Supporting Information

Highly Stereoselective Cyclopropanation of Diazo Weinreb Amides Catalyzed by Chiral Ru(II)-*Amm*-Pheox Complexes

Soda Chanthamath,* Hamada S. A. Mandour, Tong Thi Minh Thu, Kazutaka Shibatomi and Seiji Iwasa*

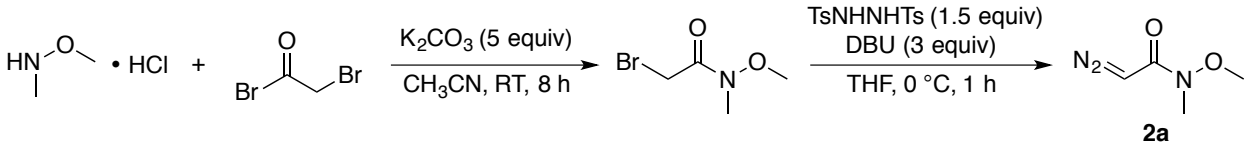
Department of Environmental and Life Sciences, Toyohashi University of Technology, 1-1 Tempaku-cho, Toyohashi, Aichi 441-8580, JAPAN

CONTENTS:

General: All reactions were performed under an atmosphere of argon unless otherwise noted. Dichloromethane (CH_2Cl_2) was purchased from Kanto Chemical Co., Inc.. Acetonitrile was purchased from Wako Pure Chemical Industries, Ltd.. All reactions were monitored by thin layer chromatography (TLC), glass plates pre-coated with silica gel Merck KGaA 60 F_{254}, layer thickness 0.2 mm. All the starting materials are commercially available and were used after purification. The products were visualized by irradiation with UV light or by treatment with a solution of phosphomolybdic acid or by treatment with a solution of *p*-anisaldehyde. Flash column chromatography was performed using silica gel (Merck, Art. No.7734). ^{1}H NMR (500 MHz, 400 MHz) and ^{13}C NMR (500 MHz, 400 MHz) spectra were recorded on JEOL JNM-ECX500, JEOL JNM-ECS400 spectrometer. Chemical shifts are reported as δ values (ppm) relative to $CDCl_3$ (7.26 ppm). Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Optical rotations were performed with a JASCO P-1030 polarimeter at the sodium D line (1.0 ml sample cell). DART mass (positive mode) analyses were performed on a LC-TOF JMS-T100LP.

1. Synthesis of various diazo Weinreb amides

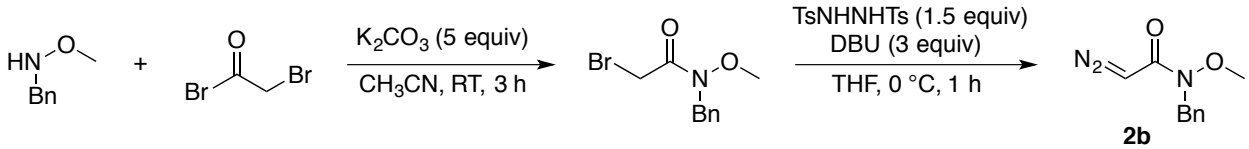
N-Methoxy-*N*-methyldiazoacetamide (MMD) (2a)



2a

According to Fukuyama method,[1] to a solution of *N,O*-dimethylhydroxylamine hydrochloride (100.0 mg, 1 mmol) and potassium carbonate (708.3 mg, 5 mmol) in acetonitrile, bromoacetyl bromide (88.8 µL, 1 mmol) was added drop wise with stirring at room temperature. The reaction mixture was stirred for 8 h. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and extracted with water and methylene chloride. The organic layer was dried over Na_2SO_4, and concentrated. The residue was dissolved in THF and *N,N*-ditosylhydrazine (TsNHNHTs) (520.2 mg, 1.5 mmol) was added then DBU (456 µL, 3 mmol) was added drop wise at 0 °C. The reaction mixture was stirred until the reaction was finished. The progress of the reaction was monitored by TLC. After the reaction was completed within 1 h, the reaction was quenched using saturated soln. of $NaHCO_3$ then reaction mixture was extracted with water and diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography with a mixture of (*n*-Hexane/EtOAc) (2/1 (v/v)) to give the corresponding diazo Weinreb amide **2a** (49% yield) as yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.15 (s, 3H), 3.64 (s, 3H), 5.32 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.36, 46.40, 61.56, 168.39 ppm. IR (neat) ν 2359, 2341, 2108, 1623 cm^{-1}. HRMS (DART) calcd for $C_4H_7N_3O_2$ $[M+NH_4]^+$: 147.0882 found: 147.0885.

N-Benzyl-*N*-methoxydiazoacetamide (BMD) (2b)

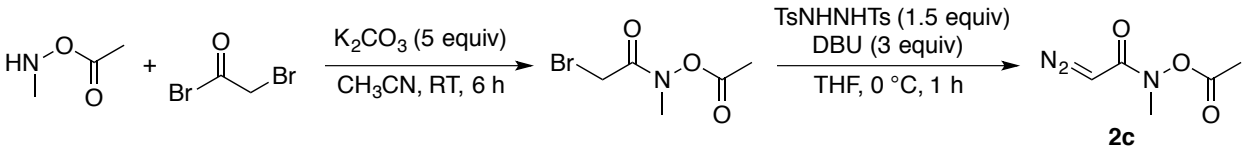


2b

According to Fukuyama method,[1] in a 50 mL two nick flask a mixture of *N*-benzyl-*O*-methylhydroxylamine (66 mg, 0.48 mmol) and K_2CO_3 (332.5 mg, 2.4 mmol) were dissolved in 15 mL of dry CH_3CN. Then from the side arm of the flask bromoacetyl bromide (41.5 µL, 0.48 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. The progress of the reaction was monitored by TLC and ^{1}H NMR. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and extracted with water and methylene chloride. The organic layer was dried

over Na_2SO_4, and concentrated. The residue was dissolved in THF and *N,N*-ditosylhydrazine (TsNHNHTs) (245 mg, 0.7 mmol) was added then DBU (215 µL, 1.44 mmol) was added drop wise at 0 °C. The reaction mixture was stirred until the reaction was finished. The progress of the reaction was monitored by TLC. After the reaction was completed within 1 h, the reaction was quenched using saturated soln. of $NaHCO_3$ then reaction mixture was extracted with water and diethyl ether. The organic layer was dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography with a mixture of (*n*-Hexane/EtOAc) (9/1 (v/v)) to give the corresponding diazo Weinreb amide **2b** (44% yield) as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (s, 3H), 4.73 (s, 2H), 5.32 (s, 1H), 7.10-7.12 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.75, 50.43, 62.58, 127.82, 128.49, 128.64, 136.47, 168.49 ppm. IR (neat) ν 2395, 2341, 2108, 1622 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{11}N_3O_2$ $[M+NH_4]^+$: 223.1195 found: 223.1192.

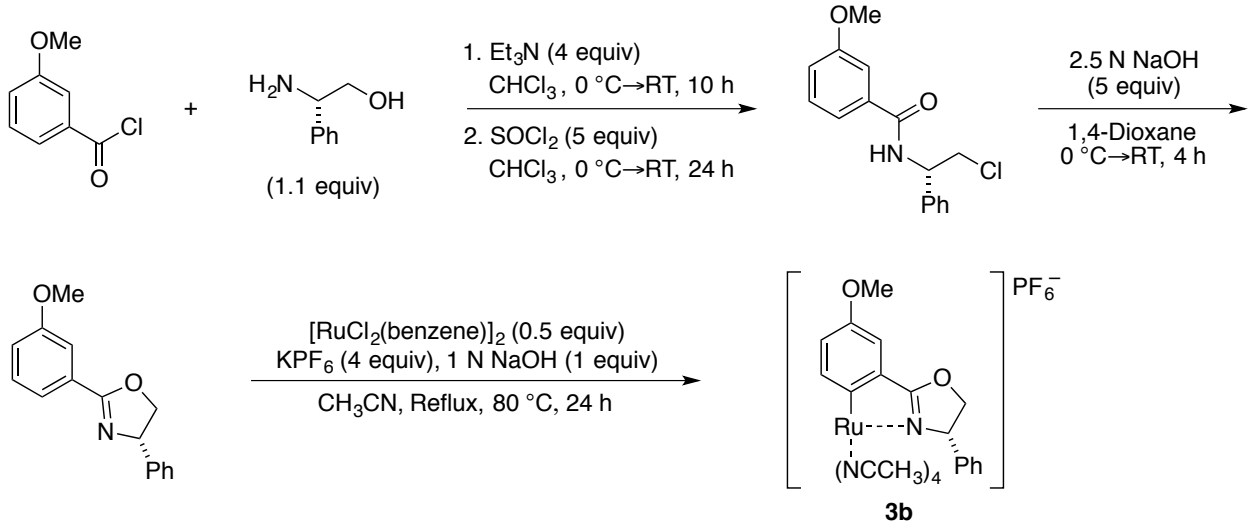
_N_-Acetoxy-_N_-methyldiazoacetamide (AMD) (2c)



According to Fukuyama method,[1] to a solution of *O*-acetyl-*N*-methyl hydroxylamine (100 mg, 0.79 mmol) and potassium carbonate (550 mg, 3.94 mmol) in 20 mL of dry acetonitrile then bromoacetyl bromide (47 µL, 0.79 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 6 h. The reaction was monitored by TLC and ^{1}H NMR. After the reaction was completed, the reaction mixture was evaporated and extracted with water and dichloromethane. The organic layer was dried over Na_2SO_4, and concentrated. Then the residue was dissolved in THF and ditosylhydrazine (TsNHNHTs) (403 mg, 1.2 mmol) was added. After that DBU (354 µL, 2.38 mmol) was added drop wise at 0 °C. The reaction mixture was stirred until the reaction was finished. The progress of the reaction was monitored by TLC. After the reaction was completed within 1 h, saturated solution of $NaHCO_3$ was added to quench the reaction and the mixture was extracted with water and diethyl ether. The organic layer was dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography with a mixture of (*n*-Hexane/EtOAc) (3/1 (v/v)) to give the corresponding diazo Weinreb amide **2c** (46% yield) as yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (s, 3H), 3.26 (s, 3H), 4.99 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.65, 36.47, 46.99, 167.760, 168.02 ppm. IR (neat) ν 2359, 2341, 2113, 1796, 1682,1643 cm^{-1}. HRMS (DART) calcd for $C_5H_7N_3O_3$ $[M+NH_4]^+$: 175.0831 found: 175.0833.

2. Synthesis of Ru(II)-Pheox complexes

Ru(II)-Pheox (3b)



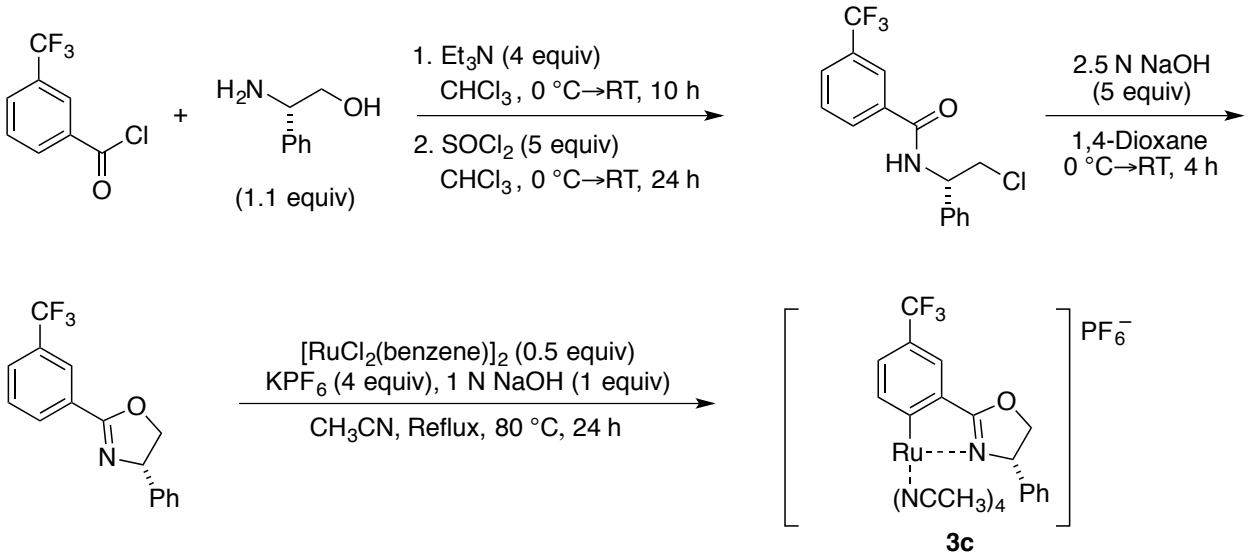
3b

To a mixture of (*S*)-(+)-2-phenylglycinol (300.0 mg, 2.18 mmol) and Et_3N (1.2 mL, 8.72 mmol) in $CHCl_3$ (7 mL), a solution of 3-methoxybenzoyl chloride (339.0 mg, 1.98 mmol) in $CHCl_3$ (4 mL) was added dropwise with magnetic stirring at 0 °C. After the stirring for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (12 mL) and treated with $SOCl_2$ (0.7 mL, 9.94 mmol) at 0 °C. After stirring for 24 h at room temperature, the solvent and excess $SOCl_2$ were removed under reduced pressure. Sat. $NaHCO_3$ (aq.) (30 mL) was added to the residue with stirring for 5 min. The organic product was extracted with CH_2Cl_2 (3 × 25 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. By using a sonicator, the solid residue was dissolved in 1,4-dioxane (10 mL) and 2.5 N NaOH (aq.) (316.8 mg, 7.9 mmol) was added slowly at 0 °C, then the reaction mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum, followed by addition of water (25 mL) and CH_2Cl_2 (3 × 25 mL) for extraction. The solvent was evaporated under vacuum to afford (*S*)-2-(3-methoxyphenyl)-4-phenyl-4,5-dihydrooxazole ligand (87% yield). $[\alpha]^{28}_D = -34.6$ (c 1.00, $CHCl_3$), ^{1}H NMR (125 MHz, $CDCl_3$) δ 3.84 (s, 3H), 4.26 (t, J = 16.8 Hz, 1H), 4.78 (t, J = 18.7 Hz, 1H) 5.38 (t, J = 17.9 Hz, 1H), 7.06 (dd, J = 1.91, 10.3 Hz, 1H), 7.25-7.37 (m, 6H), 7.62 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.54, 70.25, 75.30, 112.87, 118.49, 121.06, 126,88, 127.77, 128.89, 129.57, 142.45, 159.64, 164.79 ppm. IR (neat) 3019, 2963, 1603, 1478 cm^{-1}, HRMS (DART) calcd for $C_{16}H_{15}NO_2$ $[M+H]^+$: 254.1181 found: 254.1186.

A two necked round bottom flask (100 mL) fitted with a magnetic stirring bar and a reflux condenser was charged with (*S*)-2-(3-methoxyphenyl)-4-phenyl-4,5-dihydrooxazole (300.0 mg, 1.18 mmol), $[RuCl_2(benzene)]_2$ (2.59 mg, 0.59 mmol), and KPF_6 (871.7 mg, 4.7 mmol). The reaction flask was

evacuated and backfilled with argon. Through the side arm CH_3CN (20 mL, degassed) and NaOH (aq.) (47.2 mg, 1.18 mmol) were injected. The suspended reaction mixture was refluxed for 24 h at 80 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_3CN/CH_2Cl_2 (1/10 (v/v)) to give the desired complex **3b** (67% yield) as a green solid. ^{1}H NMR (500 MHz, CD_3CN) δ 1.99 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H) 2.40 (s, 3H), 3.76 (s, 3H, CH_3CN), 4.49 (t, J = 8.0 Hz, 1H), 5.09 (t, J = 8.0 Hz, 2H), 6.84 (d, J = 10.7 Hz, 1H), 7.09 (d, J = 2.7 Hz, 1H), 7.31-7.41 (m, 5H), 7.70 (d, J =7.6 Hz, 1H). ^{13}C NMR (125 MHz, CD_3CN) δ 0.88, 3.04, 3.13, 3.38, 54.98, 68.22, 78.05, 110.42, 121.27, 121.51, 122.49, 128.09, 128.13, 134.44, 138.60, 141.47, 155.31, 174.07, 174.89 ppm.

Ru(II)-Pheox (3c)



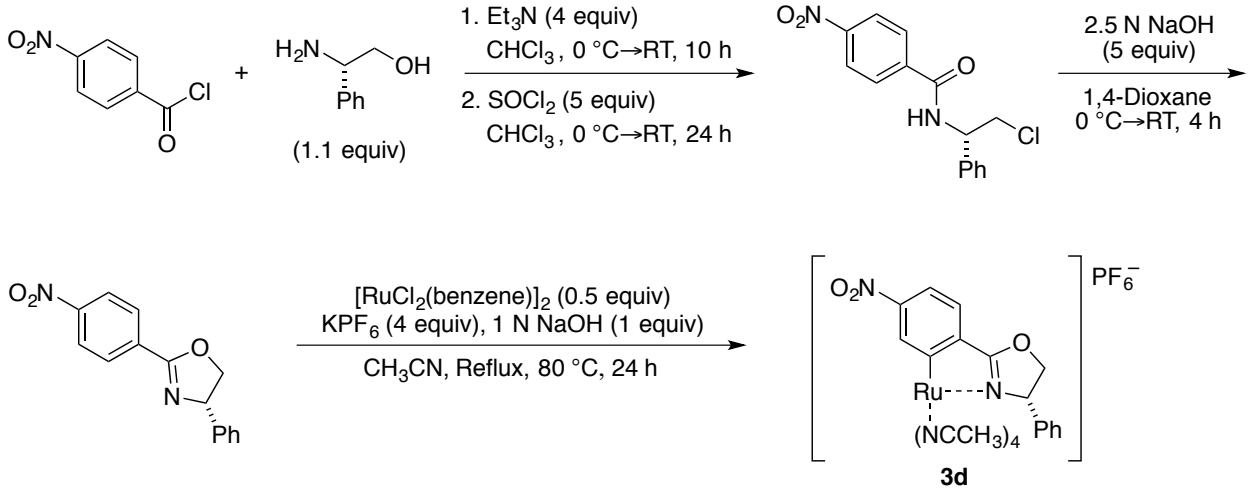
3c

To a mixture of (*S*)-(+)-2-phenylglycinol (244.0 mg, 1.78 mmo) and Et_3N (0.9 mL, 6.46 mmol) in $CHCl_3$ (7 mL), a solution of 3-(trifluoromethyl)benzoyl chloride (333.0 mg, 1.6 mmol) in $CHCl_3$ (4 mL) was added drop wise with magnetic stirring at 0 °C. After the stirring for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (12.0 mL) and treated with $SOCl_2$ (0.58 mL, 8 mmol) at 0 °C. After stirring for 24 h at room temperature, the solvent and excess $SOCl_2$ were removed under reduced pressure. Sat. $NaHCO_3$ (aq.) (30 mL) was added to the residue with stirring for 5 min. the organic product was extracted with CH_2Cl_2 (3 × 25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. By using a sonicator, the solid residue was dissolved in 1,4-dioxane (10 mL) and 2.5 N NaOH (aq.) (256.0 mg, 6.4 mmol) was added slowly at 0 °C, then the reaction mixture was stirred for 4 h at room temperature. The solvent was removed under

vacuum, followed by addition of water (25 mL) and CH_2Cl_2 (3 x 25 mL) for extraction. The solvent was evaporated under vacuum to afford (*S*)-4-phenyl-2-(3-(trifluoromethyl)phenyl)-4,5-dihydrooxazole ligand (59% yield). $[\alpha]^{28}_D = -43.6$ (c 1.00, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 (t, *J* = 16.8 Hz, 1H), 4.83 (t, *J* = 18.7 Hz, 1H), 5.42 (t, *J* = 18.7 Hz, 1H), 7.29-7.39 (m, 5H), 7.56 (t, *J* = 15.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 8.35 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.33, 75.23, 125.54, 126.83, 127.92, 128.15, 128.55, 128.96, 129.11, 130.97, 131.23, 131.76, 142.00, 163.58 ppm. IR (neat) 3072, 2981, 1674 cm^{-1}. HRMS (DART) calcd for $C_{15}H_{12}N_2O_3$ $[M+H]^+$: 292.0949 found: 292.0943.

A two necked round bottom flask (100.0 mL) fitted with a magnetic stirring bar and a reflux condenser was charged with the (*S*)-4-phenyl-2-(3-(trifluoromethyl)phenyl)-4,5-dihydrooxazole ligand (200 mg, 0.67 mmol), $[RuCl_2(benzene)]_2$ (171.7 mg, 0.34 mmol), and KPF_6 (493.1 mg, 2.68 mmol). The reaction flask was evacuated and backfilled with argon. Through the side arm CH_3CN (20 mL, degassed) and NaOH (aq.) (26.8 mg, 0.67 mmol) were injected. The suspended reaction mixture was refluxed for 24 h at 80 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_3CN/CH_2Cl_2 (1/20 (v/v)) to give the desired complex **3c** (43% yield) as a faint green solid. ^{1}H NMR (500 MHz, CD_3CN) δ 1.93 (s, 3H), 1.99 (s, 3H), 2.11 (s, 3H), 2.42 (s, 3H), 4.53 (t, *J* = 5.4 Hz, 1H), 5.12 (d, *J* = 8.5 Hz, 2H), 7.34-7.42 (m, 6H), 7.65 (d, *J* = 5.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, CD_3CN) δ 0.86, 2.82, 2.98, 3.32, 68.24, 78.38, 121.72, 121.80, 122.04, 124.10, 124.49, 128.16, 128.30, 135,58, 139.15, 141.03, 174.27, 197.19 ppm. IR (neat) ν 2964,2293, 1641, 1473 cm^{-1}.

Ru(II)-Pheox (3d)



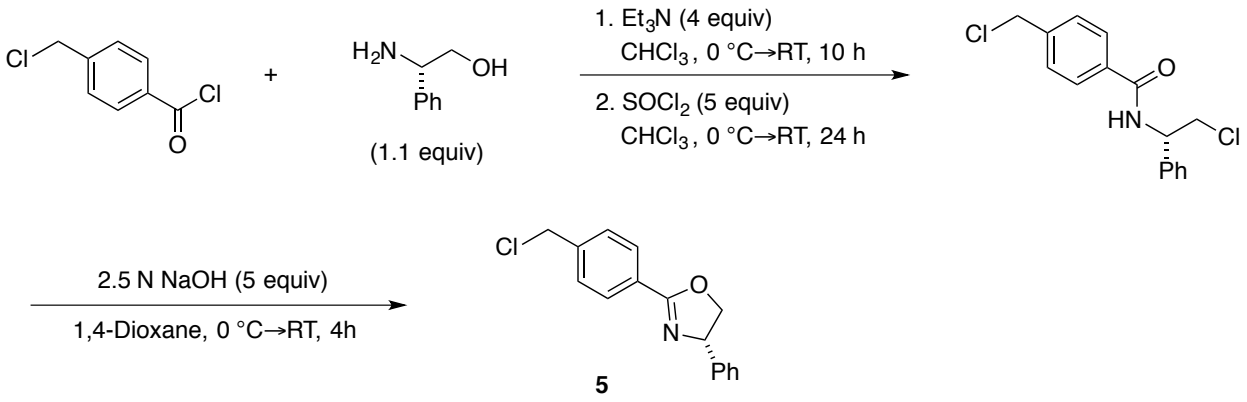
To a mixture of (*S*)-(+)-2-phenylglycinol (244.0 mg, 1.78 mmol) and Et_3N (0.9 mL, 6.4 mmol) in $CHCl_3$ (7 mL), a solution of 4-nitrobenzoyl chloride (296.0 mg, 1.6 mmol) in $CHCl_3$ (4 mL) was added drop

wise with magnetic stirring at 0 °C. After the stirring for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (12 mL) and treated with $SOCl_2$ (0.58 mL, 8 mmol) at 0 °C. After stirring for 24 h at room temperature, the solvent and excess $SOCl_2$ were removed under reduced pressure. Sat. $NaHCO_3$ (aq.) (30 mL) was added to the residue with stirring for 5 min. the organic product was extracted with CH_2Cl_2 (3 × 25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. By using a sonicator, the solid residue was dissolved in 1,4-dioxane (10 mL) and 2.5 N NaOH (aq.) (256 mg, 6.4 mmol) was added slowly at 0 °C, then the reaction mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum, followed by addition of water (25 mL) and CH_2Cl_2 (3 × 25 mL) for extraction. The solvent was evaporated under vacuum to afford (*S*)-2-(4-nitrophenyl)-4-phenyl-4,5-dihydrooxazole ligand (62% yield). $[\alpha]^{27}_D = -72.5$ (c 1.00, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (t, *J* = 15.6 Hz, 1H), 4.85 (t, *J* = 18.7 Hz, 1H) 5.43 (t, *J* = 18.7 Hz, 1H), 7.28-7.38 (m, 5H), 8.19 (d, *J* = 11.0 Hz, 2H), 8.27 (d, *J* = 11.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.48, 75.41, 123.67, 126.80, 128.02, 129.00, 129.60, 133.45, 141.66, 149.72, 163.00 ppm. IR (neat) 3065, 2949, 1631, 1481 cm^{-1}, HRMS (DART) calcd for $C_{15}H_{12}N_2O_3$ $[M+H]^+$: 269.0926 found: 269.0923.

A two necked round bottom flask (100 mL) fitted with a magnetic stirring bar and a reflux condenser was charged with (*S*)-2-(4-nitrophenyl)-4-phenyl-4,5-dihydrooxazole ligand (200.0 mg, 0.75 mmol), $[RuCl_2(benzene)]_2$ (187.6 mg, 0.38 mmol) and KPF_6 (552.0 mg, 3.0 mmol). The reaction flask was evacuated and backfilled with argon. Through the side arm CH_3CN (20 mL, degassed) and NaOH (aq.) (30.0 mg, 0.75 mmol) were injected. The suspended reaction mixture was refluxed for 24 h at 80 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_3CN/CH_2Cl_2 (1/20 (v/v)) to give the desired complex **3d** (86% yield) as a green solid. ^{1}H NMR (500 MHz, CD_3CN) δ 1.93 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H) 2.45 (s, 3H), 4.60 (t, *J* = 26.4 Hz, 1H), 5.17 (d, *J* = 23.7 Hz, 2H), 7.33-7.46 (m, 5H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 10.7 Hz, 1H), 8.55 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (125 MHz, CD_3CN) δ 1.10, 3.00, 3.04, 3.43, 68.52, 78.51, 115.70, 121.89, 122.18, 123.21, 125.80, 128.38, 128.48, 131.40, 140.73, 141.60, 147.81, 174.02, 190.57 ppm. IR (neat) ν 2972,2289, 1664 cm^{-1}.

3. Synthesis of Ru(II)-*Amm*-Pheox complexes

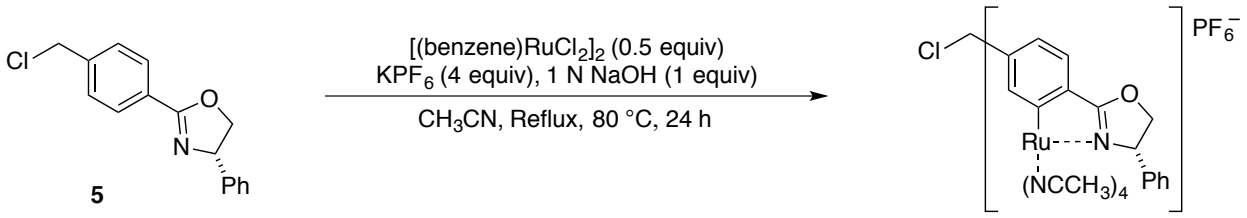
(Chloromethyl)phenyl-Pheox (5)



5

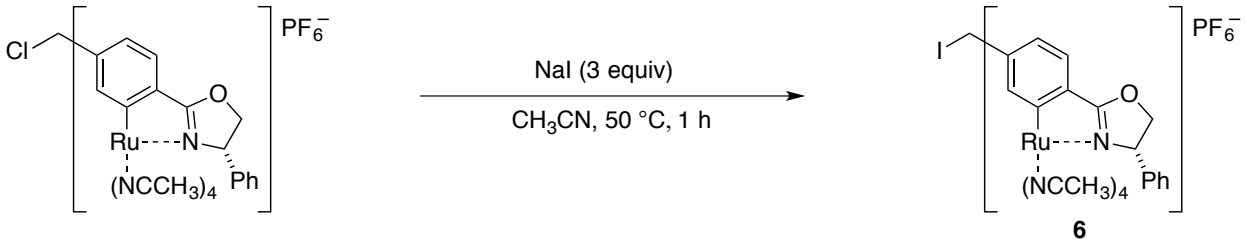
To a mixture of (*S*)-(+)-2-phenylglycinol (301.0 mg, 2.19 mmol) and Et_3N (0.8 mL, 7.96 mmol) in $CHCl_3$ (7.0 mL), a solution of 4-(chloromethyl)benzoyl chloride (376.0 mg, 1.99 mmol) in $CHCl_3$ (4.00 mL) was added dropwise with magnetic stirring at 0 °C. After the stirring for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (12.0 mL) and treated with $SOCl_2$ (1.2 mL, 9.95 mmol) at 0 °C. After stirring for 24 h at room temperature, the solvent and the excess of $SOCl_2$ were removed under reduced pressure. Sat. $NaHCO_3$ (aq.) (30 mL) was added to the residue with stirring for 5 min. the organic product was extracted with CH_2Cl_2 (3 × 25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. By using a sonicator, the solid residue was dissolved in 1,4-dioxane (10 mL) and 2.5 N NaOH (aq.) (398.0 mg, 9.95 mmol) was added slowly at 0 °C, then the reaction mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum, followed by addition of water (25 mL) and CH_2Cl_2 (3 × 25 mL) for extraction. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel (EtOAc/*n*-Hexane) (1/10 (v/v)) to afford (*S*)-2-(4-(chloromethyl)phenyl)-4-phenyl-4,5-dihydrooxazole **5** (86% yield) as a pale yellow solid. R_f = 0.53 (*n*-Hexane/EtOAc) (2/1 (v/v)). $[\alpha]^{24}_D$ = −20.1 (c 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 (t, *J* = 15.7 Hz, 1H), 4.6 (s, 2H), 4.75 (t, *J* = 18.6 Hz, 1H), 5.36 (t, *J* = 17.4 Hz, 1H), 7.31-7.40 (m, 5H), 7.46 (d, *J* = 7.6 Hz, 2H), 8.07 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.73, 70.28, 75.07, 126.88, 127.72, 127.82, 128.70, 128.93, 129.01, 140.93, 142.40, 164.30. IR (neat) 3078, 2915, 1614, 1492 cm^{-1}. HRMS (DART) calcd for $C_{16}H_{14}ClNO$ $[M+H]^+$: 272.0844 found: 272.0847.

Ru(II)-(chloromethyl)phenyl-Pheox



A two necked round bottom flask (100.0 ml) fitted with a magnetic stirring bar and a reflux condenser was charged with a mixture of (*S*)-2-(4-(chloromethyl)phenyl)-4-phenyl-4,5-dihydrooxazole ligand **5** (149 mg, 0.55 mmol), $[RuCl_2(benzene)]_2$ (137 mg, 0.28 mmol), and KPF_6 (412 mg, 2.24 mmol). The reaction flask was evacuated and backfilled with argon. Through the side arm CH_3CN (20 mL, degassed) and NaOH (aq.) (22 mg, 0.55 mmol) was injected. The suspended reaction mixture was refluxed for 24 h at 80 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_3CN/CH_2Cl_2 (1/20 (v/v)) to give the desired complex Ru(II)-(chloromethyl)phenyl-Pheox (96% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.10 (s, 3H), 2.14 (s, 3H) 2.47 (s, 3H), 4.51 (t, *J* = 15.8 Hz, 1H), 4.70 (s, 2H), 5.12 (t, *J* = 18.6 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 7.31-7.43 (m, 5H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.12, 4.02, 4.05, 4.39, 47.52, 67.76, 78.11, 120.43, 120.78, 121.37, 121.88, 125.94, 127.97, 128.34, 134.76, 137.87, 138.22, 141.48, 174.67, 186.67 ppm. IR (neat) ν 2271, 1621, 1455 cm^{-1}.

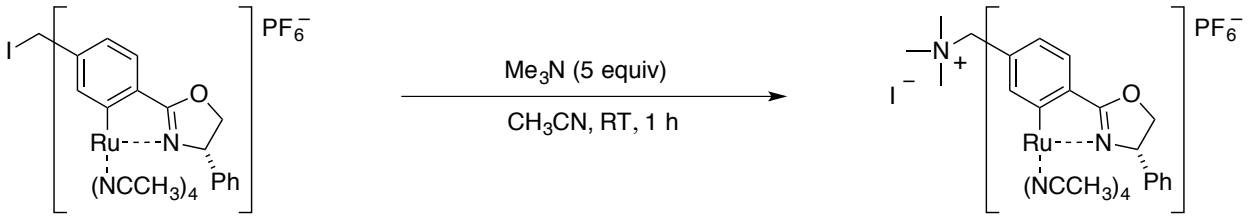
Ru(II)-(iodomethyl)phenyl-Pheox (6)



A mixture of Ru(II)-(chloromethyl)phenyl-Pheox complex (590.0 mg, 0.86 mmol), NaI (376.0 mg, 2.59 mmol) were placed in a two necked flask equipped with a magnetic stirring bar and a reflux condenser. The system was evacuated and backfilled with argon. CH_3CN (dry) (15 mL) was injected. The reaction mixture was refluxed for 1 h at 50 °C. During period of reaction time, the white crystalline salt (NaCl) was formed as a side product. The reaction was monitored by ^{1}H NMR until the conversion was completely finished. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_3CN/CH_2Cl_2 (1/20 (v/v)) to afford Ru(II)-

(iodomethyl)phenyl-Pheox complex **6** (98% yield) as a dark green color. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.44 (s, 3H), 4.49 (t, *J* = 5.4 Hz, 1H), 4.59 (s, 2H), 5.08 (dd, *J* = 6.1 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.30-7.41 (m, 6H), 7.87 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (125 MHz, CD_3CN) δ 1.02, 3.10, 3.51, 7.90, 68.11, 78.13, 121.52, 121.66, 122.71, 125.79, 128.16, 128.40, 134.60, 138.04, 140.28, 141.40, 174.60, 187.62 ppm. IR (neat) ν 2359, 2341, 2271, 1619, cm^{-1}.

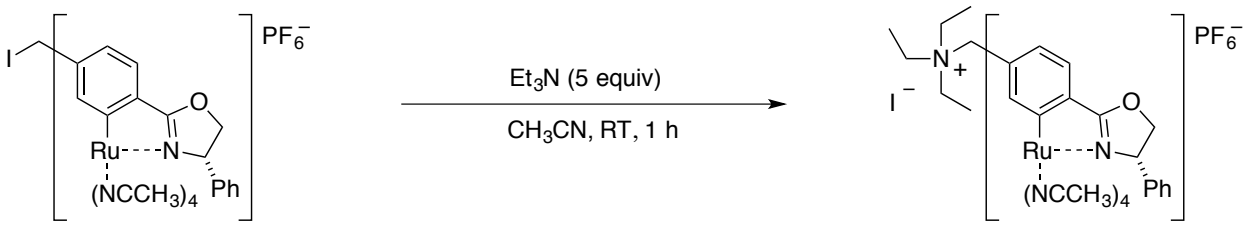
Ru(II)-*Amm*-Pheox (7a)



6 **7a**

Into a schlenktype flask equipped with a magnetic stirring Ru(II)-(iodomethyl)phenyl-Pheox complex **6** (100.0 mg, 0.13 mmol) was added. The system was evacuated and backfilled with argon. Trimethylamine (44 μL, 0.65 mmol) and CH_3CN (dry) (5 mL) was injected from the side arm. The reaction mixture was stirred at room temperature for 1 h. The reaction progress was monitored by ^{1}H NMR and TLC until the reaction was finished. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_3CN/CH_2Cl_2 (1/5 (v/v)) to afford the desired product **7a** (47% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 1.93 (s, 3H), 1.97 (s, 3H), 2.10 (s, 3H), 2.43 (s, 3H), 3.01 (s, 9H), 4.39 (s, 2H), 4.53 (t, *J* = 29.4 Hz, 1H), 5.12 (d, *J* = 3.0 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 1H), 7.31-7.37 (m, 3H), 7.39-7.42 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 2.89, 3.29, 3.41, 3.56, 53.23, 69.07, 71.07, 79.05, 121.89, 122.58, 122.82, 123.97, 125.48, 126.34, 129.08, 129.34, 138.12, 142.18, 143.81, 175.47, 189.93 ppm. IR (neat) ν 2 359, 2341, 2273, 1622 cm^{-1}.

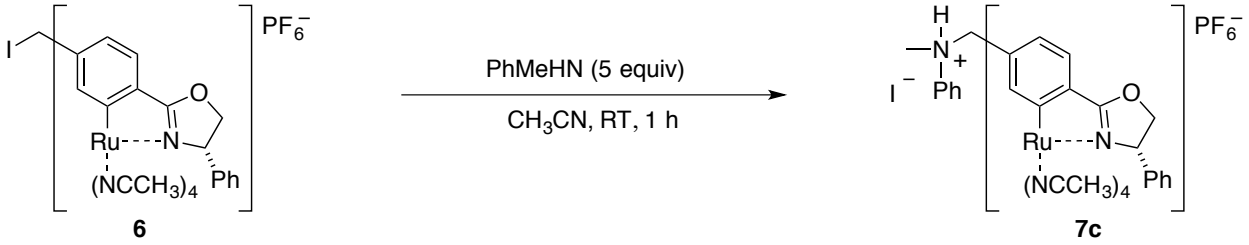
Ru(II)-*Amm*-Pheox (7b)



6 **7b**

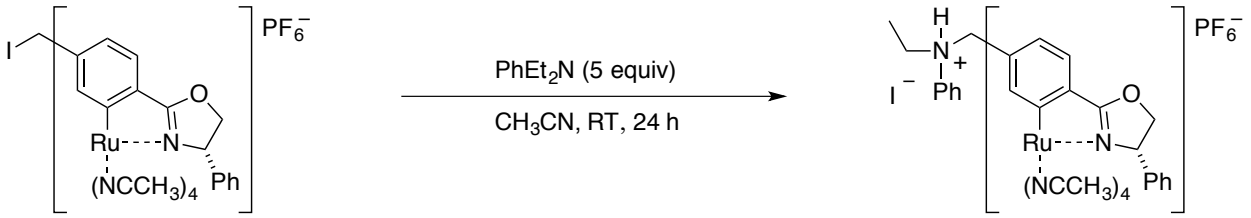
Into a schlenktype flask equipped with a magnetic stirring Ru(II)-(iodomethyl)phenyl-Pheox complex **6** (100.0 mg, 0.13 mmol) was added. The system was evacuated and backfilled with argon. Triethylamine (90 μL, 0.65 mmol) and CH_3CN (dry) (5 mL) was injected from the side arm. The reaction mixture was stirred at room temperature for 1 h. The reaction progress was monitored by ^1H NMR and TLC until the reaction was finished. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_3CN/CH_2Cl_2 (1/5 (v/v)) to afford the desired product **7b** (42% yield). ^1H NMR (400 MHz, CD_3CN) δ 1.37 (t, J = 7.2 Hz, 9H), 1.99 (s, 3H), 2.11 (s, 3H), 2.19 (s, 3H), 2.42 (s, 3H), 3.19 (q, J = 7.2 Hz, 6H), 4.32 (s, 2H), 4.53 (t, J = 13.3 Hz, 1H), 5.12 (d, J = 25.2 Hz, 2H), 6.97 (d, J = 1.8 Hz, 1H), 7.30-7.44 (m, 5H), 7.53 (d, J = 7.3 Hz, 1H), 7.88 (s, 1H). ^{13}C NMR (125 MHz, CD_3CN) δ 2.92, 3.33, 7.27, 52.55, 61.18, 67.73, 68.80, 121.55, 121.86, 122.85, 123.64, 123.86, 125.47, 127.35, 128.31, 137.21, 141.07, 142.00, 174.43, 188.85 ppm. IR (neat) ν 2359, 2341, 2274, 1622 cm^{-1}.

Ru(II)-*Amm*-Pheox (7c)



Into a schlenktype flask equipped with a magnetic stirring Ru(II)-(iodomethyl)phenyl-Pheox complex **6** (100.0 mg, 0.129 mmol) was added. The system was evacuated and backfilled with argon. *N*-methylaniline (70 μL, 0.65 mmol) and CH_3CN (10 mL) was injected from the side arm. The reaction mixture was stirred at room temperature for 1 h. The reaction progress was monitored by ^1H NMR and TLC until the reaction was finished. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_3CN/CH_2Cl_2 (1/5 (v/v)) to afford the desired product **7c** with (41% yield.) ^1H NMR (400 MHz, CD_3CN) δ 1.93 (s, 3H), 1.98 (s, 3H), 2.11 (s, 3H), 2.26 (s, 3H), 3.04 (s, 3H), 4.45 (s, 1H), 4.58 (s, 2H), 5.07 (d, J = 3.0 Hz, 2H), 6.58-6.62 (m, 1H), 6.74-6.77 (m, 3H), 7.13-7.17 (m, 2H), 7.29-7.32 (m, 3H), 7.36-7.39 (m, 3H), 7.69 (s, 1H) ppm. ^{13}C NMR (125 MHz, CD_3CN) δ 3.04, 3.06, 38.39, 56.23, 68.03, 78.04, 112.16, 115.96, 119.24, 121.33, 121.62, 122.36, 125.68, 128.08, 128.39, 129.11, 133.37, 136.44, 140.20, 141.55, 149.83, 174.80, 186.94 ppm. IR (neat) ν 2962, 2359, 2271, 1619 cm^{-1}.

