Supporting Information

Visible-Light-Induced C−O Bond Formation for the Construction of 5- and 6-Membered Cyclic ethers and Lactones

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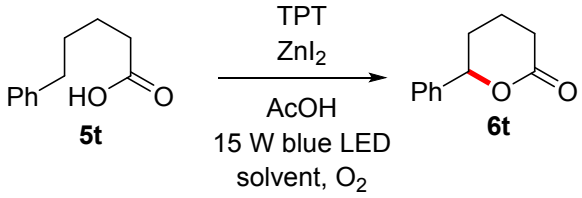
I. General Methods and Materials.

Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F^{254} plates and visualization on TLC was achieved by UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 or 600 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 or 150 MHz and was fully decoupled by broad band proton decoupling. Signals of ^{13}C spectra of carbon atom adjacent to fluorine atom of organoflouro compounds appeared as a doublet with varied coupling constants between C and F (J_{CF}). Chemical shifts were reported in ppm referenced to the centerline of a triplet at 77.0 ppm of $CDCl_3$. ^{19}F NMR was recorded on 376 or 564 MHz and was fully decoupled by broad band proton decoupling. Mass spectral data were obtained from the KAIST Basic Science Institute and KBSI (Korea Basic Science Institute) by using ESI, EI or FAB method. Commercial grade reagents and solvents were used without further purification except as indicated below.

II. Optimization of the reaction conditions

Table S1. Optimization of lactone



entry[a]	reaction time	TPT (x mol %)	ZnI_2 (x equiv)	solvent	AcOH (x equiv)	yield[b] (%)
1	24	5	0.15	CH_2Cl_2/HFIP (6:1)	1.0	48
2	24	5	0.15	CH_2Cl_2/HFIP (1:1)	1.0	28
3	24	5	0.3	CH_2Cl_2/HFIP (6:1)	1.0	50
4	24	5	0.3	CH_2Cl_2/HFIP (3:1)	1.0	54
5	24	5	0.3	CH_2Cl_2/HFIP (2:1)	1.0	49
6	24	5	0.3	CH_2Cl_2	1.0	34
7	24	5	0.3	HFIP	1.0	31
8	24	2	0.3	CH_2Cl_2/HFIP (6:1)	1.0	50
9	24	2	0.3	CH_2Cl_2/HFIP (1:1)	1.0	43
10	24	2	0.5	CH_2Cl_2/HFIP (6:1)	1.0	35
11[c]	24	5	0.3	CH_2Cl_2/HFIP (6:1)	1.0	63
12	24	5	0.3	CH_2Cl_2/HFIP (6:1)	2.0	54
13	24	5	0.3	CH_2Cl_2/HFIP (6:1)	3.0	52
14	**48**	**5**	**0.3**	**CH_2Cl_2/HFIP (6:1)**	**1.0**	**80**
15	**72**	**5**	**0.3**	**CH_2Cl_2/HFIP (6:1)**	**1.0**	**85**
16	48	4	0.2	CH_2Cl_2/HFIP (6:1)	1.0	42
17	48	3	0.3	CH_2Cl_2/HFIP (6:1)	1.0	68

[a] Reactions were conducted with 15 W blue LED for 24 hours in the cap test tube under O_2 atmosphere. [b] Yield was analyzed by ^1H NMR. [c] 0.8 mg of TPT (2 mol %) was added at reaction start and the residual catalyst (3 mol %) was added after 24 hours.

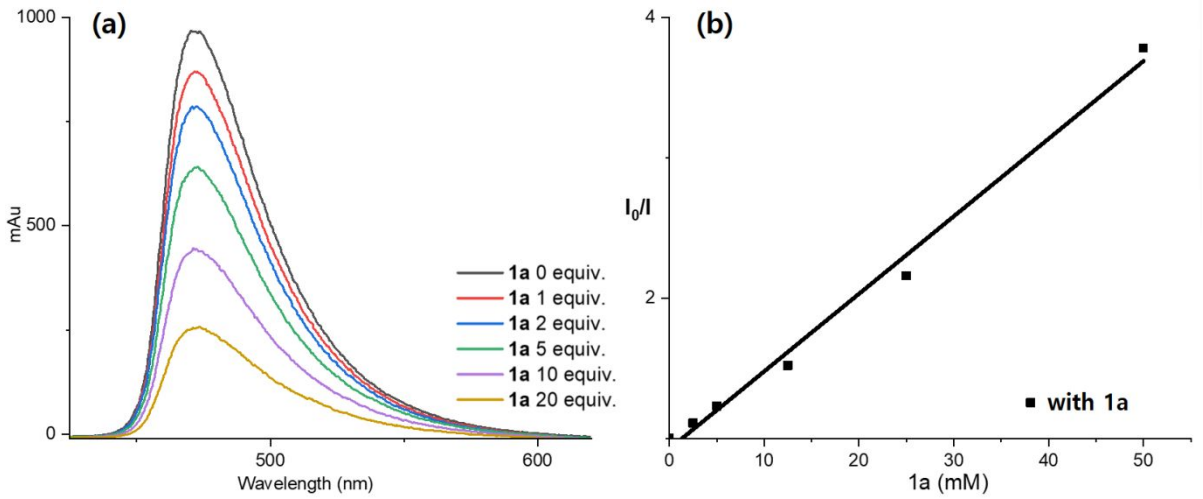
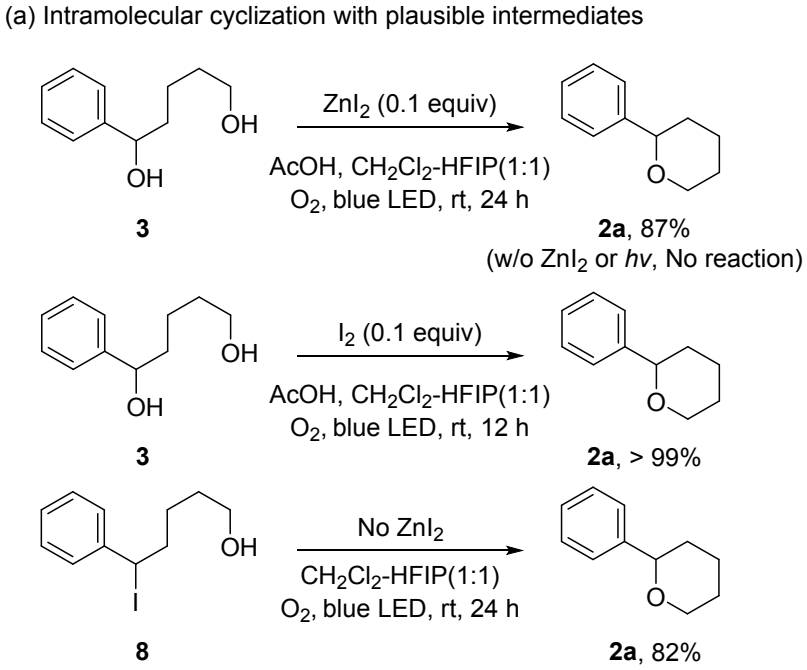


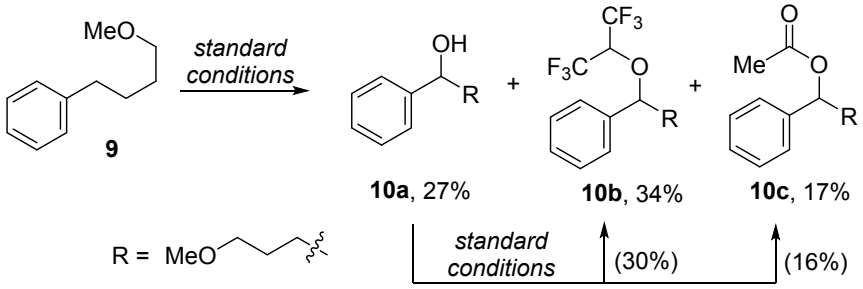
Figure S1. Stern-Volmer quenching experiment (TPT/5-phenyl pentan-1-ol ratio) (a) Fluorescence quenching of the TPT^{+} catalyst with 1a (0 to 0.05 M) under 415 nm light. (b) Quenching plot of the Stern-Volmer experiment.

III. Control experiment

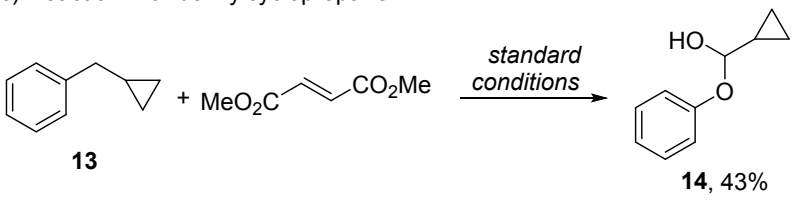
Scheme S1. Control experiment



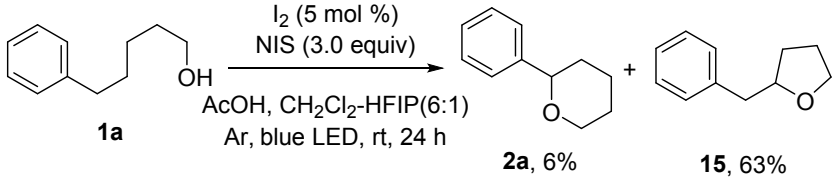
(b) Reaction with 4-methoxy butyl benzene



(c) Reaction with benzylcyclopropane



(d) Reaction with stoichiometric amount of NIS

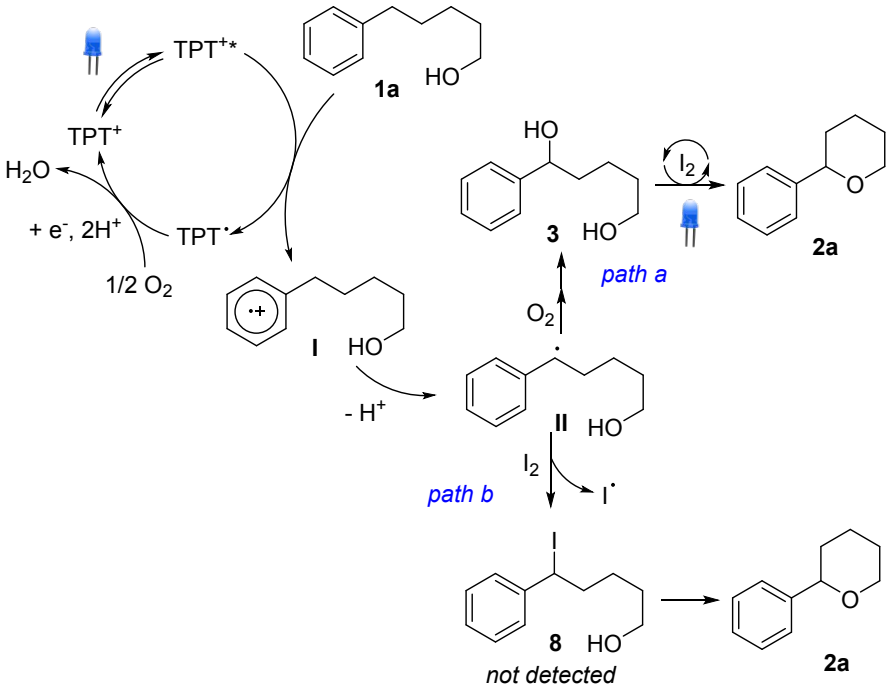


IV. Proposed mechanistic pathway

Upon single-electron transfer (SET) between the excited TPT* catalyst and **1a**, aromatic radical cation species I would be generated. By the presence of a positive charge on the aromatic system, the acidity of the benzylic hydrogens is dramatically increased (by several orders of magnitude), leading to the formation of benzylic radical intermediate II after deprotonation of intermediate I. Molecular oxygen subsequently intercepts the benzylic radical II, and invoking intermediate **3** for the C−O cyclization is reasonable (path a) since a considerable amount of **3** was isolated from the reaction mixtures, and 3 was readily cyclized under the current reaction conditions (Scheme 2a). In addition, a significant amount of Hock rearrangement product was obtained during our investigations, supporting the intermediacy of a benzylic hydroperoxide. Alternatively, I_2 is generated by photoredox catalysis, and the mechanistic possibility involving direct cyclization of iodinated intermediate 8 is also feasible (path b), although intermediate **8** could not be detected. At current stage, Hock-type rearrangement product formation cannot completely disprove the possibility of the two-electron oxidation process, but we surmised that

the formation of benzyl cations appears to be less feasible considering extremely low concentration of excited TPT* and significant amounts of O_2 or I_2 present in the reaction mixtures. Finally, cyclized product **2a** could be obtained via intramolecular cyclization of **3** or **8** as observed in the control experiments.

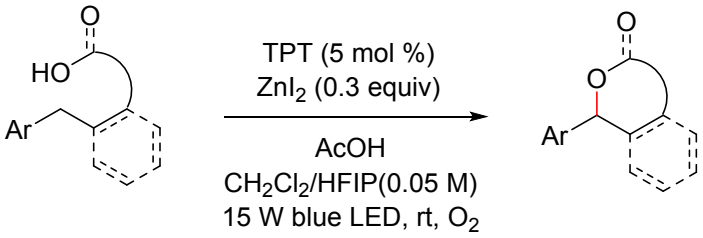
Scheme S2. Proposed mechanistic pathway



V. Experimental Procedure

Reaction set-up for the light-promoted reactions

General Procedure for Visible-Light Induced regioselective lactone / ether fromation



To oven-dried cap test tube (10 mL) was added ZnI_2 (9.6 mg, 0.3 equiv., weighed in glovebox), 2,4,6-triphenylpyrylium tetrafluoroborate (TPT, 2.0 mg, 5 mol %) and alcohols or carboxylic acids (0.1 mmol). The reaction tube was refilled with O_2 gas and 2.0 mL of solvent (DCM/HFIP 1:1 for alcohols, DCM/HFIP 6:1 for carboxylic acids) was added. The mixture was stirred under irradiation of 15 W blue LED at 30 ^{o}C for 24 to 72 hours. The completion of reaction was monitored by TLC. After reaction finished, the reaction mixture was directly filtered thorugh celite pad and concentrated in *vacuo*. The resdiue was purified by flash column chromatography on silica gel (EA/Hx 1:10 to 1:200) to afford the desired cyclized product.

1 mmol scale Procedure

To oven-dried Sealed tube (80 mL) was added ZnI_2 (95.7 mg, 0.3 equiv, weighed in glovebox), 2,4,6-triphenylpyrylium tetrafluoroborate (TPT, 19.8 mg, 5 mol %) and 2-benzyl benzoic acid (212.0 mg, 1.0 mmol). The reaction tube was filled with air atmosphere and 20.0 mL of solvent (DCM/HFIP 1:1) was added. The mixture was stirred under irradiation of 45 W blue LED (427 nm) at 30 ^{o}C for 72 hours. After reaction finished, the reaction mixture was directly filtered thorugh celite pad and concentrated in *vacuo*. The resdiue was purified by flash column chromatography on silica gel (EA/Hx 1:15) to afford 3-phenylisobenzofuran-1(3H)-one (83%, 172.2 mg) as a white solid.

VI. Cyclic voltammetry

Comparison of oxidation potentials of 1a vs. 2a:

Alcohol substrate **1a** is irreversibly oxidized at a potential of 1.78 V vs. $Ag/AgNO_3$ while the corresponding thetrahydropyran product **2a** is oxidized at a higher potential of 1.92 V vs. $Ag/AgNO_3$. **1a** is more favorably oxidized by 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) catalyst than **2a**, so the tetrahyropyran products can be formed with low possibility of decomposition.

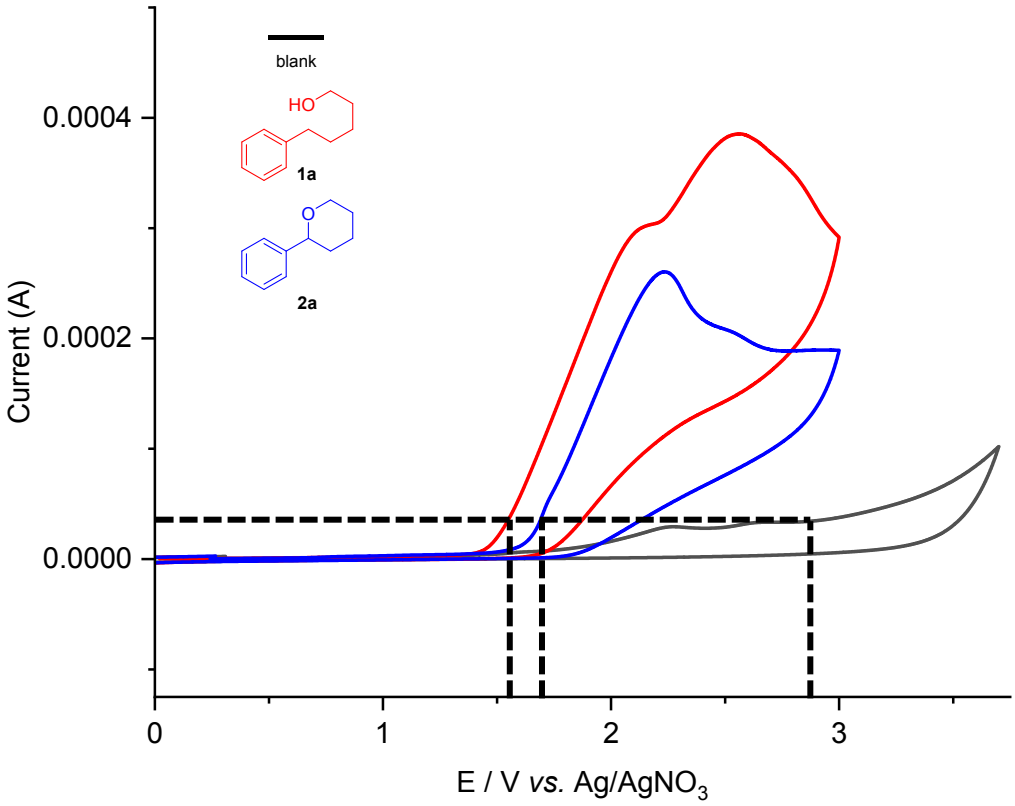
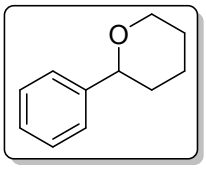
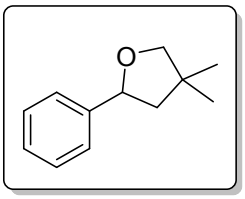


Figure S1. Cyclic voltammetry of **1a** (30 mM, red line) and **2a** (30 mM, blue line). The voltammogram for the blank electrolyte is shown for comparison (black line). Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: $Ag/0.01M\ AgNO_3$ in 0.1 M Bu_4NBF_4 ; scan rate: $50mV\ s^{-1}$.

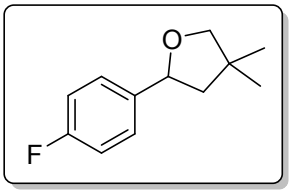
VII. Compound characterization



2-phenyltetrahydro-2H-pyran (2a). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 74% **(**12.1 mg). Pale red oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 4.33 (dd, J = 10.8, 2.3 Hz, 1H), 4.19 – 4.10 (m, 1H), 3.69 – 3.55 (m, 1H), 2.00 – 1.91 (m, 2H), 1.88 – 1.80 (m, 1H), 1.75 – 1.53 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.48, 128.42, 127.41, 125.99, 80.30, 69.15, 34.17, 26.05, 24.17. HRMS (EI+) m/z calcd. for $[C_{11}H_{14}O]^{+}$: 162.1045, found : 162.1047

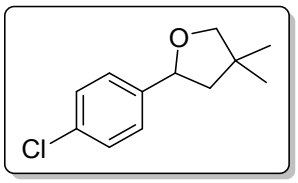


4,4-dimethyl-2-phenyltetrahydrofuran (2b). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 72% (12.7 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 5.05 (dd, J = 9.5, 6.8 Hz, 1H), 3.76 (d, J = 8.0 Hz, 1H), 3.67 (dd, J = 8.0, 0.7 Hz, 1H), 2.13 (ddd, J = 12.4, 6.7, 0.7 Hz, 1H), 1.68 (dd, J = 12.3, 9.5 Hz, 1H), 1.20 (s, 3H), 1.14 (s, 3H) ^{13}C NMR (100 MHz, CDCl3) δ 143.89, 128.46, 127.21, 125.65, 81.11, 80.92, 77.48, 77.16, 76.84, 49.97, 26.67, 26.60. HRMS (EI+) m/z calcd. for $[C_{12}H_{16}O]^{+}$: 176.1201, found : 176.1200

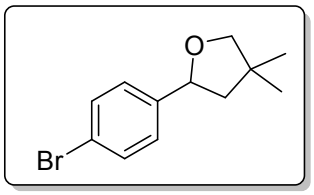


2-(4-fluorophenyl)-4,4-dimethyltetrahydrofuran (2c). Purified by flash chromatography on silica gel (EA/Hx = 1:40). Overall yield 73% (14.2 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.34 – 7.27 (m, 2H), 7.07 – 6.97 (m, 2H), 4.98 (dd, J = 9.5, 6.7 Hz, 1H), 3.71 (d, J = 8.1 Hz, 1H), 3.61 (dd, J = 8.1, 0.7 Hz, 1H), 2.11 (ddd, J = 12.3, 6.7, 0.6 Hz, 1H), 1.65 – 1.54 (m, 2H), 1.18 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (150 MHz, Methylene Chloride-d_2) δ 162.49 (d, J = 243.8 Hz), 140.54 (d, J = 3.2 Hz), 127.78 (d, J = 8.1 Hz), 115.46 (d, J = 21.3 Hz), 81.44, 80.68, 50.56, 40.68, 26.91, 26.71. ^{19}F NMR (376 MHz, CD2Cl2) δ -116.92. HRMS (EI+) m/z calcd. for $[C_{12}H_{15}FO]^{+}$: 194.1107, found :

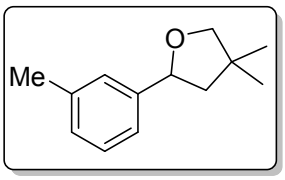
194.1110



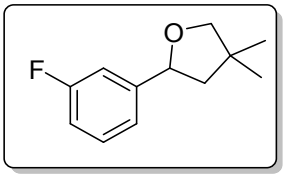
2-(4-chlorophenyl)-4,4-dimethyltetrahydrofuran (2d). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 70% (14.6 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.17 (m, 4H), 5.01 (dd, J = 9.4, 6.8 Hz, 1H), 3.73 (d, J = 8.1 Hz, 1H), 3.65 (d, J = 8.1 Hz, 1H), 2.12 (dd, J = 12.3, 6.8 Hz, 1H), 1.62 (dd, J = 12.3, 9.3 Hz, 1H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.49, 132.78, 128.58, 127.01, 81.13, 80.24, 49.99, 40.38, 26.66, 26.54. HRMS (EI+) m/z calcd. for $[C_{12}H_{15}ClO]^{+}$: 210.0811, found : 210.0809



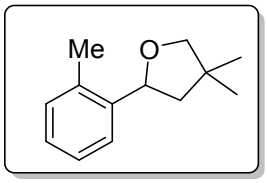
2-(4-bromophenyl)-4,4-dimethyltetrahydrofuran (2e). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 41% (10.3 mg). Coloress oil. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.47 – 7.42 (m, 2H), 7.24 – 7.18 (m, 2H), 5.00 (dd, J = 9.4, 6.9 Hz, 1H), 3.73 (d, J = 8.1 Hz, 1H), 3.65 (d, J = 8.1 Hz, 1H), 2.12 (dd, J = 12.3, 6.8 Hz, 1H), 1.61 (dd, J = 12.4, 9.4 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 143.08, 131.54, 127.37, 120.88, 81.16, 80.27, 49.98, 40.39, 26.67, 26.56. HRMS (EI+) m/z calcd. for $[C_{12}H_{15}BrO]^{+}$: 254.0306, found : 254.0303



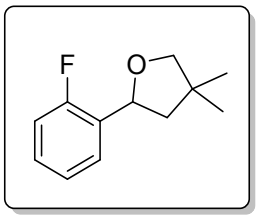
4,4-dimethyl-2-(m-tolyl)tetrahydrofuran (2f). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 38% (7.3 mg). Coloress oil. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.24 – 7.19 (m, 1H), 7.18 – 7.15 (m, 1H), 7.16 – 7.10 (m, 1H), 7.10 – 7.04 (m, 1H), 5.01 (dd, J = 9.5, 6.7 Hz, 1H), 3.75 (d, J = 8.0 Hz, 1H), 3.65 (d, J = 8.0 Hz, 1H), 2.35 (s, 3H), 2.11 (dd, J = 12.3, 6.7 Hz, 1H), 1.68 (dd, J = 12.3, 9.5 Hz, 1H), 1.20 (s, 4H), 1.14 (s, 4H). ^{13}C NMR (150 MHz, Chloroform-d) δ 143.82, 138.10, 128.37, 127.97, 126.33, 122.77, 81.14, 80.98, 49.96, 40.30, 26.75, 26.65, 21.61. HRMS (ESI+) m/z calcd. for $[C_{13}H_{18}NaO]^{+}$: 213.1250, found : 213.1240



2-(3-fluorophenyl)-4,4-dimethyltetrahydrofuran (2g). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 52% (10.0 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.22 (m, 1H), 7.12 – 7.01 (m, 2H), 6.98 – 6.87 (m, 1H), 5.04 (dd, J = 9.3, 6.9 Hz, 1H), 3.74 (d, J = 8.1 Hz, 1H), 3.66 (dd, J = 8.1, 0.7 Hz, 1H), 2.14 (ddd, J = 12.4, 6.9, 0.7 Hz, 1H), 1.64 (dd, J = 12.3, 9.3 Hz, 1H), 1.19 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 163.13 (d, J = 245.3 Hz), 146.86 (d, J = 6.7 Hz), 129.95 (d, J = 8.2 Hz), 121.13 (d, J = 2.7 Hz), 113.94 (d, J = 21.3 Hz), 112.45 (d, J = 22.0 Hz), 81.13, 80.21 (d, J = 1.9 Hz), 49.90, 40.37, 26.54, 26.52. ^{19}F NMR (376 MHz, Chloroform-d) δ -113.32. HRMS (EI+) m/z calcd. for $[C_{12}H_{15}FO]^{+}$: 194.1107, found : 194.1109

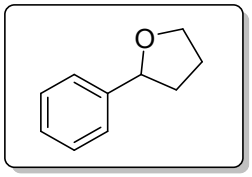


4,4-dimethyl-2-(o-tolyl)tetrahydrofuran (2h). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 58% (11.1 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.48 (m, 1H), 7.26 – 7.17 (m, 1H), 7.19 – 7.07 (m, 2H), 5.21 (dd, J = 9.1, 7.0 Hz, 1H), 3.78 (d, J = 8.1 Hz, 1H), 3.67 (d, J = 8.1 Hz, 1H), 2.28 (s, 3H), 2.18 (dd, J = 12.3, 7.1 Hz, 1H), 1.53 (dd, J = 12.3, 9.2 Hz, 1H), 1.21 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 142.34, 134.10, 130.22, 126.81, 126.28, 124.43, 80.83, 78.28, 48.52, 40.38, 26.80, 26.64, 19.35. HRMS (EI+) m/z calcd. for $[C_{13}H_{18}O]^{+}$: 190.1358, found : 190.1355

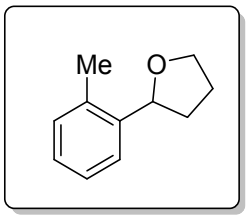


2-(2-fluorophenyl)-4,4-dimethyltetrahydrofuran (2i). Purified by flash chromatography on silica gel (EA/Hx = 1:40). Overall yield 55% (10.7 mg). Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 (td, J = 7.6, 1.4 Hz, 1H), 7.27 – 7.16 (m, 1H), 7.13 (td, J = 7.6, 0.9 Hz, 1H), 7.00 (ddd, J = 10.6, 8.1, 1.4 Hz, 1H), 5.28 (dd, J = 9.2, 7.0 Hz, 1H), 3.74 (d, J = 8.0 Hz, 1H), 2.23 (ddd, J = 12.4, 7.0, 1.3 Hz, 1H), 1.72 – 1.59 (m, 1H), 1.20 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 159.90

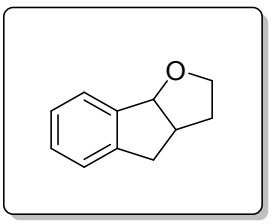
(d, J = 245.3 Hz), 131.28 (d, J = 13.5 Hz), 128.44 (d, J = 8.1 Hz), 126.71 (d, J = 4.8 Hz), 124.23 (d, J = 3.4 Hz), 115.20 (d, J = 21.3 Hz), 80.77, 75.38 (d, J = 2.6 Hz), 48.61, 40.35, 26.43, 26.41. ^{19}F NMR (376 MHz, Chloroform-d) δ -118.73. HRMS (EI+) m/z calcd. for $[C_{12}H_{15}FO]^+$: 194.1107, found : 194.1104



2-phenyltetrahydrofuran (2j). Purified by flash chromatography on silica gel (EA/Hx = 1:50). Overall yield 62% (9.0 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 4.90 (t, J = 7.2 Hz, 1H), 4.14 – 4.06 (m, 1H), 3.99 – 3.87 (m, 1H), 2.40 – 2.28 (m, 1H), 2.06 – 1.96 (m, 2H), 1.88 – 1.74 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.60, 128.43, 127.26, 125.77, 80.82, 68.82, 34.76, 26.18. HRMS (ESI+) m/z calcd. for $[C_{10}H_{12}NaO]^+$: 171.0780, found : 171.0774

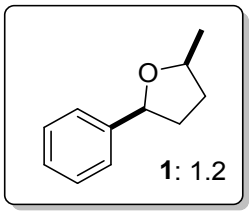


2-(o-tolyl)tetrahydrofuran (2k). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 51% (8.3 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.41 (m, 1H), 7.24 – 7.09 (m, 3H), 5.07 (t, J = 7.1 Hz, 1H), 4.19 – 4.11 (m, 1H), 4.00 – 3.88 (m, 1H), 2.42 – 2.33 (m, 1H), 2.31 (s, 3H), 2.07 – 1.95 (m, 2H), 1.75 – 1.62 (m, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 141.98, 134.35, 130.28, 126.92, 126.15, 124.72, 78.14, 68.78, 33.31, 26.19, 19.37. HRMS (EI+) m/z calcd. for $[C_{11}H_{14}O]^+$: 162.1045, found : 162.1046



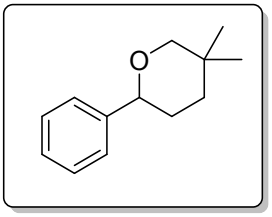
3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan (2l). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Overall yield 57% (9.1 mg, single diastereomer). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.37 (m, 1H), 7.31 – 7.21 (m, 3H), 7.25 – 7.15 (m, 2H), 5.48 (d, J = 7.1 Hz,

1H), 3.86 (ddd, J = 8.8, 7.1, 5.2 Hz, 1H), 3.63 (td, J = 8.0, 6.4 Hz, 2H), 3.22 (dd, J = 16.1, 8.8 Hz, 1H), 3.19 – 3.07 (m, 1H), 2.80 (dd, J = 16.3, 2.8 Hz, 1H), 2.27 – 2.13 (m, 1H), 1.76 – 1.62 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.21, 142.29, 128.70, 127.15, 125.80, 124.91, 87.47, 67.58, 41.27, 38.17, 34.82. HRMS (EI+) m/z calcd. for $[C_{11}H_{12}O]^+$: 160.0888, found : 160.0885

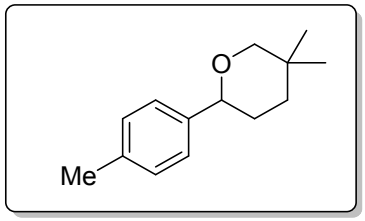


2-methyl-5-phenyltetrahydrofuran (2m) *cis*-isomer. Purified by flash chromatography on silica gel (EA/Hx = 1:50). Overall yield 52% (8.2 mg, *cis* : *trans* = 1:1.2). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 4H), 7.25 – 7.22 (m, 1H), 4.88 (t, J = 7.3 Hz, 1H), 4.17 (dq, J = 12.6, 6.2 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.14 – 2.03 (m, 1H), 1.70 – 1.56 (m, 2H), 1.37 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.67, 128.40, 127.18, 125.72, 81.18, 34.79, 33.24, 21.48. HRMS (EI+) m/z calcd. for $[C_{11}H_{14}O]^+$: 162.1045, found : 162.1044.

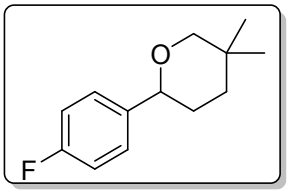
***trans-isomer* (2m)** ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 5.04 (dd, J = 8.2, 6.4 Hz, 1H), 4.36 (dp, J = 8.2, 6.0 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.22 – 2.11 (m, 1H), 1.95 – 1.79 (m, 2H), 1.32 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.15, 128.44, 127.28, 126.00, 80.40, 35.75, 34.42, 21.69. HRMS (EI+) m/z calcd. for $[C_{11}H_{14}O]^+$: 162.1045, found : 162.1044. The characterization data of **2m** was full agreement with the reported literature.[S1]



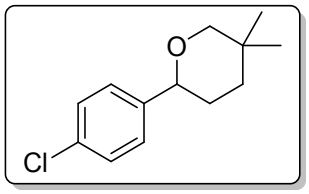
5,5-dimethyl-2-phenyltetrahydro-2H-pyran (2n). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 80% **(**15.2 mg). Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 4H), 7.30 – 7.22 (m, 1H), 4.24 (dd, J = 11.3, 2.8 Hz, 1H), 3.62 (dd, J = 11.1, 2.5 Hz, 1H), 3.35 (d, J = 11.1 Hz, 1H), 1.89 – 1.73 (m, 1H), 1.75 – 1.47 (m, 3H), 1.13 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.32, 128.43, 127.43, 126.02, 80.36, 78.87, 37.42, 30.60, 29.97, 27.37, 23.64. HRMS (EI+) m/z calcd. for $[C_{13}H_{18}O]^+$: 190.1358, found : 190.1356



5,5-dimethyl-2-(p-tolyl)tetrahydro-2H-pyran (2o). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 48% (9.8 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.22 (m, 2H), 7.18 – 7.10 (m, 2H), 4.20 (dd, J = 11.3, 2.7 Hz, 1H), 3.61 (dd, J = 11.1, 2.6 Hz, 1H), 3.33 (d, J = 11.1 Hz, 1H), 2.33 (s, 3H), 1.87 – 1.72 (m, 1H), 1.71 – 1.56 (m, 2H), 1.57 – 1.45 (m, 1H), 1.12 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 140.35, 137.02, 129.09, 125.97, 80.23, 78.87, 37.44, 30.55, 29.97, 27.38, 23.64, 21.27. HRMS (EI+) m/z calcd. for $[C_{14}H_{20}O]^{+}$: 204.1514, found : 204.1511

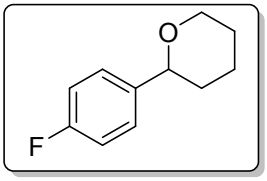


2-(4-fluorophenyl)-5,5-dimethyltetrahydro-2H-pyran (2p). Purified by flash chromatography on silica gel (EA/Hx = 1:200). Overall yield 86% **(**17.9 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.31 (m, 2H), 7.05 – 6.98 (m, 2H), 4.21 (dd, J = 11.2, 2.8 Hz, 1H), 3.61 (dd, J = 11.1, 2.6 Hz, 1H), 3.34 (dd, J = 11.1, 0.9 Hz, 1H), 1.84 – 1.70 (m, 1H), 1.70 – 1.58 (m, 2H), 1.58 – 1.46 (m, 1H), 1.12 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 162.20 (d, J = 244.7 Hz), 139.12 (d, J = 3.1 Hz), 127.66 (d, J = 8.0 Hz), 115.20 (d, J = 21.3 Hz), 79.67, 78.89, 37.32, 30.64, 29.93, 27.33, 23.60. ^{19}F NMR (376 MHz, Chloroform-d) δ -115.59. HRMS (EI+) m/z calcd. for $[C_{13}H_{17}FO]^{+}$: 208.1263, found : 208.1265

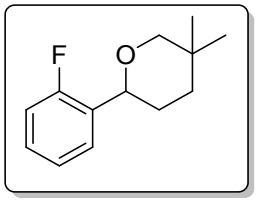


2-(4-chlorophenyl)-5,5-dimethyltetrahydro-2H-pyran (2q). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 63% **(**14.2 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 (m, 4H), 4.21 (dd, J = 10.9, 3.1 Hz, 1H), 3.61 (dd, J = 11.1, 2.5 Hz, 1H), 3.33 (dd, J = 11.1, 0.9 Hz, 1H), 1.80 – 1.46 (m, 4H), 1.11 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d)

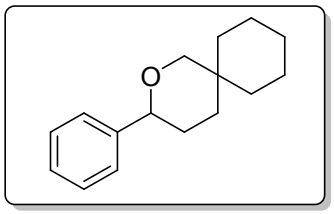
δ 141.87, 133.01, 128.55, 127.37, 79.56, 78.82, 37.27, 30.65, 29.92, 27.31, 23.59. HRMS (EI+) m/z calcd. for $[C_{13}H_{17}ClO]^+$: 224.0968, found : 224.0967



2-(4-fluorophenyl)tetrahydro-2H-pyran (2r). Purified by flash chromatography on silica gel (EA/Hx = 1:200). Overall yield 70% **(**12.6 mg). Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.27 (m, 2H), 7.06 – 6.95 (m, 2H), 4.30 (dd, J = 10.8, 2.2 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.66 – 3.55 (m, 1H), 1.98 – 1.90 (m, 1H), 1.85 – 1.78 (m, 1H), 1.73 – 1.64 (m, 2H), 1.61 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 162.18 (d, J = 244.9 Hz), 139.29 (d, J = 3.2 Hz), 127.63 (d, J = 8.0 Hz), 115.18 (d, J = 21.2 Hz), 79.60, 69.18, 34.20, 25.96, 24.08. ^{19}F NMR (376 MHz, Chloroform-d) δ -115.60 – -115.65 (m). HRMS (EI+) m/z calcd. for $[C_{11}H_{13}FO]^+$: 180.0950, found : 180.0948

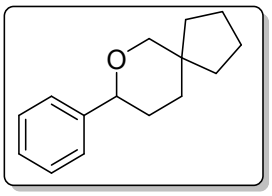


2-(2-fluorophenyl)-5,5-dimethyltetrahydro-2H-pyran (2s). Purified by flash chromatography on silica gel (EA/Hx = 1:200). Overall yield 82% **(**17.0 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.50 (m, 1H), 7.28 – 7.18 (m, 1H), 7.19 – 7.10 (m, 1H), 7.05 – 6.93 (m, 1H), 4.57 (dd, J = 9.6, 4.3 Hz, 1H), 3.63 (dd, J = 11.1, 2.3 Hz, 1H), 3.37 (d, J = 11.1 Hz, 1H), 1.81 – 1.70 (m, 2H), 1.64 – 1.52 (m, 2H), 1.14 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 159.64 (d, J = 245.6 Hz), 130.57, 128.65 (d, J = 8.4 Hz), 127.37 (d, J = 4.5 Hz), 124.36 (d, J = 3.4 Hz), 115.19 (d, J = 21.9 Hz), 78.98, 74.10 (d, J = 2.7 Hz), 37.30, 30.01, 29.65, 27.35, 23.60. ^{19}F NMR (564 MHz, Chloroform-d) δ -120.05 (dt, J = 11.6, 6.3 Hz). HRMS (EI+) m/z calcd. for $[C_{13}H_{17}FO]^+$: 208.1263, found : 208.1262

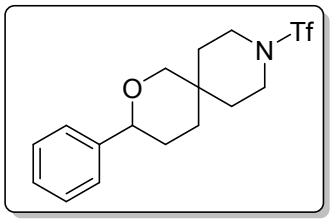


3-phenyl-2-oxaspiro[5.5]undecane (2t). Purified by flash chromatography on silica gel (EA/Hx =

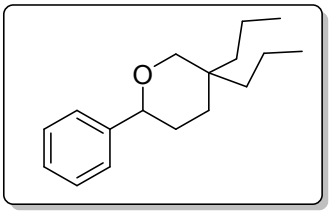
1:100). Overall yield 80% **(**18.4 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 4H), 7.29 – 7.22 (m, 1H), 4.26 (dd, J = 11.2, 2.8 Hz, 1H), 3.92 (dd, J = 11.3, 2.7 Hz, 1H), 3.27 (d, J = 11.3 Hz, 1H), 1.94 – 1.82 (m, 1H), 1.85 – 1.73 (m, 1H), 1.73 – 1.57 (m, 3H), 1.56 – 1.32 (m, 7H), 1.26 – 1.16 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.35, 128.42, 127.43, 126.04, 80.87, 36.73, 32.15, 31.36, 29.83, 26.98, 21.70, 21.65. HRMS (EI+) m/z calcd. for $[C_{16}H_{22}O]^{+}$: 230.1671, found : 230.1668



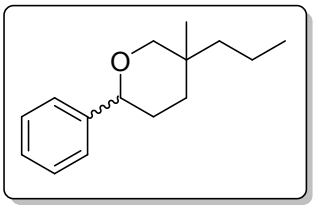
8-phenyl-7-oxaspiro[4.5]decane (2u). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 65% **(**14.1 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.29 (m, 4H), 7.30 – 7.21 (m, 1H), 4.33 – 4.25 (m, 1H), 3.68 (dd, J = 11.1, 1.9 Hz, 1H), 3.38 (dd, J = 11.0, 1.5 Hz, 1H), 2.09 – 1.97 (m, 1H), 1.81 – 1.55 (m, 8H), 1.51 – 1.37 (m, 1H), 1.37 – 1.24 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-d) δ 143.39, 128.41, 127.41, 126.04, 80.16, 76.88, 42.01, 36.89, 36.87, 34.64, 31.91, 25.34, 24.63. HRMS (EI+) m/z calcd. for $[C_{15}H_{20}O]^{+}$: 216.1514, found : 216.1514



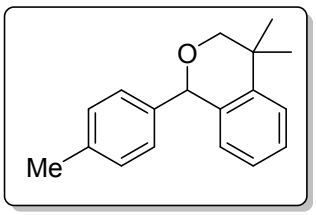
3-phenyl-9-((trifluoromethyl)sulfonyl)-2-oxa-9-azaspiro[5.5]undecane (2v). Purified by flash chromatography on silica gel (EA/Hx = 1:5). Overall yield 85% **(**31.1 mg). Yellow oil. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.35 (d, J = 4.3 Hz, 4H), 7.29 (h, J = 4.2 Hz, 1H), 4.32 (dd, J = 8.1, 6.0 Hz, 1H), 3.97 (m, 1H), 3.53 (m, 4H), 3.38 (d, J = 11.6 Hz, 2H), 1.92 (m, 2H), 1.81 – 1.74 (m, 2H), 1.57 – 1.50 (m, 1H), 1.47 (t, J = 5.9 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-d) δ 142.43, 128.54, 127.75, 125.85, 120.29 (q, J = 323.5 Hz), 80.73, 42.99, 42.42, 35.16, 30.67, 30.56, 29.27. ^{19}F NMR (564 MHz, Chloroform-d) δ -75.60. HRMS (ESI+) m/z calcd. for $[C_{16}H_{20}F_3NnaO_3S]^{+}$: 386.1008, found : 386.1006



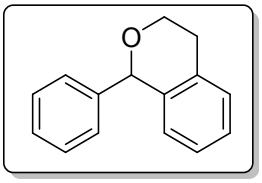
2-phenyl-5,5-dipropyltetrahydro-2H-pyran (2w). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 69% **(**17.0 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.31 (m, 4H), 7.29 – 7.22 (m, 1H), 4.25 (dd, J = 11.1, 2.9 Hz, 1H), 3.80 (dd, J = 11.3, 2.6 Hz, 1H), 3.29 (d, J = 11.3 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.71 – 1.60 (m, 1H), 1.62 – 1.50 (m, 2H), 1.48 – 1.34 (m, 1H), 1.36 – 1.16 (m, 4H), 1.16 – 1.07 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 143.43, 128.41, 127.41, 126.01, 80.54, 76.67, 39.78, 34.76, 34.17, 33.96, 30.01, 16.49, 16.07, 15.23, 15.19. HRMS (ESI+) m/z calcd. for $[C_{17}H_{26}NaO]^{+}$: 269.1876, found : 269.1879



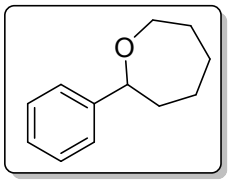
5-methyl-2-phenyl-5-propyltetrahydro-2H-pyran (2x) mixture. Purified by flash chromatography on silica gel (EA/Hx = 1:200). Overall yield 70% **(**15.6 mg, d.r. = 1.1:1). Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.31 (m, 4H), 7.30 – 7.23 (m, 1H), 4.25 (ddd, J = 11.2, 6.0, 2.8 Hz, 1H), 3.36 (dd, J = 11.1, 0.9 Hz, 1H), 1.82 – 1.59 (m, 4H), 1.55 – 1.39 (m, 2H), 1.39 – 1.21 (m, 2H), 1.17 – 1.13 (m, 1H), 1.12 (s, 2H), 0.95 (dt, J = 16.0, 7.2 Hz, 3H), 0.81 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 128.42, 127.42, 126.02, 125.99, 80.65, 80.25, 78.33, 77.79, 43.62, 37.47, 35.60, 35.18, 32.53, 32.38, 30.44, 30.13, 24.07, 20.86, 16.90, 16.23, 15.22, 15.19. HRMS (EI+) m/z calcd. for $[C_{15}H_{22}O]^{+}$: 218.1671, found : 218.1669



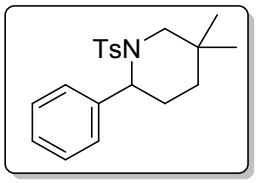
4,4-dimethyl-1-(p-tolyl)isochromane (2y). Purified by flash chromatography on silica gel (EA/Hx = 1:50). Overall yield 60% **(**15.1 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 (dd, J = 7.9, 1.3 Hz, 1H), 7.26 – 7.14 (m, 5H), 7.05 (td, J = 7.5, 1.3 Hz, 1H), 6.72 (ddt, J = 7.8, 1.5, 0.7 Hz, 1H), 5.73 (s, 1H), 3.77 (d, J = 11.2 Hz, 1H), 3.67 (d, J = 11.3 Hz, 1H), 2.36 (d, J = 0.7 Hz, 3H), 1.44 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.65, 139.51, 137.95, 136.22, 129.23, 129.04, 127.03, 126.83, 125.66, 125.51, 80.62, 75.32, 33.86, 29.50, 26.09, 21.34. HRMS (EI+) m/z calcd. for $[C_{18}H_{20}O]^{+}$: 252.1514, found : 252.1510



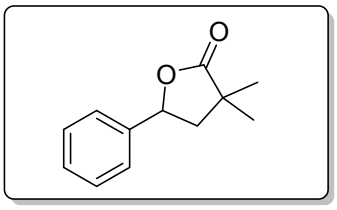
1-phenylisochromane (2z). Purified by flash chromatography on silica gel (EA/Hx = 1:50). Overall yield 51% (10.6 mg). Coloress oil. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.38 – 7.28 (m, 5H), 7.20 – 7.14 (m, 2H), 7.08 (tt, J = 5.6, 2.5 Hz, 1H), 6.76 (d, J = 7.7 Hz, 1H), 5.74 (s, 1H), 4.20 (ddd, J = 11.1, 5.5, 3.8 Hz, 1H), 3.94 (ddd, J = 11.1, 9.5, 3.8 Hz, 1H), 3.15 (td, J = 9.8, 4.7 Hz, 1H), 2.82 (dt, J = 16.4, 4.0 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 142.38, 137.53, 134.02, 129.05, 128.87, 128.56, 128.23, 127.07, 126.76, 126.07, 79.81, 64.02, 29.00. HRMS (ESI+) m/z calcd. for $[C_{15}H_{14}NaO]^+$: 233.0937, found 233.0955



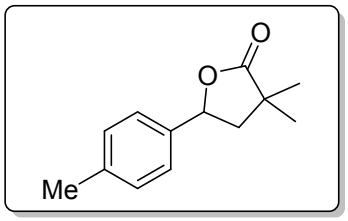
2-phenyloxepane (2aa). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Overall yield 17% (3.1 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.29 (m, 4H), 7.26 – 7.20 (m, 1H), 4.58 (dd, J = 9.2, 3.9 Hz, 1H), 3.98 (ddd, J = 12.4, 6.4, 4.6 Hz, 1H), 3.73 (ddd, J = 12.2, 7.5, 4.1 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.91 – 1.79 (m, 3H), 1.80 – 1.71 (m, 2H), 1.69 – 1.60 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 144.80, 128.36, 126.99, 125.86, 81.53, 68.88, 38.05, 31.18, 26.88, 26.06. The characterization data of **6o** was full agreement with the reported literature.[S2]



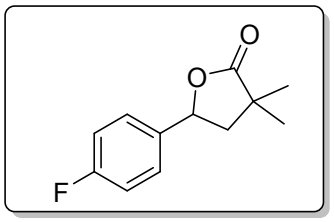
5,5-dimethyl-2-phenyl-1-tosylpiperidine (2ab). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 71% **(**24.2 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.65 (d, J = 8.2 Hz, 2H), 7.33 – 7.22 (m, 4H), 7.24 – 7.11 (m, 3H), 5.19 (t, J = 4.0 Hz, 1H), 3.38 (d, J = 13.5 Hz, 1H), 2.87 (d, J = 13.5 Hz, 1H), 2.41 (s, 3H), 2.24 – 2.00 (m, 2H), 1.27 – 1.13 (m, 2H), 0.77 (d, J = 17.9 Hz, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 143.59, 139.79, 139.12, 130.00, 128.92, 127.46, 127.19, 55.96, 53.08, 32.98, 30.72, 28.87, 26.30, 24.36, 21.76. HRMS (EI+) m/z calcd. for $[C_{20}H_{25}NO_2S]^+$: 343.1606, found : 343.1610



3,3-dimethyl-5-phenyldihydrofuran-2(3H)-one (6a). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 74% **(**14.1 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.28 (m, 5H), 5.45 (dd, J = 9.9, 6.3 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.08 (dd, J = 12.9, 9.9 Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 181.79, 139.63, 128.85, 128.47, 125.45, 77.73, 46.21, 40.88, 25.10, 24.37. HRMS (ESI+) m/z calcd. for $[C_{12}H_{14}NaO_2]^+$: 213.0886, found : 213.0885

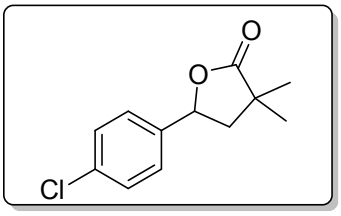


3,3-dimethyl-5-(p-tolyl)dihydrofuran-2(3H)-one (6b). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 69% **(**14.0 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.27 – 7.16 (m, 4H), 5.42 (dd, J = 10.0, 6.2 Hz, 1H), 2.45 (dd, J = 12.9, 6.2 Hz, 1H), 2.36 (s, 3H), 2.07 (dd, J = 12.8, 10.0 Hz, 1H), 1.36 (s, 3H), 1.31 (d, J = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 181.86, 138.34, 136.54, 129.50, 125.54, 77.80, 46.21, 40.93, 25.12, 24.35, 21.28. HRMS (ESI+) m/z calcd. for $[C_{13}H_{16}NaO_2]^+$: 227.1043, found : 227.1052

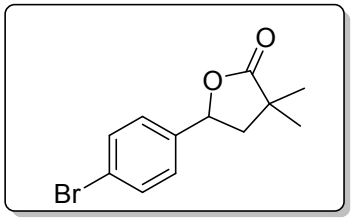


5-(4-fluorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6c). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 65% **(**13.5 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.28 (m, 2H), 7.14 – 7.02 (m, 2H), 5.42 (dd, J = 10.0, 6.2 Hz, 1H), 2.47 (dd, J = 12.9, 6.2 Hz, 1H), 2.04 (dd, J = 12.8, 10.0 Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 181.54, 162.76 (d, J = 247.2 Hz), 135.33 (d, J = 3.2 Hz), 127.36 (d, J = 8.2 Hz), 115.82

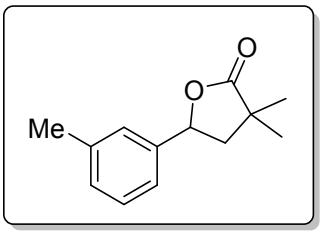
(d, J = 21.6 Hz), 46.25, 40.93, 25.07, 24.30. ^{19}F NMR (564 MHz, Methylene Chloride-d_2) δ -114.44 – -114.49 (m). HRMS (ESI+) m/z calcd. for $[C_{12}H_{13}FNaO_2]^+$: 231.0792, found : 231.0800



5-(4-chlorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6d). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 85% **(**19.1 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.41 – 7.34 (m, 2H), 7.33 – 7.25 (m, 2H), 5.41 (dd, J = 10.0, 6.2 Hz, 1H), 2.48 (dd, J = 12.9, 6.2 Hz, 1H), 2.01 (dd, J = 12.9, 10.0 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 181.72, 138.93, 134.52, 129.38, 127.51, 77.43, 46.41, 41.21, 25.21, 24.46. HRMS (ESI+) m/z calcd. for $[C_{12}H_{13}ClNaO_2]^+$: 247.0496, found : 247.0502

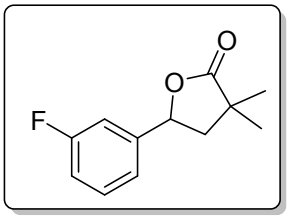


5-(4-bromophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6e). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 87% **(**23.4 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.58 – 7.51 (m, 2H), 7.28 – 7.20 (m, 2H), 5.39 (dd, J = 10.0, 6.2 Hz, 1H), 2.48 (dd, J = 12.9, 6.2 Hz, 1H), 2.00 (dd, J = 12.9, 10.0 Hz, 1H), 1.33 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 181.70, 139.44, 132.34, 127.78, 122.60, 77.43, 46.36, 41.19, 25.20, 24.45. HRMS (ESI+) m/z calcd. for $[C_{12}H_{13}BrNaO_2]^+$: 290.9991, found : 291.0001

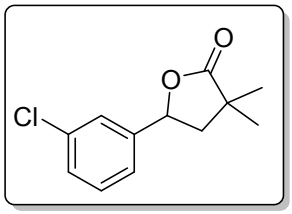


3,3-dimethyl-5-(m-tolyl)dihydrofuran-2(3H)-one (6f). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 67% **(**13.6 mg). White solid. mp 45-47 °C. ^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 7.32 – 7.24 (m, 1H), 7.21 – 7.07 (m, 3H), 5.39 (dd, J = 10.2, 6.1 Hz, 1H), 2.45 (dd, J =

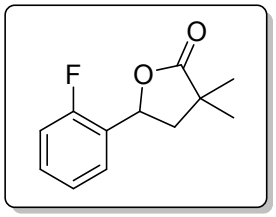
12.8, 6.2 Hz, 1H), 2.36 (s, 3H), 2.05 (dd, J = 12.9, 10.1 Hz, 1H), 1.34 (s, 4H), 1.28 (s, 4H). ^{13}C NMR (150 MHz, Methylene Chloride-d_2) δ 182.04, 140.20, 139.17, 129.60, 129.10, 126.69, 123.12, 78.28, 46.57, 41.26, 25.28, 24.53, 21.70. HRMS (EI+) m/z calcd. for $[C_{13}H_{16}O_2]^+$: 204.1150, found : 204.1149



3,3-dimethyl-5-phenyldihydrofuran-2(3H)-one (6g). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 75% **(**15.6 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.38 (td, J = 8.0, 5.9 Hz, 1H), 7.19 – 7.10 (m, 1H), 7.11 – 7.00 (m, 2H), 5.43 (dd, J = 9.9, 6.3 Hz, 1H), 2.50 (dd, J = 12.9, 6.3 Hz, 1H), 2.02 (dd, J = 12.9, 9.9 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 181.68, 163.53 (d, J = 246.0 Hz), 143.05 (d, J = 7.4 Hz), 130.99 (d, J = 8.3 Hz), 121.61 (d, J = 3.0 Hz), 115.60 (d, J = 21.2 Hz), 112.88 (d, J = 22.7 Hz), 77.28 (d, J = 2.1 Hz), 46.37, 41.14, 25.20, 24.49. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -113.01. HRMS (ESI+) m/z calcd. for $[C_{12}H_{13}FNaO_2]^+$: 231.0792, found : 231.0816

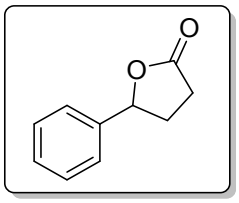


5-(3-chlorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6h). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 60% **(**13.4 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.39 – 7.29 (m, 3H), 7.28 – 7.21 (m, 1H), 5.40 (dd, J = 10.0, 6.3 Hz, 1H), 2.49 (dd, J = 12.9, 6.3 Hz, 1H), 2.02 (dd, J = 12.9, 10.0 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 181.65, 142.52, 135.10, 130.68, 128.91, 126.07, 124.21, 77.26, 46.39, 41.16, 25.19, 24.48. HRMS (EI+) m/z calcd. for $[C_{12}H_{13}ClO_2]^+$: 224.0604, found : 224.0604

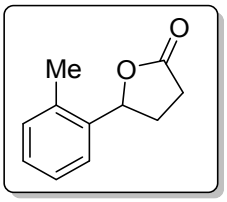


5-(2-fluorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6i). Purified by flash chromatography on

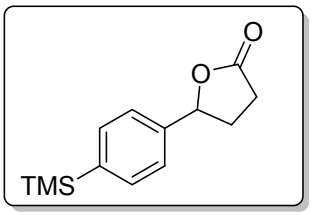
silica gel (EA/Hx = 1:10). Overall yield 62% **(**12.8 mg). Yellow solid. mp 55-57 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.44 (td, J = 7.6, 1.8 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.20 (td, J = 7.6, 1.2 Hz, 1H), 7.09 (ddd, J = 10.8, 8.2, 1.2 Hz, 1H), 5.66 (dd, J = 9.9, 6.4 Hz, 1H), 2.55 (ddd, J = 12.9, 6.5, 1.5 Hz, 1H), 2.07 (dd, J = 12.9, 9.8 Hz, 1H), 1.35 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 181.76, 160.44 (d, J = 246.5 Hz), 130.44 (d, J = 8.2 Hz), 127.60 (d, J = 12.5 Hz), 127.24 (d, J = 3.8 Hz), 125.05 (d, J = 3.5 Hz), 116.07 (d, J = 21.0 Hz), 73.16 (d, J = 3.3 Hz), 45.20 (d, J = 1.7 Hz), 40.95, 25.27, 24.72). ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -119.29. HRMS (EI+) m/z calcd. for $[C_{12}H_{13}FO_2]^+$: 208.0900, found : 208.0901



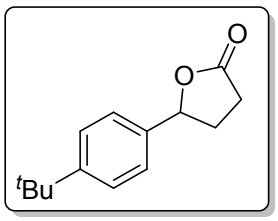
5-phenyldihydrofuran-2(3H)-one (6j). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 77% **(**12.5 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.45 – 7.28 (m, 5H), 5.48 (dd, J = 8.3, 6.1 Hz, 1H), 2.71 – 2.57 (m, 3H), 2.25 – 2.09 (m, 1H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 177.23, 140.25, 129.24, 128.92, 125.96, 81.80, 31.51, 29.54. HRMS (EI+) m/z calcd. for $[C_{10}H_{10}O_2]^+$: 162.0681, found : 162.0680



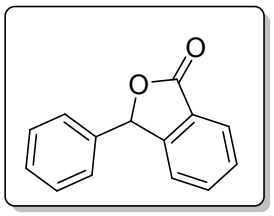
5-(o-tolyl)dihydrofuran-2(3H)-one (6k). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 67% **(**11.8 mg). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.40 – 7.30 (m, 1H), 7.29 – 7.13 (m, 3H), 5.69 (dd, J = 8.8, 5.6 Hz, 1H), 2.73 – 2.58 (m, 3H), 2.34 (s, 3H), 2.17 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 177.42, 138.40, 135.09, 131.20, 128.60, 126.87, 124.71, 79.35, 30.19, 29.29, 19.31. HRMS (ESI+) m/z calcd. for $[C_{11}H_{12}NaO_2]^+$: 199.0730, found : 199.0730



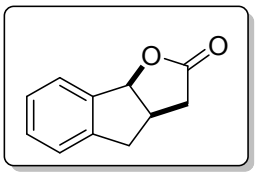
5-(4-(trimethylsilyl)phenyl)dihydrofuran-2(3H)-one (6l). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 54% **(**12.6 mg). White solid. mp 65-67 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.62 – 7.50 (m, 2H), 7.42 – 7.26 (m, 2H), 5.47 (dd, J = 8.4, 6.0 Hz, 1H), 2.75 – 2.54 (m, 3H), 2.31 – 2.09 (m, 1H), 0.28 (s, 9H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 177.27, 141.53, 140.69, 134.27, 125.23, 81.81, 31.48, 29.54. HRMS (EI+) m/z calcd. for $[C_{13}H_{18}O_2Si]^+$: 234.1078, found : 234.1078



5-(4-(tert-butyl)phenyl)dihydrofuran-2(3H)-one (6m). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 62% **(**13.5 mg). White solid. mp 56-58 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.48 – 7.40 (m, 2H), 7.33 – 7.23 (m, 2H), 5.46 (dd, J = 8.3, 6.0 Hz, 1H), 2.71 – 2.53 (m, 3H), 2.30 – 2.11 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, Methylene Chloride-d_2) δ 177.30, 152.26, 137.14, 126.23, 125.87, 81.90, 35.09, 31.62, 31.40, 29.68. HRMS (EI+) m/z calcd. for $[C_{14}H_{18}O_2]^+$: 218.1307, found : 218.1309

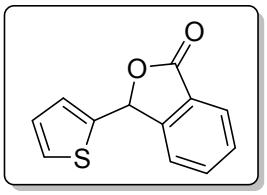


3-phenylisobenzofuran-1(3H)-one (6n). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 90% **(**19.0 mg). White solid. mp 112-114 °C . ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.94 (d, J = 7.6 Hz, 1H), 7.67 (td, J = 7.5, 1.2 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.35 (dd, J = 7.7, 1.0 Hz, 1H), 7.34 – 7.26 (m, 2H), 6.42 (s, 1H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 170.78, 150.27, 137.25, 134.87, 129.89, 129.79, 129.49, 127.50, 126.11, 125.91, 123.44, 83.17. HRMS (ESI+) m/z calcd. for $[C_{14}H_{10}O_2]^+$: 210.0681, found : 210.0681

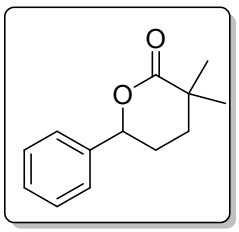


3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan-2-one (6o). Purified by flash chromatography on silica

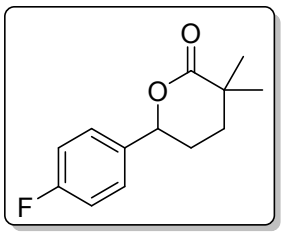
gel (EA/Hx = 1:8). Overall yield 82% **(**14.1 mg, only single *cis*-diasteromer) White solid. mp 52-54 °C ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.53 – 7.46 (m, 1H), 7.39 – 7.33 (m, 1H), 7.33 – 7.26 (m, 2H), 5.87 (d, J = 7.0 Hz, 1H), 3.47 – 3.23 (m, 2H), 2.97 – 2.79 (m, 2H), 2.46 – 2.26 (m, 1H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 177.25, 143.57, 139.59, 130.39, 127.91, 126.68, 125.89, 88.20, 38.49, 37.90, 36.14. HRMS (EI+) m/z calcd. for $[C_{11}H_{10}O_2]^+$: 174.0681, found : 174.0684. The characterization data of **6o** was full agreement with the reported literature.[S3]



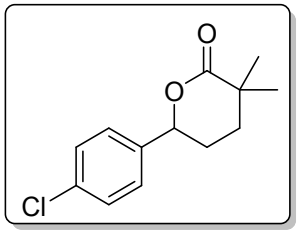
3-(thiophen-2-yl)isobenzofuran-1(3H)-one (6p). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 60% **(**12.9 mg). Yellow solid. mp 74-76 °C. ^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 7.93 (d, J = 7.7 Hz, 1H), 7.73 (t, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.43 – 7.38 (m, 2H), 7.21 – 7.16 (m, 1H), 7.08 – 7.02 (m, 1H), 6.69 (s, 1H). ^{13}C NMR (150 MHz, Methylene Chloride-d_2) δ 170.04, 149.32, 139.81, 134.93, 130.36, 128.55, 128.11, 127.68, 126.46, 125.99, 123.78, 78.43. HRMS (EI+) m/z calcd. for $[C_{12}H_8O_2S]^+$: 216.0245, found : 216.0242



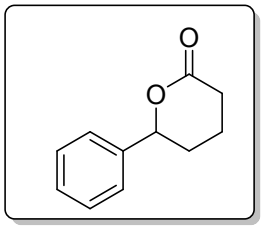
3,3-dimethyl-6-phenyltetrahydro-2H-pyran-2-one (6q). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 80% **(**16.3 mg). White solid. mp 78-80 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.29 (m, 5H), 5.38 (dd, J = 10.0, 3.9 Hz, 1H), 2.18 – 2.07 (m, 1H), 2.09 – 1.96 (m, 1H), 1.89 (ddd, J = 13.6, 11.4, 3.8 Hz, 1H), 1.79 (ddd, J = 13.6, 5.1, 3.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 177.30, 140.39, 128.71, 128.28, 125.66, 82.70, 38.36, 34.54, 28.78, 28.07, 27.93. HRMS (ESI+) m/z calcd. for $[C_{13}H_{16}NaO_2]^+$: 227.1043, found : 227.1057



