SUPPORTING INFORMATON

Palladium-Catalyzed C–C Bond Cleavage of *N*-Cyclopropyl Acylhydrazones

Hiroki Fujioka, Motohiro Yasui*, Shohei Hamada, Kohei Fukumi, Norihiko Takeda, Yusuke Kobayashi, Takumi Furuta and Masafumi Ueda*

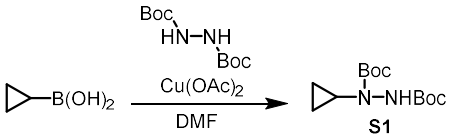
Kobe Pharmaceutical University
Motoyamakita, Higashinada, Kobe 657-8558 (Japan)
masa-u@kobepharma-u.ac.jp

1. General information

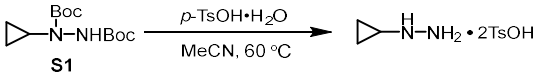
^{1}H NMR spectra were recorded at ambient temperature on JEOL ECZ400S spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane (0.00 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded at ambient temperature on a 75 MHz JEOL ECZ400S spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.00 ppm). ^{19}F NMR spectra were recorded on a 376 MHz JNM-ECZ400S. Chemical shifts are reported in ppm with $CFCl_3$ as the standard in machine setting. The high-resolution mass spectra (HRMS) were obtained using Orbitrap Mass Spectrometer (Exactive, Thermo Fisher Scientific) by the ESI technique. Melting points (uncorrected) were determined on BÜCHI M-565. Preparative Flash column chromatography was performed using KANTO CHEMICAL CO., INC. Silica Gel 60 N (spherical, neutral 40-50μm). TLC separations (PTLC) were carried out on precoated silica gel plates (E. Merck 60F254). Flash column chromatography were performed using Silicycle silica gel (siliaFlash® F60, 40-63 μm). Medium-pressure column chromatography with Biotage Isolera® was performed using Santai Technologies, Inc. iLOK-SL Series. Unless otherwise stated, all the reagents and solvents were used as received from the manufacturer. An oil bath was used as the heat source in all heating reaction condition.

2. Experimental section

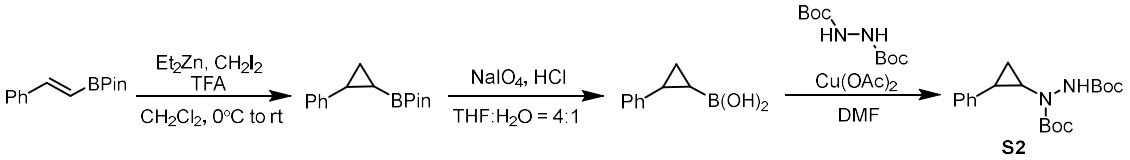
2-1. Representative procedure for synthesis of cyclopropylhydrazines[1]



To a solution of cyclopropylboronic acid (8.59 g, 100 mmol) in DMF (60 mL) were added di-*tert*-butyl azodicarboxylate (7.41 g, 32.0 mmol) and $Cu(OAc)_2$ (908 mg, 5.00 mmol). The mixture was stirred at 80 °C for 8 h, and then cooled to room temperature. After the mixture was cooled to 0 °C, 100 mL of H_2O and 200 mL of Et_2O were added. The organic layer was washed with H_2O and brine, and dried over $MgSO_4$. Then, the mixture was filtered and concentrated. The residue was purified with silica gel column chromatography (hexane/EtOAc = 9:1) to afford protected *N*-cyclopropylhydrazine **S1** (5.75 g, 21% yield).



To a solution of protected *N*-cyclopropylhydrazine **S1** (5.75g, 21 mmol) in MeCN (105 mL) was added *p*-toluenesulfonic acid monohydrate (16.0 g, 84 mmol). The mixture was stirred at 60 °C for 1 h, and then cooled to room temperature, filtered with KIRIYAMA ROHTO to afford *N*-cyclopropylhydrazine tosylate (6.26 g, 71% yield).



S2

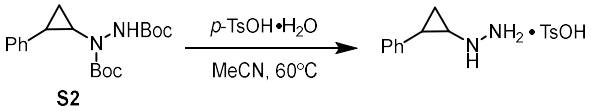
Et_2Zn (8.69 mL, 8.69 mmol in 1 M hexane) was added to CH_2Cl_2 (6.7 mL) at 0 °C. To the solution was added a solution of TFA (0.67 mL) in CH_2Cl_2 (6.7 mL) slowly. Then, the mixture was stirred at 0 °C for 30 minutes. Next, a solution of diiodomethane (700 µL, 8.69 mmol) in CH_2Cl_2 (6.7 mL) was added and the resulting reaction mixture was stirred for an additional 20 minutes at 0 °C. To the resulting solution was added *trans*-2-phenylvinylboronic acid pinacol ester in CH_2Cl_2 (6.7 mL), and the mixture was allowed to warm to room temperature and stirred for 12 h. Then, the mixture was quenched with sat. NH_4Claq. and extracted with $CHCl_3$ three times. The collected organic layers were washed with brine and dried over $MgSO_4$, filtered, and concentrated to afford crude cyclopropylboronate. To a solution of the crude cyclopropylboronate in THF/H_2O (4:1, 25 mL) was added $NaIO_4$ (1.28 g, 6.00 mmol) and stirred at room temperature for 15 minutes. Then, HCl (1.0 M, 5.1 mL) was added to the mixture and stirred for 14 h. The reaction mixture was diluted with water and extracted with EtOAc three times. The collected organic layers were washed with brine, dried over Na_2SO_4, and concentrated to afford crude cyclopropylboronic acid. The residue was dissolved in DMF (5.0 mL). To the solution were added di-*tert*-butyl azodicarboxylate (523 mg, 2.27 mmol) and $Cu(OAc)_2$ (41.0 mg, 0.23 mmol). The mixture was stirred at 80 °C for 15 h, and then cooled to 0 °C and diluted with water and Et_2O. The organic layer was collected and washed with water and brine. The resulting solution was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc = 7:3) to afford 1,2-bis(1,1-dimethyl) 1-(2-phenylcyclopropyl)-1,2-hydrazinedicarboxylate **S2** (357 mg, 24% from *trans*-2-phenylvinylboronic acid pinacol ester).

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.25 (d, J = 8.2 Hz, 2H), 7.15 (dd, J = 20.1, 6.4 Hz, 3H), 6.43 (s, 0.7H), 6.16 (s, 0.2H), 3.13 (s, 0.6H), 3.05 (s, 0.08H), 2.28 (s, 1H), 1.46 (d, J = 16.0 Hz, 18H), 1.37 (s, 0.3H), 1.19 (s, 0.9H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 155.7, 140.6, 128.2, 126.5, 125.9, 81.5, 81.2, 41.0, 28.2, 28.2, 16.3; Two carbon peak could not be detected probably due to overlapping;

HRMS (ESI) m/z calcd for $C_{19}H_{28}O_4N_2$ $[M+Na]^+$371.1941, found 371.1943.



S2

To a solution of **S2** (5.75 g, 21.0 mmol) in MeCN (105 mL) was added *p*-toluenesulfonic acid (16.0 g, 84.0 mmol). The mixture was stirred at 60 °C for 1 h, and then cooled to room temperature, filtered with KIRIYAMA ROHTO to afford *N*-(2-phenyl)cyclopropylhydrazine tosylate (206 mg, 64%).

Physical state: white solid;

Mp: 148 °C (decomp.);

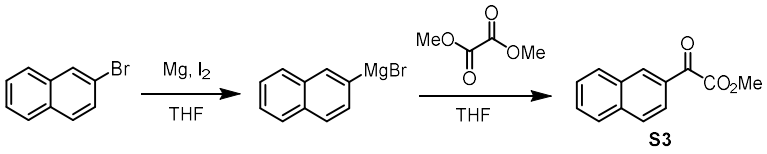
^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.66-9.51 (m, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.25 (t, J = 6.9 Hz, 2H), 7.17-7.08 (m, 5H), 2.67 (s, 1H), 2.28 (s, 3H), 2.11 (s, 1H), 1.17-1.09 (m, 2H);

^{13}C-NMR (101 MHz, DMSO-d_6) δ 145.5, 140.5, 137.8, 128.2, 128.1, 126.1, 125.8, 125.5, 40.4, 23.5, 20.8, 15.5;

HRMS (ESI) m/z calcd for $C_9H_{13}N_2$ $[M+H]^+$ 149.1073, found 149.1074.

2-2. Preparation of α-keto carbonyl compounds.

2-2-1. Synthesis of methyl 2-(naphthalen-2-yl)-2-oxoacetate

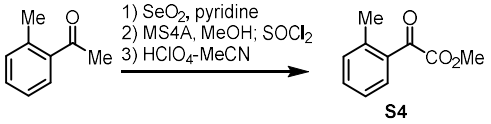


S3

To a suspension of magnesium (703 mg, 28.9 mmol) in THF (7.30 mL), was added I_2 slowly. To the resulted mixture was added the solution of 2-bromonaphthalene (5.00 g, 24.1 mmol) in THF (12 mL). After cooled to -78 °C, dimethyloxalate (1.90 g, 15.9 mmol) solution in THF was added to the reaction mixture and stirred at -78 °C for 1 h. Then, the mixture was quenched with 1M HCl and the aqueous phase was extracted with ethyl acetate and the combined organic extracts were dried over $MgSO_4$, filtered, and evaporated. 2-(Naphthalen-2-yl)-2-oxoacetate **S3** (571 mg, 11%) was obtained after purification by flash column chlomatography (hexane/EtOAc);

The spectral data were identical with those reported in the literature.[2]

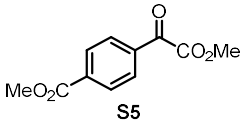
2-2-2. Representative procedure for synthesis of aryl α-keto esters from aryl ketones[3]



S4

To a solution of 2-methylacetophenone (1.34 g, 10.0 mmol) in pyridine (5.00 mL), was added SeO_2 (1.66 g, 15.0 mmol) and stirred at 100 °C under argon overnight. The mixture was cooled in an ice bath and then MS4A (60 mg) and MeOH were added (7.5 mL, 180 mmol). After the mixture was stirred for 10 min., $SOCl_2$ (3.75ml, 50.0 mmol) was added slowly and stirred at room temperature overnight. Then, $HClO_4$ (2.70 ml) and MeCN (27.3 ml) were poured into the flask, stirred for 30 min. Excess acid was neutralized by saturated Na_2CO_3 and filtered with Celite. Then, the aqueous phase was extracted with ethyl acetate three times and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated. 2-methyl-α-oxobenzene acetate **S4** (755 mg, 56%) was obtained after purification by flash column chlomatography (hexane/EtOAc);

The spectral data were identical with those reported in the literature.[3]



S5

Following to the representative procedure using 4-methoxycarbonylacetophenone (1.78 g, 10.0 mmol), SeO_2 (1.66 g, 15.0 mmol), pyridine (5.00 mL), MS4A (60 mg), MeOH (7.50 mL), $SOCl_2$ (3.75 mL), $HClO_4$ (2.70 mL) and MeCN (27.3 mL), methyl(4-(methoxycarbonyl)phenyl)glyoxylate **S5** (242 mg, 11%) was obtained after purification by flash column chromatography (hexane/EtOAc);

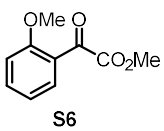
Physical state: white solid;

Mp: 96-101 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 6.8 Hz, 2H), 8.11-8.09 (m, 2H), 4.00 (d, J = 2.0 Hz, 3H), 3.97 (d, J = 2.0 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 185.2, 165.9, 163.3, 135.6, 135.4, 130.0, 129.9, 53.0, 52.6;

HRMS (ESI) m/z calcd for $C_{11}H_{10}O_5Na$ $[M+Na]^+$ 245.0420, found 245.0423.



S6

Following to the representative procedure using 2-methoxyacetophenone (751 mg, 5.00 mmol), SeO_2 (832 mg, 7.50 mmol), pyridine (2.50 mL), MS4A (300 mg), MeOH (3.60 mL), $SOCl_2$ (1.89 mL), $HClO_4$ (1.30 mL) and MeCN (13.7 mL), 3-methoxy-α-oxobenzene acetate **S6** (159 mg, 16%) was obtained after purification by flash column chromatography (hexane/EtOAc);

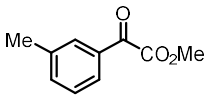
The spectral data were identical with those reported in the literature.

Physical state: Colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.91 (d, *J* = 2.4 Hz, 3H), 3.87 (d, *J* = 3.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 186.3, 165.6, 160.3, 136.4, 130.6, 122.7, 121.3, 112.0, 56.2, 52.4;

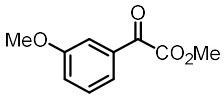
HRMS (ESI) m/z calcd for $C_{10}H_{11}O_4$ $[M+H]^+$ 195.0652, found 195.0654.



S7

Following to the representative procedure using 3-methylacetophenone (537 mg, 4.00 mmol), SeO_2 (666 mg, 6.00 mmol), pyridine (2.00 mL), MS4A (50 mg), MeOH (3.00 mL), $SOCl_2$ (1.5 mL), $HClO_4$ (1.20 mL) and MeCN (12.1 mL), 3-methyl-α-oxobenzene acetate **S7** (544 mg, 76%) was obtained after purification by flash column chromatography (hexane/EtOAc);

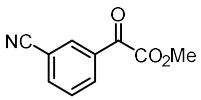
The spectral data were identical with those reported in the literature.[3]



S8

Following to the representative procedure using 3-methoxyacetophenone (751 mg, 5.00 mmol), SeO_2 (832 mg, 7.50 mmol), pyridine (2.50 mL), MS4A (300 mg), MeOH (3.60 mL), $SOCl_2$ (1.89 mL), $HClO_4$ (1.30 ml) and MeCN (13.7 ml), 3-methoxy-α-oxobenzene acetate **S8** (84.2 mg, 9%) was obtained after purification by flash column chromatography (hexane/EtOAc);

The spectral data were identical with those reported in the literature.[4]



S9

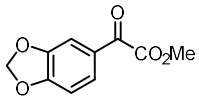
Following to the representative procedure using 3-cyanoacetophenone (728 mg, 5.00 mmol), SeO_2 (832 mg, 7.50 mmol), pyridine (2.50 mL), MS4A (300 mg), MeOH (3.60 mL), $SOCl_2$ (1.89 mL), $HClO_4$ (1.30 mL) and MeCN (13.7 mL), 3-cyano-α-oxobenzene acetate **S9** (198 mg, 21%) was obtained after purification by flash column chromatography (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.70-7.66 (m, 1H), 4.02 (d, *J* = 1.6 Hz, 3H);

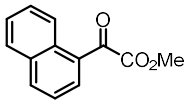
^{13}C-NMR (101 MHz, $CDCl_3$) δ 183.3, 162.5, 137.5, 133.9, 133.8, 133.4, 129.9, 117.4, 113.6, 53.3;

HRMS (ESI) m/z calcd for $C_{10}H_7O_3NNa$ $[M+Na]^+$ 212.0318, found 212.0321.



S10

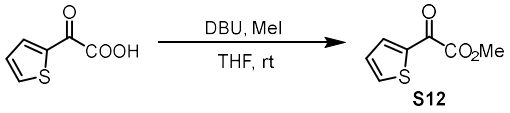
Following to the representative procedure using 3,4-methylenedioxyacetophenone (1.64 g, 10.0 mmol), SeO_2 (1.66 g, 15.0 mmol), pyridine (5.00 mL), MS4A (60 mg), MeOH (7.50 mL), $SOCl_2$ (3.75 mL), $HClO_4$ (2.70 mL) and MeCN (27.3 mL), methyl- α -oxo-1,3-benzodioxole-5-acetate **S10** (1.08 g, 52%) was obtained after purification by flash column chromatography (hexane/EtOAc);
The spectral data were identical with those reported in the literature.[5]



S11

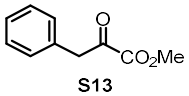
Following to the representative procedure using 1-acetonaphthone (681 mg, 4.00 mmol), SeO_2 (666 mg, 6.00 mmol), pyridine (2.00 mL), MS4A (50 mg), MeOH (3.00 mL), $SOCl_2$ (1.50 mL), $HClO_4$ (1.20 mL) and MeCN (12.1 mL), methyl- α -oxo-1-naphthalene acetate **S11** (594 mg, 69%) was obtained after purification by flash column chromatography (hexane/EtOAc);
The spectral data were identical with those reported in the literature.[2]

2-2-3. Representative procedure for synthesis of aryl α-keto esters from carboxylic acids.



S12

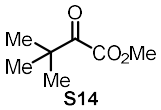
To a solution of thiopheneglyoxylic acid (625 mg, 4.00 mmol) in THF (20 mL) were added DBU (657 μL, 4.40 mmol) and MeI (1.20 mL, 20 mmol). The mixture was stirred at rt overnight, and then quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with Et_2O three times and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated. Methyl α-oxo-2-thiophene acetate **S12** (664 mg, 97%) was obtained after purification by flash column chlomatography (hexane/EtOAc);
The spectral data were identical with those reported in the literature[3].



S13

Following to the representative procedure using phenylpyruvic acid (657 mg, 4.00 mmol), DBU (657

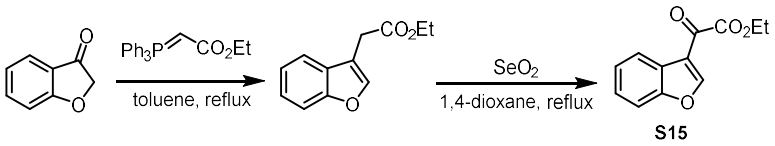
μL, 4.40 mmol), MeI (1.20 mL, 20 mmol) and THF (20 mL), methyl α-oxobenzenepropanoate **S13** (342 mg, 48%) was obtained after purification by flash column chromatography (hexane/EtOAc);
Physical state: yellow oil;
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 6.6 Hz, 2H), 7.29-7.25 (m, 1H), 6.53 (s, 1H), 6.45 (s, 1H), 3.92 (d, *J* = 1.6 Hz, 3H);
^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.7, 139.0, 134.0, 129.9, 128.5, 128.0, 111.2, 53.3;
HRMS (ESI) m/z calcd for $C_{10}H_{11}O_3$ $[M+H]^+$ 179.0703, found 179.0703.



S14

Following to the representative procedure using 3,3-dimethyl-2-oxobutanoic acid (1.30 g, 10.0 mmol), DBU (1.64 mL, 11.0 mmol), MeI (3.11 mL, 50.0 mmol) and THF (50 mL), methyl 2-oxo-3,3-dimethylbutanoate **S14** (1.54 g, quant.) was obtained after purification by flash column chromatography (hexane/EtOAc);
The spectral data were identical with those reported in the literature.[6]

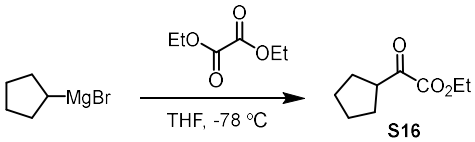
2-2-4. Synthesis of ethyl-α-oxo-3-benzofuran acetate[7,8]



S15

To a solution of coumaranone (671 mg, 5.00 mmol) in toluene (50 mL) was added ethyl triphenylphosphoranylidene acetate (2.61 g, 7.50 mmol) and stirred at reflux for 17 h. Then, the mixture was evaporated. Methyl benzofuran-3-acetate (888 mg, 87%) was obtained after purification by flash column chromatography (hexane/EtOAc).
To a solution of methyl benzofuran-3-acetate (888 mg, 4.35 mmol) in 1,4-dioxane (6.00 mL) was added SeO_2 (965 mg, 8.70 mmol) and stirred at reflux for 4 h. Then, the resulting mixture was filtered with Celite pad and the solution was evaporated. Ethyl-α-oxo-3-benzofuran acetate **S15** (682 mg, 72%) was obtained after purification by flash column chromatography (hexane/EtOAc).
The spectral data were identical with those reported in the literature.[8]

2-2-5. Synthesis of ethyl α-oxocyclopentaneacetate



S16

To a solution of diethyloxalate (466 μL, 3.00 mmol) in THF (5.00 mL) was added cyclopropylmagnesium bromide solution in THF (3.00 mL, 3.0 mmol). The mixture was stirred at -78 °C. Then, the mixture was warmed up to -10 °C and quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with Et_2O three times and the combined organic extracts were dried over Na_2SO_4, filtered and evaporated. Ethyl α-oxo cyclopentaneacetate **S16** (245 mg, 48%) was obtained after purification by flash column chlomatography (hexane/EtOAc);

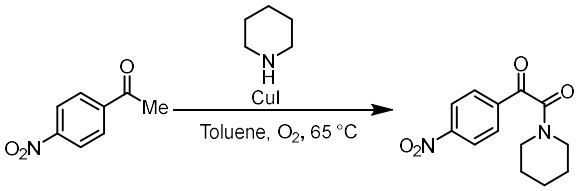
Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.36-4.30 (m, 2H), 3.54-3.46 (m, 1H), 1.90-1.81 (m, 4H), 1.65-1.64(m, 4H), 1.39-1.35 (m, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.7, 161.9, 62.2, 47.4, 28.3, 26.0, 14.0;

HRMS (ESI) m/z calcd for $C_9H_{14}O_3Na$ $[M+Na]^+$ 193.0835, found 193.0837.

2-2-6. Synthesis of 1-(4-nitrophenyl)-2-(1-piperodinyl)-1,2-ethanedione[9]

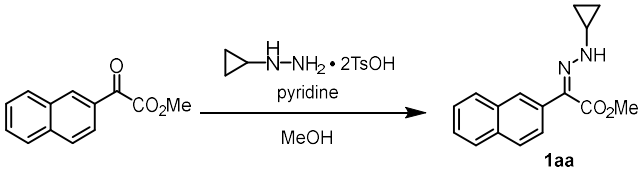


S17

To a solution of 4-nitroacetophenone (330 mg, 2.00 mmol) in toluene (5.0 mL) were added piperidine (218 μL, 2.20 mmol) and CuI (38.0 mg, 0.200 mmol). The mixture was stirred at 65 °C under O_2 for 5 h. After H_2O was added into the resulting mixture, the aqueous phase was extracted with EtOAc three times and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated. 1-(4-nitrophenyl)-2-(1-piperodinyl)-1,2-ethanedione **S17** (286 mg, 55%) was obtained after purification by flash column chromatography (hexane/EtOAc).

The spectral data were identical with those reported in the literature.[9]

2-3. Representative procedure for synthesis of *N*-cyclopropylhydrazones.



1aa

To a solution of **S3** (571 mg, 2.70 mmol) in MeOH (120 mL) were added cyclopropylhydrazine (1.11 g, 2.70 mmol) and pyridine (430 μL, 5.30 mmol). The mixture was stirred at room temperature for 18 h, and then evaporated. **1aa** (320 mg, 45%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

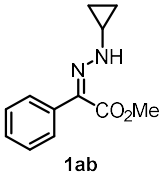
Physical state: white solid;

Mp: 72-77 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.96 (s, 1H), 7.84-7.78 (m, 3H), 7.66 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.47-7.41 (m, 2H), 3.81 (s, 3H), 3.12-3.07 (m, 1H), 0.85-0.79 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.1, 134.4, 133.2, 132.5, 128.2, 127.5, 127.2, 127.1, 126.6, 126.0, 125.8, 125.7, 51.4, 31.9, 6.3;

HRMS (ESI) m/z calcd for $C_{16}H_{17}O_2N_2$ $[M+H]^+$ 269.1285, found 269.1284.



1ab

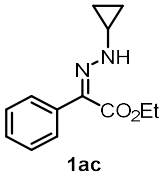
Following to the representative procedure using commercially available methyl benzoylformate (1.20 g, 7.20 mmol), cyclopropylhydrazine (3.00 g, 7.20 mmol) and pyridine (1.20 mL, 14 mmol), **1ab** (775 mg, 49%) was obtained after purification by flash column chromatography (hexane/EtOAc = 10:1);

Physical state: yellow oil;

^{1}H-NMR (600 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.50-7.48 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.24 (m, 1H), 3.77 (s, 3H), 3.07-3.03 (m, 1H), 0.82-0.75 (m, 4H);

^{13}C-NMR (151 MHz, $CDCl_3$) δ 163.9, 137.0, 128.4, 127.8, 127.0, 126.1, 51.3, 31.8, 6.2;

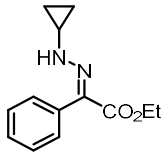
HRMS (ESI) m/z calcd for $C_{12}H_{15}O_2N_2$ $[M+H]^+$ 219.1128, found 219.1128.



1ac

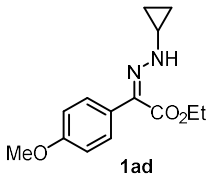
Following to the representative procedure using commercially available ethyl benzoylformate (1.07 g, 6.00 mmol), cyclopropylhydrazine (2.50 g, 6.00 mmol) and pyridine (969 μL, 12.0 mmol), **1ac** (854

mg, 61%) were obtained after purification by flash column chromatography (hexane/EtOAc);
Physical state: yellow oil;
^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.53-7.50 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.07-3.02 (m, 1H), 1.31 (t, *J* = 7.6 Hz, 3H), 0.81-0.76 (m, 4H);
^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.6, 137.1, 128.3, 127.8, 126.9, 126.3, 60.4, 31.8, 14.2, 6.2;
HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2N_2$ $[M+H]^+$ 233.1285, found 233.1286.



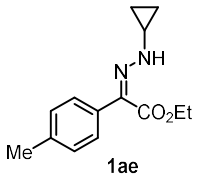
1ac'

Following to the representative procedure using commercially available ethyl benzoylformate (534 mg, 3.00 mmol), cyclopropylhydrazine (1.25 mg, 3.00 mmol) and pyridine (484 μL, 6.00 mmol), **1ac** (45.6 mg, 7%) and **1ac'** (*E*-isomer of **1ac**, 21.0 mg, 3%) were obtained after purification by flash column chromatography (hexane/EtOAc = 4:1);
Physical state: yellow oil;
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48-7.37 (m, 3H), 7.27-7.22 (m, 2H), 6.41 (s, 1H), 4.32-4.26 (m, 2H), 2.90-2.87 (m, 1H), 1.33-1.29 (m, 3H), 0.73-0.63 (m, 4H);
^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.4, 133.6, 130.5, 129.2, 129.0, 129.0, 61.1, 31.1, 14.3, 6.7;
HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2N_2$ $[M+H]^+$ 233.1285, found 233.1284.



1ad

Following to the representative procedure, commercially available ethyl 4-methoxybenzoylformate (208 mg, 1.00 mmol), cyclopropylhydrazine (417 mg, 1.00 mmol) and pyridine (161 μL, 2.00 mmol) were used and the reaction time was 4 h. **1ad** (128 mg, 12%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);
Physical state: yellow oil;
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 6.88-6.85 (m, 2H), 4.26 (q, *J* = 6.8 Hz, 2H), 3.81 (s, 3H), 3.05-2.99 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.79-0.74 (m, 4H);
^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.6, 158.7, 129.8, 129.5, 126.3, 113.2, 60.4, 55.3, 31.7, 14.2, 6.2;
HRMS (ESI) m/z calcd for $C_{14}H_{19}O_3N_2$ $[M+H]^+$ 263.1390, found 263.1388.



1ae

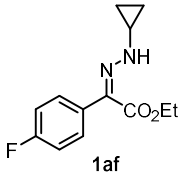
Following to the representative procedure, commercially available ethyl 4-methoxybenzoylformate (326 mg, 1.70 mmol), cyclopropylhydrazine (700 mg, 1.68 mmol) and pyridine (270 μL, 3.40 mmol) were used and the reaction time was 2 h. **1ae** (207 mg, 49%) was obtained after purification by Biotage Isolera® (hexane/EtOAc = 10:1);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 4.28-4.23 (m, 2H), 3.05-3.00 (m, 1H), 2.34 (s, 3H), 1.32-1.29 (m, 3H), 0.79-0.75 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.6, 136.7, 134.3, 128.5, 128.2, 126.5, 60.3, 31.8, 21.2, 14.2, 6.2;

HRMS (ESI) m/z calcd for $C_{14}H_{19}O_2N_2$ $[M+H]^+$ 247.1441, found 247.1441.



1af

Following to the representative procedure, commercially available ethyl-(4-fluorobenzoyl)formate (334 mg, 1.70 mmol), cyclopropylhydrazine (700 mg, 1.68 mmol) and pyridine (270 μL, 3.4 mmol) were used and the reaction time was 2 h. **1af** (212 mg, 50%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: yellow solid;

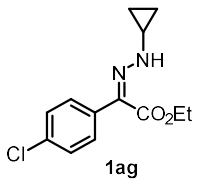
Mp: 35-40 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.50-7.46 (m, 2H), 7.00 (t, J = 8.8 Hz, 2H), 4.26 (q, J = 7.2 Hz, 2H), 3.06-3.01 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H), 0.78 (d, J = 6.8 Hz, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 245.6 Hz), 160.8, 133.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.89 Hz), 130.0 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 7.71 Hz), 125.3, 114.6 (d, $J_{C\text{-}C\text{-}F}$ = 21.2 Hz), 60.5, 31.8, 14.2, 6.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7

HRMS (ESI) m/z calcd for $C_{13}H_{16}O_2N_2F$ $[M+H]^+$ 251.1190, found 251.1192.



1ag

Following to the representative procedure, commercially available ethyl-(4-chlorobenzoyl)formate

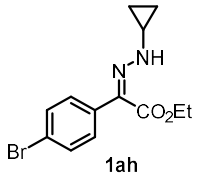
(360 mg, 1.7 mmol), cyclopropylhydrazine (700 mg, 1.68 mmol) and pyridine (270 μL, 3.4 mmol) were used and the reaction time was 5 h. **1ag** (207 mg, 46%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.48-7.45 (m, 2H), 7.30-7.26 (m, 2H), 4.26 (q, *J* = 6.8 Hz, 2H), 3.07-3.01 (m, 1H), 1.31 (t, *J* = 6.8 Hz, 3H), 0.80-0.77 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.3, 135.6, 132.6, 129.5, 127.9, 125.0, 60.5, 31.9, 14.2, 6.2;

HRMS (ESI) m/z calcd for $C_{13}H_{16}O_2N_2Cl$ $[M+H]^+$ 267.0895 found 267.0895.



1ah

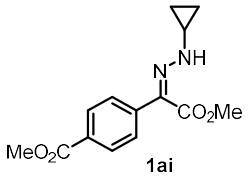
Following to the representative procedure, commercially available ethyl-(4-bromobenzoyl)formate (617 mg, 2.40 mmol), cyclopropylhydrazine (1.00 g, 2.40 mmol) and pyridine (400 μL, 4.8 mmol) were used and the reaction time was 5 h. **1ah** (403 mg, 54%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.45-7.38 (m, 4H), 4.26 (q, *J* = 7.6 Hz, 2H), 3.07-3.01 (m, 1H), 1.31 (t, *J* = 7.6 Hz, 3H), 0.80-0.77 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.3, 136.0, 130.8, 129.9, 124.9, 120.9, 60.5, 31.9, 14.2, 6.2;

HRMS (ESI) m/z calcd for $C_{13}H_{16}O_2N_2Br$ $[M+H]^+$ 311.0390, found 311.0391.



1ai

Following to the representative procedure, **S5** (165 mg, 0.743 mmol), cyclopropylhydrazine (291 mg, 0.700 mmol) and pyridine (113 μL, 1.4 mmol) were used and the reaction time was 3 h. **1ai** (79.7 mg, 41%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

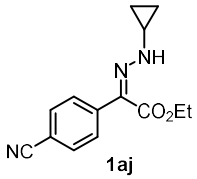
Physical state: white solid;

Mp: 75 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.00-7.97 (m, 2H), 7.62-7.59 (m, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.11-3.06 (m, 1H), 0.84-0.80 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.1, 163.8, 141.5, 129.1, 128.2, 127.9, 124.6, 52.0, 51.4, 32.1, 6.3;

HRMS (ESI) m/z calcd for $C_{14}H_{17}O_4N_2$ $[M+H]^+$ 277.1183, found 277.1182.



1aj

Following to the representative procedure, commercially available ethyl 4-cyanobenzoylformate (203 mg, 1.00 mmol), cyclopropylhydrazine (416 mg, 1.00 mmol) and pyridine (161 μL, 2.0 mmol) were used and the reaction time was 5 h. **1aj** (133 mg, 51%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

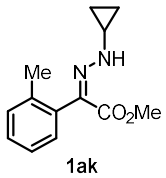
Physical state: white solid;

Mp: 66-70 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.68 (dd, J = 6.8, 1.6 Hz, 2H), 7.59 (dd, J = 6.8, 1.6 Hz, 2H), 4.29 (q, J = 7.2 Hz, 2H), 3.12-3.06 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 0.84-0.81 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.1, 141.6, 131.6, 128.4, 123.8, 119.3, 109.7, 60.7, 32.2, 14.2, 6.3;

HRMS (ESI) m/z calcd for $C_{14}H_{16}O_2N_3$ $[M+H]^+$ 258.1237, found 258.1239.



1ak

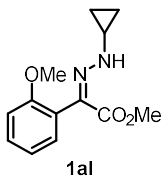
Following to the representative procedure, **S4** (115 mg, 0.645 mmol), cyclopropylhydrazine (268 mg, 0.643 mmol) and pyridine (103 μL, 1.3 mmol) were used. The mixture stirred at room temperature for 18 h. Then the mixture was heated up to 50 °C and stirred for 8 h. After the same work-up as the representative procedure, **1ak** (20.2 mg, 14%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: white solid;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.24-7.17 (m, 4H), 3.69 (s, 3H), 3.04-2.99 (m, 1H), 2.22 (s, 3H), 0.76 (t, J = 3.4 Hz, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.0, 137.2, 136.4, 130.2, 130.0, 127.8, 126.1, 125.6, 51.3, 31.6, 19.8, 6.3;

HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2N_2$ $[M+H]^+$ 233.1285, found 233.1286.



1al

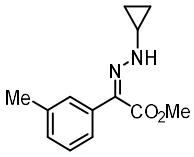
Following to the representative procedure, **S6** (159 mg, 0.819 mmol), cyclopropylhydrazine (342 mg, 0.821 mmol) and pyridine (132 μL, 1.60 mmol) were used and the reaction time was 17 h. **1al** (16.7 mg, 8%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.31-7.26 (m, 2H), 6.99-6.95 (m, 1H), 6.88-6.86 (m, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 3.02-2.97 (m, 1H), 0.77-0.72 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.0, 157.8, 130.5, 129.2, 126.8, 125.3, 120.7, 110.8, 55.6, 51.2, 31.4, 6.3;

HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3N_2$ $[M+H]^+$ 249.1234, found 249.1231.



1am

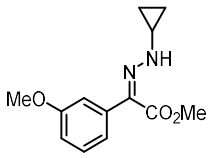
Following to the representative procedure, **S7** (132 mg, 0.741 mmol), cyclopropylhydrazine (309 mg, 0.742 mmol) and pyridine (119 μL, 1.50 mmol) were used and the reaction time was 22 h. **1am** (112 mg, 65%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 1H), 7.08 (d, J = 8.0 Hz, 1H), 3.77 (s, 3H), 3.06-3.03 (m, 1H), 2.36 (s, 3H), 0.80-0.76 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.0, 137.4, 136.9, 129.0, 128.0, 127.7, 126.3, 125.6, 51.3, 31.8, 21.5, 6.3

HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2N_2$ $[M+H]^+$ 233.1285, found 233.1284.



1an

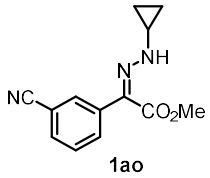
Following to the representative procedure, **S8** (84.2 mg, 0.433 mmol), cyclopropylhydrazine (181 mg, 0.434 mmol) and pyridine (69.0 μL, 0.86 mmol) were used and the reaction time was 21 h. **1an** (26.5 mg, 25%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.26-7.22 (m, 1H), 7.11-7.06 (m, 2H), 6.84-6.81 (m, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.07-3.02 (m, 1H), 0.81-0.76 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.9, 159.1, 138.3, 128.7, 125.7, 121.0, 114.2, 112.5, 55.2, 51.3, 31.9, 6.2;

HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3N_2$ $[M+H]^+$ 249.1233, found 249.1234.



1ao

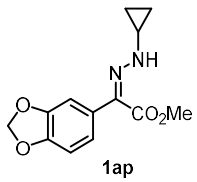
Following to the representative procedure, **S9** (189 mg, 1.00 mmol), cyclopropylhydrazine (416 mg, 1.00 mmol) and pyridine (161 μL, 2.0 mmol) were used and the reaction time was 24 h. **1ao** (110 mg, 45%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.84 (d, *J* = 0.8 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.11-3.05 (m, 1H), 0.83 (d, *J* = 5.6 Hz, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.4, 138.2, 132.4, 131.8, 130.1, 128.6, 123.2, 119.2, 111.9, 51.5, 32.2, 6.3;

HRMS (ESI) m/z calcd for $C_{13}H_{14}O_2N_3$ $[M+H]^+$ 244.1081, found 244.1079.



1ap

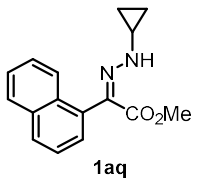
Following to the representative procedure, **S10** (400 mg, 1.92 mmol), cyclopropylhydrazine (696 mg, 1.67 mmol) and pyridine (270 μL, 3.3 mmol) were used and the reaction time was 17 h. **1ap** (117 mg, 23%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.00-6.96 (m, 2H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.94 (s, 2H), 3.77 (s, 3H), 3.05-3.00 (m, 1H), 0.79-0.75 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.8, 147.1, 146.7, 131.1, 125.7, 122.1, 109.1, 107.8, 100.9, 51.3, 31.8, 6.2;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_4N_2$ $[M+H]^+$ 263.1026, found 263.1027.



1aq

Following to the representative procedure, **S11** (175 mg, 0.815 mmol), cyclopropylhydrazine (339 mg,

0.815 mmol) and pyridine (132 µL, 1.63 mmol) were used and the reaction time was 22 h. **1aq** (60.3 mg, 28%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

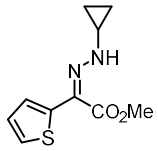
Physical state: brown solid;

Mp: 87-90 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.85-7.81 (m, 2H), 7.76 (t, *J* = 4.4 Hz, 1H), 7.49-7.41 (m, 4H), 3.60 (d, *J* = 1.6 Hz, 3H), 3.09-3.03 (m, 1H), 0.83-0.74 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.5, 134.4, 133.7, 132.8, 128.3, 128.3, 127.8, 125.8, 125.5, 125.3, 125.3, 125.1, 51.3, 31.7, 6.4;

HRMS (ESI) m/z calcd for $C_{16}H_{17}O_2N_2$ $[M+H]^+$ 269.1285, found 269.1287.



1ar

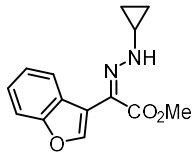
Following to the representative procedure, **S12** (181 mg, 1.06 mmol), cyclopropylhydrazine (443 mg, 1.06 mmol) and pyridine (171 µL, 2.1 mmol) were used and the reaction time was 22 h. **1ar** (52.8 mg, 22%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.31 (dd, *J* = 3.6, 1.6 Hz, 1H), 7.13-7.12 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.86 (s, 3H), 3.08-3.04 (m, 1H), 0.86-0.76 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.1, 141.1, 127.0, 124.0, 123.8, 121.3, 51.4, 32.1, 6.2;

HRMS (ESI) m/z calcd for $C_{10}H_{13}O_2N_2S$ $[M+H]^+$ 225.0692, found 225.0691.



1as

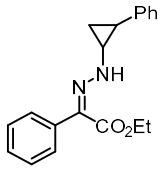
Following to the representative procedure, **S15** (207 mg, 0.948 mmol), cyclopropylhydrazine (396 mg, 0.948 mmol) and pyridine (153 µL, 1.9 mmol) were used and the reaction time was 3 h. **1as** (79.0 mg, 31%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.25-8.23 (m, 1H), 7.98 (s, 1H), 7.47-7.45 (m, 1H), 7.33-7.25 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.15-3.09 (m, 1H), 1.41 (t, *J* = 7.2 Hz, 3H), 0.88-0.83 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.2, 154.9, 143.0, 126.2, 124.3, 123.3, 122.7, 120.1, 117.1, 111.0, 60.7, 31.9, 14.2, 6.2;

HRMS (ESI) m/z calcd for $C_{15}H_{17}O_3N_2$ $[M+H]^+$ 273.1234, found 273.1234.



1at

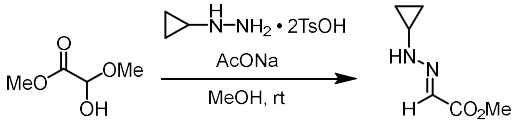
Following to the representative procedure, commercially available ethyl benzoylformate (114 mg, 0.640 mmol), (2-phenyl) cyclopropylhydrazine (315 mg, 0.983 mmol) and pyridine (103 μL, 1.3 mmol) were used and the reaction time was 13 h. **1at** (94.0 mg, 48%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.56-7.53 (m, 2H), 7.35-7.24 (m, 5H), 7.20-7.16 (m, 1H), 7.12-7.09 (m, 2H), 4.29 (q, J = 6.8 Hz, 2H), 3.25-3.21 (m, 1H), 2.32-2.27 (m, 1H), 1.60-1.55 (m, 1H), 1.32 (t, J = 6.8 Hz, 3H), 1.29-1.26 (m, 1H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.6, 140.8, 137.0, 128.4, 128.3, 127.8, 127.0, 126.5, 126.0, 125.9, 60.5, 41.8, 24.7, 15.4, 14.2;

HRMS (ESI) m/z calcd for $C_{19}H_{21}O_2N_2$ $[M+H]^+$ 309.1598, found 309.1598.



1au

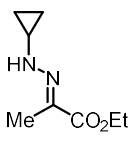
To a solution of commercially available methyl 2-hydroxy-2-methoxy acetate (100 mg, 0.831 mmol) in MeOH (3.00 mL) was added cyclopropylhydrazine (346 mg, 0.831 mmol) and AcONa (136 mg, 1.66 mmol). The mixture was stirred at room temperature for 3 h. The mixture was evaporated and extracted with $CHCl_3$ three times. Then, the mixture was dried over $MgSO_4$, filtered, and evaporated. **1au** (84.2 mg, 65%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.75 (s, 1H), 3.82 (s, 3H), 2.49-2.46 (m, 1H), 0.84 (q, J = 6.3 Hz, 2H), 0.65-0.61 (m, 2H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.3, 122.5, 51.8, 26.5, 6.4;

HRMS (ESI) m/z calcd for $C_6H_{11}O_2N_2$ $[M+H]^+$ 143.0815, found 143.0815.



1av

Following to the representative procedure, commercially available ethyl pyruvate (116 mg, 1.00 mmol), cyclopropylhydrazine (416 mg, 1.00 mmol) and pyridine (161 μL, 2.0 mmol) were used and the reaction time was 9 h. **1av** (150 mg, 88%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

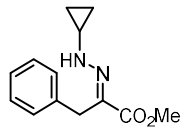
Physical state: white solid;

Mp: 54-58 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.92 (s, 1H), 4.31 (q, *J* = 5.2 Hz, 2H), 3.09-2.87 (m, 1H), 1.91 (s, 3H), 1.36 (t, *J* = 5.2 Hz, 3H), 0.82-0.68 (m, 4H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 132.6, 61.1, 31.3, 14.5, 10.2, 6.8;

HRMS (ESI) m/z calcd for $C_8H_{15}O_2N_2$ $[M+H]^+$ 171.1128, found 171.1127.



1aw

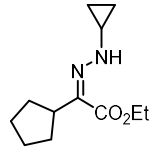
Following to the representative procedure, **S13** (125 mg, 0.701 mmol), cyclopropylhydrazine (291 mg, 0.699 mmol) and pyridine (113 μL, 1.4 mmol) were used and the reaction time was 4 h. **1aw** (65.7 mg, 40%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.24-7.20 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.20 (s, 1H), 3.85 (s, 3H), 3.84 (s, 2H), 2.89-2.83 (m, 1H), 0.69-0.64 (m, 2H), 0.55-0.51 (m, 2H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.7, 135.0, 133.2, 128.9, 127.8, 126.8, 52.4, 31.3, 30.8, 6.6;

HRMS (ESI) m/z calcd for $C_{13}H_{17}O_2N_2$ $[M+H]^+$ 233.1285, found 233.1285.



1ax

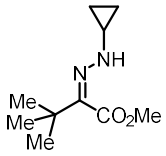
Following to the representative procedure, **S16** (170 mg, 1.00 mmol), cyclopropylhydrazine (416 mg, 1.00 mmol) and pyridine (161 μL, 2.00 mmol) were used and the reaction time was 7 h. **1ax** (110 mg, 49%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.99-2.91 (m, 1H), 2.89-2.84 (m, 1H), 1.82-1.77 (m, 2H), 1.69-1.54 (m, 6H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.68-0.66 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.7, 129.5, 59.8, 42.6, 31.3, 31.0, 25.3, 14.2, 5.9;

HRMS (ESI) m/z calcd for $C_{12}H_{21}O_2N_2$ $[M+H]^+$ 225.1598, found 225.1599.



1ay

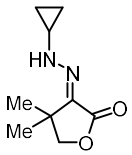
Following to the representative procedure, **S14** (132 mg, 0.915 mmol), cyclopropylhydrazine (383 mg, 0.915 mmol) and pyridine (149 μL, 1.80 mmol) were used and the reaction time was 4 h. **1ay** (97.3 mg, 53%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 3.76 (s, 4H), 2.87-2.82 (m, 1H), 1.18 (s, 9H), 0.69-0.64 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.3, 133.9, 50.6, 36.3, 31.4, 29.0, 5.7;

HRMS (ESI) m/z calcd for $C_{10}H_{19}O_2N_2$ $[M+H]^+$ 199.1441, found 199.1442.



1az

Following to the representative procedure, commercially available 2-ketopantoyl lactone (100 mg, 0.780 mmol), cyclopropylhydrazine (325 mg, 0.780 mmol) and pyridine (126 μL, 1.66 mmol) were used and the reaction time was 2 h. **1az** (95.0 mg, 67%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

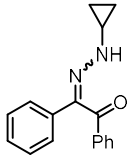
Physical state: white solid;

Mp: 96 °C (decomp.);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 4.01 (s, 2H), 3.00-2.95 (m, 1H), 1.40 (s, 7H), 0.78-0.73 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.3, 133.7, 77.6, 37.2, 31.9, 22.6, 6.8;

HRMS (ESI) m/z calcd for $C_9H_{15}O_2N_2$ $[M+H]^+$ 183.1128, found 183.1128.



1ba

Following to the representative procedure, commercially available benzil (147 mg, 0.699 mmol), cyclopropylhydrazine (291 mg, 0.699 mmol) and pyridine (113 μL, 1.40 mmol) were used and the

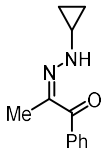
reaction time was 2 h. **1ba** (dr = 3.2:1, 62.7 mg, 24%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 8.01-7.97 (m, 7H), 7.53-7.49 (m, 12H), 7.46-7.38 (m, 11H), 7.28-7.25 (m, 11H), 7.24-7.18 (m, 2H), 6.67 (s, 3H), 3.11-3.06 (m, 1H), 2.89-2.84 (m, 3H), 0.87-0.77 (m, 4H), 0.71-0.67 (m, 14H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 190.7, 141.3, 138.5, 131.9, 131.2, 130.6, 130.5, 129.9, 129.3, 129.2, 129.0, 128.1, 127.9, 127.6, 127.0, 32.3, 31.5, 6.4, 6.3; Five carbon peaks of diastereomers could not be detected probably due to overlapping;

HRMS (ESI) (*E/Z* mixture) m/z calcd for $C_{17}H_{17}ON_2$ $[M+H]^+$ 265.1335, found 265.1336.



1bb

Following to the representative procedure, commercially available 1-phenyl-1,2-propanedione (104 mg, 0.700 mmol), cyclopropylhydrazine (291 mg, 0.700 mmol) and pyridine (161 μL, 1.40 mmol) were used and the reaction time was 10 h. **1bb** (97.9 mg, 69%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

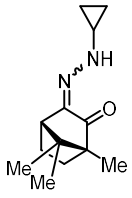
Physical state: yellow solid;

Mp: 60 °C (decomp.);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 6.8 Hz, 2H), 7.49-7.46 (m, 1H), 7.39 (t, J = 7.2 Hz, 2H), 6.21 (s, 1H), 2.95-2.90 (m, 1H), 1.98 (s, 3H), 0.74-0.71 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.4, 139.9, 137.9, 131.1, 130.6, 127.5, 31.5, 8.8, 6.5;

HRMS (ESI) m/z calcd for $C_{12}H_{15}ON_2$ $[M+H]^+$ 203.1179, found 203.1180.



1bc

Following to the representative procedure, commercially available camphorquinone (166 mg, 1.00 mmol), cyclopropylhydrazine (416 mg, 1.00 mmol) and pyridine (161 μL, 2.00 mmol) were used and the reaction time was 9 h. **1bc** (*E*/*Z* = 100:7, 40.6 mg, 18%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

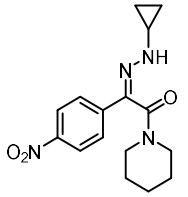
Physical state: white solid;

Mp: 87-93 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.91 (s, 1H), 2.90-2.84 (m, 1H), 2.66 (d, J = 4.4 Hz, 1H), 2.48 (d, J = 4.4 Hz, 0.07H), 1.97-1.89 (m, 1H), 1.75-1.68 (m, 1H), 1.54-1.47 (m, 1H), 1.42-1.34 (m, 1H), 0.99 (s, 3H), 0.94 (s, 3H), 0.90 (s, 0.19H), 0.83 (s, 3H), 0.69-0.64 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 204.1, 203.5, 146.5, 141.7, 59.3, 57.8, 50.7, 47.7, 45.7, 45.3, 31.4, 31.1, 30.9, 30.1, 26.0, 23.6, 20.4, 18.5, 18.1, 9.1, 8.7, 6.9, 6.7, 6.3, 6.2; One carbon peak could not be detected probably due to overlapping;

HRMS (ESI) m/z calcd for $C_{13}H_{21}ON_2$ $[M+H]^+$ 221.1648, found 221.1648.



1ca

To a solution of **S17** (127 mg, 0.569 mmol) in EtOH (5.70 ml), cyclopropylhydrazine (237 mg, 0.569 mmol) and pyridine (92.0 μL, 1.14 mmol) were added. The mixture was stirred at rt for 12 h, then heated 70 °C and stirred overnight. The mixture was evaporated. **1ca** (61.4 mg, 34%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

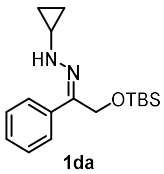
Physical state: yellow solid;

Mp: 99 °C (decomp.);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 11.2 Hz, 2H), 6.53 (s, 1H), 3.73 (s, 2H), 3.18 (t, J = 5.6 Hz, 2H), 2.95-2.89 (m, 1H), 1.66 (s, 4H), 1.42 (s, 2H), 0.76-0.67 (m, 4H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.1, 146.9, 140.7, 136.9, 125.1, 124.0, 47.2, 42.2, 31.5, 26.8, 25.7, 24.3, 6.4;

HRMS (ESI) m/z calcd for $C_{16}H_{21}O_3N_4$ $[M+H]^+$ 317.1608, found 317.1607.



1da

To a solution of 2-(tert-Butyldimethylsilyloxy)acetophenone (264 mg, 1.06 mmol) in CH_2Cl_2 (5.30 mL), cyclopropylhydrazine (440 mg, 1.06 mmol) and pyridine (171 μL, 2.12 mmol) were added. The mixture was stirred at room temperature for 6 h. After the same work-up as representative procedure, **1da** (22.6 mg, 7%) was obtained after purification by Biotage Isolera® (hexane/EtOAc);

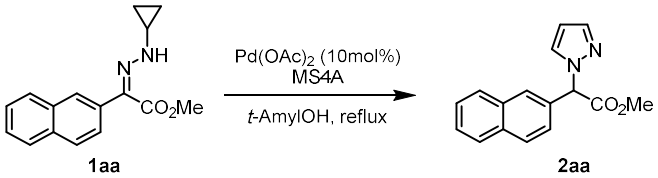
Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 5H), 5.56 (s, 1H), 4.43 (s, 2H), 2.63-2.58 (m, 1H), 0.80 (s, 9H), 0.61-0.51 (m, 4H), -0.04 (s, 6H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 147.0, 133.3, 128.8, 128.5, 128.2, 67.6, 30.9, 25.8, 18.2, 6.2, -5.4;

HRMS (ESI) m/z calcd for $C_{17}H_{29}ON_2Si$ $[M+H]^+$ 305.2044, found 305.2044.

2-4. Representative Procedure for C–C bond cleavage reaction of *N*-cyclopropylhydrazones



1aa 2aa

N-cyclopropylhydrazone **1aa** (32.1 mg, 0.120 mmol), $Pd(OAc)_2$ (2.7 mg, 0.012 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.20 mL). The mixture was stirred at reflux for 4 h. Then, the mixture was cooled to room temperature, filtered with Celite and evaporated. The residue was purified by PTLC (hexane/EtOAc = 7:3) to afford pyrazole **2aa** (25.6 mg, 80%).

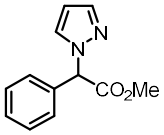
Physical state: yellow solid;

Mp: 97-99 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 4H), 7.61 (d, J = 2.0 Hz, 1H), 7.54-7.47 (m, 3H), 7.42 (d, J = 2.0 Hz, 1H), 6.40 (s, 1H), 6.27 (t, J = 2.0 Hz, 1H), 3.83 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.5, 140.0, 133.4, 133.1, 131.0, 129.3, 129.1, 128.2, 128.0, 127.7, 127.0, 126.7, 125.5, 106.1, 67.9, 52.9;

HRMS (ESI) m/z calcd for $C_{16}H_{15}O_2N_2$ $[M+H]^+$ 267.1128, found 267.1127.



2ab

Following to the representative procedure, **1ab** (32.2 mg, 0.148 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol) and MS4A (100 mg) were used and the reaction time was 23 h. **2ab** (20.2 mg, 64%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

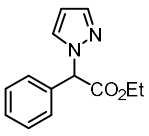
Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 1.6 Hz, 1H), 7.42-7.38 (m, 6H), 6.26 (t, J = 2.0 Hz, 1H), 6.23 (s, 1H), 3.80 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.4, 139.9, 133.8, 129.4, 129.2, 129.2, 128.4, 106.1, 67.8, 52.9;

HRMS (ESI) m/z calcd for $C_{12}H_{13}O_2N_2$ $[M+H]^+$ 217.0972, found 217.0973.

The spectral data were identical with those reported in the literature.[10,11]



2ac

Following to the representative procedure, **1ac** (22.8 mg, 0.0982 mmol), $Pd(OAc)_2$ (2.2 mg, 0.0098 mmol) and MS4A (86.0 mg) were used and the reaction time was 7 h. **2ac** (12.5 mg, 55%) was obtained after purification by PTLC (hexane/EtOAc = 3:1);

Following to the representative procedure, **1ac** (660 mg, 2.84 mmol), $Pd(OAc)_2$ (62.9 mg, 0.280 mmol) and MS4A (2.49 g) were used and the reaction time was 10 h. **2ac** (291 mg, 44%) was obtained after purification by flash column chlomatography (hexane/EtOAc);

Following to the representative procedure, **1ac'** (21.0 mg, 0.0904 mmol), $Pd(OAc)_2$ (2.0 mg, 0.0090 mmol) and MS4A (79.0 mg) were used and the reaction time was 6 h. **2ac** (11.1 mg, 53%) was obtained after purification by PTLC (hexane/EtOAc = 3:1);

Physical state: yellow solid;

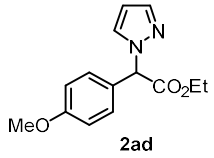
Mp: 43-47 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.0 Hz, 1H), 7.40-7.38 (m, 6H), 6.26 (t, J = 2.4 Hz, 1H), 6.21 (s, 1H), 4.33-4.20 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.0, 139.8, 134.0, 129.3, 129.2, 129.1, 128.4, 106.0, 67.9, 62.1, 14.0;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2N_2$ $[M+H]^+$ 231.1128, found 231.1130.

The spectral data were identical with those reported in the literature.[12]



2ad

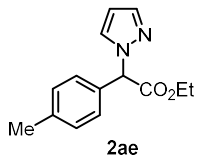
Following to the representative procedure, **1ad** (34.2 mg, 0.13 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol) and MS4A (100 mg) were used and the reaction time was 5 h. **2ad** (15.8 mg, 47%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 1.2 Hz, 1H), 7.36-7.33 (m, 3H), 6.95-6.92 (m, 2H), 6.25 (t, J = 1.6 Hz, 1H), 6.15 (s, 1H), 4.33-4.20 (m, 2H), 3.82 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.2, 160.3, 139.8, 129.9, 129.1, 125.8, 114.5, 105.9, 67.3, 62.0, 55.3, 14.0;

HRMS (ESI) m/z calcd for $C_{14}H_{17}O_3N_2$ $[M+H]^+$ 261.1234, found 261.1232.



2ae

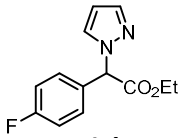
Following to the representative procedure, **1ae** (35.4 mg, 0.140 mmol), $Pd(OAc)_2$ (3.2 mg, 0.014 mmol) and MS4A (100 mg) were used and the reaction time was 24 h. **2ae** (22.4 mg, 64%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 1.6 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.25 (t, J = 1.6 Hz, 1H), 6.18 (s, 1H), 4.34-4.20 (m, 2H), 2.37 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.1, 139.8, 139.3, 130.8, 129.8, 129.1, 128.4, 105.9, 67.6, 62.0, 21.2, 14.0;

HRMS (ESI) m/z calcd for $C_{14}H_{17}O_2N_2$ $[M+H]^+$ 245.1285, found 245.1284.



