Electronic Supplementary Information for

Weak Base-Promoted Selective Rearrangement of Oxaziridines to Amides via Visible-Light Photoredox Catalysis

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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.

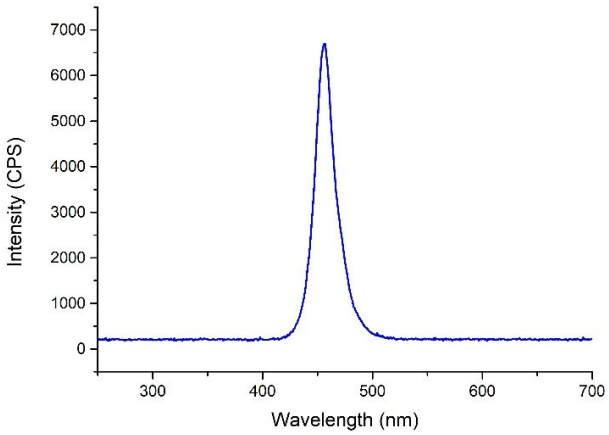
The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F_{254}), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into a *p*-anisaldehyde solution (5.6 mL of *p*-anisaldehyde, 2.3 mL acetic acid and 3.0 mL of concentrated sulfuric acid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

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), bs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. 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 $[M+H]^{+}$. 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 CH instrument (CHI600E model).

II. Reaction Setup

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

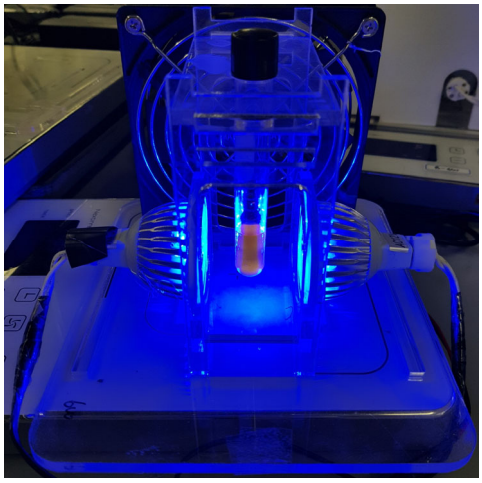
MR16 3 W blue LEDs spotlight



Emission spectrum of 3 W blue LEDs

Figure S1. Description for 3 W blue LED spotlight lamp

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

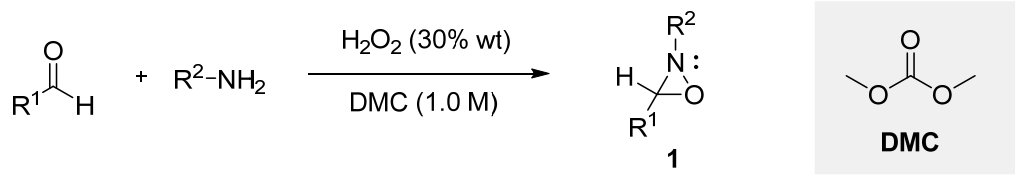


** A fan was used to maintain the internal and external temperature of the reaction vial at 20 ~ 30 °C.

Figure S2. reaction setup

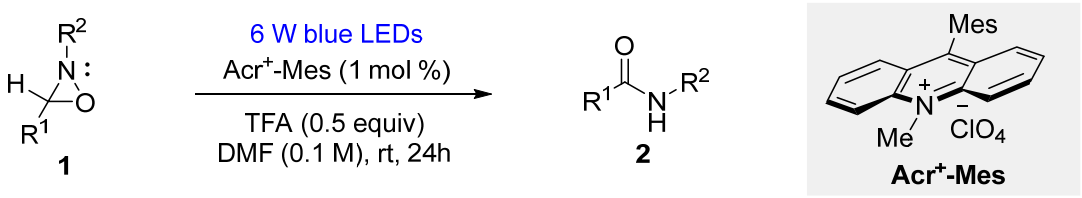
III. Preparation of oxaziridines 1

All the utilized aryl and alkyl oxaziridines **1** had been prepared by following the reported protocol.[1]



IV. General procedure and characterization data of products

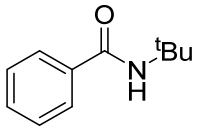
A. General procedure for rearrangement oxaziridines 1 to amides 2



To a re-sealable pressure tube (13 x 100 mm) with a magnetic stirrer bar was charged with oxaziridine **1** (0.2 mmol, 1.0 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 DMF (2 mL, 0.1 M for **1**). 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 for 24h. After the reaction was completed, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography contained ethyl acetate/hexanes as the eluent to afford the corresponding amide **2**.

B. Characterization data of amides 2

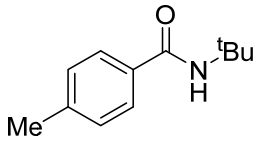
N-(tert-butyl)benzamide (2a).[2]



2a

Following the general procedure using 15% ethyl acetate in hexanes as eluant, **2a** was obtained as a white solid (33.7 mg, 95% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.60 (m, 2H), 7.60 – 7.31 (m, 3H), 6.01 (bs, 1H), 1.45 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.99, 135.96, 131.12, 128.51, 126.78, 51.65, 28.93.

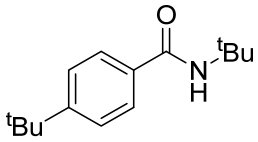
N-(tert-butyl)-4-methylbenzamide (2b).[3]



2b

Following the general procedure using 15% ethyl acetate in hexanes as eluant, **2b** was obtained as a white solid (26.8 mg, 70% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.55 (m, 2H), 7.26 – 7.15 (m, 2H), 5.92 (bs, 1H), 2.38 (s, 3H), 1.46 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.95, 141.48, 133.14, 129.20, 126.79, 51.59, 29.01, 21.50.

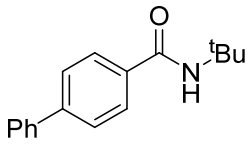
N,4-di-tert-butylbenzamide (2c).[3]



2c

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2c** was obtained as a white solid (25.3mg, 54% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.57 (m, 2H), 7.49 – 7.33 (m, 2H), 5.93 (bs, 1H), 1.46 (s, 9H), 1.32 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.97, 154.61, 133.17, 126.63, 125.50, 51.59, 34.96, 31.30, 29.02.

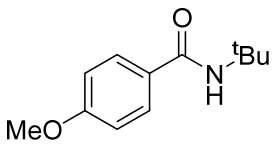
N-(tert-butyl)-[1,1'-biphenyl]-4-carboxamide (2d).[4]



2d

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2d** was obtained as a white solid (45.6 mg, 90% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 2H), 7.67 – 7.54 (m, 4H), 7.51 – 7.32 (m, 3H), 6.07 (bs, 1H), 1.50 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.70, 143.90, 140.15, 134.63, 128.97, 127.98, 127.34, 127.25, 127.18, 51.72, 28.98.

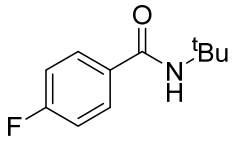
N-(tert-butyl)-4-methoxybenzamide (2e).[3]



2e

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2e** was obtained as a white solid (12.5 mg, 30% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 2H), 6.95 – 6.85 (m, 2H), 5.88 (bs, 1H), 3.83 (s, 3H), 1.46 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.57, 161.98, 128.58, 128.32, 113.74, 55.53, 51.59, 29.08.

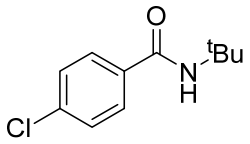
N-(tert-butyl)-4-fluorobenzamide (2f).[3]



2f

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2f** was obtained as a white solid (25.0 mg, 64% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.61 (m, 2H), 7.13 – 6.94 (m, 2H), 5.99 (bs, 1H), 1.44 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.98, 164.50 (d, J = 251.0 Hz), 132.15 (d, J = 3.3 Hz), 129.10 (d, J = 8.8 Hz), 115.44 (d, J = 21.8 Hz), 51.78, 28.91.; ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.13.

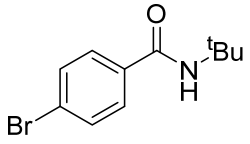
N-(tert-butyl)-4-chlorobenzamide (2g).[3]



2g

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2g** was obtained as a white solid (40.7 mg, 96% yield); R_f= 0.40 (ethyl acetate:hexanes, 1:10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.40 – 7.30 (m, 2H), 5.95 (bs, 1H), 1.45 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.96, 137.32, 134.36, 128.76, 128.29, 51.90, 28.93.

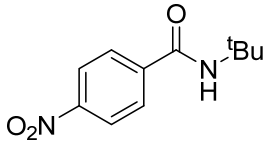
4-bromo-N-(tert-butyl)benzamide (2h).[3]



2h

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2h** was obtained as a white solid (45.1 mg, 88% yield); R_f= 0.40 (ethyl acetate:hexanes, 1:10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.46 (m, 4H), 5.95 (bs, 1H), 1.45 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.04, 134.82, 131.73, 128.49, 125.74, 51.91, 28.92.

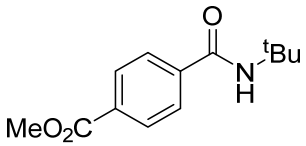
N-(tert-butyl)-4-nitrobenzamide (2i).[2]



2i

Following the general procedure using 25% ethyl acetate in hexanes as eluant, **2i** was obtained as a white solid (33.8 mg,76% yield); R_f= 0.20 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 – 8.16 (m, 2H), 7.91 – 7.80 (m, 2H), 6.10 (bs, 1H), 1.47 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.01, 149.35, 141.63, 128.06, 123.79, 52.38, 28.81.

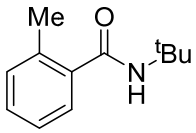
methyl 4-(tert-butylcarbamoyl)benzoate (2j).[2]



2j

Following the general procedure using 25% ethyl acetate in hexanes as eluant, **2j** was obtained as a white solid (46.9 mg, 99% yield); R_f= 0.25 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.87 – 7.72 (m, 2H), 5.96 (bs, 1H), 3.94 (s, 3H), 1.48 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.44, 166.14, 139.93, 132.33, 129.79, 126.89, 52.43, 51.99, 28.87.

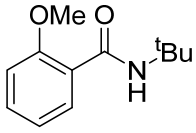
N-(tert-butyl)-2-methylbenzamide (2k).[3]



2k

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2k** was obtained as a white solid (25.2 mg, 66% yield); R_f= 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 7.22 – 7.11 (m, 2H), 5.56 (bs, 1H), 2.43 (s, 3H), 1.46 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.81, 138.01, 135.58, 130.92, 129.51, 126.54, 125.76, 51.84, 28.99, 19.68.

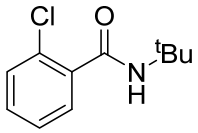
N-(tert-butyl)-2-methoxybenzamide (2l).[3]



2l

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2l** was obtained as a oil (37.3 mg, 90% yield); R_f= 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.13 (m, 1H), 7.84 (bs, 1H), 7.48 – 7.36 (m, 1H), 7.13 – 7.01 (m, 1H), 6.99 – 6.90 (m, 1H), 3.95 (s, 3H), 1.46 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.20, 157.26, 132.41, 131.96, 122.79, 121.35, 111.38, 55.95, 51.04, 29.00.

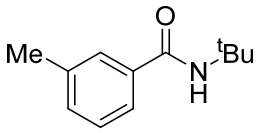
N-(tert-butyl)-2-chlorobenzamide (2m).[3]



2m

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2m** was obtained as a white solid (37.3 mg, 88% yield); R_f= 0.4 (ethyl acetate:hexanes, 1:10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 1H), 7.41 – 7.27 (m, 3H), 5.91 (bs, 1H), 1.48 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.98, 136.60, 130.94, 130.51, 130.15, 129.85, 127.14, 52.31, 28.90.

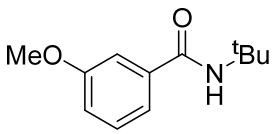
N-(tert-butyl)-3-methylbenzamide (2n).[3]



2n

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2n** was obtained as a white solid (32.9 mg, 86% yield); R_f= 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 2H), 7.34 – 7.22 (m, 2H), 5.96 (bs, 1H), 2.38 (s, 3H), 1.47 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.20, 138.38, 135.99, 131.87, 128.43, 127.59, 123.74, 51.64, 28.97, 21.46.

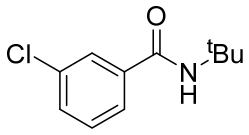
N-(tert-butyl)-3-methoxybenzamide (2o).[3]



2o

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2o** was obtained as a white solid (40.2 mg, 97% yield); R_f= 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 3H), 7.10 – 6.96 (m, 1H), 5.94 (bs, 1H), 3.85 (s, 3H), 1.47 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.79, 159.84, 137.46, 129.46, 118.49, 117.40, 112.18, 55.47, 51.68, 28.91.

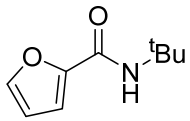
N-(tert-butyl)-3-chlorobenzamide (2p).[3]



2p

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2p** was obtained as a white solid (38.1mg, 90% yield); R_f= 0.40 (ethyl acetate:hexanes, 1:10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 1H), 7.60 – 7.50 (m, 1H), 7.43 – 7.32 (m, 1H), 7.34 – 7.23 (m, 1H), 6.14 (bs, 1H), 1.45 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.66, 137.74, 134.50, 131.01, 129.74, 127.17, 124.91, 51.87, 28.80.

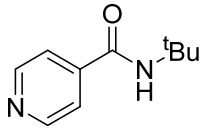
N-(tert-butyl)furan-2-carboxamide (2q).[2]



2q

Following the general procedure using 30% ethyl acetate in hexanes as eluant, **2q** was obtained as a white solid (20.1 mg, 60% yield); R_f= 0.20 (ethyl acetate:hexanes, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 1H), 7.04 (d, *J* = 3.5 Hz, 1H), 6.46 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.19 (bs, 1H), 1.45 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.92, 148.94, 143.41, 113.58, 112.22, 51.57, 29.05.

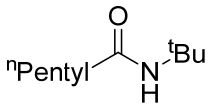
N-(tert-butyl)isonicotinamide (2r).[5]



2r

Following the general procedure using 30% ethyl acetate in hexanes as eluant, **2r** was obtained as a white solid (28.6 mg, 80% yield); R_f= 0.20 (ethyl acetate:hexanes, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 – 8.62 (m, 2H), 7.57 – 7.49 (m, 2H), 6.14 (bs, 1H), 1.44 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.97, 150.49, 143.02, 120.90, 52.22, 28.79.

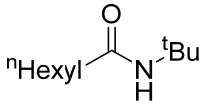
N-(tert-butyl)hexanamide (2s).



2s

Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2s** was obtained as a white solid (27.5 mg, 80% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:15); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30 (bs, 1H), 2.06 (t, *J* = 7.7 Hz, 2H), 1.57 (tt, *J* = 7.6, 7.1 Hz, 2H), 1.34 (s, 9H), 1.30 – 1.18 (m, 4H), 0.87 (t, *J* = 6.7 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.69, 51.12, 37.81, 31.51, 28.94, 25.59, 22.55, 14.07.

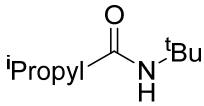
N-(tert-butyl)heptanamide (2t).



2t

Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2t** was obtained as a white solid (26.3 mg, 71% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:15); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (bs, 1H), 2.06 (t, *J* = 7.5 Hz, 2H), 1.65 – 1.49 (m, 2H), 1.32 (s, 9H), 1.30 – 1.23 (m, 6H), 0.86 (t, *J* = 6.6 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.67, 51.12, 37.86, 31.69, 28.99, 28.95, 25.87, 22.62, 14.15.

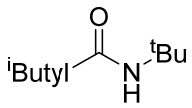
N-(tert-butyl)isobutyramide (2u).[6]



2u

Following the general procedure using 15% ethyl acetate in hexanes as eluant, **2u** was obtained as a white solid (15.5 mg, 54% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:15); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.24 (bs, 1H), 2.20 (hept, *J* = 6.8 Hz, 1H), 1.33 (s, 9H), 1.10 (d, *J* = 6.9 Hz, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.54, 50.94, 36.47, 28.95, 19.82.

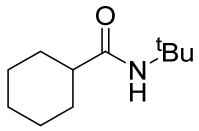
N-(tert-butyl)-3-methylbutanamide (2v).[2]



2v

Following the general procedure using 5% ethyl acetate in hexanes as eluant, **2v** was obtained as a white solid (18.9 mg, 60% yield); R_f = 0.40 (ethyl acetate:hexanes, 1:15); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22 (bs, 1H), 2.17 – 2.01 (m, 1H), 1.93 (d, *J* = 7.2 Hz, 2H), 1.34 (s, 9H), 0.93 (d, *J* = 6.5 Hz, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.04, 51.08, 47.10, 28.87, 26.26, 22.40.

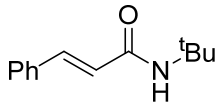
N-(tert-butyl)cyclohexanecarboxamide (2w).[7]



2w

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **2w** was obtained as a white solid (31.6 mg, 86% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:15); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (bs, 1H), 2.03 – 1.86 (m, 1H), 1.86 – 1.72 (m, 4H), 1.70 – 1.60 (m, 1H), 1.50 – 1.35 (m, 2H), 1.33 (s, 9H), 1.29 – 1.18 (m, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.70, 50.85, 46.41, 29.87, 28.96, 25.87.

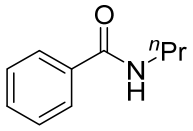
N-(tert-butyl)cinnamamide (2x).[2]



2x

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2x** was obtained as a white solid (24.4mg, 60% yield); R_f = 0.30 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 15.5 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.39 – 7.29 (m, 3H), 6.35 (d, *J* = 15.5 Hz, 1H), 5.59 (bs, 1H), 1.43 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.34, 140.33, 135.08, 129.56, 128.87, 127.82, 122.09, 51.62, 28.98.

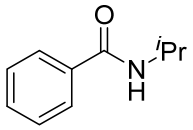
N-propylbenzamide (2y).[8]



2y

Following the general procedure using 15% ethyl acetate in hexanes as eluant, **2y** was obtained as a white solid (30.1 mg, 92% yield); R_f= 0.35 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.68 (m, 2H), 7.52 – 7.32 (m, 3H), 6.40 (bs, 1H), 3.46 – 3.24 (m, 2H), 1.70 – 1.50 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.72, 134.93, 131.36, 128.59, 126.96, 41.85, 23.00, 11.54.

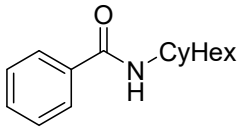
N-isopropylbenzamide (2z).[2]



2z

Following the general procedure using 15% ethyl acetate in hexanes as eluant, **2z** was obtained as a white solid (31.0 mg, 95% yield); R_f= 0.35 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 2H), 7.54 – 7.34 (m, 3H), 6.24 (bs, 1H), 4.40 – 4.18 (m, 1H) 1.26 (d, *J* = 6.6 Hz, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.94, 134.87, 131.38, 128.56, 126.97, 42.05, 22.87.

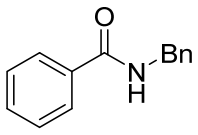
N-cyclohexylbenzamide (2aa).[2]



2aa

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **2aa** was obtained as a white solid (34.6 mg, 85% yield); R_f= 0.25 (ethyl acetate:hexanes, 1:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.63 (m, 2H), 7.59 – 7.34 (m, 3H), 5.97 (bs, 1H), 4.08 – 3.88 (m, 1H), 2.14 – 1.94 (m, 2H), 1.83 – 1.56 (m, 4H), 1.51 – 1.35 (m, 2H), 1.29 – 1.18 (m, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.76, 135.24, 131.38, 128.66, 126.95, 48.79, 33.39, 25.71, 25.05.

N-benzylbenzamide (2ab).[9]



2ab

Following the general procedure using 25% ethyl acetate in hexanes as eluant, **2ab** was obtained as a white solid (25.4 mg, 60% yield); R_f = 0.35 (ethyl acetate:hexanes, 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.69 (m, 2H), 7.55 – 7.22 (m, 8H), 6.57 (bs, 1H), 4.63 (d, *J* = 5.7 Hz, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.50, 138.30, 134.47, 131.67, 128.90, 128.70, 128.03, 127.73, 127.08, 44.23.

V. Electrochemical measurements

Cyclic voltammograms

Electrochemical study was performed using a CH instrument (CHI600E model). The redox potentials of substrates (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 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.

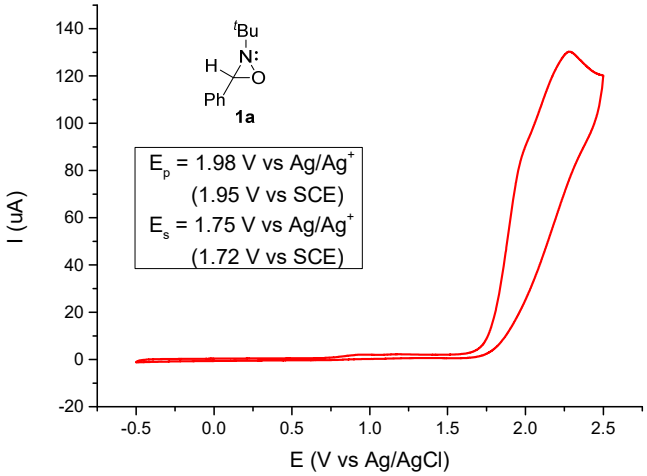


Figure S3. Cyclic voltammogram study for **1a**

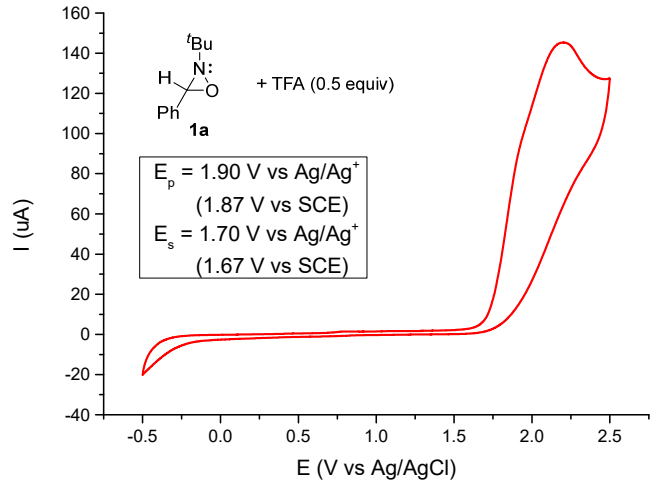


Figure S4. Cyclic voltammogram study for **1a** with TFA (0.5 equiv)

VI. Mechanistic studies

A. UV-Visible study

i. UV-Visible absorption of Acr^{+}-Mes

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

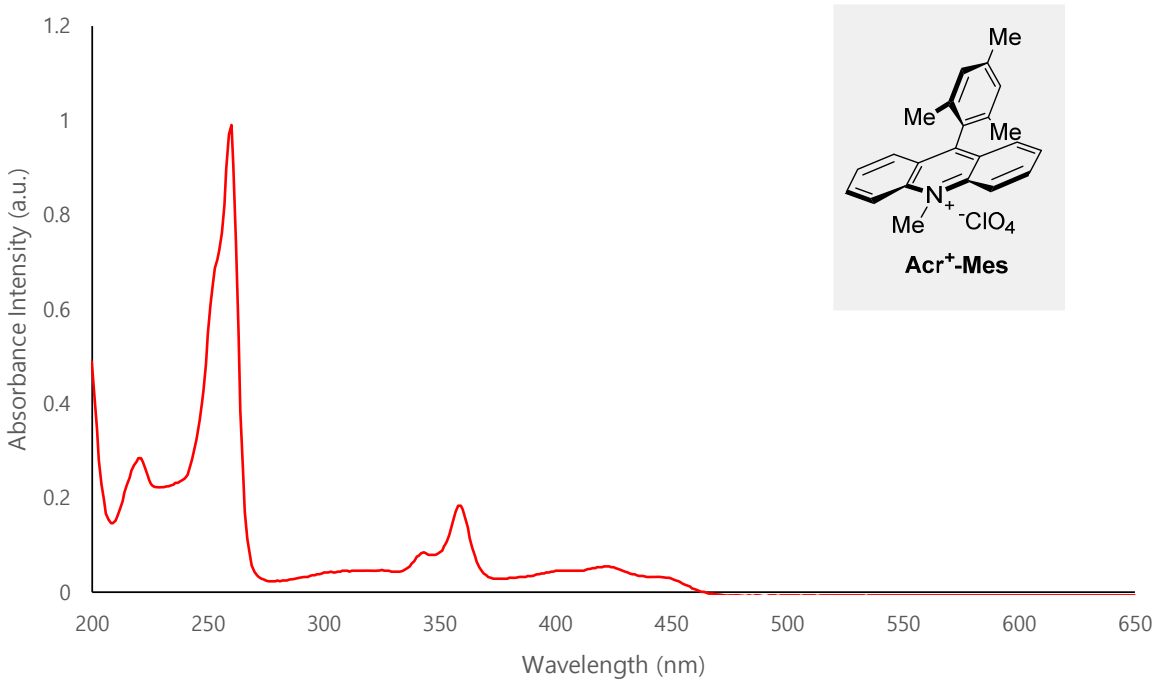


Figure S5. UV-Visible absorption spectra of Acr^{+}-Mes

ii. UV-Visible absorption of **1a** and **1a** with TFA (0.5 equiv)

A solution of 1.0 x 10^{-5} M in CH_3CN of substrates were prepared and UV-Visible absorption spectrum was measured.

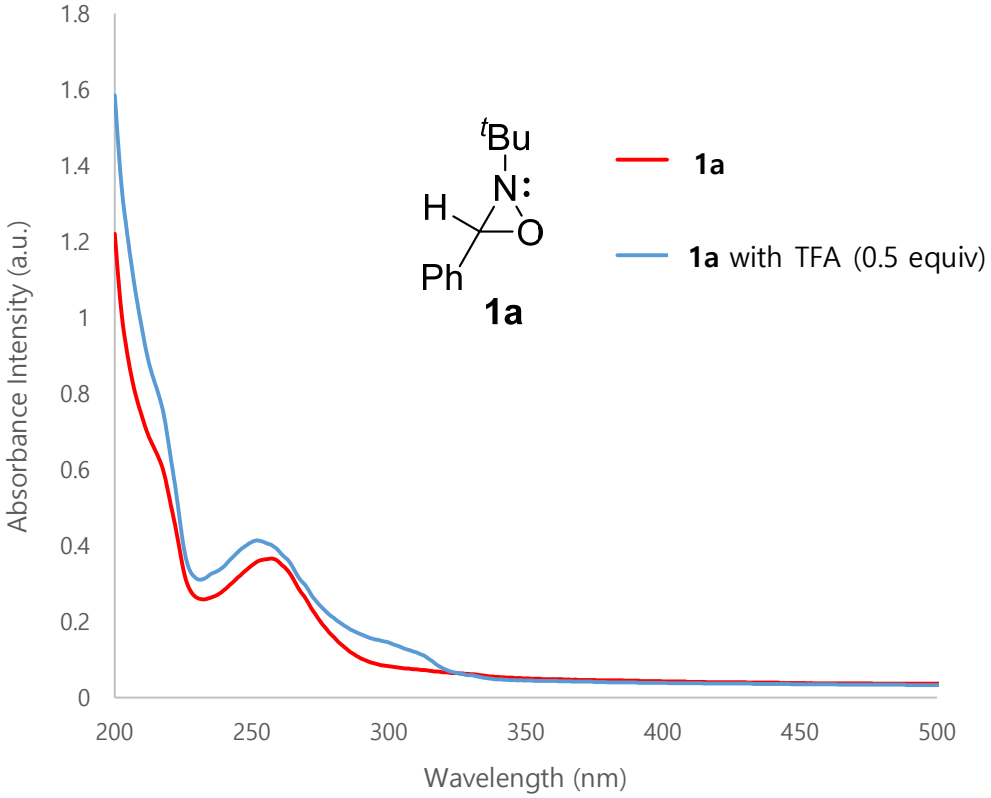


Figure S6. UV-Visible absorption spectra of **1a** and **1a** with TFA (0.5 equiv)

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** and **1a** with TFA (0.5 equiv) were 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 S7 supports that reaction mechanism occuring through single electron transfer (SET). Similar study was performed with Acr^{+}-Mes solution and **1a** with TFA (0.5 equiv). The quenching of the emission intensity of the catalyst with **1a** with TFA solution was observed as presented in Figure S8. This study shows that TFA enhanced quenching by **1a** of Acr^{+}-Mes catalysts. The quenching experiments demonstrated that the luminescence was quenched in proportion to the concentration of **1a** and **1a** with TFA (Figure S9).

