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Supporting Information for

Formal Giese Addition of C(sp^3)–H Nucleophiles Enabled by Visible Light Mediated Ni Catalysis of Triplet Enone Diradicals

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Table of Contents

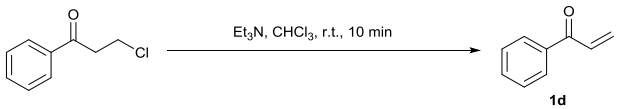
1. General Information

Unless otherwise noted, all reactions were performed under inert conditions. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a Bruker DPX-300 (300 MHz) spectrometer or Varian 400 and 500 NMR (400 and 500 MHz), and the residual solvent signal was used as a reference. High-resolution mass spectrometry (HRMS) was performed at the Organic Chemistry Research Center in Sogang University using the ESI method. Chemical shifts are reported in ppm and coupling constants are given in Hz. Gas chromatography (GC) was carried out using a 7980B GC system (Agilent Technologies) equipped with an HP-5 column and a flame ionization detector (FID). Reactions were monitored by thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates, and visualized either using UV light (254 nm) or by staining with potassium permanganate and heating. Tetrahydrofuran (THF) and toluene were dried using a PureSolv solvent purification system. Deuterated compounds were purchased from Cambridge Isotope Laboratories, Inc. and Sigma-Aldrich Corporation. 34 W Blue LED lamps purchased from Kessil (Kessil H150 Grow light-Blue) were used for all the visible light photocatalytic reactions. Cyclic voltammetry was measured using a CHI604B potentiostat (CH Instruments). UV–Vis spectra were recorded on an Agilent 8453 UV–Vis spectrophotometer with ChemStation software. Fluorescence spectra were recorded on a Photon Technology International (PTI) QM-400 spectrofluorometer with FelixGX software.

2. Substrate Preparation

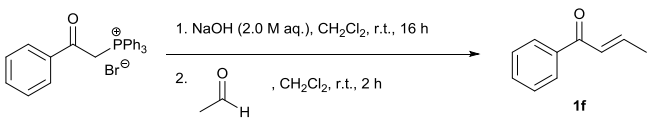
All Giese acceptor substrates not listed individually below were purchased from commercial sources (Alfa Aesar, TCI, or Sigma-Aldrich) with highest available purity and were used as received. Other Giese acceptors were synthesized following the procedures shown below using chemicals purchased from commercial sources in the highest available purity without further purification. All physical and spectroscopic properties of the synthesized materials agreed with previously reported data. Giese donors other than THF and toluene were purchased from commercial sources in the highest available purity and were degassed prior to use. The photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was synthesized from literature procedure.[1]

Phenyl vinyl ketone (1d)



Compound **1d** was prepared according to a previous literature procedure with slight modifications.[2] More specifically, to a stirred solution of 3-chloropropiophenone (933 mg, 5.0 mmol) in $CHCl_3$ (10 mL) at room temperature was added Et_3N (1.0 mL, 10.0 mmol). After stirring the resulting mixture for 10 min, a large quantity of white precipitate was obtained. This mixture was then diluted with NH_4Cl (sat aq., 10 mL) and water (5 mL), extracted with CH_2Cl_2 (3 × 5 mL), dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexanes/EtOAc, 9:1) to afford **1d** (661 mg, 5.0 mmol, >99%) as a colorless oil. All physical and spectroscopic data were in accordance with the literature.[2]

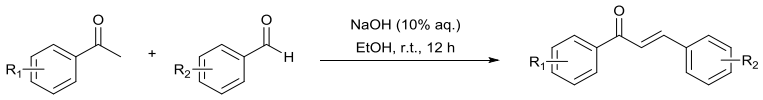
(*E*)-1-Phenylbut-2-en-one (1f)



Compound **1f** was prepared according to a previous literature procedure with slight modifications.[3] More specifically, to a biphasic mixture of CH_2Cl_2 (20 mL) and NaOH (2.0 M aq., 10 mL) was added (2-oxo-2-phenylethyl)triphenylphosphonium bromide[4] (2.30 g, 5.0 mmol). The resulting mixture was stirred for 16 h at

room temperature before the layers were separated. The aqueous layer was then extracted with CH_2Cl_2 (1 × 10 mL) and the combined organic layers were dried using anhydrous Na_2SO_4. Without filtering, to the resulting suspension was added acetaldehyde (3 mL, 3 × 1 mL in 30 min intervals) and stirring continued for 1 h. The resulting mixture was concentrated under reduced pressure, and the obtained residue was purified by flash column chromatography (silica gel, hexanes/EtOAc, 9:1) to afford **1f** (599 mg, 4.10 mmol, 82%) as a colorless oil. All physical and spectroscopic data were in accordance with the literature.[3]

General chalcones (1h–1j, 1q, 1z, 1aa, 1ab)

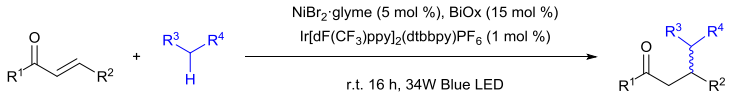


Chalcones (**1h–1j, 1q, 1z, 1aa, 1ab**) were synthesized via a previously reported Claisen-Schmidt condensation procedure with slight modifications.[5] More specifically, to a 20 mL vial equipped with a PTFE-coated stirrer bar were added the corresponding benzaldehyde (3.0 mmol, 1.0 equiv.), acetophenone (3.0 mmol, 1.0 equiv.), and ethanol (9.0 mL). NaOH (10% aq., 6.0 mL) was then added to the resulting solution and subsequently stirred for 12 h at room temperature. In the majority of cases, a precipitate formed, which was filtered and washed with a 1:1 ethanol/water solution. The obtained solid was dissolved in CH_2Cl_2, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure to afford the corresponding analytically pure chalcones. Alternatively, when no precipitates were formed, the reaction mixture was extracted with EtOAc, dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexanes/EtOAc, gradient elution) to afford the corresponding chalcones. All physical and spectroscopic data were in accordance with the literature.[6]

4'-Chalconecarboxylic acid methyl ester (1r)

Compound **1r** was synthesized following the general procedure outlined above, but replacing ethanol with methanol. All physical and spectroscopic data were in accordance with the literature.[7]

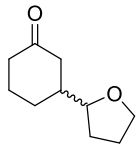
3. General Procedure for the Formal Giese Reaction



To a vial equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and the corresponding C-H donor (2.0 mL or 4.0 mL depending on acceptor). Where appropriate, MeCN (0.5 mL) was added. The resulting solution was stirred for 5 min to give a green suspension before $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.) and corresponding acceptor (0.20 mmol, 1.0 equiv.) were added. The resulting mixture was stirred for 16 h under 34W blue LED irradiation with fan cooling. The resulting mixture was filtered through a short pad of Celite®, eluted with CH_2Cl_2, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexanes/EtOAc gradient elution) to afford the desired product.

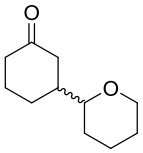
4. Characterization Data

Where the reactions yielded diastereomeric mixtures, these ratios were determined by ^1H NMR spectroscopy. All integrations were normalized with respect to the minor stereoisomer. As separation was not feasible, all peaks were recorded.



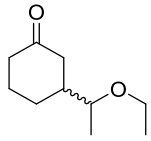
3-(Tetrahydro-2H-furan-2-yl)cyclohexan-1-one (2a)

Colorless oil, 30.5 mg (0.181 mmol, 91% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.87 – 3.65 (m, 6H), 3.65 – 3.55 (m, 1.5H), 2.49 (m, 1.5H), 2.41 – 2.19 (m, 7.5H), 2.20 – 2.08 (m, 6H), 1.99 – 1.72 (m, 10H), 1.72 – 1.33 (m, 7.5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 211.6, 211.3, 82.4, 82.3, 68.0, 67.9, 44.7, 44.2, 43.7, 43.6, 41.5, 41.4, 29.2, 29.1, 28.2, 27.7, 25.8, 25.8, 25.1, 25.0; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{10}H_{16}O_2Na$, 191.1048; found: 191.1045.



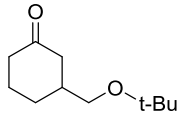
3-(Tetrahydro-2H-pyran-2-yl)cyclohexan-1-one (3a)

Colorless oil, 22.2 mg (0.122 mmol, 61% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.01 – 3.94 (m, 2.5H), 3.39 (td, *J* = 11.4, 3.1 Hz, 2.5H), 3.15 (dd, *J* = 11.1, 3.1 Hz, 1H), 3.11 – 3.03 (m, 1.5H), 2.52 – 2.45 (m, 1H), 2.35 (dd, *J* = 14.1, 1.8 Hz, 4H), 2.29 – 2.17 (m, 5H), 2.10 – 2.01 (m, 4H), 1.90 – 1.75 (m, 5H), 1.65 – 1.40 (m, 15.5H), 1.37 – 1.25 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.2, 212.0, 80.7, 80.6, 68.8, 68.7, 44.5, 44.1, 43.9, 43.3, 41.5, 41.5, 28.9, 28.6, 27.6, 26.4, 26.12, 26.1, 25.1, 25.0, 23.6, 23.5; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{11}H_{18}O_2Na$, 205.1204; found: 205.1202.



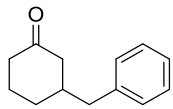
3-(1-Ethoxyethyl)cyclohexan-1-one (4a)

Colorless oil, 28.0 mg (0.164 mmol, 82% yield), 1:1 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 – 3.50 (m, 2H), 3.46 – 3.32 (m, 2H), 3.32 – 3.20 (m, 2H), 2.60 – 2.44 (m, 1H), 2.44 – 2.16 (m, 7H), 2.17 – 1.94 (m, 3H), 1.93 – 1.75 (m, 3H), 1.75 – 1.35 (m, 4H), 1.25 – 1.05 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.2, 212.2, 77.9, 77.8, 64.4, 64.3, 44.5, 44.4, 44.4, 43.5, 41.5, 27.5, 26.3, 25.1, 16.7, 16.6, 15.5, 15.5; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{10}H_{18}O_2Na$, 193.1204; found: 193.1200.



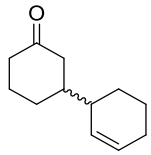
3-(*tert*-butoxymethyl)cyclohexan-1-one (5a)

Colorless oil, 26.3 mg (0.143 mmol, 71% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.26 (d, *J* = 5.6 Hz, 2H), 2.50 – 1.87 (m, 7H), 1.78 – 1.57 (m, 1H), 1.56 – 1.38 (m, 1H), 1.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.0, 72.6, 65.7, 45.0, 41.5, 39.7, 28.2, 27.5, 24.97; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{11}H_{20}O_2Na$, 207.1361; found: 207.1356.



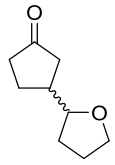
3-Benzylcyclohexan-1-one (6a)

Colorless oil, 15.5 mg (0.082 mmol, 41% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 – 7.24 (m, 2H), 7.24 – 7.16 (m, 1H), 7.16 – 7.08 (m, 2H), 2.70 – 2.55 (m, 2H), 2.43 – 2.31 (m, 2H), 2.31 – 2.19 (m, 1H), 2.14 – 1.98 (m, 3H), 1.93 – 1.82 (m, 1H), 1.72 – 1.53 (m, 1H), 1.45 – 1.30 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.7, 139.42, 129.1, 128.4, 126.2, 47.9, 43.0, 41.4, 40.9, 30.9, 25.1; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{13}H_{17}O$, 189.1279; found: 189.1274.



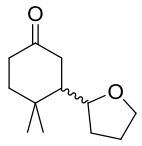
3-(1-Cyclohex-1-enyl)cyclohexan-1-one (7a)

Colorless oil, 25.8 mg (0.145 mmol, 72% yield), 1:1 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.78 – 5.71 (m, 1H), 5.59 – 5.52 (m, 1H), 2.42 – 2.31 (m, 2H), 2.29 – 2.20 (m, 1H), 2.18 – 2.04 (m, 3H), 1.94 – 1.79 (m, 2H), 1.79 – 1.67 (m, 3H), 1.65 – 1.40 (m, 4H), 1.39 – 1.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.4, 129.1, 128.9, 128.8, 128.6, 45.3, 45.1, 43.7, 41.5, 40.1, 40.0, 28.5, 28.2, 25.7, 25.5, 25.5, 25.4, 25.3, 25.3, 21.9, 21.8; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{12}H_{19}O$, 179.1436; found: 179.1430.



3-(Tetrahydro-2H-furan-2-yl)cyclopentan-1-one (2b)

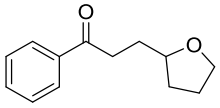
Colorless oil, 28.4 mg (0.184 mmol, 92% yield), 1:1 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.90 – 3.79 (m, 2H), 3.79 – 3.66 (m, 4H), 2.45 – 1.83 (m, 18H), 1.80 – 1.62 (m, 2H), 1.59 – 1.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 219.3, 219.0, 82.4, 82.0, 68.1, 68.1, 41.9, 41.8, 41.8, 41.6, 38.2, 38.2, 30.0, 30.0, 26.2, 26.0, 25.9, 25.8; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_9H_{14}O_2Na$, 177.0891; found: 177.0886.



4,4-Dimethyl-3-(tetrahydrofuran-2-yl)cyclohexan-1-one (2c)

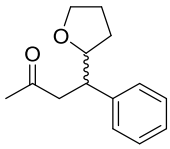
Colorless oil, 30.5 mg (0.155 mmol, 78% yield), 1:1 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.17 (t, *J* = 7.6 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.77 – 3.65 (m, 3H), 2.50 – 2.37 (m, 3H), 2.36 – 2.23 (m, 4H), 2.23 – 2.11 (m, 1H), 1.95 – 1.79 (m, 8H), 1.72 – 1.62 (m, 3H), 1.62 – 1.42 (m, 3H), 1.14 (dd, *J* = 16.3, 10.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.4, 212.1, 79.8, 77.3, 68.7, 67.3, 50.6, 50.0, 41.0, 39.5, 39.2, 37.9, 37.9, 37.0, 32.9, 32.6, 30.9, 30.1, 29.4, 28.9, 25.9, 25.8, 23.1, 20.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{12}H_{20}O_2Na$,

219.1361; found: 219.1356.



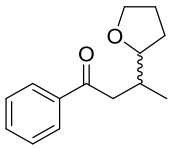
1-Phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2d)

Colorless oil, 37.3 mg (0.183 mmol, 91% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 – 7.89 (m, 2H), 7.64 – 7.51 (m, 1H), 7.51 – 7.37 (m, 2H), 4.00 – 3.82 (m, 2H), 3.74 (td, *J* = 7.8, 6.5 Hz, 1H), 3.25 – 3.00 (m, 2H), 2.15 – 1.77 (m, 5H), 1.66 – 1.42 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.1, 137.0, 132.9, 128.5, 128.1, 78.5, 67.7, 35.5, 31.5, 30.0, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{16}O_2Na$, 227.1048; found: 227.1043.



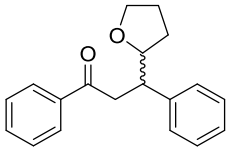
4-Phenyl-4-(tetrahydrofuran-2-yl)butan-2-one (2e)

Colorless oil, 31.0 mg (0.142 mmol, 71% yield), 1:1 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 – 7.22 (m, 6H), 7.21 – 7.13 (m, 4H), 4.13 – 4.03 (m, 1H), 4.01 – 3.90 (m, 1H), 3.87 – 3.76 (m, 1H), 3.76 – 3.69 (m, 1H), 3.70 – 3.62 (m, 1H), 3.37 – 3.28 (m, 1H), 3.22 – 3.13 (m, 1H), 3.14 – 3.05 (m, 1H), 2.99 – 2.83 (m, 2H), 2.76 – 2.65 (m, 1H), 2.04 (d, *J* = 3.6 Hz, 6H), 1.92 – 1.40 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.2, 200.0, 137.5, 137.4, 132.9, 132.8, 128.5, 128.5, 128.5, 128.2, 128.2, 83.4, 82.7, 68.2, 67.8, 42.8, 42.0, 35.3, 33.8, 29.6, 28.2, 26.1, 26.0, 16.7, 15.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{14}H_{18}O_2Na$, 241.1204; found: 241.1200.



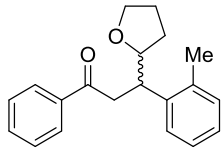
1-Phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2f)

Colorless oil, 38.5 mg (0.176 mmol, 88% yield), 1:1 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 – 7.90 (m, 4H), 7.64 – 7.50 (m, 2H), 7.50 – 7.38 (m, 4H), 3.98 – 3.71 (m, 5H), 3.65 (dd, *J* = 14.4, 7.8 Hz, 2H), 3.40 (dd, *J* = 16.2, 4.0 Hz, 1H), 3.25 – 3.02 (dd, *J* = 16.0, 4.6 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.53 – 2.36 (m, 1H), 2.35 – 2.15 (m, 1H), 2.10 – 1.80 (m, 6H), 1.74 – 1.48 (m, 2H), 1.11 – 0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.2, 200.0, 137.5, 137.4, 132.9, 132.8, 128.5, 128.5, 128.5, 128.2, 128.2, 83.4, 82.7, 68.2, 67.8, 42.8, 42.0, 35.3, 33.8, 29.6, 28.2, 26.1, 26.0, 16.7, 15.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{14}H_{18}O_2Na$, 241.1204; found: 241.1200.



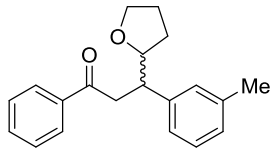
1,3-Diphenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2g)

Colorless oil, 41.1 mg (0.147 mmol, 73% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 – 7.90 (m, 5.5H), 7.59 – 7.50 (m, 3H), 7.49 – 7.39 (m, 6H), 7.39 – 7.15 (m, 10.5H), 4.26 – 4.15 (m, 1H), 4.15 – 4.03 (m, 1.5H), 3.92 – 3.65 (m, 6.5H), 3.62 – 3.25 (m, 6H), 2.00 – 1.64 (m, 7H), 1.64 – 1.47 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 198.9 142.3, 141.4, 137.4, 137.3, 132.9, 132.7, 129.1, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 126.6, 126.6, 82.7, 81.8, 68.3, 68.0, 46.9, 45.1, 42.6, 41.8, 30.2, 29.0, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{20}O_2Na$, 303.1361; found: 303.1356.



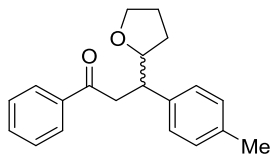
1-Phenyl-3-(tetrahydrofuran-2-yl)-3-(*o*-tolyl)propan-1-one (2h)

Colorless oil, 40.0 mg (0.136 mmol, 68% yield), 1:1 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 – 7.82 (m, 4H), 7.60 – 7.48 (m, 2H), 7.48 – 7.33 (m, 4H), 7.26 – 6.97 (m, 8H), 4.24 – 4.01 (m, 2H), 4.01 – 3.86 (m, 2H), 3.87 – 3.64 (m, 4H), 3.57 – 3.42 (m, 2H), 3.33 (dd, *J* = 17.9, 9.8 Hz, 2H), 2.46 (d, *J* = 9.0 Hz, 6H), 2.04 – 1.59 (m, 6H), 1.62 – 1.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2, 199.0, 140.9, 139.9, 137.4, 137.2, 137.0, 136.7, 132.9, 132.7, 130.5, 130.1, 128.5, 128.4, 128.1, 128.0, 127.4, 126.4, 126.2, 126.2, 126.1, 125.9, 83.4, 82.0, 68.1, 68.0, 43.2, 41.9, 41.0, 39.1, 29.8, 28.8, 26.1, 25.7, 20.3, 20.3; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{22}O_2Na$, 317.1517; found: 317.1514.



1-Phenyl-3-(tetrahydrofuran-2-yl)-3-(*m*-tolyl)propan-1-one (2i)

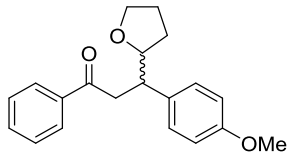
Colorless oil, 41.7 mg (0.142 mmol, 71% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 – 7.87 (m, 4.5H), 7.57 – 7.46 (m, 3H), 7.46 – 7.37 (m, 4.5H), 7.20 – 7.10 (m, 4.5H), 7.10 – 7.02 (m, 3H), 7.02 – 6.94 (m, 3H), 4.21 – 4.11 (m, 1H), 4.07 (dt, *J* = 9.0, 6.6 Hz, 1.5H), 3.90 – 3.79 (m, 1.5H), 3.76 (dd, *J* = 14.1, 7.8 Hz, 1.5H), 3.69 (ddd, *J* = 20.2, 12.5, 6.1 Hz, 3H), 3.58 – 3.46 (m, 2H), 3.46 – 3.39 (m, 1H), 3.35 (td, *J* = 8.9, 4.3 Hz, 1.5H), 3.33 – 3.21 (m, 2H), 2.31 (d, *J* = 5.1 Hz, 7.5H), 1.95 – 1.63 (m, 7H), 1.59 – 1.45 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.0, 198.9, 142.2, 141.3, 137.9, 137.5, 137.5, 137.3, 132.9, 132.6, 129.8, 129.0, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.4, 127.3, 125.9, 125.2, 82.8, 81.8, 68.3, 68.0, 46.8, 45.0, 42.6, 41.7, 30.2, 29.0, 25.9, 25.6, 21.5; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{22}O_2Na$, 317.1517; found: 317.1513.



1-Phenyl-3-(tetrahydrofuran-2-yl)-3-(*p*-tolyl)propan-1-one (2j)

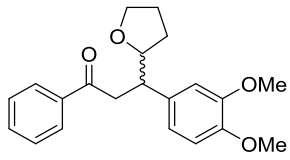
Colorless oil, 44.9 mg (0.153 mmol, 76% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (t, *J* = 7.2 Hz, 4.5H), 7.62 – 7.48 (m, 3H), 7.48 – 7.36 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 3H), 7.10 (d, *J* = 7.2 Hz, 5H), 4.18 (td, *J* = 7.0, 4.2 Hz, 1H), 4.14 – 4.03 (m, 1.5H), 3.93 – 3.64 (m, 6H), 3.61 – 3.20 (m, 6.5H), 2.31 (d, *J* = 3.7 Hz, 7.5H), 2.00 – 1.46 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 198.9, 139.2, 138.2, 137.4, 137.3, 136.1, 136.0, 132.8, 132.6, 129.1, 128.9, 128.5, 128.4, 128.1, 128.0, 128.0, 82.8, 81.9, 77.3, 77.0, 76.8, 68.3, 68.0, 46.5, 44.7, 42.7, 41.8, 30.1, 29.0, 25.9, 25.6, 21.0; HRMS-ESI (m/z) $[M+Na]^+$ calcd

for $C_{20}H_{22}O_2Na$, 317.1517; found: 317.1513.



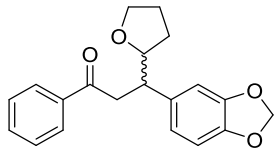
3-(4-Methoxyphenyl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2k)

Colorless oil, 46.6 mg (0.150 mmol, 75% yield), 3:2 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (t, *J* = 8.9 Hz, 4.5H), 7.57 – 7.44 (m, 3H), 7.45 – 7.33 (m, 4.5H), 7.23 (d, *J* = 9.1 Hz, 2.5H), 7.15 (d, *J* = 8.5 Hz, 3.5H), 6.76 (dd, *J* = 21.0, 19.4 Hz, 4.5H), 4.13 (dd, *J* = 10.9, 6.8 Hz, 1H), 4.01 (dt, *J* = 33.1, 16.6 Hz, 1.5H), 3.89 – 3.78 (m, 2H), 3.79 – 3.70 (m, 8H), 3.70 – 3.60 (m, 3.5H), 3.52 – 3.37 (m, 3H), 3.37 – 3.16 (m, 3.5H), 1.94 – 1.63 (m, 7H), 1.59 – 1.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 199.0, 158.2, 158.2, 137.4, 137.2, 134.3, 133.3, 132.8, 132.6, 129.9, 129.1, 128.4, 128.4, 128.1, 128.0, 113.8, 113.5, 82.8, 81.9, 68.3, 68.0, 55.1, 55.1, 46.1, 44.2, 42.7, 42.0, 30.1, 29.0, 25.9, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{22}O_3Na$, 333.1497; found: 333.1462.



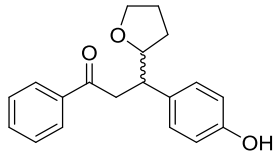
3-(3,4-Dimethoxyphenyl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2l)

Colorless oil, 47.5 mg (0.153 mmol, 70% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (t, *J* = 7.6 Hz, 4.5H), 7.60 – 7.49 (m, 3H), 7.49 – 7.36 (m, 4.5H), 6.97 – 6.83 (m, 2H), 6.83 – 6.71 (m, 6H), 4.25 – 4.18 (m, 1H), 4.06 (dt, *J* = 15.7, 8.0 Hz, 1.5H), 3.92 – 3.80 (m, 16.5H), 3.80 – 3.61 (m, 6H), 3.51 – 3.44 (m, 2.5H), 3.42 – 3.18 (m, 2.5H), 2.00 – 1.68 (m, 7H), 1.64 – 1.44 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.3, 199.1, 148.7, 148.5, 147.6, 137.5, 137.3, 134.9, 133.9, 132.9, 132.7, 128.5, 128.4, 128.2, 128.1, 128.0, 121.1, 119.9, 112.3, 111.7, 111.1, 110.8, 82.8, 81.9, 68.4, 68.0, 55.9, 55.9, 55.8, 55.8, 46.6, 44.8, 42.7, 42.1, 30.2, 29.1, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{21}H_{24}O_4Na$, 363.1572; found: 363.1567.



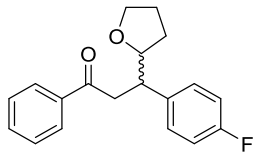
3-(Benzo[*d*][1,3]dioxol-5-yl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2m)

Colorless oil, 41.0 mg (0.126 mmol, 63% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 – 7.85 (m, 4.5H), 7.61 – 7.47 (m, 3H), 7.47 – 7.36 (m, 5H), 6.91 – 6.65 (m, 7.5H), 5.96 – 5.83 (m, 5H), 4.18 – 4.06 (m, 1H), 4.06 – 3.93 (m, 1.5H), 3.90 – 3.79 (m, 1.5H), 3.79 – 3.58 (m, 5H), 3.49 – 3.38 (m, 3H), 3.34 – 3.19 (m, 3H), 1.97 – 1.66 (m, 7H), 1.63 – 1.45 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.0, 198.8, 147.6, 147.4, 146.1, 137.4, 137.2, 136.1, 135.1, 132.9, 132.7, 128.5, 128.4, 128.1, 128.0, 122.2, 121.3, 109.2, 108.4, 108.2, 107.9, 100.8, 100.8, 82.8, 81.9, 68.3, 68.0, 46.6, 44.8, 42.7, 42.1, 30.1, 29.1, 25.9, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{20}O_4Na$, 347.1259; found: 347.1256.



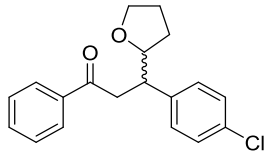
3-(4-Hydroxyphenyl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2n)

Pale yellow solid, 36.0 mg (0.121 mmol, 61% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 – 7.87 (m, 4.5H), 7.53 (dd, *J* = 10.3, 4.3 Hz, 3H), 7.43 (t, *J* = 7.5 Hz, 5H), 7.14 (t, *J* = 9.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 3H), 6.66 (dd, *J* = 9.5, 8.4 Hz, 5H), 6.01 (br, 2.5H), 4.25 – 4.15 (m, 1H), 4.07 (dt, *J* = 13.2, 6.6 Hz, 1.5H), 3.95 – 3.63 (m, 7H), 3.47 (s, 2.5H), 3.39 – 3.20 (m, 3H), 1.95 – 1.45 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.1, 199.5, 154.6, 137.2, 137.1, 133.6, 133.1, 132.9, 132.7, 130.0, 129.2, 128.5, 128.5, 128.2, 115.4, 115.2, 82.9, 82.2, 68.3, 68.1, 46.4, 44.5, 42.8, 42.1, 30.1, 29.1, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{20}O_3Na$, 319.1310; found: 319.1305.



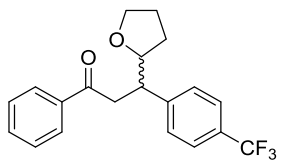
3-(4-Fluorophenyl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2o)

Colorless oil, 44.7 mg (0.150 mmol, 75% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 – 7.89 (m, 4.5H), 7.61 – 7.49 (m, 2.5H), 7.49 – 7.39 (m, 5H), 7.37 – 7.19 (m, 5.5H), 7.02 – 6.92 (m, 5H), 4.17 (td, *J* = 7.2, 4.1 Hz, 1H), 4.13 – 3.96 (m, 1.5H), 3.93 – 3.63 (m, 6H), 3.58 – 3.23 (m, 6H), 1.97 – 1.66 (m, 7H), 1.62 – 1.44 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.9, 198.7, 163.3, 163.2, 160.1, 156.0, 138.0, 138.0, 137.3, 137.1, 137.0, 136.9, 133.03 132.8, 130.6, 130.5, 129.7, 129.6, 128.6, 128.5, 128.1, 128.0, 115.4, 115.1, 115.1, 114.8, 82.6, 81.7, 68.3, 68.1, 46.1, 44.3, 42.5, 42.1, 30.1, 29.1, 25.9, 25.7; ^{19}F NMR (375 MHz, $CDCl_3$) δ = −116.4 (1.5F), −116.7 (1F); HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{19}FO_2Na$, 321.1267; found: 321.1261.



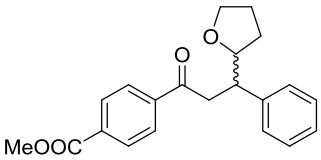
3-(4-Chlorophenyl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2p)

Colorless oil, 48.5 mg (0.154 mmol, 77% yield), 3:2 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (t, *J* = 8.3 Hz, 4H), 7.55 – 7.45 (m, 2.5H), 7.45 – 7.38 (m, 4.5H), 7.30 – 7.14 (m, 9H), 4.16 – 4.08 (m, 1H), 4.01 (m, *J* = 15.3, 6.8 Hz, 1.5H), 3.87 – 3.77 (m, 2H), 3.79 – 3.71 (m, 1.5H), 3.71 – 3.63 (m, 3H), 3.52 – 3.41 (m, 3H), 3.41 – 3.31 (m, 1.5H), 3.32 – 3.20 (m, 1.5H), 1.92 – 1.62 (m, 7H), 1.53 – 1.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 198.5, 140.8, 139.8, 137.2, 137.1, 133.1, 132.9, 132.3, 130.5, 129.6, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 82.4, 81.6, 68.3, 68.1, 46.2, 44.4, 42.3, 41.9, 30.1, 29.1, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{19}ClO_2Na$, 337.0971; found: 337.0968.



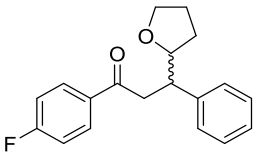
3-(4-Trifluoromethyl)-1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2q)

Colorless oil, 38.2 mg (0.110 mmol, 55% yield), 1:1 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (t, *J* = 8.1 Hz, 3H), 7.57 – 7.49 (m, 5H), 7.49 – 7.37 (m, 8H), 4.18 (dd, *J* = 12.0, 7.3 Hz, 1H), 4.07 (dd, *J* = 15.4, 6.9 Hz, 1H), 3.86 (dd, *J* = 14.6, 7.4 Hz, 1H), 3.81 – 3.67 (m, 4H), 3.63 – 3.57 (m, 1H), 3.53 – 3.48 (m, 2H), 3.46 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.34 (dd, *J* = 17.1, 9.3 Hz, 1H), 1.97 – 1.68 (m, 6H), 1.52 – 1.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.4, 198.2, 146.5, 145.6, 137.1, 137.0, 133.1, 133.0. 129.4, 128.8 (q, *J* = 32.2 Hz), 128.8 (q, *J* = 32.2 Hz), 128.6, 128.6, 128.5, 128.0, 128.0, 125.4 (q, *J* = 3.7 Hz), 125.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 286.9 Hz), 124.2 (q, *J* = 287.0 Hz), 82.2, 81.5, 68.3, 68.1, 46.5, 44.8, 42.0, 41.8, 30.1, 29.2, 25.8, 25.6; ^{19}F NMR (375 MHz, $CDCl_3$) δ = −62.5 (3F), −62.5 (3F); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{20}H_{20}F_3O_2$, 349.1415; found: 349.1411.



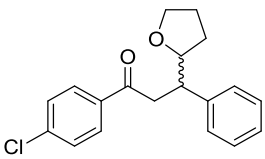
Methyl 4-(3-phenyl-3-(tetrahydrofuran-2-yl)propanoyl)benzoate (2r)

Colorless oil, 33.9 mg (0.101 mmol, 50% yield), 2:1 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (dd, *J* = 8.5, 1.9 Hz, 6H), 7.97 (t, *J* = 7.7 Hz, 6H), 7.38 – 7.10 (m, 15H), 4.20 (td, *J* = 7.2, 3.7 Hz, 1H), 4.15 – 4.05 (m, 2H), 3.96 (d, *J* = 0.9 Hz, 9H), 3.90 – 3.67 (m, 8H), 3.62 – 3.45 (m, 3H), 3.45 – 3.24 (m, 4H), 1.99 – 1.65 (m, 9H), 1.65 – 1.45 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7, 198.5, 166.3, 166.3, 142.0, 141.0, 140.7, 140.5, 133.7, 133.5, 129.8, 129.7, 129.0, 128.6, 128.2, 128.2, 128.0, 127.9, 126.8, 126.7, 82.7, 81.7, 68.3, 68.0, 52.4, 47.1, 45.0, 43.1, 42.1, 30.2, 29.7, 28.9, 25.9, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{21}H_{22}O_4Na$, 361.1416; found: 361.1414.



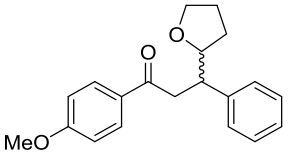
1-(4-Fluorophenyl)-3-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2s)

Colorless oil, 42.4 mg (0.142 mmol, 71% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 – 7.90 (m, 4.5H), 7.35 – 7.30 (m, 3H), 7.30 – 7.22 (m, 7.5H), 7.22 – 7.15 (m, 2.5H), 7.12 – 7.04 (m, 5H), 4.17 (td, *J* = 7.1, 4.0 Hz, 1H), 4.08 (dt, *J* = 9.2, 6.6 Hz, 1.5H), 3.88 – 3.80 (m, 1.5H), 3.79 – 3.73 (m, 1.5H), 3.72 – 3.64 (m, 3.5H), 3.56 – 3.40 (m, 3H), 3.40 – 3.33 (m, 1.5H), 3.26 (dd, *J* = 16.5, 8.8 Hz, 1.5H), 1.93 – 1.65 (m, 7H), 1.58 – 1.46 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.4, 197.3, 165.6 (d, *J* = 254 Hz), 166.5 (d, *J* = 254 Hz), 142.1, 141.1, 133.8 (d, *J* = 3 Hz), 133.7 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.3 Hz), 130.6 (d, *J* = 9.3 Hz), 129.0, 128.5, 128.2, 128.1, 126.7, 126.6, 115.5 (d, *J* = 21.9 Hz), 115.4 (d, *J* = 21.8 Hz), 82.7, 81.7, 68.3, 68.0, 47.0, 45.1, 42.5, 41.6, 30.2, 29.0, 25.9, 25.6; ^{19}F NMR (375 MHz, $CDCl_3$) δ = −105.6 (1F), −106.1 (1.5F); HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{19}FO_2Na$, 321.1267; found: 321.1262.



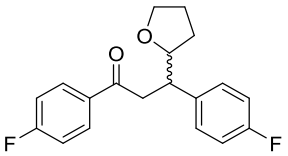
1-(4-Chlorophenyl)-3-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2t)

Colorless oil, 45.2 mg (0.144 mmol, 72% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 – 7.81 (m, 4.5H), 7.46 – 7.36 (m, 5H), 7.36 – 7.17 (m, 13H), 4.19 (td, *J* = 7.1, 4.0 Hz, 1H), 4.10 (dt, *J* = 9.1, 6.6 Hz, 1.5H), 3.90 – 3.65 (m, 7H), 3.59 – 3.43 (m, 2.5H), 3.43 – 3.33 (m, 1.5H), 3.26 (dd, *J* = 16.2, 8.7 Hz, 1.5H), 2.01 – 1.63 (m, 7H), 1.63 – 1.44 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.8, 197.7, 142.1, 141.1, 139.3, 139.1, 135.8, 135.6, 129.5, 129.5, 129.1, 128.8, 128.7, 128.5, 128.2, 126.7, 126.7, 82.7, 81.7, 68.3, 68.0, 47.1, 45.1, 42.6, 41.7, 30.2, 29.0, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{19}ClO_2Na$, 337.0971; found: 337.0965.



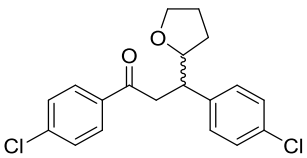
1-(4-Methoxyphenyl)-3-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2u)

Colorless oil, 47.9 mg (0.154 mmol, 77% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 – 7.85 (m, 4.5H), 7.39 – 7.12 (m, 13.5H), 6.95 – 6.85 (m, 4.5H), 4.19 (dt, *J* = 10.7, 7.0 Hz, 1H), 4.11 (dt, *J* = 8.9, 6.7 Hz, 1.5H), 3.93 – 3.61 (m, 14.5H), 3.6 – 3.5 (m, 1H), 3.42 (ddd, *J* = 12.8, 8.7, 4.8 Hz, 3H), 3.30 (dd, *J* = 16.0, 9.0 Hz, 1.5H), 2.01 – 1.63 (m, 7H), 1.63 – 1.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.5, 197.4, 163.4, 163.2, 142.4, 141.5, 130.5, 130.4, 130.3, 129.1, 128.4, 128.3, 128.1, 126.6, 126.5, 113.6, 113.6, 82.7, 81.8, 68.3, 68.0, 55.4, 46.9, 45.2, 42.1, 41.5, 30.2, 29.1, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{22}O_3Na$, 333.1467; found: 333.1462.



1,3-Bis(4-fluorophenyl)-3-(tetrahydrofuran-2-yl)propan-1-one (2v)

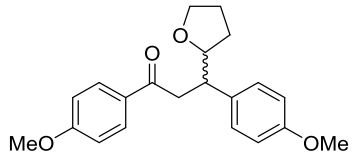
Colorless oil, 42.9 mg (0.136 mmol, 68% yield), 3:2 mixture of diastereomers; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 – 7.89 (m, 4.5H), 7.36 – 7.27 (m, 2.5H), 7.27 – 7.18 (m, 3H), 7.15 – 7.04 (m, 5H), 7.04 – 6.91 (m, 5H), 4.20 – 4.11 (m, 1H), 4.11 – 3.99 (m, 1.5H), 3.94 – 3.62 (m, 7H), 3.59 – 3.32 (m, 4H), 3.25 (dd, *J* = 16.4, 9.1 Hz, 1.5H), 1.98 – 1.65 (m, *J* = 20.1, 14.0, 7.3, 5.1 Hz, 7H), 1.60 – 1.39 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.3, 197.1, 165.7 (d, *J* = 254.6 Hz), 165.5 (d, *J* = 254.2 Hz), 163.2 (d, *J* = 244.6 Hz), 163.1 (d, *J* = 254.7 Hz), 137.8 (d, *J* = 3.3 Hz), 136.8 (d, *J* = 3.3 Hz), 133.7 (d, *J* = 3.0 Hz), 133.6 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.3 Hz), 130.6 (d, *J* = 9.4 Hz), 130.5 (d, *J* = 7.6 Hz), 129.6 (d, *J* = 7.8 Hz), 115.6 (d, *J* = 22.0 Hz), 115.5 (d, *J* = 21.8 Hz), 115.3 (d, *J* = 21.2 Hz), 114.5 (d, *J* = 21 Hz), 82.6, 81.6, 68.3, 68.1, 46.2, 44.3, 42.5, 42.0, 30.2, 29.0, 25.9, 25.7; ^{19}F NMR (375 MHz, $CDCl_3$) δ = −105.4 (1F), −105.8 (1.5F), −116.3 (1.5F), −116.5 (1F); HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{18}F_2O_2Na$, 339.1173; found: 339.1168.



