Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Controllable One-Pot Synthesis for Scaffold Diversity via Visible-Light Photoredox Catalyzed Giese Reaction and Further Transformation

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I. General Experimental Information

All reactions were run under an atmosphere of argon. Acetonitrile was purchased from Sigma-Aldrich chemical company and degassed by bubbling of nitrogen gas for 30 minutes. Pressure tubes (13 x 100 mm, PYREXPLUS, and 50 mL flask, purchased from Chem Glass) were dried in oven for overnight and cooled under a stream of nitrogen prior to use. All commercial reagents were used directly without further purification.

The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F_{254}), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into a *p*-anisaldehyde solution (5.6 mL of *p*-anisaldehyde, 2.3 mL acetic acid and 3.0 mL of concentrated sulfuric acid in 200 mL of ethanol). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using Hexanes-EtOAc (v/v).

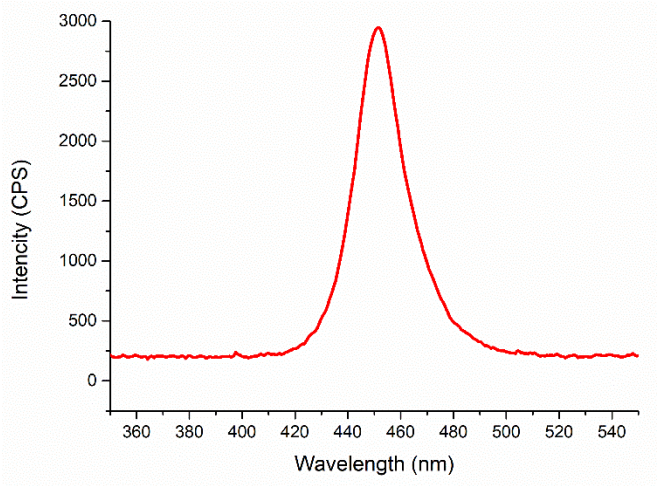
Infrared spectra were recorded on a Shimadzu (IRaffinity-1S). High-resolution mass spectra (EI) were obtained on a Jeol JMS 700 HRMS at the Korea Basic Science Center (KBSI), Daegu, Korea. Accurate masses are reported for the molecular ion $[M^+]$ or $[M+H]^+$. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, ^{19}F NMR) were recorded with a Bruker 300 or 400 MHz spectrometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. The following abbreviations are used: m (multiplet), s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Absorption spectra of the photocatalysts and emission spectra of the visible light sources were measured on a Varian Carry 100, Horiba Fluoromax-4P spectrophotometer. Cyclic voltammograms were recorded on a Bio-Logic (SP-300 model).

For Continuous Flow Processes, Vapourtec E-Series Integrated Flow Chemistry System (Vapourtec Ltd, part # 50-1307) and UV-150 photochemical reactor (Vapourtec Ltd, part # 50-1453) were used. 2 mL and 10 mL of UV-150 reactor (bore and wall, 1.3 x 0.15 nm, Vapourtec Ltd, part # 50-1289 and 50-1287) were used. 420 nm (Vapourtec Ltd, part # 50-1445) and 450 nm (Vapourtec Ltd, part # 50-1448) were used. 20 mL of Large diameter tubular reactor for rapid mixing (Vapourtec Ltd, part # 50-1426) was used. An organometallic chemistry kit (Vapourtec Ltd, part # 50-1311) was also used. This kit consists of a series of tubes and needles that enable reagents to be aspirated from bottles sealed with septa while inert gas is supplied into the bottles to replace the volume removed.

II. Reaction Setup

Irradiation of photochemical reactions was carried out using two MR16 3W blue LED spotlight lamp [*Specification of 3W blue LED: Power (3W), Voltage (12V), Wavelength (450 nm)] for milligram scale reaction. The pictures of two utilized spotlight lamps and their description are given below:

MR16 3W blue LEDs spotlight



Emission spectrum of 3W blue LEDs

Figure S1. Description for 3 W blue LED spotlight lamp

To milligram scale, two MR16 3W blue LEDs spotlight lamp are positioned 3 cm away from the reaction vial using customized reactor that was made by acrylic plate.

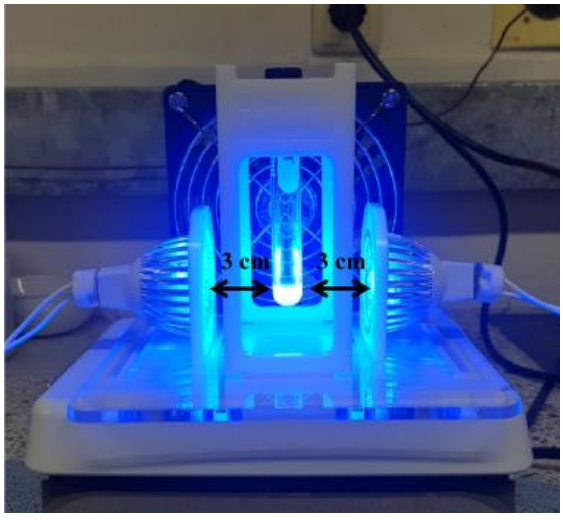


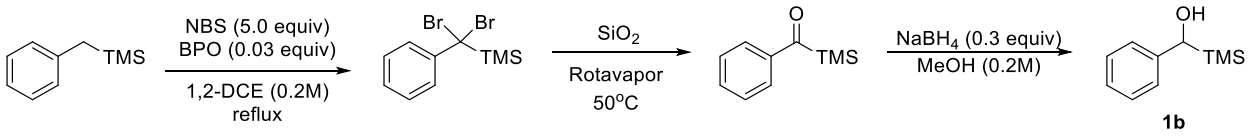
Figure S2. Milligram scale reaction setup

****In the optimized reaction conditions, the reaction is not significantly affected by temperature. The fan was used or not used according to the external temperature to maintain 20 ~ 30 ℃ in reactor.**

III. Preparation of various starting materials

A. Preparation of α-TMS-alcohols

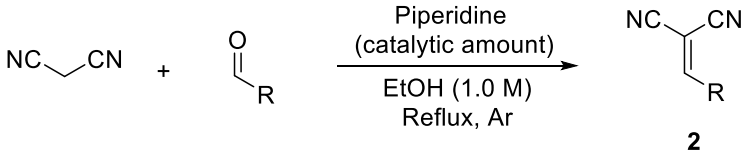
1-Trimethylsilylmethanol **1a** was bought from Combi-Block and TCI and 2nd α-TMS-alcohol **1b** was prepared through reported method.[1]

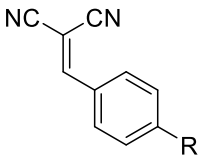


The ^{1}H NMR data of **1b** was in accordance with the literature.
Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.23 – 7.14 (m, 3H), 4.53 (s, 1H), 3.11 (brs, 1H), 0.02 (s, 9H).

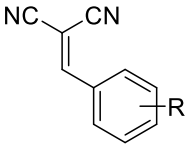
B. Preparation of electron deficient alkene derivatives

All the utilized aromatic or aliphatic electron deficient alkene derivatives (**2a**-**2p**) had been synthesized by following the reported protocol.[2] The spectroscopic data of **2** were in accordance with the literature.

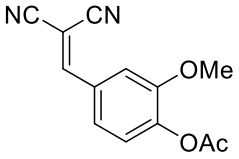




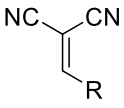
2a (R = H)
2b (R = Me)
2c (R = ^{t}**Bu**)
2d (R = Ph)
2e (R = OMe)
2f (R = OH)
2g (R = F)
2h (R = Cl)
2i (R = Br)
2j (R = I)
2k (R = CO_2Me)



2l (R = *o*-OMe)
2m (R = *m*-OMe)



2n

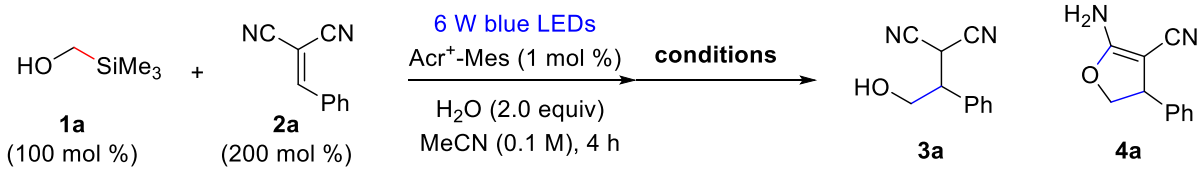


2o (R = *i*-Pr)
2p (R = Cy)

IV. Optimization of controllable one-pot protocol

We established controllable one-pot synthesis methods to obtain each desired product, i.e., **4a**, α-cyano-γ-butyrolactone **5a**, and γ-butyrolactone **6a** (manuscript, Scheme 2). The photoredox-catalyzed Giese reaction of $TMSCH_2OH$ **1a** with benzalmalononitrile **2a** provided **3a** and **4a** as a mixture after column chromatography. By analysis of ^1H NMR analysis of the crude products have revealed that **3a** is a single product and **4a** is formed via intramolecular cyclization during purification by flash column chromatography. Several reaction conditions were tested to obtain a single major product, either **3a** or **4a**. **3a** was isolated as a single product using eluent containing 1% formic acid (Table 1S, entry 3), and **4a** was obtained under weak basic conditions (TEA, K_2CO_3, etc.) or silica gel (Table S1, entries 4-10. After further optimization, we developed one-pot protocol for synthesis of 2, 3-dihydrofuran **4a** *via* photoredox catalyzed Giese reaction, followed by intramolecular cyclization in the presence of TEA (1 equiv) for 4 h (Table 1S, entry 9).

Table S1. Optimization of the reaction conditions for one-pot synthesis of 2, 3-dihydrofuran **4a**[a]

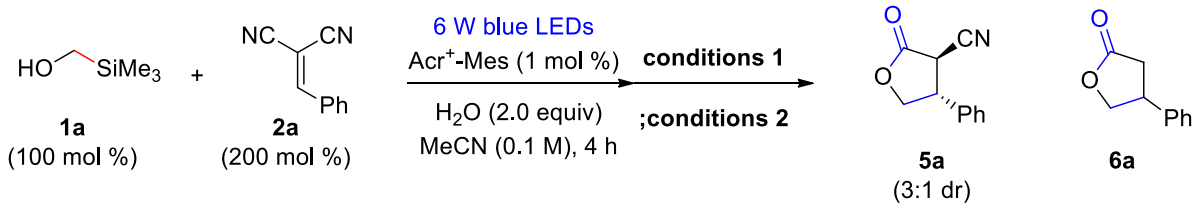


entry	condtions			results	
	reagent	time (h)	column conditions	ratio (**3a**:**4a**)[b]	yield (%)[c]
1	-	-	SiO_2[d]	mixture[e]	-
2	-	-	neutral AlO_2[d]	mixture[e]	-
3	**-**	**-**	**1% HCO_2H[f]**	**3a only**	**90**
4	SiO_2 (1.5 g)	24	SiO_2[d]	**4a** only	90
5	SiO_2 (1.5 g)	6	SiO_2[d]	**4a** only	90
6	K_2CO_3 (2.0 equiv)	24	SiO_2[d]	**4a** only	90
7	TEA (2.0 equiv)	1	SiO_2[d]	**4a** only	90
8	TEA (1.0 equiv)	1	SiO_2[d]	1:1	-
9	**TEA (1.0 equiv)**	**4**	**SiO_2[d]**	**4a only**	**90**
10	TEA (0.5 equiv)	4	SiO_2[d]	1:1	-
11	-	-	1% TEA[f]	mixture[e]	-

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Acr^+-Mes (1 mol %), H_2O (2.0 equiv), MeCN (0.1 M) with 6 W blue LEDs (450 nm) irradiation for 4 h at room temperature under argon in pressure tubes. [b]The ratio of **3a** and **4b** was determined by ^1H NMR. [c]Isolated yield by flash column chromatography. [d]Stationary phase of column chromatography. [e]The ratio of **3a** and **4b** is depend on the time of column chromatography. [F]Additive in eluent of column chromatography.

In addition, the **5a** can be obtained via direct hydrolysis of cyclic imine **4a′** in a one-pot fashion because **4a** and **4a′** are equilibrated via tautomerism. **4a** is continuously converted to **4a′** in its equilibrium state, and **4a′** is hydrolyzed to **5a** under acidic conditions. To develop a one-pot procedure for the generation of **5a**, Amberlite ™ IR 120 was used as an acid because it can be easily removed using a filter after the completion of reaction. Furthermore, the cyclization of **3a** followed by hydrolysis and decarboxylation in the presence of HCl and acetic acid under reflux affords **6a** via one-pot multistep synthesis. Finally, we developed controllable one-pot protocols for the synthesis of diverse scaffolds such as **3a**, **4a**, **5a**, and **6a** in good yields.

Table S2. Optimization of the reaction conditions for one-pot synthesis of α-cyano-γ-butyrolactone **5** and γ-butyrolactone **6**[a]



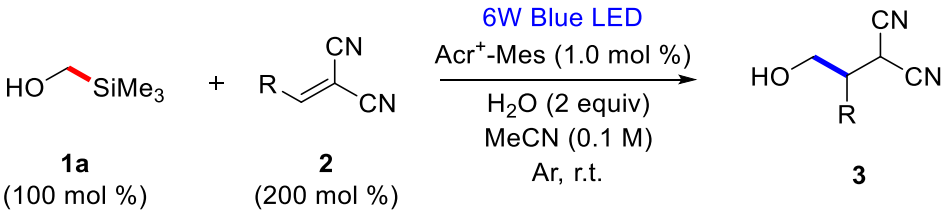
1a (100 mol %) **2a** (200 mol %) **5a** (3:1 dr) **6a**

entry	condtions 1		condtions 2		yield	
	reagent	time (h)	reagent	time (h)	**5a** (%)[b]	**6a** (%)[b]
1	TEA (1.0 equiv)	4	Amberlite (1 g)	1	60	-
2	TEA (1.0 equiv)	4	Amberlite (1 g), H_2O (0.2 mL)	1	64	-
3	TEA (1.0 equiv)	4	Amberlite (1.5 g), H_2O (0.2 mL)	1	74	-
4	**TEA (1.0 equiv)**	**4**	**Amberlite (1.5 g), H_2O (0.2 mL)**	**2**	**78**	-
5	*conc* HCl (0.5 mL) AcOH (0.34 M), 120 °C	12	-	-	60	29
6	*conc* HCl (1.0 mL) AcOH (0.04 M), 120 °C	12	-	-	37	50
7	***conc* HCl (2.0 mL) AcOH (0.1 M), 120 °C**	**12**	-	-	-	**75**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Acr$^+$-Mes (1 mol %), H_2O (2.0 equiv), MeCN (0.1 M) with 6 W blue LEDs (450 nm) irradiation for 4 h at room temperature under argon in pressure tubes. [b]Isolated yield by flash column chromatography.

V. General procedure and characterization data of products

A. General procedure and characterization data of alcohols 3



1a (100 mol %) **2** (200 mol %) **3**

To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with $TMSCH_2OH$ **1a** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (0.82 mg, 0.002 mmol, 1.0 mol %) under argon atmosphere. The reaction mixture was dissolved by degassed acetonitrile (2 mL, 0.1 M for **1a**) and H_2O (0.4 mmol, 2.0 equiv). The reaction mixture was irradiating with 2 x 3W blue LEDs using our customized milligram scale reaction set up (as shown in Figure S2) under constant stirring condition at room temperature (20 ~ 30 °C). After the reaction was completed, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography with 1 % formic acid contained ethyl acetate/hexanes as the eluent to afford the corresponding alcohol **3**.

2-(2-hydroxy-1-phenylethyl)malononitrile (3a).[3] Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3a** was obtained as a colorless liquid (33.5 mg, 90% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.30 (m, 5H), 4.47 (d, *J* = 6.1 Hz, 1H), 4.10 (dd, *J* = 6.7, 2.7 Hz, 2H), 3.44 (ddd, *J* = 6.4 Hz, 1H), 1.99 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4, 129.5, 129.5, 128.2, 112.3, 111.8, 62.4, 48.2, 26.0.

2-(2-hydroxy-1-(p-tolyl)ethyl)malononitrile (3b). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3b** was obtained as a colorless liquid (34.0 mg, 85% yield); R_f = 0.45 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 4H), 4.43 (d, *J* = 6.1 Hz, 1H), 4.05 (d, *J* = 6.6 Hz, 2H), 3.39 (td, *J* = 6.6, 6.1 Hz 1H), 2.37 (s, 3H), 2.08 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 131.3, 130.1, 128.1, 112.4, 111.9, 62.4, 47.9, 26.1, 21.3; FTIR (neat) : υ 532, 816, 1041, 1079, 1119, 1217, 1367, 1431, 1515, 1737, 2920, 2968, 3017, 3459; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O$ (M^+) 200.0949, found 200.0950.

2-(1-(4-(tert-butyl)phenyl)-2-hydroxyethyl)malononitrile (3c). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3c** was obtained as a colorless liquid (43.1 mg, 89% yield); R_f = 0.47 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.32 – 7.26 (m, 2H), 4.46 (d, *J* = 5.9 Hz, 1H), 4.07 (d, *J* = 6.6 Hz, 2H), 3.42 (td, *J* = 6.4 Hz, 1H), 2.07 (bs, 1H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 131.2, 127.9, 126.4, 112.4, 111.9, 62.5, 47.8, 34.8, 31.3, 26.0; FTIR (neat) : υ 533, 833, 1030, 1216, 1363, 1442, 1737, 2925, 2959,

3456; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O$ (M^+) 200.0950, found 200.0949.

2-(1-([1, 1'-biphenyl]-4-yl)-2-hydroxyethyl)malononitrile (3d). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3d** was obtained as a colorless liquid (48.2 mg, 92% yield); R_f = 0.43 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.54 (m, 4H), 7.52 – 7.32 (m, 5H), 4.50 (d, *J* = 6.1 Hz, 1H), 4.15 (d, *J* = 6.4 Hz, 2H), 3.50 (td, *J* = 6.4 Hz, 1H), 1.88 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 140.2, 133.2, 129.0, 128.7, 128.2, 127.9, 127.3, 112.3, 111.8, 62.5, 48.0, 26.0; FTIR (neat) : υ 501, 524, 563, 694, 732, 763, 840, 1049, 1072, 1195, 1226, 1365, 1411, 1489, 1581, 1705, 2908, 3032, 3464 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{15}H_{18}N_2O$ (M^+) 242.1419, found 242.1418.

2-(2-hydroxy-1-(4-methoxyphenyl)ethyl)malononitrile (3e). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3e** was obtained as a colorless liquid (39.3 mg, 91% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 6.98 – 6.89 (m, 2H), 4.43 (dd, *J* = 5.9 Hz, 1H), 4.05 (dd, *J* = 7.0, 3.3 Hz, 2H), 3.82 (s, 3H), 3.39 (ddd, *J* = 6.5 Hz, 1H), 2.05 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 129.4, 126.2, 114.8, 112.4, 111.9, 62.5, 55.5, 47.6, 26.3; FTIR (neat) : υ 540, 833, 1033, 1180, 1257, 1365, 1512, 1581, 1612, 1743, 2229, 2908, 3510 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0902.

2-(2-hydroxy-1-(4-hydroxyphenyl)ethyl)malononitrile (3f). Following the general procedure using 33% Acetone in hexanes as eluant, **3f** was obtained as a colorless liquid (20.2mg, 50% yield); R_f = 0.30 (acetone:hexanes, 1:2); ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.51 (bs, 1H), 7.43 – 7.17 (m, 2H), 7.01 – 6.79 (m, 2H), 4.94 (d, *J* = 6.3 Hz, 1H), 4.54 (bs, 1H), 3.97 (d, *J* = 6.0 Hz, 2H), 3.49 (td, *J* = 7.5, 6.2 Hz, 1H); ^{13}C NMR (75 MHz, Acetone-d_6) δ 158.5, 130.4, 127.8, 116.4, 114.3, 113.8, 63.0, 48.1, 27.0; FTIR (neat) : υ 540, 741, 833, 910, 1034, 1227, 1365, 1450, 1520, 1612, 1743, 2908, 3425 cm^{-1}

2-(1-(4-fluorophenyl)-2-hydroxyethyl)malononitrile (3g). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3g** was obtained as a colorless liquid (32.6 mg, 80% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.17 – 7.07 (m, 2H), 4.46 (d, *J* = 6.0 Hz, 1H), 4.06 (d, *J* = 6.5 Hz, 2H), 3.43 (td, *J* = 6.4 Hz, 1H), 2.18 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (d, J = 245.9 Hz), 137.6 (d, J = 3.2 Hz), 128.8 (d, J = 8.1 Hz), 112.2, 111.7, 62.2, 47.5, 26.1; FTIR (neat) : υ 544, 833, 1035, 1155, 1224, 1434, 1473, 1512, 1597, 1660, 2183, 3333 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{11}H_9FN_2O$ (M^+) 204.0699, found 204.0701.

2-(1-(4-chlorophenyl)-2-hydroxyethyl)malononitrile (3h). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3h** was obtained as a colorless liquid (39.4 mg, 90% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 4.46 (d, *J* = 6.1 Hz, 1H), 4.07 (d, *J* = 6.1 Hz, 2H), 3.42 (dt, *J* = 7.2, 6.0 Hz, 1H), 1.98

(bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 132.9, 129.7, 129.6, 112.1, 111.6, 62.2, 47.6, 25.9; FTIR (neat) : υ 532, 831, 1039, 1087, 1227, 1362, 1415, 1493, 1594, 1658, 1738, 2906, 3468 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{11}H_9ClN_2O$ (M^+) 220.0403, found 220.0401.

2-(1-(4-bromophenyl)-2-hydroxyethyl)malononitrile (3i). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3i** was obtained as a colorless liquid (39.7mg, 75% yield); R_f = 0.45 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.30 – 7.21 (m, 2H), 4.46 (d, J = 6.2 Hz, 1H), 4.07 (dd, J = 6.5, 1.6 Hz, 2H), 3.47 – 3.34 (m, 1H), 1.99 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.4, 132.7, 132.0, 129.9, 123.7, 112.1, 111.6, 62.1, 47.6, 25.8; FTIR (neat) : υ 506, 825, 1011, 1041, 1072, 1404, 1489, 1581, 1651, 2183, 2229, 2901, 3510 cm^{-1}

2-(2-hydroxy-1-(4-iodophenyl)ethyl)malononitrile (3j). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3j** was obtained as a colorless liquid (33.7mg, 54% yield); R_f = 0.45 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 4.46 (d, J = 6.2 Hz, 1H), 4.06 (dd, J = 6.4, 2.0 Hz, 2H), 3.45 – 3.32 (m, 1H), 1.99 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 134.0, 131.7, 130.1, 112.1, 111.6, 95.5, 62.1, 47.8, 25.7; FTIR (neat) : υ 513, 818, 1003, 1065, 1404, 1489, 1582, 2230, 2314, 2901, 3518 cm^{-1}

methyl 4-(1, 1-dicyano-3-hydroxypropan-2-yl)benzoate (3k). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3k** was obtained as a colorless liquid (43.6 mg, 89% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.49 – 7.43 (m, 2H), 4.51 (d, *J* = 6.4 Hz, 1H), 4.11 (d, *J* = 5.4 Hz, 2H), 3.93 (s, 3H), 3.50 (td, *J* = 6.3 Hz, 1H), 2.17 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 139.4, 131.2, 130.6, 128.4, 112.0, 111.5, 62.1, 52.5, 48.1, 25.6; FTIR (neat) : υ 709, 771, 856, 964, 1041, 1080, 1110, . 1195, 1288, 1435, 1612, 1658, 1712, 2183, 2908, 2954, 3456 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{13}H_{12}N_2O_3$ (M^+) 244.0848, found 244.0848.

2-(2-hydroxy-1-(2-methoxyphenyl)ethyl)malononitrile (3l). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3l** was obtained as a colorless liquid (35.8 mg, 83% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 2H), 7.06 – 6.91 (m, 2H), 4.47 (d, *J* = 7.0 Hz, 1H), 4.14 – 4.01 (m, 2H), 3.95 (ddd, *J* = 7.2, 5.3 Hz, 1H), 3.87 (s, 3H), 2.15 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 130.2, 128.6, 122.8, 121.2, 112.4, 112.4, 111.2, 62.0, 55.6, 42.0, 24.7; FTIR (neat) : υ 756, 1026, 1118, 1249, 1296, 1465, 1496, 1597, 1705, 1735, 2260, 2908, 3502 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0900.

2-(2-hydroxy-1-(3-methoxyphenyl)ethyl)malononitrile (3m). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3m** was obtained as a colorless liquid (38.8 mg, 90% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 1H), 6.99 – 6.84 (m, 3H), 4.44 (d, *J* = 6.3 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.82 (s, 3H), 3.40 (ddd, *J* = 6.4

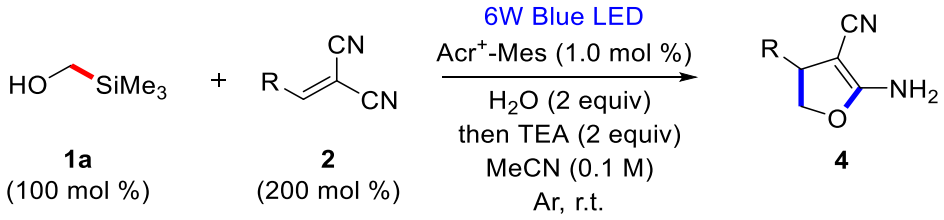
Hz, 1H), 2.02 (t, J = 4.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 135.9, 130.6, 120.3, 114.6, 114.2, 112.3, 111.9, 62.4, 55.5, 48.2, 25.9; FTIR (neat) : υ 702, 786, 1041, 1157, 1234, 1265, 1365, 1458, 1489, 1604, 1735, 2908, 3502 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0900.

4-(1,1-dicyano-3-hydroxypropan-2-yl)-2-methoxyphenyl acetate (3n). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3n** was obtained as a colorless liquid (40.5 mg, 75% yield); R_f = 0.15 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 1H), 6.99 – 6.89 (m, 2H), 4.44 (d, J = 6.0 Hz, 1H), 4.01 (d, J = 6.6 Hz, 2H), 3.85 (s, 4H), 3.38 (td, J = 6.4 Hz, 1H), 2.33 (s, 3H), 2.32 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 151.7, 140.5, 133.3, 123.7, 120.5, 112.4, 112.2, 111.8, 62.3, 56.2, 48.1, 25.9, 20.8; FTIR (neat) : υ 1033, 1126, 1157, 1203, 1273, 1373, 1427, 1465, 1512, 1604, 1759, 2916, 3510 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{14}H_{14}N_2O_4$ (M^+) 274.0954, found 274.0957.

2-(1-hydroxy-3-methylbutan-2-yl)malononitrile (3o). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3o** was obtained as a colorless liquid (22.8 mg, 75% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.25 (d, J = 4.5 Hz, 1H), 4.01 (dd, J = 11.1, 3.5 Hz, 1H), 3.75 (dd, J = 11.2, 7.1 Hz, 1H), 2.14 – 1.99 (m, 2H), 1.71 (bs, 1H), 1.14 (d, J = 6.5 Hz, 3H), 1.06 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.1, 112.5, 60.2, 48.2, 28.2, 23.0, 21.4, 19.3; FTIR (neat) : υ 1049, 1072, 1226, 1373, 1465, 1651, 1705, 1735, 2175, 2260, 2900, 2970, 3448 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_8H_{12}N_2O$ (M^+) 152.0950, found 152.0951.

2-(1-cyclohexyl-2-hydroxyethyl)malononitrile (3p). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3p** was obtained as a colorless liquid (31.9mg, 83% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (d, J = 4.7 Hz, 1H), 3.99 (dd, J = 11.1, 4.2 Hz, 1H), 3.74 (dd, J = 11.1, 8.1 Hz, 1H), 2.12 – 2.01 (m, 1H), 1.89 – 1.78 (m, 4H), 1.73 – 1.64 (m, 1H), 1.36 – 1.00 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.15, 112.64, 60.24, 47.70, 37.80, 31.51, 29.76, 26.31, 26.18, 26.07, 22.66; FTIR (neat) : υ 702, 756, 1026, 1265, 1427, 1450, 1497, 1597, 1689, 1798, 2183, 2361, 2916, 3348 cm^{-1}

B. General procedure and characterization data of 2,3-dihydrofuran 4



To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with $TMSCH_2OH$ **1a** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (0.82 mg, 0.002 mmol, 1.0 mol %) under argon atmosphere. The reaction mixture was dissolved by degassed acetonitrile (2 mL, 0.1 M for **1a**) and H_2O (0.4 mmol, 2.0 equiv). The reaction mixture was irradiating with 2 x 3W blue LEDs using our customized milligram scale reaction set up (as shown in Figure S2) under constant stirring condition at room temperature (20 ~ 30 °C). After addition reaction was completed, triethylamine (0.2 mmol, 1.0 equiv) was added to reaction mixture at room temperature. After 4 h, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography with ethyl acetate/hexanes as the eluent to afford the corresponding 2,3-dihydrofuran **4**.

2-amino-4-phenyl-4,5-dihydrofuran-3-carbonitrile (4a).[4] Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4a** was obtained as a white solid (33.5 mg, 90% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.31 – 7.23 (m, 3H), 4.85 (bs, 2H), 4.77 (dd, *J* = 9.3, 8.5 Hz, 1H), 4.37 (dd, *J* = 9.3, 6.1 Hz, 1H), 4.27 (dd, *J* = 8.5, 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 141.9, 129.0, 127.6, 127.2, 119.2, 78.8, 57.3, 47.7; FTIR (neat) : υ 686, 1021, 1450, 1589, 1650, 2200, 3300, 3445 cm^{-1}.

2-amino-4-(p-tolyl)-4,5-dihydrofuran-3-carbonitrile (4b). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4b** was obtained as a white solid (34 mg, 85% yield); R_f = 0.45 (ethyl acetate:hexanes, 1:2); Melting point: 119~121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 4H), 4.96 (bs, 2H), 4.73 (dd, *J* = 9.3, 8.5 Hz, 1H), 4.33 (dd, J = 9.3, 6.2 Hz, 1H), 4.22 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 138.9, 137.3, 129.7, 127.1, 119.1, 79.0, 57.6, 47.4, 21.2; FTIR (neat) : υ 816, 1038, 1440, 1592, 1642, 2186, 2923, 3217, 3328, 3399 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O$ (M^+) 200.0950, found 200.0949.

2-amino-4-(4-(tert-butyl)phenyl)-4,5-dihydrofuran-3-carbonitrile (4c). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4c** was obtained as a yellow solid (43.1 mg, 89% yield); R_f = 0.47 (ethyl acetate:hexanes, 1:2); Melting point: 168~169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.22 – 7.16 (m, 2H), 4.75 (dd, *J* = 8.5 Hz, 1H), 4.68 (bs, 2H), 4.35 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.28 (dd, *J* = 8.1, 6.2 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 167.9, 150.6, 138.7, 126.9, 126.0, 118.8, 79.1, 58.4, 47.3, 34.6, 31.5; FTIR (neat) : υ 836, 1043, 1444, 1599, 1640, 2173, 2356, 2961, 3188, 3214, 3282, 3321, 3410 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{15}H_{18}N_2O$ (M^+) 242.1419, found 242.1418.

4-([1,1'-biphenyl]-4-yl)-2-amino-4,5-dihydrofuran-3-carbonitrile (4d). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4d** was obtained as a brown solid (48.2 mg, 92% yield); R_f = 0.43 (ethyl acetate:hexanes, 1:2); Melting point: 201~202.5 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.50 – 7.39 (m, 2H), 7.39 – 7.30 (m, 3H), 4.81 (dd, *J* = 9.3, 8.6 Hz, 1H), 4.77 (bs, 2H), 4.42 (dd, *J* = 9.3, 6.1 Hz, 1H), 4.32 (dd, *J* = 8.6, 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 140.7, 140.7, 140.6, 128.8, 127.8, 127.5, 127.3, 127.1, 118.6, 78.9, 58.1, 47.4; FTIR (neat) : υ 696, 741, 915, 1039, 1587, 1651, 2172, 2331, 2361, 3219, 3328 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{17}H_{14}N_2O$ (M^+) 262.1106, found 262.1106.

2-amino-4-(4-methoxyphenyl)-4,5-dihydrofuran-3-carbonitrile (4e). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4e** was obtained as a white solid (39.3 mg, 91% yield); R_f= 0.35 (ethyl acetate:hexanes, 1:2); Melting point: 184~185 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 2H), 6.93 – 6.83 (m, 2H), 4.80 – 4.65 (m, 3H), 4.33 (dd, *J* = 9.3, 6.2 Hz, 1H), 4.23 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 159.1, 133.8, 128.3, 114.5, 79.2, 58.4, 55.5, 47.1; FTIR (neat) : υ 834, 1026, 1178, 1254, 1441, 1474, 1511, 1607, 1669, 2189, 3208, 3227, 3346, 3422 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0902.

2-amino-4-(4-hydroxyphenyl)-4,5-dihydrofuran-3-carbonitrile (4f). Following the general procedure using 33% Acetone in hexanes as eluant, **4f** was obtained as a colorless liquid (12.1mg, 30% yield); R_f= 0.30 (acetone:hexanes, 1:2); ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.28 (s, 1H), 7.16 – 7.04 (m, 2H), 6.87 – 6.74 (m, 2H), 6.40 (s, 2H), 4.73 (dd, *J* = 9.3, 8.6 Hz, 1H), 4.26 (dd, *J* = 9.3, 6.0 Hz, 1H), 4.12 (dd, *J* = 8.6, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, Acetone) δ 169.2, 157.4, 134.7, 129.0, 119.2, 116.3, 79.2, 56.9, 47.8; FTIR (neat) : υ 548l, 833, 1034, 1173, 1227, 1443, 1512, 1589, 1651, 2183, 3225, 3279, 3348 cm^{-1}

2-amino-4-(4-fluorophenyl)-4,5-dihydrofuran-3-carbonitrile (4g). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4g** was obtained as a yellow solid (32.6 mg, 80% yield); R_f= 0.40 (ethyl acetate:hexanes, 1:2); Melting point: 141~142 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 2H), 7.09 – 6.98 (m, 2H), 4.87 (bs, 2H), 4.75 (dd, *J* = 9.4, 8.7 Hz, 1H), 4.35 (dd, *J* = 9.4, 6.1 Hz, 1H), 4.22 (dd, *J* = 8.7, 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 162.3 (d, J = 245.9 Hz), 137.6 (d, J = 3.2 Hz), 128.8 (d, J = 8.1 Hz), 118.7, 116.0 (d, J = 21.5 Hz), 78.9, 57.9, 47.1; FTIR (neat) : υ 833, 1026, 1157, 1242, 1435, 1512, 1597, 1658, 2183, 3055, 3332 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{11}H_9FN_2O$ (M^+) 204.0699, found 204.0701.

2-amino-4-(4-chlorophenyl)-4,5-dihydrofuran-3-carbonitrile (4h).[5] Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4h** was obtained as a white solid (39.4 mg,

90% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.24 – 7.17 (m, 2H), 4.84 (bs, 2H), 4.76 (dd, *J* = 9.4, 8.7 Hz, 1H), 4.34 (dd, *J* = 9.4, 6.0 Hz, 1H), 4.22 (dd, *J* = 8.7, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 140.4, 133.5, 129.3, 128.6, 118.4, 78.8, 57.9, 47.3; FTIR (neat) : υ 737, 836, 1029, 1096, 1219, 1365, 1428, 1695, 1594, 1661, 1740, 2179, 2364, 3222, 3337, 3439 cm^{-1}.

2-amino-4-(4-bromophenyl)-4,5-dihydrofuran-3-carbonitrile (4i). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4i** was obtained as a white powder (39.7mg, 75% yield); R_f = 0.45 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 2H), 7.19 – 7.10 (m, 2H), 4.83 (bs, 2H), 4.76 (dd, J = 9.4, 8.7 Hz, 1H), 4.33 (dd, J = 9.4, 6.0 Hz, 1H), 4.22 (dd, J = 8.7, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 140.9, 132.2, 129.0, 121.6, 118.6, 78.6, 57.5, 47.3; FTIR (neat) : υ 818, 1034, 1435, 1481, 1589, 1659, 2183, 3217, 3263 3333, 3433 cm^{-1}

2-amino-4-(4-iodophenyl)-4,5-dihydrofuran-3-carbonitrile (4j). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4j** was obtained as a white powder (33.7mg, 54% yield); R_f = 0.45 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.05 – 6.98 (m, 2H), 4.82 (bs, 2H), 4.76 (dd, J = 9.3, 8.6 Hz, 1H), 4.31 (dd, J = 9.3, 6.0 Hz, 1H), 4.22 (dd, J = 8.6, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 141.6, 138.2, 129.2, 118.6, 93.1, 78.6, 57.5, 47.4; FTIR (neat) : υ 818, 1011, 1026, 1435, 1474, 1589, 1659, 2183, 3209, 3333, 3418 cm^{-1}

methyl 4-(5-amino-4-cyano-2,3-dihydrofuran-3-yl)benzoate (4k). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4k** was obtained as a brown solid (43.6 mg, 89% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:2); Melting point: 134~137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 7.96 (m, 2H), 7.39 – 7.28 (m, 2H), 4.97 (bs, 2H), 4.78 (dd, *J* = 9.5, 8.8 Hz, 1H), 4.41 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.26 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 166.9, 147.1, 130.5, 129.6, 127.3, 118.6, 78.4, 57.3, 52.3, 47.7; FTIR (neat) : υ 481, 711, 768, 817, 860, 963, 971, 1033, 1109, 1197, 1288, 1442, 1477, 1599, 1655, 1730, 2169, 2954, 2979, 3003 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{13}H_{12}N_2O_3$ (M^+) 244.0848, found 244.0848.

2-amino-4-(2-methoxyphenyl)-4,5-dihydrofuran-3-carbonitrile (4l). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4l** was obtained as a colorless liquid (35.8 mg, 83% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.5, 1.8 Hz, 1H), 7.25 (td, J = 7.8, 1.8 Hz, 1H), 6.98 (td, J = 7.5, 1.1 Hz, 1H), 6.87 (dd, J = 8.2, 1.1 Hz, 1H)., 4.87 (bs, 2H), 4.80 (dd, *J* = 9.7, 8.3 Hz, 1H), 4.69 (dd, *J* = 9.7, 5.1 Hz, 1H), 4.16 (dd, *J* = 8.3, 5.2 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 156.9, 130.1, 128.5, 127.3, 120.9, 119.5, 110.4, 78.4, 55.5, 55.0, 41.3; FTIR (neat) : υ 699, 756, 1018, 1257, 1496, 1651, 1681, 2184, 2340, 2361, 3223, 3276, 3342, 3410 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0900.

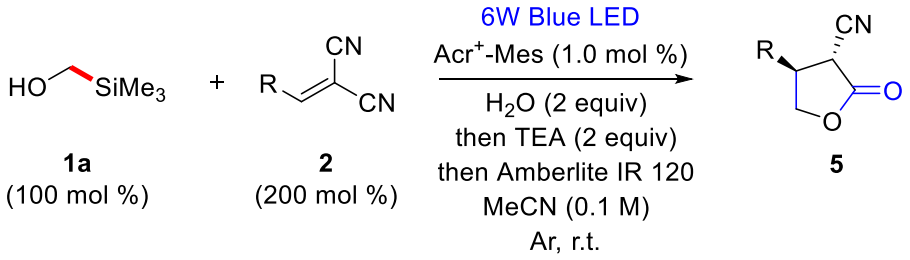
2-amino-4-(3-methoxyphenyl)-4,5-dihydrofuran-3-carbonitrile (4m). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4m** was obtained as a white solid (38.8 mg, 90% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); Melting point: 154~155 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 1H), 4.80 (bs, 2H), 4.78 (dd, *J* = 8.6 Hz, 1H), 4.87 – 4.68 (m, 3H), 4.34 (dd, *J* = 8.9, 6.1 Hz, 1H), 4.27 (dd, *J* = 8.2, 6.1 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 160.2, 143.5, 130.1, 119.5, 118.6, 113.0, 112.9, 78.9, 58.2, 55.4, 47.8; FTIR (neat) : υ 699, 782, 886, 1030, 1045, 1145, 1259, 1439, 1476, 1491, 1584, 1605, 1664, 2184, 2340, 2361, 3223, 3276, 3342, 3410 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0900.

4-(5-amino-4-cyano-2,3-dihydrofuran-3-yl)-2-methoxyphenyl acetate (4n). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4n** was obtained as a white solid (40.5 mg, 75% yield); R_f = 0.15 (ethyl acetate:hexanes, 1:2); Melting point: 156~157 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 – 6.97 (m, 1H), 6.88 – 6.81 (m, 2H), 4.88 (bs, 2H), 4.74 (dd, *J* = 9.3, 8.6 Hz, 1H), 4.36 (dd, *J* = 9.3, 6.1 Hz, 1H), 4.26 (dd, *J* = 8.6, 6.2 Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 168.3, 151.5, 140.8, 139.1, 123.3, 119.4, 118.8, 111.2, 78.7, 57.4, 56.1, 47.7, 20.8; FTIR (neat) : υ 1034, 1118, 1196, 1273, 1435, 1512, 1597, 1659, 1766, 2183, 3217, 3341 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{14}H_{14}N_2O_4$ (M^+) 274.0954, found 274.0957.

2-amino-4-isopropyl-4,5-dihydrofuran-3-carbonitrile (4o). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4o** was obtained as a colorless liquid (22.8 mg, 75% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (bs, 2H), 4.39 (dd, *J* = 9.2 Hz, 1H), 4.16 (dd, *J* = 9.0, 5.2 Hz, 1H), 3.05 (ddd, *J* = 9.3, 5.3 Hz, 1H), 1.85 – 1.69 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 120.1, 74.2, 55.0, 48.1, 32.0, 19.2, 18.6; FTIR (neat) : υ 1041, 1435, 1475, 1596, 1662, 2179, 2362, 3213, 3266, 3331, 3403 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_8H_{12}N_2O$ (M^+) 152.0950, found 152.0951.

2-amino-4-cyclohexyl-4,5-dihydrofuran-3-carbonitrile (4p). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4p** was obtained as a colorless liquid (31.9mg, 83% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2);^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (bs, 2H), 4.39 (dd, *J* = 9.1 Hz, 1H), 4.21 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.02 (ddd, *J* = 9.3, 5.4 Hz, 1H), 1.89 – 1.62 (m, 5H), 1.51 – 1.33 (m, 1H), 1.31 – 0.91 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.22, 120.20, 74.55, 55.12, 47.45, 42.13, 29.86, 29.26, 26.48, 26.29; FTIR (neat) : υ 525, 748, 910, 1219, 1366, 1435, 1659, 1736, 2947, 2970, 3017 cm^{-1}

C. General procedure and characterization data of of α-cyano-γ-butyrolactone 5



To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with $TMSCH_2OH$ **1a** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (0.82 mg, 0.002 mmol, 1.0 mol %) under argon atmosphere. The reaction mixture was dissolved by degassed acetonitrile (2 mL, 0.1 M for **1a**) and H_2O (0.4 mmol, 2.0 equiv). The reaction mixture was irradiating with 2 x 3W blue LEDs using our customized milligram scale reaction set up (as shown in Figure S2) under constant stirring condition at room temperature (20 ~ 30 °C). After addition reaction was completed, triethylamine (0.2 mmol, 1.0 equiv) was added to reaction mixture at room temperature. After 4 h, Amberlite® IR120 hydrogen form (1.5 g) and H_2O (0.2 mL) was added to reaction mixture at room temperature. After 2 h, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography with ethyl acetate/hexanes as the eluent to afford the corresponding α-cyano-γ-butyrolactone **5**.

2-oxo-4-phenyltetrahydrofuran-3-carbonitrile (5a). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5a** was obtained as a white liquid (27.8 mg, 74% yield, 3:1 dr); R_f = 0.50 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.27 (m, 5H), 4.75 (dd, *J* = 9.3, 8.0 Hz, 1H), 4.35 (dd, *J* = 10.3, 9.4 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.83 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 133.9, 129.8, 129.3, 127.0, 114.4, 72.3, 46.8, 39.4; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.27 (m, 5H), 4.71 – 4.63 (m, 2H), 4.12 (d, J = 8.5 Hz, 1H), 4.07 – 3.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 135.7, 129.6, 129.2, 127.3, 112.9, 73.1, 44.0, 39.3; FTIR (neat) : υ 702, 757, 1016, 1164, 1793, 2253, 2352, 2904 cm^{-1}.

2-amino-4-(p-tolyl)-4,5-dihydrofuran-3-carbonitrile (5b). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5b** was obtained as a white liquid (36.2 mg, 63% yield, 3:1 dr); R_f = 0.55 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.13 (m, 4H), 4.73 (dd, *J* = 9.3, 7.9 Hz, 1H), 4.32 (dd, *J* = 10.3, 9.3 Hz, 1H), 4.09 – 3.99 (m, 1H), 3.78 (d, *J* = 11.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 139.3, 130.8, 130.4, 126.8, 114.4, 72.3, 46.6, 39.5, 21.2; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 4H), 4.72 – 4.58 (m, 2H), 4.08 (d, *J* = 8.4 Hz, 1H), 4.03 – 3.95 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 139.1, 132.5, 130.3, 127.1,

112.9, 73.2, 43.7, 39.4, 21.3; FTIR (neat) : υ 498, 815, 1018, 1165, 1225, 1372, 1521, 1743, 1782, 2250, 2356, 2923 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{11}NO_2$ (M^+) 201.0790, found 201.0790.

4-(4-(tert-butyl)phenyl)-2-oxotetrahydrofuran-3-carbonitrile (5c). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5c** was obtained as a white solid (32.5 mg, 56% yield, >20:1 dr); Melting point: 128~130 ^oC; R_f = 0.57 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.31 – 7.22 (m, 2H), 4.76 (dd, *J* = 9.4, 8.0 Hz, 1H), 4.37 (dd, *J* = 10.3, 9.3 Hz, 1H), 4.09 (ddd, *J* = 11.9, 10.3, 7.9 Hz, 1H), 3.83 (d, *J* = 11.8 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 152.5, 130.7, 126.6, 126.5, 114.2, 72.2, 46.5, 39.4, 34.7, 31.2; FTIR (neat) : υ 521, 1221, 1367, 1745, 2331, 2365, 2965 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{15}H_{17}NO_2$ (M^+) 243.1259, found 243.1261.

4-([1,1'-biphenyl]-4-yl)-2-oxotetrahydrofuran-3-carbonitrile (5d). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5d** was obtained as a yellowish solid (35.4 mg, 79% yield, 4:1 dr); Melting point: 133~135 ^oC; R_f = 0.53 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.31 (m, 9H), 4.80 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.39 (dd, *J* = 10.2, 9.4 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.82 (d, *J* = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 142.4, 140.0, 132.8, 129.1, 128.5, 128.0, 127.4, 127.2, 114.2, 72.2, 46.7, 39.5; syn isomer (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.32 (m, 9H), 4.76 – 4.68 (m, 2H), 4.78 – 4.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 142.2, 140.1, 134.3, 132.7, 129.0, 128.3, 127.9, 127.8, 112.8, 73.0, 43.9, 39.2; FTIR (neat) : υ 700, 767, 841, 1020, 1157, 1225, 1366, 1487, 1742, 1788, 2361, 2919 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{17}H_{13}NO_2$ (M^+) 263.0946, found 263.2950.

4-(4-methoxyphenyl)-2-oxotetrahydrofuran-3-carbonitrile (5e). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5e** was obtained as a white solid (32 mg, 64% yield, 4.4:1); R_f = 0.50 (ethyl acetate:hexanes, 1:2); Melting point: 101~102 ^oC; anti isomer (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.99 – 6.91 (m, 2H), 4.72 (dd, J = 9.4, 7.9 Hz, 1H), 4.31 (dd, J = 10.3, 9.4 Hz, 1H), 4.08 – 3.96 (m, 1H), 3.82 (s, 3H), 3.73 (d, J = 11.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 160.2, 128.2, 125.7, 115.1, 114.3, 72.4, 55.5, 46.4, 39.7; syn isomer (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.68 – 4.60 (m, 2H), 4.16 – 3.93 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 160.1, 128.5, 127.4, 115.0, 112.9, 73.3, 55.4, 43.5, 39.5; FTIR (neat) : υ 836, 1017, 1163, 1228, 1372, 1512, 1743, 1782, 2315, 2364, 2917 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{11}NO_3$ (M^+) 217.0739, found 217.0741.

4-(4-fluorophenyl)-2-oxotetrahydrofuran-3-carbonitrile (5g). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5g** was obtained as a yellow liquid (42.3 mg, 50% yield, 3.4:1 dr); R_f = 0.50 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.08 (m, 4H), 4.75 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.32 (dd, *J* = 10.3, 9.4 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.77 (d, *J* = 11.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 163.1

(d, J = 249.2 Hz), 129.7 (d, J = 3.4 Hz), 128.8 (d, J = 8.3 Hz), 116.9 (d, J = 21.8 Hz), 114.1, 72.1, 46.3, 39.6; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.08 (m, 4H), 4.73 – 4.60 (m, 2H), 4.09– 4.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 163.0 (d, J = 249.0 Hz), 131.4 (d, J = 3.4 Hz), 129.2 (d, J = 8.4 Hz), 116.8 (d, J = 21.8 Hz), 112.7, 73.0, 43.4, 39.4; FTIR (neat) : υ 709, 833, 1018, 1165, 1242, 1512, 1604, 1789, 2252, 2908, 3610 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{11}H_8FNO_2$ (M^+) 205.0539, found 205.0537.

4-(4-chlorophenyl)-2-oxotetrahydrofuran-3-carbonitrile (5h).[6] Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5h** was obtained as a white solid (16.2 mg, 73% yield, 3.6:1 dr); R_f = 0.50 (ethyl acetate:hexanes, 1:2); Melting point: 114~115 ºC; anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.35 (m, 2H), 7.29 – 7.20 (m, 2H), 4.75 (dd, *J* = 9.3, 8.0 Hz, 1H), 4.32 (dd, *J* = 10.3, 9.3 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.79 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 135.4, 132.4, 130.1, 128.3, 114.0, 71.9, 46.3, 39.4; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.18 – 7.07 (m, 2H), 4.70 – 4.59 (m, 2H), 4.14 – 3.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 135.4, 129.9, 128.8, 128.7, 72.8, 43.5, 39.2; FTIR (neat) : υ 832, 1019, 1057, 1096, 1164, 1224, 1384, 1512, 1787, 2253, 2911 cm^{-1}.

4-(4-bromophenyl)-2-oxotetrahydrofuran-3-carbonitrile (5i). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5i** was obtained as a white liquid (31.8 mg, 60% yield, 4.4:1 dr); R_f = 0.55 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.51 (m, 2H), 7.24 – 7.12 (m, 2H), 4.76 (dd, J = 9.4, 8.0 Hz, 1H), 4.32 (dd, J = 10.2, 9.4 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.75 (d, J = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 2H), 7.23 – 7.14 (m, 2H), 4.72 – 4.59 (m, 2H), 4.13 – 3.93 (m, 2H); FTIR (neat) : υ 818, 1011, 1072, 1165, 1381, 1489, 1790, 2253, 2307 cm^{-1}.

4-(4-iodophenyl)-2-oxotetrahydrofuran-3-carbonitrile (5j). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5j** was obtained as a white liquid (25.0 mg, 40% yield, 8:1 dr); R_f = 0.55 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 2H), 7.12 – 6.99 (m, 2H), 4.75 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.31 (dd, *J* = 10.2, 9.4 Hz, 1H), 4.13 – 4.01 (m, 1H), 3.75 (d, *J* = 11.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 138.9, 133.6, 129.1, 128.8, 114.0, 71.8, 46.5, 39.2; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 2H), 7.12 – 6.99 (m, 2H), 4.71 – 4.58 (m, 2H), 4.11 – 3.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 168.6, 140.0, 138.8, 138.3, 128.2, 95.0, 72.7, 43.7, 39.0; FTIR (neat) : υ 818, 1011, 1065, 1157, 1381, 1142, 1489, 1790, 2253, 2910 cm^{-1}.

methyl 4-(4-cyano-5-oxotetrahydrofuran-3-yl)benzoate (5k). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5h** was obtained as a white liquid (27.3 mg, 70%

yield, 3.6:1 dr); R_f = 0.40 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.43 – 7.38 (m, 2H), 4.78 (dd, *J* = 9.3, 7.9 Hz, 1H), 4.37 (dd, *J* = 10.3, 9.3 Hz, 1H), 4.21 – 4.11 (m, 1H), 3.93 (s, 3H), 3.88 (d, *J* = 11.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 166.3, 140.5, 131.0, 130.9, 127.1, 114.1, 71.8, 52.5, 46.6, 39.1; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.37 – 7.32 (m, 2H), 4.78 – 4.65 (m, 2H), 4.19 – 4.05 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 166.4, 140.5, 131.1, 131.0, 127.4, 112.6, 72.6, 52.5, 43.9, 39.0; FTIR (neat) : υ 703, 771, 819, 857, 1017, 1113, 1161, 1289, 1433, 1613, 1721, 1793, 2253, 2905, 2954 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{13}H_{11}NO_4$ (M^+) 245.0688, found 245.0685.

4-(2-methoxyphenyl)-2-oxotetrahydrofuran-3-carbonitrile (5l). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5l** was obtained as a colorless liquid (35.3 mg, 69% yield, 3:1 dr); R_f = 0.45 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 1H), 7.20 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.03 – 6.93 (m, 2H), 4.66 (dd, *J* = 8.7 Hz, 1H), 4.47 (dd, *J* = 9.2 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.13 – 4.09 (m, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 157.5, 130.6, 130.0, 121.7, 121.5, 115.1, 111.5, 71.0, 55.5, 44.9, 36.3; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 1H), 7.13 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.04 – 6.94 (m, 2H), 4.75 – 4.68 (m, 1H), 4.51 – 4.47 (m, 1H), 4.17 – 4.05 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 157.3, 130.5, 129.2, 124.8, 121.2, 113.4, 72.4, 55.3, 40.2, 37.6; FTIR (neat) : υ 709, 756, 1018, 1119, 1165, 1249, 1388, 1465, 1496, 1597, 1782, 2252, 2839, 2908, 2978 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{11}NO_3$ (M^+) 217.0739, found 217.0741.

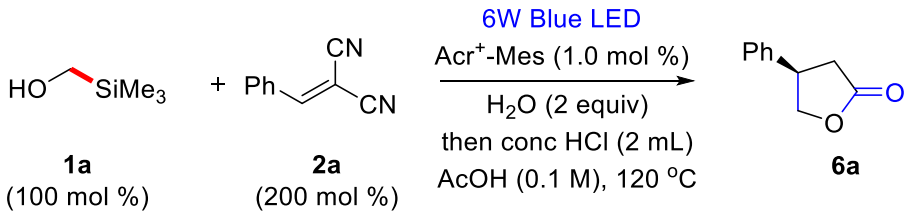
4-(3-methoxyphenyl)-2-oxotetrahydrofuran-3-carbonitrile (5m). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5m** was obtained as a white solid (35.3 mg, 70% yield, 3.6:1 dr); R_f = 0.45 (ethyl acetate:hexanes, 1:2); Melting point: 109~110 ºC; anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 1H), 6.94 – 6.77 (m, 3H), 4.73 (dd, *J* = 9.4, 8.0 Hz, 1H), 4.33 (dd, *J* = 10.3, 9.3 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.83 (s, 3H), 3.80 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 160.5, 135.5, 130.9, 118.9, 114.4, 114.2, 113.2, 72.2, 55.5, 46.8, 39.3; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 1H), 6.95 – 6.77 (m, 3H), 4.71 – 4.62 (m, 2H), 4.11 (d, *J* = 8.7 Hz, 1H) 4.02 – 3.95 (m, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 160.3, 137.2, 130.8, 119.3, 113.4, 112.9, 73.1, 55.4, 44.0, 39.2; FTIR (neat) : υ 694, 787, 864, 1018, 1165, 1265, 1496, 1604, 1790, 2252, 2908 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{12}H_{11}NO_3$ (M^+) 217.0739, found 217.0739.

4-(1,1-dicyano-3-hydroxypropan-2-yl)-2-methoxyphenyl acetate (5o). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5o** was obtained as a yellow liquid (35.3 mg, 54% yield, 5:1 dr); R_f = 0.20 (ethyl acetate:hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 7.04 (m, 1H), 6.91 – 6.81 (m, 2H), 4.74 (dd, J = 9.4, 8.0 Hz, 1H), 4.34 (dd, J = 10.2, 9.4 Hz, 1H), 4.05 (ddd, J = 10.9, 10.1, 7.9 Hz, 1H), 3.85 (s, 3H), 3.79 (d, J = 11.7 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 167.3, 152.1, 140.4, 132.9, 124.1,

118.8, 114.3, 111.3, 72.0, 56.2, 46.7, 39.5, 20.8; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.47 (dd, *J* = 9.5, 7.1 Hz, 1H), 4.19 (dd, *J* = 9.5, 8.1 Hz, 1H), 3.71 (d, *J* = 8.4 Hz, 1H), 2.53 (dddd, *J* = 8.3, 7.1 Hz, 1H), 2.14 – 2.00 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 167.8, 151.9, 134.2, 124.0, 119.6, 112.8, 111.5, 72.9, 56.2, 44.1, 39.1, 31.1; FTIR (neat) : υ 1018, 1126, 1165, 1203, 1273, 1373, 1427, 1458, 1512, 1604, 1651, 1782, 2252, 2916, 3741cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{14}H_{13}NO_5$ (M^+) 275.0794, found 275.0796.

4-isopropyl-2-oxotetrahydrofuran-3-carbonitrile (5p). Following the general procedure using 20% ethyl acetate in hexanes as eluant, **5p** was obtained as a colorless liquid (35.3 mg, 54% yield, 5:1 dr); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (dd, *J* = 9.3, 8.0 Hz, 1H), 3.98 (dd, *J* = 10.0, 9.4 Hz, 1H), 3.40 (d, *J* = 11.4 Hz, 1H), 2.69 (dddd, *J* = 11.4, 10.0, 8.3 Hz, 1H), 1.82 (dhept, *J* = 8.5, 6.7 Hz, 1H), 1.14 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 115.4, 71.1, 48.2, 36.4, 31.4, 20.6, 19.8; syn isomer (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.47 (dd, *J* = 9.5, 7.1 Hz, 1H), 4.19 (dd, *J* = 9.5, 8.1 Hz, 1H), 3.71 (d, *J* = 8.4 Hz, 1H), 2.53 (dddd, *J* = 8.3, 7.1 Hz, 1H), 2.14 – 2.00 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 112.7, 70.9, 45.4, 36.1, 28.9, 21.3, 18.7; FTIR (neat) : υ 709, 1018, 1172, 1227, 1389, 1466, 1789, 2252, 2901, 2963 cm^{-1}.

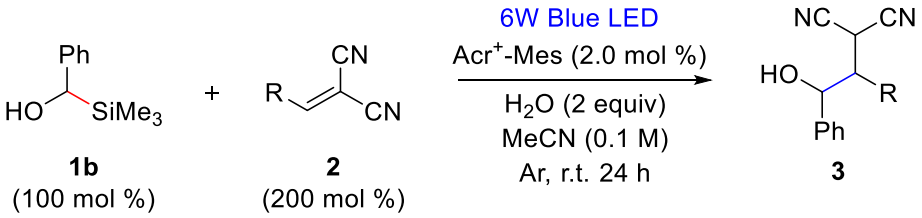
D. Procedure and characterization data of γ-butyrolactone 6a[7]



To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged wit h $TMSCH_2OH$ **1a** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (0.82 mg, 0.002 mmol, 1.0 mol %) under arg on atmosphere. The reaction mixture was dissolved by degassed acetonitrile (2 mL, 0.1 M for **1a**) and H_2O (0.4 mmol, 2.0 equiv). The reaction mixture was irradiating with 2 x 3W blue LEDs using our customized milligram scale reaction set up (as shown in Fig ure S2) under constant stirring condition at room temperature (20 ~ 30 ℃). After additio n reaction was completed, conc. HCl (2.0 mL) and acetic acid (2.0 mL, 0.1 M for **1a**) were added to reaction mixture at 120 ℃. After 12 h, the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL) and the mixture was extracted with ethyl acetate (three times),

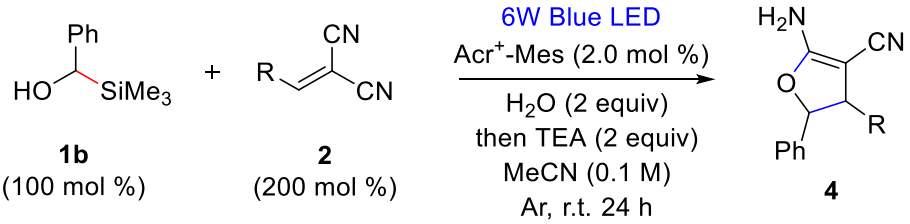
dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with 10% ethyl acetate in hexanes as eluent. The product **6a** was obtained as a white solid in the yield of 75% (24.3 mg). R_f = 0.60 (ethyl acetate:Hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 7.26 – 7.24 (m, 2H), 4.67 (dd, *J* = 9.0, 7.9 Hz, 1H), 4.27 (dd, *J* = 9.0, 8.0 Hz, 1H), 3.80 (dddd, *J* = 8.3 Hz, 1H), 2.93 (dd, *J* = 17.5, 8.7 Hz, 1H), 2.68 (dd, *J* = 17.5, 9.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.54, 139.48, 129.21, 127.79, 126.79, 74.14, 41.17, 35.78.