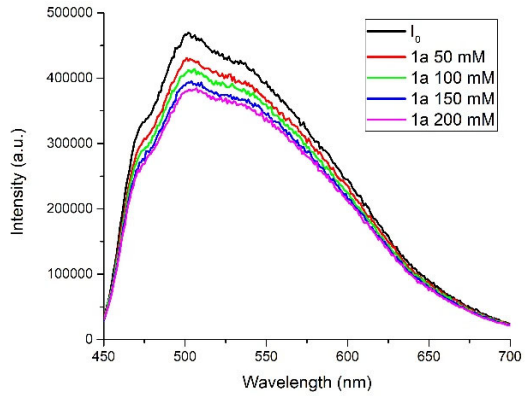


Figure S7. Luminescence quenching by **1a**

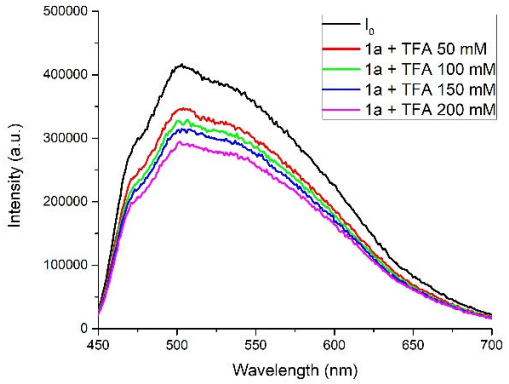


Figure S8. Luminescence quenching by **1a** with TFA (0.5 equiv)

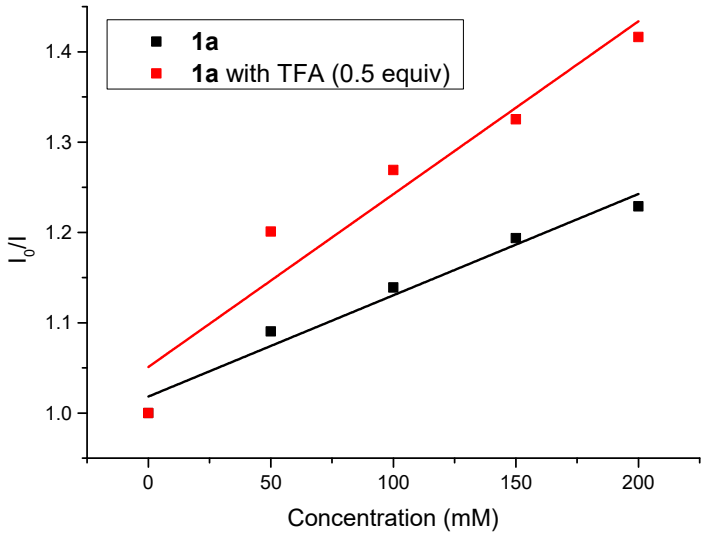
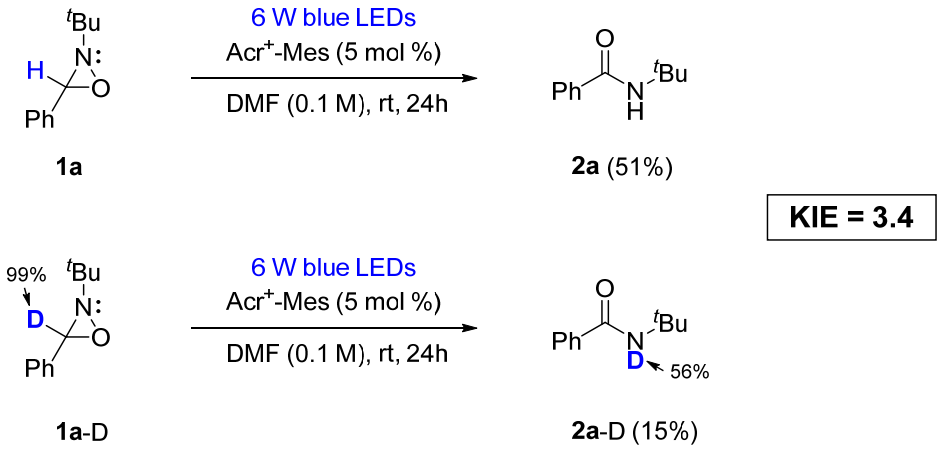


Figure S9. Stern–Volmer plot **1a** and **1a** with TFA

C. Control experiments

i. Deuterium labelling experiment

To get insight about the proton transfer from carbon to nitrogen at oxaziridine **1a** for our proposed mechanism, control experiments were performed using deuterated oxaziridine **1a**-D as starting material keeping other parameters unchanged. By ^{1}H NMR analysis of crude mixture, it was confirmed that deuterium shifts from carbon to the nitrogen of the amide **2a**-D. The decrease in the deuterium ratio is expected to be due to the trace amount of water in the DMF. And we measured kinetic isotope effect (KIE) value for rearrangement from oxaziridine 1a to amide 2a by compare reaction yield of oxaziridine **1a** and oxaziridine **1a**-D. The KIE values indicate that proton transfer steps are a late-determining step, which is consistent with the proposed mechanism.



Scheme S1. Deuterium labelling experiment

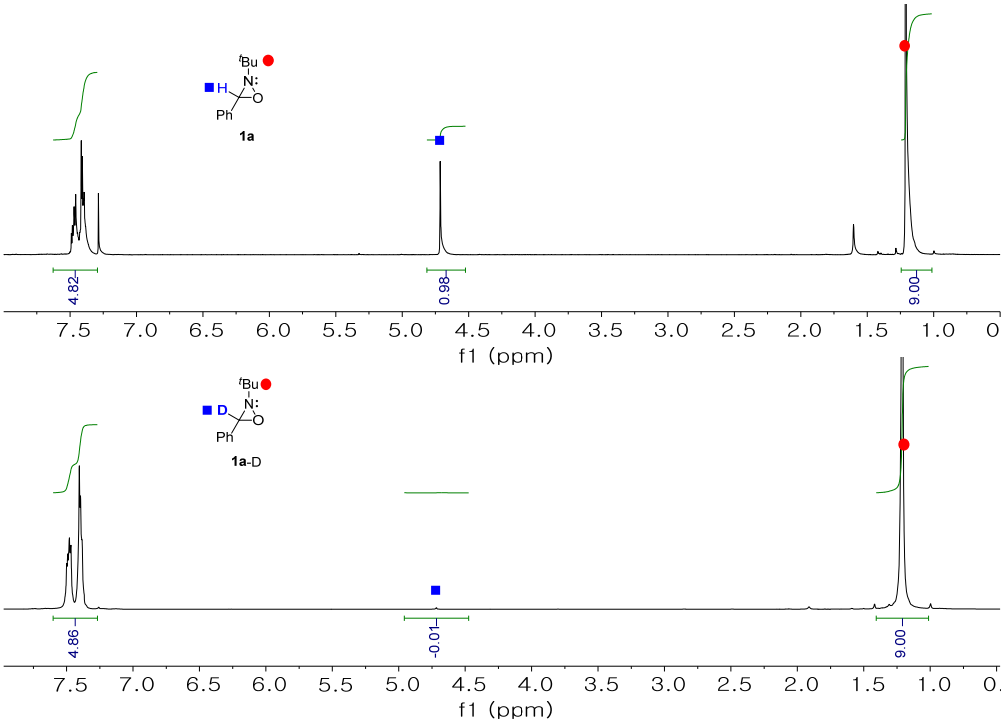


Figure S10. ^{1}H NMR of **1a** and **1a**-D

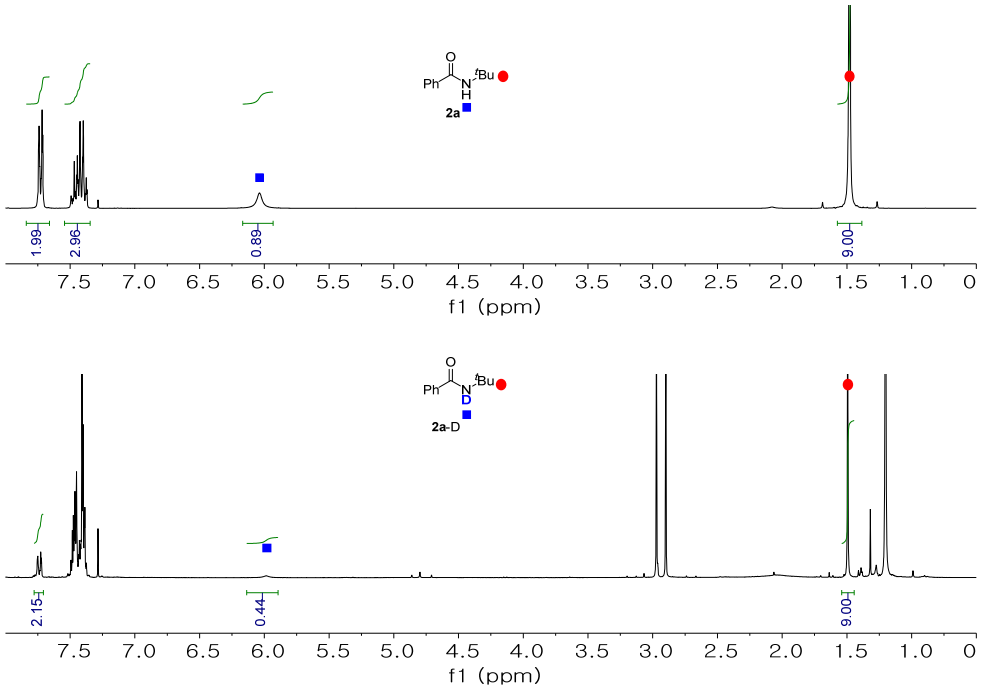
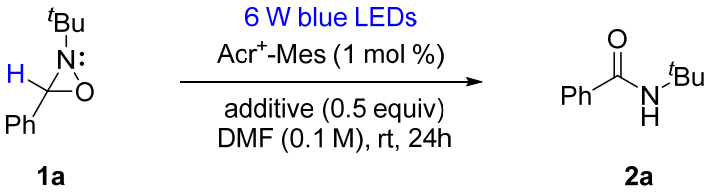


Figure S11. ^{1}H NMR of **1a** and crude of **2a**-D

ii. Carboxylate Salt effect in rearrangement of oxaziridines to amides

We proposed two major roles of TFA to improves reactivity. 1) The trifluoroacetate improves reactivity of deprotonation step because it is more basic than other solvents. 2) The TFA increases the concentration of protons in the reaction solution to facilitate the protonation step converting intermediate **II** to **III**. To prove second role of TFA, we examined rearrangement of oxazridine to amide with carboxylate salts that can only act as a base and not as a source of protons. The reaction using carboxylate salts instead of TFA or AcOH as additive shown low conversion and yield (Table S1). As these results indicate that both roles of TFA are important to improve reactivity.

Table S1. Rearrangement of oxazridine to amide with carboxylate salts



1a **2a**

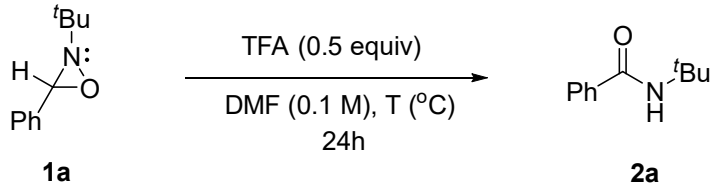
entry	additive	yield (%)[a]
1	AcONa	7
2	CF_3CO_2Na	18

[a] Yield determined by GC (internal standard: decane)

iii. Thermal rearrangement of oxaziridines to amides

We used a fan in the photoreactor to keep the reaction temperature below 30 degrees. Internal and external temperatures of photoreactor were frequently monitored to minimize the effect of reaction temperature. Additionally, we examined thermal rearrangement of oxaziridine **1a** to amide **2a** with various temperature conditions. The thermal rearrangement of oxaziridines did not occur at room temperature and requires a high temperature (In Table S2).

Table S2. Thermal rearrangement of **1a** to **2a**



1a **2a**

entry	temperature (°C)	yield (%)[a]
1	25	nd
2	50	23
3	70	60
4	90	90

[a] Yield determined by GC (internal standard: decane). nd = not detected.

D. On-off experiment

The on-off experiment of the light source was performed for weak base-promoted selective rearrangement of oxaziridines to amides by visible-light photoredox catalysis. This experiment proved that this conversion of oxaziridine **1a** to amide **2a** induced by the light source.

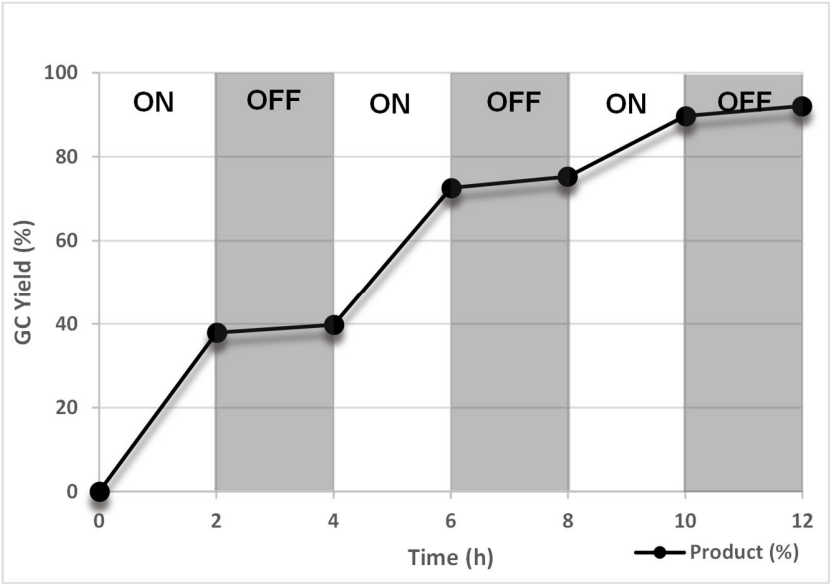


Figure S12. On-off experiment

VII. DFT calculation

Computation details

A computational study based on density functional theory (DFT) was performed to verify the experimentally proposed reaction mechanism and the detailed dependence of chemical reactivity on the base species. The molecular geometries were optimized using the hybrid PBE0 functional[10] and 6-31G(d,p) basis set implemented in Gaussian 16 program suite.[11] The frequency calculations were carried out with the same functional and basis set as those used in the geometry optimization to confirm local minima and to obtain a thermal contribution to the reaction energy diagram which is corrected by Gibbs free energy obtained at 298.15 K and 1 atm. The polarizable continuum model using the integral equation formalism (IEFPCM) was employed to take account for the influence of solvent medium, dimethylformamide (DMF) [ε = 37.219] and acetonitrile (MeCN) [dielectric constant ε = 35.688], on geometric and electronic structures.[12] Spin density was analyzed to elucidate the spatial distribution of unpaired electron in oxidized oxaziridine radical species.

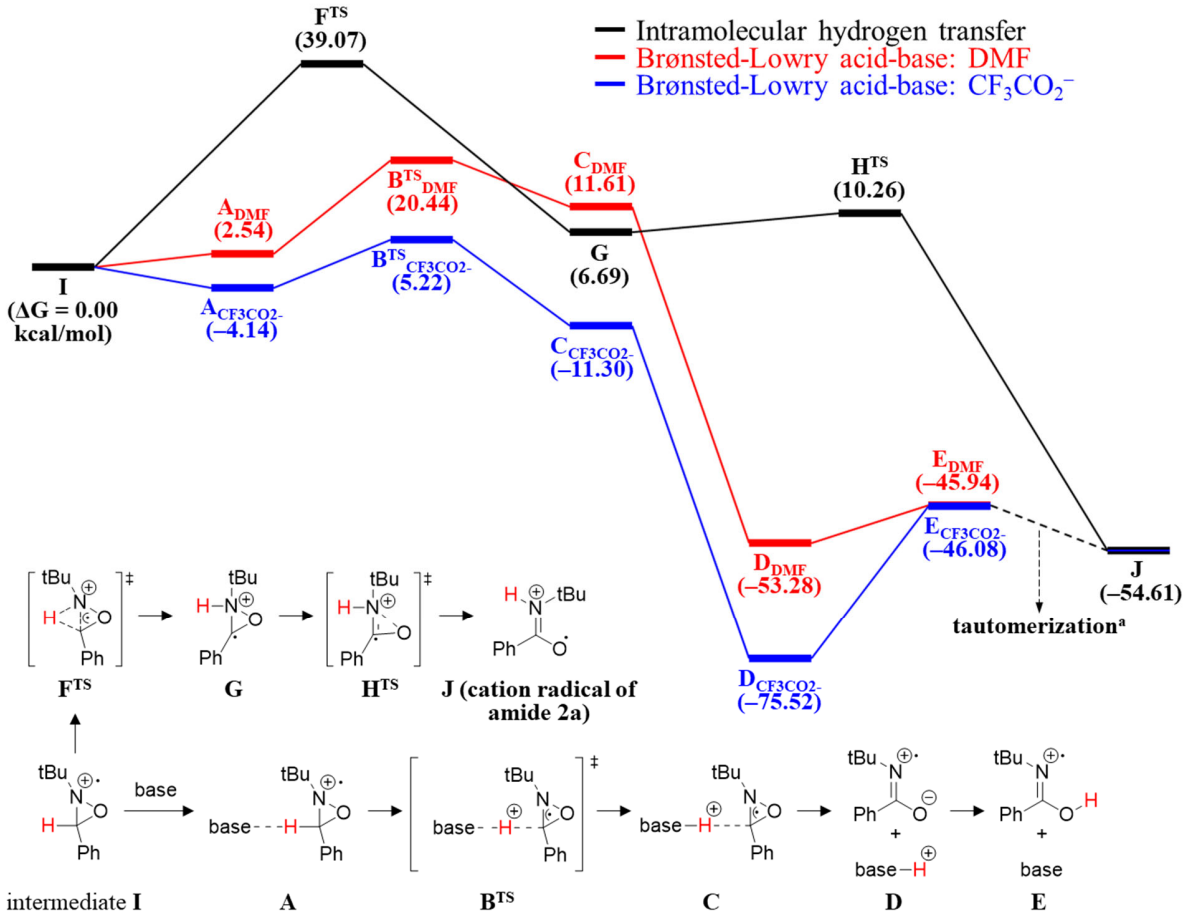


Figure S12. Reaction energy profiles for the rearrangement of cation radical intermediate **I**, i.e., oxidized oxaziridine **1a**, via Brønsted–Lowry acid–base reaction mechanism (from **I** to **E**), where DMF (red line) and trifluoroacetate (blue line) were used as base species, and via intramolecular hydrogen transfer mechanism (from **I** to **J**, black line). The solvent medium of DMF was considered using the IEFPCM method for evaluating all reaction energy profiles. All energy values are related to the Gibbs free energy (ΔG in kcal/mol) at 298.15 K and 1 atm. ([a] Notably, it is expected that tautomerization from **E** to **J** did not occur in our experiment because the one-electron reduction of cation radical **E** is generally faster than tautomerization.)

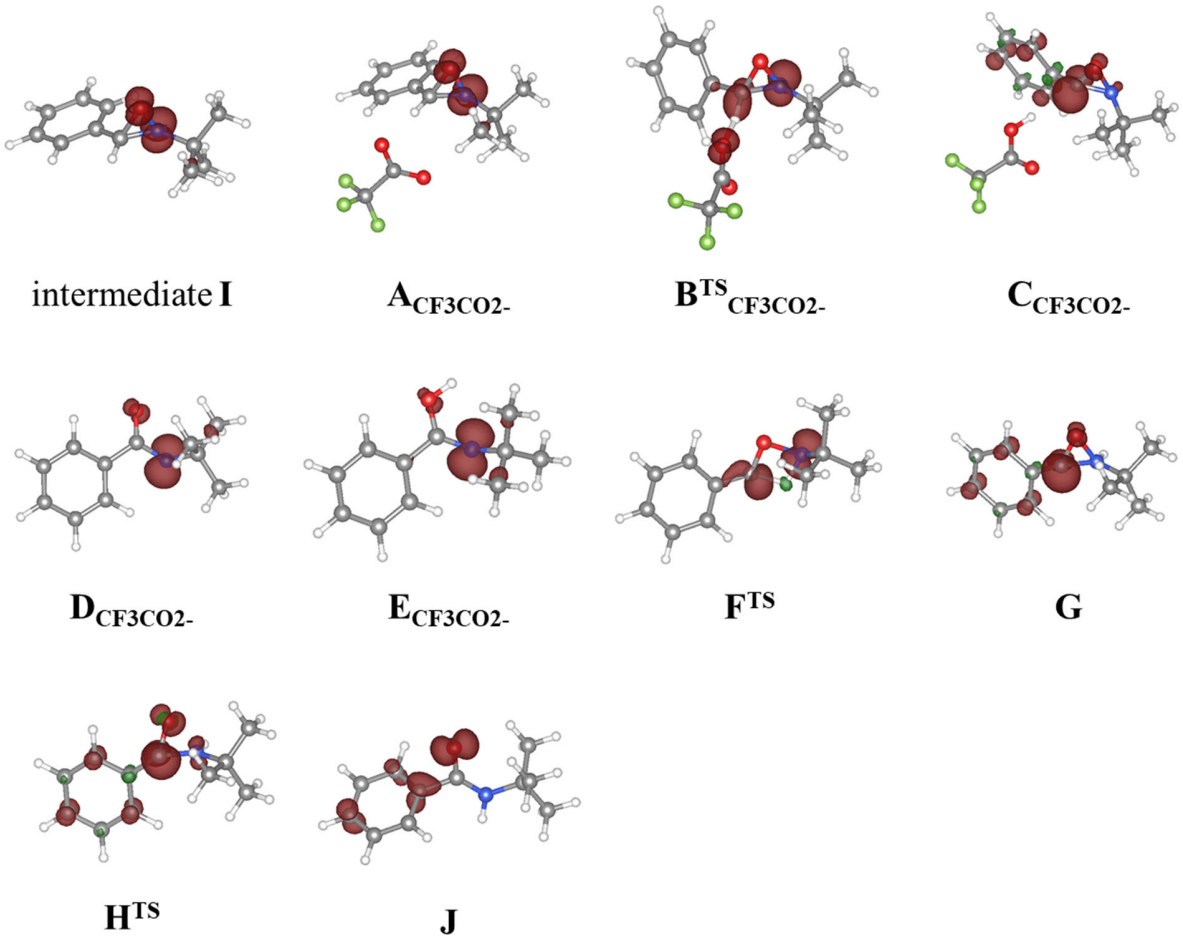


Figure S13. Optimized geometries and spin densities for the rearrangement of cation radical intermediate **I**, i.e., oxidized oxaziridine **1a**, via Brønsted–Lowry acid–base reaction mechanism (from **I** to **E**), where trifluoroacetate was used as base species, and intramolecular hydrogen transfer mechanism (from **I** to **J**). See Figure S1 for corresponding reaction energy profiles.

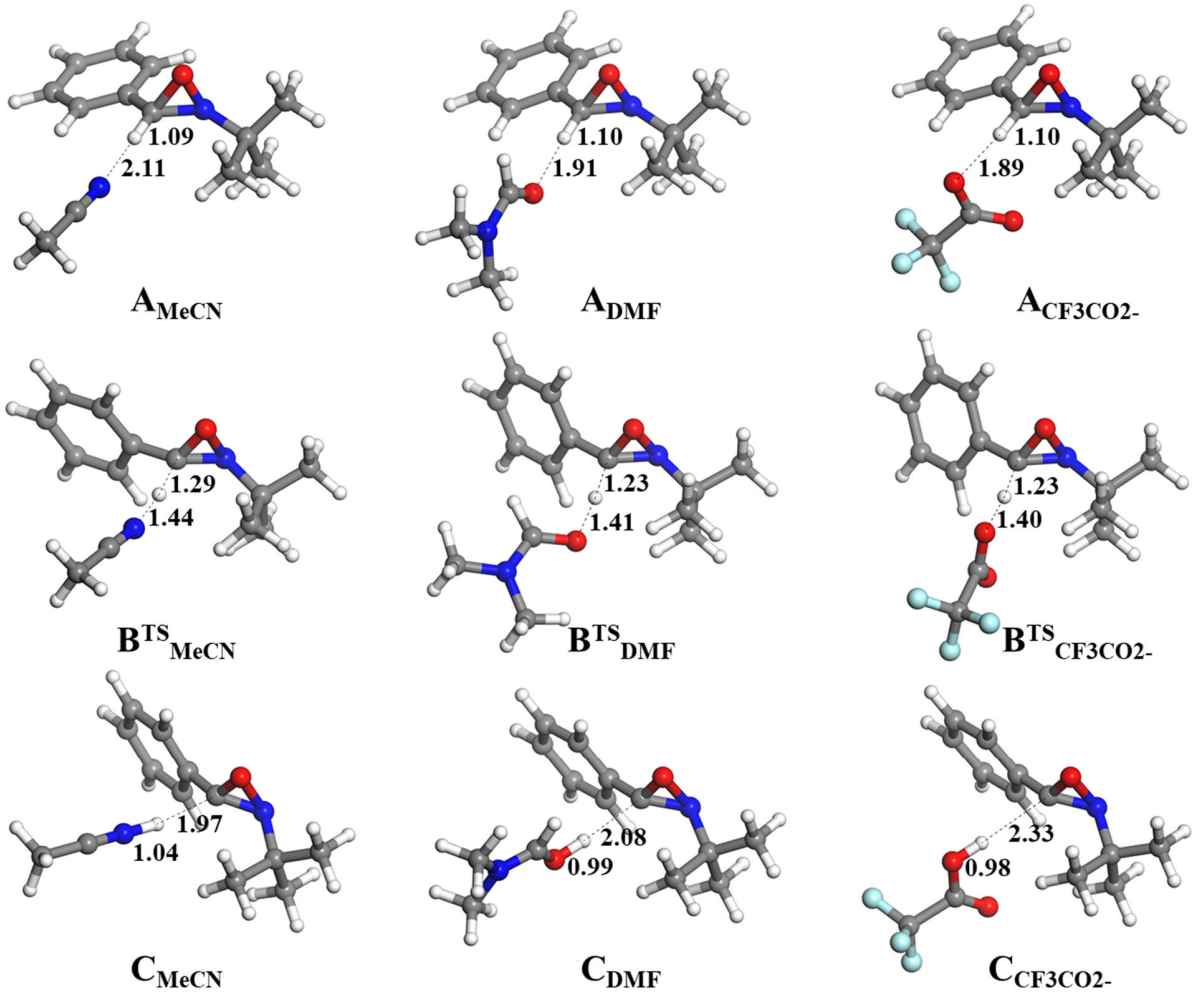


Figure S14. Optimized geometries for the deprotonation of intermediate **I** with base species, MeCN, DMF, and trifluoroacetate. Selected interatomic distances are in Å.