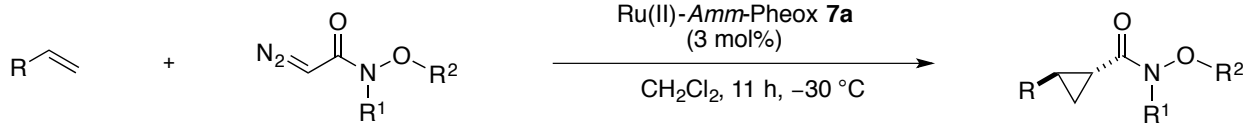
Ru(II)-*Amm*-Pheox (7d)



6 **7d**

Into a schlenktype flask equipped with a magnetic stirring Ru(II)-(iodomethyl)phenyl-Pheox complex **6** (100.0 mg, 0.13 mmol) was added. The system was evacuated and backfilled with argon. *N,N*-diethylaniline (82 μL, 0.65 mmol) and CH_3CN (dry) (10 mL) was injected from the side arm. The reaction mixture was stirred at room temperature for 24 h. The reaction progress was monitored by ^1H NMR and TLC until the reaction was finished. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_3CN/CH_2Cl_2 (1/20 (v/v)) to afford the desired product **7d** (54% yield). ^1H NMR (500 MHz, CD_3CN) δ 1.17 (t, *J* = 16.8 Hz, 3H), 1.97 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 2.23 (s, 3H), 3.51 (q, *J* = 7.26, 14.14 Hz, 2H), 4.68 (t, *J* = 7.26 Hz, 1H), 4.55 (s, 2H), 5.06 (t, *J* = 7.64 Hz, 2H), 5.42 (s, 1H), 6.56 (t, *J* = 14.52 Hz, 1H), 6.71 (d, *J* = 8.03 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 1H), 7.12 (t, *J* = 16.0 Hz, 2H), 7.31-7.33 (m, 3H), 7.37-7.40 (m, 3H), 7.74 (s, 1H). ^{13}C NMR (125 MHz, CD_3CN) δ 3.05, 11.67, 45.32, 53.96, 68.03, 78.04, 112.01, 115.55, 119.06, 122.34, 125.67, 128.08, 128.10, 128.39, 129.15, 133.28, 136.25, 140.59, 141.56, 148.62, 174.81, 186.88 ppm. IR (neat) ν 2957, 2397, 1654 cm^{-1}.

4. General procedure for asymmetric cyclopropanation of olefins with diazo Weinreb amides



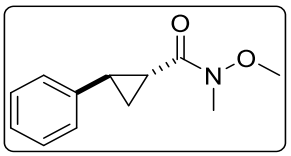
1 (5 equiv) **2** **4**

To a solution of Ru(II)-*Amm*-Pheox **7a** (3 mol%) and olefins (5 equiv) in CH_2Cl_2 under argon atmosphere at −30 °C, diazo Weinreb amides **2a–c** solution in CH_2Cl_2 was slowly added using a syringe pump over 10 h. After 10 h the syringe was washed with additional 1 mL of CH_2Cl_2 and the reaction mixture was stirred for additional 1 h. The progress of the reaction was monitored by TLC, ^1H NMR. After the reaction finished, the mixture was concentrated using reduced pressure and the residue was purified by column chromatography on silica gel eluted with (*n*-Hexane/EtOAc) to give the desired cyclopropane product.

The *trans/cis* ratio was determined from the crude ^{1}H NMR spectra and the ee value was determined by chiral HPLC analysis.

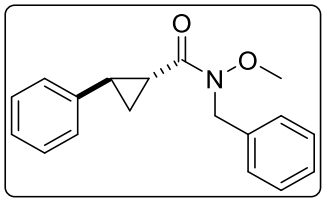
5. Analytical Data for Asymmetric Cyclopropanation Reaction Products

N-Methoxy-*N*-methyl-2-phenylcyclopropanecarboxamide (4a)



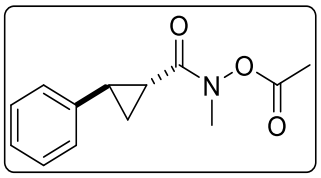
According to the typical procedure for asymmetric cyclopropanation reaction between styrene (133.0 μL, 1.16 mmol) and *N*-methoxy-*N*-methyldiazoacetamide (MMD) (30.0 mg, 0.23 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (3/1 (v/v)) as an eluent to give the desired product in 80% yield as yellow oil. $[\alpha]^{29}_{D} = -142.6$ (c 2.06, $CHCl_3$). *trans/cis* = 83/17, 90% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.26-1.32 (m, 1H), 1.56-1.63 (m, 1H), 2.36 (s br, 1H), 2.46-2.53 (m, 1H), 3.20 (s, 3H), 3.65 (s, 3H), 7.1-7.3 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer) δ 16.57, 21.66, 26.00, 32.70, 61.79, 126.32, 128.01, 128.52, 140.88, 173.16. IR (neat) ν 2936, 2359, 2341, 1653 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral AS-H), UV detector 230 nm, eluent: Hex/IPA = 20/1, Flow late = 1.0 mL/min, tR = 9.88 min (minor product), tR = 11.90 min (major product). HRMS (DART) calcd for $C_{12}H_{15}NO_2$ $[M+H]^+$: 206.1181 found: 206.1188.

N-Benzyl-*N*-methoxy-2-phenylcyclopropanecarboxamide (4b)



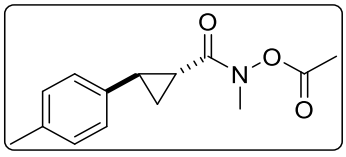
According to the typical procedure for asymmetric cyclopropanation reaction between styrene (83.7 μL, 0.73 mmol) and *N*-benzyl-*N*-methoxydiazoacetamide (BMD) (30.0 mg, 0.146 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 70% yield as yellow oil. $[\alpha]^{28}_{D} = -147.6$ (c 1.98, $CHCl_3$). *trans/cis* = 80:20, 80% *trans* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 1.32-1.36 (m, 1H), 1.68-1.72 (m, 1H), 2.46 (s br, 1H), 2.55-2.59 (m, 1H), 3.63 (s, 3H), 4.79 (d, *J* = 15.26 Hz, 1H), 4.88 (d, *J* = 15.26 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) (*trans* isomer) δ 16.89, 21.95, 26.28, 49.48, 62.84, 126.33, 126.45, 127.76, 128.47, 128.58, 128.69, 136.64, 140.82, 173.37 ppm. IR (neat) ν 3030, 2359, 2341, 1653 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral AS-H), UV detector 254 nm, eluent: Hex/IPA = 20/1, Flow late = 0.5 mL/min, tR = 23.17 min (minor product), tR = 24.97 min (major product). HRMS (DART) calcd for $C_{18}H_{19}NO_2$ $[M+H]^+$: 282.1494 found: 282.1491.

***N*-Acetoxy-*N*-methyl-2-phenylcyclopropanecarboxamide (4c)**



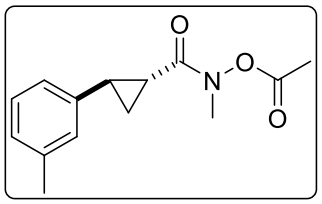
According to the typical procedure for asymmetric cyclopropanation reaction between styrene (110.0 μL, 0.95 mmol) and methyl *N*-acetoxy-*N*-diazomethylacetamide (AMD) (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 98% yield as yellow oil. $[\alpha]^{25}_{D}$ = −135.4 (c 3.83, $CHCl_3$). *trans/cis* = 98/2, 92% *trans* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 1.26-1.32 (m, 1H), 1.61-1.66 (m, 1H), 1.87-1.93 (m, 1H), 2.06 (s, 3H), 2.41-2.48 (m, 1H), 3.32 (s, 3H), 7.07 (d, *J* =7.3 Hz, 2H), 7.17-7.24 (m, 1H), 7.26-7.29 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 15.83, 18.35, 22.65, 26.22, 35.90, 126.33, 126.56, 128.58, 140.38, 168.62, 172.54 ppm. IR (neat) ν 3029, 2953, 1781, 1791, 1667, 1604 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral IE), UV detector 220 nm, eluent: Hex/IPA = 9/1, Flow late = 1.0 mL/min, tR = 19.07 min (minor product), tR = 21.96 min (major product). HRMS (DART) calcd for $C_{13}H_{15}NO_3$ $[M+H]^+$: 234.1130 found: 234.1134.

***N*-Acetoxy-*N*-methyl-2-(*p*-tolyl)cyclopropanecarboxamide (4d)**



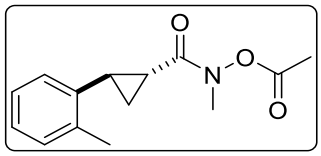
According to the typical procedure for asymmetric cyclopropanation reaction between 4-methylstyrene (126.0 μL, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (AMD) (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1(v/v)) as an eluent to give the desired product in 96% yield as yellow oil. $[\alpha]^{28}_{D}$ = −160.3 (c 2.12, $CHCl_3$). *trans/cis* = 96/4, 94% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.24-1.30 (m, 1H), 1.60-1.65 (m, 1H), 1.83-1.88 (m, 1H), 2.02 (s, 3H), 2.27 (s, 3H), 2.40-2.45 (m, 1H), 3.32 (s, 3H), 6.97 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (*trans* isomer) δ (100 MHz, $CDCl_3$) 15.76, 18.39, 21.09, 22.45, 26.00, 36.06, 126.30, 129.23, 136.15, 137.31, 168.59, 172.61 ppm. IR (neat) ν 2923, 2360, 2341, 1794, 1666 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral OJ-H), UV detector 220 nm, eluent: Hex/IPA = 50/1, Flow late = 1.0 mL/min, tR = 33.49 min (minor product), tR = 43.77 min (major product). HRMS (DART) calcd for $C_{14}H_{17}NO_3$ $[M+H]^+$: 248.1286 found: 248.1287.

_N_-Acetoxy-_N_-methyl-2-(_m_-tolyl)cyclopropanecarboxamide (4e)



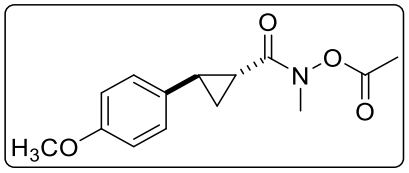
According to the typical procedure for asymmetric cyclopropanation reaction between 3-methylstyrene (125.0 μL, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (AMD) (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 94% yield as colorless oil. $[\alpha]^{26}_{D} = -142.4$ (c 2.12, $CHCl_3$). *trans/cis* = 99/1, 92% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.27-1.32 (m, 1H), 1.61-1.66 (m, 1H), 1.86-1.90 (m, 1H), 2.05 (s, 3H), 2.30 (s, 3H), 2.40-2.74 (m, 1H), 3.32 (s, 3H), 6.86-6.90 (m, 2H), 6.99 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 14.9 Hz, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 15.79, 18.39, 21.47, 22.52, 26.18, 36.09, 123.29, 127.25, 127.31, 128.48, 138.16, 140.33, 168.59, 172.48 ppm. IR (neat) ν 2922, 2359, 1793, 1668 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral OJ-H), UV detector 220 nm, eluent: Hex/IPA = 50/1, Flow late = 1.0 mL/min, tR = 27.70 min (minor product), tR = 30.90 min (major product). HRMS (DART) calcd for $C_{14}H_{17}NO_3$ $[M+H]^+$: 248.1286 found: 248.1282.

_N_-Acetoxy-_N_-methyl-2-(_o_-tolyl)cyclopropanecarboxamide (4f)



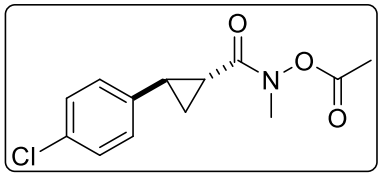
According to the typical procedure for asymmetric cyclopropanation reaction between 2-methylstyrene (125.3 μL, 0.95 mmol) and and *N*-acetoxy-*N*-methyldiazoacetamide (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 97% yield as yellow oil. $[\alpha]^{27}_{D} = -66.7$ (c 1.73, $CHCl_3$). *trans/cis* = 99/1, 90% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.28-1.39 (m, 1H), 1.54-1.63 (m, 1H), 1.78-1.85 (m, 1H), 2.13 (s, 3H), 2.36 (s, 3H), 2.51-2.59 (m, 1H), 3.35 (s, 3H), 6.94-6.96 (m, 1H), 7.09-7.16 (m, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 15.31, 18.53, 19.64, 20.51, 24.47, 36.52, 125.71, 125.92, 126.77, 130.02, 138.16, 138.29, 168.30, 172.99 ppm. IR (neat) ν 2953, 2359, 1793, 1664 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral OJ-H), UV detector 220 nm, eluent: Hex/IPA = 50/1, Flow late = 1.0 mL/min, tR = 21.90 min (minor product), tR = 26.64 min (major product). HRMS (DART) calcd for $C_{14}H_{17}NO_3$ $[M+H]^+$: 248.1286 found: 248.1282.

***N*-Acetoxy-2-(4-methoxyphenyl)-*N*-methylcyclopropanecarboxamide (4g)**



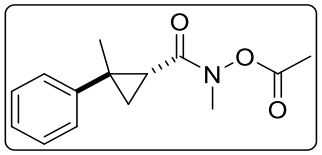
According to the typical procedure for asymmetric cyclopropanation reaction between 4-methoxy styrene (127.8 μL, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (AMD) (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 93% yield as yellow oil. $[\alpha]^{23}_{D}$ = −122.9 (c 1.32, $CHCl_3$). *trans/cis* = 93/7, 96% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.22-1.25 (m, 1H), 1.57-1.61 (m, 1H), 1.77-1.81 (m, 1H), 2.03 (s, 3H), 2.13 (s, 3H), 2.37-2.44 (m, 1H), 3.30 (s, 3H), 3.74 (s, 3H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (*trans* isomer) δ 15.53, 18.40, 22.33, 25.72, 36.05, 55.37, 113.97, 127.52, 132.31, 158.31, 168.63, 172.86 ppm. IR (neat) ν 2936, 2359, 1793, 1663 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral AS-H), UV detector 220 nm, eluent: Hex/IPA = 20/1, Flow late = 1.0 mL/min, tR = 24.85 min (minor product), tR = 27.60 min (major product). HRMS (DART) calcd for $C_{14}H_{17}NO_4$ $[M+H]^+$: 264.1235 found: 264.1239.

***N*-Acetoxy-2-(4-chlorophenyl)-*N*-methylcyclopropanecarboxamide (4h)**



According to the typical procedure for asymmetric cyclopropanation reaction between 4-chlorostyrene (141.0 μL, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 94% yield as pale yellow oil. $[\alpha]^{25}_{D}$ = −142.1 (c 1.76, $CHCl_3$). *trans/cis* = 99/1, 92% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.23-1.28 (m, 1H), 1.62-1.67 (m, 1H), 1.74-1.87 (m, 1H), 2.04 (s, 3H), 2.41-2.48 (m, 1H), 3.30 (s, 3H), 6.98 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H) ppm. ^{13}C NMR (*trans* isomer) δ (100 MHz, $CDCl_3$) δ 15.80, 18.40, 22.64, 25.56, 35.90, 127.72, 128.66, 132.21, 138.93, 168.56, 172.22 ppm. IR (neat) ν 2928, 2359, 1793, 1667 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral IE), UV detector 220 nm, eluent: Hex/IPA = 9/1, Flow late = 1.0 mL/min, tR = 16.43 min (minor product), tR = 19.83 min (major product). HRMS (DART) calcd for $C_{13}H_{14}ClNO_3$ $[M+H]^+$: 268.0749 found: 268.0743.

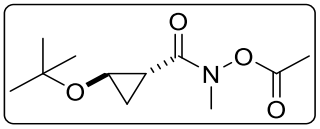
***N*-Acetoxy-*N*,2-dimethyl-2-phenylcyclopropanecarboxamide (4i)**



According to the typical procedure for asymmetric cyclopropanation reaction between α-methylstyrene (124.0 μL, 0.95 mmol) and *N*-acetoxy-*N*-

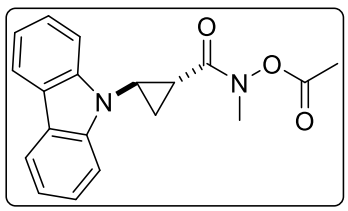
methyldiazoacetamide (AMD) (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 96% yield as colorless oil. $[\alpha]^{27}_{D}$ = +16.6 (c 1.87, $CHCl_3$). *trans/cis* = 96:4, 74% *trans* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 1.43 (s, 3H), 1.44-1.48 (m, 1H), 1.56-1.58 (m, 1H), 1.82-2.00 (m, 4H), 3.34 (s, 3H), 7.16-7.30 (m, 5H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (*trans* isomer) δ 18.36, 18.95, 19.29, 28.14, 29.57, 35.71, 126.35, 126.39, 128.57, 145.65, 168.65, 171.07 ppm. IR (neat) ν 2956, 2360, 1792, 1670 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral IC3), UV detector 230 nm, eluent: Hex/IPA = 9/1, Flow late = 1.0 mL/min, tR = 17.85 min (major product), tR = 28.29 min (minor product). HRMS (DART) calcd for $C_{14}H_{17}NO_3$ $[M+H]^+$: 248.1286 found: 248.1282.

_N_-Acetoxy-2-(*tert*-butoxy)-_N_-methylcyclopropanecarboxamide (4j)



According to the typical procedure for asymmetric cyclopropanation reaction between 2-methyl-2-(vinyloxy)propane (124.9 μL, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (AMD) (30 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 95% yield as yellow oil. $[\alpha]^{24}_{D}$ = −13.6 (c 1.90, $CHCl_3$). *trans/cis* = 99/1, 91% *trans* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 1.09-1.14 (m, 1H), 1.22 (s, 9H), 1.26-1.31 (m, 1H), 1.77-1.80 (m, 1H), 2.20 (s, 3H), 3.30 (s br, 3H), 3.54-3.57 (m, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 15.54, 18.56, 20.01, 28.01, 35.94, 54.66, 75.62, 168.42, 172.43 ppm. IR (neat) ν 2976, 2359, 1796, 1661 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral IE), UV detector 220 nm, eluent: Hex/IPA = 8/2, Flow late = 1.0 mL/min, tR = 13.27 min (major product), tR = 14.19 min (minor product). HRMS (DART) calcd for $C_{11}H_{19}NO_4$ $[M+H]^+$: 230.1392 found: 230.1390.

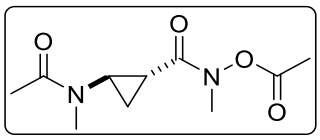
_N_-Acetoxy-2-(9*H*-carbazol-9-yl)-_N_-methylcyclopropanecarboxamide (4k)



According to the typical procedure for asymmetric cyclopropanation reaction between *N*-vinylcarbazole (183.6 mg, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (AMD) (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (2/1 (v/v)) as an eluent to give the desired product in 99% yield as colorless oil. $[\alpha]^{25}_{D}$ = +53.3 (c 3.04, $CHCl_3$). *trans/cis* = 99/1, 96% *trans* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer) δ 1.68-1.82 (m, 1H), 2.00-2.04 (m, 1H), 2.15 (s, 3H), 2.25-2.42 (m, 1H), 3.48 (s, 3H), 3.85-3.88 (m, 1H) 7.26 (t, *J* = 14.95, 2H), 7.47-7.56 (m, 4H), 8.06 (d, *J* = 7.63, 2H) ppm. ^{13}C

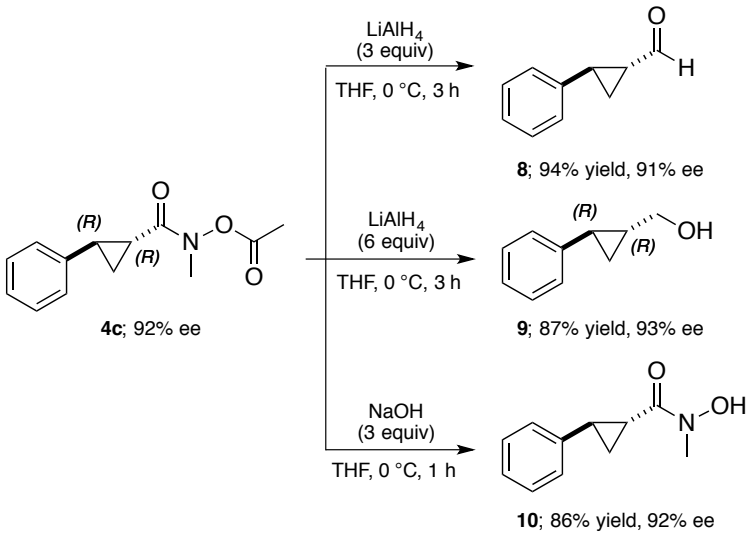
NMR (100 MHz, $CDCl_3$) (*trans* isomer) δ 16.93, 18.66, 19.89, 32.92, 36.11, 109.95, 119.81, 120.46, 123.21, 126.04, 140.84, 168.52, 171.45 ppm. IR (neat) ν 2933, 1792, 1666 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral IC), UV detector 220 nm, eluent: Hex/IPA = 9/1, Flow late = 1.0 mL/min, tR = 15.36 min (major product), tR = 17.18 min (minor product). HRMS (DART) calcd for $C_{19}H_{18}N_2O_3$ $[M+H]^+$: 323.1395 found: 323.1394.

***N*-Acetoxy-*N*-methyl-2-(*N*-methylacetamido)cyclopropanecarboxamide (4l)**

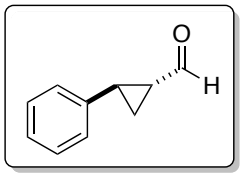


According to the typical procedure for asymmetric cyclopropanation reaction between vinyl acetate (87.94 μL, 0.95 mmol) and *N*-acetoxy-*N*-methyldiazoacetamide (30.0 mg, 0.19 mmol). The resulting mixture was purified by silica gel column chromatography with *n*–Hexane/EtOAc (3/1 (v/v)) as an eluent to give the desired product in 86% yield as colorless oil. $[\alpha]^{28}_D$ = −5.4 (c 0.49, $CHCl_3$). *trans/cis* = 91:9, 76% *trans* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 1.29-1.34 (m, 1H), 1.52-1.57 (m, 1H), 1.92-1.97 (m, 1H), 2.12 (s, 3H), 2.23 (s, 3H), 2.85 (s, 3H), 3.20-3.24 (m, 1H), 3.31 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (*trans* isomer) δ 17.99, 18.59, 21.44, 22.48, 33.54, 35.77, 40.31, 168.36, 170.95, 173.16 ppm. IR (neat) ν 2929, 2359, 1792, 1654 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral AS-H), UV detector 230 nm, eluent: Hex/IPA = 6/4, Flow late = 1.0 mL/min, tR = 12.34 min (major product), tR = 15.62 min (minor product). HRMS (DART) calcd for $C_{10}H_{16}N_2O_4$ $[M+NH_4]^+$: 246.1453 found: 246.1456.

6. Synthetic transformations of cyclopropyl Weinreb amides

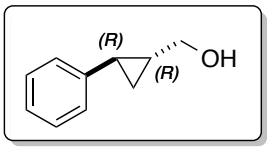


2-Phenylcyclopropanecarbaldehyde (8)



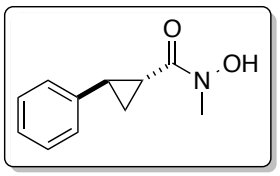
Under argon atmosphere, to a solution of *N*-acetoxy-*N*-methyl-2-phenylcyclopropanecarboxamide **4c** (50 mg, 0.21 mmol) in THF (3 mL), was added $LiAlH_4$ (24 mg, 0.63 mmol) in small portions at 0 °C. After stirring for 1 h at 0 °C, H_2O (50 μL), 20% NaOH (aq) (50 μL), H_2O (100 μL) was added successively, and then stirred at room temperature for 2 h, after which the reaction was quenched by adding excess amount of saturated NH_4Cl aqueous solution, followed by extraction with diethyl ether. The organic phase was washed with brine and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using *n*–Hexane/EtOAc (2/1 (v/v)) as eluent to give the corresponding aldehyde **8** (94% yield, *trans/cis* = 99:1, 91% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51-1.55 (m, 1H), 1.71-1.75 (m, 1H), 2.14-2.19 (m, 1H), 2.60-2.64 (m, 1H), 7.10 (d, *J* = 7.63 Hz, 2H), 7.20-7.30 (m, 3H), 9.31 (d, *J* = 4.59, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.57, 26.68, 33.91, 126.34, 126.93, 128.70, 139.04, 199.83 ppm.[2] The ee value was determined by HPLC analysis. Column (Chiral AD3), UV detector 230 nm, eluent: Hex/IPA = 6/4, Flow late = 0.5 mL/min, tR = 10.37 min (minor product), tR = 11.42 min (major product).

((1*R*,2*R*)-2-phenylcyclopropyl)methanol (9)



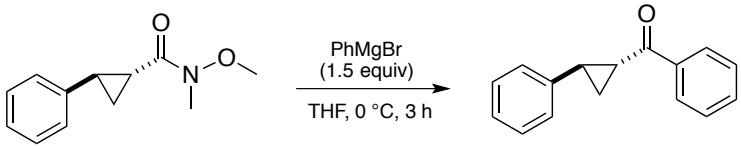
Under argon atmosphere, to a solution of *N*-acetoxy-*N*-methyl-2-phenylcyclopropanecarboxamide **4c** (50 mg, 0.21 mmol) in 3 mL THF, was added $LiAlH_4$ (48 mg, 1.26 mmol) in small portions at 0 °C. After stirring for 1 h at 0 °C, 100 μL H_2O, 100 μL 20% NaOH (aq), 200 μL H_2O was added successively, and then stirred at room temperature for 2 h, after which the reaction was quenched by adding excess amount of saturated NH_4Cl aqueous solution, followed by extraction with diethyl ether. The organic phase was washed with brine and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum *n*-Hexane/EtOAc (2/1 (v/v)) as eluent to give the corresponding alchohol **9** (87% yield, *trans/cis* = 99:1, 93% ee). $[\alpha]^{26}_D$ = −69.3 (c 0.49, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94-0.98 (m, 2H), 1.42-1.49 (m, 1H), 1.80-1.84 (m, 1H), 3.58-3.65 (m, 2H), 7.06 (d, *J* = 6.12 Hz, 2H), 7.15 (t, *J* = 7.26 Hz, 1H), 7.24-7.27 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.95, 21.38, 25.41, 66.70, 125.75, 125.90, 128.44, 142.49 ppm.[3] The ee value was determined by HPLC analysis. Column (Chiral OD-H), UV detector 254 nm, eluent: Hex/IPA = 9/1, Flow late = 0.5 mL/min, tR = 15.18 min (minor product), tR = 21.53 min (major product).

_N_-Hydroxy-_N_-methyl-2-phenylcyclopropanecarboxamide (10)



In a two way flask, NaOH aqua solution (15.4 mg, 0.39 mmol) was added from the side arm of the flask to a solution of *N*-acetoxy-*N*-methyl-2-phenylcyclopropanecarboxamide **4c** (30.0 mg, 0.13 mmol) in THF at 0 °C and the reaction mixture was stirred for 1 h. The reaction progress was monitored using TLC. After the end of the reaction, the reaction mixture was concentrated and extracted using diethyl ether and the organic layer was dried using sodium sulfate anhydrous. Then the organic solvent was removed using reduced pressure and the residue was purified using column chromatography *n*-Hexane/EtOAc (1/1 (v/v)) to give the desired product **10** (86% yield, *trans/cis* = 99:1, 92% ee). $[\alpha]^{29}_{D}$ = −79.2 (c 1.56, $CHCl_3$). ^{1}H NMR (500 MHz, CD_3OD) δ 1.27 (m, 1H), 1.45 (m, 1H), 2.32 (m, 1H), 2.59 (m, 1H), 3.21 (s, 3H), 3.27 (m, 1H), 7.09 (m, 3H), 7.21 (m, 2H) ppm. ^{13}C NMR (125 MHz, CD_3OD) δ 15.42, 21.11, 25.20, 35.37, 125.82, 125.97, 128.13, 140.79, 173.19 ppm. IR (neat) ν 3169, 2923, 2360, 2341, 1605 cm^{-1}. The ee value was determined by HPLC analysis. Column (Chiral IE), UV detector 230 nm, eluent: Hex/IPA = 9/1, Flow late = 1.0 mL/min, tR = 7.43 min (minor product), tR = 8.06 min (major product). HRMS (DART) calcd for $C_{11}H_{13}NO_2$ $[M+H]^+$: 192.1022 found: 192.1024.

Phenyl(2-phenylcyclopropyl)methanone (11)



4a; 90% ee

11; 89% yield, 90% *trans* ee

Under argon atmosphere, to a solution of *N*-methoxy-*N*-methyl-2-phenylcyclopropanecarboxamide **4a** (30.0 mg, 0.15 mmol) in 3 mL THF, was added PhMgBr (1 M in THF, 35 μL, 0.45 mmol) at 0 °C. After stirring for 2 h at 0 °C, the reaction was quenched by adding excess amount of saturated NH_4Cl aqueous solution, followed by extraction with diethyl ether. The organic phase was washed with brine and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using petroleum Et_2O/EtOAc (10/1 (v/v)) as eluent to give the corresponding ketone (89% yield, 90% *trans* ee). ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer) δ 1.52-1.57 (m, 1H), 1.89-1.94 (m, 1H), 2.66-2.71 (m, 1H), 2.87-2.91 (m, 1H), 7.16-7.32 (m, 5H), 7.40-7.47 (m, 3H), 7.97-7.99 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (*trans* isomer) δ 19.37, 29.41, 30.13, 126.32, 126.70, 128.09, 128.67, 133.02, 137.80, 140.58, 198.69 ppm.[4] The ee value was determined by HPLC analysis. Column (Chiral AD), UV detector 254 nm, eluent: Hex/IPA = 60/1, Flow late = 0.5 mL/min, tR = 18.58 min (minor product), tR = 31.41 min (major product).

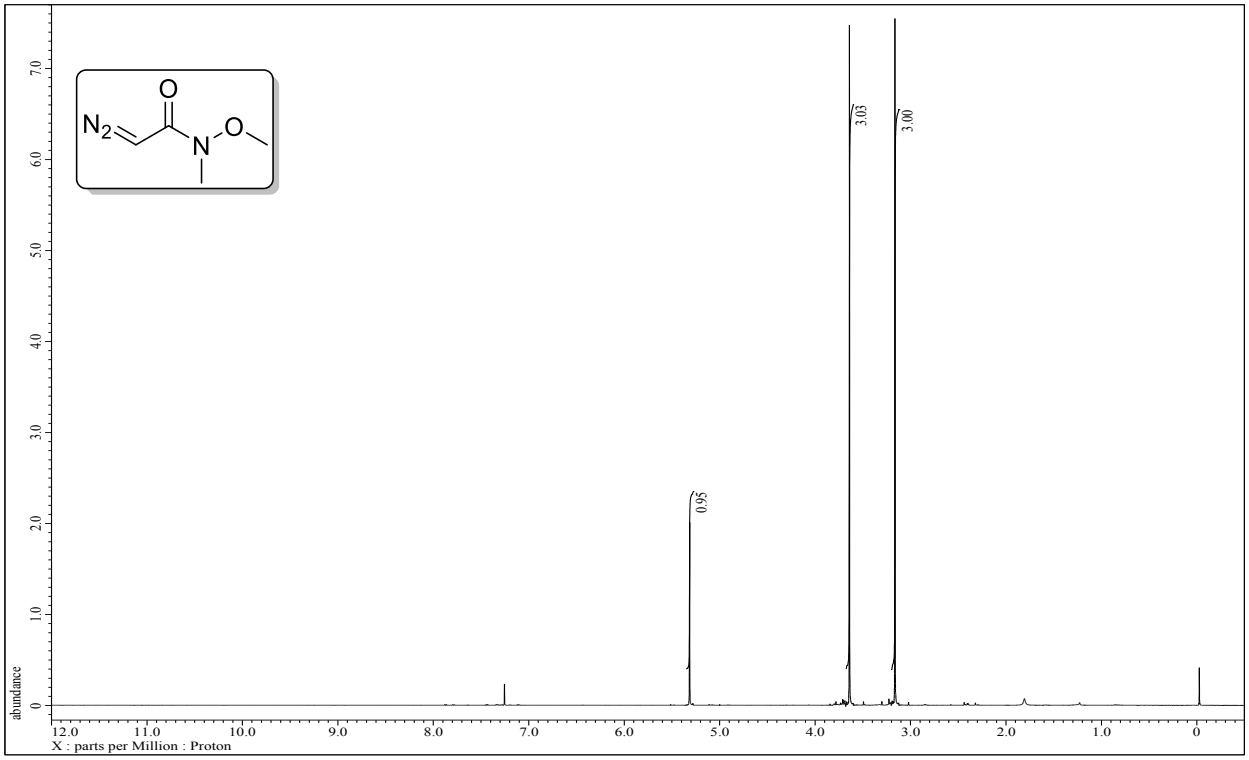
References:

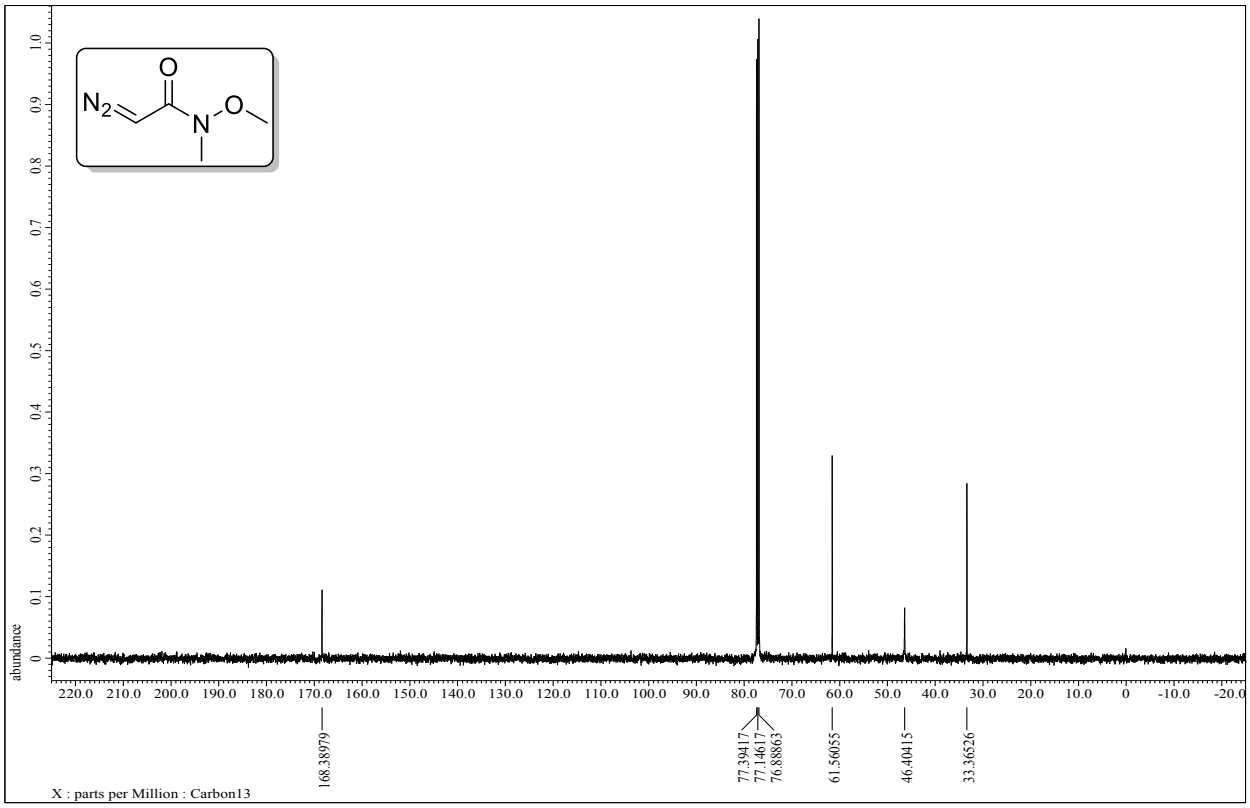
1. T. Toma, J. Shimokawa, T. Fukuyama, *Org. Lett.,* 2007*,* **9***,* 3195.

2. A. Isao, M. Atsunori, Y. Hisashi, *J. Am. Chem. Soc.*, 1985, **107**, 8254.

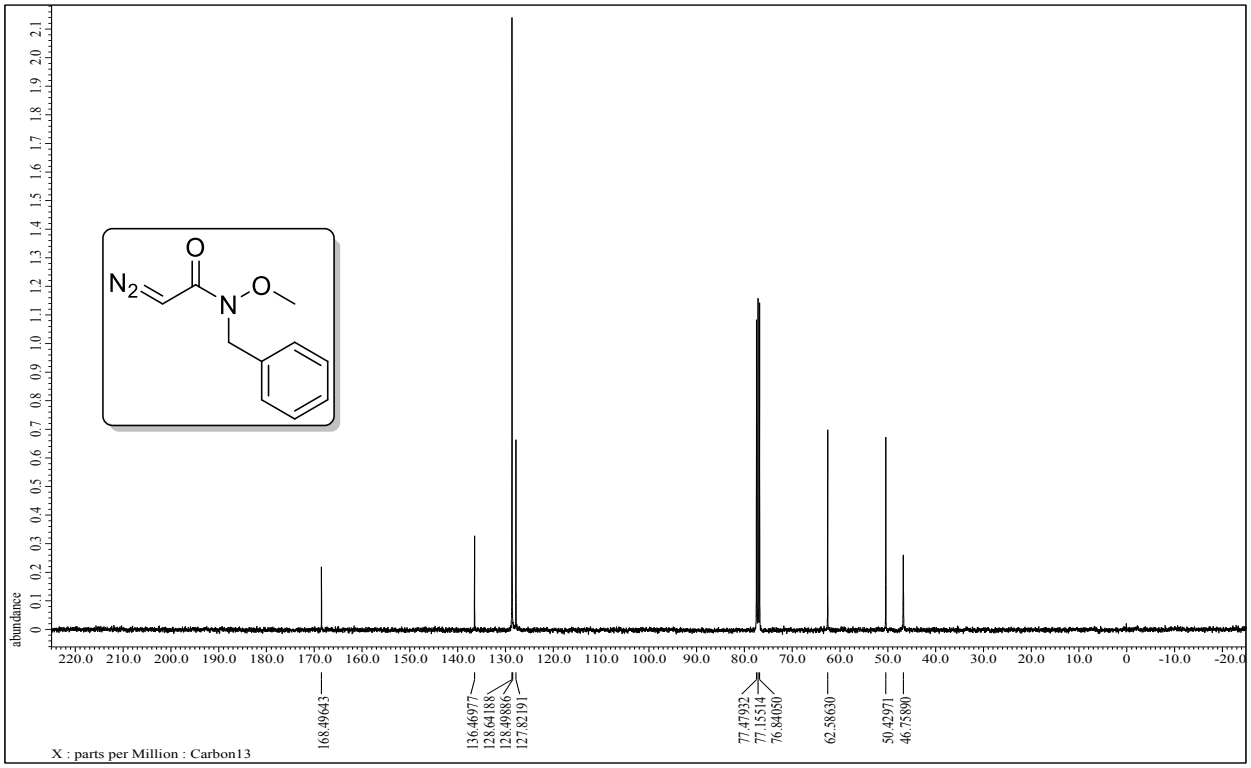
3. P. Jörg, C. M. Anja, W. Thorsten, W. Andreas, *Adv. Synth. Catal.,* 2003, **345**, 1273.

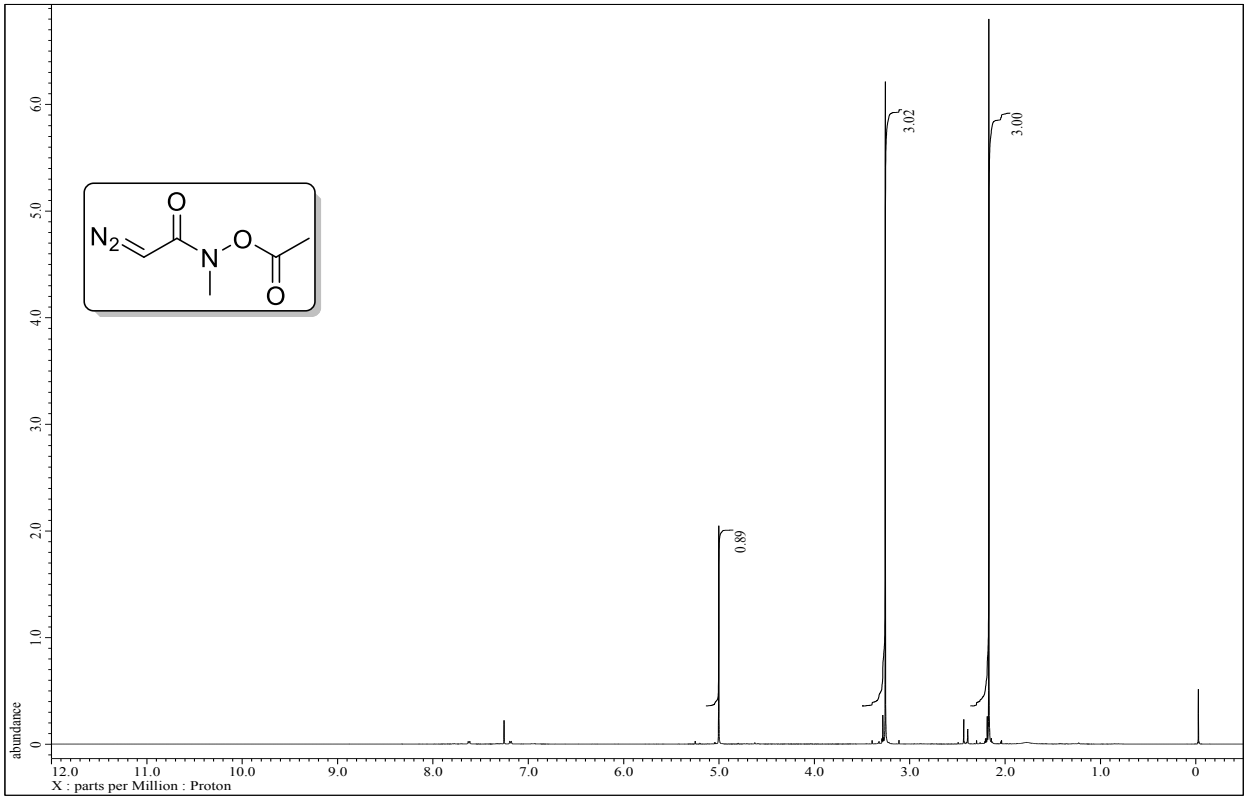
4. M. Olaf, W. Pablo, *Helv. Chim. Acta.,* 2003, **68**, 865.

