# Supporting Information

## Total Synthesis of Breviscapin B via Intramolecular Dehydrative Etherification

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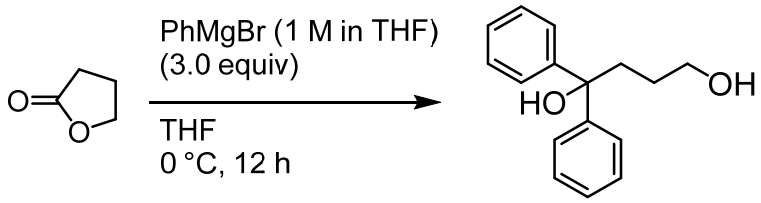
## 2. Experimental Section

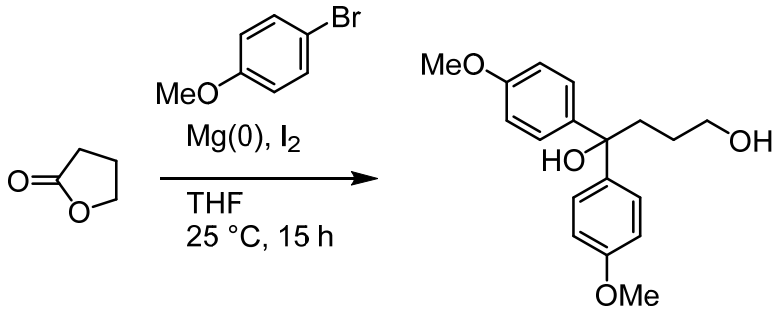
### General information

Melting points were recorded on a Yamato melting point apparatus model MP-500P and were uncorrected. Optical rotations were measured using a JASCO P1020 digital polarimeter at the sodium D line (589 nm). IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber ($cm^{-1}$). $^{1}H$ NMR spectra were recorded on JEOL ECZ-500 (500 MHz) spectrometer or chemical shifts are reported relative to internal standard (tetramethylsilane; $\delta_H$ 0.00, $CDCl_3$; $\delta_H$ 7.26, $CD_3OD$; $\delta_H$ 3.31). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, hept = heptet, m = multiplet, br = broad), coupling constant and integration. $^{13}C$ $\{^{1}H\}$ NMR spectra were recorded on JEOL ECZ-500 (150 MHz) spectrometer. The following internal references were used: $CDCl_3$ (δ 77.03), $CD_3OD$ (δ 49.00). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100. High-resolution mass spectra (HRMS) were recorded on JEOL AccuTOF and Waters Xevo G2-S QTOF system. Flash column chromatography was performed with YAMAZEN EPCLC-W-Prep 2XY equipped with YAMAZEN Universal Column Premium or CHROMATOREX Q-Pack columns. Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F254 plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. All non-aqueous reactions were carried out in flame-dried glassware under argon atmosphere unless otherwise noted. Reagents and solvents were purified by standard means.

**The preparation of diols:**

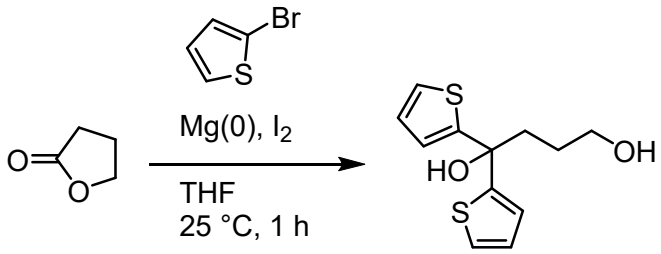



**1,1-Diphenylbutane-1,4-diol (11a)**[1]**:** Phenylmagnesium bromide (1.07 M in THF, 14.6 mL, 15.6 mmol) was added to a solution of γ-butyrolactone (448 mg, 5.2 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at the same temperature for 12 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 4:1 → 0:1 hexane/EtOAc) to afford **11a** (697 mg, 55%) as a white solid; TLC $R_f$ = 0.35 (1:1 hexane/ EtOAc); mp 93.3–96.5 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 7.5 Hz, 4H), 7.31 (dd, $J$ = 7.5, 7.5 Hz, 4H), 7.22 (dd, $J$ = 7.5, 7.5 Hz, 2H), 3.67 (t, $J$ = 6.9 Hz, 2H), 3.23 (br s, 1H), 2.43 (t, $J$ = 6.9 Hz, 2H), 1.93 (br s, 1H), 1.58 (quint, $J$ = 6.9 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 147.2, 128.3, 126.9, 126.2, 78.0, 63.3, 39.1, 27.3.

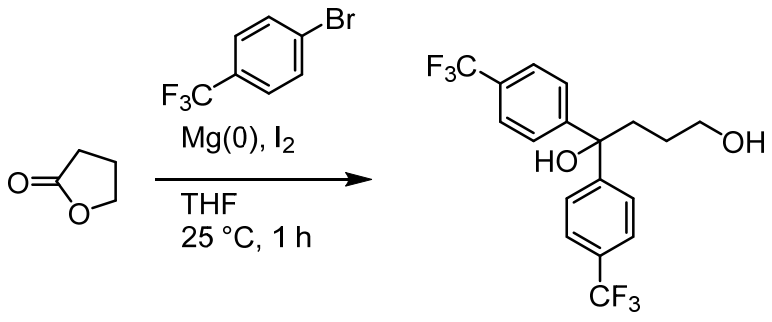



**1,1-Bis(4-methoxyphenyl)butane-1,4-diol (11b)**[1]**:** 4-Bromoanisole (3.0 mL, 4.5 g, 24.0 mmol) was added to a stirred mixture of magnesium turnings (583 mg, 24.0 mmol) and a few crystals of iodine in THF (80 mL) at 25 °C under argon. The mixture was stirred at 25 °C for 1 h. γ-Butyrolactone (0.762 mL, 861 mg, 10.0 mmol) in THF (20 mL) was added and the mixture was stirred at 25 °C for 15 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) at 0 °C and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 1:1 → 0:1 hexane/$Et_2O$) to afford **11b** (1.61 g, 53%) as a white solid; TLC $R_f$ = 0.50 (100% $Et_2O$); mp 50.9–54.0 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ

7.31 (d, $J$ = 8.6 Hz, 4H), 6.83 (d, $J$ = 8.6 Hz, 4H), 3.78 (s, 6H), 3.66 (t, $J$ = 5.7 Hz, 2H), 2.86 (br s, 1H), 2.37 (t, $J$ = 7.5 Hz, 2H), 1.74 (br s, 1H), 1.61−1.55 (m, 2H); $^{13}$C {$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 158.4, 139.7, 127.5, 113.5, 77.6, 63.4, 55.4, 39.3, 27.4.

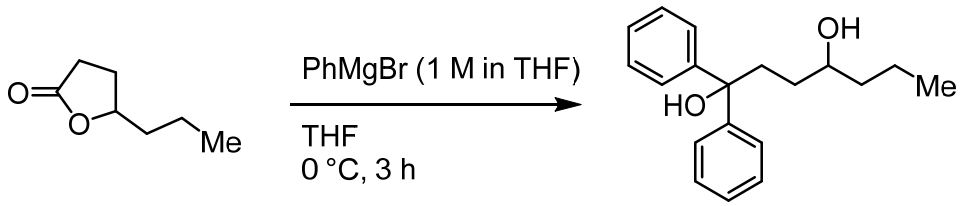



**1,1-Di(thiophen-2-yl)butane-1,4-diol (11c)**[1]**:** 2-Bromothiophene (2.87 mL, 4.89 g, 30.0 mmol) was added to a stirred mixture of magnesium turnings (802 mg, 33.0 mmol) and a few crystals of iodine in THF (40 mL) at 25 °C under argon. The mixture was stirred at 25 °C for 1 h. γ-Butyrolactone (0.667 mL, 861 mg, 10.0 mmol) in THF (10 mL) was added and the mixture was stirred at 25 °C for 1 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) at 0 °C and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 4:1 → 0:1 hexane/EtOAc) to afford **11c** (1.75 g, 69%) as a white solid; TLC $R_f$ = 0.40 (1:1 hexane/EtOAc); mp 94.2−96.3 °C; $^{1}$H NMR (500 MHz, $CD_3OD$) δ 7.23 (dd, $J$ = 5.2, 1.2 Hz, 2H), 6.98 (dd, $J$ = 3.4, 1.2 Hz, 2H), 6.93 (dd, $J$ = 5.2, 3.4 Hz, 2H), 3.56 (t, $J$ = 6.9 Hz, 2H), 2.38−2.35 (m, 2H), 1.65−1.59 (m, 2H); $^{13}$C {$^{1}$H} NMR (125 MHz, $CD_3OD$) δ 154.0, 127.4, 125.2, 124.6, 76.7, 63.1, 42.9, 28.5.

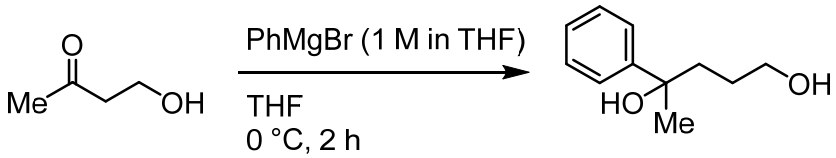



**1,1-Bis(4-(trifluoromethyl)phenyl)butane-1,4-diol (11d):** 4-Bromobenzotrifluoride (2.76 mL, 4.5 g, 20.0 mmol) was added to a stirred mixture of magnesium turnings (583 mg, 24.0 mmol) and a few crystals of iodine in THF (40 mL) at 25 °C under argon. The mixture was stirred at 25 °C for 1 h. γ-Butyrolactone (0.333 mL, 431 mg, 5.0 mmol) in THF (10 mL) was added and the mixture was stirred

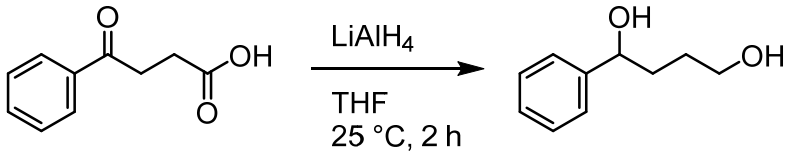
at 25 °C for 2 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) at 0 °C and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 4:1 → 0:1 hexane/EtOAc) to afford **11d** (486 mg, 26%) as a yellow solid; TLC $R_f$ = 0.34 (100% EtOAc); mp 122.5−123.2 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 8H), 4.07 (br s, 1H), 3.74 (t, $J$ = 6.3 Hz, 2H), 2.50 (t, $J$ = 6.3 Hz, 2H), 1.72 (br s, 1H), 1.63 (quint, $J$ = 6.3 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 150.6, 129.4 (q, $J_{C\text{-}F}$ = 32.6 Hz), 126.5, 125.4, 126.4 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.2 (q, $J_{C\text{-}F}$ = 271.6 Hz), 77.3, 63.0, 39.3, 26.7; IR (ATR): 3344, 2938, 1617, 1411, 1321, 1161, 1119, 1067, 1016 cm$^{-1}$; HRMS (DART) *m/z*: $[M+NH_4]^+$ Calcd for $C_{18}H_{20}F_6NO_2$ 396.1398; found 396.1391.