1,3-Bis(4-chlorophenyl)-3-(tetrahydrofuran-2-yl)propan-1-one (2w)

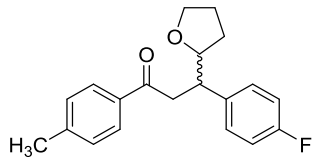
Colorless oil, 54.3 mg (0.155 mmol, 78% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 11.5, 8.6 Hz, 5H), 7.39 (dd, *J* = 8.3, 4.7 Hz, 5H), 7.28 – 7.21 (m, 7H), 7.18 (d, *J* = 8.3 Hz, 3H), 4.15 – 4.09 (m, 1H), 4.05 – 3.98 (m, 1.5H), 3.83 (dd, *J* = 14.6, 7.2 Hz, 2H), 3.75 (dd, *J* = 14.2, 7.6 Hz, 1.5H), 3.71

– 3.63 (m, 3.5H), 3.52 – 3.46 (m, 1H), 3.43 (dd, *J* = 11.6, 6.6 Hz, 1.5H), 3.33 (td, *J* = 9.0, 4.2 Hz, 1.5H), 3.21 (dd, *J* = 16.8, 9.1 Hz, 1.5H), 1.94 – 1.65 (m, 7H), 1.57 – 1.42 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.5, 197.3, 140.6, 139.5, 139.5, 139.3, 135.5, 135.4, 132.4, 130.4, 129.5, 129.5, 129.4, 128.8, 128.8, 128.6, 128.3, 82.4, 81.5, 68.3, 68.1, 46.3, 44.4, 42.3, 41.8, 30.2, 29.0, 25.8, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{18}Cl_2O_2Na$, 371.0582; found: 371.0577.



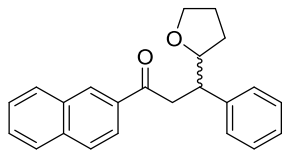
1,3-Bis(4-methoxyphenyl)-3-(tetrahydrofuran-2-yl)propan-1-one (2x)

Colorless oil, 54.4 mg (0.160 mmol, 80% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 13.0, 8.9 Hz, 4.5H), 7.27 – 7.22 (m, 2.5H), 7.16 (d, *J* = 8.6 Hz, 3H), 6.91 – 6.86 (m, 5H), 6.82 – 6.77 (m, 5H), 4.16 – 4.10 (m, 1H), 4.07 – 4.00 (m, 1.5H), 3.88 – 3.82 (m, 10H), 3.78 – 3.73 (m, 8.5H), 3.72 – 3.65 (m, 2H), 3.61 (dd, *J* = 16.6, 4.1 Hz, 1.5H), 3.50 – 3.43 (m, 1H), 3.39 (dd, *J* = 14.2, 6.8 Hz, 1.5H), 3.31 (td, *J* = 9.0, 3.9 Hz, 1.5H), 3.22 (dd, *J* = 16.2, 9.2 Hz, 1.5H), 1.93 – 1.64 (m, 7H), 1.57 – 1.45 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.7, 197.5, 163.3, 163.1, 158.1, 158.1, 134.4, 133.4, 130.5, 130.4, 130.4, 130.3, 129.9, 129.1, 113.8, 113.6, 113.5, 113.5, 82.9, 81.9, 68.3, 68.0, 55.4, 55.1, 46.1, 44.4, 42.2, 41.7, 30.1, 29.1, 25.9, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{21}H_{24}O_4Na$, 363.1572; found: 363.1567.



3-(4-Fluorophenyl)-3-(tetrahydrofuran-2-yl)-1-(p-tolyl)propan-1-one (2y)

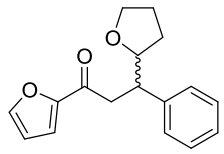
Colorless oil, 43.5 mg (0.139 mmol, 70% yield), 3:2 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (t, *J* = 8.7 Hz, 4.5H), 7.31 – 7.25 (m, 2.5H), 7.23 – 7.16 (m, 8H), 6.93 (t, *J* = 8.6 Hz, 5H), 4.15 – 4.09 (m, 1H), 4.06 – 3.97 (m, 1.5H), 3.87 – 3.79 (m, 2H), 3.79 – 3.71 (m, 1.5H), 3.70 – 3.64 (m, 2.5H), 3.61 (d, *J* = 4.0 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.44 – 3.32 (m, 3H), 3.24 (dd, *J* = 16.5, 9.3 Hz, 1.5H), 2.37 (d, *J* = 2.3 Hz, 7.5H), 1.94 – 1.60 (m, 7H), 1.54 – 1.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 198.2, 161.6 (d, *J* = 244.4 Hz), 161.5 (d, *J* = 244.5 Hz), 143.8, 143.5, 138.0 (d, *J* = 3.3 Hz), 137.0 (d, *J* = 3.2 Hz), 134.8, 134.6, 130.4 (d, *J* = 7.7 Hz), 129.6 (d, *J* = 7.8 Hz), 129.2, 129.1, 128.2, 128.1, 115.2 (d, *J* = 21.1 Hz), 114.8 (d, *J* = 21.0 Hz), 82.6, 81.7, 68.3, 68.1, 46.0, 44.4, 42.3, 41.9, 30.1, 29.1, 25.8, 25.6, 21.6; ^{19}F NMR (375 MHz, $CDCl_3$) δ = −116.5 (1.5F), −116.8 (1F); HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{21}FO_2Na$, 335.1423; found: 335.1418.



1-(Naphthalen-2-yl)-3-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2z)

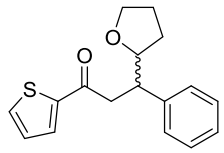
Pale yellow solid, 28.3 mg (0.086 mmol, 43% yield), 3:2 mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 11.1 Hz, 2.5H), 8.01 – 7.91 (m, 5H), 7.87 – 7.82 (m, 4.5H), 7.60 – 7.50 (m, 5H), 7.37 (d, *J* = 7.6 Hz, 1.5H), 7.32 – 7.24 (m, 8.5H), 7.23 – 7.14 (m, 3H), 4.23 (td, *J* = 7.0, 3.7 Hz, 1H), 4.17 – 4.09 (m, 1.5H), 3.91 – 3.81 (m, 3H), 3.81 – 3.75 (m, 1.5H), 3.75 – 3.67 (m, 2H), 3.67 – 3.58 (m, 2.5H), 3.48 – 3.39 (m, 3.5H), 1.96 – 1.67 (m, 7H), 1.60 – 1.52 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.9, 198.8, 142.3, 141.3, 135.4, 134.7,

132.5, 129.7, 129.6, 129.5, 129.5, 129.1, 128.5, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 127.7, 127.7, 126.7, 126.6, 126.6, 1240, 123.9, 82.8, 81.8, 68.3, 68.0, 47.1, 45.2, 42.6, 41.9, 30.2, 29.1, 25.9, 25.7; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{23}H_{22}O_2Na$, 353.1517; found: 353.1513.



1-(Furan-2-yl)-3-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (2aa)

Colorless oil, 30.4 mg (0.112 mmol, 56% yield), 3:2 mixture of diastereomers; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2.5H), 7.29 – 7.21 (m, 8H), 7.21 – 7.15 (m, 3H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.10 (d, *J* = 3.5 Hz, 1.5H), 6.49 – 6.44 (m, 2H), 4.19 – 4.13 (m, 1H), 4.11 – 4.04 (m, 1.5H), 3.87 – 3.80 (m, 2H), 3.78 – 3.71 (m, 1.5H), 3.71 – 3.66 (m, 2H), 3.54 – 3.47 (m, 2.5H), 3.37 (td, *J* = 8.8, 5.3 Hz, 1.5H), 3.31 (dd, *J* = 7.1, 4.5 Hz, 1.5H), 3.18 – 3.11 (m, 1.5H), 1.93 – 1.65 (m, 7H), 1.58 – 1.49 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.0, 187.9, 153.0, 152.9, 146.2, 146.0, 141.9, 141.0, 129.0, 128.4, 128.2, 128.1, 126.7, 126.6, 117.1, 116.6, 112.1, 112.0, 82.7, 81.7, 68.3, 68.0, 46.7, 45.1, 42.3, 41.6, 30.1, 29.0, 25.8, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{18}O_3Na$, 293.1154; found: 293.1148.



3-Phenyl-3-(tetrahydrofuran-2-yl)-1-(thiophen-2-yl)propan-1-one (2ab)

Colorless oil, 33.4 mg (0.117 mmol, 58% yield), 3:2 mixture of diastereomers; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (ddd, *J* = 9.5, 3.8, 1.1 Hz, 2.5H), 7.59 (ddd, *J* = 7.9, 5.0, 1.0 Hz, 2.5H), 7.39 – 7.30 (m, 2.5H), 7.31 – 7.25 (m, 7H), 7.25 – 7.16 (m, 3H), 7.13 – 7.06 (m, 2.5H), 4.24 – 4.16 (m, 1H), 4.16 – 4.06 (m, 1.5H), 3.93 – 3.59 (m, 7H), 3.59 – 3.50 (m, 1H), 3.47 – 3.34 (m, 3H), 3.26 (dd, *J* = 15.9, 8.8 Hz, 1.5H), 1.99 – 1.65 (m, 7H), 1.58 – 1.50 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.8, 191.8, 144.8, 144.6, 142.0, 141.0, 133.5, 133.2, 132.0, 131.6, 129.1, 128.5, 128.2, 128.2, 128.0, 127.9, 126.7, 126.7, 82.6, 81.6, 68.3, 68.1, 47.0, 45.4, 43.3, 42.7, 30.2, 29.1, 25.9, 25.6; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{18}O_2SNa$, 309.0925; found: 309.0920.

5. Cyclic Voltammetry Data

CV measurements of the substrate and Ni-added substrate were carried out as outlined below.

(a) Calibration of the Reference Electrode

<Electrode Composition>

Working electrode: glassy carbon.

Reference electrode: Ag/AgCl in KCl (aq).

Counter electrode: Pt sheet.

<Procedure>

Ferrocene (**Fc**, 0.001 M) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in acetonitrile (20 mL) were transferred to an electrochemical cell equipped with the above three-electrode system. The cyclic voltammogram was obtained using a potentiostat with a scan rate 0.1 V/s and a scan range of 0.0 to 0.6 V.

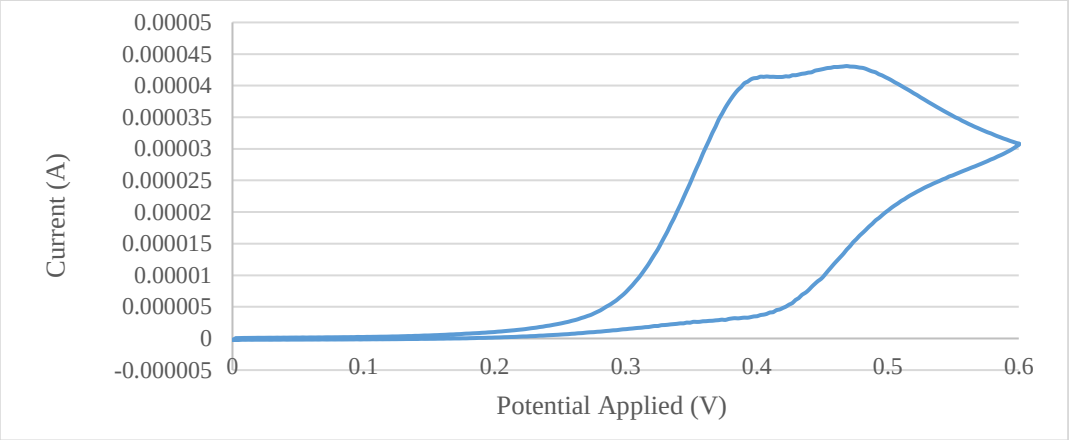


Figure S1. Cyclic Voltammogram of Fc/Fc$^+$

Measured: $E_{1/2}$[**Fc**/**Fc**$^+$] = 0.443 V vs Ag/AgCl

Reference: $E_{1/2}$[**Fc**/**Fc**$^+$] = 0.380 V vs S.C.E. (Saturated Calomel Electrode)

The conversion constant was measured to be +0.063 V (theoretical: +0.044 V)

(b) Enone 1a

<Electrode Composition>

Working electrode: glassy carbon.

Reference electrode: Ag/AgCl in KCl (aq).

Counter electrode: Pt sheet.

<Procedure>

1a (0.001 M) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in acetonitrile (20 mL) were transferred to an electrochemical cell equipped with the above three-electrode system. The cyclic voltammogram was obtained by using a potentiostat with a scan rate 0.05 V/s and a scan range of −2.5 to 1.0 V.

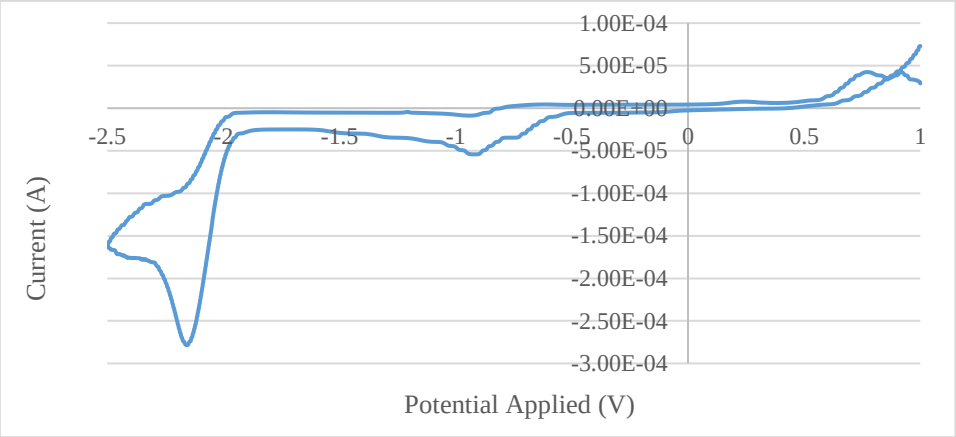


Figure S2. Cyclic Voltammogram of 1a/1a^{-}

The peak reduction potential of **1a/1a**$^{-}$ was observed to be −2.16 V (or −2.10 V vs. S.C.E.). This result clearly indicates that the reduction of **1a** by the Ir photocatalyst (E^{o} [Ir(II)/Ir(III)] = −1.37 V) is not feasible. This data also corresponds well with the estimated reduction potential reported in the literature[8] (see also the empirical formula and the experimental data for **1b**).

(c) Enone 1a + Ni catalyst

<Electrode Composition>

Working electrode: glassy carbon.

Reference electrode: Ag/AgCl in KCl (aq).

Counter electrode: Pt sheet.

<Procedure>

1a (0.001 M), $NiBr_2$·glyme (0.001 M), BiOx (0.0015 M) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in acetonitrile (20 mL) were transferred to an electrochemical cell equipped with the above three-electrode system. The cyclic voltammogram was obtained by using a potentiostat with a scan rate 0.05 V/s and a scan range of −2.5 to 1.0 V.

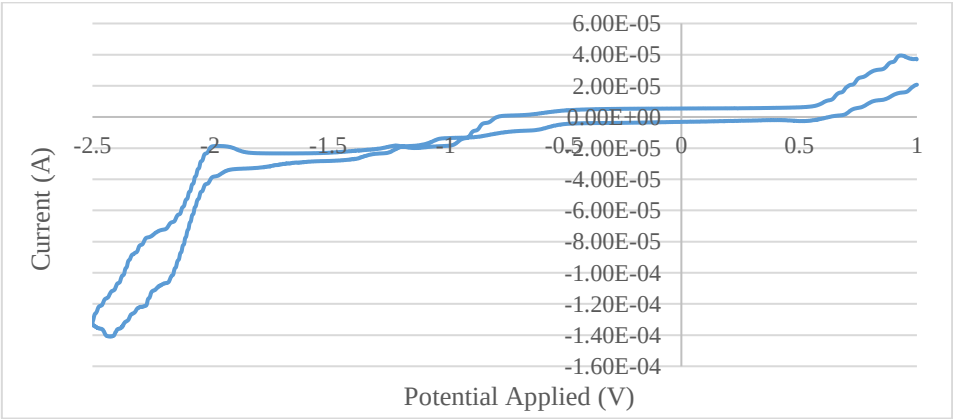
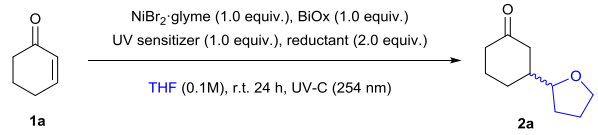


Figure S3. Cyclic Voltammogram of 1a/1a^{-} + Ni Catalyst

The cyclic voltammogram indicates that even under Ni activation, the reduction of **1a** by the photocatalyst fails to take place (E^{o} < −2.0 V). The new complex patterns correspond to the Ni redox processes.

6. UV Sensitizer Study

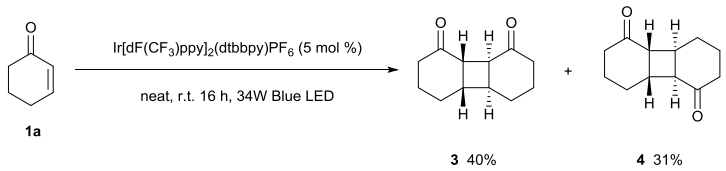
For the experiments outlined in Scheme 2a (see the main manuscript for further details), the following procedure was employed.



To a quartz tube equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (61.7 mg, 0.20 mmol, 1.0 equiv.), BiOx (2,2'-bis(2-oxazoline)) (28.0 mg, 0.20 mmol, 1.0 equiv.), and THF (2.0 mL). The resulting solution was stirred for 5 min to give a green suspension before indicated UV sensitizer (0.20 mmol, 1.0 equiv), Mn powder (dried at 120 °C overnight, 22.0 mg, 0.4 mmol, 2.0 equiv.) where indicated, and **1a** (19.2 mg, 0.20 mmol, 1.0 equiv) were added. This mixture was stirred for 24 h under UV lamp irradiation with fan cooling. After this time, dodecane (20.0 µL, 0.088 mmol) was added as an internal standard, and the product yield was determined by GC.

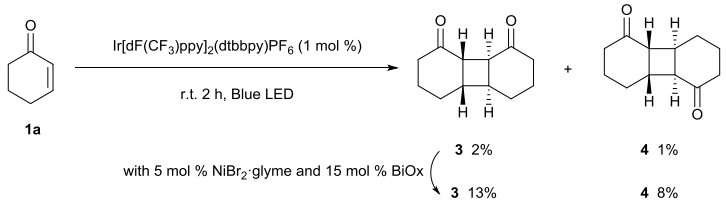
7. Photodimerization Study

For the experiments shown in Scheme 2b (see the main manuscript for further details), the following procedure was employed:



To a vial equipped with a PTFE-coated stirrer bar were added **1a** (192 mg, 2.0 mmol, 1.0 equiv) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (112.2 mg, 0.1 mmol, 0.05 equiv.). The photocatalyst was soluble in **1a** and gave a homogeneous solution. The resulting mixture was stirred for 16 h under 34W blue LED irradiation with fan cooling, after which time the resulting crude mixture was filtered through a short pad of Celite®, eluted with CH_2Cl_2, and concentrated under reduced pressure. The obtained residue was analyzed by ^1H NMR spectroscopy to determine the yields of the dimerized products.

To check the effect of the Ni catalyst in the dimerization event, the dimerization experiments were also conducted with a shortened reaction time and a lowered catalyst loading as follows:



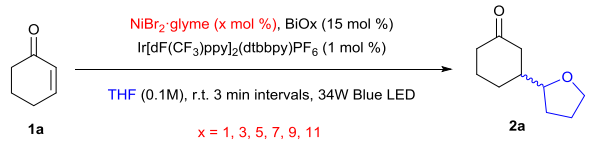
Procedure without the Ni catalyst: To a vial equipped with a PTFE-coated stirrer bar were added **1a** (192 mg, 2.0 mmol, 1.0 equiv) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (22.4 mg, 0.02 mmol, 0.01 equiv.). The photocatalyst was soluble in **1a** and gave a homogeneous solution. The resulting mixture was stirred for 2 h under 34W blue LED irradiation with fan cooling, after which time the resulting crude mixture was filtered through a short pad of Celite®, eluted with CH_2Cl_2, and concentrated under reduced pressure. The obtained residue was analyzed GC following the addition of dodecane (200 µL) to determine the yields of the dimerized products.

Procedure with Ni catalyst: To a vial equipped with a PTFE-coated stirrer bar were added **1a** (192 mg, 2.0 mmol, 1.0 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (22.4 mg, 0.02 mmol, 0.01 equiv.), $NiBr_2$·glyme (30.8 mg, 0.1 mmol, 0.05 equiv.), and BiOx (2,2'-bis(2-oxazoline)) (42.0 mg, 0.3 mmol, 0.15 equiv.). The resulting mixture was stirred for 2 h under 34W blue LED irradiation with fan cooling, after which time the resulting crude mixture was filtered

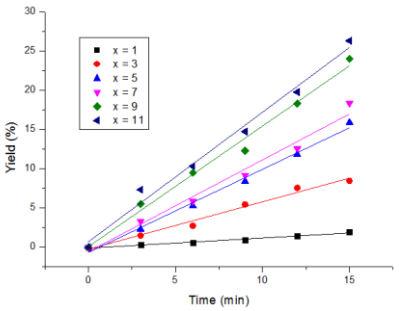
through a short pad of Celite®, eluted with CH_2Cl_2, and concentrated under reduced pressure. The obtained residue was analyzed GC following the addition of dodecane (200 µL) to determine the yields of the dimerized products.

8. Ni Kinetic Order Experiments

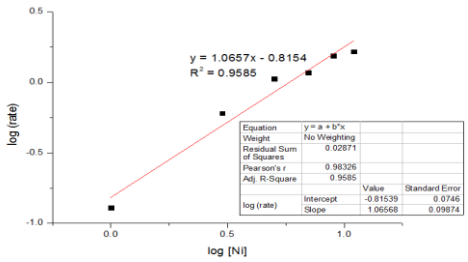
To determine the kinetic order with respect to the Ni catalyst, initial rate measurements and the determination of the kinetic order were carried out as follows:



To 6 vials equipped each with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (0.71 mg per 0.01 equiv., 0.002 mmol per 0.01 equiv., respectively 0.01, 0.03, 0.05, 0.07, 0.09, 0.11 equiv), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and THF (2.0 mL). The resulting solution was stirred for 5 min to give a green suspension prior to the addition of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.) and dodecane (20 µL, 0.088 mmol), and **1a** (19.2 mg, 0.20 mmol, 1.0 equiv). The resulting mixture was stirred under 34 W blue LED irradiation with fan cooling, and aliquots of each vial were taken every 3 min for analysis by GC to obtain the individual initial rates and determine the Ni kinetic order. The results are outlined below in Figure S4.



Equation	y = a + b*x						
Weight	No Weighting						
Residual Sum of Squares	0.05217	0.98932	1.34239	4.09455	4.15184	5.34503	
Pearson's r	0.99019	0.99147	0.99622	0.99064	0.99446	0.99383	
Adj. R-Square	0.9756	0.97877	0.99058	0.97671	0.9862	0.98461	
		Value	Standard Error				
x = 1	Intercept	-0.0961	0.08266				
	Slope	0.12899	0.0091				
x = 3	Intercept	-0.22605	0.35994				
	Slope	0.60303	0.03963				
x = 5	Intercept	-0.64971	0.41927				
	Slope	1.05936	0.04616				
x = 7	Intercept	-0.55705	0.73225				
	Slope	1.17023	0.08062				
x = 9	Intercept	0.08781	0.73736				
	Slope	1.53645	0.08118				
x = 11	Intercept	0.71157	0.83663				
	Slope	1.65019	0.09211				

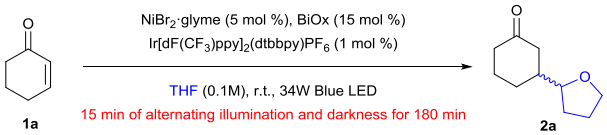


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.02871		
Pearson's r	0.98326		
Adj. R-Square	0.9585		
		Value	Standard Error
log (rate)	Intercept	-0.81539	0.0746
	Slope	1.06568	0.09874

Figure S4. Ni Kinetic Order Measurement

9. On/Off Study

For the on/off study, the following procedure was employed.



To a vial equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and THF (2.0 mL). The resulting solution was stirred for 5 min to give a green suspension prior to the addition of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002

mmol, 0.01 equiv.), dodecane (20 μL, 0.088 mmol), and **1a** (19.2 mg, 0.20 mmol, 1.0 equiv). The resulting mixture was then stirred in alternating illumination and darkness with intervals of 15 min (34 W blue LED irradiation with fan cooling or no irradiation). Aliquots of the reaction mixture were taken upon alternating and analyzed by GC to obtain the corresponding product yields. Product formation was observed only during illumination.

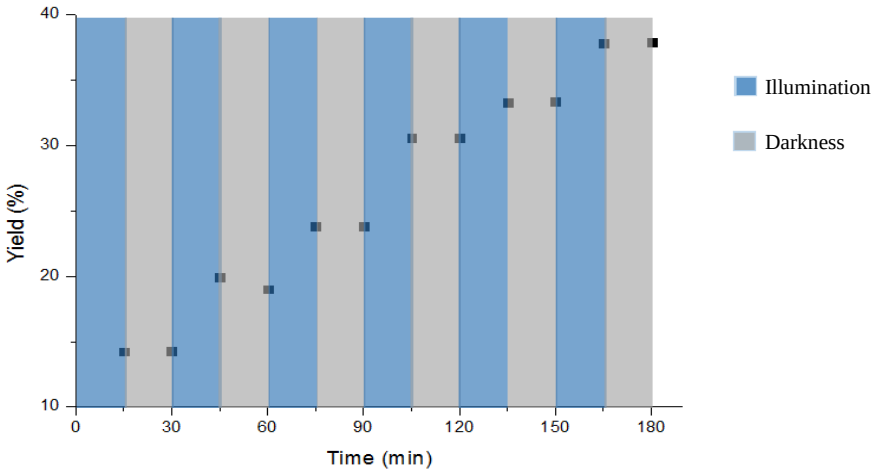


Figure S5. On/Off Study

10. Quantum Yield Measurement

Quantum yield was measured following a procedure reported by the Yoon group.[9]

<Actinometry>

The photon flux was measured following standard actinometry with potassium ferrioxalate. Potassium ferrioxlalate solution was prepared by dissolving 737 mg of potassium ferrioxalate in 15 mL of 0.05 M sulfuric acid. The solution was rigorously mixed for full solvation. Separately, 25 mg of 1,10-phenanthroline and 5.63 g of sodium acetate was dissolved in 25 mL of 0.5 M sulfuric acid. All solutions were handled in the dark at all times. 2.0 mL of the ferrioxalate solution was transferred to a cuvette and irradiated for 90.0 seconds at 436 nm with a slit size of 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the irradiated solution. Separately, 2.0 mL of the ferrioxalate solution was taken and mixed with 0.35 mL of the phenanthroline solution for comparison. After 1 h, the absorbance of the solutions was measured at 510 nm.

Conversion of the ferrioxalate solution could be calculated using the equation:

$$\text{mol } Fe^{2+} = \frac{V\Delta A}{l \cdot \varepsilon}$$

Here, V is the volume of the solution, ΔA is the difference in absorbance at 510 nm, l is the cuvette dimension, and ε is the molar absorption coefficient.

The photon flux could be calculated using the equation:

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\emptyset \cdot t \cdot f}$$

Here, $\emptyset$ is the quantum yield of ferrioxalate, t is the irradiation time, f is the fraction of light absorbed by the ferrioxalate solution at 436 nm.

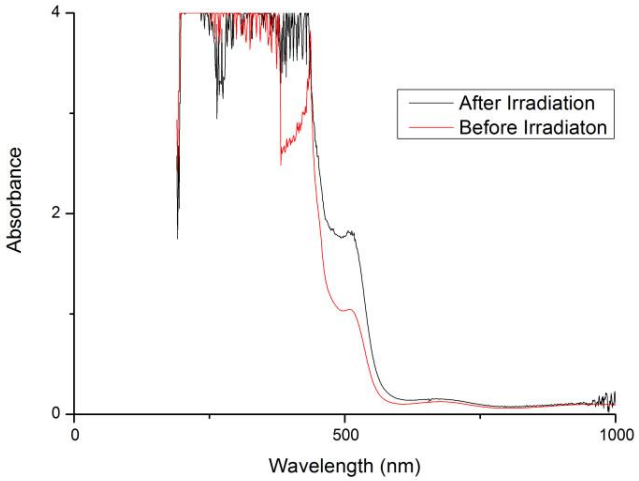


Figure S6. Absorbance of the Ferrioxalate Solutions

From the above absorption spectra, ΔA = 0.769123.

Therefore,

$$\text{mol } Fe^{2+} = \frac{V\Delta A}{l \cdot \varepsilon} = \frac{0.00235 \cdot 0.769123}{1 \cdot 11000} \text{ mol} = 1.628323 \times 10^{-7} \text{ mol}$$

Then,

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\emptyset \cdot t \cdot f} = \frac{1.628323 \cdot 10^{-7}}{1.01 \cdot 90 \cdot 0.99833} \text{ einstein/s} = 1.794331 \times 10^{-9} \text{ einstein/s}$$

<Absorption Spectrum of 1 mM Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 in THF>

For quantum yield measurement, absorption spectrum of 1 mM Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 in THF was obtained to match the standard reaction condition.

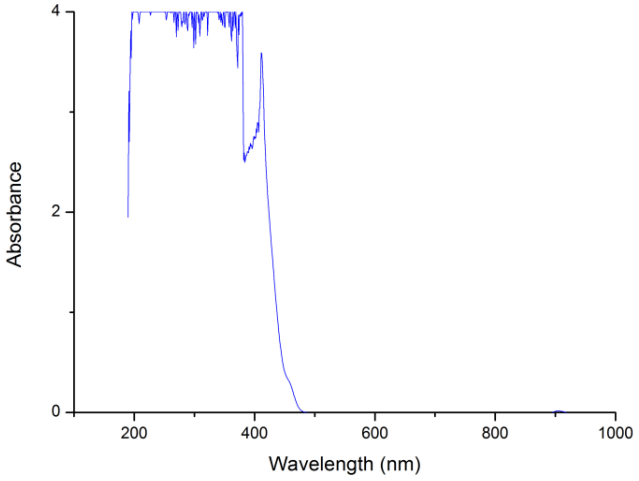
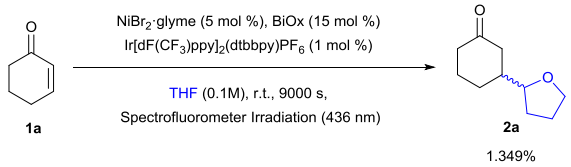


Figure S7. Absorbance of 1 mM Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 in THF

Absorbance at 436 nm = 1.086399.

Fraction of light absorbed at 436 nm = $1 - 10^{-1.086399} = 0.91804$.

<Quantum Yield Measurement>



To a sealable cuvette equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (3.1 mg, 0.010 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.030 mmol, 0.15 equiv.), and THF (2.0 mL). The resulting solution was stirred for 5 min to give a green suspension prior to the addition of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.0020 mmol, 0.01 equiv.) and **1a** (19.2 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was sealed and irradiated for 9000 s (2.5 h) under the identical conditions with the actinometry. The resulting mixture was analyzed by GC following the addition of dodecane (20 μL, 0.088 mmol) as an internal standard to give 1.349% yield of the desired product.

$$\text{mol product} = 1.349\% \cdot 0.20\ \text{mmol} = 2.698 \cdot 10^{-6}\ \text{mol}$$

$$\text{Quantum yield} = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f} = \frac{2.698 \cdot 10^{-6}}{1.794331 \cdot 10^{-10} \cdot 9000 \cdot 0.91804} = 0.18$$

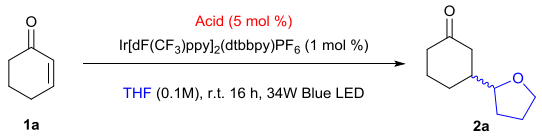
Here, flux is the photon flux, t is irradiation time, and f is the fraction of light absorbed at 436 nm as obtained above.

11. Reaction with Other Lewis or Brønsted Acids

During reaction optimization, a number of Lewis and Brønsted acids were tested, especially those known to be efficient activators for photoredox reactions.[10] However, these reagents generally provided unsuccessful results, with zero conversion, or the formation of no isolable products, presumably due to polymerization.

Procedure: To a vial equipped with a PTFE-coated stirrer bar were added the corresponding acid (0.01 mmol, 0.05 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.), **1a** (19.2 mg, 0.20 mmol, 1.0 equiv), and THF (2.0 mL). The resulting mixture was stirred for 16 h under 34W blue LED irradiation with fan cooling. The resulting mixture was analyzed by GC following the addition of dodecane (20 μL, 0.088 mmol) as an internal standard to determine the product yield.

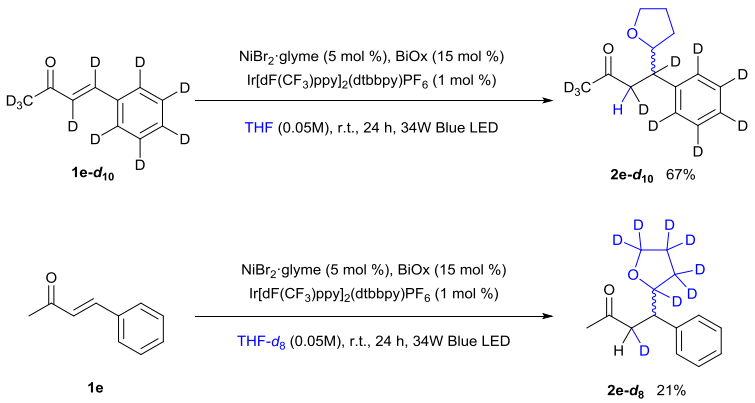
Table S1. Acid Screening Experiments



entry	Acid	yield (%)
1	CH_3COOH	0
2	CF_3COOH	0
3	*p*-TsOH	4
4	$Sc(OTf)_3$	0
5	$Eu(OTf)_3$	0
6	$Gd(OTf)_3$	0
7	$La(OTf)_3$	0
8	$Mg(OTf)_2$	0
9	$LiBF_4$	0
10	$Cu(OTf)_2$	0
11	$Fe(acac)_2$	0
12	$Zn(OTf)_2$	2
13	$Mn(OAc)_2$	1
14	TMSOTf	3

12. α-Deuteration Study

To confirm α-deuterium incorporation, the reaction was conducted using **1e** and THF-d_8. **1e** was chosen as the substrate as its deuterated form **1e-*d*$_{10}$** was readily available, and so cross-referencing was therefore possible.



Procedure: To a vial equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and either THF or THF-d_8 (4.0 mL). The

resulting solution was stirred for 5 min to give a green suspension prior to the addition of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.) and either **1e** or **1e-*d*$_{10}$** (0.20 mmol, 1.0 equiv). The resulting mixture was stirred for 24 h under 34W blue LED irradiation with fan cooling, then filtered through a short pad of Celite®, eluted with CH_2Cl_2, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexanes/EtOAc gradient elution) to afford the desired product.

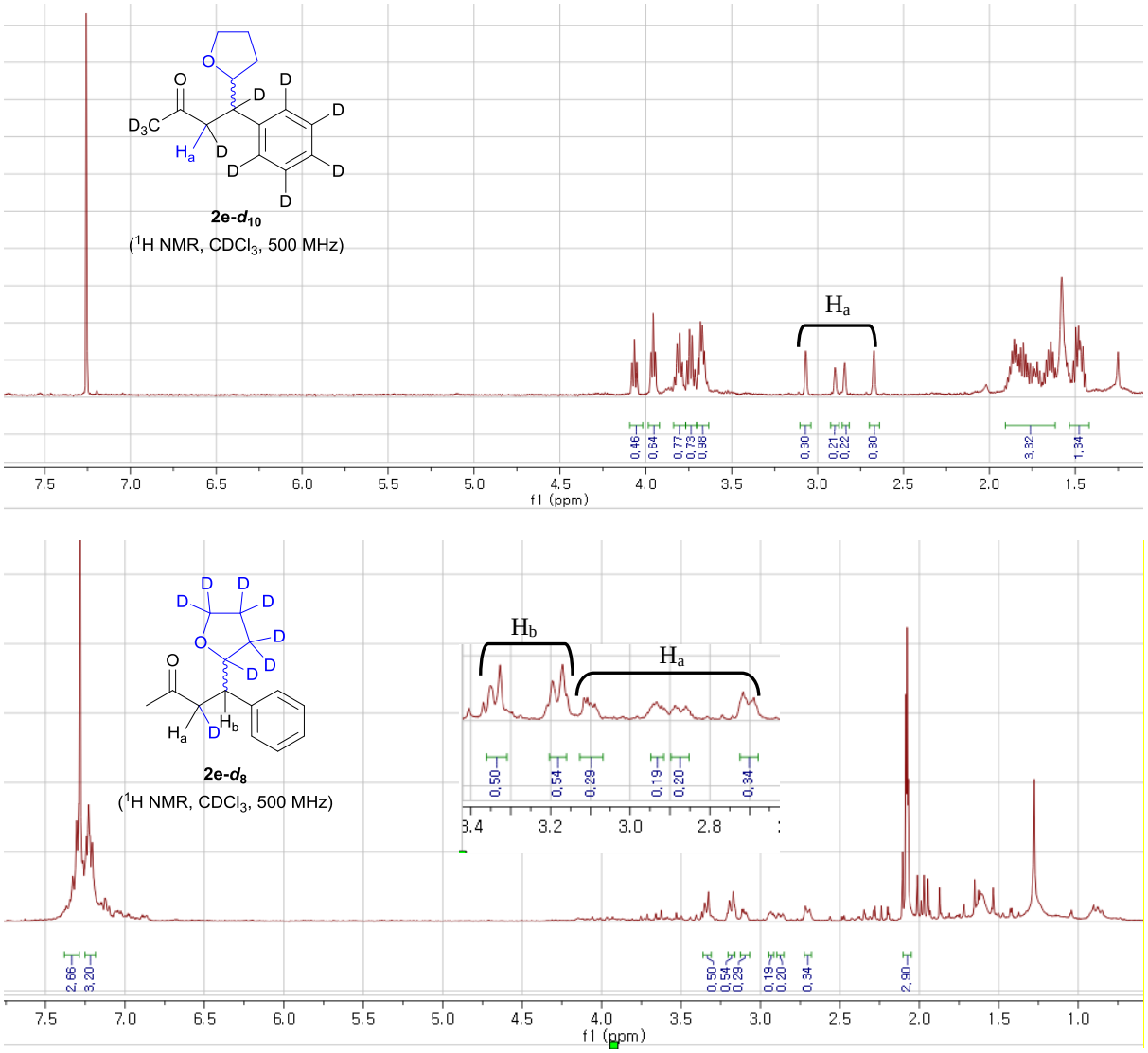


Figure S8. ^{1}H NMR Spectra of Deuterated Products 2e-*d*$_{10}$ and 2e-*d*$_8$

In the NMR spectra of **2e-*d*$_{10}$**, the four diastereomers were observed in a 3:3:2:2 ratio as shown in the characteristic splitting pattern in the 2.5~3.5 ppm region. Similarly, for **2e-*d*$_8$**, identical pattern was observed in the corresponding region, with additional splitting patterns due to the α-proton. The integrations also indicate a mixture of 4 diastereomers, in a 3:3:2:2 ratio. Clearly, the ^{1}H NMR spectra shown in Figure S8 confirm that the THF α-oxy C–H(D) was fully transferred to the α-position of the substrate enone. As no other peaks corresponding to the product were observed, the full carbonyl α-deuterium content of **2e-*d*$_8$** was confirmed. The incorporation of deuterium was further confirmed by ^{2}D NMR spectroscopy using $CDCl_3$ as the reference (see Figure S9).