VIII. References

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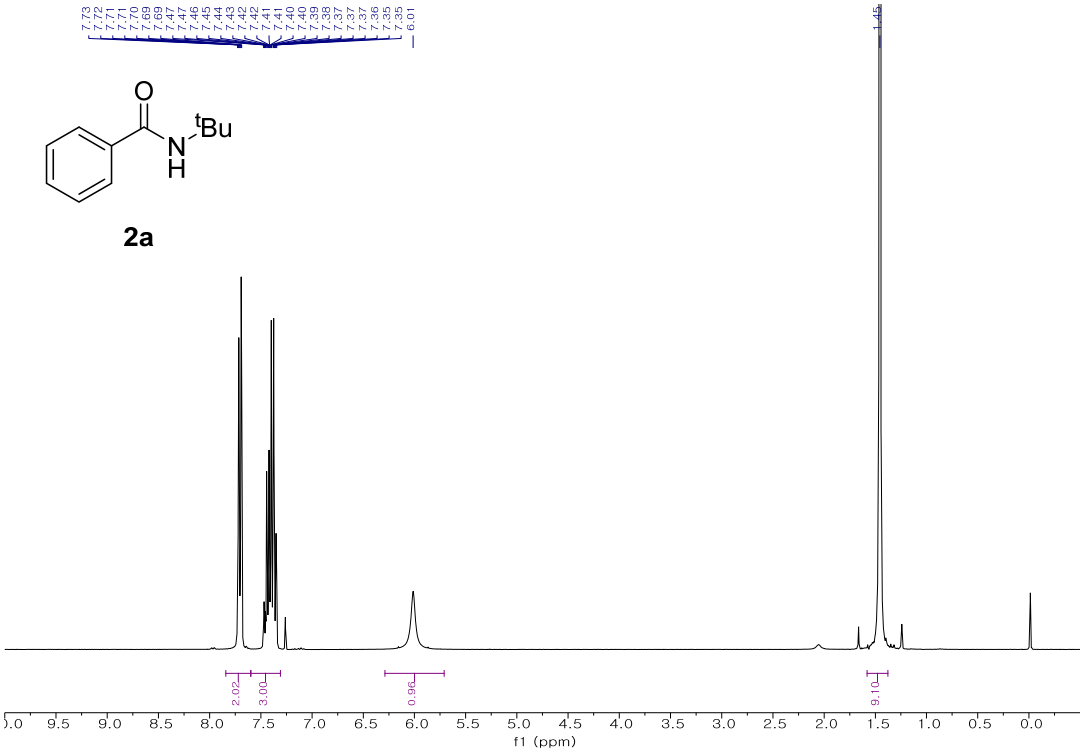
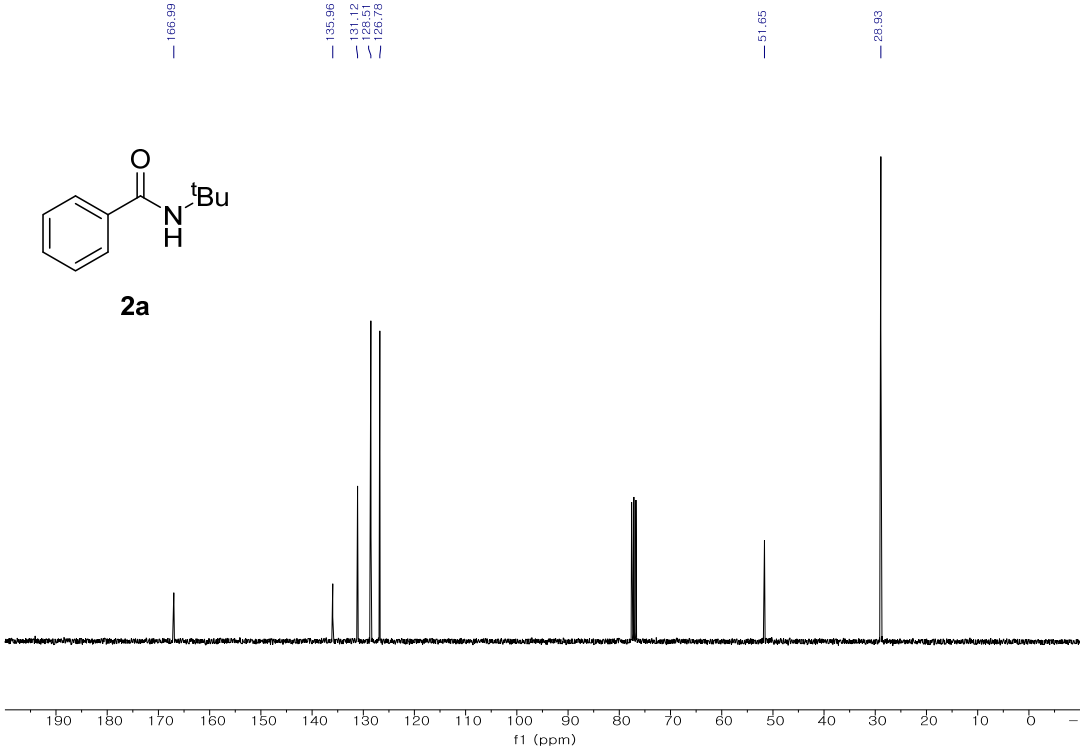
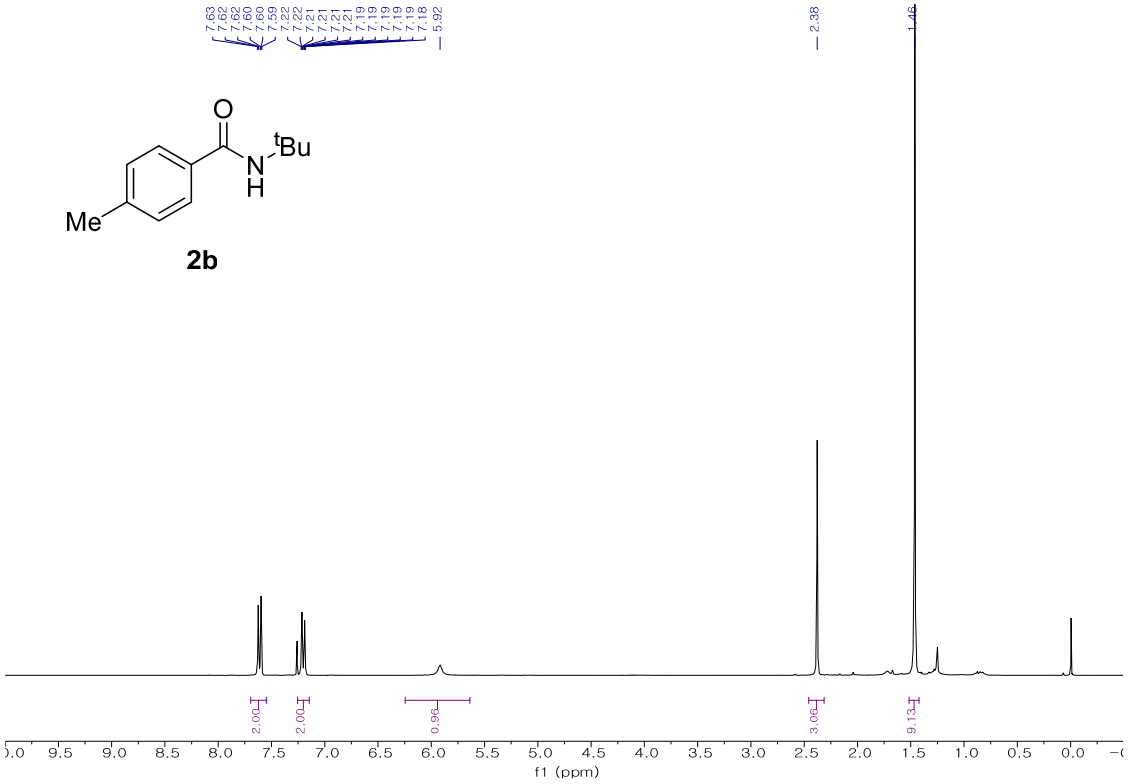
IX. ^{1}H and ^{13}C and ^{19}F NMR Spectral



