# *Supporting Information*

## Ir(III)-Catalyzed Stereoselective Haloamidation of Alkynes Enabled by Ligand Participation

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## I .General Information

Unless otherwise stated, all commercial reagents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 $F_{254}$ plates. Visualization on TLC was achieved by the use of UV light (254 nm), treatment with acidic anisaldehyde, 10% ninhydrin in ethanolm, 5% phosphormolybdic acid in ethanol, or ceric ammonium molybdate stain followed by heating. Silica-gel column chromatography was performed using a CombiFlash® $R_f$ $^+$ system with RediSep® $R_f$ Silica columns (230 – 400 mesh) using a proper eluent system. Air sensitive liquid and solutions were transferred via syringe or cannula by using degassed solvents. Concentration of solution was carried out by using a rotary evaporator and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on Brucker Avance 400 MHz or Agilent Technologies DD2 600 MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak (e.g. $CHCl_3$ in $CDCl_3$: 7.26 ppm) or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Carbon 13 nuclear magnetic resonance spectroscopy ($^{13}$C NMR) was recorded on Brucker Avance (100 MHz) or Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. $^{19}$F NMR was recorded on Agilent Technologies DD2 (564 MHz). Frequencies are given in reciprocal centimeters ($cm^{-1}$) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using FAB or EI method. Melting point was measured with Buchi Melting Point M-565. X-ray diffraction data was collected on a Bruker SMART APEX II coated with Paraton-*N* oil under a stream of $N_2$ (g) at 120 K. Crystal of **12**, **16** and **29** were coated with parabar oil and the diffraction data measured at 100 K with synchrotron radiation ($\lambda$ = 0.70000 Å) on a Rayonix MX225HS detector at BL2D-SMC with a silicon (111) double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program was used for data collection (detector distance is 66 mm, omega scan; $\Delta\omega$ = 1°, exposure time is 1 sec per frame) and HKL3000sm (Ver. 716.7) was used for cell refinement, reduction and absorption correction. The crystal structures of **12, 16** and **29** were solved by SHELX structure solution program and refined by full-matrix least-squares calculations with the SHELXL. The NMR spectral data for the $BAr^F_4$ anion ($BAr^F_4$ = B{3,5-$(CF_3)_2C_6H_3$}$_4$) are identical for all complexes in dichloromethane-$d_2$ and are not repeated below. B($Ar^F$ )$_4$: **$^1$H NMR** δ 7.72 (s, 8H, *o*-Ar), 7.54 (s, 4H, *p*-Ar); **$^{13}$C NMR** δ 161.9 (q, *J* = 49.7 Hz, *ipso*-Ar), 134.9 (*o*-Ar), 128.9 (q, *J* = 33.9 Hz, *m*-Ar), 124.7 (q, *J* = 273.5 Hz, *C*$F_3$), 117.7 (*p*-Ar); **$^{19}$F NMR** δ -62.71.

## II. Procedures for the Preparation of Starting Materials

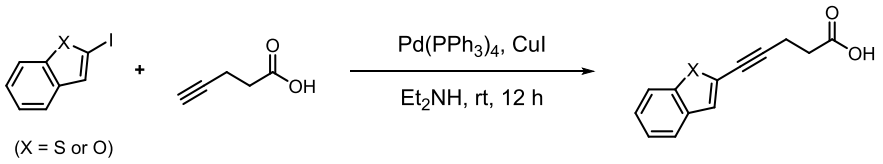
### 1. Preparation of Ir complex I

**I** was synthesized according to the previously reported procedure.[1]

### 2. Preparation of Carboxylic Acids

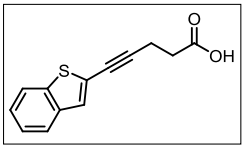
5-Phenylpent-4-ynoic acid,[2] 5-(4-methoxyphenyl)pent-4-ynoic acid,[3] 5-(4-chlorophenyl)pent-4-ynoic acid,[3] 5-{4-(trifluoromethyl)phenyl}pent-4-ynoic acid,[3] 5-(4-nitrophenyl)pent-4-ynoic acid,[3] 2-methyl-5-phenylpent-4-ynoic acid,[4] 3-methyl-5-phenylpent-4-ynoic acid,[5], 7-phenylhepta-4,6-diynoic acid,[6] 2-(phenylethynyl)benzoic acid,[7] 2-(cyclohex-1-en-1-ylethynyl)benzoic acid,[7] 2-(cyclopropylethynyl)benzoic acid,[8] and 2-(3,3-dimethylbut-1-yn-1-yl)benzoic acid[7] were synthesized according to the previously reported procedures.

### 3. Preparation of 5-(benzofuran-2-yl)pent-4-ynoic acid and 5-(benzo[*b*]thiophen-2-yl)pent-4-ynoic acid[2]



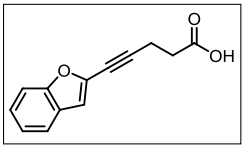

A solution of 2-iodobenzofuran or 2-iodobenzo[*b*]thiophene (24.5 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol) and CuI (456 mg, 2.4 mmol) in $Et_2NH$ (20 mL) was stirred at room temperature for 10 min. To the resulting mixture, a solution of carboxylic acid (20.4 mmol) in $Et_2NH$ (15 mL) was added. The reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was diluted with EtOAc (10 mL) and water (20 mL). The aqueous layer was washed with EtOAc (20 mL x 3). To the aqueous layer was added aqueous 2N HCl until pH = 1 ~ 2 to protonate the carboxylate ion and the aqueous layer was extracted with EtOAc (25 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: *n*-hexane/EtOAc = 4:1 ~ 2:1) to obtain the desired product.

**5-(Benzo[*b*]thiophen-2-yl)pent-4-ynoic acid**



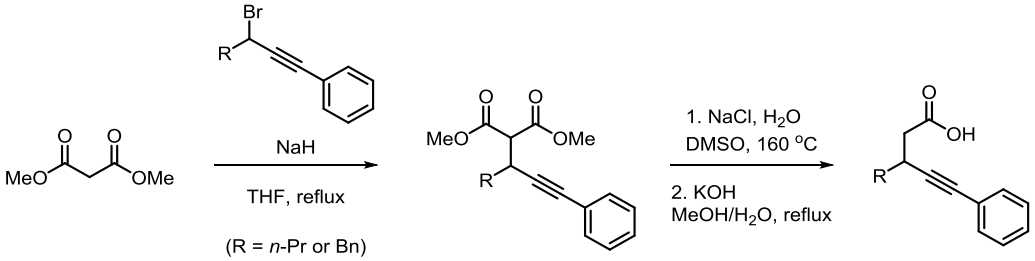
Yellow solid (2.2 g, 65%); **m.p.** 151-153 °C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$, *one proton of carboxylic acid, COO**H**, is not observed due to broadness*) δ 7.76 – 7.73 (m, 2H), 7.37 – 7.35 (m, 3H), 2.81 (t, *J* = 7.1 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 176.7, 140.2, 139.5, 128.6, 125.7, 125.1, 124.1, 123.8, 122.3, 94.5, 75.0, 33.2, 15.8; **IR** ($cm^{-1}$) 2916, 2138, 1690, 1427, 1409, 1204; **HRMS** (EI) m/z calcd. for $C_{13}H_{10}O_2S$ $[M]^+$: 230.0402, found: 230.0403.

**5-(Benzofuran-2-yl)pent-4-ynoic acid**



White solid; **m.p.** 130-132 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$, *one proton of carboxylic acid, COO**H**, is not observed due to broadness*) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.30 – 7.24 (m, 1H), 6.92 (s, 1H), 2.87 (t, *J* = 6.8 Hz, 2H), 2.78 (t, *J* = 6.9 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 177.8, 155.0, 139.2, 128.0, 125.8, 123.6, 121.5, 111.4, 111.2, 94.8, 72.1, 33.1, 15.6; **IR** ($cm^{-1}$) 2922, 2233, 1720, 1694, 1570, 1429, 1412, 1307, 1215; **HRMS** (EI) m/z calcd. for $C_{13}H_{10}O_3$ $[M]^+$: 214.0630, found: 214.0632.

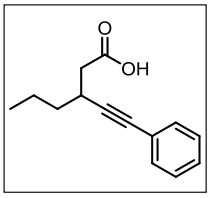
**4. Preparation of 3-(phenylethynyl)hexanoic acid and 3-benzyl-5-phenylpent-4-ynoic acid[5]**




To a 0 °C suspension of NaH (1.1 equiv) was prepared via dropwise addition of dimethylmalonate (3.0 equiv). Stirring at 0 °C (in ice bath) for 5 min was followed by dropwise addition of (3-bromohex-1-yn-1-yl)benzene or (3-bromobut-1-yne-1,4-diyl)dibenzene (1.0 equiv). The reaction mixture was then heated to reflux for about 12 h, cooled to room temperature and quenched with a saturated $NH_4Cl$ (aq) solution. The mixture was extracted with $Et_2O$ (x 4), washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude alkylation products were then purified using silica column chromatography (eluent: *n*-hexane/ EtOAc = 20:1 ~ 4:1).

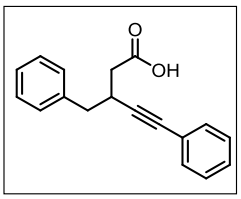
A round-bottom flask was charged with the alkylated products (1.0 equiv), NaCl (21.0 equiv), water (2.0 equiv) and DMSO (30 mL). The reactions were observed to be complete after heating at 160 ºC for 8 h. The crude mixture was cooled to room temperature, diluted with water (30 mL), extracted with $CH_2Cl_2$ (x 4). After that, the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give yellow liquids. These crude esters (1 equiv) was taken up into MeOH (9 mL), water (5 mL) and KOH (2.2 equiv) added. The mixture was heated to reflux for 2 h, cooled to rt, and acidified to pH 1 using 6N HCl. The cloudy solution was then extracted with $Et_2O$ (x 4), the combined organic layers washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture were then purified using silica column chromatography (eluent: *n*-hexane/EtOAc = 4:1 ~ 2:1) to give the desired carboxylic acids.

**3-(Phenylethynyl)hexanoic acid**




Prepared according to general procedure on a 17.1 mmol scale. Yellow oil (2.1 g, two steps yield from (3-bromohex-1-yn-1-yl)benzene: 77%); **$^1$H NMR** (600 MHz, $CD_2Cl_2$, *one proton of carboxylic acid, COO**H**, is not observed due to broadness*) δ 7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 3H), 3.08 (p, *J* = 7.3, 6.7 Hz, 1H), 2.68 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.60 (dd, *J* = 15.8, 6.6 Hz, 1H), 1.67 – 1.56 (m, 3H), 1.56 – 1.46 (m, 1H), 0.98 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 176.9, 131.5, 128.2, 127.8, 123.5, 91.2, 82.0, 39.7, 36.7, 28.4, 20.4, 13.5.

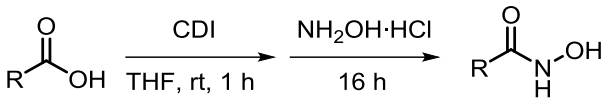
**3-Benzyl-5-phenylpent-4-ynoic acid**




Prepared according to general procedure on a 7.1 mmol scale. Yellow oil (1.5 g, two steps yield from (3-bromobut-1-yne-1,4-diyl)dibenzene: 81%); **$^1$H NMR** (600 MHz, $CD_2Cl_2$, *one proton of carboxylic acid, COO**H**, is not observed due to broadness*) δ 7.37 – 7.31 (m, 6H), 7.31 – 7.24 (m, 4H), 3.33 (tt, *J* = 7.7, 6.6 Hz, 1H), 2.99 – 2.88 (m, 2H), 2.71 – 2.59 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 177.0, 138.9, 131.7 129.7, 128.5, 128.5, 128.2, 126.9, 123.5, 90.9, 83.2, 40.8, 39.1, 30.9.

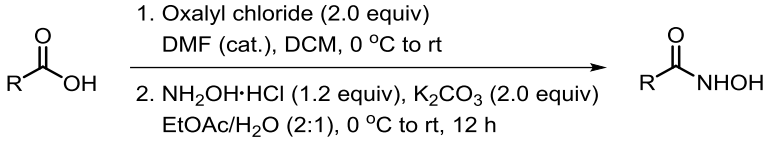
## 5. Preparation of Hydroxamic Acids

### General procedure A: One-Pot Synthesis of Hydroxamic Acids from Carboxylic Acids[1]




1,1'-Carbonyldiimidazole (CDI, 15 mmol, 1.5 equiv) was added to a solution of carboxylic acid (10 mmol) in dry tetrahydrofuran (THF, 30 mL). The reaction mixture was stirred for 1 h. Powdered hydroxylamine hydrochloride (1.39 g, 20 mmol) was added. The resulting mixture was stirred overnight (about 16 h). The mixture was diluted with 5% aq. $KHSO_4$ (30 mL) and extracted with EtOAc (2 x 30 mL). The combined organic phase was washed with brine (50 mL) and dried over $MgSO_4$. The extract was filtered and concentrated under reduced pressure and the crude mixture was purified by silica gel column chromatography (eluent: dichloromethane/methanol = 30:1 ~ 10:1) to obtain the hydroxamic acid.

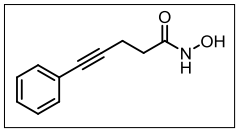
### General procedure B: One-Pot Synthesis of Hydroxamic Acids from Carboxylic Acids[1]




Oxalyl chloride (4.0 mmol) and DMF (2 drops) were added to a solution of the carboxylic acid (2.0 mmol) in dichloromethane (30 mL) at 0 °C. The mixture was allowed to stir at room temperature for 2.5 ~ 4 h, then the reaction mixture was concentrated, and the crude product was used directly in the next reaction.

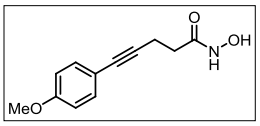
Hydroxylamine hydrochloride (1.2 equiv) was added to a biphasic mixture of $K_2CO_3$ (2.0 equiv) in a 2:1 mixture of EtOAc (16 mL) and $H_2O$ (8 mL). The resulting solution was cooled to 0°C followed by dropwise addition of the unpurified acid chloride dissolved in a minimum amount of EtOAc under ambient conditions. The flask containing the acid chloride was then rinsed with additional EtOAc. The reaction was warmed to room temperature for stirring additional 12 h. The phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by recrystallization (dichloromethane + few drops of methanol/*n*-pentane) or silica chromatography (eluent: dichloromethane/methanol = 30:1 ~ 10:1) to afford the desired hydroxamic acid.

**5-Phenylpent-4-ynyl hydroxamic acid**



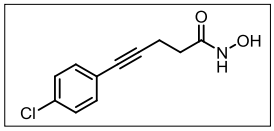
Prepared according to general procedure **A** from 5-phenylpent-4-ynoic acid on a 11.0 mmol scale. White solid (1.79 g, 86%); **m.p.** 108-110 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.49 (s, 1H), 8.82 (s, 1H), 7.37 – 7.33 (m, 5H), 2.63 (t, $J$ = 7.2 Hz, 2H), 2.24 (t, $J$ = 7.2 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.3, 131.2, 128.5, 128.0, 123.0, 89.5, 80.7, 31.5, 15.1; **IR** (cm$^{-1}$) 3281 ,3051, 2768, 2110, 1662, 1623, 1561, 1440, 1082, 985; **HRMS** (EI) m/z calcd. for $C_{11}H_{11}NO_2$ $[M]^+$: 189.0790, found: 189.0791.

**5-(4-Methoxyphenyl)pent-4-ynyl hydroxamic acid**



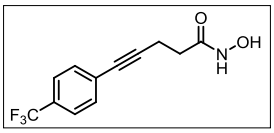
Prepared according to general procedure **A** from 5-(4-methoxyphenyl)pent-4-ynoic acid on a 10.0 mmol scale. White solid (1.53 g, 70%); **m.p.** 131-133 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.48 (s, 1H), 8.81 (s, 1H), 7.30 (d, $J$ = 8.6 Hz, 2H), 6.90 (d, $J$ = 8.6 Hz, 2H), 3.75 (s, 3H), 2.60 (t, $J$ = 7.2 Hz, 2H), 2.22 (t, $J$ = 7.2 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.3, 158.9, 132.7, 115.0, 114.1, 87.7, 80.5, 55.1, 31.7, 15.1; **IR** (cm$^{-1}$) 3270, 3039, 2780, 1656, 1605, 1566, 1508, 1440, 1245; **HRMS** (EI) m/z calcd. for $C_{12}H_{13}NO_3$ $[M]^+$: 219.0895, found: 219.0898.

**5-(4-Chlorophenyl)pent-4-ynyl hydroxamic acid**



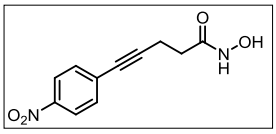
Prepared according to general procedure **A** from 5-(4-chlorophenyl)pent-4-ynoic acid on a 8.5 mmol scale. White solid (1.60 g, 84%); **m.p.** 167-169 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.49 (s, 1H), 8.82 (s, 1H), 7.44 – 7.36 (m, 4H), 2.63 (s, 2H), 2.24 (s, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.2, 133.0, 132.7, 128.7, 121.9, 90.8, 79.5, 31.4, 15.1; **IR** (cm$^{-1}$) 3262, 3062, 2704, 1660, 1621, 1565, 1487, 1433, 1079, 984, 823; **HRMS** (EI) m/z calcd. for $C_{11}H_{10}ClNO_2$ $[M]^+$: 223.0400, found: 223.0401.

**5-{4-(Trifluoromethyl)phenyl}pent-4-ynyl hydroxamic acid**



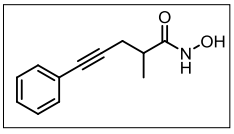
Prepared according to general procedure **A** from 5-{4-(trifluoromethyl)phenyl}pent-4-ynoic acid on a 10.0 mmol scale. Off-white solid (2.13 g, 83%); **m.p.** 141-143 °C; **$^{1}$H NMR** (600 MHz, DMSO-$d_6$) δ 10.51 (s, 1H), 8.84 (s, 1H), 7.71 (d, $J$ = 8.2 Hz, 2H), 7.58 (d, $J$ = 8.0 Hz, 2H), 2.68 (t, $J$ = 7.2 Hz, 2H), 2.26 (t, $J$ = 7.2 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.2, 132.0, 128.0 (q, $J$ = 32.0 Hz), 127.3, 125.4 (q, $J$ = 3.6 Hz), 124.0 (q, $J$ = 272.2 Hz), 92.8, 79.5, 31.3, 15.2; **$^{19}$F NMR** (564 MHz, DMSO-$d_6$) -61.3 (s); **IR** (cm$^{-1}$) 3264, 3026, 2165, 1981, 1608, 1509, 1326, 1250, 1166, 1125, 1069; **HRMS** (EI) m/z calcd. for $C_{12}H_{10}F_3NO_2$ $[M]^+$: 257.0664, found: 257.0660.

**5-(4-Nitrophenyl)pent-4-ynyl hydroxamic acid**



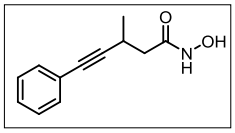
Prepared according to general procedure **A** from 5-(4-nitrophenyl)pent-4-ynoic acid on a 3.0 mmol scale. Off-white solid (0.61 g, 87%); **m.p.** 148-150 °C; **$^{1}$H NMR** (600 MHz, DMSO-$d_6$) δ 10.52 (s, 1H), 8.85 (s, 1H), 8.20 (d, $J$ = 7.3 Hz, 2H), 7.63 (d, $J$ = 8.2 Hz, 2H), 2.71 (t, $J$ = 7.1 Hz, 2H), 2.28 (t, $J$ = 7.0 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.6, 146.9, 132.9, 130.4, 124.2, 96.1, 79.8, 31.6, 15.8; **IR** (cm$^{-1}$) 3383, 3262, 3066, 2217, 1672, 1636, 1591, 1505, 1432, 1339; **HRMS** (EI) m/z calcd. for $C_{11}H_{10}N_2O_4$ $[M]^+$: 234.0641, found: 234.0643.

**2-Methyl-5-phenylpent-4-ynyl hydroxamic acid**



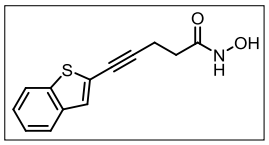
Prepared according to general procedure **B** from 2-methyl-5-phenylpent-4-ynoic acid on a 3.5 mmol scale. White solid (0.63 g, 90%); **m.p.** 130-132 °C; **$^{1}$H NMR** (600 MHz, DMSO-$d_6$) δ 10.54 (s, 1H), 8.83 (s, 1H), 7.41 – 7.31 (m, 5H), 2.63 – 2.53 (m, 1H), 2.46 – 2.36 (m, 2H), 1.11 (d, $J$ = 6.7 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 170.8, 131.2, 128.5, 128.0, 123.0, 88.6, 81.4, 36.6, 23.3, 17.3; **IR** (cm$^{-1}$) 3207, 3038, 2913, 1680, 1625, 1539, 1488, 1453; **HRMS** (EI) m/z calcd. for $C_{12}H_{13}NO_2$ $[M]^+$: 203.0946, found: 203.0948.

**3-Methyl-5-phenylpent-4-ynyl hydroxamic acid**



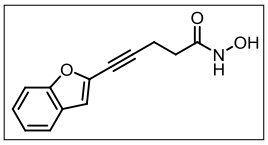
Prepared according to general procedure **A** from 3-methyl-5-phenylpent-4-ynoic acid on a 12.2 mmol scale. White solid (1.93 g, 78%); **m.p.** 121-123 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.50 (s, 1H), 8.84 (s, 1H), 7.38 – 7.30 (m, 5H), 3.07 (h, *J* = 7.1 Hz, 1H), 2.25 (dd, *J* = 13.9, 7.4 Hz, 1H), 2.15 (dd, *J* = 13.9, 7.4 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$, *one carbon merged to solvent peak*) δ 167.1, 131.7, 129.0, 128.5, 123.4, 94.2, 81.1, 23.4, 20.9; **IR** (cm$^{-1}$) 3181, 3009, 2898, 1628, 1540, 1485, 1440, 1428; **HRMS** (EI) m/z calcd. for $C_{12}H_{13}NO_2$ $[M]^+$: 203.0946, found: 203.0949.

**5-(Benzo[*b*]thiophen-2-yl)pent-4-ynyl hydroxamic acid**



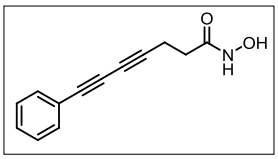
Prepared according to general procedure **A** from 5-(benzo[*b*]thiophen-2-yl)pent-4-ynoic acid on a 7.0 mmol scale. Yellow solid (1.6 g, 97%); **m.p.** 152-154 °C; **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.52 (s, 1H), 8.86 (s, 1H), 7.91 (m, 1H), 7.81 (m, 1H), 7.54 (s, 1H), 7.39 (m, 2H), 2.73 (t, *J* = 6.8 Hz, 2H), 2.28 (t, *J* = 6.8 Hz, 2H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$) δ 167.2, 138.9, 138.8, 128.4, 125.6, 125.0, 123.9, 122.8, 122.2, 96.2, 74.1, 31.1, 15.4; **IR** (cm$^{-1}$) 3272, 3054, 2720, 1658, 1614, 1556, 1417, 1079; **HRMS** (EI) m/z calcd. for $C_{13}H_{11}NO_2S$ $[M]^+$: 245.0510, found: 245.0509.

**5-(Benzofuran-2-yl)pent-4-ynyl hydroxamic acid**



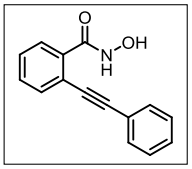
Prepared according to general procedure **A** from 5-(benzofuran-2-yl)pent-4-ynoic acid on a 6.5 mmol scale. Off-white solid; **m.p.** 132-134 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.53 (s, 1H), 8.86 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 7.0 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.0, 153.9, 138.1, 127.2, 125.6, 123.5, 121.3, 111.0, 110.8, 96.6, 71.2, 30.8, 15.1; **IR** (cm$^{-1}$) 3146, 3053, 2912, 2241, 1629, 1561, 1472, 1448, 1422, 1327, 1253, 1199; **HRMS** (EI) m/z calcd. for $C_{13}H_{11}NO_3$ $[M]^+$: 229.0739, found: 229.0741.

**7-Phenylhepta-4,6-diynyl hydroxamic acid**



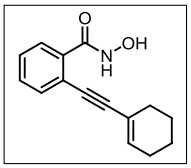
Prepared according to general procedure **A** from 7-phenylhepta-4,6-diynoic acid on a 5.0 mmol scale. White solid (0.95 g, 89%); **m.p.** 128-130 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.51 (s, 1H), 8.86 (s, 1H), 7.53 (d, $J$ = 7.0 Hz, 2H), 7.45 (t, $J$ = 7.4 Hz, 1H), 7.40 (t, $J$ = 7.3 Hz, 2H), 2.64 (t, $J$ = 7.0 Hz, 2H), 2.22 (t, $J$ = 7.0 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.4, 132.8, 130.0, 129.3, 121.2, 85.2, 75.4, 74.6, 65.4, 31.2, 15.6; **IR** (cm$^{-1}$) 3191, 3044, 2914, 1632, 1544, 1489, 1429, 1378, 1077; **HRMS** (EI) m/z calcd. for $C_{13}H_{11}NO_2$ $[M]^+$: 213.0790, found: 213.0793.

**2-(Phenylethynyl)benzyl hydroxamic acid**



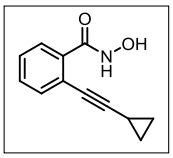
Prepared according to general procedure **A** from 2-(phenylethynyl)benzoic acid on a 1.3 mmol scale. White solid (0.21 g, 67%); **m.p.** 160-162 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.98 (s, 1H), 9.19 (s, 1H), 7.61 (d, $J$ = 7.6 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.50 (m, $J$ = 7.6, 4.9 Hz, 1H), 7.48 – 7.39 (m, 5H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) 164.5, 137.3, 132.4, 131.4, 129.8, 128.9, 128.7, 128.5, 127.9, 122.4, 120.5, 92.6, 87.7; **IR** (cm$^{-1}$) 3165, 3047, 2214, 1613, 1537, 1493, 1440, 1393, 1167; **HRMS** (EI) m/z calcd. for $C_{15}H_{11}NO_2$ $[M]^+$: 237.0790, found: 237.0791.

**2-(Cyclohex-1-en-1-ylethynyl)benzyl hydroxamic acid**



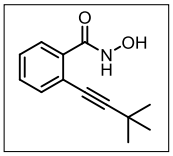
Prepared according to general procedure **B** from 2-(cyclohex-1-en-1-ylethynyl)benzoic acid on a 3.0 mmol scale. White solid (0.61 g, 85%); **m.p.** 128-130 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.85 (s, 1H), 9.11 (s, 1H), 7.47 – 7.40 (m, 2H), 7.38 (s, 2H), 6.20 – 6.14 (m, 1H), 2.17 – 2.07 (m, 4H), 1.66 – 1.51 (m, 4H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 165.0 137.5, 136.0, 132.7, 130.1, 128.4, 128.3, 121.5, 120.7, 95.0, 85.6, 29.0, 25.7, 22.2, 21.5; **IR** (cm$^{-1}$) 3284, 3146, 2895, 2197, 1610, 1589, 1534, 1458, 1315, 1264, 1166; **HRMS** (EI) m/z calcd. for $C_{15}H_{15}NO_2$ $[M]^+$: 241.1103, found: 241.1105.

**2-(Cyclopropylethynyl)benzyl hydroxamic acid**



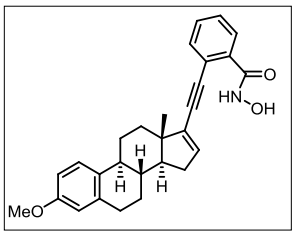
Prepared according to general procedure **B** from 2-(cyclopropylethynyl)benzoic acid on a 8.5 mmol scale. White solid (0.94 g, 55%); **m.p.** 135-137 °C; **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.79 (s, 1H), 9.12 (s, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 1.50 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.91 – 0.84 (m, 2H), 0.73 (dt, *J* = 4.8, 3.1 Hz, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 165.1, 137.7, 132.9, 130.0, 128.2, 127.9, 121.8, 97.9, 74.0, 9.0, 0.5; **IR** (cm$^{-1}$) 3243, 2898, 2225, 1631, 1510, 1475, 1308, 1166, 1024, 953, 901, 755; **HRMS** (EI) m/z calcd. for $C_{12}H_{11}NO_2$ $[M]^+$: 201.0790, found: 201.0787.

**2-(3,3-Dimethylbut-1-yn-1-yl)benzyl hydroxamic acid**



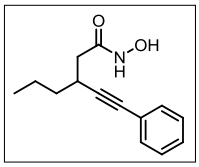
Prepared according to general procedure **B** from 2-(3,3-dimethylbut-1-yn-1-yl)benzoic acid on a 4.0 mmol scale. Off-white solid (0.85 g, 96%); **m.p.** 88-90 °C; **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.77 (d, *J* = 2.1 Hz, 1H), 9.06 (d, *J* = 2.1 Hz, 1H), 7.43 – 7.32 (m, 4H), 1.27 (s, 9H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 164.9, 137.7, 132.6, 130.0, 128.3, 128.1, 121.7, 102.6, 77.6, 31.0, 28.2; **IR** (cm$^{-1}$) 3350, 3167, 2967, 2233, 1639, 1593, 1519, 1458, 1363, 1272, 1199, 1161, 1021, 895; **HRMS** (EI) m/z calcd. for $C_{13}H_{15}NO_2$ $[M]^+$: 217.1103, found: 217.1102.

***N*-hydroxy-2-[{(8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl}ethynyl]benzamide**



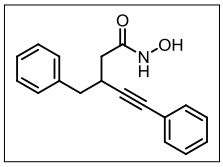
Prepared according to general procedure **B** from 2-[{(8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl}ethynyl]benzoic acid on a 1.0 mmol scale. Off-white solid (0.34 g, 84%); **m.p.** 158-159 °C; **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ 10.84 (s, 1H), 9.05 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.42 (ddd, *J* = 7.7, 5.1, 3.8 Hz, 1H), 7.38 (d, *J* = 4.3 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.66 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.60 (d, *J* = 2.5 Hz, 1H), 6.12 (s, 1H), 3.67 (s, 3H), 2.83 – 2.74 (m, 2H), 2.30 (ddd, *J* = 16.1, 6.3, 3.2 Hz, 2H), 2.22 (t, *J* = 11.1 Hz, 1H), 2.11 (dd, *J* = 15.9, 13.1 Hz, 1H), 2.02 (d, *J* = 10.6 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.56 (tt, *J* = 13.9, 7.2 Hz, 1H), 1.52 – 1.44 (m, 3H), 1.44 – 1.33 (m, 1H), 1.28 – 1.18 (m, 1H), 0.85 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 164.9, 157.5, 137.8, 137.5, 137.3, 136.8, 133.0, 132.6, 130.1, 128.6, 128.3, 126.3, 121.4, 114.0 111.9, 91.5, 89.0, 55.4, 55.3, 48.7, 44.3, 37.6, 34.5, 32.1, 29.6, 27.7, 26.6, 16.7; **IR** (cm$^{-1}$) 3362, 3205, 2927, 2196, 1655, 1609, 1498, 1463, 1281, 1254, 1235, 755, 735; **HRMS** (FAB) m/z calcd. for $C_{28}H_{29}NO_3$ $[M+H]^+$: 427.2147, found: 428.2229.

**3-(Phenylethynyl)hexanyl hydroxamic acid**



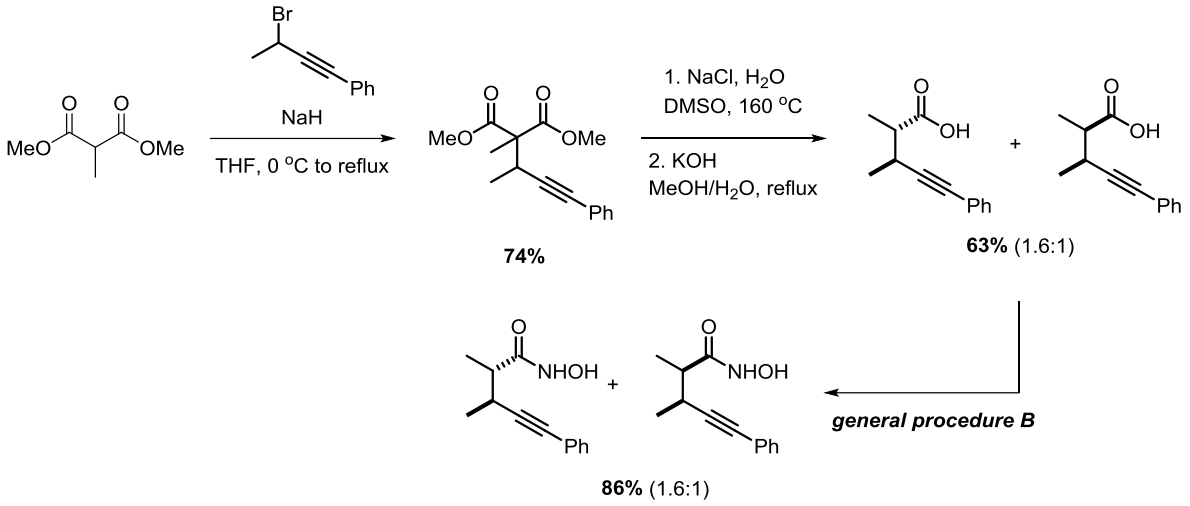
Prepared according to general procedure **A** from 3-(phenylethynyl)hexanoic acid on a 9.3 mmol scale. White solid (1.7 g, 84%); **m.p.** 90-92 °C; **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.50 (s, 1H), 8.84 (s, 1H), 7.39 – 7.30 (m, 5H), 3.03 – 2.96 (m, 1H), 2.20 (qd, $J$ = 14.0, 7.4 Hz, 2H), 1.58 – 1.45 (m, 2H), 1.45 – 1.38 (m, 2H), 0.92 (t, $J$ = 6.8 Hz, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$) δ 167.2, 131.7, 129.0, 128.4, 123.5, 93.0, 82.1, 38.6, 36.6, 28.7, 20.4, 14.2; **IR** (cm$^{-1}$) 3203, 3051, 2915, 1627, 1540, 1488, 1342, 1270, 1072, 985, 757, 737, 692; **HRMS** (EI) m/z calcd. for $C_{14}H_{17}NO_2$ $[M]^+$: 231.1259, found: 231.1260.

**3-Benzyl-5-phenylpent-4-ynyl hydroxamic acid**



Prepared according to general procedure **A** from 3-benzyl-5-phenylpent-4-ynoic acid on a 5.7 mmol scale. White solid (1.2 g, 76%); **m.p.** 85-87 °C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 9.03 (br, 1H), 8.74 (br, 1H), 7.39 – 7.34 (m, 2H), 7.34 – 7.22 (m, 8H), 3.31 (p, $J$ = 7.1, 6.5 Hz, 1H), 2.85 (ddt, $J$ = 21.4, 13.3, 7.1 Hz, 2H), 2.38 – 2.25 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 169.4, 138.5, 131.5, 129.4, 128.3, 128.2, 128.0, 126.6, 123.1, 90.4, 83.7, 40.6, 38.0, 31.0; **IR** (cm$^{-1}$) 3212, 3051, 2915, 1627, 1540, 1488, 1442, 1352, 1072, 985, 757, 737, 692.

**6. Preparation of (±)-(2,3-*anti*)-2,3-dimethyl-5-phenylpent-4-ynyl hydroxamic acid and (±)-(2,3-*syn*)-2,3-dimethyl-5-phenylpent-4-ynyl hydroxamic acid**

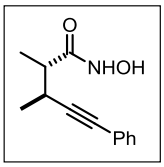



To a 0 ºC suspension of NaH (1.0 equiv) in dry THF was prepared via dropwise addition of dimethyl methylmalonate (2.0 equiv). Stirring at 0 ºC (in ice bath) for 5 min was followed by dropwise addition of (3-bromobut-1-yn-1-yl)benzene (15 mmol, 1.0 equiv). The reaction mixture was then heated to reflux for about 12 h, cooled to room temperature and quenched with a saturated $NH_4Cl$ (aq) solution. The mixture was extracted with ethyl acetate (x 4), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude alkylation products were then purified using silica column chromatography (eluent: *n*-hexane/ EtOAc = 20:1 ~ 4:1) to afford dimethyl 2-methyl-2-(4-phenylbut-3-yn-2-yl)malonate in 74% yield (3.1 g).

A round-bottom flask was charged with dimethyl 2-methyl-2-(4-phenylbut-3-yn-2-yl)malonate (1.0 equiv), NaCl (21.0 equiv), water (2.0 equiv) and DMSO (30 mL). The reactions were observed to be complete after heating at 160 ºC for 8 h. The crude mixture was cooled to room temperature, diluted with water (30 mL), extracted with $CH_2Cl_2$ (x 4). After that, the combined organic layers were washed with brine, dried by $MgSO_4$ and concentrated under reduced pressure to give yellow liquids. These crude esters (1 equiv) was taken up into MeOH (9 mL), water (5 mL) and KOH (2.2 equiv) added. The mixture was heated to reflux for 6 h, cooled to rt, and basified using 1N KOH. The crude mixture was washed by $Et_2O$ (x 4), and acidified to pH 1 using 1N HCl. The cloudy solution was then extracted with $Et_2O$ (x 4), the combined organic layers washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was used for next step without further purification (68%, 2 steps yield from malonate, diastereomeric ratio is measured to be 1.6 by $^1H$ NMR spectroscopy).

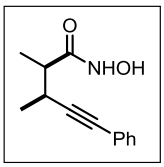
2,3-Dimethyl-5-phenylpent-4-ynyl hydroxamic acid was prepared according to general procedure **B** from 2,3-dimethyl-5-phenylpent-4-ynoic acid on a 7.1 mmol scale to afford a mixture of two diastereomers in 86% yield (1.3 g, major:minor = 1.6:1, measured by $^{1}$H NMR spectroscopy). Two diastereomers were separated by silica column chromatography (eluent: dichloromethane/methanol = 100:0 ~ 95:5)

**(±)-(2,3-*anti*)-2,3-Dimethyl-5-phenylpent-4-ynyl hydroxamic acid**



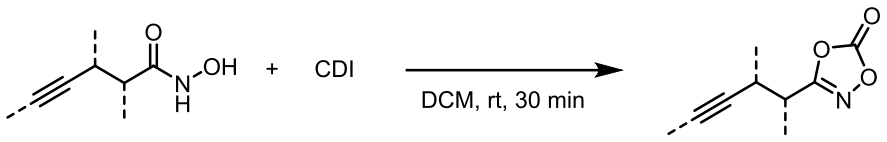

Major diastereomer: White solid; **m.p.** 153-155 °C; **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 8.45 (s, 1H), 7.79 (s, 1H), 7.45 – 7.36 (m, 2H), 7.35 – 7.24 (m, 3H), 2.91 (p, *J* = 7.2 Hz, 1H), 2.35 (p, *J* = 7.1 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 4H), 1.25 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 168.1, 131.4, 128.3, 128.1, 122.8, 89.1, 83.3, 36.9, 29.9, 17.8, 13.4; **IR** ($cm^{-1}$) 3169, 3038, 2913, 1628, 1489, 1019, 972, 759, 693, 482; **HRMS** (ESI) m/z calcd. for $C_{13}H_{15}NO_2$ $[M+Na]^+$: 240.0990, found: 240.1087.

**(±)-(2,3-*syn*)-2,3-Dimethyl-5-phenylpent-4-ynyl hydroxamic acid**



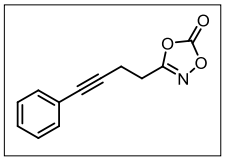

Minor diastereomer: White solid; **m.p.** 121-123 °C; **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 8.49 (br, 1H), 8.36 (br, 1H), 7.44 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 2.96 (p, *J* = 7.0 Hz, 1H), 2.27 (p, *J* = 7.0 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 172.6, 131.4, 128.2, 127.9, 123.3, 91.4, 82.6, 43.7, 30.0, 18.6, 15.3; **IR** ($cm^{-1}$) 3205, 3036, 2976, 2905, 1625, 1537, 1489, 1371, 1265, 1044, 975, 945, 738, 689, 432; **HRMS** (ESI) m/z calcd. for $C_{13}H_{15}NO_2$ $[M+Na]^+$: 240.0990, found: 240.1072.

**7. Preparation of 3-substituted-1,4,2-dioxazol-5-ones[1]**



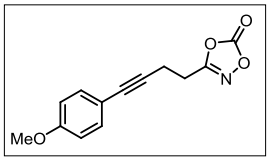

To a stirred solution of hydroxamic acid (5.0 mmol) in dichloromethane (50 mL) was added 1,1′-carbonyldiimidazole (0.81 g, 5.0 mmol) in one portion at room temperature. After stirring for 30 min, the reaction mixture was quenched with 1 N HCl (30 mL), extracted with dichloromethane three times (50 mL x 3) and dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude mixture was filtered through a pad of silica and washed with dichloromethane (10 mL x 2). The filtrate was concentrated under reduced pressure to afford 3-substituted 1,4,2-dioxazol-5-ones.

**3-(4-Phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (1, Scheme 2)**



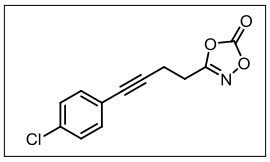
Prepared according to general procedure from 5-phenylpent-4-ynyl hydroxamic acid on a 8.5 mmol scale. White solid (1.7 g, 93%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.86 (t, *J* = 7.1 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 165.1, 153.9, 131.6, 128.3, 128.3, 122.6, 84.9, 83.2, 24.8, 15.6; **IR** ($cm^{-1}$) 1867, 1823, 1638, 1490, 1145; **HRMS** (EI) m/z calcd. for $C_{12}H_9NO_3$ $[M]^+$: 215.0582, found: 215.0581.

**3-{4-(4-Methoxyphenyl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



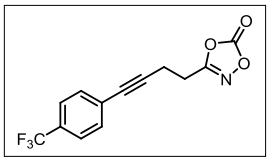

Prepared according to general procedure from 5-(4-methoxyphenyl)pent-4-ynyl hydroxamic acid on a 2.5 mmol scale. Off-white solid (0.50 g, 89%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.84 (t, *J* = 7.1 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 166.0, 160.1, 154.5, 133.4, 115.3, 114.4, 84.2, 82.9, 55.7, 25.3, 15.9; **IR** ($cm^{-1}$) 1856, 1826, 1633, 1605, 1509, 1289, 1247, 1148; **HRMS** (EI) m/z calcd. for $C_{13}H_{11}NO_4$ $[M]^+$: 245.0688, found: 245.0686.

**3-{4-(4-Chlorophenyl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



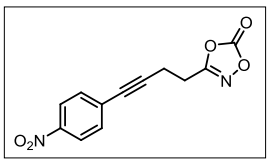
Prepared according to general procedure from 5-(4-chlorophenyl)pent-4-ynyl hydroxamic acid on a 6.0 mmol scale. Yellowish oil (1.5 g, 99%); **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 165.2, 154.0, 134.6, 133.0, 128.8, 121.3, 86.1, 82.3, 24.8, 15.7; **IR** ($cm^{-1}$) 1868, 1827, 1641, 1489, 1149, 1090, 981, 829, 739; **HRMS** (EI) m/z calcd. for $C_{12}H_8ClNO_3$ $[M]^+$: 249.0193, found: 249.0195.

**3-[4-{4-(Trifluoromethyl)phenyl}but-3-yn-1-yl]-1,4,2-dioxazol-5-one**



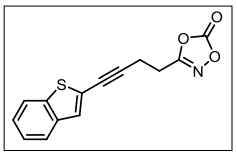
Prepared according to general procedure from 5-{4-(trifluoromethyl)phenyl}pent-4-ynyl hydroxamic acid on a 4.0 mmol scale. Colorless oil (3.7 g, 92%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$ δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H), 2.89 (t, *J* = 7.0 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.8, 154.4, 132.4, 130.2 (q, *J* = 32.6 Hz), 127.2, 125.7 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 272.1 Hz), 88.5, 81.9, 25.0, 15.9; **IR** ($cm^{-1}$) 1870, 1829, 1665, 1616, 1323, 1166, 1136, 1105, 1067; **HRMS** (EI) m/z calcd. for $C_{13}H_8F_3NO_3$ $[M]^+$: 283.0456, found: 283.0456.

**3-{4-(4-Nitrophenyl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



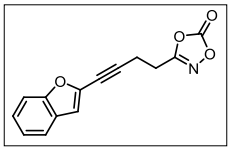
Prepared according to general procedure from 5-(4-nitrophenyl)pent-4-ynyl hydroxamic acid on a 2.5 mmol scale. Off-white solid (0.61 g, 94%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 3.00 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.2, 153.9, 147.1, 132.4, 129.6, 123.5, 90.9, 81.1, 24.4, 15.5; **IR** ($cm^{-1}$) 2227, 1871, 1854, 1825, 1640, 1590, 1509, 1489, 1337, 1304, 1287; **HRMS** (EI) m/z calcd. for $C_{12}H_8N_2O_5$ $[M]^+$: 260.0433, found: 260.0435.

**3-{4-(Benzo[*b*]thiophen-2-yl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



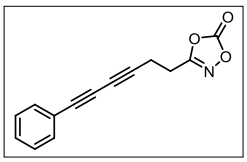
Prepared according to general procedure from 5-(benzo[*b*]thiophen-2-yl)pent-4-ynyl hydroxamic acid on a 6.0 mmol scale. White solid (1.3 g, 80%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.76 (m, 2H), 7.41 (s, 1H), 7.37 (m, 2H), 3.00 (t, *J* = 6.7 Hz, 2H), 2.94 (t, *J* = 6.7 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.7, 154.4, 140.4, 139.4, 129.2, 126.0, 125.2, 124.2, 123.1, 122.4, 91.9, 76.7, 25.0, 16.2; **IR** ($cm^{-1}$) 1863, 1819, 1632, 1431, 1224, 1151, 977, 750, 726; **HRMS** (EI) m/z calcd. for $C_{14}H_9NO_3S$ $[M]^+$: 271.0303, found: 271.0305.

**3-{4-(Benzofuran-2-yl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



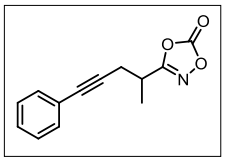
Prepared according to general procedure from 5-(benzofuran-2-yl)pent-4-ynyl hydroxamic acid on a 4.4 mmol scale. Off-white liquid (1.1 g, 97%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.28 – 7.22 (m, 1H), 6.93 (s, 1H), 3.04 – 2.92 (m, 4H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.5, 155.1, 154.3, 138.5, 127.9, 126.0, 123.7, 121.6, 111.9, 111.5, 92.3, 73.6, 24.7, 15.9; **IR** ($cm^{-1}$) 1864, 1826, 1638, 1449, 1144, 981, 751; **HRMS** (EI) m/z calcd. for $C_{14}H_9NO_4$ $[M]^+$: 255.0532, found: 255.0531.

**3-(6-Phenylhexa-3,5-diyn-1-yl)-1,4,2-dioxazol-5-one**



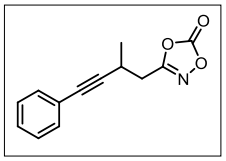
Prepared according to general procedure from 7-phenylhepta-4,6-diynyl hydroxamic acid on a 3.2 mmol scale. White solid (0.67 g, 89%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 7.0 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.0, 153.9, 132.5, 129.3, 128.4, 121.3, 79.4, 76.2, 73.2, 67.1, 24.3, 15.5; **IR** ($cm^{-1}$) 1861, 1828, 1633, 1425, 1147, 976, 758, 692; **HRMS** (EI) m/z calcd. for $C_{14}H_9NO_3$ $[M]^+$: 239.0582, found: 239.0580.

**3-(5-Phenylpent-4-yn-2-yl)-1,4,2-dioxazol-5-one**



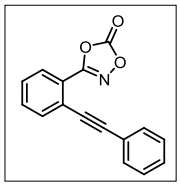
Prepared according to general procedure from 2-methyl-5-phenylpent-4-ynyl hydroxamic acid on a 2.9 mmol scale. Colorless oil (0.55 g, 84%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.30 (m, 3H), 3.17 (h, *J* = 6.9 Hz, 1H), 2.83 (qd, *J* = 17.0, 6.6 Hz, 2H), 1.48 (d, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 168.9, 154.6, 132.0, 128.8, 128.7, 123.3, 84.8, 83.9, 31.7, 23.7, 15.7; **IR** ($cm^{-1}$) 1871, 1822, 1627, 1490, 1254, 1149, 975, 755, 690; **HRMS** (EI) m/z calcd. for $C_{13}H_{11}NO_3$ $[M]^+$: 229.0739, found: 229.0739.

**3-(2-Methyl-4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (25, equation 1)**



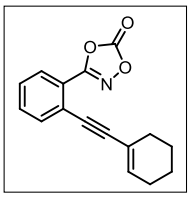
Prepared according to general procedure from 3-methyl-5-phenylpent-4-ynyl hydroxamic acid on a 2.0 mmol scale. Colorless oil (0.30 g, 66%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.41 – 7.37 (m, 2H), 7.34 – 7.30 (m, 3H), 3.20 (h, *J* = 6.9 Hz, 1H), 2.93 – 2.86 (m, 2H), 1.42 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.0, 154.1, 131.5, 128.3, 128.2, 122.8, 89.8, 82.7, 32.1, 23.8, 20.5; **IR** ($cm^{-1}$) 1876, 1826, 1634, 1489, 1361, 1146, 981, 755, 691; **HRMS** (EI) m/z calcd. for $C_{13}H_{11}NO_3$ $[M]^+$: 229.0739, found: 229.0738.

**3-{2-(Phenylethynyl)phenyl}-1,4,2-dioxazol-5-one (28, equation 2)**



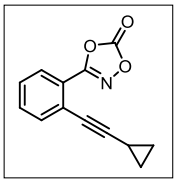
Prepared according to general procedure from 2-(phenylethynyl)benzyl hydroxamic acid on a 1.70 mmol scale. Additional recrystallization by dichloromethane/*n*-pentane should be required to obtain the high-purity compound. White solid (0.38 g, 85%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.60 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.39 (m, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 163.9, 154.3, 134.4, 133.4, 132.1, 129.7, 129.1, 129.1, 129.0, 123.1, 122.8, 121.7, 97.2, 86.7; **IR** ($cm^{-1}$) 3064, 2245, 2219, 1855, 1828, 1608, 1496, 1361, 1277, 1168, 1057, 967, 752, 688; **HRMS** (EI) m/z calcd. for $C_{16}H_9NO_3$ $[M]^+$: 263.0582, found: 263.0584.

**3-{2-(Cyclohex-1-en-1-ylethynyl)phenyl}-1,4,2-dioxazol-5-one**



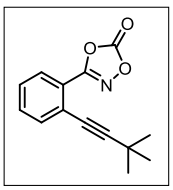
Prepared according to general procedure from 2-(cyclohex-1-en-1-ylethynyl)benzyl hydroxamic acid on a 2.5 mmol scale. Additional recrystallization by dichloromethane/*n*-pentane should be required to obtain the high-purity compound. White solid (0.44 g, 67%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.84 – 7.77 (m, 1H), 7.67 – 7.58 (m, 2H), 7.54 – 7.44 (m, 1H), 6.36 (tt, *J* = 4.0, 1.8 Hz, 1H), 2.29 (ddd, *J* = 8.2, 4.2, 26 Hz, 2H), 2.22 (dh, *J* = 8.5, 2.5 Hz, 2H), 1.77 – 1.63 (m, 4H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 163.5, 153.9, 137.5, 133.7, 132.8, 128.6, 128.0, 123.3, 120.9, 120.5, 99.0, 83.7, 28.5, 25.9, 22.2, 21.4; **IR** ($cm^{-1}$) 2933, 2861, 2201, 1858, 1831, 1607, 1493, 1348, 1169, 969, 756; **HRMS** (EI) m/z calcd. for $C_{16}H_{13}NO_3$ $[M]^+$: 267.0895, found: 267.0897.

**3-{2-(Cyclopropylethynyl)phenyl}-1,4,2-dioxazol-5-one**



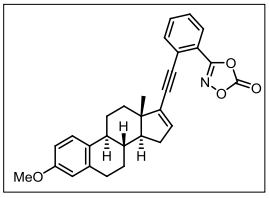
Prepared according to general procedure from 2-(cyclopropylethynyl)benzyl hydroxamic acid on a 4.3 mmol scale. Additional recrystallization by dichloromethane/*n*-pentane should be required to obtain the high-purity compound. White solid (0.61 g, 62%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.44 (ddd, *J* = 8.0, 6.6, 2.3 Hz, 1H), 1.56 – 1.47 (m, 1H), 0.96 (qd, *J* = 5.4, 2.2 Hz, 2H), 0.90 (ddd, *J* = 5.2, 4.1, 2.5 Hz, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 163.6, 153.9, 133.9, 132.7, 128.5, 127.7, 123.5, 121.2, 102.3, 72.6, 8.6, 0.3; **IR** ($cm^{-1}$) 2227, 1857, 1831, 1599, 1507, 1344, 969, 952, 753; **HRMS** (EI) m/z calcd. for $C_{13}H_9NO_3$ $[M]^+$: 227.0582, found: 227.0586.

**3-{2-(3,3-Dimethylbut-1-yn-1-yl)phenyl}-1,4,2-dioxazol-5-one**



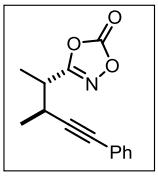
Prepared according to general procedure from 2-(3,3-dimethylbut-1-yn-1-yl)benzyl hydroxamic acid on a 3.7 mmol scale. Additional recrystallization by dichloromethane/*n*-pentane should be required to obtain the high-purity compound. White solid (0.65 g, 72%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.45 (ddd, *J* = 7.9, 6.0, 2.8 Hz, 1H), 1.34 (s, 9H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 163.7, 154.0, 133.8, 132.7, 128.5, 127.8, 123.7, 121.4, 106.6, 76.1, 30.1, 28.3; **IR** ($cm^{-1}$) 2971, 2243, 1860, 1829, 1265, 969, 736; **HRMS** (EI) m/z calcd. for $C_{14}H_{13}NO_3$ $[M]^+$: 243.0895, found: 243.0898.

**3-[2-({(8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H* cyclopenta[a]phenanthren-17-yl)ethynyl}phenyl]-1,4,2-dioxazol-5-one**



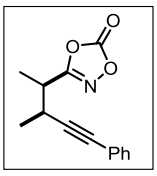
Prepared according to general procedure on a 0.76 mmol scale. Additional recrystallization by dichloromethane/*n*-pentane should be required to obtain the high-purity compound. White solid (0.23 g, 68%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (td, *J* = 7.7, 1.1 Hz, 1H), 7.49 (td, *J* = 7.8, 1.1 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.69 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 6.30 – 6.27 (m, 1H), 3.76 (s, 3H), 2.95 – 2.84 (m, 2H), 2.40 (ddd, *J* = 16.2, 6.2, 3.1 Hz, 2H), 2.32 (t, *J* = 10.4 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.11 (dd, *J* = 8.4, 2.3 Hz, 1H), 1.97 – 1.93 (m, 1H), 1.74 – 1.66 (m, 1H), 1.63 (t, *J* = 11.4 Hz, 3H), 1.47 (qd, *J* = 11.9, 6.7 Hz, 1H), 0.97 (s, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 163.4, 157.5, 153.8, 138.8, 137.9, 137.0, 134.1, 132.9, 132.7, 128.6, 128.2, 125.9, 123.1, 120.8, 113.7, 111.2, 93.2, 89.3, 55.5, 55.0, 48.8, 44.3, 37.6, 34.7, 32.2, 29.6, 27.7, 26.5, 16.2; **IR** ($cm^{-1}$) 2937, 2923, 2854, 2834, 2189, 1852, 1821, 1609, 1488, 1344, 1255, 1051, 1035, 960, 805, 754; **HRMS** (EI) m/z calcd. for $C_{29}H_{27}NO_4$ $[M]^+$: 453.1940, found: 453.1942.

**3-{(±)-(2,3-*anti*)-3-methyl-5-phenylpent-4-yn-2-yl}-1,4,2-dioxazol-5-one (17, Table 2)**



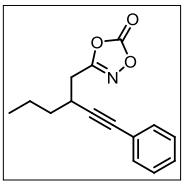
Prepared according to general procedure from (±)-(2,3-*anti*)-2,3-dimethyl-5-phenylpent-4-ynyl hydroxamic acid on a 0.9 mmol scale. Yellowish oil (0.20 g, 91%); **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 3H), 3.09 – 3.02 (m, 2H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.36 (d, *J* = 6.8 Hz, 4H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$); **IR** ($cm^{-1}$) 2983, 2940, 2881, 1625, 1490, 1453, 1251, 1153, 1070, 973; **HRMS** (ESI) m/z calcd. for $C_{14}H_{13}NO_3$ $[M+Na]^+$: 266.0788, found: 266.0798.

**3-{(±)-(2,3-*syn*)-3-Methyl-5-phenylpent-4-yn-2-yl}-1,4,2-dioxazol-5-one (19, Table 2)**



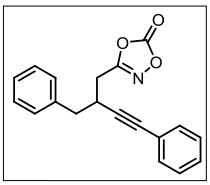
Prepared according to general procedure from (±)-(2,3-*syn*)-2,3-dimethyl-5-phenylpent-4-ynyl hydroxamic acid on a 0.94 mmol scale. Yellowish oil (0.16 g, 70%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.43 – 7.37 (m, 2H), 7.35 – 7.29 (m, 3H), 3.16 (p, *J* = 7.0 Hz, 1H), 2.98 (p, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.37 (d, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 168.3, 154.1, 131.5, 128.2, 128.1, 122.9, 88.71, 83.6, 36.7, 29.4, 18.5, 12.4; **IR** ($cm^{-1}$) 2984, 2940, 2879, 1625, 1490, 1454, 1340, 1243, 1156, 1056, 967, 934; **HRMS** (ESI) m/z calcd. for $C_{14}H_{13}NO_3$ $[M+Na]^+$: 266.0788, found: 266.0796.

**3-{2-(Phenylethynyl)pentyl}-1,4,2-dioxazol-5-one (21, Table 2)**



Prepared according to general procedure from 3-(phenylethynyl)hexanyl hydroxamic acid on a 2.5 mmol scale. Colorless oil (0.60 g, 94%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.43 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.38 – 7.31 (m, 3H), 3.17 – 3.07 (m, 1H), 2.92 (d, *J* = 7.5 Hz, 2H), 1.73 – 1.61 (m, 3H), 1.61 – 1.50 (m, 1H), 1.03 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.2, 154.1, 131.5, 128.3, 128.2, 122.8, 88.8, 83.7, 36.7, 30.7, 29.0, 20.3, 13.4; **IR** ($cm^{-1}$) 2959, 2933, 2873, 1864, 1826, 1635, 1489, 1365, 1337, 1145, 980, 755, 691; **HRMS** (EI) m/z calcd. for $C_{15}H_{15}NO_3$ $[M]^+$: 257.1052, found: 257.1049.

**3-(2-Benzyl-4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (23, Table 2)**

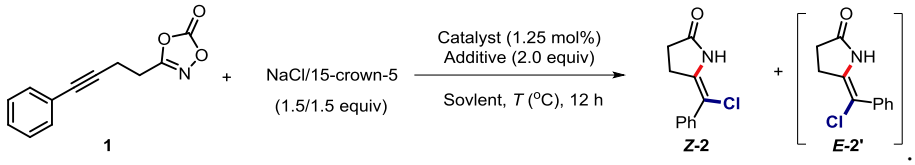


Prepared according to general procedure from 3-benzyl-5-phenylpent-4-ynyl hydroxamic acid on a 2.5 mmol scale. Colorless oil (0.88 mg, 96%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.44 – 7.23 (m, 10H), 3.36 (dt, *J* = 14.1, 7.2 Hz, 1H), 3.10 – 2.94 (m, 2H), 2.94 – 2.81 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.0, 154.0, 137.5, 131.5, 129.3, 128.5, 128.3, 128.3, 127.0, 122.6, 88.2, 84.6, 40.6, 31.0, 29.9; **IR** ($cm^{-1}$) 3062, 3029, 2926, 1870, 1827, 1634, 1490, 1365, 1143, 979, 754, 691; **HRMS** (EI) m/z calcd. for $C_{19}H_{15}NO_3$ $[M]^+$: 305.1052, found: 305.1049.

## III. Procedures of the Optimization Study (Table 1)

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added 3-(4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (**1**, 0.1 mmol), catalyst, sodium chloride (0.15 mmol), 15-crown-5 (0.15 mmol), additive and solvent (0.6 mL). The reaction mixture was vigorously stirred in a pre-heated oil bath at the indicated temperature for 12 h, and concentrated under reduced pressure. The crude yield (**2**+**2'**) and ratio of *Z*/*E*-isomers (**2**:**2'**) were measured by using $^1$H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

**Table S1**. Optimization study for catalytic chloroamidation of dioxazolone **1**

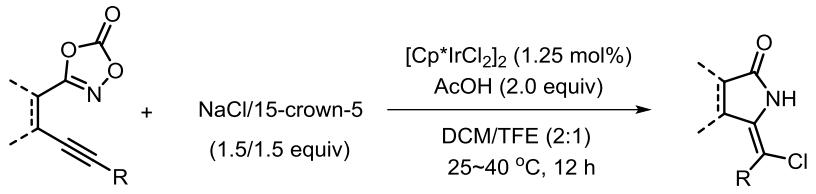



| Entry | Catalyst | Additive | *T* (°C) | Solvent | **2+2'** (%) | **2:2'** |
|---|---|---|---|---|---|---|
| 1 | $[Cp^*IrCl_2]_2$ | AcOH | 40 | DCM | 40 | >20:1 |
| 2 | $[Cp^*IrCl_2]_2$ | AcOH | 40 | TFE | 86 | 10.2:1 |
| 3 | $[Cp^*IrCl_2]_2$ | AcOH | 40 | HFIP | 90 | 5.9:1 |
| 4 | $[Cp^*IrCl_2]_2$ | AcOH | 40 | DCM/TFE = 2:1 | >95 | >20:1 |
| 5 | $[Cp^*IrCl_2]_2$ | PhCOOH | 40 | DCM/TFE = 2:1 | 66 | >20:1 |
| 6 | $[Cp^*IrCl_2]_2$ | *o*-$NO_2C_6H_4COOH$ | 40 | DCM/TFE = 2:1 | 85 | 4.7:1 |
| 7 | $[Cp^*IrCl_2]_2$ | $CF_3COOH$ | 40 | DCM/TFE = 2:1 | 77 | 2.9:1 |
| 8 | $[Cp^*IrCl_2]_2$ | - | 40 | DCM/TFE = 2:1 | 11 | >20:1 |
| 9[a] | $[Cp^*IrCl_2]_2$ | AcOH | 40 | DCM/TFE = 2:1 | >95 | >20:1 |
| 10 | $[Cp^*IrCl_2]_2$ | AcOH | 25 | DCM/TFE = 2:1 | >95 | >20:1 |
| 11[b] | $[Cp^*IrCl_2]_2$ | AcOH | 40 | DCM/TFE = 2:1 | 33 | >20:1 |
| 12[c] | $[Cp^*IrCl_2]_2$ | AcOH | 40 | DCM/TFE = 2:1 | >95 | >20:1 |
| 13 | $[Cp^*RhCl_2]_2$ | AcOH | 40 | DCM/TFE = 2:1 | <5 | - |
| 14 | $[RuCl_2(p\text{-cymene})]_2$ | AcOH | 40 | DCM/TFE = 2:1 | 36 | >20:1 |
| 15 | - | AcOH | 40 | DCM/TFE = 2:1 | - | - |

DCM = dichloromethane; TFE=2,2,2-trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol; AcOH =acetic acid. [a]In the presence of $NaBAr^F_4$ (5 mol%). [b]In the absence of 15-crown-5. [c]($n$-$Bu_4N$)Cl (1.5 equiv) was used instead of NaCl/15-crown-5.

# IV. Procedures of the Ir-catalyzed Haloamidation of Dioxazolones

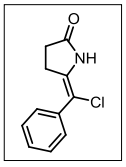
### 1. Procedure of the Ir-catalyzed Chloroamination of Dioxazolones (Table 2)




To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $[Cp^*IrCl_2]_2$ (2.0 mg, 1.25 mol%), 1,4,2-dioxazol-5-one (0.2 mmol), sodium chloride (17.5 mg, 0.3 mmol) and dichloromethane/2,2,2-trifluoroethanol = 2:1 (1.2 mL) under atmospheric condition and stirred for 1 min. To the vial were added acetic acid (22.9 μL, 0.4 mmol) and 15-crown-5 (59.3 μL, 0.3 mmol), and then sealed. The reaction mixture was vigorously stirred at 25 °C or in a pre-heated oil bath at 40 °C for 12 h, filtered through a pad of celite with dichloromethane (10 mL × 4) and concentrated under reduced pressure. Desired product was obtained by silica column chromatography (eluent: *n*-hexane/EtOAc, 10:1 ~ 4:1).

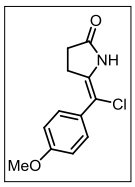
※ Note: When compounds **2**–**6**, **10, 11, 18** and **20** were purified, deactivated silica (by flushing with 2% trimethylamine-*n*-hexane solution) should be used to prevent *Z*/*E* isomerization during the course of column chromatography.

**(*Z*)-5-{Chloro(phenyl)methylene}pyrrolidin-2-one (2, Table 2)**



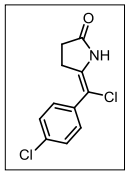

*The reaction was performed at 25 °C.* White solid (34 mg, 82%); **m.p.** 76-78 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.54 (s, 1H), 7.46 – 7.34 (m, 4H), 7.33 – 7.27 (m, 1H), 2.95 – 2.87 (m, 2H), 2.62 – 2.54 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 175.8, 136.0, 136.0, 128.3, 128.1, 127.7, 103.6, 30.3, 25.3; **IR** ($cm^{-1}$) 3151, 3049, 1742, 1686, 1653, 1442, 1399, 1339, 1305, 1226, 877, 746, 694, 667; **HRMS** (EI) m/z calcd. for $C_{11}H_{10}ClNO$ $[M]^+$: 207.0451, found: 207.0450.

**(*Z*)-5-{Chloro(4-methoxyphenyl)methylene}pyrrolidin-2-one (3, Table 2)**



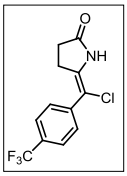
*The reaction was performed at at 25 °C.* White solid (35 mg, 74%); **m.p.** 94-96 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.56 (s, 1H), 7.35 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 2.90 – 2.82 (m, 2H), 2.61 – 2.52 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 175.9, 159.4, 135.3, 129.8, 128.6, 113.9, 103.7, 55.5, 30.6, 25.4; **IR** ($cm^{-1}$) 3161, 2920, 1708, 1659, 1604, 1509, 1392, 1337, 1289, 1250, 1215, 1175, 1028, 831, 578; **HRMS** (EI) m/z calcd. for $C_{12}H_{12}ClNO_2$ $[M]^+$: 237.0557, found: 237.0558.

**(*Z*)-5-{Chloro(4-chlorophenyl)methylene}pyrrolidin-2-one (4, Table 2)**



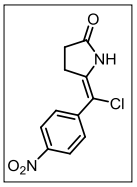
*The reaction was performed at 25 °C.* White solid (37 mg, 76%); **m.p.** 171-173 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.59 (s, 1H), 7.42 – 7.30 (m, 4H), 2.93 – 2.86 (m, 2H), 2.63 – 2.55 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 176.0, 137.0, 135.0, 133.5, 129.7, 128.7, 102.7, 30.5, 25.6; **IR** ($cm^{-1}$) 3144, 3040, 1710, 1647, 1492, 1407, 1340, 1299, 1229, 1090, 1011, 959, 893, 834, 787; **HRMS** (EI) m/z calcd. for $C_{11}H_9Cl_2NO$ $[M]^+$: 241.0061, found: 241.0060.

**(*Z*)-5-[Chloro{4-(trifluoromethyl)phenyl}methylene]pyrrolidin-2-one (5, Table 2)**



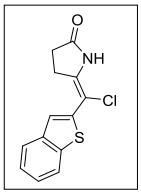
*The reaction was performed at 25 °C.* White solid (30 mg, 54%); **m.p.** 170-172 °C; **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 8.34 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 2.97 – 2.92 (m, 2H), 2.65 – 2.60 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 176.2, 140.0, 138.2, 129.1 (q, *J* = 32.5 Hz), 128.3, 125.3 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 271.8 Hz), 102.4, 30.3, 25.5; **$^{19}$F NMR** (564 MHz, $CD_2Cl_2$) δ -62.99; **IR** ($cm^{-1}$) 3169, 1716, 1654, 1611, 1422, 1322, 1223, 1160, 1107, 1067, 839; **HRMS** (EI) m/z calcd. for $C_{12}H_9ClF_3NO$ $[M]^+$: 275.0325, found: 275.0327.

**(*Z*)-5-{Chloro(4-nitrophenyl)methylene}pyrrolidin-2-one (6, Table 2)**



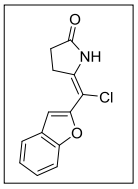
*The reaction was performed at 25 °C.* Yellow solid (21 mg, 42%); **m.p.** 225-227 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.25 – 8.19 (m, 2H), 7.75 (s, 1H), 7.66 – 7.58 (m, 2H), 3.06 – 2.98 (m, 2H), 2.68 – 2.60 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 175.6, 146.6, 142.8, 139.9, 128.6, 123.8, 102.3, 30.4, 26.1; **IR** ($cm^{-1}$) 3153, 1715, 1614, 1573, 1503, 1331, 1298, 1198, 1110, 849, 752; **HRMS** (EI) m/z calcd. for $C_{11}H_9ClN_2O_3$ $[M]^+$: 252.0302, found: 252.0298.

**(*Z*)-5-(Benzo[*b*]thiophen-2-ylchloromethylene)pyrrolidin-2-one (7, Table 2)**



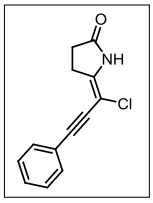
*The reaction was performed at 40 °C.* Off-white solid (43 mg, 81%); **m.p.** 168-170 °C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.66 (s, 1H), 7.38 – 7.34 (m, 2H), 7.32 (td, *J* = 7.7, 7.2, 1.2 Hz, 1H), 3.20 – 3.14 (m, 2H), 2.73 – 2.67 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 193.7, 175.9, 139.7, 139.6, 139.0, 138.7, 125.2, 124.9, 123.9, 122.4, 122.2, 30.6, 26.2; **IR** ($cm^{-1}$) 3160, 3067, 1715, 1630, 1391, 1345, 1297, 1233, 734; **HRMS** (EI) m/z calcd. for $C_{13}H_{10}ClNOS$ $[M]^+$: 263.0172, found: 263.0172.

**(*Z*)-5-(Benzofuran-2-ylchloromethylene)pyrrolidin-2-one (8, Table 2)**



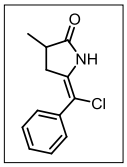
*The reaction was performed at 40 °C.* Off-white solid (41 mg, 83%); **m.p.** 183-185°C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.68 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.76 (s, 1H), 3.39 – 3.34 (m, 2H), 2.72 – 2.66 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 176.1, 155.3, 152.8, 141.5, 139.7, 128.8, 124.6, 123.6, 121.1, 111.2, 104.1, 30.3, 26.1; **IR** ($cm^{-1}$) 3163, 3056, 1716, 1648, 1400, 1304, 1279, 1230, 732; **HRMS** (EI) m/z calcd. for $C_{13}H_{10}ClNO_2$ $[M]^+$: 247.0400, found: 247.0396.