E. Procedure and characterization data of controllable one-pot reaction with 2nd α-silyl alcohol 1b



2-(2-hydroxy-1, 2-diphenylethyl)malononitrile (3ba). To a re-sealable pressure tube (13 x 1 00 mm) with a magnetic stir bar was charged with 2nd α-silyl alcohol **1b** (0.2 mmol, 1.0 equiv), benzalmalonitrile **2a** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridinium perc hlorate (Acr^+-Mes) (1.64 mg, 0.004 mmol, 2.0 mol %) under argon atmosphere. The reac tion mixture was dissolved by degassed acetonitrile (2 mL, 0.1 M for **1b**) and H_2O (0.4 mmol, 2.0 equiv). The reaction mixture was irradiating with 2 x 3W blue LEDs using o ur customiszed milligram scale reaction set up (as shown in Figure S2) under constant st irring condition at room temperature (20 ~ 30 °C). After the reaction was completed, the solvent was removed under reduced pressure and residue was purified by silica gel colu mn chromatography with 1% formic acid contained 10% ethyl acetate in hexanes as elue nt. Coupling product **3ba** was obtained as a colorless liquid in the yield of 71% (37.2 mg, 1.37:1 dr). R_f = 0.47 (ethyl acetate:Hexanes, 1:2); (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H), 7.28 – 7.12 (m, 5H), 5.16 (d, *J* = 10.3 Hz, 1H), 4.77 (d, *J* = 4.5 Hz, 1H), 3.46 (dd, *J* = 10.4, 4.4 Hz, 2H), 2.43 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 133.9, 129.3, 129.1, 128.9, 128.8, 126.8, 112.4, 112.2, 74.6, 53.5, 26.7; (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.25 – 7.12 (m, 5H), 5.33 (d, *J* = 6.1 Hz, 1H), 4.15 (d, *J* = 8.3 Hz, 1H), 3.41 (dd, *J* = 8.4, 6.1 Hz, 1H), 2.43 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 133.1, 129.3, 129.1, 129.0, 128.7, 126.3, 112.3, 111.9, 73.7, 53.6, 26.9; FTIR(neat) : υ 701, 754, 1033, 1172, 1273, 1428, 1477, 1496, 1592, 1654, 2185, 2363, 3351 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{17}H_{14}N_2O$ (M^+) 262.1106, found 262.1108. 275.0796.

2-(2-hydroxy-2-phenyl-1-(p-tolyl)ethyl)malononitrile (3bh). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **3bh** was obtained as a green liquid (38.6mg, 65% yield, 1.1:1dr); R_f= 0.45 (ethyl acetate:hexanes, 1:2); (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.10 (m, 9H), 5.37 (d, *J* = 5.5 Hz, 1H), 4.23 (d, *J* = 8.8 Hz, 1H), 3.43 (dd, *J* = 9.0, 5.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 135.3, 131.6, 130.7, 129.2, 129.0, 129.0, 126.1, 112.1, 111.8, 73.4, 53.1, 26.8; (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.10 (m, 9H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.82 (d, *J* = 4.4 Hz, 1H), 3.52 – 3.46 (dd, *J* = 10.1, 4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 135.2, 132.3, 130.2, 129.4, 129.1, 128.9, 126.8, 112.2, 112.0, 74.5, 52.9, 26.6; FTIR(neat) : υ 525, 895, 1219, 1366, 1435, 1736, 2970, 3009, 3456 cm^{-1}

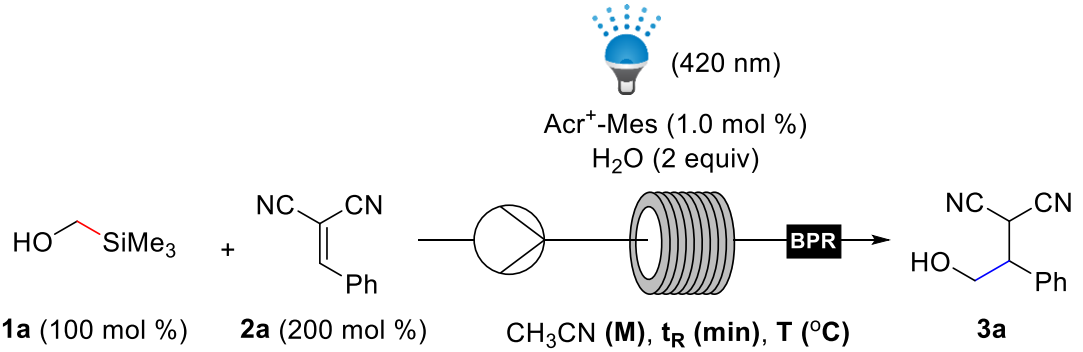


2-amino-4, 5-diphenyl-4, 5-dihydrofuran-3-carbonitrile (4ba). To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with 2nd α-silyl alcohol **1b** (0.2 m mol, 1.0 equiv), benzalmalonitrile **2a** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridi nium perchlorate (Acr^+-Mes) (1.64 mg, 0.004 mmol, 2.0 mol %) under argon atmosphere. The reaction mixture was dissolved by degassed acetonitrile (2 mL, 0.1 M for **1b**) and H_2O (0.4 mmol, 2.0 equiv). The reaction mixture was irradiating with 2 x 3W blue LED s using our customized milligram scale reaction set up (as shown in Figure S2) under co nstant stirring condition at room temperature (20 ~ 30 ℃). After the reaction was completed, triethylamine (0.2 mmol, 1.0 equiv) was added to reaction mixture at room temperature. After 4 h, the solvent was removed under reduced pressure and residue was p urified by silica gel column chromatography with 10% ethyl acetate in hexanes as eluent. 2, 3-dihydrofuran **4ba** was obtained as a green liquid in the yield of 68% (35.6 mg, 1.66:1 dr). R_f = 0.47 (ethyl acetate:Hexanes, 1:2); (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 7H), 7.13 – 6.99 (m, 2H), 6.96 – 6.83 (m, 1H), 5.33 (d, *J* = 6.9 Hz, 1H), 4.95 (bs, 2H), 4.30 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 137.5, 135.4, 128.7, 128.1, 128.0, 128.0, 127.3, 118.7, 88.9, 57.7, 53.0; (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 7H), 7.13 – 6.99 (m, 2H), 6.96 – 6.83 (m, 1H), 5.93 (d, *J* = 8.9 Hz, 1H), 5.02 (bs, 2H), 4.54 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 141.0, 139.1, 129.2, 129.1, 129.1, 128.0, 127.6, 125.9, 118.7, 92.8, 56.7, 53.0; FTIR (neat) : υ 702, 763, 1026, 1172, 1265, 1435, 1496, 1597, 1658, 1782, 2183, 2924, 3032, 3224, 3348 cm^{-1}; HRMS *m/z* (EI) : calcd. For $C_{17}H_{14}N_2O$ (M^+) 262.1106, found 262.1108. 275.0796.

2-amino-4-(4-chlorophenyl)-5-phenyl-4,5-dihydrofuran-3-carbonitrile (4bh). Following the general procedure using 33% ethyl acetate in hexanes as eluant, **4bh** was obtained as a green liquid (35.6mg, 60% yield, 1.1:1dr); R_f = 0.45 (ethyl acetate:hexanes, 1:2); (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 6.73 (m, 9H), 5.28 – 5.22 (m, 3H), 4.27 (d, *J* = 7.2 Hz, 1H); NMR (75 MHz, $CDCl_3$) δ 167.5, 139.4, 136.3, 133.6, 129.3, 129.1, 129.0, 128.2, 125.8, 118.7, 92.5, 56.2, 56.0; (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 6.73 (m, 9H), 5.91 (d, J = 8.9 Hz, 1H), 5.20 (s, 2H), 4.51 (d, J = 8.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 138.7, 135.1, 132.9, 130.0, 129.0, 128.1, 128.0, 126.2, 119.0, 88.3, 56.5, 52.4; FTIR (neat) : υ 509, 548, 617, 702, 733, 833, 910, 1018, 1095, 1211, 1265, 1358, 1435, 1489, 1589, 1659, 2183, 2931, 3032, 3170, 3217, 3279, 3341, 3456 cm^{-1}

VI. Optimization and procedure for controllable synthesis of diverse scaffolds in continuous flow processes

Table S3. Optimization table for photoredox catalyzed Giese reaction in continuous flow process[a]



entry	reactor size (mL)	t_R (min)	flow rate (uL/min)	T (°C)	c (M)	yield (%)[b]
1	5	15	333	30	0.1	75
2	5	30	167	30	0.1	79
3	5	50	100	30	0.1	78
4	5	15	333	50	0.3	57
5	5	15	333	50	0.1	88
6	5	15	333	80	0.1	93
7	**10**	**15**	**667**	**80**	**0.1**	**97 (98)[b]**
8	10	10	1000	80	0.1	86
9	10	5	2000	80	0.1	65

[a]Yields determined by ^{1}H-NMR analysis of the crude reaction mixture using 1,3-benzodioxole as the internal starndard, [b]isolated yield (0.5 mmol scale).

The homogenous reaction solution in the presence of photocatalyst, Acr$^+$-Mes (1 mol %), was pumped through the reactor at a flow rate 333 μL min^{-1} (residence time of 15 min), irradiating with a 420 nm LED lamp with flow wizard program, delivering the corresponding alcohol **3a** in 75% ^{1}H NMR yield. Although there was no significant improvement seen with longer residence time (Table S3, entry 2 and 3), a modest increase in temperature improved the yield to 93% with same residence time of 15 min (Table S3, entry 5 and 6). To provide the same amount of alcohol product **3a** in a shorter collection time, a higher concentration (0.3 M) was conducted (Table S3, entry 4). However, the yield of desired product was decreased from 88% to 57% due to decreased photon concentration by higher absorbance of reaction mixture at the higher concentration based on the Beer-Lambert law. Further variation in wavelength of visible light, such as 450 nm, and residence time (Table S3, entry 7-9) did not avail further improvement. Finally, the desired alcohol **3** was isolated in 98% yield on a 0.5 mmol scale with the extremely shorter residence time of 15 min (Table S3, entry 7) compared to the reaction in batch on a 0.2 mmol scale with 4 hours.

A. Procedure for synthesis of alcohol 3a in continuous flow process

(Optimal conditions on 0.5 mmol scale, Table S3, entry 7)

A screw-cap reaction tube (20 mm × 150 mm, Fisher Scientific, part # 14-959-37C) was capped with a Teflon/silicone septum screw cap (Fisher Scientific, part # 033407G) and insert (Fisher Scientific, part # 03394B). The reaction tube was charged with benzalmalononitrile **2a** (462 mg, 3.0 mmol, 2 equiv), 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (6.2 mg, 0.015 m mol, 1.0 mol %). The reaction tube was recapped, the septum was punctured with a needle attached to a Schlenk line, and the tube was evacuated and backfilled with nitrogen (This process was repeated a total of three times). Degassed acetonitrile (15 mL) was added, followed by $TMSCH_2OH$ **1a** (0.2 mL, 1.5 mmol, 1 equiv) and HPLC water (54 uL, 3.0 mmol, 2 equiv) via syringe.

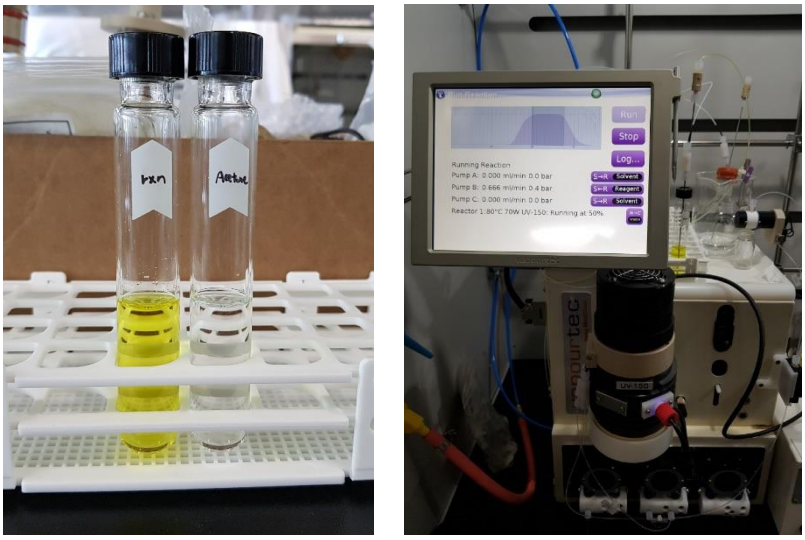
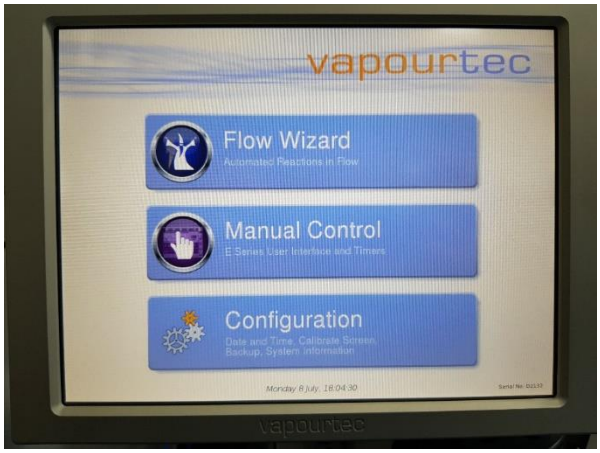


Figure S3. Measurement method for the total volume of the reaction mixture (left), A Vapourtec E series flow reactor fitted with a UV-150 photoreactor (10 mL) (right)

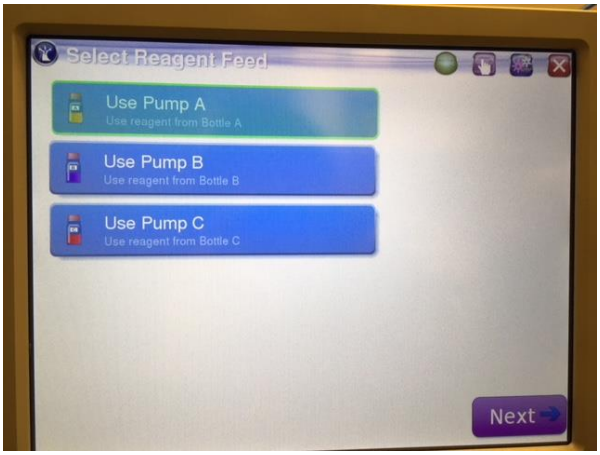
The total volume of the reaction mixture was measured by adding acetone via syringe to a reaction tube of the same size until the same level as the reaction mixture was reached. *[Note: The error range is estimated to be less than 0.2 mL]* (Figure S3, left). The reaction mixture was placed on top of the Vapourtec E-series. Nitrogen gas was connected to the reaction mixture with the organometallic chemistry kit. The UV-150 photoreactor (10 mL) was washed with degassed acetonitrile (Figure S3, right).

Step by step guide for using the software



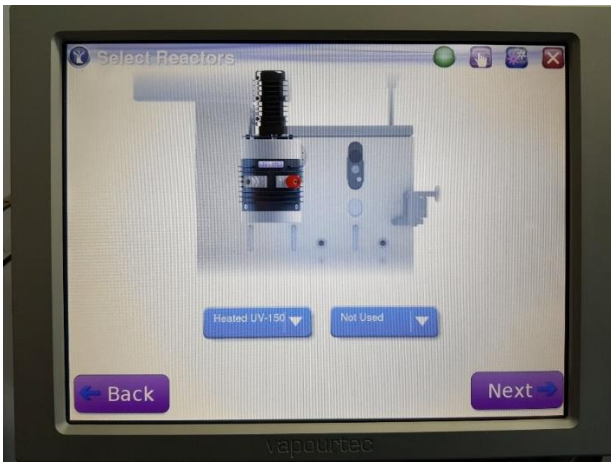
1. The manual control is selected by choosing the second option from the first menu loaded.

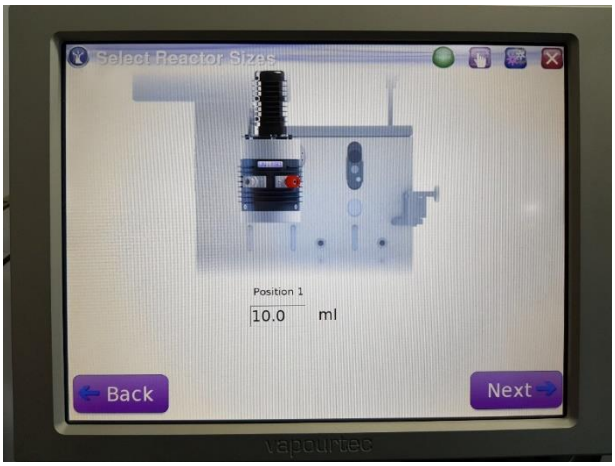
2. Press the “prime” button to inject 0.55 mL of the reaction solution before running the reaction.



3. Go back to the initial menu loaded, and select the flow wizard by choosing the first option.

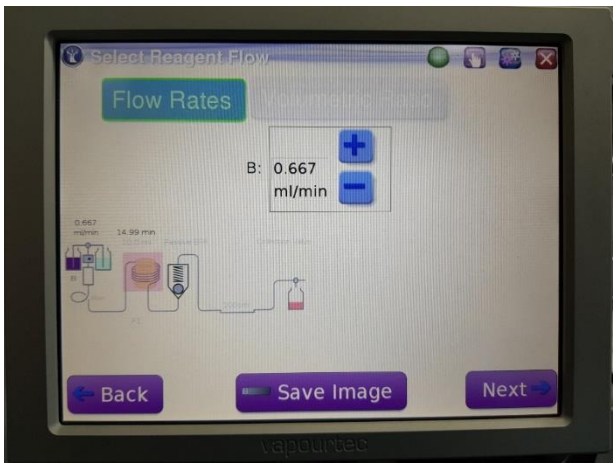
4. The first screen asks which pumps are to be used for the reaction. Press the button for “Use Pump A”, and press next

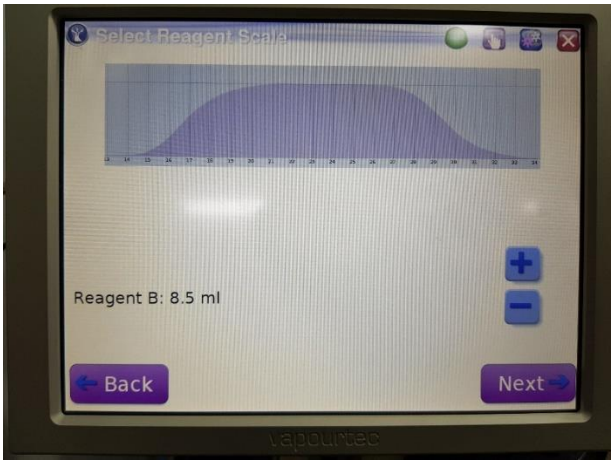




5. The next screen allows one or two reactors to be configured. Push the button for the left position and choose the heated UV-150 reactor.

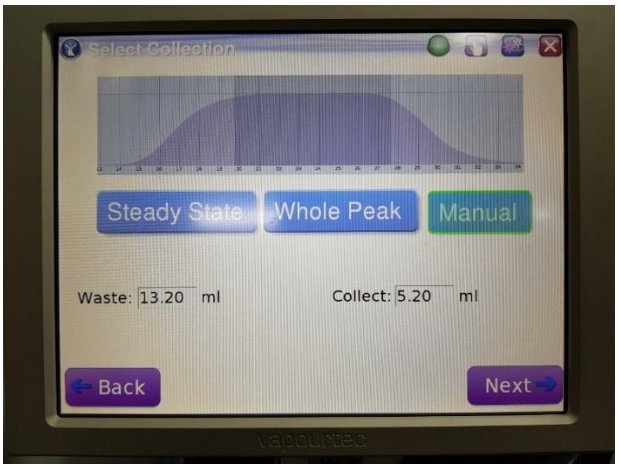
6. Set the reactor volume (10 mL).

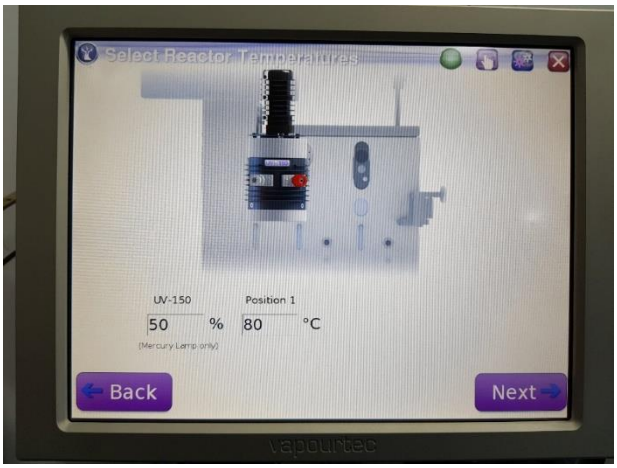




7. The interface then displays a diagram showing the equipment that has been specified. Subsequently, set the flow rate (0.667 mL/min).

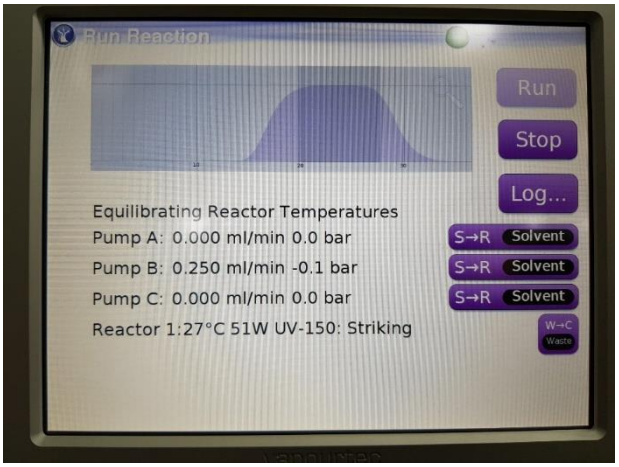
8. Press the button to set the scale of the reaction (8.5 mL). *[Note: the diagram shows a prediction of the dispersion with respect to time]*





9. Using this dispersion prediction, the system offers three choices. Press the button for manual, and select the specific scale for collection. The grey colored selected range could be adjusted by changing the volume of waste.

10. The power of UV-150 does not need to be adjusted (left). Set the desired temperature (80 ºC).



11. Hit “Run” to begin the reaction.

The reaction solution was pumped through the 10 mL of tubing reactor at 80 ºC with a flow rate of 667 μL min^{-1} (residence time of 15 min), irradiating with a 420 nm LEDs lamp with the flow wizard program. After the reaction solution had entered the reactor, it was followed with degassed acetonitrile at the same flow rate. 0.5 mmol of the crude reaction mixture was collected in a 20 mL vial. After the reaction was completed, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography with 1% formic acid contained 33% ethyl acetate/hexanes as the eluent, **3a** was obtained as a colorless liquid (91.7 mg, 98% yield); R_f = 0.40 (ethyl aceate:hexanes, 1:2) *[Note: The calibration of the pump tubing is required before the use for the accuracy]*

- Total volume of the reaction mixture: 15.6 mL (1.5 mmol)

- Injection volume of the reaction mixture: 8.5 mL

- Collected volume of the crude residue from steady state: 5.20 mL (0.5 mmol)

- Flow rate: 667 μL min^{-1}

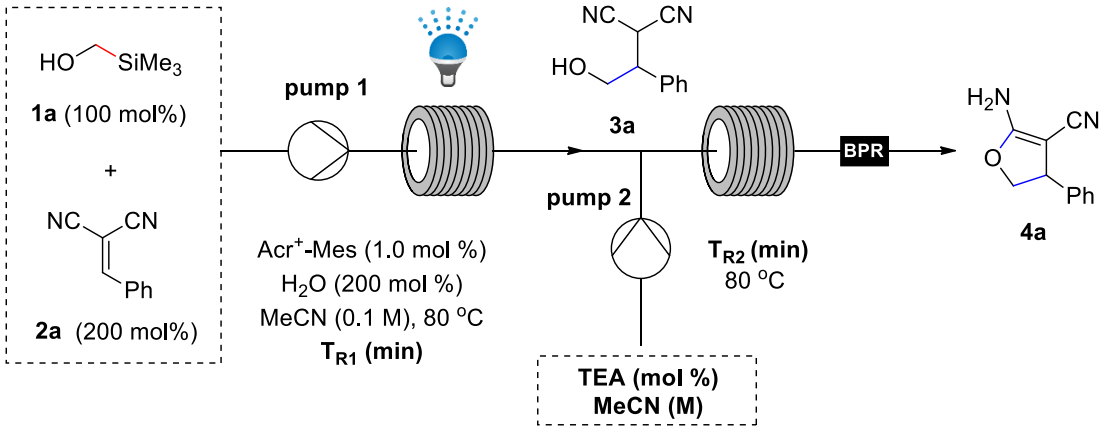
- Residence time: 15 min

[Note: Back pressure regulator (0.1 bar) was used due to the volatility of acetonitrile at 80 ºC]

B. Optimization and procedure for controllable synthesis of 2,3-dihydrofuran 4a in continuous flow process

For scaffold diversity, further transformation in the presence of 200 mol % of Et_3N as a base after a visible-light-mediated Giese reaction was conducted in continuous flow process. Variation in residence time of 2nd reactor was explored, and 25 min of the residence time was deemed optimal (Table S4, entry 1–3). Under these optimal conditions, lower loadings of Et_3N were also conducted (Table S4, entry 4 and 5), the desired product **4a** was obtained in 88% yield with the use of 150 mol % of Et_3N. Finally, **4a** was isolated in 93% yield by increasing residence time of both reactor 1 and 2 (Table S4, entry 6).

Table S4. Optimization for controllable synthesis of 2,3-dihydrofuran **4a** in a continuous flow process[a]



entry	t_R (min)	flow rate (uL/min)	t_R (min)	flow rate (uL/min)	TEA (mol %)	c (M)	BPR (bar)	yield of **3a** (%)[a]	yield of **4a** (%)[a]
1	15	667	15	667	200	0.20	3.9	49	51
2	15	667	20	333	200	0.40	3.6	22	78
3	**15**	**667**	**25**	**133**	**200**	**1.00**	**3.0**	**trace**	**95 (95)[b]**
4	15	667	25	133	120	0.60	3.4	18	82
5	15	667	25	133	150	0.75	3.4	12	88
6	**18**	**555**	**30**	**111**	**150**	**0.75**	**3.9**	**trace**	**93 (93)[b]**

[a]Yields determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3-benzodioxole as the internal standard; [b]isolated yield (0.5 mmol scale).

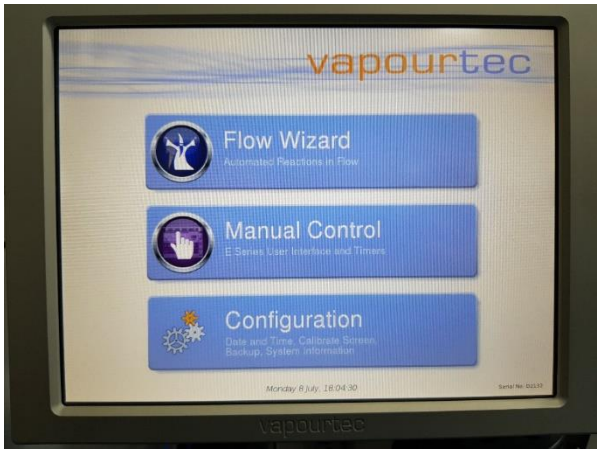
(Optimal conditions on 0.5 mmol scale, Table S4, entry 6)

A screw-cap reaction tube (20 mm × 150 mm, Fisher Scientific, part # 14-959-37C) was capped with a Teflon/silicone septum screw cap (Fisher Scientific, part # 033407G) and insert (Fisher Scientific, part # 03394B).

The 1st reaction tube was charged with benzalmalononitrile **2a** (462 mg, 3.0 mmol , 2 equiv), 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (6.2 mg, 0.015 mmol, 1.0 mol %). The reaction tube was recapped, the septum was punctured with a needle attached to a Schlenk line, and the tube was evacuated and backfilled with nitrogen (This process was repeated a total of three times). Degassed acetonitrile (15 mL) was added, followed by $TMSCH_2OH$ **1a** (0.2 mL, 1.5 mmol, 1 equiv) and HPLC water (54 uL, 3.0 mmol, 2 equiv) via syringe.

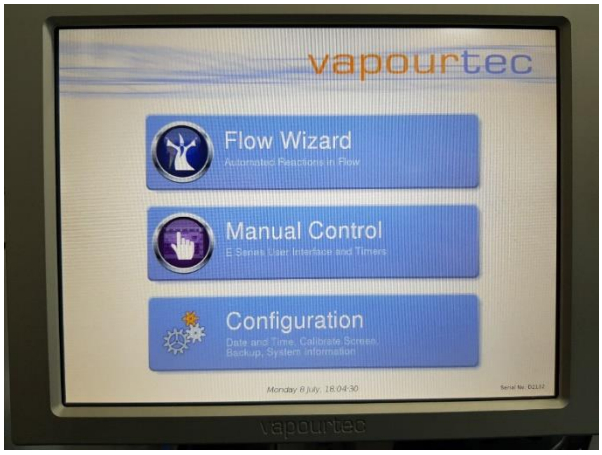
The 2nd reaction tube was charged with Et_3N (1.05 mL, 7.5 mmol). The reaction tube was recapped, the septum was punctured with a needle attached to a Schlenk line, and the tube was evacuated and backfilled with nitrogen (This process was repeated a total of three times).To afford 0.75 M of reaction solution, degassed acetonitrile (10 mL) was added via syringe.

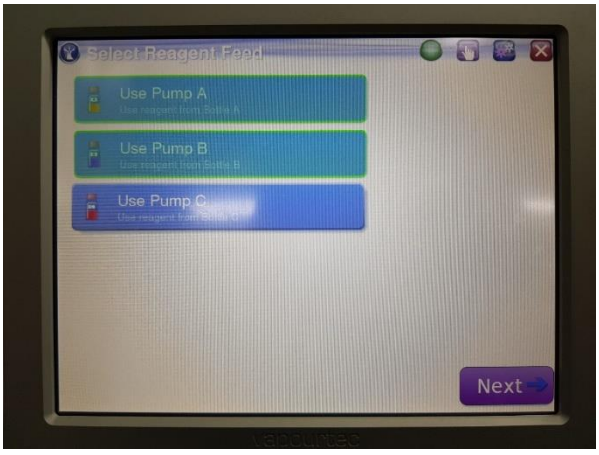
Step by step guide for using the software



1. The manual control is selected by choosing the second option from the first menu loaded.

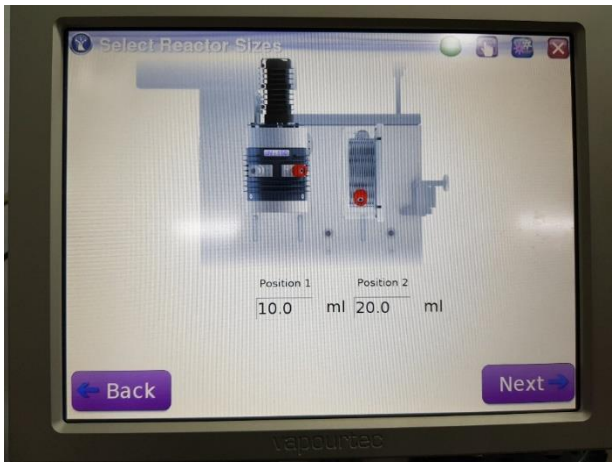
2. Press the “prime” button to inject 0.55 mL of the reaction solution before running the reaction.

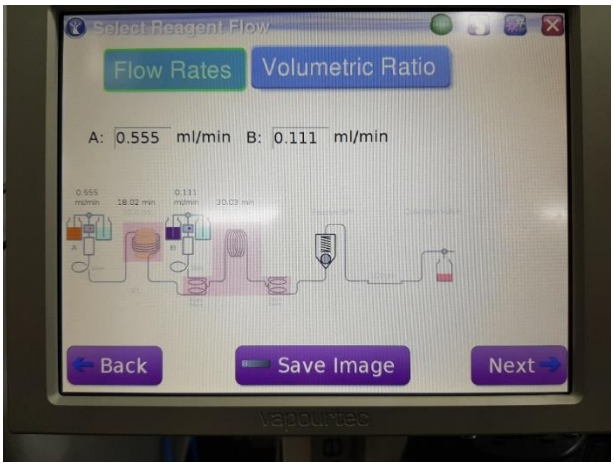




3. Go back to the initial menu loaded, and select the flow wizard by choosing the first option.

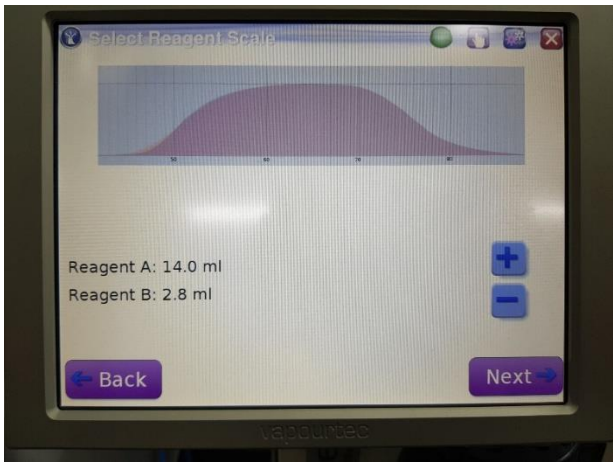
4. The first screen asks which pumps are to be used for the reaction. Press the button for “Use Pump A and B”, and press next

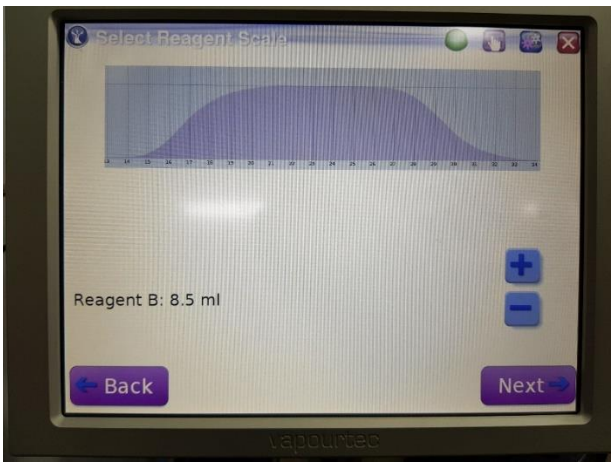




5. The next screen allows two reactors to be configured. Push the button for the left position and choose the heated UV-150 reactor. Also push the button for the right position and choose the mixer reactor. And set the reactor volumes (10 mL for position 1 and 20 mL for position 2, respectively).

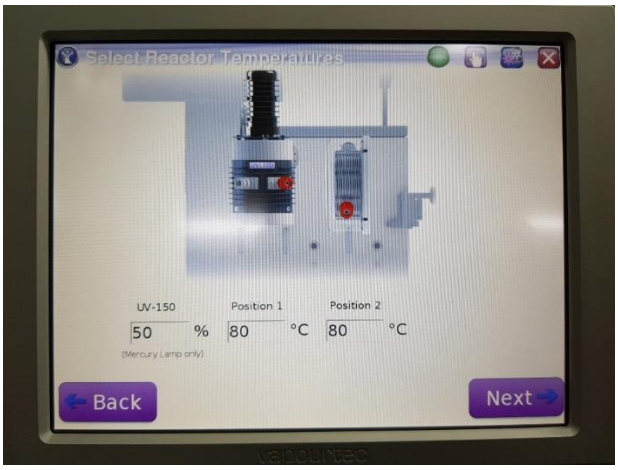
6. The interface then displays a diagram showing the equipment that has been specified. Subsequently, set the flow rate (0.555 mL/min for pump A and 0.111 mL/min for pump B, respectively).

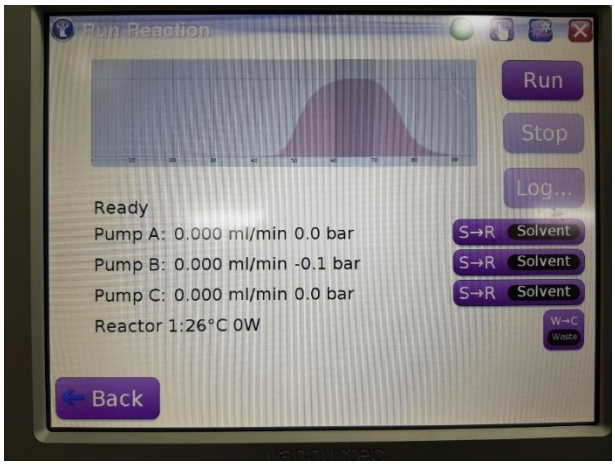




7. Press the button to set the scale of the reaction. *[Note: the diagram shows a prediction of the dispersion with respect to time]*

8. Using this dispersion prediction, the system offers three choices. Press the button for manual, and select the specific scale for collection. The grey colored selected range could be adjusted by changing the volume of waste.

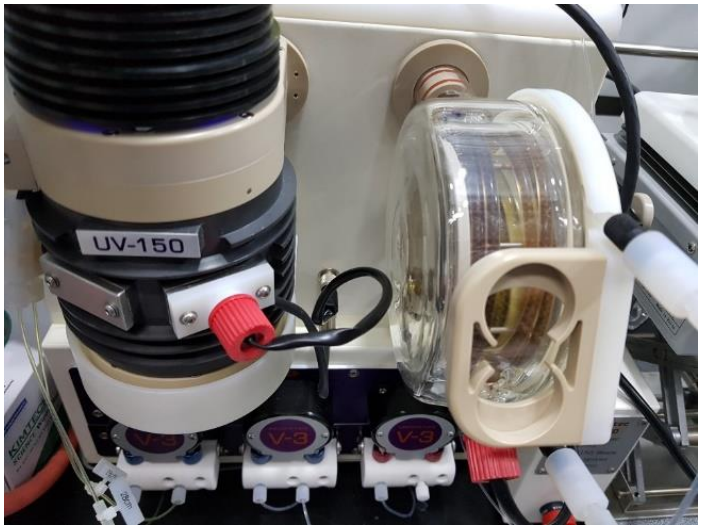




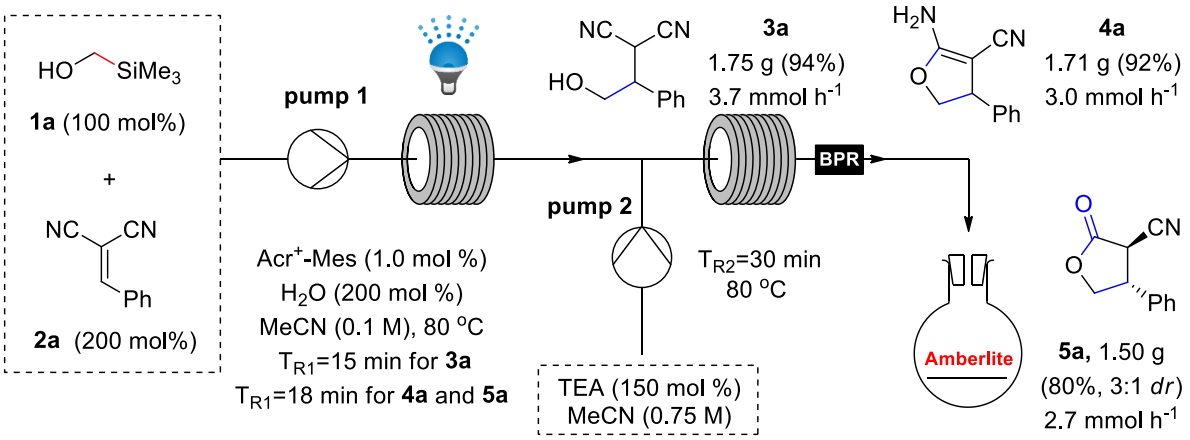
9. The power of UV-150 does not need to be adjusted (left). Set the desired temperature (80 ºC for both position 1 and 2).

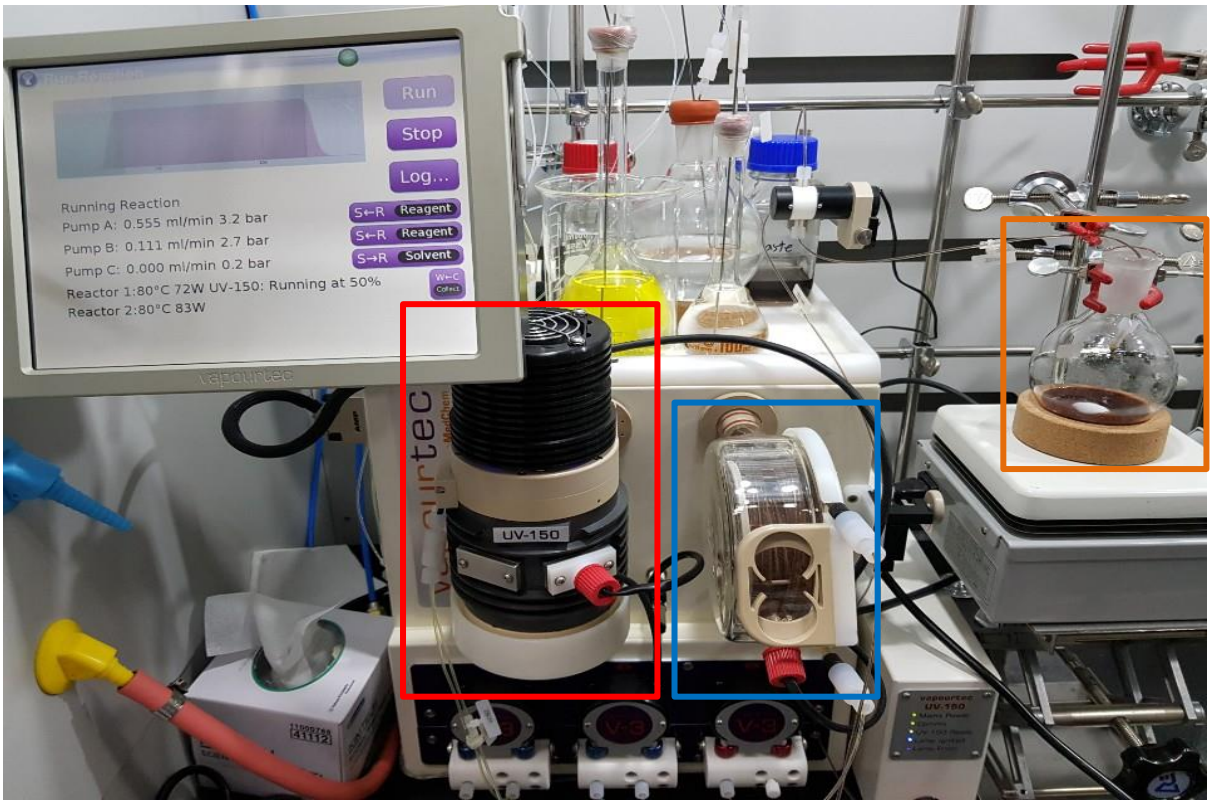
10. Hit "Run" to begin the reaction.

After the 1st reaction solution had entered the reactor 1 (UV-150 photoreactor), followed by reactor 2 (large diameter tubular reactor for rapid mixing) with the 2nd reaction solution of Et_3N (0.75 M in degassed acetonitrile), it was followed with degassed acetonitrile at the same flow rate. 0.5 mmol of the crude reaction mixture (6.02 mL) was collected in a 20 mL vial. After the reaction was completed, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography with 33% ethyl acetate/hexanes as the eluent, **4a** was obtained as a white solid (86.5 mg, 93% yield); R_f = 0.40 (ethyl aceate:hexanes, 1:2) *[Note: The calibration of the pump tubing is required before the use for the accuracy, And back pressure regulator (3.9 bar) was used due to the volatility of acetonitrile and Et_3N at 80 ºC]*



C. Controllable synthesis for diverse scaffolds in a continuous flow process on 10 mmol scale





(Controllable Synthesis of alcohol 3a in continuous flow process on 10 mmol scale)

A 200 mL of volumetric flask was capped with a septum. The reaction flask was charged with benzalmalononitrile **2a** (6.16 g, 40 mmol, 2 equiv), 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (82.4 mg, 0.2 mmol, 1.0 mol %). The reaction flask was recapped, the septum was punctured with a needle attached to a Schlenk line, and the flask was evacuated and backfilled

with nitrogen (This process was repeated a total of three times). Degassed acetonitrile (100 mL) was added, followed by $TMSCH_2OH$ **1a** (2.60 mL, 20 mmol, 1 equiv) and HPLC water (0.72 mL, 40 mmol, 2 equiv) via syringe. To afford 0.1 M of reaction solution, degassed acetonitrile was added to scale of 200 mL of volumetric flask. The reaction solution was pumped through the 10 mL of tubing reactor at 80 °C with a flow rate of 667 μL min^{-1} (residence time of 15 min), irradiating with a 420 nm LEDs lamp with the flow wizard program. After the reaction solution had entered the reactor, it was followed with degassed acetonitrile at the same flow rate. 10 mmol of the crude reaction mixture (100 mL) was collected in a 250 mL of round bottom flask. After the reaction was completed, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography with 1% formic acid contained 33% ethyl acetate/hexanes as the eluent, **3a** was obtained as a colorless liquid (1.75 g, 94% yield); R_f = 0.40 (ethyl aceate:hexanes, 1:2) *[Note: The calibration of the pump tubing is required before the use for the accuracy. And back pressure regulator (0.1 bar) was used due to the volatility of acetonitrile at 80 °C]*

(Controllable Synthesis of 2,3-dihydrofuran 4a in continuous flow process on 10 mmol scale)

For the 1st reaction solution, a 250 mL of volumetric flask was capped with a septum. The reaction flask was charged with benzalmalononitrile **2a** (7.70 g, 50 mmol, 2 equiv), 9-mesityl-10-methyla cridinium perchlorate (Acr^+-Mes) (103.0 mg, 0.25 mmol, 1.0 mol %). The reaction flask was recapped, the septum was punctured with a needle attached to a Schlenk line, and the flask was evacuated and backfilled with nitrogen (This process was repeated a total of three times). Degassed acetonitrile (150 mL) was added, followed by $TMSCH_2OH$ **1a** (3.24 mL, 25 mmol, 1 equiv) and HPLC water (0.90 mL, 50 mmol, 2 equiv) via syringe. To afford 0.1 M of reaction solution, degassed acetonitrile was added to scale of 250 mL of volumetric flask via syringe.

For the 2nd reaction solution, a 100 mL of volumetric flask was charged with Et_3N (10.45 mL, 75 mmol). The reaction flask was recapped, the septum was punctured with a needle attached to a Schlenk line, and the flask was evacuated and backfilled with nitrogen (This process was repeated a total of three times). To afford 0.75 M of reaction solution, degassed acetonitrile was added to scale of 100 mL of volumetric flask via syringe.

After the 1st reaction solution had entered the reactor 1 (UV-150 photoreactor), followed by reactor 2 (large diameter tubular reactor for rapid mixing) with the 2nd reaction solution of Et_3N (0.75 M in degassed acetonitrile), it was followed with degassed acetonitrile at the same flow rate. 10 mmol of the crude reaction mixture (120.48 mL) was collected in a 250 mL of round bottom flask. After the reaction was completed, the solvent was removed under reduced pressure and residue

was purified by silica gel column chromatography with 33% ethyl acetate/hexanes as the eluent, **4a** was obtained as a white solid (1.71 g, 92% yield); R_f = 0.40 (ethyl aceate:hexanes, 1:2) *[Note: The calibration of the pump tubing is required before the use for the accuracy, And back pressure regulator (3.9 bar) was used due to the volatility of acetonitrile and Et_3N at 80 °C]*

(Controllable Synthesis of α-cyano-γ-butyrolactone 5a in continuous flow process on 10 mmol scale)

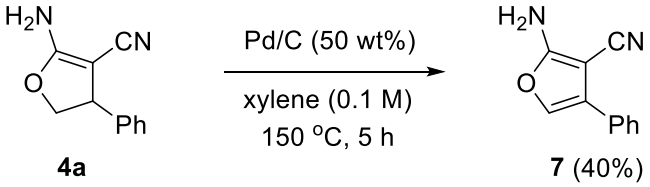
For the 1st reaction solution, a 250 mL of volumetric flask was capped with a septum. The reaction flask was charged with benzalmalononitrile **2a** (7.70 g, 50 mmol, 2 equiv), 9-mesityl-10-methyla cridinium perchlorate (Acr^+-Mes) (103.0 mg, 0.25 mmol, 1.0 mol %). The reaction flask was recapped, the septum was punctured with a needle attached to a Schlenk line, and the flask was evacuated and backfilled with nitrogen (This process was repeated a total of three times). Degassed acetonitrile (150 mL) was added, followed by $TMSCH_2OH$ **1a** (3.24 mL, 25 mmol, 1 equiv) and HPLC water (0.90 mL, 50 mmol, 2 equiv) via syringe. To afford 0.1 M of reaction solution, degassed acetonitrile was added to scale of 250 mL of volumetric flask via syringe.

For the 2nd reaction solution, a 100 mL of volumetric flask was charged with Et_3N (10.45 mL, 75 mmol). The reaction flask was recapped, the septum was punctured with a needle attached to a Schlenk line, and the flask was evacuated and backfilled with nitrogen (This process was repeated a total of three times). To afford 0.75 M of reaction solution, degassed acetonitrile was added to scale of 100 mL of volumetric flask via syringe.

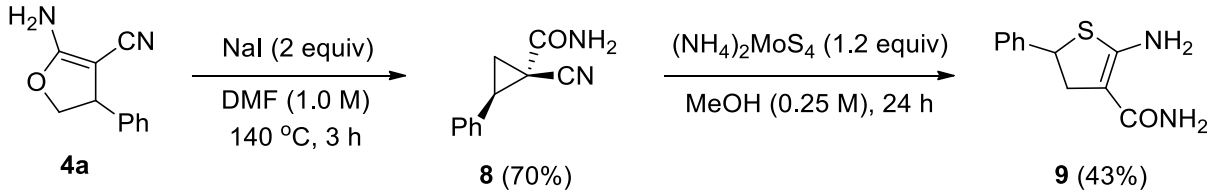
After the 1st reaction solution had entered the reactor 1 (UV-150 photoreactor), followed by reactor 2 (large diameter tubular reactor for lapid mixing) with the 2nd reaction solution of Et_3N (0.75 M in degassed acetonitrile), it was followed with degassed acetonitrile at the same flow rate. 10 mmol of the crude reaction mixture (120.48 mL) was collected in a 250 mL of round bottom flask in the presence of Amberlite® IR120 hydrogen form (30 g) and H_2O (6 mL) while stirring. After the collection was completed, the crude mixture was stirred for 30 min at room temperature. And the solvent was removed under reduced pressure and residue was purified by silica gel c olumn chromatography with 20% ethyl acetate/hexanes as the eluent, **5a** was obtained as a colorless liquid (1.50 g, 80% yield, 3:1 dr); R_f = 0.50 (ethyl aceate:hexanes, 1:2); anti isomer (major isomer) *[Note: The calibration of the pump tubing is required before the use for the accuracy, And back pressure regulator (3.9 bar) was used due to the volatility of acetonitrile and Et_3N at 80 °C]*

VII. Synthetic application of synthesized products

A. Conversion of 2,3-dihydrofuran 4a to diverse scaffolds



2-amino-4-phenylfuran-3-carbonitrile (7).[8] The 2,3-dihydrofuran **4a** (0.53 mmol, 1.0 equiv) was dissolved in xylene (5.3 mL, 0.1 M for **4a**) degassed by N_2 and Pd/C (50 mg, 50 wt%) was added. The suspension was stirred at 150 °C for 5 h. After completion of the reaction, the mixture was filtered through Celite, which was washed with CH_2Cl_2, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatog raphy with 10% ethyl acetate in hexanes as eluent. Furan **7** was obtained as brown solid in the yield of 40% (39 mg). R_f = 0.25 (ethyl acetate:Hexanes, 1:2); ^{1}H NMR (300 MHz, Acetone-d_6) δ 7.64 – 7.57 (m, 2H), 7.45 – 7.30 (m, 3H), 7.29 (s, 1H), 6.76 (bs, 2H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 166.2, 131.7, 129.8, 129.7, 128.7, 127.0, 126.7, 116.1, 67.2. FTIR (neat): υ 702, 1026, 1442, 1597, 1651, 2183, 2360, 3178, 3217, 3271, 3325, 3441 cm^{-1}.

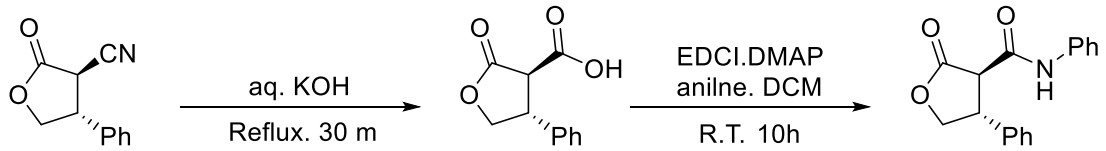


anti-1-cyano-2-phenylcyclopropane-1-carboxamide (8).[9] The 2,3-dihydrofuran **4a** (0.2 mmol, 1.0 equiv) was dissolved in DMF (0.2 mL, 1.0 M for **4a**) and sodium iodide (60 mg, 1.0 eq uiv) was added. The reaction mixture was stirred at 140 °C for 3 h. After completion of the reaction, the solvent was removed *in vacuo* and cold water was added to the residue The mixture was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatogr aphy with 20% ethyl acetate in hexanes as eluent. Cyclopropane **8** was obtained as white solid in the yield of 70% (26 mg). R_f = 0.40 (ethyl acetate:Hexanes, 1:1); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.67 (d, J = 11.1 Hz, 2H), 7.44 – 7.25 (m, 5H), 3.03 (dd, J = 9.1, 8.1 Hz, 1H), 2.23 (dd, J = 8.1, 5.4 Hz, 1H), 1.98 (dd, J = 9.1, 5.4 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.3, 134.4, 128.4, 128.4, 127.8, 118.0, 32.7, 23.6, 20.0. FTIR (neat): υ 524, 1219, 1365, 1435, 1681, 1735, 2947,

2970, 3016, 3155, 3448 cm^{-1}.

2-amino-5-phenyl-4,5-dihydrothiophene-3-carboxamide (9). [9] Cyclopropane **8** (0.21 mmol, 1. 0 equiv) was dissolved in MeOH (0.8 mL, 1.0 M for **8**) and ammonium tetrathiomolybdate (65 mg, 1.2 equiv) was added. The reaction mixture was stirred at room temperature for 48 h. the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with 2% MeOH in dichloromethane as eluent. 2,3-dihydrothiophene **9** was obtained as white solid in the yield of 43% (20 mg). R_f = 0.40 (Dichloromethane:MeOH, 20:1); ^{1}H NMR (300 MHz, Acetone-d_6) δ 7.52 – 7.45 (m, 2H), 7.37 – 7.24 (m, 3H), 7.17 (bs, 2H), 5.75 (bs, 2H), 4.95 – 4.83 (m, 1H), 3.35 (dd, *J* = 13.5, 8.5 Hz, 1H), 3.07 (dd, *J* = 13.5, 7.3 Hz, 1H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 169.4, 160.5, 143.5, 129.5, 128.4, 128.1, 91.6, 50.6, 42.9. FTIR (neat): υ 694, 763, 1319, 1404, 1496, 1627, 2322, 2360, 3178, 3332, 3448 cm^{-1}.

B. Conversion of α-cyano-γ-butyrolactone 5a to γ-butyrolactone derivatives

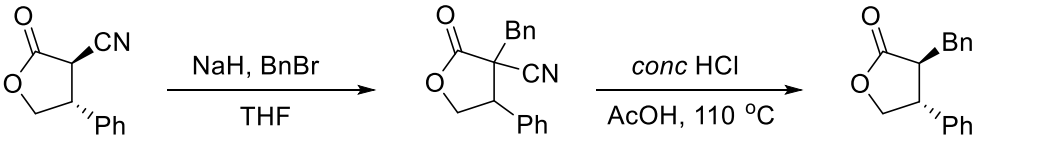


5a (3:1 dr) **S10** (68%) **10** (74%)

2-oxo-4-phenyltetrahydrofuran-3-carboxylic acid (S10). A mixture of **5a** (1.87 g, 10 mmol) and aqueous KOH solution (1 g/4 ml) was stirred at room temperature for 30 min. The mixture was poured into saturated aqueous $NaHCO_3$. The aqueous layer was collected and added 2N HCl upto pH 3~4. The extract was washed with dichloromethane and dried over Na_2SO_4. **S10** was obtained by recrystallization (dichloromethane) as a white solid (1.41 g, 68%); R_f = 0.10 (ethyl acetate:hexanes, 1:1); ^{1}H NMR (300 MHz, CD_3CN) δ 7.46 – 7.21 (m, 5H), 4.68 (t, *J* = 9.8, 7.7 Hz, 1H), 4.23 (dd, *J* = 9.8, 8.1 Hz, 1H), 4.14 (td, *J* = 10.4, 7.6 Hz, 1H), 3.85 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_3CN) δ 172.9, 168.9, 137.9, 129.9, 128.9, 128.2, 73.0, 53.5, 46.5; FTIR (neat) : υ 694, 756, 1018, 1157, 1219, 1280, 1725, 1774, 3170 cm^{-1}

2-oxo-N,4-diphenyltetrahydrofuran-3-carboxamide (10). EDCI (0.72 mmol, 1.5 equiv) and DMAP (0.24 mmol, 0.5 equiv) was added to solution of **S10** (100mg, 0.48 mmol) in dichloromethane (9.6 ml, 0.05 M for **S10**) at 0 °C. After the mixture was stirred for 30 min, the solution was added with aniline (1.92 mmol, 4 equiv) at 0 °C. The reaction mixture was quenched with H_2O (10 mL) and the mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated *in vacuo.* The residue was purified by silica gel column chromatography with 20% ethyl acetate in hexanes as eluent. **10** was obtained as white solid in the

yield of 74% (99 mg). R_f = 0.60 (ethyl acetate:Hexanes, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.56 – 7.48 (m, 2H), 7.44 – 7.28 (m, 7H), 7.17 – 7.07 (m, 1H), 4.84 – 4.71 (m, 1H), 4.44 – 4.30 (m, 2H), 3.79 – 3.70 (m, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 162.4, 138.9, 137.3, 129.4, 129.2, 128.1, 127.4, 124.9, 120.2, 73.4, 53.5, 43.1; FTIR (neat) : υ 694, 756, 1018, 1149, 1311, 1422, 1496, 1550, 1604, 1666, 1774, 2368, 3325 cm^{-1}



5a (3:1 dr) **S11** (85%) **11** (76%, 14.2:1 dr)

3-benzyl-2-oxo-4-phenyltetrahydrofuran-3-carbonitrile (S11). To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with 2-oxo-4-phenyltetrahydrofuran-3-carbonitrile **5a** (0.2 mmol, 1.0 equiv), NaH (0.24 mmol, 1.2 equiv) and THF (2.0 mL, 0.1 M). After 10 min, BnBr (0.24 mmol, 1.2 equiv) was added to reaction mixture. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was quenched with H_2O (10 mL) and the mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated *in vacuo.* The residue was purified by silica gel column chromatography with 10% ethyl acetate in hexanes as eluent. The product S**11** was obtained as a white solid in the yield of 85% (47.1 mg) as single diastereosiomer. R_f = 0.55 (ethyl acetate:Hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.11 (m, 11H), 4.45 (dd, *J* = 9.6, 7.4 Hz, 1H), 4.30 (dd, *J* = 9.6, 7.3 Hz, 1H), 3.55 (dd, *J* = 7.4 Hz, 7.3 Hz, 1H), 3.44 (d, *J* = 14.1 Hz, 1H), 3.22 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 134.4, 132.9, 130.6, 129.4, 129.2, 129.2, 128.6, 128.2, 115.8, 71.1, 51.3, 47.3, 39.9; FTIR (neat) : υ 702, 748, 910, 1018, 1172, 1396, 1419, 1458, 1519, 1535, 1651, 1681, 1782, 3618, 3649, 3672, 3741, 3865 cm^{-1}.