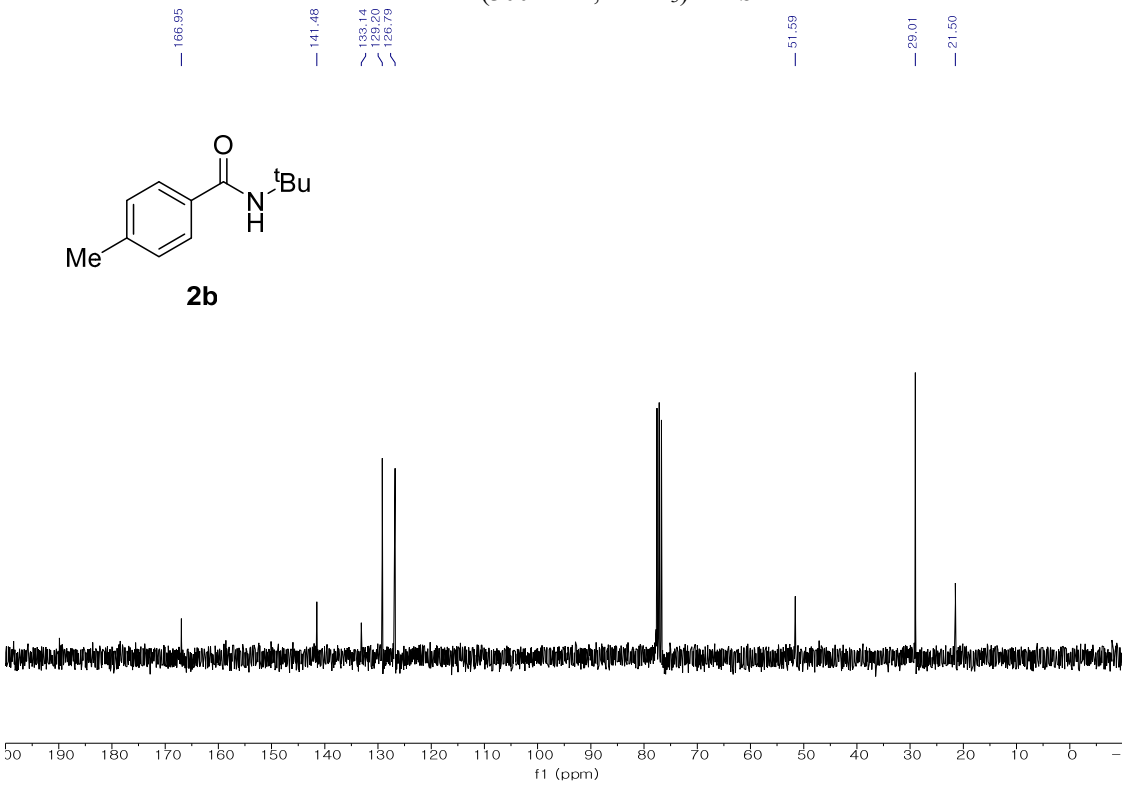
^{1}H-NMR (300 MHz, $CDCl_3$) of **2a**



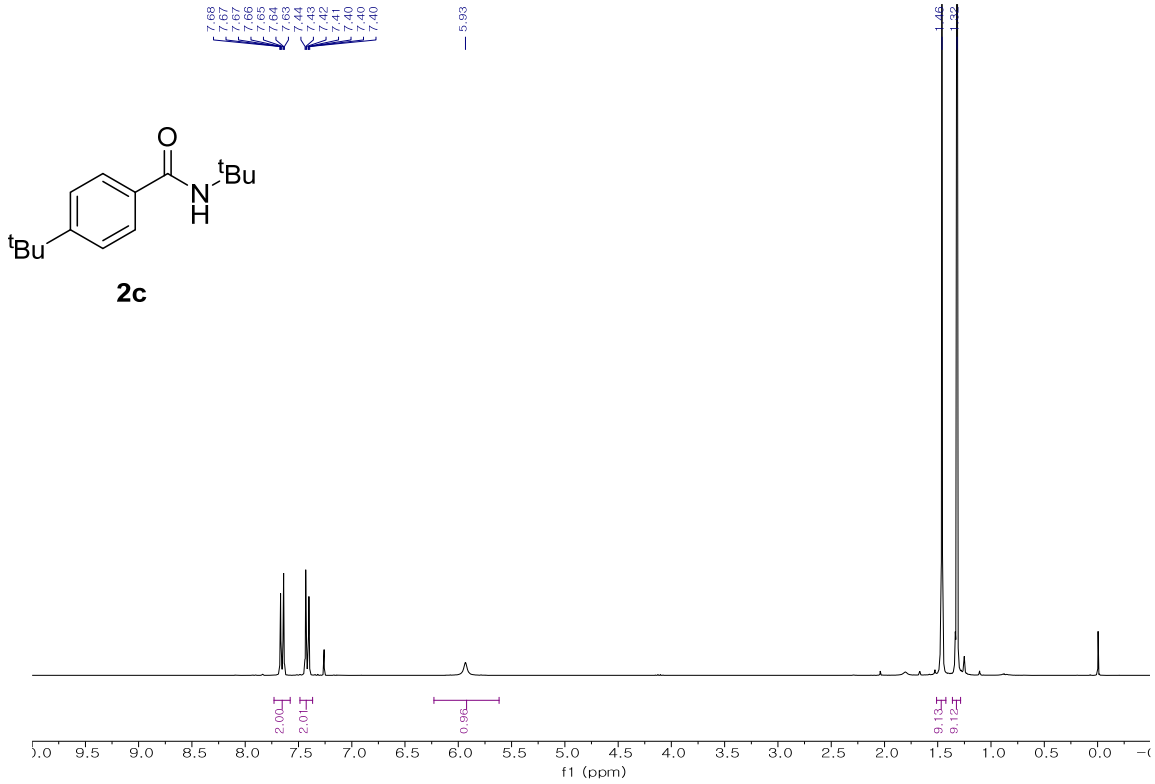
^{13}C-NMR (75 Hz, $CDCl_3$) of **2a**



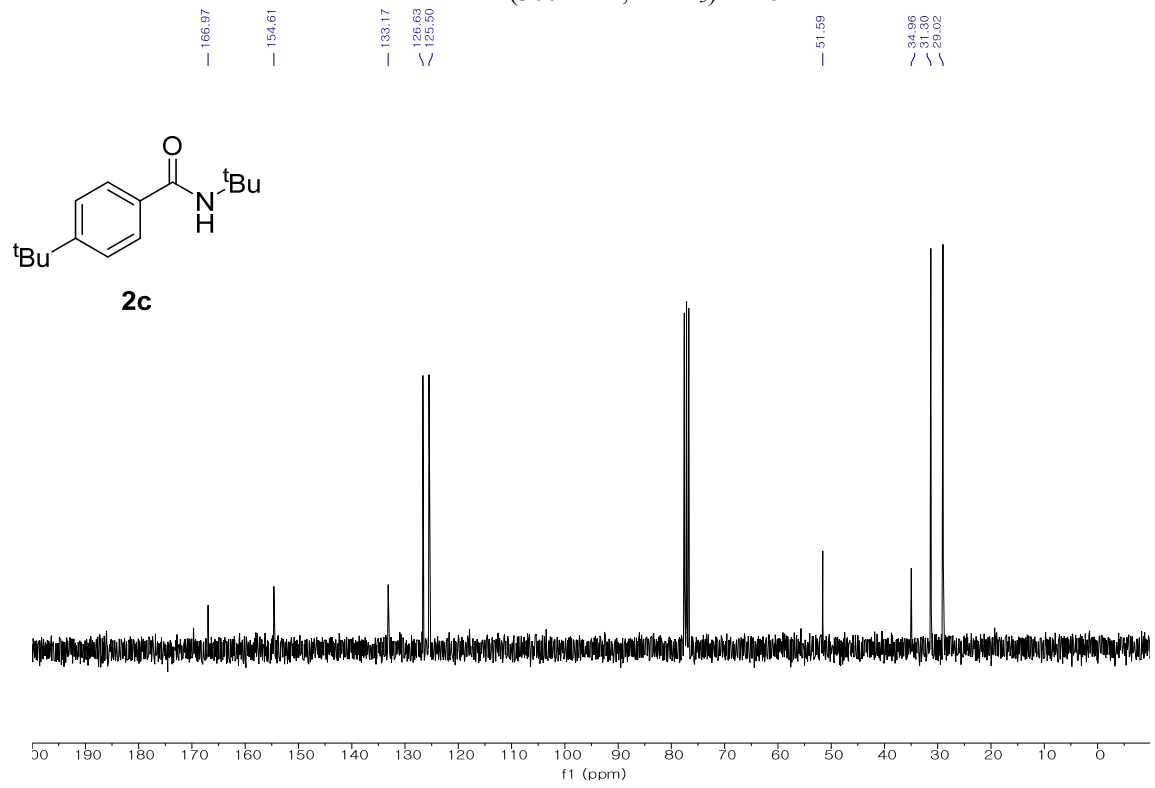
^{1}H-NMR (300 MHz, $CDCl_3$) of **2b**



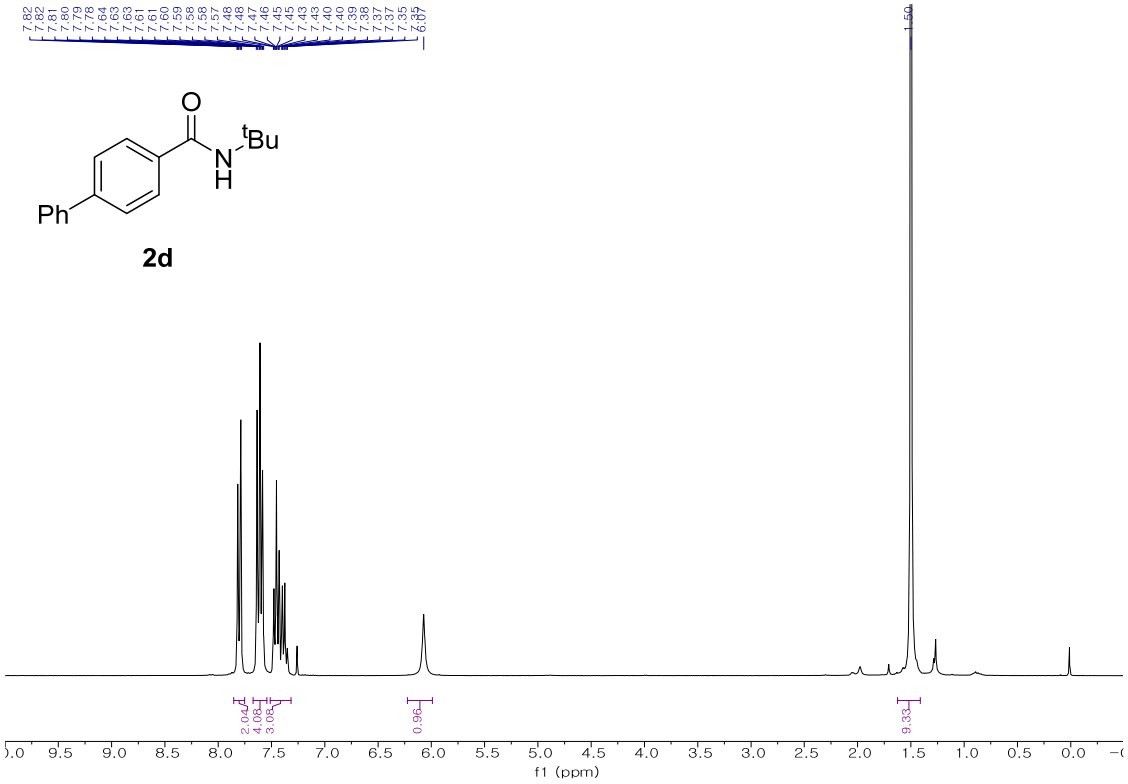
^{13}C-NMR (75 Hz, $CDCl_3$) of **2b**



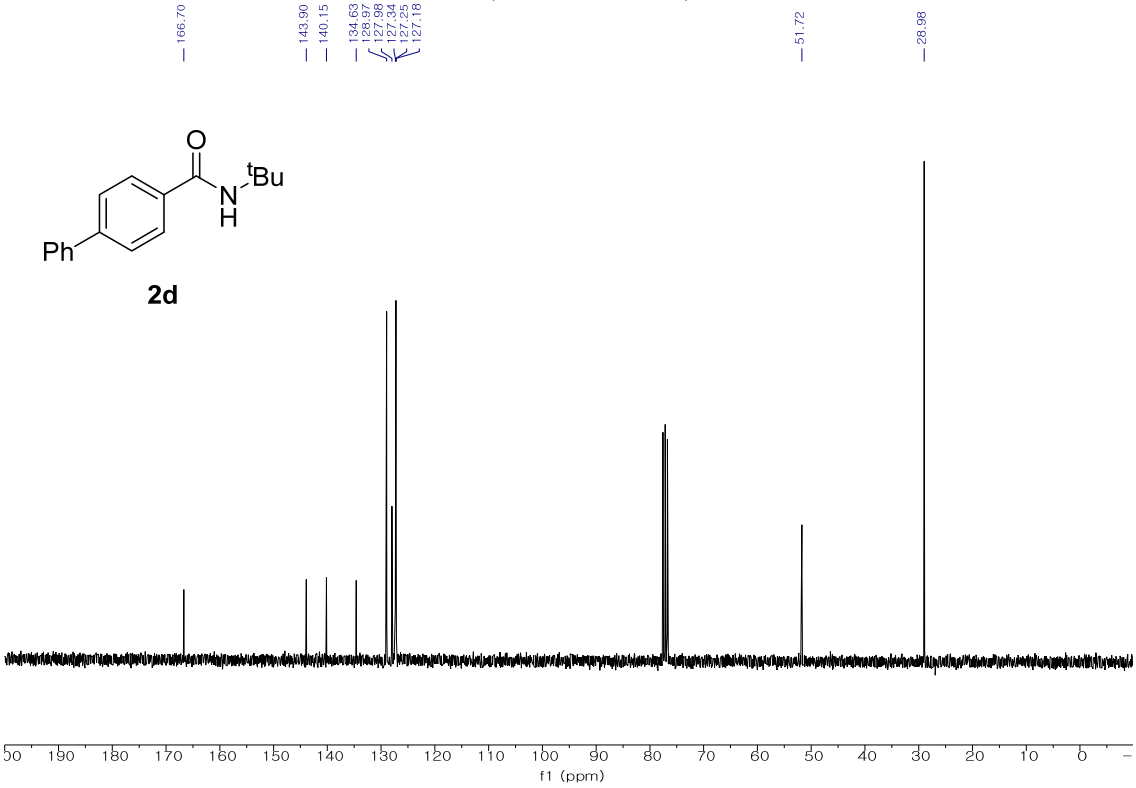
^{1}H-NMR (300 MHz, $CDCl_3$) of **2c**



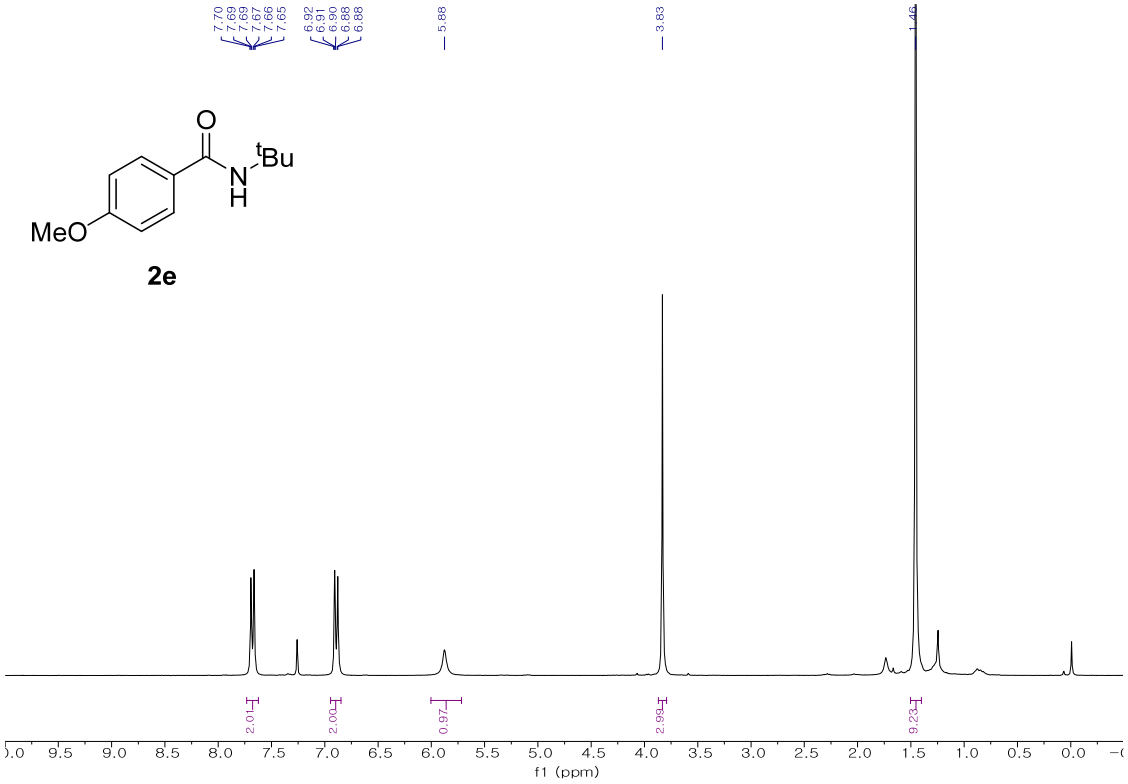
^{13}C-NMR (75 Hz, $CDCl_3$) of **2c**



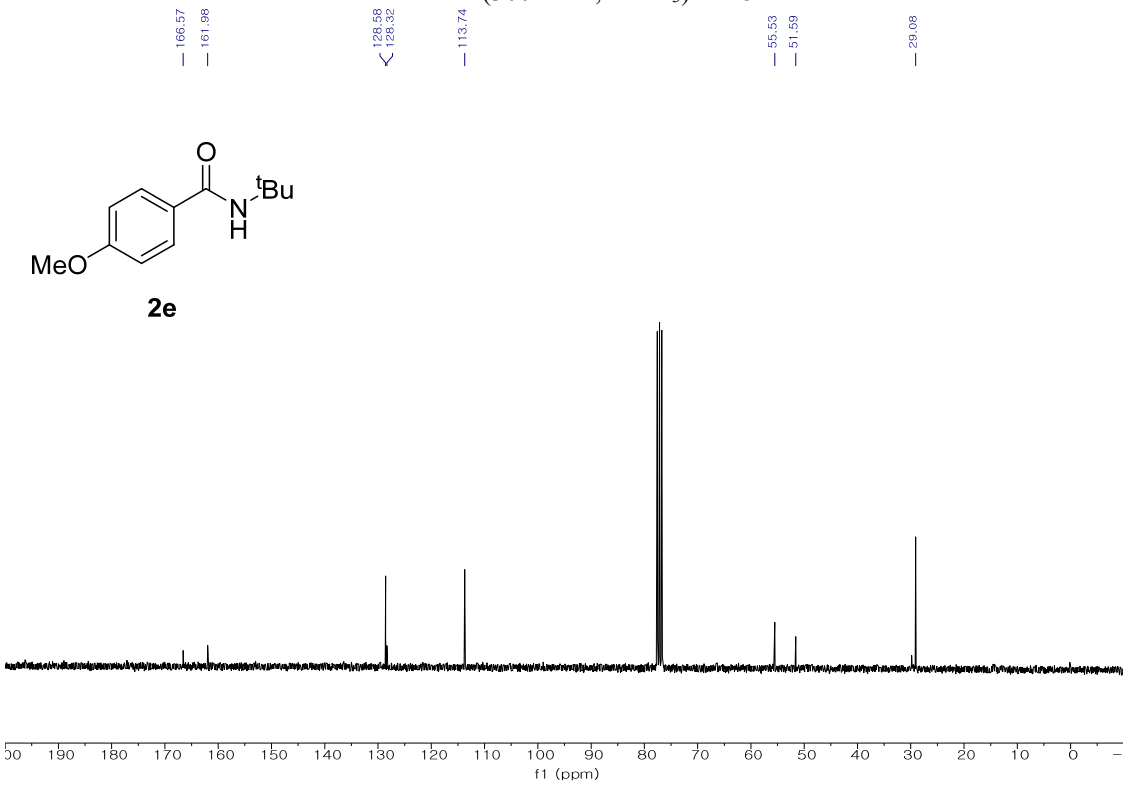
^{1}H-NMR (300 MHz, $CDCl_3$) of **2d**



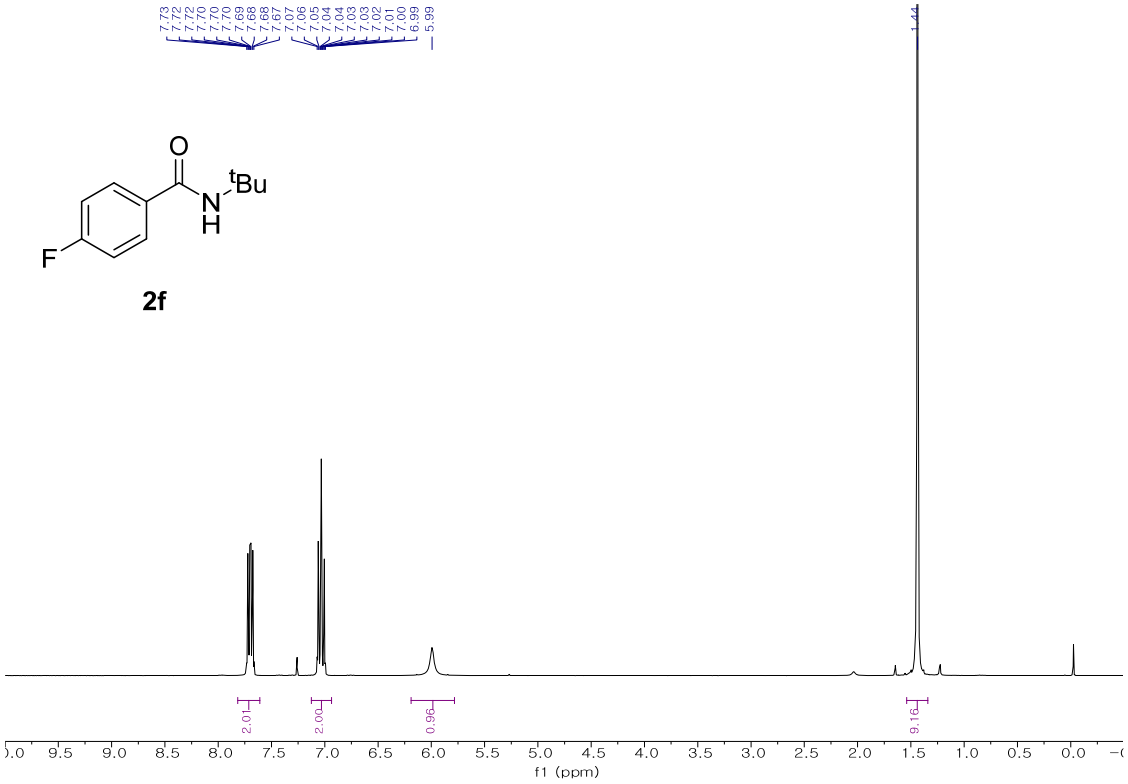
^{13}C-NMR (75 Hz, $CDCl_3$) of **2d**



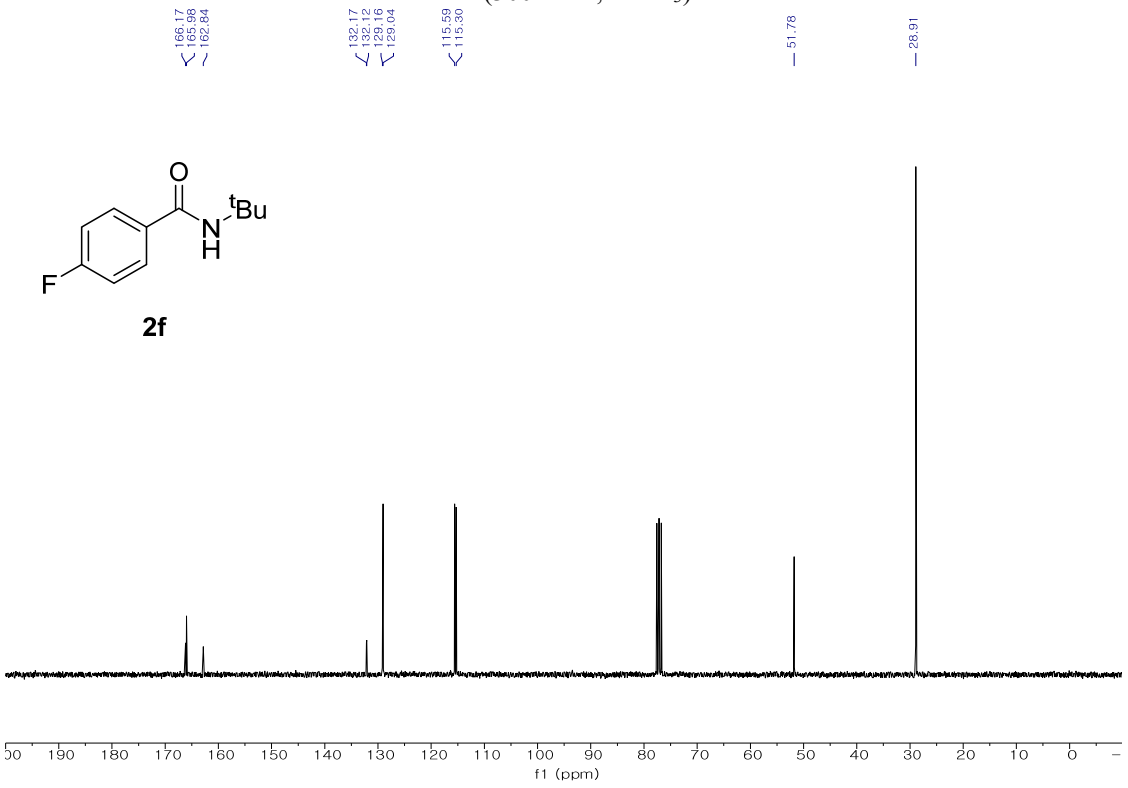
^{1}H-NMR (300 MHz, $CDCl_3$) of **2e**



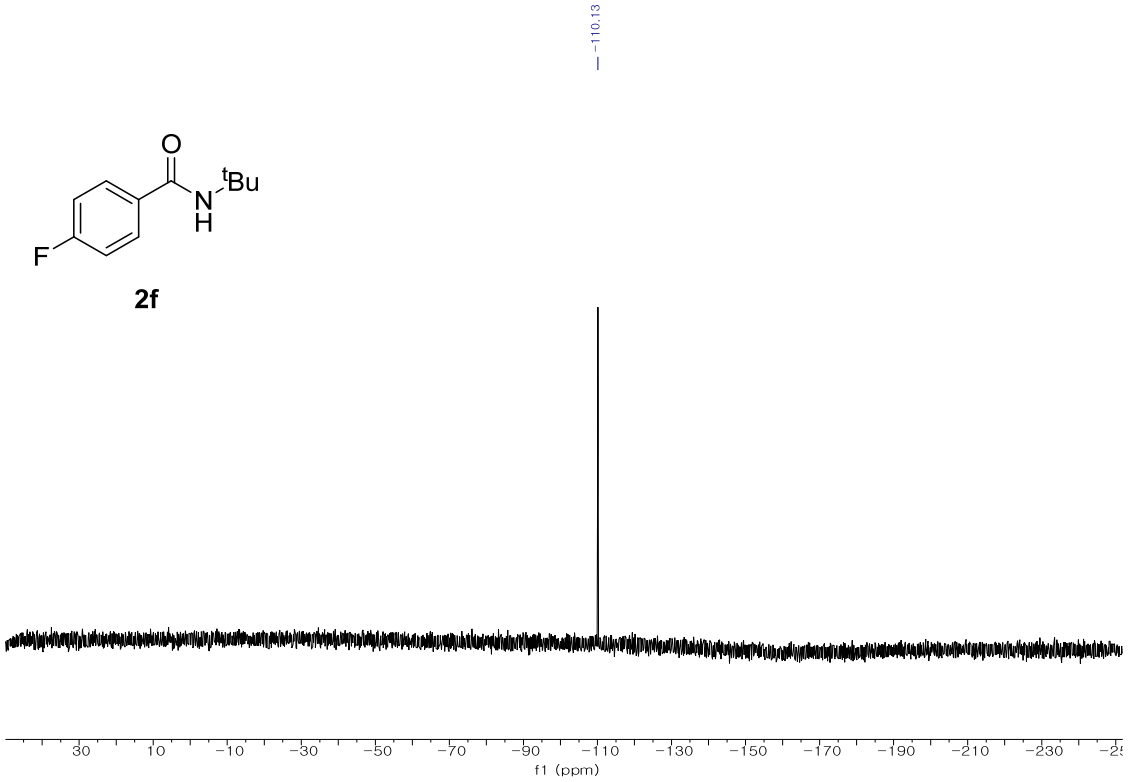
^{13}C-NMR (75 Hz, $CDCl_3$) of **2e**



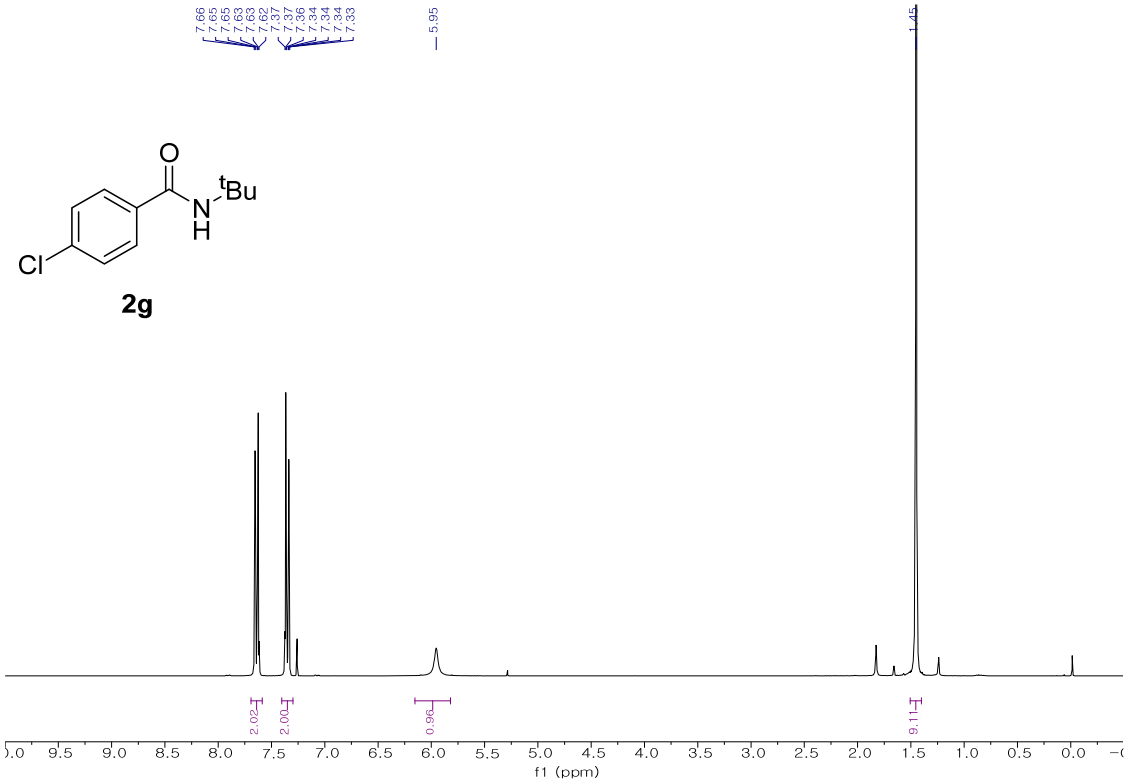
^{1}H-NMR (300 MHz, $CDCl_3$) of **2f**



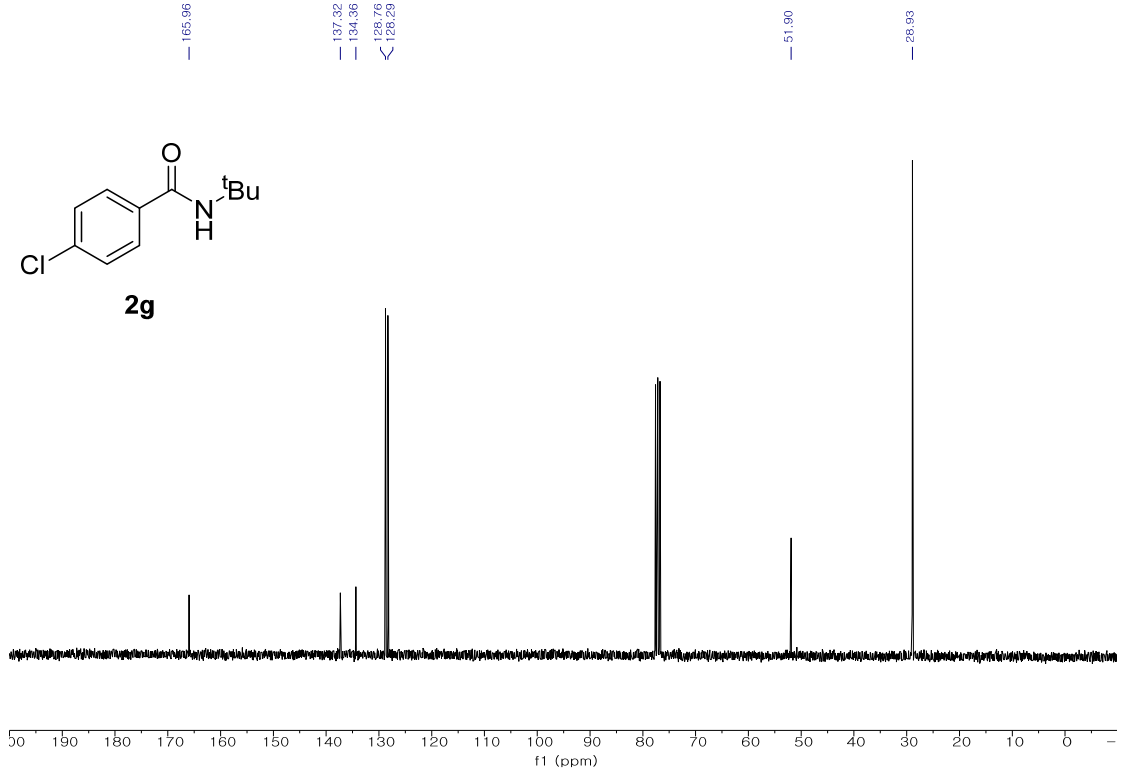
