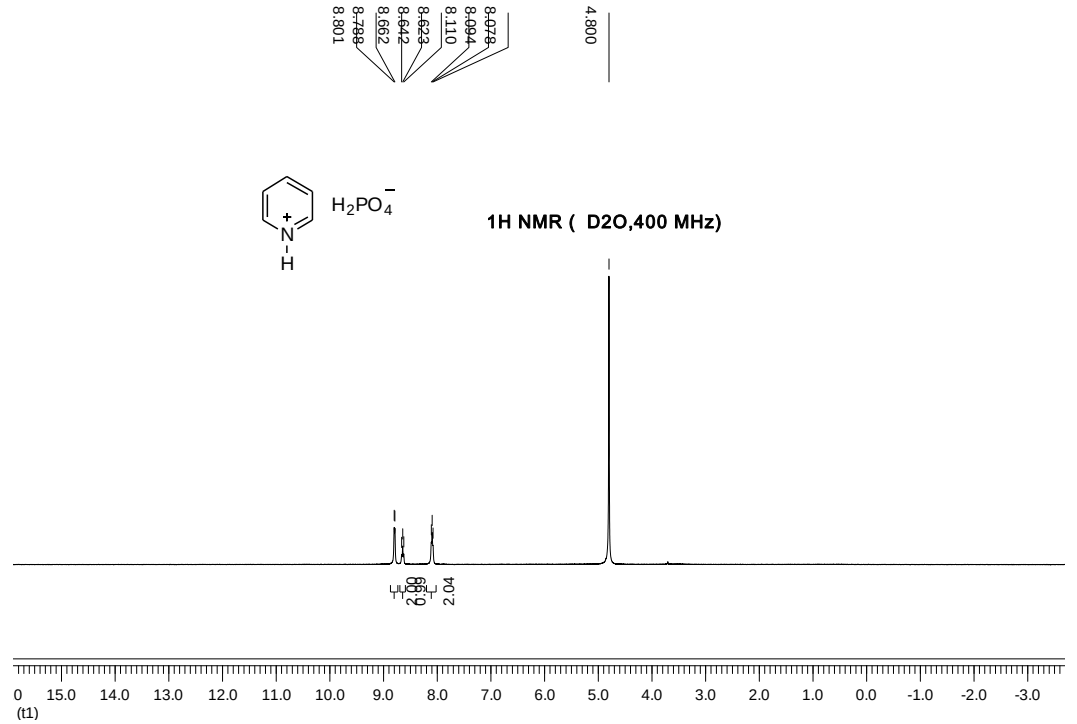


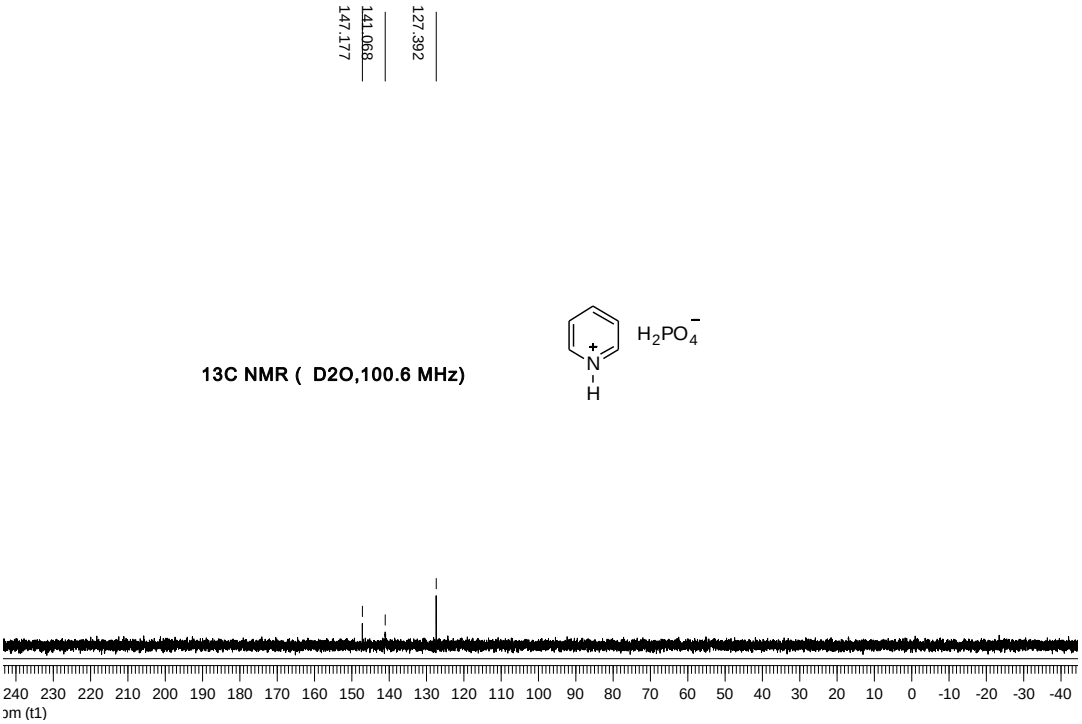
$HPyHSO_4$: pyridin-1-ium bisulfate



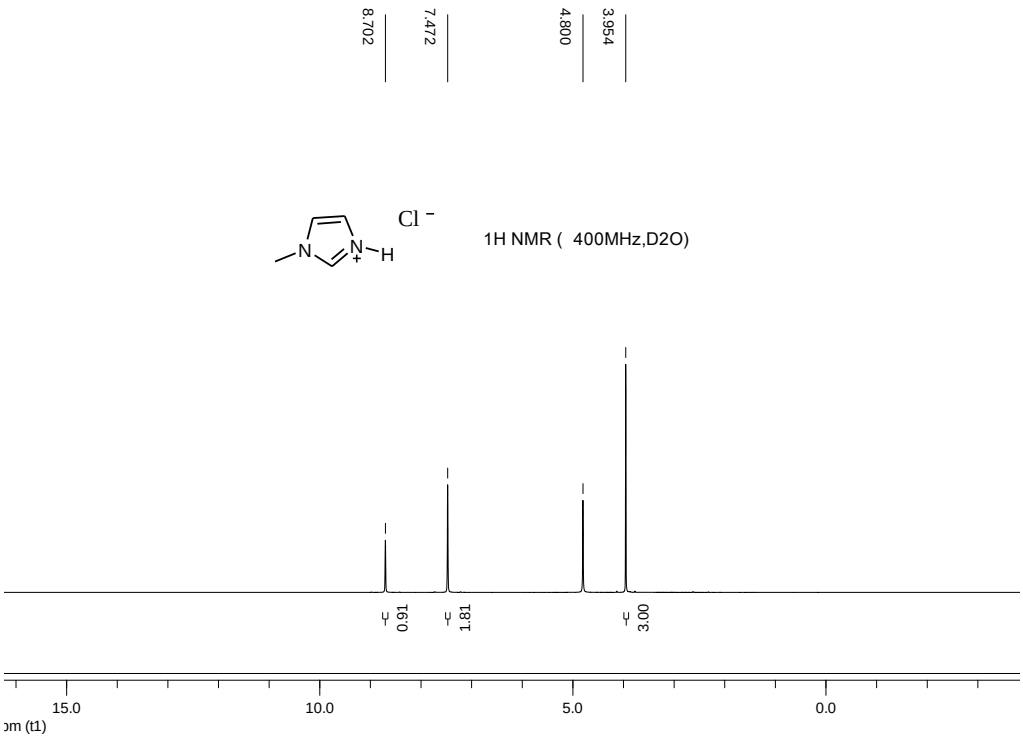


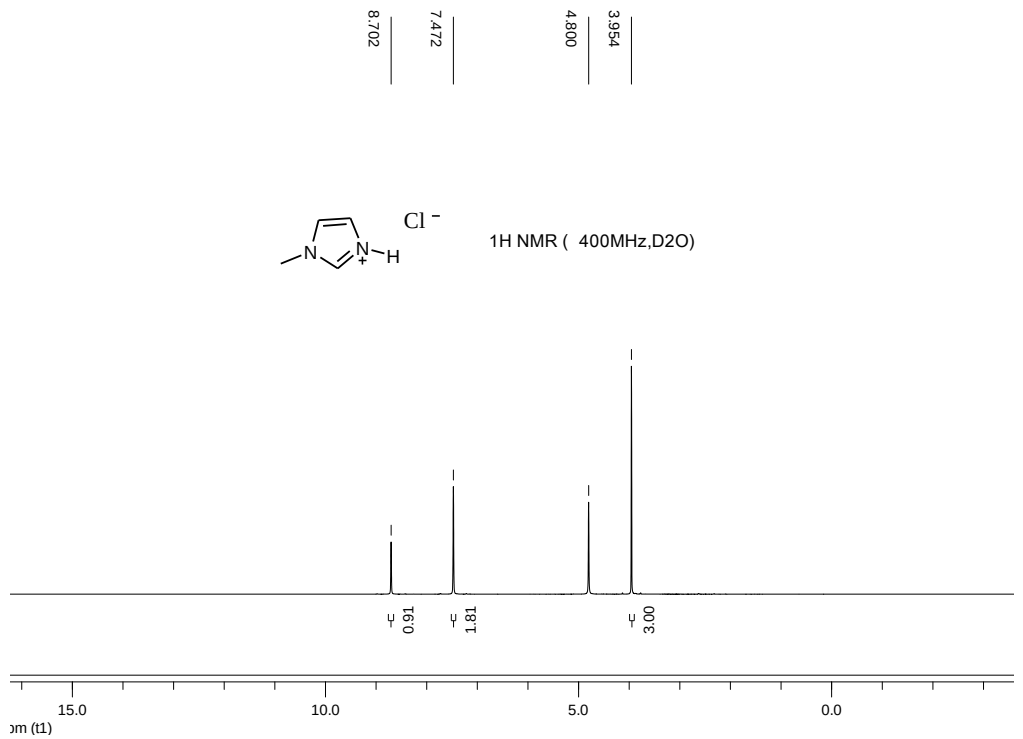
$HPyH_2PO_4$: pyridin-1-ium dihydrogen phosphate



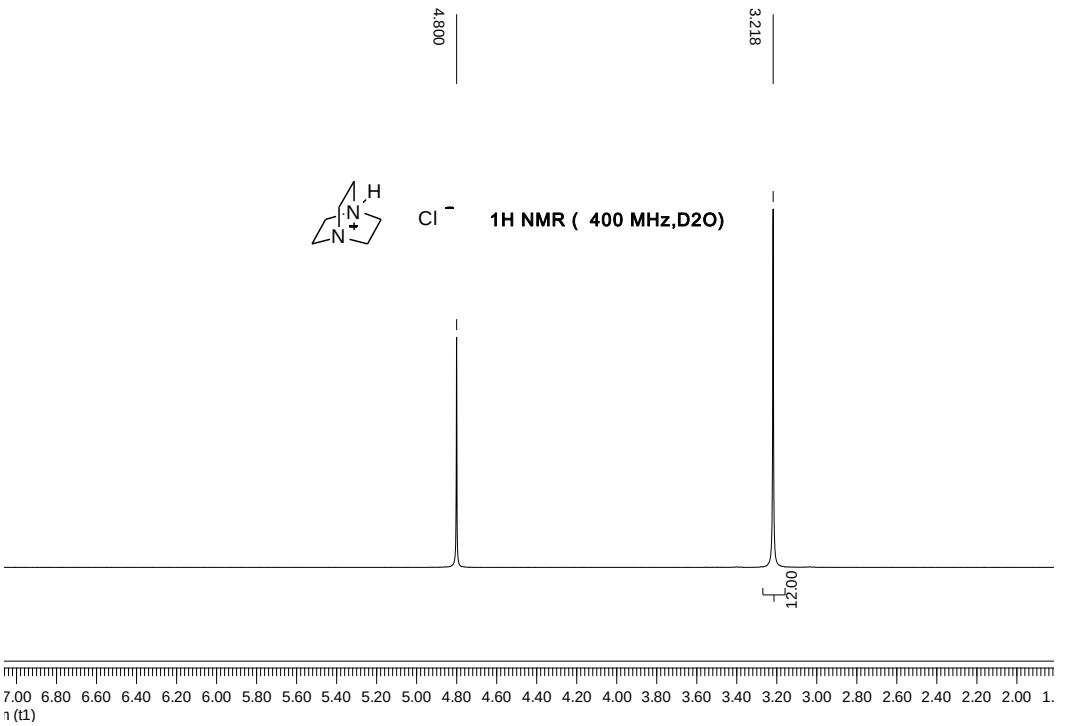


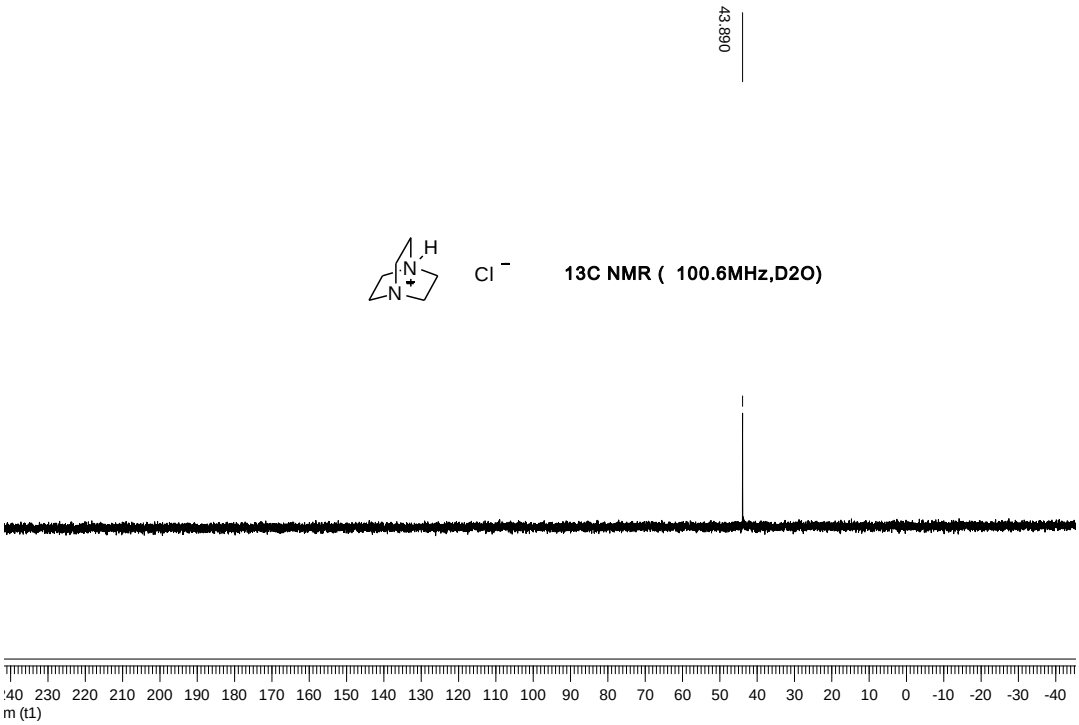
HMImCl: 1-hydro-3-methylimidazolium chloride