**(*Z*)-5-(1-Chloro-3-phenylprop-2-yn-1-ylidene)pyrrolidin-2-one (9, Table 2)**



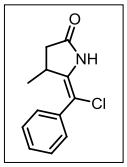

*2.5 mol% of [Cp*IrCl$_2$]$_2$ was applied at 40 °C.* White solid (30 mg, 65%); **m.p.** 163–165 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.89 (s, 1H), 7.49 – 7.43 (m, 2H), 7.39 – 7.34 (m, 3H), 3.04 – 2.96 (m, 2H), 2.69 – 2.61 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 176.3, 145.7, 131.4, 128.8, 128.6, 122.6, 94.1, 86.7, 83.8, 30.0, 25.3; **IR** ($cm^{-1}$) 3137, 3047, 1722, 1640, 1594, 1304, 1234, 801, 751, 684, 576; **HRMS** (EI) m/z calcd. for $C_{13}H_{10}ClNO$ $[M]^+$: 231.0451, found: 231.0447.

**(*Z*)-5-{Chloro(phenyl)methylene}-3-methylpyrrolidin-2-one (10, Table 2)**



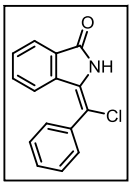

*The reaction was performed at 25 °C.* White solid (21 mg, 47%); **m.p.** 161-163 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.55 (s, 1H), 7.46 – 7.33 (m, 4H), 7.33 – 7.26 (m, 1H), 3.11 (dd, *J* = 16.2, 9.2 Hz, 1H), 2.74 (dp, *J* = 9.2, 7.2 Hz, 1H), 2.57 (dd, *J* = 16.3, 6.7 Hz, 1H), 1.25 (d, *J* = 7.3 Hz, 3H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 178.6, 136.4, 134.9, 128.5, 128.3, 127.9, 104.0, 36.9, 34.3, 16.4; **IR** ($cm^{-1}$) 3210, 1720, 1657, 1225, 746, 696, 634; **HRMS** (EI) m/z calcd. for $C_{12}H_{12}ClNO$ $[M]^+$: 221.0607, found: 221.0610.

**(*Z*)-5-{Chloro(phenyl)methylene}-4-methylpyrrolidin-2-one (11, Table 2)**



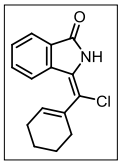

*The reaction was performed at 25 °C.* White solid (38 mg, 86%); **m.p.** 126-128 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.52 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 3.42 – 3.29 (m, 1H), 2.86 (dd, *J* = 17.7, 9.3 Hz, 1H), 2.16 (dd, *J* = 17.7, 2.9 Hz, 1H), 0.93 (d, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 174.7, 140.9, 136.3, 129.0, 128.5, 128.2, 104.1, 38.9, 31.4, 19.8; **IR** ($cm^{-1}$) 3219, 1718, 1666, 1399, 1340, 1229; **HRMS** (EI) m/z calcd. for $C_{12}H_{12}ClNO$ $[M]^+$: 221.0607, found: 221.0606.

**(Z)-3-{Chloro(phenyl)methylene}isoindolin-1-one (12, Table 2)**



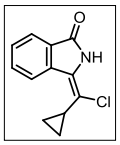
*The reaction was performed at 40 °C.* White solid (32 mg, 63%); 226-228 °C; **$^{1}$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.95 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.50 (m, 5H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 167.2, 136.4, 135.6, 132.5, 132.3, 131.2, 130.5, 130.4, 129.7, 129.5, 124.0, 123.0, 113.3; **IR** ($cm^{-1}$) 3168, 1709, 1657, 1472, 1400, 1365, 1305, 750, 690; **HRMS** (EI) m/z calcd. for $C_{15}H_{10}ClNO$ $[M]^+$: 255.0451, found: 255.0453.

**(*Z*)-3-{Chloro(cyclohex-1-en-1-yl)methylene}isoindolin-1-one (13, Table 2)**



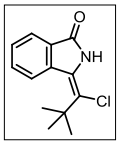
*2.5 mol% of $[Cp^*IrCl_2]_2$ was applied at 40 °C.* White solid (37 mg, 71%); **m.p.** 196-198 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.96 (s, 1H), 7.86 – 7.82 (m, 1H), 7.81 (dt, *J* = 1.5, 0.7 Hz, 1H), 7.56 (td, *J* = 7.6, 1.3 Hz, 1H), 7.49 (td, *J* = 7.5, 0.9 Hz, 1H), 6.15 (tt, *J* = 3.7, 1.6 Hz, 1H), 2.37 – 2.29 (m, 2H), 2.29 – 2.22 (m, 2H), 1.87 – 1.79 (m, 2H), 1.79 – 1.72 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 166.4, 135.6, 133.6, 133.5, 132.1, 130.7, 130.0, 128.8, 123.4, 122.8, 117.4, 26.6, 25.7, 22.4, 21.7; **IR** ($cm^{-1}$) 2920, 2154, 1698, 772, 681; **HRMS** (EI) m/z calcd. for $C_{15}H_{14}ClNO$ $[M]^+$: 259.0764, found: 259.0767.

**(*Z*)-3-{Chloro(cyclopropyl)methylene}isoindolin-1-one (14, Table 2)**



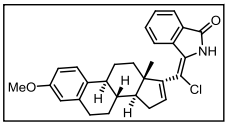
*2.5 mol% of $[Cp^*IrCl_2]_2$ was applied at 40 °C.* White solid (22 mg, 50%); **m.p.** 186-188 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.99 (d, *J* = 7.9 Hz, 1H), δ 7.87 (br, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.65 (td, *J* = 7.7, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 0.9 Hz, 1H), 2.28 (tt, *J* = 8.2, 5.1 Hz, 1H), 1.15 – 1.07 (m, 2H), 1.04 – 0.95 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 166.1, 135.0, 132.2, 131.8, 130.8, 128.8, 123.7, 123.4, 118.8, 14.7, 8.7; **IR** ($cm^{-1}$) 3169, 2920, 1697, 1648, 1605, 1469, 1304, 1196, 1146, 1105, 1042, 999, 748, 724, 692; **HRMS** (EI) m/z calcd. for $C_{12}H_{10}ClNO$ $[M]^+$: 219.0451, found: 219.0449.

**(*Z*)-3-(1-Chloro-2,2-dimethylpropylidene)isoindolin-1-one (15, Table 2)**



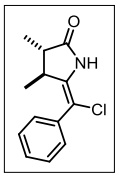
*2.5 mol% of [Cp*IrCl$_2$]$_2$ was applied at 40 °C.* White solid (20 mg, 42%); **m.p.** 152–154 °C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.89 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.66 (td, *J* = 7.9, 1.2 Hz, 1H), 7.55 – 7.51 (m, 1H), 1.56 (s, 9H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 165.8, 133.8, 132.0, 131.6, 131.3, 129.1, 128.6, 126.3, 123.8, 37.0, 30.2; **IR** (cm$^{-1}$) 3202, 3057, 2959, 2927, 1699, 1595, 1472, 1458, 1312, 1228, 764, 698, 587; **HRMS** (EI) m/z calcd. for $C_{13}H_{14}ClNO$ [M]$^+$: 235.0764, found: 235.0761.

**(*Z*)-3-[Chloro{(8*S*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl}methylene]isoindolin-1-one (16, Table 2)**



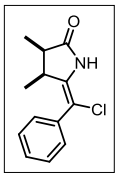
*2.5 mol% of [Cp*IrCl$_2$]$_2$ was applied at 40 °C. The reaction was performed on a 0.1 mmol scale.* White solid (35 mg, 79%); **m.p.** 253-255°C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.90 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.47 (m, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.65 (s, 1H), 6.22 (s, 1H), 3.76 (s, 3H), 2.93 (qd, *J* = 16.6, 14.2, 5.4 Hz, 2H), 2.51 (ddd, *J* = 16.1, 6.4, 3.3 Hz, 1H), 2.39 – 2.29 (m, 3H), 2.07 – 1.99 (m, 2H), 1.94 (td, *J* = 11.5, 6.6 Hz, 1H), 1.74 (q, *J* = 10.6 Hz, 2H), 1.68 – 1.59 (m, 1H), 1.53 (dd, *J* = 11.9, 6.6 Hz, 1H), 1.14 (s, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 166.1, 157.5, 148.7, 137.9, 136.1, 135.6, 132.6, 132.0, 131.9, 130.8, 129.0, 125.9, 123.5, 122.7, 113.7, 111.2, 111.0, 57.3, 55.0, 49.4, 44.1, 37.4, 34.7, 32.0, 29.6, 27.7, 26.4, 16.7; **IR** (cm$^{-1}$) 2928, 1702, 1608, 1498, 1470, 1254, 1147, 1103, 1032, 761, 694; **HRMS** (EI) m/z calcd. for $C_{28}H_{28}ClNO_2$ [M]$^+$: 445.1809, found: 445.1810.

***trans*-(*Z*)-5-{Chloro(phenyl)methylene}-3,4-dimethylpyrrolidin-2-one (18, Table 2)**



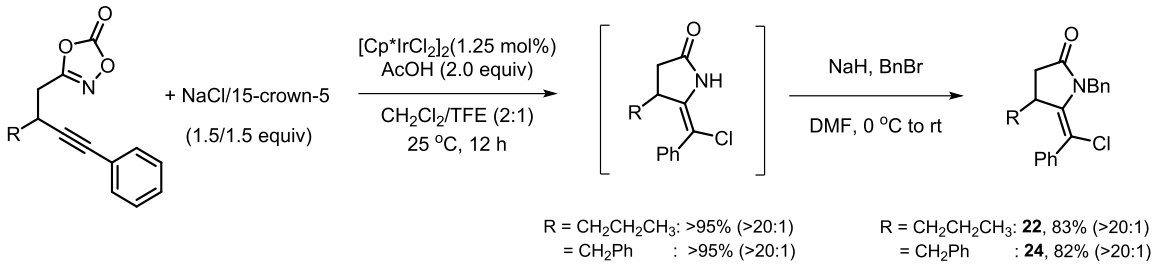
*The reaction was performed at 25 °C.* The stereochemistry of the product was confirmed by 1D NOE experiment; White solid (38 mg, 80%); **m.p.** 180-182 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.51 (s, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.30 (m, 2H), 2.92 (qd, *J* = 7.0, 4.4 Hz, 1H), 2.28 (qd, *J* = 7.4, 4.4 Hz, 1H), 1.27 (d, *J* = 7.4 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$); **IR** (cm$^{-1}$) 3202, 3053, 2971, 2928, 2871, 1714, 1650, 1444, 1394, 1351, 1319, 1227, 769; **HRMS** (ESI) m/z calcd. for $C_{13}H_{14}ClNO$ [M+Na]$^+$: 258.0656, found: 258.0741.

***cis*-(*Z*)-5-{Chloro(phenyl)methylene}-3,4-dimethylpyrrolidin-2-one (20, Table 2)**




*The reaction was performed at 25 °C.* The stereochemistry of the product was confirmed by 1D NOE experiment; White solid (27 mg, 57%); **m.p.** 177-179 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.49 – 7.41 (m, 3H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 3.32 (dt, *J* = 14.5, 7.3 Hz, 1H), 2.88 (p, *J* = 7.6 Hz, 1H), 1.09 (d, *J* = 7.5 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 177.4, 140.3, 136.3, 129.1, 128.5, 128.1, 104.3, 40.4, 35.7, 14.3, 9.4; **IR** ($cm^{-1}$) 3190, 2976, 2929, 2868, 1713, 1644, 1392, 1356, 1224; **HRMS** (ESI) m/z calcd. for $C_{13}H_{14}ClNO$ $[M+Na]^+$: 258.0656, found: 258.0720.

**2. Procedure for the Ir-catalyzed chloroamidation of *β*-substituted dioxazolones (Table 2)**

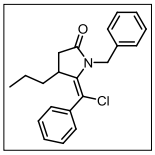



To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $[Cp^*IrCl_2]_2$ (2.0 mg, 1.25 mol%), 1,4,2-dioxazol-5-one (0.2 mmol), sodium chloride (17.5 mg, 0.3 mmol) and dichloromethane/2,2,2-trifluoroethanol = 2:1 (1.2 mL) under atmospheric condition and stirred for 1 min. To the vial were added acetic acid (22.9 μL, 0.4 mmol) and 15-crown-5 (59.3 μL, 0.3 mmol), and then sealed. The reaction mixture was vigorously stirred at 25 °C for 12 h, concentrated under reduced pressure. The crude mixture was diluted with EtOAc (10 mL), washed by brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. This crude mixture was used for next step without further purification.

To a 0 °C suspension of the crude mixture, NaH (60 % dispersion in mineral oil, 1.5 equiv) and anhydrous DMF (2 mL) was dropwisely added benzyl bromide (2.0 equiv) under argon atmosphere. The suspension allowed to stir at 25 °C for 1 h. The reaction mixture was diluted with EtOAc (15 mL), washed by brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Desired product was obtained by silica column chromatography (eluent: *n*-hexane/EtOAc, 20:1 ~ 5:1).

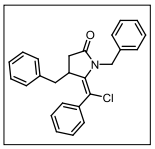
※ Note: Two compounds **22** and **24** were smoothly decomposed even at room temperature. Thus, after purification, **22** and **24** should be stored in refrigerator.

**(*Z*)-1-Benzyl-5-{chloro(phenyl)methylene}-4-propylpyrrolidin-2-one (22, Table 2)**



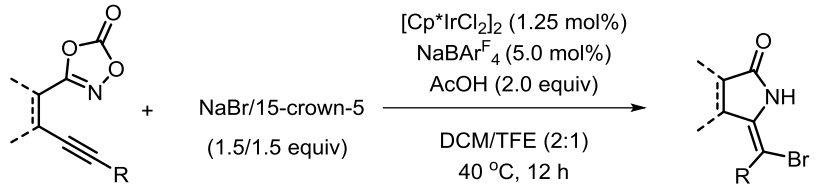
Colorless resin (56 mg, 83%); **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.42 – 7.24 (m, 10H), 5.29 (d, *J* = 15.8 Hz, 1H), 5.22 (d, *J* = 15.7 Hz, 1H), 3.00 – 2.89 (m, 1H), 2.69 (dd, *J* = 17.1, 8.5 Hz, 1H), 2.22 (dd, *J* = 17.0, 1.3 Hz, 1H), 1.16 – 1.00 (m, 3H), 1.00 – 0.83 (m, 1H), 0.54 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 176.6, 141.6, 139.1, 138.4, 130.1, 128.8, 128.6, 128.5, 127.2, 127.1, 105.2, 45.4, 37.5, 36.3, 35.5, 19.2, 13.2; **IR** ($cm^{-1}$) 3059, 3029, 2960, 2931, 2872, 1689, 1632, 1599, 1449, 696.

**(*Z*)-1,4-Dibenzyl-5-{chloro(phenyl)methylene}pyrrolidin-2-one (24, Table 2)**



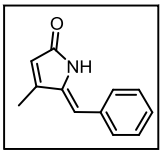
Beige solid (64 mg, 82%); **m.p.** 117–119 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.45 – 7.34 (m, 7H), 7.34 – 7.26 (m, 3H), 7.14 (dd, *J* = 5.0, 1.9 Hz, 3H), 6.67 – 6.60 (m, 2H), 5.26 (d, *J* = 15.7 Hz, 1H), 5.15 (d, *J* = 15.7 Hz, 1H), 3.23 – 3.14 (m, 1H), 2.61 – 2.50 (m, 2H), 2.27 – 2.17 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) δ 176.1, 140.7, 139.0, 138.4, 138.2, 130.1, 129.0, 129.0, 128.7, 128.7, 128.6, 127.3, 127.0, 126.7, 105.7, 45.5, 40.0, 40.0, 34.6; **IR** ($cm^{-1}$) 3059, 3027, 2923, 1721, 1689, 1648, 1494, 1443, 1353, 1181, 746, 697.

**3. Procedure of the Ir-catalyzed bromoamination of dioxazolones (equations 1 and 2)**



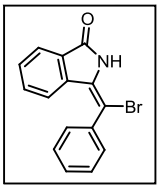

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $[Cp^*IrCl_2]_2$ (2.0 mg, 1.25 mol%), sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (8.8 mg, 5.0 mol%), 1,4,2-dioxazol-5-one (0.2 mmol), sodium bromide (30.8 mg, 0.3 mmol) and dichloromethane/2,2,2-trifluoroethanol = 2:1 (1.2 mL) under atmospheric condition and stirred for 1 min. To the vial were added acetic acid (22.9 μL, 0.4 mmol) and 15-crown-5 (59.3 μL, 0.3 mmol), and then sealed. The reaction mixture was vigorously stirred in a pre-heated oil bath at 40 °C for 12 h, filtered through a pad of celite with dichloromethane (10 mL × 4) and concentrated under reduced pressure. Desired product was obtained by silica column chromatography (eluent: *n*-hexane/EtOA = 10:1 ~ 4:1).

**(*Z*)-5-Benzylidene-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (27, equation 1)**



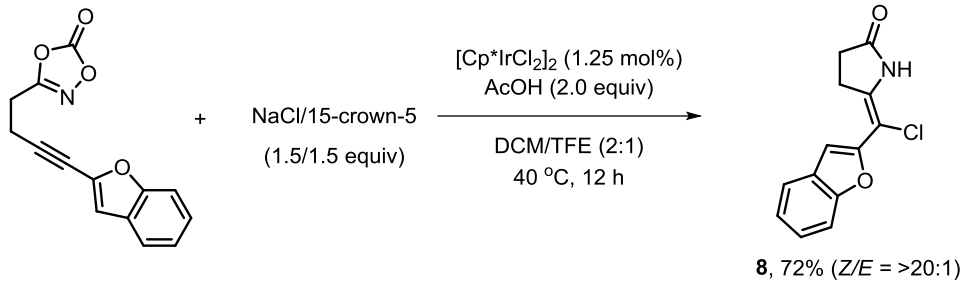

The reaction of 3-(2-methyl-4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one under the above conditions gave (*Z*)-5-(bromo(phenyl)methylene)-4-methylpyrrolidin-2-one in >95% NMR yield and 8.2:1 of *Z*/*E* ratio (measured by $^1$H NMR spectroscopy) in crude mixture. However, after silica column chromatography, debromonated **27** was obtained as a single product. Yellow solid (37 mg, 99%); **m.p.** 103-105 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 9.77 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 6.67 (s, 1H), 6.14 (s, 1H), 2.32 (s, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 197.2, 176.3, 160.9, 157.0, 153.7, 153.4, 153.3, 142.7, 141.8, 35.9; **IR** ($cm^{-1}$) 3219, 2920, 2850, 1662, 1641, 1455, 1326, 963, 819, 755, 685, 523; **HRMS** (EI) m/z calcd. for $C_{12}H_{11}NO$ $[M]^+$: 185.0841, found: 185.0839.

**(*Z*)-3-{Bromo(phenyl)methylene}isoindolin-1-one (29, equation 2)**




White solid (52 mg, 86%); **m.p.** 213-215 °C; **$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.97 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.51 (m, 5H), 7.44 (td, *J* = 7.5, 0.8 Hz, 1H), 7.28 (td, *J* = 7.9, 1.1 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 167.2, 138.1, 135.7, 134.1, 132.6, 131.5, 130.6, 130.2, 129.7, 129.6, 124.0, 123.3, 103.6; **IR** ($cm^{-1}$) 2917, 2849, 1700, 1652, 1468, 1301, 1229, 1102, 720, 691; **HRMS** (EI) m/z calcd. for $C_{15}H_{10}BrNO$ $[M]^+$: 298.9946, found: 298.9948.

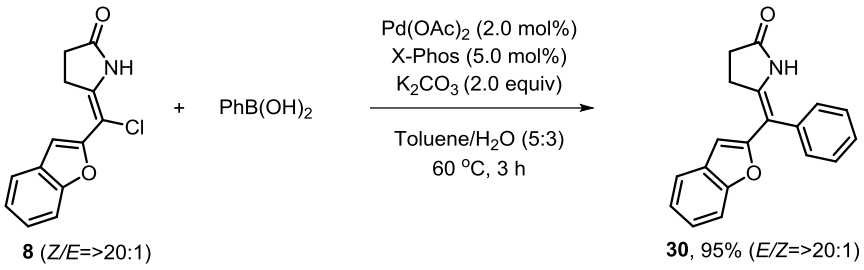
**4. Procedure for chloroamidation of dioxazolone on a gram-scale (Scheme 4)**




**8**, 72% (*Z*/*E* = >20:1)

To a 100 mL round flask with a stir bar were added $[Cp^*IrCl_2]_2$ (39.8 mg, 1.25 mol%), 3-{4-(benzofuran-2-yl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one (1.02 g, 4.0 mmol), sodium chloride (0.35 g, 6.0 mmol) and DCM/TFE = 2:1 (24 mL) under atmospheric condition and stirred for 1 min. To the vial were added acetic acid (0.46 mL, 8.0 mmol) and 15-crown-5 (1.2 mL, 6.0 mmol), and then sealed. The reaction mixture was vigorously stirred in a pre-heated oil bath at 40 °C for 12 h, and concentrated under reduced pressure. The crude mixture was diluted with EtOAc (50 mL), washed by brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by recrystallization using dichloromethane/*n*-pentane at -30 °C. The precipitate was filtered and washed with dichloromethane/*n*-pentane = 1:10 to afford the desired product **8** in 72% yield (0.71 g).

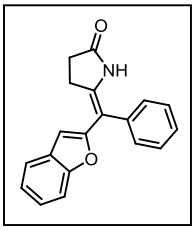
**5. Procedure for Suzuki cross coupling reaction of 8 (Scheme 4)[9]**




**8** (*Z*/*E*=>20:1) **30**, 95% (*E*/*Z*=>20:1)

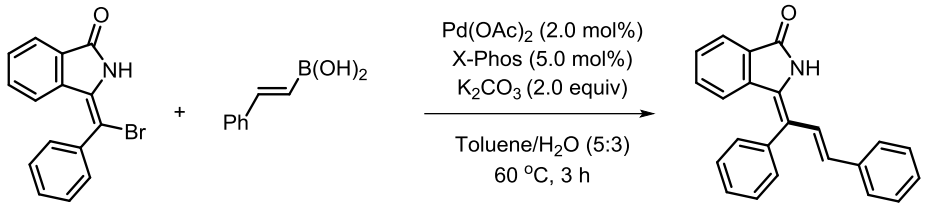
To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $Pd(OAc)_2$ (0.5 mg, 2.0 mol%), X-phos (2.4 mg, 5.0 mol%), **8** (24.8 mg, 0.1 mmol), phenylboronic acid (24.4 mg, 0.2 mmol) and $K_2CO_3$ (41.5 mg, 0.3 mmol). To the vial were added Ar-bubbled toluene/water = 5:3 (0.34 mL) under atmospheric condition and then sealed. The reaction mixture was vigorously stirred at 60 °C for 3 h. After cooling, the reaction mixture was diluted with EtOAc and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: *n*-hexane/EtOAc = 4:1 ~ 2:1) to obtain the desired product **30**.

**(*E*)-5-{Benzofuran-2-yl(phenyl)methylene}pyrrolidin-2-one (30, Scheme 4)**




White solid (28 mg, 95%); The *E*/*Z* ratio was measured to be >20:1 by $^1$H NMR spectroscopic analysis of the unpurified reaction mixture; The stereochemistry of the product was confirmed by 1D NOE experiment; **m.p.** 145-147 °C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 7.48 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.36 – 7.32 (m, 2H), 7.22 – 7.18 (m, 1H), 7.18 – 7.13 (m, 1H), 7.06 (s, 1H), 6.07 (s, 1H), 3.51 – 3.44 (m, 2H), 2.68 – 2.62 (m, 2H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 176.6, 157.6, 154.9, 140.0, 137.0, 130.6, 129.8, 129.3, 128.5, 123.8, 123.2, 120.5, 110.9, 106.6, 103.7, 30.1, 26.5; **IR** ($cm^{-1}$) 3416, 3247, 3055, 1714, 1634, 1441, 1379, 1298, 1253, 1208, 731, 699; **HRMS** (EI) m/z calcd. for $C_{19}H_{15}NO_2$ $[M]^+$: 289.1103, found: 289.1104.

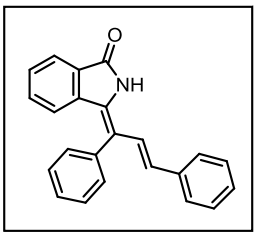
**6. Procedure for Suzuki cross coupling reaction of 29 (Scheme 4)[9]**




**29** (*Z*/*E*=>20:1) ***E,E*-32**, 93% (*E*/*Z*=>20:1)

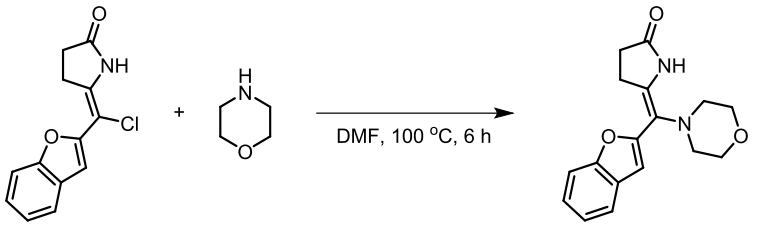
To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $Pd(OAc)_2$ (0.5 mg, 2.0 mol%), X-phos (2.4 mg, 5.0 mol), **29** (25.6 mg, 0.1 mmol), (*E*)-Phenylethenylboronic acid (29.6 mg, 0.2 mmol) and $K_2CO_3$ (41.5 mg, 0.3 mmol). To the vial were added Ar-bubbled toluene/water = 5:3 (0.34 mL) under atmospheric condition and then sealed. The reaction mixture was vigorously stirred at 60 °C for 3 h. After cooling, the reaction mixture was diluted with EtOAc and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: *n*-hexane/EtOAc = 4:1 ~ 2:1) to obtain the desired product **32**.

**(*E*)-3-{(*E*)-1,3-Diphenylallylidene}isoindolin-1-one (32, Scheme 4)**




Fluorescent yellow solid (30 mg, 93%); The *E*/*Z* ratio was measured to be >20:1 by $^1$H NMR spectroscopic analysis of the unpurified reaction mixture; The stereochemistry of the product (*E*,*E*) was confirmed by X-ray crystallographic analysis; **m.p.** 279-281 °C; **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 11.03 (s, 1H), 7.98 (d, *J* = 15.5 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.58 (m, *J* = 4.8, 1.6 Hz, 3H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 6.8 Hz, 4H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 15.5 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 169.6, 137.9, 137.3, 137.0, 134.8, 132.3, 132.1, 131.0, 130.9, 129.5, 129.1, 128.8, 128.8, 128.5, 127.5, 127.0, 124.6, 124.4, 123.5; **IR** ($cm^{-1}$) 2917, 2848, 1686, 1606, 1449, 1307, 1211, 1152, 961, 765, 696, 596; **HRMS** (EI) m/z calcd. for $C_{23}H_{17}NO$ $[M]^+$: 323.1310, found: 323.1306.

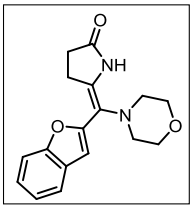
**7. Procedure for nucleophilic addition of 8 using morpholine**




**8** (*Z*/*E* = >20:1) **31**, 75% (*Z*/*E* = 1.9:1)

To an oven-dried screwed vial equipped with a stir bar were added **8** (0.1 mmol, 24.8 mg), morpholine (0.2 mmol) and DMF (0.3 mL) under ambient atmosphere. The mixture was allowed to stir at 100 °C for 6 h. After cooling, the reaction mixture was diluted with EtOAc and washed with brine and water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: *n*-hexane/EtOAc = 4:1 ~ 2:1) to obtain the desired product **31**.

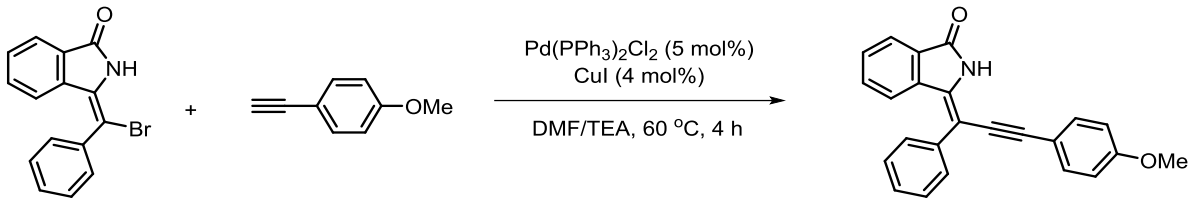
**(*Z*/*E*)-5-{Benzofuran-2-yl(morpholino)methylene}pyrrolidin-2-one (31, Scheme 4)**




White solid (22 mg, 75%); The *Z*/*E* ratio was measured to be 1.9:1 by $^1$H NMR spectroscopic analysis of the unpurified reaction mixture; The stereochemistry of the product confirmed by 1D NOE experiment.

**Major isomer** (*Z* configuration) **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.14 (s, 1H), 7.58 – 7.51 (m, 1H), 7.50 – 7.44 (m, 1H), 7.27 – 7.19 (m, 2H), 6.57 (s, 1H), 3.82 – 3.70 (m, 4H), 3.13 – 3.04 (m, 2H), 3.00 – 2.94 (m, 4H), 2.66 – 2.58 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) 176.0, 154.2, 153.4, 140.8, 129.0, 124.1, 123.2, 120.7, 115.3, 111.1, 104.1, 68.2, 51.3, 30.6, 24.4; **minor isomer** (*E* configuration) δ 8.64 (s, 1H), 7.58 – 7.51 (m, 1H), 7.50 – 7.44 (m, 1H), 7.27 – 7.19 (m, 2H), 6.67 (s, 1H), 3.82 – 3.70 (m, 4H), 3.13 – 3.04 (m, 2H), 3.04 – 2.99 (m, 4H), 2.58 – 2.47 (m, 2H); **$^{13}$C NMR** (100 MHz, $CD_2Cl_2$) 177.7, 154.2, 153.8, 140.8, 128.9, 124.1, 123.6, 120.9, 115.1, 111.1, 102.3, 68.4, 51.2, 28.8, 25.2; **IR** ($cm^{-1}$) 3233, 2926, 2848, 1708, 1635, 1452, 1374, 1296, 1253, 1110, 870, 749, 650; **HRMS** (EI) m/z calcd. for $C_{17}H_{18}N_2O_3$ $[M]^+$: 298.1317, found: 298.1315.

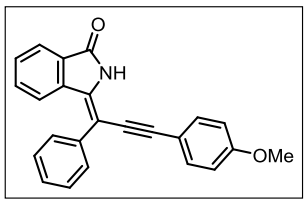
**8. Procedure for Sonogashira cross coupling reaction of 29 (Scheme 4)**




**29** (*Z*/*E* = >20:1) **33**, 82% (*Z*/*E* = >20:1)

To an oven-dried screwed vial equipped with a stir bar were added lactam **29** (0.1 mmol, 30 mg), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (4 mol%), DMF (1.0 mL) and TEA (0.15 mL) under argon atmosphere. The reaction mixture was stirred for 5 min at room temperature. A solution of the 4-ethynylanisole (0.2 mmol) in DMF (1 mL) was added dropwise over 5 min. The mixture was allowed to stir at 60 °C for 4 h. After cooling, the reaction mixture was diluted with EtOAc and washed with brine and water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: *n*-hexane/EtOAc = 10:1) to obtain desired product **33**.

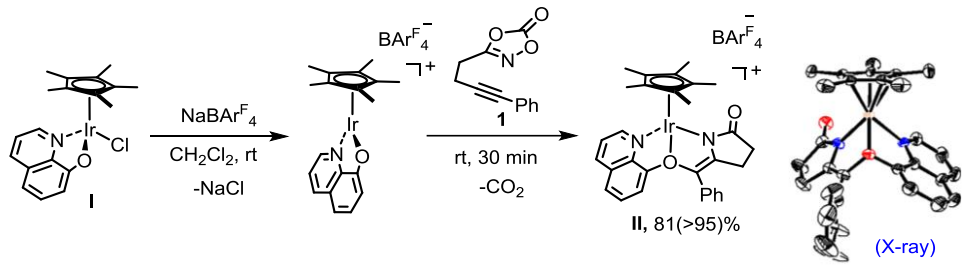
**(*Z*)-3-{3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-ylidene}isoindolin-1-one (33, Scheme 4)**




Yellow solid (29 mg, 82%); The *Z*/*E* ratio was measured to be >20:1 by $^1$H NMR spectroscopic analysis of the unpurified reaction mixture; The stereochemistry of the product was assigned as *Z* based on the literature;[10] **m.p.** 220-222 °C; **$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.20 (s, 1H), 7.85 – 7.76 (m, 1H), 7.60 – 7.54 (m, 2H), 7.54 – 7.41 (m, 6H), 7.32 (td, *J* = 7.9, 1.2 Hz, 1H), 6.94 – 6.87 (m, 3H), 3.83 (s, 3H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 166.6, 160.2, 138.2, 135.9, 135.1, 133.0, 131.8, 130.7, 129.7, 129.3, 128.9, 128.6, 123.5, 123.3, 114.5, 114.1, 104.8, 99.4, 86.4, 55.3; **IR** ($cm^{-1}$) 2920, 2848, 2174, 1698, 1598, 1508, 1247, 831, 765, 701; **HRMS** (EI) m/z calcd. for $C_{24}H_{17}NO_2$ $[M]^+$: 351.1259, found: 351.1258.

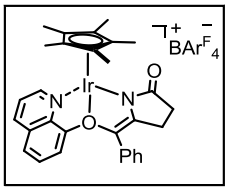
# V. Procedures of Mechanistic Studies

### 1. Stoichiometric reaction of iridium I with dioxazolone 1 (Scheme 2)



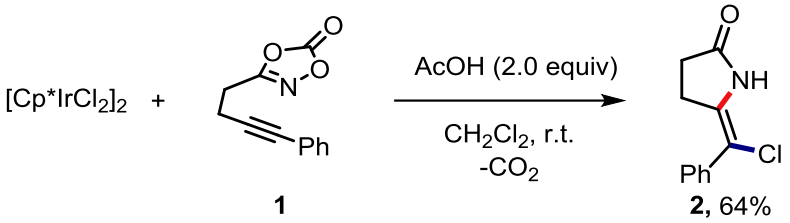

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added iridium catalyst **I** (50.7 mg, 0.1 mmol), sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (88.6 mg, 0.1 mmol) and dichloromethane (1.2 mL) under atmospheric conditions and stirred. After 1 min, the vial was charged with 3-(4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (**1**, 21.5 mg, 0.1 mmol). The reaction mixture was vigorously stirred at room temperature for 30 min, filtered through a pad of celite with dichloromethane (10 mL × 3) and concentrated under reduced pressure. The crude yield of **II** (>95 %) was measured with respect to 1,1,2,2-tetrachloroethane as an internal standard. The crude mixture was purified by recrystallization (dichloromethane/*n*-pentane at -20 °C) to afford alkyne-inserted iridium complex **II**.

**Alkyne-inserted iridium complex (II, Scheme 2)**




Orange solid (123 mg, 81%); **m.p.** 125-127 °C **$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ 9.07 (d, *J* = 5.0 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 3H), 7.35 (t, *J* = 7.9 Hz, 2H), 2.99 – 2.87 (m, 1H), 2.72 – 2.60 (m, 2H), 2.58 – 2.48 (m, 1H), 1.70 (s, 15H); **$^{13}$C NMR** (150 MHz, $CD_2Cl_2$) δ 180.9, 156.8, 152.1, 145.9, 140.7, 140.1, 138.8, 132.6, 131.1, 129.7, 129.6, 127.9, 127.0, 126.9, 125.1, 122.6, 89.3($Cp^*$), 32.0, 24.3, 9.4($Cp^*$); **IR** ($cm^{-1}$) 1640, 1503, 1354, 1277, 1124, 887, 839, 713, 682, 671; **HRMS** (FAB) m/z calcd. for $C_{30}H_{30}IrN_2O_2$ $[M]^+$: 643.1937, found: 643.1940.

**2. Stoichiometric reaction of $[Cp^*IrCl_2]_2$ with dioxazolone 1 (Scheme 3)**




To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $[Cp^*IrCl_2]_2$ (19.9 mg, 0.025 mmol), dioxazolone **1** (10.7 mg, 0.05 mmol), acetic acid (0.1 mmol) and dichloromethane (0.6 mL) under atmospheric conditions and stirred. The reaction mixture was vigorously stirred at room temperature for 1 h, filtered through a pad of celite with dichloromethane (10 mL × 3) and concentrated under reduced pressure. The crude yield of **2** (64%) was measured with respect to 1,1,2,2-tetrachloroethane (8.2 mg, 0.05 mmol) as an internal standard.

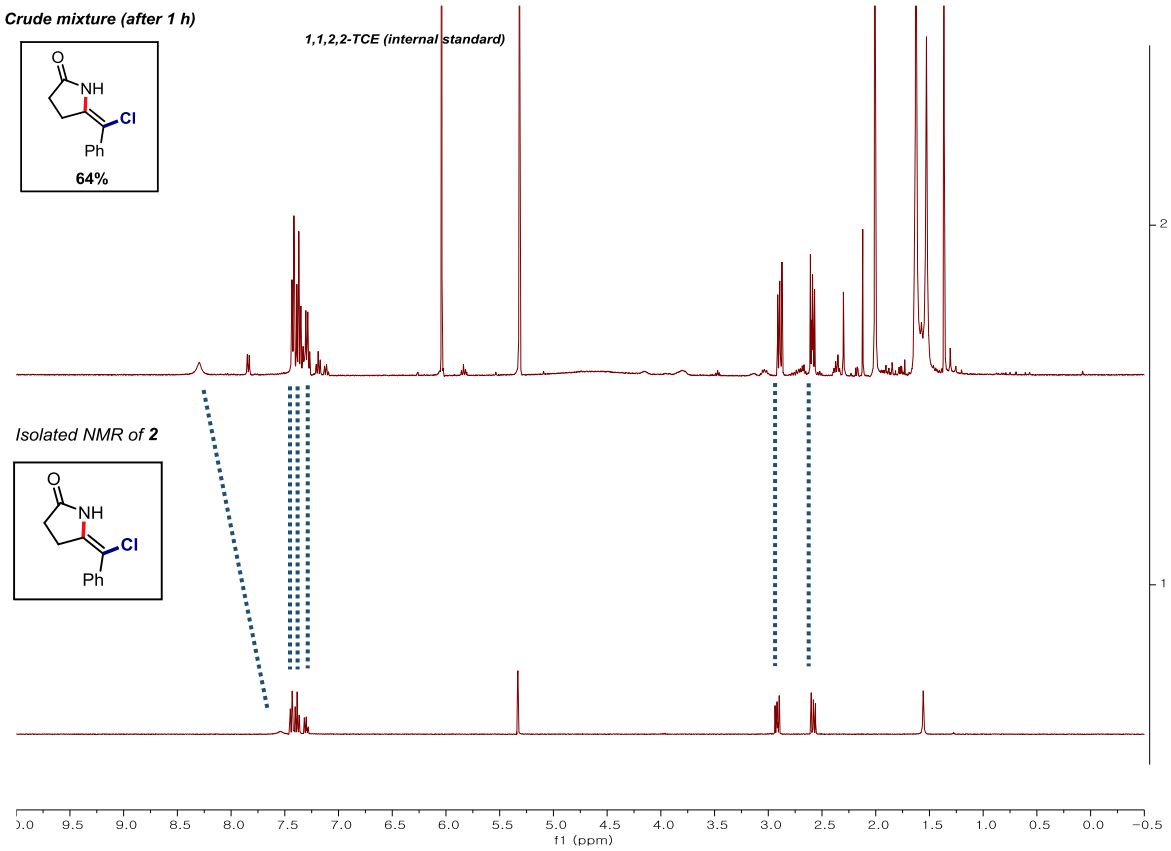
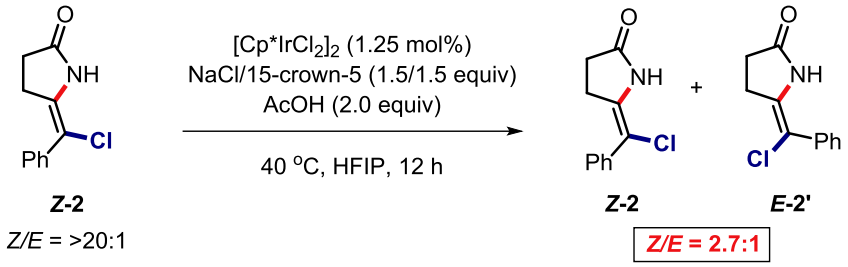


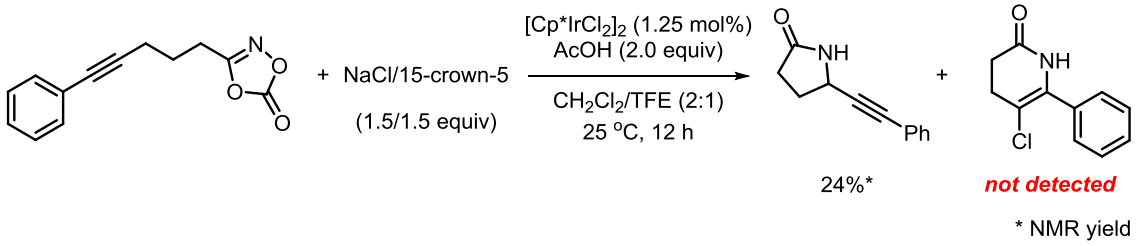

**Figure S1**. $^1$H NMR of the crude reaction mixture

**3. Test reaction to see whether the isomerization of initially generated *Z*-products may occur (Ref 14)**




To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $[Cp^*IrCl_2]_2$ (1.0 mg, 1.25 mol%), 1,4,2-dioxazol-5-one (0.1 mmol), sodium chloride (8.8 mg, 0.15 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (0.6 mL) under atmospheric condition and stirred for 1 min. To the vial were added acetic acid (11.3 μL, 0.2 mmol) and 15-crown-5 (29.6 μL, 0.15 mmol), and then sealed. The reaction mixture was vigorously stirred in a pre-heated oil bath at 40 °C for 12 h, and concentrated under reduced pressure. The *Z*/*E* ratio (**2**:**2**') was measured to be 2.7:1 by $^1$H NMR spectroscopic analysis of the unpurified reaction mixture.

**4. The catalytic reaction of 3-(5-phenylpent-4-yn-1-yl)-1,4,2-dioxazol-5-one (Ref 15)**




To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added $[Cp^*IrCl_2]_2$ (1.0 mg, 1.25 mol%), 3-(5-phenylpent-4-yn-1-yl)-1,4,2-dioxazol-5-one (0.1 mmol), sodium chloride (8.8 mg, 0.15 mmol) and dichloromethane/2,2,2-trifluoroethanol = 2:1 (0.6 mL) under atmospheric condition and stirred for 1 min. To the vial were added acetic acid (11.3 μL, 0.2 mmol) and 15-crown-5 (29.6 μL, 0.15 mmol), and then sealed. The reaction mixture was vigorously stirred in a pre-heated oil bath at 40 °C for 12 h, and concentrated under reduced pressure. We observed 5-(phenylethynyl)pyrrolidin-2-one in 24% crude yield (measured by $^1$H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.) presumably via a C−H insertion pathway. However, the corresponding 6-membered lactam was not formed at all.

# VI. Computational Studies

### 1. Computational details

All DFT calculations were carried out with Gaussian 09 program.[11] All structures were optimized by B3LYP functionals[12] with a mixed basis sets of Los Alamos National Laboratory doubleζ (LANL2DZ) ECP basis set[13] for Ir atom and 6-31G(d,p) basis sets for other main group atoms. Thermodynamic parameters including Gibbs free energies at 298 K were obtained by frequency calculations. Transition states are realized by the presence of single negative frequency. We carried out intrinsicreaction coordinate (IRC) calculations to confirm that the computed transition states properly connect the reactant and the product structures along the reaction trajectory. Electronic energies of optimized structures were further corrected by single point calculations of M06 functionals[14] with SDD basis sets for Ir atom and 6-311++G(d,p) basis sets for other atoms. Solvation of dichloromethane (DCM) was considered by single point calculation with integral equation formalism PCM model.[15] The effectiveness of the calculations with B3LYP followed by M06 functionals was reported by previous literatures.[16] Figures of three-dimensional molecular structures were prepared using CYLview.[17]

### 2. Calculations of potential energy surface for stoichiometric reaction of 1 with I (Scheme 2b)

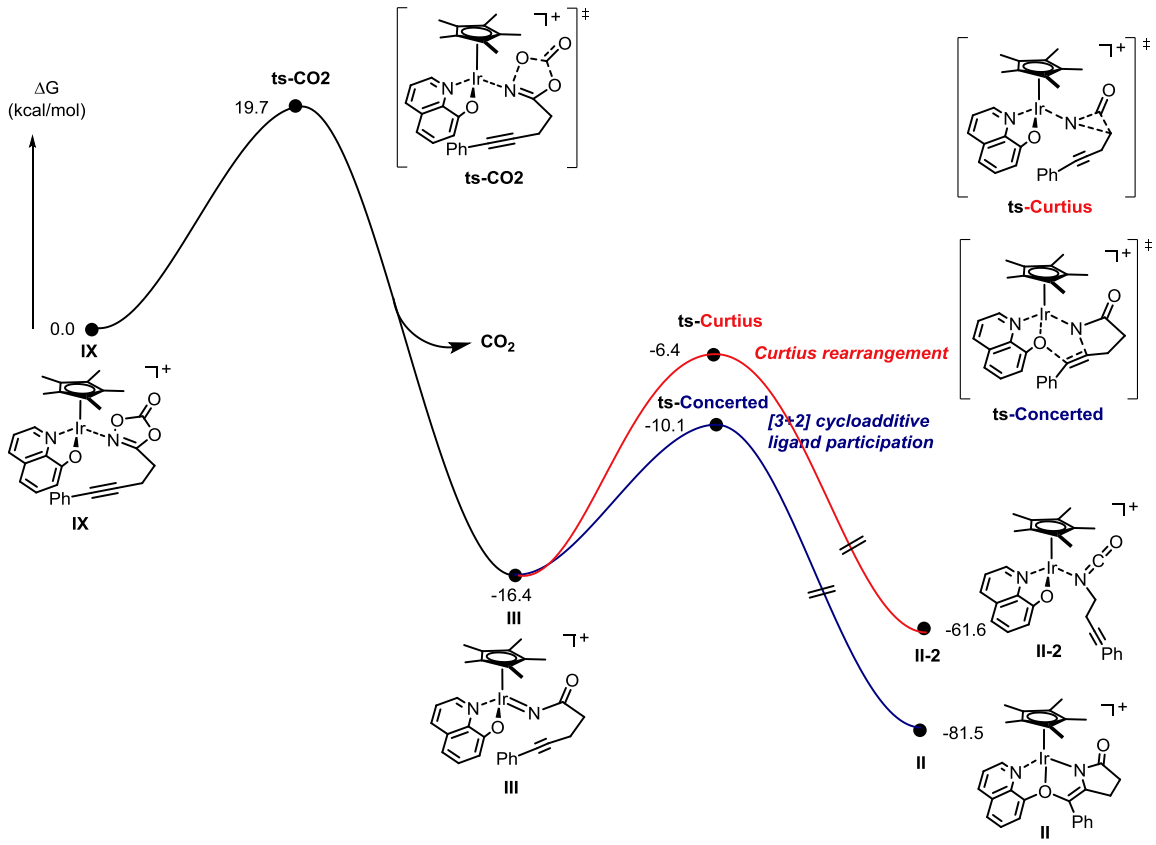



**Figure S2.** Potential energy surface for stoichiometric reaction of **1** with **I**

**3. Relaxed PES scanning to consider the intermediacy of vinyl cation species**

To find out the optimized geometry for the structure of vinyl cation, relaxed PES scanning was conducted as a function of O1-C1 distance of the iridium **II** at every 0.1 Å interval from 1.47 to 4.47 Å to explore the local minimum (calculated by B3LYP/6-31G*//LANL2DZ method, modredundant option in Gaussian 09). However, it was observed that no stationary structure was obtained from relaxed PES scanning. Instead, all of the initially guessed structures drifted down to the original **II** structure.

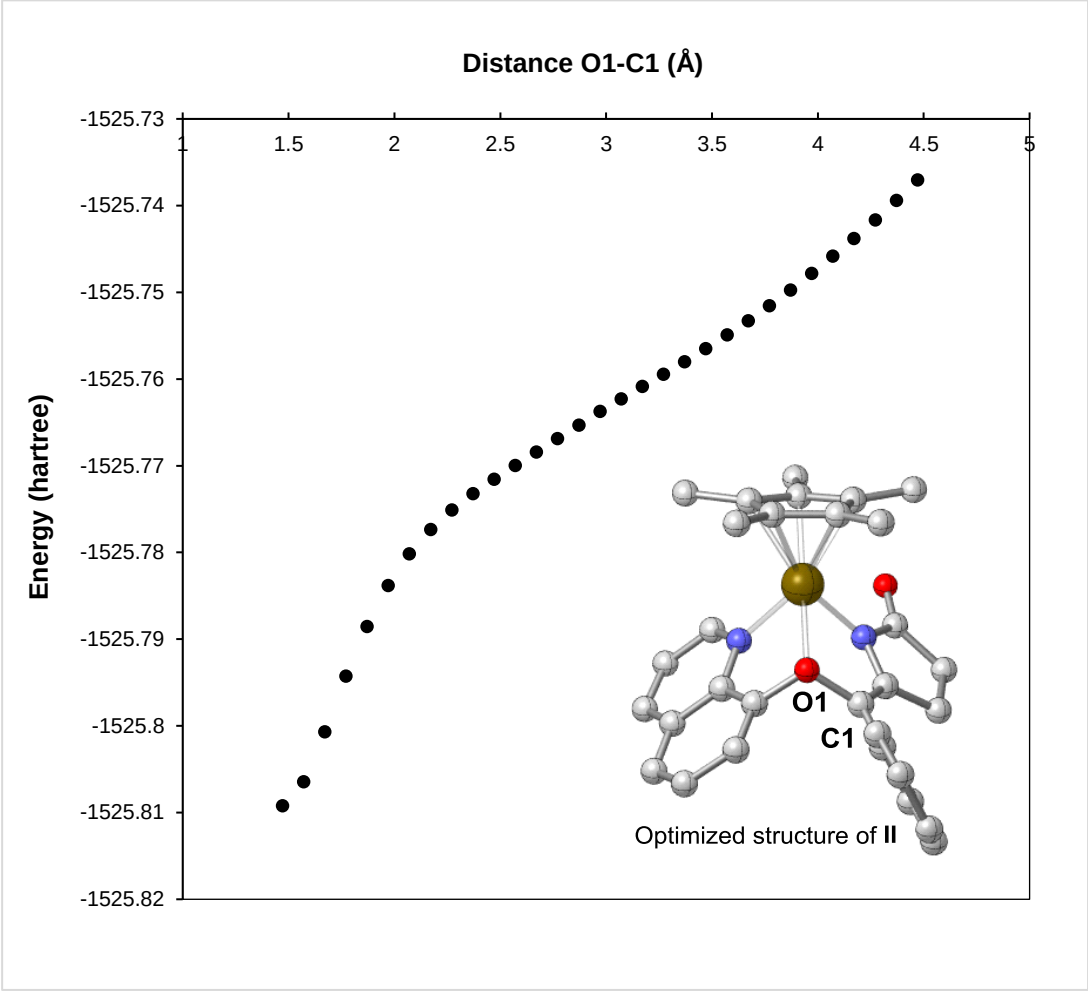



**Figure S3**. Relaxed PES scanning as a function of O1-C1 distance of **II**

**4. Calculations of potential energy surface for chloroamidation (Scheme 3b)**

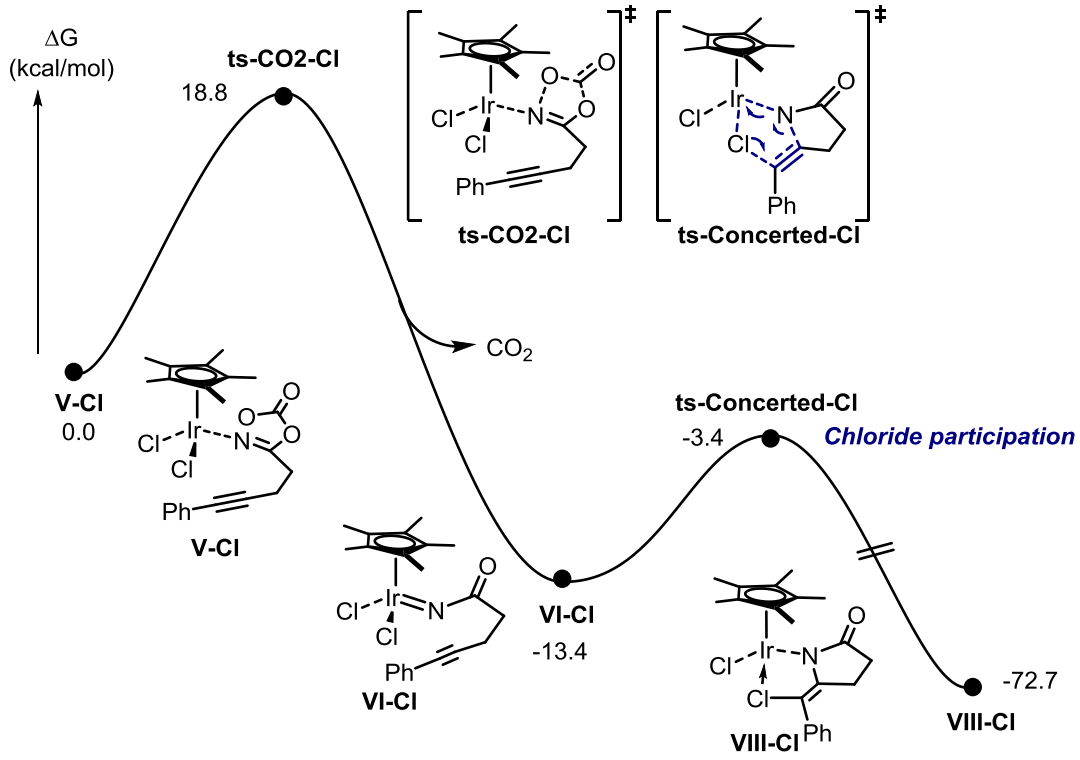



**Figure S4.** Potential energy surface for chloroamidation

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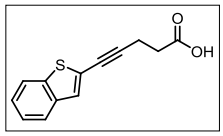
# *Appendix I*

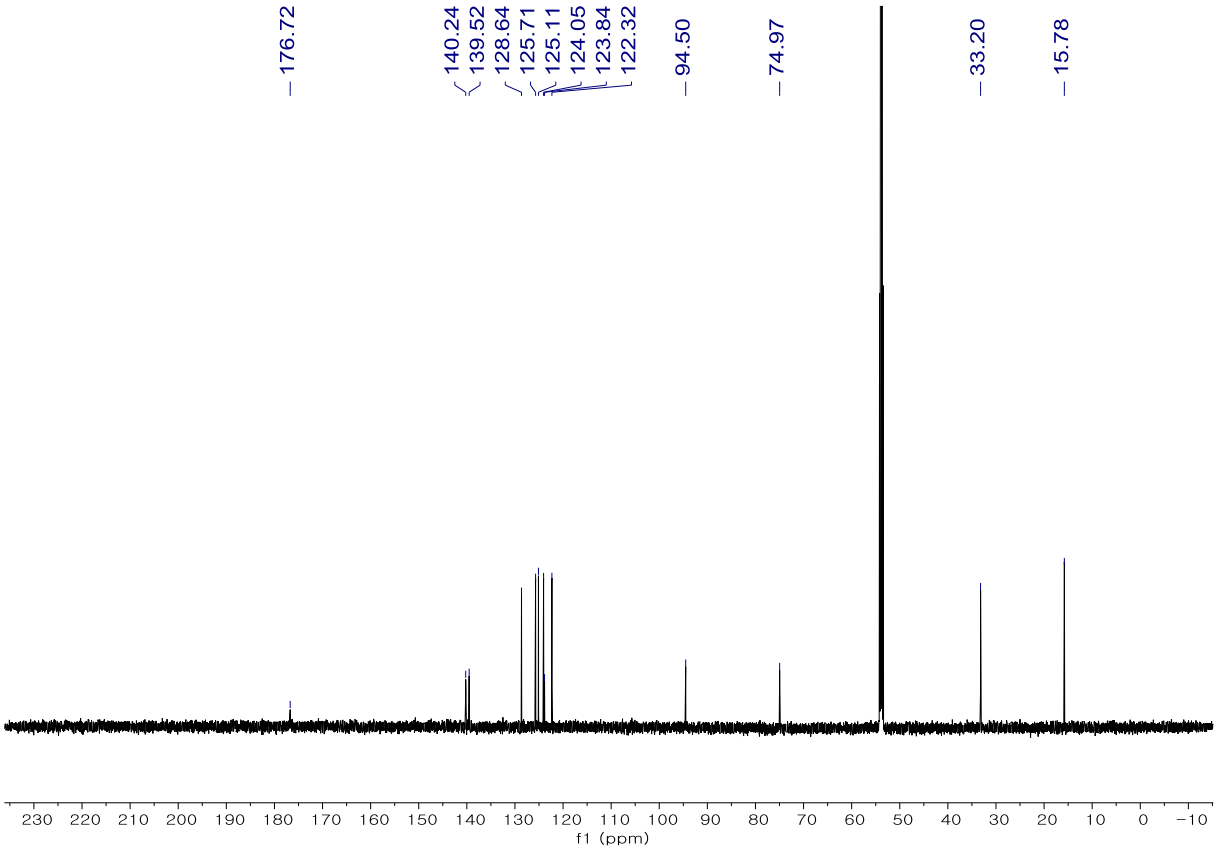
# *(Spectral Copies of $^{1}H$, $^{13}C$ and $^{19}F$ NMR of Compounds Obtained in this Study)*