3-benzyl-4-phenyldihydrofuran-2(3H)-one (11).[10] To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with 3-benzyl-2-oxo-4-phenyltetrahydrofuran-3-carbonitrile S**11** (0.2 mmol, 1.0 equiv), *conc.* HCl (35 equiv), AcOH (0.34 M). The reaction mixture was stirred at 110 °C for 12 h. The reaction mixture was quenched with saturated $NaHCO_3$ (10 mL) and the mixture was extracted with ethyl acetate (three times), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with 10% ethyl acetate in hexanes as eluent. The product **11** was obtained as a white solid in the yield of 76% (38.3 mg, 14.2:1 dr). R_f = 0.60 (ethyl acetate:Hexanes, 1:2); anti isomer (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.10 (m, 10H), 4.41 (dd, *J* = 9.0, 8.2 Hz, 1H), 4.09 (dd, *J* = 9.3 Hz, 9.3 Hz, 1H), 3.37 (ddd, *J* = 9.8, 8.1 Hz, 1H), 3.22 – 3.04 (m, 2H), 3.07 – 2.91 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 138.0, 137.2, 129.8, 129.2, 128.6, 127.8, 127.5, 126.9, 72.5, 48.0, 45.7, 33.8; syn isomer (minor isomer) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.07 (m, 6H), 7.09 – 6.99 (m, 2H),

6.99 – 6.89 (m, 2H), 4.58 (dd, J = 9.3, 5.9 Hz, 1H), 4.47 (d, J = 1.1 Hz, 1H), 3.60 (t, J = 7.6 Hz, 1H), 3.34 – 3.20 (m, 1H), 3.22 – 2.93 (m, 1H), 2.30 (dd, J = 14.7, 10.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 138.7, 136.5, 129.0, 128.8, 128.5, 128.0, 127.5, 126.5, 125.5, 72.7, 46.3, 44.6, 31.7; FTIR (neat) : υ 494, 617, 702, 756, 910, 1018, 1141, 1180, 1350, 1450, 1496, 1604, 1774, 2916, 3032, 3062 cm^{-1}.

VIII. Electrochemical measurements

Cyclic voltammograms

Electrochemical study was performed using a Bio-Logic (SP-300 model). The redox potentials of the **1** (vs Ag/AgCl) were determined through cyclic voltammetry using a 5.0 mM solution of that material in 0.1 M solution of Bu_4NPF_6 (purged MeCN with N_2). Measurements employed a glassy carbon disk electrode, platinum wire counter electrode, 3.0 M NaCl Ag/AgCl reference electrode, a scan rate 50 mV/s. The obtained value was referenced to Ag/AgCl and converted to SCE by subtracting 0.032 V.

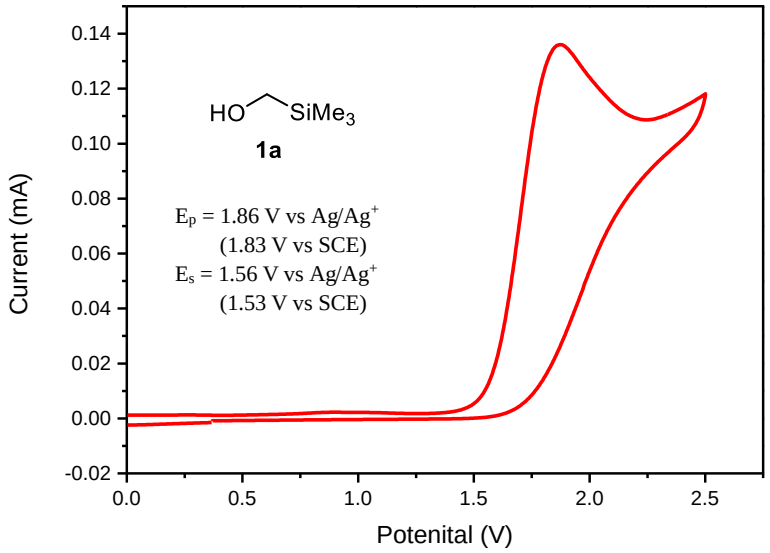


Figure S4. Cyclic voltammogram study for **1a**

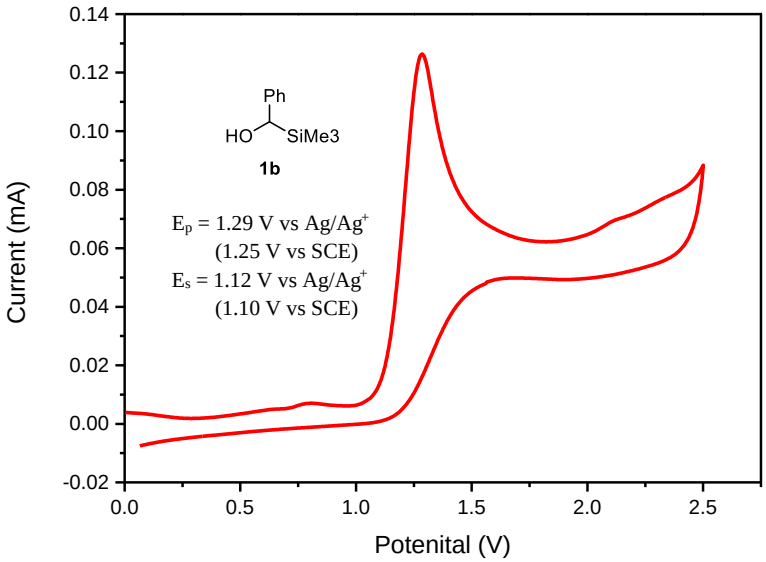


Figure S5. Cyclic voltammogram study for **1b**

IX. Mechanistic studies

A. UV-Visible study

A solution of 1.0 x 10^{-5} M in CH_3CN of the catalyst 9-mesityl-10-mehtylacridinium perchlorate (Acr^+-Mes) was prepared and UV-Visible absorption spectrum was measured. This graph showed that 9-mesityl-10-mehtylacridinium perchlorate has absorption at 430~455 wavelength (blue LEDs).

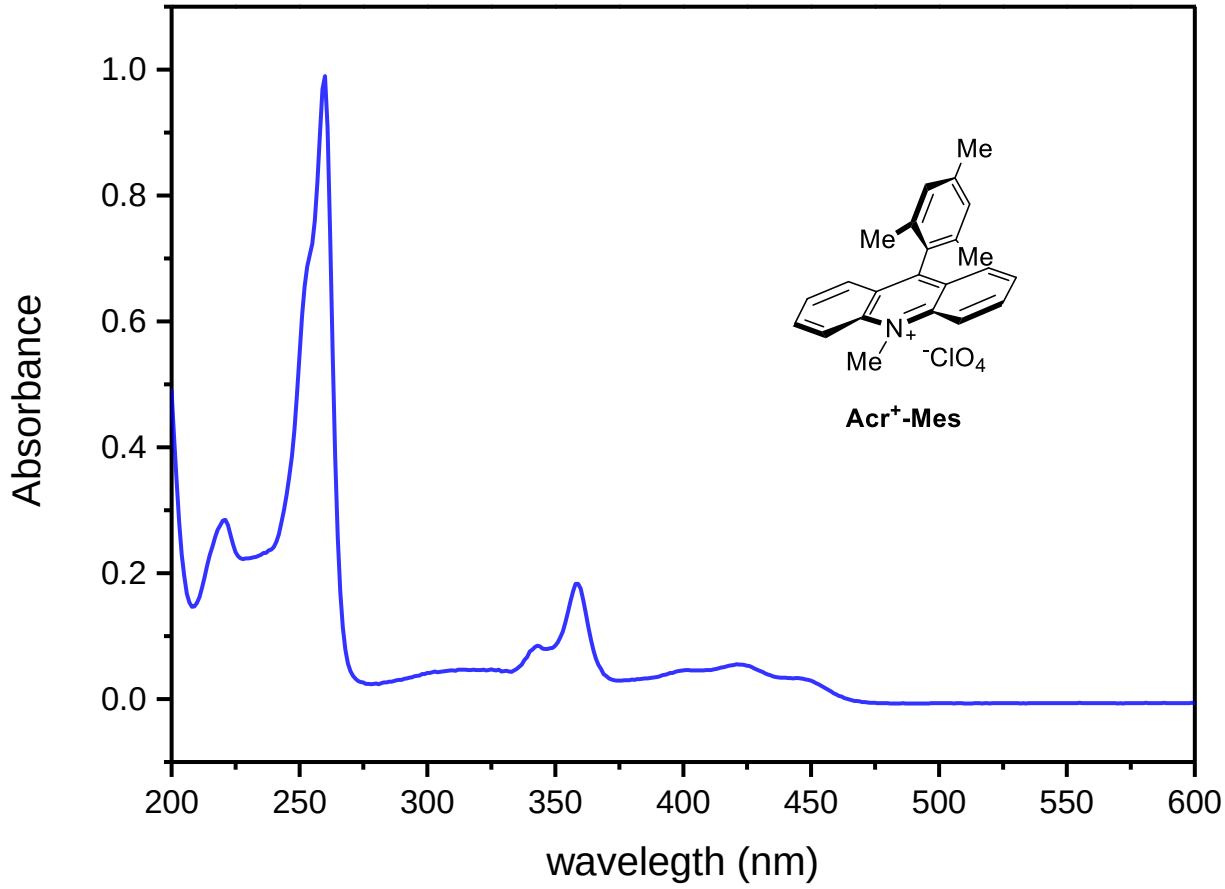


Figure S6. UV-Visible absorption spectra of 9-mesityl-10-mehtylacridinium perchlorate

B. Luminescence quenching Study

The emission spectra were collected using Horiba Fluoromax-4P spectrophotometer. Catalyst Acr^+-Mes (9-mesityl-10-methylacridinium perchlorate) was excited at 435 nm in CH_3CN solution and the emission intensity was observed at ~499 nm. CH_3CN was degassed with a stream of argon gas for 30 min. In a typical experiment, the emission spectrum of a 1.0 x 10^{-4} (M) solution of Acr^+-Mes in CH_3CN solution was collected. Then, **1a** was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_o and I signify the intensities of the emission in the absence and presence of the quencher at ~499 nm. The steady decrease of the emission intensity of the Acr^+-Mes catalyst solution with the gradual increase of the amount of **1a** as presented in Figure S6 and Figure S7 supports that reaction mechanism occuring through reductive quenching cycle.

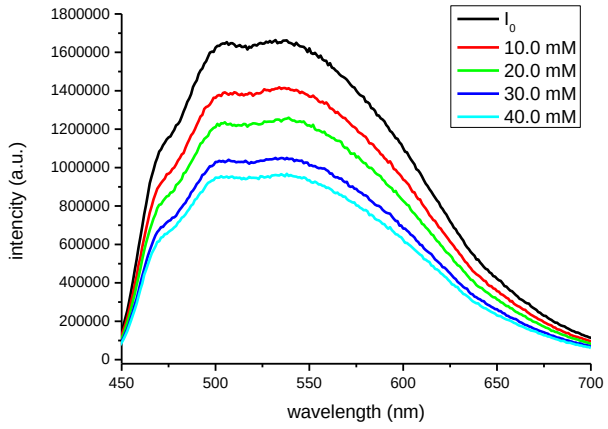


Figure S7. Luminescence quenching by **1a**

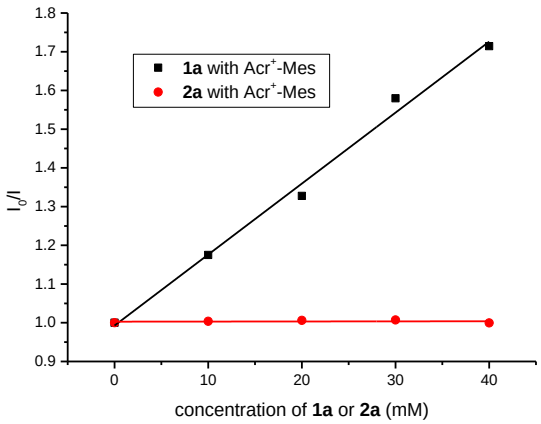


Figure S8. Stern-Volmer plot

C. Deuterium labelling experiment

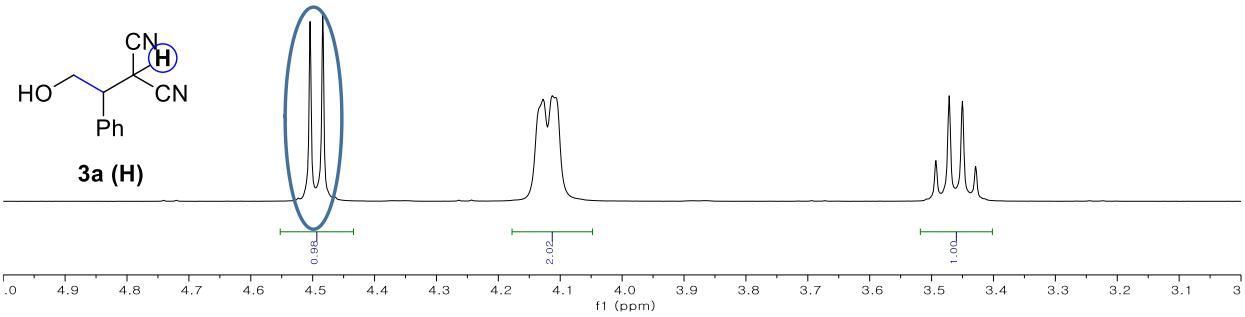
To get insight about the proton source for our proposed mechanism, control experiments were performed with D_2O instead of using H_2O as additive keeping other parameters unchanged. ^1H NMR confirmed the presence of deuterium atom in the final crude product (^1H NMR spectrum of crude product is attached in below).

1a (100 mol %)

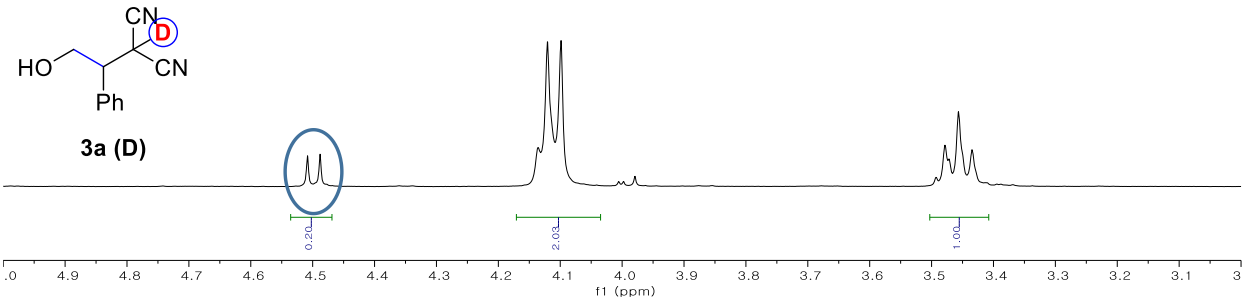
2a (200 mol %)

3a (D:H = 8.0:2.0)

^1H NMR of **3a** (H)

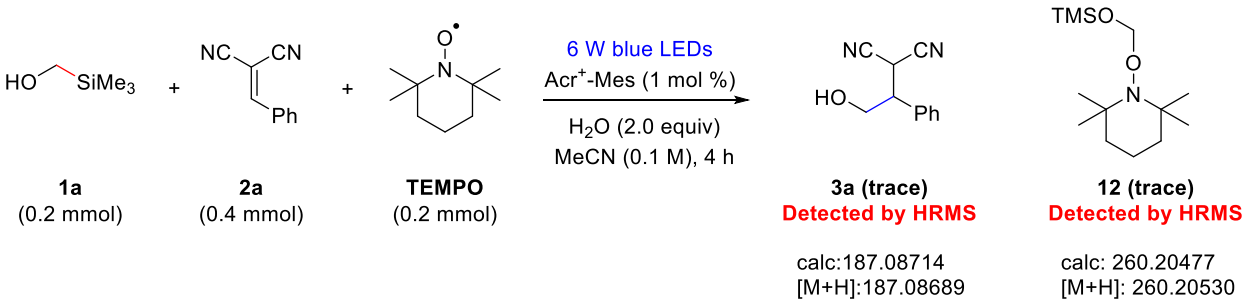


^1H NMR of Crude **3a** (D)



D. Radical trapping experiments

To get some mechanistic insight into the reaction mechanism, radical trapping experiments was performed using TEMPO as radical scavenger. The visible photoredox catalyzed Giese reaction with TEMPO provided only trace amount of alcohol **3a.** In addition, trace amount of TMS protected hydroxymethyl-TEMPO coupling product **12** was detected by HRMS (Please see next section **IX. Mechanistic studies, E** that provide proposed mechanism for generation of TMS protected hydroxy methyl radical). These results indicate that reaction involve radical mechanism. In addition, we conducted luminescence quenching study of photoredox catalyst (Acr^+-Mes) with TEMPO to confirm that the catalyst is activated in the presence of TEMPO. The photocatalyst was quenched by TEMPO but it still active in the presence of 100 ~200 equiv of TEMPO. This result indicates that activity of photoredox catalyst is reduced but still remains active by TEMPO.



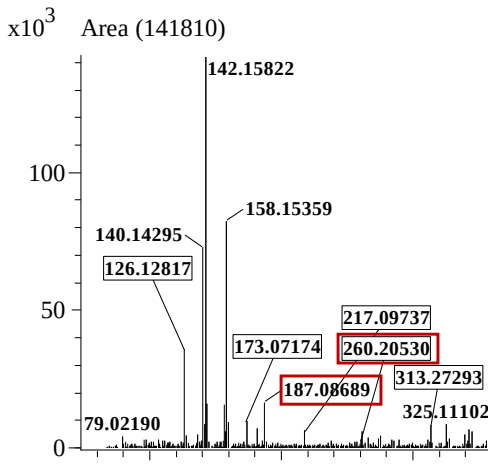


Figure S9. HRMS

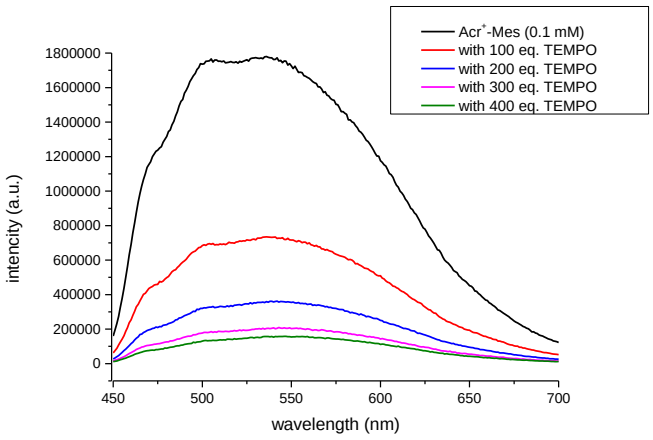
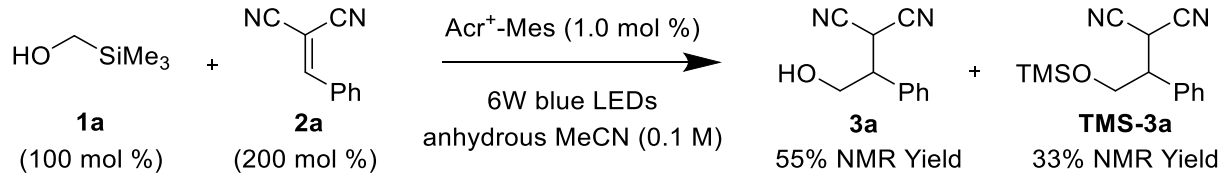


Figure S10. Luminescence quenching by TEMPO

E. Proposed mechanism for TMS-protected alcohol product, TMS-3a in anhydrous conditions



To a re-sealable pressure tube (13 x 100 mm) with a magnetic stir bar was charged with $TMSCH_2OH$ **1a** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) (0.82 mg, 0.002 mmol, 1.0 mol %) under argon atmosphere. The reaction mixture was dissolved by *degassed anhydrous acetonitrile* (2 mL, 0.1 M for **1a**). The reaction mixture was irradiating with 2 x 3W blue LEDs using our customized milligram scale reaction set up (as shown in Figure S2) under constant stirring condition at room temperature (20 ~ 30 ℃). After the reaction was completed, yields determined by ^{1}H-NMR analysis of the crude reaction mixture using 1,3-benzodioxole as the internal standard.

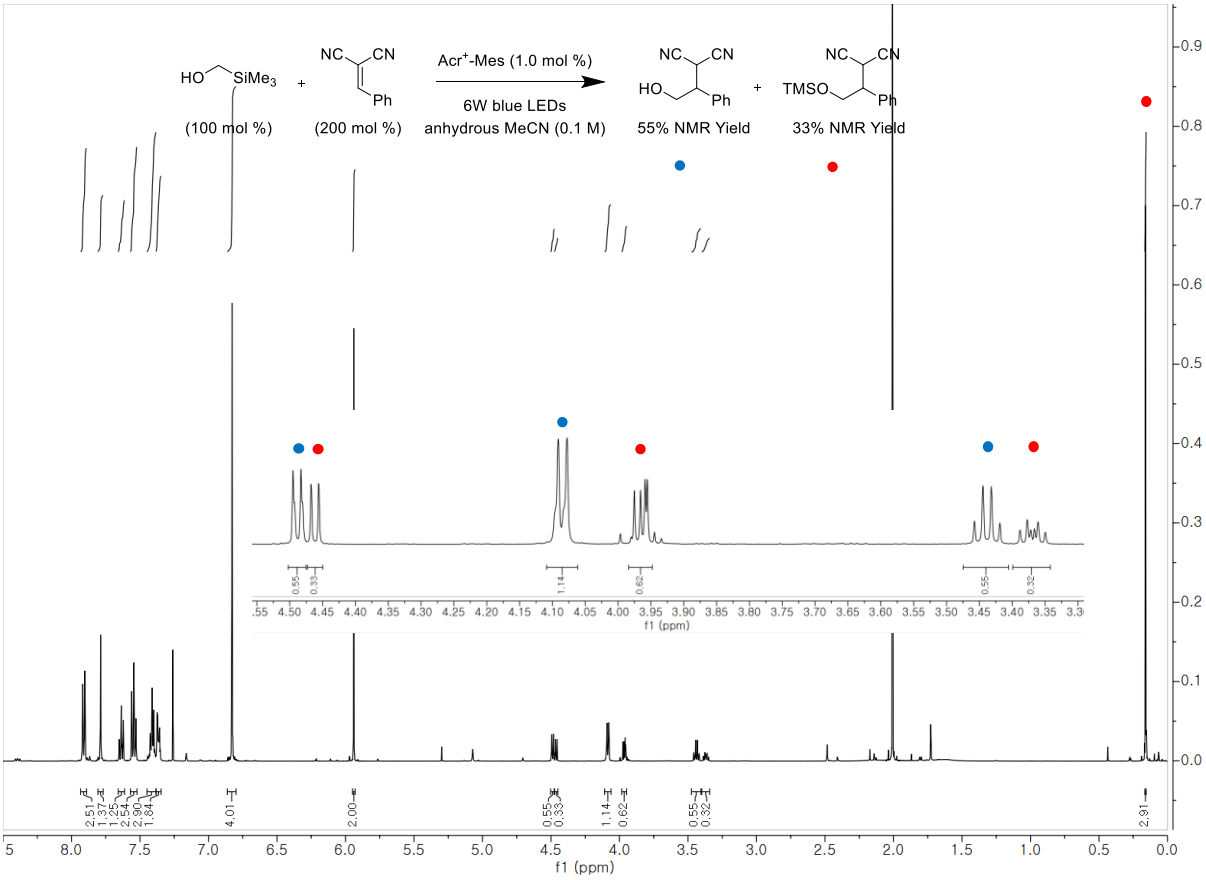


Figure S11. ^{1}H NMR spectrum of crude mixture

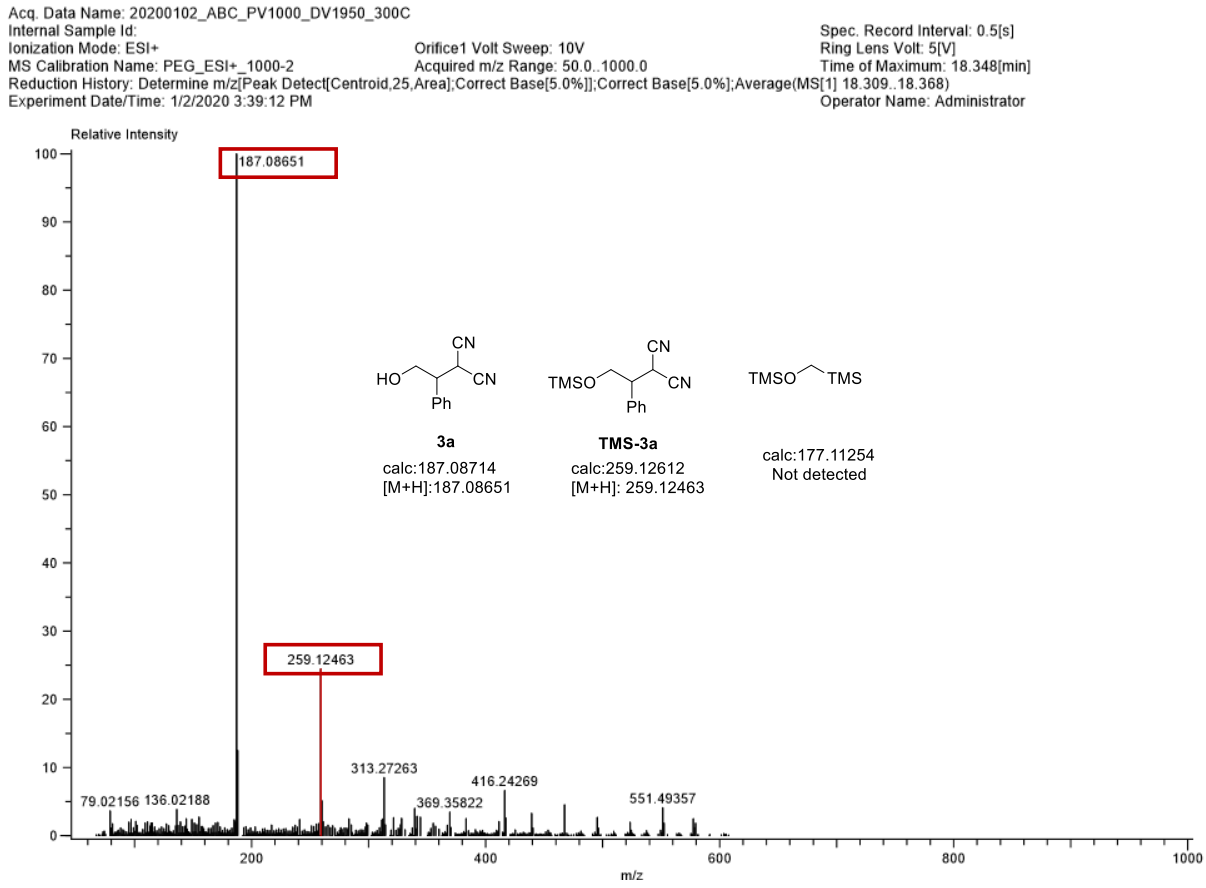
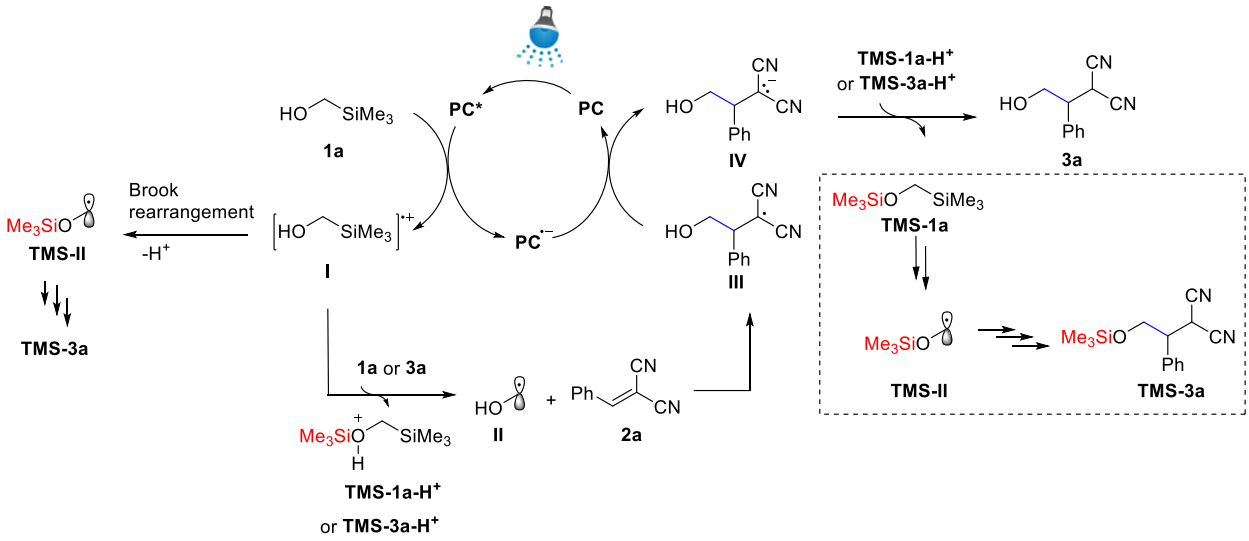


Figure S12. HRMS spectrum of crude mixture



Scheme S1. Proposed mechanism in anhydrous conditions

In the proposed mechanism (manuscript, Scheme 5), a proton source, such as $HOCH_2TMS$ **1a** and water, is essential for the completion of the photoredox-catalyzed Giese reaction. To verify the role of water as a proton source, the use of anhydrous MeCN under optimal conditions was explored and the yield decreased by 16% (manuscript, Table 1, entry 10). In addition, we examined extreme anhydrous conditions (using sigma-aldrich Sure/Seal™ anhydrous MeCN) to understand mechanism. We obtained TMS protected Giese addition product **TMS-3a** that was analyzed by crude NMR and HRMS. We proposed mechanism for generation of **TMS-3a** in anhydrous conditions in Scheme S1. Single-electron oxidation of $TMSCH_2OH$ **1a** by excited Fukuzumi acridium (Acr^+-Mes*) generates a cation radical **I**, which is desilylated with a **1a** or **3a** to produce the hydroxymethyl radical **II** in anhydrous conditions. The addition of hydroxymethyl radical **II** to benzalmalonitrile **2a** produce produces α-cyano radical **III**. Further single-electron reduction of α-cyano radical **III** by reduced Fukuzumi acridium (Acr•-Mes) provides α-cyano anion **IV**. Alcohol **3a** and **TMS-1a** were produced by the protonation of α-cyano anion **IV** with **TMS-1a-H$^+$** or **TMS-3a-H$^+$**. **TMS-1a** is converted to silyl protected hydroxymethyl radical **TMS-II** by photoredox catalyzed single electron oxidation and desilylation. The radical **TMS-II** can also be generated from a cation radical **I** via brook rearrangement in another pathway.[11] Finally, TMS protected product **TMS-3a** can be generated from radical **TMS-II** via further steps. Based on this result, a trace amount of water plays a key role as a proton source to prevent undesired pathways. Therefore, for better reproducibility, two equivalents of water were used as an additive (manuscript, Table 1, entries 11–12).

X. References

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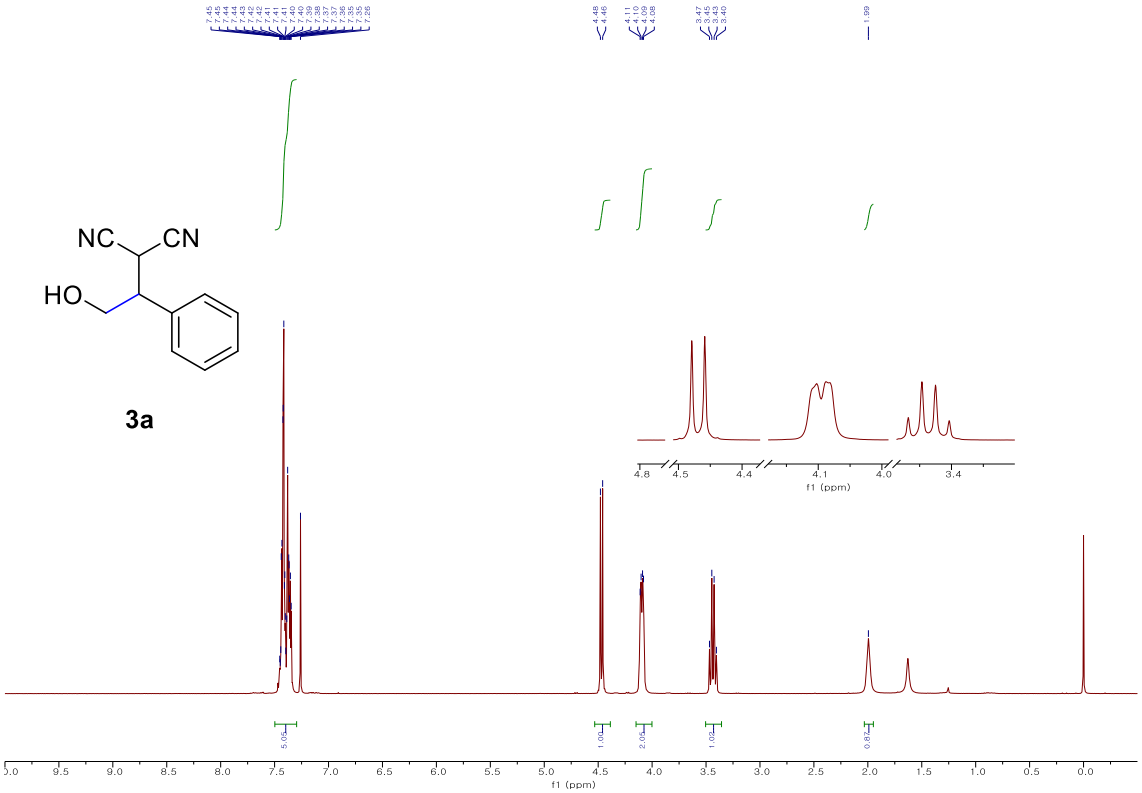
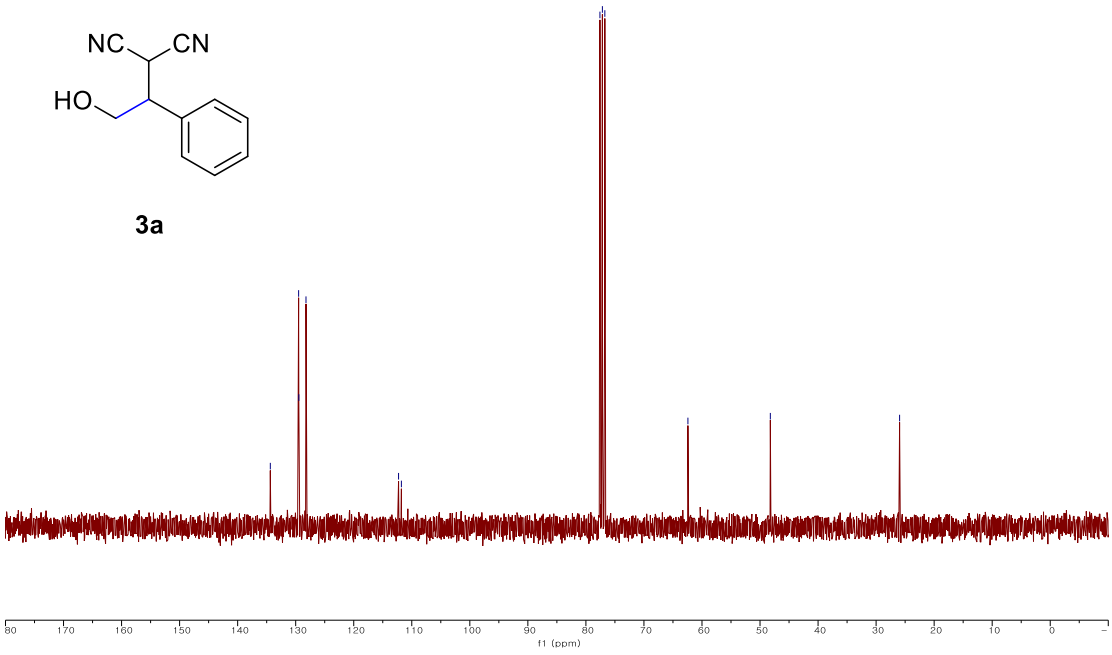
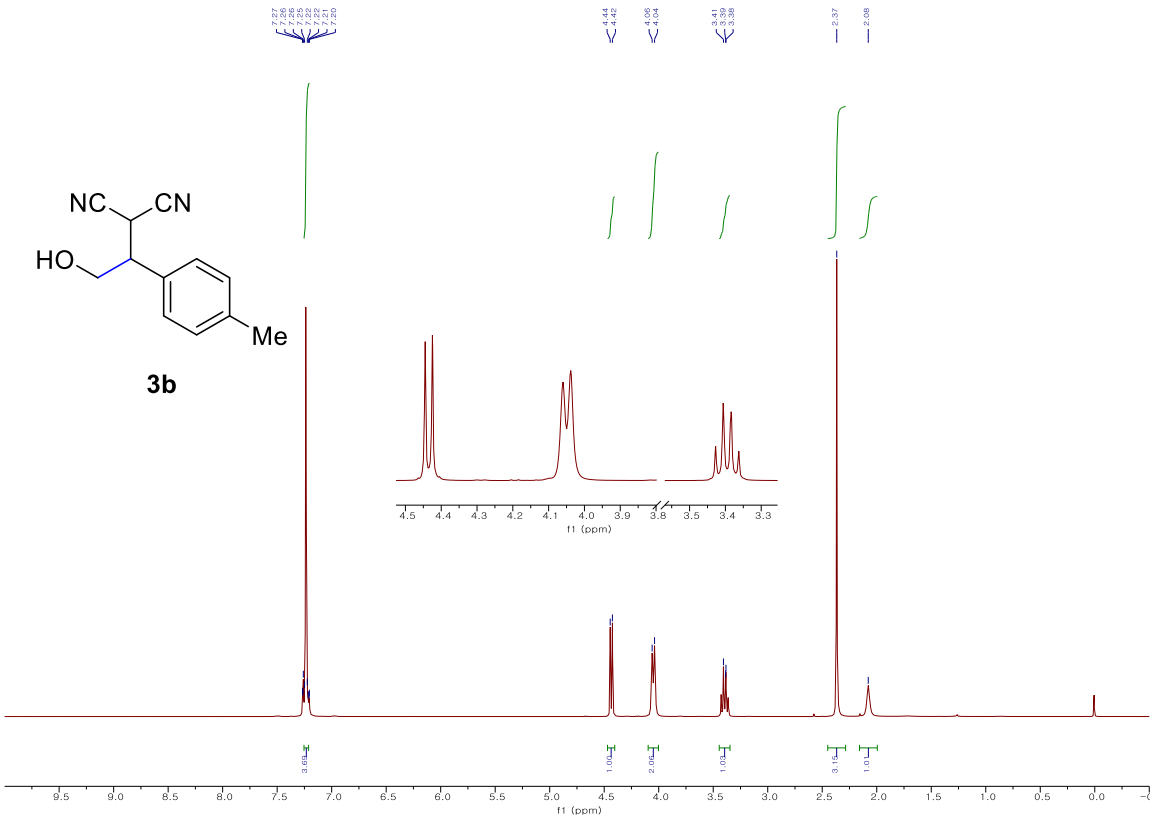
XI. ^{1}H and ^{13}C NMR Spectral



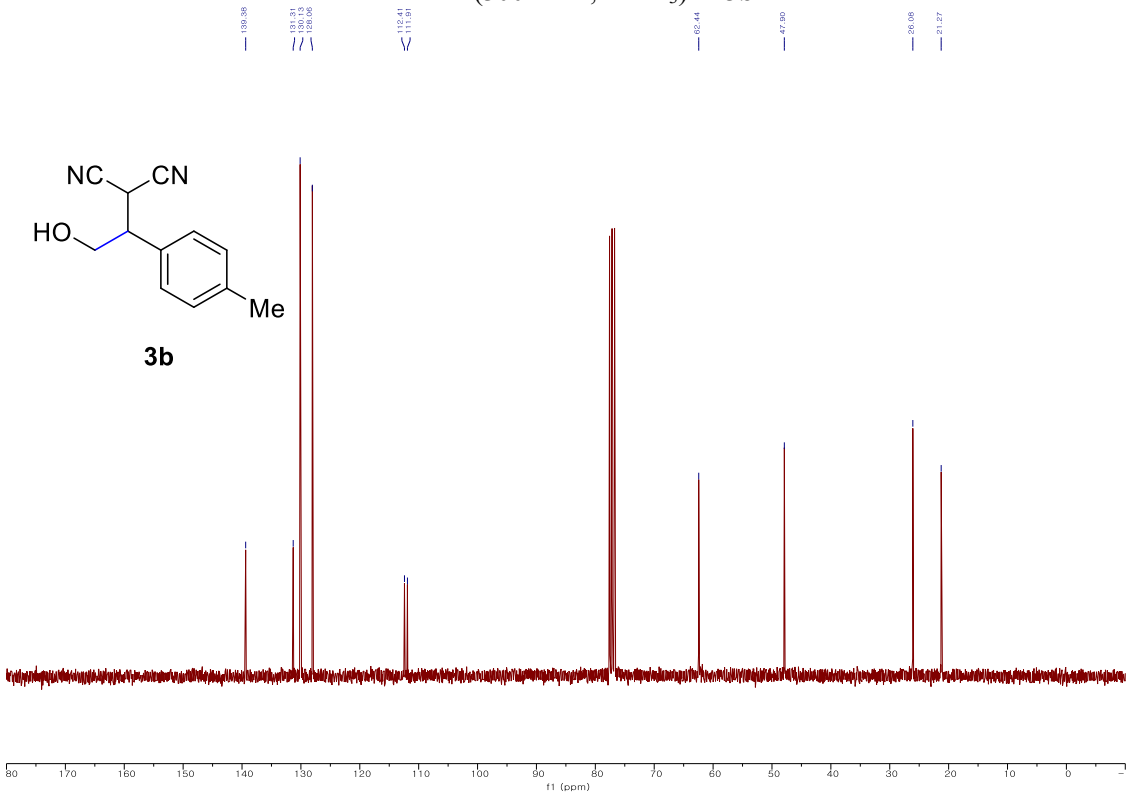
^{1}H-NMR (300 MHz, $CDCl_3$) of **3a**



^{13}C-NMR (75Hz, $CDCl_3$) of **3a**



^{1}H-NMR (300 MHz, $CDCl_3$) of **3b**



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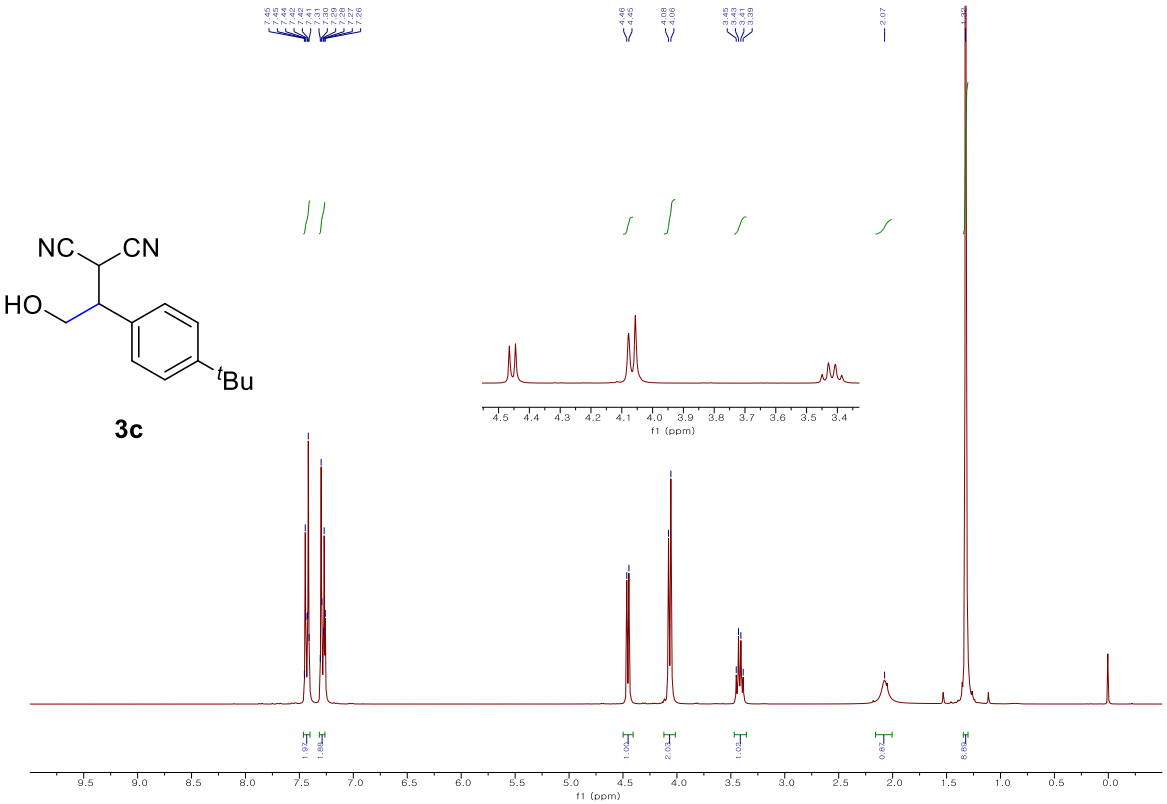
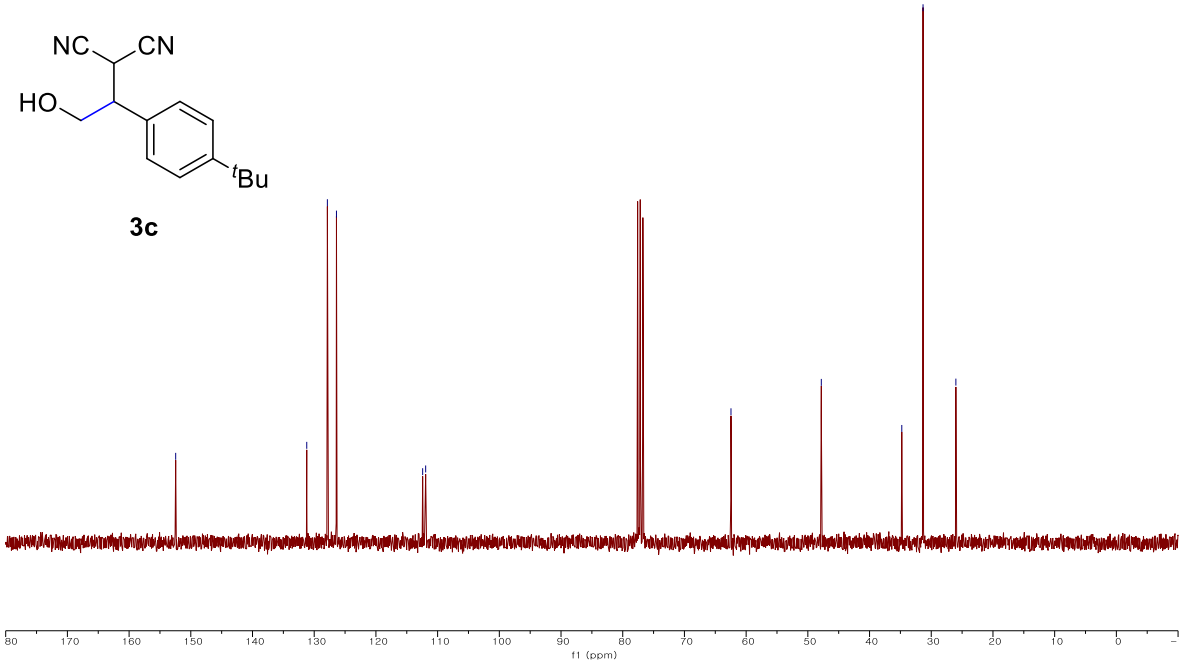


^{1}H-NMR (300 MHz, $CDCl_3$) of **3c**



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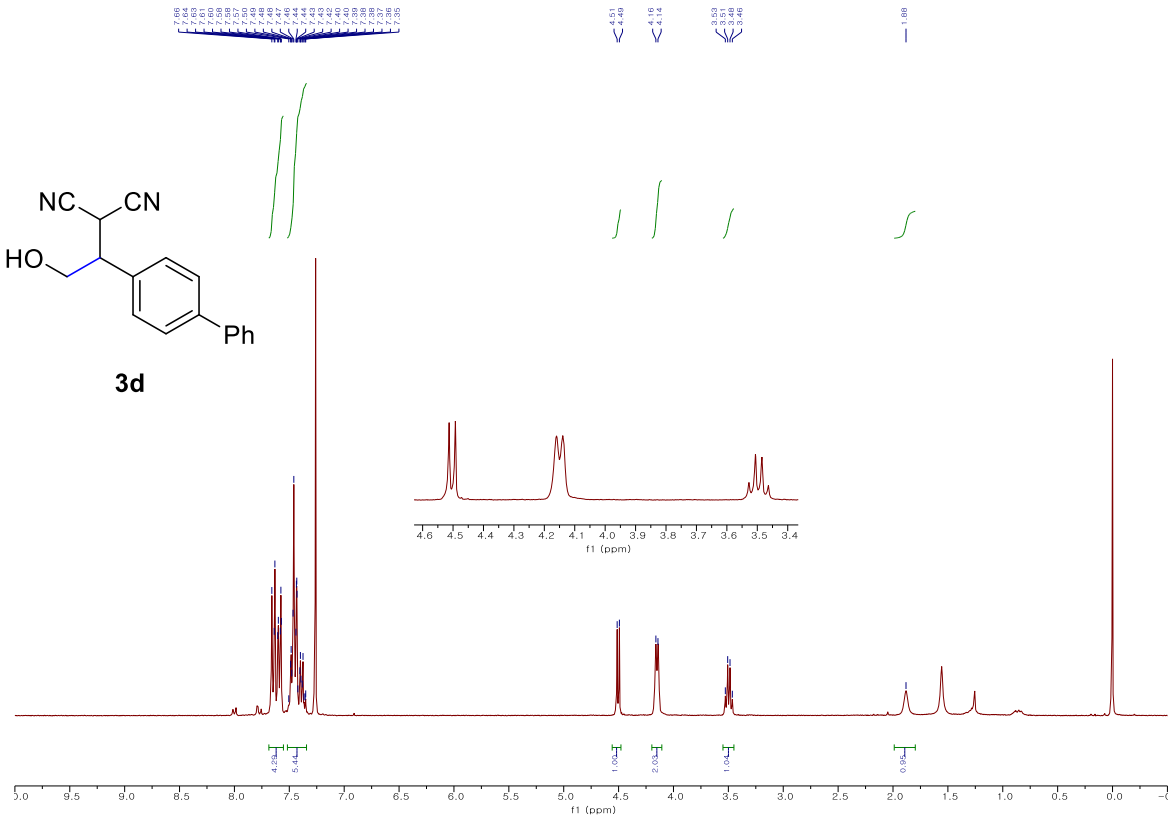
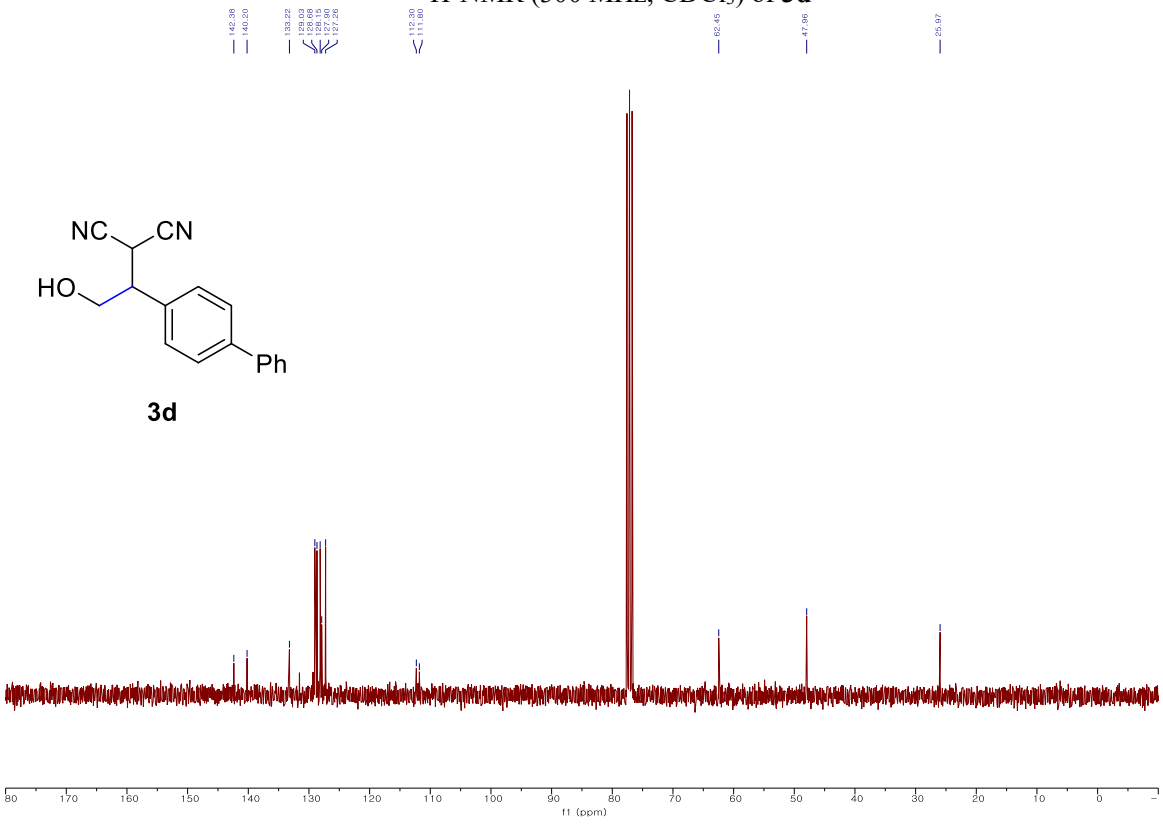


^{1}H-NMR (300 MHz, $CDCl_3$) of **3d**



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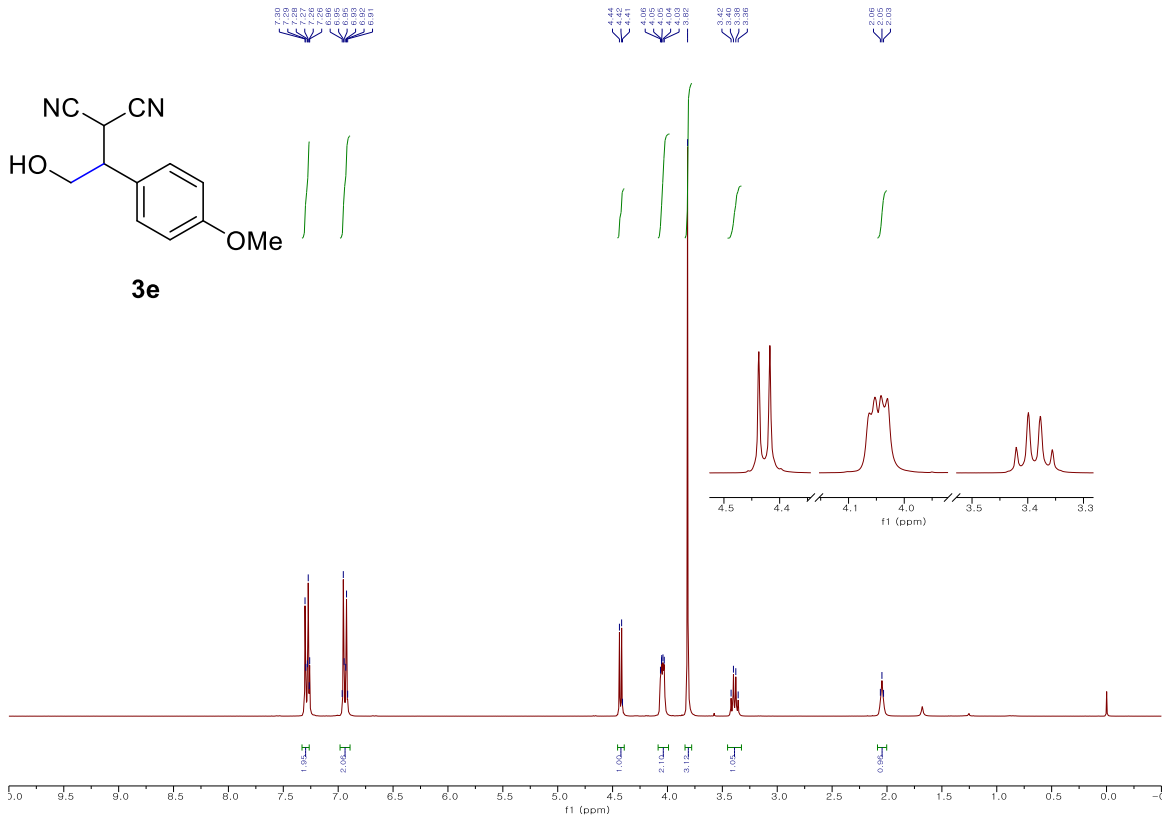

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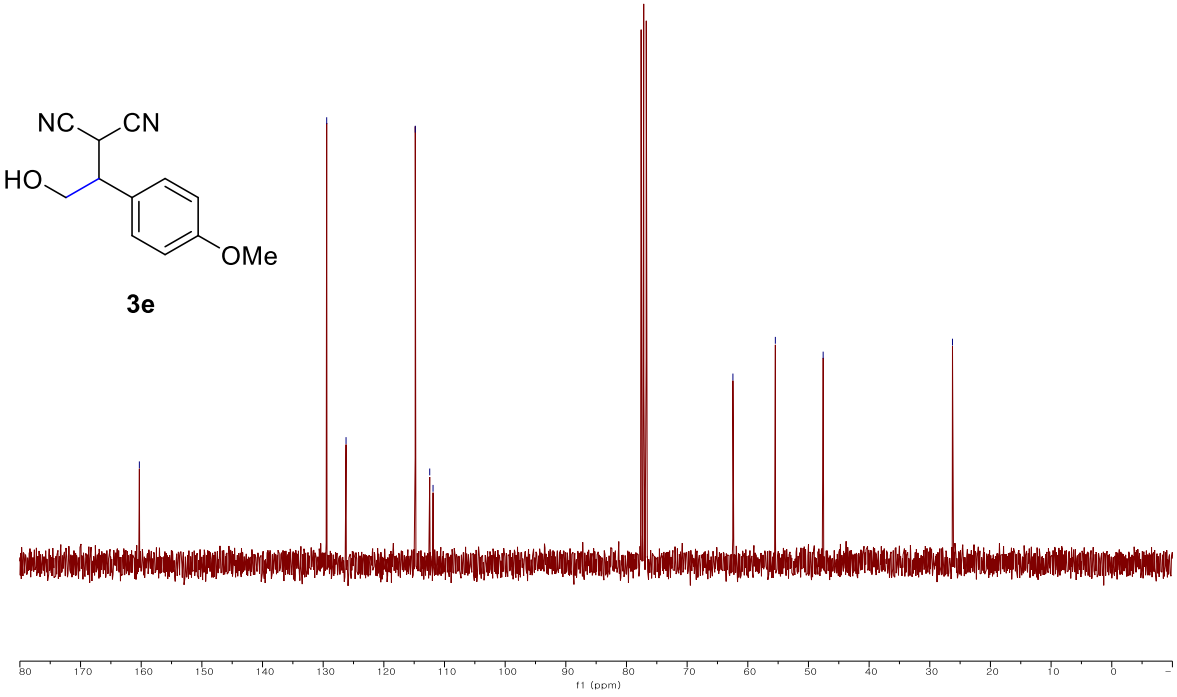
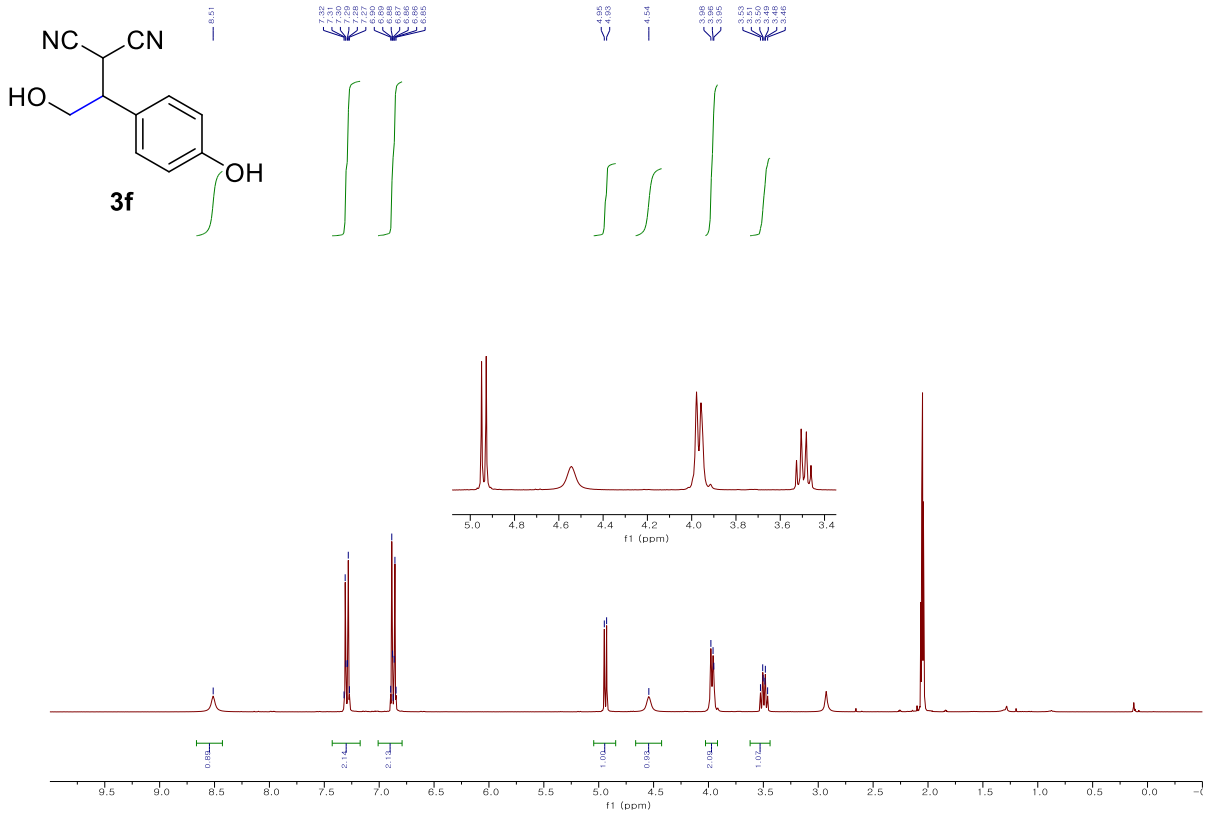
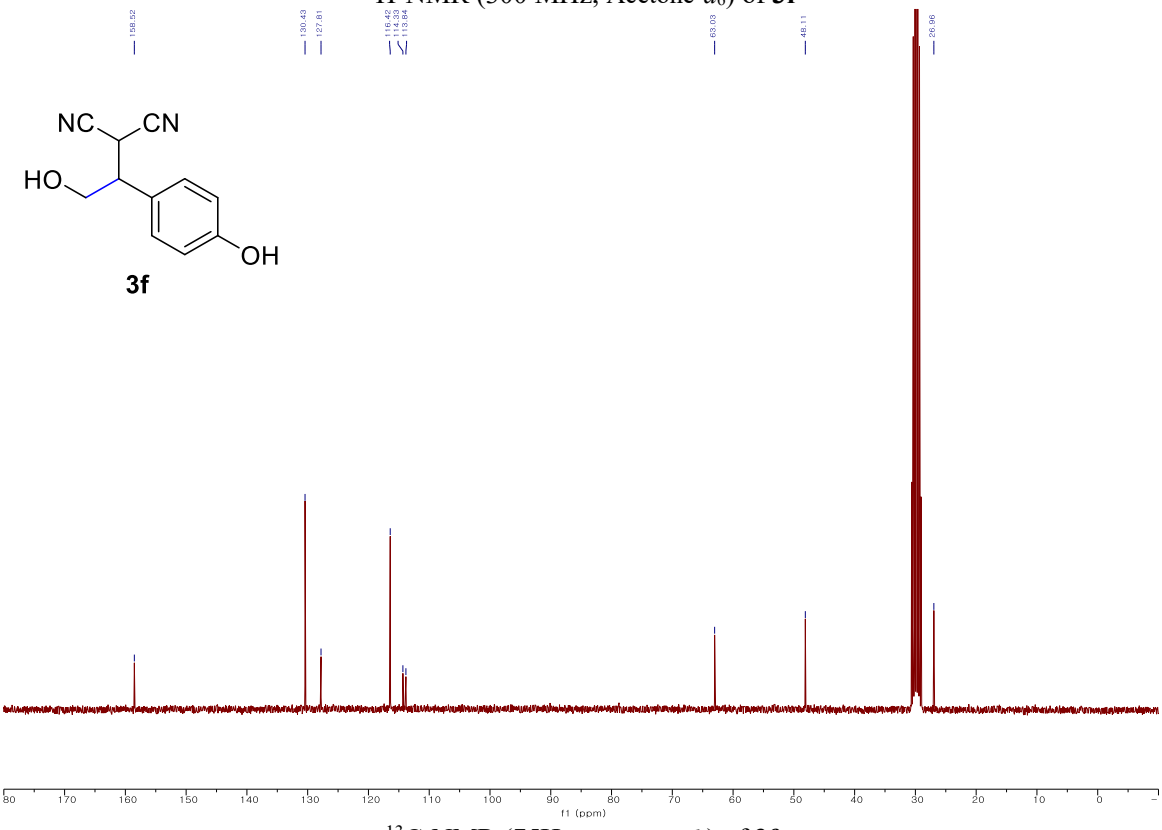