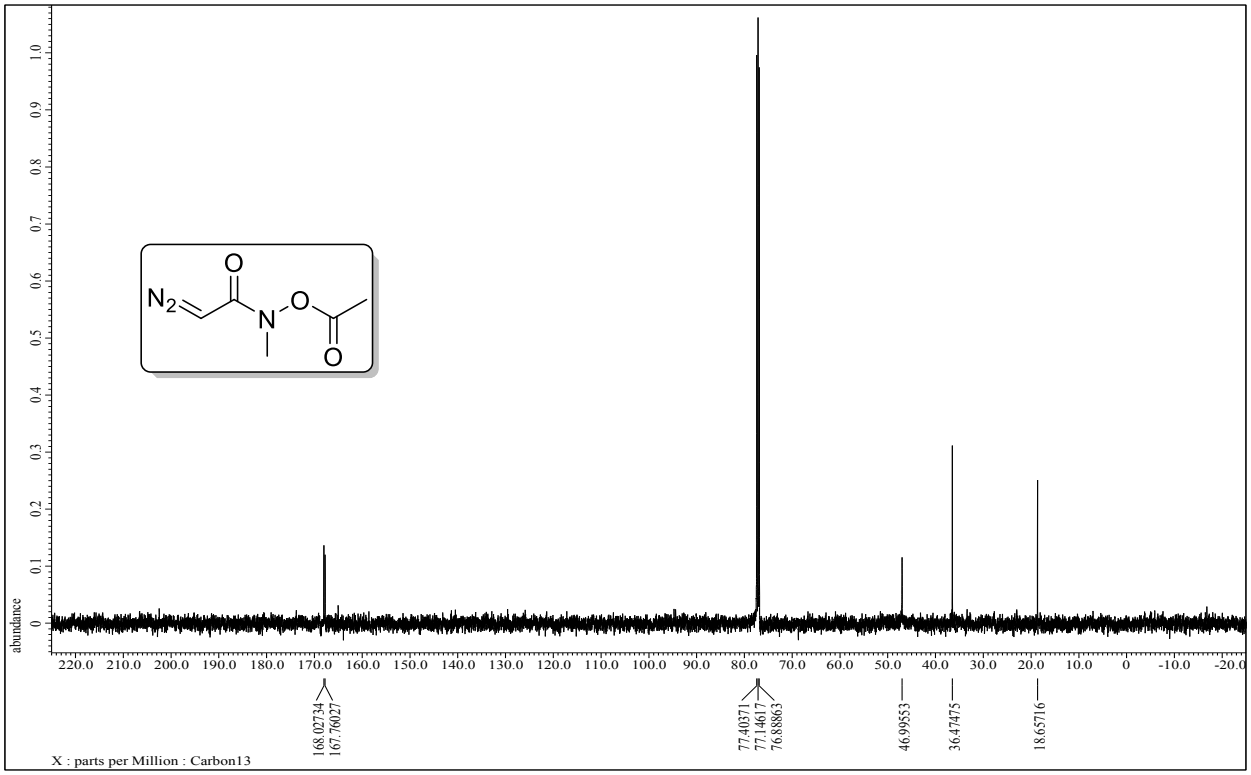

O
N2
N
O
0.95
3.03
3.00
abundance
X : parts per Million : Proton

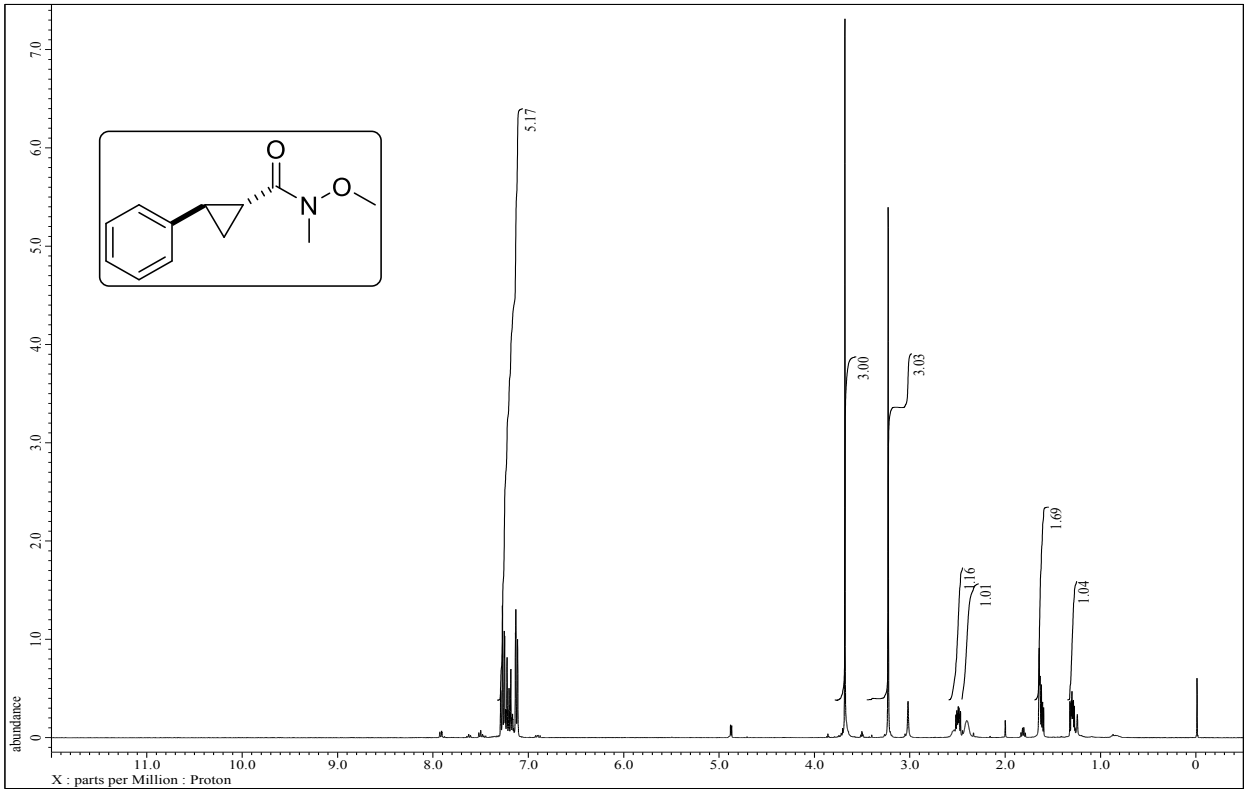

O
N2
N
O
abundance
168.38979
77.39417
77.14617
76.88863
61.56055
46.40415
33.36526
X : parts per Million : Carbon13

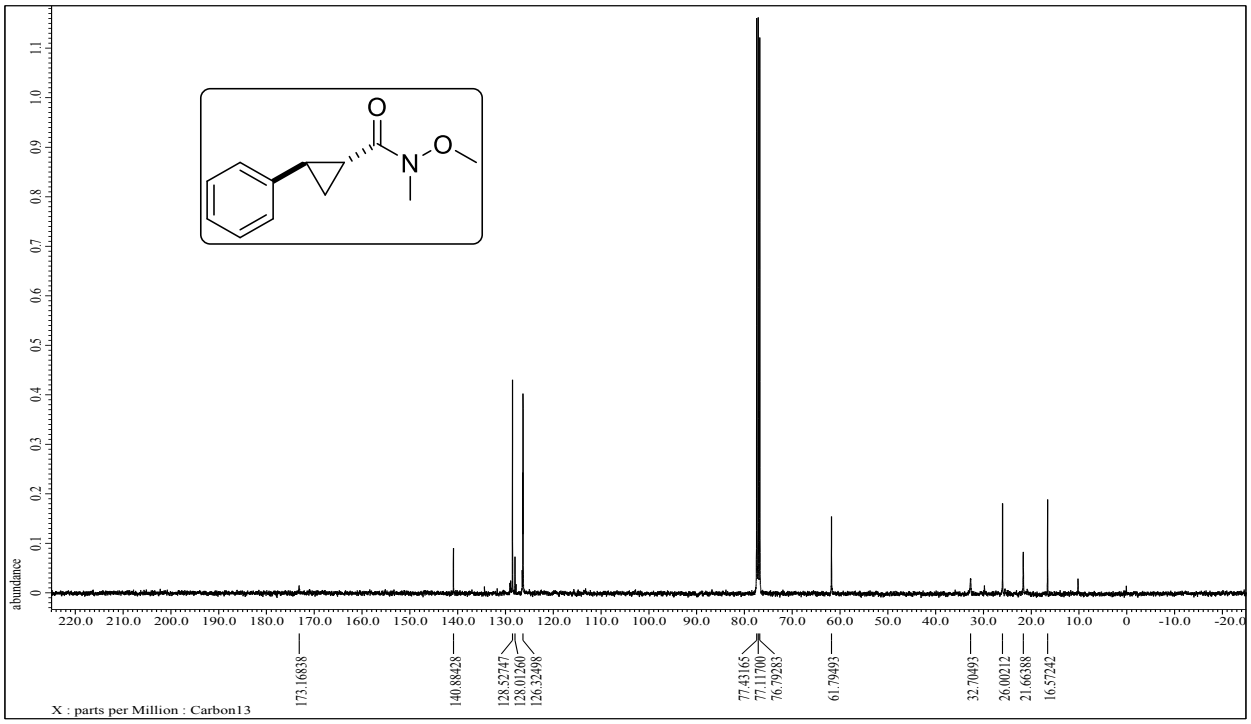

O
N2
N
O
5.31
0.96
2.16
3.00
abundance
X : parts per Million : Proton

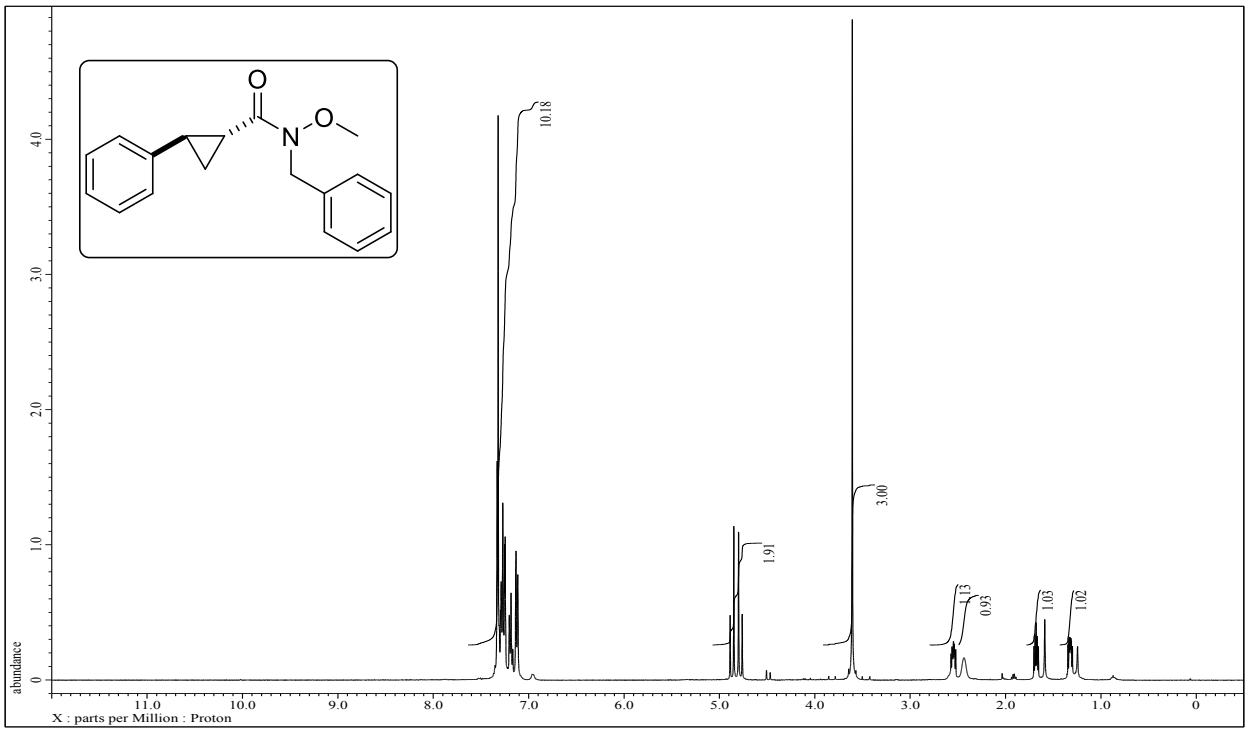

O
N2
N
O
abundance
168.49643
136.46977
128.64188
128.49886
127.82191
77.47932
77.15514
76.84050
62.58630
50.42971
46.75890
X : parts per Million : Carbon13

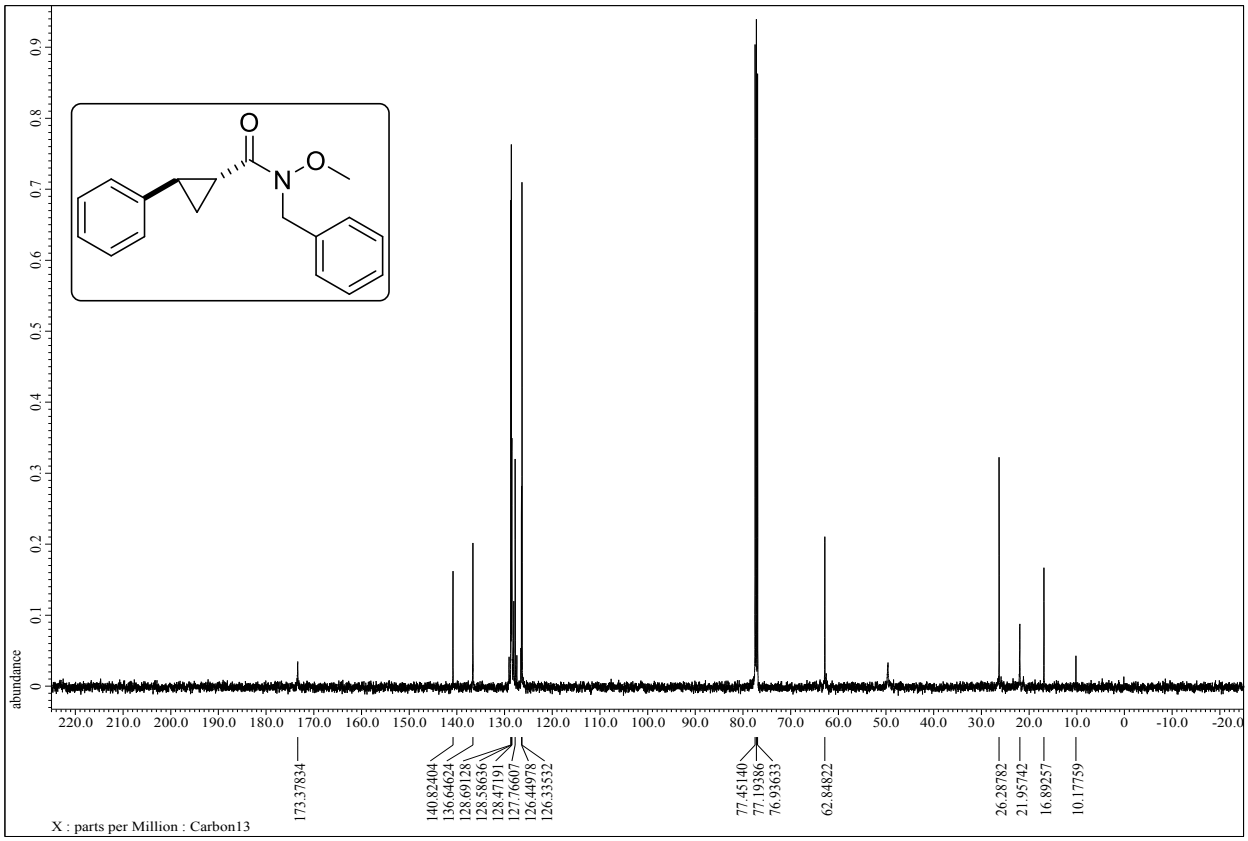

abundance
X : parts per Million : Proton
0.89
3.02
3.00

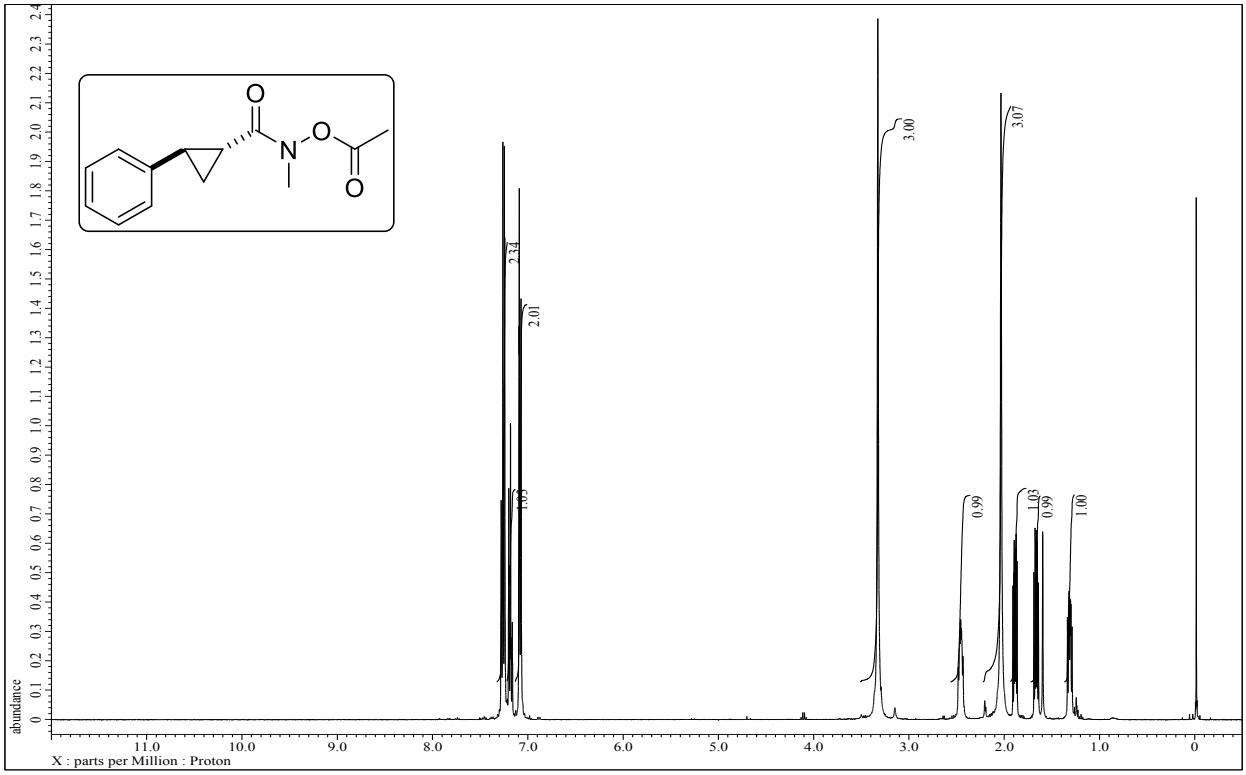

abundance
X : parts per Million : Carbon13
168.02734
167.76027
77.40371
77.14617
76.88863
46.99553
36.47475
18.65716

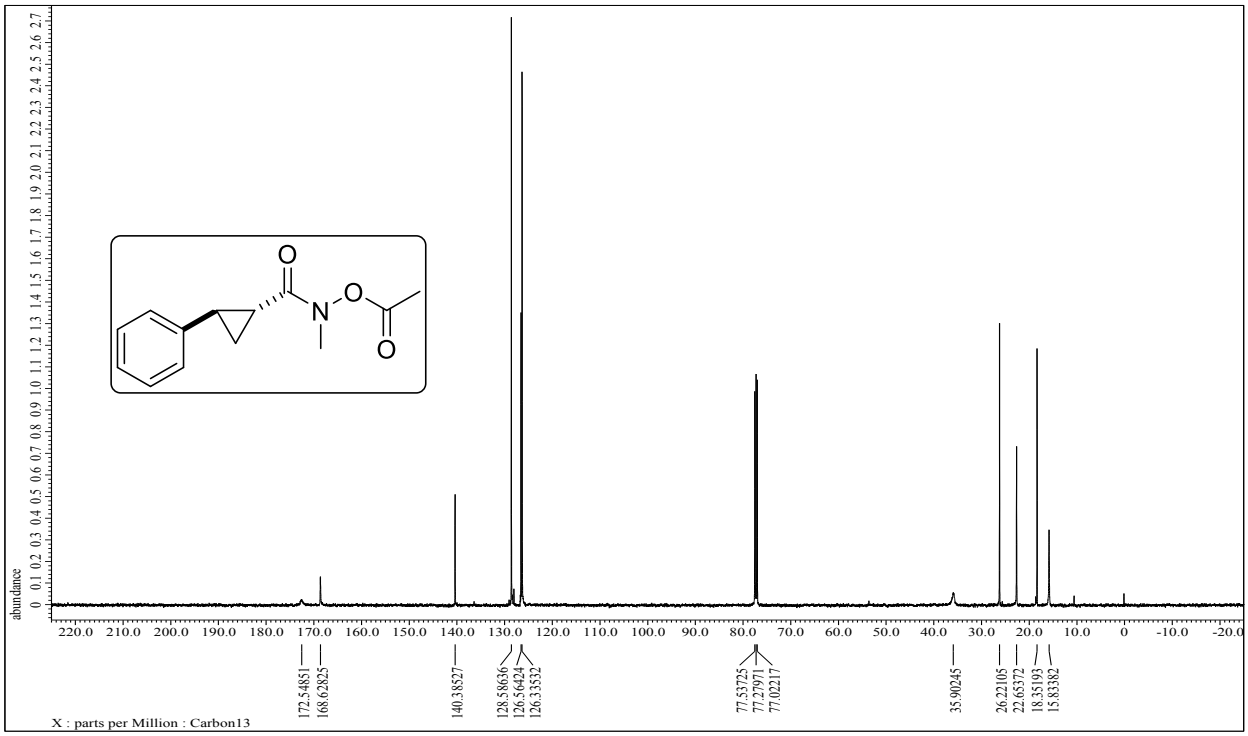

O
N
O
5.17
3.00
3.03
1.69
1.16
1.01
1.04
abundance
X : parts per Million : Proton

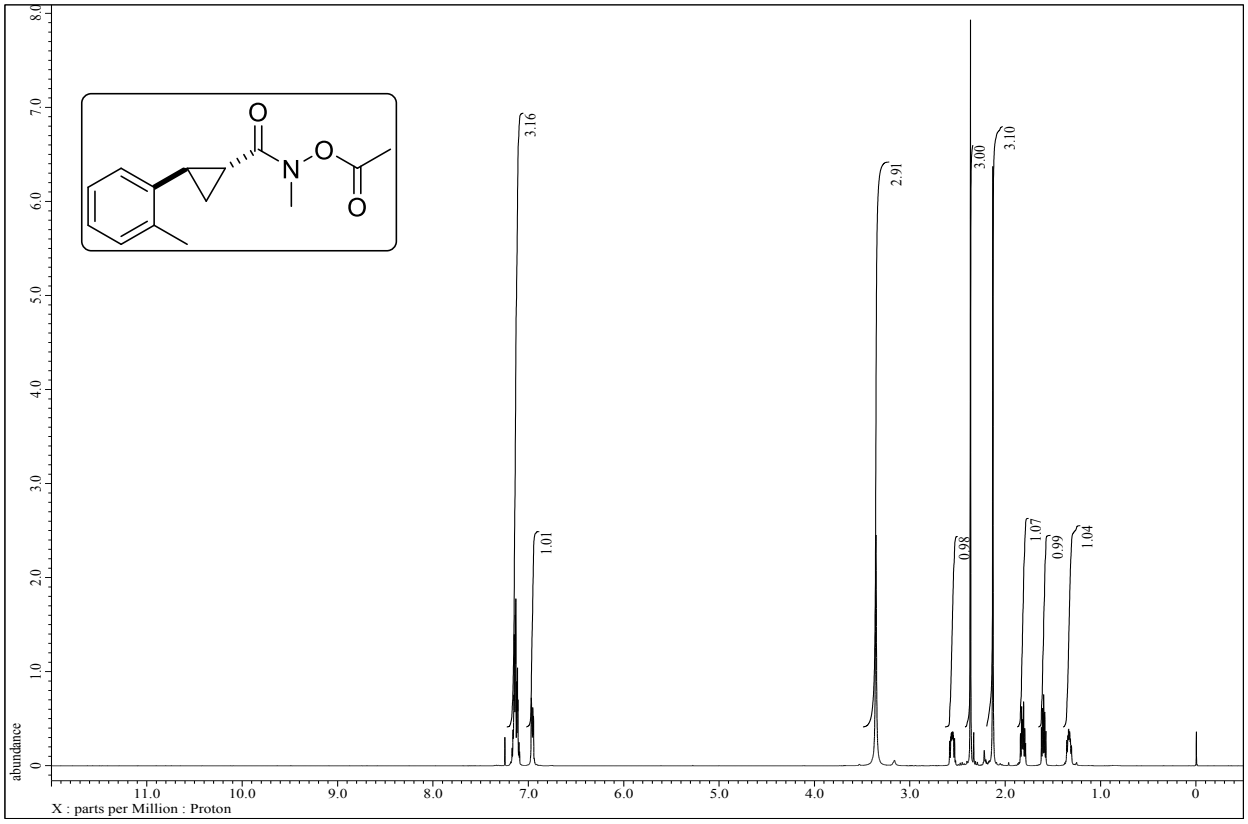

O
N
O
abundance
173.16838
140.88428
128.52747
128.01260
126.32498
77.43165
77.11700
76.79283
61.79493
32.70493
26.00212
21.66388
16.57242
X : parts per Million : Carbon13

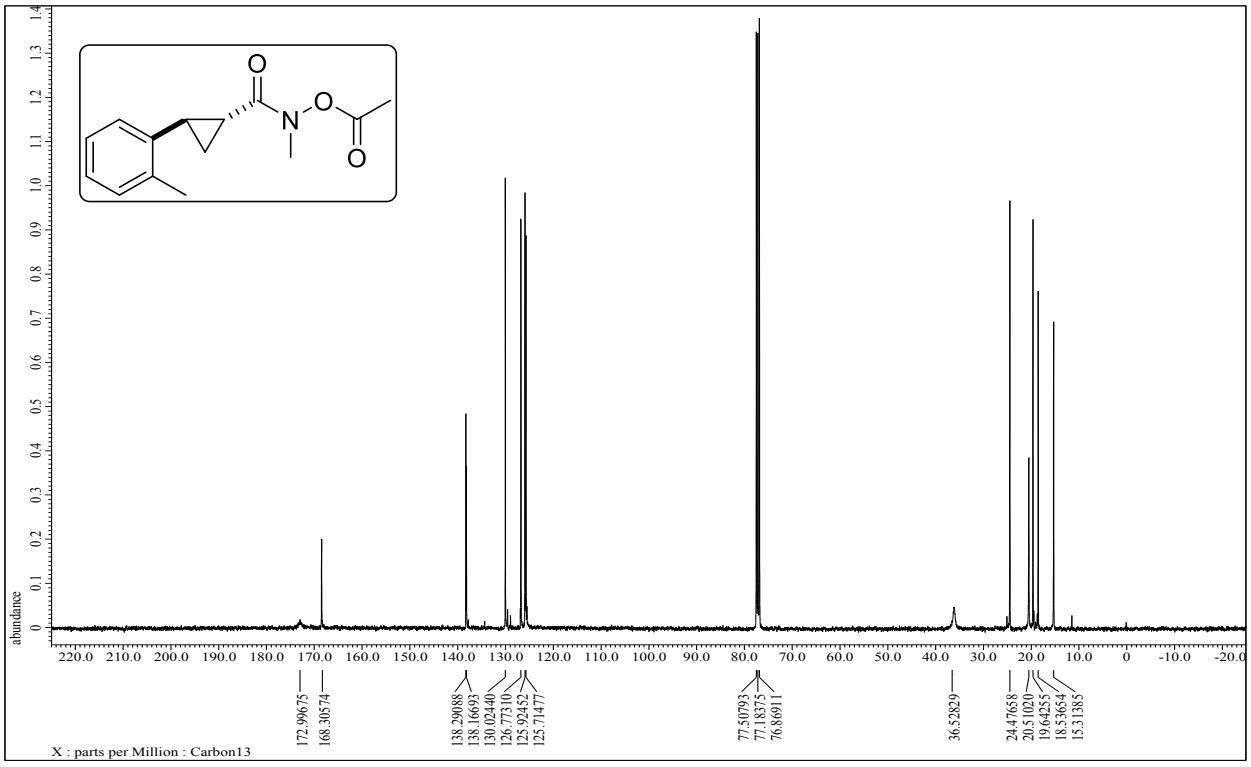

O
N
O
10.18
3.00
1.91
1.13
0.93
1.03
1.02
abundance
X : parts per Million : Proton

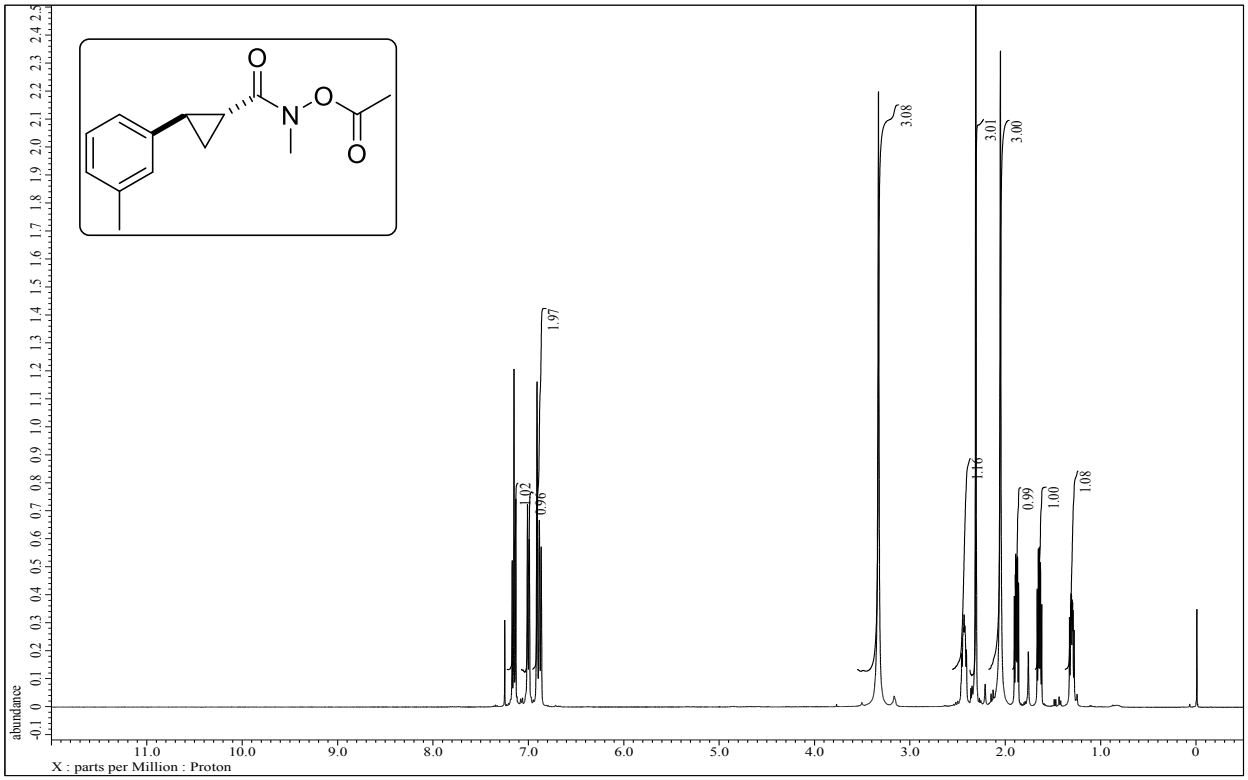

O
N
O
abundance
173.37834
140.82404
136.64624
128.69128
128.58636
128.47191
127.76607
126.44978
126.33532
77.45140
77.19386
76.93633
62.84822
26.28782
21.95742
16.89257
10.17759
X : parts per Million : Carbon13

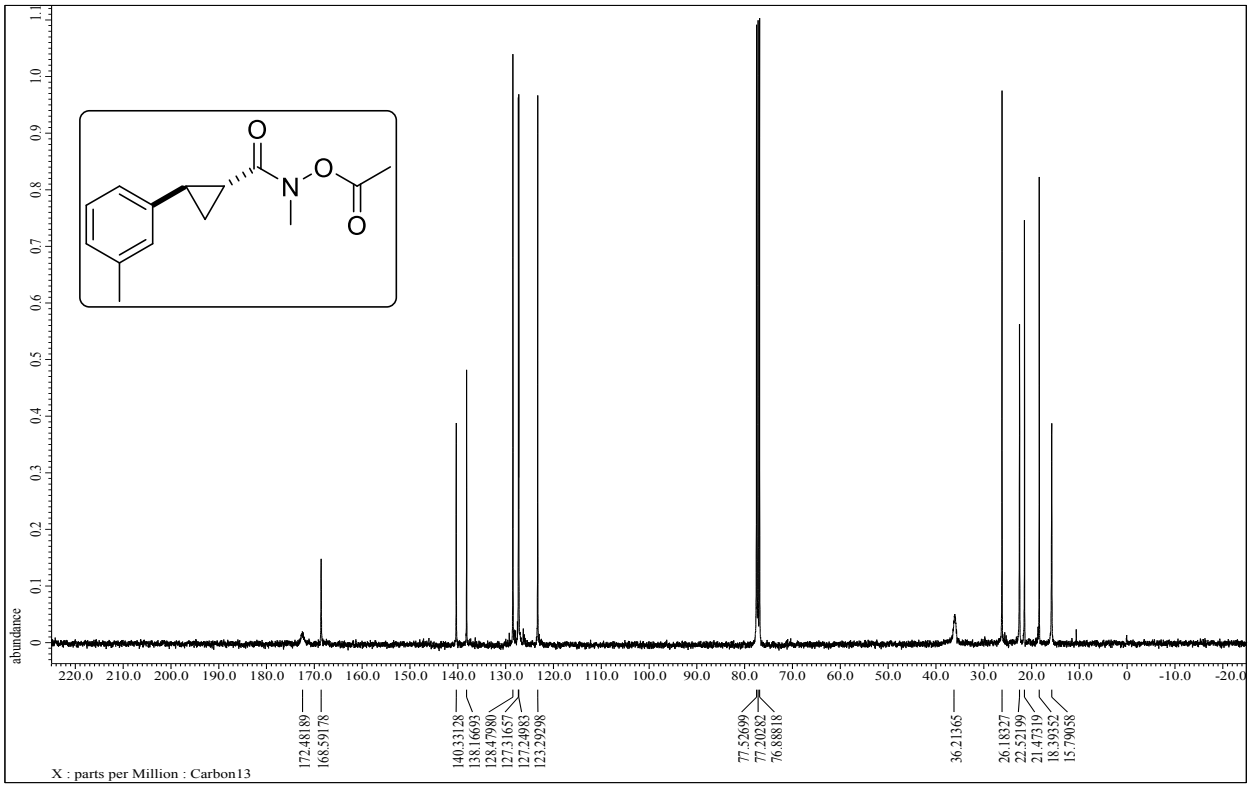

abundance
X : parts per Million : Proton
2.34
2.01
1.03
3.00
3.07
0.99
1.03
0.99
1.00

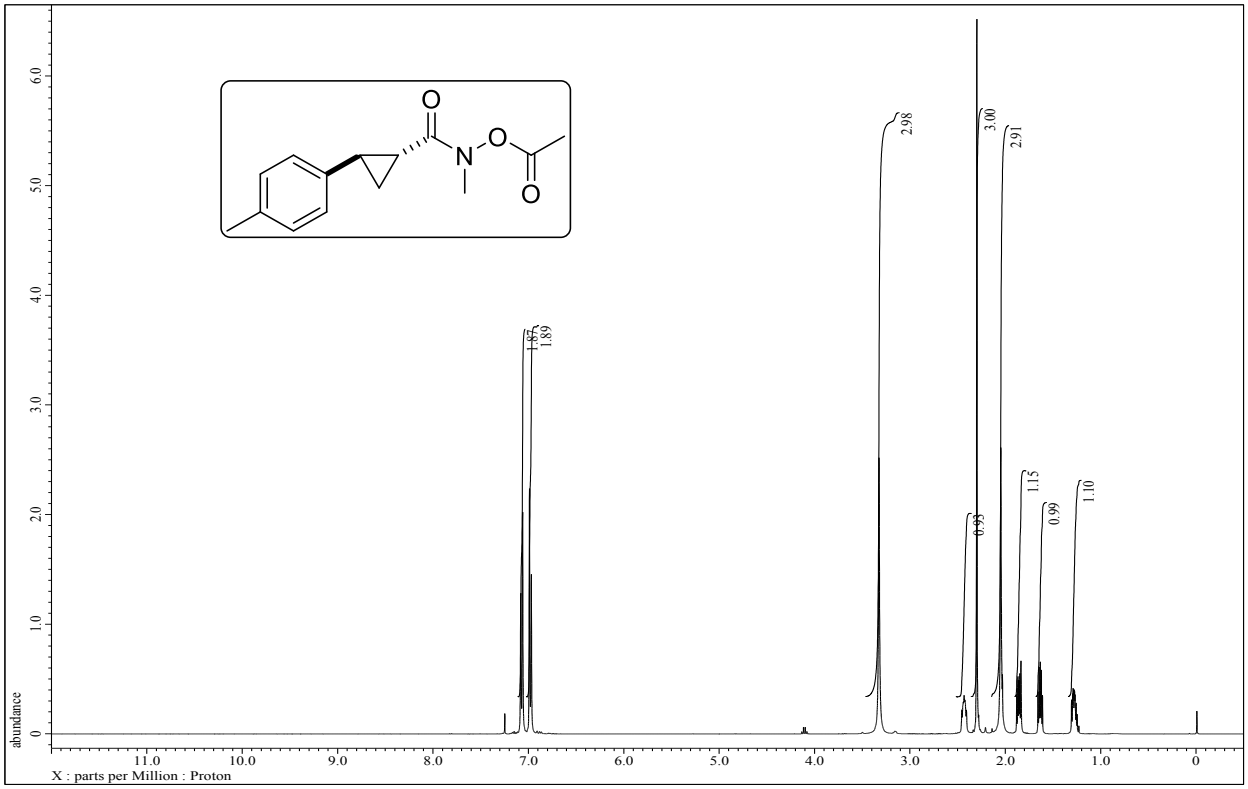

abundance
X : parts per Million : Carbon13
172.54851
168.62825
140.38527
128.58636
126.56424
126.33532
77.53725
77.27971
77.02217
35.90245
26.22105
22.65372
18.35193
15.83382

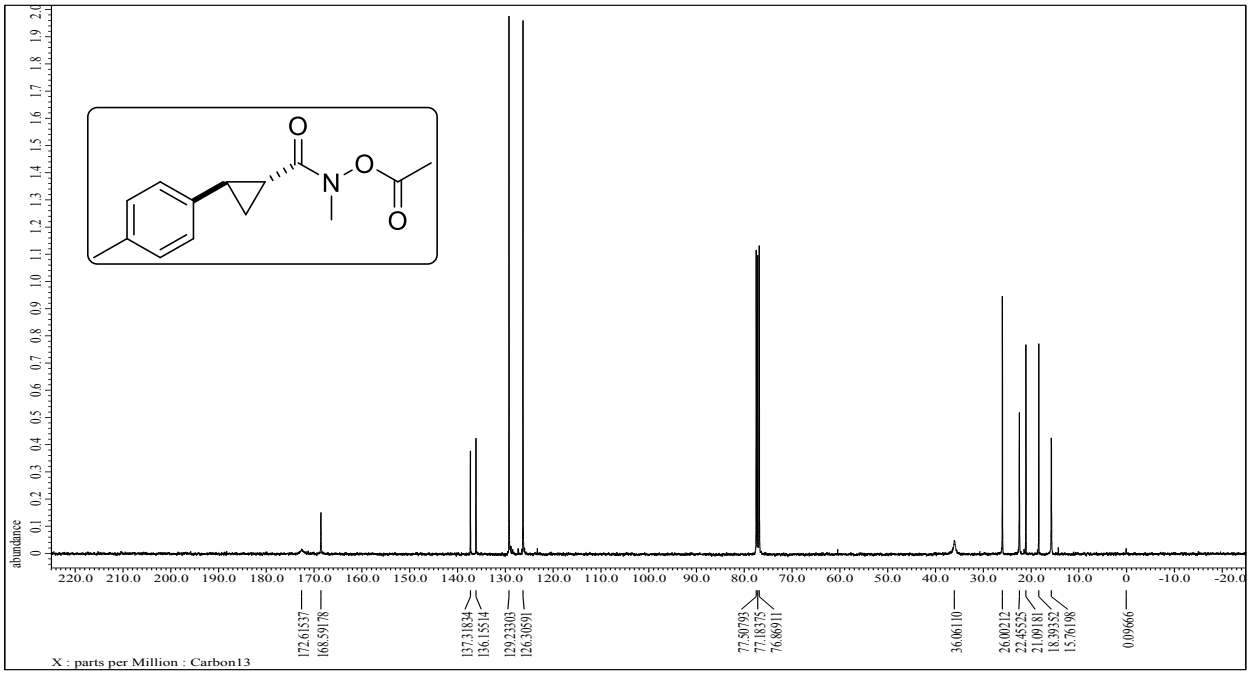

3.16
2.91
3.00
3.10
1.01
0.98
1.07
0.99
1.04
abundance
X : parts per Million : Proton