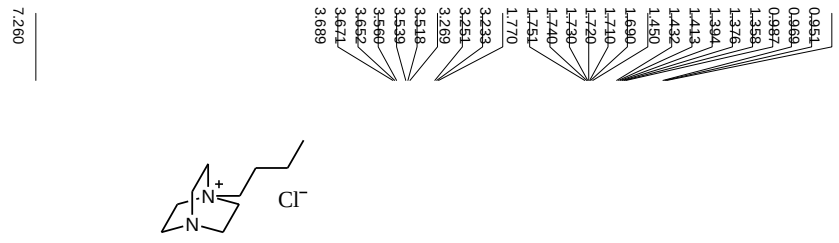


HDABCOCl: 1-hydro-4-aza-1-azaniabicyclo-[2.2.2]octane chloride

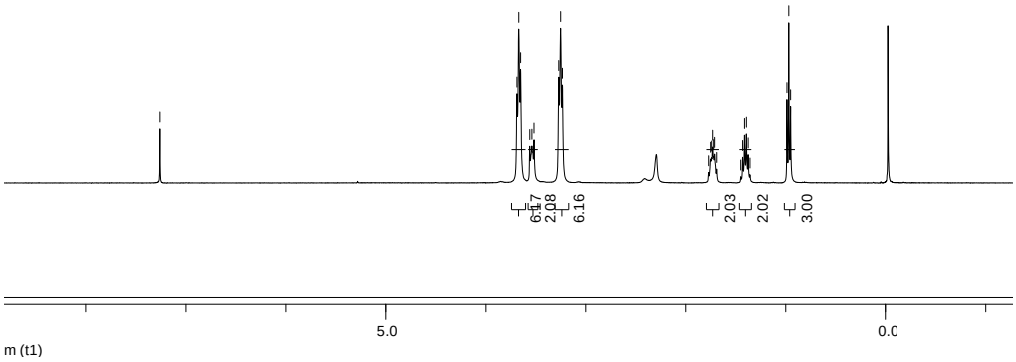


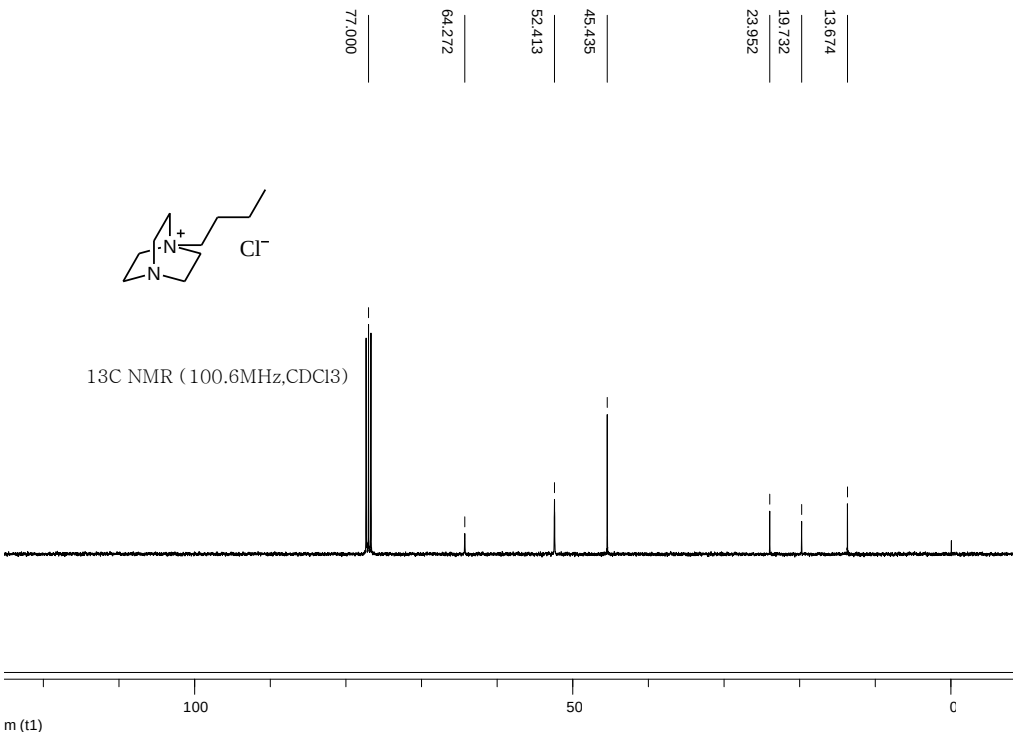


[C_4DABCO]Cl: 1-butyl-4-aza-1-azaniabicyclo[2.2.2]octane chloride



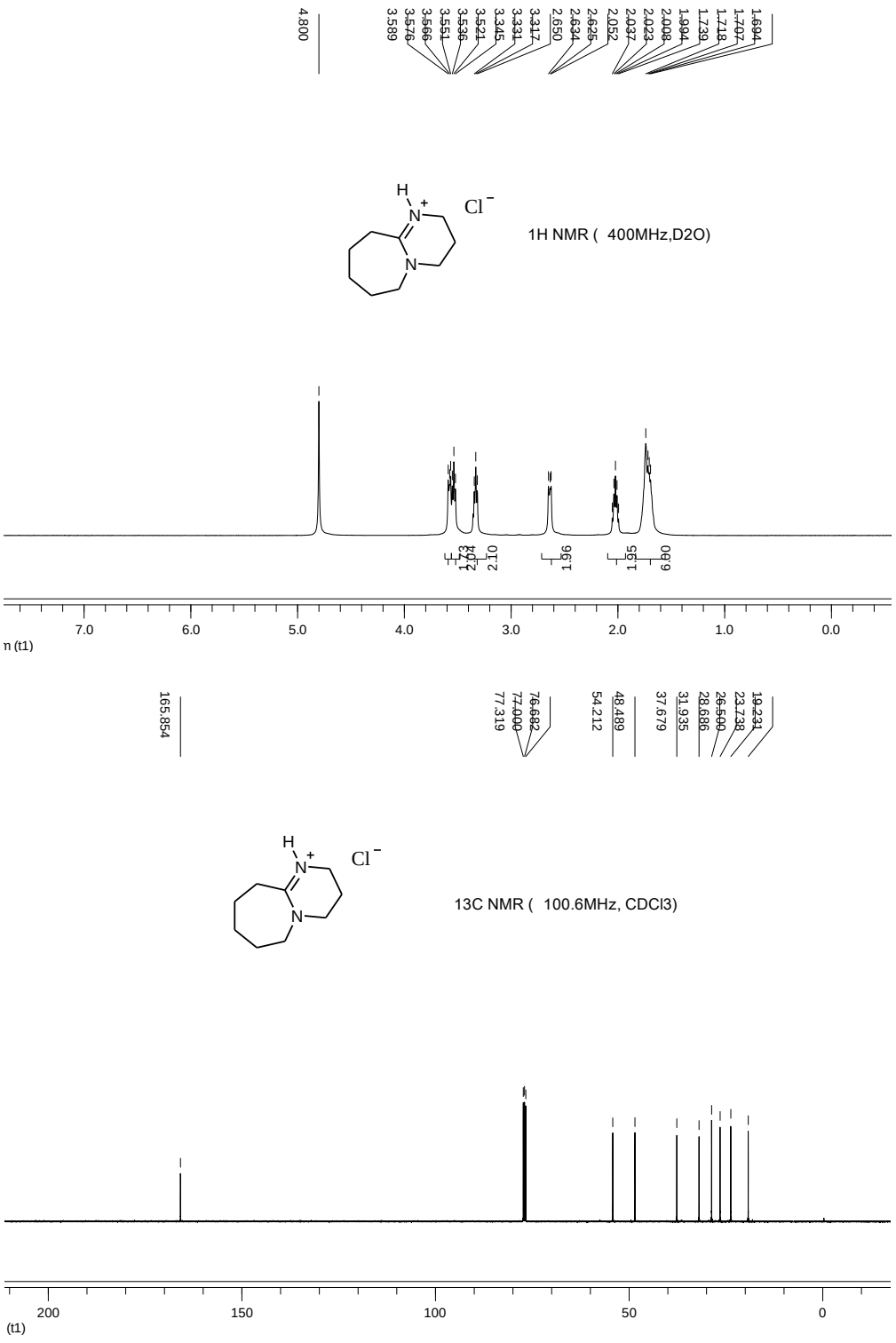
1H NMR (400MHz,CDCl3)



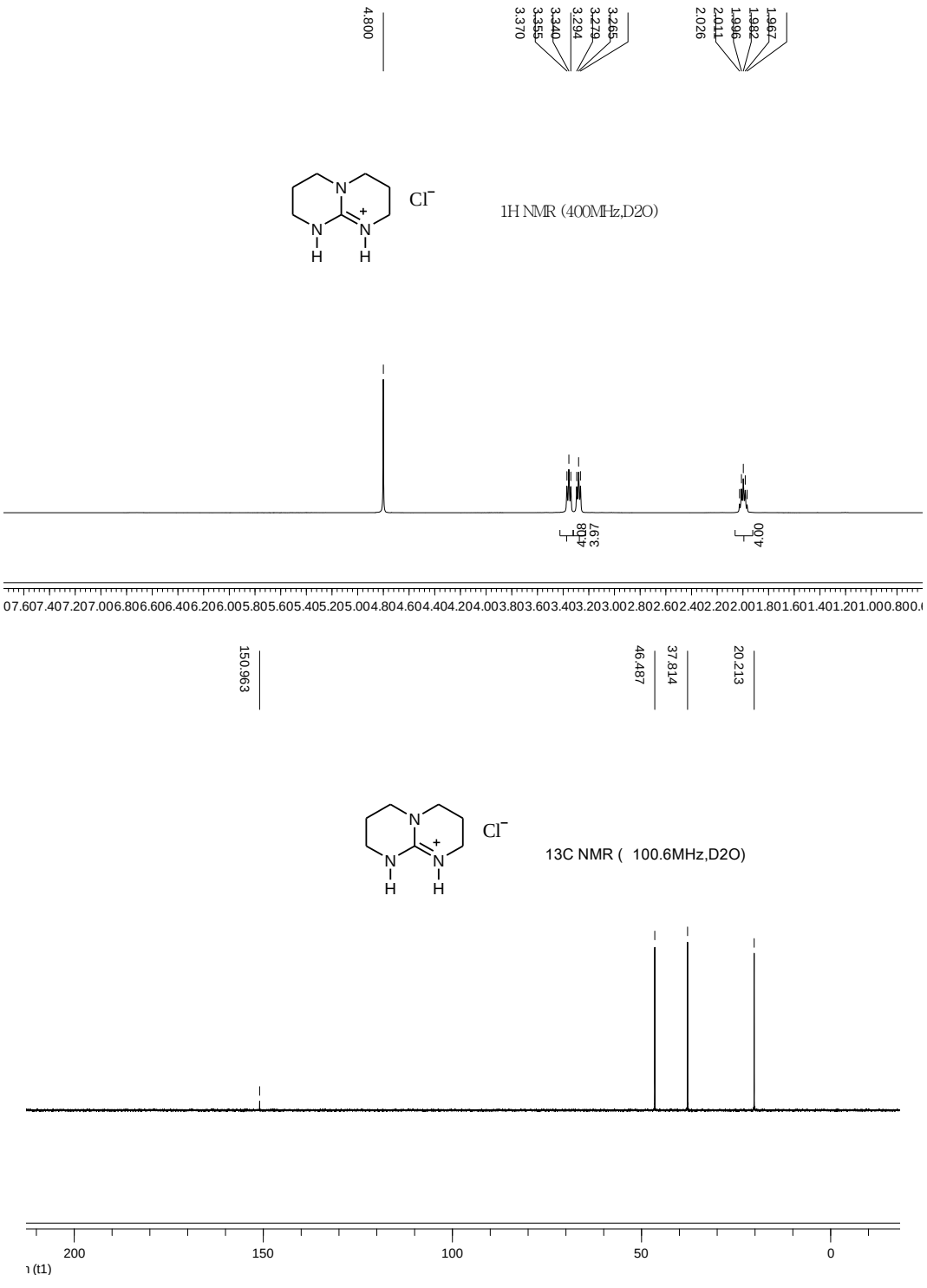


13C NMR (100.6MHz,CDCl3)

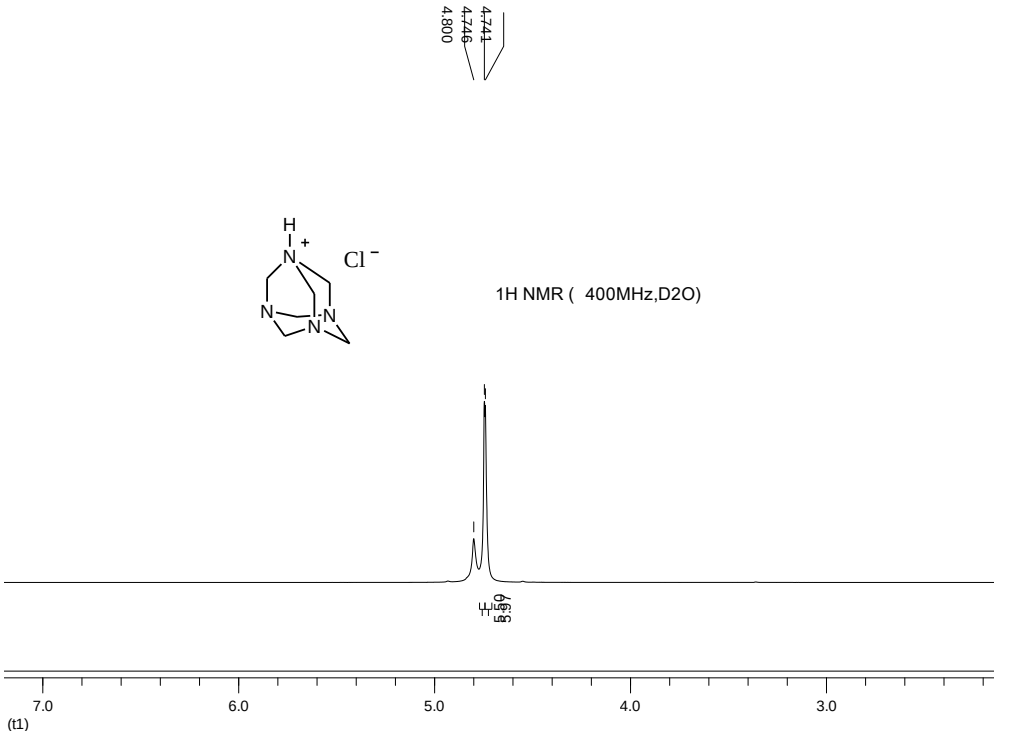
HDBUCl: 1,8-diazabicyclo[5.4.0]undec-7-enium chloride