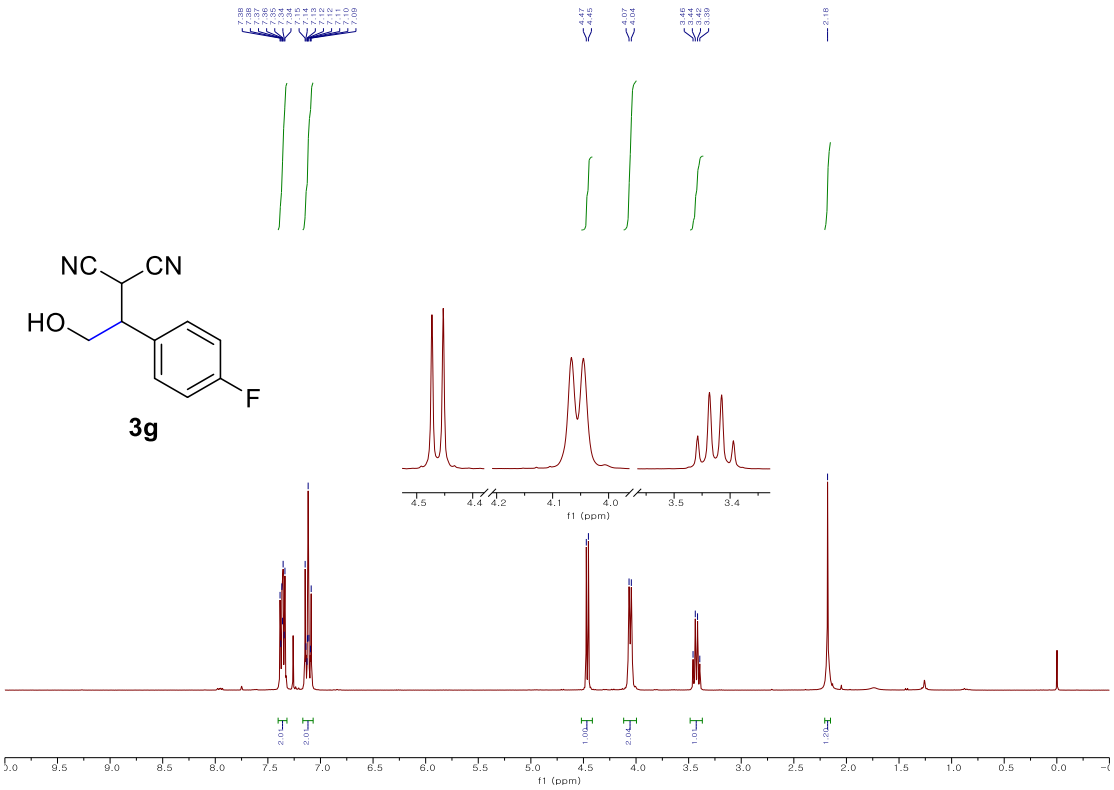
^{13}C-NMR (75Hz, $CDCl_3$) of **3e**



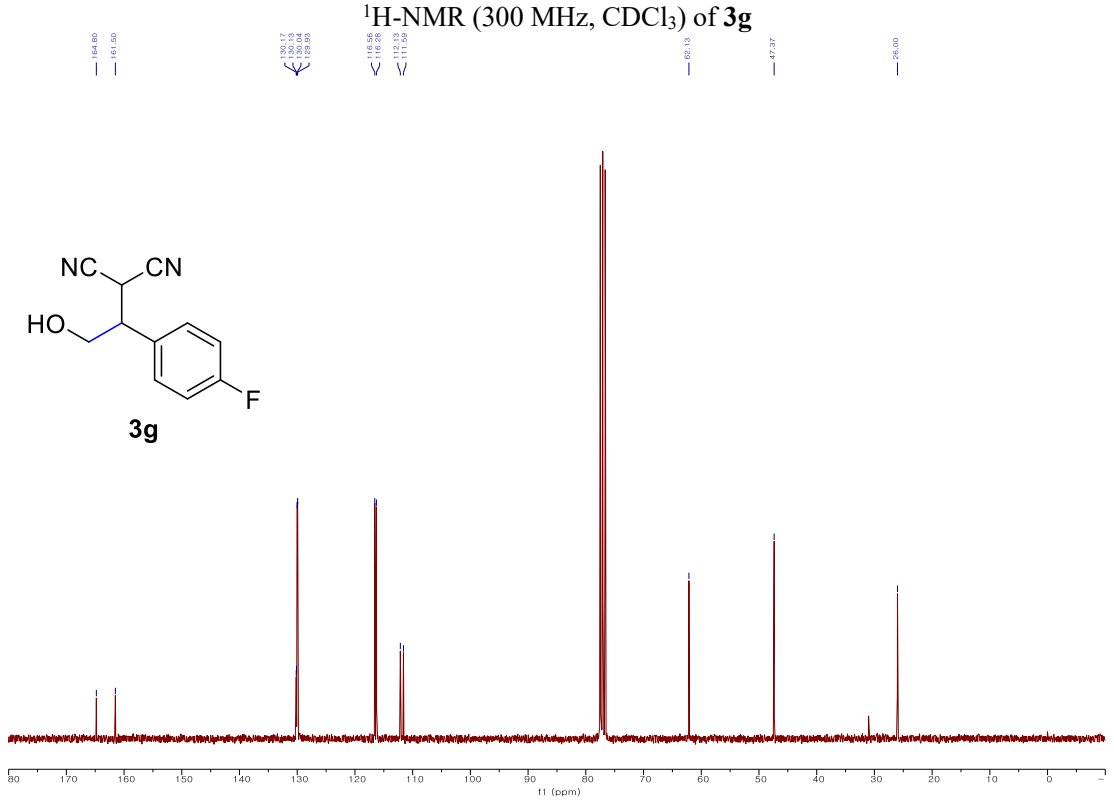
^{1}H-NMR (300 MHz, Acetone-d_6) of **3f**



^{13}C-NMR (75Hz, Acetone-d_6) of **3f**



^{1}H-NMR (300 MHz, $CDCl_3$) of **3g**



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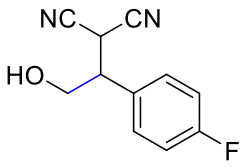
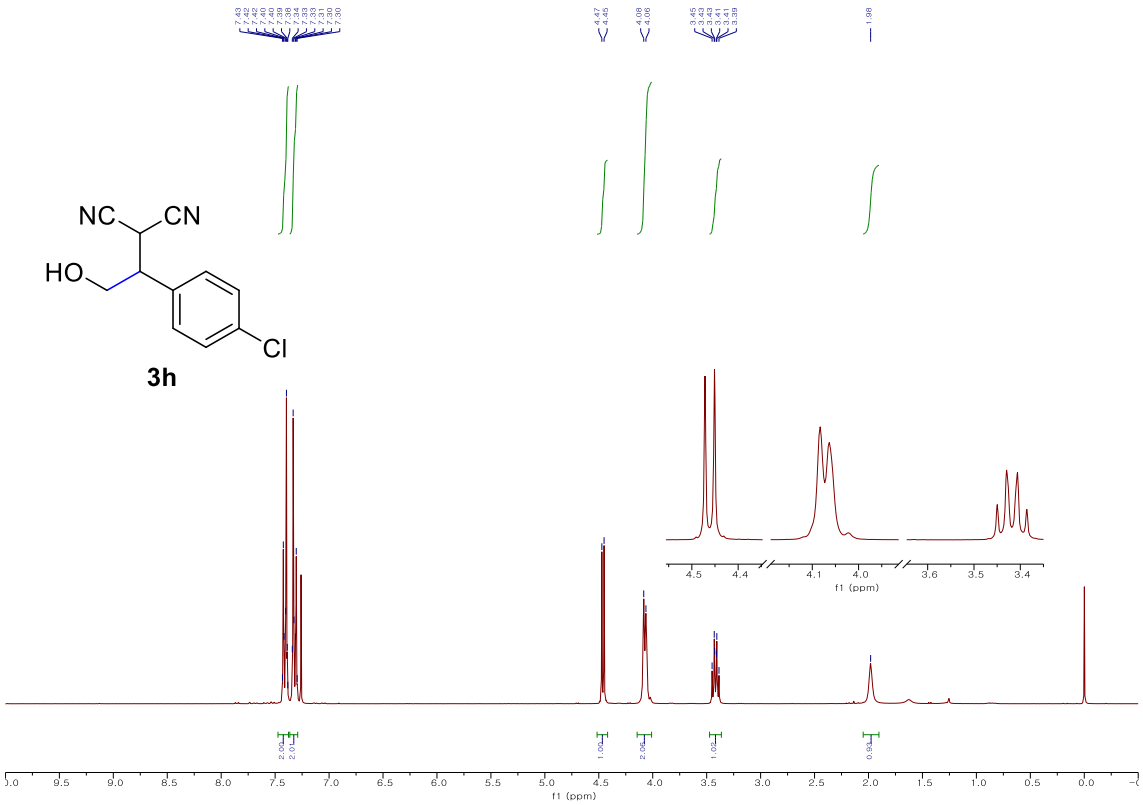
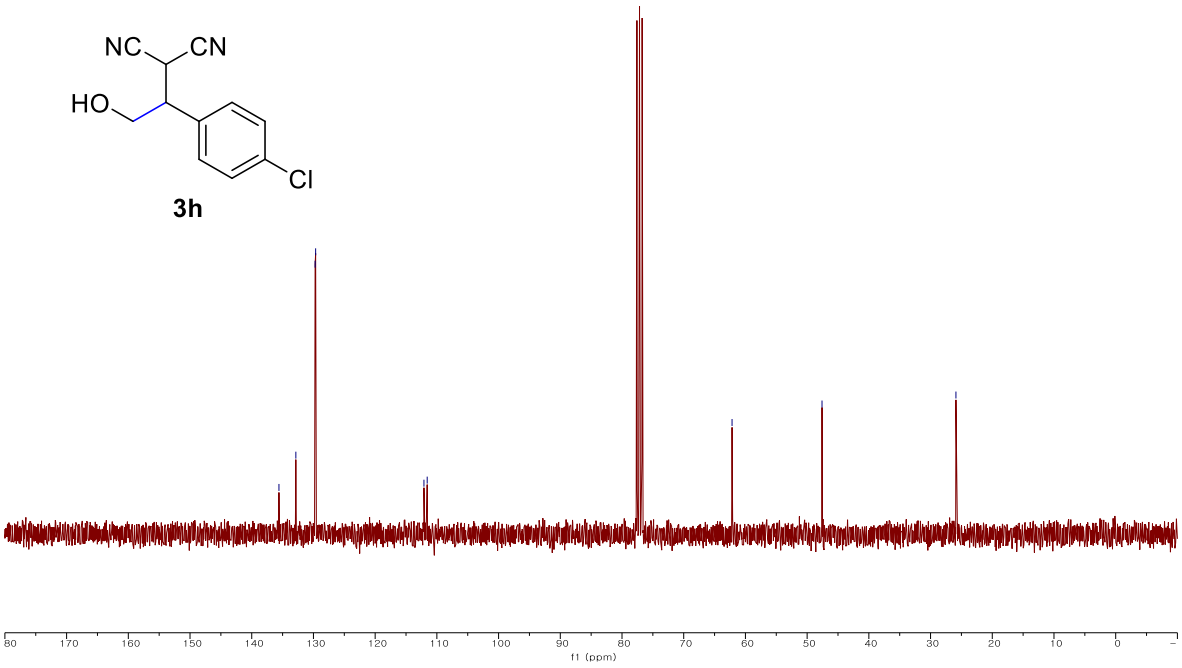


3g

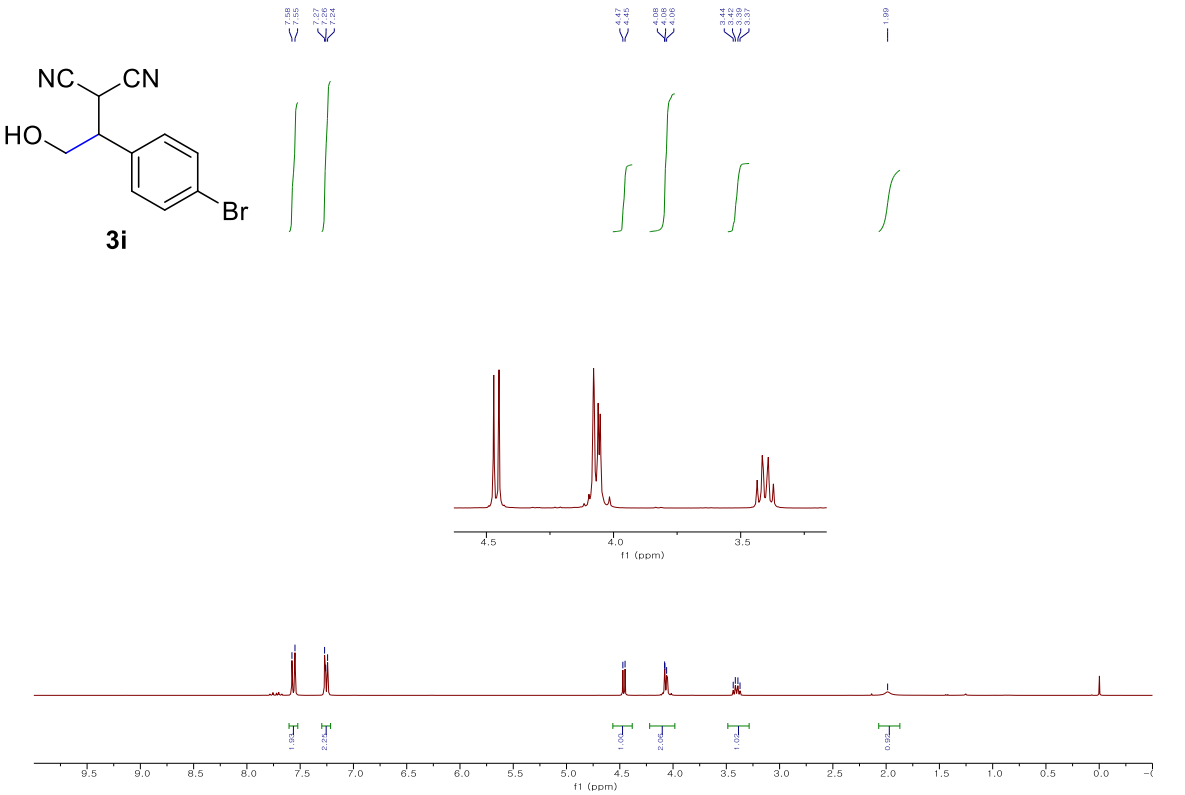
^{19}F-NMR (282 MHz, $CDCl_3$) of **3g**



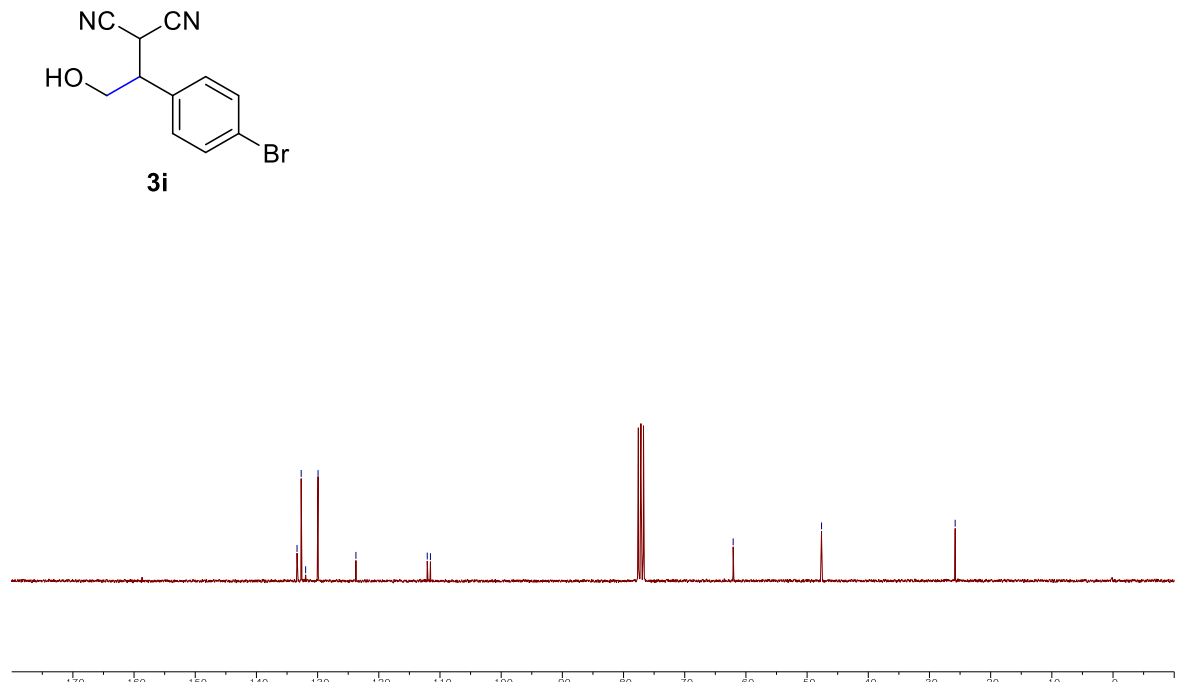
^{1}H-NMR (300 MHz, $CDCl_3$) of **3h**



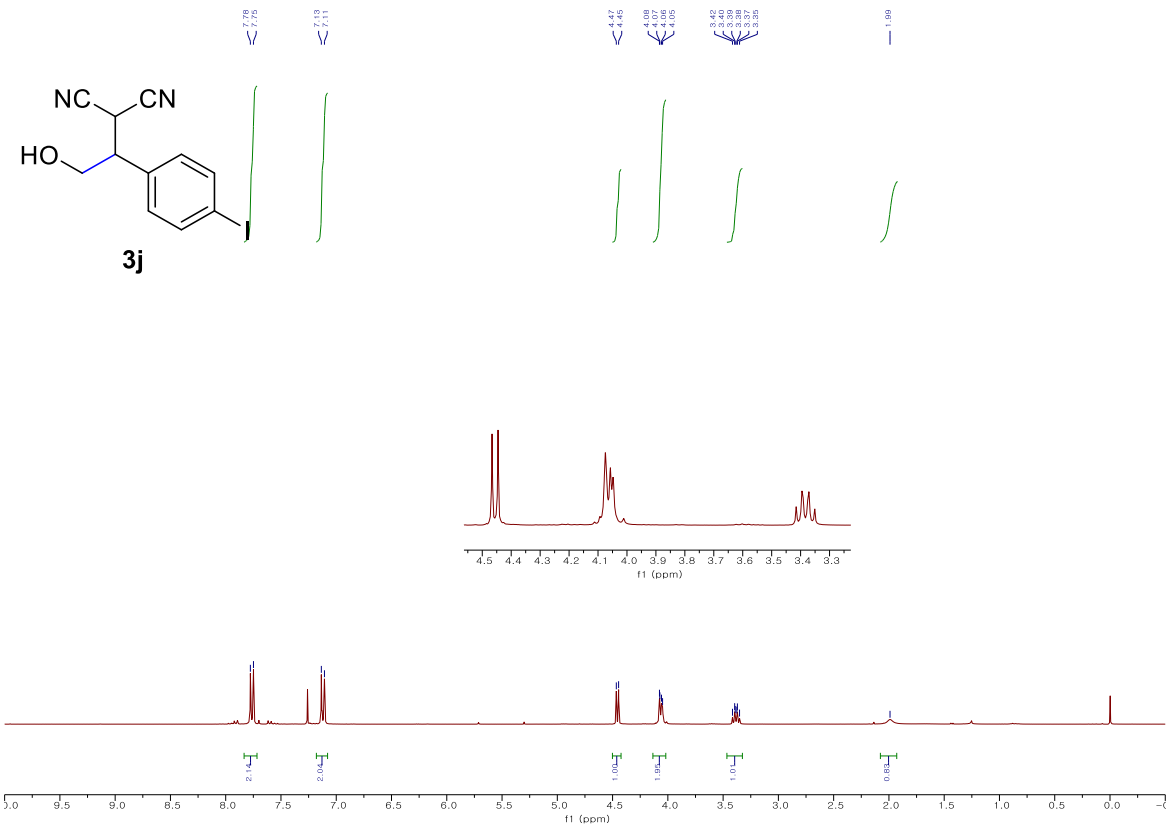
^{13}C-NMR (75Hz, $CDCl_3$) of **3h**



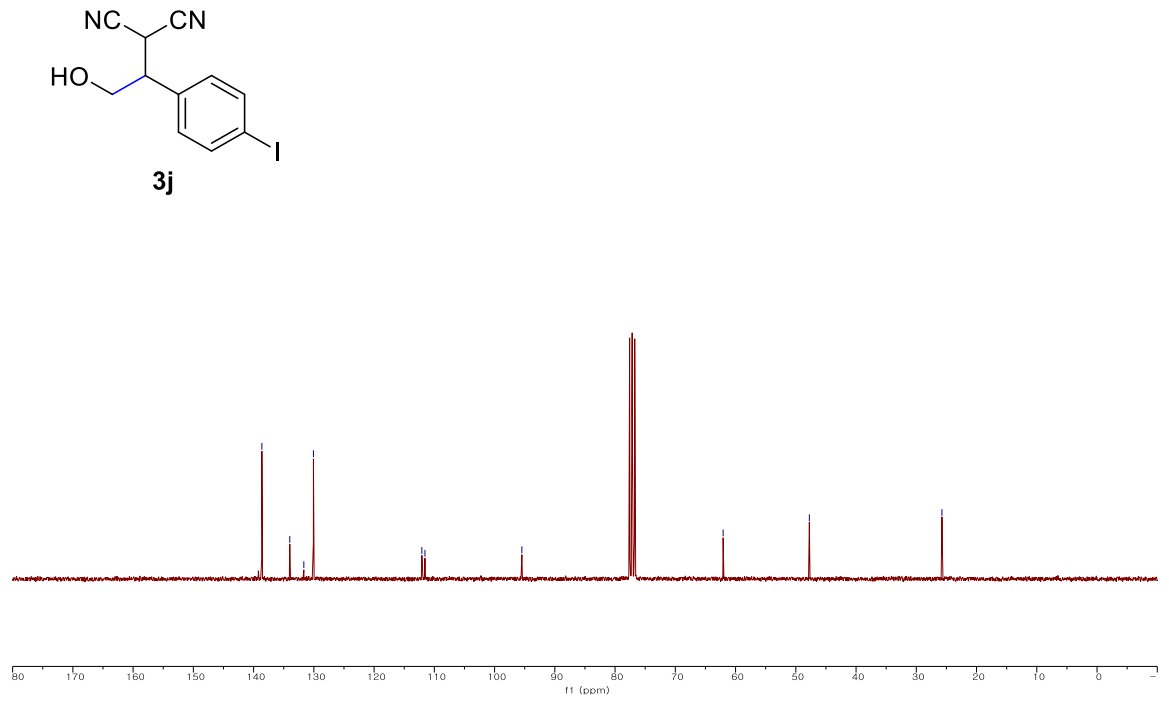
^{1}H-NMR (300 MHz, $CDCl_3$) of **3i**



^{13}C-NMR (75Hz, $CDCl_3$) of **3i**



^{1}H-NMR (300 MHz, $CDCl_3$) of **3j**



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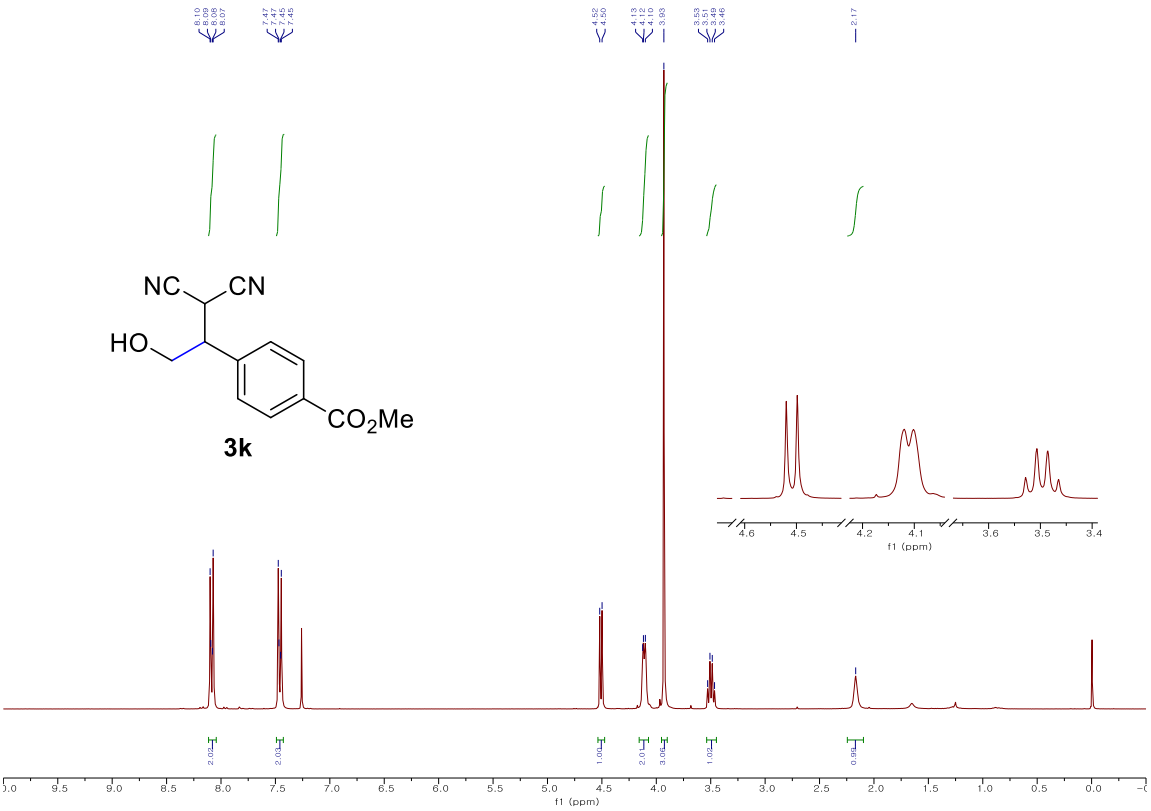
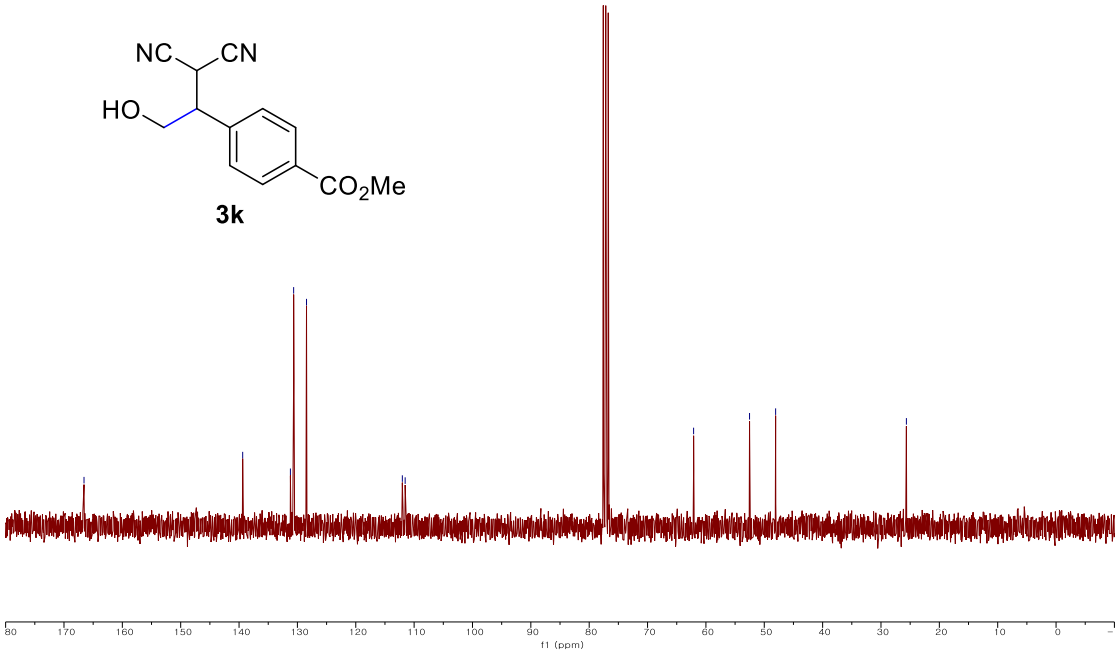
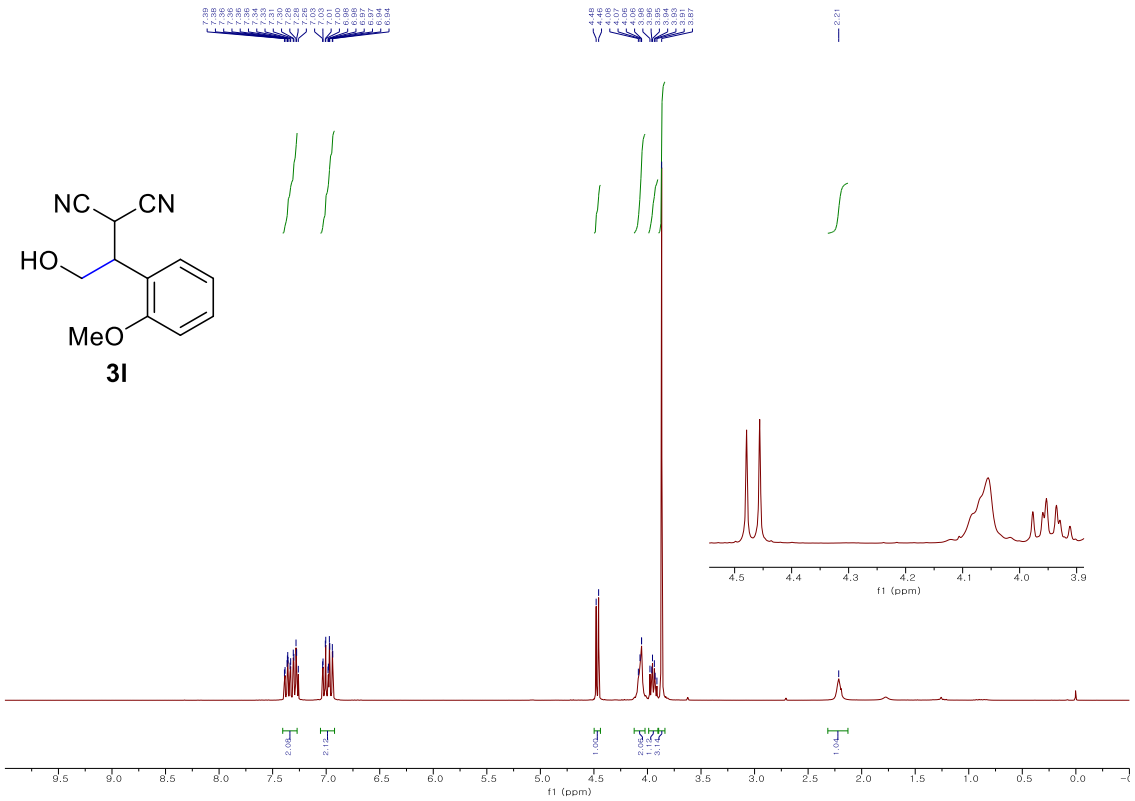


