Supporting Information

Dehalogenative Deuteration of Alkyl and Aryl Bromides by Thiyl Radical Catalysis under Visible-Light Irradiation

Jiin Lee[a] and Sunggi Lee*[ab]

[a]Department of physics and Chemistry, DGIST, 333 Techno Jungang-daero, Dalseong-gun, Daegu 42988

[b]Center for Basic Science, DGIST, 333 Techno Jungang-daero, Dalseong-gun, Daegu 42988

Table of Contents

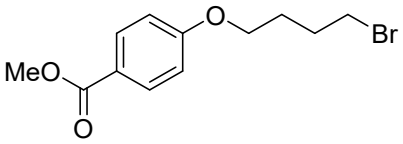
1. General Consideration

All chemicals and solvents were used without further purifications. ^{1}H, ^{13}C spectra were recorded on a Bruker Avance III-400 spectrometer. The chemical shifts reported in ppm relative to residual solvent $CDCl_3$, CD_3CN, CD_3OD, or added TMS as an internal reference. Splitting patterns are designated as follows: br; broad, s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dt; double of triplet, td; triple of doublet, dd; double of doublet. Flash chromatography was carried out on Merck silica 60 (230-400 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F_{254} plates. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu). IR spectra were recorded by SHIMADZU IRAffiinity-1S. Blue light LEDs were purchased from Kessil (A160WE, PR 160 440 nm, and PR 160 390 nm).

2. Experimental Section

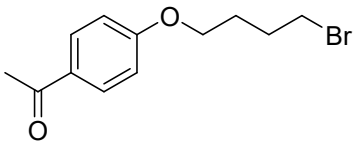
2-1. Preparation of Substrate

methyl 4-(4-bromobutoxy)benzoate (1c)



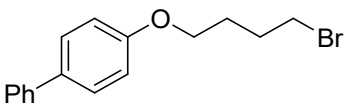
In a 50 mL RBF, 1,4-dibromobutane (6.48 g, 3.58 mL, 30 mmol, 3.0 equiv.) was added in a mixture of methyl 4-hydroxybenzoate (1.52 g, 10 mmol, 1.0 equiv.) and potassium carbonate (1.93 g, 14 mmol, 1.4 equiv.) in acetone (18.0 mL). The reaction mixture was refluxed for 18 hours. Solid was filtered, and solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (Hx/EtOAc = 3/1 ~ 2/1) to afford **1c** (1.0 g, 35%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.89 (m, 2H), 6.95 – 6.74 (m, 2H), 4.05 (t, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.15 – 2.02 (m, 2H), 2.02 – 1.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 162.6, 131.6, 122.6, 114.0, 67.0, 51.5, 33.2, 29.3, 27.7. **IR**: 2951, 1722, 1508, 1280, 1253, 1170, 1043, 848 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{15}BrO_3$ 286.0205; Found 286.0202.

1-(4-(4-bromobutoxy)phenyl)ethenone (1d)



In a 20 mL vial, 1,4-dibromobutane (2.16 g, 1.20 ml, 10 mmol, 2.0 equiv.) was added in a mixture of methyl 4'-hydroxyacetophenone (681 mg, 5 mmol, 1.0 equiv.) and potassium carbonate (1.04 g, 7.5 mmol, 1.5 equiv.) in acetone (15.0 mL). The reaction mixture was stirred for 18 hours at room temperature. Solid was filtered, and solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (Hx/EtOAc = 2/1) to afford **1d** as a white solid (680 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.87 (m, 2H), 7.02 – 6.85 (m, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.56 (s, 3H), 2.08 (m, 2H), 2.04 – 1.91 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 162.7, 130.6, 130.4, 114.1, 67.1, 33.2, 29.3, 27.7, 26.3. **IR**: 2951, 2870, 1741, 1672, 1598, 12553, 1020, 815 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{15}BrO_2$ 270.0255; Found 270.0253.

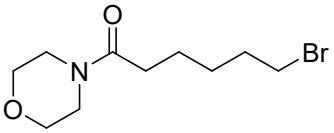
4-(4-bromobutoxy)-1,1'-biphenyl (1e)



In a 20 mL vial, 1,4-dibromobutane (1.30 g, 720 µL, 6 mmol, 1.2 equiv.) was added in a mixture of 4-phenylphenol (851 mg, 5 mmol, 1.0 equiv.), potassium iodide (41.5 mg, 0.25 mmol, 5 mol %) and potassium carbonate (1.04 g, 7.5 mmol, 1.5 equiv.) in acetone (15.0 mL). The reaction mixture was refluxed for 12 hours. Solid was filtered, and solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (Hx/ EtOAc = 20/1~5/1) to afford **1e** as a white solid (560 mg, 37%). **^{1}H NMR** (400 MHz,

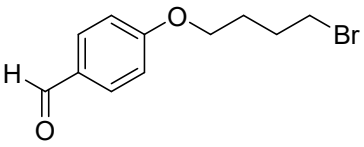
$CDCl_3$) δ 7.58 – 7.49 (m, 4H), 7.41 (m, 2H), 7.33 – 7.28 (m, 1H), 7.01 – 6.92 (m, 2H), 4.05 (t, *J* = 6.0 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.10 (m, 2H), 2.02 – 1.90 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.7, 66.9, 33.4, 29.5, 27.9. **IR**: 2943, 2873, 2362, 1523, 1487, 1253, 1180, 1043, 896 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{16}H_{17}BrO$ 304.0463; Found 304.0461.

6-bromo-1-morpholinohexan-1-one (1f)



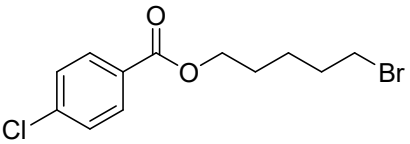
1f was synthesized according to known literature procedures.[1] In a dried 50 mL RBF, morpholine (784 mg, 787 µL, 9.0 mmol, 1.8 equiv.) and triethyl amine (1.01 g, 1.39 mL, 10.0mmol, 2.0 equiv.) was added in a solution of 6-bormohexanoyl chloride (1.07g, 765 µL, 5.0 mmol, 1.0 equiv.) in CH_2Cl_2 (20.0 mL). Solution was stirred for 12 hours at room temperature. Crude mixture was washed with 3 M HCl solution. Aqueous layer was removed and $NaHCO_3$ (aq) was added in organic layer. Organic layer was extracted with CH_2Cl_2 and dried over $MgSO_4$. Solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (Hx/EtOAc =1/2) to afford **1f** as a colorless oil (130 mg, 9.8%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.73 – 3.58 (m, 6H), 3.49 – 3.44 (m, 2H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.33 (m, 2H), 1.89 (m, 2H), 1.67 (m, 2H), 1.54 – 1.41 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 66.9, 66.7, 46.0, 42.0, 33.6, 32.8, 32.6, 28.0, 24.2. **IR**: 2972, 284, 1597, 1433, 1228, 1114, 1029, 846 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{10}H_{18}BrNO_2$ 263.0521; Found 263.0522.

4-(4-bromobutoxy)benzaldehyde (1h)



In a 50 mL RBF, 1,4-dibromobutane (4.32 g, 20.0 mmol, 2.0 equiv.) was added in a mixture of 4-hydroxybenzaldehyde (1.22 g, 10.0 mmol, 1.0 equiv.) and potassium carbonate (1.38 g, 10.0 mmol, 1.0 equiv.) in acetone (30.0 mL). The reaction mixture was refluxed for 24 hours. Solid was filtered, and solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **1h** as a colorless oil (1.87 g, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.93 – 7.72 (m, 2H), 7.06 – 6.76 (m, 2H), 4.09 (t, *J* = 5.9 Hz, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 2.16 – 2.04 (m, 2H), 2.04 – 1.94 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 163.9, 132.0, 130.0, 114.7, 67.3, 33.2, 29.3, 27.7. **IR**: 2954, 2740, 2569, 2104, 1691, 1598, 1251, 1157, 831 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{11}H_{13}BrO_2$ 256.0099; Found 256.0097.

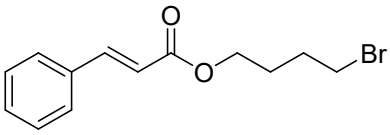
5-bromopentyl 4-chlorobenzoate (1i)



In a 50 mL RBF, cesium carbonate (4.89 g, 15.0 mmol, 1.5 equiv.) and 4-chlorobenzoic acid (1.57 g, 10.0 mmol, 1.0 equiv.) was added in a solution of 1,5-dibromopentane (4.60 g, 20.0 mmol, 2.0 equiv.) in DMF (25.0 mL). The reaction mixture was stirred for 12 hours at room temperature. The reaction mixture was filtered, and the filtrate was concentrated under the reduced pressure. The

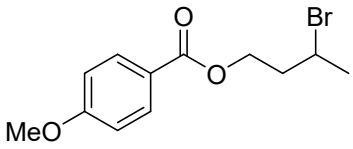
crude product was purified by silica gel column chromatography (Hx/EtOAc = 20/1) to afford **1i** as a colorless oil (3.06 g, 34%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.45 – 7.36 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 2.00 – 1.90 (m, 2H), 1.85 – 1.76 (m, 2H), 1.66 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 139.3, 130.9, 128.8, 128.7, 64.8, 33.4, 32.2, 27.8, 24.7. **IR**: 2951, 2939, 1720, 1271, 1091, 904 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{14}BrClO_2$ 305.9844; Found 305.9840.

4-bromobutyl cinnamate (1j)



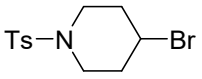
In a 50 mL RBF, trans-cinnamic acid (1.46 g, 10 mmol, 1.0 equiv.) and cesium carbonate (2.28 g, 7.0 mmol, 0.7 equiv.) was added in a solution of 1.4-dibromobutane (6.48 g, 30.0 mmol, 3.0 equiv.) in DMF (25.0 mL). Reaction mixture was stirred for 12 hours at room temperature. Reaction mixture was filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1 ~ 10/1) to afford **1j** as a colorless oil (2.83 g, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.43 – 7.33 (m, 3H), 6.44 (m, 1H), 4.25 (t, *J* = 6.3 Hz, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.08 – 1.95 (m, 2H), 1.94 – 1.83 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 145.0, 134.4, 130.4, 129.0, 128.1, 118.0, 63.5, 33.1, 29.4, 27.4. **IR**: 2966, 2899, 1710, 1637, 1251, 1165, 979 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{13}H_{15}BrO_2$ 282.0255; Found 282.0254.

3-bromobutyl 4-methoxybenzoate (1k)



In a 25 mL RBF, 1,3-dibromobutane (2.16 g, 1.20 mL, 10.0 mmol, 2.0 equiv.) was added in a solution of p-anisic acid (761 mg, 5.0 mmol, 1.0 equiv.) and cesium carbonate (2.44 g, 7.5 mmol, 1.5 equiv.) in DMF (12.5 mL) solution. Reaction mixture was stirred for 12 hours at room temperature. Filtrate was collected and solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **1k** as a colorless oil (750 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 2H), 6.95 – 6.90 (m, 2H), 4.55 – 4.47 (m, 1H), 4.45 – 4.36 (m, 1H), 4.35 – 4.25 (m, 1H), 3.86 (s, 3H), 2.32 – 2.09 (m, 2H), 1.79 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 163.5, 131.6, 122.5, 113.7, 62.7, 55.5, 47.0, 39.9, 26.6. **IR**: 2958, 2839, 1604, 1510, 1274, 1253, 110, 950 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{15}BrO_3$ 286.0205; Found 286.0206.

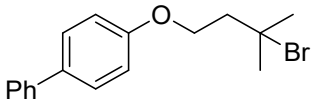
4-bromo-1-tosylpiperidine (1l)[2]



In a 50 mL RBF, triphenylphosphine (2.26 g, 8.6 mmol, 1.1 equiv.) and carbon tetrabromide (2.60 g, 8.2 mmol, 1.0 equiv.) was added in a solution of 1-tosylpiperidin-4-ol (2.0 g, 7.8 mmol, 1.0 equiv.) in CH_2Cl_2 (15.0 mL). Reaction mixture was stirred for 16 hours at room temperature. Na_2CO_3 (aq) was added in a reaction mixture, and crude mixture was extracted with Et_2O and dried over $MgSO_4$. Solvent was evaporated under reduced pressure and the crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **1l** as a white solid (1.64 g, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m,

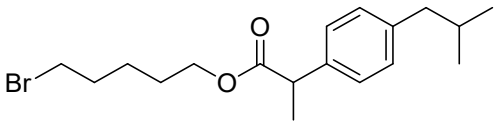
2H), 7.39 – 7.30 (m, 2H), 4.31 – 4.19 (m, 1H), 3.25 – 3.14 (m, 2H), 3.14 – 3.04 (m, 2H), 2.45 (s, 3H), 2.25 – 2.13 (m, 2H), 2.11 – 1.98 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 133.4, 129.8, 127.6, 47.8, 43.8, 34.7, 21.6. **IR**: 2926, 2860, 1340, 1157, 1008, 927, 858 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{16}BrNO_2S$ 319.0065; Found 319.0047.

4-(3-bromo-3-methylbutoxy)-1,1'-biphenyl (1m)[3, 4]



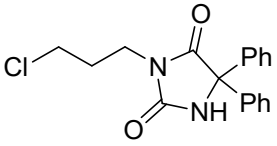
In a 25 mL RBF, 4-phenylphenol (749 mg, 4.4 mmol, 1.1 equiv.), and K_2CO_3 (663 mg, 4.8 mmol, 1.2 equiv.) was added in a solution of 3-hydroxy-3-methylbutyl 4-methylbenzenesulfonate (1.03 g, 4.0 mmol, 1.0 equiv.) in DMF (10.0 mL). The reaction mixture was stirred for 12 hours at 80 °C, then quenched with H_2O (15.0 mL) and extracted with CH_2Cl_2 and dried over $MgSO_4$. Solvent was evaporated under reduced pressure. The crude product was used for next step without purification. In a dried Schlenk flask, the crude alcohol (in a minimal amount of CH_2Cl_2) was added in a solution of LiBr (695 mg, 8.0 mmol), and 48 wt% Hydrobromic acid (900 μL, 8.0 mmol) under argon atmosphere at 0˚C. The reaction mixture was allowed to warm to room temperature and stirred for 12 hours. The reaction mixture was diluted with ethyl acetate, and quenched with H_2O, and $NaHCO_3$ (aq). The crude mixture was extracted with ethyl acetate and dried over $MgSO_4$. Solvent was evaporated under reduced pressure and the crude mixture was purified by silica gel column chromatography (Hx/EtOAC = 10/1) to afford **1m** as a white solid (687 mg, 55% overall two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 4H), 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 1H), 7.03 – 6.94 (m, 2H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.34 (t, *J* = 6.6 Hz, 2H), 1.88 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 140.8, 134.0, 128.7, 128.2, 126.8, 126.7, 114.8, 66.2, 65.3, 45.9, 34.9. **IR**: 2937, 1606, 1485, 1247, 1122, 1031, 833 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{17}H_{19}BrO$ 318.0619; Found 318.0621.

5-bromopentyl 2-(4-isobutylphenyl)propanoate (1n)



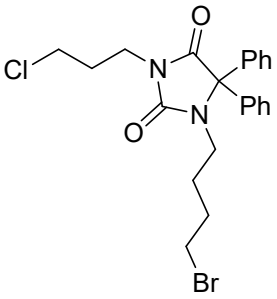
In a dried 25 mL RBF, 1,5-dibromopentane (2.23 g, 1.32 mL, 9.7 mmol, 2.0 equiv.) was added in a solution of ibuprofen (1.00 g, 4.85 mmol, 1.0 equiv.) and potassium carbonate (2.01 g, 14.5 mmol, 3 equiv.) in DMF (9.70 mL). Reaction mixture was stirred for 24 hours at room temperature. Filtrate was collected and solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography. (Hx/EtOAc = 20/1~ 10/1) to afford **1n** as a colorless oil (720 mg, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.13 – 7.07 (m, 2H), 4.14 – 4.00 (m, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.33 (t, *J* = 6.8 Hz, 2H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.93 – 1.72 (m, 3H), 1.68 – 1.54 (m, 2H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.45 – 1.33 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 140.5, 137.8, 129.3, 127.2, 64.2, 45.2, 45.0, 33.4, 32.2, 30.2, 27.7, 24.5, 22.4, 18.4. **IR**: 2954, 2872, 1732, 1163, 945 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{18}H_{27}BrO_2$ 354.1194; Found 354.1197.

3-(3-chloropropyl)-5,5-diphenylimidazolidine-2,4-dione



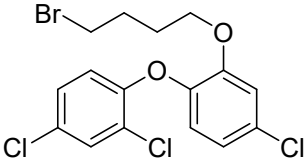
In a 20 mL vial, NaH 60% in mineral oil (200 mg, 5.0 mmol, 1.0 equiv.) was added in a solution of 5,5-diphenyl hydantoin (1.26 g, 5.0 mmol, 5.0 mmol, 1.0 equiv.) in DMF (15.0 mL) and stirred for 30 minutes at 50 °C. Then, 1,3-chloropropane (1.97 g, 1.2 mL, 15.0 mnol, 2.5 equiv.) was added and stirred at 50 °C. After 18 hours, solution was quenched by 1 N HCl (20.0 mL) and extracted with EtOAc. Solvent was evaporated under reduced pressure. Crude mixture was added to a solution of lithium chloride (636 mg, 15.0 mmol, 3.0 equiv.) in DMF (15.0 mL) and stirred at 90 °C. After 12 hours, the reaction mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. White solid was obtained (1.13 g, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 10H), 3.65 (t, *J* = 6.9 Hz, 2H), 3.42 (t, *J* = 6.5 Hz, 2H), 2.11 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.3, 156.8, 139.1, 128.9, 128.6, 126.8, 70.1, 41.8, 36.7, 31.0. **IR**: 2956, 1703, 1448, 1417 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{18}H_{17}ClN_2O_2$ 328.0979; Found 328.0979.

1-(4-bromobutyl)-3-(3-chloropropyl)-5,5-diphenylimidazolidine-2,4-dione (1o)



In a 20 mL vial, 1,4-dibromobutane (1.1 g, 0.6 mL, 5.0 mmol, 5.0 equiv.) was added in a solution of 3-(3-chloropropyl)-5,5-diphenylimidazolidine-2,4-dione (329 mg, 1.0 mmol, 1.0 equiv.) and potassium carbonate (207 mg, 1.5 equiv.) and potassium iodide (9 mg, 5 mol%) in acetone (5.0 mL) solution. Reaction mixture was stirred for 4 hours at room temperature. Solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAC = 5/1) to afford **1o** as a white solid (204 mg, 44%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 6H), 7.29 – 7.22 (m, 4H), 3.76 (t, *J* = 6.9 Hz, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 3.43 – 3.35 (m, 2H), 3.13 (t, *J* = 6.7 Hz, 2H), 2.20 – 2.10 (m, 2H), 1.59 – 1.50 (m, 2H), 1.10 – 0.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 155.7, 137.0, 129.1, 129.0, 128.2, 74.9, 41.8, 41.2, 37.0, 32.6, 31.0, 29.9, 26.8. **IR**: 2954, 1710, 1450, 1242, 1045 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{22}H_{24}BrClN_2O_2$ 464.0689; Found 464.0687.

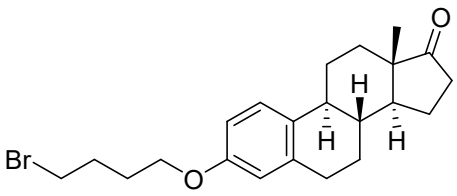
2-(4-bromobutoxy)-4-chloro-1-(2,4-dichlorophenoxy)benzene (1p)



In a 50 mL RBF, 1,4-dibromobutane (1.62 g, 0.91 mL,7.5 mmol, 1.5 equiv.) was added in a solution of 5-chloro-2-(2,4-dichlorophenoxy)phenol (1.45 mg, 5.0 mmol, 1.0 equiv.) and potassium carbonate (691 mg, 5.0mmol, 1.0 equiv.) in acetone (20.0 mL) solution. Reaction mixture was stirred for 12 hours at room temperature. Filtrate was collected and solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1 ~ 10/1) to afford **1p** as a colorless oil (1.71 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 1H), 7.14 – 7.05 (m, 1H), 7.02 – 6.91 (m, 3H), 6.68 – 6.49 (m, 1H), 3.95 (t, *J* = 5.4 Hz, 2H), 3.32 (t, *J* = 6.1 Hz, 2H), 1.89 – 1.63 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.6, 150.8, 142.9, 130.7, 130.2, 127.8, 127.6, 124.3, 122.4, 121.2, 117.6, 114.8, 68.0, 33.1, 29.0, 27.5. **IR**: 2941,

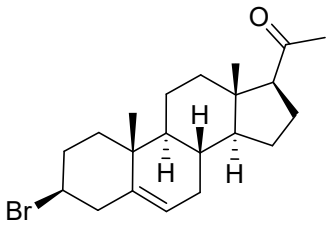
2841, 1598, 1471, 1230, 904 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{16}H_{14}BrCl_3O_2$ 423.9219; Found 423.9214.

(8R,9S,13S,14S)-3-(4-bromobutoxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (1q)



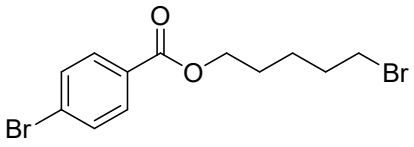
In a 20 ml vial, 1,4-dibromobutane (432.0 mg, 239 μL, 2.00 mmol, 2.0 equiv.) was added in a mixture of estrone (270.0 mg, 1.00 mmol, 1.0 equiv.), potassium iodide (8.3 mg, 0.05 mmol, 5 mol%), and potassium carbonate (207 mg, 1.50 mmol, 1.5 equiv.) in acetone (3.0 mL). The reaction mixture was refluxed for 12 hours. Solid was filtered, and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (Hx/EtOAc = 10/1~3/1) to afford **1q** as a white solid (210mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 1H), 6.70 (dd, J_1 = 8.6, J_2 = 2.8 Hz, 1H), 6.67 – 6.60 (m, 1H), 3.97 (t, J = 6.0 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.93 – 2.86 (m, 2H), 2.50 (dd, J = 18.8, 8.6 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.31 – 2.21 (m, 1H), 2.21 – 2.11 (m, 1H), 2.10 – 1.86 (m, 7H), 1.71 – 1.37 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.9, 156.9, 137.8, 132.2, 126.4, 114.6, 112.1, 66.8, 50.4, 48.0, 44.0, 38.4, 35.9, 33.5, 31.6, 29.7, 29.5, 28.0, 26.6, 25.9, 21.6, 13.9. **IR**: 3736, 2962, 2873, 1732, 1253, 1004 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{22}H_{29}BrO_2$ 406.1333; Found 406.1340.

1-((8S,9S,10R,13S,14S,17S)-3-bromo-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethenone (1r)



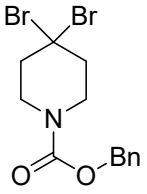
In a dried 50 mL RBF, carbon tetrabromide (1.99 g, 6.0 mmol, 1.2 equiv.) was added in a solution of 5-Pregnen-3β-ol-20-one (1.57 g, 5.0 mmol, 1.0 equiv.) and triphenylphosphine (1.44 g, 5.5 mmol, 1.1 equiv.) in dichloromethane (20.0 mL). Reaction mixture was stirred for 12 hours at room temperature. Reaction mixture was filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **1r** as a white solid (140 mg, 7.4%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.43 – 5.29 (m, 1H), 3.98 – 3.84 (m, 1H), 2.79 – 2.68 (m, 1H), 2.62 – 2.56 (m, 1H), 2.56 – 2.49 (m, 1H), 2.22 – 2.16 (m, 2H), 2.12 (s, 3H), 2.10 – 1.93 (m, 3H), 1.93 – 1.82 (m, 1H), 1.74 – 1.38 (m, 7H), 1.29 – 1.11 (m, 3H), 1.04 (s, 3H), 1.00 – 0.94 (m, 1H), 0.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.5, 141.6, 122.0, 63.7, 56.8, 52.3, 50.1, 44.2, 44.0, 40.2, 38.8, 36.4, 34.3, 31.7, 31.7, 31.5, 24.5, 22.9, 20.9, 19.3, 13.2. **IR**: 2933, 2850, 1701, 1359, 1105 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{21}H_{31}BrO$ 380.1540; Found 380.1539.

5-bromopentyl 4-bromobenzoate (1s)



In a 20 mL vial, cesium carbonate (2.44 g, 7.5 mmol, 1.5 equiv.) and 4-bromobenzoic acid (1.01 g, 5.0 mmol, 1.0 equiv.) was added in a solution of 1,5-dibromopentane (2.30 g, 10.0 mmol, 2.0 equiv.) in DMF (12.5 mL). The reaction mixture was stirred for 12 hours at room temperature. The reaction mixture was filtered, and the filtrate was concentrated under the reduced pressure. The crude product was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **1s** as a colorless oil (1.75 g, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.82 (m, 2H), 7.64 – 7.54 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 1.99 – 1.87 (m, 2H), 1.86 – 1.74 (m, 2H), 1.69 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 131.7, 131.1, 129.3, 128.0, 64.9, 33.4, 32.3, 27.9, 24.7. **IR**: 2958, 2866, 1720, 1589, 1269, 1012, 846 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{12}H_{14}Br_2O_2$ 349.9341; Found 349.9328.

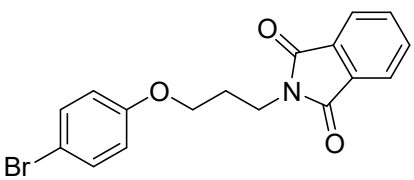
benzyl 4,4-dibromopiperidine-1-carboxylate (1t)



In a 50 mL RBF, molecular sieves 3Å (1 g), methanol (5.0 mL) and hydrazine hydrate (0.97 ml, 20.0 mmol, 20.0 equiv.) were added successively with stirring. After 20 min, a methanol (5.0 mL) solution of benzyl 4-Oxo-1-piperidinecarboxylate (233 mg, 1.0 mmol, 1.0 equiv.) was added to the reaction mixture and the mixture was stirred for 2 hours. Molecular sieves were filtered off and washed with diethyl ether. The filtrate was concentrated under reduced pressure and the excess hydrazine was further removed from the residue under high vacuum. The crude mixture of hydrazone was used in next step without any further purification.

To a THF solution of *t*-butanol (222 mg, 287 µL, 3 mmol, 3.0 equiv.) was added a hexane solution of 1.8 M *n*-butyllithium (1.67 mL, 3.0 mmol, 3.0 equiv.) at 0 ˚C and the reaction mixture was stirred for 5 min. Copper(II) bromide (1.34 g, 6.0 mmol, 6.0 equiv.) was added to the mixture. The ice bath was removed and stirred for 20 min. Crude hydrazone in THF (3.0 mL) was added dropwise to the reaction mixture. After 1 hour, the reaction was quenched by addition of 25% NH_3 aqueous solution. The organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4. Solvent was concentrated under reduced pressure. The residue was purified by silica gel chromatography (Hx/EtOAc = 5/1) to give **1t** (182 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 5.13 (s, 2H), 3.70 – 3.55 (m, 4H), 2.63 – 2.43 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 136.4, 128.6, 128.2, 128.0, 67.5, 65.9, 47.9, 42.6. **IR**: 2920, 1697, 1427, 1276, 1002 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{13}H_{15}Br_2NO_2$ 376.9750; Found 376.9456.

2-(3-(4-bromophenoxy)propyl)isoindoline-1,3-dione (3d)

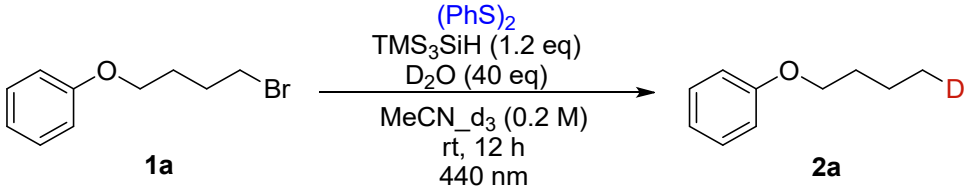


In a 20 mL vial, n-(3-bromopropyl)phthalimide (295 mg, 1.1 mmol), 4-bromophenol (173 mg, 1.0 mmol), and potassium carbonate (138 mg, 1.0 mmol) was added then 5.0 mL of DMF was added. Reaction mixture was stirred for 12 hours at 60˚C. Reaction mixture was concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1)

to afford **3d** as a white solid (288 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.76 – 7.68 (m, 2H), 7.35 – 7.27 (m, 2H), 6.71 – 6.64 (m, 2H), 3.99 (t, *J* = 6.0 Hz, 2H), 3.90 (t, *J* = 6.8 Hz, 2H), 2.23 – 2.12 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 157.8, 134.0, 132.2, 132.2, 123.3, 116.3, 113.0, 66.0, 35.4, 28.2. **IR**: 3064, 2943, 1699, 1377, 1236, 1029 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{17}H_{14}BrNO_3$ 359.0157; Found 359.0155.

2-1. Reaction Optimization

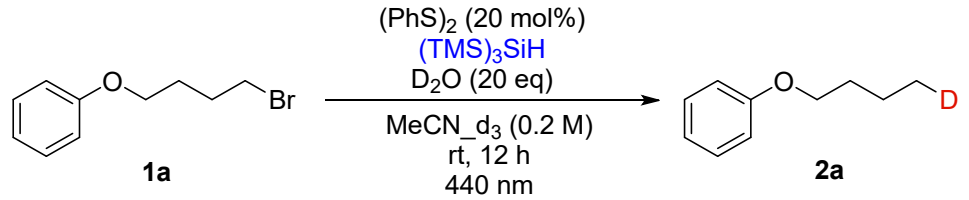
Table S1. Diphenyl disulfide equivalent screening[a]



entry	equivalent ($(PhS)_2$)	yield [b] (%)	D-inc[c] (%)
1	0	n.d.[d]	0
2	0.1	98	98
3	0.2	99	98
4	0.5	65	93
5	1.0	22	92

[a]Reaction conditions (0.1 mmol scale): 4-phenoxybutylbromide **1a** 0.1 mmol, diphenyl disulfide, $(TMS)_3SiH$ (1.2 eq) and D_2O (40 eq) in MeCN_d_3 (0.2 M), 440 nm blue LED irradiation for 12 h under Ar. [b, c]yields and D-inc were measured by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [d]Not detected.

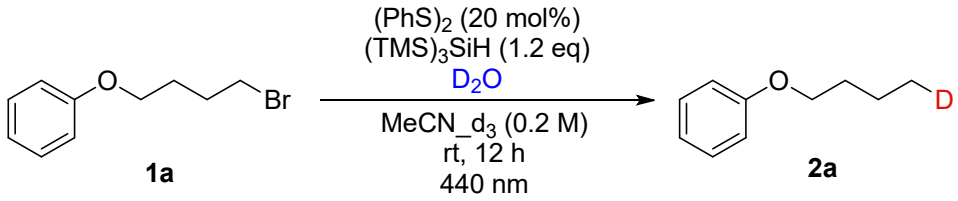
Table S2. TTMSS equivalent screening[a]



entry	equivalent (TTMSS)	yield [b] (%)	D-inc[c] (%)
1	0	n.d.[d]	0
2	0.5	30	90
3	1.0	83	92
4	1.2	93	87
5	1.5	100	88
6	2.0	100	87

[a]Reaction conditions (0.1 mmol scale): 4-phenoxybutylbromide **1a** 0.1 mmol, 20 mol% of diphenyl disulfide, $(TMS)_3SiH$ and D_2O (20 eq) in MeCN_d_3 (0.2 M), 440 nm blue LED irradiation for 12 h under Ar. [b, c]yields and D-inc were measured by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [d]Not detected.

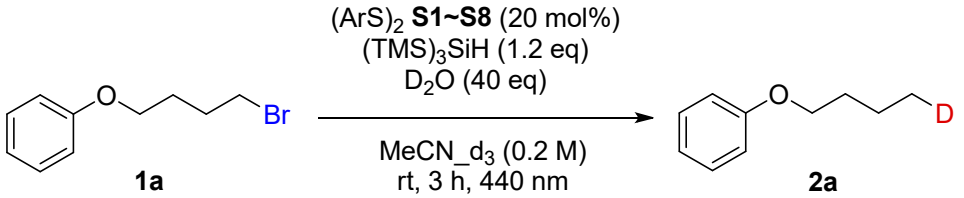
Table S3. D_2O screening[a]

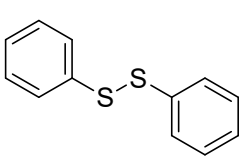


entry	equivalent (D_2O)	yield [b] (%)	D-inc[c] (%)
1	0	86	0
2	10	100	81
3	20	100	88
4	30	100	89
5	40	100	98
6	50	100	88

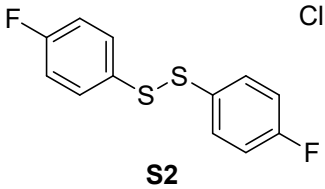
[a]Reaction conditions (0.1 mmol scale): 4-phenoxybutylbromide **1a** 0.1 mmol, 20 mol% of diphenyl disulfide, $(TMS)_3SiH$ (1.2 eq) and D_2O in MeCN_d_3 (0.2 M), 440 nm blue LED irradiation for 12 h under Ar. [b, c]yields and D-inc were measured by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard.

Table S4. Catalyst screening[a]

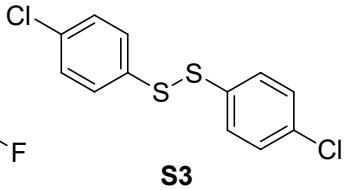




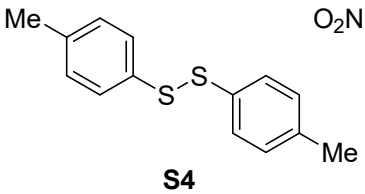
S1
99%, 98% D



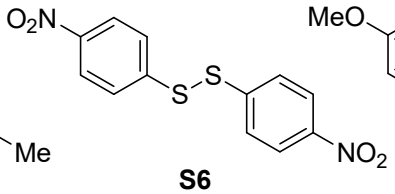
S2
90%, 99% D



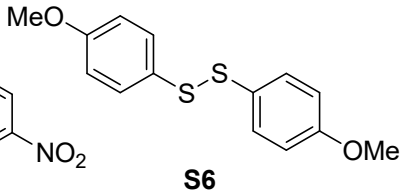
S3
96%, 98% D



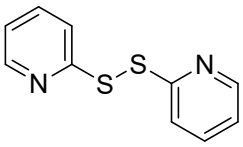
S4
93%, 96% D



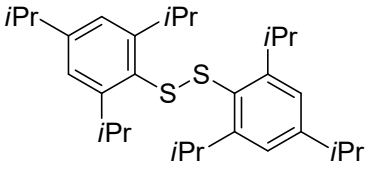
S6
5%, 41% D



S6
75%, 83% D



S7
53%, 79% D



S8
55%, 75% D

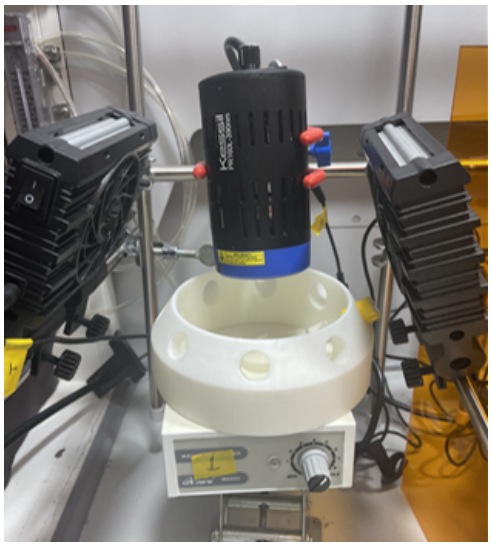
[a]Reaction conditions (0.1 mmol scale): 4-phenoxybutylbromide **1a** 0.1 mmol, 20 mol% of $(ArS)_2$, $(TMS)_3SiH$ (1.2 eq) and D_2O in MeCN_d_3 (0.2 M), 440 nm blue LED irradiation for 3 h under Ar. Yields and D-inc were measured by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard.

2-3. Deuteration of Alkyl Bromides

Deuteration of alkyl or alkyl bromides:

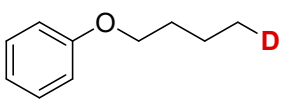
All experiments were performed in frame-dried glassware using argon as protective gas. Solvents were transferred by using syringe and were introduced into the vial through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC). NMR yield was measured with dibromomethane as an internal standard and isolated yield was obtained by flash chromatography using silica gel. D-incorporation was determined by NMR or GC-MS using crude mixtures or isolated compounds.

General Procedure for deuteration of alkyl bromides (**General Procedure A**). In an oven-dried 4 ml vial, tris(trimethylsilyl)silane (1.2 equiv.) was added in a solution of diphenyl disulfide (20 mol%), alkyl bromide (0.1 mmol-0.6 mmol, 1.0 equiv.) and D_2O (40.0 equiv.) in MeCN (0.2 M) under argon atmosphere. The vial was sealed with electric tape and stirred for 3-72 hours at room temperature (~30 ˚C under irradiation) under 440 nm irradiation (440 nm, Kessil LEDs lamp). After the reaction was completed, the solvent was evaporated under reduced pressure. Deuterated product was isolated by column chromatography on silica gel (hexane/ethyl acetate).



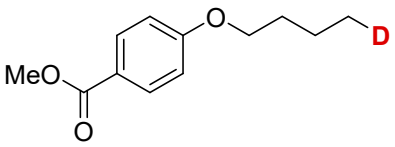
Reaction setup for **General Procedure A & B** with Kessil lamp (160WE, PR 160 440 nm, and PR 160 390 nm).

(4-*d*-butoxy)benzene (2a)[5]



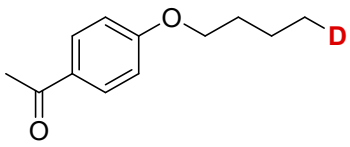
Compound was synthesized from (4-bromobutoxy)benzene according to General Procedure A on a 0.2 mmol scale. NMR yield and Deuterium incorporation was observed via ^{1}H NMR. Spectrum in accordance with literature: *Nat. Commun.* 2022, **13**, 3774.

Methyl 4-(butoxy-4-*d*)benzoate (2c)



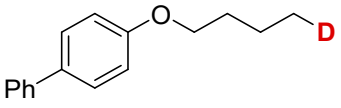
Following General Procedure A, diphenyl disulfide (4.4 mg, 0.02 mmol, 20 mol%), tris(trimethylsilyl)silane (37.0 μL, 0.12 mmol, 1.2 equiv.), **1c** (28.7 mg, 0.10 mmol, 1.0 equiv.), D_2O (80.0 μL, 4.00 mmol, 40.0 equiv.), and MeCN (0.5 mL) were reacted for 3 hours. Then, TBAF (1.0 mL, 1.0 M solution in THF) was added in the reaction mixture and stirred for 10 minutes. Solvent was evaporated under the reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 50/1) to **2c** (18.1 mg, 87%, 94 % D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 6.93 – 6.85 (m, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.88 (s, 3H), 1.87 – 1.72 (m, 2H), 1.55 – 1.44 (m, 2H), 1.02 – 0.92 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 163.0, 131.6, 122.3, 114.1, 67.9, 51.8, 31.1, 19.1, 13.5 (t, *J* = 19.2 Hz). **IR**: 2951, 2872, 1716, 1435, 1251, 1103, 1010 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{15}DO_3$ 209.1162; Found 209.1160.

1-(4-butoxyphenyl-4-*d*)ethenone (2d)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1d** (54.2 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. Then, TBAF (1.0 mL, 1.0 M solution in THF) was added in the reaction mixture and stirred for 10 minutes. Solvent was evaporated under the reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1~10/1) to afford **2d** (21.7 mg, 56%, 94 % D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 6.98 – 6.87 (m, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.55 (s, 3H), 1.87 – 1.72 (m, 2H), 1.53 – 1.43 (m, 2H), 1.03 – 0.92 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 163.2, 130.6, 130.2, 114.2, 68.0, 31.1, 26.3, 19.1, 13.5 (t, *J* = 19.2 Hz). **IR**: 2949, 2889, 1666, 1600, 1244, 999 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{15}DO_2$ 193.1213; Found 193.1214.

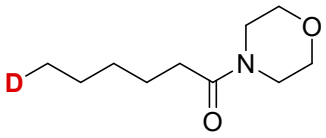
4-(butoxy-4-*d*)-1,1'-biphenyl (2e)



Following General Procedure A, diphenyl disulfide (4.4 mg, 0.02 mmol, 20 mol%), tris(trimethylsilyl)silane (37.0 μL, 0.12 mmol, 1.2 equiv.), **1e** (30.5 mg,

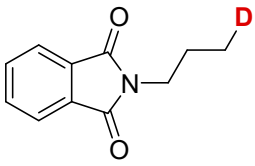
0.10 mmol, 1.0 equiv.), D_2O (80.0 μL, 4.00 mmol, 40.0 equiv.), and MeCN (0.5 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **2e** (22.7 mg, 70%, 95% D) as a white solid**. ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.40 (m, 4H), 7.37 – 7.30 (m, 2H), 7.27 – 7.20 (m, 1H), 6.94 – 6.86 (m, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.49 – 1.39 (m, 3H), 0.95 – 0.87 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 140.9, 133.6, 128.7, 128.1, 126.7, 126.6, 114.8, 67.8, 31.4, 19.2, 13.6 (t, *J* = 19.2 Hz). **IR**: 2951, 2926, 2858, 1606, 1271, 1251, 1068, 839 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{16}H_{17}DO$ 227.1420; Found 227.1418.

1-morpholinohexan-1-one-6-*d* (2f)



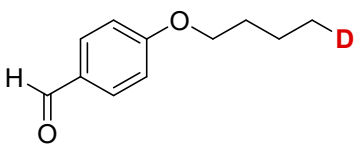
Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1f** (52.8 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **2f** (37.3 mg, 67%, 97 % D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.69 – 3.63 (m, 4H), 3.63 – 3.57 (m, 2H), 3.49 – 3.40 (m, 2H), 2.34 – 2.23 (m, 2H), 1.69 – 1.55 (m, 2H), 1.38 – 1.25 (m, 4H), 0.92 – 0.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 67.0, 66.7, 46.1, 41.9, 33.1, 31.6, 25.0, 22.4, 13.7 (t, *J* = 19.1 Hz). **IR**: 2954, 2926, 2850, 1643, 1271, 1114, 850 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{10}H_{18}DNO_2$ 186.1479; Found 186.1478.

2-(propy-3-*d*)lisoindoline-1,3-dione (2g)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1g** (53.6 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **2g** (23.0 mg, 60%, 92 % D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.73 – 7.67 (m, 2H), 3.71 – 3.58 (m, 2H), 1.76 – 1.65 (m, 2H), 0.99 – 0.90 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 133.8, 132.2, 123.2, 39.6, 21.8, 11.0 (t, *J* = 19.3 Hz). **IR**: 2949, 2924, 2852, 1697, 1396, 1041, 885 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{11}H_{10}DNO_2$ 190.0853; Found 190.0851.

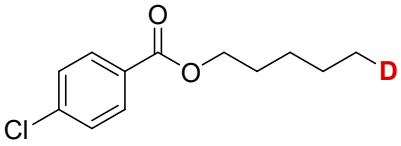
4-(4-*d*-butoxy)benzaldehyde (2h)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20

mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1h** (61.1 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. Then, TBAF (1.0 mL, 1.0 M solution in THF) was added in the reaction mixture and stirred for 10 minutes. Solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1) to afford **2h** (67%-NMR yield, 97% D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.88 – 7.76 (m, 2H), 7.02 – 6.88 (m, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.54 – 1.45 (m, 2H), 1.02 – 0.94 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 164.3, 132.0, 129.8, 114.8, 68.1, 31.1, 19.1, 13.5 (t, *J* = 19.3 Hz). **IR**: 2872, 2825, 1693, 1600, 1255, 1215, 1026 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{11}H_{13}DO_2$ 179.1057; Found 179.1053.

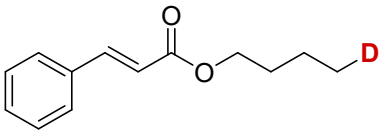
Pentyl-5-*d* 4-chlorobenzoate (2i)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1i** (61.1 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. Then, TBAF (1.0 mL, 1.0 M solution in THF) was added in the reaction mixture and stirred for 10 minutes. Solvent was evaporated under the reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 30/1) to afford **2i** (38.9 mg, 85%, 92% D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.43 – 7.38 (m, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.47 – 1.32 (m, 4H), 0.95 – 0.87 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 139.2, 130.9, 129.0, 128.7, 65.4, 28.4, 28.2, 22.3, 13.7, (t, *J* = 19.1 Hz). **IR**: 2951, 2933, 1720, 1595, 1269, 1091, 1014, 958 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{14}DClO_2$ 227.0823; Found 227.0820.

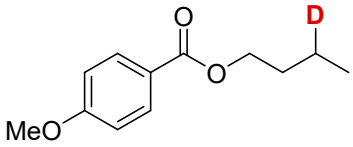
1398, 1112, 1012, 846 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{14}DBrO_2$ 271.0318; Found 271.0315.

Butyl-4-*d* cinnamate (2j)



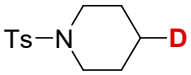
Following General Procedure A, diphenyl disulfide (26.2 mg, 0.12 mmol, 20 mol%), tris(trimethylsilyl)silane (222.0 μL, 0.72 mmol, 1.2 equiv.), **1j** (170.0 mg, 0.60 mmol, 1.0 equiv.), D_2O (480.0 μL, 24.00 mmol, 40.0 equiv.), and MeCN (3.0 mL) were reacted for 72 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 100/1~30/1) to afford **2j** (65.8 mg, 53%, 99% D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.41 – 7.34 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.50 – 1.37 (m, 2H), 0.99 – 0.93 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.5, 30.8, 19.1, 13.5 (t, *J* = 19.2 Hz). **IR**: 2953, 2873, 1712, 1637, 1201, 1166, 979 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{13}H_{15}DO_2$ 205.1213; Found 205.1211.

3-*d*-butyl 4-methoxybenzoate (2k)



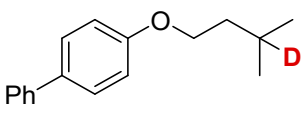
Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1k** (57.4 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1) to afford **2k** (31.5 mg, 75%, 96% D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 7.92 (m, 2H), 6.95 – 6.86 (m, 2H), 4.29 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 1.77 – 1.68 (m, 2H), 1.52 – 1.40 (m, 1H), 1.00 – 0.93 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 163.3, 131.5, 123.0, 113.6, 64.5, 55.4, 30.8, 18.9 (t, *J* = 19.2 Hz), 13.7. **IR**: 2962, 2873, 1606, 1510, 1456, 1276, 1103, 1031, 846 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{15}DO_3$ 209.1162; Found 209.1160.

4-*d*-1-tosylpiperidine (2l)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1l** (63.6 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to≂ afford **2l** (48.1 mg, 85%, 95% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.03 – 2.89 (m, 4H), 2.43 (s, 3H), 1.67 – 1.58 (m, 4H), 1.44 – 1.35 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 133.4, 129.5, 127.7, 46.9, 25.1, 23.2 (t, *J* = 19.4 Hz), 21.5. **IR**: 2922, 2829, 1716, 1327, 1163, 927 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{16}DNO_2S$ 240.1043; Found 240.1045.

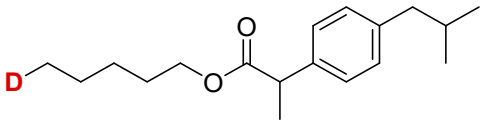
4-(3-methylbutoxy-3-*d*)-1,1'-biphenyl (2m)



Following General Procedure A, diphenyl disulfide (4.4 mg, 0.02 mmol, 20 mol%), tris(trimethylsilyl)silane (37.0 μL, 0.12 mmol, 1.2 equiv.), **1m** (31.9 mg, 0.10 mmol, 1.0 equiv.), D_2O (80.0 μL, 4.00 mmol, 40.0 equiv.), and MeCN (0.5 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1) to afford **2m** (15.0 mg, 62%, 83% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 4H), 7.44 – 7.40 (m, 2H), 7.34 – 7.28 (m, 1H), 7.04 – 6.91 (m, 2H), 4.04 (t, *J* = 6.7 Hz, 2H), 1.70 (t, *J* = 6.6 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 140.9, 133.6, 128.7, 128.1, 126.7, 126.6, 114.8, 66.5, 37.9, 24.6 (t, *J* = 19.4 Hz), 22.5. **IR**: 2953, 2868, 1724, 1521, 1477, 1247, 1051, 827 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd.

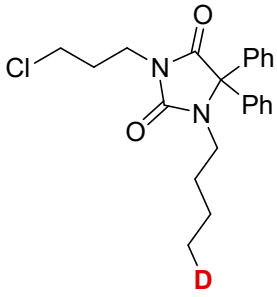
for. $C_{17}H_{19}DO$ 241.1577; Found 241.1574.

5-*d*-pentyl 2-(4-isobutylphenyl)propanoate (2n)



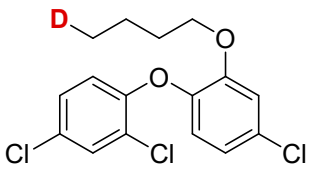
Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1n** (71.1 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1) to afford **2n** (49.0 mg, 88%, 82% D) as a colorless oil (D-incorporation was determined by GC-MS). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 7.11 – 7.05 (m, 2H), 4.05 (t, *J* = 6.7 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.92 – 1.77 (m, 1H), 1.63 – 1.51 (m, 2H), 1.48 (d, *J* = 7.1 Hz, 3H), 1.33 – 1.15 (m, 4H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.87 – 0.80 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 140.4, 137.9, 129.3, 127.2, 64.8, 45.2, 45.1, 30.2, 28.2, 27.9, 22.4, 22.1, 18.5, 13.6 (t, *J* = 19.1 Hz). **IR**: 2931, 2906, 2868, 1735, 1236, 1201, 1161, 879 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{18}H_{27}DO_2$ 277.2152; Found 277.2150.

1-(4-*d*-butyl)-3-(3-chloropropyl)-5,5-diphenylimidazolidine-2,4-dione (2o)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1o** (92.8 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **2o** (57.3 mg, 74%, 99 % D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 6H), 7.23 – 7.15 (m, 4H), 3.68 (t, *J* = 6.9 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.29 – 3.17 (m, 2H), 2.13 – 2.01 (m, 2H), 1.00 – 0.89 (m, 2H), 0.85 – 0.73 (m, 2H), 0.61 – 0.53 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 155.6, 137.2, 128.9, 128.8, 128.3, 74.9, 42.0, 41.9, 37.0, 31.1, 30.0, 19.9, 13.3, 13.1, 12.9. **IR**: 2916, 1454, 1421, 1134 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{22}H_{24}DClN_2O_2$ 385.1667; Found 385.1667.

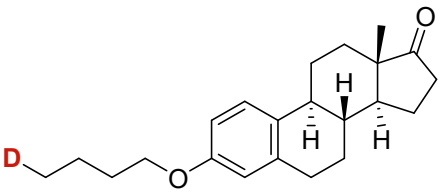
2-(butyl-4-*d*)oxy-4-chloro-1-(2,4-dichlorophenoxy)benzene (2p)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1p** (63.6 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column

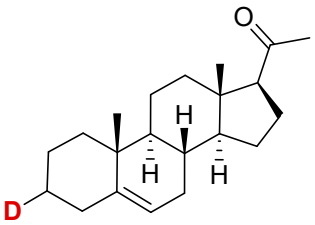
chromatography (Hx/EtOAc = 20/1) to afford **2p** (48.1 mg, 81%, 99% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.5 Hz, 1H), 7.08 (dd, J_1 = 8.8, J_2 = 2.6 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.91 (dd, J_1 = 8.3, J_2 = 2.4 Hz, 1H), 6.63 (d, J = 8.8 Hz, 1H), 3.91 (t, J = 6.3 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.27 – 1.19 (m, 2H), 0.87 – 0.80 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 151.1, 143.0, 130.6, 130.1, 127.7, 127.5, 124.4, 122.2, 120.8, 117.8, 114.7, 68.8, 30.9, 18.8, 13.3 (t, J = 19.2 Hz). **IR**: 2978, 2862, 1496, 1473, 1230, 1114, 935 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{16}H_{14}DCl_3O_2$ 354.0200; Found 354.0202.

(8R,9S,13S,14S)-3-(butoxy-4-*d*)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (2q)



Following General Procedure A, diphenyl disulfide (4.4 mg, 0.02 mmol, 20 mol%), tris(trimethylsilyl)silane (37.0 μL, 0.12 mmol, 1.2 equiv.), **1q** (28.7 mg, 0.10 mmol, 1.0 equiv.), D_2O (80.0 μL, 4.00 mmol, 40.0 equiv.), and MeCN (0.5 mL) were reacted for 12 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1) to afford **2q** (23.0 mg, 70%, 90% D) as a white solid (D-incorporation was determined by GC-MS). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 1H), 6.71 (dd, J_1 = 8.6, J_2 = 2.8 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 3.93 (t, J = 6.5 Hz, 2H), 2.93 – 2.84 (m, 2H), 2.50 (dd, J_1 = 18.8, J_2 = 8.6 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.29 – 2.21 (m, 1H), 2.20 – 1.91 (m, 4H), 1.80 – 1.70 (m, 2H), 1.68 – 1.39 (m, 8H), 1.00 – 0.92 (m, 2H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.0, 157.2, 137.7, 131.8, 126.3, 114.6, 112.1, 67.6, 50.5, 48.0, 44.0, 38.4, 35.9, 31.6, 31.4, 29.7, 26.6, 25.9, 21.6, 19.2, 13.9, 13.6 (t, J = 19.2 Hz). **IR**: 2929, 2858, 1732, 1492, 1053, 1053 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{22}H_{29}DO_2$ 327.2309; Found 327.2308.