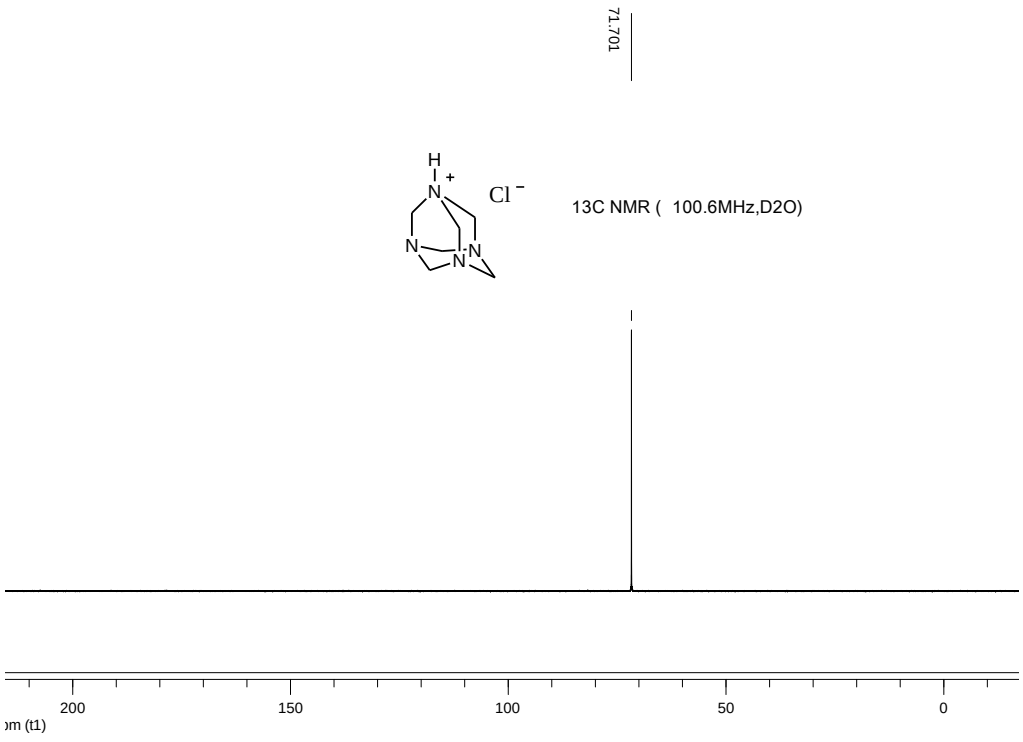


HTBDCl: 1,5,7-triazabicyclo[4.4.0]dec-5-enium chloride

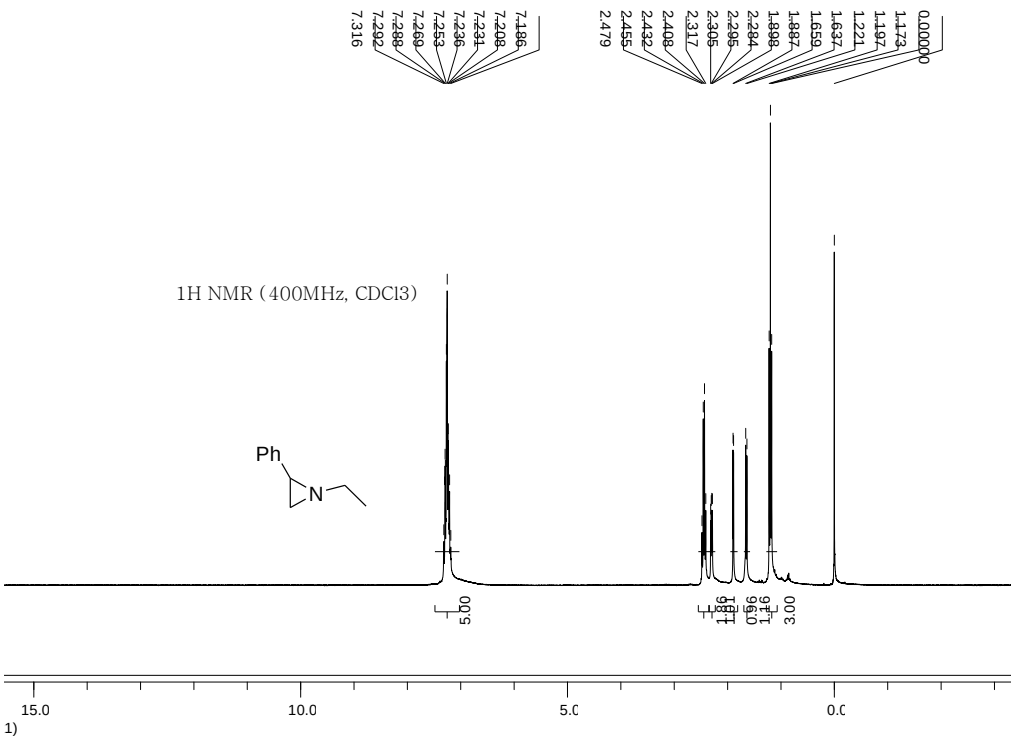


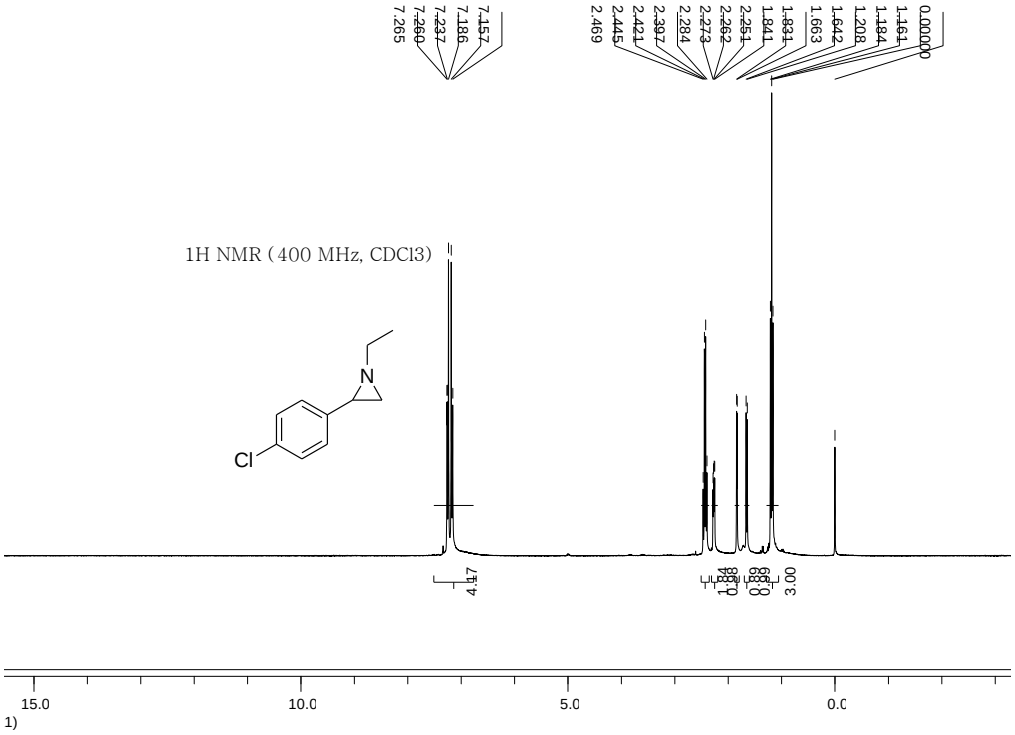
HHMTACl: 1,3,5,7-tetraazatricyclo[1.1.1.1.1.1]dec-1-anium chloride