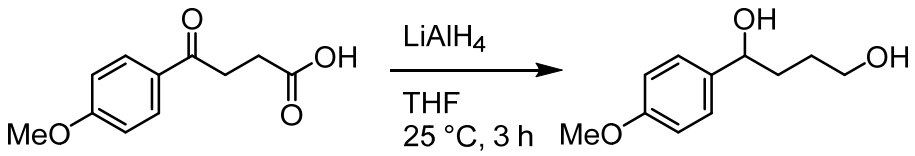

**1,1-Diphenylheptane-1,4-diol (11e):** Phenylmagnesium bromide (1.07 M in THF, 20.4 mL, 21.8 mmol) was added to a solution of γ-heptanolactone (0.70 mL, 700 mg, 5.5 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at the same temperature for 3 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 1:0 → 7:3 $CH_2Cl_2$/EtOAc) to afford **11e** (460 mg, 30%) as a white solid; TLC $R_f$ = 0.45 (6:1 $CH_2Cl_2$/EtOAc); mp 105.3−106.7 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, $J$ = 8.0 Hz, 4H), 7.30−7.26 (m, 4H), 7.21−7.18 (m, 2H), 3.62−3.57 (m, 2H), 2.42 (t, $J$ = 7.5 Hz, 2H), 2.12 (br s, 1H), 1.54−1.49 (m, 1H), 1.42−1.32 (m, 4H), 1.27−1.22 (m, 1H), 0.87 (t, $J$ = 6.9 Hz, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 147.5, 147.2, 128.2, 182.2, 126.8, 126.8, 126.3, 126.2, 78.0, 72.2, 39.8, 38.1, 31.6, 19.0, 14.1; IR (ATR): 3414, 3294, 3058, 2955, 2929, 2869, 1598, 1492, 1446, 1406, 1323, 1211, 1164, 1122, 1058, 1015 cm$^{-1}$; HRMS (DART) m/z: $[M+NH_4]^+$ Calcd for $C_{19}H_{28}NO_2$ 302.2120; found 302.2122.



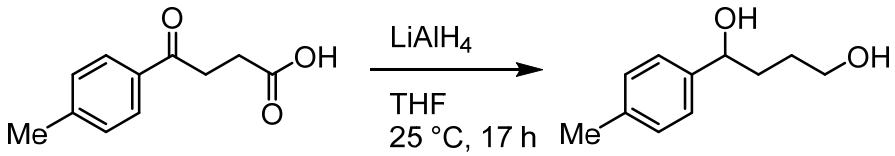

**4-Phenylpentane-1,4-diol (11f)**[2]**:** Phenylmagnesium bromide (1.07 M in THF, 14.0 mL, 15.0 mmol) was added to a solution of 5-hydroxy-2-pentanone (0.511 mL, 511 mg, 5.0 mmol) in THF (20 mL) at 0 °C and the mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 4:1 → 0:1 hexane/EtOAc) to afford **11f** (509 mg, 56%) as a colorless oil; TLC $R_f$ = 0.35 (1:1 hexane/EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 8.0 Hz, 2H), 7.33 (dd, $J$ = 8.0, 8.0 Hz, 2H), 7.23 (dd, $J$ = 8.0, 8.0 Hz, 1H), 3.63−3.55 (m, 2H), 3.00 (br s, 1H), 2.33 (br s, 1H), 2.03−1.97 (m, 1H), 1.91−1.85 (m, 1H), 1.56 (s, 3H), 1.49 (quint, $J$ = 6.3 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 148.1, 128.2, 126.5, 125.0, 74.4, 63.0, 41.3, 30.7, 27.3.



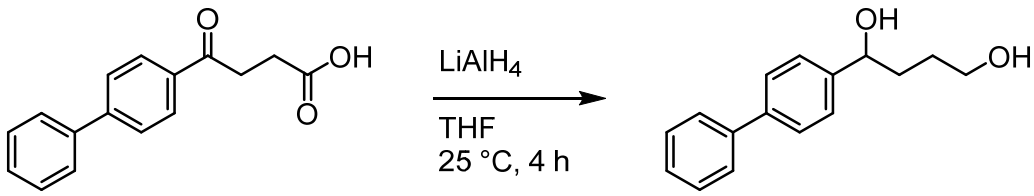

**1-Phenylbutane-1,4-diol (11g)**[3]**:** A solution of 3-benzoylpropionic acid (890 mg, 5.0 mmol) in THF (5 mL) was added dropwise to a stirred mixture of lithium aluminium hydride (569 mg, 15.0 mmol) in THF (20 mL) at 0 °C and the mixture was stirred at 25 °C for 2 h. The reaction was quenched by sequential addition of $H_2O$ (0.57 mL), 15% sodium hydroxide solution (0.57 mL) and $H_2O$ (1.14 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 4:1→1:4 hexane/EtOAc) to afford **11g** (538 mg, 65%) as a white solid; TLC $R_f$ = 0.42 (9:1 $CH_2Cl_2$/MeOH); mp 64.0−65.8 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37−7.33 (m, 4H), 7.29−7.26 (m, 1H), 4.73 (t, $J$ = 6.3 Hz, 1H), 3.73−3.65 (m, 2H), 2.15 (br s, 2H), 1.87 (q, $J$ = 6.9 Hz, 2H), 1.75−1.62 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 144.8, 128.6, 127.7, 125.9, 74.6, 63.1, 36.3, 29.3.



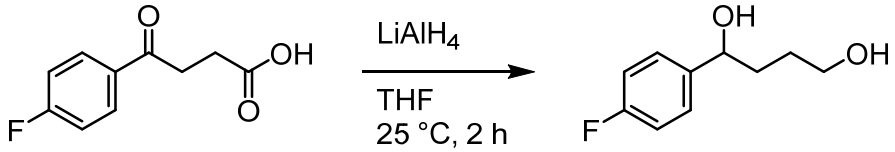

**1-(4-Methoxyphenyl)butane-1,4-diol (11h)**[3]**:** A solution of 3-(4-methoxybenzoyl)propionic acid (1.04 g, 5.0 mmol) in THF (5 mL) was added dropwise to a stirred mixture of lithium aluminium hydride (569 mg, 15.0 mmol) in THF (20 mL) at 0 °C and the mixture was stirred at 25 °C for 3 h. The reaction was quenched by sequential addition of $H_2O$ (0.57 mL), 15% sodium hydroxide solution (0.57 mL) and $H_2O$ (1.14 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:0→9:1 $CH_2Cl_2$/ MeOH) to afford **11h** (739 mg, 75%) as a white solid; TLC $R_f$ = 0.40 (9:1 $CH_2Cl_2$/ MeOH); mp 64.0–65.8 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, $J$ = 8.6 Hz, 2H), 6.88 (d, $J$ = 8.6 Hz, 2H), 4.67 (dd, $J$ = 7.5, 5.7 Hz, 1H), 3.80 (s, 3H), 3.71–3.63 (m, 2H), 2.20 (br s, 2H), 1.88–1.80 (m, 2H), 1.73–1.59 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 159.2, 137.0, 127.2, 114.0, 74.2, 63.1, 55.4, 36.2, 29.5.



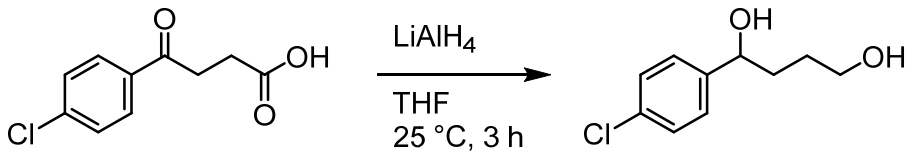

**1-(*p*-Tolyl)butane-1,4-diol (11i)**[3]**:** A solution of 4-(4-methylphenyl)-4-oxobutyric acid (1.00 g, 5.2 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (592 mg, 15.6 mmol) in THF (20 mL) at 0 °C and the mixture was stirred at 25 °C for 17 h. The reaction was quenched by sequential addition of $H_2O$ (0.60 mL), 15% sodium hydroxide solution (0.60 mL) and $H_2O$ (1.20 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:1→0:1 hexane/ $Et_2O$) to afford **11i** (708 mg, 69%) as a colorless oil; TLC $R_f$ = 0.45 (100% $Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 4.70 (t, $J$ = 6.9 Hz, 1H), 3.72–3.65 (m, 2H), 2.37 (br s, 1H), 2.34 (s, 3H), 2.01 (br s, 1H), 1.88–1.83 (m, 2H), 1.73–1.63 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 141.8, 137.3, 129.3, 125.9, 74.4, 63.0, 36.3, 29.4, 21.2.



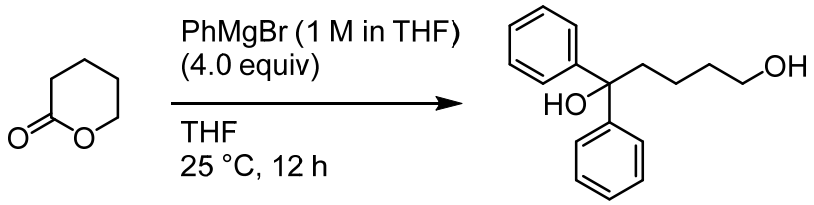

**1-[(1,1'-Biphenyl)-yl]butane-1,4-diol (11j)**[4]**:** A solution of fenbufen (1.00 g, 3.93 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (448 mg, 11.8 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 4 h. The reaction was quenched by sequential addition of $H_2O$ (0.45 mL), 15% sodium hydroxide solution (0.45 mL) and $H_2O$ (0.90 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:1→0:1 hexane/$Et_2O$) to afford **11j** (823 mg, 86%) as a white solid; TLC $R_f$ = 0.45 (100% $Et_2O$); mp 78.4–82.0°C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 4H), 7.44 (dd, $J$ = 8.0, 8.0 Hz, 4H), 7.35 (dd, $J$ = 8.0, 8.0 Hz, 1H), 4.80 (t, $J$ = 6.3 Hz, 1H), 3.76–3.69 (m, 2H), 2.53 (br s, 1H), 1.95 (br s, 1H), 1.92 (q, $J$ = 6.9 Hz, 2H), 1.80–1.66 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 143.8, 140.9, 140.6, 128.9, 127.4, 127.3, 127.2, 126.3, 74.3, 63.0, 36.3, 29.3.



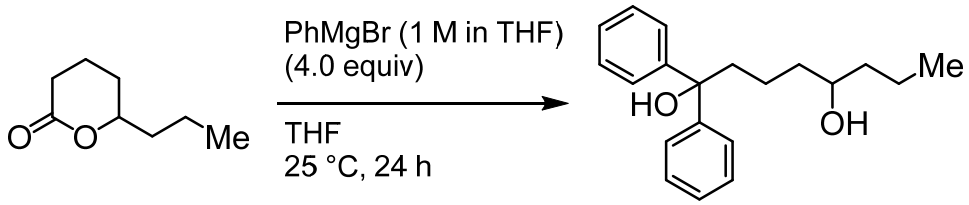

**1-(4-Fluorophenyl)butane-1,4-diol (11k)**[5]**:** A solution of 3-(4-fluorobenzoyl)propionic acid (981 mg, 5.0 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (569 mg, 15.0 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 2 h. The reaction was quenched by sequential addition of $H_2O$ (0.57 mL), 15% sodium hydroxide solution (0.57 mL) and $H_2O$ (1.14 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:1→0:1 hexane/EtOAc) to afford **11k** (666 mg, 72%) as a pale yellow oil; TLC $R_f$ = 0.35 (1:4 hexane/EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, $J$ = 8.6, 5.7 Hz, 2H), 6.97 (dd, $J$ = 8.6, 8.6 Hz, 2H), 4.57 (t, $J$ = 6.3 Hz, 1H), 4.35 (br s, 1H), 3.79 (br s, 1H), 3.58–3.48 (m, 2H), 1.73 (q, $J$ = 6.9 Hz, 2H), 1.61–1.50 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 162.1 (d, $J_{C\text{-}F}$ = 245.1 Hz), 140.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.5 (d, $J_{C\text{-}F}$ = 8.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.7 Hz), 73.5, 62.5, 36.5, 29.0.