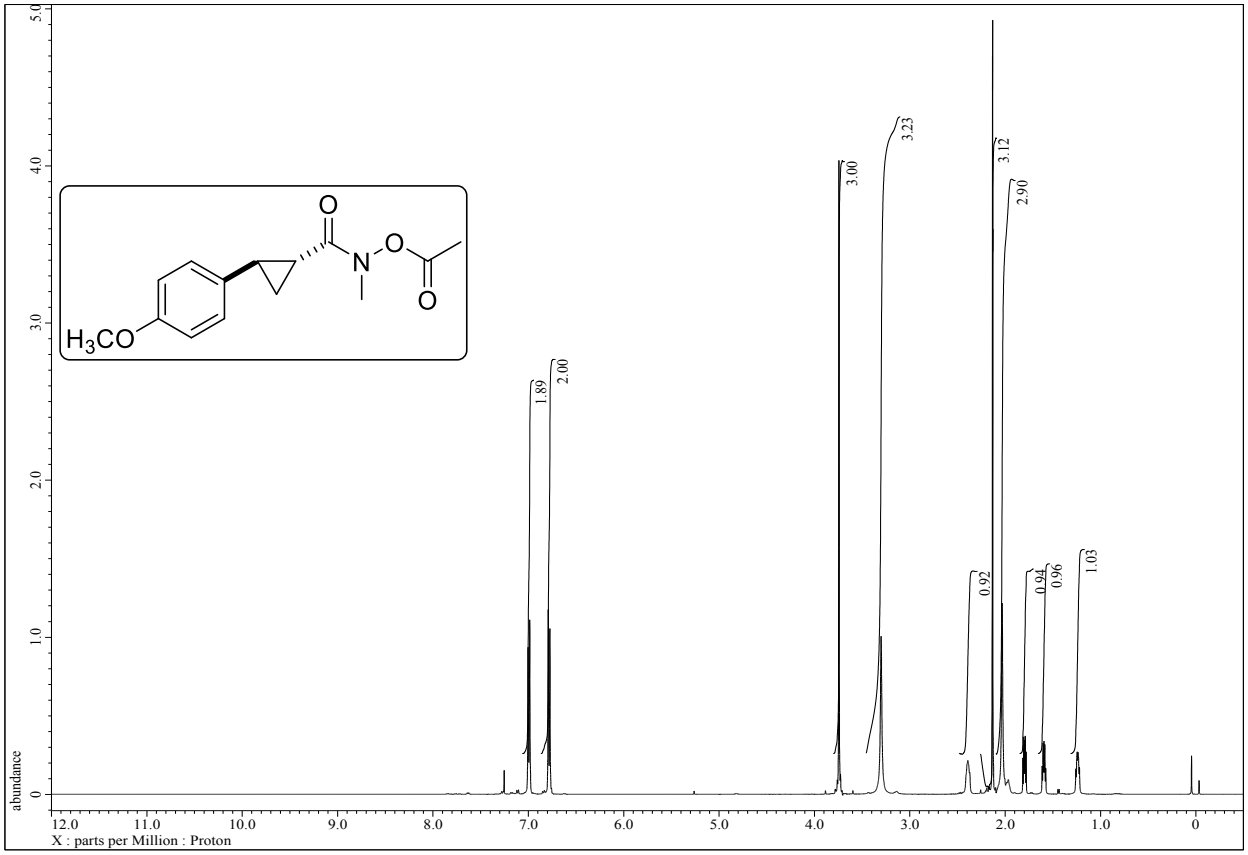

172.99675
168.30574
138.29088
138.16693
130.02440
126.77310
125.92452
125.71477
77.50793
77.18375
76.86911
36.52829
24.47658
20.51020
19.64255
18.53654
15.31385
abundance
X : parts per Million : Carbon13

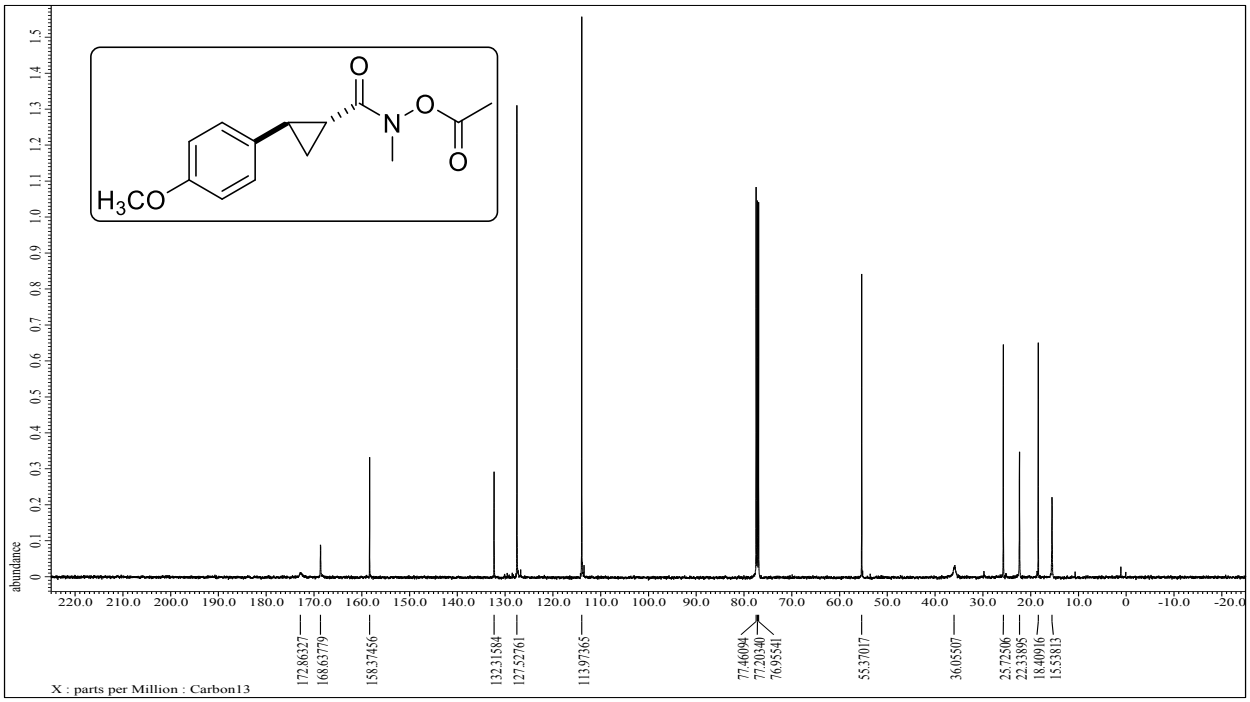

abundance
X : parts per Million : Proton
3.08
3.01
3.00
1.97
1.16
1.08
1.02
0.99
1.00
0.96

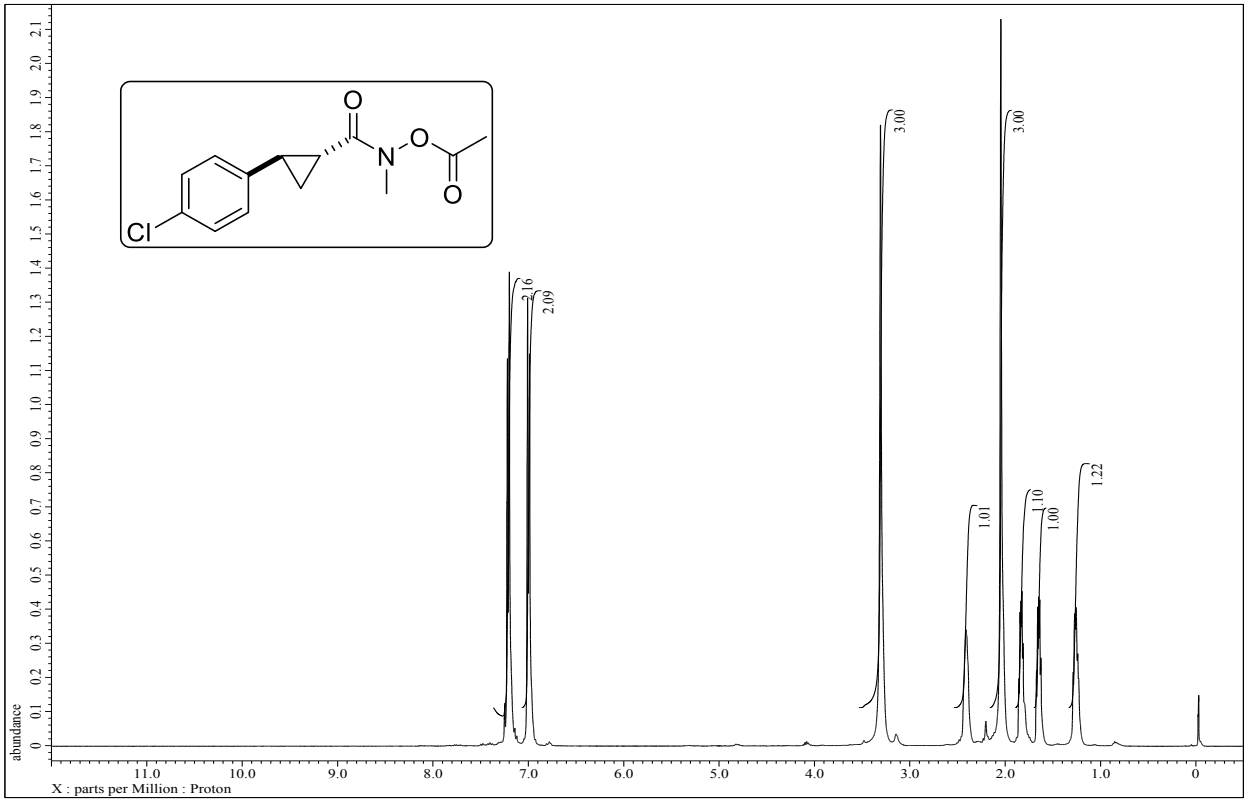

abundance
X : parts per Million : Carbon13
172.48189
168.59178
140.33128
138.16693
128.47980
127.31657
127.24983
123.29298
77.52699
77.20282
76.88818
36.21365
26.18327
22.52199
21.47319
18.39352
15.79058


abundance
X : parts per Million : Proton
1.87
1.89
2.98
3.00
2.91
0.93
1.15
0.99
1.10

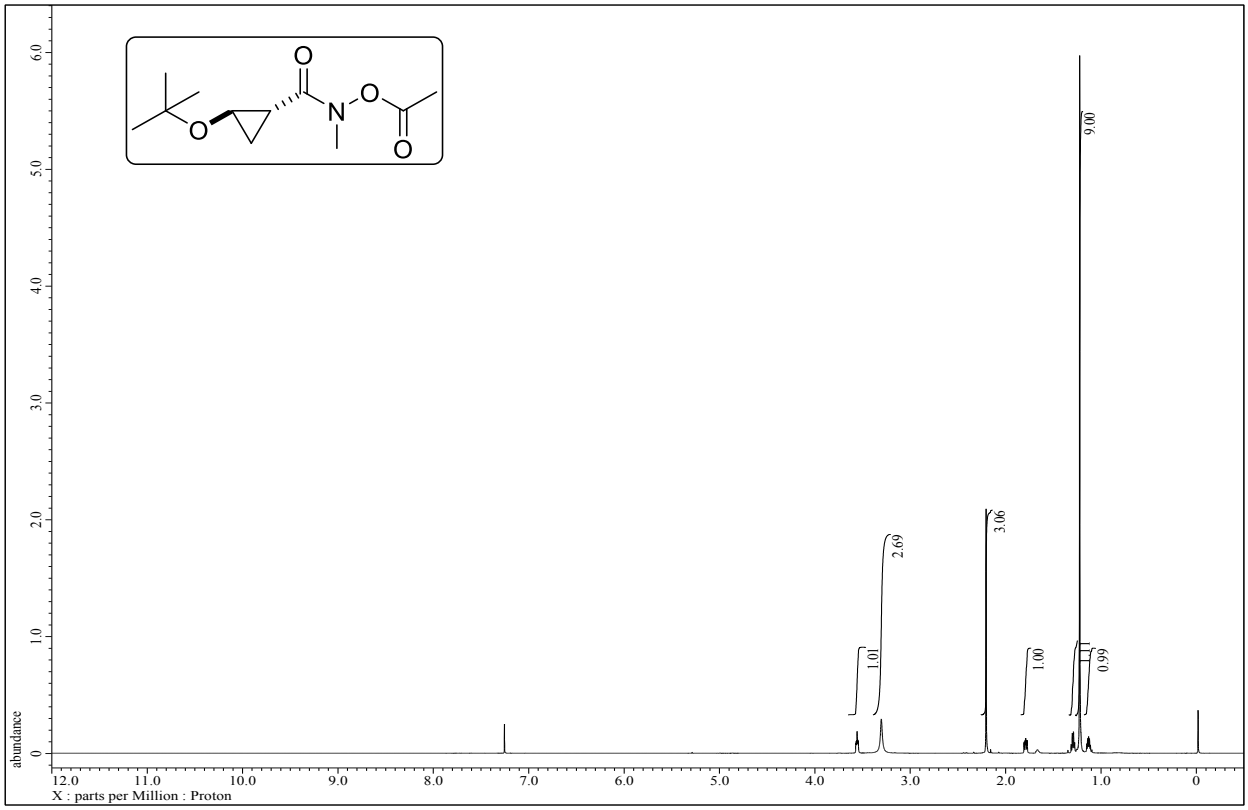

abundance
X : parts per Million : Carbon13
172.61537
168.59178
137.31834
136.15514
129.23303
126.30591
77.50793
77.18375
76.86911
36.06110
26.00212
22.45525
21.09181
18.39352
15.76198
0.09666

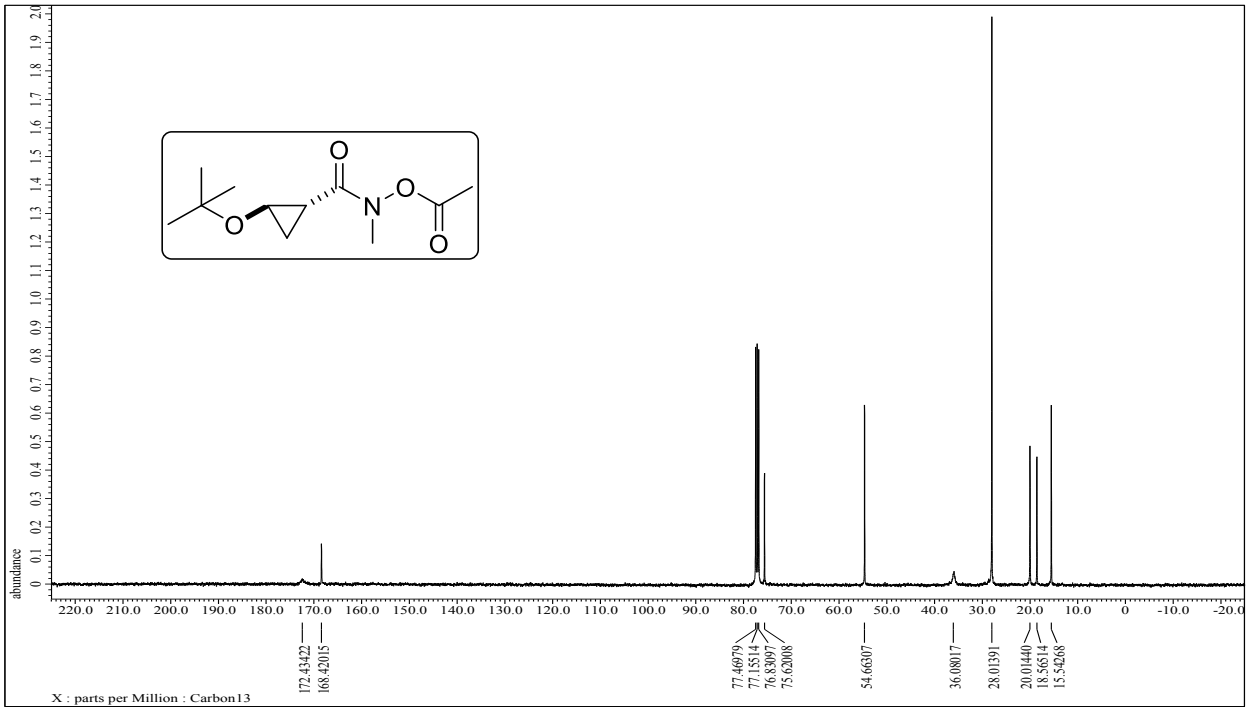

O
N
O
O
H3CO
1.89
2.00
3.00
3.23
3.12
2.90
0.92
0.94
0.96
1.03
abundance
X : parts per Million : Proton

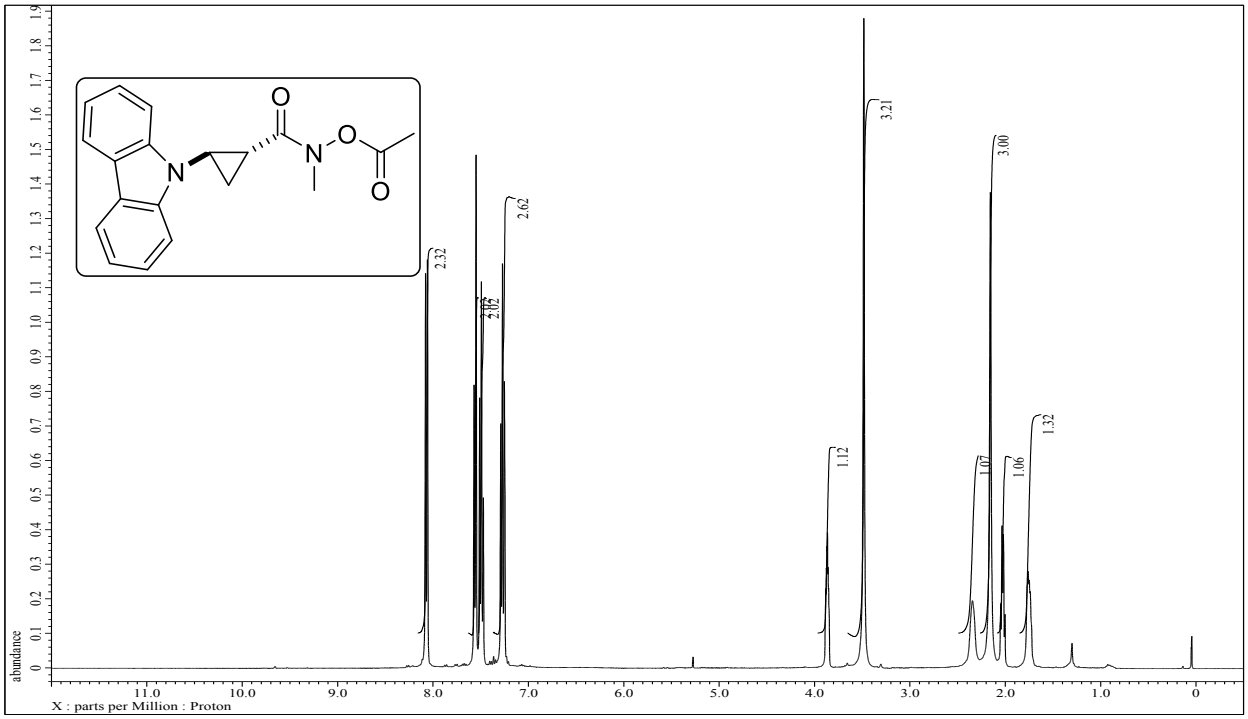

O
N
O
O
H3CO
abundance
172.86327
168.63779
158.37456
132.31584
127.52761
113.97365
77.46094
77.20340
76.95541
55.37017
36.05507
25.72506
22.33895
18.40916
15.53813
X : parts per Million : Carbon13

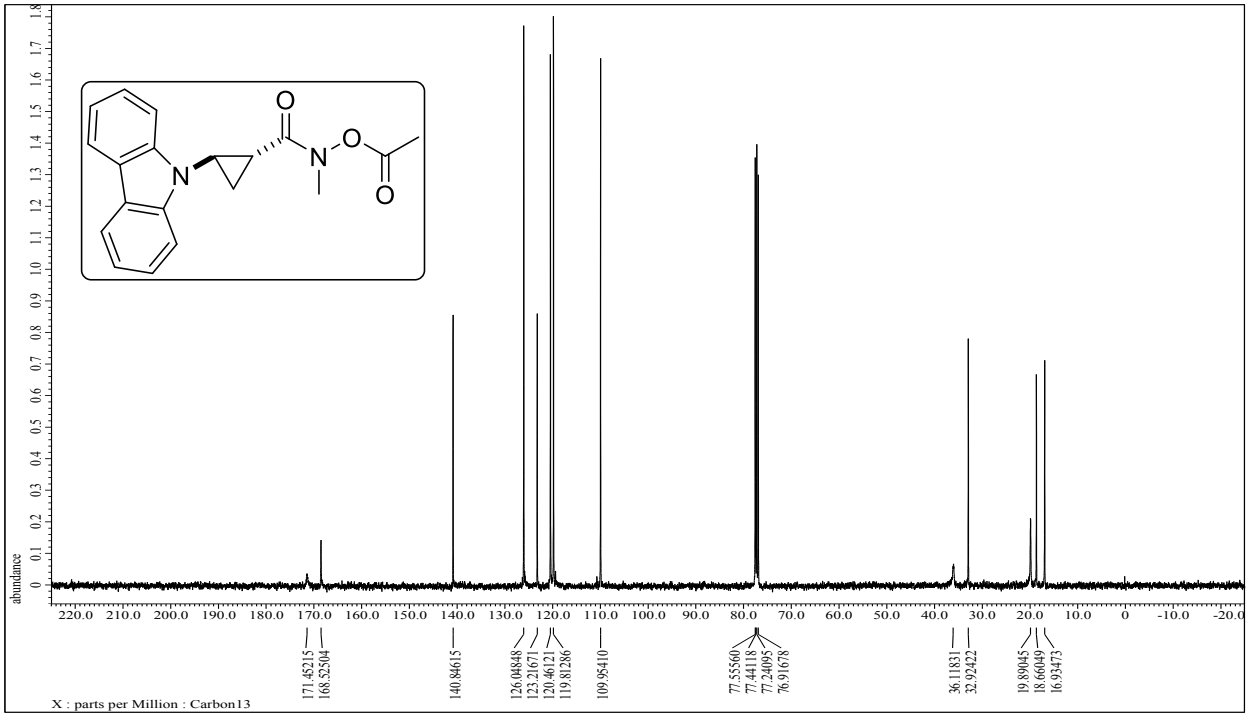

abundance
X : parts per Million : Proton
3.00
3.00
2.16
2.09
1.01
1.10
1.00
1.22
Cl

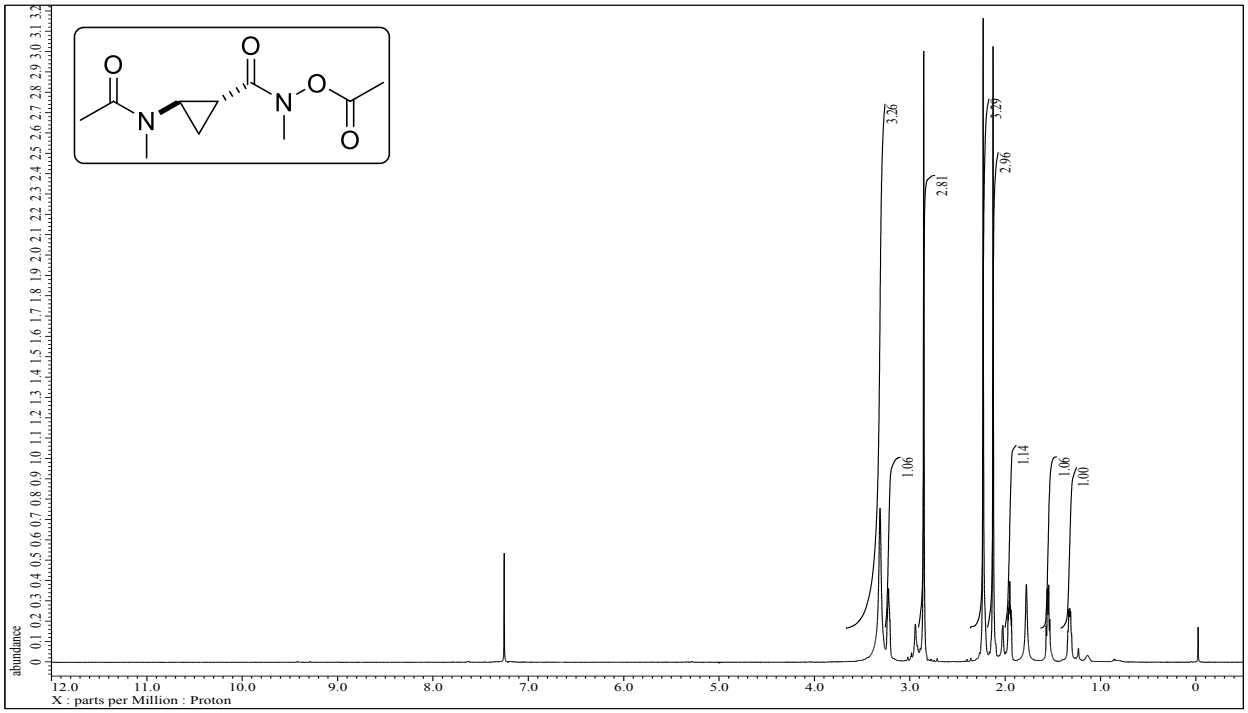

abundance
X : parts per Million : Carbon13
172.22446
168.56317
138.93922
132.21735
128.66095
127.72656
77.48885
77.16468
76.85004
36.00389
25.56353
22.64594
18.40306
15.80011
Cl

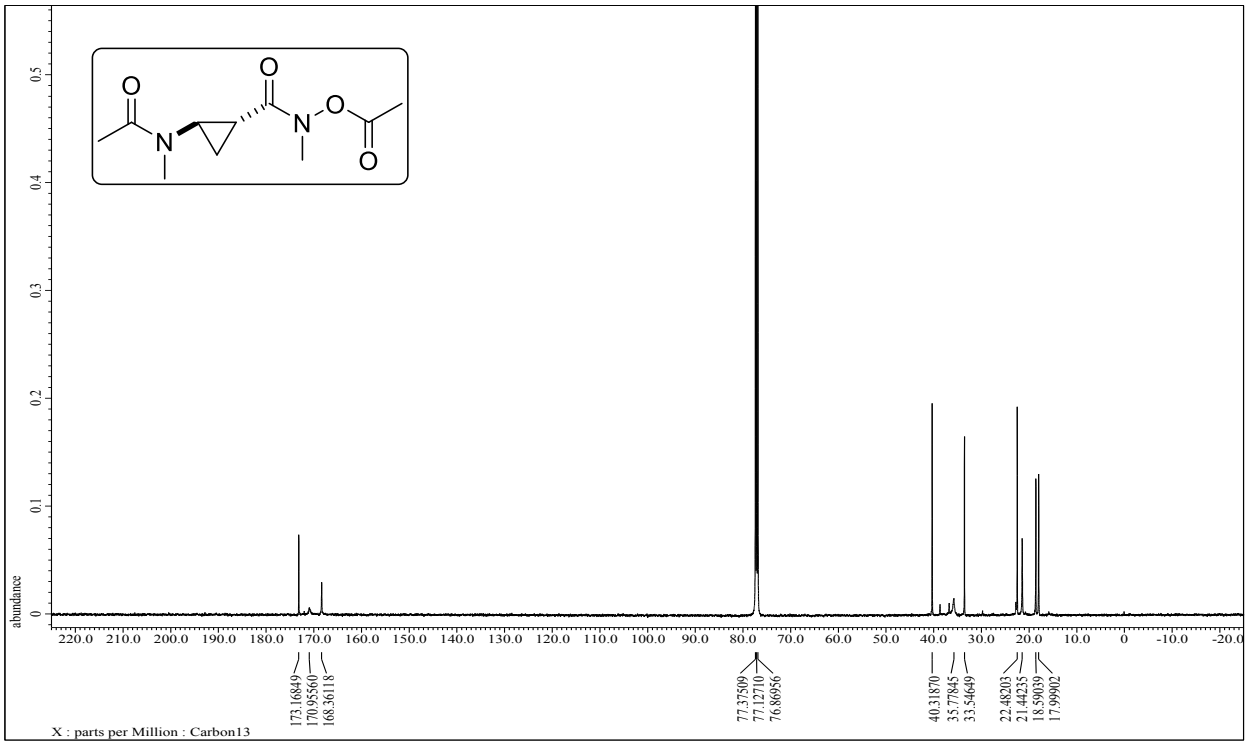

abundance
X : parts per Million : Proton
1.01
2.69
3.06
1.00
0.99
9.00

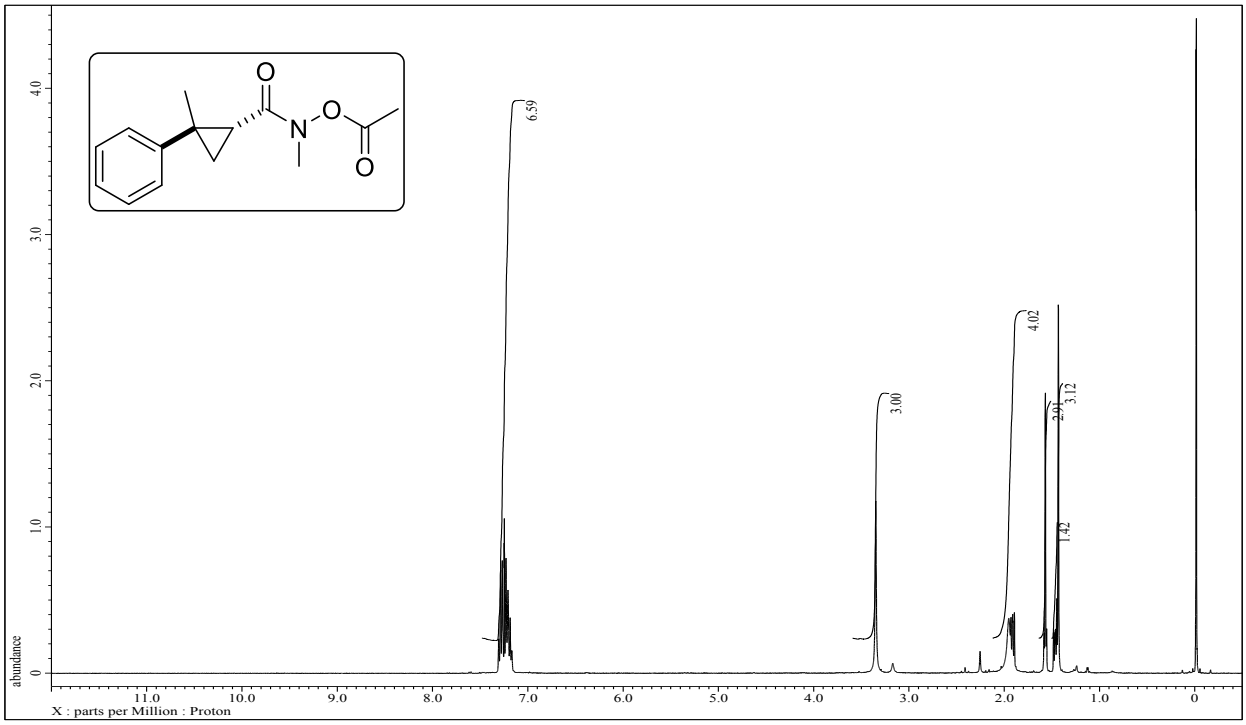

abundance
X : parts per Million : Carbon13
172.43422
168.42015
77.44679
77.15514
76.83097
75.62008
54.66307
36.08017
28.01391
20.01440
18.56514
15.54268

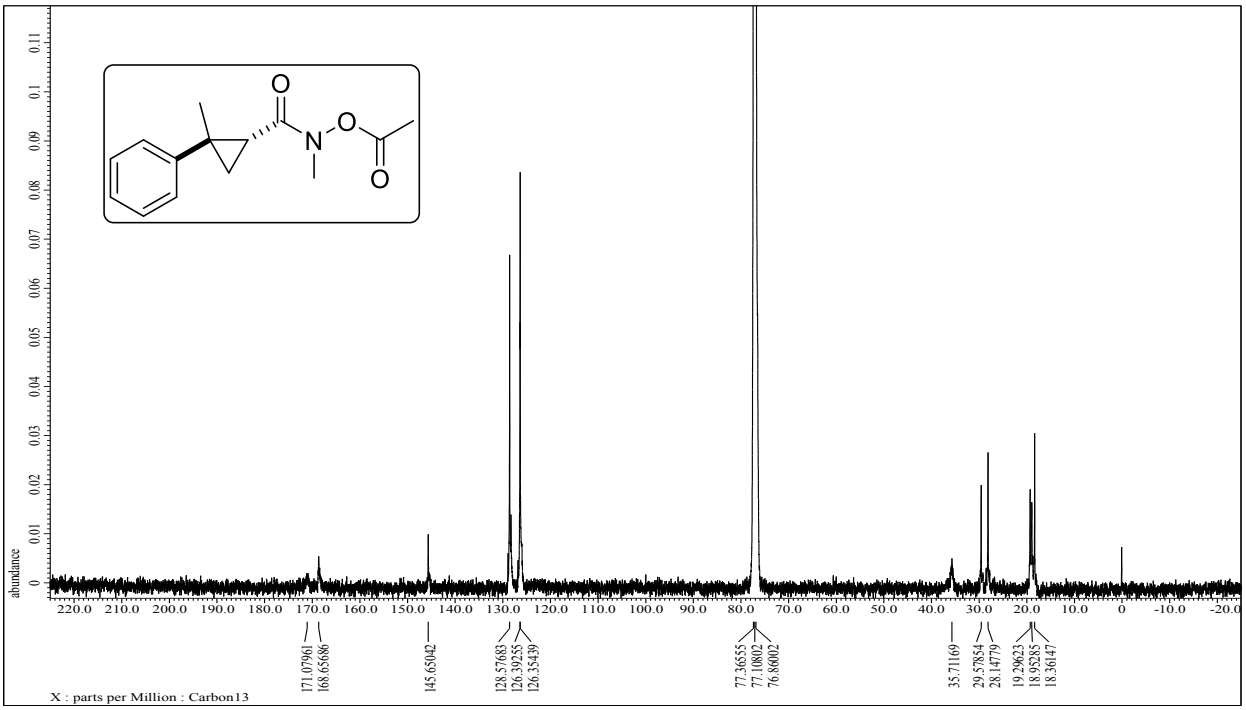

abundance
X : parts per Million : Proton
2.32
2.62
3.21
3.00
1.12
1.32
1.07
1.06

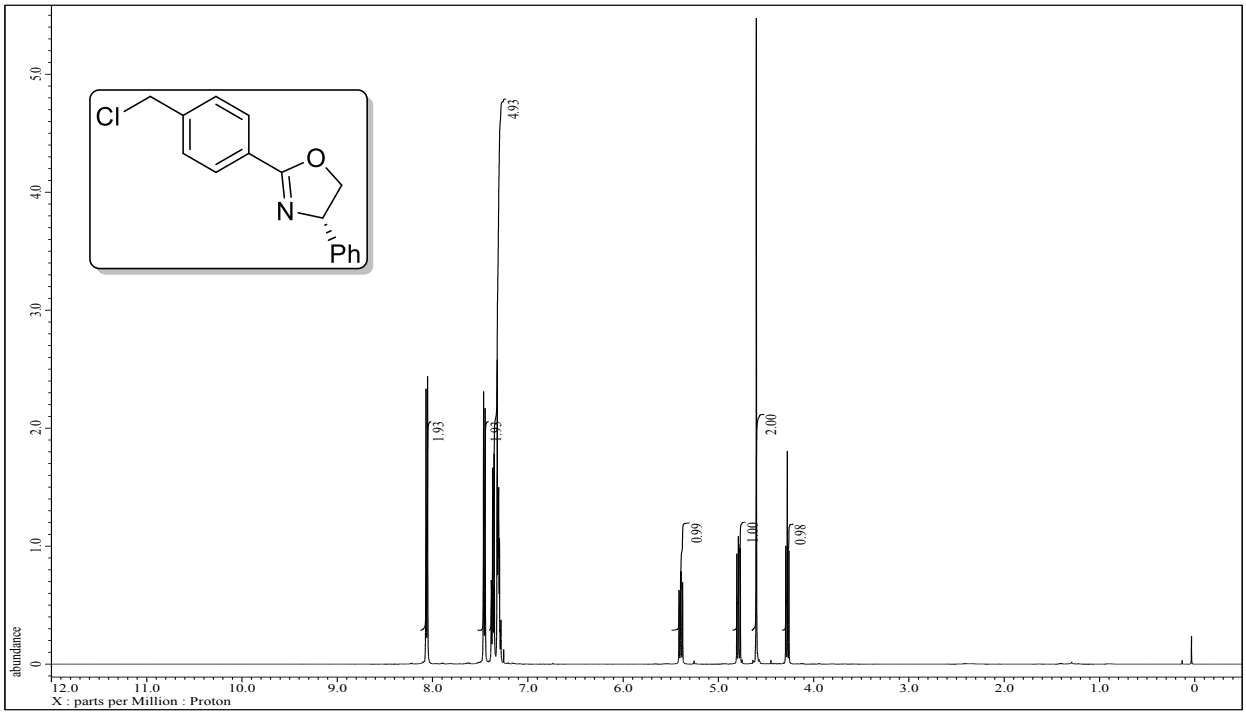

abundance
X : parts per Million : Carbon13
171.45215
168.52504
140.84615
126.04848
123.21671
120.46121
119.81286
109.95410
77.55560
77.44118
77.24095
76.91678
36.11831
32.92422
19.89045
18.66049
16.93473

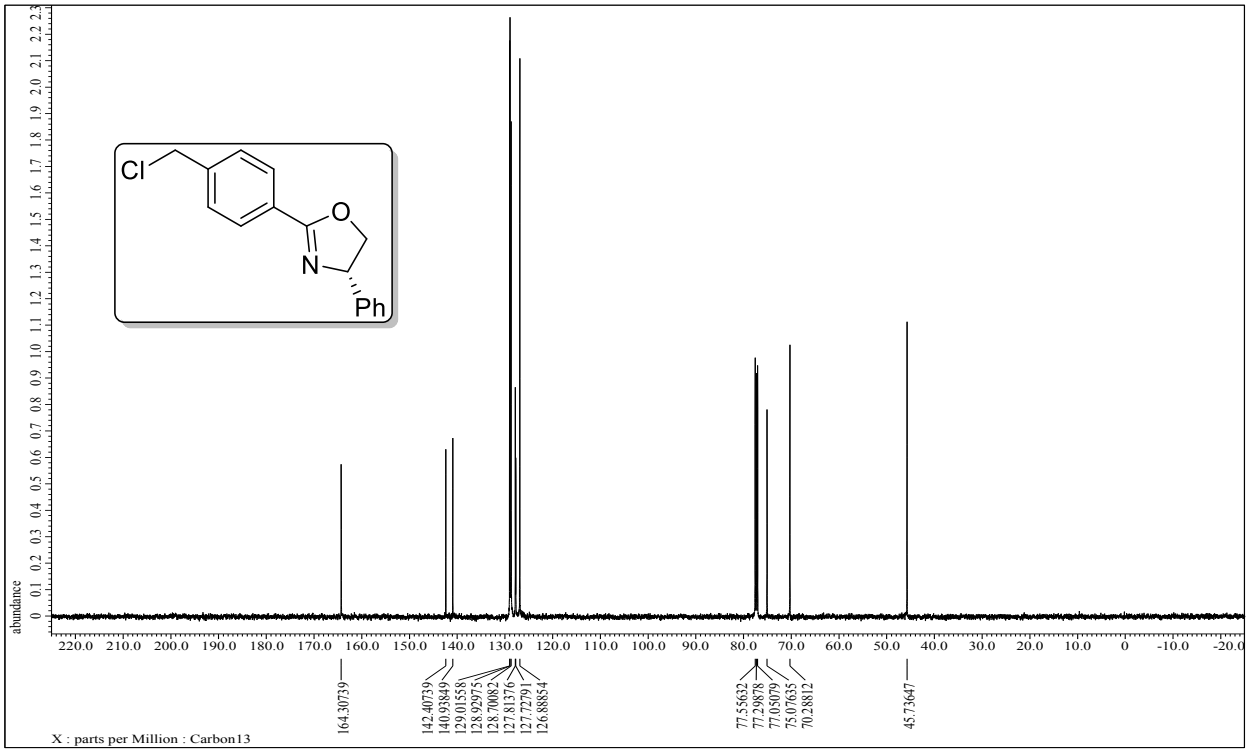

abundance
X : parts per Million : Proton
3.26
2.81
3.29
2.96
1.14
1.06
1.06
1.00

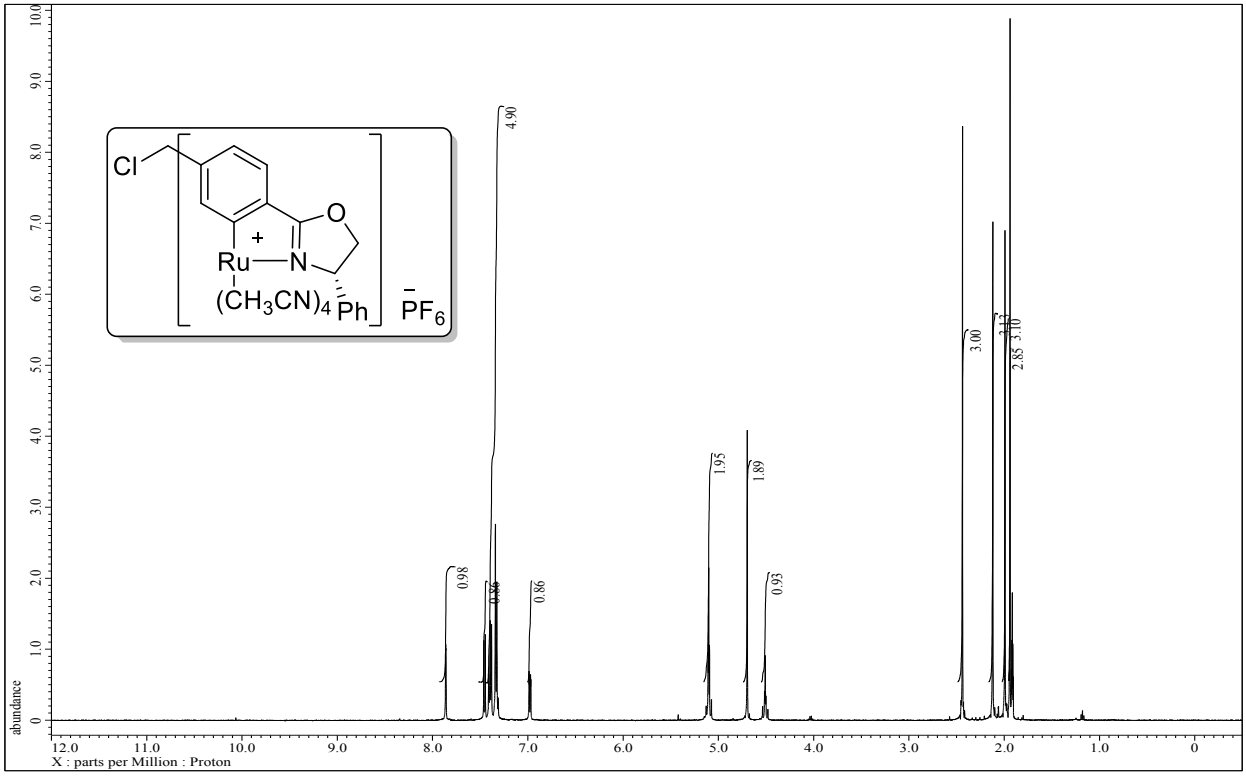

abundance
X : parts per Million : Carbon13
173.16849
170.95560
168.36118
77.37509
77.12710
76.86956
40.31870
35.77845
33.54649
22.48203
21.44235
18.59039
17.99902