**5-(Benzo[*b*]thiophen-2-yl)pent-4-ynoic acid**

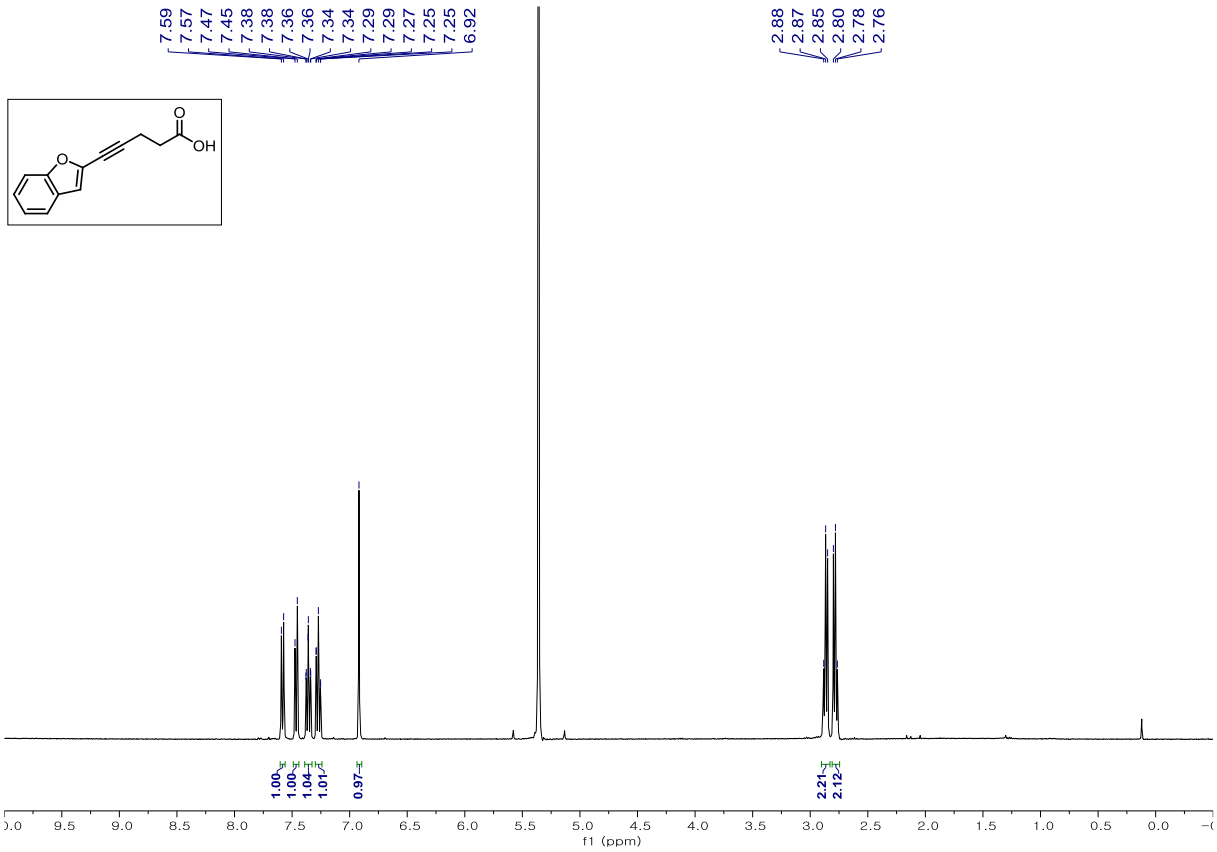


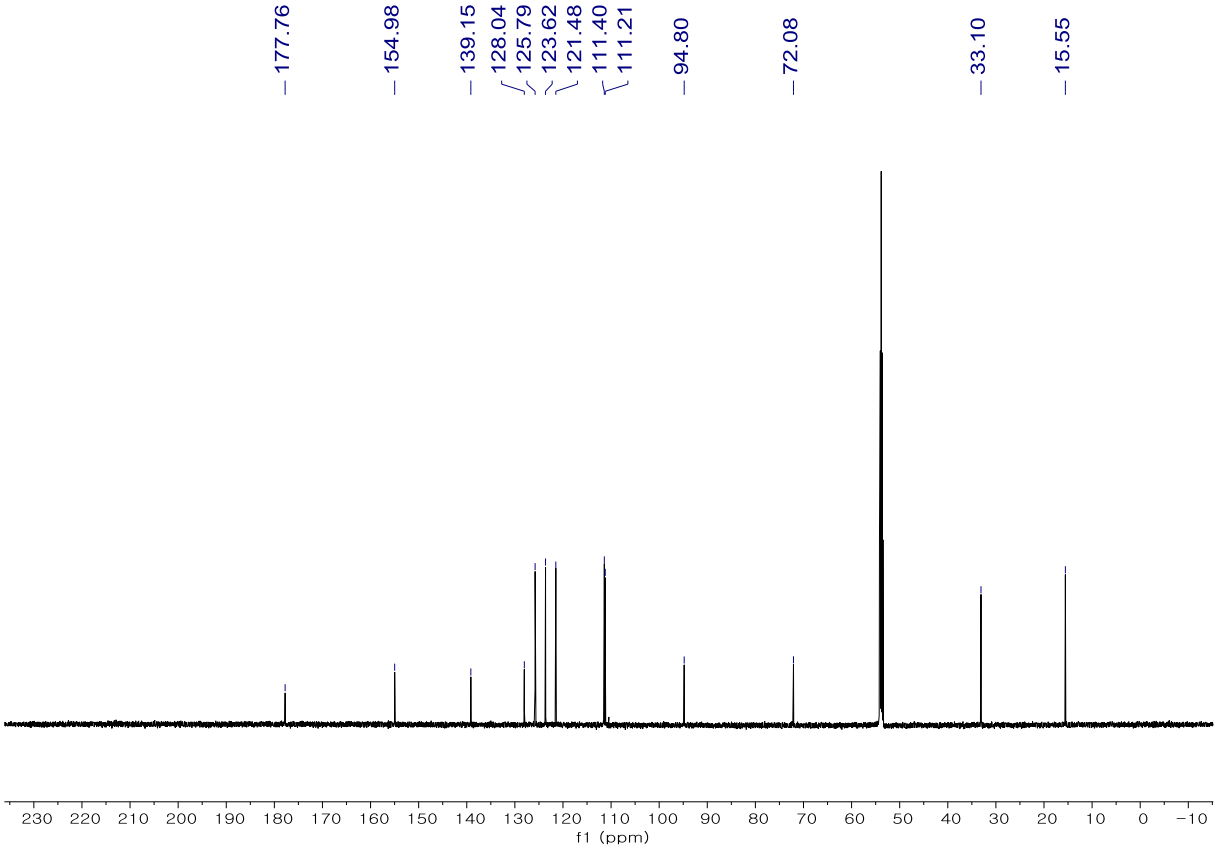




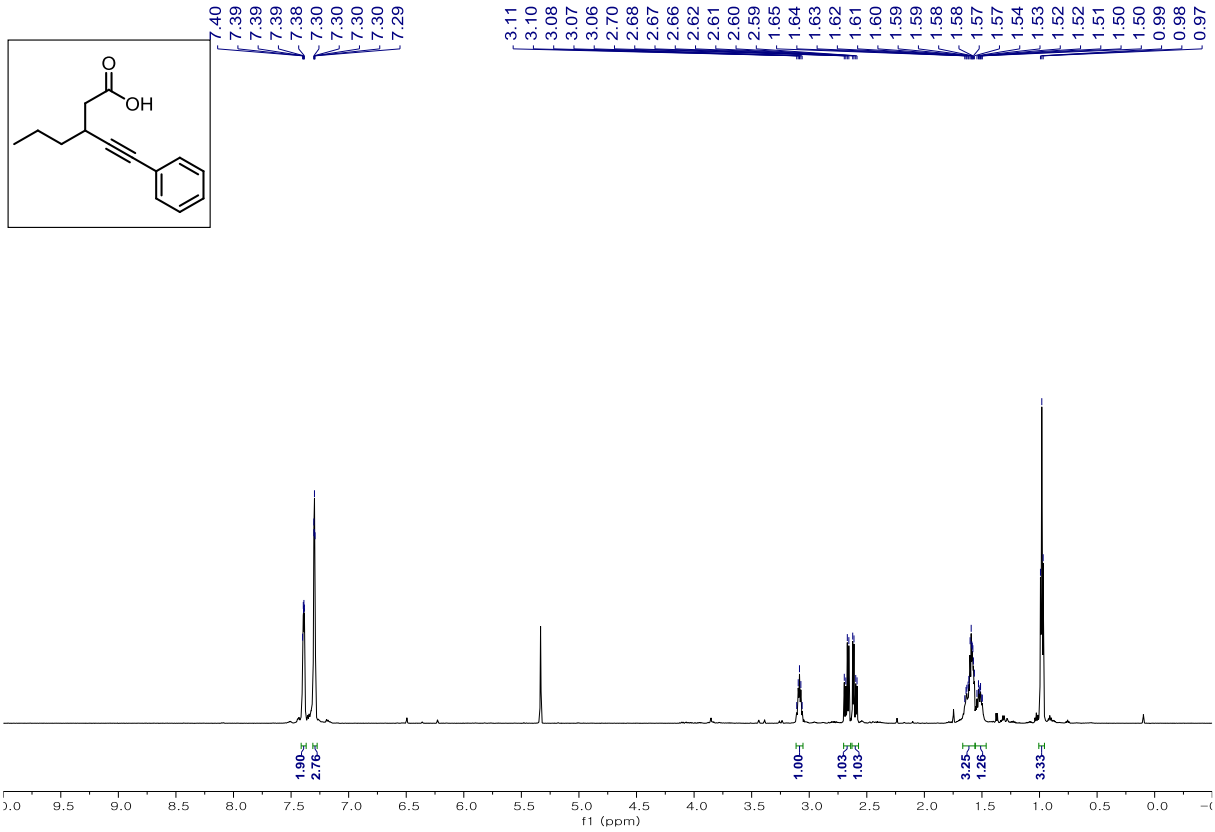


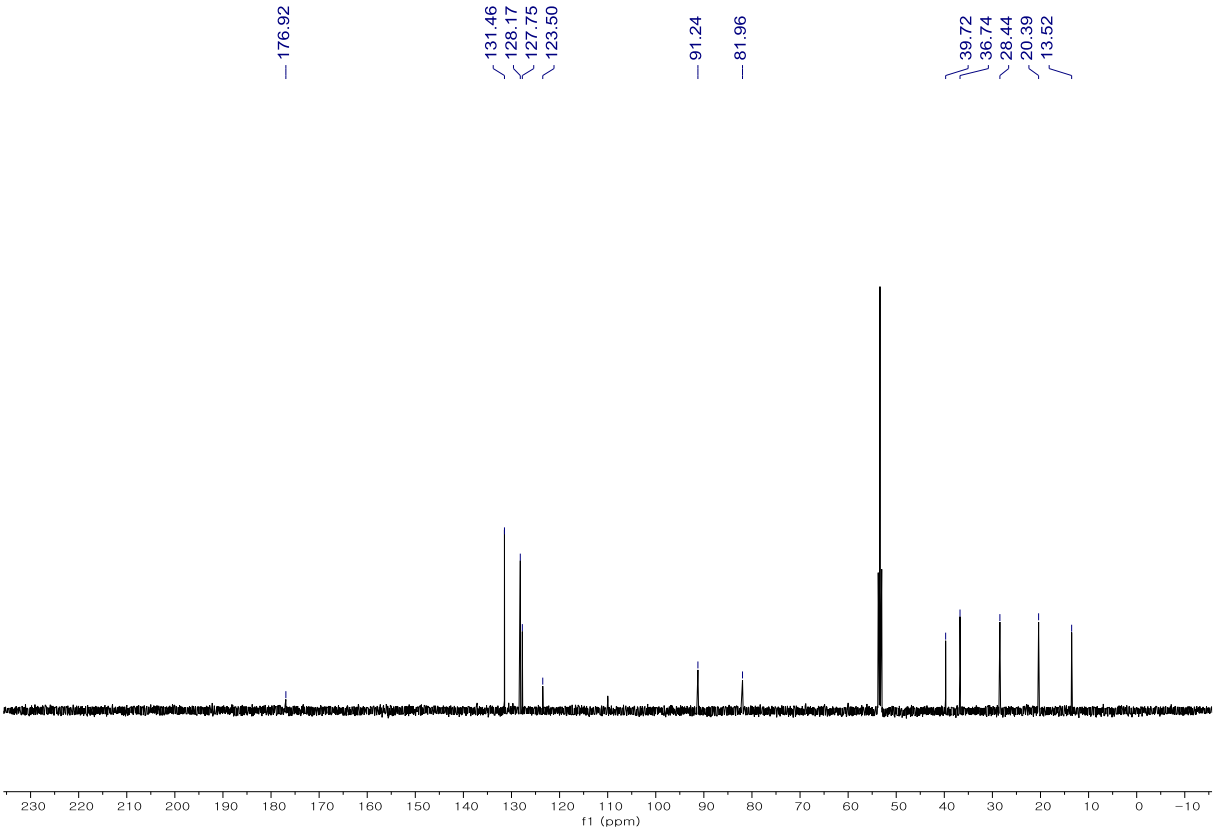
## 5-(Benzofuran-2-yl)pent-4-ynoic acid



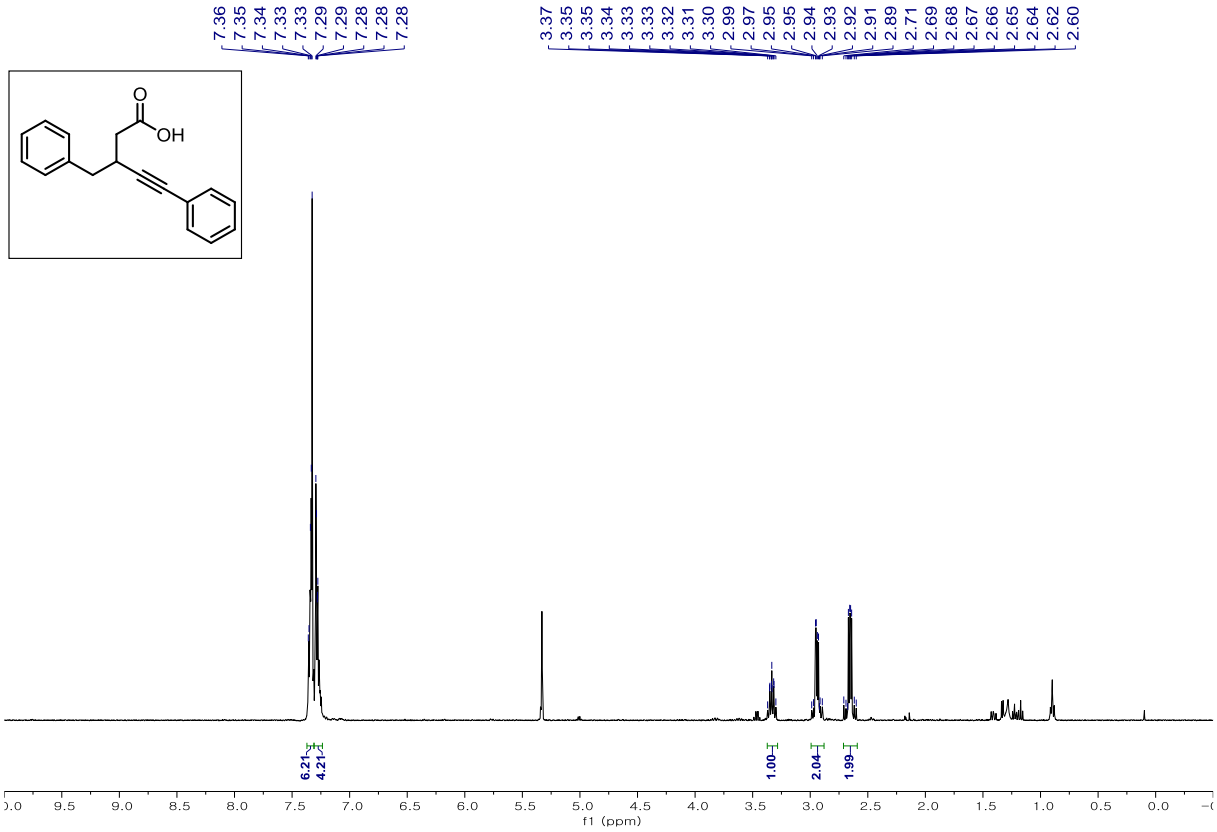



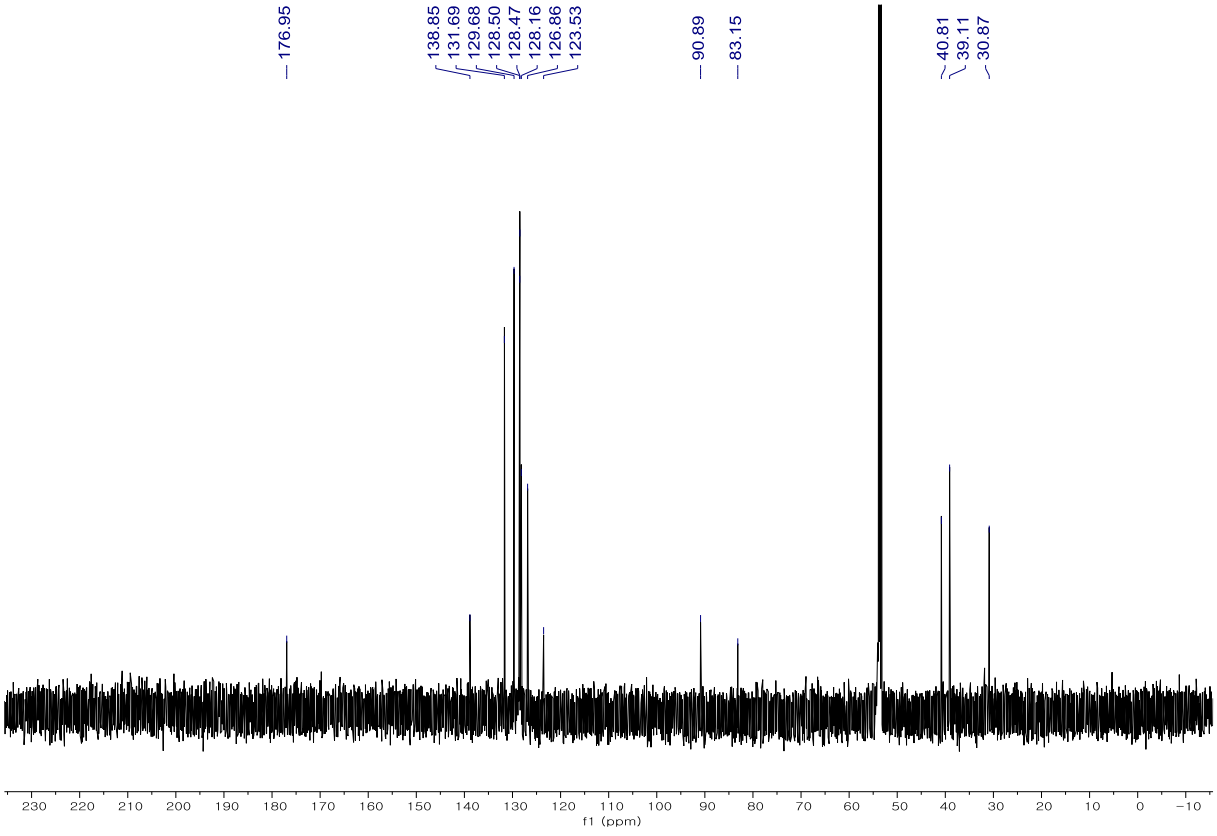
## 3-(Phenylethynyl)hexanoic acid



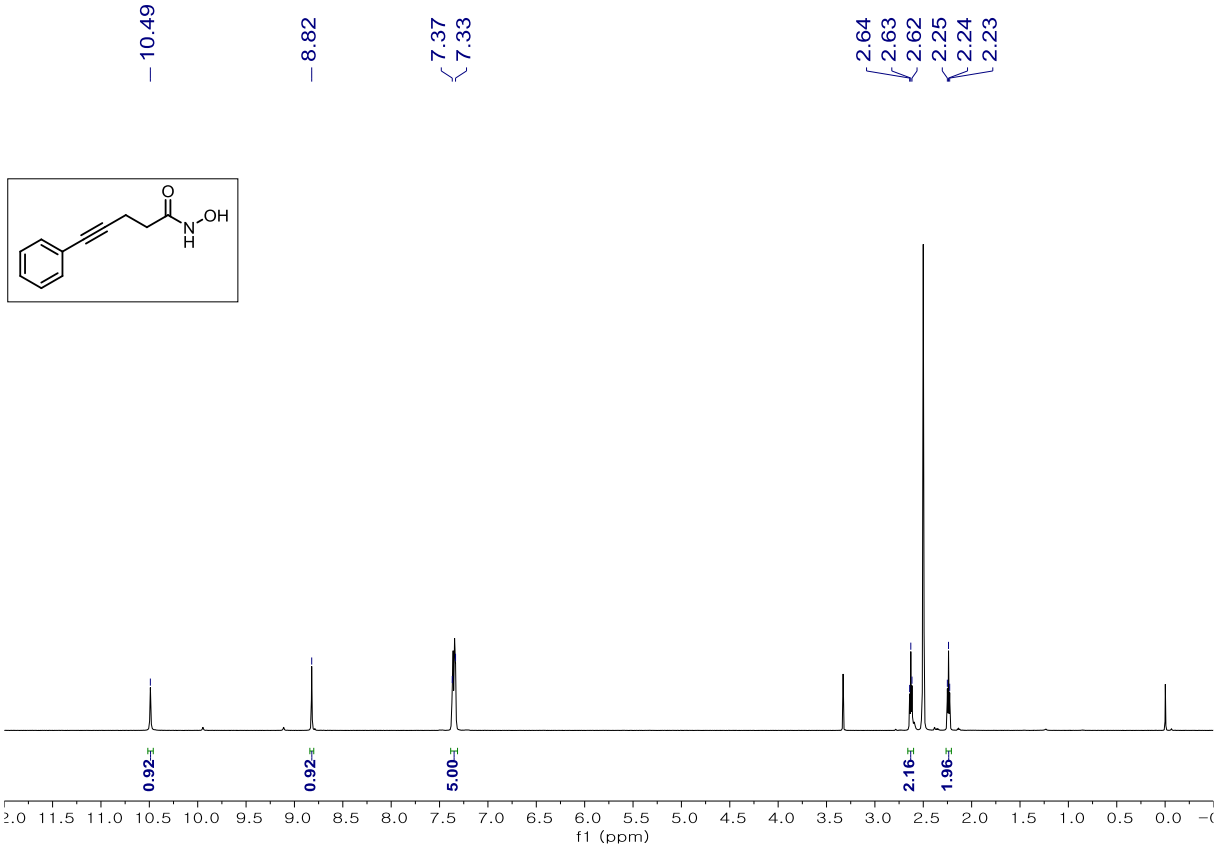



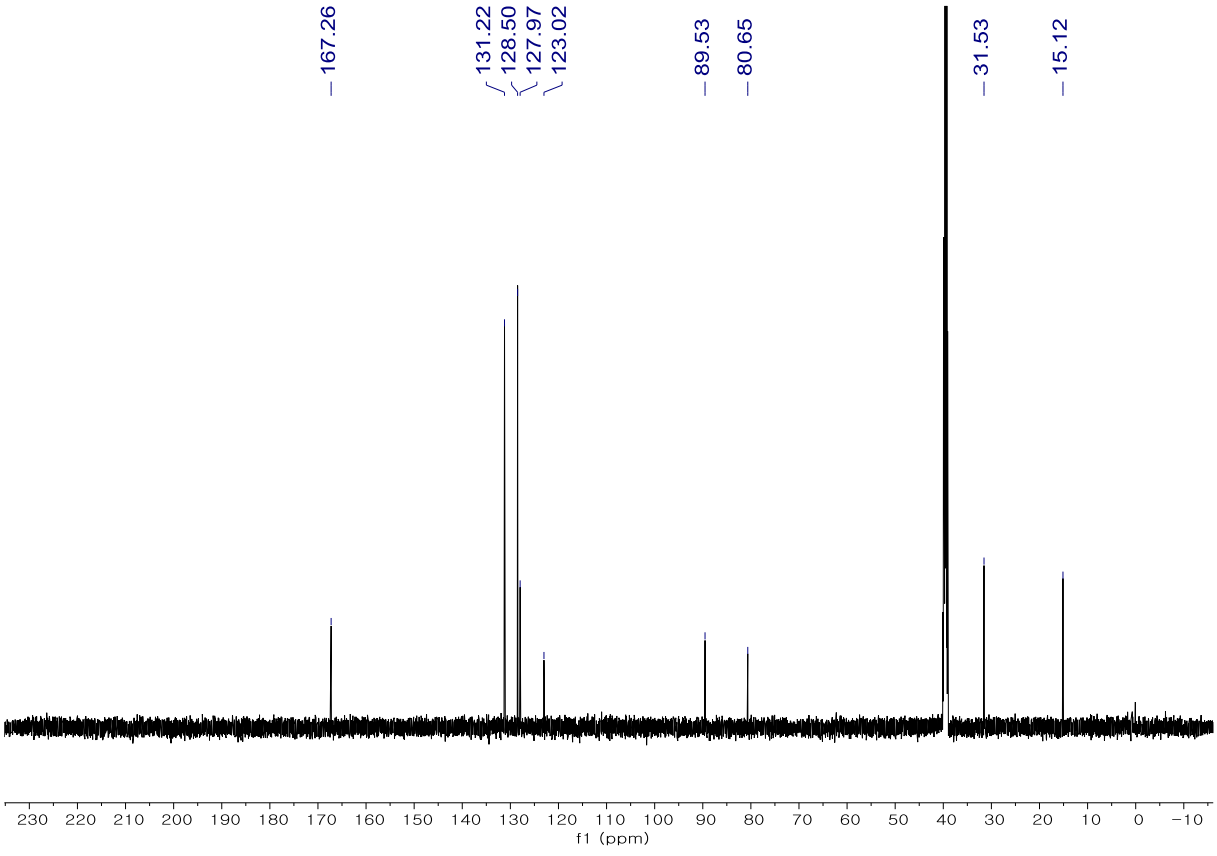
**3-Benzyl-5-phenylpent-4-ynoic acid**



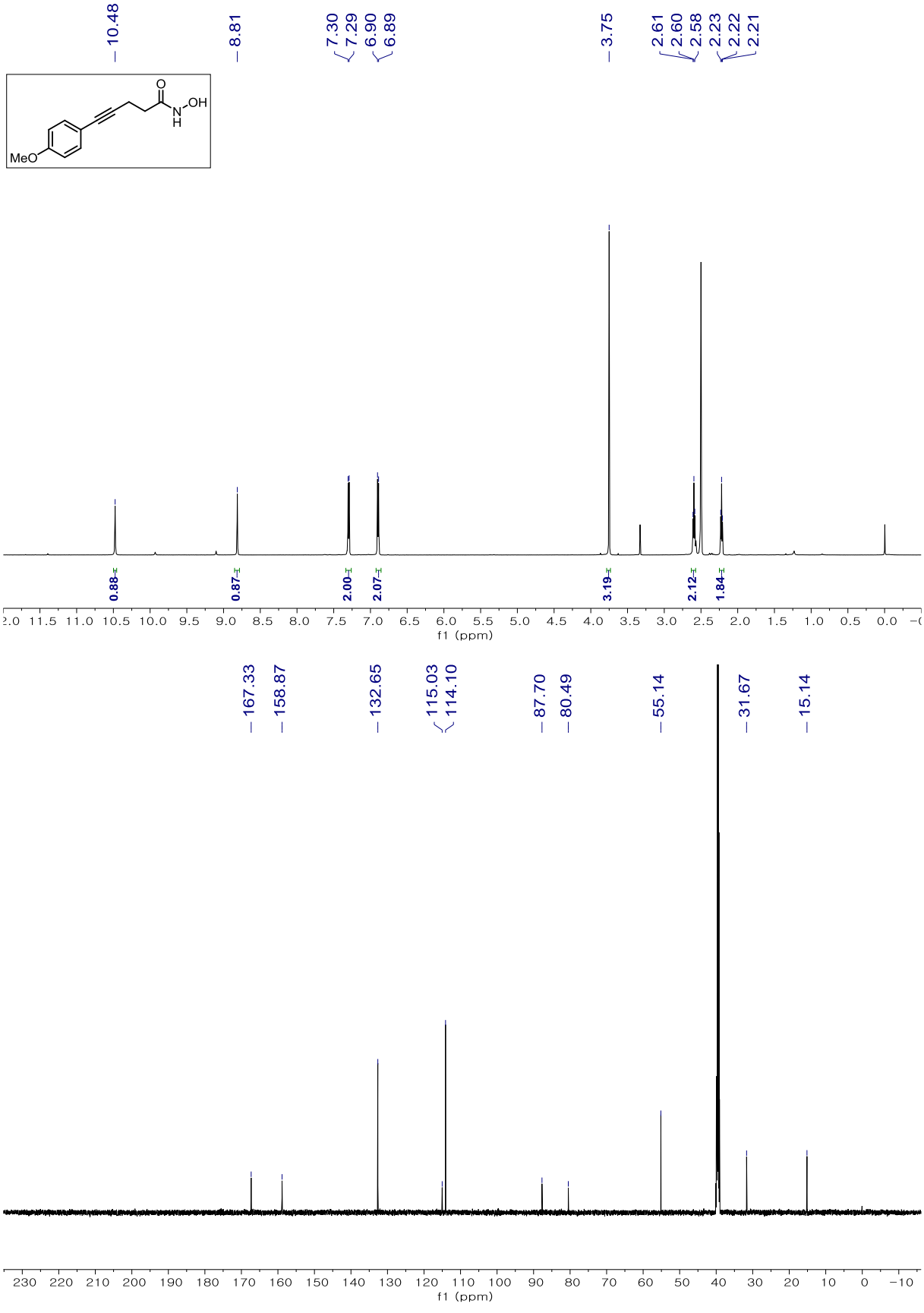



**5-Phenylpent-4-ynyl hydroxamic acid**

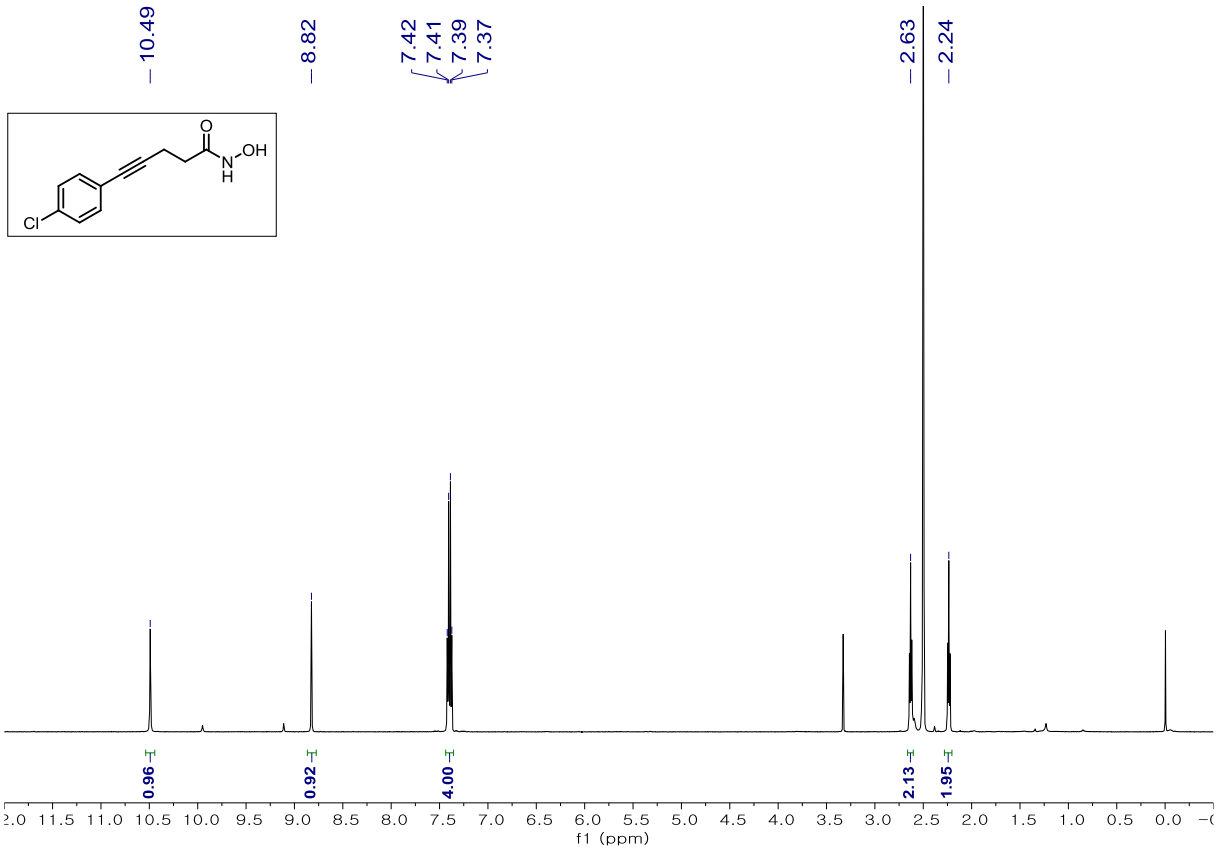


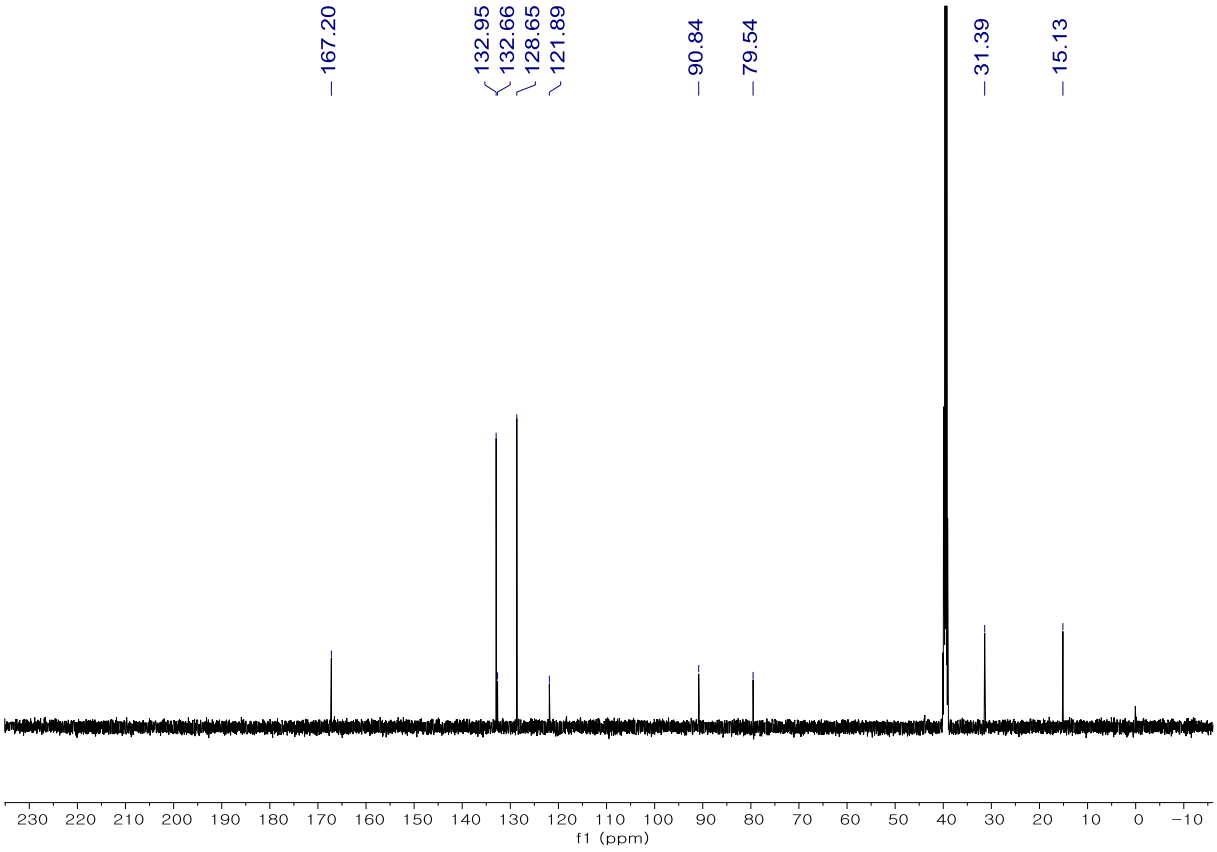



**5-(4-Methoxyphenyl)pent-4-ynyl hydroxamic acid**

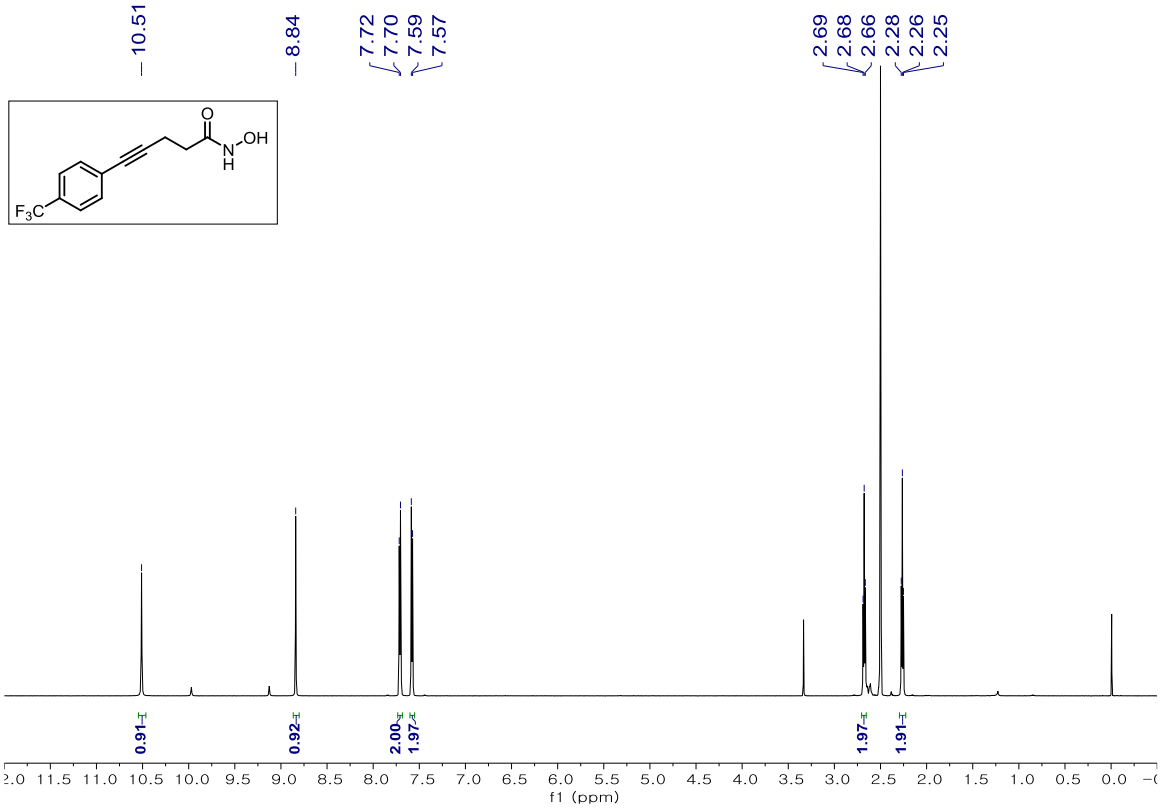


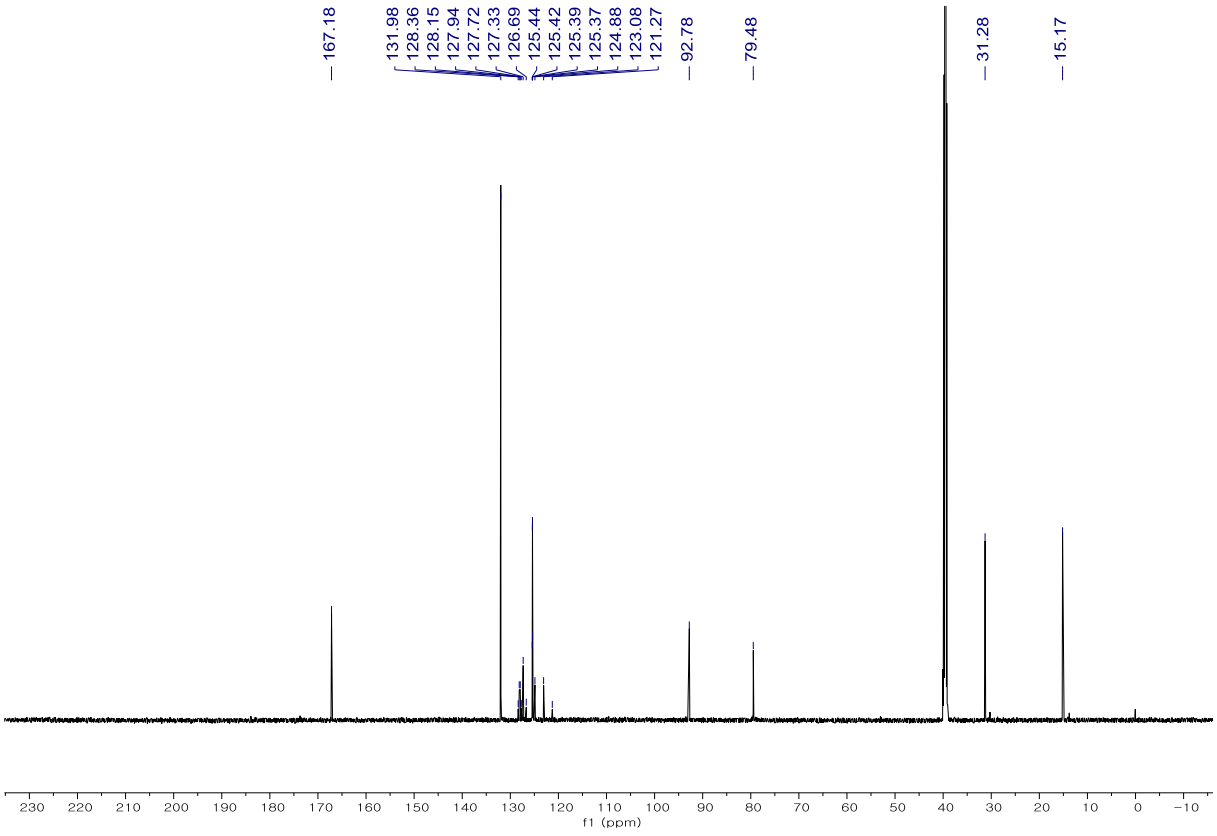
**5-(4-Chlorophenyl)pent-4-ynyl hydroxamic acid**

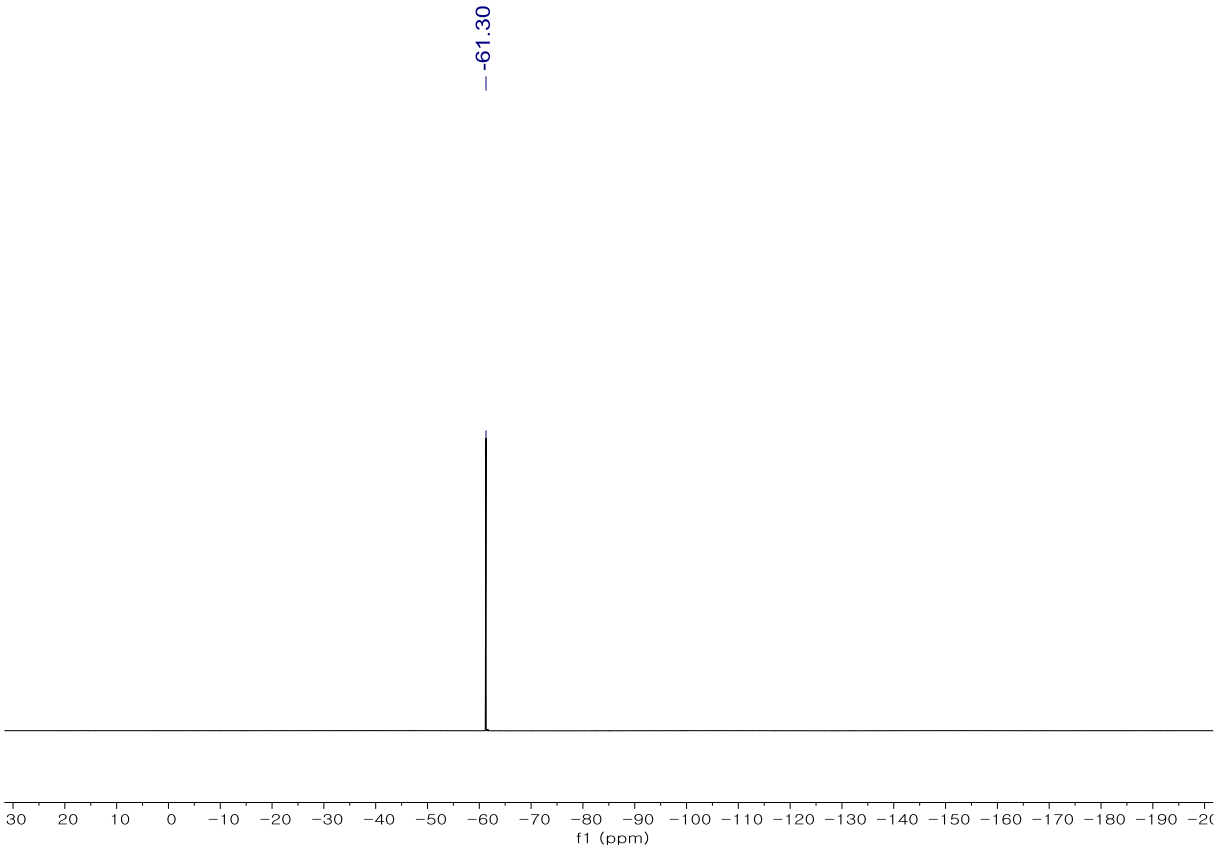


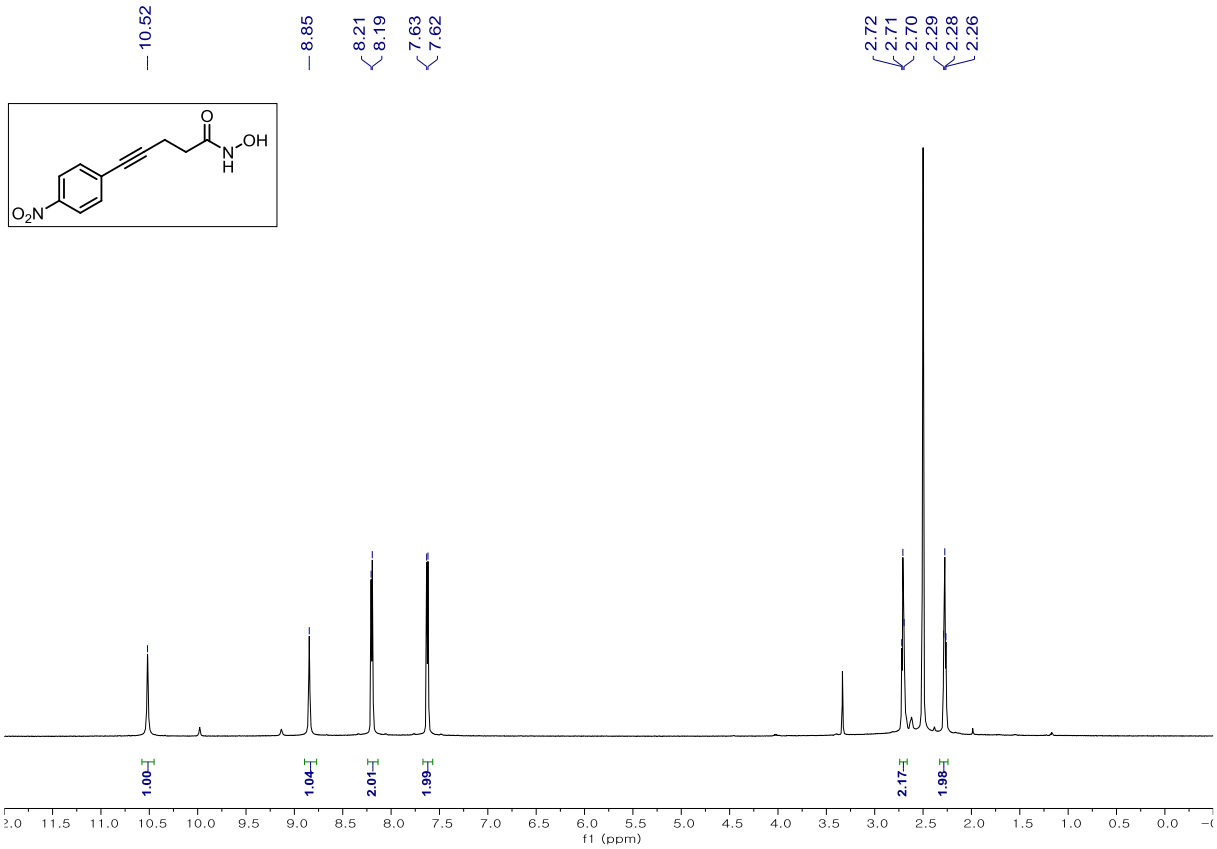
**5-{4-(Trifluoromethyl)phenyl}pent-4-ynyl hydroxamic acid**

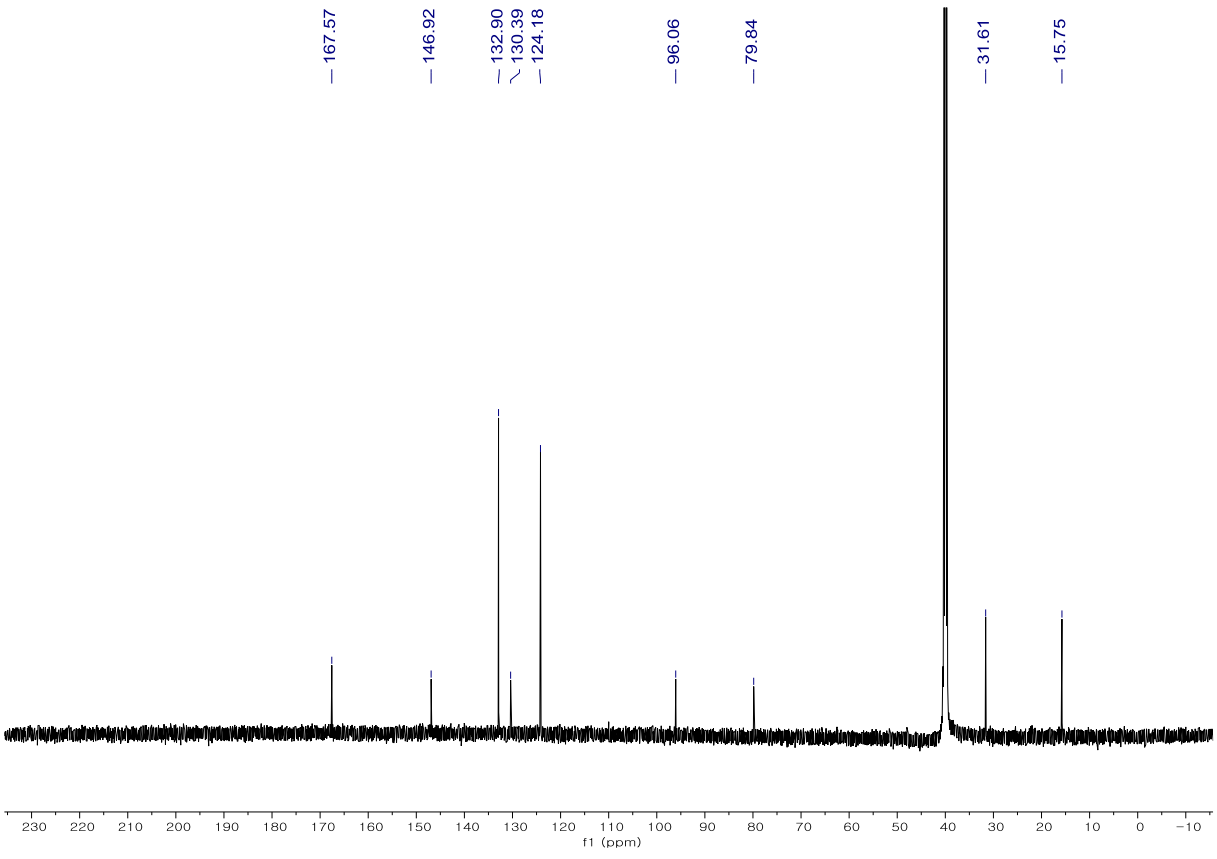


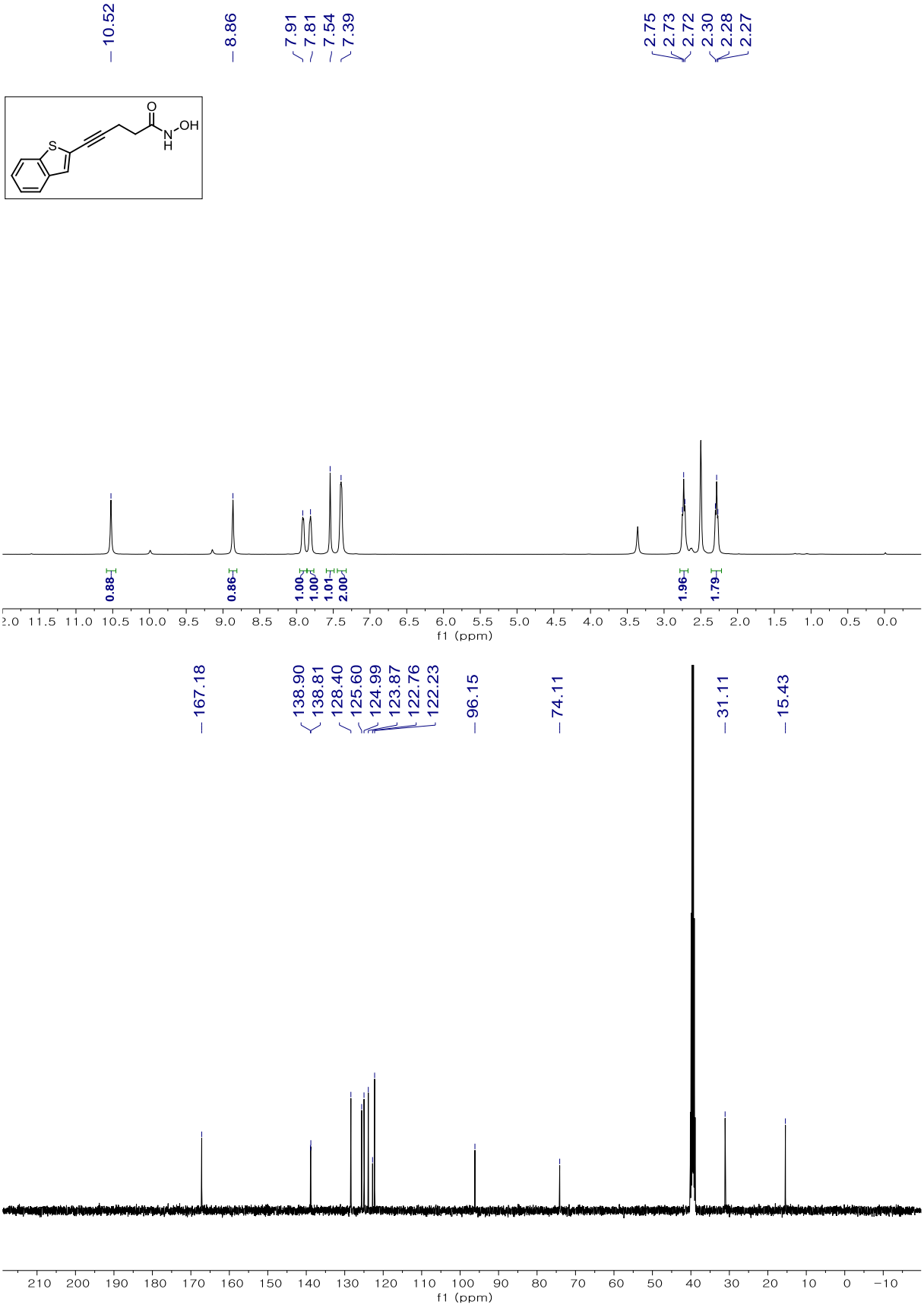

-61.30
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

## 5-(4-Nitrophenyl)pent-4-ynyl hydroxamic acid

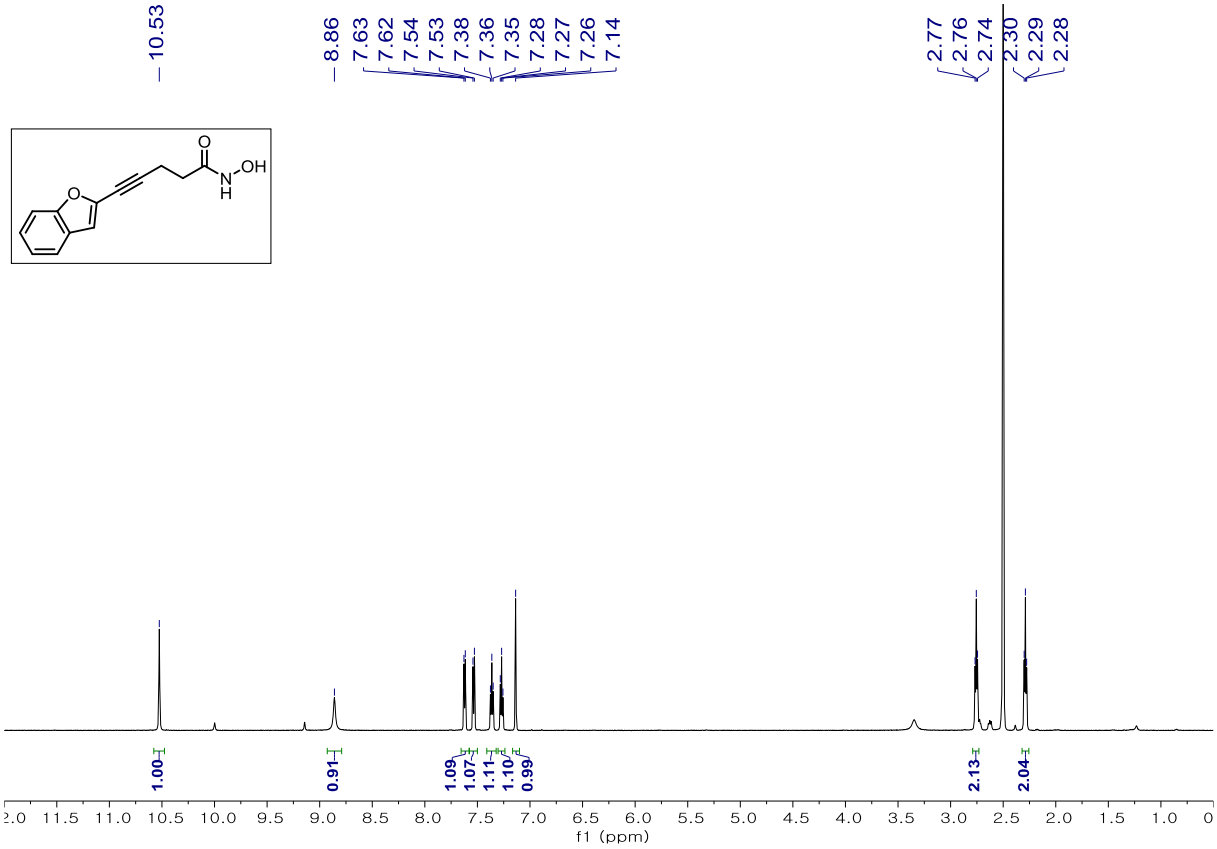


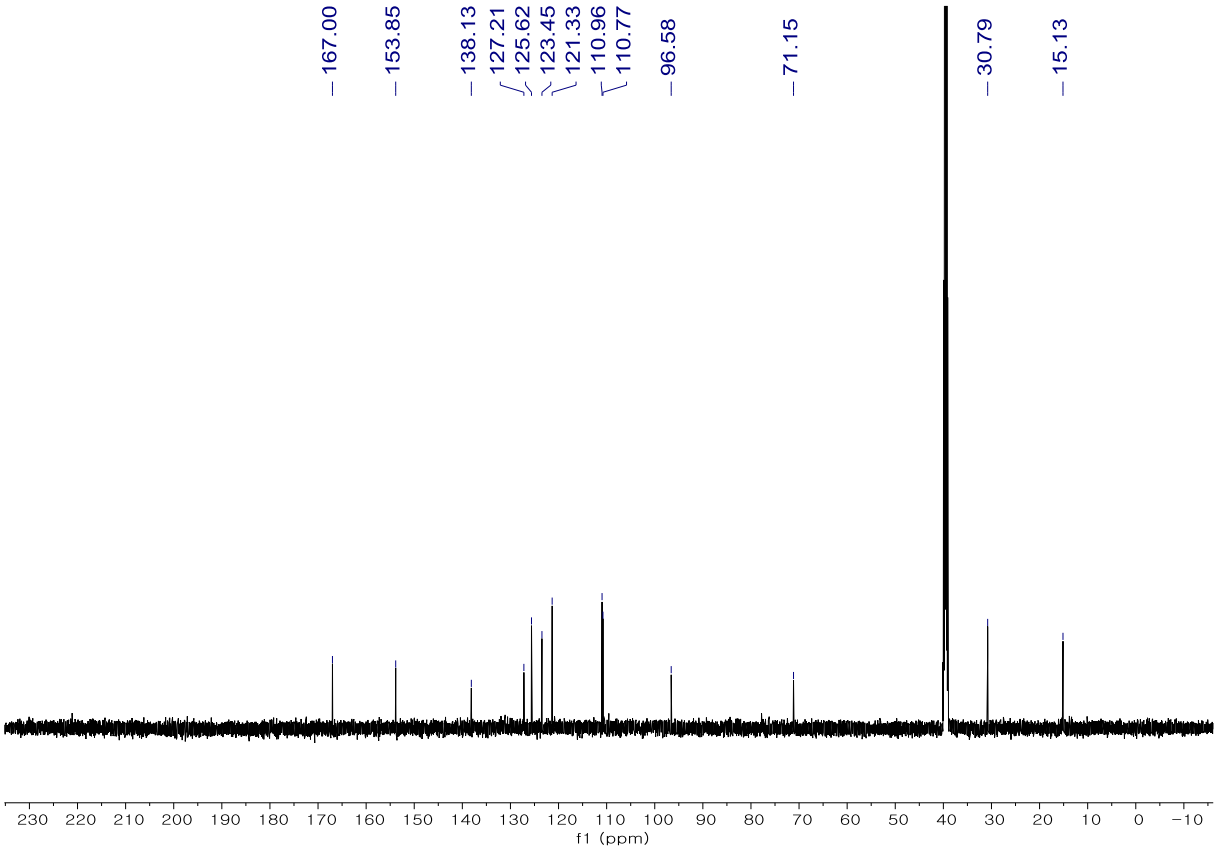



**5-(Benzo[*b*]thiophen-2-yl)pent-4-ynyl hydroxamic acid**

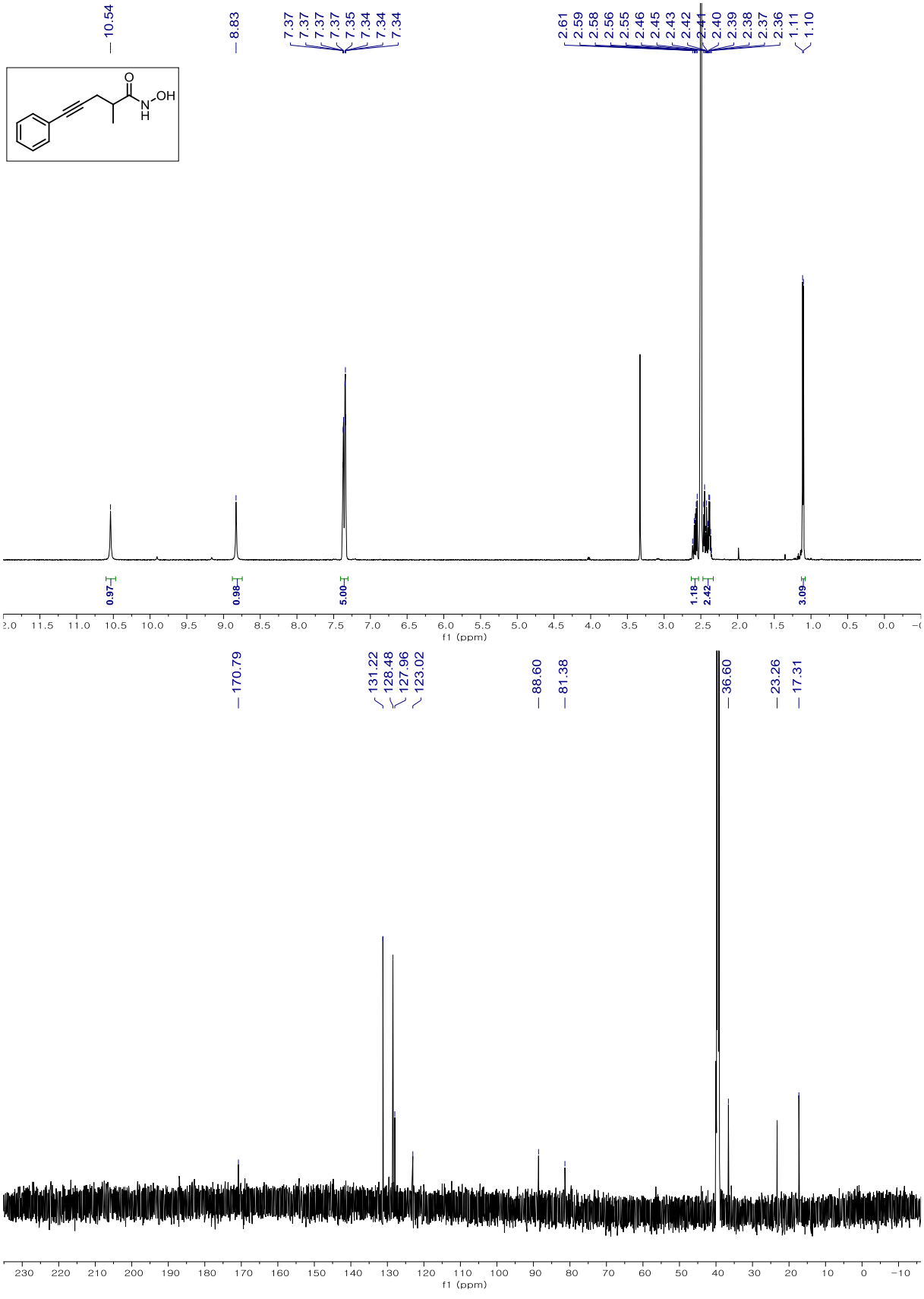


**5-(Benzofuran-2-yl)pent-4-ynyl hydroxamic acid**

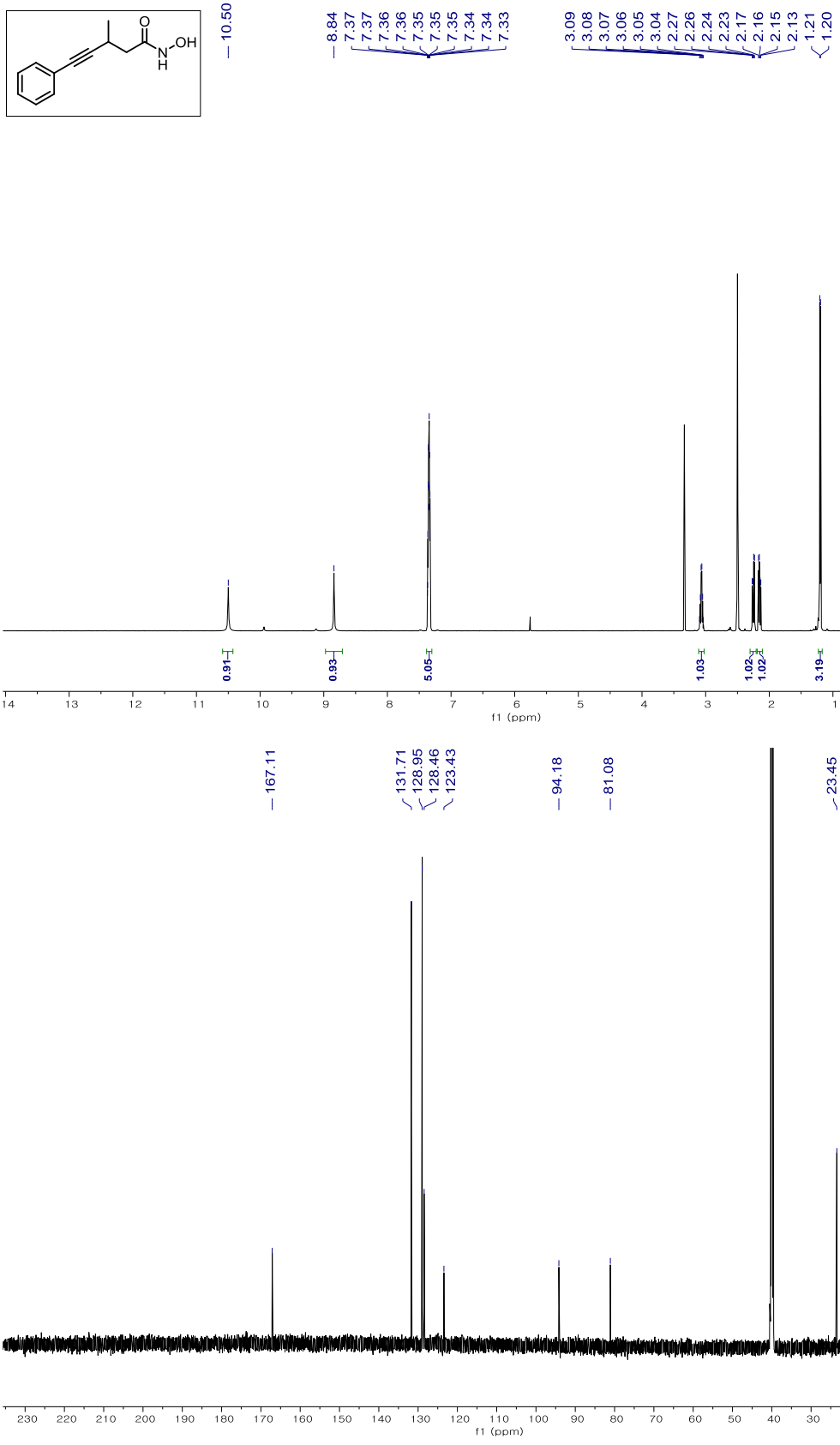


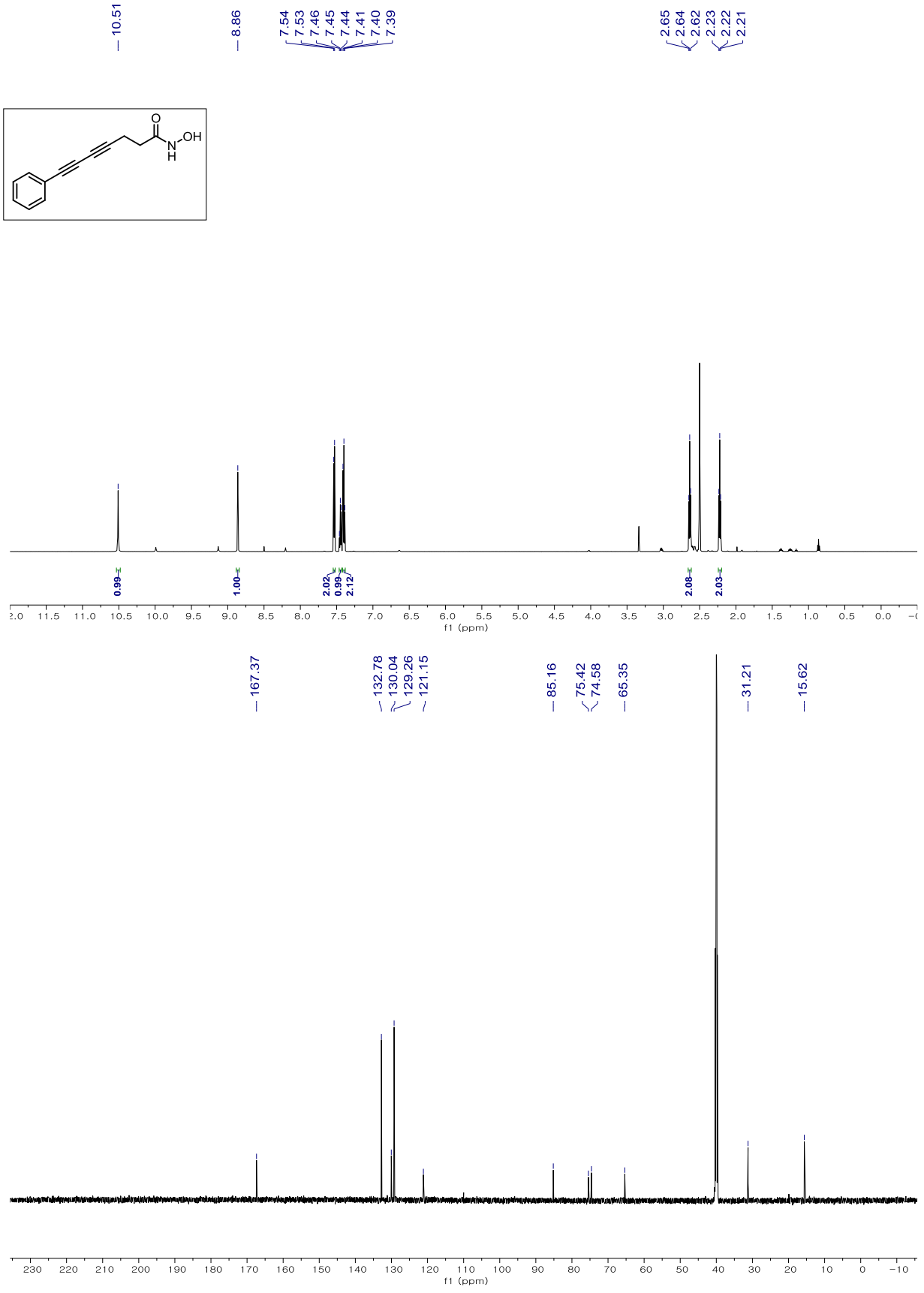
**2-Methyl-5-phenylpent-4-ynyl hydroxamic acid**



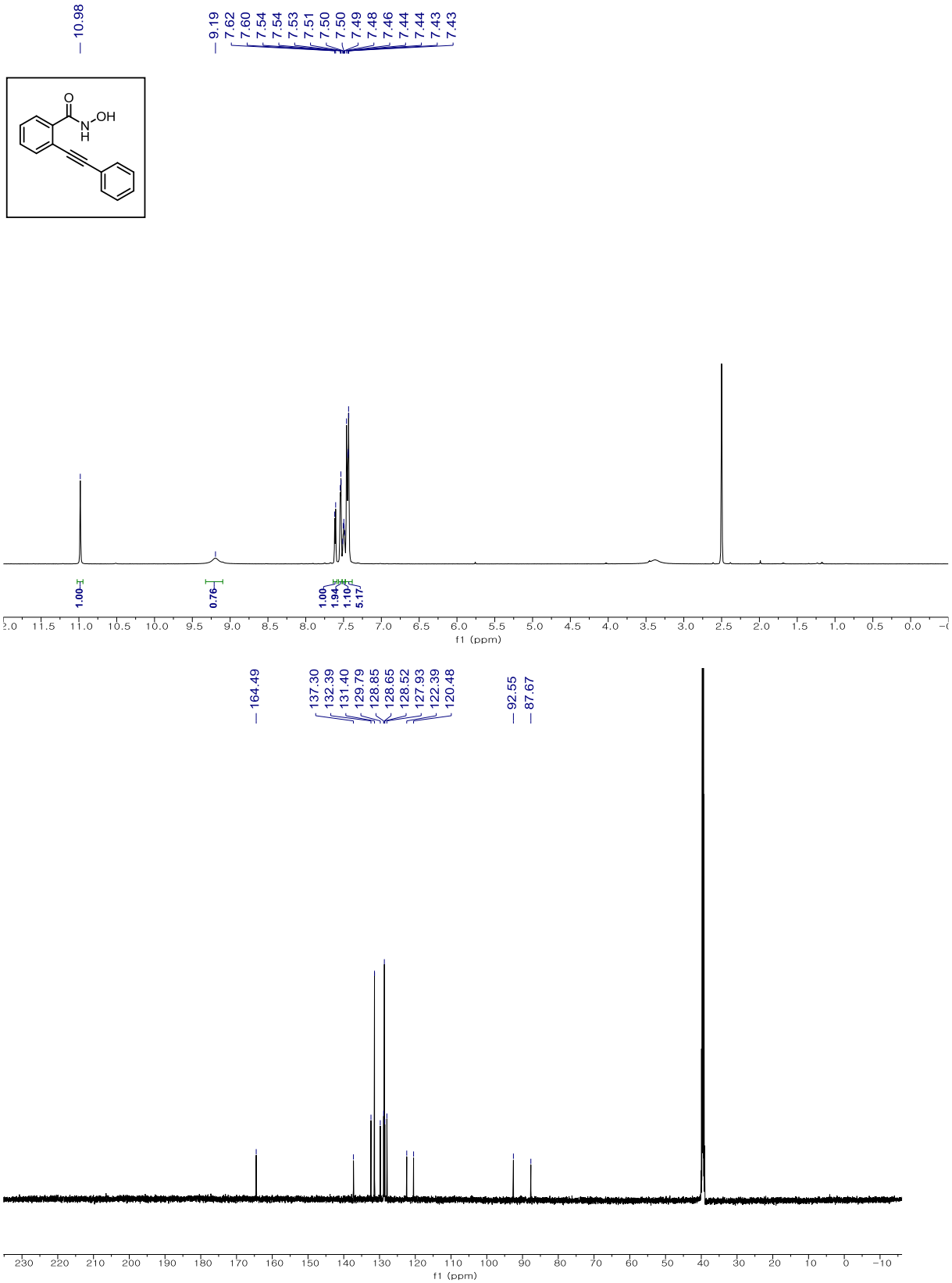
## 3-Methyl-5-phenylpent-4-ynyl hydroxamic acid



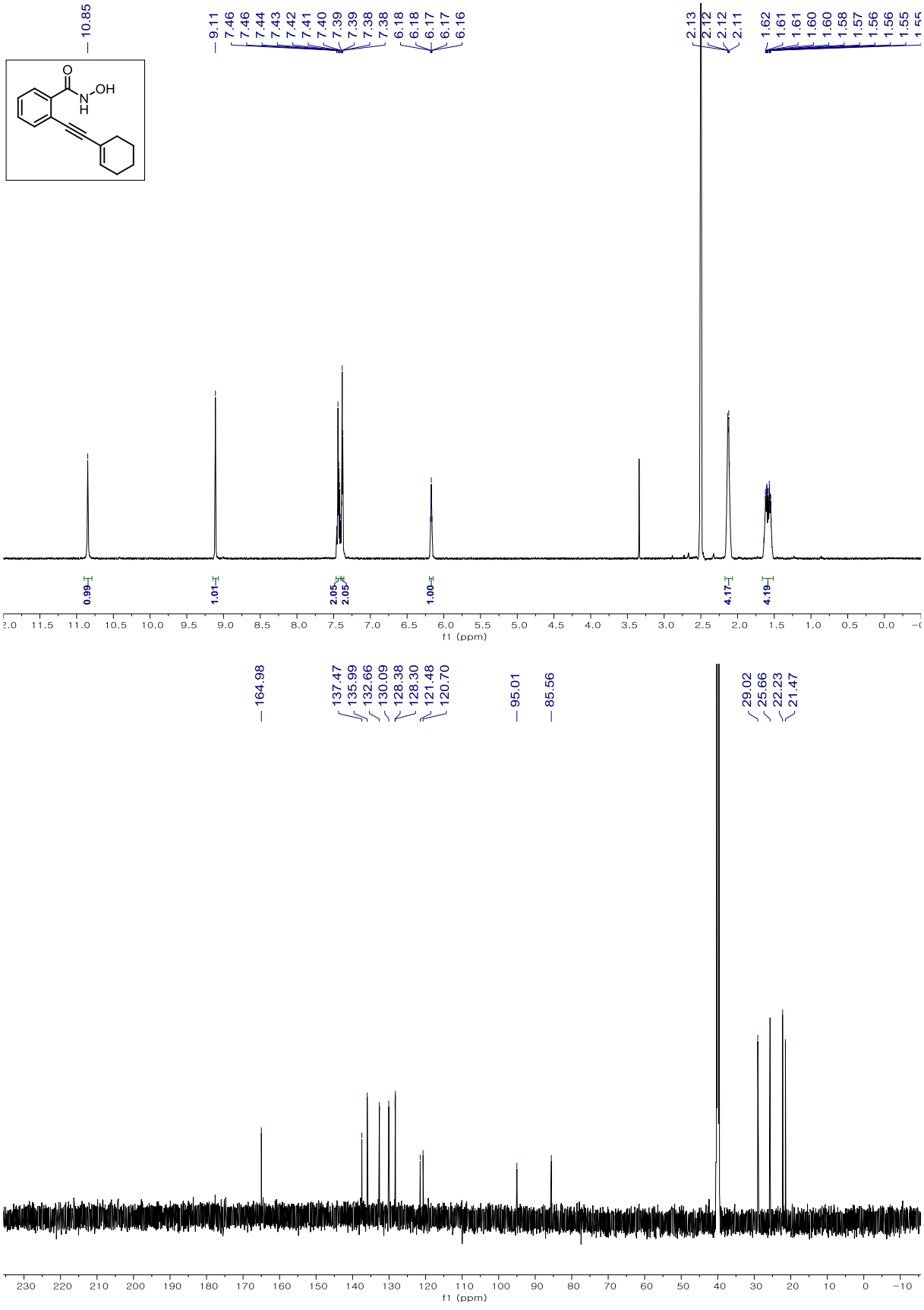
**7-Phenylhepta-4,6-diynyl hydroxamic acid**



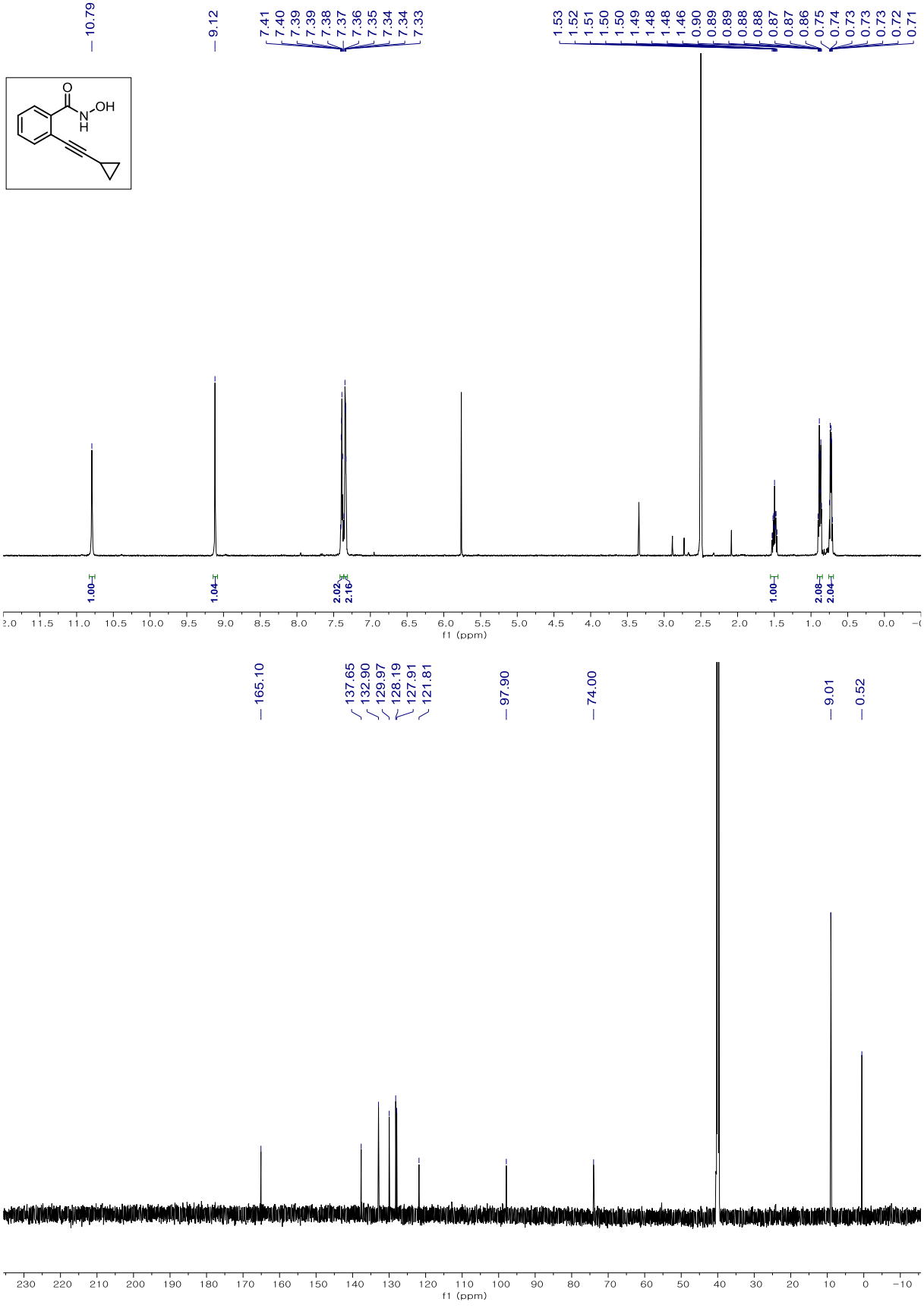
## 2-(Phenylethynyl)benzyl hydoxamic acid