^{13}C-NMR (75 Hz, $CDCl_3$) of **2f**



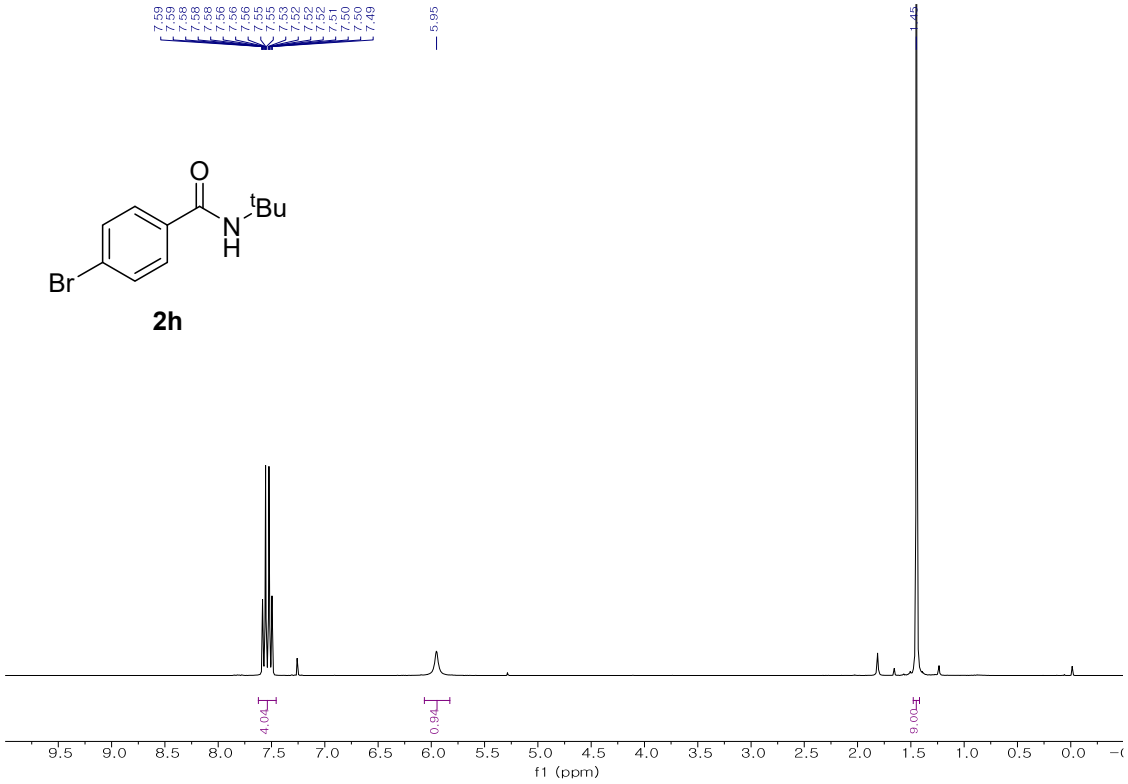
^{19}F-NMR (282 Hz, $CDCl_3$) of **2f**



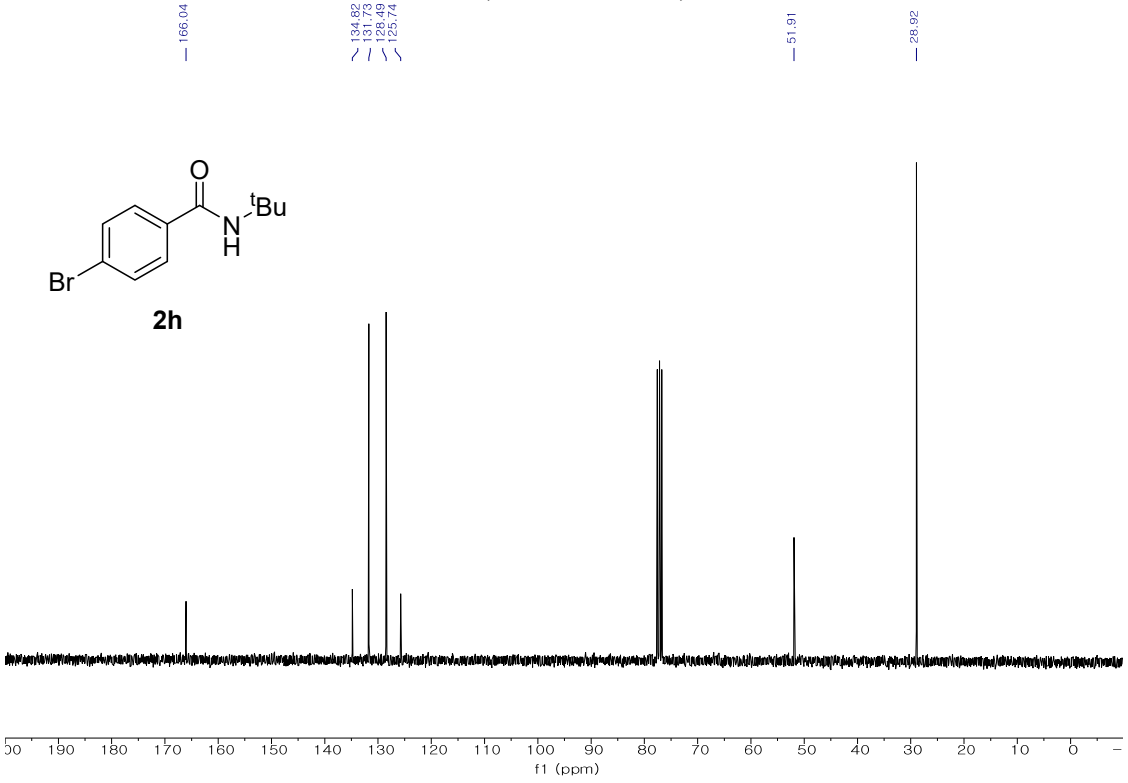
^{1}H-NMR (300 MHz, $CDCl_3$) of **2g**



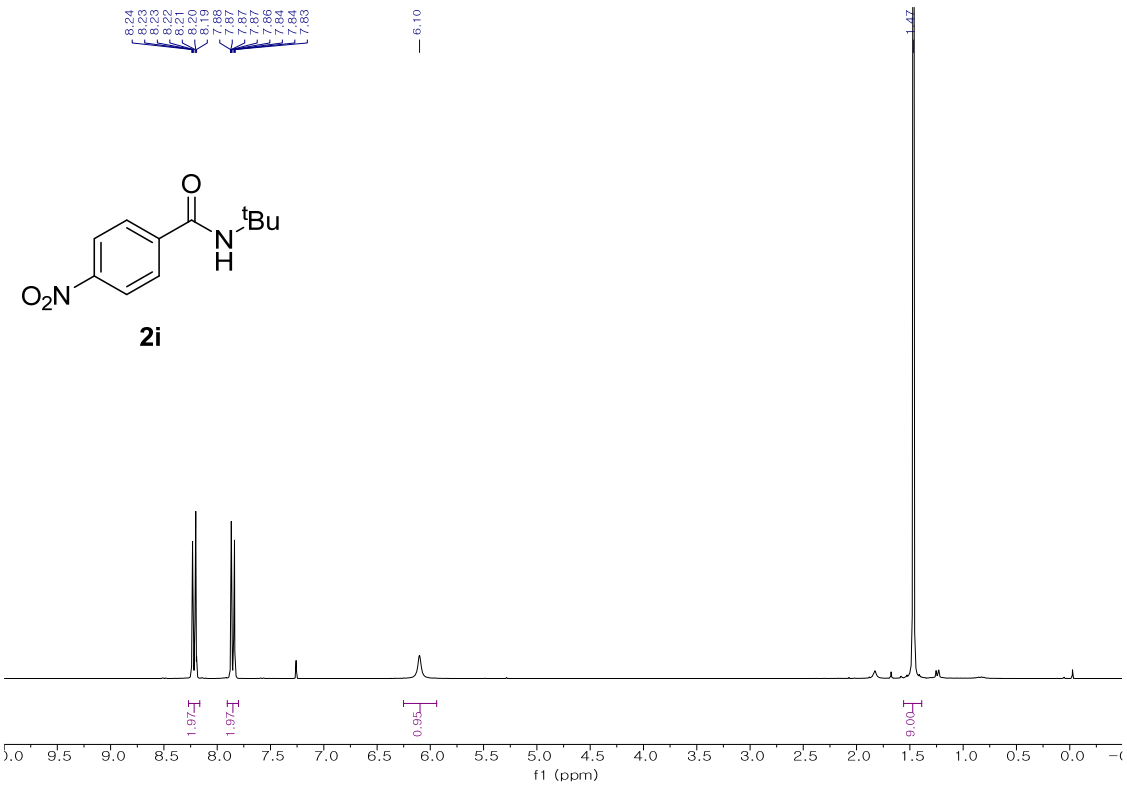
^{13}C-NMR (75 Hz, $CDCl_3$) of **2g**



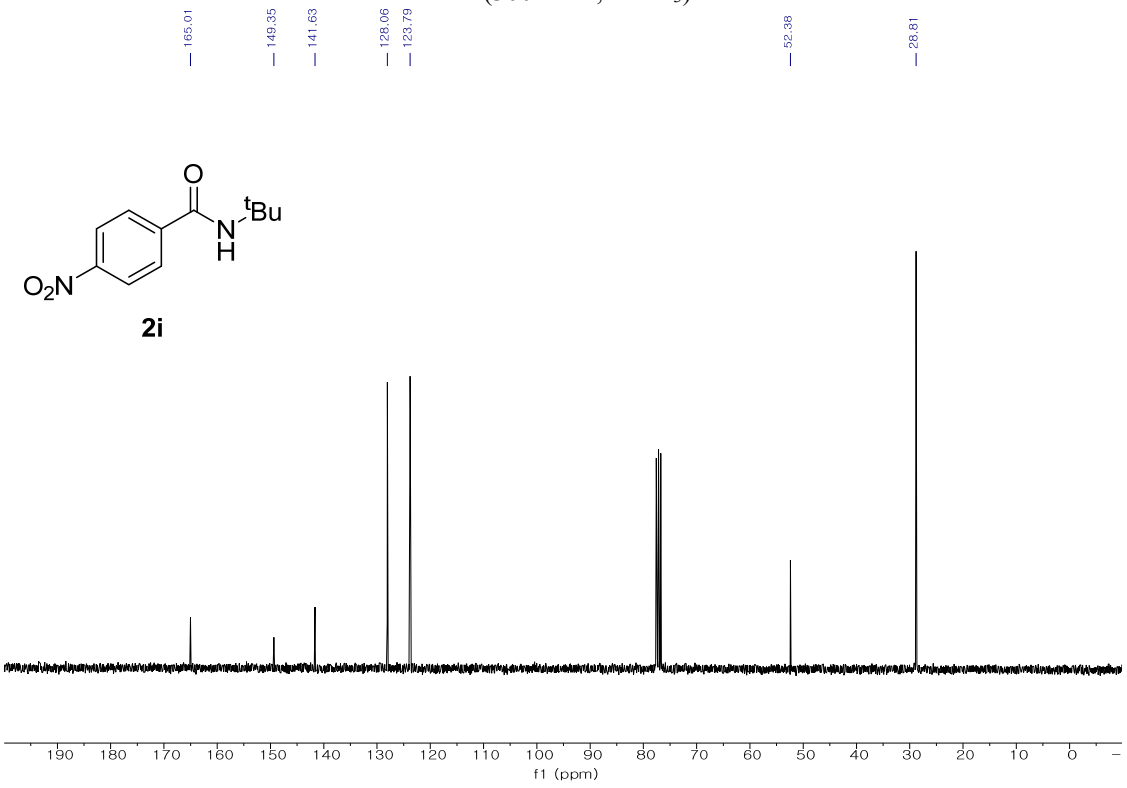
^{1}H-NMR (300 MHz, $CDCl_3$) of **2h**



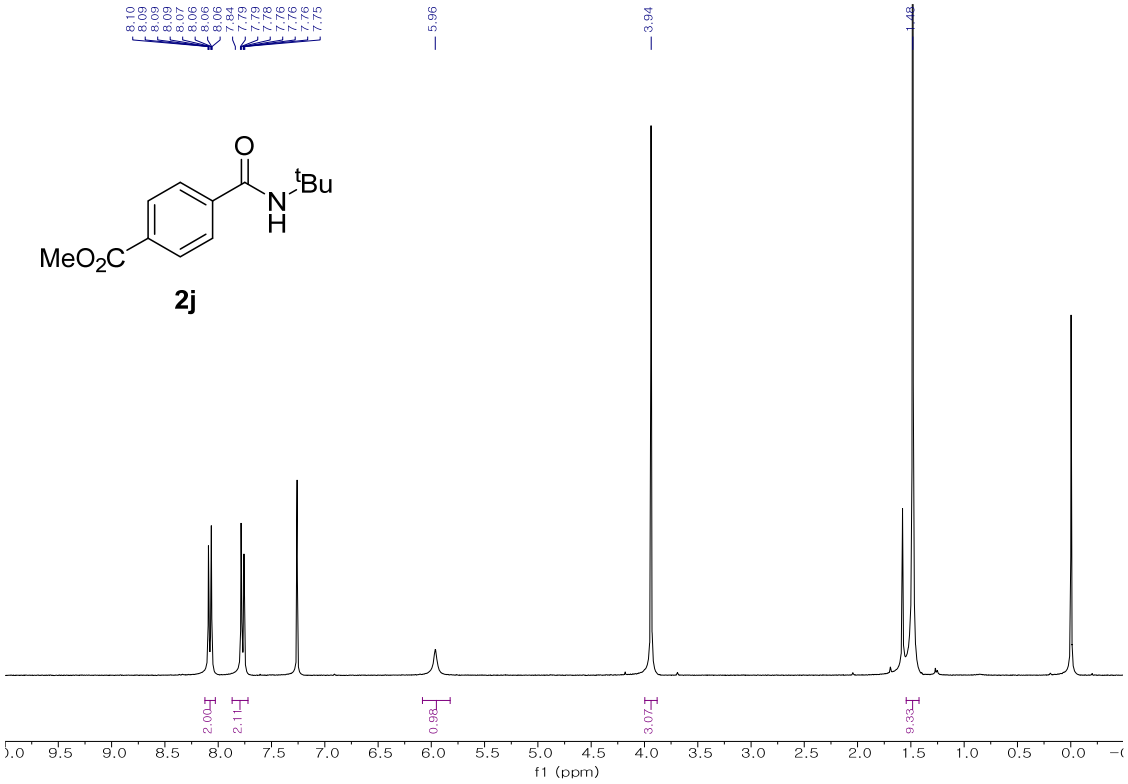
^{13}C-NMR (75 Hz, $CDCl_3$) of **2h**



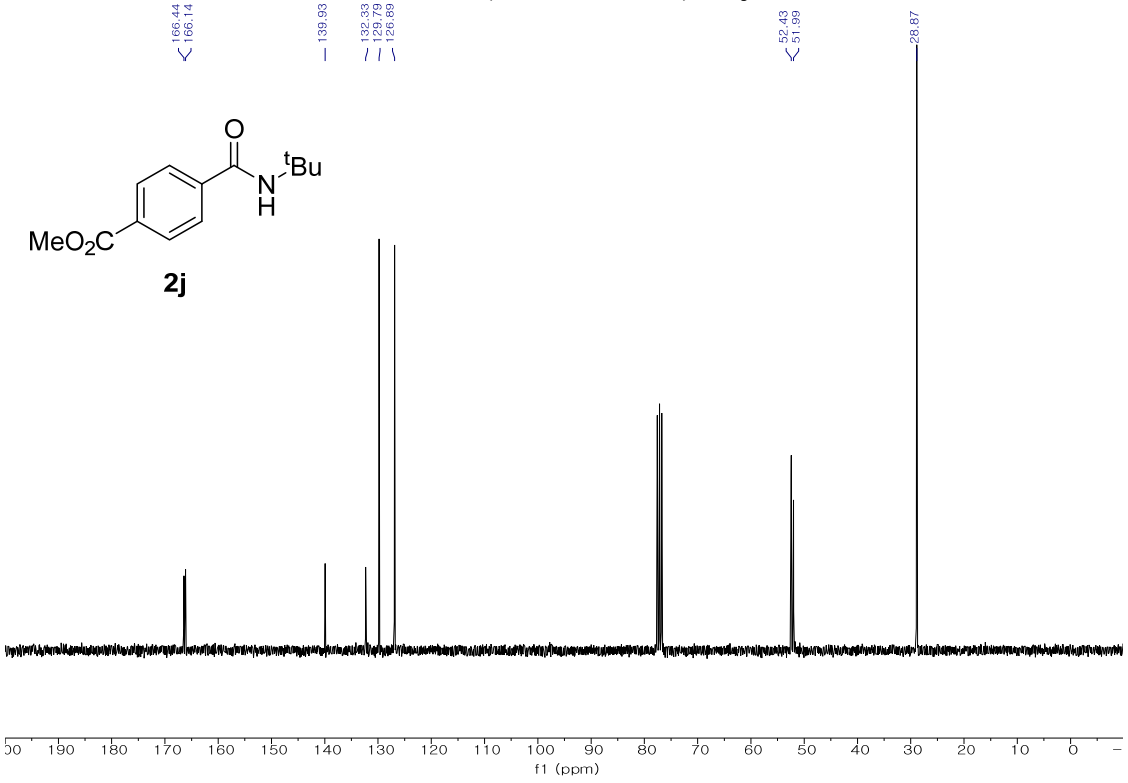
^{1}H-NMR (300 MHz, $CDCl_3$) of **2i**



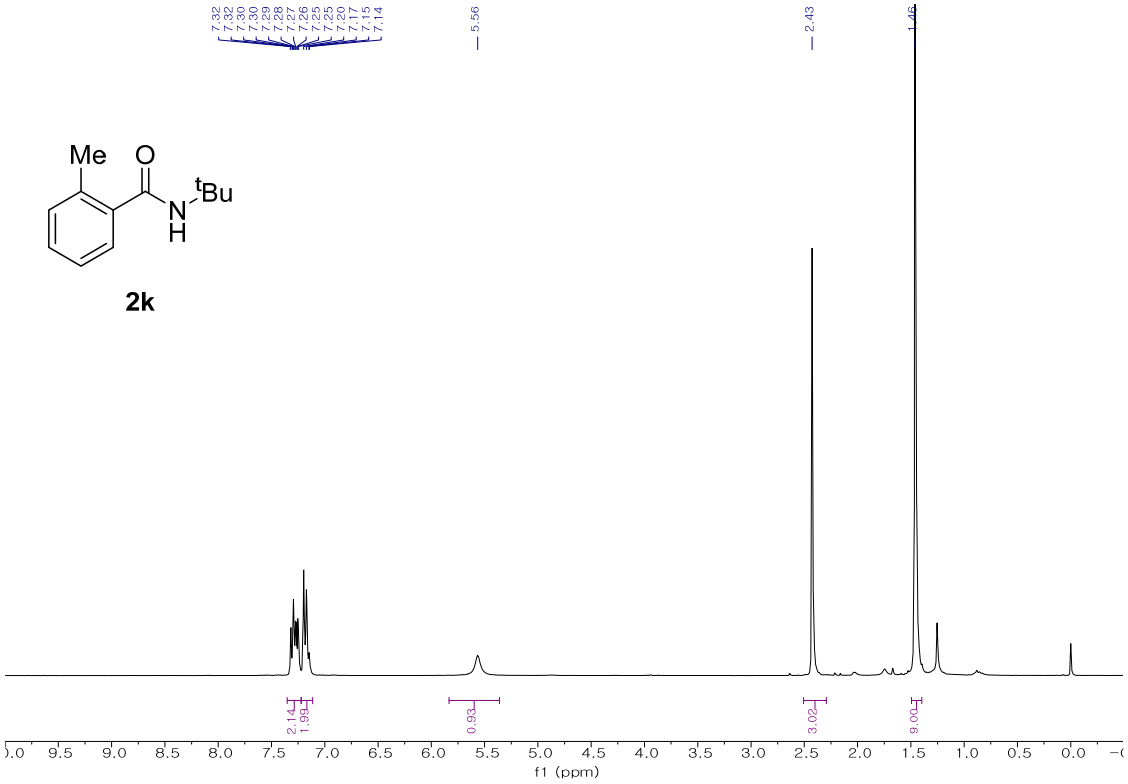
^{13}C-NMR (75 Hz, $CDCl_3$) of **2i**



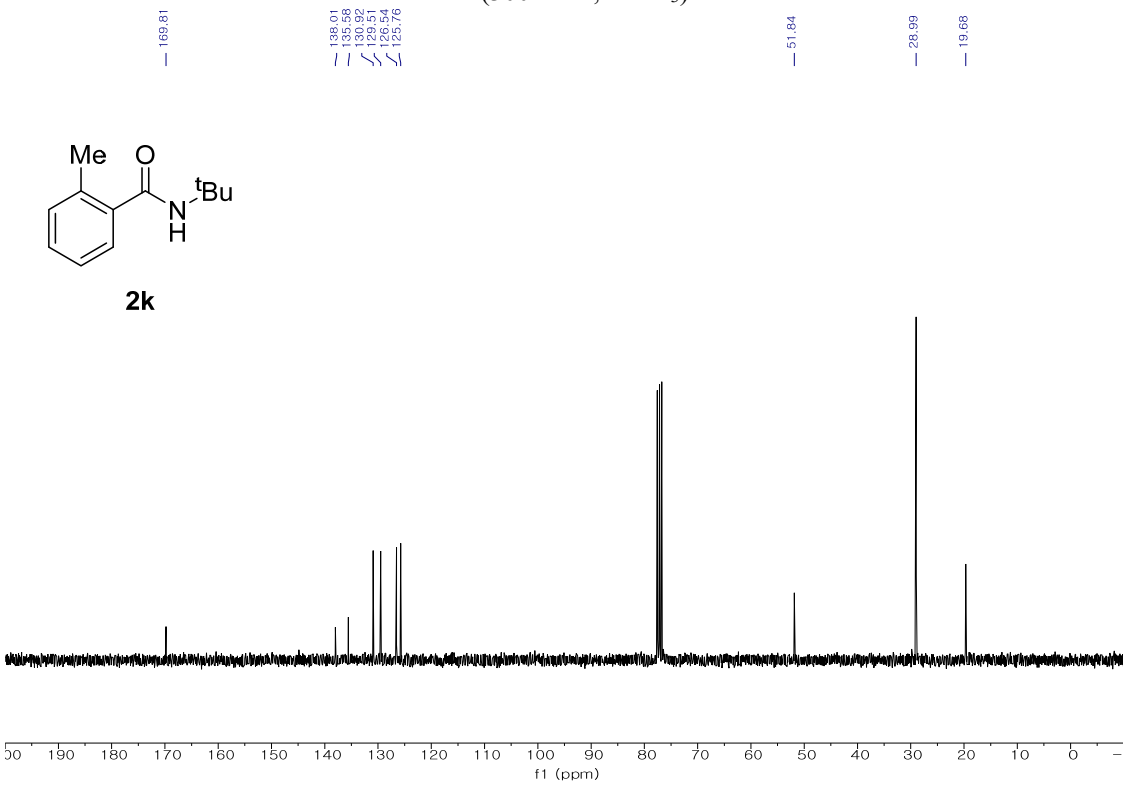
^{1}H-NMR (300 MHz, $CDCl_3$) of **2j**



^{13}C-NMR (75 Hz, $CDCl_3$) of **2j**



^{1}H-NMR (300 MHz, $CDCl_3$) of **2k**



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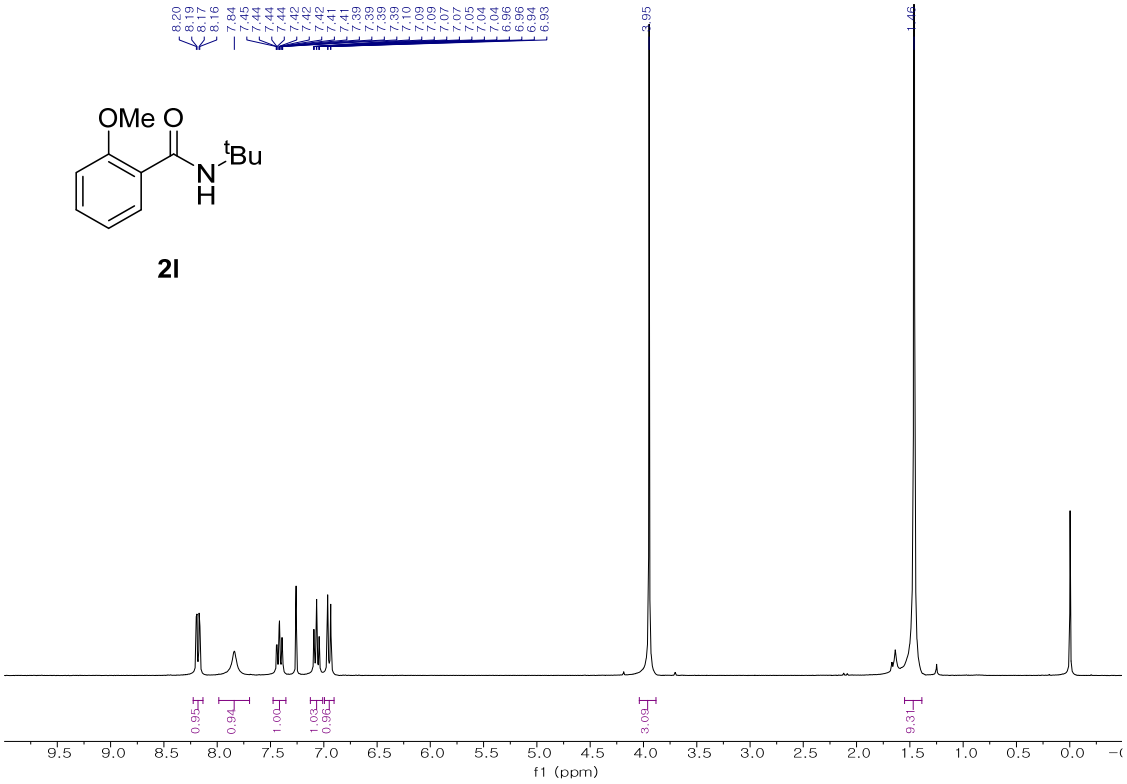
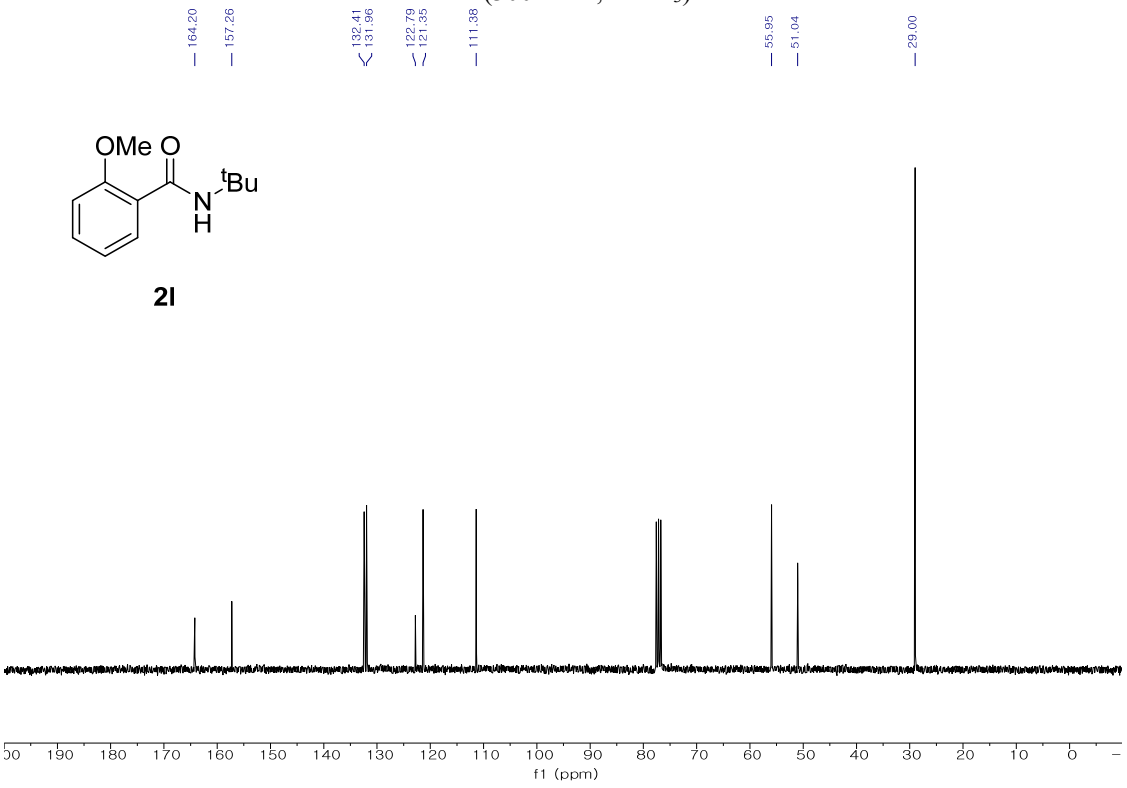
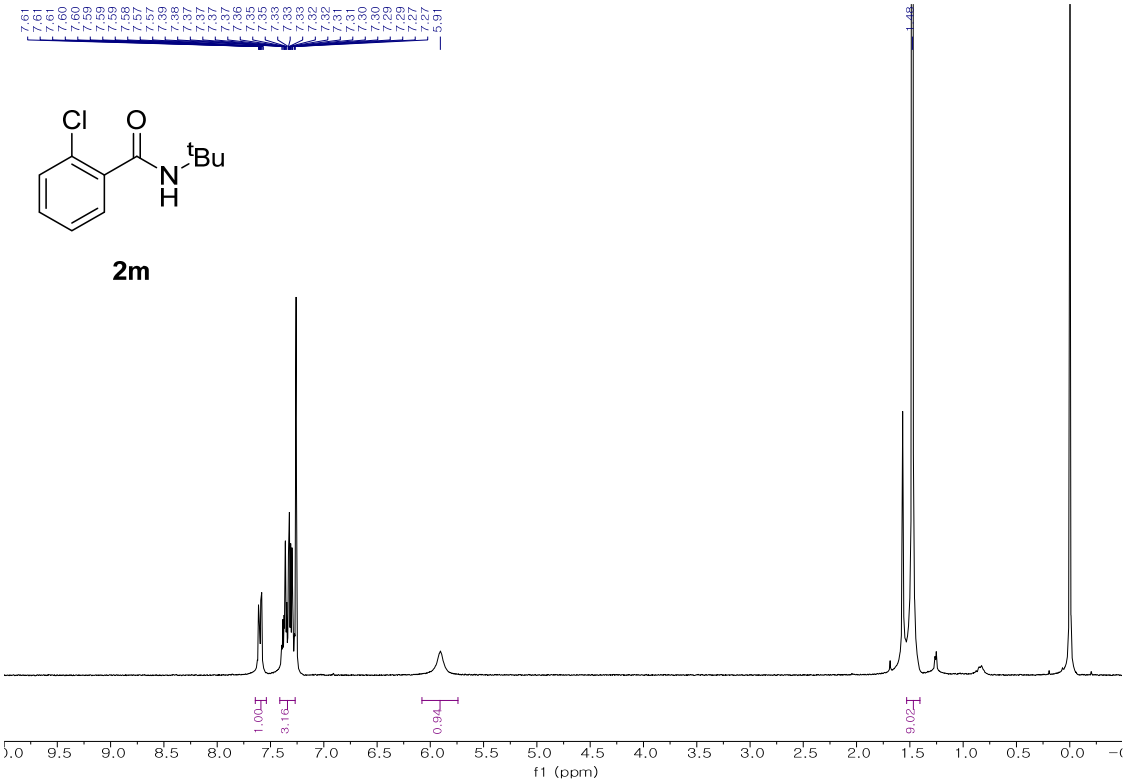