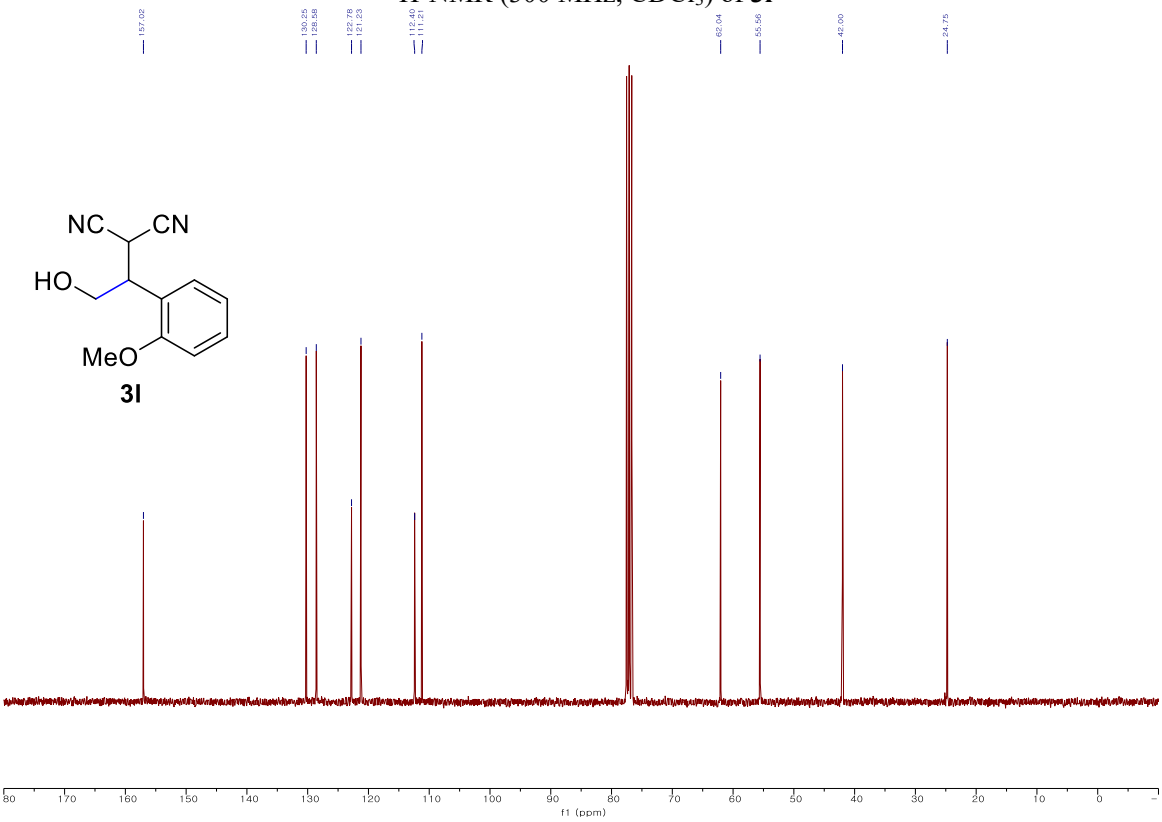
^{1}H-NMR (300 MHz, $CDCl_3$) of **3k**



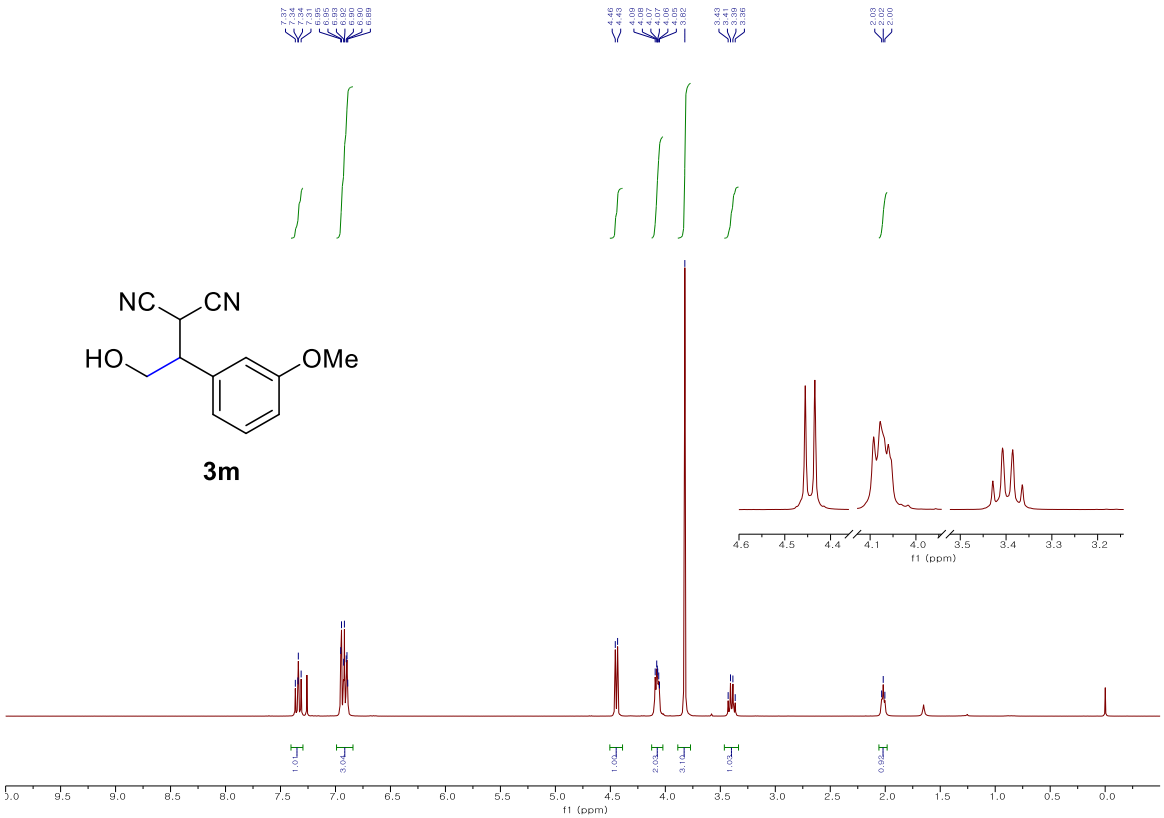
^{13}C-NMR (75Hz, $CDCl_3$) of **3k**



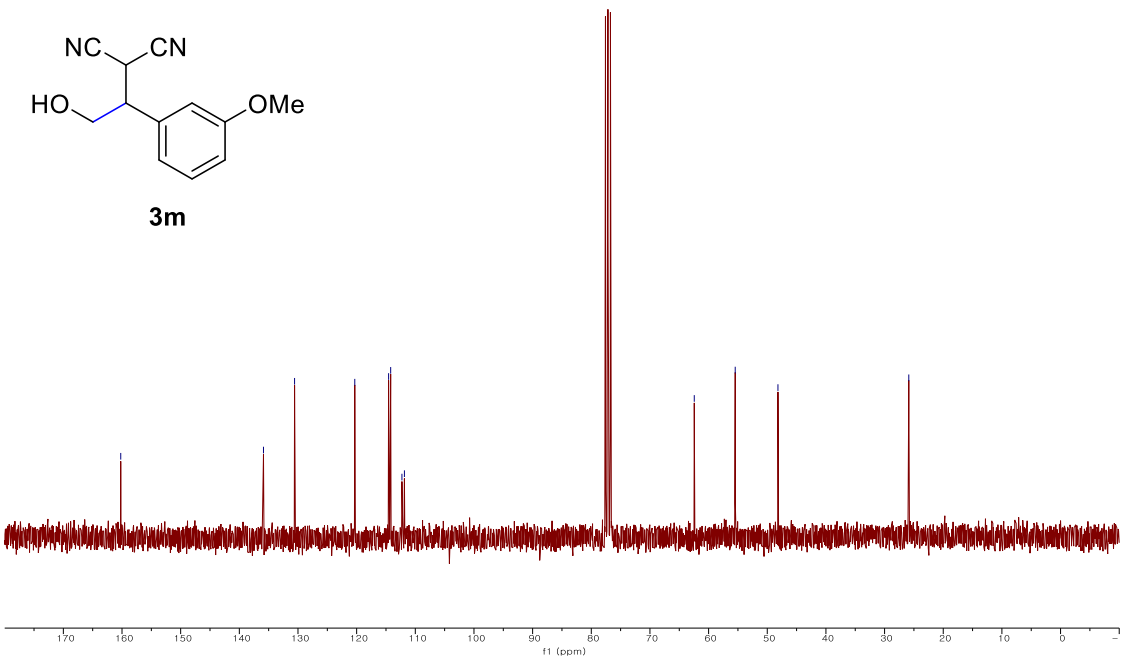
^{1}H-NMR (300 MHz, $CDCl_3$) of **3l**



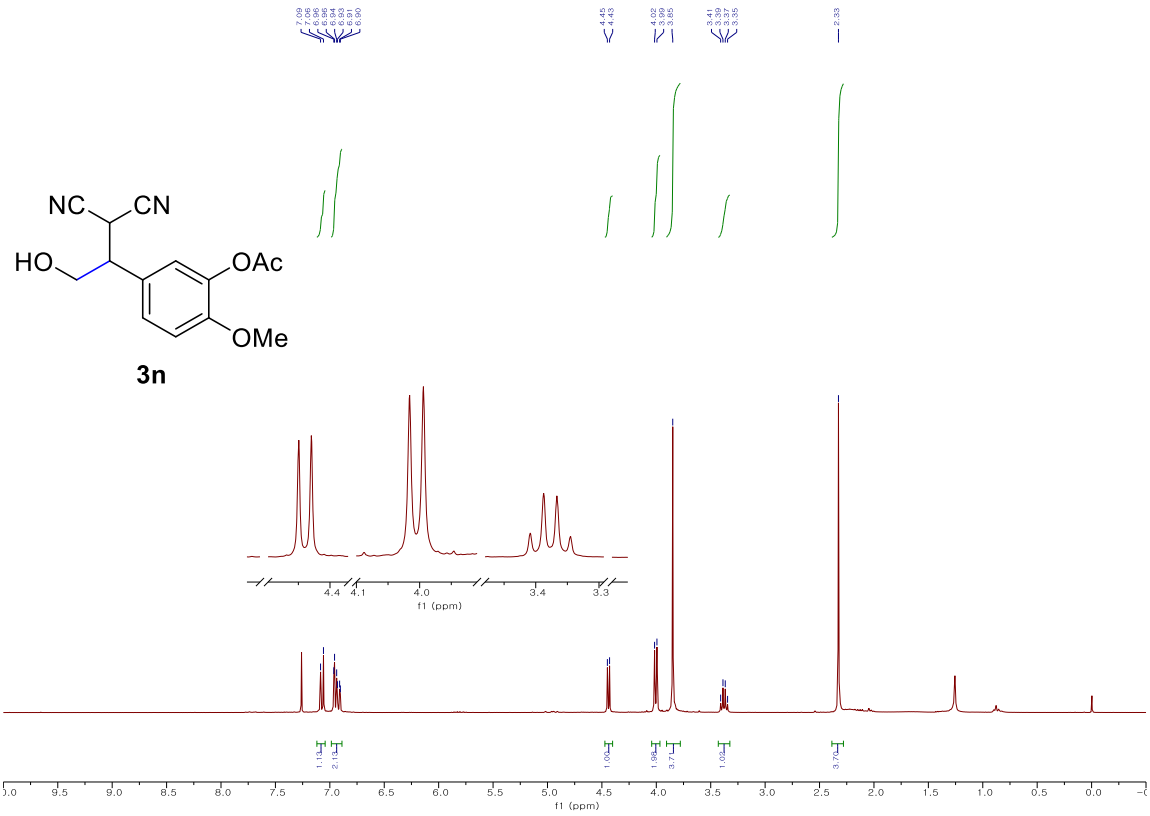
^{13}C-NMR (75Hz, $CDCl_3$) of **3l**



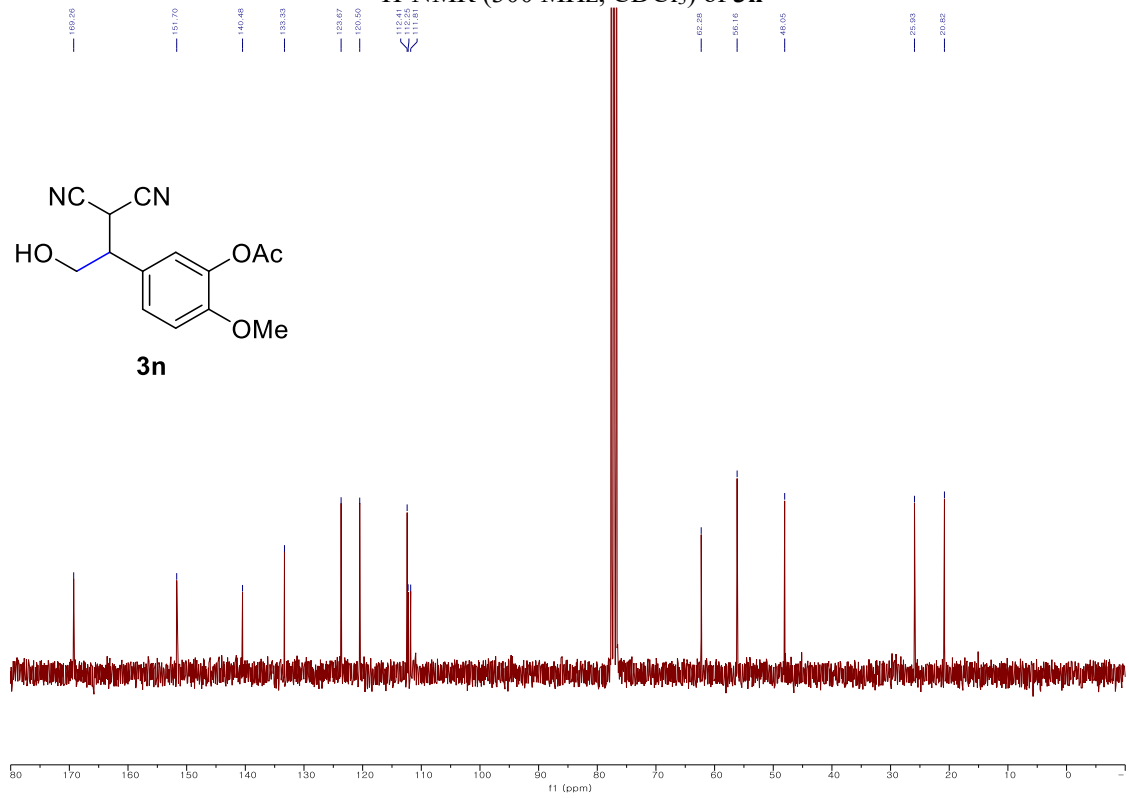
^{1}H-NMR (300 MHz, $CDCl_3$) of **3m**



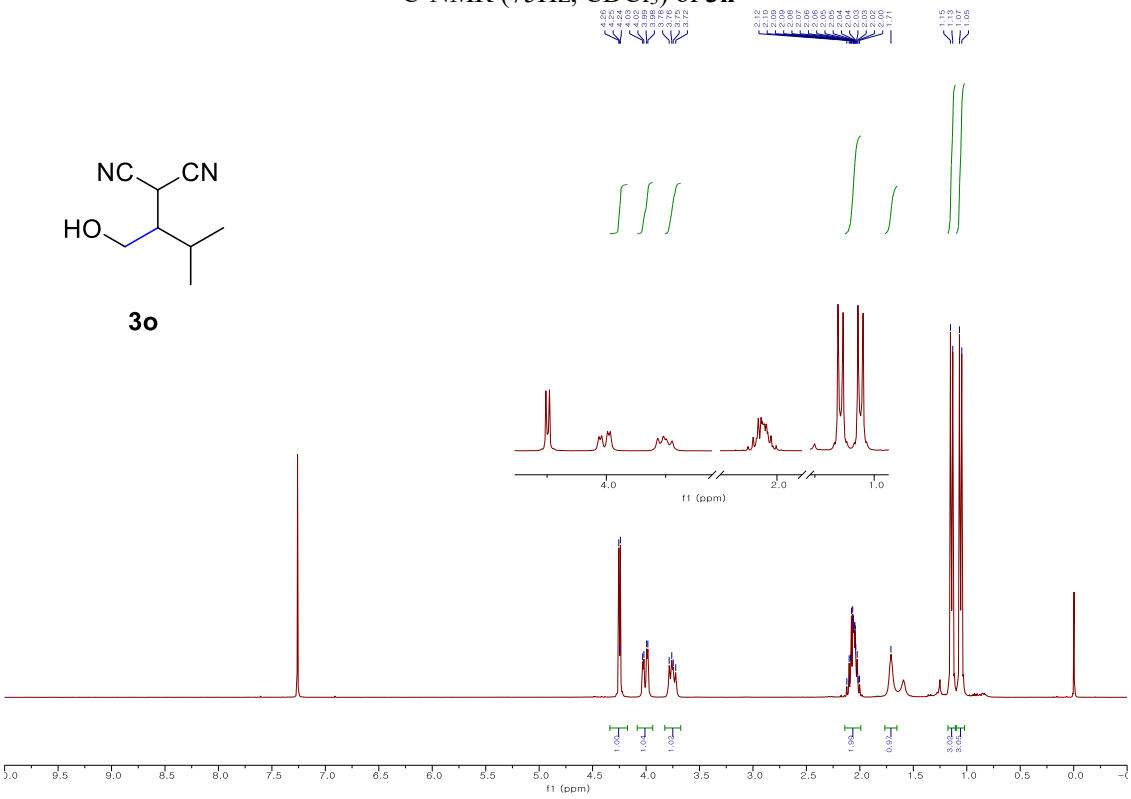
^{13}C-NMR (75Hz, $CDCl_3$) of **3m**



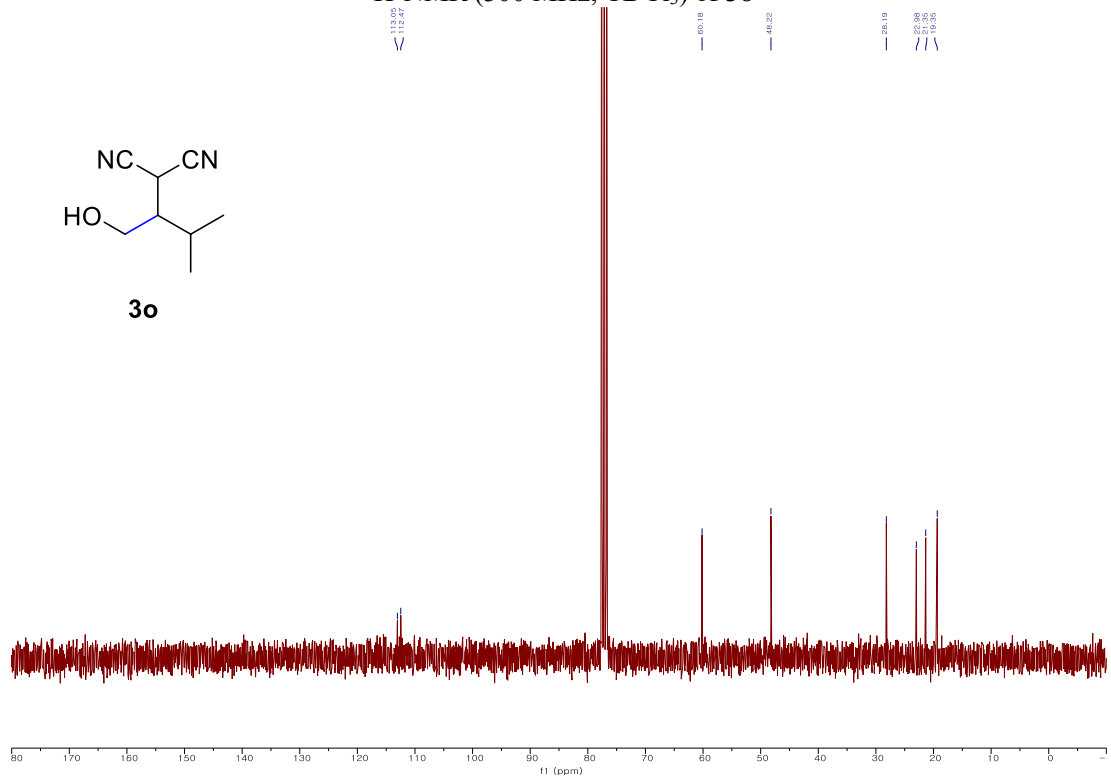
^{1}H-NMR (300 MHz, $CDCl_3$) of **3n**



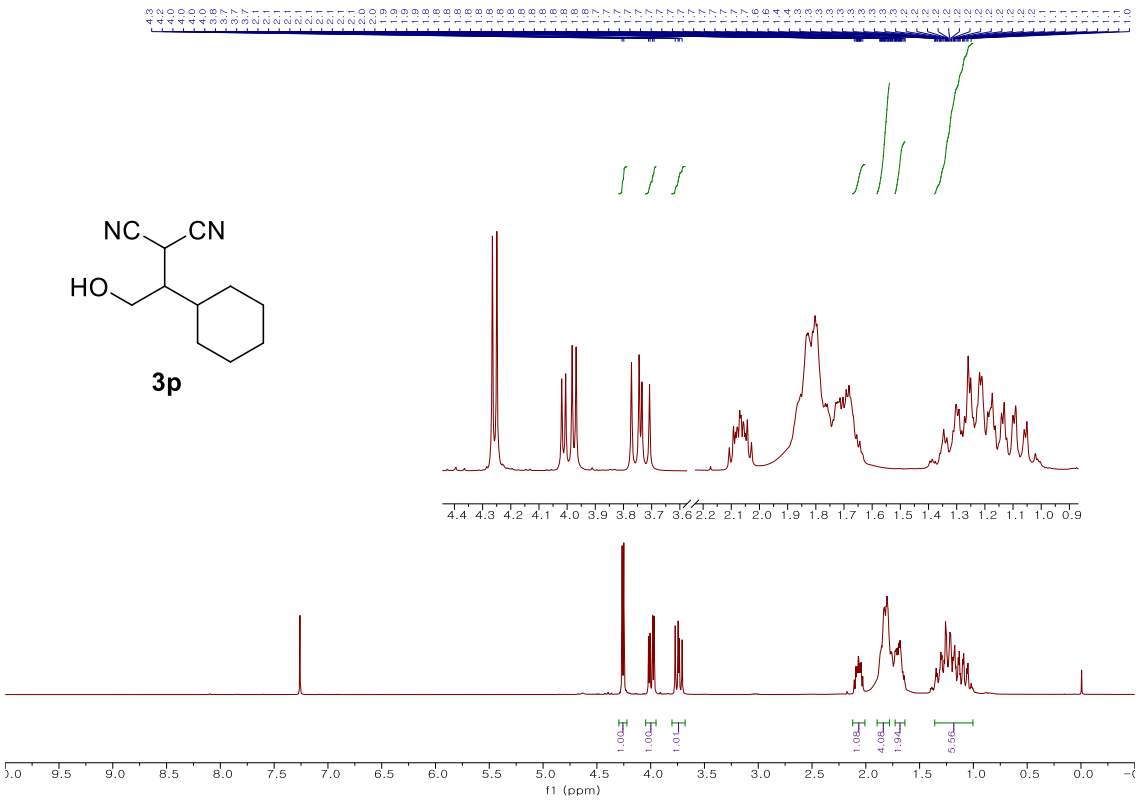
^{13}C-NMR (75Hz, $CDCl_3$) of **3n**



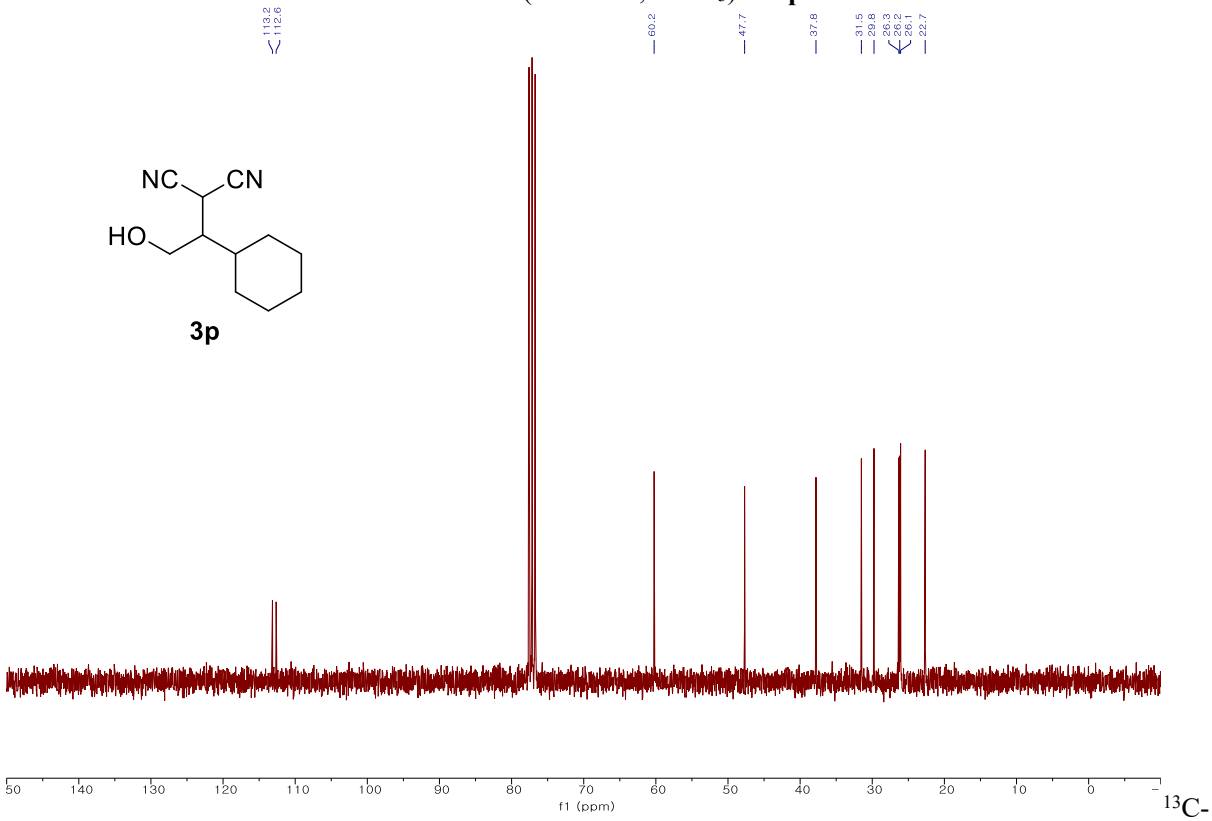
^{1}H-NMR (300 MHz, $CDCl_3$) of **3o**



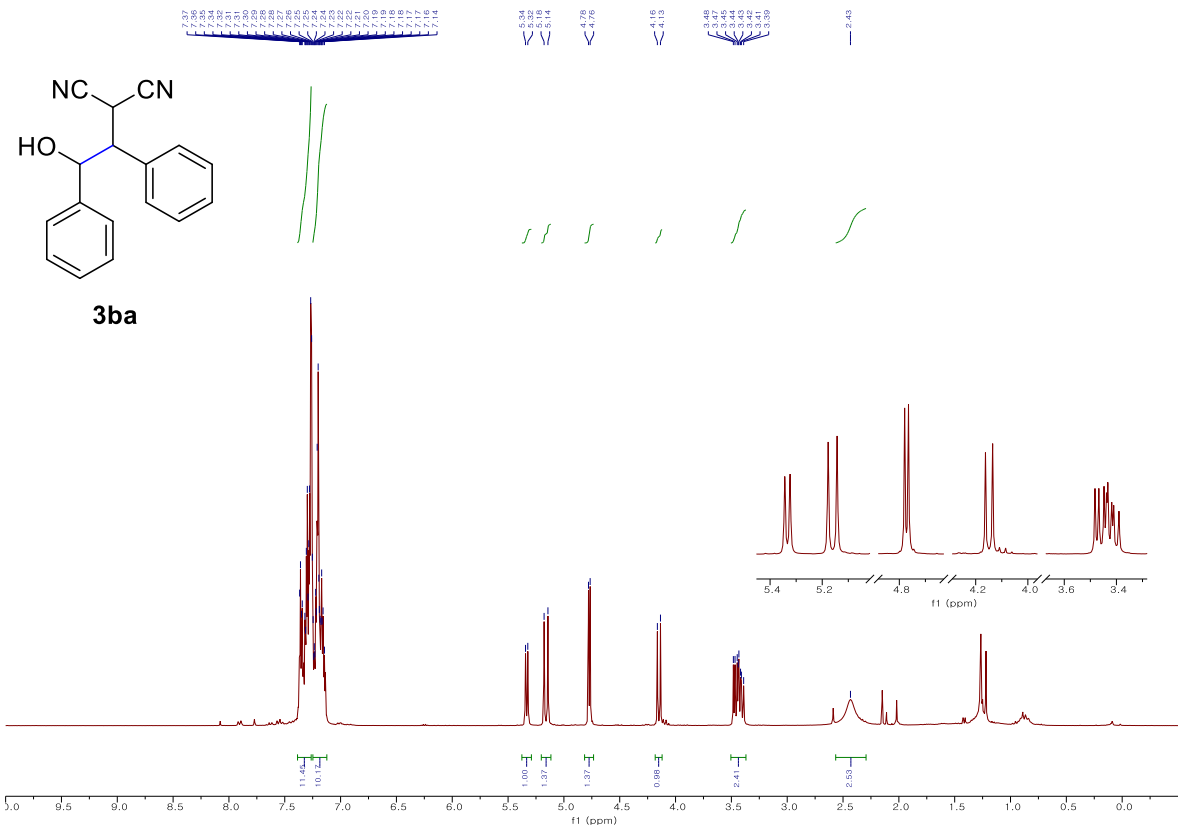
^{13}C-NMR (75Hz, $CDCl_3$) of **3o**



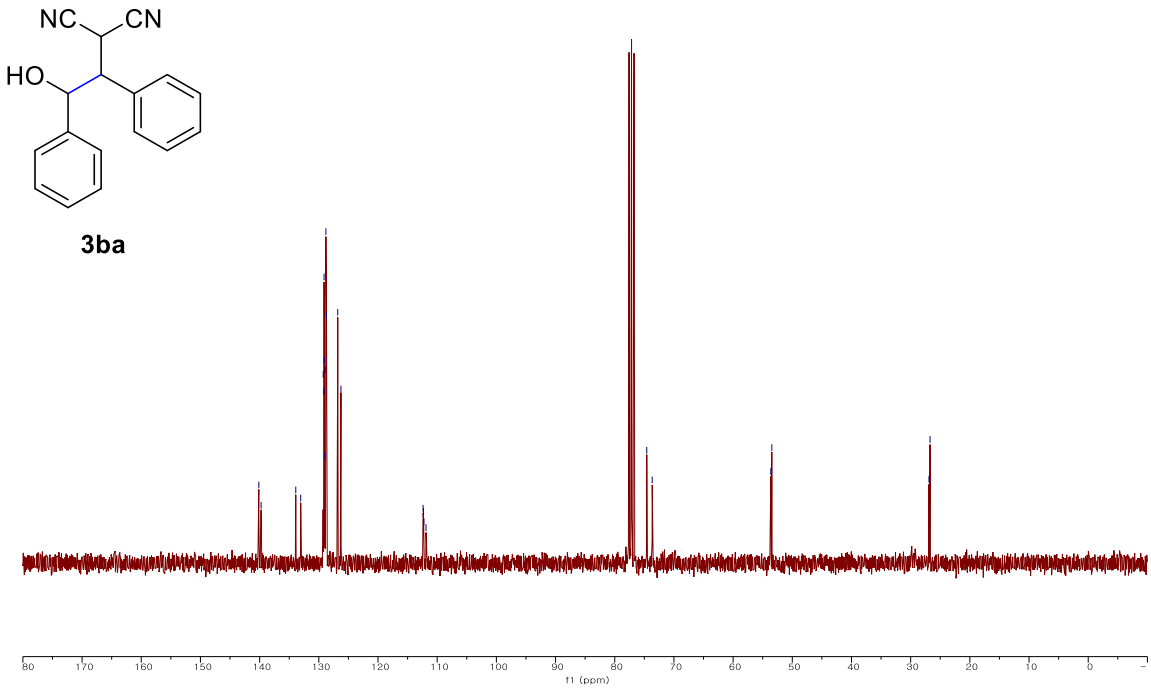
^{1}H-NMR (300 MHz, $CDCl_3$) of **3p**



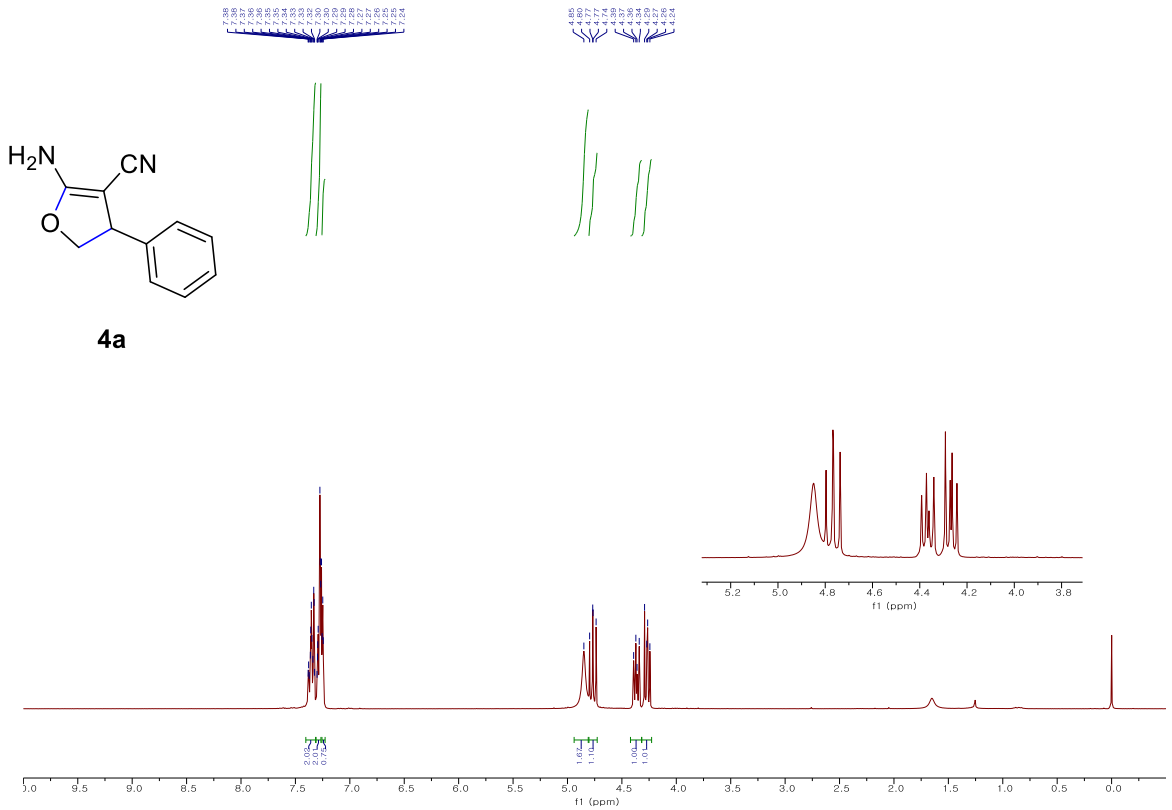
^{13}C-NMR (75Hz, $CDCl_3$) of **3p**



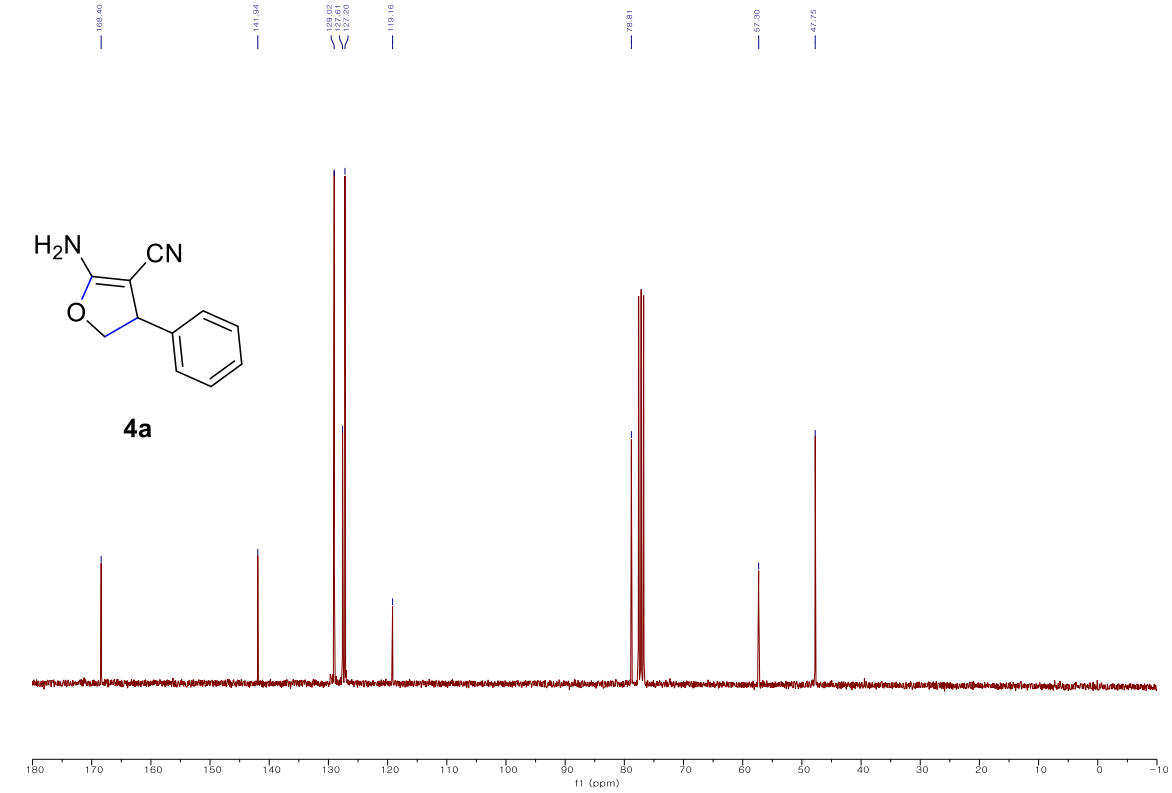
^{1}H-NMR (300 MHz, $CDCl_3$) of **3ba**



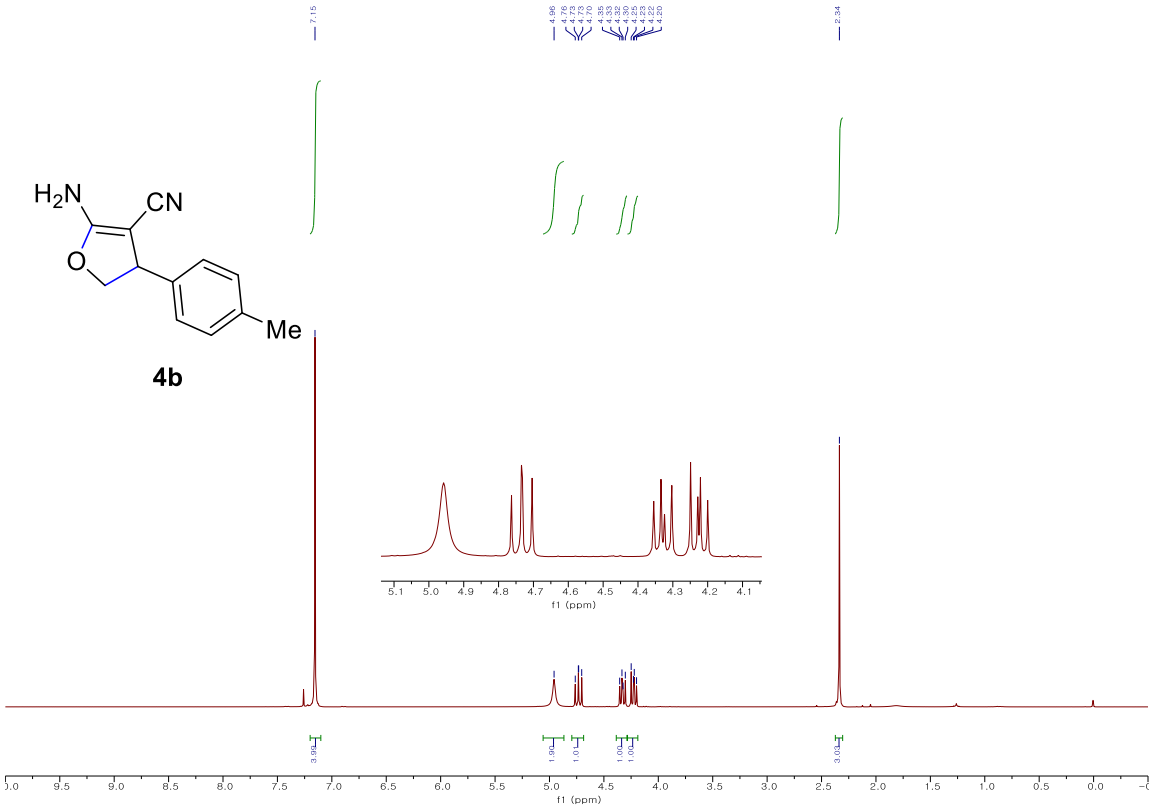
^{13}C-NMR (75Hz, $CDCl_3$) of **3ba**



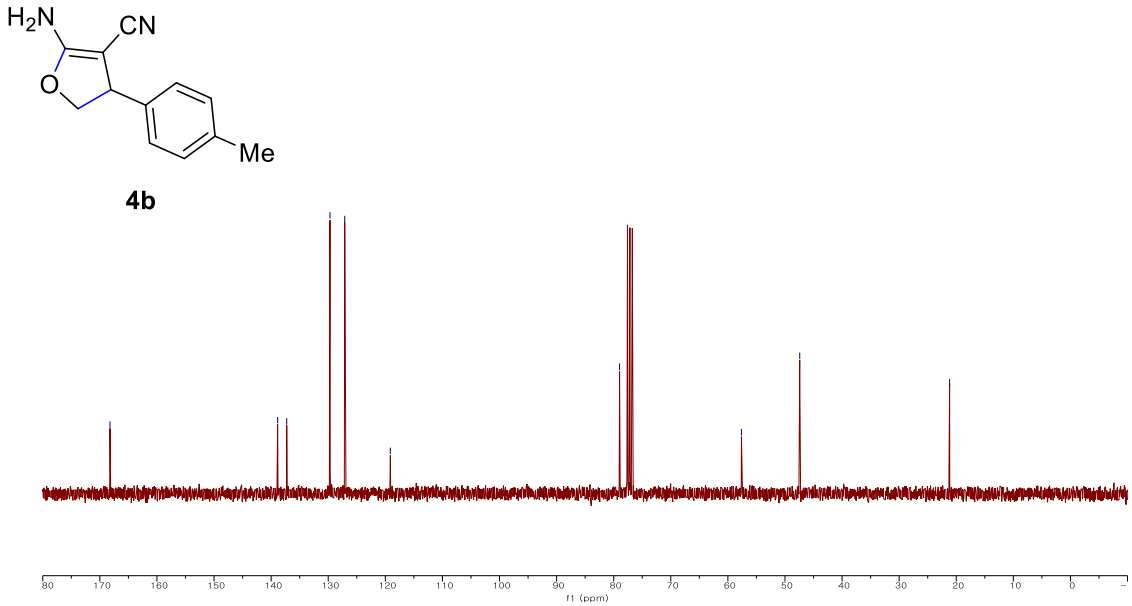
^{1}H-NMR (300 MHz, $CDCl_3$) of **4a**



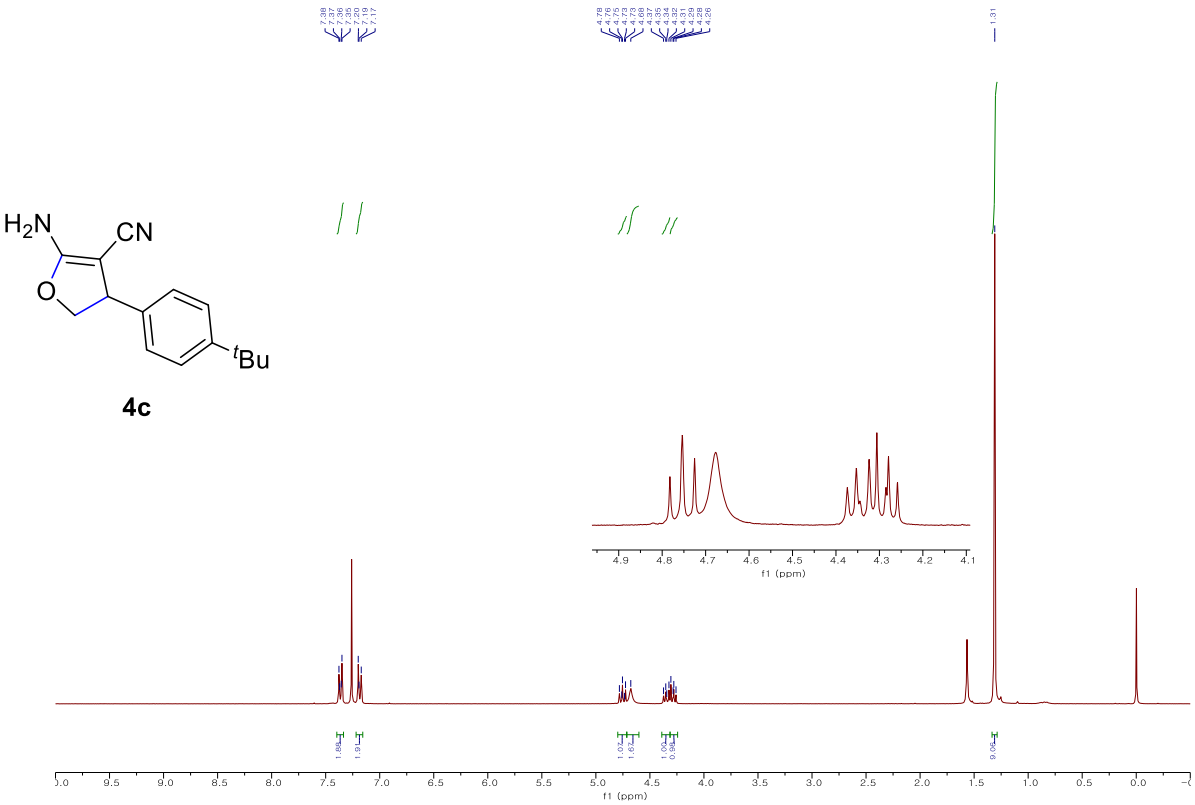
^{13}C-NMR (75Hz, $CDCl_3$) of **4a**



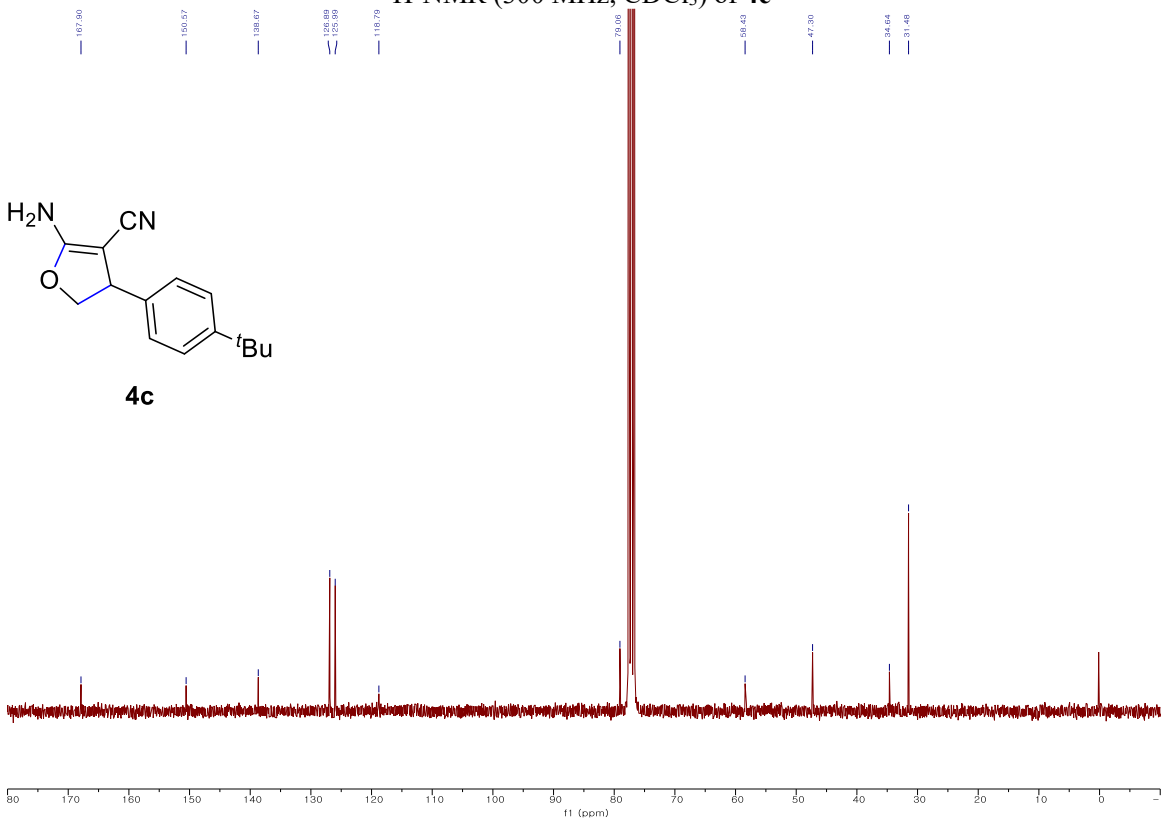
^{1}H-NMR (300 MHz, $CDCl_3$) of **4b**



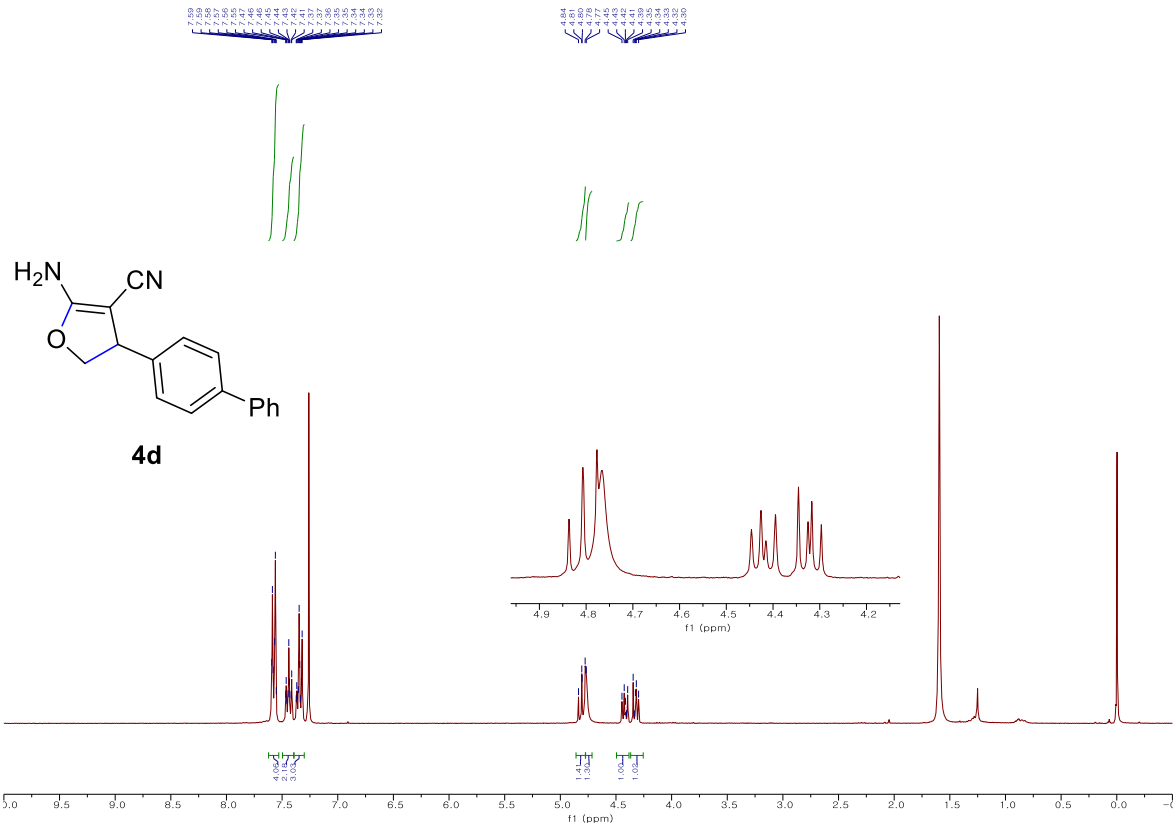
^{13}C-NMR (75Hz, $CDCl_3$) of **4b**



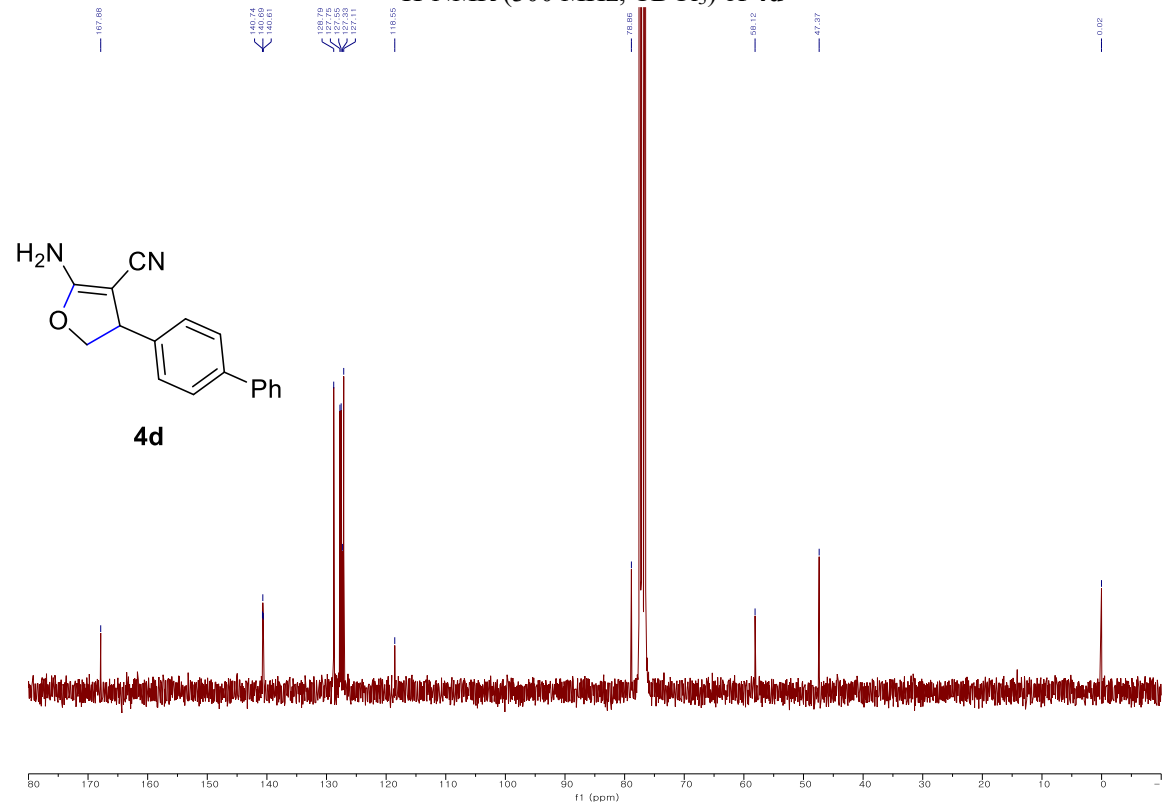
^{1}H-NMR (300 MHz, $CDCl_3$) of **4c**



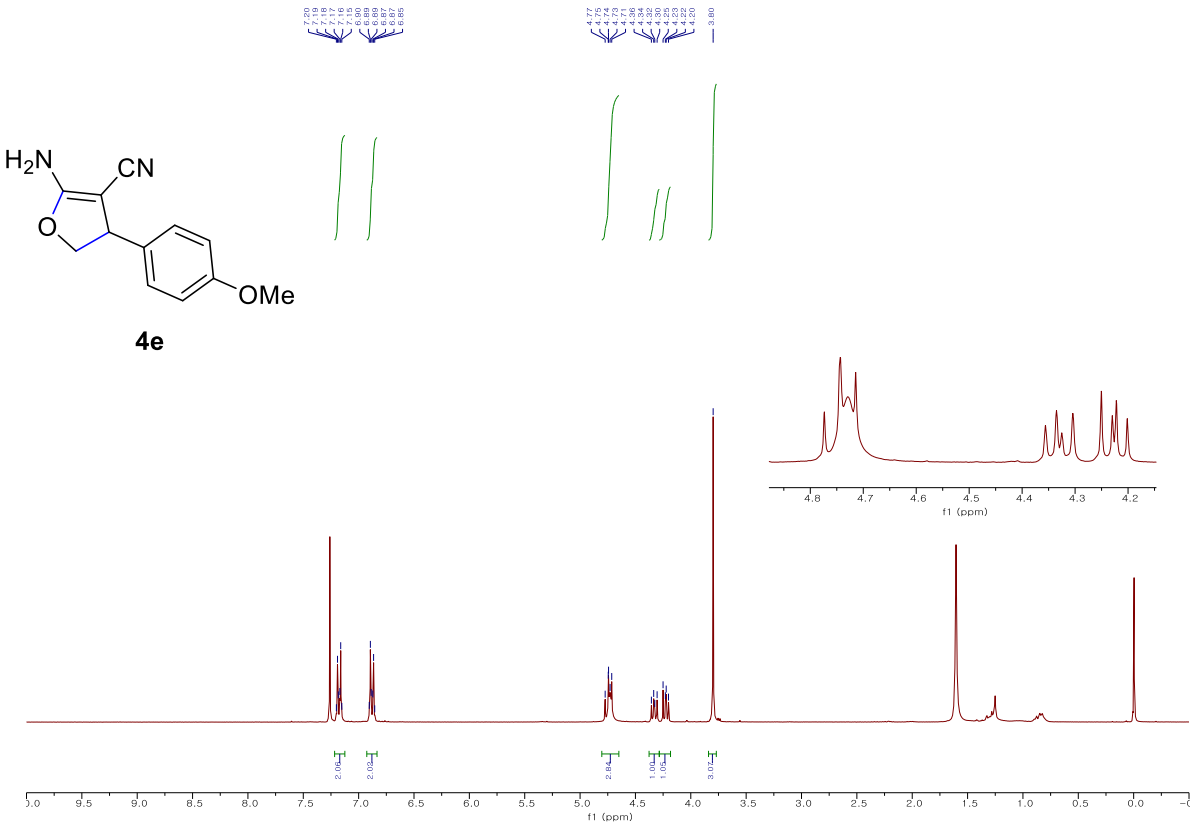
^{13}C-NMR (75Hz, $CDCl_3$) of **4c**



^{1}H-NMR (300 MHz, $CDCl_3$) of **4d**



^{13}C-NMR (75Hz, $CDCl_3$) of **4d**



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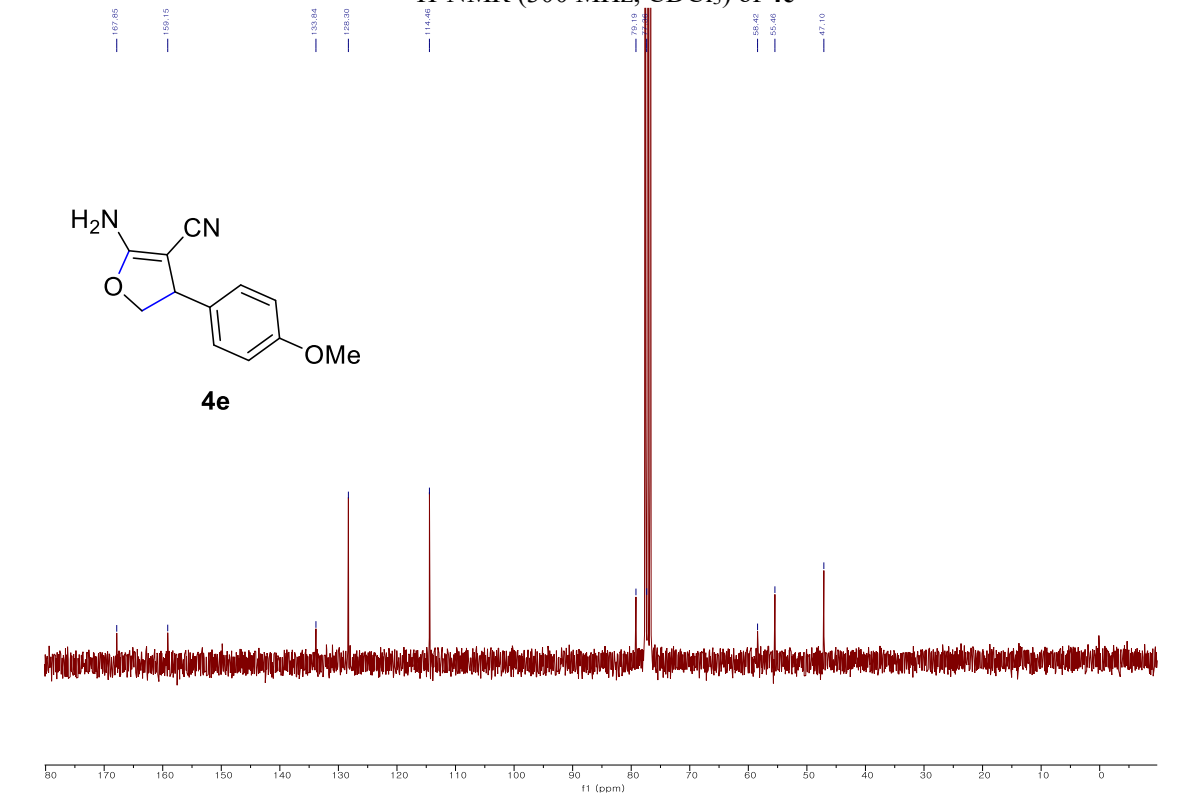

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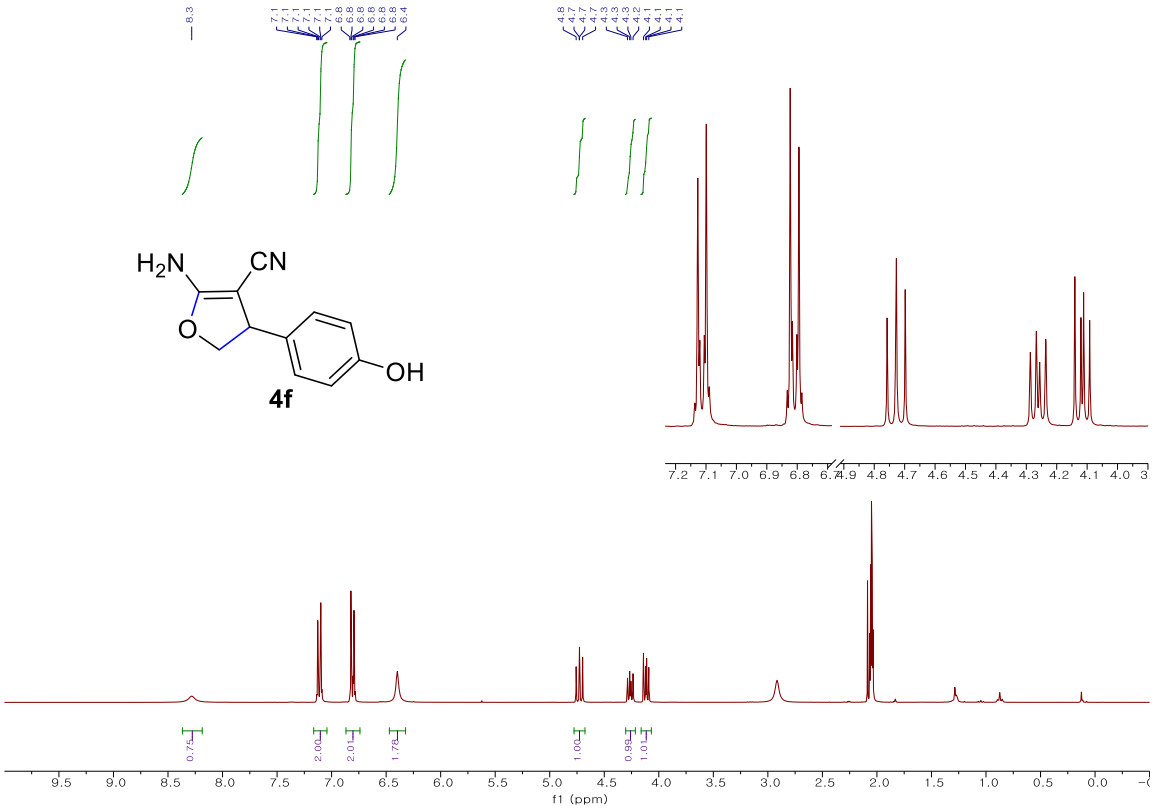
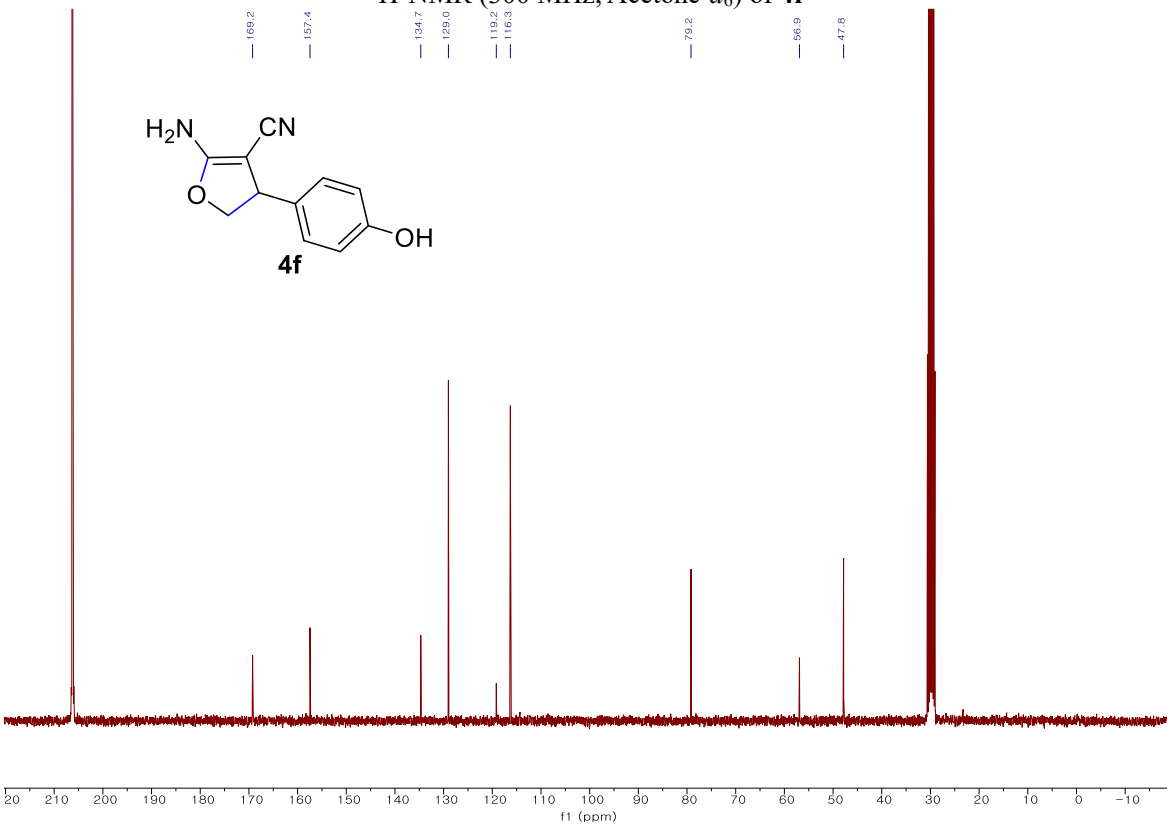
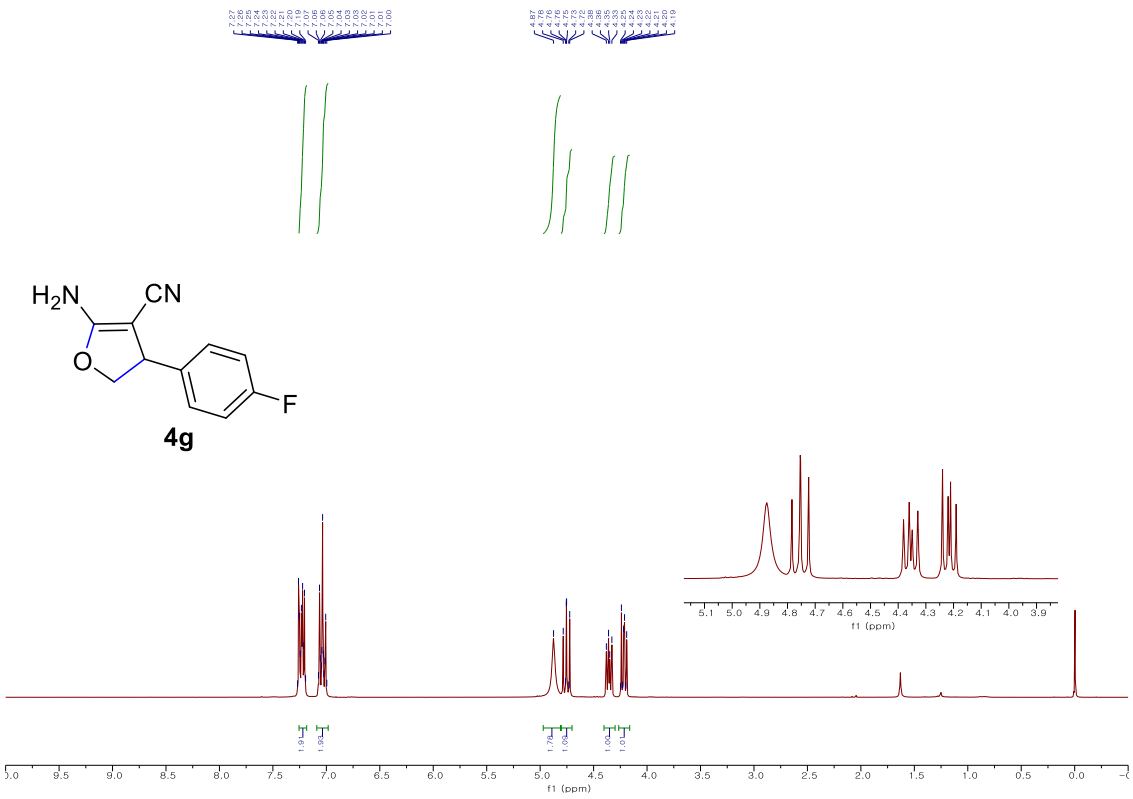


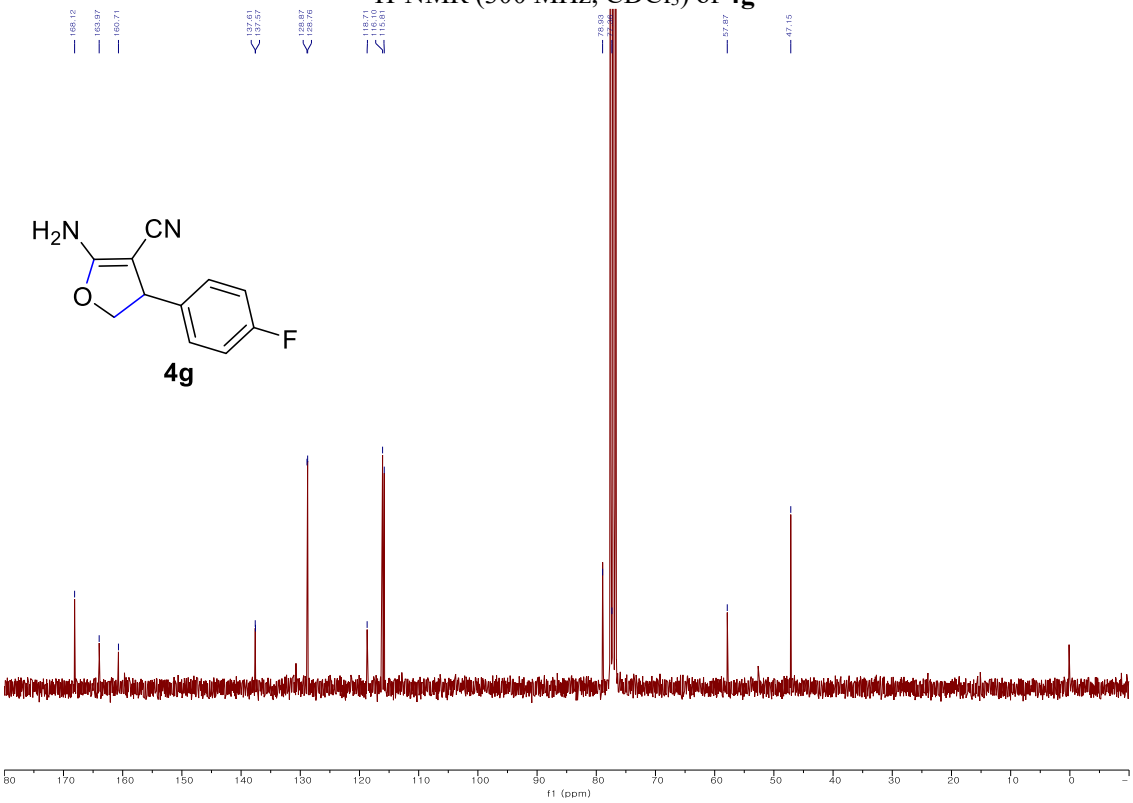
^{1}H-NMR (300 MHz, Acetone-d_6) of **4f**



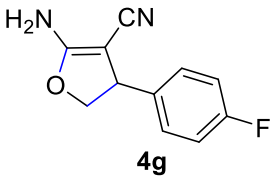
^{13}C-NMR (75Hz, Acetone-d_6) of **4f**



^{1}H-NMR (300 MHz, $CDCl_3$) of **4g**

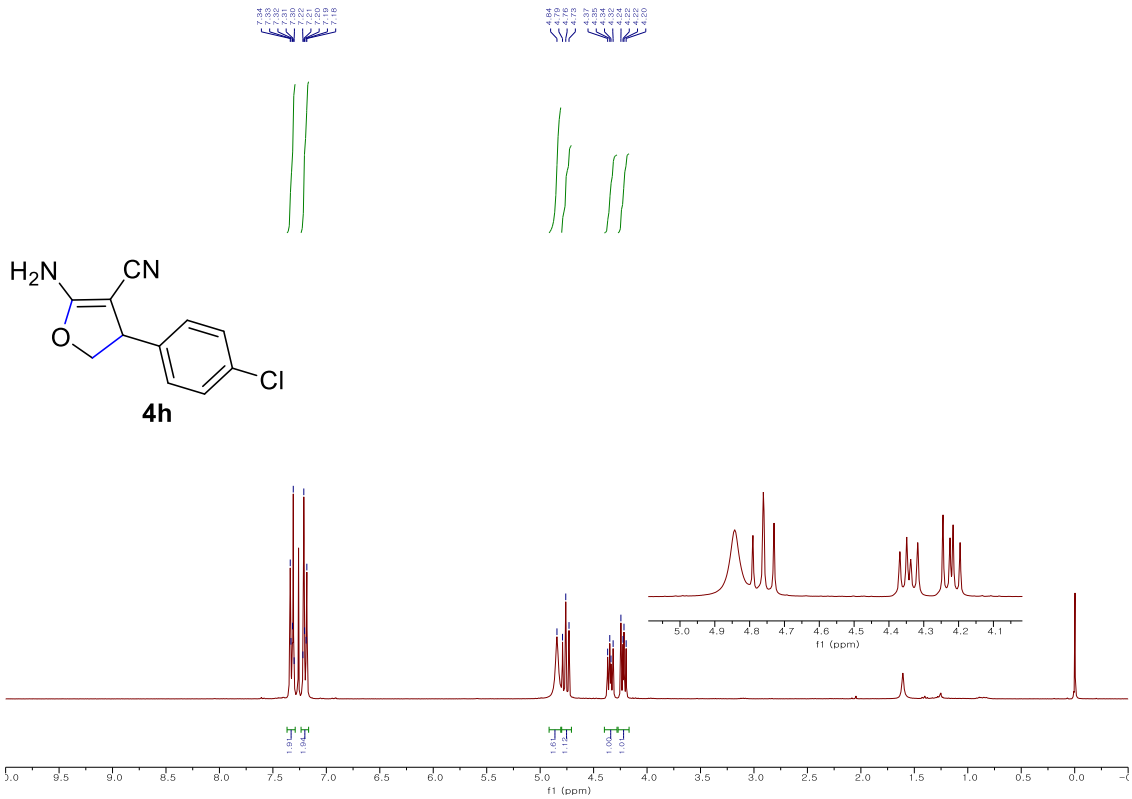


^{13}C-NMR (75Hz, $CDCl_3$) of **4g**

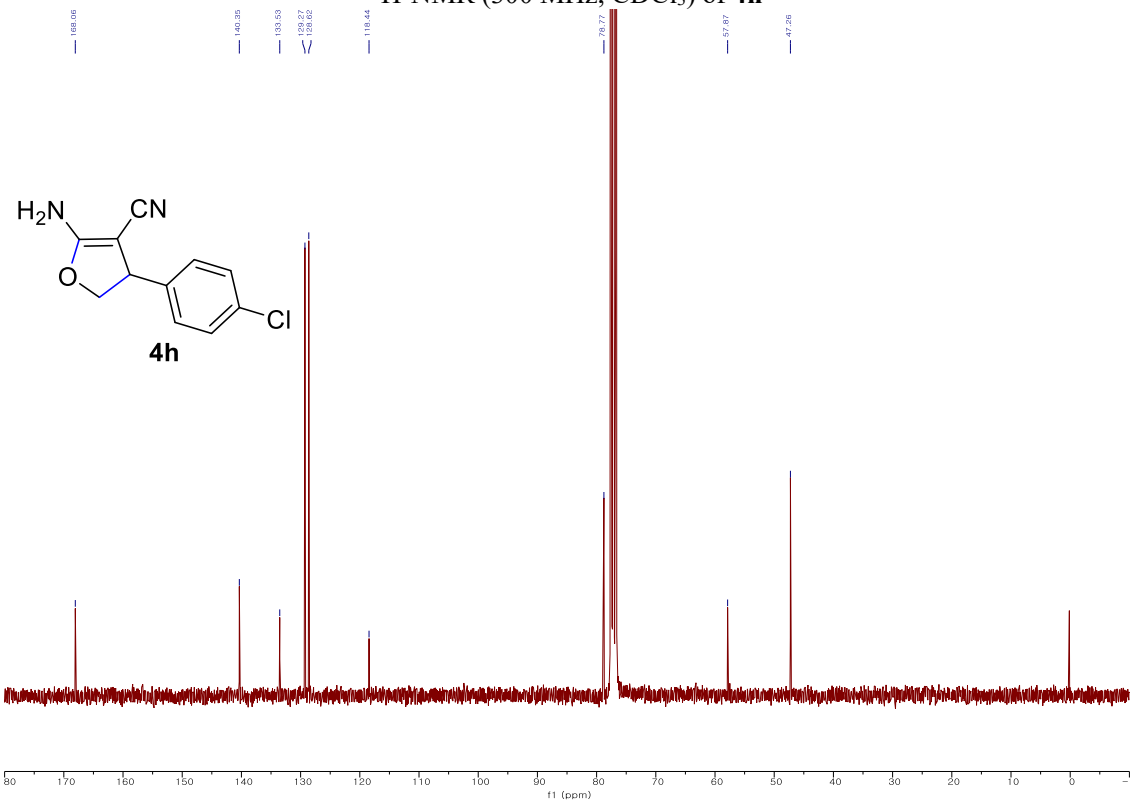


4g

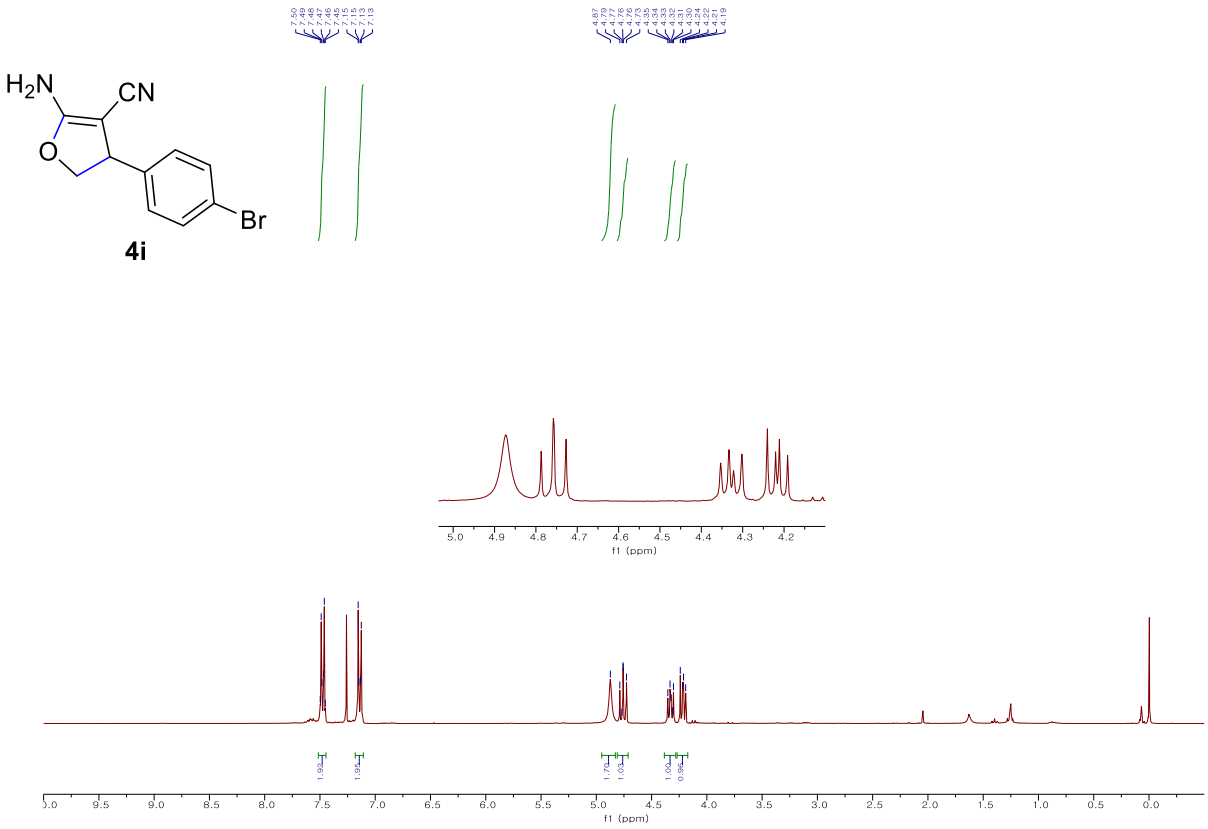
^{19}F-NMR (282 MHz, $CDCl_3$) of **4g**