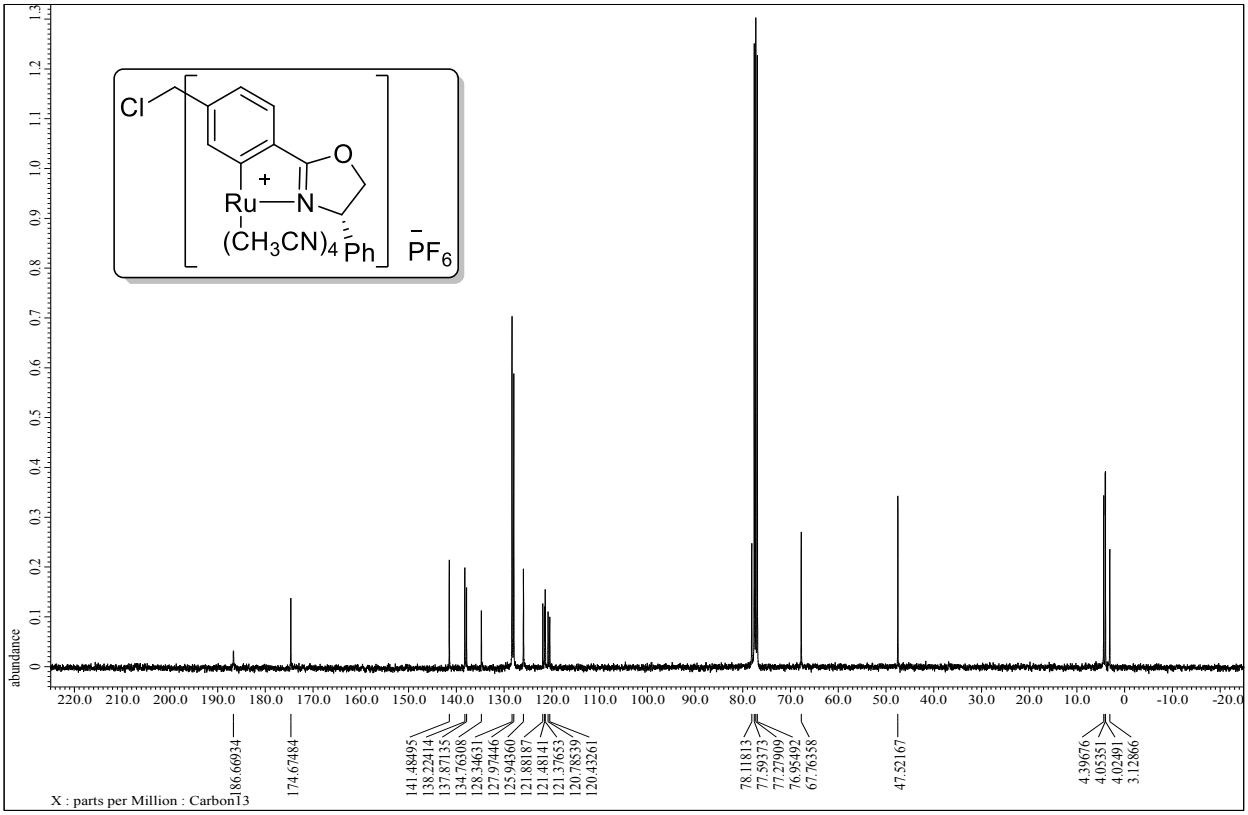

O
N
O
O
6.59
3.00
4.02
3.12
2.07
1.42
abundance
X : parts per Million : Proton

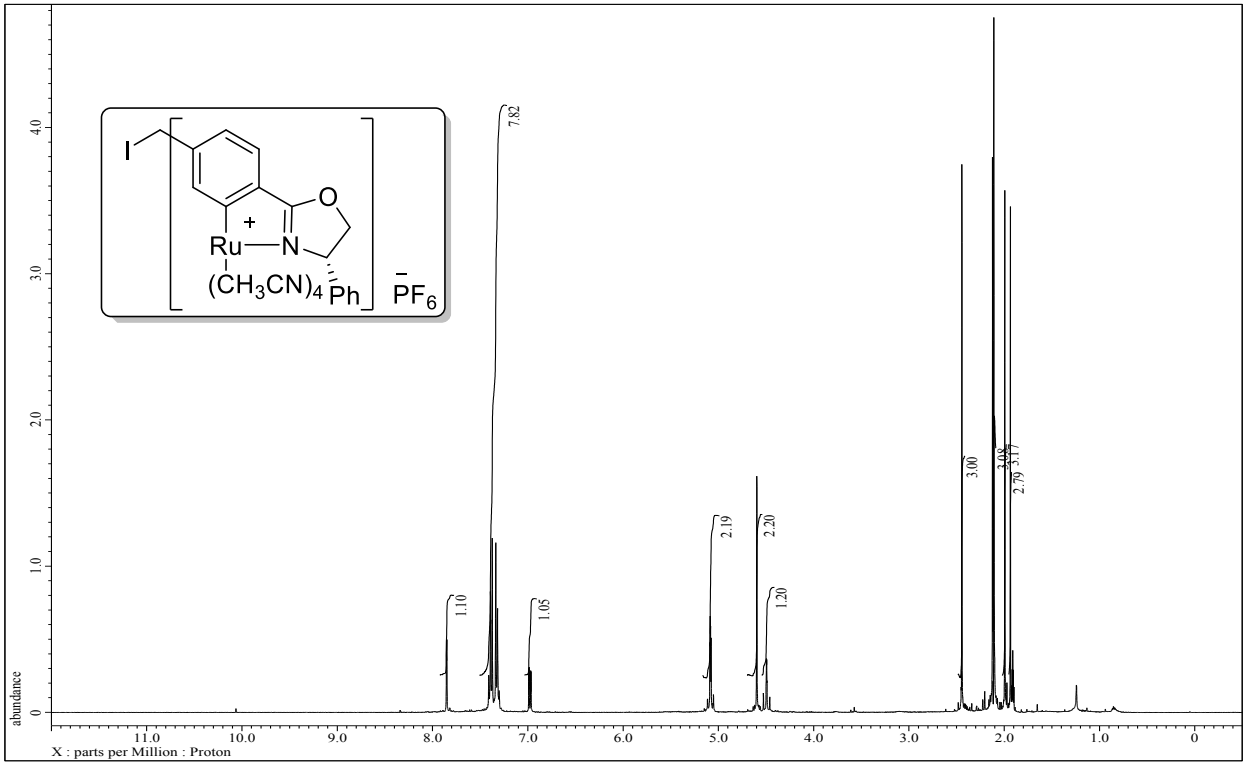

O
N
O
O
abundance
171.07961
168.65686
145.65042
128.57683
126.39255
126.35439
77.36555
77.10802
76.86002
35.71169
29.57854
28.14779
19.29623
18.95285
18.36147
X : parts per Million : Carbon13

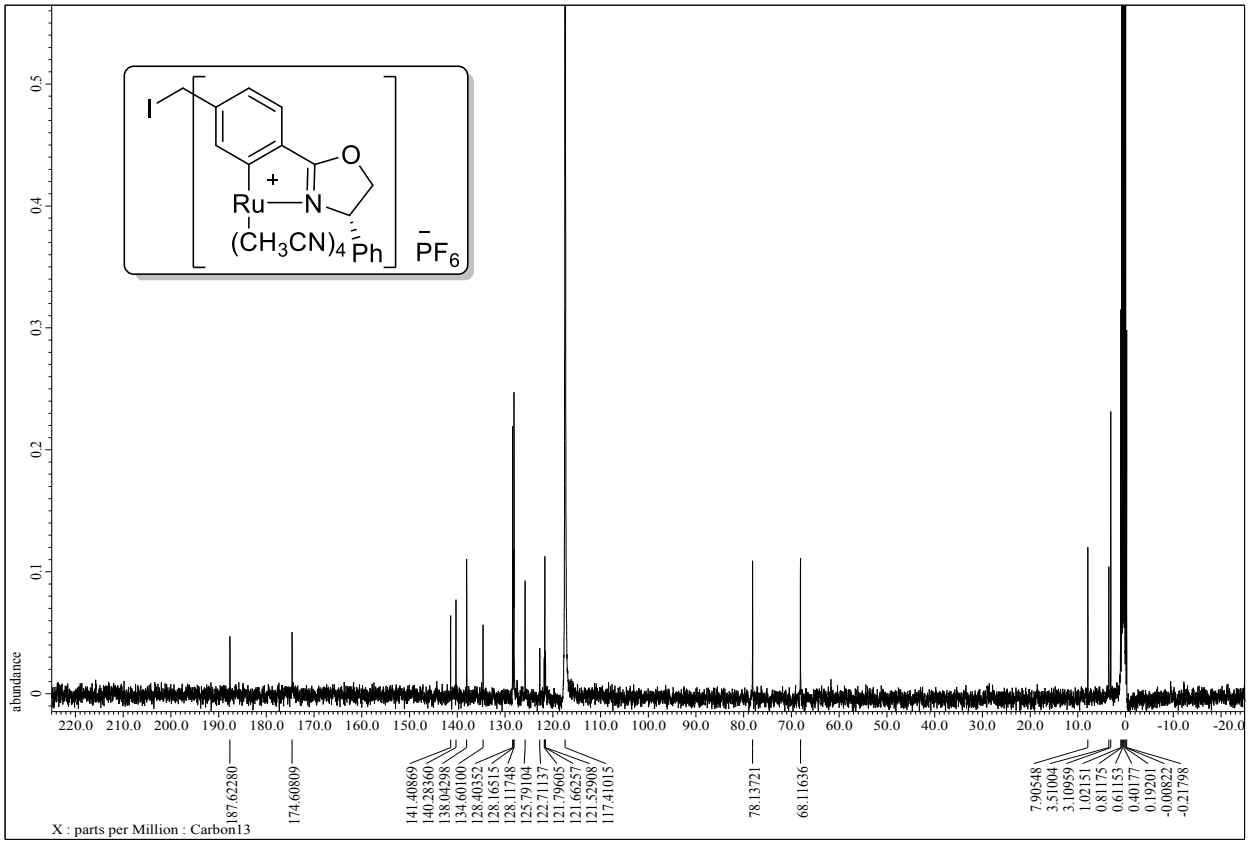

Cl
O
N
Ph
4.93
1.93
1.93
2.00
0.99
1.00
0.98
abundance
X : parts per Million : Proton

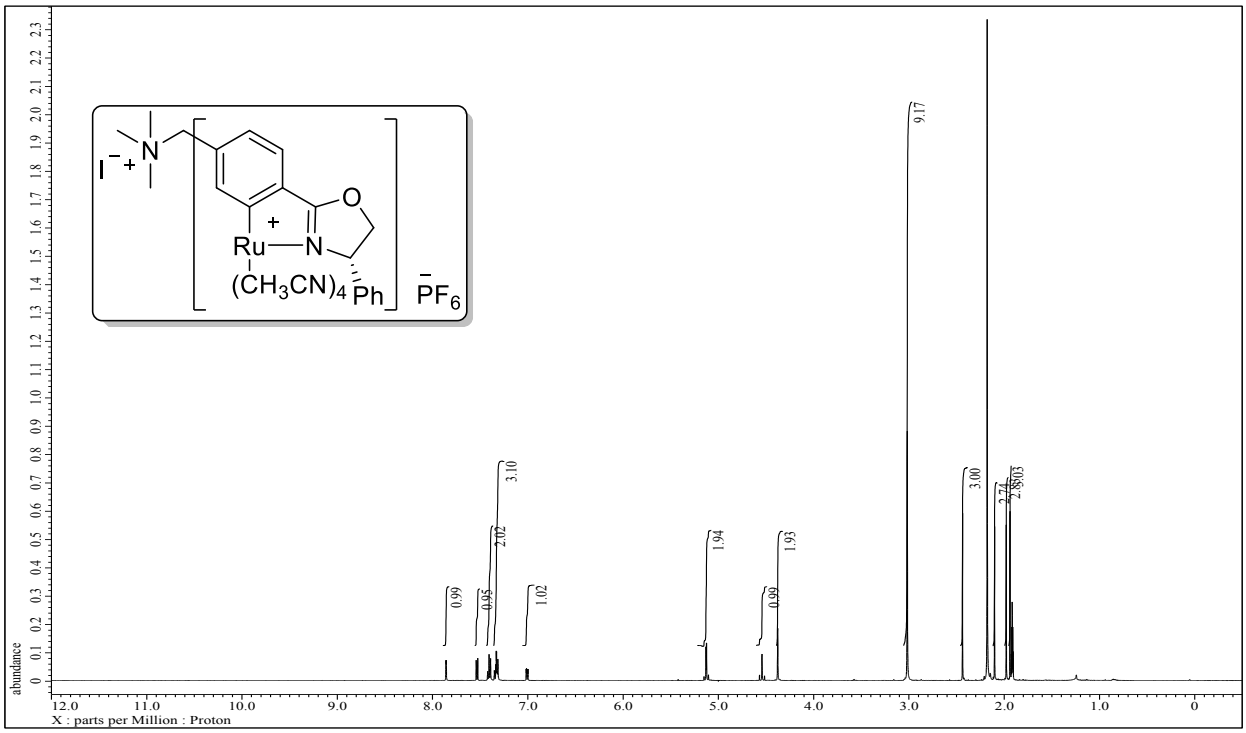

Cl
O
N
Ph
abundance
164.30739
142.40739
140.93849
129.01558
128.92975
128.70082
127.81376
127.72791
126.88854
77.35632
77.29878
77.05079
75.07635
70.28812
45.73647
X : parts per Million : Carbon13

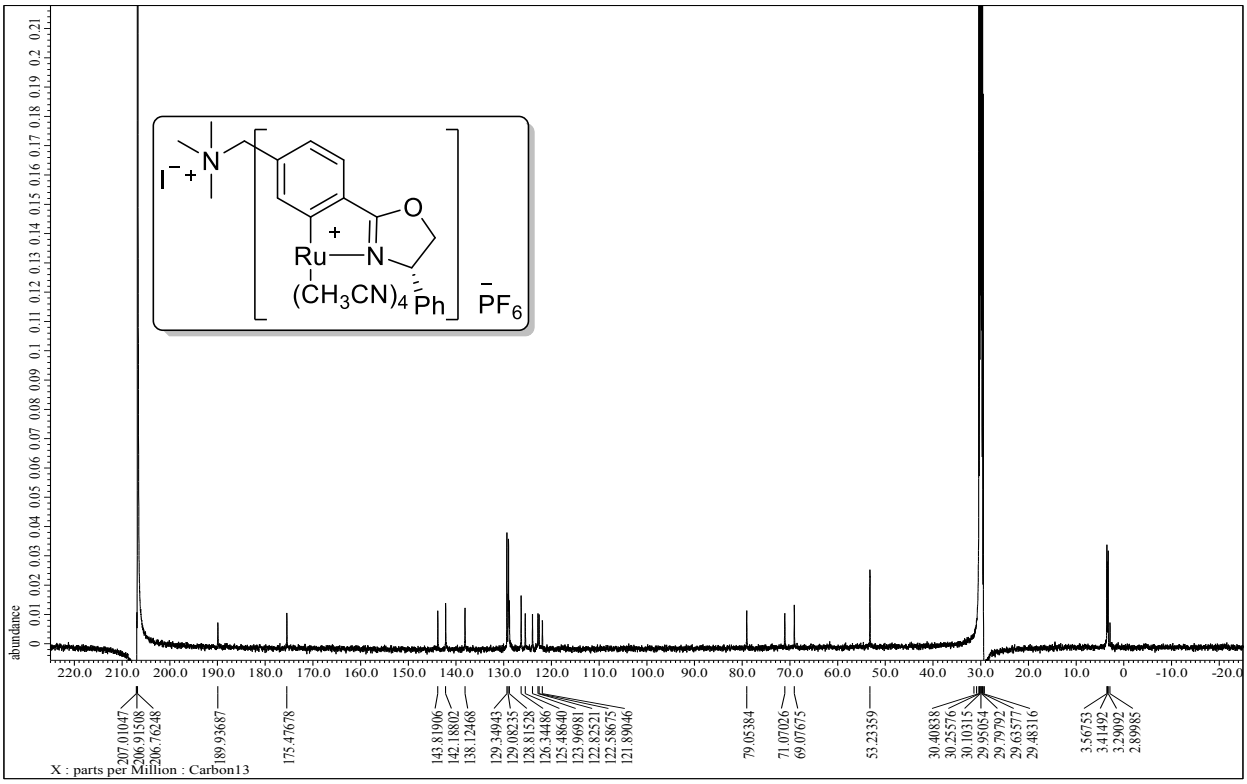

Cl
O
Ru
N
(CH3CN)4
Ph
PF6
4.90
3.00
1.95
1.89
0.98
0.86
0.93
abundance
X : parts per Million : Proton

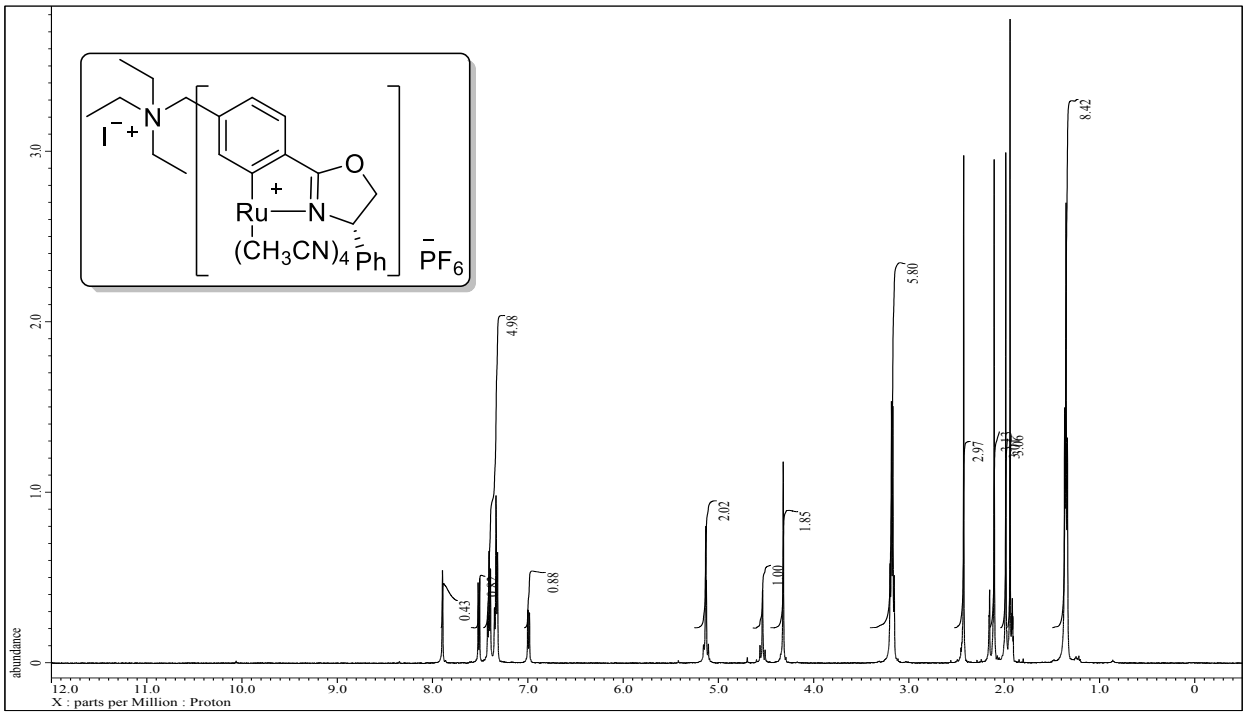

Cl
O
Ru
N
(CH3CN)4
Ph
PF6
abundance
186.66934
174.67484
141.48495
138.22414
137.87135
134.76308
128.34631
127.97446
125.94360
121.88187
121.48141
121.37653
120.78539
120.43261
78.11813
77.59373
77.27909
76.95492
67.76358
47.52167
4.39676
4.05351
4.02491
3.12866
X : parts per Million : Carbon13

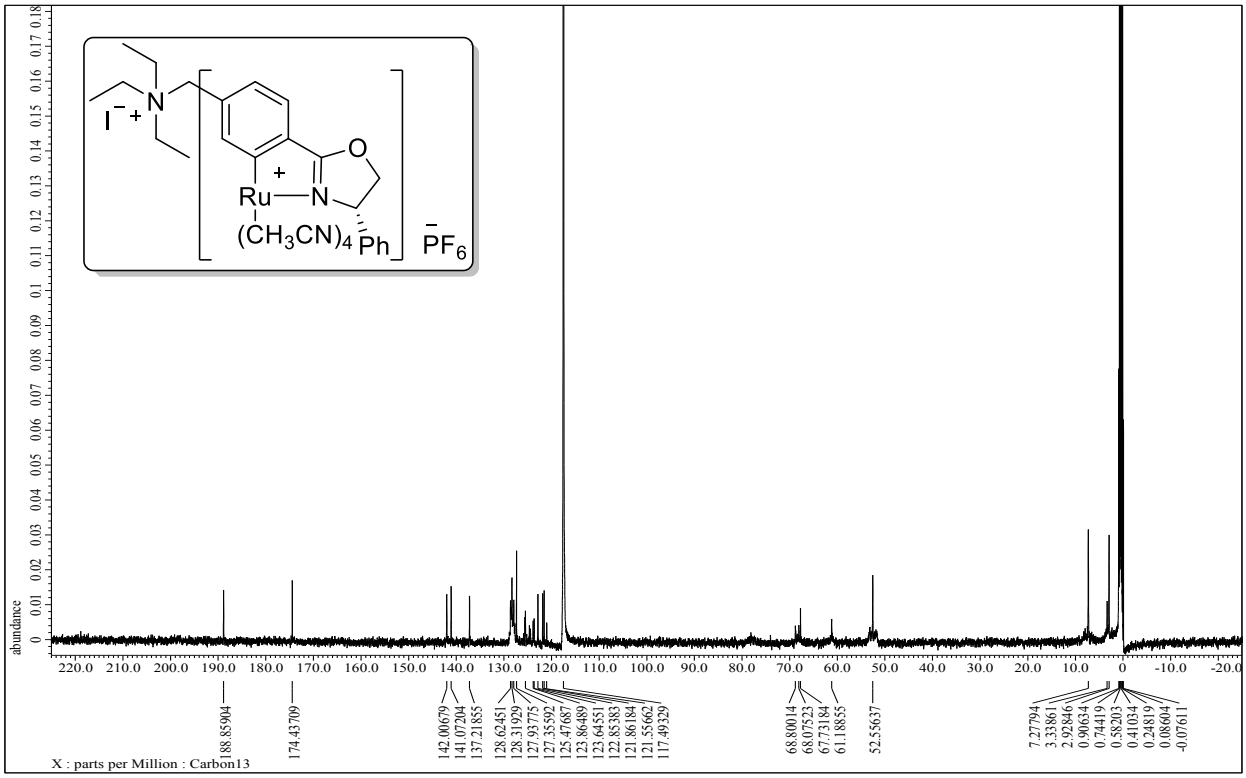

I
O
+
Ru—N
(CH3CN)4
Ph
PF6
7.82
1.10
1.05
2.19
2.20
1.20
3.00
3.08
3.17
2.79
abundance
X : parts per Million : Proton

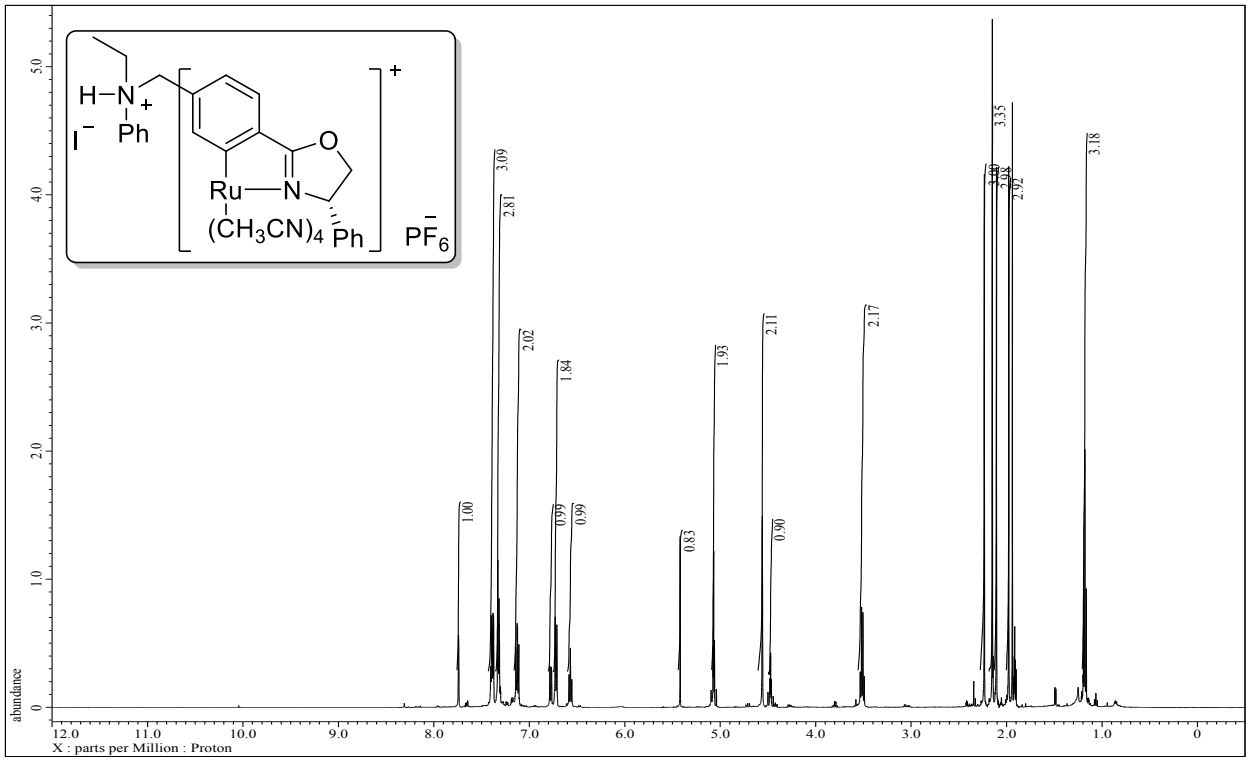

I
O
+
Ru—N
(CH3CN)4
Ph
PF6
abundance
187.62280
174.60809
141.40869
140.28360
138.04298
134.60100
128.40352
128.16515
128.11748
125.79104
122.71137
121.79605
121.66257
121.52908
117.41015
78.13721
68.11636
7.90548
3.51004
3.10959
1.02151
0.81175
0.61153
0.40177
0.19201
-0.00822
-0.21798
X : parts per Million : Carbon13

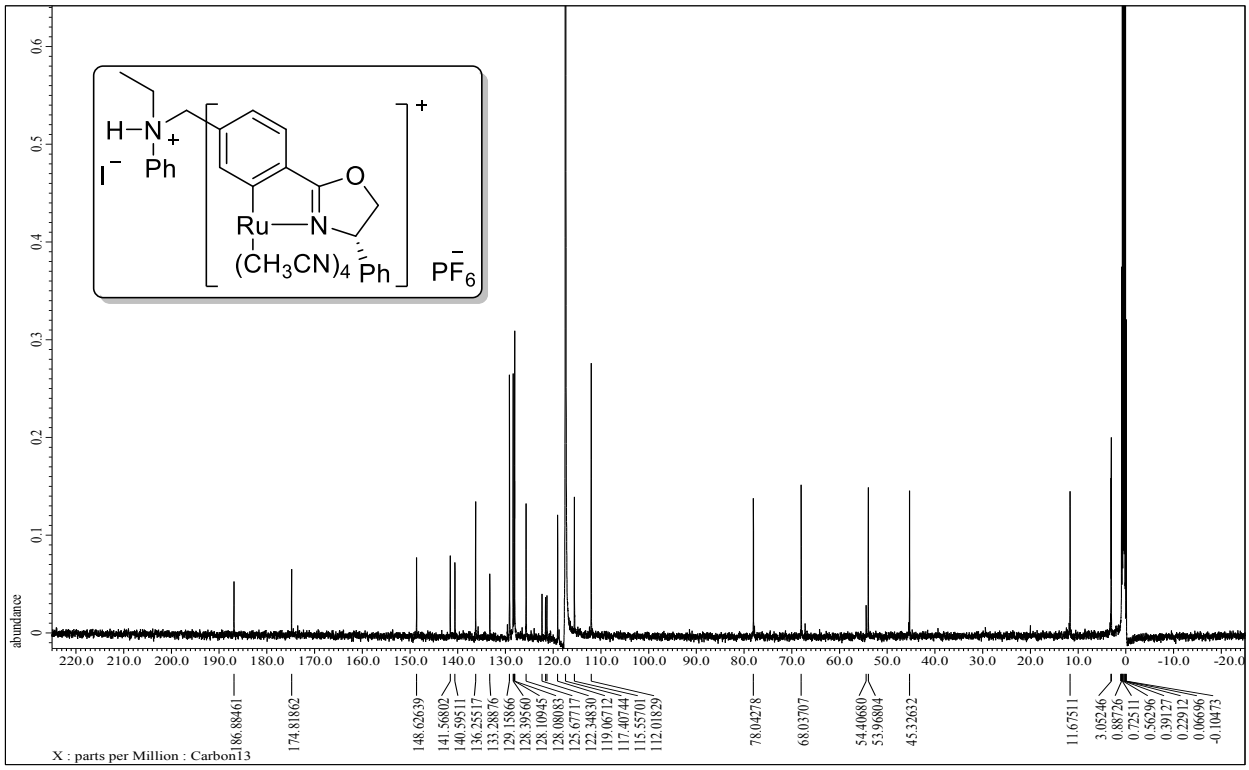

abundance
X : parts per Million : Proton
0.99
0.95
2.02
3.10
1.02
1.94
0.99
1.93
9.17
3.00
2.74
2.80

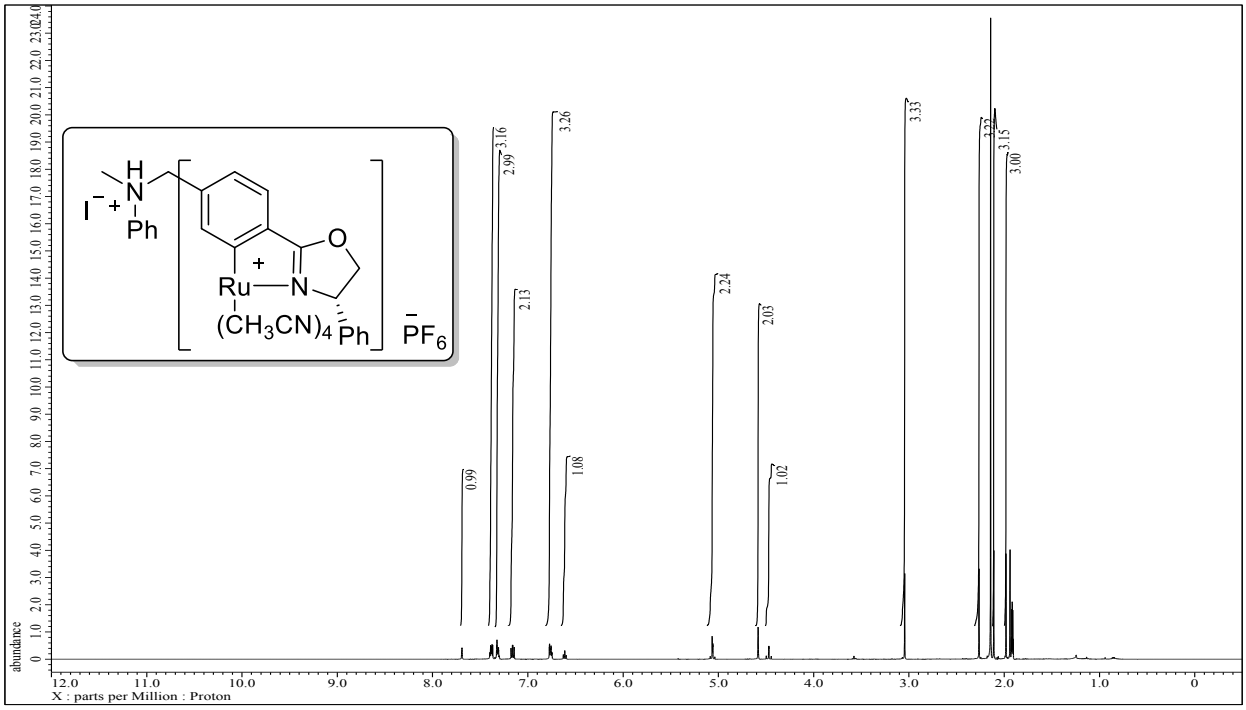

abundance
X : parts per Million : Carbon13
207.01047
206.91508
206.76248
189.93687
175.47678
143.81906
142.18802
138.12468
129.34943
129.08235
126.81528
126.34486
125.48640
123.96981
122.82521
122.58675
121.89046
79.05384
71.07026
69.07675
53.23359
30.40838
30.25576
30.10315
29.95054
29.79792
29.63577
29.48316
3.56753
3.41492
3.29092
2.89985

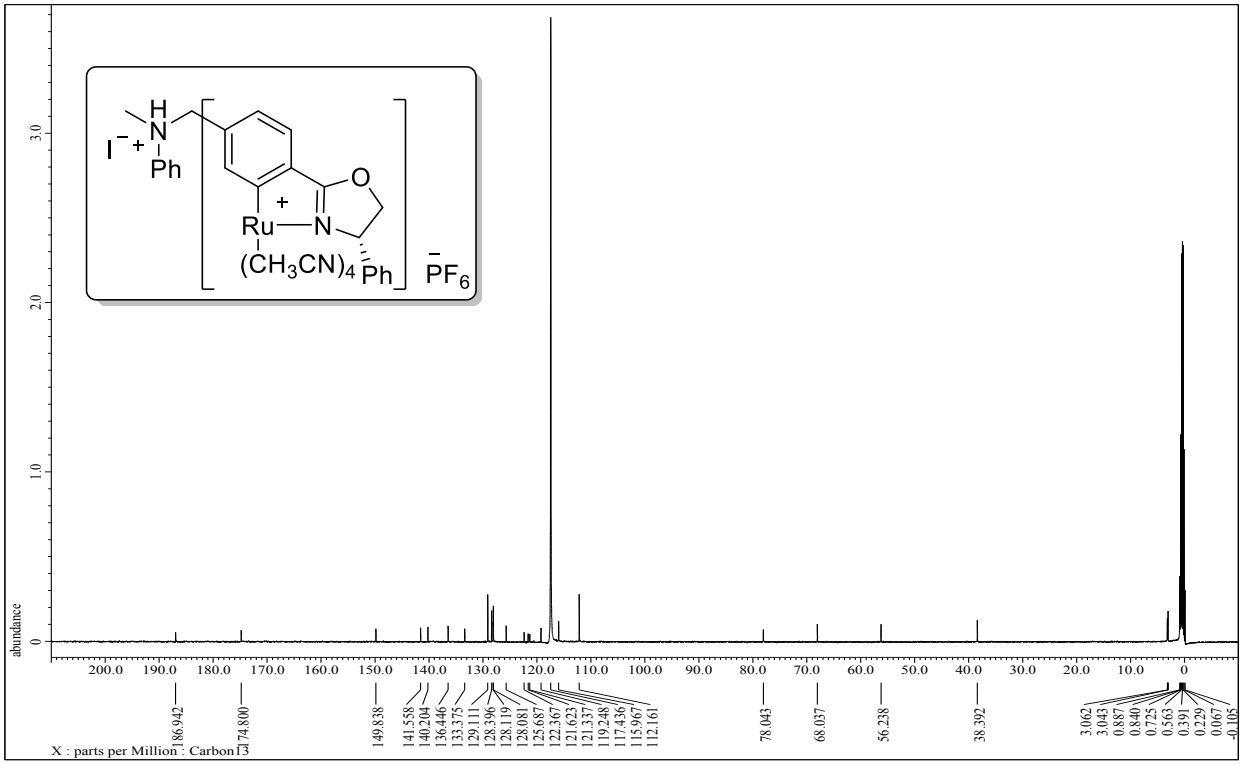

abundance
X : parts per Million : Proton
4.98
5.80
8.42
2.02
1.85
1.00
0.88
0.43
2.97

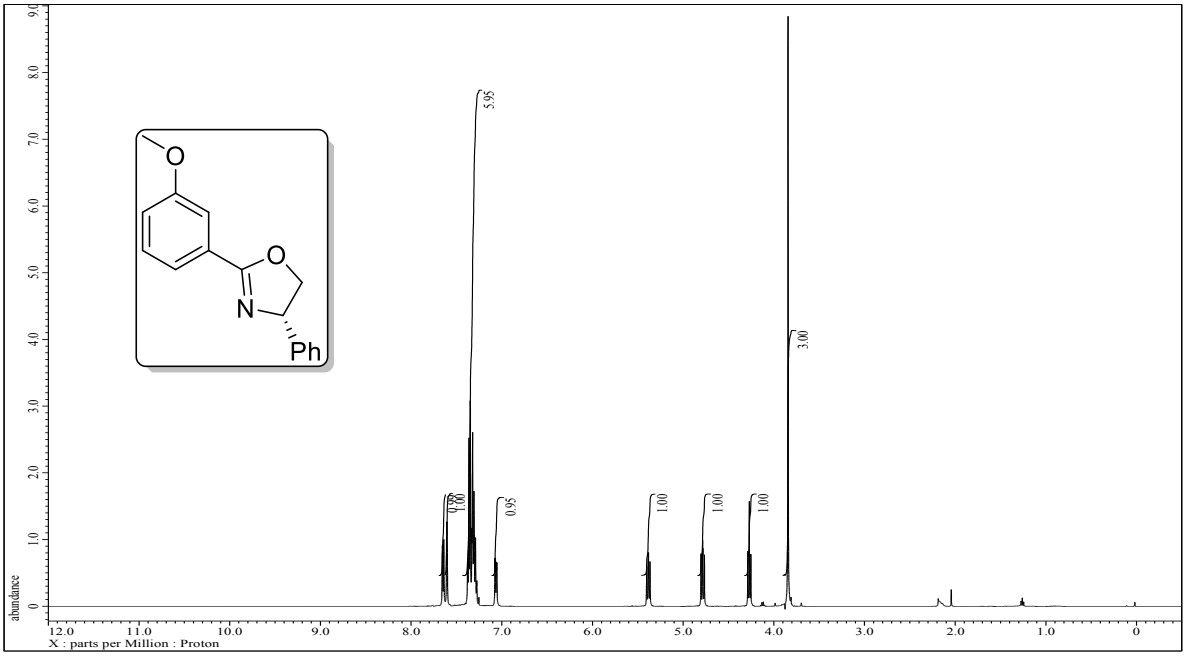

abundance
X : parts per Million : Carbon13
188.85904
174.43709
142.00679
141.07204
137.21855
128.62451
128.31929
127.93775
127.35592
125.47687
123.86489
123.64551
122.85383
121.86184
121.55662
117.49329
68.80014
68.07523
67.73184
61.18855
52.56537
7.27794
3.33861
2.92846
0.90634
0.74419
0.58203
0.41034
0.24819
0.08604
-0.07611