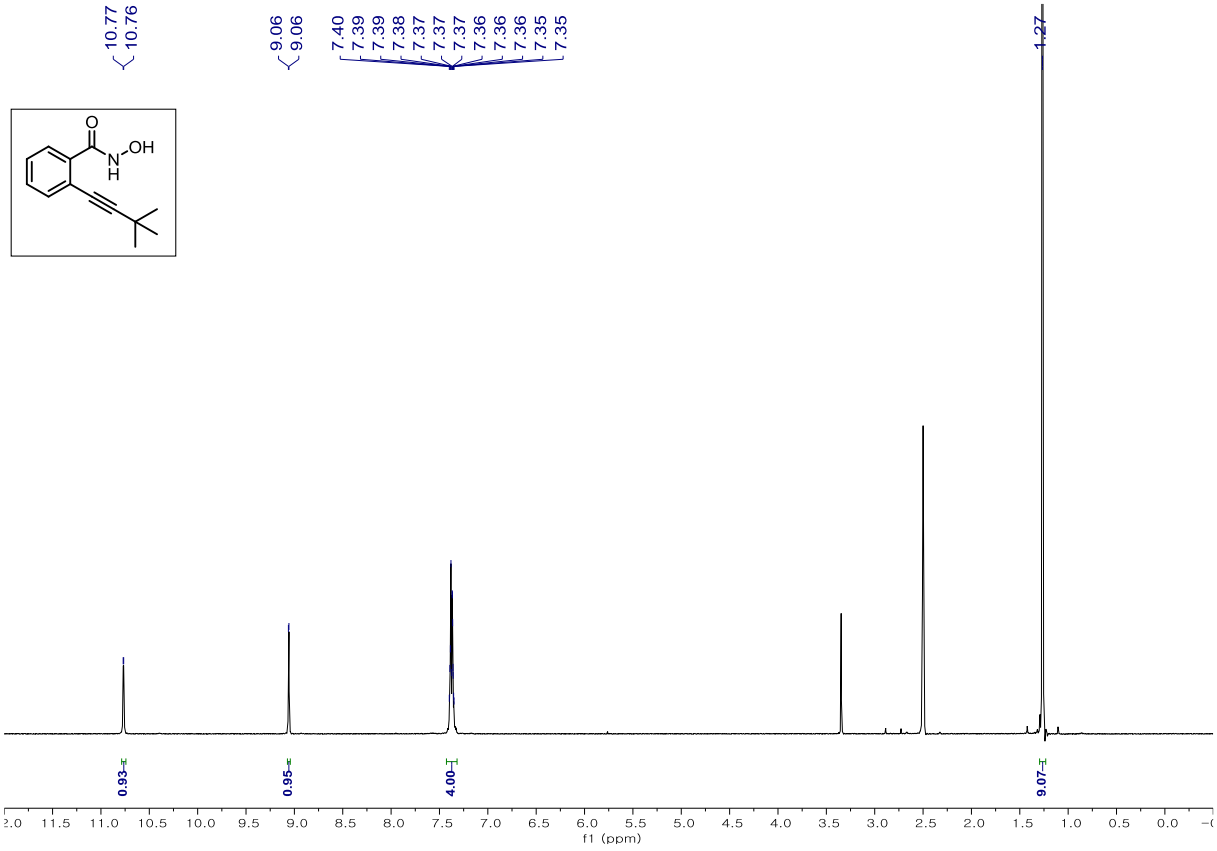
## 2-(Cyclohex-1-en-1-ylethynyl)benzyl hydroxamic acid

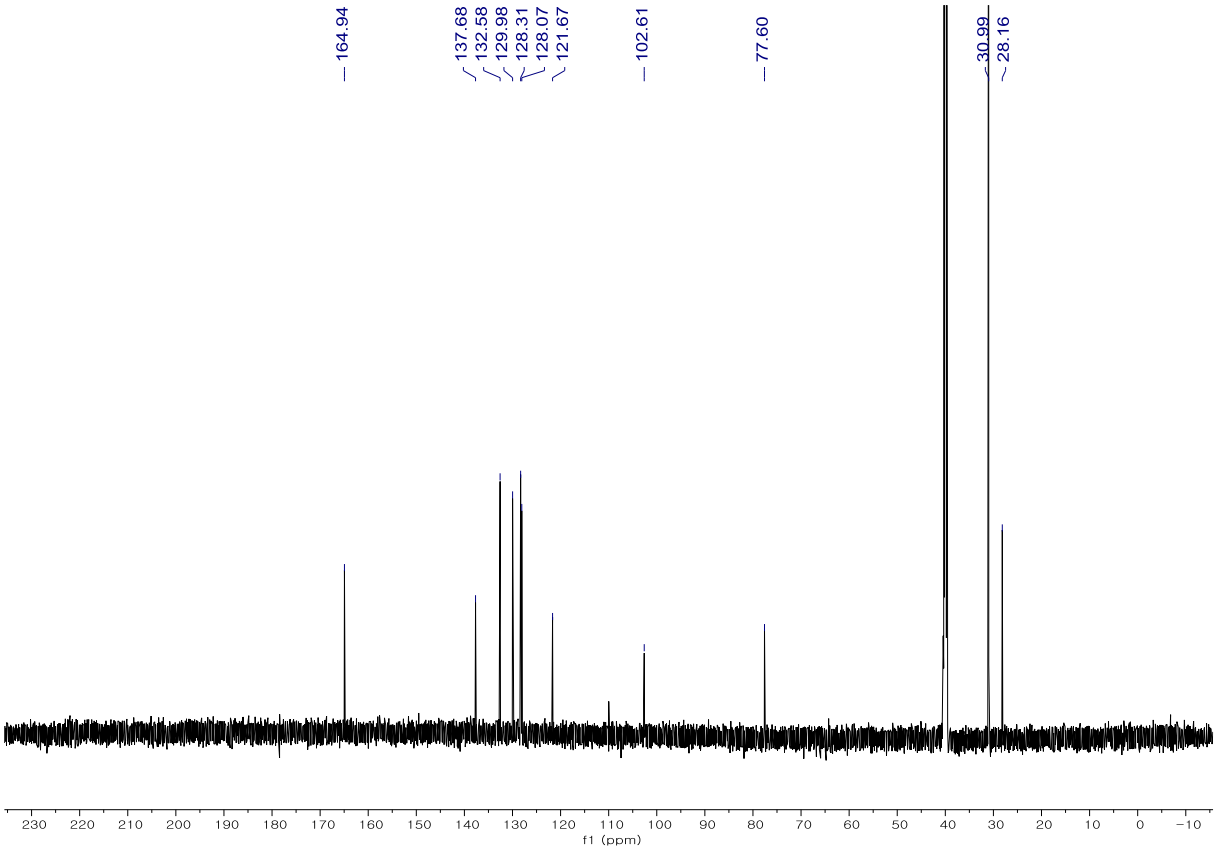


## 2-(Cyclopropylethynyl)benzyl hydroxamic acid

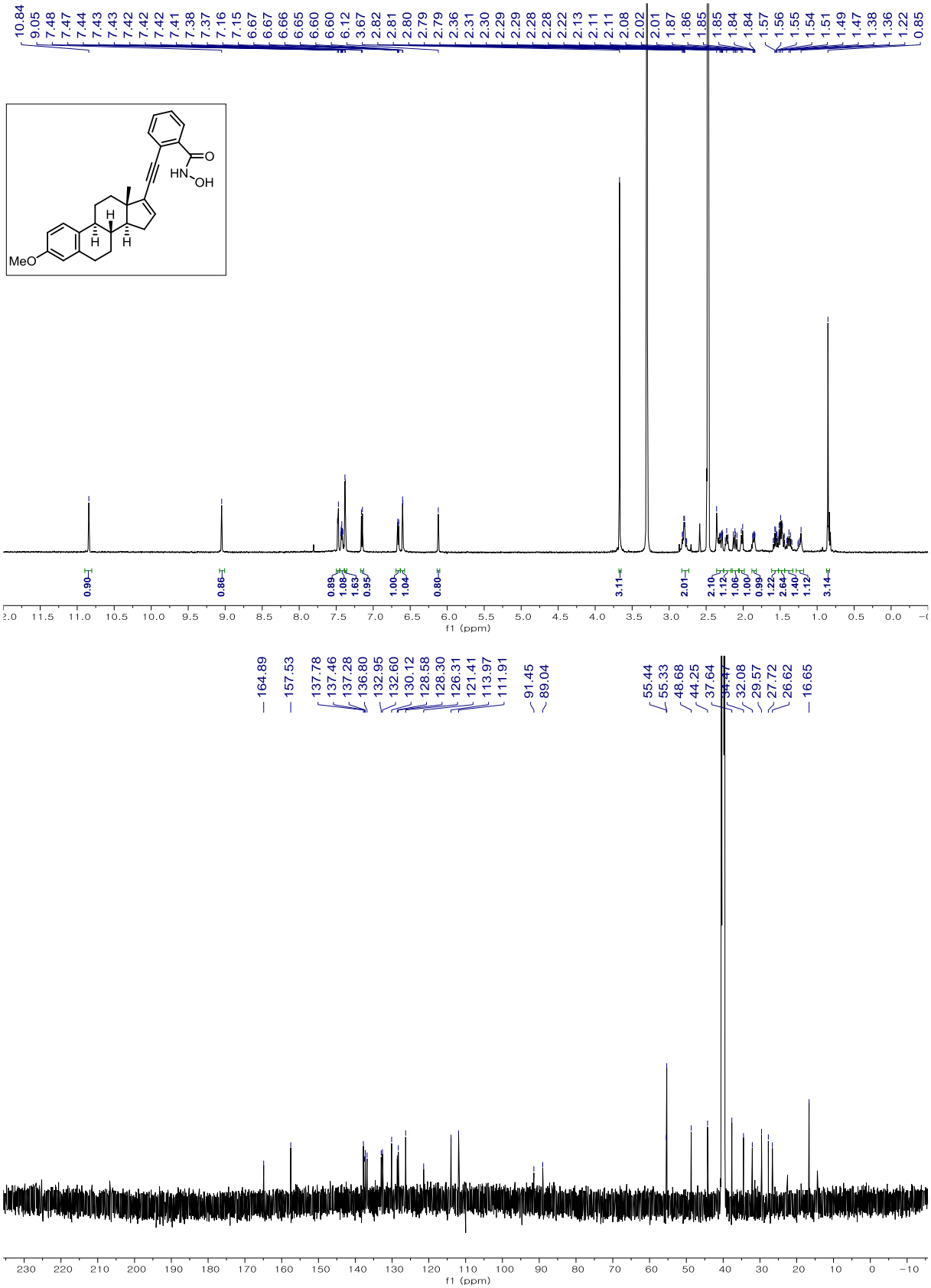


## 2-(3,3-Dimethylbut-1-yn-1-yl)benzyl hydroxamic acid

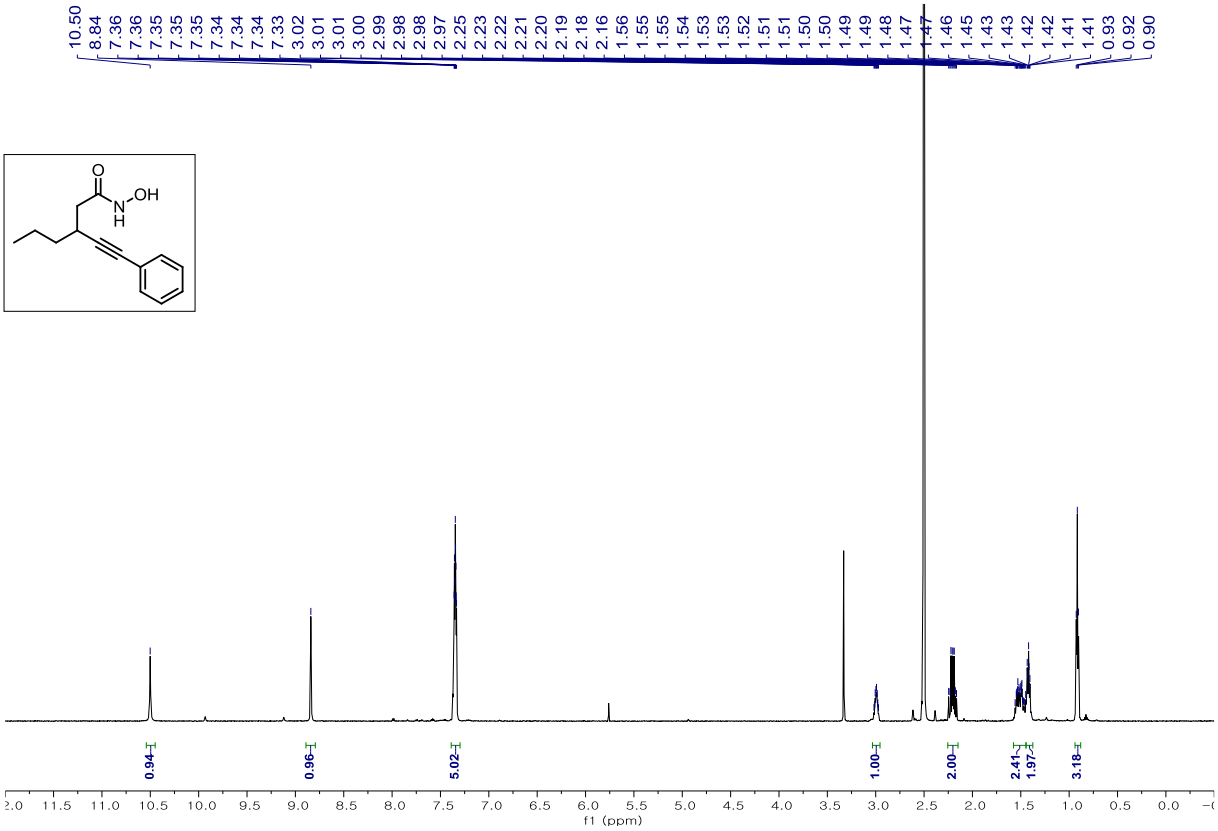


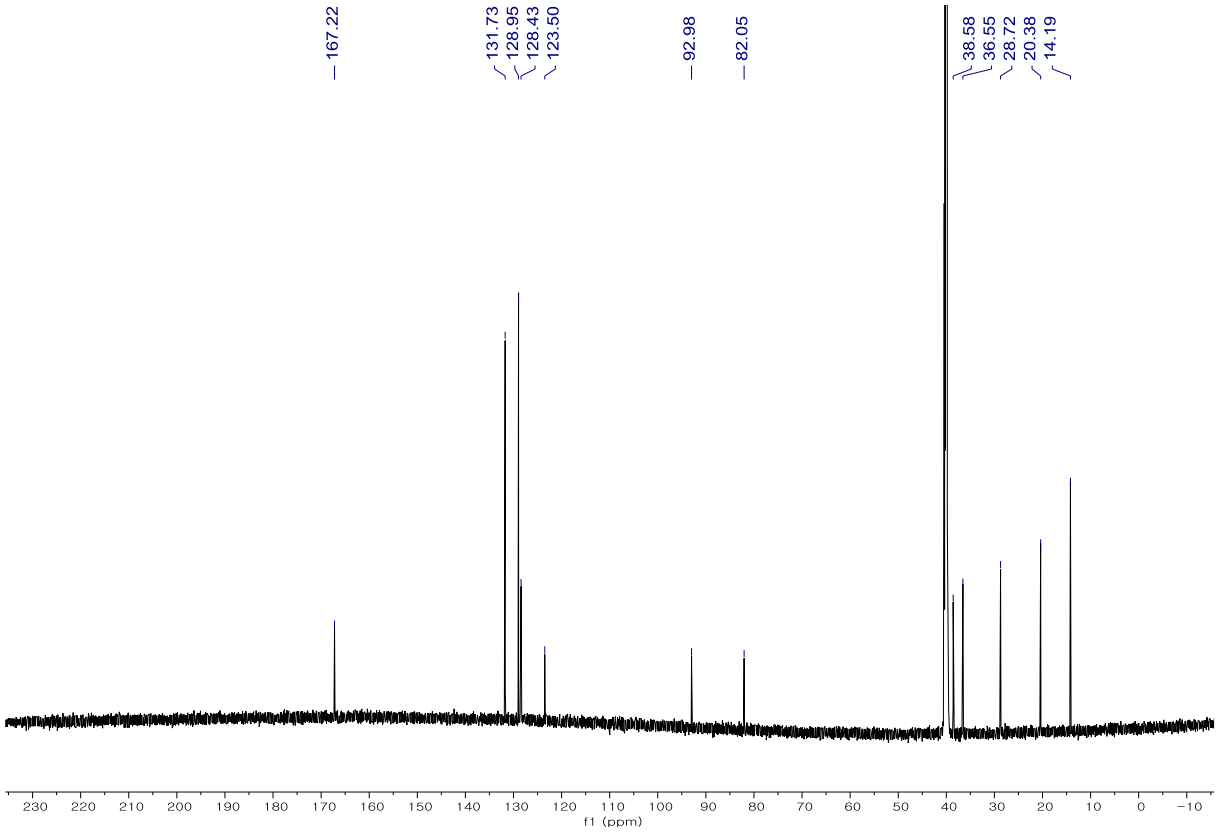



***N*-hydroxy-2-[{(8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[a]phenanthren-17-yl}ethynyl]benzamide**

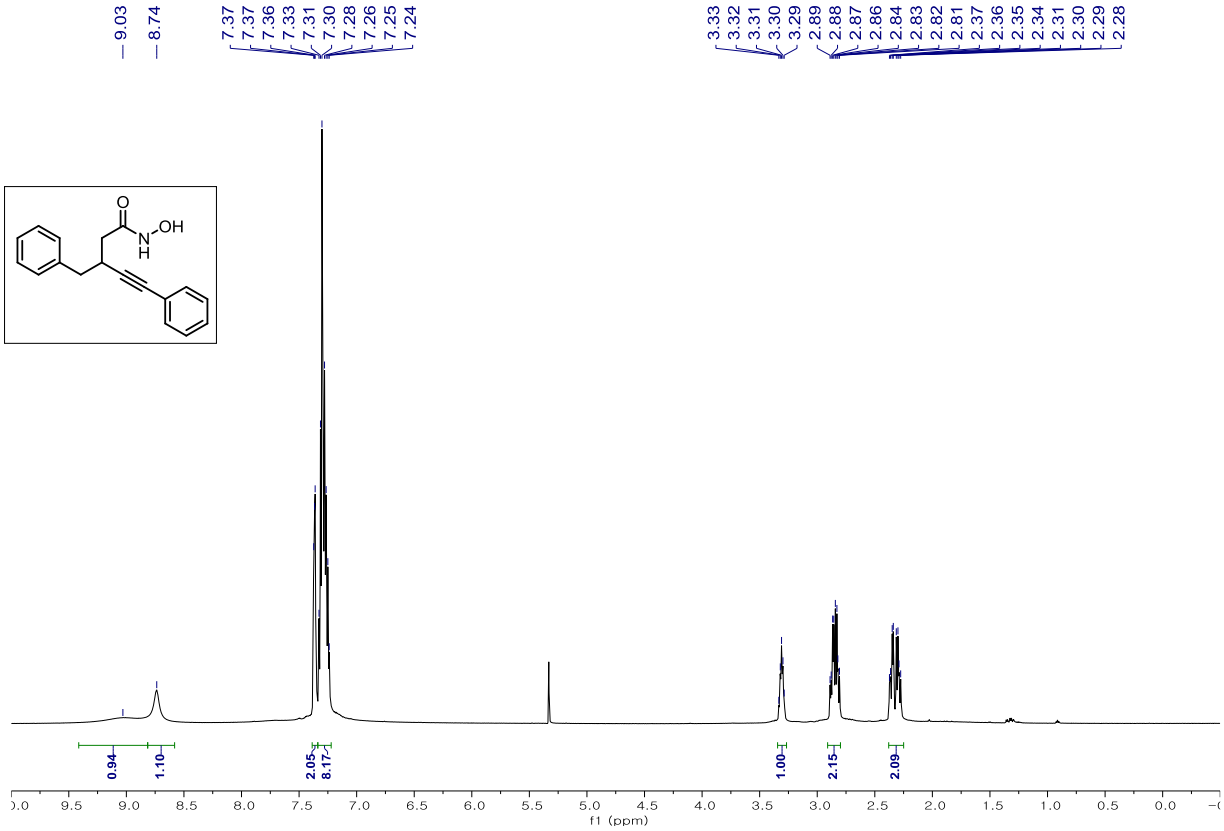


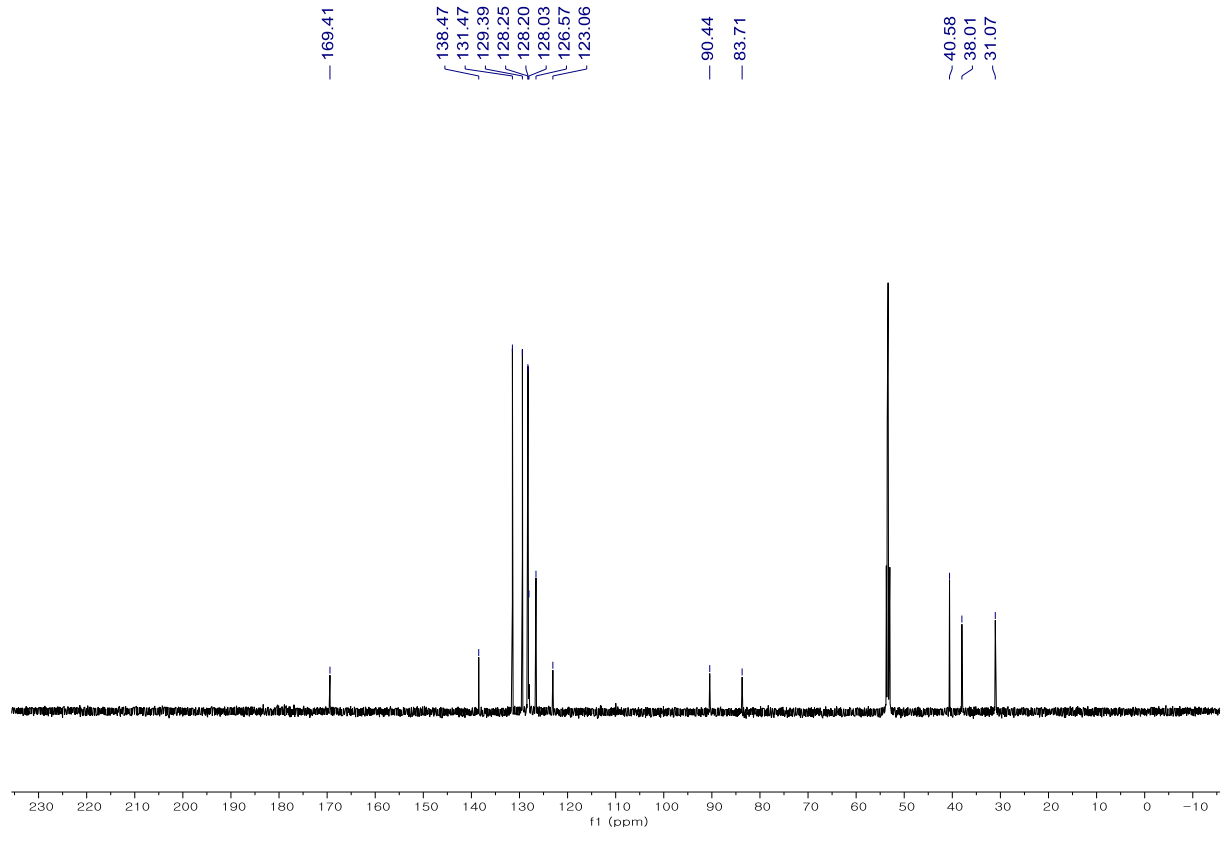
## 3-(Phenylethynyl)hexanyl hydroxamic acid



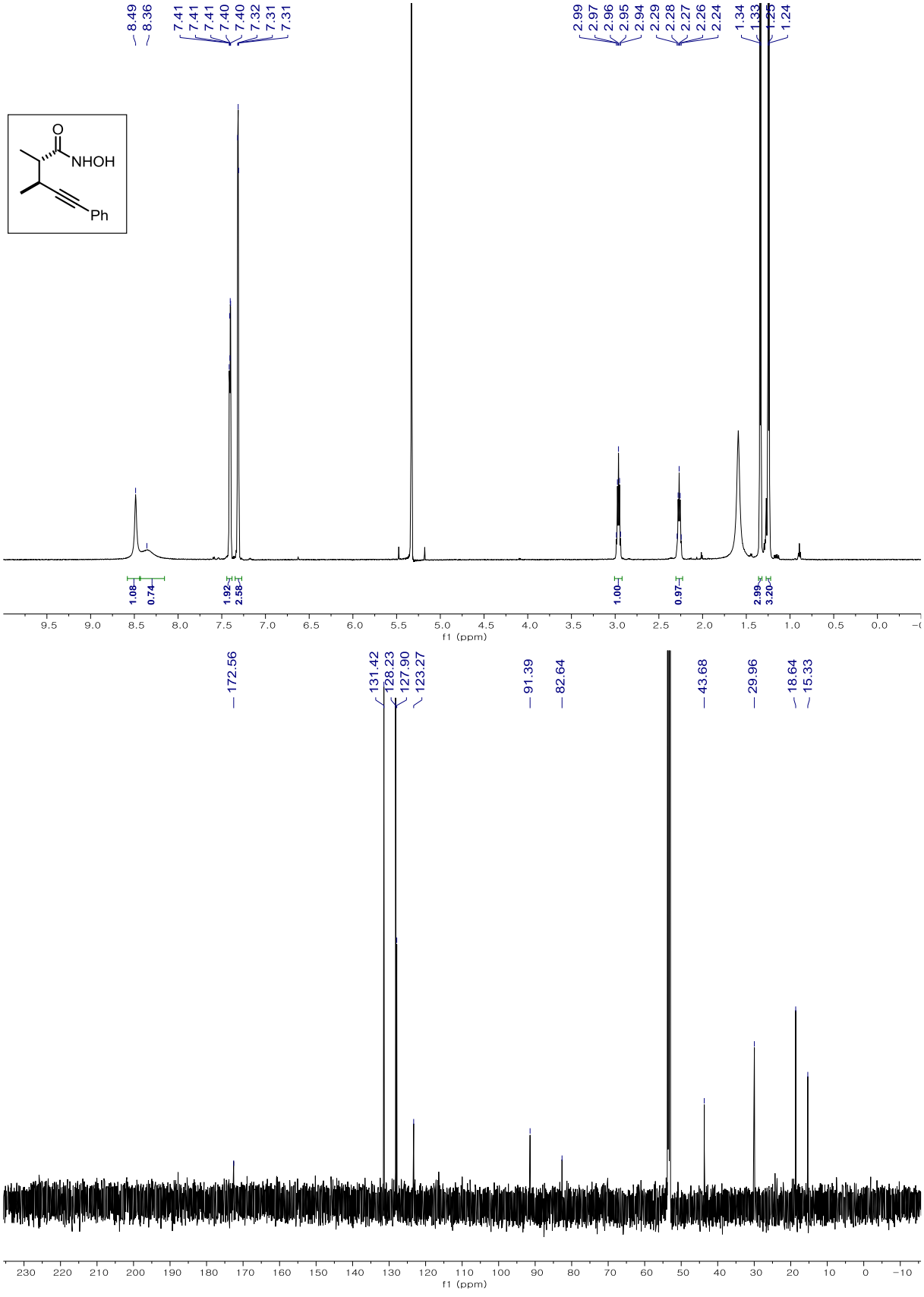



**3-Benzyl-5-phenylpent-4-ynyl hydroxamic acid**

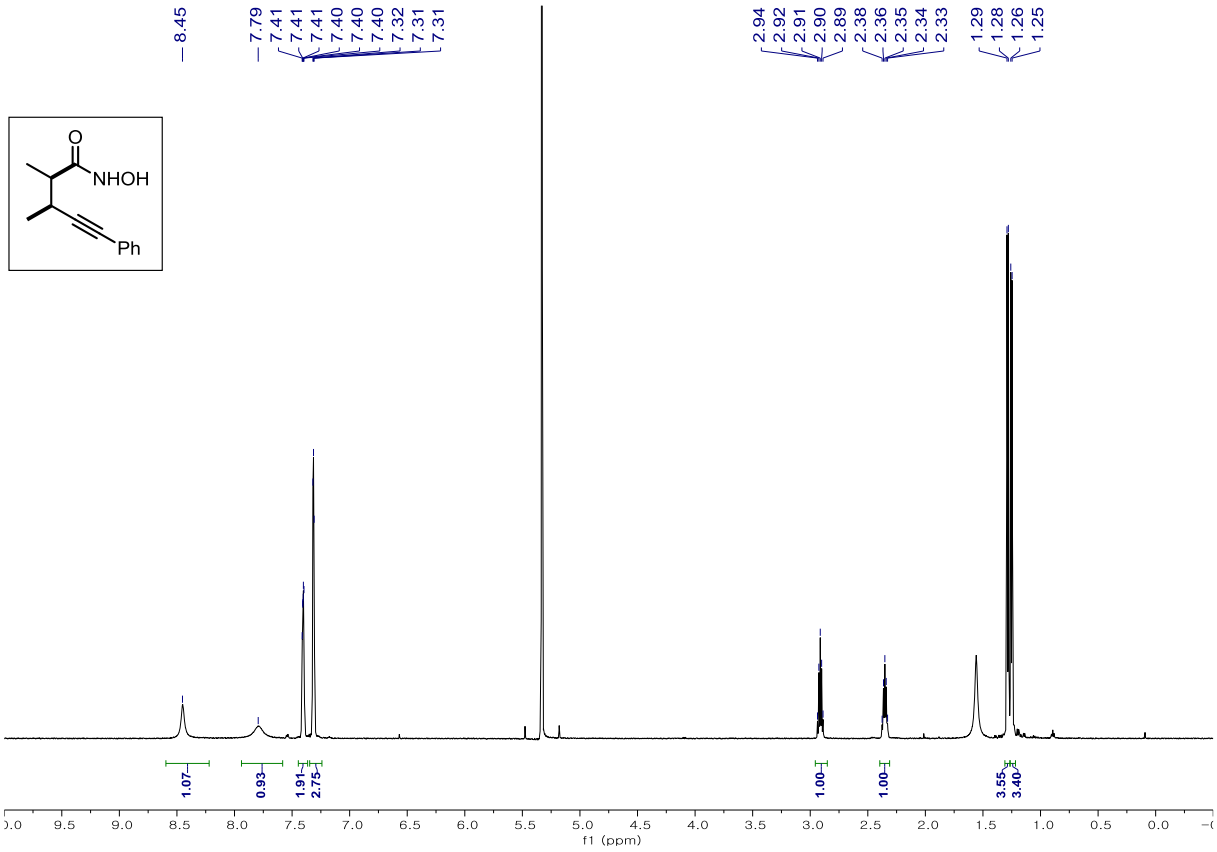


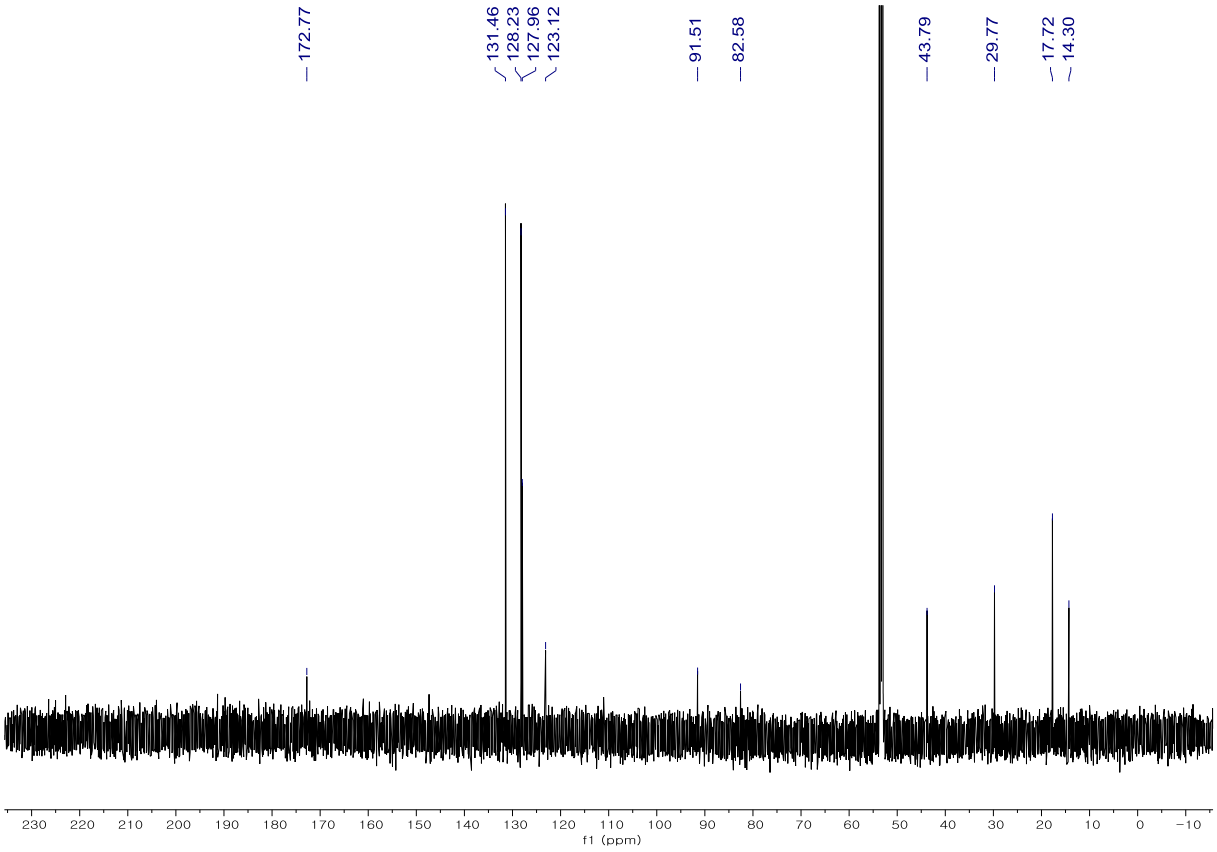



**(±)-(2,3-*anti*)-2,3-Dimethyl-5-phenylpent-4-ynyl hydroxamic acid**

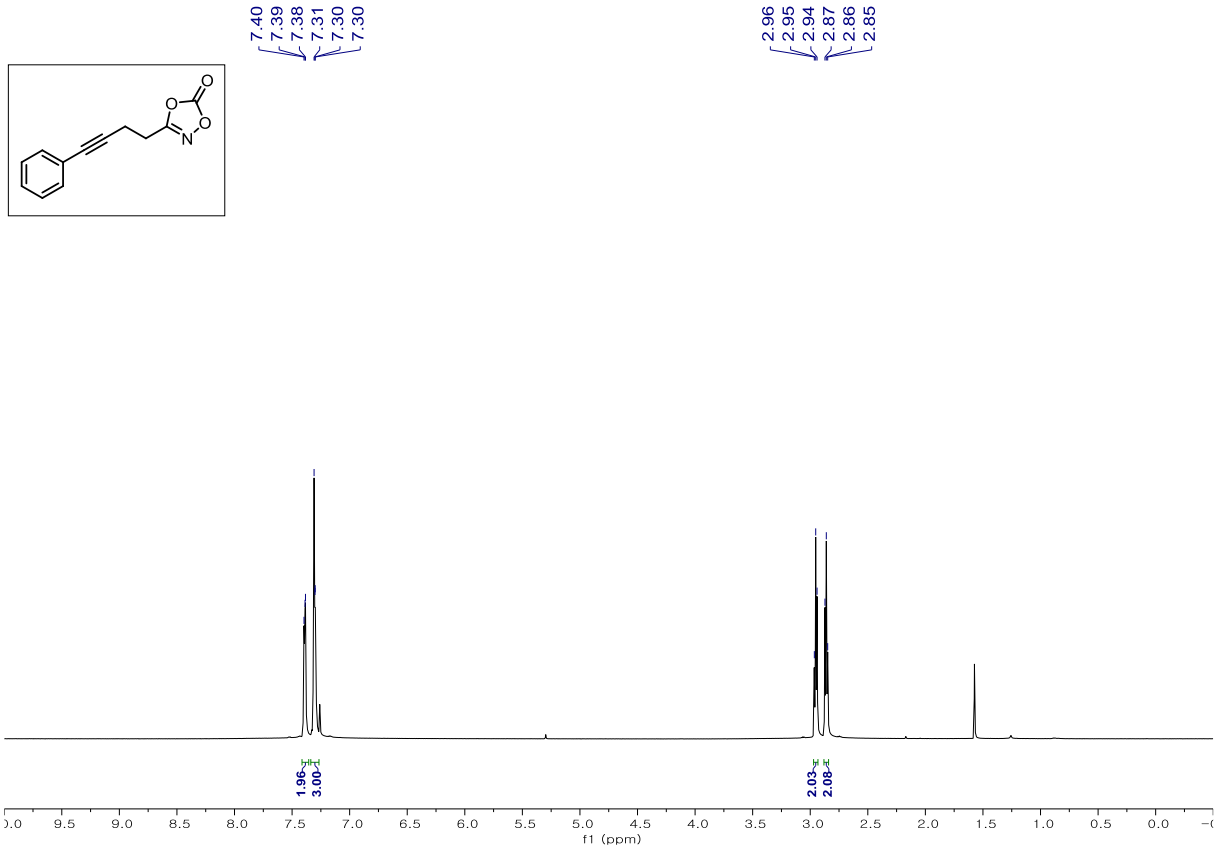


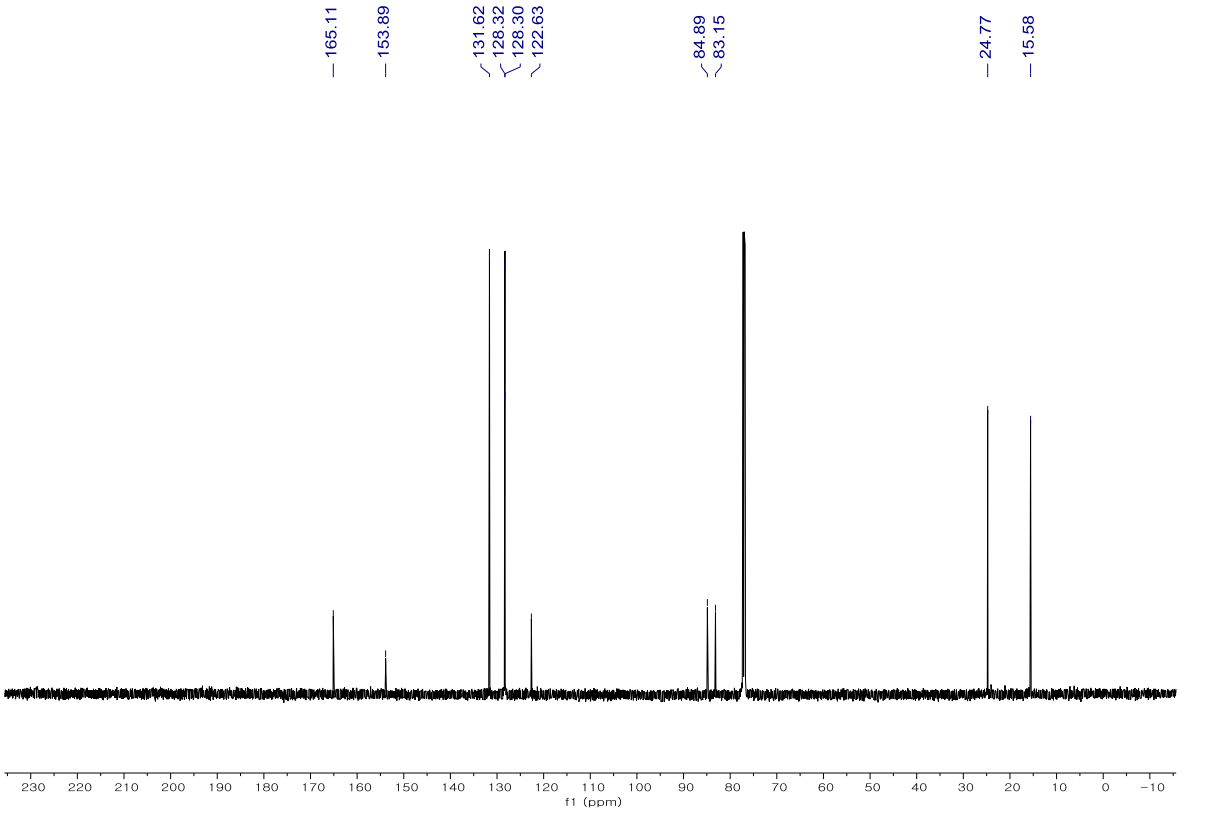
**(±)-(2,3-*syn*)-2,3-Dimethyl-5-phenylpent-4-ynyl hydroxamic acid**



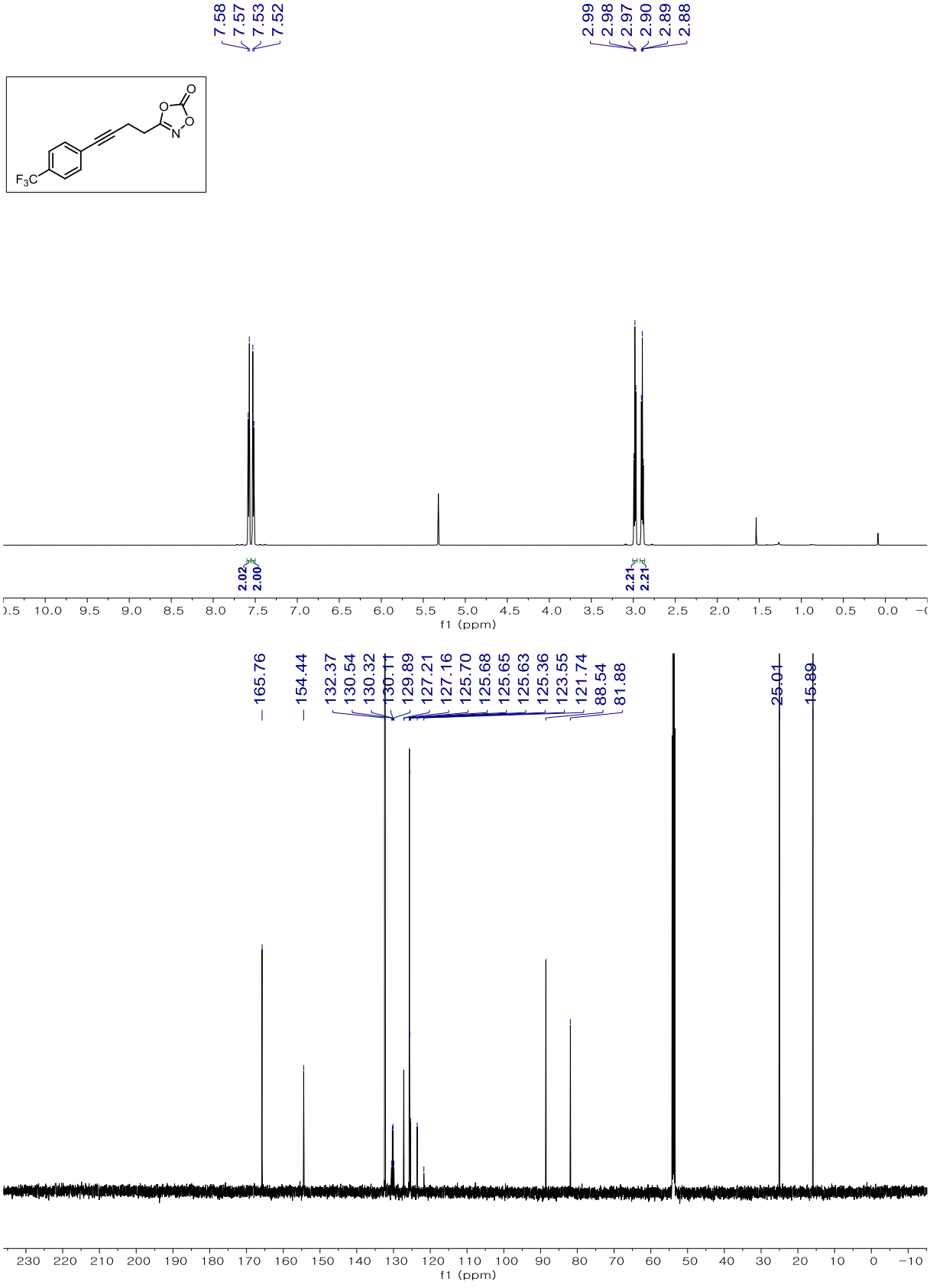



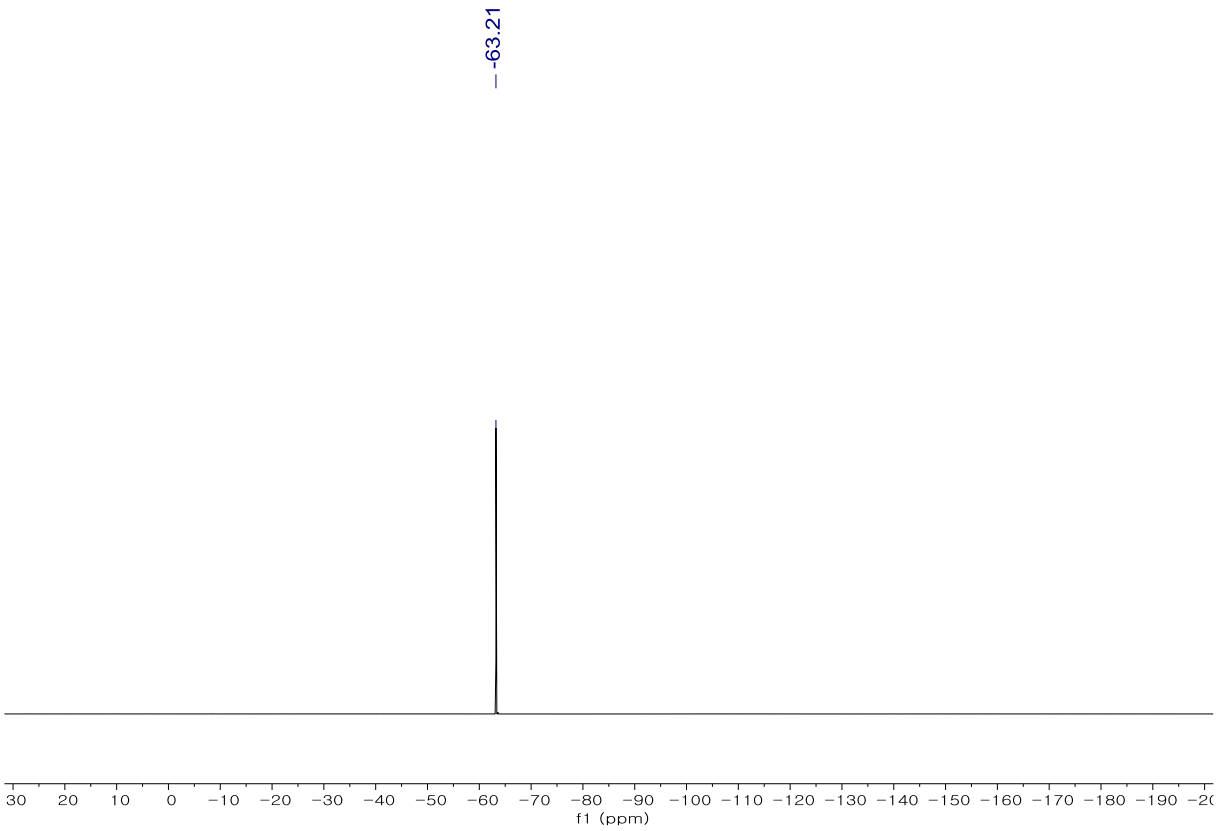
**3-(4-Phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (1, Scheme 2)**



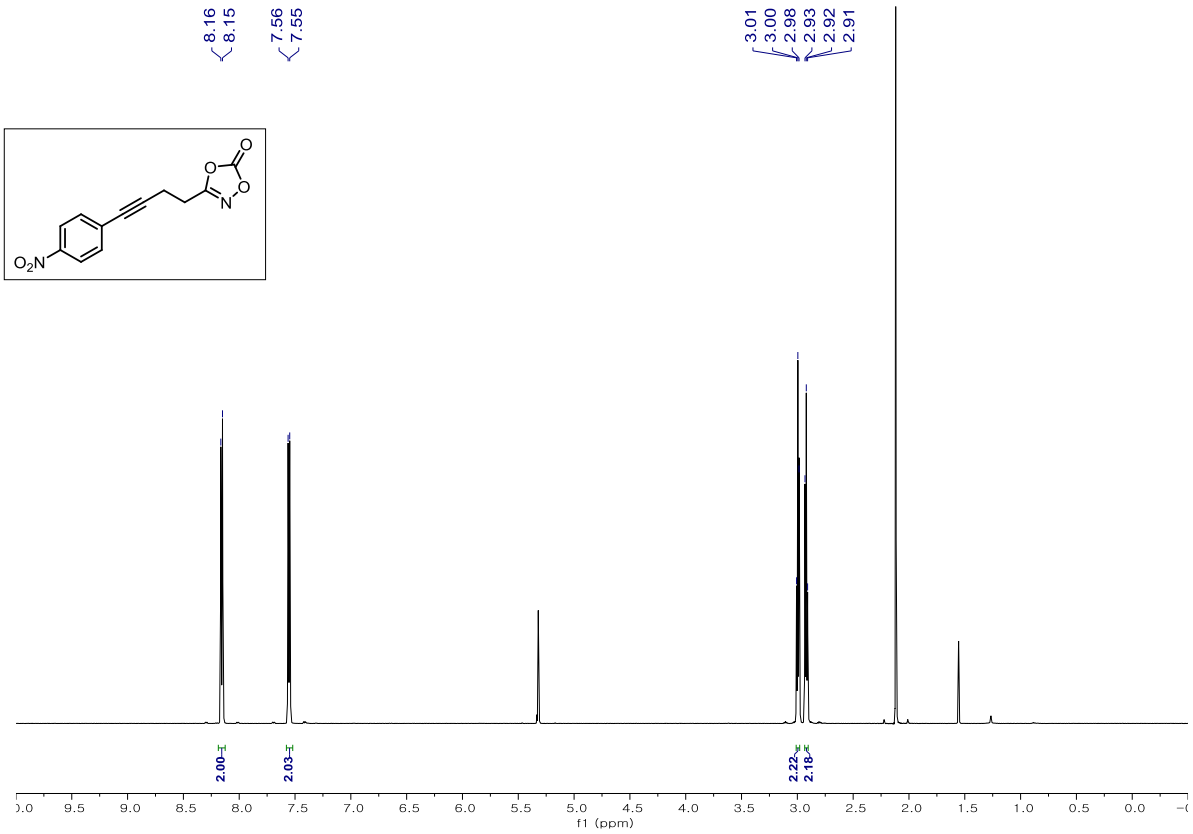



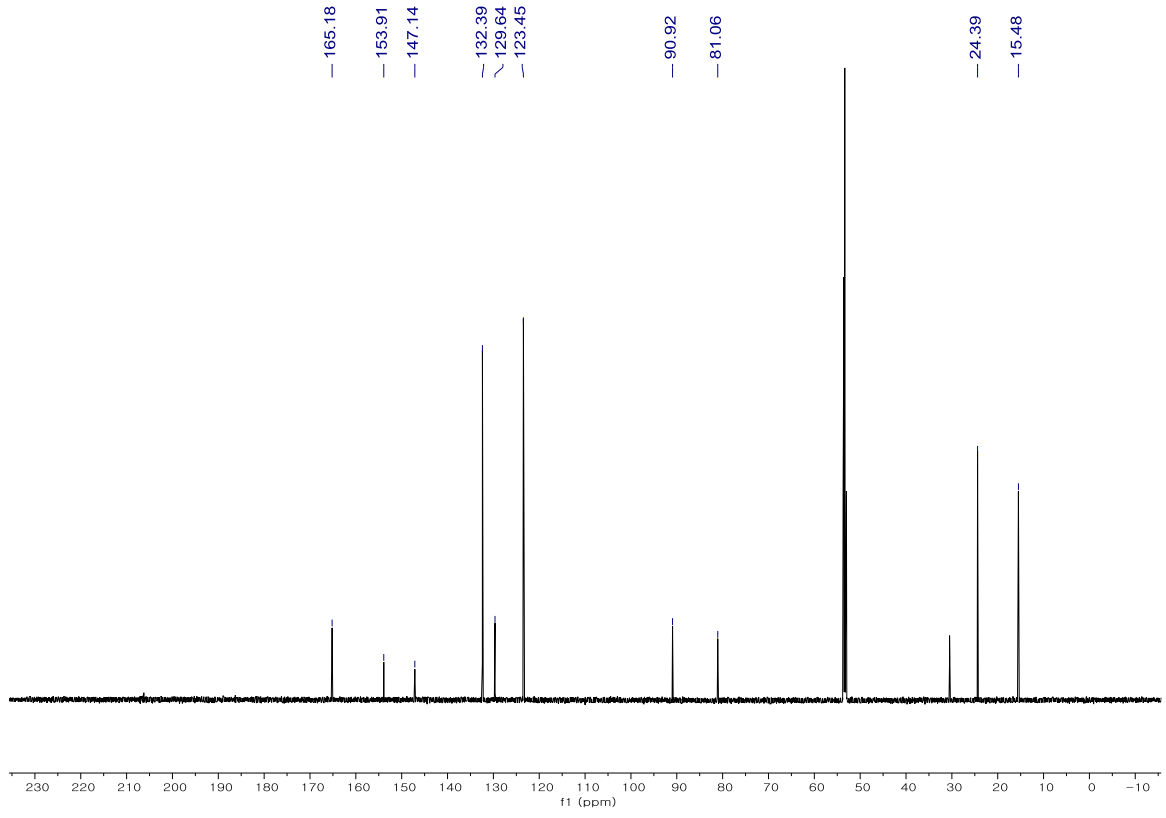
**3-[4-{4-(Trifluoromethyl)phenyl}but-3-yn-1-yl]-1,4,2-dioxazol-5-one**



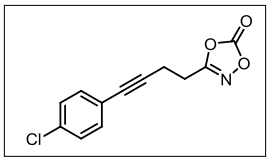

-63.21
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20
f1 (ppm)

**3-{4-(4-Nitrophenyl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



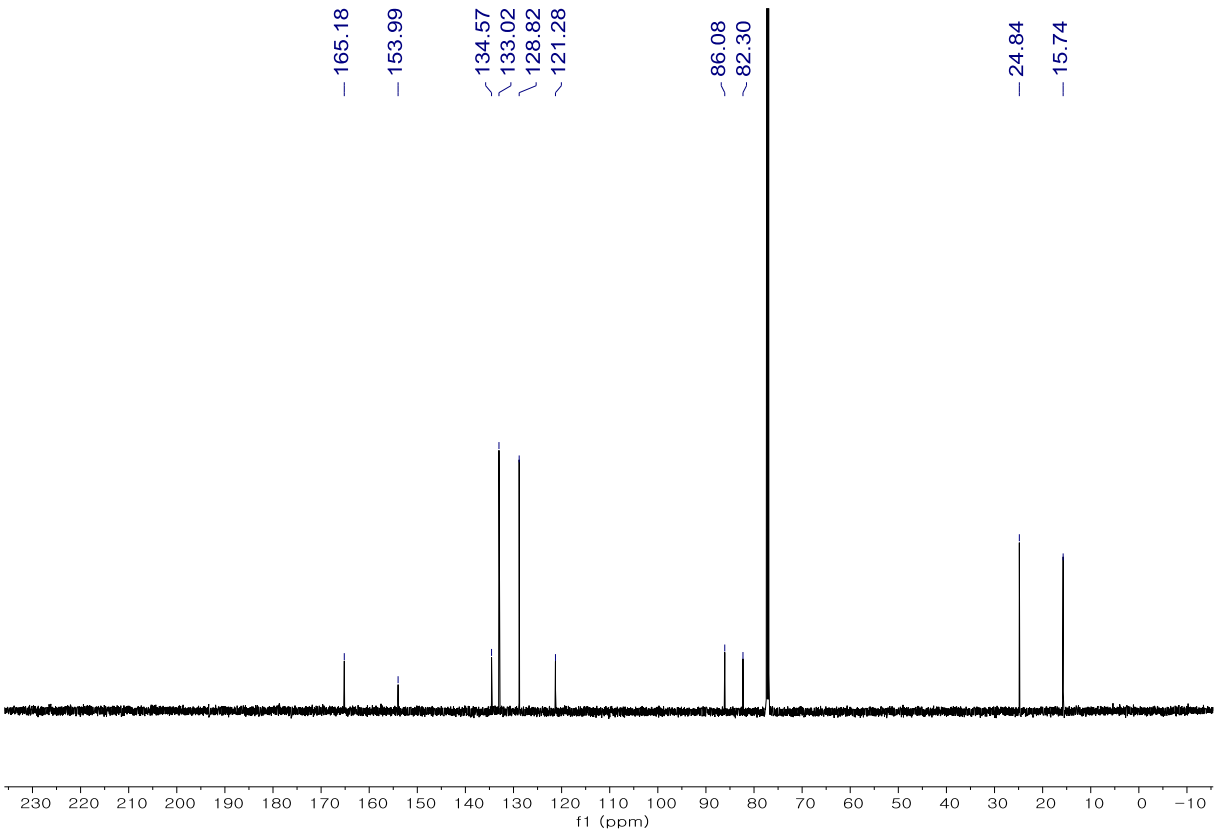



**3-{4-(4-Chlorophenyl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**

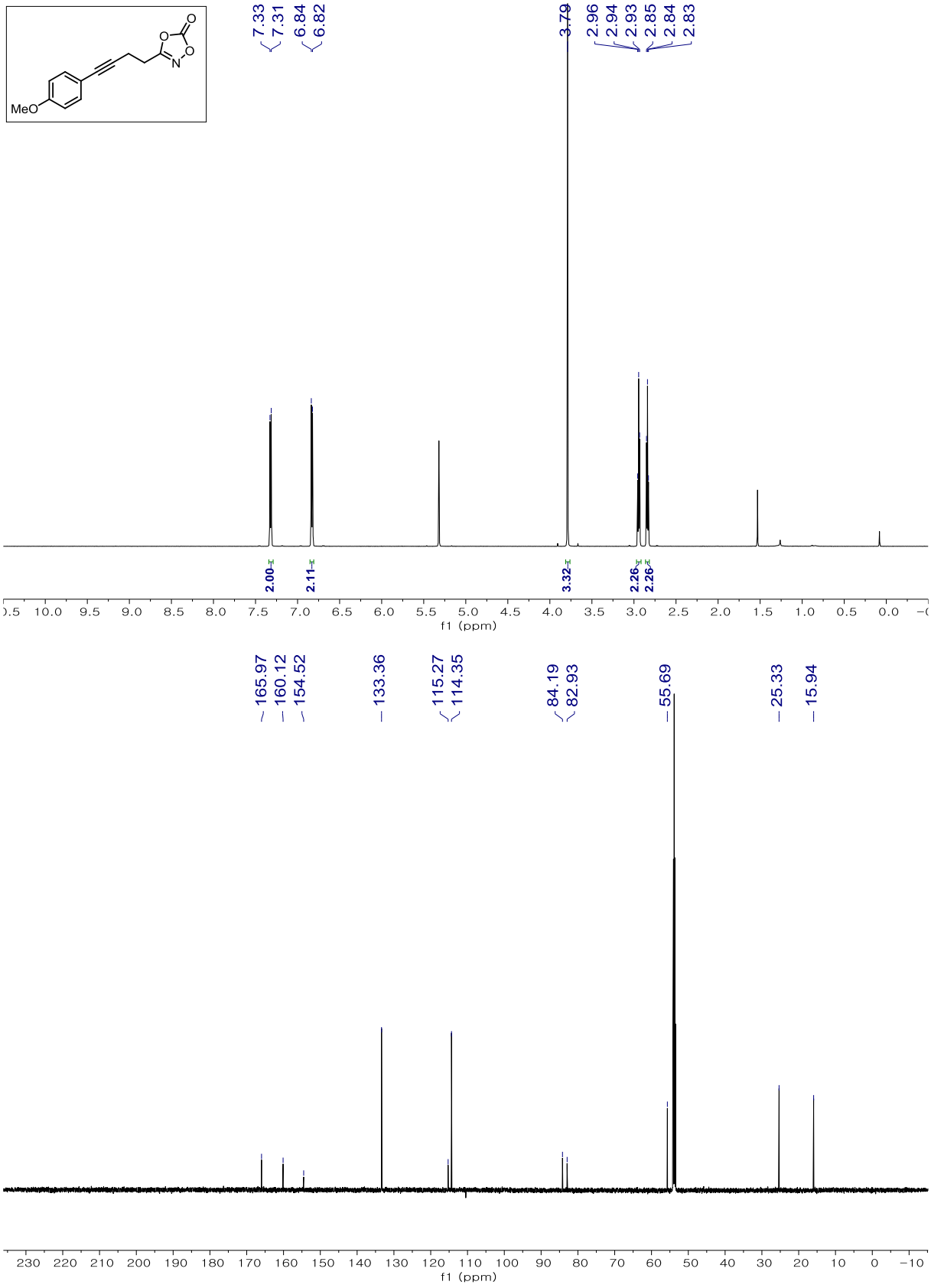




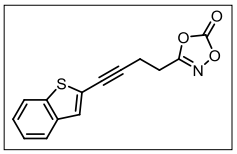




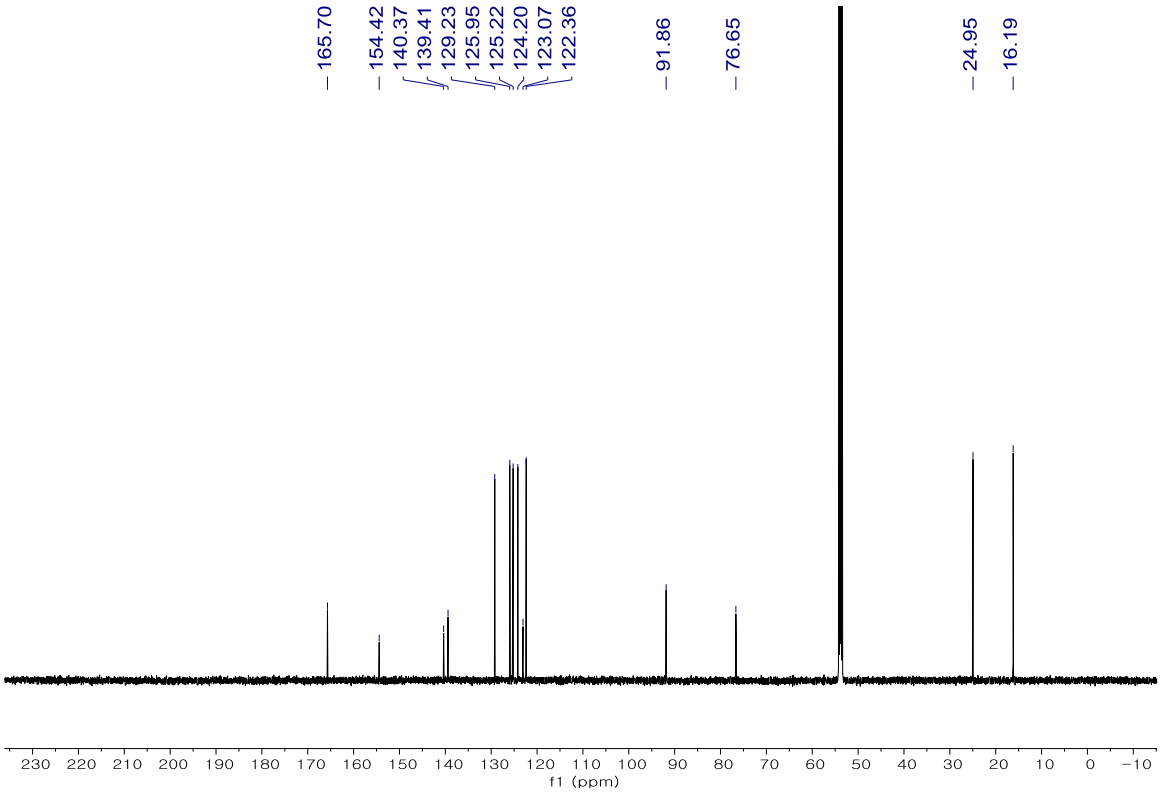
**3-{4-(4-Methoxyphenyl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



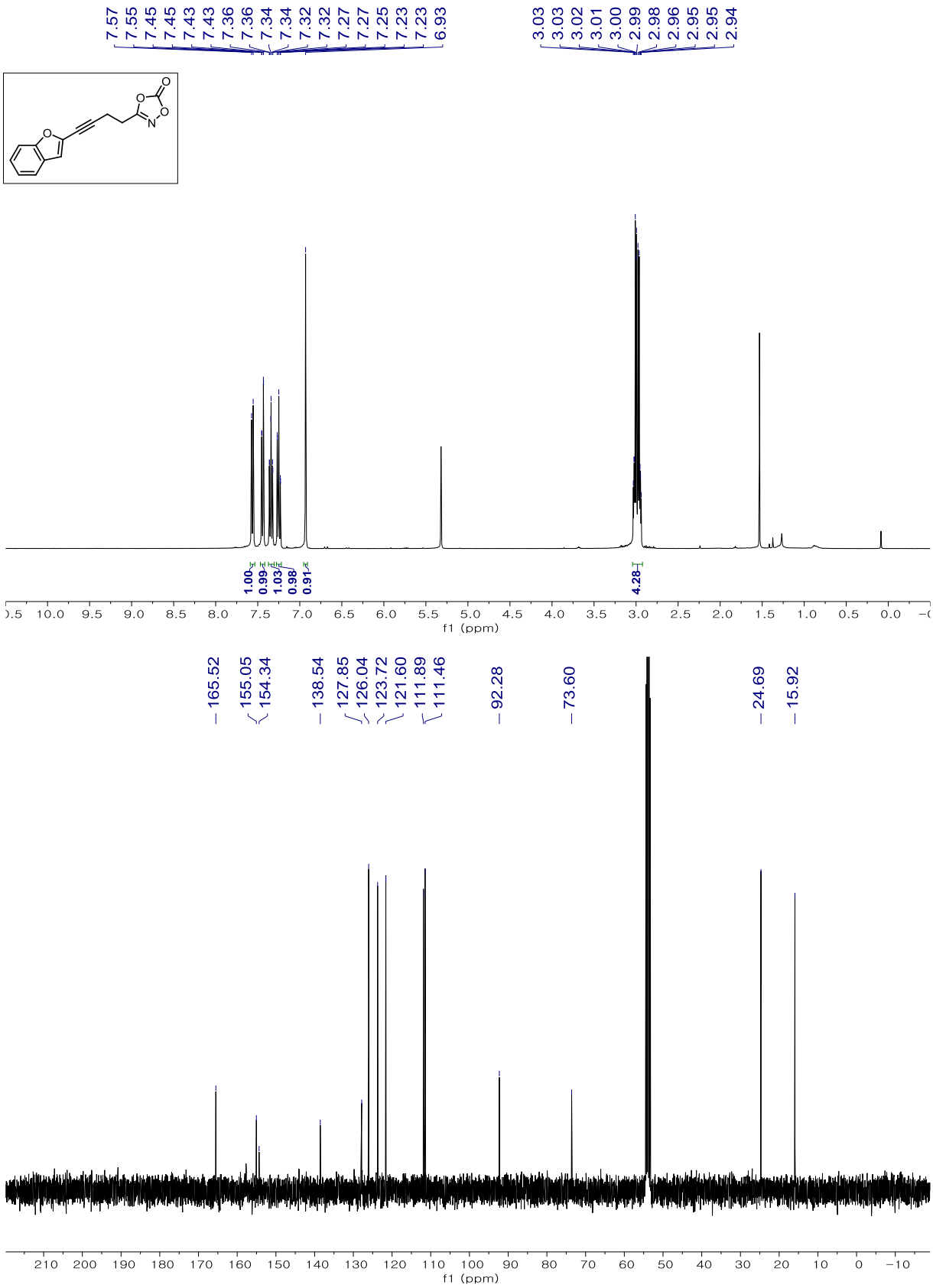
**3-{4-(Benzo[*b*]thiophen-2-yl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



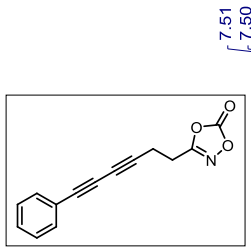


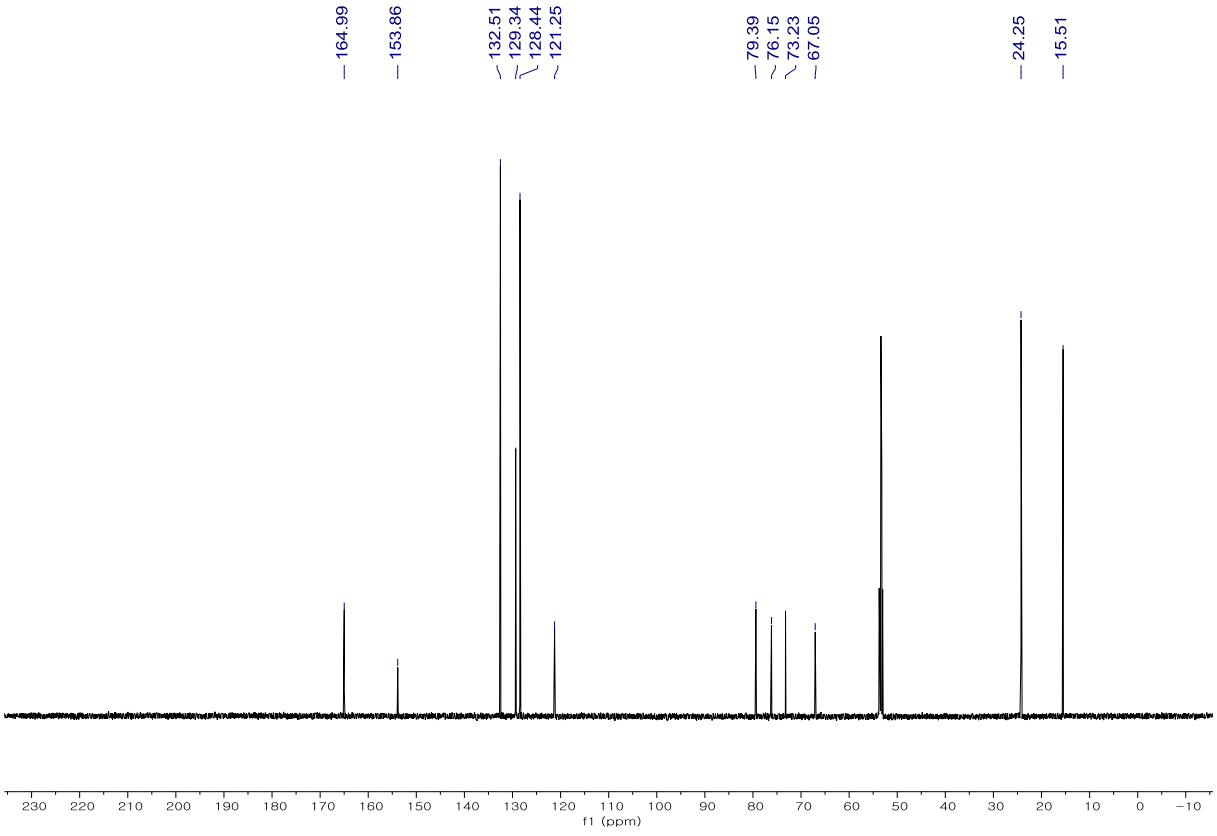
**3-{4-(Benzofuran-2-yl)but-3-yn-1-yl}-1,4,2-dioxazol-5-one**