2af

Following to the representative procedure, **1af** (32.0 mg, 0.128 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol) and MS4A (100 mg) were used and the reaction time was 6 h. **2af** (18.5 mg, 58%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

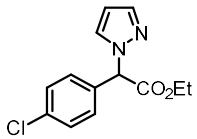
Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.42-7.37 (m, 3H), 7.13-7.08 (m, 2H), 6.29 (t, J = 2.4 Hz, 1H), 6.19 (s, 1H), 4.34-4.21 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.8, 163.1 (d, $J_{C\text{-}F}$ = 249.5 Hz), 140.0, 130.3 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 8.67Hz), 129.9 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.89 Hz), 129.1, 116.2 (d, $J_{C\text{-}C\text{-}F}$ = 22.2 Hz), 106.2, 67.1, 62.2, 14.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7

HRMS (ESI) m/z calcd for $C_{13}H_{14}O_2N_2F$ $[M+H]^+$ 249.1034, found 249.1035.



2ag

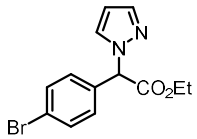
Following to the representative procedure, **1ag** (37.9 mg, 0.142 mmol), $Pd(OAc)_2$ (3.2 mg, 0.014 mmol) and MS4A (100 mg) were used and the reaction time was 12 h. **2ag** (26.9 mg, 72%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.44 (d, J = 2.4 Hz, 1H), 7.40-7.38 (m, 2H), 7.34-7.32 (m, 2H), 6.29 (t, J = 2.4 Hz, 1H), 6.17 (s, 1H), 4.34-4.21 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.5, 140.0, 135.4, 132.6, 129.7, 129.3, 129.2, 106.3, 67.1, 62.3, 14.0;

HRMS (ESI) m/z calcd for $C_{13}H_{14}O_2N_2Cl$ $[M+H]^+$ 265.0738, found 265.0738.



2ah

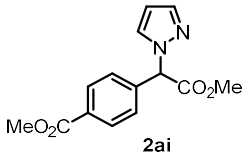
Following to the representative procedure, **1ah** (40.6 mg, 0.130 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol) and MS4A (100 mg) were used and the reaction time was 24 h. **2ah** (3.5 mg, 9%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 3H), 7.43 (d, *J* = 2.8 Hz, 1H), 7.26-7.24 (m, 2H), 6.28 (t, *J* = 2.0 Hz, 1H), 6.14 (s, 1H), 4.33-4.20 (m, 2H), 1.26 (t, *J* = 6.8 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.5, 140.0, 133.1, 132.3, 129.9, 129.2, 123.6, 106.3, 67.2, 62.3, 14.0;

HRMS (ESI) m/z calcd for $C_{13}H_{14}O_2N_2{}^{79}Br$ $[M+H]^+$ 309.0233, found 309.0232, $C_{13}H_{14}O_2N_2{}^{81}Br$ $[M+H]^+$ 311.0213, found 311.0211.



2ai

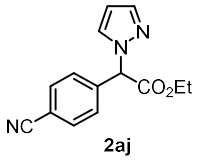
Following to the representative procedure, **1ai** (26.6 mg, 0.0962 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and MS4A (82.0 mg) were used and the reaction time was 24 h. **2ai** (15.9 mg, 60%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.59 (s, 1H), 7.47-7.44 (m, 3H), 6.31 (d, *J* = 0.8 Hz, 1H), 6.29 (s, 1H), 3.93 (s, 3H), 3.83 (t, *J* = 0.8 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.8, 166.3, 140.1, 138.7, 131.0, 130.3, 129.4, 128.3, 106.5, 67.4, 53.1, 52.3;

HRMS (ESI) m/z calcd for $C_{14}H_{15}O_4N_2$ $[M+H]^+$ 275.1026, found 275.1025.



2aj

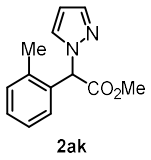
Following to the representative procedure, **1aj** (42.6 mg, 0.165 mmol), $Pd(OAc)_2$ (3.7 mg, 0.017 mmol) and MS4A (100 mg) were used and the reaction time was 24 h. **2aj** (15.6 mg, 37%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.35 (t, *J* = 2.4 Hz, 1H), 6.25 (s, 1H), 4.37-4.25 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.7, 140.3, 139.5, 132.7, 129.5, 128.8, 118.1, 113.1, 106.8, 67.2, 62.6, 14.0;

HRMS (ESI) m/z calcd for $C_{14}H_{14}O_2N_3$ $[M+H]^+$ 256.1081, found 256.1081.



2ak

Following to the representative procedure, **1ak** (20.2 mg, 0.0873 mmol), $Pd(OAc)_2$ (2.0 mg, 0.0089 mmol) and MS4A (74.0 mg) were used and the reaction time was 18 h. **2ak** (11.7 mg, 58%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

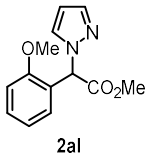
Physical state: white solid;

Mp: 80-82 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.2 Hz, 1H), 7.34-7.23 (m, 4H), 7.17 (d, *J* = 2.4 Hz, 1H), 6.43 (s, 1H), 6.23 (t, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 2.24 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.1, 139.9, 138.0, 132.0, 131.3, 129.5, 129.1, 127.6, 126.6, 106.0, 65.0, 52.8, 19.1;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2N_2$ $[M+H]^+$ 231.1128, found 231.1126.



2al

Following to the representative procedure, **1al** (16.7 mg, 0.0673 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0067 mmol) and MS4A (60.0 mg) were used and the reaction time was 9 h. **2al** (10.0 mg, 60%) was obtained

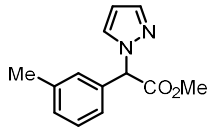
after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.6 Hz, 1H), 7.41-7.36 (m, 2H), 7.29-7.26 (m, 1H), 7.02-6.94 (m, 2H), 6.53 (s, 1H), 6.26 (t, *J* = 2.0 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.0, 157.0, 139.7, 130.7, 129.5, 129.2, 122.9, 121.0, 111.2, 105.8, 62.6, 55.7, 52.8;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_3N_2$ $[M+H]^+$ 247.1077, found 247.1075.



2am

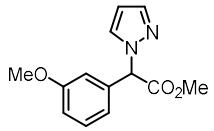
Following to the representative procedure, **1am** (26.8 mg, 0.115 mmol), $Pd(OAc)_2$ (2.6 mg, 0.012 mmol) and MS4A (98.0 mg) were used and the reaction time was 9 h. **2am** (10.3 mg, 39%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 3H), 6.27 (t, *J* = 2.4 Hz, 1H), 6.20 (s, 1H), 3.81 (s, 3H), 2.37 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.6, 139.9, 139.1, 133.5, 130.2, 129.2, 129.1, 129.1, 125.4, 106.0, 67.8, 52.9, 21.4;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2N_2$ $[M+H]^+$ 231.1128, found 231.1128.



2an

Following to the representative procedure, **1an** (26.3 mg, 0.110 mmol), $Pd(OAc)_2$ (2.4 mg, 0.011 mmol) and MS4A (95.0 mg) were used and the reaction time was 6 h. **2an** (16.1 mg, 62%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

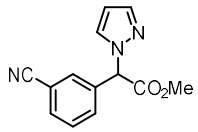
Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.2 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 6.99-6.92 (m, 3H), 6.28 (t, *J* = 2.0 Hz, 1H), 6.20 (s, 1H), 3.81 (s, 1H), 3.80 (s, 1H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.3, 160.1, 139.9, 135.1, 130.2, 129.3, 120.5, 114.8, 114.2, 106.1, 67.7, 55.3, 52.9;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_3N_2$ $[M+H]^+$ 247.1077, found 247.1076.

The spectral data were identical with those reported in the literature. [11]



2ao

Following to the representative procedure, **1ao** (48.0 mg, 0.200 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and MS4A (168 mg) were used and the reaction time was 24 h. **2ao** (32.1 mg, 68%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

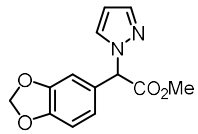
Physical state: yellow solid;

Mp: 101-103 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.51 (m, 6H), 6.35 (d, J = 2.0 Hz, 1H), 6.23 (s, 1H), 3.85 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.2, 140.5, 136.1, 132.7, 132.4, 131.6, 129.9, 129.4, 118.0, 113.4, 106.9, 66.8, 53.3;

HRMS (ESI) m/z calcd for $C_{13}H_{12}O_2N_3$ $[M+H]^+$ 242.0924, found 242.0922.



2ap

N-cyclopropylhydrazone **1ap** (33.8 mg, 0.129 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol) and MS4A (110 mg) were dissolved in *t*-AmylOH (1.29 mL). The mixture was stirred at reflux for 19 h. Then the mixture was transferred to sealed tube and stirred at 150 °C for 9 h. After the same work-up as representative procedure, **2ap** (11.0 mg, 33%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

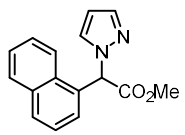
Physical state: yellow solid;

Mp: 49- 52 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 1.6 Hz, 1H), 7.42 (d, J = 2.4 Hz, 1H), 6.90-6.88 (m, 2H), 6.84-6.82 (m, 1H), 6.28 (t, J = 2.4 Hz, 1H), 6.12 (s, 1H), 6.00 (s, 2H), 3.80 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.5, 148.5, 148.3, 140.0, 129.1, 127.2, 122.5, 108.8, 108.7, 106.0, 101.6, 67.4, 52.9;

HRMS (ESI) m/z calcd for $C_{13}H_{12}O_4N_2Na$ $[M+H]^+$ 283.0689, found 283.0687.



2aq

Following to the representative procedure, **1aq** (24.7 mg, 0.0921 mmol), $Pd(OAc)_2$ (2.1 mg, 0.0092 mmol) and MS4A (77.0 mg) were used and the reaction time was 10 h. **2aq** (15.3 mg, 62%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

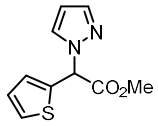
Physical state: yellow solid;

Mp: 81-86 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94-7.87 (m, 3H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.53-7.47 (m, 4H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.02 (s, 1H), 6.19 (t, *J* = 2.0 Hz, 1H), 3.85 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.1, 140.1, 134.0, 131.5, 130.5, 129.4, 128.9, 127.5, 126.4, 126.1, 125.1, 122.7, 106.1, 64.9, 52.9;

HRMS (ESI) m/z calcd for $C_{16}H_{15}O_2N_2$ $[M+H]^+$ 267.1128, found 267.1130.



2ar

Following to the representative procedure, **1ar** (25.5 mg, 0.114 mmol), $Pd(OAc)_2$ (2.5 mg, 0.011 mmol) and MS4A (97.0 mg) were used and the reaction time was 18 h. **2ar** (18.8 mg, 74%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

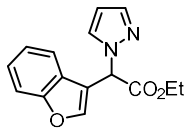
Physical state: yellow solid;

Mp: 41-45 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.6 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.19-7.18 (m, 1H), 7.04 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.44 (s, 1H), 6.30 (t, *J* = 2.0 Hz, 1H), 3.83 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.6, 140.1, 135.1, 129.0, 128.5, 127.7, 127.1, 106.3, 62.9, 53.2;

HRMS (ESI) m/z calcd for $C_{10}H_{11}O_2N_2S$ $[M+H]^+$ 223.0536, found 223.0533.



2as

Following to the representative procedure, **1as** (26.1 mg, 0.0958 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and MS4A (86.0 mg) were used and the reaction time was 10 h. **2as** (15.5 mg, 60%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow solid;

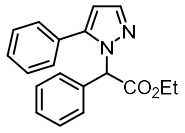
Mp: 49-52 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.45 (d, *J* =

2.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.26-7.21 (m, 1H), 6.42 (d, *J* = 1.2 Hz, 1H), 6.27 (t, *J* = 2.0 Hz, 1H), 4.36-4.24 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.2, 155.4, 144.3, 140.0, 129.2, 125.7, 125.3, 123.4, 120.0, 114.5, 111.8, 106.3, 62.4, 59.7, 14.0;

HRMS (ESI) m/z calcd for $C_{15}H_{15}O_3N_2$ $[M+H]^+$ 271.1077, found 271.1075.



2at

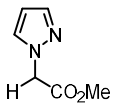
N-cyclopropylhydrazone **1at** (30.2 mg, 0.0980 mmol), $Pd(OAc)_2$ (2.2 mg, 0.0098 mmol) and MS4A (87.0 mg) were dissolved in *t*-AmylOH (980 μL). After the mixture was stirred at 140 °C in a sealed tube for 21 h, $Pd(OAc)_2$ (2.2 mg, 0.0100 mmol) was added and stirred for 4 h. Then, the mixture was cooled to room temperature, filtered with Celite and evaporated. The residue was purified by PTLC (Hexane/EtOAc = 7: 3) to afford pyrazole **2at** (11.4 mg, 38%).

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.44 (t, *J* = 2.0 Hz, 3H), 7.35 (s, 7H), 7.26 (s, 2H), 6.33 (s, 1H), 6.02 (s, 1H), 4.22 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.6, 144.6, 139.8, 135.1, 130.4, 129.2, 128.9, 128.8, 128.7, 128.5, 106.4, 64.6, 62.0, 14.0; One carbon peak could not be detected probably due to overlapping;

HRMS (ESI) m/z calcd for $C_{19}H_{19}O_2N_2$ $[M+H]^+$ 307.1441, found 307.1439.



2au

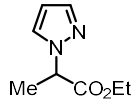
Following to the representative procedure, **1au** (12.0 mg, 0.0844 mmol), $Pd(OAc)_2$ (1.9 mg, 0.0085 mmol) and MS4A (100 mg) were used and the reaction time was 32 h. **2au** (4.1 mg, 35%) was obtained after purification by PTLC (hexane/EtOAc = 1:1);

Physical state: brown oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 6.34 (t, *J* = 2.0 Hz, 1H), 4.95 (s, 2H), 3.78 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.3, 140.2, 130.6, 106.6, 52.9, 52.7;

HRMS (ESI) m/z calcd for $C_6H_9O_2N_2$ $[M+H]^+$ 141.0659, found 141.0658.



2av

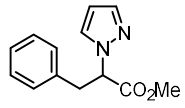
Following to the representative procedure, **1av** (20.0 mg, 0.117 mmol), $Pd(OAc)_2$ (2.6 mg, 0.012 mmol) and MS4A (100 mg) were used and the reaction time was 8 h. **2av** (15.3 mg, 78%) was obtained after purification of silica gel short column (hexane/EtOAc).

Physical state: brown oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 0.8 Hz, 2H), 6.32 (t, J = 0.8 Hz, 1H), 5.11 (q, J = 7.2 Hz, 1H), 4.23-4.17 (m, 2H), 1.81-1.79 (m, 3H), 1.27-1.23 (m, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.6, 139.5, 128.1, 106.0, 61.7, 59.5, 17.5, 14.0;

HRMS (ESI) m/z calcd for $C_8H_{13}O_2N_2$ $[M+H]^+$ 169.0972, found 169.0970.



2aw

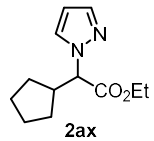
Following to the representative procedure, **1aw** (23.7 mg, 0.102 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and MS4A (83.0 mg) were used and the reaction time was 5 h. **2aw** (10.3 mg, 44%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.25-7.19 (m, 3H), 7.02 (dd, J = 7.6, 2.0 Hz, 2H), 6.23 (t, J = 2.4 Hz, 1H), 5.15 (t, J = 7.2 Hz, 1H), 3.73 (s, 3H), 3.49 (d, J = 7.6 Hz, 2H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.8, 139.8, 136.1, 129.5, 128.9, 128.5, 127.0, 105.9, 65.6, 52.7, 38.2;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2N_2$ $[M+H]^+$ 231.1126, found 231.1128.



2ax

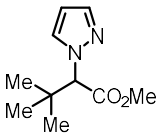
Following to the representative procedure, **1ax** (24.3 mg, 0.109 mmol), $Pd(OAc)_2$ (2.4 mg, 0.011 mmol) and MS4A (93.0 mg) were used and the reaction time was 12 h. **2ax** (16.5 mg, 68%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 2.0 Hz, 1H), 7.50 (d, J = 1.2 Hz, 1H), 6.31 (t, J = 1.6 Hz, 1H), 4.73 (d, J = 11.2 Hz, 1H), 4.26-4.13 (m, 2H), 2.77-2.67 (m, 1H), 1.89-1.81 (m, 1H), 1.75-1.51 (m, 6H), 1.45-1.35 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.0, 139.0, 128.3, 106.1, 69.0, 61.5, 42.7, 29.6, 29.6, 25.3, 24.8, 14.1;

HRMS (ESI) m/z calcd for $C_{12}H_{19}O_2N_2$ $[M+H]^+$ 223.1441, found 223.1442.



2ay

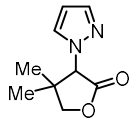
N-cyclopropylhydrazone **1ay** (21.0 mg, 0.106 mmol), $Pd(OAc)_2$ (2.4 mg, 0.011 mmol) and MS4A (91.0 mg) were dissolved in *t*-AmylOH (1.06 mL). After the mixture was stirred at 130 °C in a sealed tube for 13 h, $Pd(OAc)_2$ (2.4 mg, 0.011 mmol) was added and stirred for 11 h. After the same work-up as representative procedure, **2ay** (3.8 mg, 18%) was obtained after purification by PTLC (hexane/EtOAc = 7:3).

Physical state: colorless oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 6.30 (t, *J* = 2.0 Hz, 1H), 4.94 (s, 1H), 3.75 (s, 3H), 1.02 (s, 9H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.6, 138.4, 129.7, 105.8, 73.0, 52.0, 36.0, 26.9

HRMS (ESI) m/z calcd for $C_{10}H_{17}O_2N_2$ $[M+H]^+$ 197.1284, found 197.1285.



2az

Following to the representative procedure, **1az** (32.1 mg, 0.175 mmol), $Pd(OAc)_2$ (3.9 mg, 0.017 mmol) and MS4A (100 mg) were used and the reaction time was 13 h. **2az** (27.0 mg, 86%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

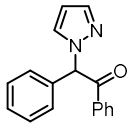
Physical state: white solid;

Mp: 78-81 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.2 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 6.33 (t, *J* = 2.0 Hz, 1H), 4.90 (s, 1H), 4.25 (d, *J* = 8.8 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 1.35 (s, 3H), 0.80 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.9, 140.6, 130.2, 106.0, 69.0, 41.9, 24.3, 20.0;

HRMS (ESI) m/z calcd for $C_9H_{13}O_2N_2$ $[M+H]^+$ 181.0972, found 181.0970.



2ba

Following to the representative procedure, **1ba** (17.9 mg, 0.068 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0067 mmol) and MS4A (60.0 mg) were used and the reaction time was 17 h. **2ba** (6.8 mg, 38%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

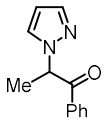
Physical state: yellow solid;

Mp: 95-98 °C;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.59-7.52 (m, 2H), 7.44-7.38 (m, 8H), 7.22 (s, 1H), 6.30 (t, J = 2.0 Hz, 1H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.6, 139.6, 134.7, 134.1, 133.8, 129.8, 129.5, 129.4, 129.1, 128.9, 128.8, 106.0, 70.1;

HRMS (ESI) m/z calcd for $C_{17}H_{15}ON_2$ $[M+H]^+$ 263.1179, found 263.1178.



2bb

Following to the representative procedure, **1bb** (26.9 mg, 0.134 mmol), $Pd(OAc)_2$ (3.0 mg, 0.013 mmol) and MS4A (118 mg) were used and the reaction time was 7 h. **2bb** (11.8 mg, 44%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

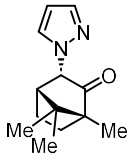
Physical state: brown solid;

Mp: 79 °C (decomp);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.58-7.52 (m, 3H), 7.44 (t, J = 7.8 Hz, 2H), 6.29 (s, 1H), 6.08 (q, J = 7.2 Hz, 1H), 1.76 (d, J = 7.2 Hz, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 195.6, 139.4, 134.6, 133.8, 128.8, 128.7, 127.9, 106.4, 60.9, 18.0;

HRMS (ESI) m/z calcd for $C_{12}H_{13}ON_2$ $[M+H]^+$ 201.1022, found 201.1023.



2bc

Following to the representative procedure, **1bc** (19.1 mg, 0.0867 mmol), $Pd(OAc)_2$ (2.0 mg, 0.0089 mmol) and MS4A (74.0 mg) were used and the reaction time was 5 h. **2bc** (11.3 mg, 60%) was obtained

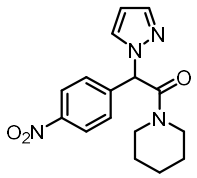
after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 (d, J = 2.4 Hz, 1H), 6.27-6.26 (m, 1H), 5.01 (d, J = 4.4 Hz, 1H), 2.63 (t, J = 4.4 Hz, 1H), 1.89-1.78 (m, 1H), 1.75-1.65 (m, 1H), 1.57-1.48 (m, 1H), 1.10-1.00 (m, 1H), 1.07 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 212.4, 139.9, 129.1, 105.3, 67.4, 59.2, 49.5, 43.9, 30.8, 19.8, 19.7, 19.1, 9.5;

HRMS (ESI) m/z calcd for $C_{13}H_{19}ON_2$ $[M+H]^+$ 219.1492, found 219.1490.



2ca

Following to the representative procedure, **1ca** (26.5 mg, 0.0838 mmol), $Pd(OAc)_2$ (1.9 mg, 0.0084 mmol) and MS4A (75 mg) were used and the reaction time was 9 h. **2ca** (14.3 mg, 54%) was obtained after purification by PTLC (hexane/EtOAc = 7:3);

Physical state: yellow solid;

Mp: 93-98 °C;

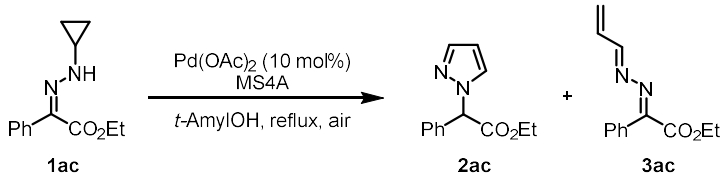
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25-8.21 (m, 2H), 7.58 (d, J = 1.2 Hz, 1H), 7.54 (d, J = 2.8 Hz, 1H), 7.44-7.42 (m, 2H), 6.64 (s, 1H), 6.34 (t, J = 2.4 Hz, 1H), 3.71-3.58 (m, 2H), 3.45-3.29 (m, 2H), 1.64-1.54 (m, 4H), 1.36-1.25 (m, 2H);

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.7, 148.0, 142.7, 140.0, 129.7, 129.0, 124.1, 106.9, 64.9, 47.0, 43.8, 26.1, 25.4, 24.2;

HRMS (ESI) m/z calcd for $C_{16}H_{19}O_3N_4$ $[M+H]^+$315.1452, found 315.1450.

2-5. Mechanistic studies

2-5-1. Identification of reaction intermediates



1ac 2ac 3ac

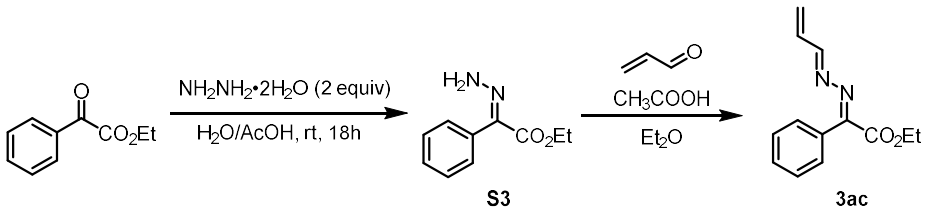
N-cyclopropylhydrazone **1ac** (23.6 mg, 0.102 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and MS4A (92.0 mg) were dissolved in *t*-AmylOH (1.0 mL). The mixture was stirred at reflux under air for 30 min. After the mixture was cooled to room temperature, the mixture was filtered through

Celite® and evaporated. The residue was analyzed by ^{1}H NMR ($CDCl_3$) using triphenyl methane (21.5 mg, 0.0880 mmol) as internal standard. The azine **3ac** was calculated as 22% NMR yield, pyrazole **2ac** as 4% and *N*-cyclopropylhydrazone **1ac** as 43%.

N-cyclopropylhydrazone **1ac** (26.5 mg, 0.114 mmol), $Pd(OAc)_2$ (2.6 mg, 0.012 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.1 mL). The mixture was stirred at reflux under air for 1 h. After the mixture was cooled to room temperature, the mixture was filtered through Celite® and evaporated. The residue was analyzed by ^{1}H NMR ($CDCl_3$) using triphenyl methane (22.1mg, 0.0904 mmol) as internal standard. The azine **3ac** was calculated as 26% NMR yield, pyrazole **2ac** as 19% and *N*-cyclopropylhydrazone **1ac** as 17%.

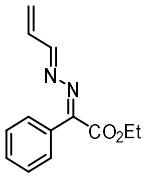
N-cyclopropylhydrazone **1ac** (26.1 mg, 0.112 mol), $Pd(OAc)_2$ (2.5 mg, 0.011 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.1 mL). The mixture was stirred at reflux under air for 2 h. After the mixture was cooled to room temperature, the mixture was filtered through Celite® and evaporated. The residue was analyzed by ^{1}H NMR ($CDCl_3$) using triphenyl methane (23.0 mg, 0.0941 mmol) as internal standard. The azine **3ac** was calculated as 15% NMR yield, pyrazole **2ac** as 42% and *N*-cyclopropylhydrazone **1ac** as 2%.

N-cyclopropylhydrazone **1ac** (27.1 mg, 0.117 mmol), $Pd(OAc)_2$ (2.62 mg, 0.012 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.2 mL). The mixture was stirred at reflux under air for 17 h. After the mixture was cooled to room temperature, the mixture was filtered through Celite® and evaporated. The residue was analyzed by ^{1}H NMR ($CDCl_3$) using triphenyl methane (25.2 mg, 0.103 mmol) as internal standard. The pyrazole **2ac** was calculated as 79% NMR yield.



Azine **3ac** was synthesized by the following procedure; To a solution of hydrazine monohydrate (600 μL, 10.0 mmol) in H_2O/AcOH = 1:1 (800 μL), ethylbenzoylformate (795 μL, 5.00 mmol) was added dropwise. The mixture was stirred at room temperature overnight. The resulting mixture was diluted with water and extracted with EtOAc three times. The collected organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford crude hydrazone **S3**. To a solution of crude hydrazone **S3** in Et_2O (5.0 mL) were added acrolein (67.0 μL, 1.00 mmol) and AcOH (20 μL). The mixture was stirred at room temperature for 4 h, and then evaporated. Azine **3ac** (66.0 mg, 29%) was obtained after

purification with flash column chromatography (hexane/EtOAc = 7:3);



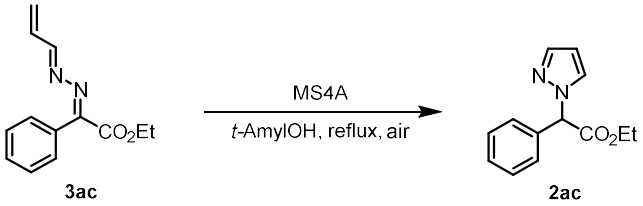
3ac

Physical state: yellow oil;

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.6 Hz, 1H), 7.80-7.78 (m, 2H), 7.55-7.42 (m, 4H), 6.71-6.61 (m, 1H), 5.89-5.85 (m, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H);

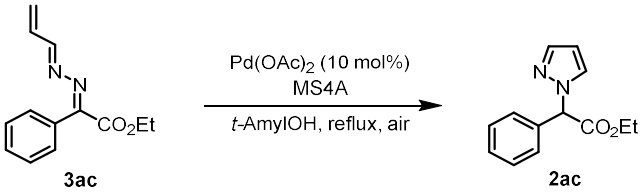
^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.6, 164.3, 161.7, 134.3, 131.6, 131.5, 129.4, 128.8, 127.5, 61.6, 14.3;

HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2N_2$ $[M+H]^+$ 231.1128, found 231.1127.



3ac **2ac**

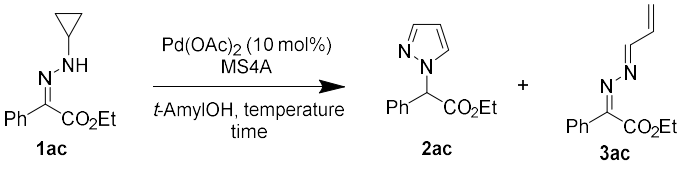
Azine **3ac** (27.2 mg, 0.118 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.2 mL). The mixture was stirred at reflux under air for 7 h. After cooled to rt, the mixture was filtered through Celite® and evaporated. The residue was purified by PTLC (hexane/EtOAc = 7:3) to afford pyrazole **2ac** (21.1 mg, 78%).



3ac **2ac**

Azine **3ac** (24.8 mg, 0.108 mmol), $Pd(OAc)_2$ (2.4 mg, 0.011 mmol) and MS4A (92.0 mg) were dissolved in *t*-AmylOH (1.1 mL). The mixture was stirred at reflux under air for 8 h. After cooled to rt, the mixture was filtered through Celite® and evaporated. The residue was purified by PTLC (hexane/EtOAc = 7:3) to afford pyrazole **2ac** (17.8 mg, 72%).

2-5-2. Control experiments (Reaction temperature).



entry	temperature	time	2ac[a]	3ac[a]
1	60 °C	23 h	21%	38%
2	80 °C	23 h	66%	0%
3	105 °C	17 h	79%	0%

[a] NMR yield using a triphenylmethane as a internal standard.

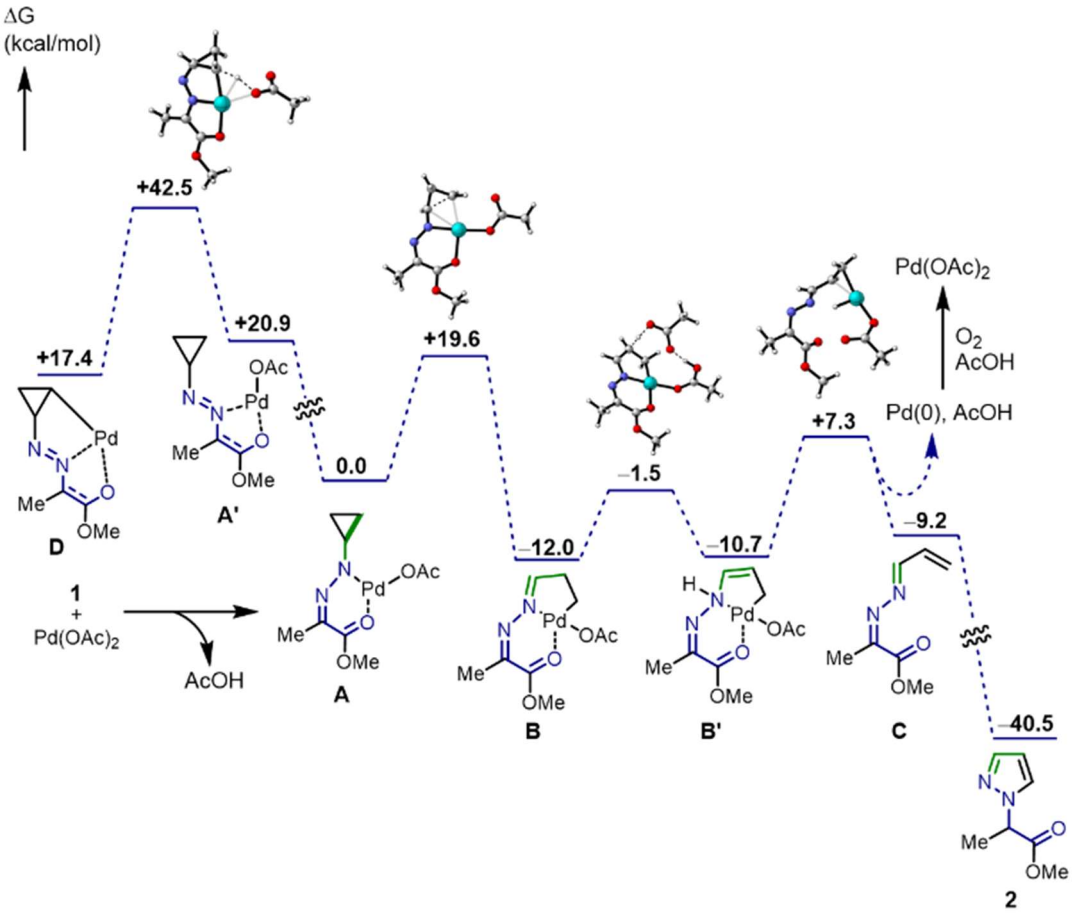
N-cyclopropylhydrazone **1ac** (25.9 mg, 0.112 mmol), $Pd(OAc)_2$ (2.5 mg, 0.011 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.1 mL). The mixture was stirred at 60 °C under air for 23 h. After the mixture was cooled to room temperature, the mixture was filtered through Celite® and evaporated. The residue was analyzed by ^{1}H NMR ($CDCl_3$) using triphenyl methane (26.6 mg, 0.109 mmol) as internal standard. The azine **3ac** was calculated as 38% NMR yield, pyrazole **2ac** as 21%.

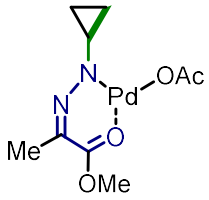
N-cyclopropylhydrazone **1ac** (29.7 mg, 0.128 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol) and MS4A (100 mg) were dissolved in *t*-AmylOH (1.3 mL). The mixture was stirred 80 °C under air for 23 h. After the mixture was cooled to room temperature, the mixture was filtered through Celite® and evaporated. The residue was analyzed by ^{1}H NMR ($CDCl_3$) using triphenyl methane (28.1 mg, 0.115 mmol) as internal standard. The pyrazole **2ac** was calculated as 66% NMR yield.

3. DFT calculations

The molecular geometries for each transition states were first estimated with the *Reaction plus* software package, based on the nudged elastic band method,[15] and were subsequently re-optimized using the Gaussian 16 software package.[16] Once the stationary points were obtained at B97D/6-31G+(d, p)-def2TZV (Lanl2DZ for Pd) level,[17–20] the harmonic vibrational frequencies were calculated at the same level to estimate the Gibbs free energy. The nature of the stationary points was characterized *via* vibrational analysis. All of the Gibbs free energy values reported in this paper were calculated for a temperature of 298.15 K. The transition structure reported was optimized without constraints and the intrinsic reaction coordinate (IRC) route was calculated in both directions toward the corresponding minima for each transition-state structure. The IRC calculation failed to reach the energy minima on the potential energy surface for the transition states, and we therefore carried out

geometry optimizations as a continuation of the IRC path. For each optimized structure (potential energy minimum or transition state computed at B97D/6-31G+(d, p)-def2TZV (Lanl2DZ for Pd) level), additional single-point energy calculations in the presence of chlorobenzene were performed at the same level. The 3D optimized structural figures in this paper were displayed by the CYLview visualization program.[21]





A

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -888.148 Hartree

RMS Gradient Norm = 1.357e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 0.806392 Debye

Polarizability (?) = 186.15633 a.u.

Point Group = C1

Molecular Mass = 319.99884 amu

Job cpu time: 0 days 0 hours 9 minutes 45.3 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.148 Hartree

Zero-point Energy Correction = 0.225096 Hartree

Thermal Correction to Energy = 0.244167 Hartree

Thermal Correction to Enthalpy = 0.245112 Hartree

Thermal Correction to Free Energy = 0.175058 Hartree

EE + Zero-point Energy = -887.9229 Hartree

EE + Thermal Energy Correction = -887.90383 Hartree

EE + Thermal Enthalpy Correction = -887.90289 Hartree

EE + Thermal Free Energy Correction = -887.97294 Hartree

E (Thermal) = 153.217 kcal/mol

Heat Capacity (Cv) = 66.252 cal/mol-kelvin

Entropy (S) = 147.439 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

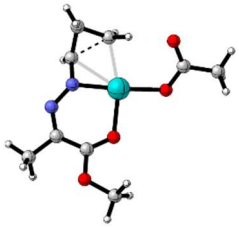
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.15772 Hartree



TS of **A** to **B**

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -888.109 Hartree

RMS Gradient Norm = 2.05e-07 Hartree/Bohr

Imaginary Freq = 1

Dipole Moment = 4.6693763 Debye

Polarizability (?) = 185.76033 a.u.

Point Group = C1

Molecular Mass = 319.99884 amu

Job cpu time: 0 days 0 hours 11 minutes 19.5 seconds.

Thermo Tab Data Section:

Imaginary Freq = 1

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.109 Hartree

Zero-point Energy Correction = 0.22219 Hartree

Thermal Correction to Energy = 0.241022 Hartree

Thermal Correction to Enthalpy = 0.241966 Hartree

Thermal Correction to Free Energy = 0.173658 Hartree

EE + Zero-point Energy = -887.8868 Hartree

EE + Thermal Energy Correction = -887.86797 Hartree

EE + Thermal Enthalpy Correction = -887.86703 Hartree

EE + Thermal Free Energy Correction = -887.93534 Hartree

E (Thermal) = 151.243 kcal/mol

Heat Capacity (Cv) = 65.944 cal/mol-kelvin

Entropy (S) = 143.767 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

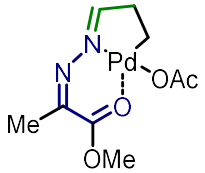
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.12516 Hartree



B

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -888.15572 Hartree

RMS Gradient Norm = 8.292e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 7.8355929 Debye

Polarizability (?) = 183.897 a.u.

Point Group = C1

Molecular Mass = 319.99884 amu

Job cpu time: 0 days 0 hours 10 minutes 3.1 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.15572 Hartree

Zero-point Energy Correction = 0.223323 Hartree

Thermal Correction to Energy = 0.242619 Hartree

Thermal Correction to Enthalpy = 0.243564 Hartree

Thermal Correction to Free Energy = 0.172917 Hartree

EE + Zero-point Energy = -887.93239 Hartree

EE + Thermal Energy Correction = -887.9131 Hartree

EE + Thermal Enthalpy Correction = -887.91215 Hartree

EE + Thermal Free Energy Correction = -887.9828 Hartree

E (Thermal) = 152.246 kcal/mol

Heat Capacity (Cv) = 67.114 cal/mol-kelvin

Entropy (S) = 148.689 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

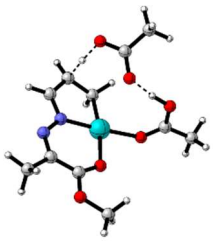
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.17472 Hartree



TS of **B** to **B'**

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C11H18N2O6Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -1117.0687 Hartree

RMS Gradient Norm = 6.51e-07 Hartree/Bohr

Imaginary Freq = 1

Dipole Moment = 3.1427077 Debye

Polarizability (?) = 226.46933 a.u.

Point Group = C1

Molecular Mass = 380.01997 amu

Job cpu time: 0 days 0 hours 20 minutes 42.0 seconds.

Thermo Tab Data Section:

Imaginary Freq = 1

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -1117.0687 Hartree

Zero-point Energy Correction = 0.27912 Hartree

Thermal Correction to Energy = 0.303315 Hartree

Thermal Correction to Enthalpy = 0.304259 Hartree

Thermal Correction to Free Energy = 0.222463 Hartree

EE + Zero-point Energy = -1116.7896 Hartree

EE + Thermal Energy Correction = -1116.7654 Hartree

EE + Thermal Enthalpy Correction = -1116.7645 Hartree

EE + Thermal Free Energy Correction = -1116.8463 Hartree

E (Thermal) = 190.333 kcal/mol

Heat Capacity (Cv) = 84.446 cal/mol-kelvin

Entropy (S) = 172.153 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C11H18N2O6Pd

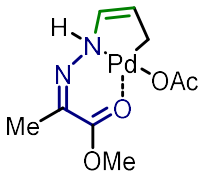
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -1117.0809 Hartree



B'

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C11H18N2O6Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -1117.0903 Hartree

RMS Gradient Norm = 5.662e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 3.4031855 Debye

Polarizability (?) = 210.37667 a.u.

Point Group = C1

Molecular Mass = 380.01997 amu

Job cpu time: 0 days 0 hours 20 minutes 15.9 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -1117.0903 Hartree

Zero-point Energy Correction = 0.284129 Hartree

Thermal Correction to Energy = 0.309021 Hartree

Thermal Correction to Enthalpy = 0.309965 Hartree

Thermal Correction to Free Energy = 0.227344 Hartree

EE + Zero-point Energy = -1116.8062 Hartree

EE + Thermal Energy Correction = -1116.7813 Hartree

EE + Thermal Enthalpy Correction = -1116.7804 Hartree

EE + Thermal Free Energy Correction = -1116.863 Hartree

E (Thermal) = 193.914 kcal/mol

Heat Capacity (Cv) = 86.506 cal/mol-kelvin

Entropy (S) = 173.891 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C11H18N2O6Pd

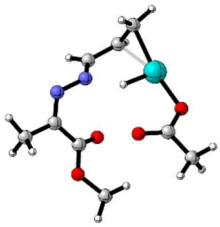
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -1117.1005 Hartree



TS of **B'** to **C**

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -888.1084 Hartree

RMS Gradient Norm = 6.28e-07 Hartree/Bohr

Imaginary Freq = 1

Dipole Moment = 3.3307199 Debye

Polarizability (?) = 179.039 a.u.

Point Group = C1

Molecular Mass = 319.99884 amu

Job cpu time: 0 days 0 hours 12 minutes 12.4 seconds.

Thermo Tab Data Section:

Imaginary Freq = 1

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.1084 Hartree

Zero-point Energy Correction = 0.217867 Hartree

Thermal Correction to Energy = 0.237248 Hartree

Thermal Correction to Enthalpy = 0.238193 Hartree

Thermal Correction to Free Energy = 0.167882 Hartree

EE + Zero-point Energy = -887.89053 Hartree

EE + Thermal Energy Correction = -887.87115 Hartree

EE + Thermal Enthalpy Correction = -887.8702 Hartree

EE + Thermal Free Energy Correction = -887.94051 Hartree

E (Thermal) = 148.876 kcal/mol

Heat Capacity (Cv) = 67.511 cal/mol-kelvin

Entropy (S) = 147.981 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

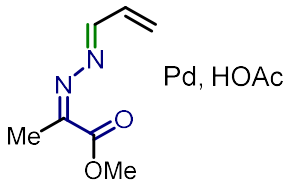
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.12573 Hartree



C

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -888.14357 Hartree

RMS Gradient Norm = 7.35e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 5.0263615 Debye

Polarizability (?) = 185.268 a.u.

Point Group = C1

Molecular Mass = 319.99884 amu

Job cpu time: 0 days 0 hours 10 minutes 33.0 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.14357 Hartree

Zero-point Energy Correction = 0.222602 Hartree

Thermal Correction to Energy = 0.242858 Hartree

Thermal Correction to Enthalpy = 0.243802 Hartree

Thermal Correction to Free Energy = 0.169869 Hartree

EE + Zero-point Energy = -887.92097 Hartree

EE + Thermal Energy Correction = -887.90071 Hartree

EE + Thermal Enthalpy Correction = -887.89977 Hartree

EE + Thermal Free Energy Correction = -887.9737 Hartree

E (Thermal) = 152.396 kcal/mol

Heat Capacity (Cv) = 68.508 cal/mol-kelvin

Entropy (S) = 155.607 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

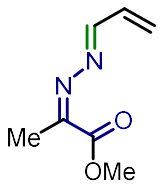
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.15397 Hartree



C

Calculation Type = FREQ

Calculation Method = RB97D

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -532.19975 Hartree

RMS Gradient Norm = 1.208e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 1.9878389 Debye

Polarizability (?) = 114.66267 a.u.

Point Group = C1

Job cpu time: 0 days 0 hours 2 minutes 19.0 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -532.19975 Hartree

Zero-point Energy Correction = 0.160591 Hartree

Thermal Correction to Energy = 0.173441 Hartree

Thermal Correction to Enthalpy = 0.174385 Hartree

Thermal Correction to Free Energy = 0.119784 Hartree

EE + Zero-point Energy = -532.03916 Hartree

EE + Thermal Energy Correction = -532.02631 Hartree

EE + Thermal Enthalpy Correction = -532.02537 Hartree

EE + Thermal Free Energy Correction = -532.07997 Hartree

E (Thermal) = 108.836 kcal/mol

Heat Capacity (Cv) = 43.976 cal/mol-kelvin

Entropy (S) = 114.918 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

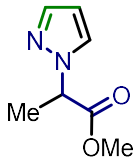
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -532.20711 Hartree



2

Calculation Type = FREQ

Calculation Method = RB97D

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -532.24546 Hartree

RMS Gradient Norm = 2.446e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 3.7857682 Debye

Polarizability (?) = 90.126333 a.u.

Point Group = C1

Job cpu time: 0 days 0 hours 2 minutes 1.0 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -532.24546 Hartree

Zero-point Energy Correction = 0.164093 Hartree

Thermal Correction to Energy = 0.175653 Hartree

Thermal Correction to Enthalpy = 0.176597 Hartree

Thermal Correction to Free Energy = 0.12526 Hartree

EE + Zero-point Energy = -532.08137 Hartree

EE + Thermal Energy Correction = -532.06981 Hartree

EE + Thermal Enthalpy Correction = -532.06886 Hartree

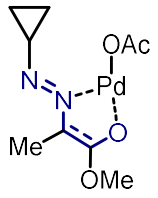
EE + Thermal Free Energy Correction = -532.1202 Hartree

E (Thermal) = 110.224 kcal/mol

Heat Capacity (Cv) = 41.07 cal/mol-kelvin

Entropy (S) = 108.047 cal/mol-kelvin

Calculation Type = SP
Calculation Method = RB97D
Basis Set = Gen/def2TZV
Charge = 0
Spin = Singlet
Solvation = scrf=solvent=chlorobenzene
E(RB97D) = -532.25353 Hartree



A'

Calculation Type = FREQ
Calculation Method = RB97D
Formula = C9H14N2O4Pd
Basis Set = Gen/def2TZV
Charge = 0
Spin = Singlet
Solvation = None
E(RB97D) = -888.10879 Hartree
RMS Gradient Norm = 9.131e-06 Hartree/Bohr
Imaginary Freq = 0
Dipole Moment = 2.3365251 Debye
Polarizability (?) = 186.16867 a.u.
Point Group = C1
Molecular Mass = 319.99884 amu
Job cpu time: 0 days 0 hours 11 minutes 4.4 seconds.

Thermo Tab Data Section:
Imaginary Freq = 0
Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.10879 Hartree

Zero-point Energy Correction = 0.222923 Hartree

Thermal Correction to Energy = 0.242205 Hartree

Thermal Correction to Enthalpy = 0.24315 Hartree

Thermal Correction to Free Energy = 0.173375 Hartree

EE + Zero-point Energy = -887.88587 Hartree

EE + Thermal Energy Correction = -887.86658 Hartree

EE + Thermal Enthalpy Correction = -887.86564 Hartree

EE + Thermal Free Energy Correction = -887.93542 Hartree

E (Thermal) = 151.986 kcal/mol

Heat Capacity (Cv) = 66.793 cal/mol-kelvin

Entropy (S) = 146.853 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

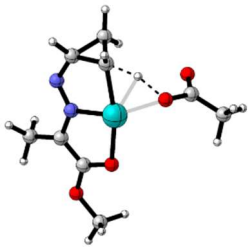
Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.12266 Hartree



TS of **A'** to **D**

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

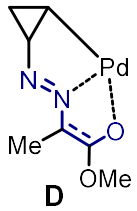
Charge = 0

Spin = Singlet
Solvation = None
E(RB97D) = -888.07143 Hartree
RMS Gradient Norm = 2.74e-07 Hartree/Bohr
Imaginary Freq = 1
Dipole Moment = 1.9287079 Debye
Polarizability (?) = 181.819 a.u.
Point Group = C1
Molecular Mass = 319.99884 amu
Job cpu time: 0 days 0 hours 11 minutes 59.4 seconds.

Thermo Tab Data Section:
Imaginary Freq = 1
Temperature = 298.15 Kelvin
Pressure = 1 atm
Frequencies scaled by = 1
Electronic Energy (EE) = -888.07143 Hartree
Zero-point Energy Correction = 0.217974 Hartree
Thermal Correction to Energy = 0.236724 Hartree
Thermal Correction to Enthalpy = 0.237668 Hartree
Thermal Correction to Free Energy = 0.168776 Hartree
EE + Zero-point Energy = -887.85345 Hartree
EE + Thermal Energy Correction = -887.8347 Hartree
EE + Thermal Enthalpy Correction = -887.83376 Hartree
EE + Thermal Free Energy Correction = -887.90265 Hartree
E (Thermal) = 148.547 kcal/mol
Heat Capacity (Cv) = 66.208 cal/mol-kelvin
Entropy (S) = 144.996 cal/mol-kelvin

Calculation Type = SP
Calculation Method = RB97D
Formula = C9H14N2O4Pd
Basis Set = Gen/def2TZV
Charge = 0
Spin = Singlet
Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.08365 Hartree



D

Calculation Type = FREQ

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = None

E(RB97D) = -888.1176 Hartree

RMS Gradient Norm = 5.93e-07 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 2.3609399 Debye

Polarizability (?) = 173.565 a.u.

Point Group = C1

Molecular Mass = 319.99884 amu

Job cpu time: 0 days 0 hours 10 minutes 20.7 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -888.1176 Hartree

Zero-point Energy Correction = 0.223842 Hartree

Thermal Correction to Energy = 0.242801 Hartree

Thermal Correction to Enthalpy = 0.243745 Hartree

Thermal Correction to Free Energy = 0.174332 Hartree

EE + Zero-point Energy = -887.89376 Hartree

EE + Thermal Energy Correction = -887.8748 Hartree

EE + Thermal Enthalpy Correction = -887.87385 Hartree

EE + Thermal Free Energy Correction = -887.94327 Hartree

E (Thermal) = 152.36 kcal/mol

Heat Capacity (Cv) = 67.077 cal/mol-kelvin

Entropy (S) = 146.091 cal/mol-kelvin

Calculation Type = SP

Calculation Method = RB97D

Formula = C9H14N2O4Pd

Basis Set = Gen/def2TZV

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(RB97D) = -888.12913 Hartree

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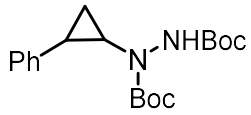
5. NMR spectra



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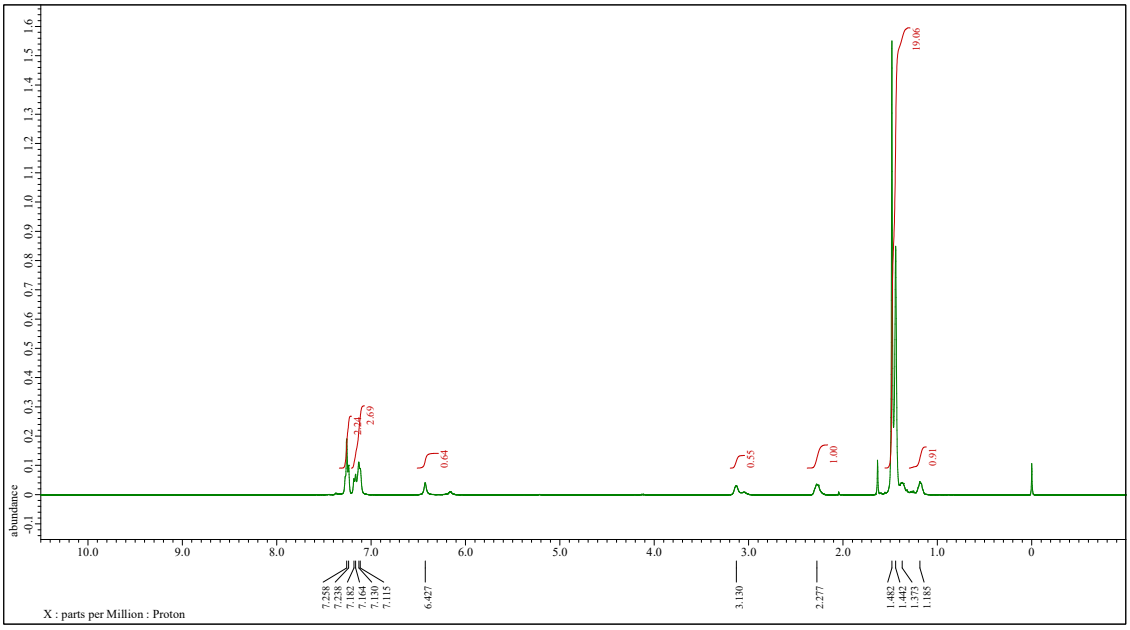

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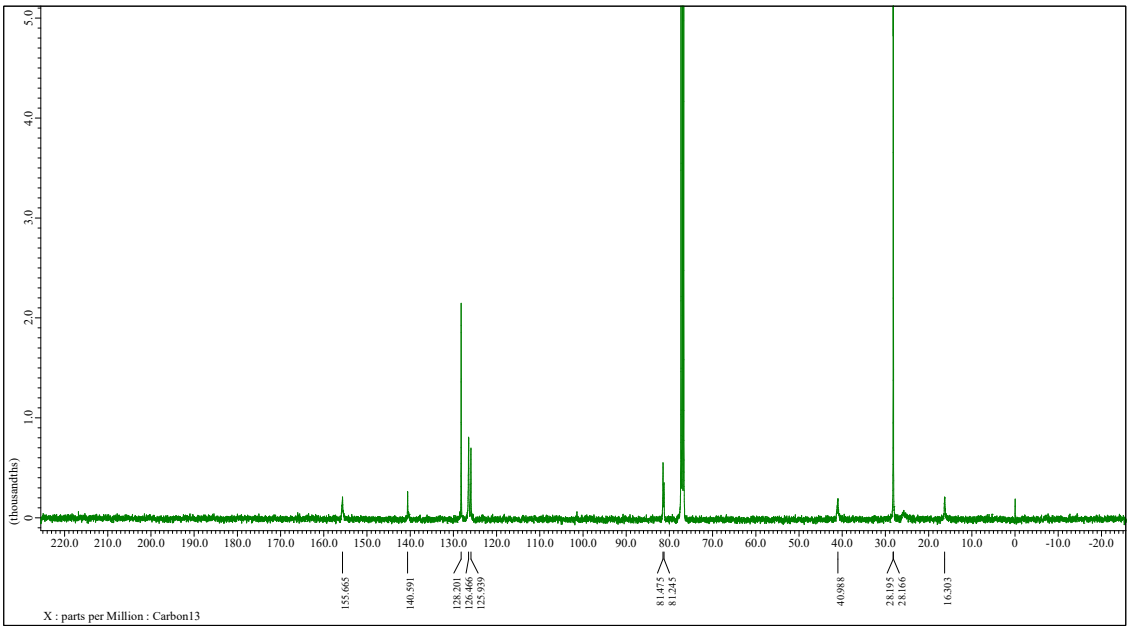

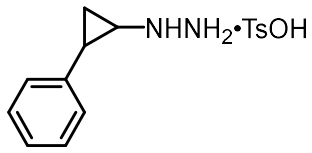

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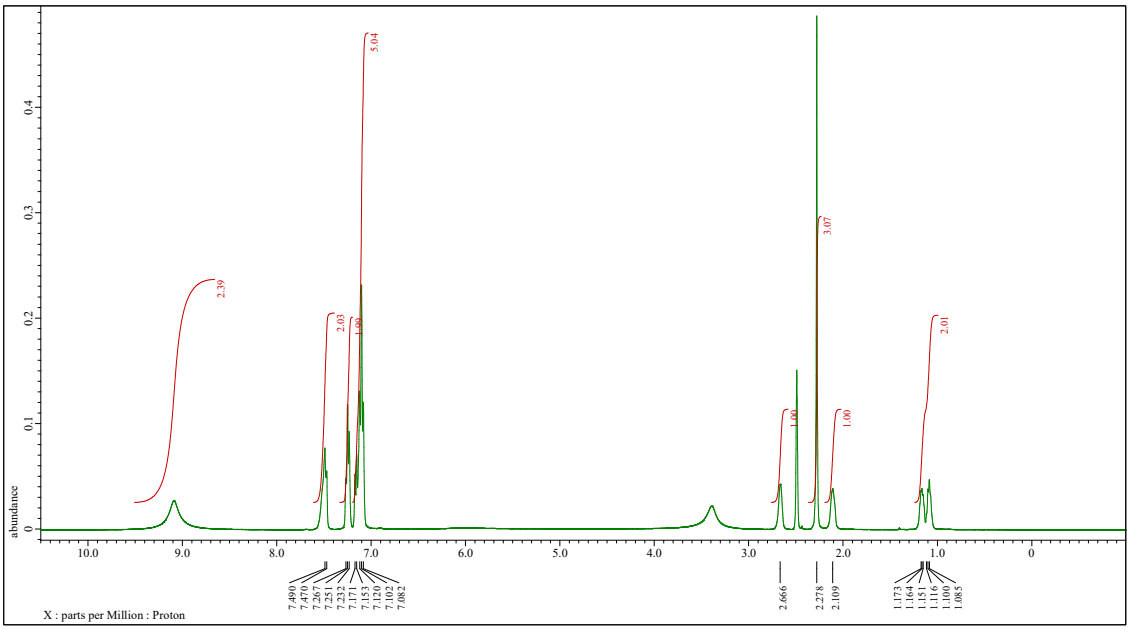