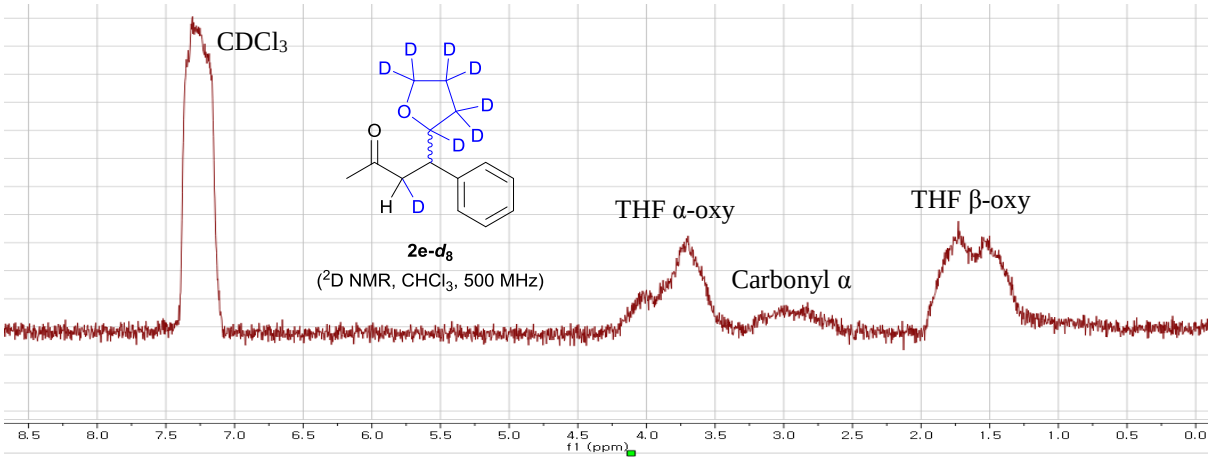
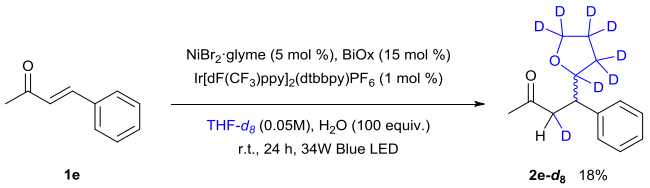


Figure S9. ^{2}D NMR of 2e-d_8

The reaction was also conducted using water as the additive. The deuterium content was not affected by the external addition of water.



Procedure: To a vial equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and THF-d_8 (4.0 mL). The resulting solution was stirred for 5 min to give a green suspension before $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.), H_2O (0.36 mL, 20.0 mmol, 100 equiv.) and **1e** (29.2 mg, 0.20 mmol, 1.0 equiv) were added. The resulting mixture was stirred for 24 h under 34W blue LED irradiation with fan cooling. The resulting mixture was dried (anhydrous $MgSO_4$), filtered through a short pad of Celite®, eluted with CH_2Cl_2, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexanes/EtOAc gradient elution) to afford the desired product (8.1 mg, 0.036 mmol, 18%). All physical and spectroscopic data for the obtained product were identical with the above-described product.

13. Stern-Volmer Quenching Study

Stern-Volmer quenching study was conducted with 100 μM $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in MeCN. In-situ generated $Ni(BiOx)Br_2$ complex (by pre-mixing equimolar amounts of $NiBr_2$·glyme and BiOx) and **1a** was used as quenchers. Samples were excited at 380 nm and peak emissions were observed at 470 nm to construct the Stern-Volmer regression.

The fluorescence spectra and the Stern-Volmer regression data is presented below.

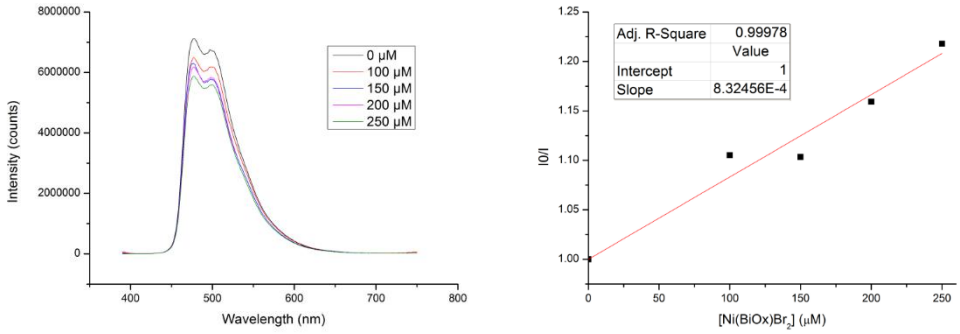


Figure S10. Stern-Volmer Quenching Study with Ni(BiOx)Br_2

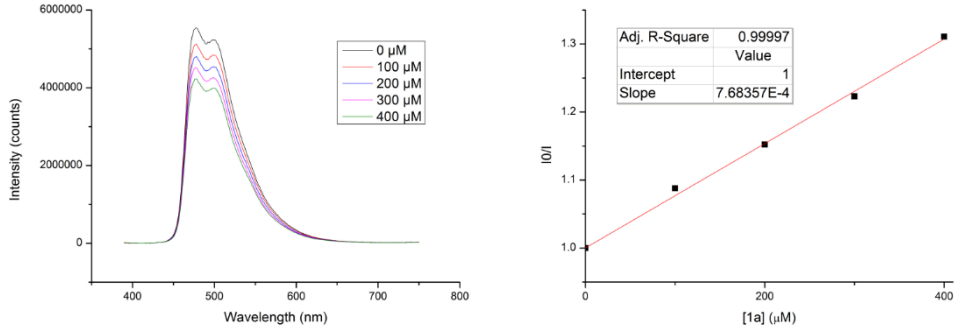
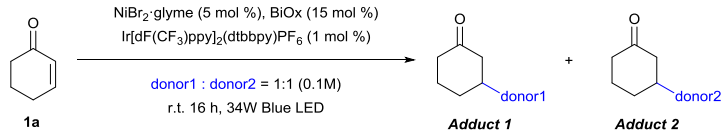


Figure S11. Stern-Volmer Quenching Study with 1a

The Ni catalyst and **1a** shows very similar degrees of quenching, with the difference of quenching rate k_q ~ 8%. This shows that the fluorescent energy of the Ir photocatalyst could be transferred to both the Ni catalyst and **1a**.

14. Competition Experiment

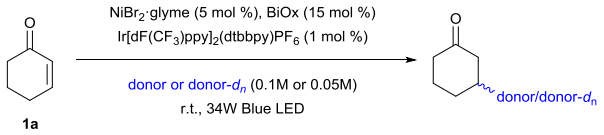
For the competition experiments shown in Scheme 4a (see the main manuscript for further information), the following procedure was employed:



To a vial equipped with a PTFE-coated stirrer bar were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and two Giese donors as indicated (1.0 mL each). The resulting solution was stirred for 5 min to give a green suspension before Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 0.01 equiv.), and **1a** (19.2 mg, 0.20 mmol, 1.0 equiv) were added. The resulting mixture was stirred for 16 h under 34W blue LED lamp irradiation with fan cooling. The resulting mixture was analyzed by GC after the addition of dodecane (20 μL, 0.088 mmol) as an internal standard to determine the product yields.

15. Kinetic Isotope Experiment

For kinetic isotope effect experiments, the following procedure was employed:



donor	THF	toluene	cyclohexene
k_H/k_D	3.13	1.40	1.45

To two vials equipped with PTFE-coated stirrer bars were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and respectively the non-deuterated and deuterated Giese donors (2.0 mL for THF, 4.0 mL for toluene and cyclohexene). In the case of toluene and cyclohexene, MeCN (0.5 mL) was added. The resulting solution was stirred for 5 min to reach a green suspension prior to the addition of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.), dodecane (20 μL, 0.088 mmol), and **1a** (19.2 mg, 0.20 mmol, 1.0 equiv). The resulting mixture was stirred under 34W blue LED lamp irradiation with fan cooling. Aliquots of the reaction mixture were taken every 5 min (THF), 10 min (cyclohexene), or 20 min (toluene), and analyzed by GC to determine the product yields. The initial rates were compared and the kinetic isotope effect was measured.

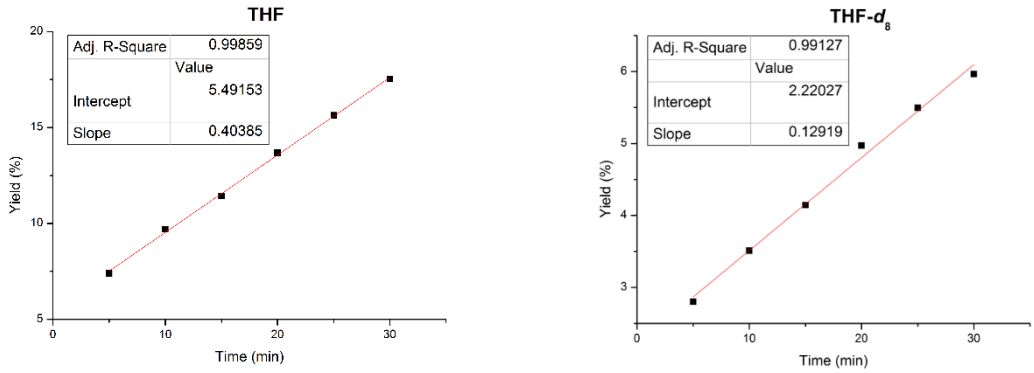


Figure S12. KIE Measurement with THF (KIE value k_H/k_D = 3.13 for THF).

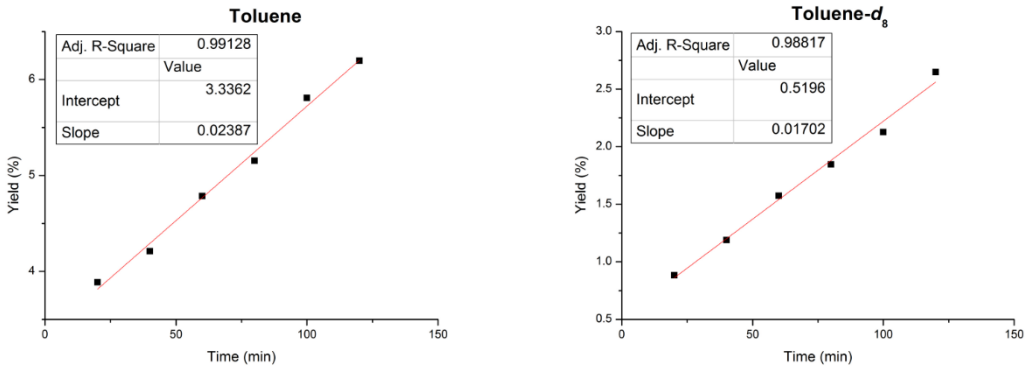


Figure S13. KIE Measurement with Toluene (KIE value k_H/k_D = 1.40 for toluene).

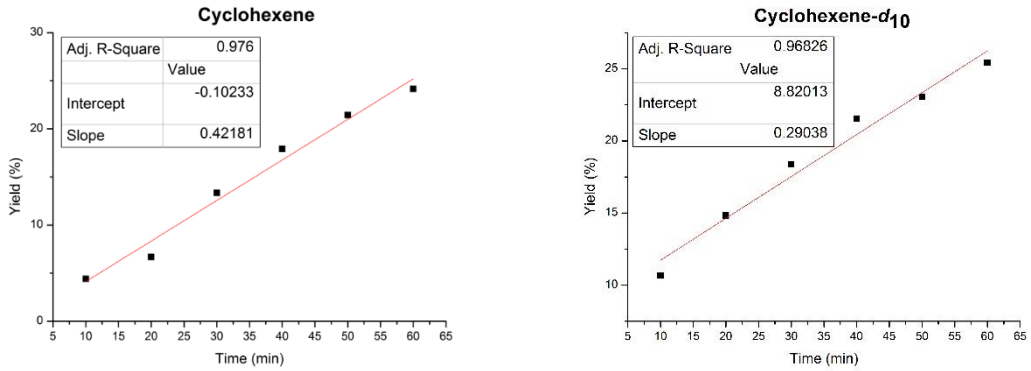
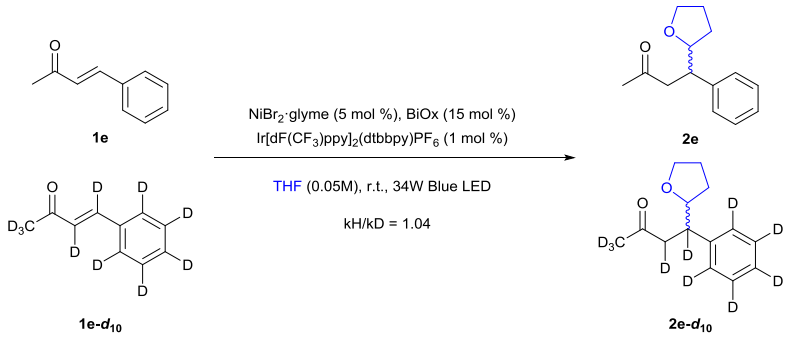


Figure S14. KIE Measurement with Cyclohexene (KIE value k_H/k_D = 1.45 for cyclohexene).

Although not included in the manuscript, the kinetic isotope effect with respect to the Giese acceptor was also measured. Due to substrate availability, **1e** was used to obtain the KIE value.



Procedure: To two vials equipped with PTFE-coated stirrer bars were added $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 0.05 equiv.), BiOx (2,2'-bis(2-oxazoline)) (4.2 mg, 0.03 mmol, 0.15 equiv.), and THF (4.0 mL). The resulting solution was stirred for 5 min to give a green suspension prior to the addition of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv.), dodecane (20 μL, 0.088 mmol), and **1e** or **1e-*d*$_{10}$** (29.2 mg and 30.6 mg respectively, 0.20 mmol, 1.0 equiv). The resulting mixture was stirred under 34W blue LED lamp irradiation with fan cooling. Aliquots of the reaction mixture was taken every 5 min and analyzed by GC to determine the product yield. The initial rates were compared and the kinetic isotope effect was measured (k_H/k_D = 1.04). The results indicate no KIE effect with respect to **1e**, thereby confirming that the HAT step is the rate-limiting step at least when THF is employed as the Giese donor.

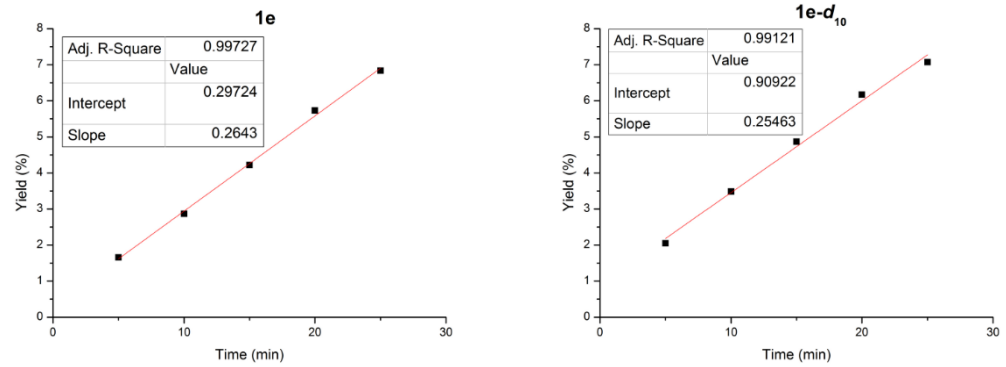
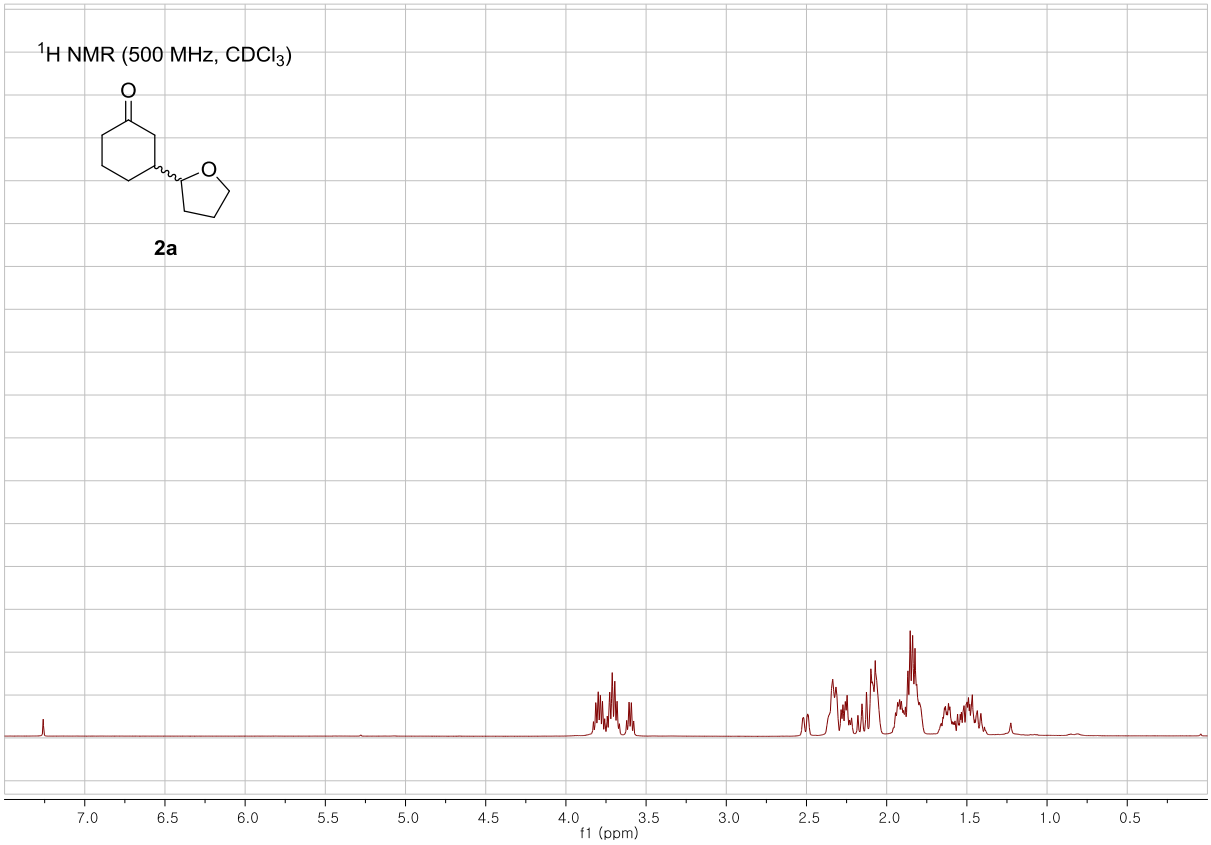


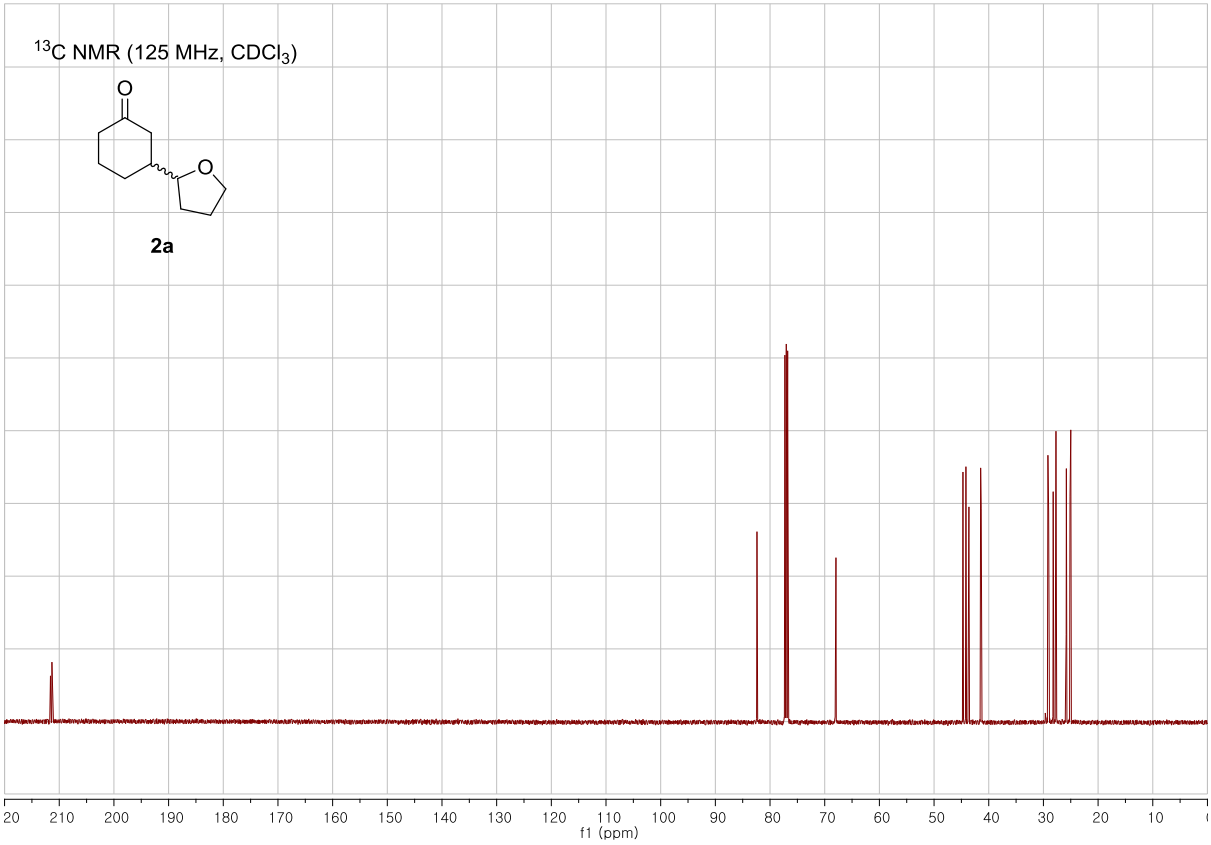
Figure S15. KIE Measurement with 2e (KIE value k_H/k_D = 1.04).

16. References

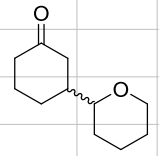
(1) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712.
(2) Chanthamath, S.; Takaki, S.; Shibatomi, K.; Iwasa, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 5818.
(3) Therkelsen, F. D.; Hansen, A. L. L.; Pedersen, E. B.; Nielsen, C. *Org. Biomol. Chem.* **2003**, *1*, 2908.
(4) Li, Y.; Wang, Q.; Yang, X.; Xie, F.; Li, X. *Org. Lett.* **2017**, *19*, 3410.
(5) Kellogg, R. M.; Nieuwenhuijzen, J. W.; Pouwer, K.; Vries, T. R.; Broxterman, Q. B.; Grimbergen, R. F. P.; Kaptein, B.; La Crois, R. M.; de Wever, E.; Zwaagstra, K.; van der Laan, A. C. *Synthesis* **2003**, 1626.
(6) (a) Kazi, I.; Guha, S.; Sekar, G. *Org. Lett.* **2017**, *19*, 1244. (b) Guo, T. L.; Jiang, Q. B.; Yu, L. K.; Yu, Z. K. *Chinese J. Catal.* **2015**, *36*, 78.
(7) Wu, X. F.; Neumann, H.; Spannenberg, A.; Schulz, T.; Jiao, H. J.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 14596.
(8) House, H. O.; Huber, L. E.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 8471.
(9) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426.
(10) (a) Yoon, T. P. *Acc. Chem. Res.* **2016**, *49*, 2307. (b) Fukuzumi, S.; Jung, J.; Lee, Y.-M.; Nam, W. *Asian J. Org. Chem.* **2017**, *6*, 397.

17. ^{1}H NMR and ^{13}C NMR Spectra



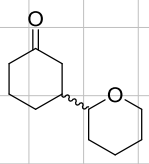


^{1}H NMR (500 MHz, $CDCl_3$)

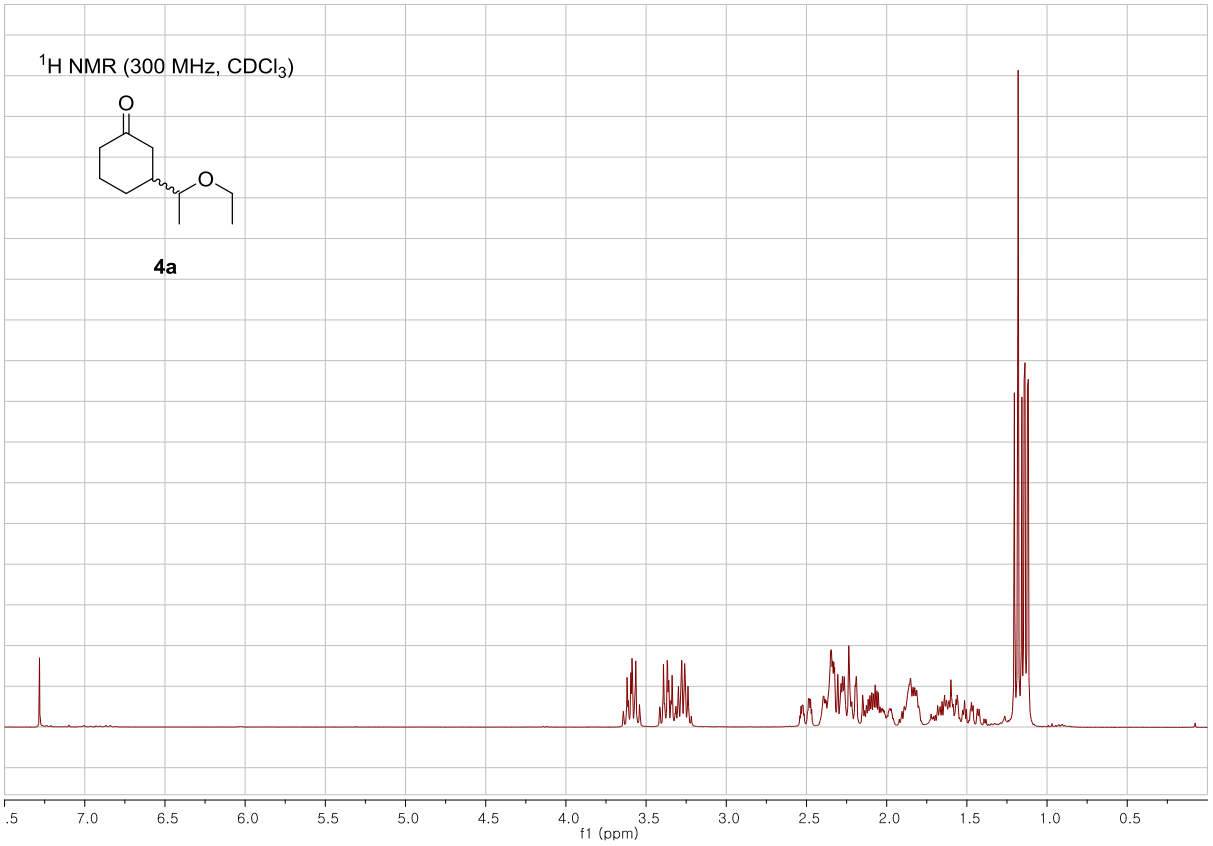


3a

^{13}C NMR (125 MHz, $CDCl_3$)



3a


^{1}H NMR (300 MHz, $CDCl_3$)
O
O
4a
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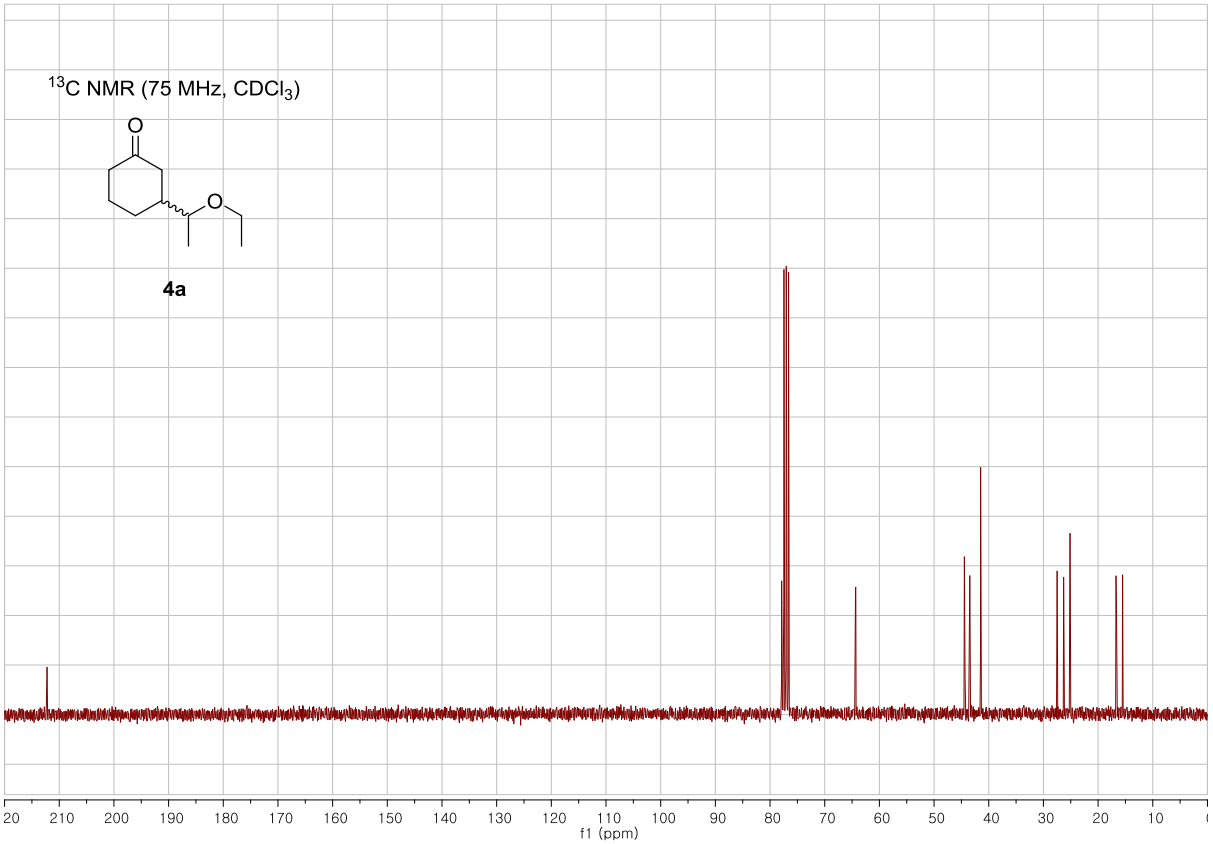
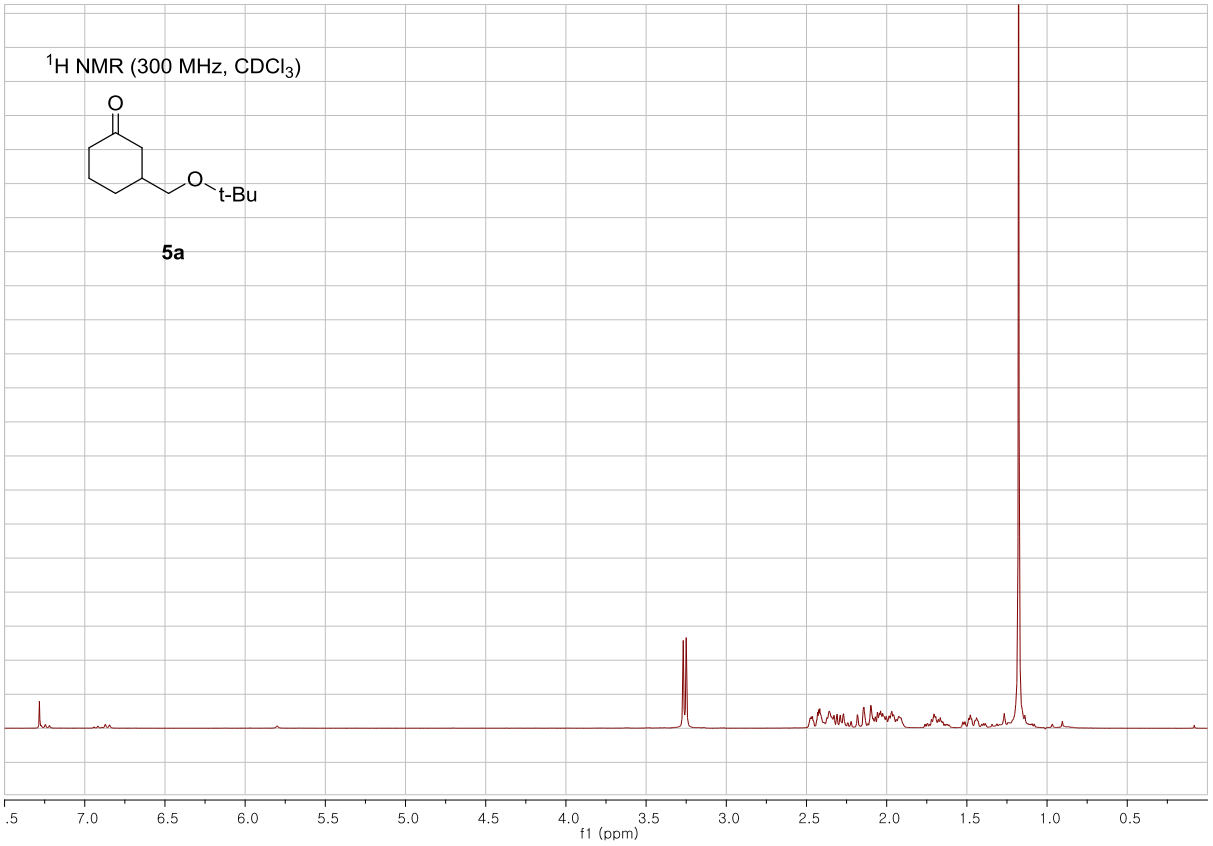
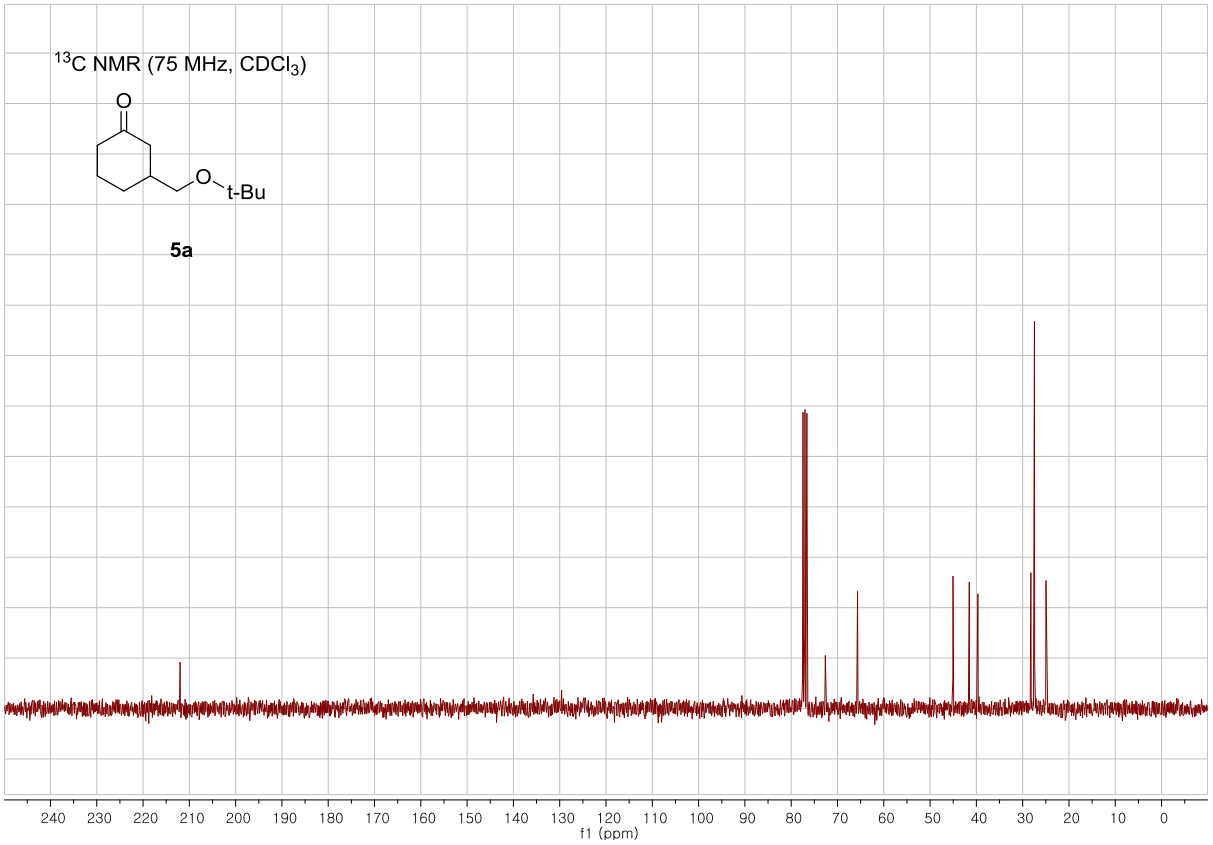
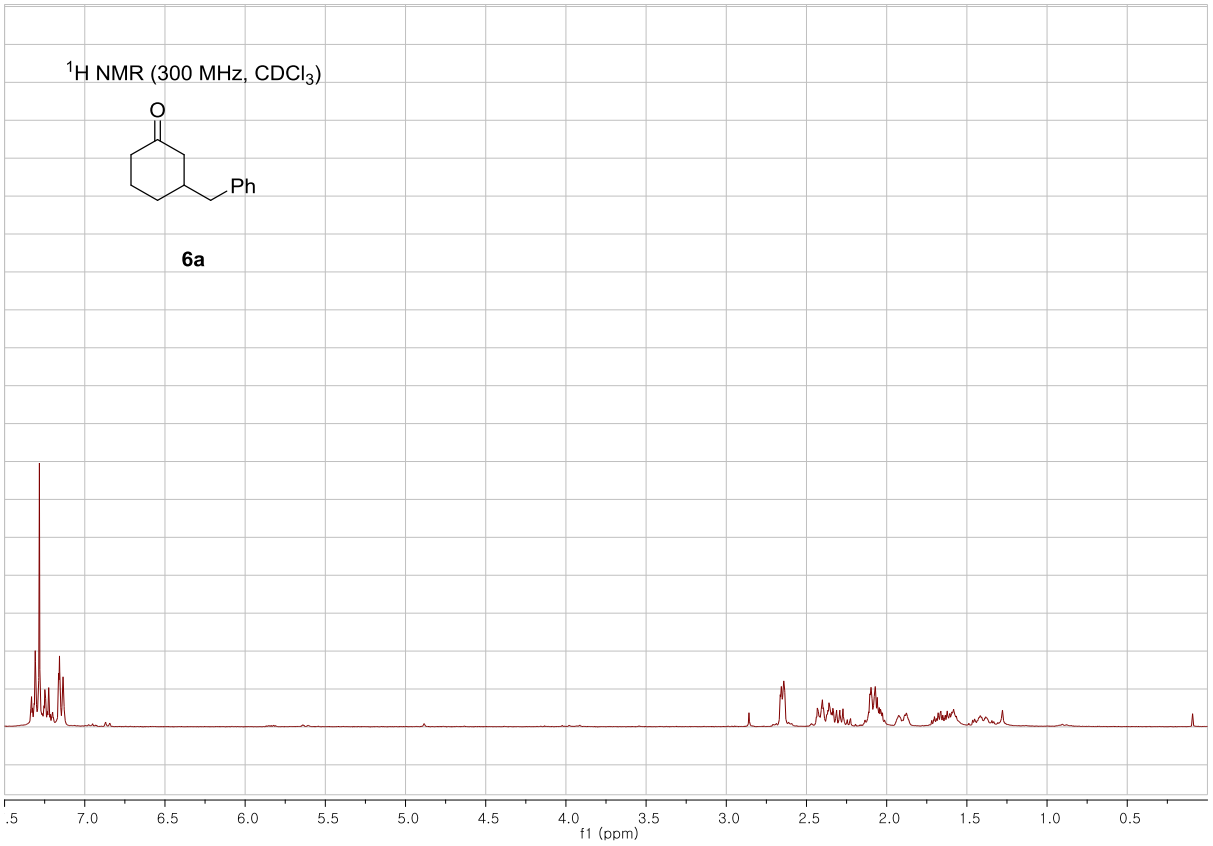
f1 (ppm)


^{13}C NMR (75 MHz, $CDCl_3$)
O
O
4a
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


^{1}H NMR (300 MHz, $CDCl_3$)
O
O
t-Bu
5a
.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