6-(4-fluorophenyl)-3,3-dimethyltetrahydro-2H-pyran-2-one (6r). Purified by flash chromatography on silica gel (EA/Hx = 1:15). Overall yield 63% **(**13.9 mg). Pale yellow solid. mp 108-110 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.38 – 7.30 (m, 2H), 7.13 – 7.03 (m, 2H), 5.34 (d, J = 3.6 Hz, 1H), 2.11 – 2.02 (m, 1H), 2.01 – 1.91 (m, 1H), 1.92 – 1.83 (m, 1H), 1.82 – 1.75 (m, 1H), 1.34 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 177.23, 163.03 (d, J = 245.7 Hz), 137.10 (d, J = 3.0 Hz), 128.06 (d, J = 8.3 Hz), 115.91 (d, J = 21.7 Hz), 82.51, 38.63, 34.99, 29.27, 28.21, 28.15. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -114.83. HRMS (EI+) m/z calcd. for $[C_{13}H_{15}FO_2]^+$: 222.1056, found : 222.1053

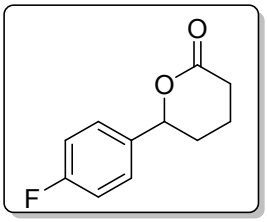


6-(4-chlorophenyl)-3,3-dimethyltetrahydro-2H-pyran-2-one (6s). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 65% **(**15.5 mg). White solid. mp 90-92 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.43 – 7.35 (m, 2H), 7.34 – 7.26 (m, 2H), 5.34 (d, J = 3.6 Hz, 1H), 2.13 – 2.05 (m, 1H), 2.03 – 1.84 (m, 2H), 1.82 – 1.73 (m, 1H), 1.34 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 177.15, 139.81, 134.27, 129.23, 127.62, 82.35, 38.65, 34.89, 29.20, 28.18, 28.12. HRMS (EI+) m/z calcd. for $[C_{13}H_{15}ClO_2]^+$: 238.0761, found : 238.0759

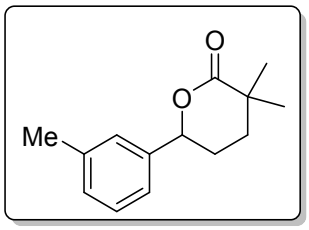


6-phenyltetrahydro-2H-pyran-2-one (6t). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 85% **(**15.0 mg). White solid. mp 45-47 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.45 – 7.31 (m, 5H), 5.33 (dd, J = 10.6, 3.4 Hz, 1H), 2.67 (dtd, J = 17.7, 6.3, 1.2 Hz, 1H),

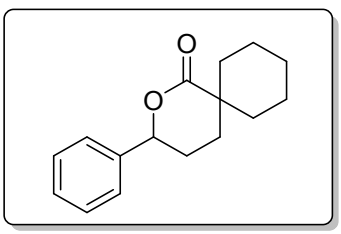
2.53 (dt, J = 17.7, 7.9 Hz, 1H), 2.20 – 2.09 (m, 1H), 2.03 – 1.92 (m, 2H), 1.90 – 1.80 (m, 1H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 171.51, 140.72, 129.10, 128.73, 126.32, 82.14, 31.05, 30.01, 19.23. HRMS (EI+) m/z calcd. for $[C_{11}H_{12}O_2]^+$: 176.0837, found : 176.0837



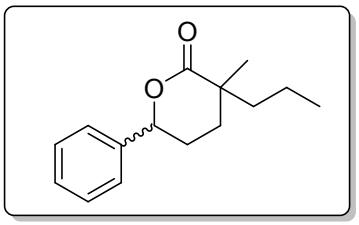
6-(4-fluorophenyl)tetrahydro-2H-pyran-2-one (6u). Purified by flash chromatography on silica gel (EA/Hx = 1:15). Overall yield 77% **(**14.8 mg). White solid. mp 81-83 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.28 (m, 2H), 7.13 – 7.00 (m, 2H), 5.32 (dd, J = 10.7, 3.3 Hz, 1H), 2.71 (dt, J = 17.8, 6.3 Hz, 1H), 2.57 (dt, J = 17.8, 7.9 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.05 – 1.92 (m, 2H), 1.94 – 1.74 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 171.26, 162.69 (d, J = 246.9 Hz), 135.67 (d, J = 3.3 Hz), 127.69 (d, J = 8.4 Hz), 115.66 (d, J = 21.6 Hz), 81.16, 30.68, 29.53, 18.75. ^{19}F NMR (564 MHz, Methylene Chloride-d_2) δ -114.72 (ddd, J = 8.8, 5.4, 3.5 Hz). HRMS (EI+) m/z calcd. for $[C_{11}H_{11}FO_2]^+$: 194.0743, found : 194.0744



3,3-dimethyl-6-(m-tolyl)tetrahydro-2H-pyran-2-one (6v). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 50% (11.0 mg). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.22 (m, 1H), 7.19 – 7.07 (m, 3H), 5.34 (dd, J = 10.0, 3.9 Hz, 1H), 2.36 (s, 3H), 2.17 – 1.94 (m, 2H), 1.92 – 1.84 (m, 1H), 1.79 (ddd, J = 13.6, 5.1, 3.8 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 177.35, 140.36, 138.47, 129.02, 128.59, 126.32, 122.73, 82.77, 38.38, 34.62, 28.81, 28.10, 27.97, 21.58. HRMS (ESI+) m/z calcd. for $[C_{14}H_{18}NaO_2]^+$: 241.1199, found : 241.1194

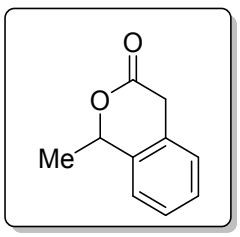


3-phenyl-2-oxaspiro[5.5]undecan-1-one (6w). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Overall yield 63% **(**15.4 mg). White solid. mp 85-87 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.30 (m, 5H), 5.34 (dd, J = 10.1, 3.4 Hz, 1H), 2.18 – 2.04 (m, 3H), 2.06 – 1.85 (m, 2H), 1.85 – 1.53 (m, 6H), 1.49 – 1.38 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 177.34, 140.53, 128.68, 128.23, 125.70, 81.73, 41.94, 35.77, 33.93, 28.84, 28.49, 25.58, 21.09, 20.99. HRMS (EI+) m/z calcd. for $[C_{16}H_{20}O_2]^+$: 244.1463, found : 244.1467



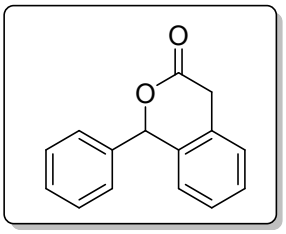
3-methyl-6-phenyl-3-propyltetrahydro-2H-pyran-2-one (6x-major). Purified by flash chromatography on silica gel (EA/Hx = 1:20). Yield 38% (8.7 mg of major diastereomer) Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 5H), 5.30 (dd, J = 10.2, 3.2 Hz, 1H), 2.15 – 1.93 (m, 3H), 1.85 (ddd, J = 12.9, 12.0, 4.1 Hz, 1H), 1.74 – 1.64 (m, 1H), 1.57 – 1.38 (m, 2H), 1.34 (s, 3H), 1.32 – 1.25 (m, 1H), 1.01 – 0.92 (m, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 176.81, 140.40, 128.71, 128.34, 125.75, 82.59, 43.13, 42.21, 31.71, 29.06, 27.11, 17.85, 14.57. HRMS (ESI+) m/z calcd. for $[C_{15}H_{20}NaO_2]^+$: 255.1356, found : 255.1364

3-methyl-6-phenyl-3-propyltetrahydro-2H-pyran-2-one (6x-minor). Purified by flash chromatography on silica gel (EA/Hx = 1:20). Yield 23% (5.3 mg of minor diastereomer). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.28 (m, 5H), 5.39 (dd, J = 9.4, 4.0 Hz, 1H), 2.17 – 2.08 (m, 1H), 2.06 – 1.98 (m, 1H), 1.92 (ddd, J = 13.9, 5.7, 3.6 Hz, 1H), 1.79 – 1.66 (m, 2H), 1.64 – 1.58 (m, 1H), 1.40 – 1.35 (m, 1H), 1.33 (s, 3H), 1.32 – 1.28 (m, 1H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 176.98, 140.50, 128.70, 128.22, 125.66, 82.25, 42.43, 41.71, 31.57, 28.71, 26.22, 17.49, 14.66. HRMS (ESI+) m/z calcd. for $[C_{15}H_{20}NaO_2]^+$: 255.1356, found : 255.1353

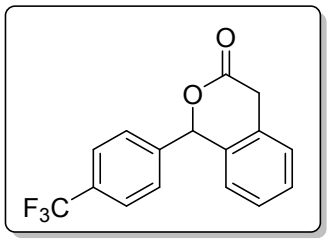


1-methylisochroman-3-one (6y). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 65% **(**10.5 mg). Pale yellow oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.39 –

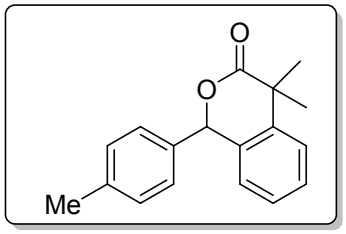
7.29 (m, 2H), 7.33 – 7.24 (m, 2H), 7.27 – 7.18 (m, 1H), 5.47 (q, J = 6.7 Hz, 1H), 3.71 (s, 2H), 1.73 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 171.01, 136.65, 131.65, 129.07, 127.88, 127.62, 124.12, 76.86, 36.79, 19.44. HRMS (EI+) m/z calcd. for $[C_{10}H_{10}O_2]^+$: 162.0681, found : 162.0679



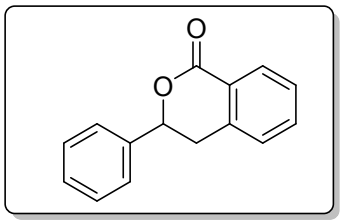
1-phenylisochroman-3-one (6z). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 76% **(**17.0 mg). Pale yellow solid. mp 74-76 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.34 (m, 4H), 7.34 – 7.21 (m, 4H), 7.04 – 6.92 (m, 1H), 6.41 (s, 1H), 3.75 (d, J = 18.2 Hz, 1H), 3.64 (d, J = 18.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 170.69, 137.04, 134.75, 131.12, 129.09, 129.02, 128.90, 127.62, 127.45, 127.45, 126.18, 82.20, 36.66. HRMS (ESI+) m/z calcd. for $[C_{15}H_{12}NaO_2]^+$: 247.0730, found : 247.0726



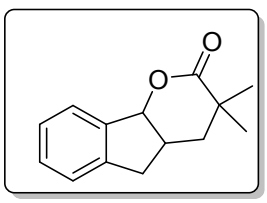
1-(4-(trifluoromethyl)phenyl)isochroman-3-one (6aa). Purified by flash chromatography on silica gel (EA/Hx = 30:1). Overall yield 65% **(**19.0 mg). Yellow solid. mp 126-128 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.71 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.37 – 7.25 (m, 2H), 6.92 (d, J = 7.8 Hz, 1H), 6.46 (s, 1H), 3.79 (d, J = 18.3 Hz, 1H), 3.64 (d, J = 18.3 Hz, 1H). ^{13}C NMR (150 MHz, Methylene Chloride-d_2) δ 170.29, 141.79, 134.71, 131.83, 131.39 (q, J = 32.5 Hz), 129.76, 128.58, 126.35, 126.32, 126.29, 125.73 – 121.65 (m), 81.68, 37.02. ^{19}F NMR (564 MHz, Methylene Chloride-d_2) δ -61.12. HRMS (EI+) m/z calcd. for $[C_{16}H_{11}F_3O_2]^+$: 292.0711, found : 292.0708



4,4-dimethyl-1-(p-tolyl)isochroman-3-one (6ab). Purified by flash chromatography on silica gel (EA/Hx = 30:1). Overall yield 72% **(**19.2 mg). White solid. mp 112-114 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.44 (dd, J = 7.9, 1.4 Hz, 1H), 7.38 (tdd, J = 7.9, 1.4, 0.7 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.19 (td, J = 7.5, 1.3 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.49 (s, 1H), 2.40 (s, 3H), 1.65 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 175.57, 140.59, 139.53, 136.13, 134.55, 129.93, 129.46, 128.64, 127.16, 126.73, 124.93, 81.42, 42.57, 27.00, 25.70, 21.53. HRMS (ESI+) m/z calcd. for $[C_{18}H_{18}NaO_2]^+$: 289.1199, found : 289.1196



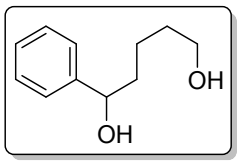
3-phenylisochroman-1-one (6ac). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 72% **(**16.1 mg). Whit solid. mp 87-89 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 8.10 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 (td, J = 7.5, 1.4 Hz, 1H), 7.54 – 7.36 (m, 6H), 7.32 (ddq, J = 7.6, 1.2, 0.6 Hz, 1H), 5.56 (dd, J = 12.0, 3.2 Hz, 1H), 3.34 (ddt, J = 16.4, 11.9, 1.1 Hz, 1H), 3.15 (dd, J = 16.5, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 165.43, 139.07, 138.70, 134.04, 130.57, 128.82, 128.78, 128.01, 127.48, 126.25, 125.29, 80.09, 35.74. HRMS (EI+) m/z calcd. for $[C_{15}H_{12}O_2]^+$: 224.0837, found : 224.0840. X-ray crystallographic data of **6ac** is provided in *Appendix I*. The similar structure of **6ac** is also reported in the literature.[S4]



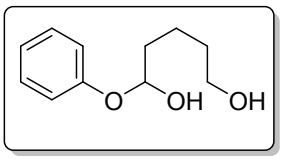
3,3-dimethyl-4,4a,5,9b-tetrahydroindeno[1,2-b]pyran-2(3H)-one (6ad). Purified by flash chromatography on silica gel (EA/Hx = 1:8). Overall yield 50% (10.8 mg of single diasteromer). White solid. mp 105-107 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.50 (m, 1H), 7.36 – 7.28 (m, 2H),

7.24 (ddd, J = 7.2, 1.9, 0.9 Hz, 1H), 5.90 (d, J = 7.7 Hz, 1H), 3.25 (dd, J = 16.1, 7.8 Hz, 1H), 3.13 – 2.99 (m, 1H), 2.74 (dd, J = 16.1, 2.7 Hz, 1H), 1.80 (dd, J = 13.6, 6.4 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.39 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 176.95, 140.71, 140.26, 129.32, 127.42, 125.78, 125.18, 84.83, 38.91, 37.72, 37.53, 33.17, 27.13, 24.75. HRMS (ESI+) m/z calcd. for $[C_{14}H_{16}NaO_2]^+$: 239.1043, found : 239.1042

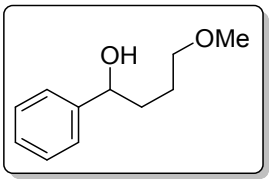
Control experiment



phenylpentane-1,5-diol (3). Purified by flash chromatography on silica gel (EA/Hx = 3:1). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 4.68 (dd, J = 7.6, 5.6 Hz, 1H), 3.62 (t, J = 6.4 Hz, 2H), 1.91 – 1.83 (m, 1H), 1.73 (ddt, J = 13.5, 9.6, 5.7 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.54 – 1.46 (m, 1H), 1.45 – 1.32 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.89, 128.61, 127.70, 125.99, 74.65, 62.82, 38.82, 32.57, 22.13. HRMS (EI+) m/z calcd. for $[C_{11}H_{16}O_2]^+$: 180.1150, found : 180.1150

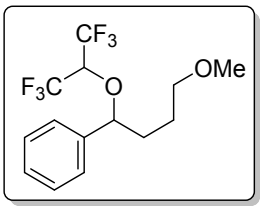


1-phenoxypentane-1,5-diol (4). Purified by flash chromatography on silica gel (EA/Hx = 2:1). Coloress oil. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.43 – 7.27 (m, 5H), 4.89 (t, J = 6.9 Hz, 1H), 3.57 (t, J = 6.4 Hz, 2H), 1.94 – 1.81 (m, 1H), 1.73 – 1.63 (m, 1H), 1.59 – 1.51 (m, 2H), 1.49 – 1.40 (m, 1H), 1.37 – 1.28 (m, 1H). ^{13}C NMR (150 MHz, Methylene Chloride-d_2) δ 141.58, 129.12, 128.68, 127.43, 88.63, 63.03, 34.75, 33.14, 22.62. HRMS (ESI+) m/z calcd. for $[C_{11}H_{16}NaO_3]^+$: 219.0992, found : 219.0991

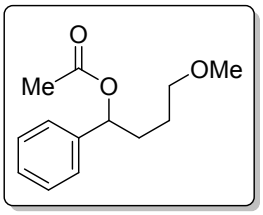


4-methoxy-1-phenylbutan-1-ol (10a). Purified by flash chromatography on silica gel (EA/Hx = 1:5).

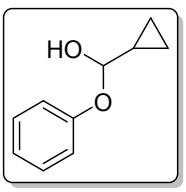
Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 4.70 (dd, J = 7.2, 5.4 Hz, 1H), 3.42 (t, J = 6.0 Hz, 2H), 3.34 (s, 3H), 1.92 – 1.80 (m, 2H), 1.78 – 1.56 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.97, 128.47, 127.42, 125.94, 74.24, 72.94, 58.71, 36.72, 26.32. HRMS (EI+) m/z calcd. for $[C_{11}H_{16}O_2]^+$: 180.1150, found : 180.1152



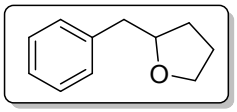
(1-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxybutyl)benzene (10b). Purified by flash chromatography on silica gel (EA/Hx = 1:100). Coloress oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 4.66 (dd, J = 8.0, 5.4 Hz, 1H), 3.97 (hept, J = 6.0 Hz, 1H), 3.44 – 3.33 (m, 2H), 3.30 (s, 3H), 2.12 – 2.00 (m, 1H), 1.88 – 1.68 (m, 2H), 1.56 – 1.46 (m, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 138.41, 129.22, 128.93, 127.86, 124.50 – 119.74 (m), 85.48, 72.85 (dt, J = 64.0, 32.1 Hz), 72.35, 58.68, 34.35, 26.02. ^{19}F NMR (564 MHz, Chloroform-d) δ -72.49 (dq, J = 15.4, 9.3 Hz), -73.52 – -73.69 (m). HRMS (FAB+) m/z calcd. for $[C_{14}H_{17}OF_6O_2]^+$: 331.1127, found : 331.1130



4-methoxy-1-phenylbutyl acetate (10c). Purified by flash chromatography on silica gel (EA/Hx = 1:10). pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 5.75 (dd, J = 7.8, 6.1 Hz, 1H), 3.39 – 3.34 (m, 2H), 3.30 (s, 3H), 2.07 (s, 3H), 2.02 – 1.91 (m, 1H), 1.90 – 1.80 (m, 1H), 1.70 – 1.58 (m, 2H), 1.55 – 1.44 (m, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 170.47, 140.75, 128.58, 128.03, 126.64, 75.97, 72.35, 58.69, 33.17, 25.87, 21.38. HRMS (EI+) m/z calcd. for $[C_{13}H_{18}O_3]^+$: 222.1256, found : 222.1258



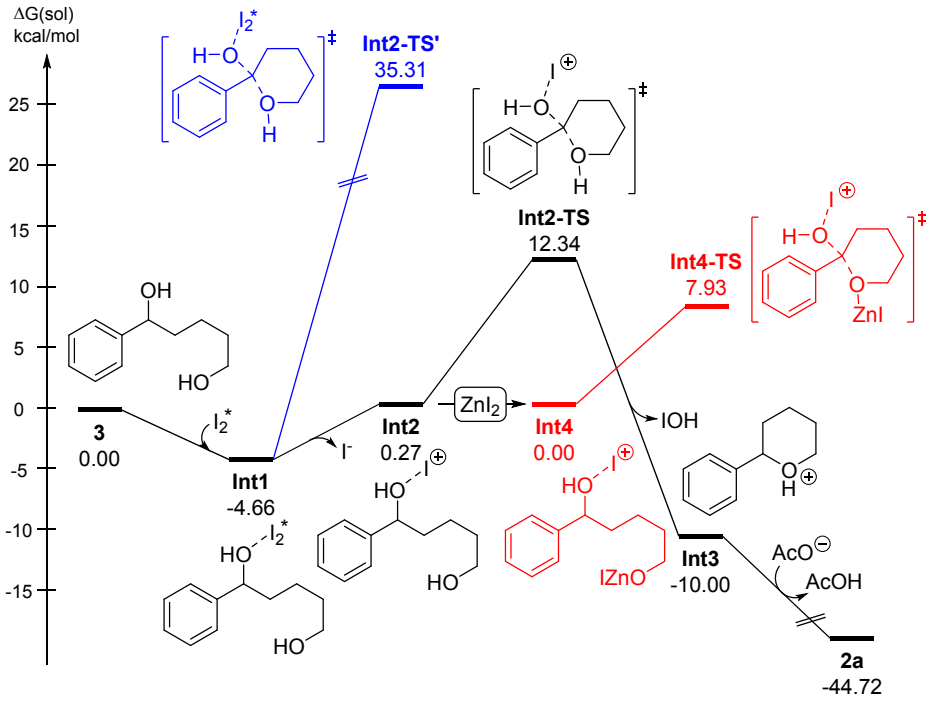
cyclopropyl(phenoxy)methanol (14). Purified by flash chromatography on silica gel (EA/Hx = 1:10). Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (s, 1H), 7.41 – 7.38 (m, 4H), 7.38 – 7.31 (m, 1H), 4.26 (d, J = 8.8 Hz, 1H), 1.24 – 1.12 (m, 1H), 0.77 – 0.65 (m, 1H), 0.64 – 0.47 (m, 2H), 0.38 – 0.26 (m, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 140.04, 128.75, 128.40, 127.10, 92.41, 14.74, 4.72, 2.43. HRMS (ESI+) m/z calcd. for $[C_{10}H_{13}O_2]^+$: 165.0910, found : 165.0912

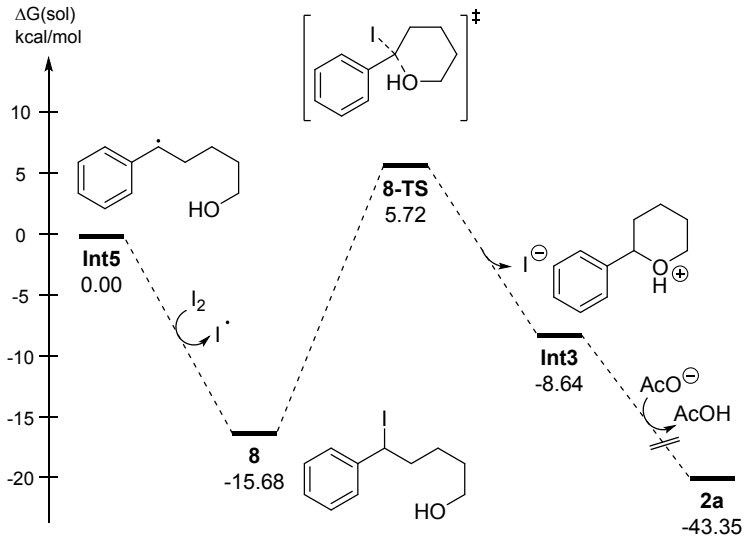


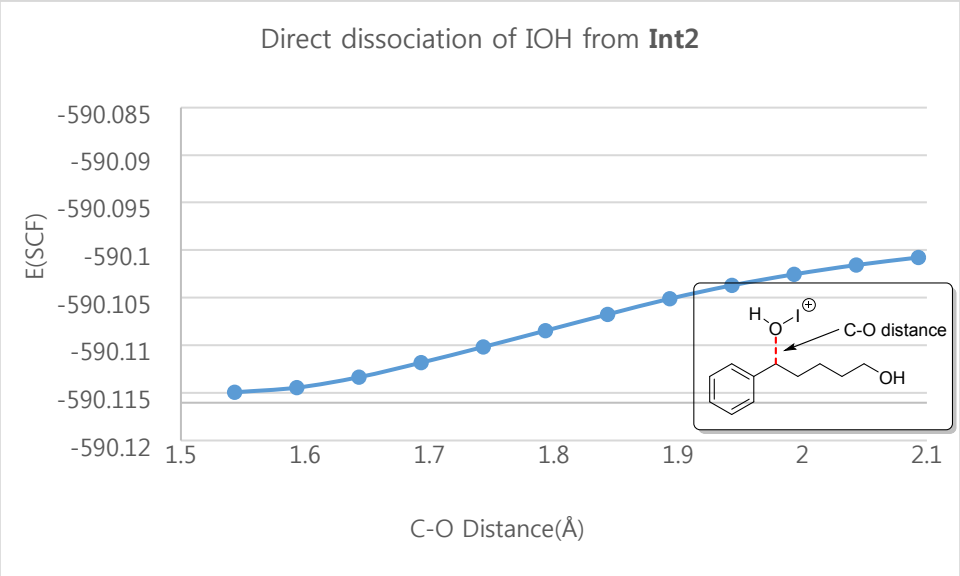
2-benzyltetrahydrofuran (15). Purified by flash chromatography on silica gel (EA/Hx = 1:30). Pale red oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 4.13 – 4.02 (m, 1H), 3.95 – 3.84 (m, 1H), 3.79 – 3.69 (m, 1H), 2.93 (dd, J = 13.5, 6.5 Hz, 1H), 2.75 (dd, J = 13.6, 6.5 Hz, 1H), 1.97 – 1.80 (m, 3H), 1.61 – 1.50 (m, 1H). The characterization data of **15** was full agreement with the reported literature.[S5]

VIII. Computational Details

All calculations were conducted using DFT[S6] as implemented in Gaussian 09 software[S7] of ab initio quantum chemistry programs with Minnesota functional M06-2X[S8] Geometry optimization of all species was carried out using a mixed basis set of LanL2DZ[S9] for I and Zn and 6-31+G(d) basis set for other atoms. Frequency analysis was performed to ensure the stationary point as minimum or transition state. For the solvent effect of hexafluoroisopropanol, the SMD solvation model was used with parameters adapted for HFIP.[S10,S11] The single-point calculation was carried out by using M06-2X with a mixed basis set of SDD[S12] for I and Zn and 6-311+G(2d,p) basis set for other atoms.







- Cartesian coordinates of optimized structures (Å)

3

Lowest three frequencies(cm^{-1}): 33.4683, 47.0545, 54.3209

C	-4.31896500	-0.82111000	0.46556200
C	-3.78466100	-1.10424100	-0.79112400
C	-2.53698000	-0.59198400	-1.15096800
C	-1.81065400	0.20194600	-0.25997200
C	-2.35296600	0.48228200	0.99905400
C	-3.60005700	-0.02505400	1.35998100
H	-4.34153200	-1.71736600	-1.49485700
H	-2.12424900	-0.80688700	-2.13520000
H	-1.79325200	1.10523200	1.69313900
H	-4.01288200	0.19986700	2.34000200
H	-5.29222100	-1.21412100	0.74691800
C	-0.43649200	0.72210600	-0.63490300
C	0.66926400	-0.10055100	0.02183100
C	2.07323600	0.34049000	-0.38665400
H	0.51580300	-1.15441100	-0.24468400
C	4.55936600	-0.04720800	-0.10978000
C	3.16044600	-0.50360600	0.27735600
H	2.21308100	1.39519300	-0.12021800
H	2.17040800	0.27303200	-1.47997800
H	4.71843400	0.99120300	0.19883600
H	4.68661700	-0.09351300	-1.20136100
H	3.06210500	-0.44899300	1.36972300
H	3.03547900	-1.55919800	-0.00572700
O	5.58174000	-0.79876900	0.53664600
H	5.50903500	-1.72239100	0.24700800
H	-0.32418300	0.65715400	-1.72822700

H	0.55254600	-0.02302500	1.11216800
O	-0.25106300	2.07160300	-0.21513400
H	-0.94983400	2.61713100	-0.61194100

Int1

Lowest three frequencies(cm^{-1}): 21.4027, 24.8898, 30.7131

I	-0.04179800	-1.95114800	-1.07484800
I	-2.28109600	-0.93231000	1.13075200
C	5.18853100	0.19801800	1.54385900
C	5.29811500	1.28860900	0.68288200
C	4.20527500	1.67557900	-0.09579200
C	2.99466200	0.98369000	-0.01616600
C	2.89101900	-0.10846700	0.85450300
C	3.98193000	-0.50157100	1.62669800
H	6.23365500	1.83663500	0.61291500
H	4.29347900	2.52323500	-0.77228800
H	1.95214400	-0.65314000	0.92831100
H	3.89083200	-1.35116700	2.29785600
H	6.03784600	-0.10692200	2.14877400
C	1.81144900	1.41793300	-0.85530600
C	0.61691400	1.85311200	-0.01755400
C	-0.60120700	2.24037300	-0.85420600
H	0.93767900	2.70551500	0.59538000
C	-2.95926800	3.15311000	-0.79519900
C	-1.68450400	2.90299400	-0.00486100
H	-1.00884000	1.34312500	-1.33949100
H	-0.29387500	2.92212400	-1.66034000
H	-3.37702500	2.20358200	-1.14577000
H	-2.74368600	3.77125800	-1.67972900
H	-1.92399300	2.26675000	0.85708700
H	-1.30789400	3.85809600	0.38980500
O	-3.98377400	3.75586400	-0.01150600
H	-3.65002900	4.60375500	0.32407200
H	2.12215800	2.25860000	-1.49274600
H	0.34669200	1.04496600	0.67623000
O	1.36140900	0.36406800	-1.72550500
H	2.12568100	0.01710900	-2.22004200

Int2

Lowest three frequencies(cm^{-1}): 25.0761, 41.0465, 63.1163

C	4.32408300	-1.64102800	-0.63583200
C	3.99507100	-1.85231800	0.70349100
C	2.68950700	-1.63658100	1.13673900
C	1.70477100	-1.20853500	0.23703200
C	2.03942200	-1.00613600	-1.10876700

C	3.34688400	-1.21975500	-1.53919100
H	4.74997000	-2.19279200	1.40582600
H	2.42605700	-1.81420500	2.17740000
H	1.28648500	-0.68545500	-1.82303500
H	3.60215600	-1.06180300	-2.58282100
H	5.34095100	-1.81124300	-0.97805500
C	0.32265400	-0.97448900	0.76110900
C	-0.85248800	-1.22825700	-0.15065600
C	-2.20100500	-0.93348100	0.50523000
H	-0.78774200	-2.28982100	-0.42258200
C	-4.71199000	-1.01422700	0.24118900
C	-3.36658900	-1.30947600	-0.40713700
H	-2.26837700	0.13353400	0.75682100
H	-2.27202800	-1.48749100	1.45117400
H	-4.79118500	0.05200500	0.47685300
H	-4.80982400	-1.57276900	1.18339100
H	-3.29908600	-0.75277500	-1.35090900
H	-3.31125300	-2.37867700	-0.65600100
O	-5.80694500	-1.29854000	-0.61982900
H	-5.81626400	-2.25249300	-0.80081400
H	0.18121900	-1.47999100	1.72226100
H	-0.74918200	-0.66252900	-1.08495700
O	0.20345200	0.48901200	1.23585600
H	0.86996000	0.66028300	1.94311500
I	0.20253100	2.07958800	-0.09066300

Int2-TS'

Lowest three frequencies(cm^{-1}): -395.6011, 25.1248, 38.1204

C	0.59122100	-3.20451900	1.99875000
C	1.36700800	-3.48573200	0.86909900
C	1.86574900	-2.44320600	0.10000200
C	1.59093900	-1.11139700	0.45049000
C	0.81391300	-0.83722200	1.58436600
C	0.31642300	-1.88435000	2.35547700
H	1.57566000	-4.51494200	0.59314700
H	2.46368400	-2.64863200	-0.78504100
H	0.57657200	0.18649500	1.85519600
H	-0.29463700	-1.66804800	3.22660800
H	0.19712900	-4.01995900	2.59895600
C	2.10637700	-0.04781100	-0.39861800
C	1.76820100	1.39402600	-0.23396900
C	2.72876000	2.33043500	-0.97140000
H	1.72121100	1.65085500	0.83089400
H	0.74936800	1.50418200	-0.62562800
C	4.80226100	1.05305300	-0.25581100
C	4.10971900	2.40240700	-0.31858600
H	2.28704600	3.33159700	-0.99058600
H	2.82188200	2.00203400	-2.01527500

H	5.77966400	1.11724800	0.23302800
H	4.94400600	0.63119600	-1.25535400
H	4.75624600	3.08882100	-0.87769800
H	4.01763700	2.80677400	0.69920700
O	4.00413100	0.07892800	0.44652200
H	2.65057400	-0.34984700	-1.28489100
H	3.90750500	0.35025500	1.37961500
I	-1.74003800	-0.98396100	-1.18572500
I	-2.17056600	1.62740700	0.82683700
O	0.50629300	-0.26538100	-2.07612600
H	0.66168900	-1.07312000	-2.60307200

Int2-TS

Lowest three frequencies(cm^{-1}): -167.5359, 40.9889, 46.7693

C	0.97921500	3.62847500	0.28063400
C	0.61550300	3.20615000	-1.00101900
C	-0.04518700	1.99435900	-1.16842500
C	-0.34579800	1.19486700	-0.05750200
C	0.02268700	1.61980800	1.22289000
C	0.68082700	2.83767200	1.38959100
H	0.84634200	3.82239600	-1.86469700
H	-0.33496900	1.65801800	-2.16152300
H	-0.19539600	1.00810300	2.09332500
H	0.96382800	3.16477700	2.38561300
H	1.49194600	4.57681100	0.41395400
C	-0.99518200	-0.11847800	-0.29047000
C	-1.45502200	-0.98941800	0.86072400
C	-2.55655600	-1.98497900	0.47524000
H	-1.81526800	-0.34564100	1.66830100
H	-0.58279700	-1.51895600	1.26487000
C	-3.96945300	-0.17888700	-0.62756400
C	-3.93684600	-1.33299600	0.36098000
H	-2.59586300	-2.77091400	1.23618900
H	-2.29731500	-2.47956800	-0.47161700
H	-4.97006300	0.26056300	-0.69950900
H	-3.68449200	-0.51994100	-1.63005800
H	-4.67646400	-2.08058800	0.05070200
H	-4.24728900	-0.96417200	1.34838600
O	-3.01366600	0.83198700	-0.28039700
H	-1.50314300	-0.21183700	-1.24304400
H	-3.35618800	1.34613300	0.47143300
I	2.15631700	-1.15161800	-0.01101100
O	0.34707000	-0.99218200	-0.93712000
H	0.03997500	-1.88729200	-1.20910400

Int3

Lowest three frequencies(cm^{-1}): 49.9083, 88.2609, 130.4507

C	3.67876200	0.06120100	-0.20947200
C	3.10510800	-1.02545200	0.45266900
C	1.73076000	-1.05583400	0.66976700
C	0.92044900	-0.00295700	0.22885700
C	1.49946500	1.08355100	-0.43555000
C	2.87667600	1.11239200	-0.65247100
H	3.72781300	-1.84364800	0.80246300
H	1.27627000	-1.89731100	1.18819800
H	0.88964000	1.91441900	-0.77853600
H	3.32365600	1.95991500	-1.16374800
H	4.75173400	0.08977900	-0.37708800
C	-0.55756900	-0.09334800	0.47592900
C	-1.36115700	1.18746500	0.57710400
C	-2.85426400	0.89159300	0.74285700
H	-1.19832200	1.80432700	-0.31524600
H	-0.97227500	1.74570200	1.43568900
C	-2.58076000	-1.22955300	-0.56563200
C	-3.37274700	0.04803900	-0.42261600
H	-3.40941100	1.83217000	0.79590600
H	-3.02050500	0.35867300	1.68756800
H	-2.80479100	-1.80571200	-1.46334600
H	-2.62767700	-1.87063200	0.31668900
H	-4.41995600	-0.23470800	-0.27092100
H	-3.32144700	0.61542100	-1.36034900
O	-1.12590800	-0.91337600	-0.68075600
H	-0.76568200	-0.75970700	1.31788000
H	-0.93012900	-0.46426100	-1.53775500

Int4

Lowest three frequencies(cm^{-1}): 23.3358, 37.7723, 39.5500

C	7.33843800	-2.12123600	-0.27326800
C	6.91394000	-2.12427300	1.05623900
C	5.61223100	-1.74036300	1.36630600
C	4.72786500	-1.34494600	0.35383700
C	5.15855900	-1.34846600	-0.97887000
C	6.46070200	-1.73679500	-1.28756300
H	7.59094300	-2.43342700	1.84695800
H	5.27196100	-1.75746700	2.39980200
H	4.48529200	-1.05716800	-1.77962000
H	6.78929800	-1.74160900	-2.32241200
H	8.35190500	-2.42427700	-0.51994300
C	3.34754000	-0.91565900	0.74451800
C	2.24068300	-1.01036600	-0.27693000
C	0.89099200	-0.52734600	0.25175200
H	2.18470500	-2.07212500	-0.55078300
C	-1.59800200	-0.35293700	-0.17994300

C	-0.25100100	-0.82671500	-0.71696000
H	0.93580100	0.55362200	0.44251700
H	0.69019800	-1.01129600	1.21770500
H	-1.53481000	0.73681100	0.00241600
H	-1.75269100	-0.82138000	0.81051100
H	-0.06450800	-0.34074000	-1.68430700
H	-0.30784200	-1.90754000	-0.90450500
O	-2.62953100	-0.66508000	-1.07308700
H	3.04398700	-1.38074900	1.68890000
H	2.50876400	-0.46636900	-1.19134500
O	3.39147900	0.55737300	1.19907400
H	3.94786400	0.63607200	2.01003800
I	3.90043900	2.06885000	-0.11871500
Zn	-4.43588200	-0.40780300	-0.49947000
I	-6.92330000	0.06092300	0.34806600

Int4-TS

Lowest three frequencies(cm^{-1}): -318.9965, 32.3000, 36.4336

C	0.23319400	-2.94691700	1.78198700
C	0.70741000	-2.00718500	2.70347400
C	1.00389400	-0.71582200	2.28432100
C	0.82846200	-0.35065900	0.94167200
C	0.36178200	-1.29708900	0.02166000
C	0.05796200	-2.59143000	0.44593000
H	0.84385100	-2.28437000	3.74459300
H	1.37088000	0.02301600	2.99279500
H	0.23377400	-1.03562400	-1.02560100
H	-0.31543800	-3.31791100	-0.26937200
H	-0.00208900	-3.95576600	2.10895500
C	1.19730900	1.02195300	0.52814600
C	0.83631700	1.56513000	-0.83580000
C	0.72666500	3.09374800	-0.87799500
H	-0.11573400	1.12419700	-1.15266700
H	1.57920700	1.21185700	-1.56287200
C	-0.77482300	3.19761800	1.18589400
C	-0.57152600	3.62333200	-0.26485400
H	0.78586300	3.41357400	-1.92355500
H	1.58994100	3.54237600	-0.36542200
H	-1.69086100	3.66273000	1.58279600
H	0.05905700	3.59153600	1.79437300
H	-0.58526700	4.71877200	-0.32738800
H	-1.42207800	3.25734900	-0.86055800
O	-0.80353900	1.79840900	1.32990300
H	1.33306000	1.72555000	1.34133800
I	3.89673800	-0.53655800	-0.75656300
O	2.95408600	0.82521100	0.42368100
H	3.35941100	1.71028100	0.28321400
Zn	-2.27754000	0.73299200	0.69106900

I	-3.58620300	-0.89593900	-0.91528500

2a

Lowest three frequencies(cm^{-1}): 29.2076, 86.6713, 140.5268

C	3.66833100	-0.01240100	-0.17954300
C	2.97690100	-1.19362200	0.10032300
C	1.59723800	-1.16762800	0.28538100
C	0.88169900	0.03369900	0.19347400
C	1.58121100	1.20974400	-0.08820000
C	2.96670000	1.18709200	-0.27151200
H	3.51426300	-2.13548700	0.17468300
H	1.06035800	-2.08837100	0.49879100
H	1.05545800	2.15651900	-0.17035200
H	3.49407700	2.11182400	-0.49055500
H	4.74509300	-0.02947800	-0.32479600
C	-0.61818900	0.00315100	0.42325700
C	-1.35979400	1.29828000	0.09925000
C	-2.86438000	1.11204700	0.31411700
H	-1.15863700	1.56984700	-0.94600700
H	-0.98461200	2.10867000	0.73449000
C	-2.51085600	-1.32222100	-0.09786300
C	-3.36362700	-0.11266700	-0.45284300
H	-3.40602900	2.01282100	0.00556400
H	-3.06010500	0.97055500	1.38672900
H	-2.77744500	-2.19651600	-0.69787900
H	-2.64096700	-1.58010800	0.96680300
H	-4.41351400	-0.32450500	-0.21873200
H	-3.29256200	0.06695300	-1.53365300
O	-1.13354000	-1.07732700	-0.35347800
H	-0.79845100	-0.23695600	1.48768200

Int5

Lowest three frequencies(cm^{-1}): 17.5921, 61.3010, 65.6140

C	-4.53160400	0.49429000	0.02365000
C	-4.19834200	-0.86652100	0.04694100
C	-2.87046500	-1.26312200	0.03033000
C	-1.81712300	-0.31004900	-0.00936900
C	-2.17741700	1.06377400	-0.03322800
C	-3.51146700	1.45055000	-0.01758200
H	-4.98417700	-1.61706000	0.07912300
H	-2.61724200	-2.32112800	0.04856700
H	-1.39889400	1.82181900	-0.06529300
H	-3.76250800	2.50810300	-0.03658400
H	-5.57271400	0.80369200	0.03659000
C	-0.46321400	-0.73899100	-0.01836600

C	0.71372500	0.18199000	-0.03283900
H	-0.27486500	-1.81113800	-0.00343600
C	2.04803500	-0.56491000	-0.04265700
H	0.67786000	0.85070200	0.84303800
H	0.66325900	0.84916000	-0.90856200
C	4.56827400	-0.38501000	-0.04147700
C	3.25064300	0.37500700	-0.00122500
H	2.10186000	-1.19327600	-0.94243800
H	2.08533300	-1.24540700	0.81919500
H	4.65466500	-0.94323100	-0.97942200
H	4.61134800	-1.11109800	0.78359300
H	3.21607900	1.07190600	-0.84910900
H	3.21247100	0.97967900	0.91662600
O	5.70293100	0.47394300	-0.00181700
H	5.69781400	0.94368600	0.84758600

8

Lowest three frequencies(cm^{-1}): 45.2752, 54.0664, 62.3206

C	-4.10750100	2.07532500	-0.28014200
C	-3.27182500	1.70196200	-1.33641600
C	-2.05761700	1.07154800	-1.07992700
C	-1.65873200	0.80610300	0.23670600
C	-2.50330400	1.17662500	1.28778000
C	-3.72087400	1.80969900	1.03205600
H	-3.56875900	1.90201600	-2.36226600
H	-1.41907300	0.77316600	-1.90826200
H	-2.20371400	0.96992000	2.31287400
H	-4.36420000	2.09369100	1.86022300
H	-5.05461000	2.56792500	-0.48149500
C	-0.32753600	0.18550200	0.54372800
C	0.85773000	0.90212300	-0.09057100
C	2.22974500	0.40945700	0.36274100
H	0.74690200	1.95988900	0.19327100
H	0.78384500	0.86152700	-1.18438400
C	4.72776400	0.78160100	0.24379800
C	3.35557200	1.30433800	-0.15538300
H	2.39032800	-0.61829400	0.01274800
H	2.26124800	0.37991600	1.46119300
H	4.87547200	-0.23416800	-0.15057600
H	4.81185200	0.73014300	1.33409400
H	3.30070500	1.36746400	-1.25207500
H	3.23793500	2.32379600	0.23413900
O	5.78554600	1.63352200	-0.18166600
H	-0.19251300	0.10502300	1.62395900
I	-0.35465400	-1.94861500	-0.06934000
H	5.76636800	1.68071000	-1.15130700

8-TS

Lowest three frequencies(cm^{-1}): -338.8962, 47.1255, 51.1937

C	-3.91697000	-0.91511000	0.13407500
C	-3.25912700	-0.83102700	-1.09649300
C	-1.87807400	-0.67768500	-1.13690200
C	-1.13572500	-0.60907800	0.05033900
C	-1.79915300	-0.69758300	1.27963000
C	-3.18453600	-0.84915800	1.31932900
H	-3.82513200	-0.88278900	-2.02220300
H	-1.36094700	-0.60565000	-2.09105400
H	-1.23969600	-0.63054200	2.20888200
H	-3.69213500	-0.91168700	2.27771300
H	-4.99663800	-1.03103600	0.16710400
C	0.33192500	-0.46055000	-0.02296200
C	1.21698200	-0.73945400	1.17878700
C	2.67288700	-1.00358100	0.78338500
H	0.81230700	-1.61936500	1.69571800
H	1.15350600	0.08372600	1.89300500
C	1.97167000	-2.67615700	-0.99566400
C	2.87477600	-2.40264500	0.19598500
H	3.30789200	-0.89347800	1.66867000
H	2.99625600	-0.23758800	0.06476200
H	2.10885300	-3.69141500	-1.38353700
H	2.17981900	-1.97439200	-1.81079100
H	3.91652500	-2.53592200	-0.11979500
H	2.67686800	-3.15501100	0.97281200
O	0.58998100	-2.47002200	-0.66558300
H	0.76756500	-0.42062000	-1.00918100
I	0.50592900	2.12493900	-0.13683300
H	0.29295400	-3.18365500	-0.07231500

I_2*

Frequency(cm^{-1}): 160.7947

I	0.00000000	0.00000000	1.57747200
I	0.00000000	0.00000000	-1.57747200

IOH

Lowest three frequencies(cm^{-1}): 576.8086, 1134.4391, 3755.9189

I	0.01503300	-0.29616700	0.00000000
O	0.01503300	1.71240200	0.00000000
H	-0.91702200	1.99762400	0.00000000

AcOH

Lowest three frequencies(cm^{-1}): 90.7605, 444.3858, 559.1302

C	1.39134800	-0.12033600	-0.00018500
H	1.66751900	-0.72699800	-0.86746600
H	1.91949000	0.83233500	-0.02721400
H	1.67108400	-0.67675600	0.89949500
C	-0.08779300	0.11983000	-0.00085800
O	-0.63118300	1.20257300	0.00012200
O	-0.78635300	-1.02946800	-0.00024400
H	-1.73913300	-0.81039300	0.00242100

AcO^-

Lowest three frequencies(cm^{-1}): 53.2357, 455.8012, 630.7904

C	-1.34568400	-0.05318400	-0.00001200
H	-1.72089100	-1.07984200	-0.00002300
H	-1.73153300	0.47140000	0.88159700
H	-1.73152700	0.47142000	-0.88161200
C	0.19262500	-0.00008200	-0.00000700
O	0.70076500	1.15258100	0.00000300
O	0.81202300	-1.09550400	0.00001600

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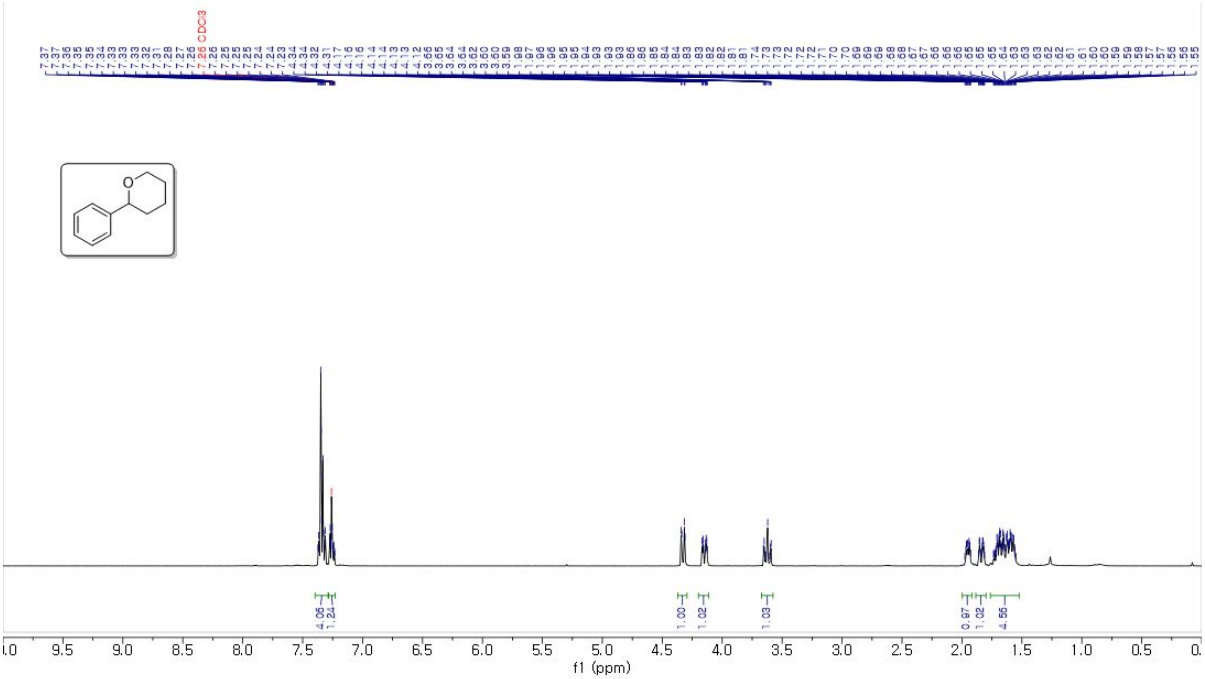
Appendix I

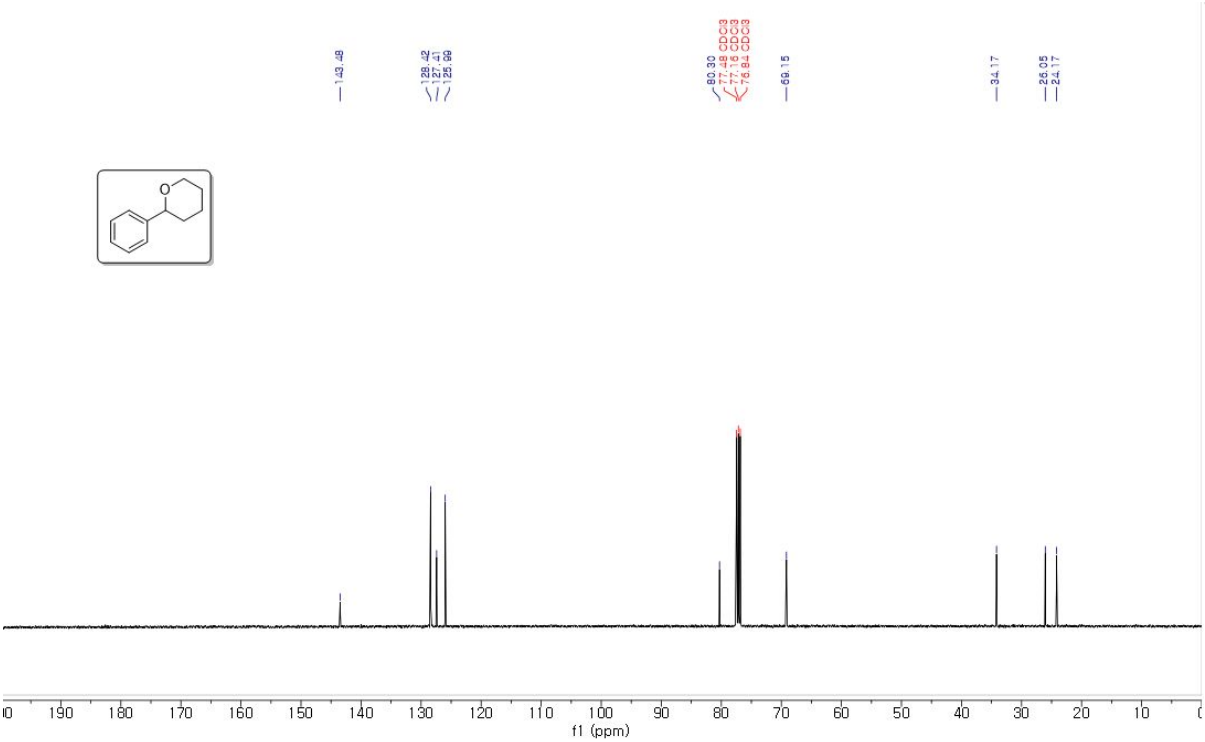
Spectral Copies of ^{1}H, ^{13}C and ^{31}P NMR Data Obtained in this Study

2-phenyltetrahydro-2H-pyran (2a)

400 MHz, ^{1}H NMR in $CDCl_3$

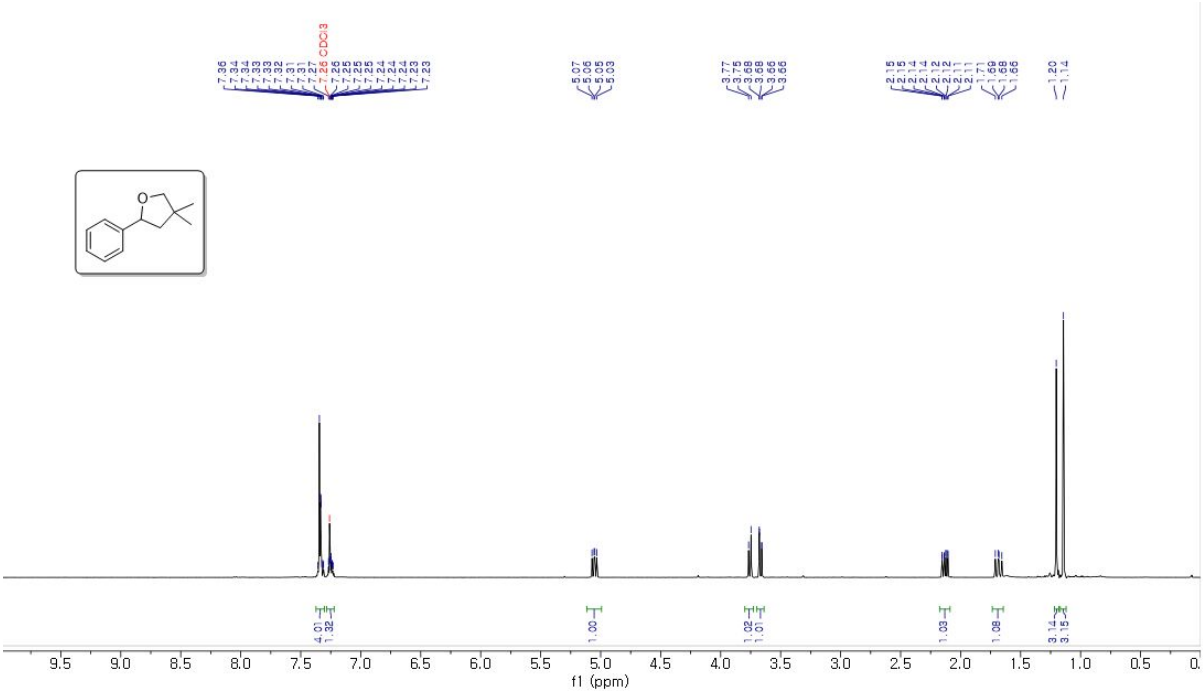


100 MHz, ^{13}C NMR in $CDCl_3$

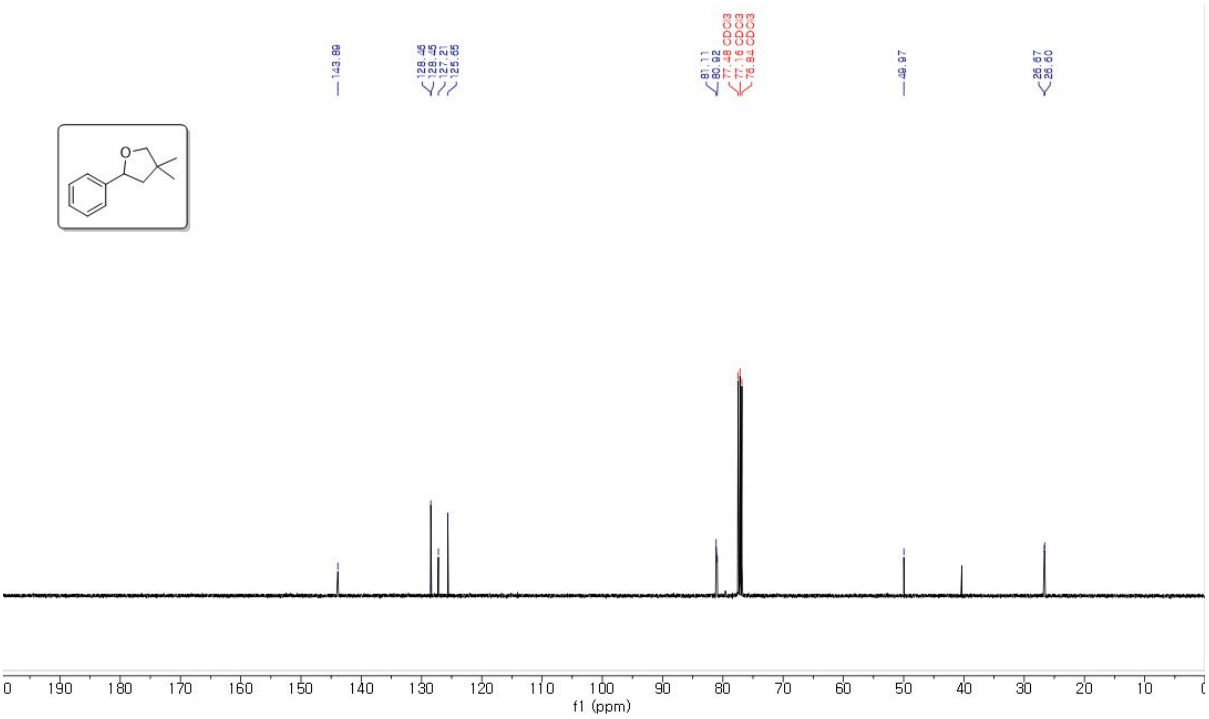


4,4-dimethyl-2-phenyltetrahydrofuran (2b)

400 MHz, ^{1}H NMR in $CDCl_3$

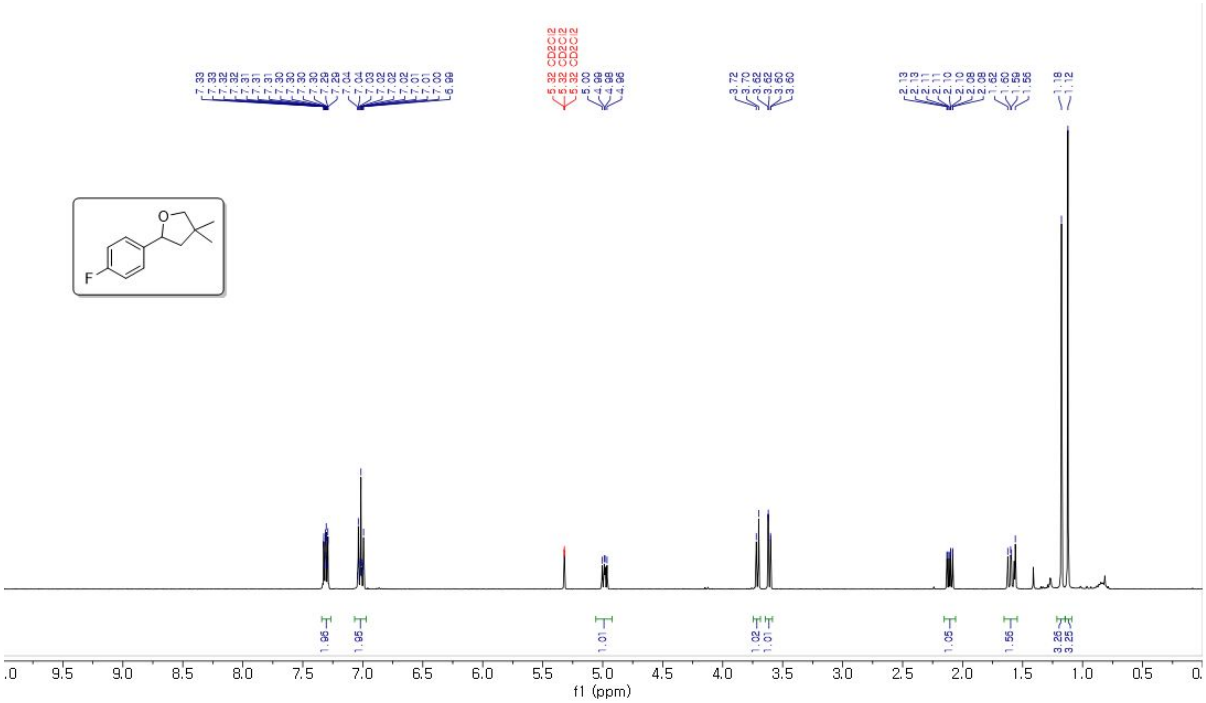


100 MHz, ^{13}C NMR in $CDCl_3$

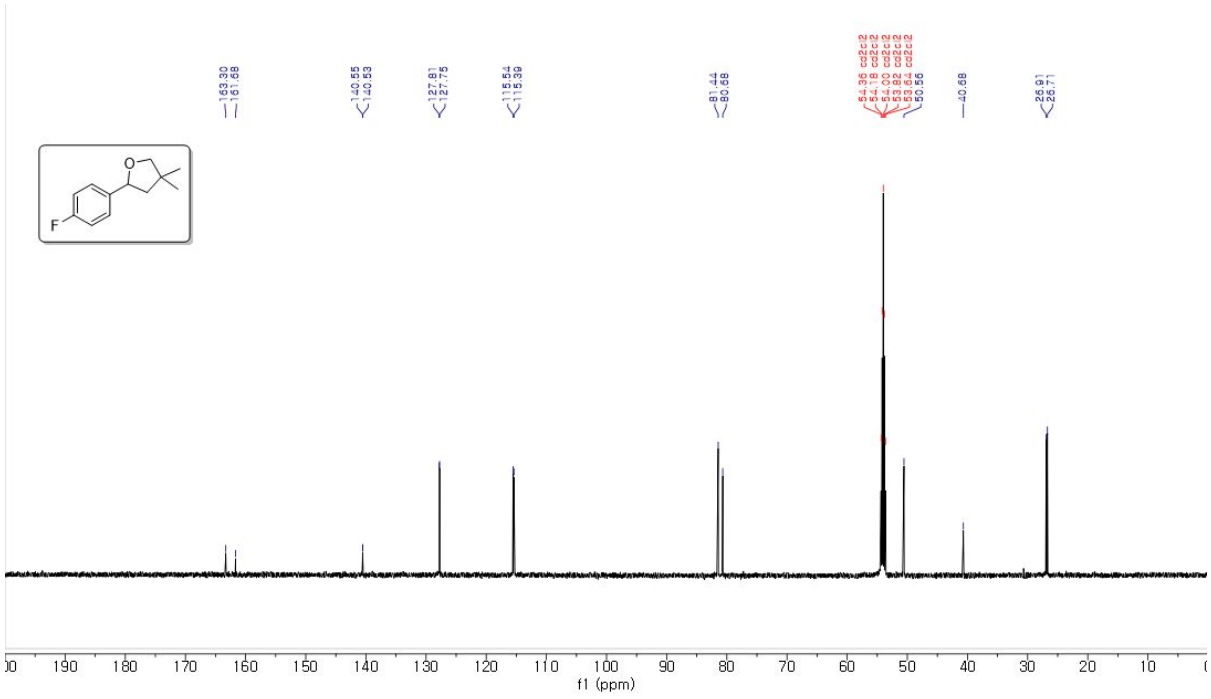


2-(4-fluorophenyl)-4,4-dimethyltetrahydrofuran (2c)