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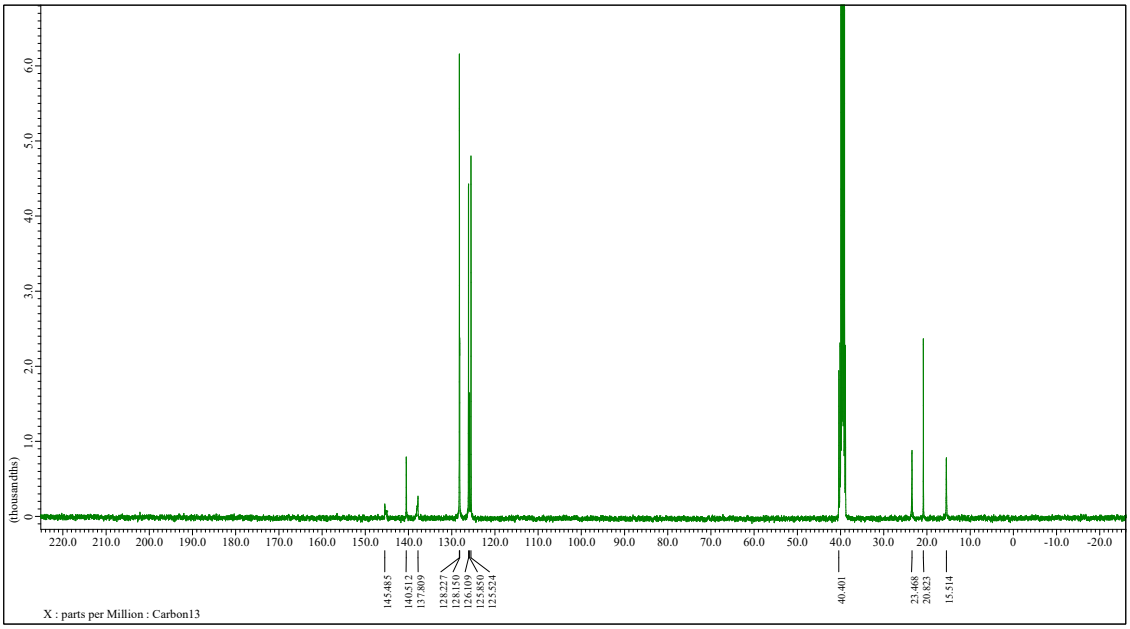

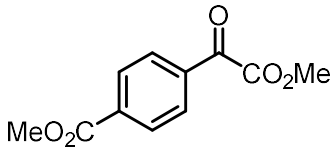

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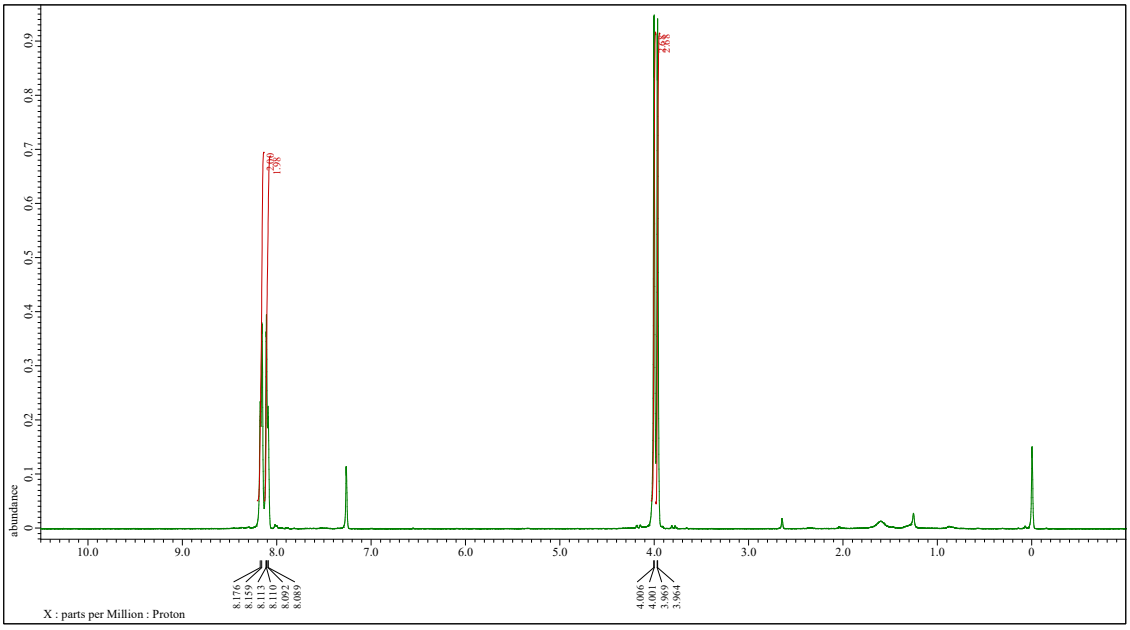

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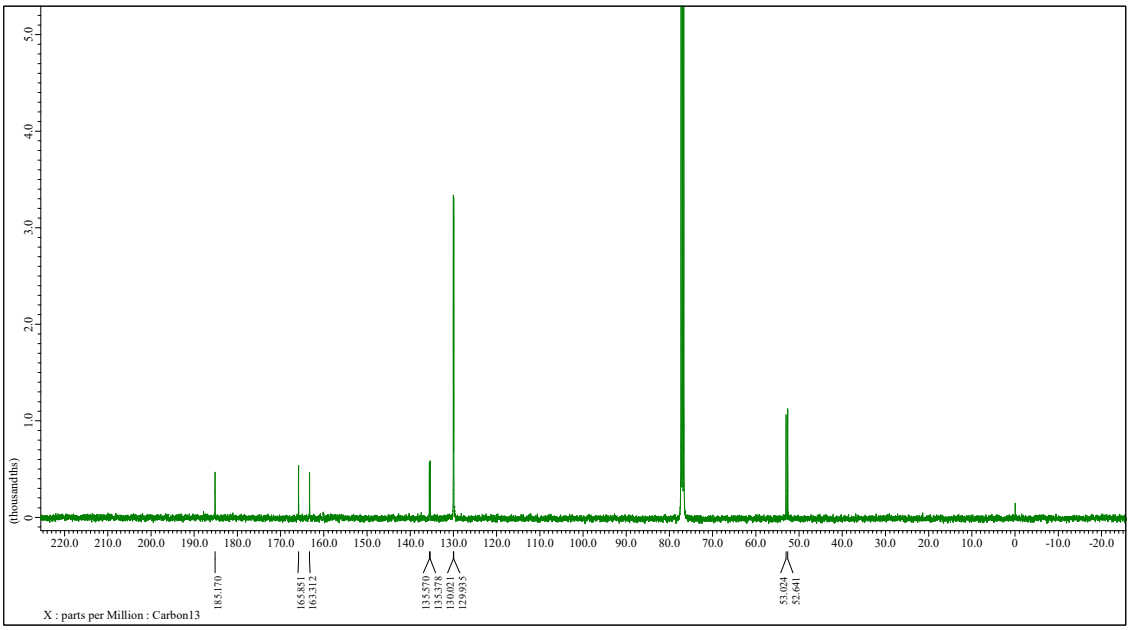

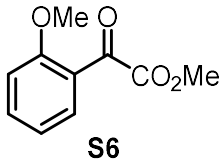

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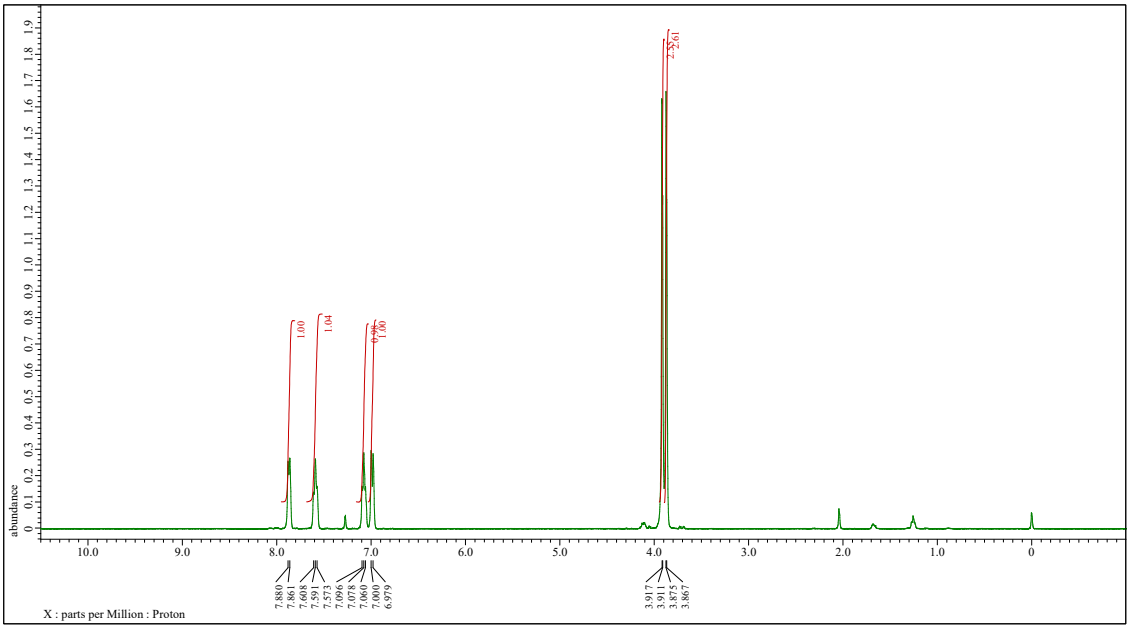

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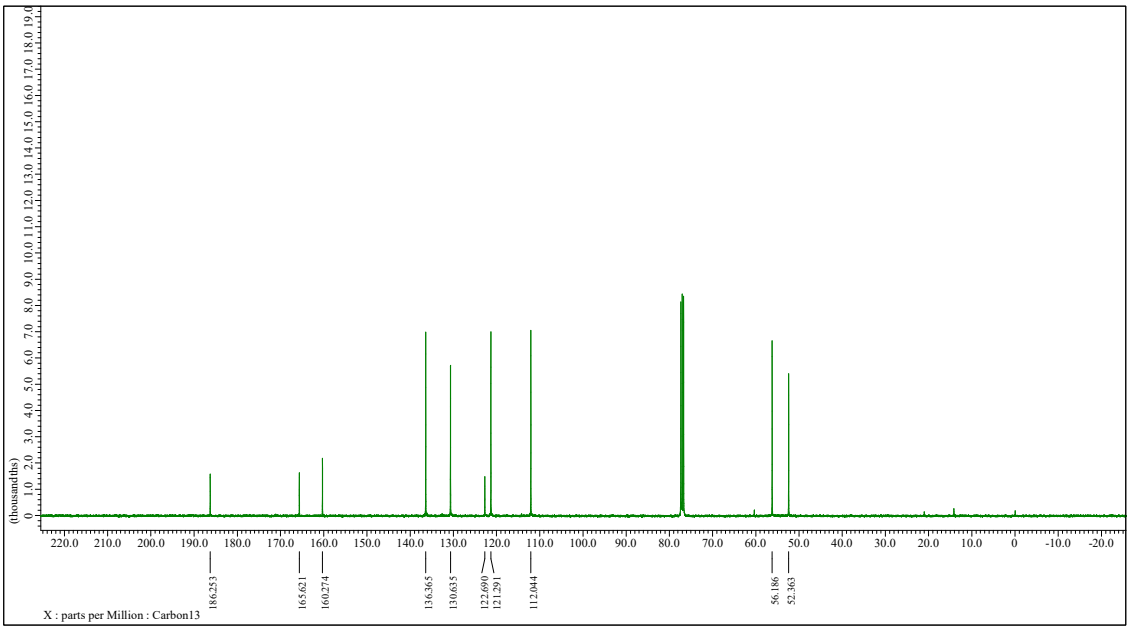

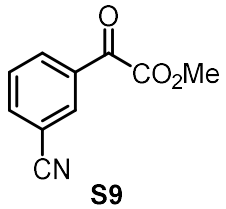

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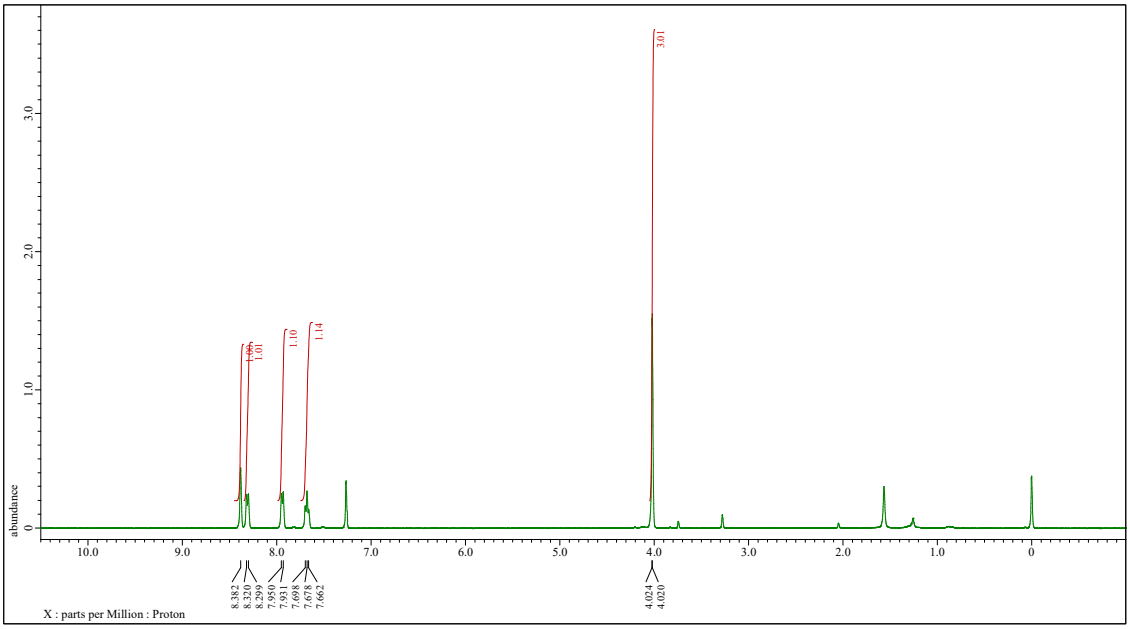

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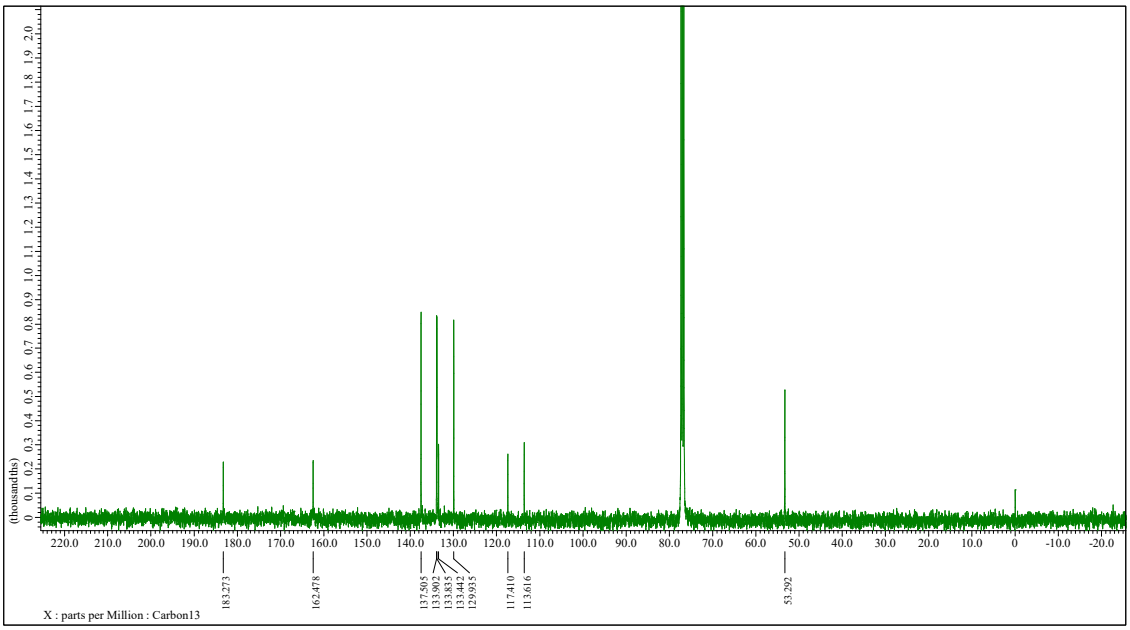

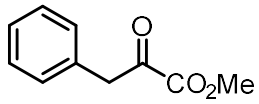

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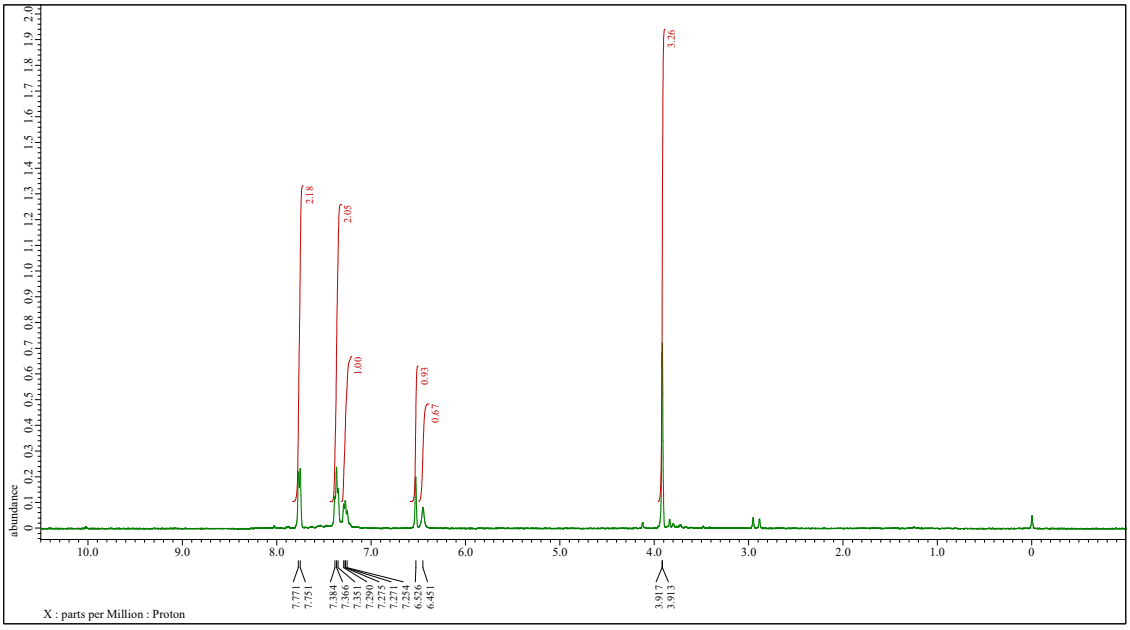

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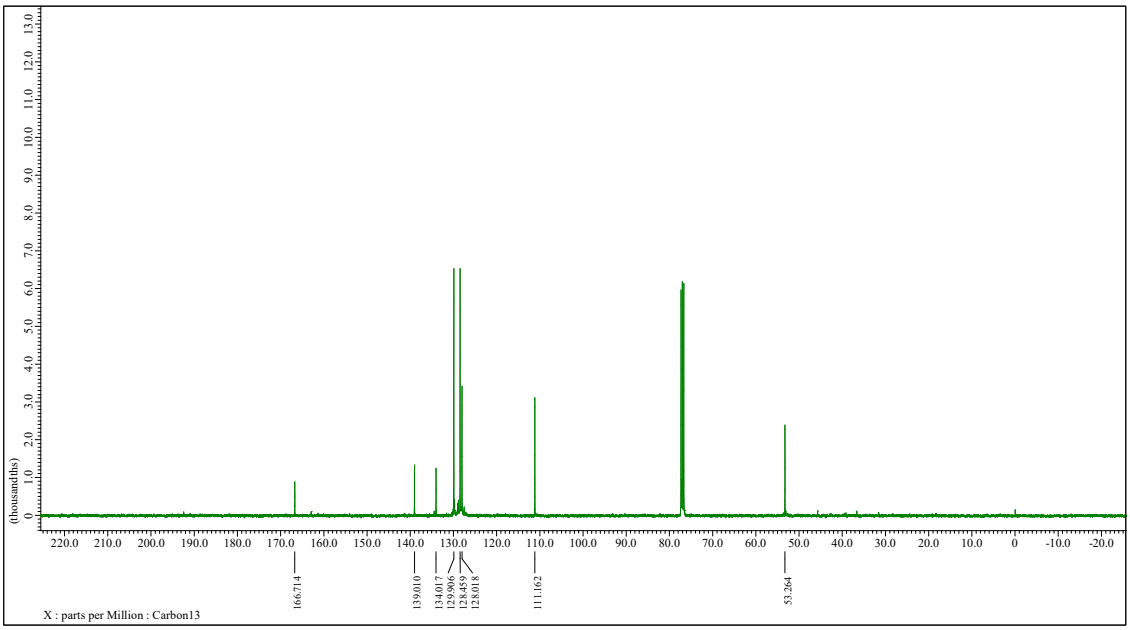

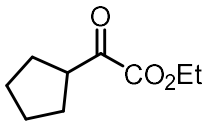

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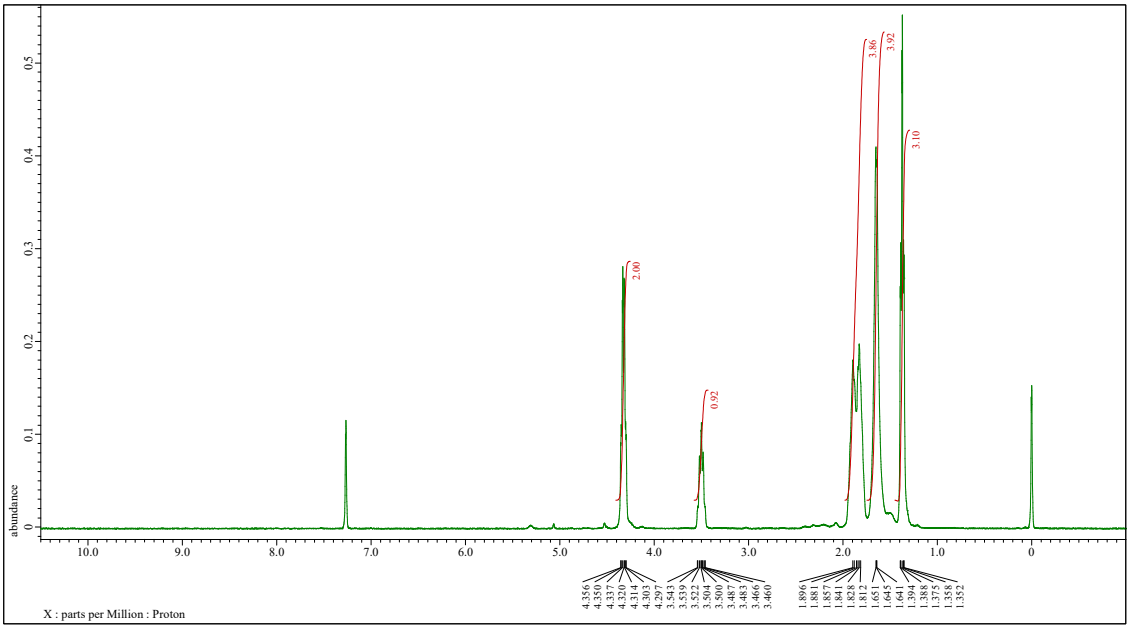

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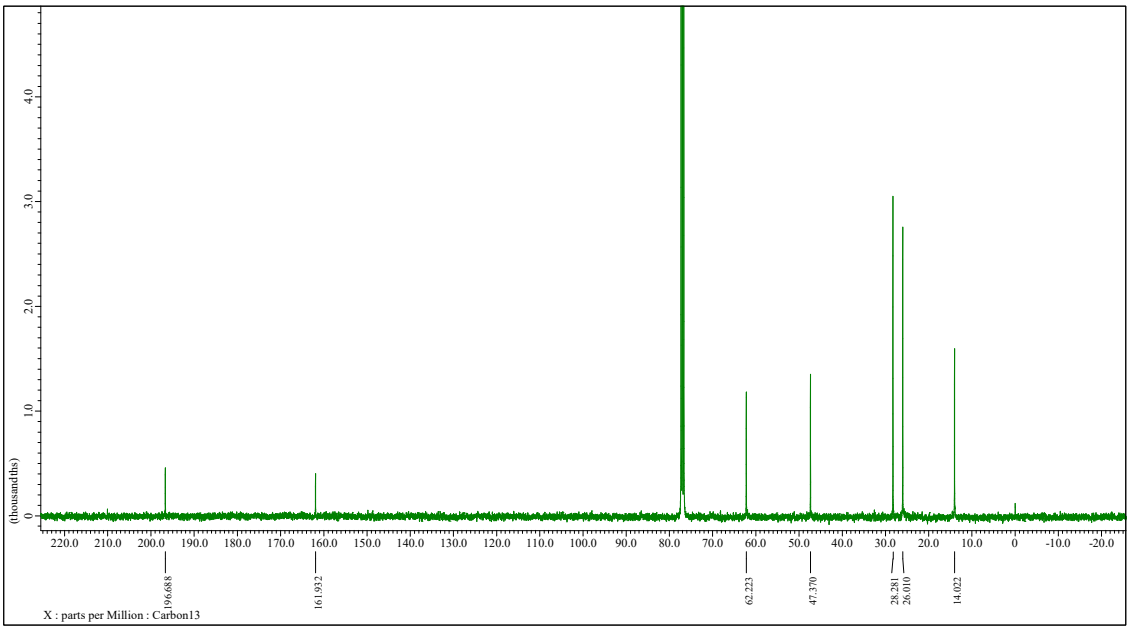

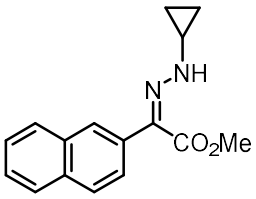

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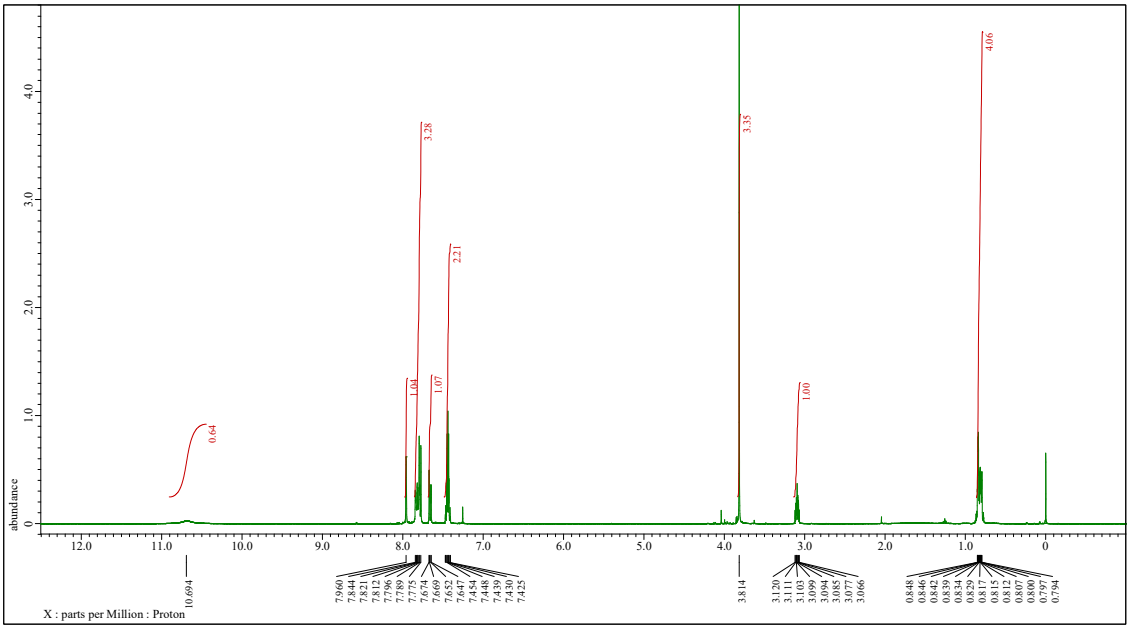

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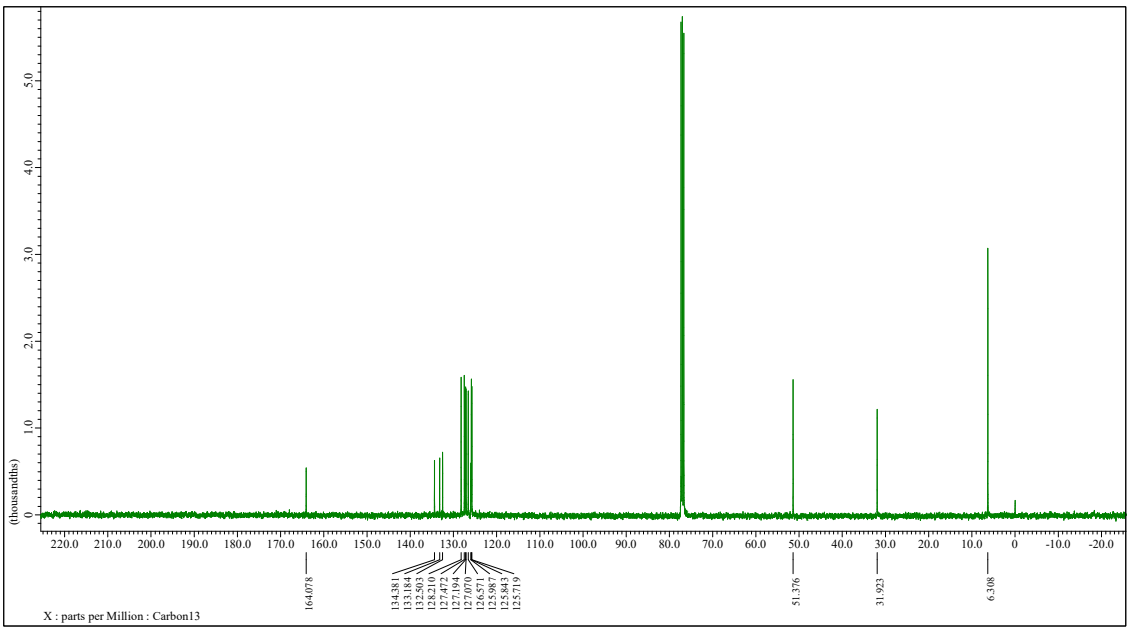
(thousandths)
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1.0
2.0
3.0
4.0
5.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
164.078
134.381
133.184
132.503
128.210
127.472
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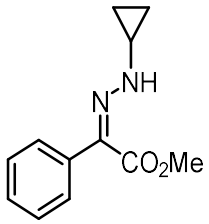

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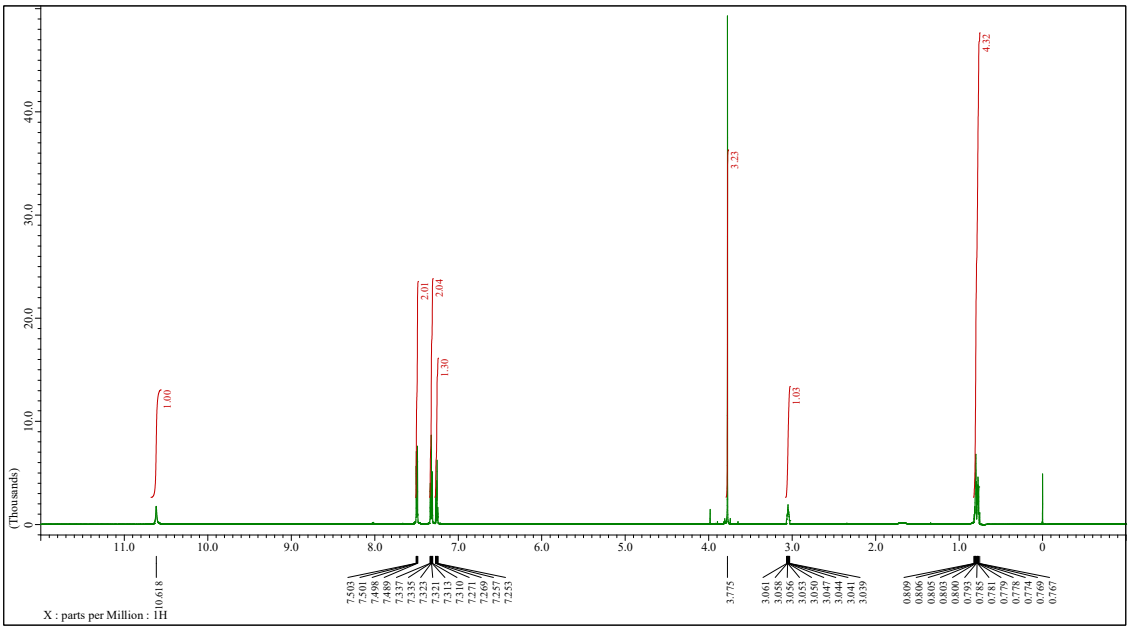

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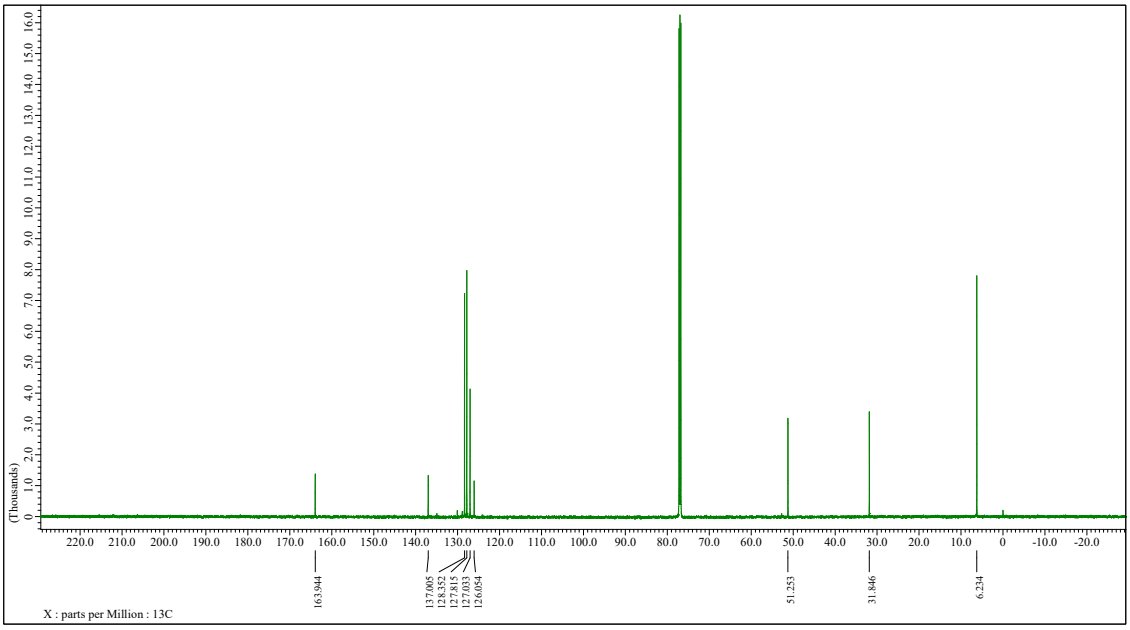

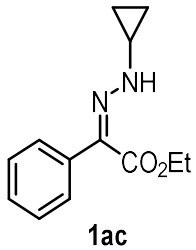

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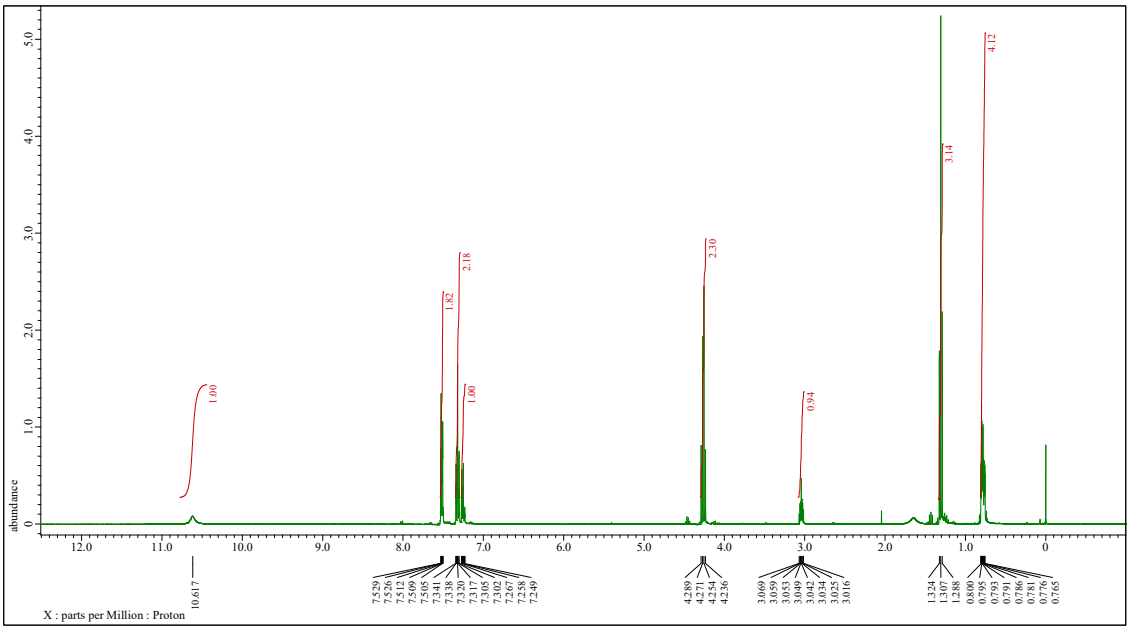

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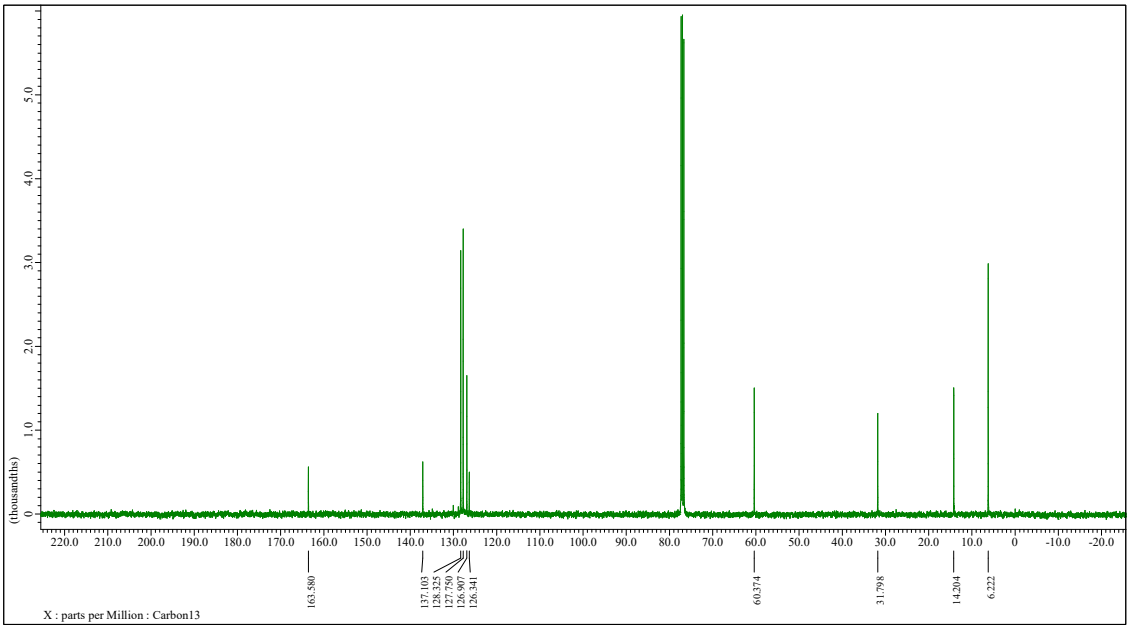

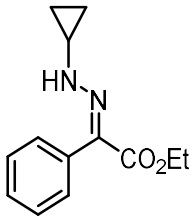

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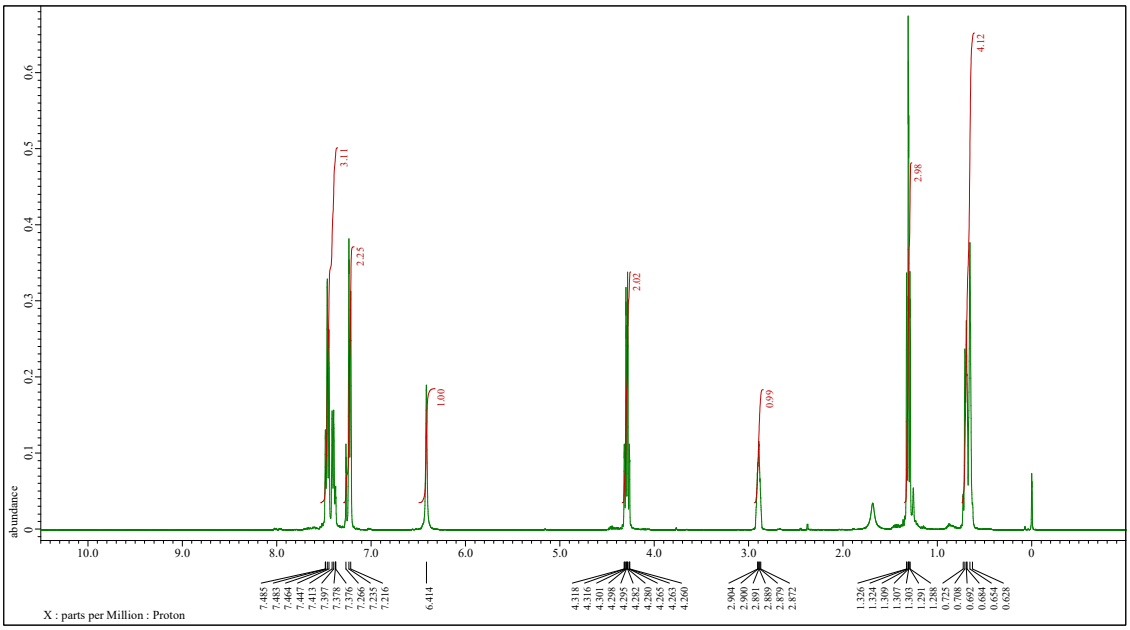

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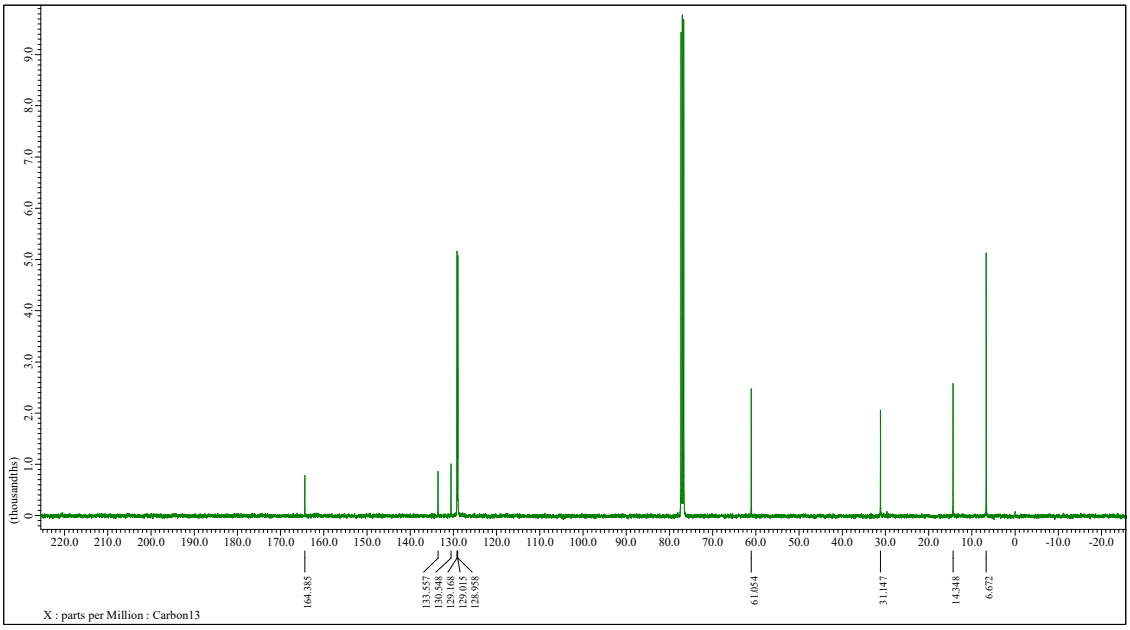

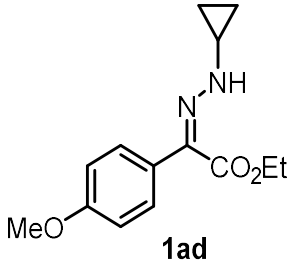

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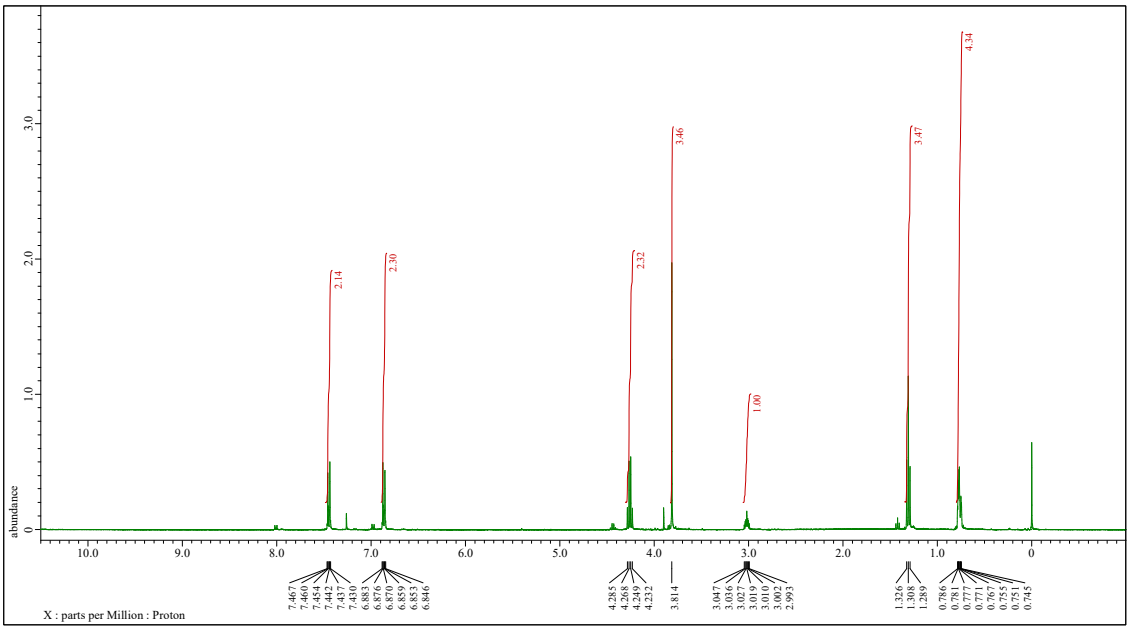

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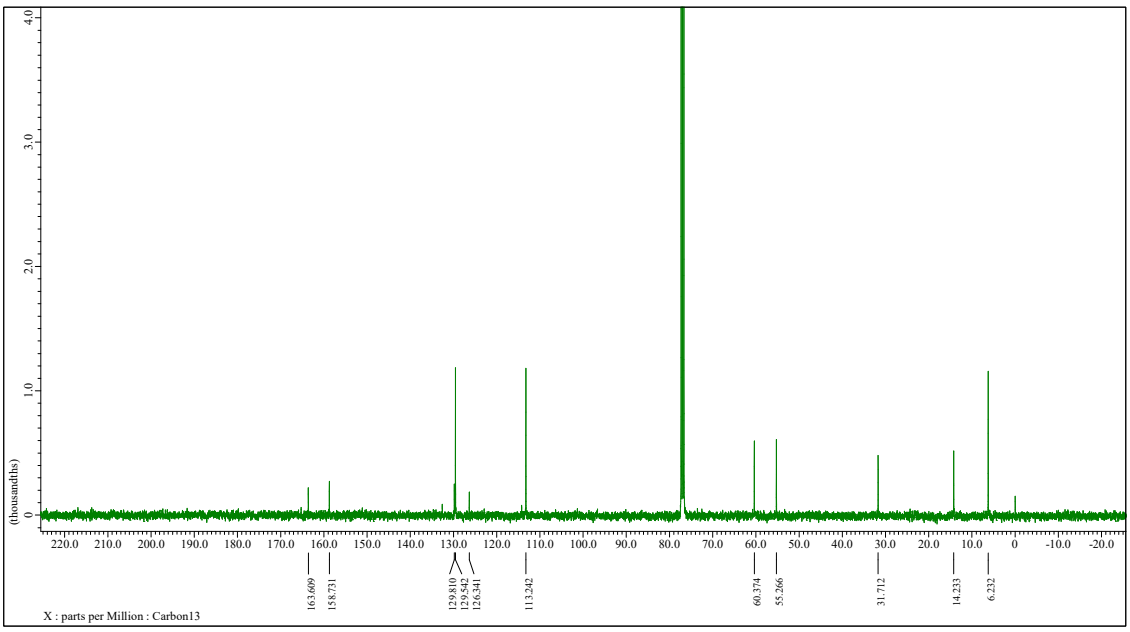

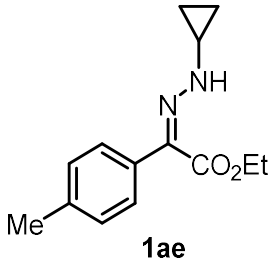

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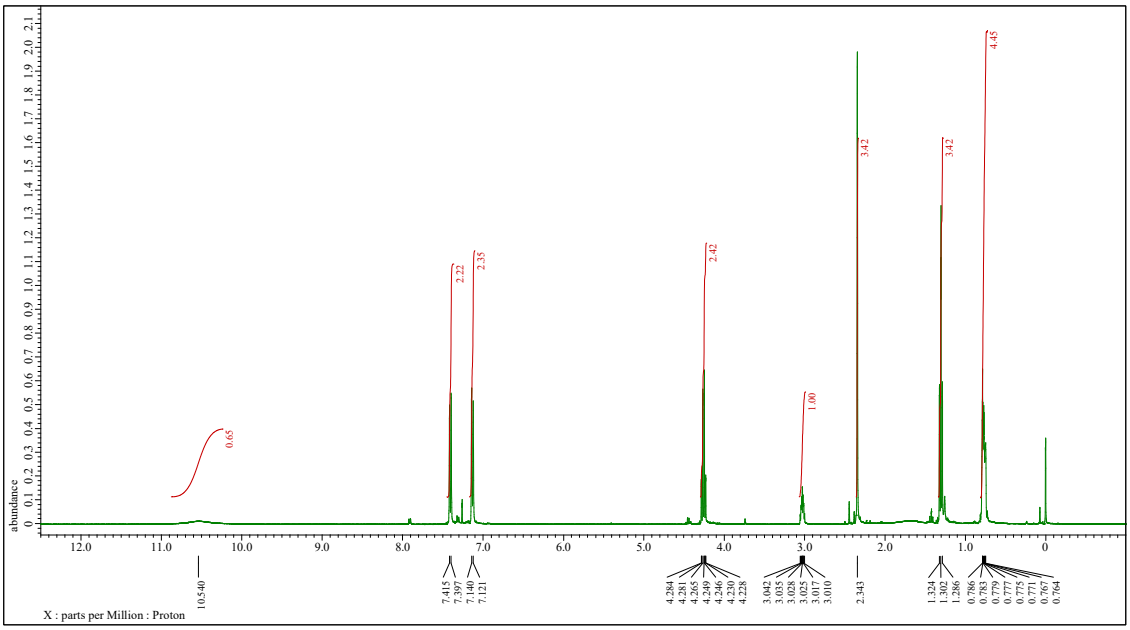
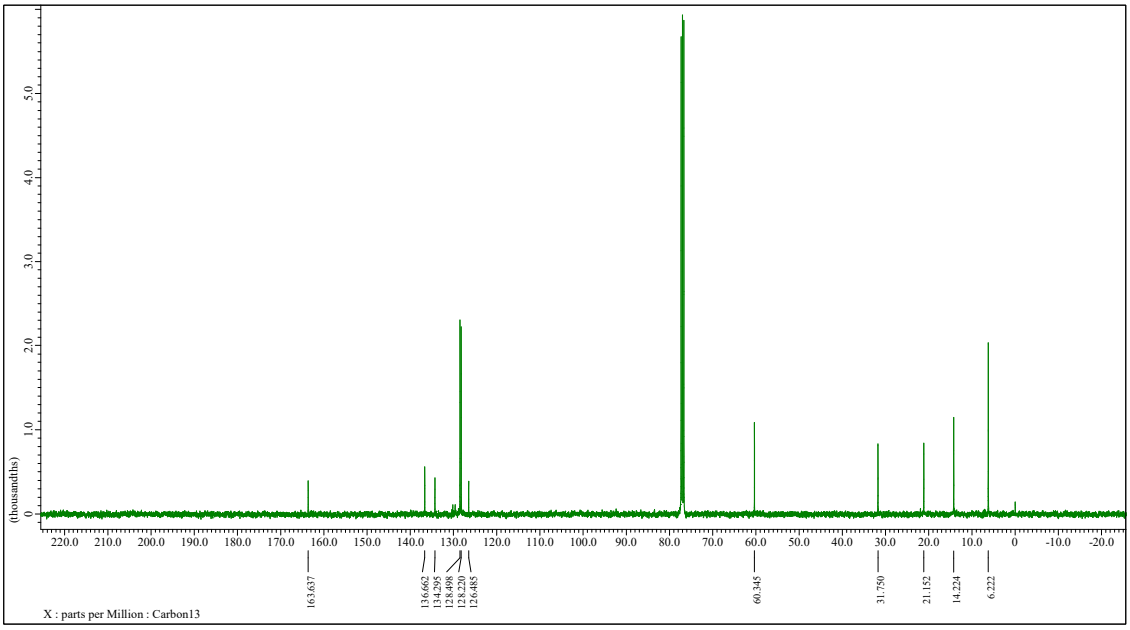
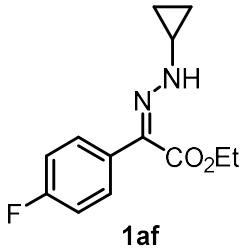


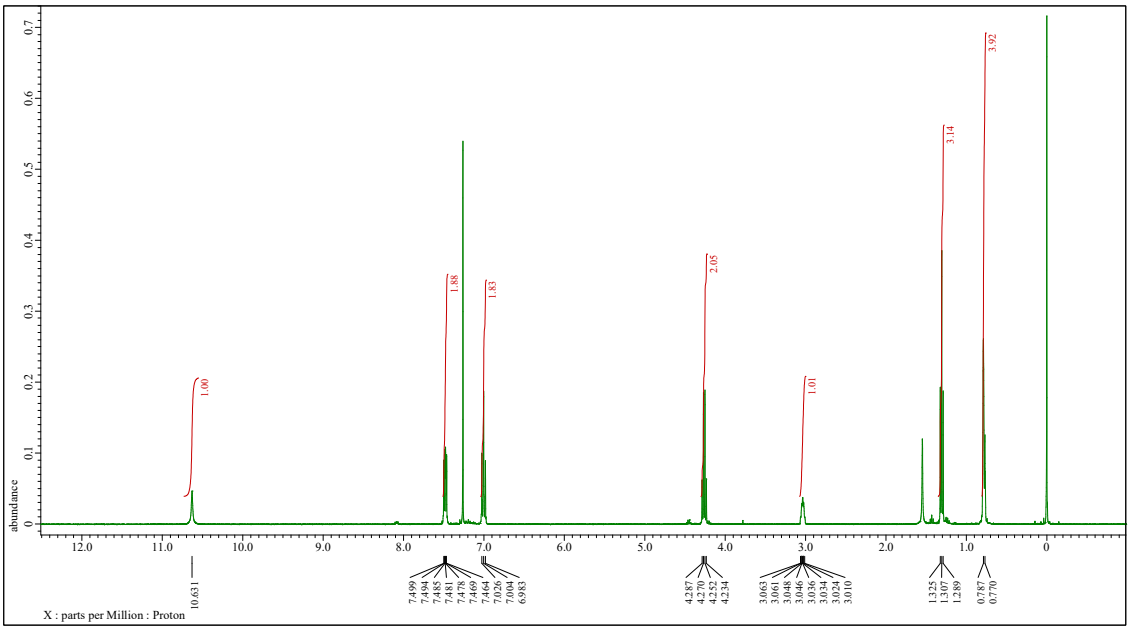
^{13}C-NMR (101 MHz, $CDCl_3$)