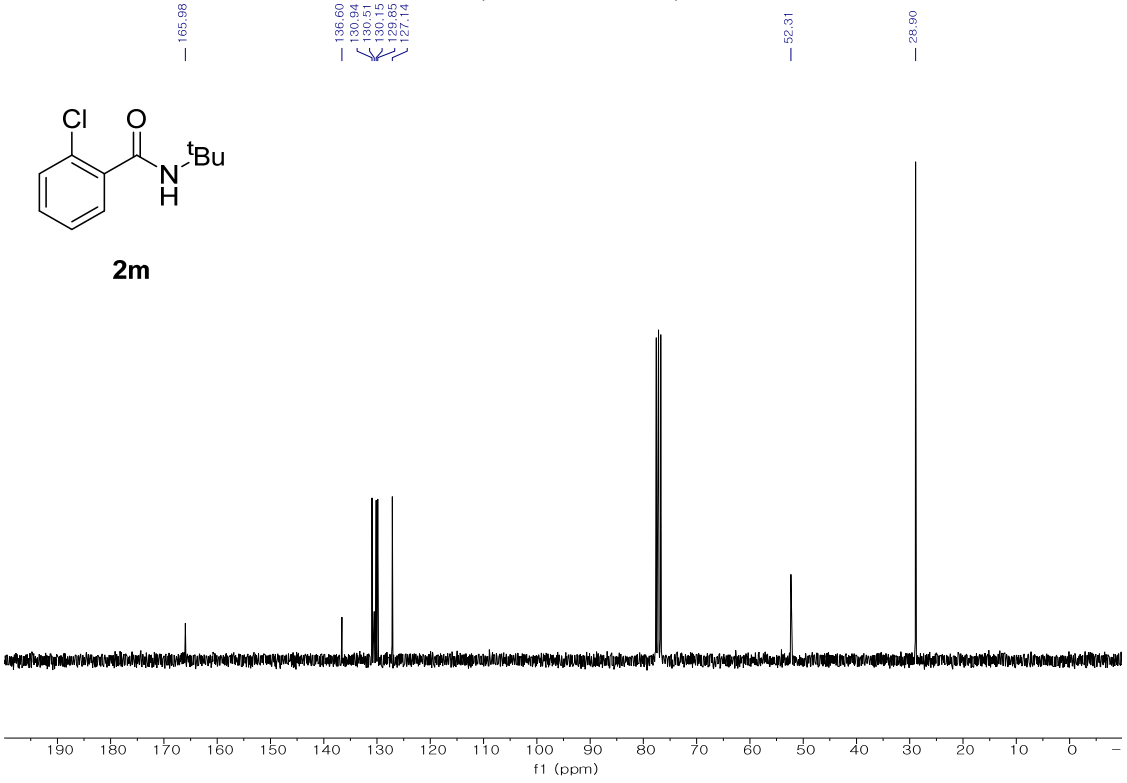
^{1}H-NMR (300 MHz, $CDCl_3$) of **2l**



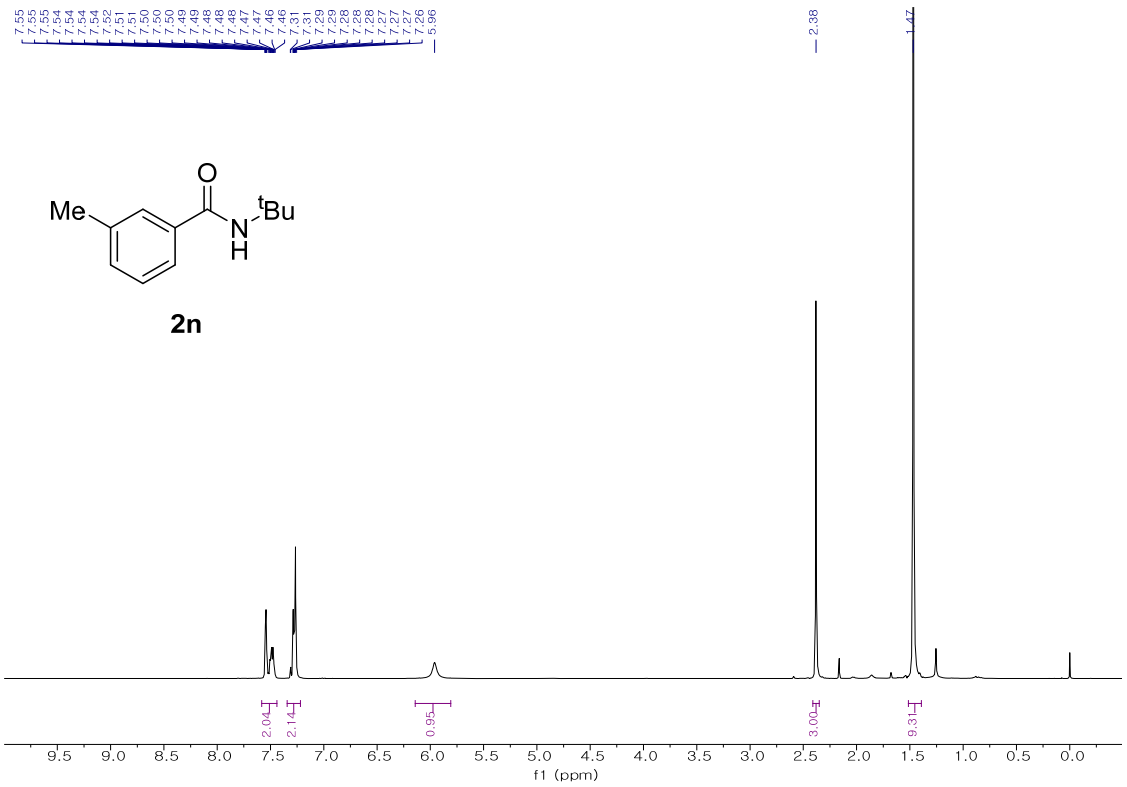
^{13}C-NMR (75 Hz, $CDCl_3$) of **2l**



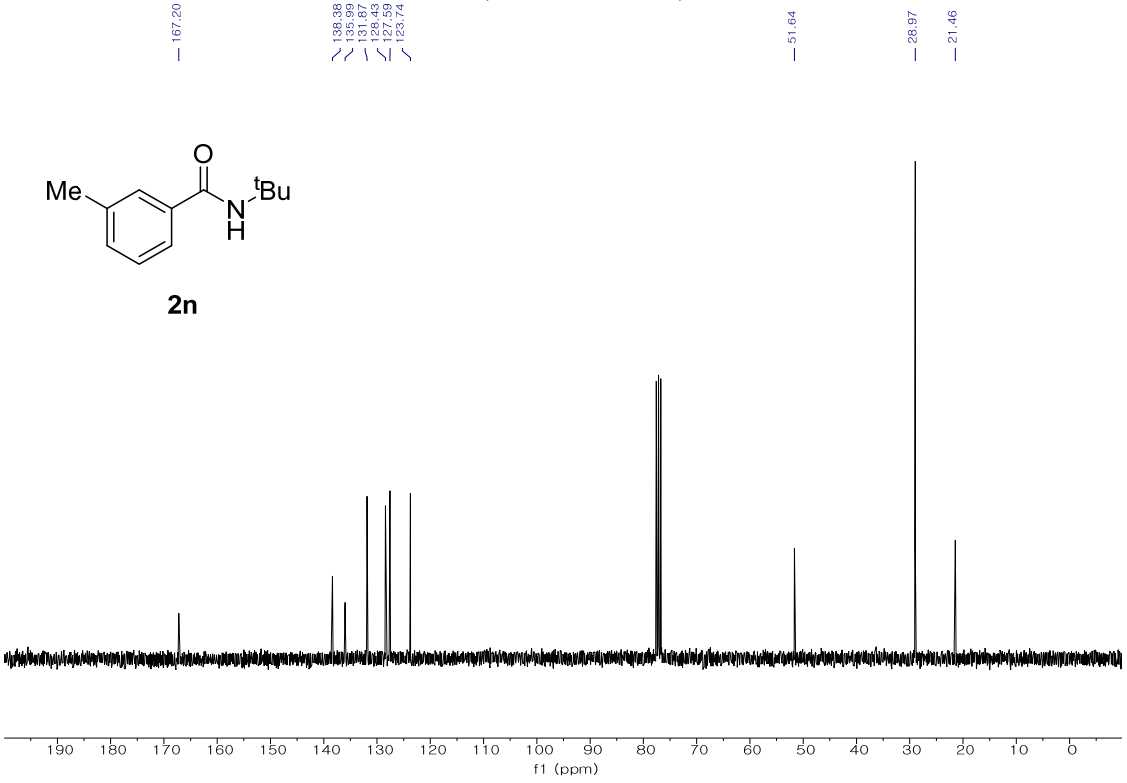
^{1}H-NMR (300 MHz, $CDCl_3$) of **2m**



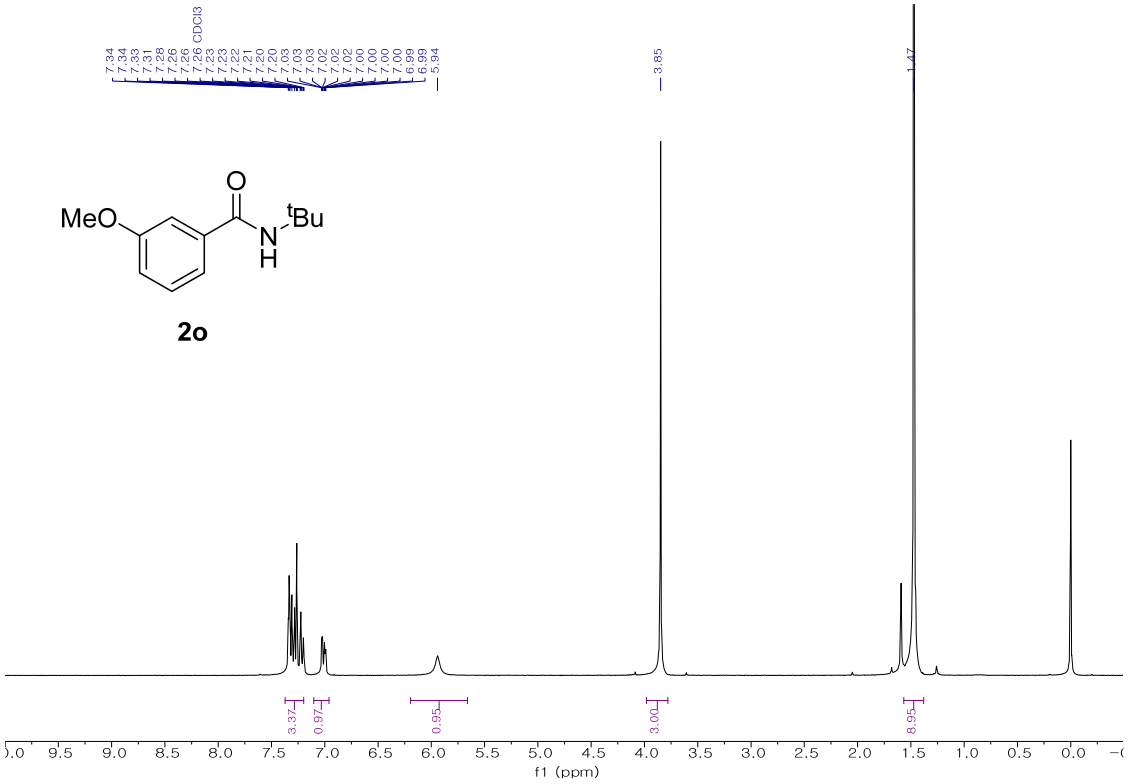
^{13}C-NMR (75 Hz, $CDCl_3$) of **2m**



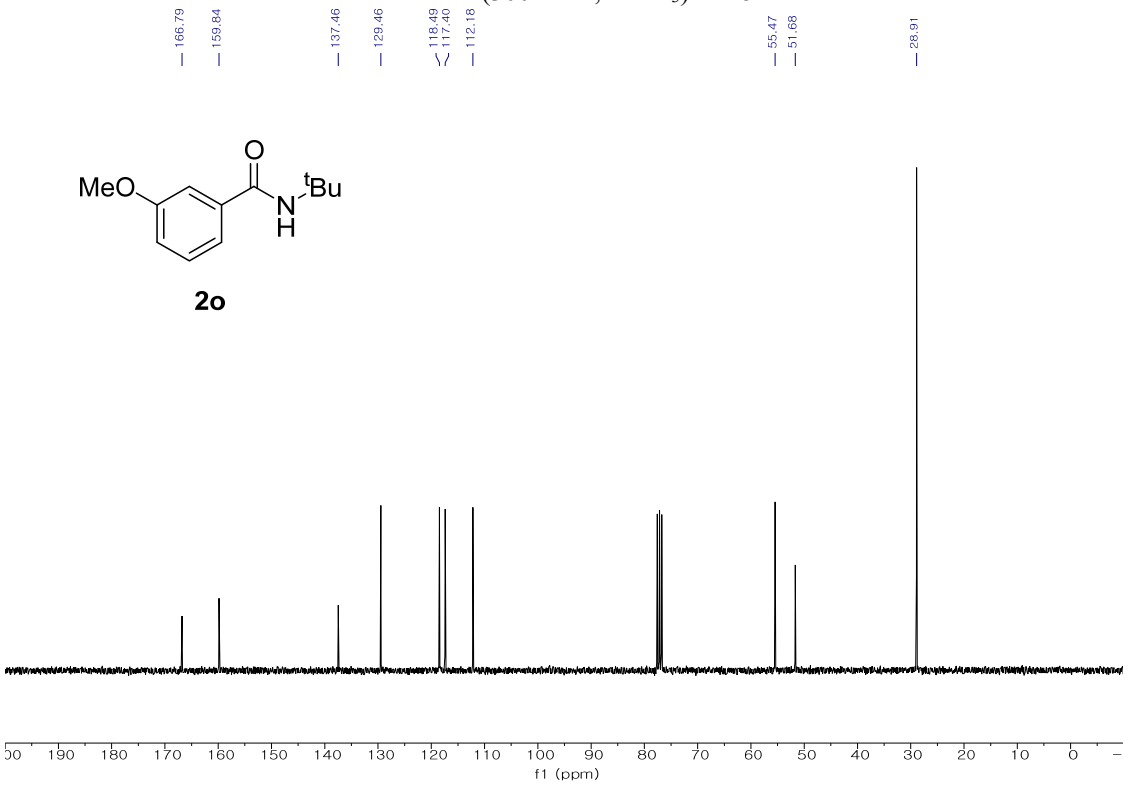
^{1}H-NMR (300 MHz, $CDCl_3$) of **2n**



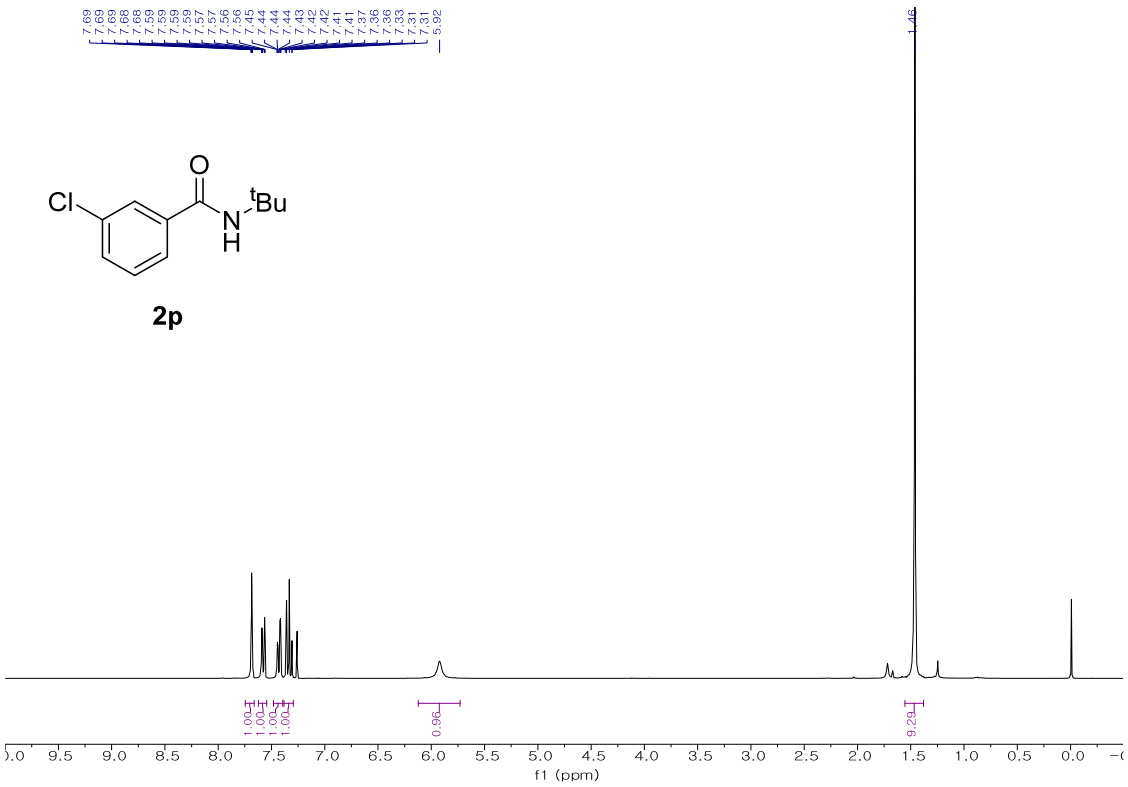
^{13}C-NMR (75 Hz, $CDCl_3$) of **2n**



^{1}H-NMR (300 MHz, $CDCl_3$) of **2o**



^{13}C-NMR (75 Hz, $CDCl_3$) of **2o**



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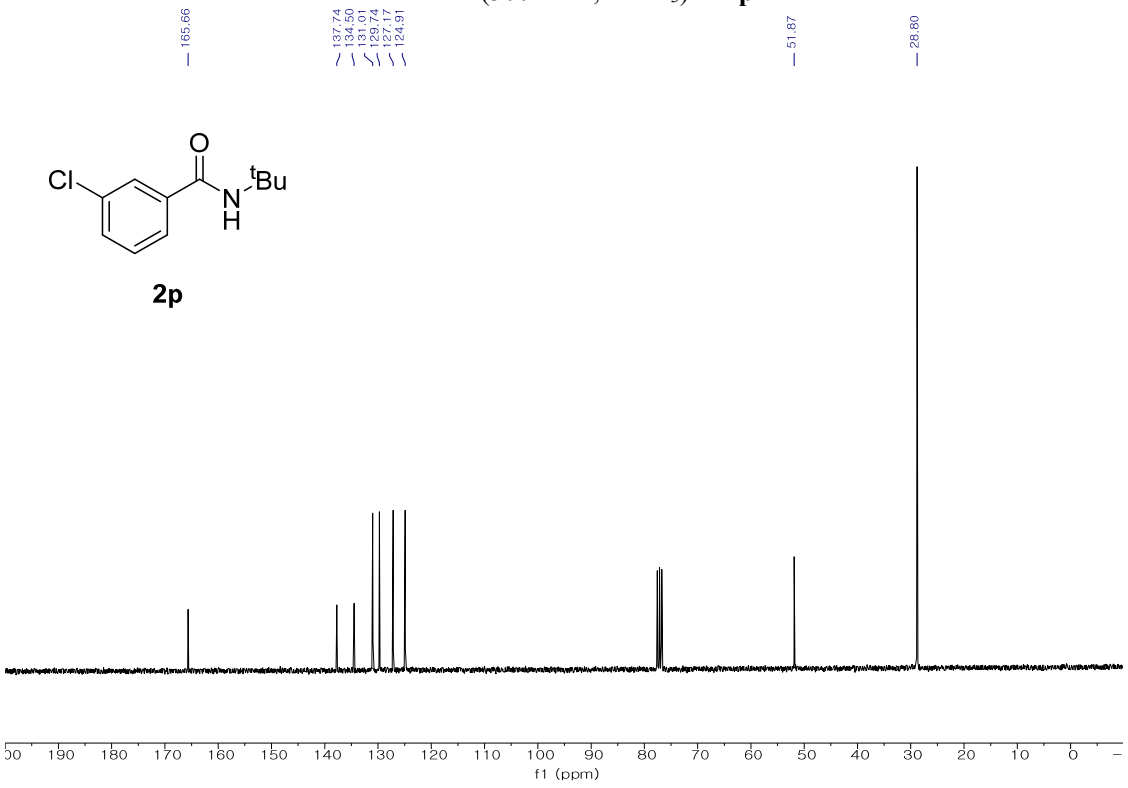
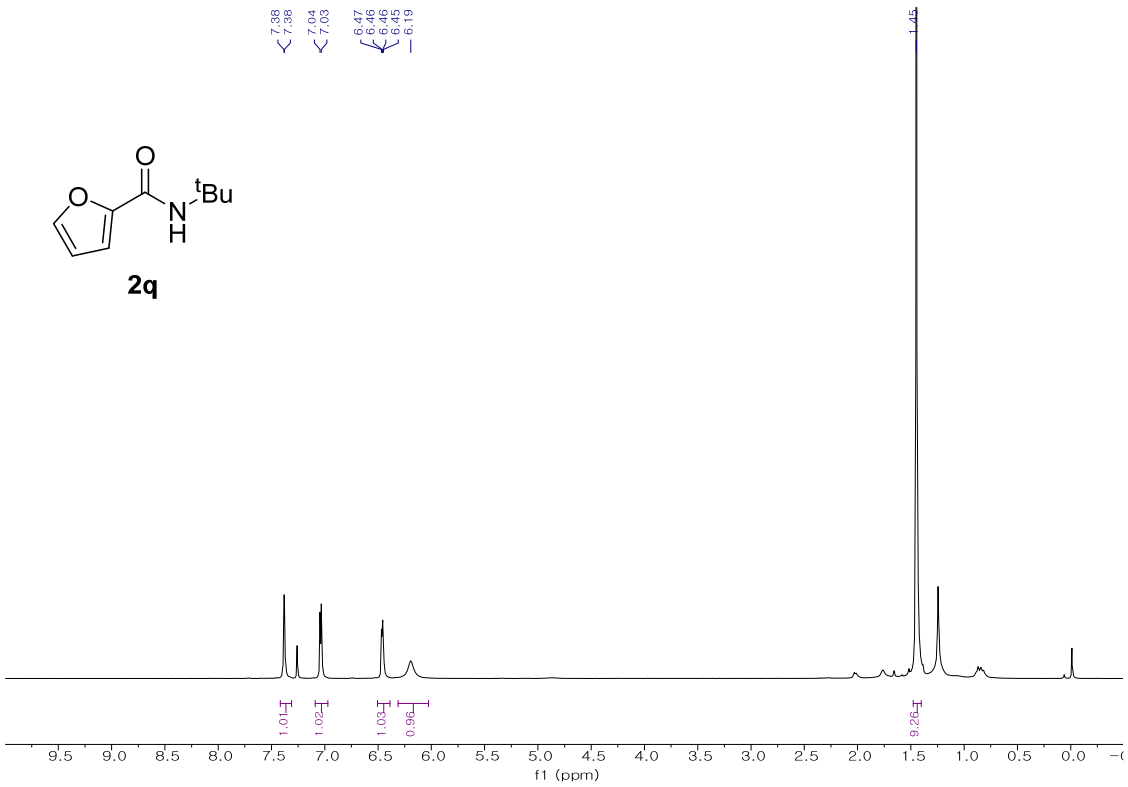
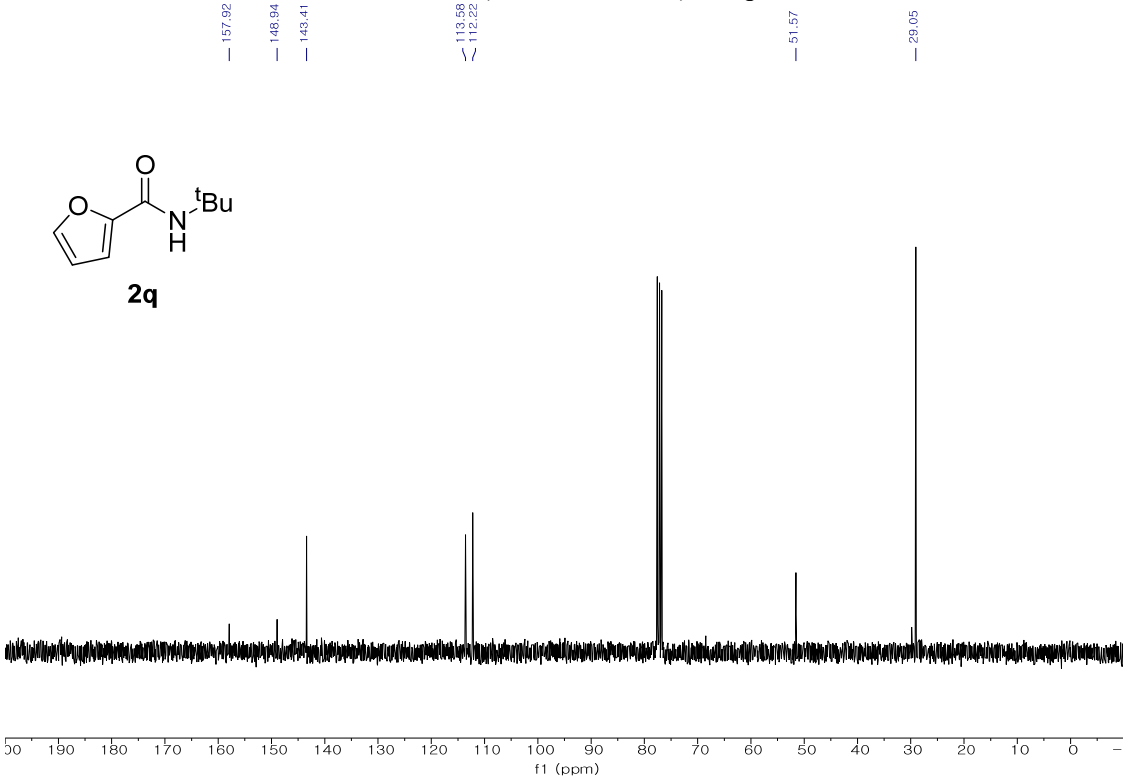