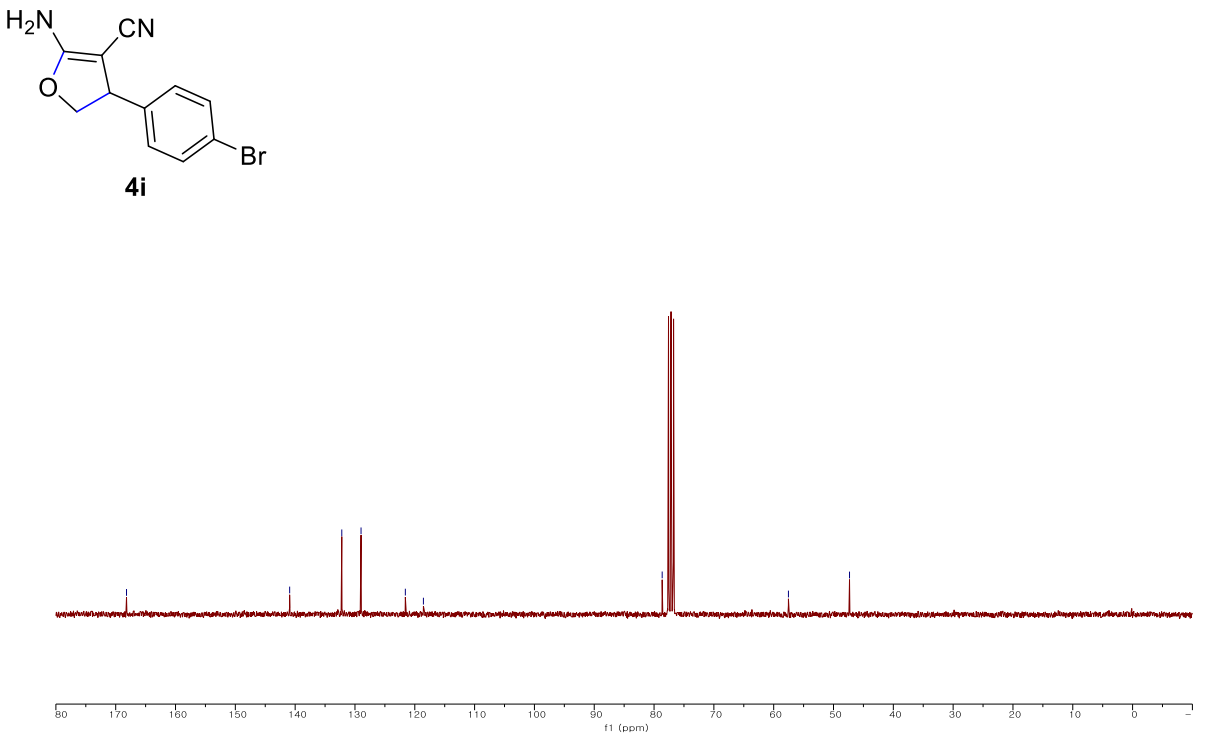
^{1}H-NMR (300 MHz, $CDCl_3$) of **4h**



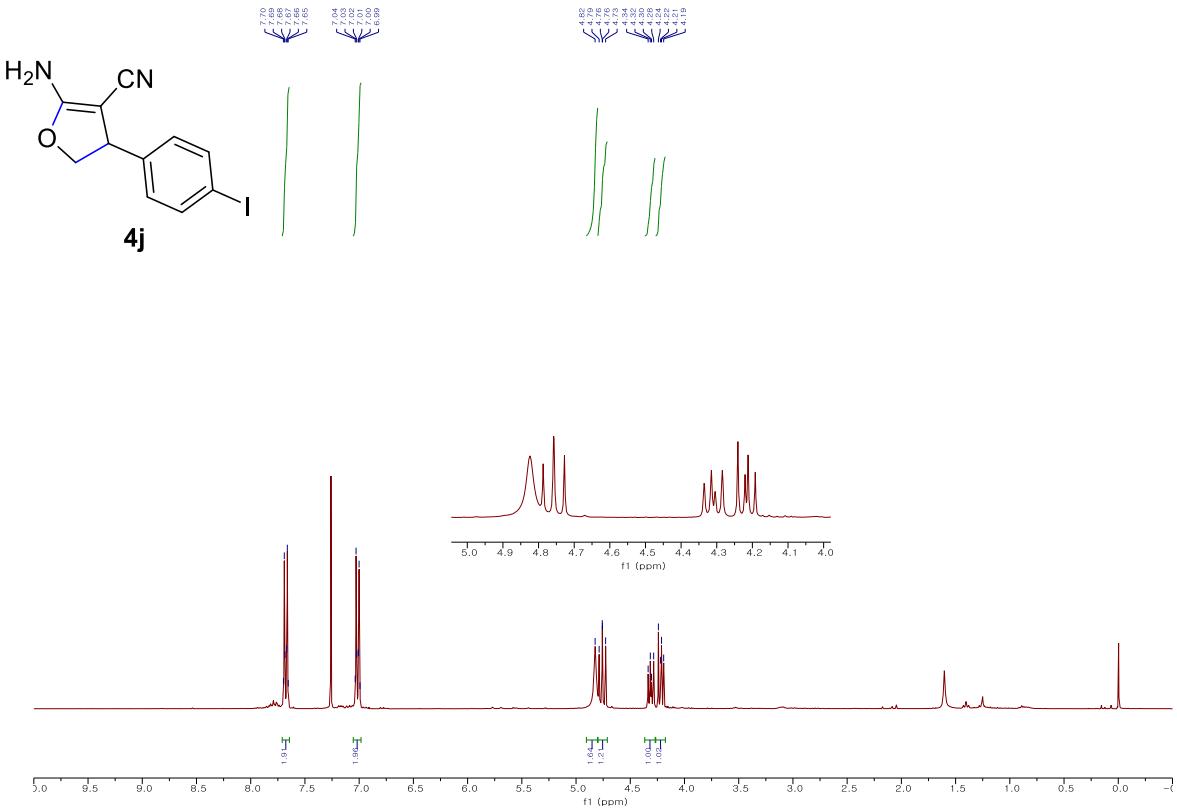
^{13}C-NMR (75Hz, $CDCl_3$) of **4h**



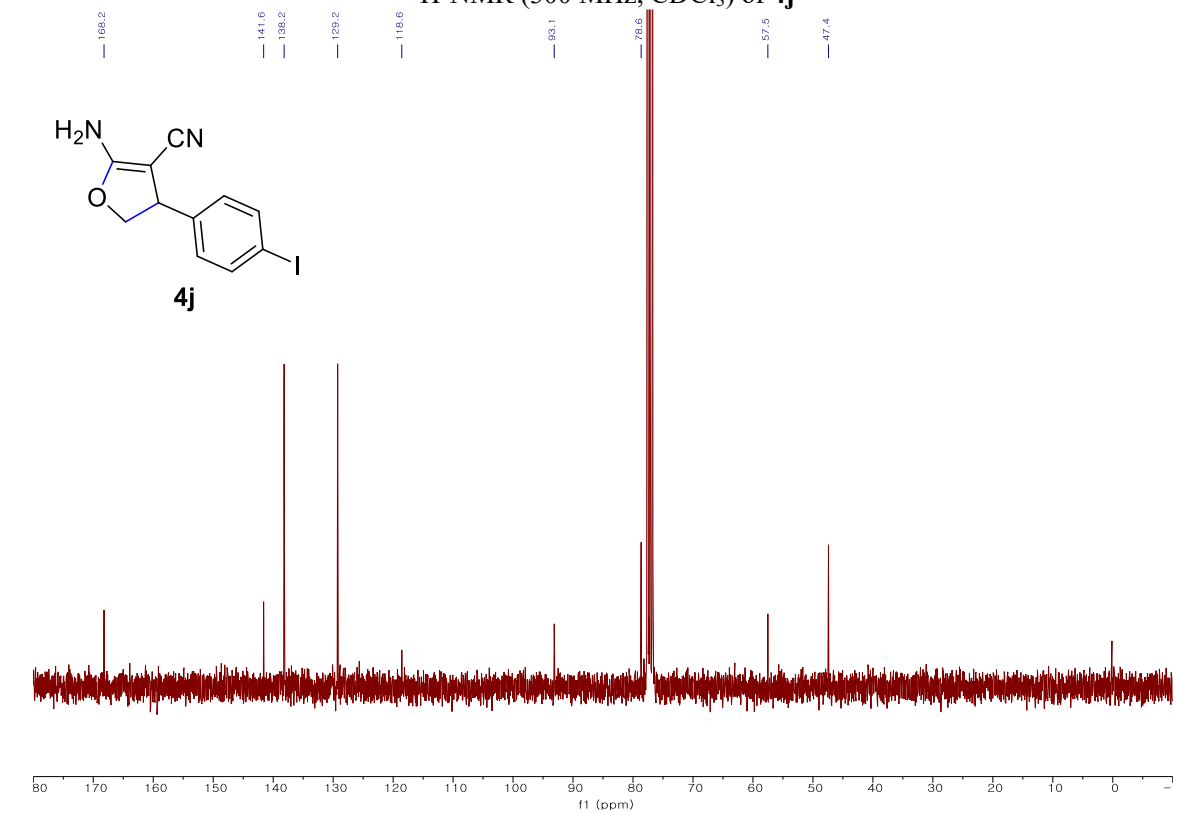
^{1}H-NMR (300 MHz, $CDCl_3$) of **4i**



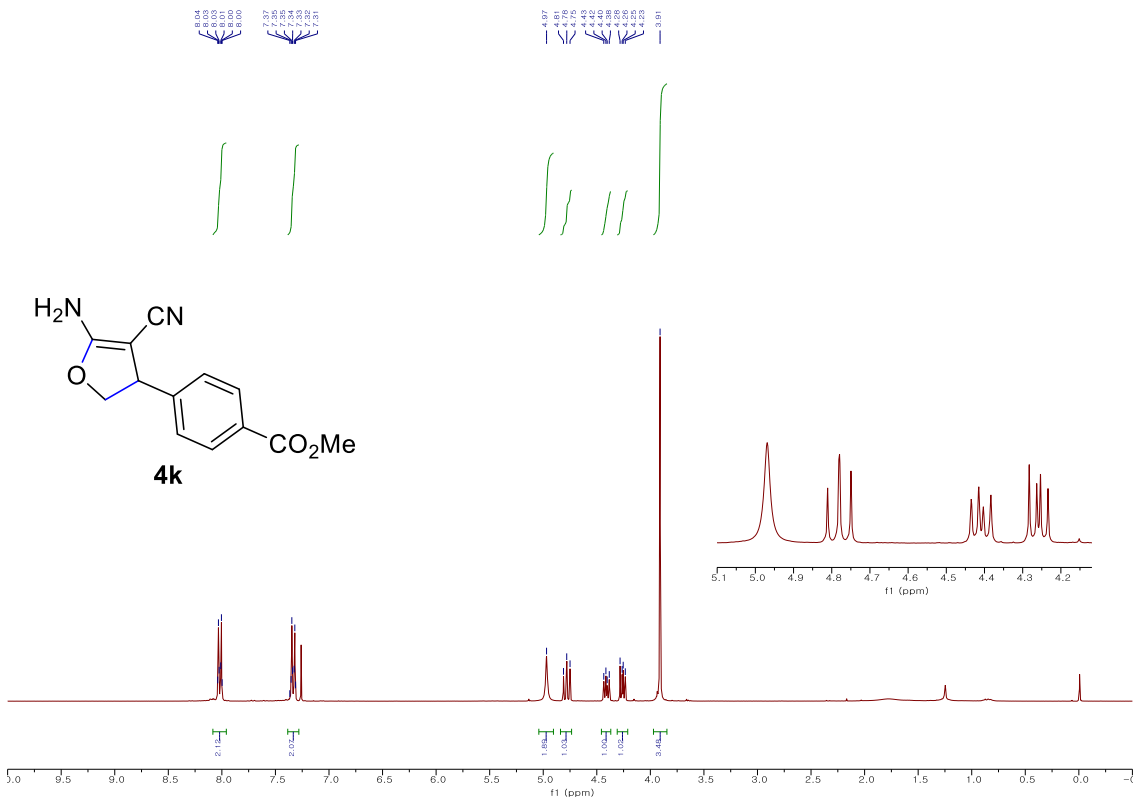
^{13}C-NMR (75Hz, $CDCl_3$) of **4i**



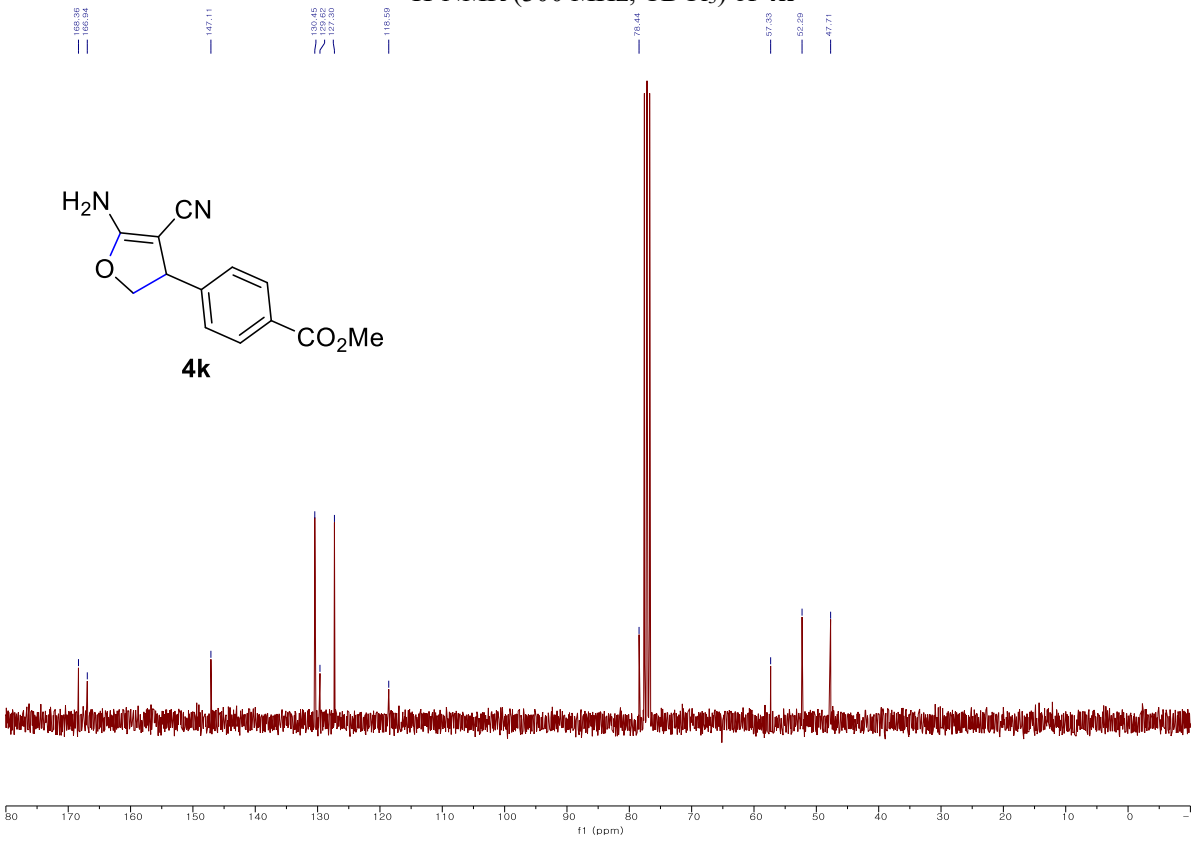
^{1}H-NMR (300 MHz, $CDCl_3$) of **4j**



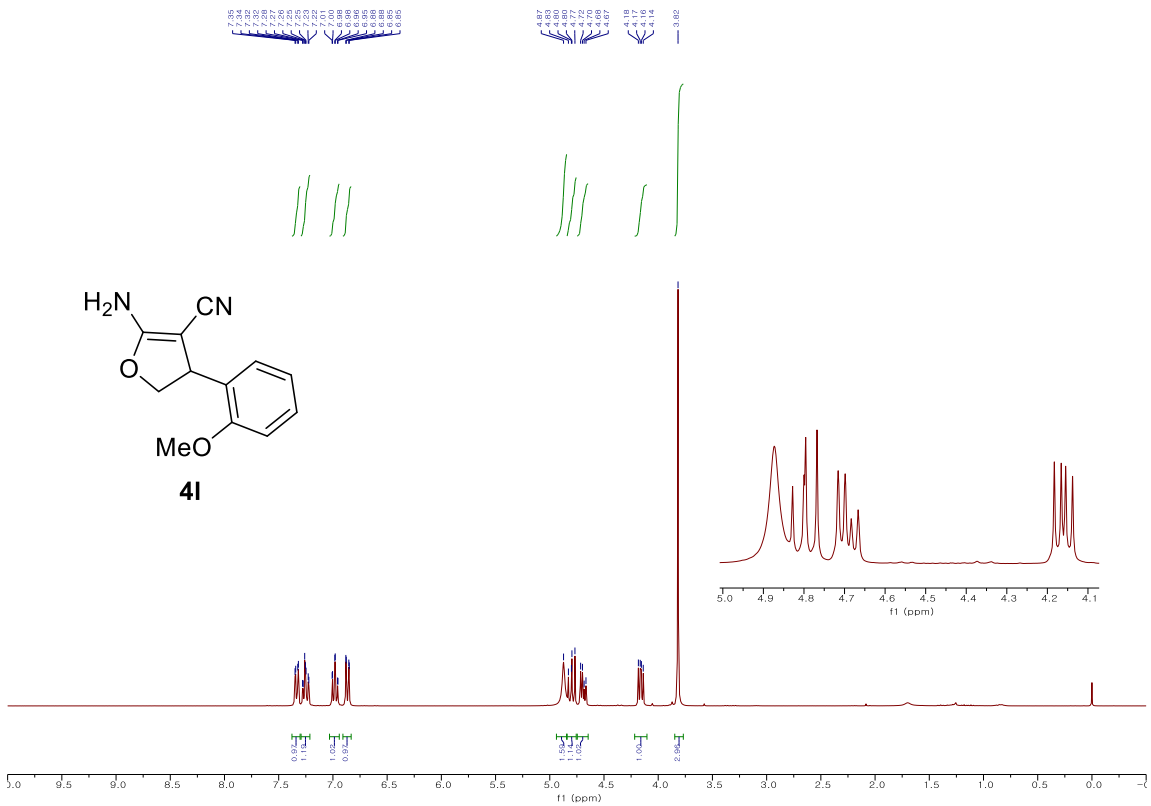
^{13}C-NMR (75Hz, $CDCl_3$) of **4j**



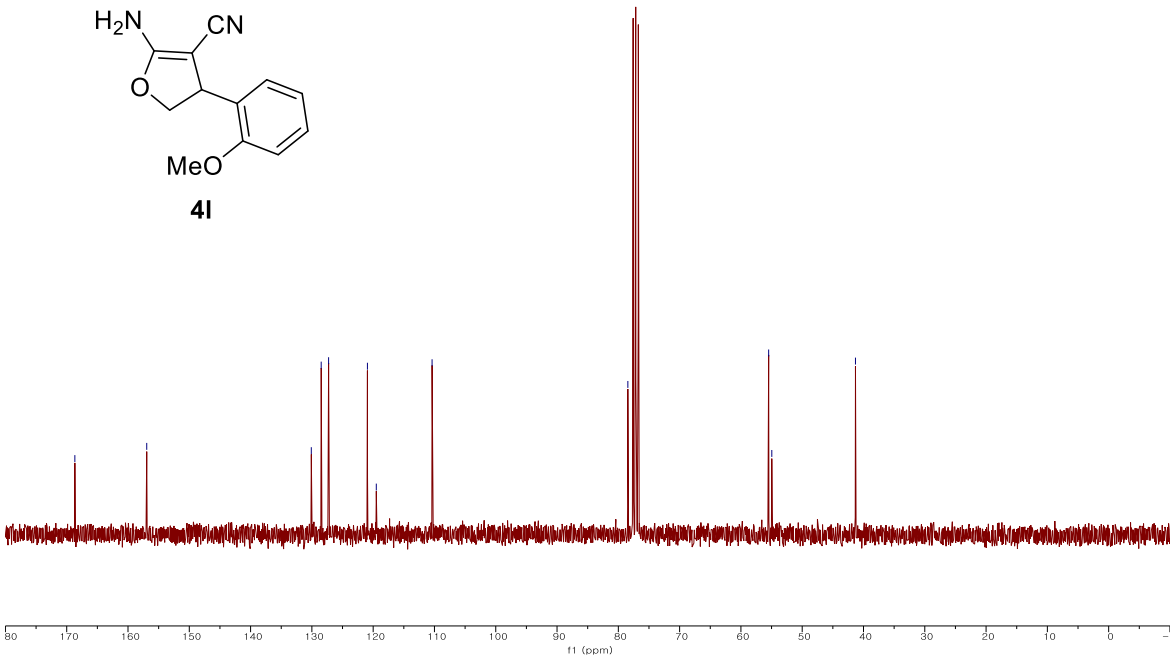
^{1}H-NMR (300 MHz, $CDCl_3$) of **4k**



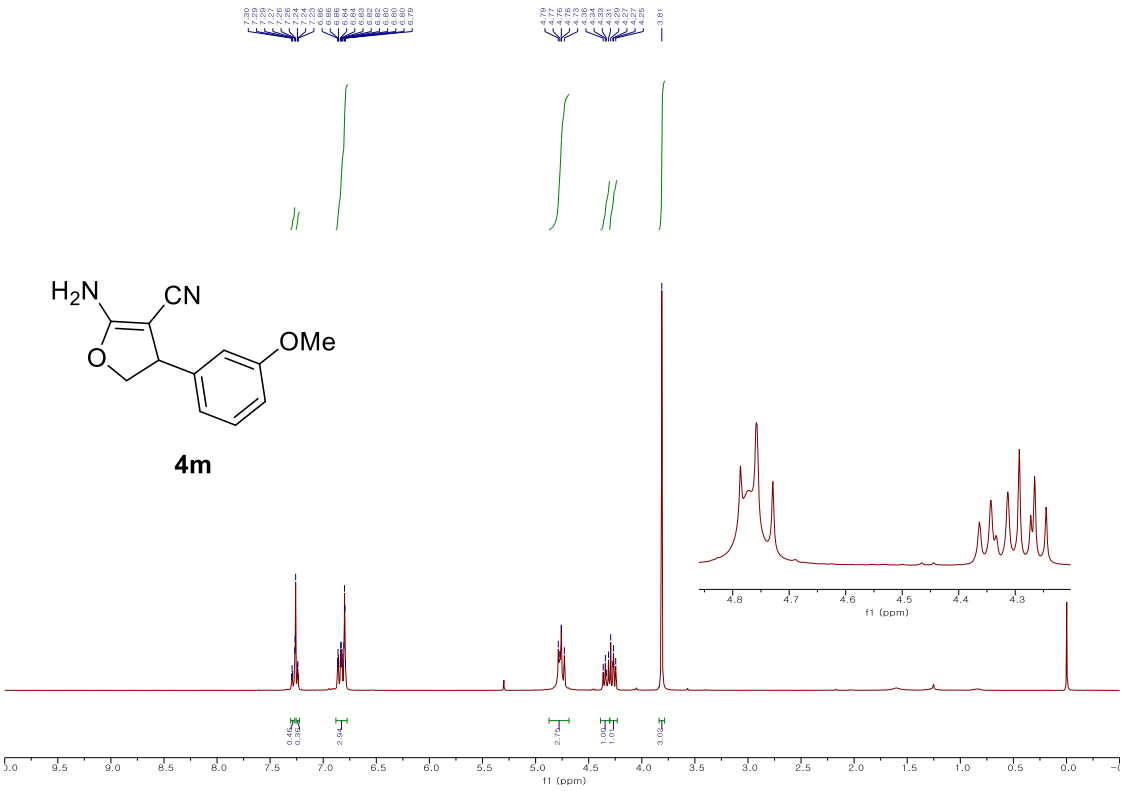
^{13}C-NMR (75Hz, $CDCl_3$) of **4k**



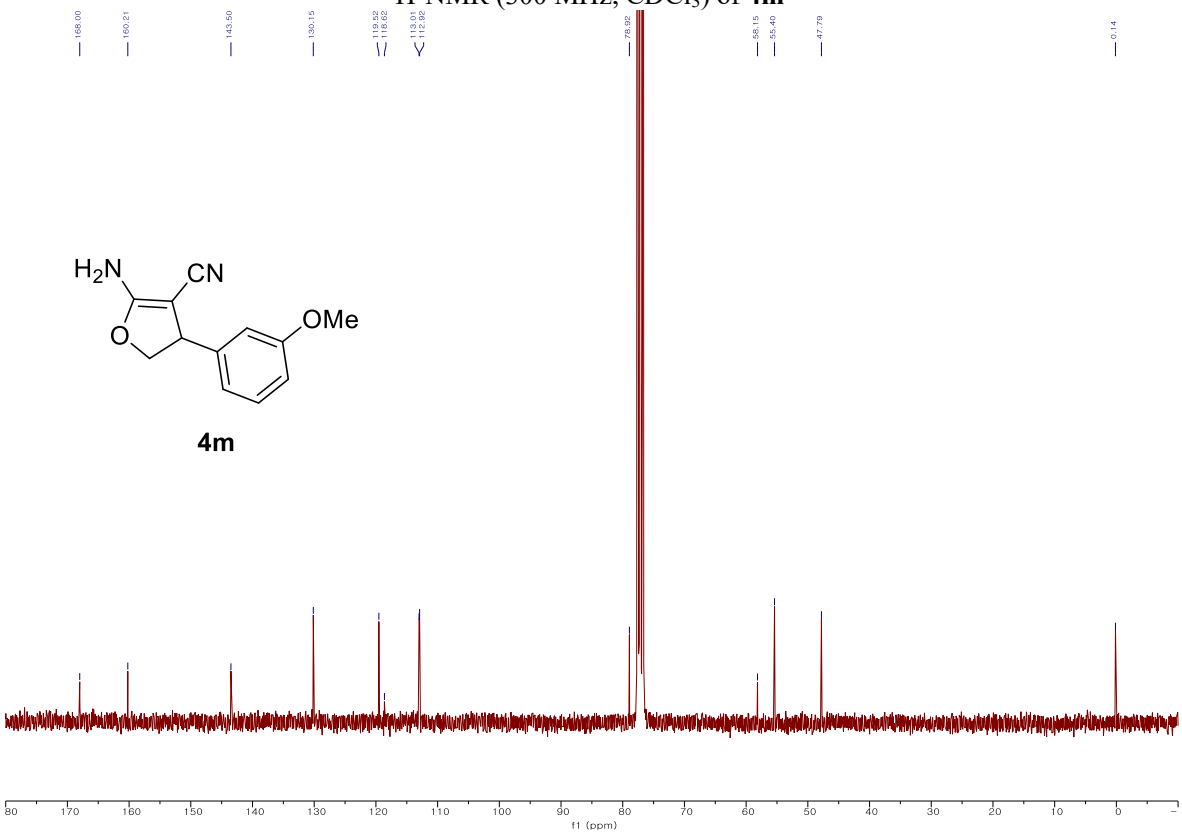
^{1}H-NMR (300 MHz, $CDCl_3$) of **4l**



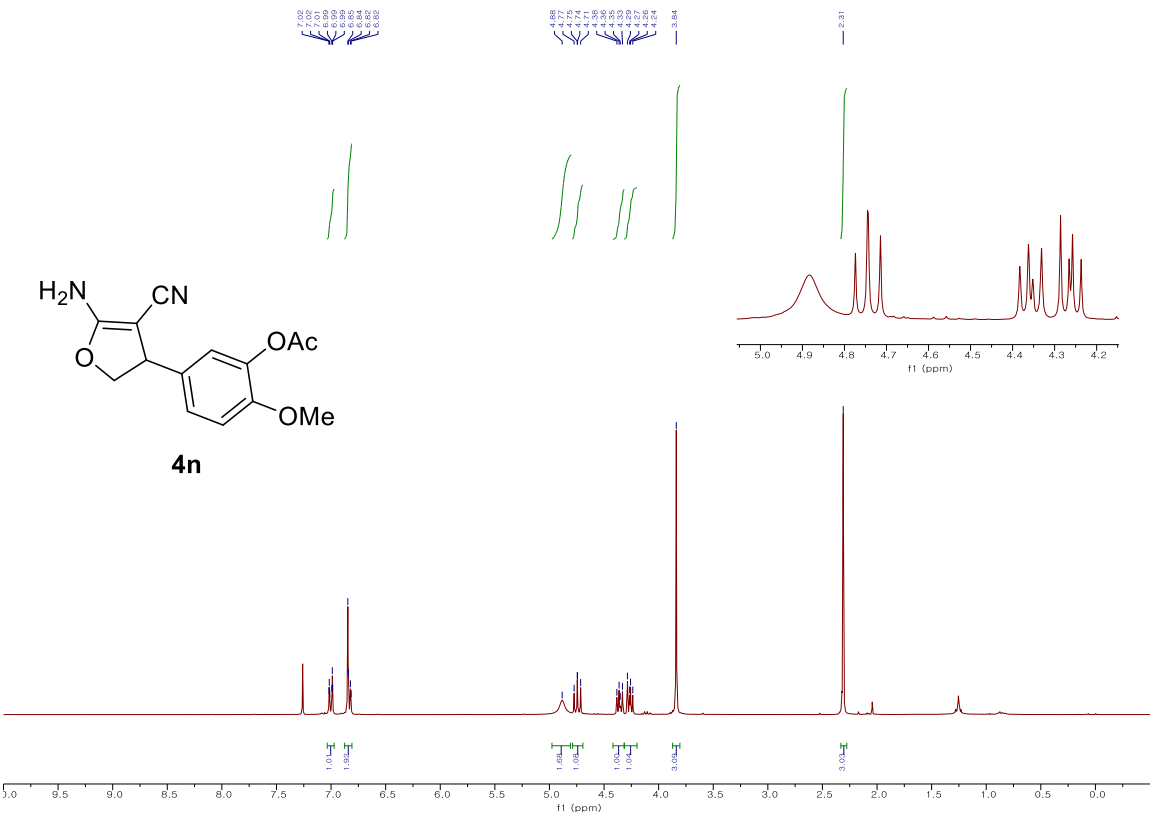
^{13}C-NMR (75Hz, $CDCl_3$) of **4l**



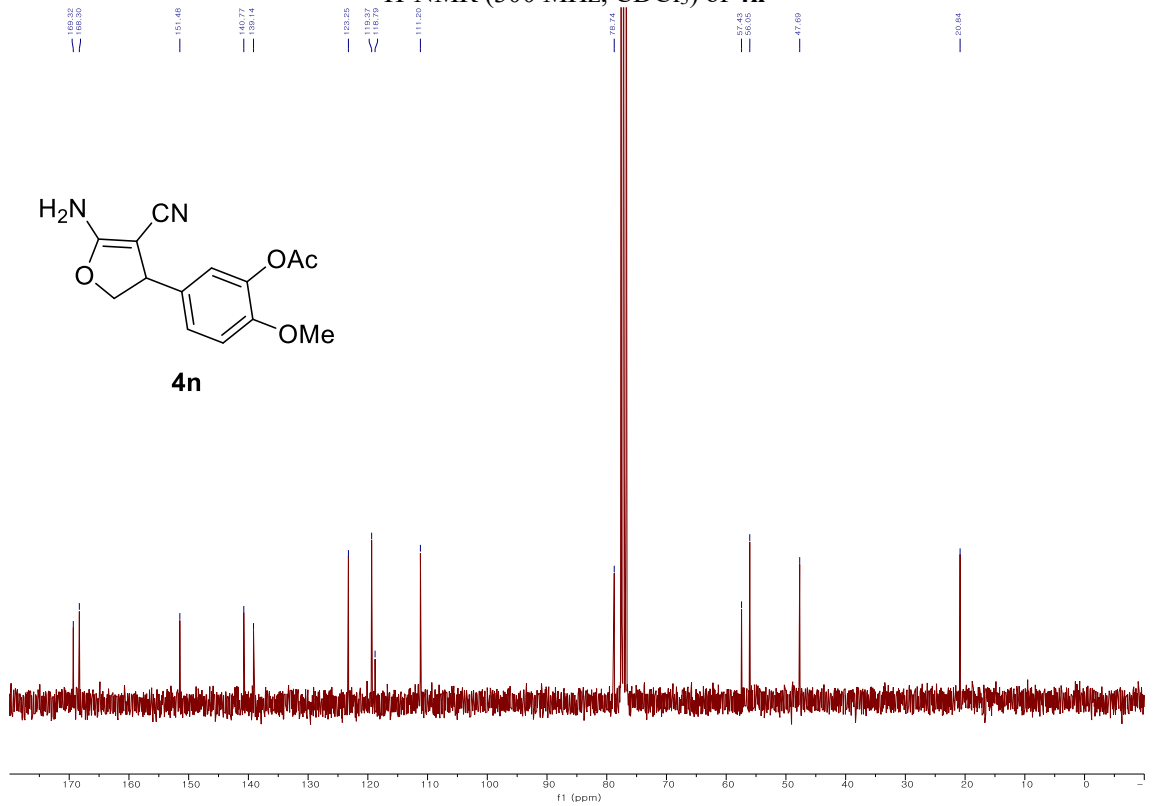
^{1}H-NMR (300 MHz, $CDCl_3$) of **4m**



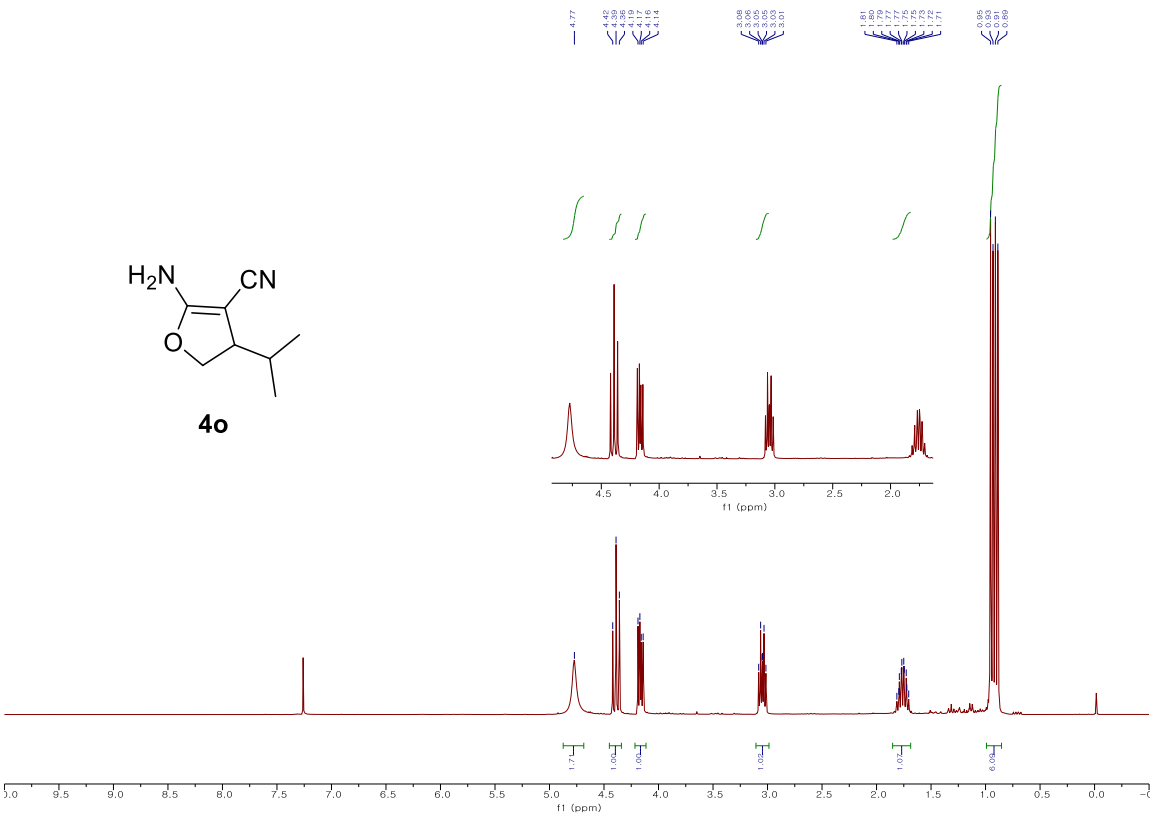
^{13}C-NMR (75Hz, $CDCl_3$) of **4m**



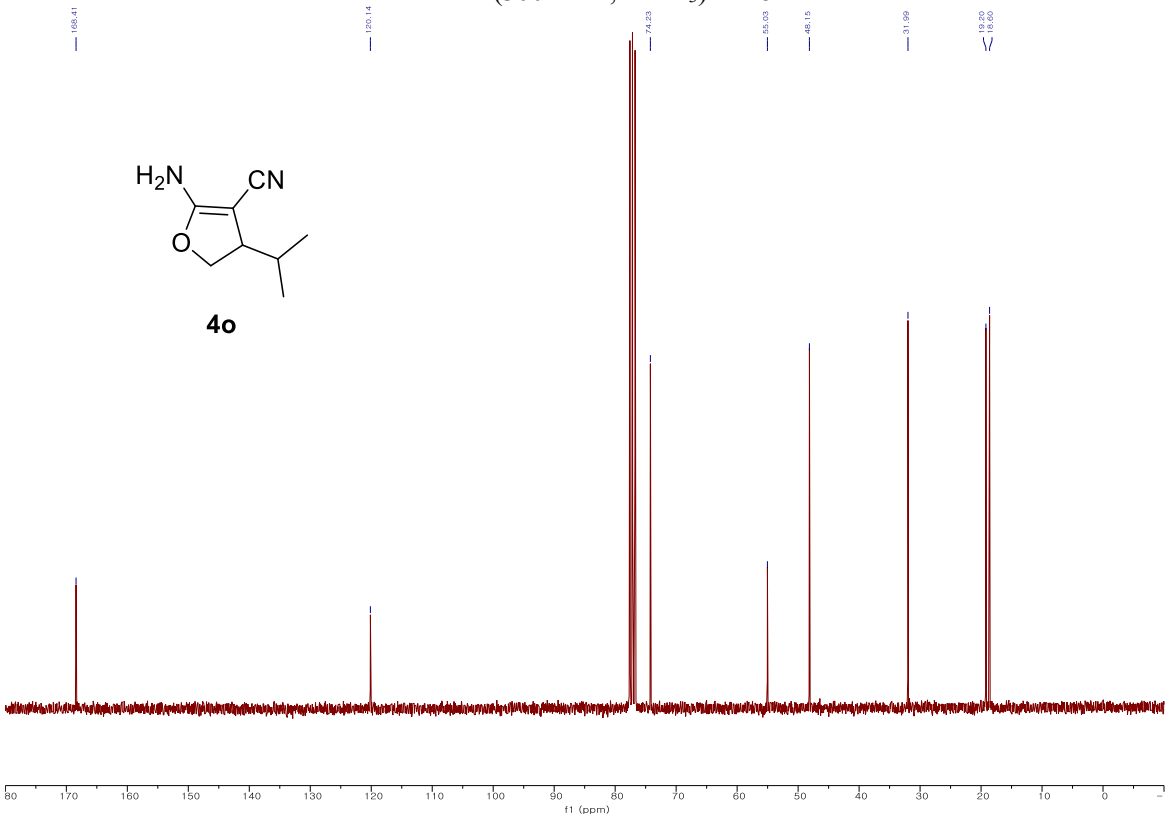
^{1}H-NMR (300 MHz, $CDCl_3$) of **4n**



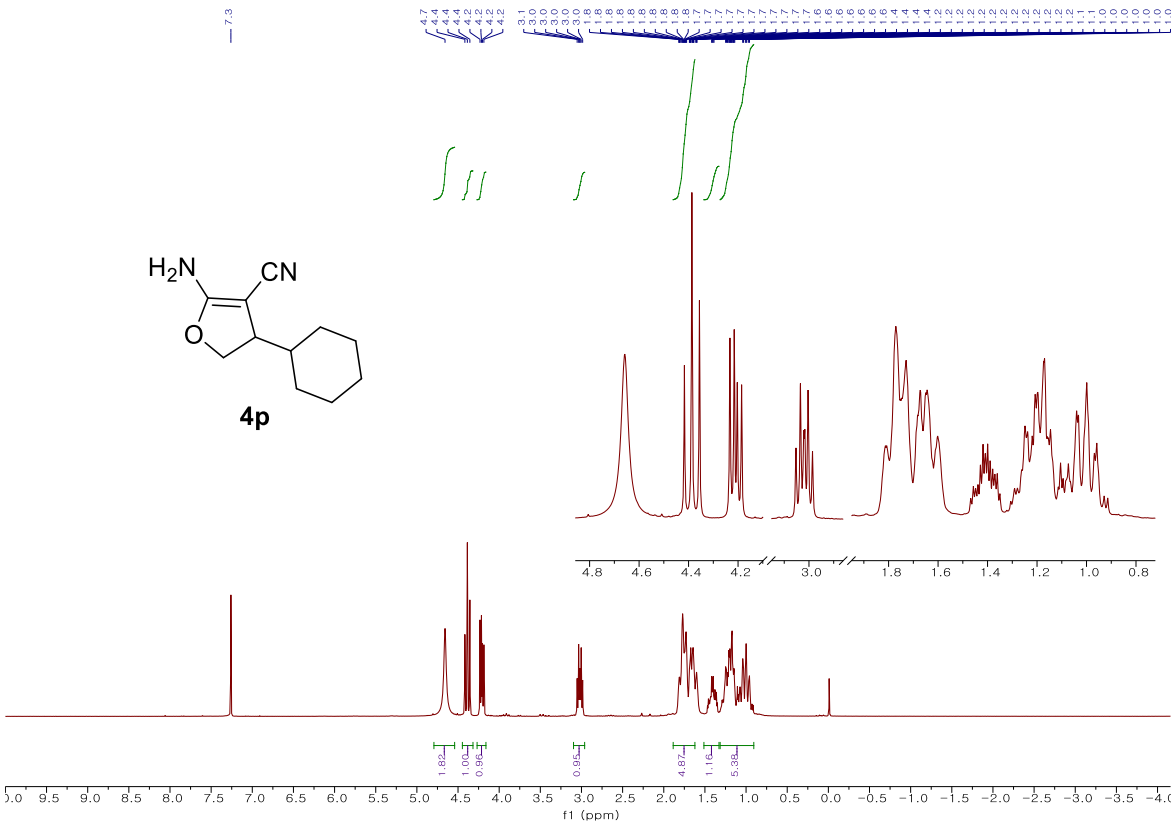
^{13}C-NMR (75Hz, $CDCl_3$) of **4n**



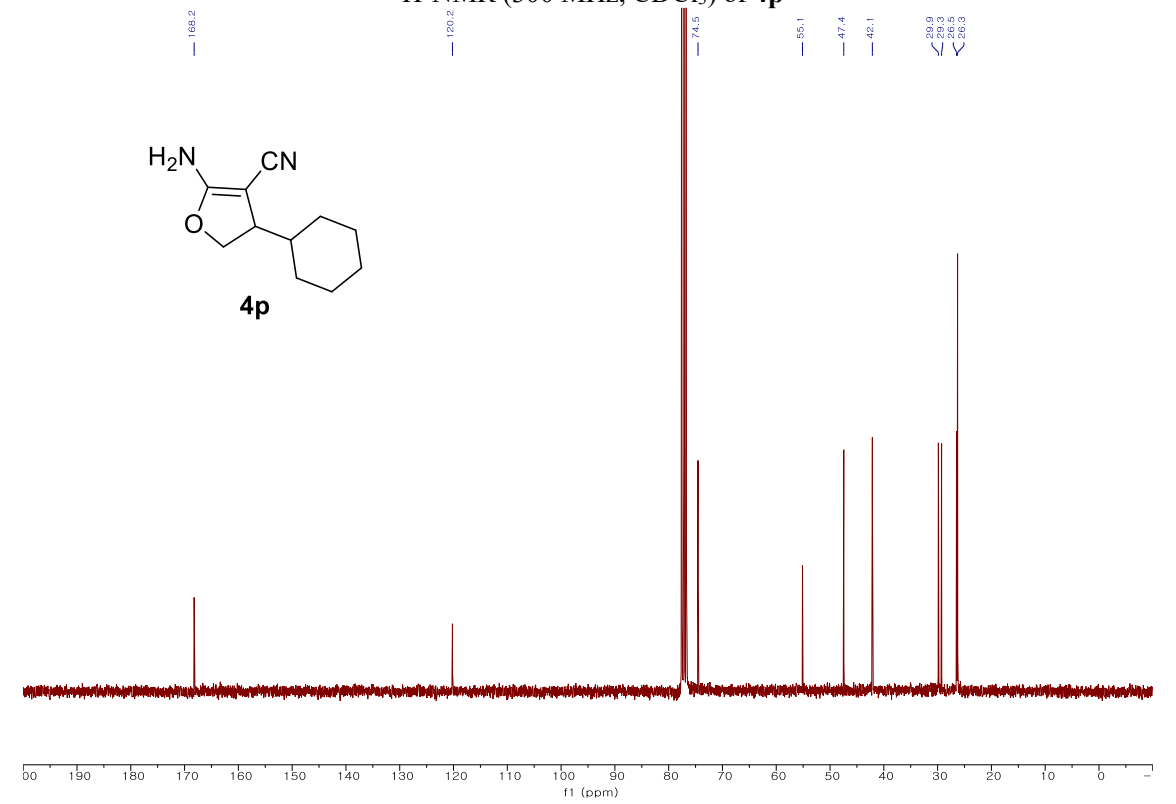
^{1}H-NMR (300 MHz, $CDCl_3$) of **4o**



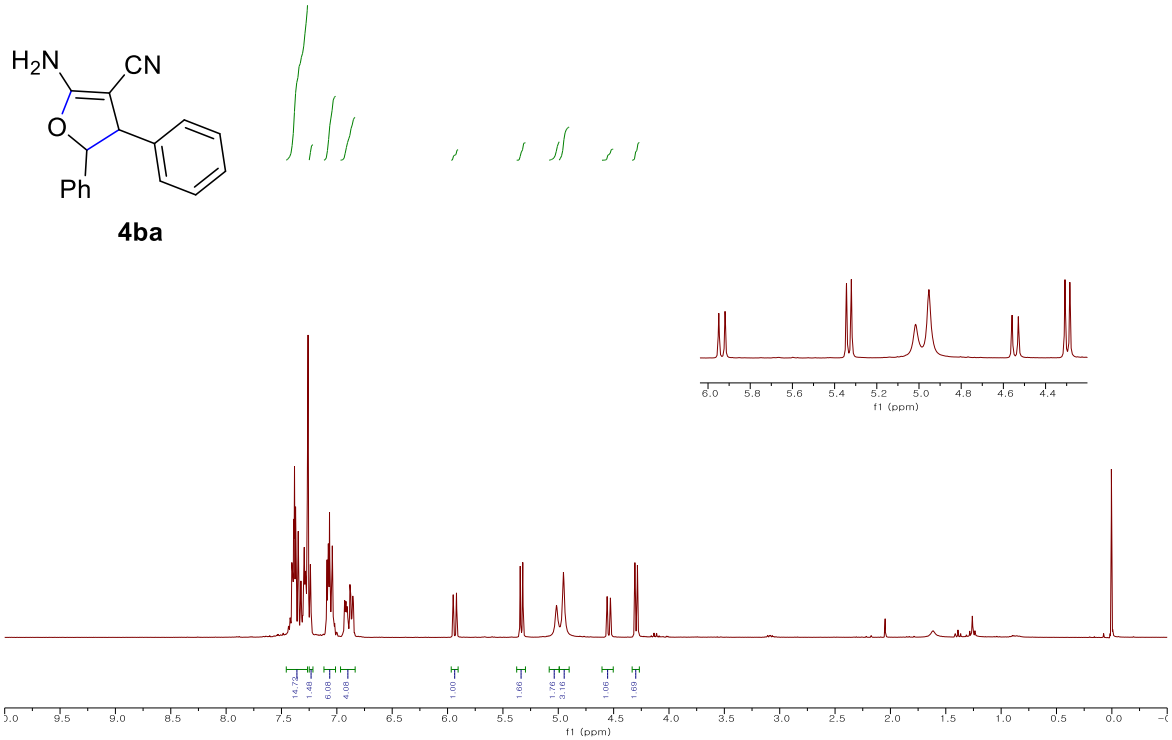
^{13}C-NMR (75Hz, $CDCl_3$) of **4o**



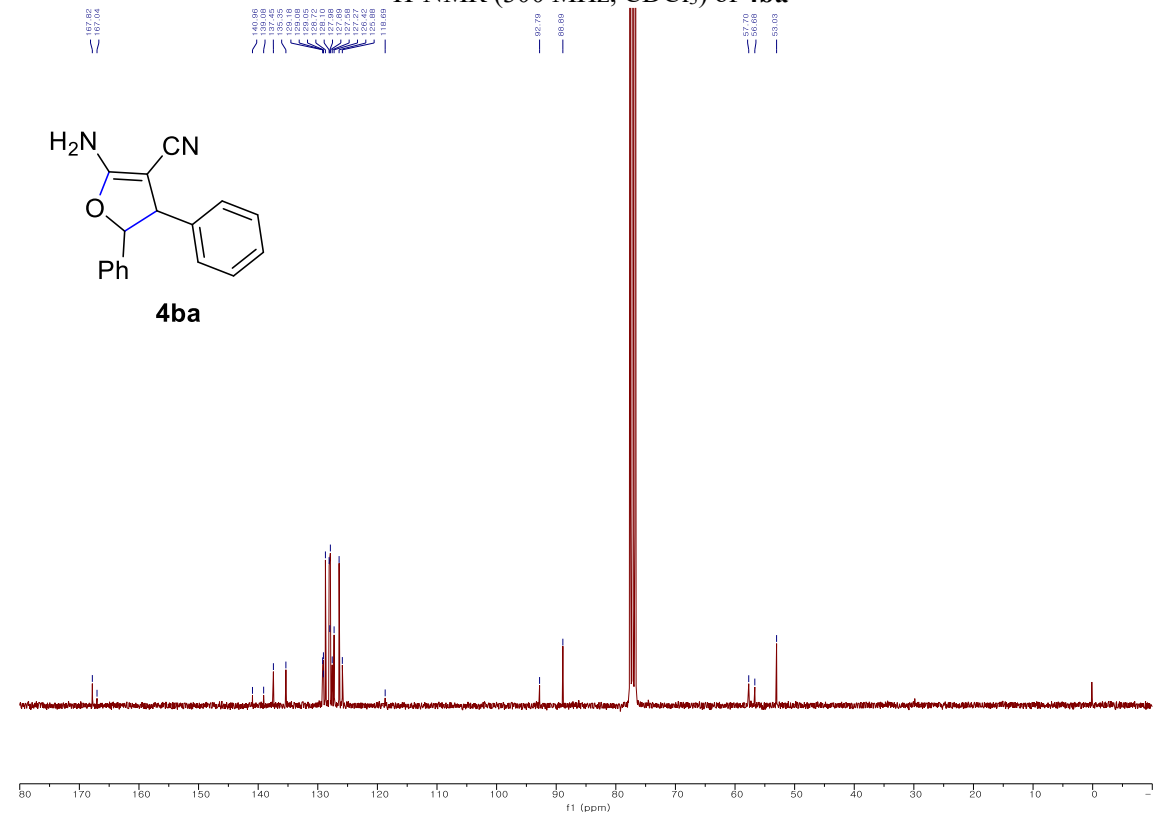
^{1}H-NMR (300 MHz, $CDCl_3$) of **4p**



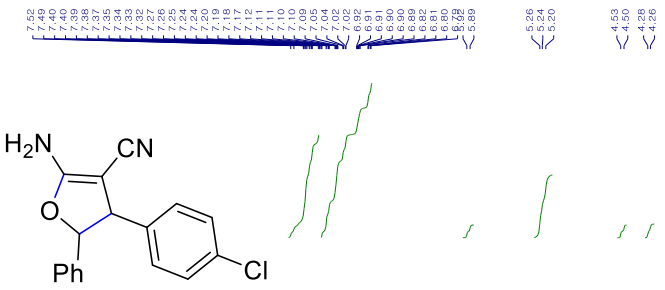
^{13}C-NMR (75Hz, $CDCl_3$) of **4p**



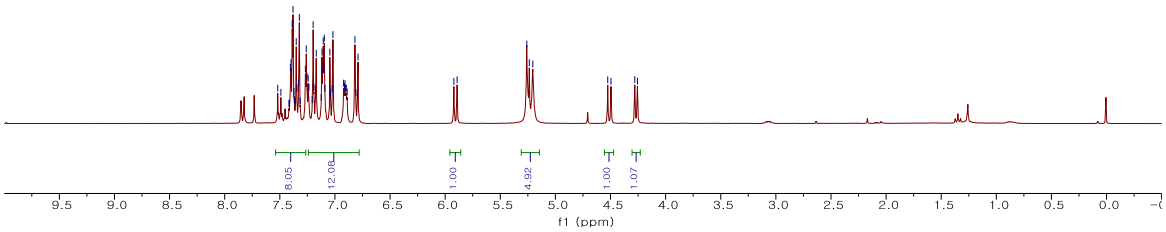
^{1}H-NMR (300 MHz, $CDCl_3$) of **4ba**