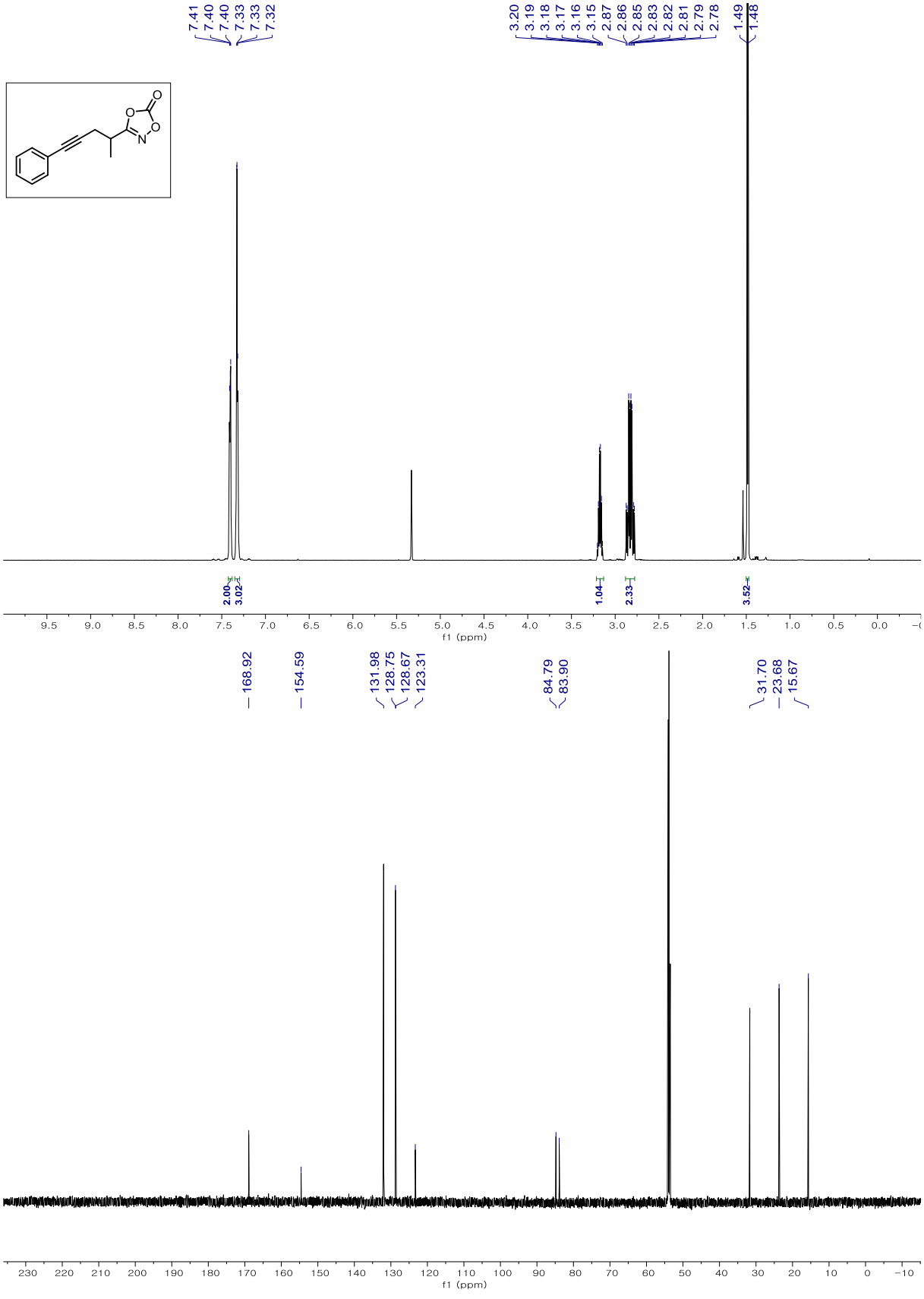
**3-(6-Phenylhexa-3,5-diyn-1-yl)-1,4,2-dioxazol-5-one**



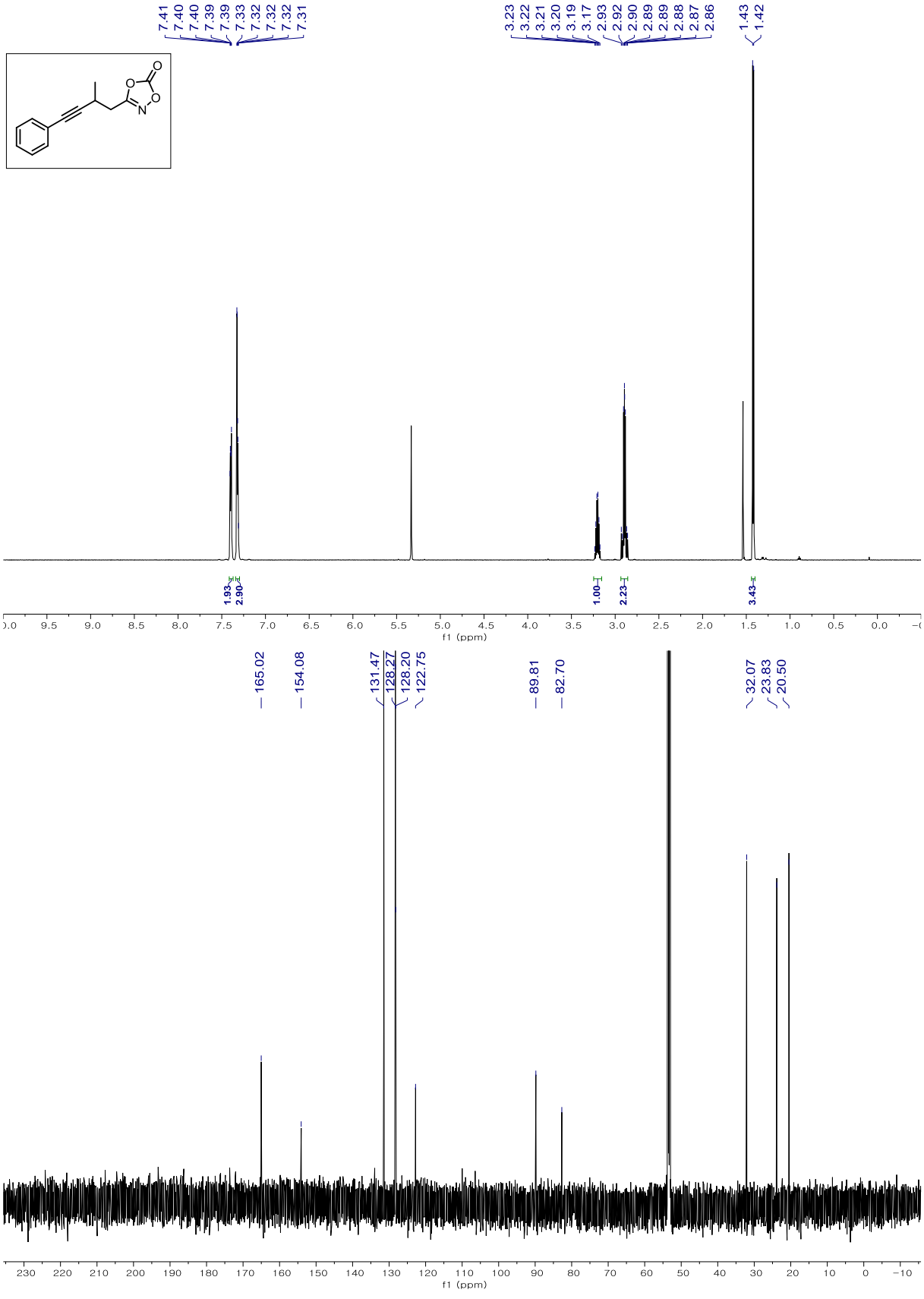


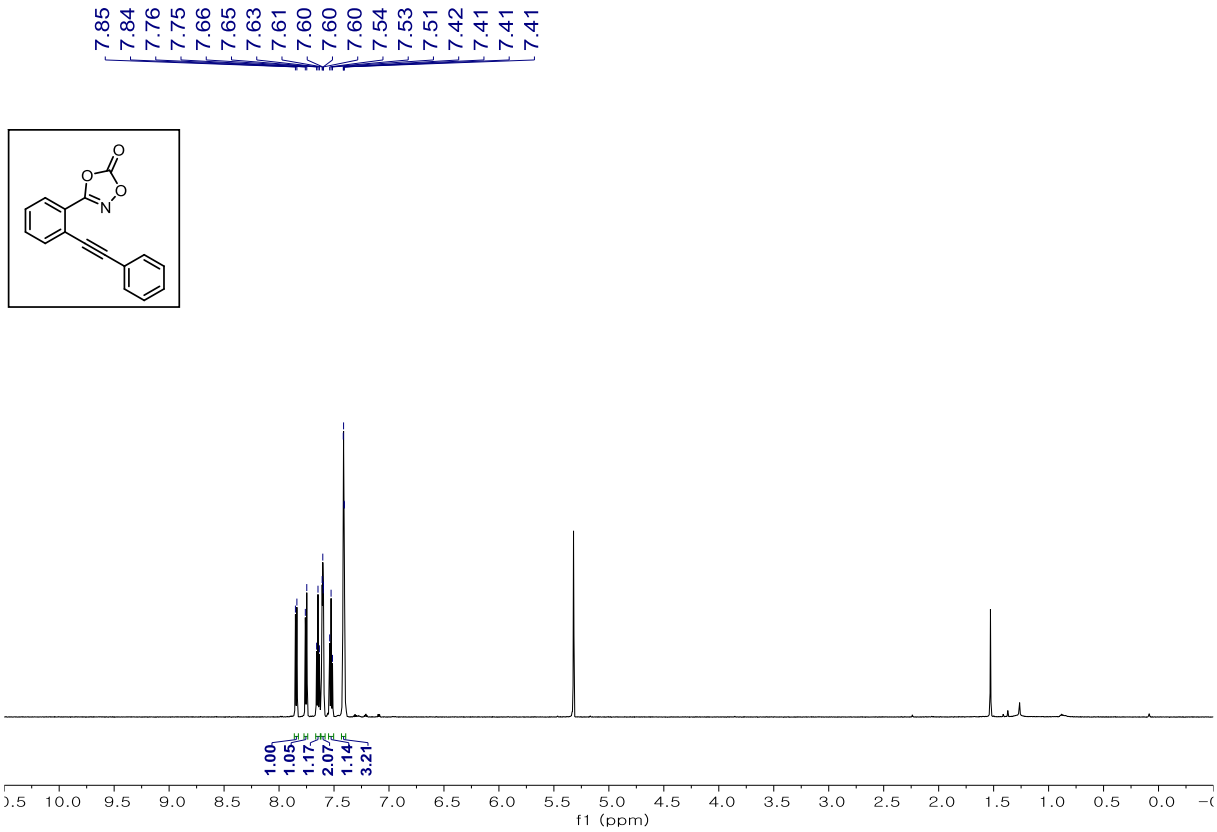
**3-(5-Phenylpent-4-yn-2-yl)-1,4,2-dioxazol-5-one**

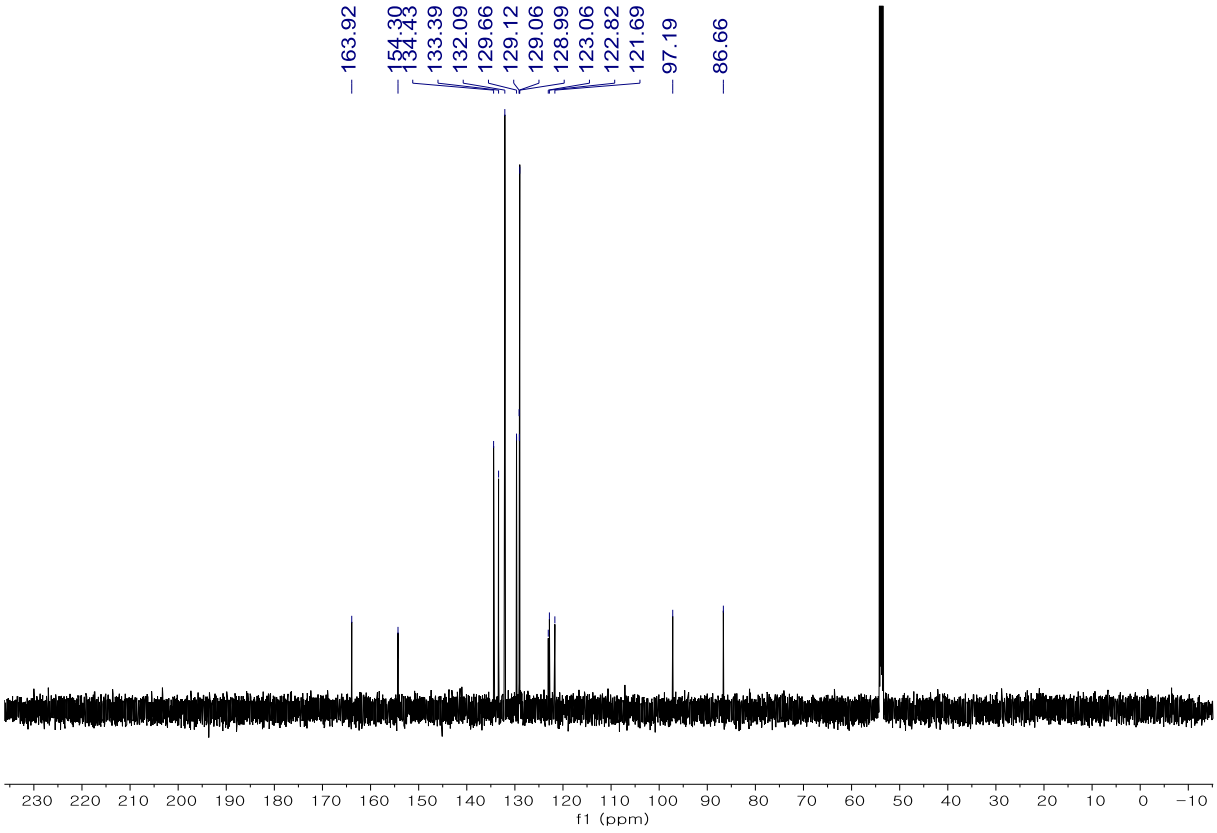


**3-(2-Methyl-4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (25, equation 1)**

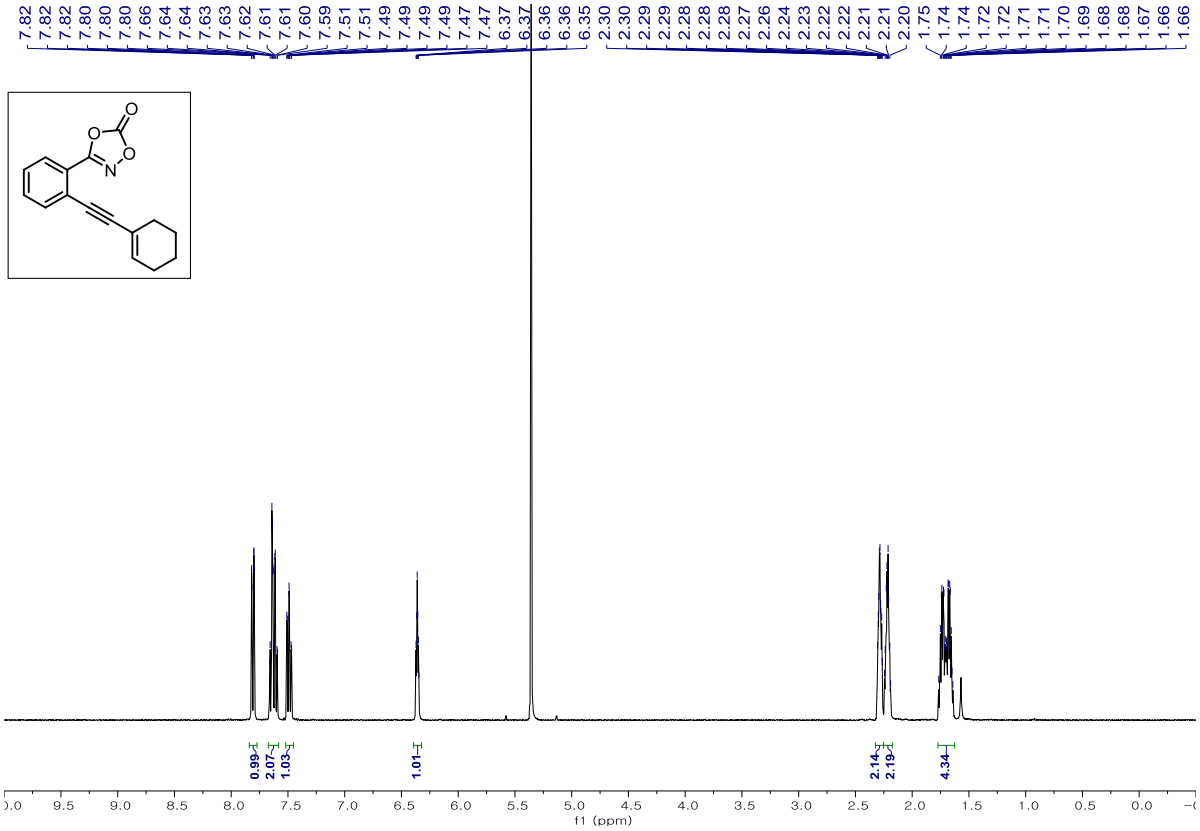


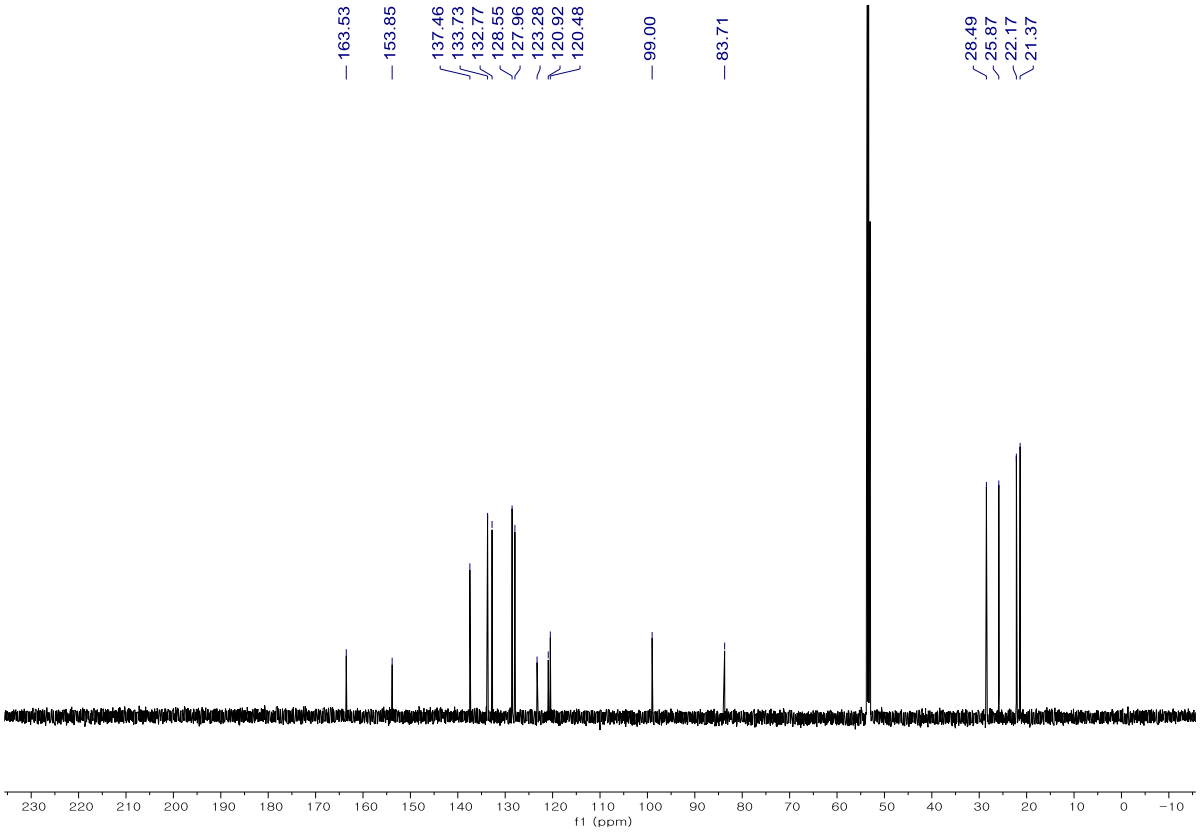
**3-{2-(Phenylethynyl)phenyl}-1,4,2-dioxazol-5-one (28, equation 2)**



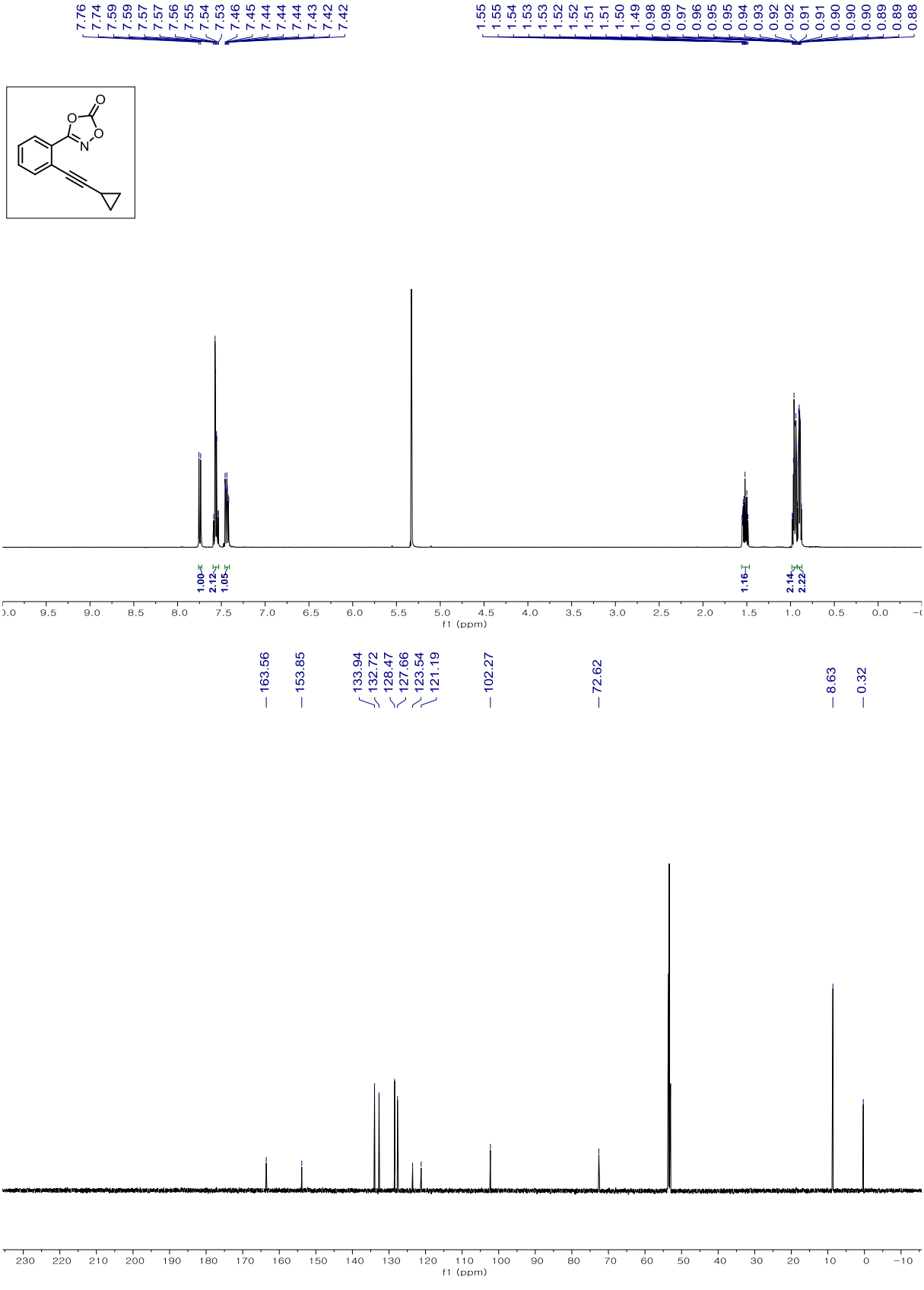



**3-{2-(Cyclohex-1-en-1-ylethynyl)phenyl}-1,4,2-dioxazol-5-one**

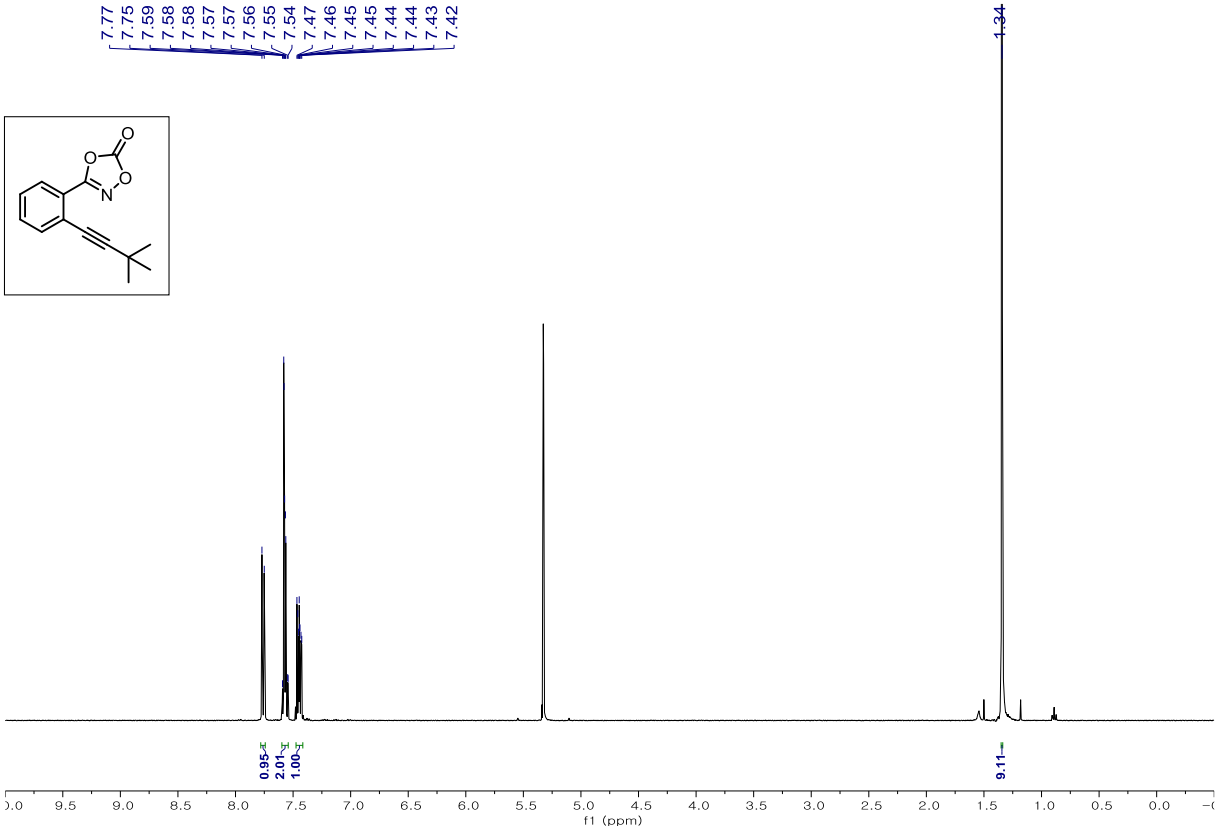


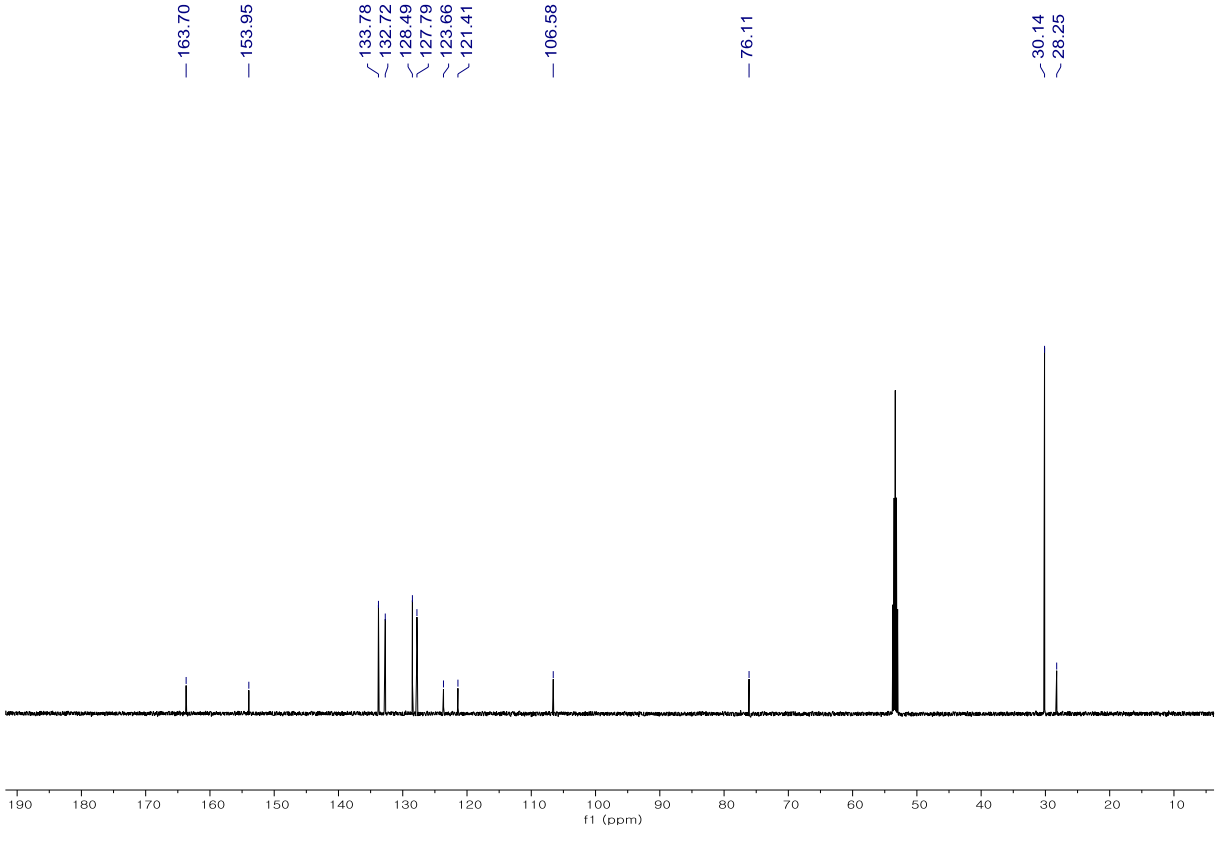



**3-{2-(Cyclopropylethynyl)phenyl}-1,4,2-dioxazol-5-one**

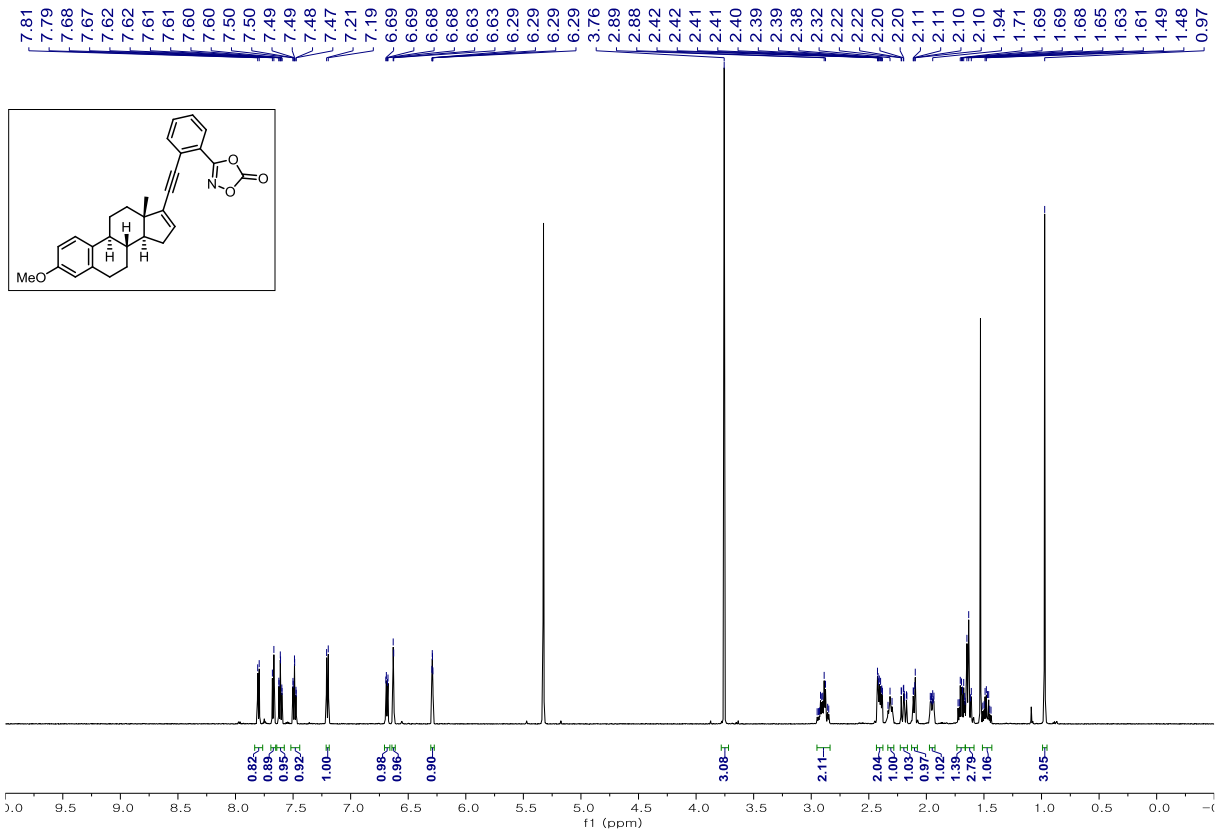


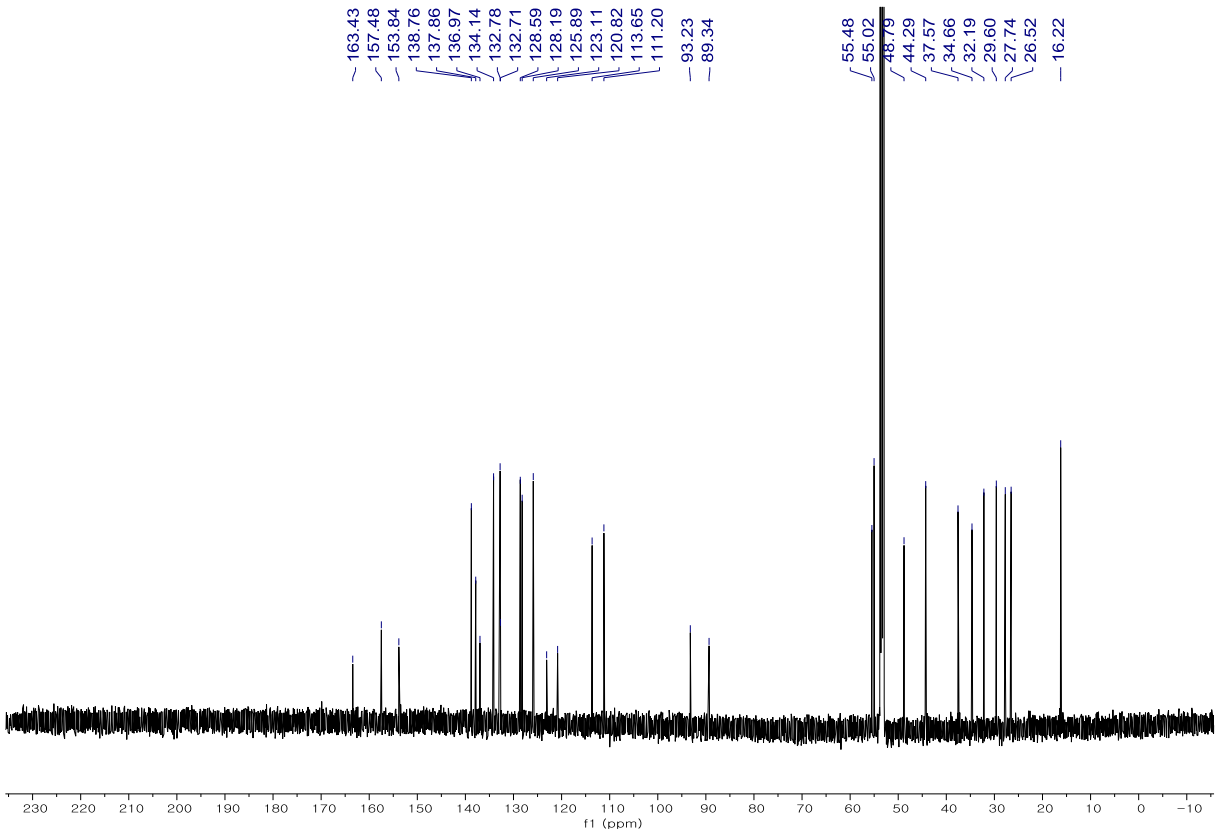
**3-{2-(3,3-Dimethylbut-1-yn-1-yl)phenyl}-1,4,2-dioxazol-5-one**



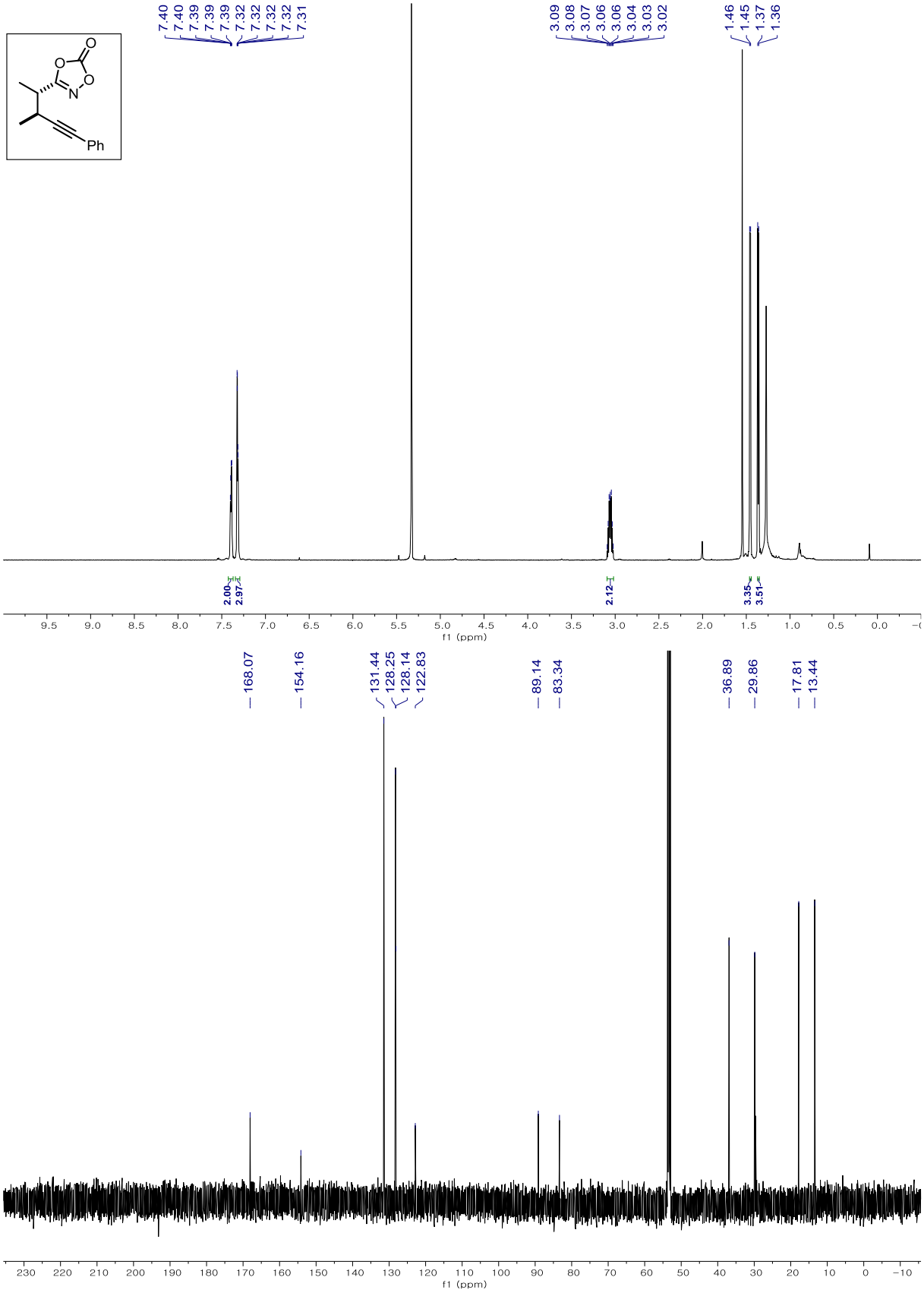



**3-[2-({(8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H* cyclopenta[a]phenanthren-17-yl)ethynyl}phenyl]-1,4,2-dioxazol-5-one**

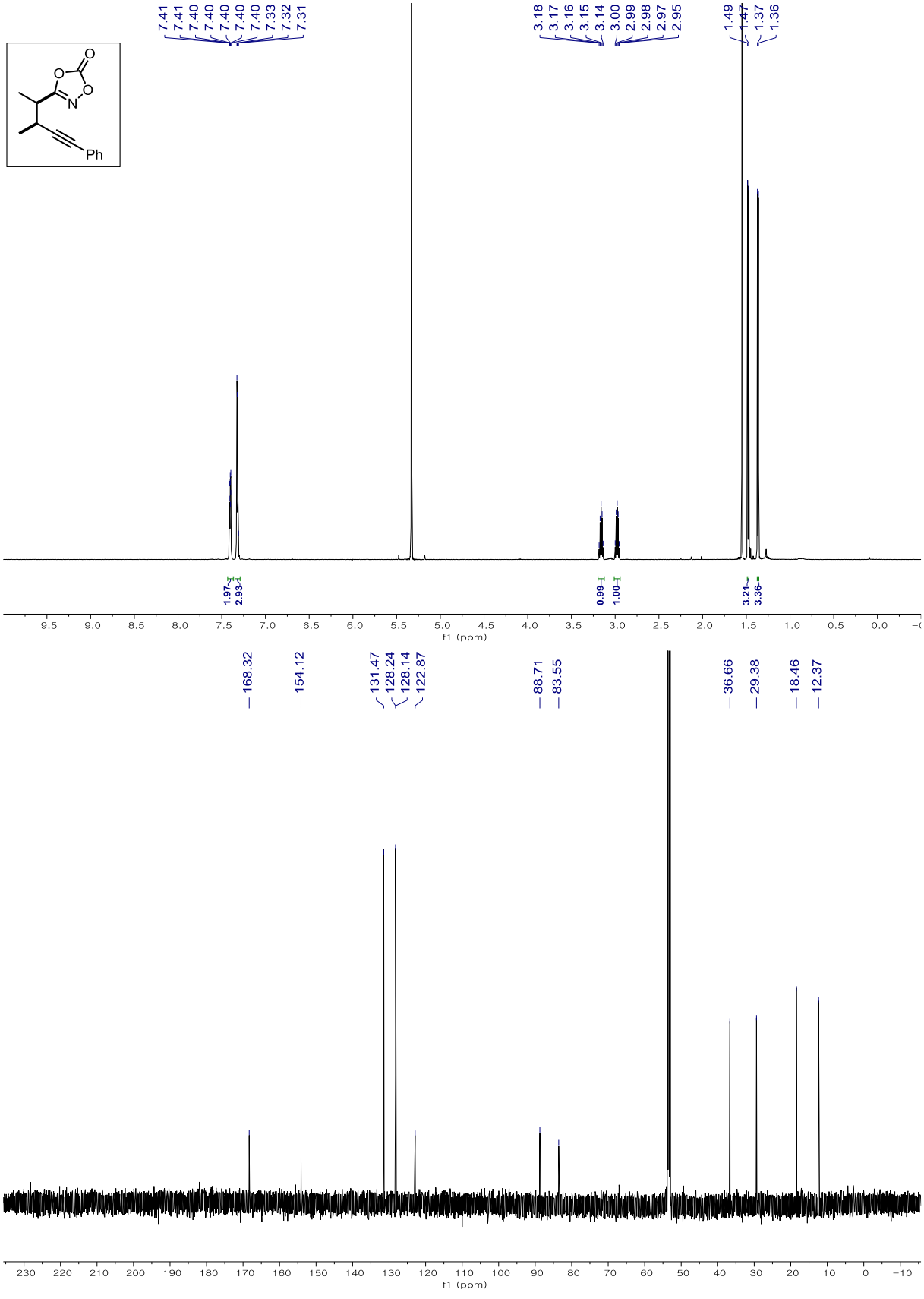


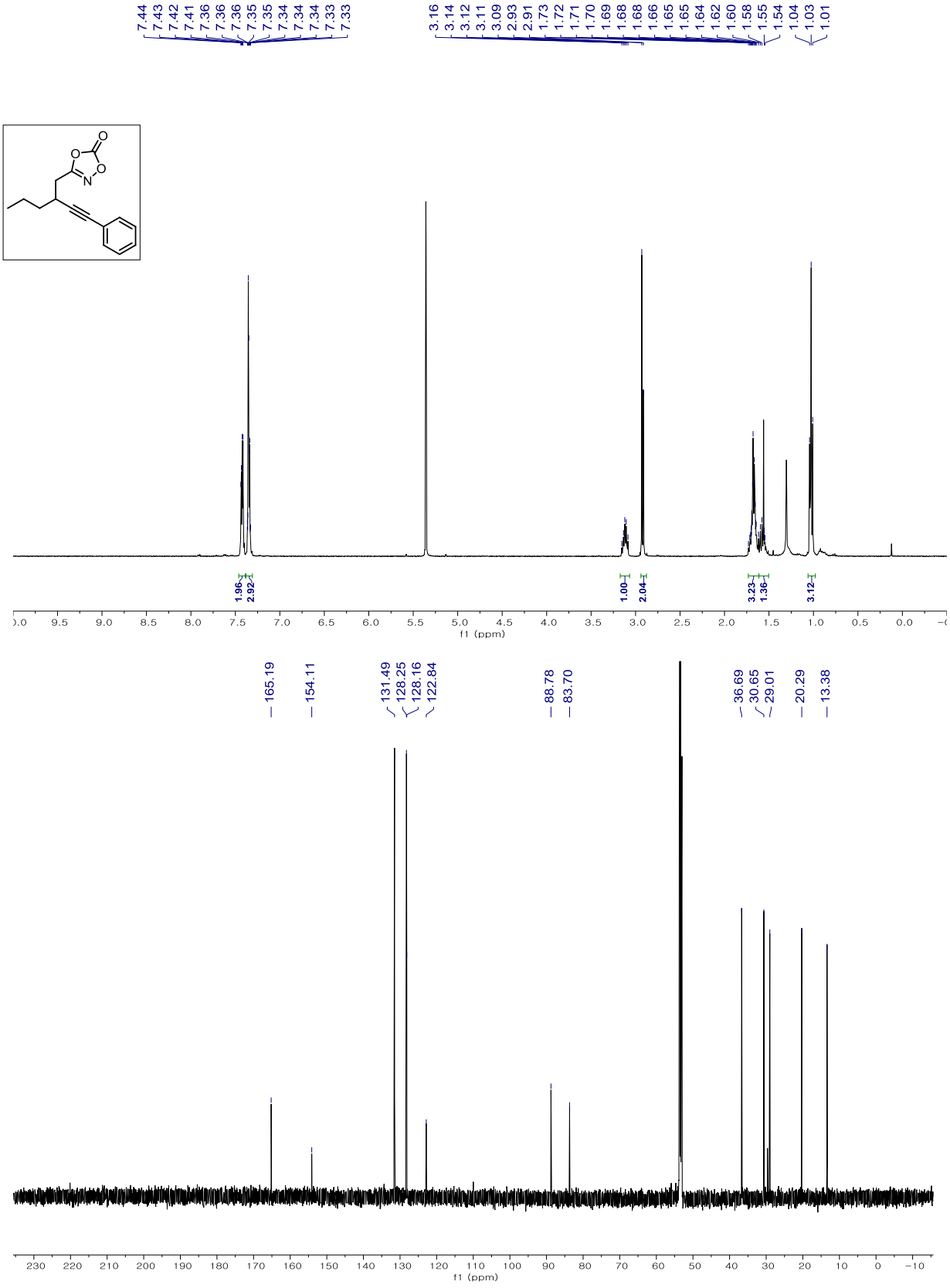
**3-{(±)-(2,3-*anti*)-3-methyl-5-phenylpent-4-yn-2-yl}-1,4,2-dioxazol-5-one (17, Table 2)**



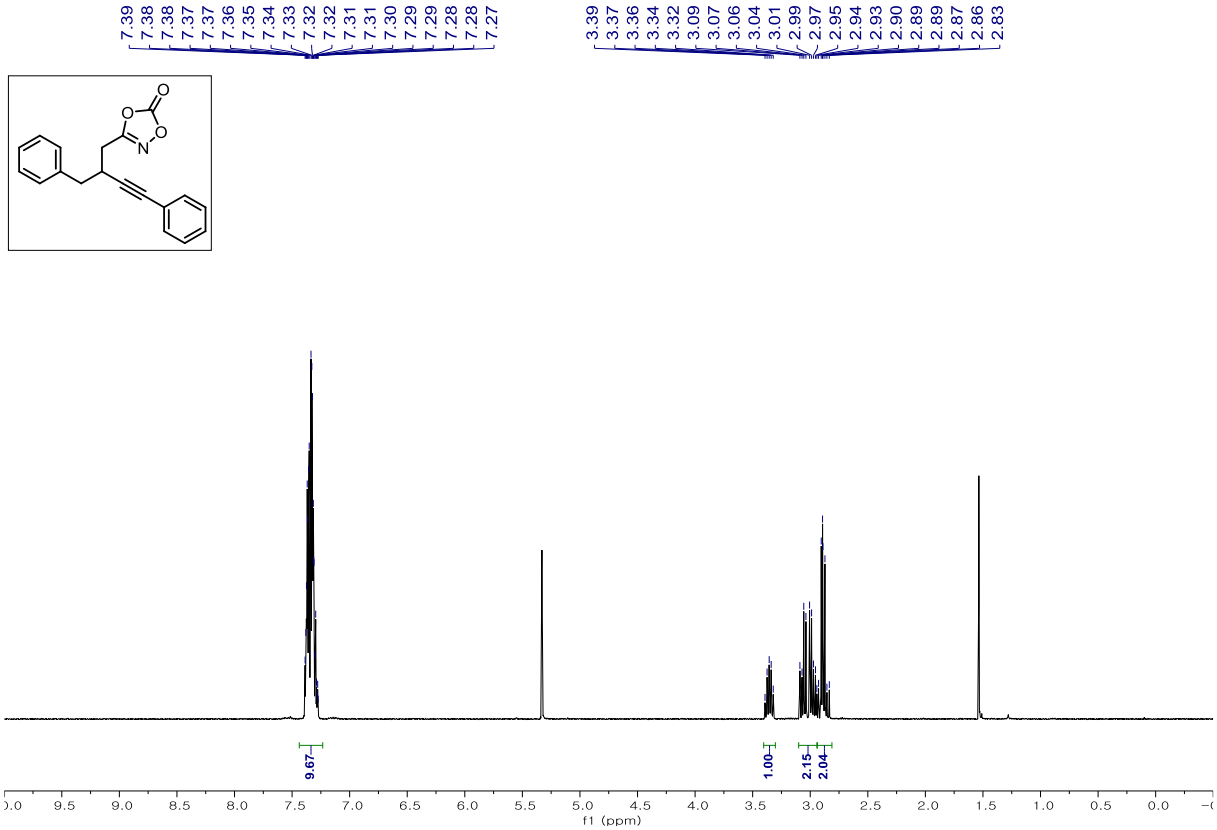
**3-{(±)-(2,3-*syn*)-3-Methyl-5-phenylpent-4-yn-2-yl}-1,4,2-dioxazol-5-one (19, Table 2)**