1-((8S,9S,10R,13S,14S,17S)-3-*d*-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethenone (2r)



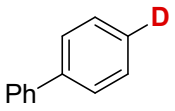
Following General Procedure A, diphenyl disulfide (4.4 mg, 0.02 mmol, 20 mol%), tris(trimethylsilyl)silane (37.0 μL, 0.12 mmol, 1.2 equiv.), **1r** (37.9 mg, 0.10 mmol, 1.0 equiv.), D_2O (80.0 μL, 4.00 mmol, 40.0 equiv.), and MeCN (0.5 mL) were reacted for 12 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1) to afford **2r** (18.4 mg, 61%, 93% D) as a white solid (D-incorporation was determined by GC-MS). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.30 – 5.23 (m, 1H), 2.53 (t, J = 9.0 Hz, 1H), 2.27 – 2.15 (m, 2H), 2.12 (s, 3H), 2.06 – 1.94 (m, 3H), 1.88 – 1.78 (m, 1H), 1.75 – 1.40 (m, 9H), 1.29 – 1.11 (m, 3H), 1.08 – 1.01 (m, 2H), 0.99 (s, 3H), 0.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 143.7, 118.7, 63.8, 57.1, 50.5, 44.0, 39.9, 39.0, 37.6, 32.8, 31.8, 31.8, 31.6, 27.6 (t, J = 19.2 Hz), 24.5, 22.8, 22.4, 20.8, 19.5, 13.3. **IR**: 2939, 2868, 1730, 1394, 1249, 1065, 968 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for.

$C_{21}H_{31}DO$ 301.2516; Found 301.2513.

2-4. Deuteration of Aryl Bromides

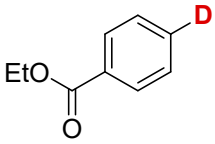
General Procedure for deuteration of aryl bromides (**General Procedure B**). In an oven-dried 4 ml vial, tris(trimethylsilyl)silane (74.6 mg, 92.6 µL, 1.5 equiv.) was added in a solution of dibutyl disulfide (7.1 mg, 7.6 µL, 20 mol%), aryl bromide (0.2 mmol, 1.0 equiv.), thiophenol (11.0 mg, 10.0 µL, 0.5 equiv.) and D_2O (160 µL, 40.0 equiv.) in MeCN (0.2 M) under argon atmosphere. The vial was sealed with electric tape and stirred for 12 hours at room temperature (~30˚C under irradiation) or 80˚C under 390 nm irradiation (390 nm Kessil LEDs lamp). After the reaction was completed, the solvent was evaporated under reduced pressure. Deuterated product was isolated by column chromatography on silica gel (hexane/ethyl acetate).

1,1'-biphenyl-4-*d* (4a)[3]



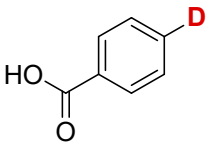
Compound was synthesized from 4-bromo-1,1'-biphenyl according to General Procedure B on a 0.2 mmol scale. 71% yield, and 86% D was observed via ^{1}H NMR. Spectrum in accordance with literature: *Nat. Commun.* 2021, **12**, 2894.

ethyl 4-*d*-benzoate (4b)[6]



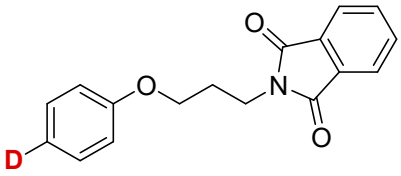
Compound was synthesized from ethyl 4-bromobenzoate according to General Procedure B on a 0.2 mmol scale. 98% yield, and 80% D was observed via ^{1}H NMR. Spectrum in accordance with literature: *Org. Chem. Front.* 2015, **2**, 1071-1075.

4-*d*-benzoic acid (4c)



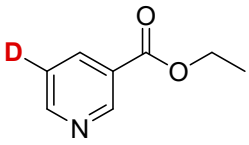
Following General Procedure B, **3c** (40.2 mg, 0.20 mmol, 1.0 equiv.) were reacted for 12 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1~1/1) to afford **4c** (11.2 mg, 45%, 84% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 2H), 7.51 – 7.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 133.5 (t, J = 24.1 Hz), 130.2, 129.3, 128.4. **IR**: 2920, 2848, 1681, 1427, 1288, 1257, 1128, 1161, 837 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_7H_5DO_2$ 123.0431; Found 123.0429.

2-(3-(4-*d*-phenoxy)propyl)isoindoline-1,3-dione (4d)



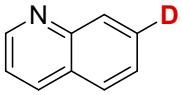
Following General Procedure B, **3d** (40.2 mg, 0.20 mmol, 1.0 equiv.) were reacted for 36 hours at 80˚C. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **4d** (37.8 mg, 67%, 86% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.75 – 7.68 (m, 2H), 7.25 – 7.20 (m, 2H), 6.84 – 6.78 (m, 2H), 4.03 (t, *J* = 6.1 Hz, 2H), 3.91 (t, *J* = 6.9 Hz, 2H), 2.25 – 2.13 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 158.7, 133.9, 132.2, 129.3, 123.3, 120.5 (t, *J* = 25.2 Hz), 114.5, 65.6, 35.5, 28.4. **IR**: 2960, 2875, 1697, 1375, 1247, 1107 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{17}H_{14}DNO_3$ 282.1115; Found 282.1113.

ethyl 5-*d*-nicotinate (4e)



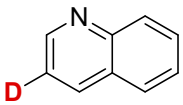
Following General Procedure B, **3e** (46.0 mg, 0.20 mmol, 1.0 equiv.) were reacted for 12 hours. After that, solvent was evaporated under reduced pressure. Then, K_2CO_3 (aq) was added in a reaction mixture, and crude mixture was extracted with EtOAc and dried over $MgSO_4$. Solvent was evaporated by reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **4e** (18.6 mg, 61%, 80% D) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 – 9.15 (m, 1H), 8.77 (s, 1H), 8.37 – 8.25 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 152.6, 150.3, 137.6, 126.6, 123.2 (t, *J* = 25.1 Hz) 61.6, 14.3. **IR**: 2981, 1722, ,1415, 1274, 1016, 858 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_8H_8DNO_2$ 152.0696; Found 152.0694.

7-*d*-quinoline (4f)



Following General Procedure B, **3f** (41.6 mg, 0.20 mmol, 1.0 equiv.) were reacted for 12 hours. After that, solvent was evaporated under reduced pressure. Then, K_2CO_3 (aq) was added in a reaction mixture, and crude mixture was extracted with EtOAc and dried over $MgSO_4$. Solvent was evaporated by reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **4f** (14.8 mg, 57%, 81% D) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 – 8.90 (m, 1H), 8.23 – 8.16 (m, 1H), 8.17 – 8.12 (m, 1H), 7.87 – 7.80 (m, 1H), 7.61 – 7.52 (m, 1H), 7.46 – 7.38 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 147.9, 136.5, 129.4 (t, *J* = 25.0 Hz), 129.1, 128.4, 127.8, 126.6, 121.1, 77.4, 77.0, 76.7. **IR**: 3051, 1593, 1490, 1126, 1031, 846 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. C_9H_6DN 130.0641; Found 130.0643.

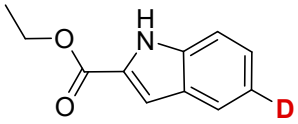
3-*d*-quinoline (4g)



Following General Procedure B, **3g** (41.6 mg, 0.20 mmol, 1.0 equiv.) were reacted for 12 hours. After that, solvent was evaporated under reduced pressure. Then, K_2CO_3 (aq) was added in a reaction mixture, and crude mixture was extracted with EtOAc and dried over $MgSO_4$. Solvent was evaporated by reduced pressure. The crude mixture was purified by silica gel column chromatography

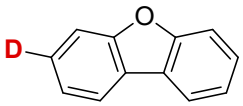
(Hx/EtOAc = 5/1) to afford **4g** (18.7 mg, 72%, 81% D) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 – 8.87 (m, 1H), 8.25 – 8.19 (m, 1H), 8.19 – 8.14 (m, 1H), 7.87 – 7.81 (m, 1H), 7.80 – 7.71 (m, 1H), 7.62 – 7.55 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 147.1, 137.2, 130.2, 128.6, 128.4, 127.9, 127.1, 120.8 (t, J = 25.2 Hz). **IR**: 3070, 1639, 1494, 1247, 1045, 839 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. C_9H_6DN 130.0641; Found 130.0642.

ethyl 5-*d*-1*H*-indole-2-carboxylate (4h)

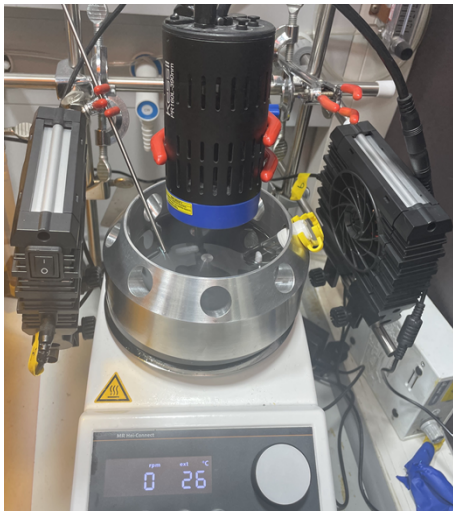


Following General Procedure B, **3f** (53.6 mg, 0.20 mmol, 1.0 equiv.) were reacted for 12 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 10/1~5/1) to afford **4h** (22.7 mg, 60%, 82% D) as a white solid. **^{1}H NMR** (400 MHz, DMSO) δ 11.86 (br, 1H), 7.79 (s, 1H), 7.62 – 7.57 (m, 1H), 7.41 – 7.36 (m, 1H), 7.30 – 7.25 (m, 1H), 4.49 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H). **NMR** (101 MHz, DMSO) δ 161.1, 137.2, 127.2, 126.6, 124.2, 121.7, 119.6 (t, J = 24.1 Hz), 112.3, 107.5, 60.1, 14.1. **IR**: 3307, 2945, 2370, 1685, 1517, 1246, 1186, 1024 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{11}H_{10}DNO_2$ 190.0853; Found 190.0855.

3-bromodibenzo[b,d]furan (4i)



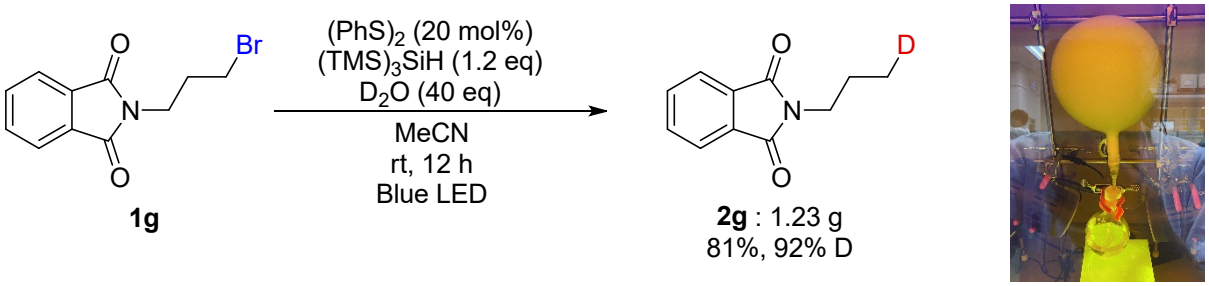
Following General Procedure B, **3i** (494 mg, 0.20 mmol, 1.0 equiv.) tris(trimethylsilyl)silane (746 mg, 926 µL, 1.5 equiv.), dibutyl disulfide (71 mg, 76 µL, 20 mol%), thiophenol (110 mg, 100 µL, 0.5 equiv.) and D_2O (1.6 mL, 40.0 equiv.) were reacted for 12 hours. After that, solvent was evaporated under reduced pressure. Then, K_2CO_3 (aq) was added in a reaction mixture, and crude mixture was extracted with EtOAc and dried over $MgSO_4$. Solvent was evaporated by reduced pressure. The crude mixture was purified by silica gel column chromatography (Hx only) to afford **4i** (256 mg, 76%, 85% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.62 – 7.56 (m, 2H), 7.51 – 7.44 (m, 1H), 7.40 – 7.32 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 126.9 (t, J = 24.7 Hz), 124.3, 122.7, 122.6, 120.7, 111.7, 111.6. **IR**: 2964, 1444, 1419, 1182, 889, 840 cm^{-1}. **HRMS (EI)** m/z:[M]$^+$: calcd. for. $C_{12}H_7DO$ 169.0638; Found 169.0636.



Reaction setup for synthesis of **4d** with Kessil lamp (160WE, PR 160 390 nm) in an aluminum holder.

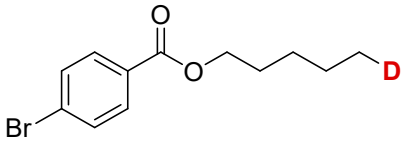
2-5. Practical Examples

Gram scale synthesis:



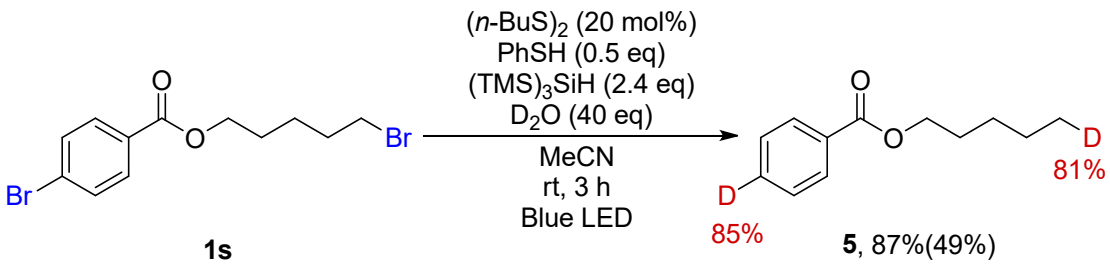
Following General Procedure A, diphenyl disulfide (349 mg, 1.6 mmol, 20 mol%), tris(trimethylsilyl)silane (2.96 mL, 9.6 mmol, 1.2 equiv.), **1f** (2.14 g, 8.0 mmol, 1.0 equiv.), D_2O (6.41 mL, 320 mmol, 40.0 equiv.), and MeCN (30.0 mL) were reacted for 12 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **2f** (1.23 g, 81%, 92 % D) as a white solid.

Pentyl-5-*d* 4-bromobenzoate (2s)



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 µL, 0.24 mmol, 1.2 equiv.), **1j** (70.0 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 µL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1~10/1) to afford **2s**(26.3 mg, 48%, 93 % D) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.63 – 7.50 (m, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.46 – 1.33 (m, 4H), 0.95 – 0.89 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 131.7, 131.1, 129.5, 127.9, 65.4, 28.4, 28.2, 22.3, 13.7 (t, *J* = 19.2 Hz). **IR**: 2954, 2935, 2860, 1722,

One-pot dehalogenative deuteration of aryl-Br & alkyl-Br:



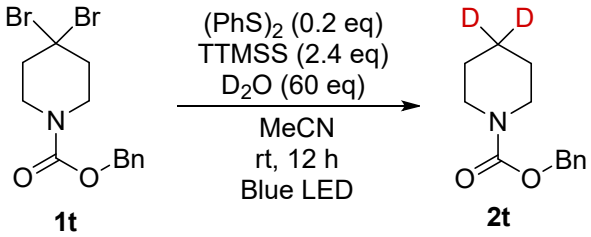
Following General Procedure B, tris(trimethylsilyl)silane (59.7 mg, 74.0 µL, 1.2 equiv.) was added in a solution of dibutyl disulfide (7.1 mg, 7.5 µL, 20 mol%), **2s** (70.0 mg, 0.2 mmol, 1.0 equiv.), thiophenol (11.0 mg, 10.0 µL, 0.5 equiv.) and D_2O (160 µL, 40.0 equiv.) in MeCN (0.2 M) under argon atmosphere. After 3 hours,

tris(trimethylsilyl)silane (59.7 mg, 74.0 μL, 1.2 equiv.) was added in a reaction mixture and stirred for another 9 hours. After the reaction was completed, the solvent was evaporated under reduced pressure. Deuterated product was isolated by column chromatography on silica gel (Hx/EtOAc = 50/1) to afford **5** as a colorless oil (19.2 mg, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.49 – 7.39 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.50 – 1.31 (m, 4H), 0.98 – 0.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 130.6, 129.5, 128.3, 128.2, 65.1, 28.5, 28.2, 22.3, 13.7 (t, J = 19.2 Hz). **IR**: 2931, 2858, 1718, 1107, 1024, 877 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{14}D_2O_2$ 194.1276; Found 194.1274.

Dehalogenative deuteration in air:

Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1g** (53.6 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 12 hours in air. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **2g** (27.0 mg, 71%, 93 % D) as a white solid

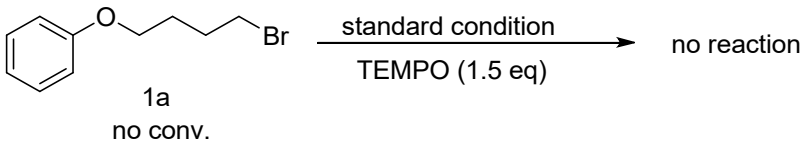
Multiple deuteration:



Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (148.0 μL, 0.48 mmol, 2.4 equiv.), **1t** (75.4 mg, 0.20 mmol, 1.0 equiv.), D_2O (217.0 μL, 12.00 mmol, 60.0 equiv.), and MeCN (1.0 mL) were reacted for 12 hours in Ar atmosphere. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 5/1) to afford **2t** (41.7 mg, 94%, 75 % D) as a colorless oil (D-incorporation was determined by GC-MS). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.13 (s, 2H), 3.49 – 3.36 (m, 4H), 1.58 – 1.44 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.4, 137.1, 128.5, 127.9, 127.8, 66.9, 44.9, 25.5, 24.0 (p, *J* = 19.5 Hz). **IR**: 2933, 2852, 1697, 1427, 1234, 1020, 839 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{13}H_{15}D_2NO_2$ 221.1385; Found 221.1382.

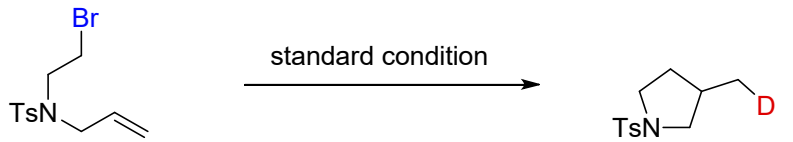
2-6. Mechanistic Study

Radical trapping experiment:



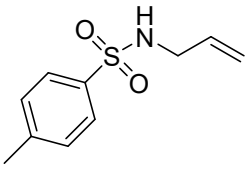
Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 μL, 0.24 mmol, 1.2 equiv.), **1a** (45.8 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 μL, 8.00 mmol, 40.0 equiv.), TEMPO (46.9 mg, 1.5 equiv.) and MeCN (1.0 mL) were reacted for 3 hours.

Radical clock experiment:



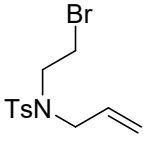
1b **2b**, 56%, 87% D

***N*-allyl-4-methylbenzenesulfonamide**



In a dried RBF, allyl bromide (1.73 mL, 20.0 mmol, 1.0 equiv.) was added in a solution of potassium carbonate (5.53 g, 40.0 mmol, 2.0 equiv.), potassium iodide (332 mg, 2.0 mmol, 0.1 equiv.) and *p*-toluenesulfonamide (6.85 g, 40.0 mmol, 2.0 equiv.) in MeCN (60.0 mL). The reaction proceeded at 80˚C for 12 hours. Filtrate was d and concentrated under reduced pressure. Crude product was purified by a silica gel column chromatography (Hx/EtOAc = 3/1). White solid was obtained (1.90 g, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.35 – 7.28 (m, 2H), 5.80 – 5.65 (m, 1H), 5.23 – 5.13 (m, 1H), 5.13 – 5.07 (m, 1H), 3.64 – 3.55 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 137.0, 133.0, 129.8, 127.2, 117.8, 45.8, 21.5. **IR**: 3246, 1303, 1317, 1157, 997 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{10}H_{13}NO_2S$ 211.0667; Found 211.0664.

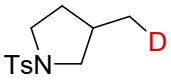
***N*-allyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide (1b)**



2-bromoethanol (591 mg, 335 μL, 4.73 mmol, 2.0 equiv.), and diisopropyl azodicarboxylate (957 mg, 932 μL, 4.73 mmol, 2.0 equiv.) was added dropwise to a stirred solution of ***N*-allyl-4-methylbenzenesulfonamide** (500 mg, 2.37 mmol, 1.0 equiv.), and triphenylphosphine (1.24 g, 4.73 mmol, 2.0 equiv.) in anhydrous THF at 0 °C. The solution was allowed to room temperature

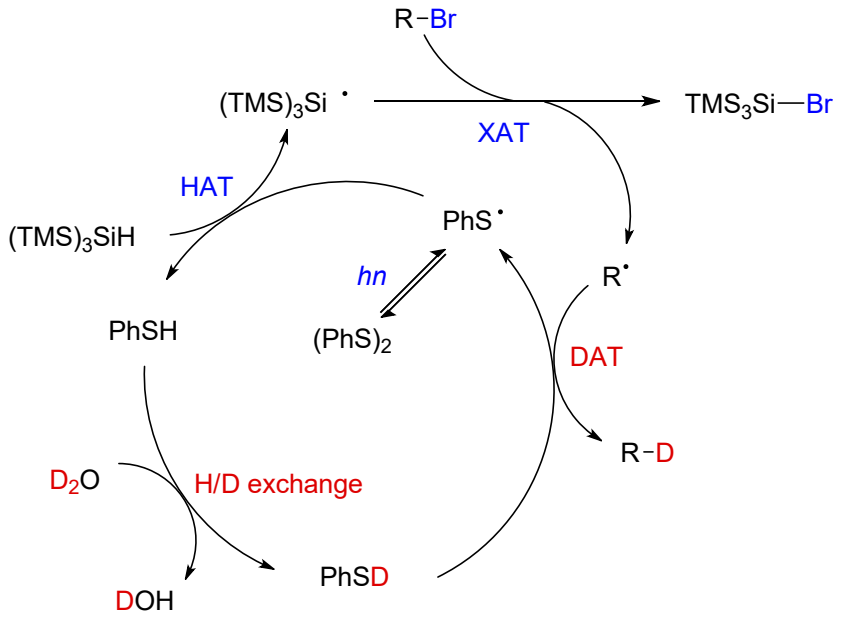
and stirred for 12 hours. After reaction was completed, solvent was evaporated under reduced pressure. Crude product was purified by silica gel column chromatography (Hx/Et_2O = 10/1) to afford **1b** as a colorless oil. (200 mg, 27% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.37 – 7.30 (m, 2H), 5.75 – 5.58 (m, 1H), 5.24 – 5.15 (m, 2H), 3.87 – 3.79 (m, 2H), 3.53 – 3.34 (m, 4H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 136.3, 132.9, 129.9, 127.2, 119.7, 52.0, 49.0, 29.3, 21.6. **IR**: 2926, 2856, 2364, 1421, 1338, 1115, 1089, 931 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{16}BrNO_2S$ 319.0065; Found 319.0060.

3-(methyl-2-*d*)-1-tosylpyrrolidine (2b)



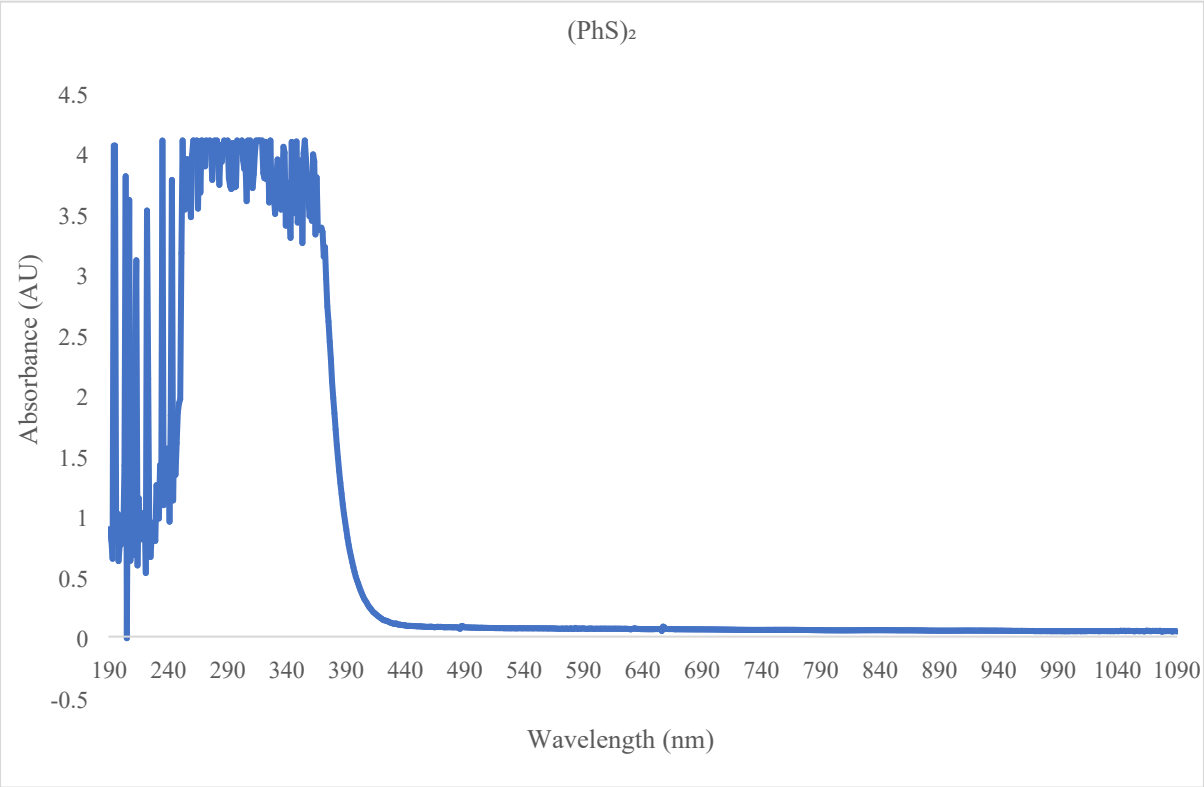
Following General Procedure A, diphenyl disulfide (8.7 mg, 0.04 mmol, 20 mol%), tris(trimethylsilyl)silane (74.0 µL, 0.24 mmol, 1.2 equiv.), **1b** (63.6 mg, 0.20 mmol, 1.0 equiv.), D_2O (160.0 µL, 8.00 mmol, 40.0 equiv.), and MeCN (1.0 mL) were reacted for 3 hours. The crude mixture was purified by silica gel column chromatography (Hx/EtOAc = 20/1~ 5/1) to afford **2b** (27.0 mg, 56%, 87% D) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.36 – 7.30 (m, 2H), 3.42 (dd, J_1 = 9.7, J_2 = 7.1 Hz, 1H), 3.39 – 3.30 (m, 1H), 3.28 – 3.17 (m, 1H), 2.75 (dd, J_1 = 9.7, J_2 = 7.8 Hz, 1H), 2.43 (s, 3H), 2.17 – 2.07 (m, 1H), 1.96 – 1.84 (m, 1H), 1.41 – 1.30 (m, 1H), 0.94 – 0.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 134.1, 129.6, 127.5, 54.7, 47.6, 33.2, 33.2, 21.5, 17.4 (t, J = 19.3 Hz). **IR**: 2924, 2883, 2852, 1332, 1037, 1016, 815 cm^{-1}. **HRMS (EI)** m/z:$[M]^+$: calcd. for. $C_{12}H_{16}DNO_2S$ 240.1043; Found 240.1040.

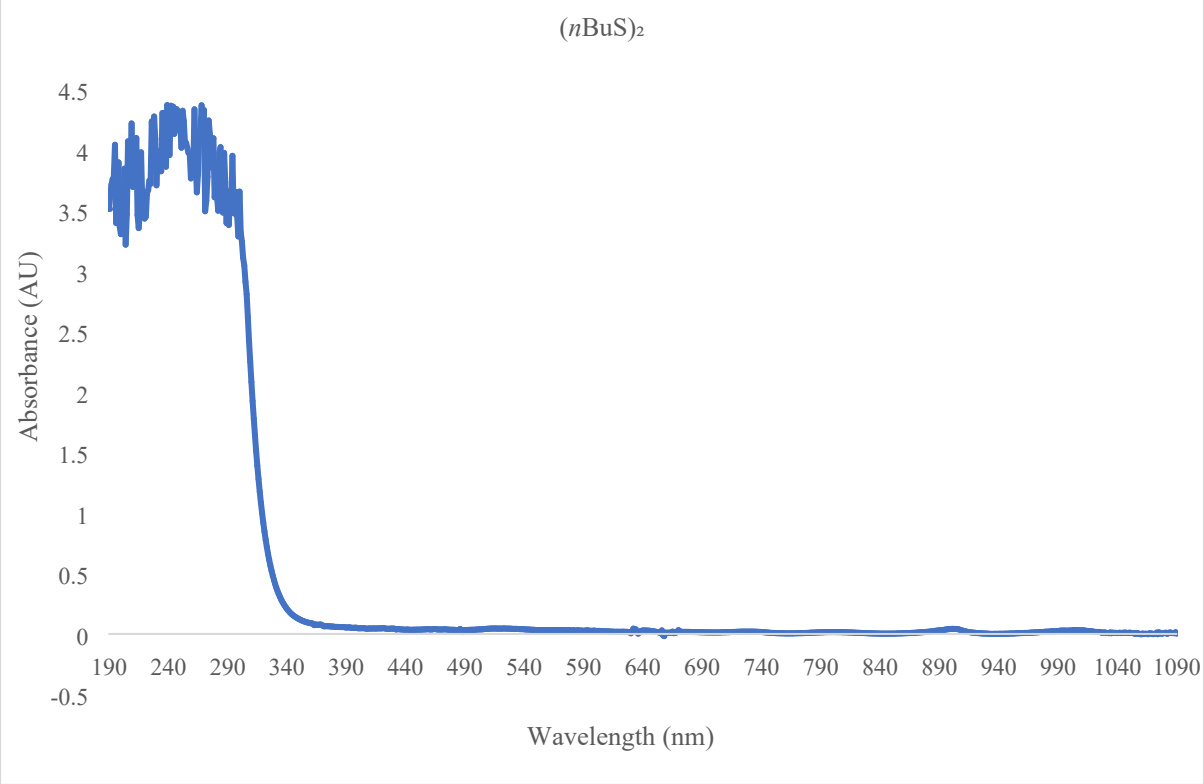
Proposed reaction design

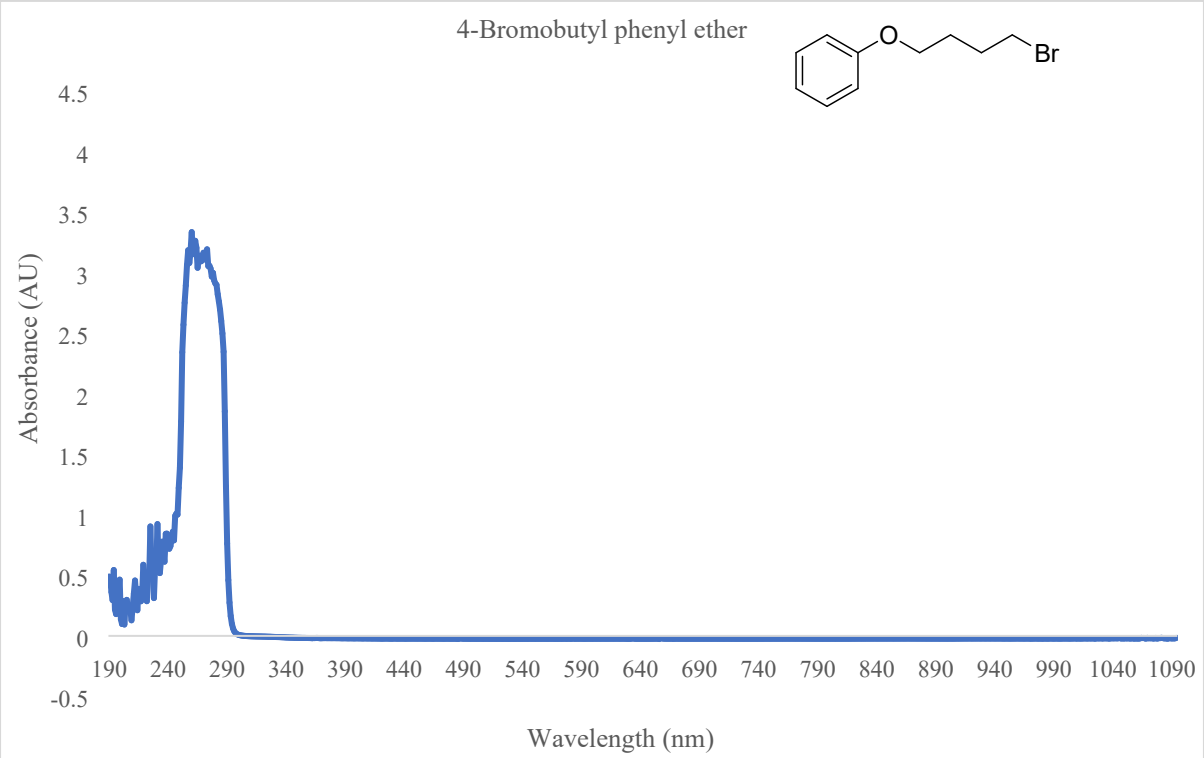


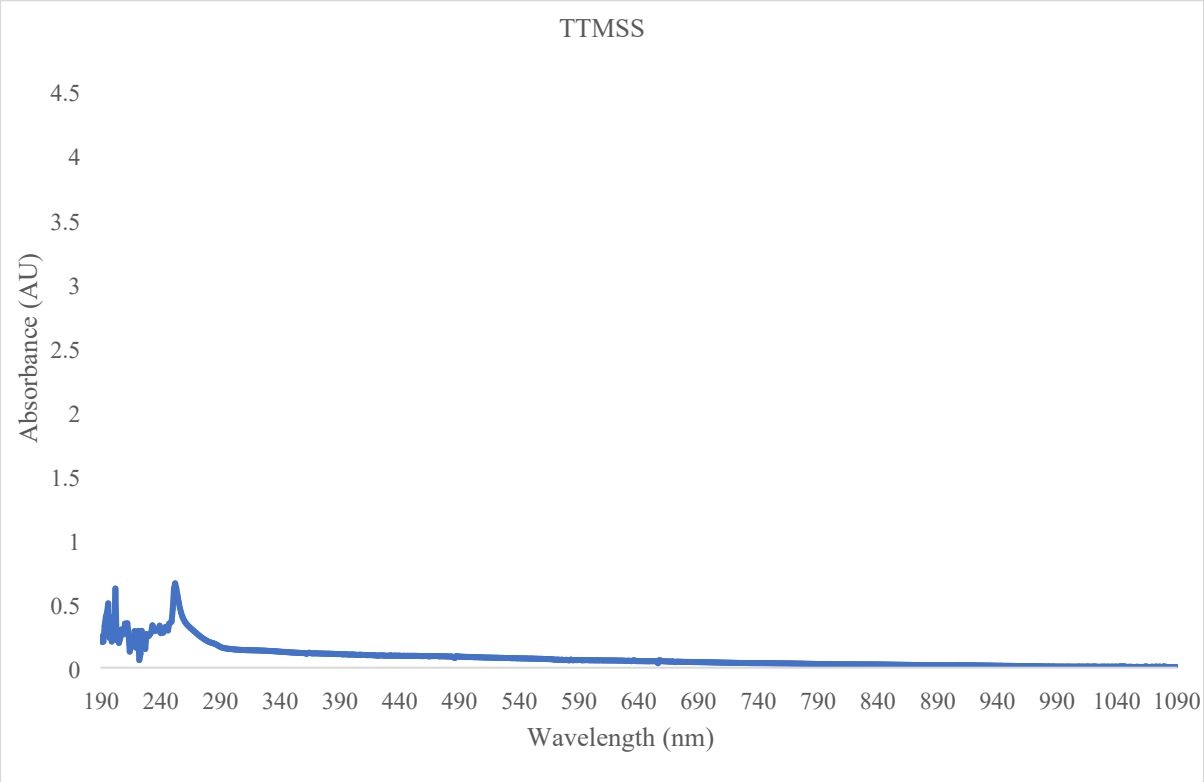
3. UV/Visible absorption spectroscopy

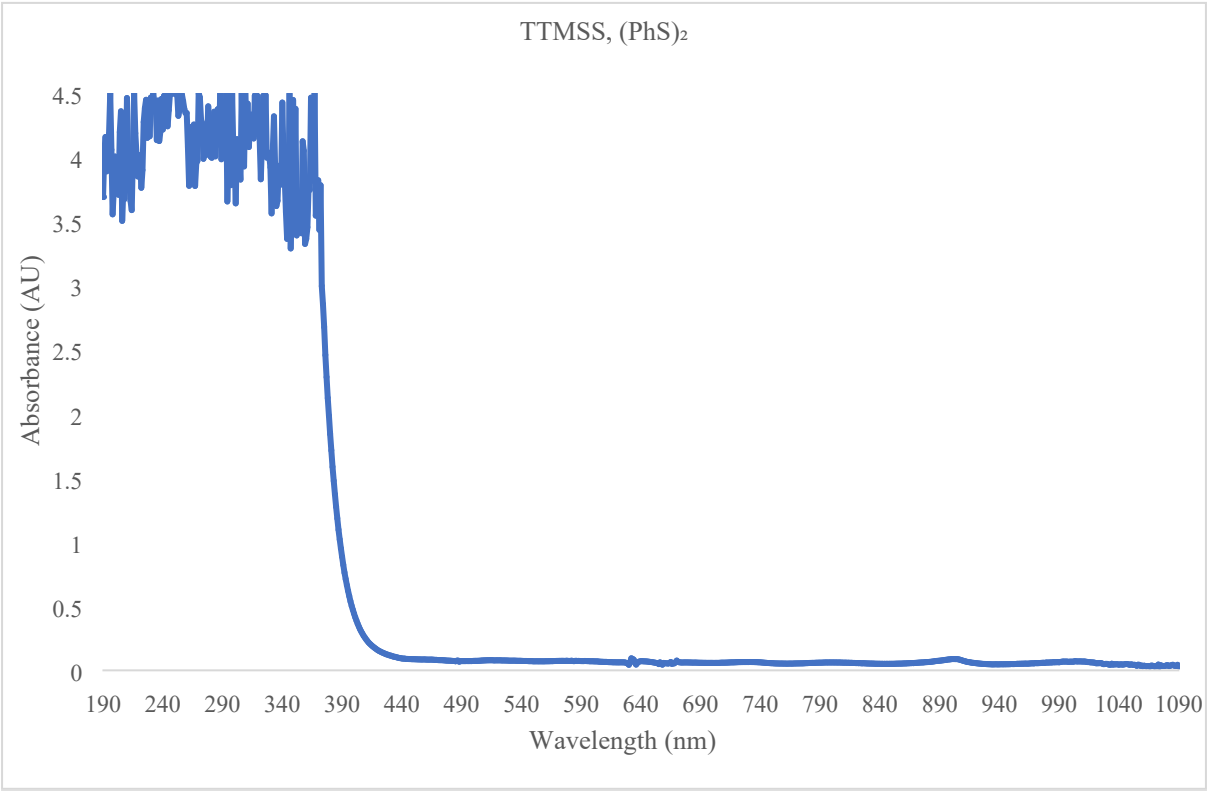
UV/Visible absorption spectra were recorded on a Cary 8454 UV-Vis spectrometer. The spectra were acquired from 190 to 1090 nm using 1 nm steps. All measurements were performed in ethyl acetate (100 mM, 2 mL).

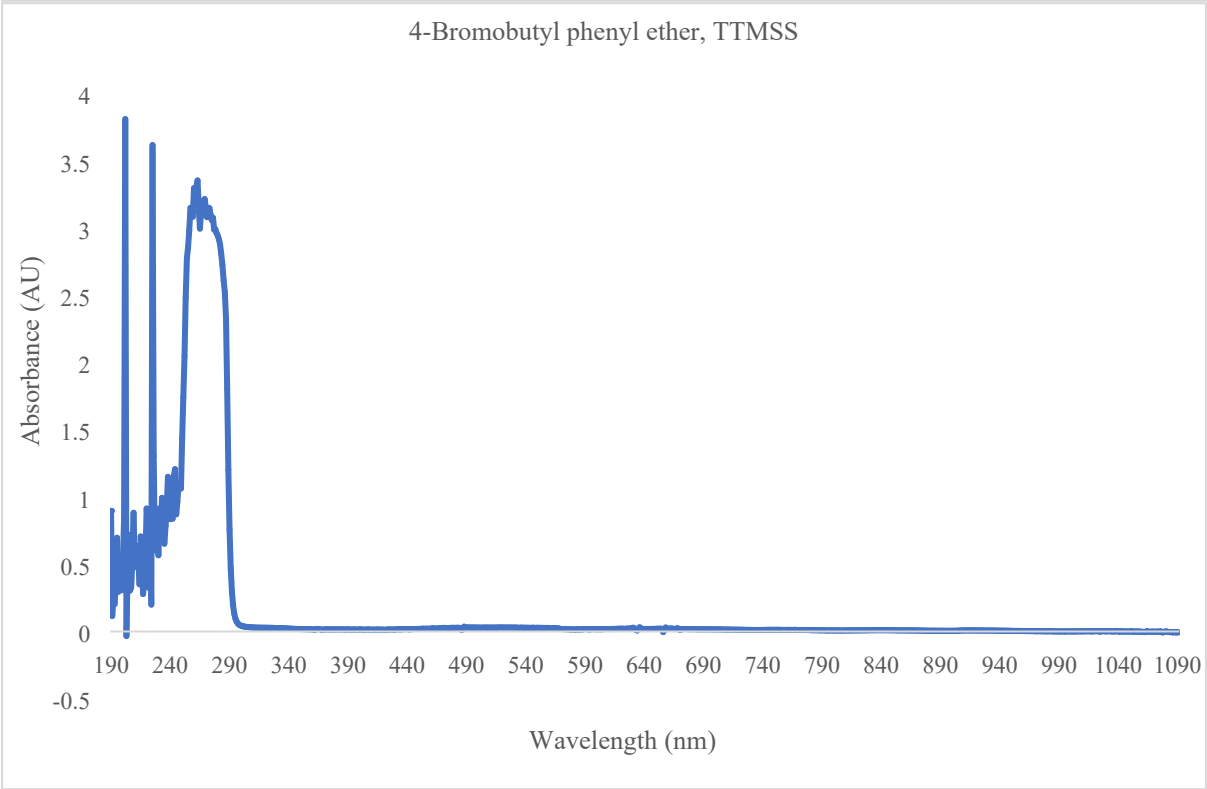


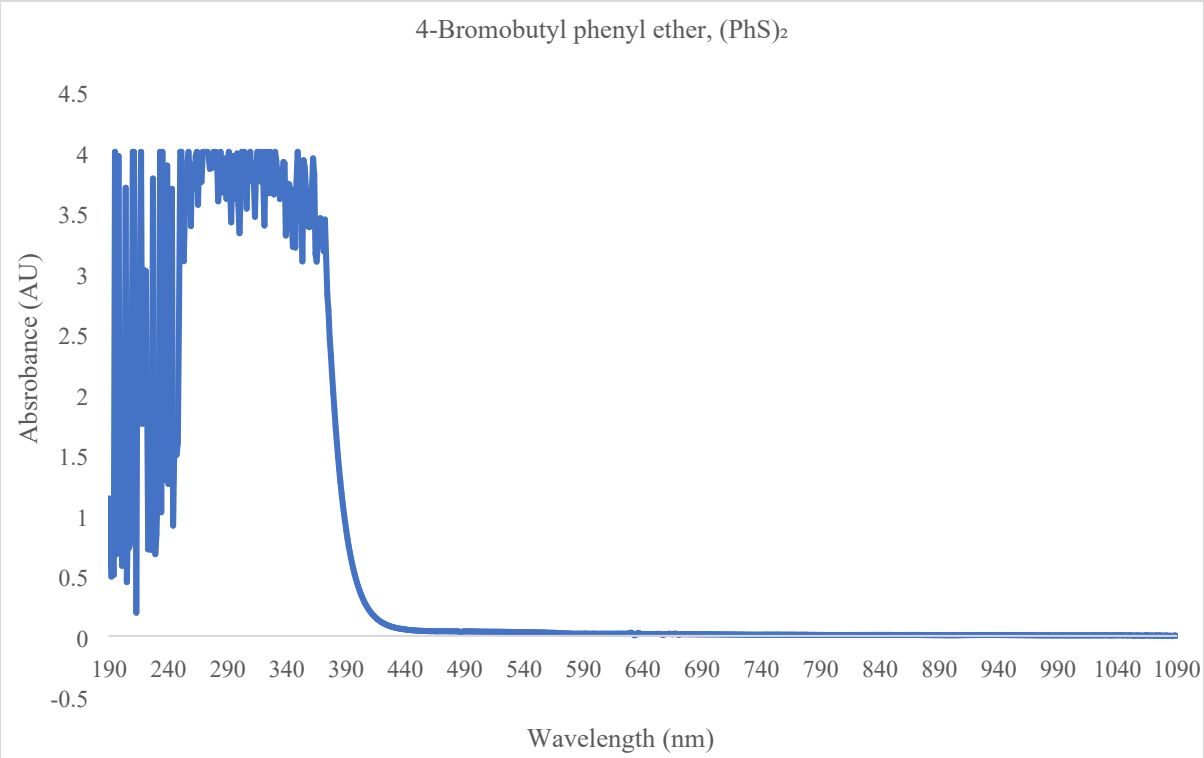


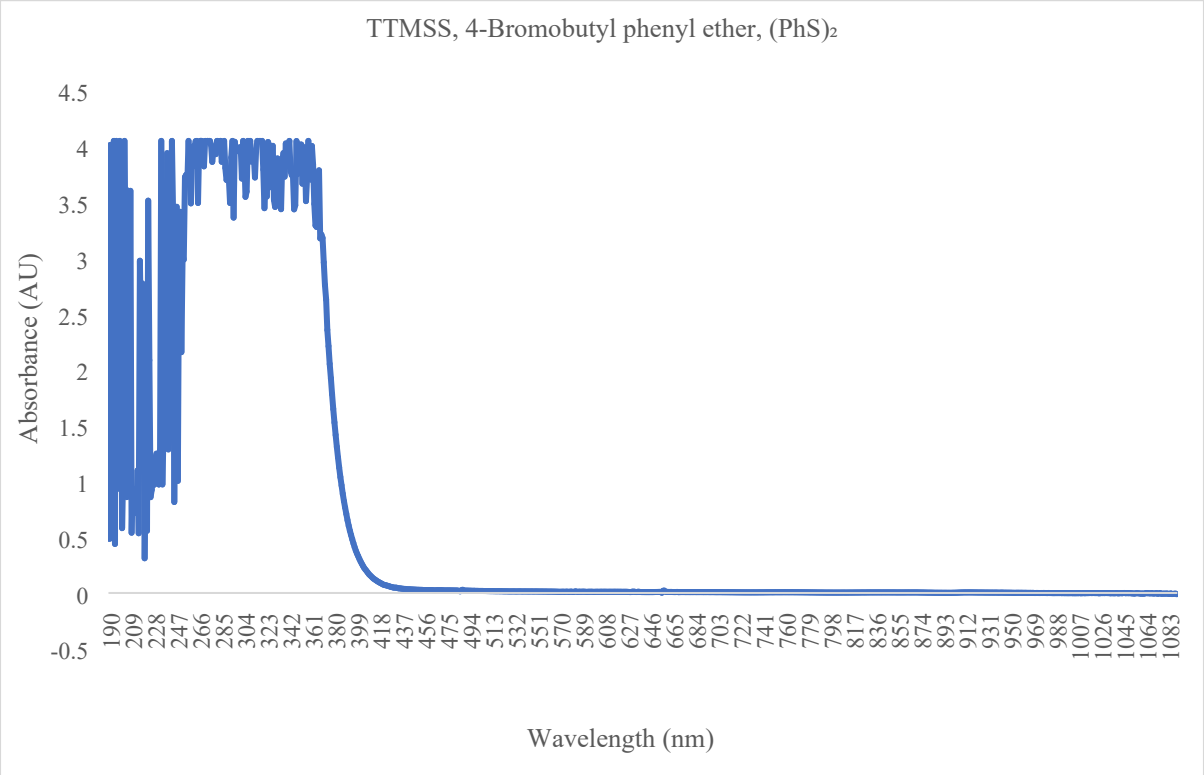

4-Bromobutyl phenyl ether
O
Br
Absorbance (AU)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
190 240 290 340 390 440 490 540 590 640 690 740 790 840 890 940 990 1040 1090
Wavelength (nm)

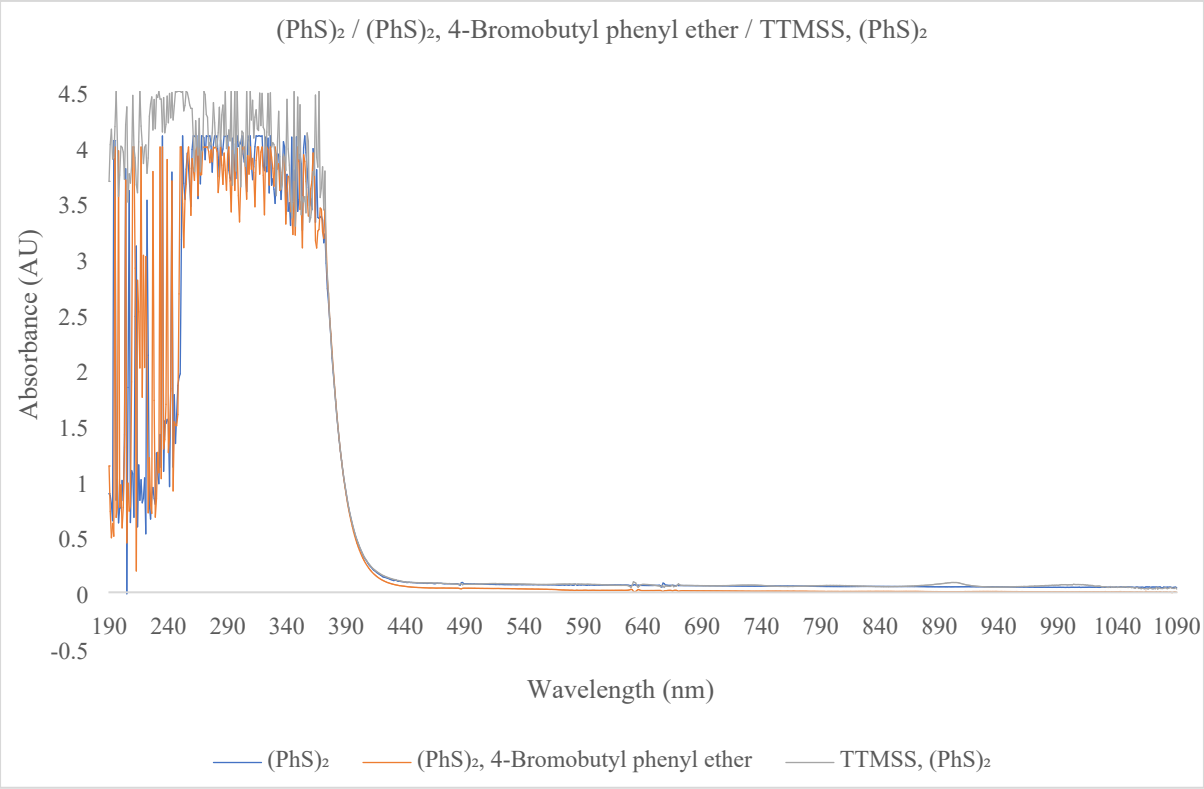

TTMSS
Absorbance (AU)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
190 240 290 340 390 440 490 540 590 640 690 740 790 840 890 940 990 1040 1090
Wavelength (nm)


TTMSS, (PhS)2
Absorbance (AU)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
190 240 290 340 390 440 490 540 590 640 690 740 790 840 890 940 990 1040 1090
Wavelength (nm)