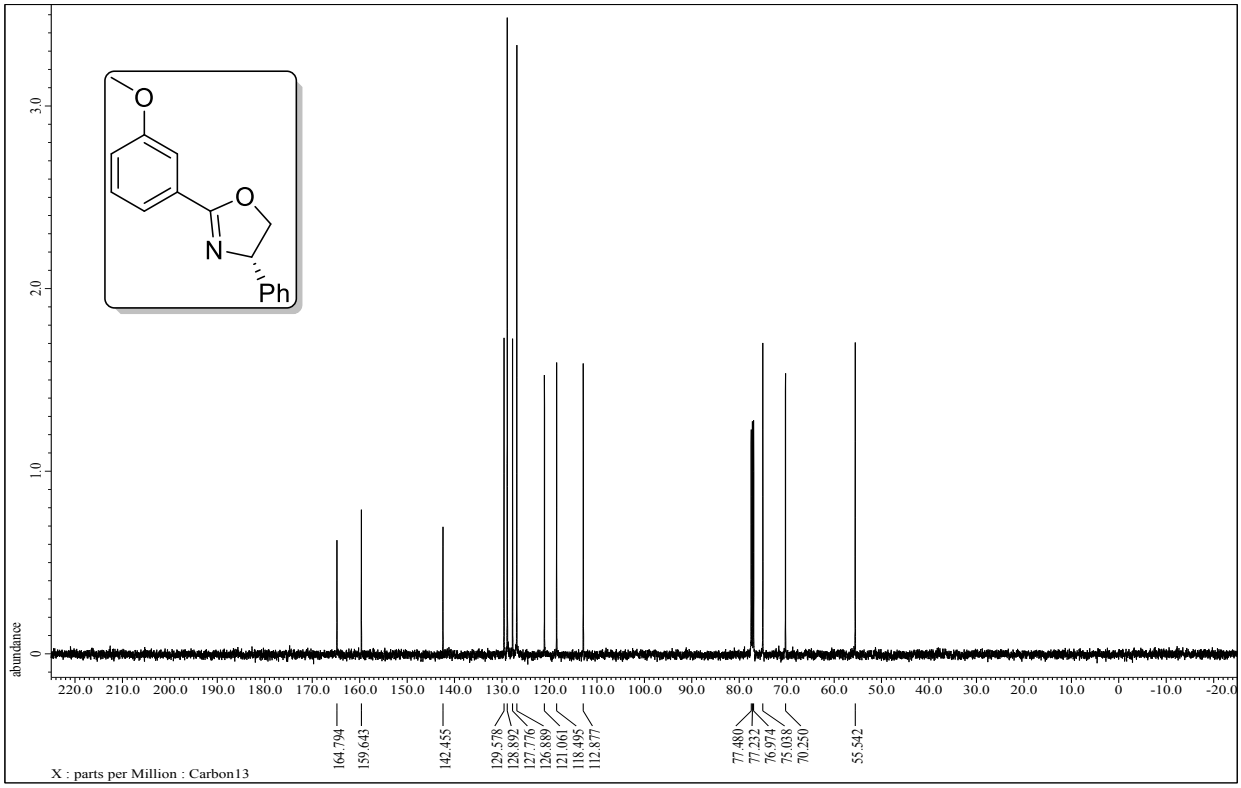

abundance
X : parts per Million : Proton
1.00
3.09
2.81
2.02
1.84
0.99
0.99
0.83
1.93
2.11
0.90
2.17
3.35
3.18
2.92
H–N+
Ph
I–
Ru—N
O
(CH3CN)4
Ph
PF6–

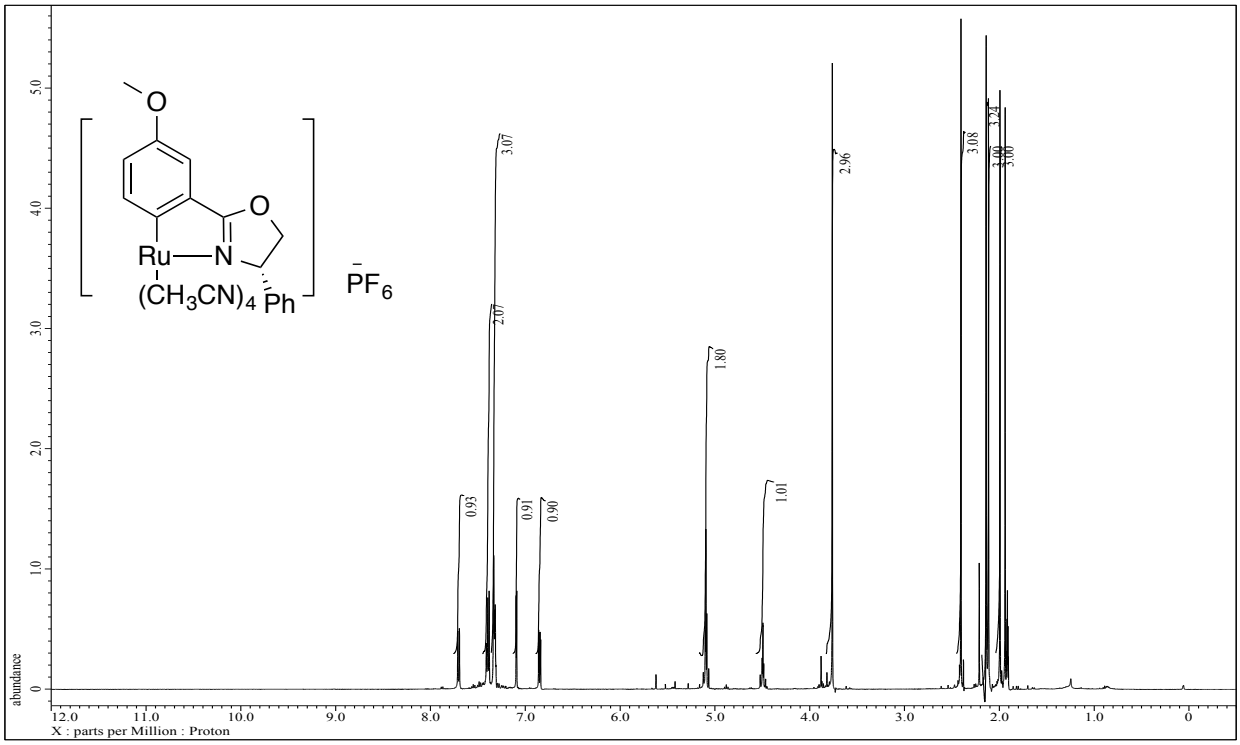

abundance
X : parts per Million : Carbon13
186.88461
174.81862
148.62639
141.56802
140.59511
136.25517
133.28876
129.15866
128.39560
128.10945
128.08083
125.67717
122.34830
119.06712
117.40744
115.55701
112.01829
78.04278
68.03707
54.40680
53.96804
45.32632
11.67511
3.05246
0.88726
0.72511
0.56296
0.39127
0.22912
0.06696
-0.10473
H–N+
Ph
I–
Ru—N
O
(CH3CN)4
Ph
PF6–

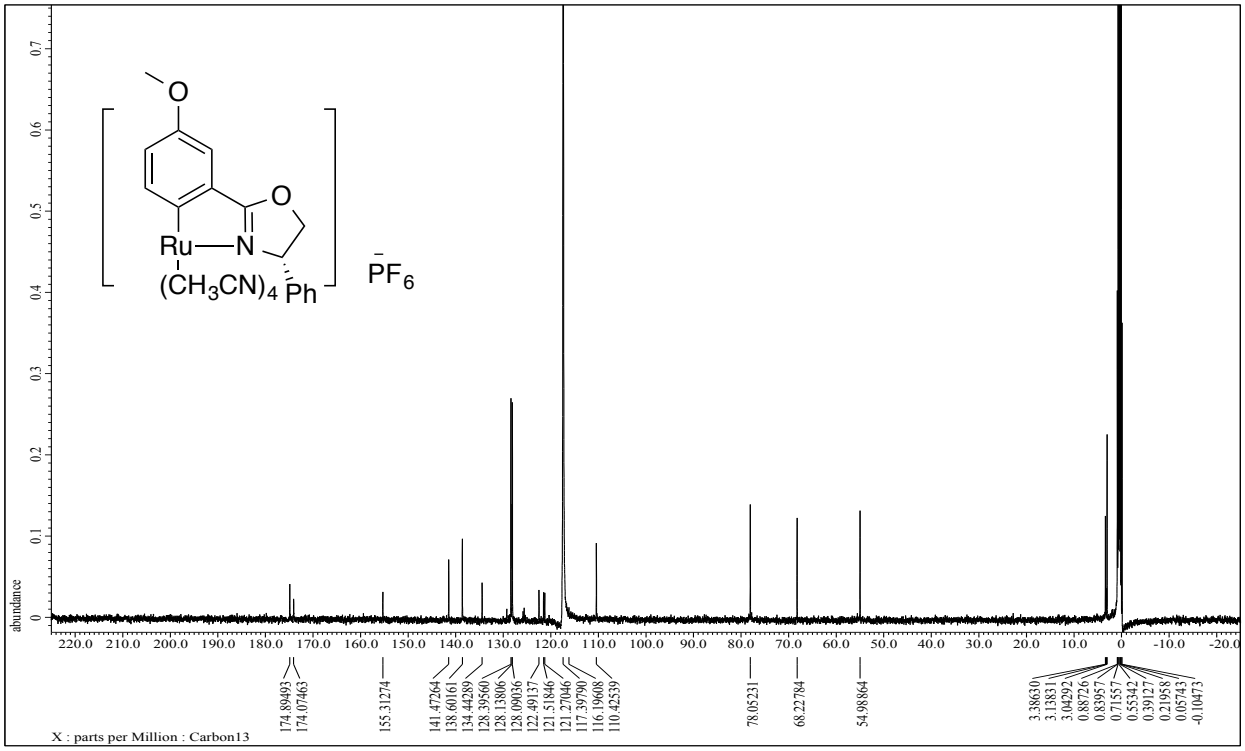

0.99
3.16
2.99
2.13
3.26
1.08
2.24
2.03
1.02
3.33
3.15
3.00
abundance
X : parts per Million : Proton

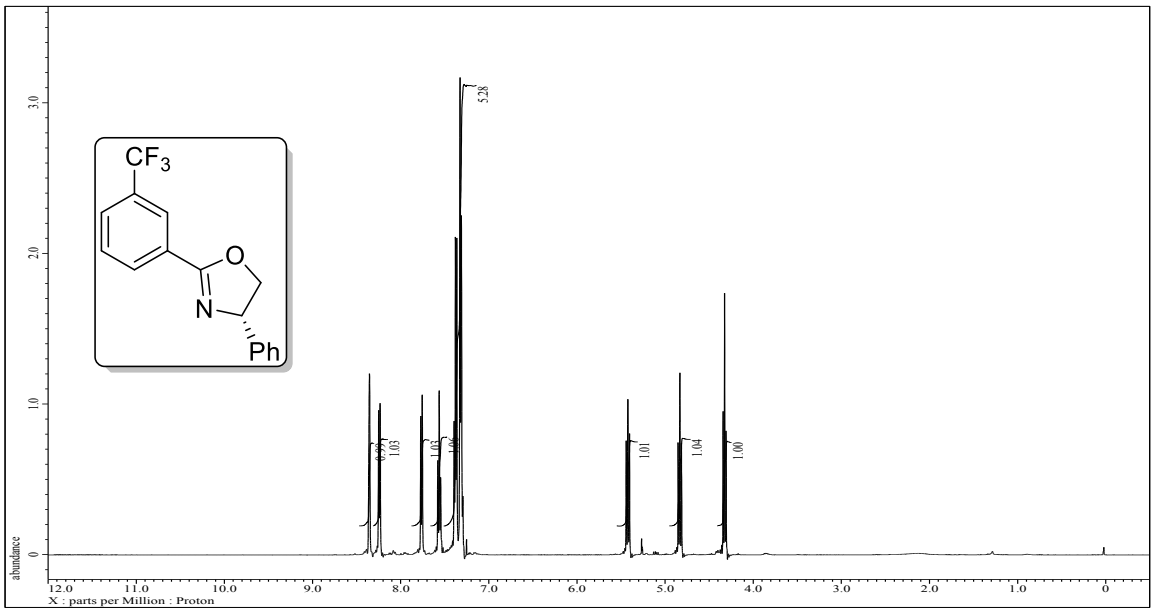

abundance
X : parts per Million : Carbon 13

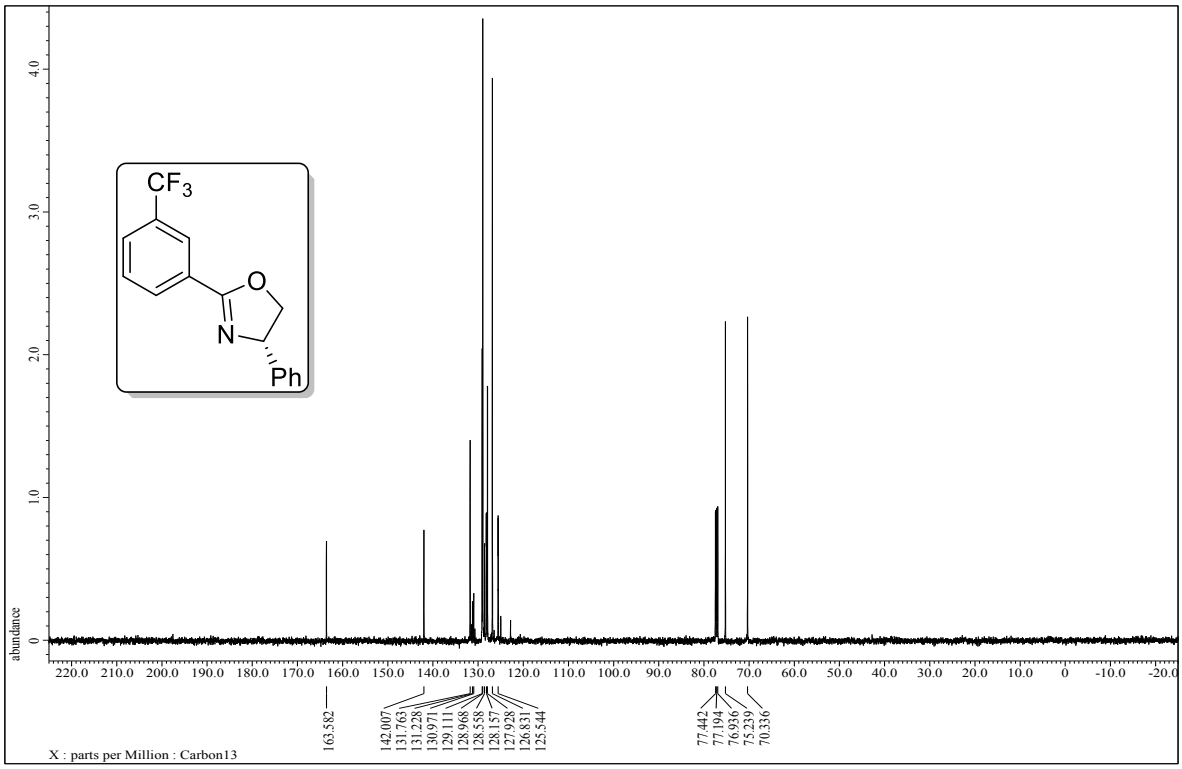

O
O
N
Ph
5.95
0.78
1.00
0.95
1.00
1.00
1.00
3.00
abundance
X : parts per Million : Proton

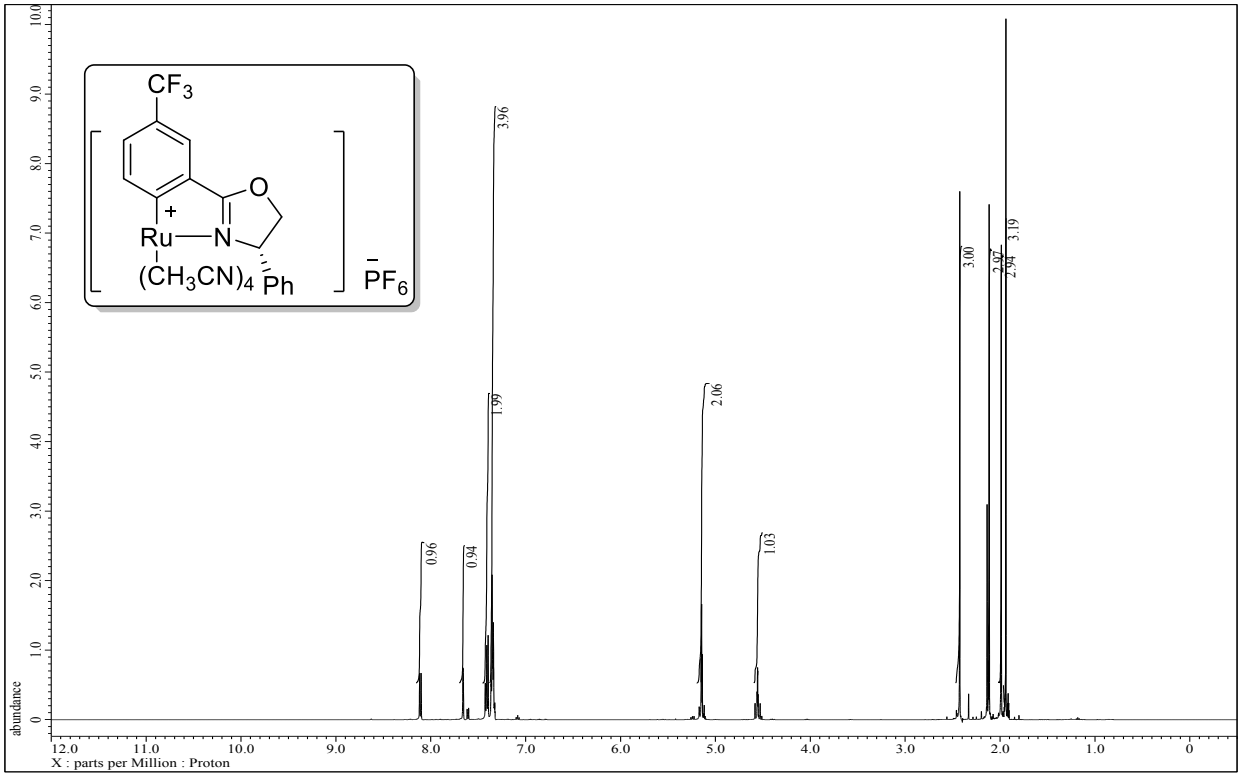

O
O
N
Ph
abundance
164.794
159.643
142.455
129.578
128.892
127.776
126.889
121.061
118.495
112.877
77.480
77.232
76.974
75.038
70.250
55.542
X : parts per Million : Carbon13

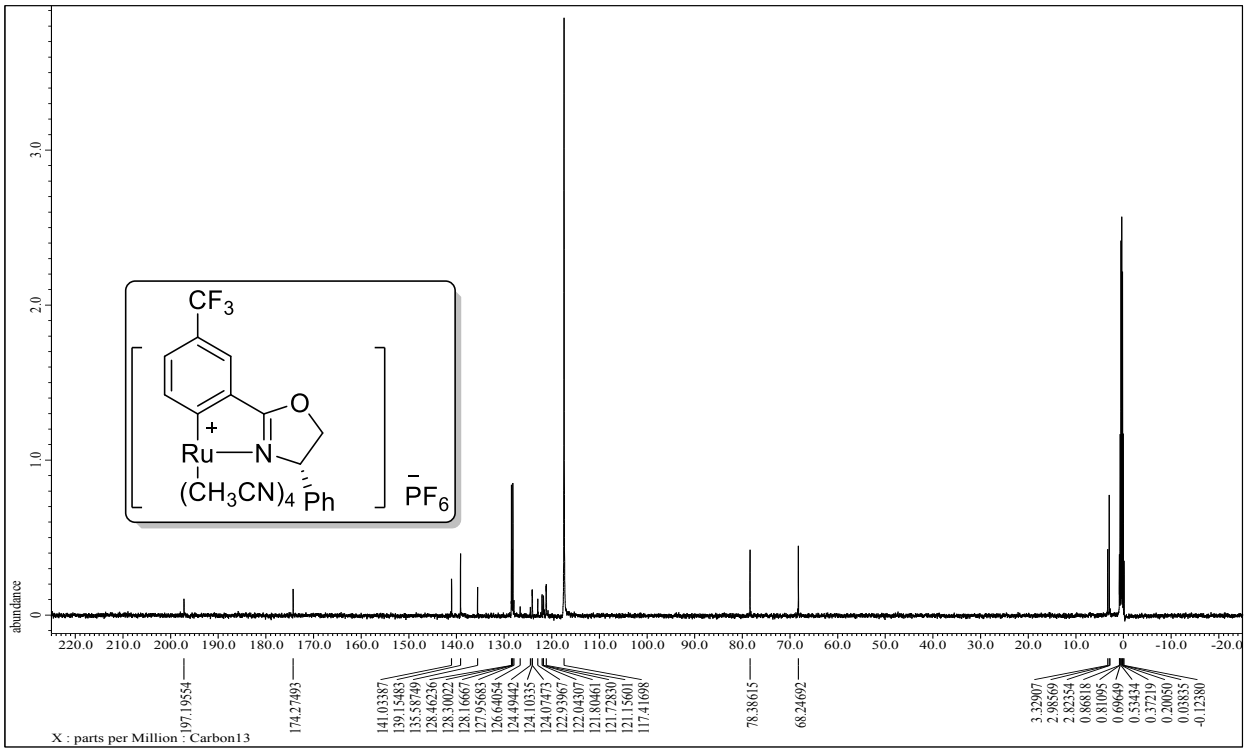

O
O
Ru—N
(CH3CN)4
Ph
PF6
0.93
3.07
2.07
0.91
0.90
1.80
1.01
2.96
3.08
3.04
3.00
3.01
abundance
X : parts per Million : Proton

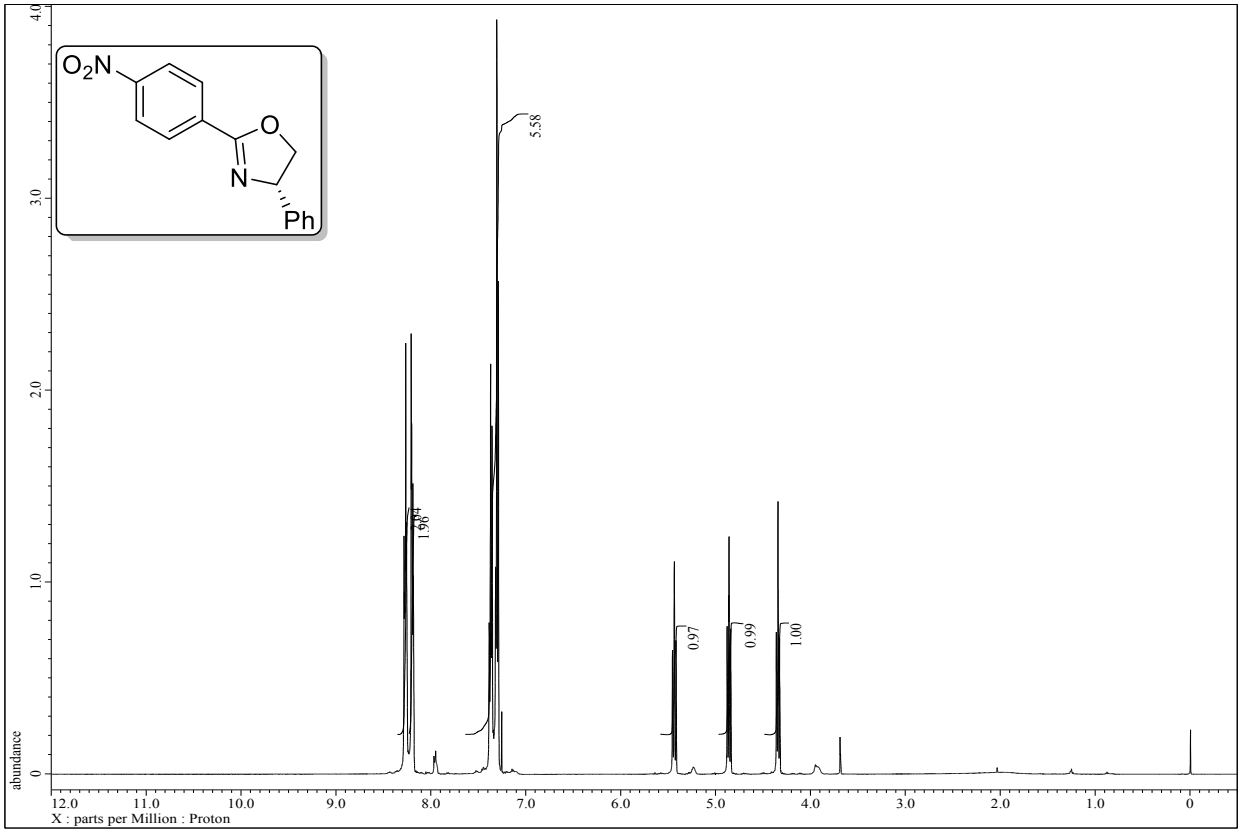

O
O
Ru—N
(CH3CN)4
Ph
PF6
abundance
174.89493
174.07463
155.31274
141.47264
138.60161
134.44289
128.39560
128.13806
128.09036
122.49137
121.51846
121.27046
117.39790
116.19608
110.42539
78.05231
68.22784
54.98864
3.38630
3.13831
3.04292
0.88726
0.83957
0.71557
0.55342
0.39127
0.21958
0.05743
-0.10473
X : parts per Million : Carbon13

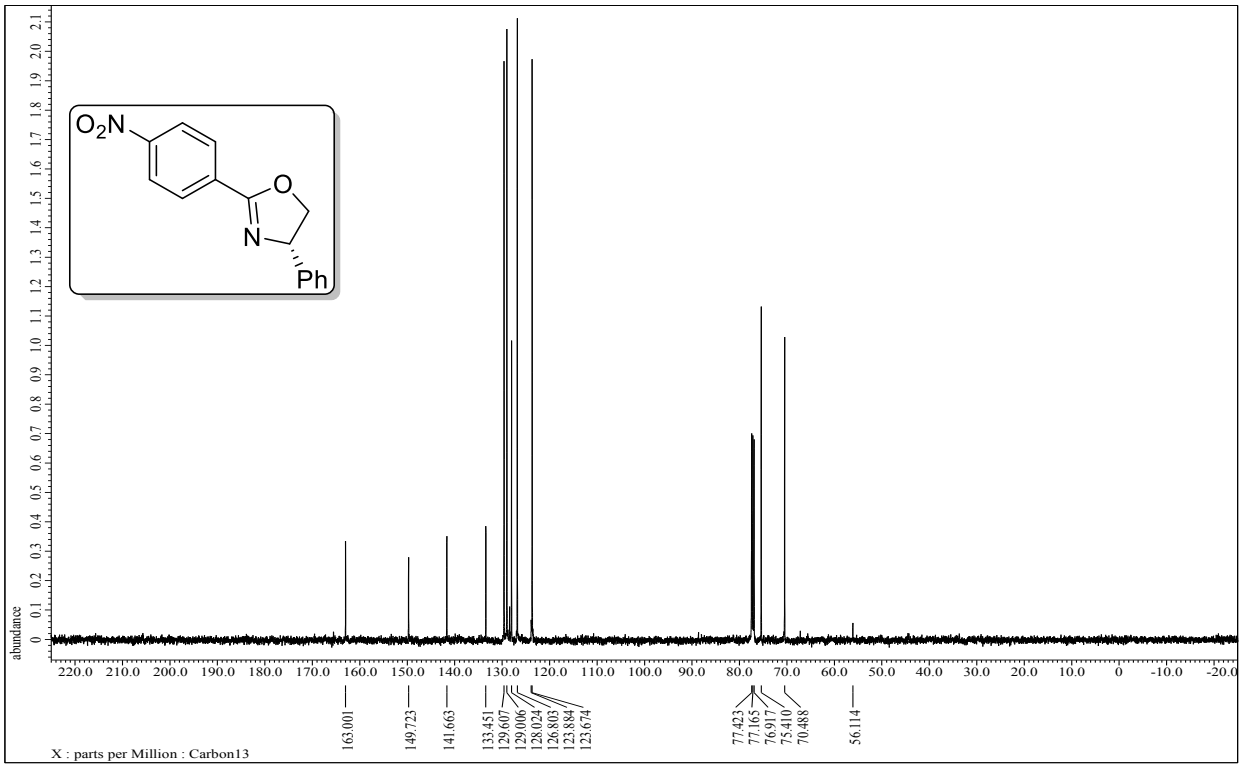

CF3
O
N
Ph
5.28
0.97
1.03
1.02
1.00
1.01
1.04
1.00
abundance
X : parts per Million : Proton

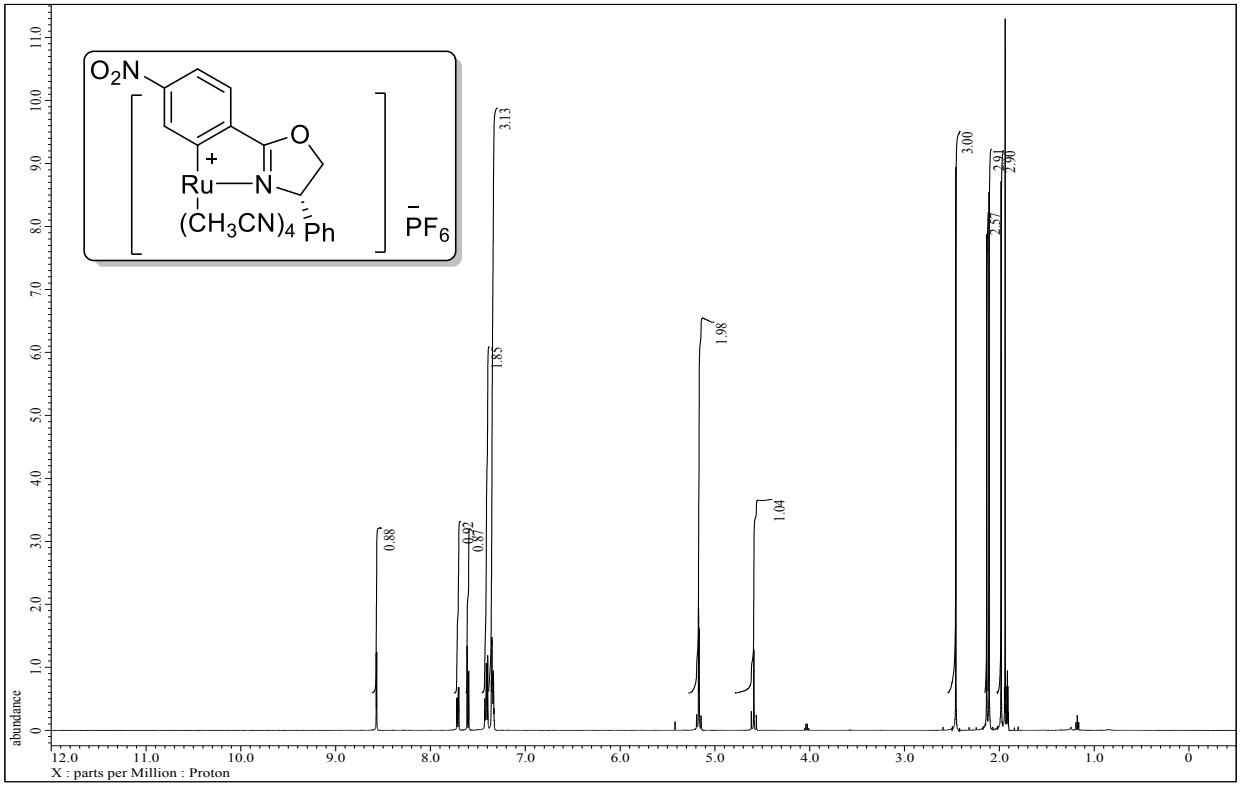

CF3
O
N
Ph
abundance
163.582
142.007
131.763
131.228
130.971
129.111
128.968
128.558
128.157
127.928
126.831
125.544
77.442
77.194
76.936
75.239
70.336
X : parts per Million : Carbon13

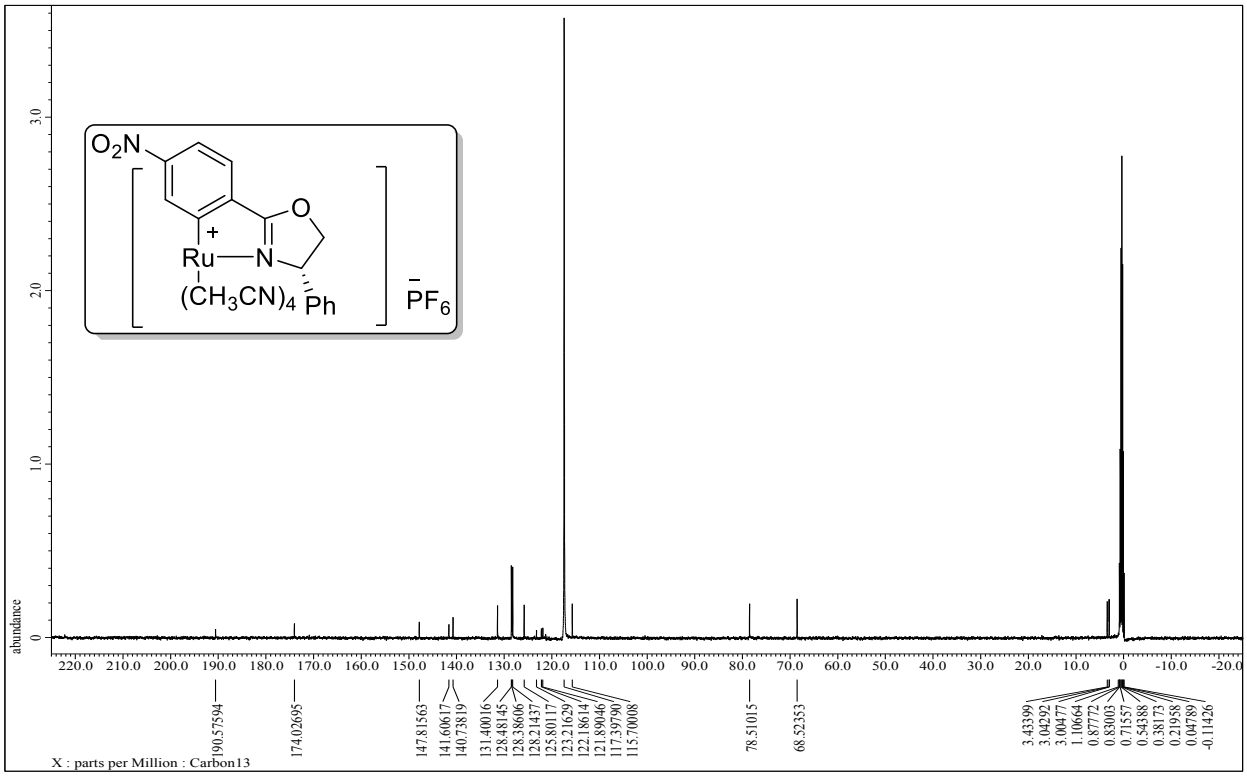

CF3
O
Ru
N
(CH3CN)4
Ph
PF6
3.96
1.99
2.06
0.96
0.94
1.03
3.00
2.97
2.94
3.19
abundance
X : parts per Million : Proton


CF3
O
Ru
N
(CH3CN)4
Ph
PF6
abundance
X : parts per Million : Carbon13
197.19554
174.27493
141.03387
139.15483
135.58749
128.46236
128.30022
128.16667
127.95683
126.64054
124.49442
124.10335
124.07473
122.93967
122.04307
121.80461
121.72830
121.15601
117.41698
78.38615
68.24692
3.32907
2.98569
2.82354
0.86818
0.81095
0.69649
0.53434
0.37219
0.20050
0.03835
-0.12380

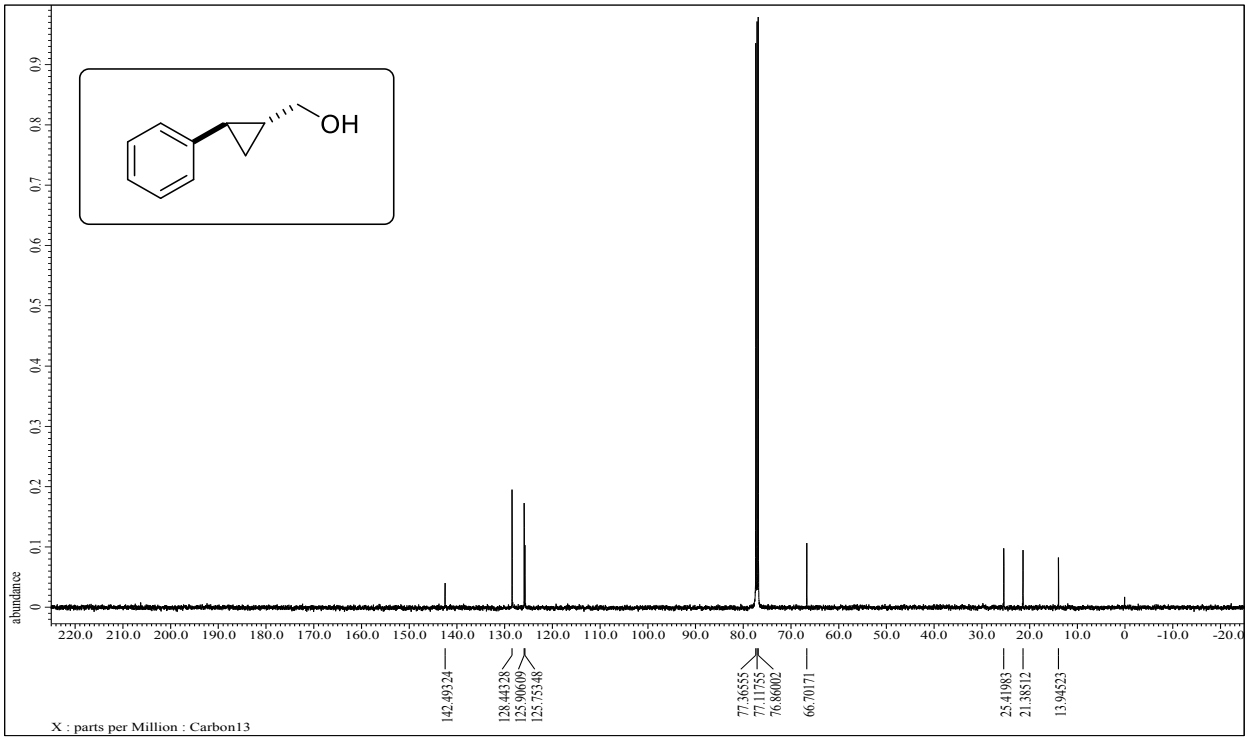

O2N
O
N
Ph
5.58
1.98
1.94
0.97
0.99
1.00
abundance
X : parts per Million : Proton

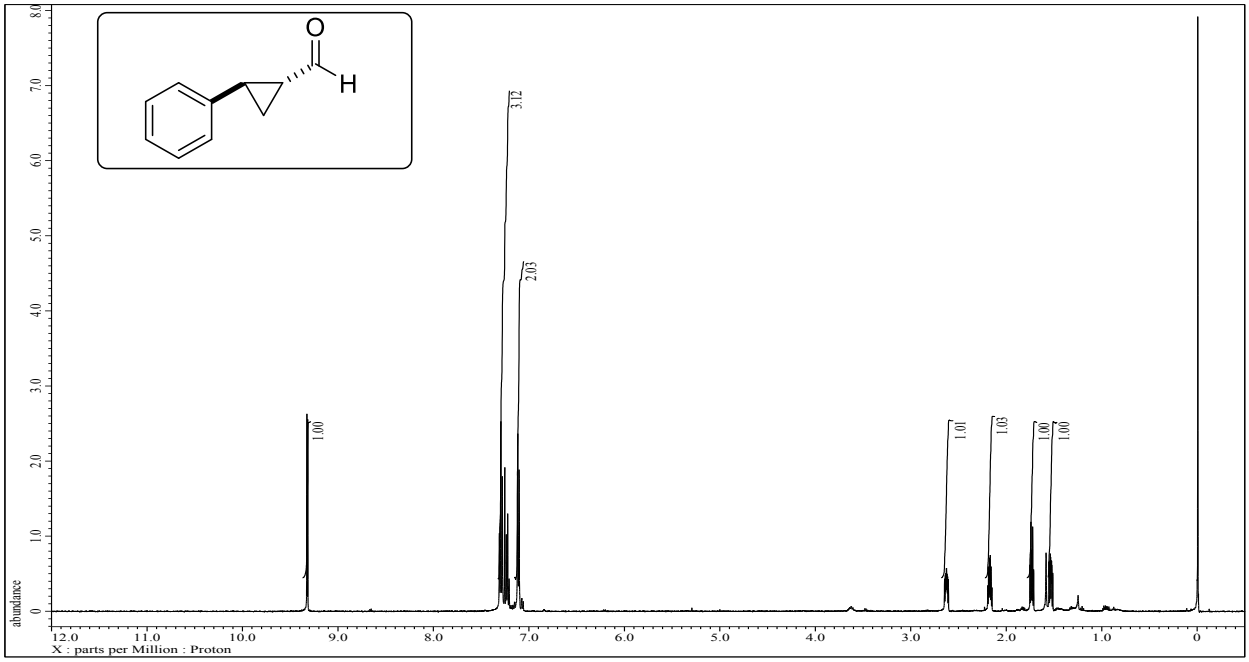

O2N
O
N
Ph
abundance
X : parts per Million : Carbon13
163.001
149.723
141.663
133.451
129.607
129.006
128.024
126.803
123.884
123.674
77.423
77.165
76.917
75.410
70.488
56.114