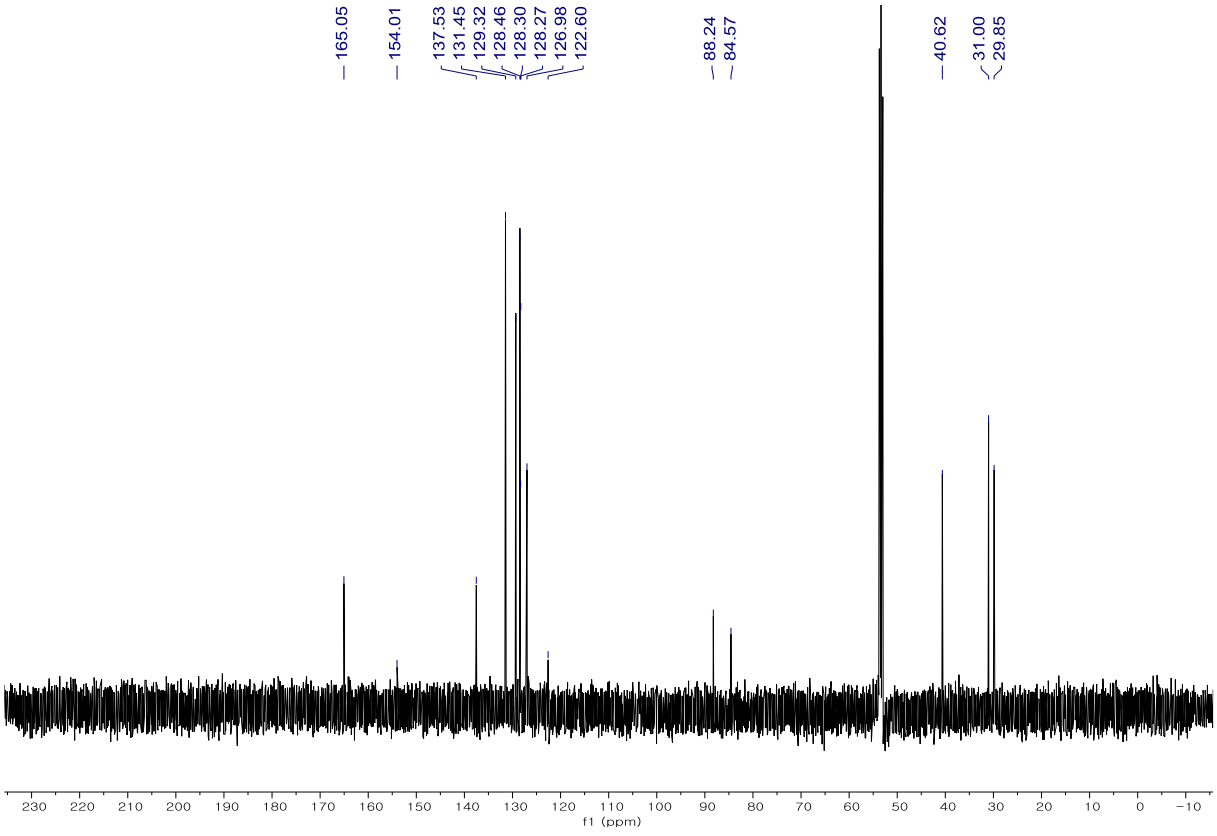


**3-{2-(Phenylethynyl)pentyl}-1,4,2-dioxazol-5-one (21, Table 2)**

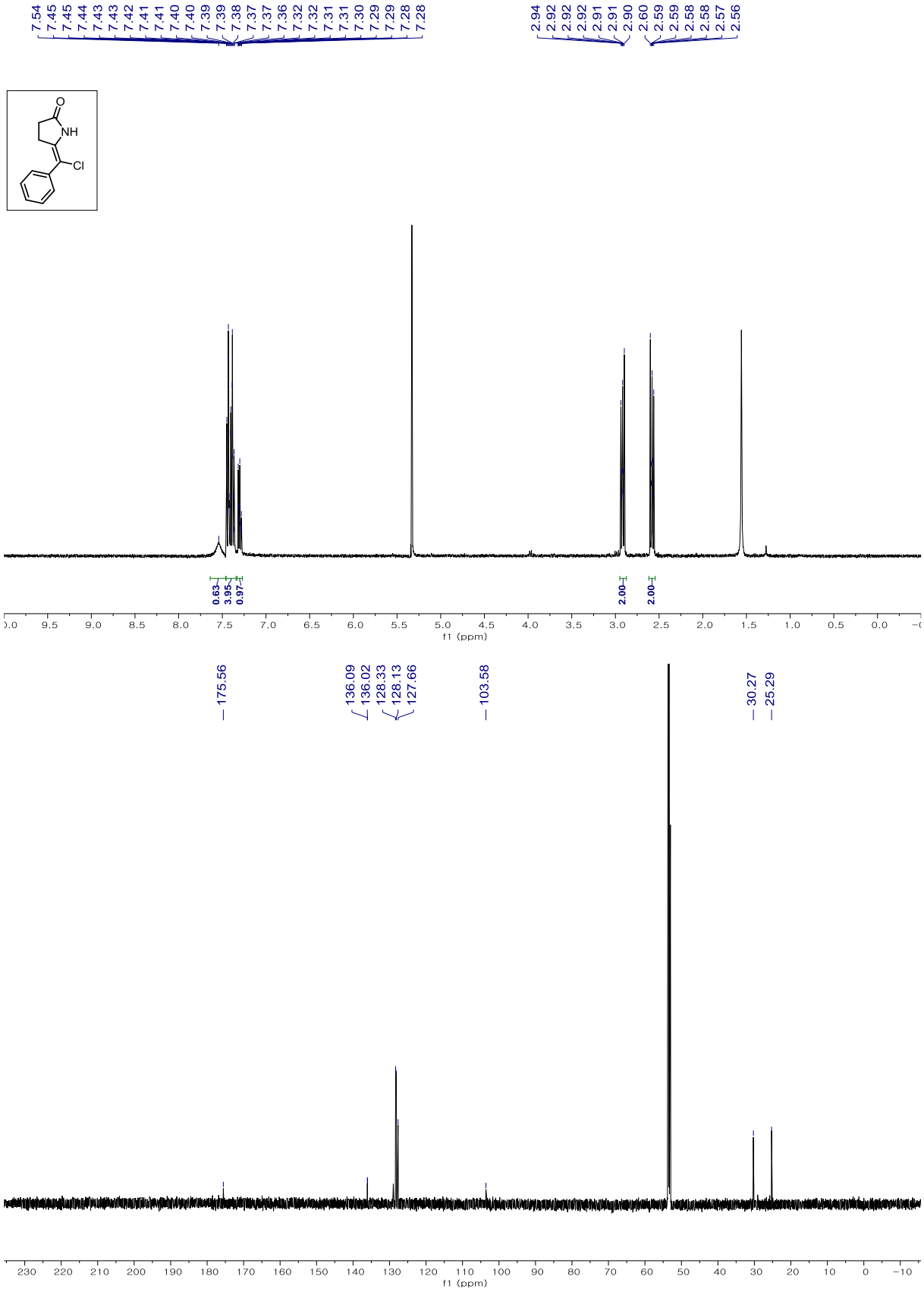


**3-(2-Benzyl-4-phenylbut-3-yn-1-yl)-1,4,2-dioxazol-5-one (23, Table 2)**

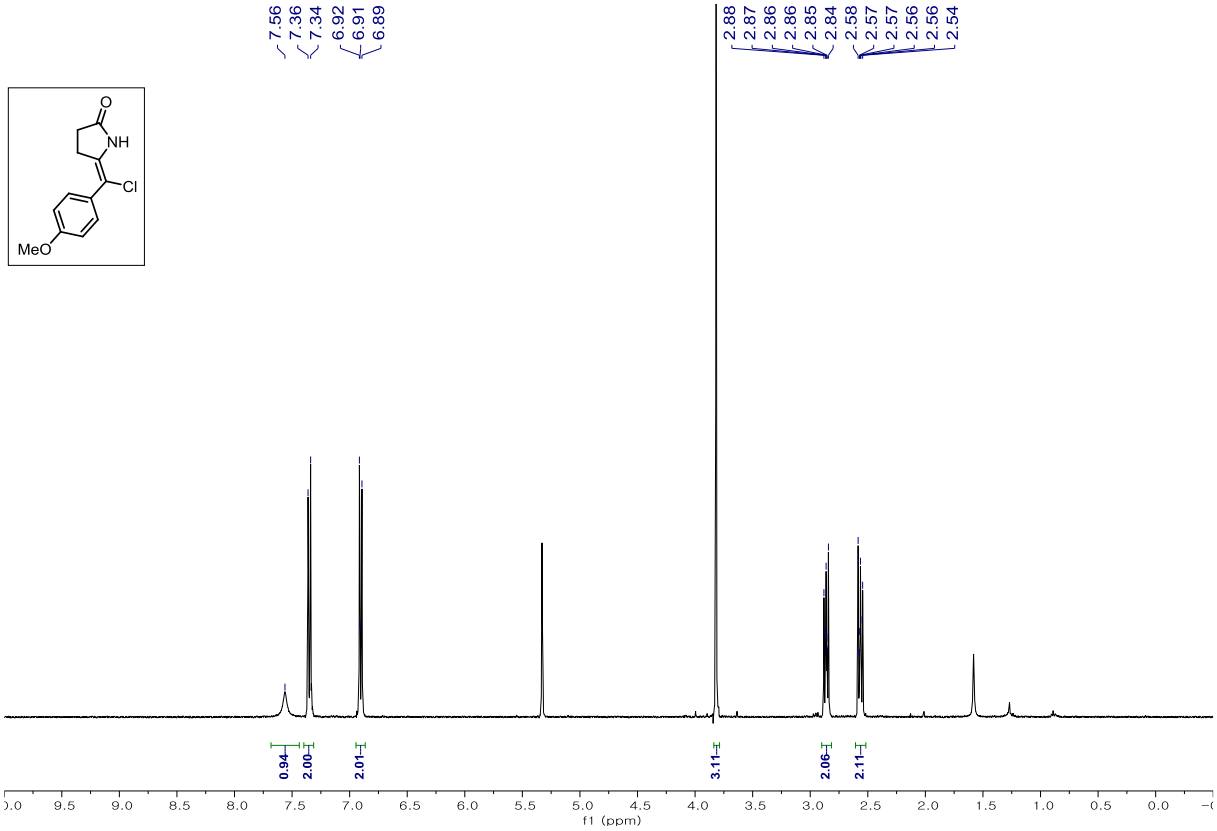


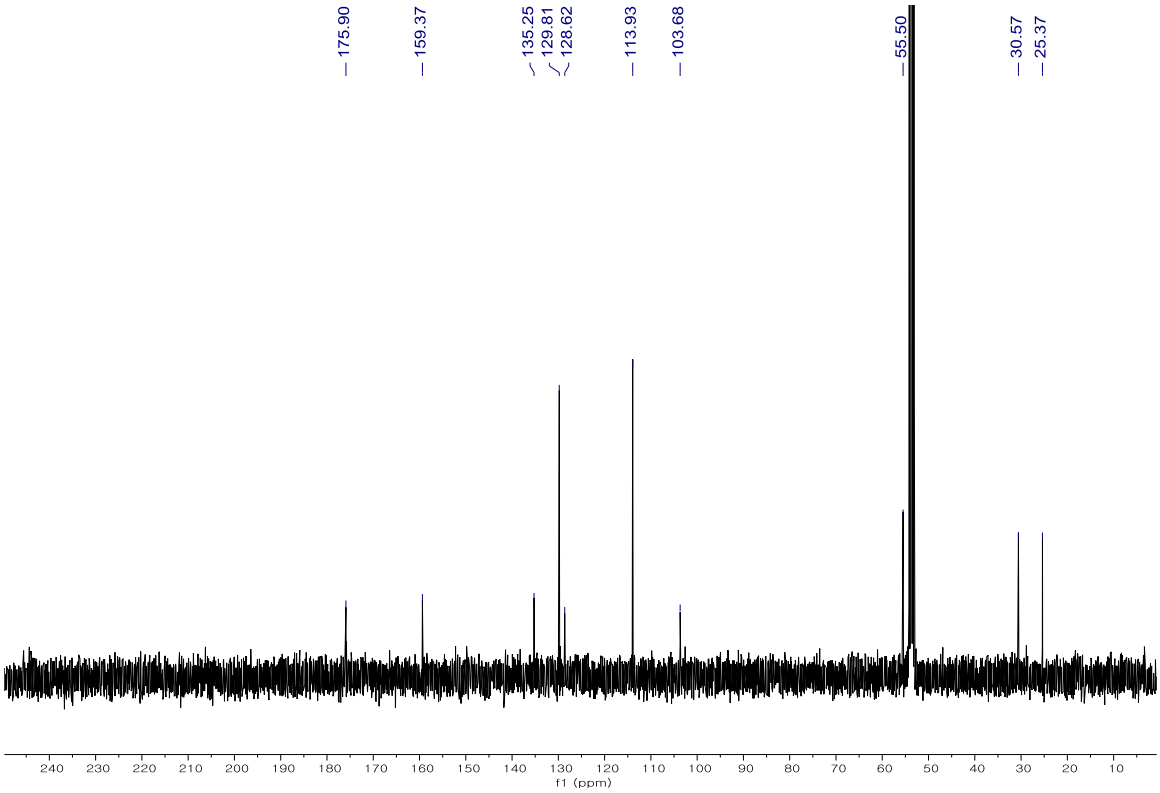



**(*Z*)-5-{Chloro(phenyl)methylene}pyrrolidin-2-one (2, Table 2)**

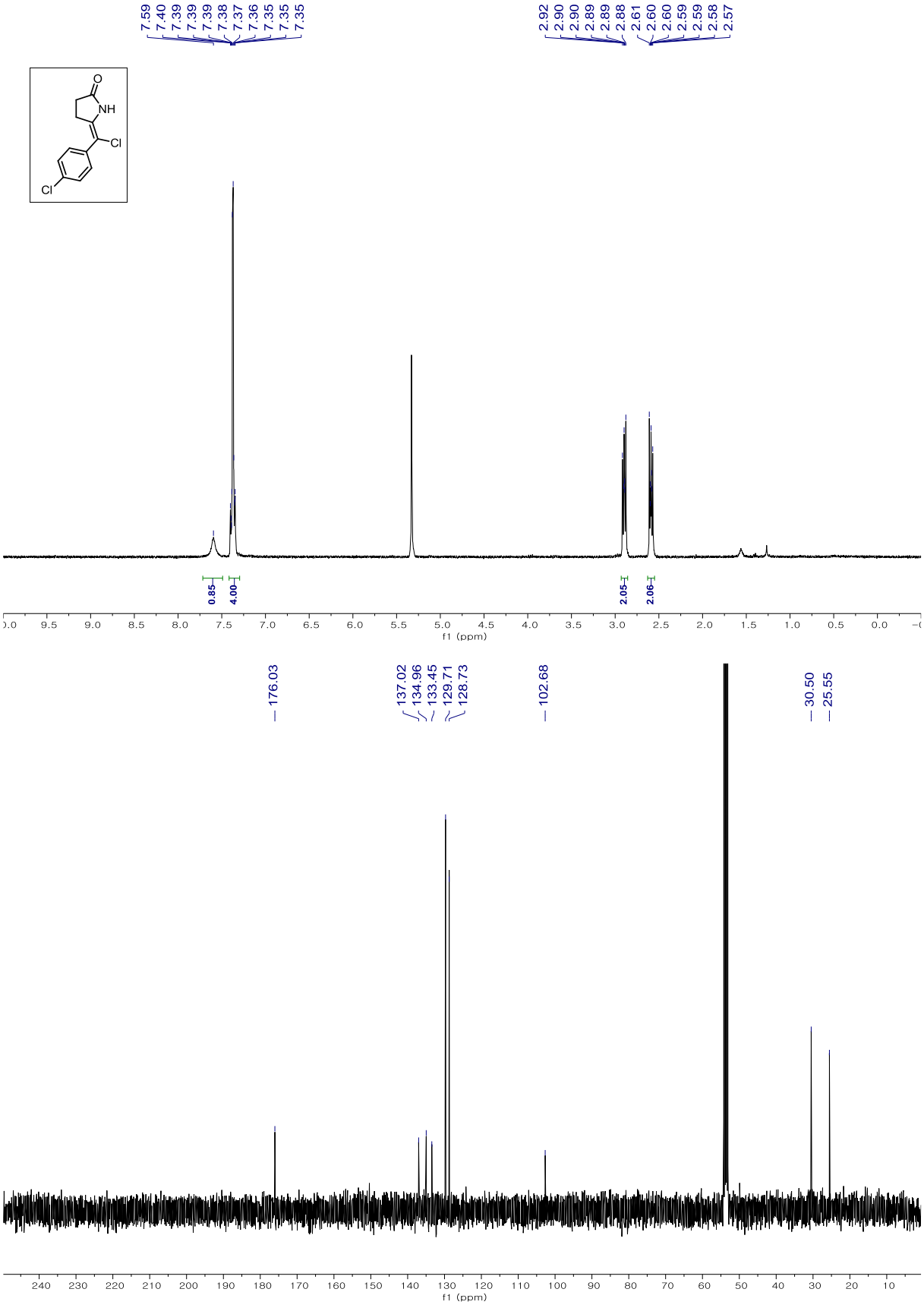


**(Z)-5-{Chloro(4-methoxyphenyl)methylene}pyrrolidin-2-one (3, Table 2)**

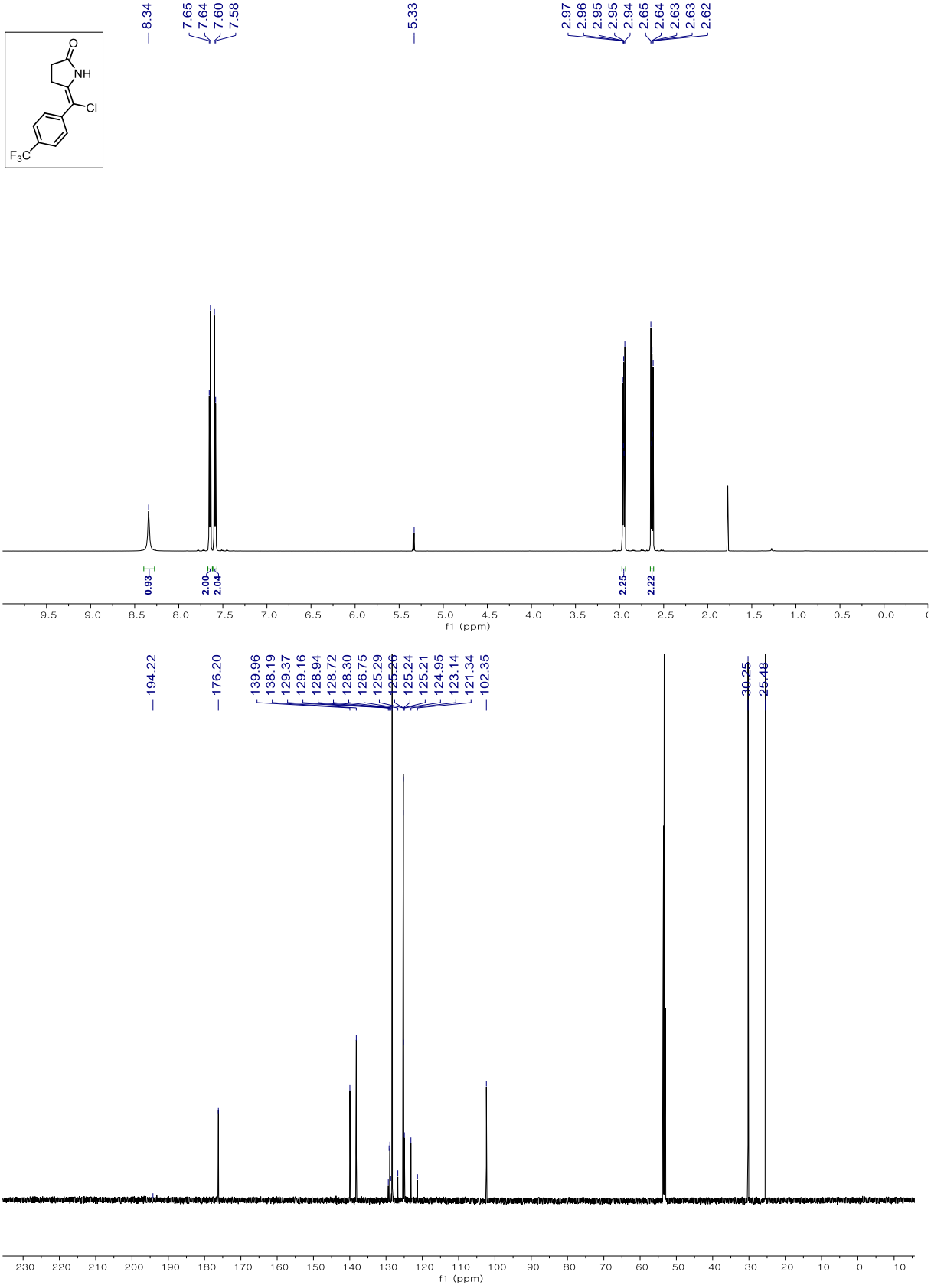


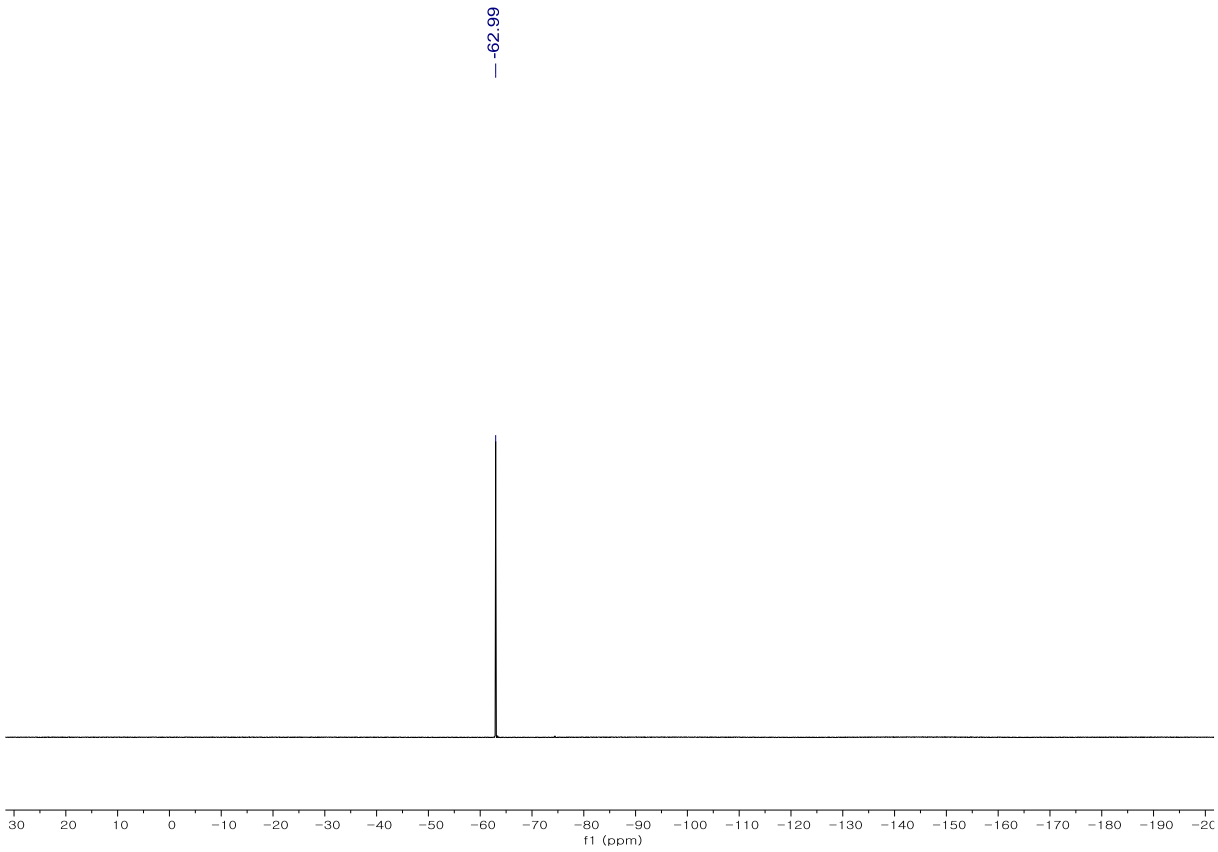



**(*Z*)-5-{Chloro(4-chlorophenyl)methylene}pyrrolidin-2-one (4, Table 2)**

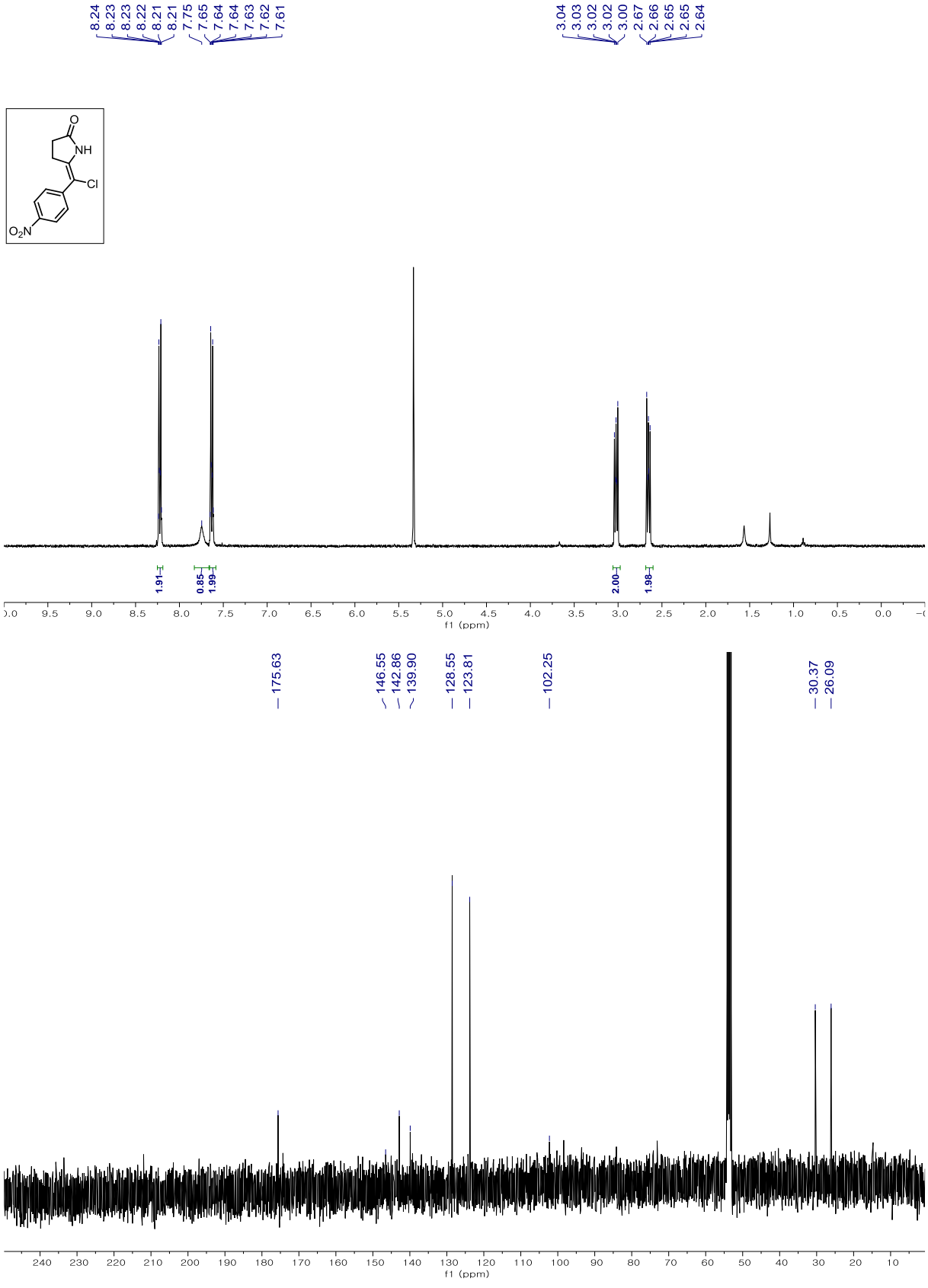


**(*Z*)-5-[Chloro{4-(trifluoromethyl)phenyl}methylene]pyrrolidin-2-one (5, Table 2)**

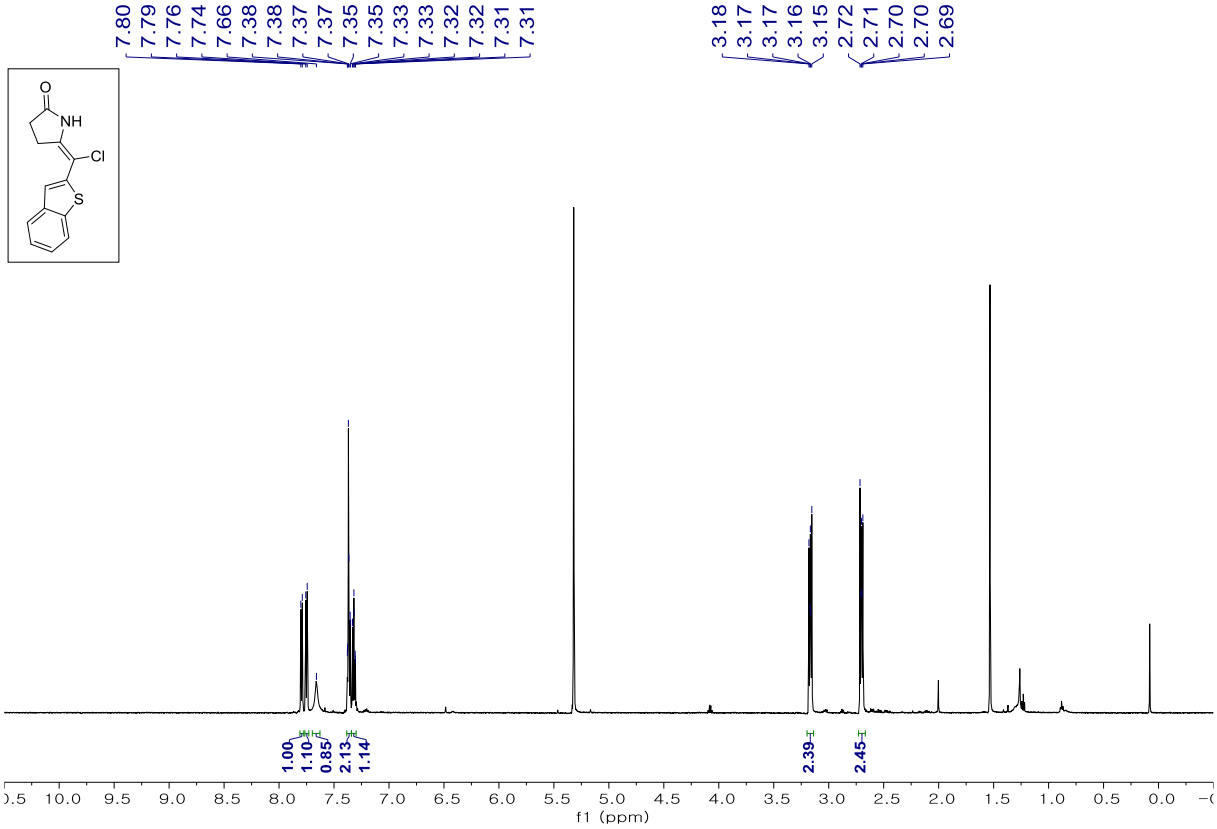


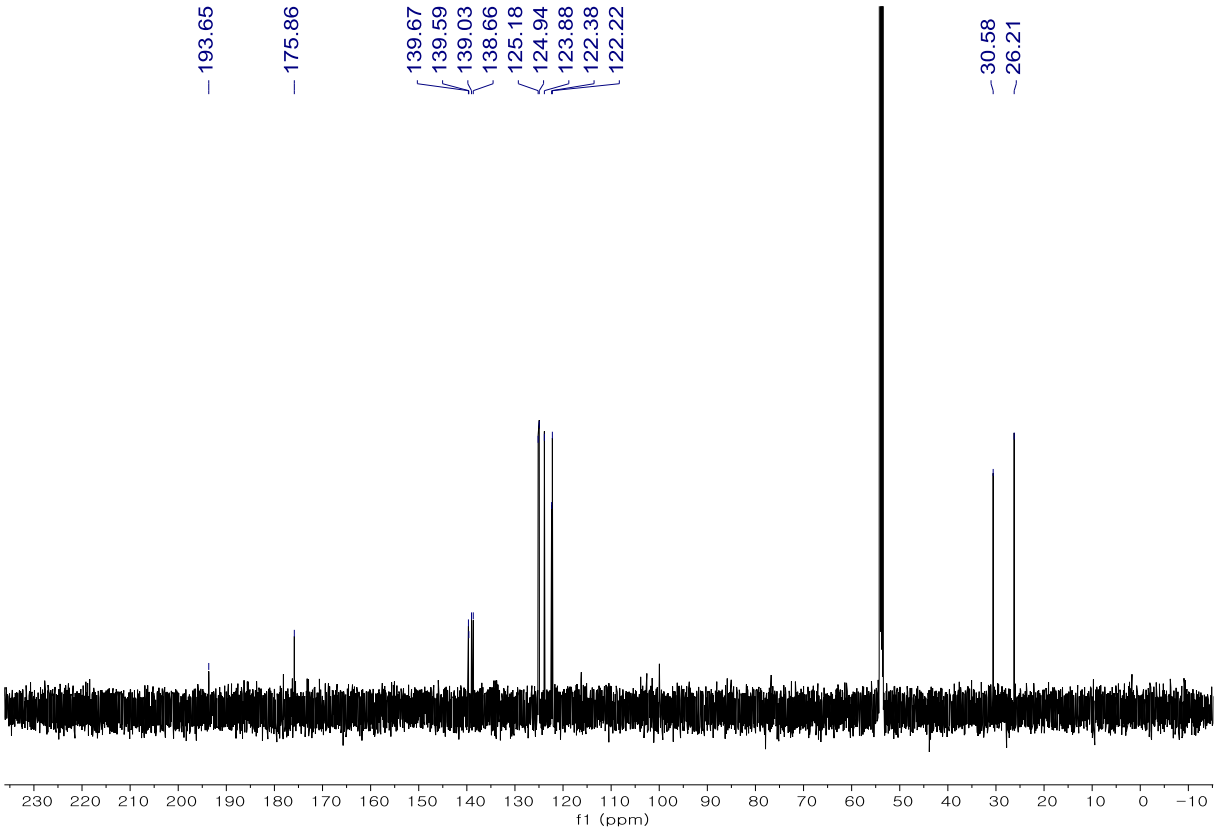

-62.99
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

**(*Z*)-5-{Chloro(4-nitrophenyl)methylene}pyrrolidin-2-one (6, Table 2)**

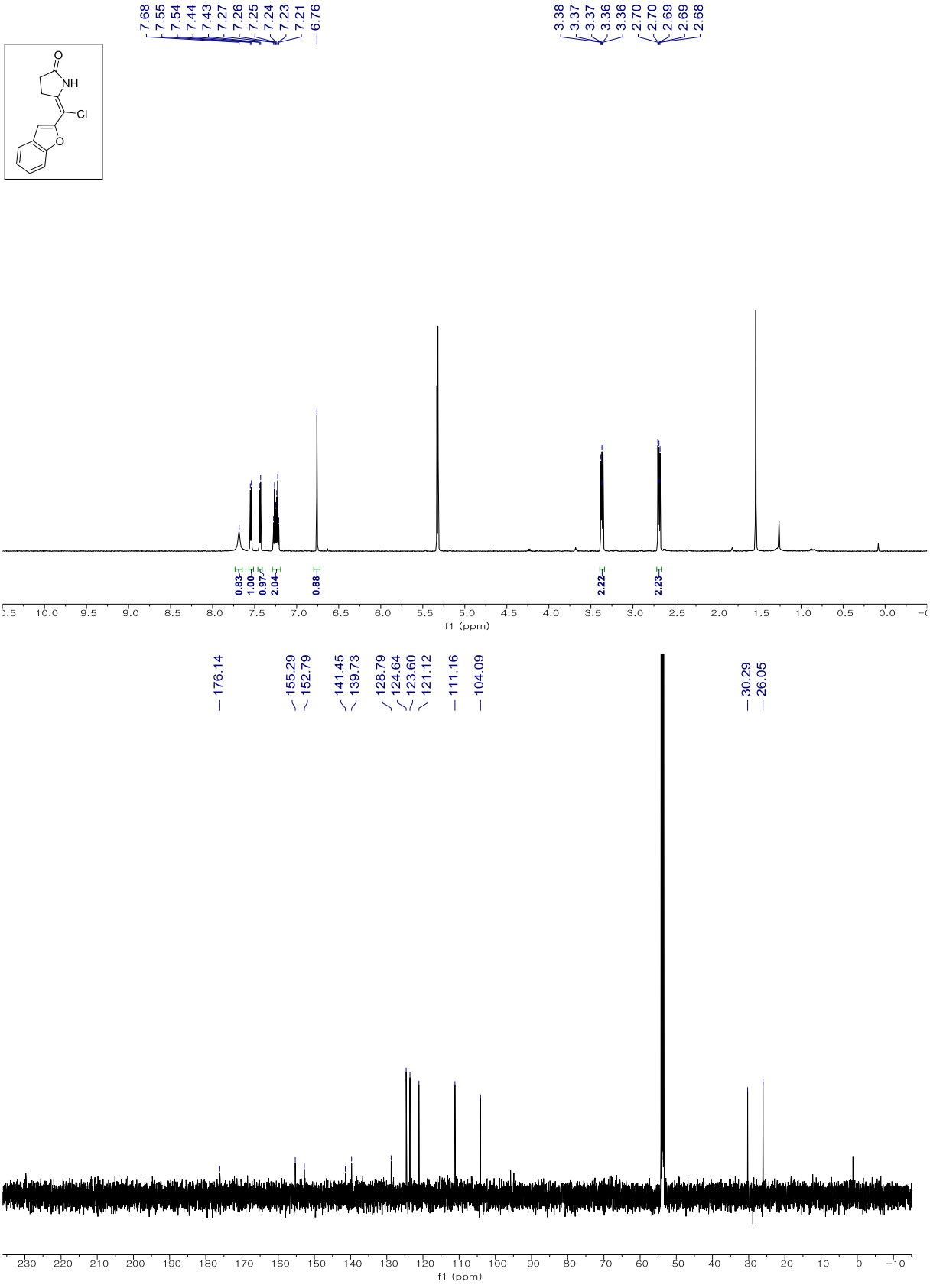


**(Z)-5-(Benzo[*b*]thiophen-2-ylchloromethylene)pyrrolidin-2-one (7, Table 2)**

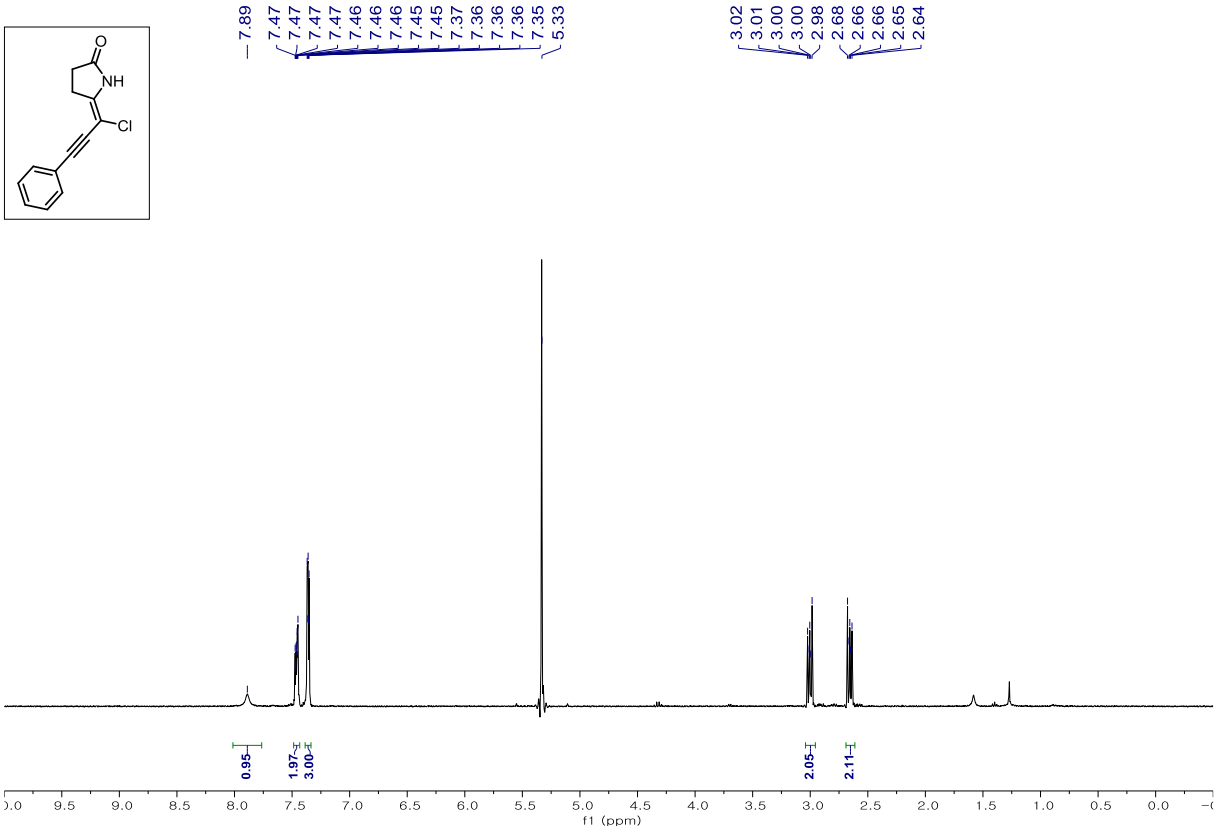


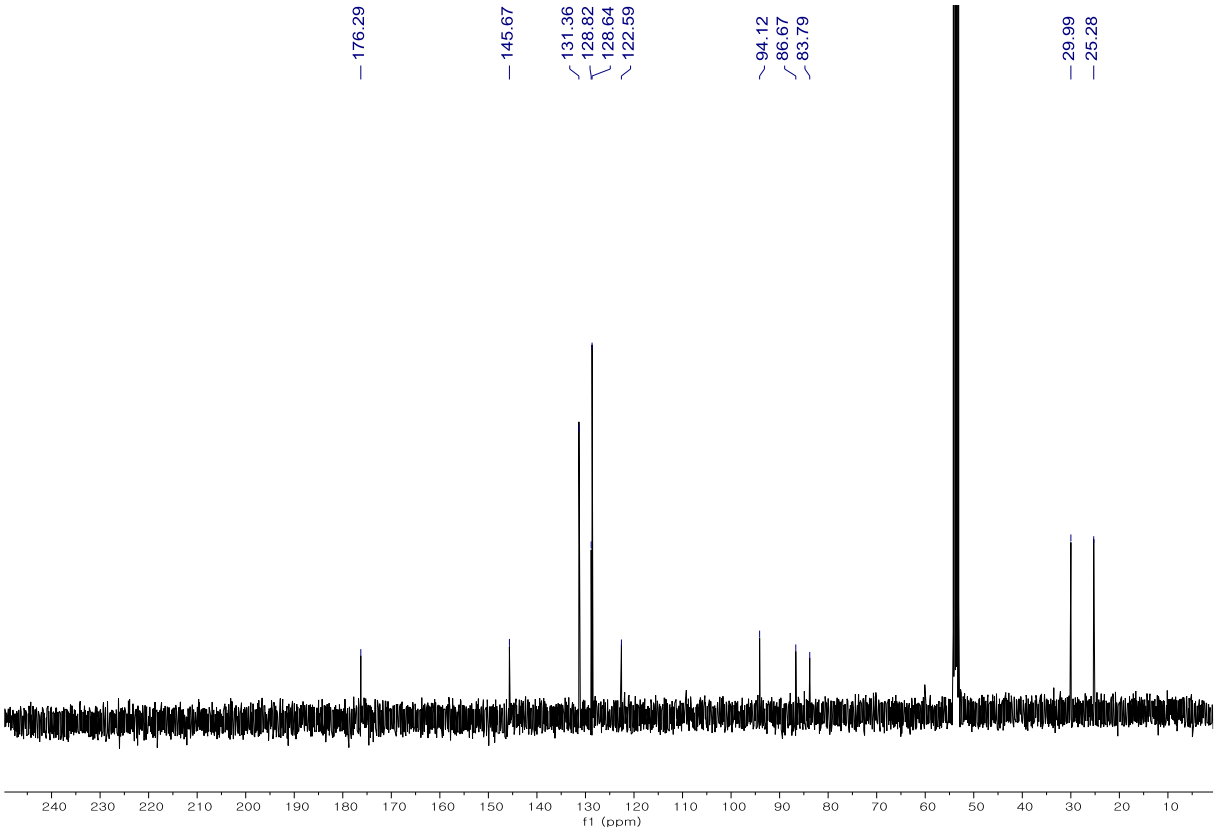



**(Z)-5-(Benzofuran-2-ylchloromethylene)pyrrolidin-2-one (8, Table 2)**

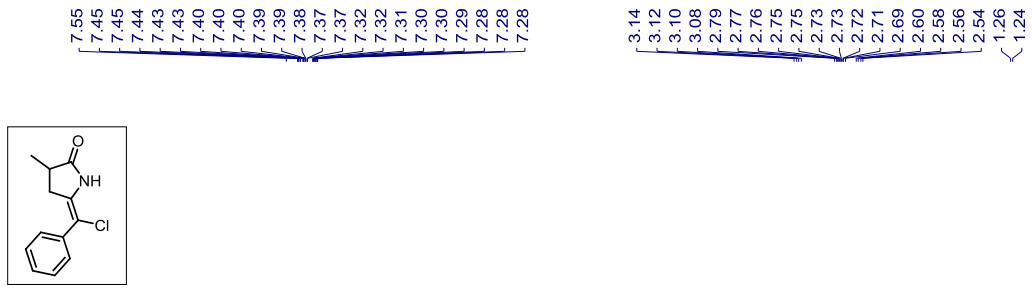


**(*Z*)-5-(1-Chloro-3-phenylprop-2-yn-1-ylidene)pyrrolidin-2-one (9, Table 2)**



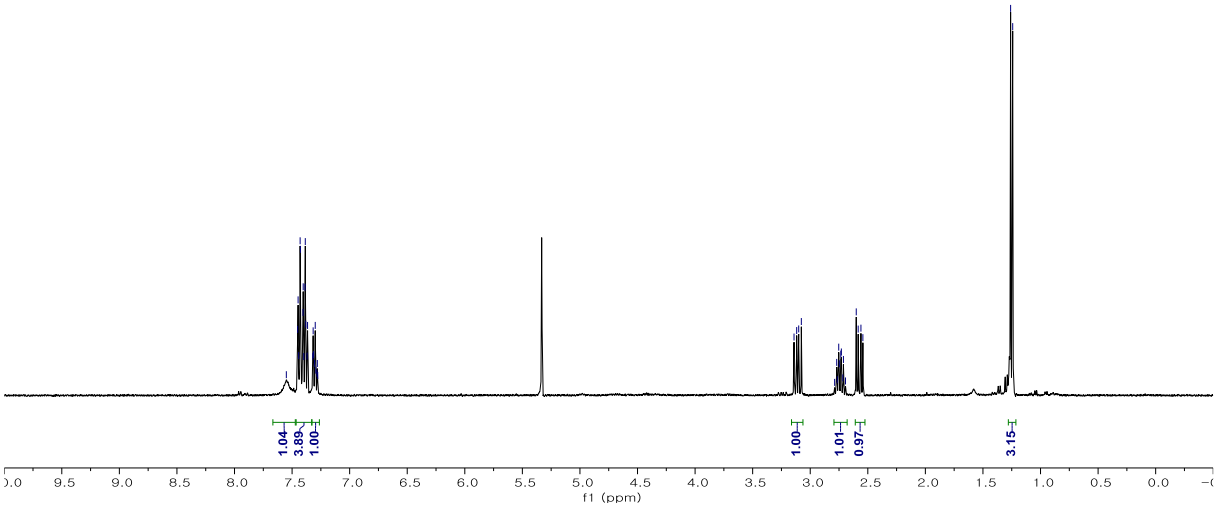



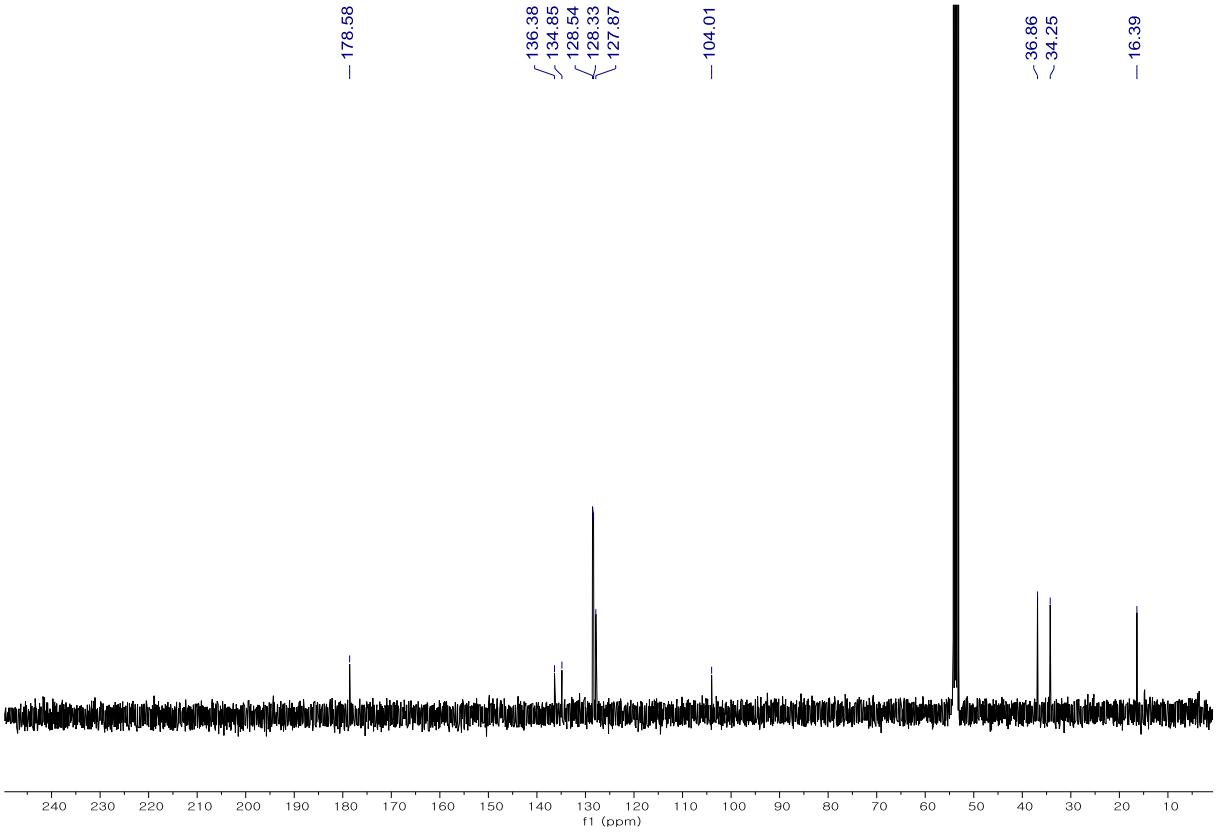
**(*Z*)-5-{Chloro(phenyl)methylene}-3-methylpyrrolidin-2-one (10, Table 2)**



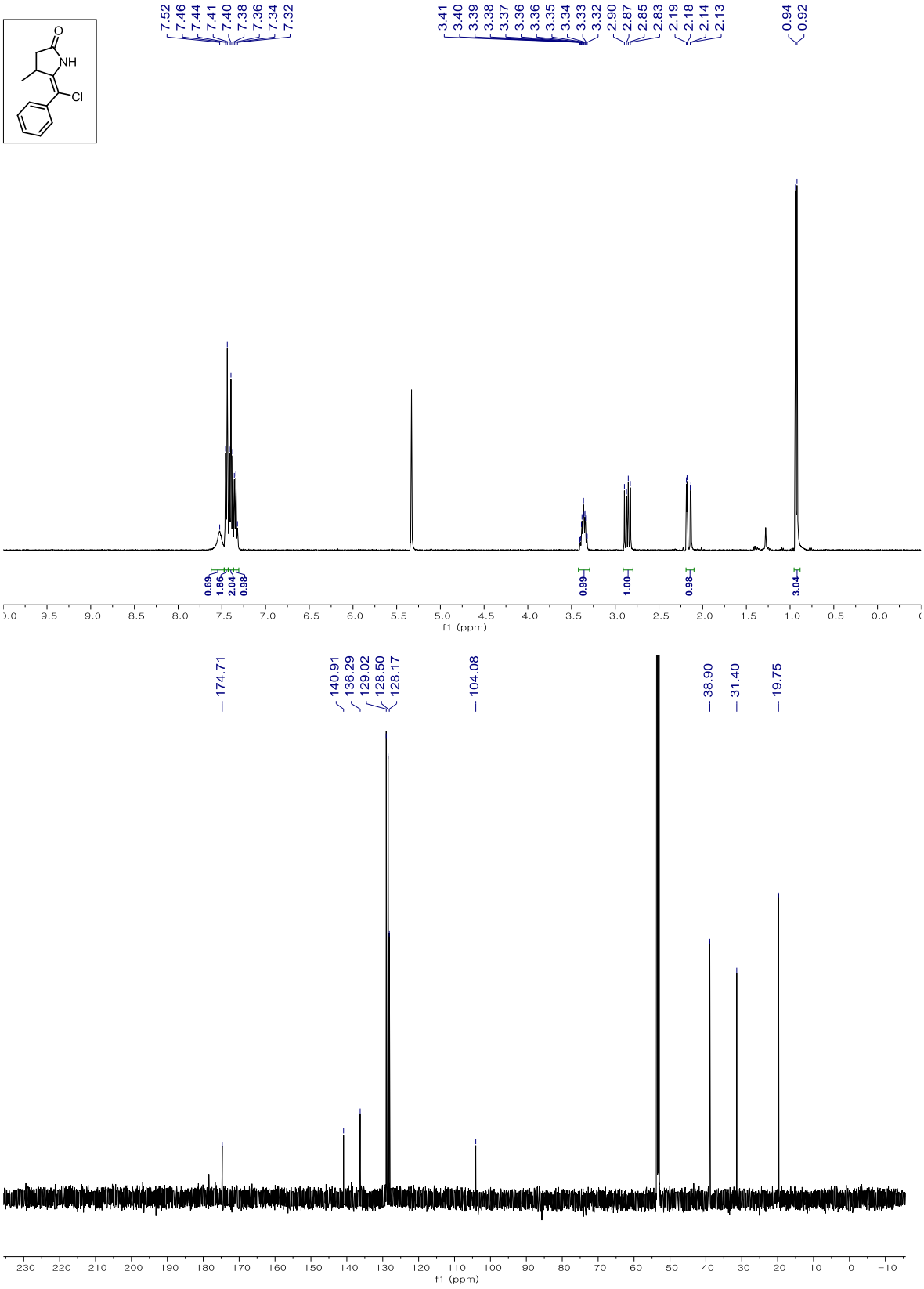




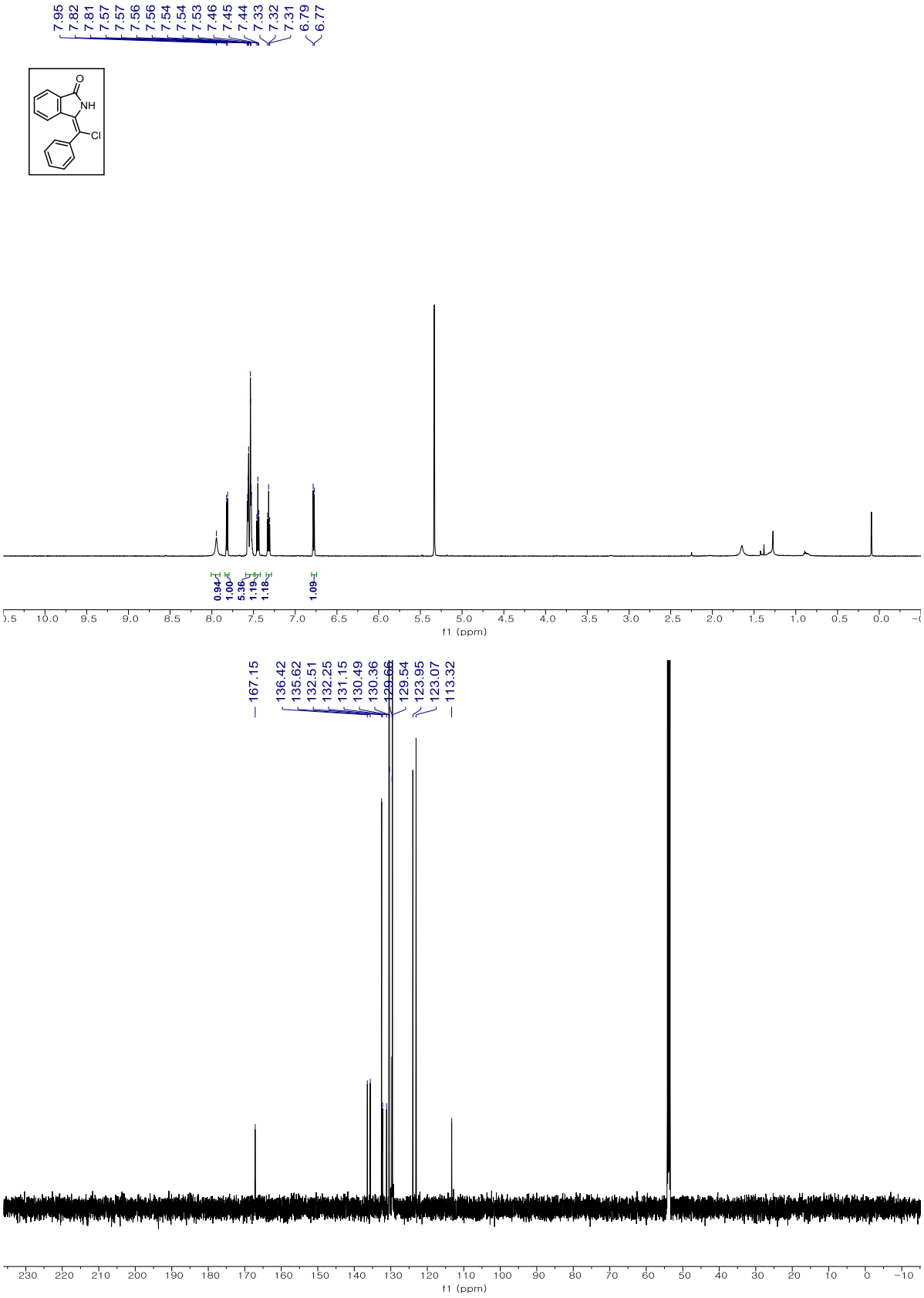


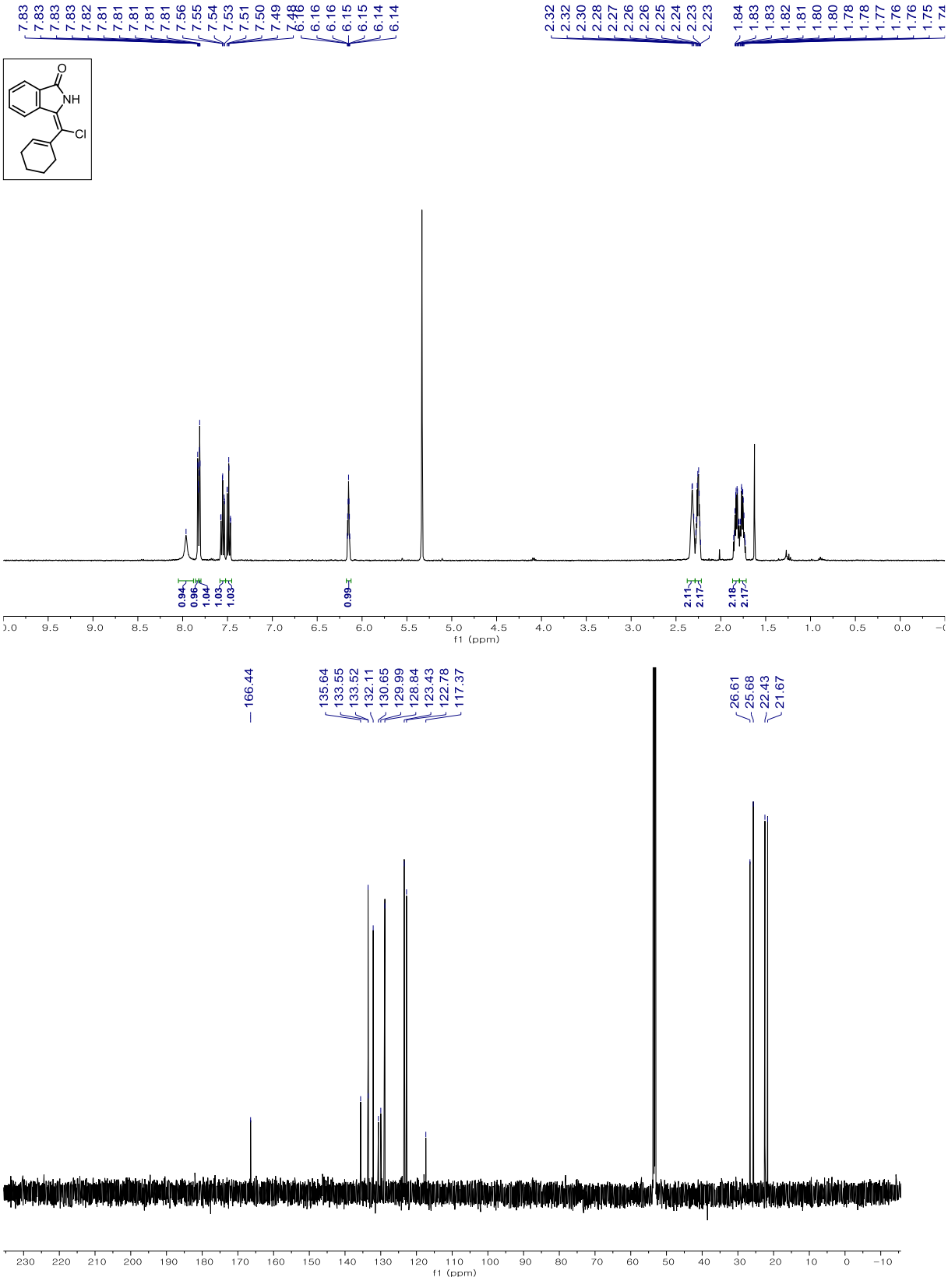
**(*Z*)-5-{Chloro(phenyl)methylene}-4-methylpyrrolidin-2-one (11, Table 2)**



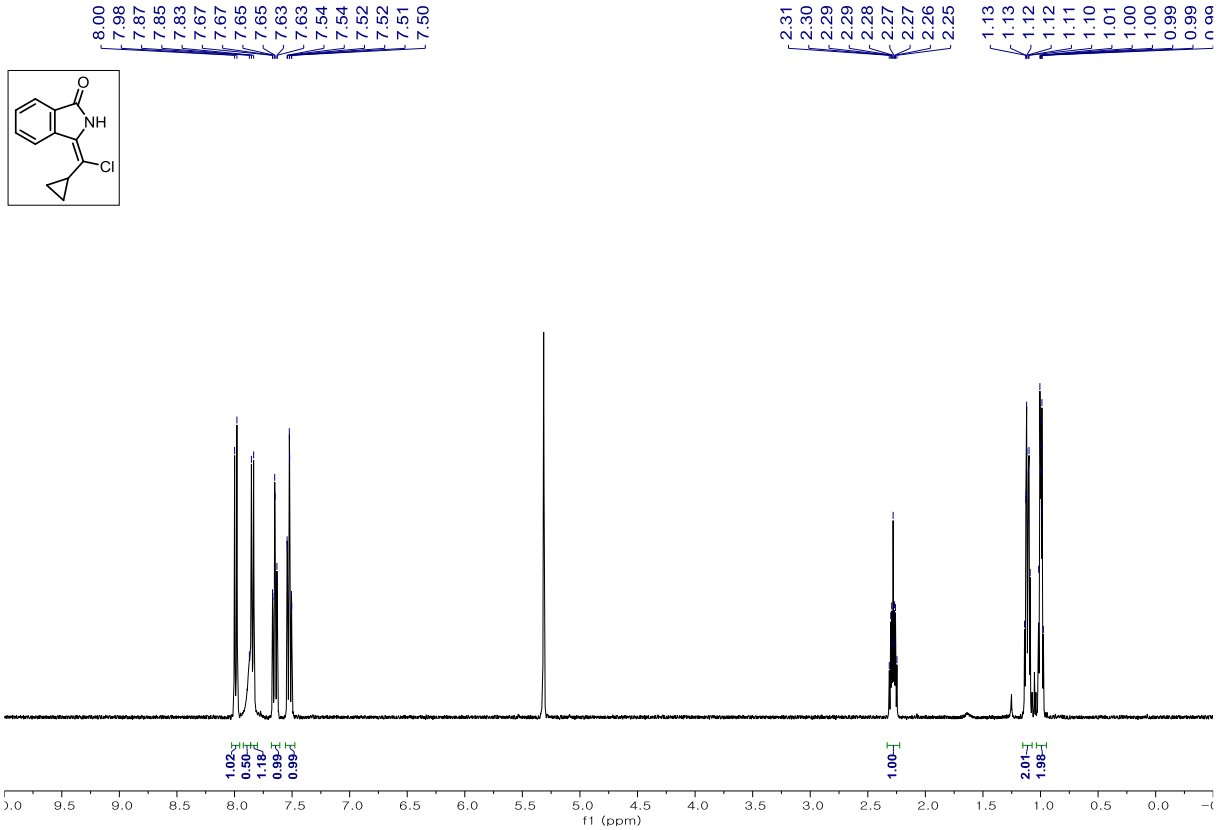
**(*Z*)-3-{Chloro(phenyl)methylene}isoindolin-1-one (12, Table 2)**

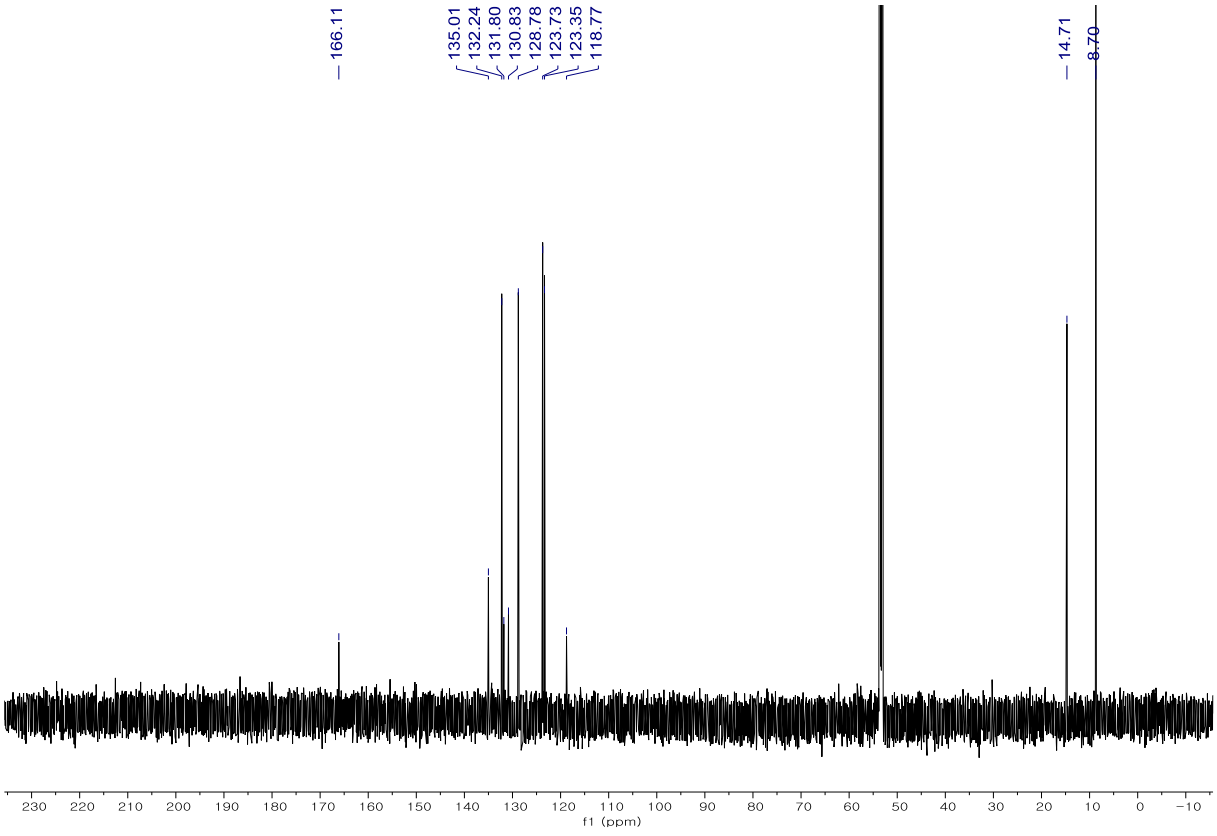


**(*Z*)-3-{Chloro(cyclohex-1-en-1-yl)methylene}isoindolin-1-one (13, Table 2)**

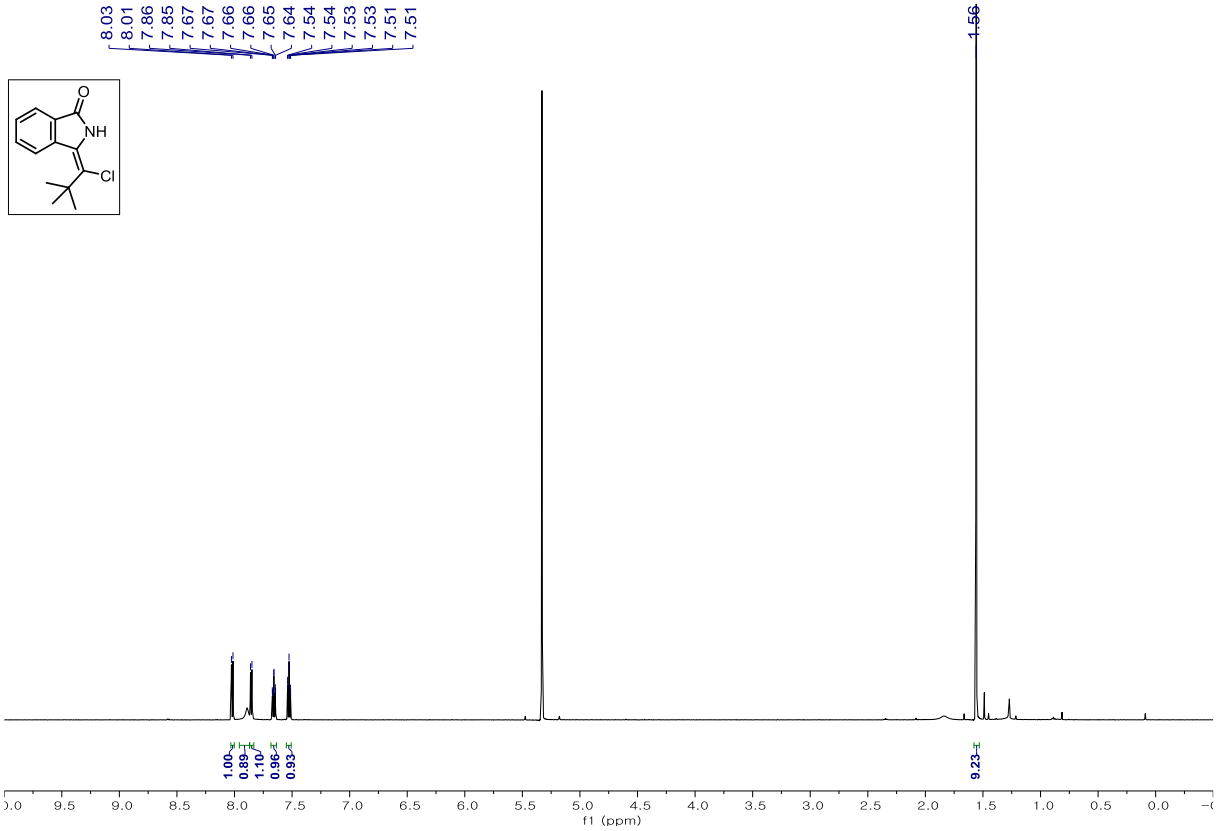


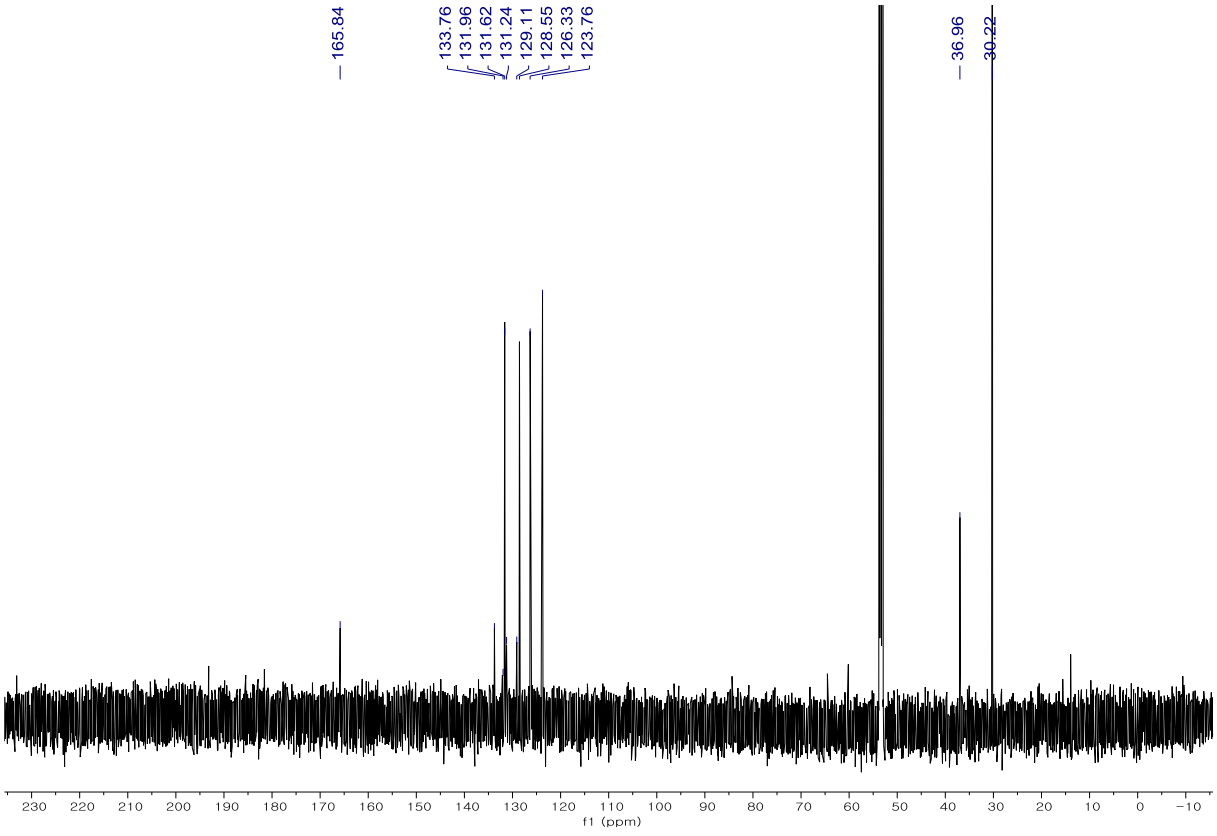
**(*Z*)-3-{Chloro(cyclopropyl)methylene}isoindolin-1-one (14, Table 2)**



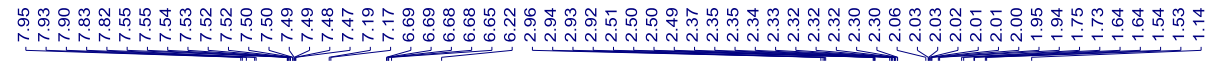



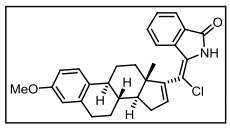
**(*Z*)-3-(1-Chloro-2,2-dimethylpropylidene)isoindolin-1-one (15, Table 2)**

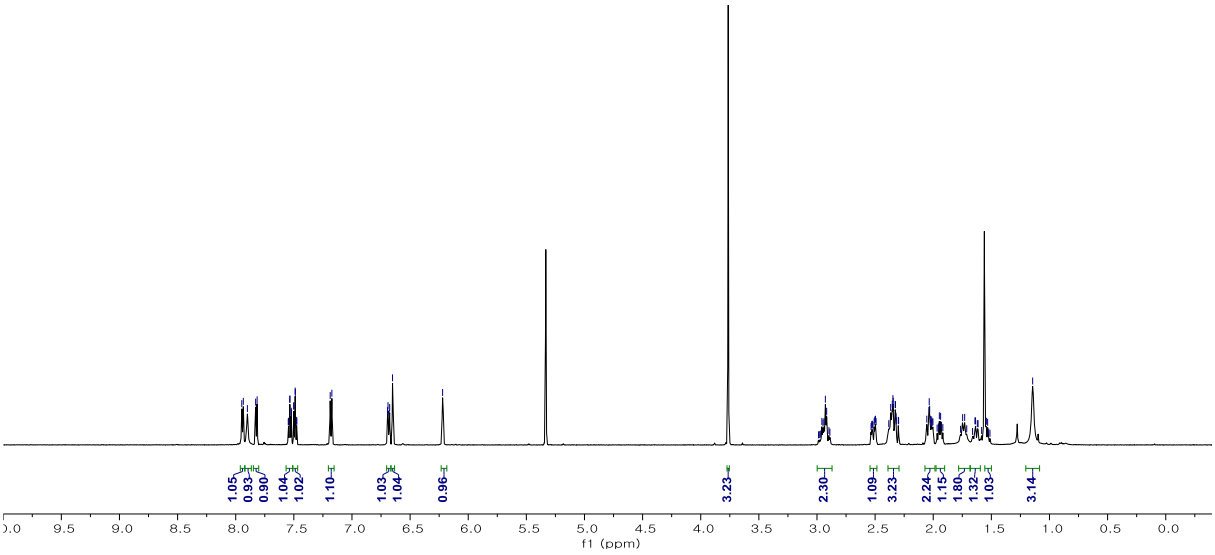


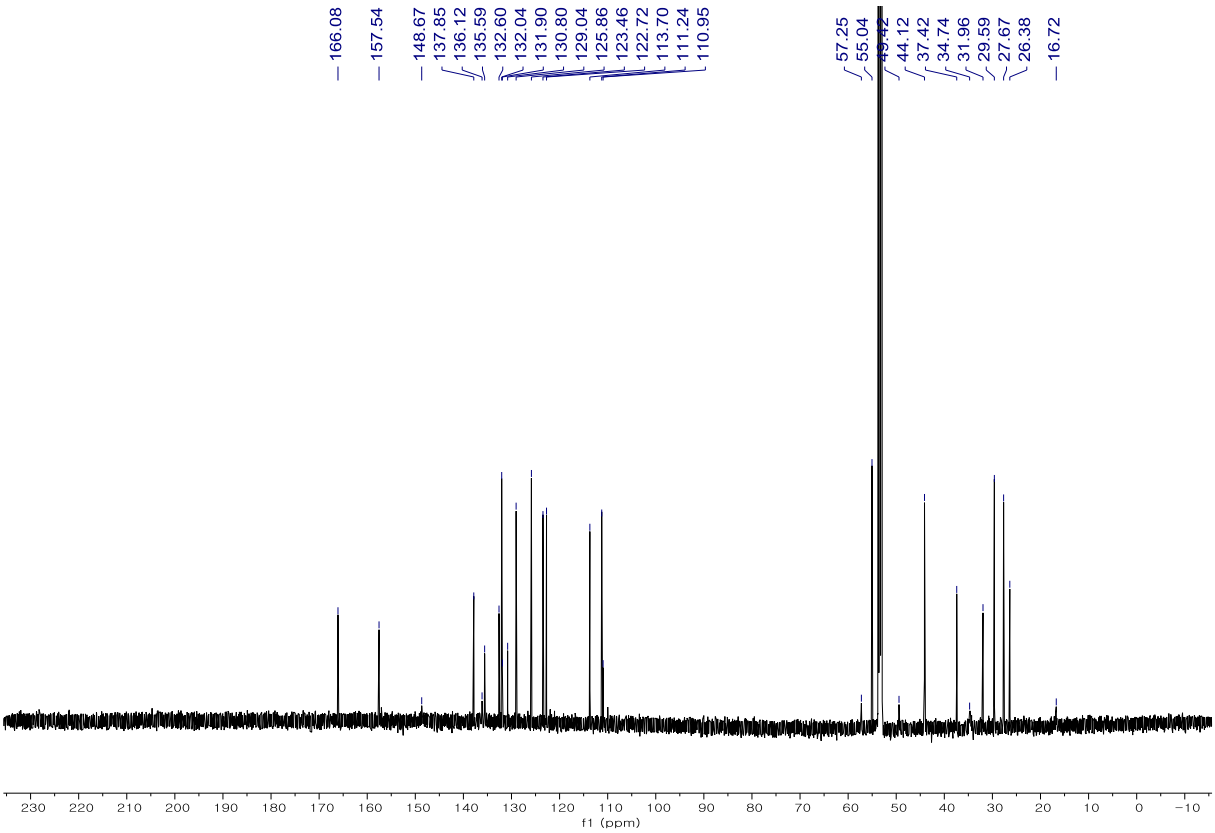



**(*Z*)-3-[Chloro{(8*S*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl}methylene]isoindolin-1-one (16, Table 2)**

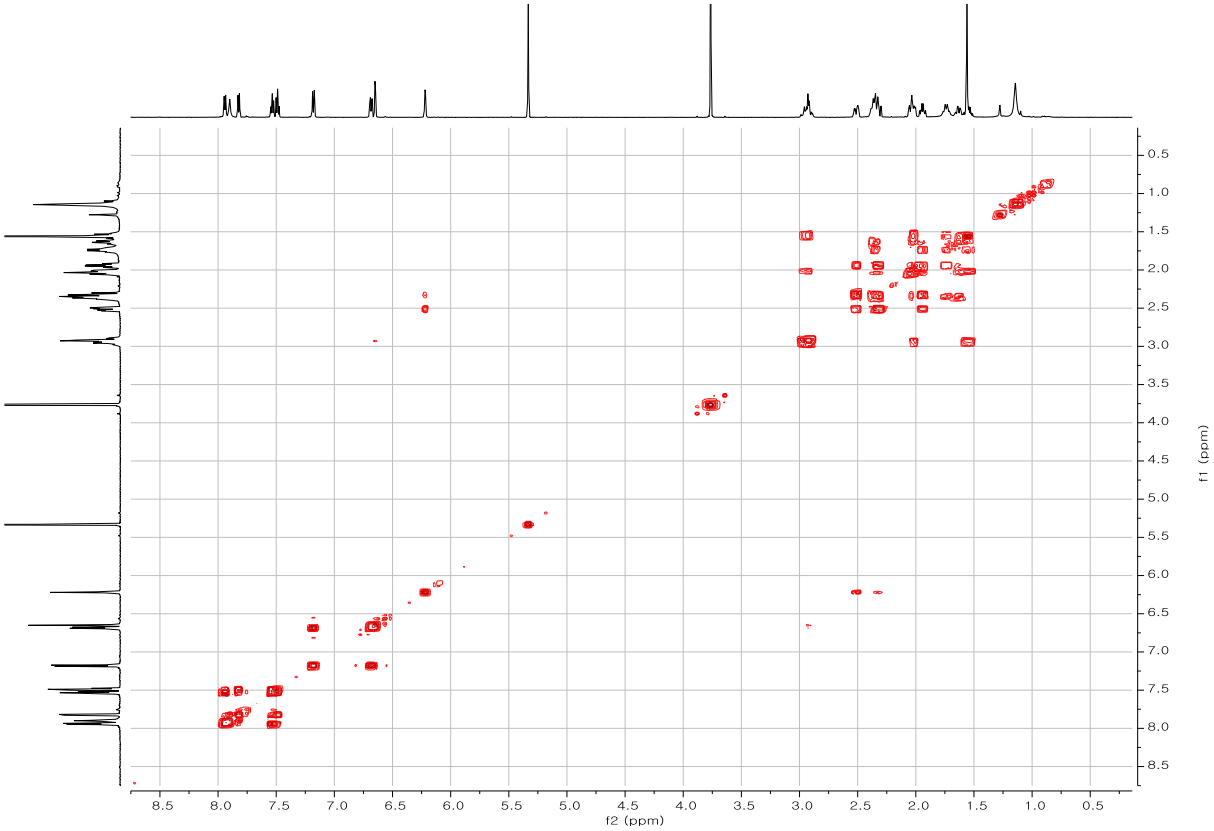


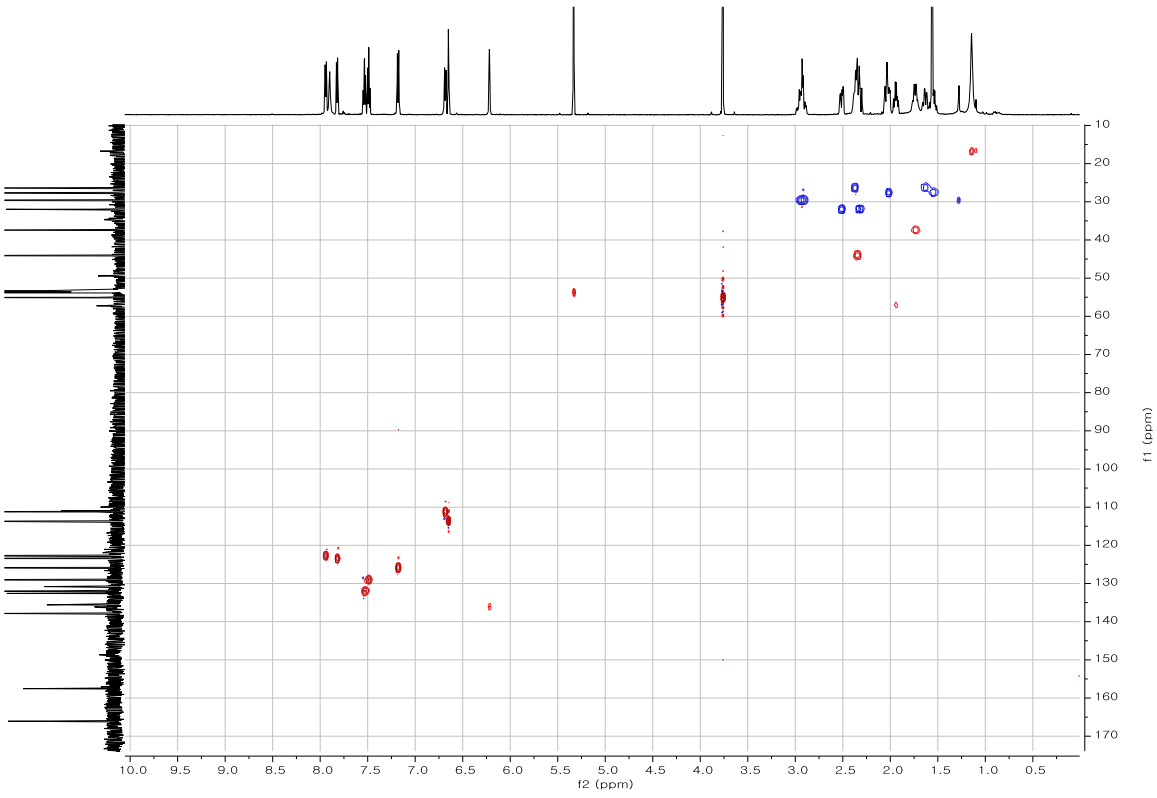



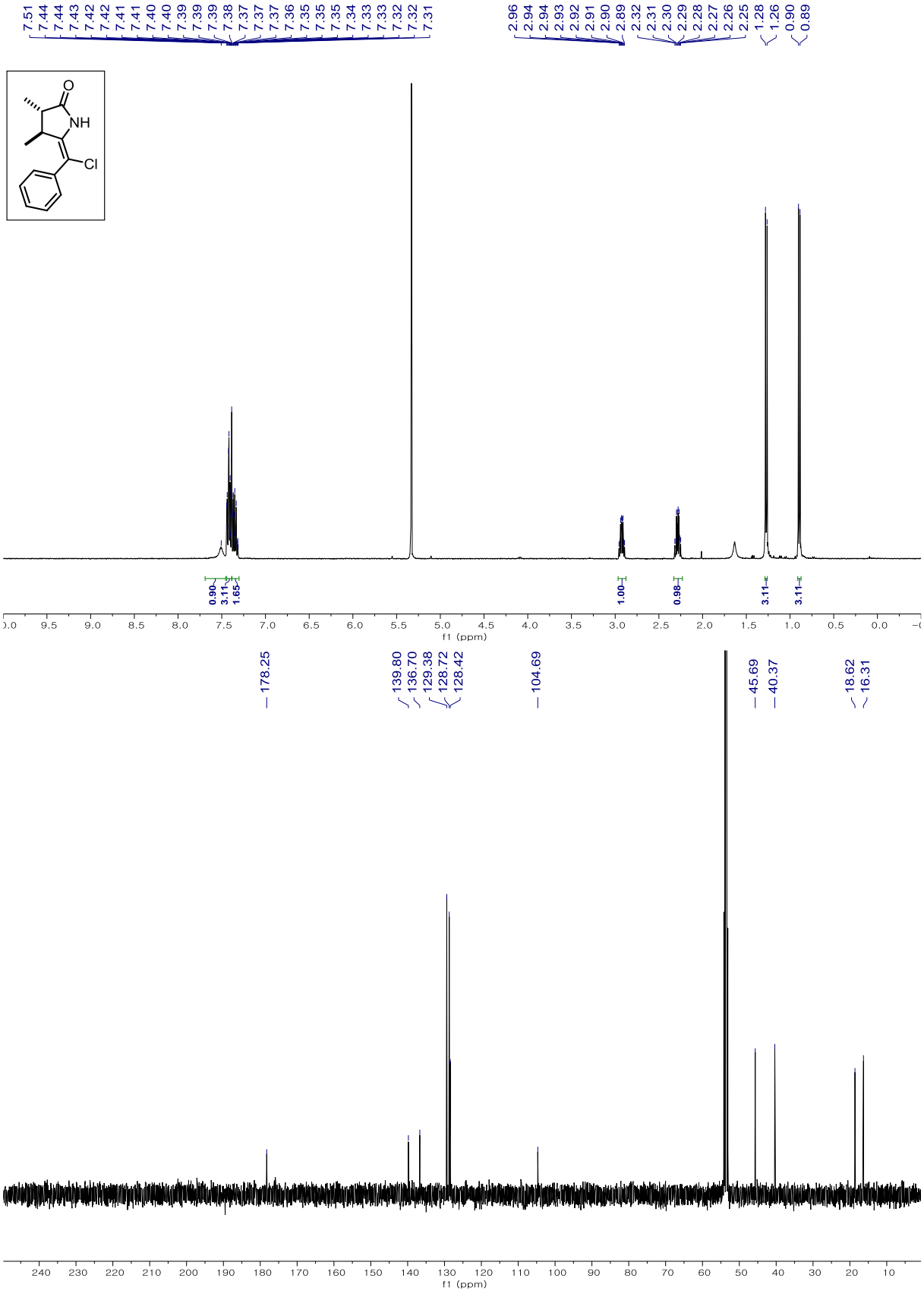
**gCOSY**



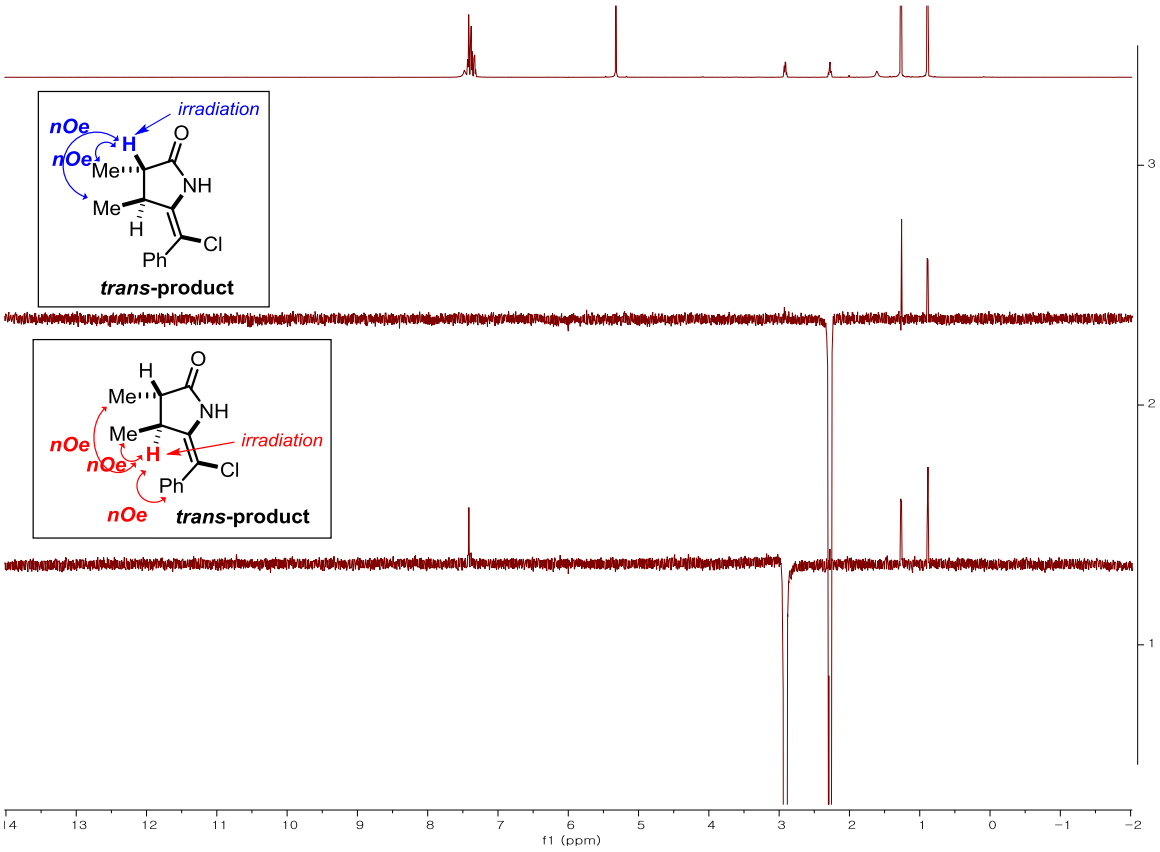

**HSQC**



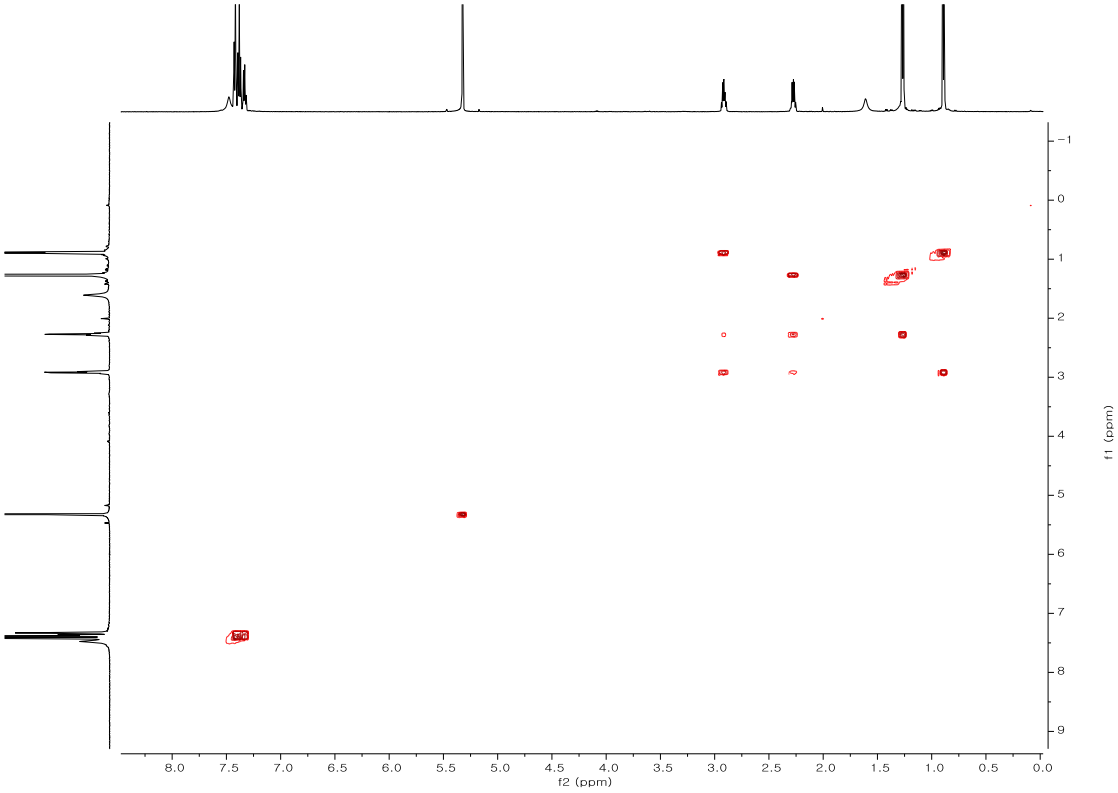
***trans*-(*Z*)-5-{Chloro(phenyl)methylene}-3,4-dimethylpyrrolidin-2-one (18, Table 2)**