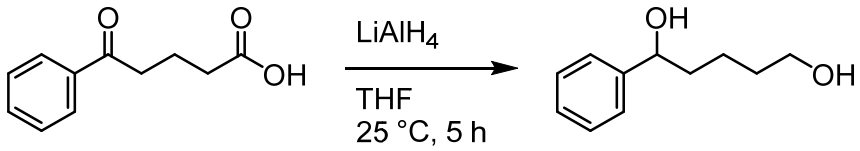

**1-(4-Chlorophenyl)butane-1,4-diol (11l)**[3]**:** A solution of 3-(4-chlorobenzoyl)propionic acid (1.00 g, 4.7 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (535 mg, 14.1 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 3 h. The reaction was quenched by sequential addition of $H_2O$ (0.54 mL), 15% sodium hydroxide solution (0.54 mL) and $H_2O$ (1.08 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:1→0:1 hexane/EtOAc) to afford **11l** (854 mg, 85%) as a pale yellow oil; TLC $R_f$ = 0.25 (1:3 hexane/EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, $J$ = 8.6 Hz, 2H), 7.26 (d, $J$ = 8.6 Hz, 2H), 4.66 (dd, $J$ = 7.5, 5.2 Hz, 1H), 3.69–3.59 (m, 2H), 3.37 (br s, 1H), 2.79 (br s, 1H), 1.84–1.76 (m, 2H), 1.69–1.59 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 143.3, 133.1, 128.6, 127.3, 73.7, 62.8, 36.6, 29.1.



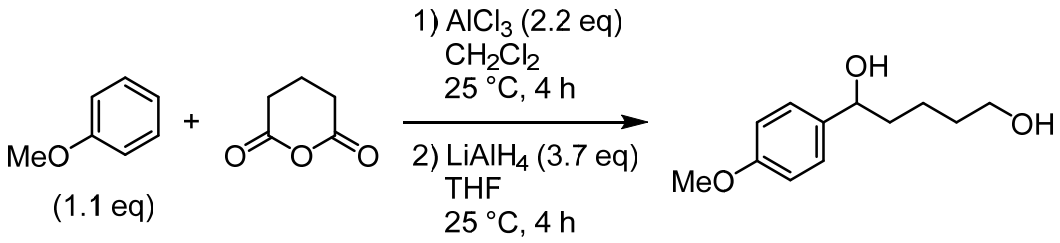

**1,1-Diphenylpentane-1,5-diol (11m):** Phenylmagnesium bromide (1.07 M in THF, 20.7 mL, 22.2 mmol) was added to a solution of $\delta$-valerolactone (0.50 mL, 555 mg, 5.5 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 12 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 1:0 → 95:5 $CH_2Cl_2$/ MeOH) to afford **11m** (664 mg, 47%) as a white solid; TLC $R_f$ = 0.45 (14:1 $CH_2Cl_2$/ MeOH); mp 78.4–81.7 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, $J$ = 7.5 Hz, 4H), 7.30 (dd, $J$ = 7.5, 7.5 Hz, 4H), 7.22 (dd, $J$ = 7.5, 7.5 Hz, 2H), 3.60 (t, $J$ = 6.3 Hz, 2H), 2.30 (t, $J$ = 8.0 Hz, 2H), 1.58 (quint, $J$ = 7.5 Hz, 2H), 1.39–1.32 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 147.1, 128.3, 127.0, 126.1, 78.4, 62.8, 41.6, 33.0, 20.2; IR (ATR): 3366, 3056, 2940, 1597, 1491, 1446, 1216, 1059, 1030 cm$^{-1}$; HRMS (DART) *m/z*: $[M+NH_4]^+$ Calcd for $C_{17}H_{24}NO_2$ 274.1807; found 274.1807.



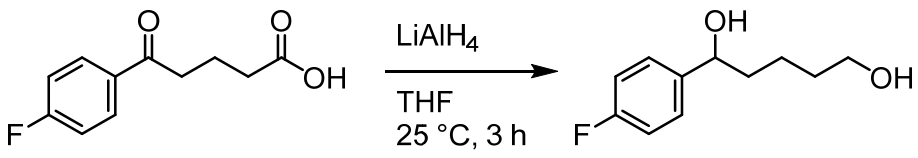

**1,1-Diphenyloctane-1,5-diol (11n):** Phenylmagnesium bromide (1.07 M in THF, 18.7 mL, 20.0 mmol) was added to a solution of δ-octanolactone (0.711 mL, 711 mg, 5.0 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 24 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 1:0 → 7:3 $CH_2Cl_2$/ EtOAc) to afford **11n** (897 mg, 60%) as a white solid; TLC $R_f$ = 0.38 (14:1 $CH_2Cl_2$/ EtOAc); mp 88.0–91.4 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, $J$ = 7.5 Hz, 4H), 7.31 (dd, $J$ =7.5, 7.5 Hz, 4H), 7.22 (dd, $J$ =7.5, 7.5 Hz, 2H), 3.60–3.55 (m, 1H), 2.35–2.25 (m, 3H), 1.50–1.28 (m, 7H), 0.90 (t, $J$ = 6.9 Hz, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ. 147.2, 128.3, 126.9, 126.1, 78.4, 71.6, 41.8, 39.8, 37.7, 20.1, 18.9, 14.2; IR (ATR): 3374, 3057, 2929, 2869, 1598, 1491, 1446, 1376, 1178, 1126, 1061, 1030 cm$^{-1}$; HRMS (DART) *m/z*: $[M+NH_4]^+$ Calcd for $C_{20}H_{30}NO_2$ 316.2277; found 316.2282.




**1-Phenylpentane-1,5-diol (11o)**[4]**:** A solution of 4-benzoylbutyric acid (961 mg, 5.0 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (569 mg, 15.0 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 5 h. The reaction was quenched by sequential addition of $H_2O$ (0.57 mL), 15% sodium hydroxide solution (0.57 mL) and $H_2O$ (1.14 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:1→0:1 hexane/$Et_2O$) to afford **11o** (772 mg, 86%) as a colorless oil; TLC $R_f$ = 0.45 (100% $Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36–7.33 (m, 4H), 7.29–7.26 (m, 1H), 4.67 (dd, $J$ = 7.5, 5.2 Hz, 1H), 3.62 (t, $J$ = 6.3 Hz, 2H), 1.86–1.79 (m, 1H), 1.76–1.69 (m, 1H), 1.60–1.46 (m, 3H), 1.41–1.32 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 144.9, 128.6, 127.7, 126.0, 74.6, 62.8, 38.8, 32.6, 22.1.

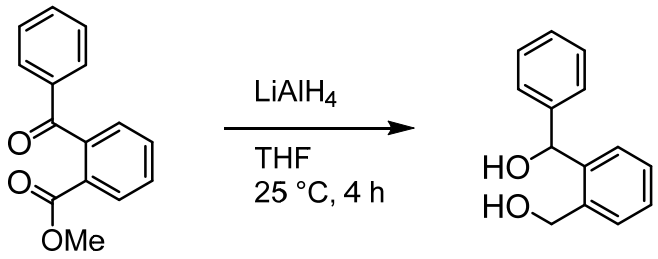



**1-(4-Methoxyphenyl)pentane-1,5-diol (11p)**[4]**:** A solution of alumimiun chloride (2.57 g, 19.3 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise to a mixture of glutaric anhydride (1.0 g, 8.8 mmol) and anisole (1.04 mL, 1.0 g, 9.7 mmol) in $CH_2Cl_2$ (25 mL) at 0 °C under argon and the mixture was stirred at 25 °C for 4 h. The reaction was quenched with 2 M potassium hydroxide solution (15 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The aqueous was acidified to pH 1–2 with aq. 2 M HCl and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated and the crude material was used directly in the next step. A solution of crude compound in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (1.23 g, 32.4 mmol) in THF (30 mL) at 0 °C and the mixture was stirred at 25 °C for 4 h. The reaction was quenched by sequential addition of $H_2O$ (1.23 mL), 15% sodium hydroxide solution (1.23 mL) and $H_2O$ (2.46 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:0→4:1 $CH_2Cl_2$/ MeOH) to afford **11p** (1.04 g, 57%) as a colorless oil; TLC $R_f$ = 0.50 (12:1 $CH_2Cl_2$/ MeOH); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, $J$ = 8.6 Hz, 2H), 6.88 (d, $J$ = 8.6 Hz, 2H), 4.62 (t, $J$ = 6.3 Hz, 1H), 3.80 (s, 3H), 3.62 (t, $J$ = 6.3 Hz, 2H), 1.85−1.79 (m, 1H), 1.74−1.69 (m, 1H), 1.62−1.56 (m, 2H), 1.52−1.43 (m, 1H), 1.38−1.29 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 159.2, 137.0, 127.3, 114.0, 74.3, 62.8, 55.4, 38.7, 32.6, 22.2.

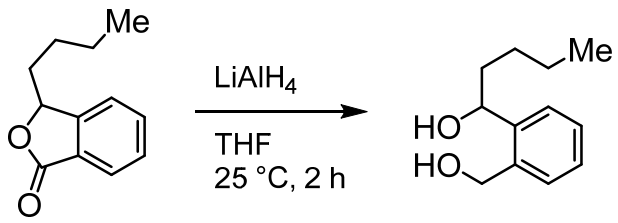



**1-(4-Fluorophenyl)pentane-1,5-diol (11q)**[4]**:** A solution of 4-(4-fluorobenzoyl)butyric acid (1.0 g, 4.8 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (542 mg, 14.3 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 3 h. The reaction was quenched by sequential addition of $H_2O$ (0.55 mL), 15% sodium hydroxide solution (0.55 mL) and $H_2O$ (1.10 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed

by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 1:1→0:1 hexane/EtOAc) to afford **11q** (832 mg, 88%) as a white solid; TLC $R_f$ = 0.28 (2:3 hexane/EtOAc); mp 70.8–72.2 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.03 (dd, $J$ = 8.6 Hz, 2H), 4.68 (t, $J$ = 6.9 Hz, 1H), 3.64 (t, $J$ = 6.3 Hz, 2H), 1.88 (br s, 1H), 1.86–1.79 (m, 1H), 1.73–1.69 (m, 1H), 1.61–1.56 (m, 2H), 1.53–1.45 (m, 1H), 1.40–1.34 (m, 1H), 1.28 (br s, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 246.3 Hz), 140.6 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.6 (d, $J_{C\text{-}F}$ = 7.2 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.7 Hz), 74.0, 62.8, 38.9, 32.5, 22.1.