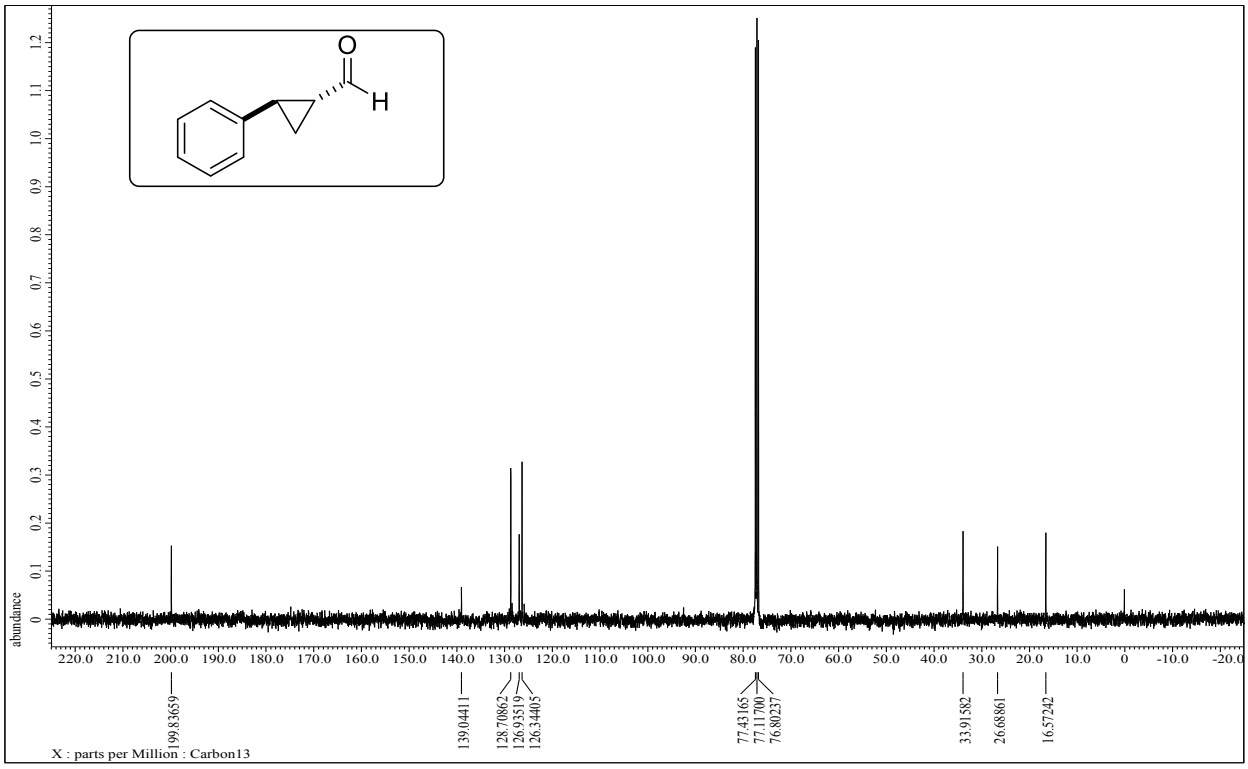

O2N
O
Ru—N
(CH3CN)4
Ph
PF6
abundance
X : parts per Million : Proton
0.88
0.92
0.87
3.13
1.85
1.98
1.04
3.00
2.91
2.90
2.57

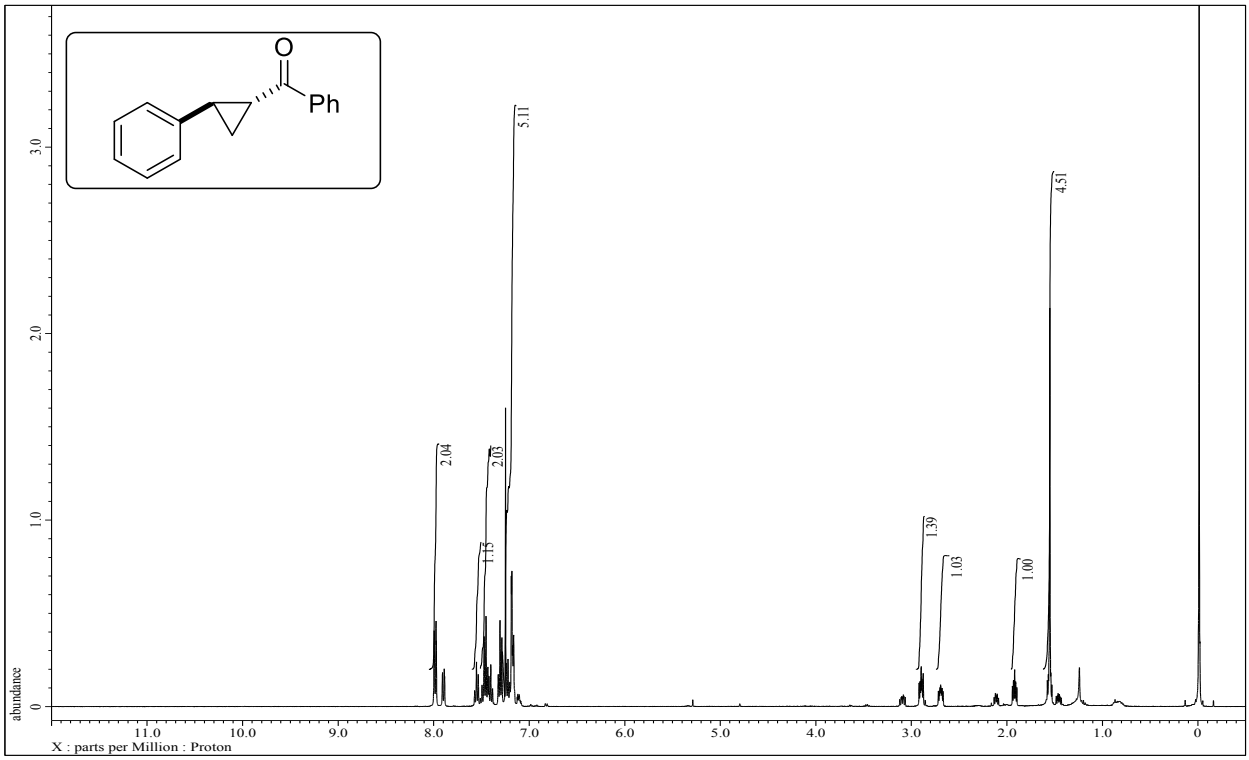

O2N
O
Ru—N
(CH3CN)4
Ph
PF6
abundance
X : parts per Million : Carbon13
190.57594
174.02695
147.81563
141.60617
140.73819
131.40016
128.48145
128.38606
128.21437
125.80117
123.21629
122.18614
121.89046
117.39790
115.70008
78.51015
68.52353
3.43399
3.04292
3.00477
1.10664
0.87772
0.83003
0.71557
0.54388
0.38173
0.21958
0.04789
-0.11426

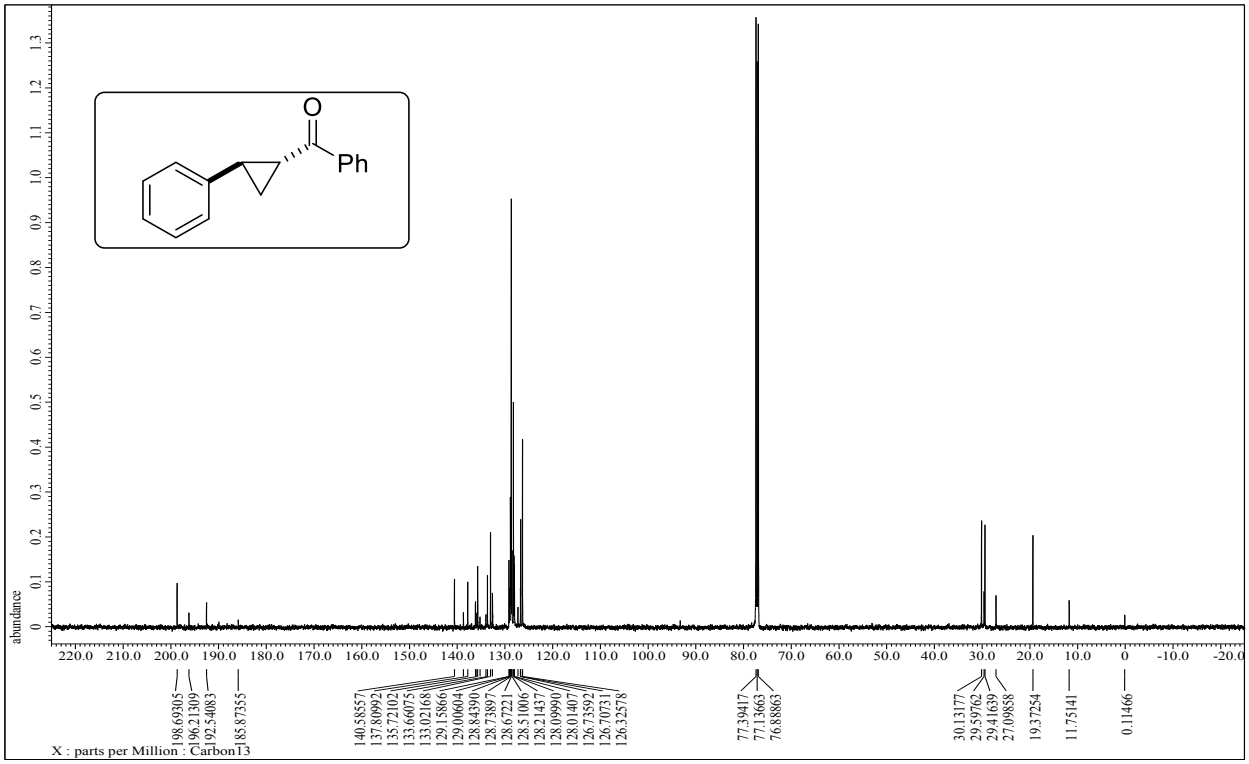

OH
abundance
X : parts per Million : Proton

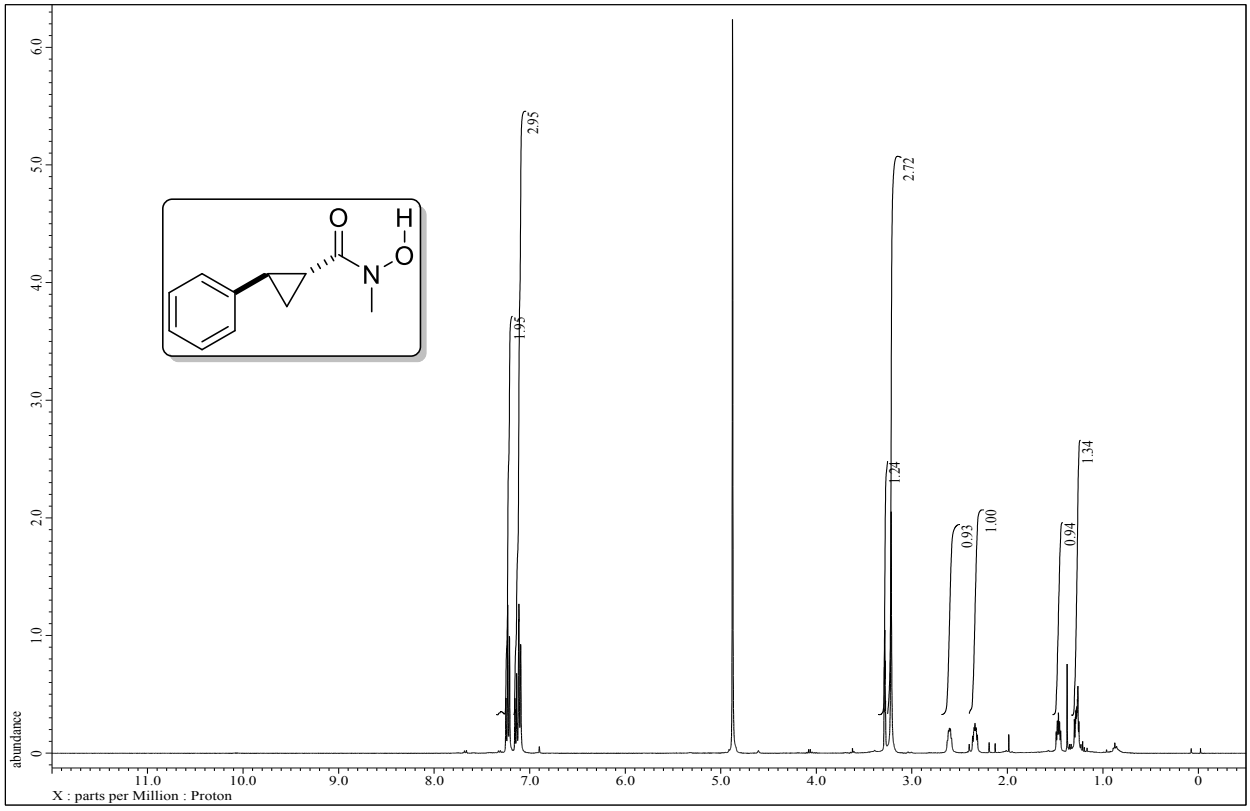

OH
abundance
142.49324
128.44328
125.90609
125.75348
77.36555
77.11755
76.86602
66.70171
25.41983
21.38512
13.94523
X : parts per Million : Carbon13

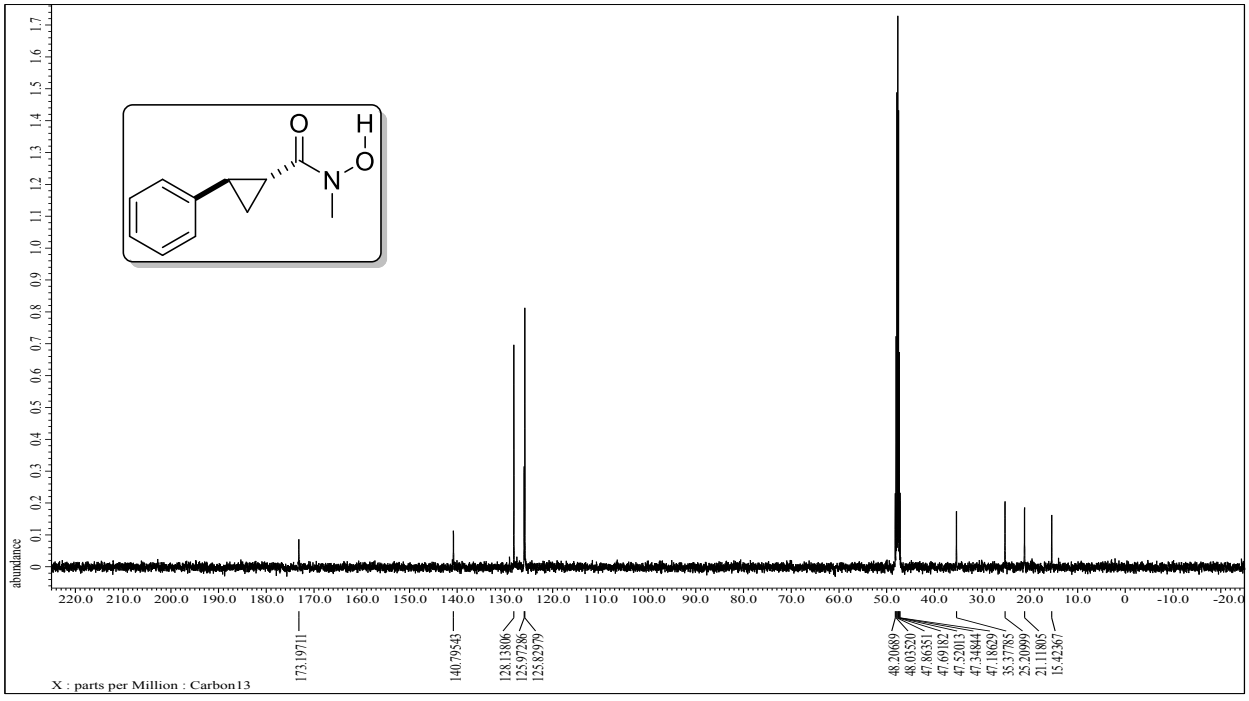

O
H
3.12
2.03
1.00
1.01
1.03
1.00
1.00
abundance
X : parts per Million : Proton

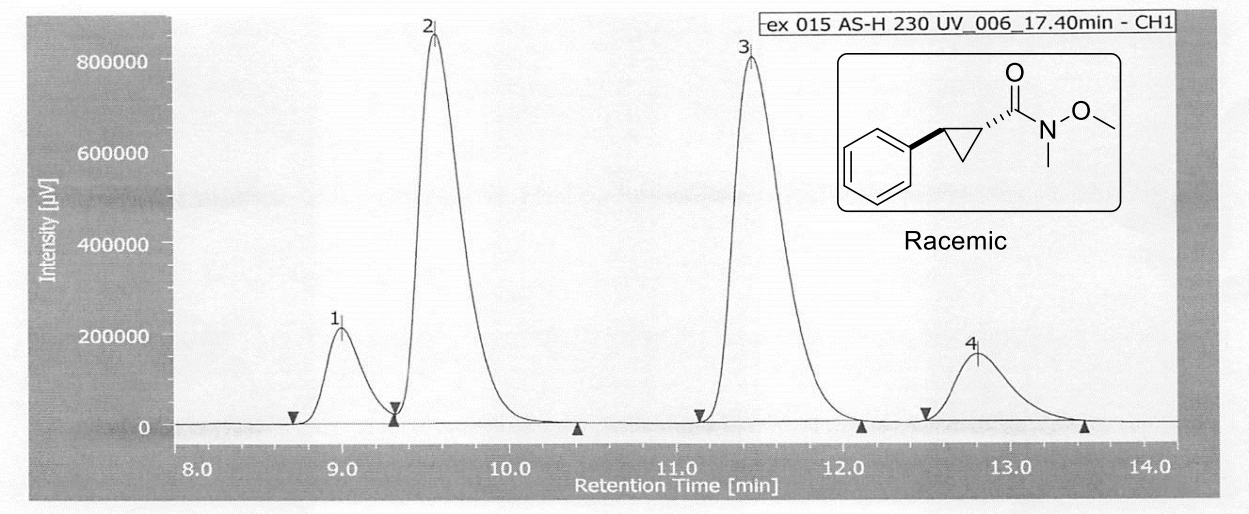

O
H
abundance
199.83659
139.04411
128.70862
126.93519
126.34405
77.43165
77.11700
76.80237
33.91582
26.68861
16.57242
X : parts per Million : Carbon13


O
Ph
5.11
4.51
2.04
2.03
1.15
1.39
1.03
1.00
abundance
X : parts per Million : Proton

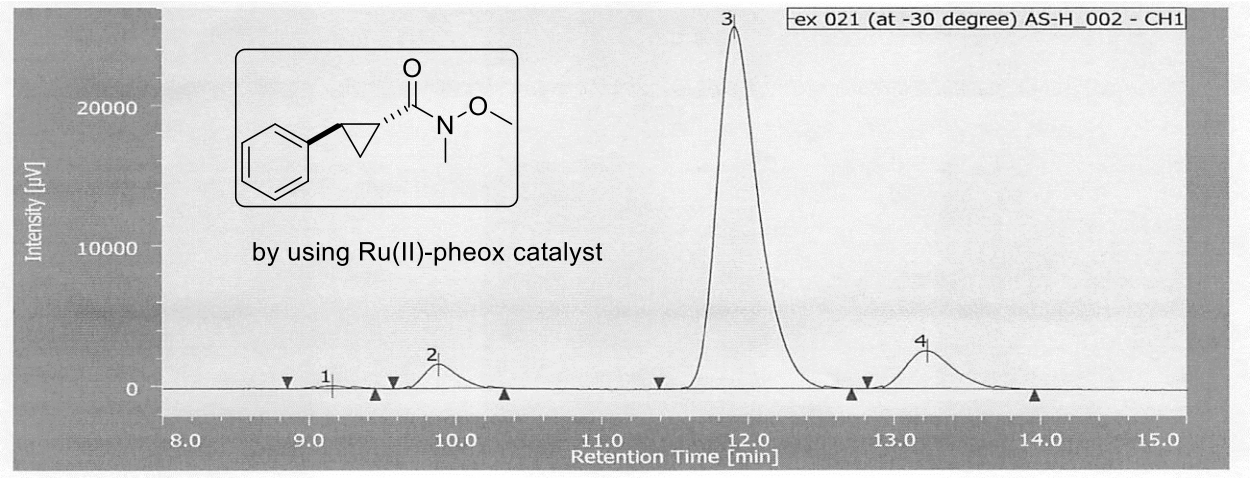

O
Ph
abundance
198.69305
196.21309
192.54083
185.87355
140.58557
137.80992
135.72102
133.66075
133.02168
129.15866
129.00604
128.84390
128.73897
128.67221
128.51006
128.21437
128.09990
128.01407
126.73592
126.70731
126.32578
77.39417
77.13663
76.88863
30.13177
29.59762
29.41639
27.09858
19.37254
11.75141
0.11466
X : parts per Million : Carbon13


abundance
X : parts per Million : Proton
2.95
1.95
2.72
1.24
0.93
1.00
0.94
1.34

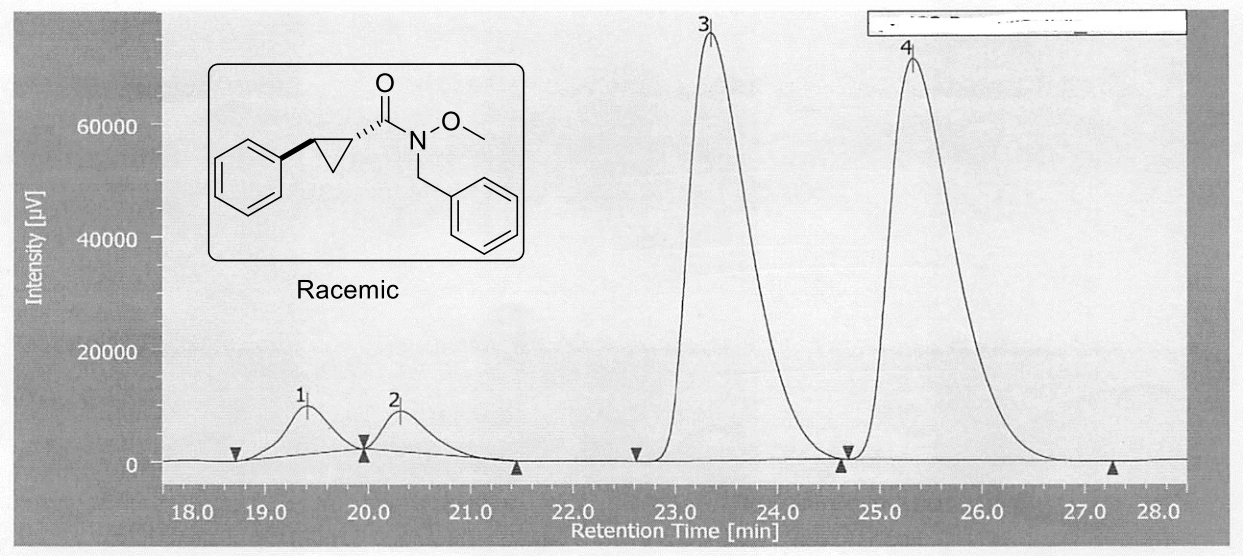

abundance
X : parts per Million : Carbon13
173.19711
140.79543
128.13806
125.97286
125.82979
48.20689
48.03520
47.86351
47.69182
47.52013
47.34844
47.18629
35.37785
25.20999
21.11805
15.42367



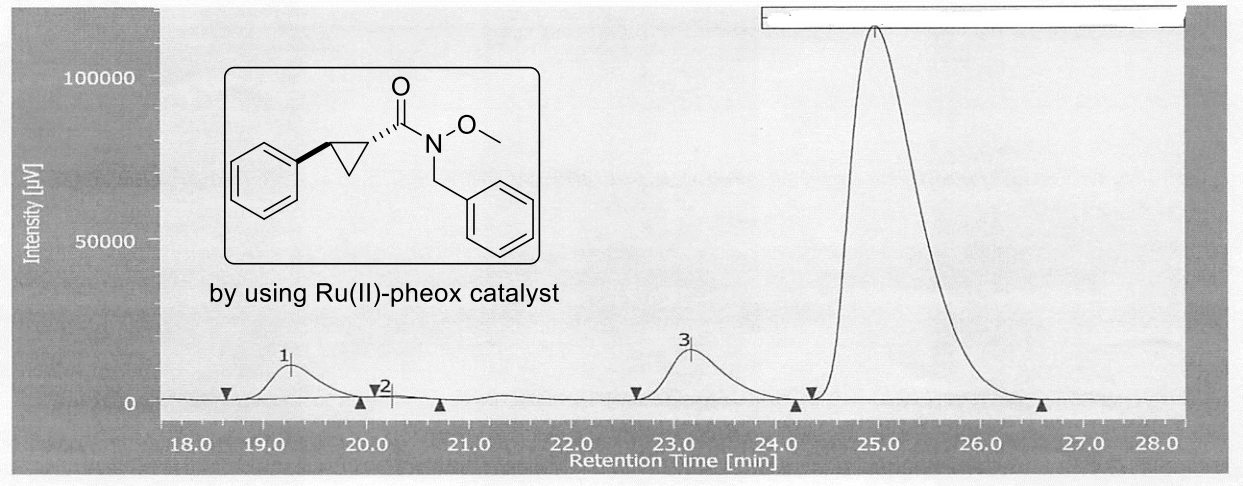
No.	Time [min]	Area [µV-sec]	Area%
1	9.00	3265624	8.635
2	9.56	15598136	39.921
3	11.45	16120920	42.626
4	12.80	3334996	8.818



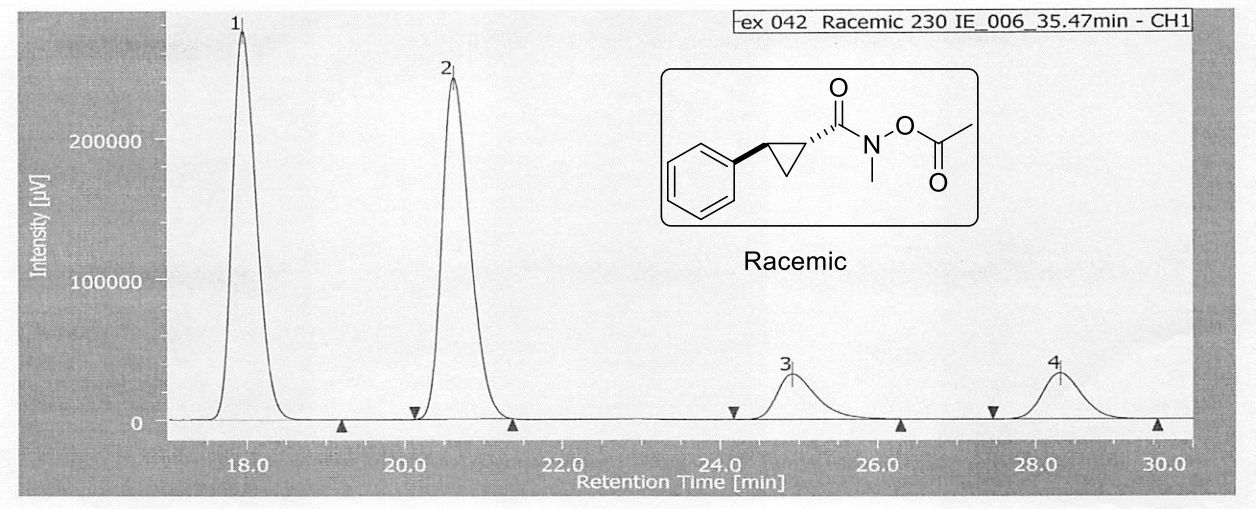
No.	Time [min]	Area [µV-sec]	Area%
1	9.1	2813	0.46
2	9.88	27635	4.58
3	11.90	509563	84.60
4	13.22	62246	10.33



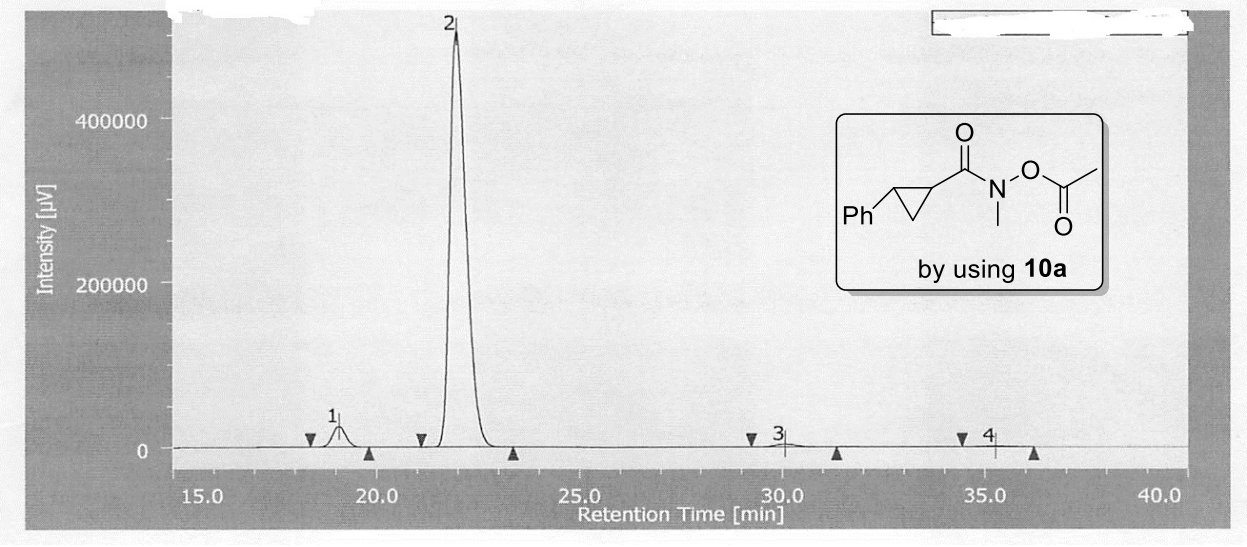
No.	Time [min]	Area [μV-sec]	Area%
1	19.4	255618	3.78
2	20.3	220606	3.26
3	23.35	3124709	46.72
4	25.32	3152161	46.67



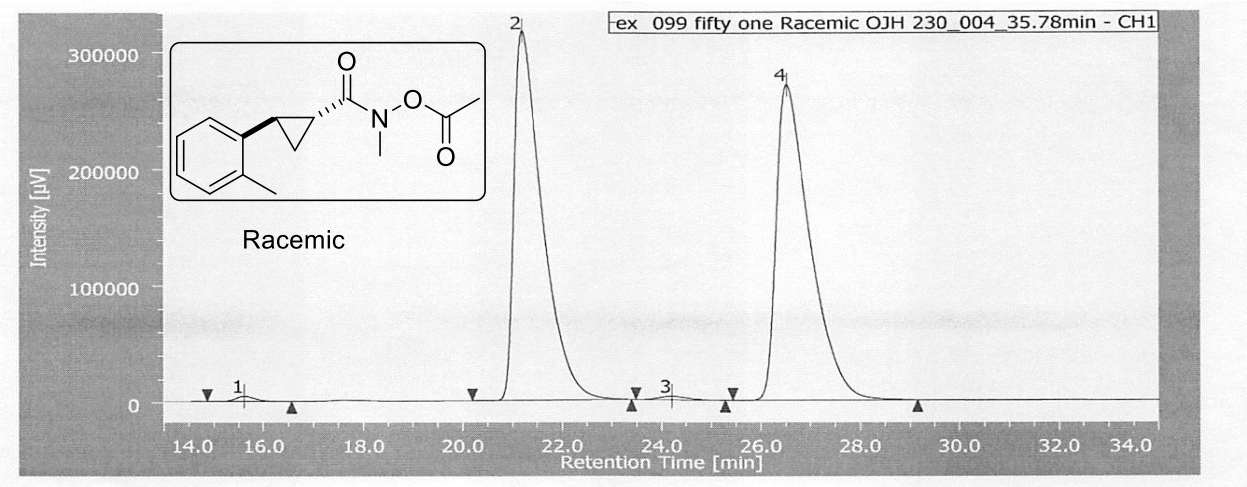
No.	Time [min]	Area [μV-sec]	Area%
1	19.2	316069	5.08
2	20.25	10671	0.17
3	23.17	573226	9.22
4	24.97	5317402	85.52



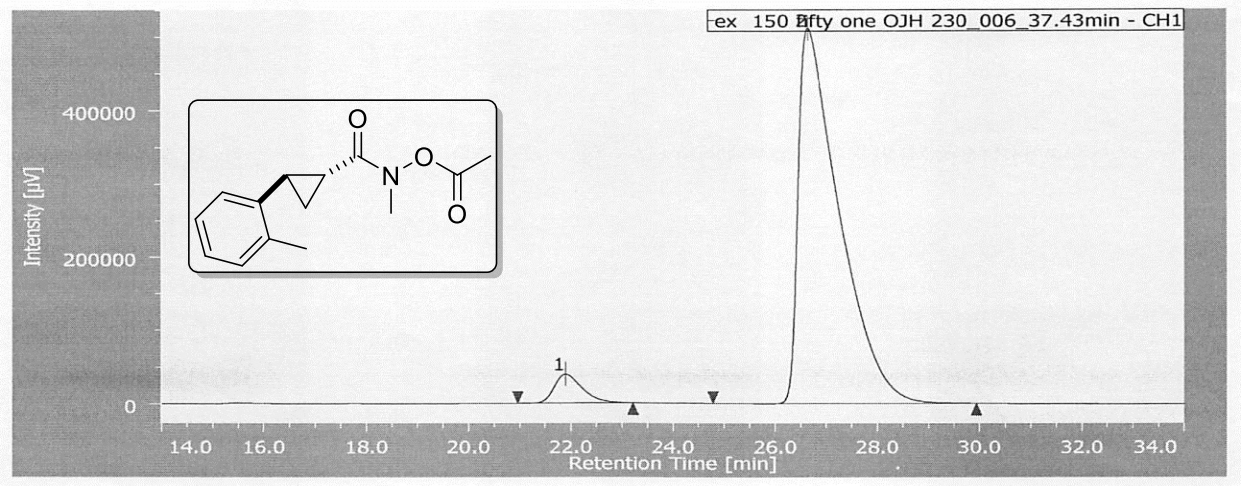
No.	Time [min]	Area [µV-sec]	Area%
1	17.95	5827797	41.74
2	20.62	5903145	41.56
3	24.91	1111962	5.51
4	28.31	1117682	5.60



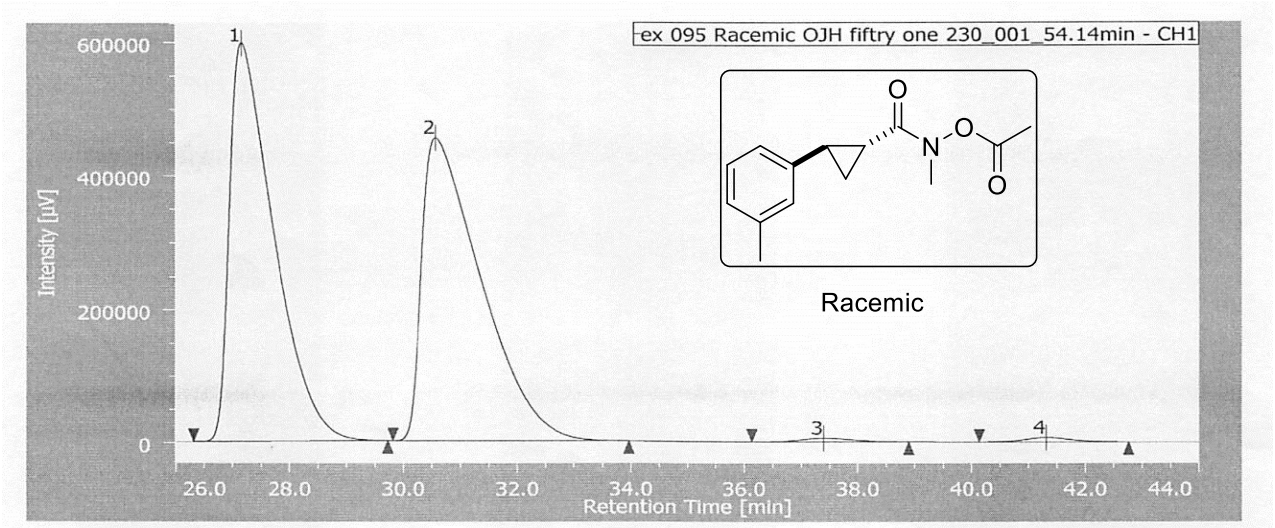
No.	Time [min]	Area [µV-sec]	Area%
1	19.07	579541	3.93
2	21.96	13994561	94.90
3	30.06	126314	0.85
4	35.25	46176	0.31



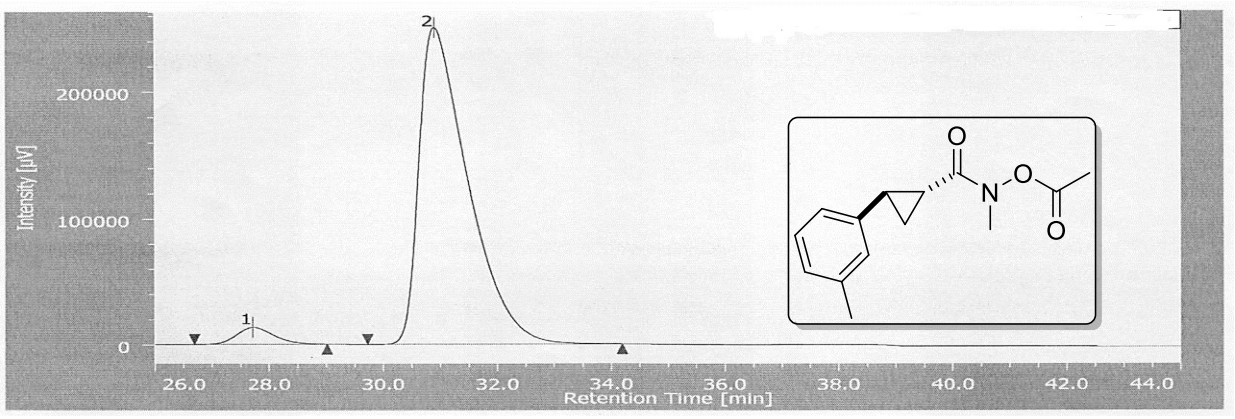
No.	Time [min]	Area [µV-sec]	% Area
1	15.60	113411	0.445
2	21.19	12557536	49.22
3	24.20	120274	0.47
4	26.51	12717093	49.85



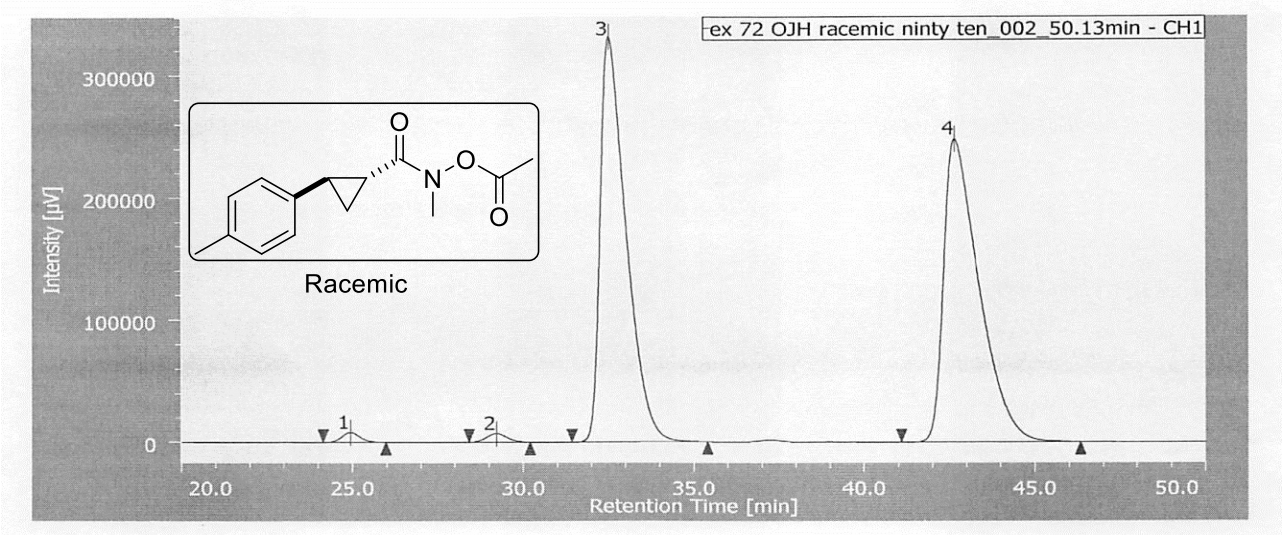
No.	Time [min]	Area [µV-sec]	Area%
1	21.90	1484504	4.94
2	26.64	28536137	95.05