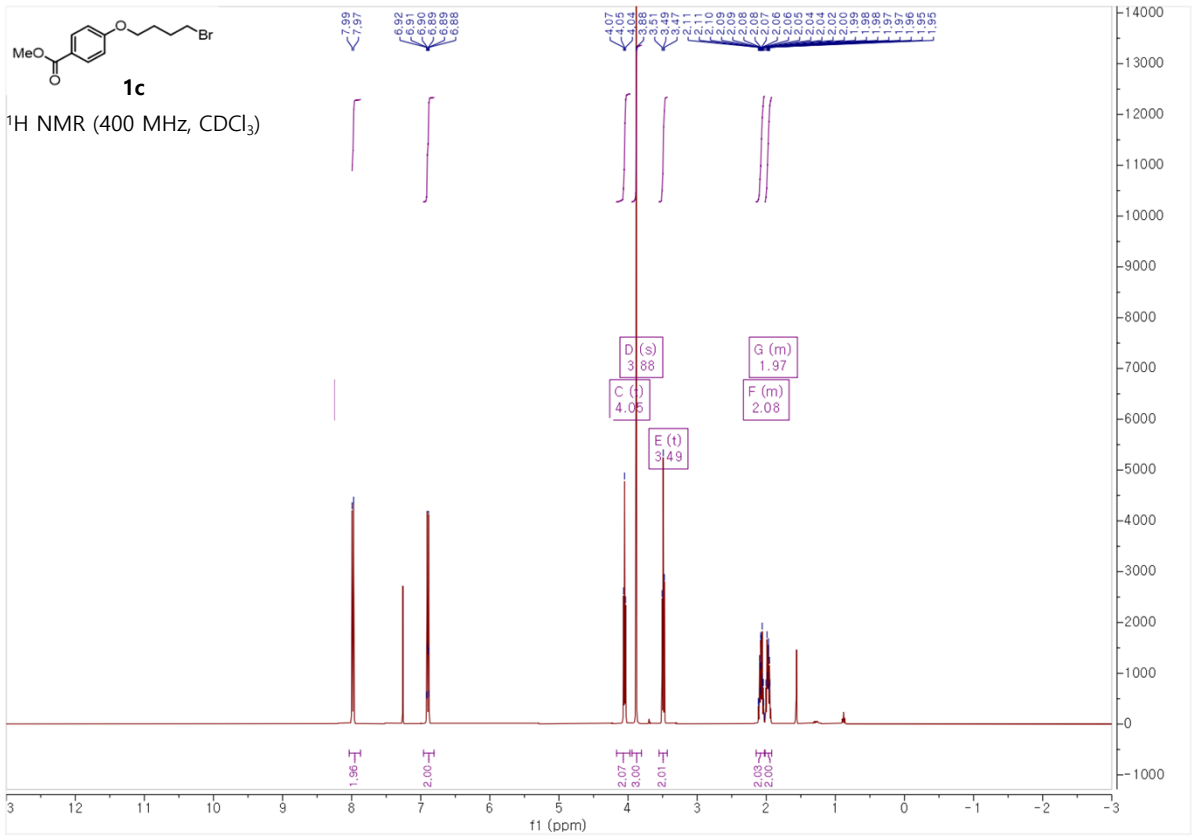

4-Bromobutyl phenyl ether, TTMSS
Absorbance (AU)
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
190 240 290 340 390 440 490 540 590 640 690 740 790 840 890 940 990 1040 1090
Wavelength (nm)

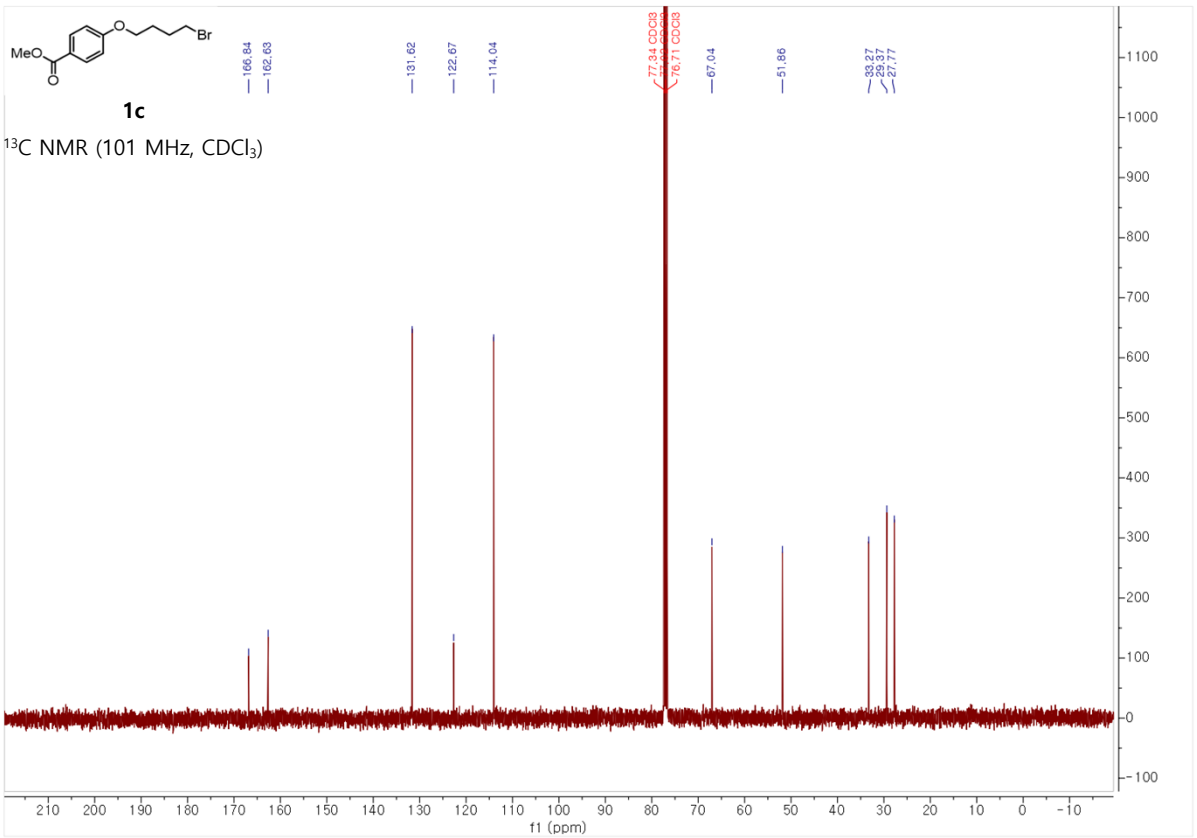

4-Bromobutyl phenyl ether, (PhS)2
Absrobance (AU)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
190 240 290 340 390 440 490 540 590 640 690 740 790 840 890 940 990 1040 1090
Wavelength (nm)

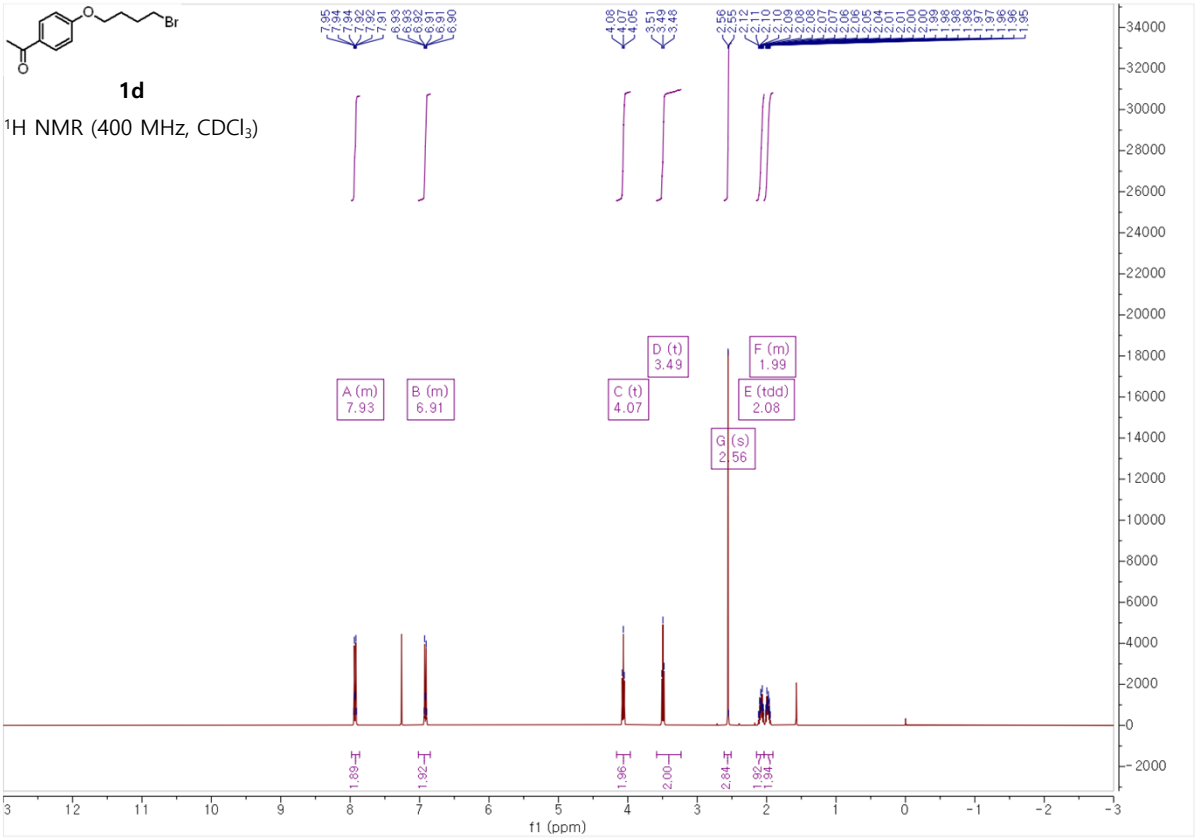

TTMSS, 4-Bromobutyl phenyl ether, (PhS)2
Absorbance (AU)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
190 209 228 247 266 285 304 323 342 361 380 399 418 437 456 475 494 513 532 551 570 589 608 627 646 665 684 703 722 741 760 779 798 817 836 855 874 893 912 931 950 969 988 1007 1026 1045 1064 1083
Wavelength (nm)

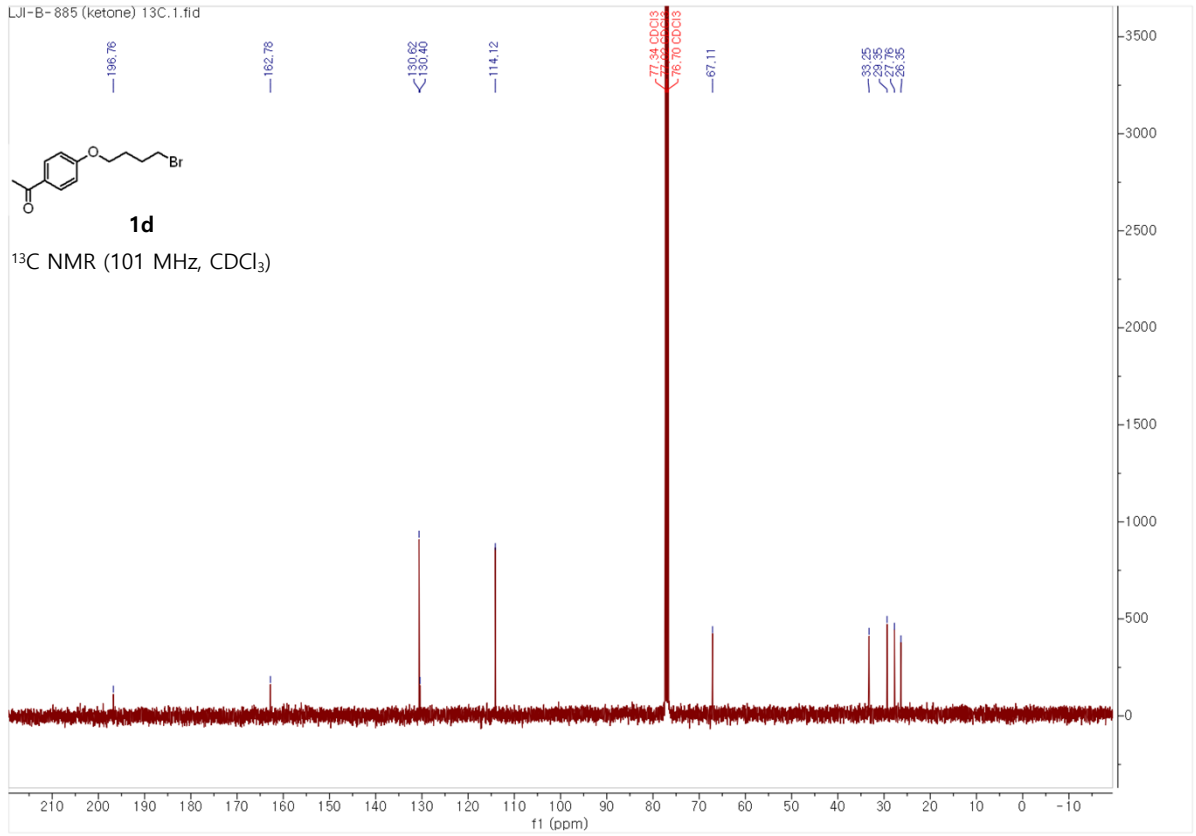

(PhS)2 / (PhS)2, 4-Bromobutyl phenyl ether / TTMSS, (PhS)2
Absorbance (AU)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
190 240 290 340 390 440 490 540 590 640 690 740 790 840 890 940 990 1040 1090
Wavelength (nm)
(PhS)2
(PhS)2, 4-Bromobutyl phenyl ether
TTMSS, (PhS)2

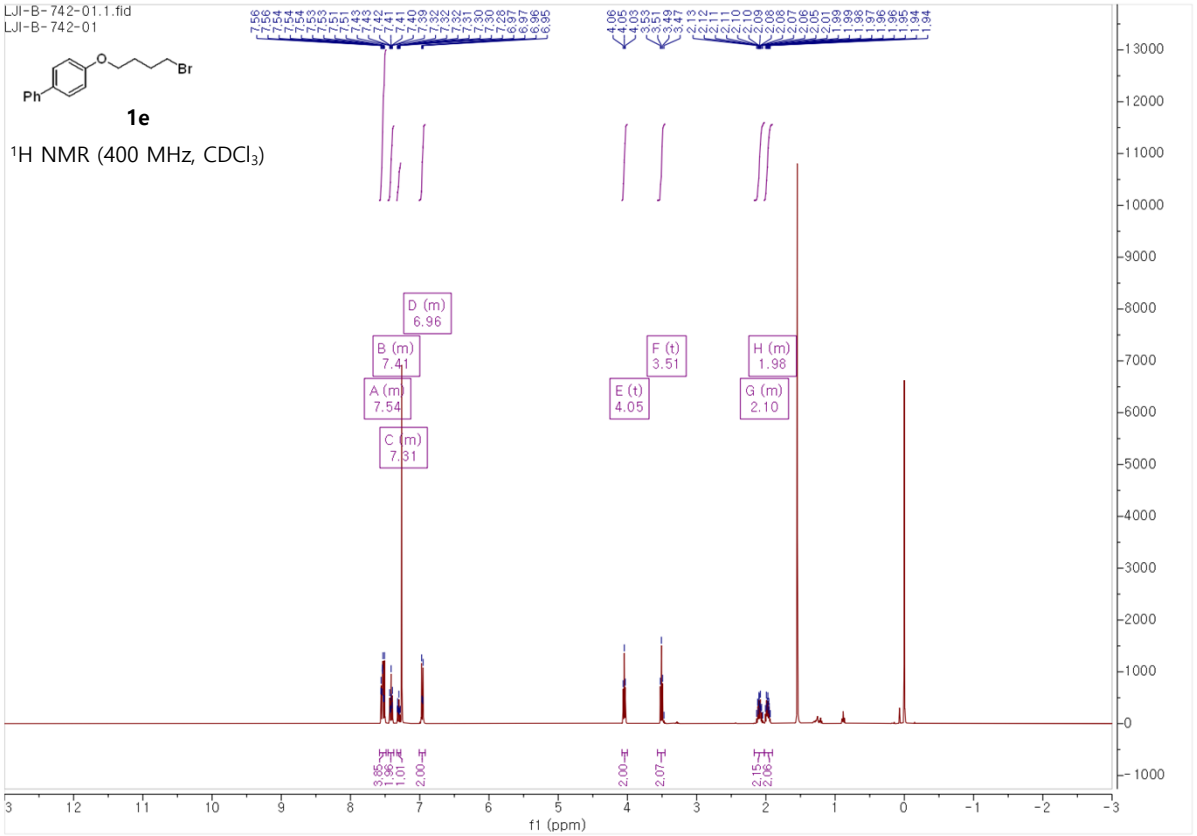
4. NMR Spectra

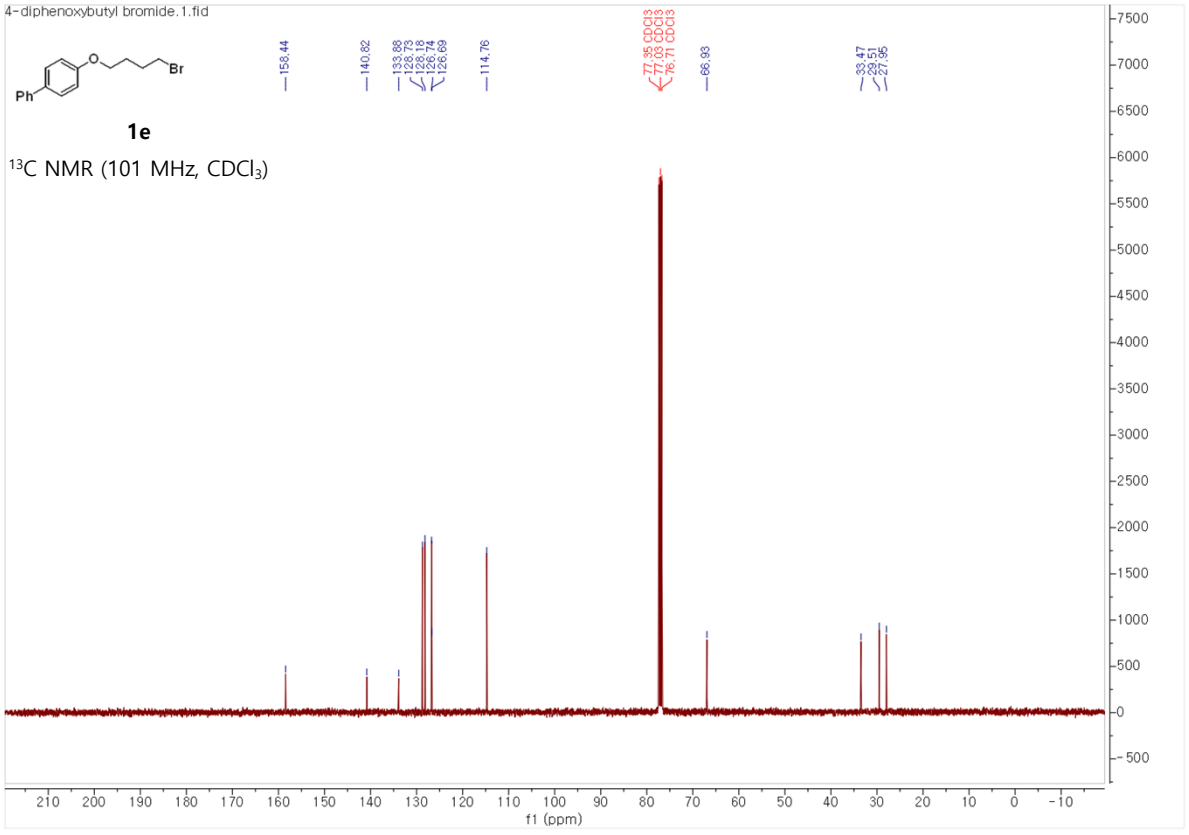


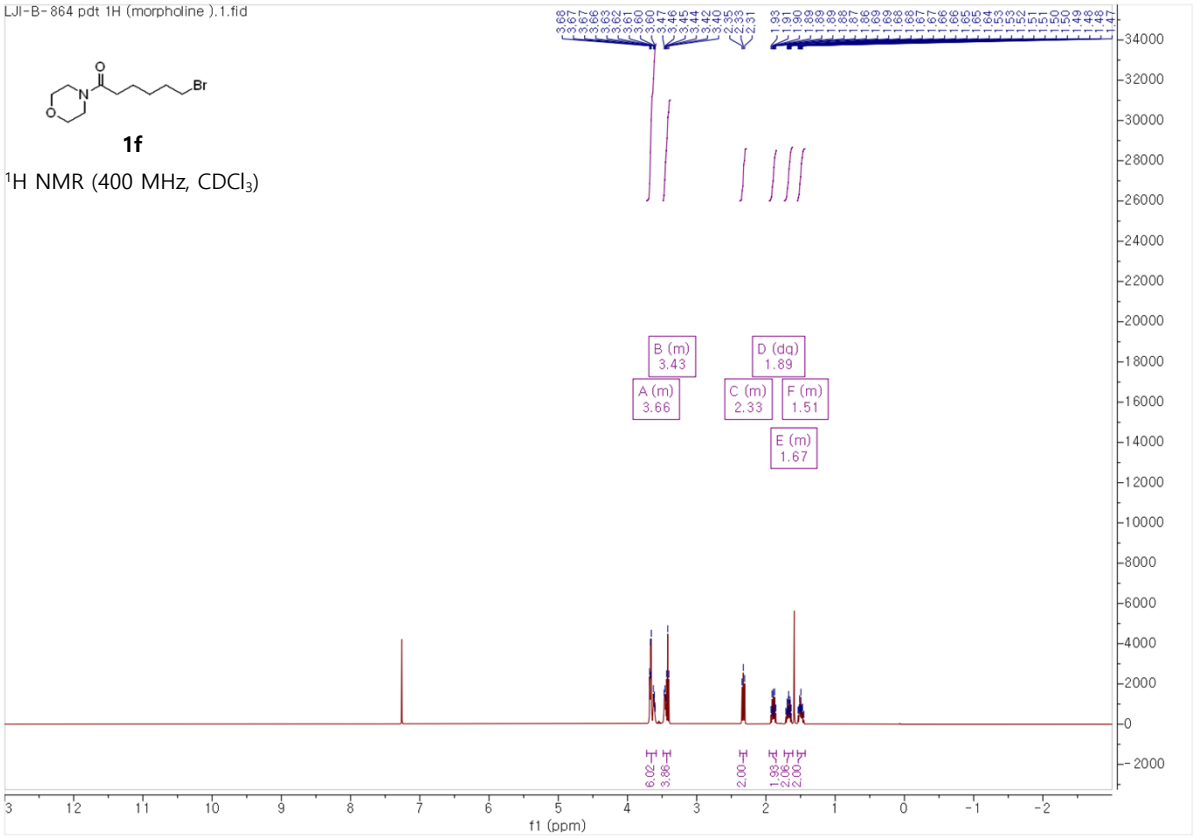



1d
1H NMR (400 MHz, CDCl3)
A (m) 7.93
B (m) 6.91
C (t) 4.07
D (t) 3.49
E (tdd) 2.08
F (m) 1.99
G (s) 2.56
f1 (ppm)


LJI-B-885 (ketone) 13C.1.fid
1d
13C NMR (101 MHz, CDCl3)
196.76
162.78
130.62
130.40
114.12
77.34 CDCl3
78.70 CDCl3
67.11
33.25
29.35
27.76
26.35
f1 (ppm)

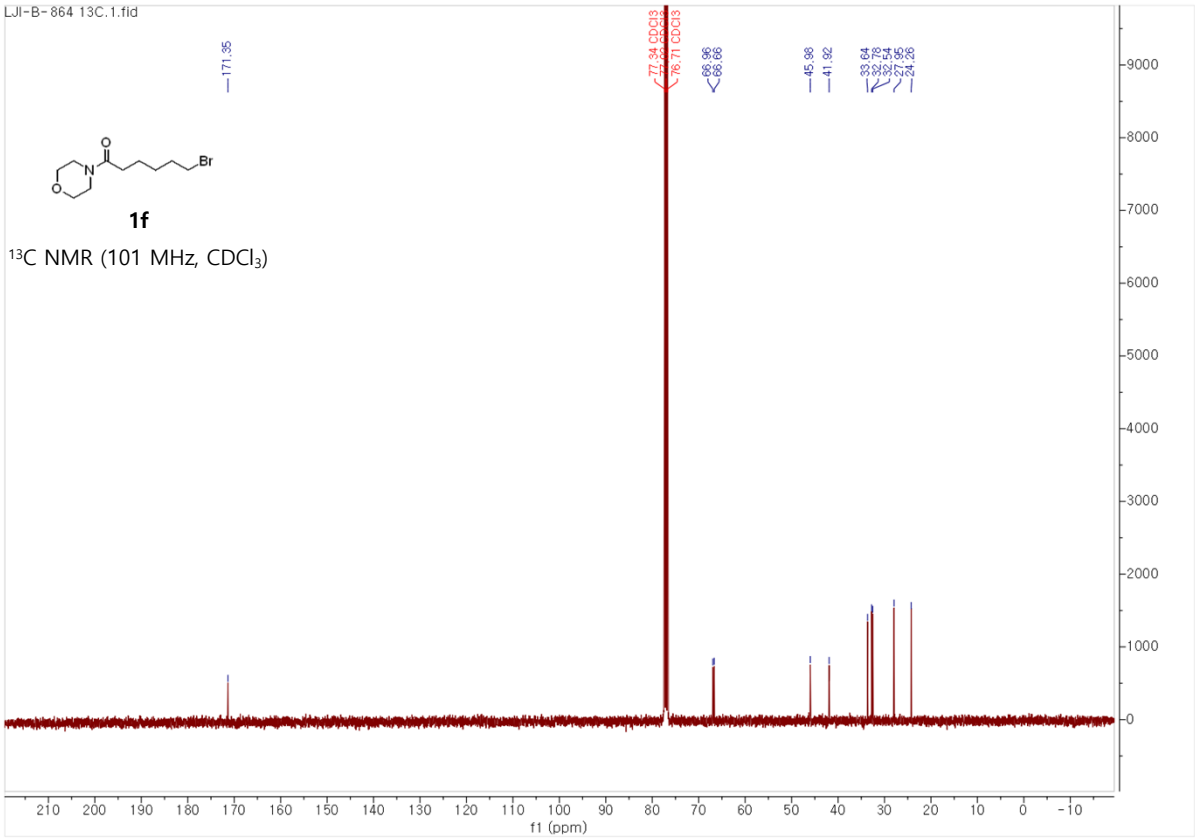

LJI-B-742-01.1.fid
LJI-B-742-01
Ph
O
Br
1e
^{1}H NMR (400 MHz, $CDCl_3$)
D (m) 6.96
B (m) 7.41
A (m) 7.54
C (m) 7.31
F (t) 3.51
E (t) 4.05
H (m) 1.98
G (m) 2.10
f1 (ppm)


4-diphenoxybutyl bromide.1.fid
Ph
O
Br
1e
^{13}C NMR (101 MHz, $CDCl_3$)
158.44
140.82
133.88
128.73
128.18
126.74
126.69
114.76
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
66.93
33.47
29.51
27.95
f1 (ppm)



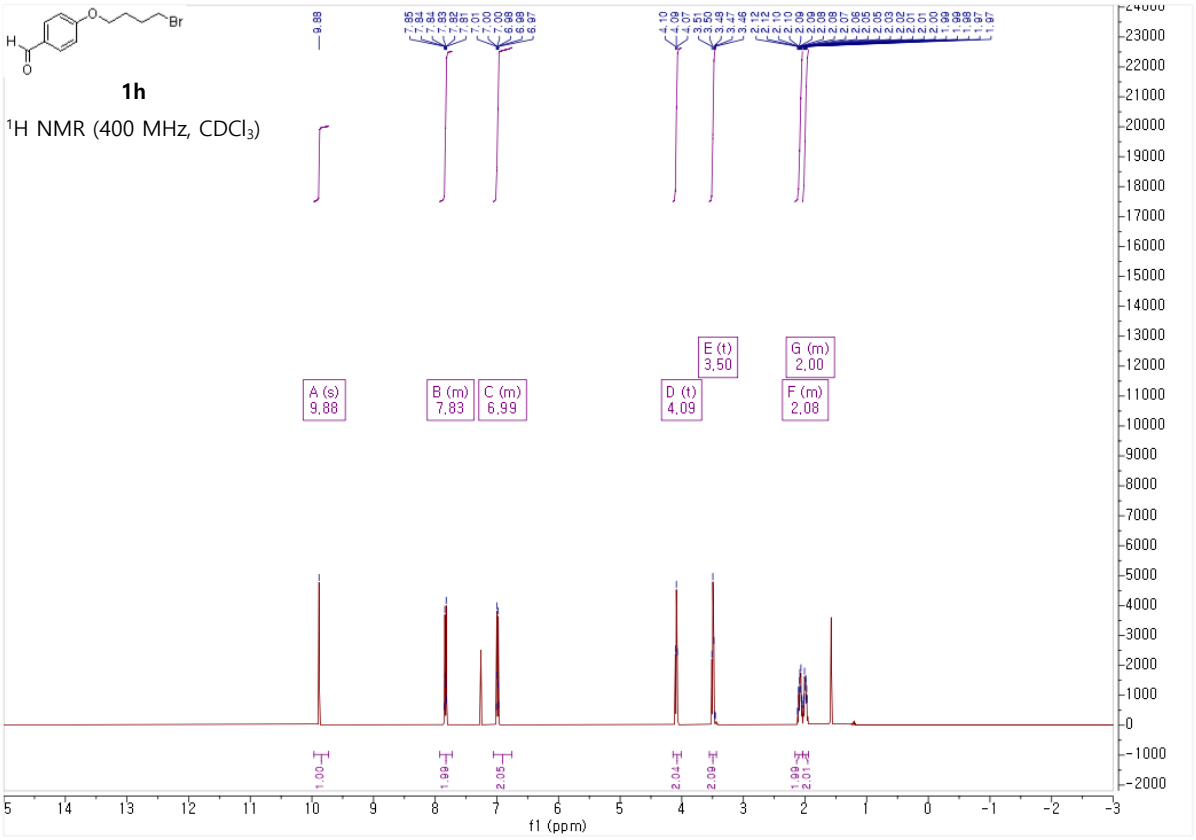
1f

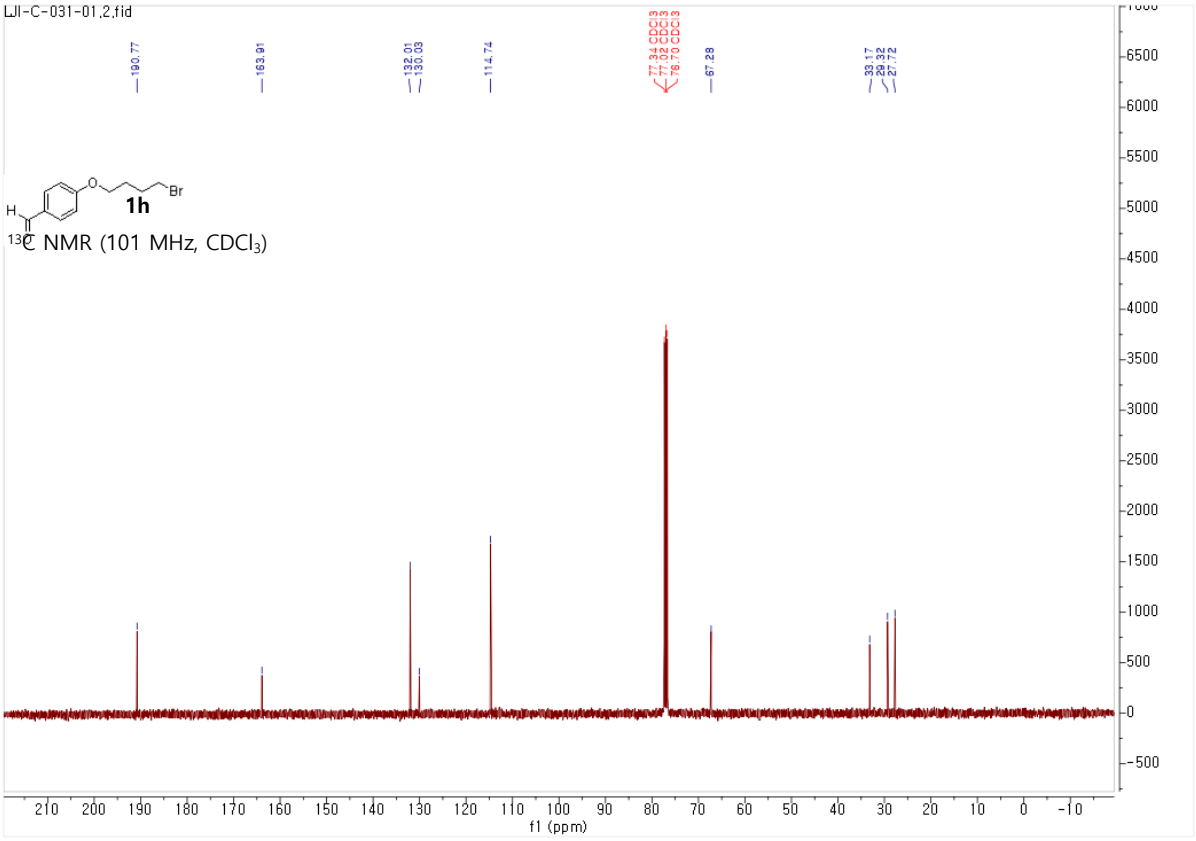
^{1}H NMR (400 MHz, $CDCl_3$)

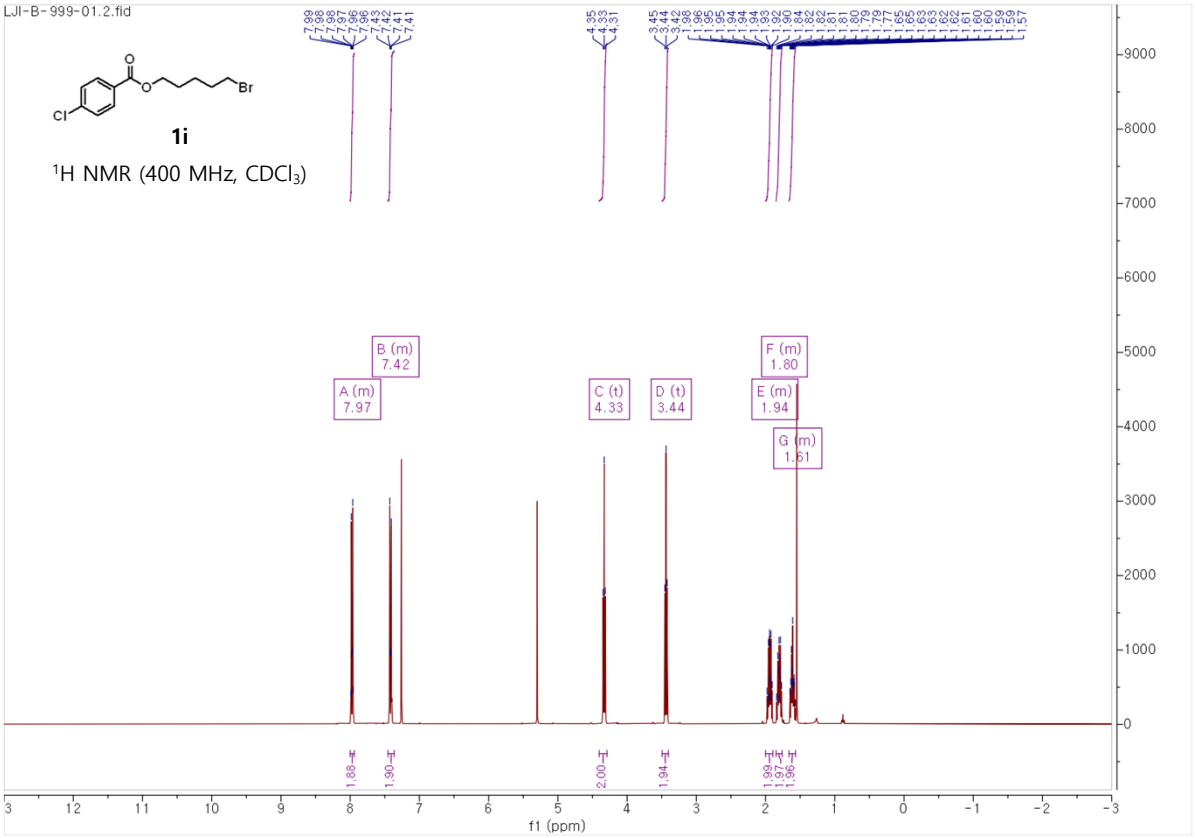


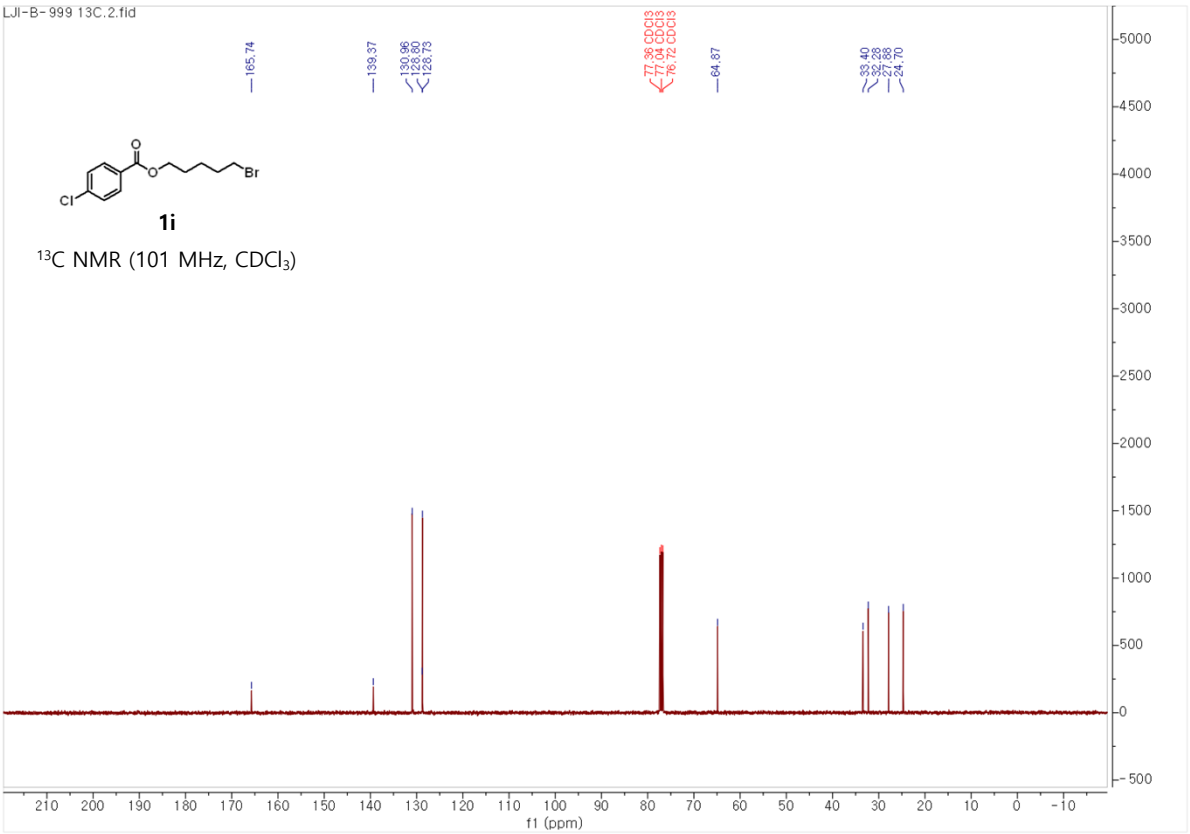
1f

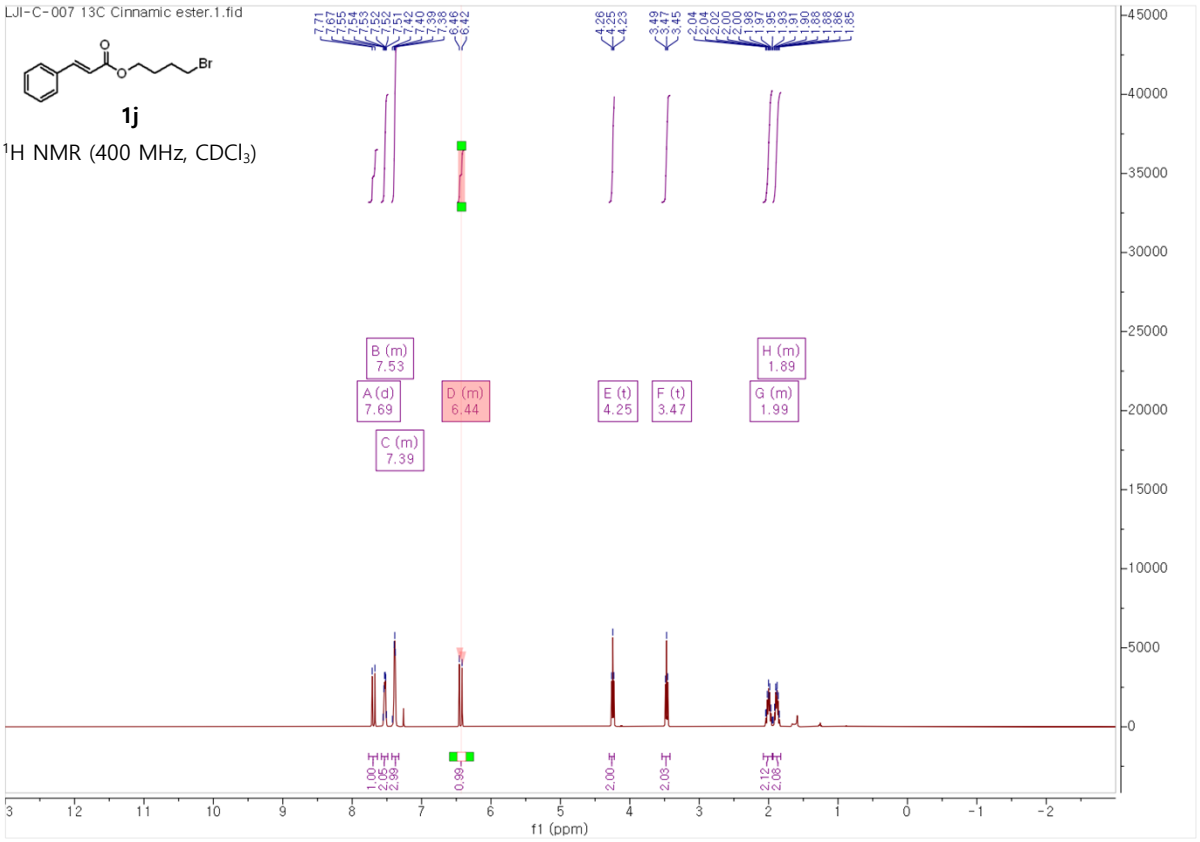
^{13}C NMR (101 MHz, $CDCl_3$)

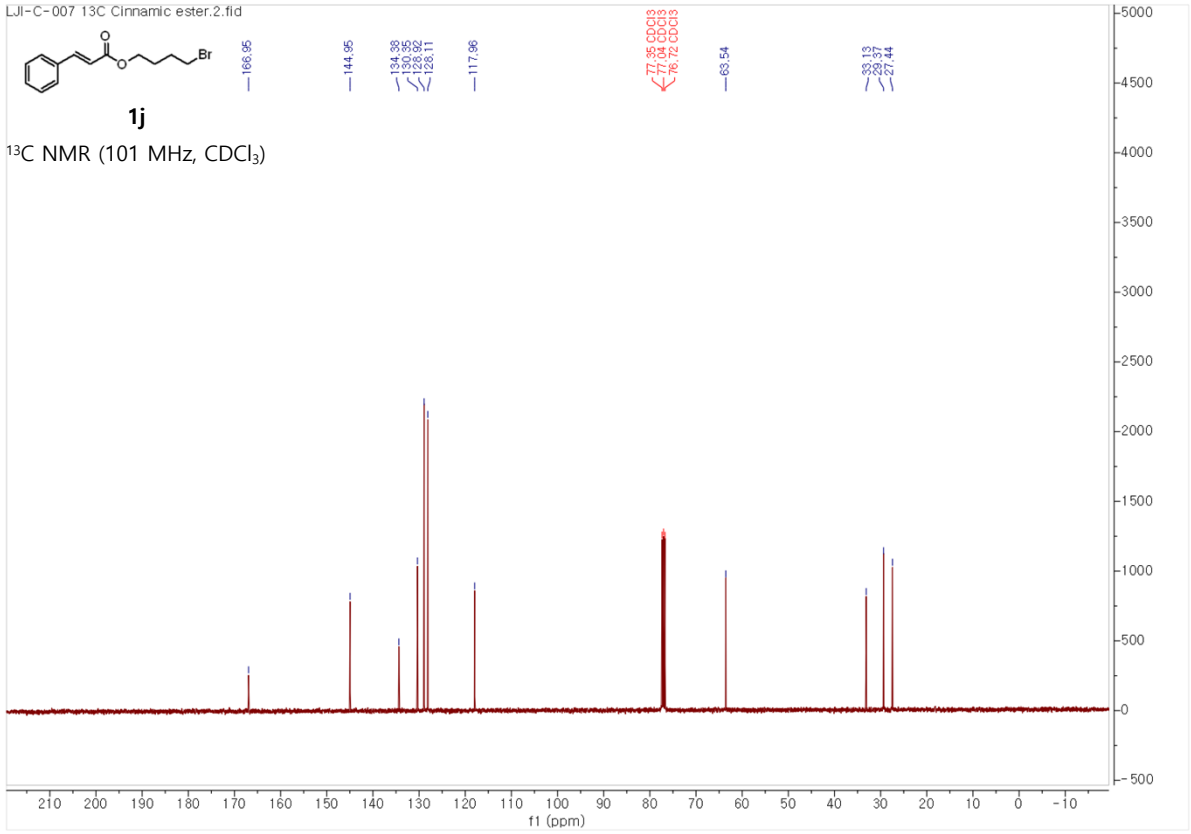

1h
^{1}H NMR (400 MHz, $CDCl_3$)
A (s) 9,88
B (m) 7,83
C (m) 6,99
D (t) 4,09
E (t) 3,50
F (m) 2,08
G (m) 2,00
f1 (ppm)

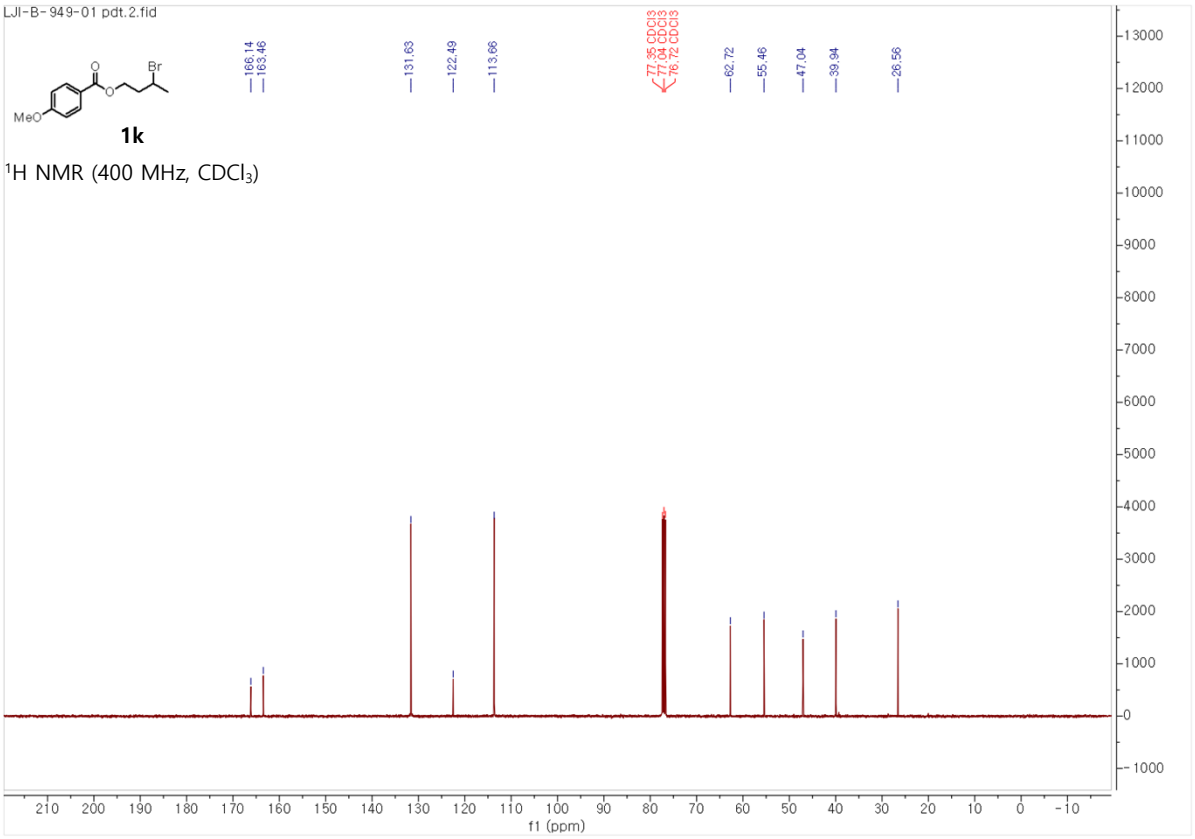

LJI-C-031-01.2.fid
1h
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


LJI-B-999-01.2.fid
1i
1H NMR (400 MHz, CDCl3)
A (m) 7.97
B (m) 7.42
C (t) 4.33
D (t) 3.44
E (m) 1.94
F (m) 1.80
G (m) 1.61
f1 (ppm)


LJI-B-999 13C.2.fid
1i
13C NMR (101 MHz, CDCl3)
165.74
139.37
130.96
128.80
128.73
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
64.87
33.40
32.29
27.88
24.70
f1 (ppm)

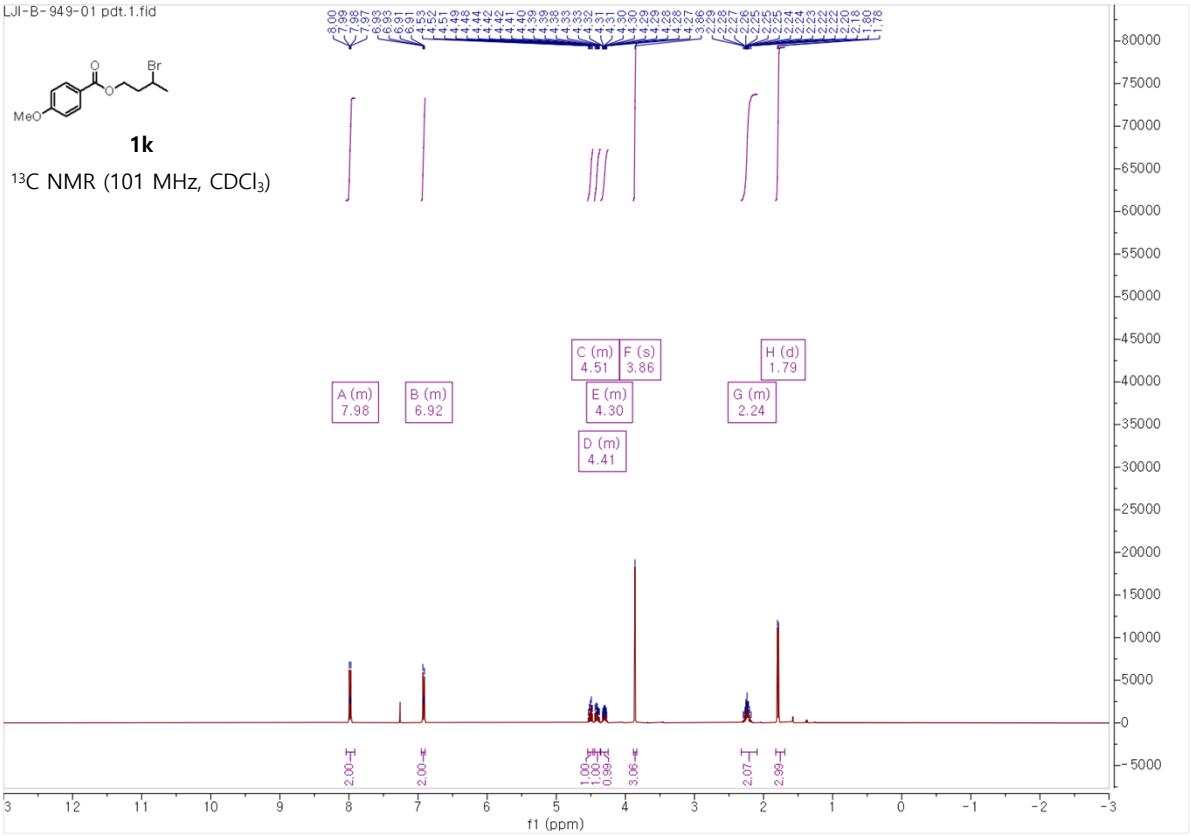

LJI-C-007 13C Cinnamic ester.1.fid
Br
1j
1H NMR (400 MHz, CDCl3)
B (m) 7.53
A (d) 7.69
D (m) 6.44
E (t) 4.25
F (t) 3.47
H (m) 1.89
G (m) 1.99
C (m) 7.39
f1 (ppm)


LJI-C-007 13C Cinnamic ester.2.fid
Br
1j
13C NMR (101 MHz, CDCl3)
166.95
144.95
134.38
130.35
128.92
128.11
117.96
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
63.54
33.13
29.37
27.44
f1 (ppm)