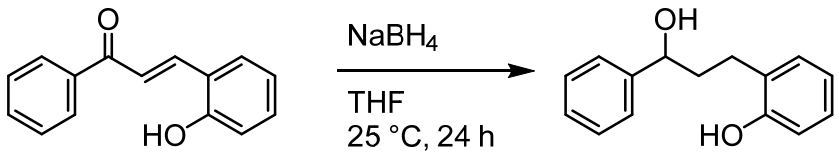



**[2-(Hydroxymethyl)phenyl](phenyl)methanol (11r)**[6]**:** A solution of methyl 2-benzoylbenzoate (1.0 g, 4.2 mmol) in THF (5 mL) was added dropwise to a mixture of lithium aluminium hydride (474 g, 12.5 mmol) in THF (10 mL) at 0 °C and the mixture was stirred at 25 °C for 4 h. The reaction was quenched by sequential addition of $H_2O$ (0.48 mL), 15% sodium hydroxide solution (0.48 mL) and $H_2O$ (0.96 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 4:1→4:6 hexane/EtOAc) to afford **11r** (859 mg, 96%) as a colorless oil; TLC $R_f$ = 0.50 (1:1 hexane/EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, $J$ = 4.6 Hz, 4H), 7.30–7.26 (m, 4H), 7.23–7.21 (m, 1H), 6.02 (s, 1H), 4.61 (d, $J$ = 12.0 Hz, 1H), 4.46 (d, $J$ = 12.0 Hz, 1H), 3.86 (br s, 1H), 2.98 (br s, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 142.7, 142.4, 138.6, 130.4, 129.0, 128.5, 128.5, 128.4, 127.5, 126.6, 74.4, 63.9.



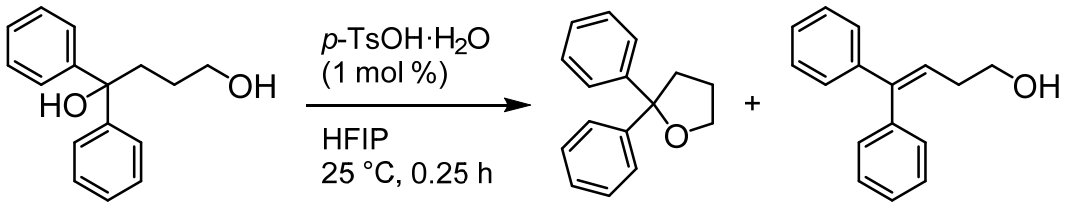

**1-[2-Hydroxymethyl)phenyl]pentan-1-ol (11s):** A solution of butylphthalide (0.533 mL, 571 mg, 3.0 mmol) in THF (10 mL) was added dropwise to a mixture of lithium aluminium hydride (171 mg, 4.5

mmol) in THF (20 mL) at 0 °C and the mixture was stirred at 25 °C for 2 h. The reaction was quenched by sequential addition of $H_2O$ (0.17 mL), 15% sodium hydroxide solution (0.17 mL) and $H_2O$ (0.34 mL) at 0 °C. The whole was filtered through a Celite pad and the precipitate was washed by EtOAc (3 × 10 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 4:1→1:1 hexane/EtOAc) to afford **11s** (537 mg, 92%) as a colorless oil; TLC $R_f$ = 0.45 (1:1 hexane/EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 7.5 Hz, 1H), 7.35−7.33 (m, 2H), 7.29 (d, $J$ = 7.5 Hz, 1H), 4.94 (t, $J$ = 6.9 Hz, 1H), 4.79 (d, $J$ = 12.0 Hz, 1H), 4.69 (d, $J$ = 12.0 Hz, 1H), 2.60 (br s, 2H), 1.95−1.88 (m, 1H), 1.86−1.79 (m, 1H), 1.52−1.45 (m, 1H), 1.40−1.28 (m, 3H), 0.91 (t, $J$ = 7.5 Hz, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 142.8, 138.3, 129.9, 128.6, 127.9, 126.7, 71.8, 63.8, 36.9, 28.6, 22.8, 14.2; IR (ATR): 3327, 2934, 1616, 1411, 1322, 1161, 1119, 1068 cm$^{-1}$; HRMS (DART) *m/z*: $[M+NH_4]^+$ Calcd for $C_{12}H_{22}NO_2$ 212.1651; found 212.1653.



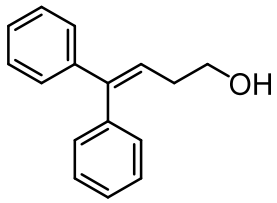

**2-(3-Hydroxy-3-phenylpropyl)phenol (11t)**[7]**:** Sodium borohydride (506 mg, 13.4 mmol) was added to a solution of (*E*)-2-hydroxychalcone (1.00 g, 4.5 mmol) in THF (20 mL) at 0 °C and the mixture was stirred at 25 °C for 24 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (10 mL) at 0 °C and the whole mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with $H_2O$ (10 mL) and brine (2 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 $CH_2Cl_2$/EtOAc) to afford **11t** (703 mg, 70%) as a pale yellow solid; TLC $R_f$ = 0.35 (8:1 $CH_2Cl_2$/ EtOAc); mp 91.9–93.5 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.33−7.25 (m, 5H), 7.13−7.09 (m, 2H), 6.88−6.83 (m, 2H), 4.60 (dd, $J$ = 10.3, 3.4 Hz, 1H), 2.97−2.91 (m, 1H), 2.75−2.70 (m, 1H), 2.13−2.06 (m, 1H), 1.97−1.90 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 154.7, 144.0, 130.7, 128.7, 128.0, 127.8, 127.3, 125.9, 120.9, 116.4, 73.1, 39.5, 26.1.

**Representative procedure for the intramolecular dehydrative etherification of diols:**

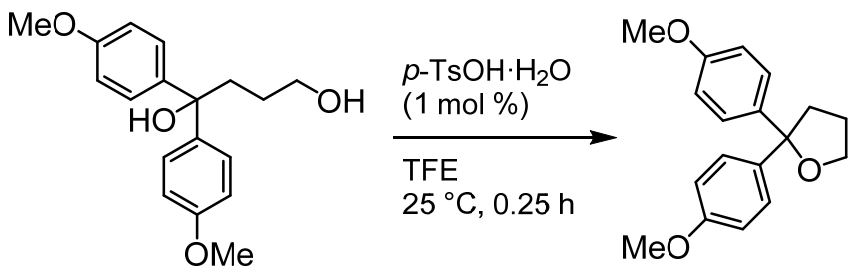



**Brønsted Acid-Catalyzed Intramolecular Dehydrative Etherification of 1,1-Diphenylbutane-1,4-diol (11a) (Entry 1 in Table 1).**

**2,2-Diphenyltetrahydrofuran (12a)**[8]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 1,1,1,3,3,3-hexafluoropropan-2-ol (0.1 mL) was added to a stirred solution of **11a** (48.5 mg, 0.20 mmol) in 1,1,1,3,3,3-hexafluoropropan-2-ol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.25 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 0:1 hexane/ $CH_2Cl_2$) to afford **12a** (42 mg, 94%) as a white solid and **13a** (2.2 mg, 5%); TLC $R_f$ = 0.20 (4:1 hexane/ $CH_2Cl_2$); mp 72.0–73.0 °C;$^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 7.5 Hz, 4H), 7.28 (dd, $J$ = 7.5, 7.5 Hz, 4H), 7.20–7.17 (m, 2H), 4.05 (t, $J$ = 7.5 Hz, 2H), 2.56 (t, $J$ = 7.5 Hz, 2H), 1.94 (quint, $J$ = 7.5 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 146.5, 128.3, 126.8, 126.0, 88.2, 67.5, 38.7, 25.6.

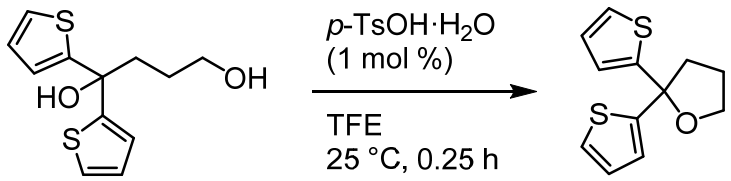



**4,4-Diphenylbut-3-en-1-ol (13a)**[9]**:** TLC $R_f$ = 0.25 (100% $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.33–7.22 (m, 6H), 7.21–7.18 (m, 2H), 6.12 (t, $J$ = 7.5 Hz, 1H), 3.79 (br s, 2H), 2.41 (q, $J$ = 7.5 Hz, 2H), 1.32 (br s, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 144.5, 142.5, 140.0, 130.0, 128.4, 128.3, 127.4, 127.3, 127.2, 125.3, 62.8, 33.5.

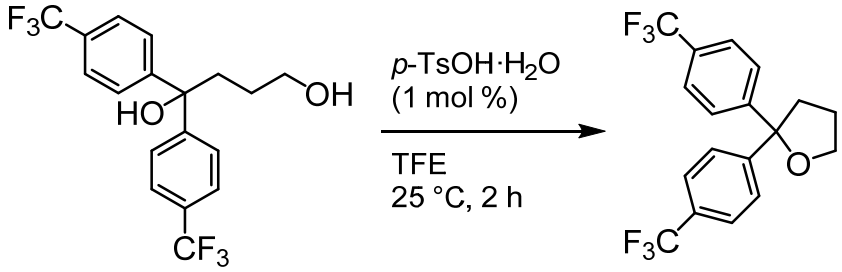



**2,2-Bis(4-methoxyphenyl)tetrahydrofuran (12b)**[10]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002

mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11b** (61.7 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.25 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:1 → 0:1 hexane/ $Et_2O$) to afford **12b** (43 mg, 97%) as a white solid; TLC $R_f$ = 0.45 (100% $Et_2O$); mp 64.6–66.0 °C;$^1$H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, $J$ = 9.2 Hz, 4H), 6.82 (d, $J$ = 9.2 Hz, 4H), 4.02 (t, $J$ = 7.5 Hz, 2H), 3.77 (s, 6H), 2.49 (t, $J$ = 6.9 Hz, 2H), 1.94 (quint, $J$ = 6.9 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 158.4, 138.9, 127.2, 113.6, 87.6, 67.4, 55.4, 38.9, 25.7.

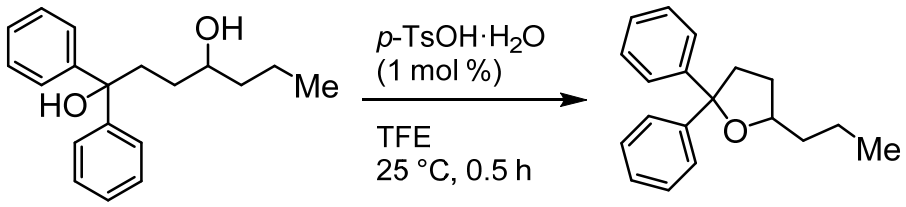



**2,2-Di(thiophen-2-yl)tetrahydrofuran (12c)**[11]**:** A solution of $p$-TsOH·$H_2O$ (0.40 mg, 0.0021 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11c** (53.5 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.25 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 2:1 hexane/ EtOAc) to afford **12c** (47 mg, 95%) as a white solid; TLC $R_f$ = 0.55 (4:1 hexane/ EtOAc); mp 55.8–58.2 °C;$^1$H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, $J$ = 5.2, 1.7 Hz, 2H), 6.93–6.91 (m, 4H), 4.12 (t, $J$ = 6.9 H, 2H), 2.61 (t, $J$ = 6.9 H, 2H), 2.08 (quint, $J$ = 6.9 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 150.8, 126.7, 124.8, 124.1, 84.7, 68.5, 42.6, 26.3.