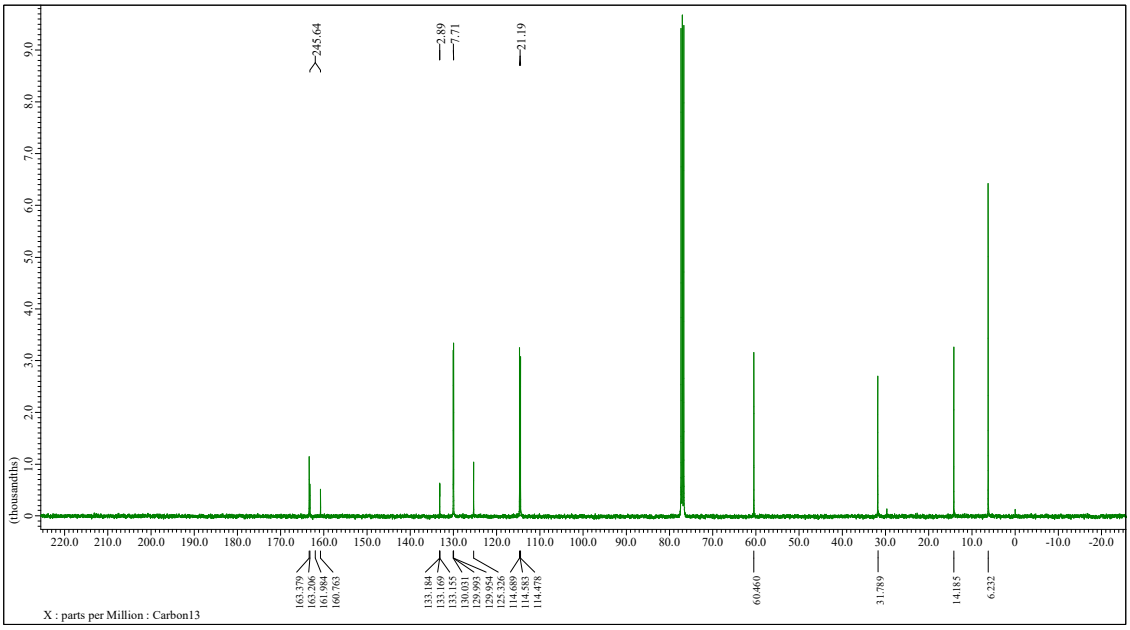


1af

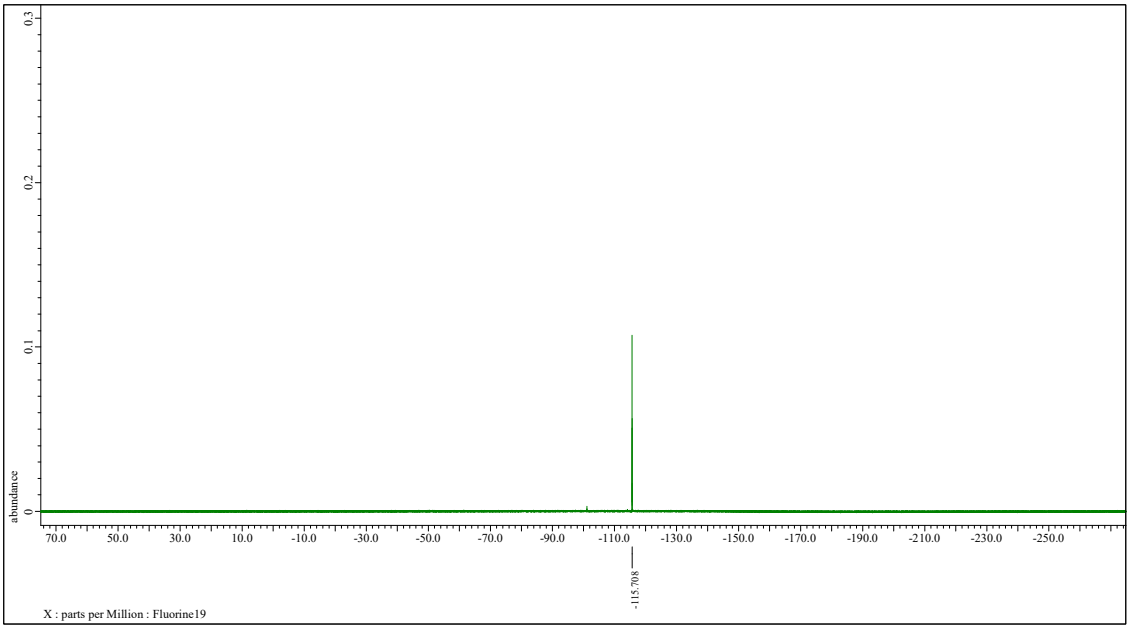
^{1}H-NMR (400 MHz, $CDCl_3$)

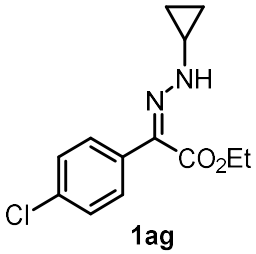


^{13}C-NMR (101 MHz, $CDCl_3$)



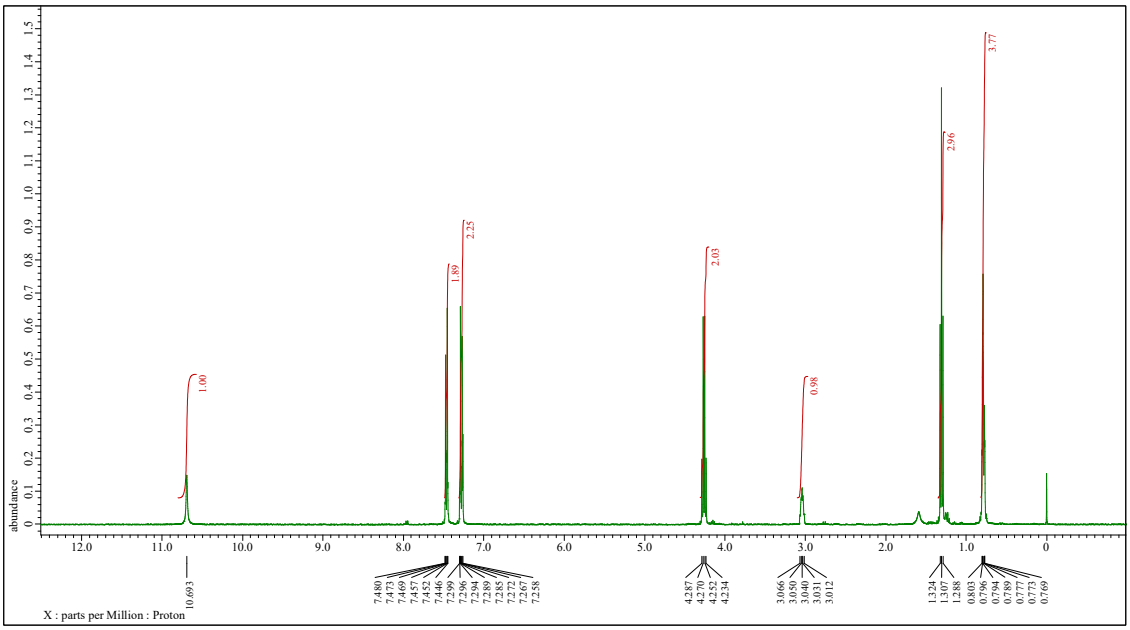
^{19}F NMR (376 MHz, $CDCl_3$)



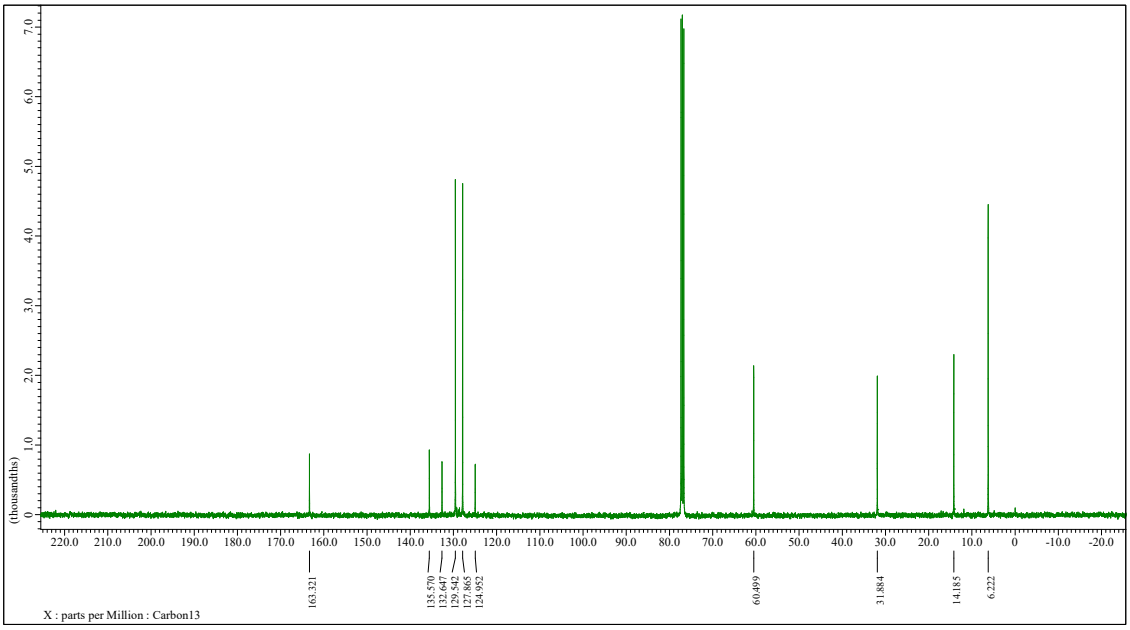


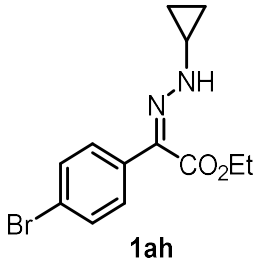
1ag

^{1}H-NMR (400 MHz, $CDCl_3$)



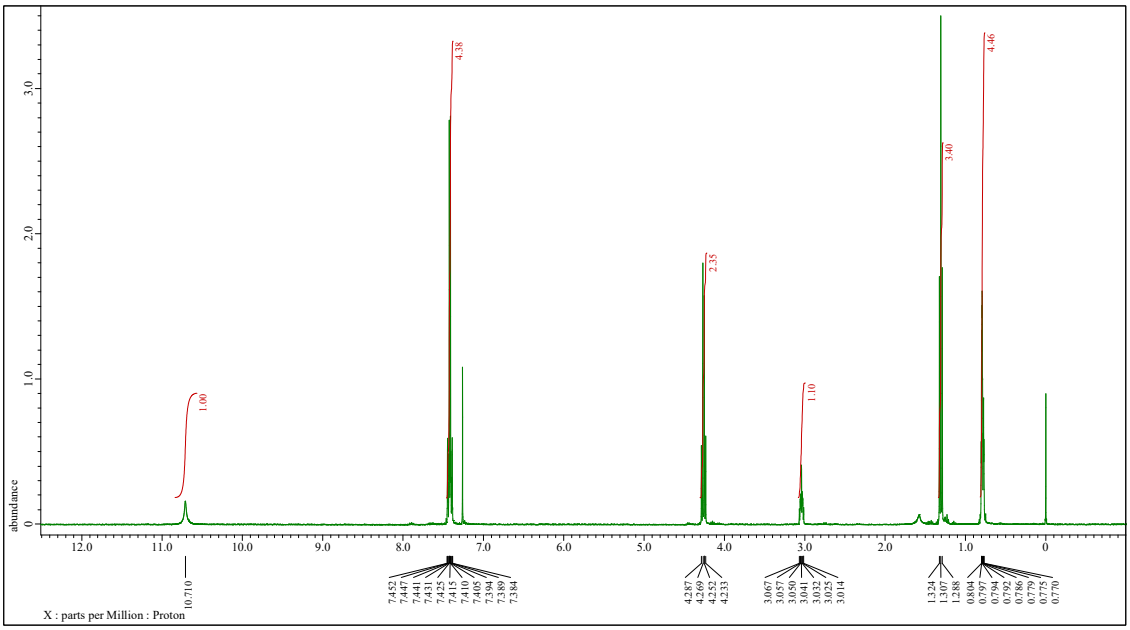
^{13}C-NMR (101 MHz, $CDCl_3$)



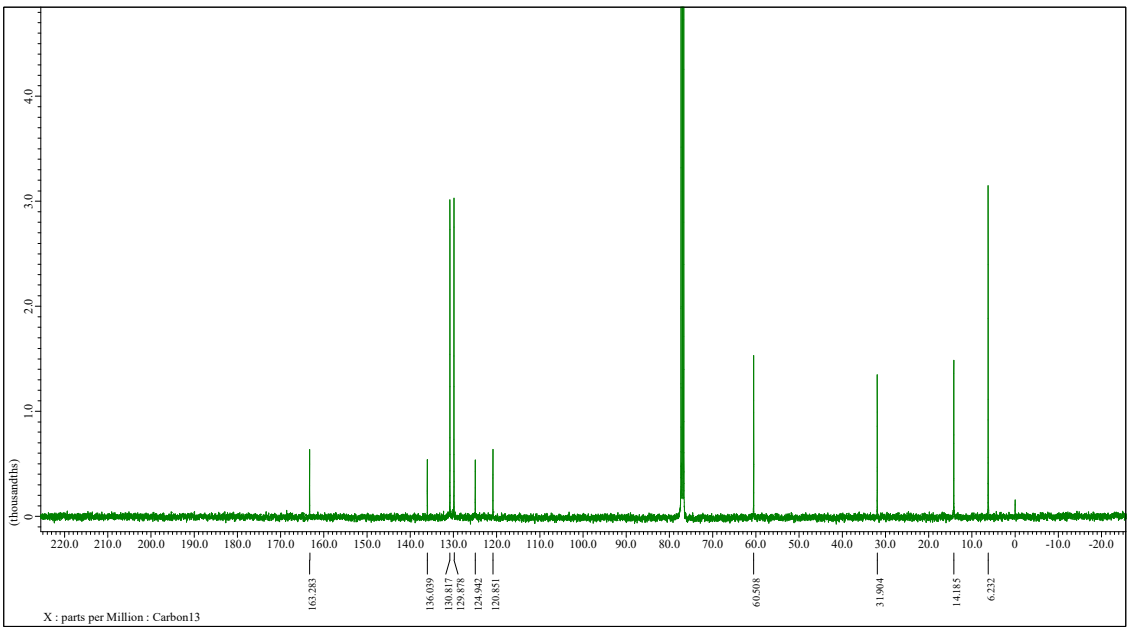


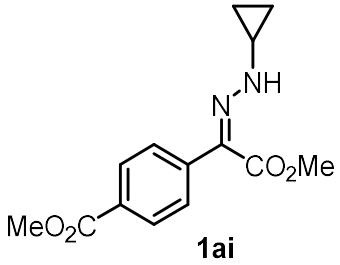
1ah

^{1}H-NMR (400 MHz, $CDCl_3$)



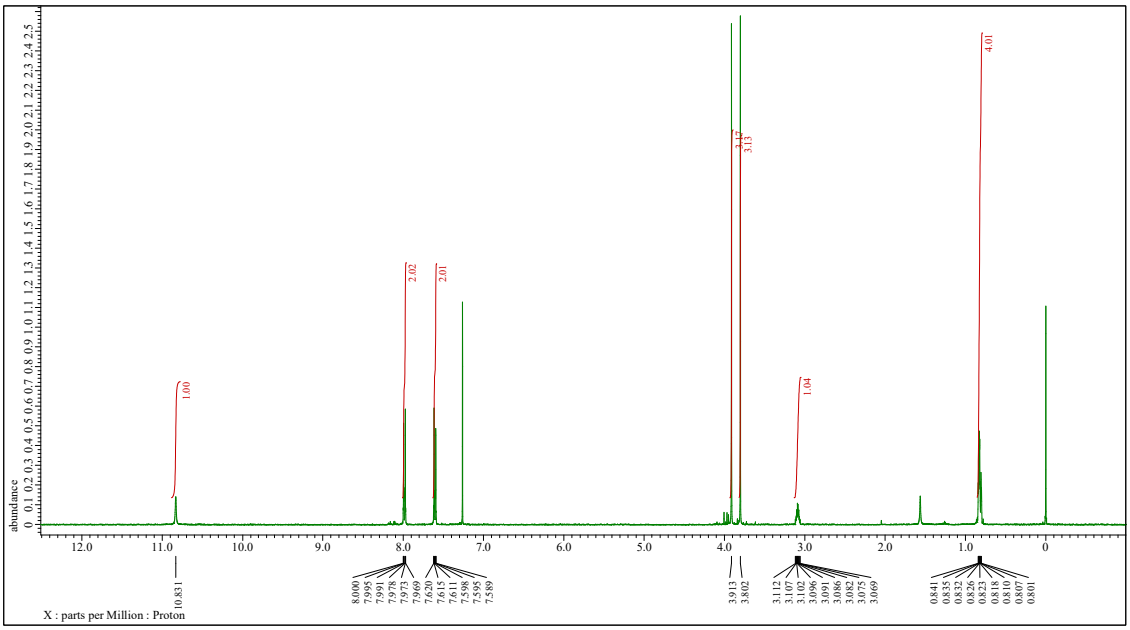
^{13}C-NMR (101 MHz, $CDCl_3$)



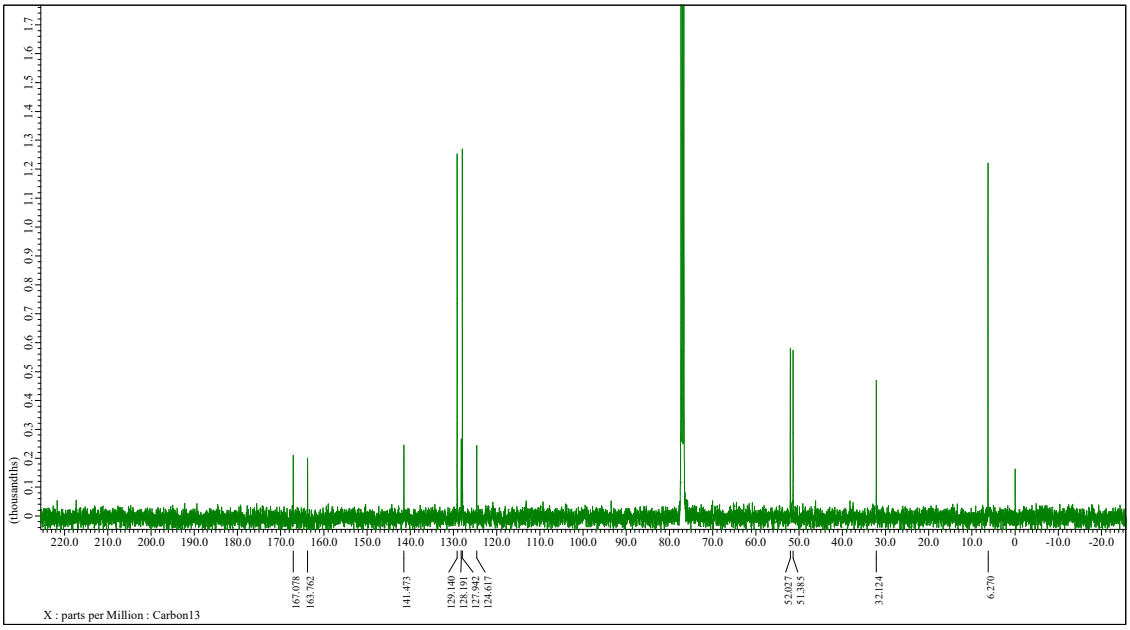


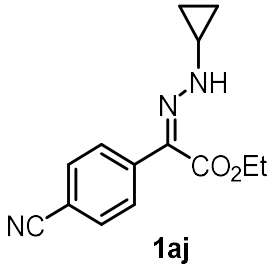
1ai

^{1}H-NMR (400 MHz, $CDCl_3$)



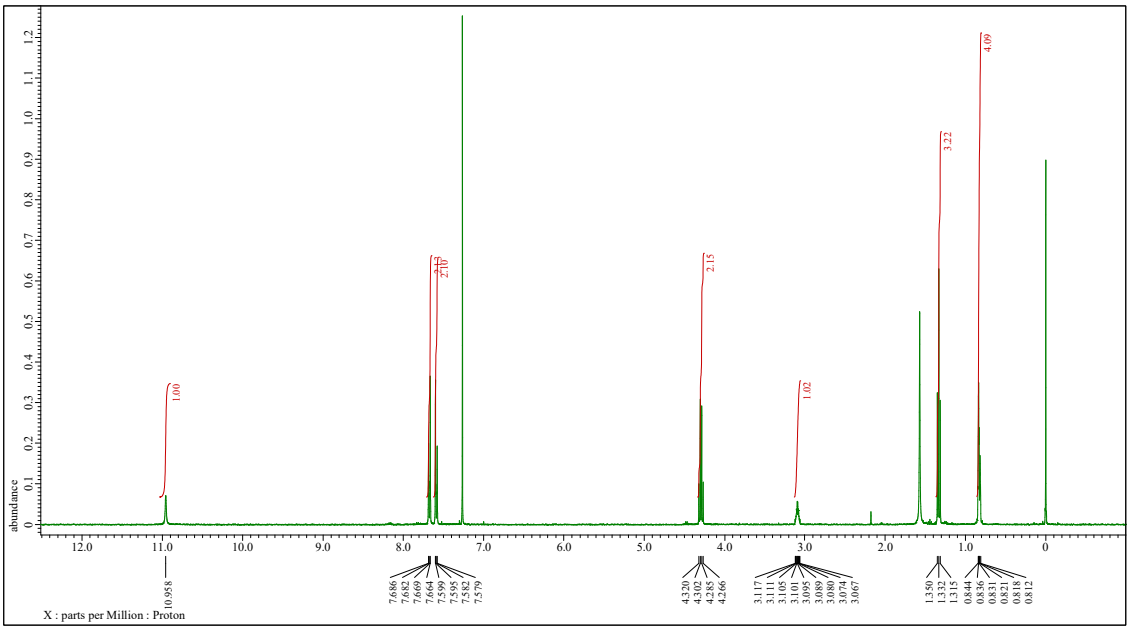
^{13}C-NMR (101 MHz, $CDCl_3$)



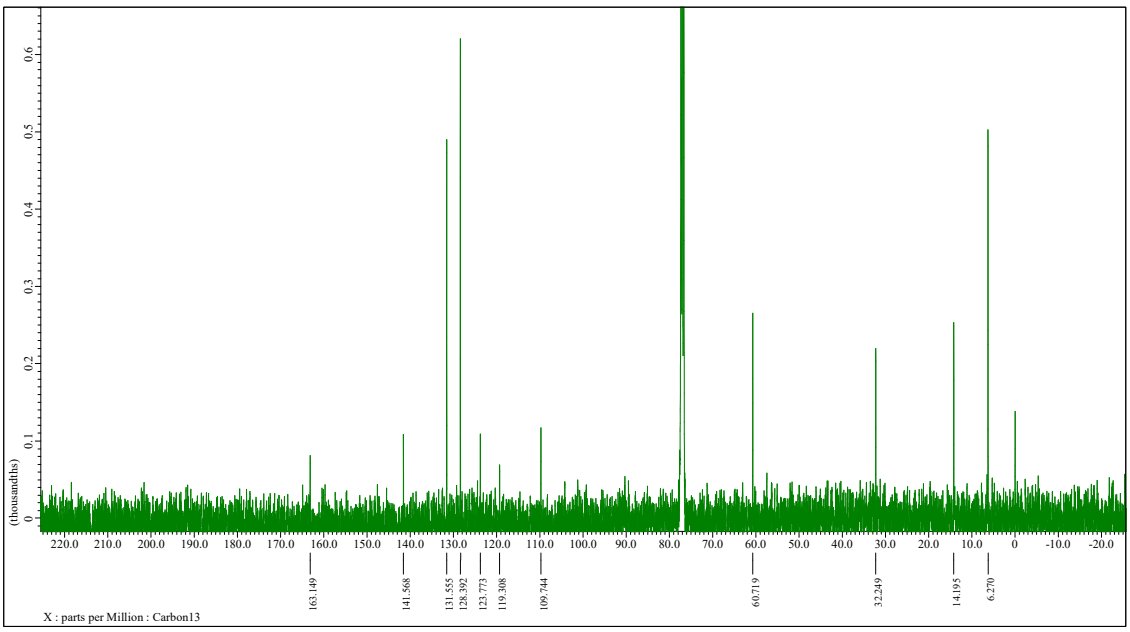


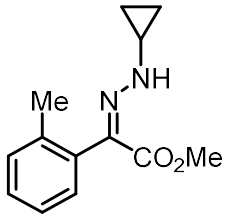
1aj

^{1}H-NMR (400 MHz, $CDCl_3$)



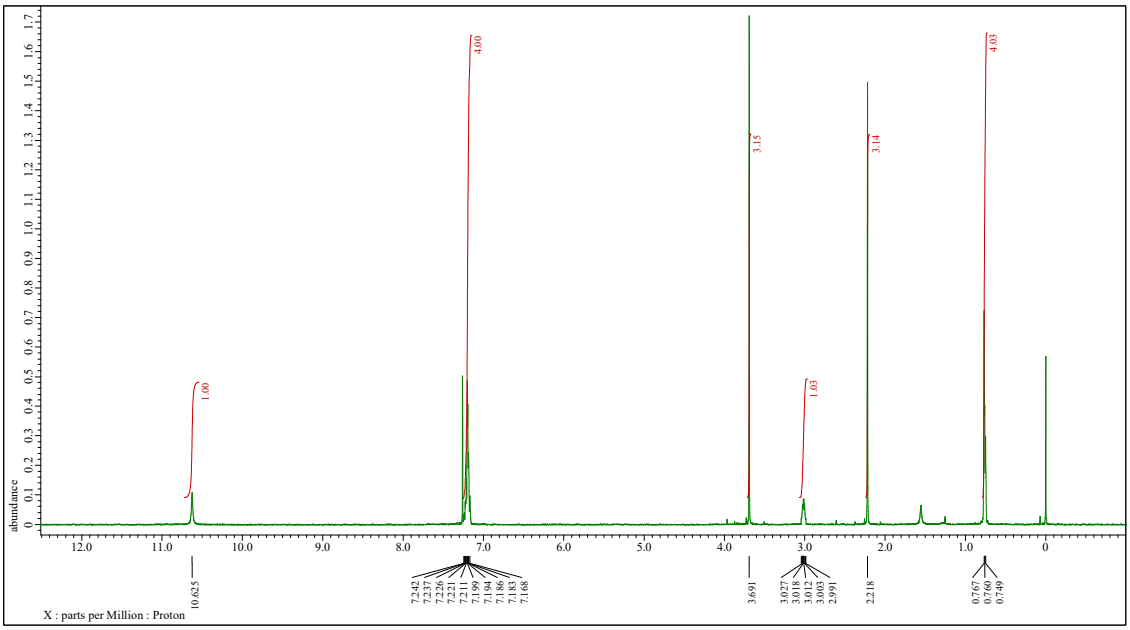
^{13}C-NMR (101 MHz, $CDCl_3$)



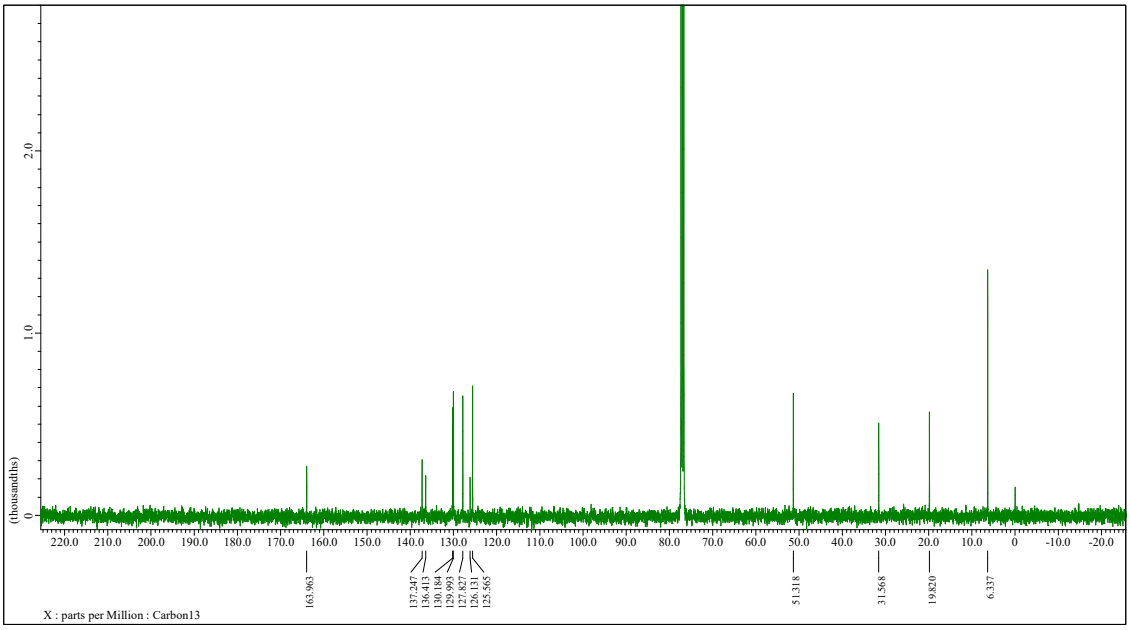


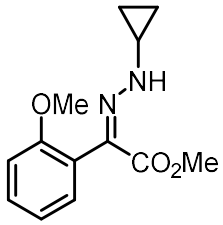
1ak

^{1}H-NMR (400 MHz, $CDCl_3$)



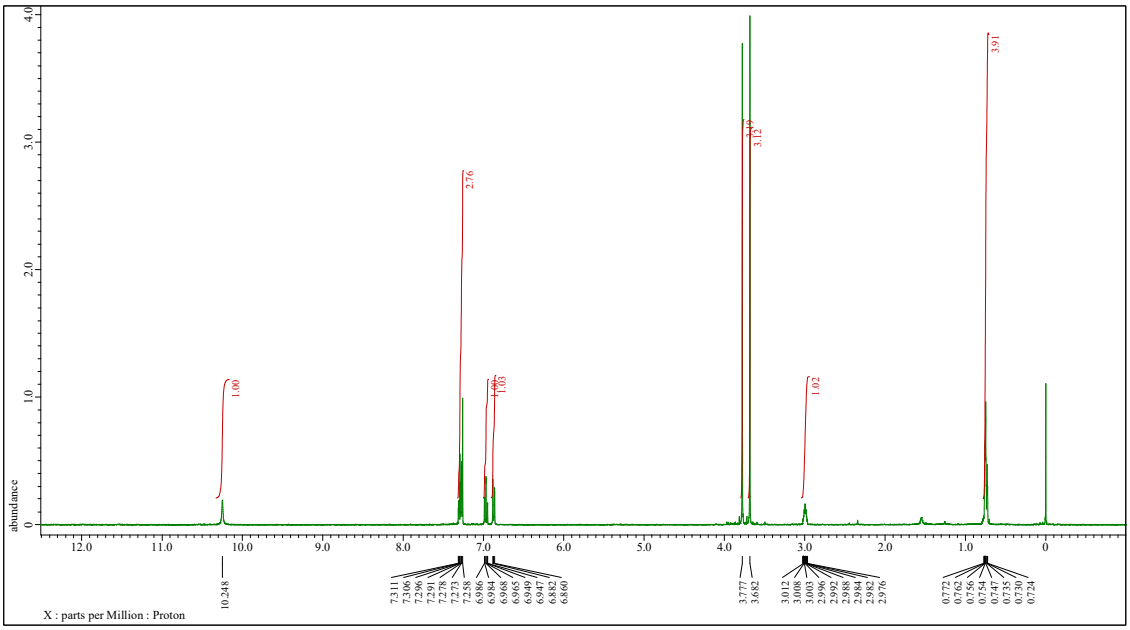
^{13}C-NMR (101 MHz, $CDCl_3$)



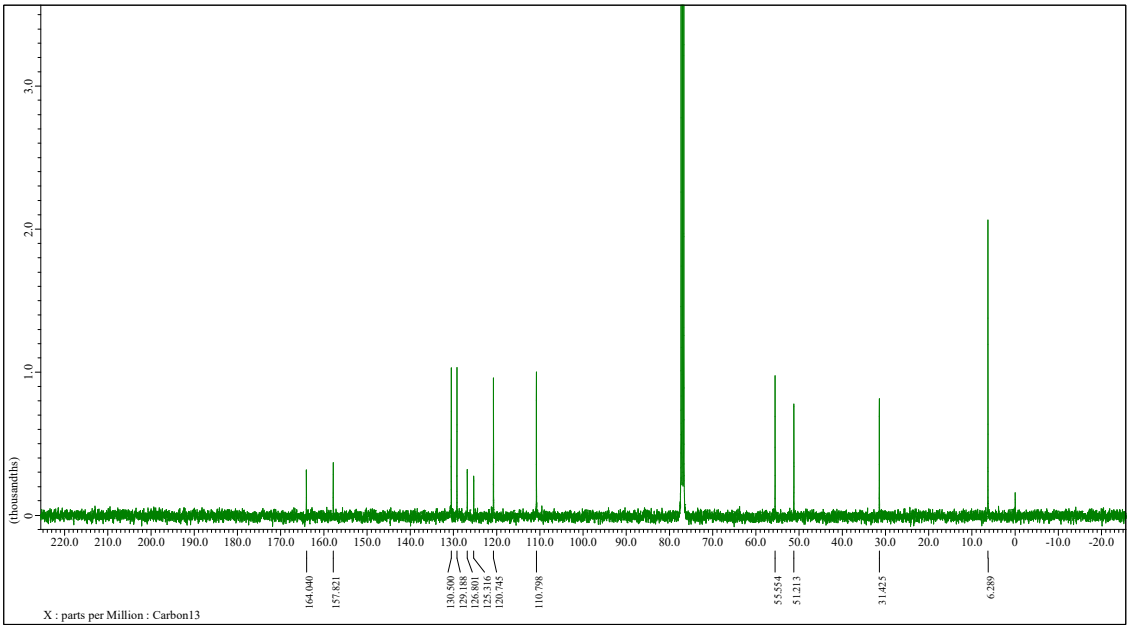


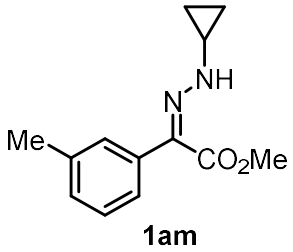
1al

^{1}H-NMR (400 MHz, $CDCl_3$)



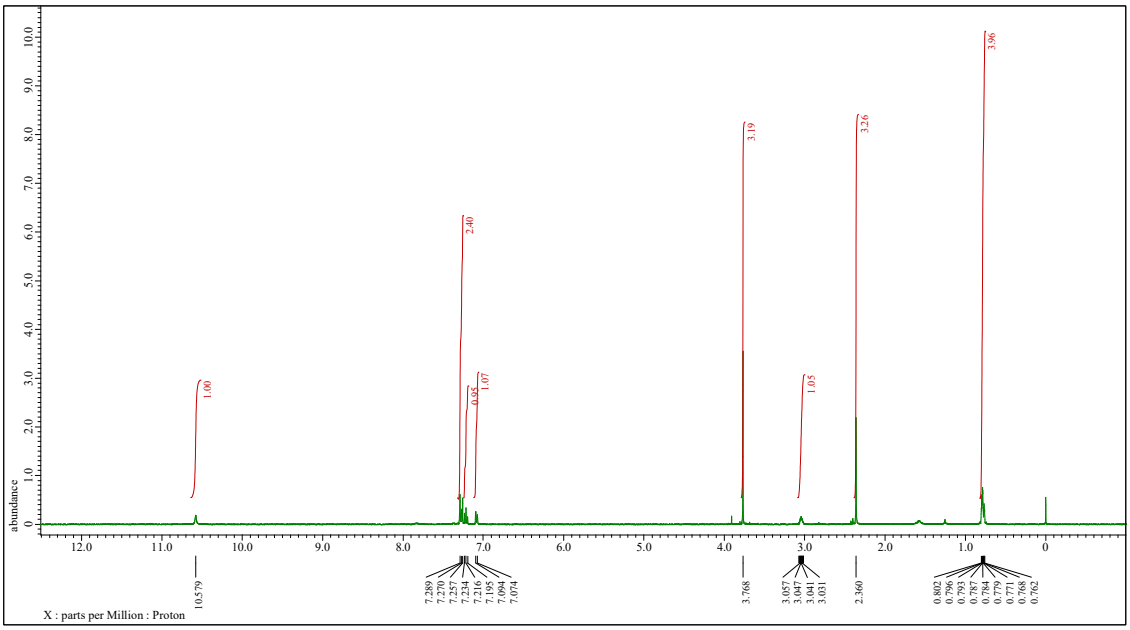
^{13}C-NMR (101 MHz, $CDCl_3$)



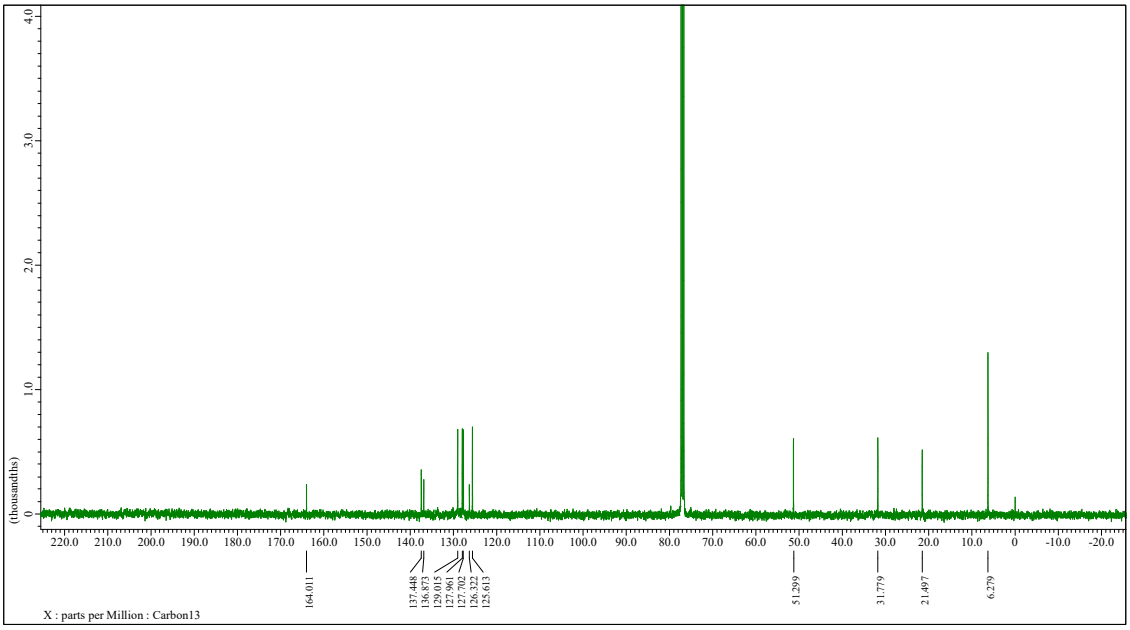


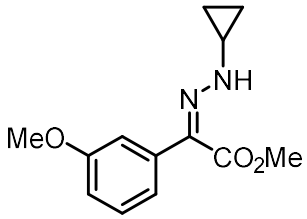
1am

^{1}H-NMR (400 MHz, $CDCl_3$)



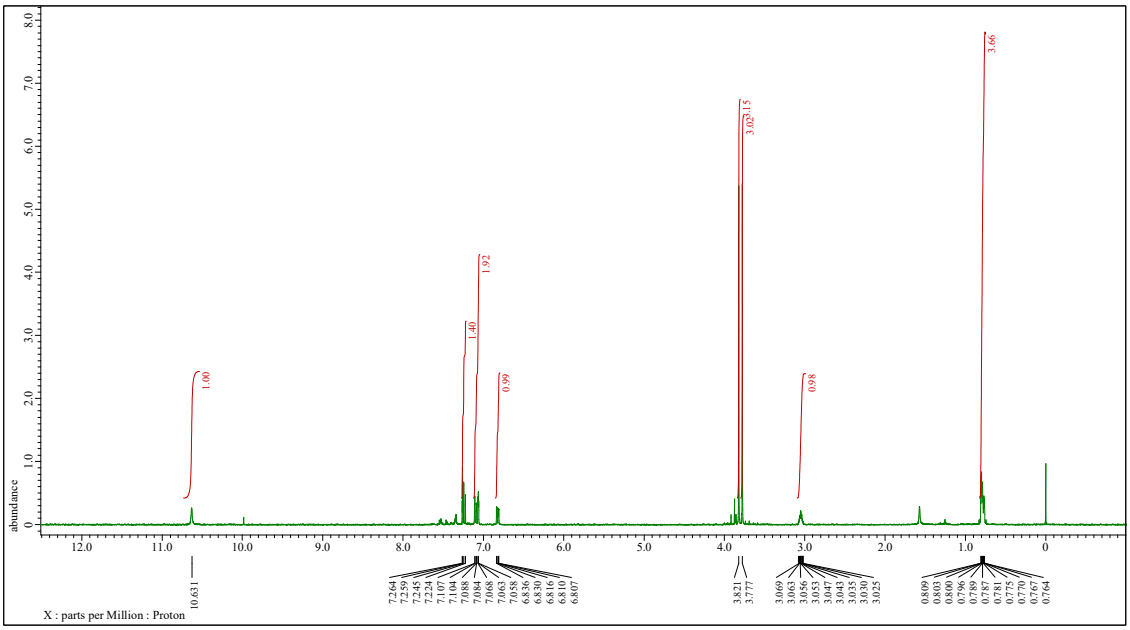
^{13}C-NMR (101 MHz, $CDCl_3$)



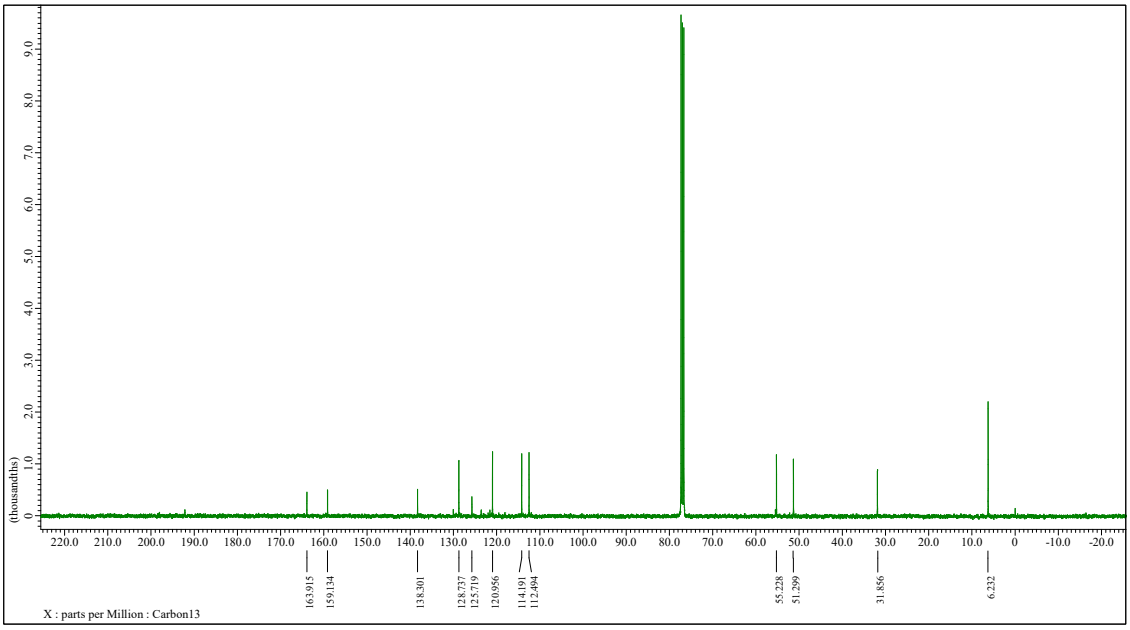


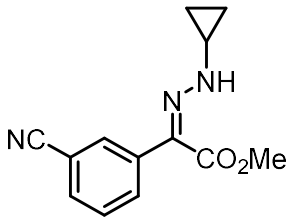
1an

^{1}H-NMR (400 MHz, $CDCl_3$)



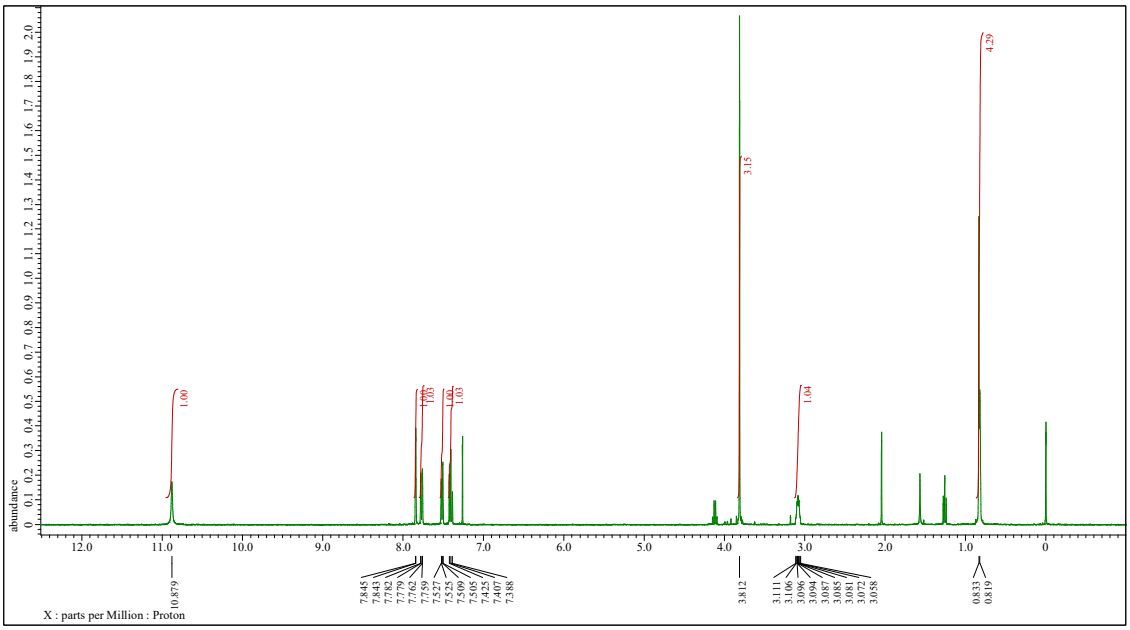
^{13}C-NMR (101 MHz, $CDCl_3$)



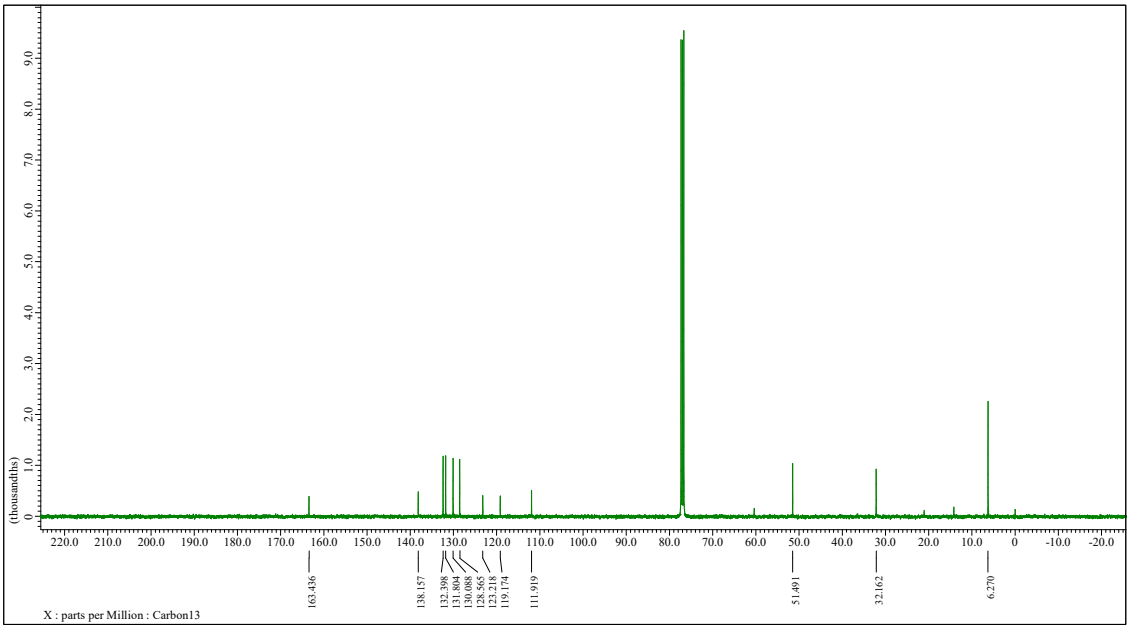


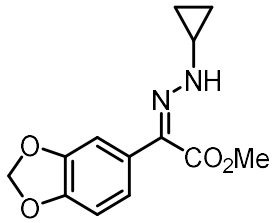
1ao

^{1}H-NMR (400 MHz, $CDCl_3$)



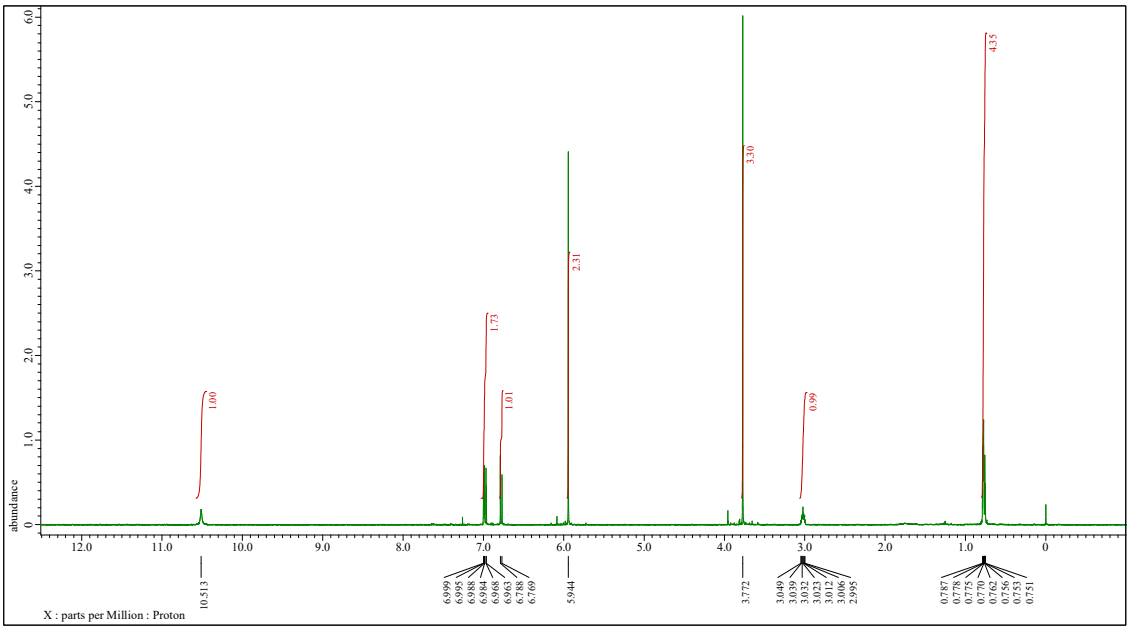
^{13}C-NMR (101 MHz, $CDCl_3$)



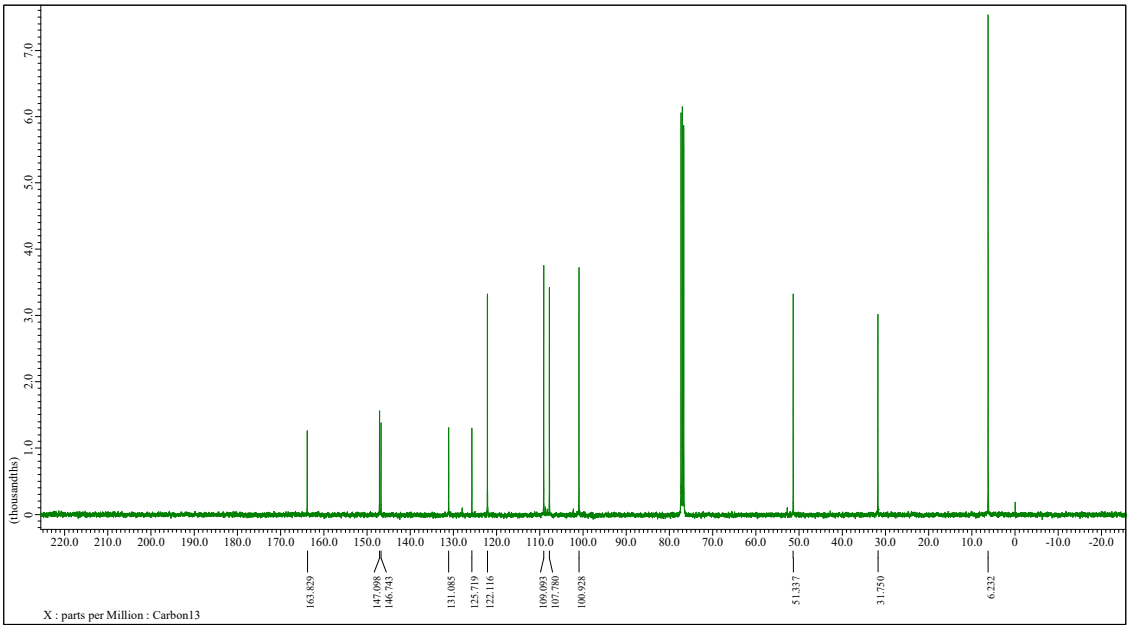


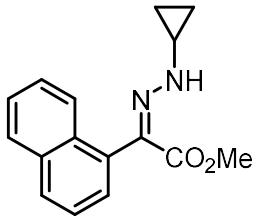
1ap

^{1}H-NMR (400 MHz, $CDCl_3$)



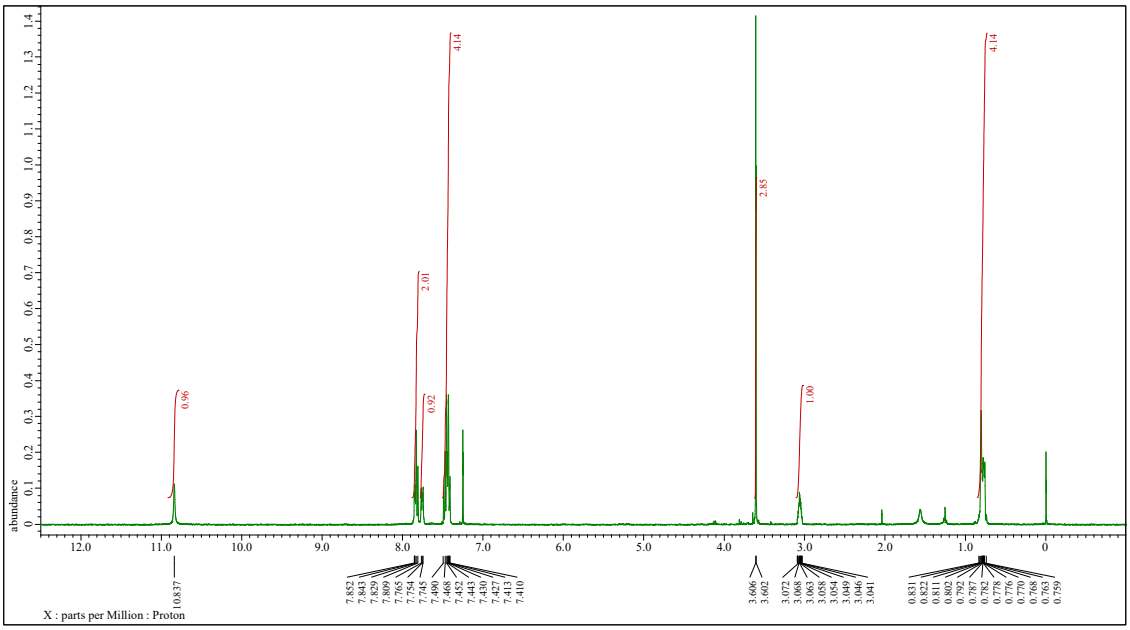
^{13}C-NMR (101 MHz, $CDCl_3$)



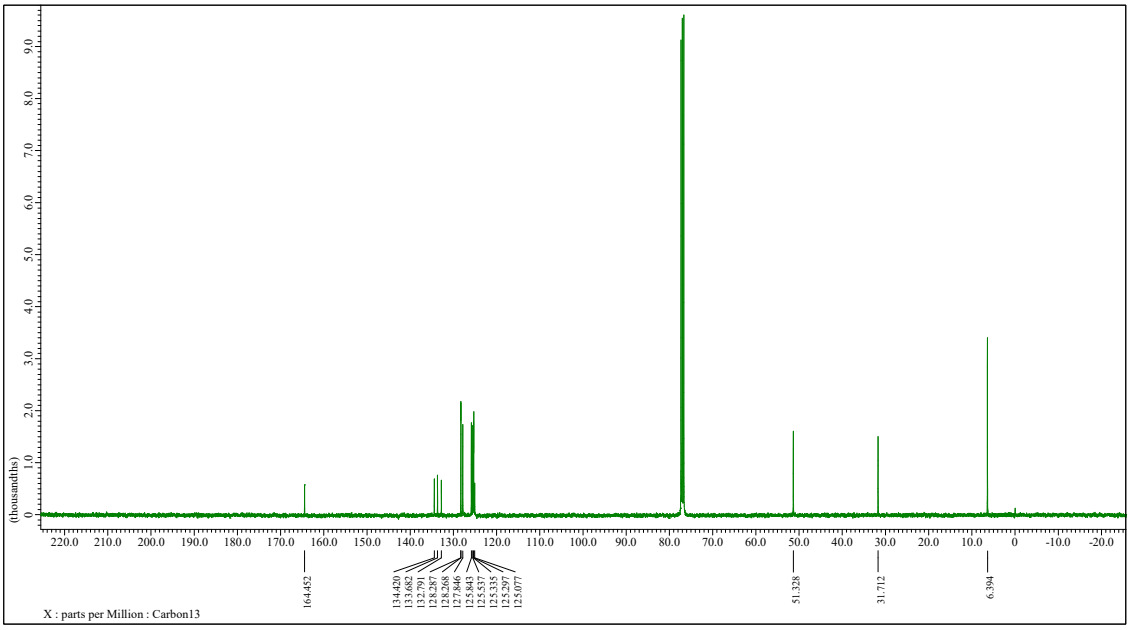


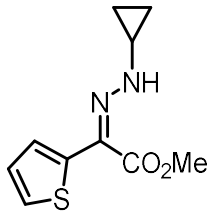
1aq

^{1}H-NMR (400 MHz, $CDCl_3$)



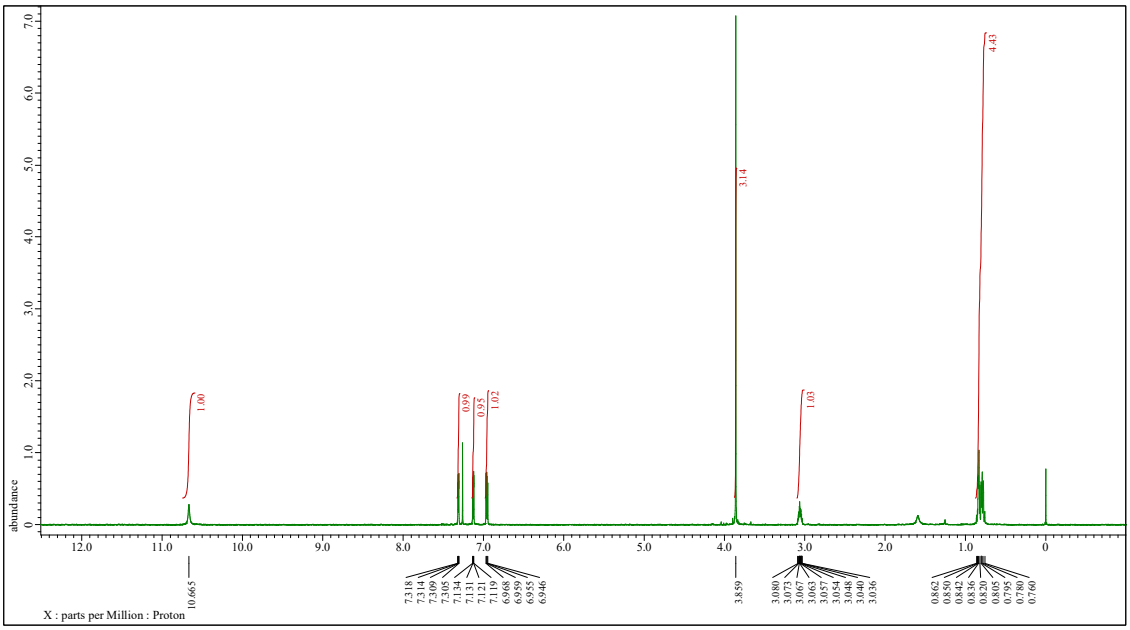
^{13}C-NMR (101 MHz, $CDCl_3$)