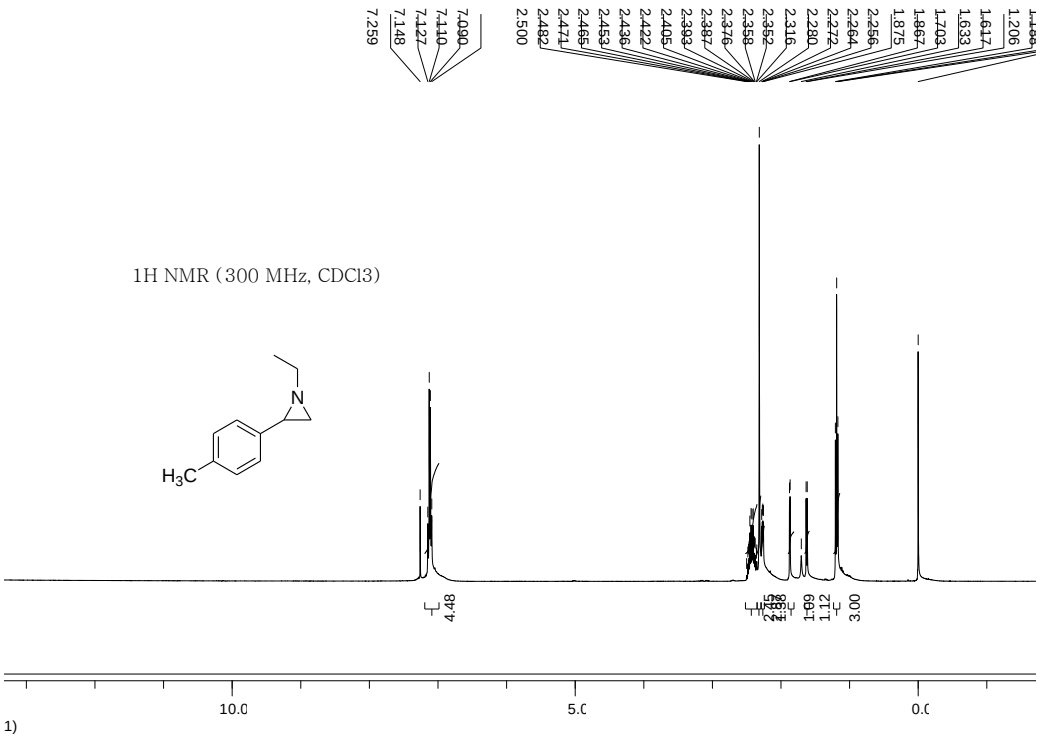


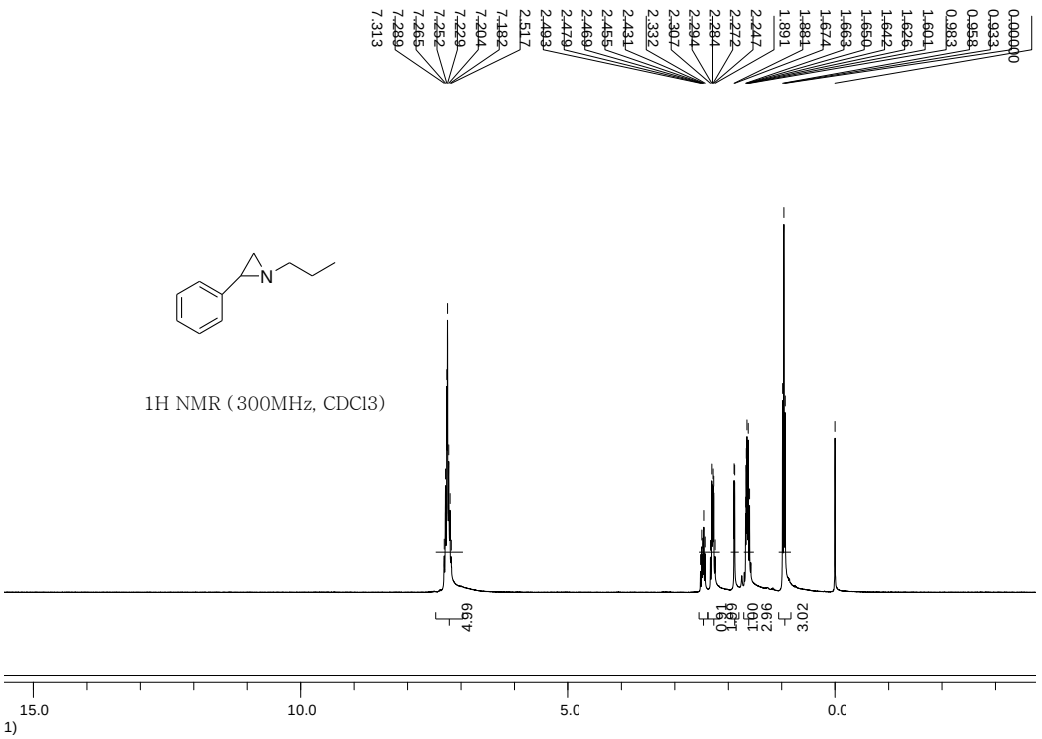


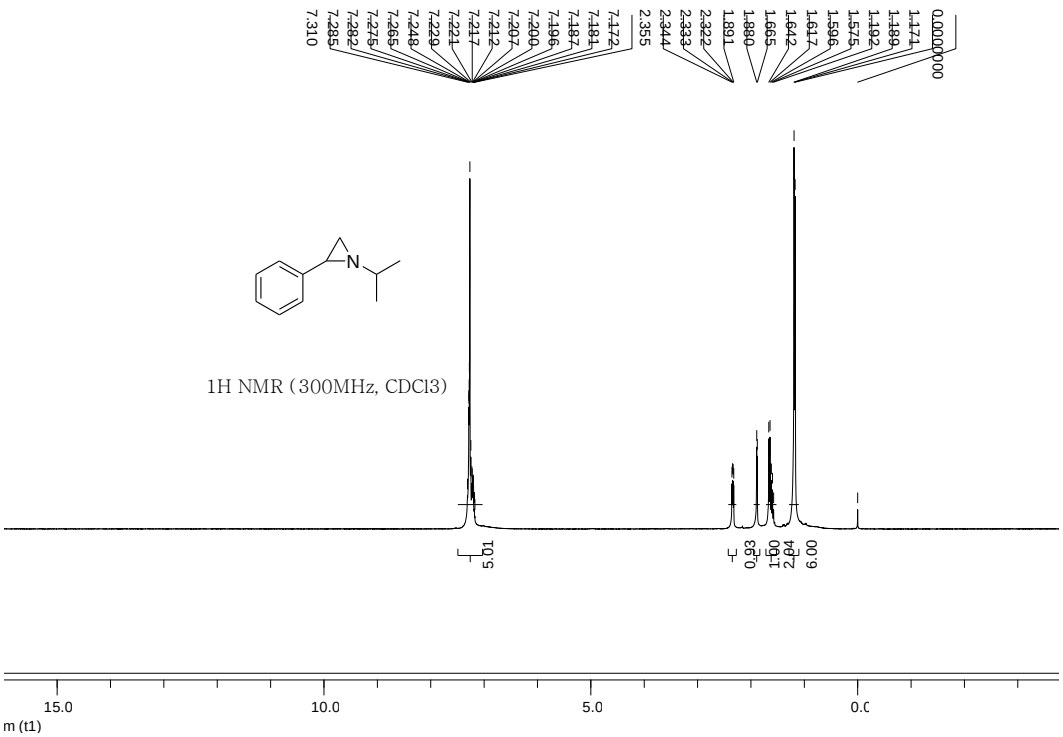
10. The ^{1}H NMR charts for aziridines

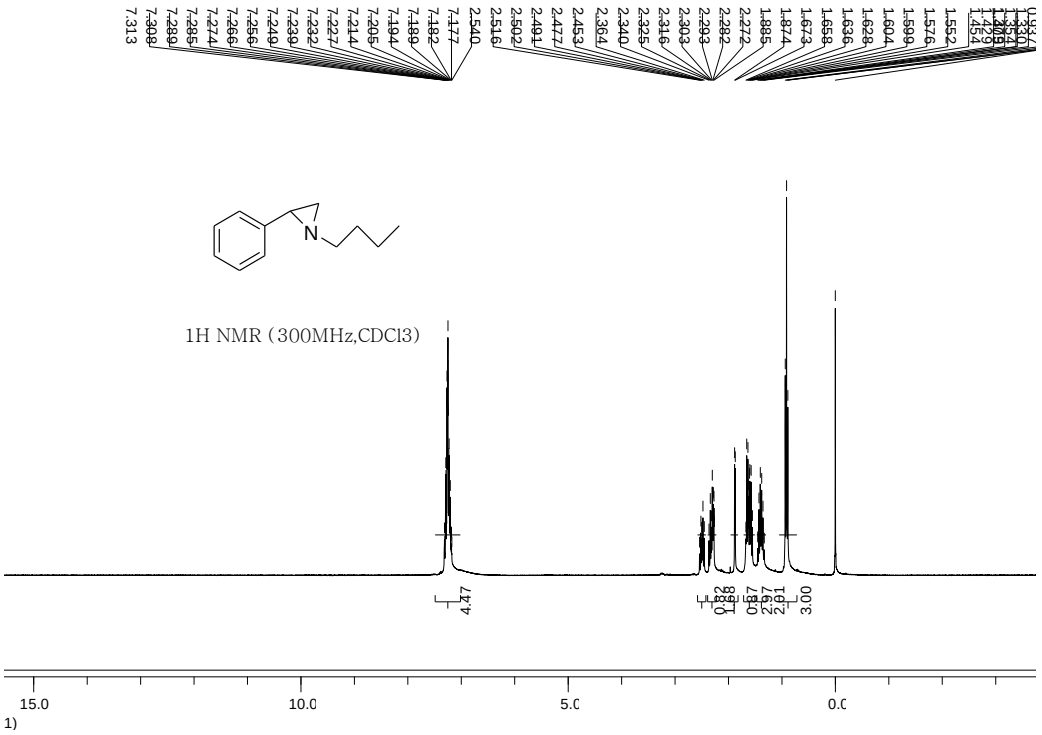


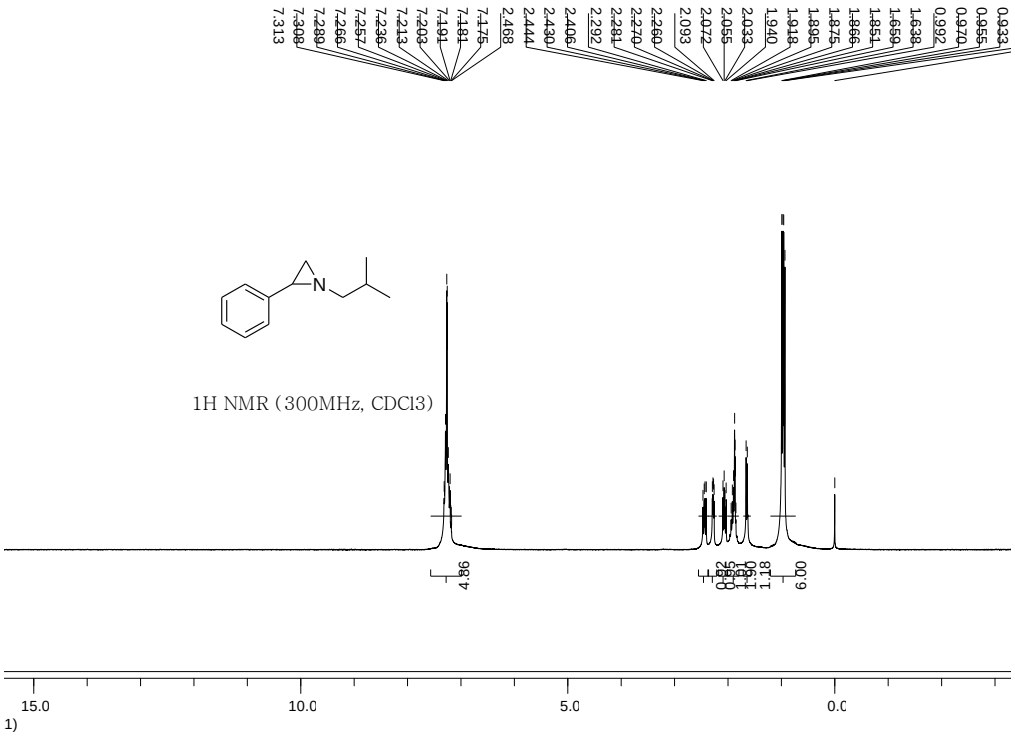


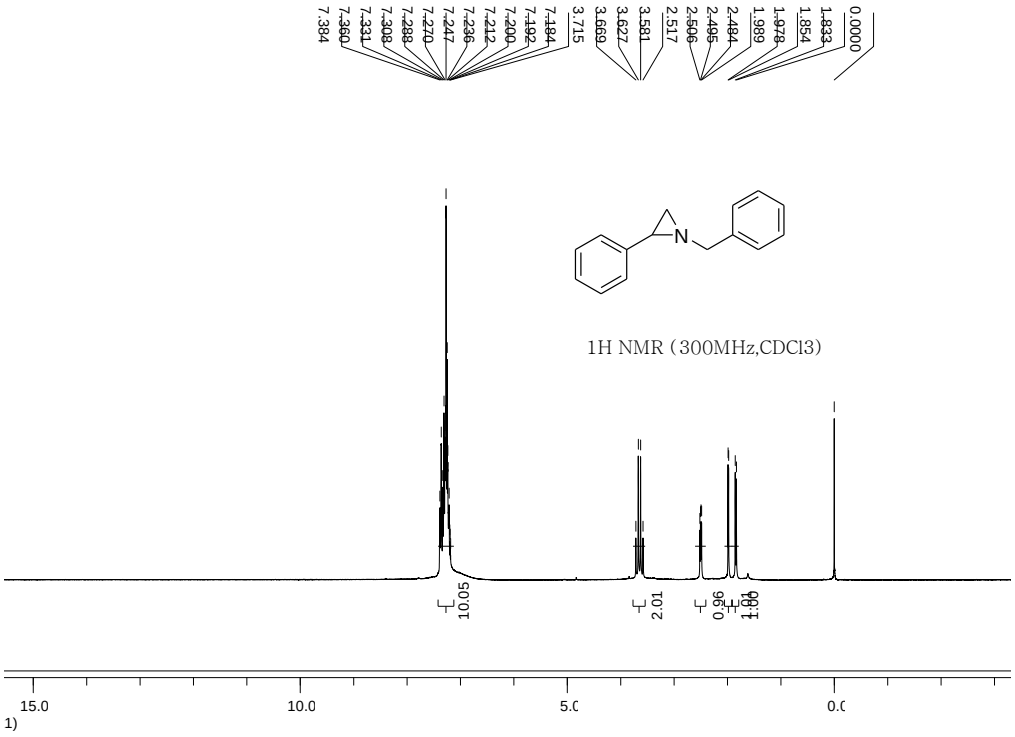

1H NMR (300 MHz, CDCl3)
N
H3C
4.48
3.00
10.0
5.0
0.0
1)

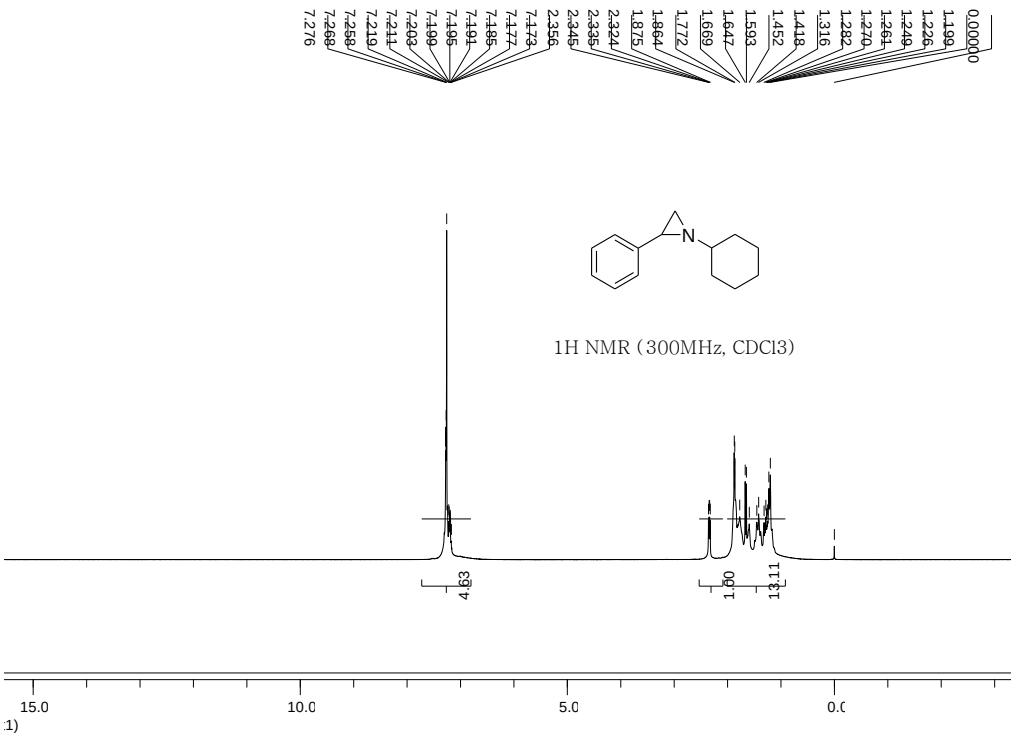

1H NMR (300MHz, CDCl3)
N
4.99
3.02
15.0
10.0
5.0
0.0
1)

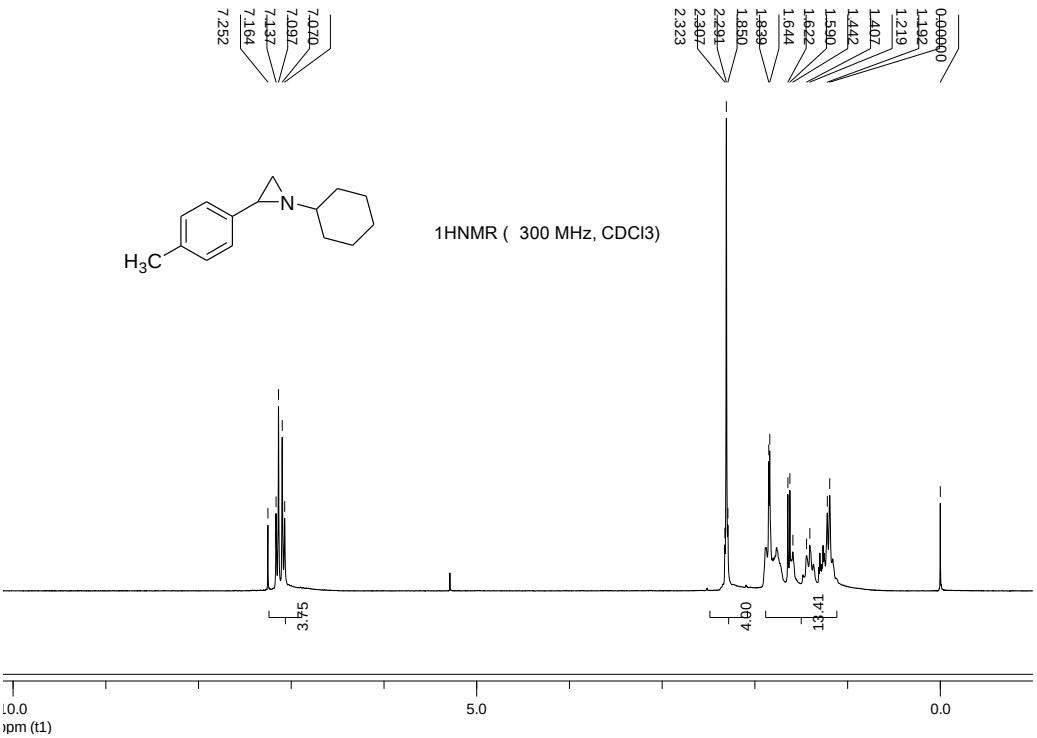

7.310
7.285
7.282
7.276
7.265
7.248
7.229
7.221
7.217
7.212
7.207
7.200
7.196
7.187
7.181
7.172
2.355
2.344
2.333
2.322
1.891
1.880
1.665
1.642
1.617
1.596
1.575
1.192
1.189
1.171
0.000000
N
1H NMR (300MHz, CDCl3)
5.01
0.93
1.00
2.04
6.00
15.0
10.0
5.0
0.0
m (t1)

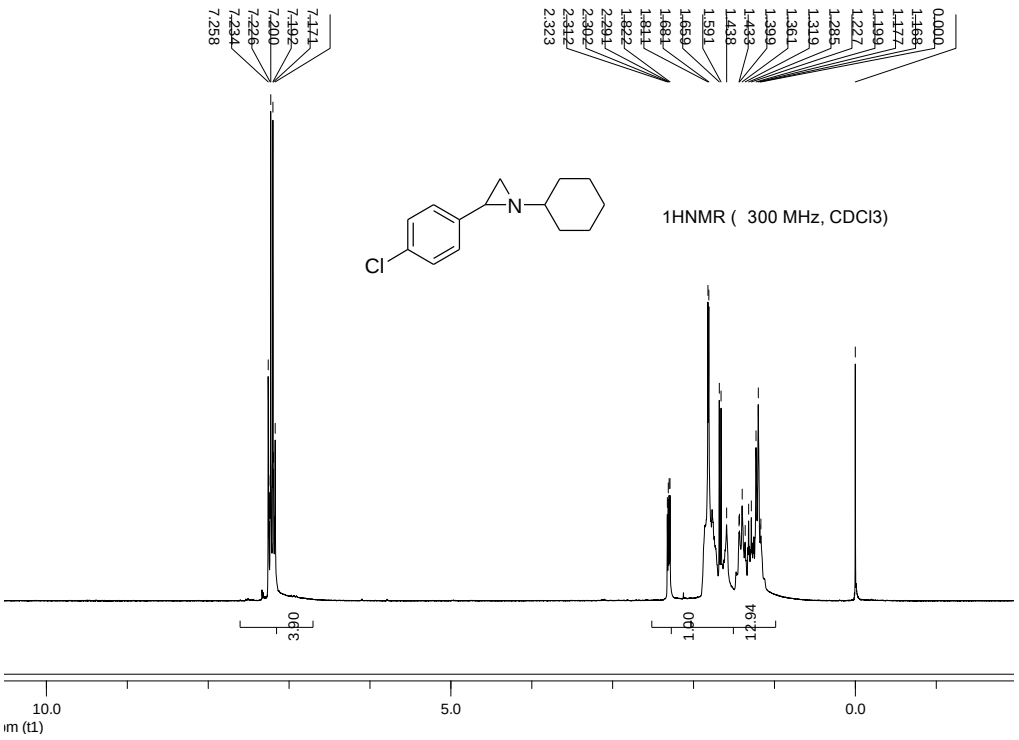

7.313
7.309
7.289
7.285
7.274
7.266
7.256
7.249
7.239
7.232
7.227
7.214
7.205
7.194
7.189
7.182
7.177
2.540
2.516
2.502
2.491
2.477
2.453
2.364
2.340
2.325
2.316
2.303
2.293
2.282
2.272
1.885
1.874
1.673
1.658
1.636
1.628
1.604
1.599
1.576
1.552
1.454
N
1H NMR (300MHz,CDCl3)
4.47
0.82
1.88
0.87
2.97
2.01
3.00
15.0
10.0
5.0
0.0
1)


7.313
7.308
7.280
7.266
7.257
7.236
7.213
7.202
7.191
7.181
7.175
2.468
2.444
2.430
2.406
2.292
2.281
2.270
2.260
2.093
2.072
2.055
2.033
1.940
1.918
1.895
1.875
1.866
1.851
1.650
1.638
0.992
0.970
0.955
0.933
N
1H NMR (300MHz, CDCl3)
4.96
18.11
6.00
15.0
10.0
5.0
0.0
1)

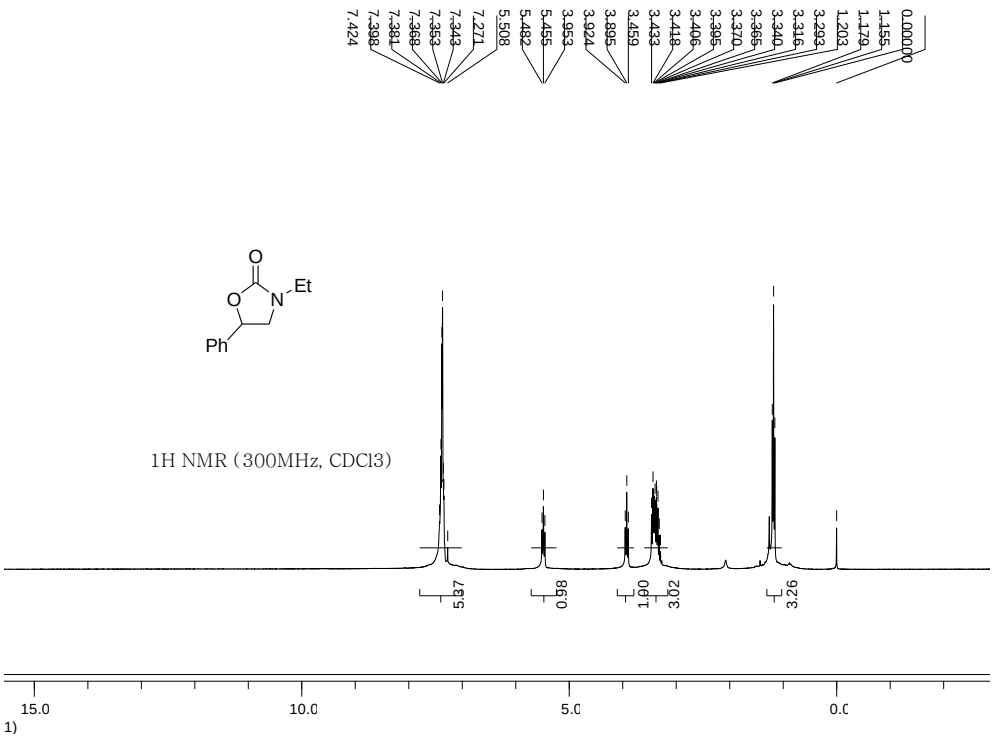

7.384
7.360
7.331
7.308
7.288
7.270
7.247
7.236
7.212
7.200
7.192
7.184
3.715
3.669
3.627
3.581
2.517
2.506
2.495
2.484
1.989
1.978
1.854
1.833
0.0000
N
1H NMR (300MHz,CDCl3)
10.05
2.01
0.96
1.00
15.0
10.0
5.0
0.0
1)