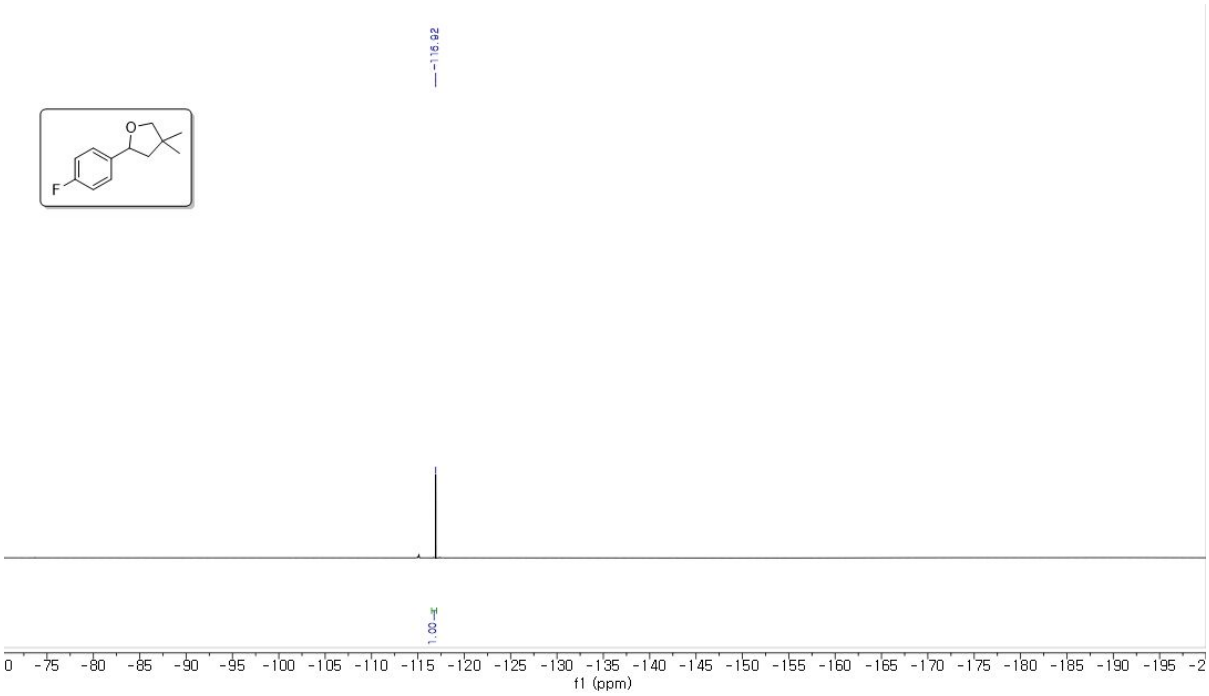
400 MHz, ^{1}H NMR in CD_2Cl_2



150 MHz, ^{13}C NMR in CD_2Cl_2

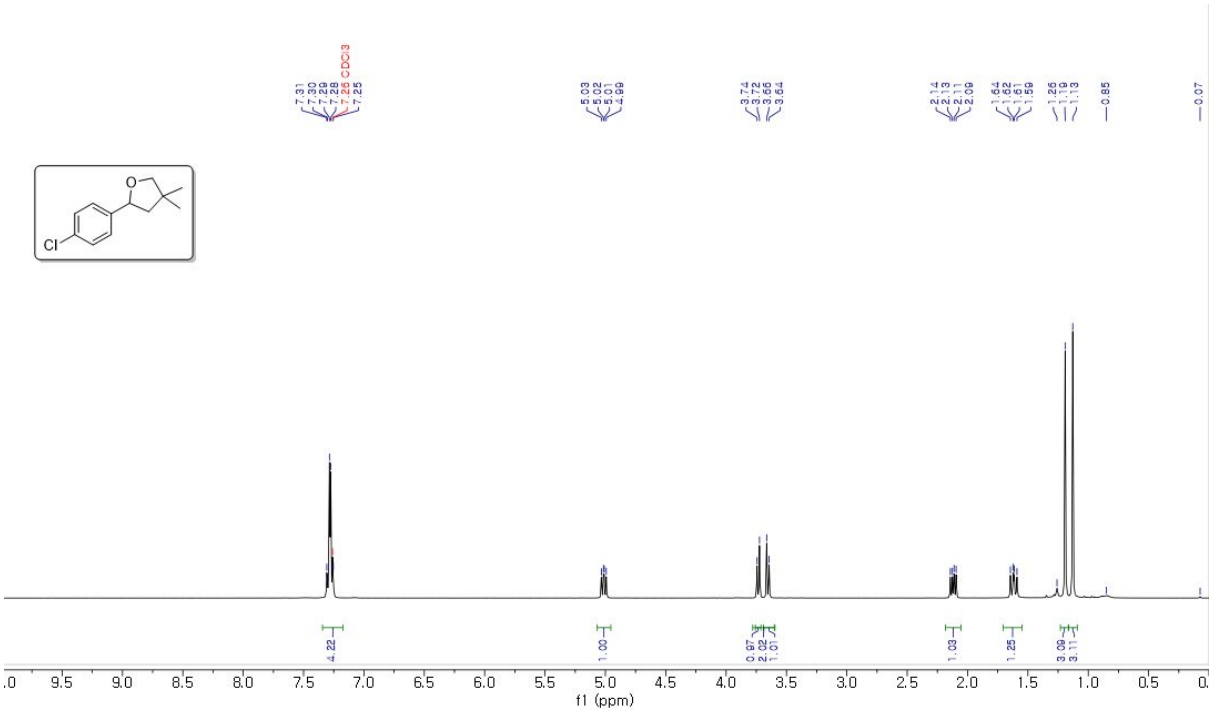


376 MHz, ^{19}F NMR in CD_2Cl_2

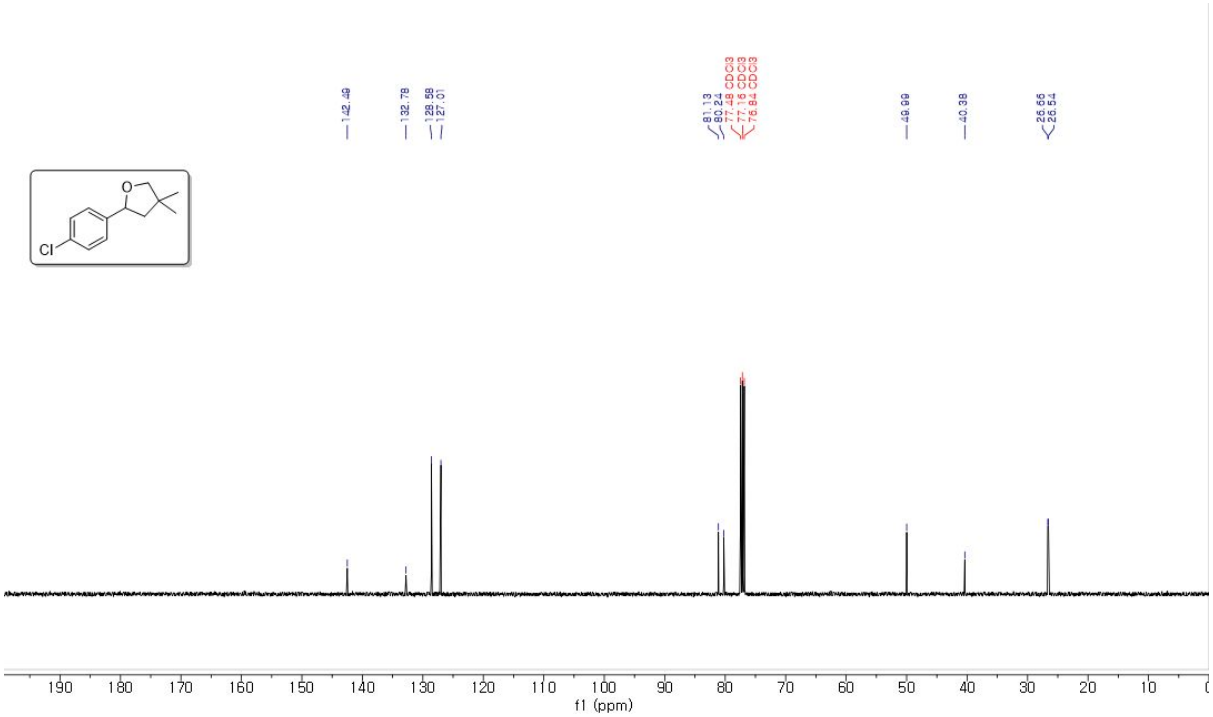


2-(4-Chlorophenyl)-4,4-dimethyltetrahydrofuran (2d)

400 MHz, ^{1}H NMR in $CDCl_3$

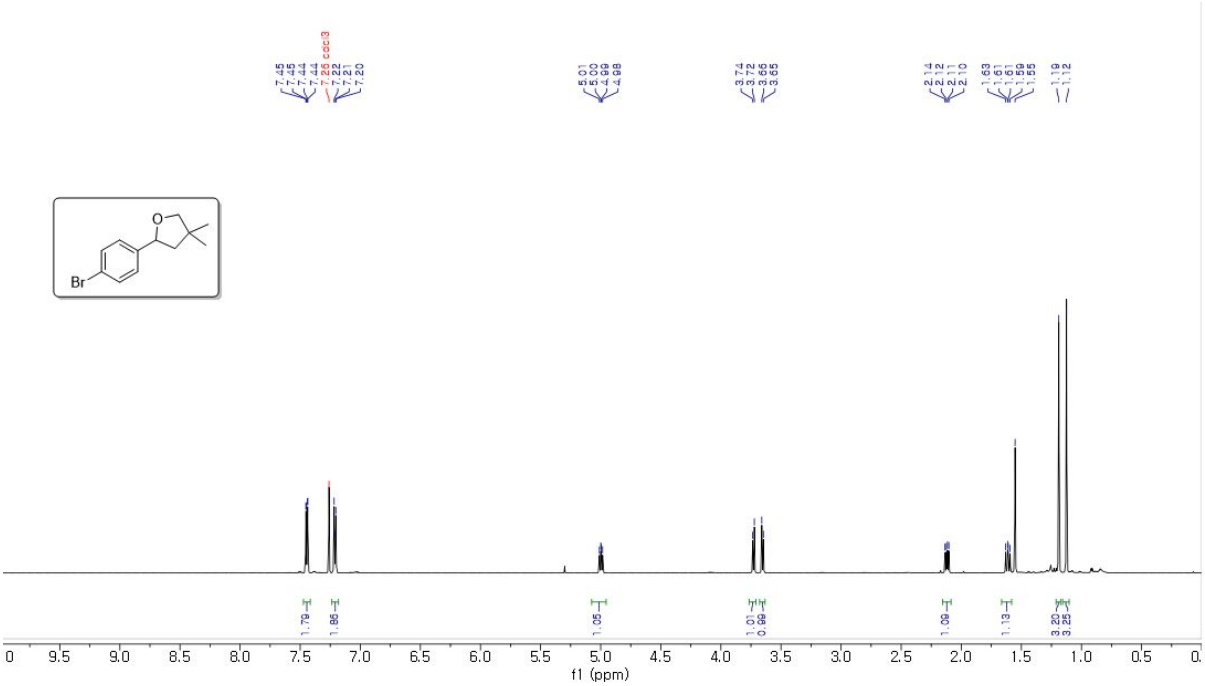


100 MHz, ^{13}C NMR in $CDCl_3$

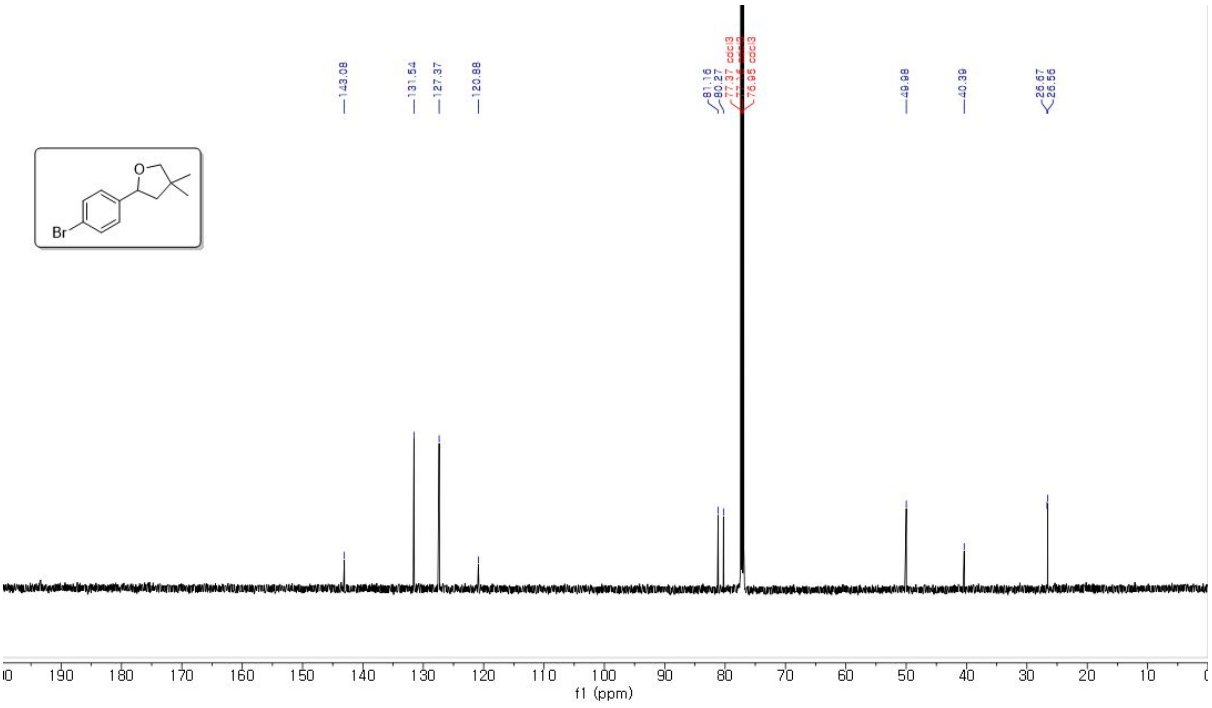


2-(4-bromophenyl)-4,4-dimethyltetrahydrofuran (2e)

600 MHz, ^{1}H NMR in $CDCl_3$

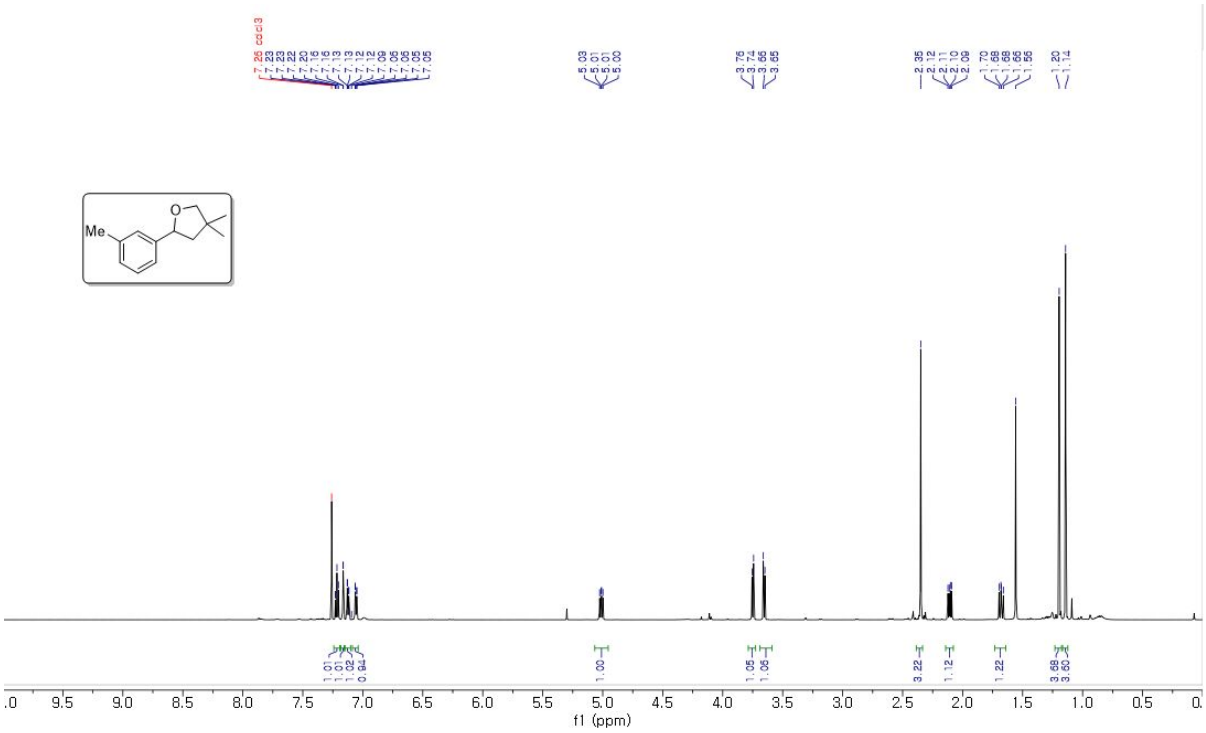


150 MHz, ^{13}C NMR in $CDCl_3$

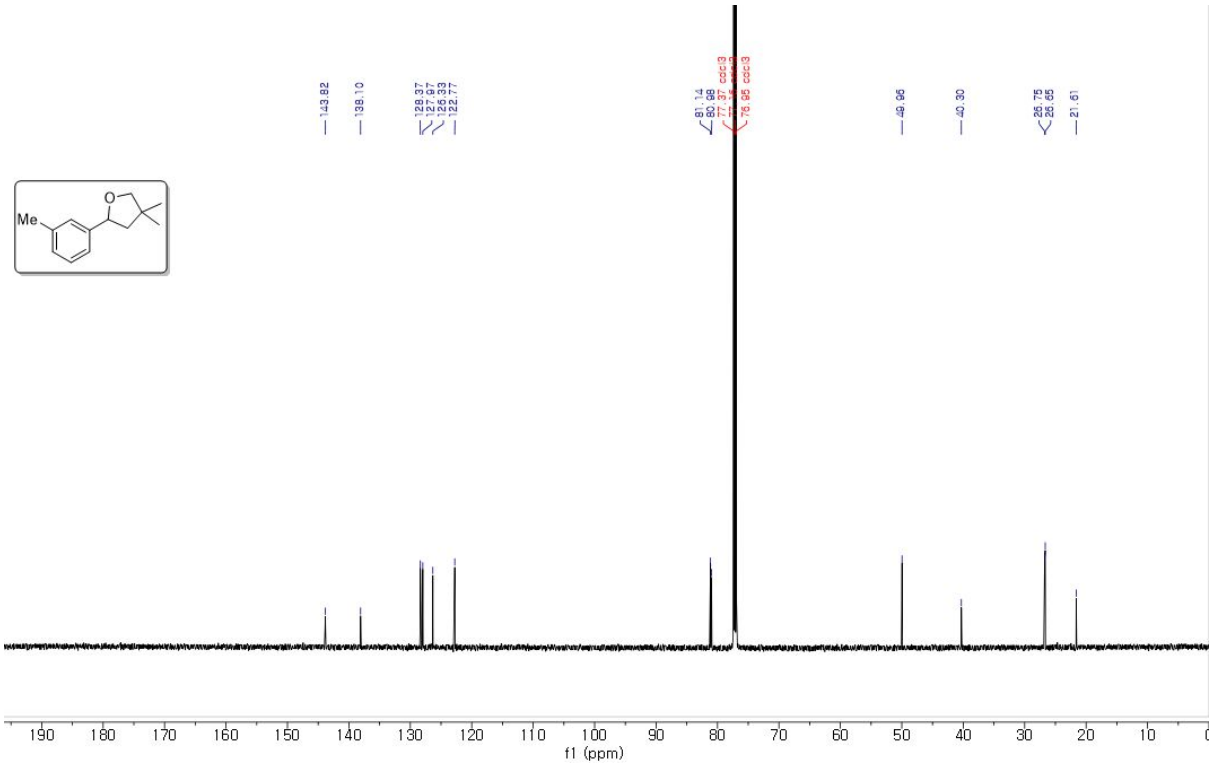


4,4-dimethyl-2-(m-tolyl)tetrahydrofuran (2f)

600 MHz, ^{1}H NMR in $CDCl_3$

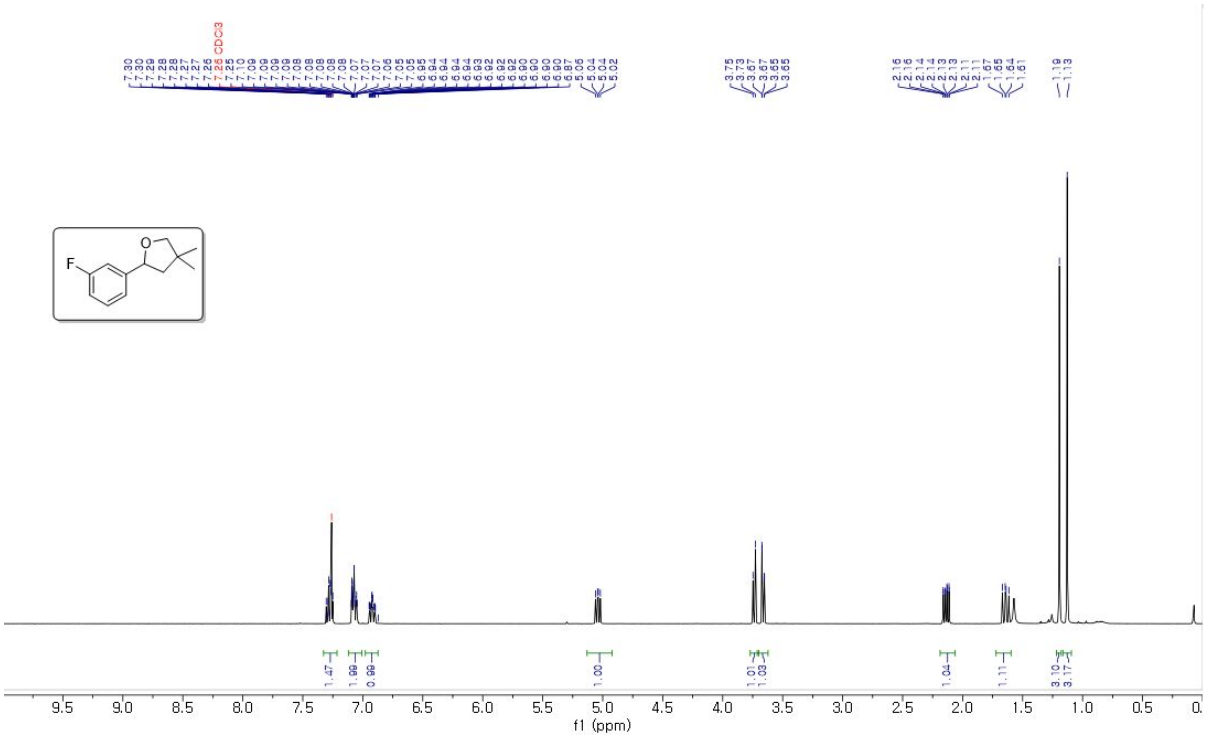


150 MHz, ^{13}C NMR in $CDCl_3$

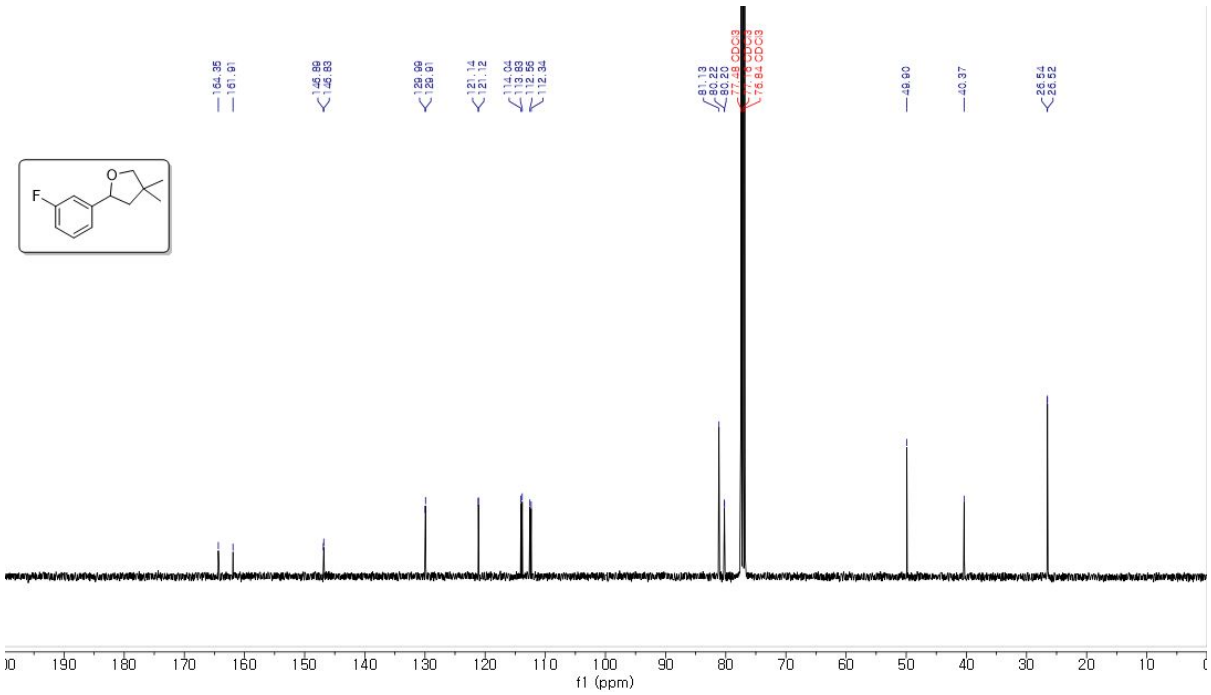


2-(3-fluorophenyl)-4,4-dimethyltetrahydrofuran (2g)

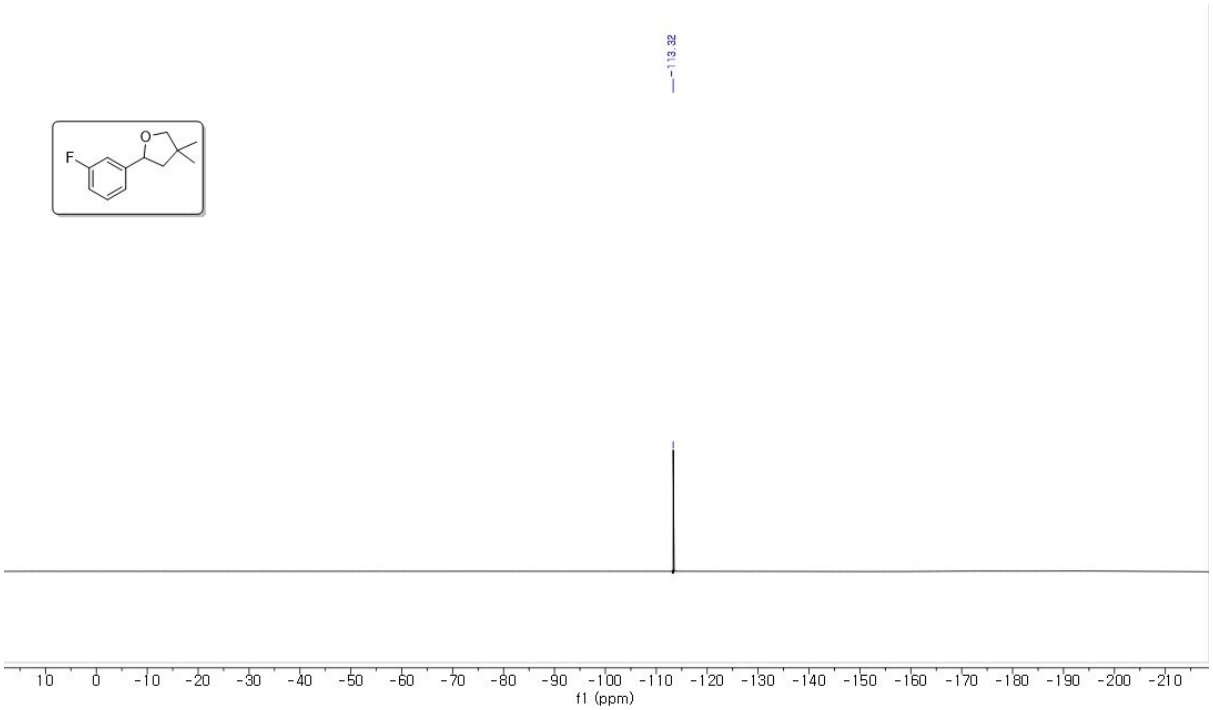
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

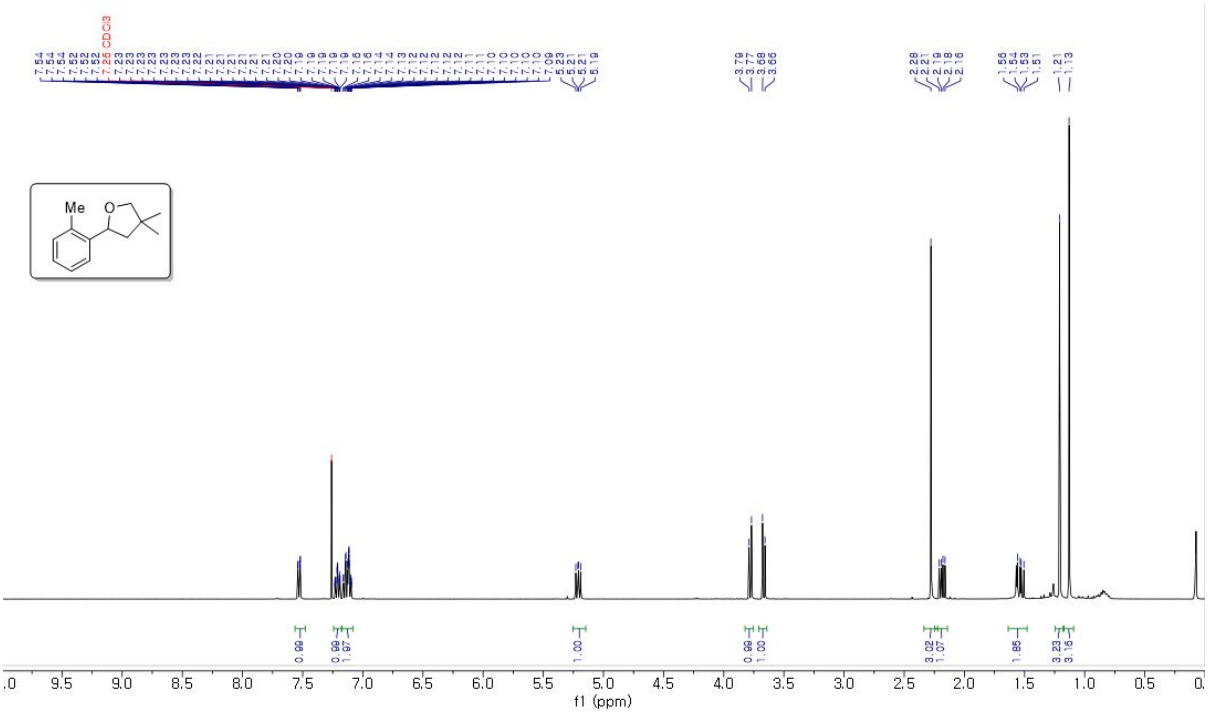


376 MHz, ^{19}F NMR in $CDCl_3$

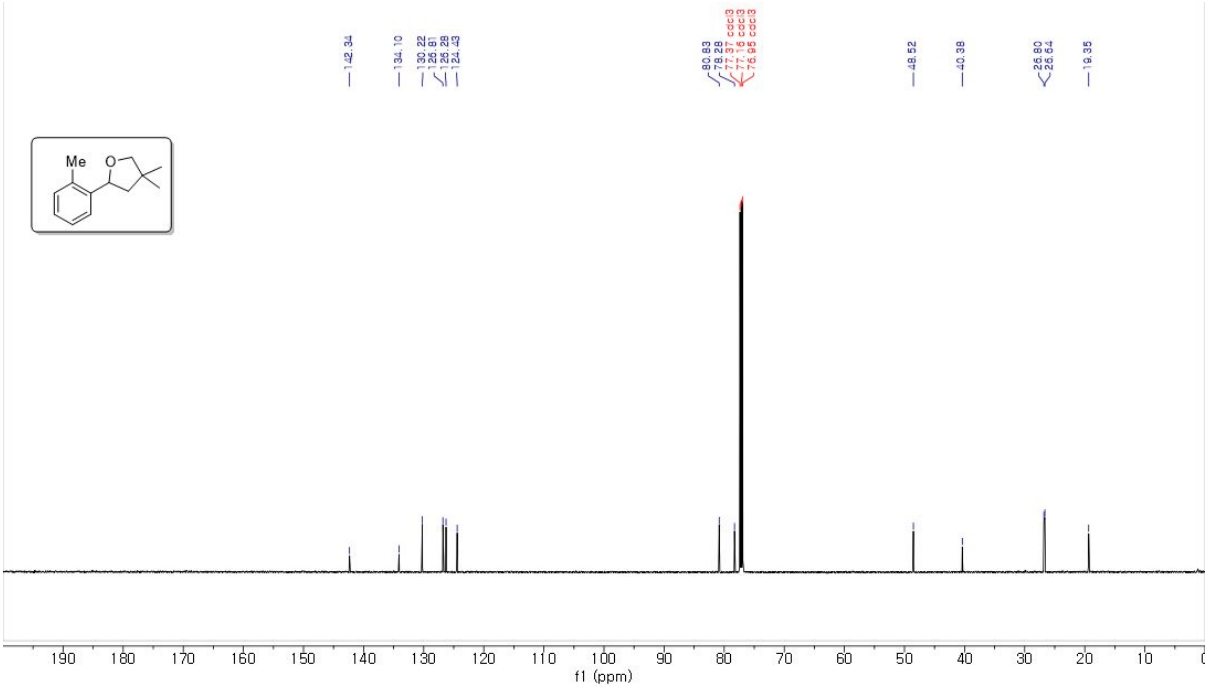


4,4-dimethyl-2-(o-tolyl)tetrahydrofuran (2h)

400 MHz, ^{1}H NMR in $CDCl_3$

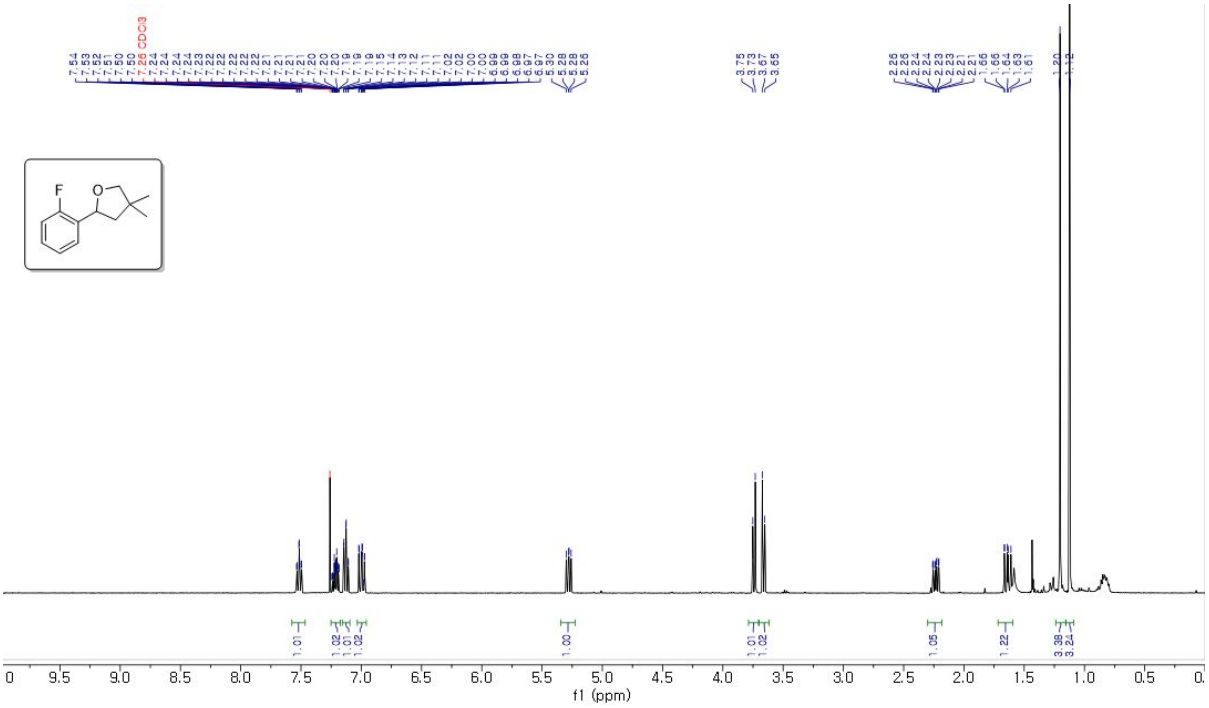


150 MHz, ^{13}C NMR in $CDCl_3$

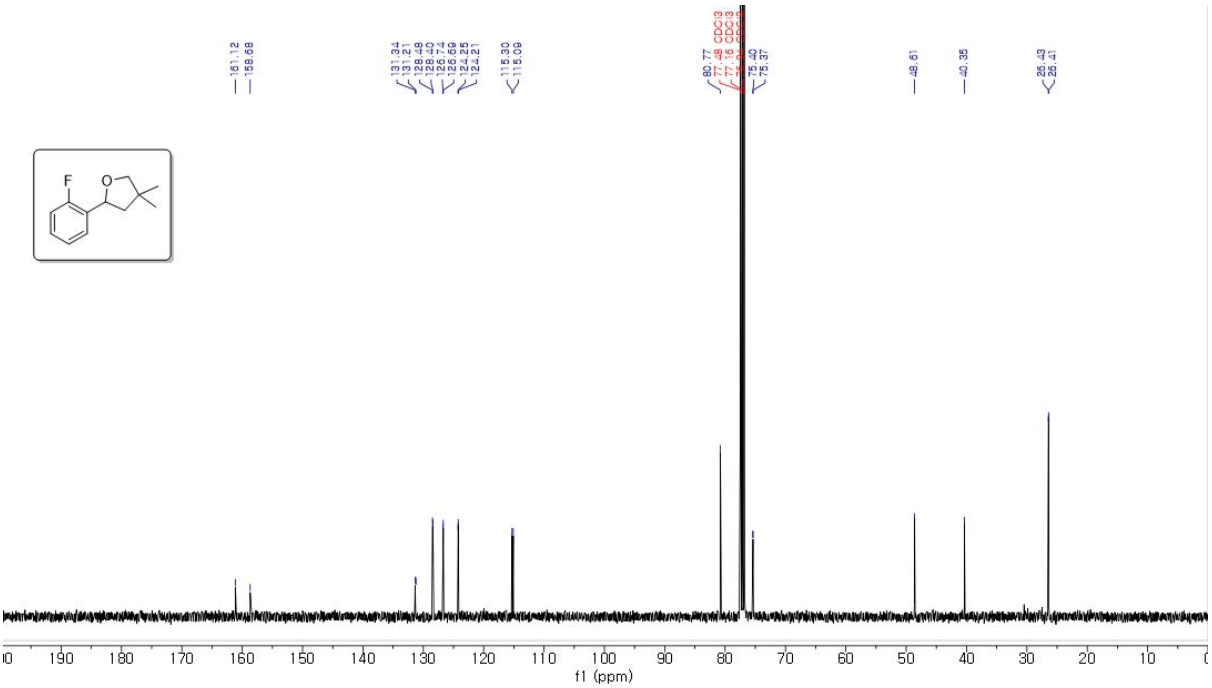


2-(2-fluorophenyl)-4,4-dimethyltetrahydrofuran (2i)

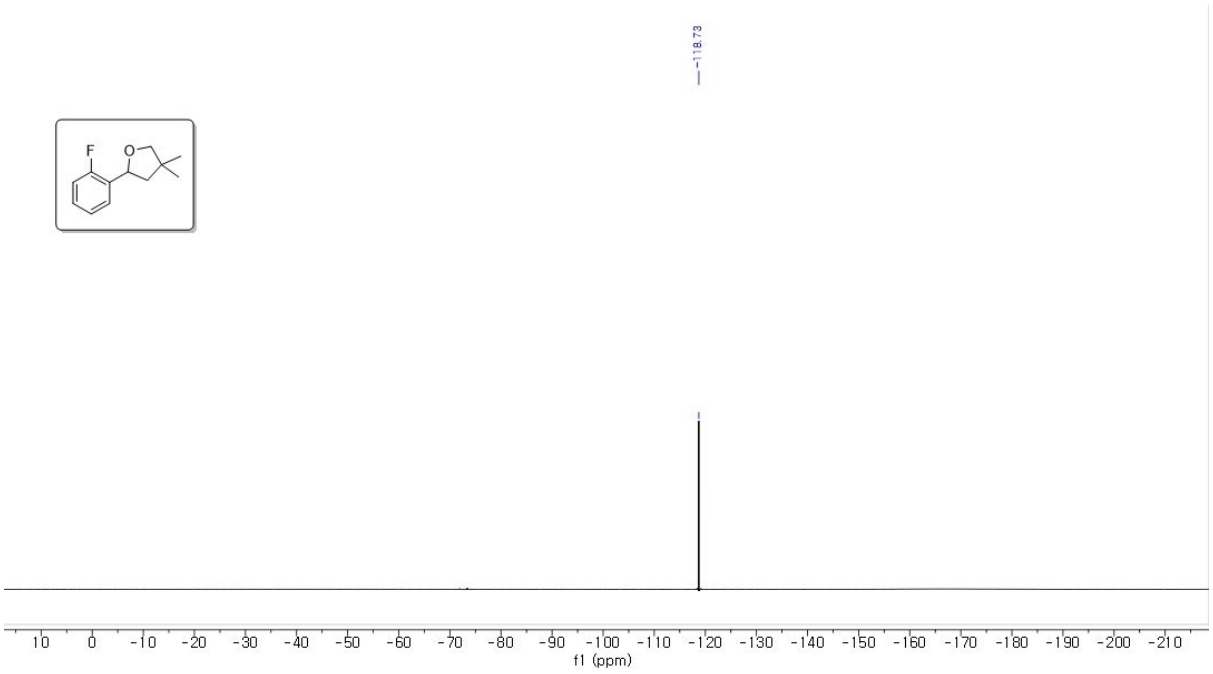
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

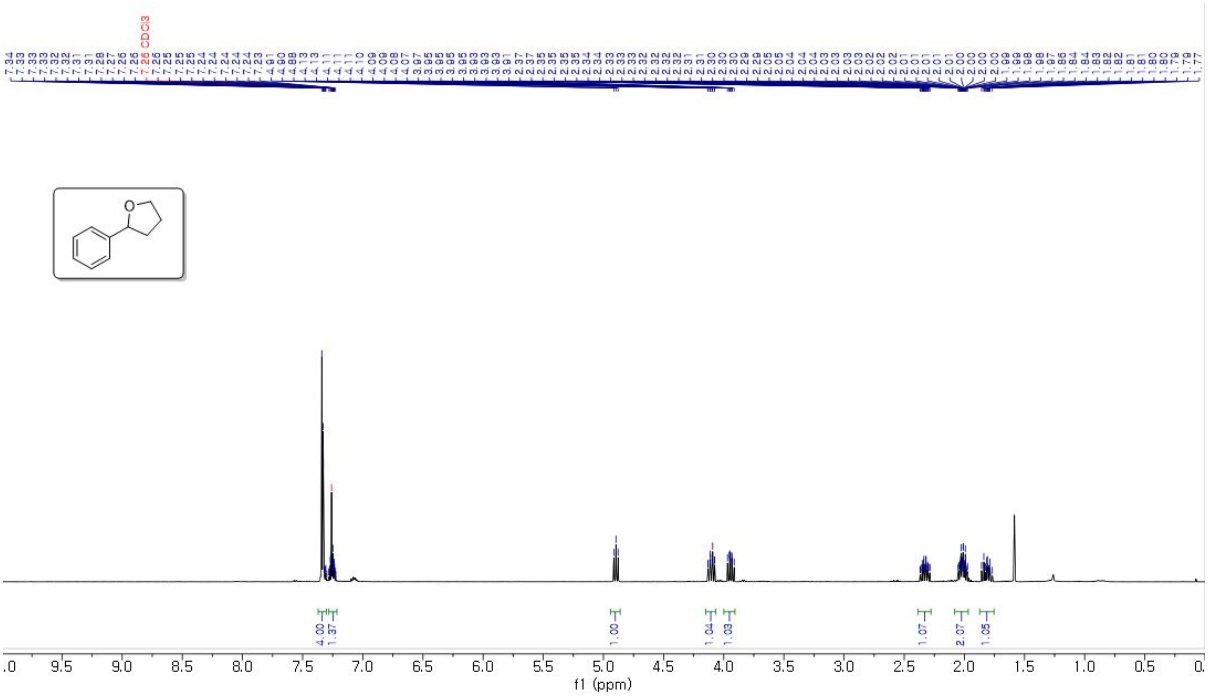


376 MHz, ^{19}F NMR in $CDCl_3$

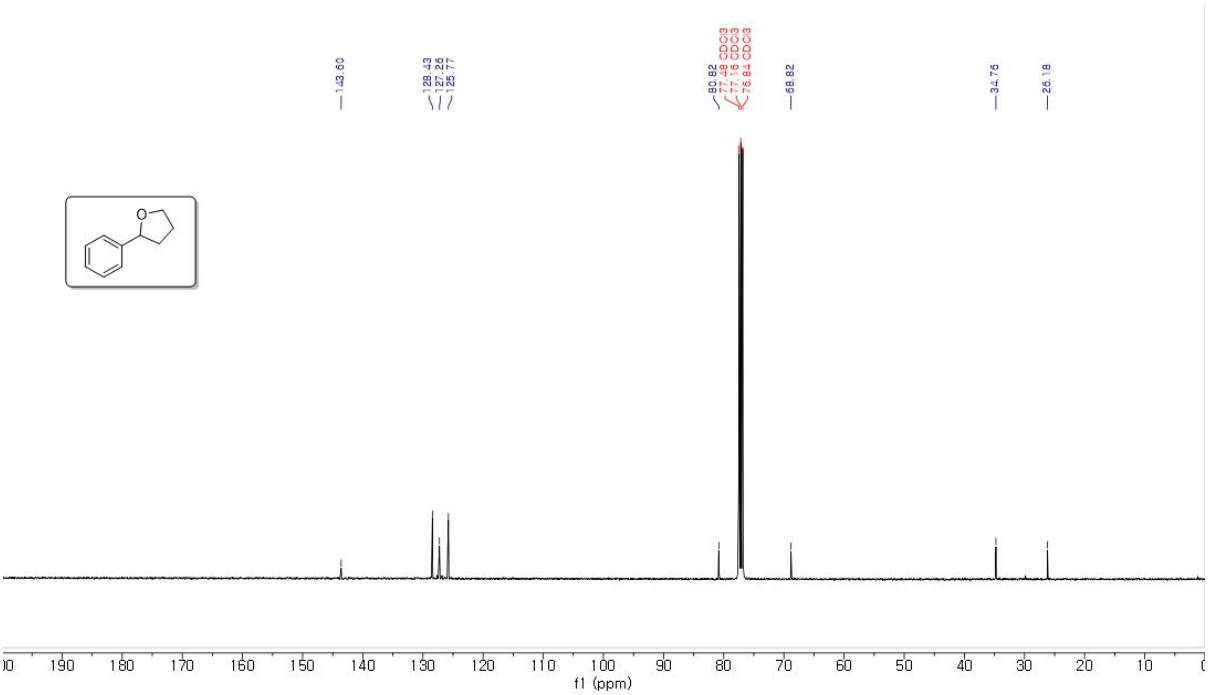


2-phenyltetrahydrofuran (2j)

400 MHz, ^{1}H NMR in $CDCl_3$

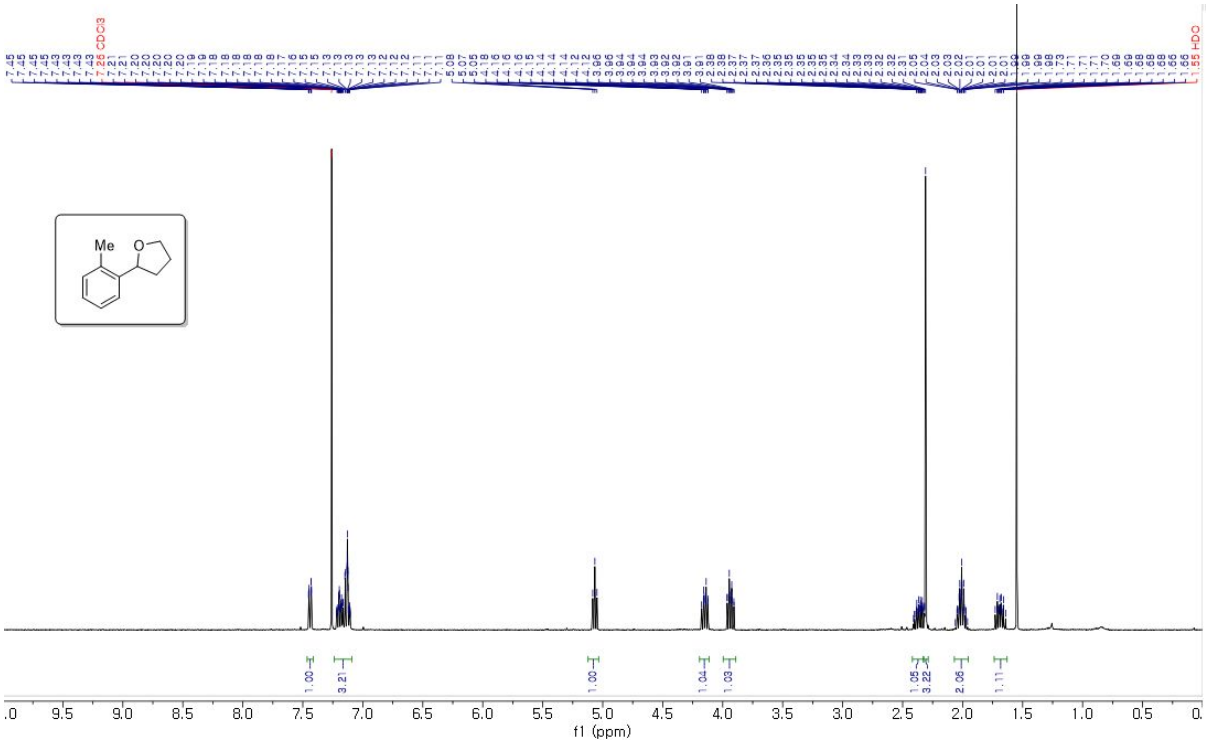


100 MHz, ^{13}C NMR in $CDCl_3$

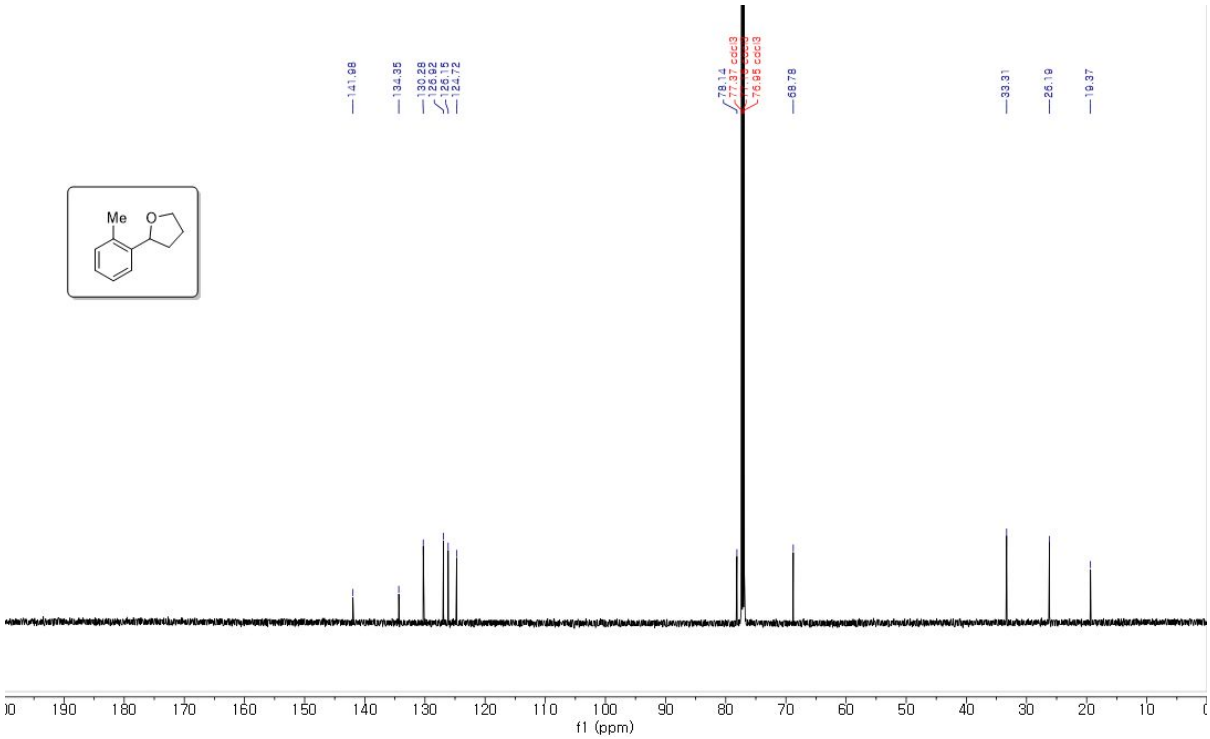


2-(o-tolyl)tetrahydrofuran (2k)

400 MHz, ^{1}H NMR in $CDCl_3$

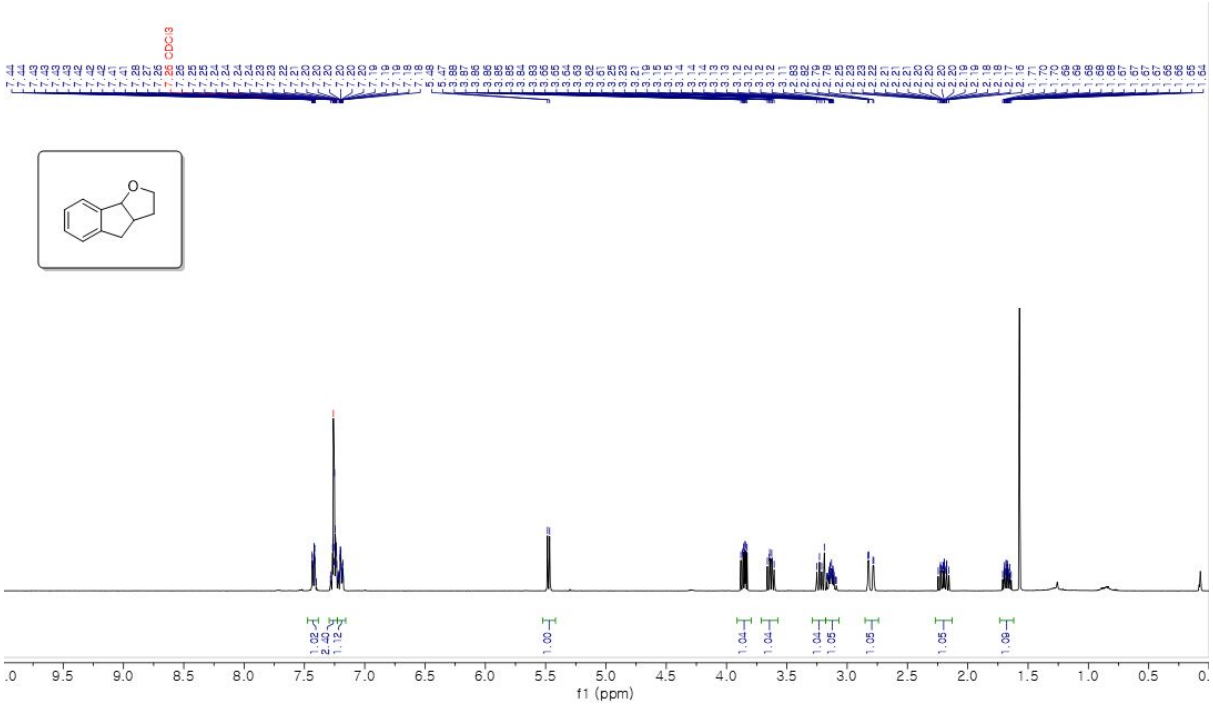


150 MHz, ^{13}C NMR in $CDCl_3$

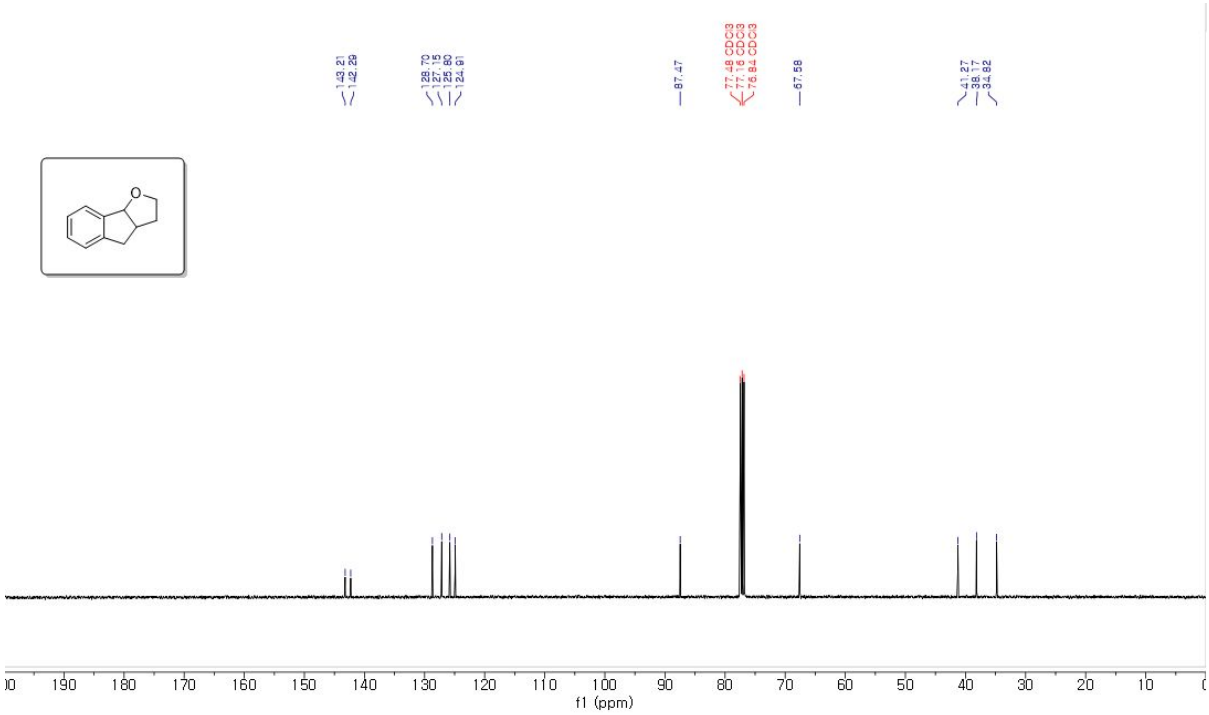


3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan (2l)

400 MHz, ^{1}H NMR in $CDCl_3$

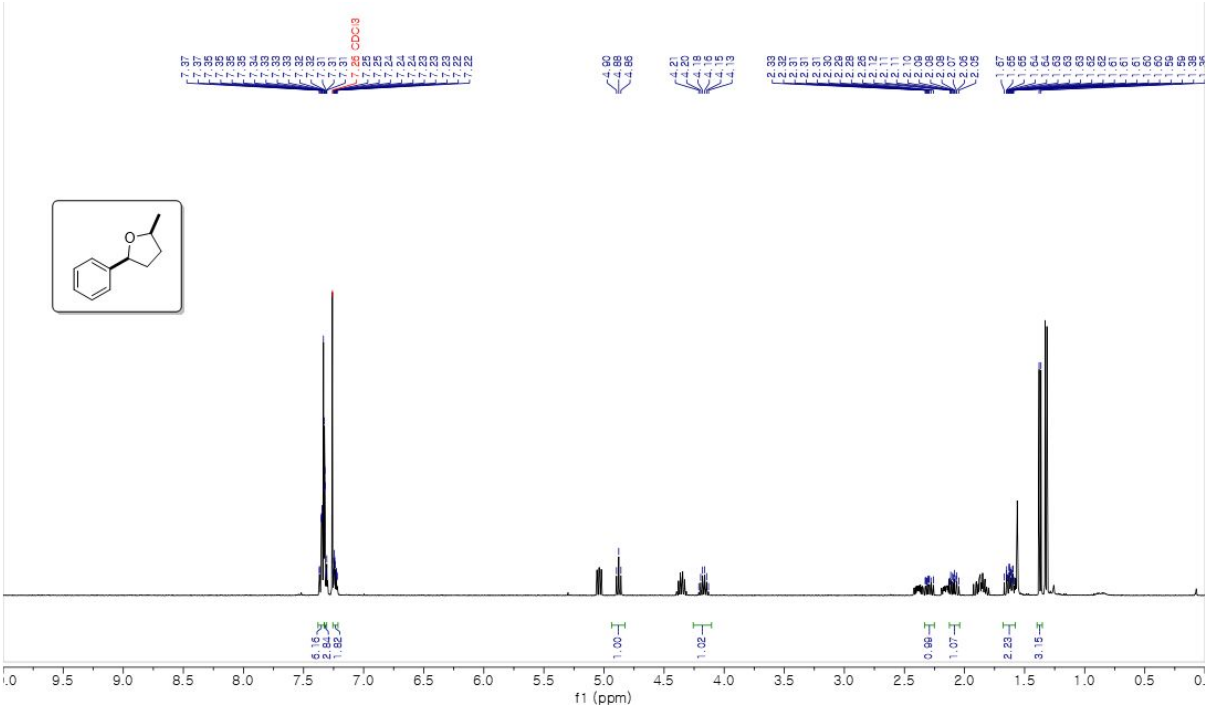


100 MHz, ^{13}C NMR in $CDCl_3$

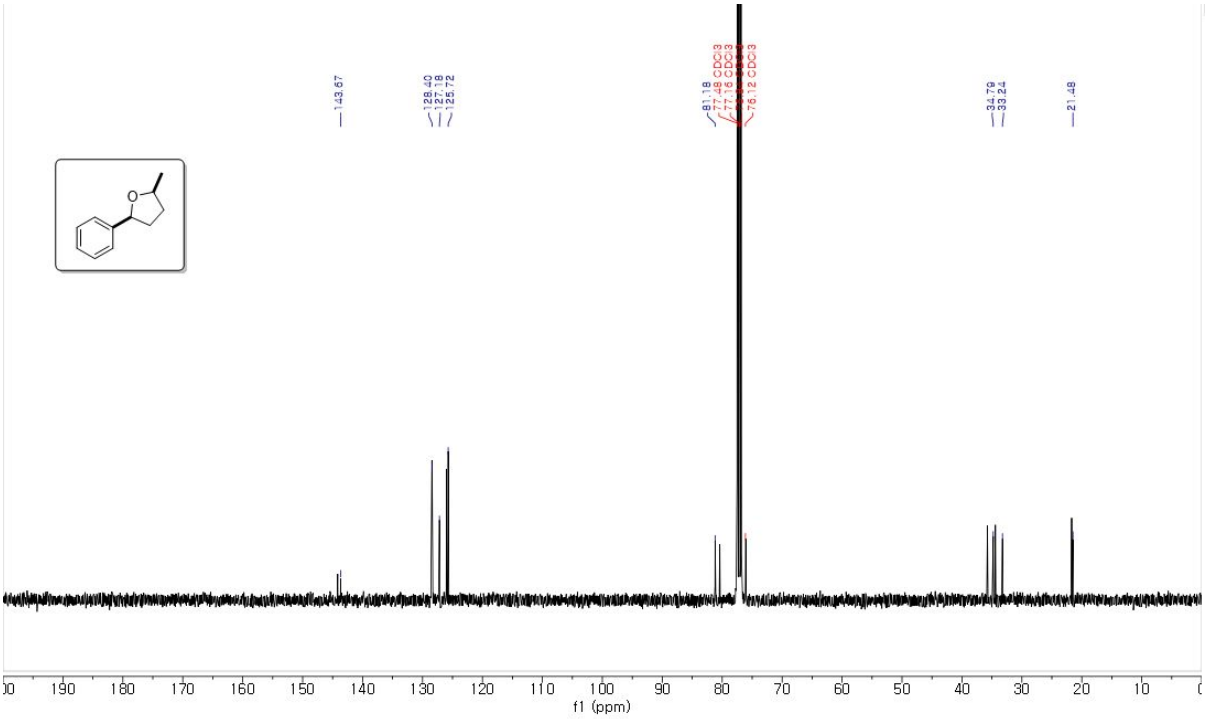


2-methyl-5-phenyltetrahydrofuran (2m – cis diastereomer) (d.r. 1: 1.17)

400 MHz, ^{1}H NMR in $CDCl_3$

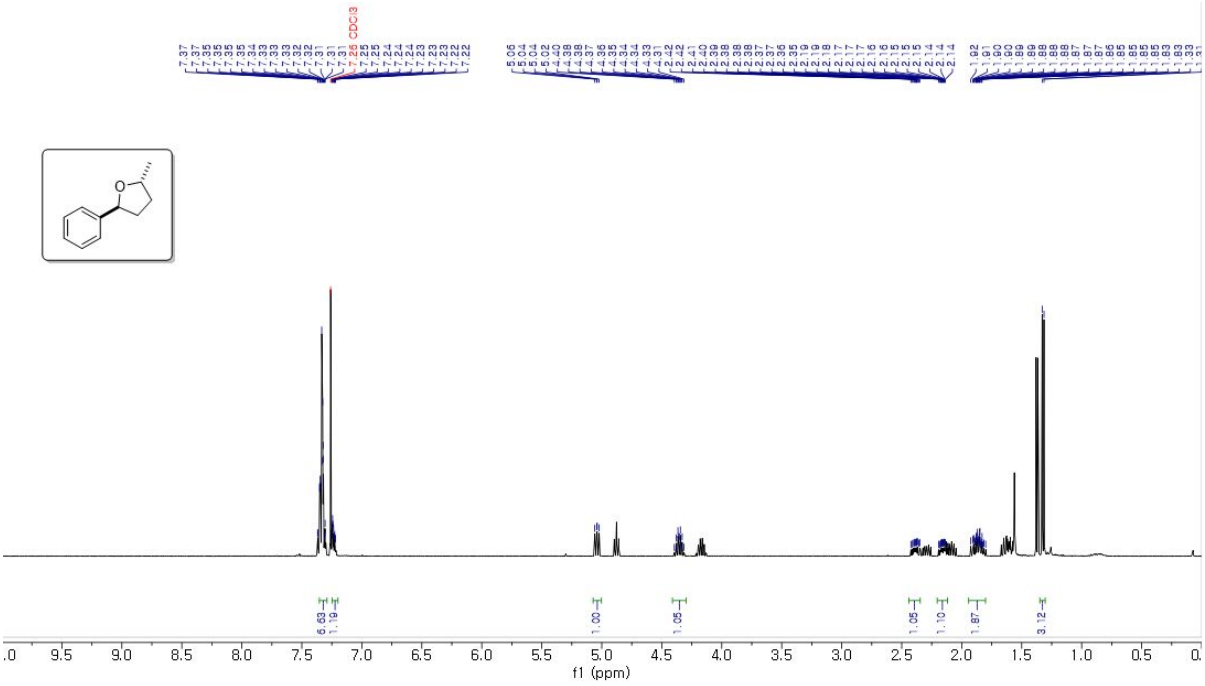


100 MHz, ^{13}C NMR in $CDCl_3$

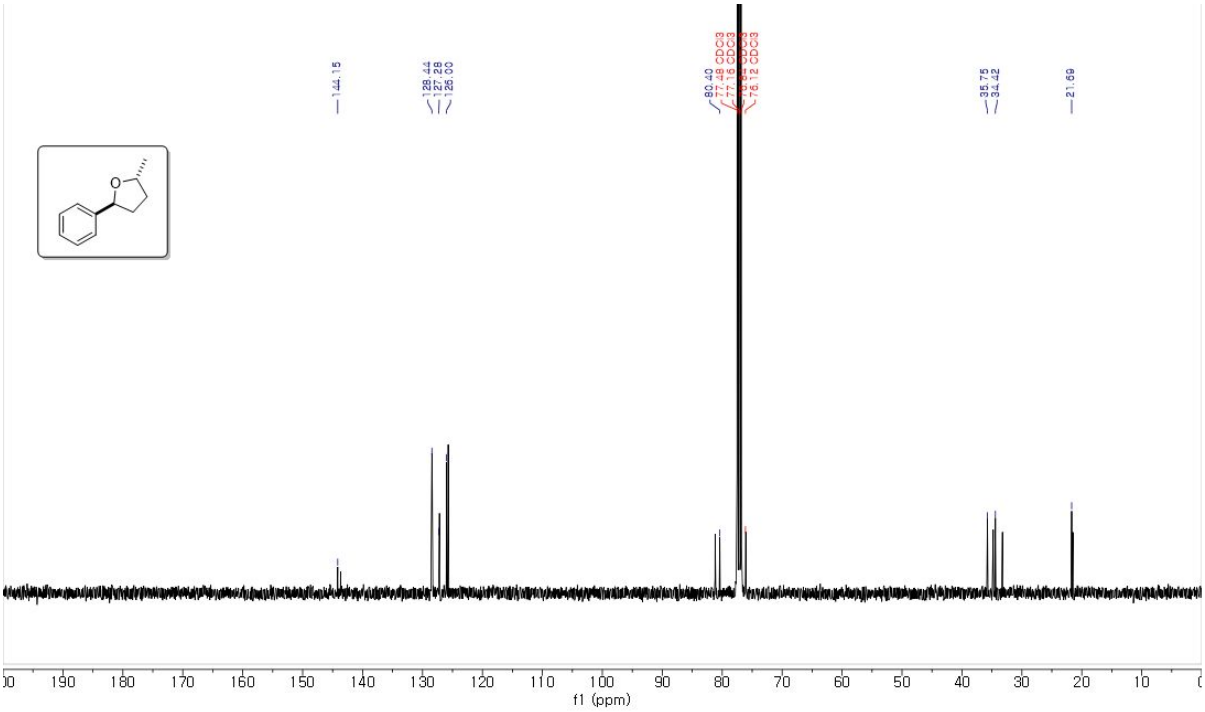


2-methyl-5-phenyltetrahydrofuran (2m- trans diastereomer)