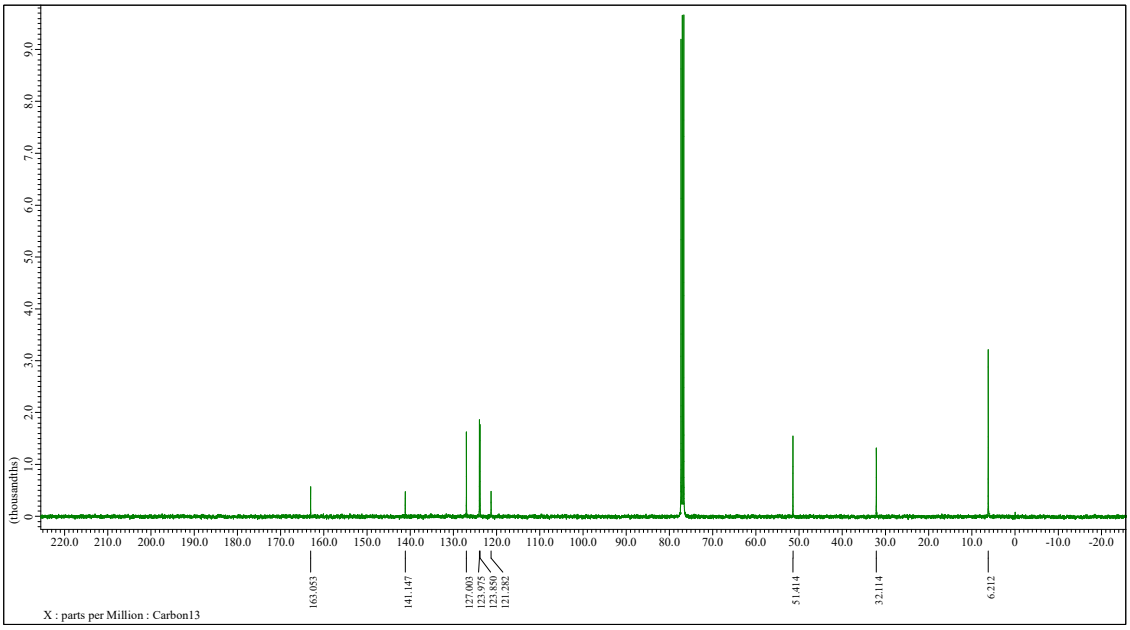


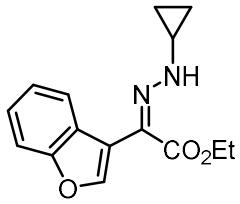
1ar

^{1}H-NMR (400 MHz, $CDCl_3$)



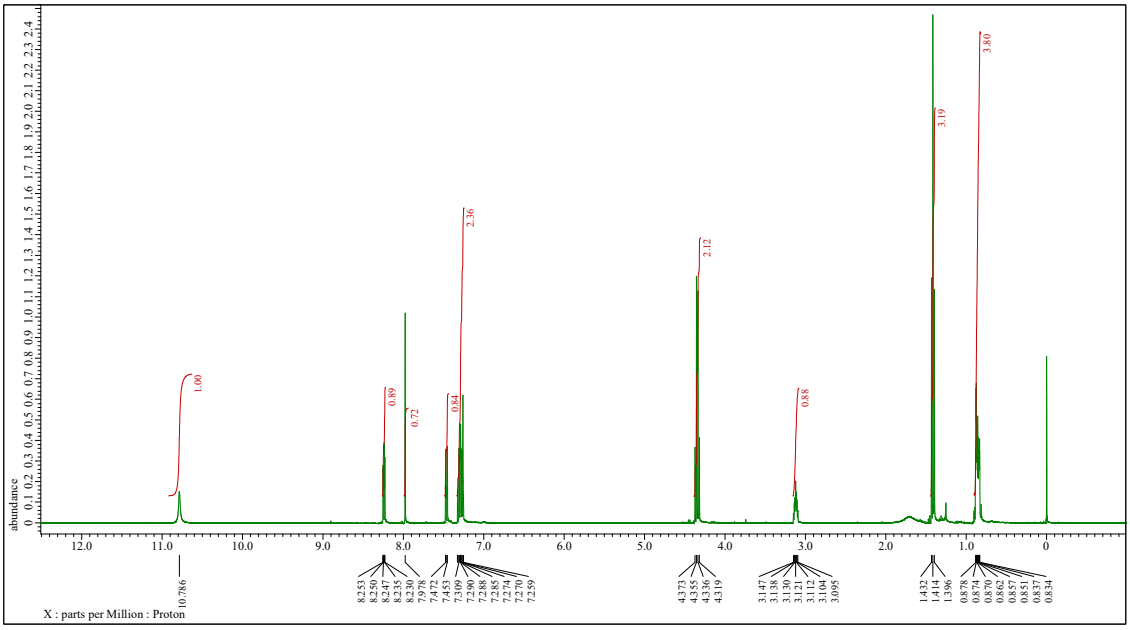
^{13}C-NMR (101 MHz, $CDCl_3$)



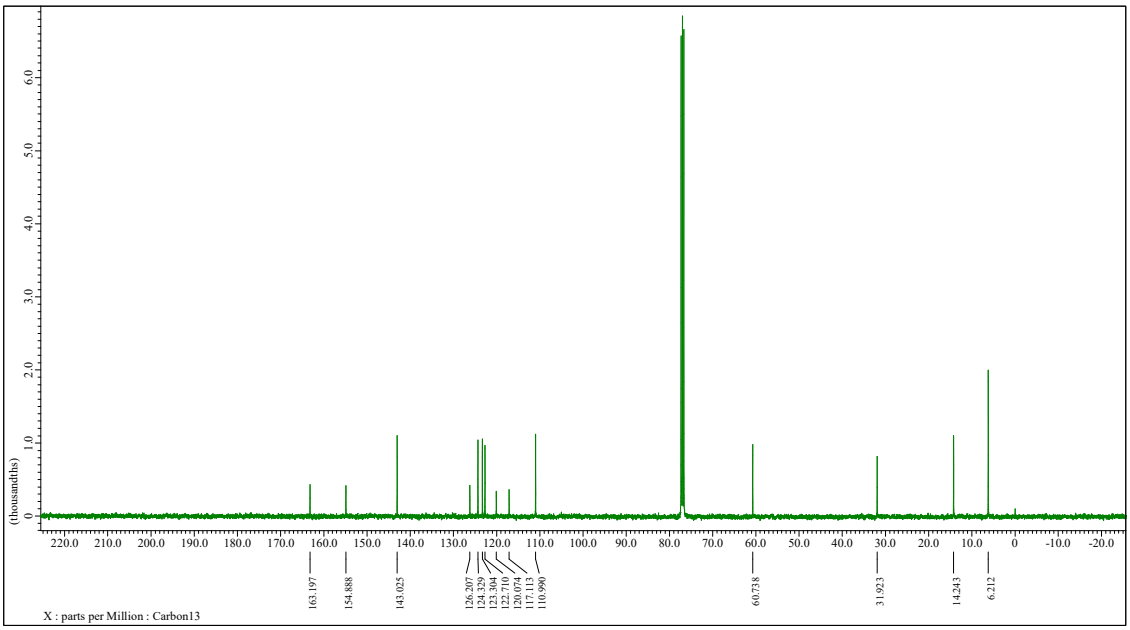


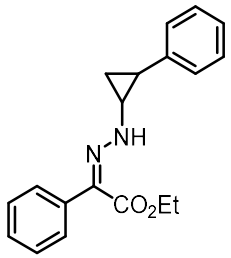
1as

^{1}H-NMR (400 MHz, $CDCl_3$)



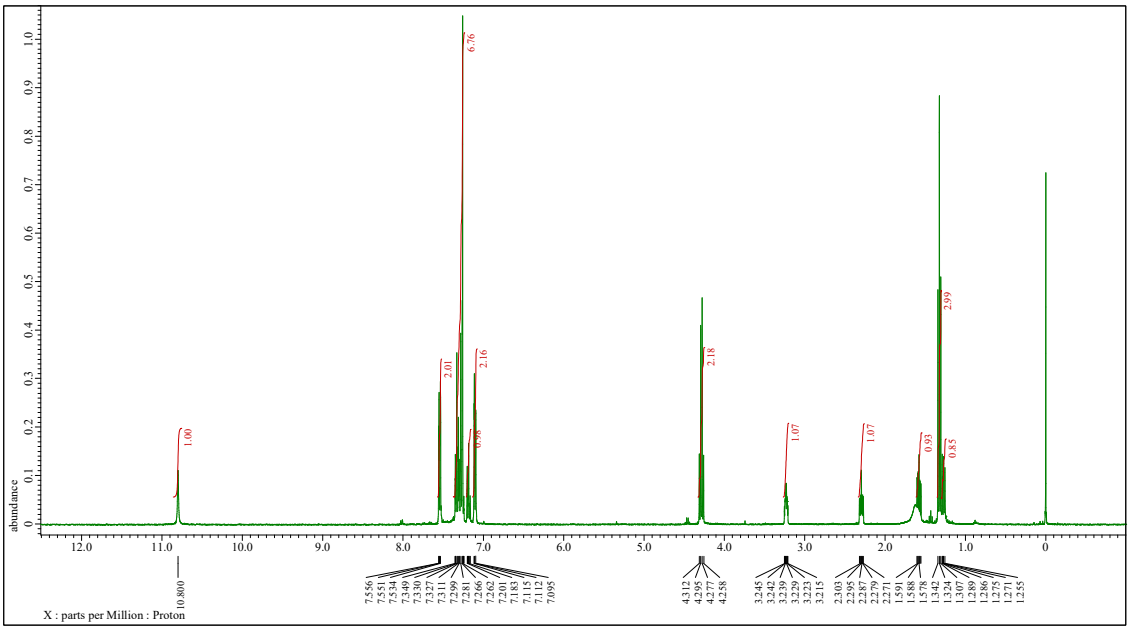
^{13}C-NMR (101 MHz, $CDCl_3$)



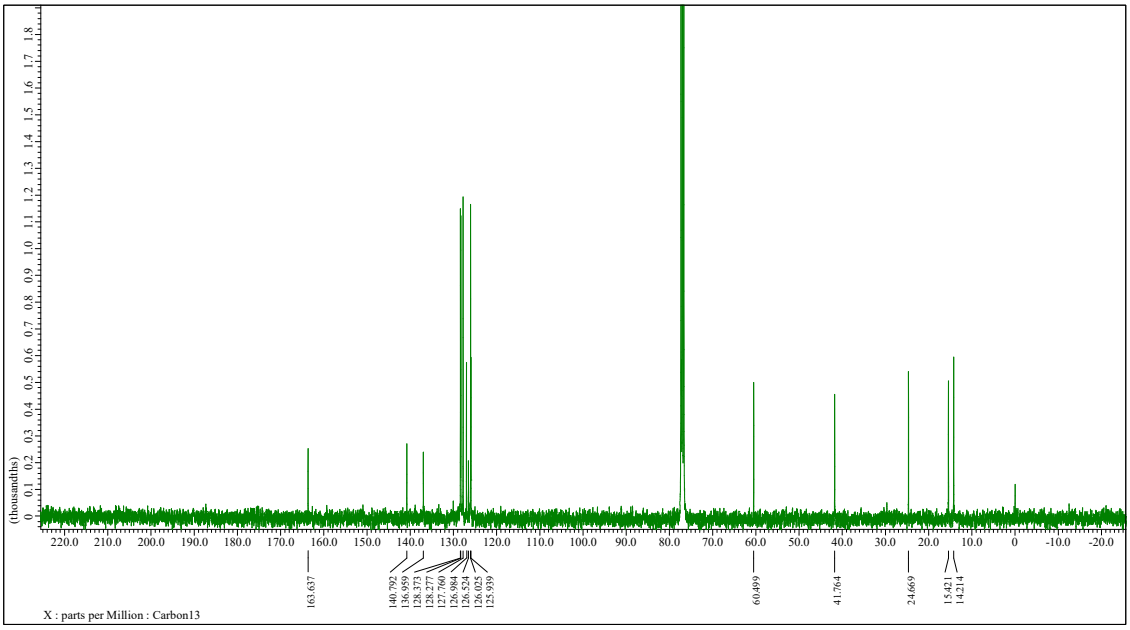


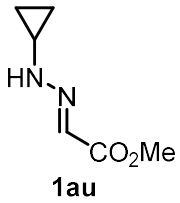
1at

^{1}H-NMR (400 MHz, $CDCl_3$)



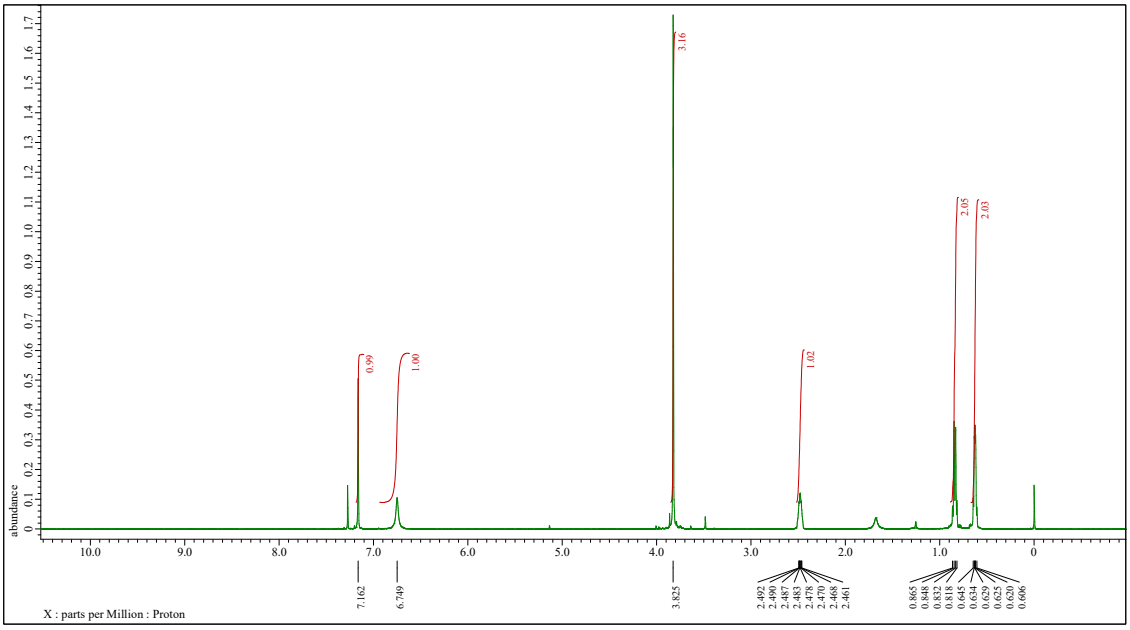
^{13}C-NMR (101 MHz, $CDCl_3$)



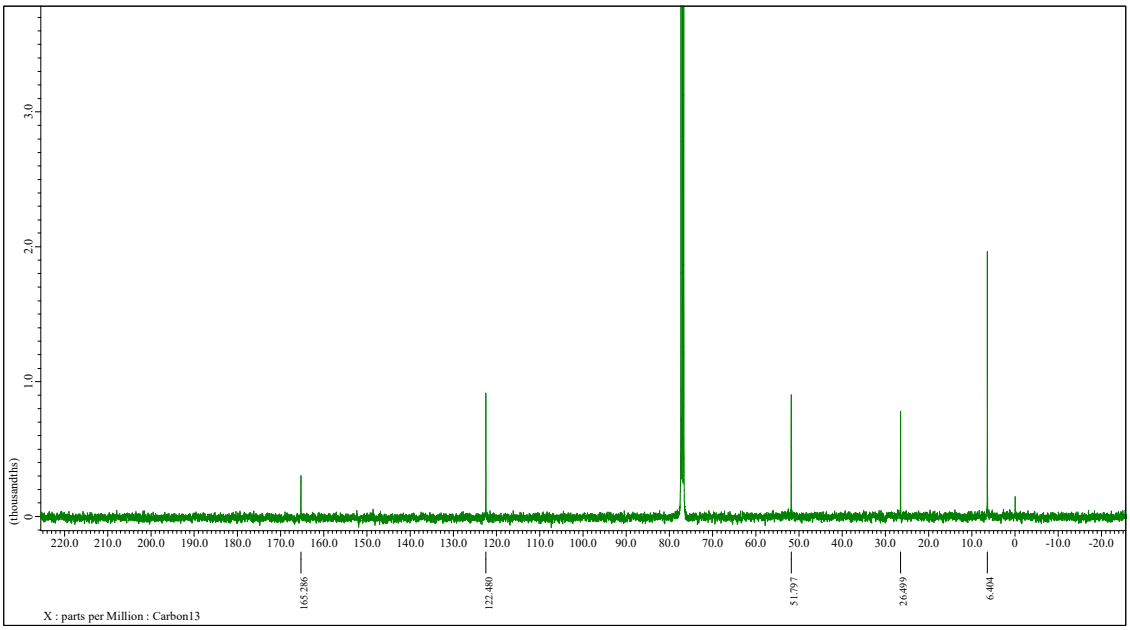


1au

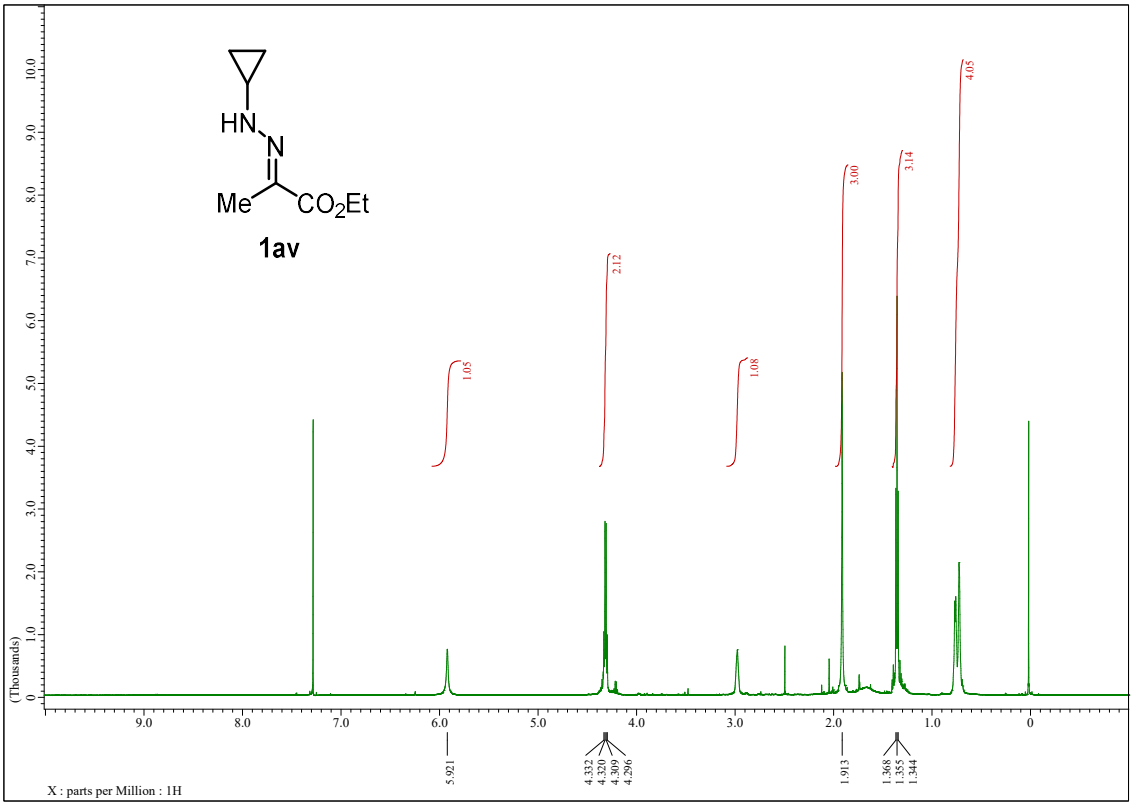
^{1}H-NMR (400 MHz, $CDCl_3$)



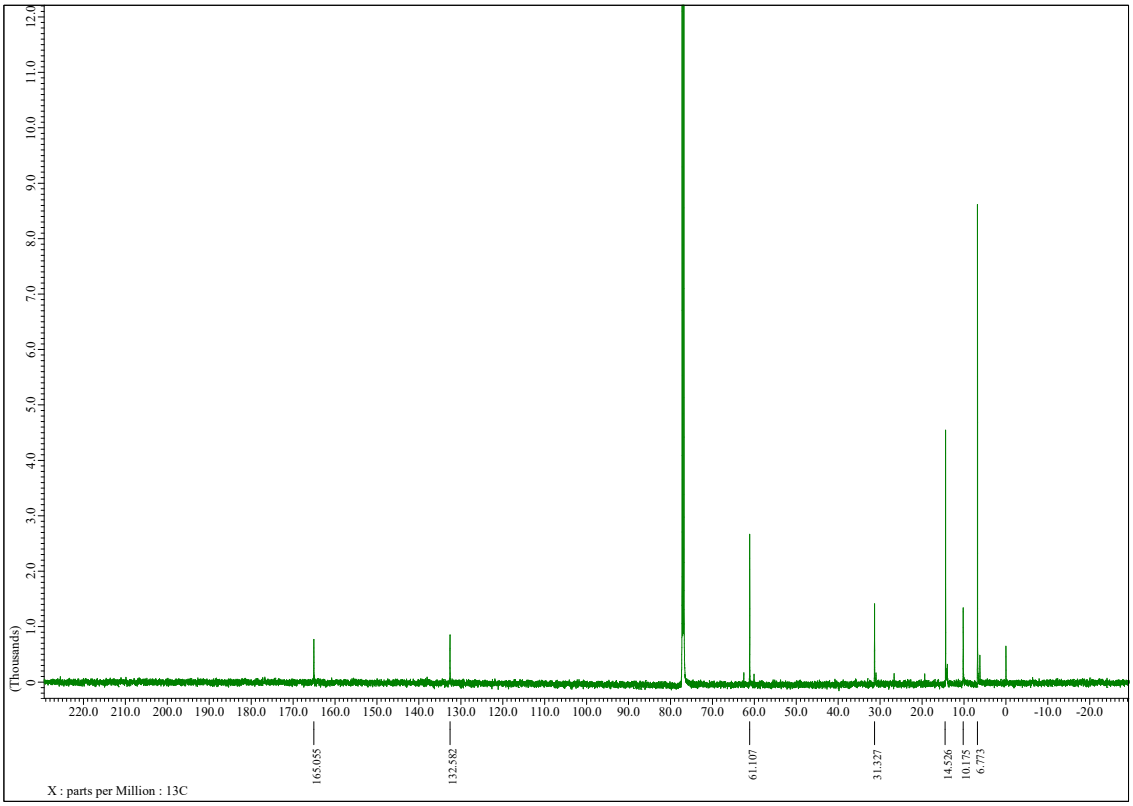
^{13}C-NMR (101 MHz, $CDCl_3$)

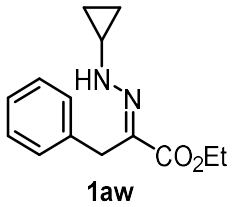


^{1}H-NMR (400 MHz, $CDCl_3$)



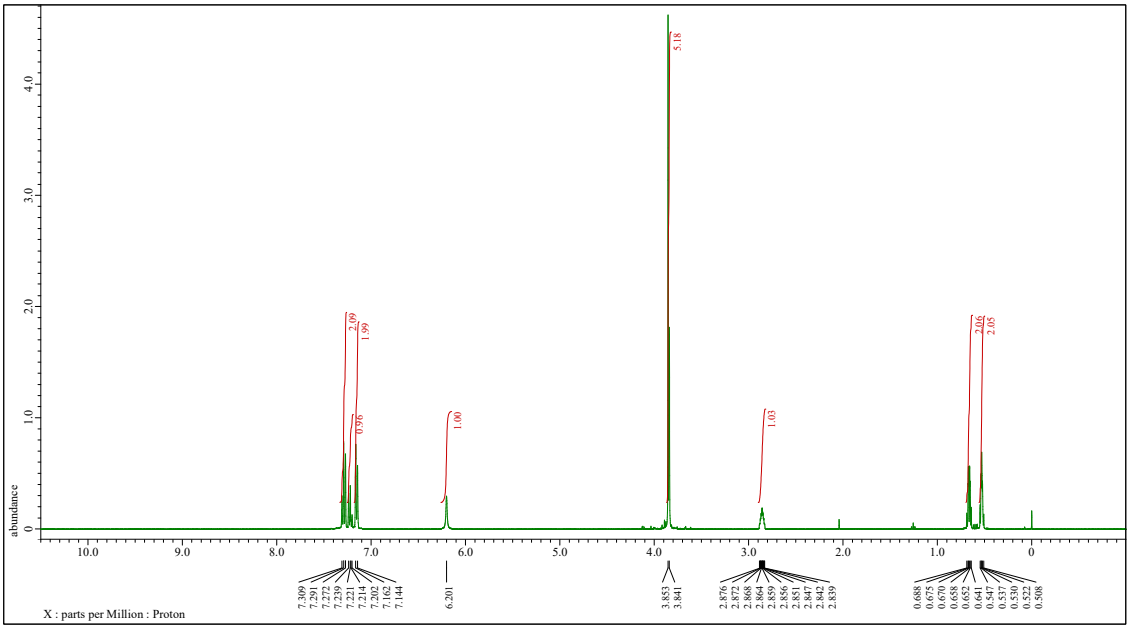
^{13}C-NMR (101 MHz, $CDCl_3$)



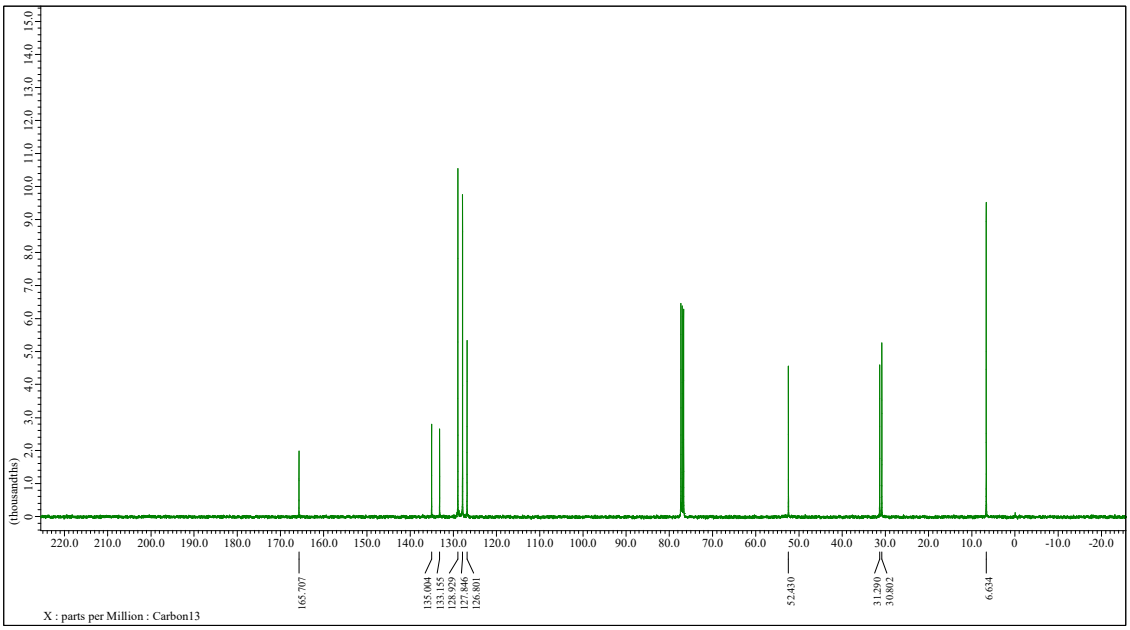


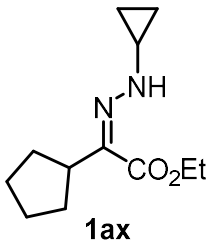
1aw

^{1}H-NMR (400 MHz, $CDCl_3$)



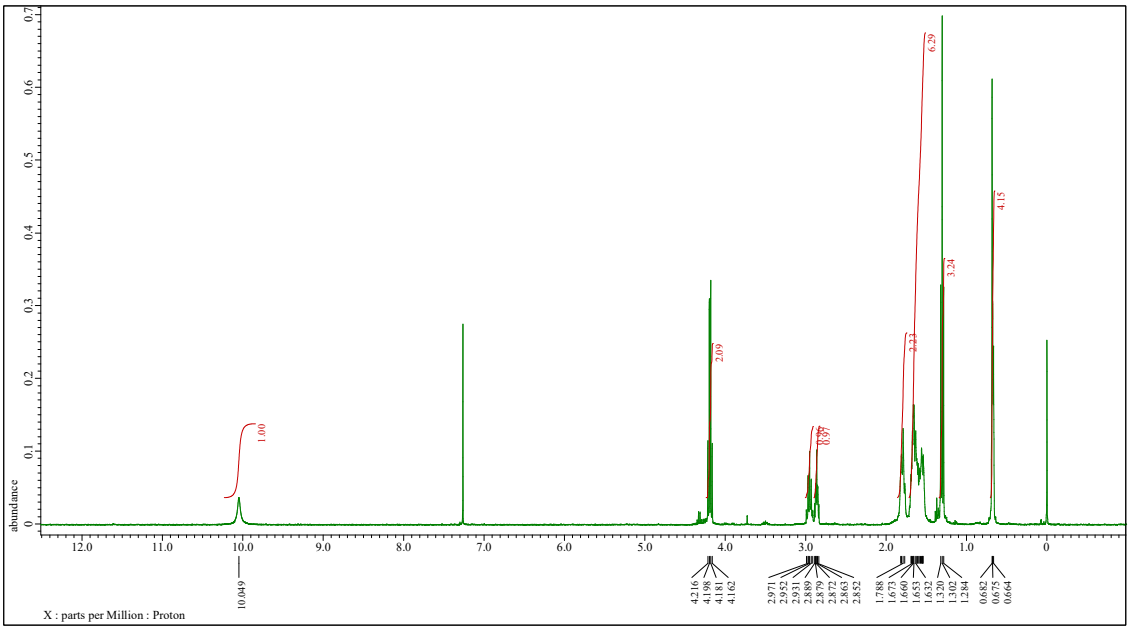
^{13}C-NMR (101 MHz, $CDCl_3$)



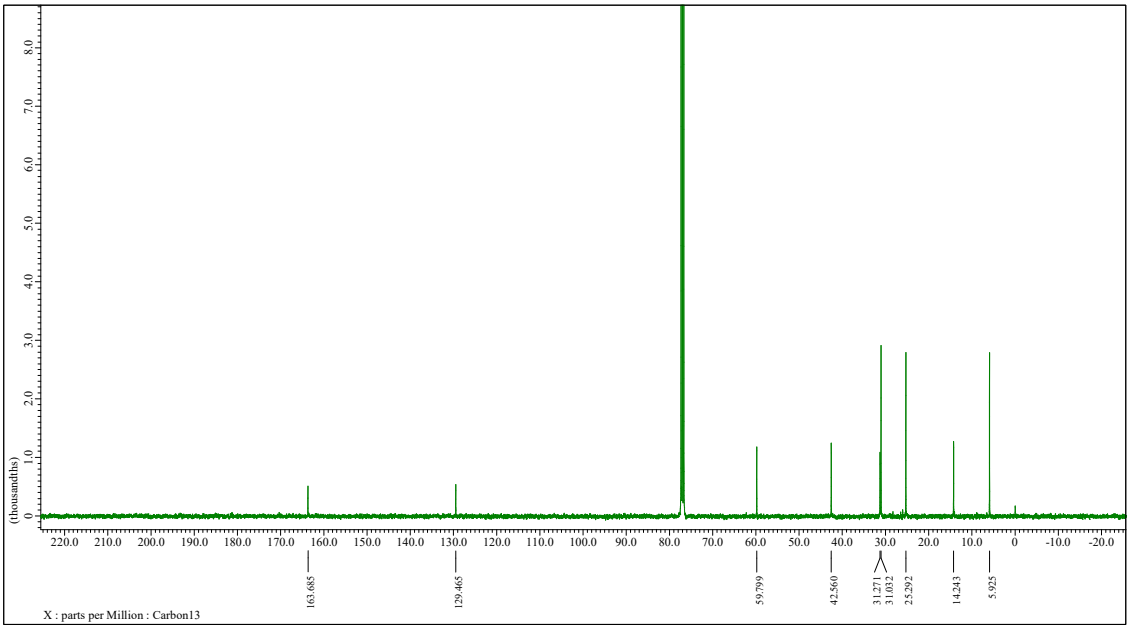


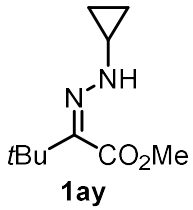
1ax

^{1}H-NMR (400 MHz, $CDCl_3$)



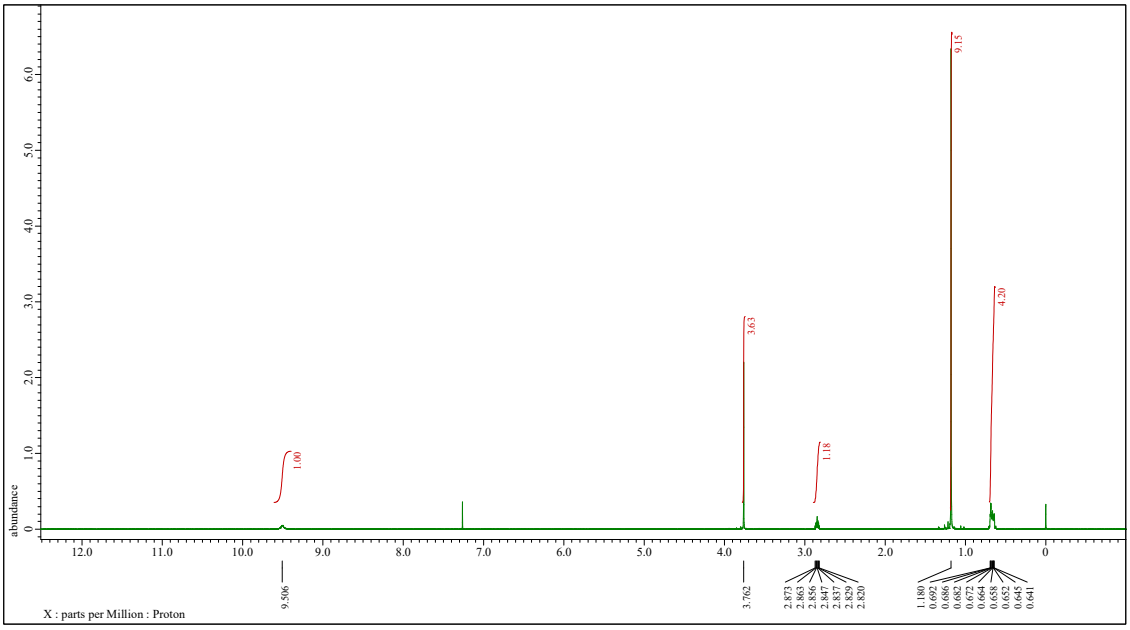
^{13}C-NMR (101 MHz, $CDCl_3$)



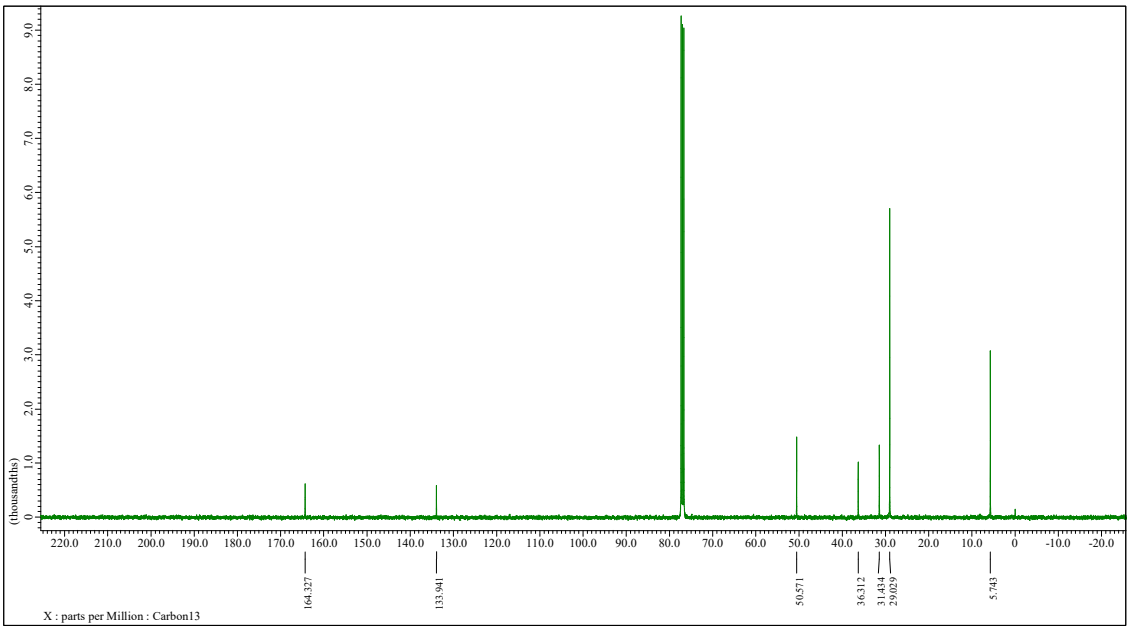


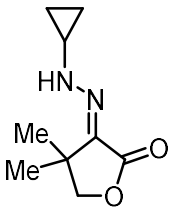
1ay

^{1}H-NMR (400 MHz, $CDCl_3$)



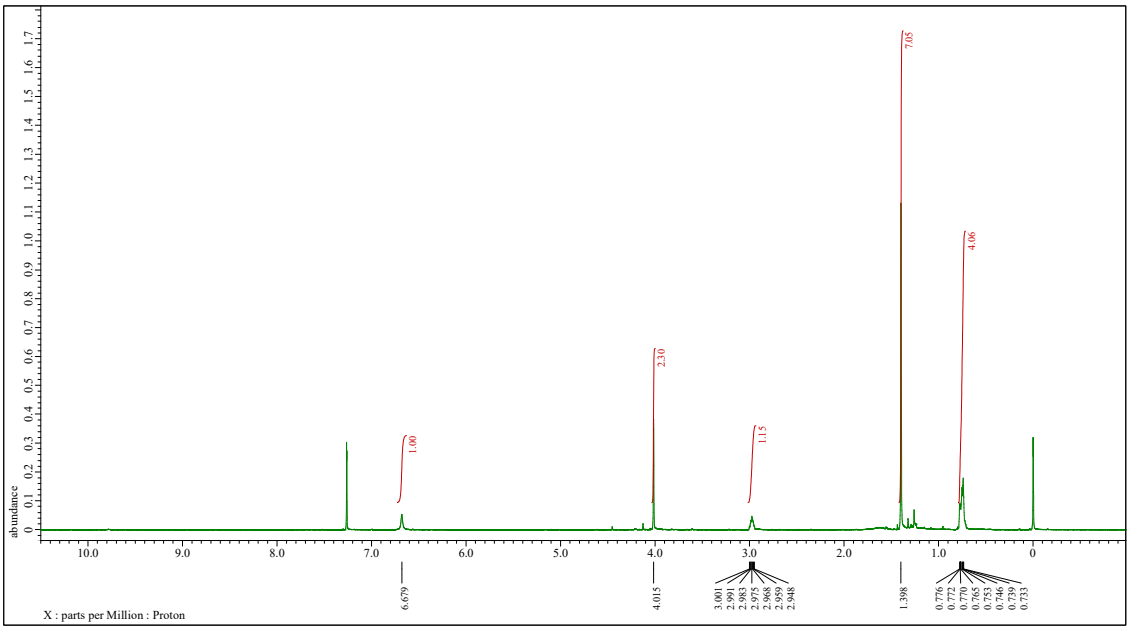
^{13}C-NMR (101 MHz, $CDCl_3$)



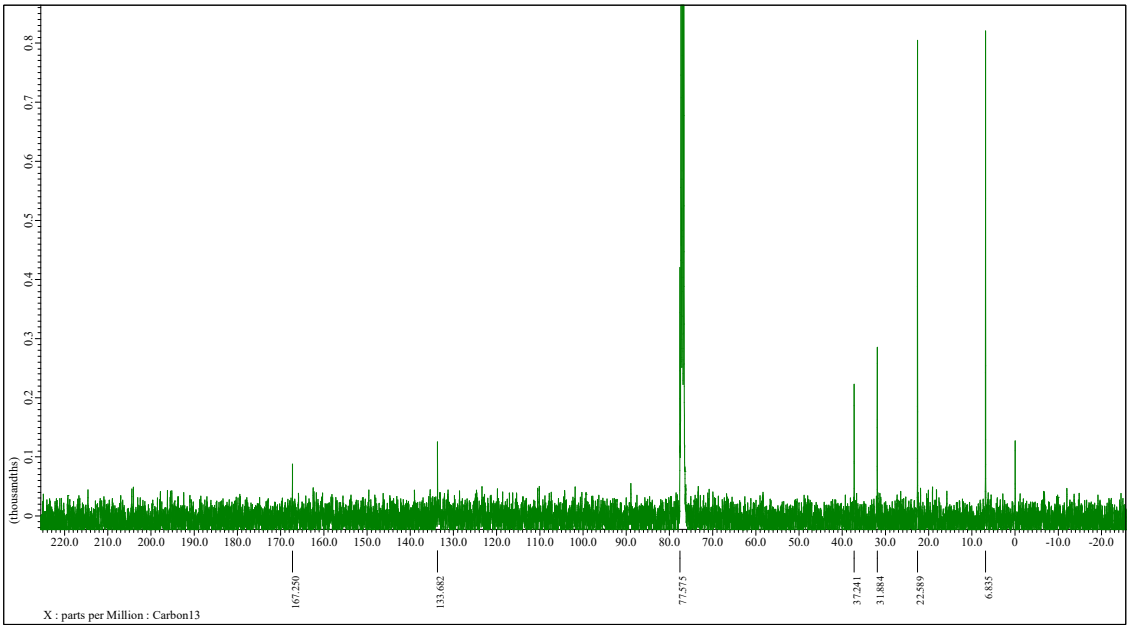


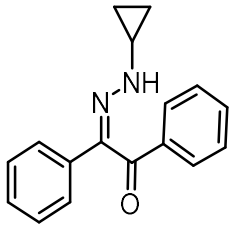
1az

^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)

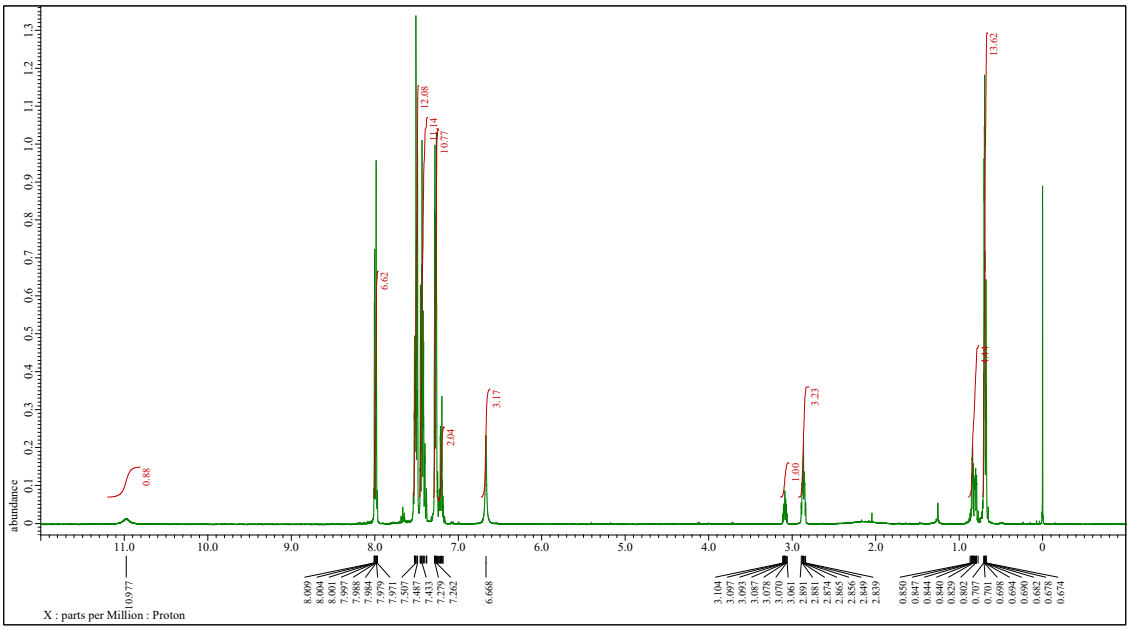




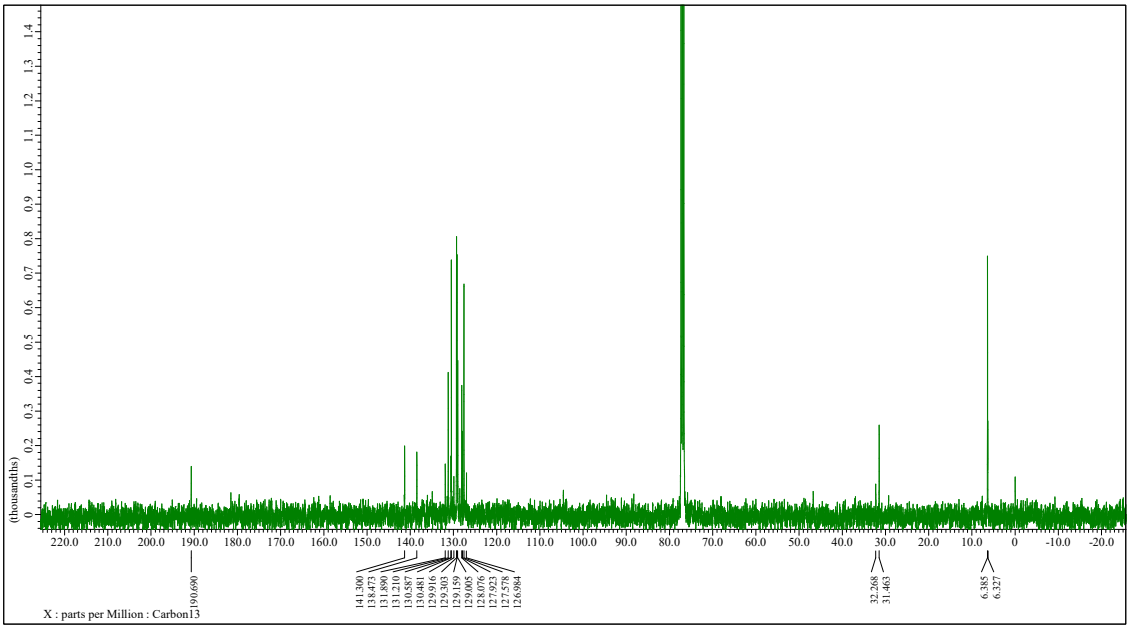
1ba

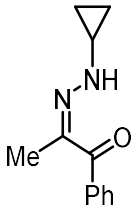
dr = 3.2:1

^{1}H-NMR (400 MHz, $CDCl_3$)



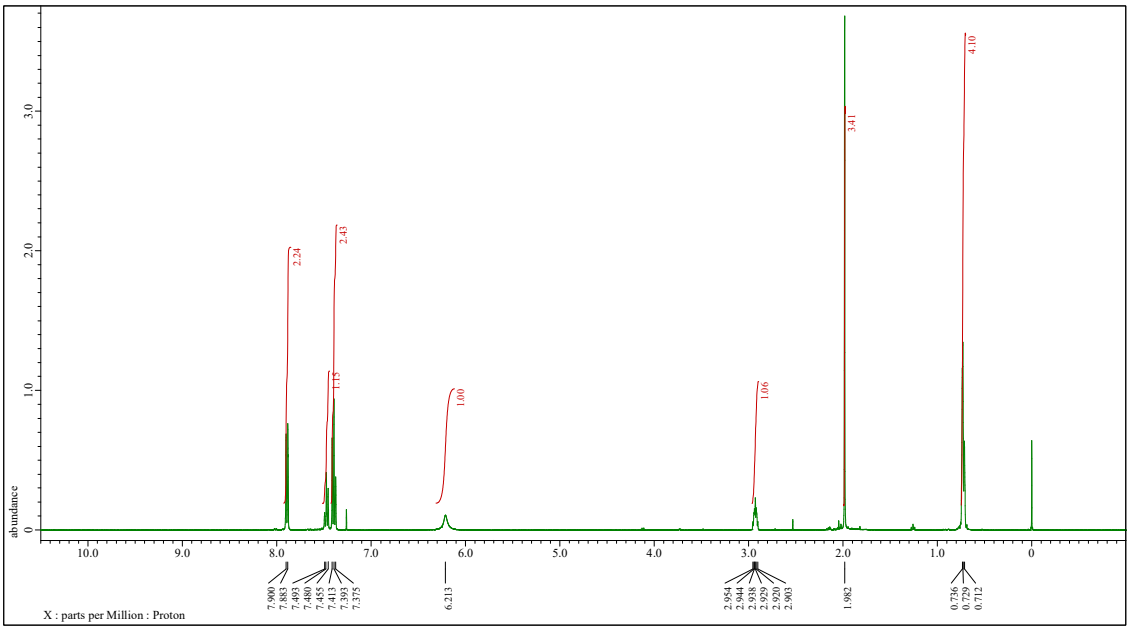
^{13}C-NMR (101 MHz, $CDCl_3$)



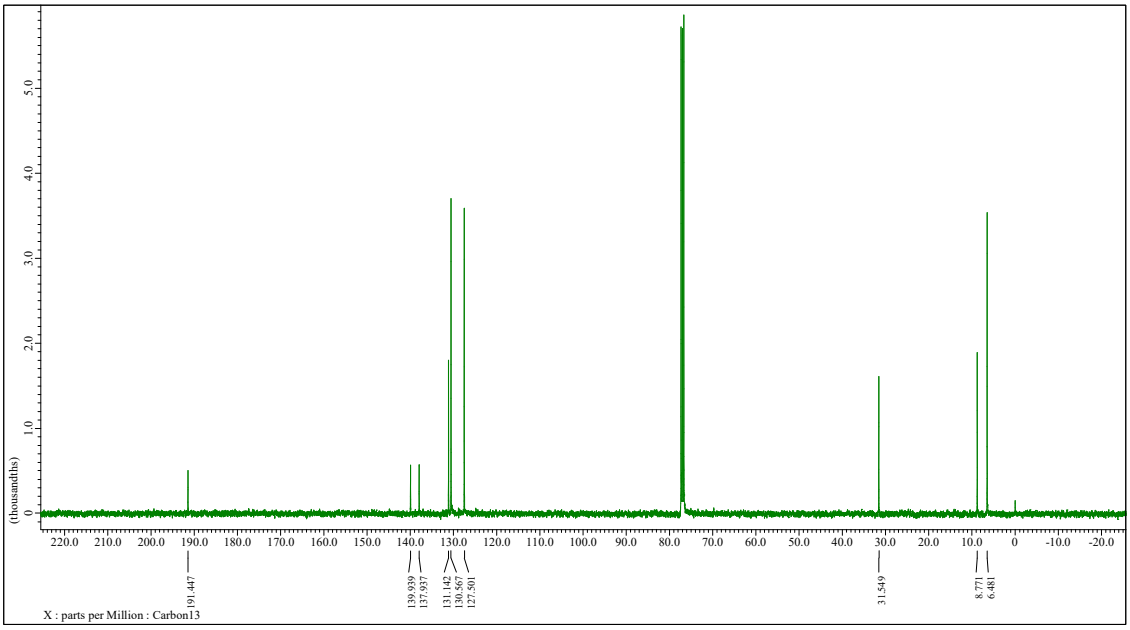


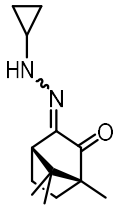
1bb

^{1}H-NMR (400 MHz, $CDCl_3$)



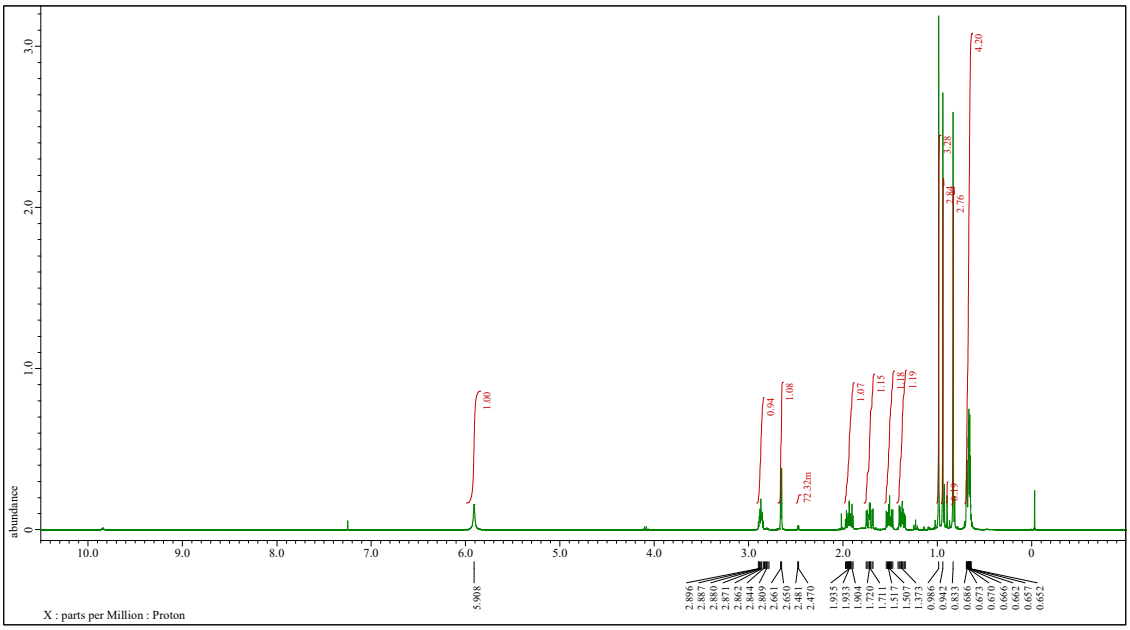
^{13}C-NMR (101 MHz, $CDCl_3$)



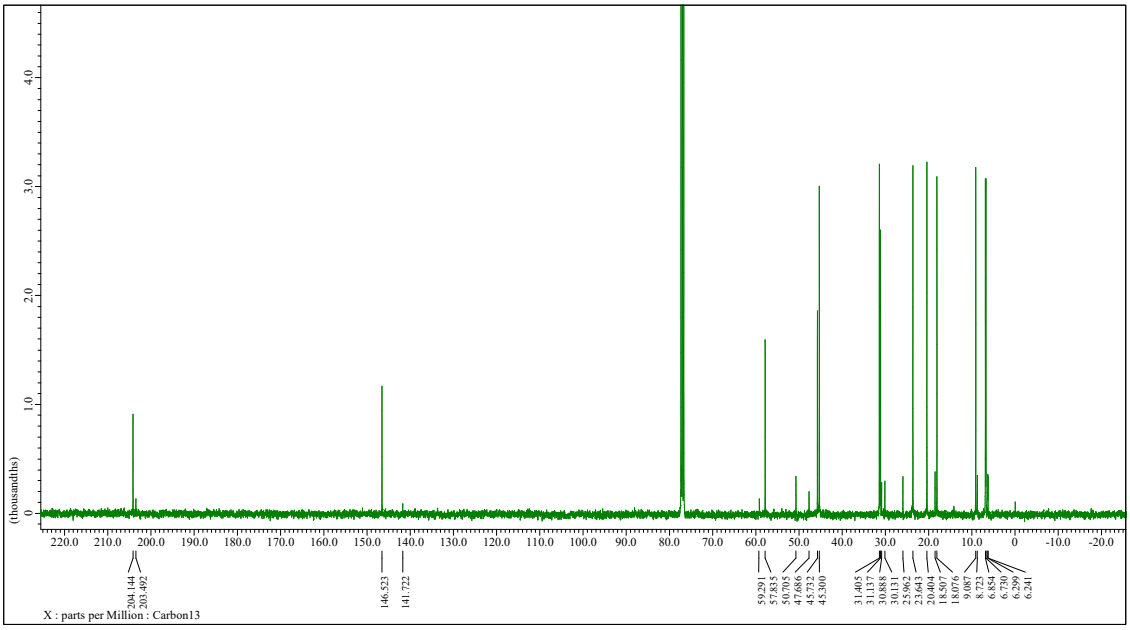


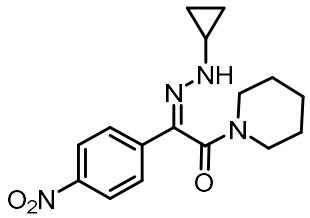
1bc dr = 100:7

^{1}H-NMR (400 MHz, $CDCl_3$)