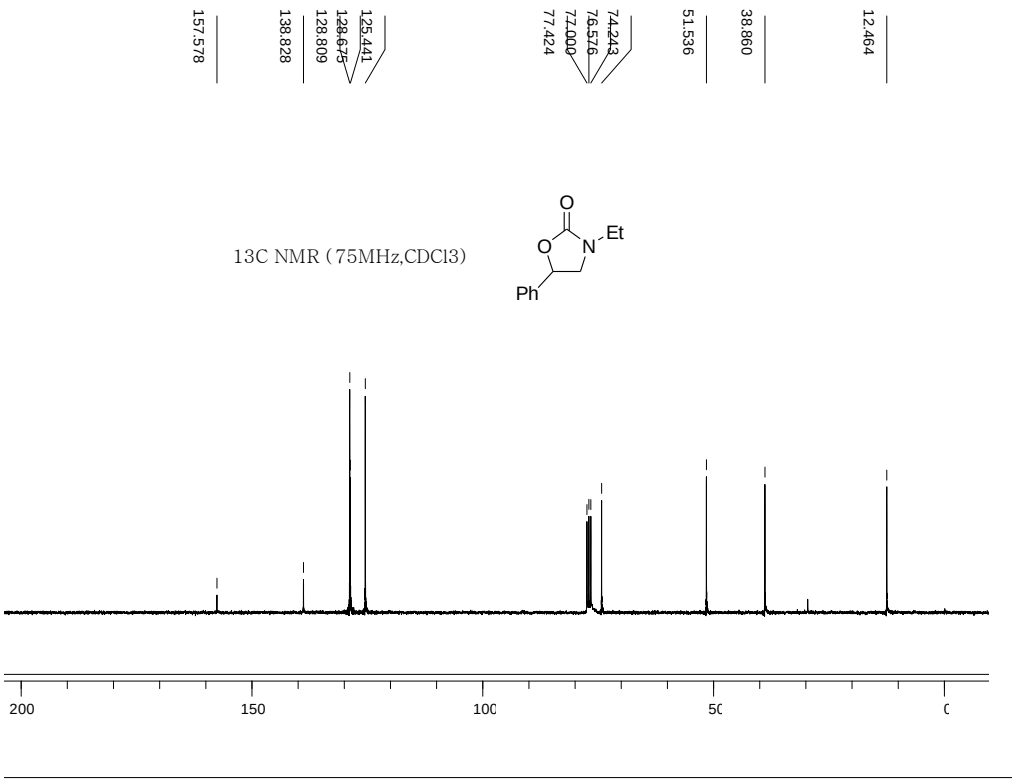

7.276
7.268
7.258
7.219
7.211
7.203
7.199
7.195
7.191
7.185
7.177
7.173
2.356
2.345
2.335
2.324
1.875
1.864
1.772
1.669
1.647
1.593
1.452
1.418
1.316
1.282
1.270
1.261
1.249
1.226
1.199
0.00000
N
1H NMR (300MHz, CDCl3)
4.93
1.00
13.11
15.0
10.0
5.0
0.0
1)

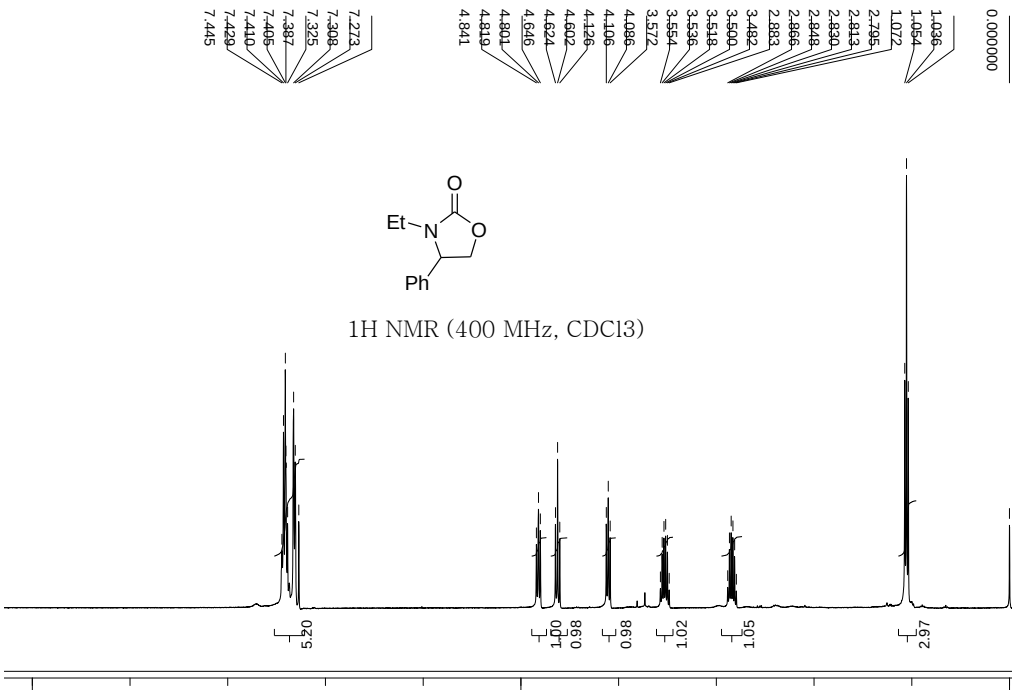

7.252
7.164
7.137
7.097
7.070
2.323
2.307
2.291
1.850
1.839
1.644
1.622
1.590
1.442
1.407
1.219
1.192
0.00000
N
H3C
1HNMR (300 MHz, CDCl3)
3.75
4.00
13.41
10.0
5.0
0.0
ppm (t1)

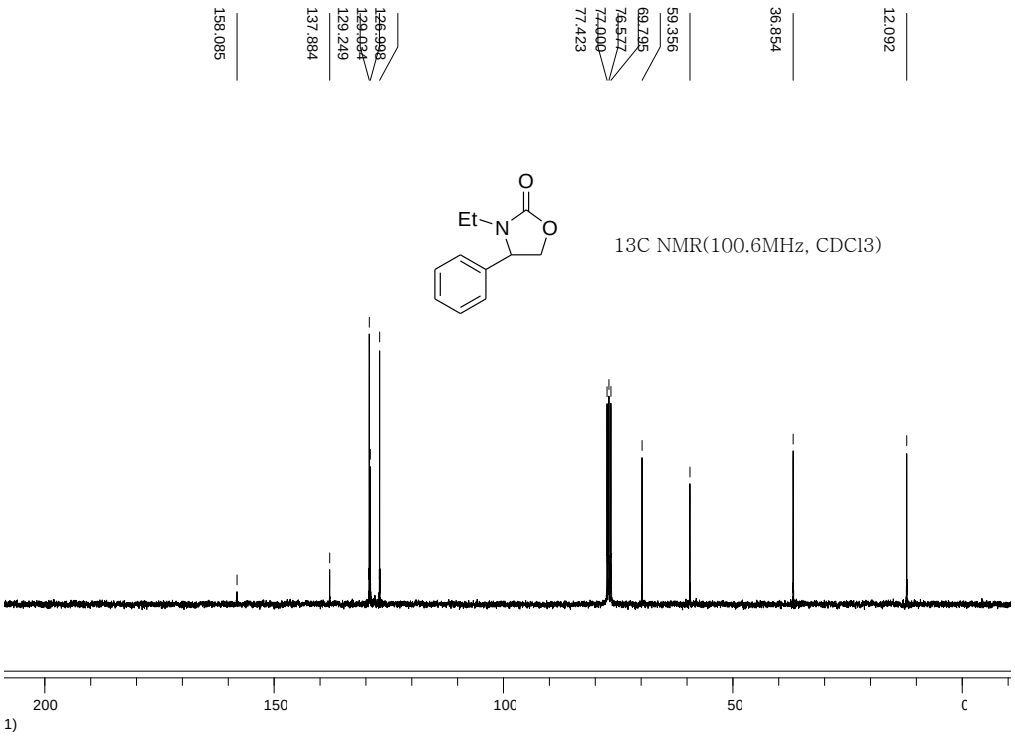


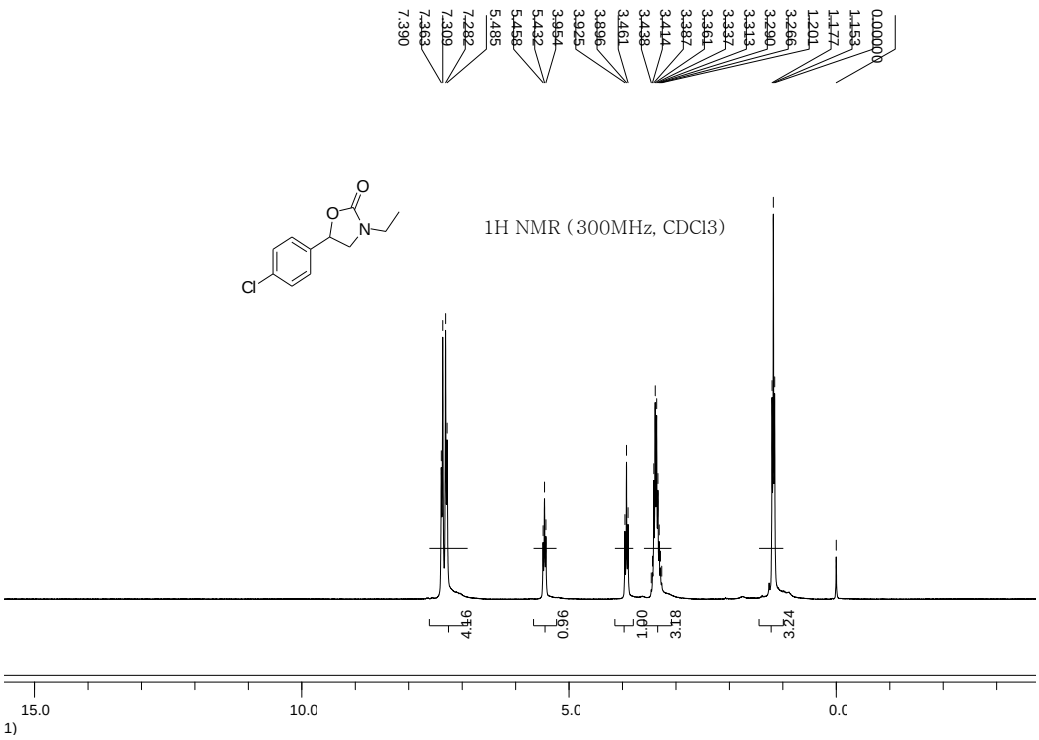
11. The ^{1}H NMR and ^{13}C NMR Charts for oxazolidinones

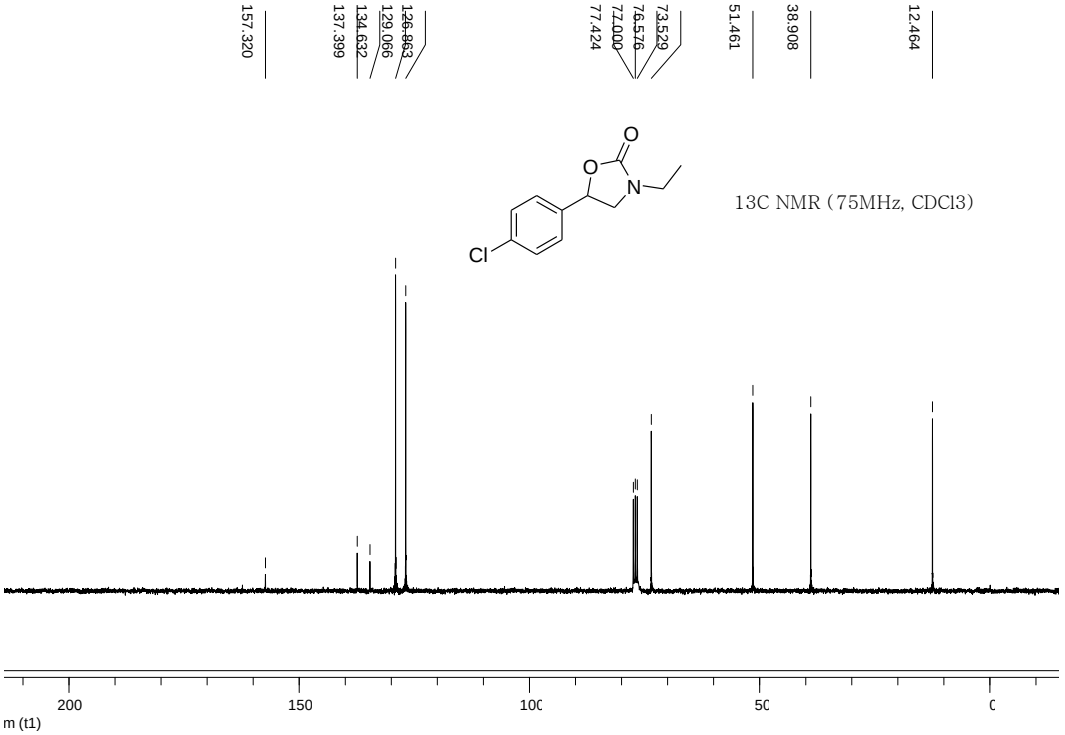


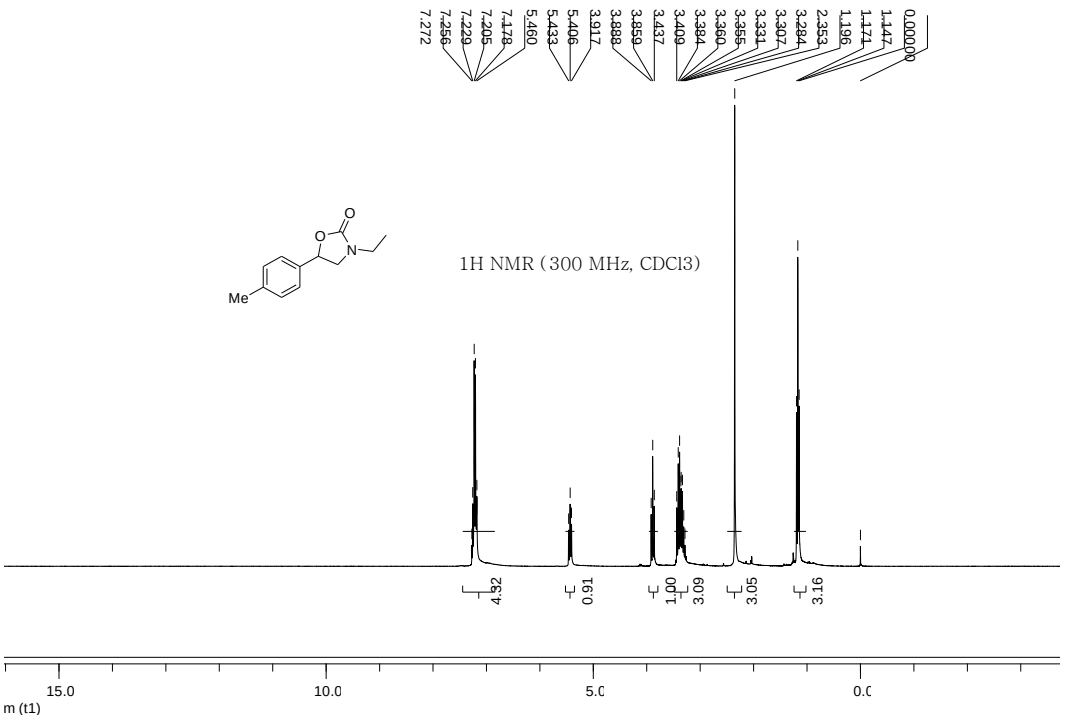

157.578
138.828
128.809
128.675
125.441
77.424
77.000
76.576
74.243
51.536
38.860
12.464
13C NMR (75MHz,CDCl3)
O
O
N
Et
Ph
200
150
100
50
0