^{13}C NMR (75 MHz, $CDCl_3$)
O
O
t-Bu
5a
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{1}H NMR (300 MHz, $CDCl_3$)
O
Ph
6a
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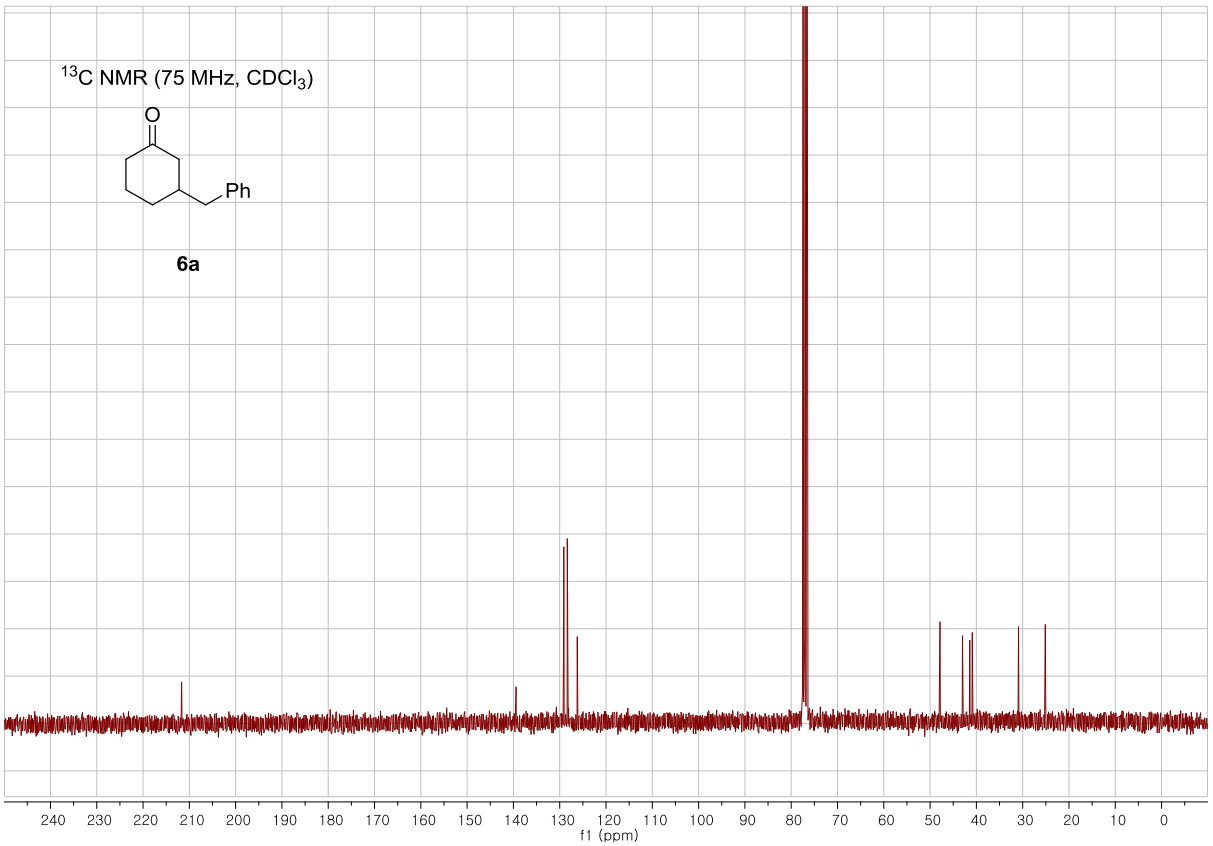
f1 (ppm)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O
Ph
6a
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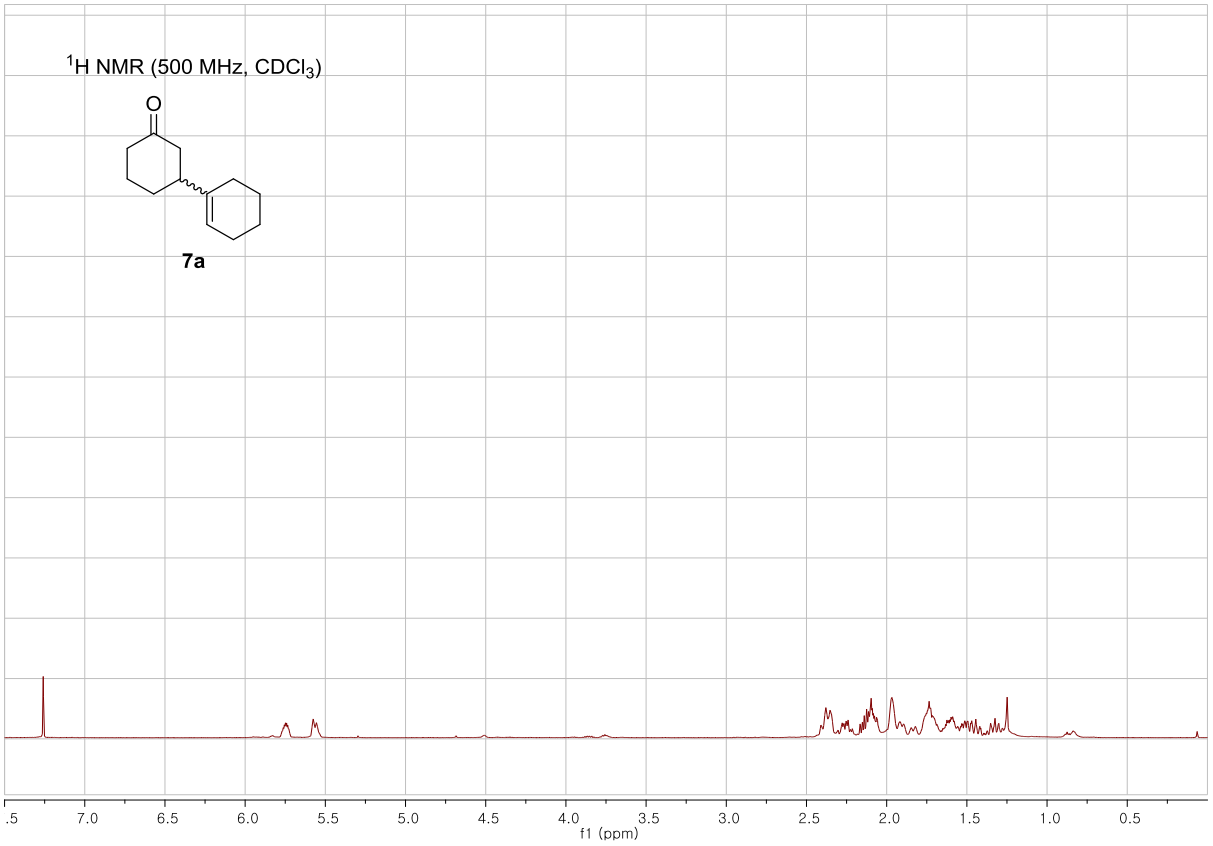
f1 (ppm)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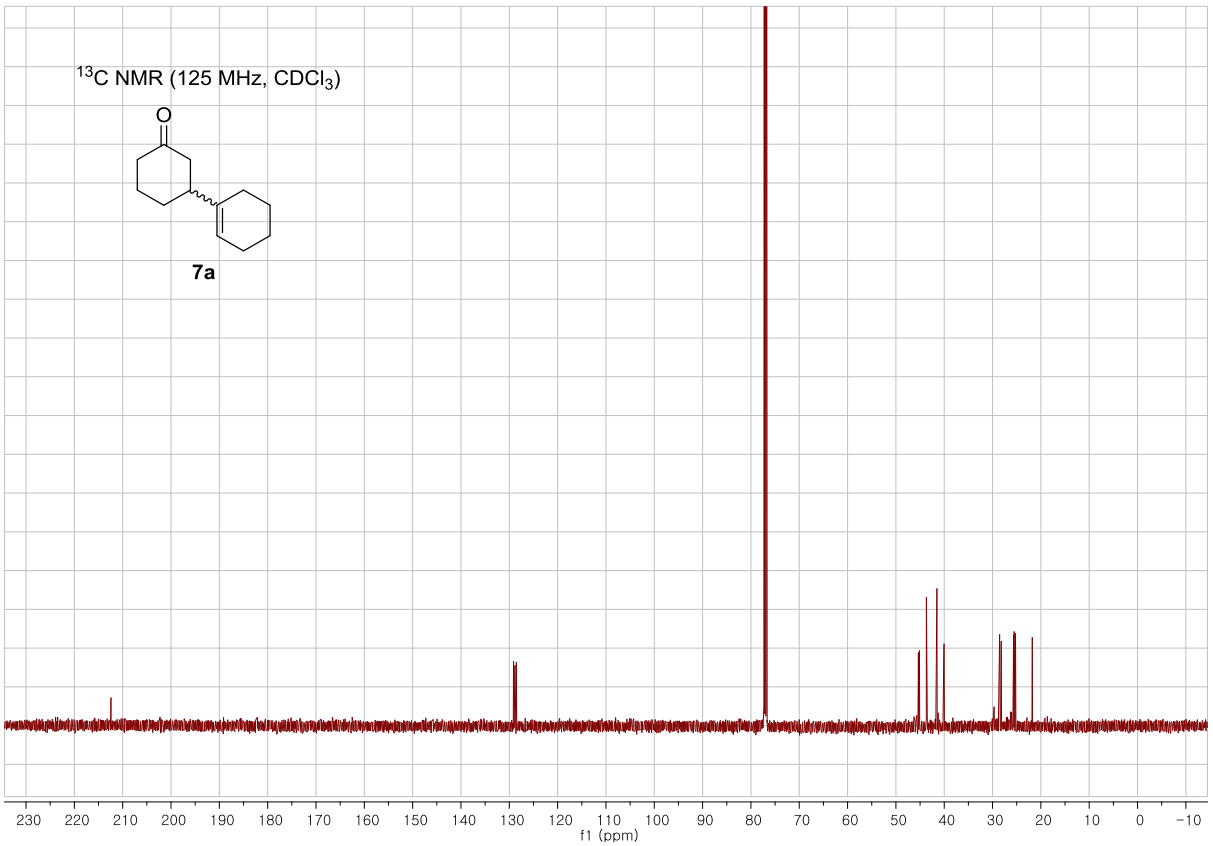
O
7a
.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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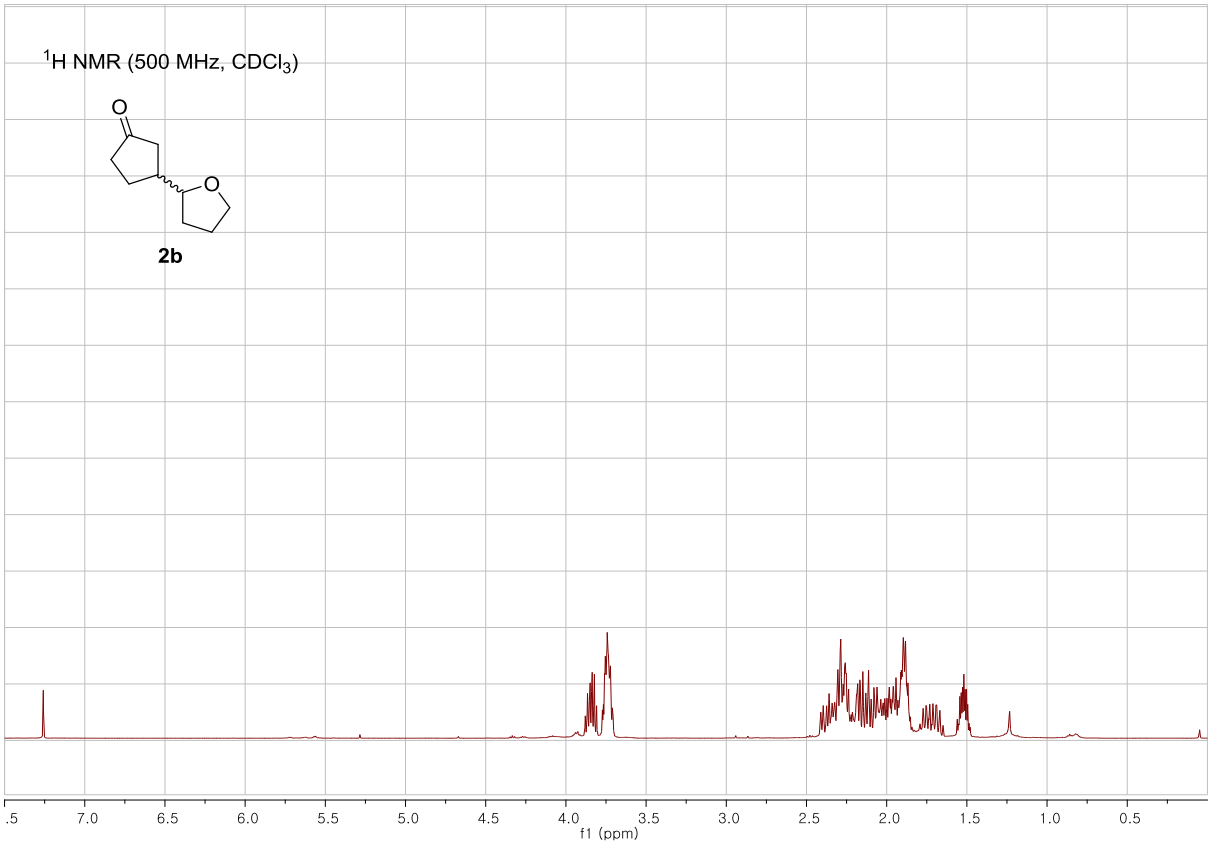
O
7a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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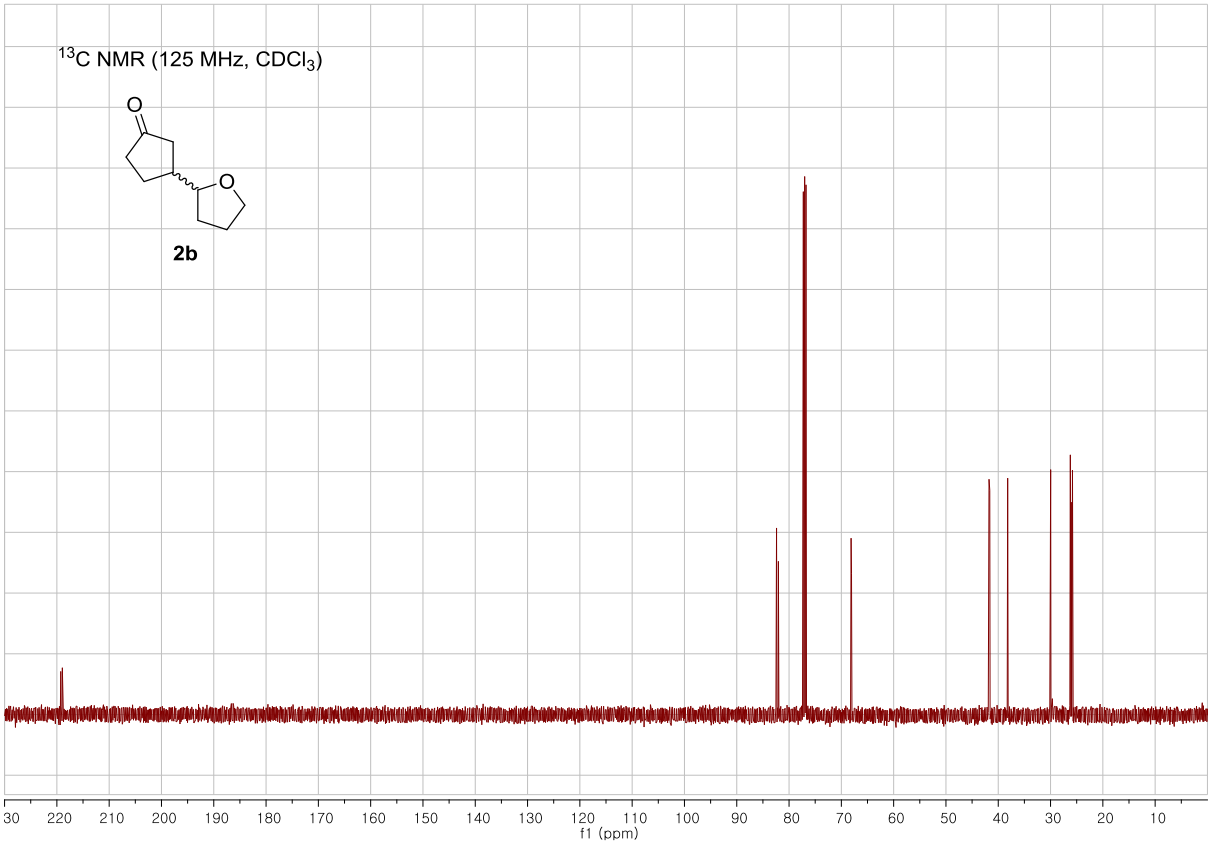
O
O
2b
.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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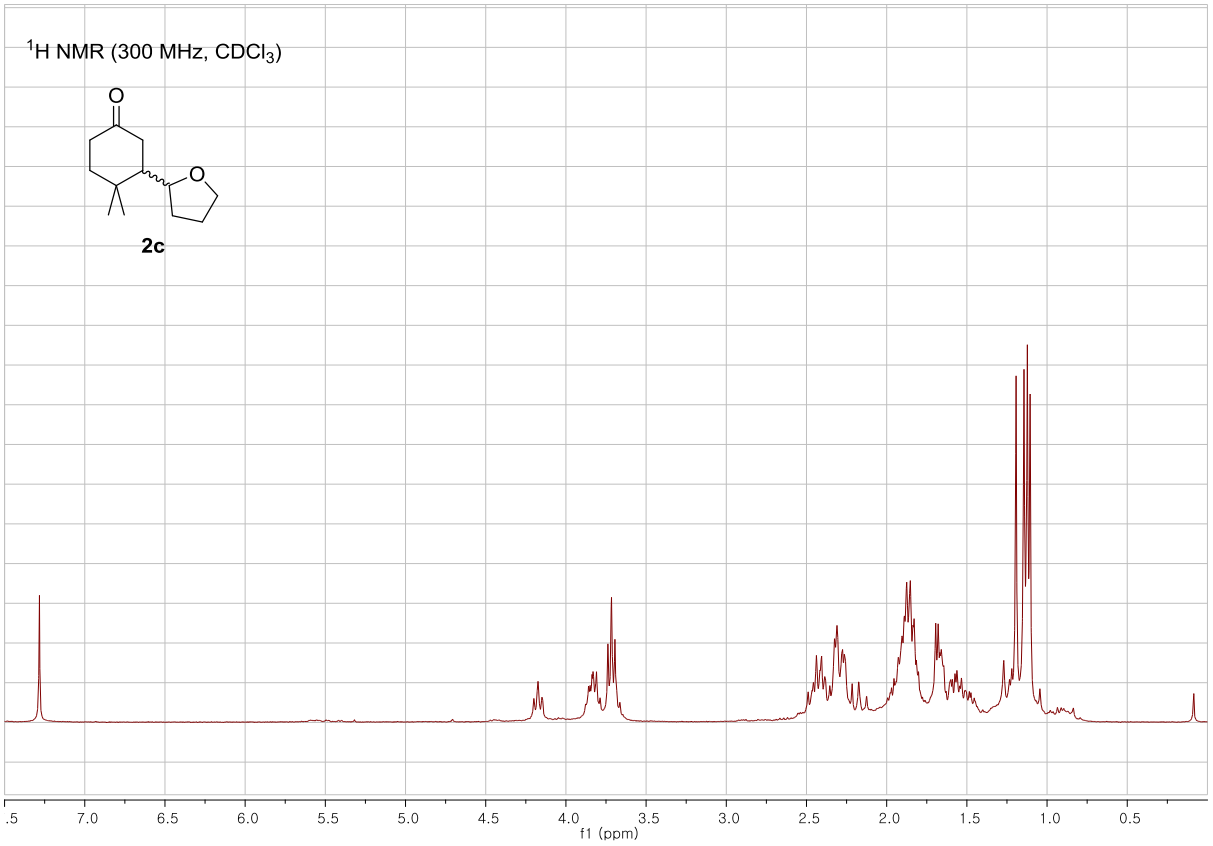
O
O
2b
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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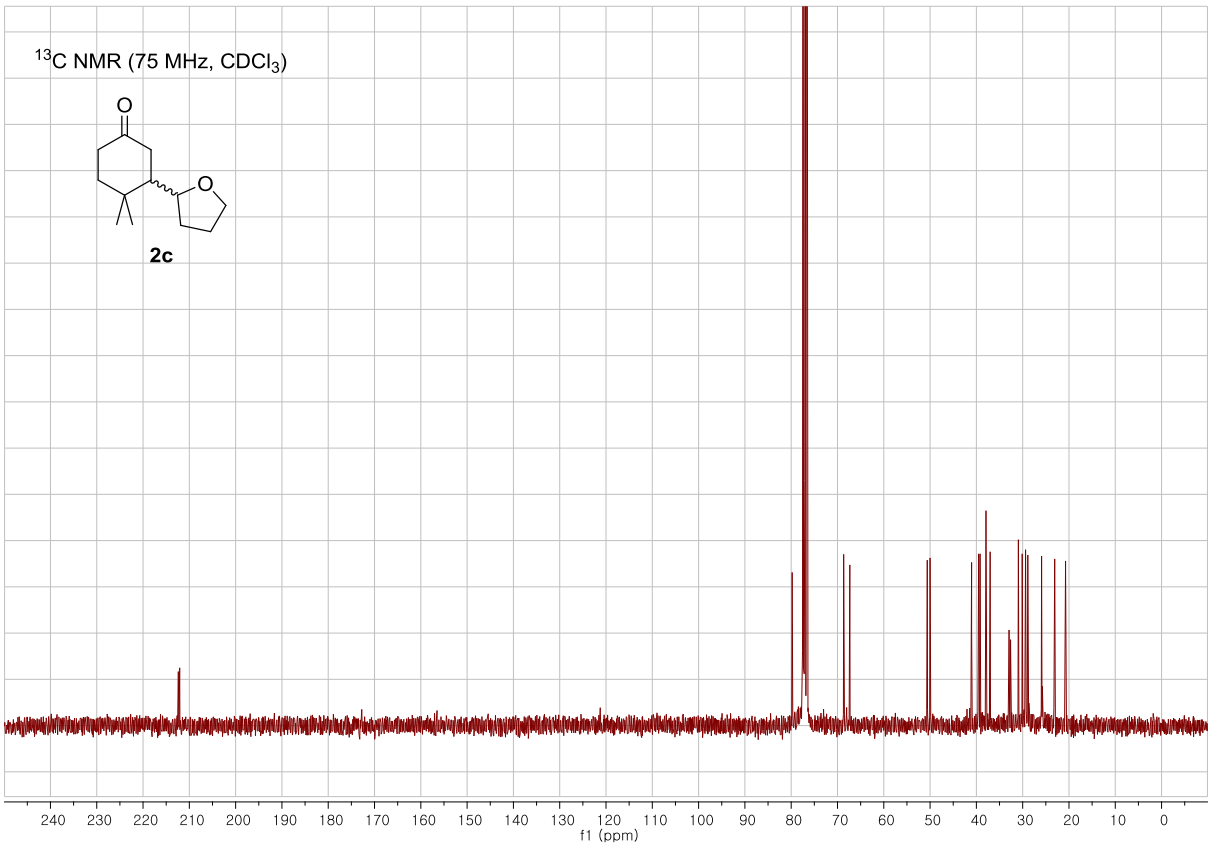
O
O
2c
.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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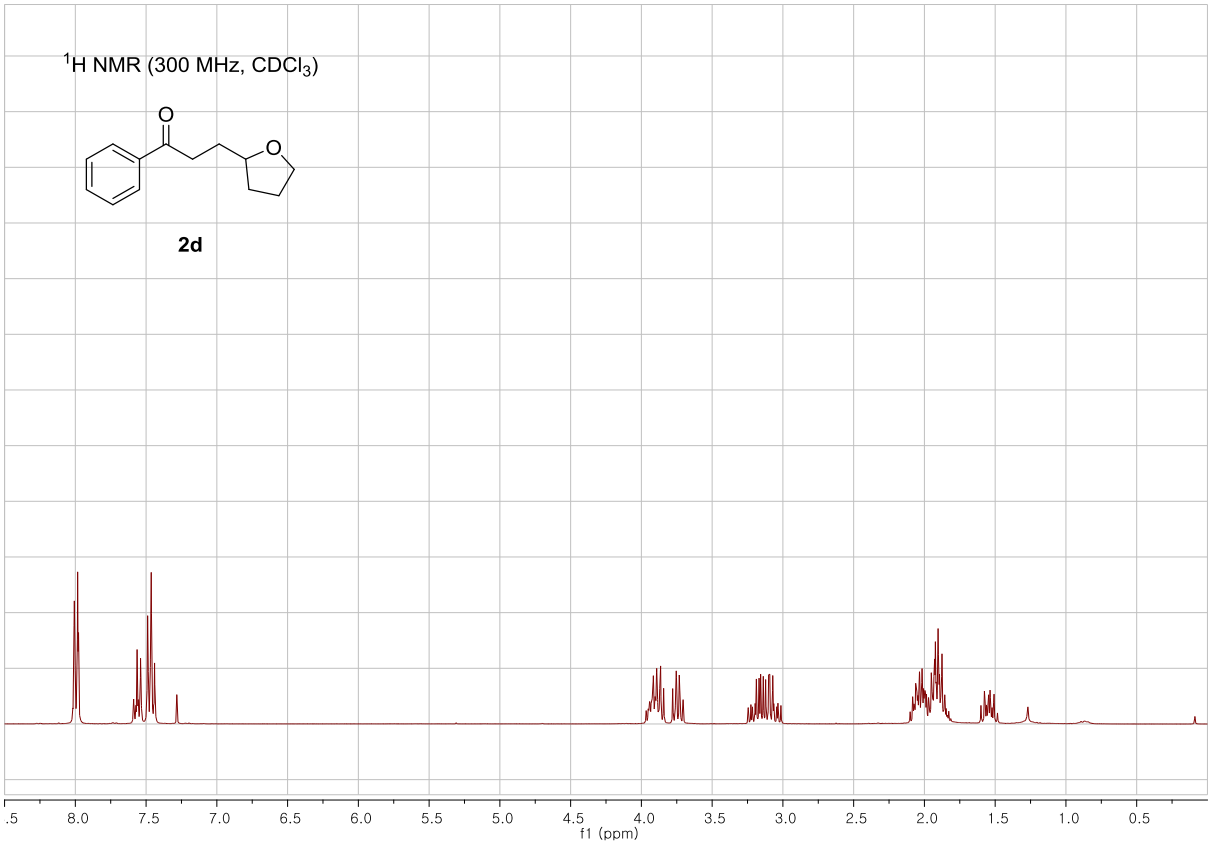
O
O
2c
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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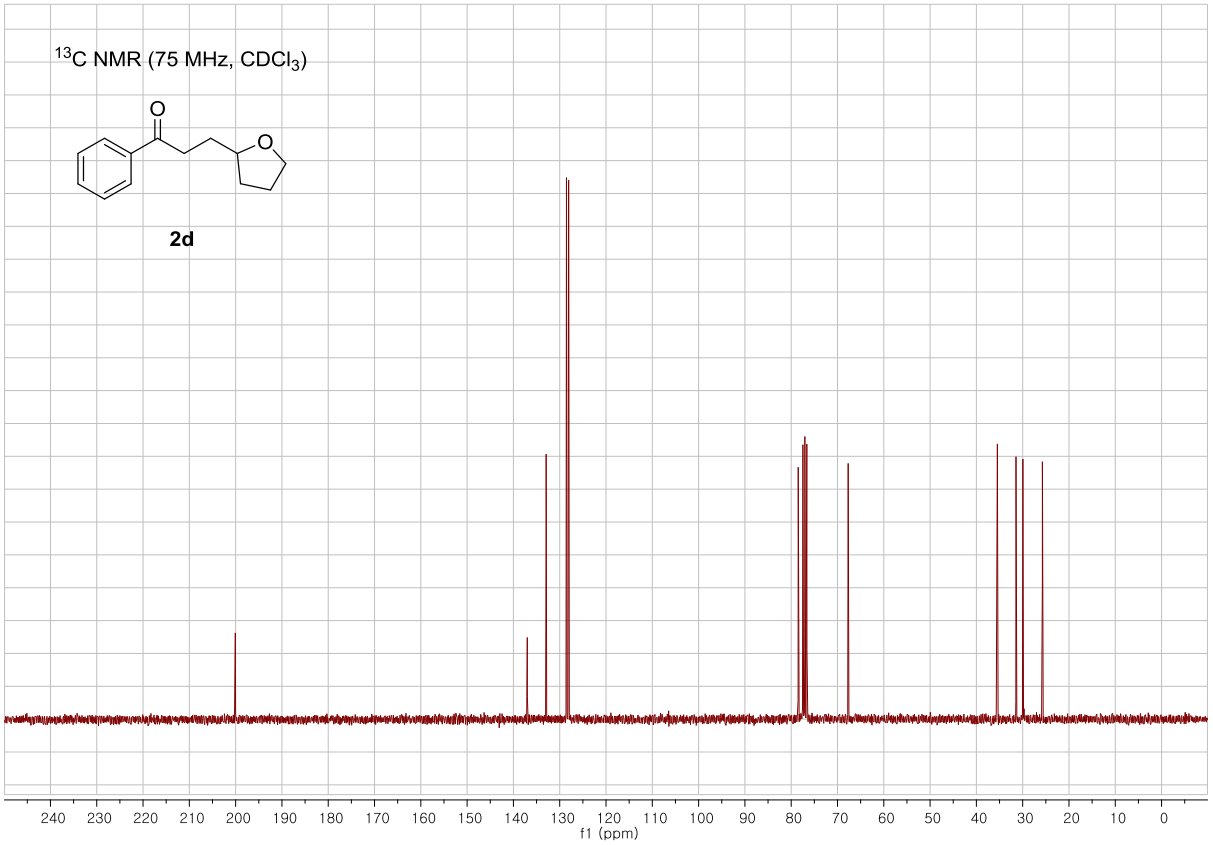
O
O
2d
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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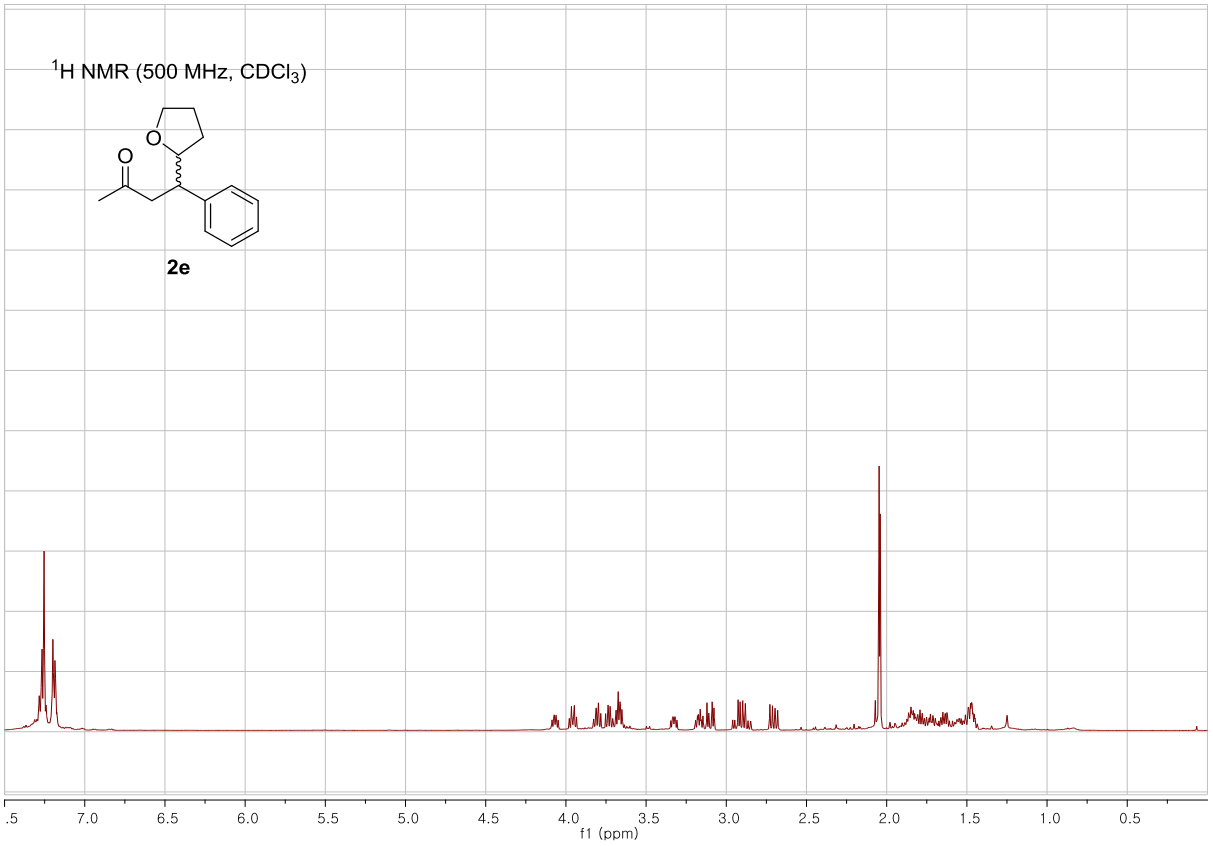
O
O
2d
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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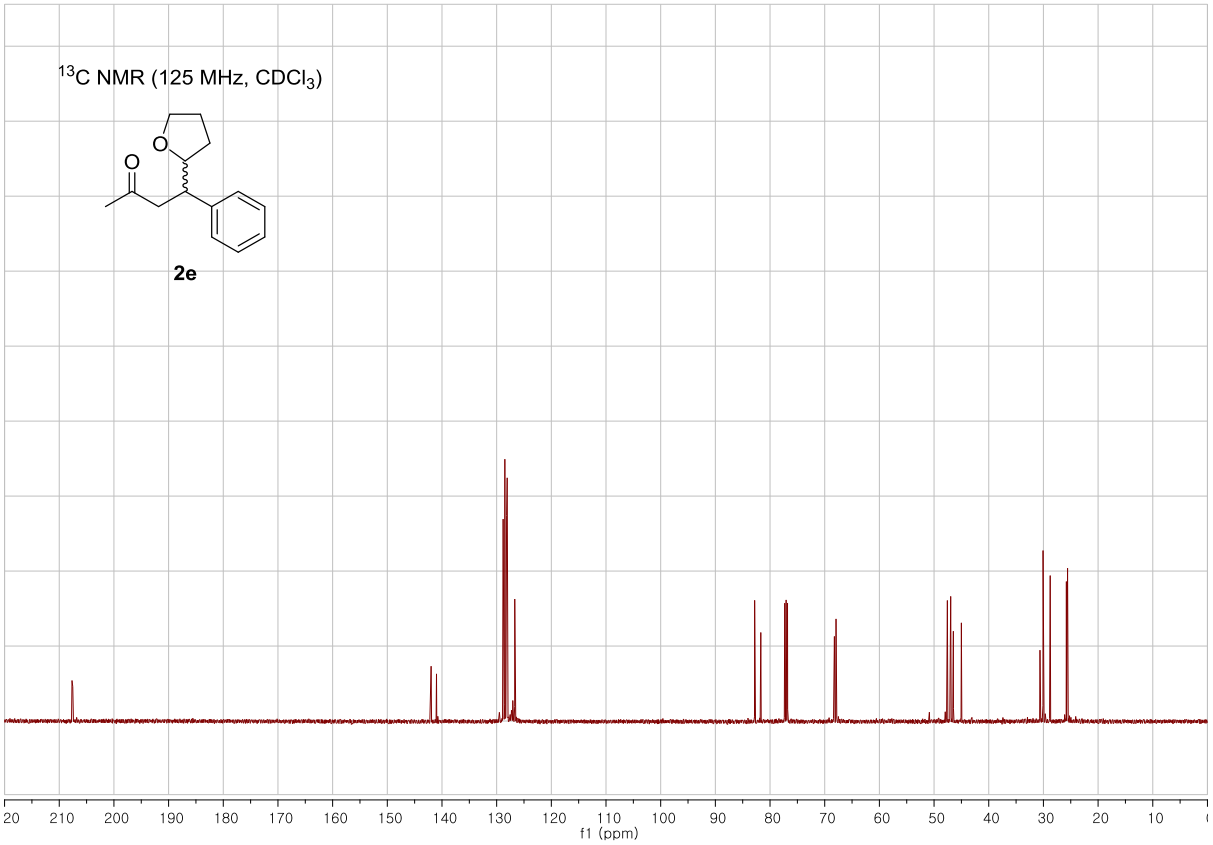
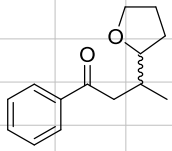
O
O
2e
.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

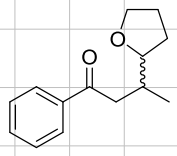

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
2e
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

^{1}H NMR (300 MHz, $CDCl_3$)