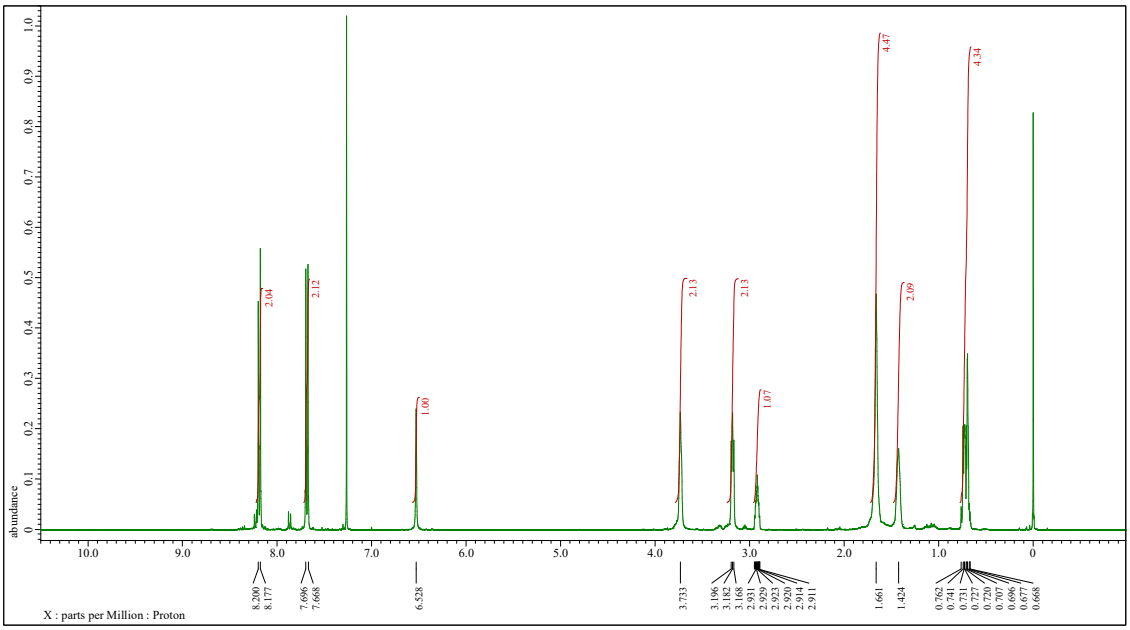
^{13}C-NMR (101 MHz, $CDCl_3$)



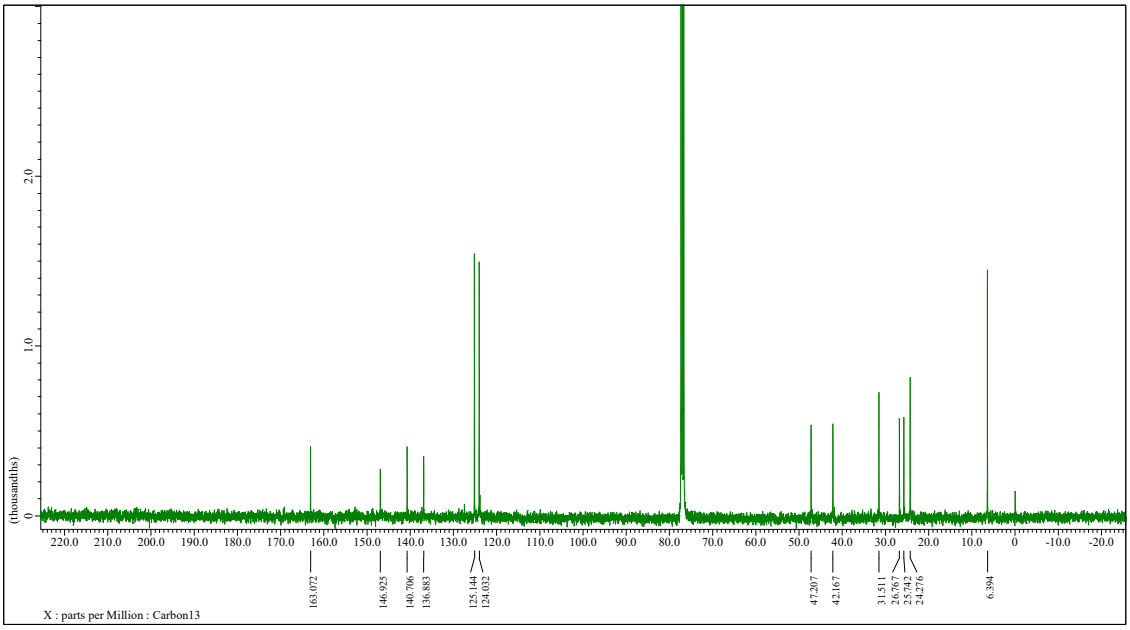


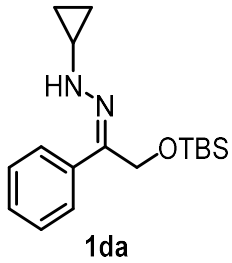
1ca

^{1}H-NMR (400 MHz, $CDCl_3$)



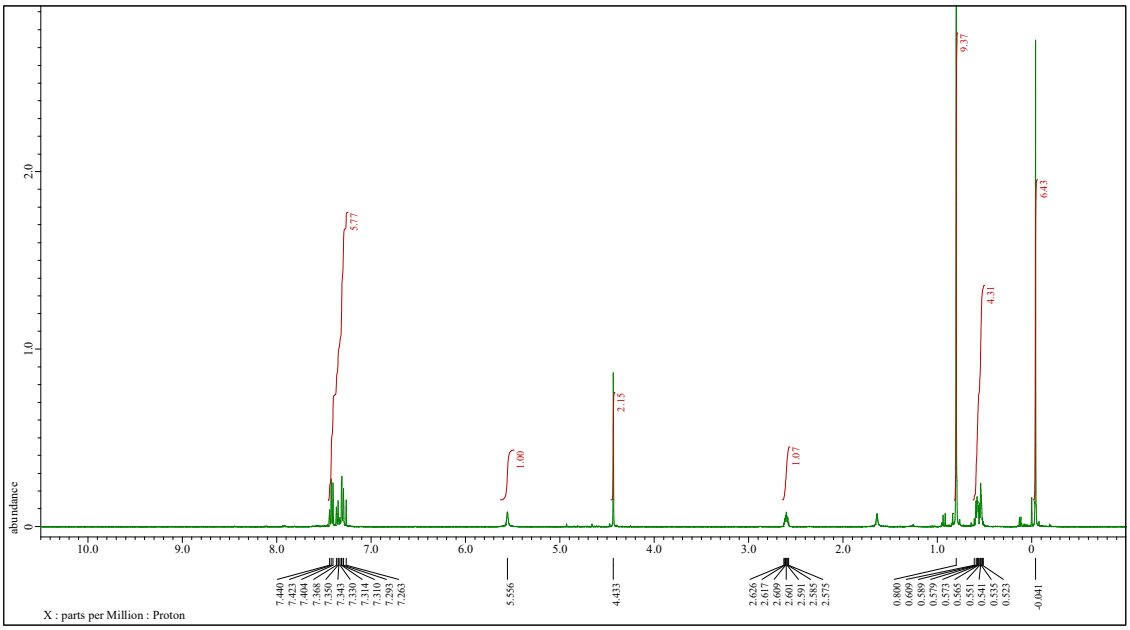
^{13}C-NMR (101 MHz, $CDCl_3$)



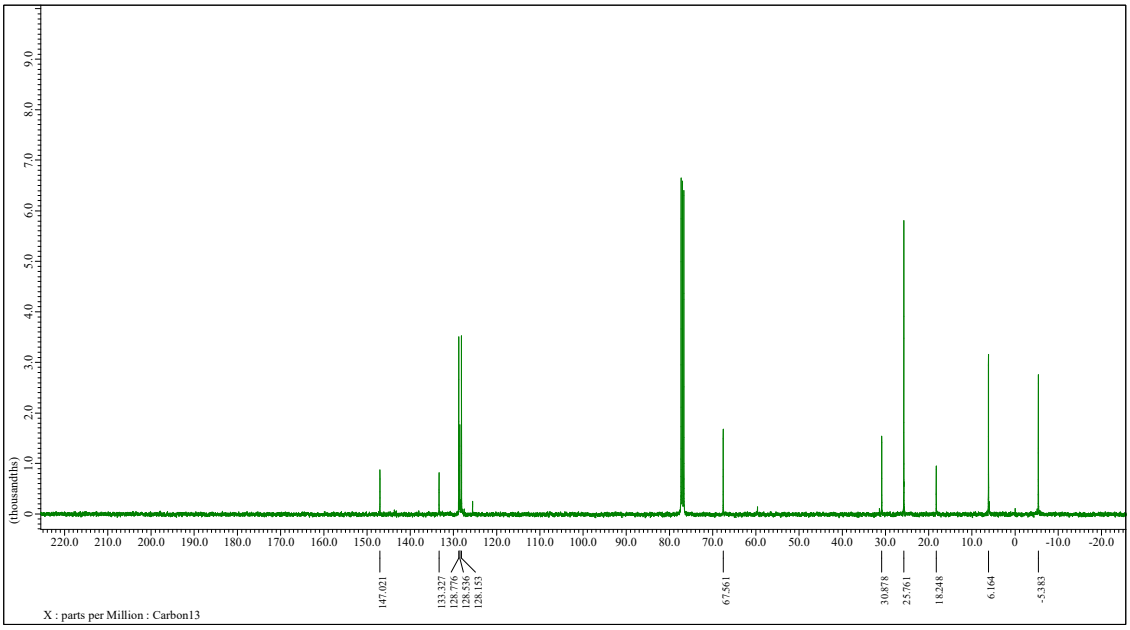


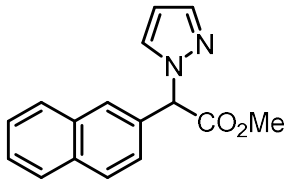
1da

^{1}H-NMR (400 MHz, $CDCl_3$)



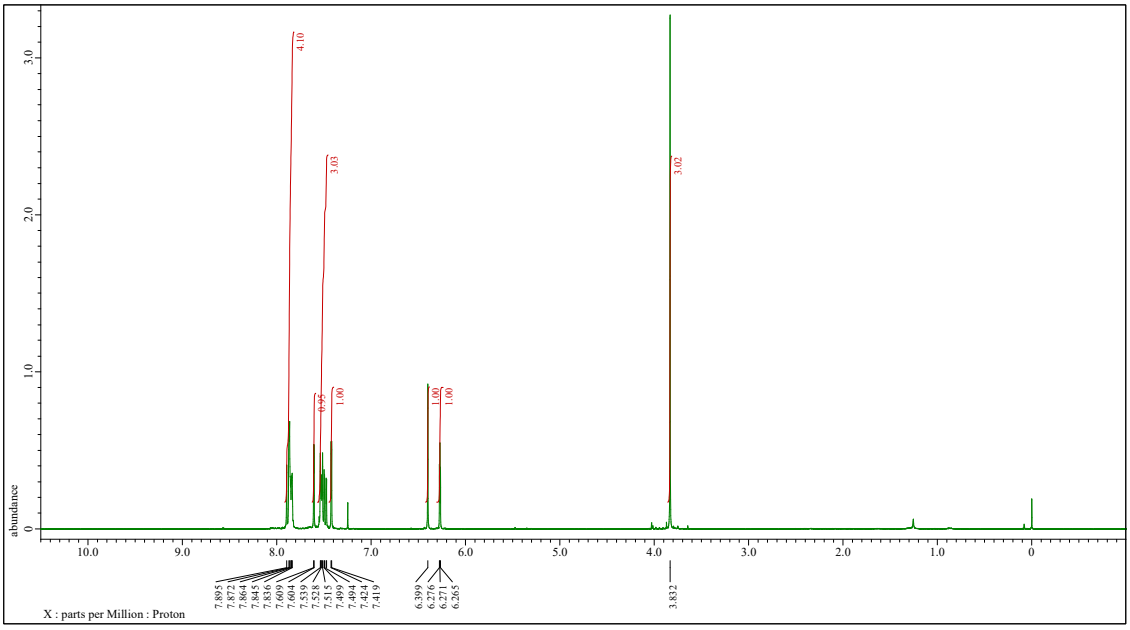
^{13}C-NMR (101 MHz, $CDCl_3$)



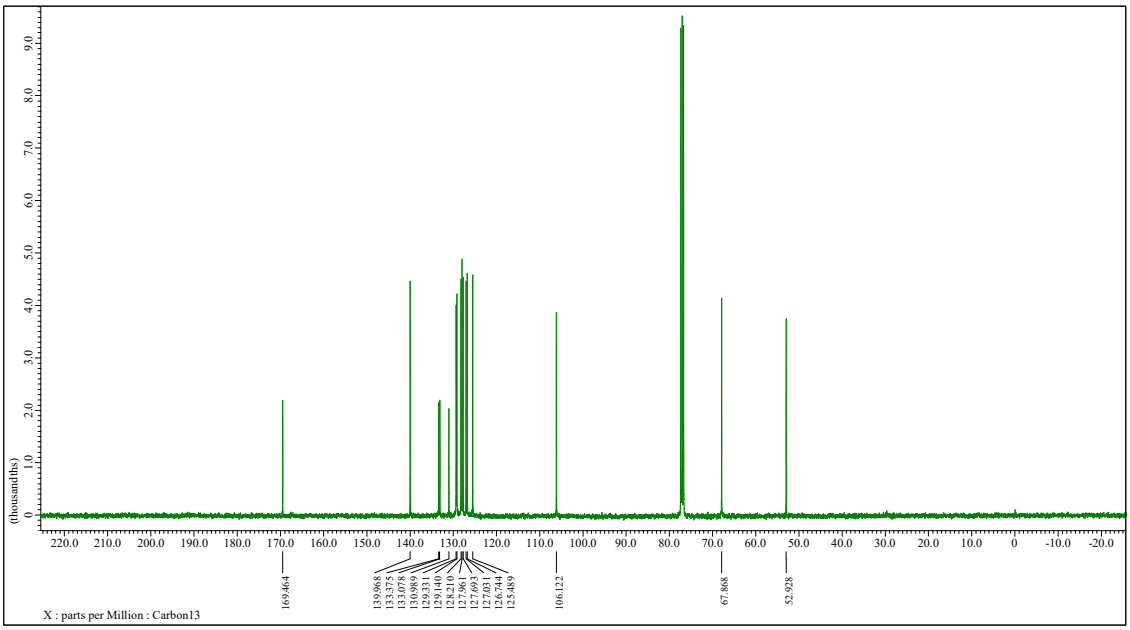


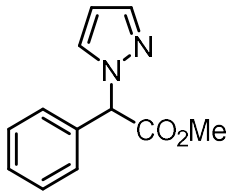
2aa

^{1}H-NMR (400 MHz, $CDCl_3$)



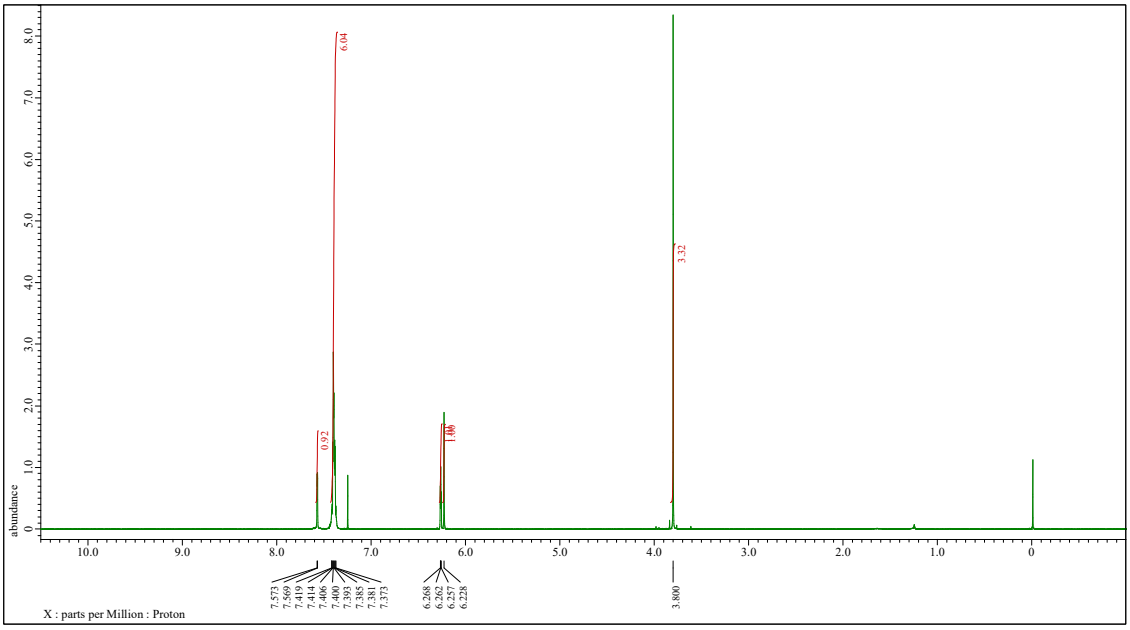
^{13}C-NMR (101 MHz, $CDCl_3$)



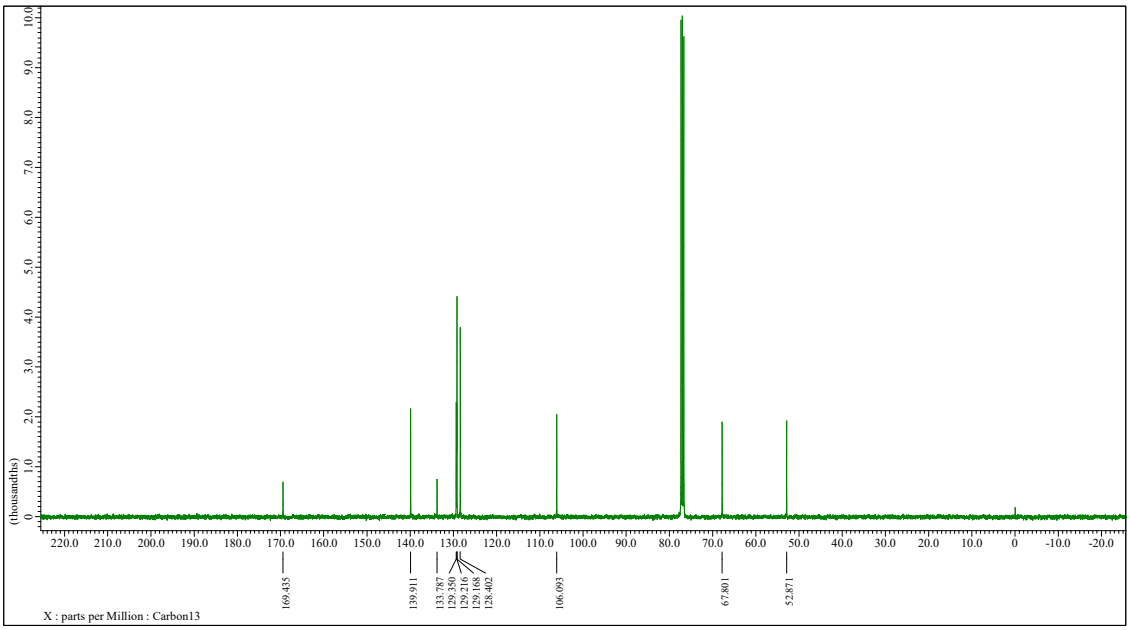


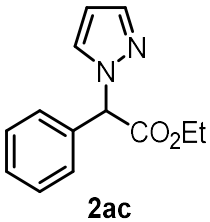
2ab

^{1}H-NMR (400 MHz, $CDCl_3$)



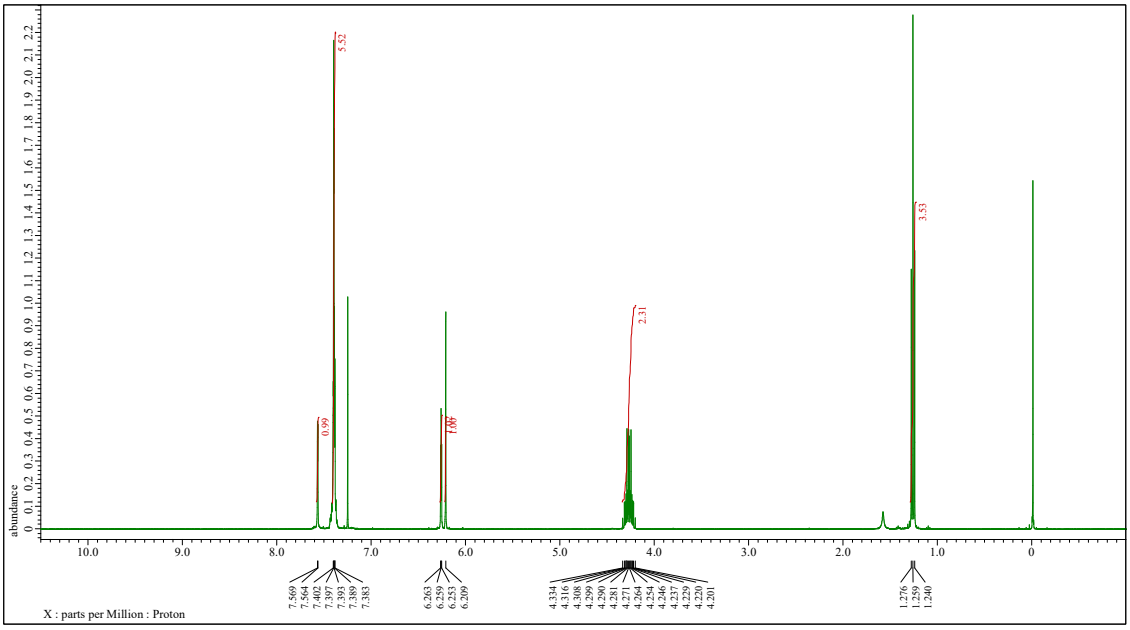
^{13}C-NMR (101 MHz, $CDCl_3$)



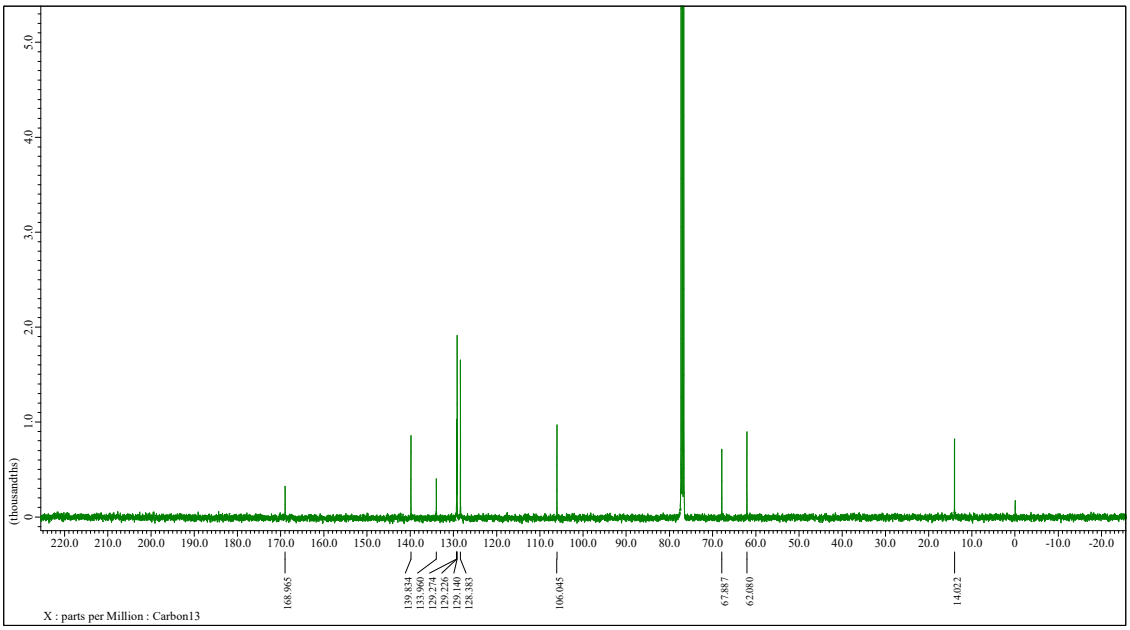


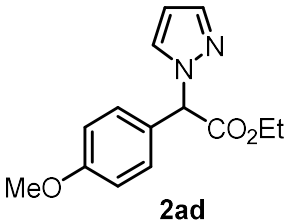
2ac

^{1}H-NMR (400 MHz, $CDCl_3$)



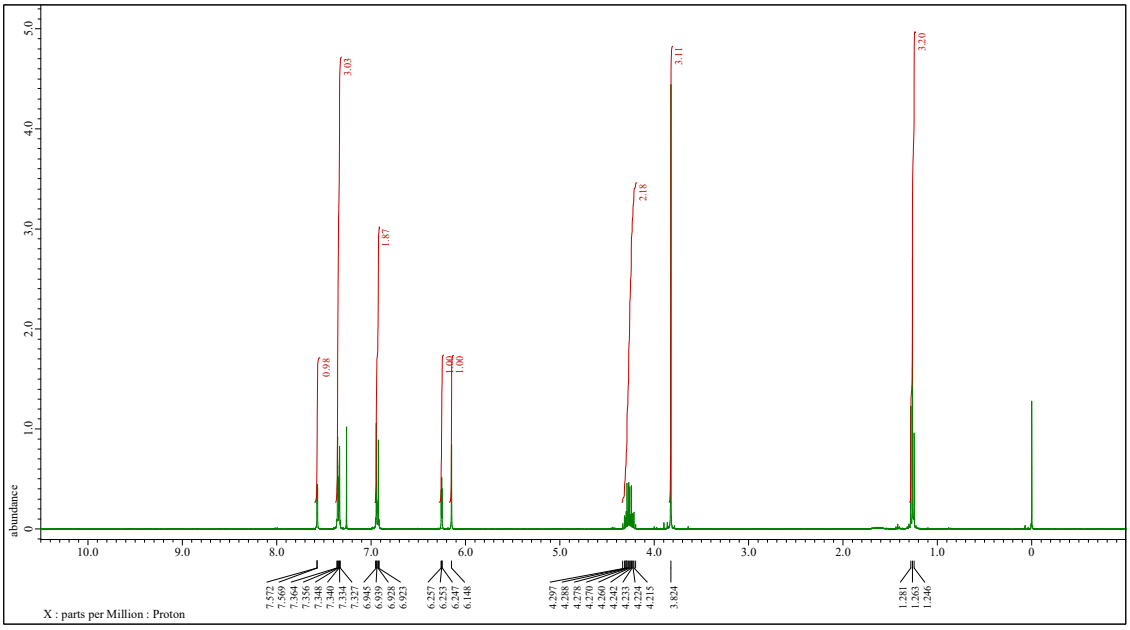
^{13}C-NMR (101 MHz, $CDCl_3$)



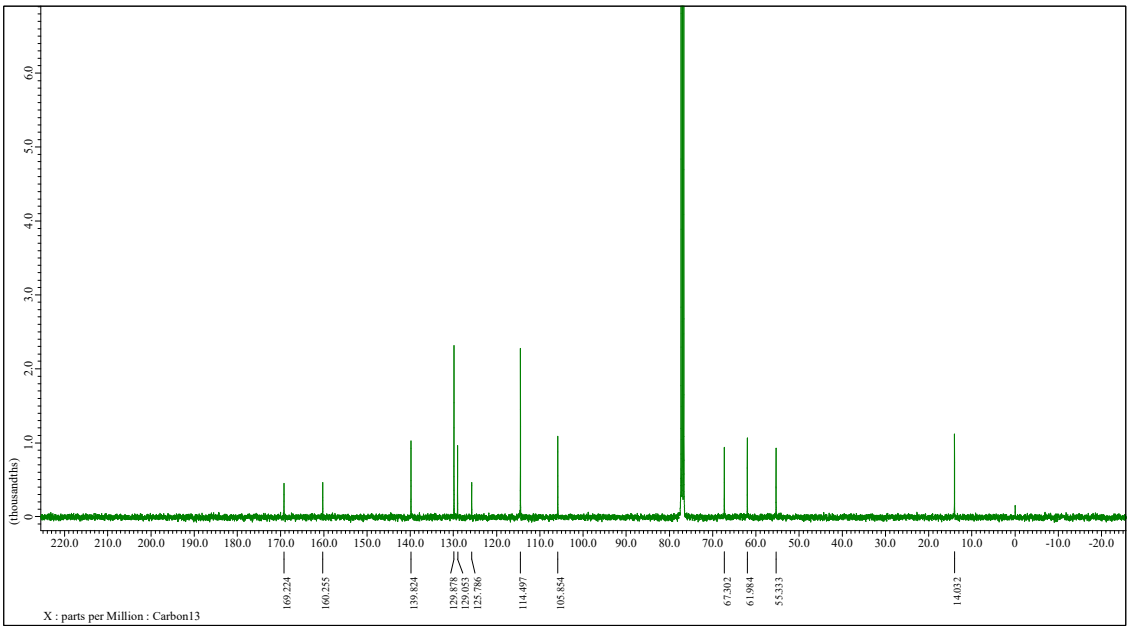


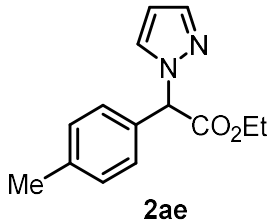
2ad

^{1}H-NMR (400 MHz, $CDCl_3$)



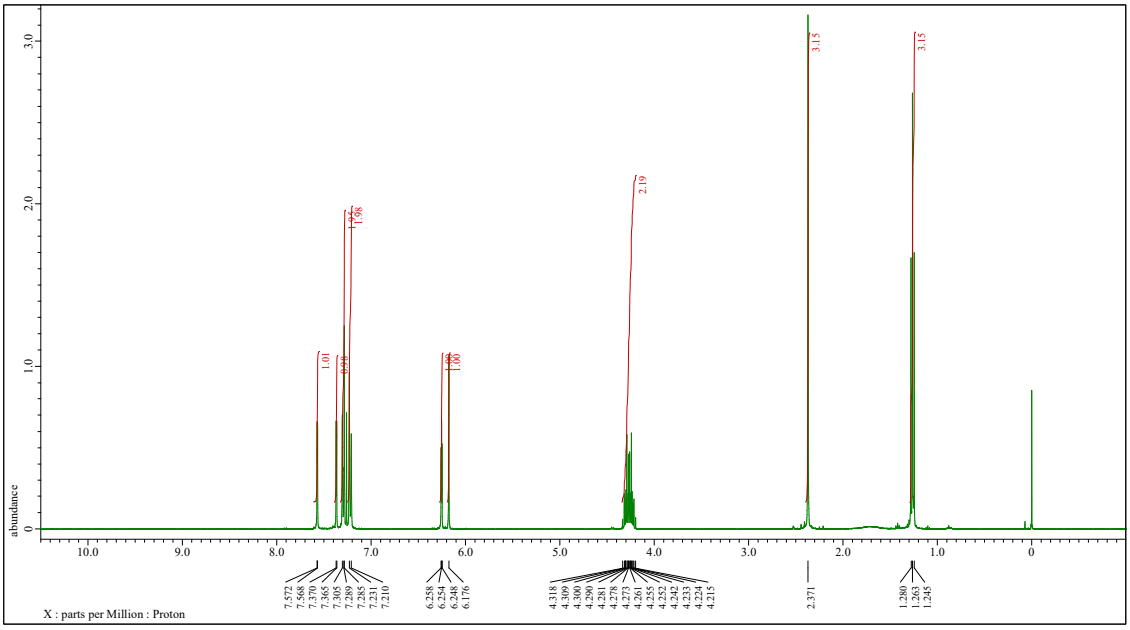
^{13}C-NMR (101 MHz, $CDCl_3$)



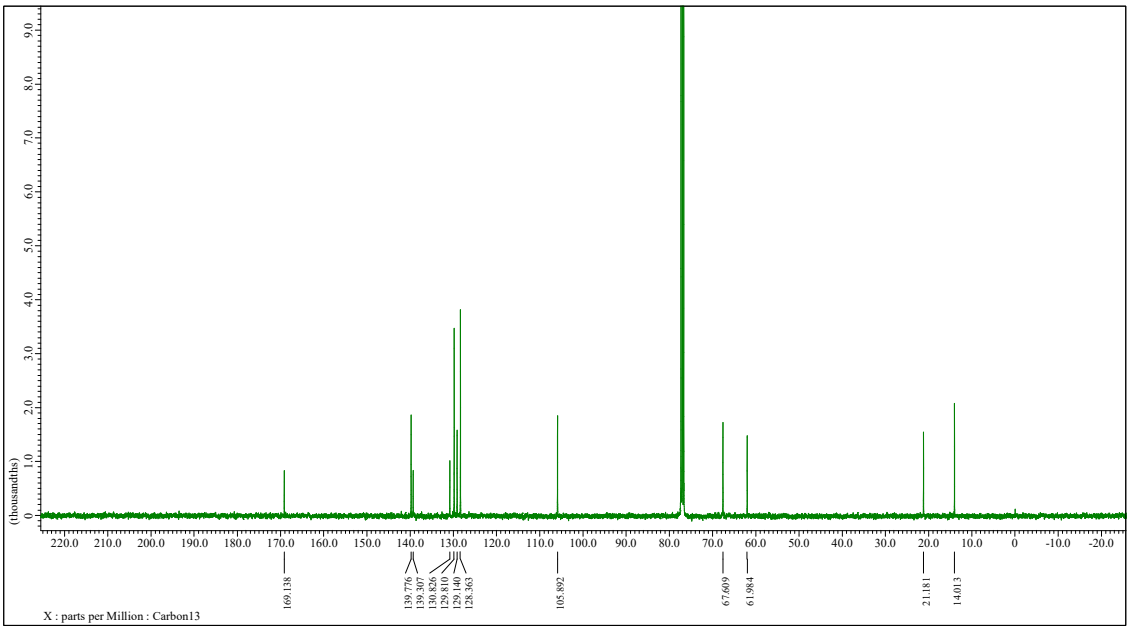


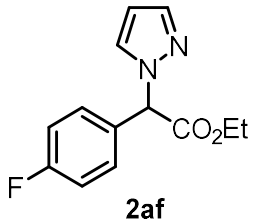
2ae

^{1}H-NMR (400 MHz, $CDCl_3$)



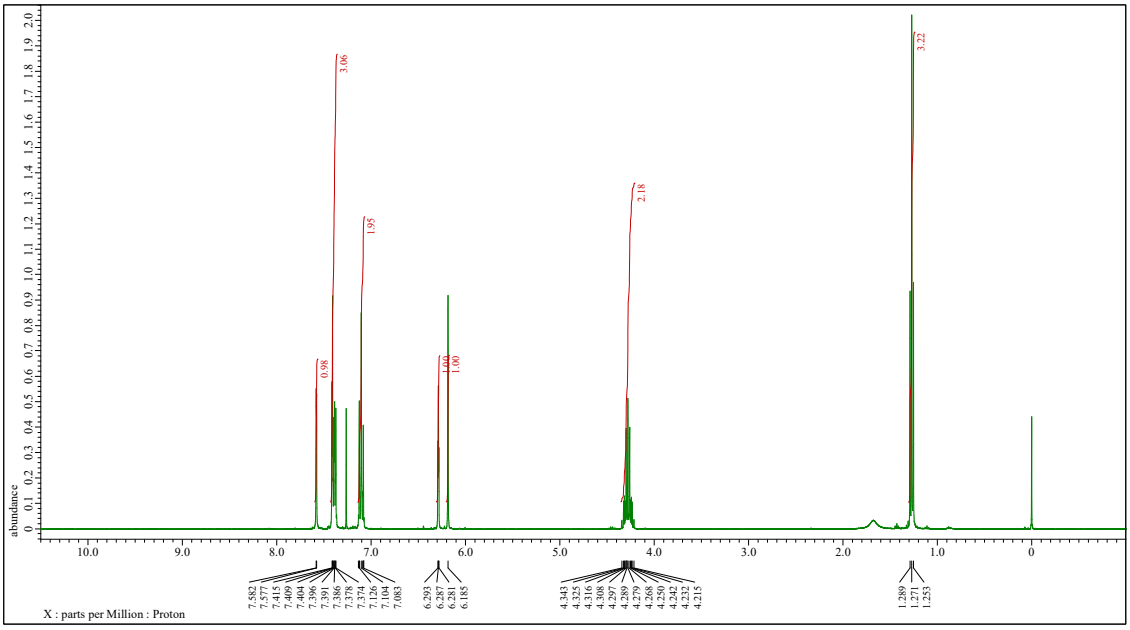
^{13}C-NMR (101 MHz, $CDCl_3$)



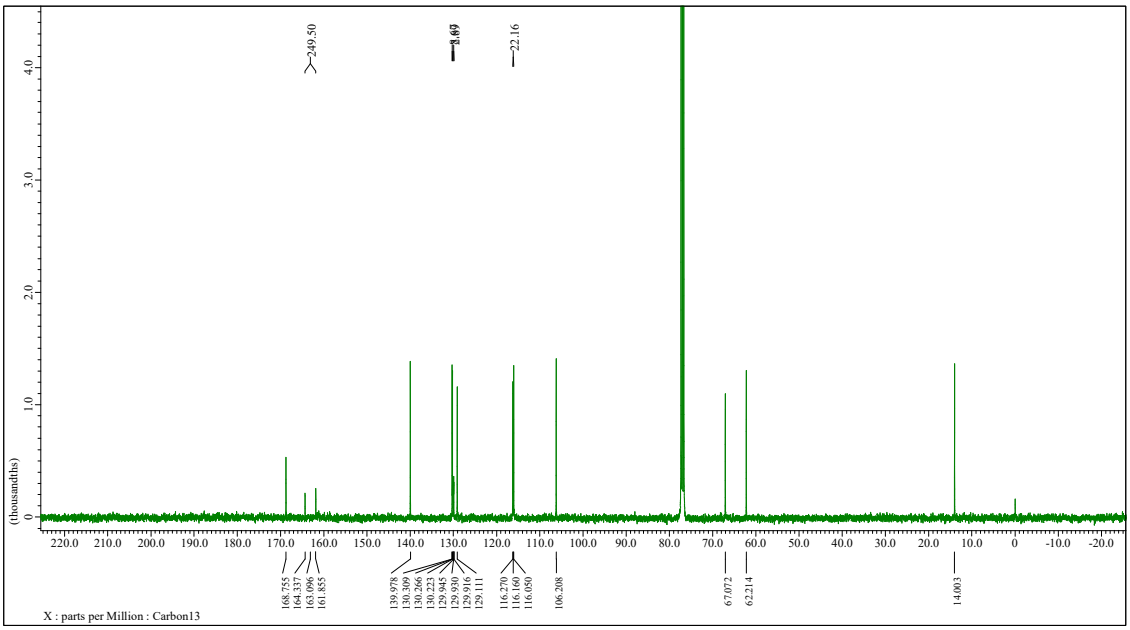


2af

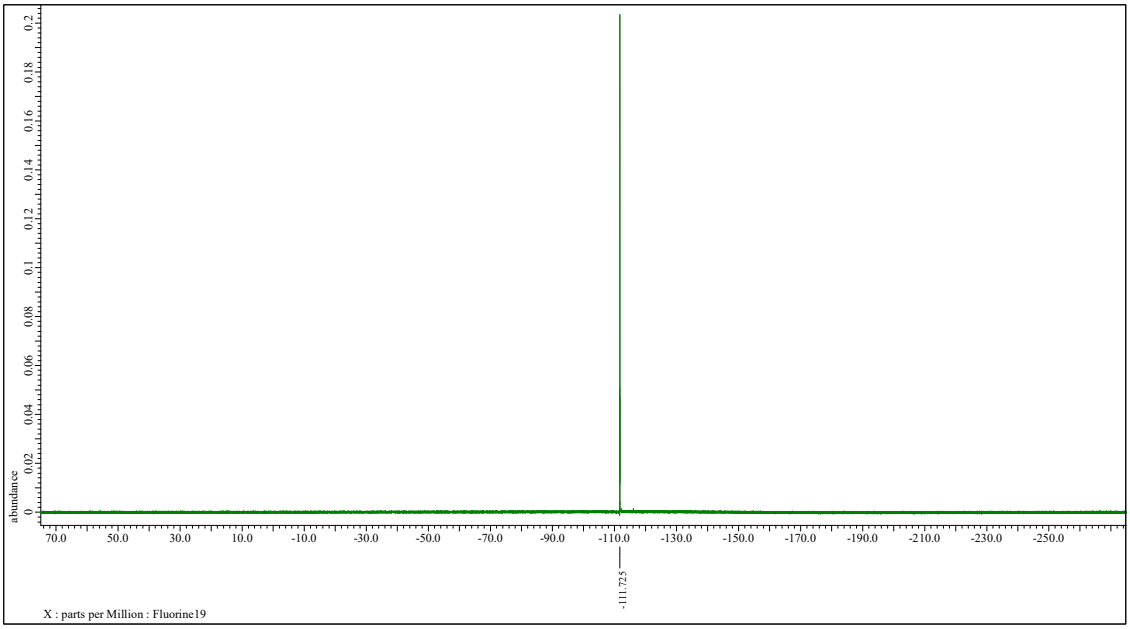
^{1}H-NMR (400 MHz, $CDCl_3$)

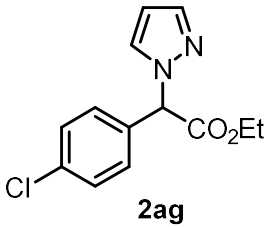


^{13}C-NMR (101 MHz, $CDCl_3$)



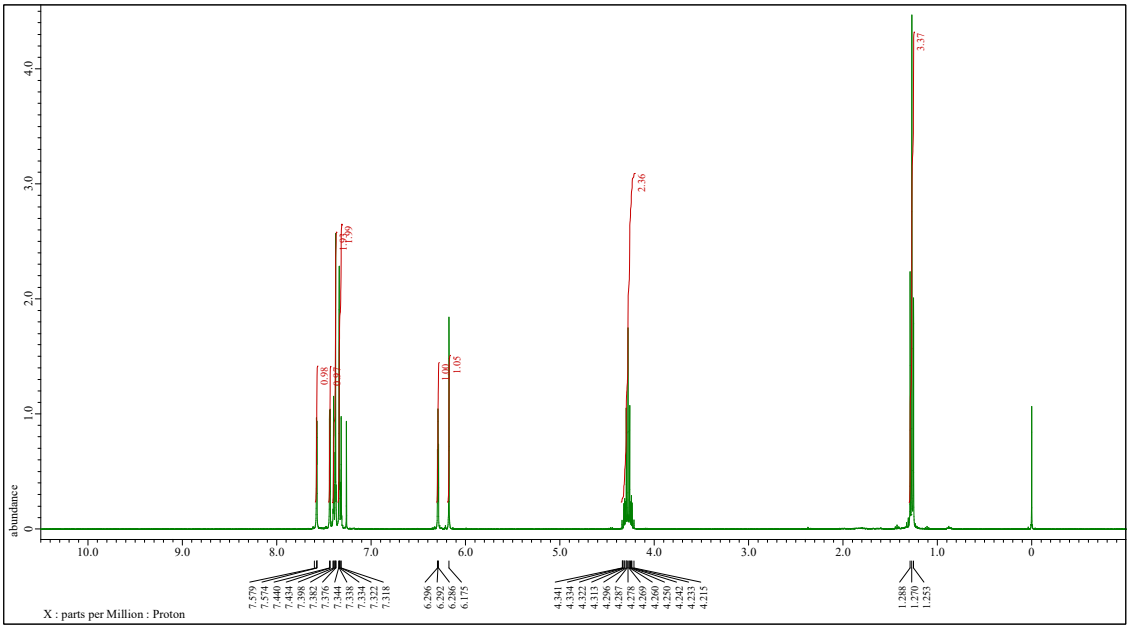
^{19}F-NMR (376 MHz, $CDCl_3$)



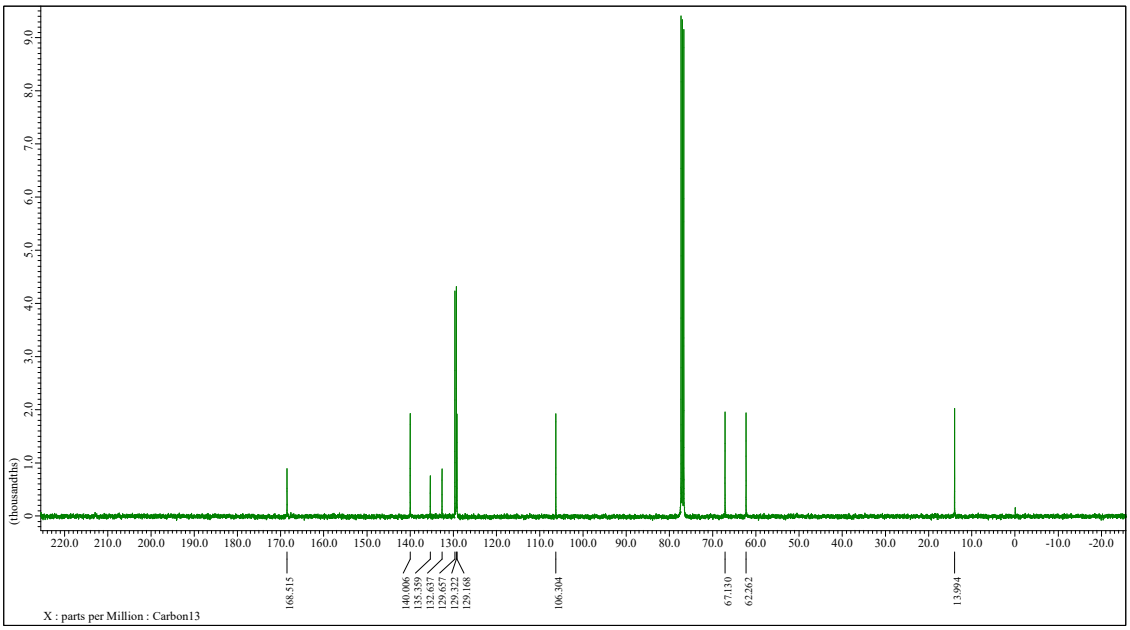


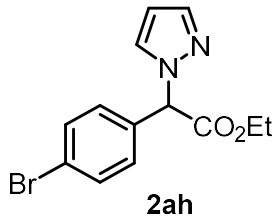
2ag

^{1}H-NMR (400 MHz, $CDCl_3$)



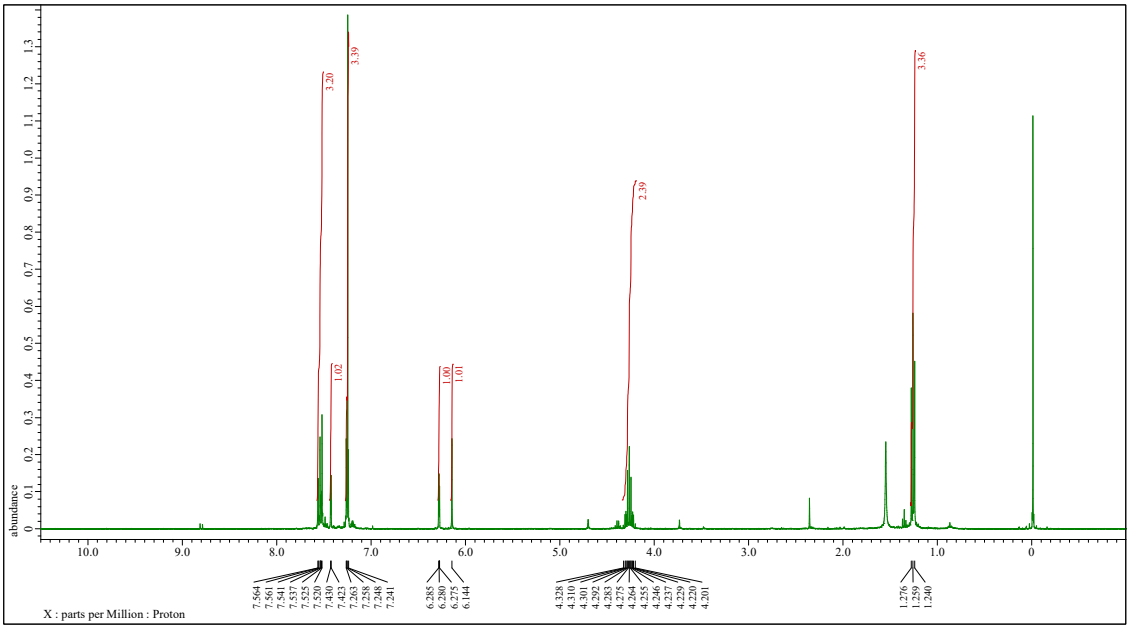
^{13}C-NMR (101 MHz, $CDCl_3$)



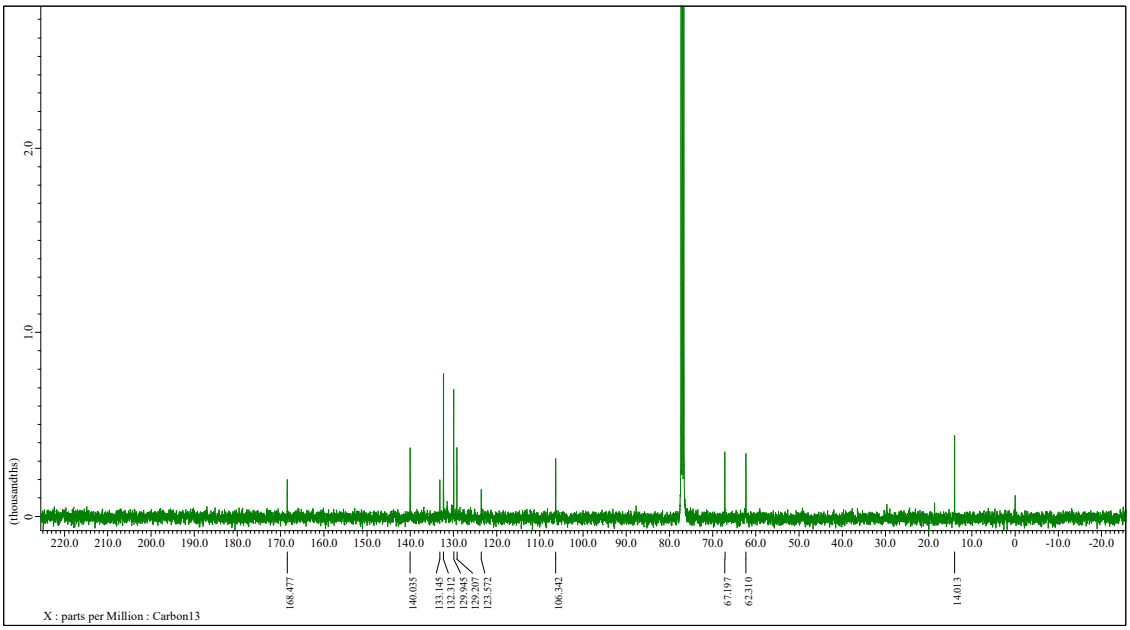


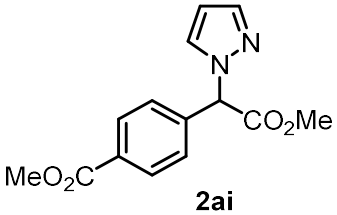
2ah

^{1}H-NMR (400 MHz, $CDCl_3$)



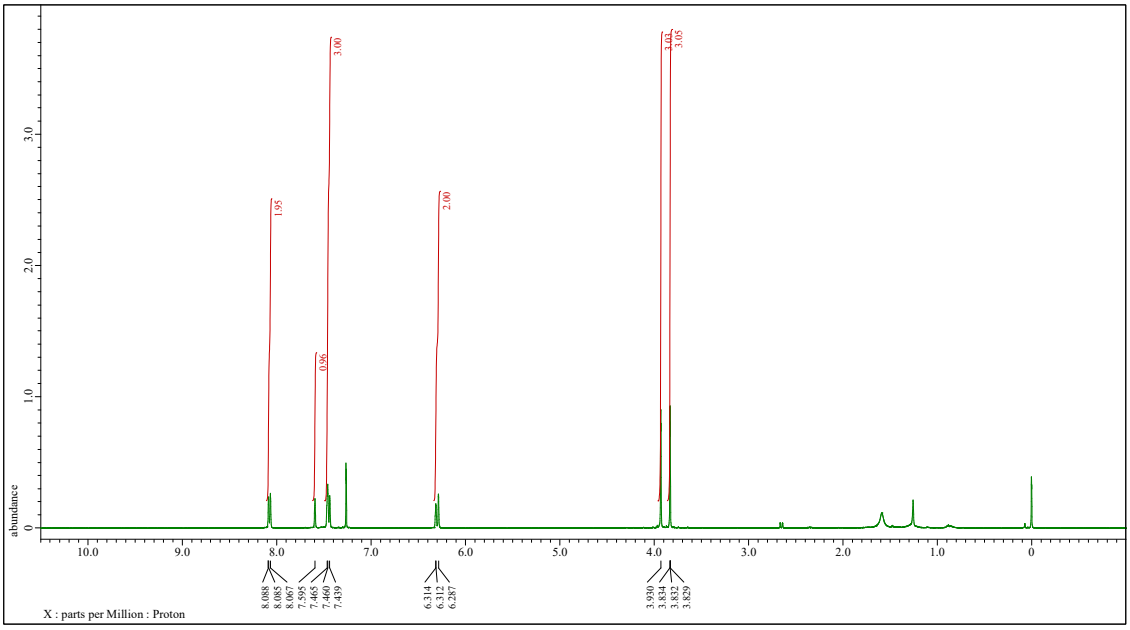
^{13}C-NMR (101 MHz, $CDCl_3$)



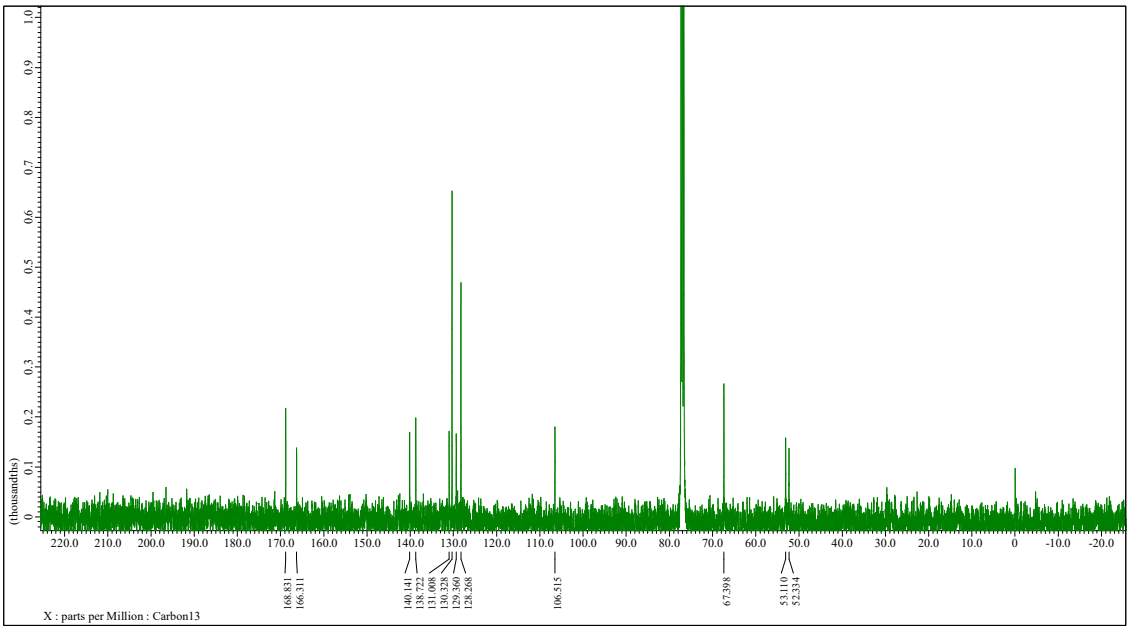


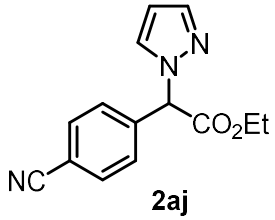
2ai

^{1}H-NMR (400 MHz, $CDCl_3$)



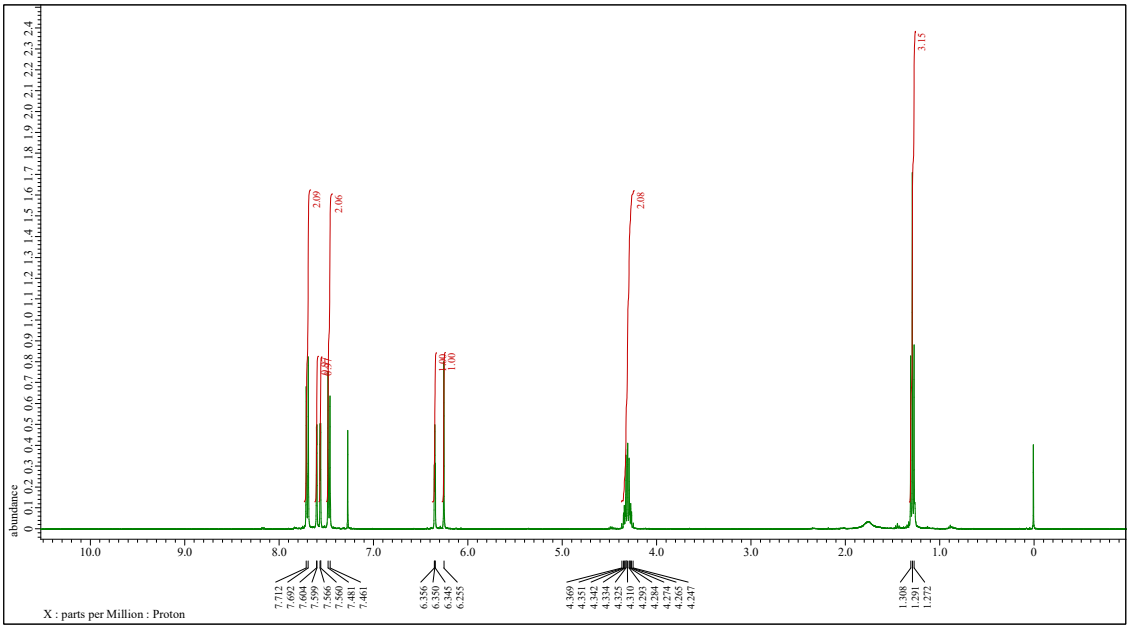
^{13}C-NMR (101 MHz, $CDCl_3$)