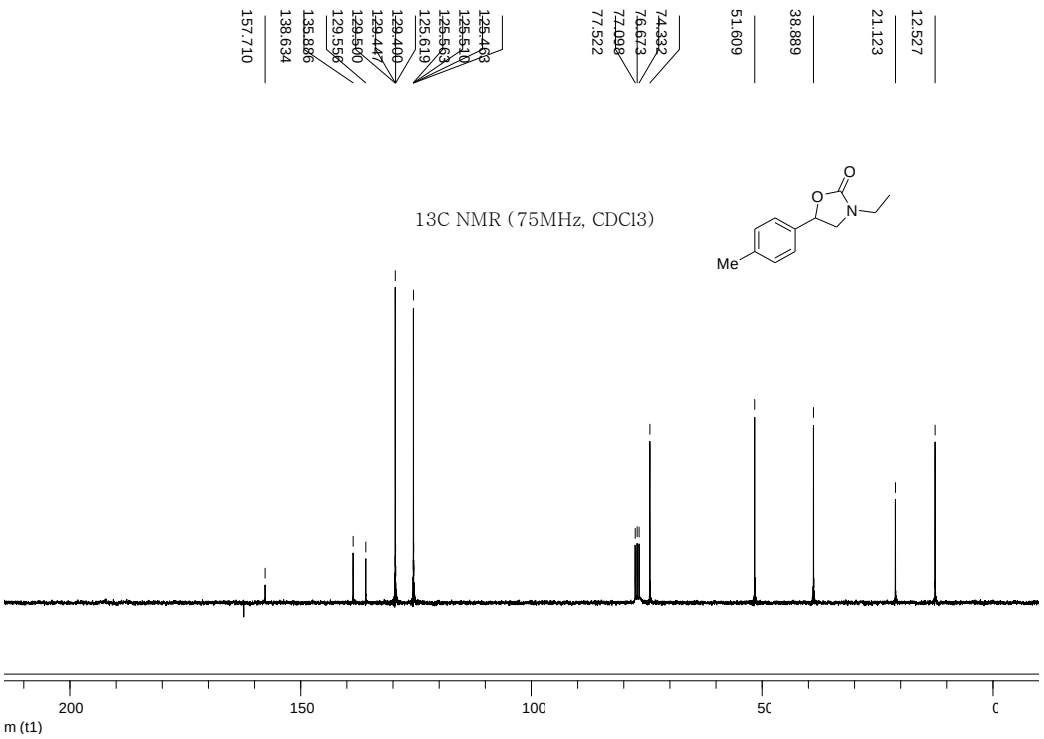

7.445
7.429
7.410
7.405
7.387
7.325
7.308
7.273
4.841
4.819
4.801
4.646
4.624
4.602
4.126
4.106
4.086
3.572
3.554
3.536
3.518
3.500
3.482
2.883
2.866
2.848
2.830
2.813
2.795
1.072
1.054
1.036
0.000000
O
Et
N
O
Ph
1H NMR (400 MHz, CDCl3)
0.75
1.00
0.98
0.98
2.01
1.05
2.97

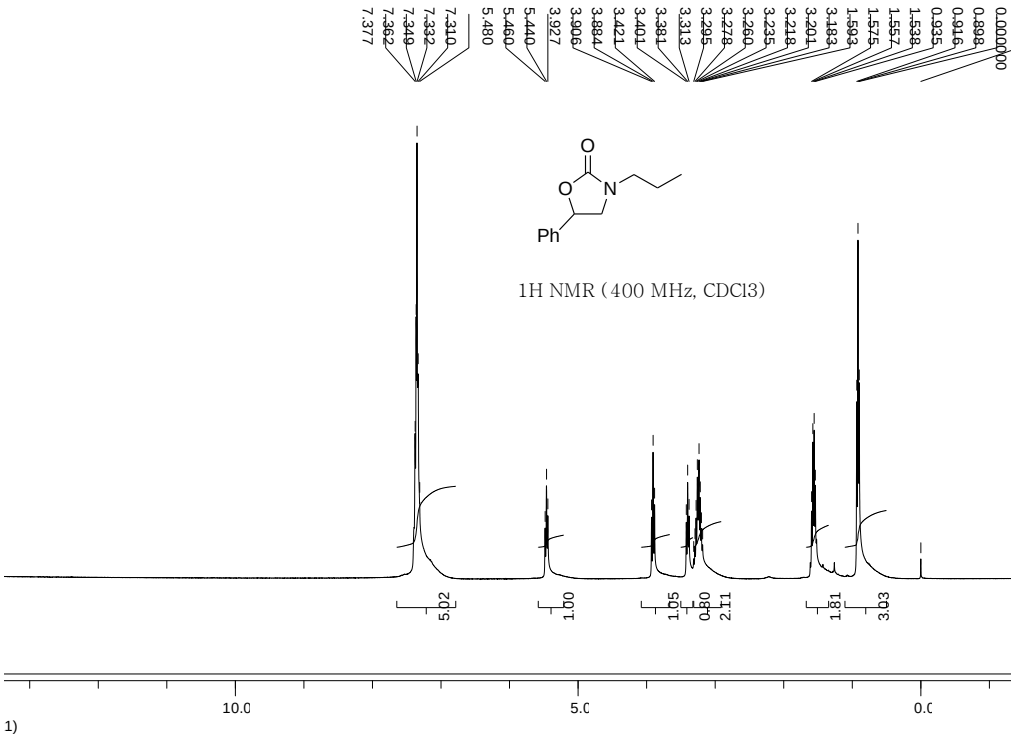

158.085
137.884
129.249
129.034
126.998
77.423
77.000
76.577
69.795
59.356
36.854
12.092
Et
N
O
O
13C NMR(100.6MHz, CDCl3)
200
150
100
50
0
1)

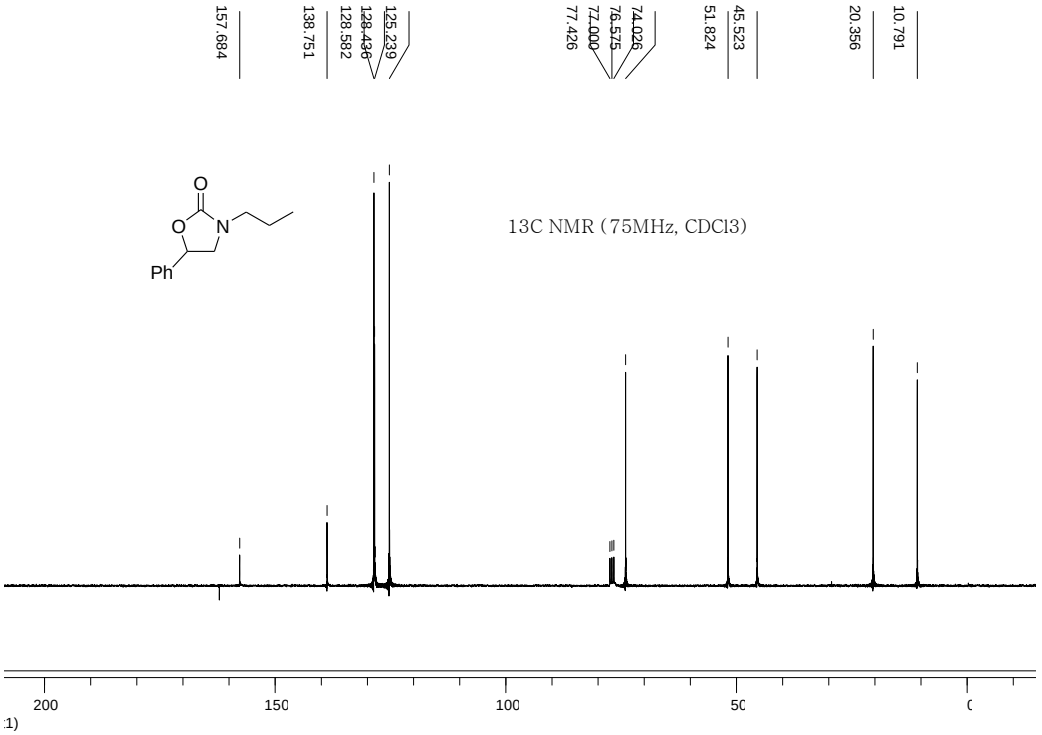

7.390
7.363
7.309
7.282
5.485
5.458
5.432
3.954
3.925
3.896
3.461
3.438
3.414
3.387
3.361
3.337
3.313
3.290
3.266
1.201
1.177
1.153
0.00000
Cl
O
O
N
1H NMR (300MHz, CDCl3)
4.16
0.90
1.00
3.18
3.24
15.0
10.0
5.0
0.0
1)

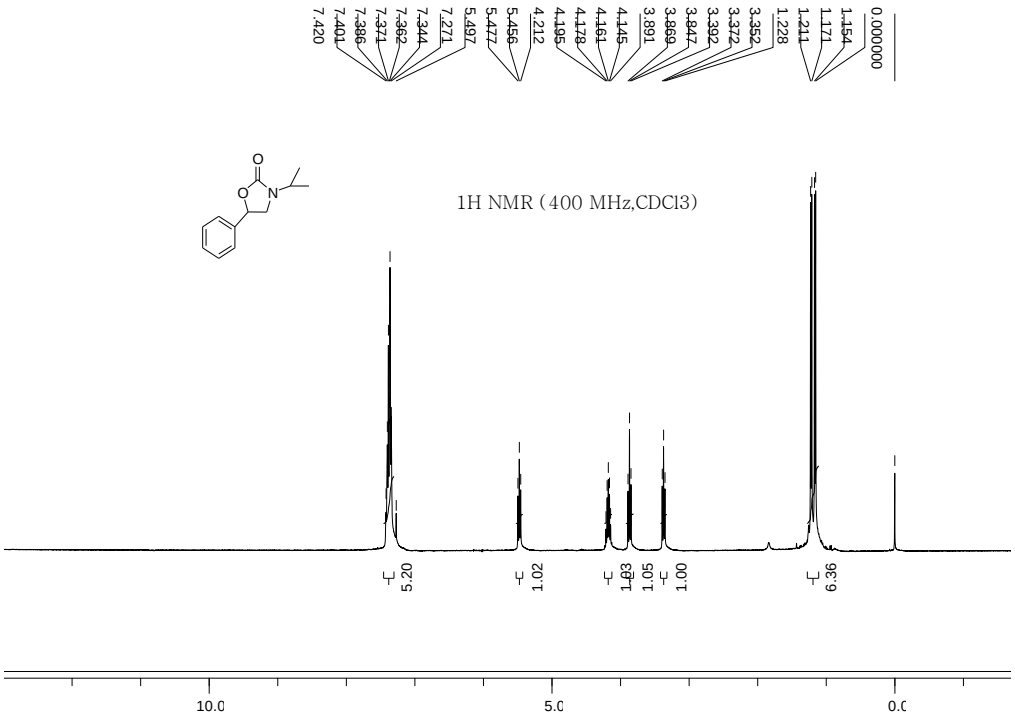

157.320
137.399
134.632
129.066
126.963
77.424
77.000
76.576
73.529
51.461
38.908
12.464
O
O
N
Cl
13C NMR (75MHz, CDCl3)
200
150
100
50
0
m (t1)

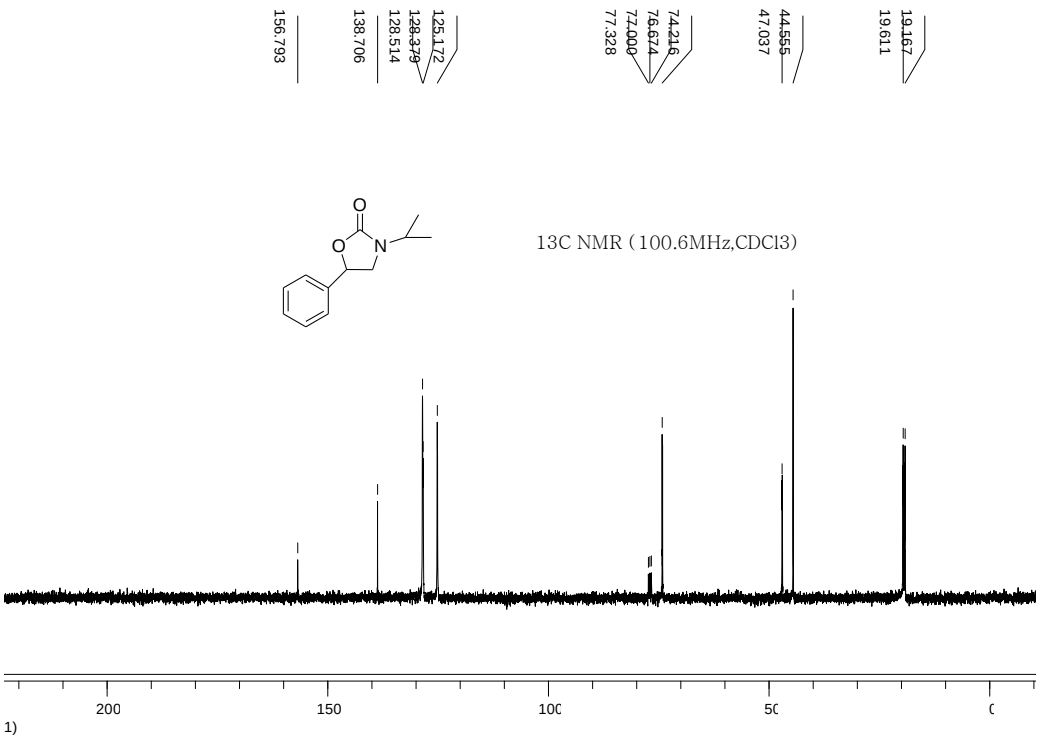

7.272
7.256
7.229
7.205
7.178
5.460
5.433
5.406
3.917
3.888
3.859
3.437
3.409
3.384
3.360
3.355
3.331
3.307
3.284
2.353
1.196
1.171
1.147
0.00000
O
O
N
Me
1H NMR (300 MHz, CDCl3)
2.32
0.91
1.00
0.93
3.05
3.16
15.0
10.0
5.0
0.0
m (t1)

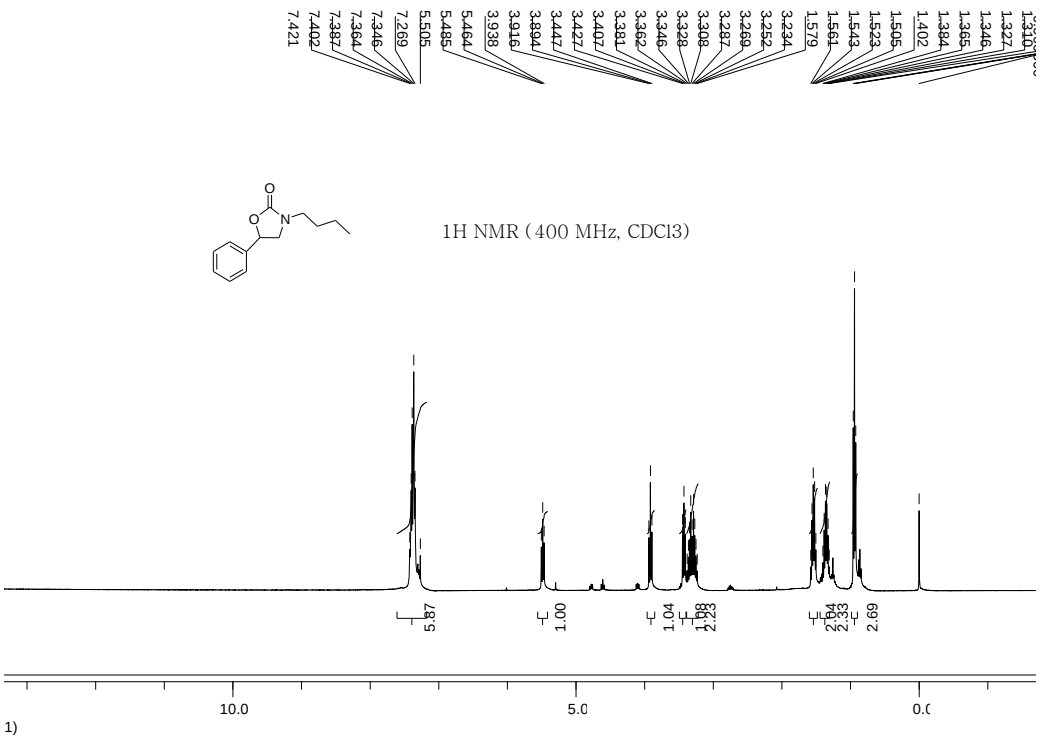

157.710
138.634
135.886
129.556
129.500
129.447
129.400
125.619
125.563
125.510
125.463
77.522
77.098
76.673
74.332
51.609
38.889
21.123
12.527
13C NMR (75MHz, CDCl3)
O
O
N
Me
200
150
100
50
0
m (t1)