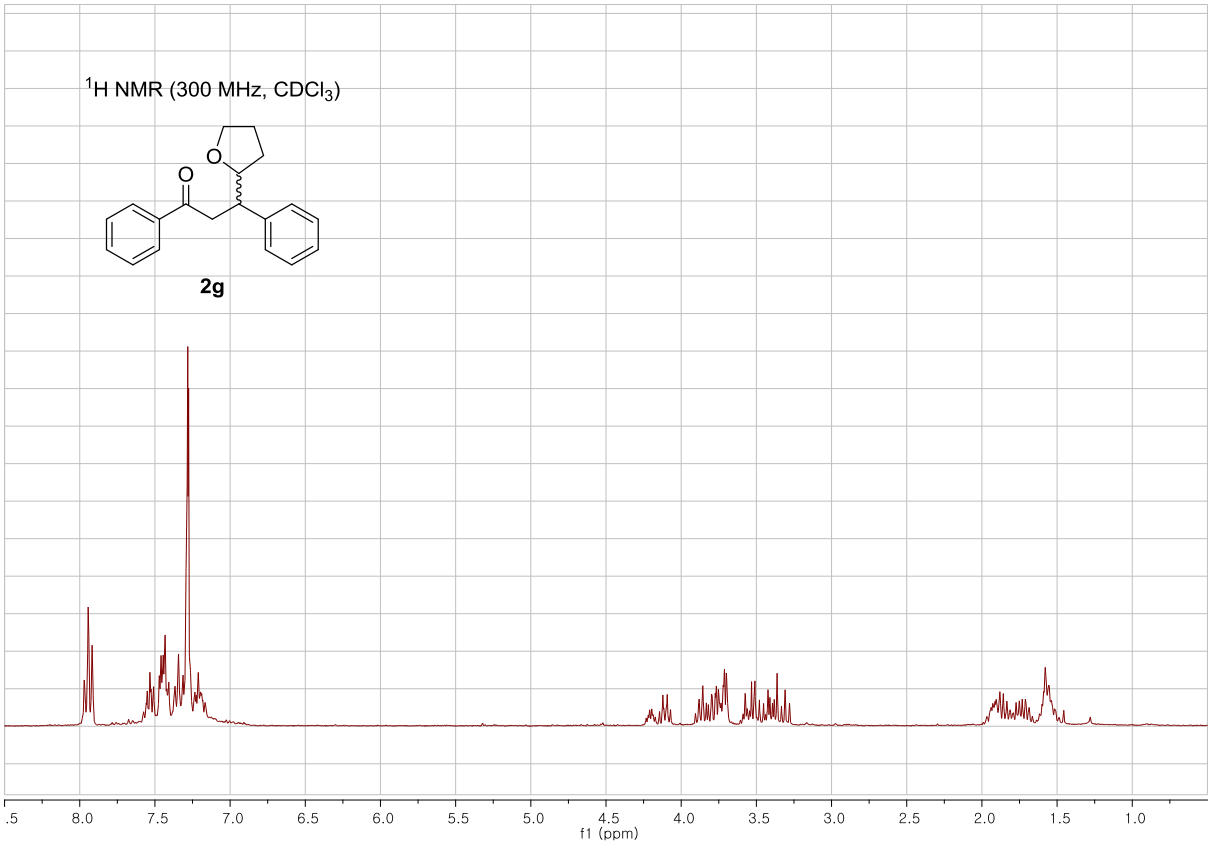


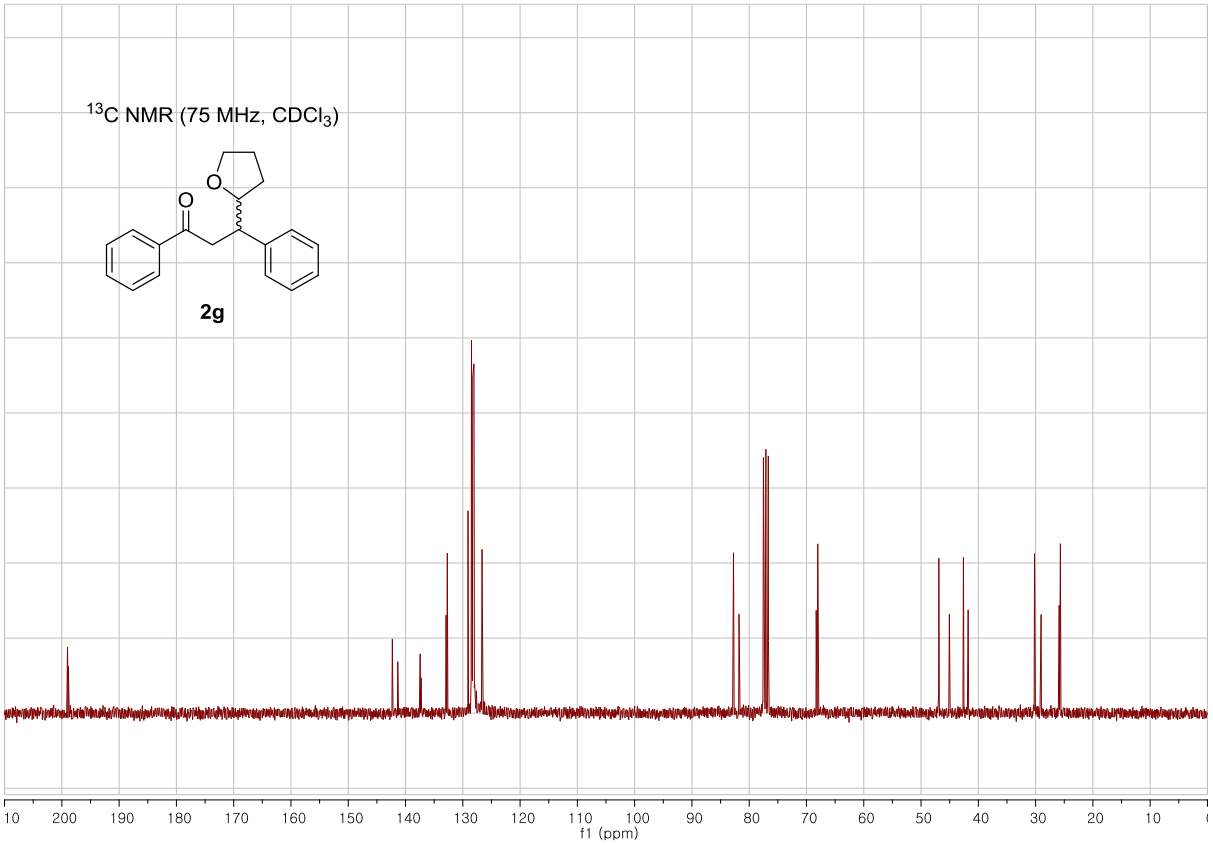
2f

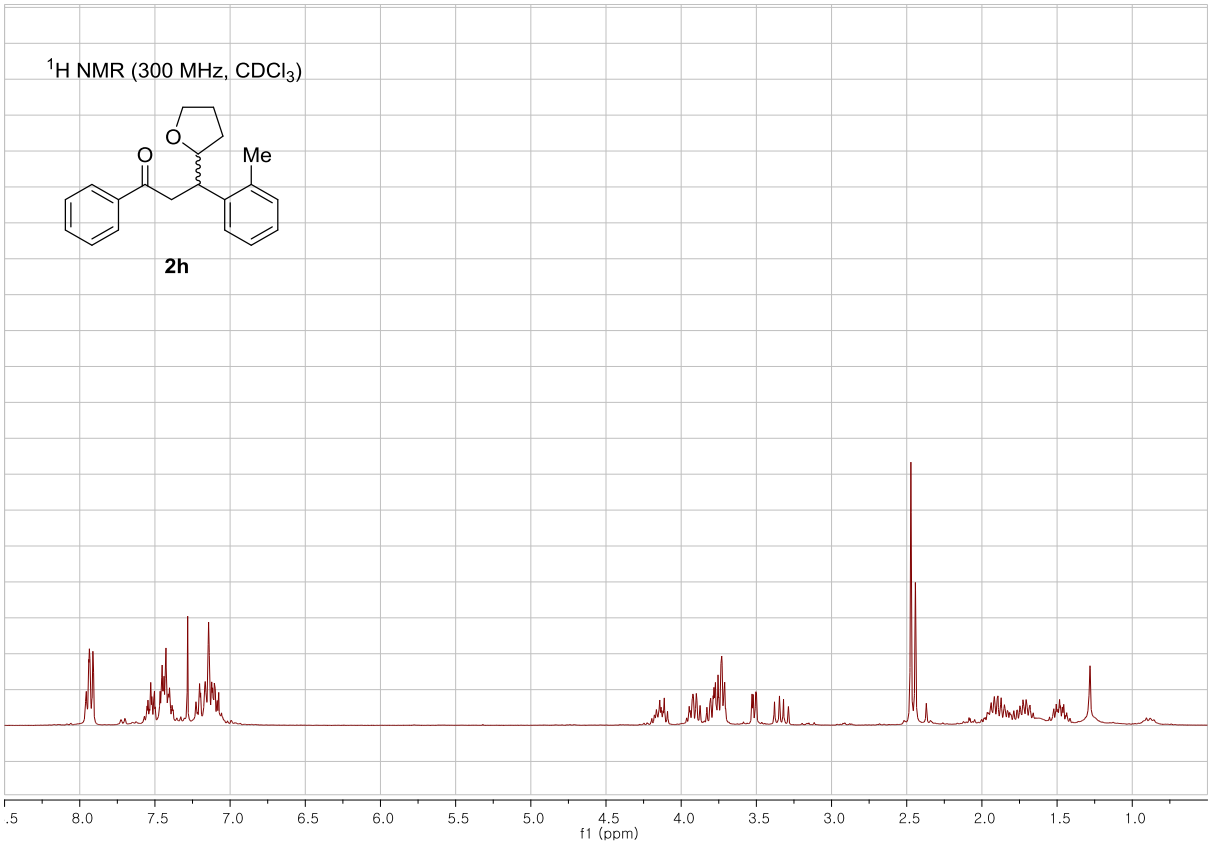
^{13}C NMR (75 MHz, $CDCl_3$)



2f


^{1}H NMR (300 MHz, $CDCl_3$)
O
O
2g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


^{13}C NMR (75 MHz, $CDCl_3$)
O
O
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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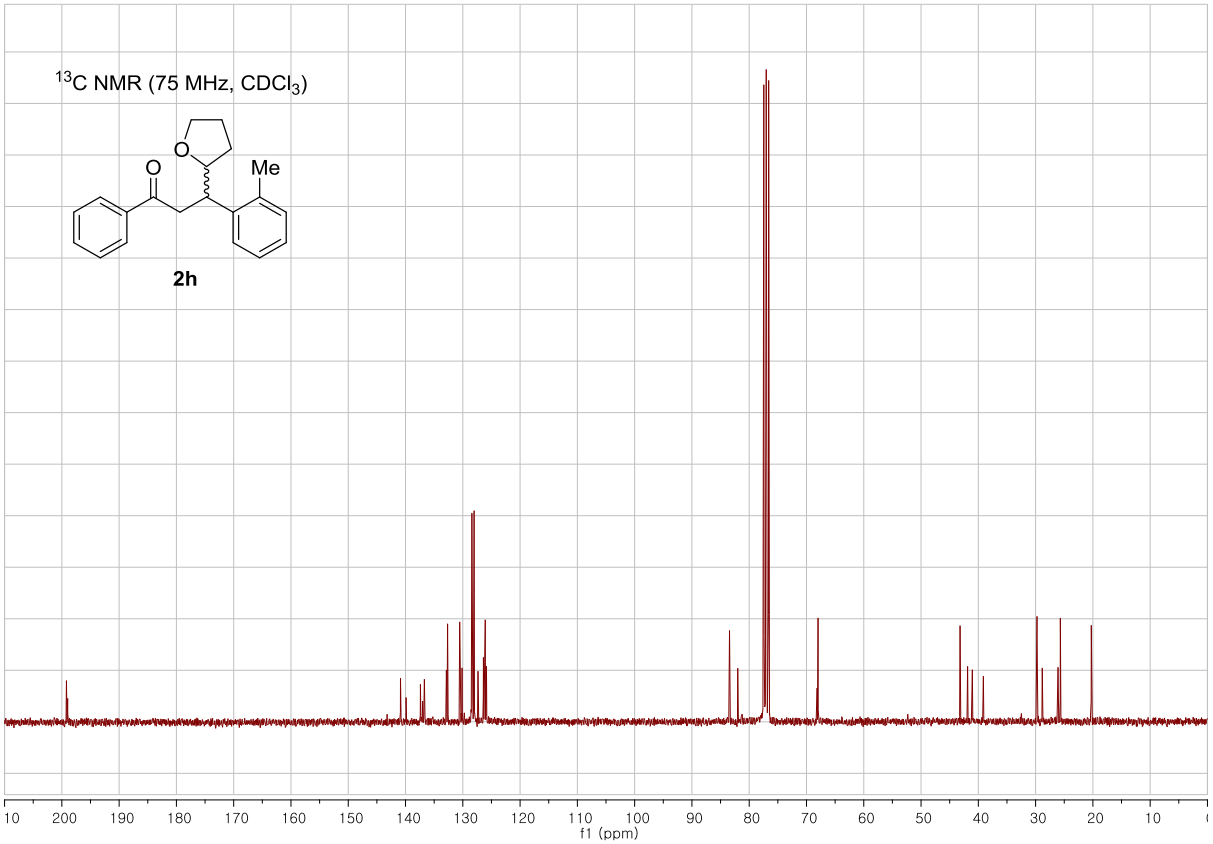
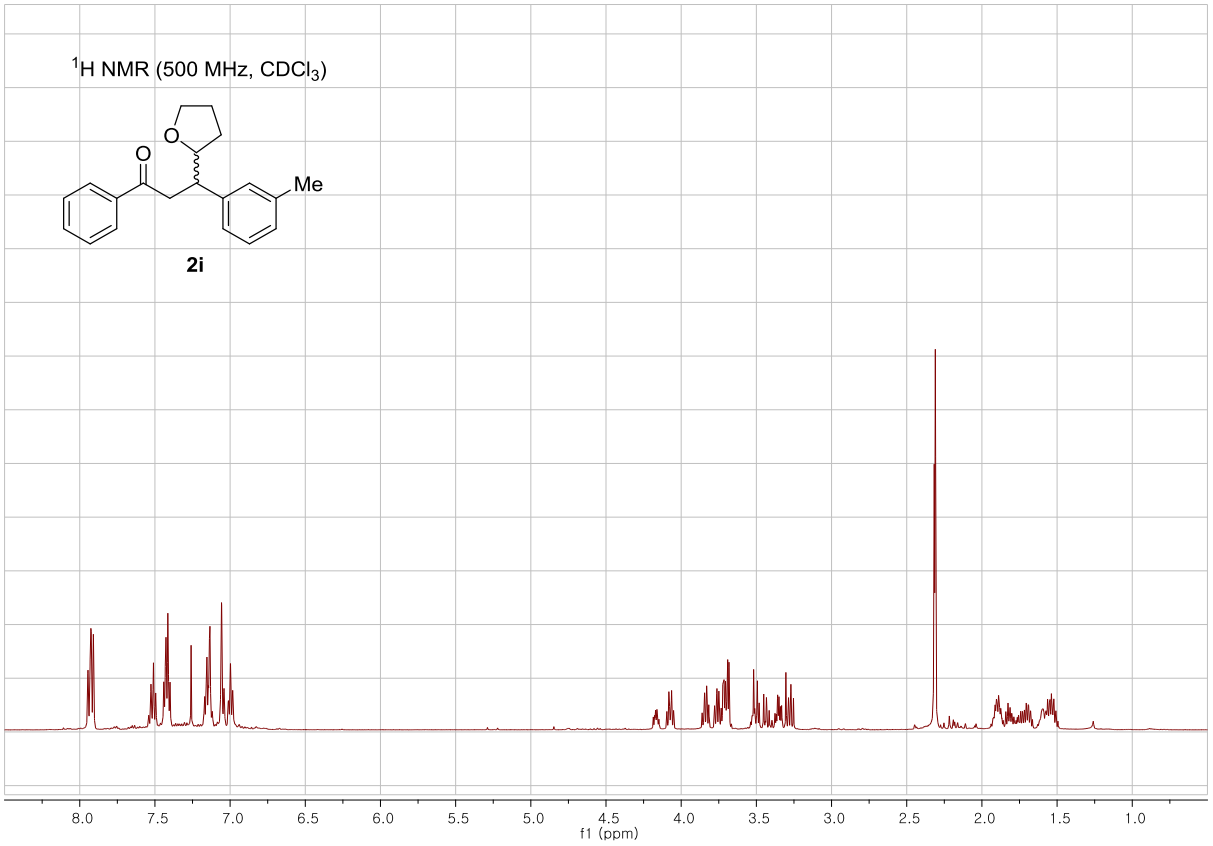
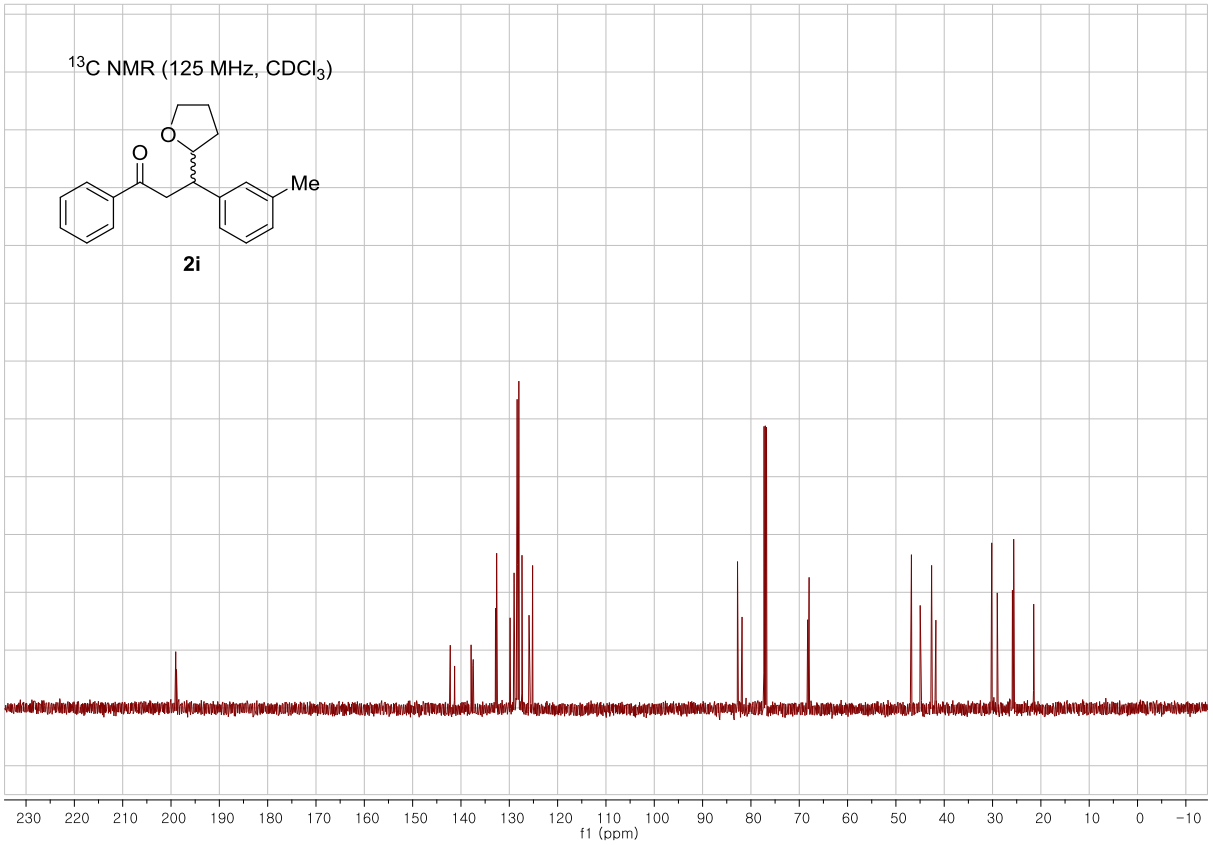
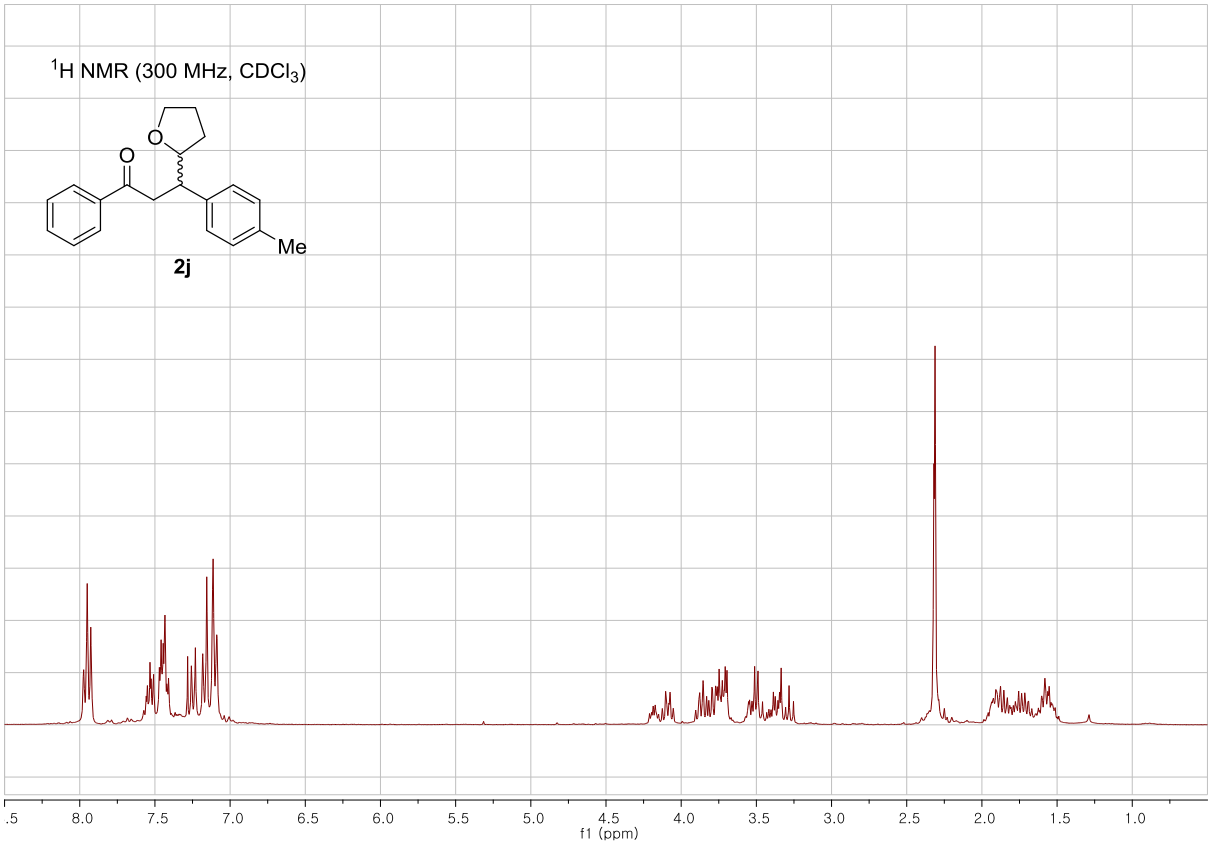
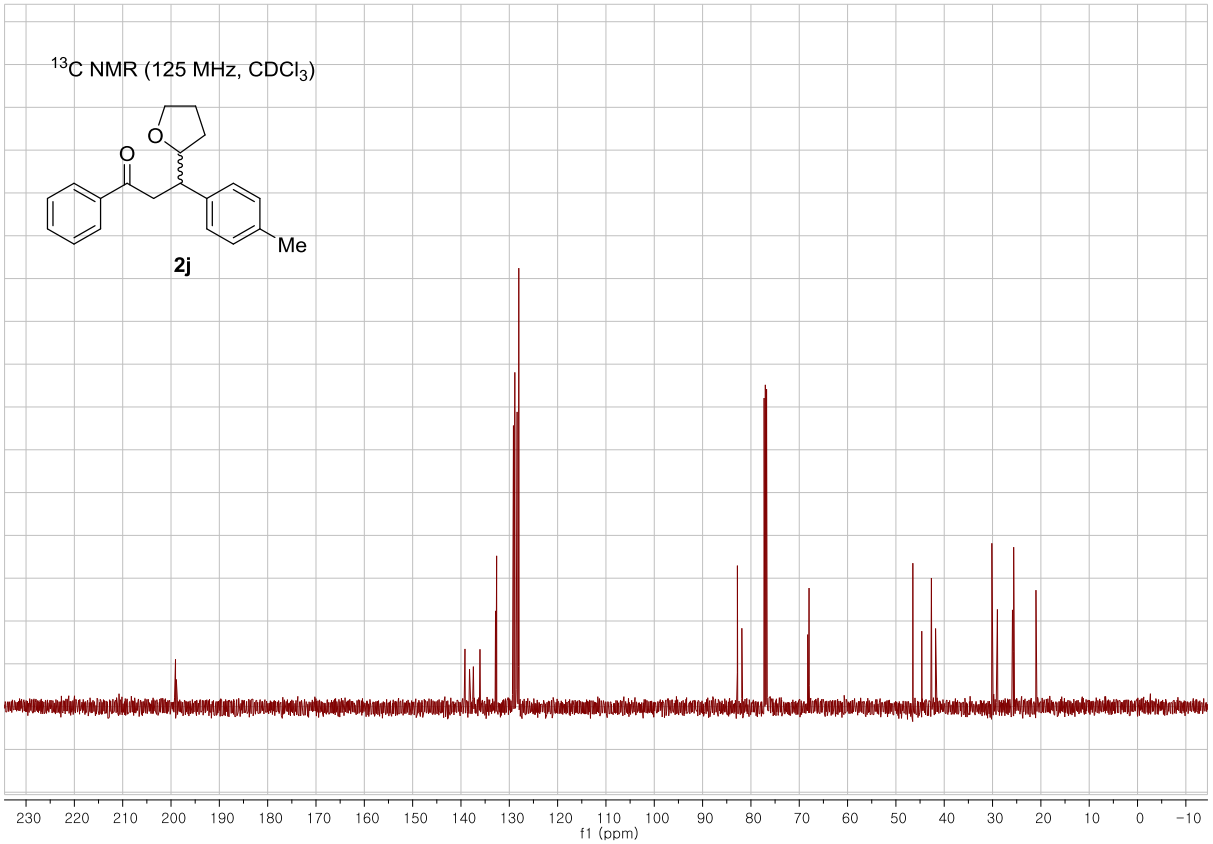
O
O
Me
2h
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

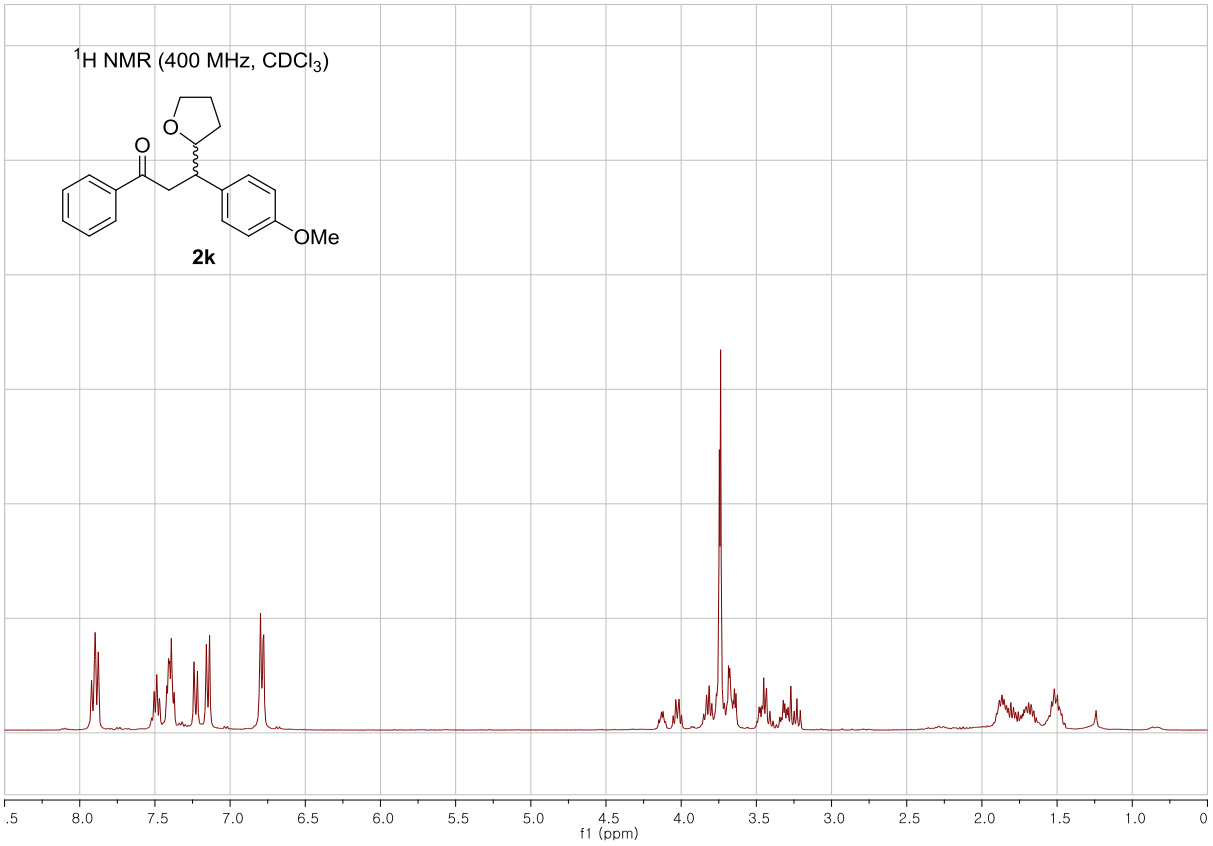

^{13}C NMR (75 MHz, $CDCl_3$)
O
O
Me
2h
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

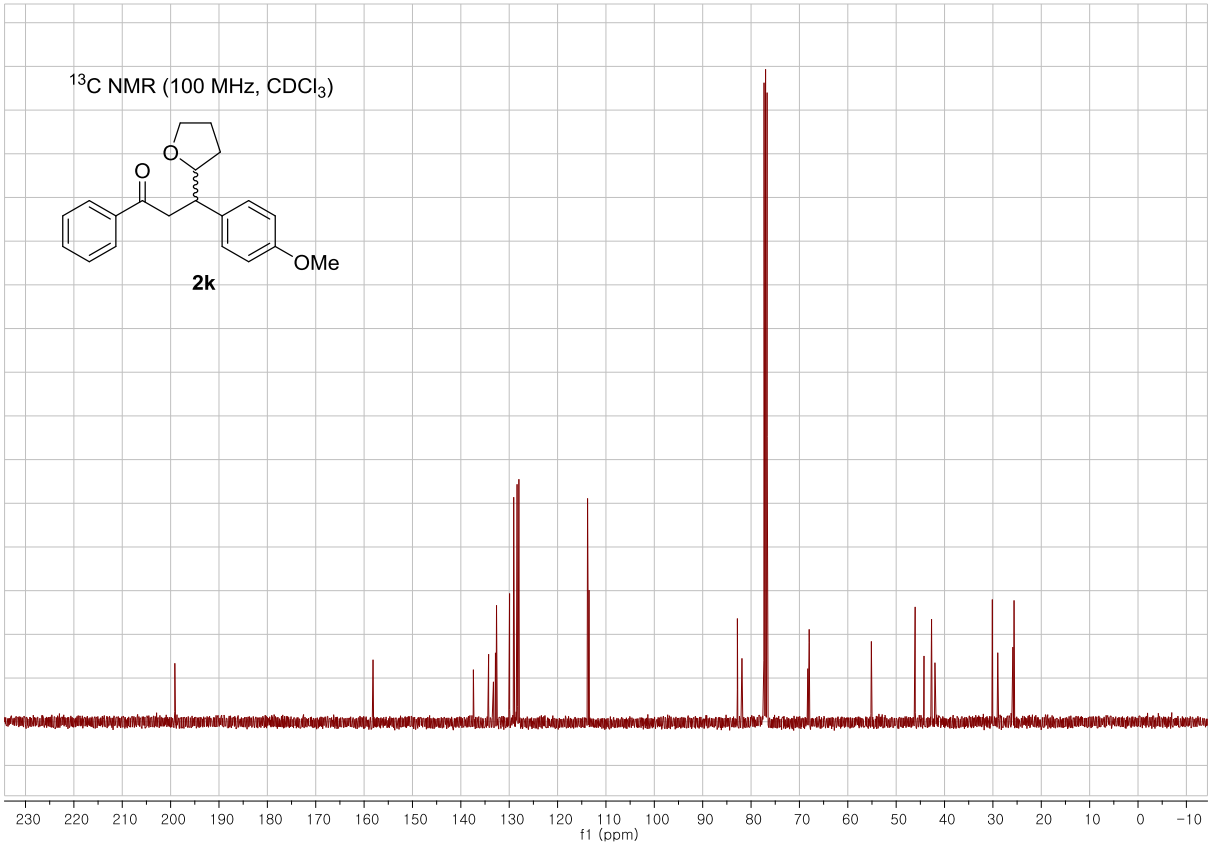

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
Me
2i
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

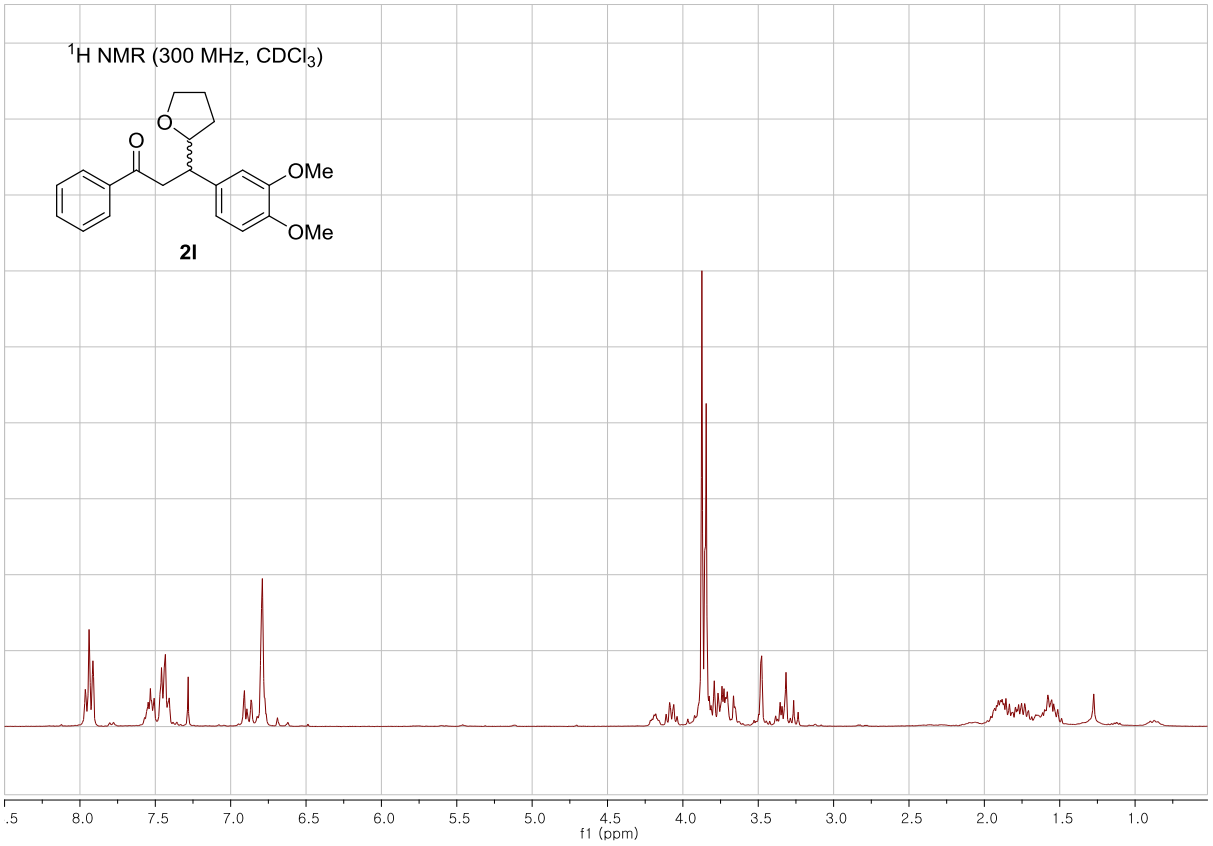

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
Me
2i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

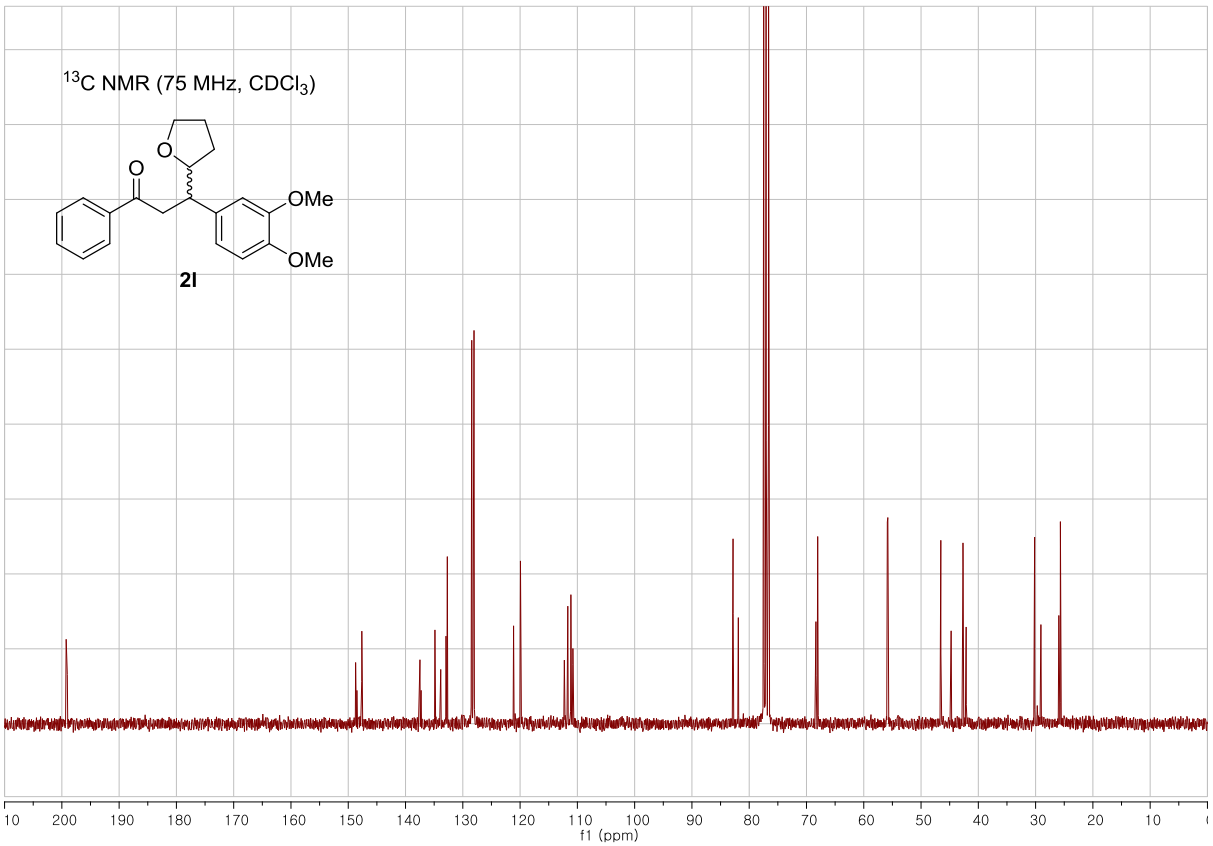

^{1}H NMR (300 MHz, $CDCl_3$)
O
O
Me
2j
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

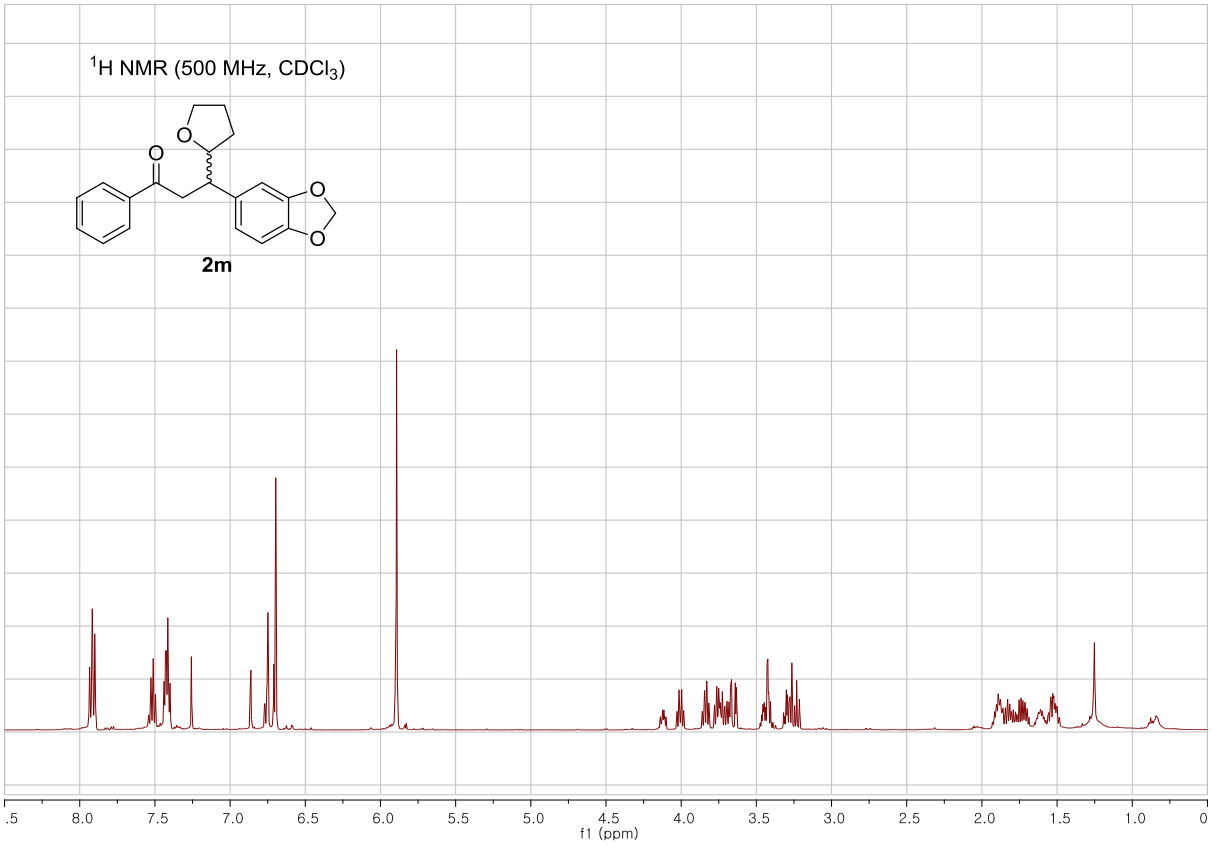

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
Me
2j
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