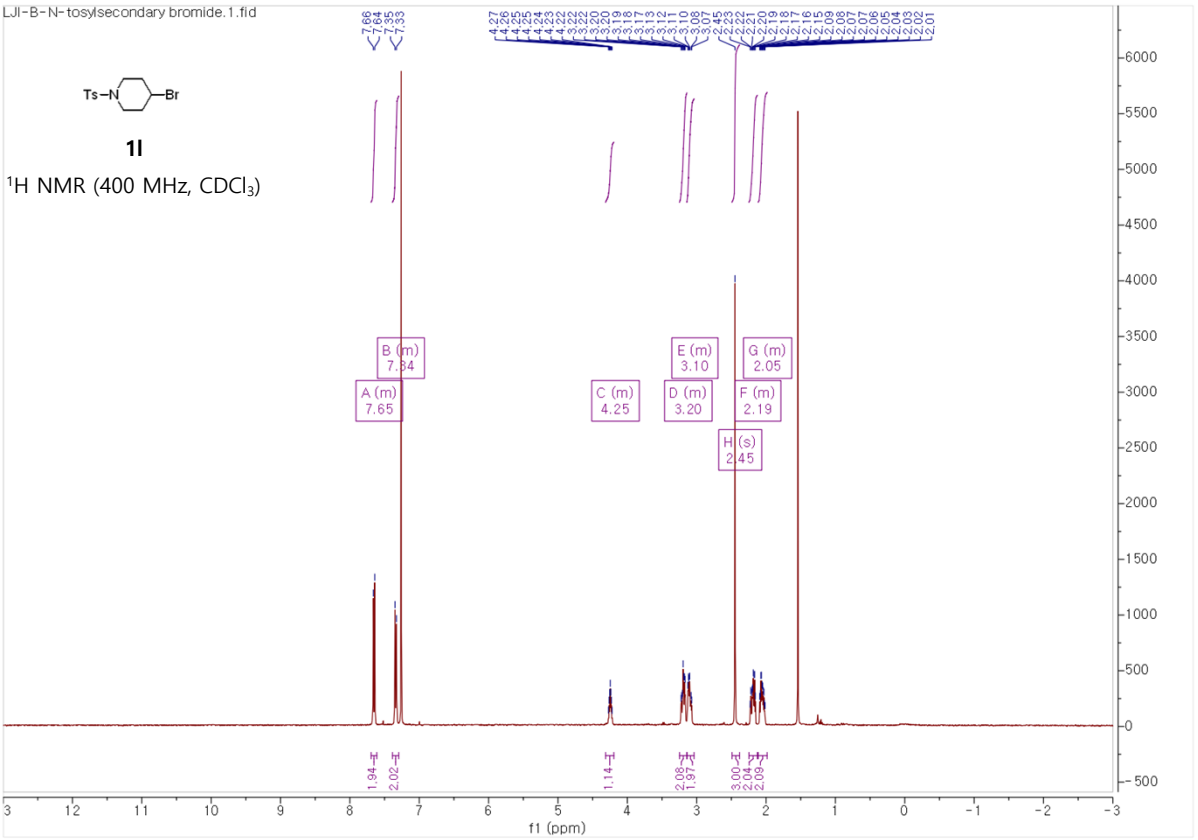
1k

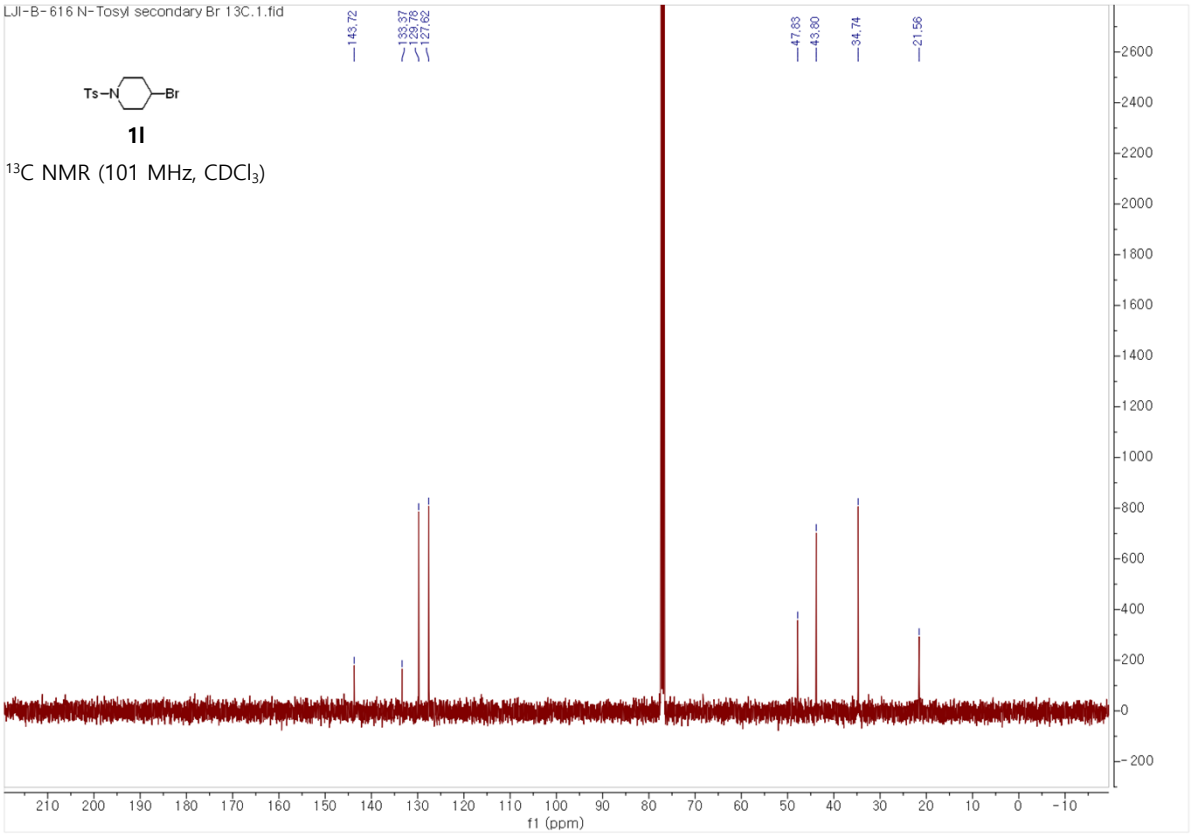
^{1}H NMR (400 MHz, $CDCl_3$)

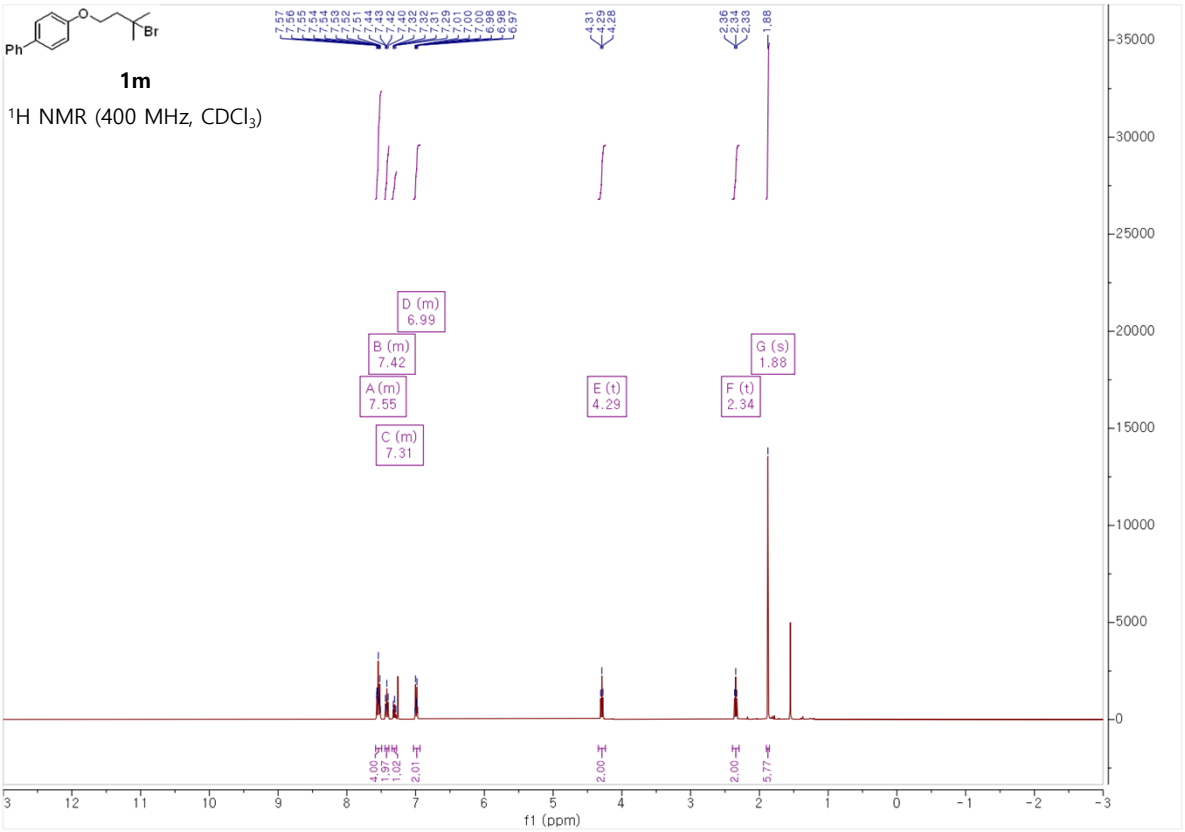


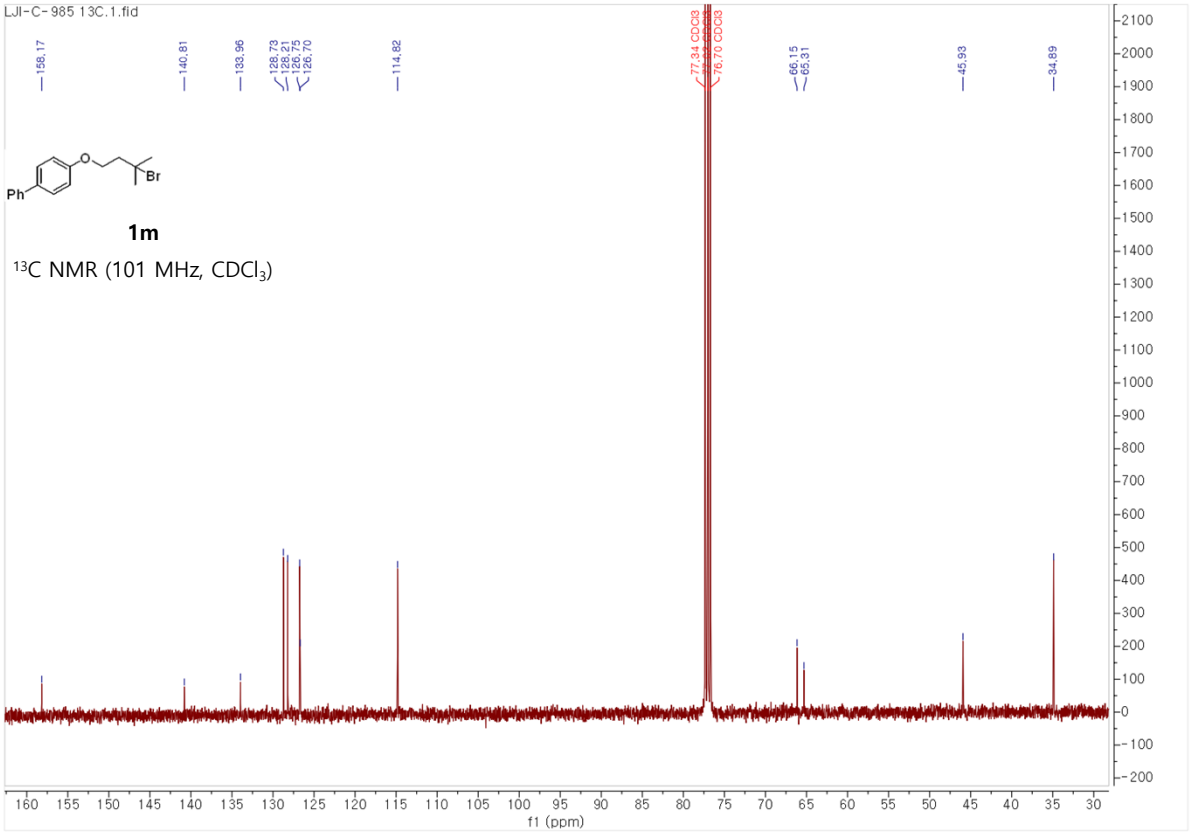
1k

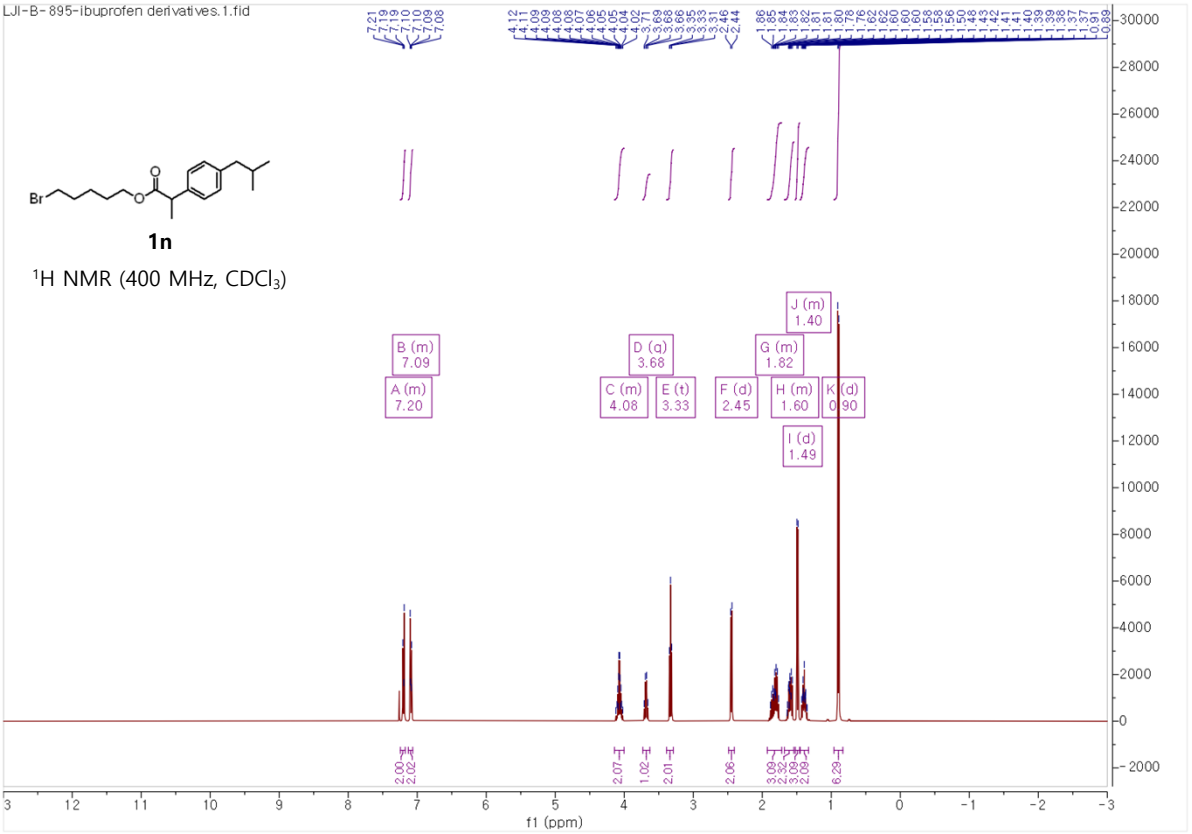
^{13}C NMR (101 MHz, $CDCl_3$)

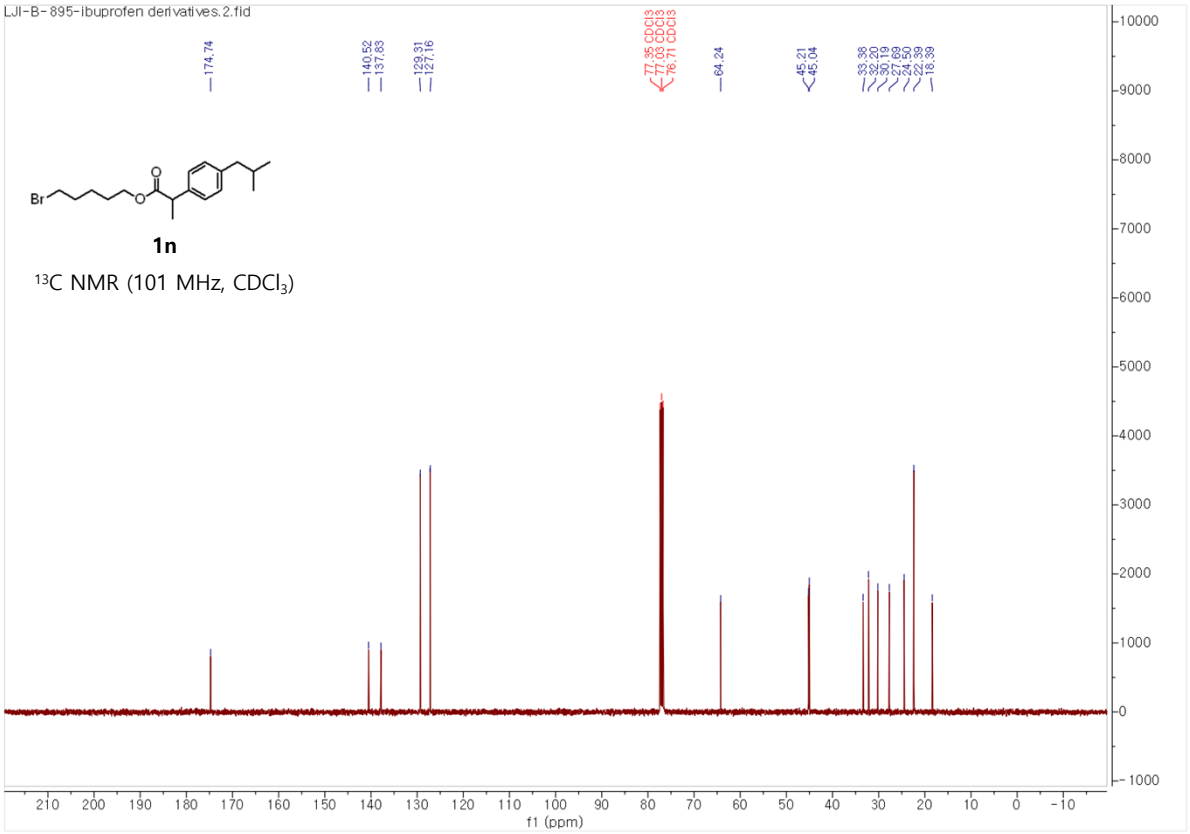

LJI-B-N-tosylsecondary bromide.1.fid
Ts–N
Br
1l
^{1}H NMR (400 MHz, $CDCl_3$)
B (m) 7.34
A (m) 7.65
C (m) 4.25
E (m) 3.10
D (m) 3.20
G (m) 2.05
F (m) 2.19
H (s) 2.45
f1 (ppm)

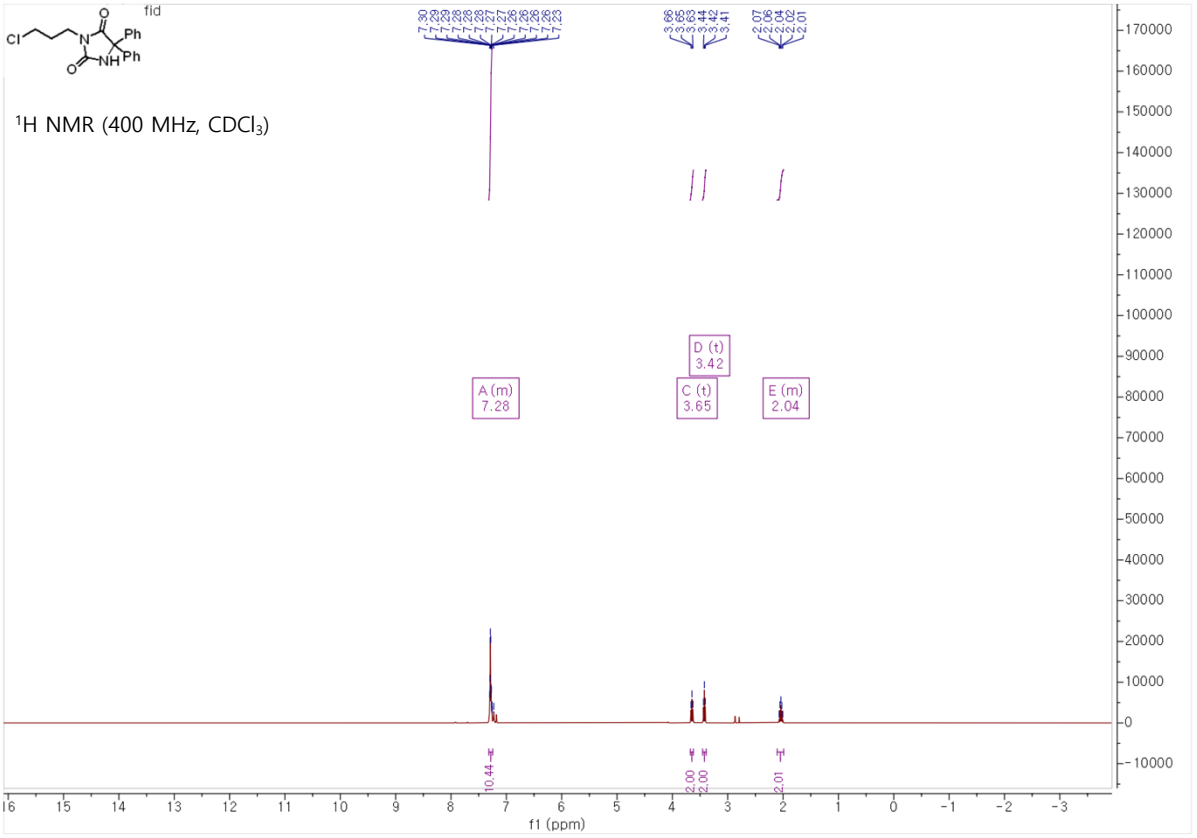

LJI-B-616 N-Tosyl secondary Br 13C.1.fid
Ts–N
Br
1l
^{13}C NMR (101 MHz, $CDCl_3$)
143.72
133.37
129.78
127.62
47.83
43.80
34.74
21.56
f1 (ppm)


Ph
Br
1m
1H NMR (400 MHz, CDCl3)
D (m) 6.99
B (m) 7.42
A (m) 7.55
C (m) 7.31
E (t) 4.29
F (t) 2.34
G (s) 1.88
f1 (ppm)

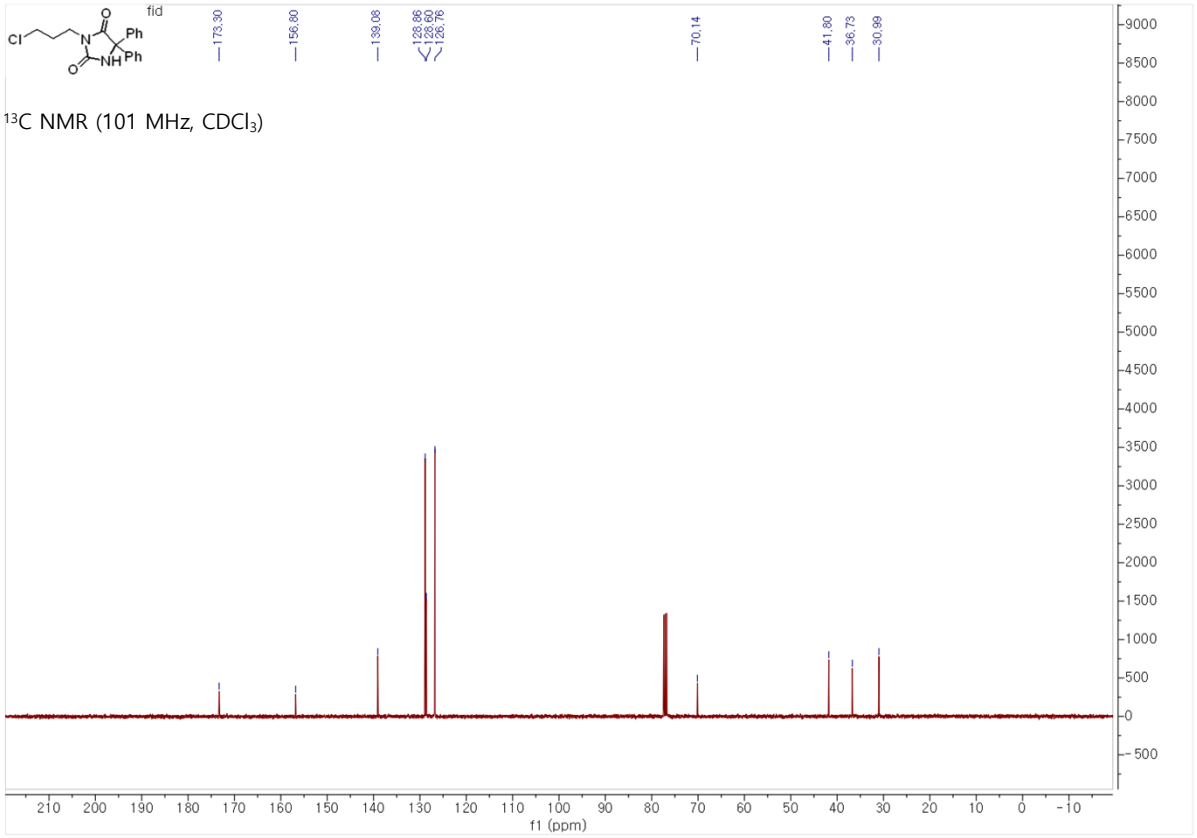

LJI-C-985 13C.1.fid
158.17
140.81
133.96
128.73
128.21
126.75
126.70
114.82
77.34 CDCl3
76.70 CDCl3
66.15
65.31
45.93
34.89
Ph
Br
1m
13C NMR (101 MHz, CDCl3)
f1 (ppm)


LJI-B-895-ibuprofen derivatives.1.fid
Br
O
O
1n
^{1}H NMR (400 MHz, $CDCl_3$)
B (m) 7.09
A (m) 7.20
D (q) 3.68
C (m) 4.08
E (t) 3.33
F (d) 2.45
G (m) 1.82
H (m) 1.60
J (m) 1.40
K (d) 0.90
I (d) 1.49
f1 (ppm)

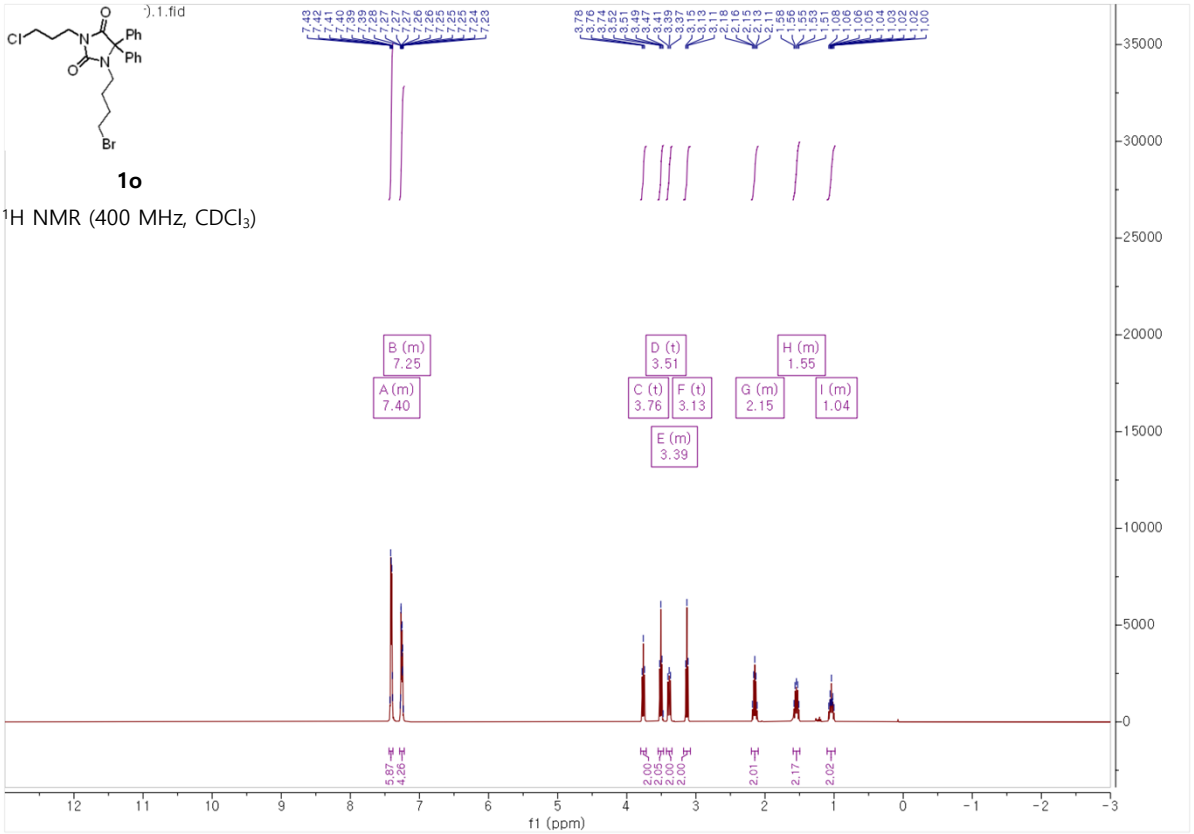

LJI-B-895-ibuprofen derivatives.2.fid
174.74
140.52
137.83
129.31
127.16
77.35 CDCl3
77.08 CDCl3
76.71 CDCl3
64.24
45.21
45.04
33.38
32.20
30.19
27.69
22.50
22.38
18.39
Br
O
O
1n
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)



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

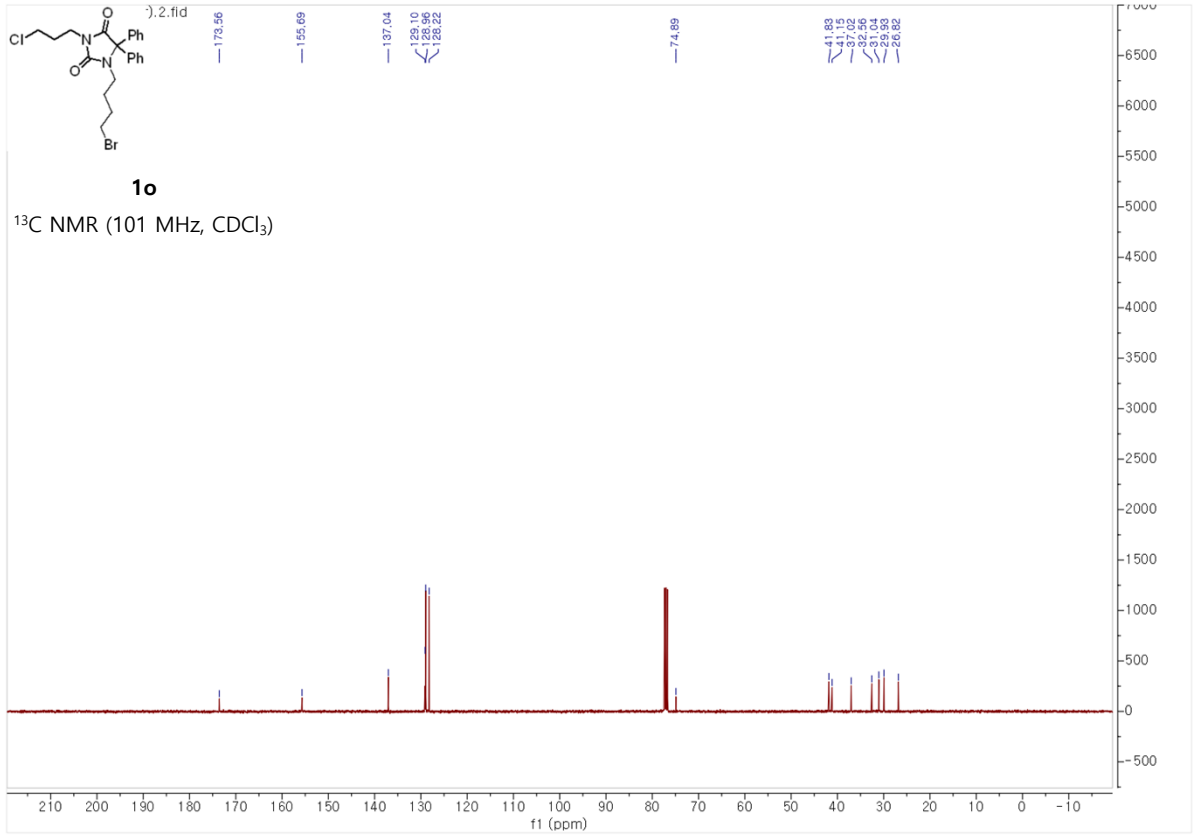


^{13}C NMR (101 MHz, $CDCl_3$)



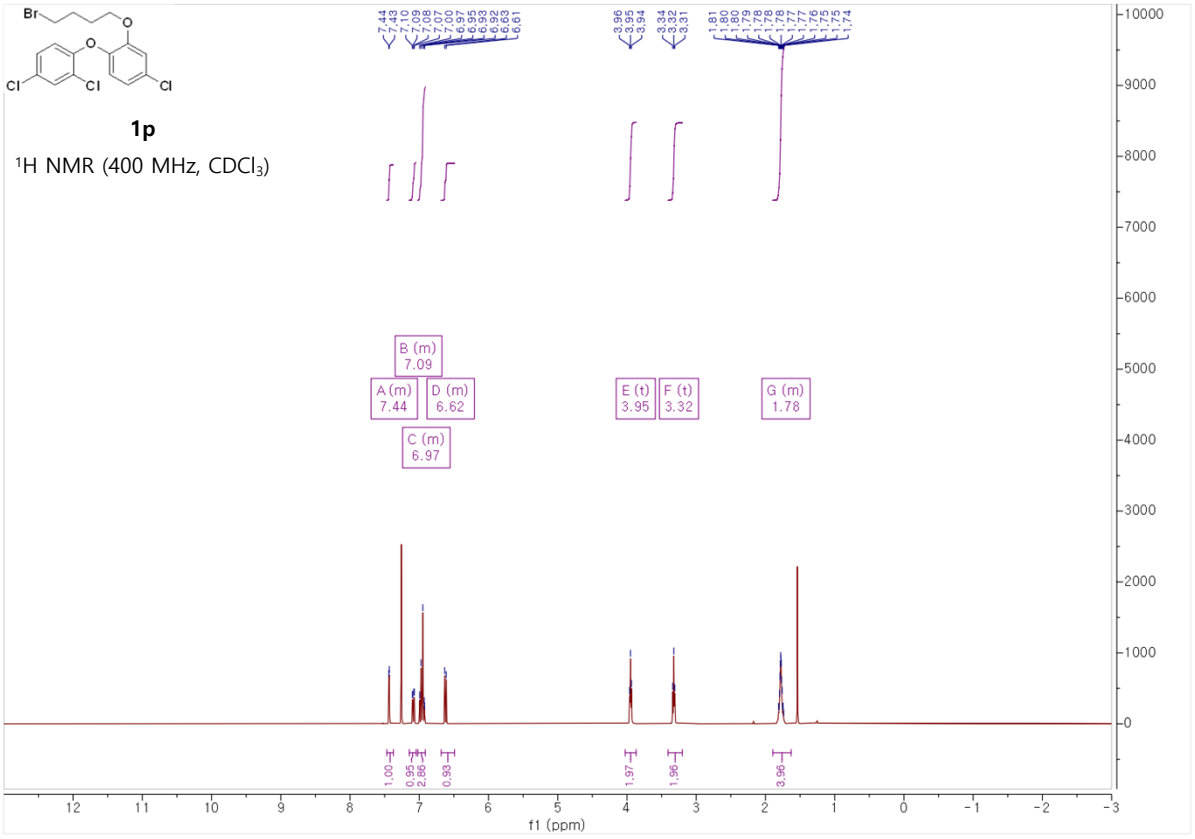
1o

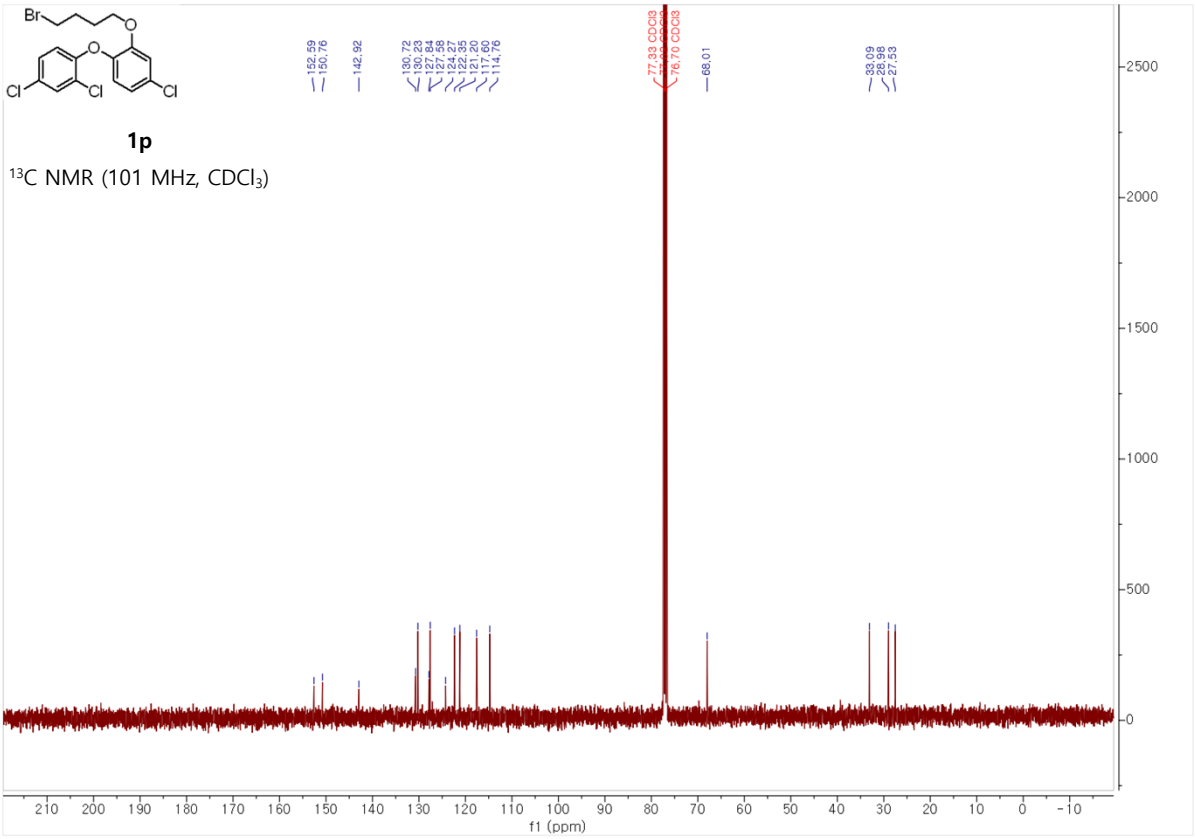
^{1}H NMR (400 MHz, $CDCl_3$)

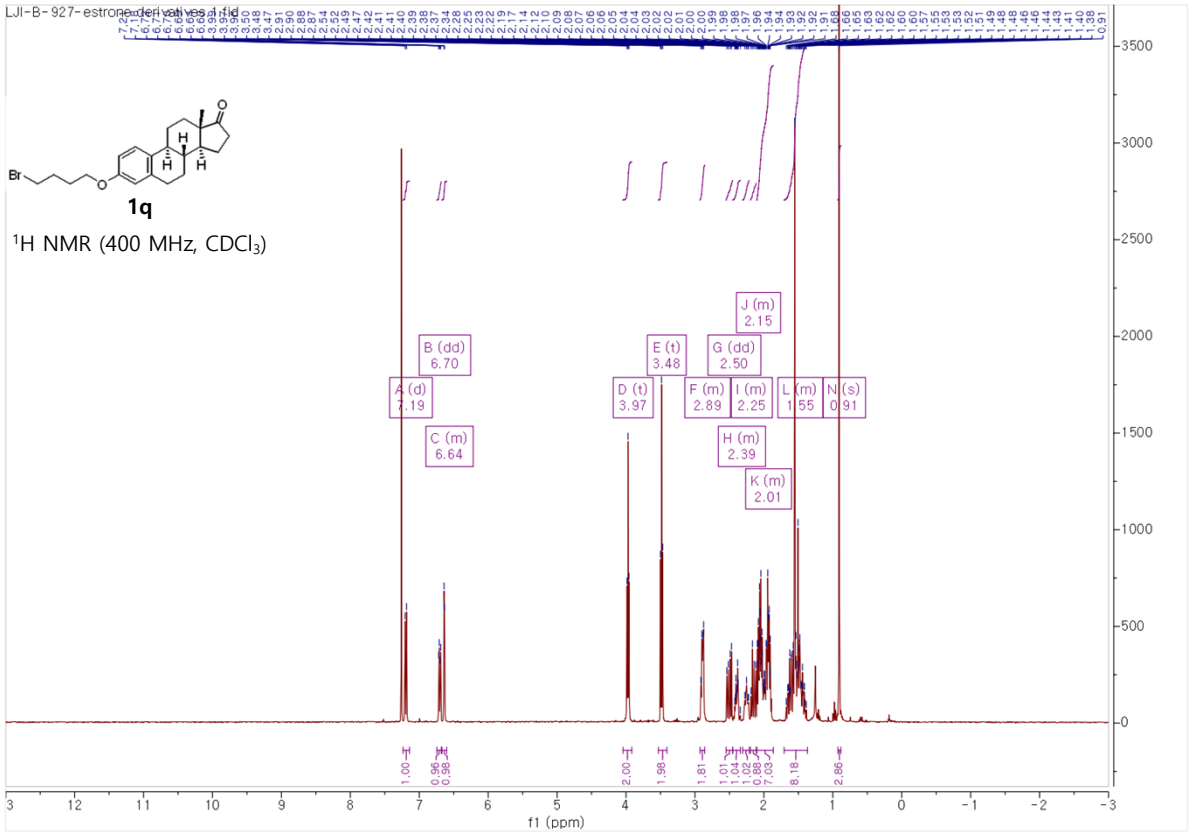


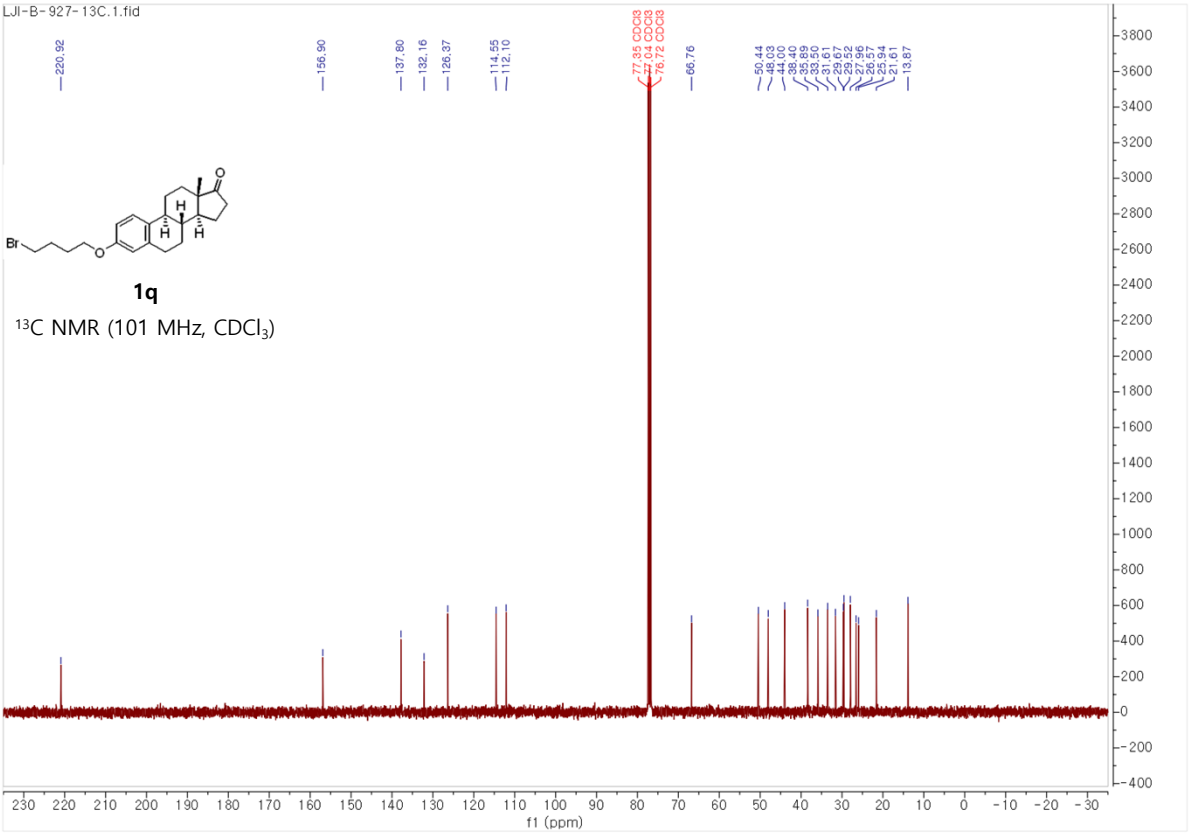
1o

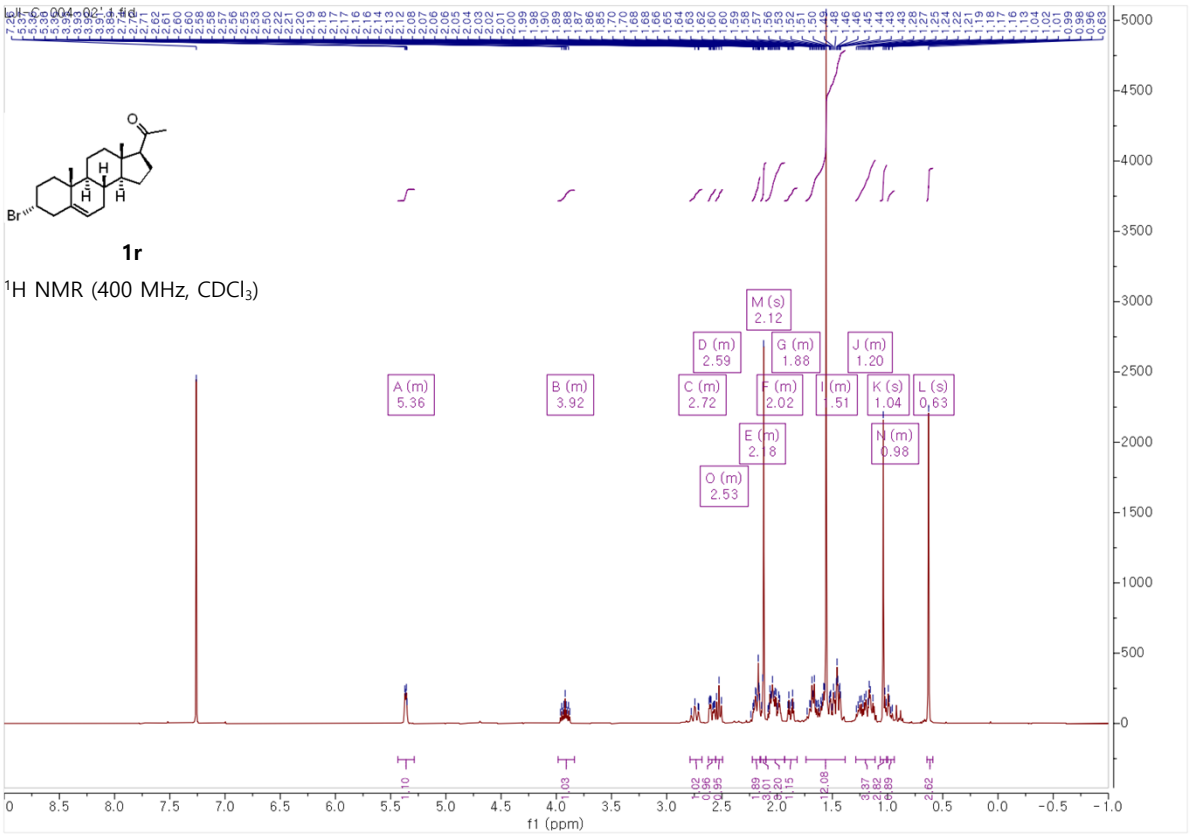
^{13}C NMR (101 MHz, $CDCl_3$)


Br
O
O
Cl
Cl
Cl
1p
1H NMR (400 MHz, CDCl3)
7.44
7.43
7.10
7.09
7.08
7.07
7.00
6.97
6.95
6.93
6.92
6.83
6.61
3.96
3.95
3.94
3.34
3.32
3.31
1.81
1.80
1.80
1.79
1.78
1.78
1.78
1.77
1.77
1.76
1.75
1.75
1.74
B (m) 7.09
A (m) 7.44
D (m) 6.62
C (m) 6.97
E (t) 3.95
F (t) 3.32
G (m) 1.78
1.00
0.95
2.86
0.93
1.97
1.96
3.96
f1 (ppm)


Br
O
O
Cl
Cl
Cl
1p
13C NMR (101 MHz, CDCl3)
152.59
150.76
142.92
130.72
130.23
127.84
127.58
124.27
122.85
121.20
117.60
114.76
77.33 CDCl3
77.00 CDCl3
76.70 CDCl3
68.01
30.09
29.98
27.53
f1 (ppm)

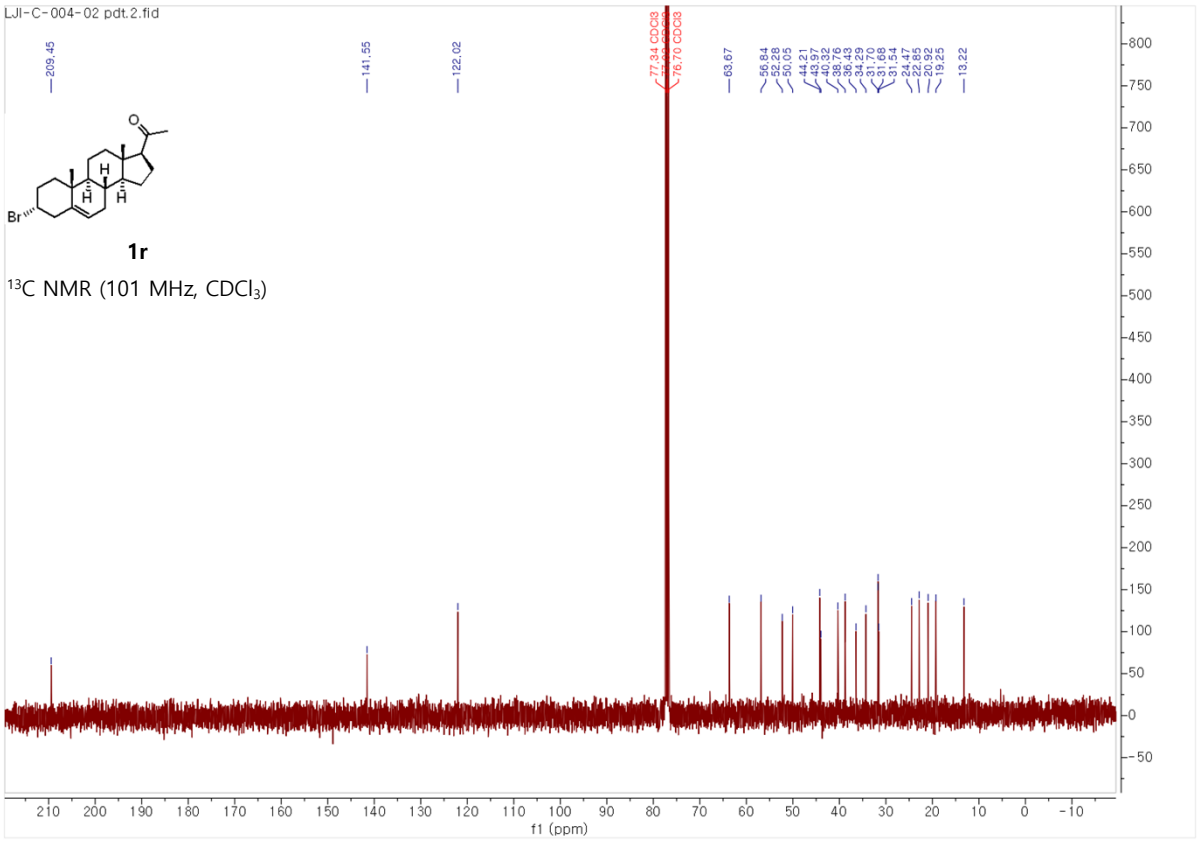

LJI-B-927-estrone-derivatives-1.fid
1q
1H NMR (400 MHz, CDCl3)
A (d) 7.19
B (dd) 6.70
C (m) 6.64
D (t) 3.97
E (t) 3.48
F (m) 2.89
G (dd) 2.50
H (m) 2.39
I (m) 2.25
J (m) 2.15
K (m) 2.01
L (m) 1.55
N (s) 0.91
f1 (ppm)