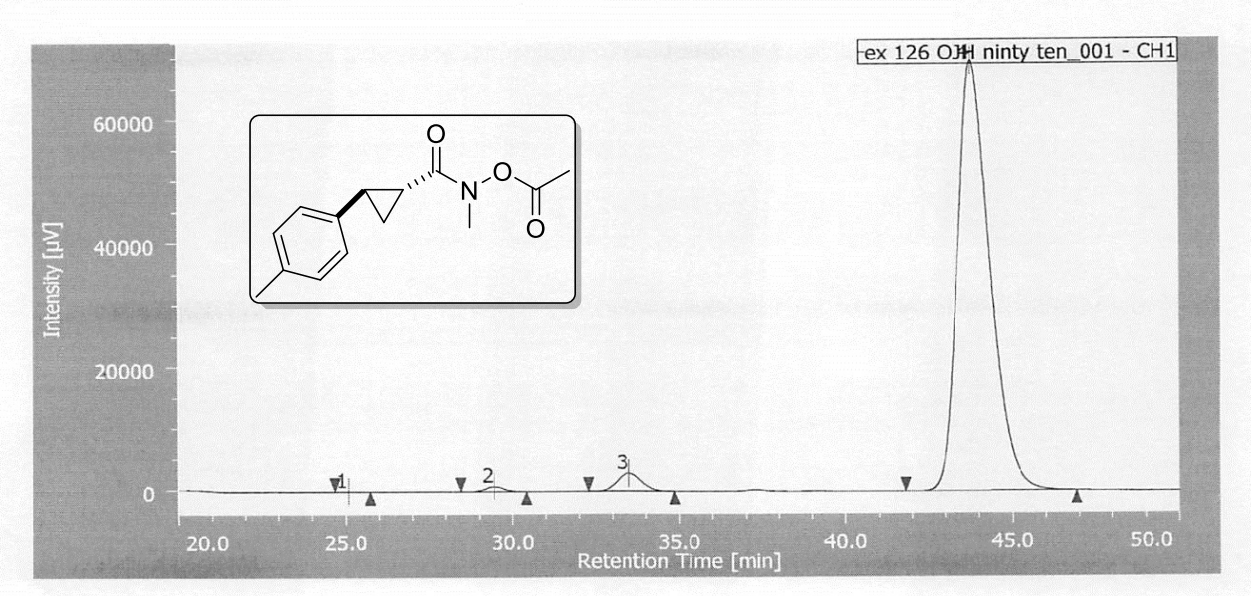
No.	Time [min]	Area [μV-sec]	Area%
1	27.15	32365942	49.07
2	30.56	32871530	49.84
3	37.39	351018	0.53
4	41.30	360042	0.54



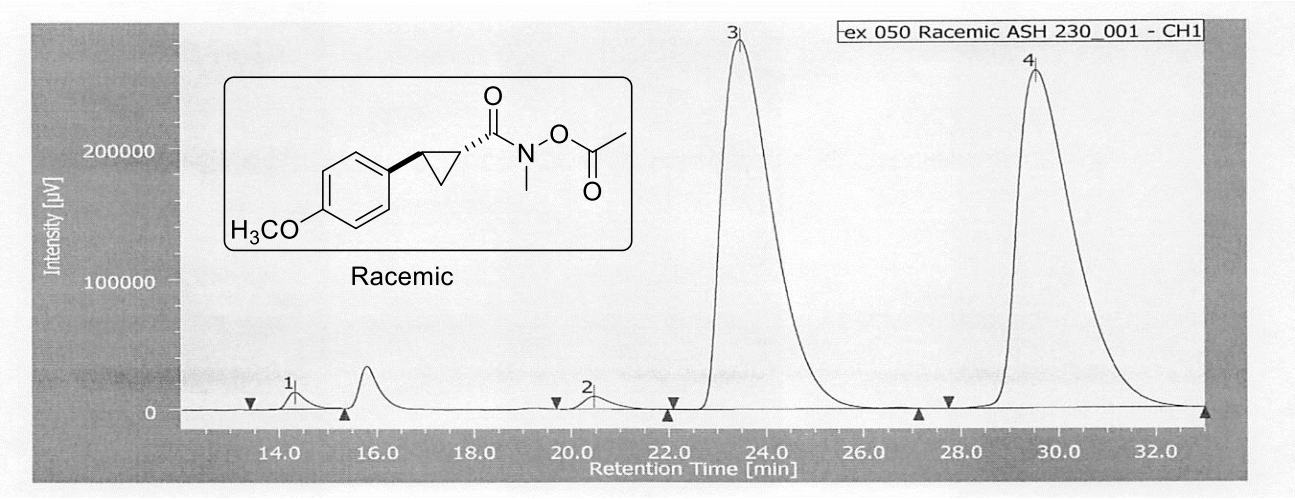
No.	Time [min]	Area [μV-sec]	Area%
1	27.70	616064	3.98
2	30.90	14861790	96.02



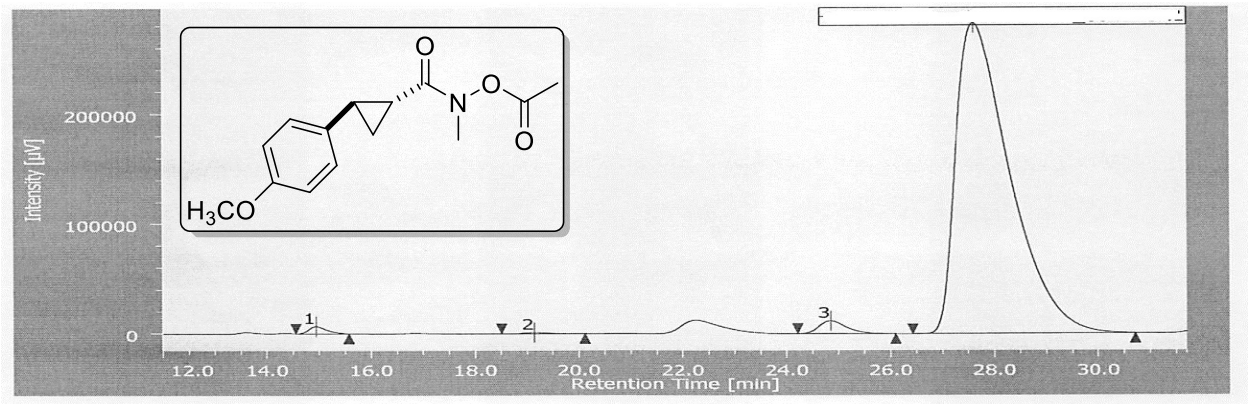
No.	Time [min]	Area[µV-sec]	Area%
1	24.94	290226	0.81
2	29.21	286204	0.79
3	32.51	17407845	48.59
4	42.65	17837736	49.79



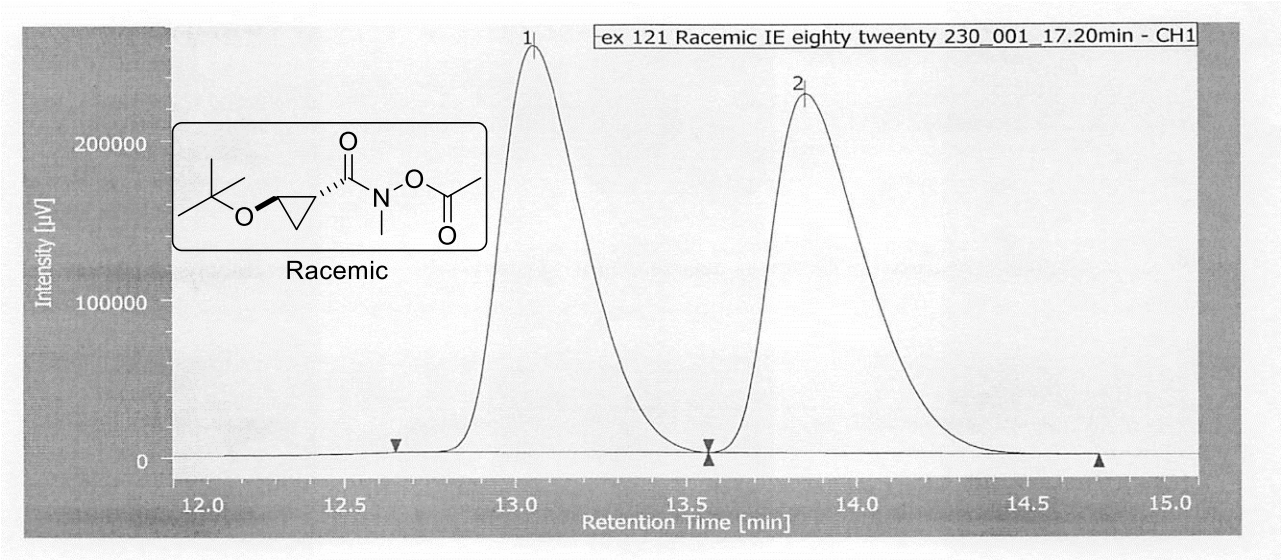
No.	Time [min]	Area [µV-sec]	Area%
1	25.07	688	0.01
2	29.44	33623	0.69
3	33.49	145031	2.99
4	43.77	4656426	96.29



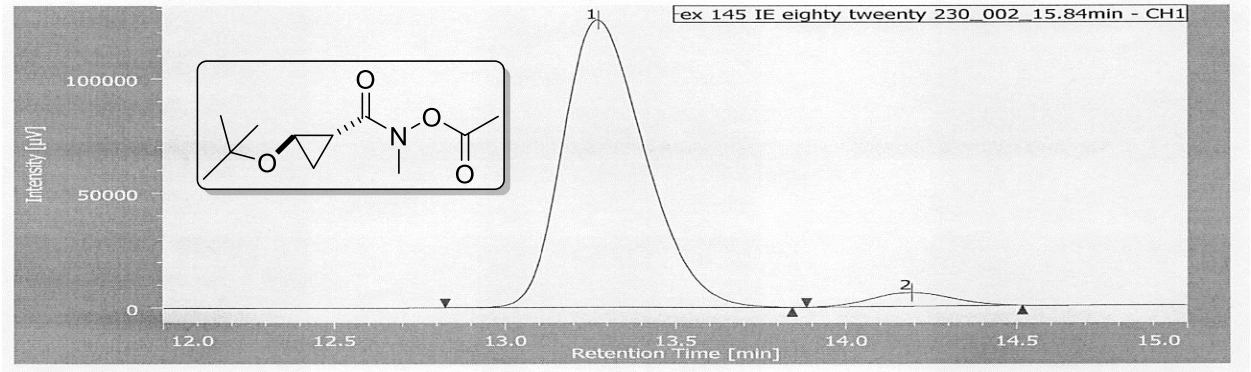
No.	Time [min]	Area [µV-sec]	Area%
1	14.33	358248	0.85
2	20.45	380165	0.90
3	23.47	20405576	48.64
4	29.55	20800479	49.59



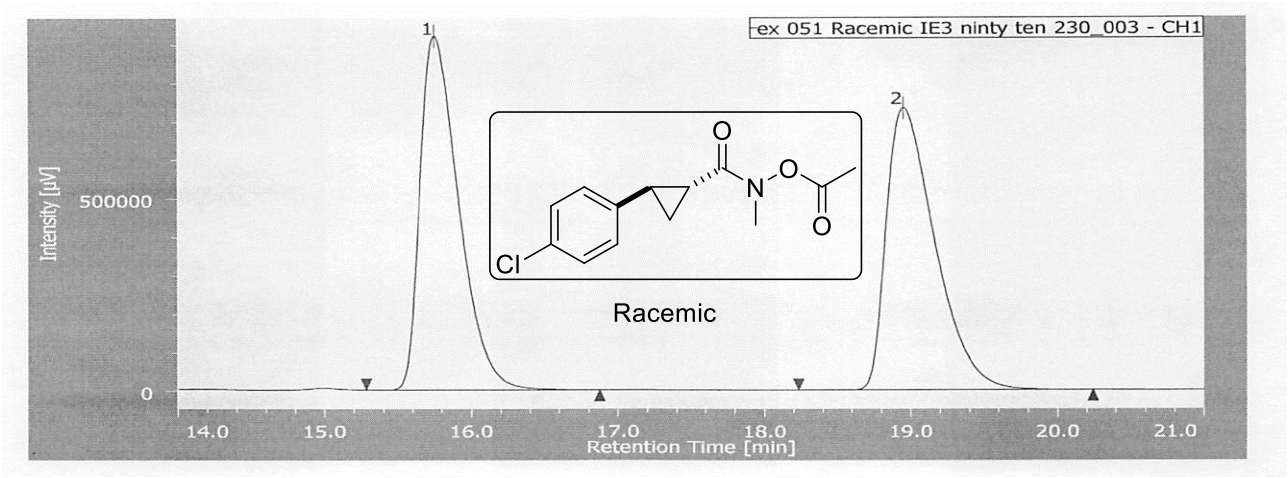
No.	Time [min]	Area [µV-sec]	Area%
1	14.94	151276	0.72
2	19.13	41741	0.2
3	24.85	422371	2.02
4	27.60	20280047	97.05



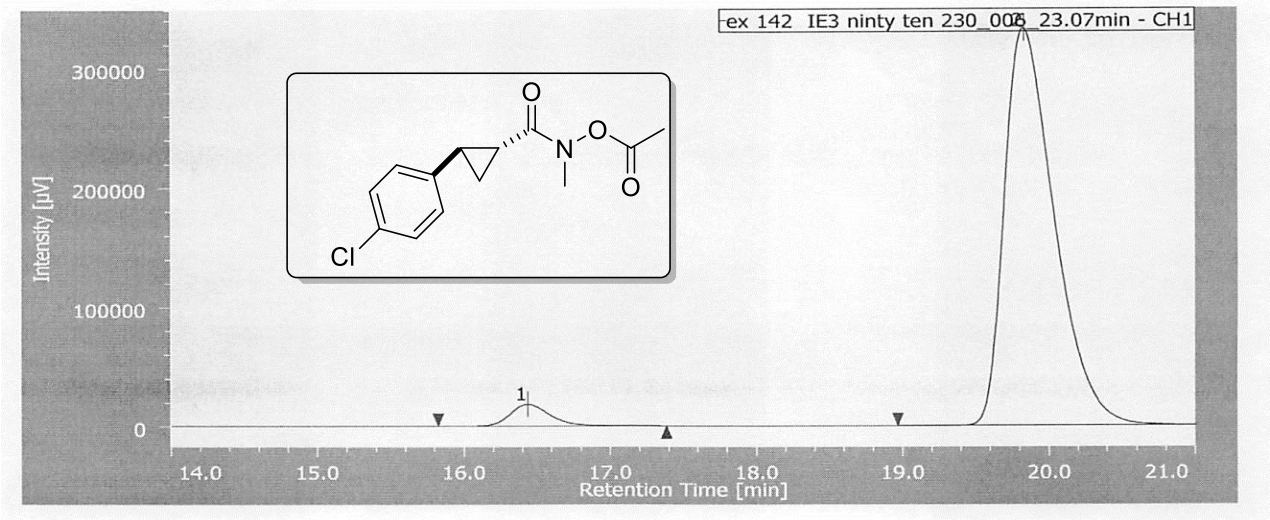
No.	Time [min]	Area [μV-sec]	Area%
1	13.05	4377598	50.18
2	13.85	4345825	49.81



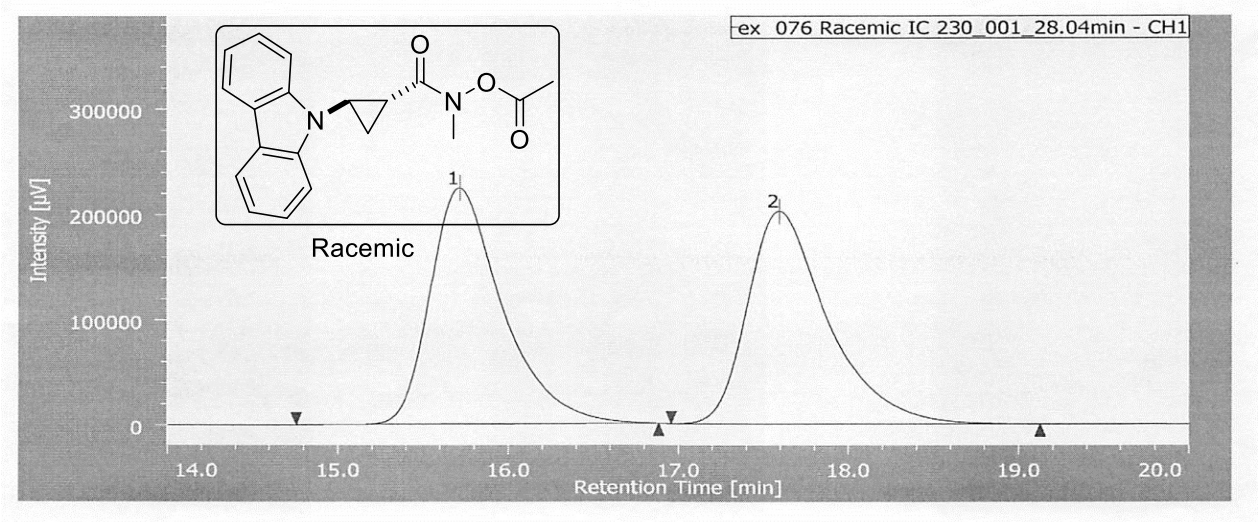
No.	Time [min]	Area [μV-sec]	Area%
1	13.27	2089043	95.414
2	14.19	100407	4.586



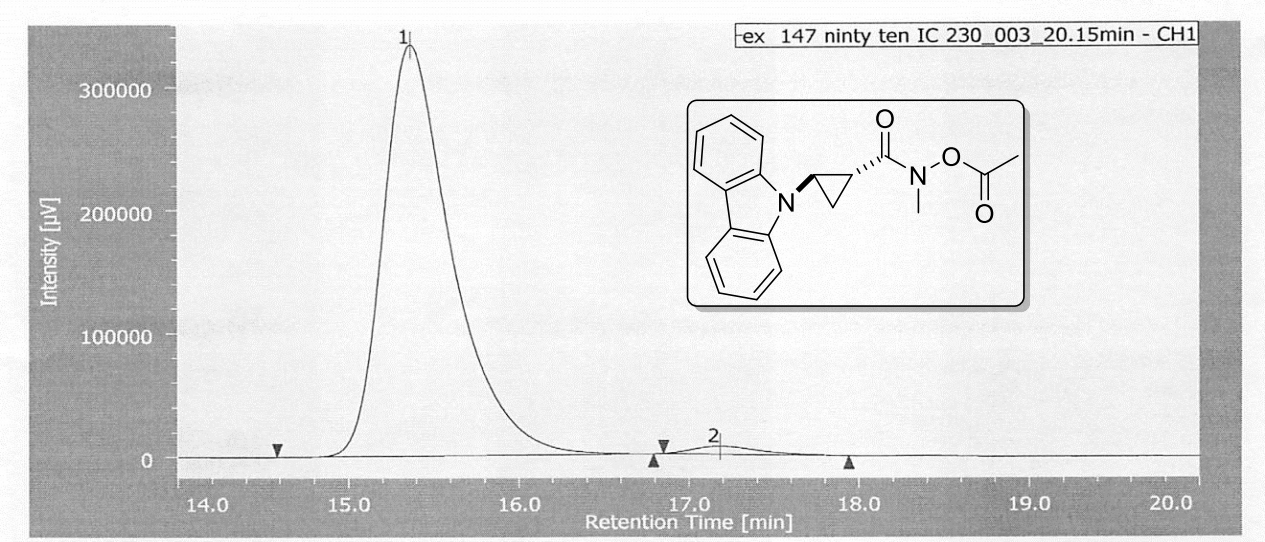
No.	Time [min]	Area [μV-sec]	Area%
1	15.75	16871308	49.978
2	18.95	16886310	50.022



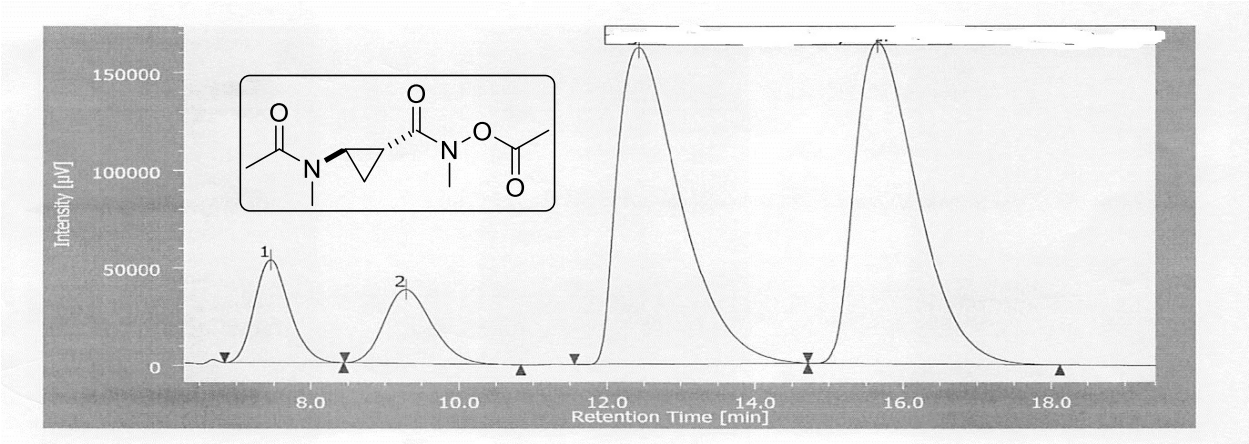
No.	Time [min]	Area [μV-sec]	Area%
1	16.43	336053	4.10
2	19.83	7847894	95.89



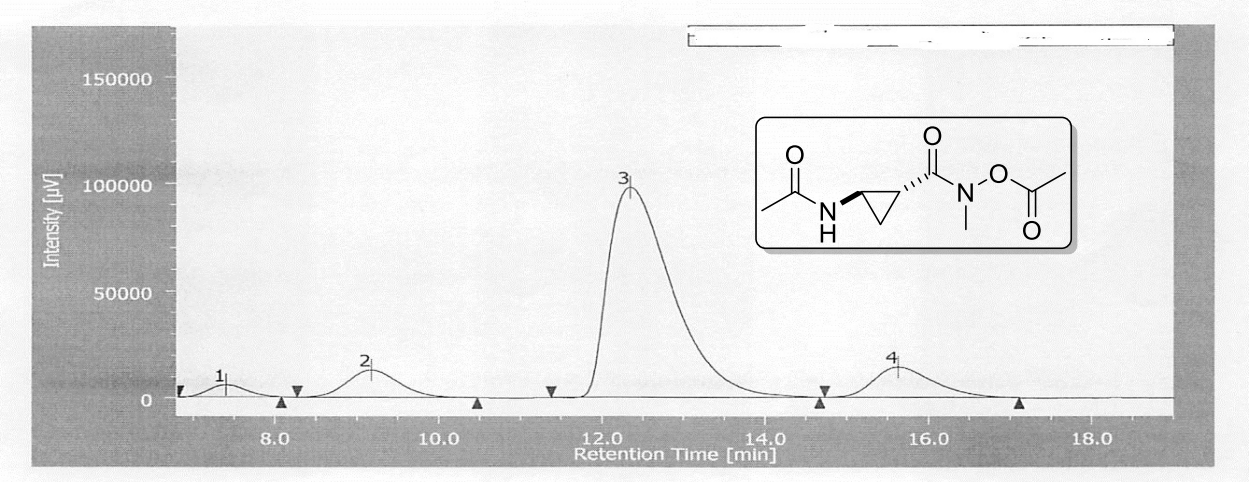
No.	Time [min]	Area [µV-sec]	Area%
1	15.71	6599946	50.02
2	17.59	6593264	49.97



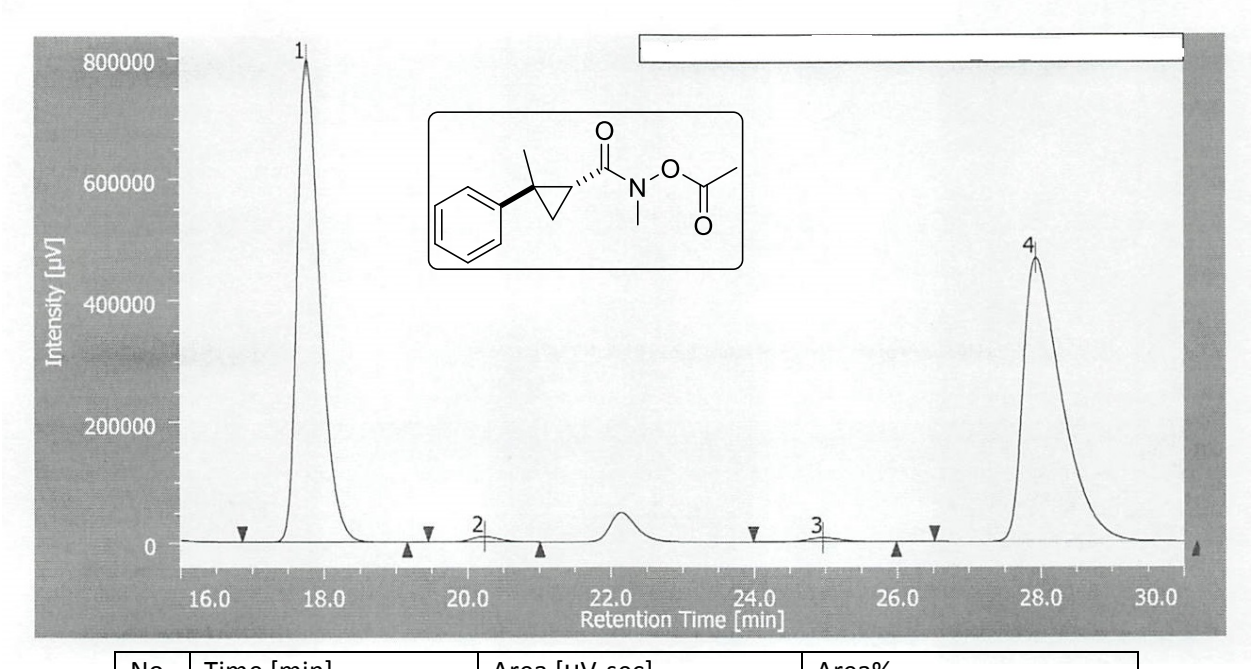
No.	Time [min]	Area [µV-sec]	Area%
1	15.36	9402883	98.071
2	17.18	178910	1.929



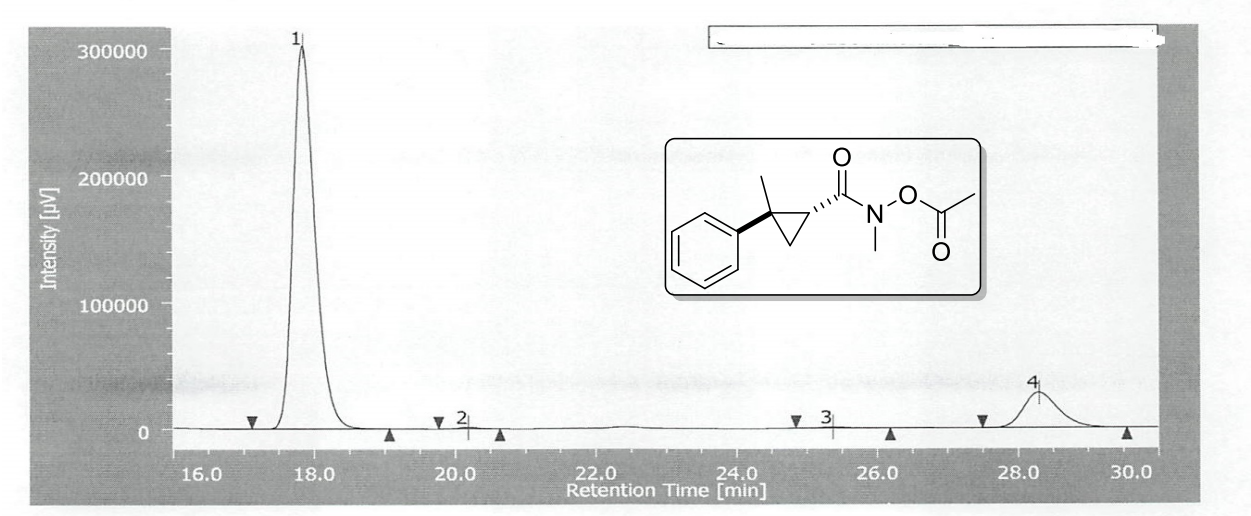
No.	Time [min]	Area [µV-sec]	Area%
1	7.45	1730152	7.61
2	9.28	1704502	7.50
3	12.42	79623440	42.35
4	15.65	79662923	42.52



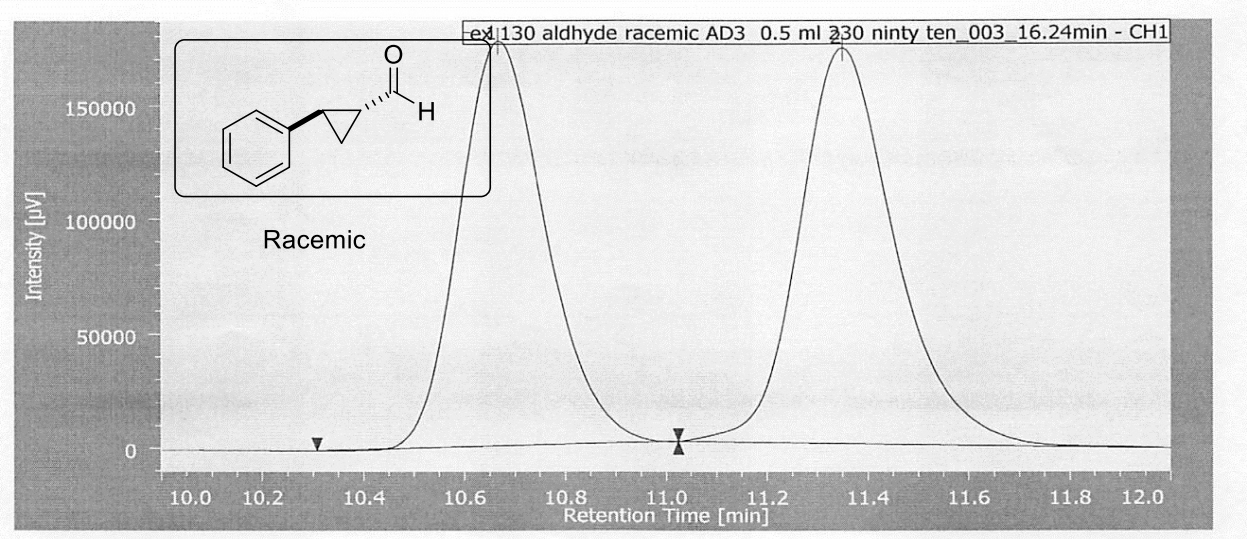
No.	Time [min]	Area [µV-sec]	Area%
1	7.40	180900	2.84
2	9.17	568128	8.13
3	12.34	5355099	78.37
4	15.62	728703	10.66



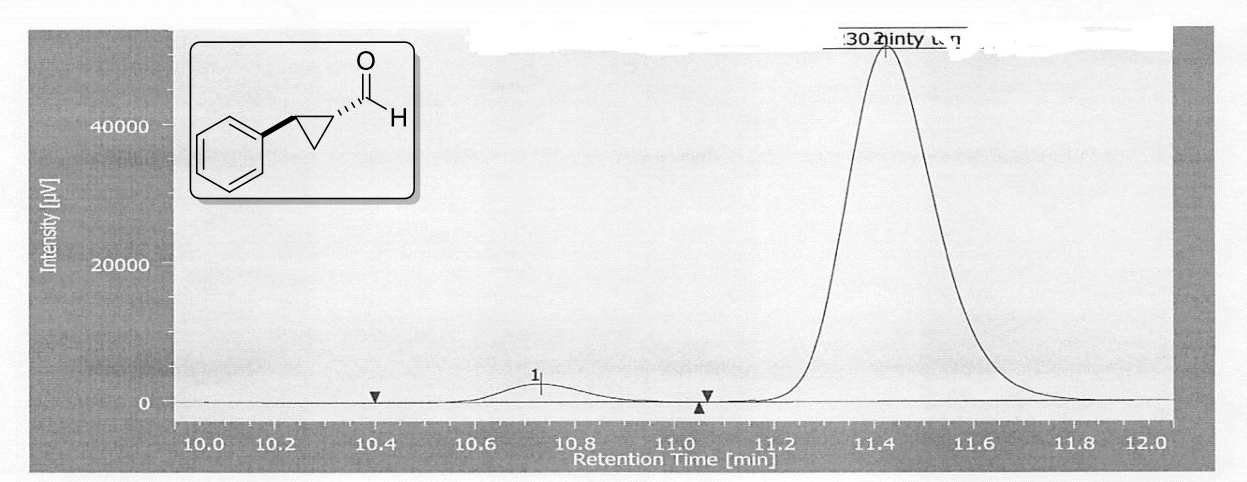
No.	Time [min]	Area [μV-sec]	Area%
1	17.75	17411767	49.24
2	20.23	250234	0.70
3	24.95	225202	0.63
4	27.93	17467118	49.40



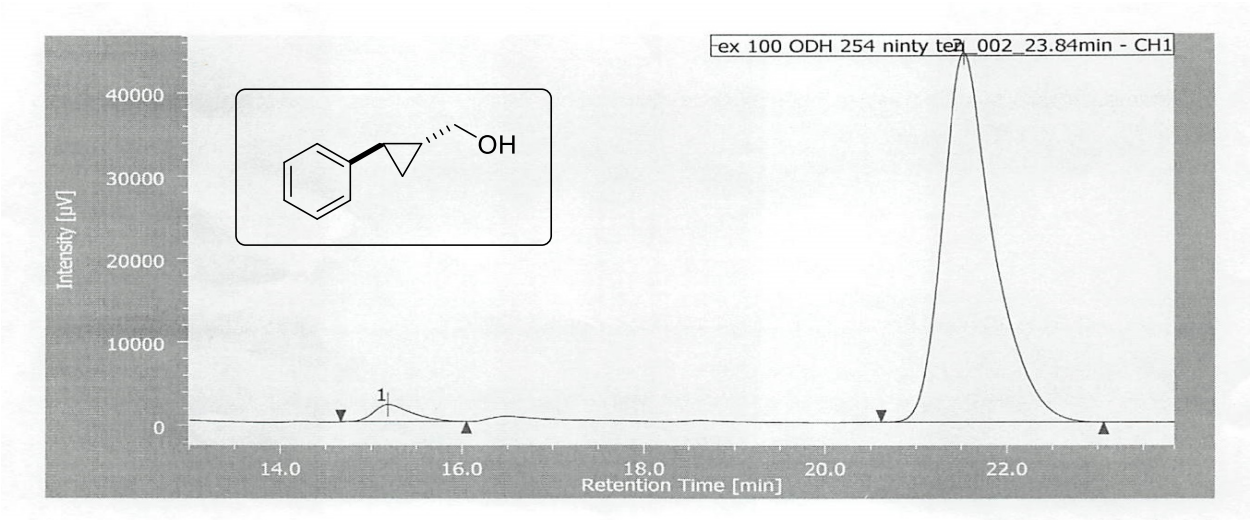
No.	Time [min]	Area [μV-sec]	Area%
1	17.85	6469084	86.36
2	20.18	23208	0.13
3	25.36	23666	0.13
4	28.29	974233	13.00



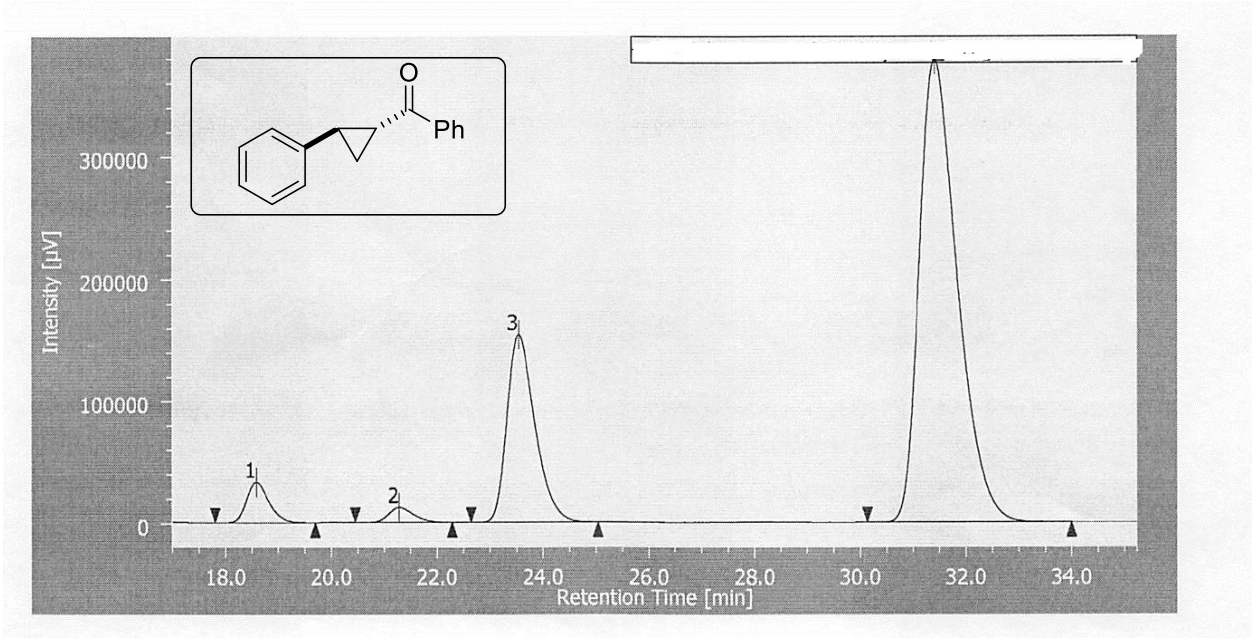
No.	Time [min]	Area [µV-sec]	Area%
1	10.66	2106736	50.79
2	11.350	2287697	49.21



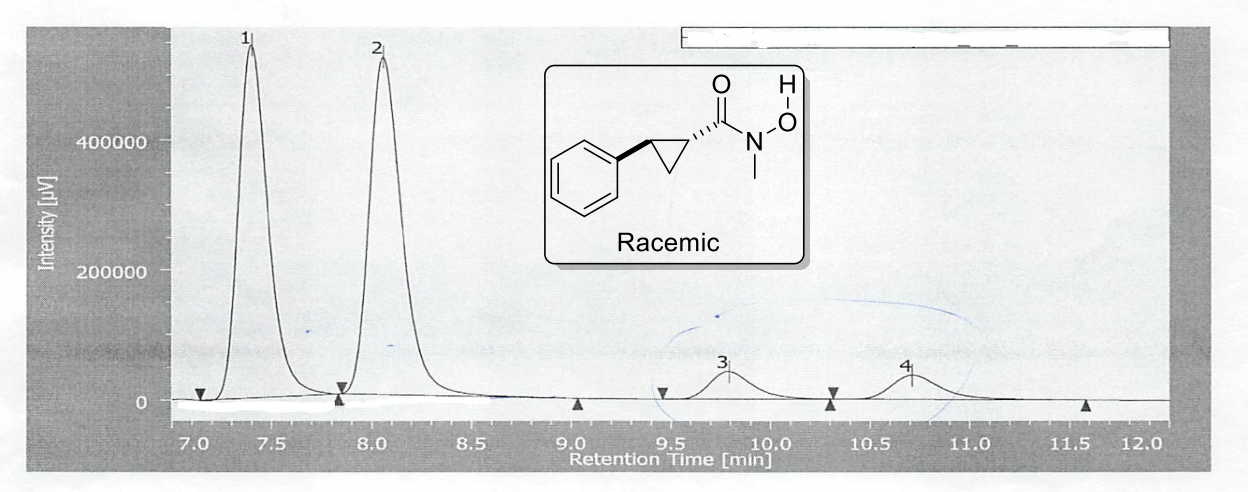
No.	Time [min]	Area [µV-sec]	Area%
1	10.37	30751	4.511
2	11.42	650977	95.48



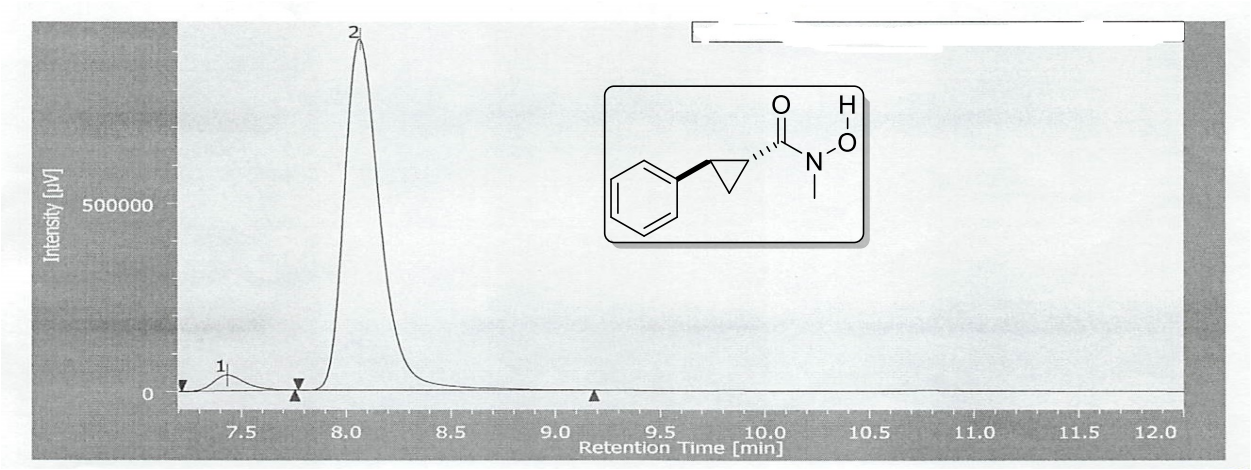
No.	Time [min]	Area [μV-sec]	Area%
1	15.18	59811	3.36
2	21.53	1715954	96.63



No.	Time [min]	Area [μV-sec]	Area%
1	18.58	970661	3.74
2	21.28	396186	1.53
3	23.54	5681480	21.93
4	31.41	18848868	72.78



No.	Time [min]	Area [μV-sec]	Area%
1	7.40	5623880	44.87
2	8.05	5952538	45.32
3	9.79	643097	5.000
4	10.70	642750	4.99



No.	Time [min]	Area [μV-sec]	Area%
1	7.43	442323	3.849
2	8.06	11050246	96.151