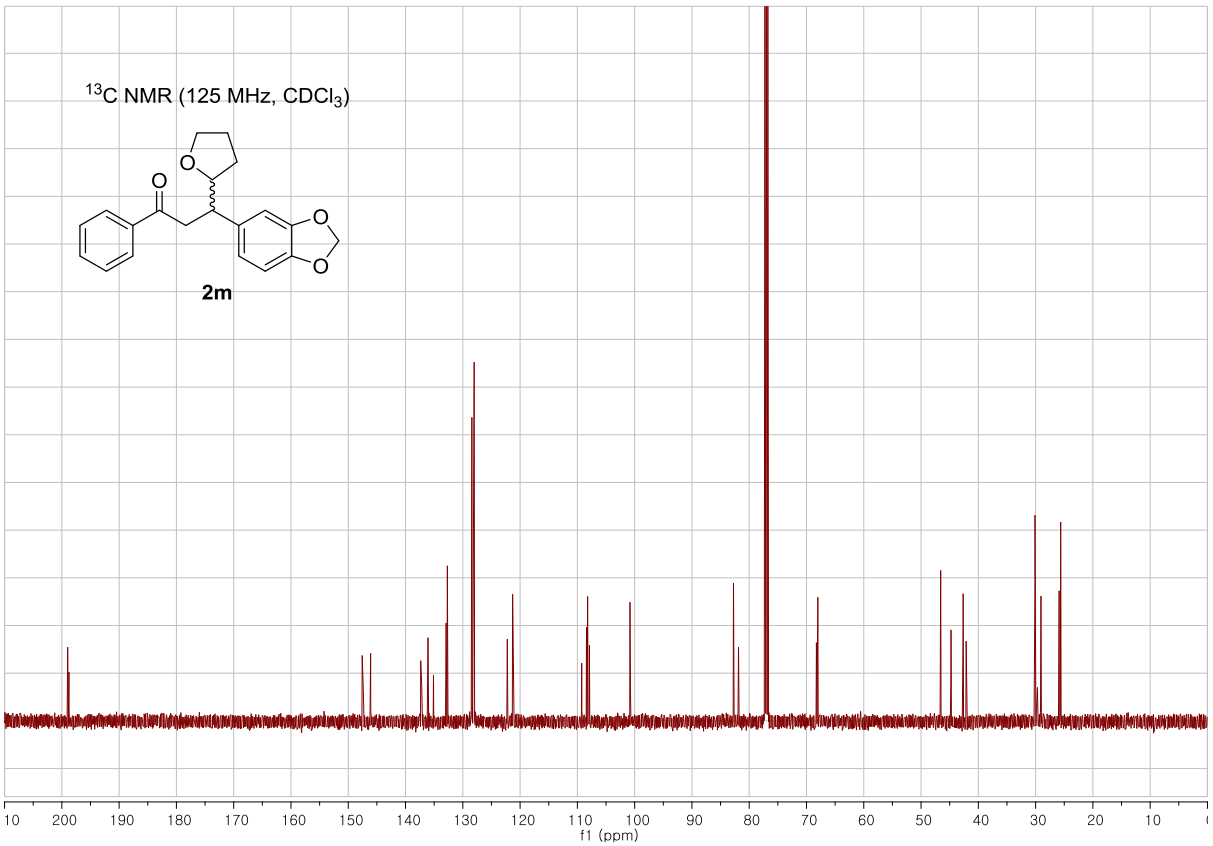

^{1}H NMR (400 MHz, $CDCl_3$)
O
O
OMe
2k
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)

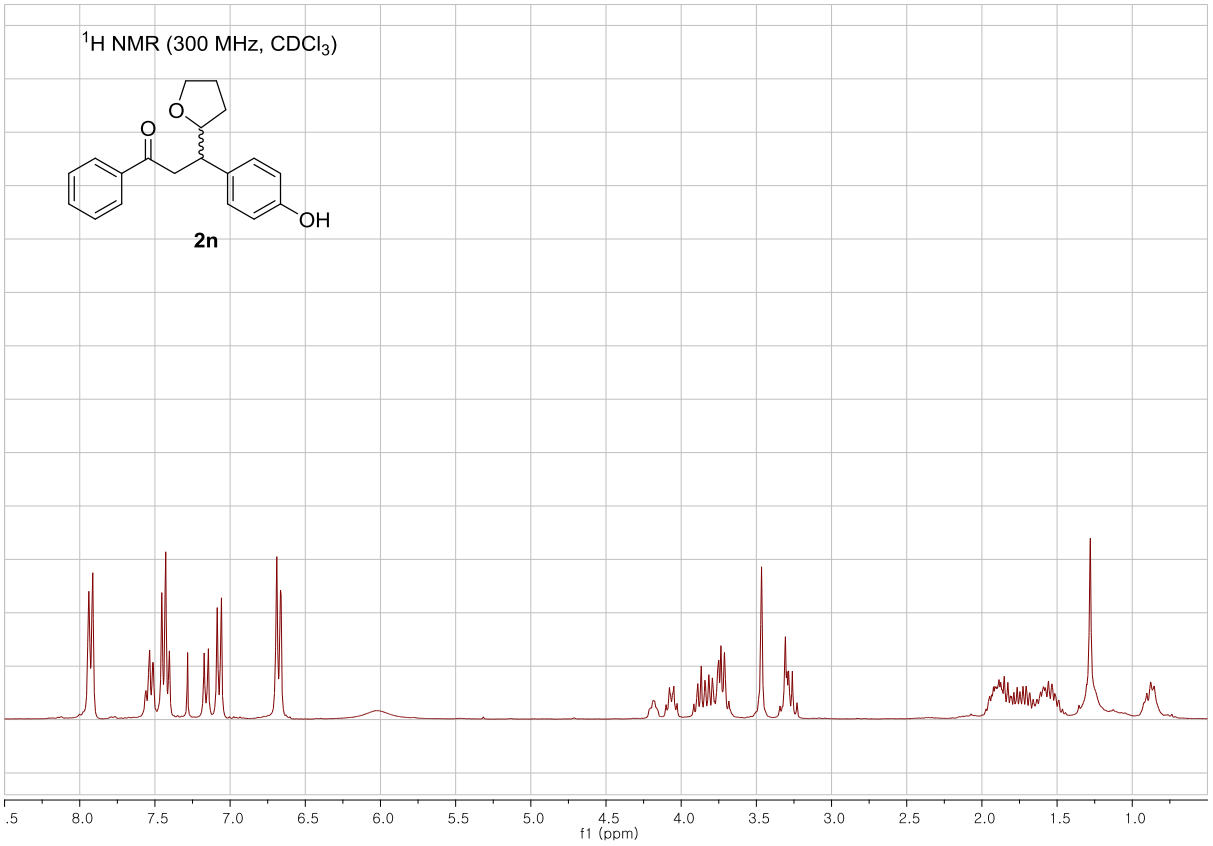

^{13}C NMR (100 MHz, $CDCl_3$)
O
O
OMe
2k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

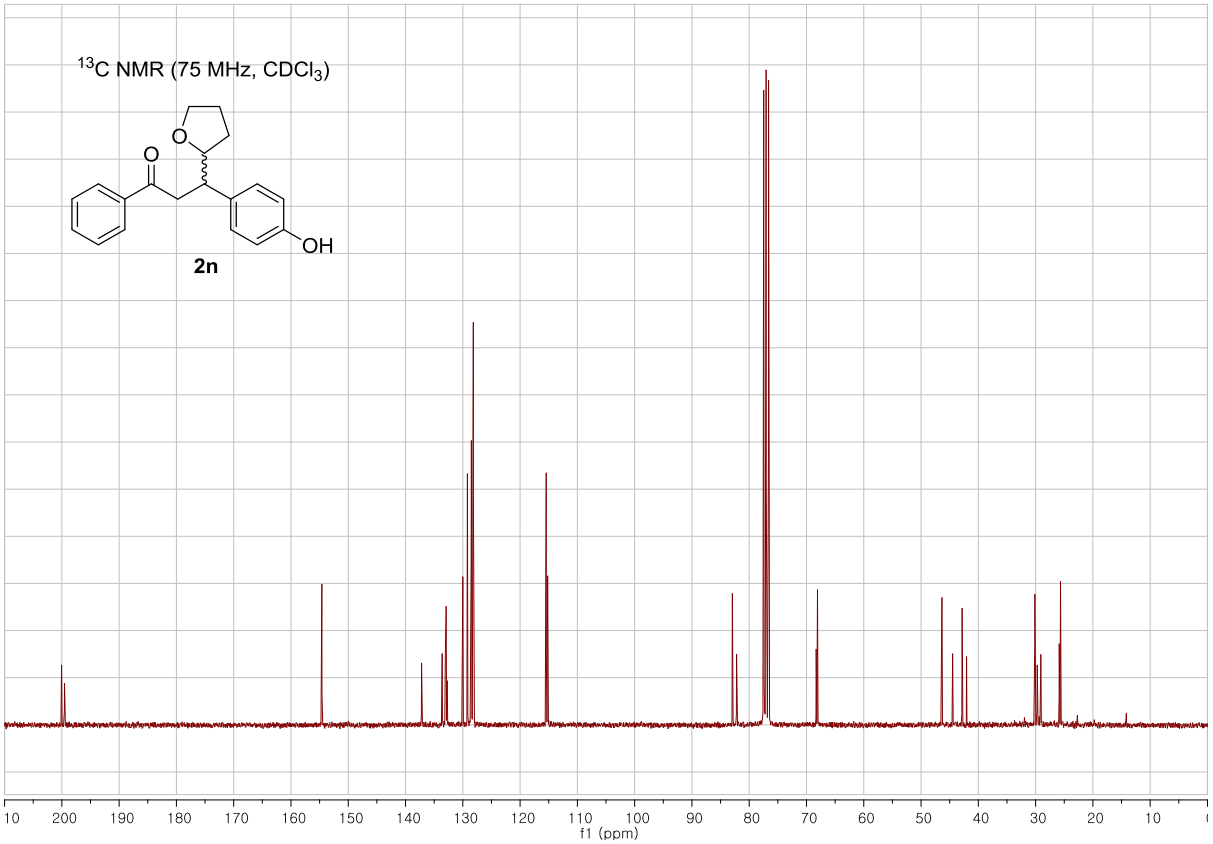

^{1}H NMR (300 MHz, $CDCl_3$)
O
O
OMe
OMe
2l
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

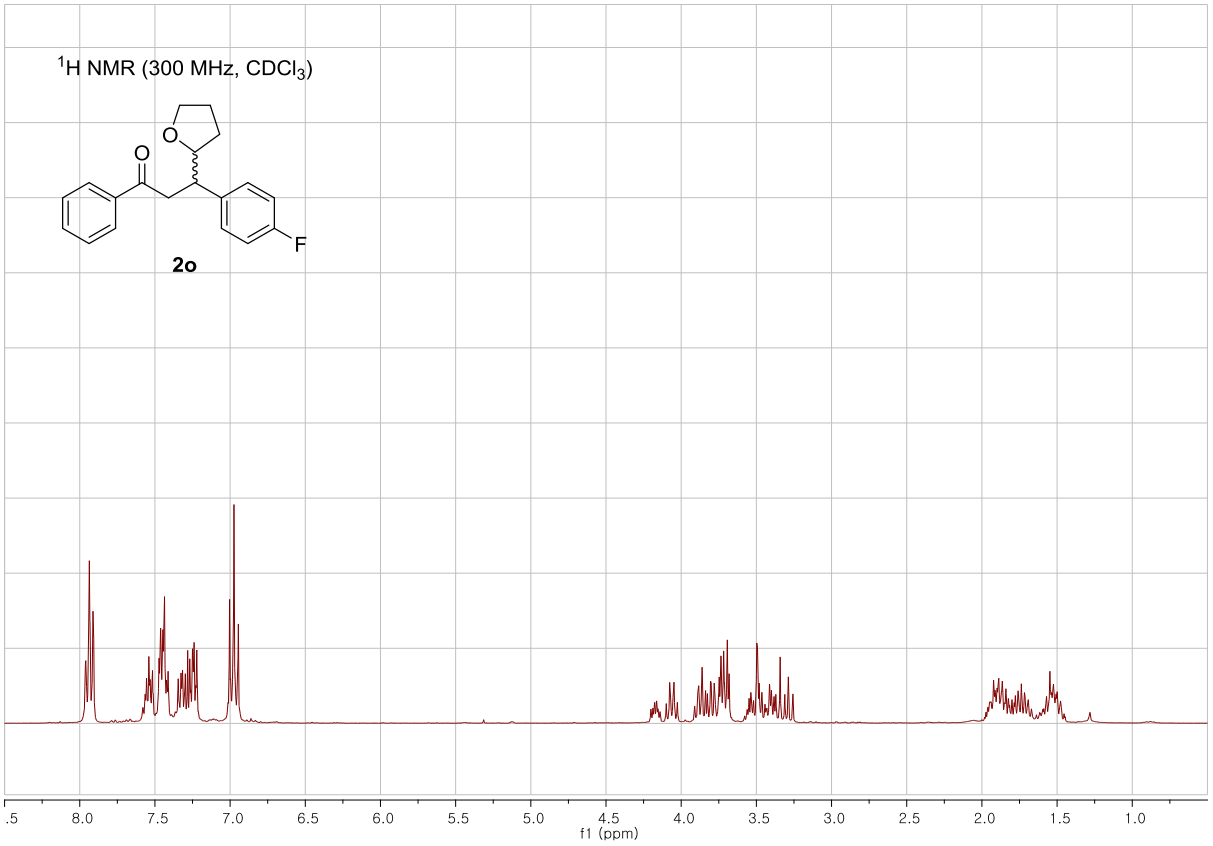

^{13}C NMR (75 MHz, $CDCl_3$)
O
O
OMe
OMe
2l
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

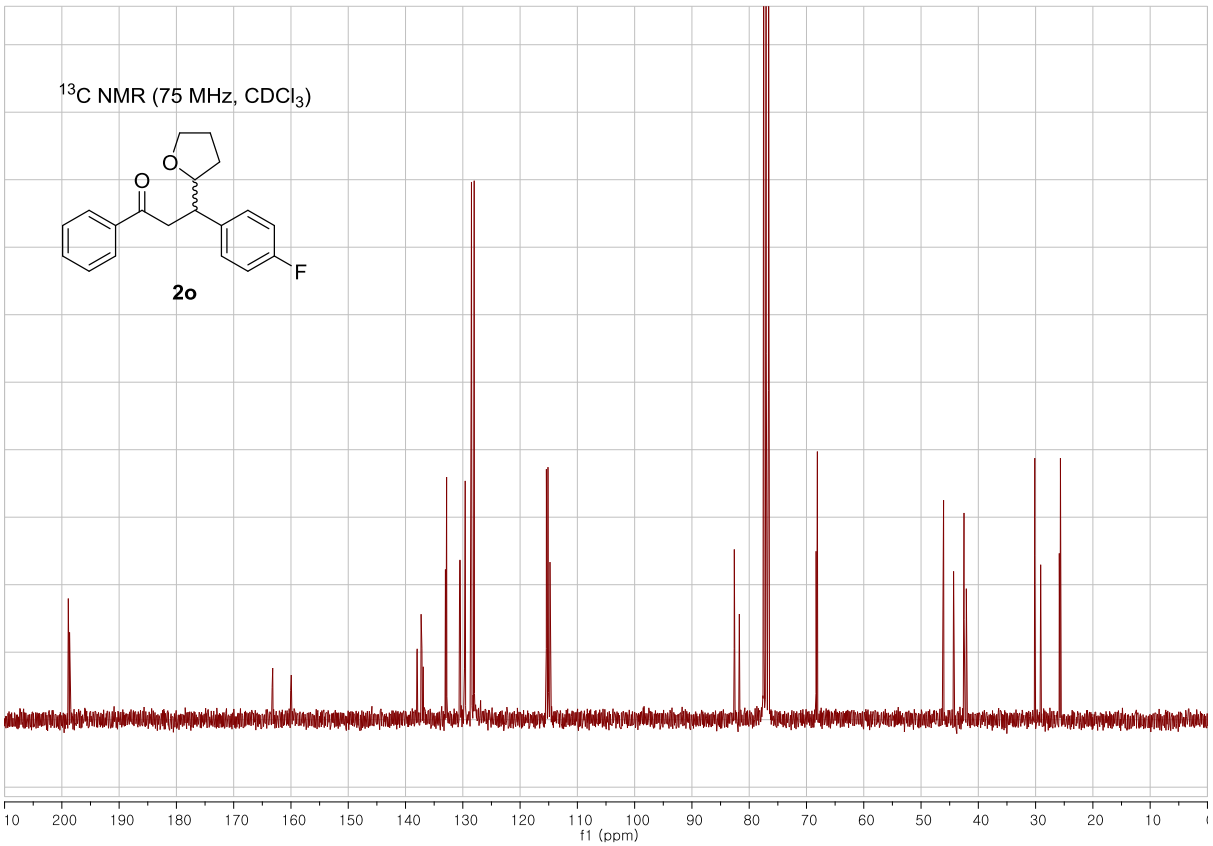

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
O
O
2m
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)

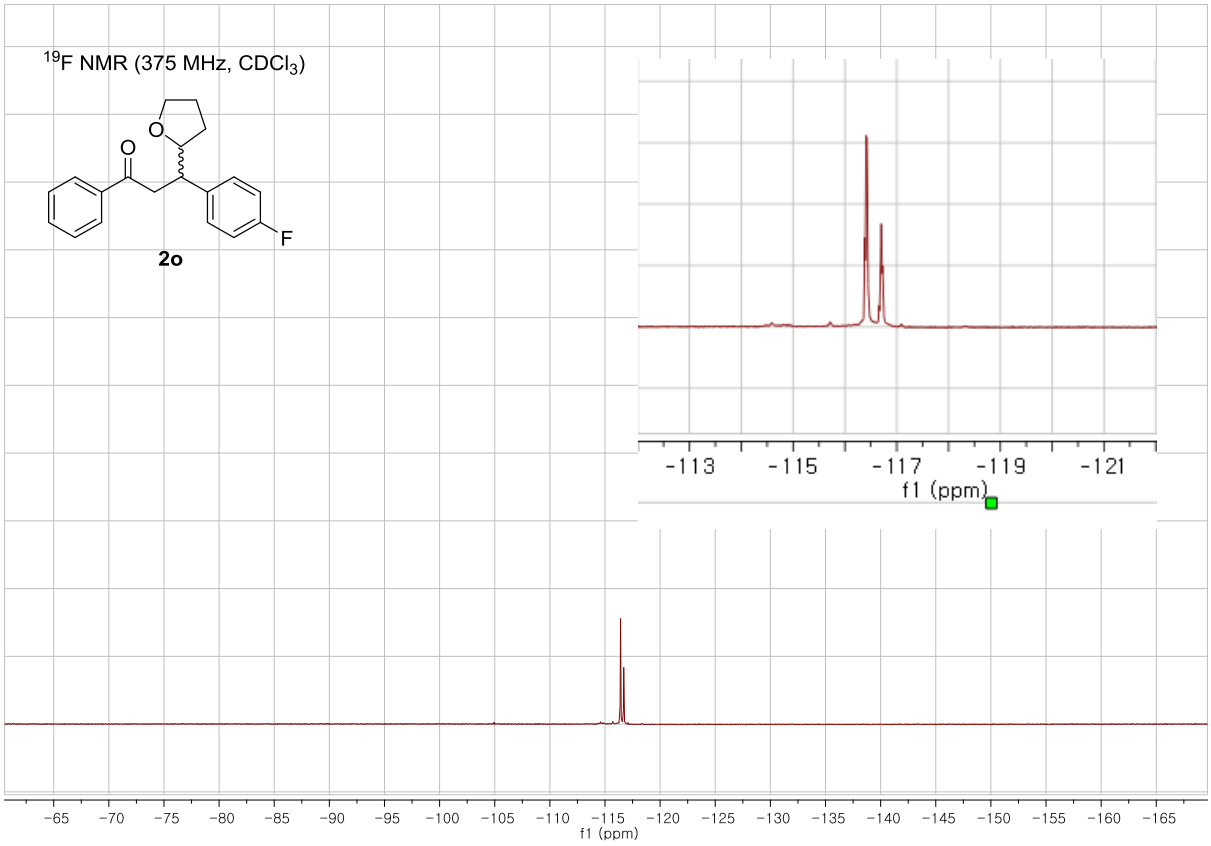

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
O
O
2m
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

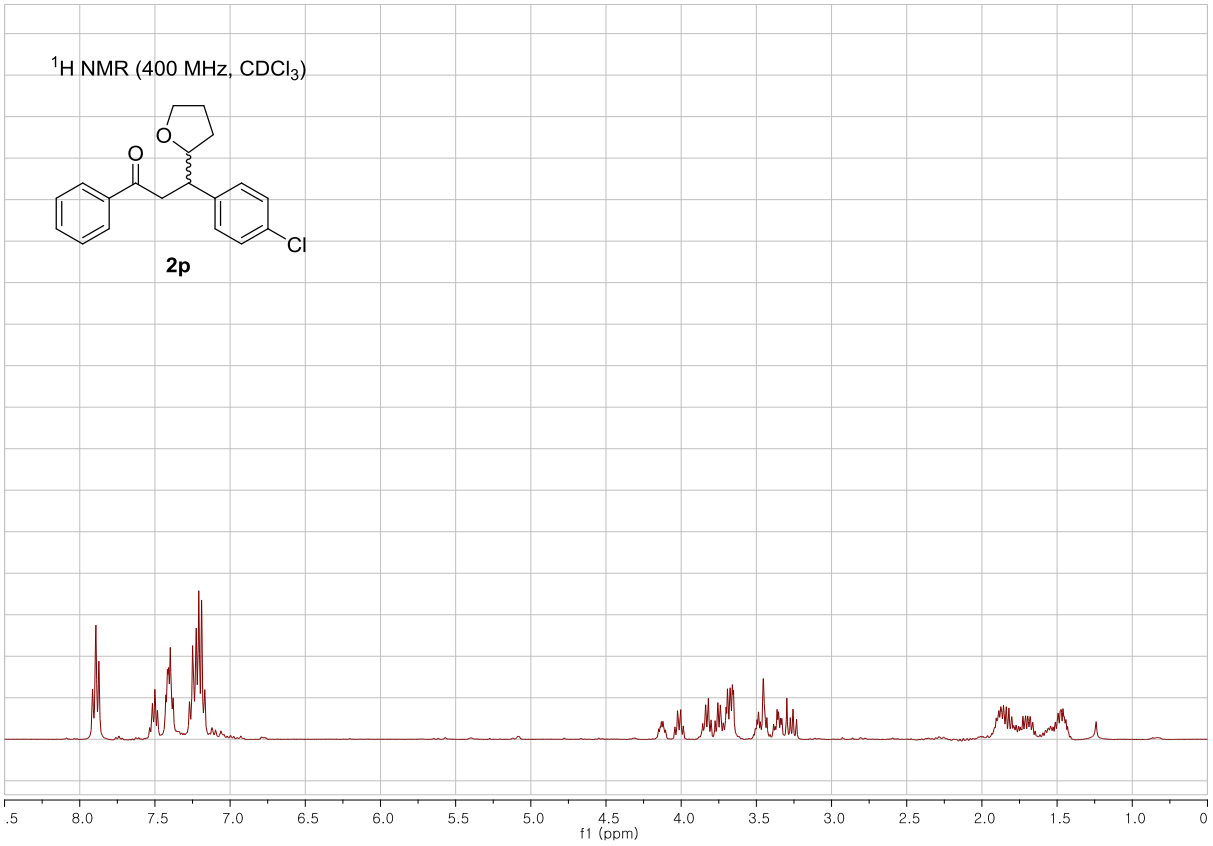

^{1}H NMR (300 MHz, CDCl$_3$)
O
O
OH
2n
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

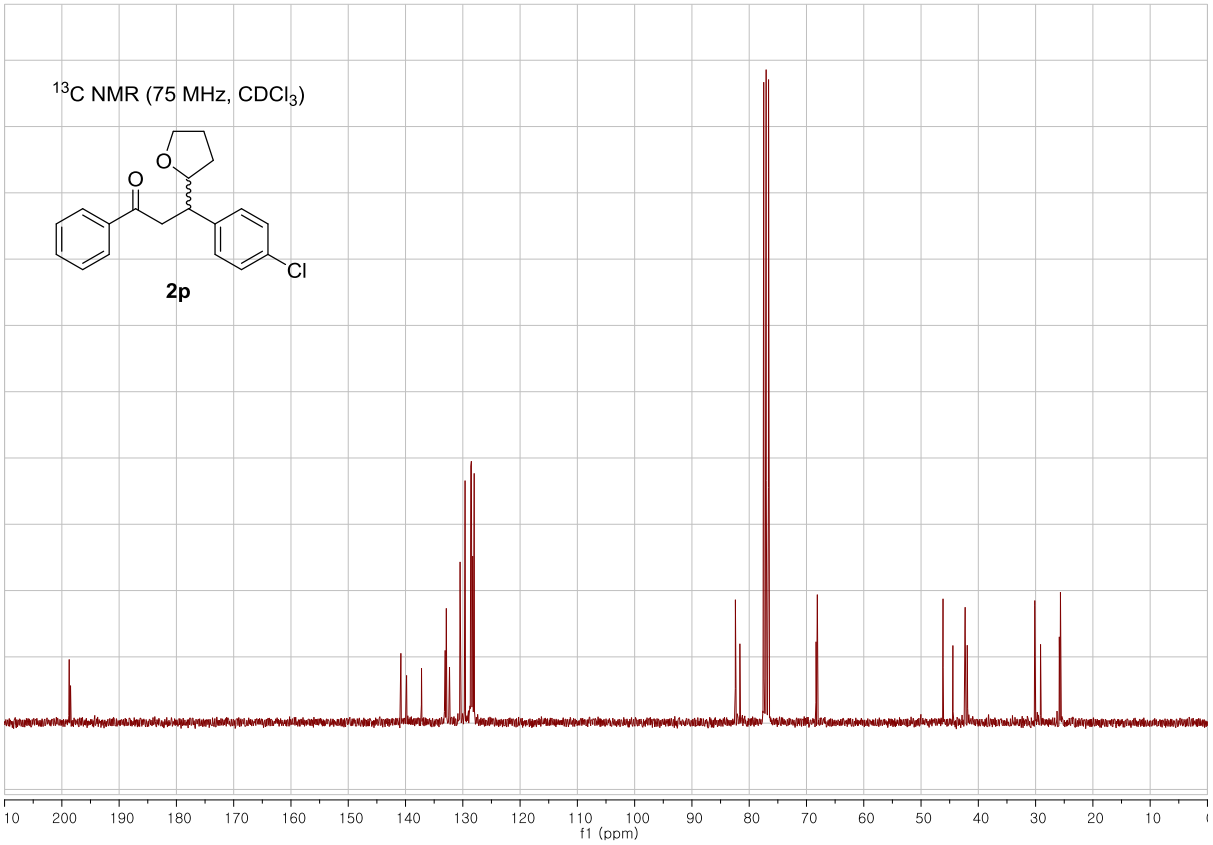

^{13}C NMR (75 MHz, CDCl$_3$)
O
O
OH
2n
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

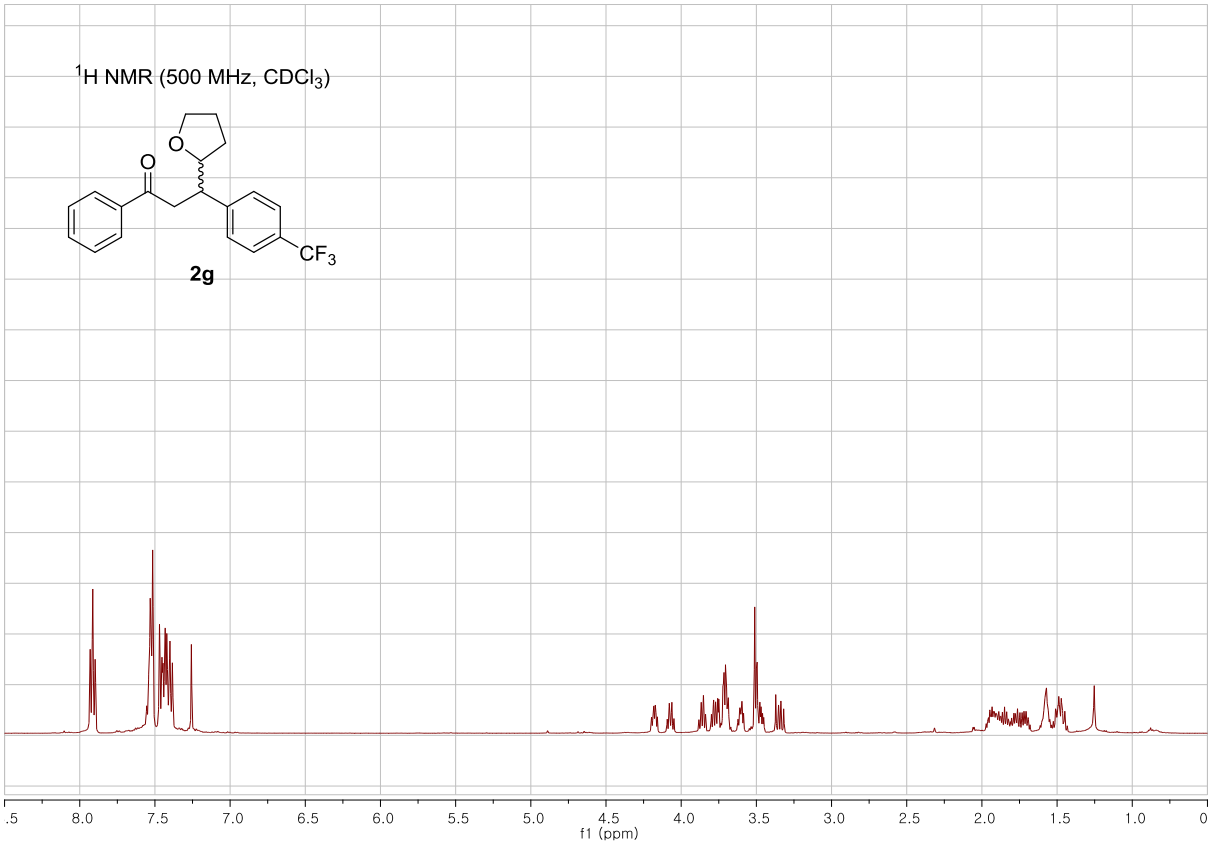

^{1}H NMR (300 MHz, $CDCl_3$)
O
O
F
2o
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

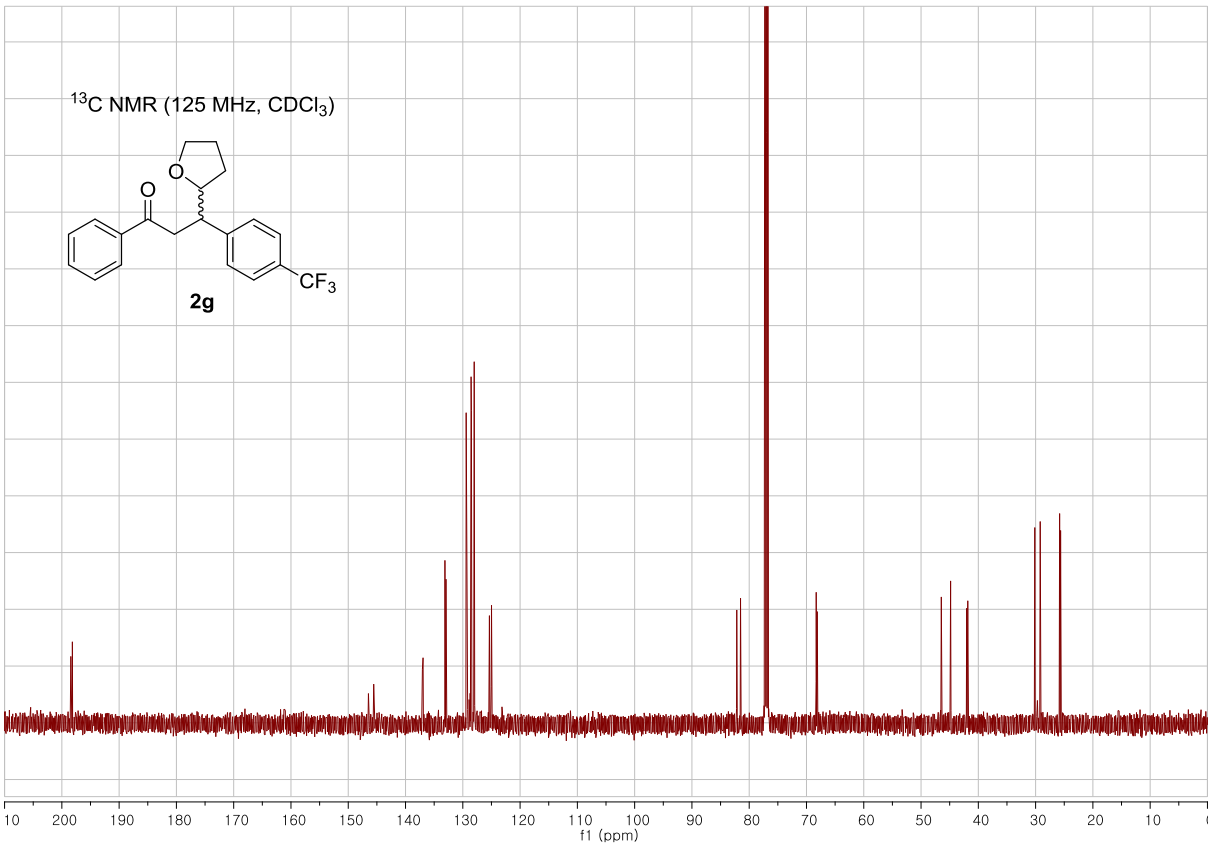

^{13}C NMR (75 MHz, $CDCl_3$)
O
O
F
2o
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

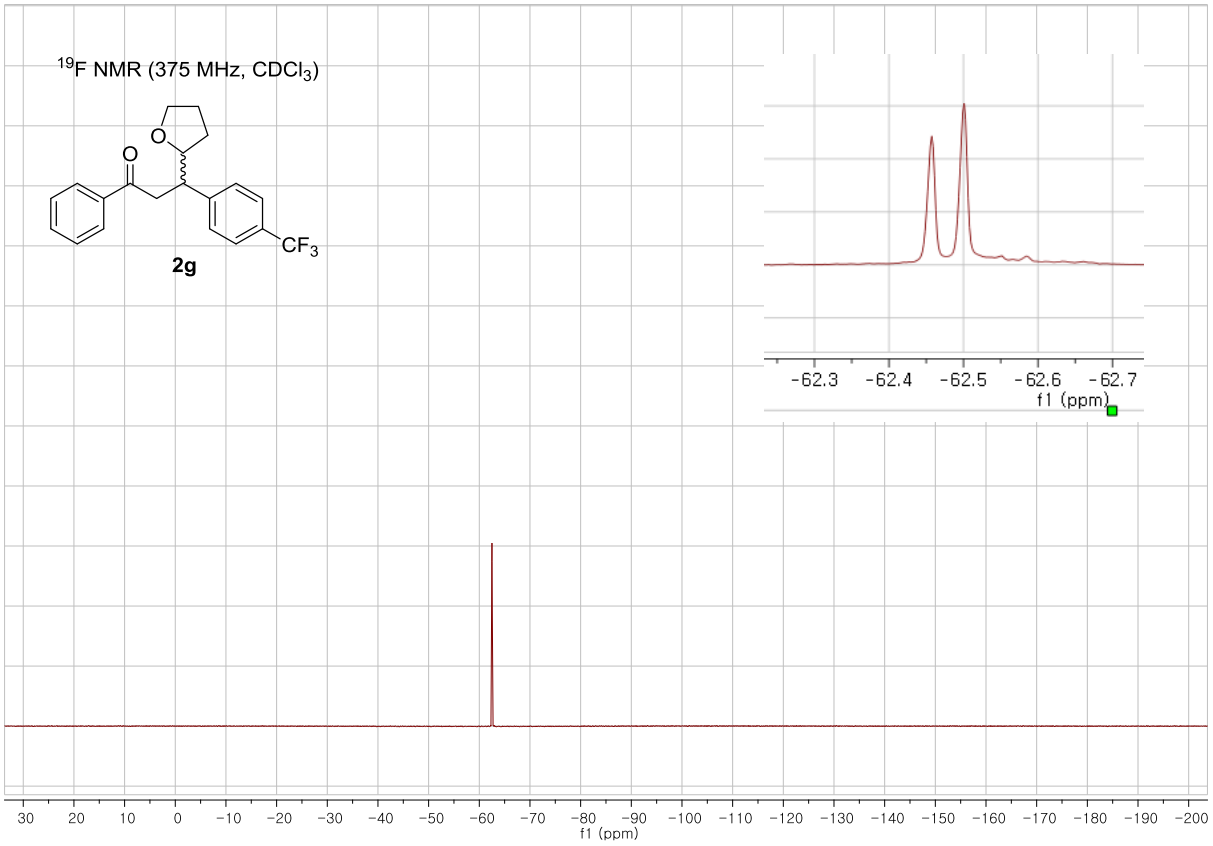

19F NMR (375 MHz, CDCl3)
O
O
F
2o
-113
-115
-117
-119
-121
f1 (ppm)
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)

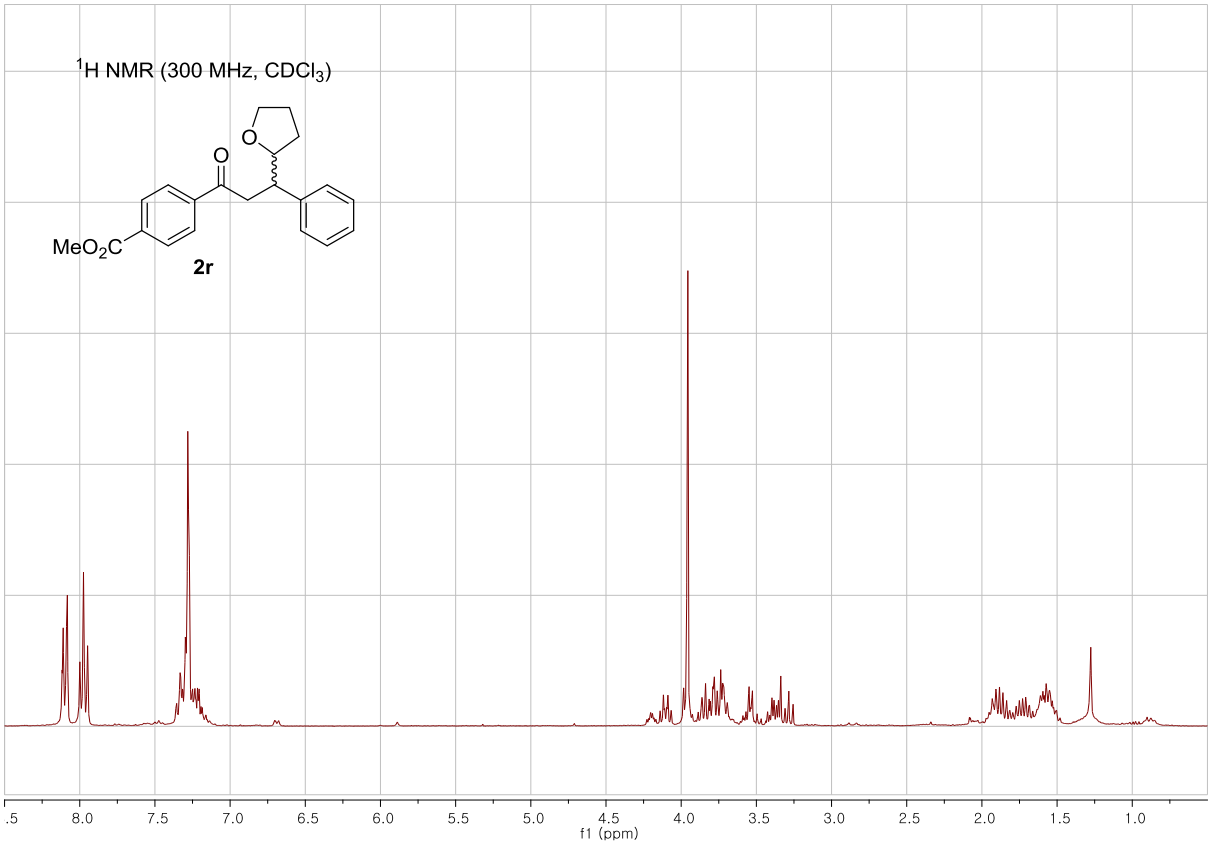

^{1}H NMR (400 MHz, $CDCl_3$)
O
O
Cl
2p
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)