LJI-B-927-13C.1.fid
1q
13C NMR (101 MHz, CDCl3)
220.92
156.90
137.80
132.16
126.37
114.55
112.10
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
66.76
50.44
48.03
44.00
38.40
35.89
33.50
31.61
29.67
29.52
27.96
26.57
25.94
21.61
13.87
f1 (ppm)



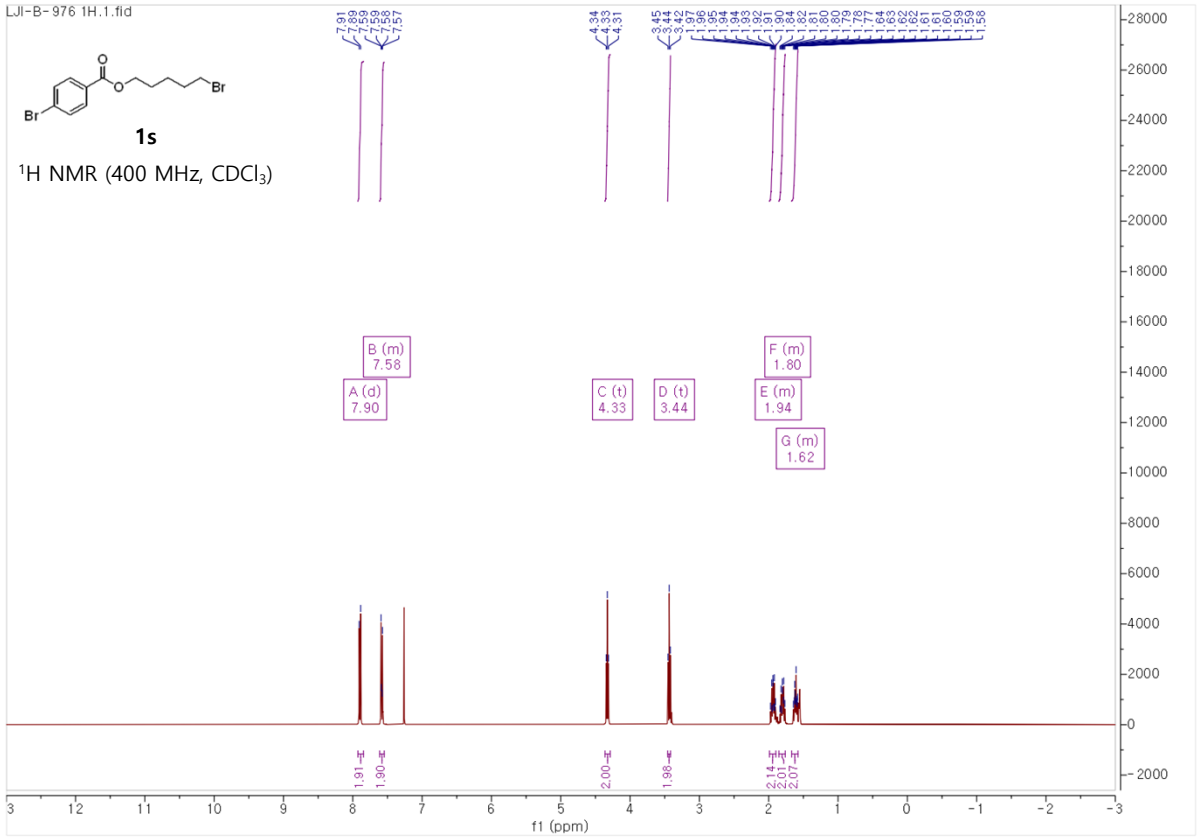
1r

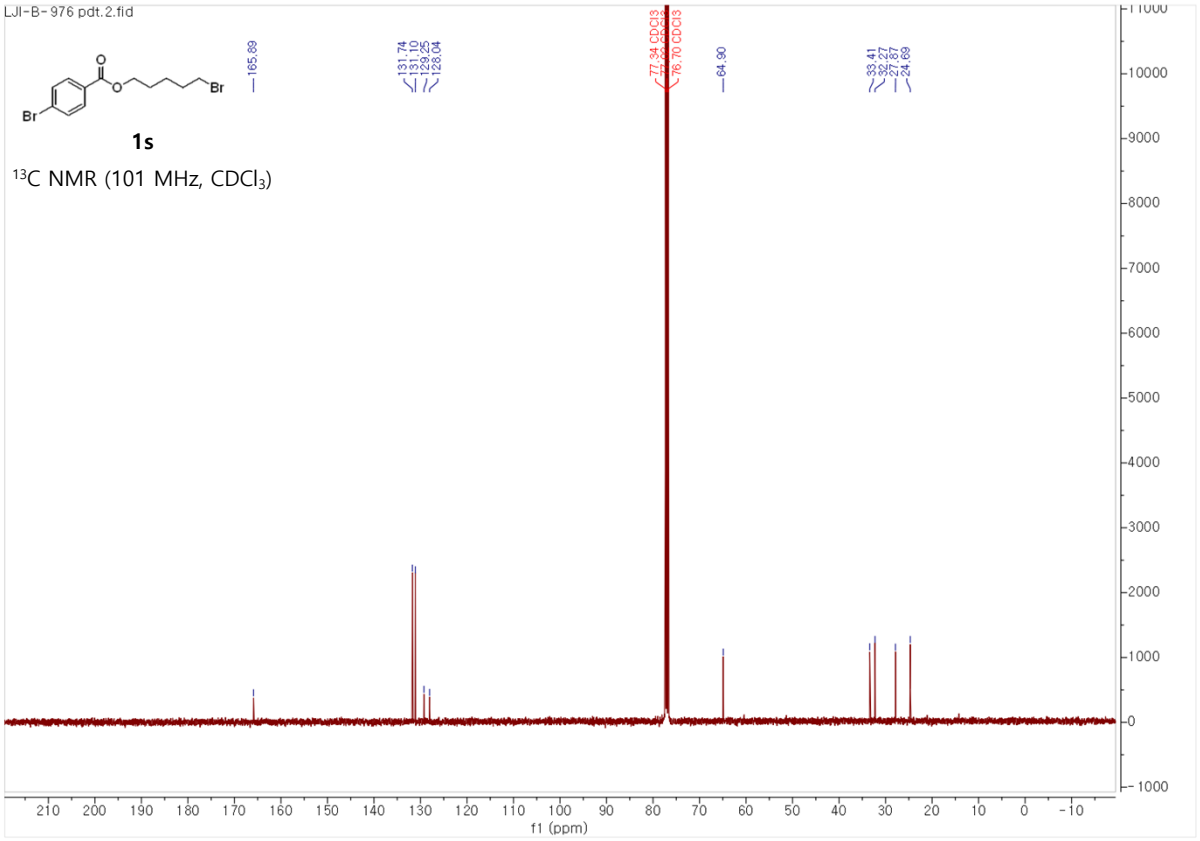
^{1}H NMR (400 MHz, $CDCl_3$)

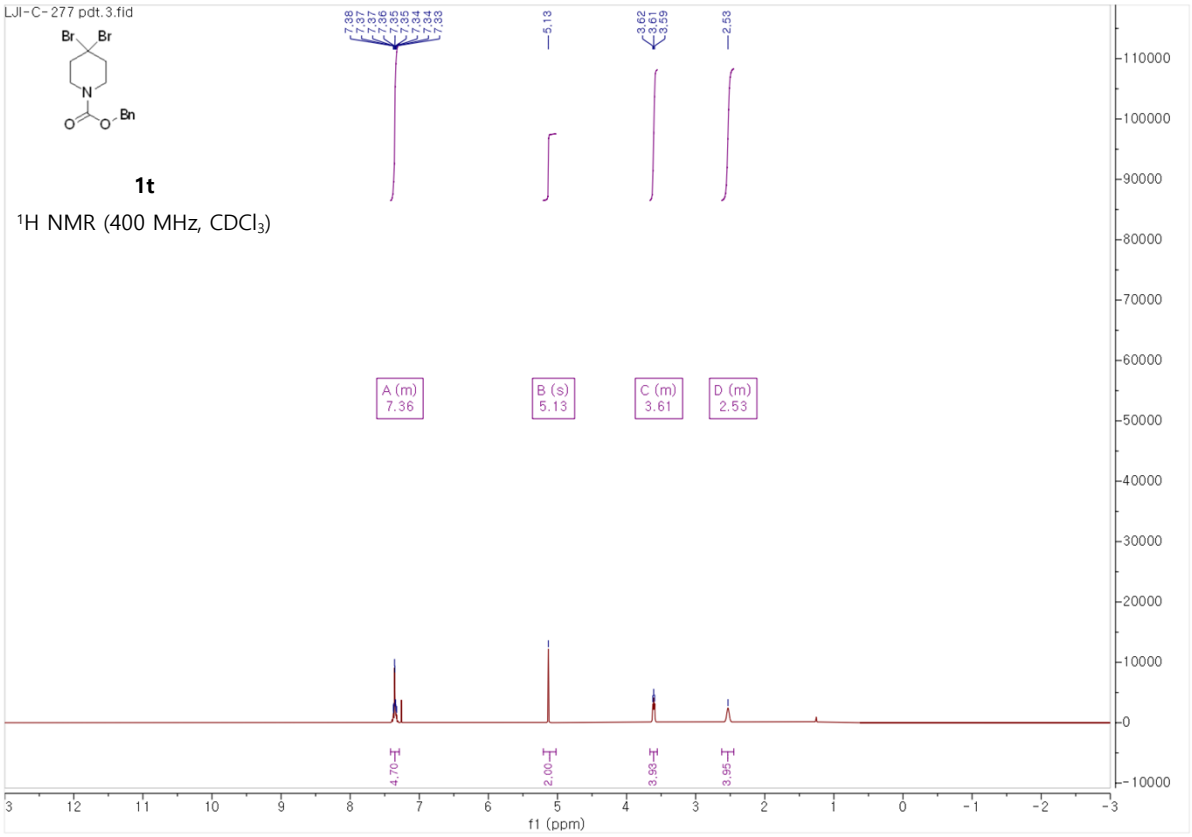


1r

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

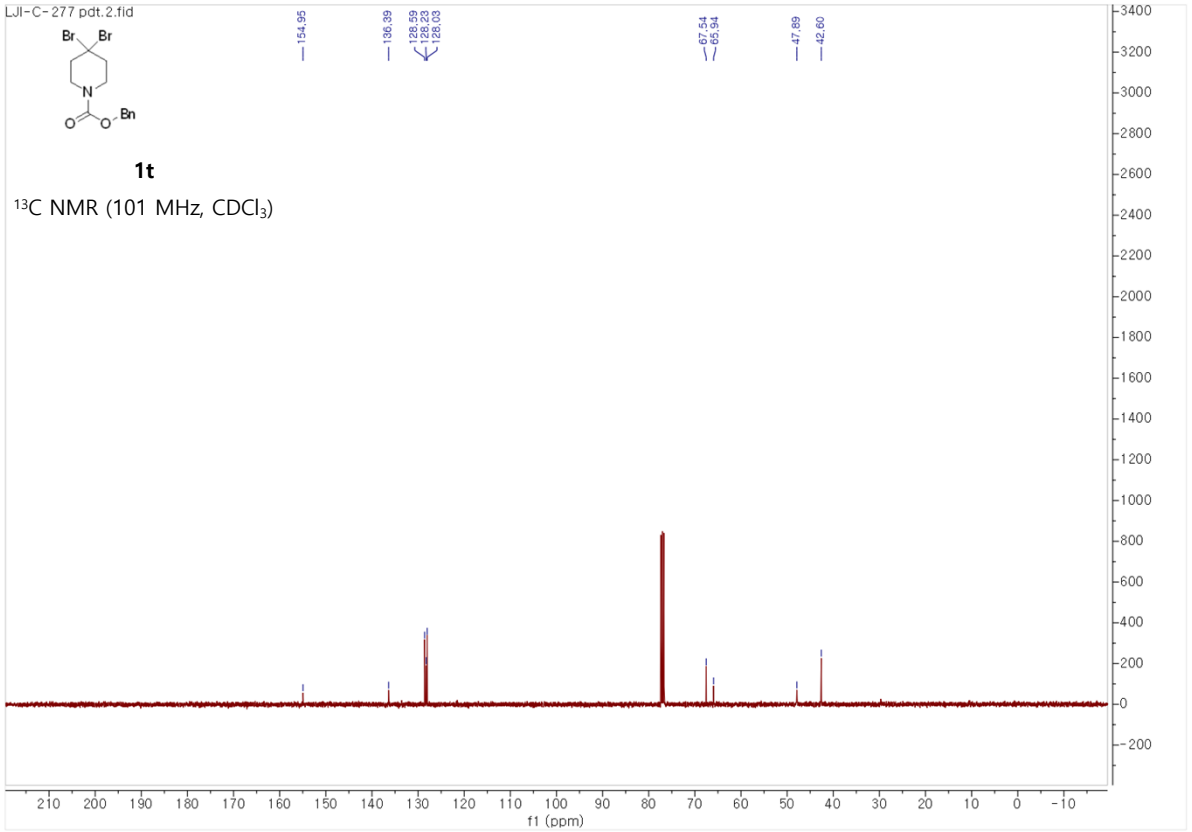

LJI-B-976 1H.1.fid
Br
O
Br
1s
^{1}H NMR (400 MHz, $CDCl_3$)
B (m) 7.58
A (d) 7.90
C (t) 4.33
D (t) 3.44
F (m) 1.80
E (m) 1.94
G (m) 1.62
1.91
1.90
2.00
1.98
2.14
2.01
2.07
f1 (ppm)


LJI-B-976 pdt.2.fid
Br
O
Br
1s
^{13}C NMR (101 MHz, $CDCl_3$)
165.89
131.74
131.10
129.25
128.04
77.34 CDCl3
77.02
76.70 CDCl3
64.90
33.41
32.27
27.87
24.69
f1 (ppm)



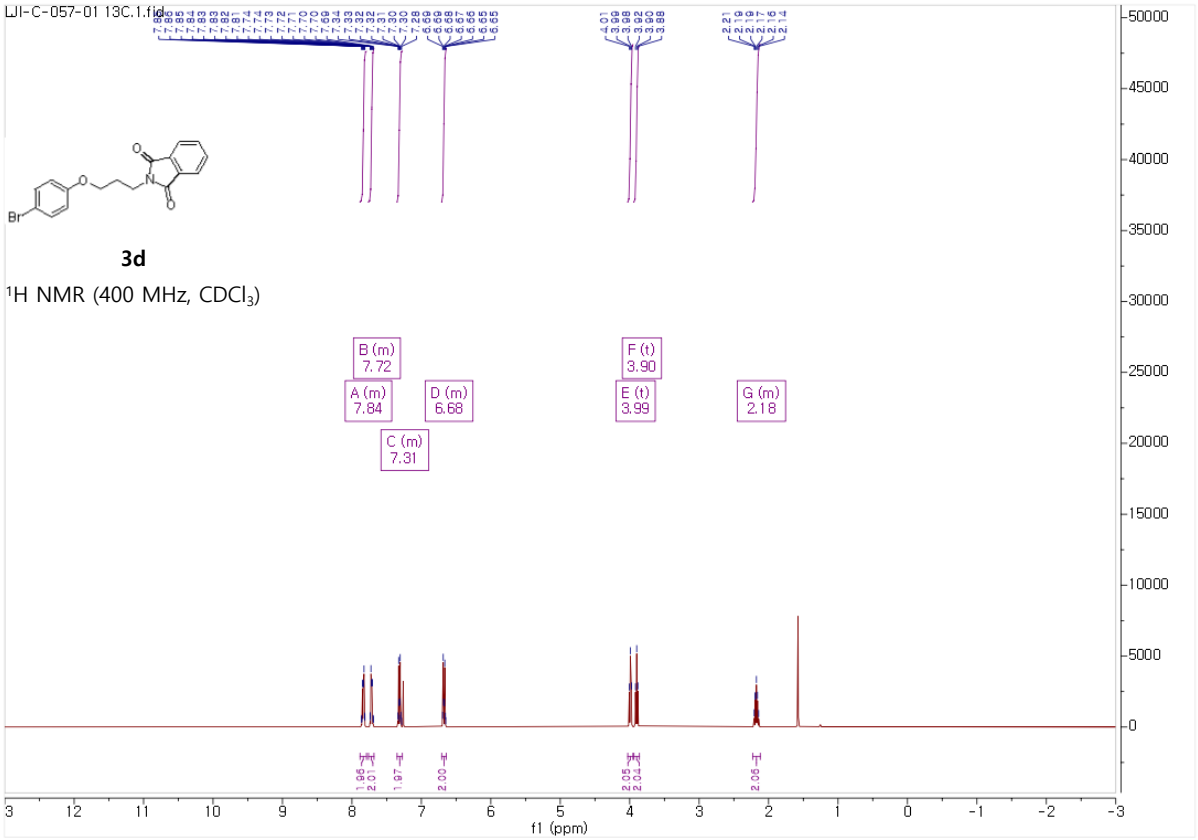
1t

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



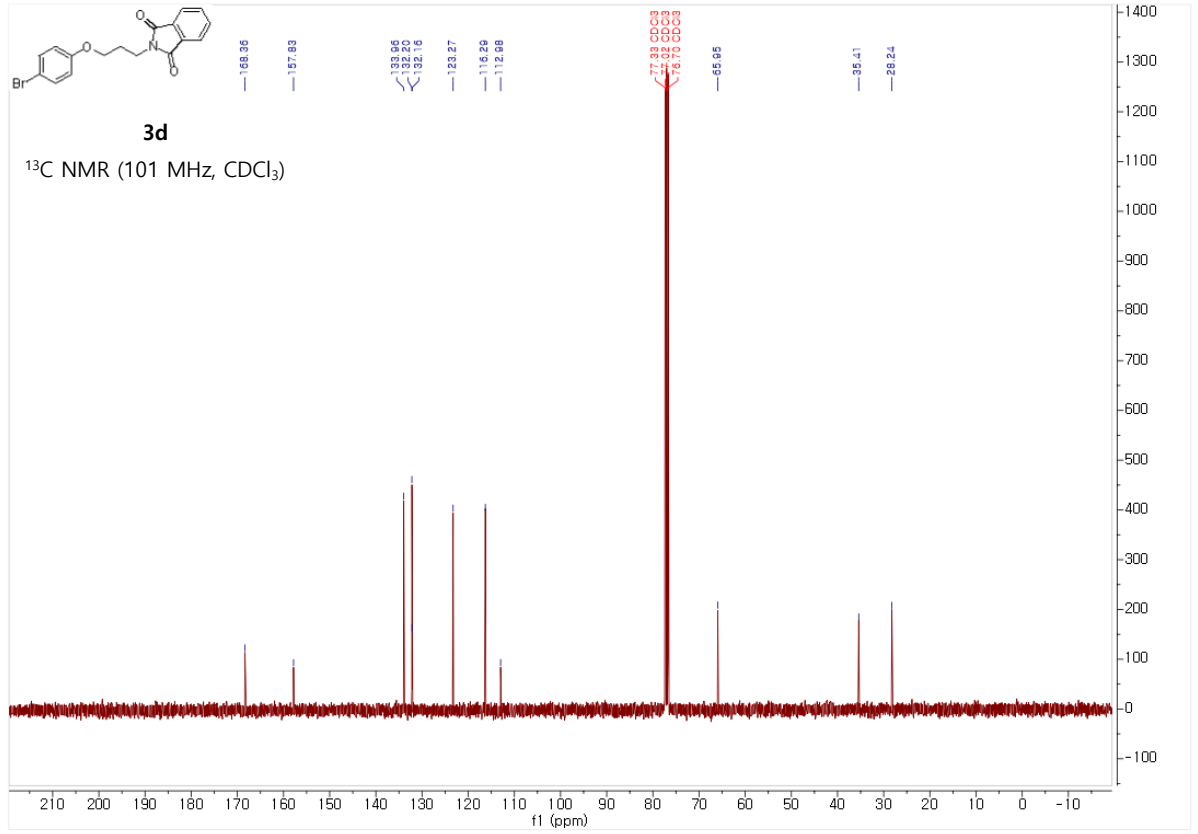
1t

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



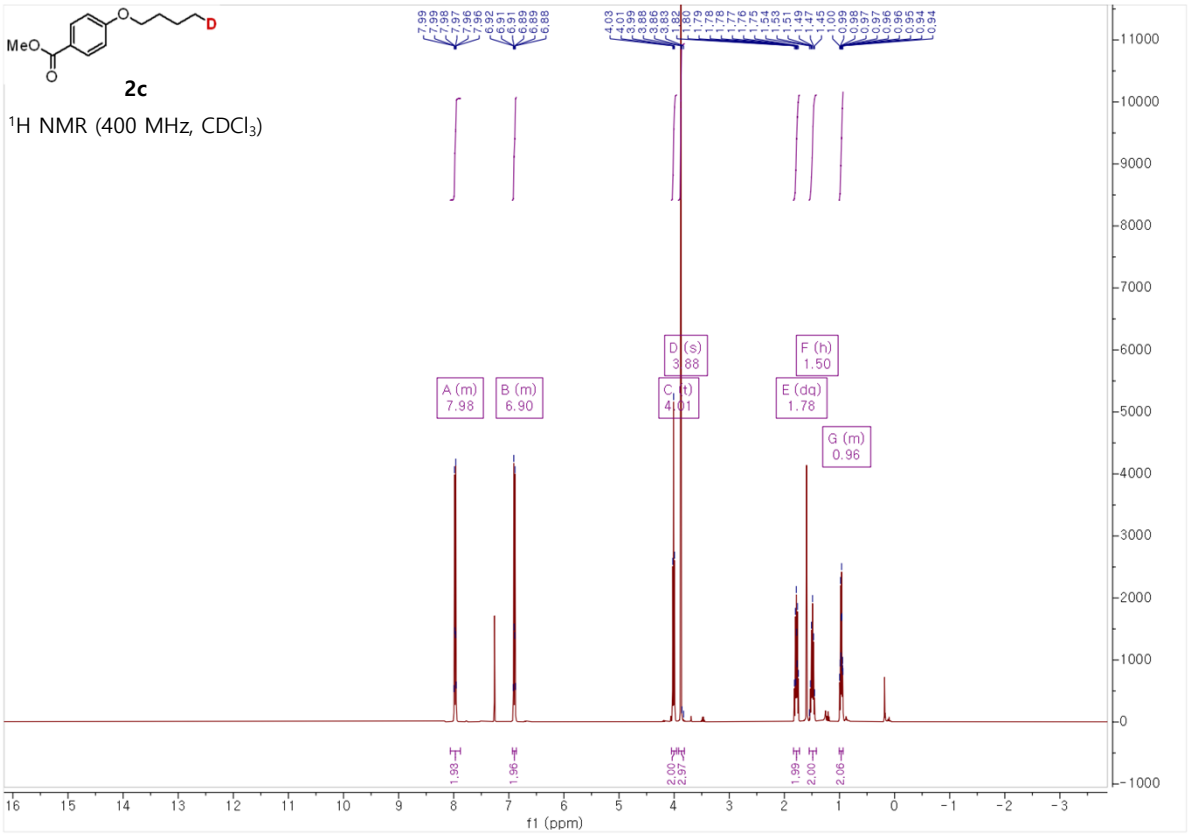
3d

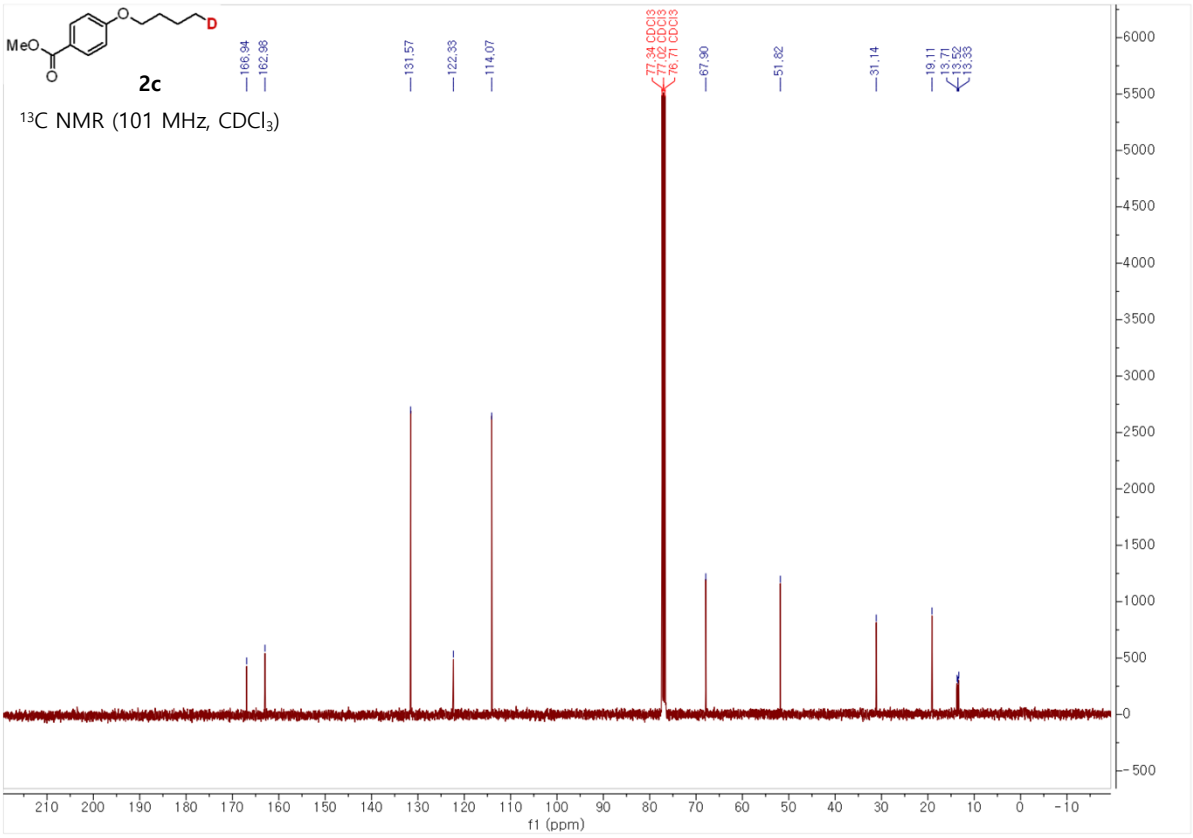
^{1}H NMR (400 MHz, $CDCl_3$)



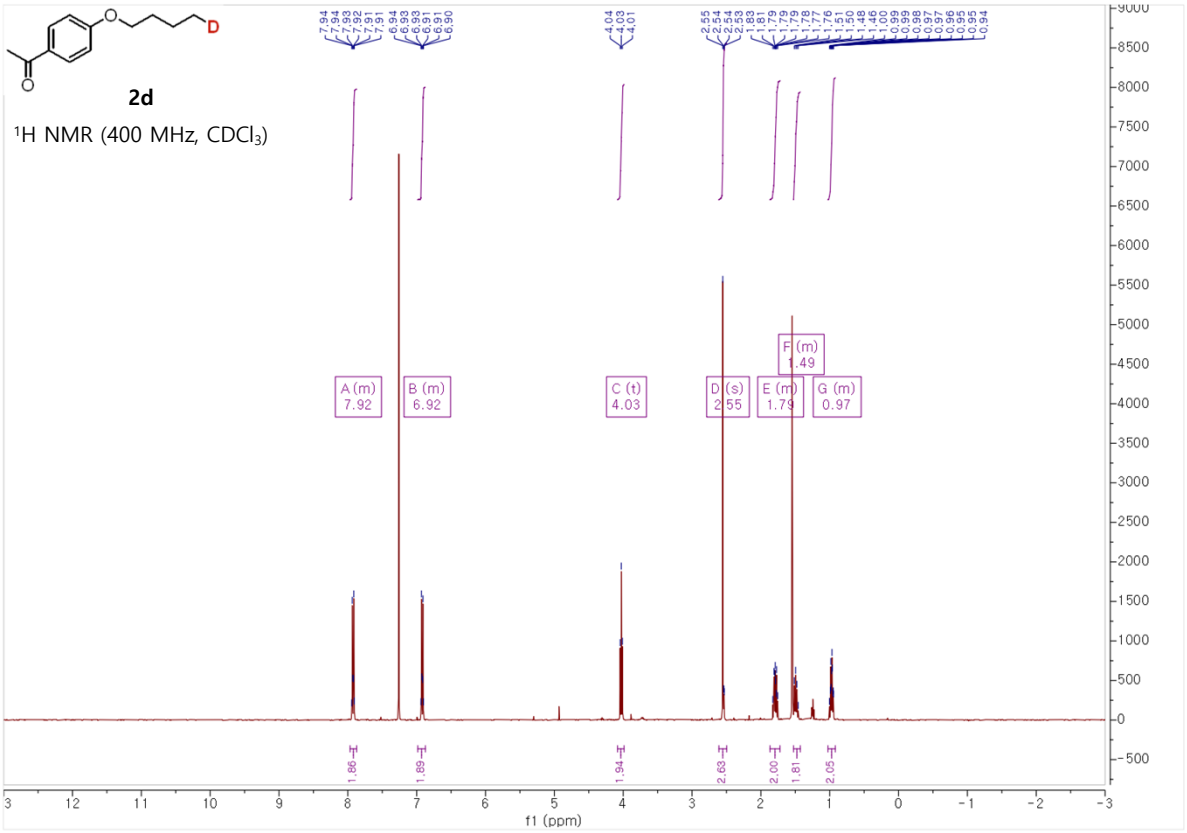
3d

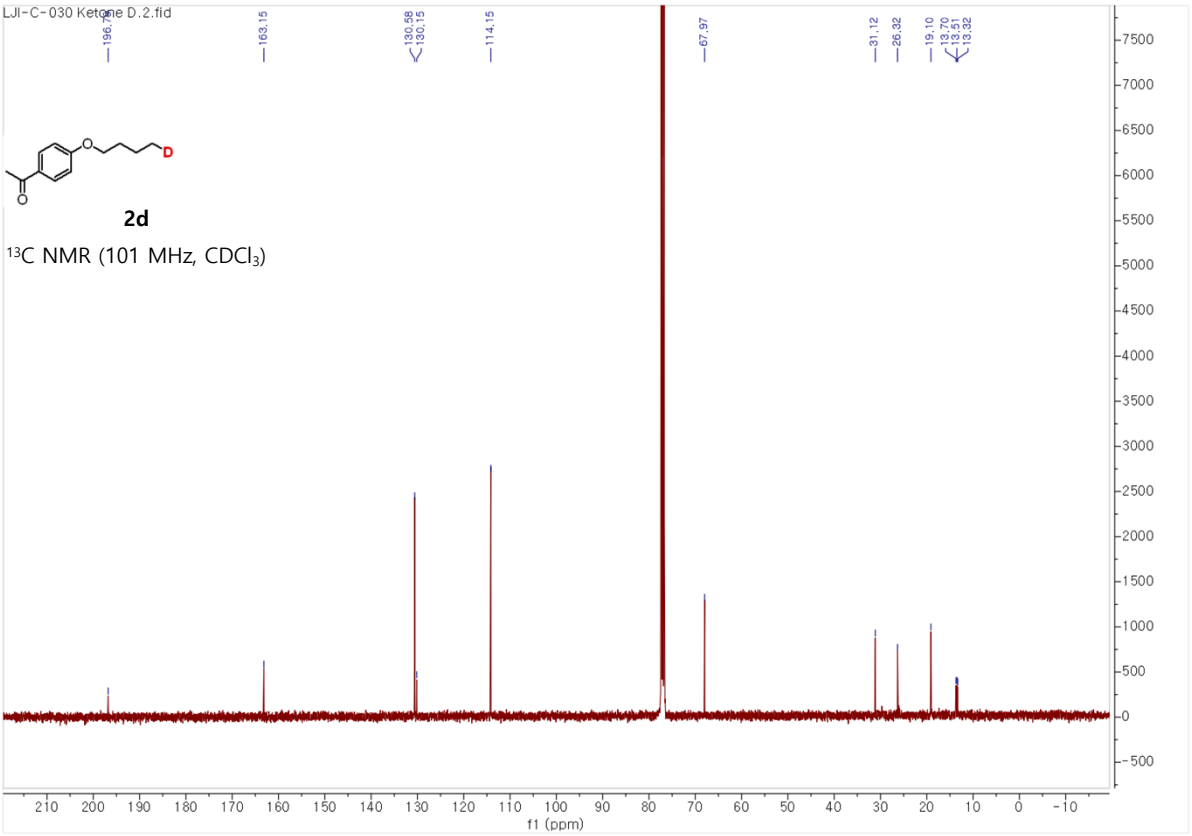
^{13}C NMR (101 MHz, $CDCl_3$)

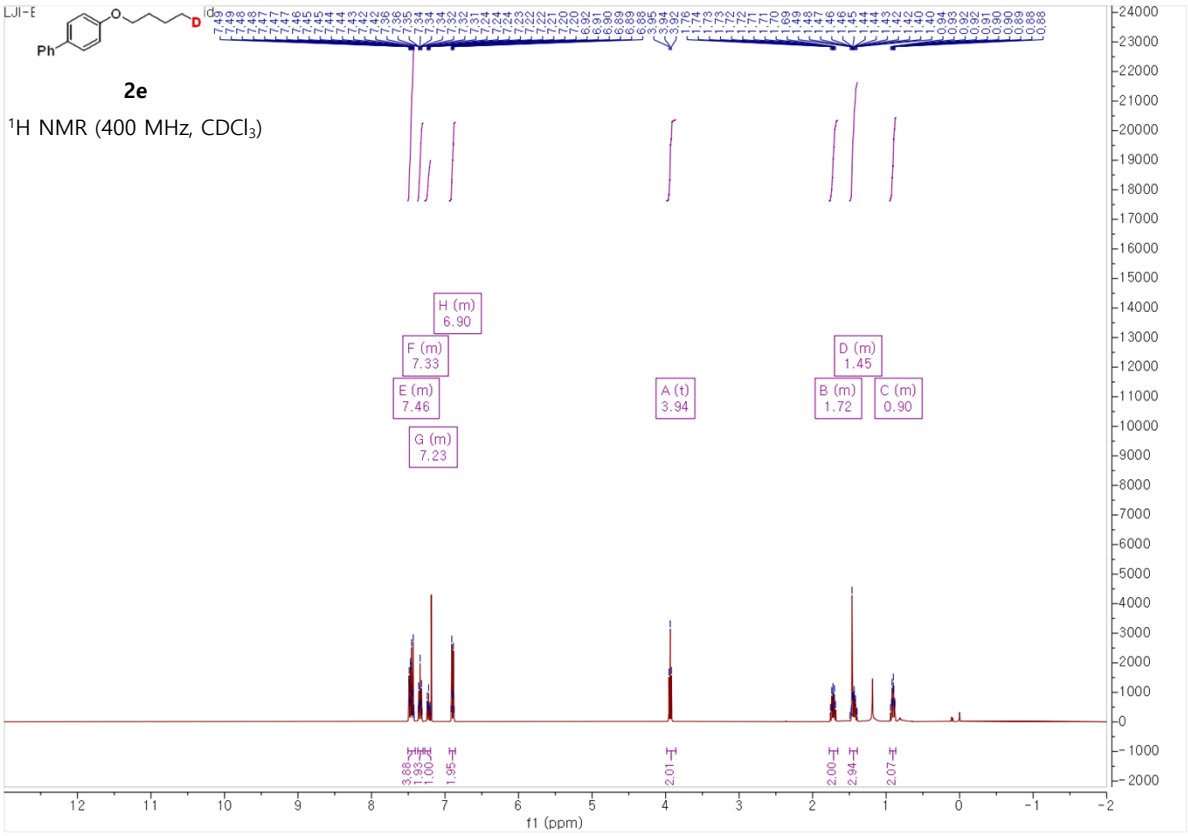

MeO
O
O
D
2c
^{1}H NMR (400 MHz, $CDCl_3$)
A (m) 7.98
B (m) 6.90
D (s) 3.88
C (t) 4.01
F (h) 1.50
E (dq) 1.78
G (m) 0.96
f1 (ppm)

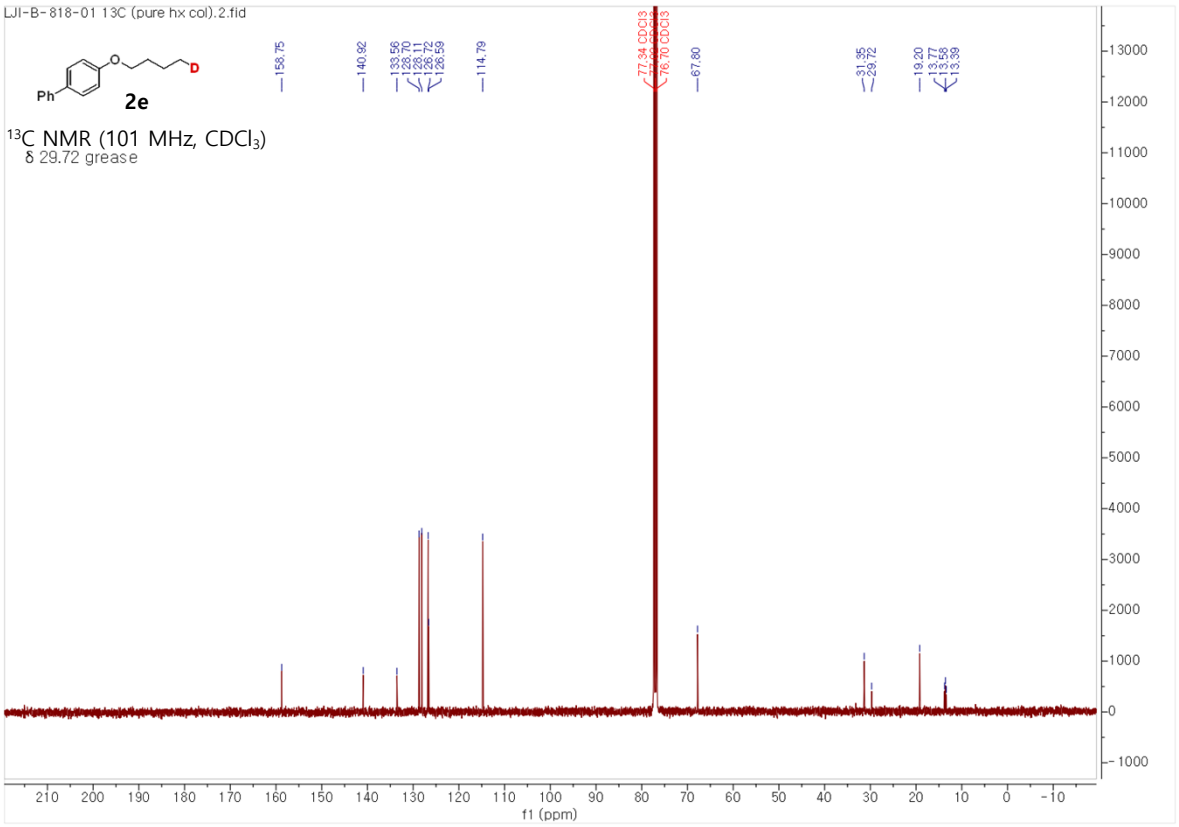

MeO
O
O
D
2c
^{13}C NMR (101 MHz, $CDCl_3$)
166.94
162.98
131.57
122.33
114.07
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
67.90
51.82
31.14
19.11
13.71
13.52
13.33
f1 (ppm)

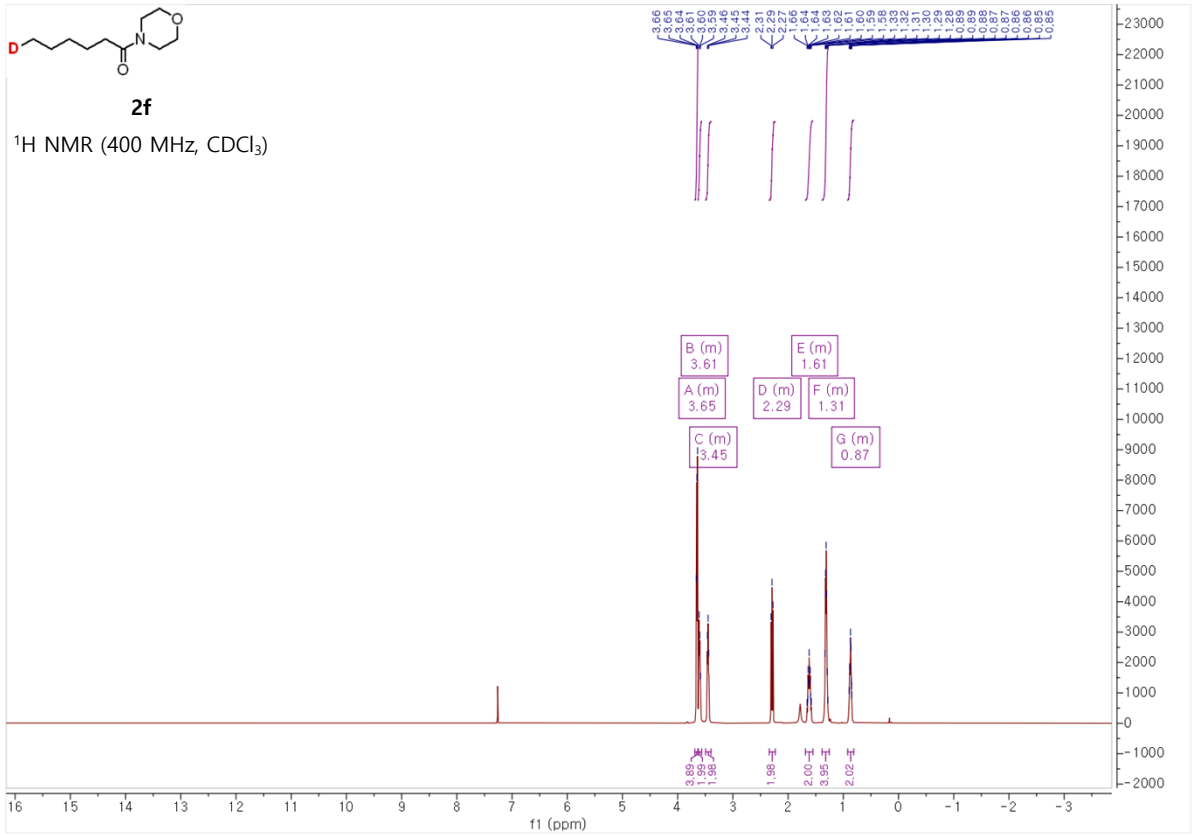
z


D
O
O
2d
1H NMR (400 MHz, CDCl3)
A (m) 7.92
B (m) 6.92
C (t) 4.03
D (s) 2.55
E (m) 1.79
F (m) 1.49
G (m) 0.97
f1 (ppm)


LJI-C-030 Ketone D.2.fid
196.79
163.15
130.58
130.15
114.15
67.97
31.12
26.32
19.10
13.70
13.51
13.32
D
O
O
2d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

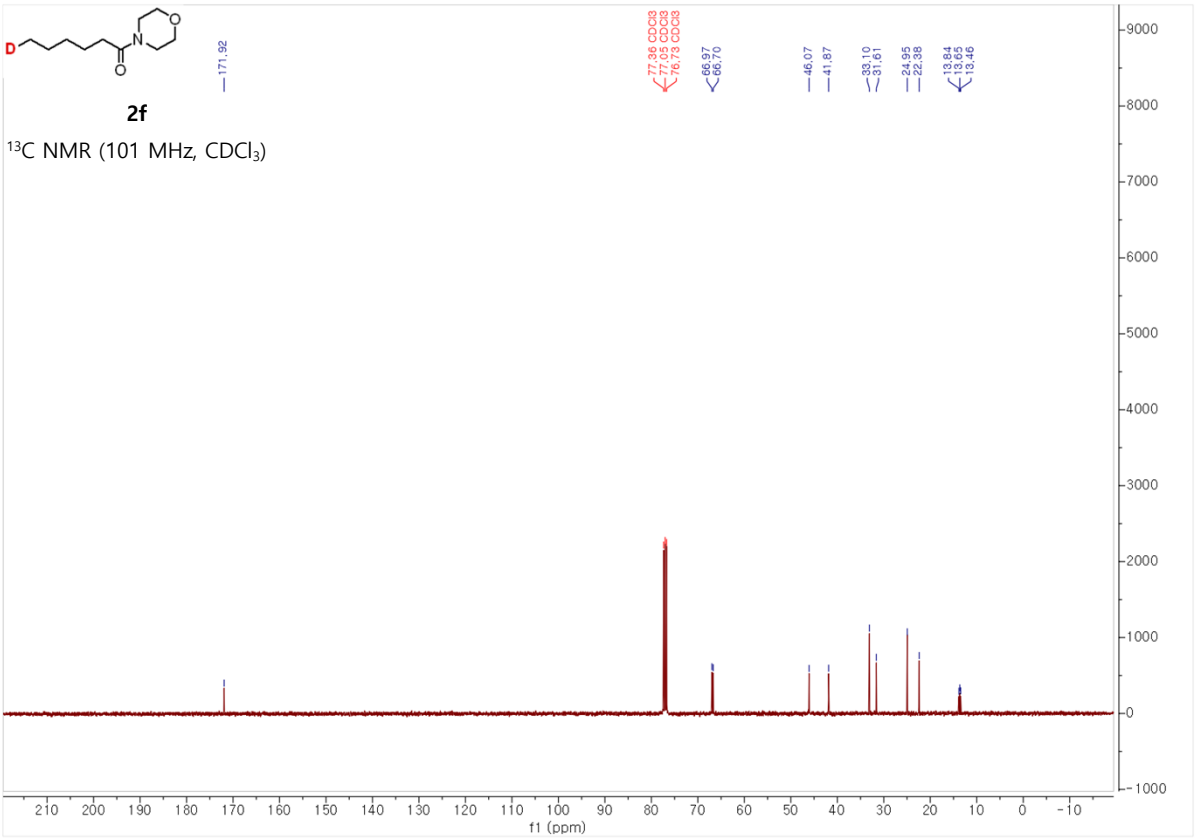

LJI-E
Ph
D
2e
1H NMR (400 MHz, CDCl3)
H (m) 6.90
F (m) 7.33
E (m) 7.46
G (m) 7.23
A (t) 3.94
D (m) 1.45
B (m) 1.72
C (m) 0.90
f1 (ppm)


LJI-B-818-01 13C (pure hx col).2.fid
Ph
D
2e
13C NMR (101 MHz, CDCl3)
δ 29.72 grease
158.75
140.92
133.56
128.70
128.11
126.72
120.59
114.79
77.34 CDCl3
77.00 CDCl3
76.70 CDCl3
67.80
31.95
29.72
19.20
13.77
13.58
13.39
f1 (ppm)



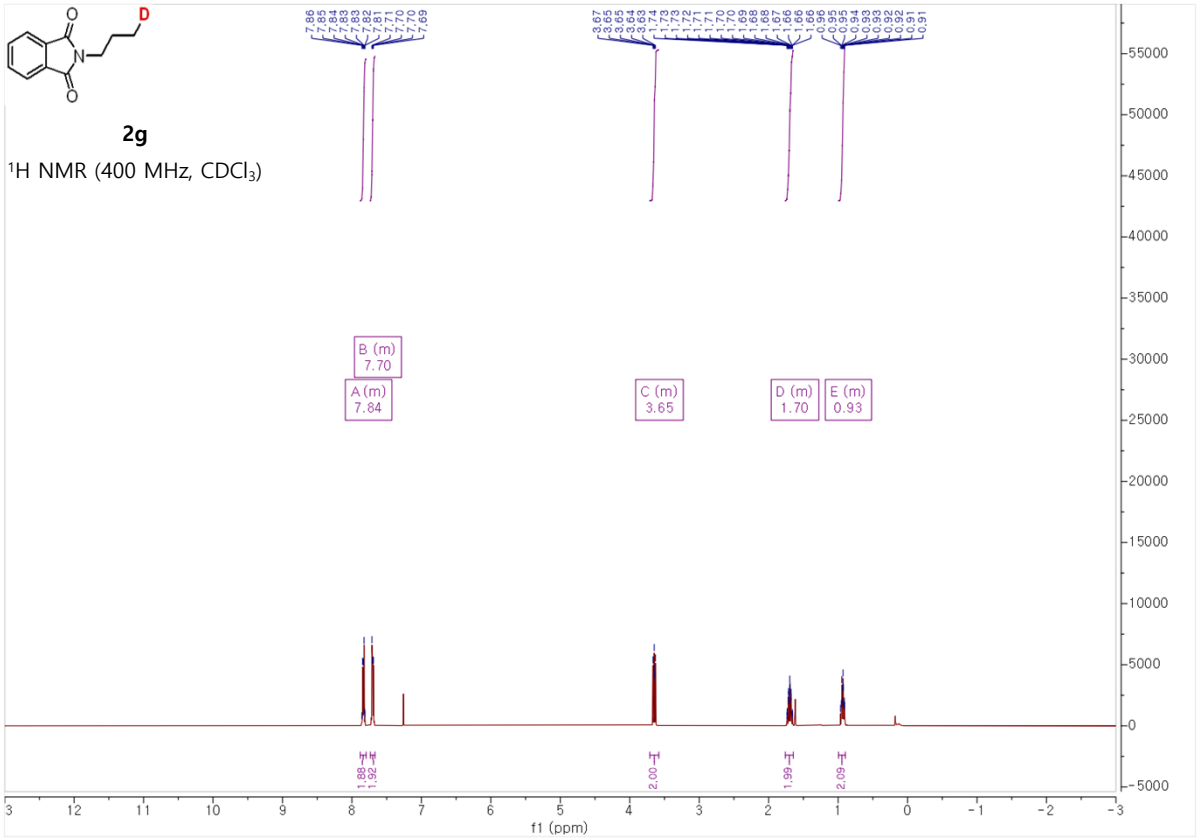
2f

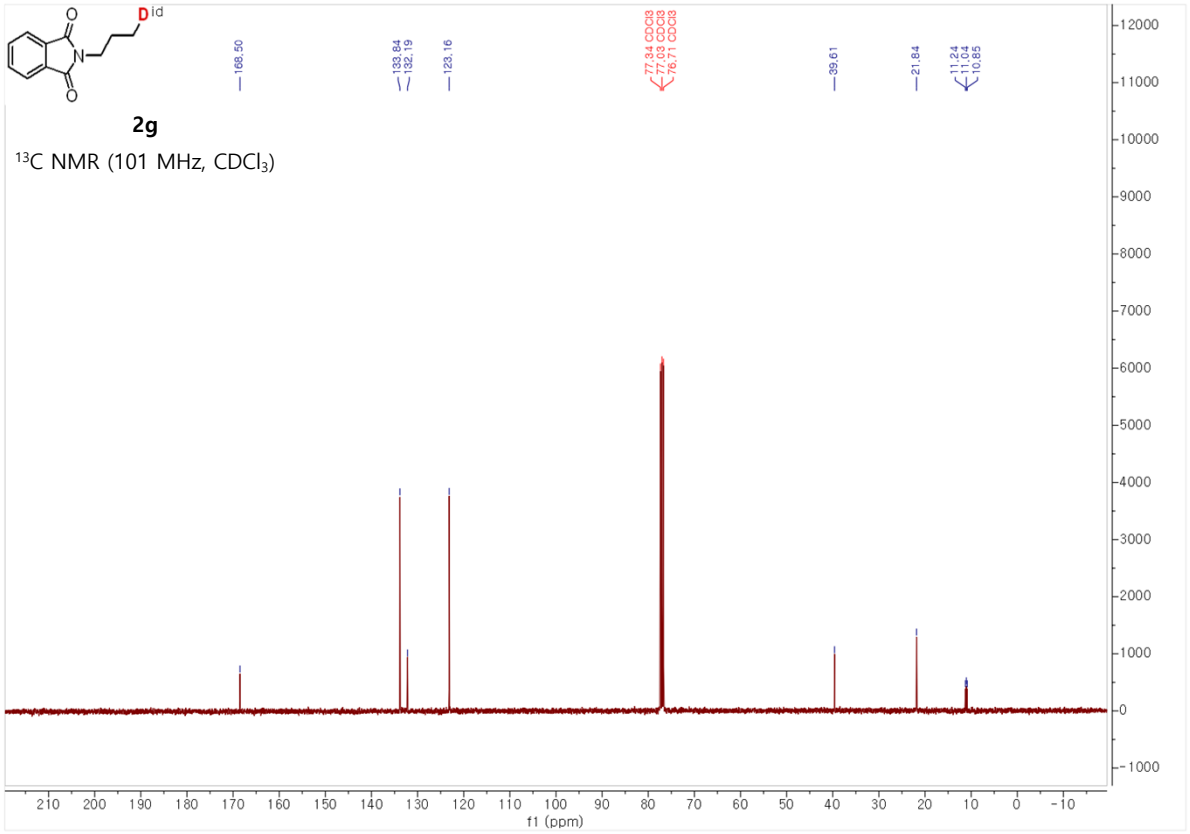
^{1}H NMR (400 MHz, $CDCl_3$)