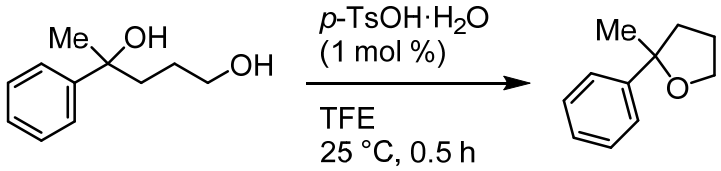



**2,2-Bis(4-(trifluoromethyl)phenyl)tetrahydrofuran (12d):** A solution of $p$-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11d** (77.0 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 2 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 1:1 hexane/ $CH_2Cl_2$) to afford **12d** (15.7 mg, 21%) as a colorless oil; TLC $R_f$ = 0.35 (4:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 8H), 4.07 (t, $J$ = 7.2 Hz, 2H), 2.59 (t, $J$ = 7.2 Hz, 2H), 1.98 (quint, $J$ = 7.2 Hz, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ

149.7, 129.4 (q, $J_{C\text{-}F}$ = 32.6 Hz), 126.2, 125.5 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.2 (q, $J_{C\text{-}F}$ = 271.6 Hz), 87.5 67.9, 38.7, 25.5; IR (ATR): 2931, 1617, 1411, 1321, 1161, 1115, 1066, 1015 $cm^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{15}F_6O$ 361.1027; found 361.1031.

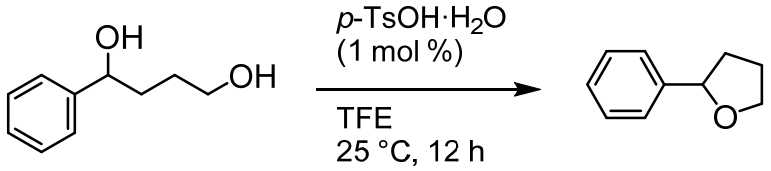



**2,2-Diphenyl-5-propyltetrahydrofuran (12e):** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11e** (57.0 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ EtOAc) to afford **12e** (42.2 mg, 93%) as a colorless oil; TLC $R_f$ = 0.50 (4:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.30–7.24 (m, 4H), 7.19–7.14 (m, 2H), 4.10 (quint, *J* = 6.9 Hz, 1H), 2.67–2.61 (m, 1H), 2.52–2.47 (m, 1H), 2.01–1.95 (m, 1H), 1.77–1.71 (m, 1H), 1.65–1.57 (m, 1H), 1.52–1.46 (m, 2H), 1.43–1.37 (m, 1H), 0.96 (t, *J* = 6.9 Hz, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 147.6, 146.9, 128.2, 128.1, 126.6, 126.7, 126.0, 125.9, 87.8, 79.0, 39.1, 38.6, 31.5, 19.6, 14.4; IR (ATR): 2956, 2870, 1598, 1489, 1446, 1377, 1226, 1182, 1024 $cm^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{23}O$ 267.1749; found 267.1751.

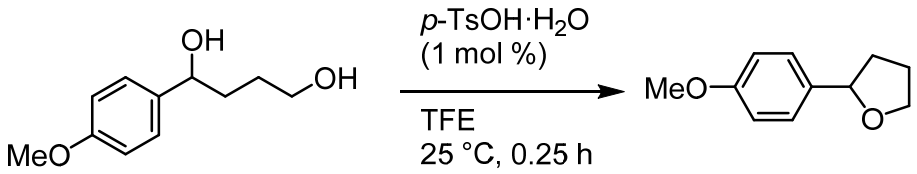



**2-Methyl-2-phenyltetrahydrofuran (12f)**[12]**:** A solution of *p*-TsOH·$H_2O$ (0.41 mg, 0.0022 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11f** (38.9 mg, 0.22 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ EtOAc) to afford **12f** (30.8 mg, 88%) as a colorless oil; TLC $R_f$ = 0.50 (4:1 hexane/ EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.21 (dd, *J* = 8.0, 8.0Hz, 1H), 4.01 (q, *J* = 7.5 Hz, 1H), 3.93–3.89 (m, 1H), 2.23–2.19 (m, 1H), 2.04–1.95 (m, 2H), 1.83–1.78 (m, 1H), 1.53 (s, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 148.3, 128.2,

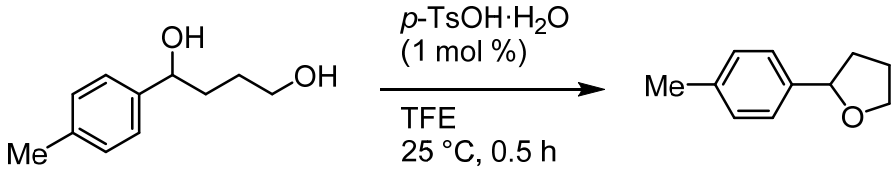
126.5, 124.8, 84.4, 67.7, 39.6, 29.8, 25.9.



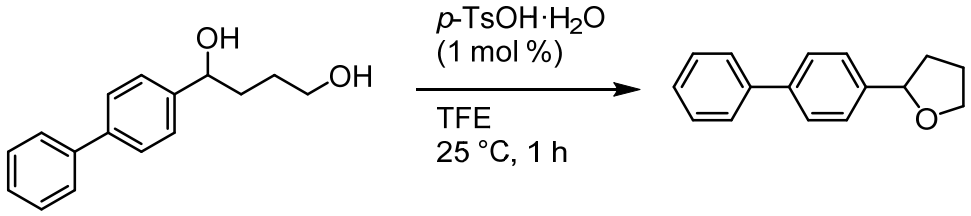

**2-Phenyltetrahydrofuran (12g)**[13]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11g** (33.3 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 12 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 1:2 hexane/ $CH_2Cl_2$) to afford **12g** (28.7 mg, 97%) as a colorless oil; TLC $R_f$ = 0.45 (1:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.33–7.32 (m, 4H), 7.26–7.23 (m, 1H), 4.89 (t, *J* = 6.9 Hz, 1H), 4.10 (q, *J* = 6.9 Hz, 1H), 3.93 (q, *J* = 6.9 Hz, 1H), 2.32 (sext, *J* = 6.9 Hz, 1H), 2.04–1.97 (m, 2H), 1.84–1.77 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 143.6, 128.4, 127.2, 125.8, 80.8, 68.8, 34.7, 26.2.



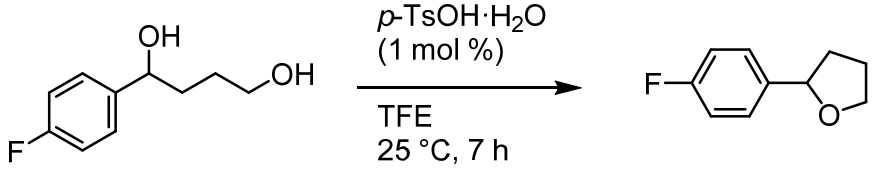

**2-(4-Methoxyphenyl)tetrahydrofuran (12h)**[3]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11h** (40.3 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.25 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:1 → 0:1 hexane/ $CH_2Cl_2$) to afford **12h** (35.9 mg, 98%) as a colorless oil; TLC $R_f$ = 0.45 (100% $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.82 (t, *J* = 6.9 Hz, 1H), 4.07 (q, *J* = 6.9 Hz, 1H), 3.90 (q, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 2.27 (sext, *J* = 6.9 Hz, 1H), 2.06–1.94 (m, 2H), 1.82–1.75 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 158.9, 135.5, 127.1, 113.8, 80.6, 68.6, 55.4, 34.6, 26.2.




**2-(*p*-Tolyl)tetrahydrofuran (12i)**[3]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11i** (41.5 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 4:1 → 1:1 hexane/ $CH_2Cl_2$) to afford **12i** (25.2 mg, 74%) as a colorless oil; TLC $R_f$ = 0.40 (1:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, $J$ = 8.0 Hz, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H), 4.85 (t, $J$ = 7.5 Hz, 1H), 4.08 (q, $J$ = 7.5 Hz, 1H), 3.91 (q, $J$ = 7.5 Hz, 1H), 2.33 (s, 3H), 2.29 (sext, $J$ = 7.5 Hz, 1H), 2.04–1.95 (m, 2H), 1.82–1.75 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 140.5, 136.8, 129.1, 125.7, 80.7, 68.7, 34.7, 26.2, 21.2.

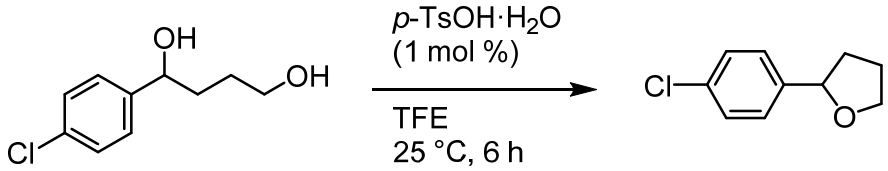



**2-[(1,1'-Biphenyl)-4-yl]tetrahydrofuran (12j)**[14]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11j** (51.2 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 1 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 1:1 hexane/ $CH_2Cl_2$) to afford **12j** (43.2 mg, 91%) as a colorless oil; TLC $R_f$ = 0.20 (4:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.58–7.55 (m, 4H), 7.44–7.40 (m, 4H), 7.32 (dd, $J$ = 7.5, 7.5 Hz, 1H), 4.93 (t, $J$ = 7.5 Hz, 1H), 4.11 (q, $J$ = 7.5 Hz, 1H), 3.95 (q, $J$ = 7.5 Hz, 1H), 2.33 (sext, $J$ = 7.5 Hz, 1H), 2.07–1.97 (m, 2H), 1.88–1.80 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 142.7, 141.1, 140.2, 128.8, 127.3, 127.2, 127.2, 126.2, 80.6, 68.8, 34.7, 26.2.

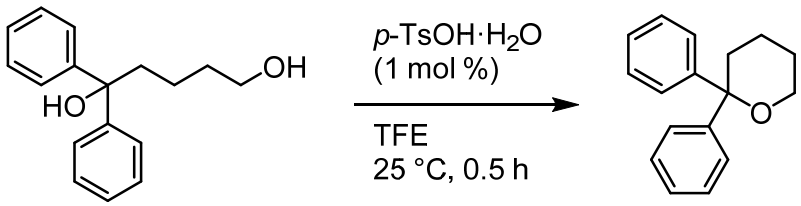



**2-(4-Fluorophenyl)tetrahydrofuran (12k)**[13]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in

2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11k** (37.2 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 7 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 4:1 → 1:4 hexane/ $CH_2Cl_2$) to afford **12k** (27.8 mg, 83%) as a colorless oil; TLC $R_f$ = 0.40 (1:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, $J$ = 8.6, 5.7 Hz, 2H), 7.01 (dd, $J$ = 8.6, 8.6 Hz, 2H), 4.85 (t, $J$ = 7.5 Hz, 1H), 4.09 (q, $J$ = 7.5 Hz, 1H), 3.92 (q, $J$ = 7.5 Hz, 1H), 2.30 (sext, $J$ = 7.5 Hz, 1H), 2.05−1.97 (m, 2H), 1.80−1.72 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 162.1 (d, $J_{C\text{-}F}$ = 245.1 Hz), 139.2 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.4 (d, $J_{C\text{-}F}$ = 8.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.7 Hz), 80.3, 68.8, 34.8, 26.1.