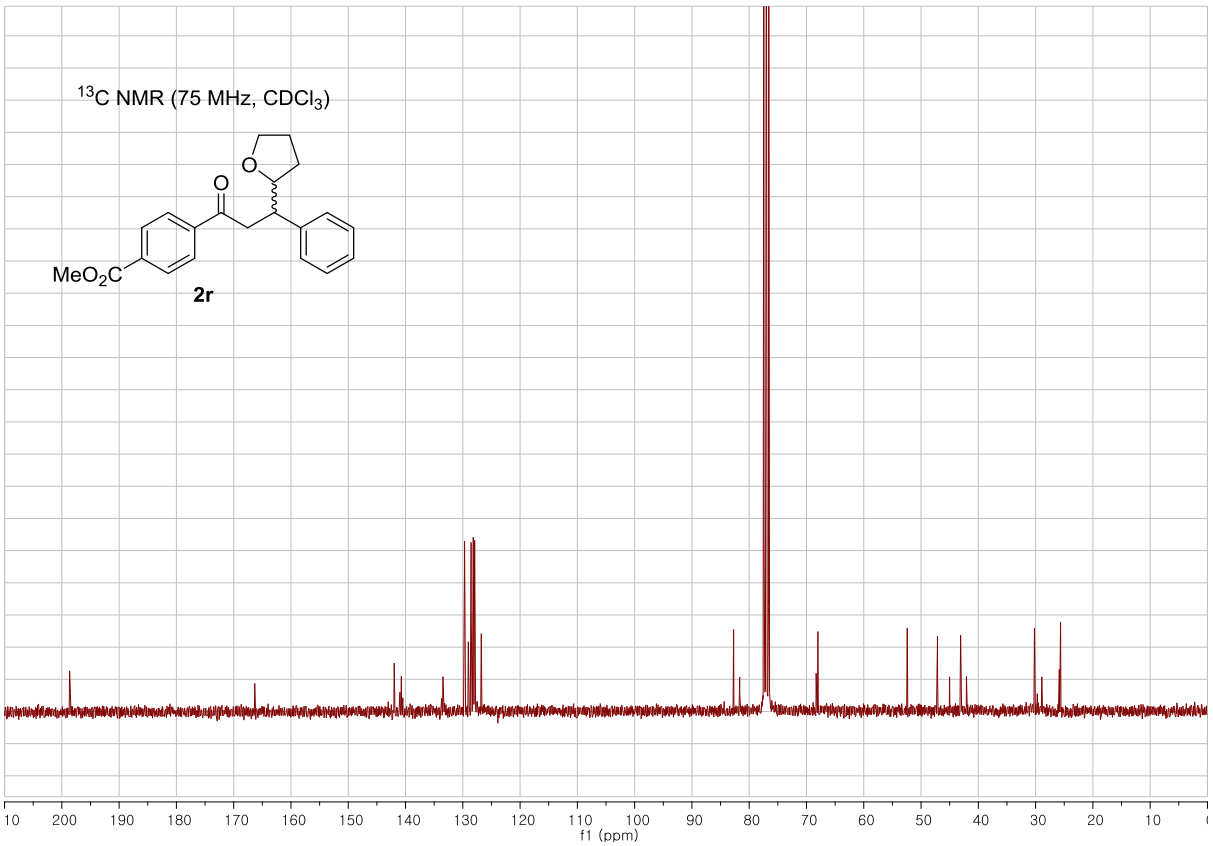

^{13}C NMR (75 MHz, $CDCl_3$)
O
O
Cl
2p
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

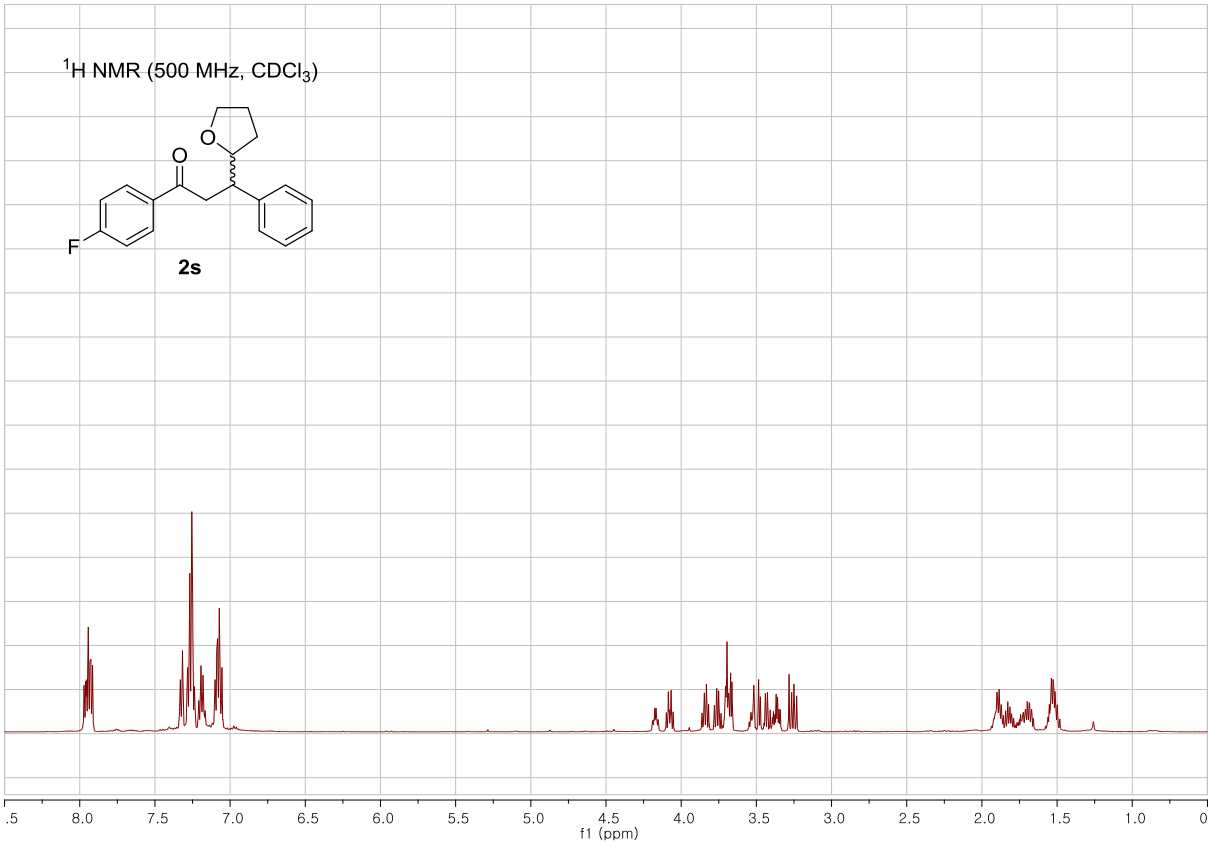

^{1}H NMR (500 MHz, CDCl$_3$)
O
O
CF$_3$
2g
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)

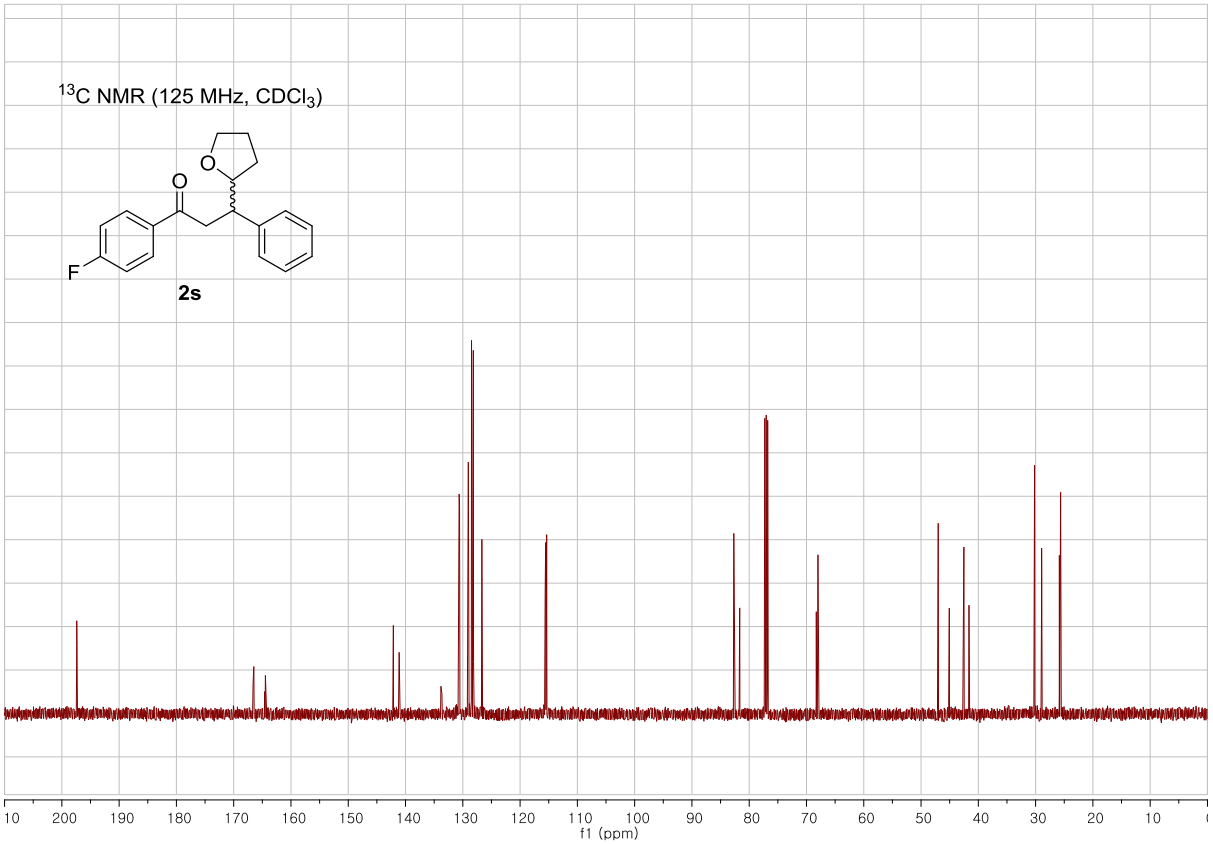

^{13}C NMR (125 MHz, CDCl$_3$)
O
O
CF$_3$
2g
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

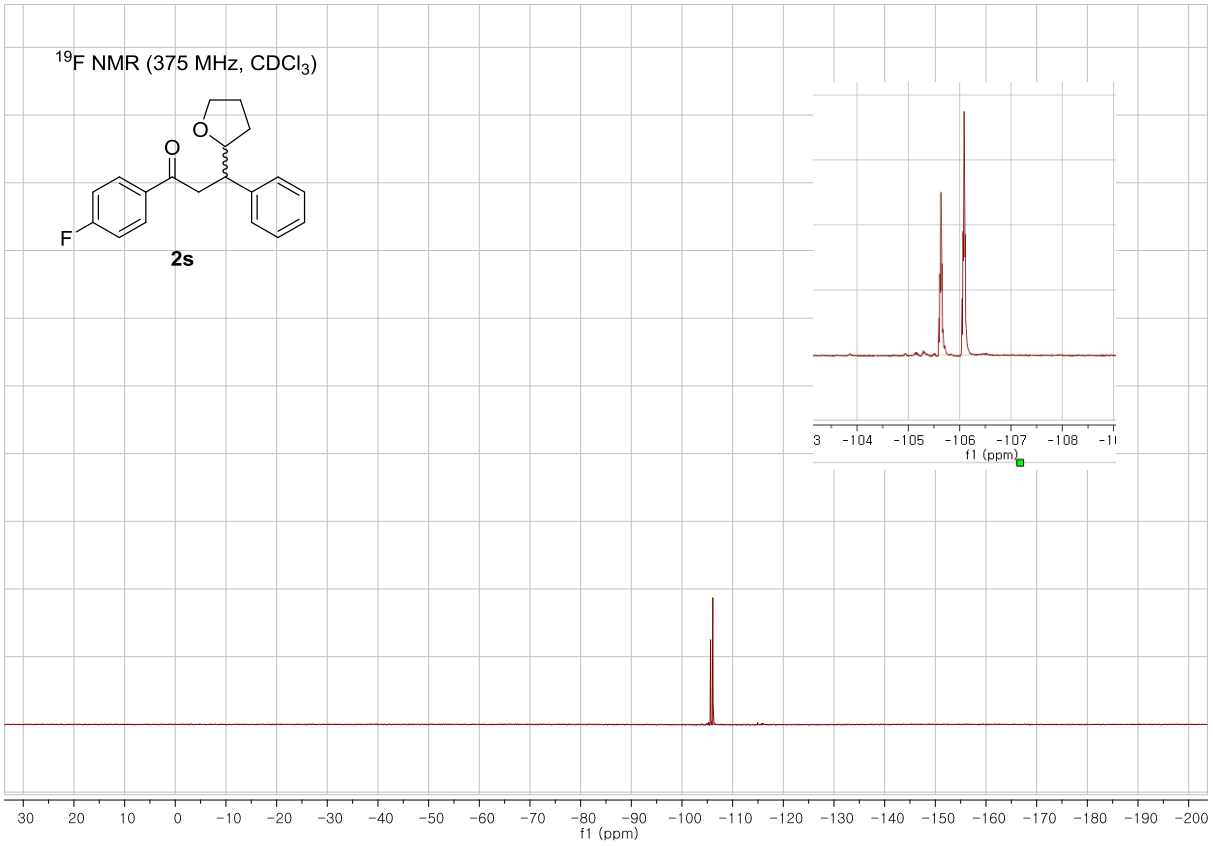

19F NMR (375 MHz, CDCl3)
O
O
CF3
2g
-62.3
-62.4
-62.5
-62.6
-62.7
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

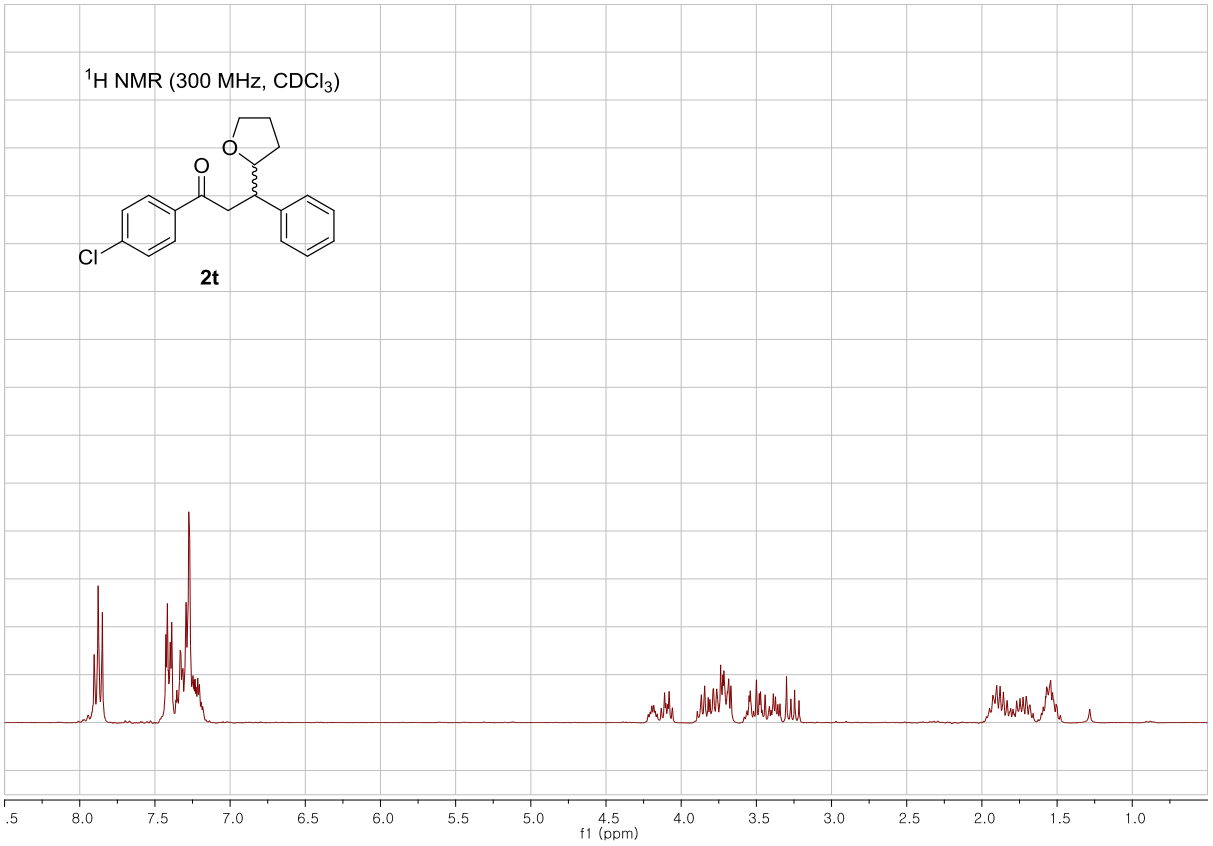

^{1}H NMR (300 MHz, CDCl$_3$)
O
O
MeO$_2$C
2r
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

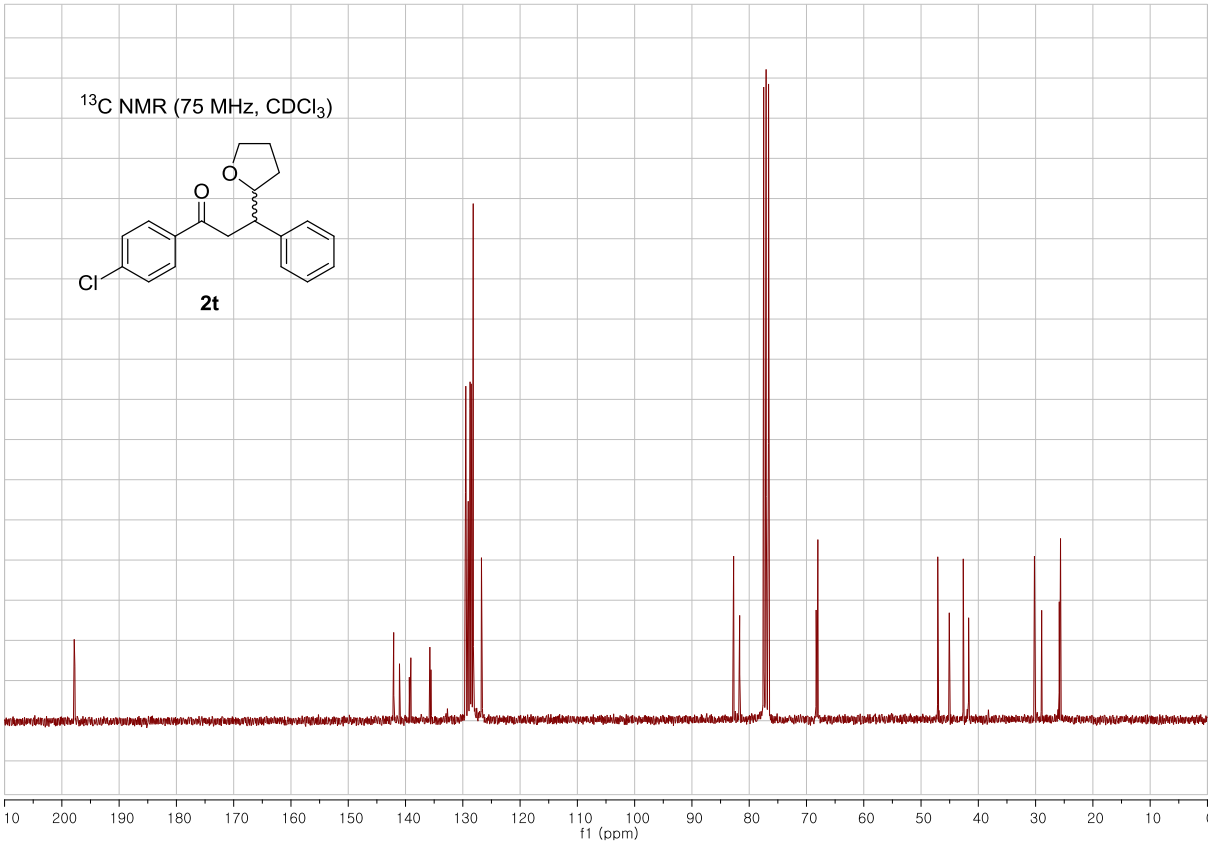

^{13}C NMR (75 MHz, CDCl$_3$)
O
O
MeO$_2$C
2r
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

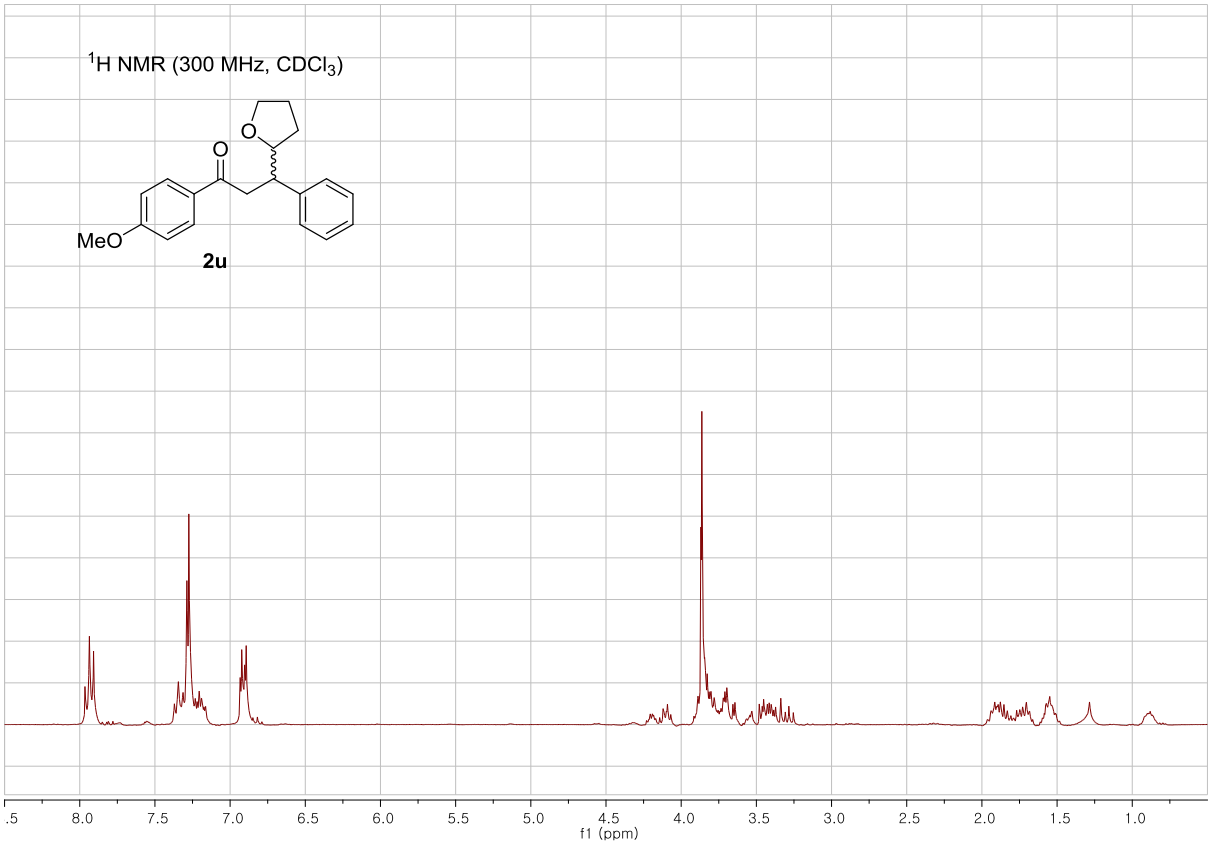

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
F
2s
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

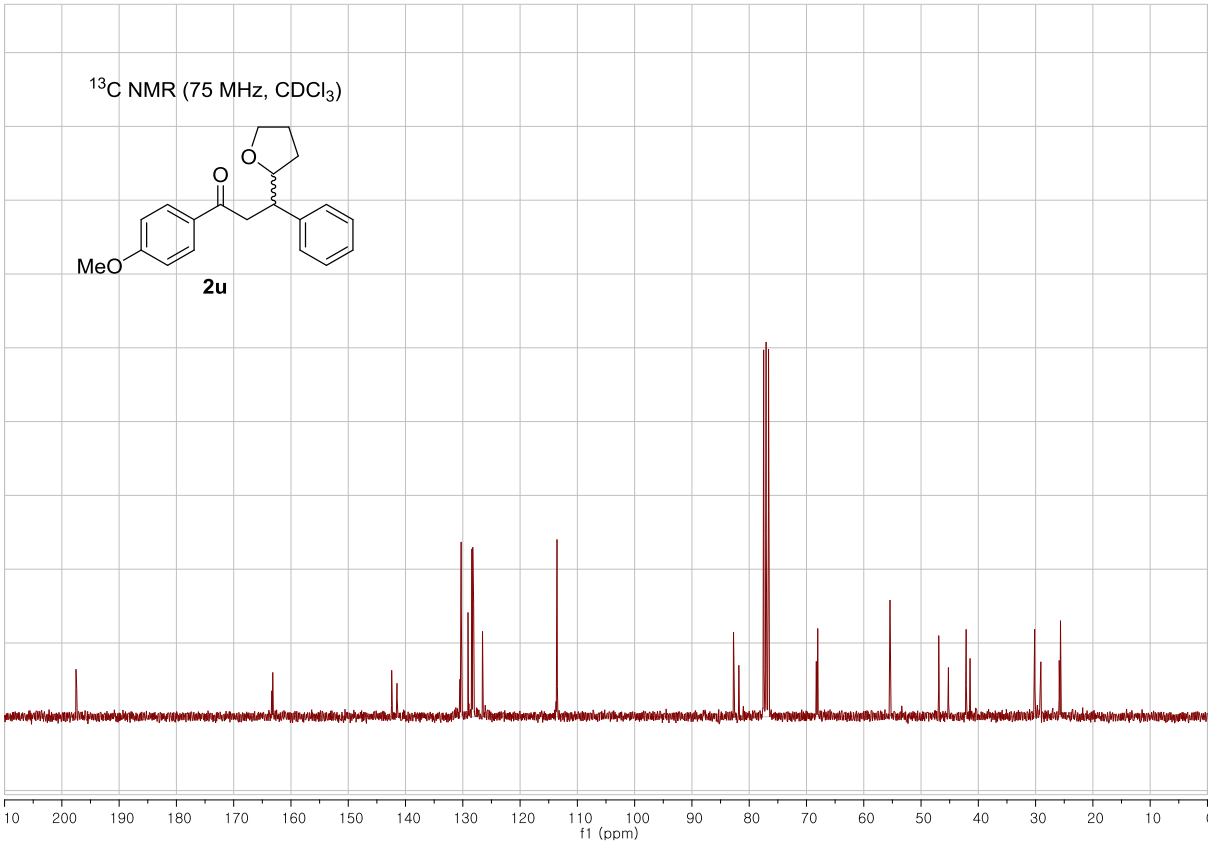

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
F
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

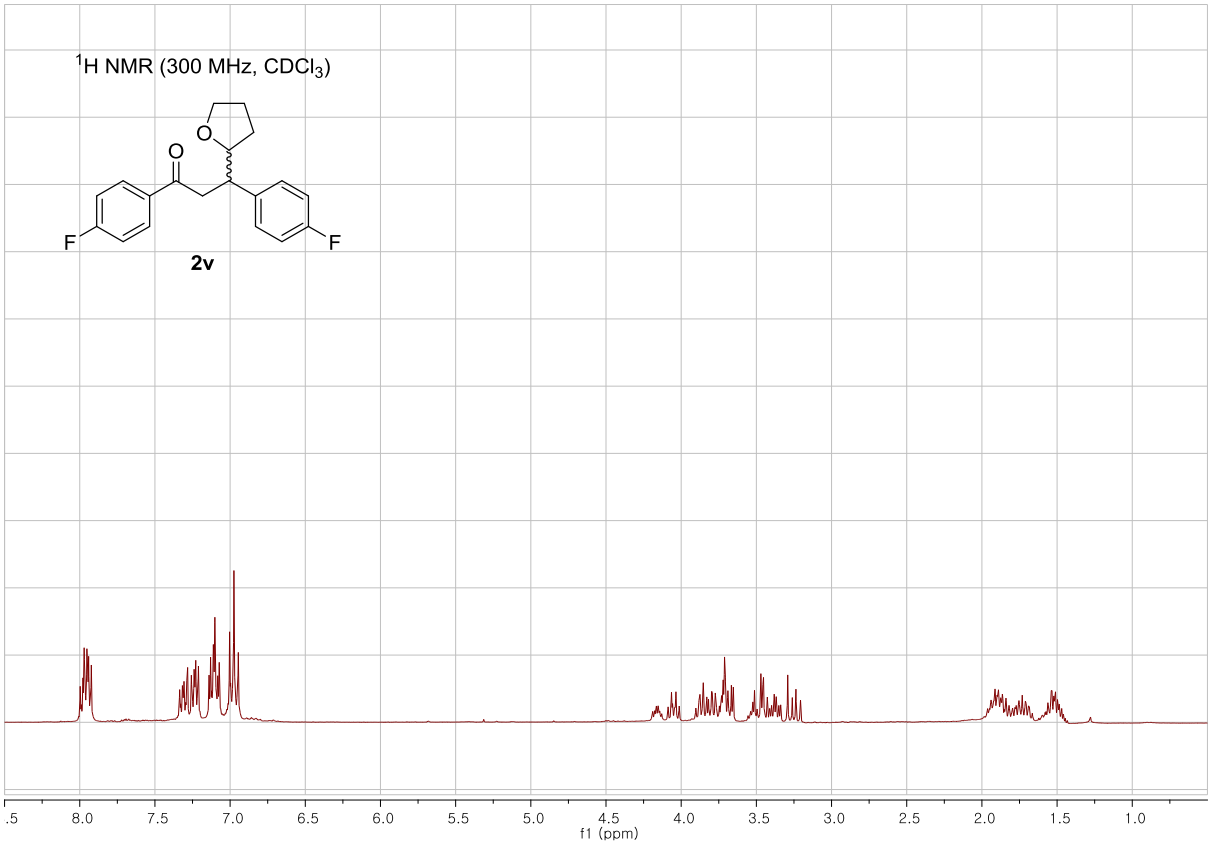

19F NMR (375 MHz, CDCl3)
O
O
F
2s
-104
-105
-106
-107
-108
f1 (ppm)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

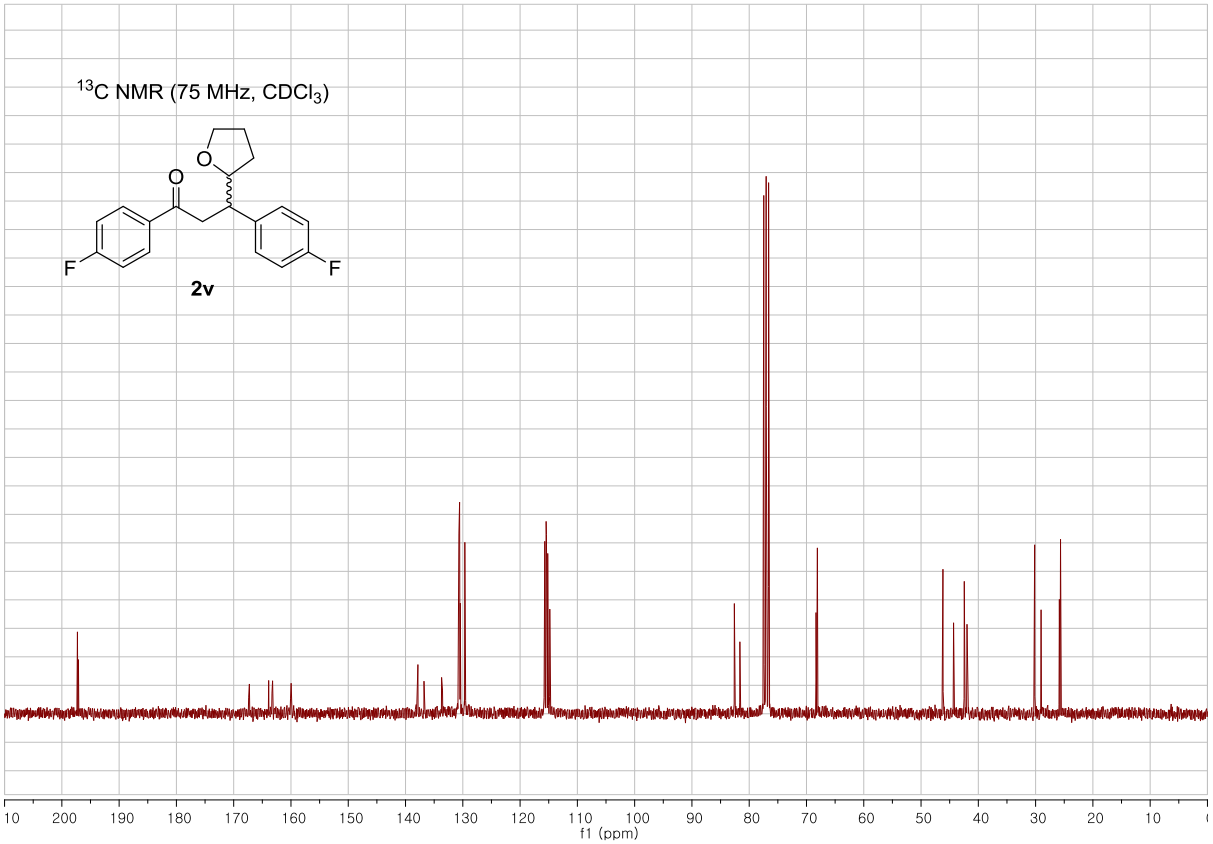

^{1}H NMR (300 MHz, $CDCl_3$)
O
O
Cl
2t
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

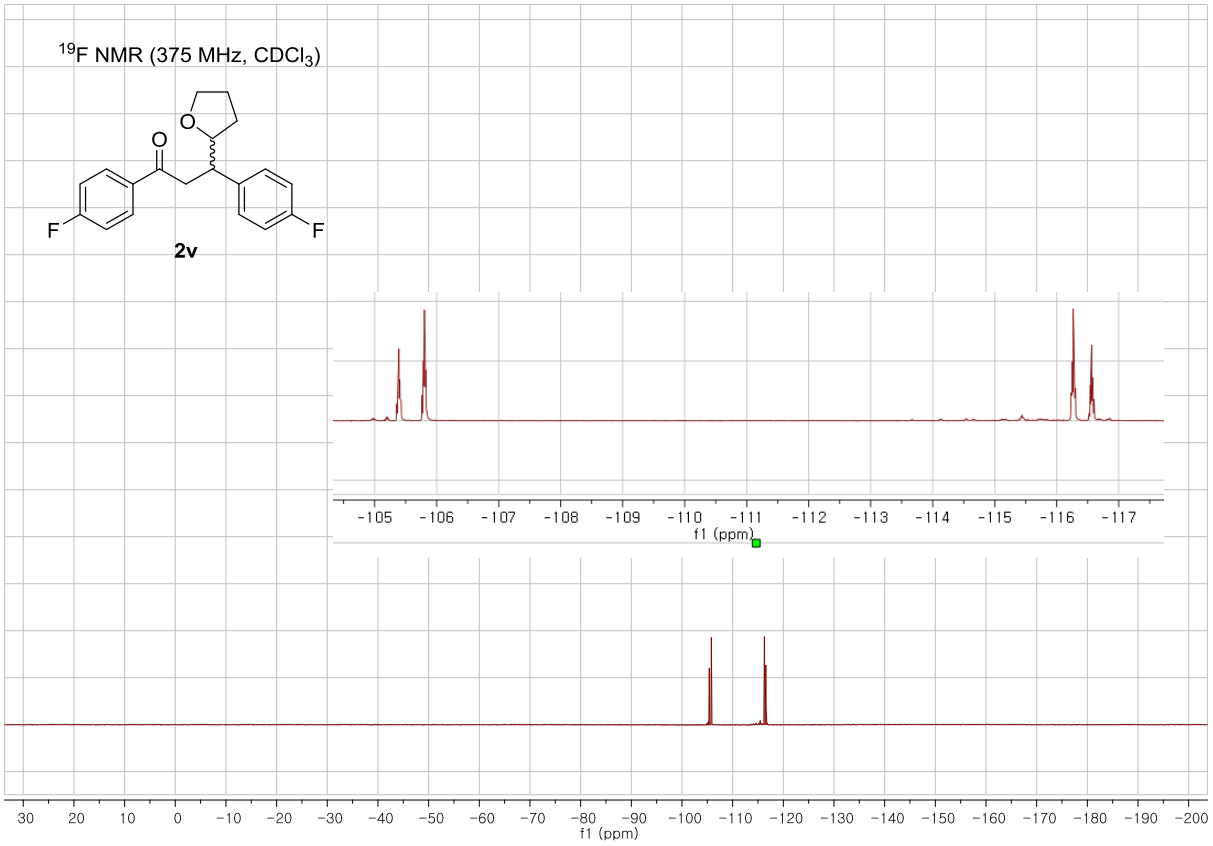

^{13}C NMR (75 MHz, $CDCl_3$)
O
O
Cl
2t
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

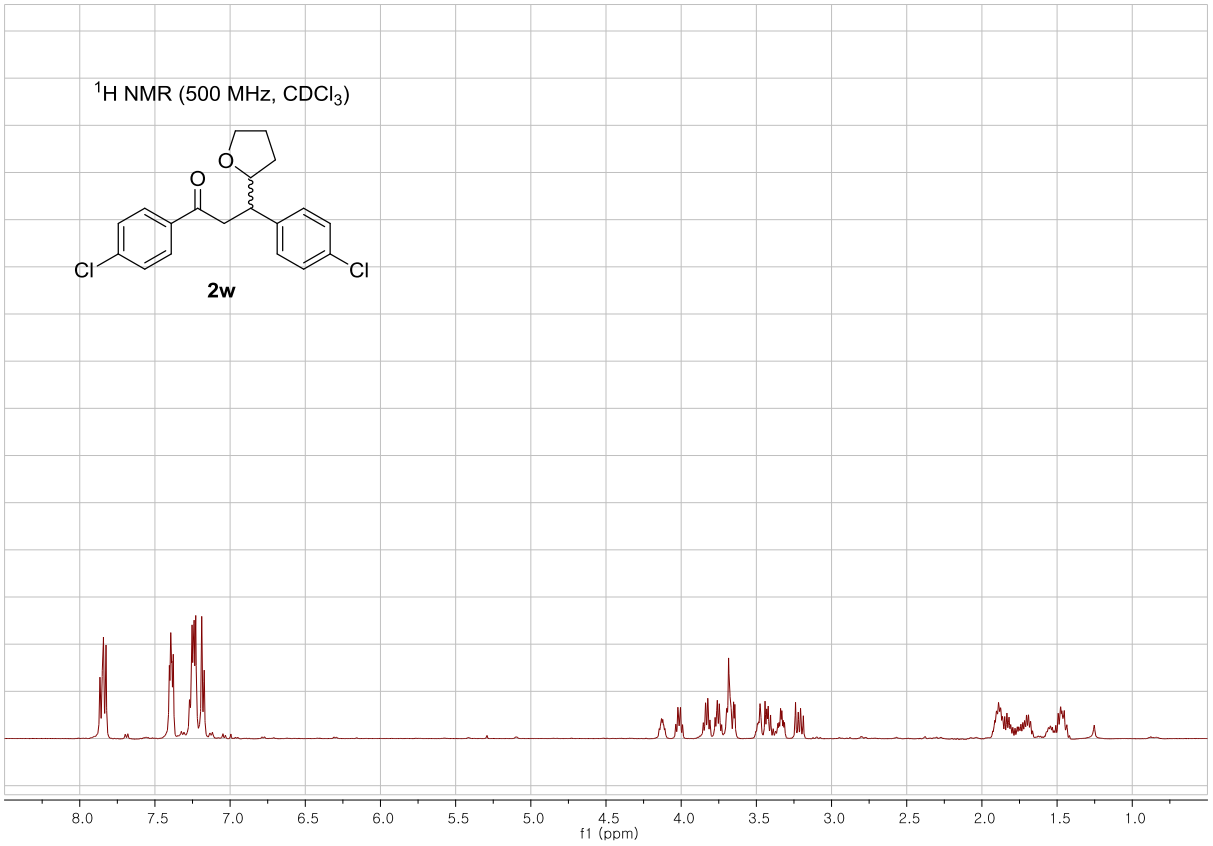

^{1}H NMR (300 MHz, $CDCl_3$)
O
O
MeO
2u
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