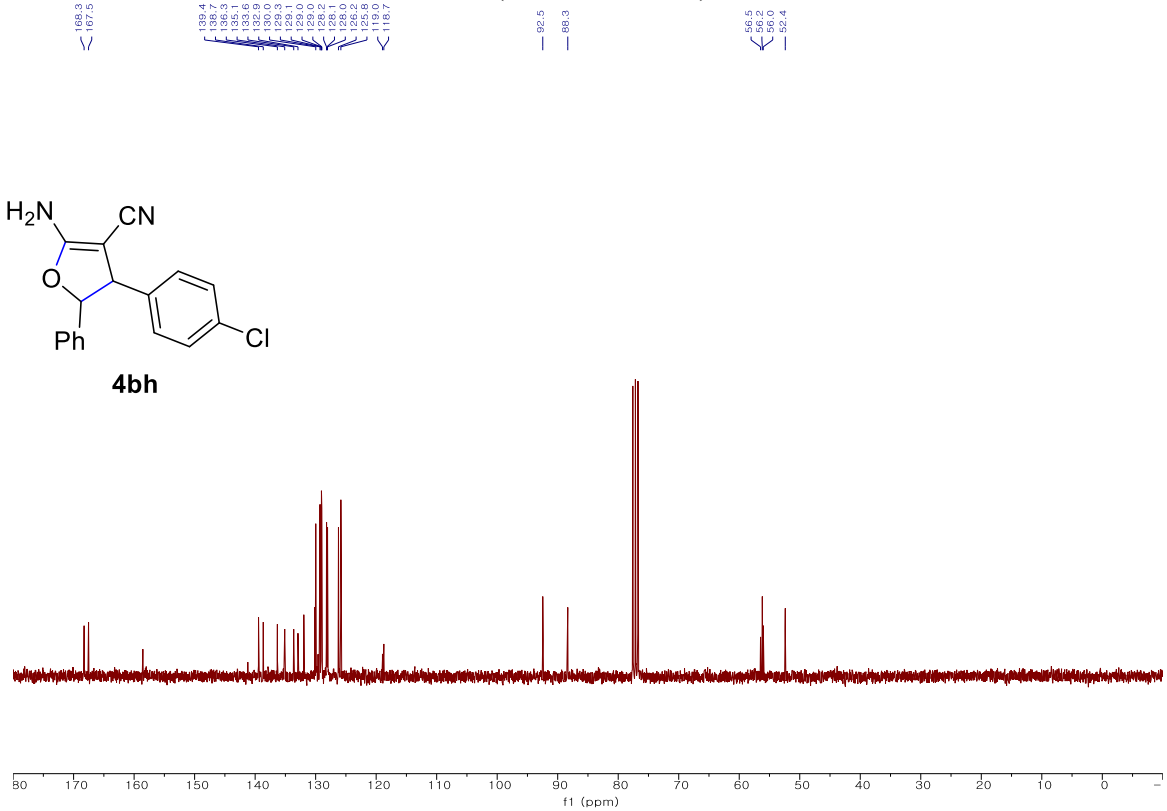
^{13}C-NMR (75Hz, $CDCl_3$) of **4ba**



4bh

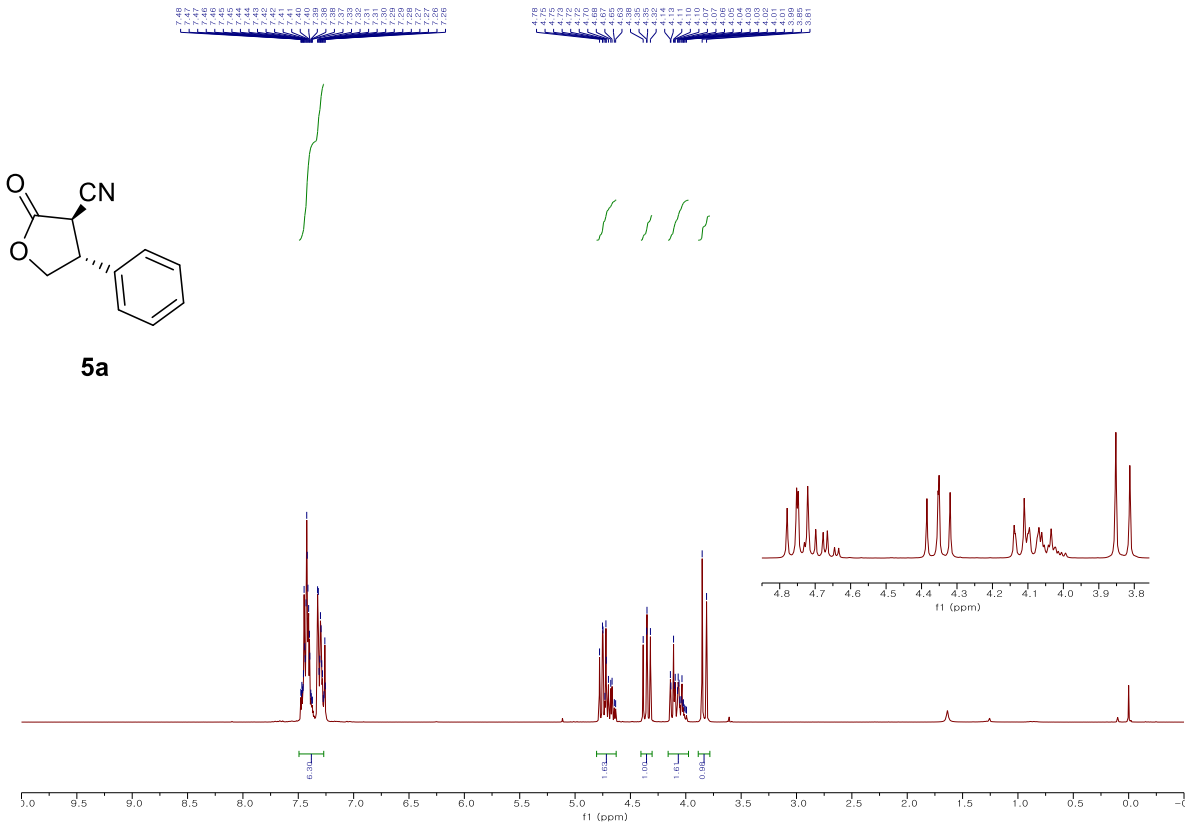


^{1}H-NMR (300 MHz, $CDCl_3$) of **4bh**

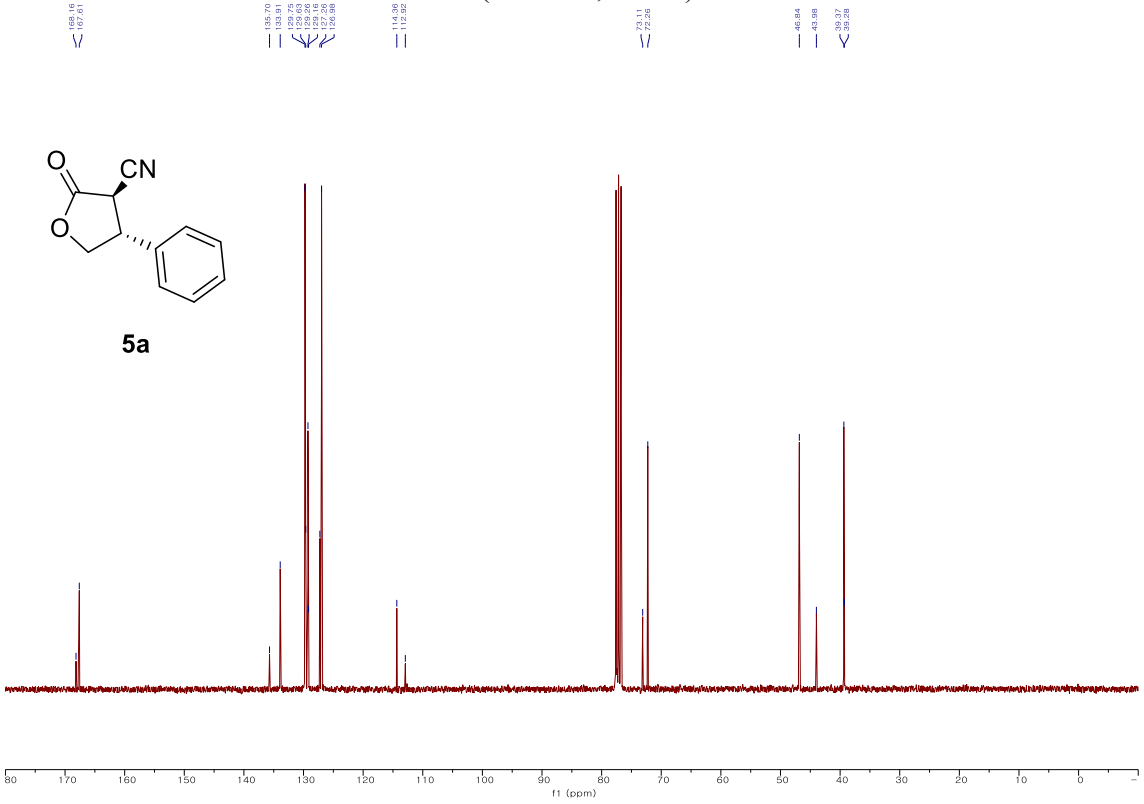


4bh

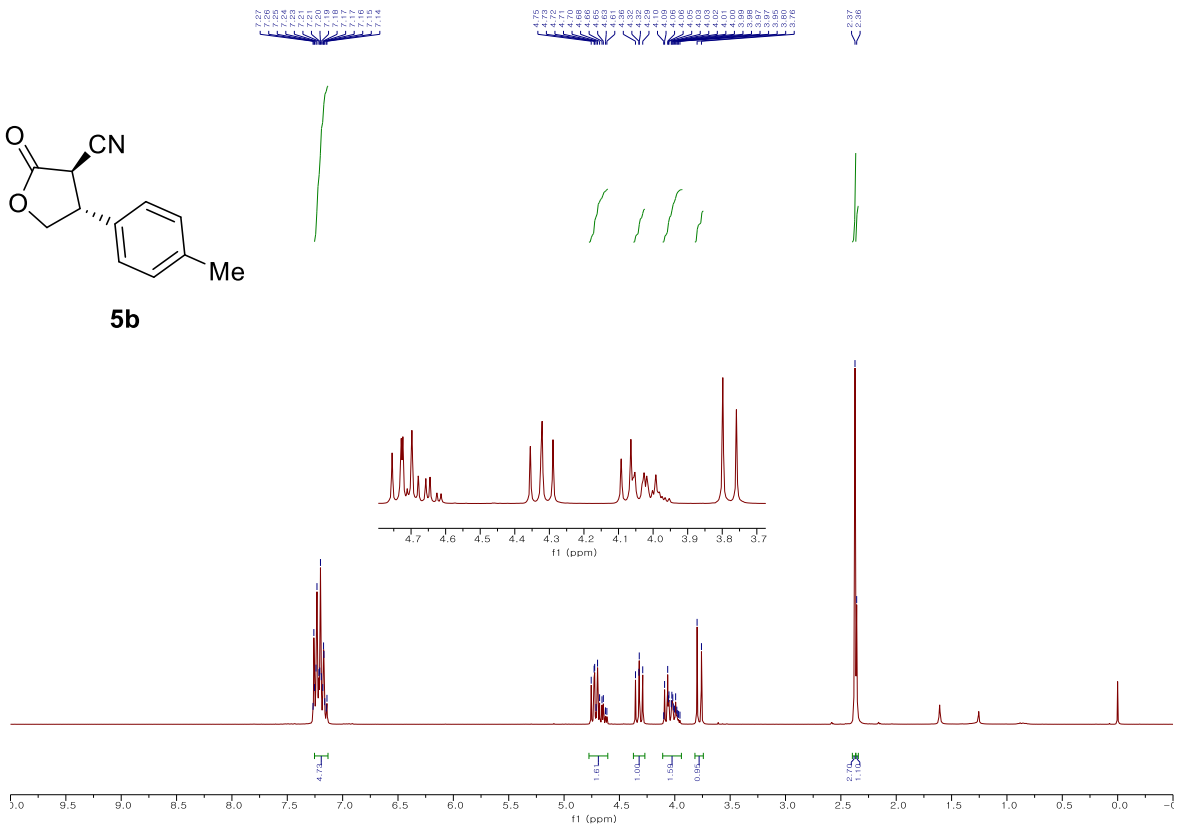
^{13}C-NMR (75Hz, $CDCl_3$) of **4bh**



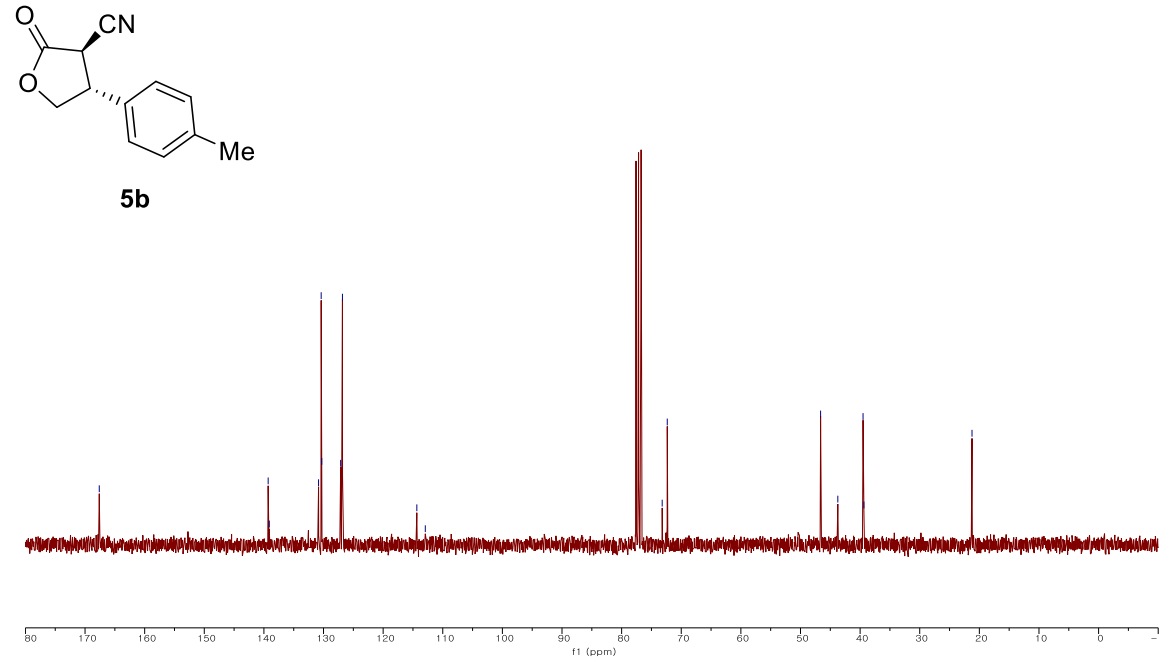
^{1}H-NMR (300 MHz, $CDCl_3$) of **5a**



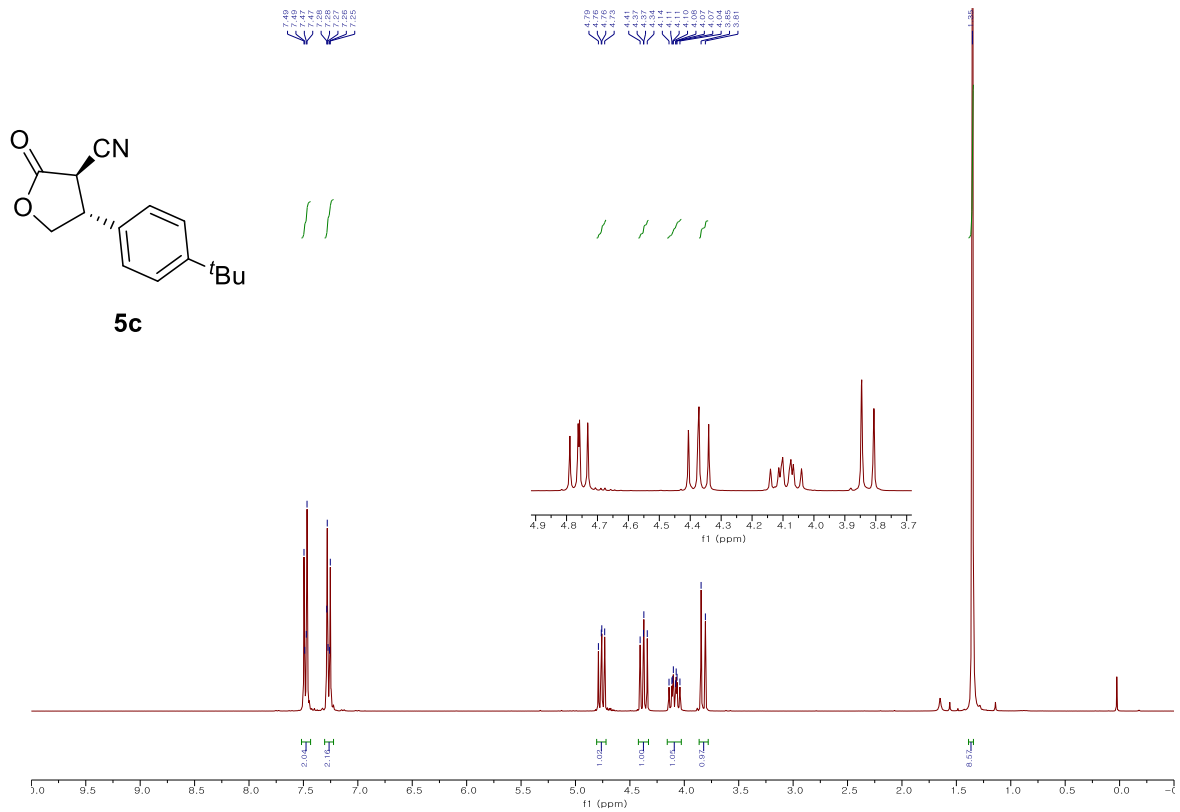
^{13}C-NMR (75Hz, $CDCl_3$) of **5a**



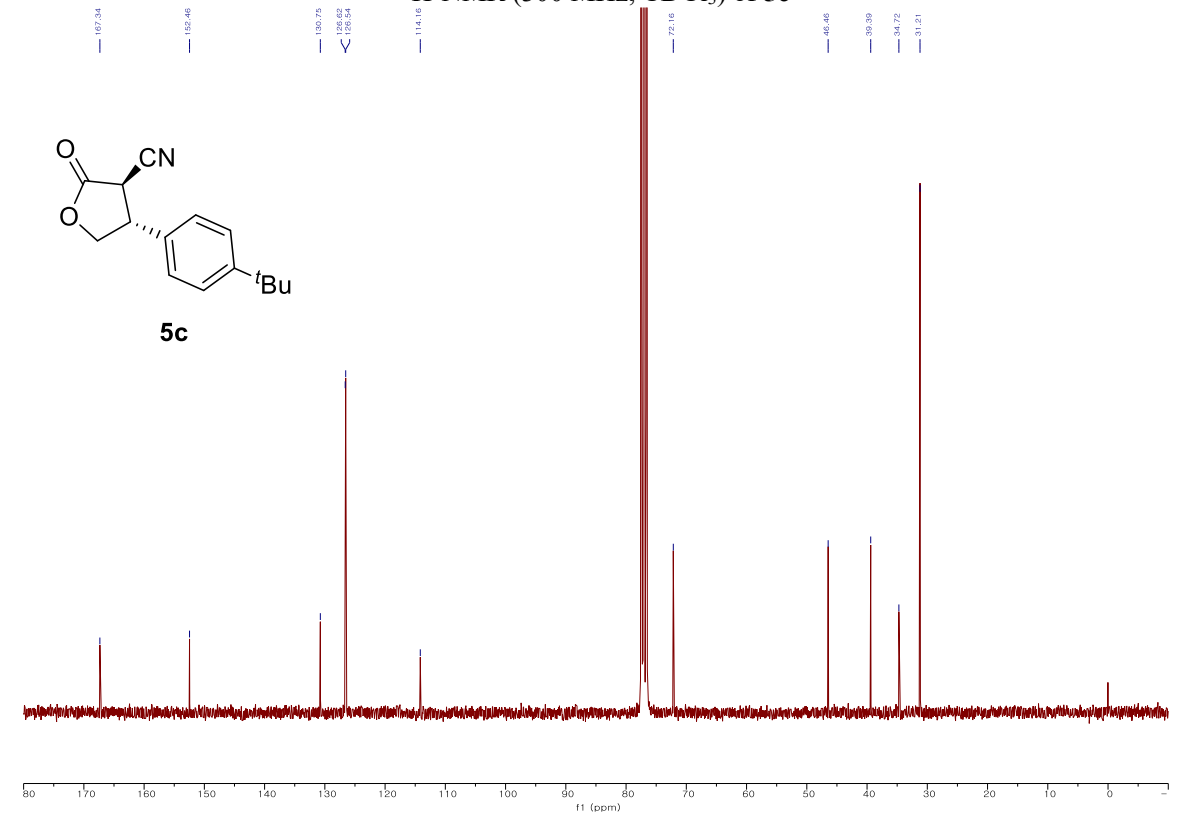
^{1}H-NMR (300 MHz, $CDCl_3$) of **5b**



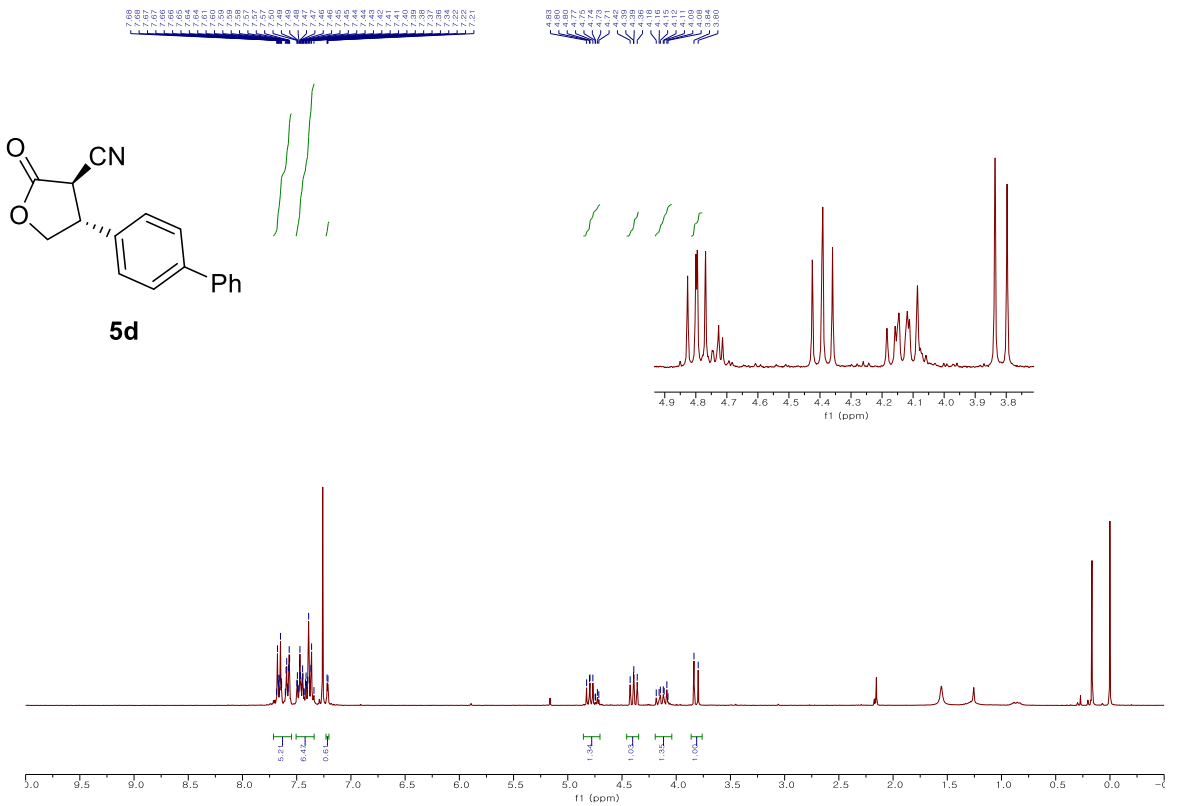
^{13}C-NMR (75Hz, $CDCl_3$) of **5b**



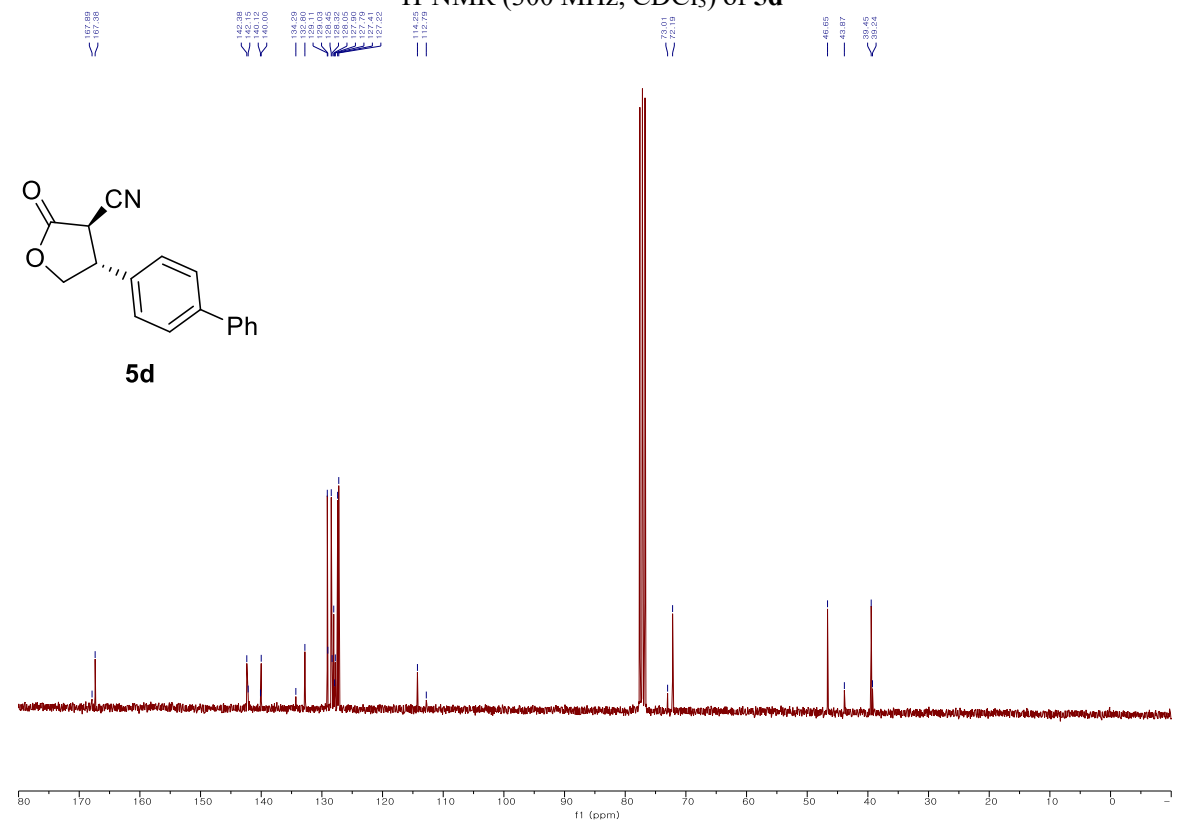
^{1}H-NMR (300 MHz, $CDCl_3$) of **5c**



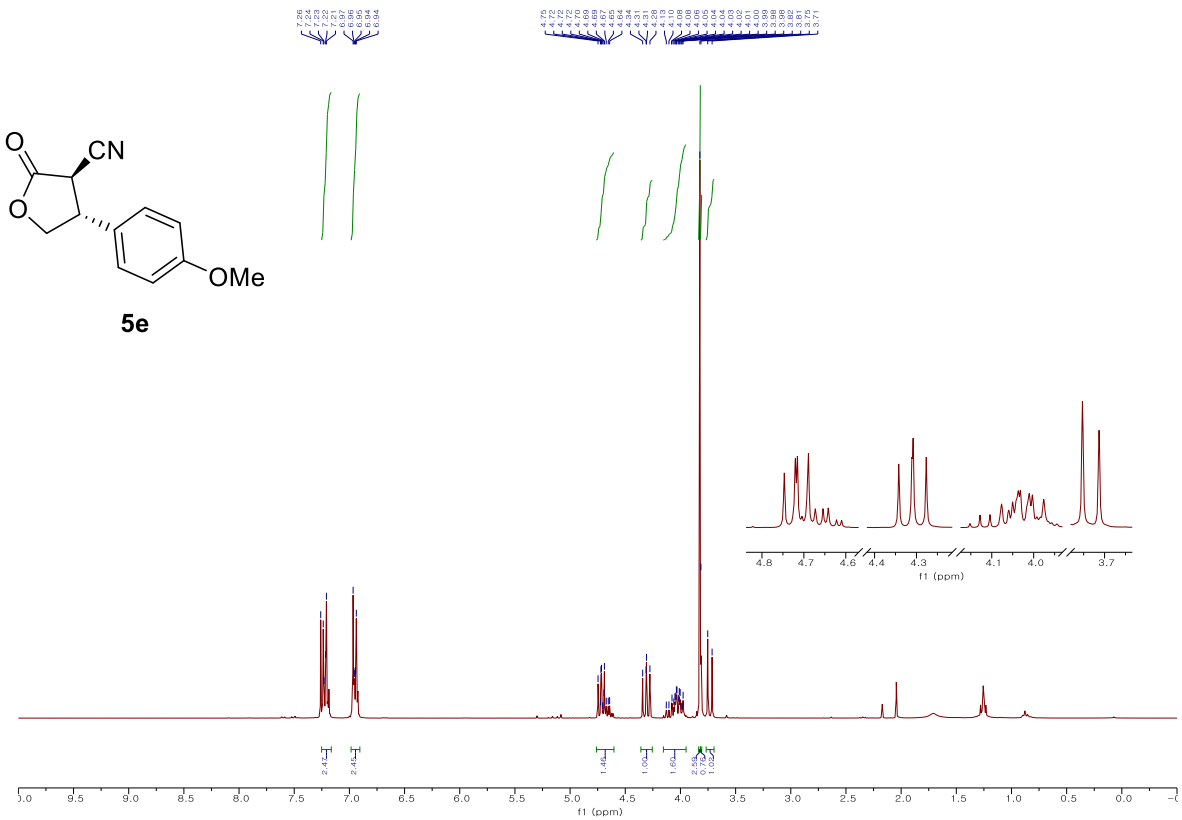
^{13}C-NMR (75Hz, $CDCl_3$) of **5c**



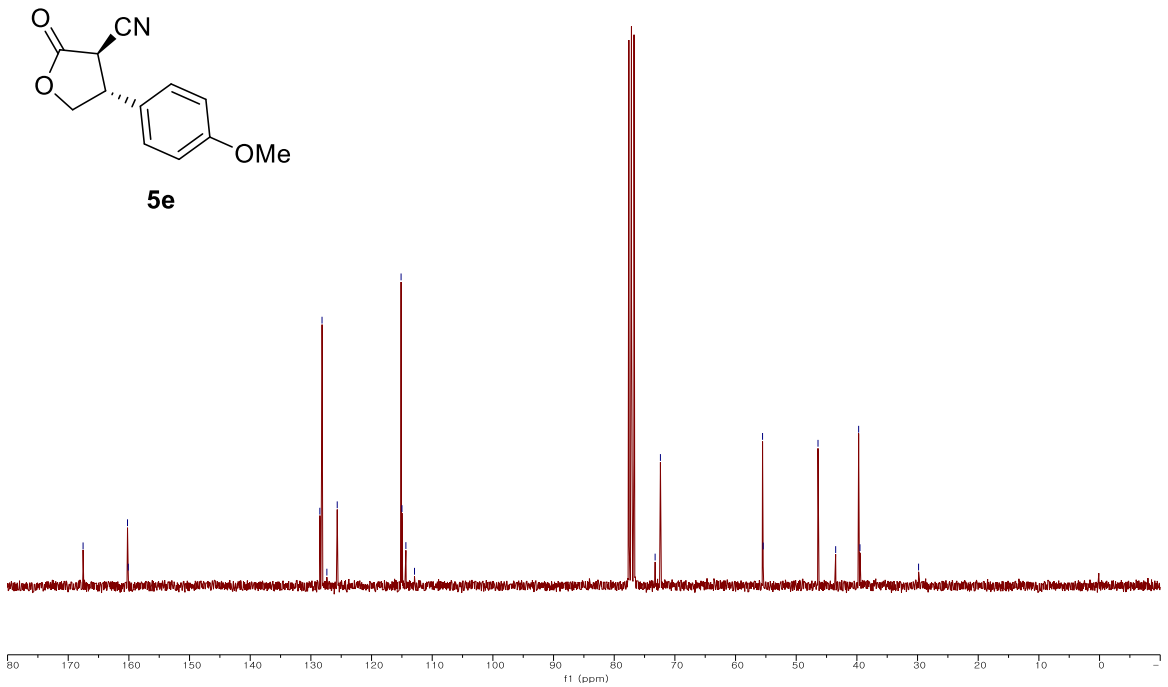
^{1}H-NMR (300 MHz, $CDCl_3$) of **5d**



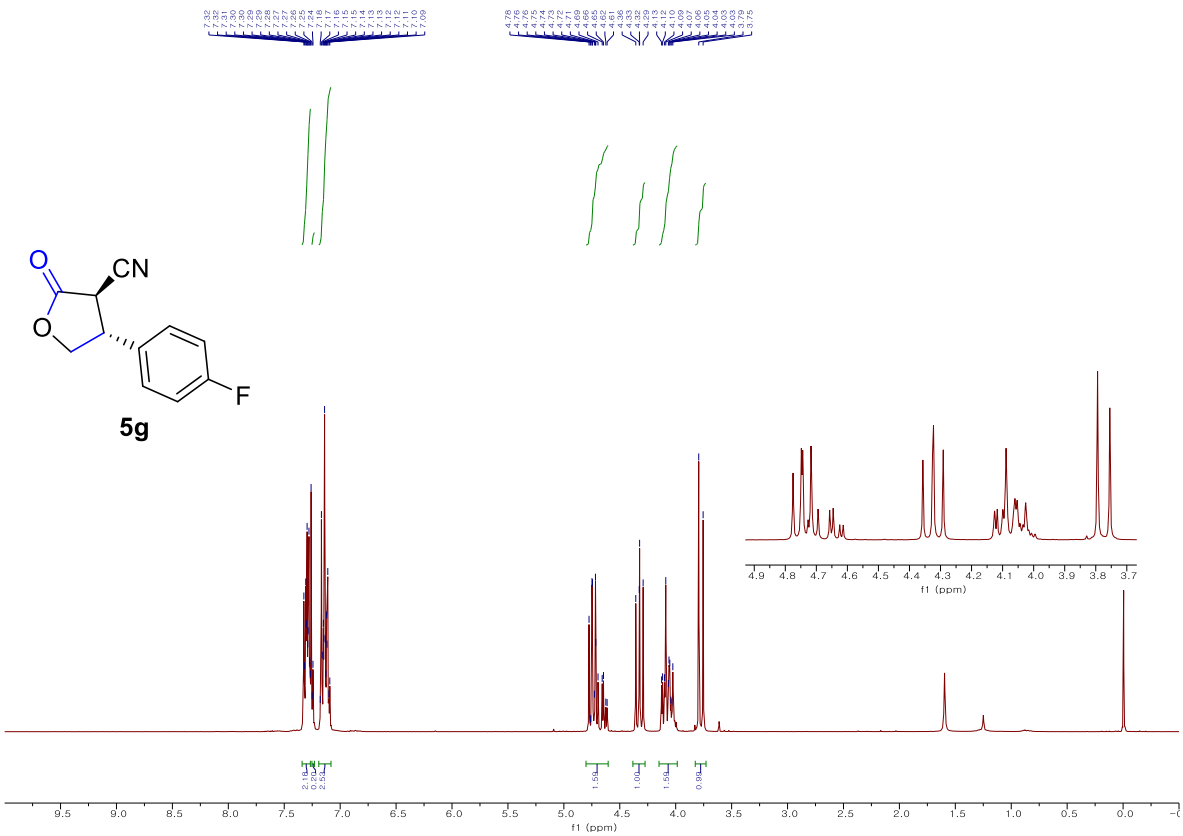
^{13}C-NMR (75Hz, $CDCl_3$) of **5d**



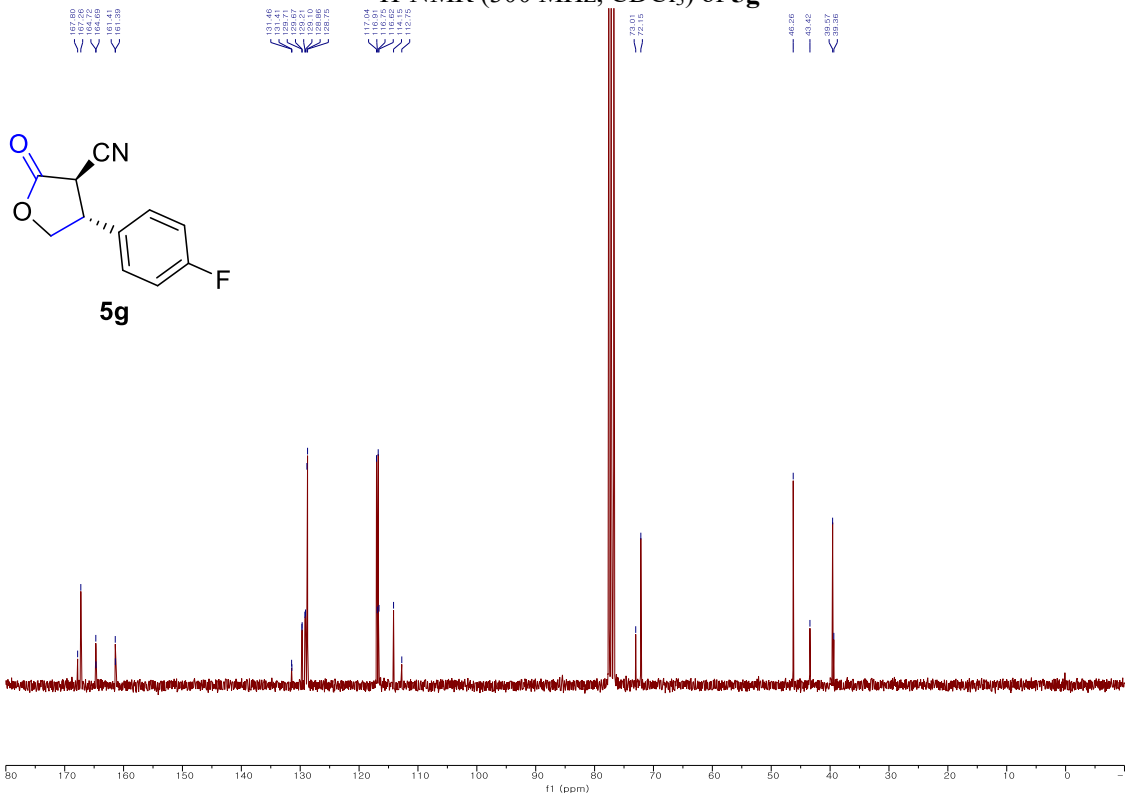
^{1}H-NMR (300 MHz, $CDCl_3$) of **5e**



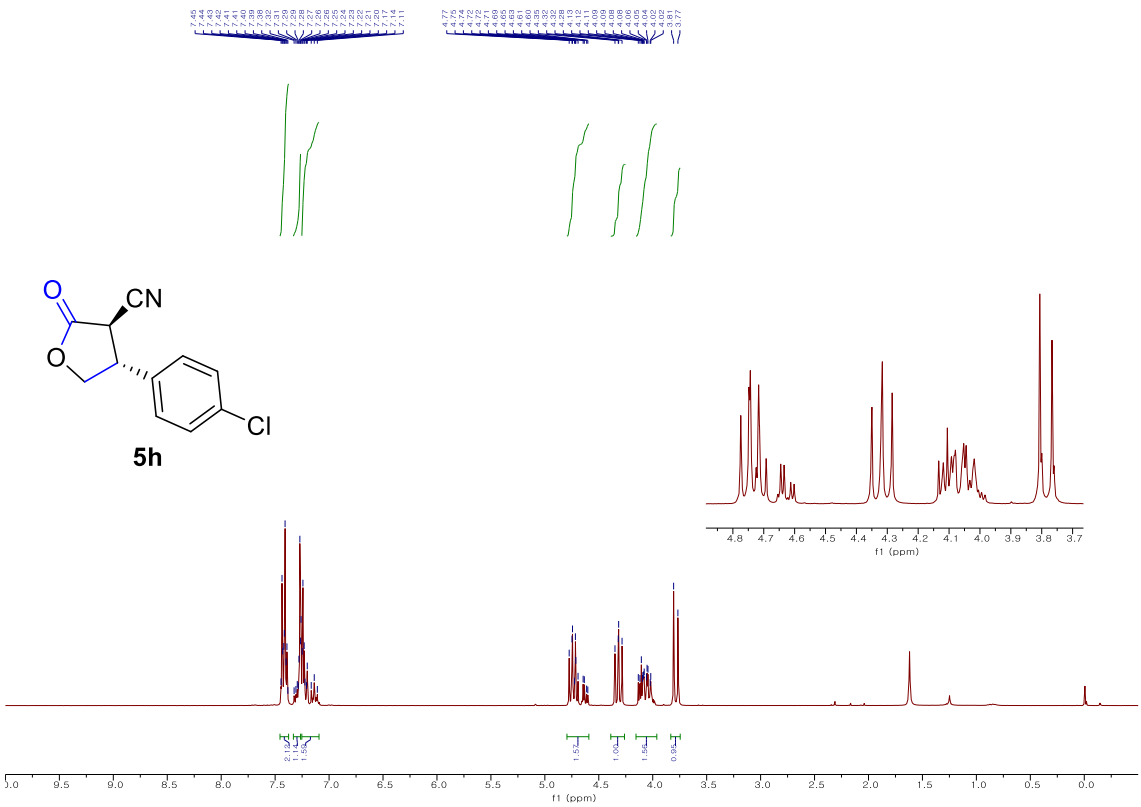
^{13}C-NMR (75Hz, $CDCl_3$) of **5e**



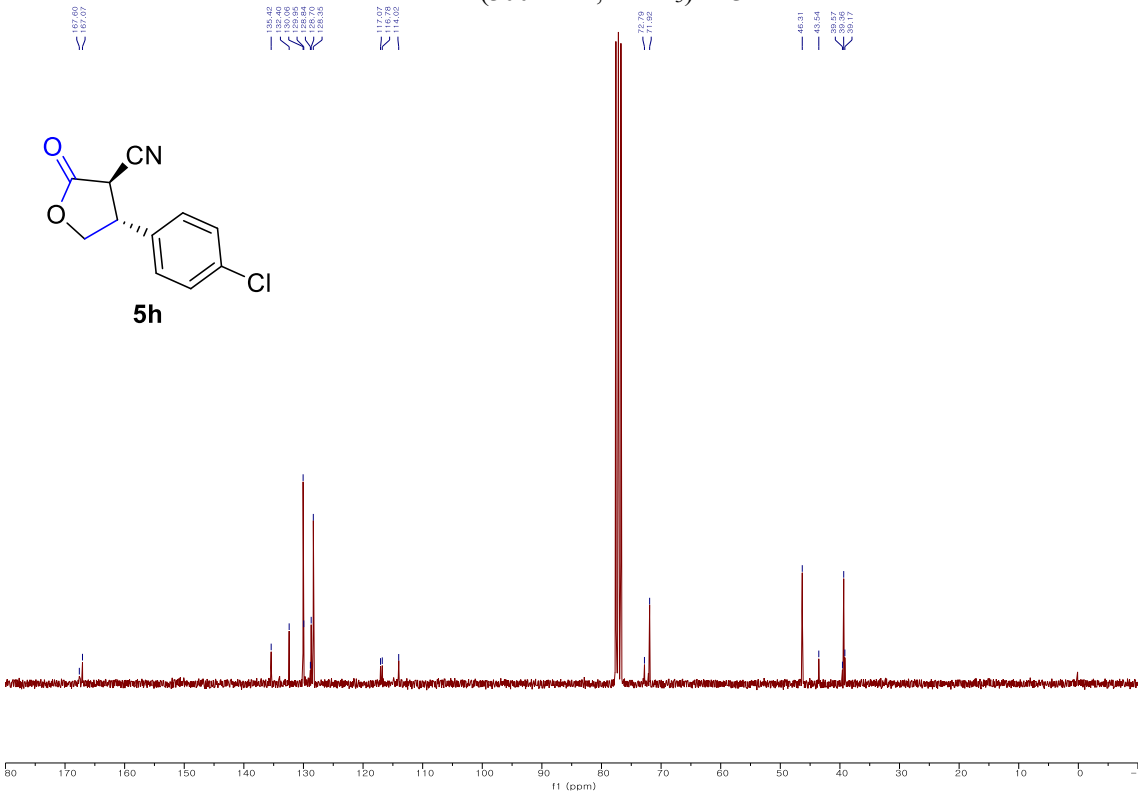
^{1}H-NMR (300 MHz, $CDCl_3$) of **5g**



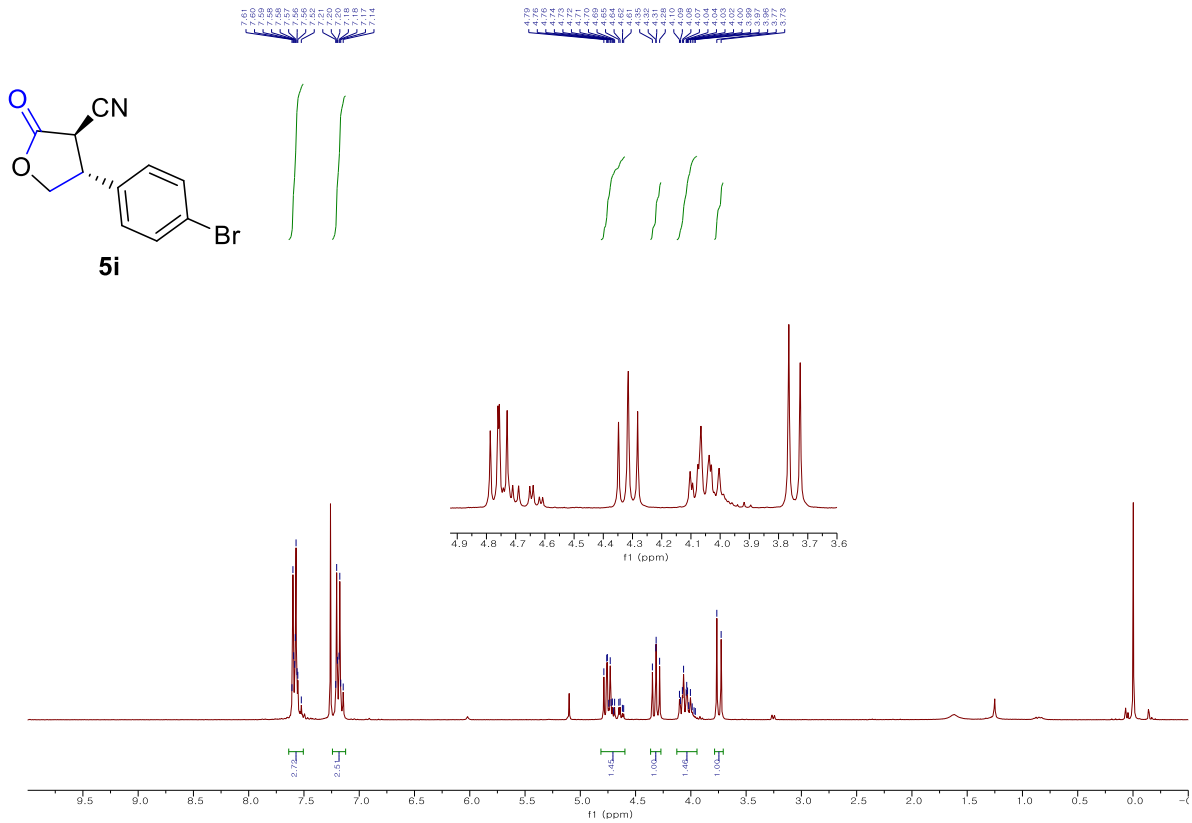
^{13}C-NMR (75Hz, $CDCl_3$) of **5g**



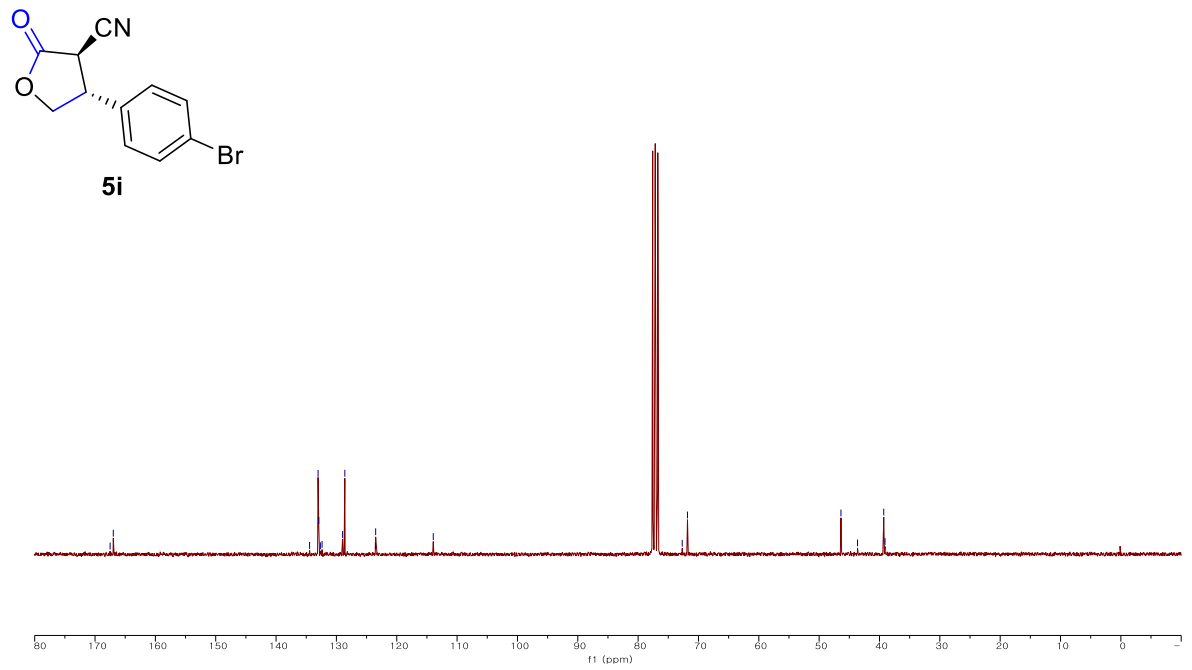
^{1}H-NMR (300 MHz, $CDCl_3$) of **5h**



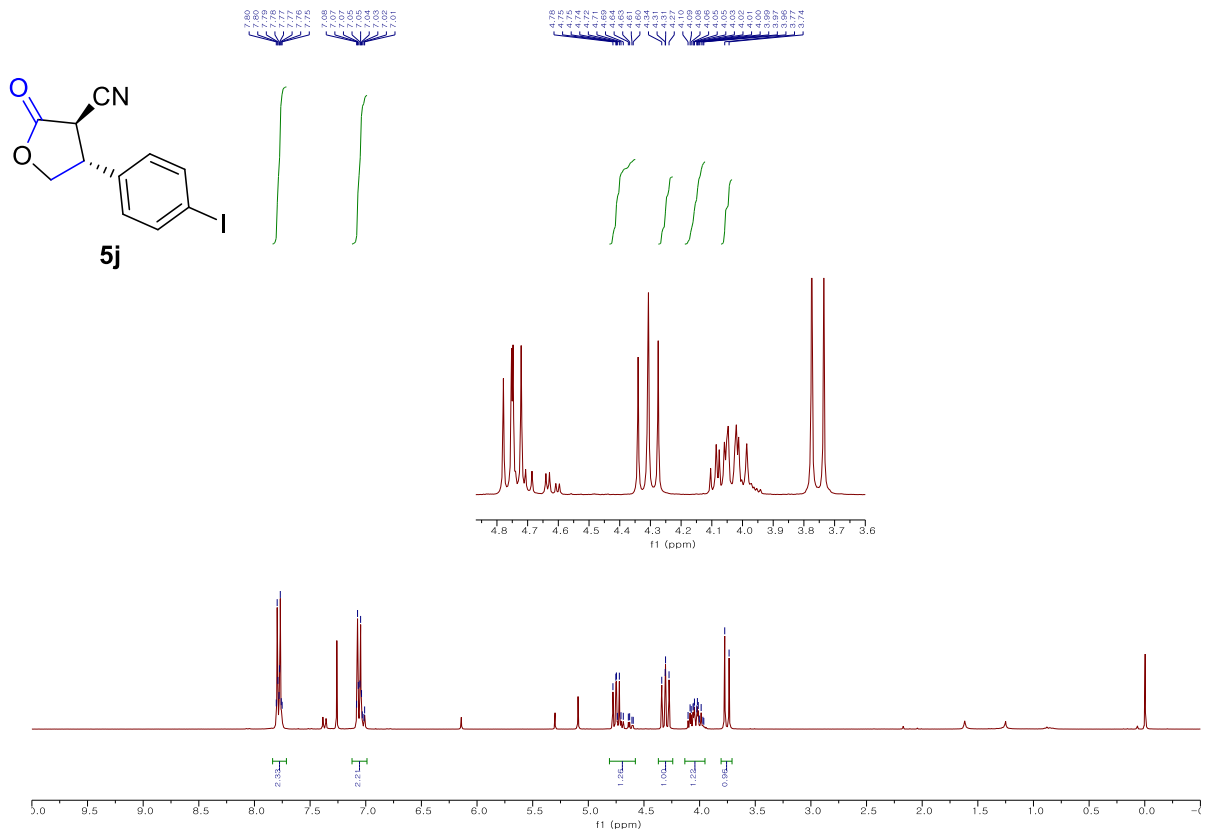
^{13}C-NMR (75Hz, $CDCl_3$) of **5h**



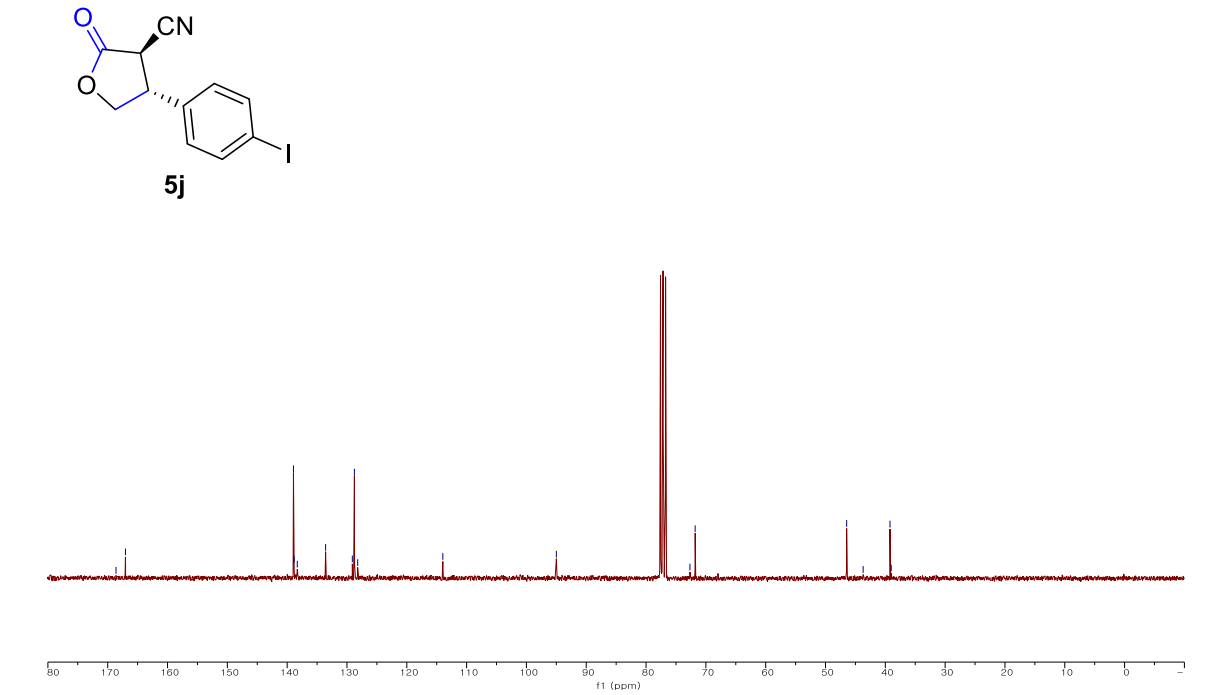
^{1}H-NMR (300 MHz, $CDCl_3$) of **5i**



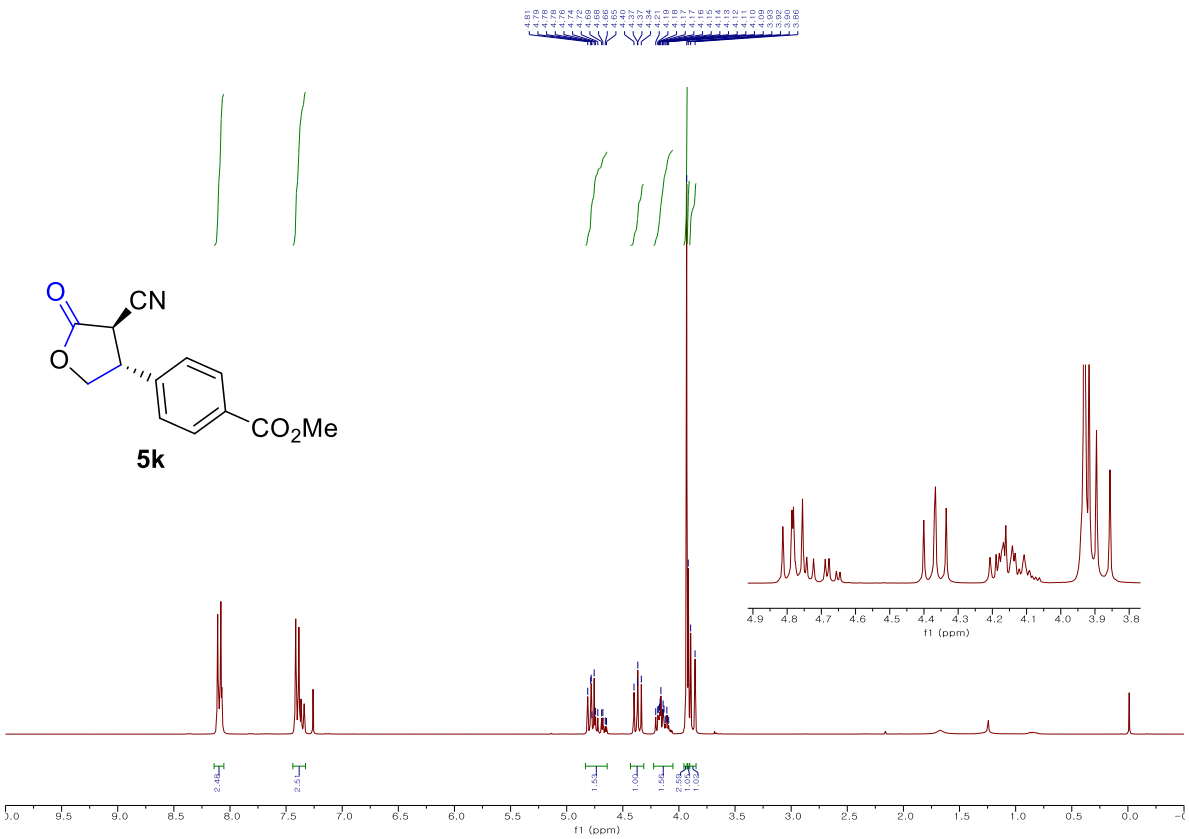
^{13}C-NMR (75Hz, $CDCl_3$) of **5i**



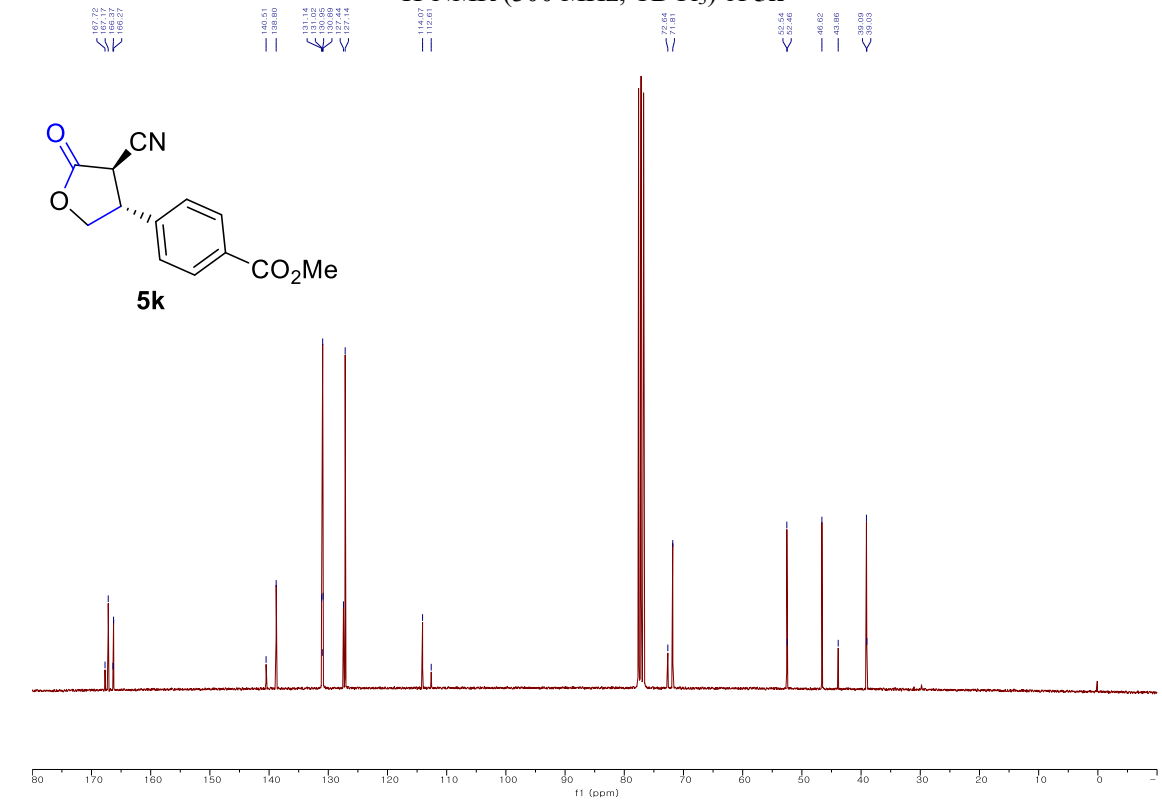
^{1}H-NMR (300 MHz, $CDCl_3$) of **5j**



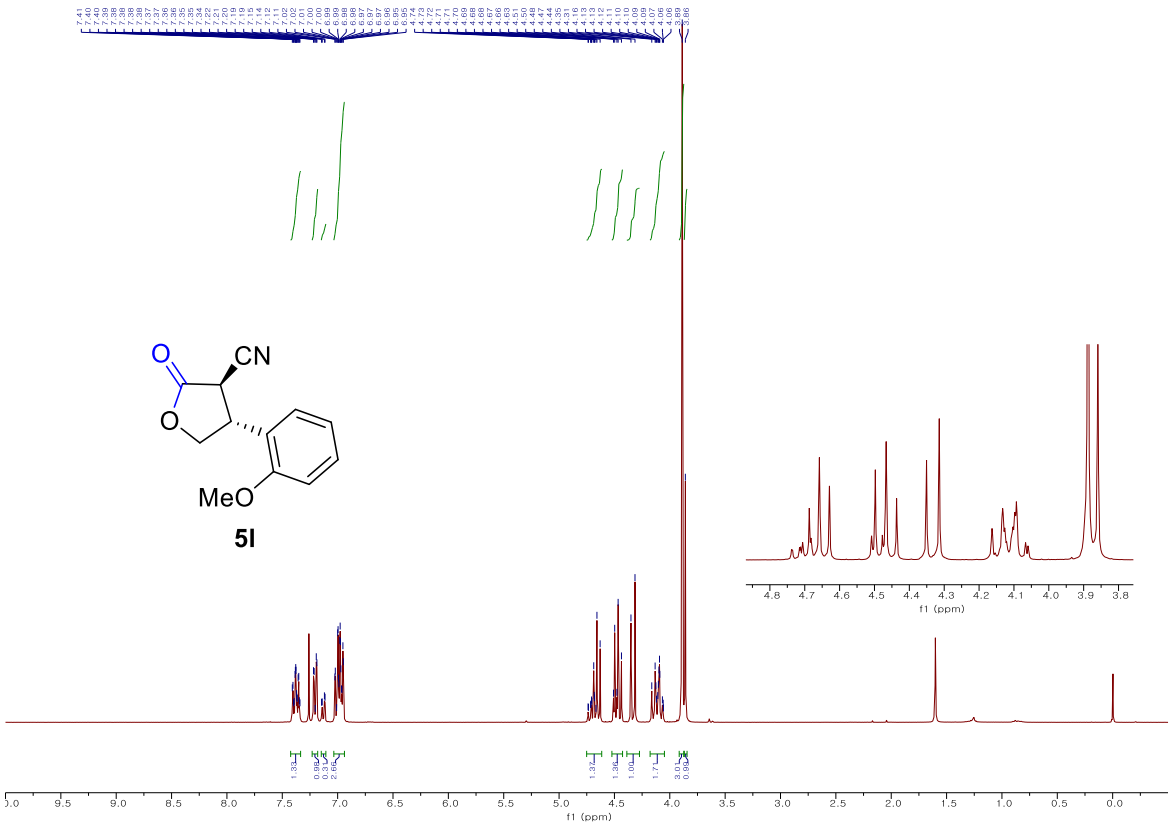
^{13}C-NMR (75Hz, $CDCl_3$) of **5j**



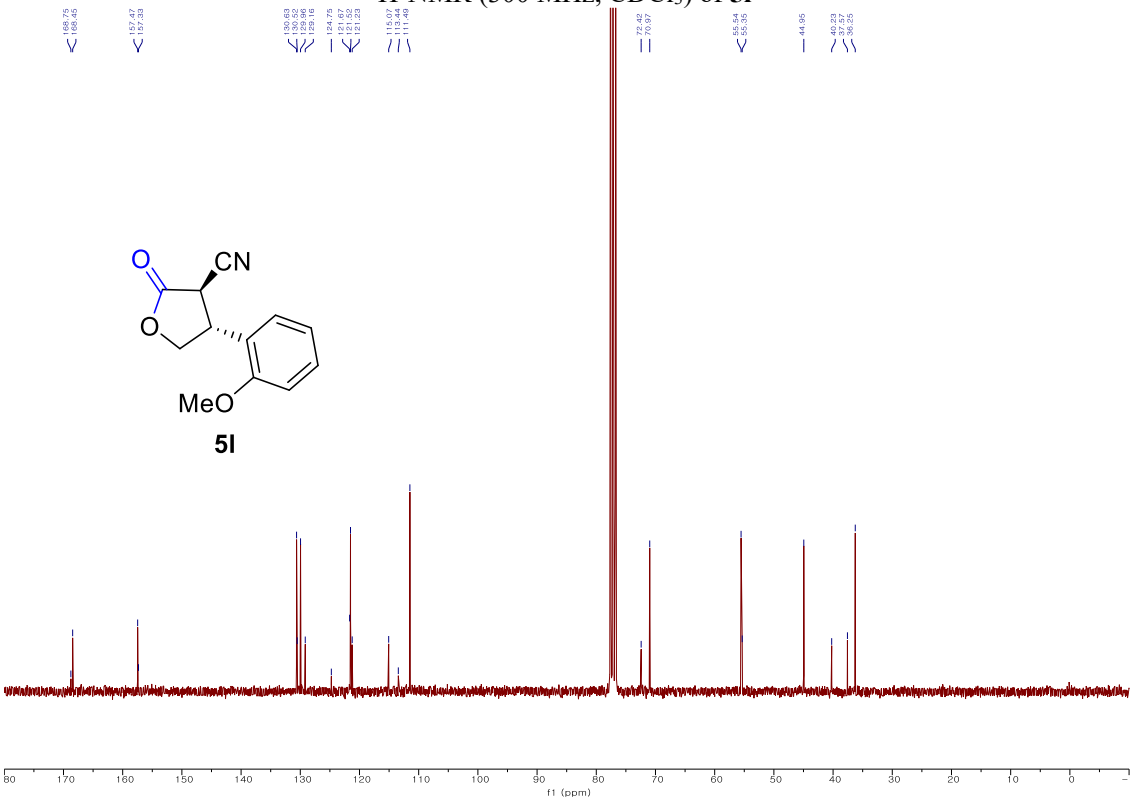
^{1}H-NMR (300 MHz, $CDCl_3$) of **5k**



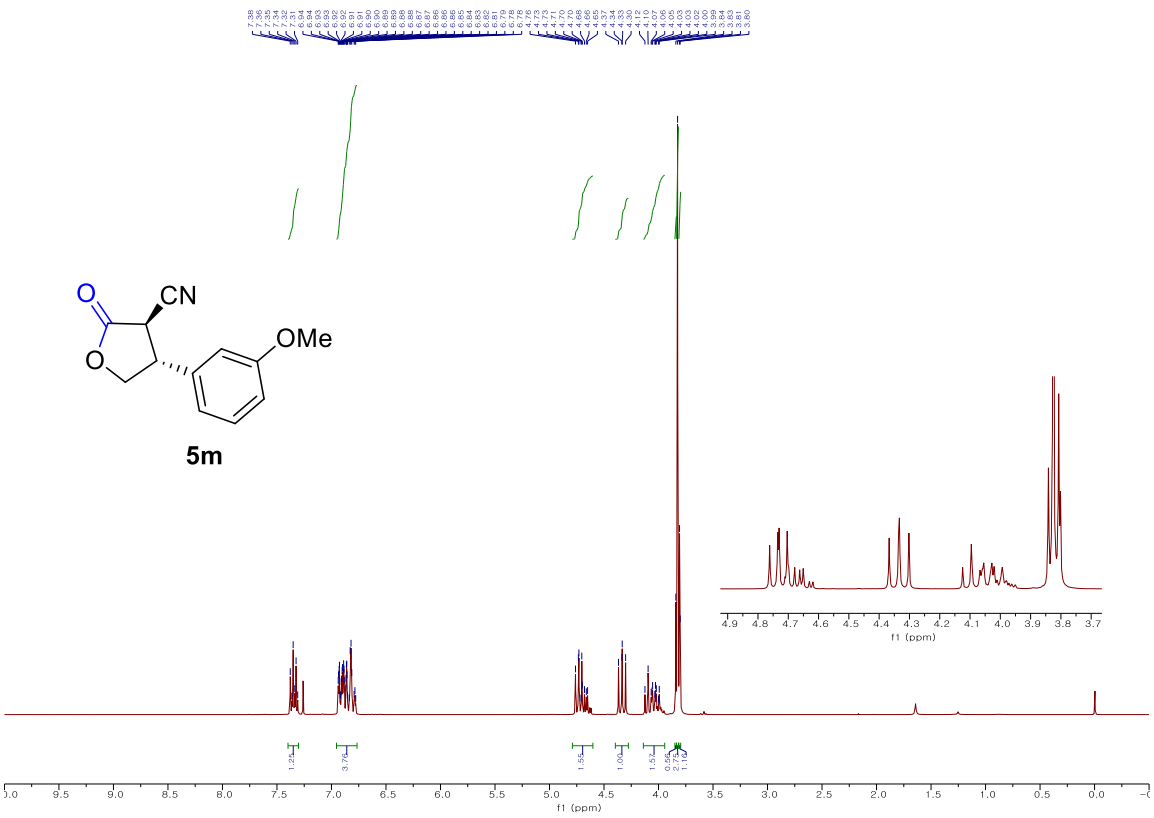