400 MHz, ^{1}H NMR in $CDCl_3$

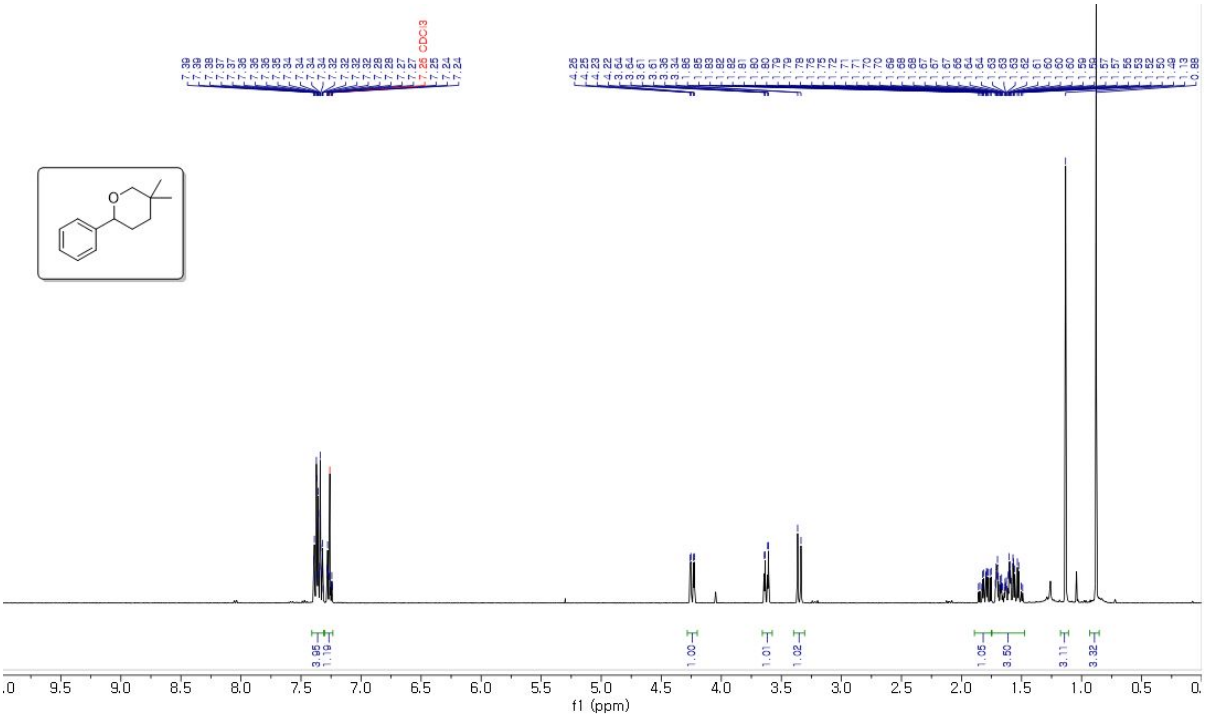


100 MHz, ^{13}C NMR in $CDCl_3$

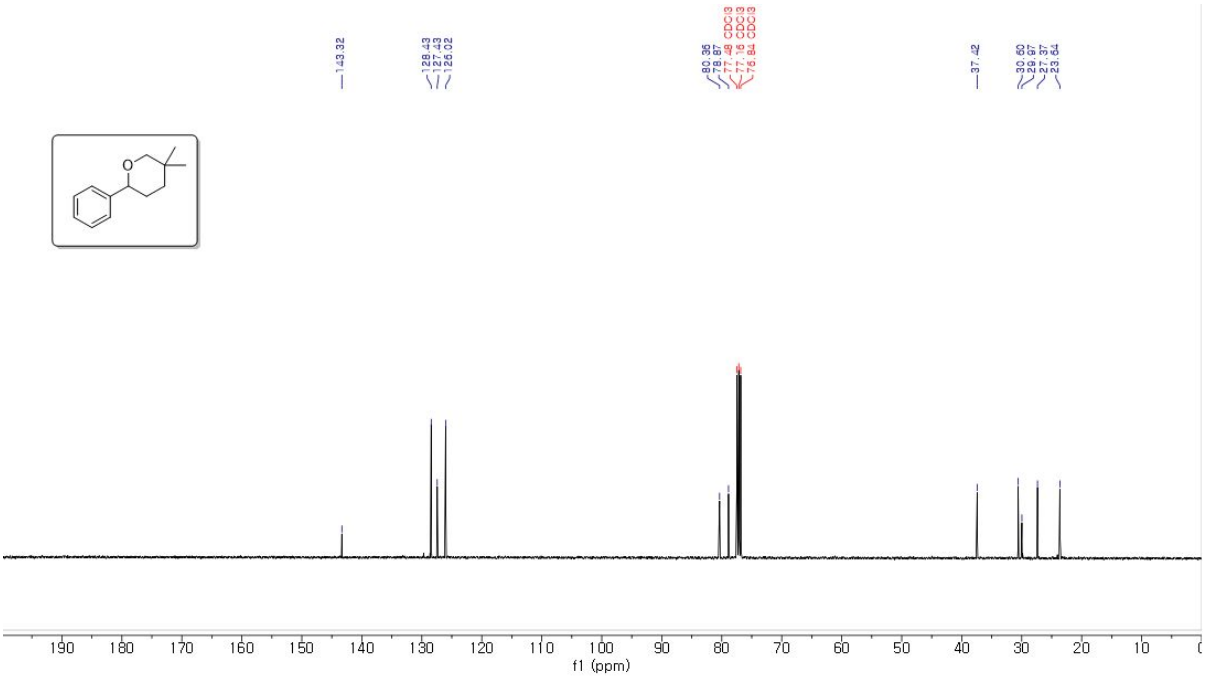


5,5-dimethyl-2-phenyltetrahydro-2H-pyran (2n)

400 MHz, ^{1}H NMR in $CDCl_3$

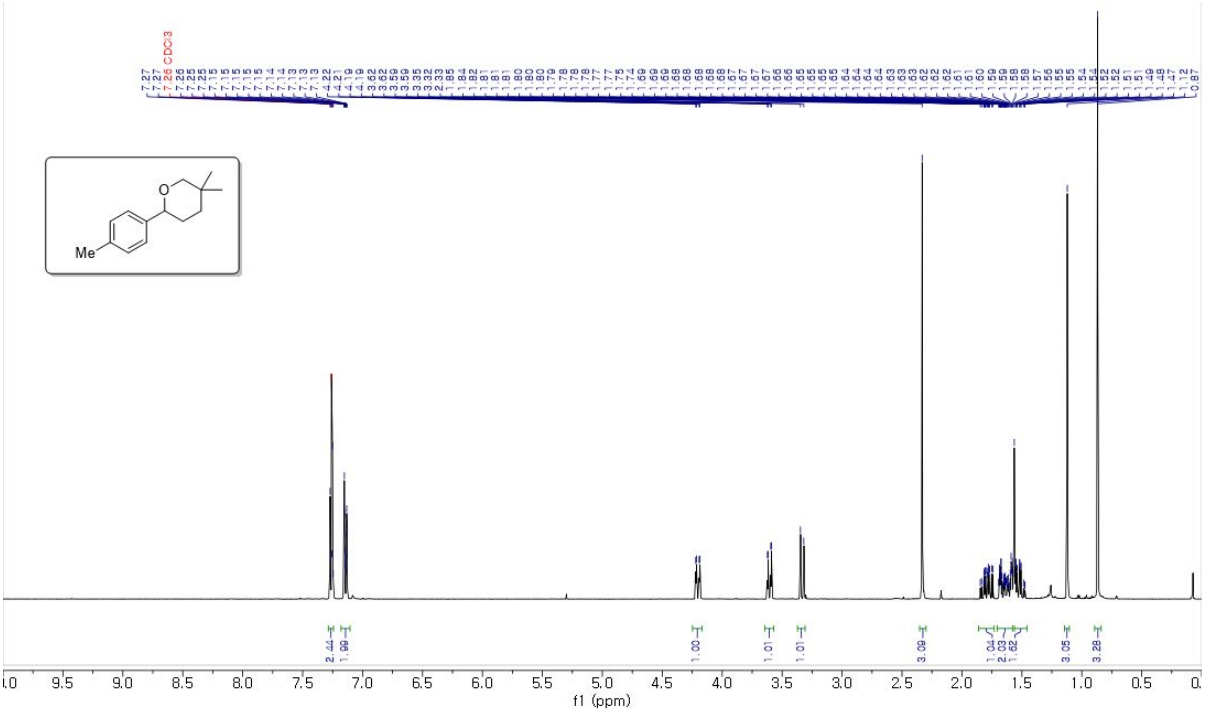


100 MHz, ^{13}C NMR in $CDCl_3$

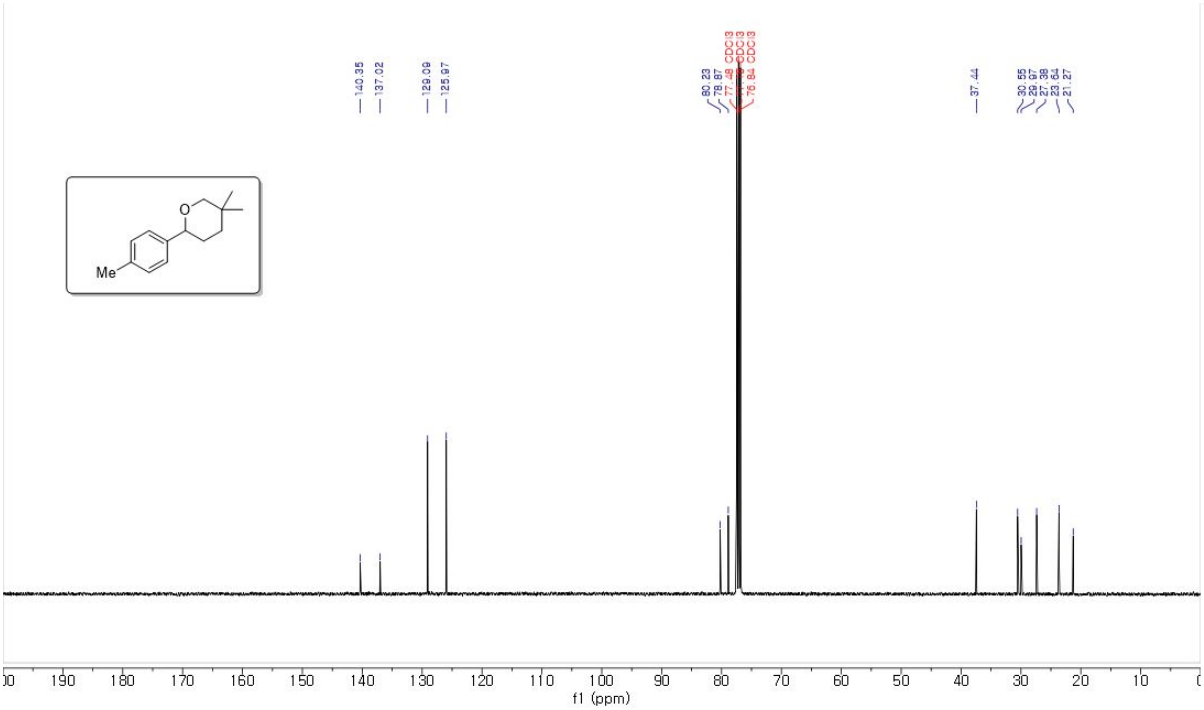


5,5-dimethyl-2-(p-tolyl)tetrahydro-2H-pyran (2o)

400 MHz, ^{1}H NMR in $CDCl_3$

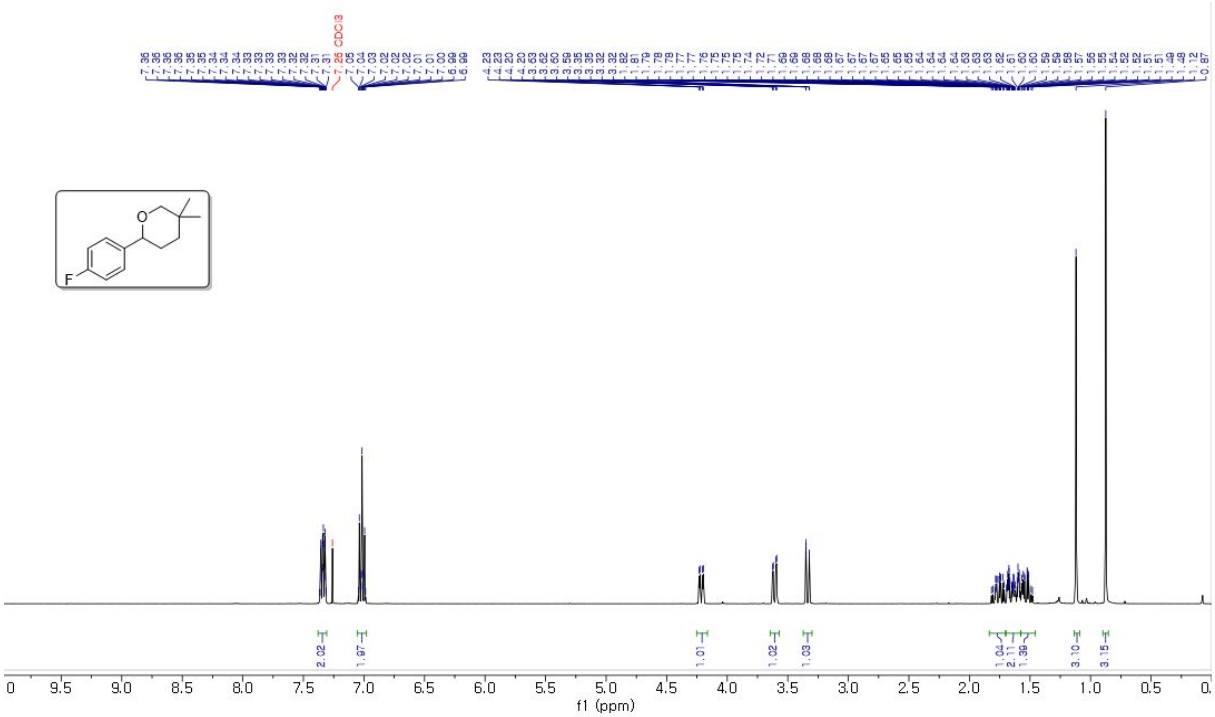


100 MHz, ^{13}C NMR in $CDCl_3$

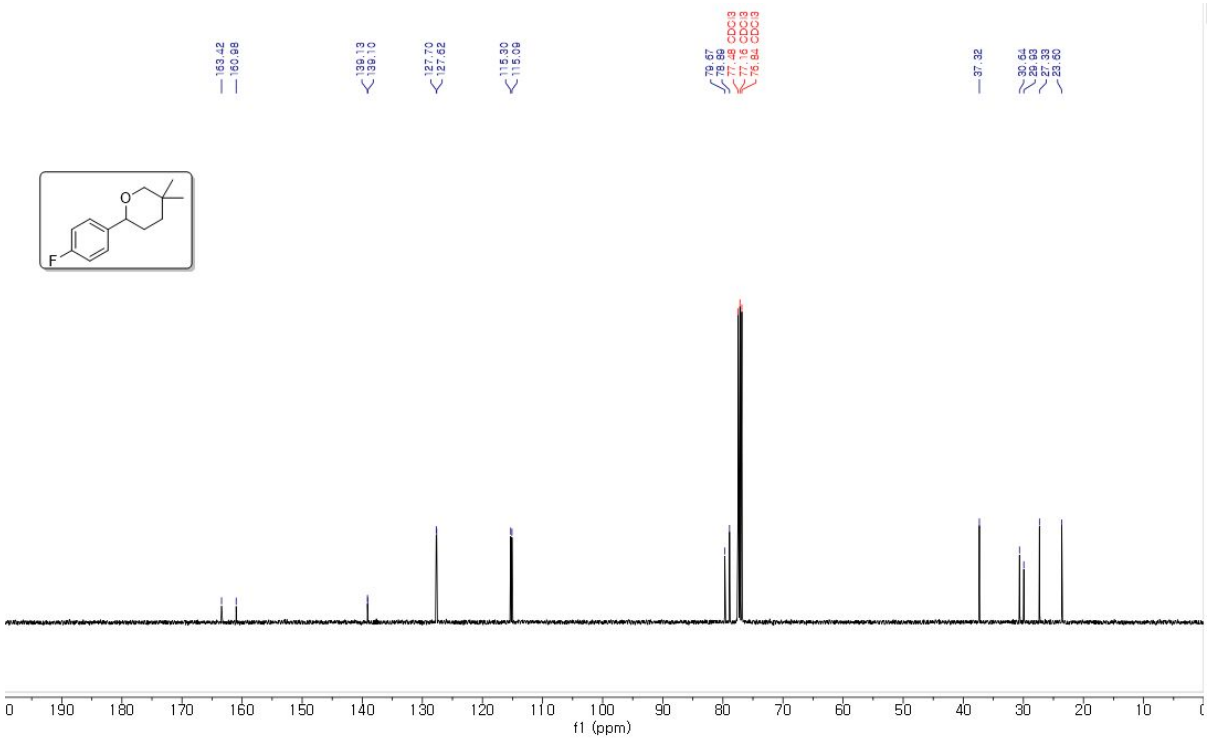


2-(4-fluorophenyl)-5,5-dimethyltetrahydro-2H-pyran (2p)

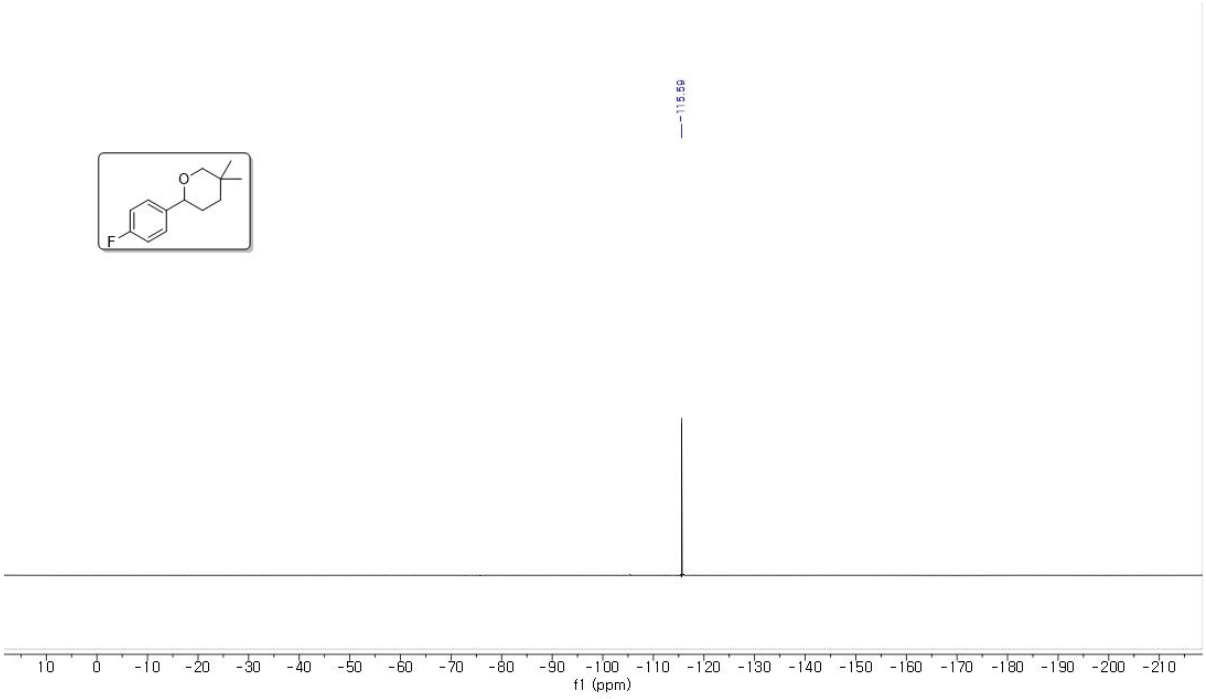
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

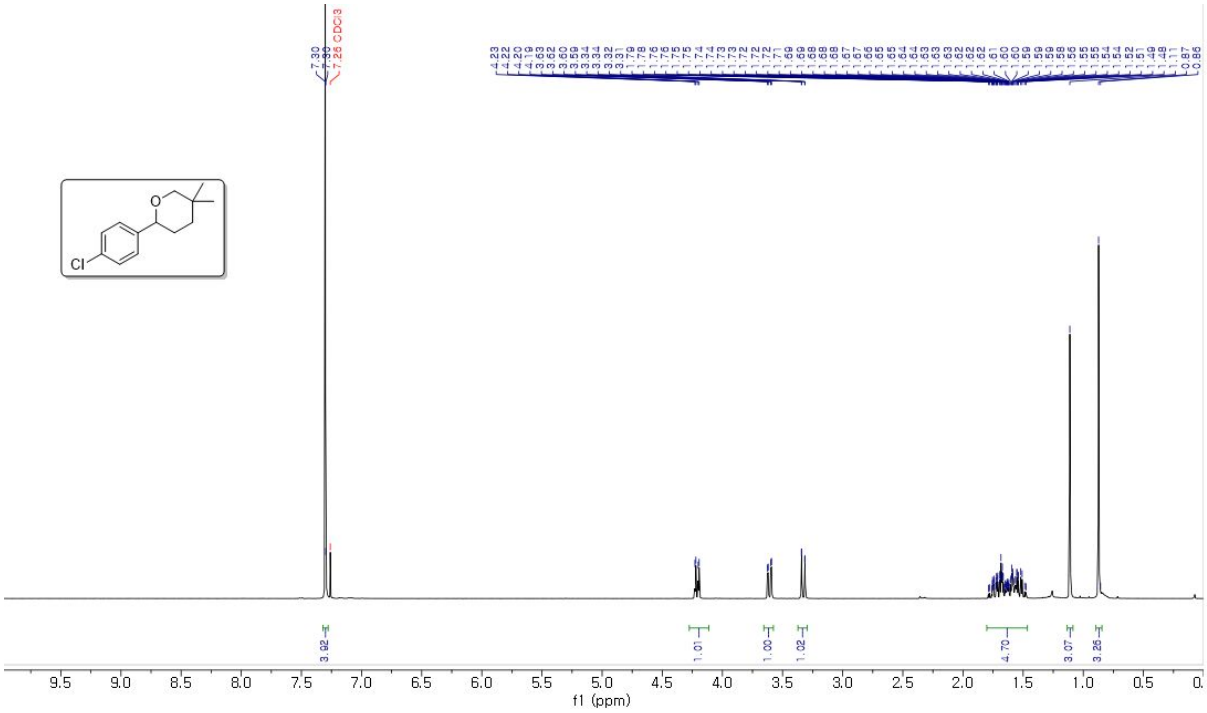


376 MHz, ^{19}F NMR in $CDCl_3$

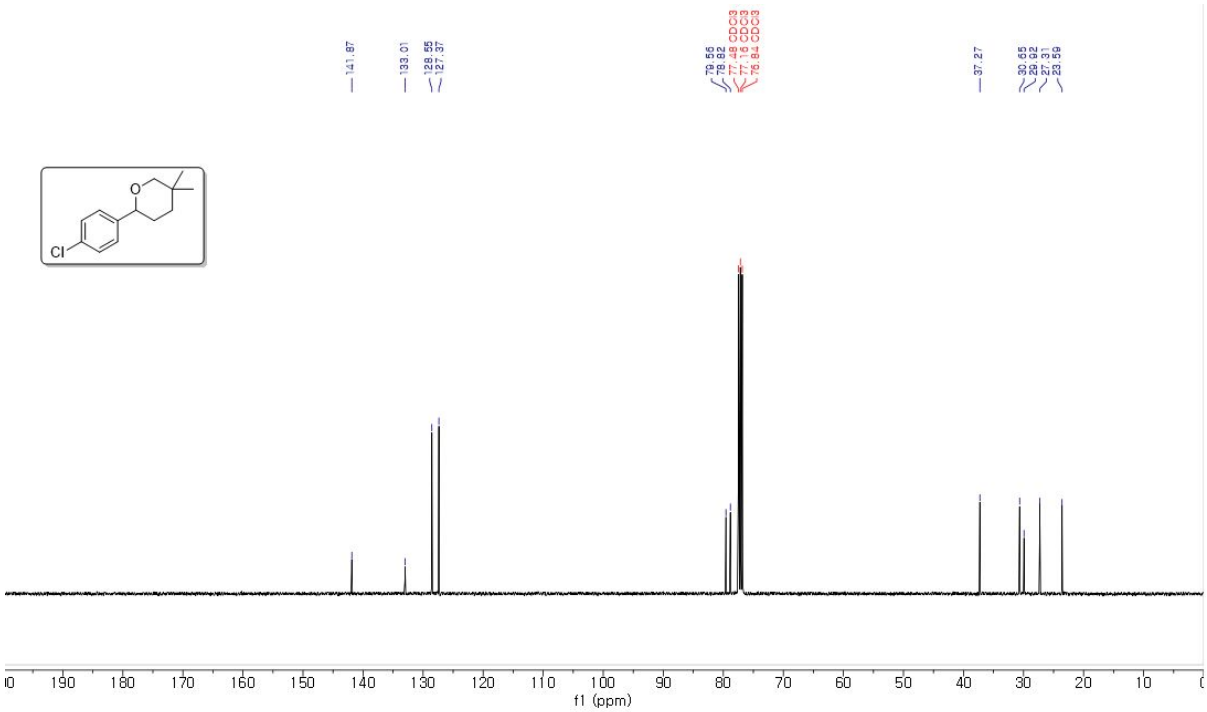


2-(4-chlorophenyl)-5,5-dimethyltetrahydro-2H-pyran (2q)

400 MHz, ^{1}H NMR in $CDCl_3$

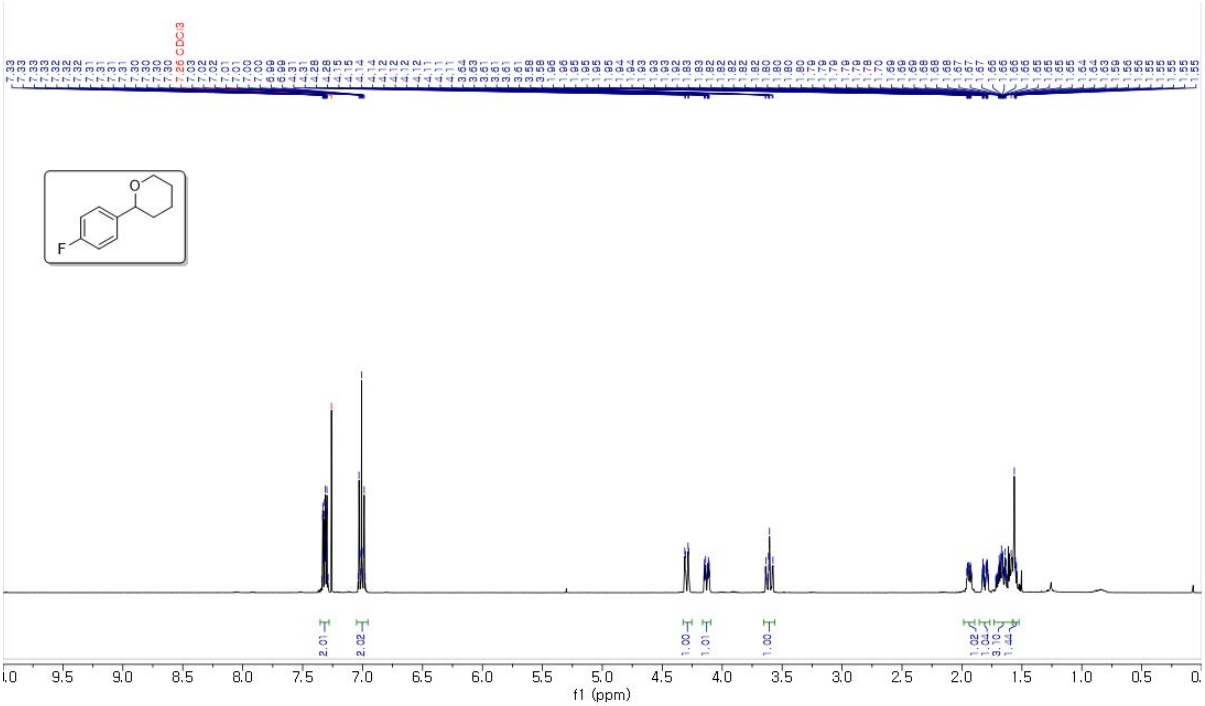


100 MHz, ^{13}C NMR in $CDCl_3$

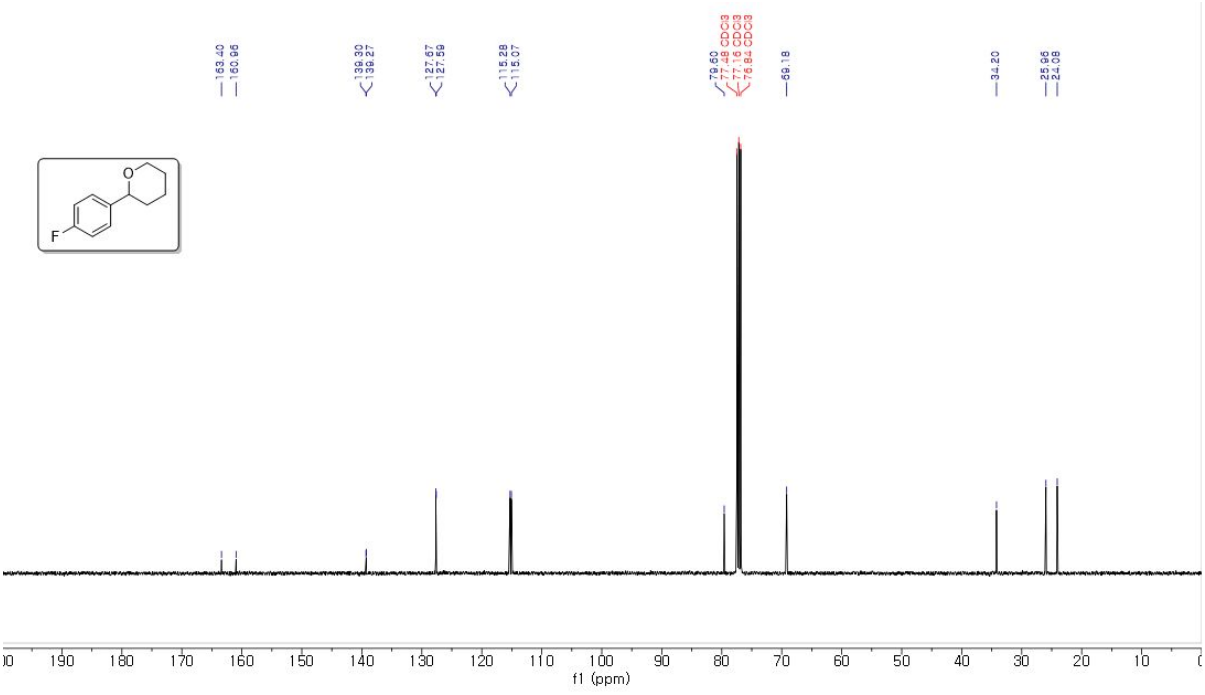


2-(4-fluorophenyl)tetrahydro-2H-pyran (2r)

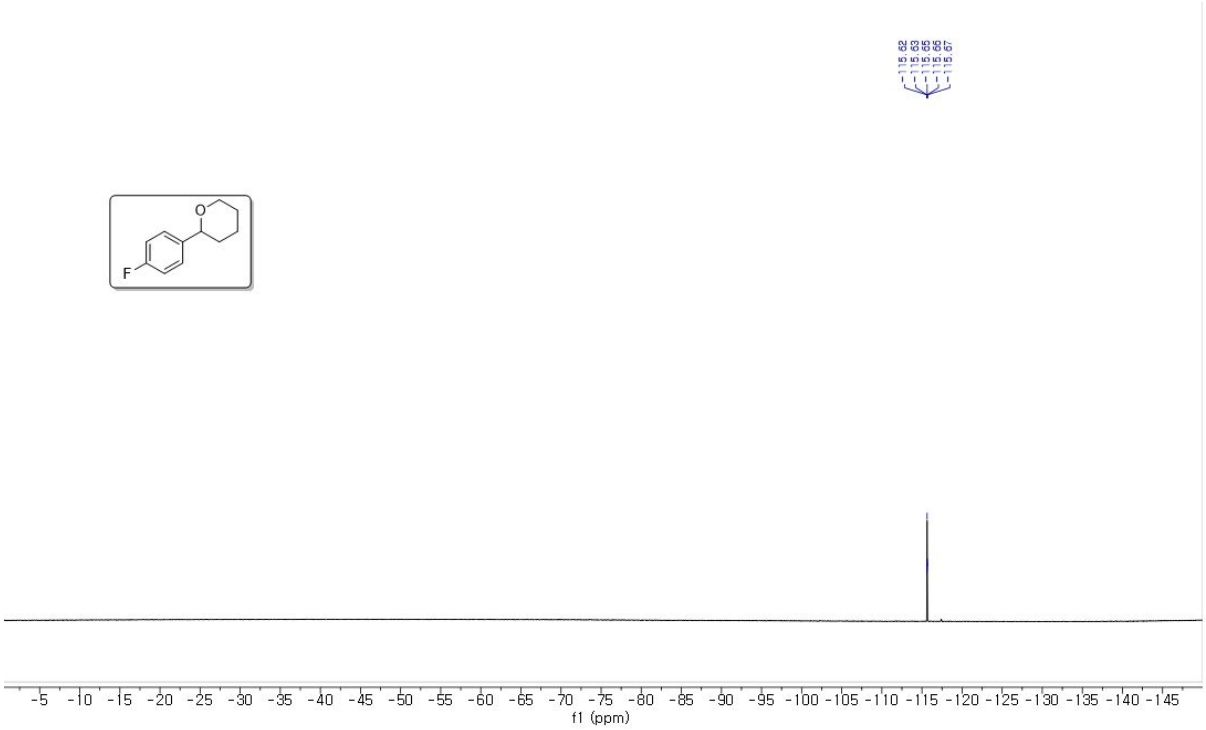
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

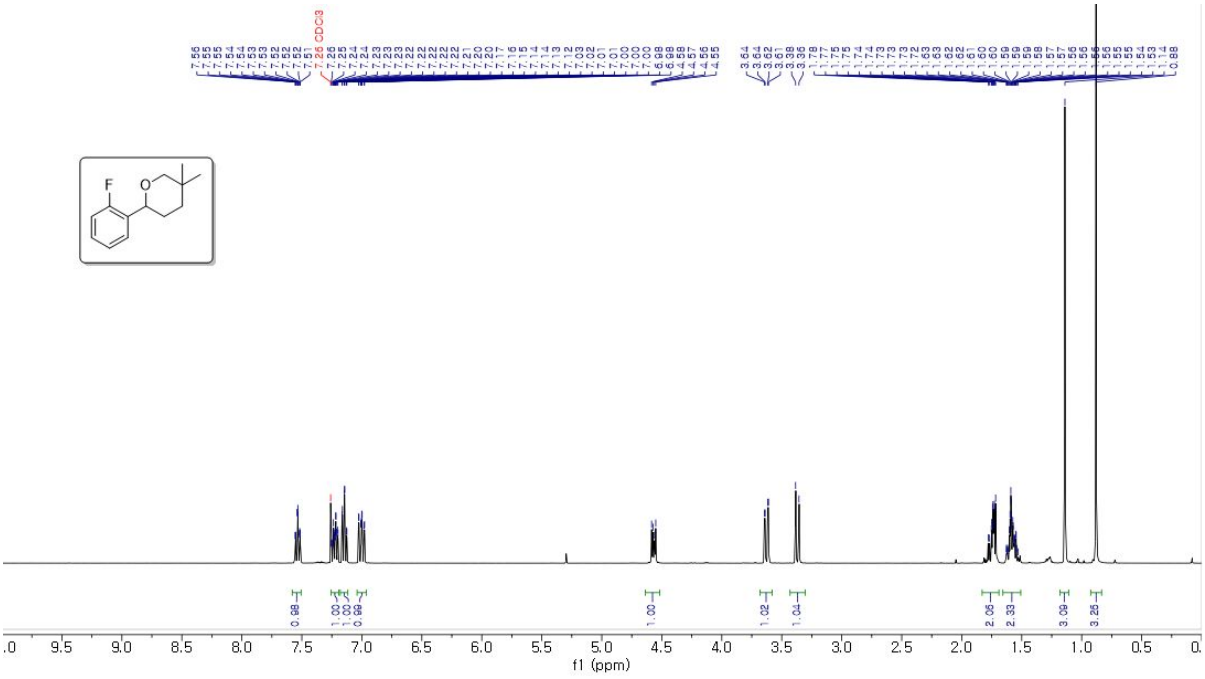


376 MHz, ^{19}F NMR in $CDCl_3$

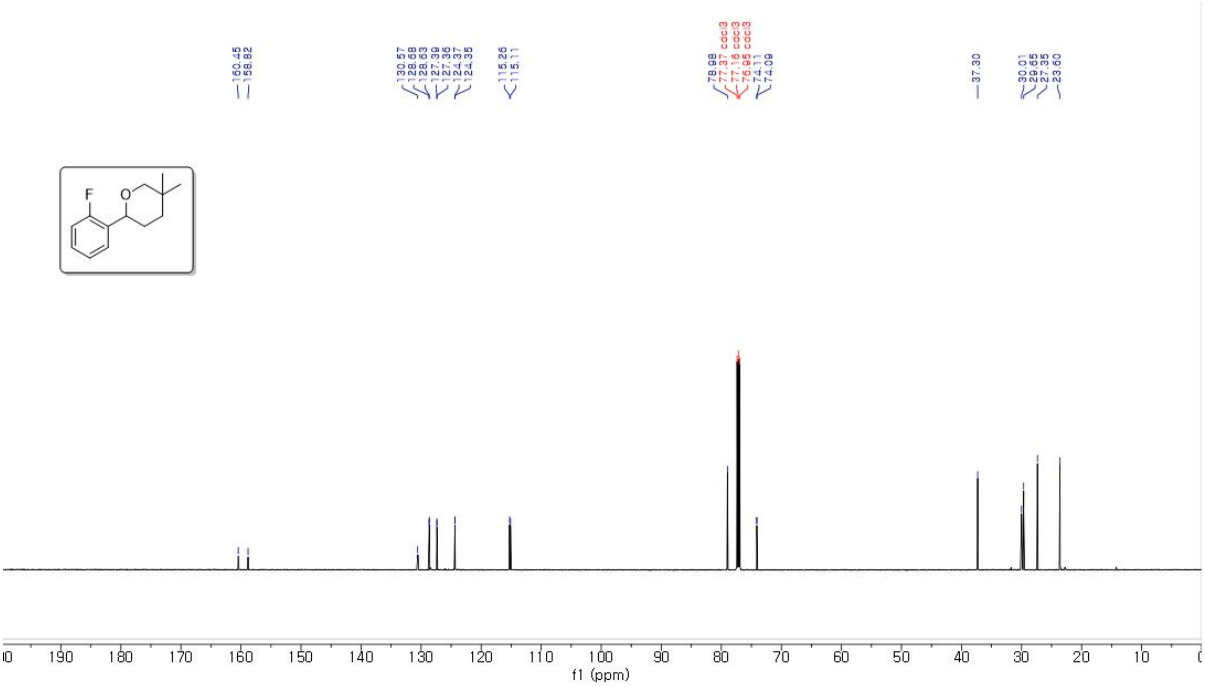


2-(2-fluorophenyl)-5,5-dimethyltetrahydro-2H-pyran (2s)

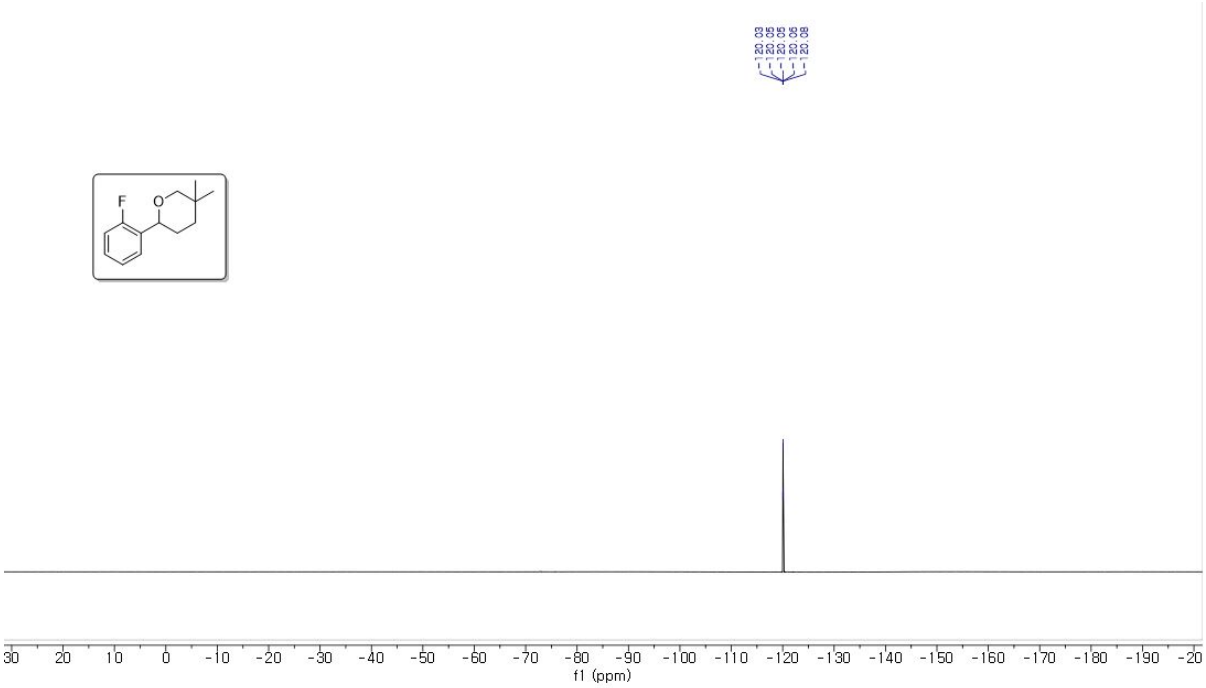
400 MHz, ^{1}H NMR in $CDCl_3$



150 MHz, ^{13}C NMR in $CDCl_3$

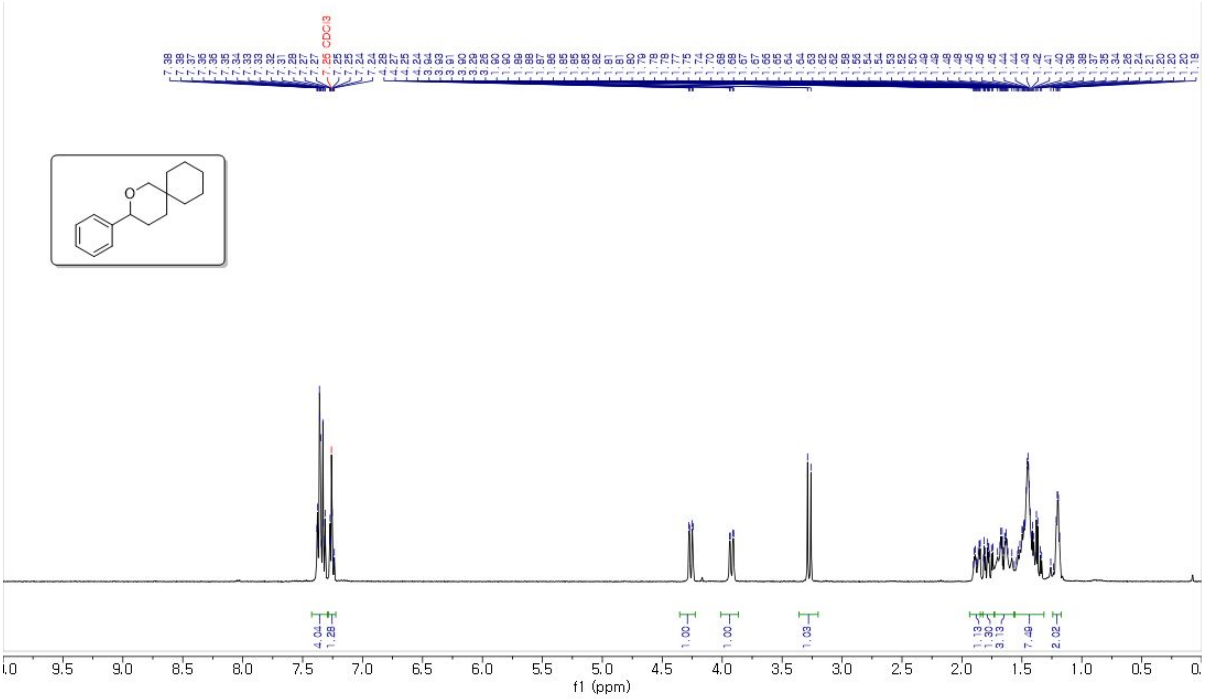


564 MHz, ^{19}F NMR in $CDCl_3$

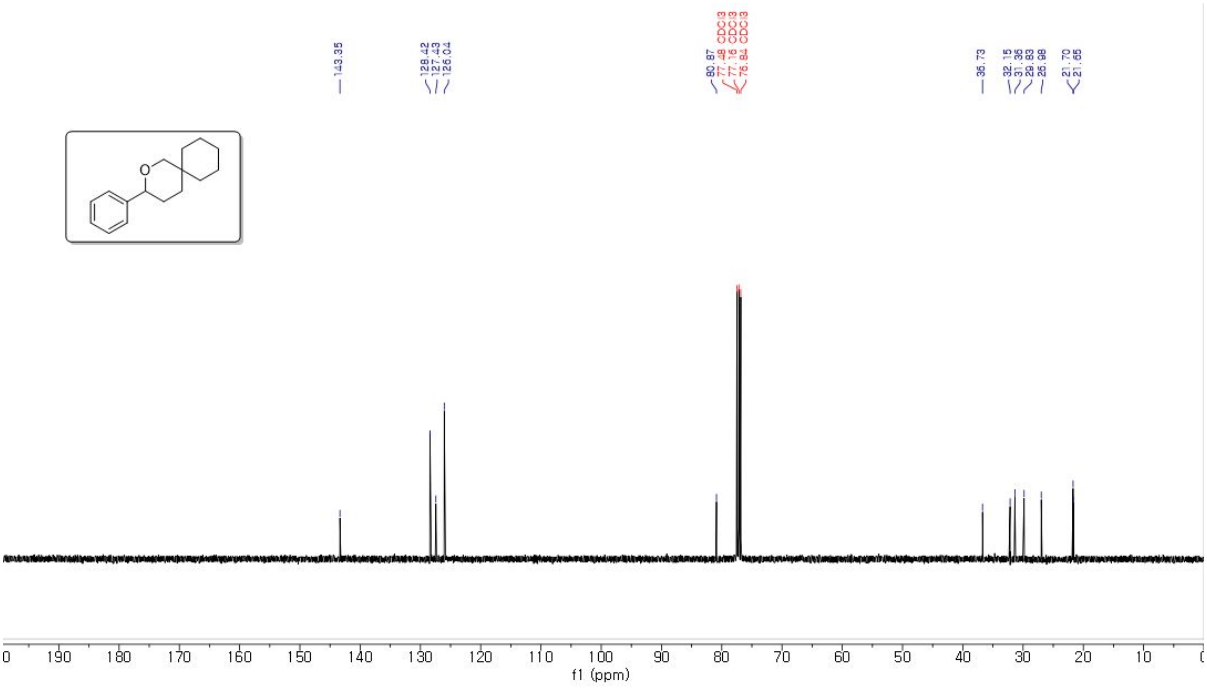


3-phenyl-2-oxaspiro[5.5]undecane (2t)

400 MHz, ^{1}H NMR in $CDCl_3$

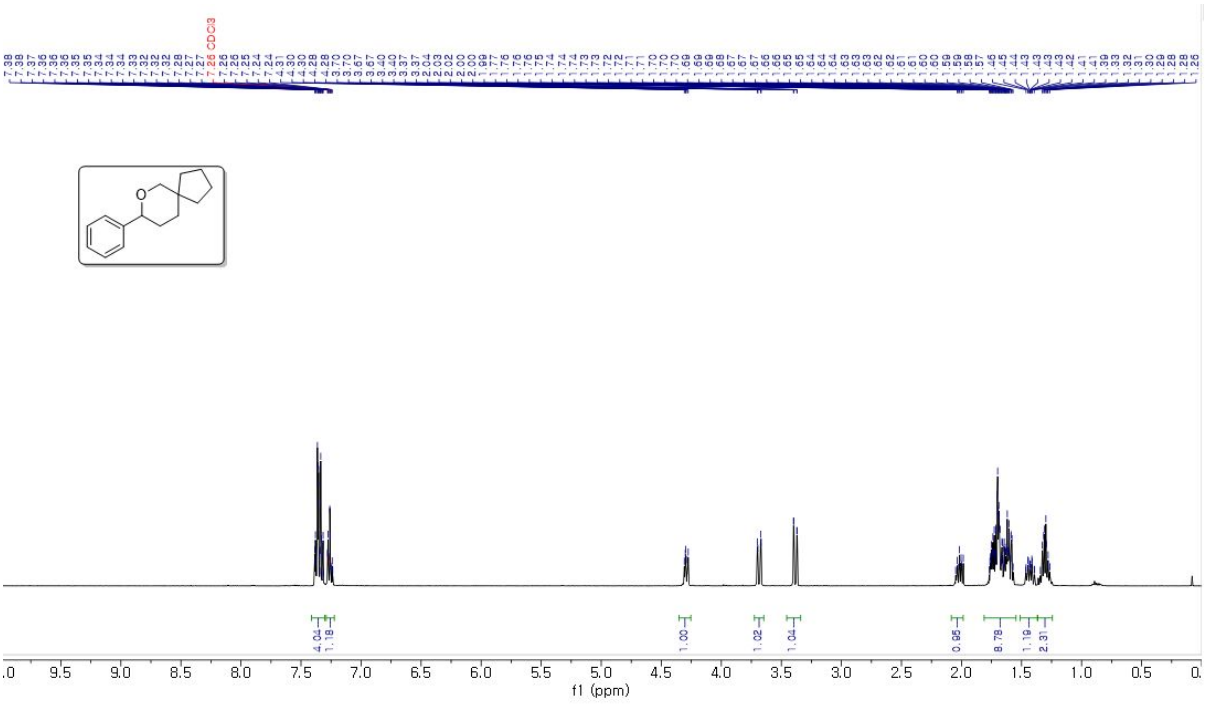


100 MHz, ^{13}C NMR in $CDCl_3$

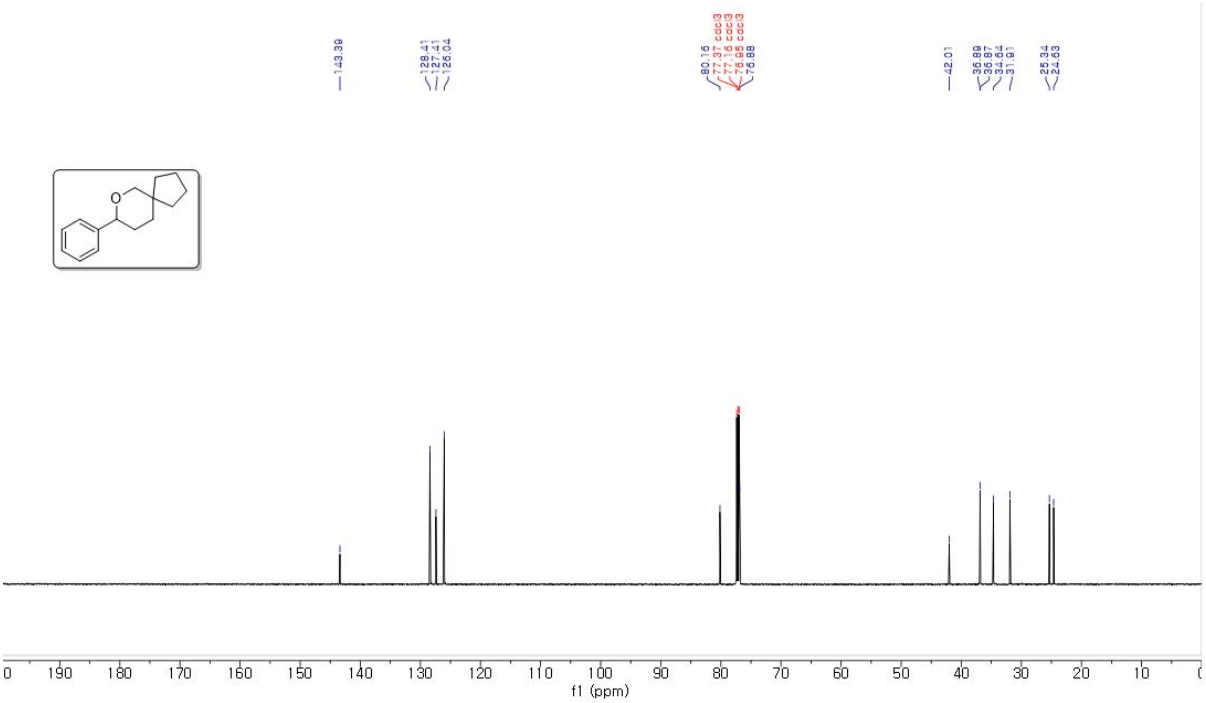


8-phenyl-7-oxaspiro[4.5]decane (2u)

400 MHz, ^{1}H NMR in $CDCl_3$

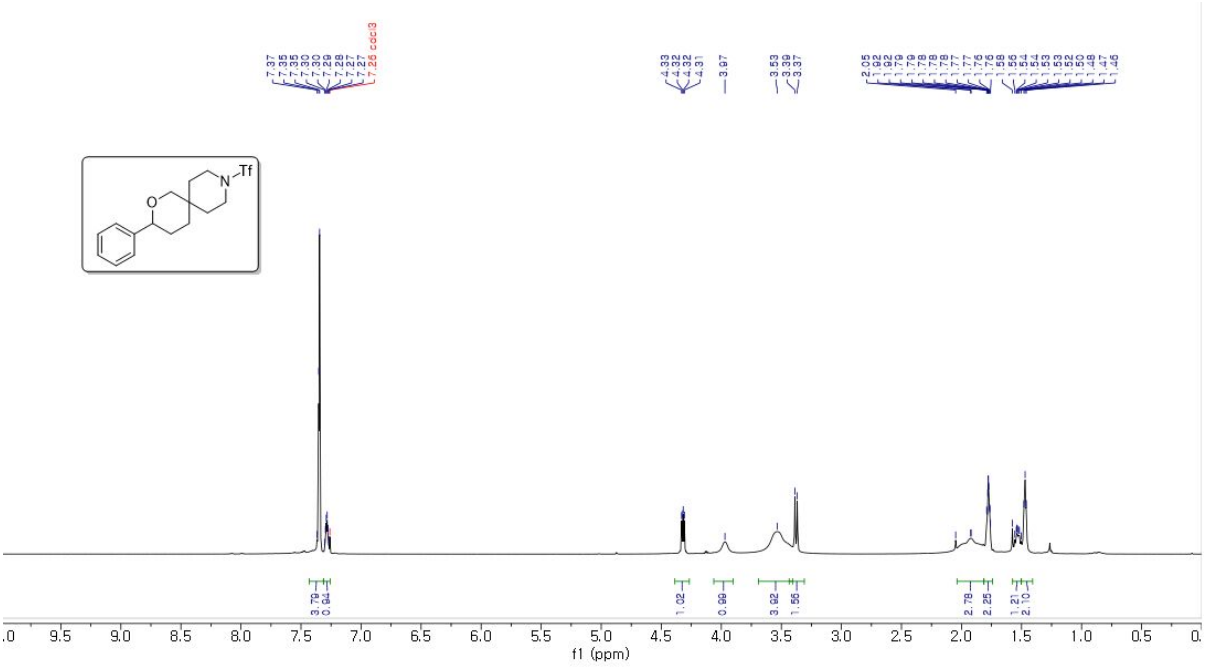


150 MHz, ^{13}C NMR in $CDCl_3$

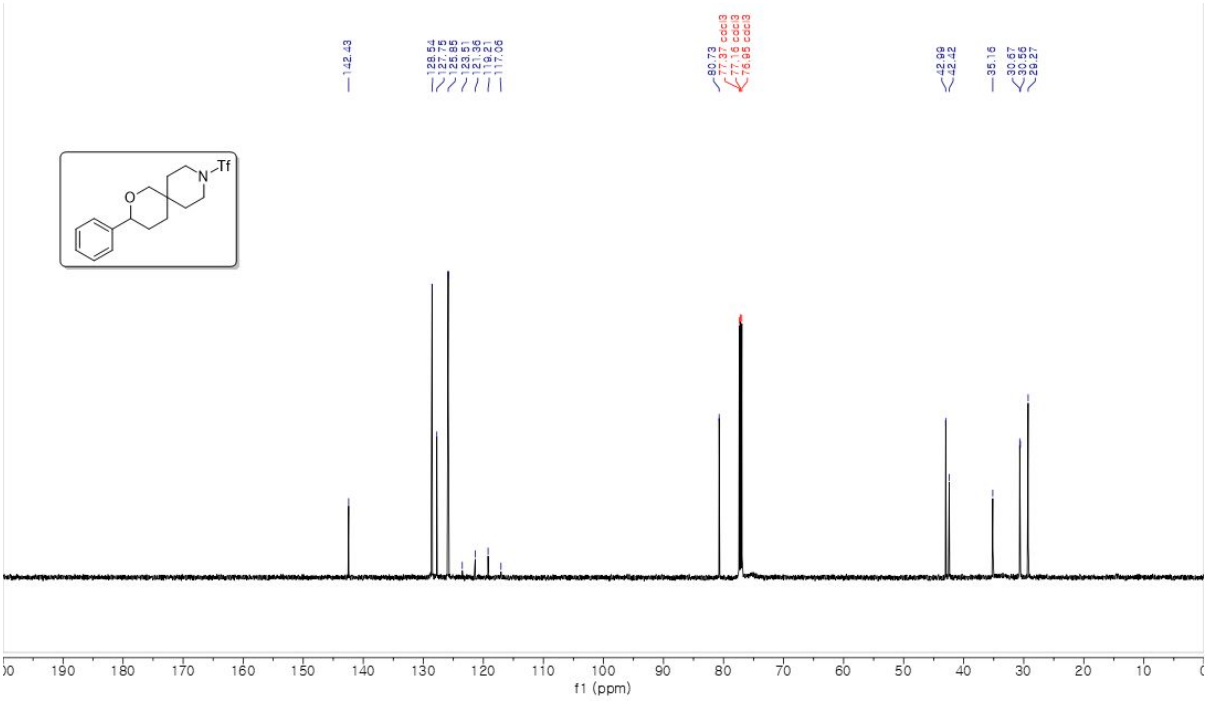


3-phenyl-9-((trifluoromethyl)sulfonyl)-2-oxa-9-azaspiro[5.5]undecane (2v)

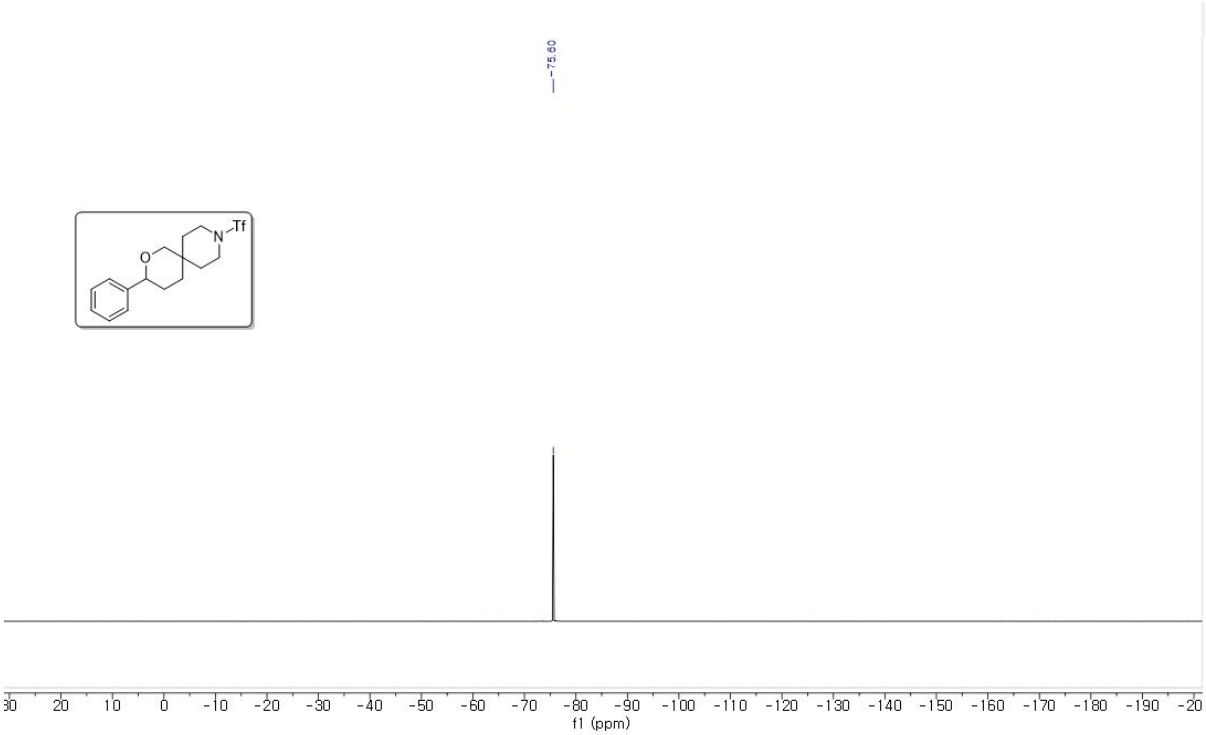
600 MHz, ^{1}H NMR in $CDCl_3$



150 MHz, ^{13}C NMR in $CDCl_3$

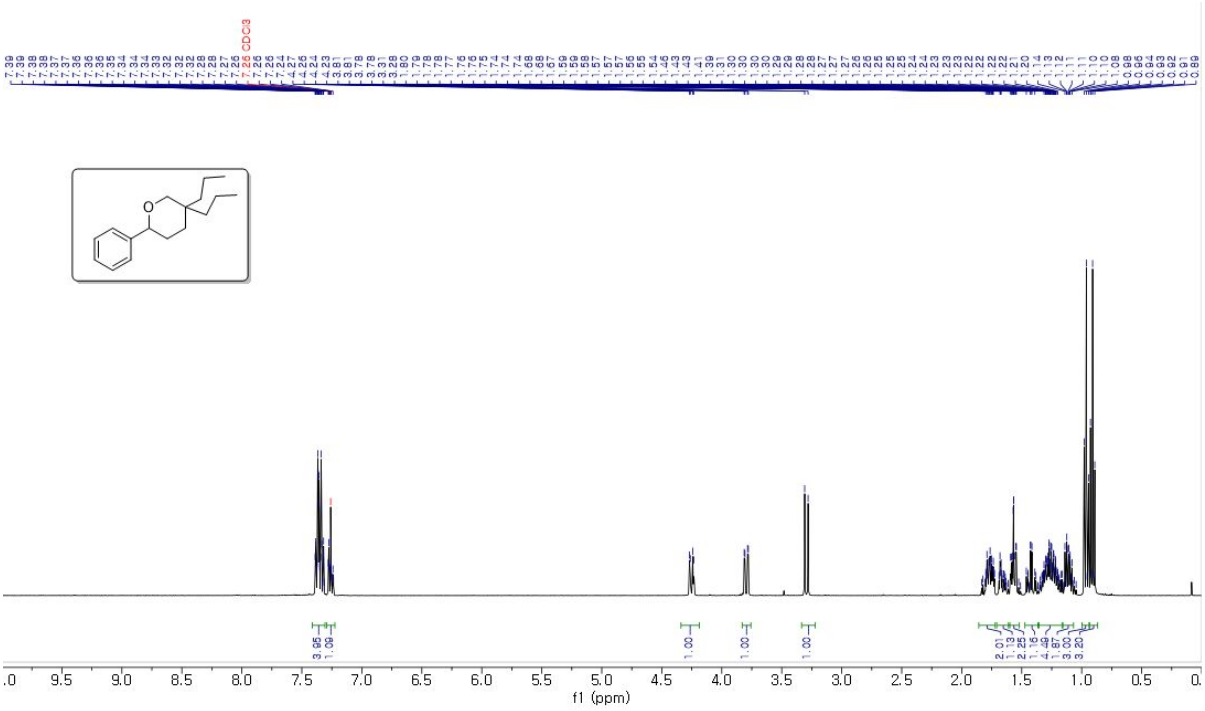


564 MHz, ^{19}F NMR in $CDCl_3$

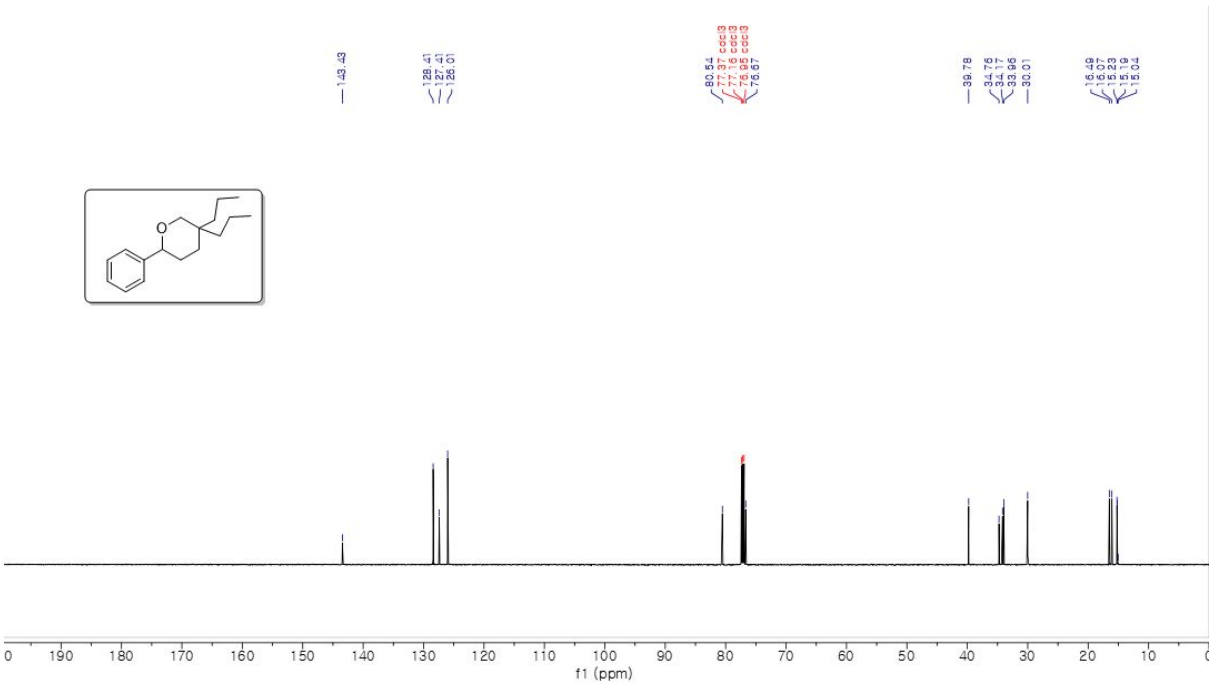


2-phenyl-5,5-dipropyltetrahydro-2H-pyran (2w)