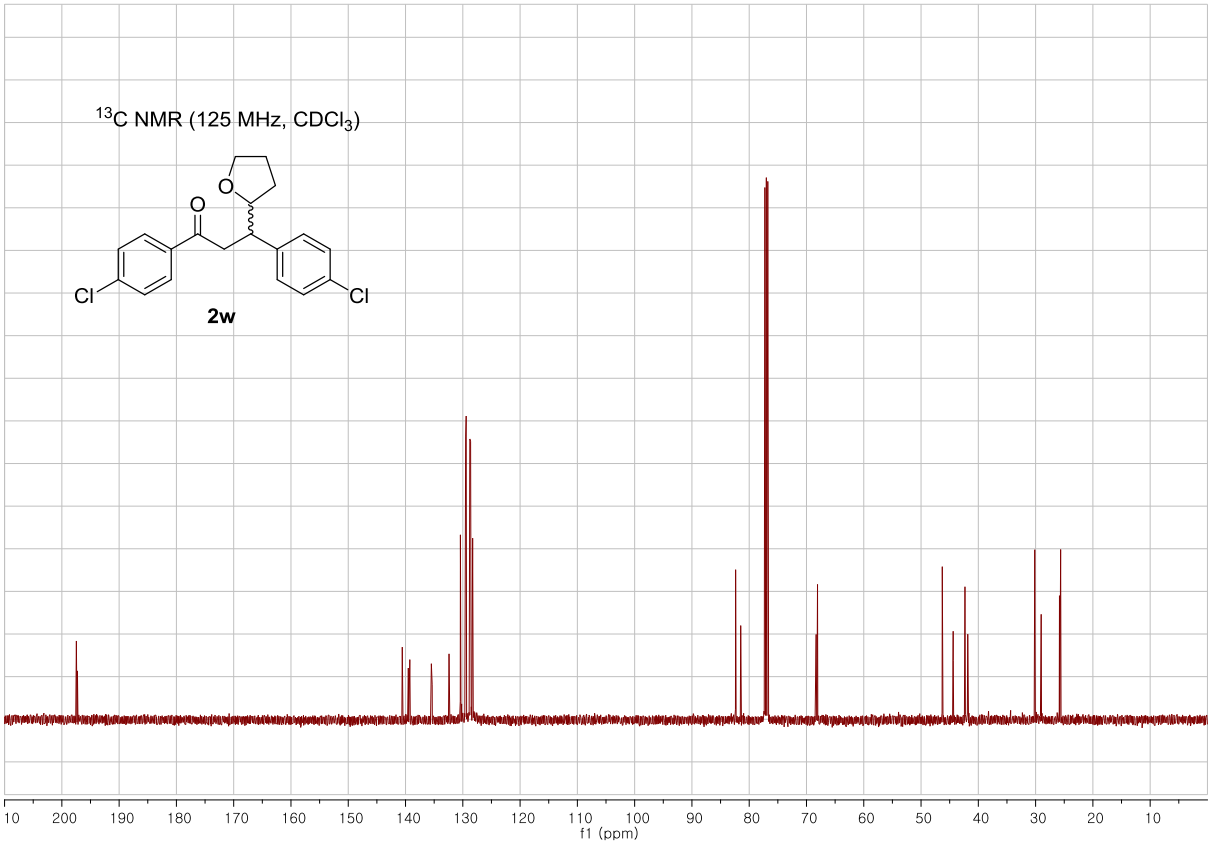

^{13}C NMR (75 MHz, $CDCl_3$)
O
O
MeO
2u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

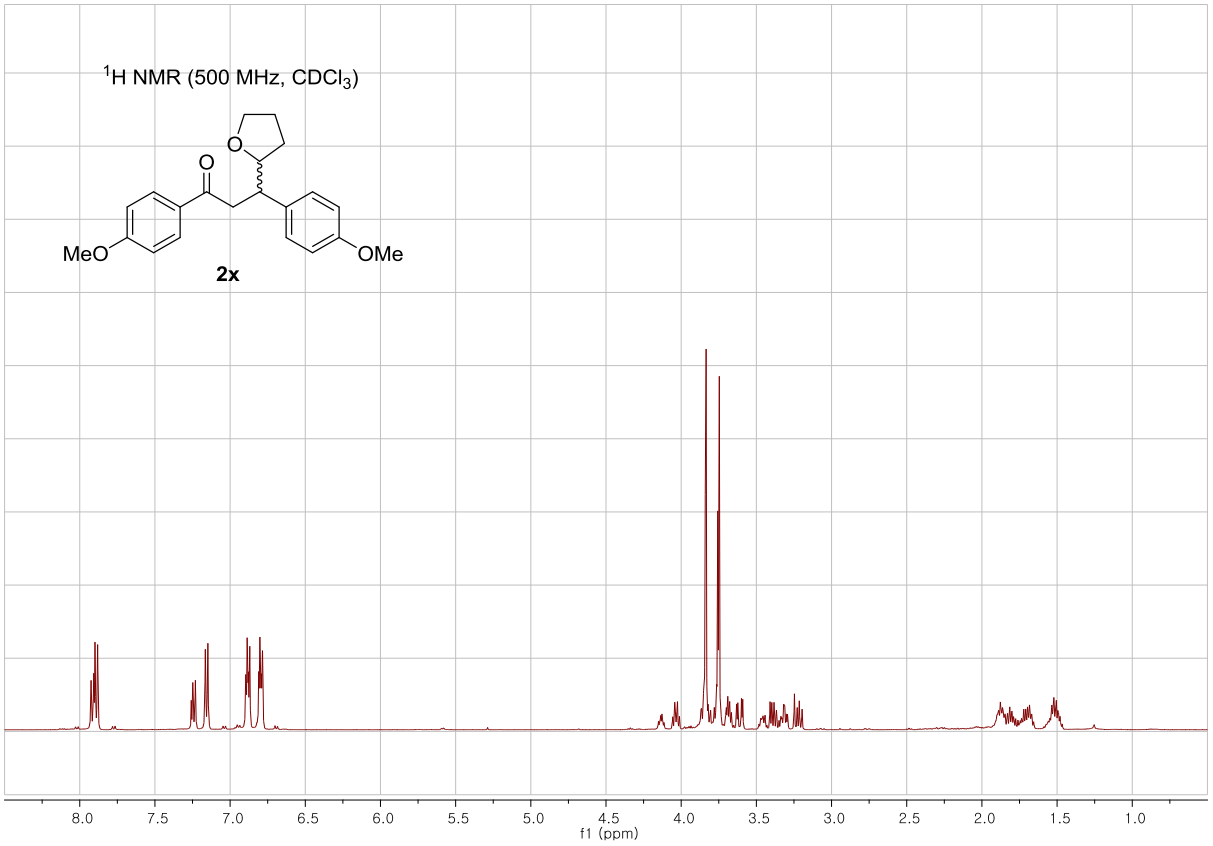

^{1}H NMR (300 MHz, CDCl$_3$)
O
O
F
F
2v
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

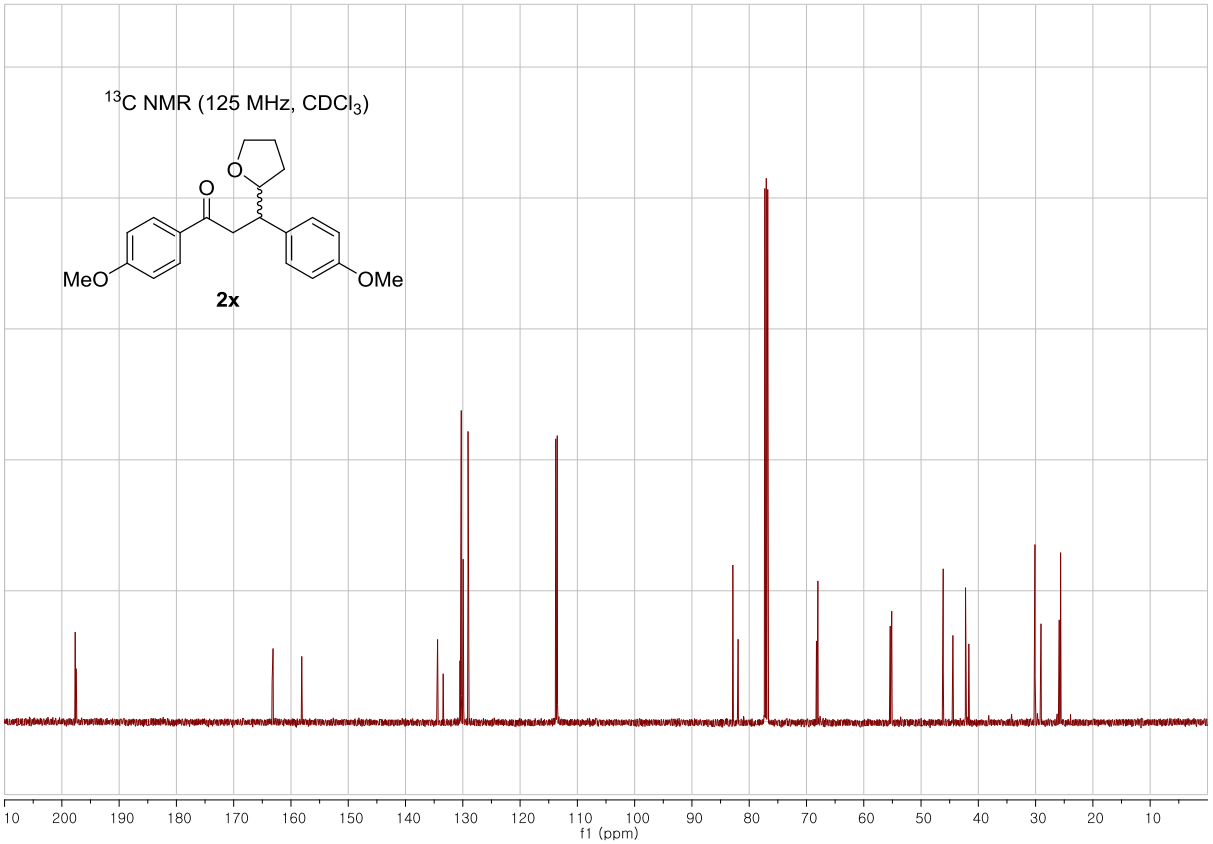

^{13}C NMR (75 MHz, CDCl$_3$)
O
O
F
F
2v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

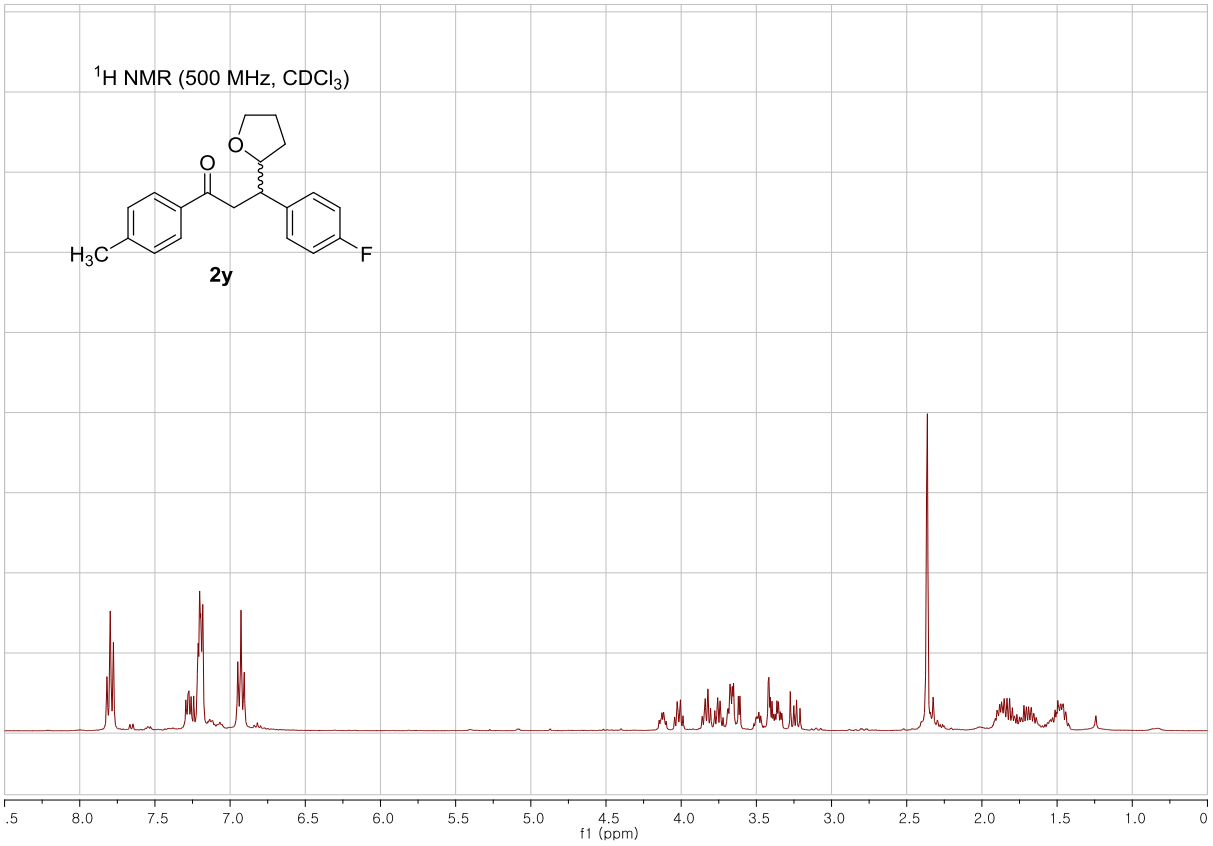

^{19}F NMR (375 MHz, $CDCl_3$)
O
O
F
F
2v
-105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

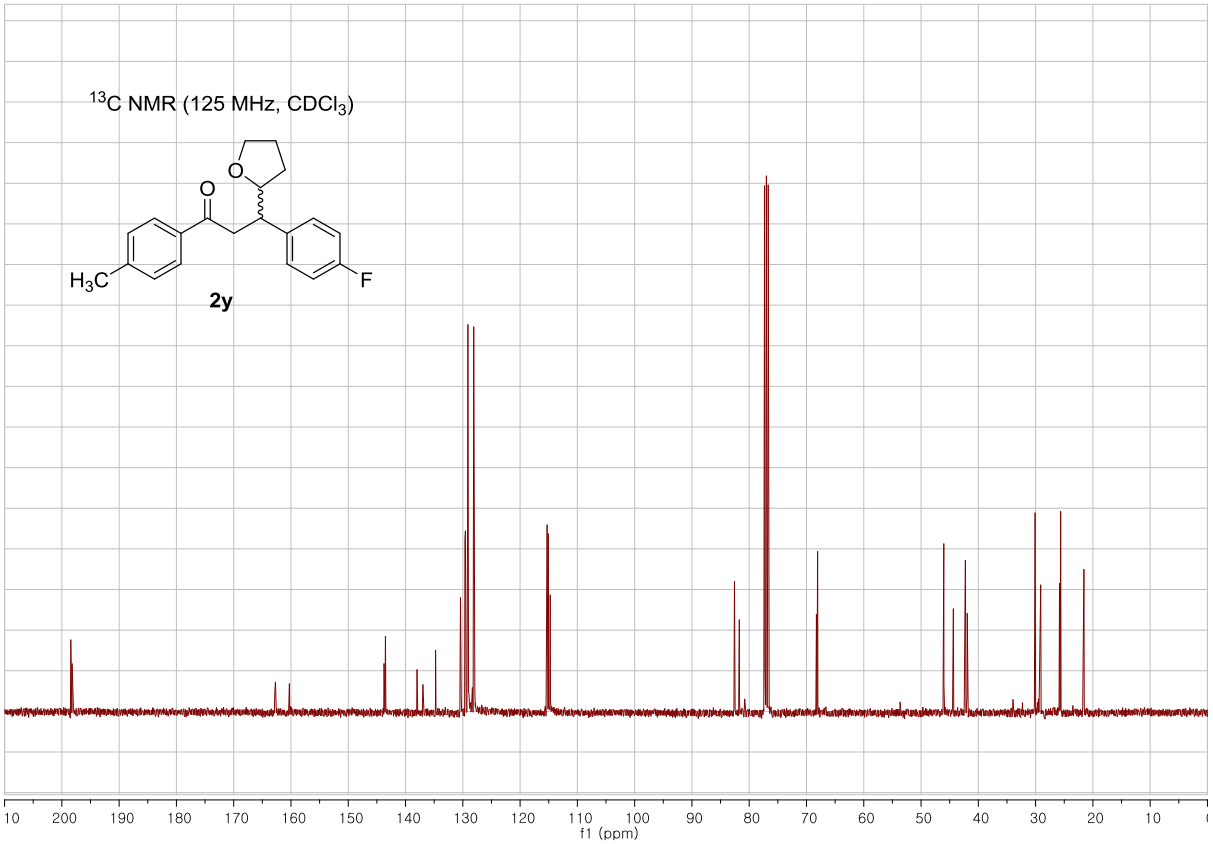

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
Cl
Cl
2w
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

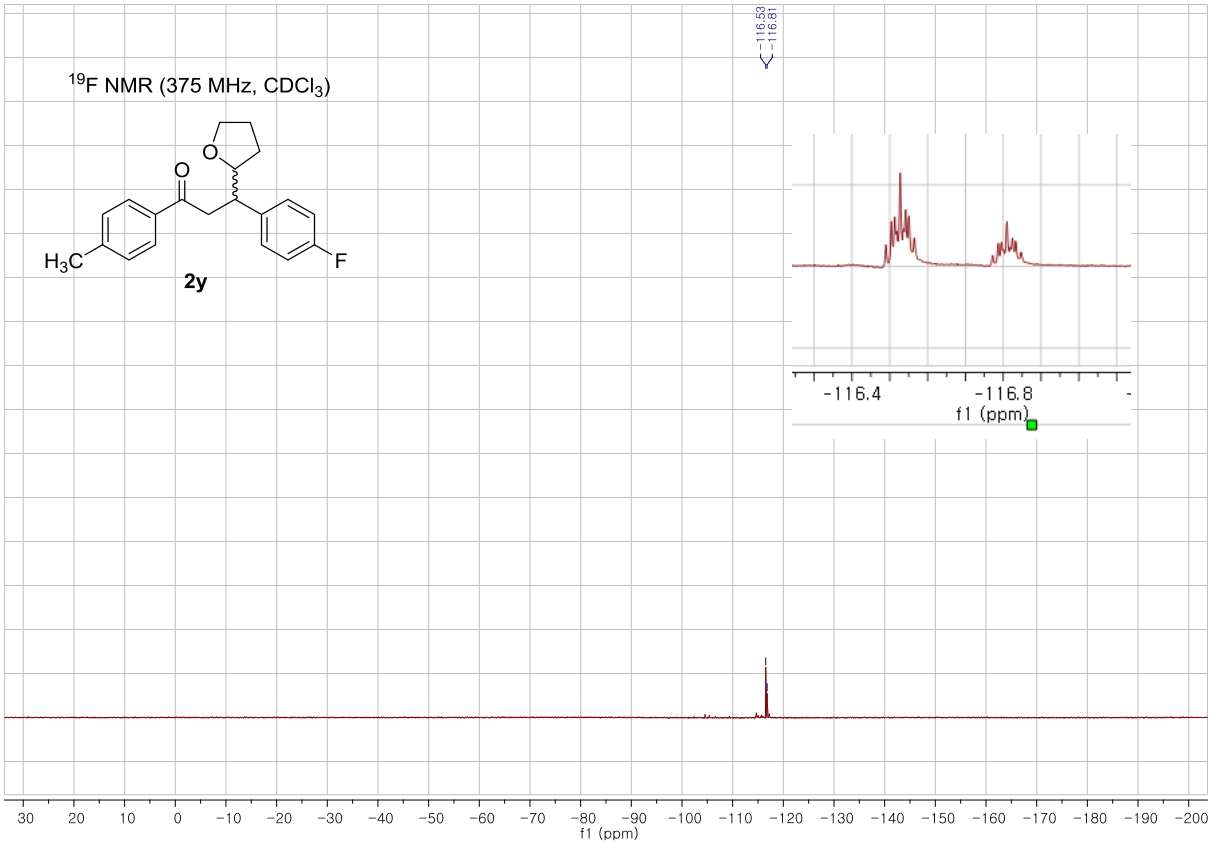

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
Cl
Cl
2w
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

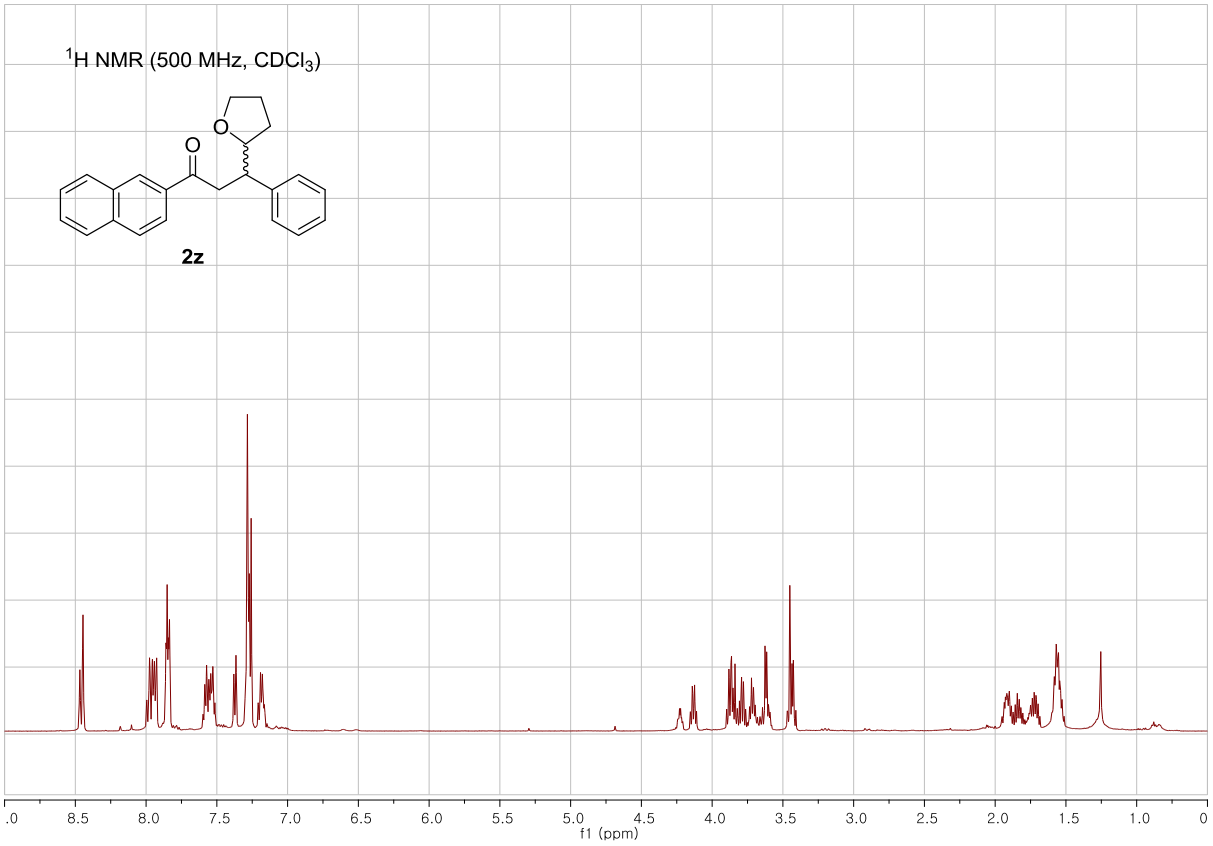

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
MeO
OMe
2x
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

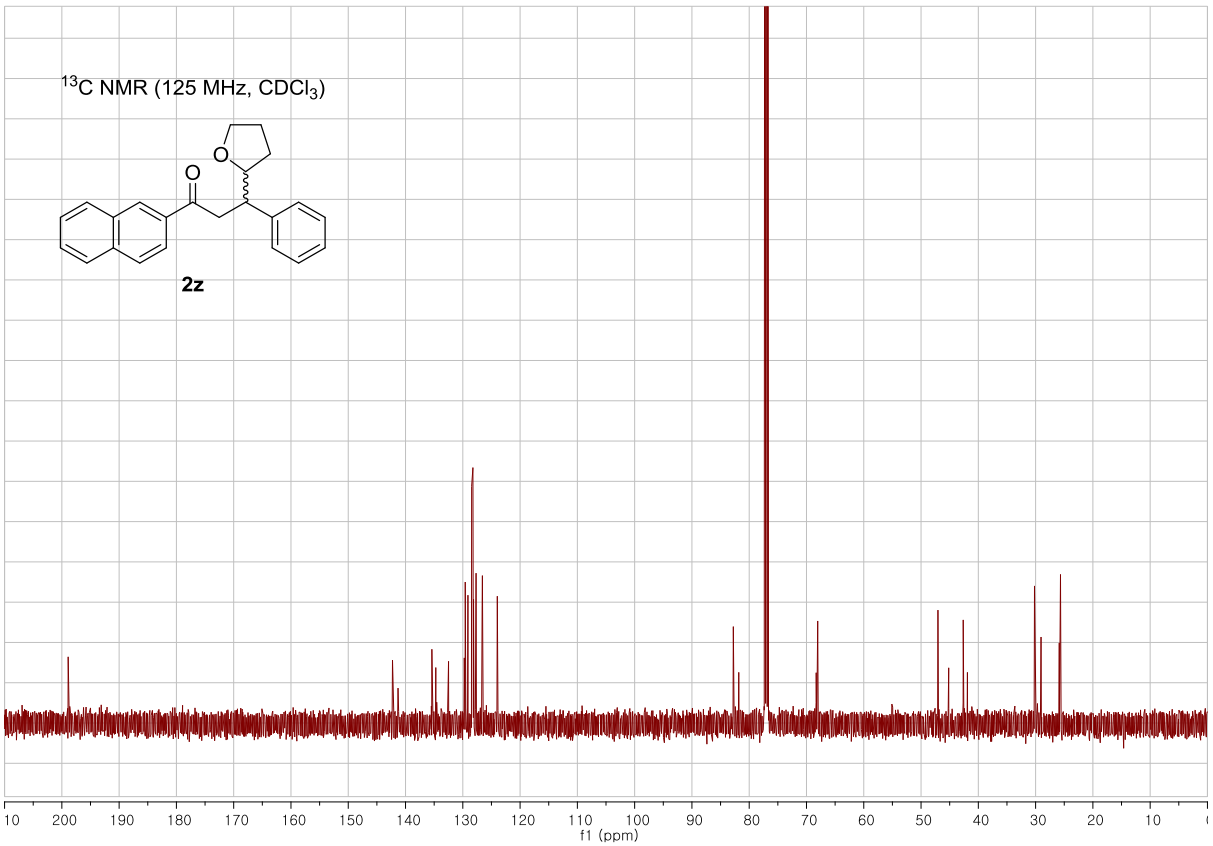

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
MeO
OMe
2x
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

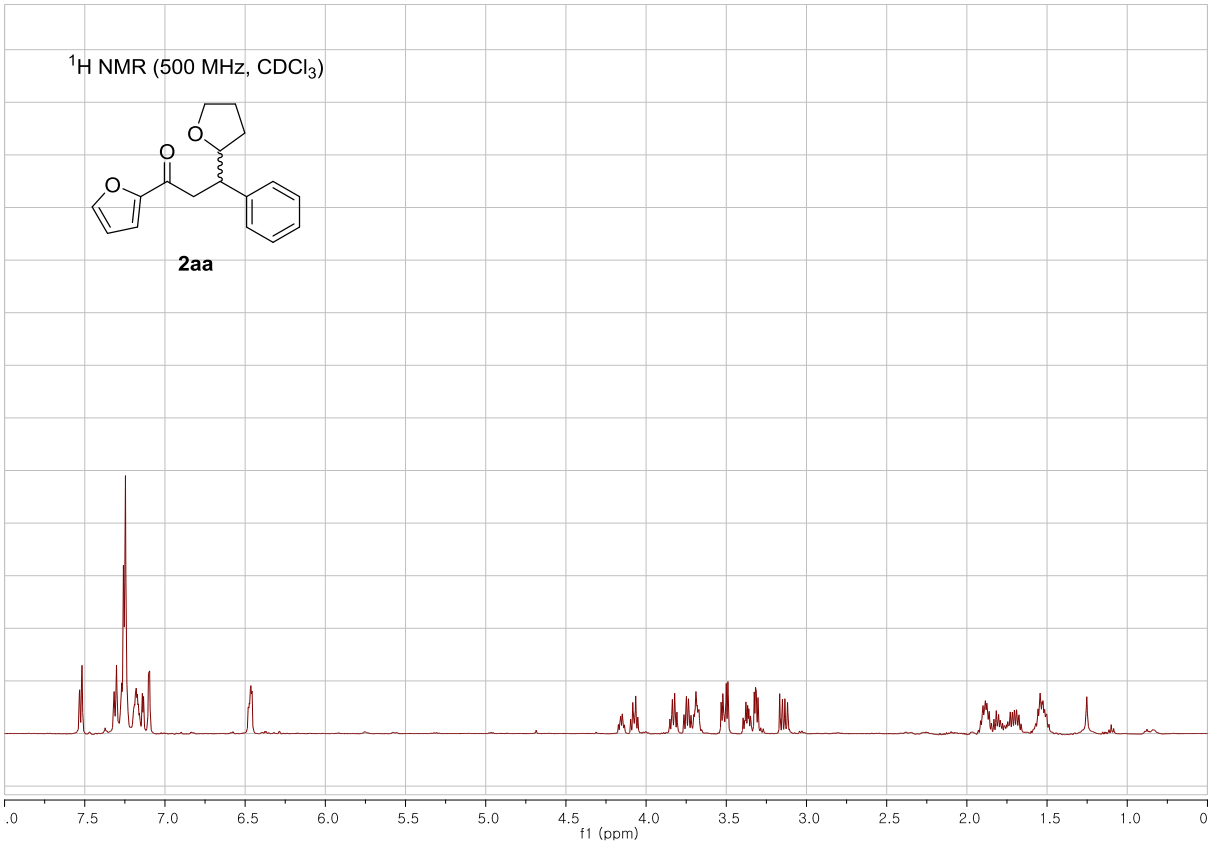

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
H_3C
F
2y
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)

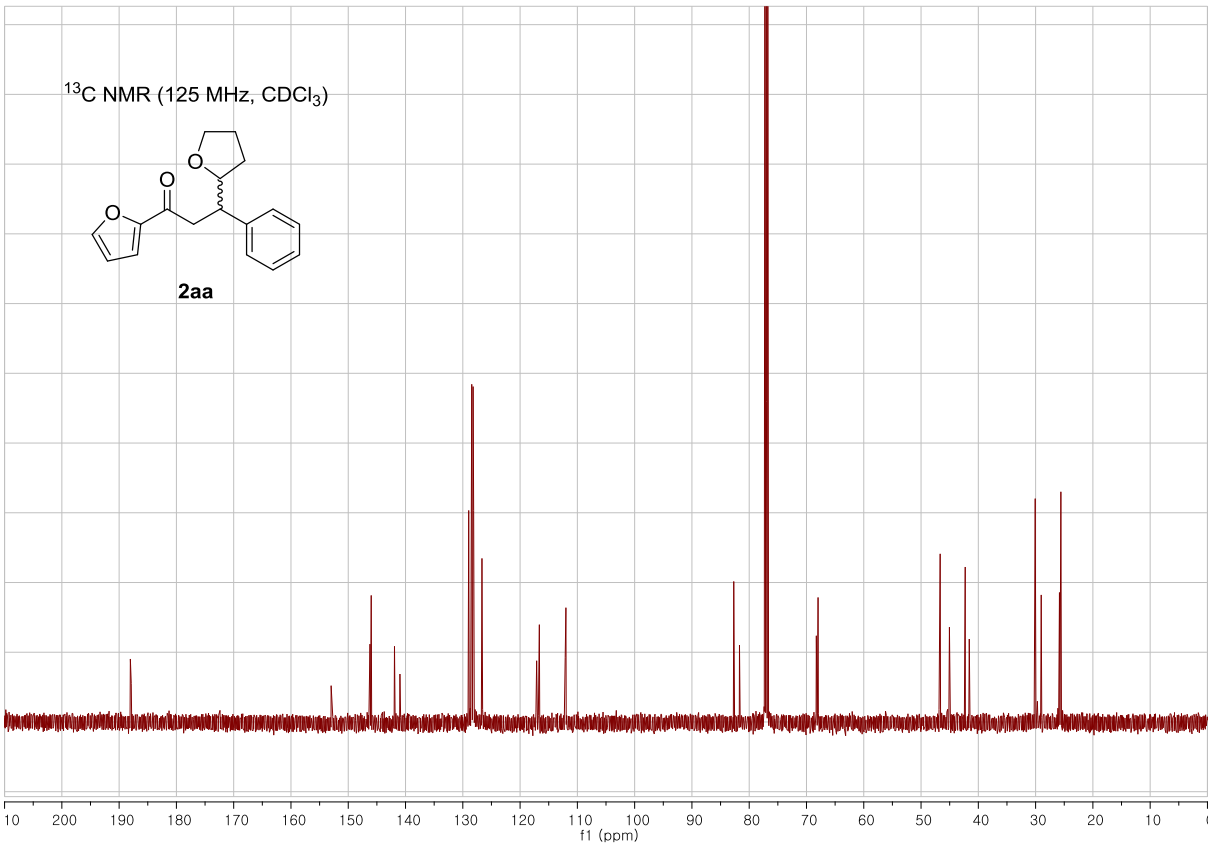

^{13}C NMR (125 MHz, $CDCl_3$)
O
O
H_3C
F
2y
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

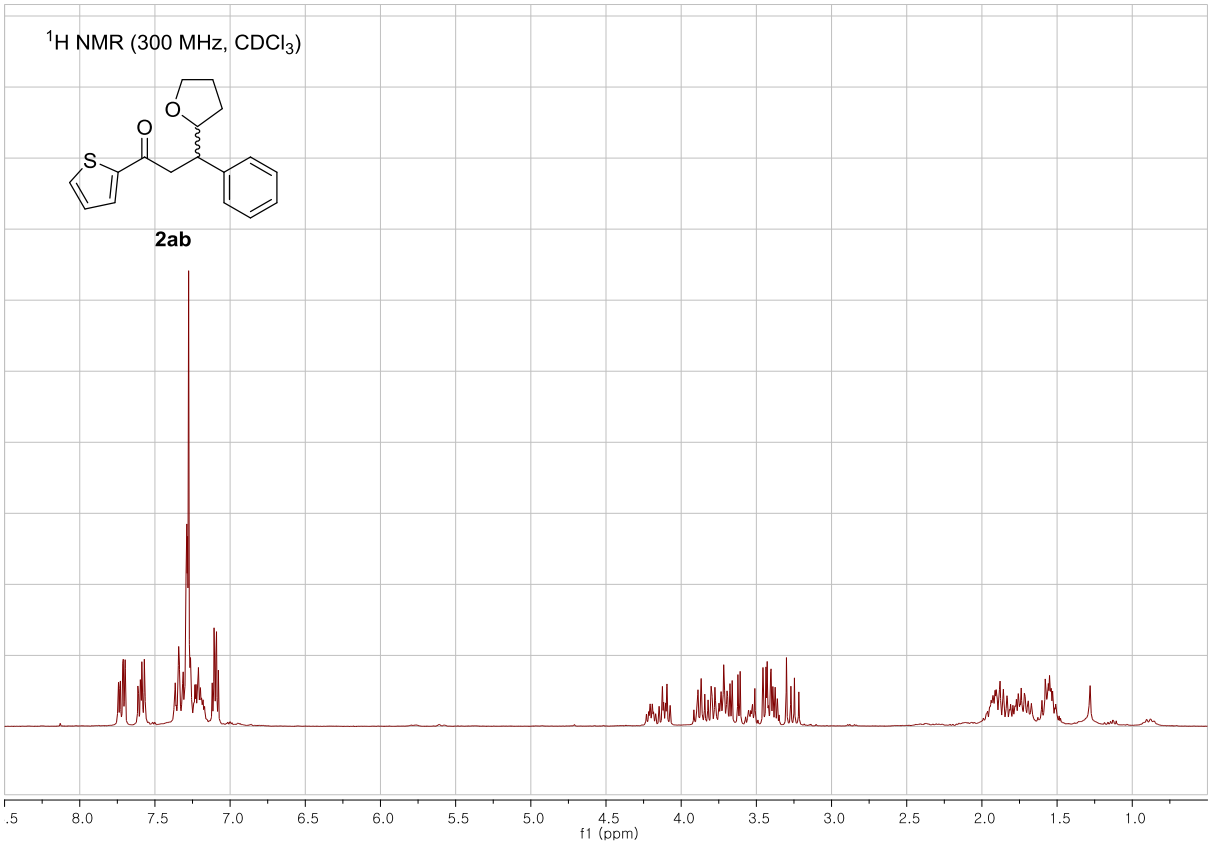

19F NMR (375 MHz, CDCl3)
O
O
H3C
F
2y
-116.53
-116.81
-116.4
-116.8
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

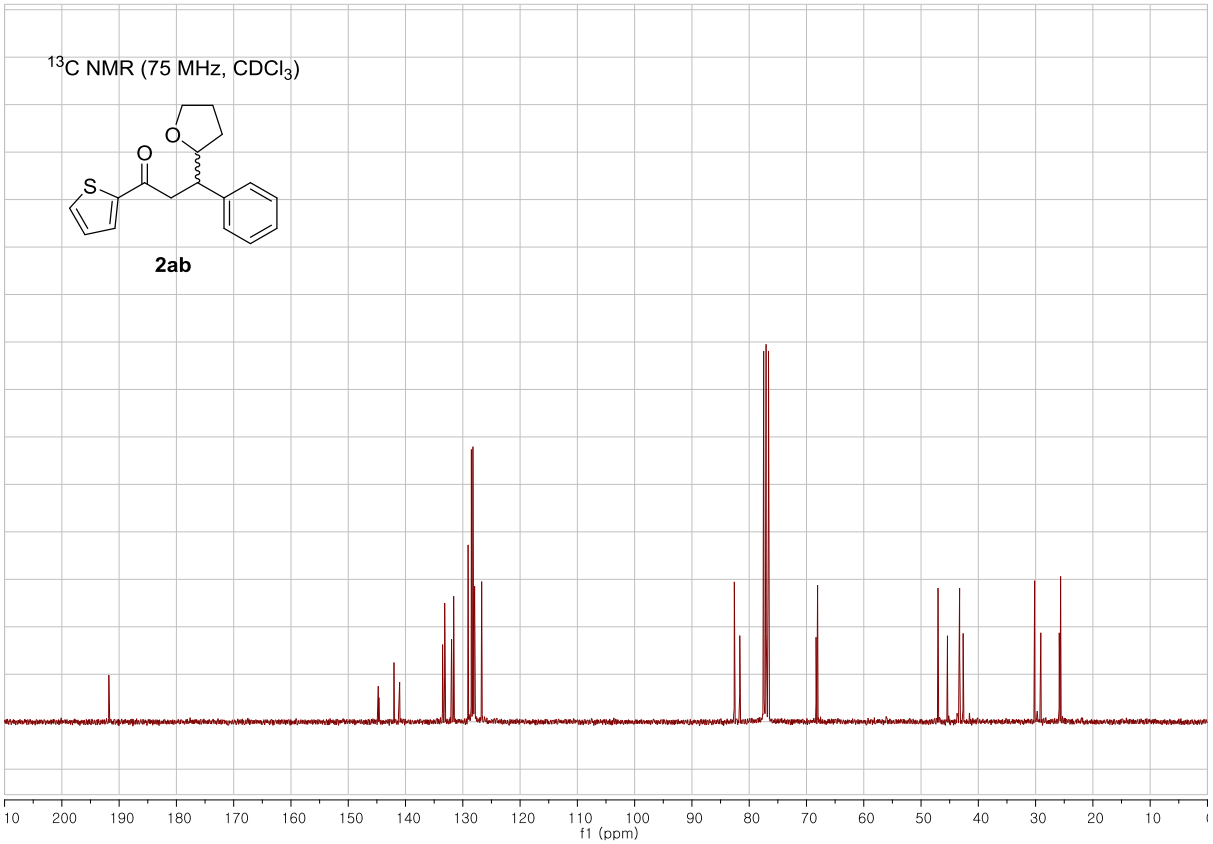

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
2z
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)


^{13}C NMR (125 MHz, $CDCl_3$)
O
O
2z
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


^{1}H NMR (500 MHz, $CDCl_3$)
2aa
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)


^{13}C NMR (125 MHz, $CDCl_3$)
2aa
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


^{1}H NMR (300 MHz, $CDCl_3$)
O
O
S
2ab
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


^{13}C NMR (75 MHz, $CDCl_3$)
O
O
S
2ab
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)