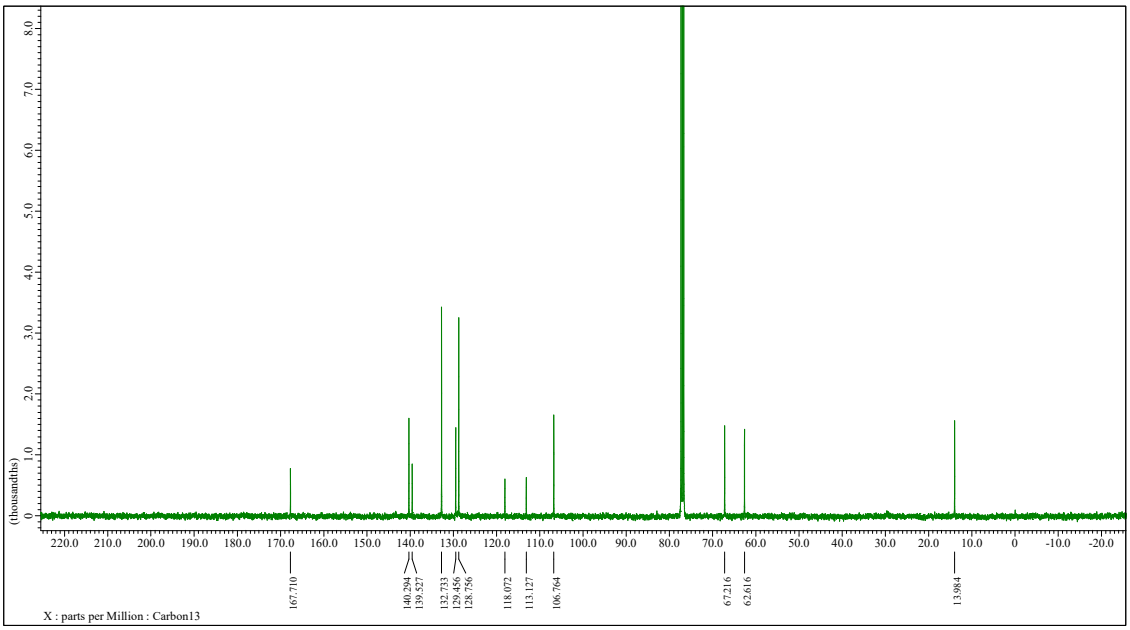


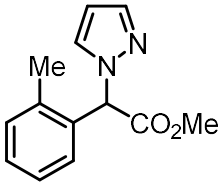
2aj

^{1}H-NMR (400 MHz, $CDCl_3$)



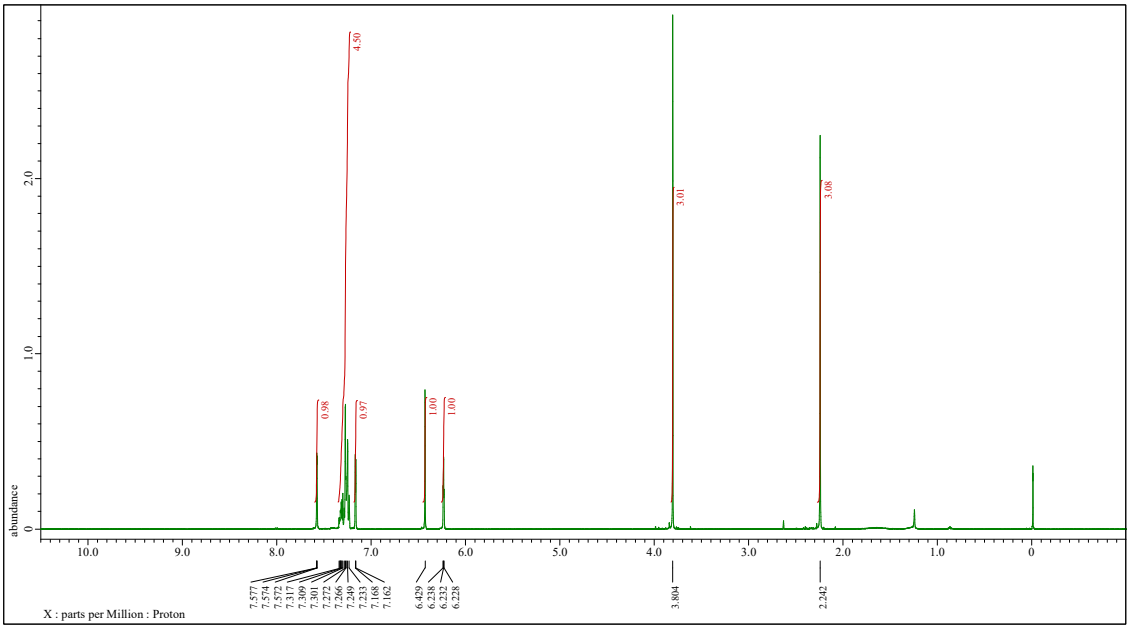
^{13}C-NMR (101 MHz, $CDCl_3$)



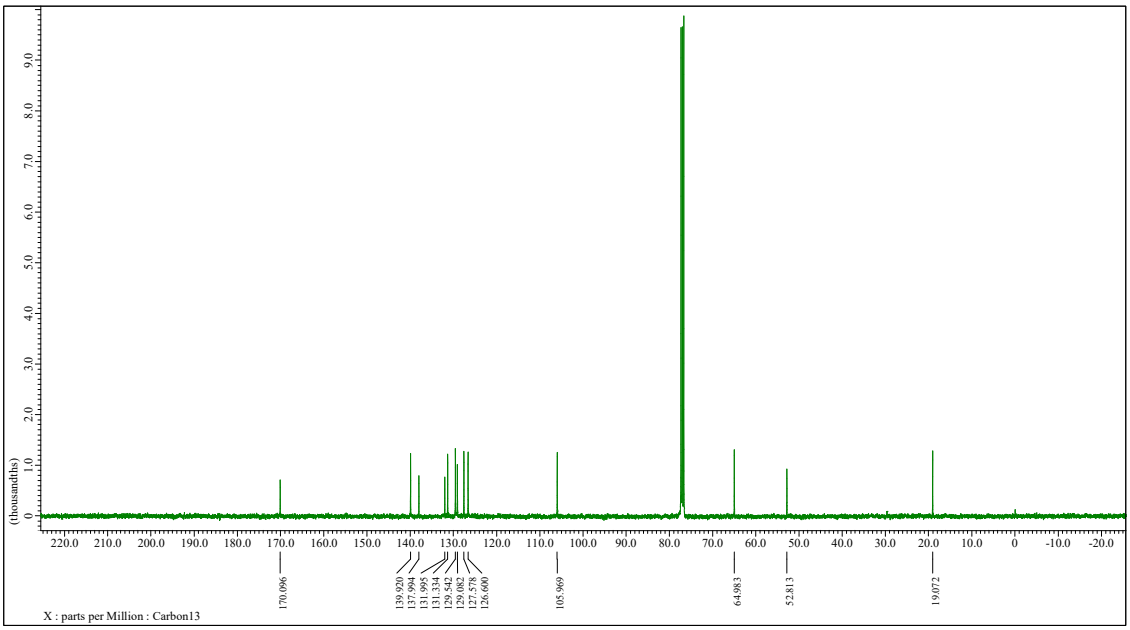


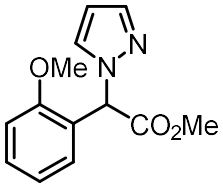
2ak

^{1}H-NMR (400 MHz, $CDCl_3$)



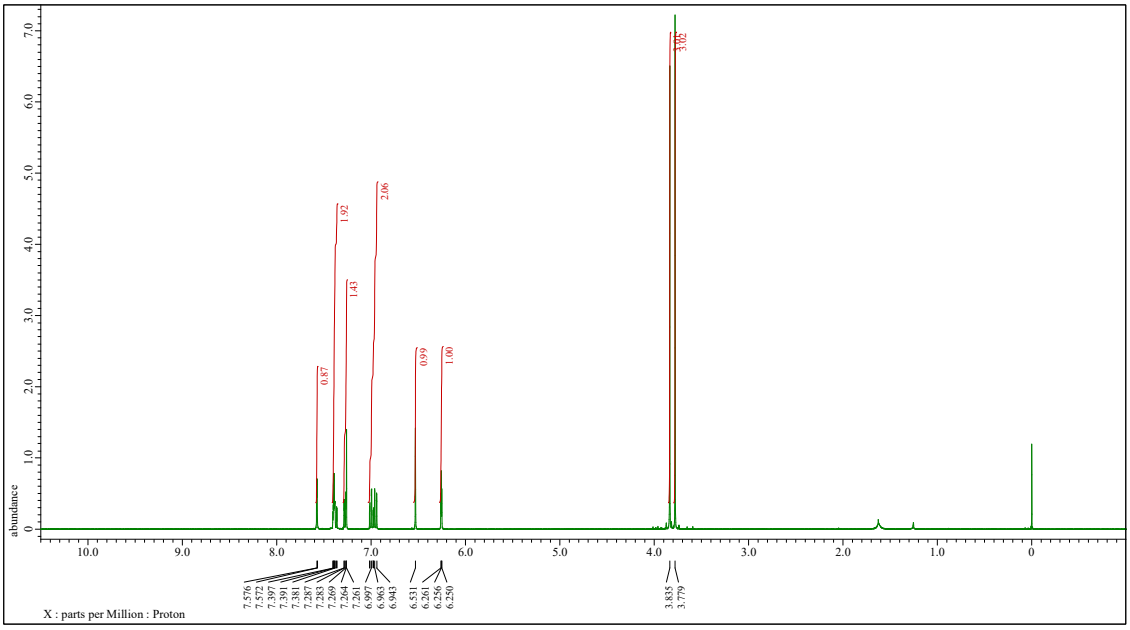
^{13}C-NMR (101 MHz, $CDCl_3$)



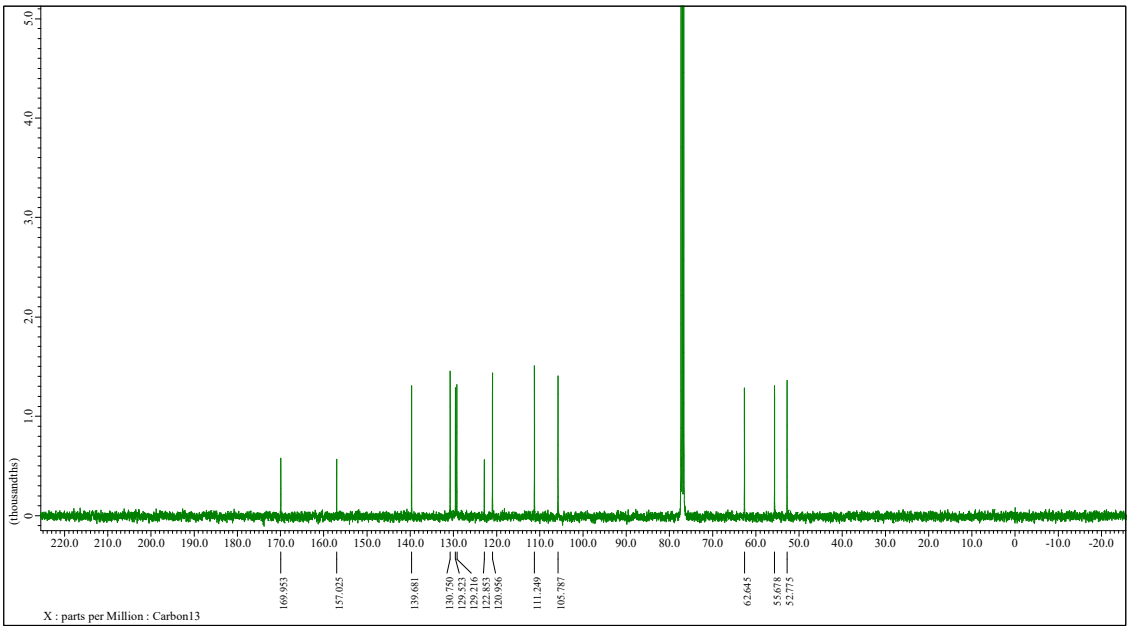


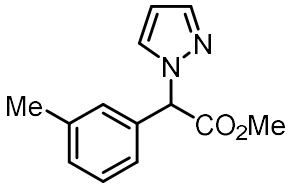
2al

^{1}H-NMR (400 MHz, $CDCl_3$)



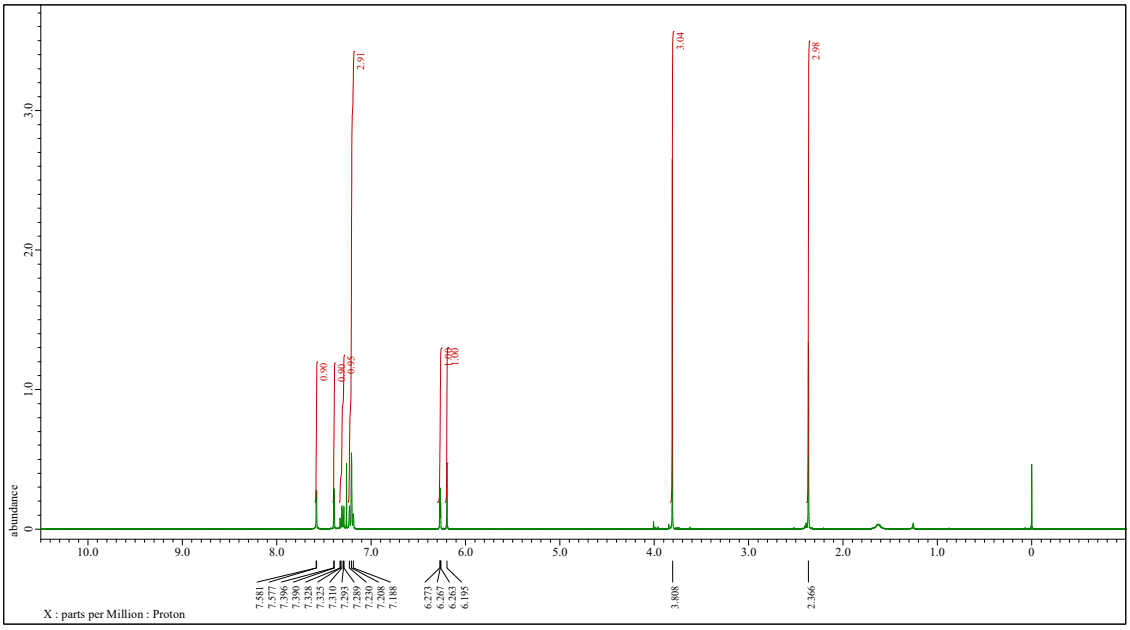
^{13}C-NMR (101 MHz, $CDCl_3$)



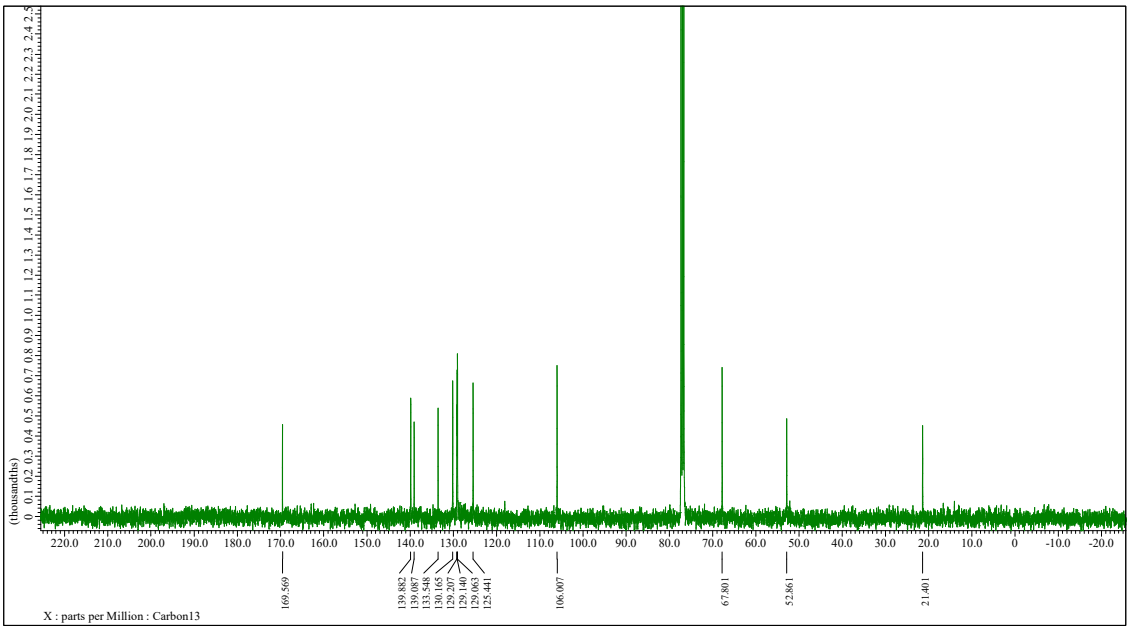


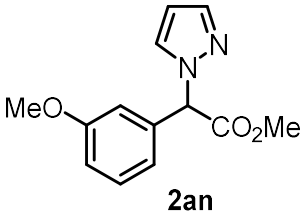
2am

^{1}H-NMR (400 MHz, $CDCl_3$)



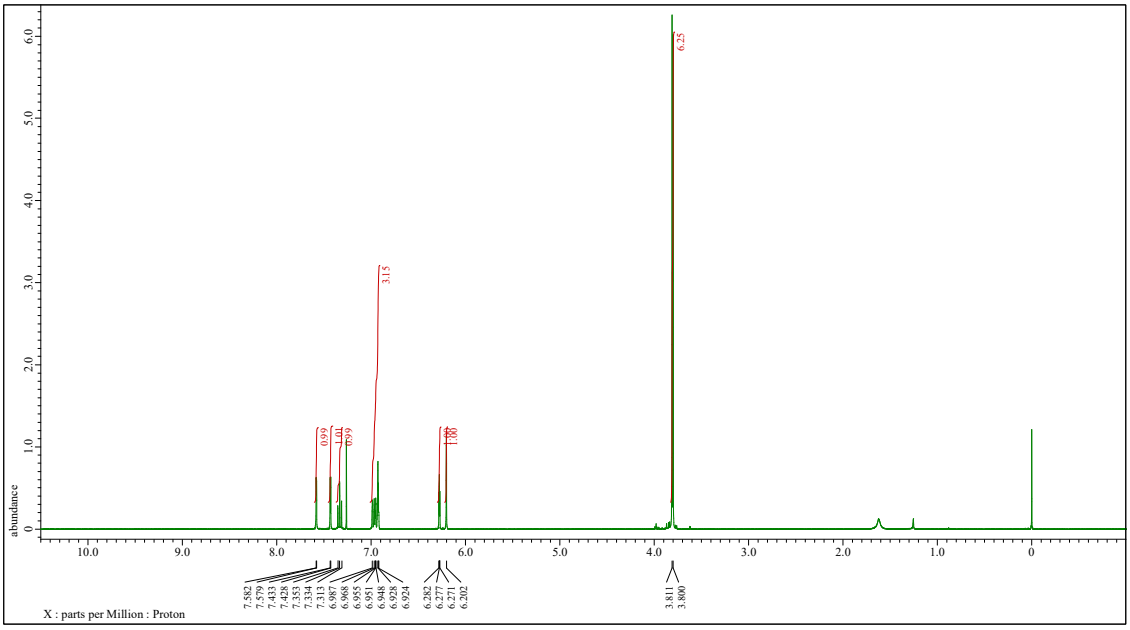
^{13}C-NMR (101 MHz, $CDCl_3$)



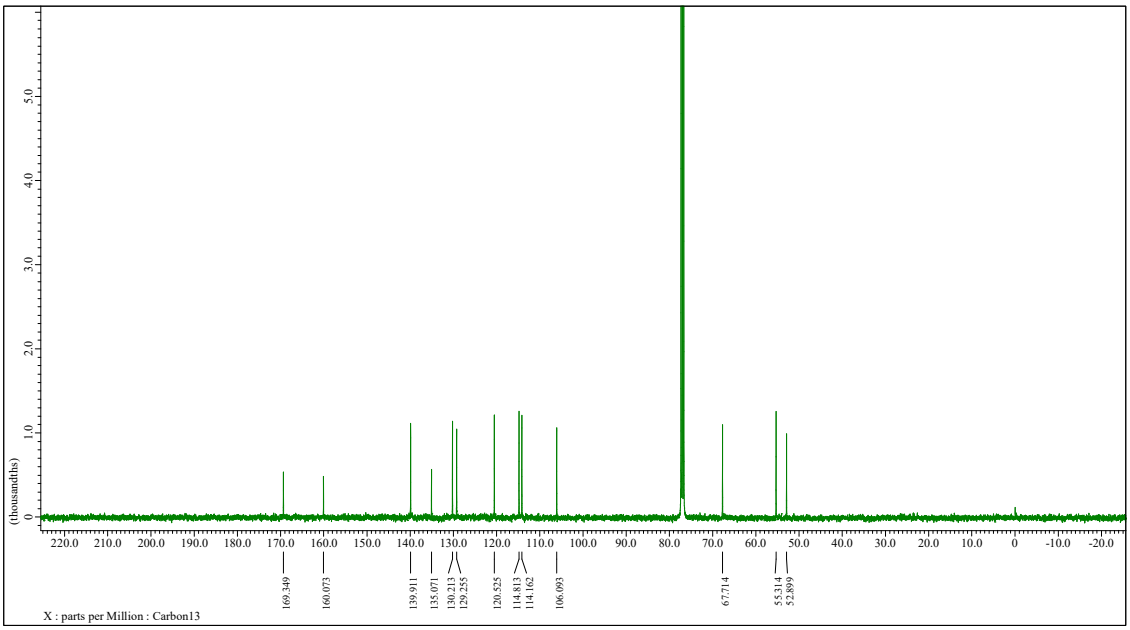


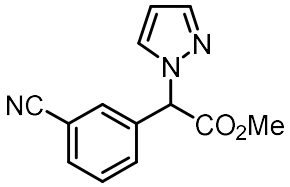
2an

^{1}H-NMR (400 MHz, $CDCl_3$)



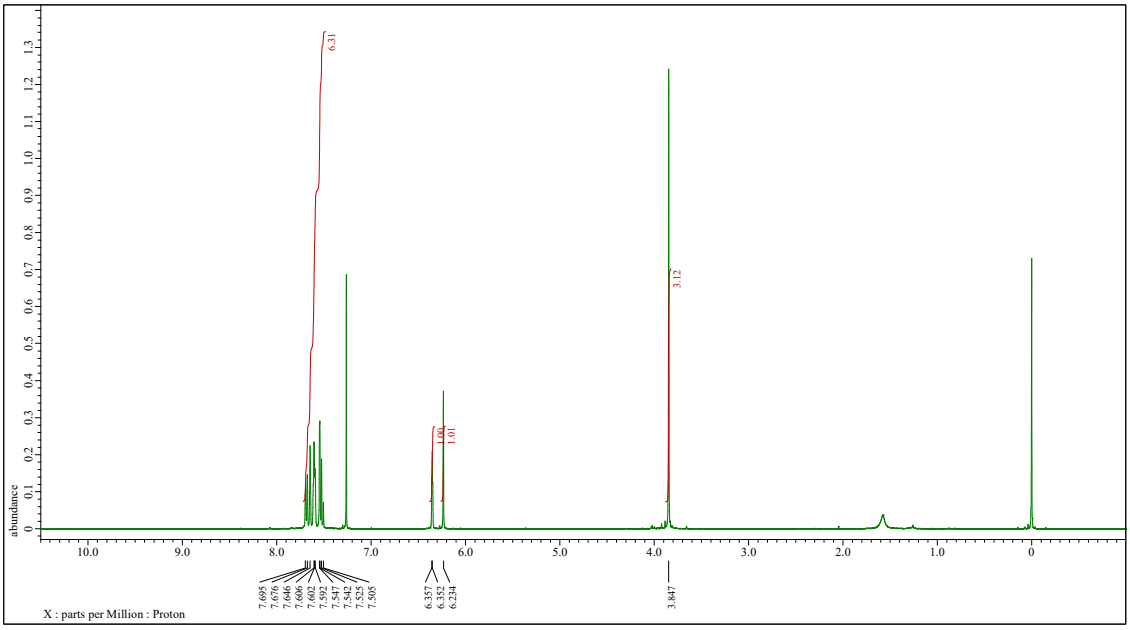
^{13}C-NMR (101 MHz, $CDCl_3$)



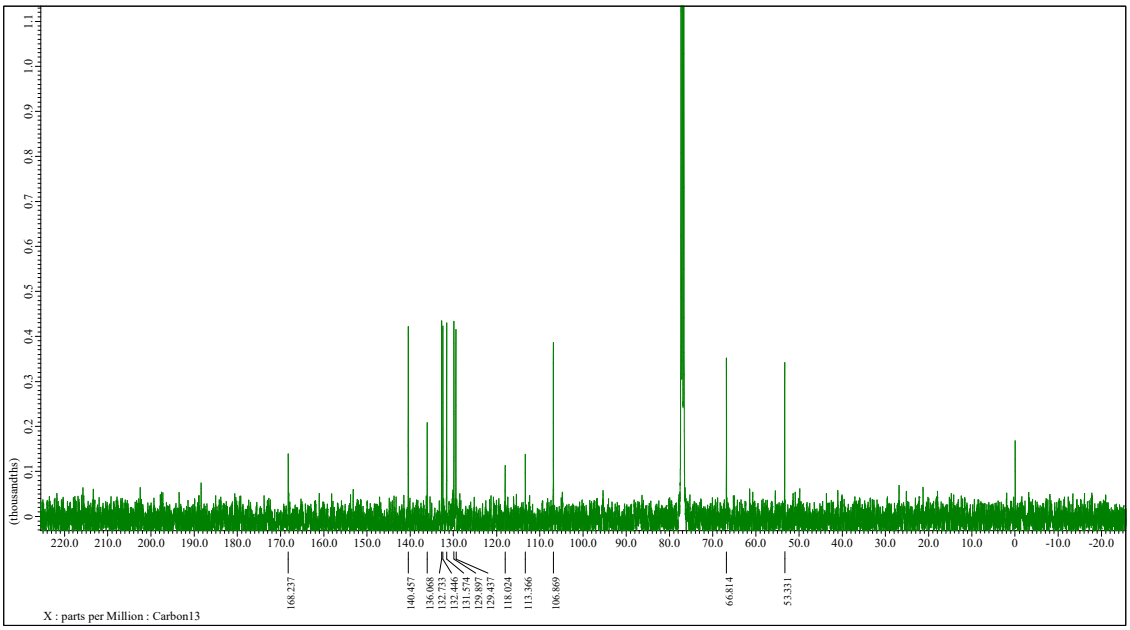


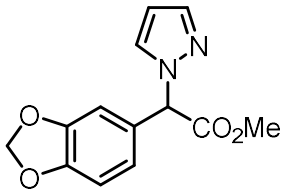
2ao

^{1}H-NMR (400 MHz, $CDCl_3$)



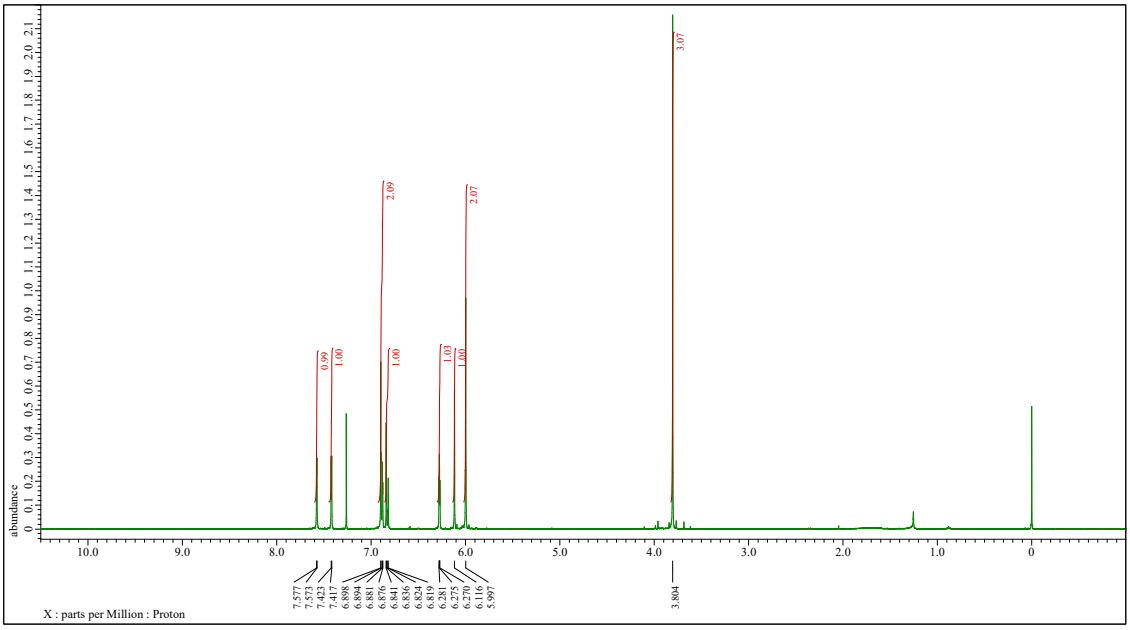
^{13}C-NMR (101 MHz, $CDCl_3$)



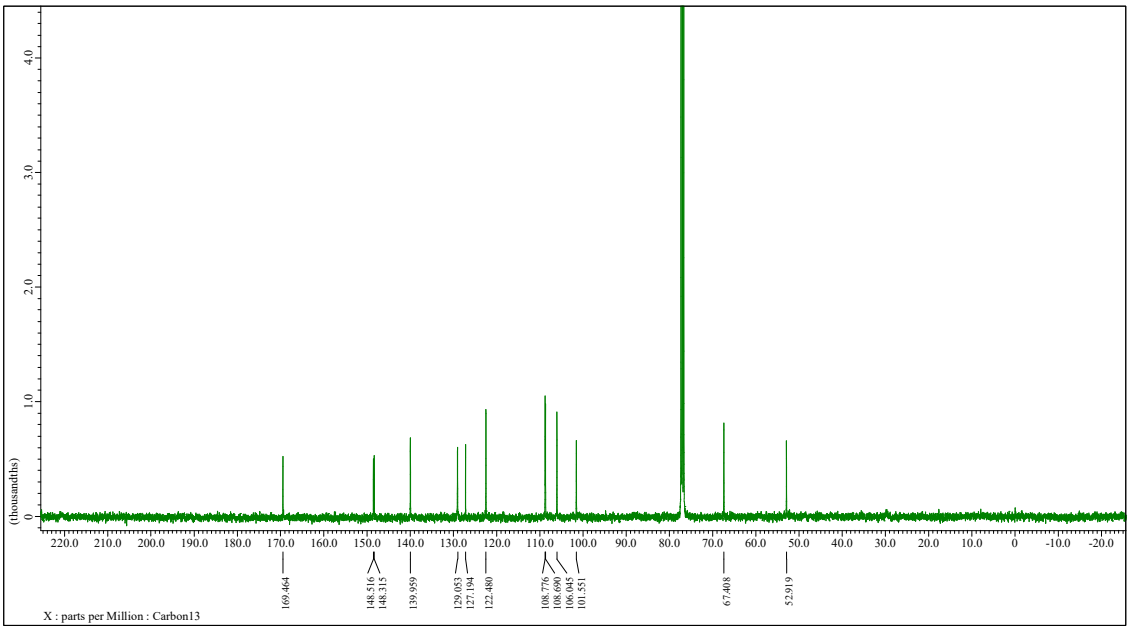


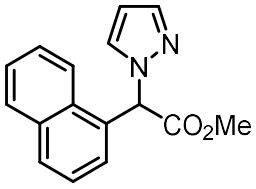
2ap

^{1}H-NMR (400 MHz, $CDCl_3$)



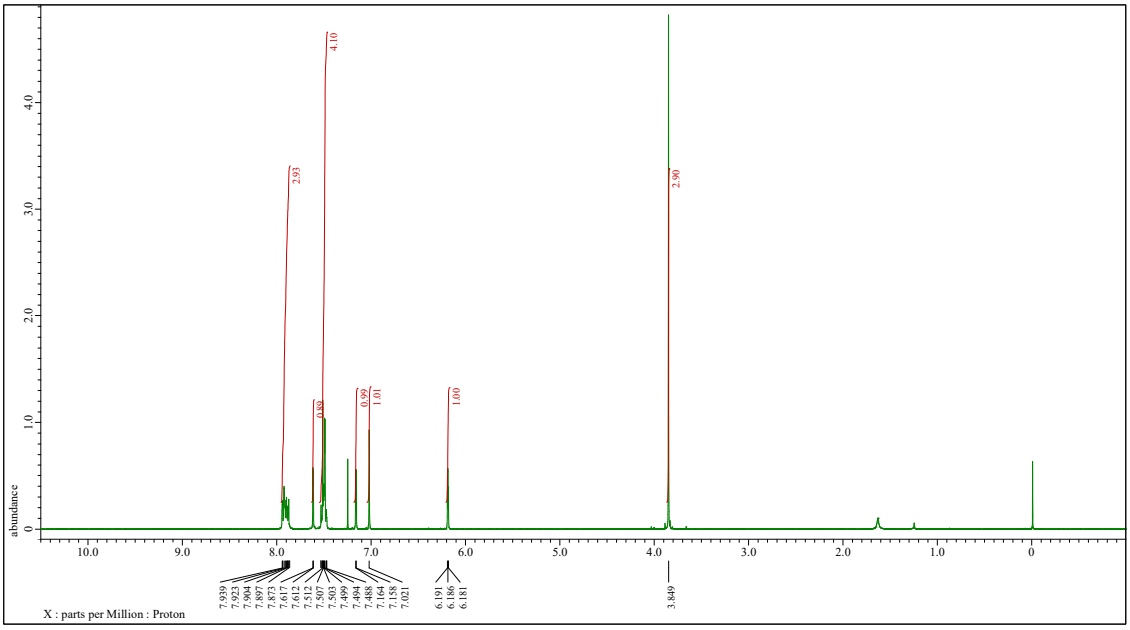
^{13}C-NMR (101 MHz, $CDCl_3$)



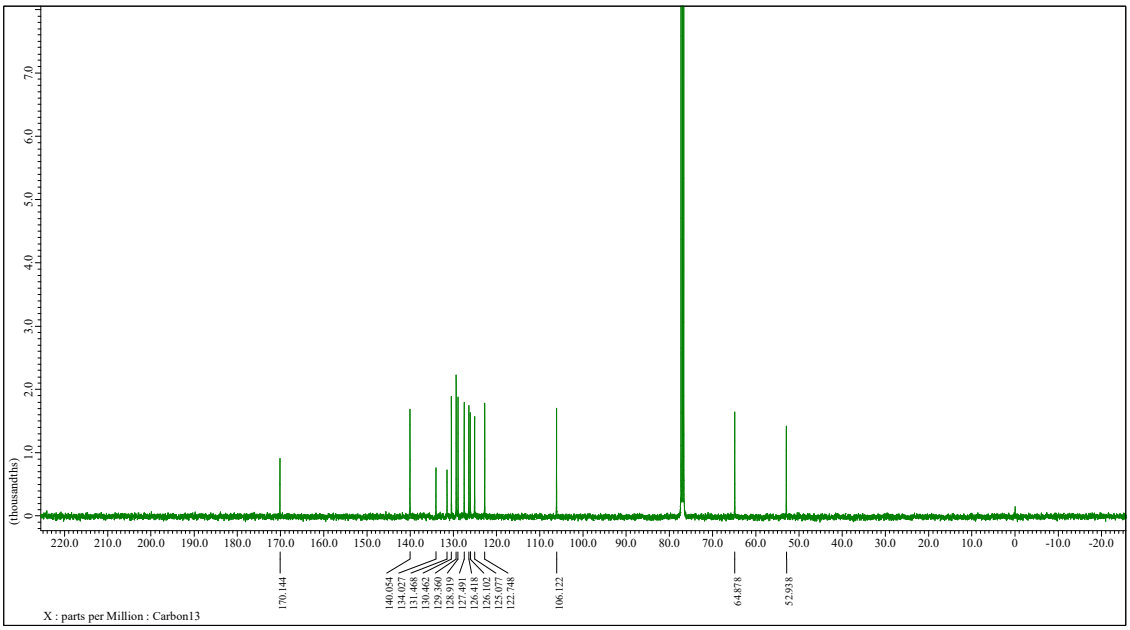


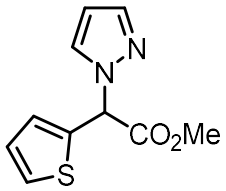
2aq

^{1}H-NMR (400 MHz, $CDCl_3$)



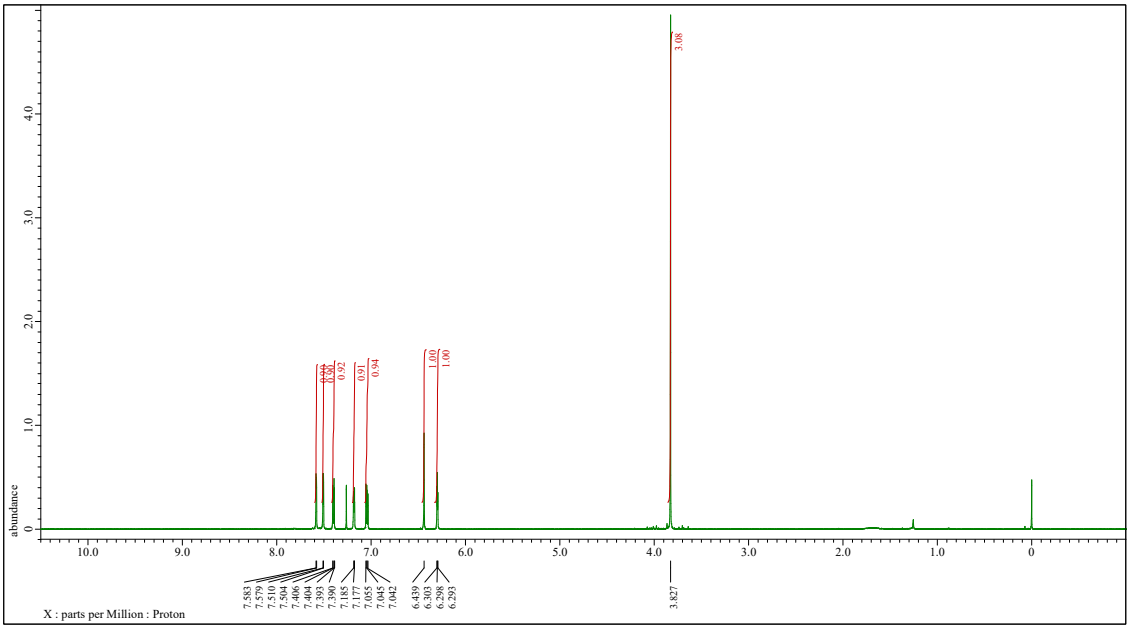
^{13}C-NMR (101 MHz, $CDCl_3$)



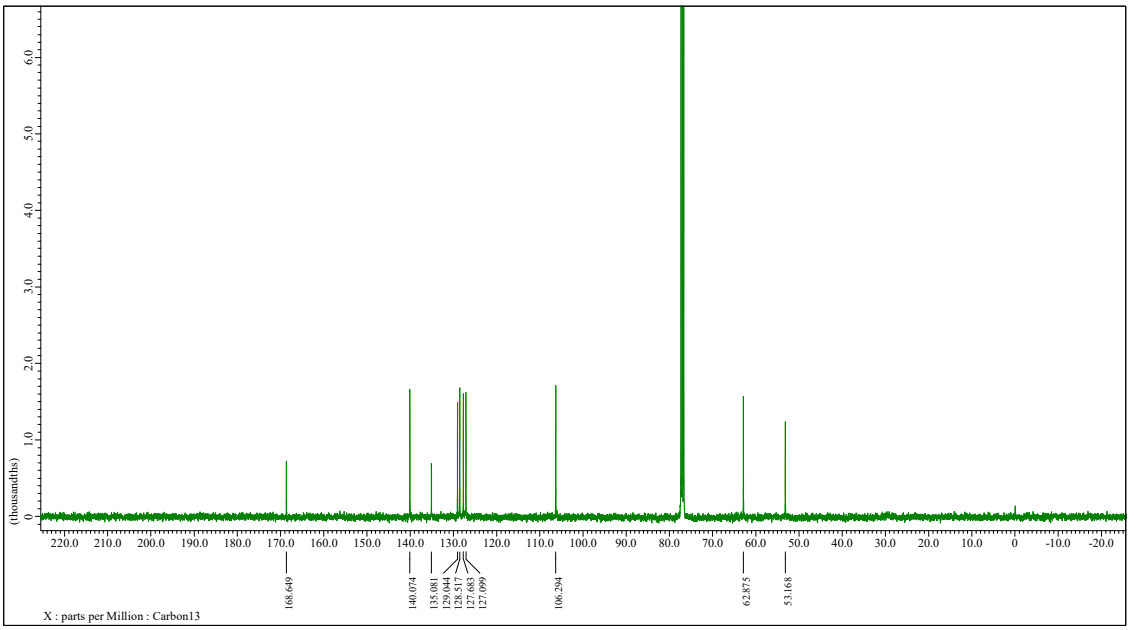


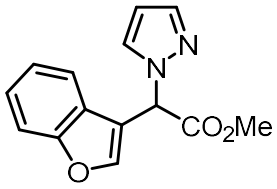
2ar

^{1}H-NMR (400 MHz, $CDCl_3$)



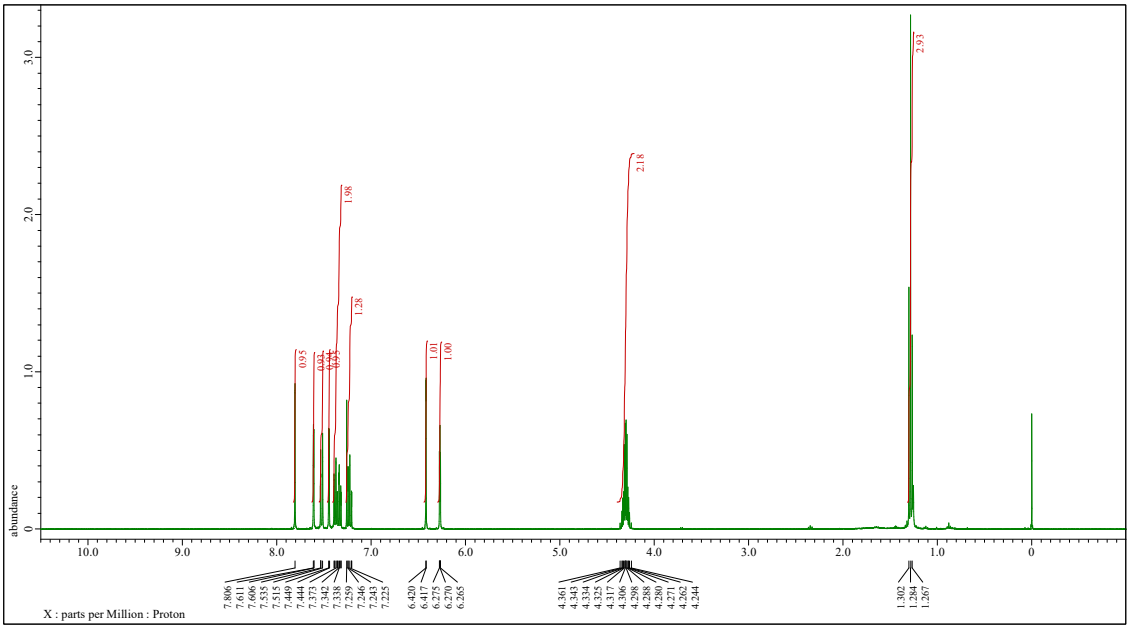
^{13}C-NMR (101 MHz, $CDCl_3$)



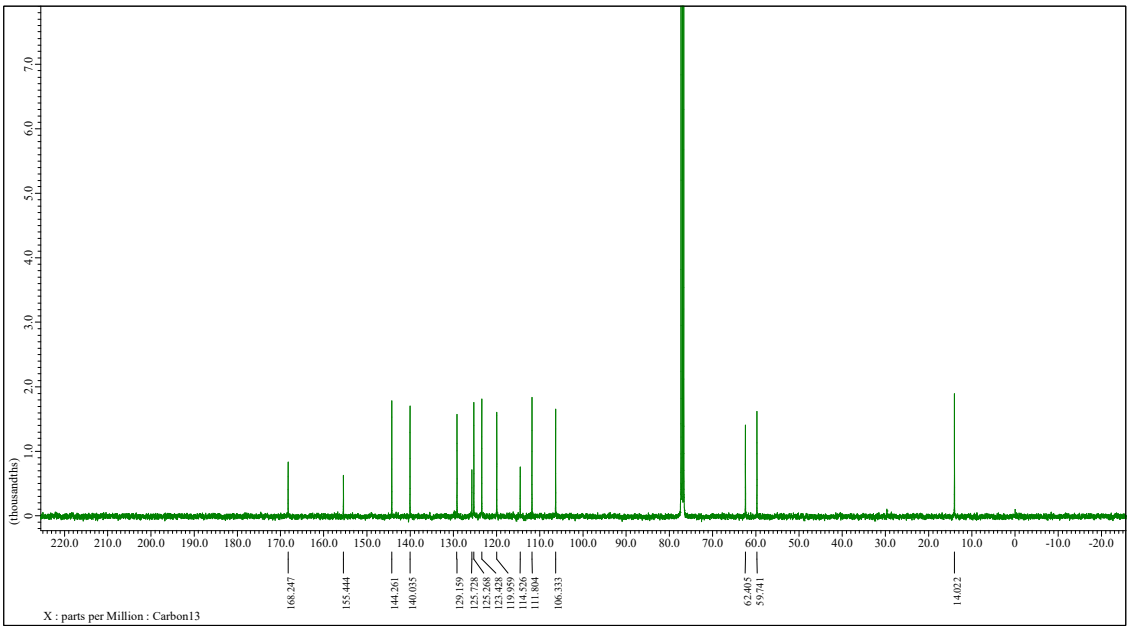


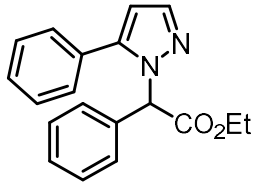
2as

^{1}H-NMR (400 MHz, $CDCl_3$)



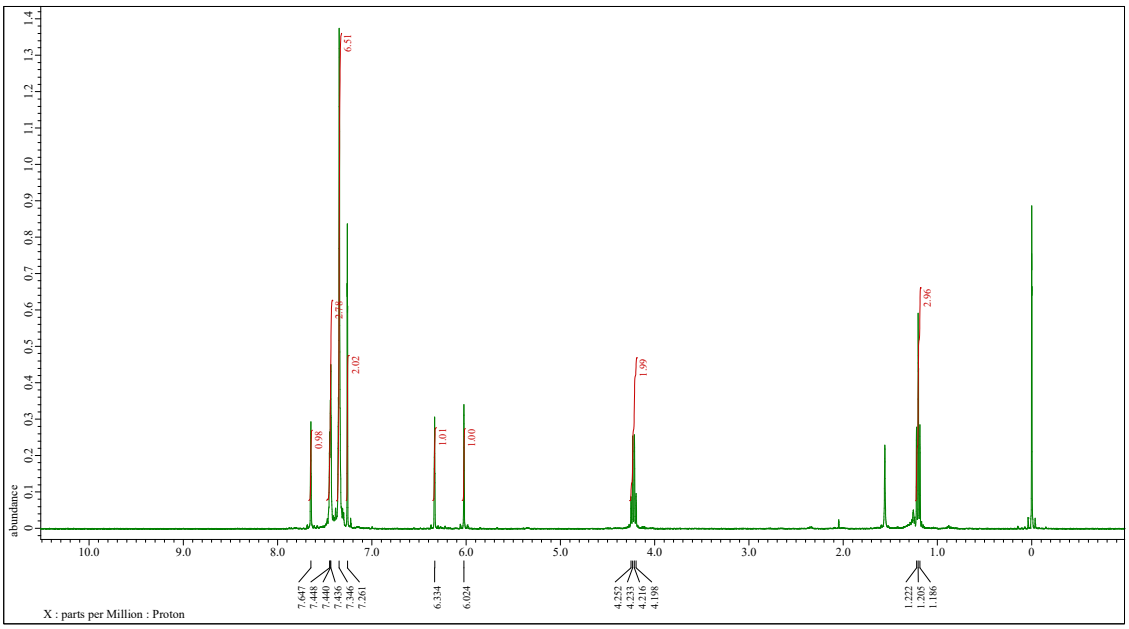
^{13}C-NMR (101 MHz, $CDCl_3$)



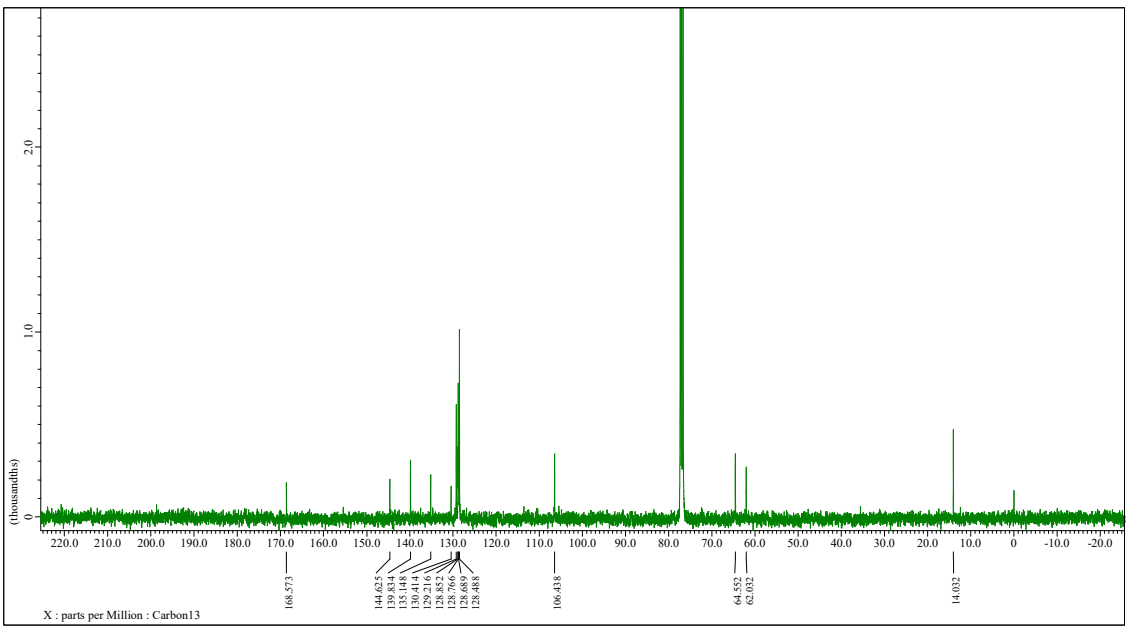


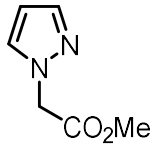
2at

^{1}H-NMR (400 MHz, $CDCl_3$)



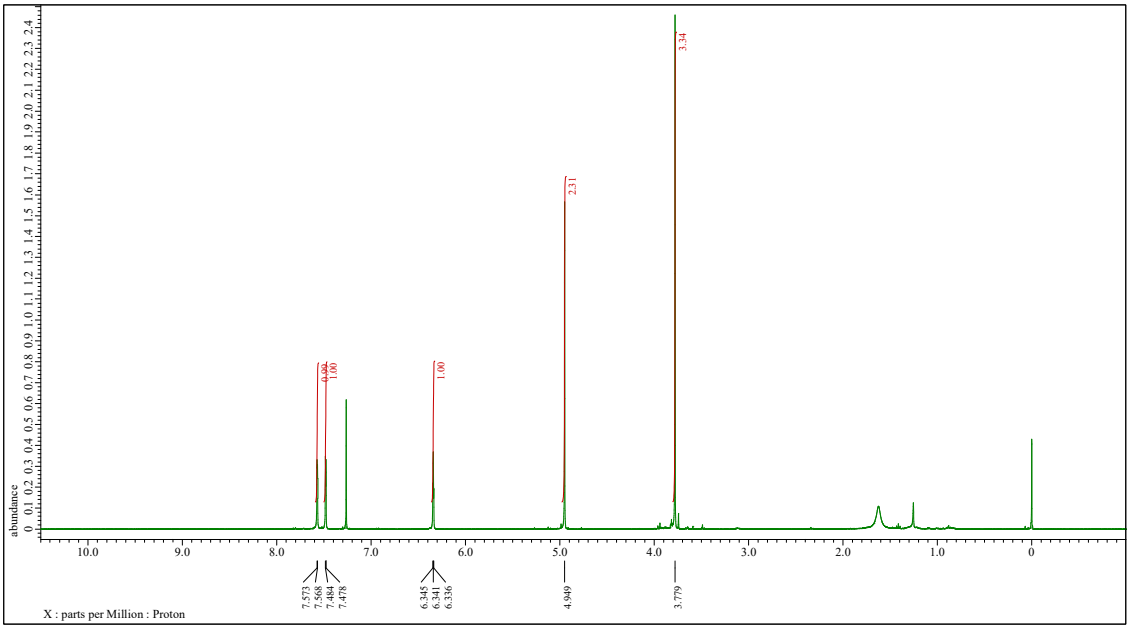
^{13}C-NMR (101 MHz, $CDCl_3$)



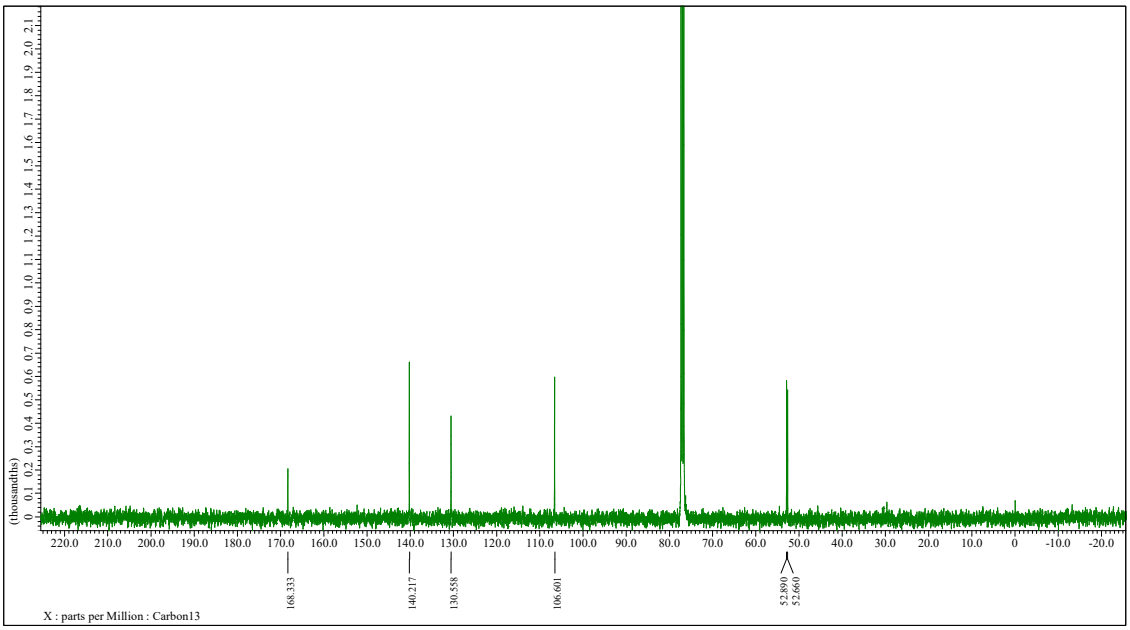


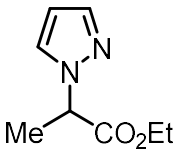
2au

^{1}H-NMR (400 MHz, $CDCl_3$)



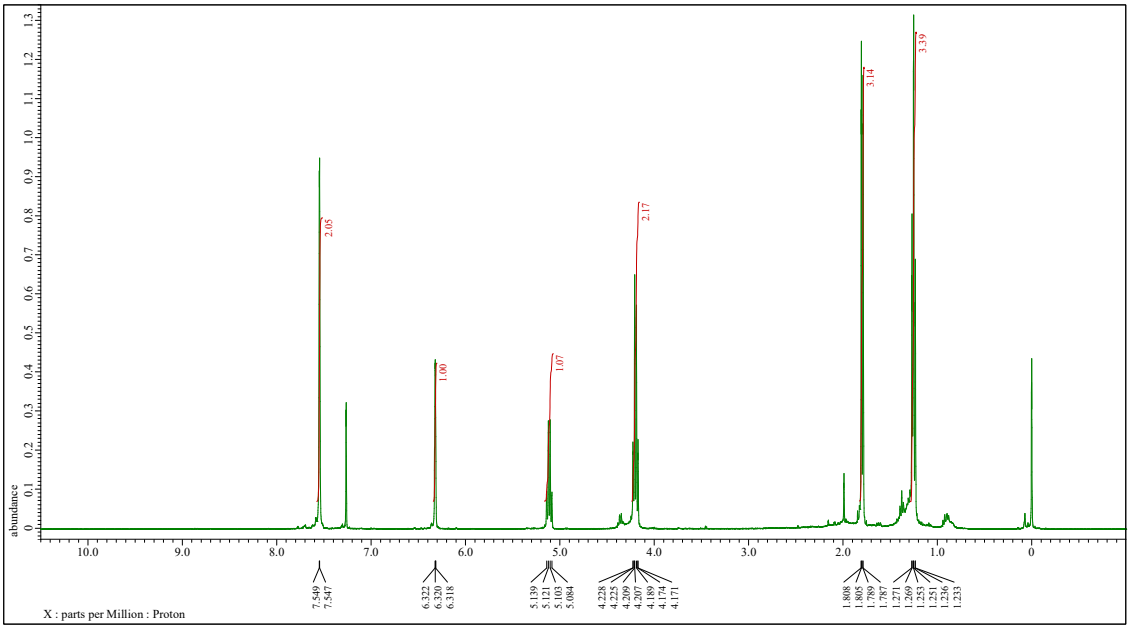
^{13}C-NMR (101 MHz, $CDCl_3$)