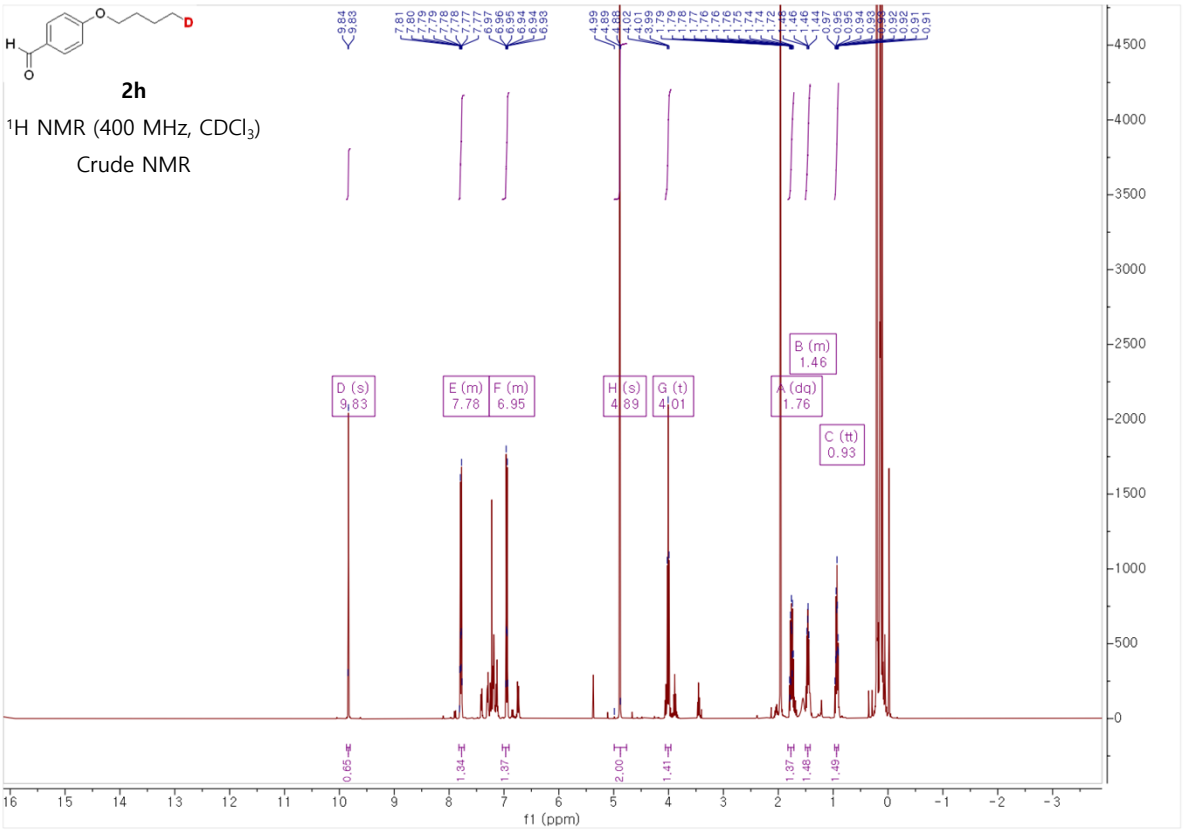


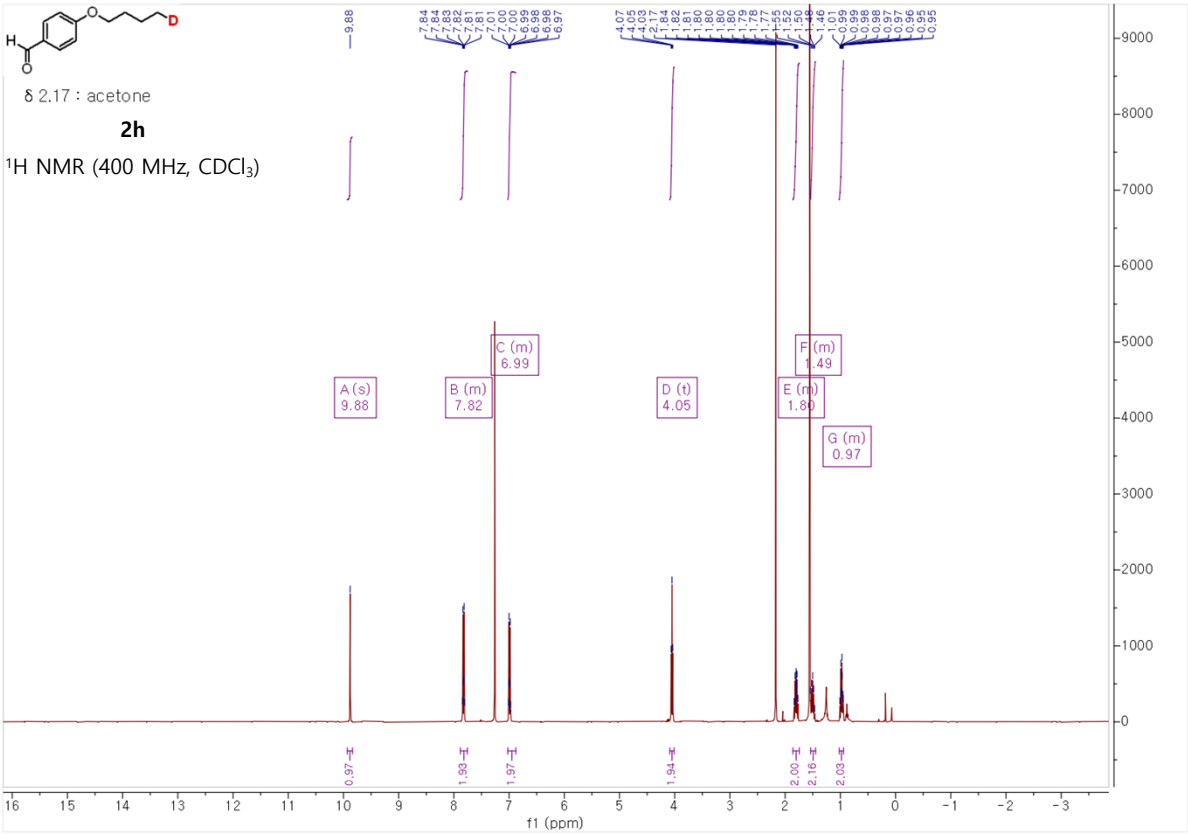
2f

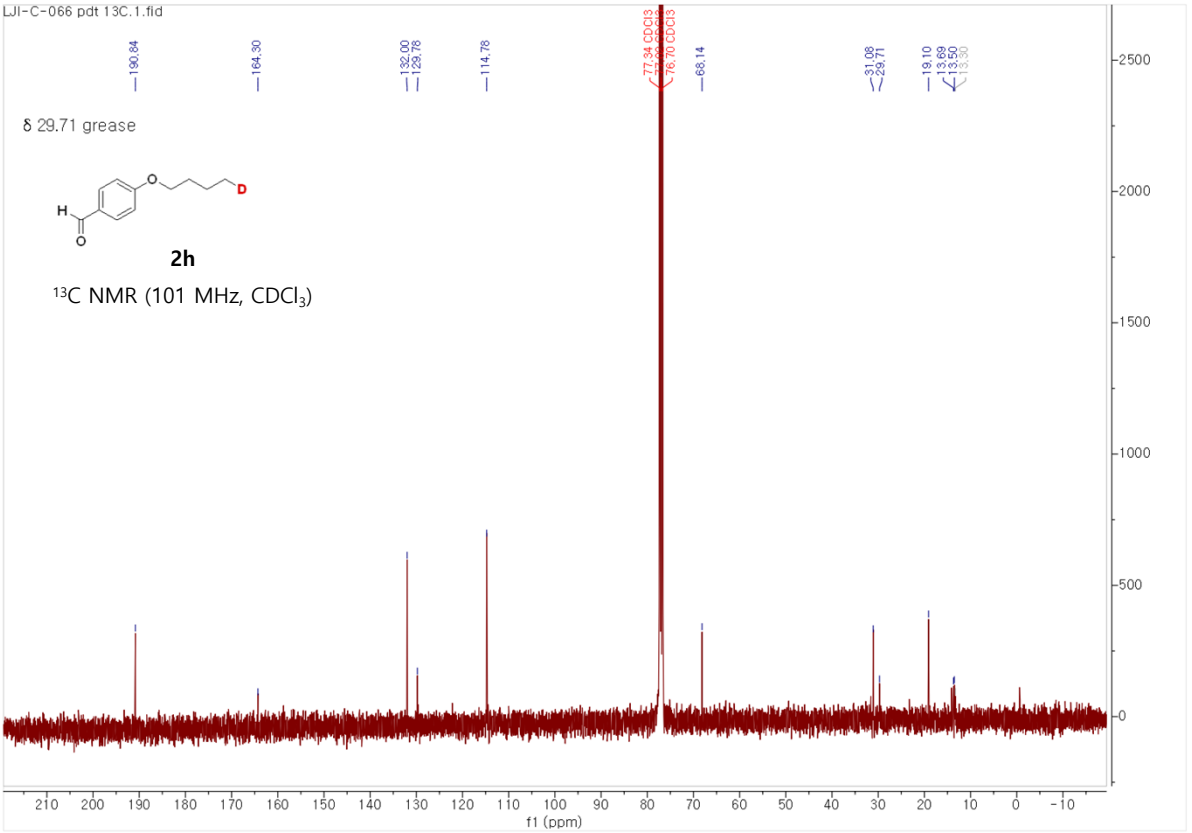
^{13}C NMR (101 MHz, $CDCl_3$)

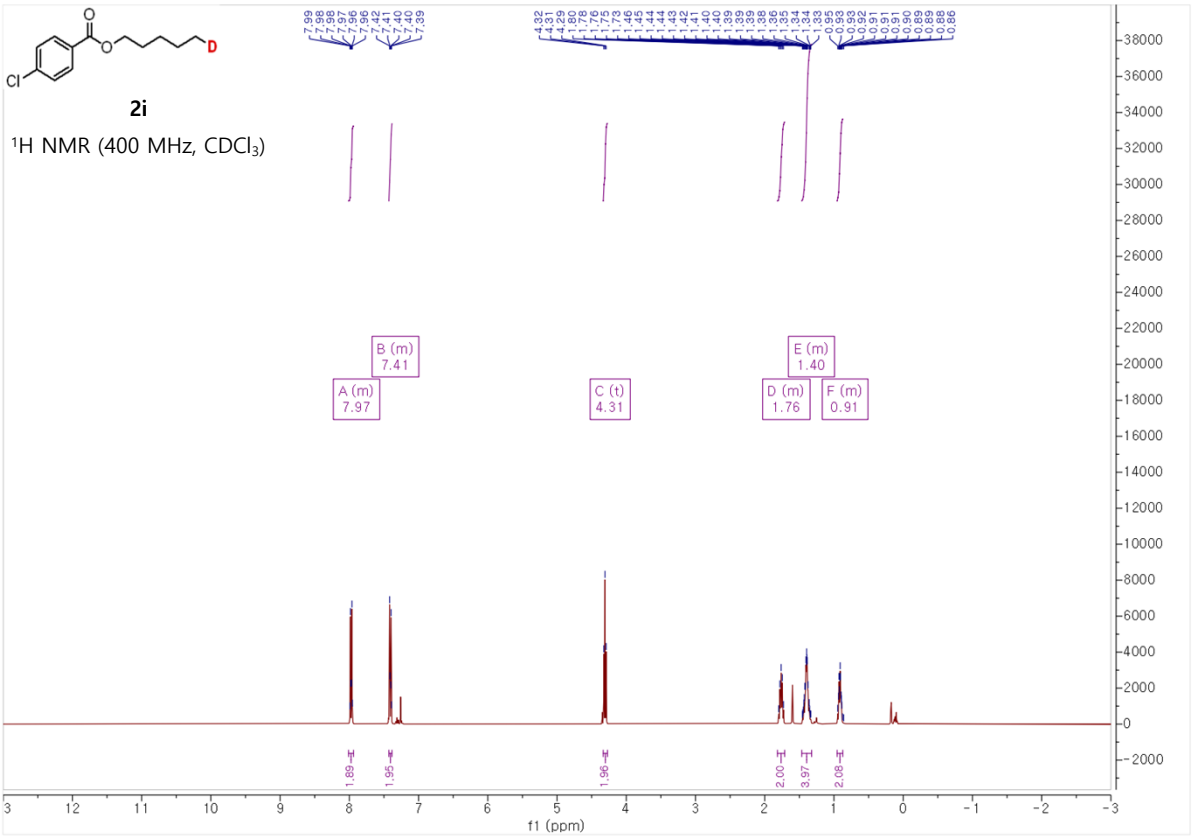

D
2g
1H NMR (400 MHz, CDCl3)
B (m) 7.70
A (m) 7.84
C (m) 3.65
D (m) 1.70
E (m) 0.93
f1 (ppm)

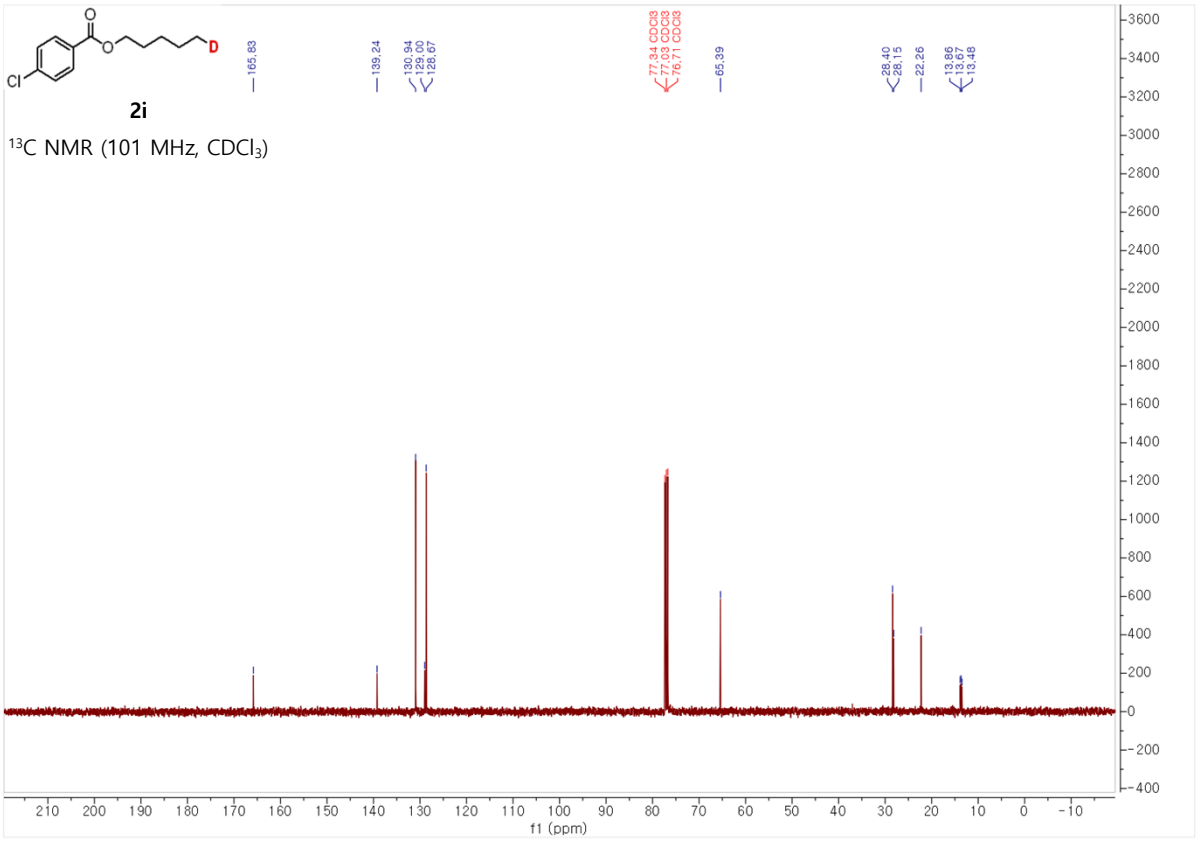

D
2g
13C NMR (101 MHz, CDCl3)
f1 (ppm)


2h
^{1}H NMR (400 MHz, $CDCl_3$)
Crude NMR
D (s) 9.83
E (m) 7.78
F (m) 6.95
H (s) 4.89
G (t) 4.01
A (dq) 1.76
B (m) 1.46
C (tt) 0.93
f1 (ppm)


δ 2.17 : acetone
2h
^{1}H NMR (400 MHz, $CDCl_3$)
A (s) 9.88
B (m) 7.82
C (m) 6.99
D (t) 4.05
E (m) 1.80
F (m) 1.49
G (m) 0.97
f1 (ppm)

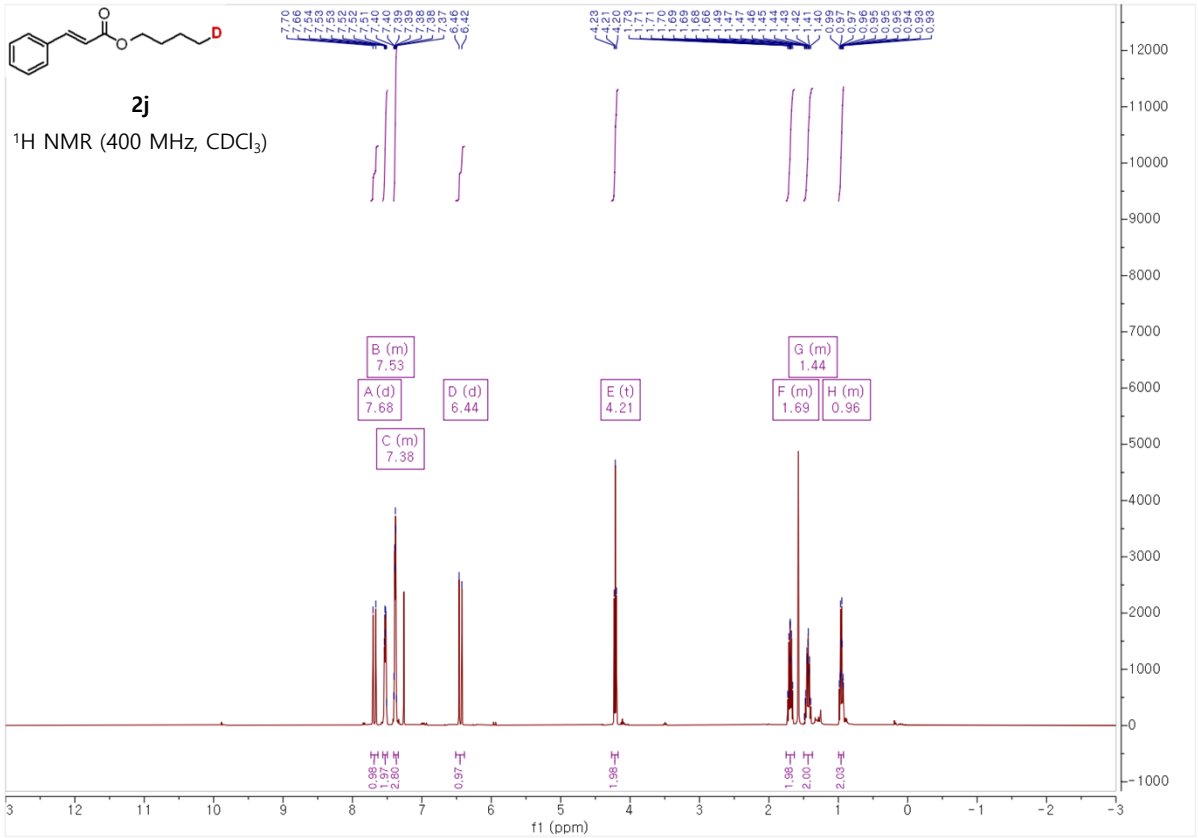

LJI-C-066 pdt 13C.1.fid
δ 29.71 grease
2h
13C NMR (101 MHz, CDCl3)
f1 (ppm)


2i
1H NMR (400 MHz, CDCl3)
A (m) 7.97
B (m) 7.41
C (t) 4.31
D (m) 1.76
E (m) 1.40
F (m) 0.91
f1 (ppm)



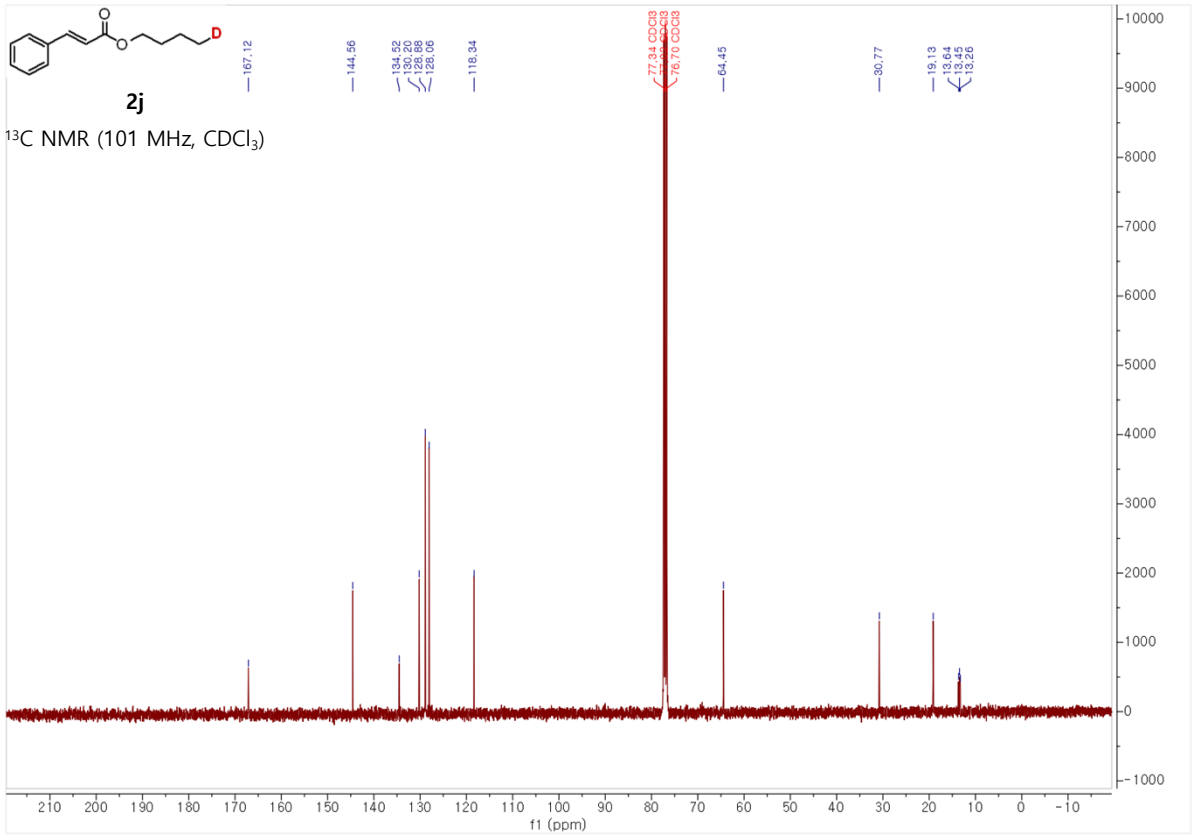
2i

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



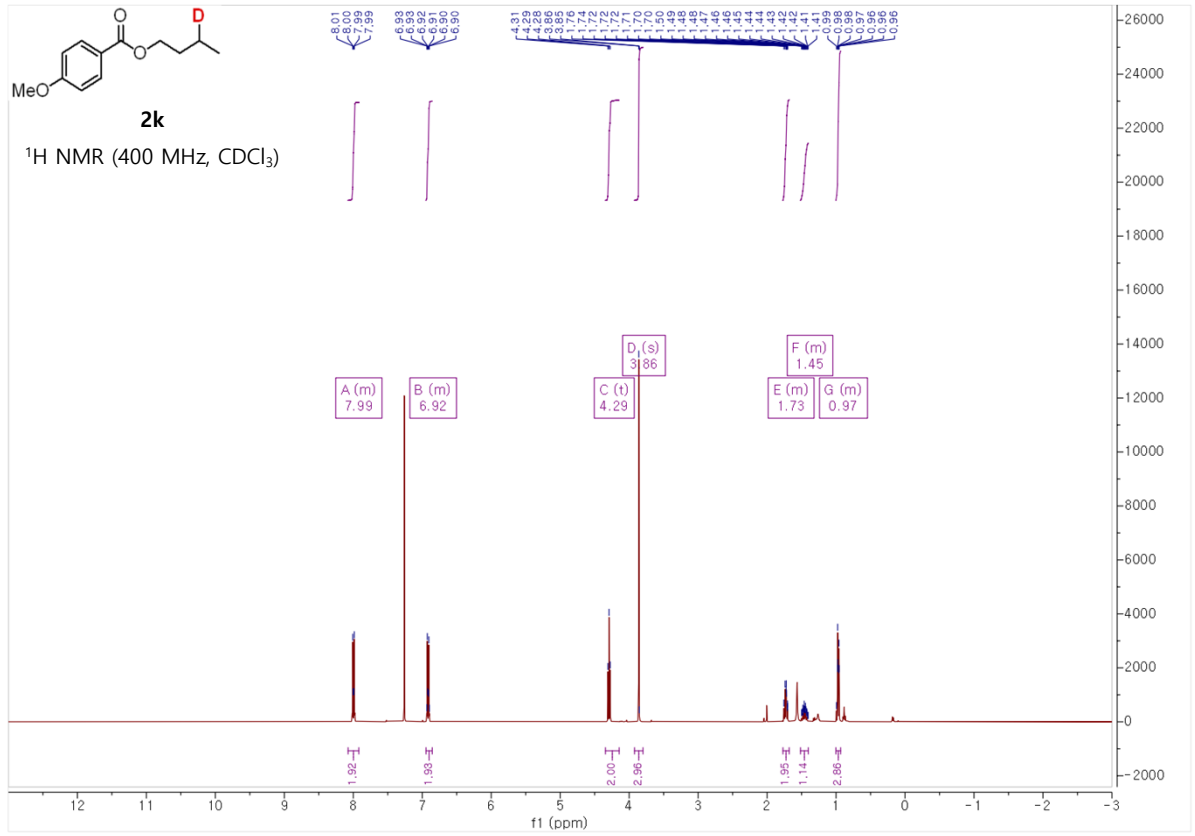
2j

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



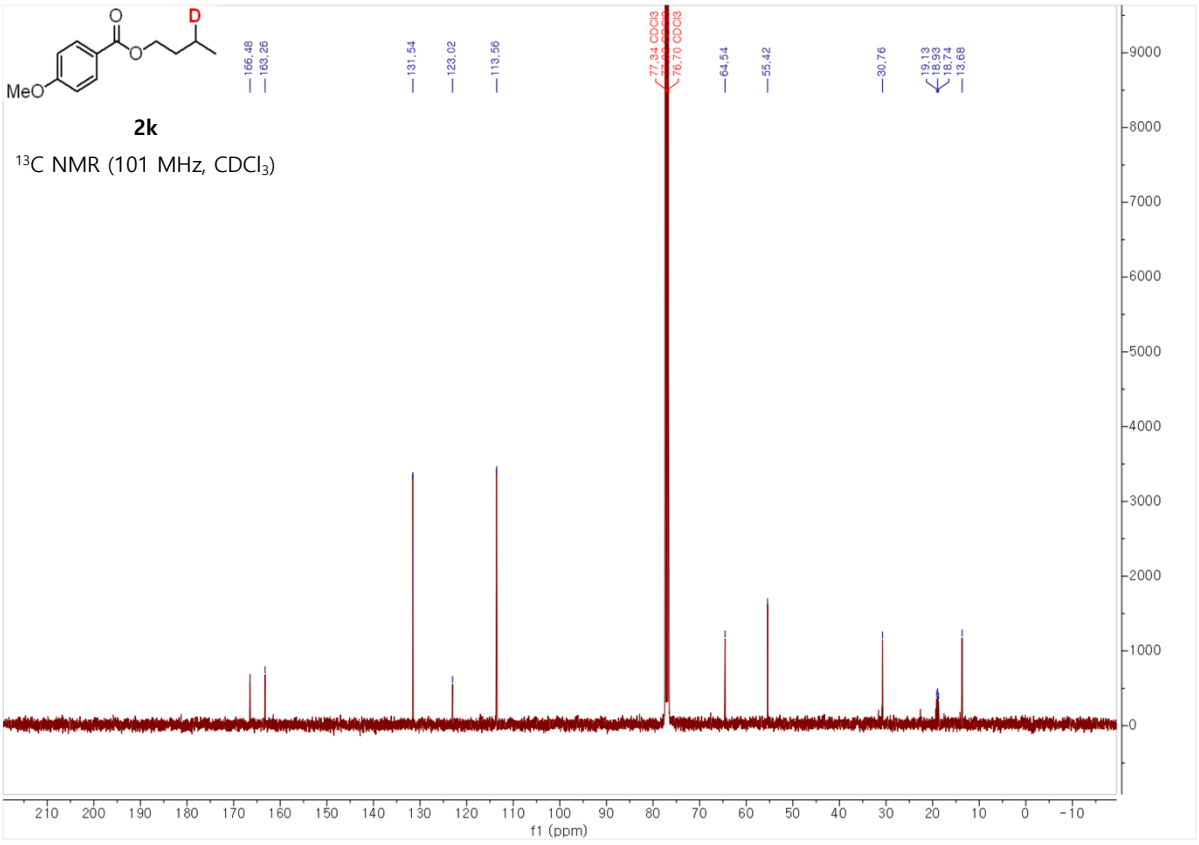
2j

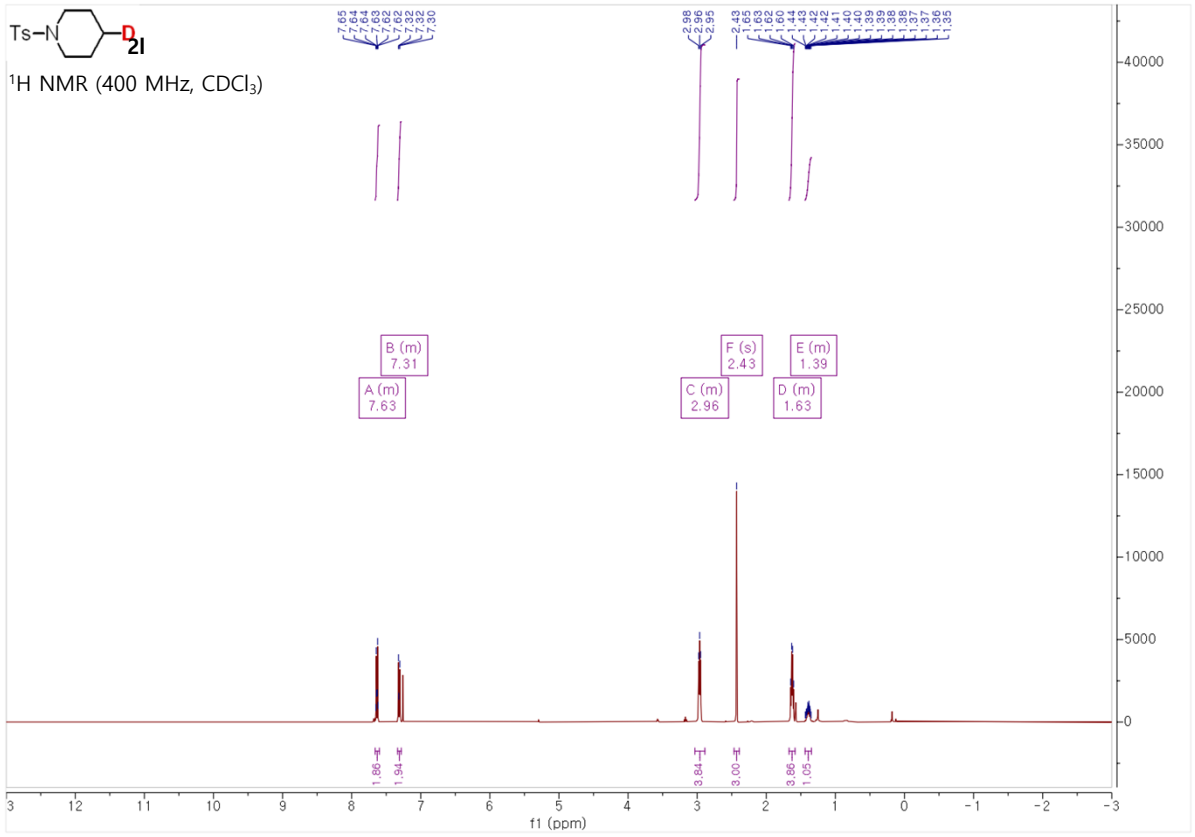
^{13}C NMR (101 MHz, $CDCl_3$)

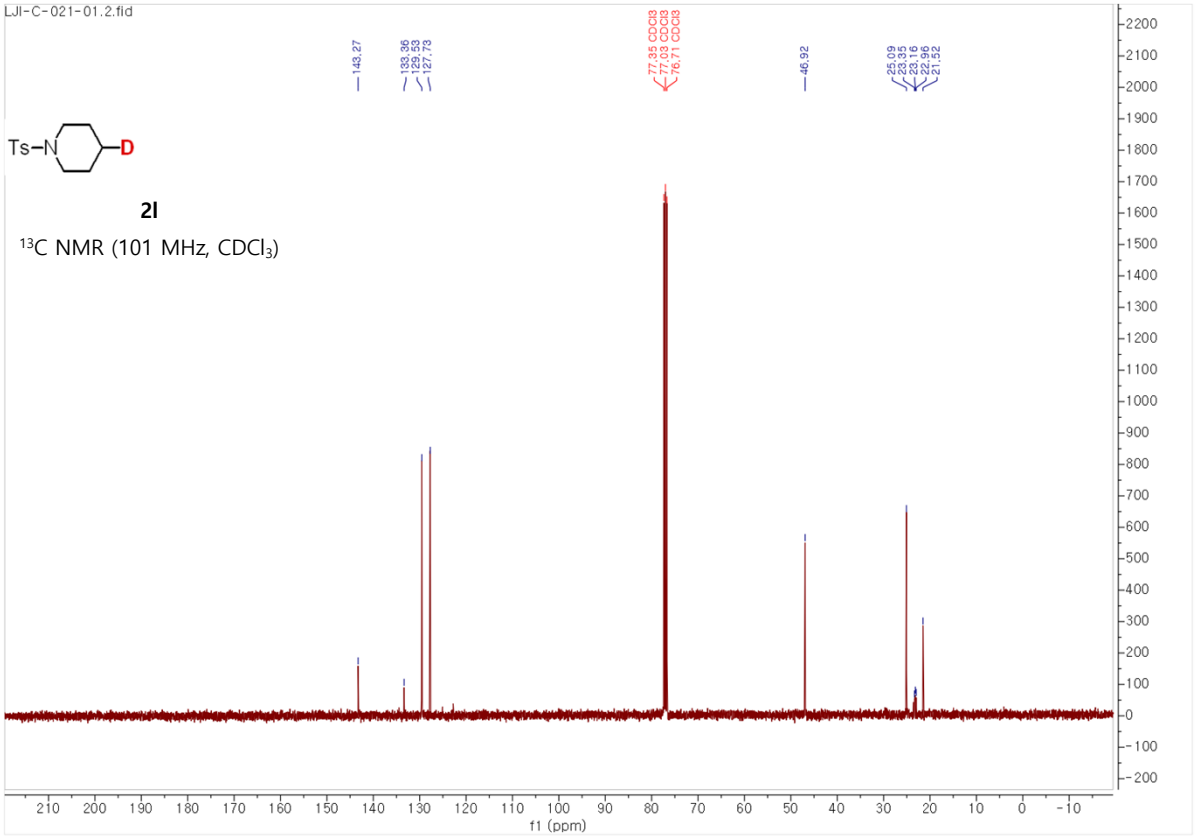


2k

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

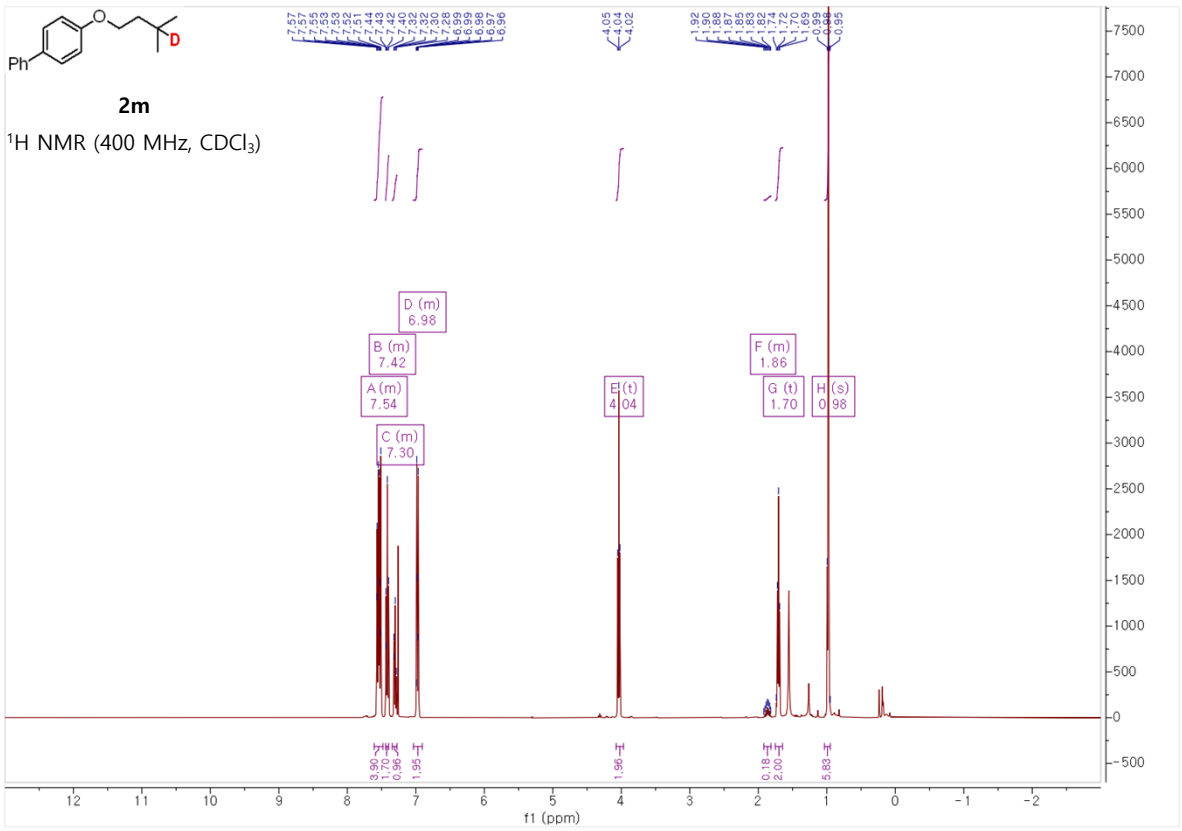

MeO
D
2k
13C NMR (101 MHz, CDCl3)
166.48
163.26
131.54
123.02
113.56
77.34 CDCl3
76.70 CDCl3
64.54
55.42
30.76
19.13
18.93
18.74
13.68
f1 (ppm)


Ts–N
D
2l
1H NMR (400 MHz, CDCl3)
B (m) 7.31
A (m) 7.63
F (s) 2.43
E (m) 1.39
C (m) 2.96
D (m) 1.63
1.86
1.94
3.84
3.00
3.86
1.05
f1 (ppm)