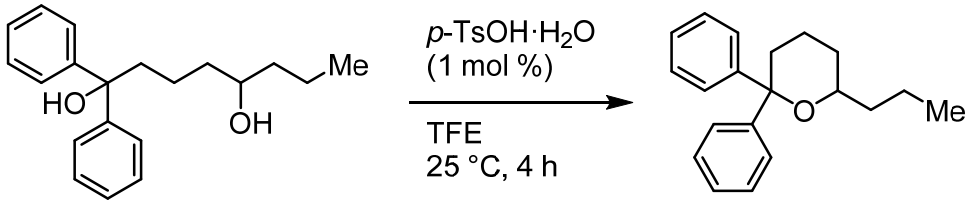



**2-(4-Chlorophenyl)tetrahydrofuran (12l)**[3]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11l** (41.2 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 6 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 2:1 hexane/ $CH_2Cl_2$) to afford **12l** (31.7 mg, 85%) as a colorless oil; TLC $R_f$ = 0.35 (4:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.30−7.25 (m, 4H), 4.86 (t, $J$ = 7.5 Hz, 1H), 4.08 (q, $J$ = 7.5 Hz, 1H), 3.93 (q, $J$ = 7.5 Hz, 1H), 2.31 (sext, $J$ = 7.5 Hz, 1H), 2.00 (quint, $J$ = 7.5 Hz, 2H), 1.78−1.71 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 142.2, 132.9, 128.5, 127.1, 80.1, 68.9, 34.8, 26.1.

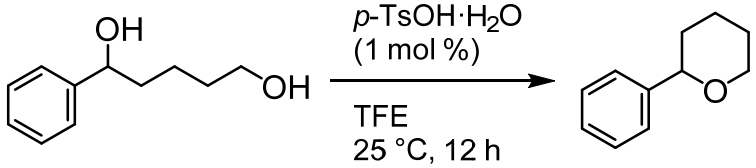



**2,2-Diphenyltetrahydro-2*H*-pyran (12m):** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11m** (51.8 mg, 0.200 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ EtOAc) to afford **12m** (45.4 mg, 94%) as a yellow solid; TLC $R_f$ = 0.50 (9:1

hexane/ EtOAc); mp 44.0–44.3 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, $J$ = 7.5 Hz, 4H), 7.30 (dd, $J$ = 7.5, 7.5 Hz, 4H), 7.18 (dd, $J$ = 7.5, 7.5 Hz, 2H), 3.17 (t, $J$ = 5.2 Hz, 2H), 2.30 (t, $J$ = 6.0 Hz, 2H), 1.75–1.71 (m, 2H), 1.63–1.58 (m, 2H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 146.2, 128.4, 126.6, 126.5, 79.9, 63.1, 35.7, 26.1, 20.7; IR (ATR): 2935, 2861, 1596, 1489, 1446, 1376, 1290, 1213, 1181, 1162, 1078, 1057, 1037, 1020 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}O$ 239.1436; found 239.1431.

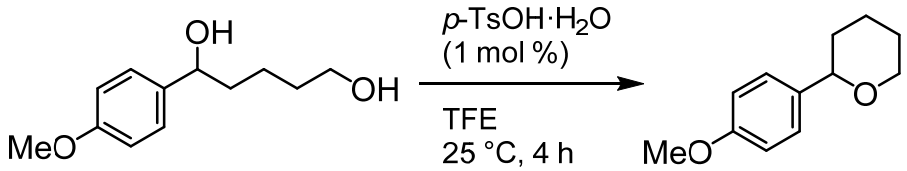



**2,2-Diphenyl-6-propyltetrahydro-2*H*-pyran (12n):** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11n** (61.5 mg, 0.21 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 4 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 9:1 hexane/ $CH_2Cl_2$) to afford **12n** (44.6 mg, 77%) as a colorless oil; TLC $R_f$ = 0.70 (9:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, $J$ = 8.6 Hz, 2H), 7.37–7.32 (m, 4H), 7.23–7.19 (m, 3H), 7.10 (dd, $J$ = 6.9, 6.9 Hz, 1H), 3.44–3.40 (m, 1H), 2.73–2.70 (m, 1H), 1.80–1.60 (m, 5H), 1.48–1.29 (m, 4H), 0.93 (t, $J$ = 6.9 Hz, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 149.9, 143.8, 128.6, 128.0, 127.7, 126.7, 126.2, 125.0, 79.7, 71.1, 39.3, 35.2, 31.7, 21.0, 18.9, 14.5; IR (ATR): 2932, 2864, 1597, 1490, 1446, 1378, 1273, 1213, 1180, 1119, 1087, 1043 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{25}O$ 281.1905; found 281.1905.

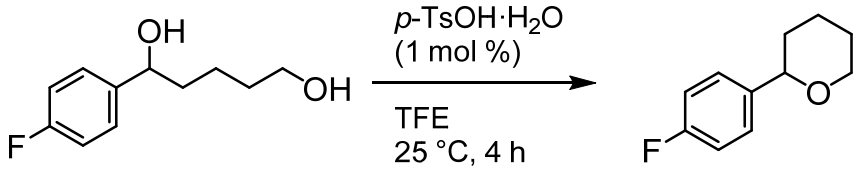



**2-Phenyltetrahydro-2*H*-pyran (12o)**[13]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11o** (39.1 mg, 0.22 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 12 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ EtOAc) to afford **12o** (33.7 mg, 96%) as a colorless oil; TLC $R_f$ = 0.40 (4:1 hexane/ EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.27–7.23 (m, 1H), 4.32 (dd, $J$ =

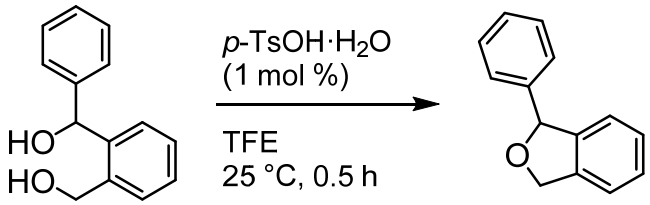
11.5, 2.3 Hz, 1H), 4.16–4.13 (m, 1H), 3.62 (ddd, $J$ = 11.5, 11.5, 2.3 Hz, 1H), 1.96–1.93 (m, 1H), 1.85–1.82 (m, 1H), 1.72–1.59 (m, 4H); $^{13}$C {$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 143.5, 128.4, 127.4, 126.0, 80.3, 69.2, 34.2, 26.0, 24.2.



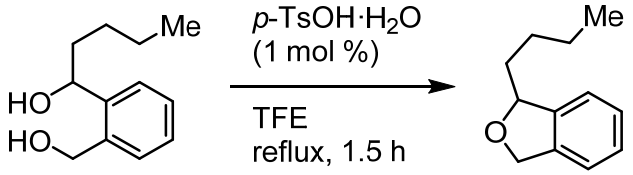

**2-(4-Methoxyphenyl)tetrahydro-2*H*-pyran (12p)**[15]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11p** (42.3 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 4 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ EtOAc) to afford **12p** (36.3 mg, 94%) as a colorless oil; TLC $R_f$ = 0.35 (4:1 hexane/ EtOAc); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, $J$ = 8.6 Hz, 2H), 6.87 (d, $J$ = 8.6 Hz, 2H), 4.28 (d, $J$ = 10.9 Hz, 1H), 4.13–4.11 (m, 1H), 3.79 (s, 3H), 3.60 (dd, $J$ = 11.5, 11.5 Hz, 1H), 1.94–1.92 (m, 1H), 1.81–1.78 (m, 1H), 1.71–1.56 (m, 4H); $^{13}$C {$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 158.9, 135.8, 127.3, 113.8, 79.9, 69.2, 55.4, 33.9, 26.0, 24.2.



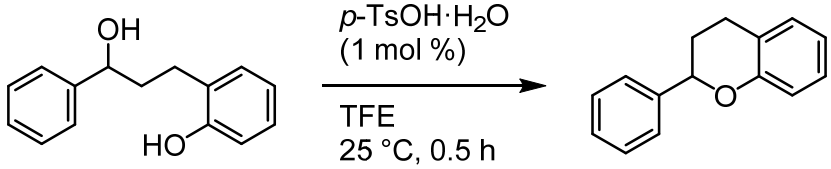

**2-(4-Fluorophenyl)tetrahydro-2*H*-pyran (12q)**[16]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11q** (39.7 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 4 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 3:7 hexane/ $CH_2Cl_2$) to afford **12q** (7.7 mg, 21%) as a colorless oil; TLC $R_f$ = 0.60 (4:1 hexane/ EtOAc); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, $J$ = 8.6, 5.2 Hz, 2H), 7.01 (dd, $J$ = 8.6, 8.6 Hz, 2H), 4.30 (dd, $J$ = 10.9, 1.7 Hz, 1H), 4.14–4.12 (m, 1H), 3.61 (ddd, $J$ = 11.5, 11.5, 2.3 Hz, 1H), 1.96–1.93 (m, 1H), 1.82–1.80 (m, 1H), 1.71–1.52 (m, 4H); $^{13}$C {$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 245.1 Hz), 139.3 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.6 (d, $J_{C\text{-}F}$ = 8.5 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.7 Hz), 79.6, 69.2, 34.2, 26.0, 24.1.




**1-Phenyl-1,3-dihydroisobenzofuran (12r)**[17]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11r** (46.0 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 4:1 → 1:1 hexane/ $CH_2Cl_2$) to afford **12r** (35.5 mg, 84%) as a yellow oil; TLC $R_f$ = 0.30 (3:1 hexane/ EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36–7.32 (m, 4H), 7.30–7.27 (m, 3H), 7.23–7.21 (m, 1H), 7.03 (d, $J$ = 7.5 Hz, 1H), 6.16 (s, 1H), 5.34 (d, $J$ = 12.0 Hz, 1H), 5.20 (d, $J$ = 12.0 Hz, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 142.3, 142.1, 139.2, 128.7, 128.2, 127.7, 127.6, 127.1, 122.4, 121.0, 86.3, 73.4.




**1-Butyl-1,3-dihydroisobenzofuran (12s)**[18]**:** A solution of *p*-TsOH·$H_2O$ (0.41 mg, 0.0022 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11s** (41.7 mg, 0.22 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred under reflux for 1.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ EtOAc) to afford **12s** (33.5 mg, 88%) as a colorless oil; TLC $R_f$ = 0.55 (4:1 hexane/ EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 2H), 7.23–7.21 (m, 1H), 7.19–7.16 (m, 1H), 5.24–5.23 (m, 1H), 5.12 (dd, $J$ = 12.0, 2.3 Hz, 1H), 5.06 (dd, $J$ = 12.0 Hz, 1H), 1.90–1.84 (m, 1H), 1.74–1.67 (m, 1H), 1.49–1.33 (m, 4H), 0.91 (t, $J$ = 7.5 Hz, 3H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 142.4, 139.6, 127.4, 127.3, 121.2, 121.1, 84.1, 72.6, 36.2, 27.5, 22.9, 14.2.