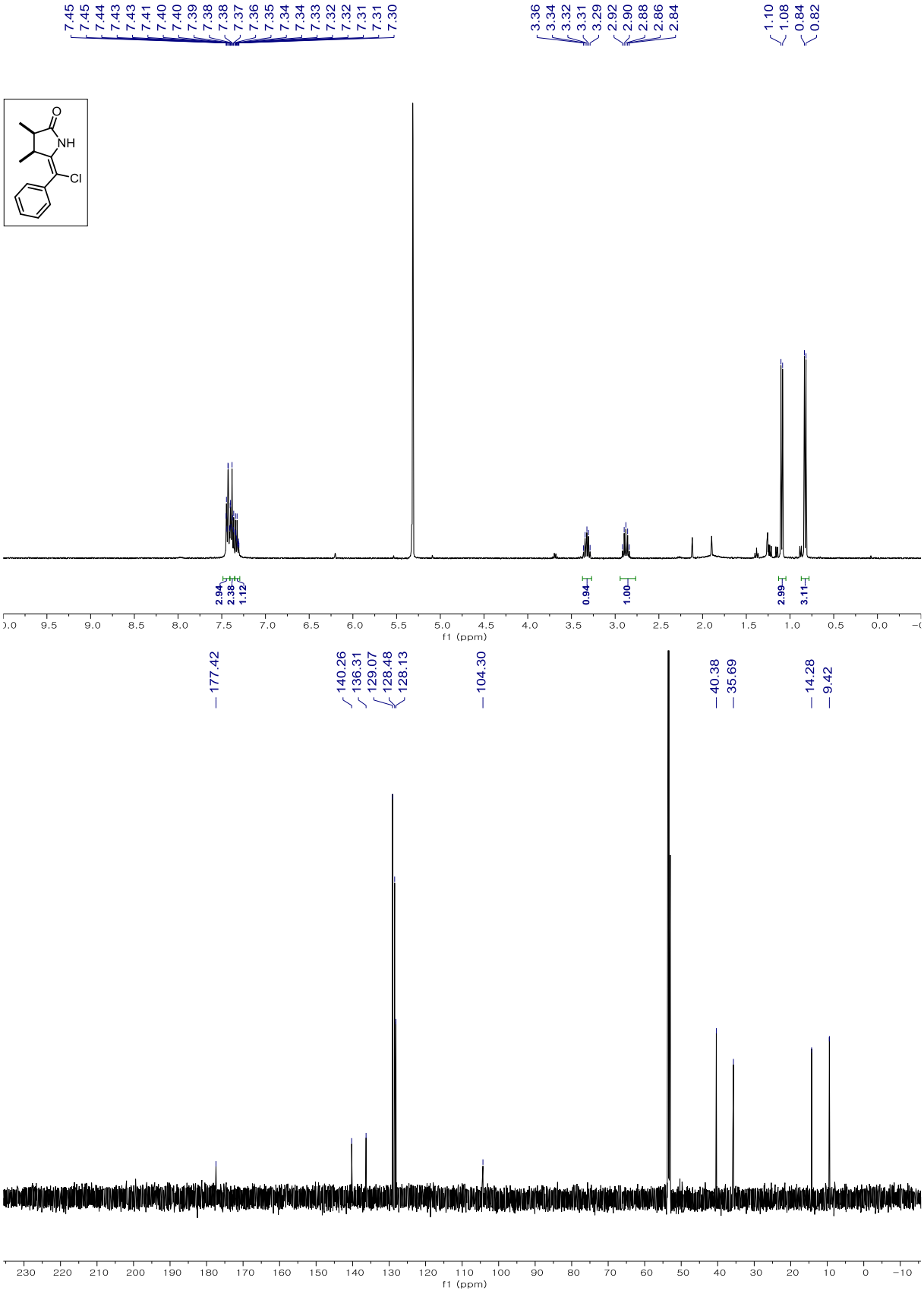
## 1D NOESY



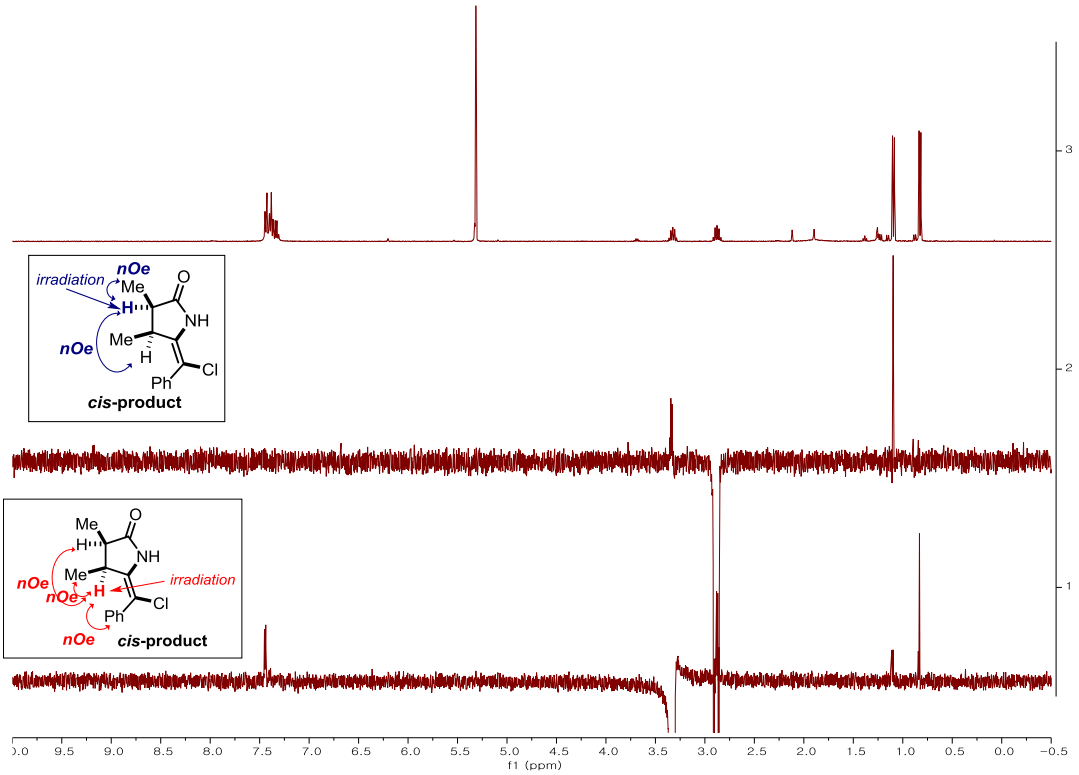

## gCOSY



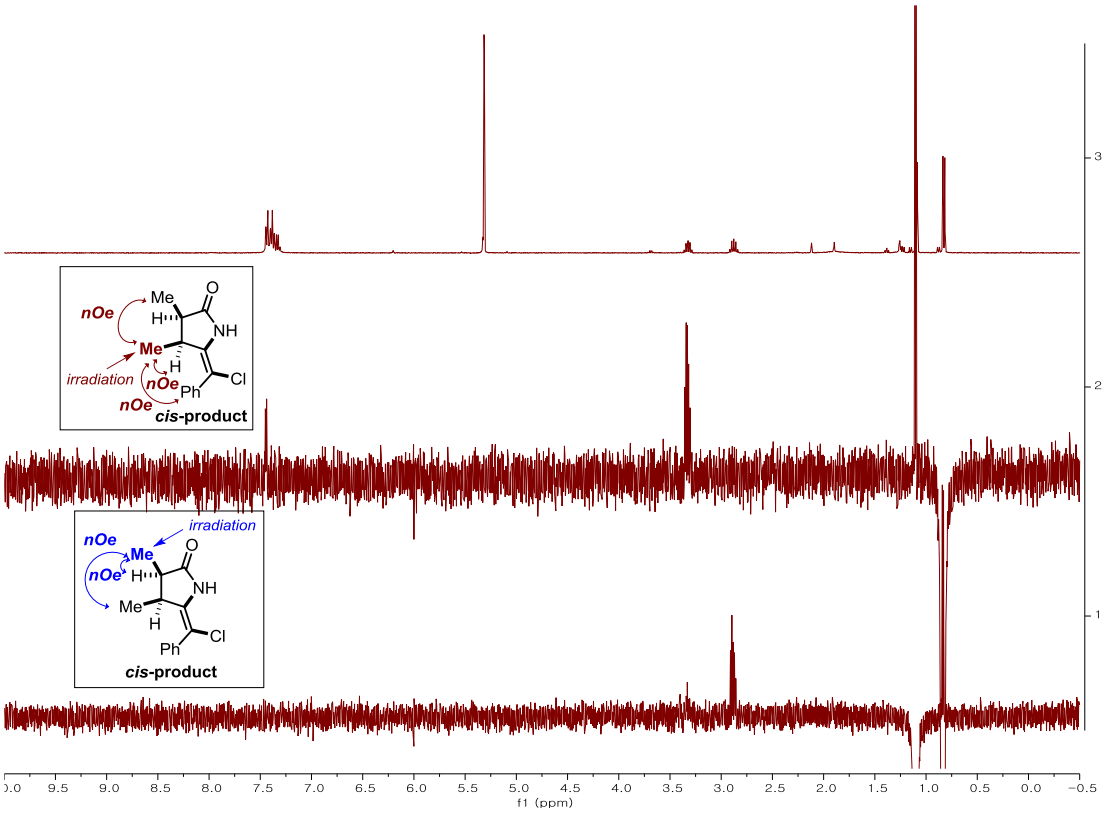
***cis*-(*Z*)-5-{Chloro(phenyl)methylene}-3,4-dimethylpyrrolidin-2-one (20, Table 2)**



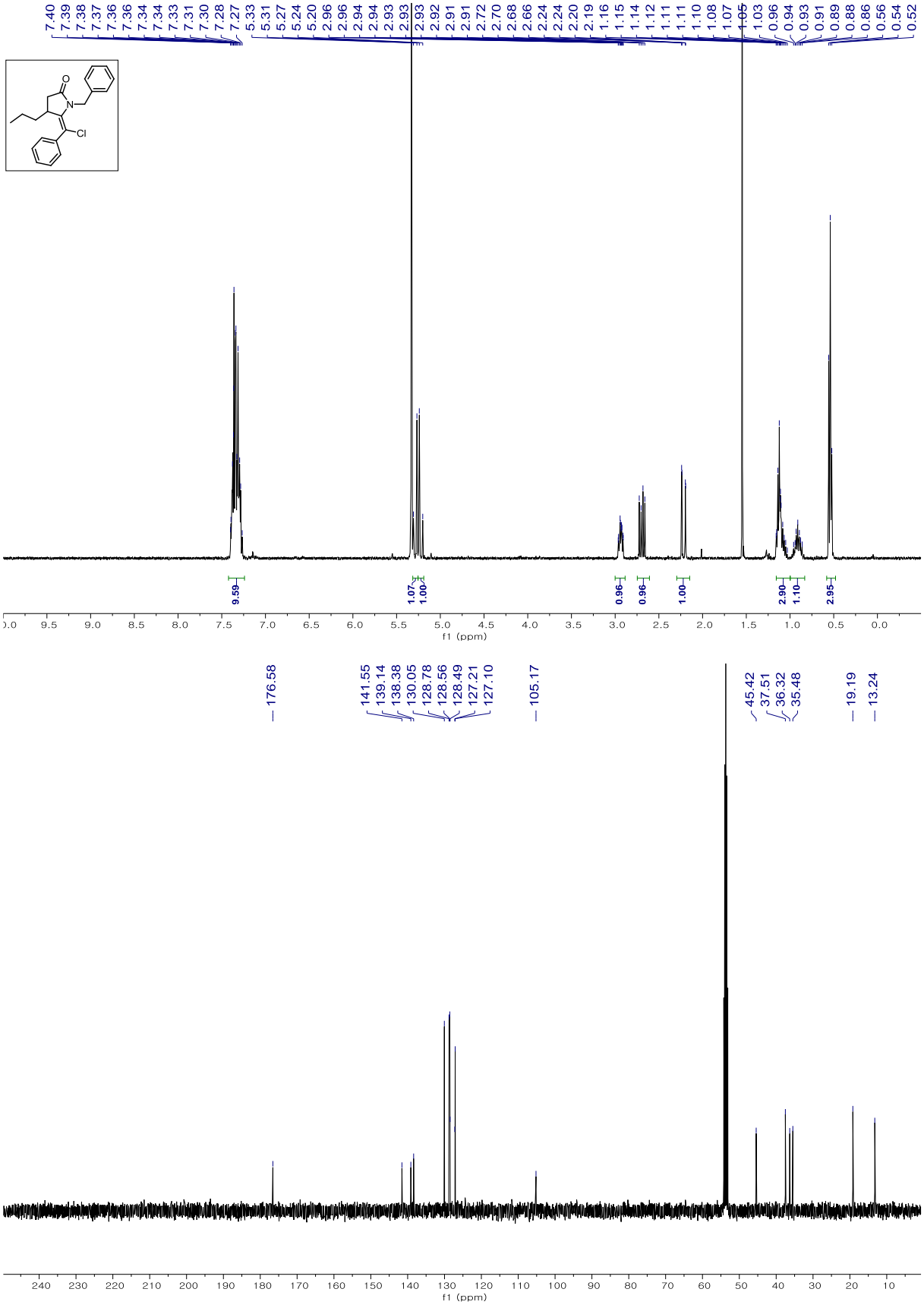
## 1D NOESY-1



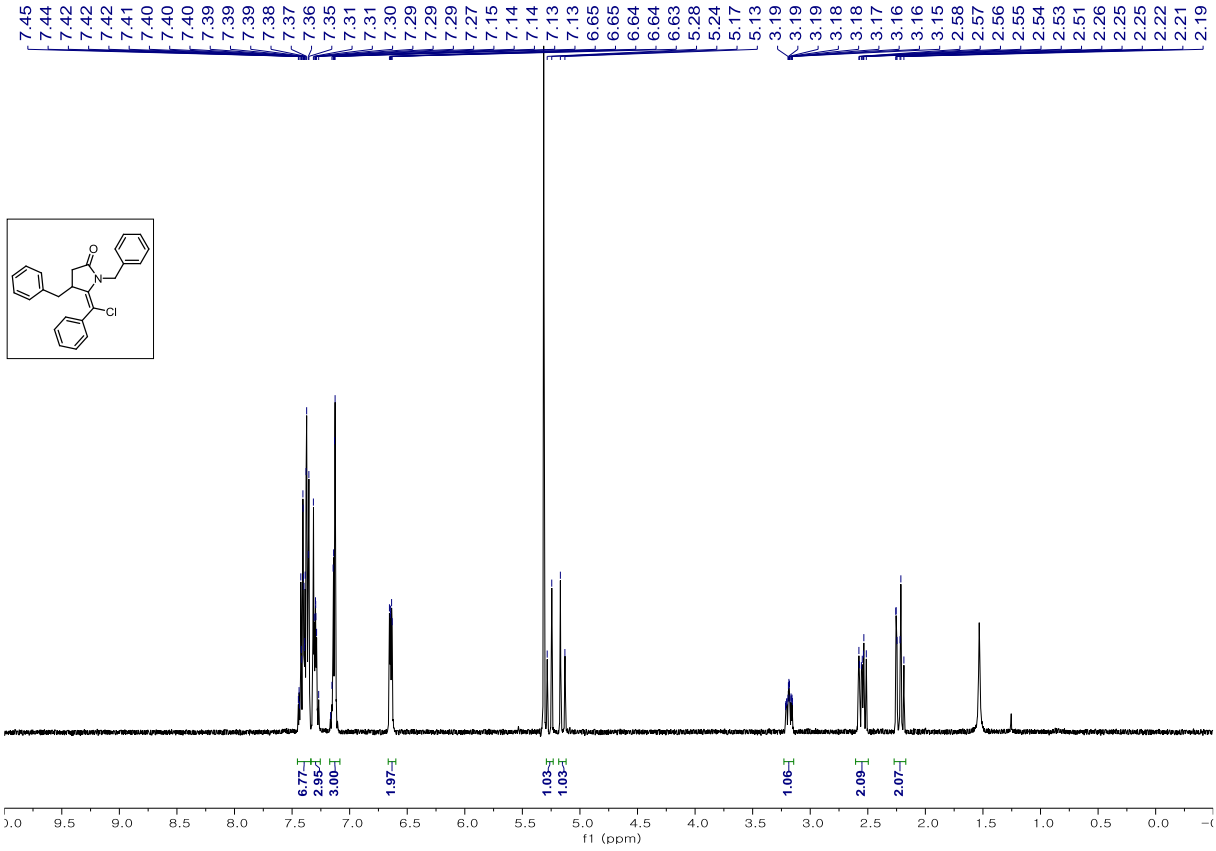

## 1D NOESY-2

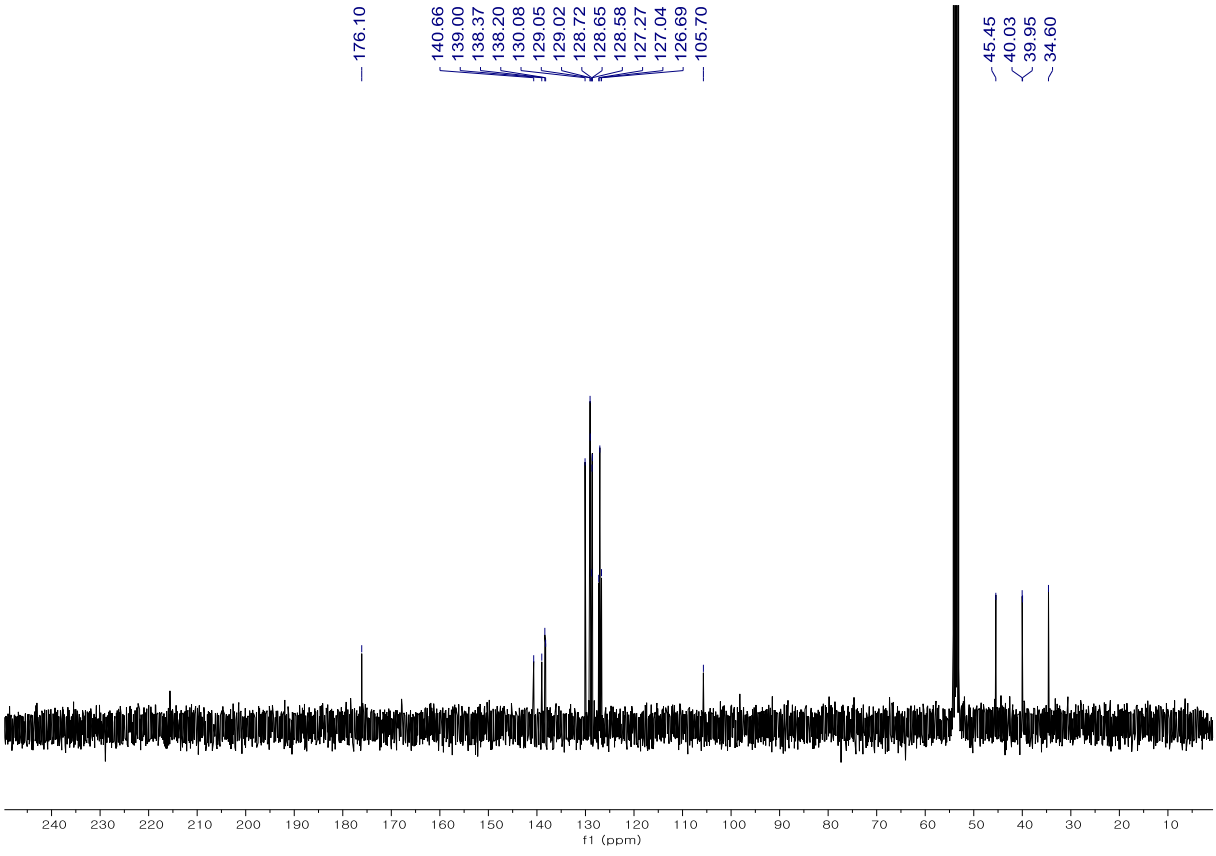


**(*Z*)-1-Benzyl-5-{chloro(phenyl)methylene}-4-propylpyrrolidin-2-one (22, Table 2)**

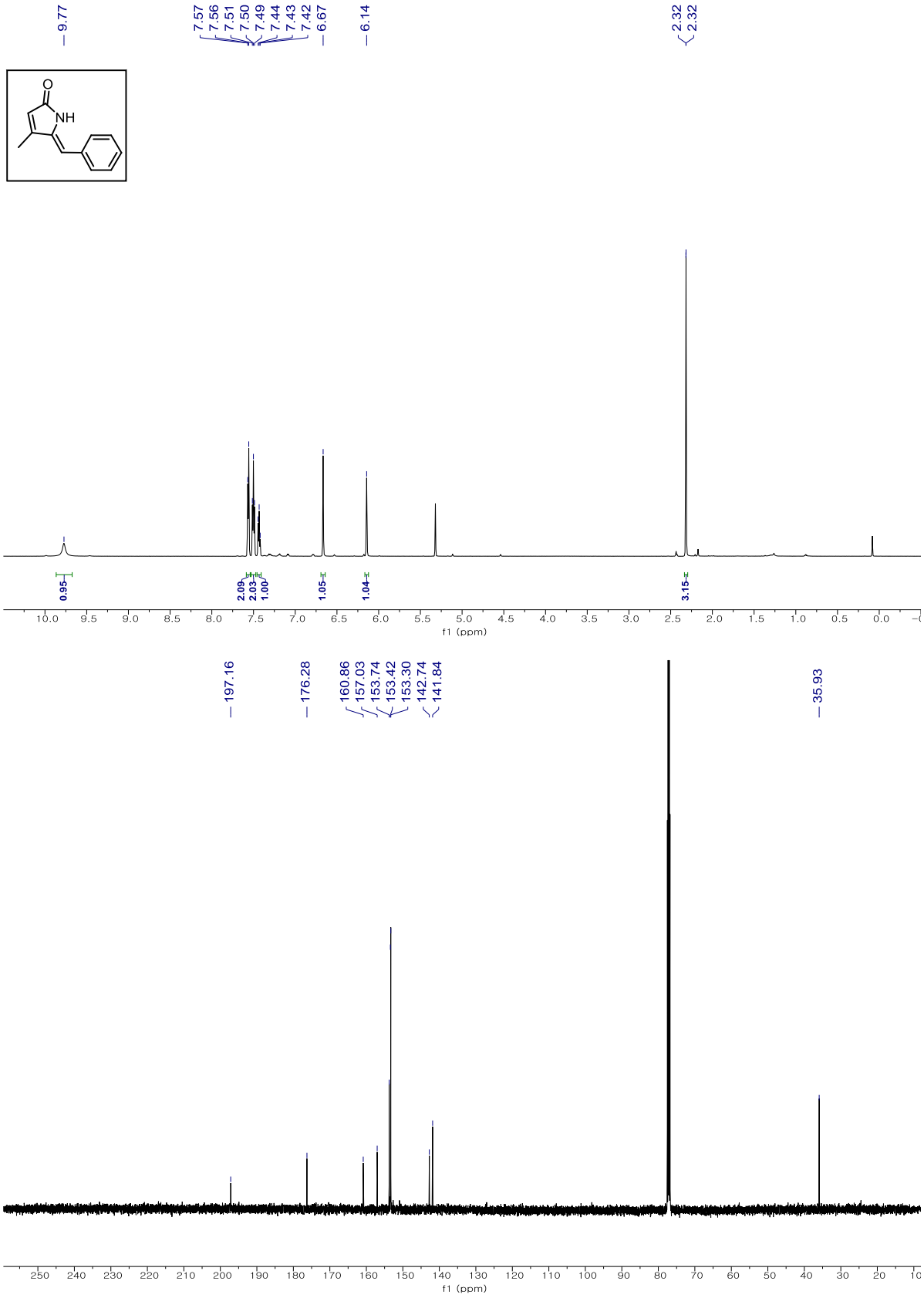


**(*Z*)-1,4-Dibenzyl-5-{chloro(phenyl)methylene}pyrrolidin-2-one (24, Table 2)**

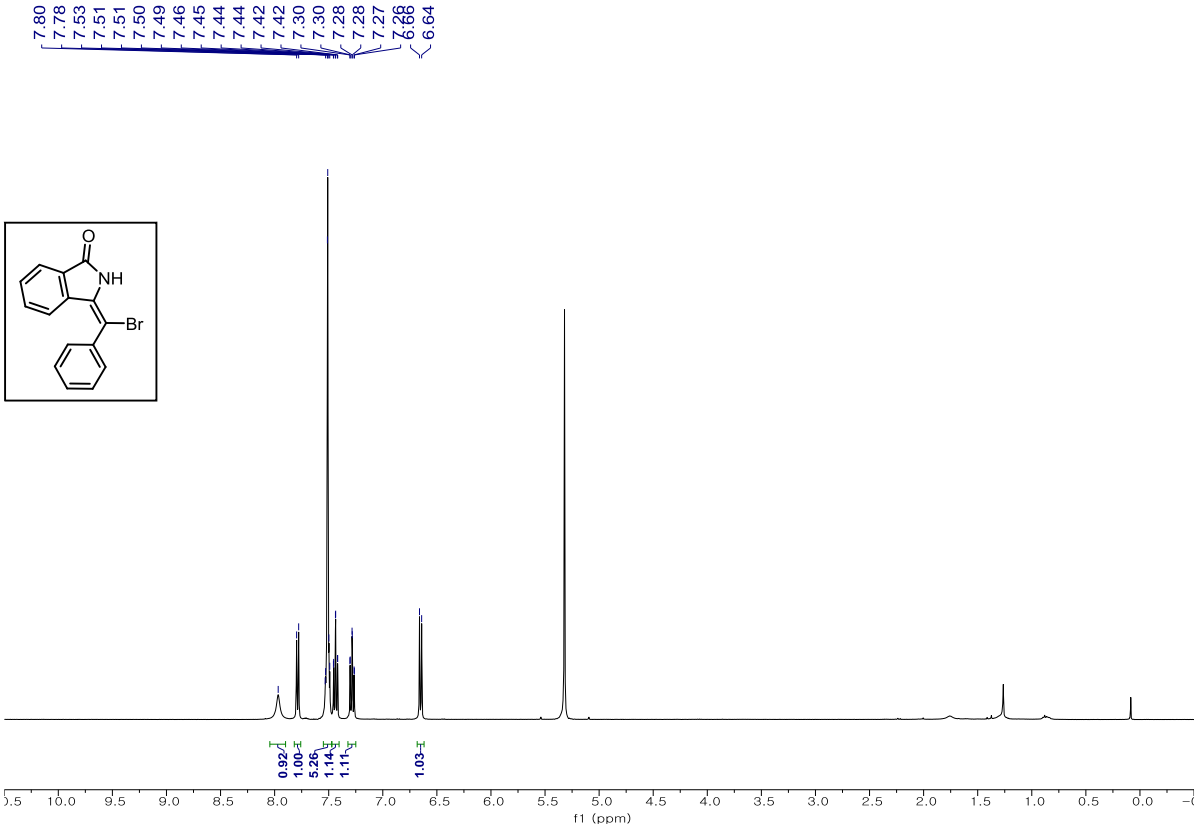


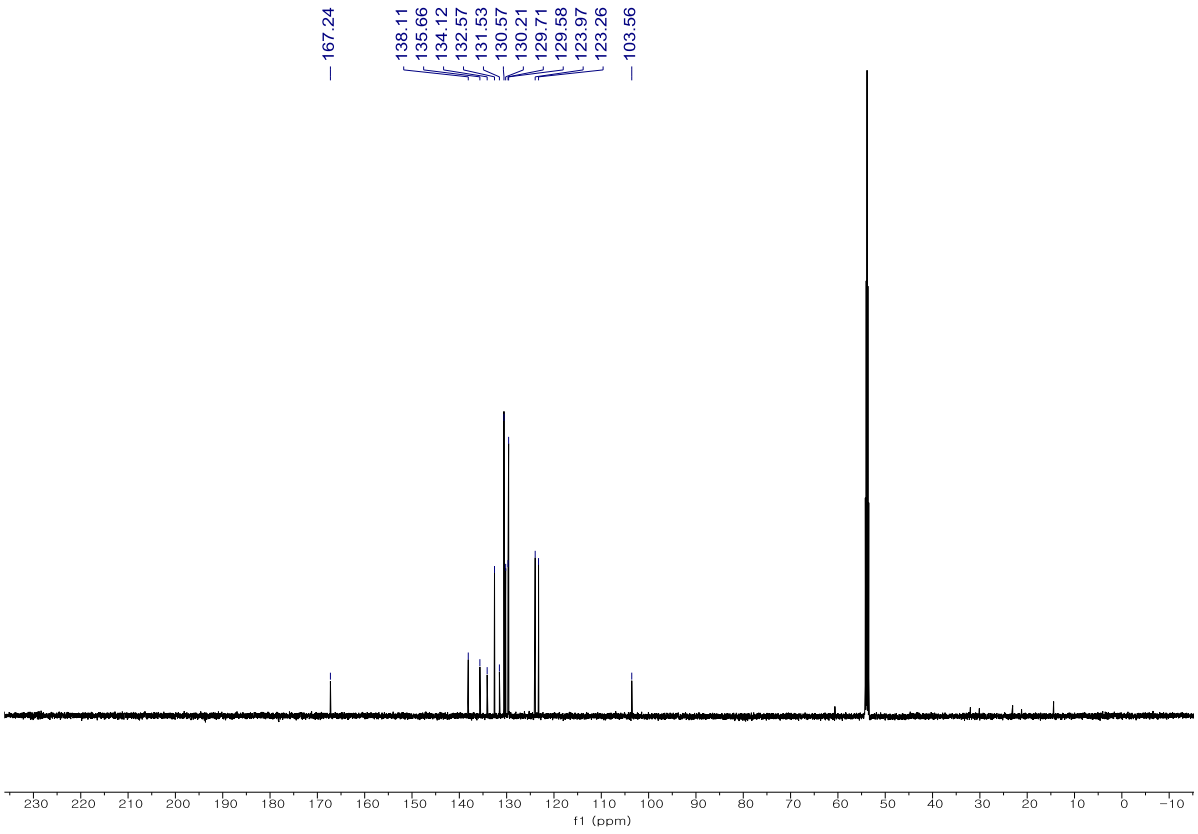



**(*Z*)-5-Benzylidene-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (27, equation 1)**

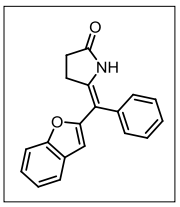


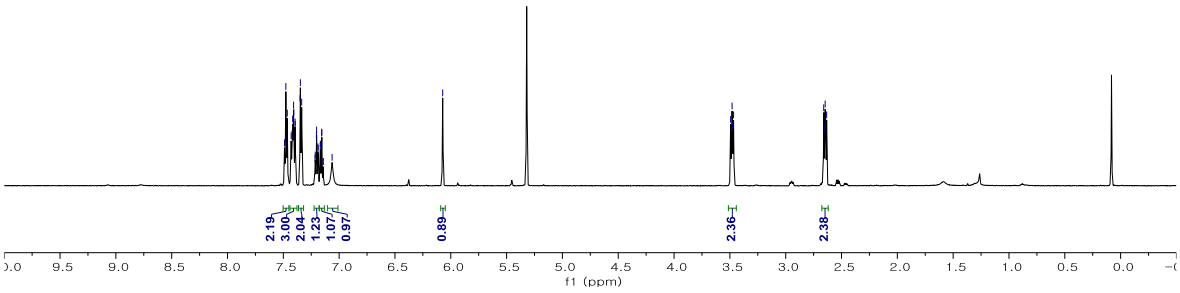
**(*Z*)-3-{Bromo(phenyl)methylene}isoindolin-1-one (29, equation 2)**

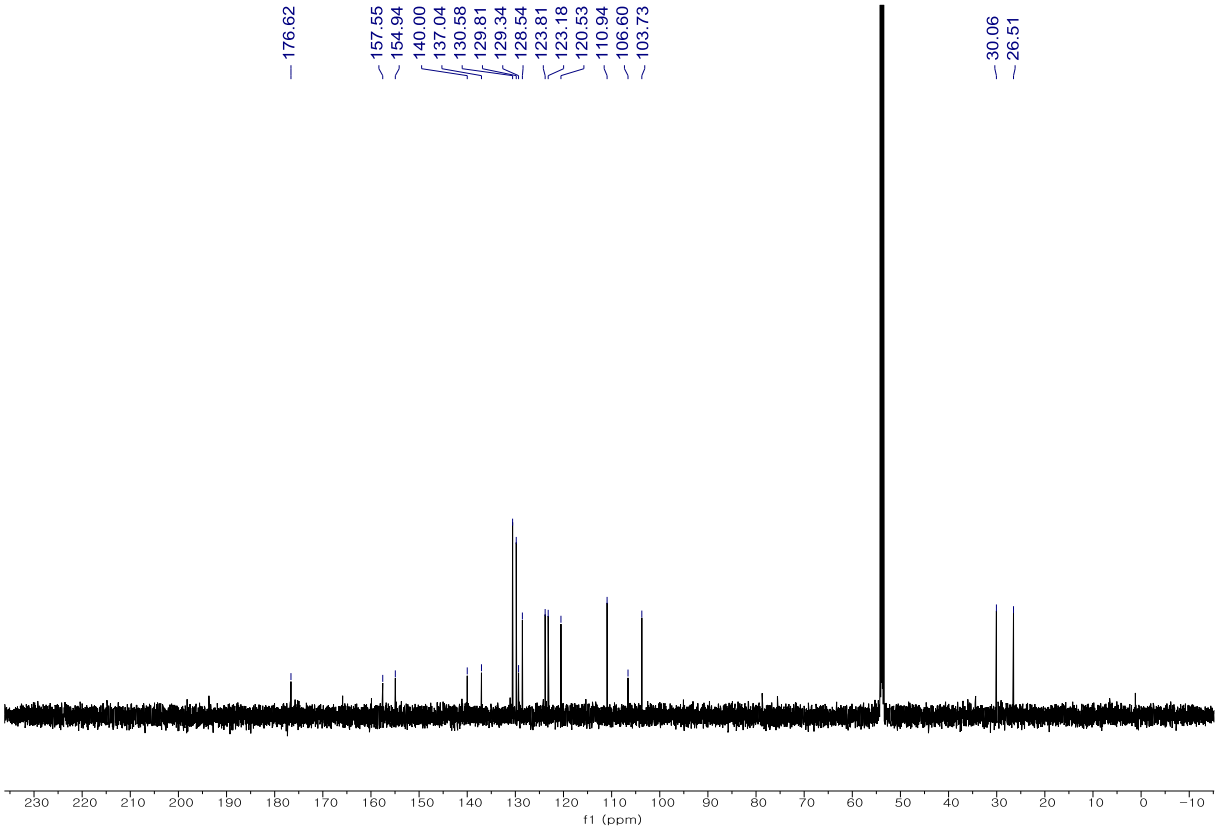


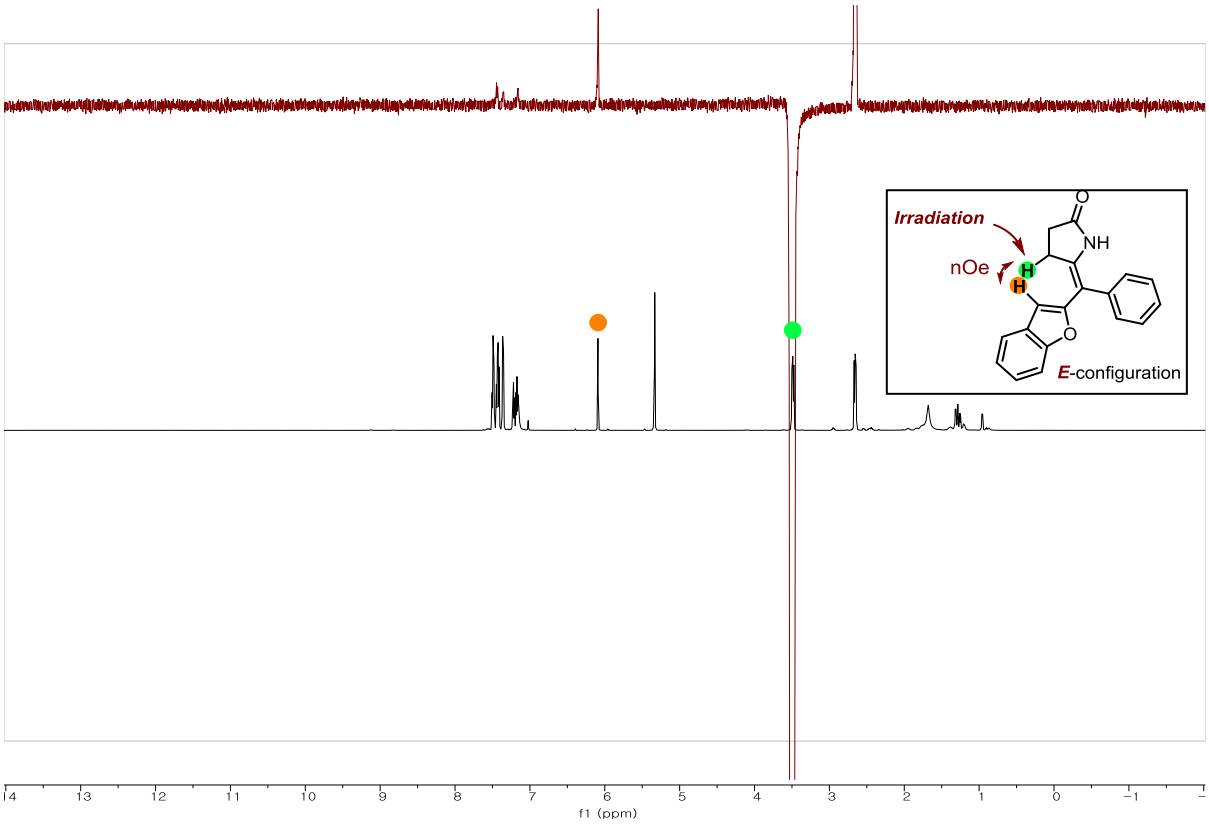
**(*E*)-5-{Benzofuran-2-yl(phenyl)methylene}pyrrolidin-2-one (30, Scheme 4)**

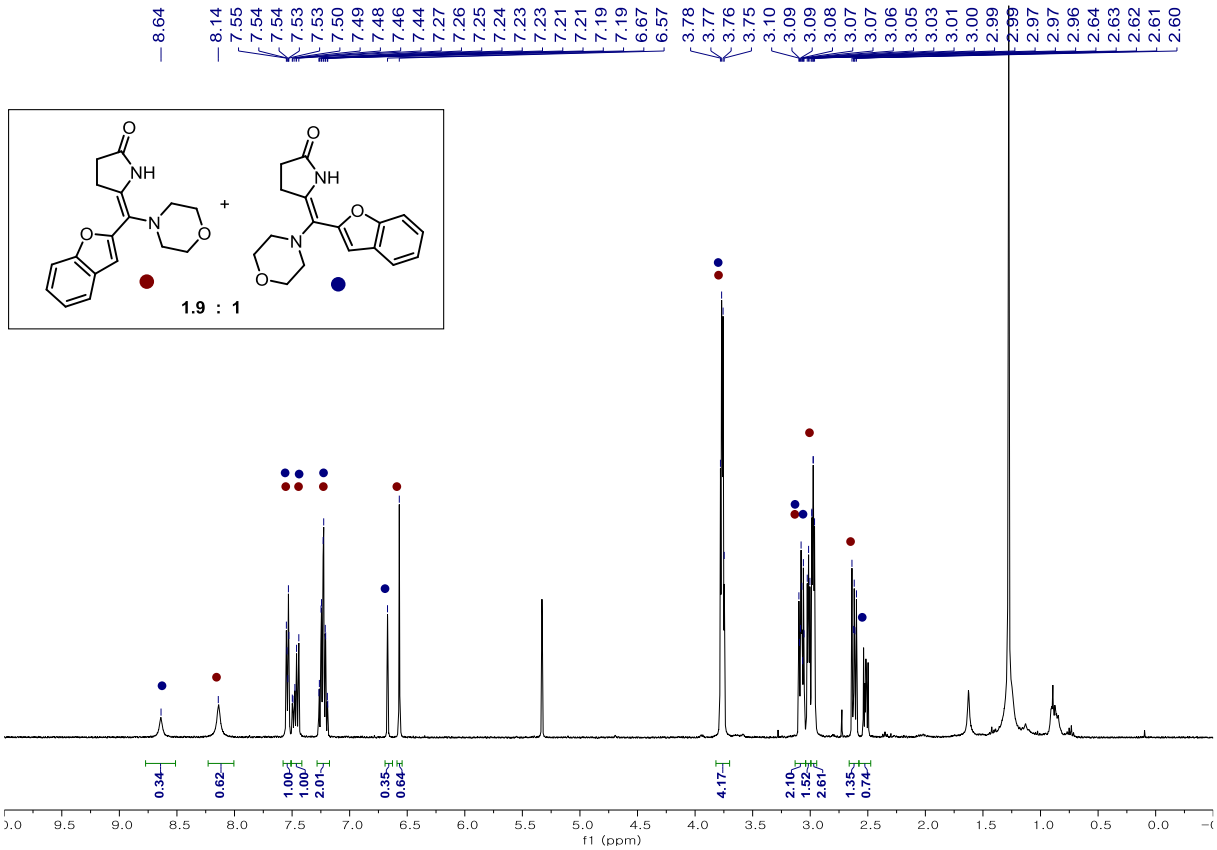



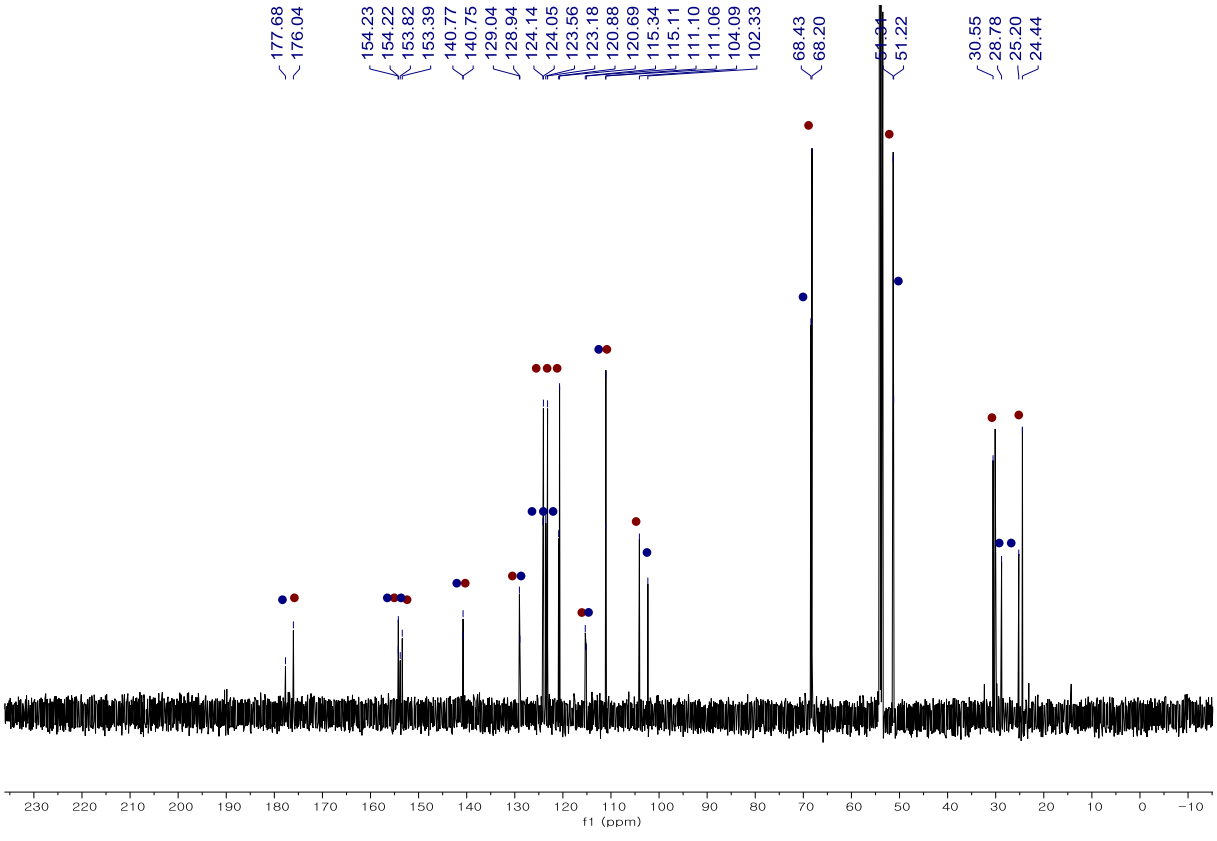



**1D NOESY**

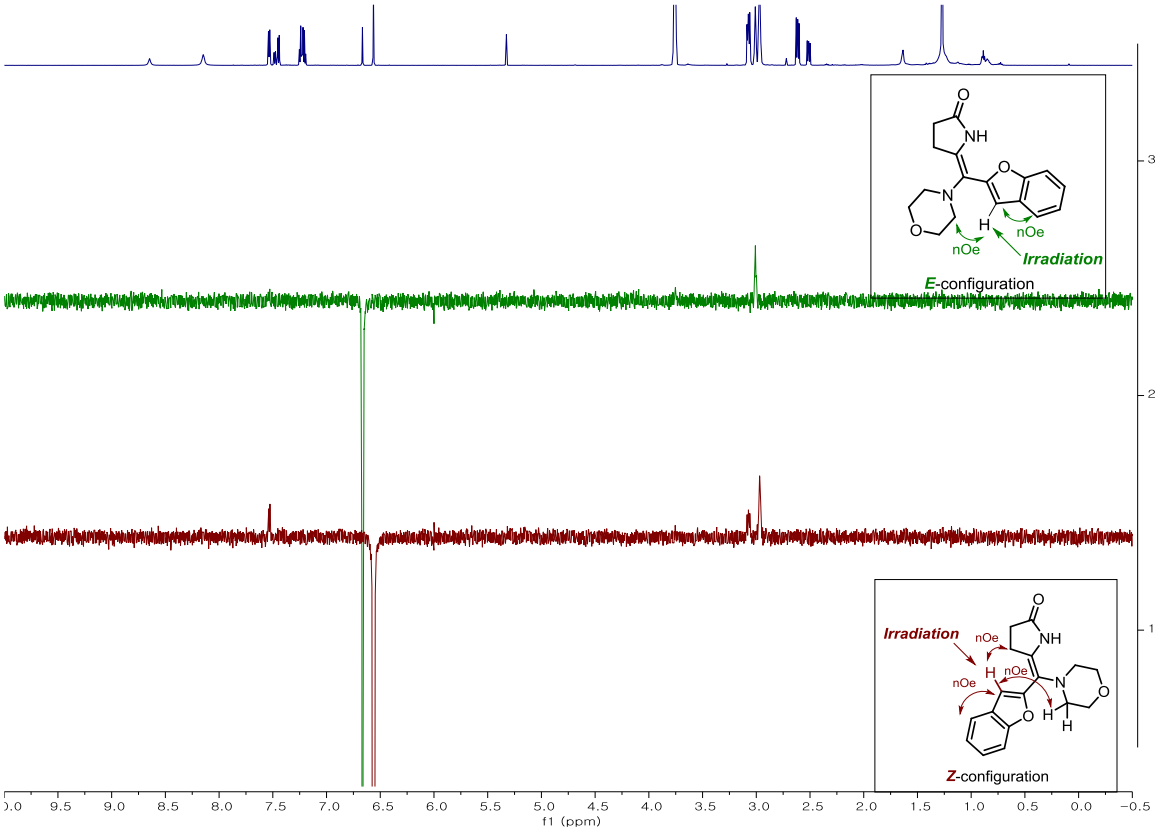

Irradiation
nOe
H
H
O
NH
O
E-configuration
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

**(*E*/*Z*)-5-{Benzofuran-2-yl(morpholino)methylene}pyrrolidin-2-one (31, Scheme 4)**

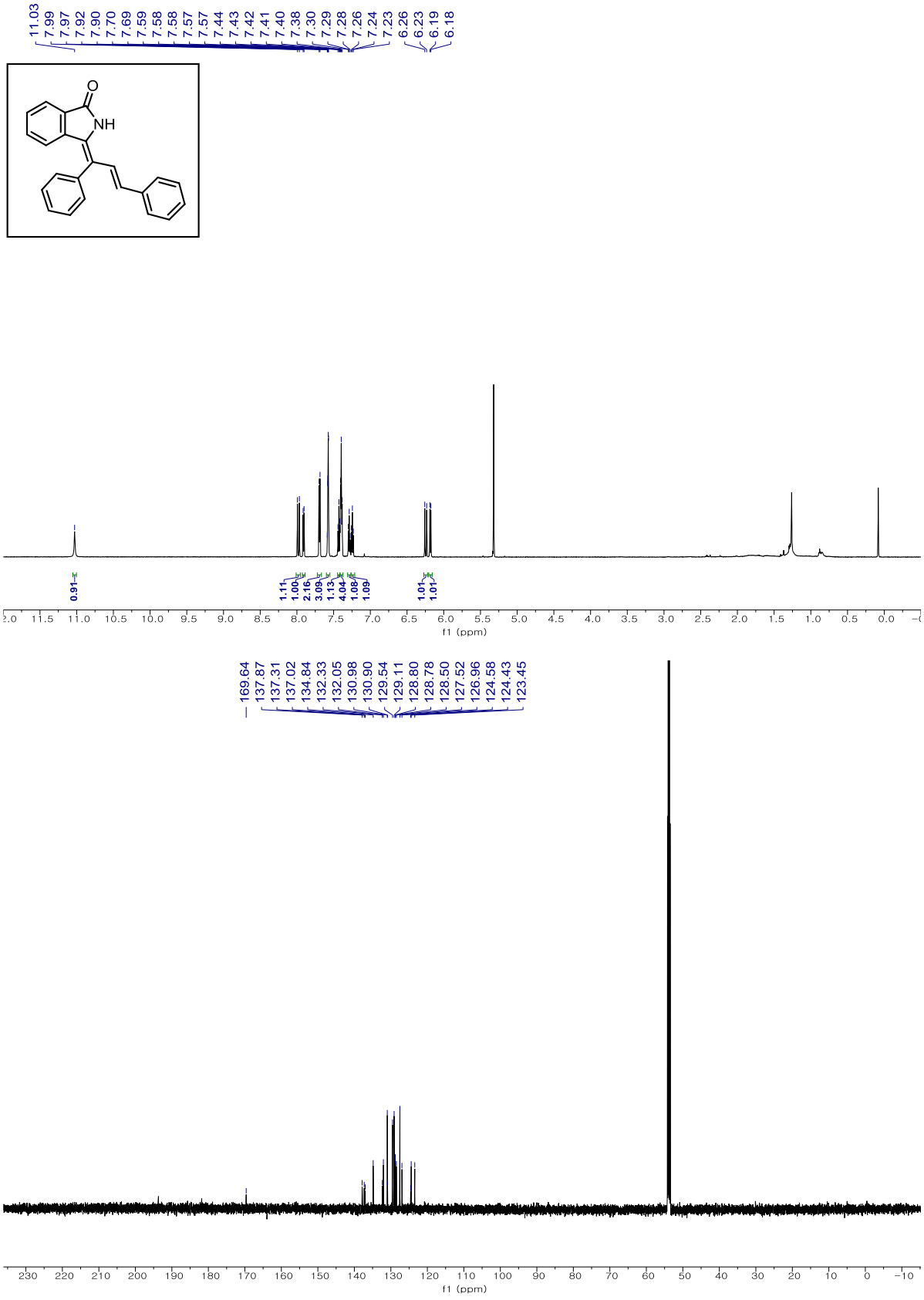


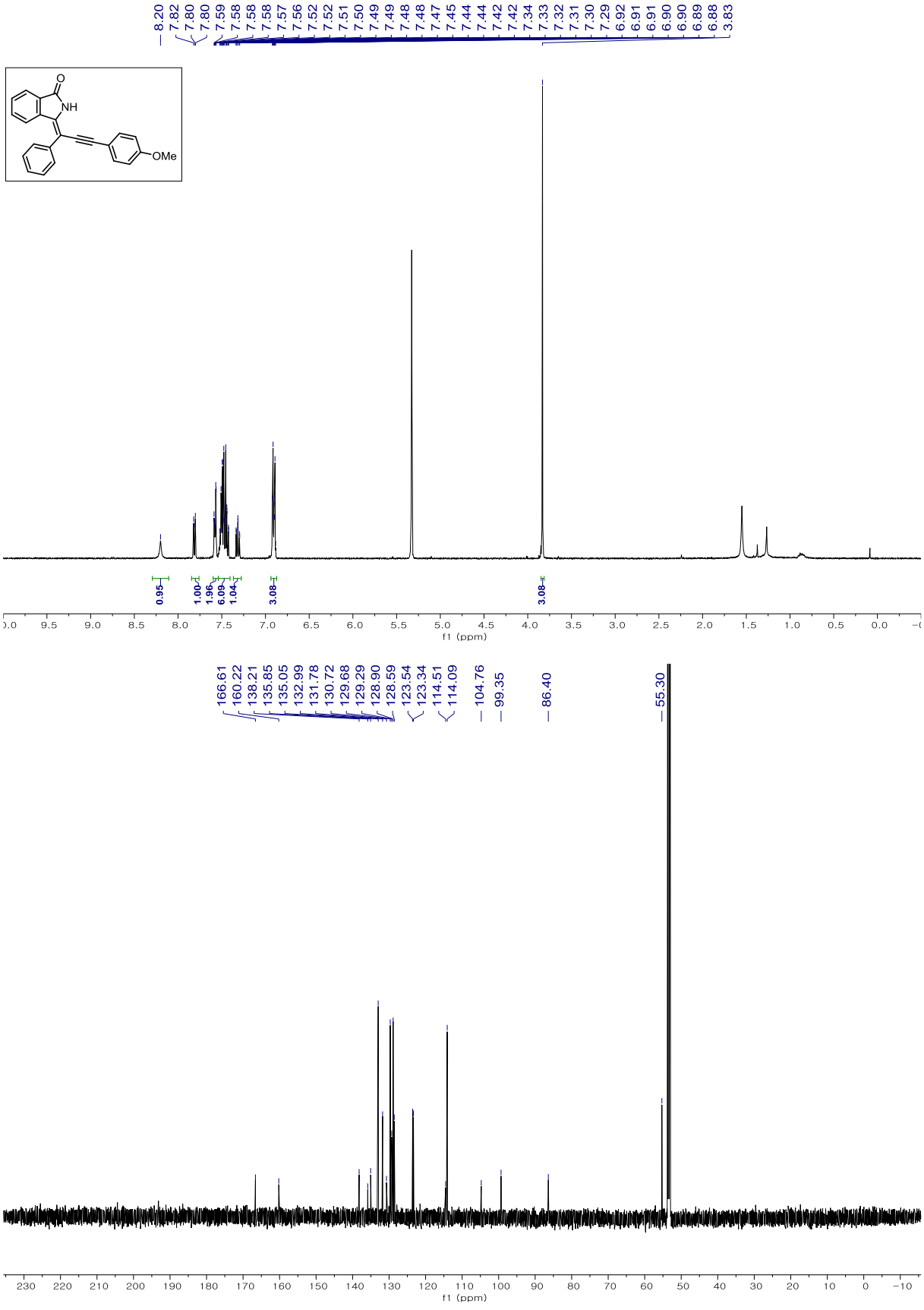
**1D NOESY**


O
NH
O
N
O
H
nOe
nOe
Irradiation
E-configuration
Irradiation
nOe
nOe
nOe
O
NH
H
N
O
H
H
Z-configuration
3
2
1
f1 (ppm)

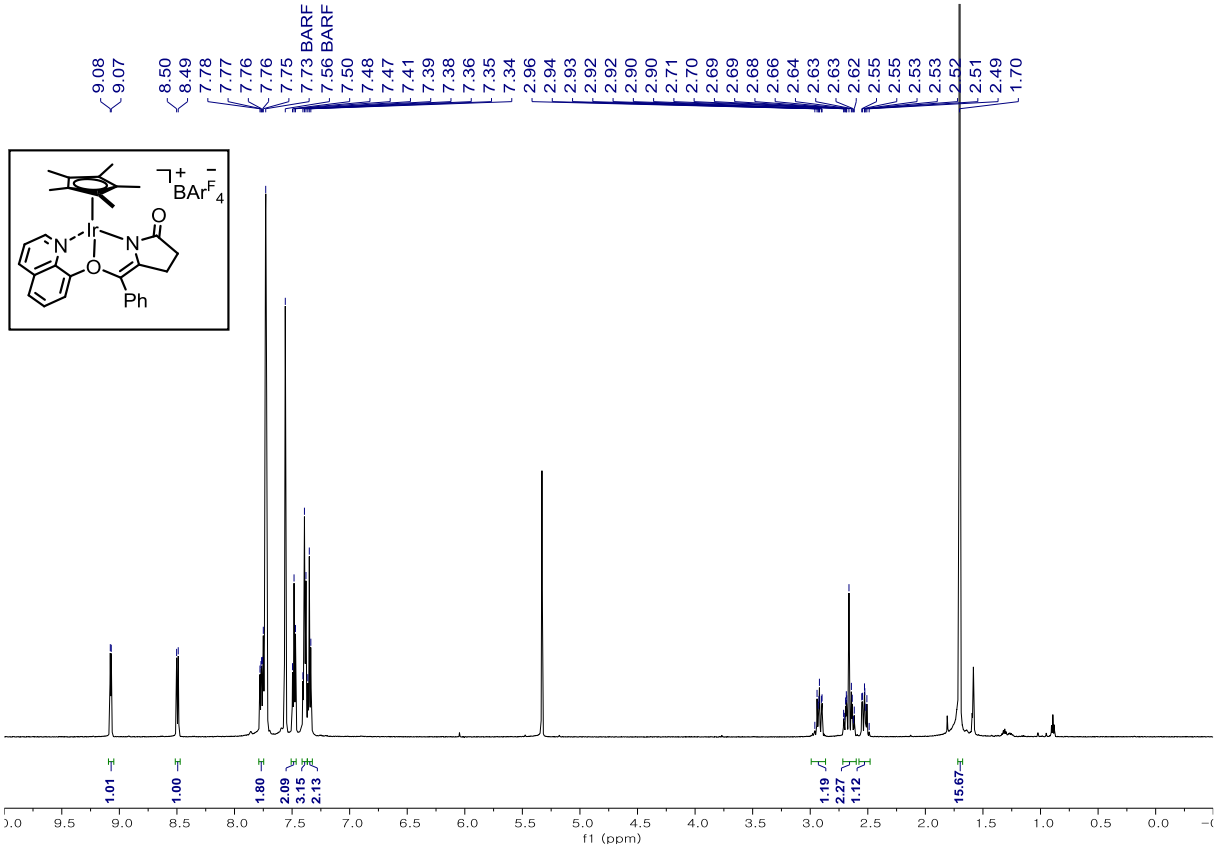
**(*E*)-3-{(*E*)-1,3-diphenylallylidene}isoindolin-1-one (32, Scheme 4)**

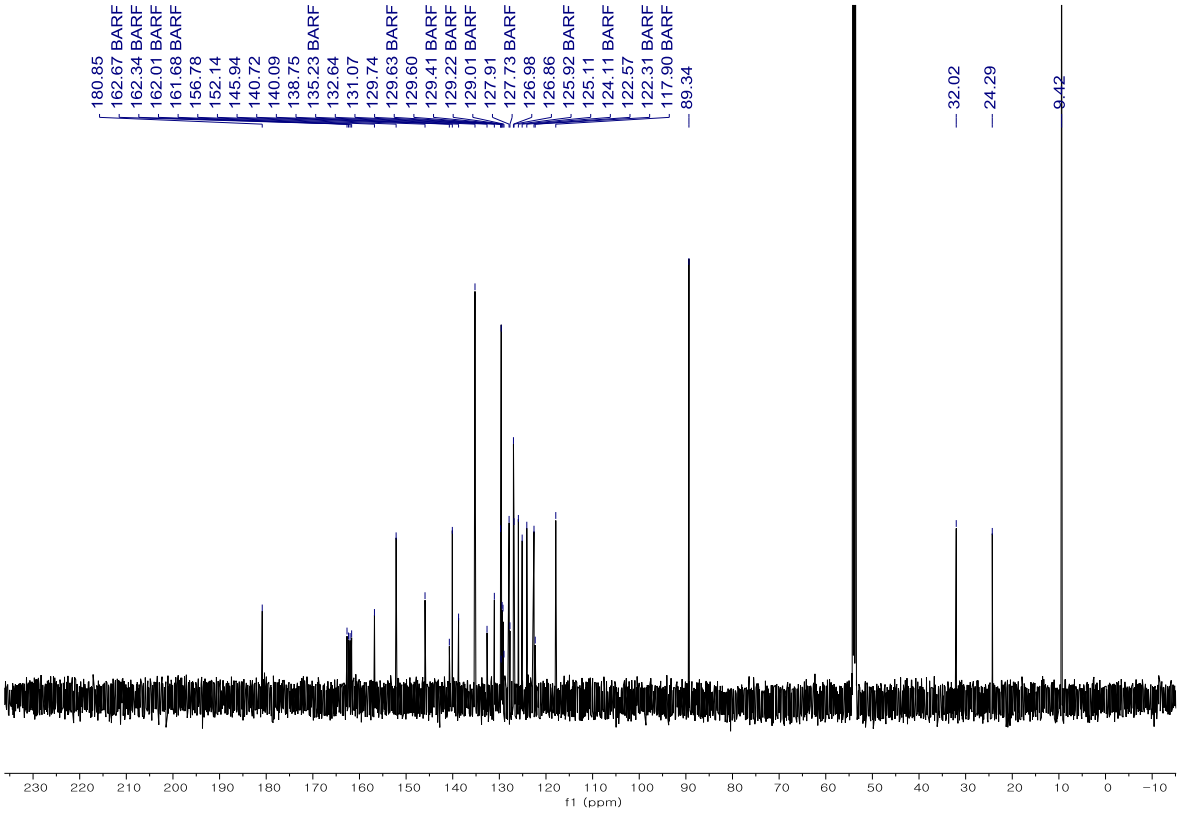


**(*Z*)-3-{3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-ylidene}isoindolin-1-one (33, Scheme 4)**



**Alkyne-inserted iridium complex (II, Scheme 2)**

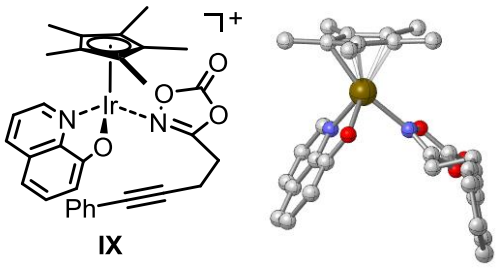


# *Appendix II*

***(Cartesian Coordinates, Structures and Computed Gibbs Free Energies for the Optimized Structures and Transition States)***

**IX (Scheme 2b)**



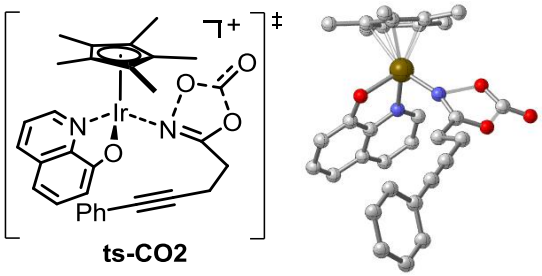

**IX**

Charge: 1, Multiplicity: 1

$G_{sol}$: -1074779.792 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -0.65892100 | -0.65714400 | -0.35947600 |
| C | -2.65187100 | -1.34285700 | -1.12816000 |
| C | -2.30694600 | -2.08438400 | 0.08906500 |
| C | -1.10776200 | -2.82377800 | -0.17023500 |
| C | -0.64434200 | -2.49014900 | -1.50786700 |
| C | -1.65367900 | -1.62170900 | -2.11169900 |
| C | -3.90174000 | -0.54001700 | -1.32491600 |
| H | -4.72885200 | -1.20139000 | -1.61011200 |
| H | -3.78551600 | 0.20812600 | -2.11106800 |
| H | -4.19662900 | -0.02051900 | -0.41077400 |
| C | -3.15364400 | -2.15535600 | 1.32444500 |
| H | -3.64872400 | -1.20257800 | 1.52620100 |
| H | -2.56436400 | -2.42515200 | 2.20297200 |
| H | -3.93796000 | -2.91189800 | 1.20274600 |
| C | -0.38472900 | -3.72926000 | 0.77643800 |
| H | -0.42581700 | -4.75995900 | 0.40669800 |
| H | -0.82695900 | -3.71018000 | 1.77338200 |
| H | 0.66477900 | -3.43736600 | 0.86642400 |
| C | 0.50839500 | -3.13503500 | -2.21862100 |
| H | 0.19106400 | -4.07627100 | -2.68355800 |
| H | 1.32358100 | -3.36041900 | -1.52786800 |
| H | 0.90498600 | -2.49201900 | -3.00741200 |
| C | -1.66274200 | -1.17294700 | -3.53990200 |
| H | -2.13009900 | -1.94822400 | -4.15925300 |
| H | -0.65287400 | -1.01509200 | -3.92434000 |
| H | -2.23743100 | -0.25454800 | -3.67857400 |
| C | 2.01208300 | -0.02300100 | 0.56893000 |
| C | 1.89367300 | 0.76648400 | -0.61072000 |
| N | 0.69396500 | 0.68668800 | -1.27410400 |
| C | 0.49303300 | 1.42392100 | -2.36209800 |
| C | 1.48871300 | 2.27951000 | -2.87417200 |
| C | 2.95598900 | 1.59981600 | -1.06893200 |
| H | -0.47661100 | 1.34268000 | -2.83809800 |
| H | 1.27474100 | 2.86173100 | -3.76329500 |
| H | 0.22832600 | 1.47230200 | 3.58879800 |
| C | -0.55298500 | 0.81805900 | 3.18592600 |
| C | -1.15255800 | 1.50325300 | 2.01575400 |
| H | -0.07199000 | -0.09576200 | 2.83377700 |
| O | -1.72091800 | 2.71835200 | 2.17773200 |
| N | -1.24318000 | 1.08222600 | 0.79353500 |
| O | -1.92048100 | 2.10117800 | 0.07062900 |
| C | -2.21634700 | 3.11782600 | 0.94119300 |
| O | -2.78096900 | 4.12892500 | 0.69500600 |
| C | 4.27172400 | 0.84102500 | 0.80952700 |
| H | 5.19715500 | 0.85546500 | 1.37738700 |
| C | 3.21539800 | 0.02522400 | 1.26775400 |
| H | 3.32854000 | -0.57190900 | 2.16647000 |
| C | 4.16241600 | 1.61896700 | -0.32884300 |
| H | 4.98353700 | 2.24585800 | -0.65984900 |
| C | 2.71048300 | 2.36125200 | -2.23984900 |
| H | 3.49025900 | 3.01146200 | -2.62603800 |
| O | 0.96742200 | -0.75582300 | 0.94819500 |
| C | -1.60074300 | 0.53255900 | 4.30315800 |
| H | -2.05813000 | 1.47660100 | 4.62301600 |
| H | -2.40981700 | -0.08386800 | 3.88992200 |
| C | -0.98587500 | -0.14258000 | 5.43905600 |
| C | -0.45204200 | -0.69447800 | 6.37782600 |
| C | 0.16792800 | -1.33331200 | 7.49687900 |
| C | 0.87933700 | -0.57179800 | 8.44421200 |
| C | 0.07378200 | -2.72788300 | 7.66777900 |
| C | 1.48105100 | -1.19485800 | 9.53436800 |
| H | 0.95022400 | 0.50357900 | 8.31674500 |
| C | 0.67810200 | -3.34208900 | 8.76157200 |
| H | -0.47697300 | -3.31671400 | 6.94118200 |
| C | 1.38254200 | -2.57905400 | 9.69618600 |
| H | 2.02600100 | -0.59946700 | 10.26059600 |
| H | 0.59837100 | -4.41772000 | 8.88681800 |
| H | 1.85151600 | -3.06122700 | 10.54850400 |