400 MHz, ^{1}H NMR in $CDCl_3$

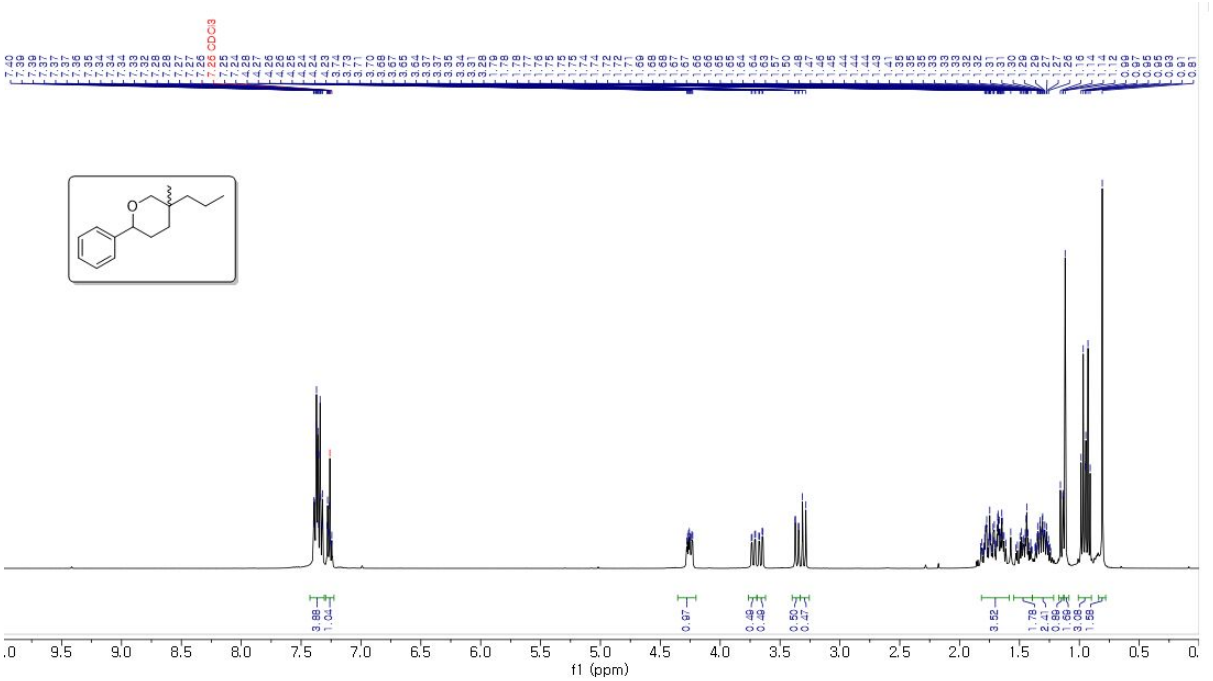


150 MHz, ^{13}C NMR in $CDCl_3$

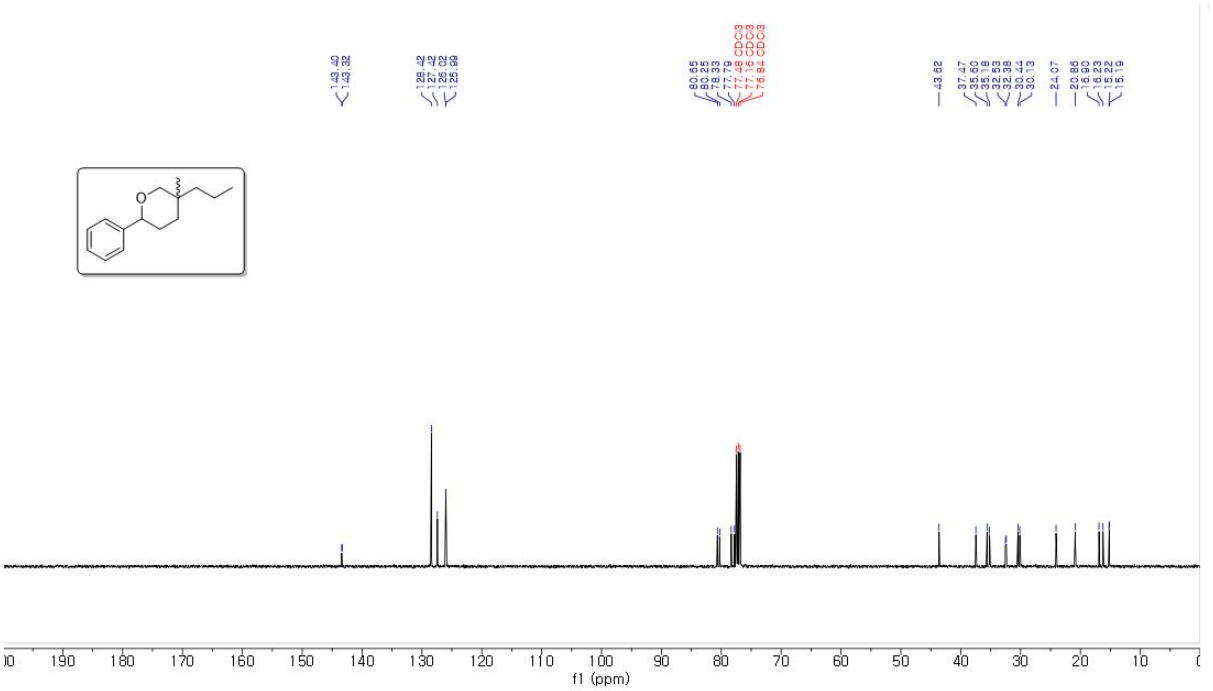


5-methyl-2-phenyl-5-propyltetrahydro-2H-pyran (2x)

400 MHz, ^{1}H NMR in $CDCl_3$

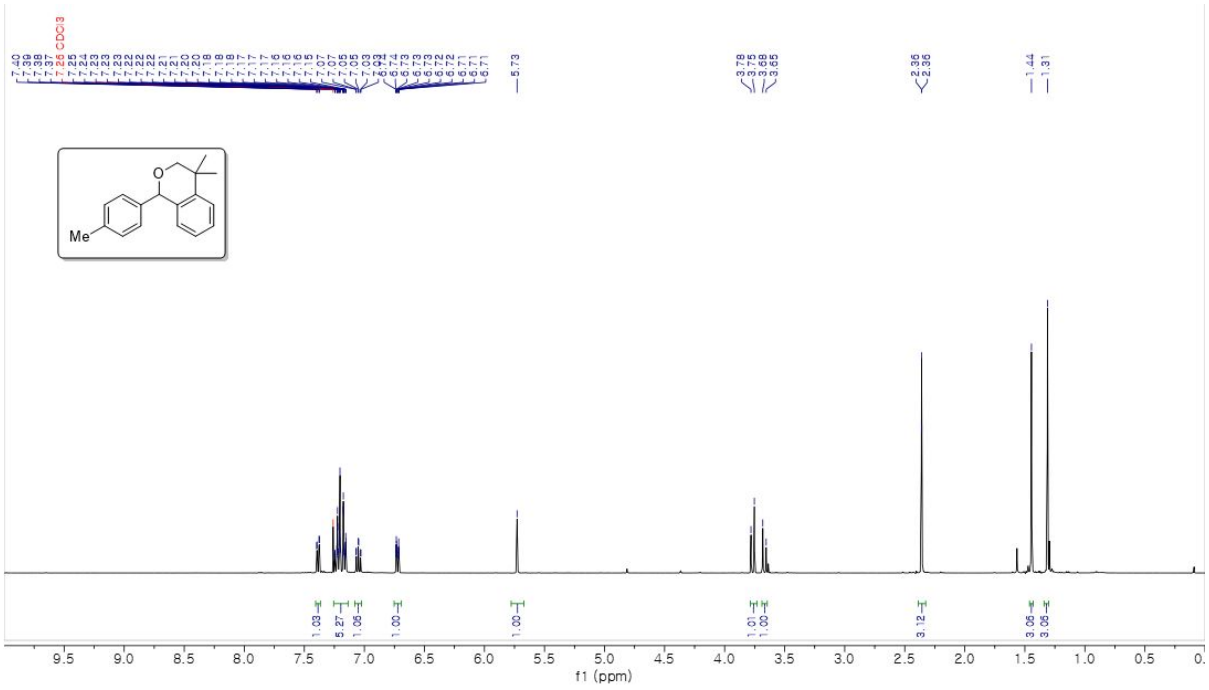


100 MHz, ^{13}C NMR in $CDCl_3$

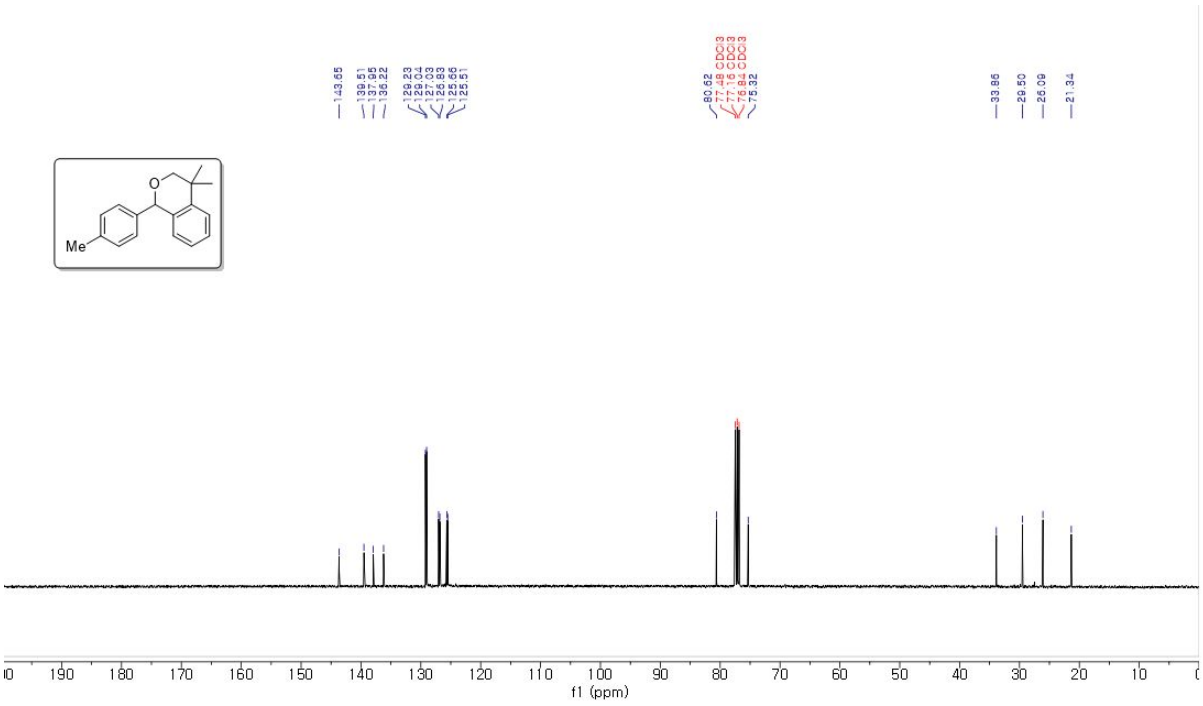


4,4-dimethyl-1-(p-tolyl)isochromane (2y)

400 MHz, ^{1}H NMR in $CDCl_3$

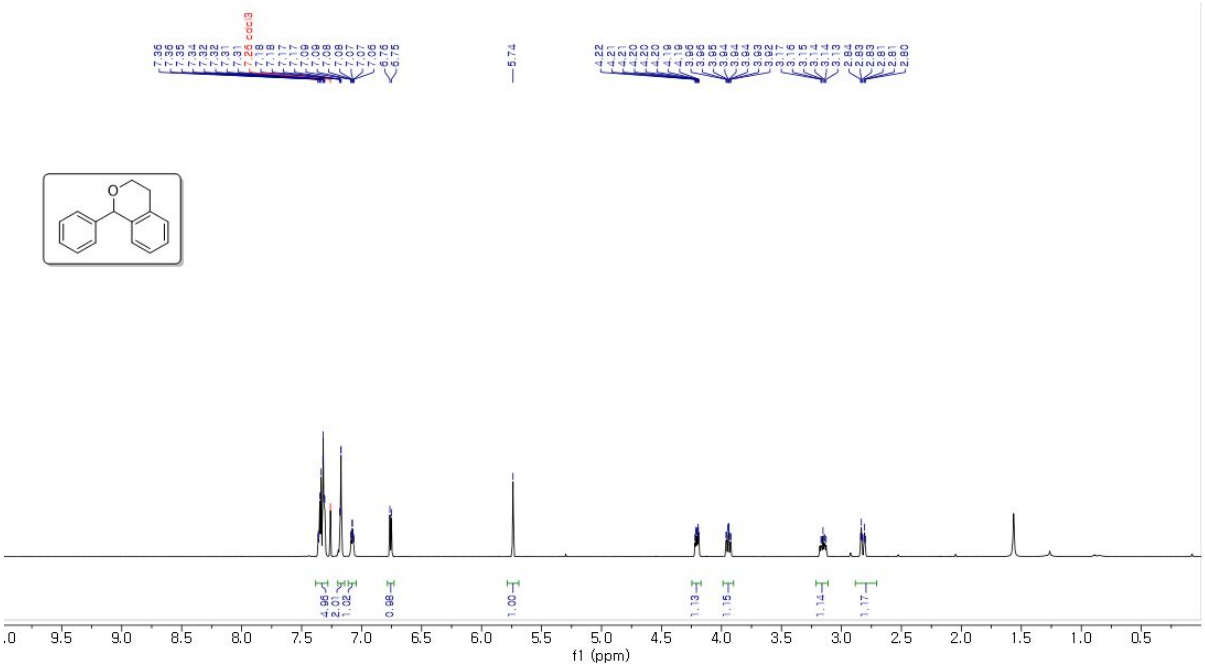


100 MHz, ^{13}C NMR in $CDCl_3$

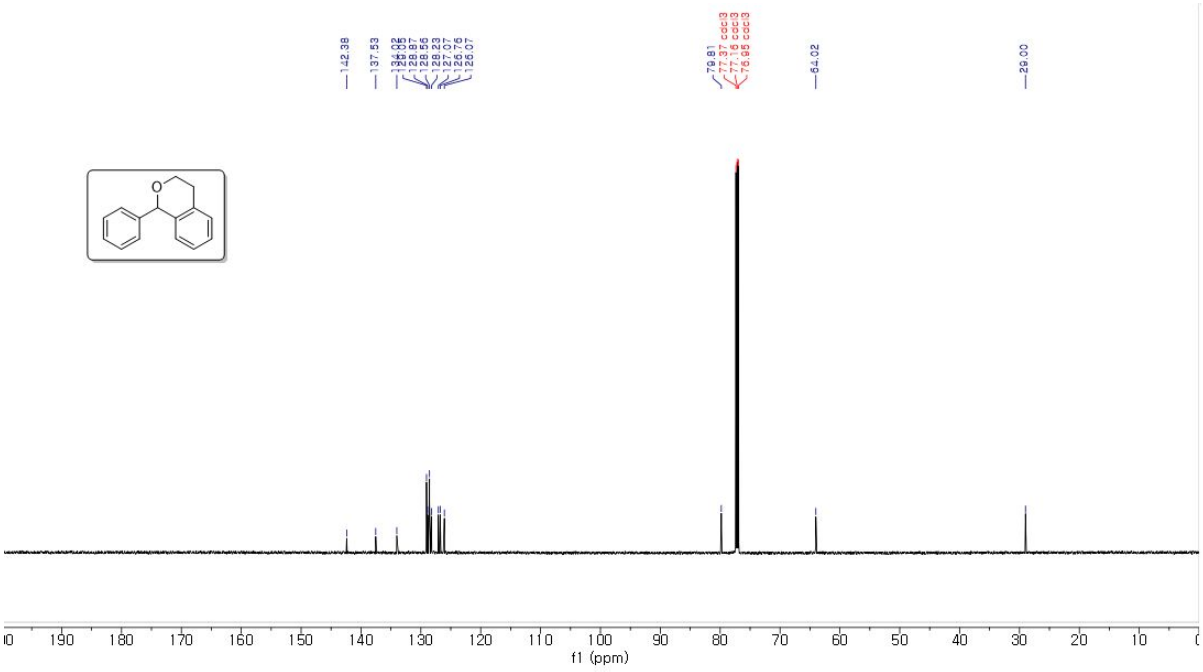


1-phenylisochromane (2z)

600 MHz, ^{1}H NMR in $CDCl_3$

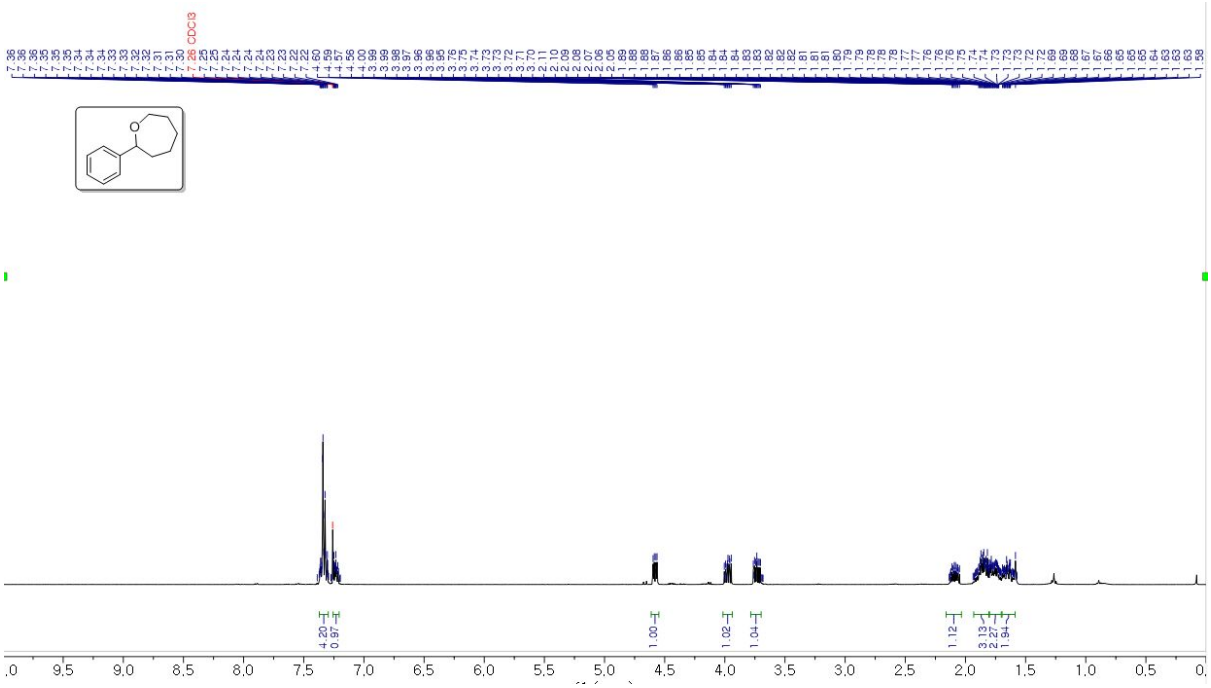


150 MHz, ^{13}C NMR in $CDCl_3$

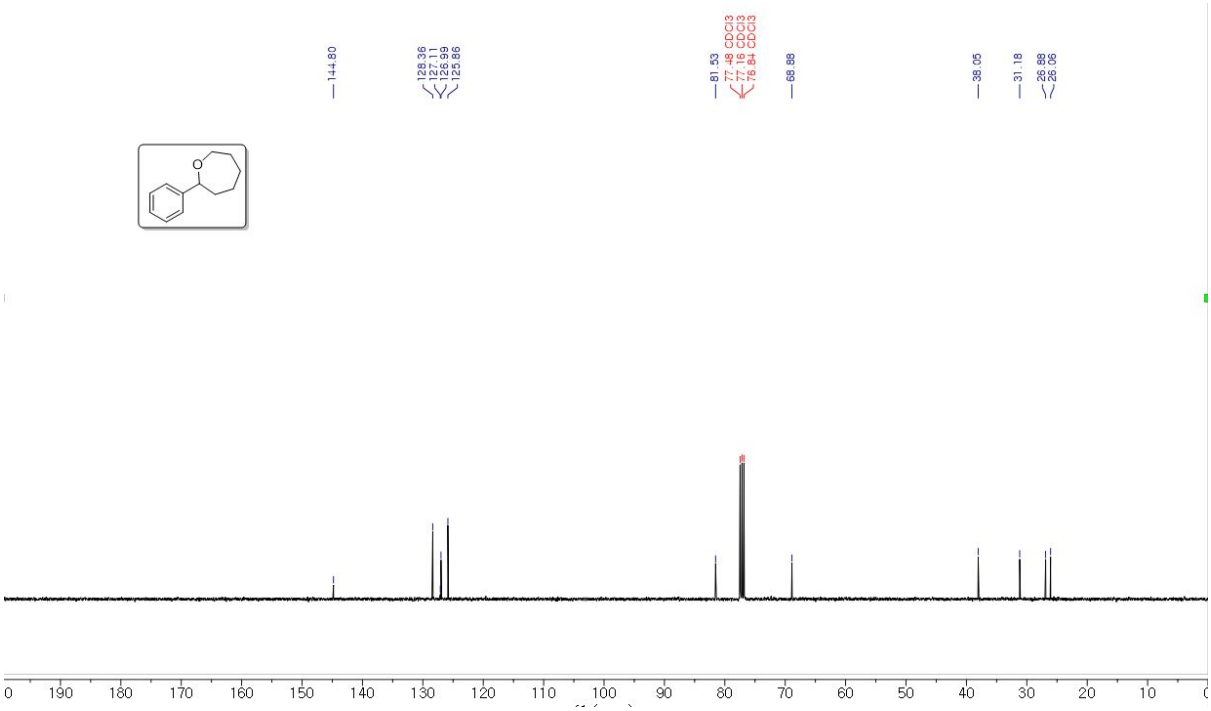


2-phenyloxepane (2aa)

400 MHz, ^{1}H NMR in $CDCl_3$

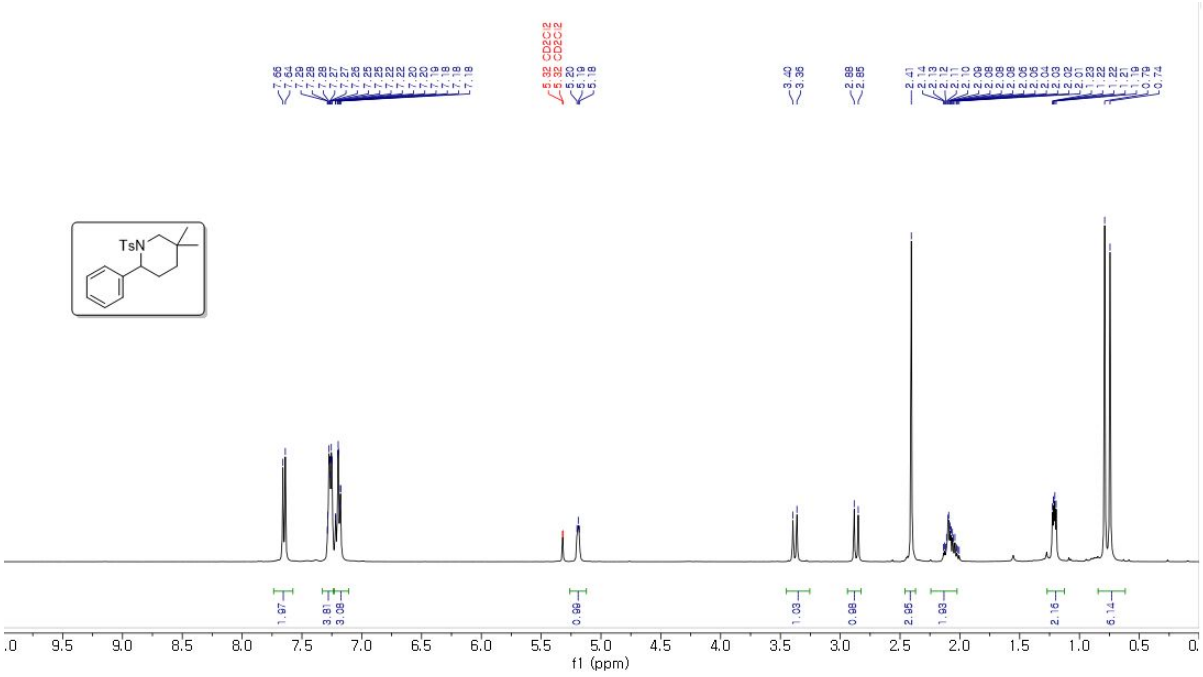


100 MHz, ^{13}C NMR in $CDCl_3$

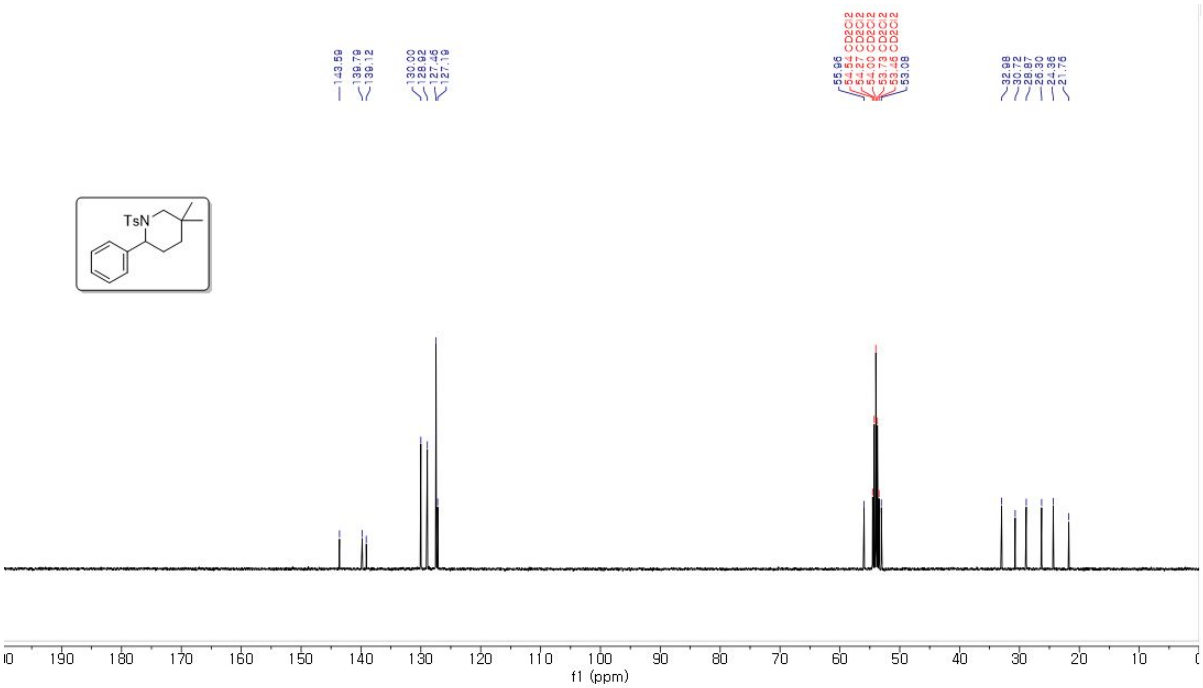


5,5-dimethyl-2-phenyl-1-tosylpiperidine (2ab)

400 MHz, ^{1}H NMR in CD_2Cl_2

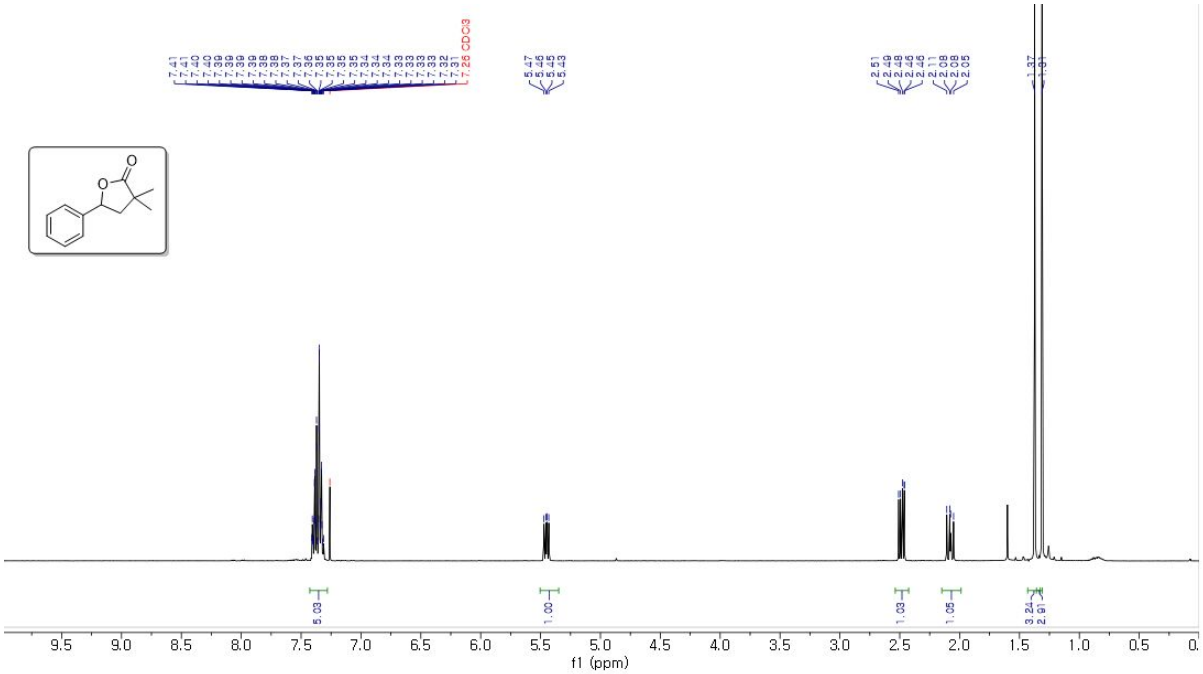


100 MHz, ^{13}C NMR in CD_2Cl_2

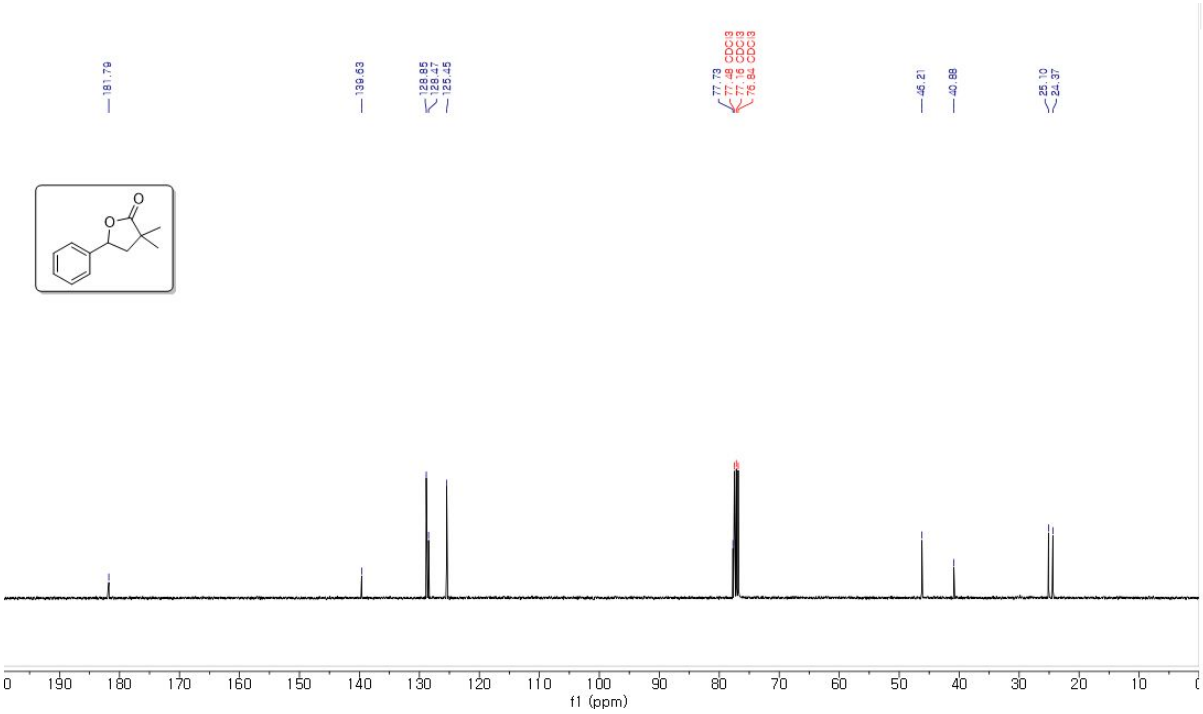


3,3-dimethyl-5-phenyldihydrofuran-2(3H)-one (6a)

400 MHz, ^{1}H NMR in $CDCl_3$

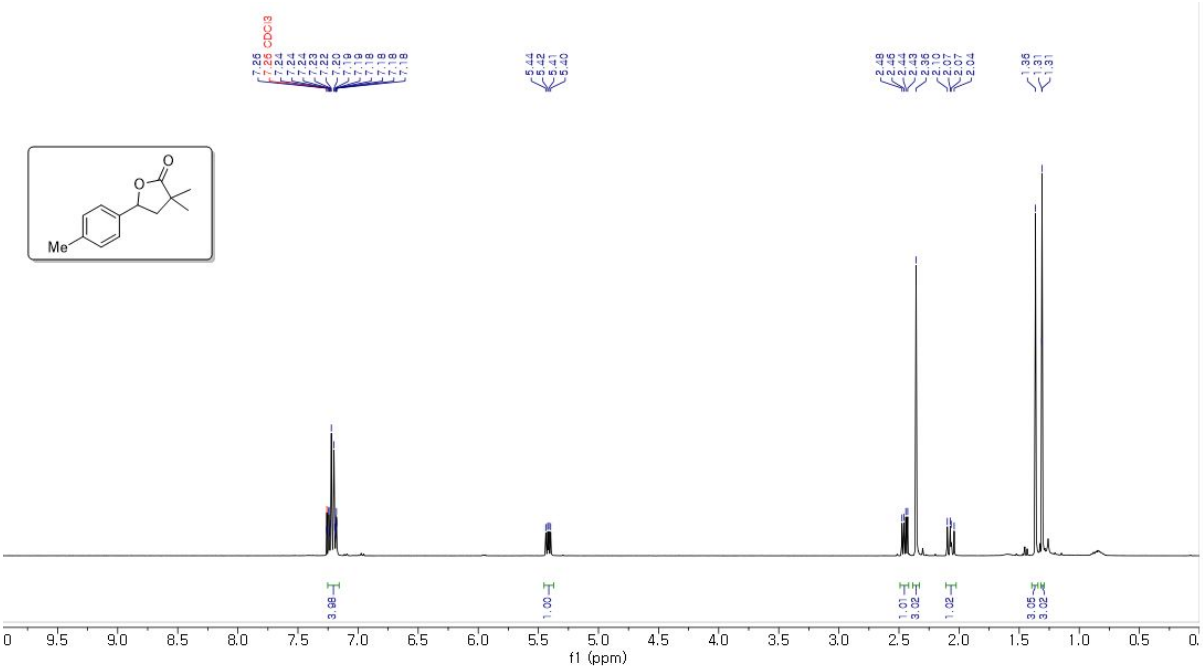


100 MHz, ^{13}C NMR in $CDCl_3$

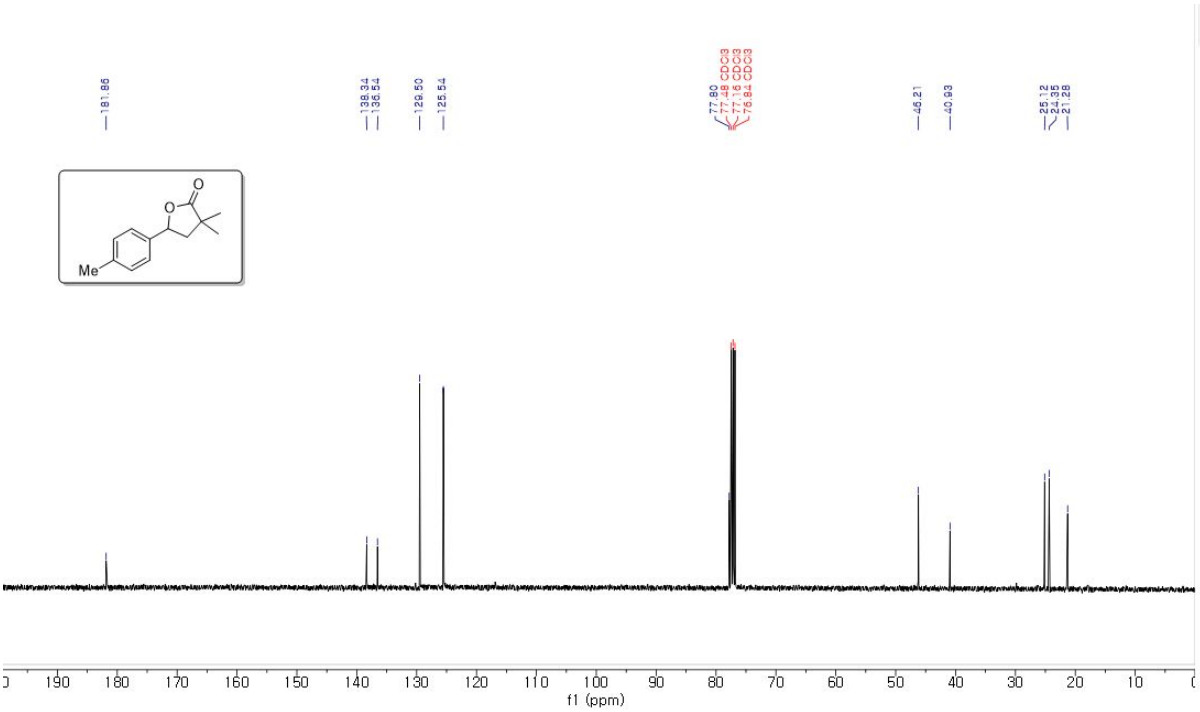


3,3-dimethyl-5-(p-tolyl)dihydrofuran-2(3H)-one (6b)

400 MHz, ^{1}H NMR in $CDCl_3$

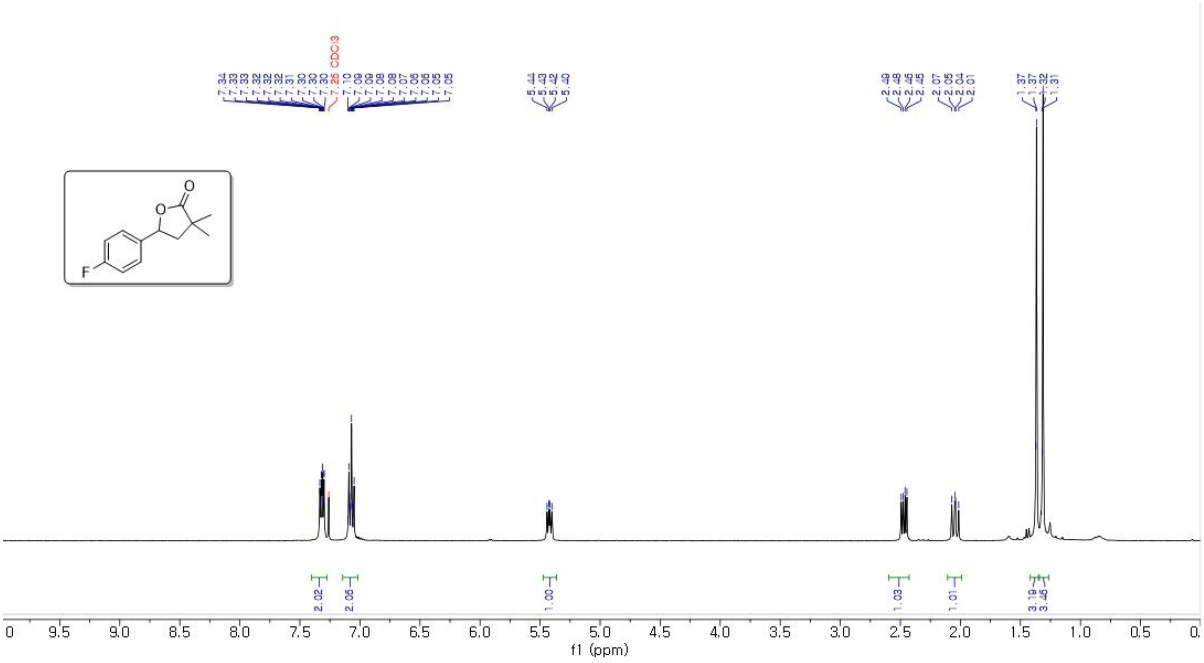


100 MHz, ^{13}C NMR in $CDCl_3$

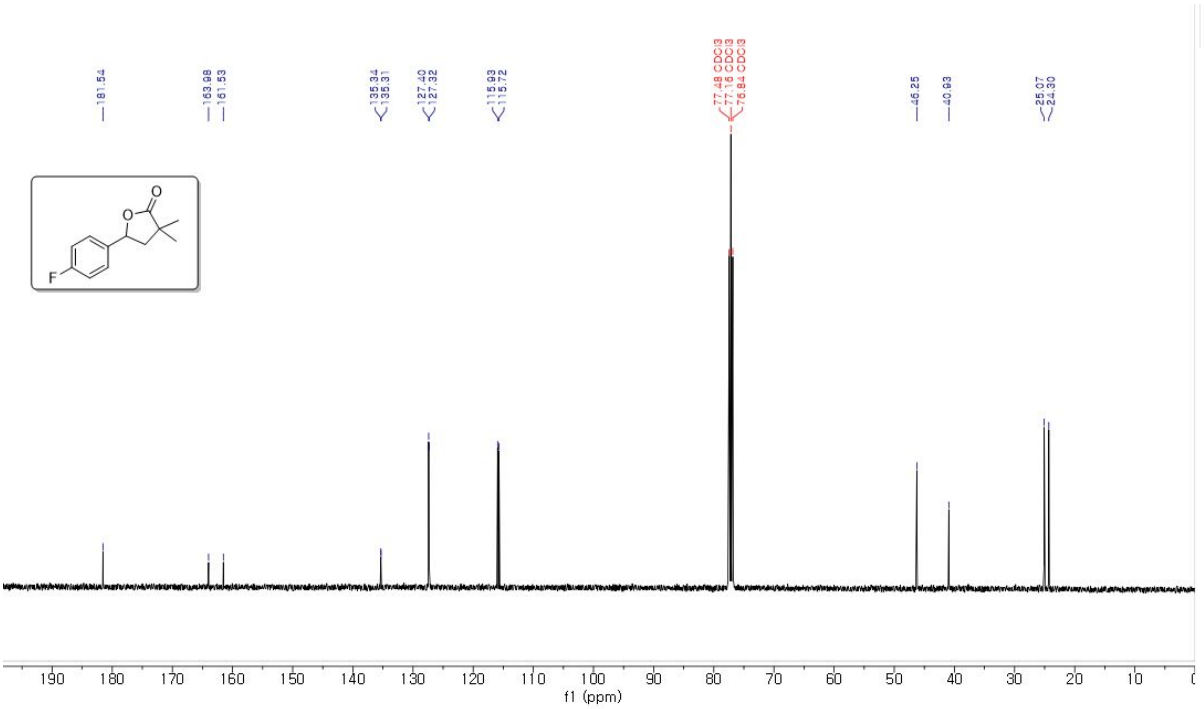


5-(4-fluorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6c)

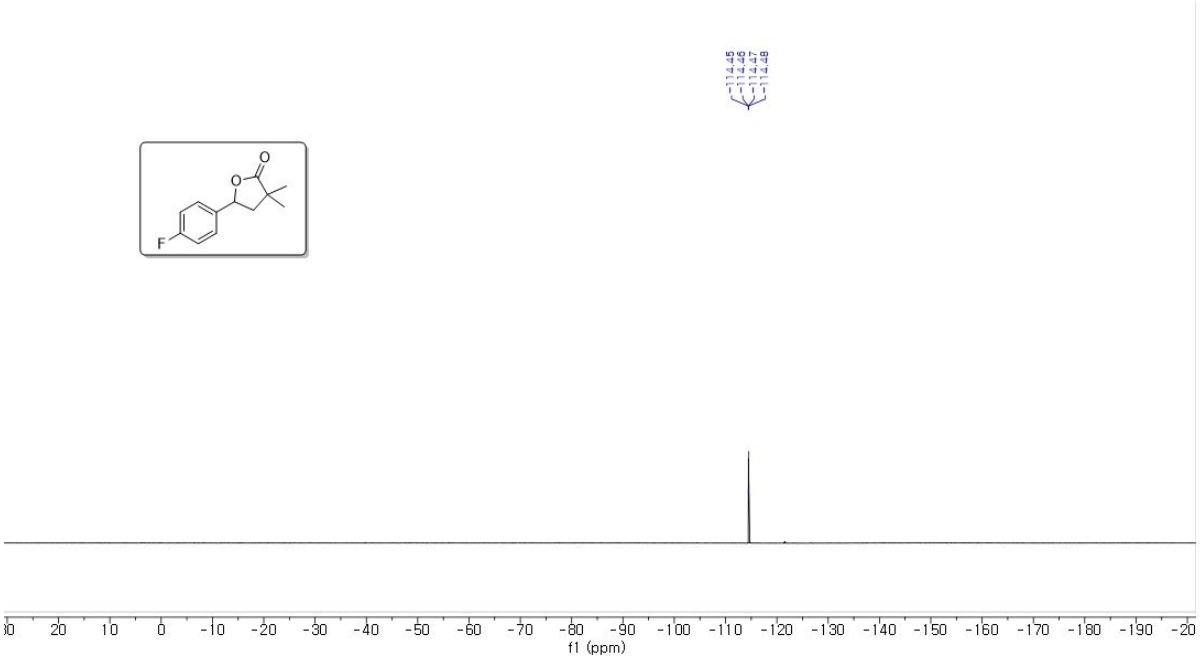
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

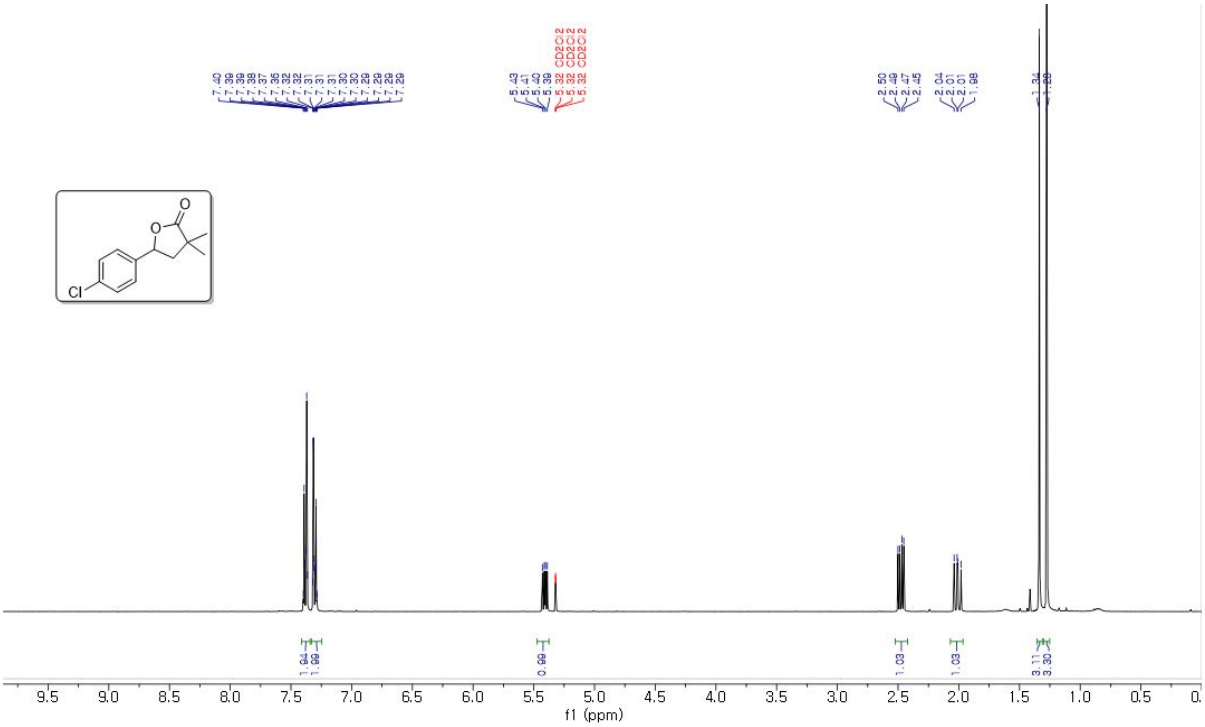


564 MHz, ^{19}F NMR in CD_2Cl_2

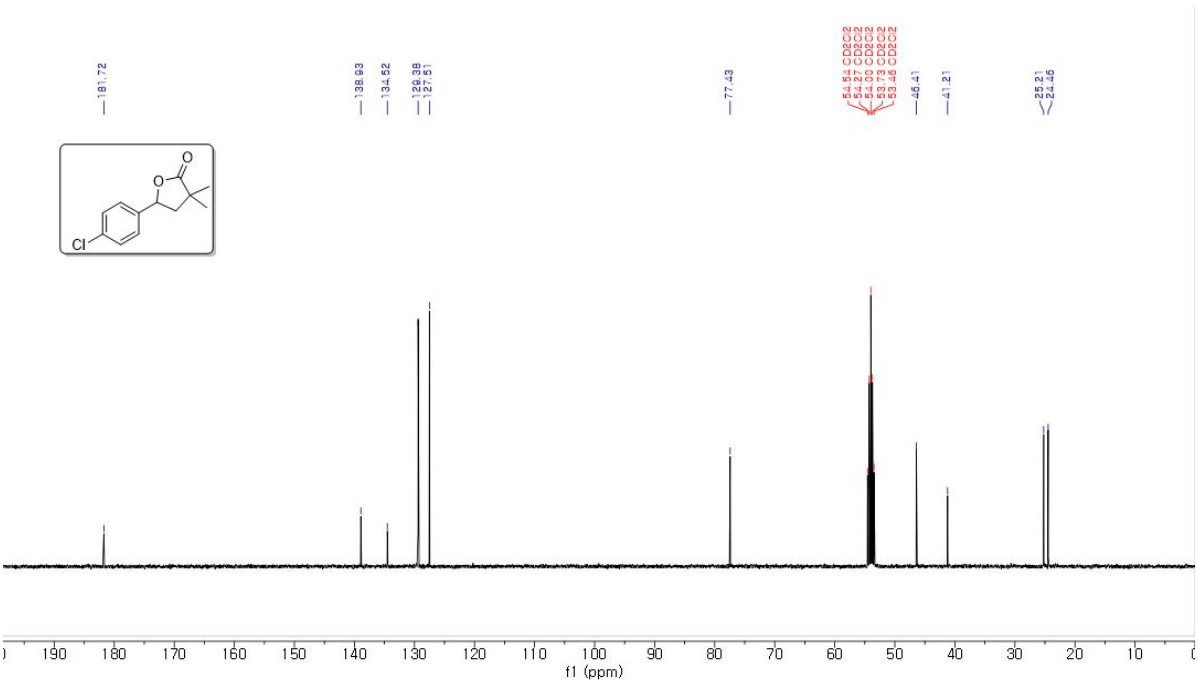


5-(4-chlorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6d)

400 MHz, ^{1}H NMR in CD_2Cl_2

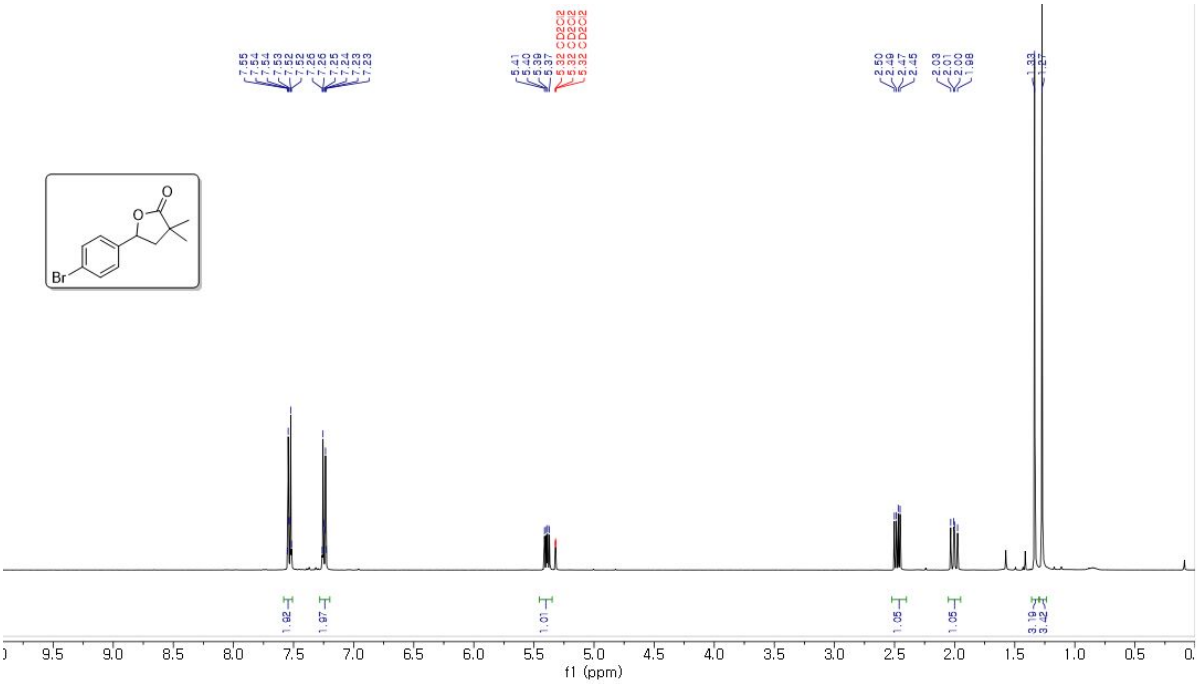


100 MHz, ^{13}C NMR in CD_2Cl_2

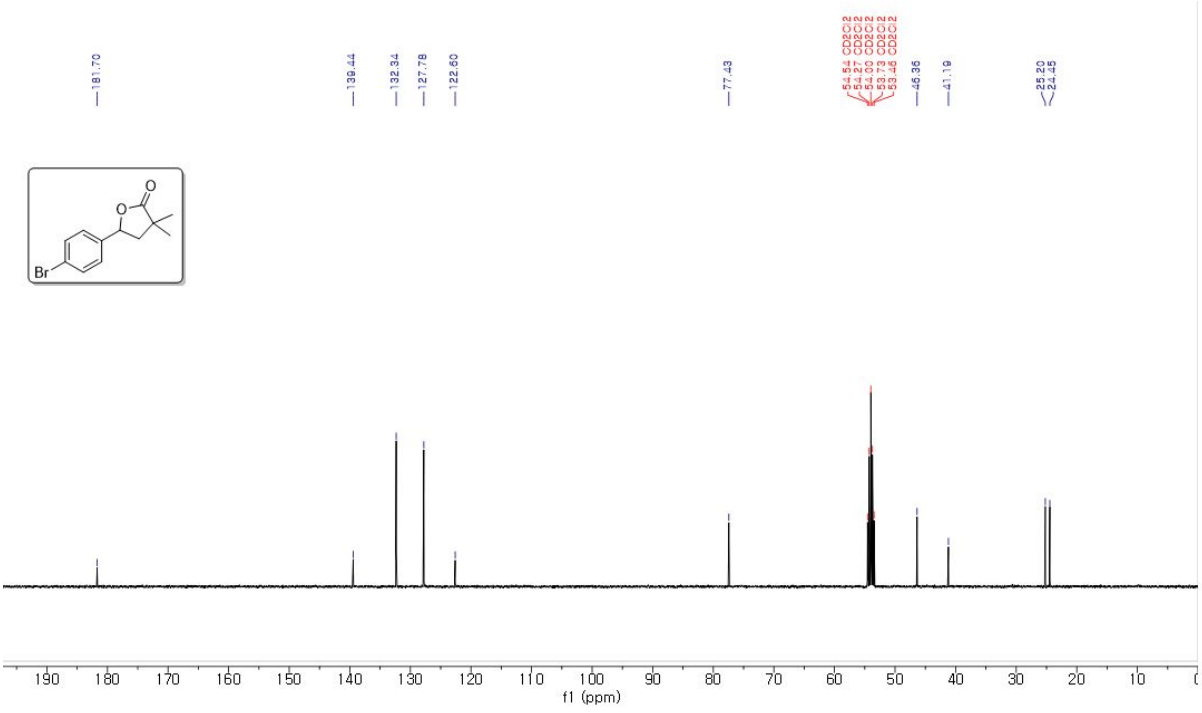


5-(4-bromophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6e)

400 MHz, ^{1}H NMR in CD_2Cl_2

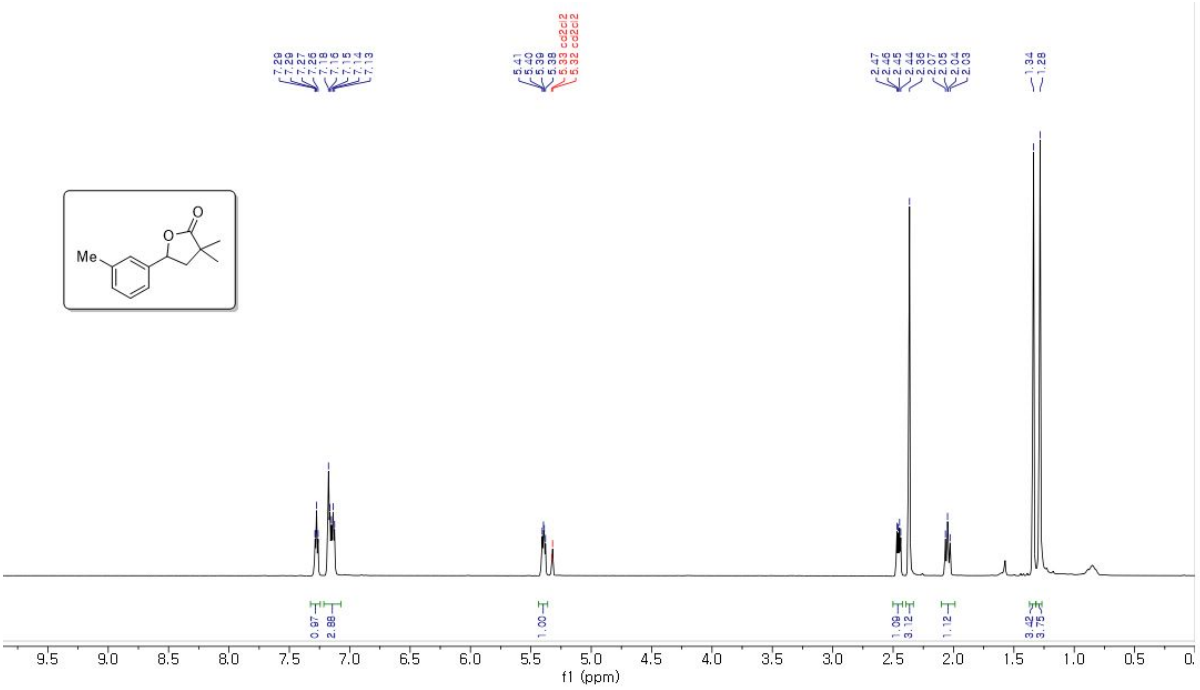


100 MHz, ^{13}C NMR in CD_2Cl_2

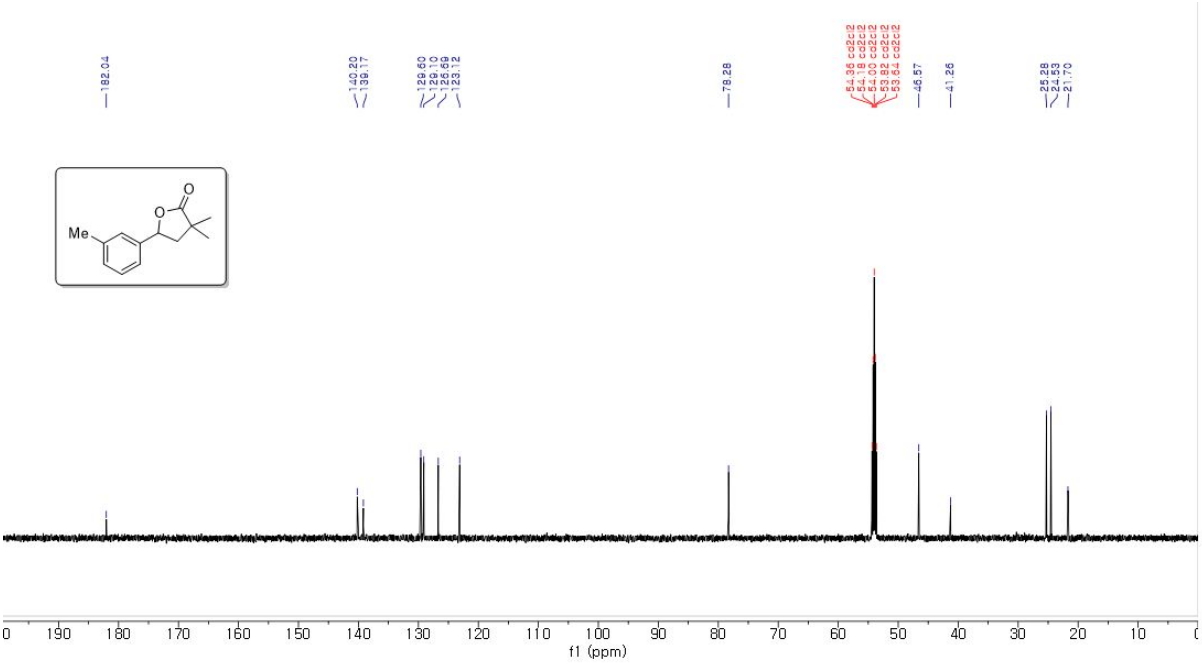


3,3-dimethyl-5-(m-tolyl)dihydrofuran-2(3H)-one (6f)