**2-phenylchromane (12t)** [19]**:** A solution of *p*-TsOH·$H_2O$ (0.38 mg, 0.002 mmol) in 2,2,2-trifluoroethanol (0.1 mL) was added to a stirred solution of **11t** (45.3 mg, 0.20 mmol) in 2,2,2-trifluoroethanol (2.0 mL) at 25 °C. The mixture was stirred at the same temperature for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:0 → 4:1 hexane/ $CH_2Cl_2$) to afford **12t** (35.1 mg, 83%) as a colorless oil; TLC $R_f$ = 0.30 (9:1 hexane/ $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43−7.36 (m, 4H), 7.31 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.12 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.87 (dd, *J* = 7.5, 7.5 Hz, 1H), 5.05 (dd, *J* = 9.7, 2.3 Hz, 1H), 3.02−2.95 (m, 1H), 2.81−2.76 (m, 1H), 2.23−2.18 (m, 1H), 2.12−2.04 (m, 1H); $^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$) δ 155.2, 141.9, 129.7, 128.6, 128.0, 127.5, 126.1, 122.0, 120.4, 117.1, 77.9, 30.1, 25.2.

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## 2. Copies of $^{1}H$ and $^{13}C$ NMR Spectra

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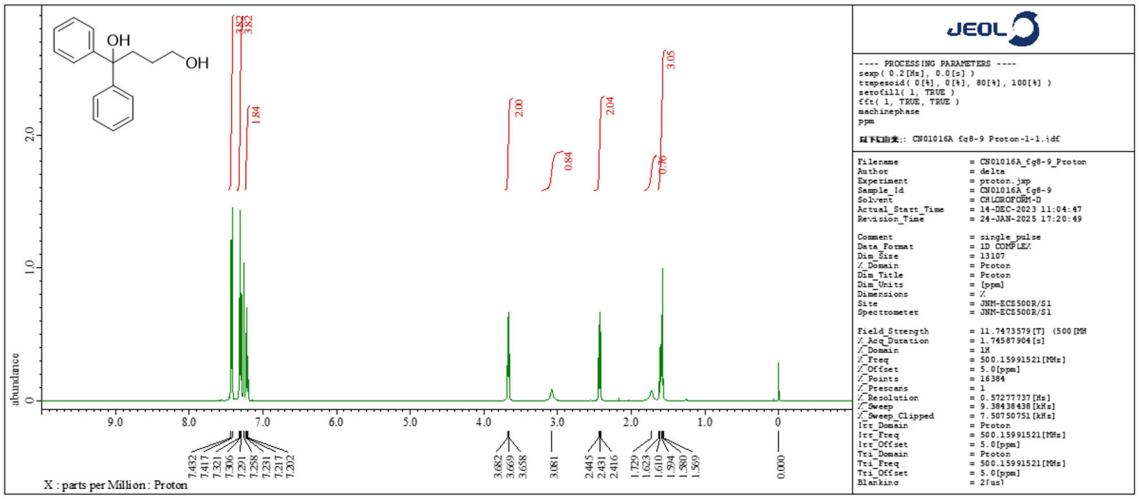


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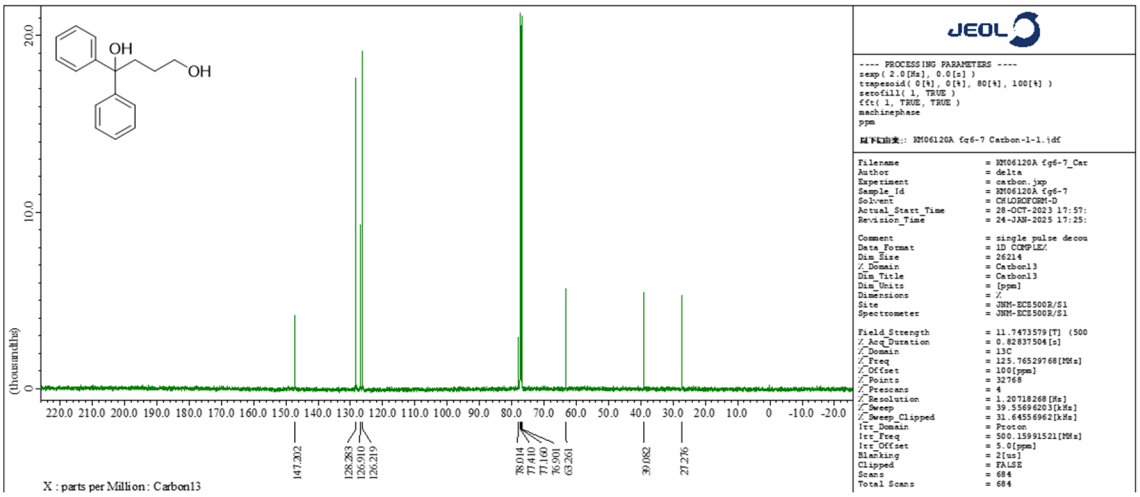


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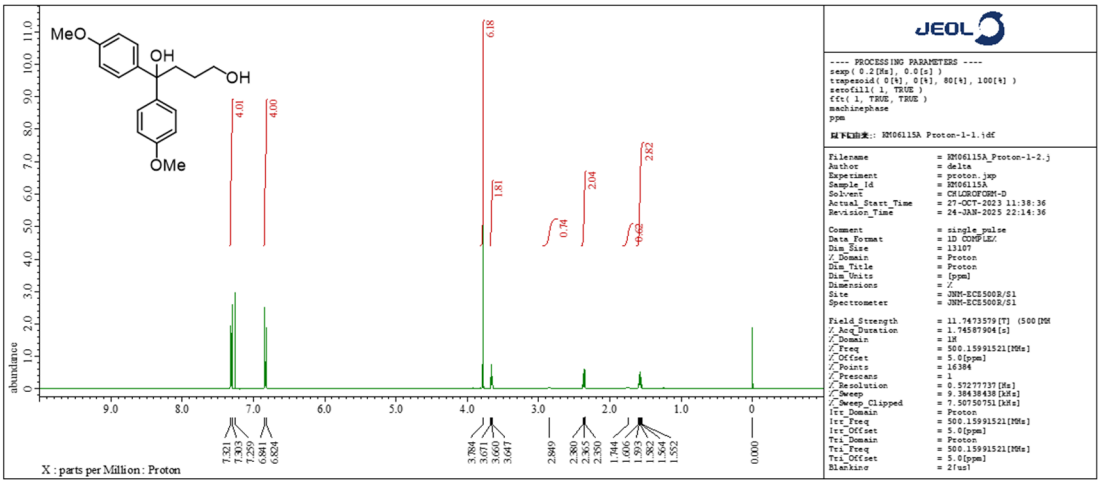

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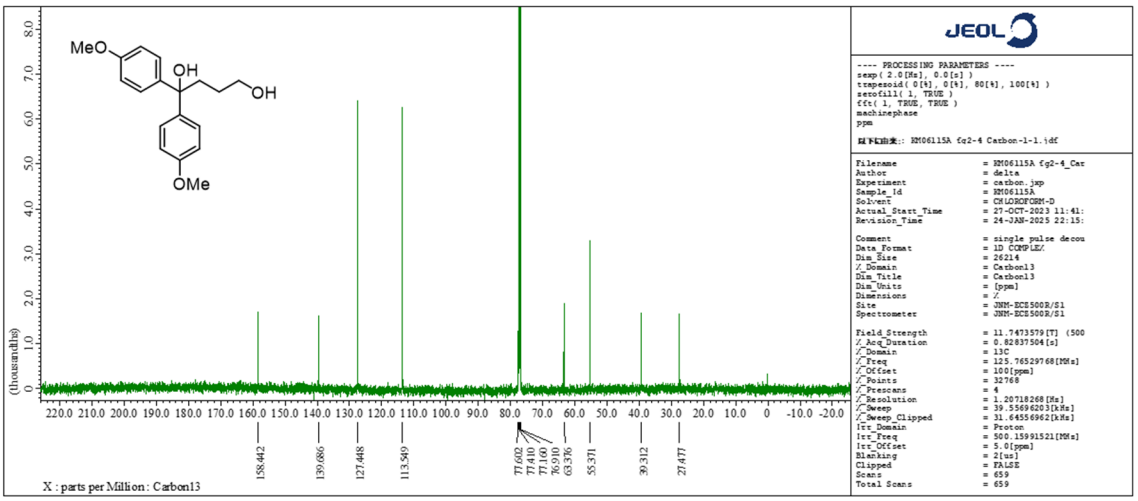


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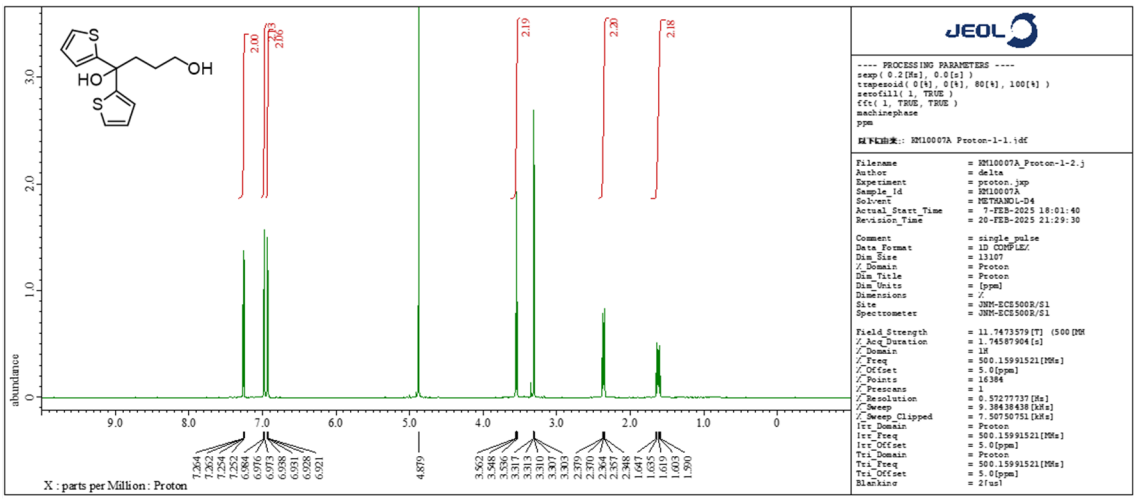


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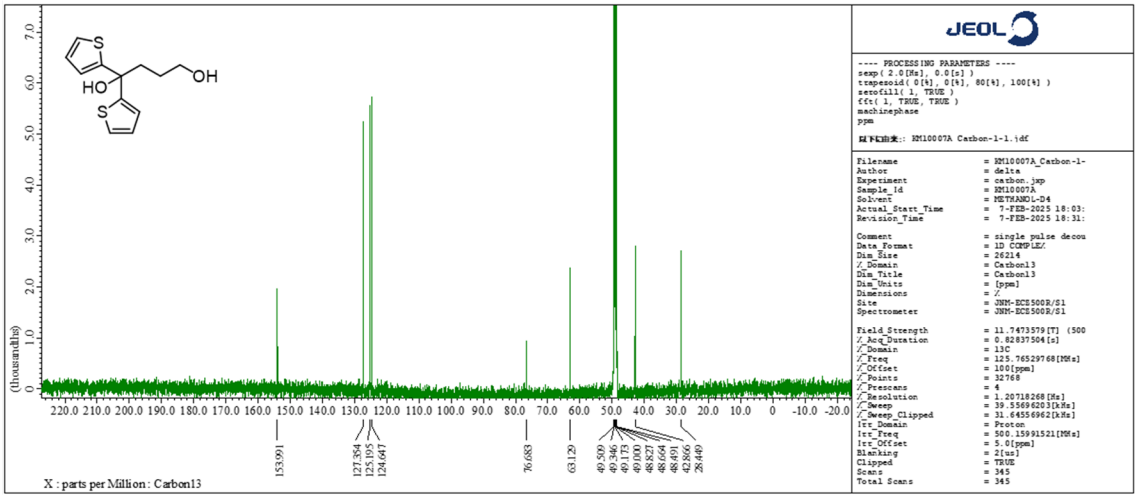