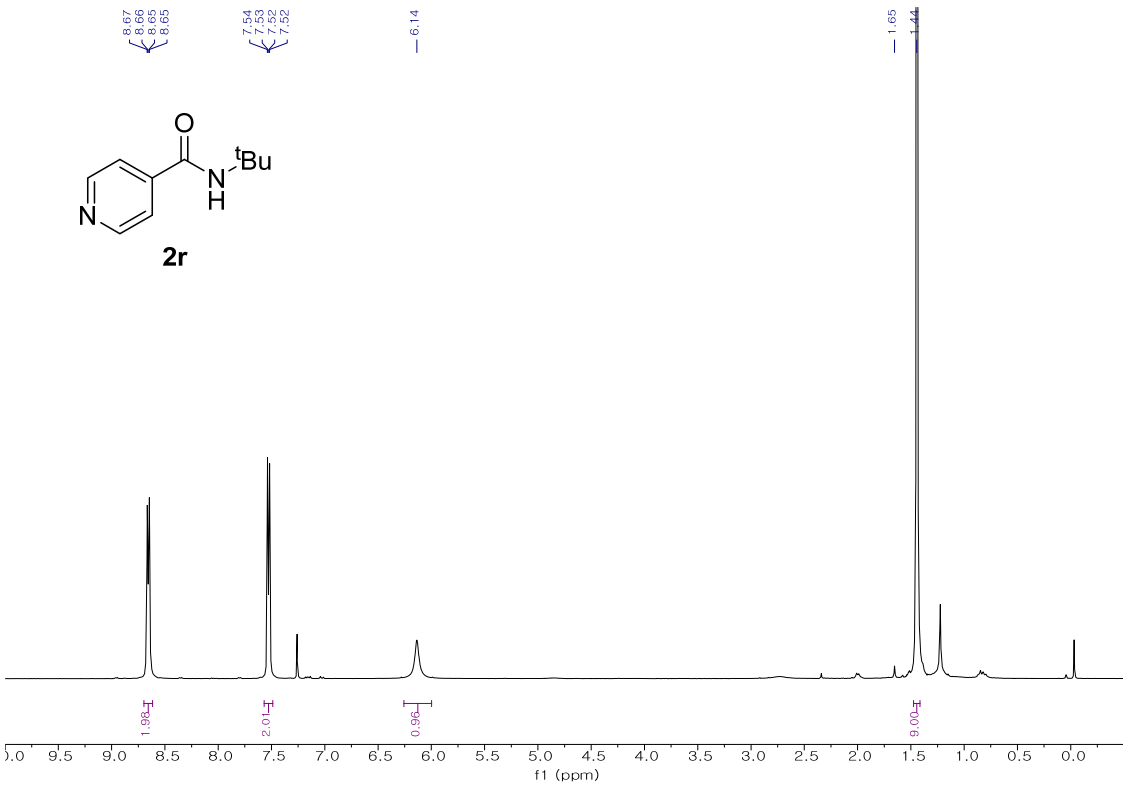
^{13}C-NMR (75 Hz, $CDCl_3$) of **2p**



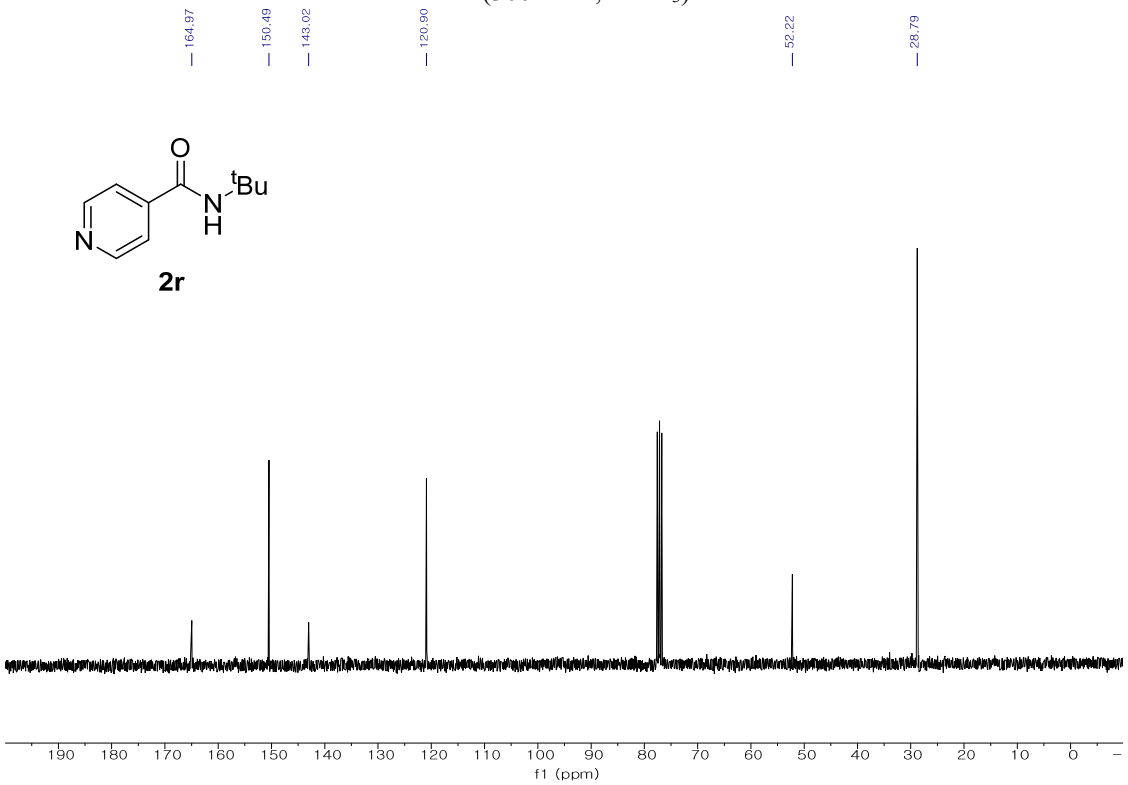
^{1}H-NMR (300 MHz, $CDCl_3$) of **2q**



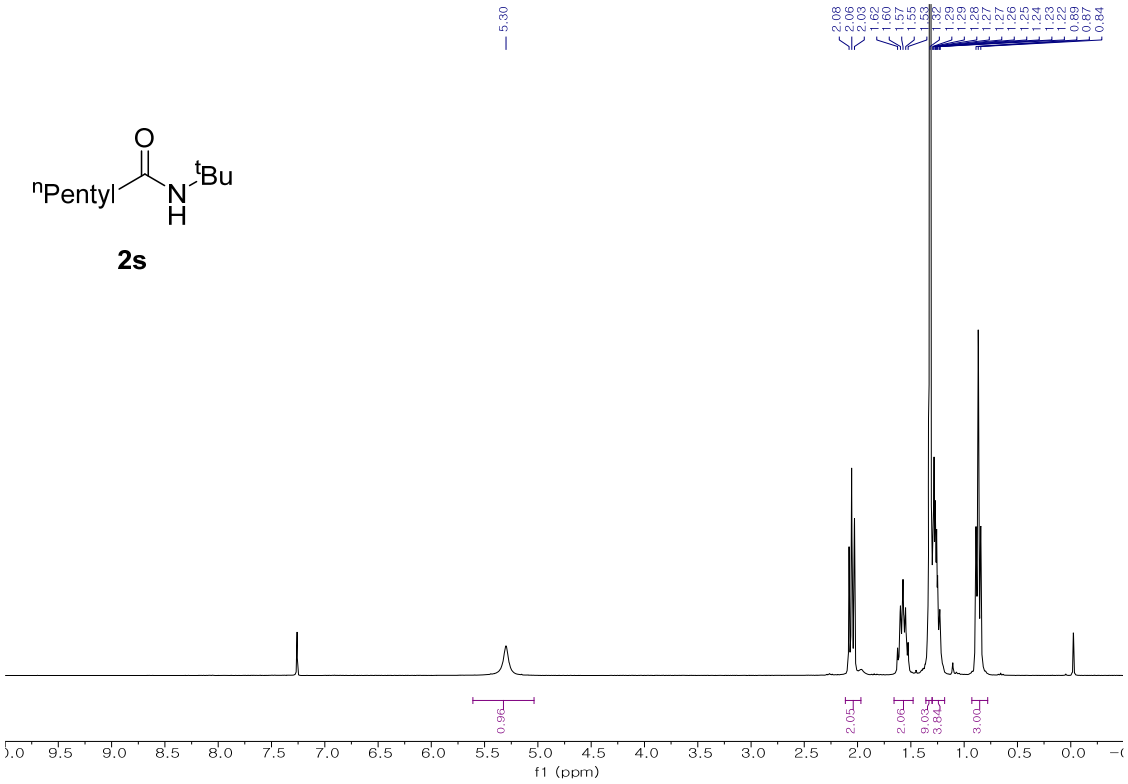
^{13}C-NMR (75 Hz, $CDCl_3$) of **2q**



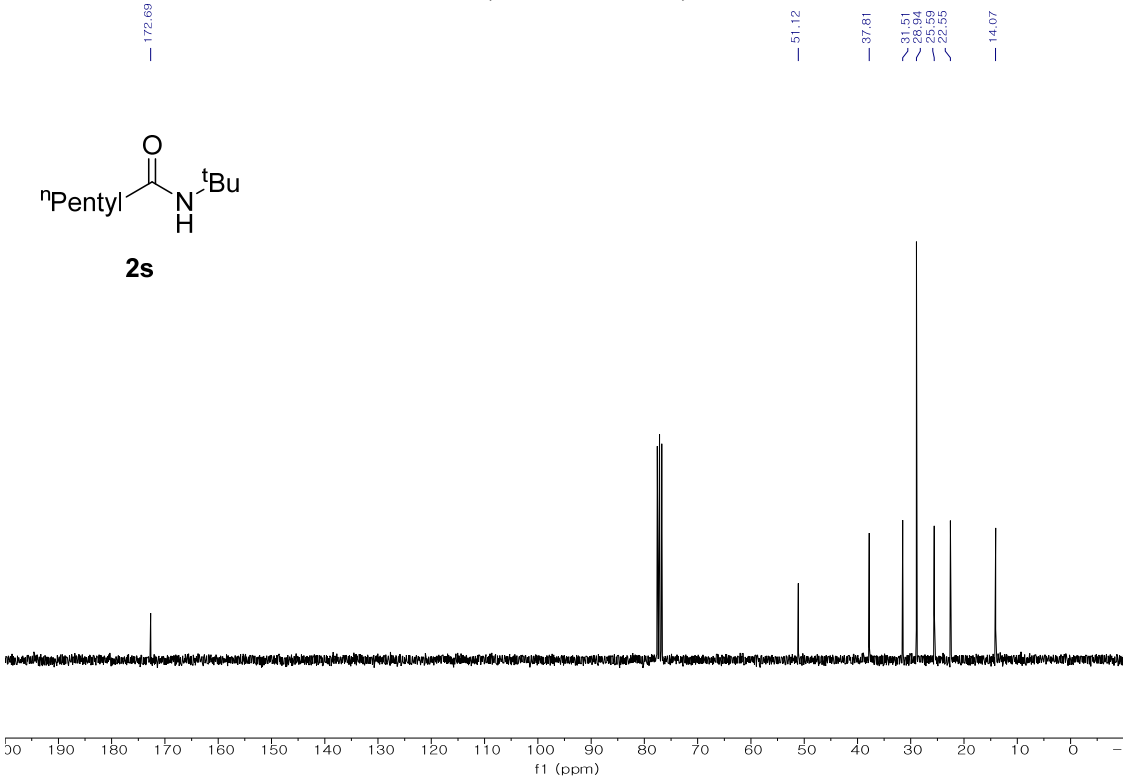
^{1}H-NMR (300 MHz, $CDCl_3$) of **2r**



^{13}C-NMR (75 Hz, $CDCl_3$) of **2r**



^{1}H-NMR (300 MHz, $CDCl_3$) of **2s**



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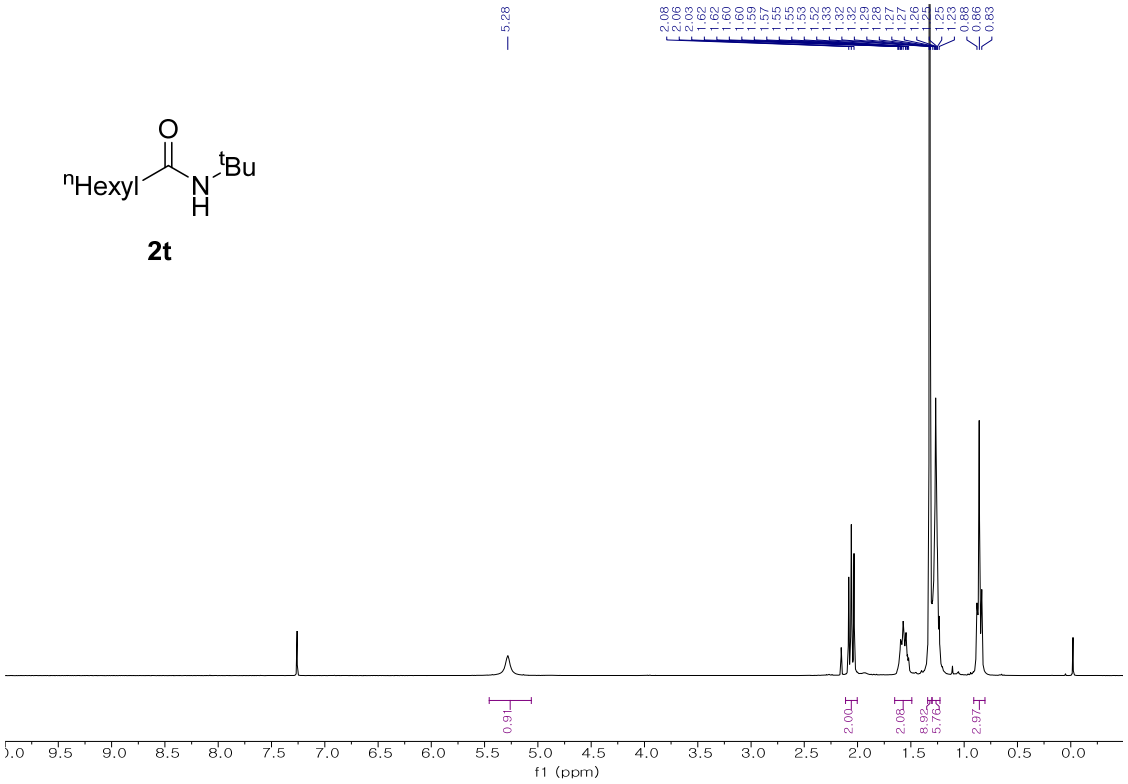
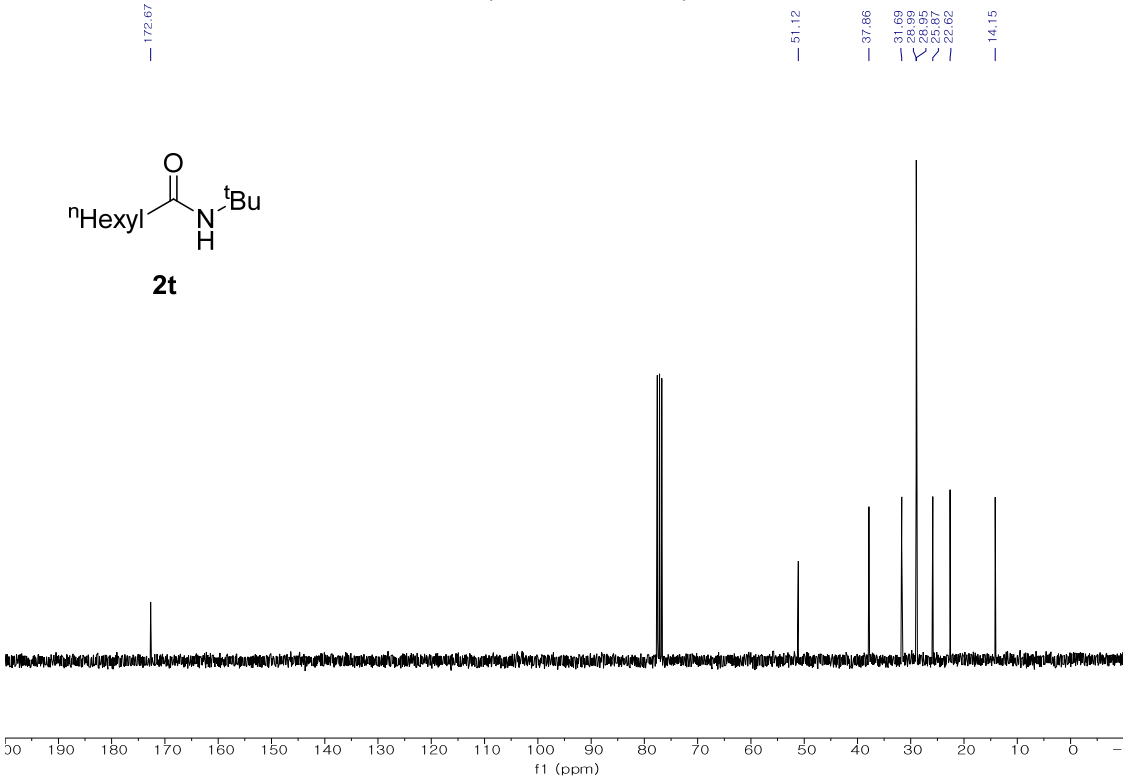
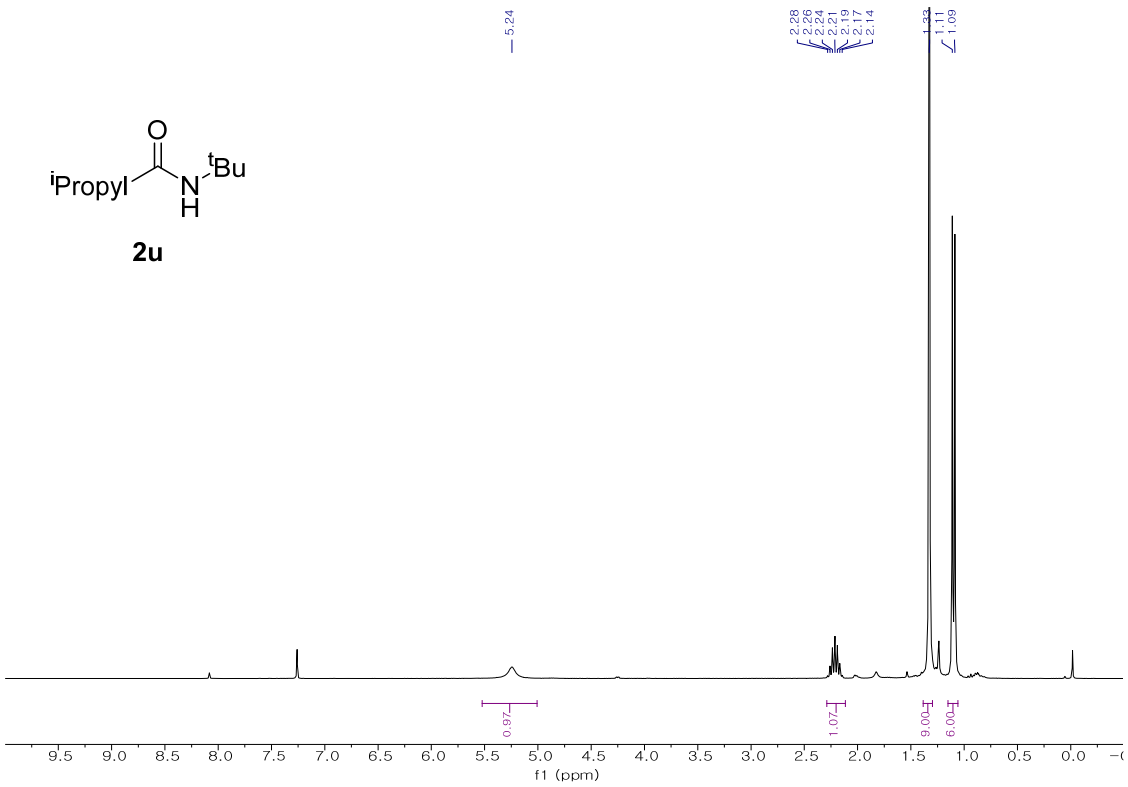