400 MHz, ^{1}H NMR in CD_2Cl_2

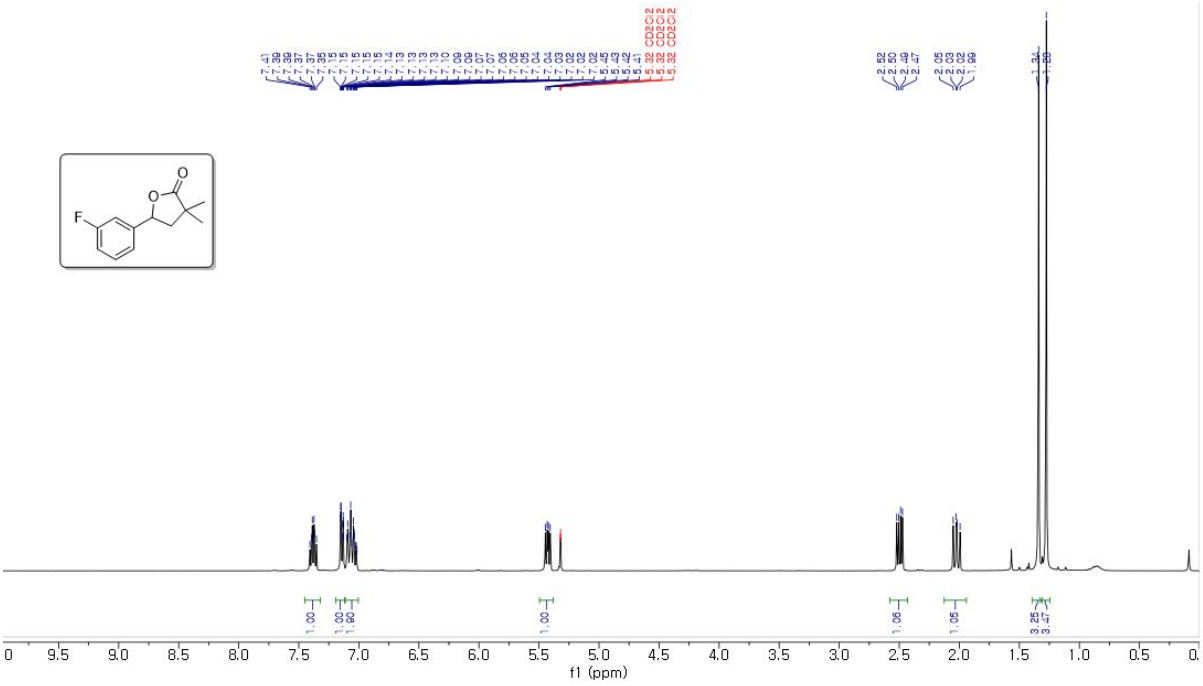


150 MHz, ^{13}C NMR in CD_2Cl_2

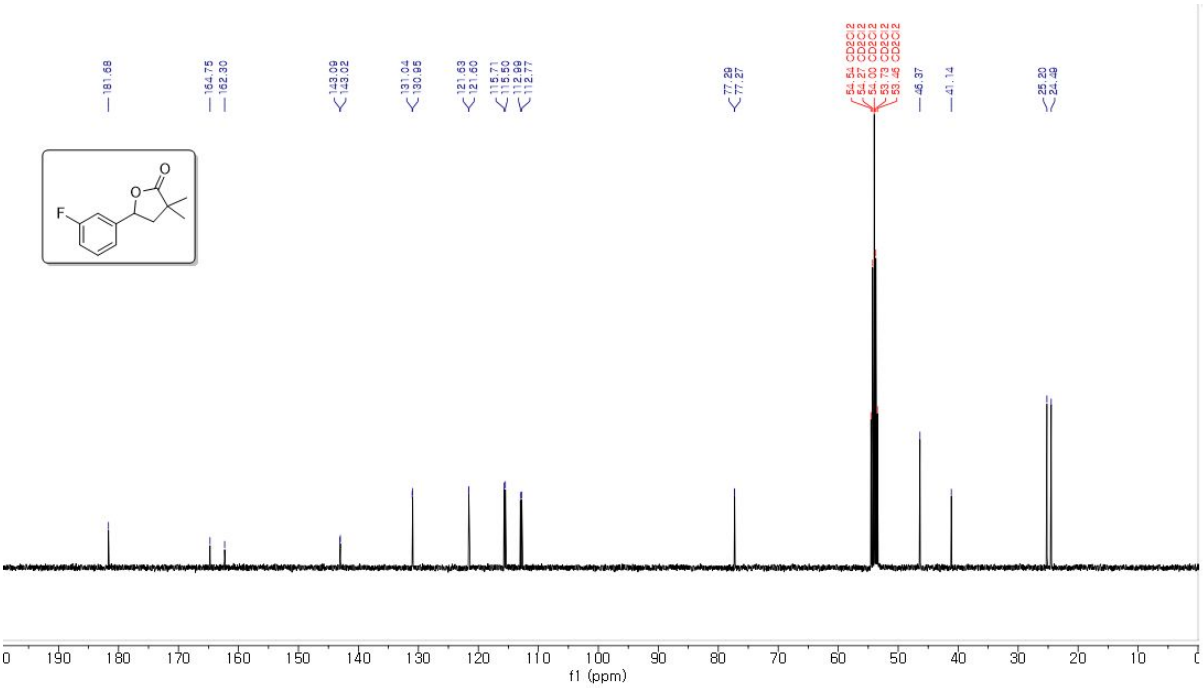


5-(3-fluorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6g)

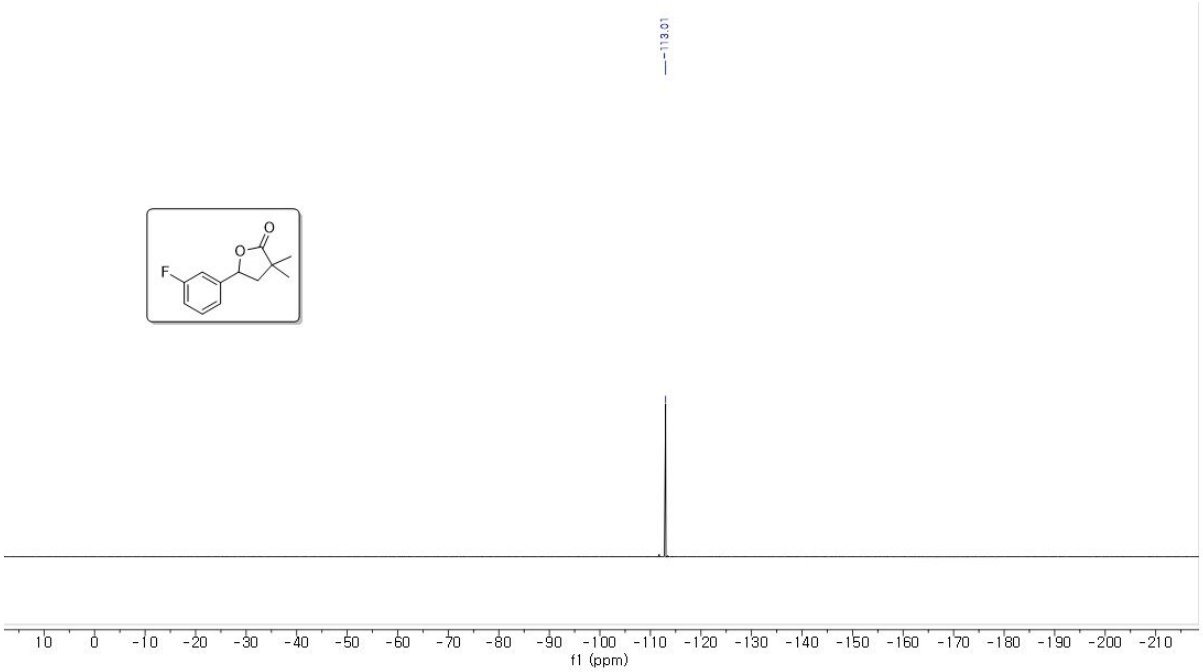
400 MHz, ^{1}H NMR in CD_2Cl_2



100 MHz, ^{13}C NMR in CD_2Cl_2

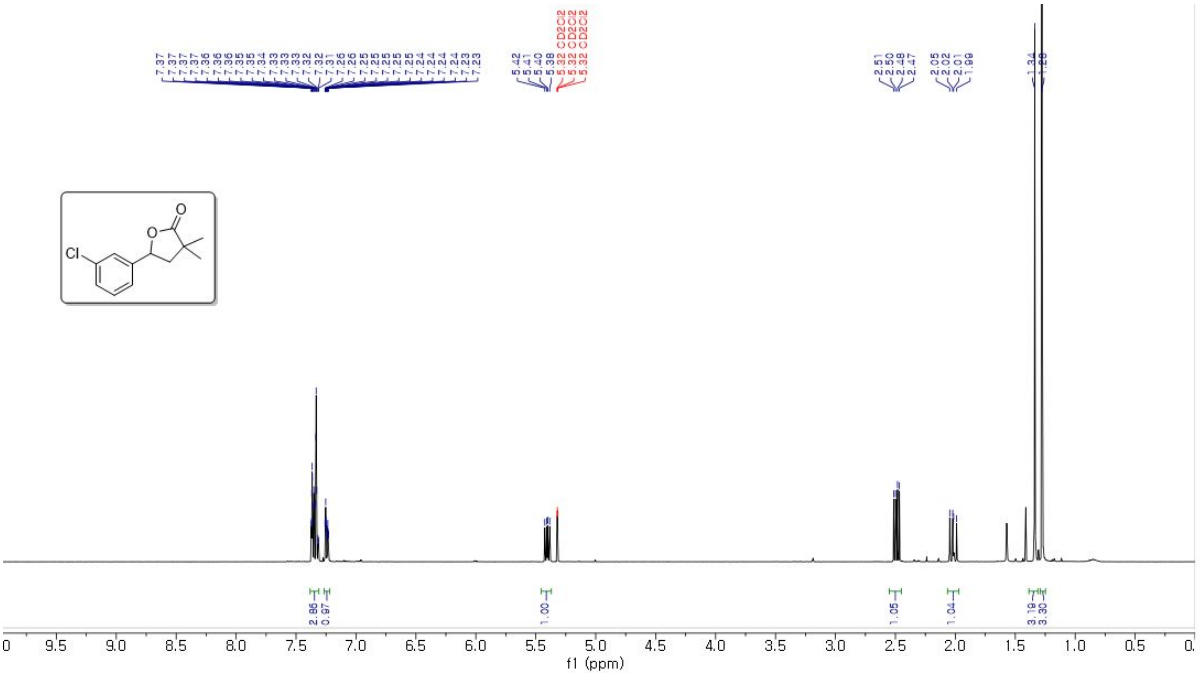


376 MHz, ^{19}F NMR in $CDCl_3$

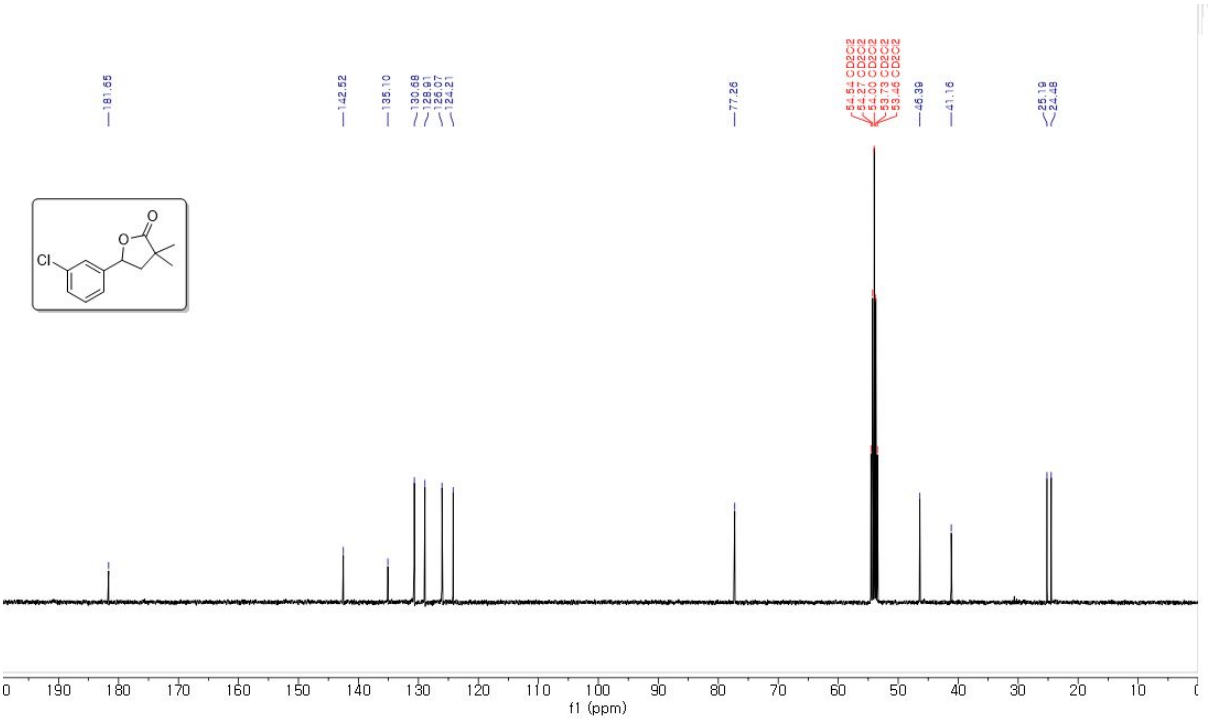


5-(3-chlorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6h)

400 MHz, ^{1}H NMR in CD_2Cl_2

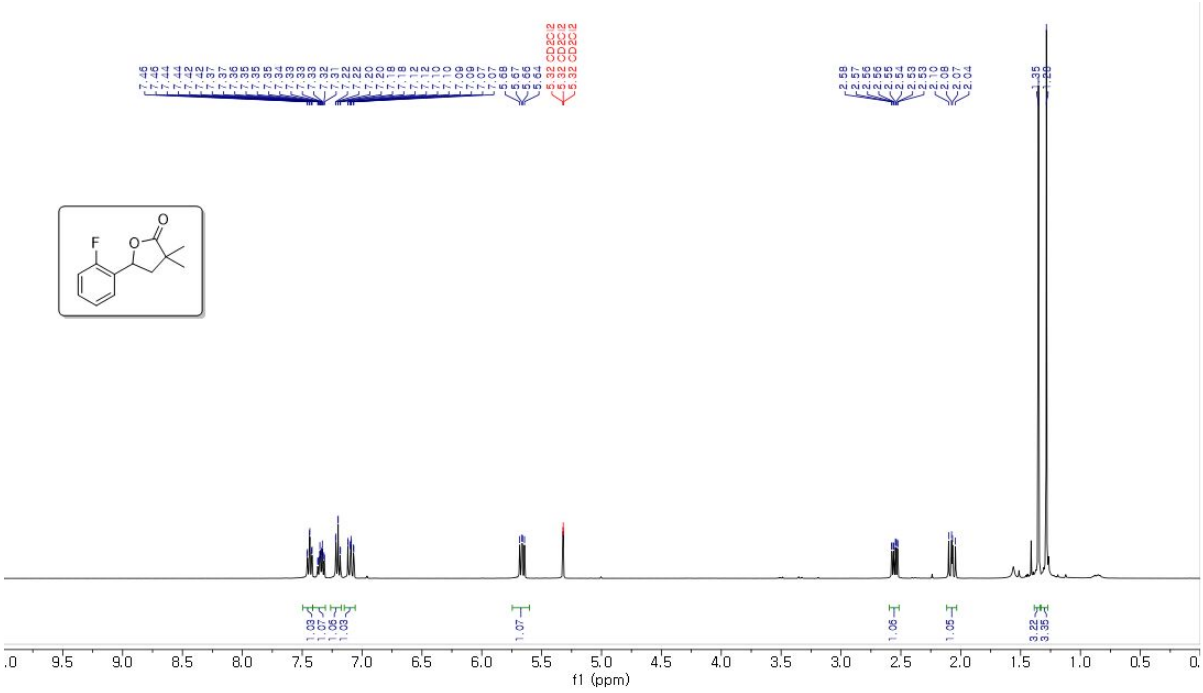


100 MHz, ^{13}C NMR in CD_2Cl_2

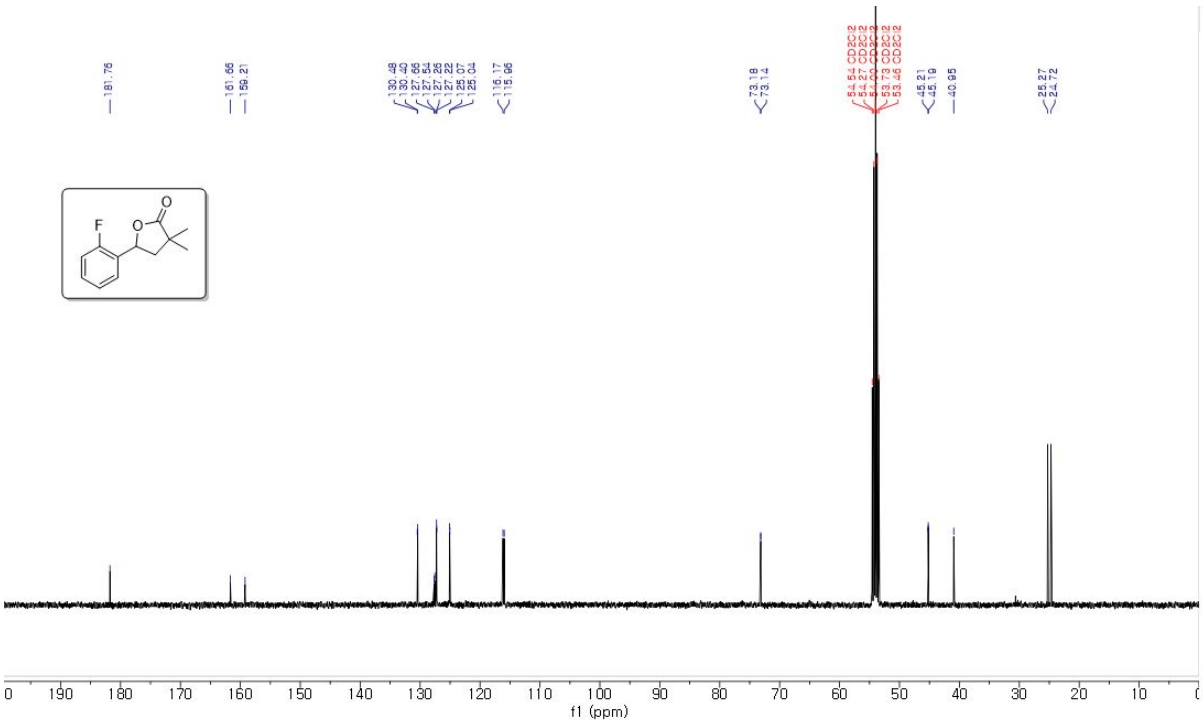


5-(2-fluorophenyl)-3,3-dimethyldihydrofuran-2(3H)-one (6i)

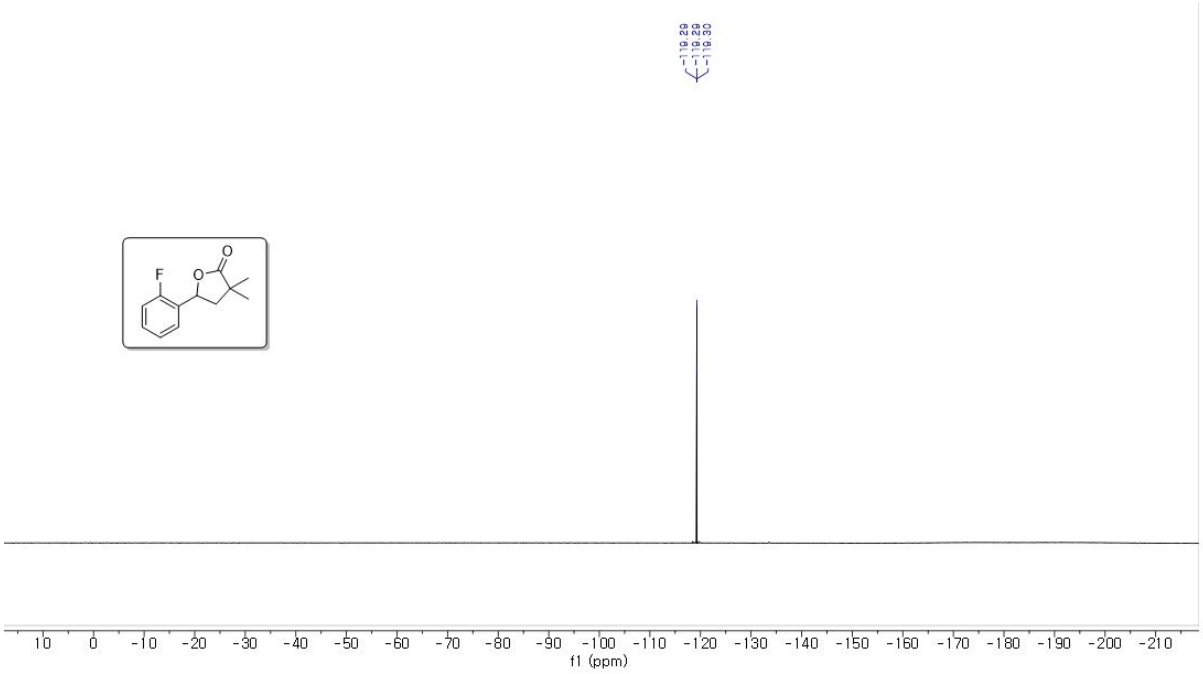
400 MHz, ^{1}H NMR in CD_2Cl_2



100 MHz, ^{13}C NMR in CD_2Cl_2

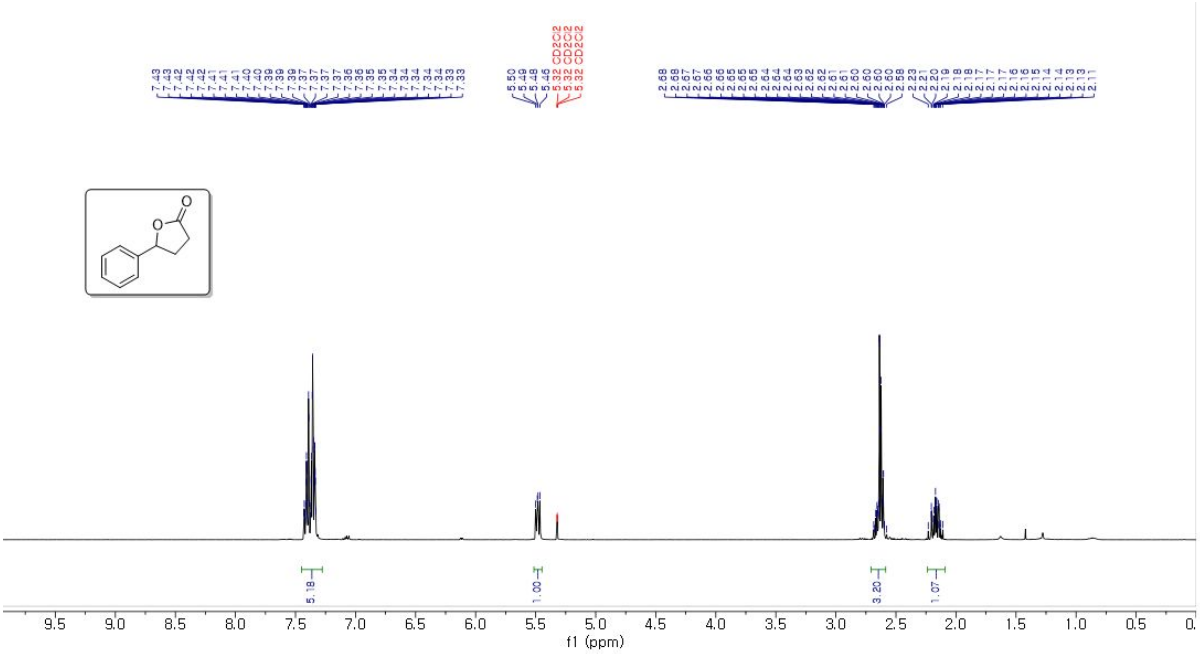


376 MHz, ^{19}F NMR in CD_2Cl_2

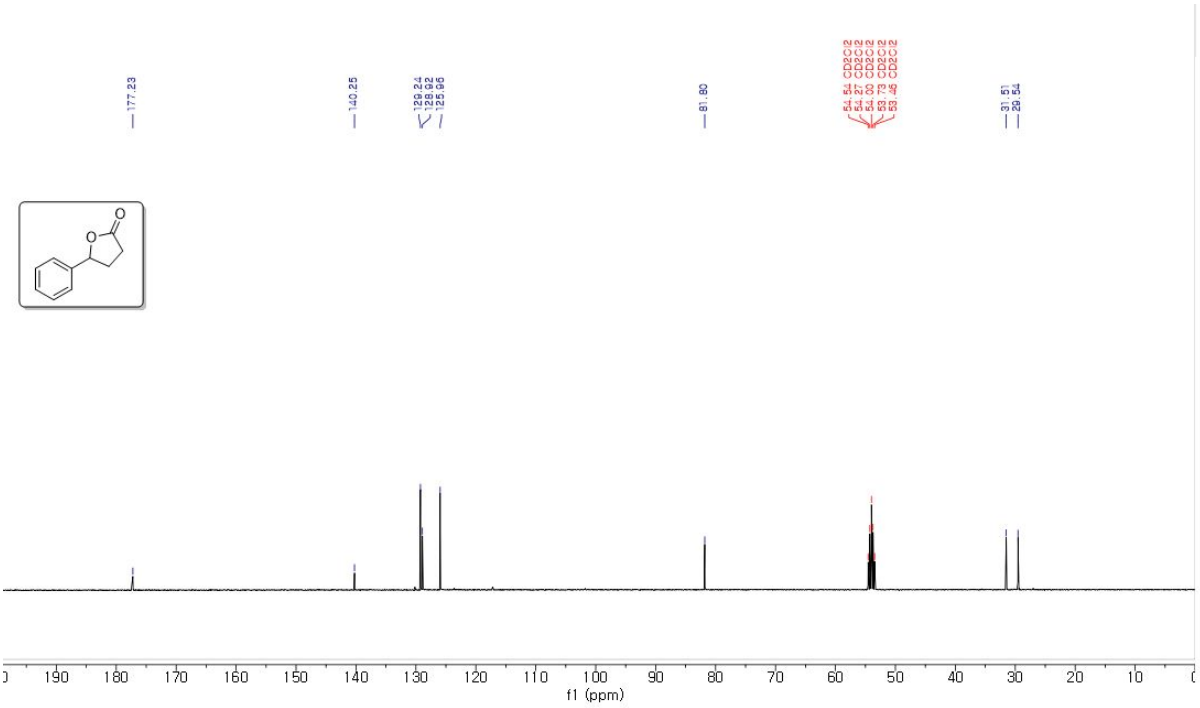


5-phenyldihydrofuran-2(3H)-one (6j)

400 MHz, ^{1}H NMR in CD_2Cl_2

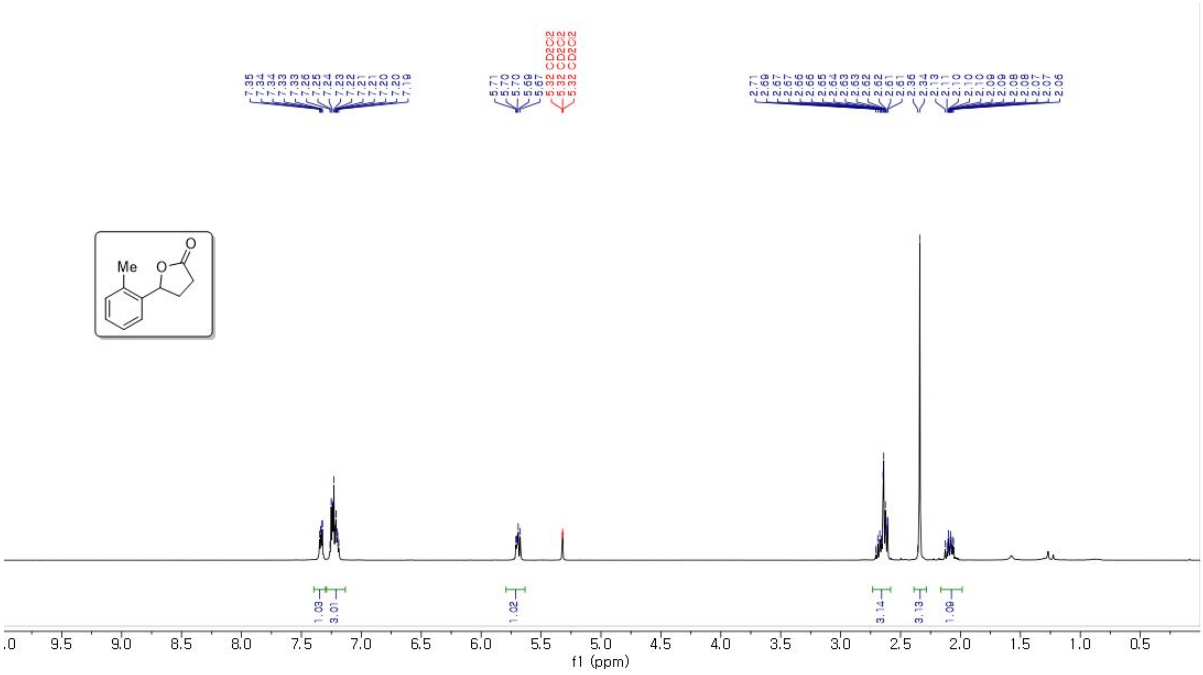


100 MHz, ^{13}C NMR in CD_2Cl_2

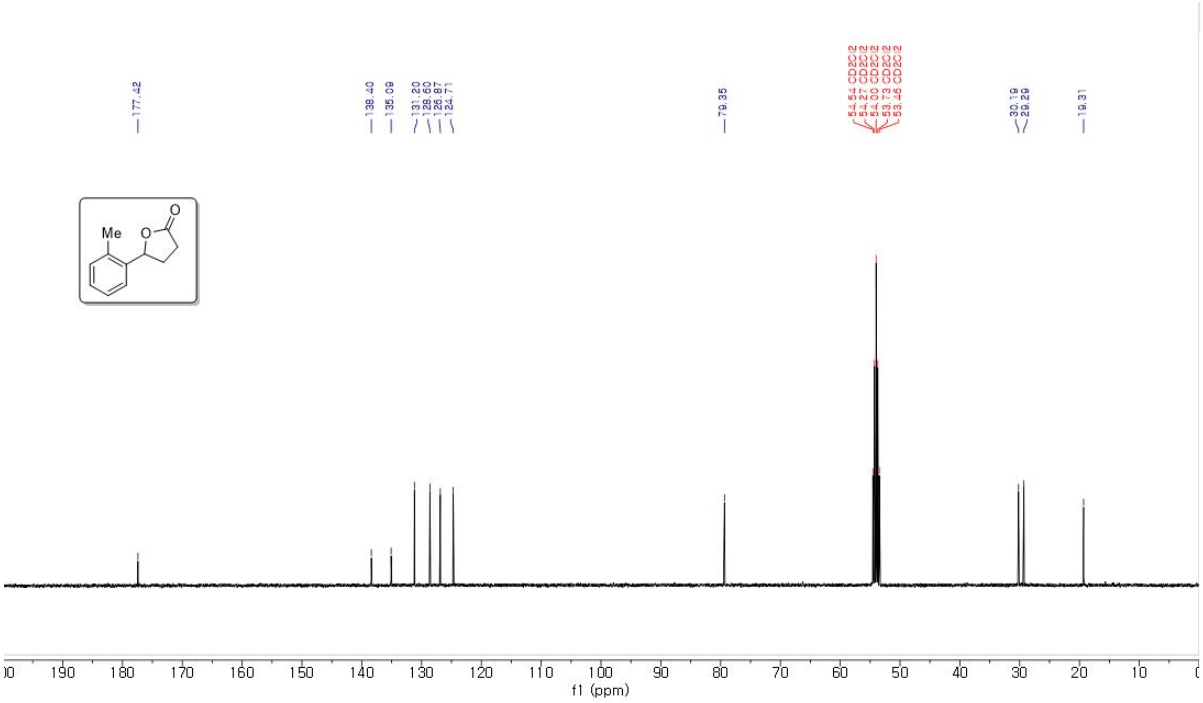


5-(o-tolyl)dihydrofuran-2(3H)-one (6k)

400 MHz, ^{1}H NMR in CD_2Cl_2

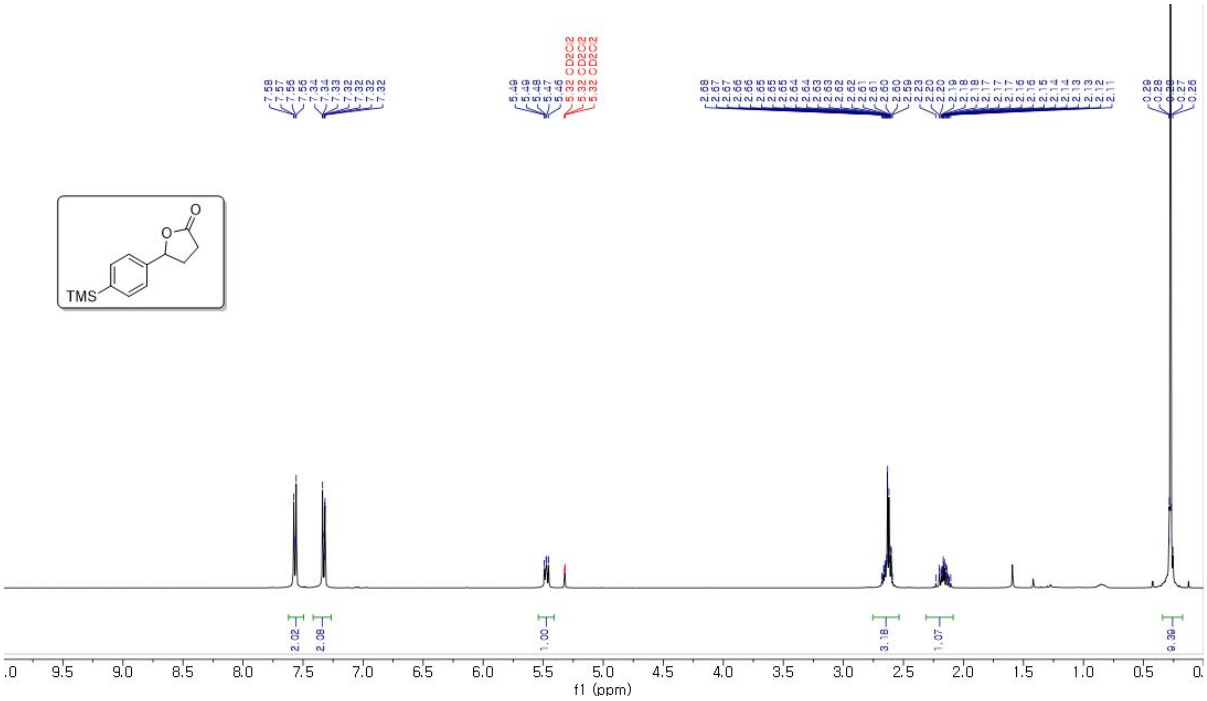


100 MHz, ^{13}C NMR in CD_2Cl_2

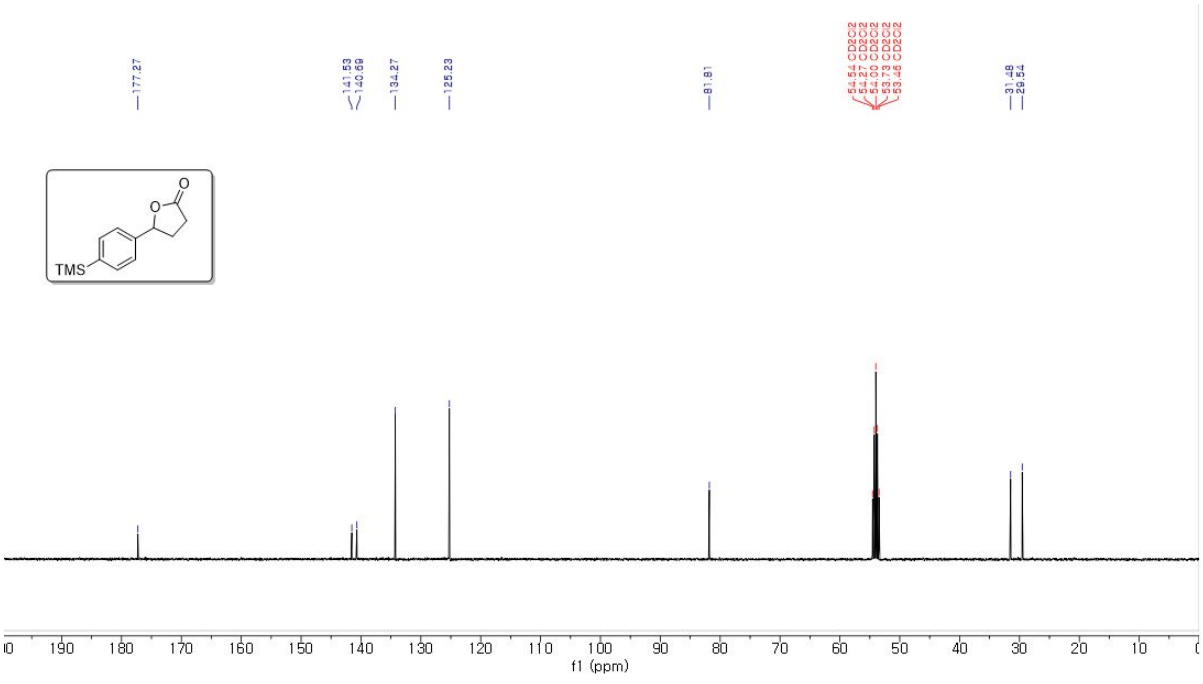


5-(4-(trimethylsilyl)phenyl)dihydrofuran-2(3H)-one (6l)

400 MHz, ^{1}H NMR in CD_2Cl_2

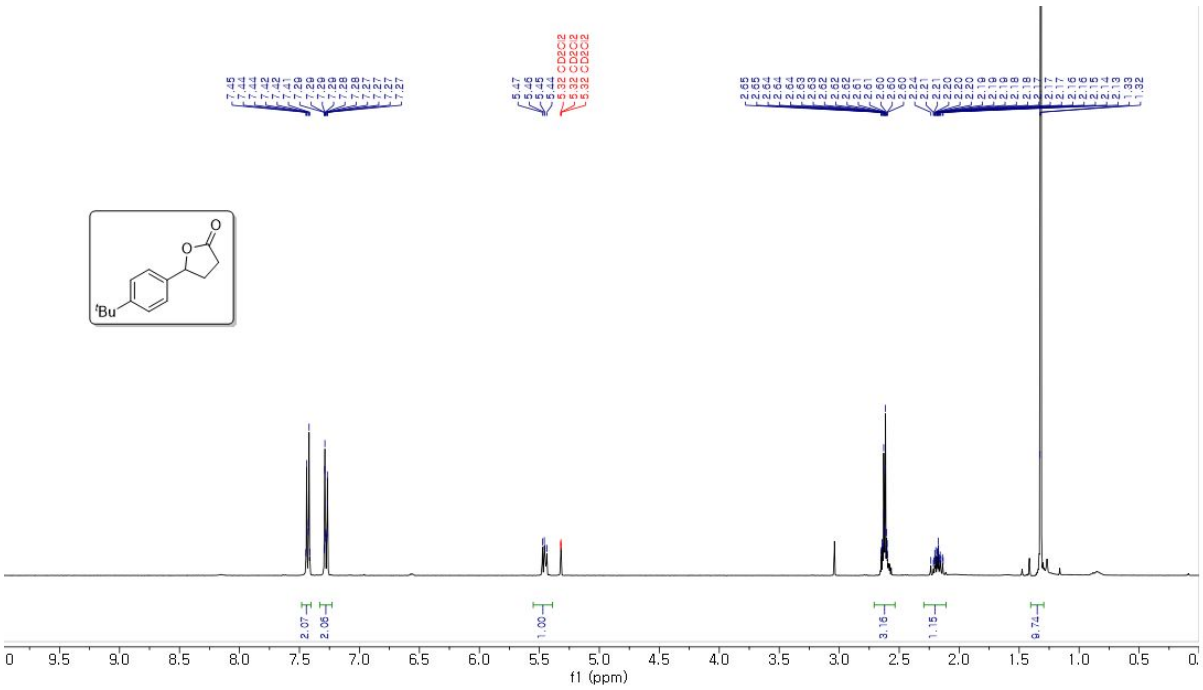


100 MHz, ^{13}C NMR in CD_2Cl_2

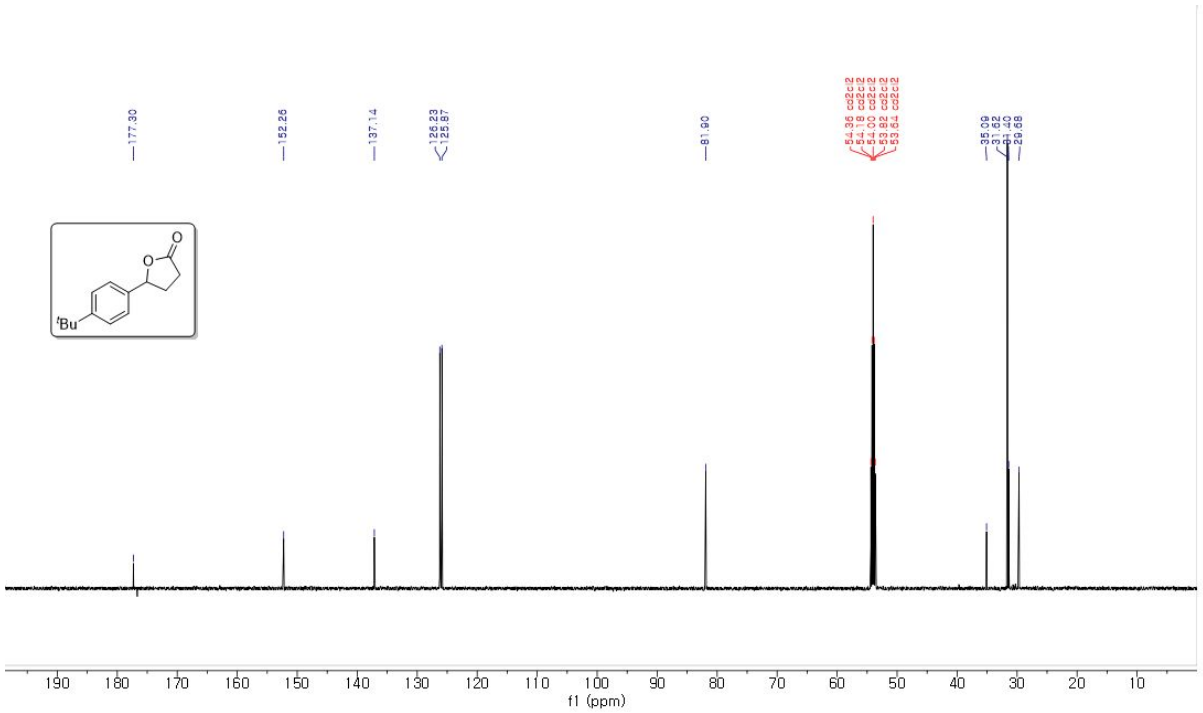


5-(4-(tert-butyl)phenyl)dihydrofuran-2(3H)-one (6m)

400 MHz, ^{1}H NMR in CD_2Cl_2

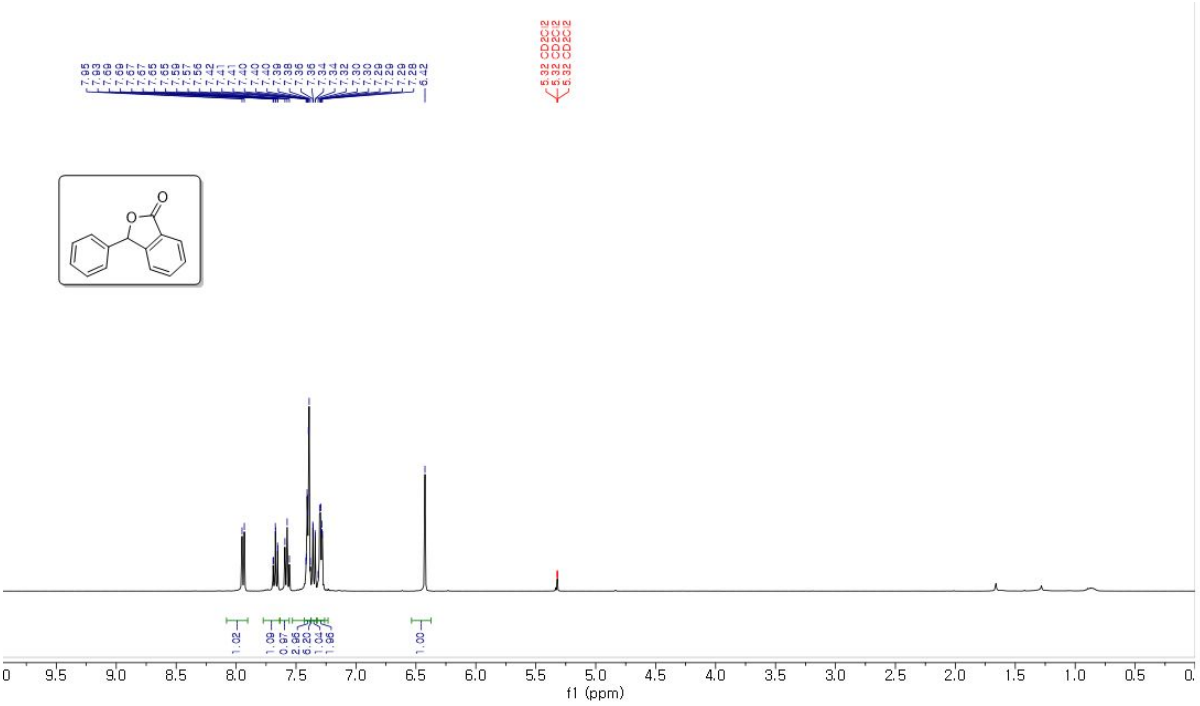


150 MHz, ^{13}C NMR in CD_2Cl_2

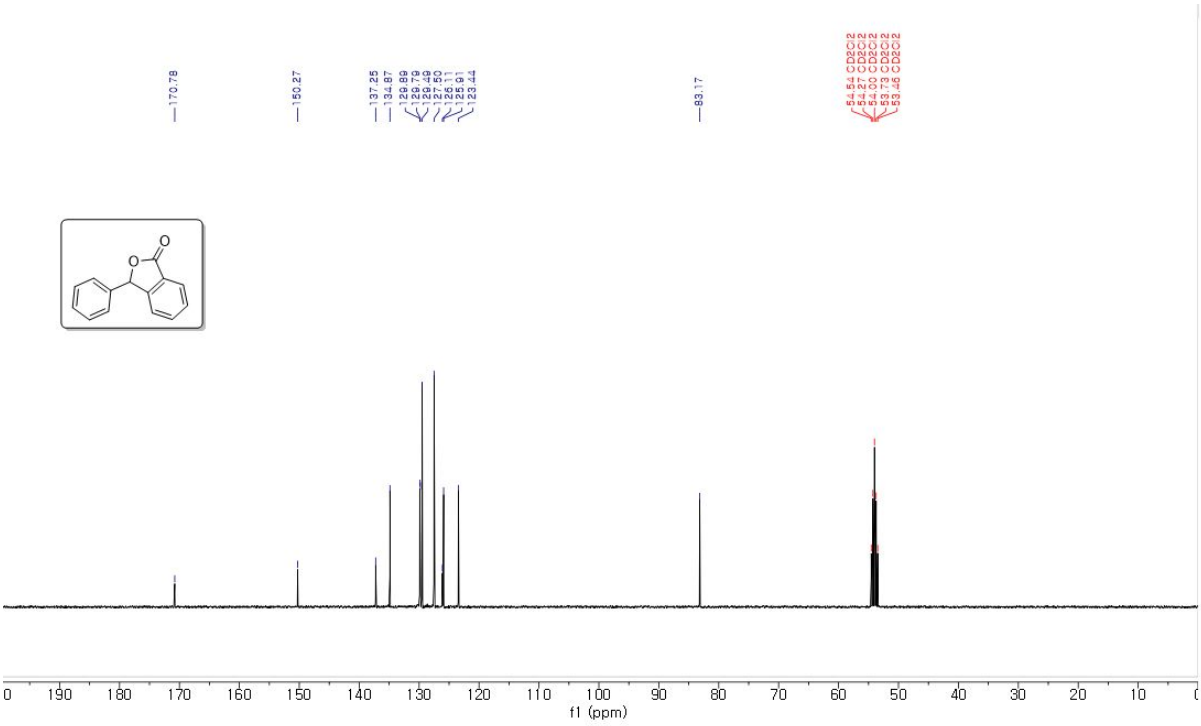


3-phenylisobenzofuran-1(3H)-one (6n)

400 MHz, ^{1}H NMR in CD_2Cl_2

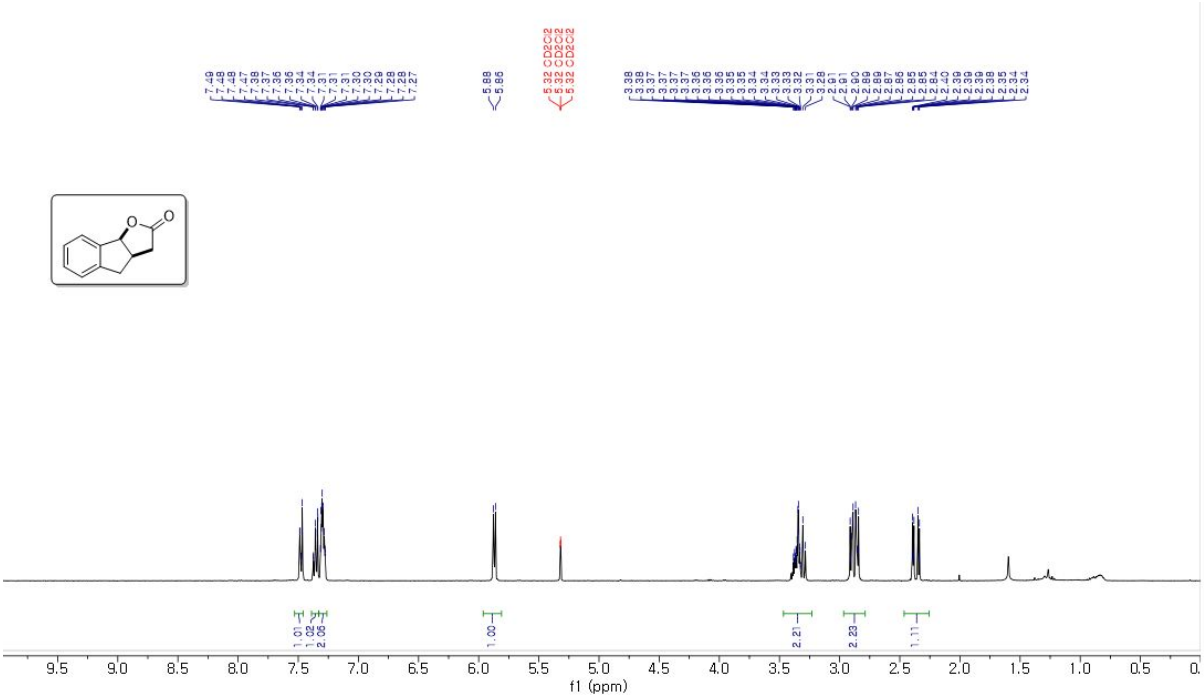


100 MHz, ^{13}C NMR in CD_2Cl_2

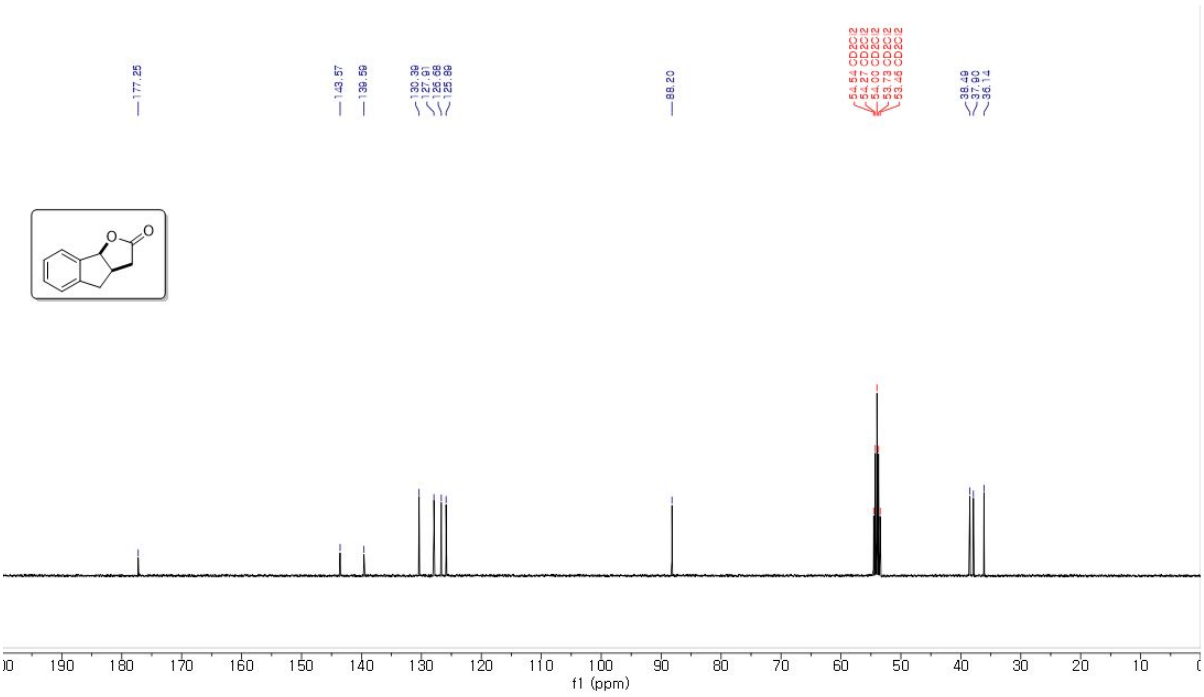


3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan-2-one (6o)

400 MHz, ^{1}H NMR in CD_2Cl_2

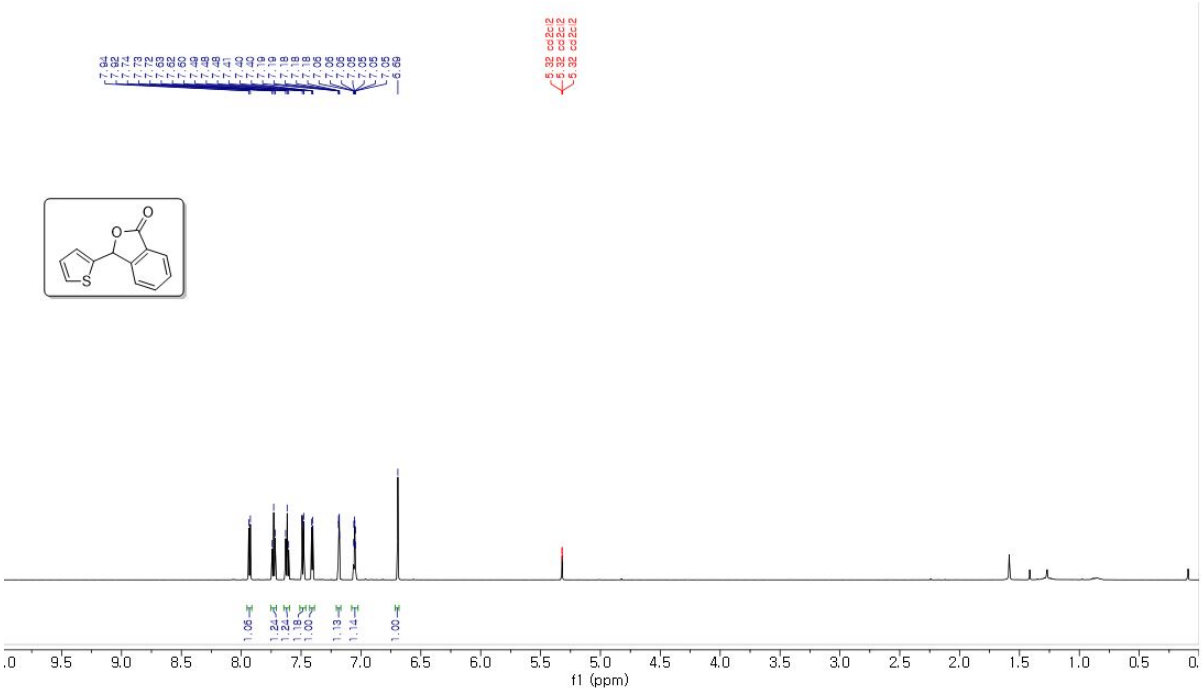


100 MHz, ^{13}C NMR in CD_2Cl_2

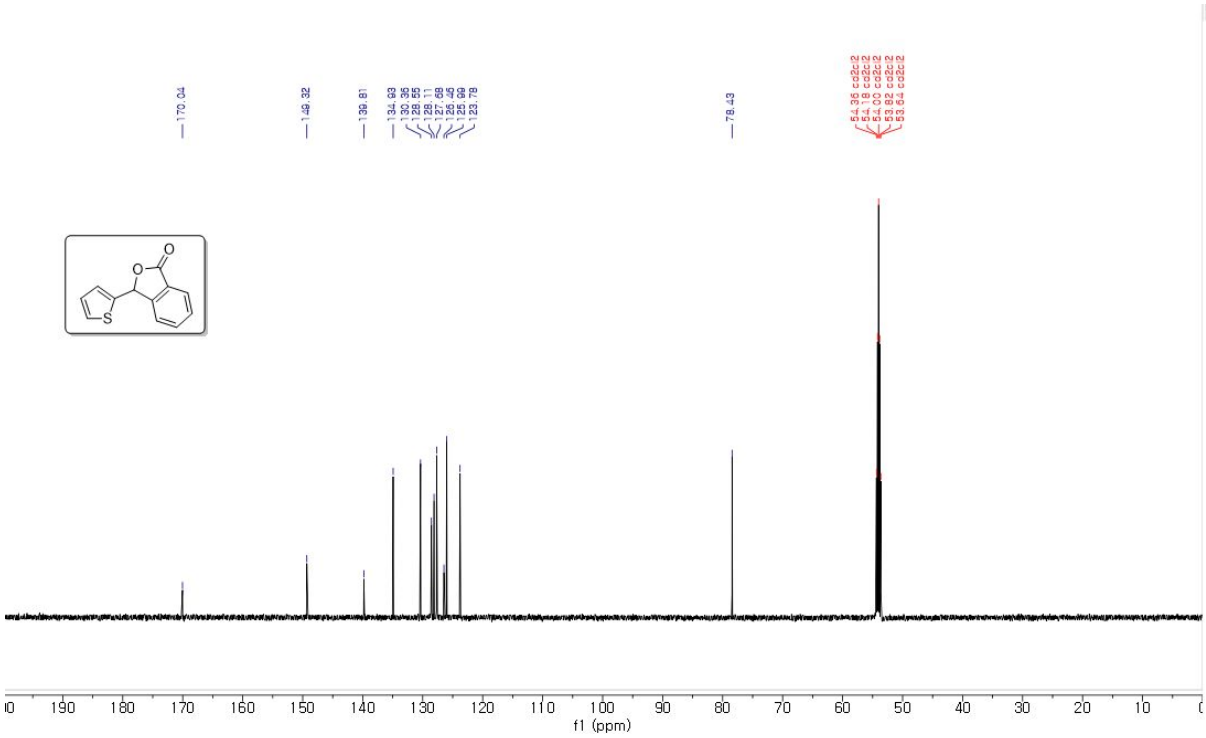


3-(thiophen-2-yl)isobenzofuran-1(3H)-one (6p)

600 MHz, ^{1}H NMR in CD_2Cl_2

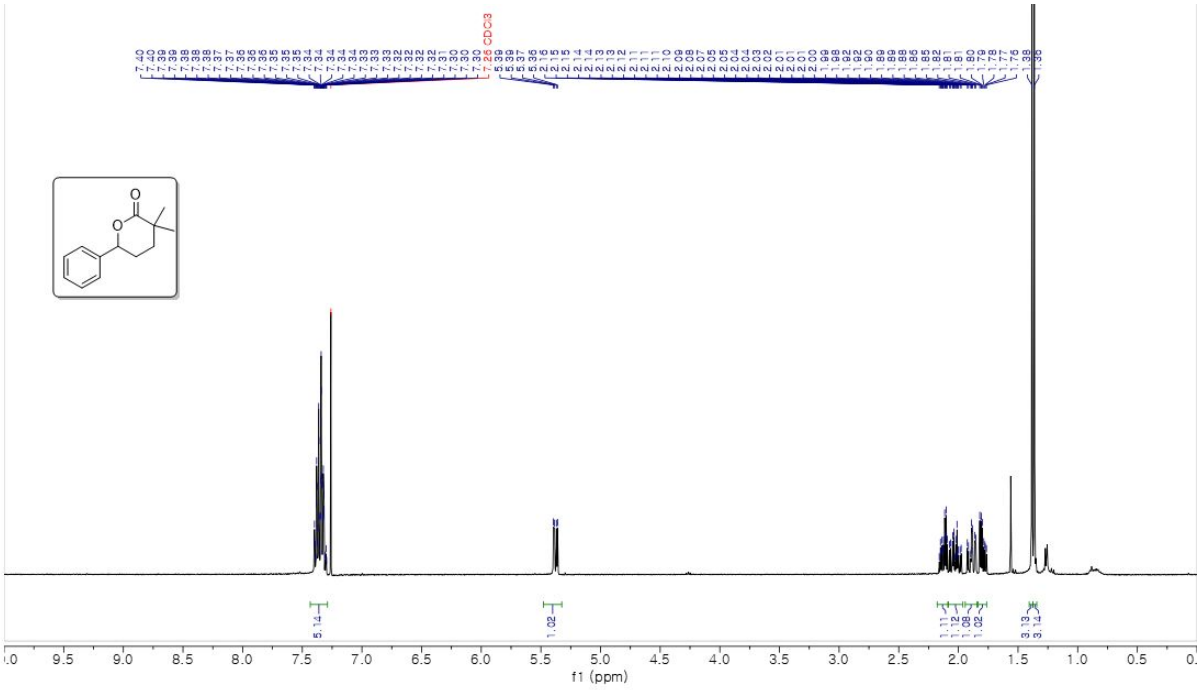


150 MHz, ^{13}C NMR in CD_2Cl_2

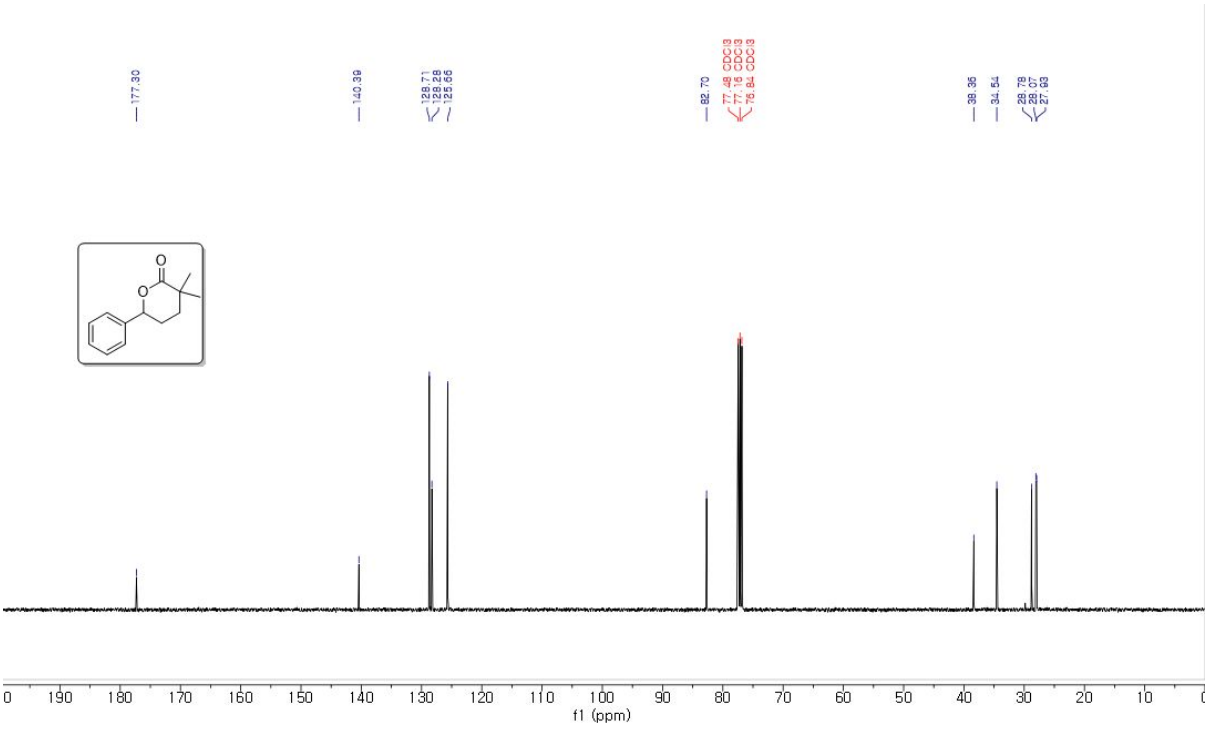


3,3-dimethyl-6-phenyltetrahydro-2H-pyran-2-one (6q)