^{13}C-NMR (75Hz, $CDCl_3$) of **5k**



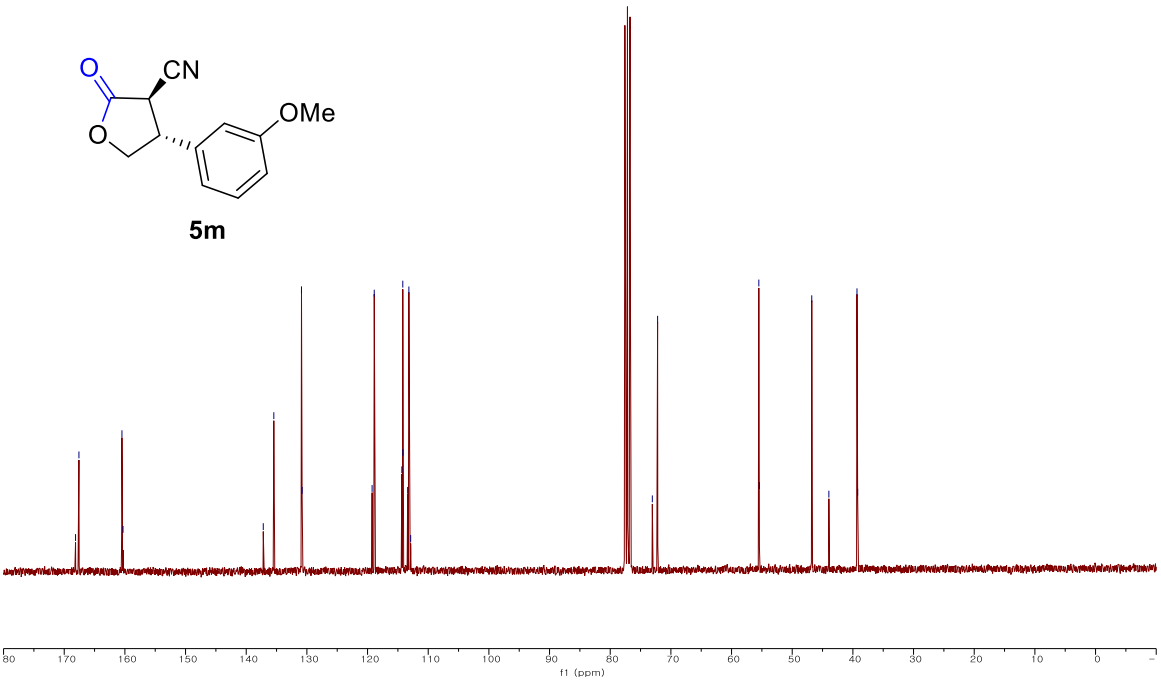
^{1}H-NMR (300 MHz, $CDCl_3$) of **5l**



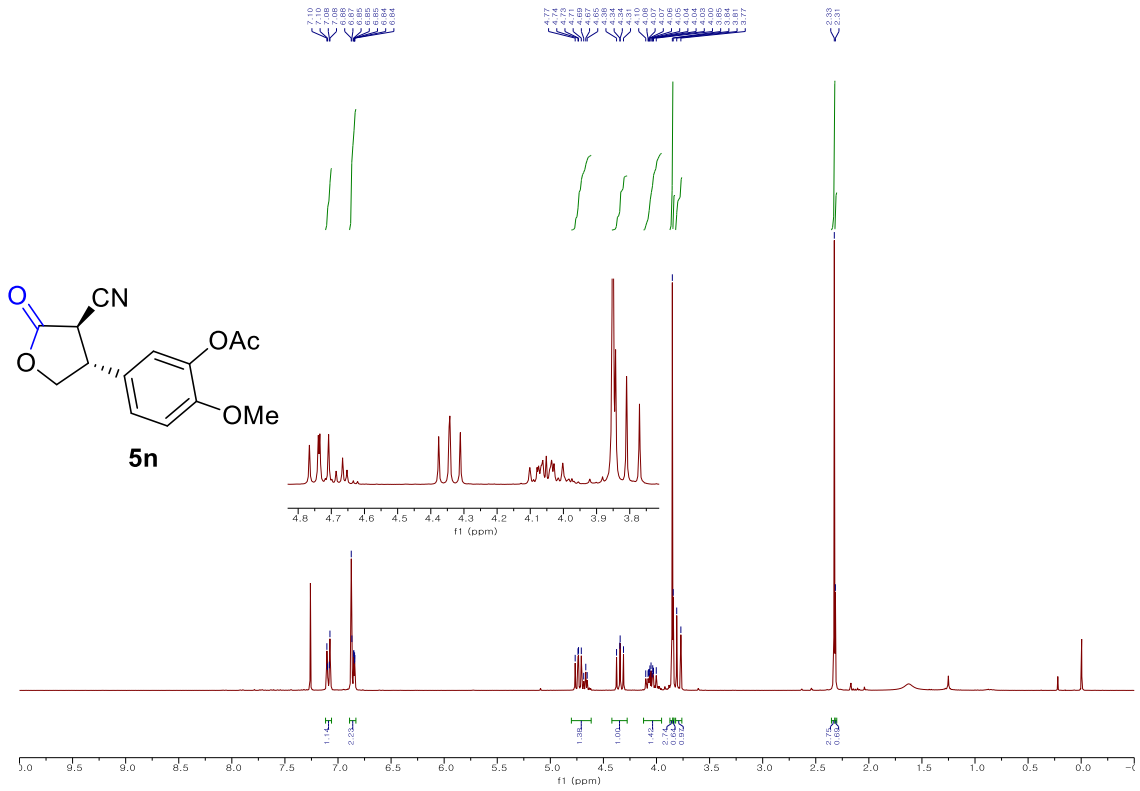
^{13}C-NMR (75Hz, $CDCl_3$) of **5l**



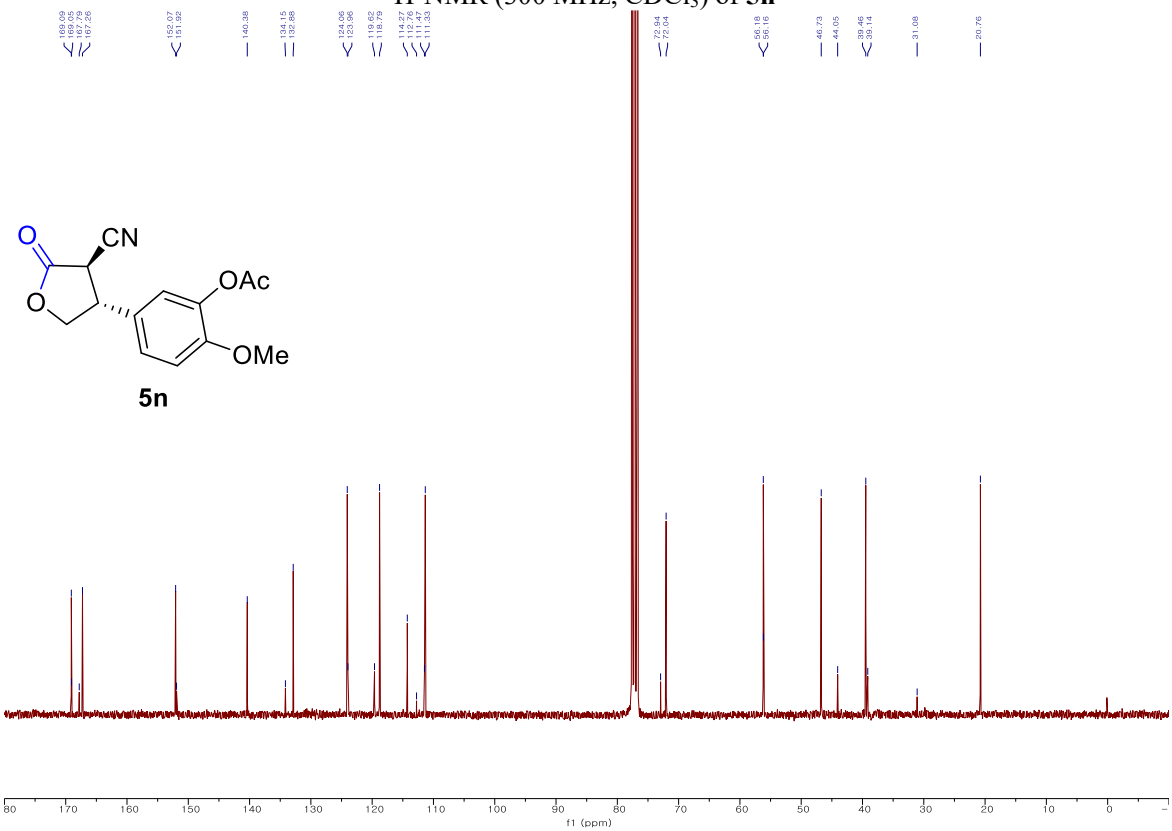
^{1}H-NMR (300 MHz, $CDCl_3$) of **5m**



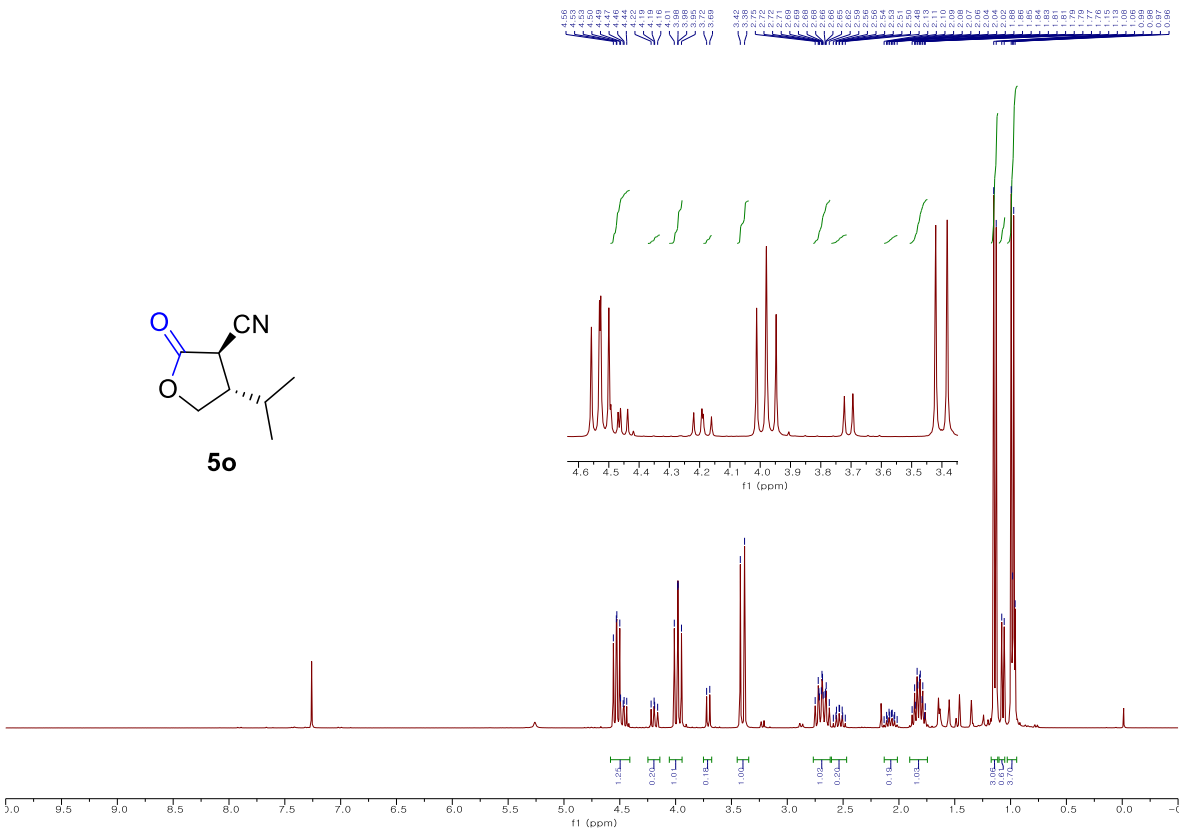
^{13}C-NMR (75Hz, $CDCl_3$) of **5m**



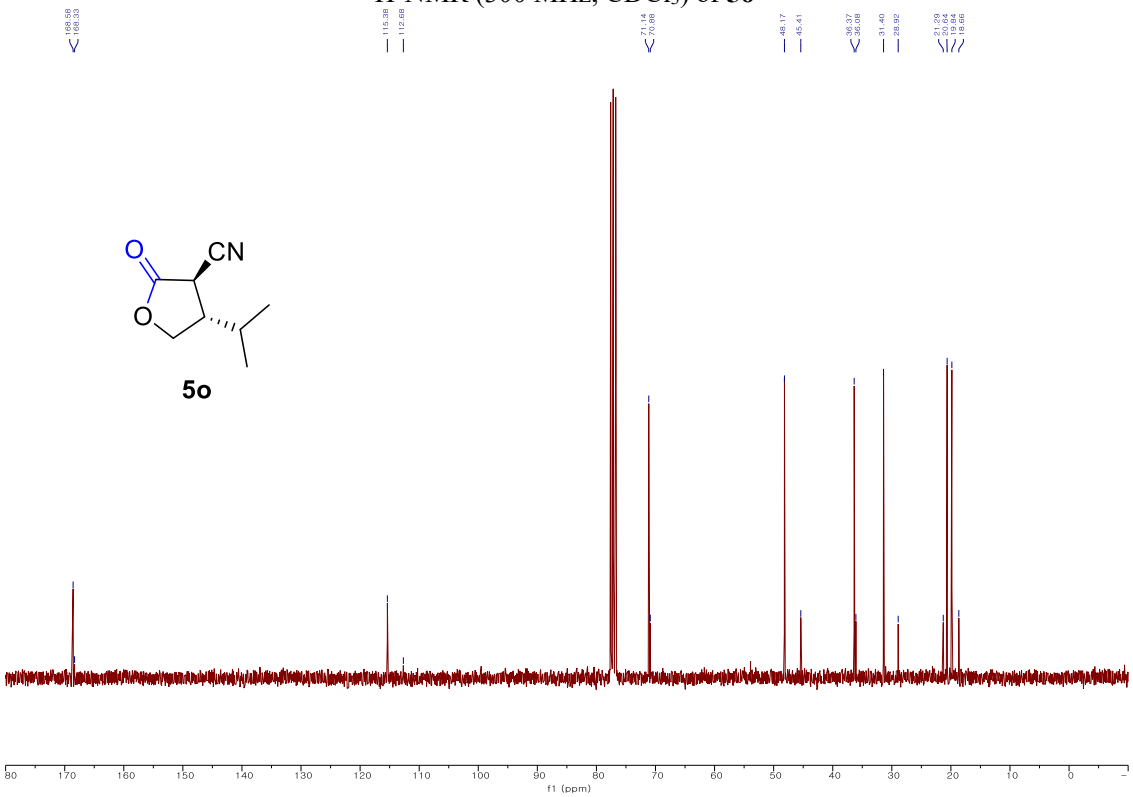
^{1}H-NMR (300 MHz, $CDCl_3$) of **5n**



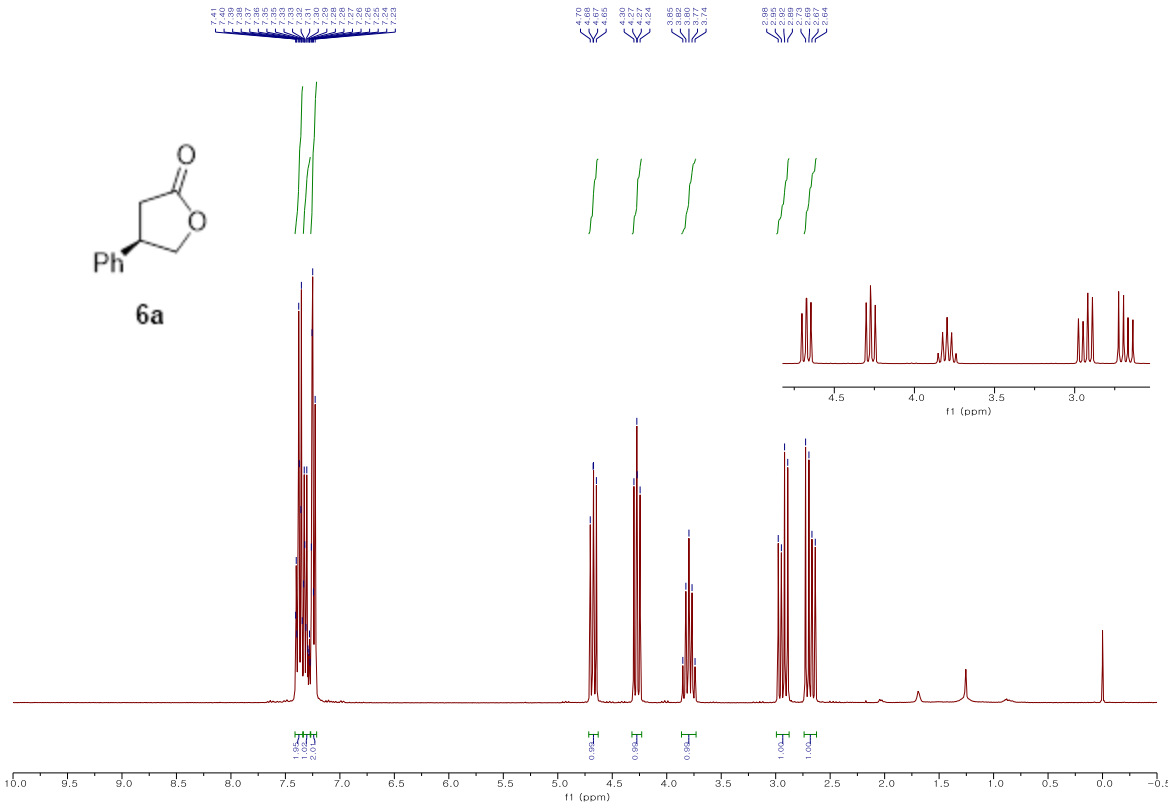
^{13}C-NMR (75Hz, $CDCl_3$) of **5n**



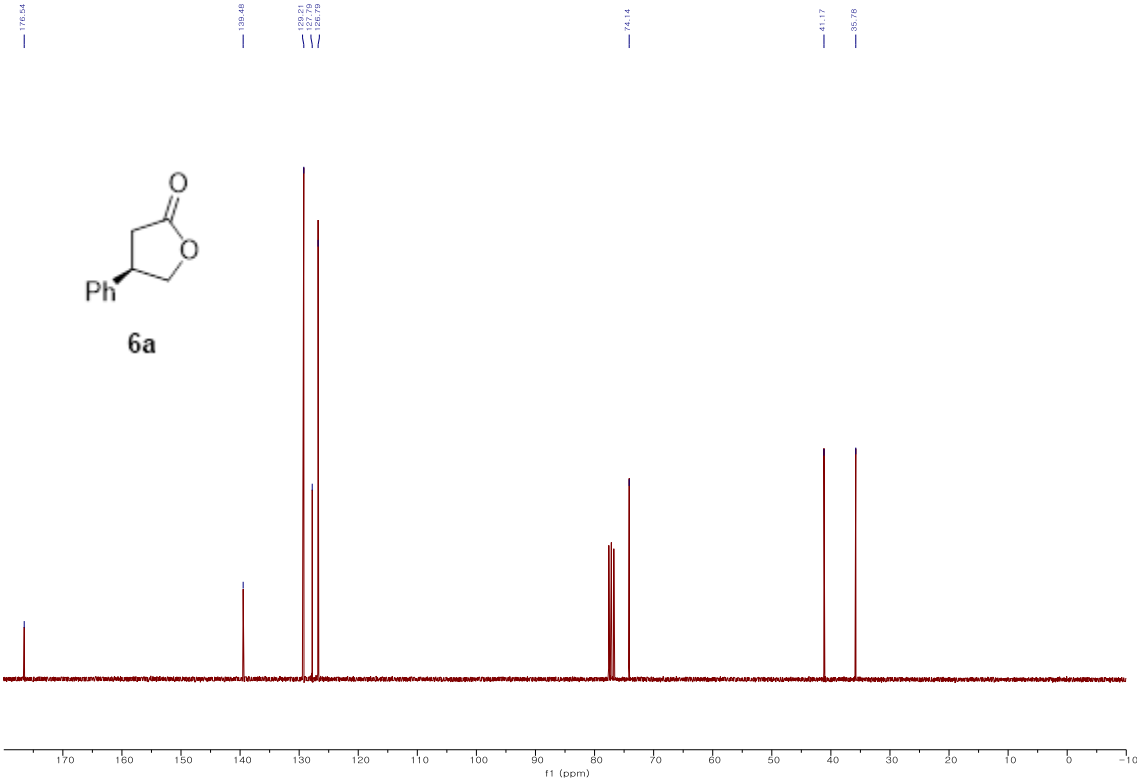
^{1}H-NMR (300 MHz, $CDCl_3$) of **5o**



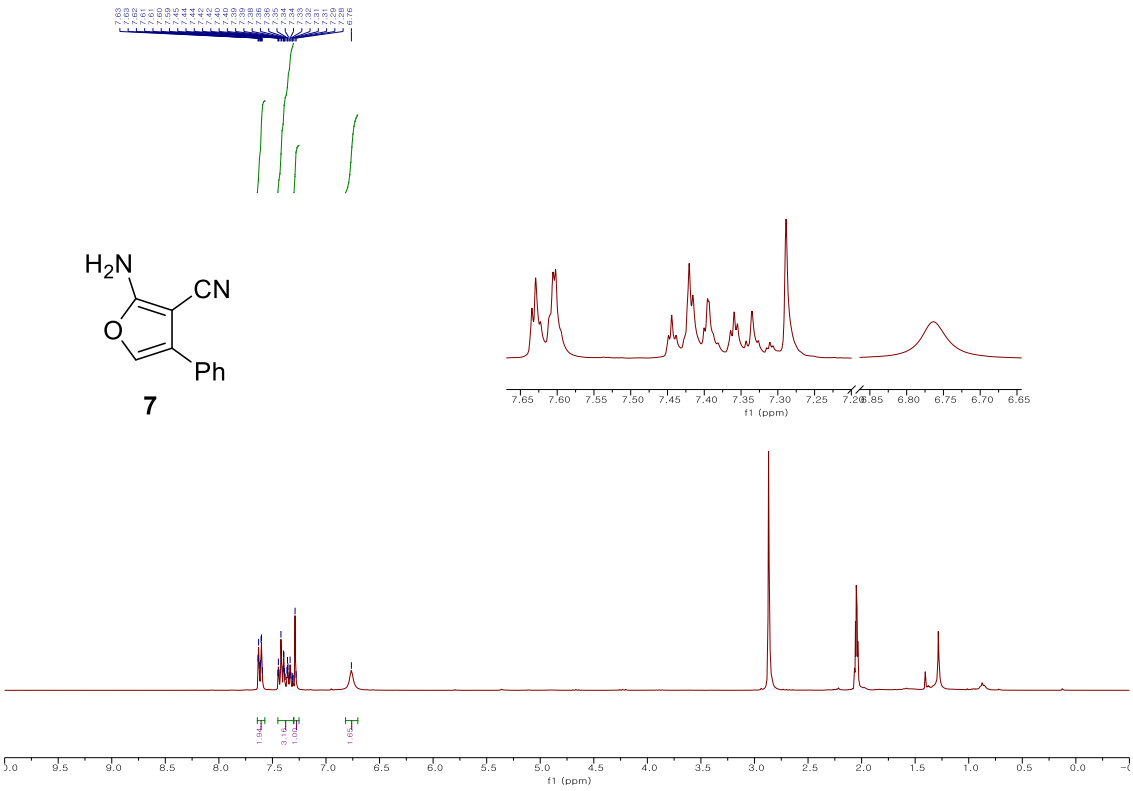
^{13}C-NMR (75Hz, $CDCl_3$) of **5o**



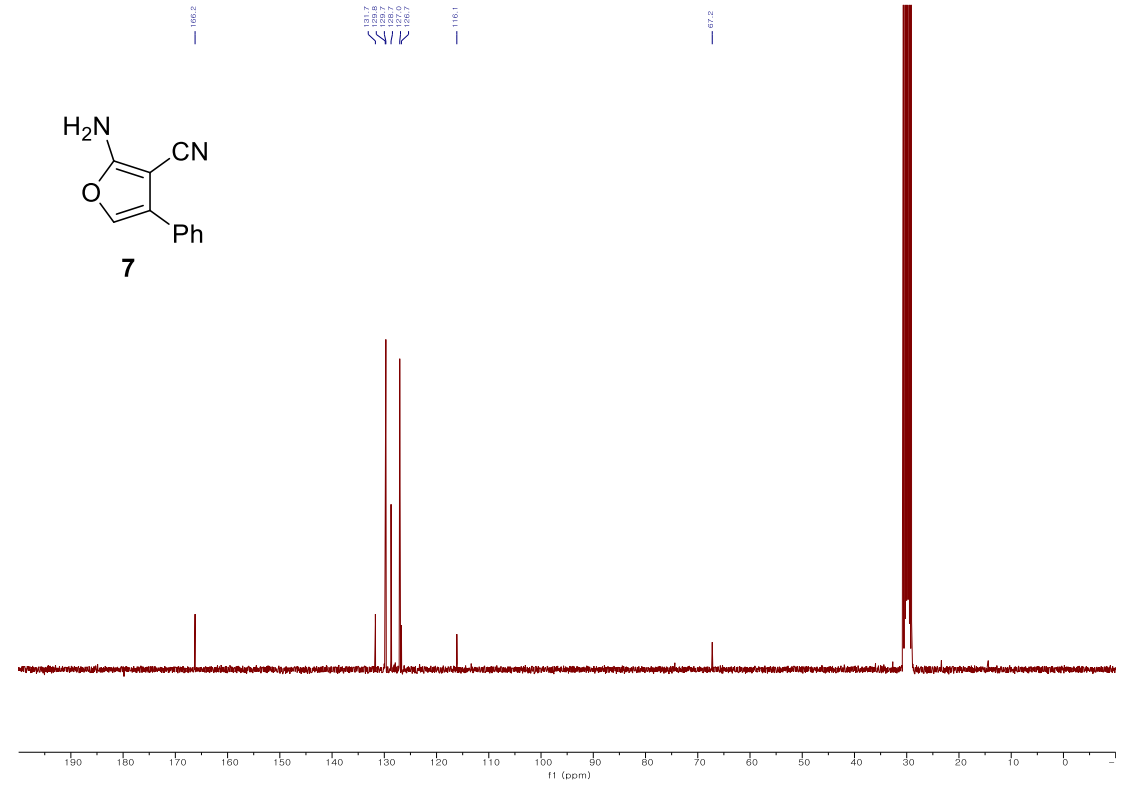
^{1}H-NMR (300 MHz, $CDCl_3$) of **6a**



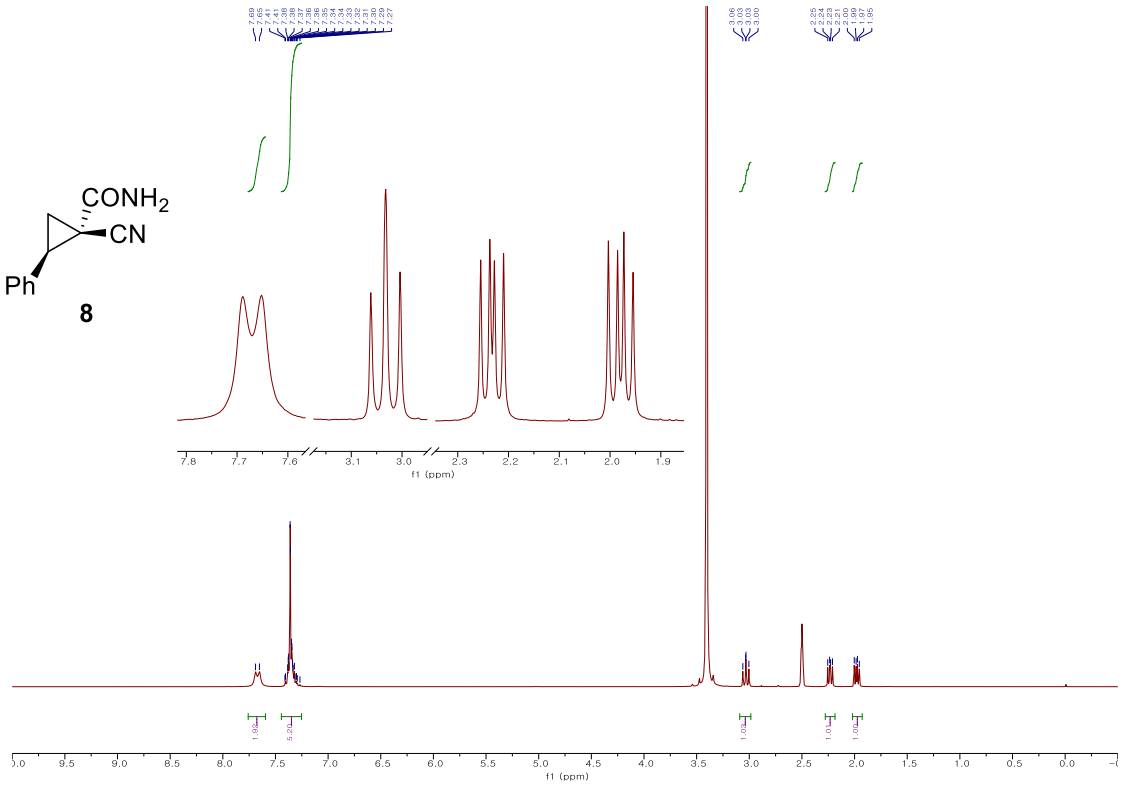
^{13}C-NMR (75Hz, $CDCl_3$) of **6a**



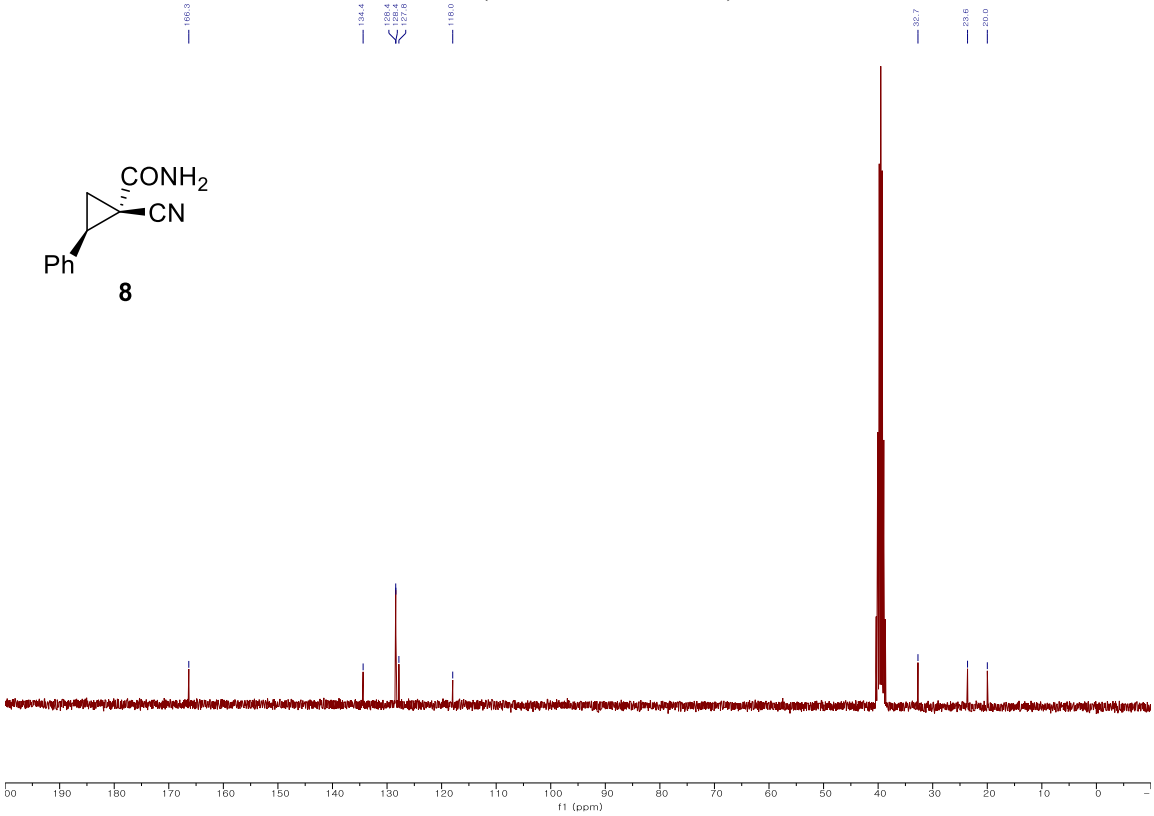
^{1}H-NMR (300 MHz, Acetone-d_6) of **7**



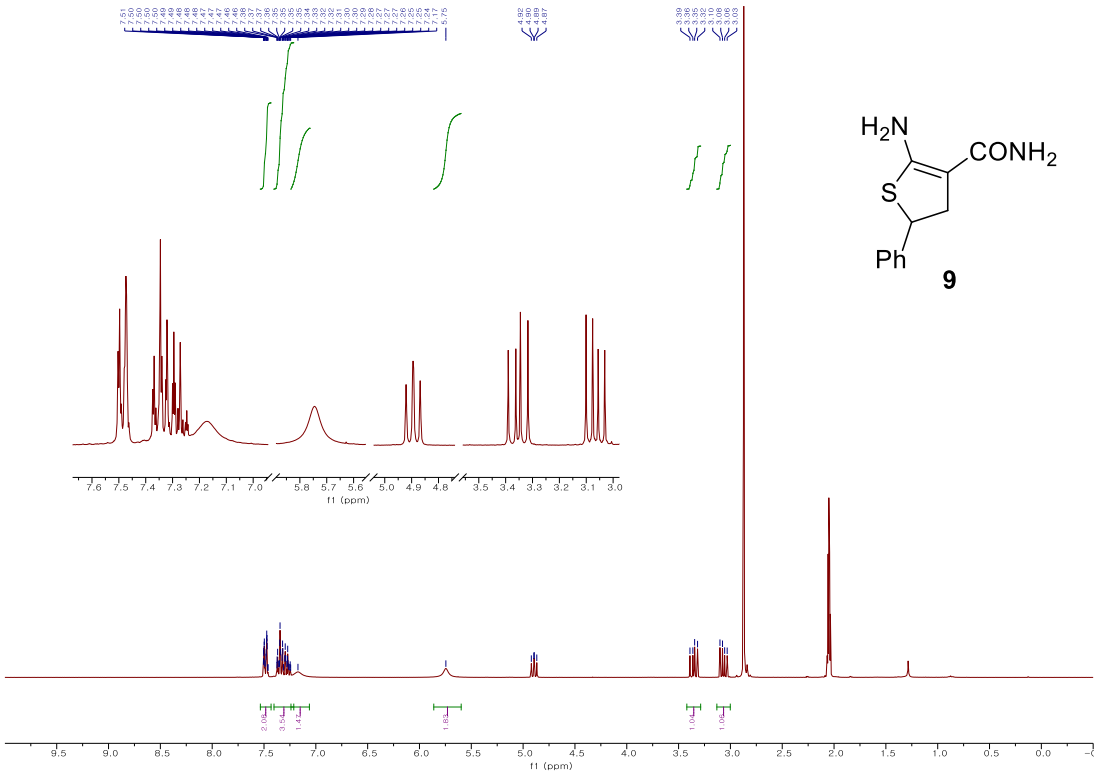
^{13}C-NMR (75Hz, Acetone-d_6) of **7**



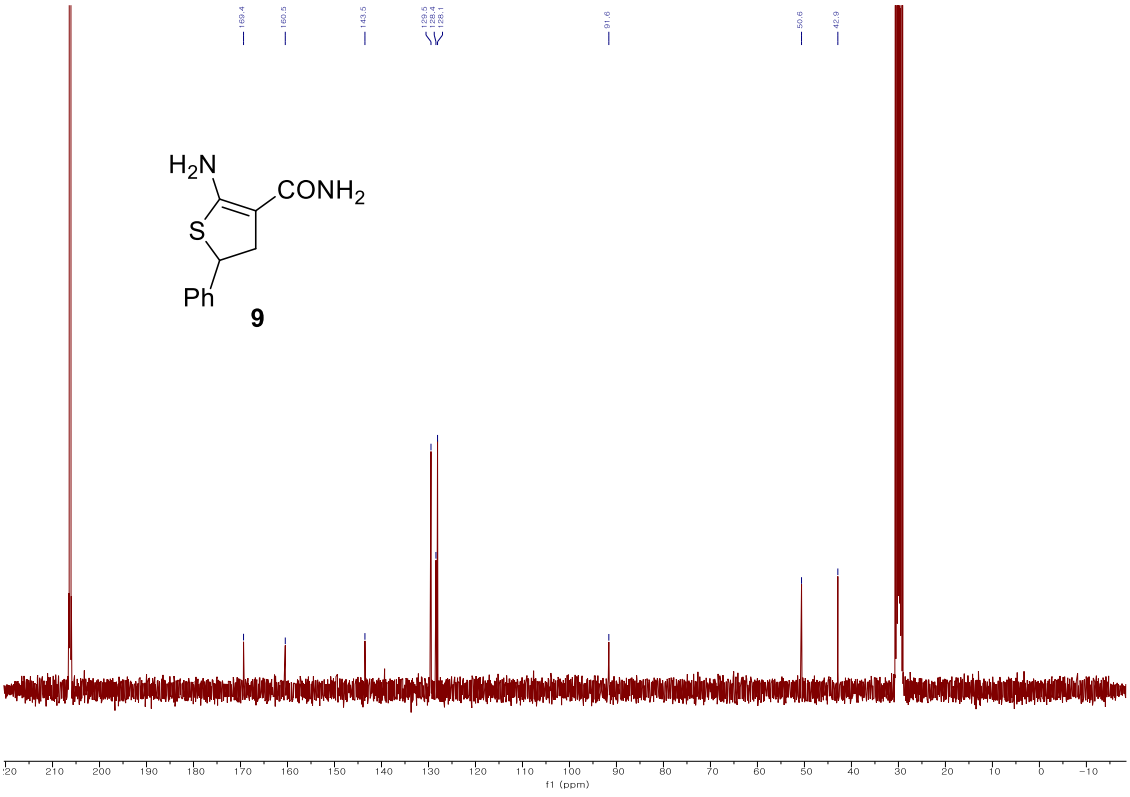
^{1}H-NMR (300 MHz, DMSO-d_6) of **8**



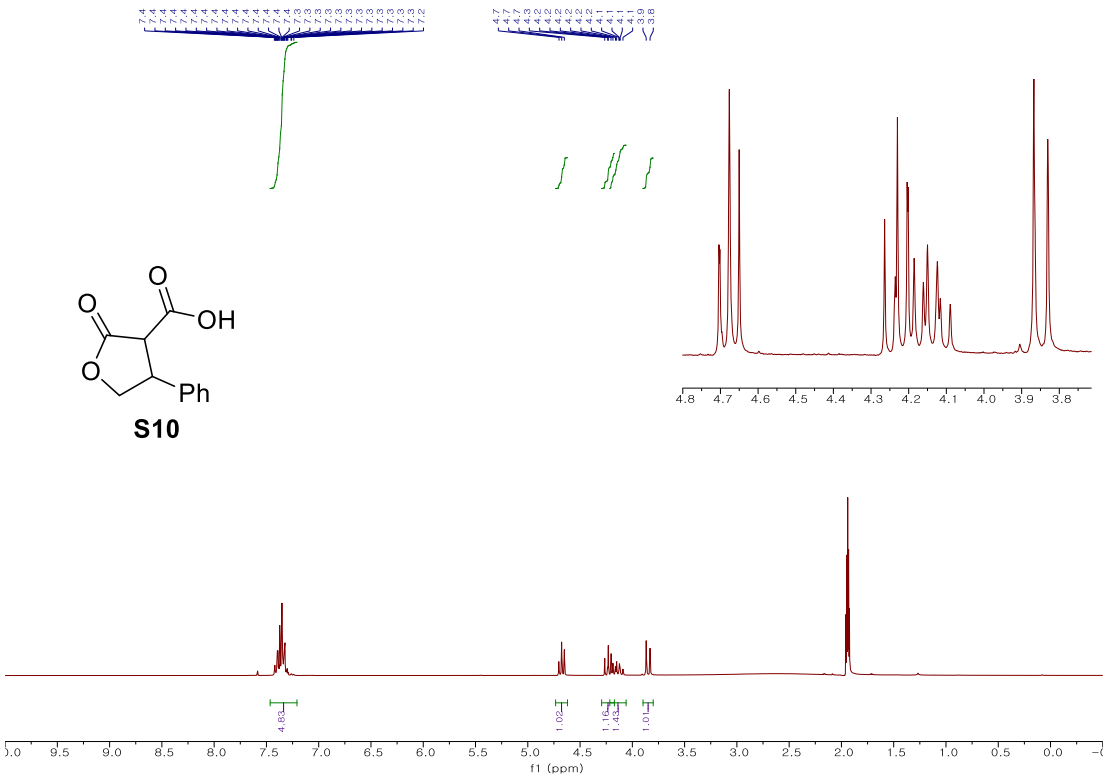
^{13}C-NMR (75Hz, DMSO-d_6) of **8**



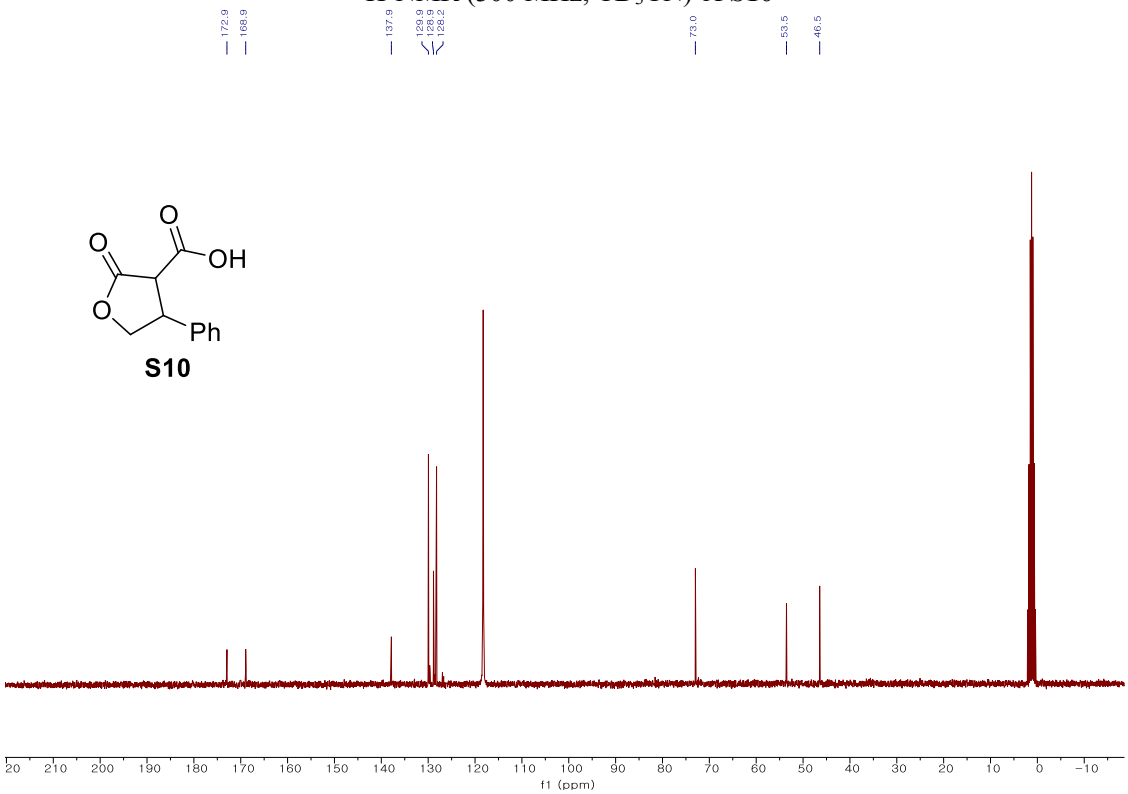
^{1}H-NMR (300 MHz, Acetone-d_6) of **9**



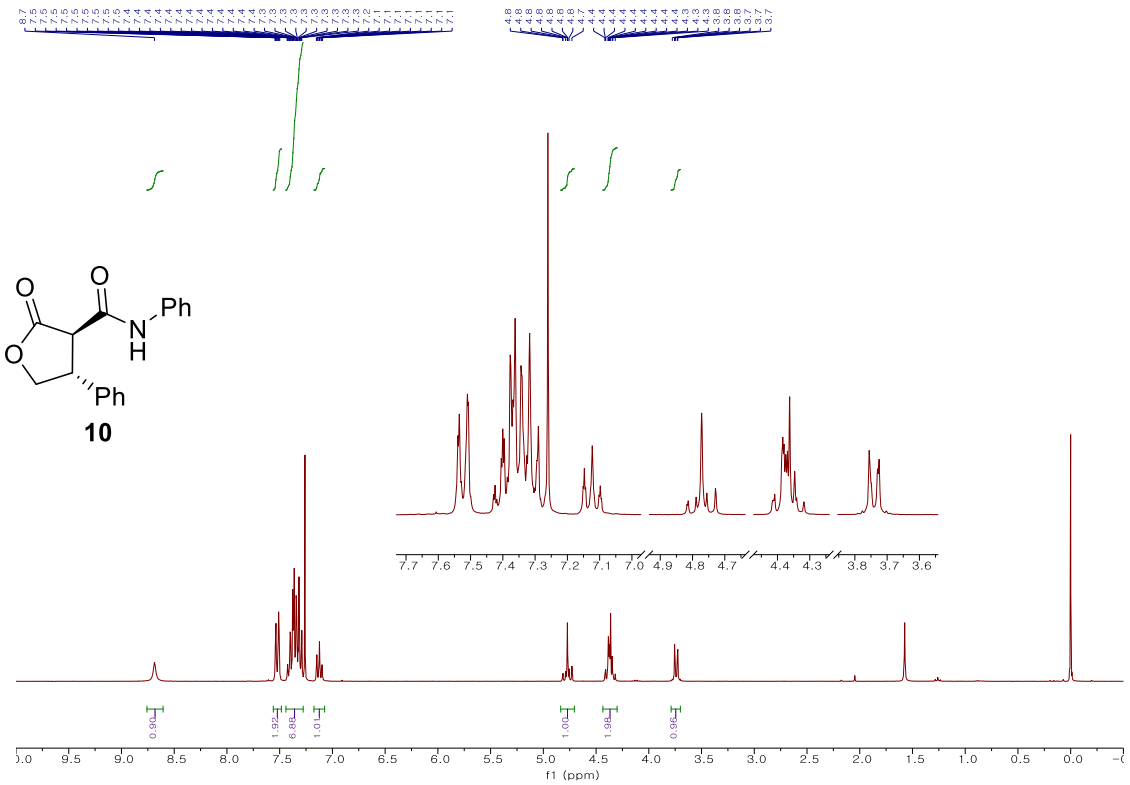
^{13}C-NMR (75Hz, Acetone-d_6) of **9**



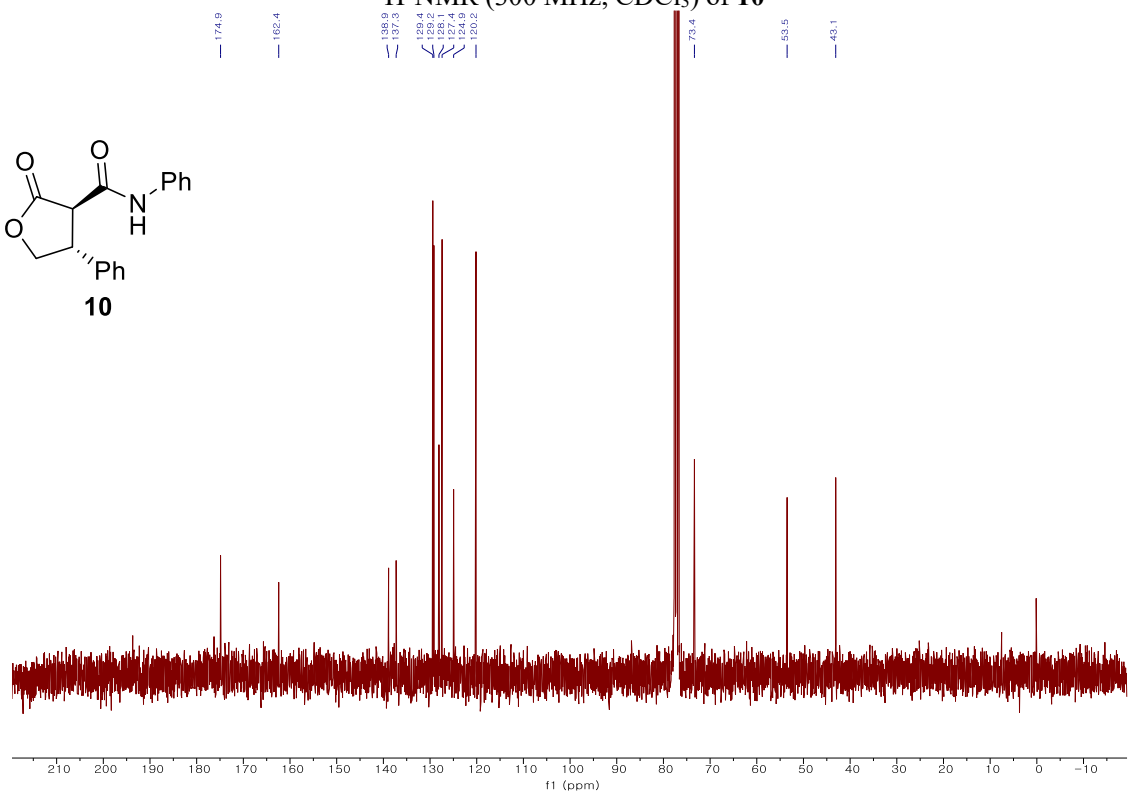
^{1}H-NMR (300 MHz, CD_3CN) of **S10**



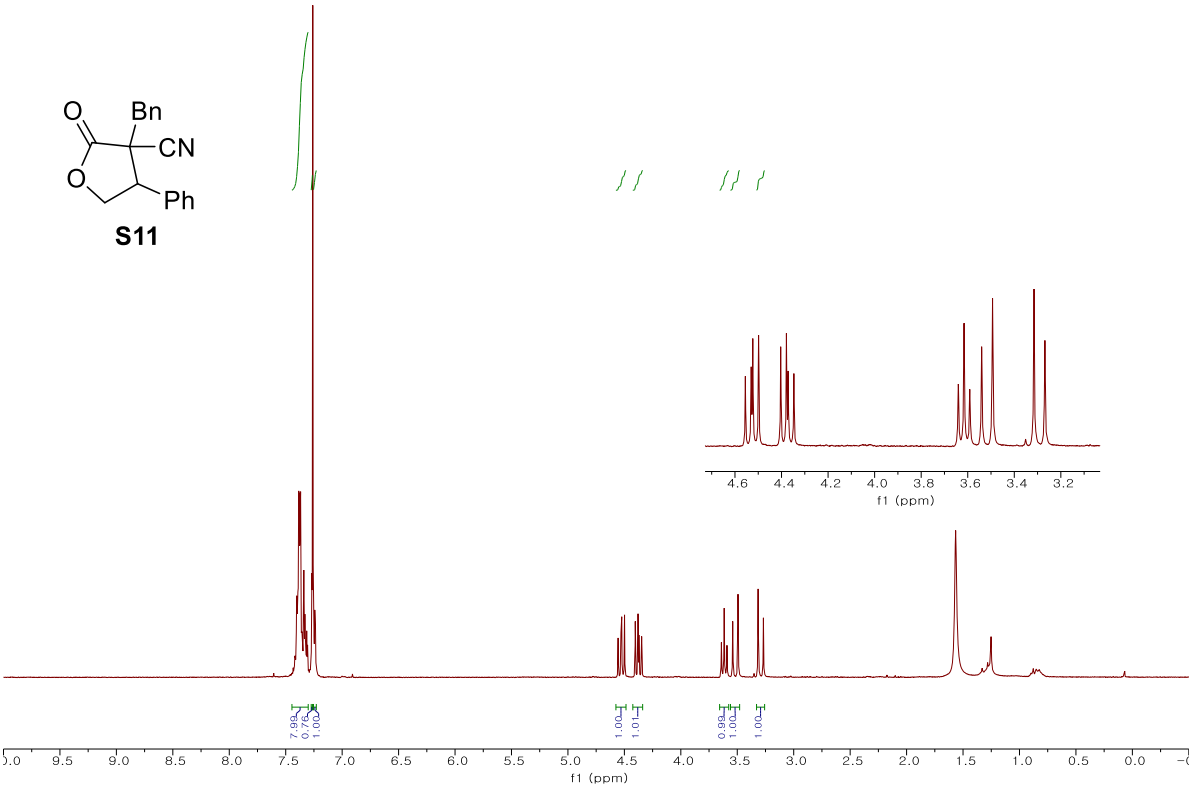
^{13}C-NMR (75Hz, CD_3CN) of **S10**



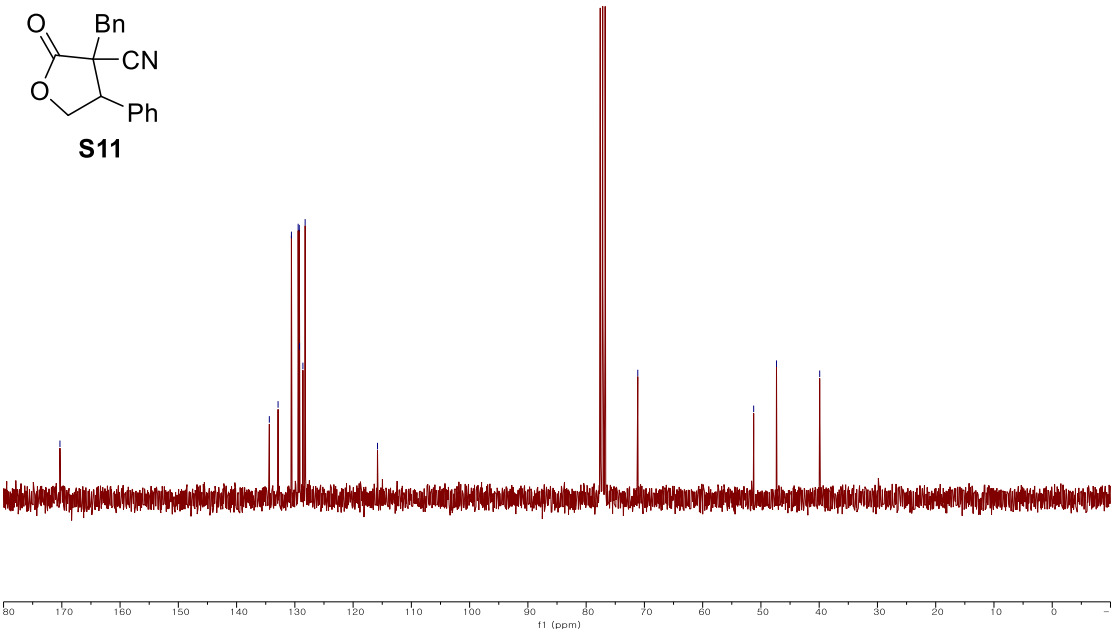
^{1}H-NMR (300 MHz, $CDCl_3$) of **10**



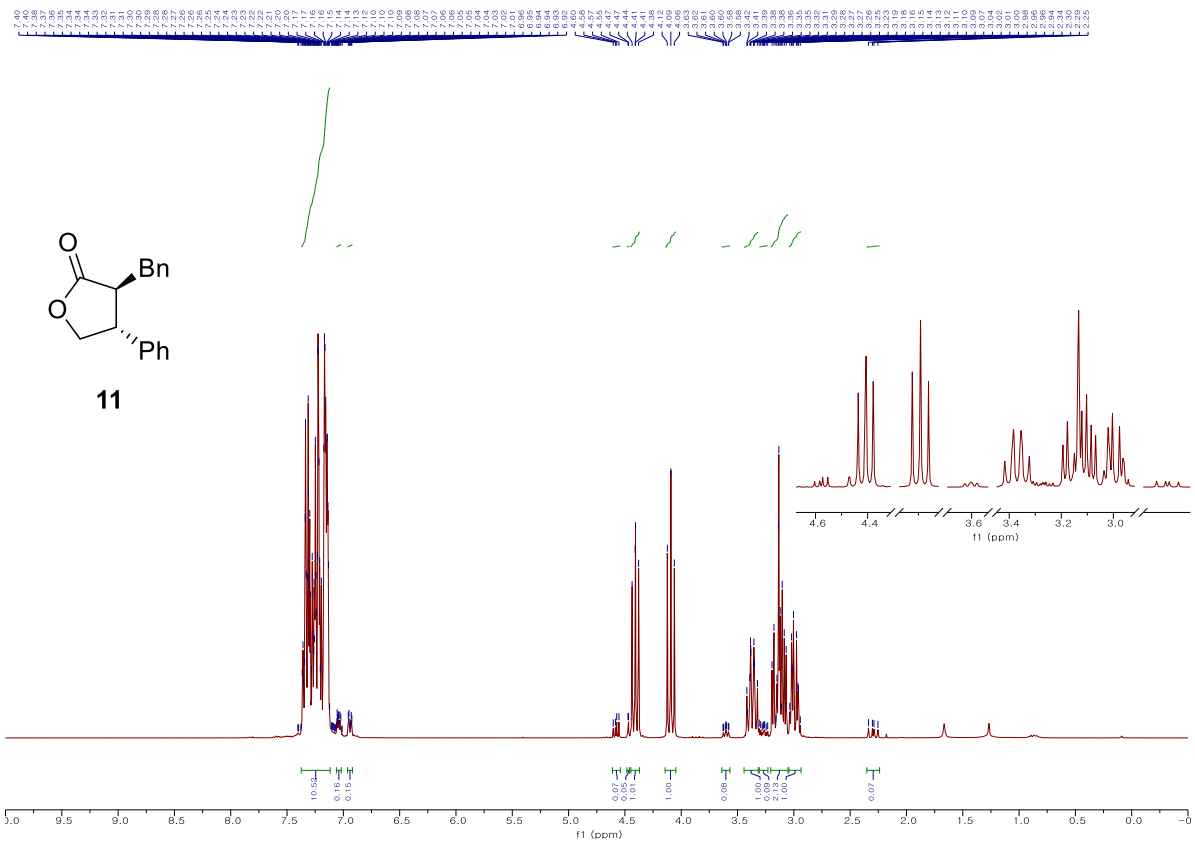
^{13}C-NMR (75Hz, $CDCl_3$) of **10**



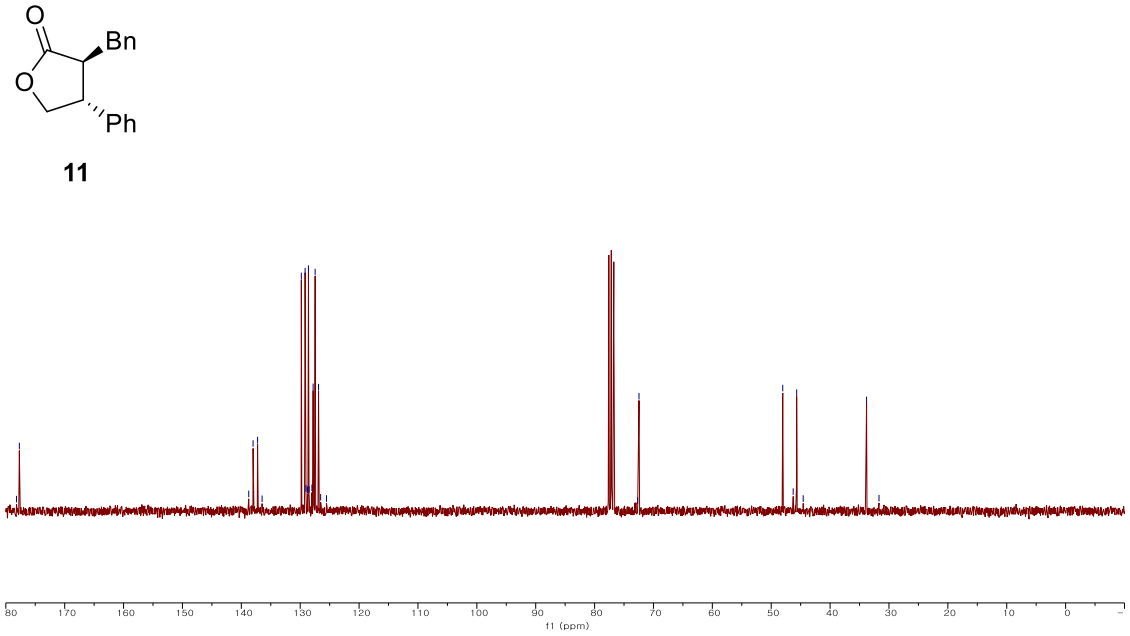
^{1}H-NMR (300 MHz, $CDCl_3$) of **S11**



^{13}C-NMR (75Hz, $CDCl_3$) of **S11**



^{1}H-NMR (300 MHz, $CDCl_3$) of **11**



^{13}C-NMR (75Hz, $CDCl_3$) of **11**