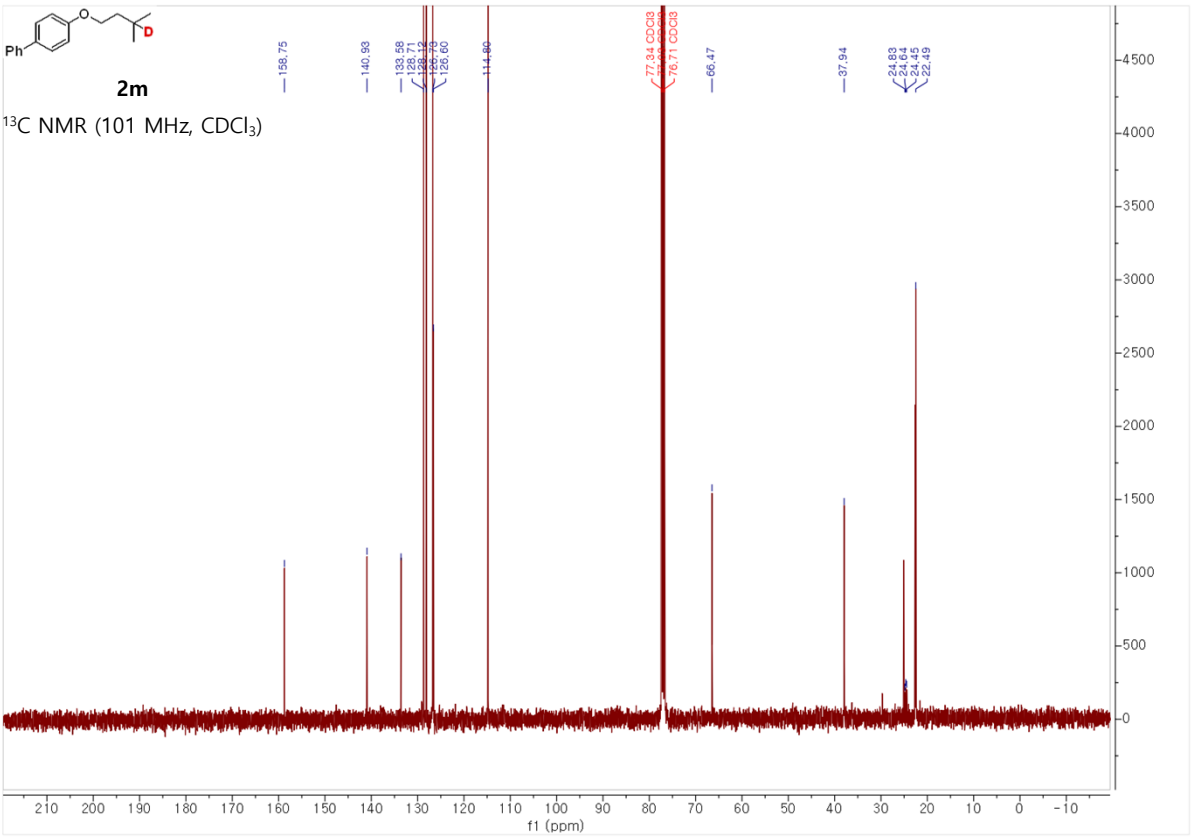
2l

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



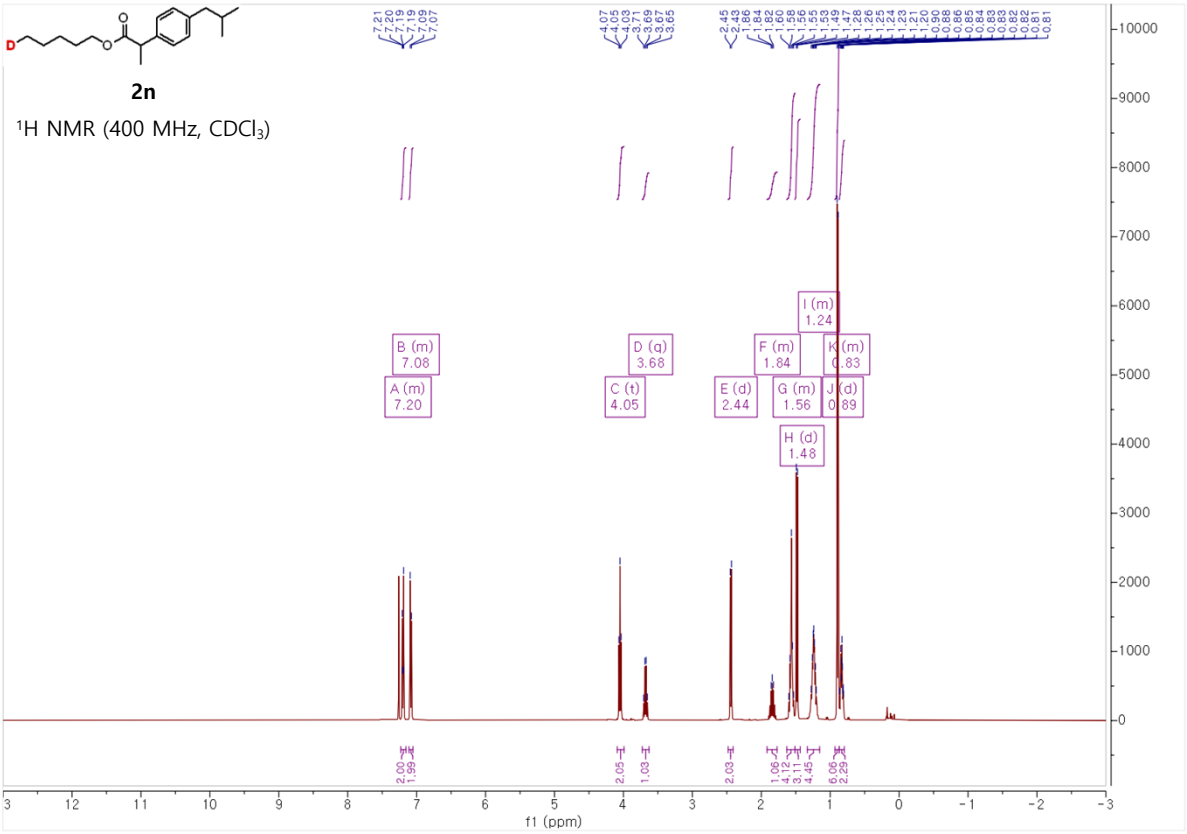
2m

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



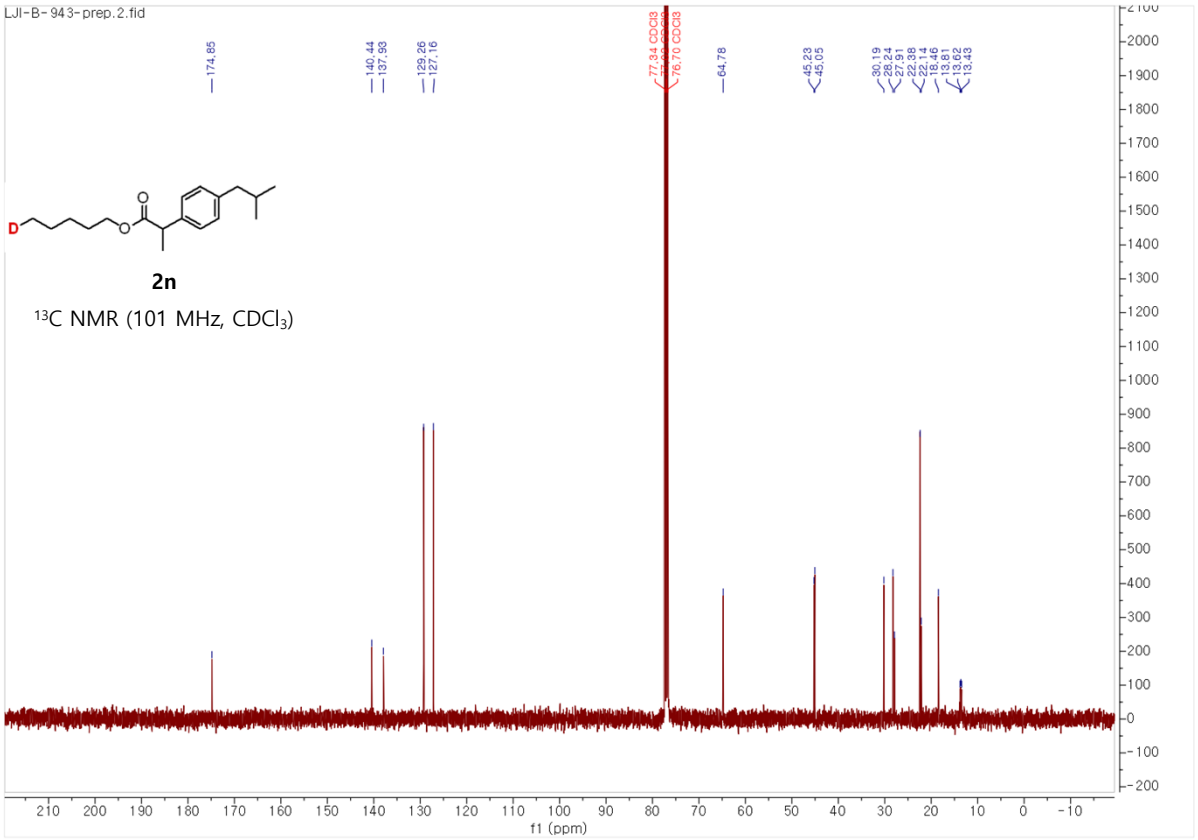
2m

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



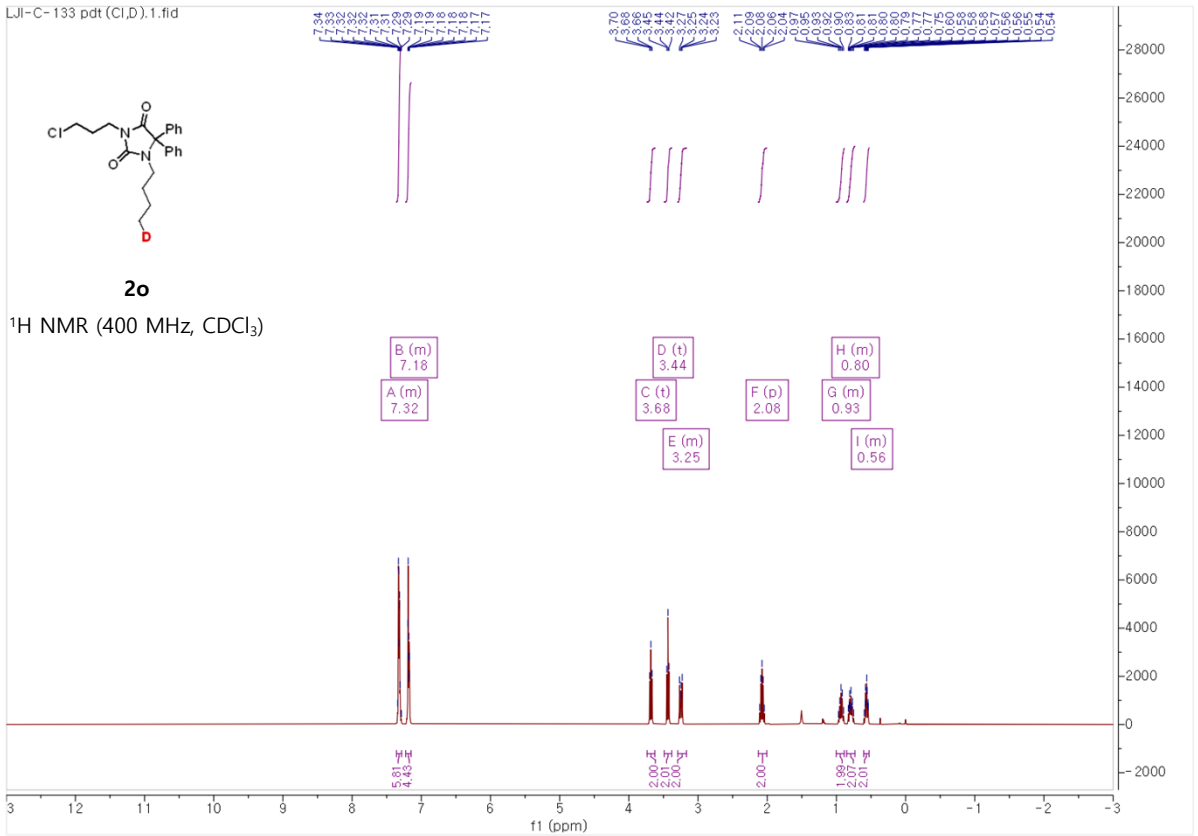
2n

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



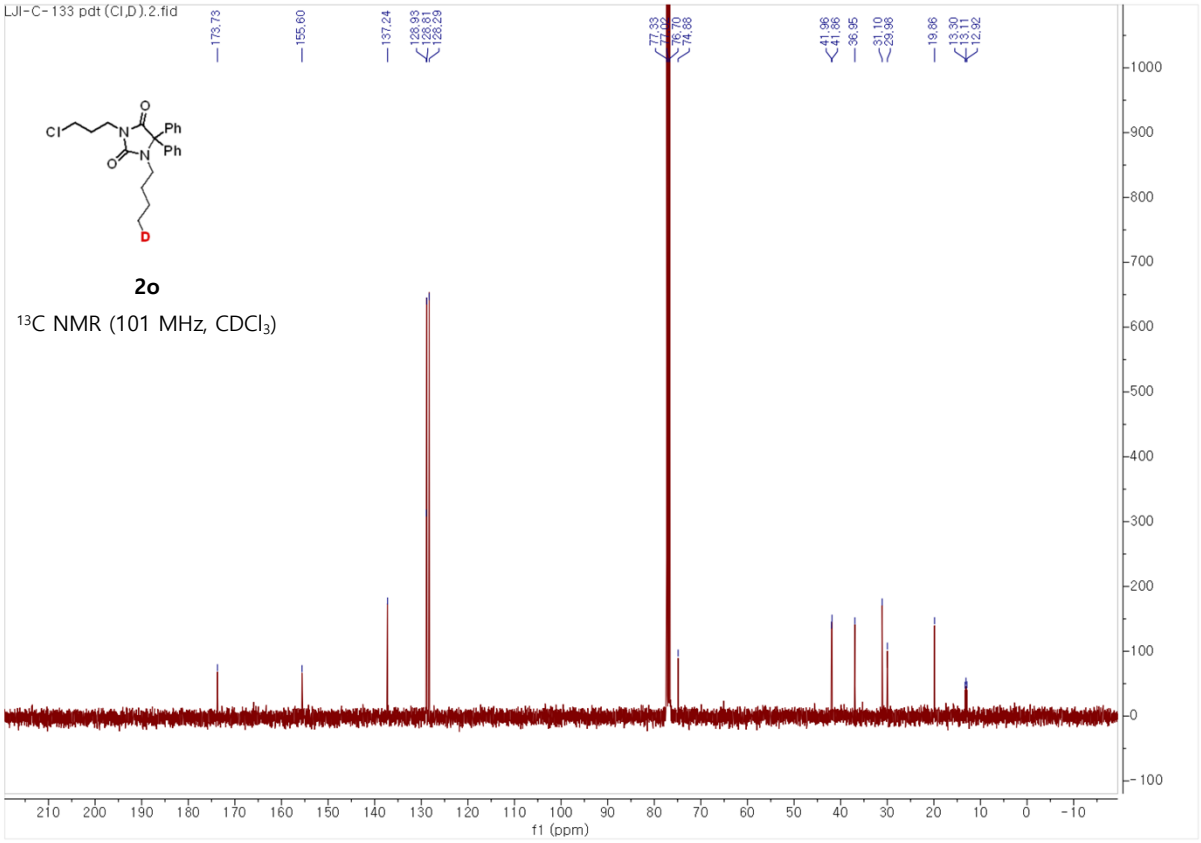
2n

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



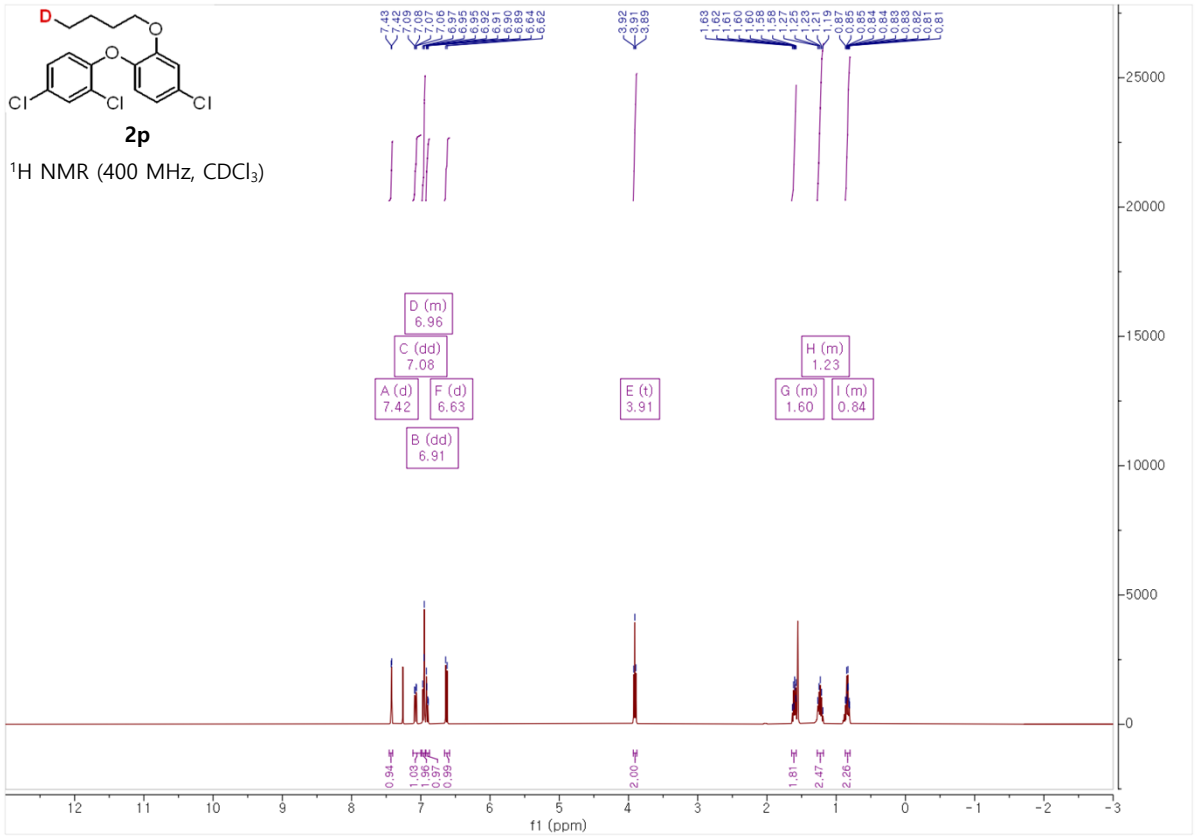
2o

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



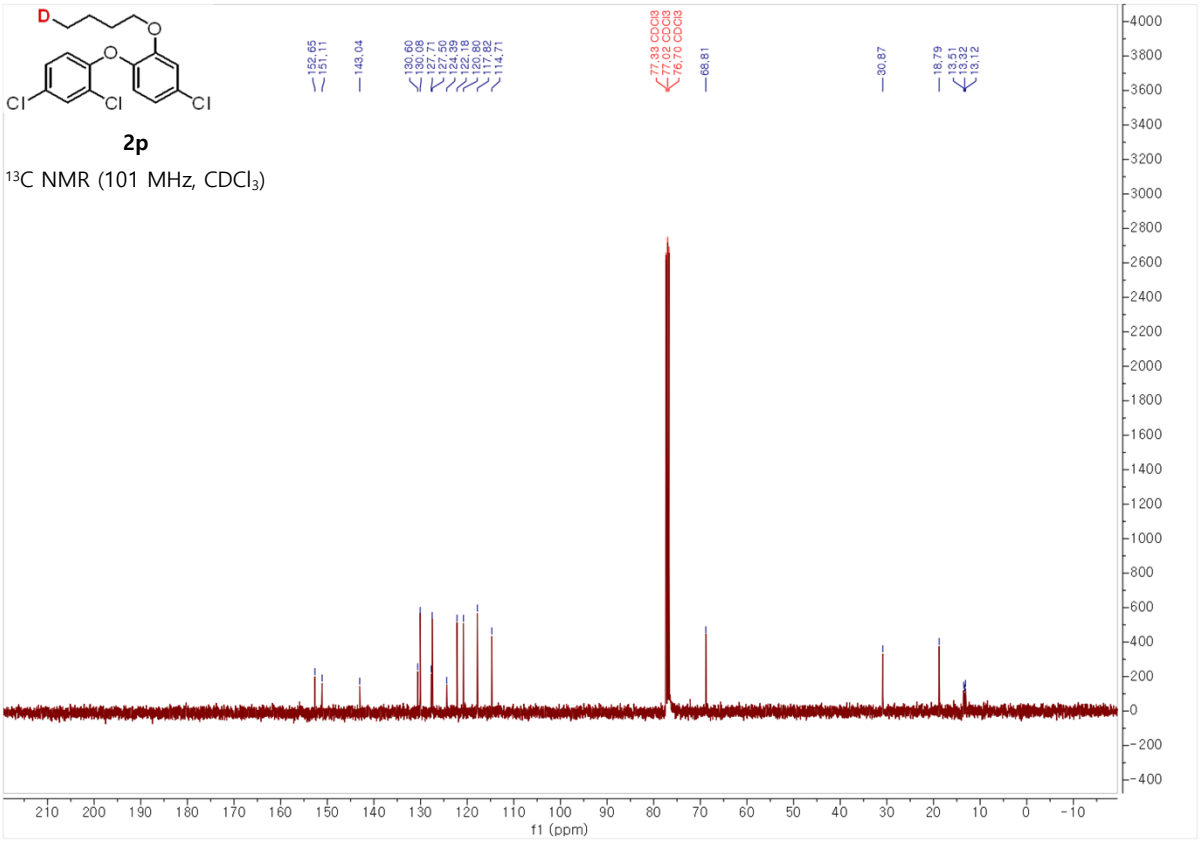
2o

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



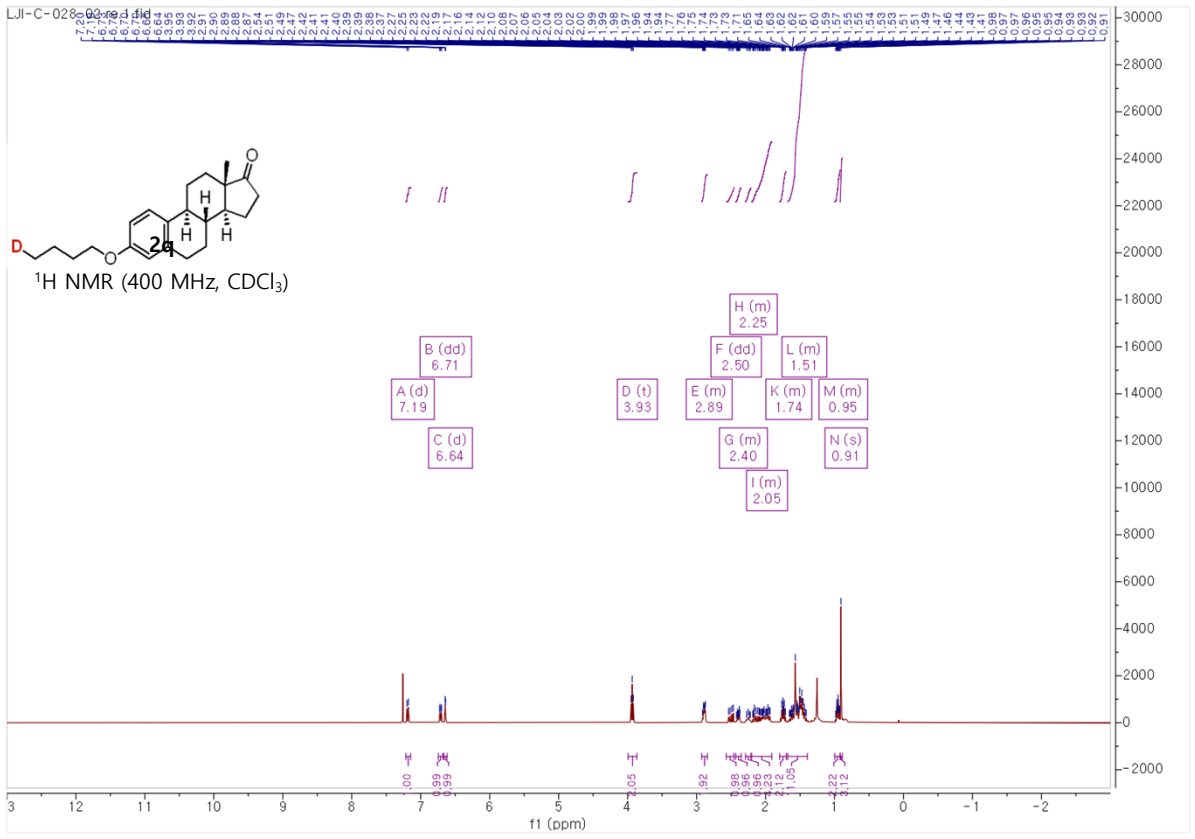
2p

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

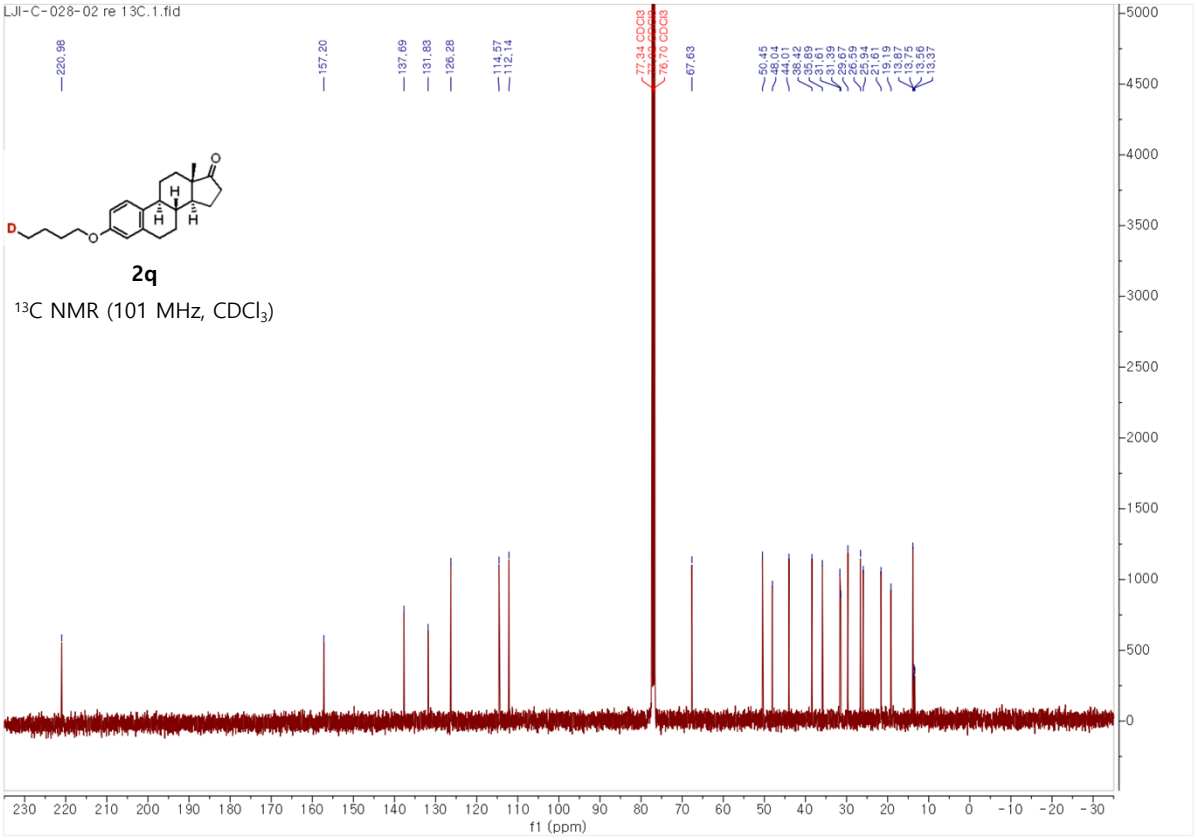


2p

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

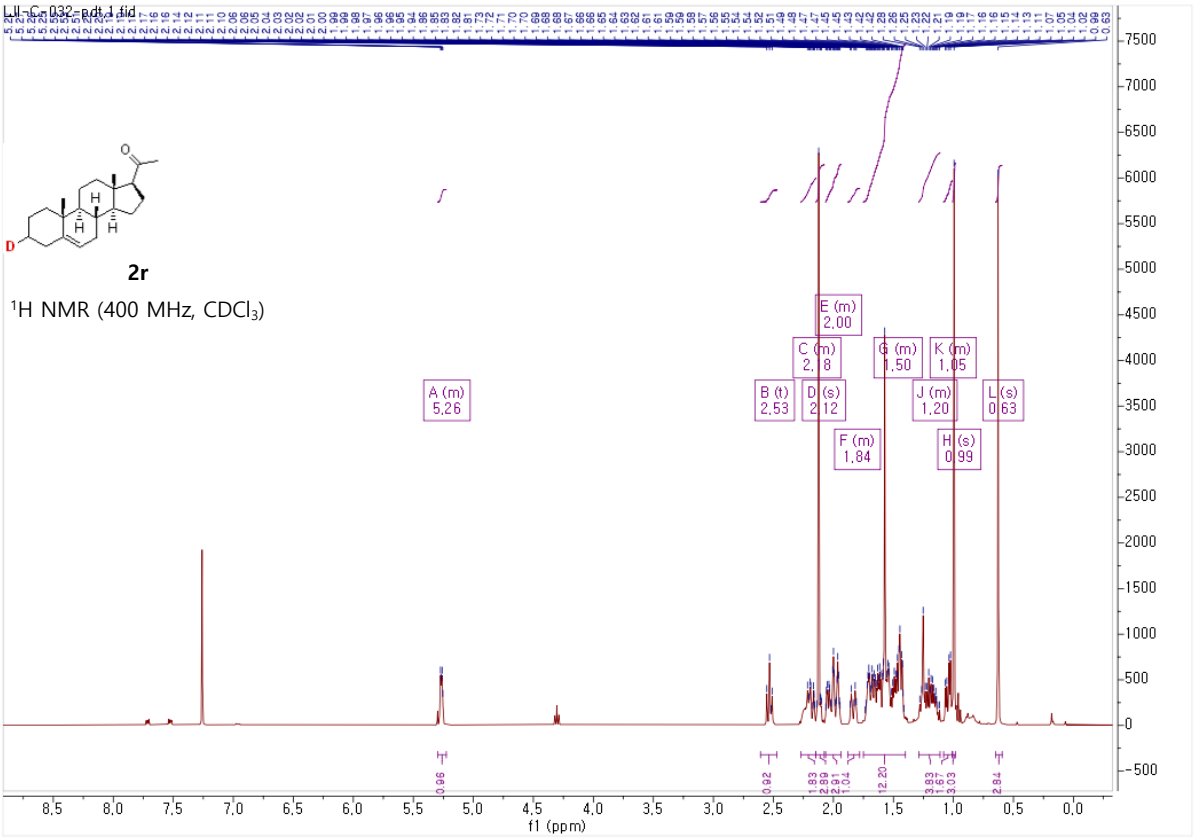


^{1}H NMR (400 MHz, $CDCl_3$)



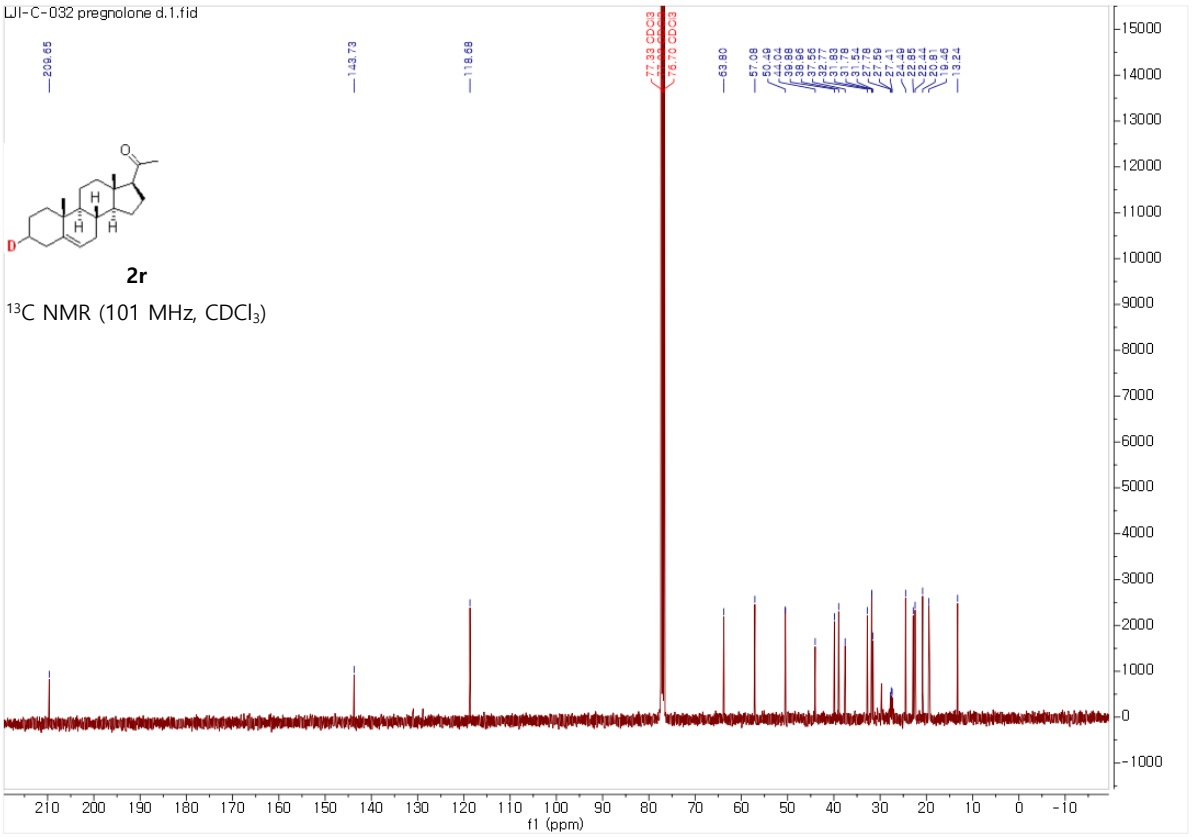
2q

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



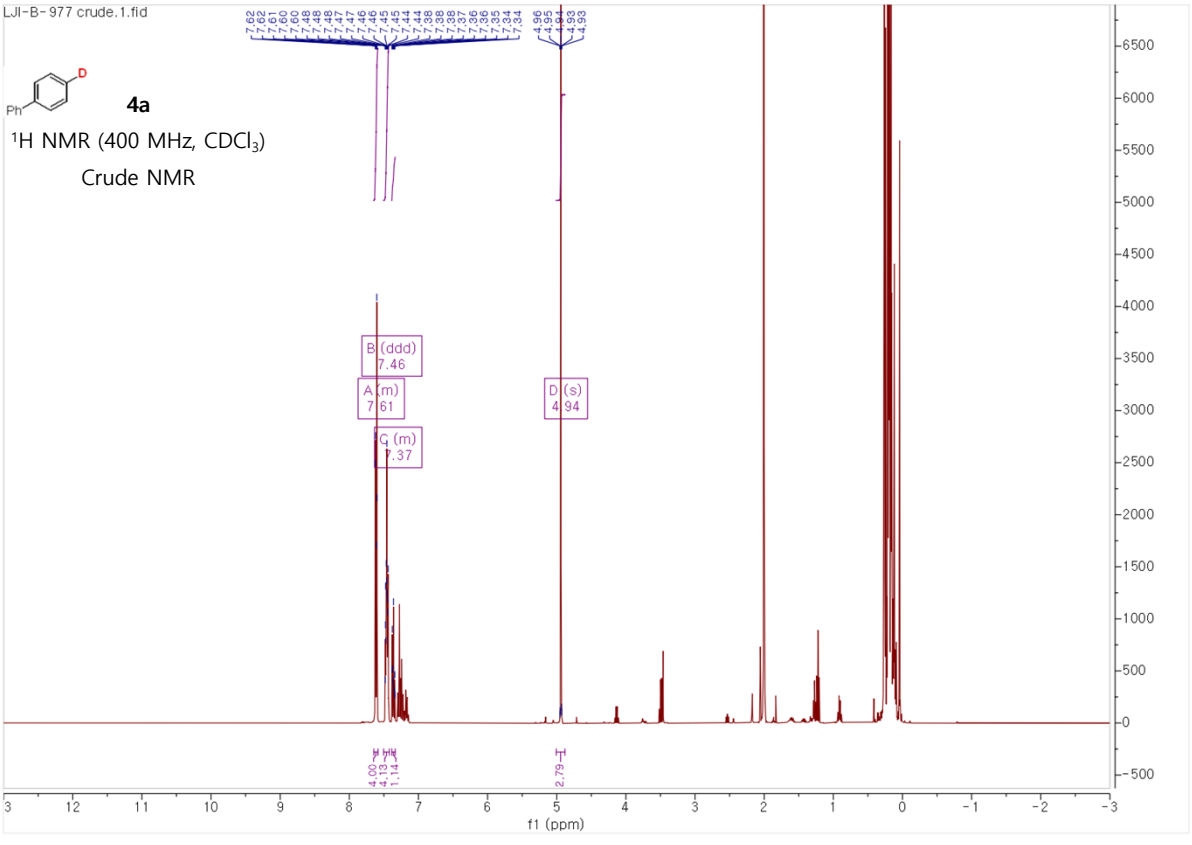
2r

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



2r

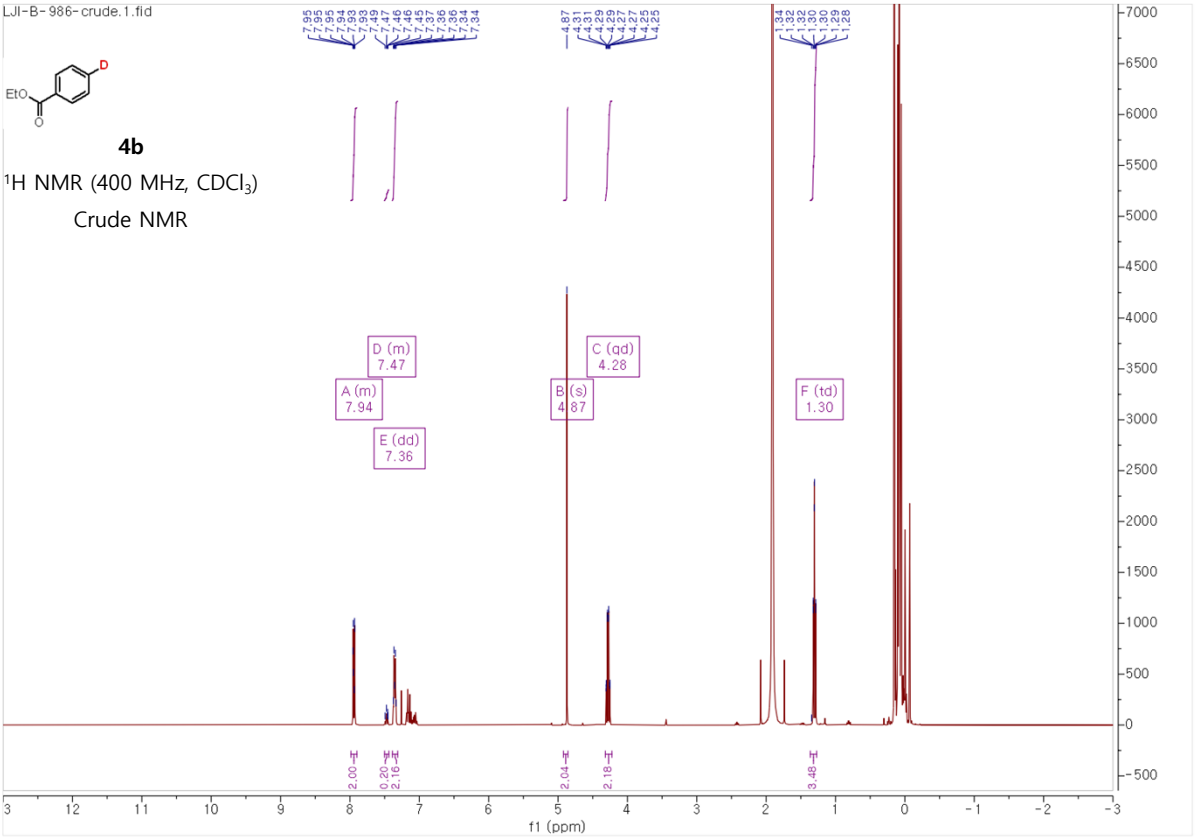
^{13}C NMR (101 MHz, $CDCl_3$)



4a

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

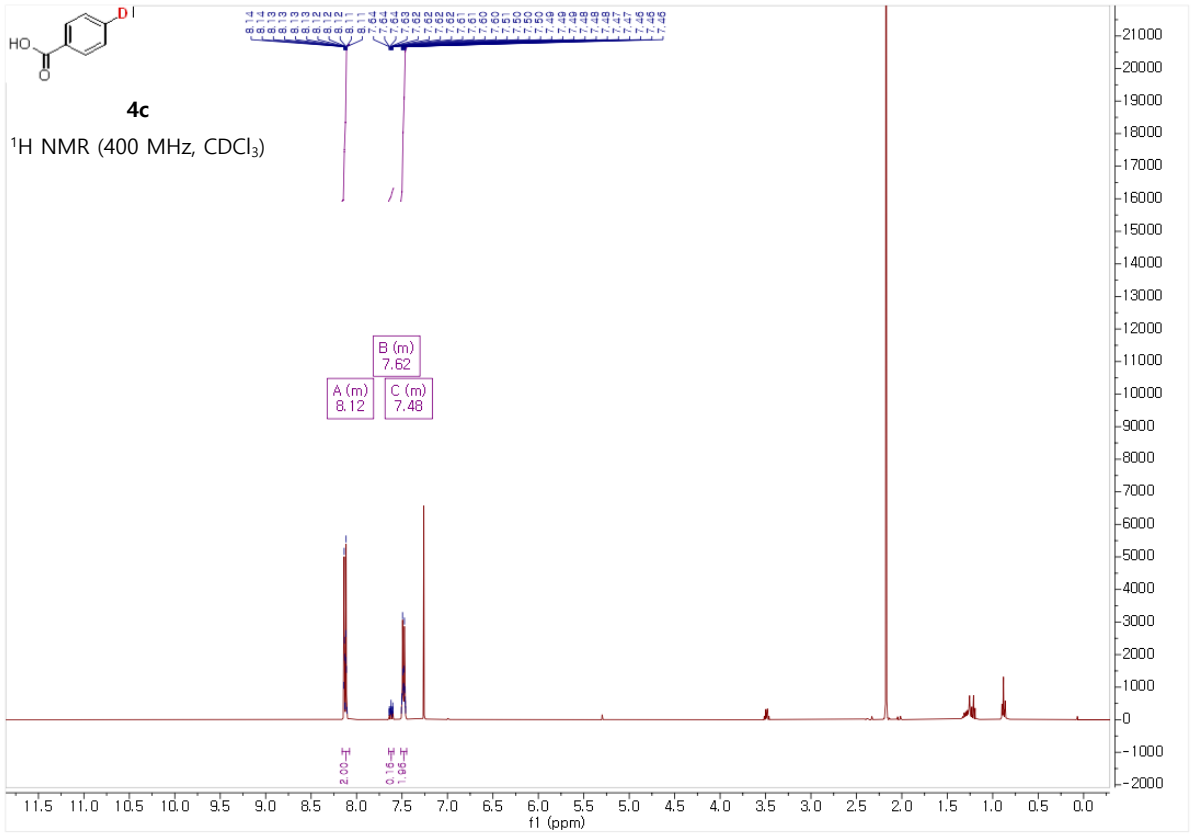
Crude NMR



4b

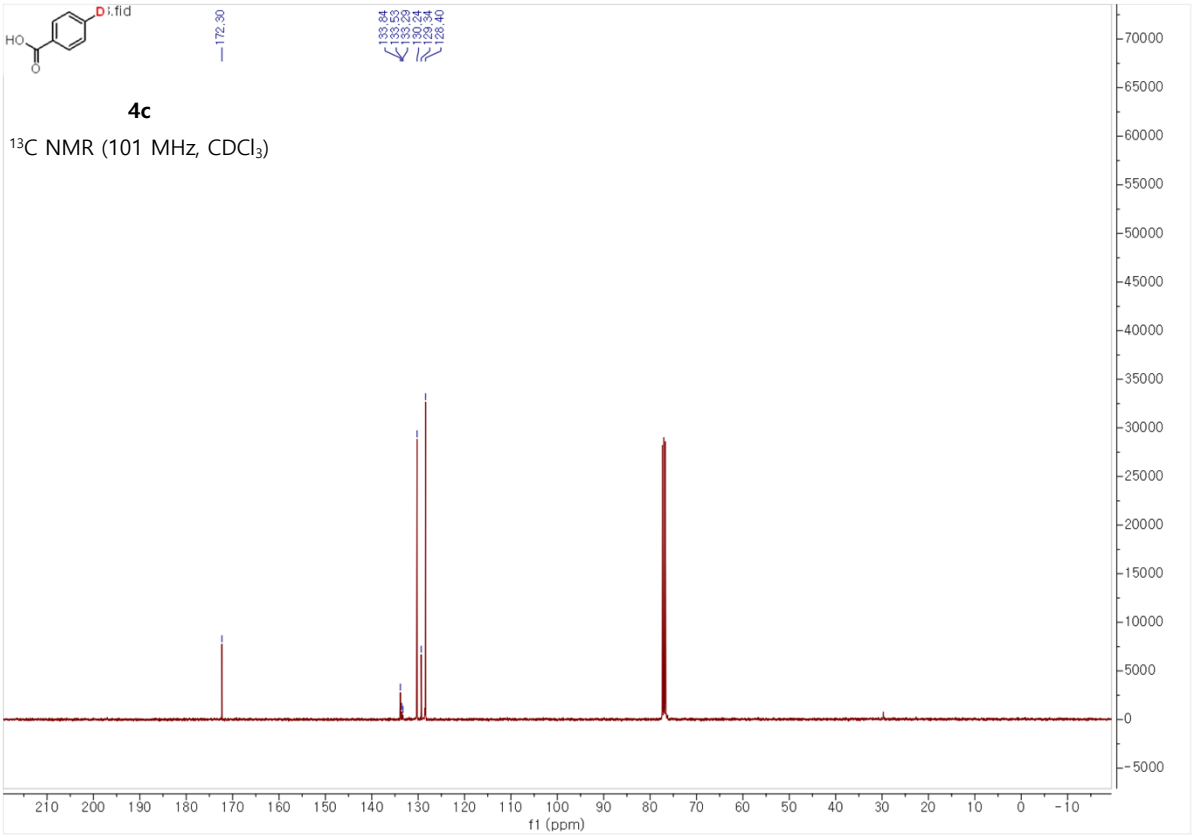
^{1}H NMR (400 MHz, $CDCl_3$)

Crude NMR



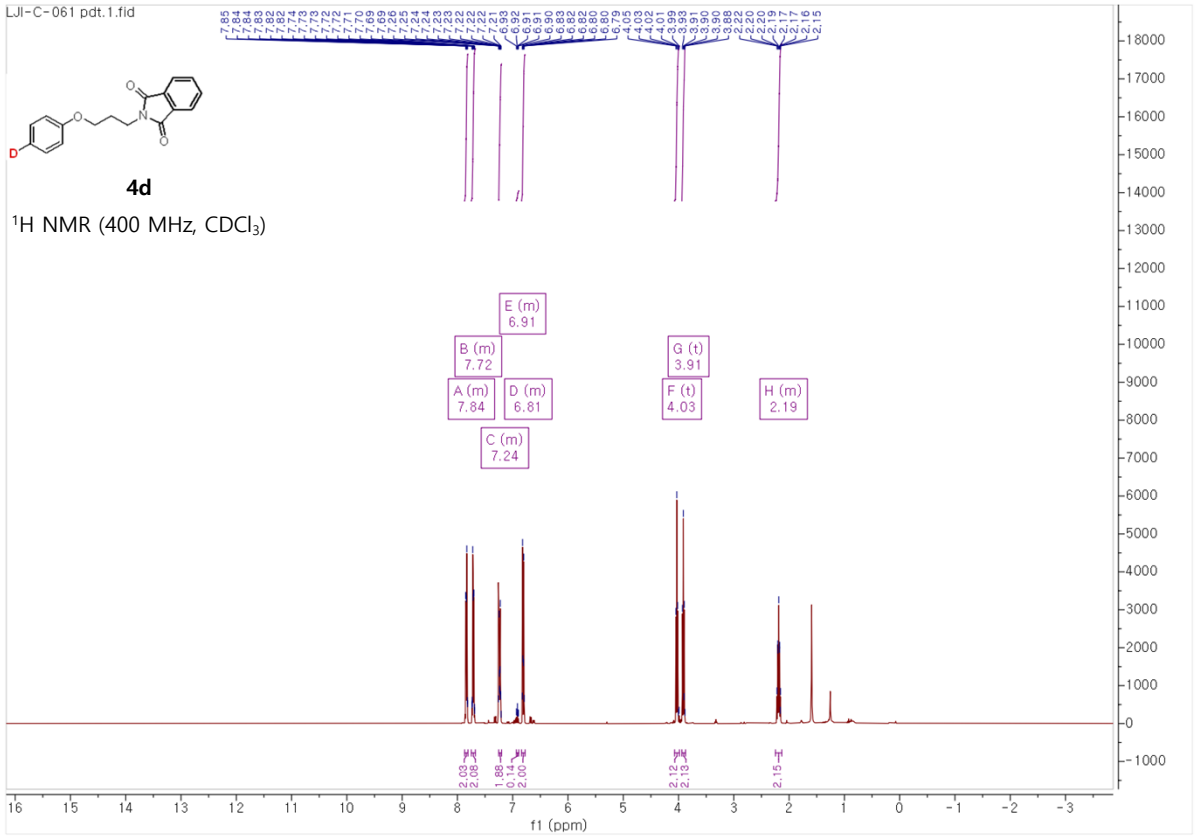
4c

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



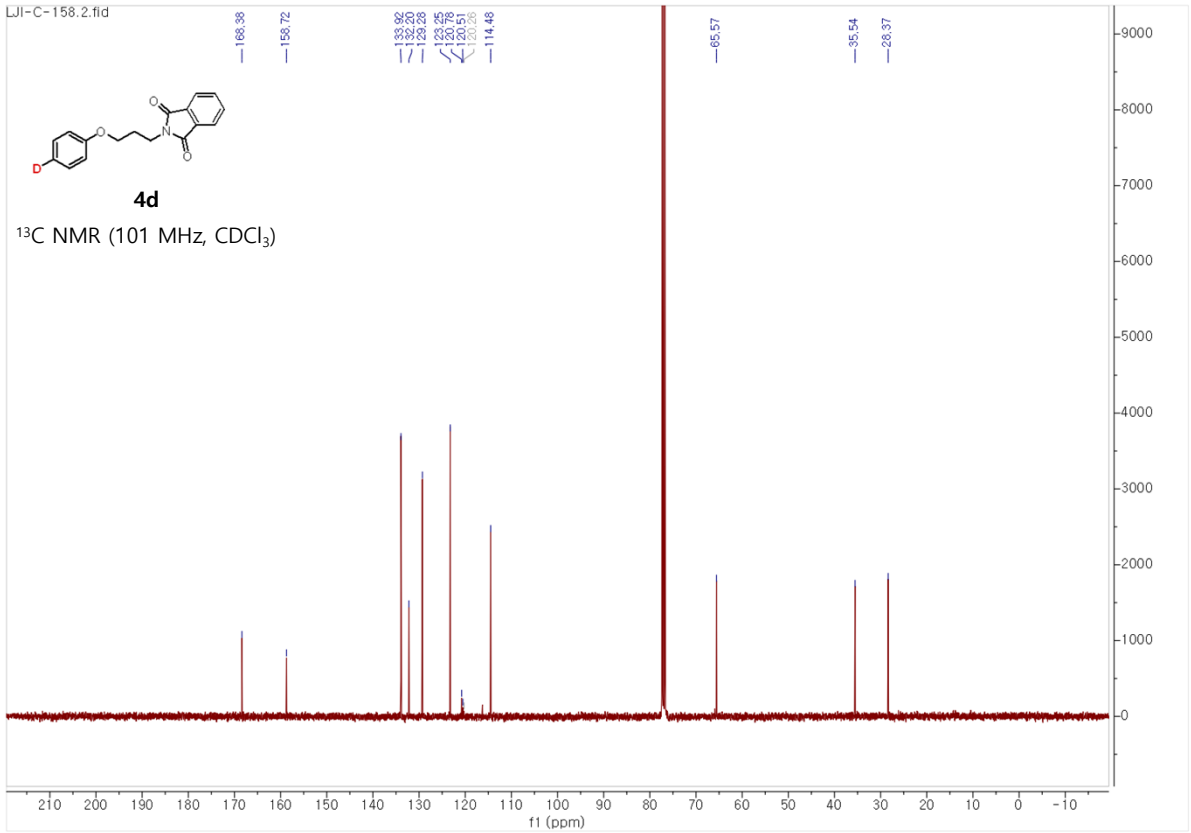
4c

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



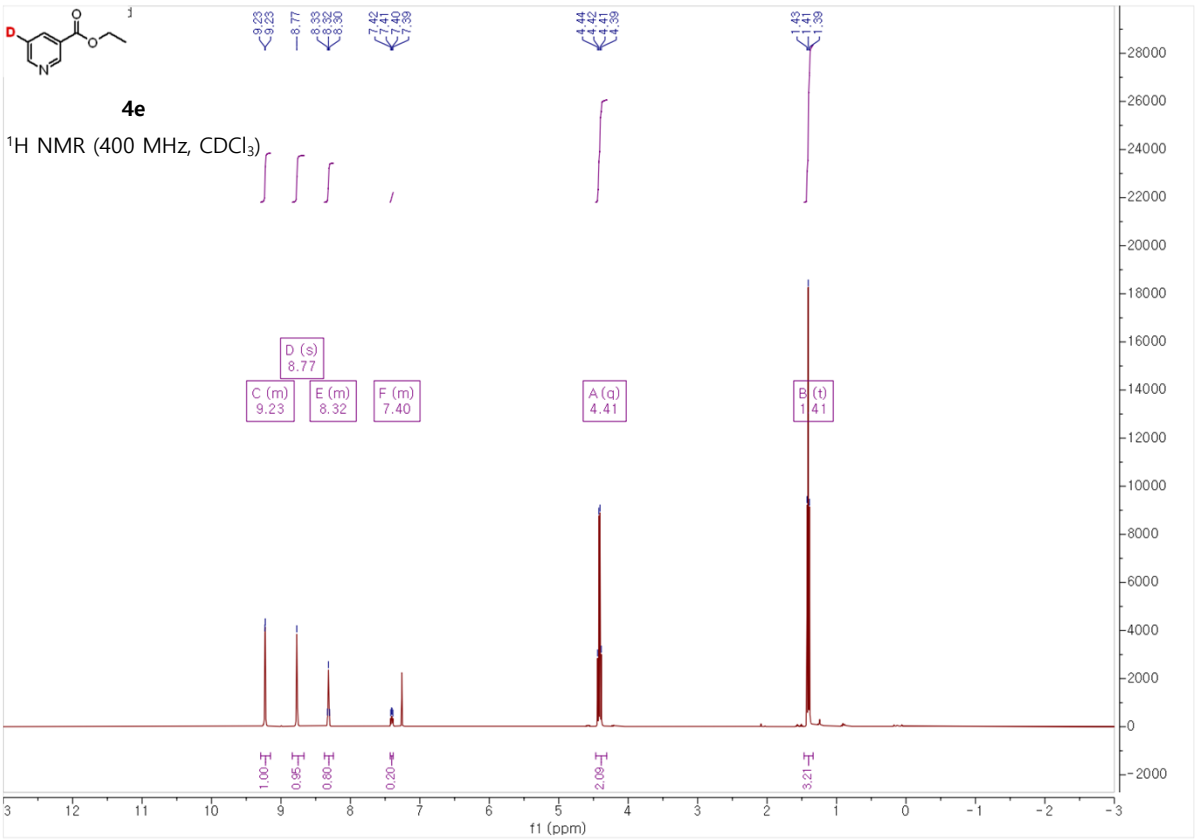
4d

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



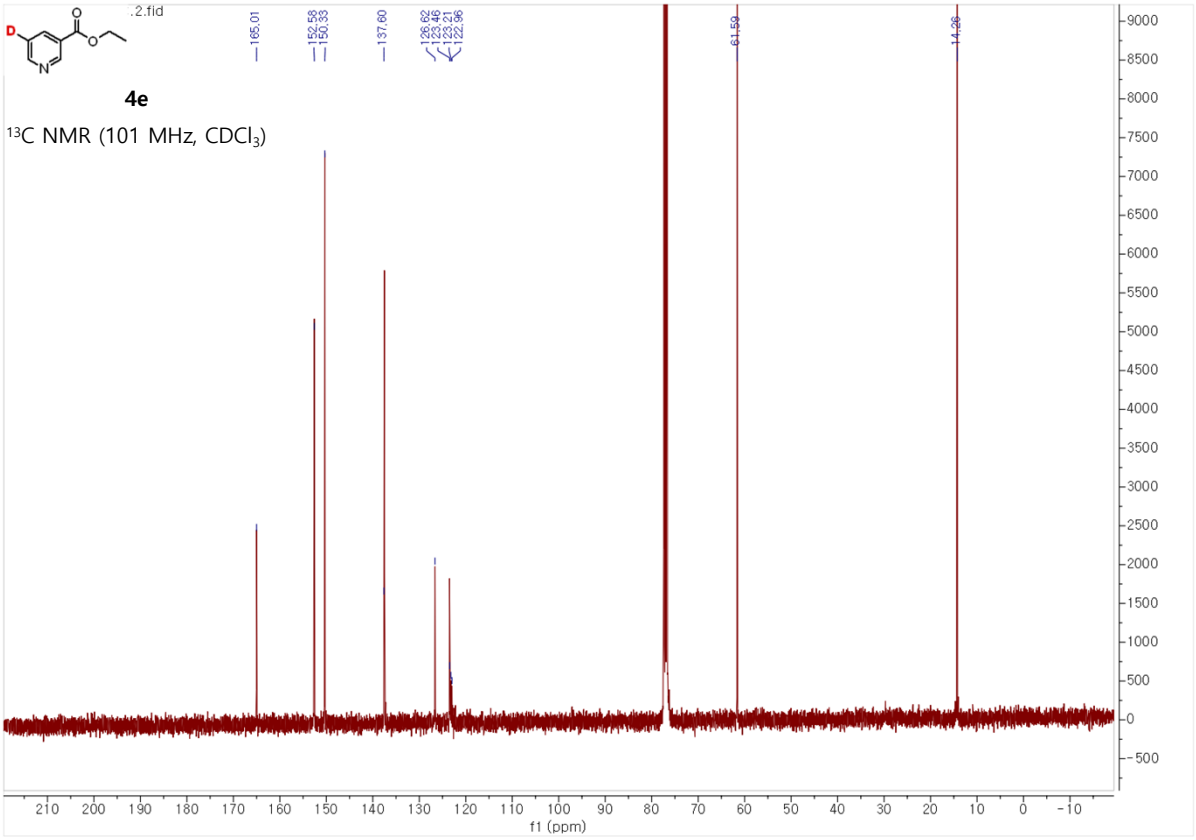
4d

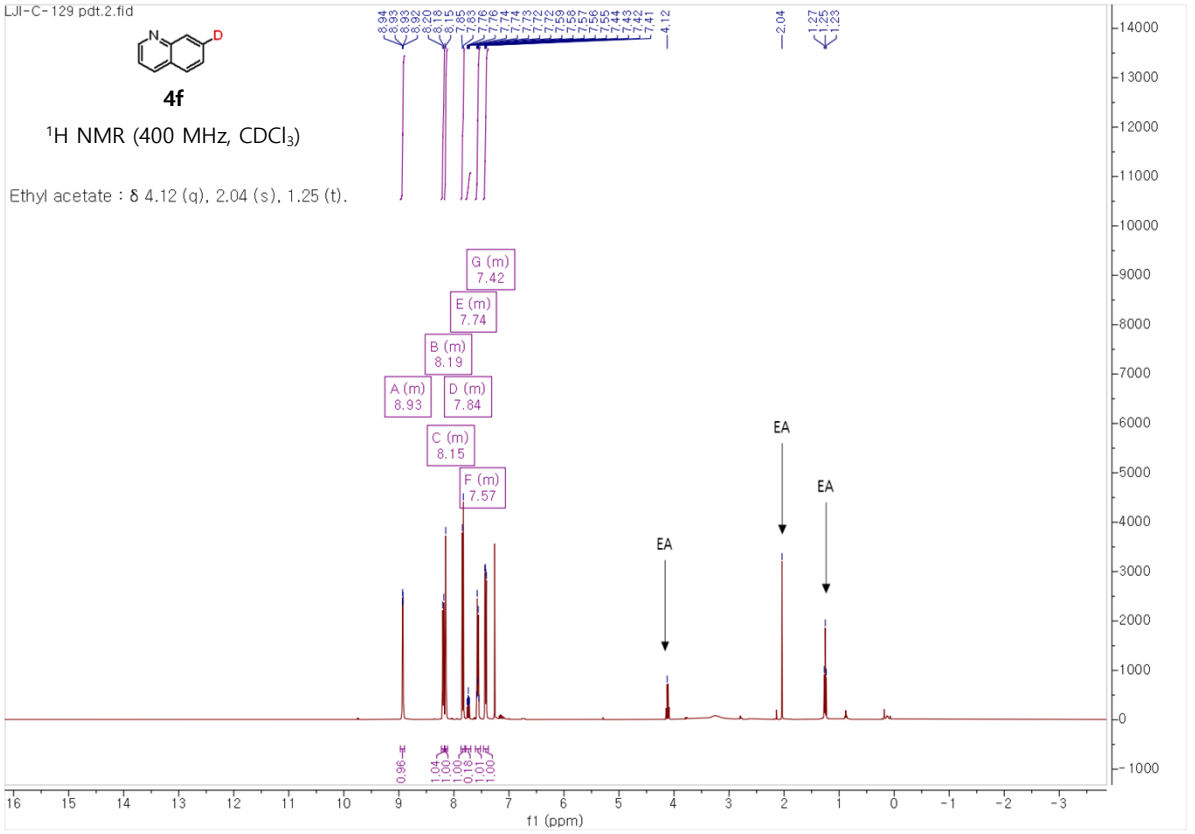
^{13}C NMR (101 MHz, $CDCl_3$)