400 MHz, ^{1}H NMR in $CDCl_3$

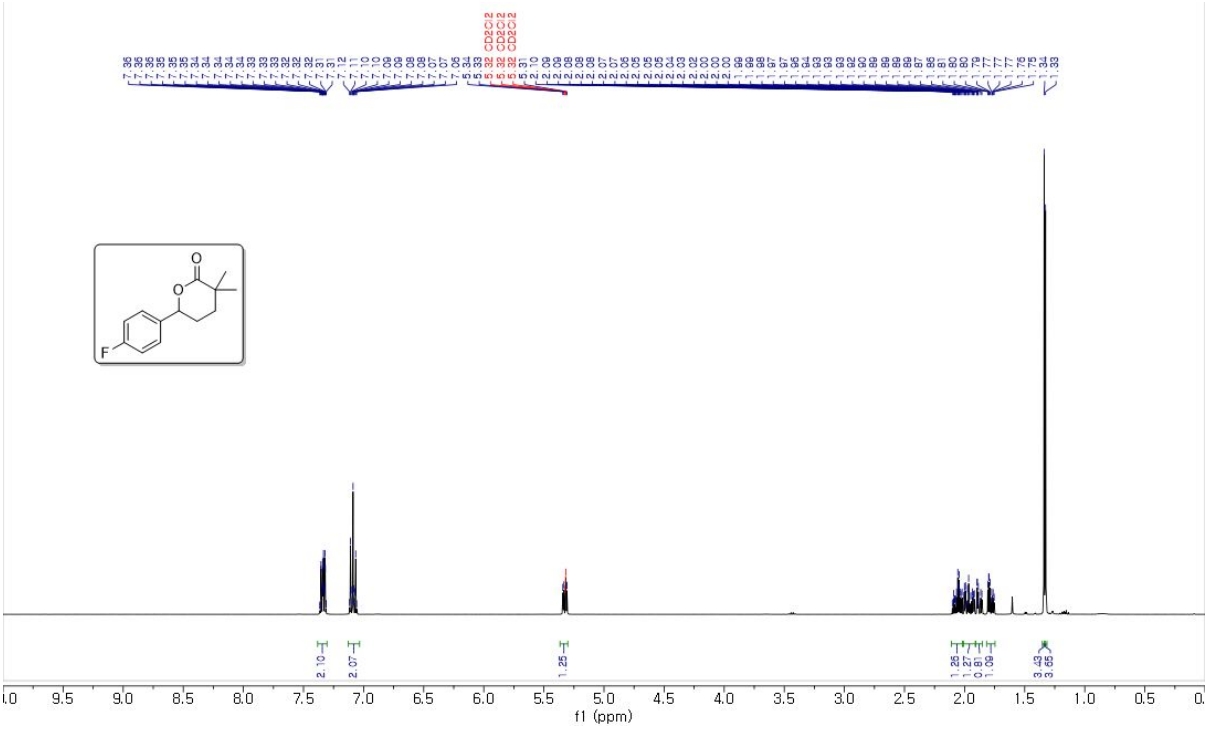


100 MHz, ^{13}C NMR in $CDCl_3$

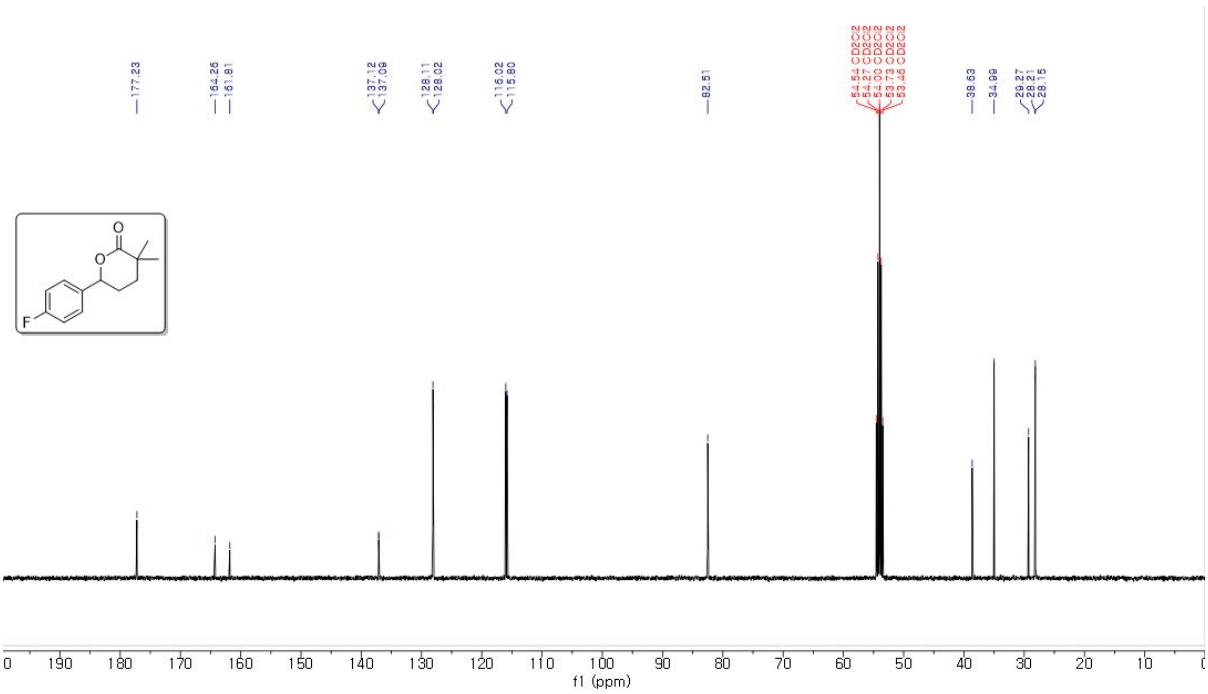


6-(4-fluorophenyl)-3,3-dimethyltetrahydro-2H-pyran-2-one (6r)

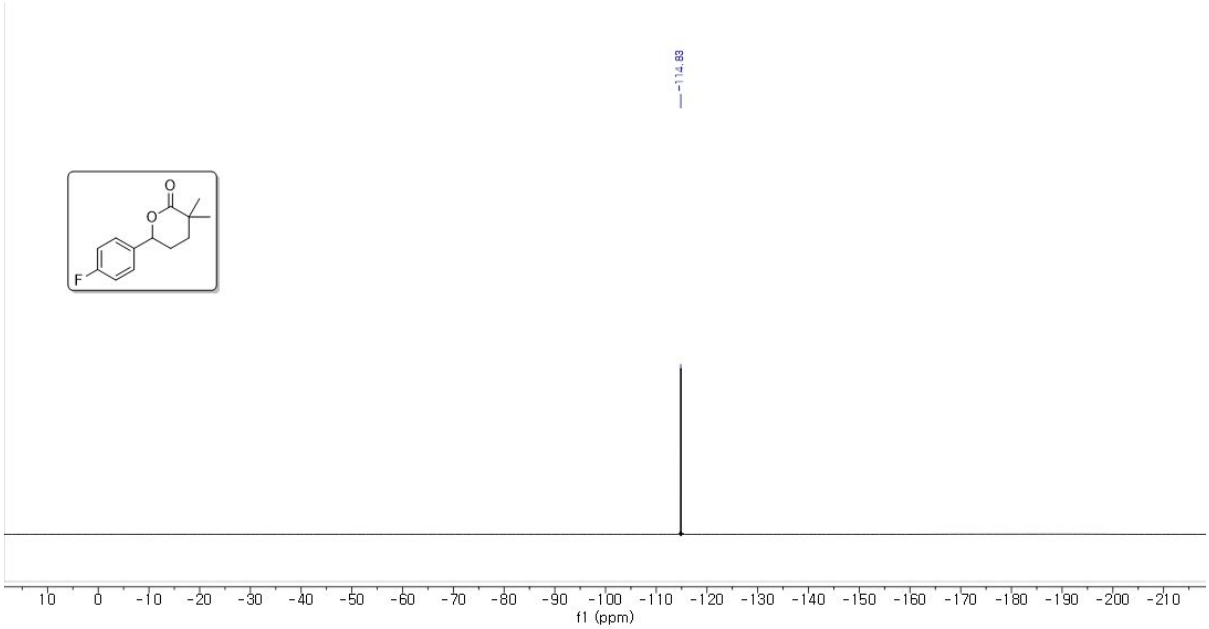
400 MHz, ^{1}H NMR in CD_2Cl_2



100 MHz, ^{13}C NMR in CD_2Cl_2

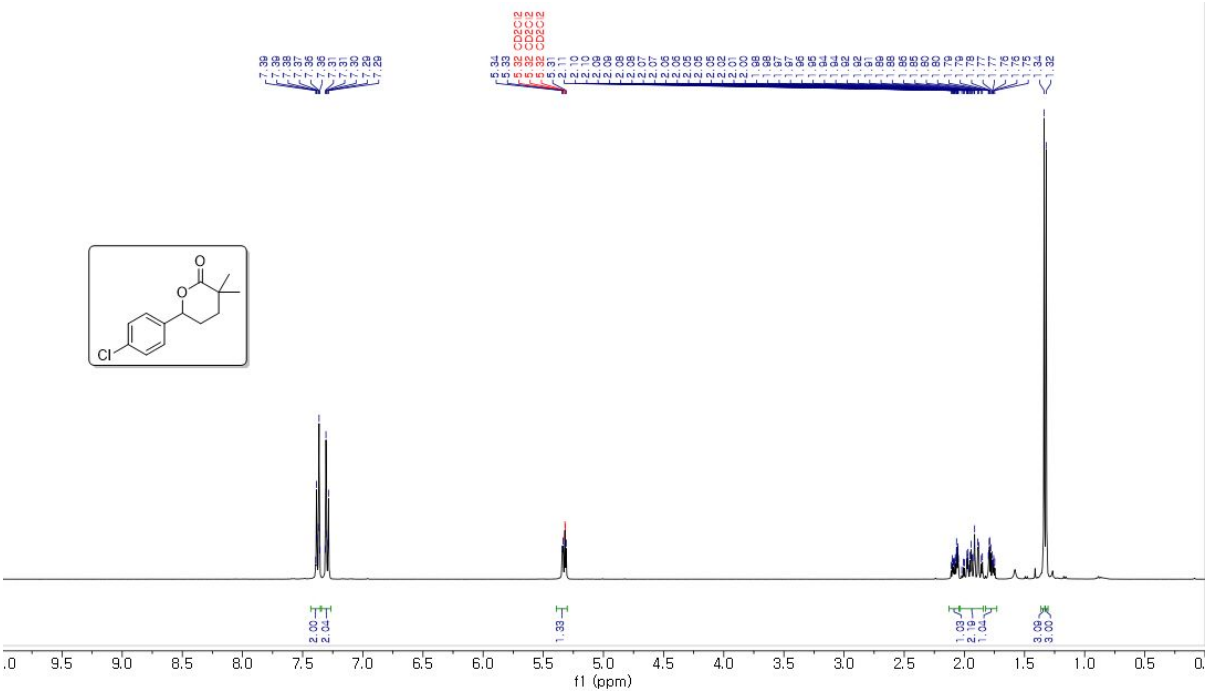


376 MHz, ^{19}F NMR in CD_2Cl_2

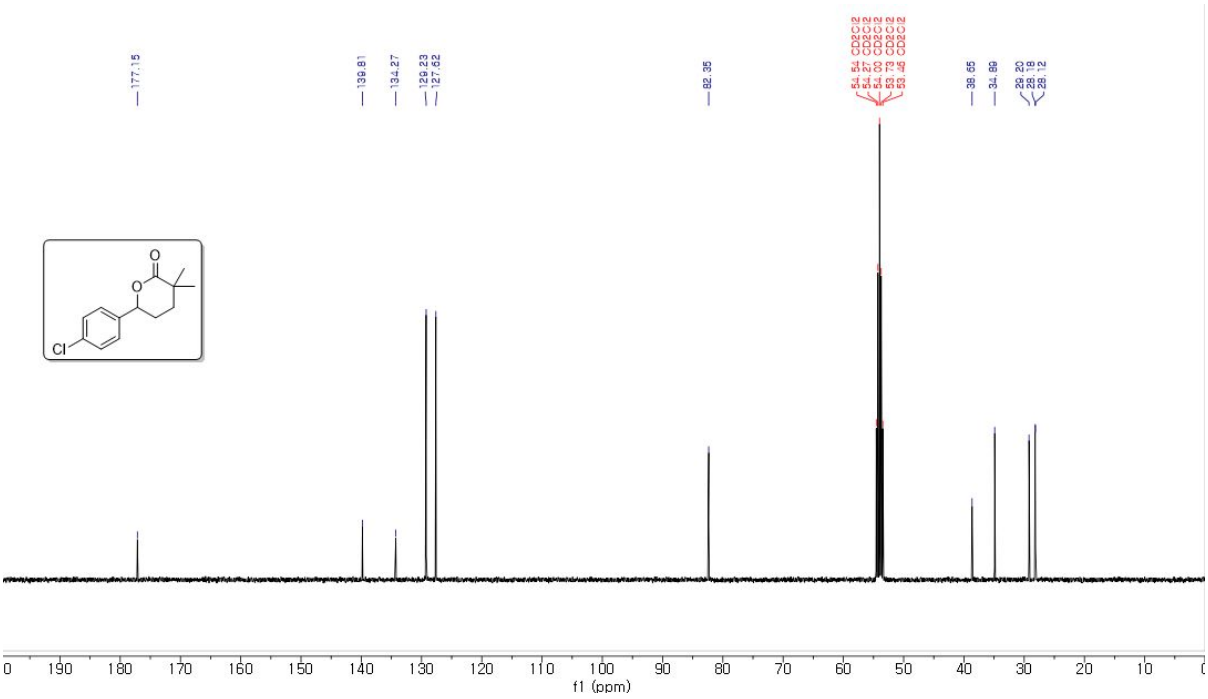


6-(4-chlorophenyl)-3,3-dimethyltetrahydro-2H-pyran-2-one (6s)

400 MHz, ^{1}H NMR in CD_2Cl_2

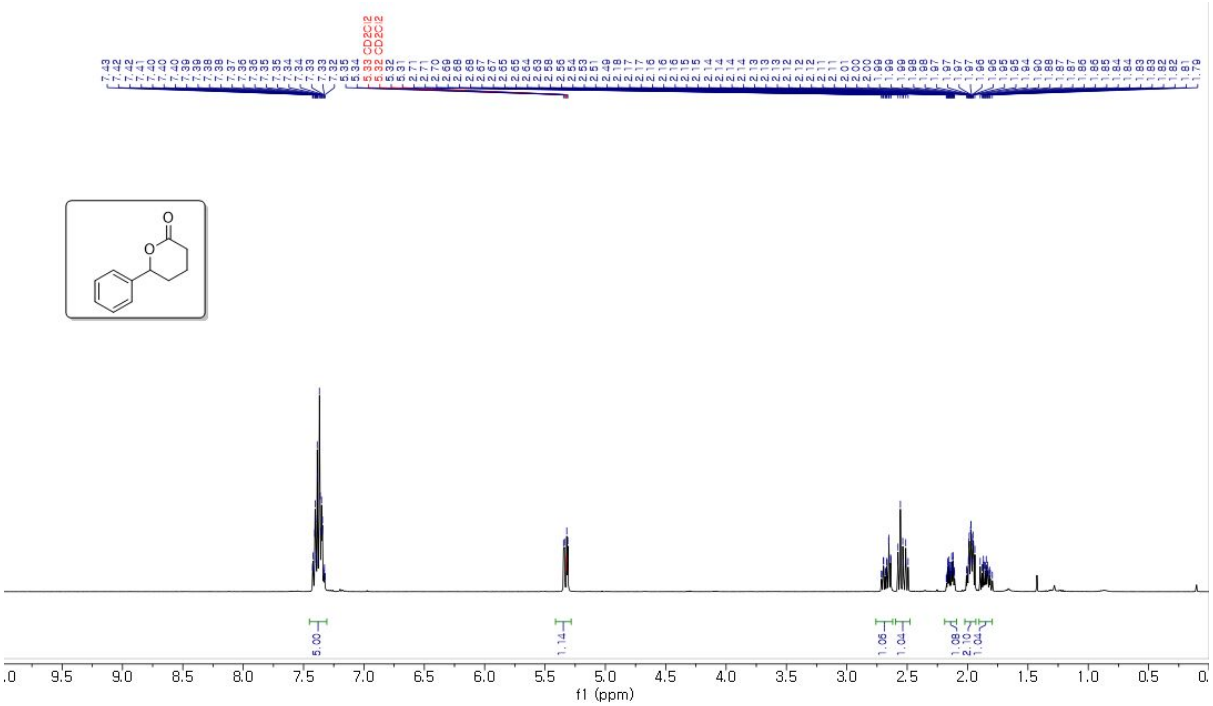


100 MHz, ^{13}C NMR in CD_2Cl_2

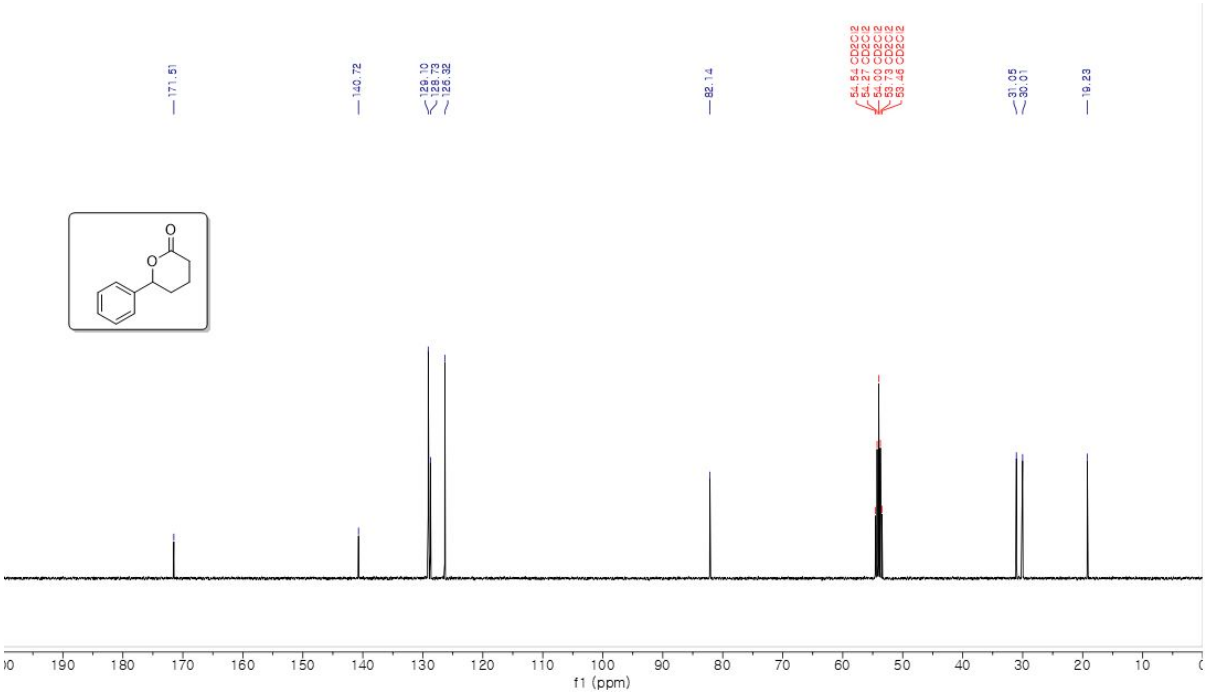


6-phenyltetrahydro-2H-pyran-2-one (6t)

400 MHz, ^{1}H NMR in CD_2Cl_2

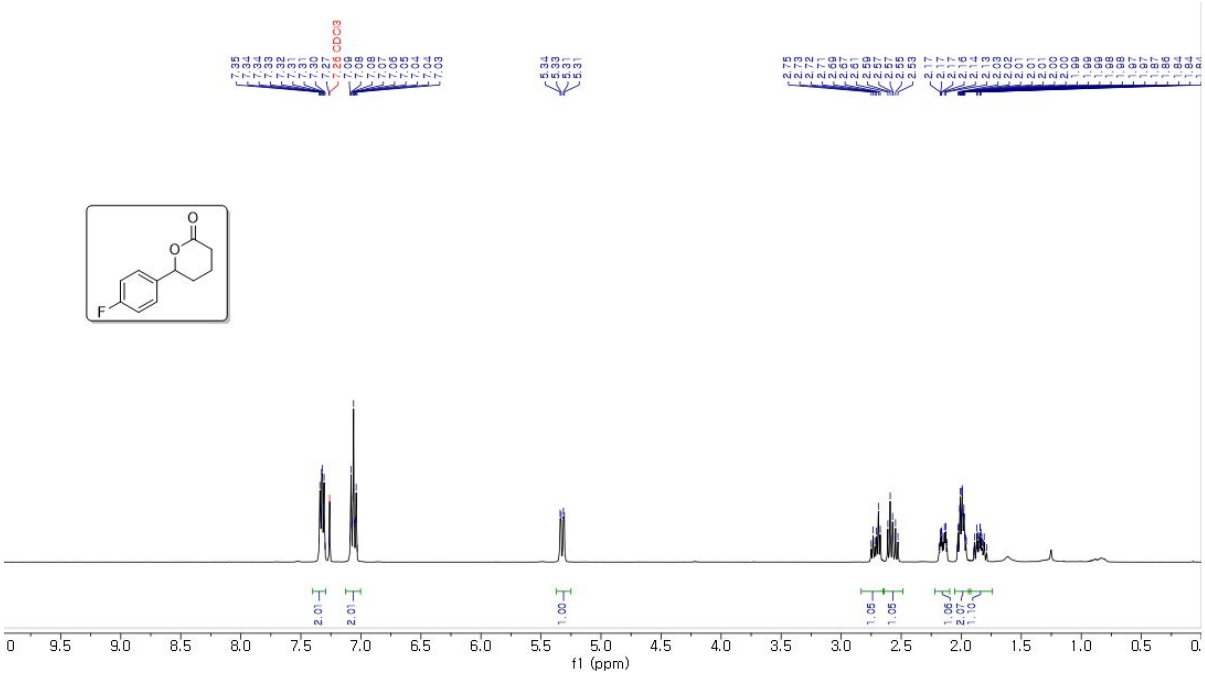


100 MHz, ^{13}C NMR in CD_2Cl_2

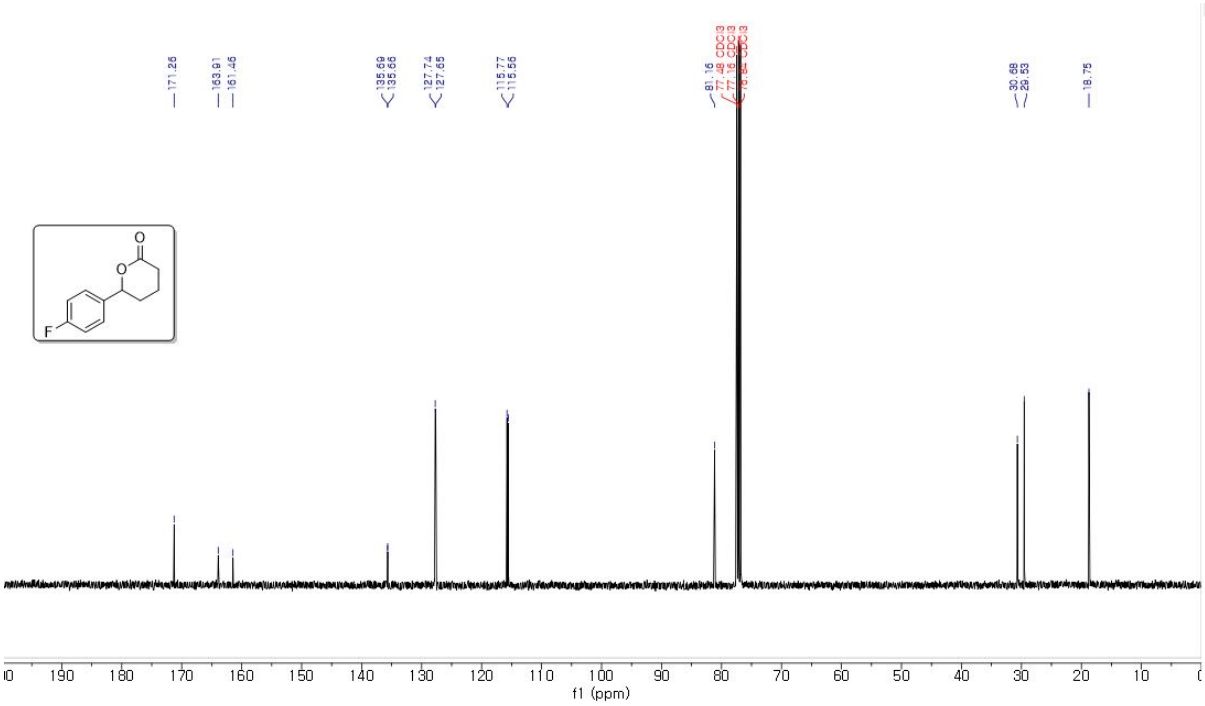


6-(4-fluorophenyl)tetrahydro-2H-pyran-2-one (6u)

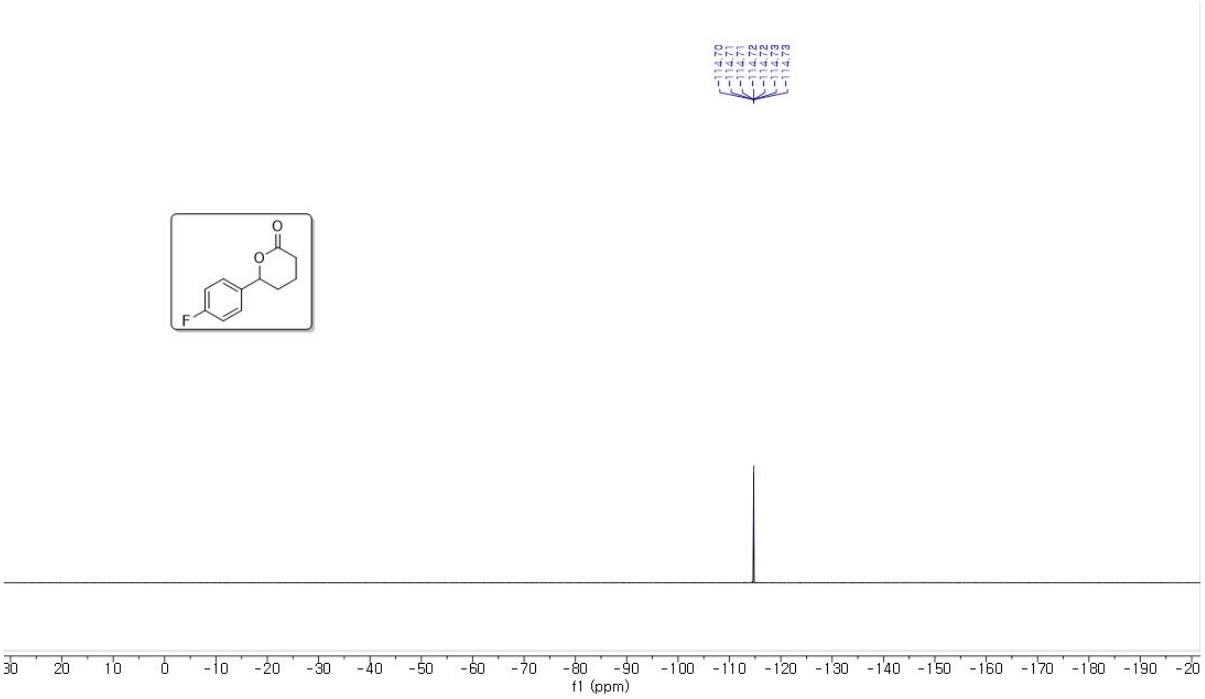
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

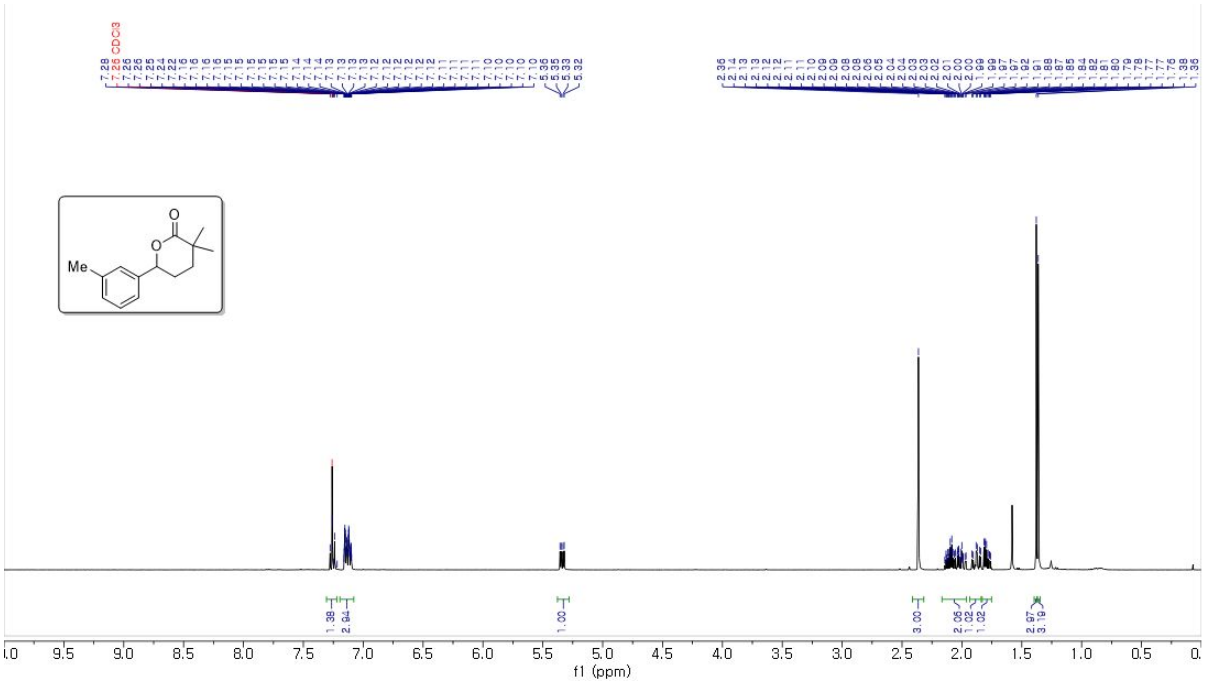


564 MHz, ^{19}F NMR in CD_2Cl_2

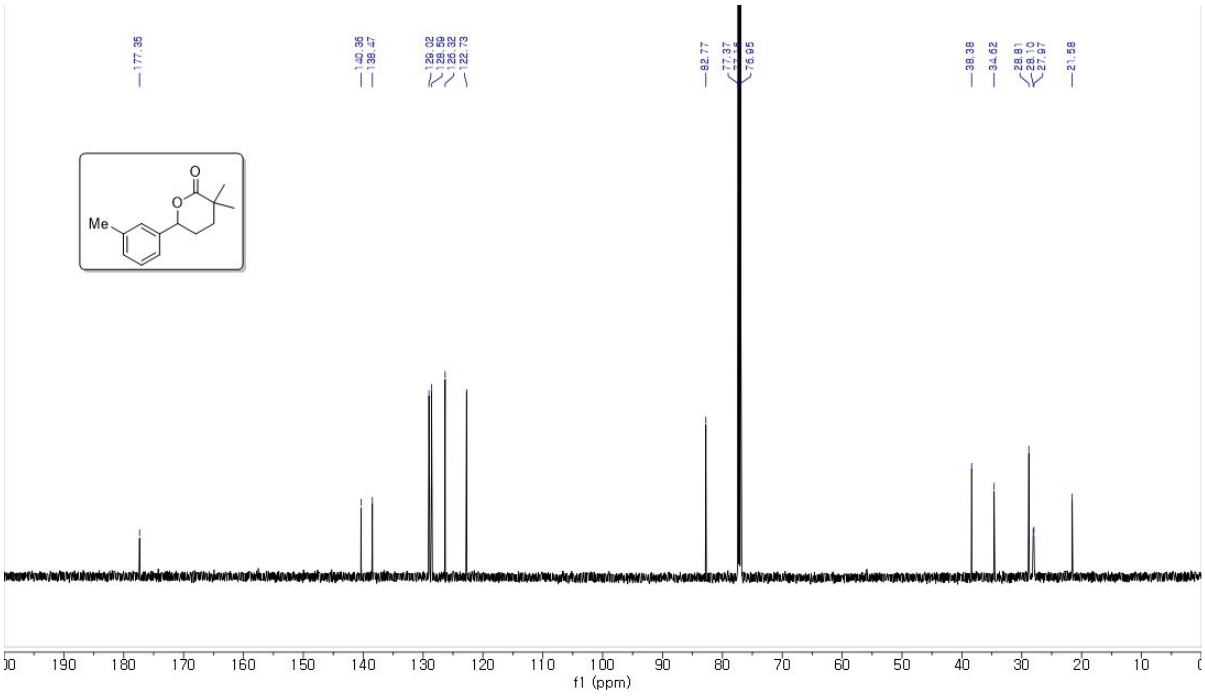


3,3-dimethyl-6-(m-tolyl)tetrahydro-2H-pyran-2-one (6v)

400 MHz, ^{1}H NMR in $CDCl_3$

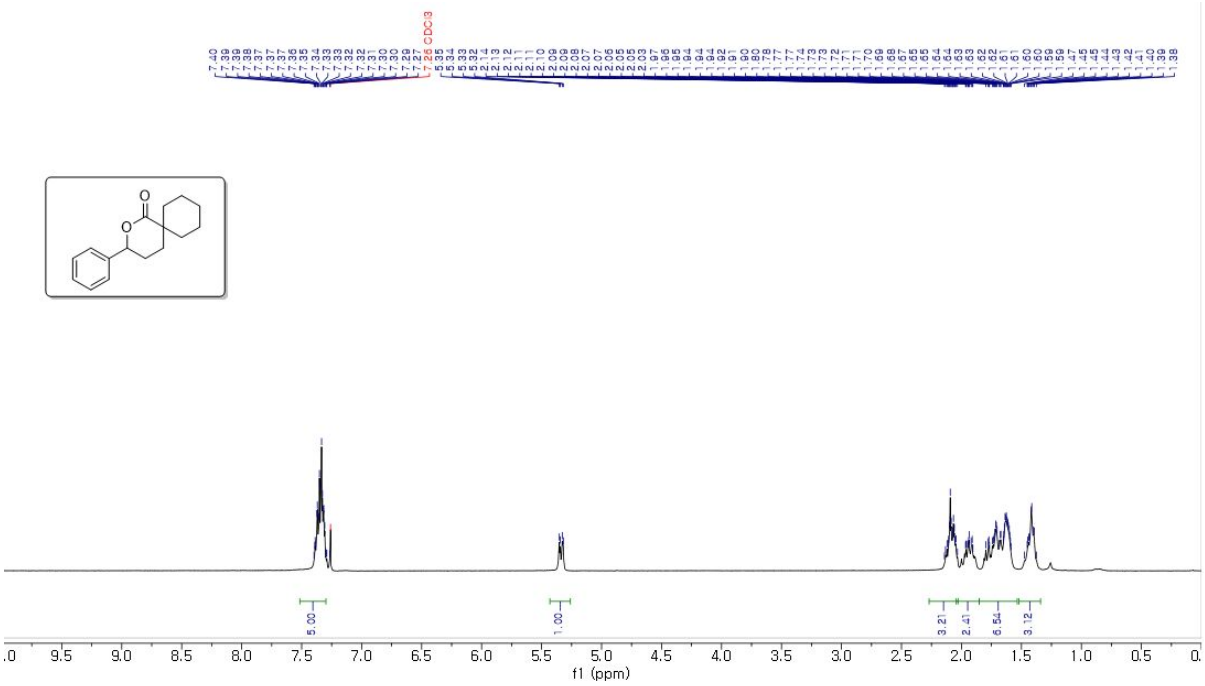


150 MHz, ^{13}C NMR in $CDCl_3$

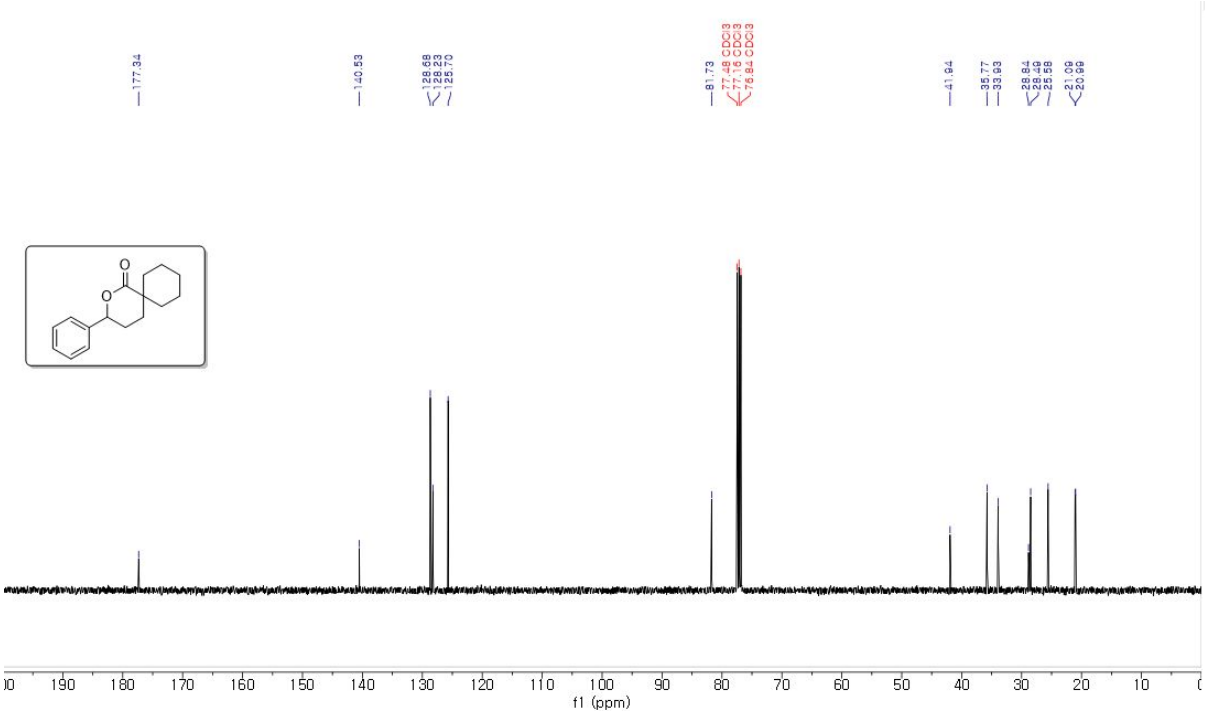


3-phenyl-2-oxaspiro[5.5]undecan-1-one (6w)

400 MHz, ^{1}H NMR in $CDCl_3$

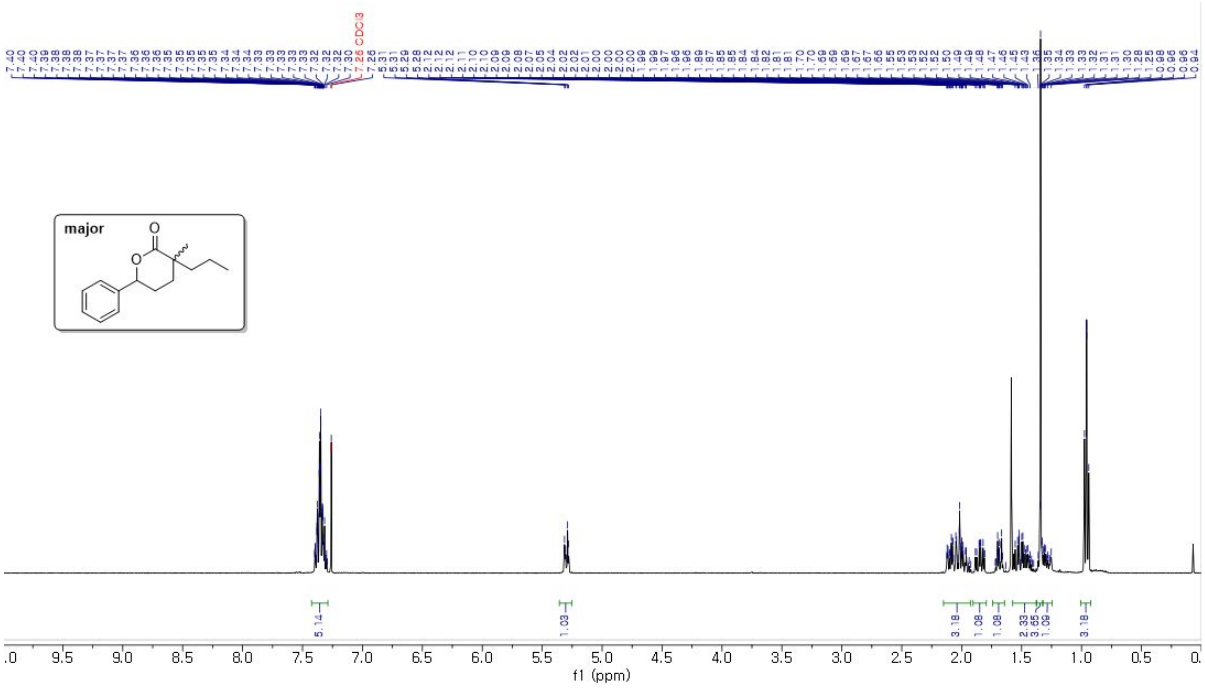


100 MHz, ^{13}C NMR in $CDCl_3$

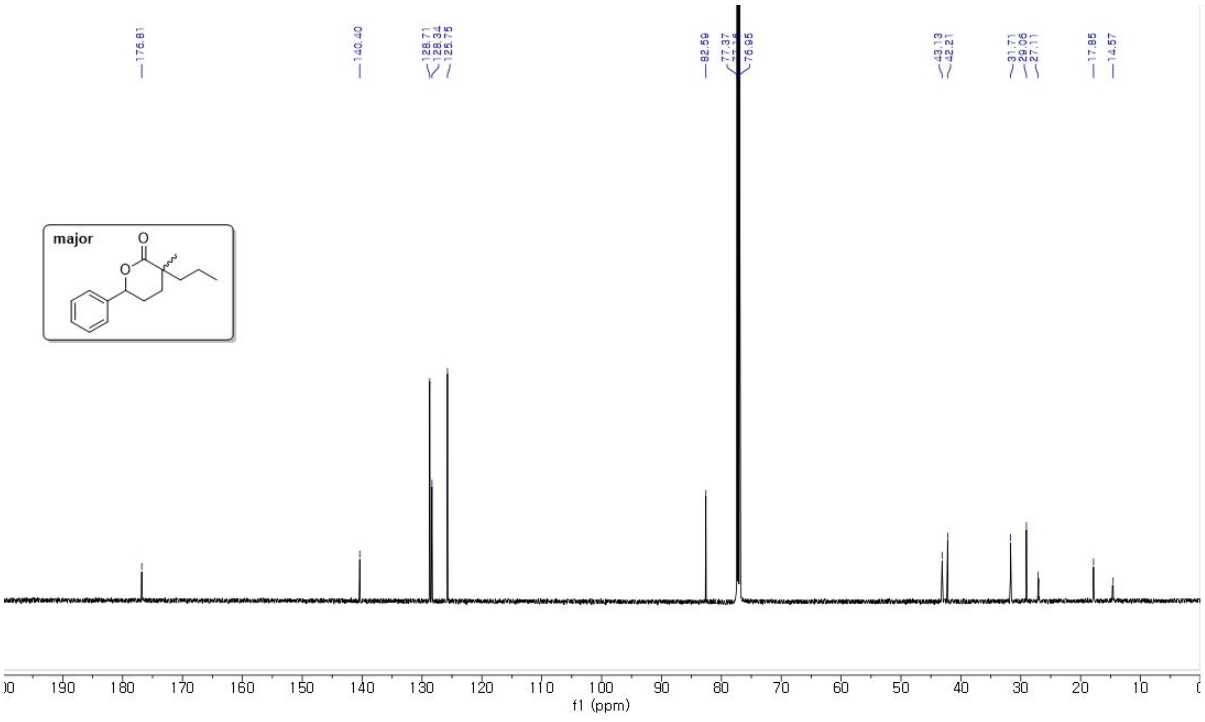


3-methyl-6-phenyl-3-propyltetrahydro-2H-pyran-2-one (6x) Major

400 MHz, ^{1}H NMR in $CDCl_3$

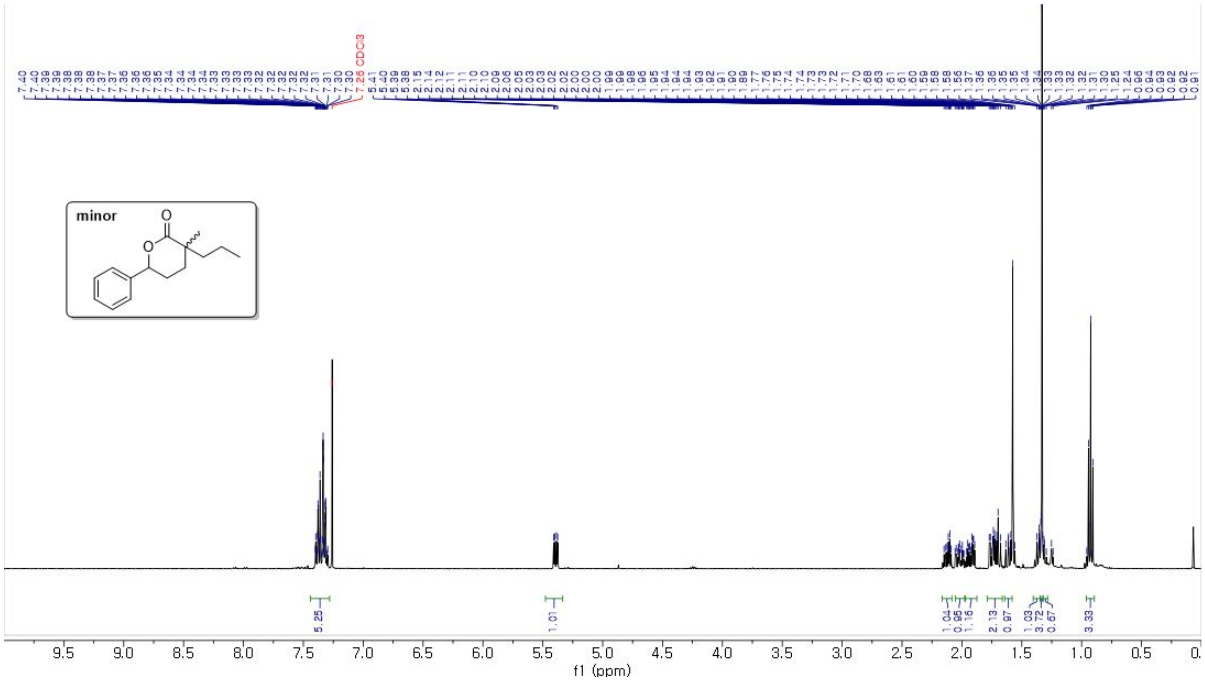


150 MHz, ^{13}C NMR in $CDCl_3$

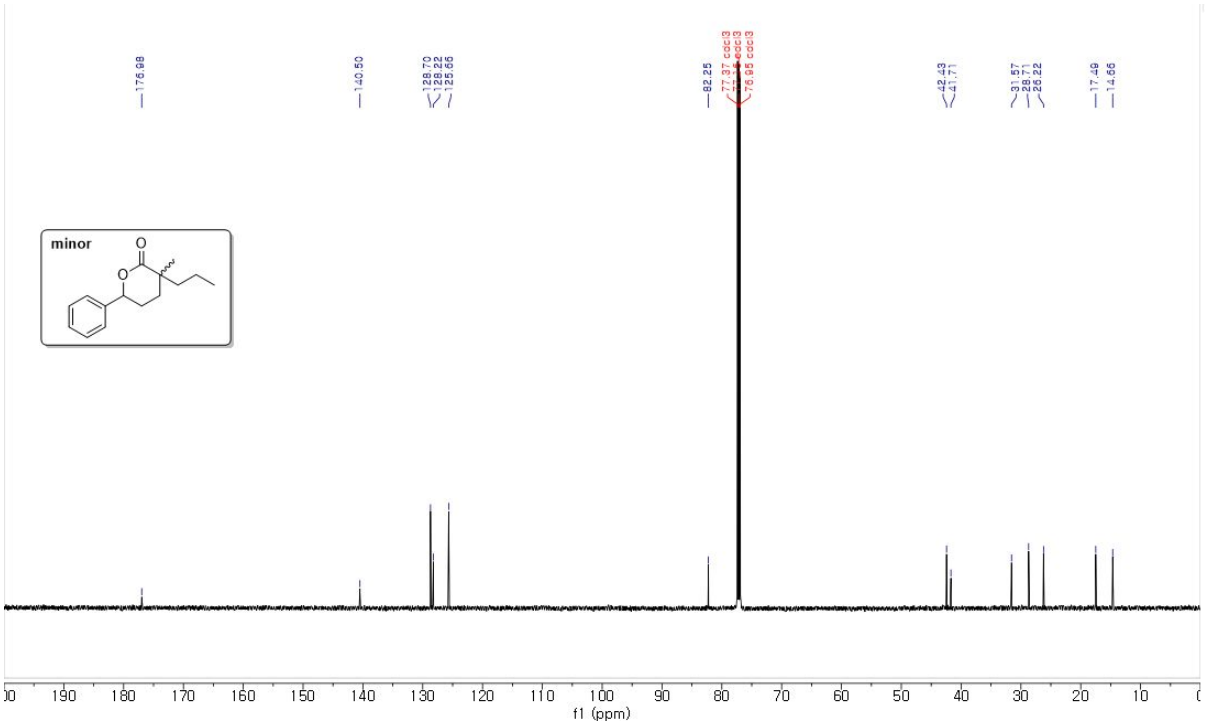


3-methyl-6-phenyl-3-propyltetrahydro-2H-pyran-2-one (6x) Minor

400 MHz, ^{1}H NMR in $CDCl_3$

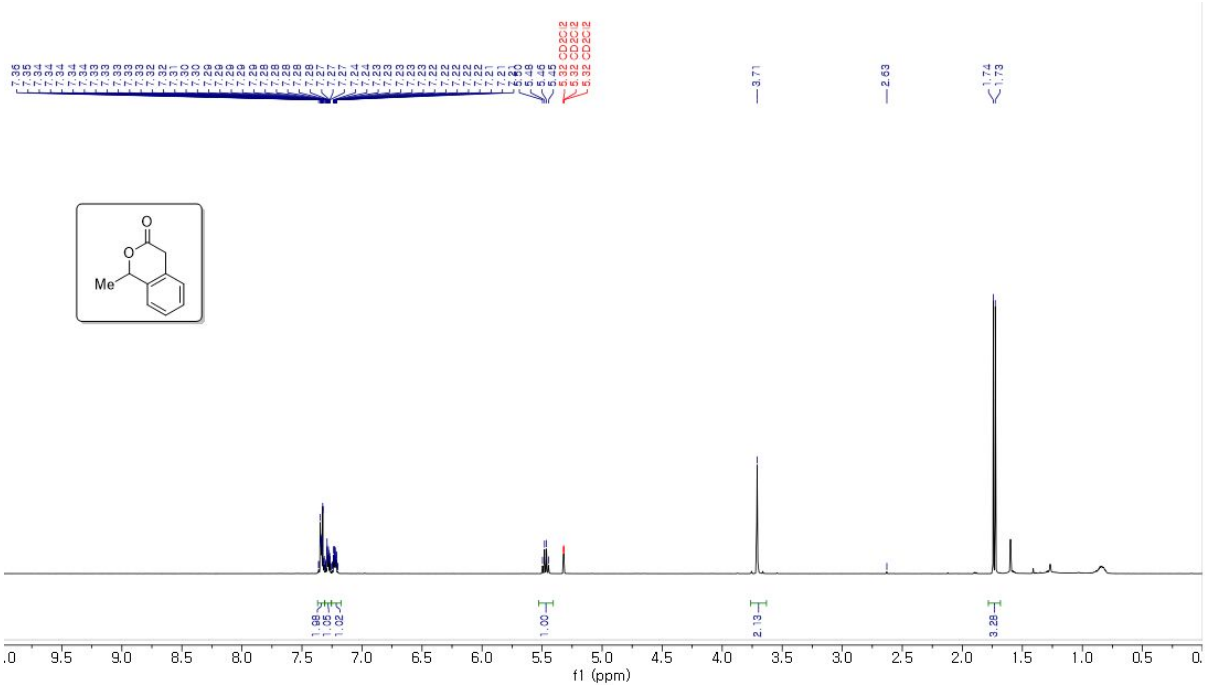


150 MHz, ^{13}C NMR in $CDCl_3$

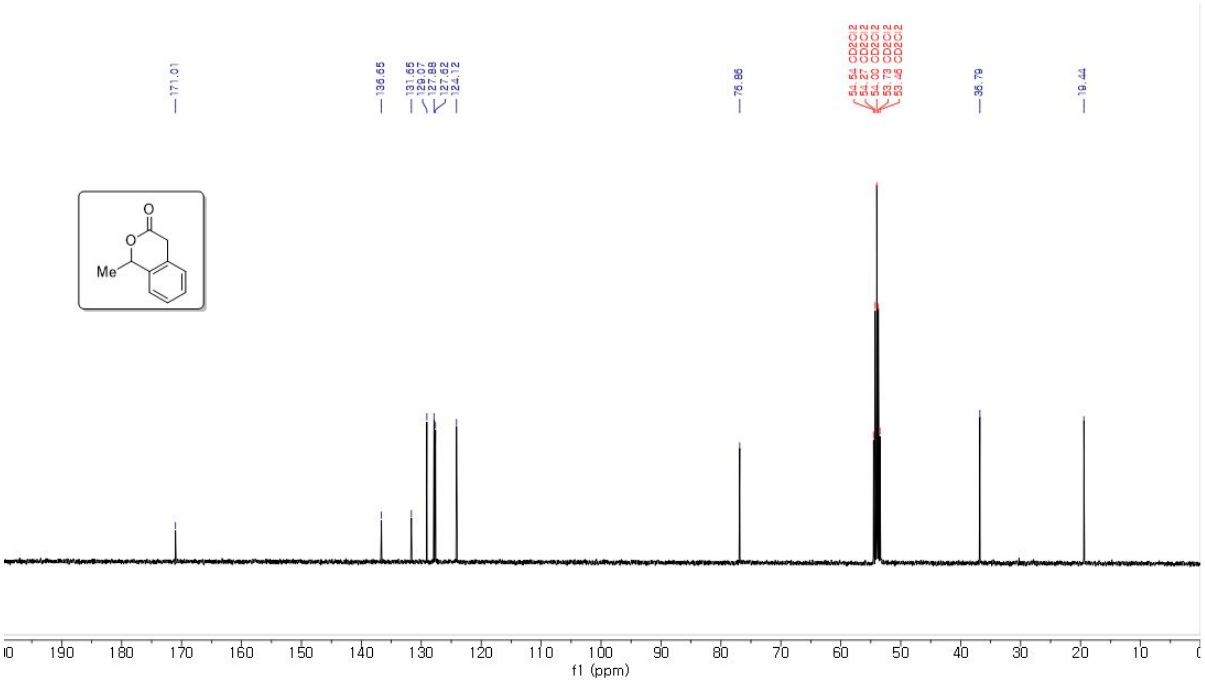


1-methylisochroman-3-one (6y)

400 MHz, ^{1}H NMR in CD_2Cl_2

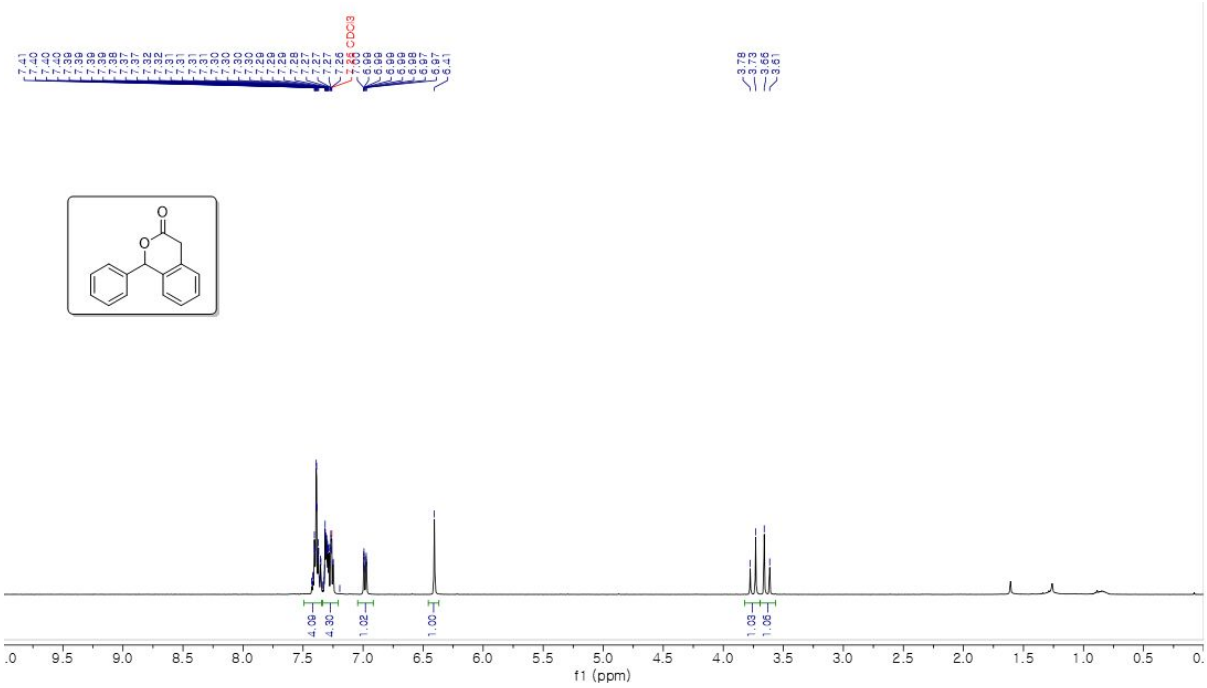


100 MHz, ^{13}C NMR in CD_2Cl_2

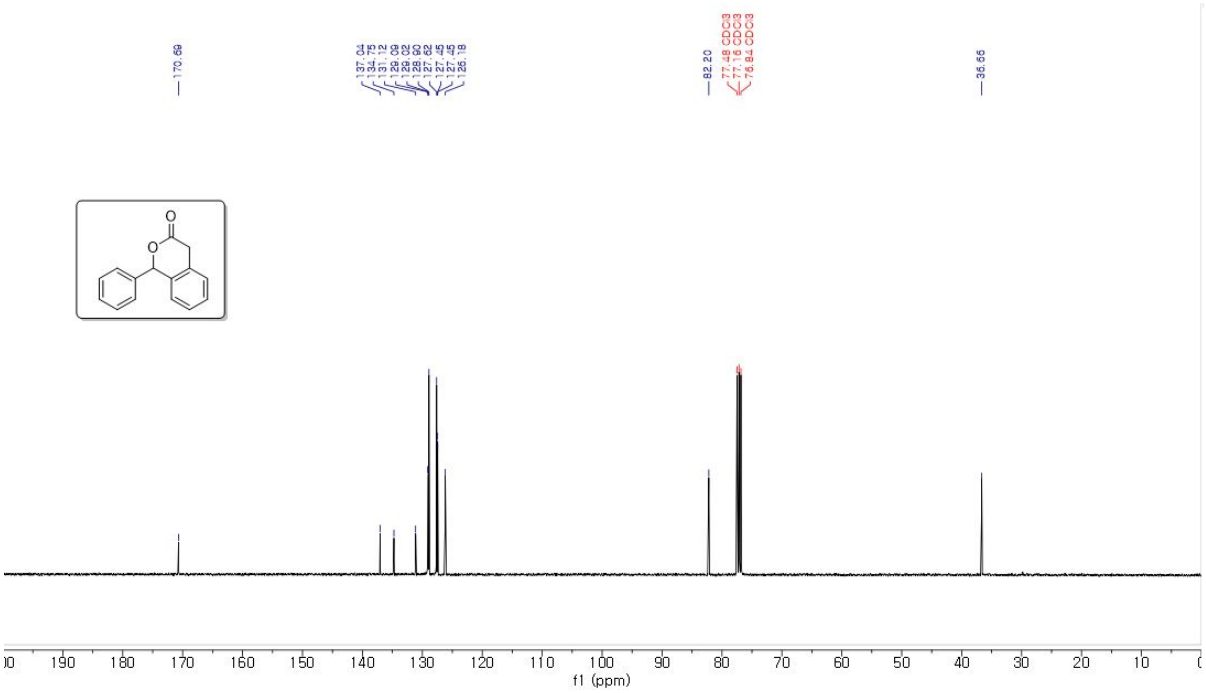


1-phenylisochroman-3-one (6z)

400 MHz, ^{1}H NMR in $CDCl_3$

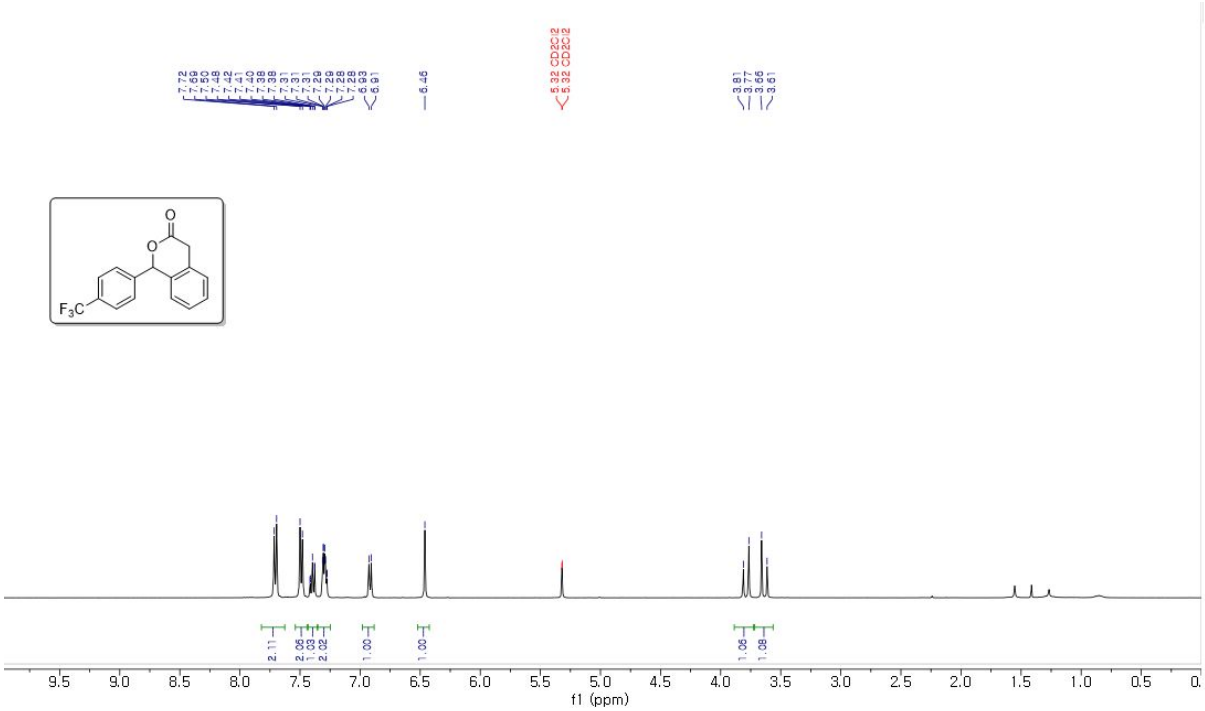


100 MHz, ^{13}C NMR in $CDCl_3$

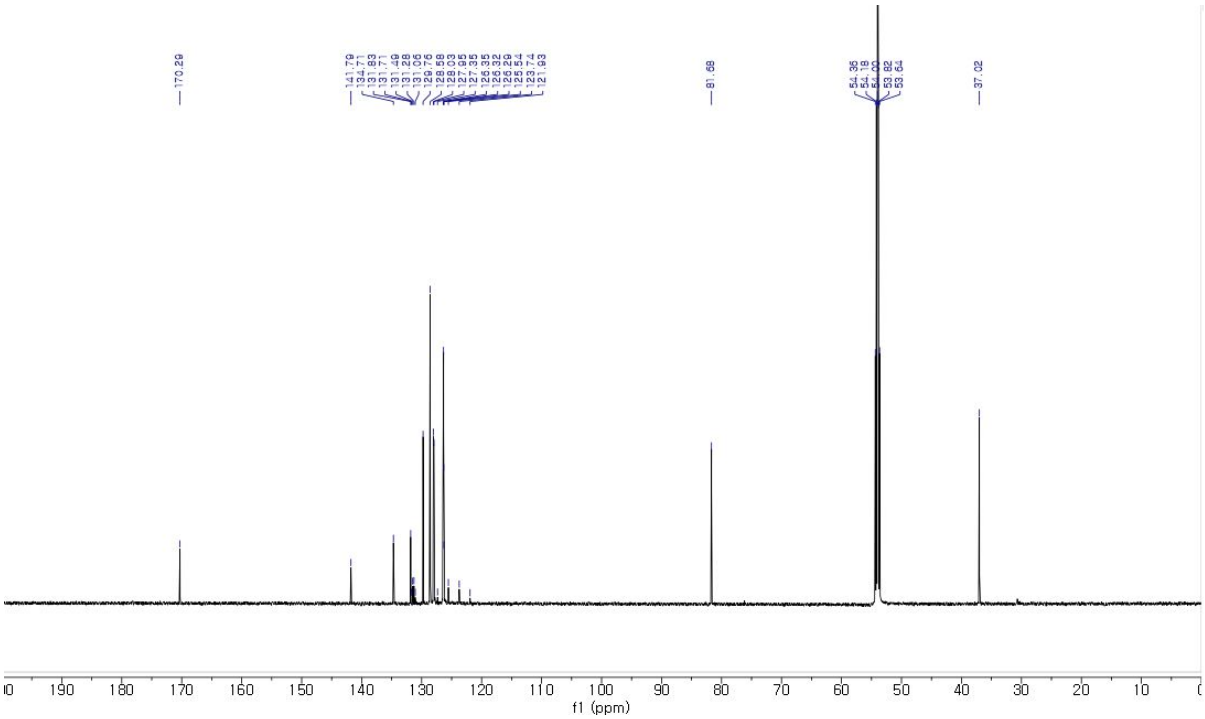


1-(4-(trifluoromethyl)phenyl)isochroman-3-one (6aa)