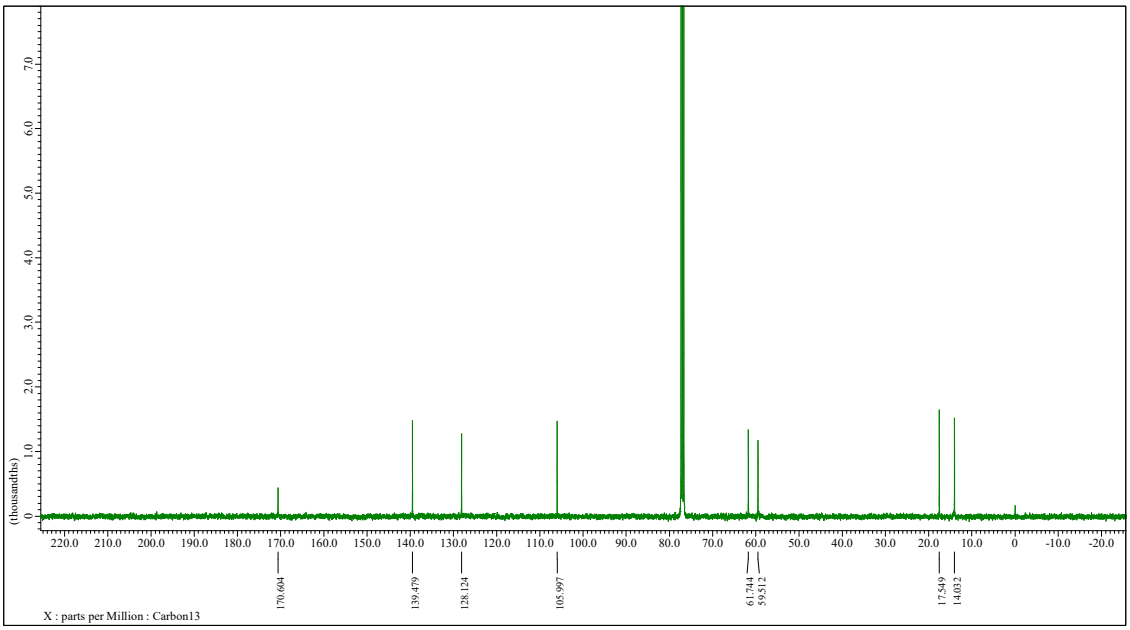


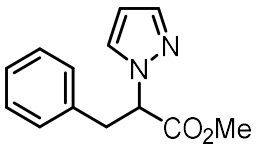
2av

^{1}H-NMR (400 MHz, $CDCl_3$)



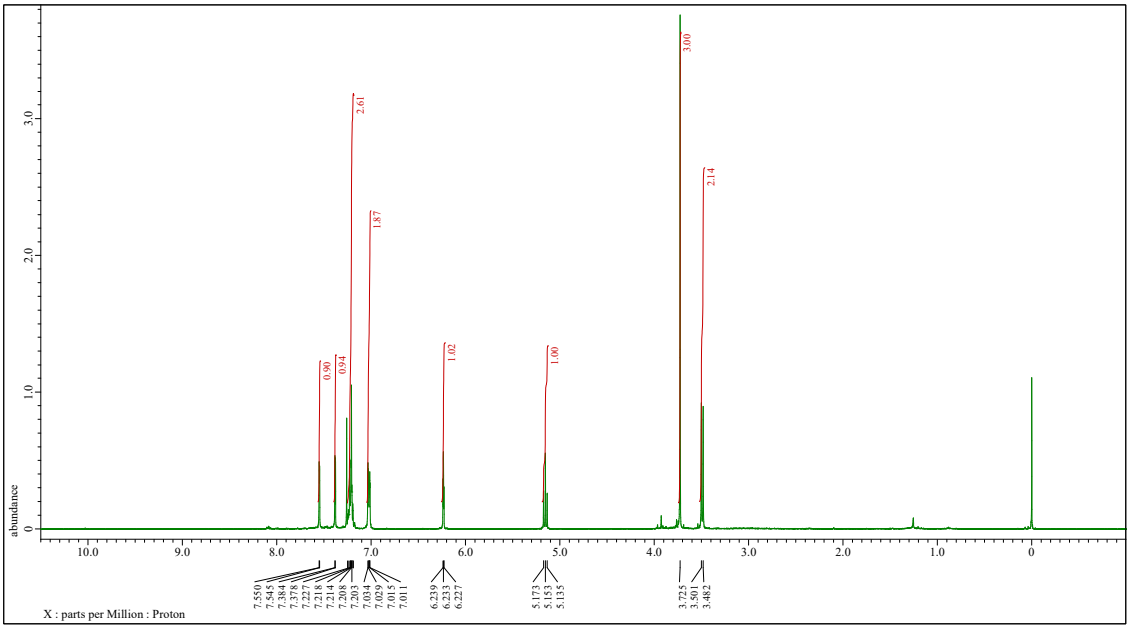
^{13}C-NMR (101 MHz, $CDCl_3$)



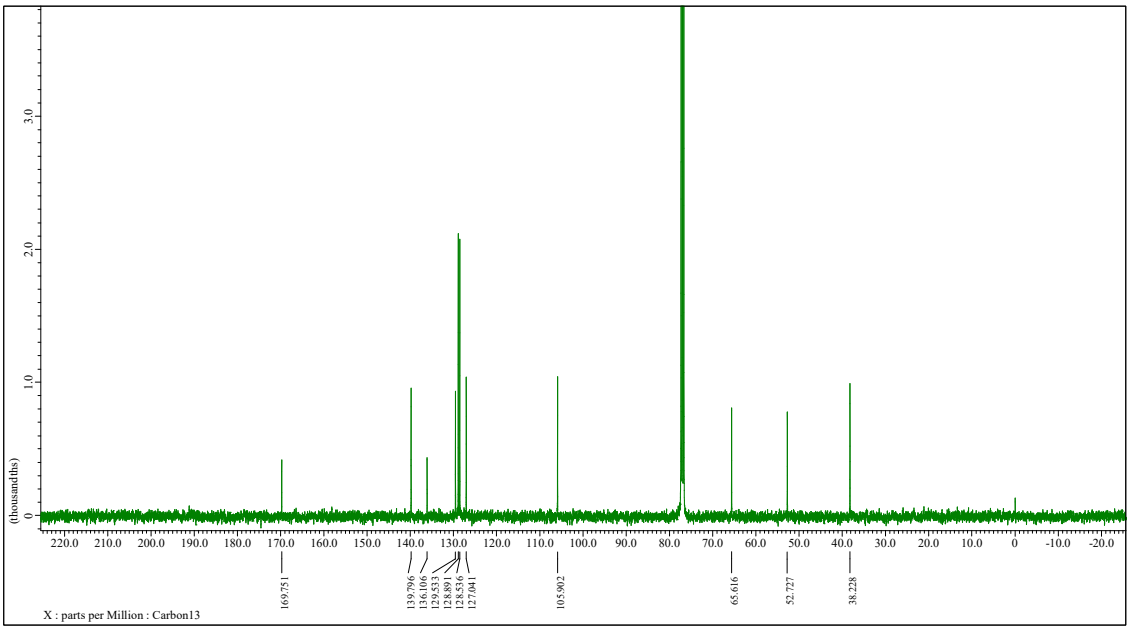


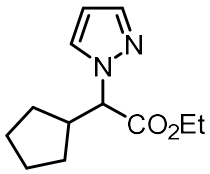
2aw

^{1}H-NMR (400 MHz, $CDCl_3$)



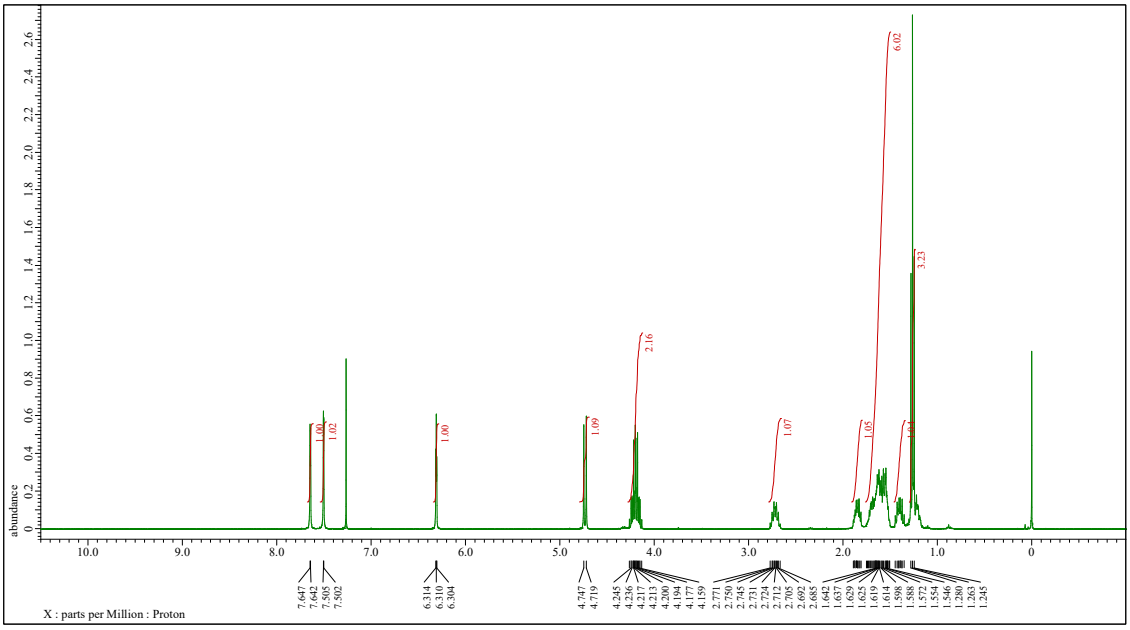
^{13}C-NMR (101 MHz, $CDCl_3$)



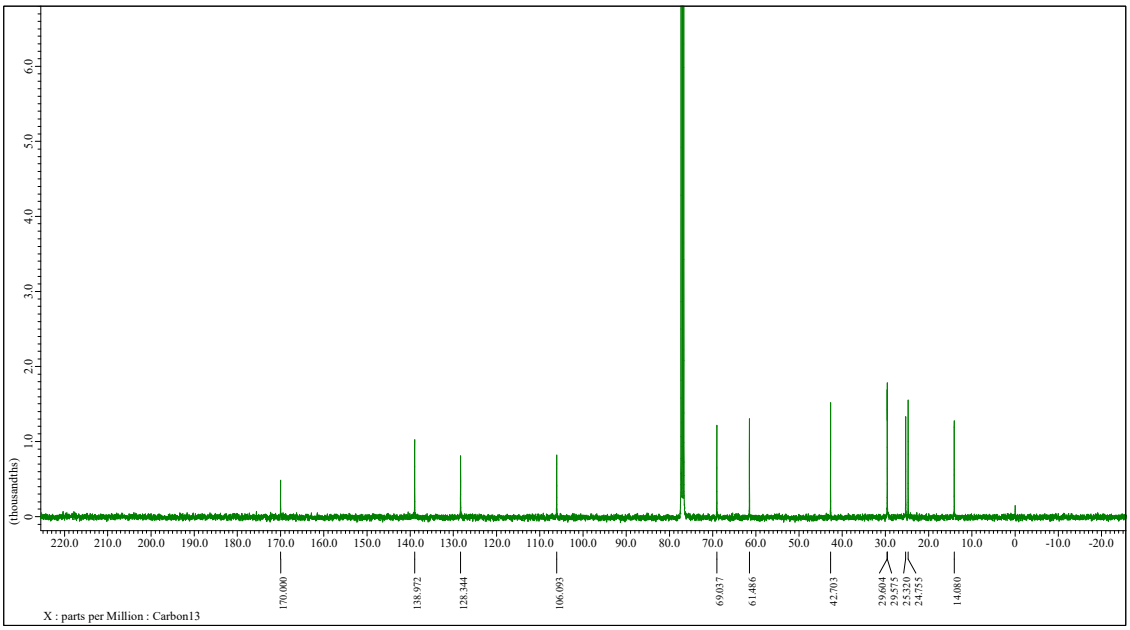


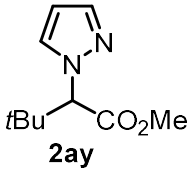
2ax

^{1}H-NMR (400 MHz, $CDCl_3$)



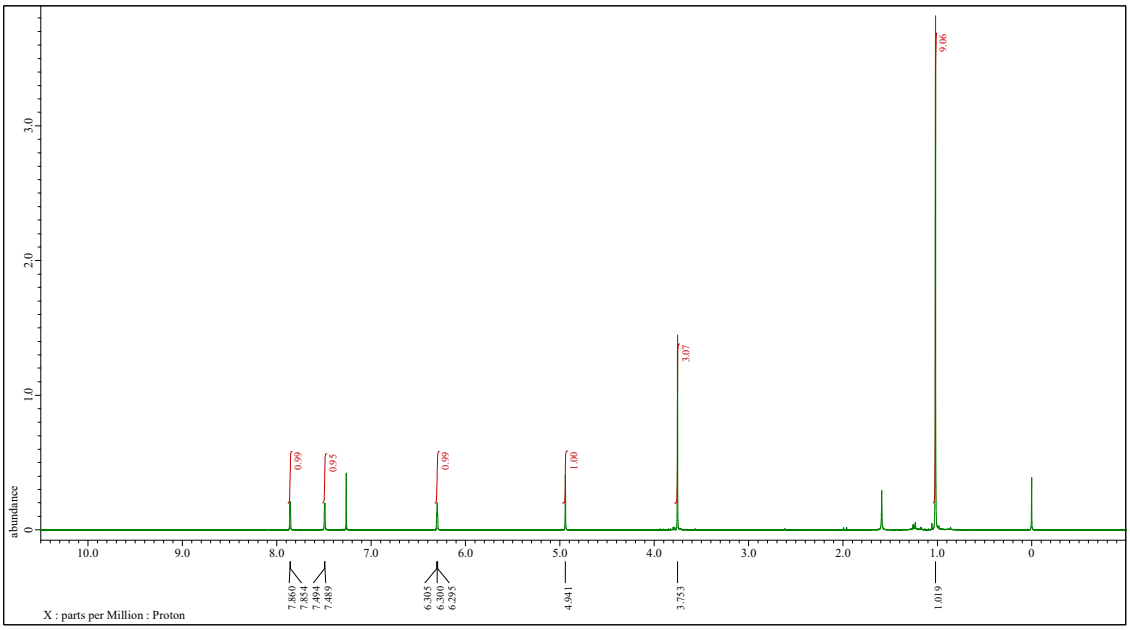
^{13}C-NMR (101 MHz, $CDCl_3$)



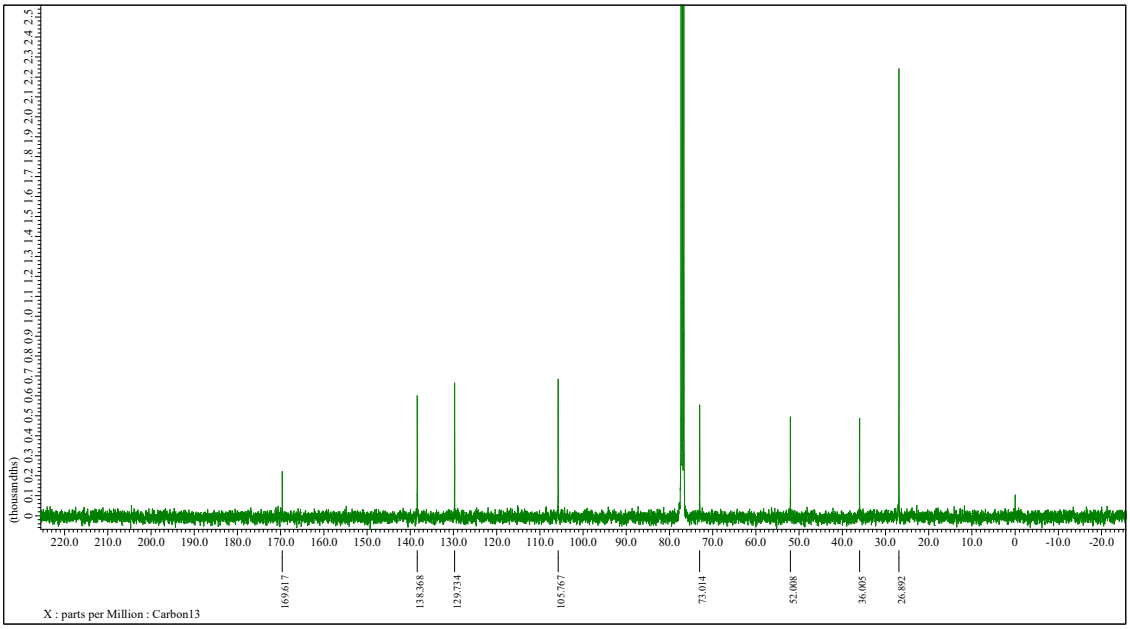


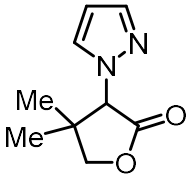
2ay

^{1}H-NMR (400 MHz, $CDCl_3$)



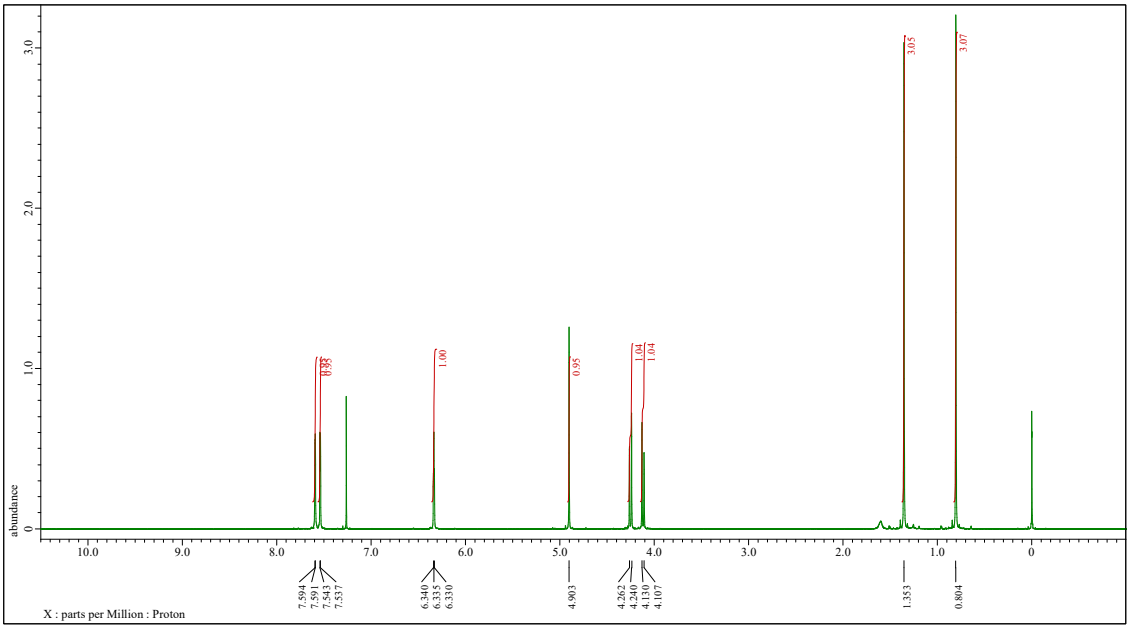
^{13}C-NMR (101 MHz, $CDCl_3$)



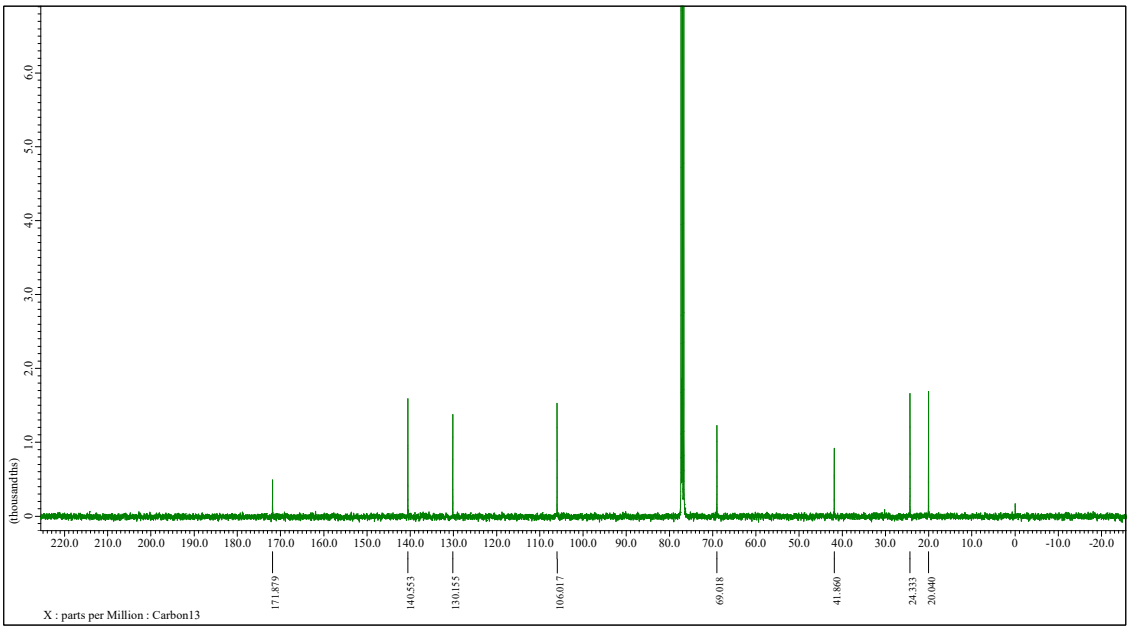


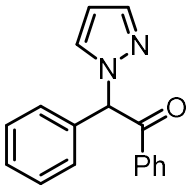
2az

^{1}H-NMR (400 MHz, $CDCl_3$)



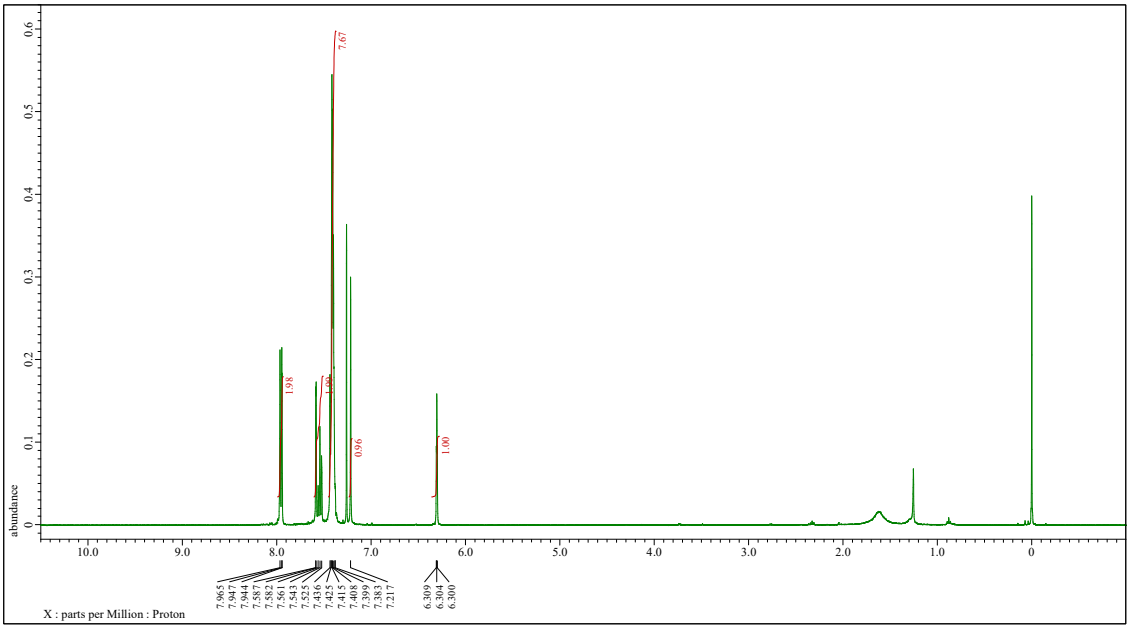
^{13}C-NMR (101 MHz, $CDCl_3$)



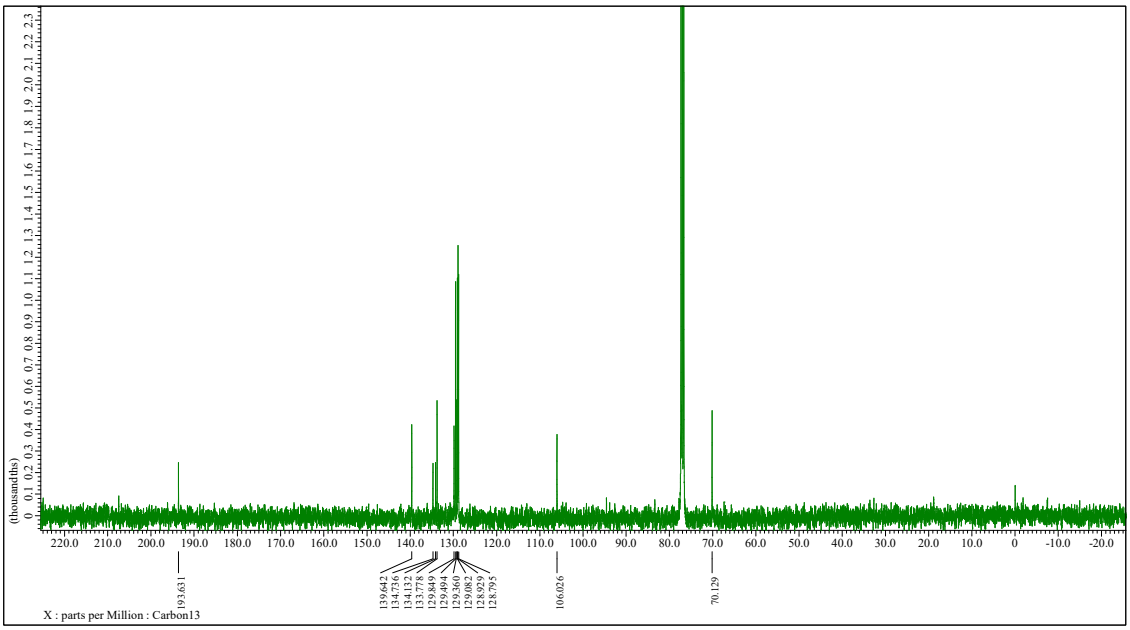


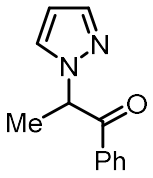
2ba

^{1}H-NMR (400 MHz, $CDCl_3$)



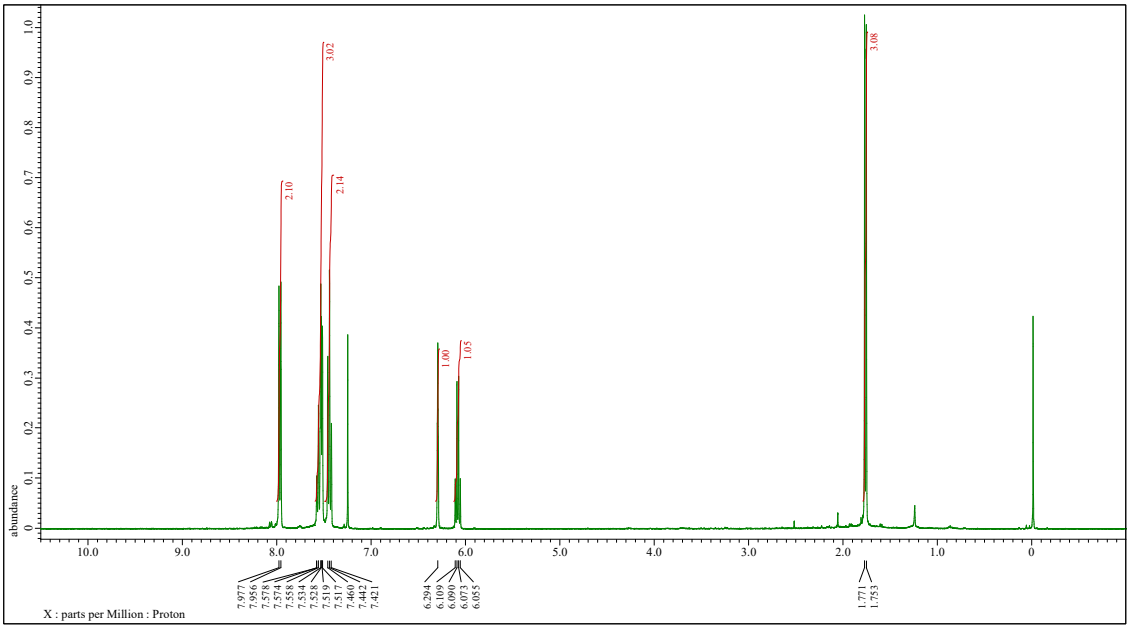
^{13}C-NMR (101 MHz, $CDCl_3$)



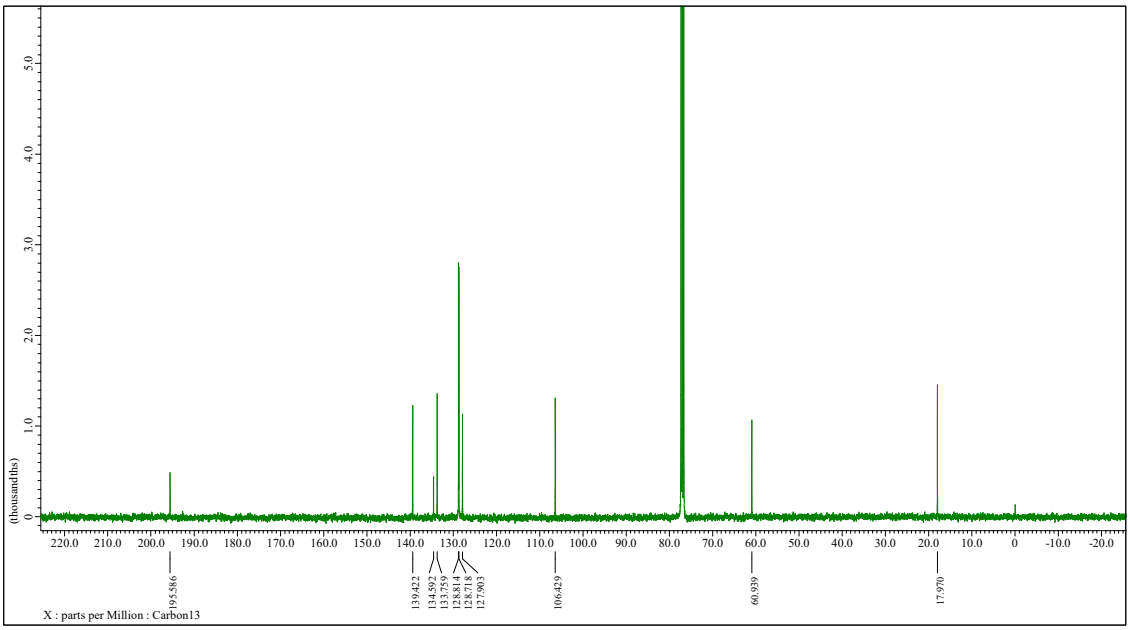


2bb

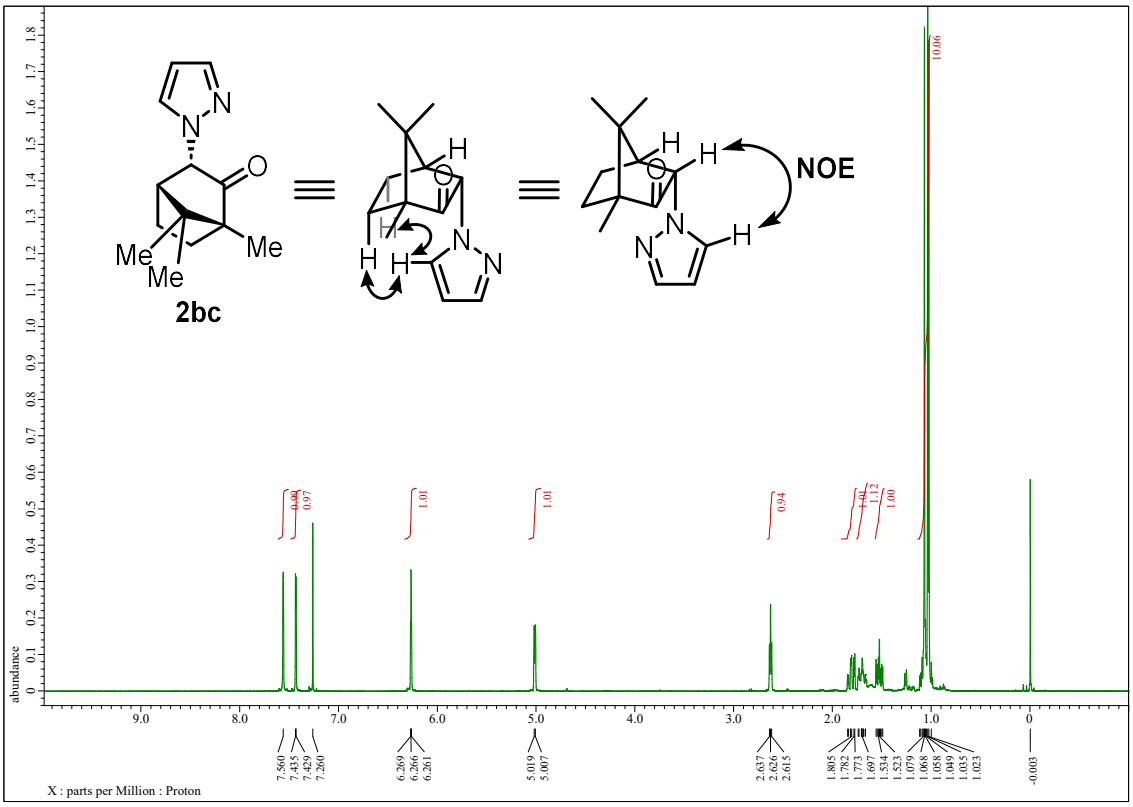
^{1}H-NMR (400 MHz, $CDCl_3$)



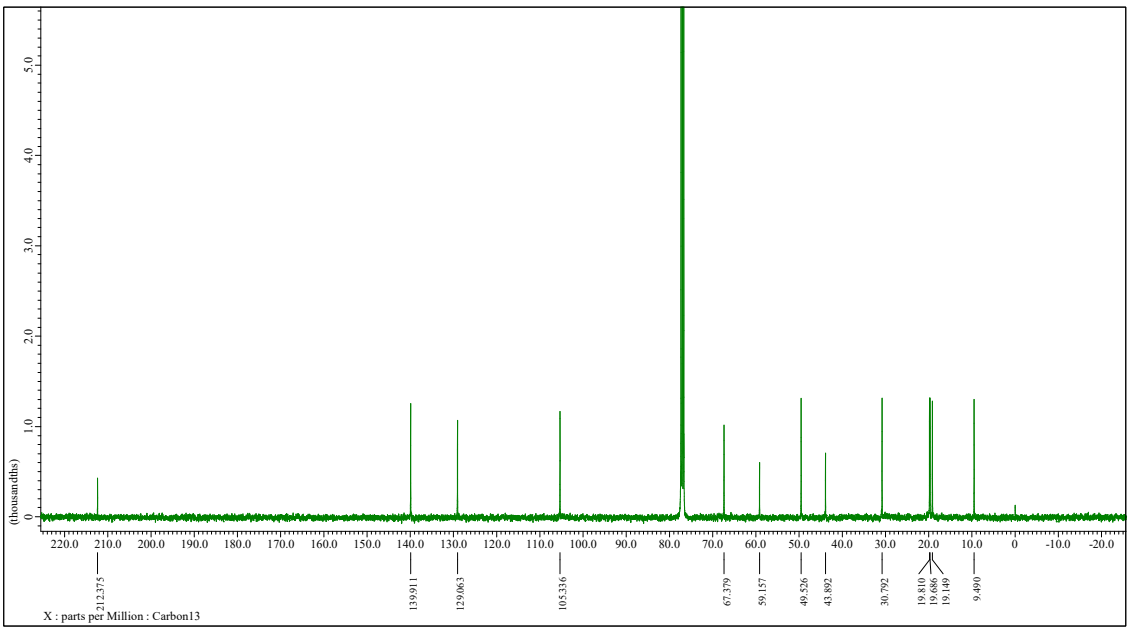
^{13}C-NMR (101 MHz, $CDCl_3$)



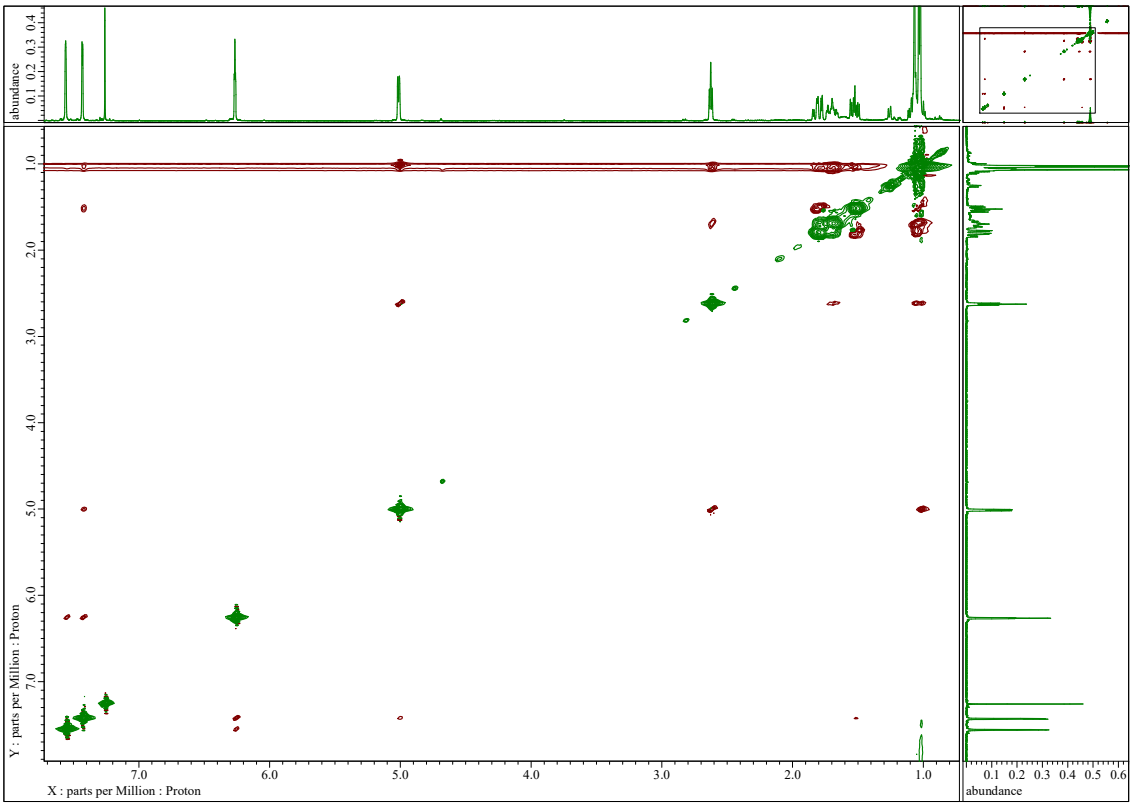
^{1}H-NMR (400 MHz, $CDCl_3$)



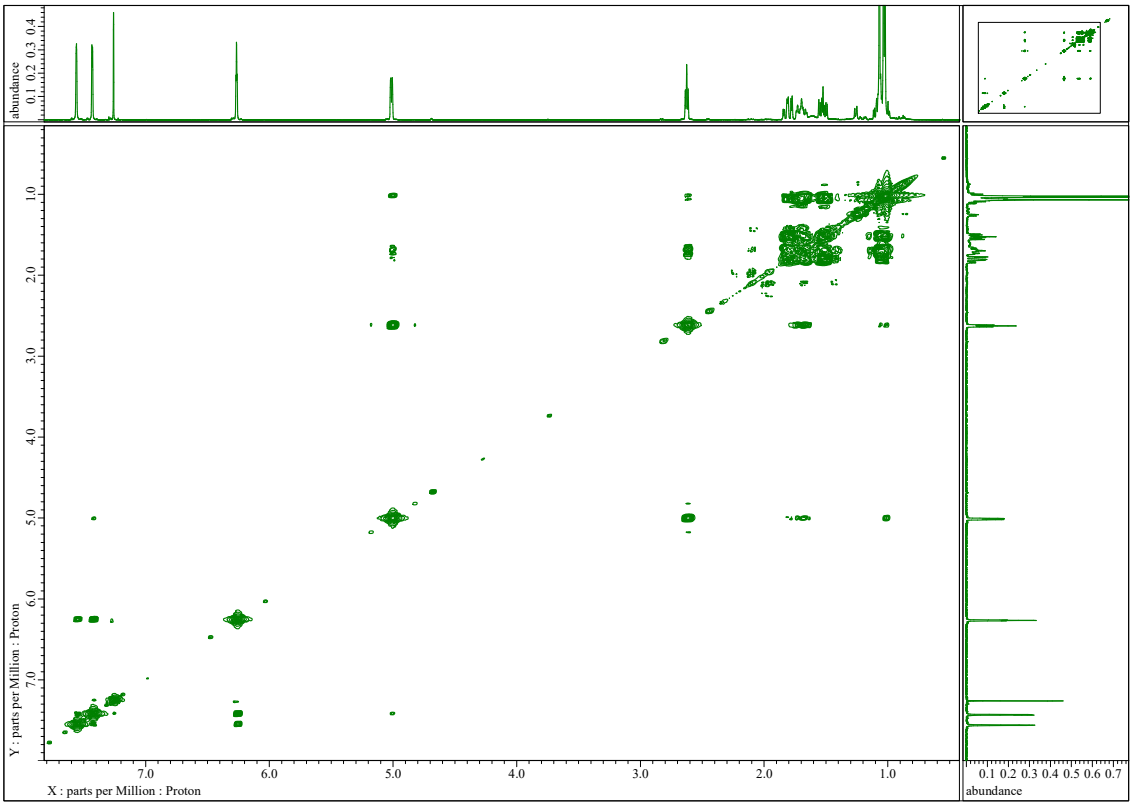
^{13}C-NMR (101 MHz, $CDCl_3$)



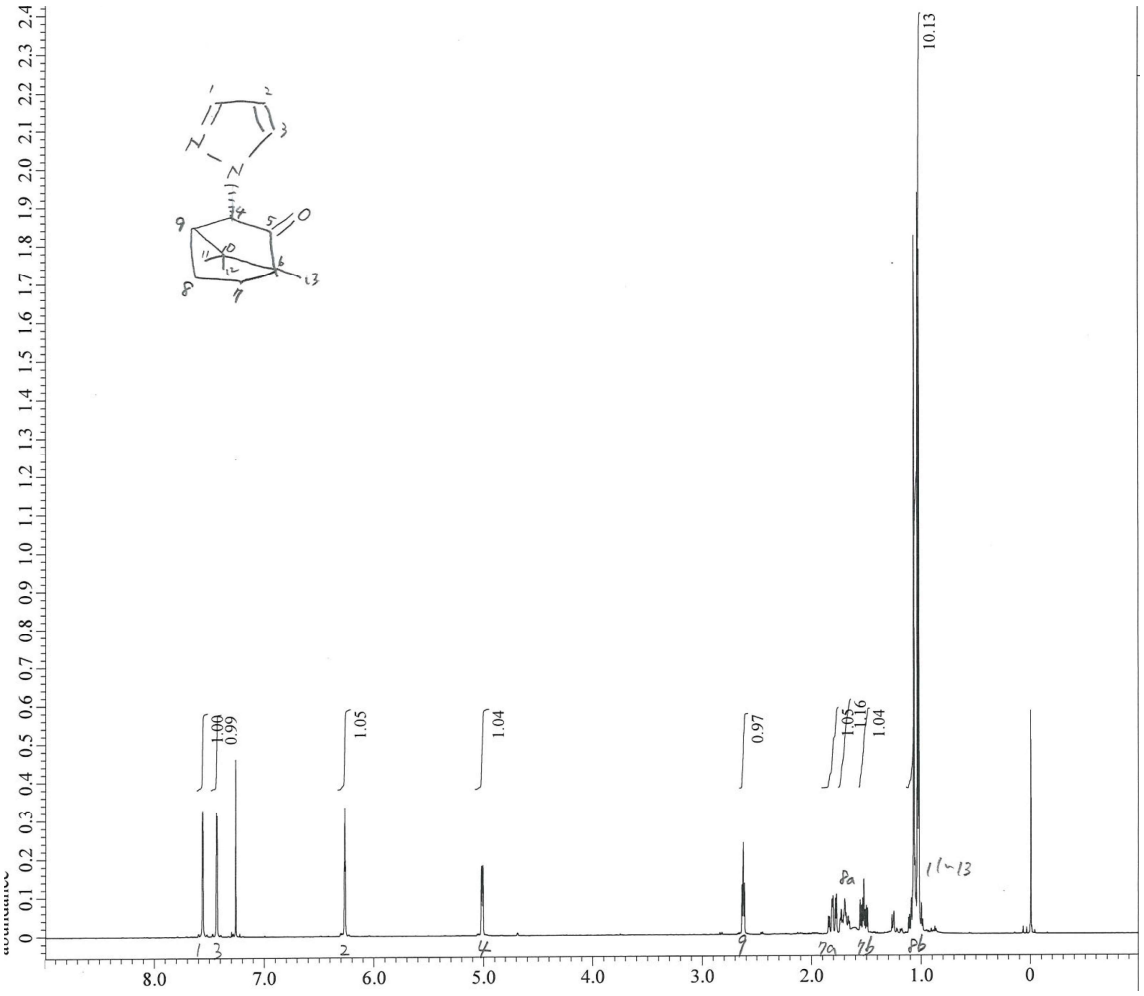
NOESY


abundance
0.1 0.2 0.3 0.4
Y : parts per Million : Proton
1.0 2.0 3.0 4.0 5.0 6.0 7.0
X : parts per Million : Proton
7.0 6.0 5.0 4.0 3.0 2.0 1.0
abundance
0.1 0.2 0.3 0.4 0.5 0.6

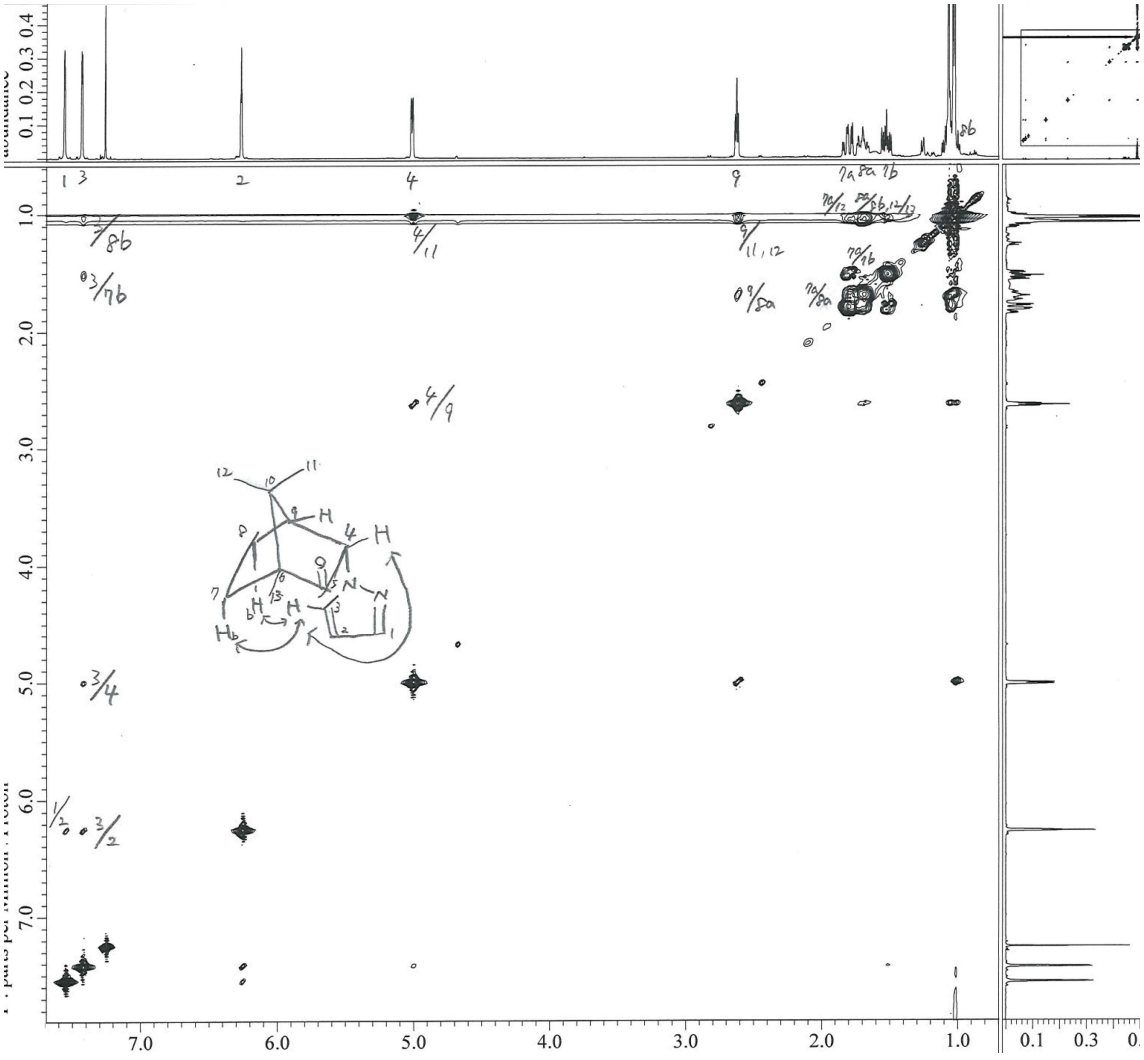
COSY

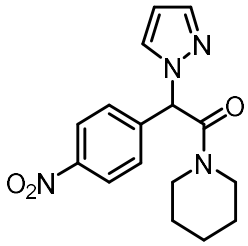

abundance
0.1 0.2 0.3 0.4
Y : parts per Million : Proton
1.0 2.0 3.0 4.0 5.0 6.0 7.0
X : parts per Million : Proton
7.0 6.0 5.0 4.0 3.0 2.0 1.0
abundance
0.1 0.2 0.3 0.4 0.5 0.6 0.7

^{1}H-NMR (400 MHz, $CDCl_3$, assigned)



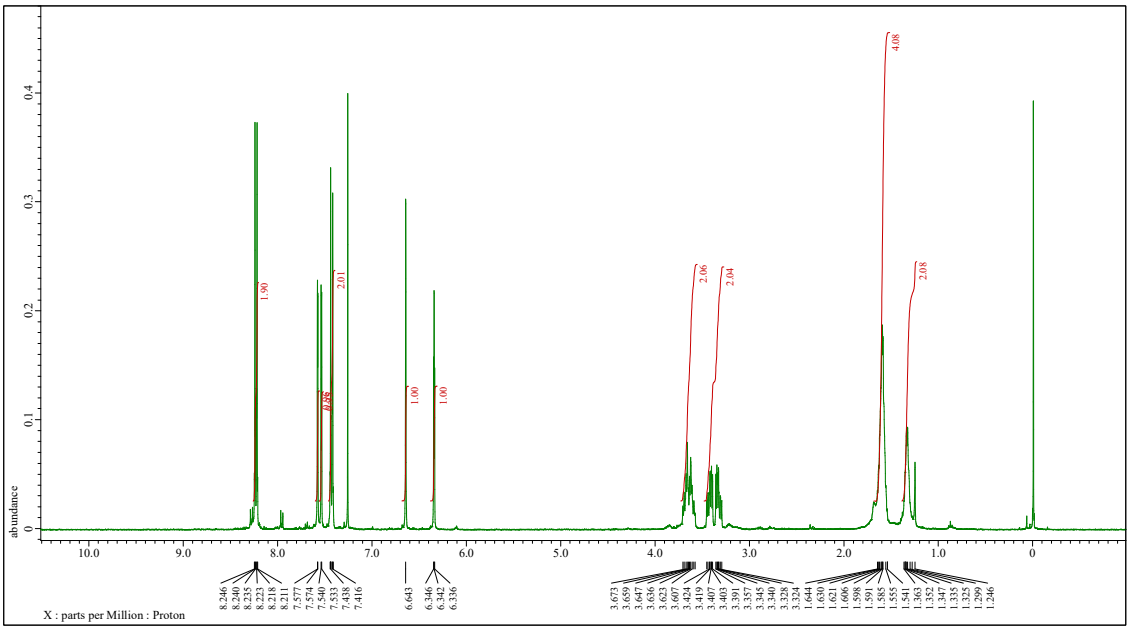
NOESY (assigned)



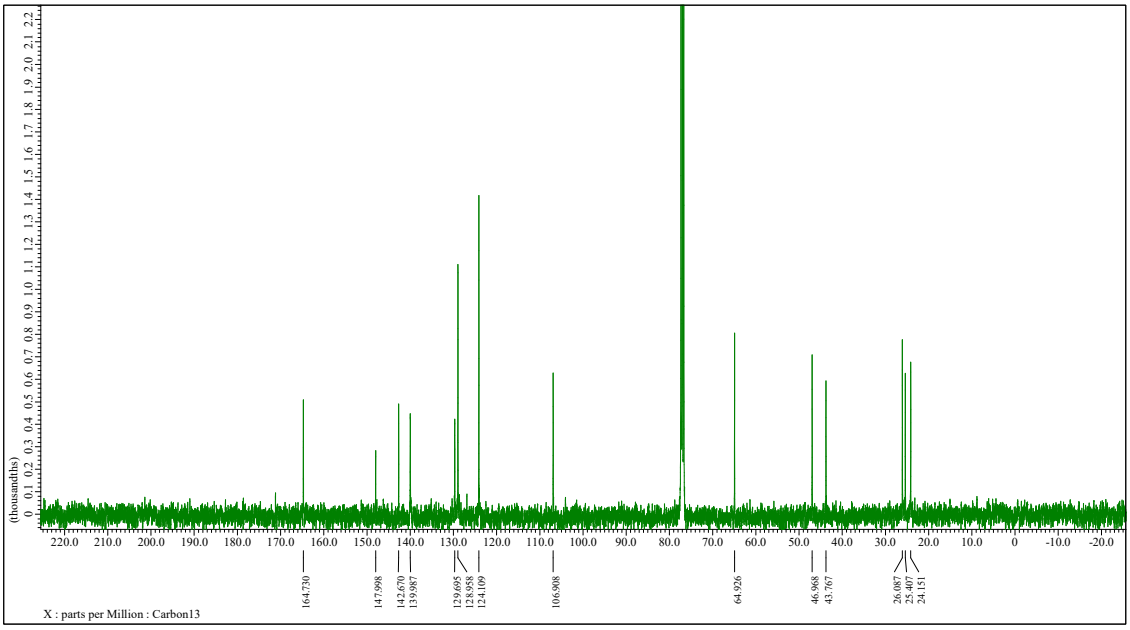


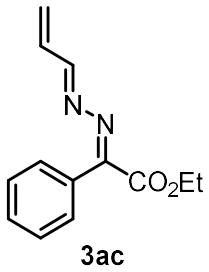
2ca

^{1}H-NMR (400 MHz, $CDCl_3$)



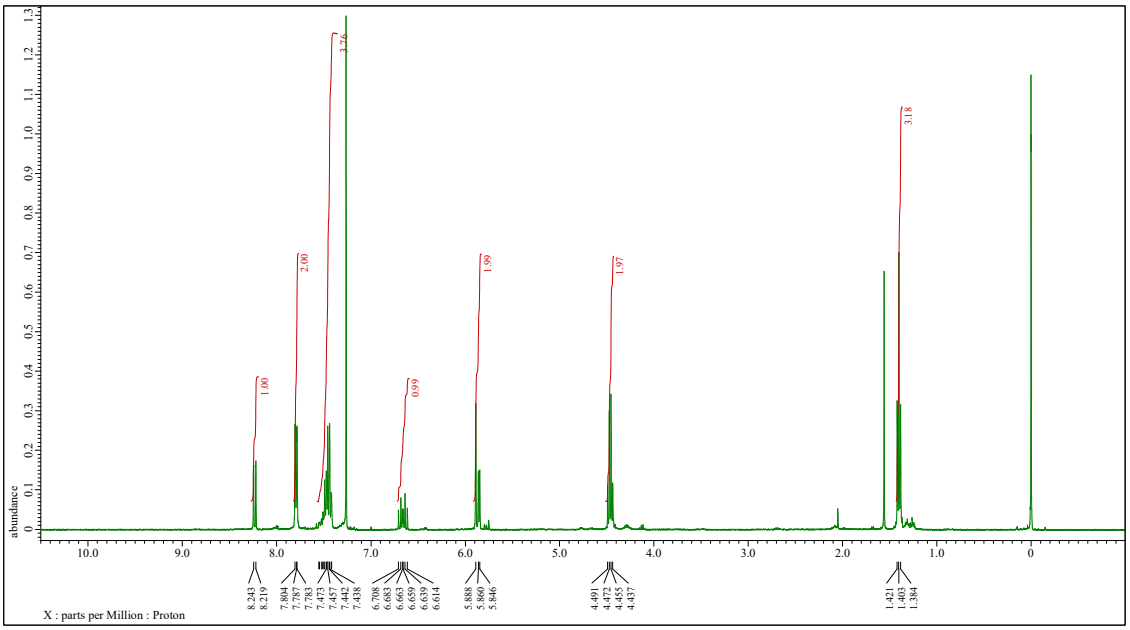
^{13}C-NMR (101 MHz, $CDCl_3$)





3ac

^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)