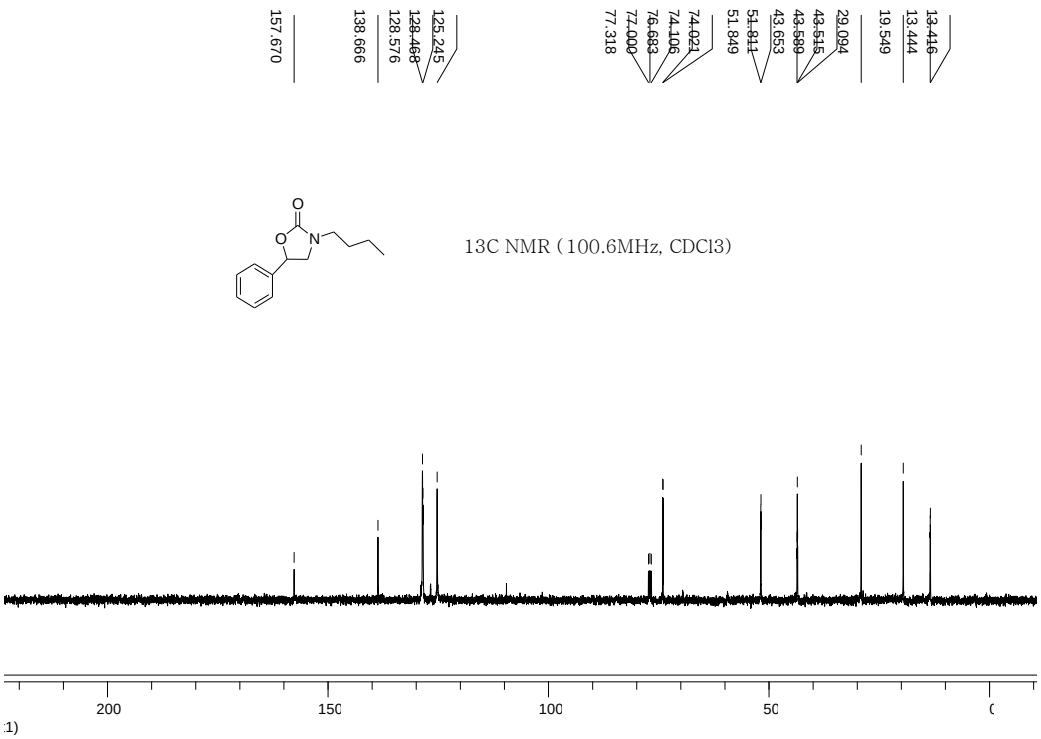

7.377
7.362
7.349
7.332
7.310
5.480
5.460
5.440
3.927
3.906
3.884
3.421
3.401
3.381
3.313
3.295
3.278
3.260
3.235
3.218
3.201
3.183
1.593
1.575
1.557
1.538
0.935
0.916
0.898
0.000000
O
O
N
Ph
1H NMR (400 MHz, CDCl3)
2.05
1.00
1.95
0.80
2.11
1.81
3.03
10.0
5.0
0.0
1)

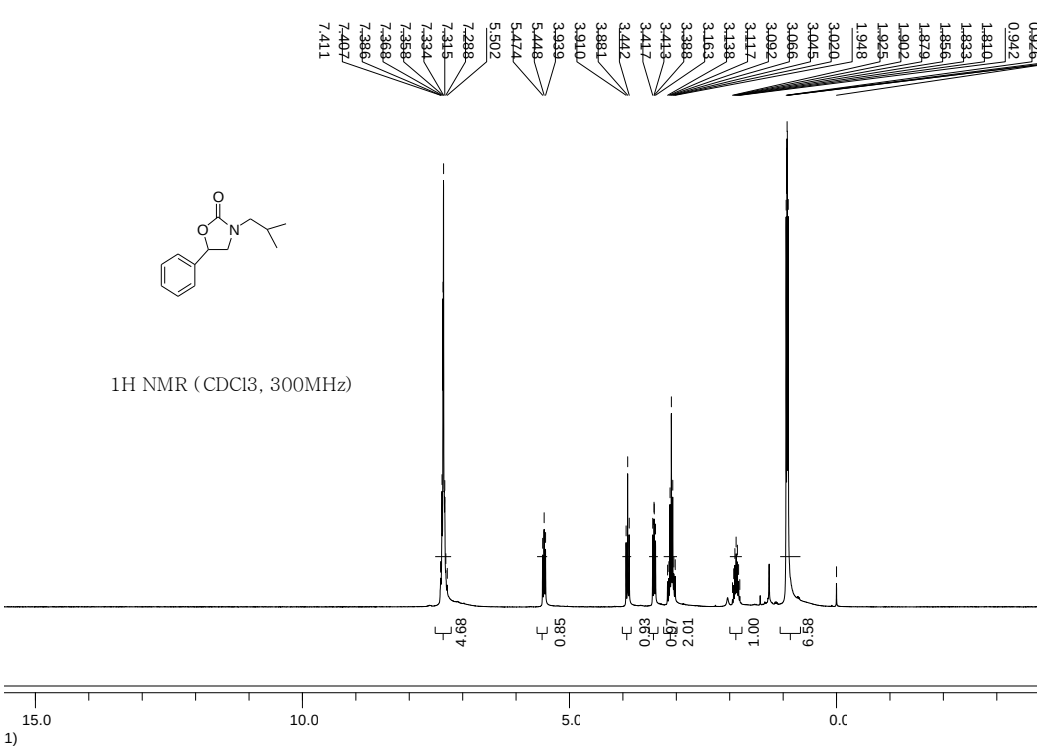

157.684
138.751
128.582
128.436
125.239
77.426
77.000
76.575
74.026
51.824
45.523
20.356
10.791
O
O
N
Ph
13C NMR (75MHz, CDCl3)
200
150
100
50
0

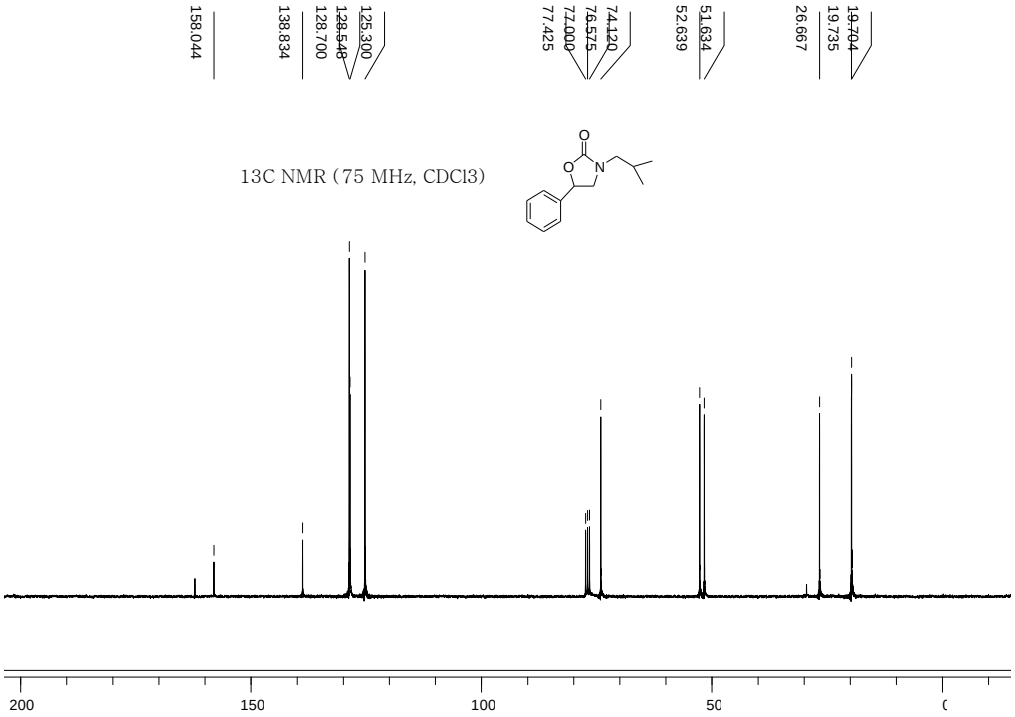

7.420
7.401
7.386
7.371
7.362
7.344
7.271
5.497
5.477
5.456
4.212
4.195
4.178
4.161
4.145
3.891
3.869
3.847
3.392
3.372
3.352
1.228
1.211
1.171
1.154
0.000000
O
O
N
1H NMR (400 MHz,CDCl3)
5.20
1.02
1.89
1.50
1.00
6.96
10.0
5.0
0.0

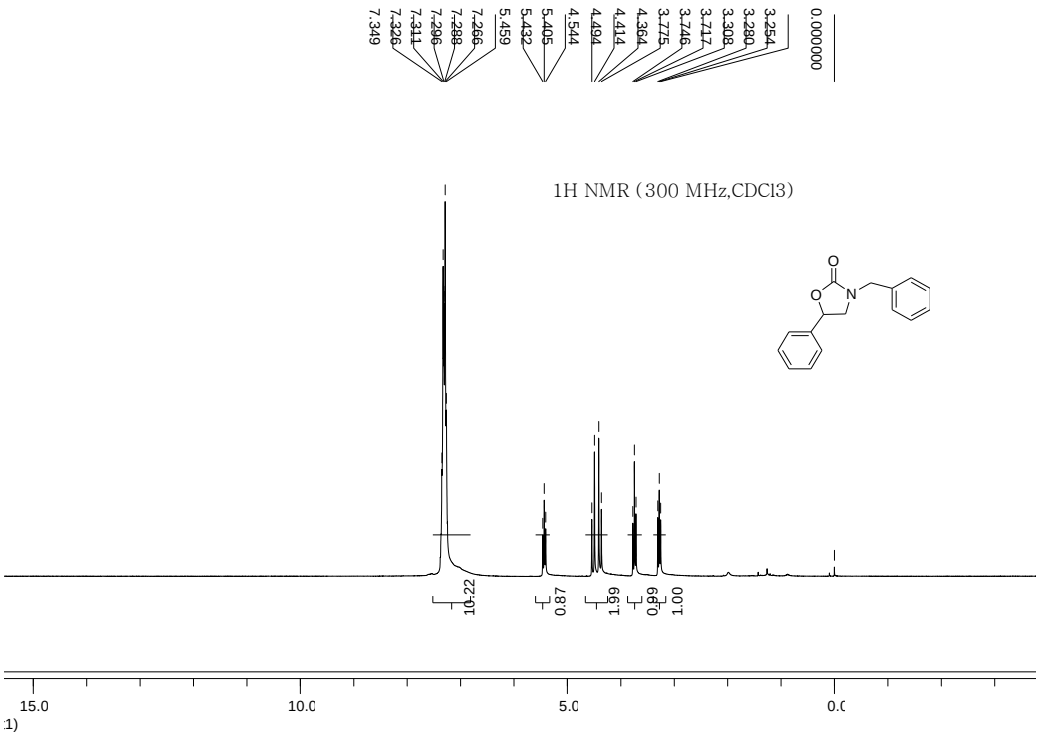

156.793
138.706
128.514
128.379
125.172
77.328
77.000
76.674
74.216
47.037
44.555
19.611
19.167
13C NMR (100.6MHz,CDCl3)
200
150
100
50
1)

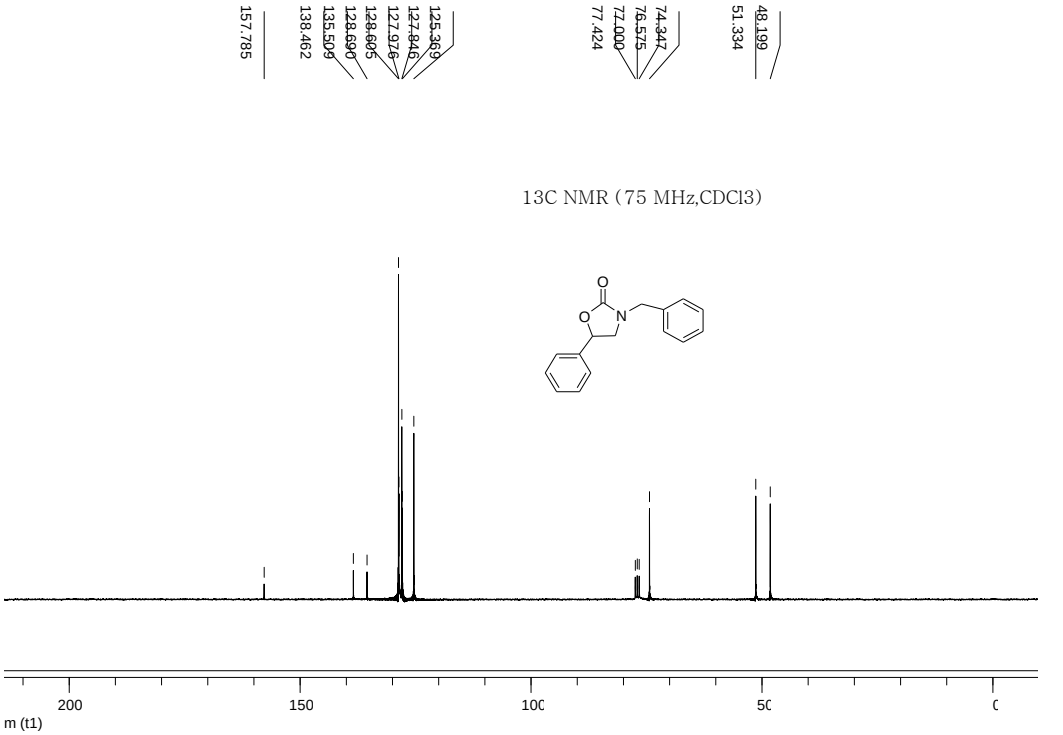

7.421
7.402
7.387
7.364
7.346
7.269
5.505
5.485
5.464
3.938
3.916
3.894
3.447
3.427
3.407
3.381
3.362
3.346
3.328
3.308
3.287
3.269
3.252
3.234
1.579
1.561
1.543
1.523
1.505
1.402
1.384
1.365
1.346
1.327
5.87
1.00
1.04
1.08
2.13
2.04
2.33
2.69
1H NMR (400 MHz, CDCl3)
10.0
5.0
1)

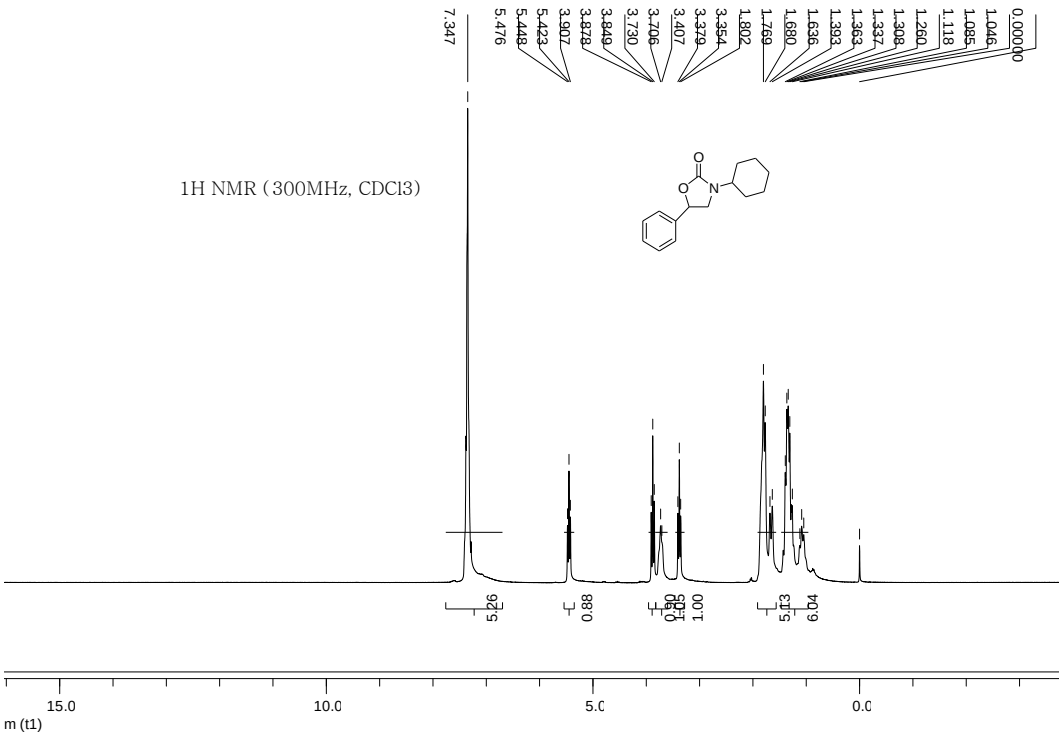

157.670
138.666
128.576
128.468
125.245
77.318
77.000
76.683
74.106
74.021
51.849
51.811
43.653
43.599
43.516
29.094
19.549
13.444
13.416
13C NMR (100.6MHz, CDCl3)
200
150
100
50