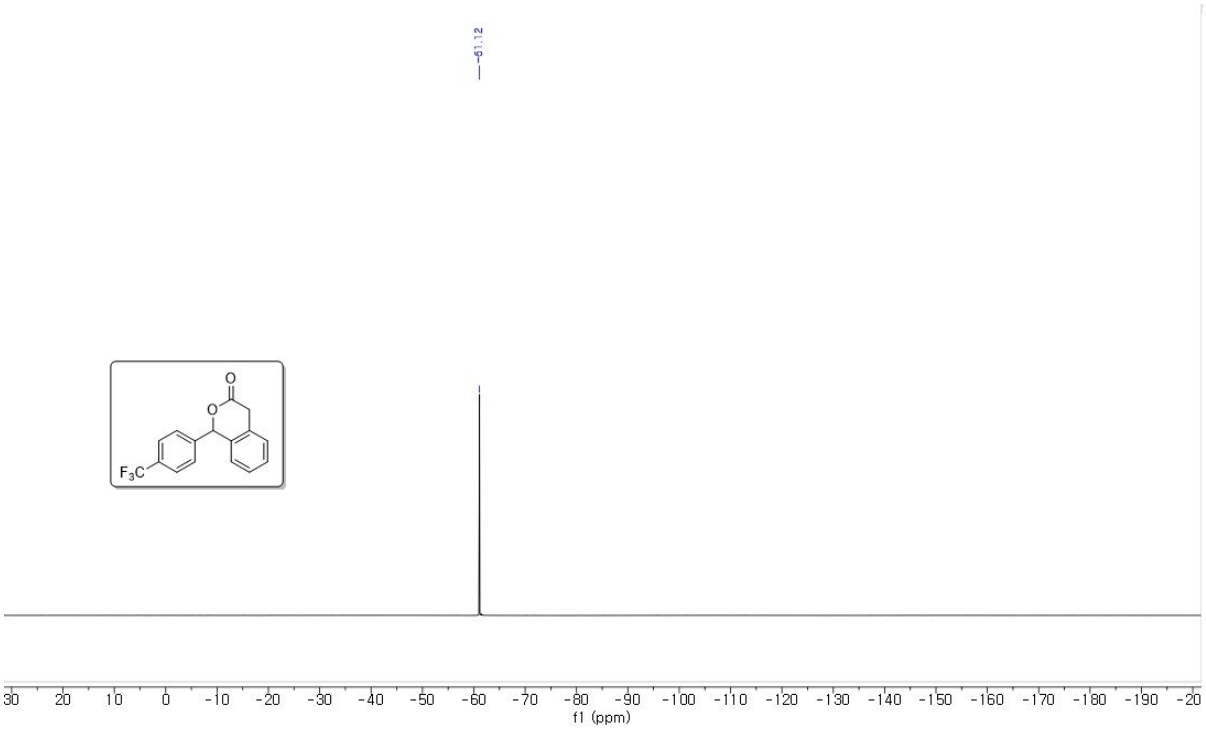
400 MHz, ^{1}H NMR in CD_2Cl_2



150 MHz, ^{13}C NMR in CD_2Cl_2

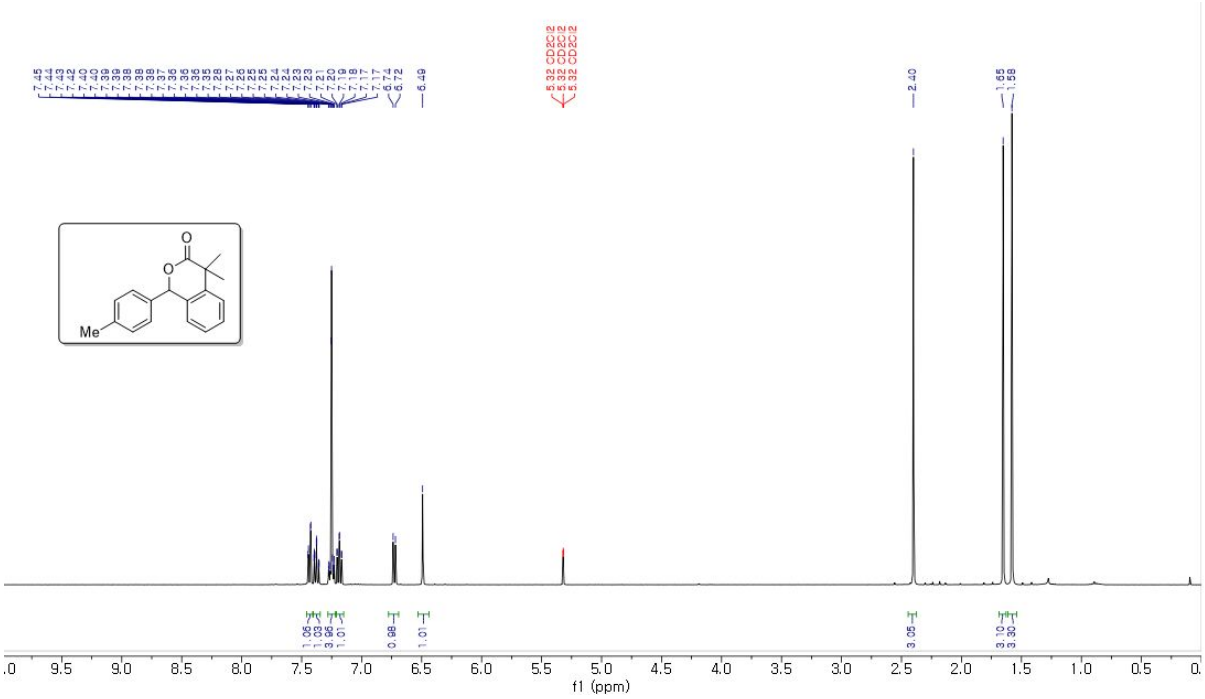


564 MHz, ^{19}F NMR in CD_2Cl_2

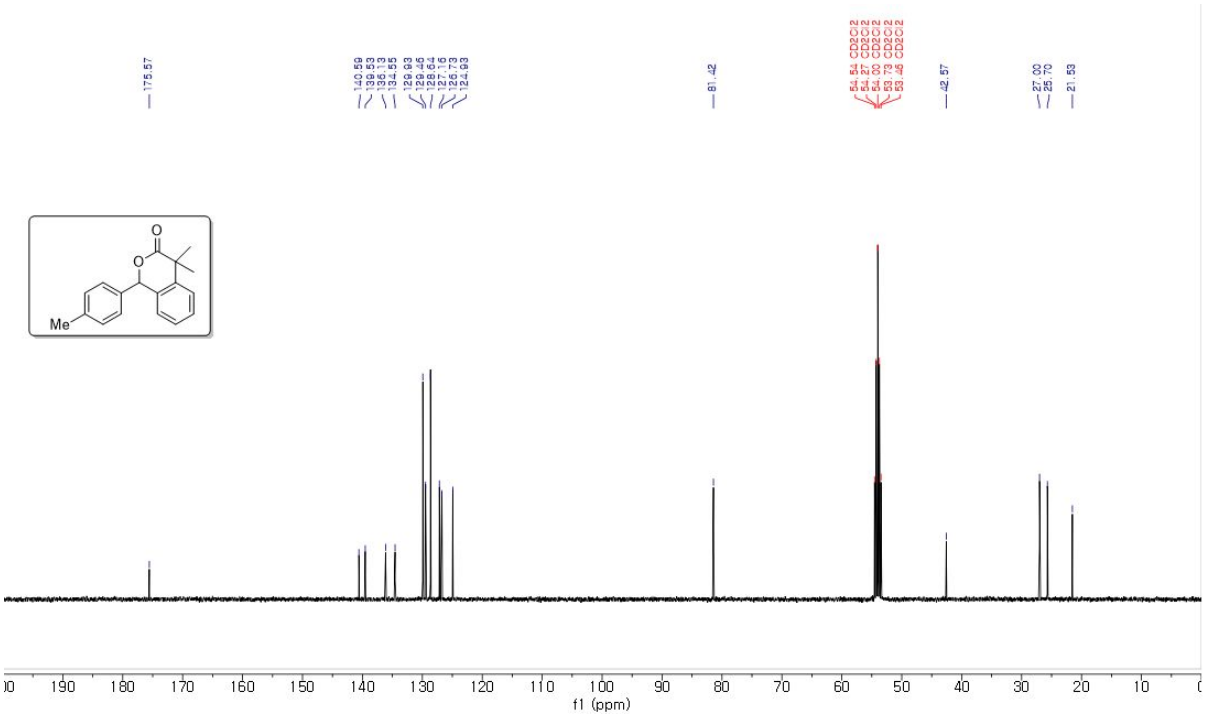


4,4-dimethyl-1-(p-tolyl)isochroman-3-one (6ab)

400 MHz, ^{1}H NMR in CD_2Cl_2

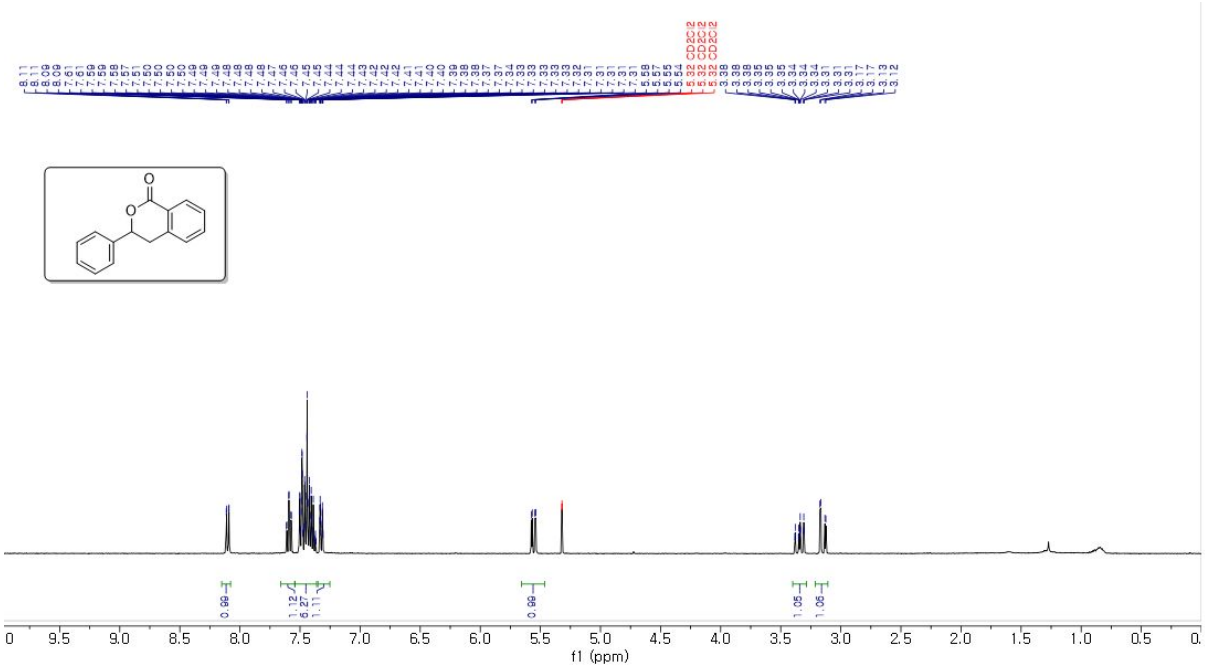


100 MHz, ^{13}C NMR in CD_2Cl_2

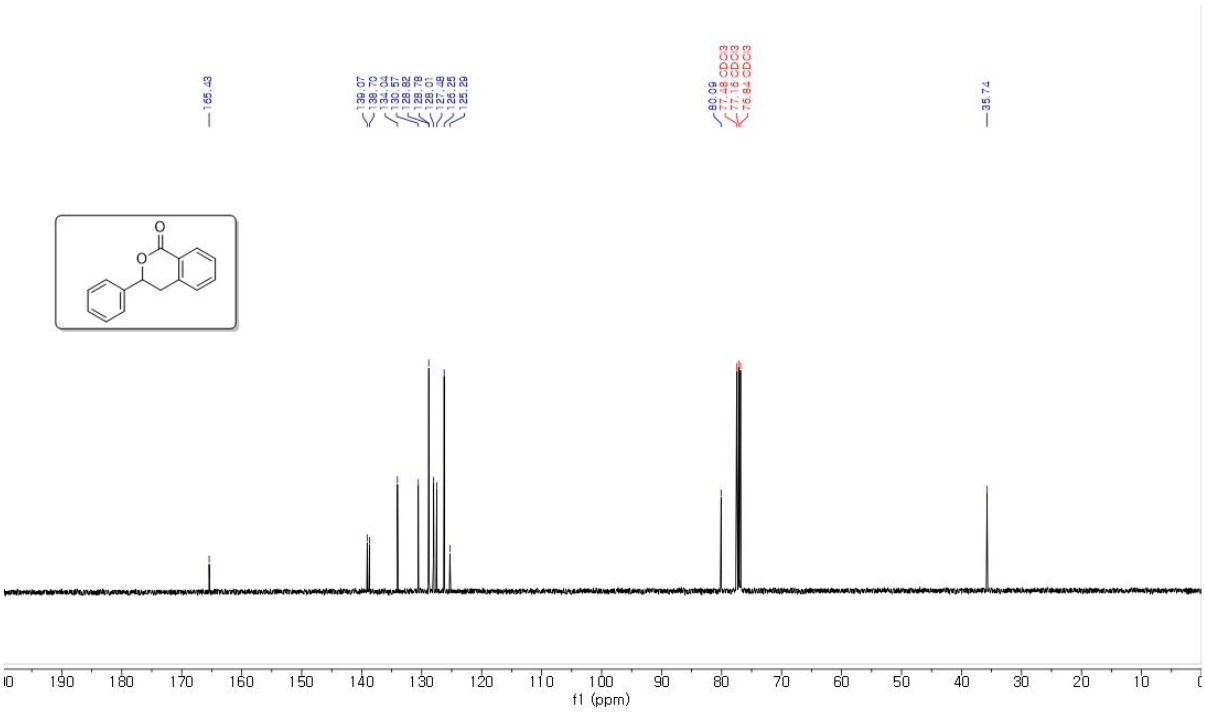


3-phenylisochroman-1-one (6ac)

400 MHz, ^{1}H NMR in CD_2Cl_2

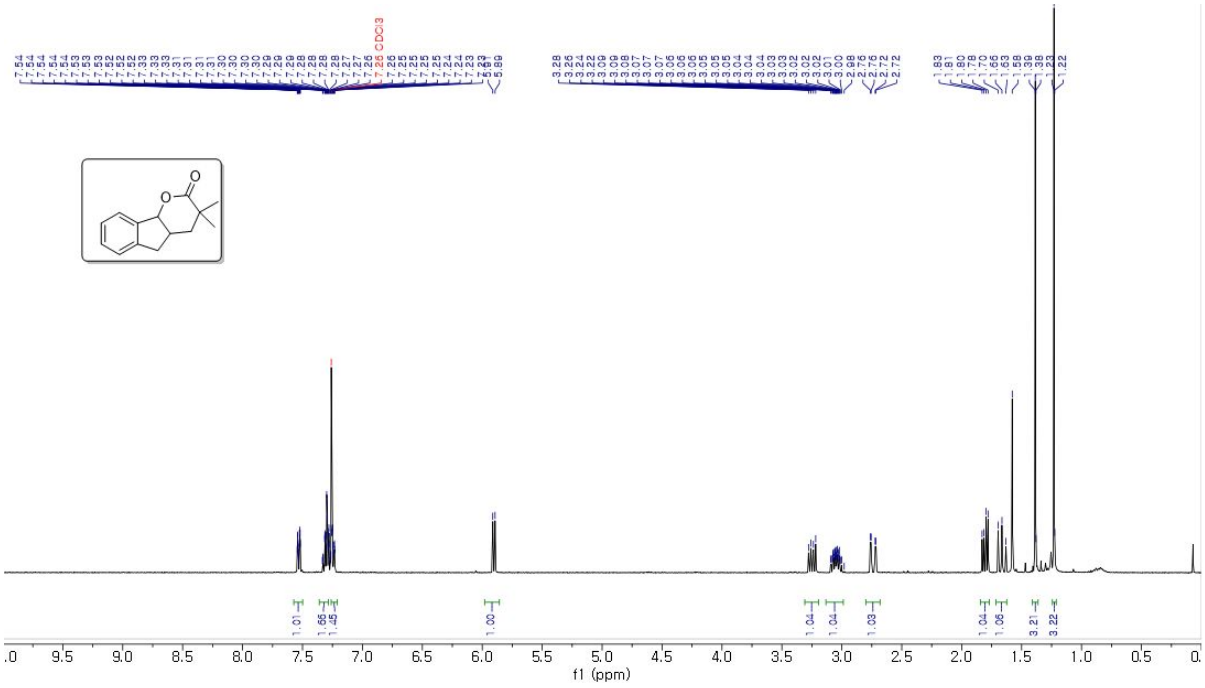


100 MHz, ^{13}C NMR in $CDCl_3$

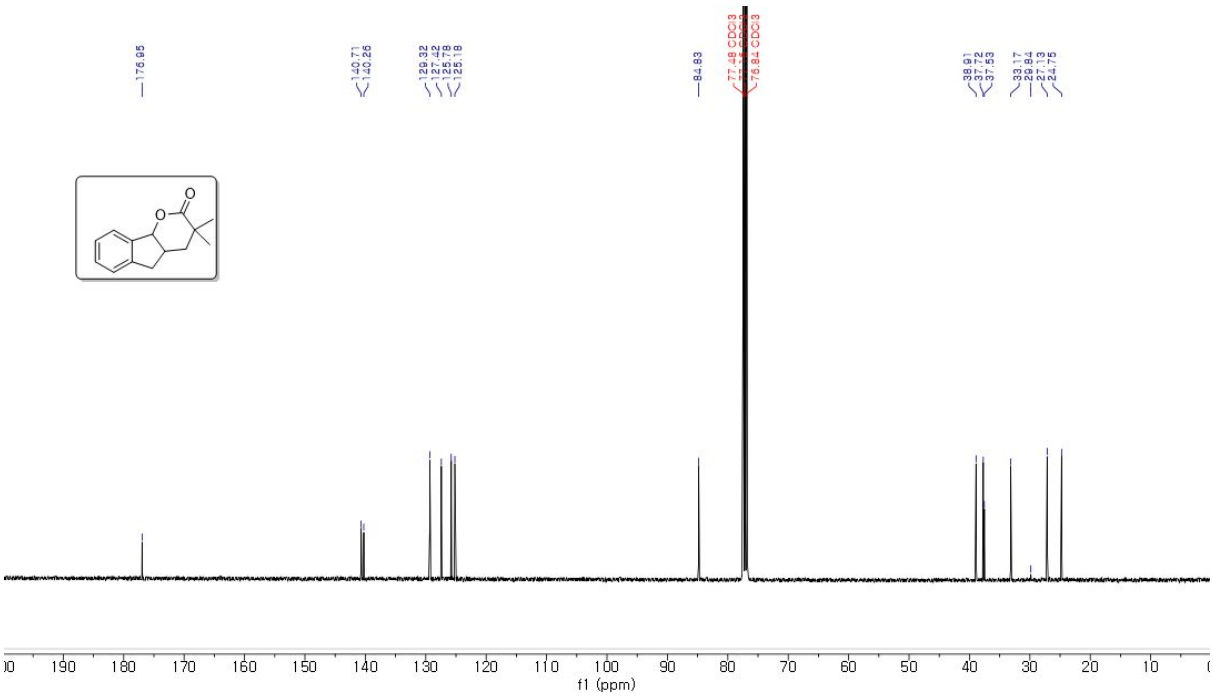


3,3-dimethyl-4,4a,5,9b-tetrahydroindeno[1,2-b]pyran-2(3H)-one (6ad)

400 MHz, ^{1}H NMR in $CDCl_3$

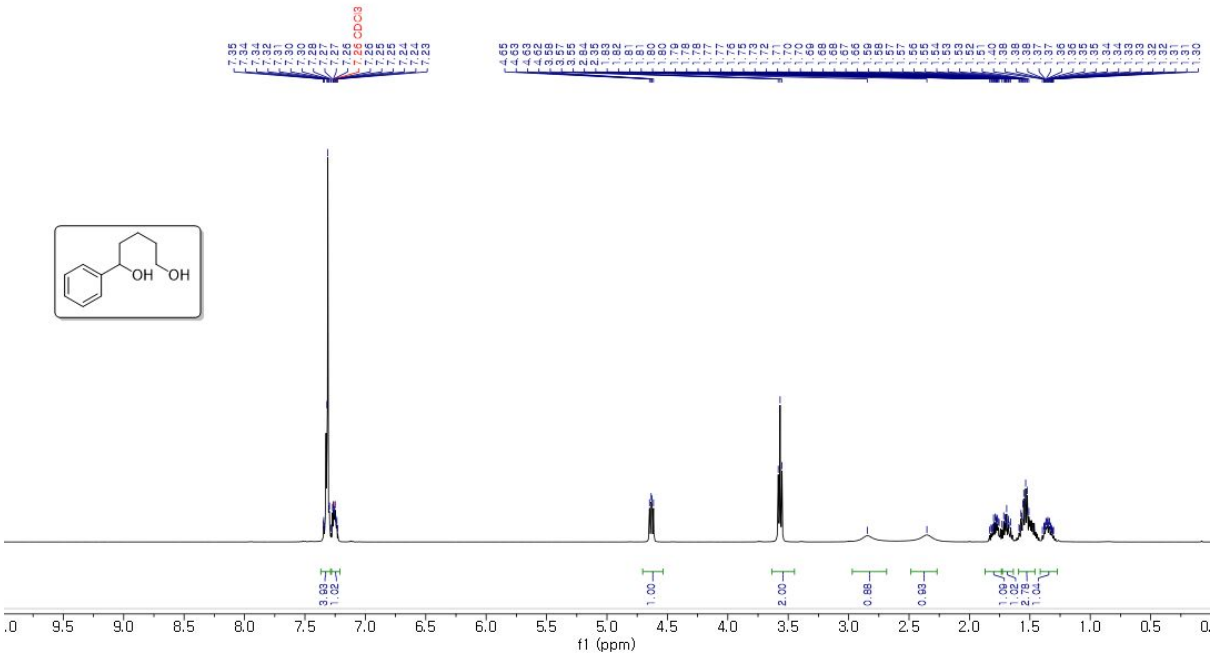


100 MHz, ^{13}C NMR in $CDCl_3$

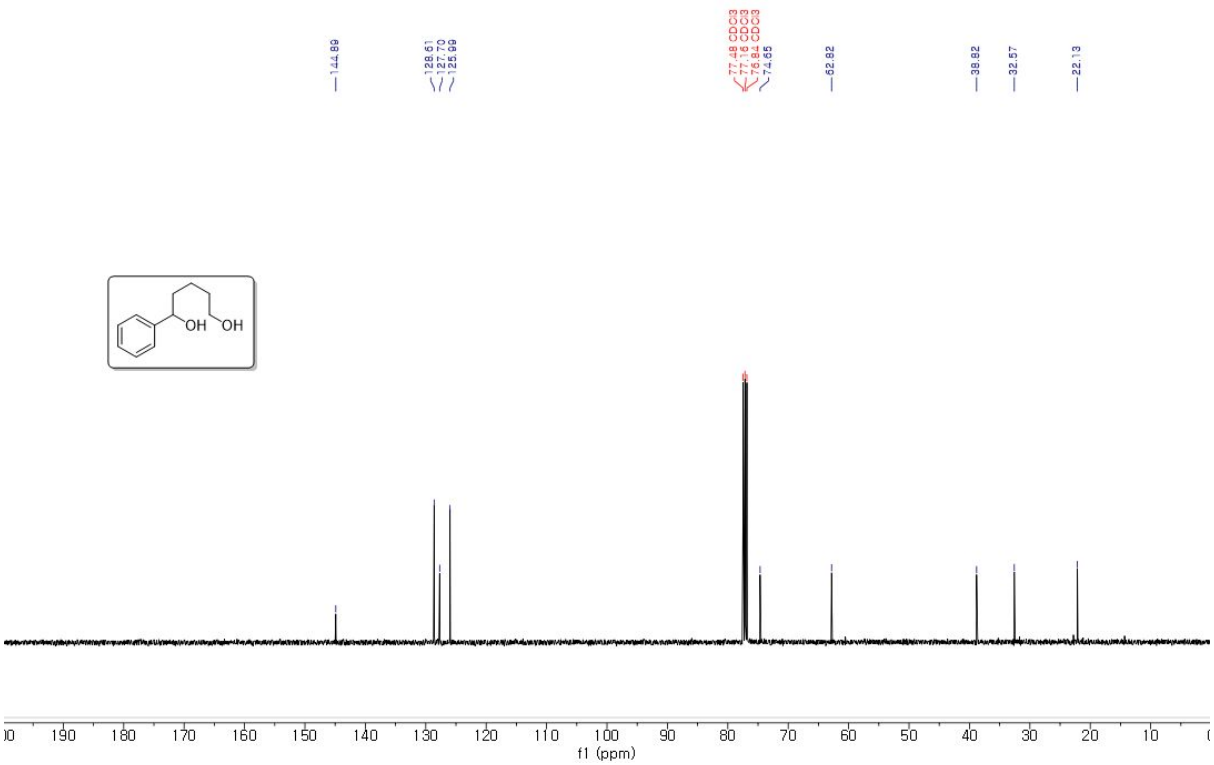


1-phenylpentane-1,5-diol (3)

400 MHz, ^{1}H NMR in $CDCl_3$

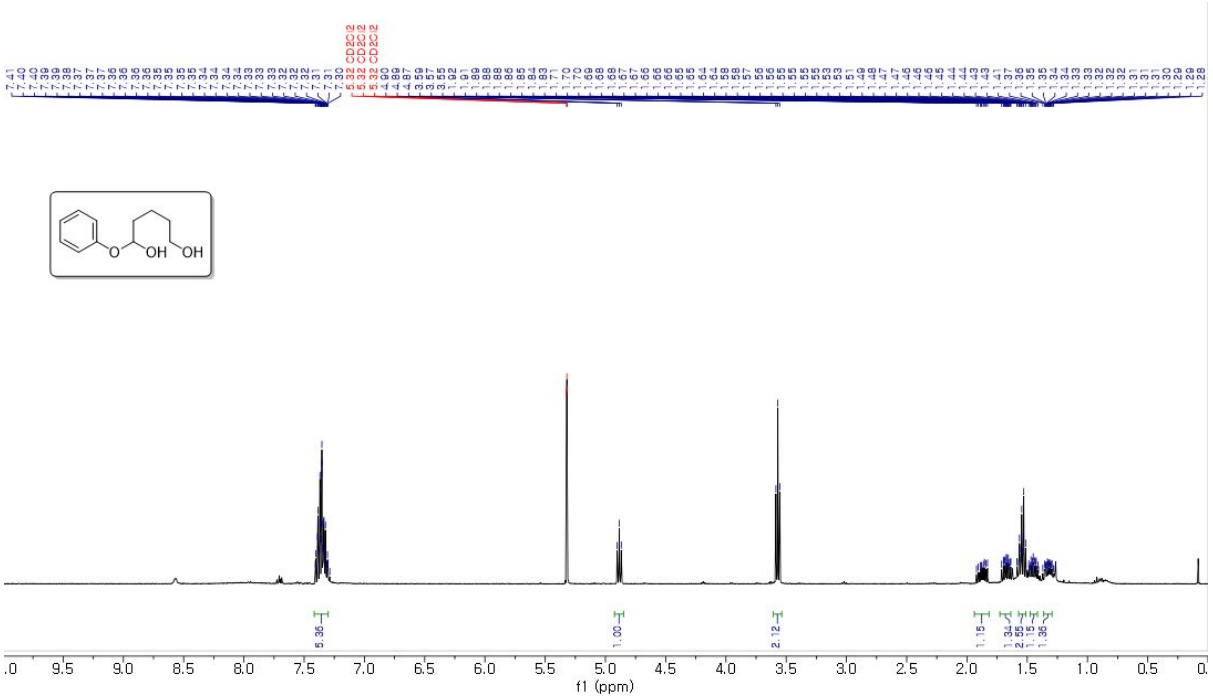


100 MHz, ^{13}C NMR in $CDCl_3$

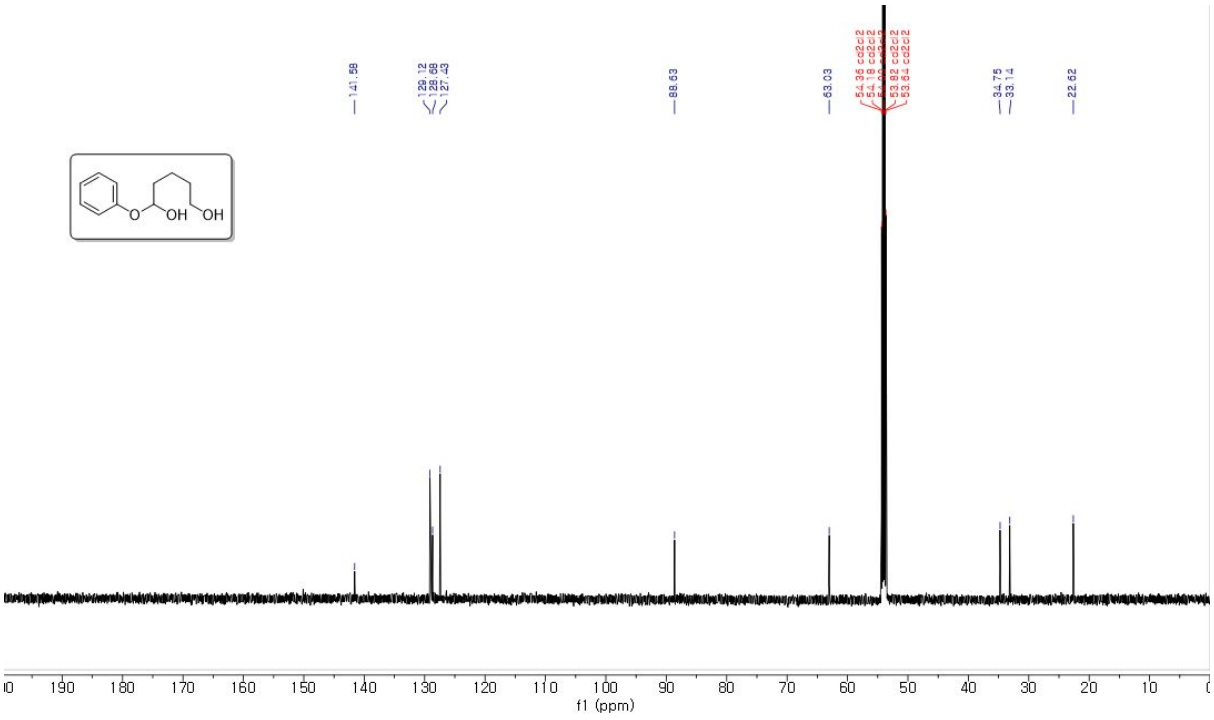


1-phenoxypentane-1,5-diol (4)

400 MHz, ^{1}H NMR in CD_2Cl_2

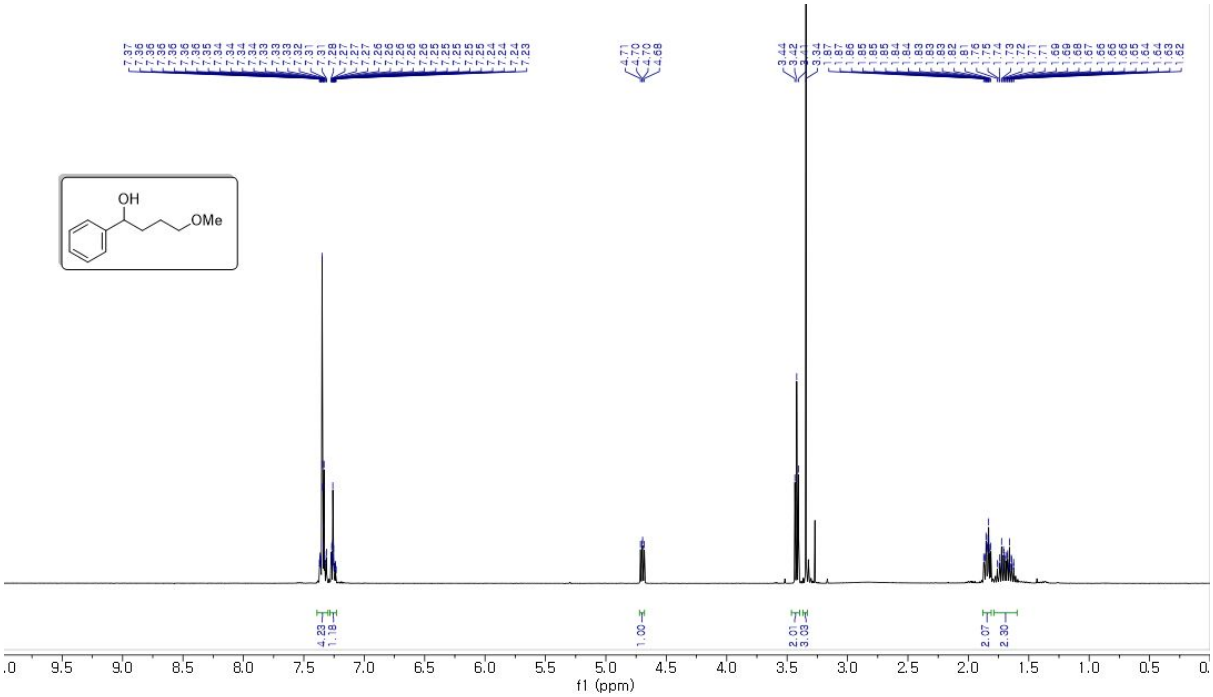


150 MHz, ^{13}C NMR in CD_2Cl_2

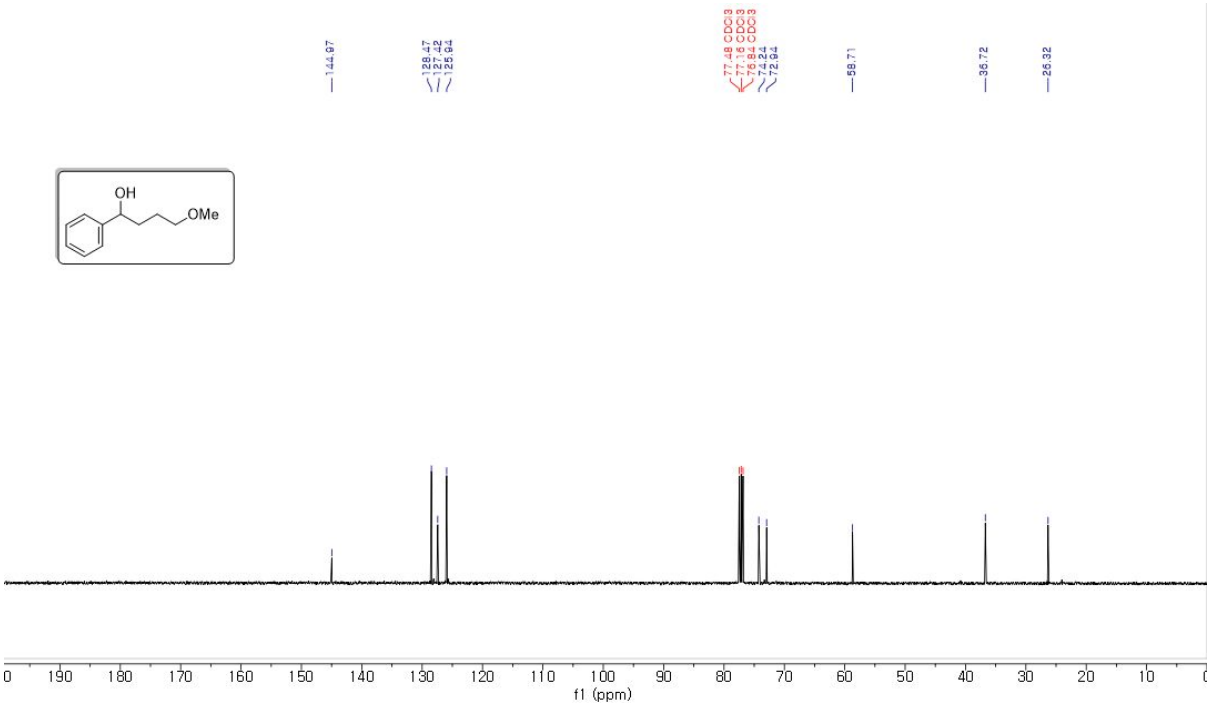


4-methoxy-1-phenylbutan-1-ol (10a)

400 MHz, ^{1}H NMR in $CDCl_3$

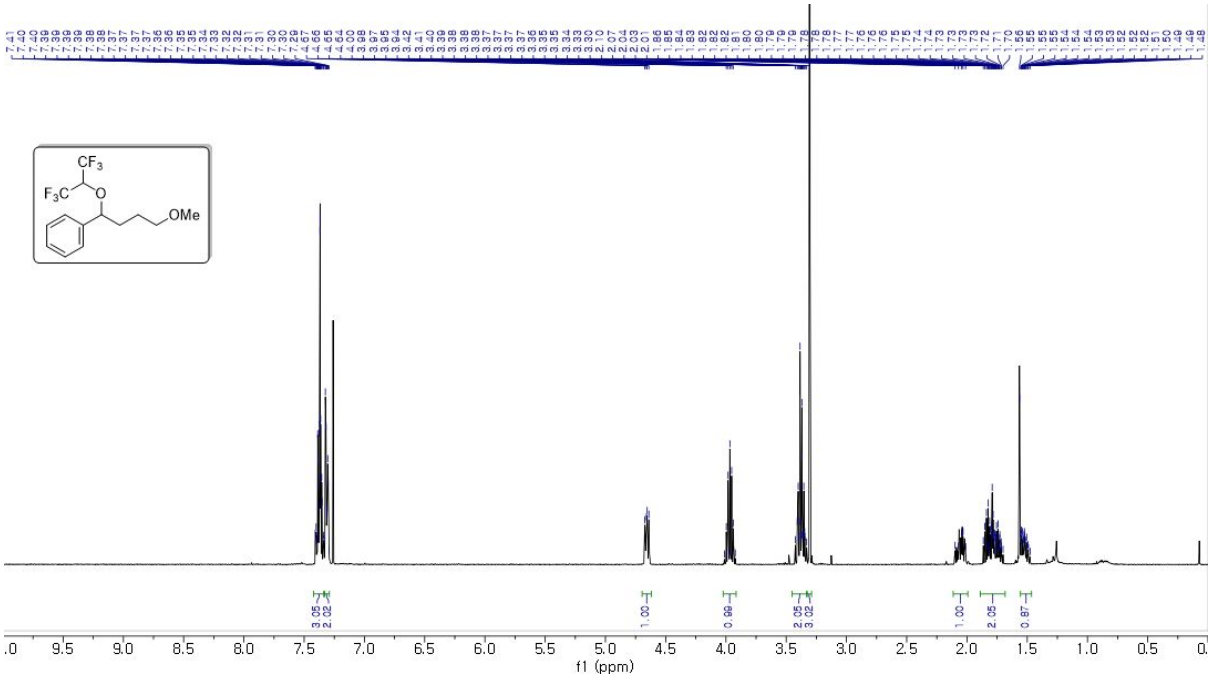


100 MHz, ^{13}C NMR in $CDCl_3$

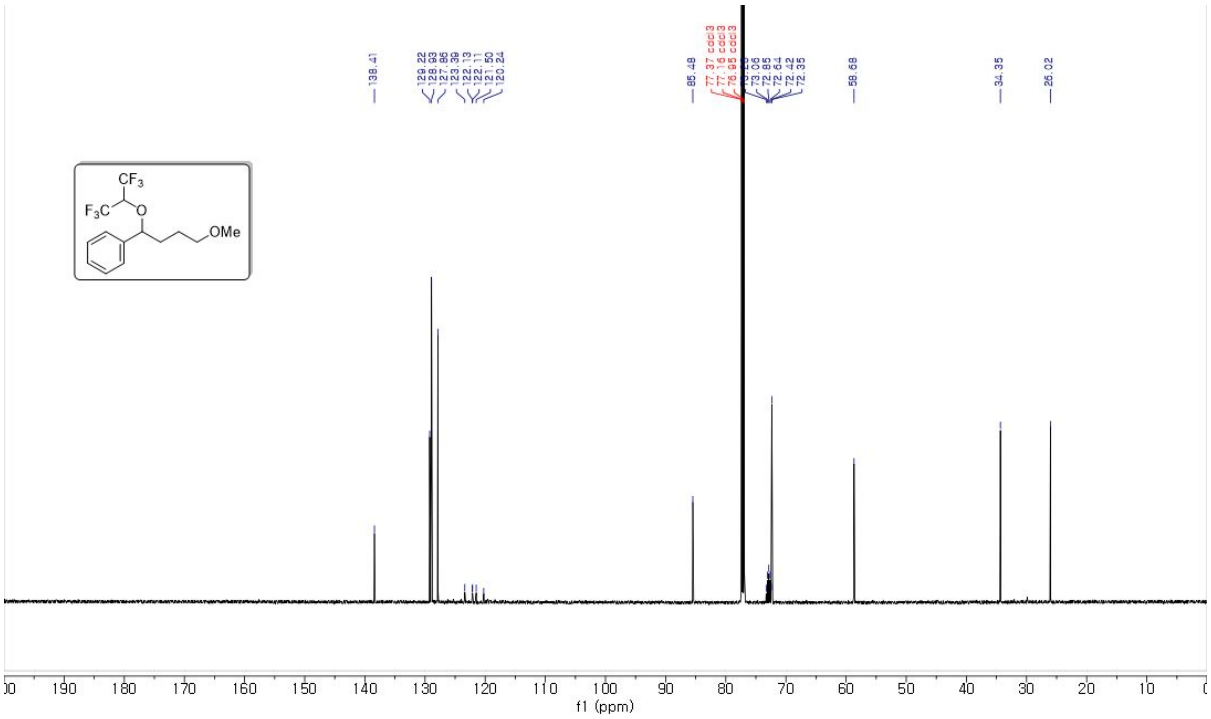


(1-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4-methoxybutyl)benzene (10b)

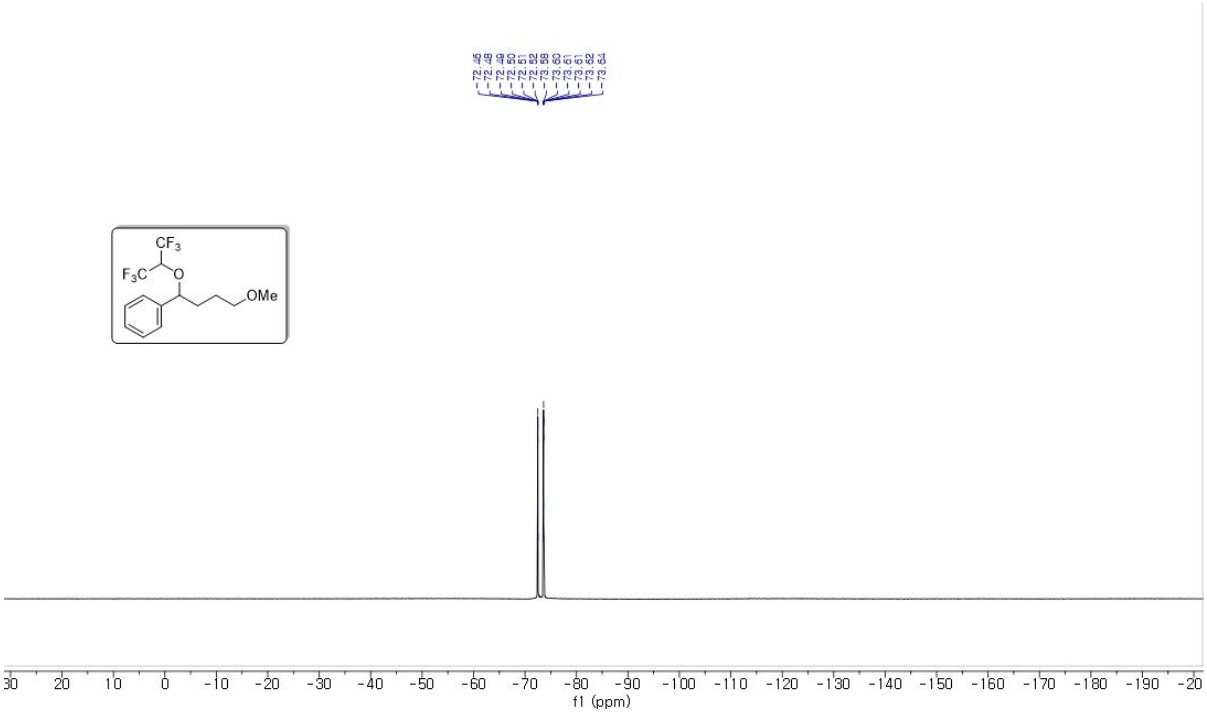
400 MHz, ^{1}H NMR in $CDCl_3$



150 MHz, ^{13}C NMR in $CDCl_3$

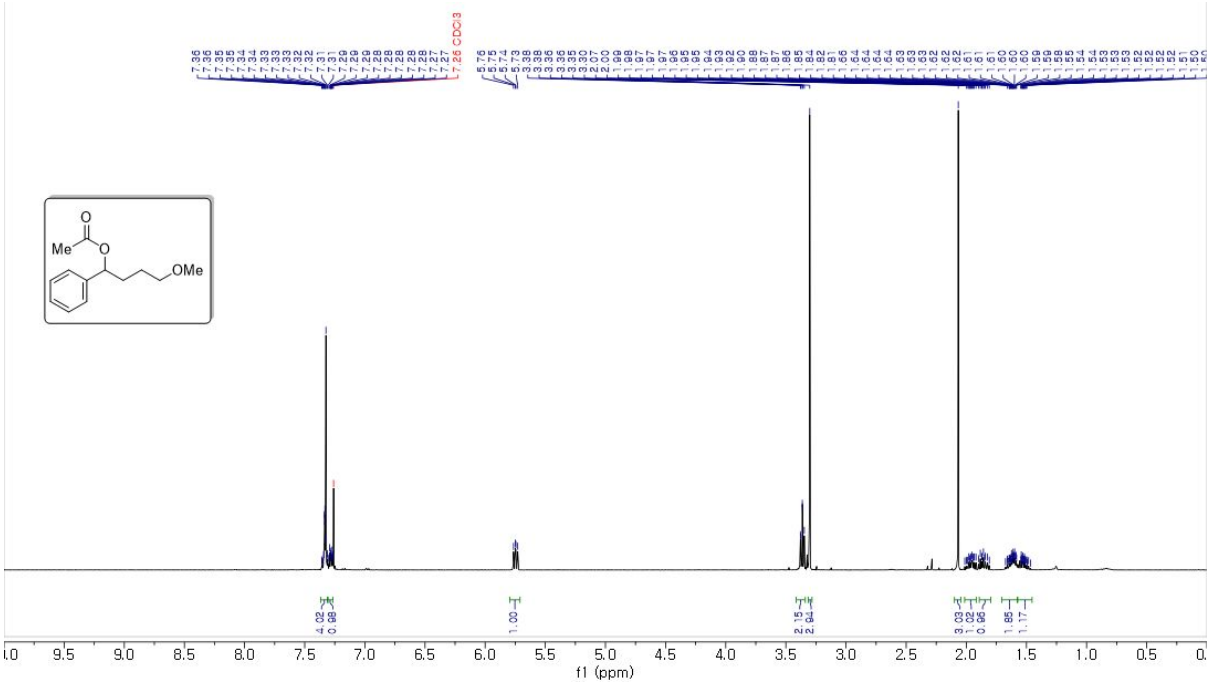


564 MHz, ^{19}F NMR in $CDCl_3$

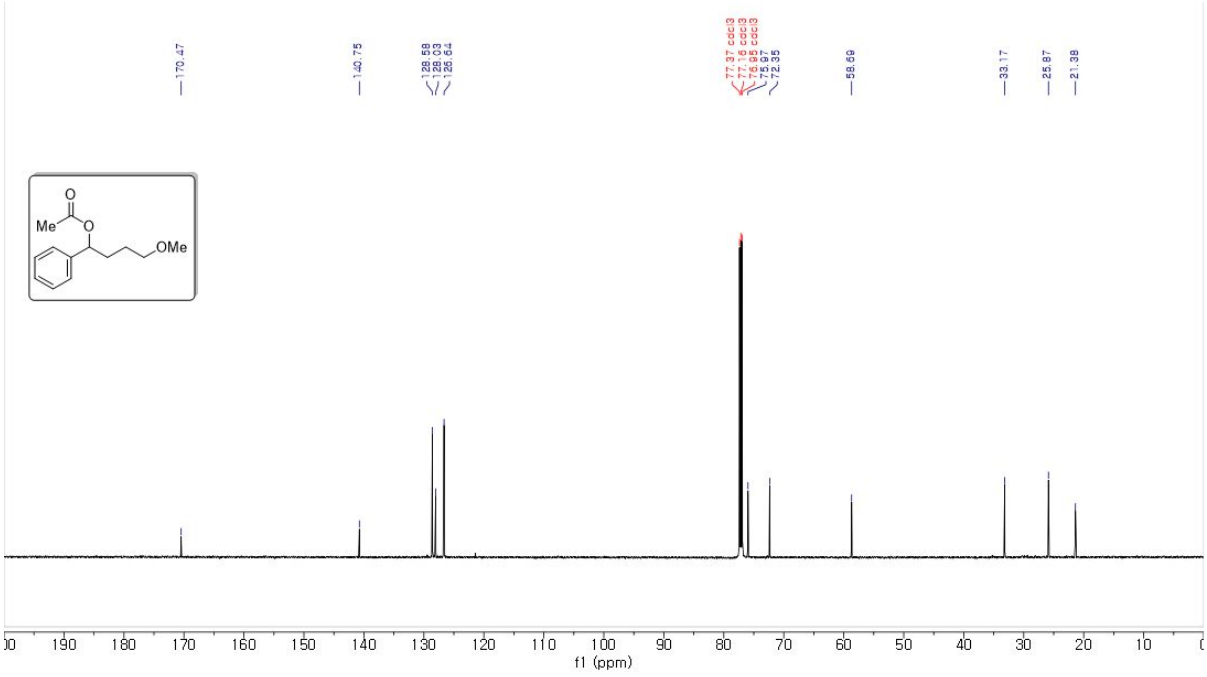


4-methoxy-1-phenylbutyl acetate (10c)

400 MHz, ^{1}H NMR in $CDCl_3$

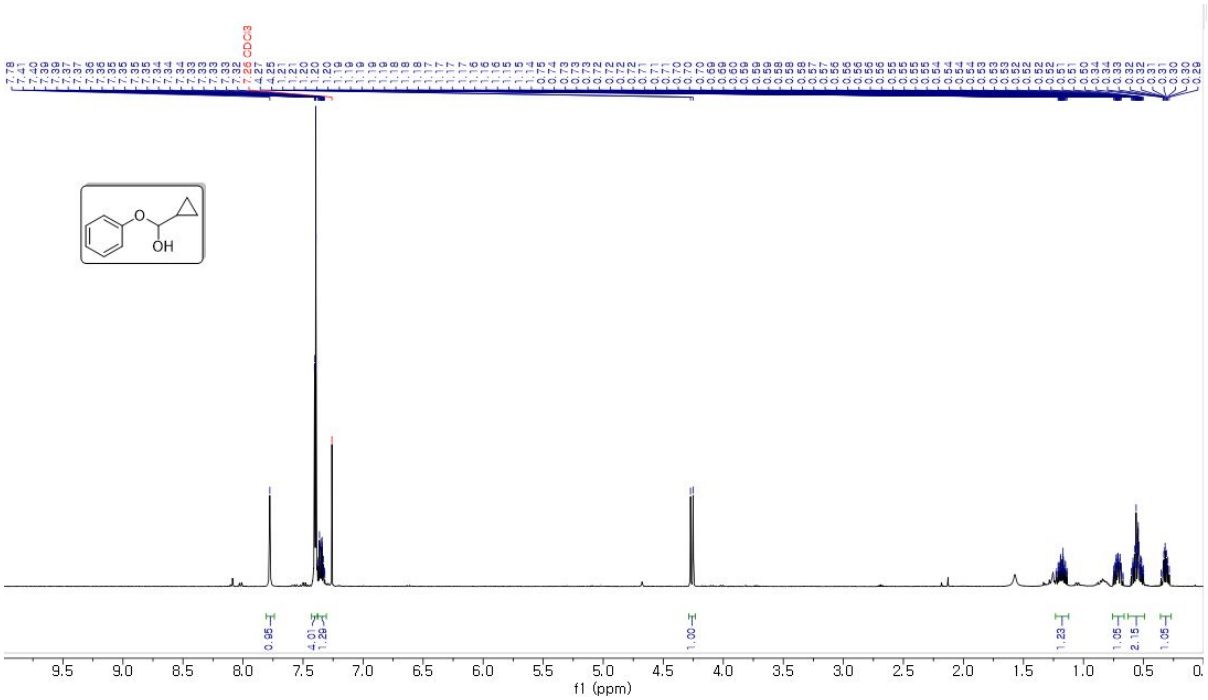


150 MHz, ^{13}C NMR in $CDCl_3$

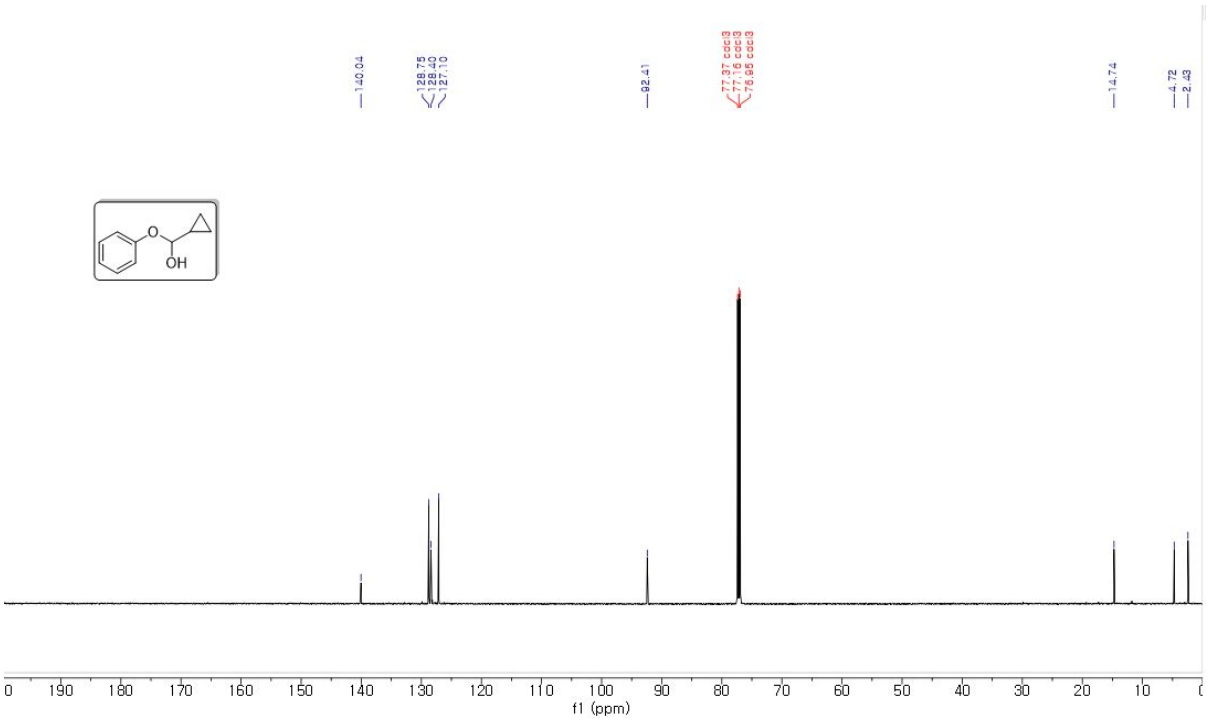


cyclopropyl(phenoxy)methanol (14)

400 MHz, ^{1}H NMR in $CDCl_3$

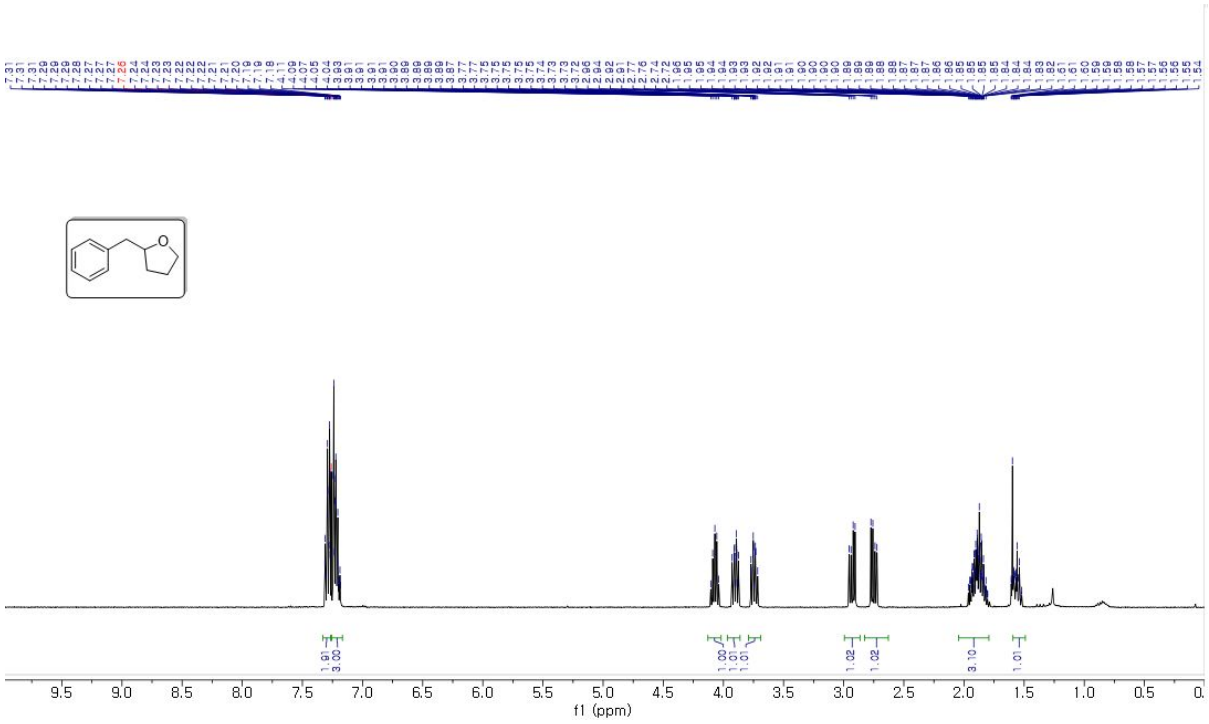


150 MHz, ^{13}C NMR in $CDCl_3$



2-benzyltetrahydrofuran (15)

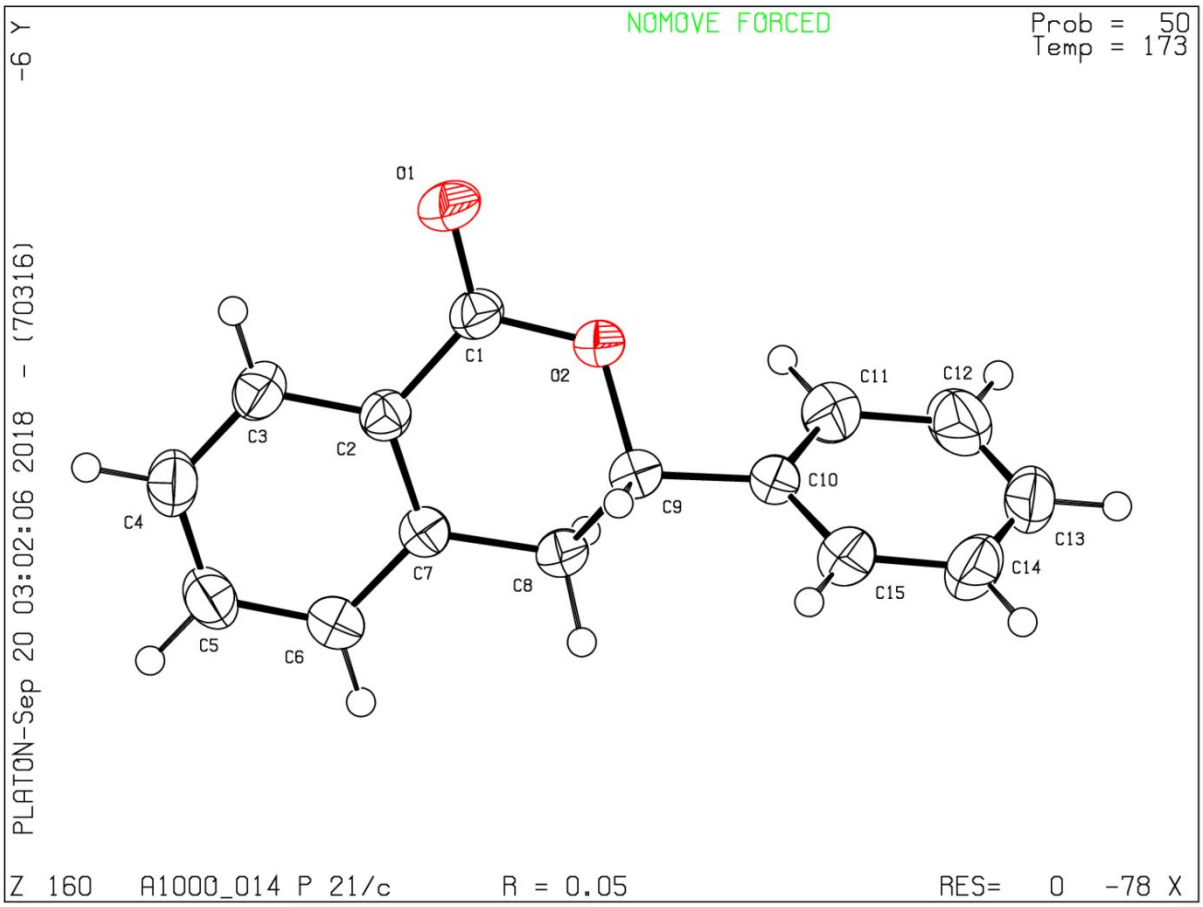
400 MHz, ^{1}H NMR in $CDCl_3$



Appendix II

Crystallographic Data for 6ac

Crystallographic Data for 6ac (CCDC : 1871380)



ORTEP representation (50% probability) of the crystal structure of **6ac**

Table 1. Crystal data and structure refinement for **A100O_014**.

Empirical formula	$C_{15}H_{12}O_2$	
Formula weight	224.25	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.713(2) Å	α = 90°
	b = 13.701(2) Å	β = 103.669(6)°
	c = 7.3792(11) Å	γ = 90°
Volume	1150.7(3) Å^3	
Z	4	

Density (calculated)	1.294 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
F(000)	472
Crystal size	0.398 x 0.143 x 0.128 mm^3
Theta range for data collection	3.207 to 29.268°.
Index ranges	−16<=h<=16, −18<=k<=18, −10<=l<=9
Reflections collected	29791
Independent reflections	3068 [R(int) = 0.0586]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6871
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3068 / 0 / 155
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1169
R indices (all data)	R1 = 0.0758, wR2 = 0.1320
Extinction coefficient	0.020(3)
Largest diff. peak and hole	0.221 and −0.174 $e \cdot Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **A100O_014**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3559(1)	6163(1)	8054(1)	53(1)
C(1)	3434(1)	6250(1)	6394(2)	35(1)
C(2)	4412(1)	6299(1)	5448(2)	31(1)
C(3)	5551(1)	6420(1)	6520(2)	41(1)
C(4)	6480(1)	6427(1)	5662(2)	46(1)
C(5)	6278(1)	6296(1)	3760(2)	46(1)
C(6)	5148(1)	6174(1)	2689(2)	41(1)
C(7)	4200(1)	6184(1)	3522(2)	32(1)
C(8)	2952(1)	6058(1)	2437(2)	37(1)
C(9)	2126(1)	6588(1)	3392(2)	36(1)
O(2)	2326(1)	6275(1)	5330(1)	39(1)
C(10)	850(1)	6394(1)	2494(2)	38(1)
C(11)	296(1)	5540(1)	2802(2)	51(1)
C(12)	-880(2)	5384(2)	1918(3)	62(1)
C(13)	-1484(1)	6072(2)	720(2)	62(1)
C(14)	-935(2)	6911(2)	392(2)	60(1)
C(15)	227(1)	7079(1)	1294(2)	48(1)

Table 3. Bond lengths [Å] and angles [°] for **A100O_014**.

O(1)-C(1)	1.2050(16)
C(1)-O(2)	1.3494(16)
C(1)-C(2)	1.4776(18)
C(2)-C(3)	1.3904(18)
C(2)-C(7)	1.3930(17)
C(3)-C(4)	1.382(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.379(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.382(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.3905(19)
C(6)-H(6)	0.9500
C(7)-C(8)	1.5012(18)
C(8)-C(9)	1.5103(19)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-O(2)	1.4582(15)
C(9)-C(10)	1.5091(19)
C(9)-H(9)	1.0000
C(10)-C(15)	1.375(2)
C(10)-C(11)	1.382(2)
C(11)-C(12)	1.394(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.369(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.366(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(2)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
O(1)-C(1)-O(2)	117.60(12)
O(1)-C(1)-C(2)	124.28(12)

O(2)-C(1)-C(2)	118.09(11)
C(3)-C(2)-C(7)	120.67(12)
C(3)-C(2)-C(1)	118.90(12)
C(7)-C(2)-C(1)	120.37(11)
C(4)-C(3)-C(2)	119.54(13)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(5)-C(4)-C(3)	120.09(13)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	120.55(14)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(7)	120.22(13)
C(5)-C(6)-H(6)	119.9
C(7)-C(6)-H(6)	119.9
C(6)-C(7)-C(2)	118.90(12)
C(6)-C(7)-C(8)	122.83(12)
C(2)-C(7)-C(8)	118.25(11)
C(7)-C(8)-C(9)	110.29(11)
C(7)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8A)	109.6
C(7)-C(8)-H(8B)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
O(2)-C(9)-C(10)	106.93(10)
O(2)-C(9)-C(8)	110.12(11)
C(10)-C(9)-C(8)	112.85(11)
O(2)-C(9)-H(9)	109.0
C(10)-C(9)-H(9)	109.0
C(8)-C(9)-H(9)	109.0
C(1)-O(2)-C(9)	119.16(10)
C(15)-C(10)-C(11)	119.03(14)
C(15)-C(10)-C(9)	118.84(13)
C(11)-C(10)-C(9)	122.11(13)
C(10)-C(11)-C(12)	120.21(16)

C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	119.92(17)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	120.05(16)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	120.29(16)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(10)-C(15)-C(14)	120.47(17)
C(10)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **A100O_014**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	48(1)	84(1)	26(1)	1(1)	9(1)	6(1)
C(1)	36(1)	41(1)	27(1)	-2(1)	6(1)	3(1)
C(2)	32(1)	31(1)	31(1)	1(1)	6(1)	2(1)
C(3)	37(1)	46(1)	35(1)	-1(1)	1(1)	0(1)
C(4)	31(1)	51(1)	52(1)	3(1)	2(1)	-3(1)
C(5)	34(1)	53(1)	55(1)	7(1)	17(1)	1(1)
C(6)	38(1)	52(1)	37(1)	2(1)	14(1)	0(1)
C(7)	31(1)	34(1)	31(1)	1(1)	8(1)	1(1)
C(8)	33(1)	53(1)	25(1)	-1(1)	6(1)	0(1)
C(9)	34(1)	44(1)	29(1)	5(1)	7(1)	0(1)
O(2)	31(1)	59(1)	27(1)	4(1)	8(1)	3(1)
C(10)	30(1)	55(1)	29(1)	1(1)	8(1)	2(1)
C(11)	43(1)	62(1)	47(1)	9(1)	8(1)	-5(1)
C(12)	50(1)	82(1)	55(1)	-9(1)	16(1)	-22(1)
C(13)	31(1)	111(2)	41(1)	-16(1)	4(1)	-1(1)
C(14)	43(1)	91(1)	43(1)	5(1)	1(1)	18(1)
C(15)	41(1)	62(1)	41(1)	7(1)	7(1)	5(1)