**ts-CO2 (Scheme 2b)**

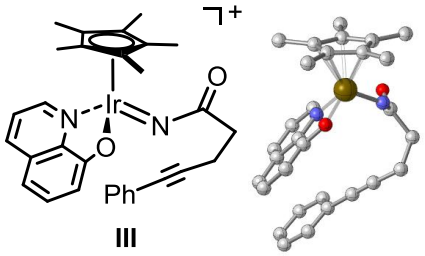



Charge: 1, Multiplicity: 1

$G_{sol}$: -1074760.054 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -1.54926100 | -0.20276800 | -0.48082200 |
| C | -2.44784800 | -2.08284000 | -1.32244900 |
| C | -1.90997400 | -1.30201400 | -2.40439900 |
| C | -2.70401100 | -0.07533200 | -2.50124400 |
| C | -3.65511200 | -0.06491300 | -1.44531500 |
| C | -3.47845800 | -1.29259300 | -0.66911400 |
| C | -2.04403000 | -3.46789200 | -0.92913600 |
| H | -2.77781700 | -4.18042000 | -1.32461200 |
| H | -2.01142800 | -3.57637500 | 0.15650700 |
| H | -1.06782000 | -3.73467900 | -1.33696700 |
| C | -0.87077400 | -1.72371500 | -3.39794700 |
| H | -0.20452800 | -2.48371200 | -2.98631400 |
| H | -0.26187100 | -0.87436400 | -3.71529200 |
| H | -1.35084100 | -2.14569100 | -4.28909800 |
| C | -2.47667600 | 0.98149900 | -3.53206300 |
| H | -2.64545000 | 0.56701900 | -4.53204700 |
| H | -1.44436000 | 1.34191300 | -3.48328400 |
| H | -3.14557800 | 1.83260200 | -3.39941900 |
| C | -4.69465900 | 0.97931400 | -1.17669500 |
| H | -5.65296800 | 0.66893200 | -1.60967200 |
| H | -4.42543400 | 1.94237300 | -1.61330500 |
| H | -4.85070900 | 1.12265500 | -0.10509300 |
| C | -4.37320000 | -1.76783500 | 0.43541200 |
| H | -5.19205300 | -2.36404400 | 0.01389100 |
| H | -4.82288900 | -0.93088000 | 0.97407400 |
| H | -3.82737600 | -2.38212800 | 1.15294400 |
| C | -0.37652800 | 2.42625100 | -0.51310500 |
| C | -1.07622100 | 2.41624500 | 0.72226300 |
| N | -1.71734400 | 1.24814500 | 1.03923200 |
| C | -2.34170000 | 1.11784300 | 2.20565000 |
| C | -2.40678000 | 2.19114800 | 3.11812400 |
| C | -1.09829500 | 3.54425400 | 1.58800900 |
| H | -2.77003700 | 0.14678300 | 2.42638400 |
| H | -2.93216300 | 2.04878800 | 4.05556500 |
| H | 2.30715500 | -0.04517500 | 1.55903000 |
| C | 1.99148100 | -0.84791100 | 0.88239900 |
| C | 0.65014000 | -1.34829400 | 1.41633500 |
| H | 1.86293900 | -0.41755000 | -0.11224100 |
| O | 0.67032500 | -2.00116300 | 2.52878500 |
| N | -0.38410200 | -1.10088100 | 0.69005900 |
| C | -0.78134400 | -2.48054300 | 3.04338500 |
| O | -1.61843900 | -2.11694100 | 2.18888000 |
| O | -0.72308400 | -3.05074500 | 4.08673300 |
| C | -0.42057100 | 4.71598400 | 1.16853100 |
| H | -0.42850500 | 5.59493200 | 1.80432000 |
| C | 0.24044600 | 4.72367300 | -0.04628800 |
| H | 0.76011200 | 5.62217200 | -0.36417900 |
| C | 0.27212000 | 3.59404500 | -0.89447500 |
| H | 0.81421800 | 3.62127400 | -1.83351500 |
| C | -1.80146500 | 3.39266600 | 2.81098100 |
| H | -1.84888200 | 4.22603500 | 3.50602000 |
| O | -0.34937400 | 1.29473000 | -1.22963100 |
| C | 3.05814500 | -1.97545500 | 0.87296100 |
| H | 3.11254200 | -2.41870200 | 1.87291000 |
| H | 2.74252000 | -2.77255300 | 0.18797100 |
| C | 4.35307600 | -1.44125000 | 0.47635800 |
| C | 5.42214500 | -0.96047600 | 0.15887300 |
| C | 6.69254100 | -0.41732900 | -0.19914500 |
| C | 7.08403500 | -0.34066000 | -1.55082900 |
| C | 7.57358900 | 0.04610600 | 0.79883000 |
| C | 8.32606500 | 0.18723000 | -1.89121100 |
| H | 6.40880800 | -0.70095400 | -2.32029000 |
| C | 8.81347600 | 0.57229700 | 0.44846200 |
| H | 7.27538800 | -0.01599300 | 1.84035700 |
| C | 9.19284600 | 0.64456000 | -0.89474900 |
| H | 8.62115300 | 0.24019500 | -2.93478900 |
| H | 9.48704600 | 0.92462700 | 1.22369900 |
| H | 10.16187900 | 1.05377100 | -1.16390800 |

**III (Scheme 2b)**



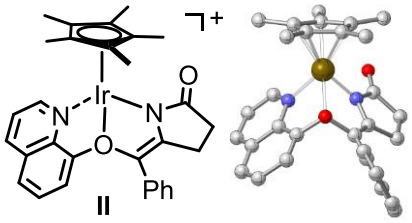

**III**

Charge: 1, Multiplicity: 1

$G_{sol}$: -956466.8225 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -0.86479000 | 0.27653100 | 0.36299600 |
| C | -2.96265400 | -0.59823700 | -0.03232700 |
| C | -3.13383000 | 0.59379000 | 0.74224200 |
| C | -2.52108200 | 0.36731000 | 2.04743600 |
| C | -1.88266000 | -0.90568700 | 2.03905900 |
| C | -2.11674800 | -1.50840600 | 0.71881800 |
| C | -3.51716400 | -0.85736000 | -1.39338700 |
| H | -4.51038800 | -1.31273700 | -1.29503200 |
| H | -2.88156100 | -1.54056500 | -1.95862200 |
| H | -3.62349700 | 0.06502100 | -1.96642200 |
| C | -3.94435700 | 1.79754200 | 0.37211400 |
| H | -4.97094700 | 1.68879500 | 0.74330100 |
| H | -3.99375000 | 1.92987100 | -0.70996700 |
| H | -3.52601600 | 2.70722300 | 0.80821000 |
| C | -2.51953600 | 1.37302700 | 3.15080200 |
| H | -3.54019500 | 1.71630800 | 3.34745600 |
| H | -1.91606400 | 2.24277200 | 2.86667900 |
| H | -2.11218000 | 0.96108700 | 4.07489400 |
| C | -1.18209200 | -1.57476300 | 3.18214700 |
| H | -1.86830300 | -2.26129300 | 3.69209100 |
| H | -0.82285800 | -0.85128200 | 3.91579500 |
| H | -0.32602900 | -2.15957900 | 2.83836800 |
| C | -1.78446000 | -2.91398200 | 0.31932100 |
| H | -2.66658700 | -3.55268200 | 0.44863000 |
| H | -0.98718800 | -3.32612500 | 0.94066100 |
| H | -1.46753000 | -2.96327600 | -0.72478500 |
| C | 1.87228900 | 0.62427600 | 1.28354700 |
| N | 1.13629600 | -0.31070500 | 0.60044100 |
| C | 1.70884100 | -1.44999700 | 0.21638700 |
| C | 3.05784700 | -1.72538100 | 0.51430800 |
| C | 3.23935100 | 0.42463800 | 1.60798200 |
| H | 1.10212700 | -2.13029800 | -0.36742100 |
| H | 3.48177400 | -2.66432300 | 0.17794400 |
| C | 0.06351900 | -0.40489400 | -2.39851400 |
| O | 0.09997800 | -1.64211900 | -2.35687200 |
| N | -0.67831200 | 0.29214900 | -1.49143900 |
| C | 3.91033100 | 1.45453700 | 2.31619000 |
| C | 1.18207100 | 1.80107400 | 1.65773100 |
| C | 1.85971800 | 2.78676800 | 2.35719300 |
| H | 1.34091600 | 3.69485800 | 2.64441000 |
| C | 3.22557400 | 2.60026200 | 2.67357600 |
| H | 3.74287400 | 3.38568300 | 3.21551700 |
| C | 0.63233100 | 0.40795900 | -3.55229100 |
| H | -0.21547100 | 0.76990300 | -4.14569200 |
| H | 1.20520400 | -0.28617300 | -4.17184700 |
| H | 4.95729300 | 1.32826800 | 2.56995400 |
| C | 3.82085700 | -0.79999700 | 1.19547300 |
| H | 4.86755200 | -0.99501300 | 1.40740900 |
| O | -0.10981100 | 1.89746000 | 1.29284800 |
| C | 2.79828300 | 1.24473700 | -2.57898200 |
| C | 3.90336400 | 0.93474700 | -2.18456200 |
| C | 5.20927300 | 0.57481000 | -1.72482300 |
| C | 5.75908600 | -0.68174600 | -2.04770600 |
| C | 5.96688800 | 1.46965400 | -0.94348400 |
| C | 7.02857900 | -1.03296900 | -1.59377600 |
| H | 5.18502700 | -1.36916000 | -2.66105800 |
| C | 7.23645600 | 1.11059300 | -0.49471000 |
| H | 5.55294000 | 2.44334600 | -0.70209200 |
| C | 7.77036400 | -0.14067900 | -0.81469100 |
| H | 7.44421400 | -2.00156800 | -1.85550900 |
| H | 7.81540700 | 1.81279200 | 0.09814000 |
| H | 8.76232700 | -0.41446200 | -0.46829700 |
| C | 1.49802400 | 1.62018600 | -3.13415300 |
| H | 0.94234000 | 2.24186800 | -2.42032600 |
| H | 1.65678100 | 2.24759500 | -4.02019300 |

**II (Scheme 2b)**



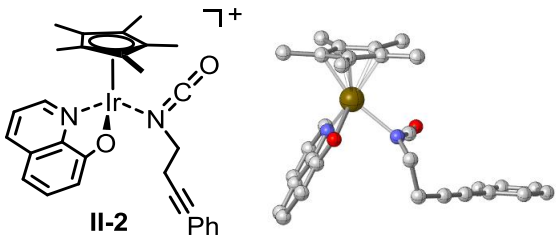

II

Charge: 1, Multiplicity: 1

$G_{sol}$: -956531.8418 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -1.02115600 | -0.30613900 | 0.18960700 |
| C | -3.07699700 | 0.30563400 | -0.38809600 |
| C | -2.51676900 | 1.30234300 | 0.46709000 |
| C | -2.25469400 | 0.68929800 | 1.77700000 |
| C | -2.63492300 | -0.67839000 | 1.70809000 |
| C | -3.06890100 | -0.96090100 | 0.33727800 |
| C | -3.61618600 | 0.50951400 | -1.76843500 |
| H | -4.69972100 | 0.67058900 | -1.70594500 |
| H | -3.43080400 | -0.36125500 | -2.39789400 |
| H | -3.17901000 | 1.38789200 | -2.24758200 |
| C | -2.33843500 | 2.75521600 | 0.14833200 |
| H | -3.22137500 | 3.32038100 | 0.47088400 |
| H | -2.20910800 | 2.91915400 | -0.92304300 |
| H | -1.47117700 | 3.17616800 | 0.66213900 |
| C | -1.75370500 | 1.42900200 | 2.98014000 |
| H | -2.58055400 | 1.96472700 | 3.46190900 |
| H | -0.99632000 | 2.16833400 | 2.70907700 |
| H | -1.31844600 | 0.75469000 | 3.72012300 |
| C | -2.60927600 | -1.67199300 | 2.82765700 |
| H | -3.61121400 | -1.76063400 | 3.26425500 |
| H | -1.92396400 | -1.37329100 | 3.62311100 |
| H | -2.31797900 | -2.66657900 | 2.48172100 |
| C | -3.66336500 | -2.24082400 | -0.16455900 |
| H | -4.75853400 | -2.18077200 | -0.14594300 |
| H | -3.37369600 | -3.08958000 | 0.46029400 |
| H | -3.33496000 | -2.43343400 | -1.18809100 |
| C | 1.57862000 | -1.32558900 | 1.23777300 |
| N | 0.37313600 | -1.79182700 | 0.77589900 |
| C | 0.11219700 | -3.09349000 | 0.83904700 |
| C | 1.00512800 | -4.01627400 | 1.41869000 |
| C | 2.51114400 | -2.18499500 | 1.88936500 |
| H | -0.83392100 | -3.41551400 | 0.42008500 |
| H | 0.73878800 | -5.06681200 | 1.43787600 |
| C | -0.70608100 | -1.11683300 | -2.79166900 |
| O | -1.66519000 | -1.87973900 | -2.78623300 |
| N | -0.18780800 | -0.47987800 | -1.68665000 |
| C | 3.70488800 | -1.62482700 | 2.41516000 |
| C | 1.89404500 | 0.04391800 | 1.06441300 |
| C | 3.04763500 | 0.57035800 | 1.59729500 |
| H | 3.27330900 | 1.62086500 | 1.46470800 |
| C | 3.95164400 | -0.27698100 | 2.28500000 |
| H | 4.85900600 | 0.15247500 | 2.69642600 |
| C | 0.09511500 | -0.69054200 | -4.02294500 |
| H | -0.59194100 | -0.24745600 | -4.74962300 |
| H | 0.53259200 | -1.57290600 | -4.49793400 |
| H | 4.41390400 | -2.27345300 | 2.91981900 |
| C | 2.18526900 | -3.56219900 | 1.96502400 |
| H | 2.87633600 | -4.24784800 | 2.44641000 |
| O | 0.98938900 | 0.81407000 | 0.30943700 |
| C | 0.88111800 | 0.34301200 | -1.99836700 |
| C | 1.49544300 | 1.07923300 | -1.04550300 |
| C | 2.44725300 | 2.18819600 | -1.15813200 |
| C | 3.49309800 | 2.16775100 | -2.09880500 |
| C | 2.30864600 | 3.32889800 | -0.34022900 |
| C | 4.35133300 | 3.25881700 | -2.23420800 |
| H | 3.64946800 | 1.28846600 | -2.71342100 |
| C | 3.17792300 | 4.40936000 | -0.46936600 |
| H | 1.50930800 | 3.36371900 | 0.39379100 |
| C | 4.20037700 | 4.38316900 | -1.42179600 |
| H | 5.15109800 | 3.22105500 | -2.96775400 |
| H | 3.05054300 | 5.27959300 | 0.16790100 |
| H | 4.87386000 | 5.22806400 | -1.52494800 |
| C | 1.15215300 | 0.29931900 | -3.49468500 |
| H | 1.06812500 | 1.29787500 | -3.93519700 |
| H | 2.16667700 | -0.05171600 | -3.69727000 |

**II-2 (Scheme 2b)**




Charge: 1, Multiplicity: 1

$G_{sol}$: -956511.9504 kcal/mol

| | | | |
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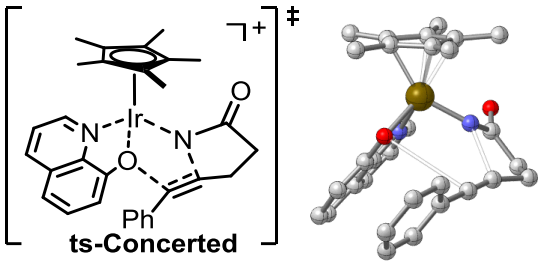
| Ir | -0.59110900 | 0.05649800 | 0.88187800 |
| C | -1.74194400 | -1.19432000 | -0.57202900 |
| C | -2.21644900 | 0.19123900 | -0.64539500 |
| C | -2.73342800 | 0.55945400 | 0.63346000 |
| C | -2.53701800 | -0.56760200 | 1.54307700 |
| C | -1.98177800 | -1.66566100 | 0.75785000 |
| C | -1.24027400 | -2.00216100 | -1.73123400 |
| H | -2.08399300 | -2.43305000 | -2.28387800 |
| H | -0.60009600 | -2.82479900 | -1.40594200 |
| H | -0.66550700 | -1.39258500 | -2.43203400 |
| C | -2.22577500 | 1.02487600 | -1.89041000 |
| H | -3.10166000 | 0.77196500 | -2.49993900 |
| H | -1.33849800 | 0.84459600 | -2.50160500 |
| H | -2.27449500 | 2.09145900 | -1.66467700 |
| C | -3.33221800 | 1.87333300 | 1.02783400 |
| H | -4.40867600 | 1.75613500 | 1.19738400 |
| H | -3.19375100 | 2.62981600 | 0.25404100 |
| H | -2.87938100 | 2.24689600 | 1.94976200 |
| C | -3.05702100 | -0.65462600 | 2.94566700 |
| H | -4.10636800 | -0.97454800 | 2.94048600 |
| H | -3.00438300 | 0.31320300 | 3.44848300 |
| H | -2.49159600 | -1.37516200 | 3.54050000 |
| C | -1.77095300 | -3.05976300 | 1.26093800 |
| H | -2.71776500 | -3.61026900 | 1.20275700 |
| H | -1.44790800 | -3.07257700 | 2.30403800 |
| H | -1.03988100 | -3.60669300 | 0.66187900 |
| C | 1.44335700 | 0.24286800 | 2.97727000 |
| N | 0.96580200 | -0.69065200 | 2.09057100 |
| C | 1.50459700 | -1.90744800 | 2.06516600 |
| C | 2.55213000 | -2.27509600 | 2.93197800 |
| C | 2.49382300 | -0.05177100 | 3.89451200 |
| H | 1.10215600 | -2.60733400 | 1.34292000 |
| H | 2.95924900 | -3.27781000 | 2.86830800 |
| C | 1.74566400 | -0.05713800 | -0.96005600 |
| O | 2.18356400 | -1.05800900 | -1.37763300 |
| N | 1.12815000 | 0.87222900 | -0.42373100 |
| C | 2.92177500 | 0.96958300 | 4.77642300 |
| C | 0.82936700 | 1.52672400 | 2.92109000 |
| C | 1.28074000 | 2.50319600 | 3.80538600 |
| H | 0.82505900 | 3.48752100 | 3.78214700 |
| C | 2.31585600 | 2.21177700 | 4.71939300 |
| H | 2.64332500 | 2.99525000 | 5.39616900 |
| C | 1.35489800 | 2.32925400 | -0.58256800 |
| H | 0.80605500 | 2.80069400 | 0.23196600 |
| H | 0.92200100 | 2.63691500 | -1.53911100 |
| H | 3.72004600 | 0.76764200 | 5.48266600 |
| C | 3.03830500 | -1.35968000 | 3.84235400 |
| H | 3.84103700 | -1.63083900 | 4.52210500 |
| O | -0.13295000 | 1.72725100 | 2.02529100 |
| C | 3.62805100 | 2.02997200 | -1.55327100 |
| C | 4.24721600 | 1.45112600 | -2.42338200 |
| C | 4.97531700 | 0.77262600 | -3.44892900 |
| C | 5.54646400 | -0.49067400 | -3.20080800 |
| C | 5.12718500 | 1.35997800 | -4.72017500 |
| C | 6.25207900 | -1.14803600 | -4.20504400 |
| H | 5.43073900 | -0.94364600 | -2.22152800 |
| C | 5.83707900 | 0.69578000 | -5.71665700 |
| H | 4.69044700 | 2.33478300 | -4.91177300 |
| C | 6.39968700 | -0.55781900 | -5.46283600 |
| H | 6.69069900 | -2.12114500 | -4.00609100 |
| H | 5.95314900 | 1.15690800 | -6.69268300 |
| H | 6.95341100 | -1.07216400 | -6.24238700 |
| C | 2.84533600 | 2.70386400 | -0.52144600 |
| H | 3.23601000 | 2.46615900 | 0.47584900 |
| H | 2.91507700 | 3.79349100 | -0.63325400 |

**ts-Concerted (Scheme 2b)**




Charge: 1, Multiplicity: 1

$G_{sol}$: -956460.4477 kcal/mol

| | | | |
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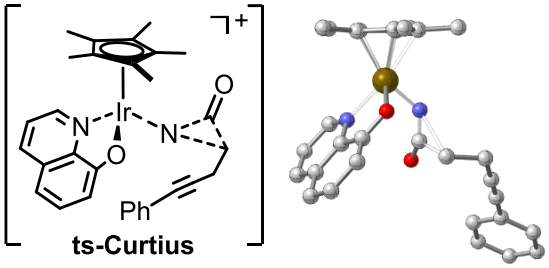
| Ir | -0.87976200 | -0.28828100 | -0.25946400 |
| C | -2.41561700 | -1.98422600 | -0.21868600 |
| C | -1.35701000 | -2.32519300 | -1.13789100 |
| C | -1.39225100 | -1.35724600 | -2.22126600 |
| C | -2.39579500 | -0.37825800 | -1.93024400 |
| C | -3.02540900 | -0.75703800 | -0.66019900 |
| C | -2.80513500 | -2.76371800 | 0.99500500 |
| H | -3.54645000 | -3.52181500 | 0.71398900 |
| H | -3.24107500 | -2.11662900 | 1.75673000 |
| H | -1.94592200 | -3.27686500 | 1.42990300 |
| C | -0.50263400 | -3.55527400 | -1.09793000 |
| H | -0.99611600 | -4.37895900 | -1.62852100 |
| H | -0.32094600 | -3.88091800 | -0.07194200 |
| H | 0.46394800 | -3.38117500 | -1.57542000 |
| C | -0.47197800 | -1.38097600 | -3.40067400 |
| H | -0.66094500 | -2.27914300 | -3.99918700 |
| H | 0.57306900 | -1.39894500 | -3.07838800 |
| H | -0.61321900 | -0.51032000 | -4.04202700 |
| C | -2.82420200 | 0.76197200 | -2.80349300 |
| H | -3.68561900 | 0.46623700 | -3.41416600 |
| H | -2.02622400 | 1.07517300 | -3.47902300 |
| H | -3.12228300 | 1.62938700 | -2.21030600 |
| C | -4.22119200 | -0.10621700 | -0.03532400 |
| H | -5.12744000 | -0.67111100 | -0.28432700 |
| H | -4.35950400 | 0.91232800 | -0.40387200 |
| H | -4.11549000 | -0.07105200 | 1.05090000 |
| C | 0.35593200 | 2.36285300 | -0.26416900 |
| N | -0.79425900 | 1.77782900 | 0.19690700 |
| C | -1.70396100 | 2.51995500 | 0.82462200 |
| C | -1.51843400 | 3.90521600 | 1.01174900 |
| C | 0.61907100 | 3.75076600 | -0.11237900 |
| H | -2.56891400 | 2.00158500 | 1.21628200 |
| H | -2.28878100 | 4.46818700 | 1.52647800 |
| C | -1.11918800 | -0.13505800 | 2.70364600 |
| O | -2.30796500 | 0.23083800 | 2.69848700 |
| N | -0.54243400 | -0.67088000 | 1.59754900 |
| C | 1.83241600 | 4.26183100 | -0.64120500 |
| C | 1.26712400 | 1.49674700 | -0.92546800 |
| C | 2.44101000 | 2.03224100 | -1.44324100 |
| H | 3.14126700 | 1.38197900 | -1.95469100 |
| C | 2.70901800 | 3.41107900 | -1.28827500 |
| H | 3.63235200 | 3.80898100 | -1.69806400 |
| C | -0.27244700 | -0.12743900 | 3.96409300 |
| H | -0.92937200 | -0.27382000 | 4.82500500 |
| H | 0.17538900 | 0.86978800 | 4.05899000 |
| H | 2.05406500 | 5.31918900 | -0.54068100 |
| C | -0.37196800 | 4.51769100 | 0.55021700 |
| H | -0.21993600 | 5.58422800 | 0.68928800 |
| O | 0.94172500 | 0.20652100 | -1.00813800 |
| C | 1.53294600 | -1.10313900 | 2.58905800 |
| C | 2.44805100 | -1.11765000 | 1.76827200 |
| C | 3.50349400 | -1.17821500 | 0.82877500 |
| C | 4.35673500 | -0.06808400 | 0.63169700 |
| C | 3.75558400 | -2.37497900 | 0.11809500 |
| C | 5.42679600 | -0.15866200 | -0.25280200 |
| H | 4.17427600 | 0.84556100 | 1.18695400 |
| C | 4.82330900 | -2.45066700 | -0.76735500 |
| H | 3.11159800 | -3.23259500 | 0.28296000 |
| C | 5.66087700 | -1.34474700 | -0.95525900 |
| H | 6.08612100 | 0.69287800 | -0.39009200 |
| H | 5.01418100 | -3.37352900 | -1.30624600 |
| H | 6.50000900 | -1.41186000 | -1.64093500 |
| C | 0.82356000 | -1.19438600 | 3.87384900 |
| H | 0.37559700 | -2.19125500 | 3.96161000 |
| H | 1.54256400 | -1.09046400 | 4.69427100 |

**ts-Curtius (Scheme 2b)**




Charge: 1, Multiplicity: 1

$G_{sol}$: -956456.8588 kcal/mol

| | | | |
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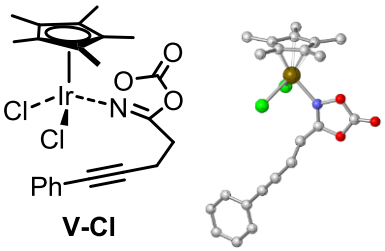
| Ir | -1.58916900 | -0.51711900 | -0.01392200 |
| C | -1.99654200 | -2.47351300 | 1.06139000 |
| C | -2.17820000 | -2.66345200 | -0.37316200 |
| C | -3.25210500 | -1.80823300 | -0.79533000 |
| C | -3.71054000 | -1.04124500 | 0.35068000 |
| C | -2.94809300 | -1.49296400 | 1.50297400 |
| C | -1.05264400 | -3.25764800 | 1.92121100 |
| H | -1.50333700 | -4.22380100 | 2.17864500 |
| H | -0.82287700 | -2.73920100 | 2.85397700 |
| H | -0.11165100 | -3.45556500 | 1.40437300 |
| C | -1.43105300 | -3.65638200 | -1.20898500 |
| H | -1.86715500 | -4.65505800 | -1.08812000 |
| H | -0.38159900 | -3.71181800 | -0.91155500 |
| H | -1.46808300 | -3.39893400 | -2.26874400 |
| C | -3.80109800 | -1.67475800 | -2.18045400 |
| H | -4.83292700 | -2.04261100 | -2.20577400 |
| H | -3.21958500 | -2.24831400 | -2.90312500 |
| H | -3.80048700 | -0.62877500 | -2.49843600 |
| C | -4.89359700 | -0.11967100 | 0.37225900 |
| H | -5.81244700 | -0.68177400 | 0.57854500 |
| H | -5.01951000 | 0.38491200 | -0.58797300 |
| H | -4.79252000 | 0.64682700 | 1.14374000 |
| C | -3.18707400 | -1.06375900 | 2.91670700 |
| H | -3.98258300 | -1.68130000 | 3.35134400 |
| H | -3.51238500 | -0.02312100 | 2.97529700 |
| H | -2.29950700 | -1.18933400 | 3.54011600 |
| C | -1.28479600 | 2.39056000 | -0.03249900 |
| N | -1.19462500 | 1.35830100 | 0.86684500 |
| C | -0.87291300 | 1.61193300 | 2.13197600 |
| C | -0.64995500 | 2.92612800 | 2.58851600 |
| C | -1.07762900 | 3.74659200 | 0.34882900 |
| H | -0.78806000 | 0.76147400 | 2.79768400 |
| H | -0.39111900 | 3.08240900 | 3.62941300 |
| C | 1.39793400 | -0.03599600 | 0.10679800 |
| O | 2.17808000 | 0.47392300 | 0.86068600 |
| N | 0.37400000 | -0.77644500 | -0.09972800 |
| C | -1.20281700 | 4.74601000 | -0.64680200 |
| C | -1.58852000 | 2.02373300 | -1.37132000 |
| C | -1.70700800 | 3.03295500 | -2.32024700 |
| H | -1.94085800 | 2.77206100 | -3.34683600 |
| C | -1.51251600 | 4.38003600 | -1.94425900 |
| H | -1.60813500 | 5.14789800 | -2.70578300 |
| C | 1.61018200 | 0.09089300 | -1.64265000 |
| H | 1.91971600 | 1.13948400 | -1.58311000 |
| H | 0.69010000 | 0.00653800 | -2.21768400 |
| H | -1.05392600 | 5.78715700 | -0.38099700 |
| C | -0.75576700 | 3.98363500 | 1.70946200 |
| H | -0.58769600 | 5.00161100 | 2.04884700 |
| O | -1.71994700 | 0.72426300 | -1.65132600 |
| C | 2.69042800 | -0.87701100 | -2.11195700 |
| H | 2.31382500 | -1.90440700 | -2.02235800 |
| H | 2.78959600 | -0.69447600 | -3.19495600 |
| C | 3.99061500 | -0.73247700 | -1.46965800 |
| C | 5.07339100 | -0.60034400 | -0.94150900 |
| C | 6.33486600 | -0.42756700 | -0.29221900 |
| C | 6.39180800 | 0.16316500 | 0.98496400 |
| C | 7.52818800 | -0.83791000 | -0.91589000 |
| C | 7.61882000 | 0.33821800 | 1.61936600 |
| H | 5.46923700 | 0.47885200 | 1.46166000 |
| C | 8.75017200 | -0.65951200 | -0.27201400 |
| H | 7.48561300 | -1.29254600 | -1.90040500 |
| C | 8.79940700 | -0.07175600 | 0.99440800 |
| H | 7.65533500 | 0.79566700 | 2.60361100 |
| H | 9.66624900 | -0.97867900 | -0.75981300 |
| H | 9.75445700 | 0.06651700 | 1.49221000 |

**V-Cl**




**V-Cl**

Charge: 0, Multiplicity: 1

$G_{sol}$: -1353631.83 kcal/mol

| | | | |
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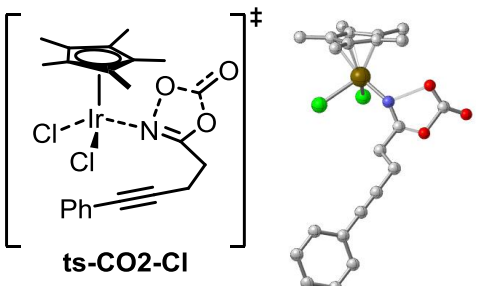
| Ir | -1.38317000 | -1.33911600 | 0.16852700 |
| C | -2.14520100 | -0.85202400 | -1.86228600 |
| C | -2.99512400 | -1.88318400 | -1.26251600 |
| C | -2.17999100 | -3.03727900 | -1.01373900 |
| C | -0.80873200 | -2.71640500 | -1.38479600 |
| C | -0.81757700 | -1.38490900 | -1.97467000 |
| C | -2.61860500 | 0.46903000 | -2.38828700 |
| H | -2.98226100 | 0.35921200 | -3.41776200 |
| H | -1.81322700 | 1.20623600 | -2.39228400 |
| H | -3.43516800 | 0.86920100 | -1.78491700 |
| C | -4.47930400 | -1.78821000 | -1.07602500 |
| H | -4.78707000 | -0.76742200 | -0.84301100 |
| H | -4.82030700 | -2.43457300 | -0.26476100 |
| H | -4.99800400 | -2.09512300 | -1.99305700 |
| C | -2.63894200 | -4.35344200 | -0.47215400 |
| H | -2.75322800 | -5.06792400 | -1.29707800 |
| H | -3.59815000 | -4.26501500 | 0.04017400 |
| H | -1.91862100 | -4.75520600 | 0.24234800 |
| C | 0.35676900 | -3.65776200 | -1.35025400 |
| H | 0.40960500 | -4.24749700 | -2.27436200 |
| H | 0.27462900 | -4.34670100 | -0.50721700 |
| H | 1.29501400 | -3.11092000 | -1.23722000 |
| C | 0.36636100 | -0.70881500 | -2.58904000 |
| H | 0.53679000 | -1.11218000 | -3.59510700 |
| H | 1.26333600 | -0.87033800 | -1.98881500 |
| H | 0.21514400 | 0.36838200 | -2.67257300 |
| H | -0.62747500 | 1.32345500 | 3.89330800 |
| C | -1.09426200 | 0.37020500 | 3.62153700 |
| C | -2.11427700 | 0.66336200 | 2.58574800 |
| H | -0.33511500 | -0.28026000 | 3.18990100 |
| O | -3.05167400 | 1.61195400 | 2.86639800 |
| N | -2.29288400 | 0.14282000 | 1.41342100 |
| O | -3.43417600 | 0.79883500 | 0.86492800 |
| C | -3.89178200 | 1.70208500 | 1.77826200 |
| O | -4.82980000 | 2.42393800 | 1.65763400 |
| C | -1.73064200 | -0.28145700 | 4.88298300 |
| H | -2.56244800 | 0.33558800 | 5.24487400 |
| H | -2.13987800 | -1.25452600 | 4.58714200 |
| C | -0.74387500 | -0.45691000 | 5.94311100 |
| C | 0.09367900 | -0.60132200 | 6.80773200 |
| C | 1.08425100 | -0.79108800 | 7.82081500 |
| C | 0.96535800 | -0.15643800 | 9.07238900 |
| C | 2.19789100 | -1.61933100 | 7.57958300 |
| C | 1.93500000 | -0.34798800 | 10.05375800 |
| H | 0.10868000 | 0.48246300 | 9.26201200 |
| C | 3.16344800 | -1.80399100 | 8.56602900 |
| H | 2.29190500 | -2.10959000 | 6.61601600 |
| C | 3.03621500 | -1.17075400 | 9.80488500 |
| H | 1.83139400 | 0.14652900 | 11.01539600 |
| H | 4.01788400 | -2.44464000 | 8.36746800 |
| H | 3.79096300 | -1.31771300 | 10.57205500 |
| Cl | 0.73666900 | -0.27118500 | 0.77942900 |
| Cl | -1.28325000 | -2.70726800 | 2.20286800 |

**ts-CO2-Cl**

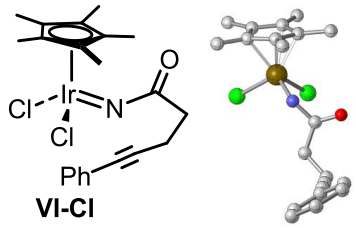



Charge: 0, Multiplicity: 1

$G_{sol}$: -1353613.047 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -1.62674700 | -0.35277100 | -0.18038300 |
| C | -2.91703500 | -0.16436400 | 1.63477400 |
| C | -2.43947500 | -1.51519400 | 1.57506600 |
| C | -3.04056900 | -2.15177000 | 0.39365200 |
| C | -3.81208500 | -1.18713200 | -0.29592600 |
| C | -3.69159600 | 0.08087300 | 0.41911100 |
| C | -2.69076200 | 0.82798400 | 2.73168300 |
| H | -3.59857800 | 0.90806700 | 3.34192100 |
| H | -2.45807700 | 1.81408100 | 2.32475600 |
| H | -1.87264300 | 0.52091100 | 3.38591200 |
| C | -1.62196800 | -2.24077900 | 2.59733900 |
| H | -1.07896300 | -1.54584500 | 3.24034000 |
| H | -0.89172000 | -2.89260200 | 2.11171600 |
| H | -2.26554900 | -2.86082700 | 3.23365900 |
| C | -2.86611900 | -3.59346000 | 0.04189200 |
| H | -3.40790400 | -4.21540100 | 0.76496800 |
| H | -1.81048700 | -3.87457200 | 0.06841900 |
| H | -3.24702900 | -3.81534400 | -0.95558400 |
| C | -4.59473200 | -1.36848200 | -1.55762500 |
| H | -5.65555200 | -1.16377300 | -1.37447700 |
| H | -4.50362600 | -2.38355800 | -1.94632800 |
| H | -4.23686600 | -0.67811300 | -2.32736900 |
| C | -4.45806900 | 1.32299200 | 0.08274000 |
| H | -5.47340500 | 1.25480900 | 0.49485200 |
| H | -4.53642000 | 1.44451300 | -0.99956300 |
| H | -3.96894600 | 2.21203800 | 0.48046500 |
| H | 2.12494900 | 1.23609700 | -1.29085900 |
| C | 1.83971300 | 1.12099400 | -0.23910500 |
| C | 0.50605400 | 1.83882400 | -0.08848600 |
| H | 1.71825900 | 0.05353900 | -0.05078700 |
| O | 0.52590000 | 3.12508200 | -0.16470000 |
| N | -0.52214600 | 1.10358800 | 0.20002800 |
| C | -0.90083200 | 3.84066500 | 0.12825300 |
| O | -1.70644600 | 2.94987000 | 0.44407000 |
| O | -0.83220200 | 5.02507300 | -0.00755400 |
| C | 2.91648400 | 1.74311100 | 0.68292400 |
| H | 2.99565300 | 2.81431000 | 0.46942600 |
| H | 2.59309100 | 1.65509500 | 1.72879000 |
| C | 4.20935000 | 1.08974700 | 0.50653800 |
| C | 5.27326400 | 0.53017100 | 0.34424600 |
| C | 6.53306000 | -0.12053200 | 0.16432400 |
| C | 7.67389200 | 0.61741100 | -0.20727400 |
| C | 6.65378700 | -1.51064000 | 0.35691700 |
| C | 8.89970700 | -0.02090000 | -0.37856200 |
| H | 7.58460100 | 1.68847300 | -0.35774300 |
| C | 7.88307100 | -2.14113500 | 0.18176900 |
| H | 5.77645500 | -2.08283500 | 0.64102700 |
| C | 9.00915300 | -1.40019900 | -0.18522900 |
| H | 9.77210000 | 0.55945600 | -0.66484400 |
| H | 7.96273600 | -3.21399200 | 0.33179100 |
| H | 9.96647300 | -1.89499500 | -0.32069600 |
| Cl | 0.01914500 | -2.02679300 | -0.75913400 |
| Cl | -1.58725000 | 0.35087700 | -2.49669600 |

**VI-Cl**



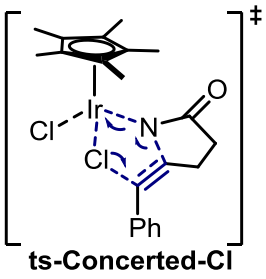

**VI-Cl**

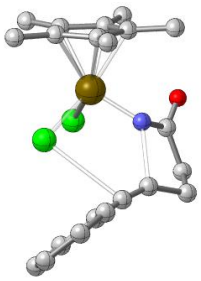
Charge: 0, Multiplicity: 1

$G_{sol}$: -1235315.858 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -1.41575700 | 0.93230500 | 0.81610100 |
| C | -2.04484000 | -1.13569200 | 0.10612600 |
| C | -3.03513700 | -0.22094400 | -0.36339000 |
| C | -3.77468700 | 0.29345700 | 0.80185700 |
| C | -3.16280300 | -0.19496000 | 1.96952500 |
| C | -2.01468200 | -1.01942100 | 1.56263800 |
| C | -1.13647300 | -2.00019800 | -0.70646300 |
| H | -1.19770400 | -3.03884100 | -0.36575600 |
| H | -0.09807700 | -1.66257600 | -0.60506300 |
| H | -1.39968500 | -1.97153700 | -1.76526800 |
| C | -3.41812600 | 0.05971100 | -1.78239700 |
| H | -4.35294800 | -0.45532000 | -2.03640900 |
| H | -2.64537900 | -0.27044900 | -2.47856300 |
| H | -3.57037200 | 1.13221500 | -1.92991700 |
| C | -4.96020700 | 1.19626600 | 0.69838300 |
| H | -5.75641800 | 0.70733400 | 0.12505300 |
| H | -4.69087500 | 2.12473400 | 0.18430700 |
| H | -5.35576000 | 1.45627700 | 1.68114600 |
| C | -3.54331700 | 0.06557000 | 3.39252500 |
| H | -3.85410100 | -0.86683600 | 3.87815500 |
| H | -4.36398500 | 0.78071800 | 3.46567700 |
| H | -2.69265300 | 0.47379800 | 3.94654900 |
| C | -1.16881300 | -1.83545800 | 2.49313300 |
| H | -1.64943300 | -2.80097900 | 2.69678700 |
| H | -1.02719000 | -1.31388800 | 3.44155300 |
| H | -0.17929200 | -2.01533700 | 2.06892800 |
| C | 1.52027000 | 0.88968600 | 0.82265100 |
| O | 2.03045800 | 0.07604200 | 1.58148300 |
| N | 0.29712100 | 0.59306900 | 0.23869800 |
| C | 2.18154400 | 2.17675900 | 0.35960600 |
| H | 1.82882500 | 2.95398500 | 1.04882300 |
| H | 1.82290600 | 2.44805700 | -0.63798900 |
| C | 4.29412200 | 1.29321400 | -0.67940500 |
| C | 4.76225800 | 0.64261600 | -1.58988600 |
| C | 5.32620700 | -0.12871700 | -2.65311900 |
| C | 5.86423400 | -1.40675900 | -2.40393700 |
| C | 5.35856000 | 0.37563400 | -3.96807000 |
| C | 6.41811100 | -2.15346100 | -3.44100400 |
| H | 5.84166000 | -1.79955200 | -1.39247200 |
| C | 5.91351000 | -0.37769500 | -4.99983300 |
| H | 4.94627300 | 1.36005200 | -4.16558700 |
| C | 6.44539300 | -1.64338500 | -4.74139800 |
| H | 6.83067600 | -3.13685000 | -3.23363600 |
| H | 5.93222900 | 0.02480400 | -6.00873700 |
| H | 6.87883800 | -2.22798800 | -5.54774200 |
| C | 3.72100900 | 2.08940400 | 0.40437500 |
| H | 4.01310200 | 1.66149300 | 1.36986600 |
| H | 4.12897300 | 3.10716800 | 0.36507700 |
| Cl | -0.57120300 | 2.04682300 | 2.77945300 |
| Cl | -2.16787900 | 3.08091900 | 0.06666800 |

**ts-Concerted-Cl**



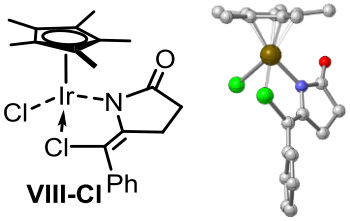



Charge: 0, Multiplicity: 1

$G_{sol}$: -1235305.839 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -0.86704900 | -0.16788200 | -0.20685200 |
| C | -2.21217600 | -0.36241200 | 1.63732500 |
| C | -1.32187700 | -1.49112800 | 1.59723300 |
| C | -1.62835100 | -2.24232300 | 0.38560900 |
| C | -2.64148400 | -1.54747900 | -0.34097700 |
| C | -2.98642100 | -0.34341100 | 0.41764500 |
| C | -2.31148300 | 0.64388700 | 2.73980200 |
| H | -3.11239700 | 0.34948800 | 3.42977800 |
| H | -2.53592900 | 1.63278100 | 2.33846200 |
| H | -1.38229500 | 0.70574900 | 3.30940800 |
| C | -0.37300800 | -1.92796700 | 2.67081200 |
| H | -0.85730000 | -2.63697400 | 3.35478300 |
| H | -0.02378200 | -1.07839200 | 3.26129900 |
| H | 0.50307600 | -2.41974900 | 2.24209200 |
| C | -0.98339400 | -3.53796200 | 0.00335700 |
| H | -1.45398700 | -4.36034100 | 0.55699100 |
| H | 0.08353600 | -3.53235200 | 0.23325300 |
| H | -1.08846600 | -3.73745400 | -1.06384100 |
| C | -3.30005900 | -1.96112400 | -1.62119600 |
| H | -4.33571800 | -2.26872900 | -1.43233600 |
| H | -2.77802900 | -2.79788400 | -2.08868900 |
| H | -3.30742900 | -1.13180200 | -2.33339900 |
| C | -4.08963300 | 0.60684500 | 0.07129900 |
| H | -5.02905500 | 0.28138500 | 0.53704400 |
| H | -4.23579100 | 0.64461300 | -1.00962900 |
| H | -3.84781700 | 1.61680300 | 0.40312400 |
| C | -0.70621900 | 2.73546700 | 0.23173200 |
| O | -1.90941900 | 2.95772700 | 0.39485100 |
| N | -0.17663200 | 1.49250000 | 0.47950500 |
| C | 0.29626500 | 3.82088600 | -0.09761000 |
| H | -0.11687200 | 4.79190200 | 0.18554200 |
| H | 0.44590800 | 3.80928700 | -1.18358700 |
| C | 1.96516300 | 2.07377300 | 0.39587400 |
| C | 2.82117200 | 1.19867300 | 0.22998000 |
| C | 3.91587600 | 0.30296600 | 0.12717200 |
| C | 4.51412900 | 0.03070900 | -1.12283400 |
| C | 4.47352100 | -0.26417800 | 1.29333600 |
| C | 5.63563200 | -0.78543900 | -1.19625000 |
| H | 4.07393900 | 0.45362500 | -2.01915000 |
| C | 5.59649900 | -1.08170200 | 1.20795100 |
| H | 4.01543000 | -0.05168300 | 2.25388100 |
| C | 6.18020000 | -1.34412200 | -0.03402600 |
| H | 6.08771000 | -0.99251100 | -2.16157900 |
| H | 6.01849800 | -1.51428800 | 2.11032800 |
| H | 7.05616900 | -1.98303600 | -0.09823900 |
| C | 1.60346600 | 3.49035600 | 0.62272100 |
| H | 1.48275400 | 3.65510200 | 1.70068900 |
| H | 2.42554000 | 4.13120000 | 0.28524600 |
| Cl | -1.22458500 | 0.92383200 | -2.35282800 |
| Cl | 1.13634800 | -1.09059900 | -1.10087600 |

## VIII-Cl




Charge: 0, Multiplicity: 1

$G_{sol}$: -1235375.075 kcal/mol

| | | | |
|---|---|---|---|
| Ir | -1.34424900 | 0.24739400 | 0.20768400 |
| C | -3.54315300 | -0.01124200 | 0.08326400 |
| C | -3.25601300 | 1.23085300 | 0.73132900 |
| C | -2.50989100 | 0.94551800 | 1.96397300 |
| C | -2.33364400 | -0.46291400 | 2.06100400 |
| C | -2.89601600 | -1.07322700 | 0.85388600 |
| C | -4.40594300 | -0.21229300 | -1.12310800 |
| H | -5.41775400 | -0.49327000 | -0.80257300 |
| H | -4.00195900 | -1.00113900 | -1.75779900 |
| H | -4.48786100 | 0.70203700 | -1.71551400 |
| C | -3.73030400 | 2.58855000 | 0.31073700 |
| H | -4.65051800 | 2.85371200 | 0.84686000 |
| H | -3.94286700 | 2.62274300 | -0.75948000 |
| H | -2.98513000 | 3.35767100 | 0.52746600 |
| C | -2.07744800 | 1.96962900 | 2.97014100 |
| H | -2.87152200 | 2.13809000 | 3.70858300 |
| H | -1.85887300 | 2.92912400 | 2.49581000 |
| H | -1.18073300 | 1.64986700 | 3.50441100 |
| C | -1.67071500 | -1.21163500 | 3.17405800 |
| H | -2.43202000 | -1.67653300 | 3.81280400 |
| H | -1.06086400 | -0.55171300 | 3.79311400 |
| H | -1.01602900 | -1.99338900 | 2.78462000 |
| C | -3.01330200 | -2.54045400 | 0.58658300 |
| H | -3.99915200 | -2.90491900 | 0.90465500 |
| H | -2.25140900 | -3.09825800 | 1.13464300 |
| H | -2.87968300 | -2.73476100 | -0.47864600 |
| C | -1.19579200 | -0.98330200 | -2.62854800 |
| O | -2.04030000 | -1.83817900 | -2.37704000 |
| N | -0.74960200 | 0.00080800 | -1.77707900 |
| C | -0.50495100 | -0.82859100 | -3.98390100 |
| H | -1.24165000 | -0.44899700 | -4.70149000 |
| H | -0.16664400 | -1.80142000 | -4.34683300 |
| C | 0.22867500 | 0.78031600 | -2.37624900 |
| C | 0.62374300 | 0.17285400 | -3.71639100 |
| H | 0.75295300 | 0.93241700 | -4.49060900 |
| H | 1.57844300 | -0.35224800 | -3.60784600 |
| C | 0.73208700 | 1.93053900 | -1.87847200 |
| Cl | 0.08810500 | 2.44362700 | -0.27285700 |
| C | 1.73984300 | 2.83328100 | -2.45150000 |
| C | 2.92208000 | 2.32284800 | -3.01858700 |
| C | 1.55061500 | 4.22888600 | -2.45599800 |
| C | 3.86073900 | 3.17400600 | -3.60180300 |
| H | 3.11520200 | 1.25663300 | -2.97783500 |
| C | 2.49678700 | 5.07654900 | -3.02551600 |
| H | 0.65108400 | 4.64583400 | -2.01344600 |
| C | 3.65397900 | 4.55370200 | -3.60898700 |
| H | 4.76600300 | 2.75591600 | -4.03312900 |
| H | 2.32727000 | 6.14970100 | -3.01996200 |
| H | 4.39027900 | 5.21621200 | -4.05447400 |
| Cl | 0.79400100 | -0.75002800 | 0.76668400 |

**$CO_2$**

Charge: 0, Multiplicity: 1

Gsol: -118329.4109 kcal/mol

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 0.00000000 |
| O | 0.00000000 | 0.00000000 | 1.16915600 |
| O | 0.00000000 | 0.00000000 | -1.16915600 |

# *Appendix III*

# *(Crystallographic Data of II, 2, 9, 12, 16, 27, 29, and 32)*

**Crystallographic data of II (Scheme 2)**

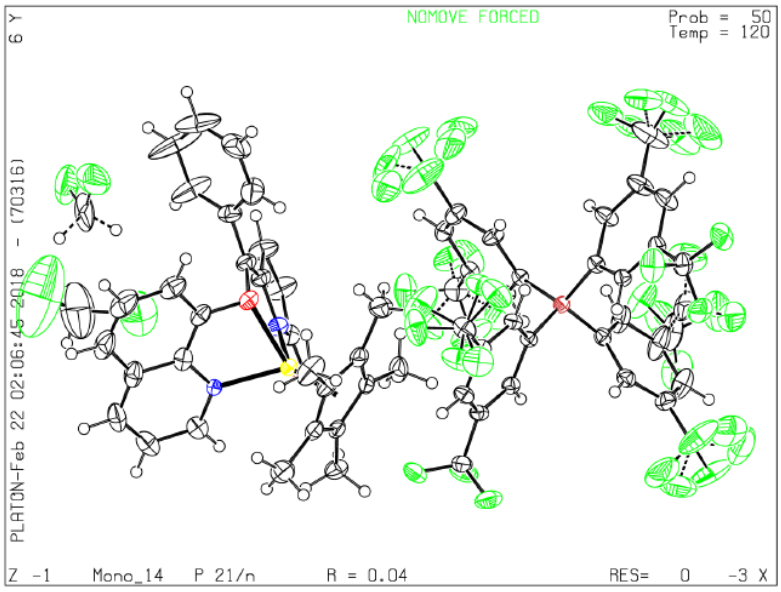



**Table S2**. Crystal data and structure refinement for **II**

| | | |
|---|---|---|
| Empirical formula | $C_{63.17}H_{42.35}BN_2O_2F_{24}Cl_{2.35}Ir$ | |
| Formula weight | 1603.76 | |
| Temperature | 120(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | a = 19.4538(8) Å | α = 90° |
| | b = 15.5386(7) Å | β = 93.348(2)° |
| | c = 21.3223(10) Å | γ = 90° |
| Volume | 6434.4(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.656 $Mg/m^3$ | |
| Absorption coefficient | 2.287 $mm^{-1}$ | |
| F(000) | 3157 | |
| Crystal size | 0.260 x 0.190 x 0.140 $mm^3$ | |
| Theta range for data collection | 2.962 to 28.366°. | |
| Index ranges | -26<=h<=25, -20<=k<=20, -28<=l<=28 | |
| Reflections collected | 158667 | |
| Independent reflections | 16037 [R(int) = 0.0802] | |
| Completeness to theta = 25.242° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7457 and 0.6248 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 16037 / 262 / 1069 | |
| Goodness-of-fit on $F^2$ | 1.056 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0378, wR2 = 0.0822 | |
| R indices (all data) | R1 = 0.0592, wR2 = 0.0919 | |
| Largest diff. peak and hole | 1.434 and –1.332 $e \cdot Å^{-3}$ | |

**Crystallographic data of 2 (Scheme 3c)**

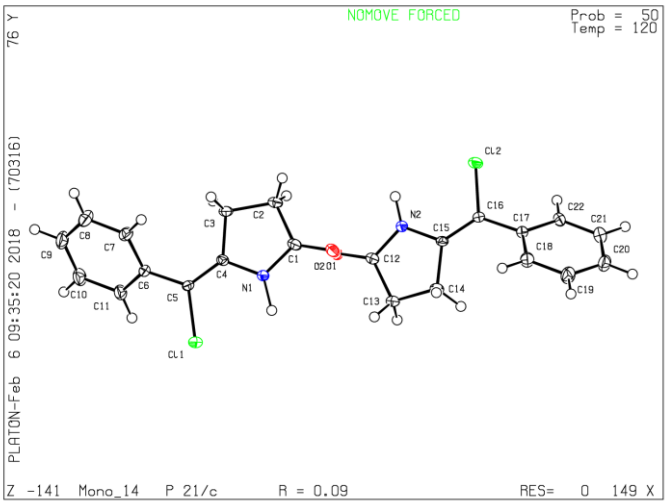



**Table S3.** Crystal data and structure refinement for **2**

| | | |
|---|---|---|
| Empirical formula | $C_{11}H_{10}NOCl$ | |
| Formula weight | 207.65 | |
| Temperature | 120(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 7.1224(8) Å | α = 90° |
| | b = 7.4835(8) Å | β = 94.938(3)° |
| | c = 37.037(4) Å | γ = 90° |
| Volume | 1966.8(4) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.403 $Mg/m^3$ | |
| Absorption coefficient | 0.351 $mm^{-1}$ | |
| F(000) | 864 | |
| Crystal size | 0.450 x 0.420 x 0.160 $mm^3$ | |
| Theta range for data collection | 2.871 to 32.700°. | |
| Index ranges | -10<=h<=10, -11<=k<=11, -56<=l<=56 | |
| Reflections collected | 45591 | |
| Independent reflections | 7218 [R(int) = 0.0415] | |
| Completeness to theta = 25.242° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.946 and 0.858 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7218 / 0 / 260 | |
| Goodness-of-fit on $F^2$ | 1.246 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0945, wR2 = 0.2350 | |
| R indices (all data) | R1 = 0.1045, wR2 = 0.2385 | |
| Extinction coefficient | 0.0013(2) | |
| Largest diff. peak and hole | 0.804 and –1.034 $e \cdot Å^{-3}$ | |

**Crystallographic data of 9 (Table 2)**

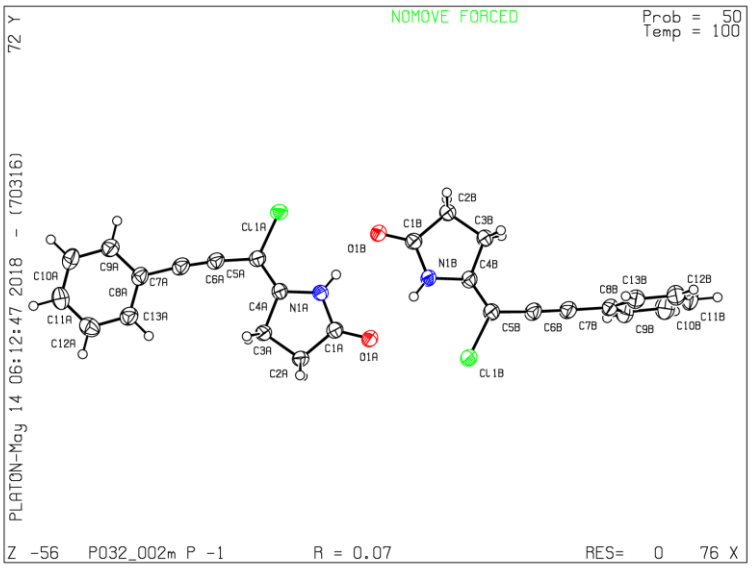



**Table S4.** Crystal data and structure refinement for **9**

| | | |
|---|---|---|
| Empirical formula | $C_{13}H_{10}NOCl$ | |
| Formula weight | 231.67 | |
| Temperature | 100(2) K | |
| Wavelength | 0.700 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 7.1030(14) Å | α = 94.46(3)° |
| | b = 7.1710(14) Å | β = 96.95(3)° |
| | c = 22.409(4) Å | γ = 98.47(3)° |
| Volume | 1115.4(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.380 $Mg/m^3$ | |
| Absorption coefficient | 0.301 $mm^{-1}$ | |
| F(000) | 480 | |
| Crystal size | 0.062 x 0.058 x 0.024 $mm^3$ | |
| Theta range for data collection | 1.812 to 27.999°. | |
| Index ranges | –9<=h<=9, –9<=k<=9, –30<=l<=30 | |
| Reflections collected | 10536 | |
| Independent reflections | 5420 [R(int) = 0.0370] | |
| Completeness to theta = 24.835° | 96.5 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 1.000 and 0.773 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5420 / 0 / 295 | |
| Goodness-of-fit on $F^2$ | 1.058 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0673, wR2 = 0.2047 | |
| R indices (all data) | R1 = 0.0783, wR2 = 0.2151 | |
| Largest diff. peak and hole | 0.689 and –0.778 $e \cdot Å^{-3}$ | |

**Crystallographic data of 12 (Table 2)**

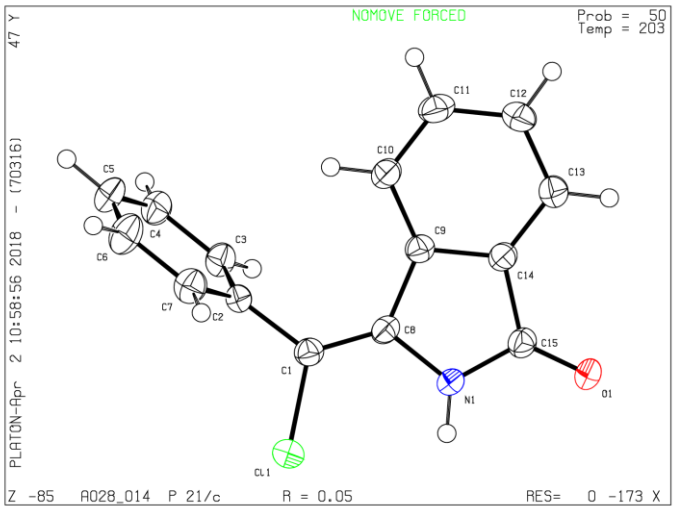



**Table S5**. Crystal data and structure refinement for **12**

| | | |
|---|---|---|
| Empirical formula | $C_{15}H_{10}NOCl$ | |
| Formula weight | 255.69 | |
| Temperature | 203(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 5.1777(2) Å | α = 90° |
| | b = 20.3335(7) Å | β = 102.0932(15)° |
| | c = 11.7701(5) Å | γ = 90° |
| Volume | 1211.67(8) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.402 $Mg/m^3$ | |
| Absorption coefficient | 0.300 $mm^{-1}$ | |
| F(000) | 528 | |
| Crystal size | 0.421 x 0.077 x 0.075 $mm^3$ | |
| Theta range for data collection | 3.488 to 28.298°. | |
| Index ranges | –6<=h<=6, –27<=k<=26, –15<=l<=15 | |
| Reflections collected | 35830 | |
| Independent reflections | 3000 [R(int) = 0.0775] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7457 and 0.7126 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3000 / 0 / 167 | |
| Goodness-of-fit on $F^2$ | 1.019 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0457, wR2 = 0.0834 | |
| R indices (all data) | R1 = 0.0752, wR2 = 0.0934 | |
| Extinction coefficient | 0.0064(10) | |
| Largest diff. peak and hole | 0.272 and –0.307 $e \cdot Å^{-3}$ | |

**Crystallographic data of 16 (Table 2)**

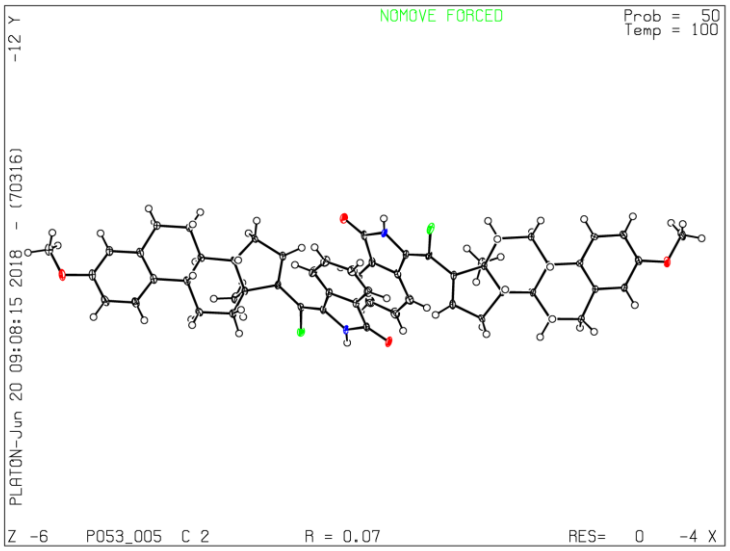



**Table S6.** Crystal data and structure refinement for **16**

| | | |
|---|---|---|
| Empirical formula | $C_{28}H_{28}NO_2Cl$ | |
| Formula weight | 445.96 | |
| Temperature | 100(2) K | |
| Wavelength | 0.670 Å | |
| Crystal system | Monoclinic | |
| Space group | *C*2 | |
| Unit cell dimensions | a = 37.321(7) Å | α = 90° |
| | b = 7.4490(15) Å | β = 101.13(3)° |
| | c = 16.822(3) Å | γ = 90° |
| Volume | 4588.6(17) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.291 $Mg/m^3$ | |
| Absorption coefficient | 0.163 $mm^{-1}$ | |
| F(000) | 1888 | |
| Crystal size | 0.123 x 0.018 x 0.015 $mm^3$ | |
| Theta range for data collection | 1.407 to 33.524°. | |
| Index ranges | -60<=h<=60, -11<=k<=11, -25<=l<=25 | |
| Reflections collected | 25545 | |
| Independent reflections | 17009 [R(int) = 0.0864] | |
| Completeness to theta = 23.703° | 99.8 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 1.000 and 0.908 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 17009 / 1 / 581 | |
| Goodness-of-fit on $F^2$ | 1.132 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0726, wR2 = 0.2002 | |
| R indices (all data) | R1 = 0.0803, wR2 = 0.2080 | |
| Absolute structure parameter | -0.04(3) | |
| Largest diff. peak and hole | 1.464 and –1.231 $e \cdot Å^{-3}$ | |

**Crystallographic data of 27 (Equation 1)**

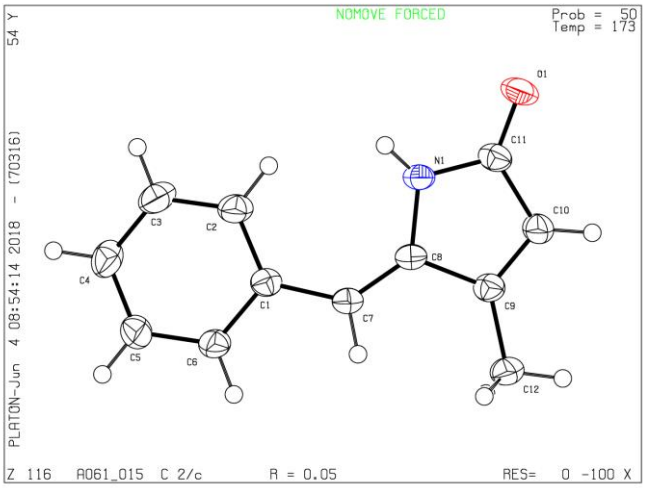



**Table S7.** Crystal data and structure refinement for **27**

| | | |
|---|---|---|
| Empirical formula | $C_{12}H_{11}NO$ | |
| Formula weight | 185.22 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | *C*2/*c* | |
| Unit cell dimensions | a = 11.286(3) Å | α = 90° |
| | b = 8.5520(18) Å | β = 102.313(8)° |
| | c = 20.170(5) Å | γ = 90° |
| Volume | 1901.9(7) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.294 $Mg/m^3$ | |
| Absorption coefficient | 0.083 $mm^{-1}$ | |
| F(000) | 784 | |
| Crystal size | 0.155 x 0.148 x 0.112 $mm^3$ | |
| Theta range for data collection | 3.014 to 30.556°. | |
| Index ranges | –16<=h<=15, –12<=k<=12, –28<=l<=28 | |
| Reflections collected | 31449 | |
| Independent reflections | 2909 [R(int) = 0.0676] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7451 and 0.7239 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2909 / 0 / 131 | |
| Goodness-of-fit on $F^2$ | 1.038 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0527, wR2 = 0.1187 | |
| R indices (all data) | R1 = 0.0872, wR2 = 0.1344 | |
| Largest diff. peak and hole | 0.190 and –0.300 $e \cdot Å^{-3}$ | |

**Crystallographic data of 29 (Equation 2)**

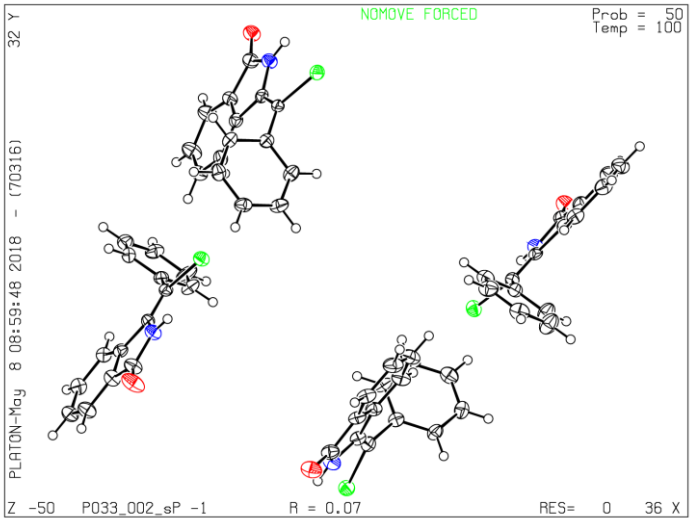



**Table S8.** Crystal data and structure refinement for **29**

| | | |
|---|---|---|
| Empirical formula | $C_{15}H_{10}NOBr$ | |
| Formula weight | 300.15 | |
| Temperature | 100(2) K | |
| Wavelength | 0.700 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 13.412(3) Å | α = 91.54(3)°. |
| | b = 14.379(3) Å | β = 106.29(3)°. |
| | c = 15.278(3) Å | γ = 106.58(3)°. |
| Volume | 2692.0(11) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.481 $Mg/m^3$ | |
| Absorption coefficient | 2.930 $mm^{-1}$ | |
| F(000) | 1200 | |
| Crystal size | 0.082 x 0.061 x 0.035 $mm^3$ | |
| Theta range for data collection | 1.465 to 27.000°. | |
| Index ranges | –17<=h<=17, –18<=k<=18, –19<=l<=19 | |
| Reflections collected | 23427 | |
| Independent reflections | 11989 [R(int) = 0.0324] | |
| Completeness to theta = 24.835° | 97.4 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 1.000 and 0.817 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11989 / 0 / 649 | |
| Goodness-of-fit on $F^2$ | 1.073 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0726, wR2 = 0.2156 | |
| R indices (all data) | R1 = 0.0782, wR2 = 0.2190 | |
| Largest diff. peak and hole | 1.834 and –1.713 $e \cdot Å^{-3}$ | |

**Crystallographic data of 32 (Scheme 4)**

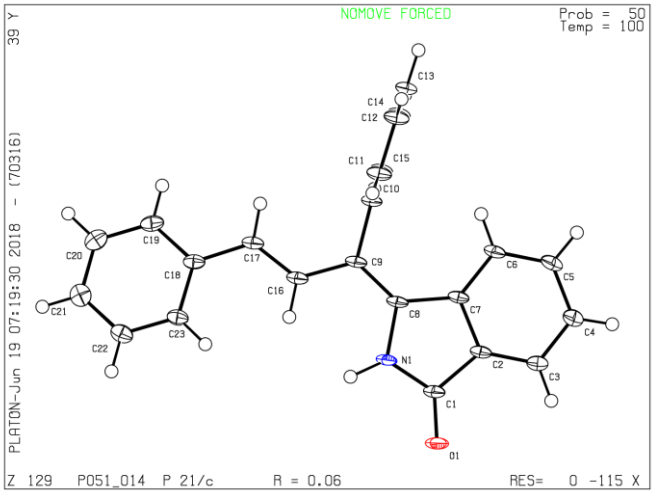



**Table S9.** Crystal data and structure refinement for **32**

| | | |
|---|---|---|
| Empirical formula | $C_{23}H_{17}NO$ | |
| Formula weight | 323.38 | |
| Temperature | 100(2) K | |
| Wavelength | 0.670 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 7.4060(15) Å | α = 90° |
| | b = 13.453(3) Å | β = 90.02(3)° |
| | c = 17.441(3) Å | γ = 90° |
| Volume | 1737.7(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.236 $Mg/m^3$ | |
| Absorption coefficient | 0.066 $mm^{-1}$ | |
| F(000) | 680 | |
| Crystal size | 0.092 x 0.022 x 0.020 $mm^3$ | |
| Theta range for data collection | 1.802 to 33.697°. | |
| Index ranges | –11<=h<=11, –20<=k<=20, –24<=l<=24 | |
| Reflections collected | 19841 | |
| Independent reflections | 6607 [R(int) = 0.0538] | |
| Completeness to theta = 23.703° | 97.1 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 1.000 and 0.919 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 6607 / 0 / 229 | |
| Goodness-of-fit on $F^2$ | 1.102 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0584, wR2 = 0.1641 | |
| R indices (all data) | R1 = 0.0666, wR2 = 0.1706 | |
| Largest diff. peak and hole | 0.456 and –0.551 $e \cdot Å^{-3}$ | |