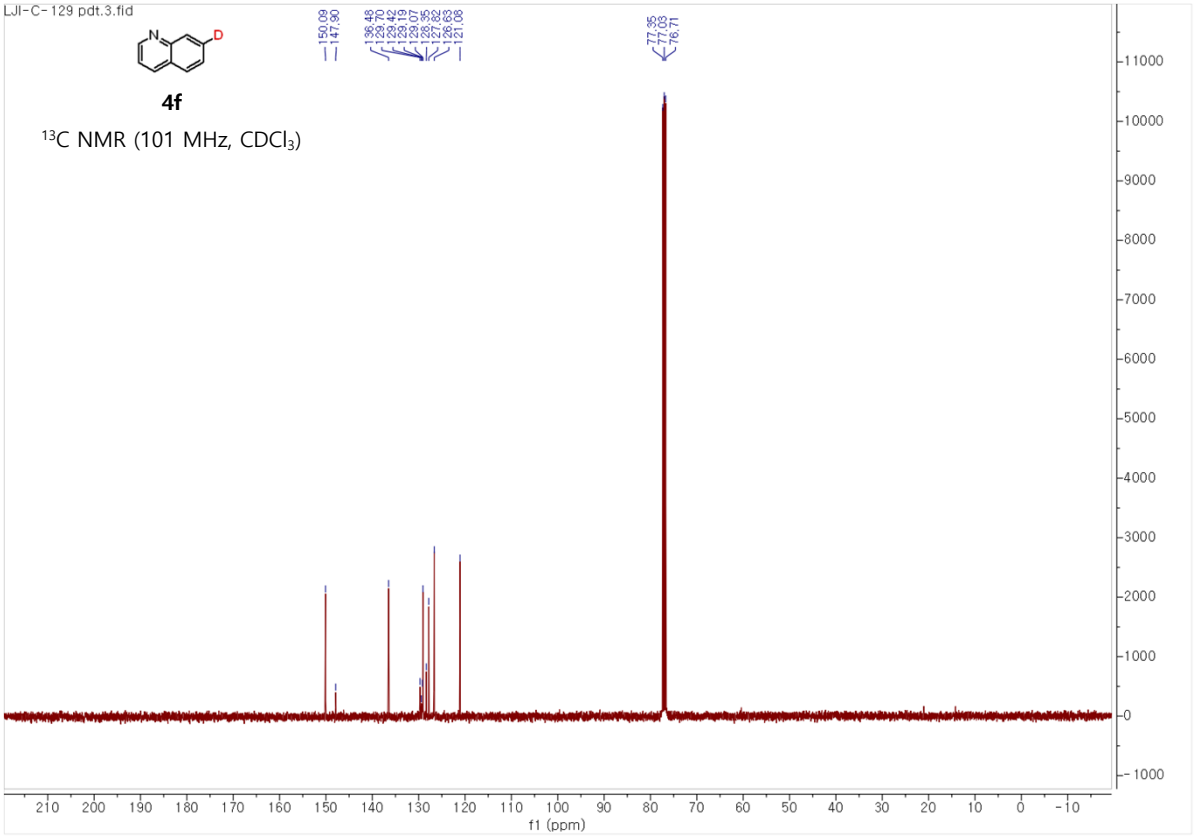


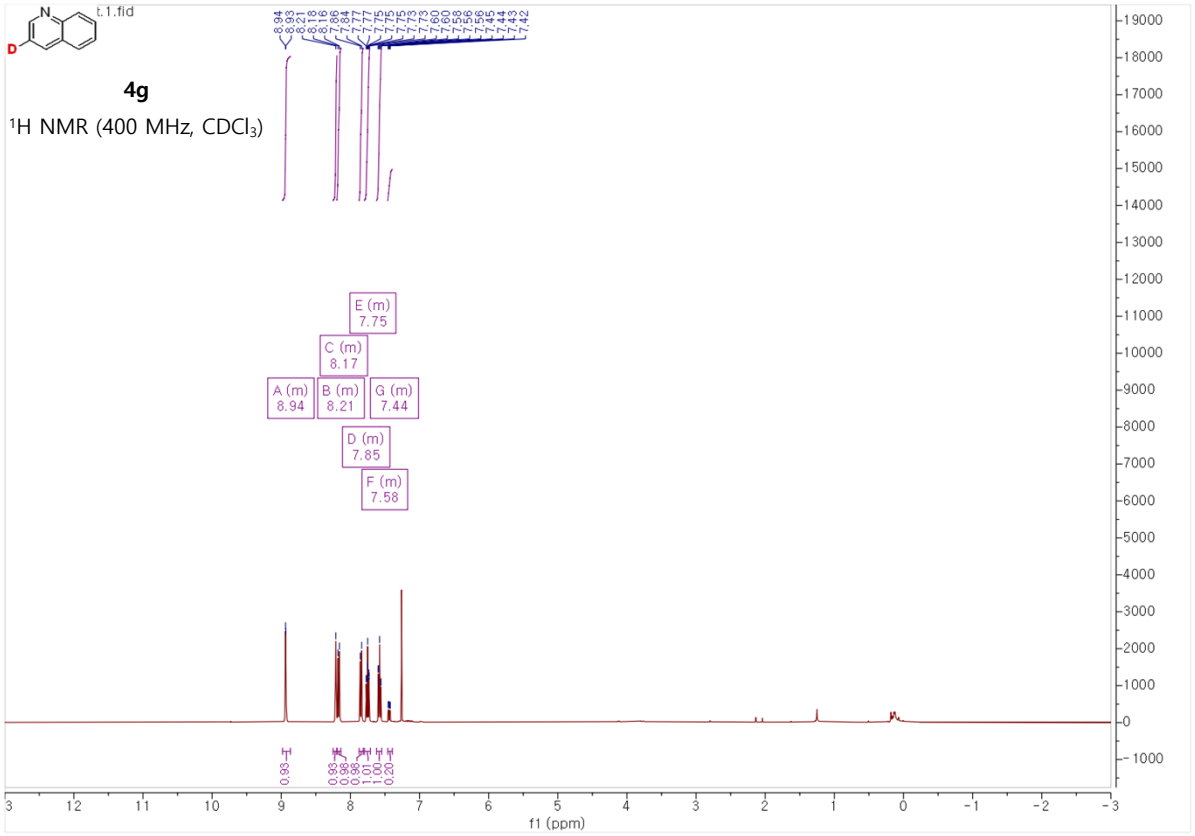
4e

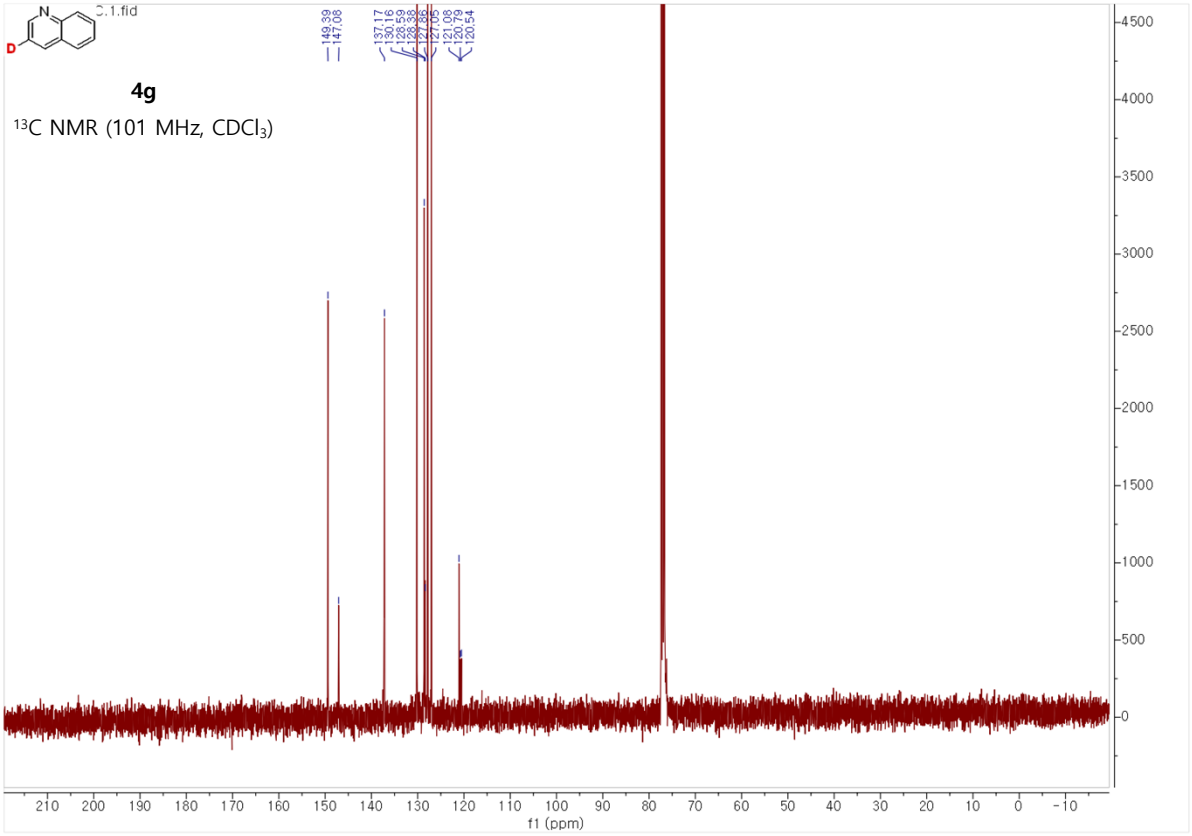
^{1}H NMR (400 MHz, $CDCl_3$)


.2.fid
D
N
O
O
4e
13C NMR (101 MHz, CDCl3)
165.01
152.58
150.33
137.60
126.62
123.46
123.21
122.86
61.59
14.26
f1 (ppm)


LJI-C-129 pdt.2.fid
N
D
4f
1H NMR (400 MHz, CDCl3)
Ethyl acetate : δ 4.12 (q), 2.04 (s), 1.25 (t).
G (m) 7.42
E (m) 7.74
B (m) 8.19
A (m) 8.93
D (m) 7.84
C (m) 8.15
F (m) 7.57
EA
EA
EA
f1 (ppm)

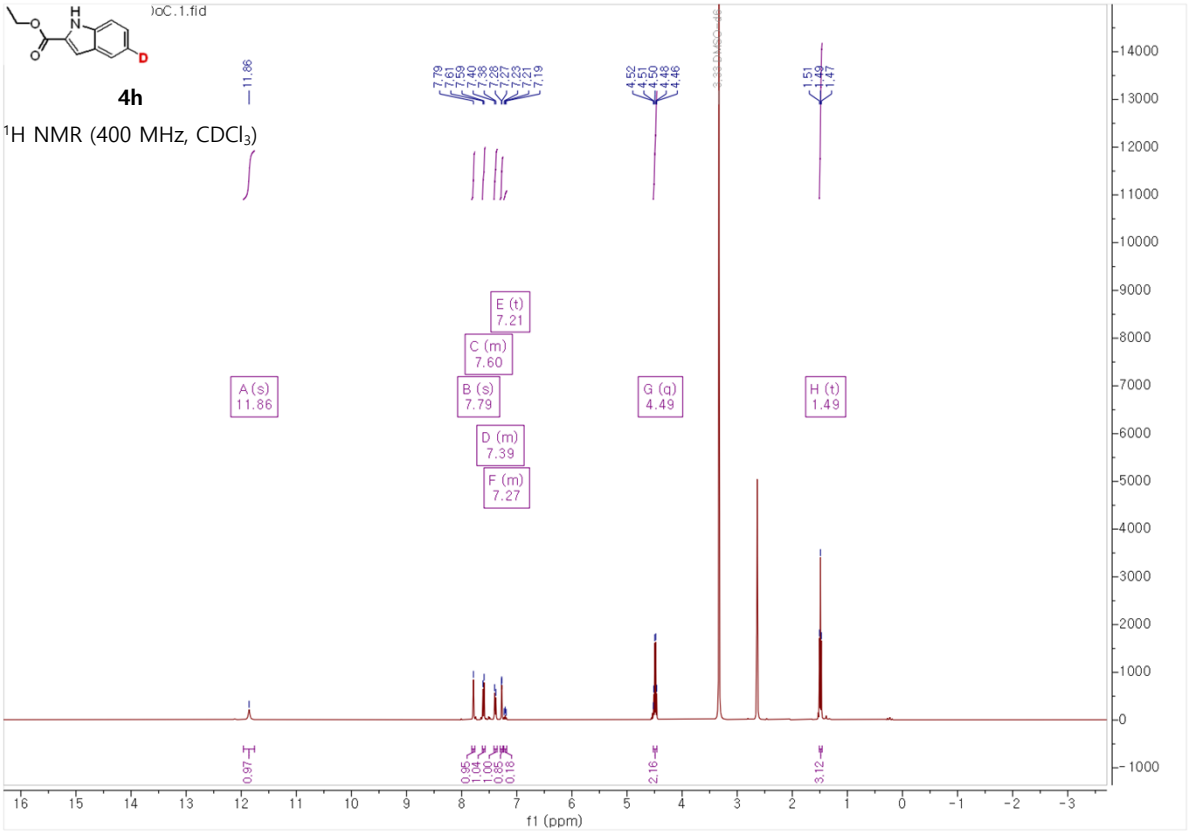

LJI-C-129 pdt.3.fid
4f
13C NMR (101 MHz, CDCl3)
150.09
147.90
136.48
129.70
129.42
129.19
129.07
128.35
127.82
126.63
121.06
77.35
77.03
76.71
f1 (ppm)


t.1.fid
4g
1H NMR (400 MHz, CDCl3)
8.94
8.93
8.21
8.18
8.16
7.86
7.84
7.77
7.75
7.73
7.60
7.58
7.56
7.45
7.44
7.43
7.42
E (m) 7.75
C (m) 8.17
A (m) 8.94
B (m) 8.21
G (m) 7.44
D (m) 7.85
F (m) 7.58
0.93
0.98
0.98
1.00
1.01
0.20
f1 (ppm)



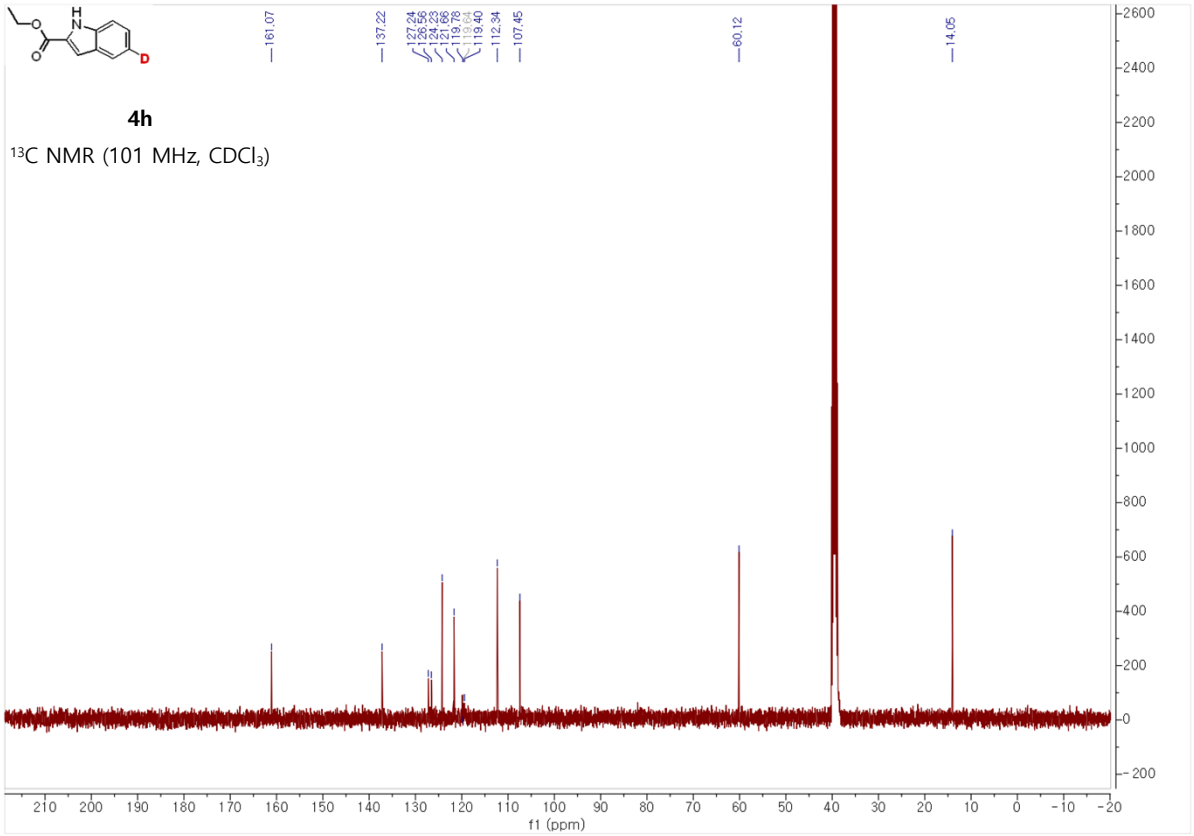
4g

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



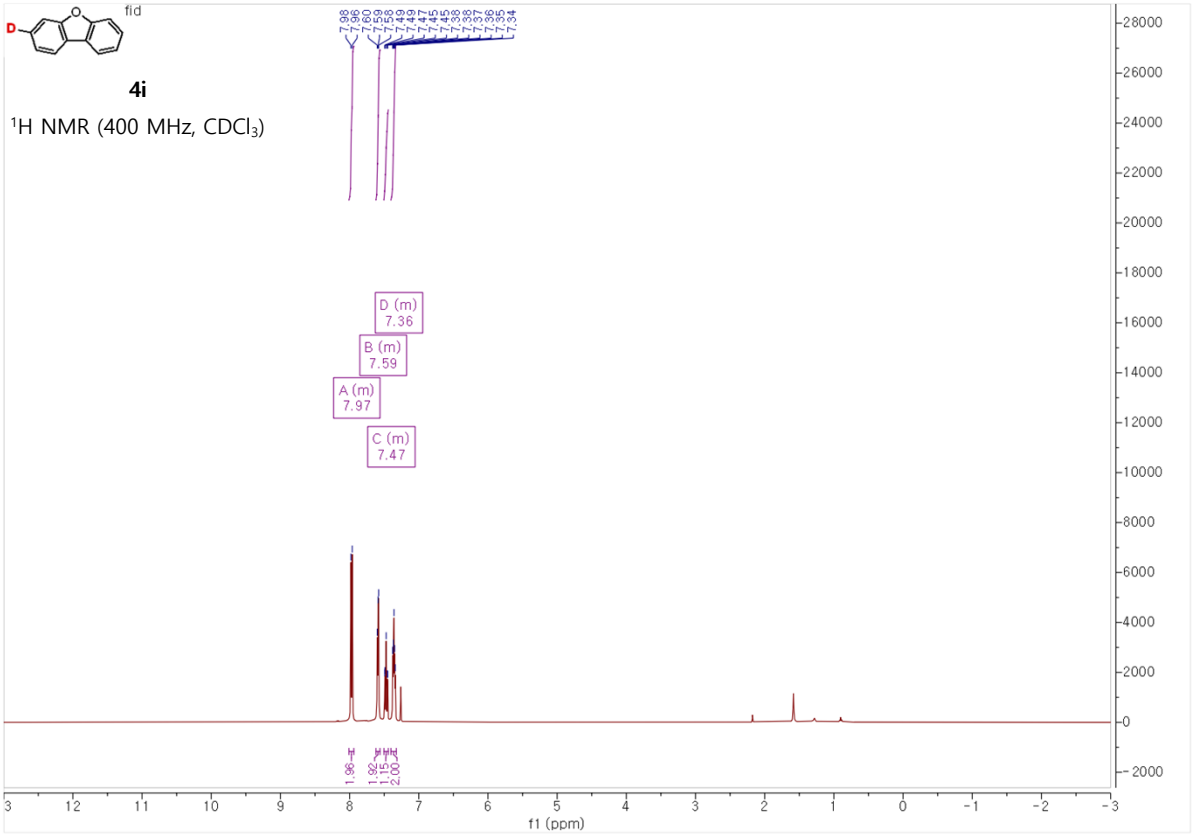
4h

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



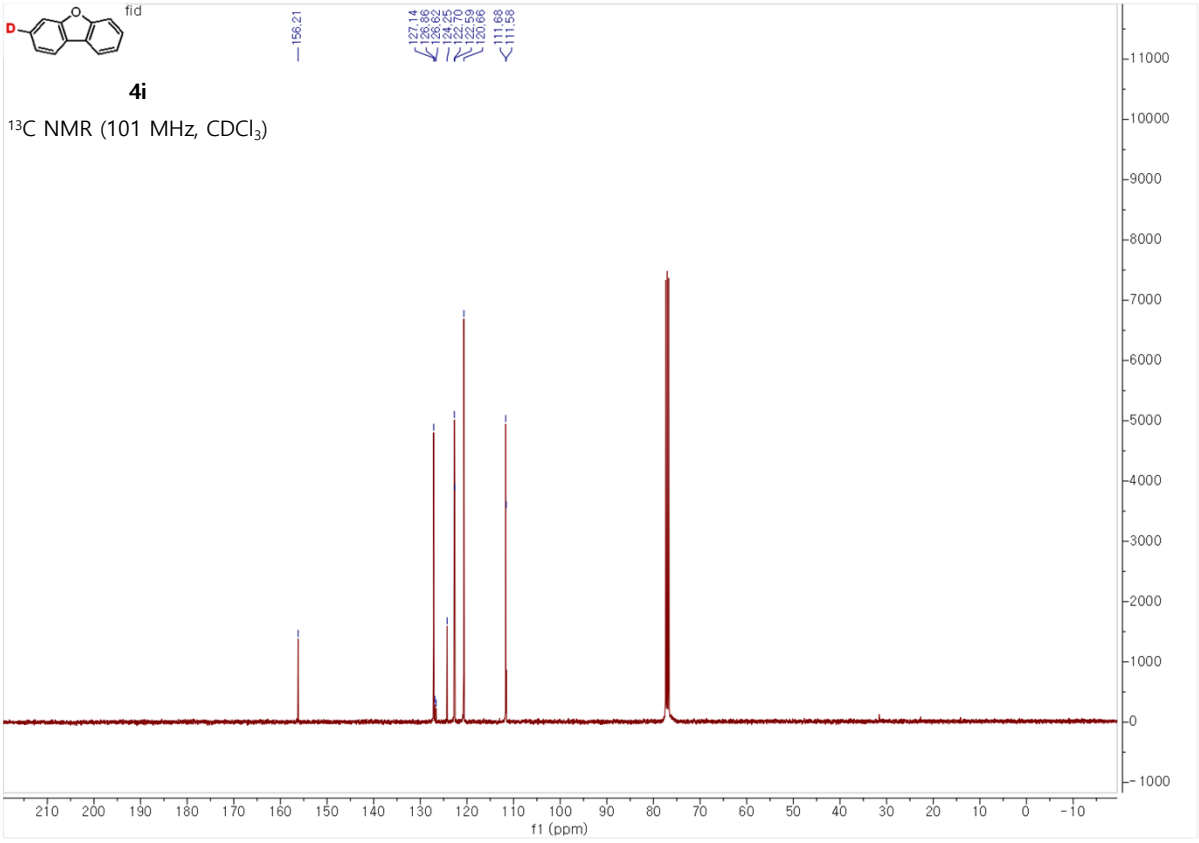
4h

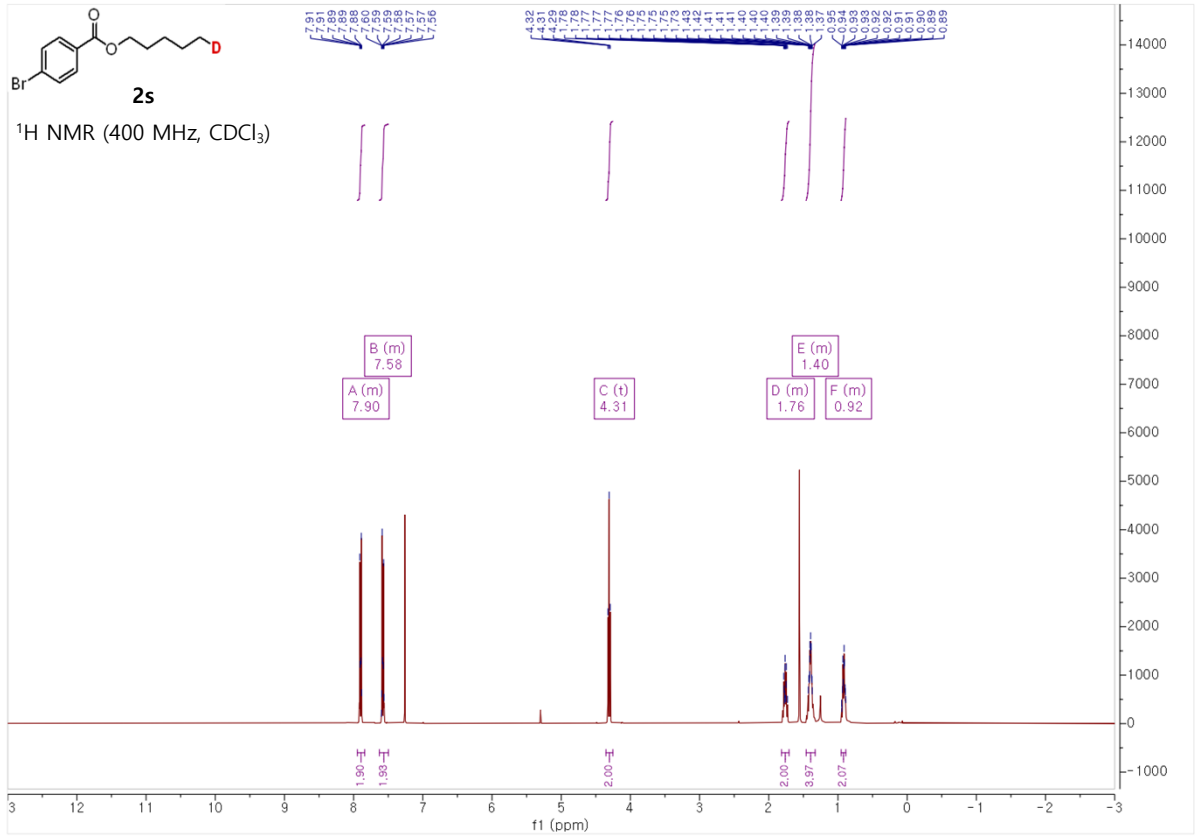
^{13}C NMR (101 MHz, $CDCl_3$)

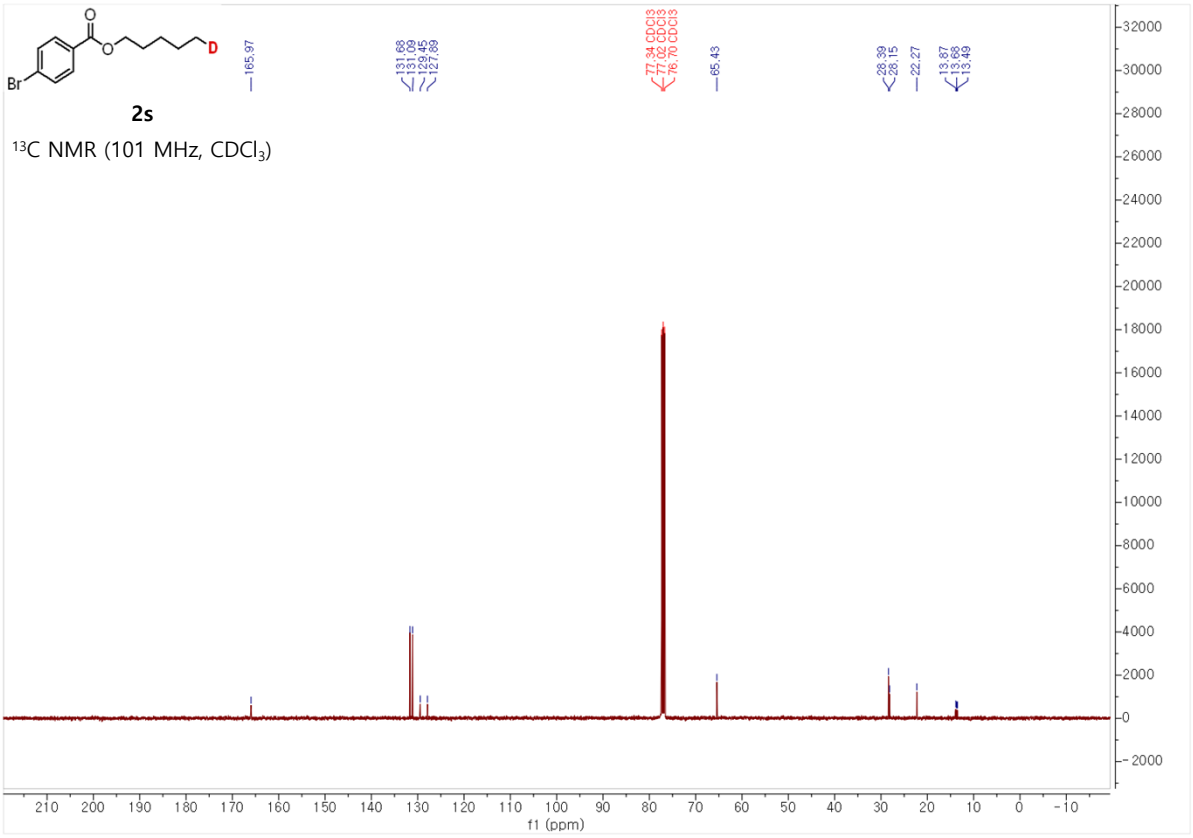


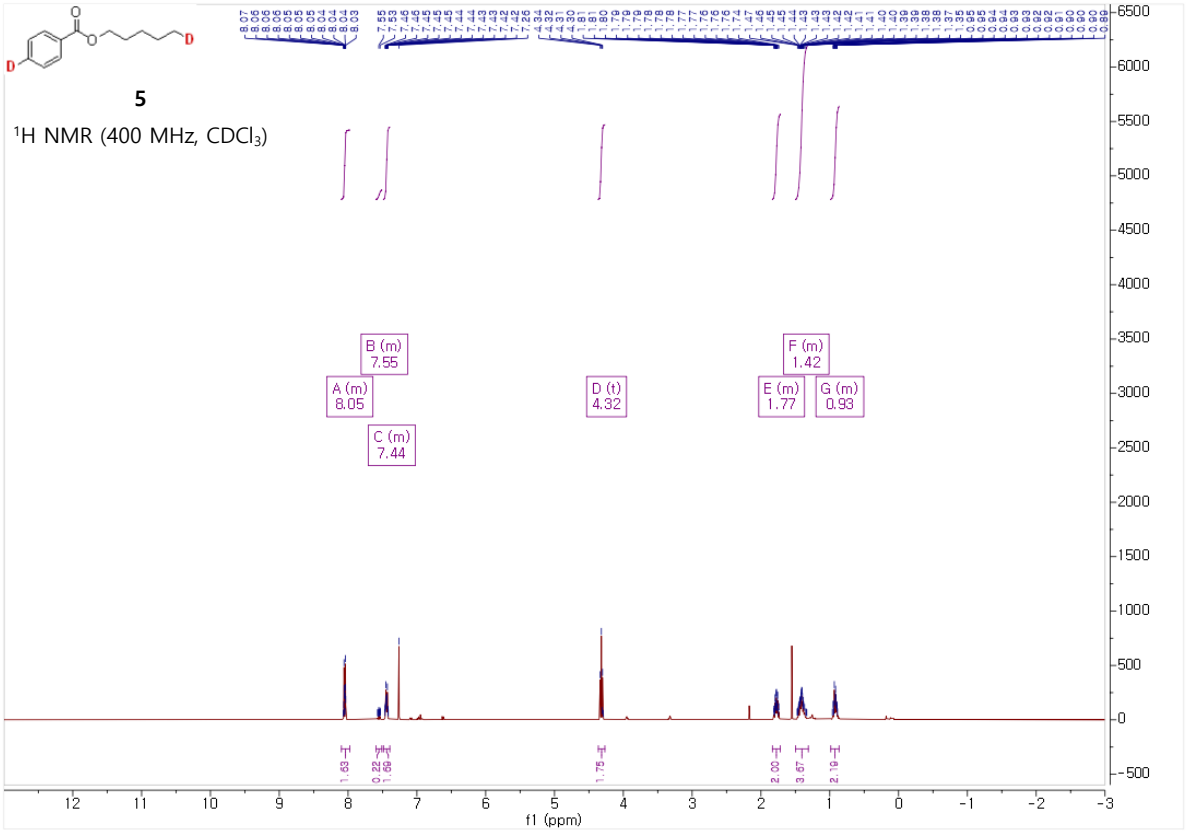
4i

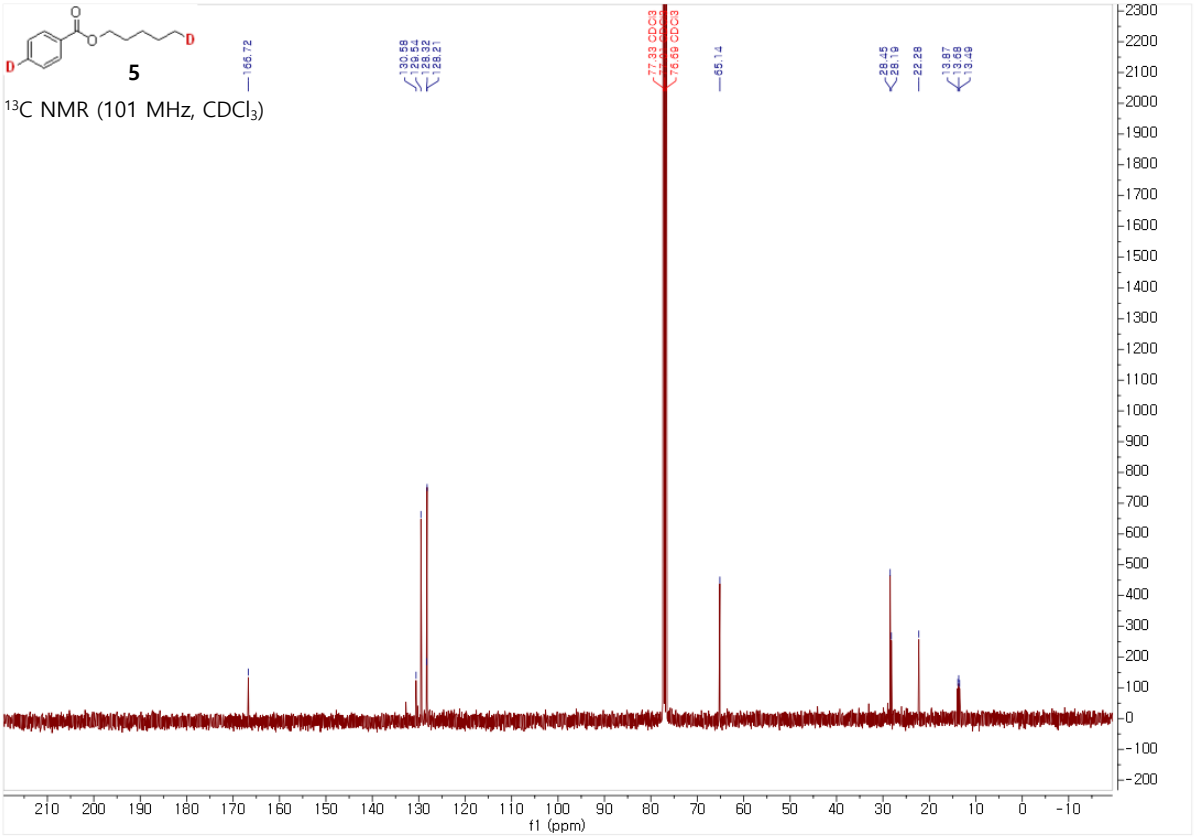
^{1}H NMR (400 MHz, $CDCl_3$)

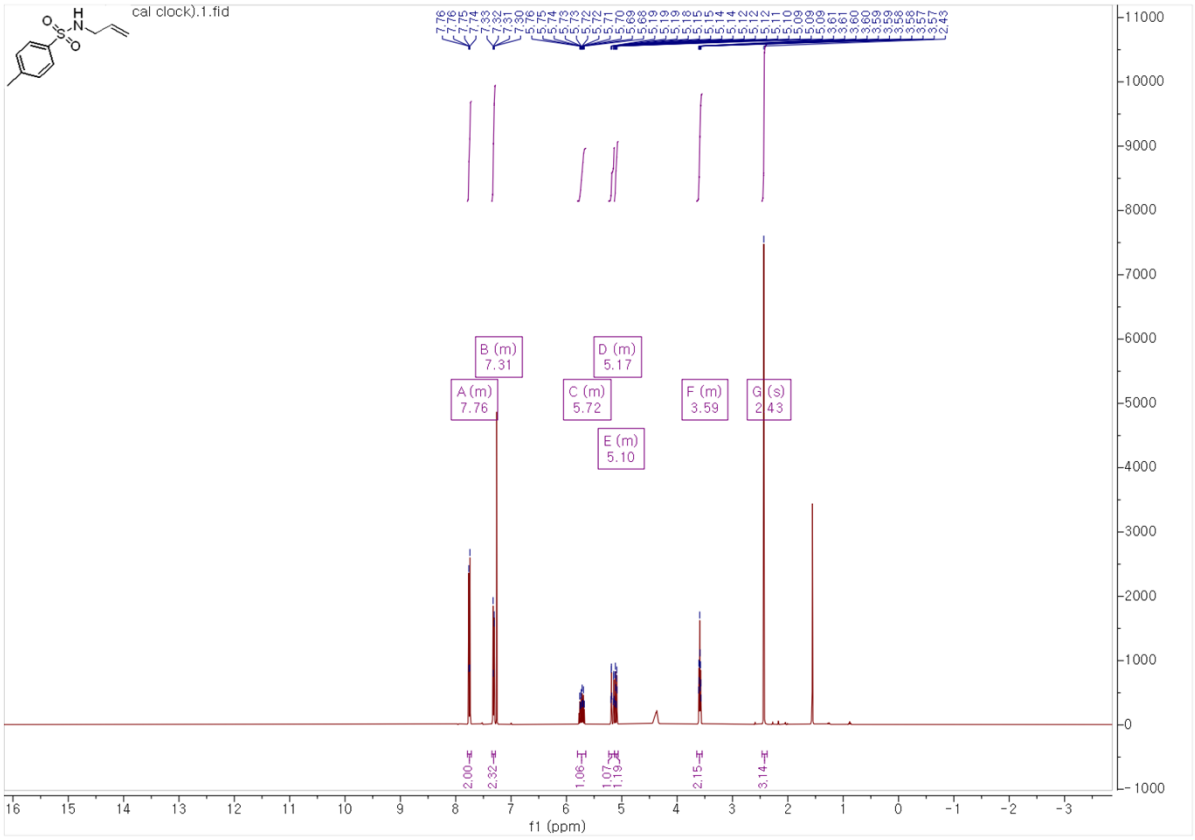

fid
D
156.21
127.14
126.86
126.62
122.75
122.70
122.59
120.66
111.68
111.58
4i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

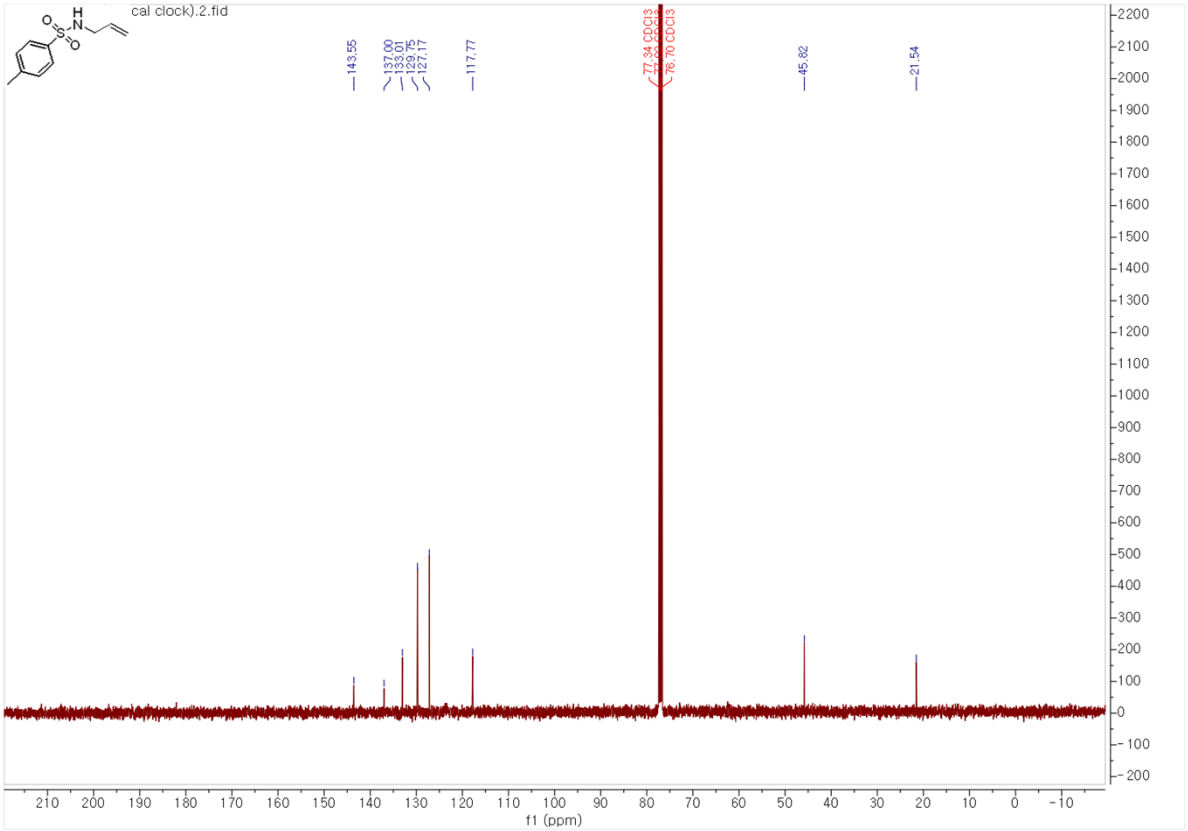

Br
O
O
D
2s
1H NMR (400 MHz, CDCl3)
B (m)
7.58
A (m)
7.90
C (t)
4.31
E (m)
1.40
D (m)
1.76
F (m)
0.92
1.90
1.93
2.00
2.00
3.97
2.07
f1 (ppm)

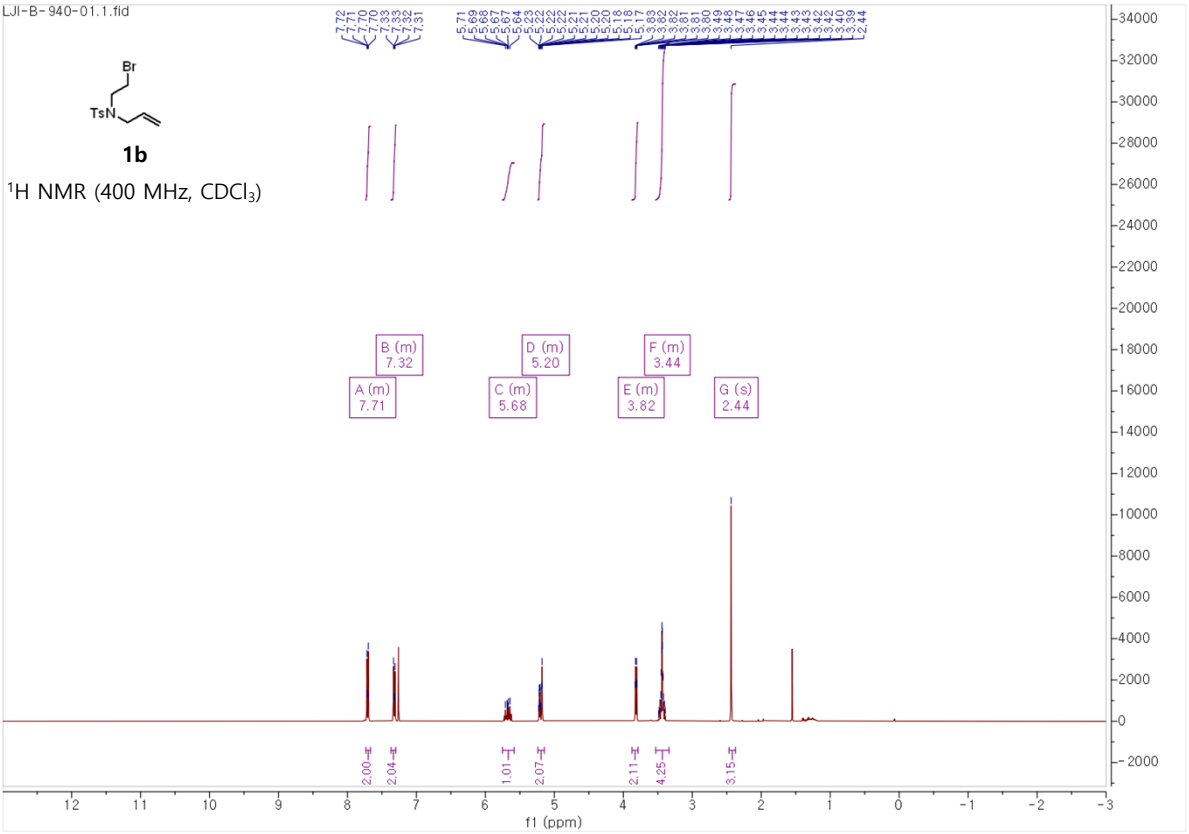

Br
D
2s
^{13}C NMR (101 MHz, $CDCl_3$)
165.97
131.68
131.09
129.45
127.69
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
65.43
28.39
28.15
22.27
13.87
13.68
13.49
f1 (ppm)


D
D
5
^{1}H NMR (400 MHz, $CDCl_3$)
B (m) 7.55
A (m) 8.05
C (m) 7.44
D (t) 4.32
F (m) 1.42
E (m) 1.77
G (m) 0.93
f1 (ppm)


5
^{13}C NMR (101 MHz, $CDCl_3$)
166.72
130.58
129.54
128.32
128.21
77.33
77.00
76.68
65.14
28.45
28.19
22.28
13.87
13.68
13.49
f1 (ppm)

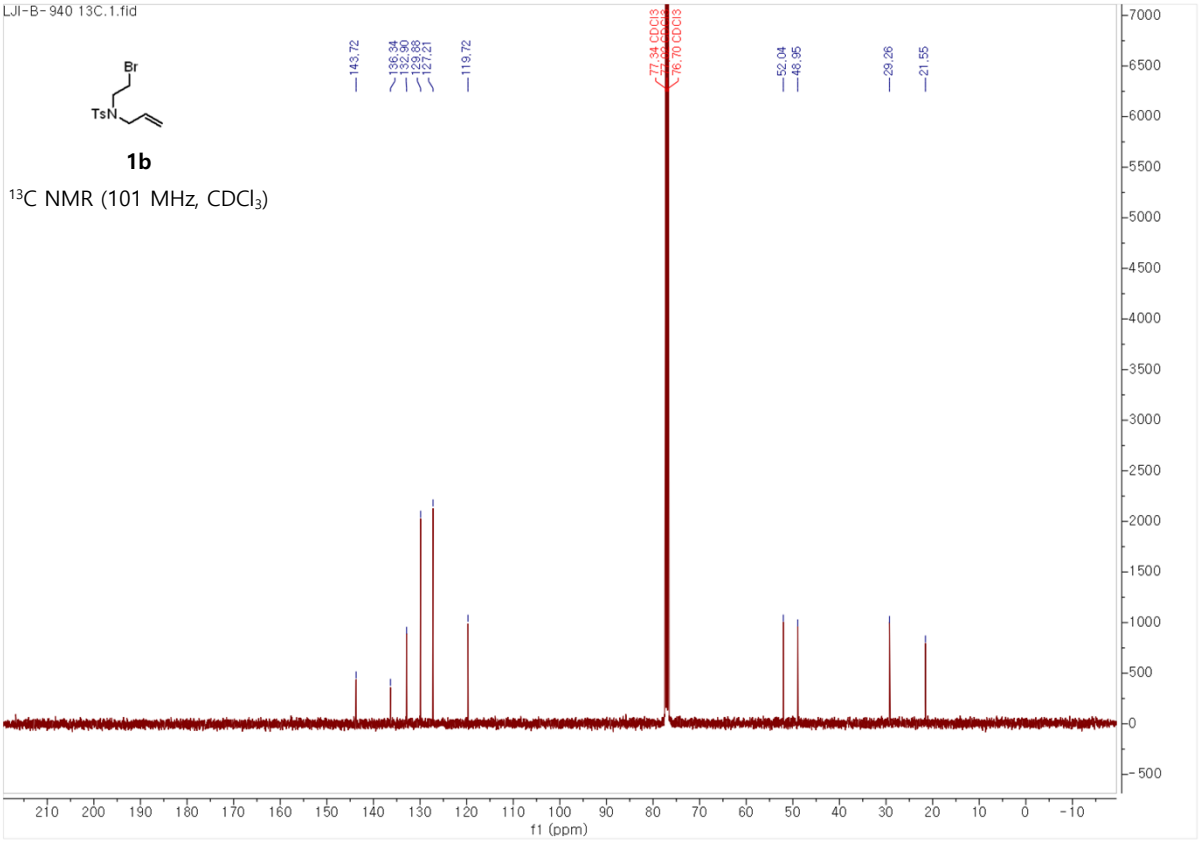

cal clock).1.fid
A (m) 7.76
B (m) 7.31
C (m) 5.72
D (m) 5.17
E (m) 5.10
F (m) 3.59
G (s) 2.43
2.00
2.32
1.06
1.07
1.19
2.15
3.14
f1 (ppm)





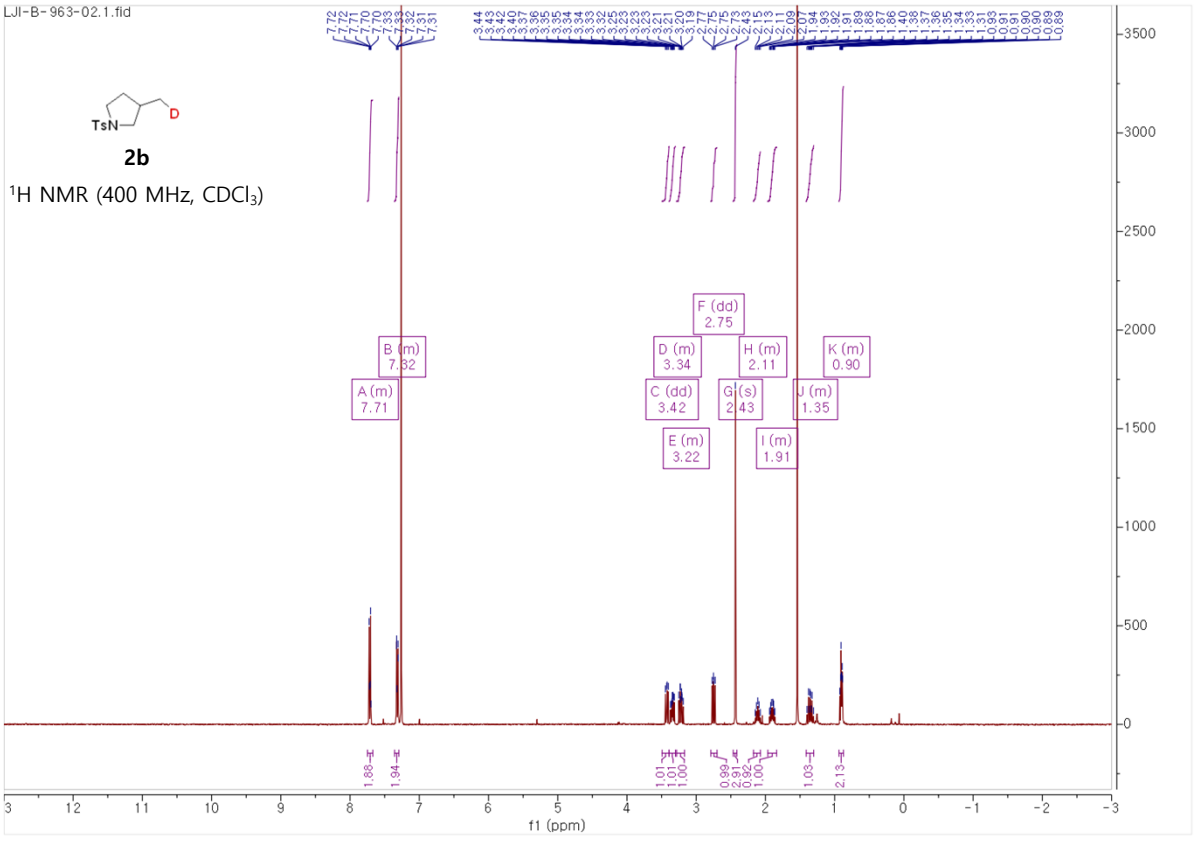
1b

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



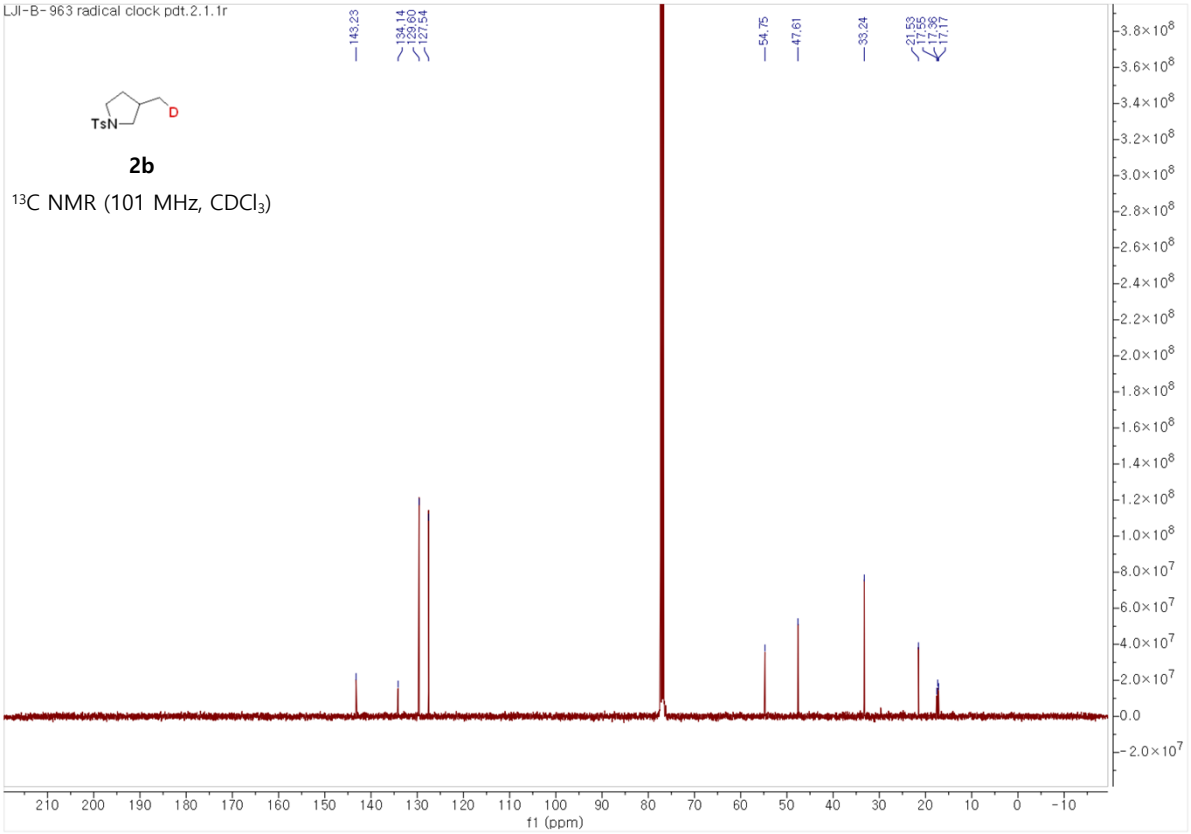
1b

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



2b

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


LJI-B-963 radical clock pdt.2.1.1r
143.23
134.14
129.60
127.54
54.75
47.61
33.24
21.53
21.55
17.36
17.17
TsN
D
2b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

5. References

1. J. H. Kirchhoff, M. R. Netherton, I. D. Hills and G. C. Fu, Boronic Acids: New Coupling Partners in Room-Temperature Suzuki Reactions of Alkyl Bromides. Crystallographic Characterization of an Oxidative-Addition Adduct Generated under Remarkably Mild Conditions, *J. Am. Chem. Soc.*, 2002, **124**, 13662-13663.
2. V. Soulard, G. Villa, D. P. Vollmar and P. Renaud, Radical Deuteration with D2O: Catalysis and Mechanistic Insights, *J. Am. Chem. Soc.*, 2018, **140**, 155-158.
3. Y. Li, Z. Ye, Y. M. Lin, Y. Liu, Y. Zhang and L. Gong, Organophotocatalytic selective deuterodehalogenation of aryl or alkyl chlorides, *Nat. Commun.*, 2021, **12**, 2894.
4. H.-M. Huang, P. Bellotti, P. M. Pflüger, J. L. Schwarz, B. Heidrich and F. Glorius, Three-Component, Interrupted Radical Heck/Allylic Substitution Cascade Involving Unactivated Alkyl Bromides, *J. Am. Chem. Soc.*, 2020, **142**, 10173-10183.
5. P. Li, C. Guo, S. Wang, D. Ma, T. Feng, Y. Wang and Y. Qiu, Facile and general electrochemical deuteration of unactivated alkyl halides, *Nat. Commun.*, 2022, **13**, 3774.
6. H.-H. Zhang, P. V. Bonnesen and K. Hong, Palladium-catalyzed Br/D exchange of arenes: selective deuterium incorporation with versatile functional group tolerance and high efficiency, *Org. Chem. Front.*, 2015, **2**, 1071-1075.