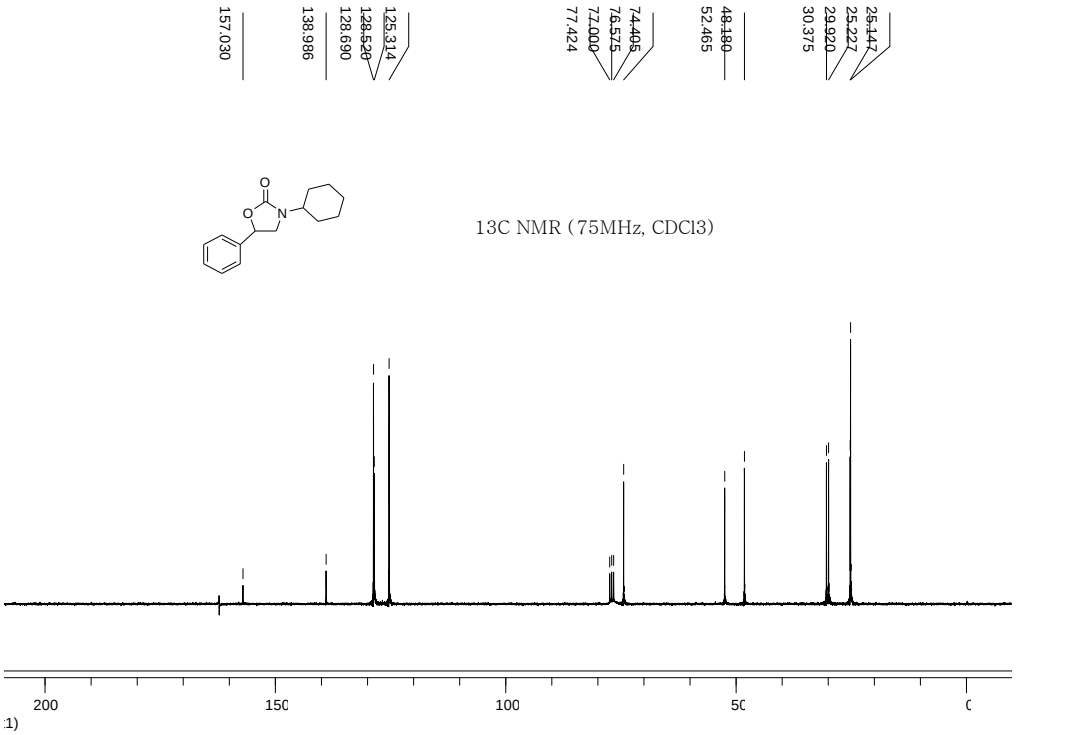

7.411
7.407
7.386
7.368
7.358
7.334
7.315
7.288
5.502
5.474
5.448
3.939
3.910
3.881
3.442
3.417
3.413
3.388
3.163
3.138
3.117
3.092
3.066
3.045
3.020
1.948
1.925
1.902
1.879
1.856
1.833
1.810
0.942
1H NMR (CDCl3, 300MHz)
4.68
0.85
3.03
7.67
10.72
1.00
5.89
15.0
10.0
5.0
0.0

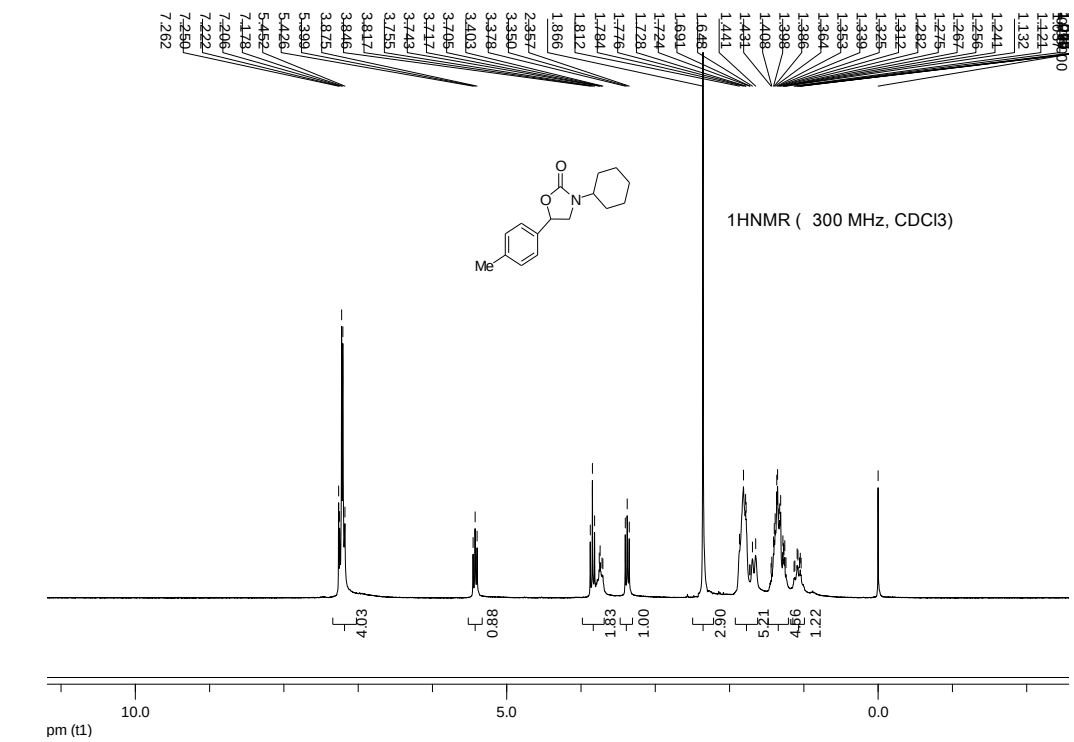

158.044
138.834
128.700
128.548
125.300
77.425
77.000
76.575
74.120
52.639
51.634
26.667
19.735
19.704
13C NMR (75 MHz, CDCl3)
O
O
N
200
150
100
50
0

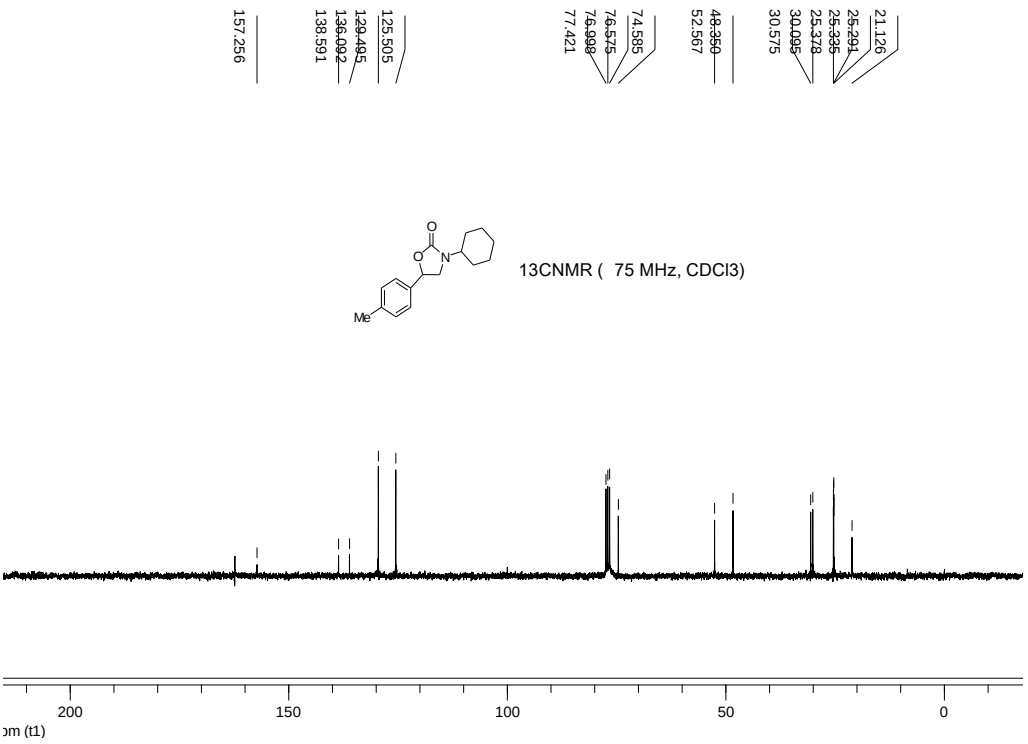

7.349
7.326
7.311
7.296
7.288
7.266
5.459
5.432
5.405
4.544
4.494
4.414
4.364
3.775
3.746
3.717
3.308
3.280
3.254
0.000000
1H NMR (300 MHz,CDCl3)
O
O
N
10.22
0.87
1.96
0.99
1.00
15.0
10.0
5.0
0.0

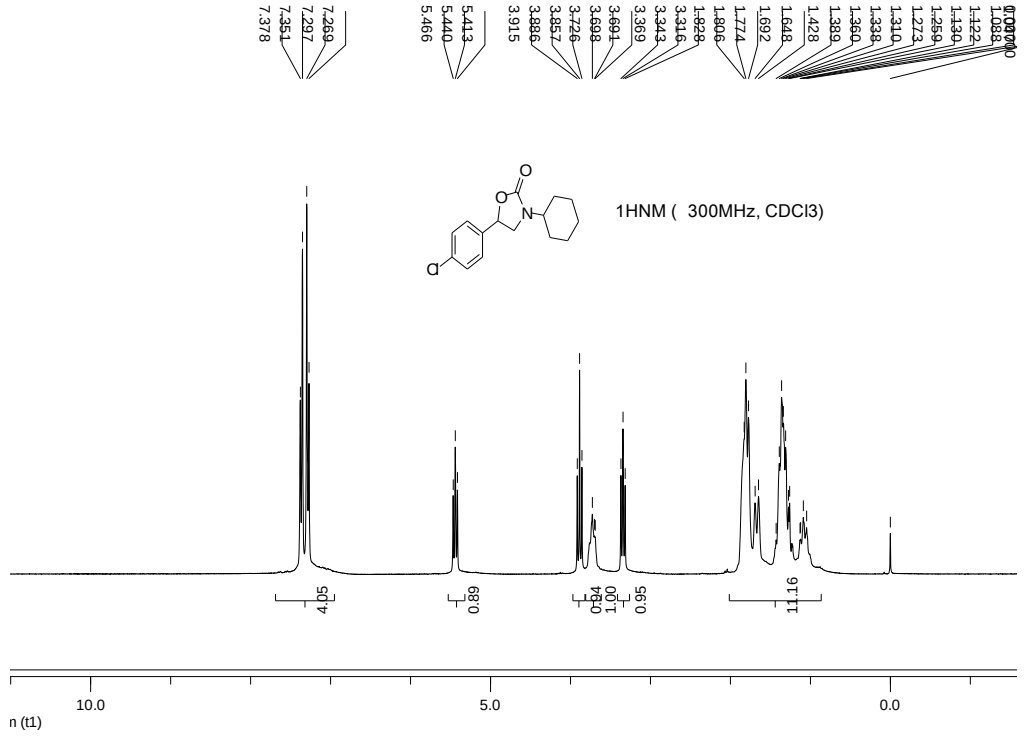

157.785
138.462
135.509
128.690
128.605
127.976
127.846
125.369
77.424
77.000
76.575
74.347
51.334
48.199
13C NMR (75 MHz,CDCl3)
O
O
N
200
150
100
50
0
m (t1)

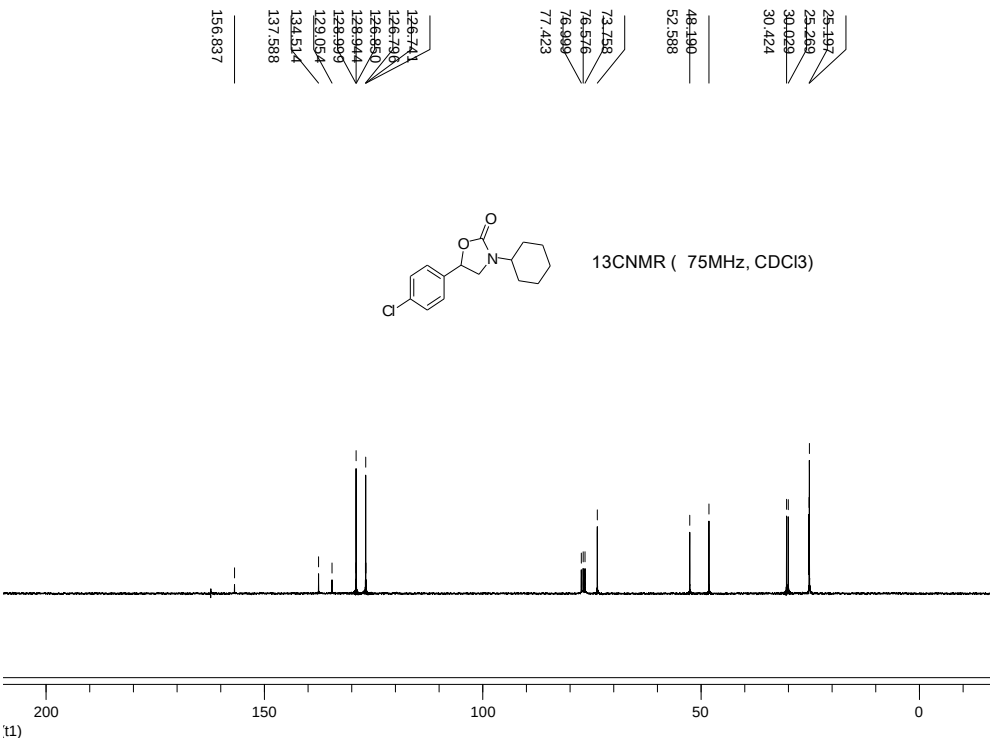

7.347
5.476
5.448
5.423
3.907
3.878
3.849
3.730
3.706
3.407
3.379
3.354
1.802
1.769
1.680
1.636
1.393
1.363
1.337
1.308
1.260
1.118
1.085
1.046
0.00000
1H NMR (300MHz, CDCl3)
O
O
N
5.26
0.88
1.00
0.90
0.85
1.13
6.04
15.0
10.0
5.0
0.0
m (t1)


157.030
138.986
128.690
128.520
125.314
77.424
77.000
76.575
74.495
52.465
48.180
30.375
29.920
25.227
25.147
13C NMR (75MHz, CDCl3)
200
150
100
50
0


7.262
7.250
7.222
7.206
7.178
5.452
5.426
5.399
3.875
3.846
3.817
3.755
3.743
3.717
3.705
3.403
3.378
3.350
2.357
1.866
1.812
1.784
1.776
1.728
1.724
1.691
1.648
1.441
1.431
1.408
1.398
1.386
1.364
1.353
1.339
1.325
1.312
1.282
1.275
1.267
1.256
1.241
1.132
1.121
Me
1HNMR (300 MHz, CDCl3)
4.03
0.88
1.83
1.00
2.90
5.21
4.56
1.22
10.0
5.0
0.0
pm (t1)


157.256
138.591
136.092
129.495
125.505
77.421
76.998
76.575
74.585
52.567
48.360
30.575
30.095
25.378
25.335
25.291
21.126
Me
13CNMR (75 MHz, CDCl3)
200
150
100
50
0
ɔm (t1)


7.378
7.351
7.297
7.269
5.466
5.440
5.413
3.915
3.886
3.857
3.726
3.698
3.691
3.369
3.343
3.316
1.828
1.806
1.774
1.692
1.648
1.428
1.389
1.360
1.338
1.310
1.273
1.259
1.130
1.122
1.088
Cl
1HNM (300MHz, CDCl3)
4.05
0.89
1.00
0.95
1.16
10.0
5.0
0.0
n (t1)


156.837
137.588
134.514
129.054
128.999
128.944
126.850
126.798
126.741
77.423
76.999
76.576
73.758
52.588
48.190
30.424
30.029
25.269
25.197
O
O
N
Cl
13CNMR (75MHz, CDCl3)
200
150
100
50
0
f1)

12. The ^{1}H NMR charts of dimer of 1a