^{1}H-NMR (300 MHz, $CDCl_3$) of **2t**

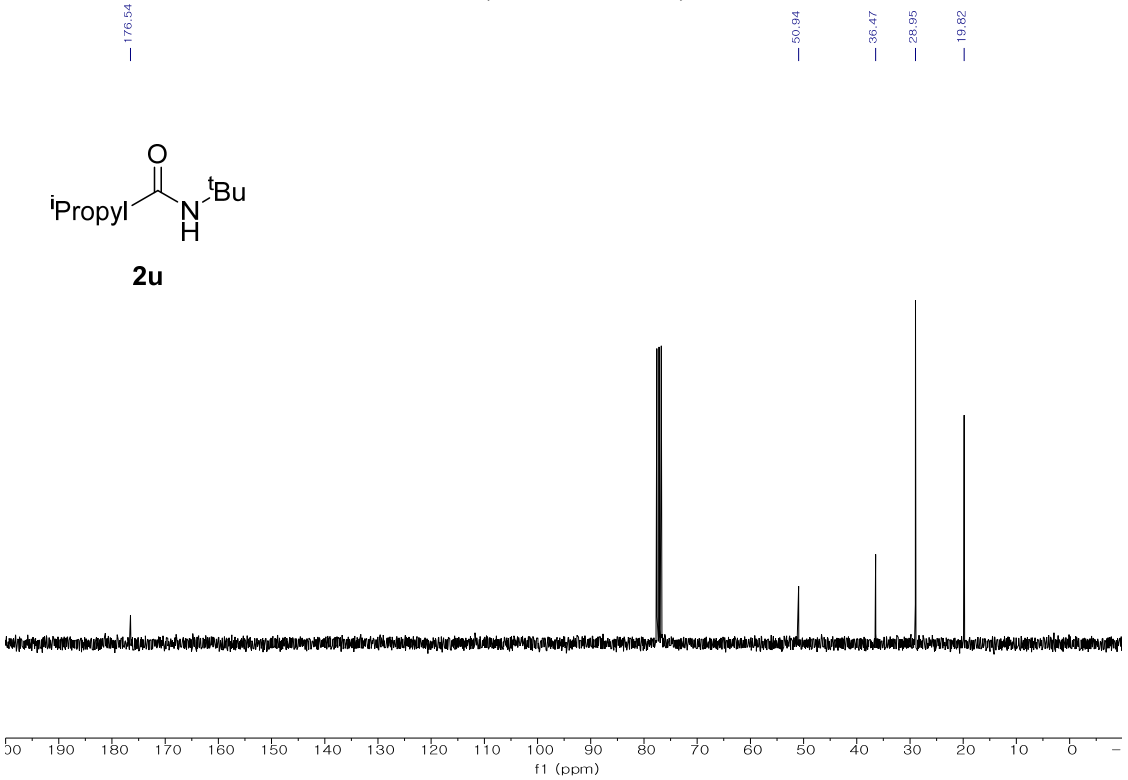


^{13}C-NMR (75 Hz, $CDCl_3$) of **2t**



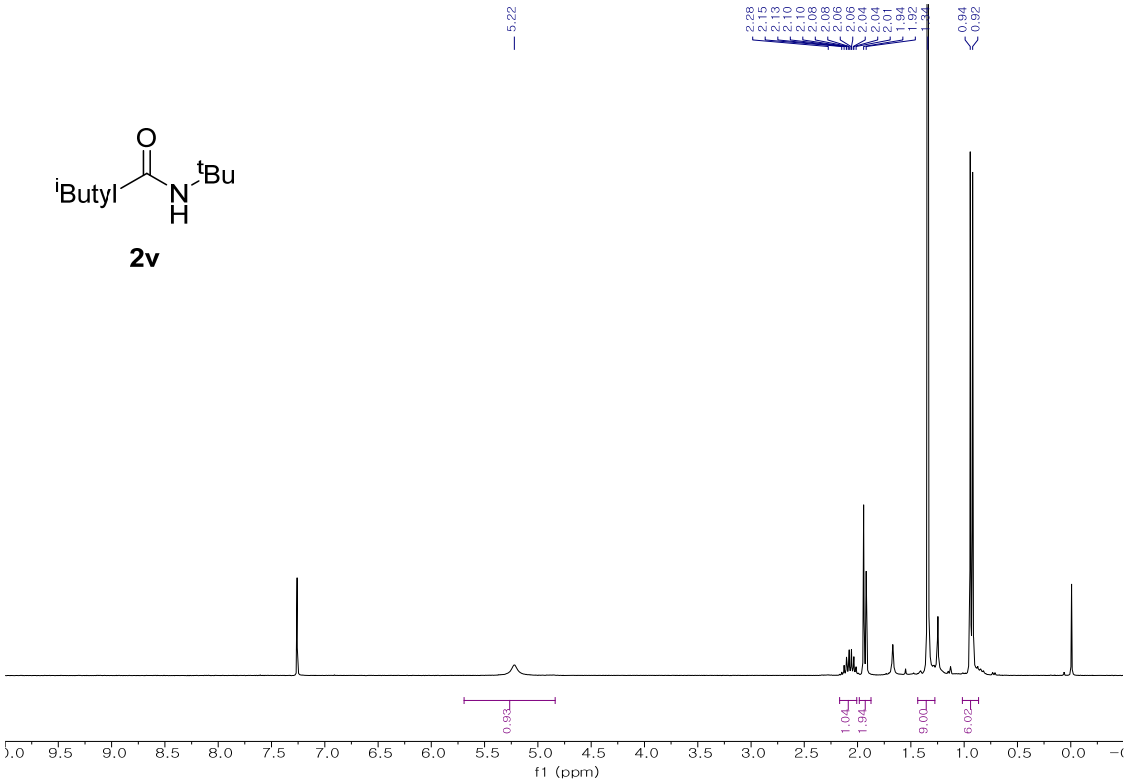
2u

^{1}H-NMR (300 MHz, $CDCl_3$) of **2u**



2u

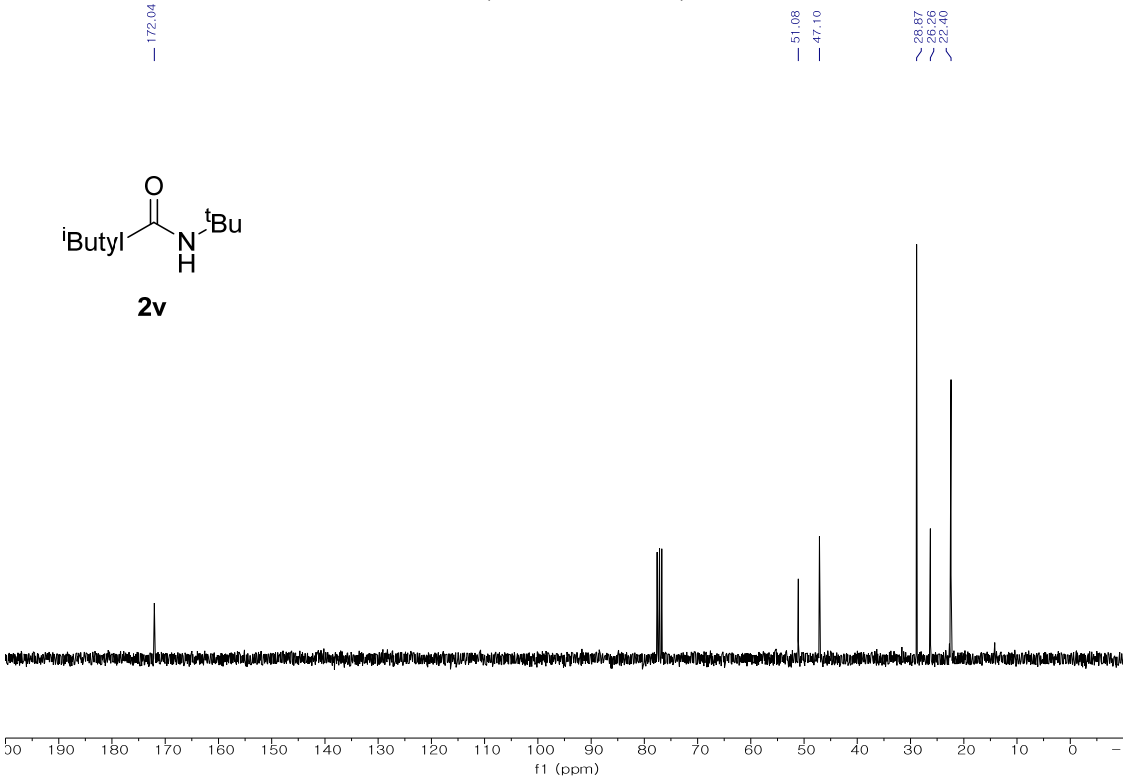
^{13}C-NMR (75 Hz, $CDCl_3$) of **2u**



^{i}Butyl, ^{t}Bu

2v

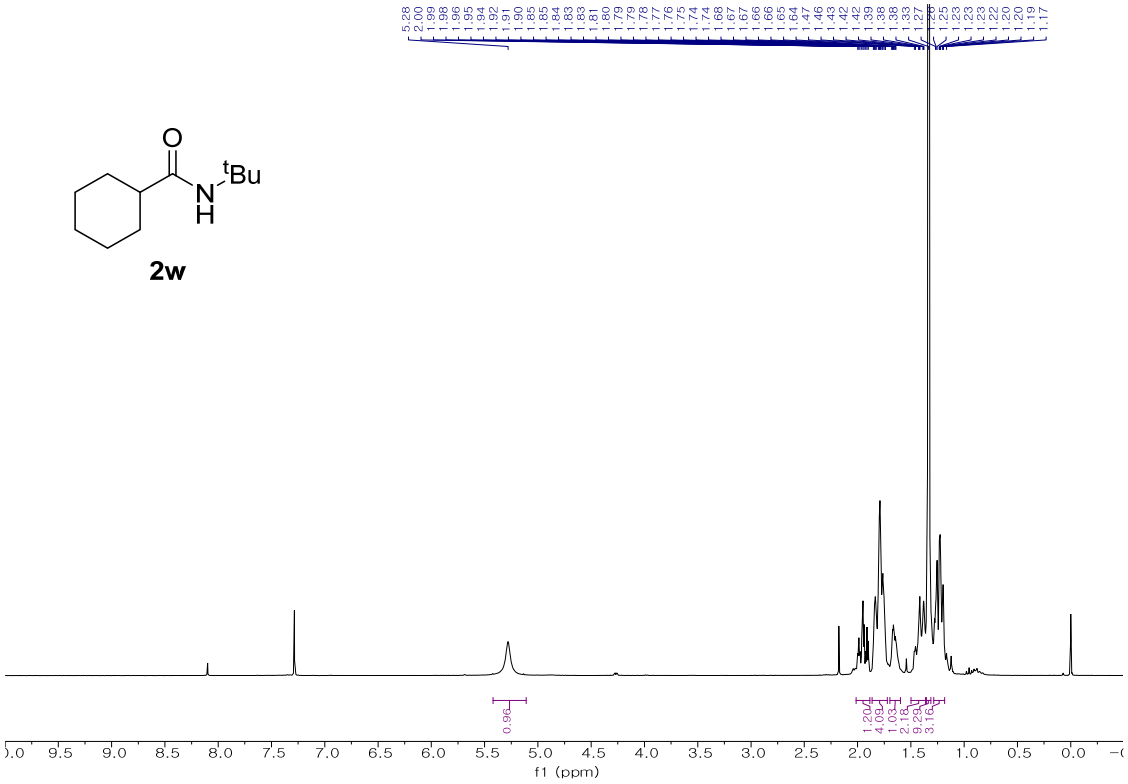
^{1}H-NMR (300 MHz, $CDCl_3$) of **2v**



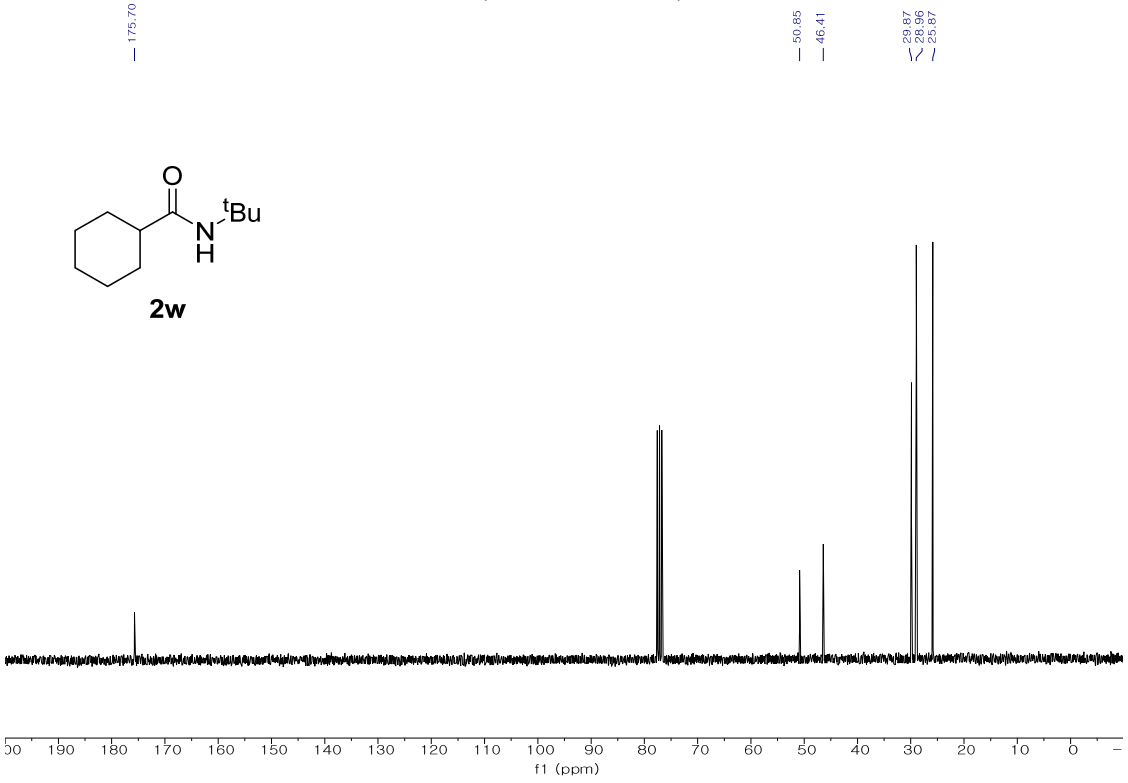
^{i}Butyl, ^{t}Bu

2v

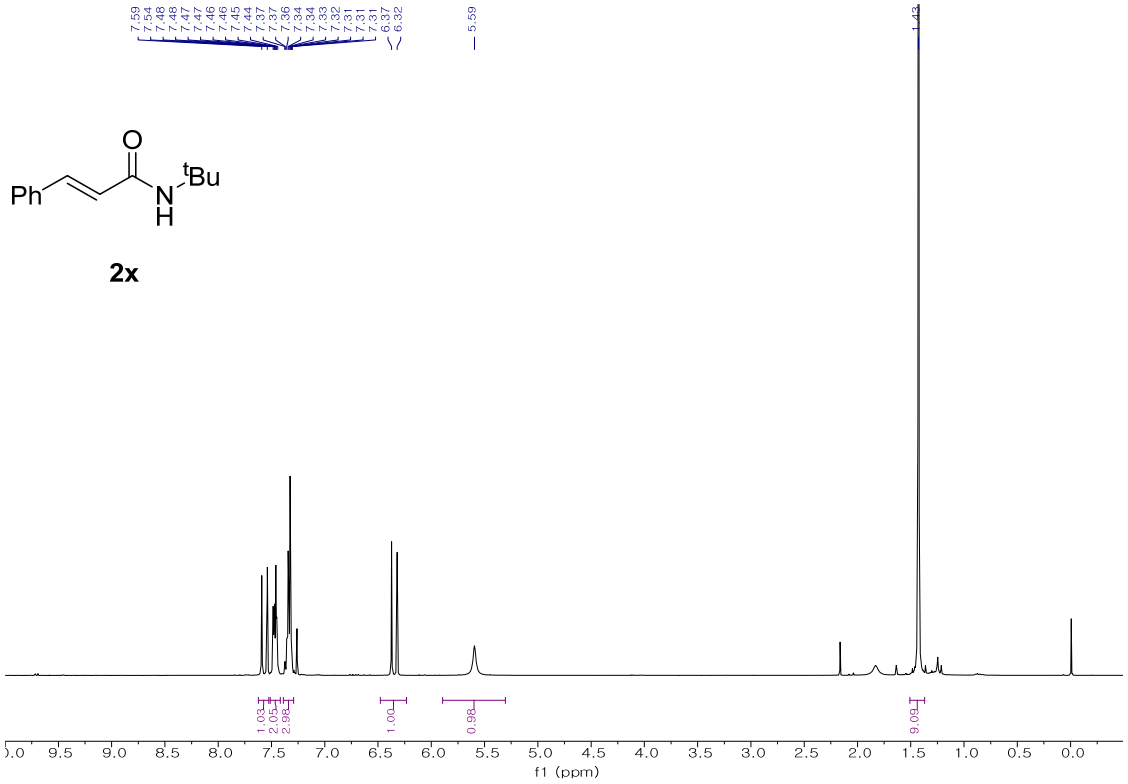
^{13}C-NMR (75 Hz, $CDCl_3$) of **2v**



^{1}H-NMR (300 MHz, $CDCl_3$) of **2w**

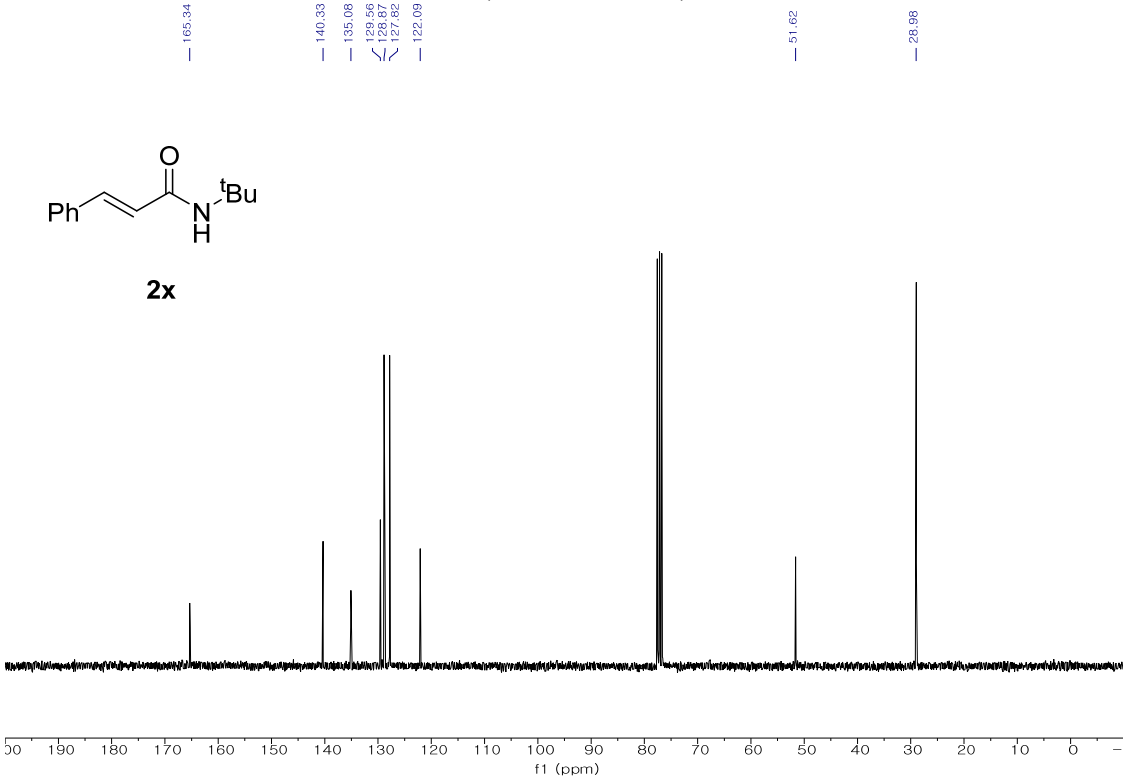


^{13}C-NMR (75 Hz, $CDCl_3$) of **2w**



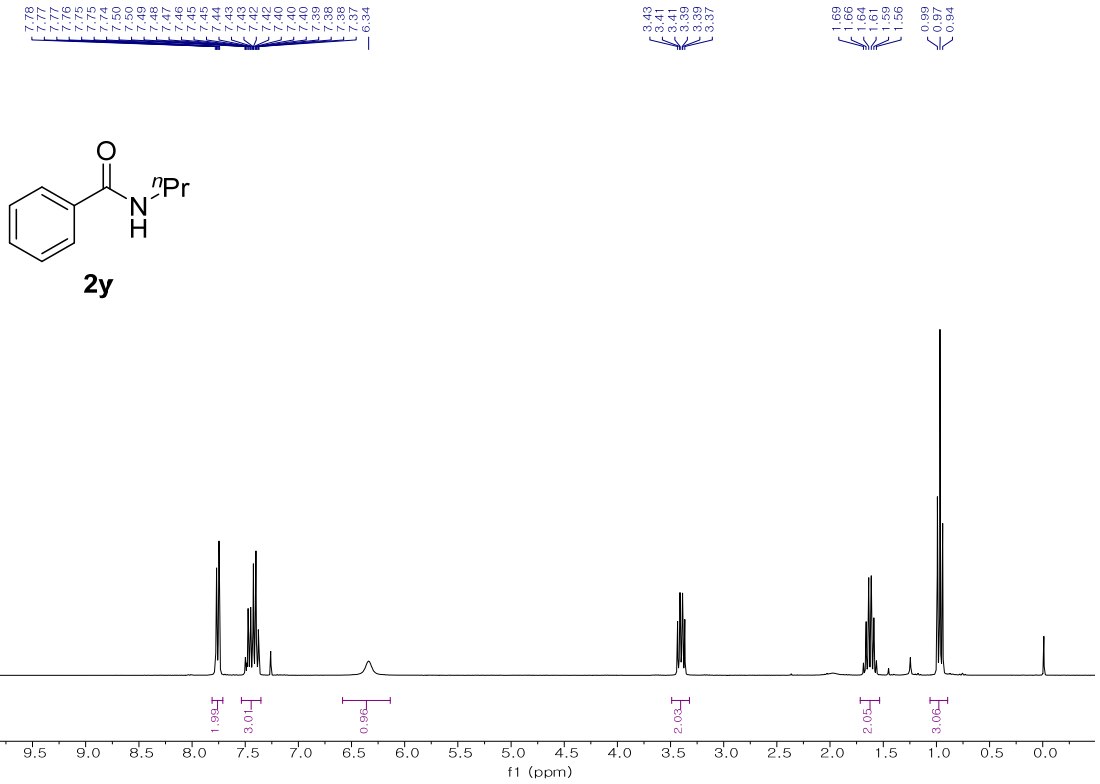
2x

^{1}H-NMR (300 MHz, $CDCl_3$) of **2x**

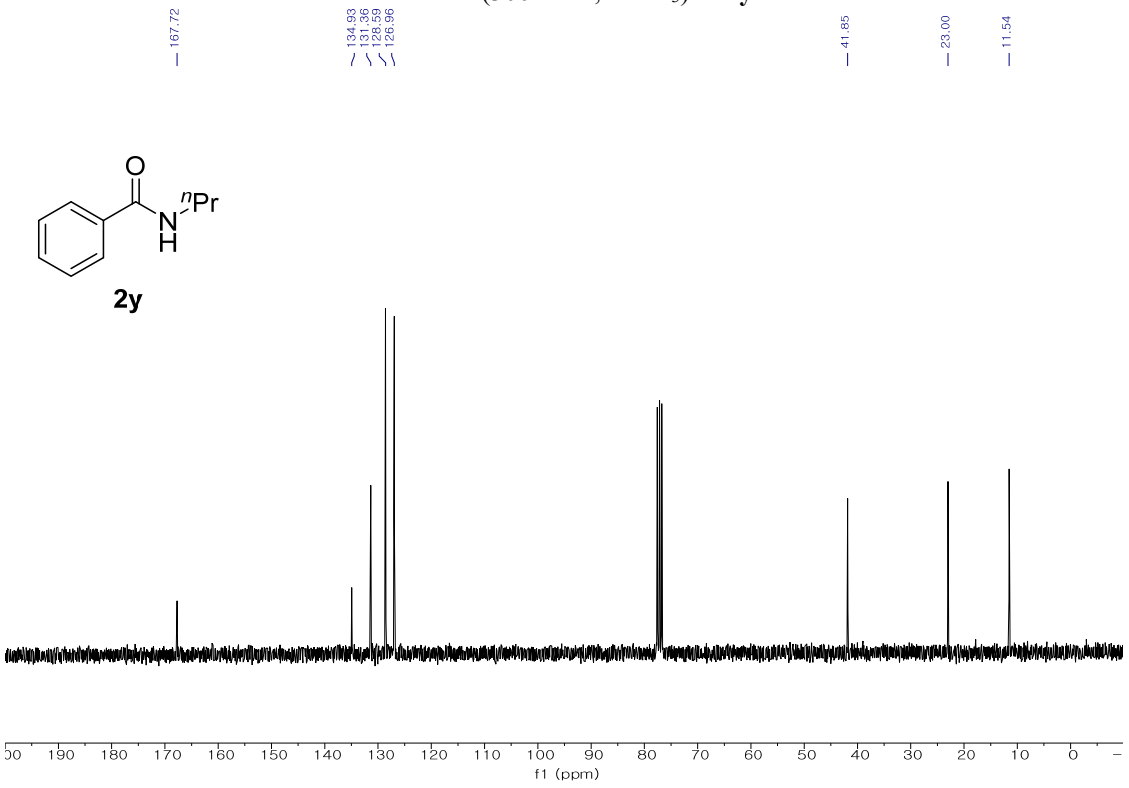


2x

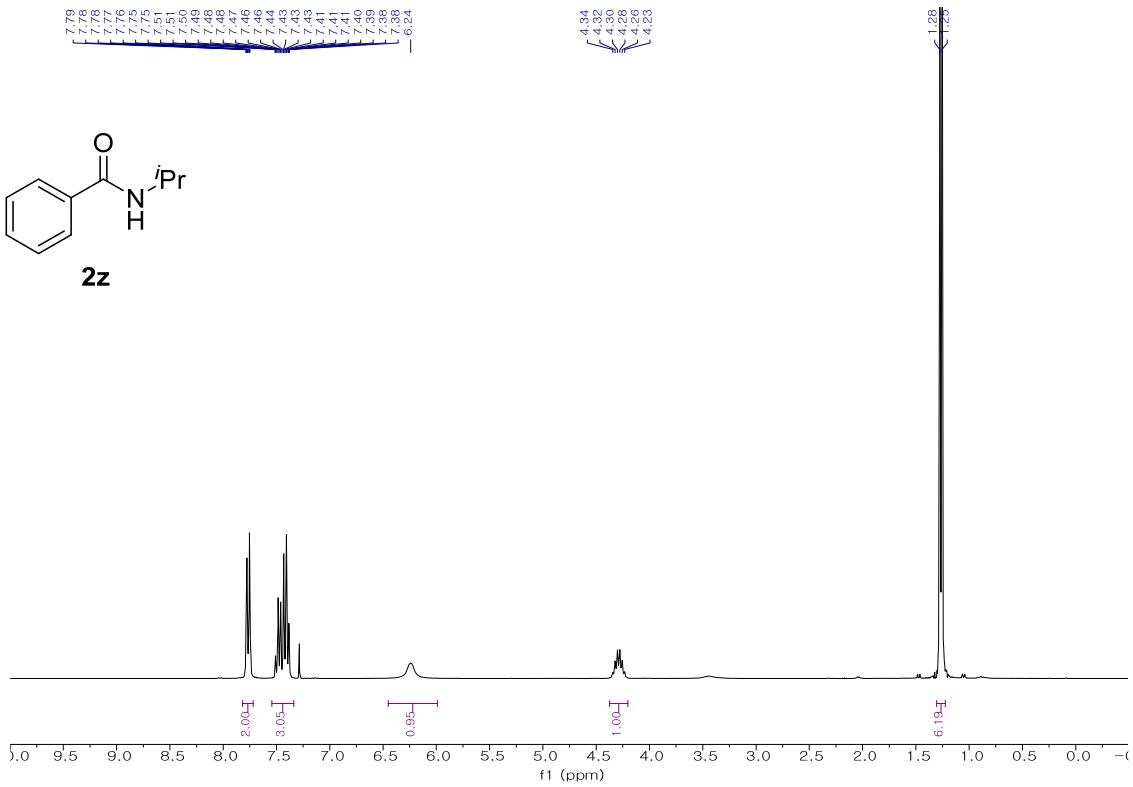
^{13}C-NMR (75 Hz, $CDCl_3$) of **2x**



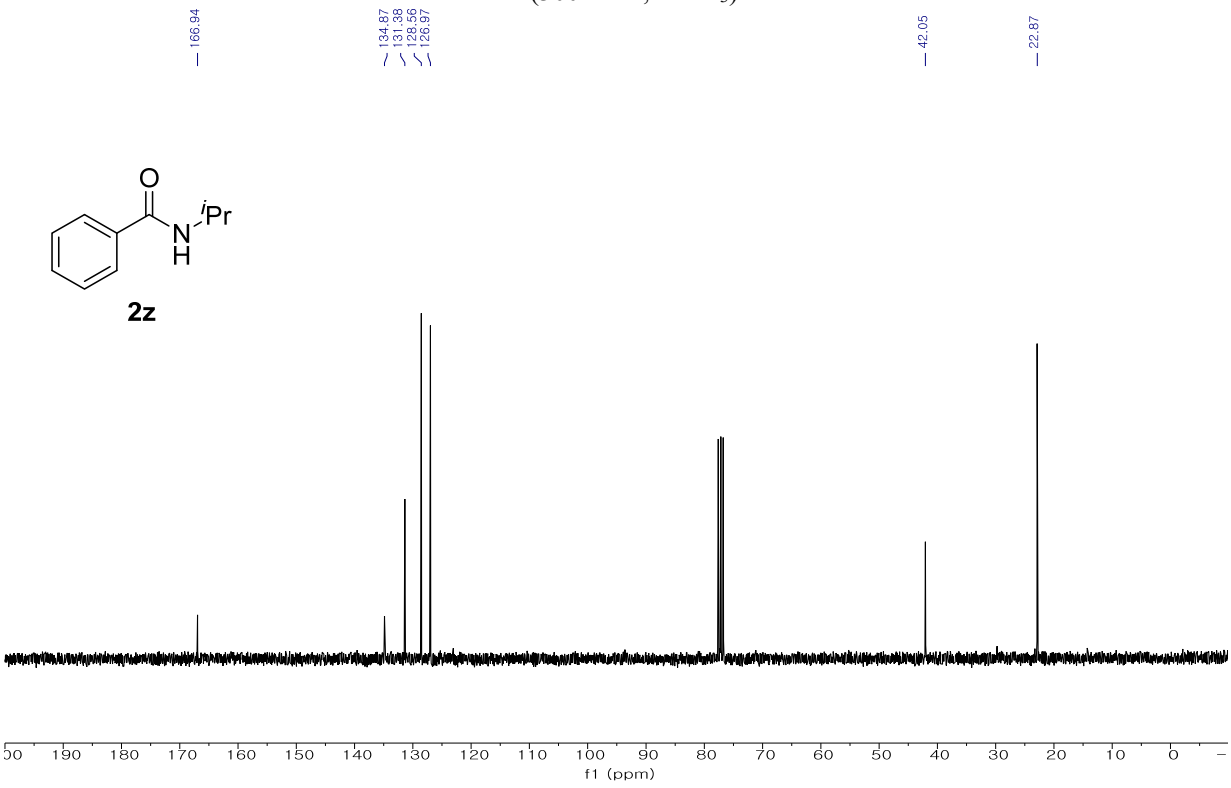
^{1}H-NMR (300 MHz, $CDCl_3$) of **2y**



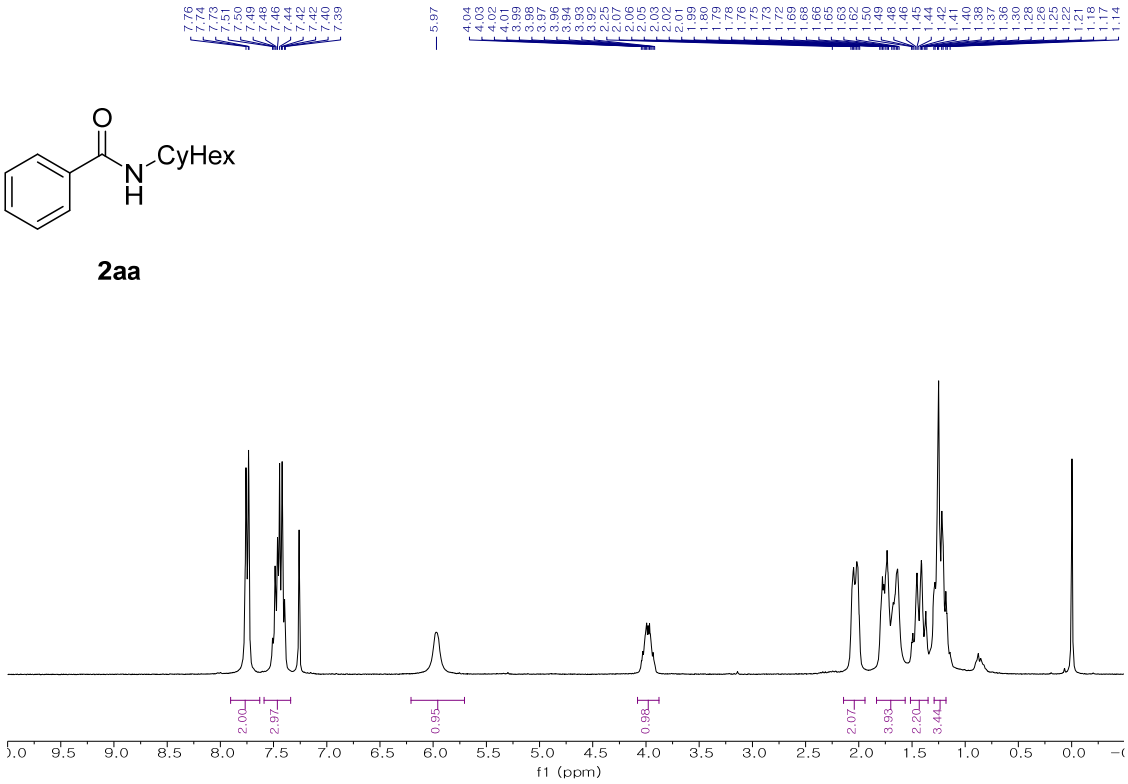
^{13}C-NMR (75 Hz, $CDCl_3$) of **2y**



^{1}H-NMR (300 MHz, $CDCl_3$) of **2z**

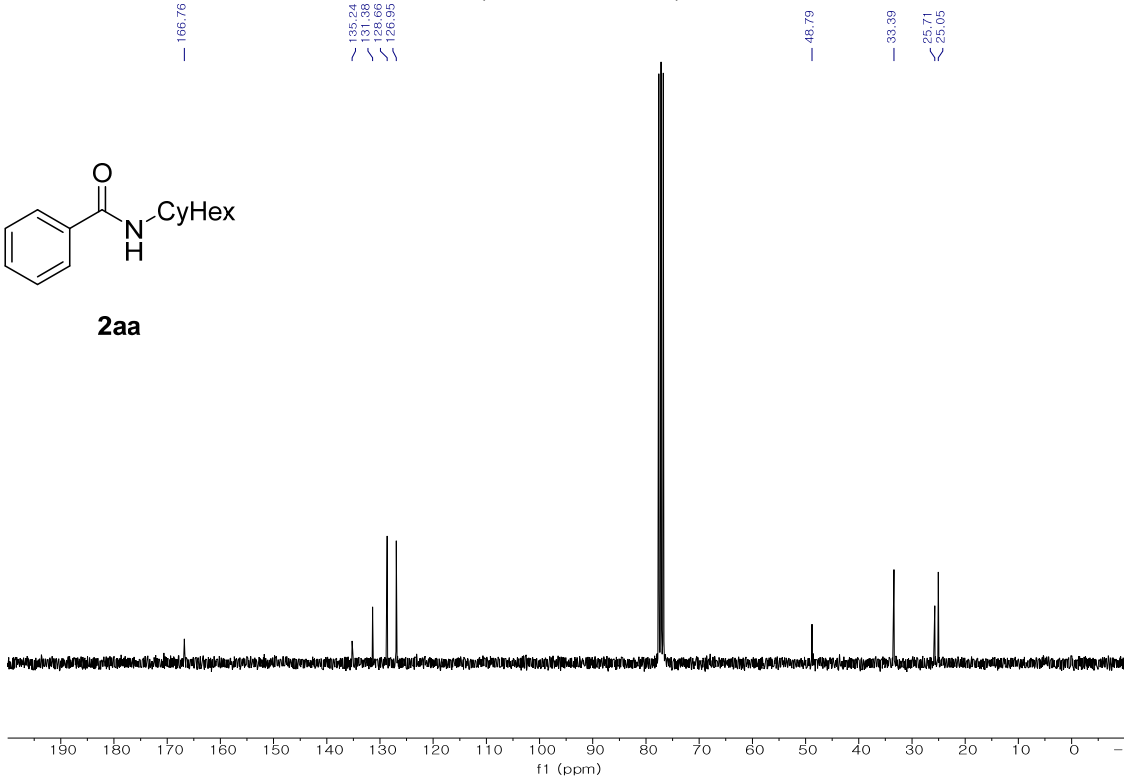


^{13}C-NMR (75 Hz, $CDCl_3$) of **2z**



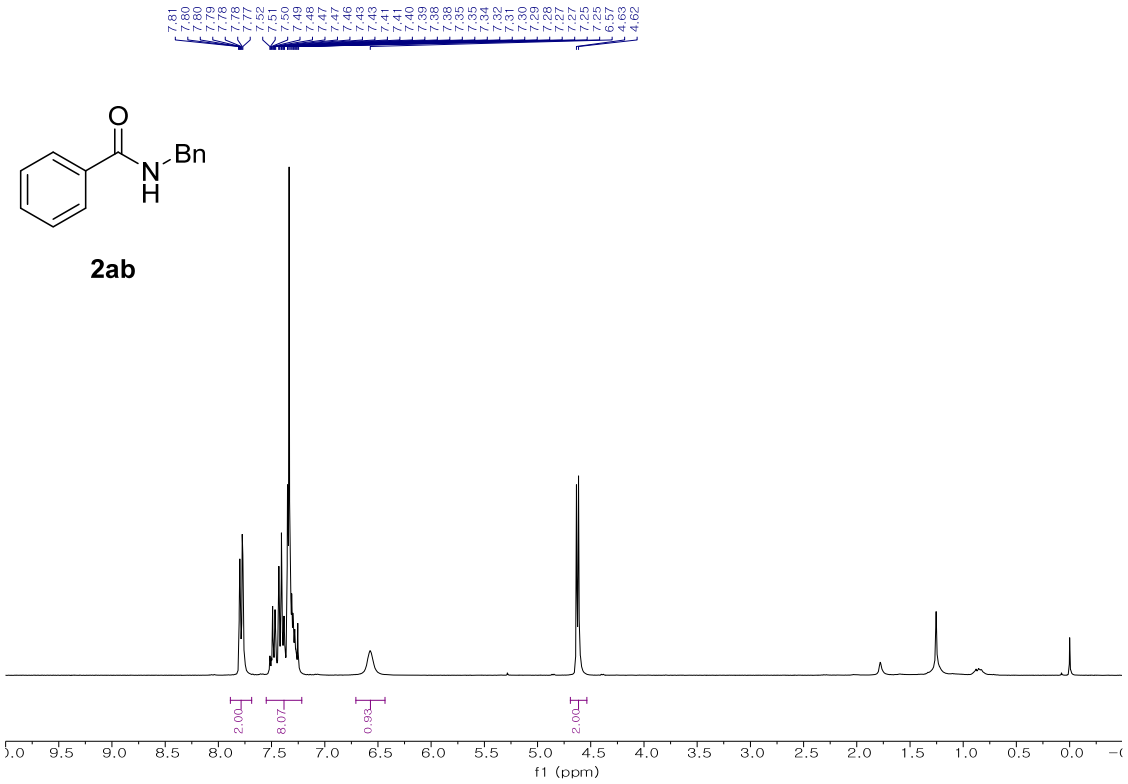
2aa

^{1}H-NMR (300 MHz, $CDCl_3$) of **2aa**

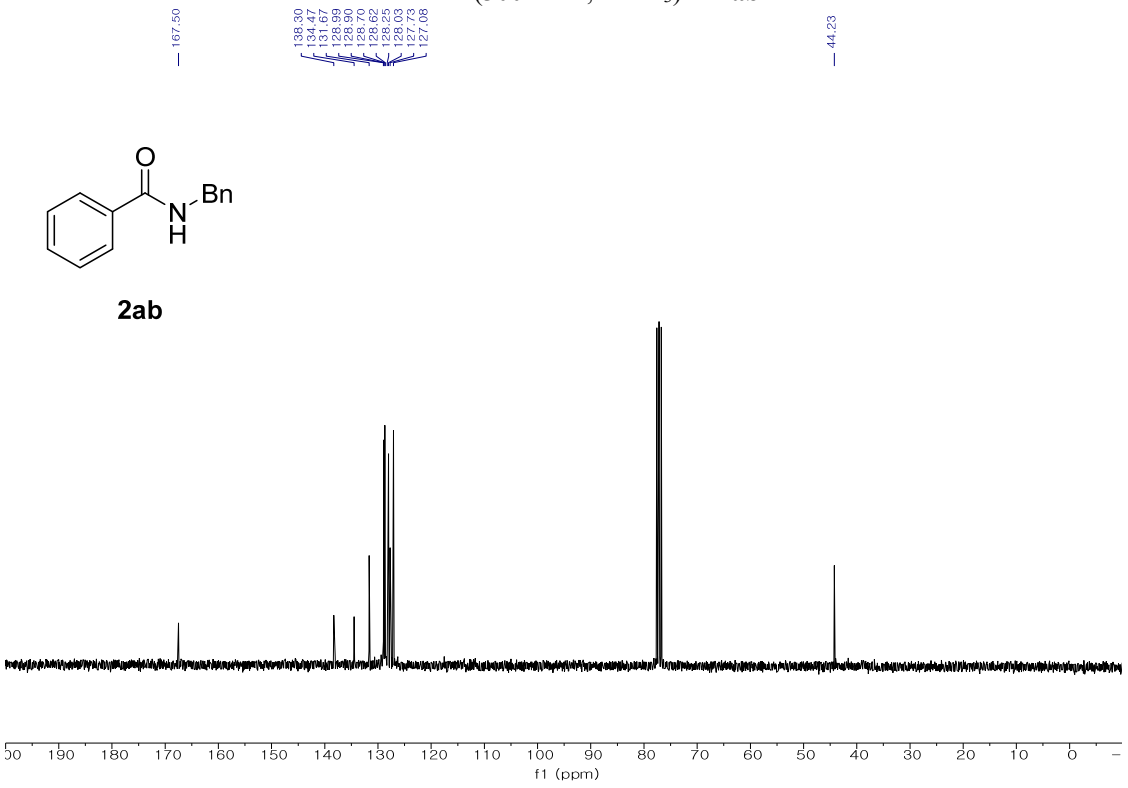


2aa

^{13}C-NMR (75 Hz, $CDCl_3$) of **2aa**



^{1}H-NMR (300 MHz, $CDCl_3$) of **2ab**



^{13}C-NMR (75 Hz, $CDCl_3$) of **2ab**