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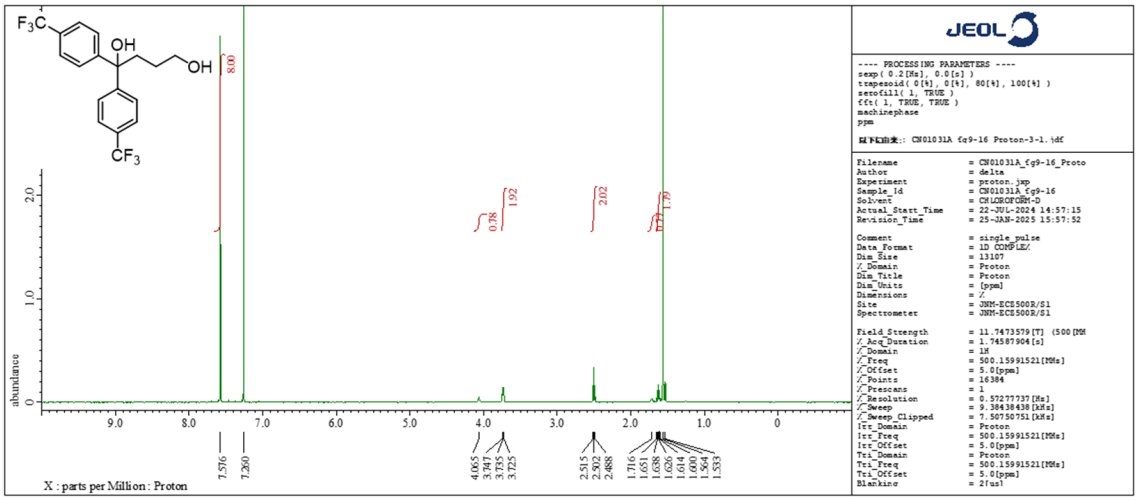

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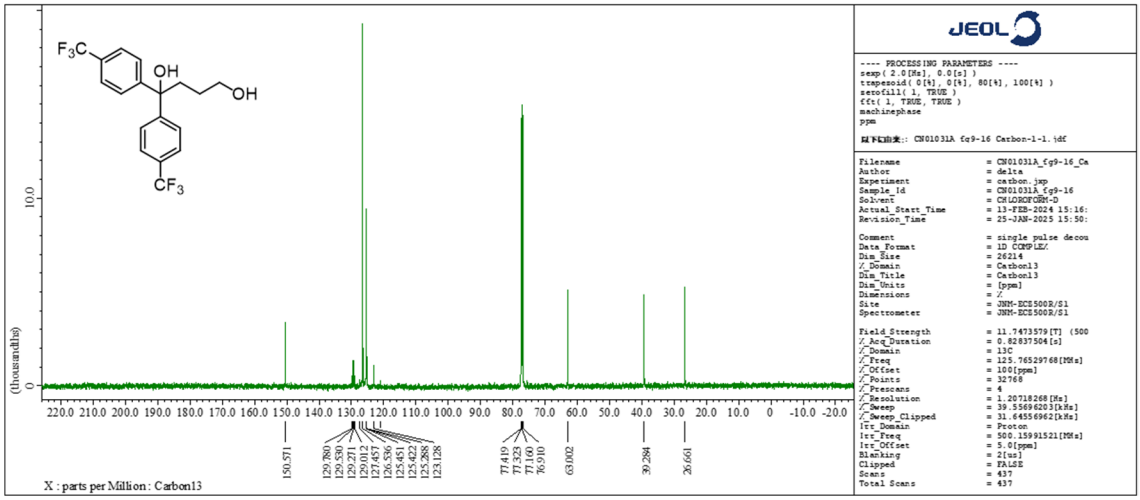

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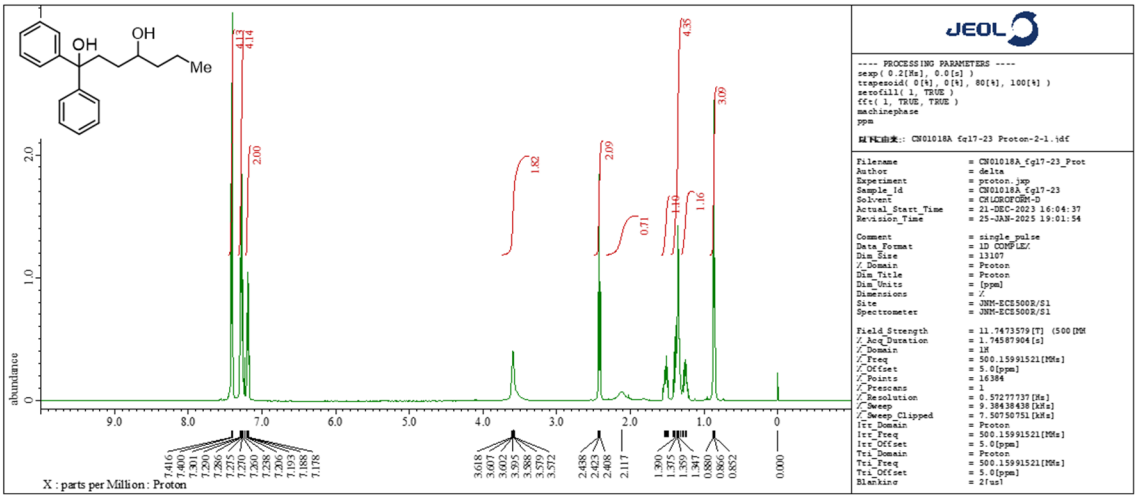

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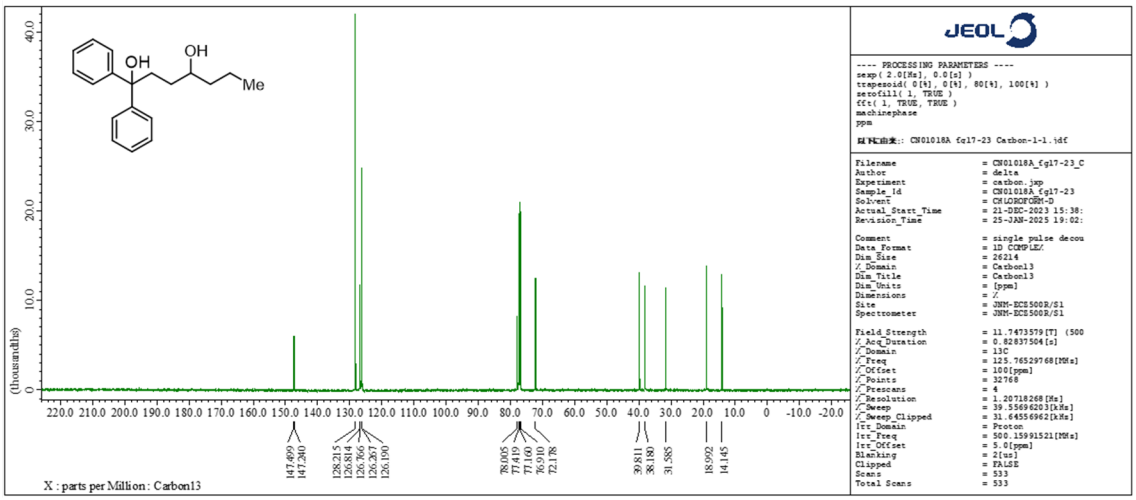


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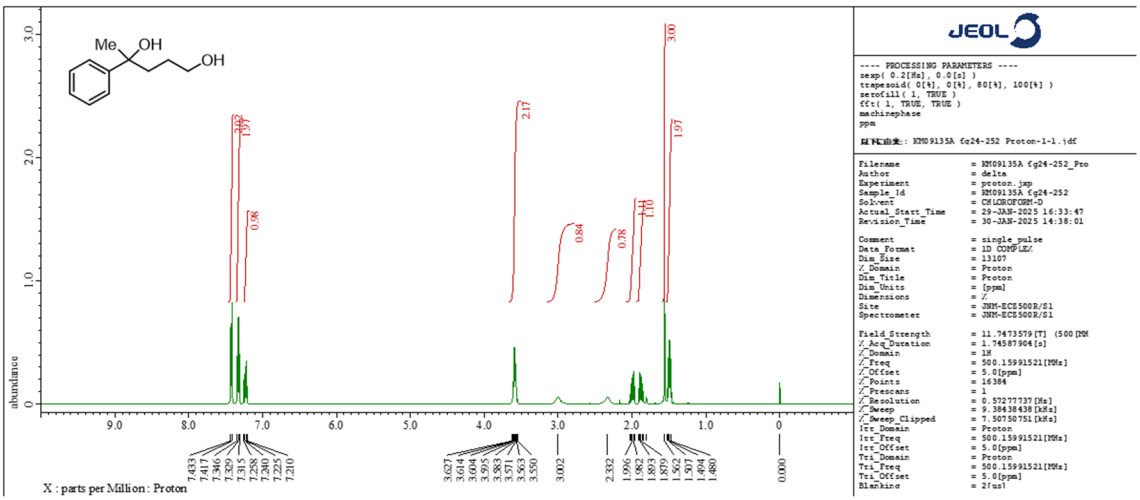


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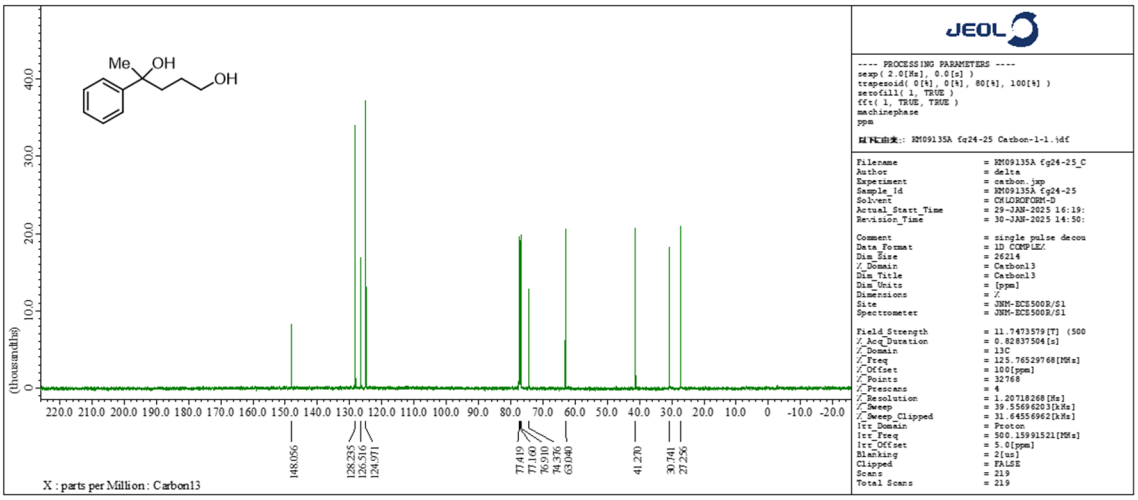

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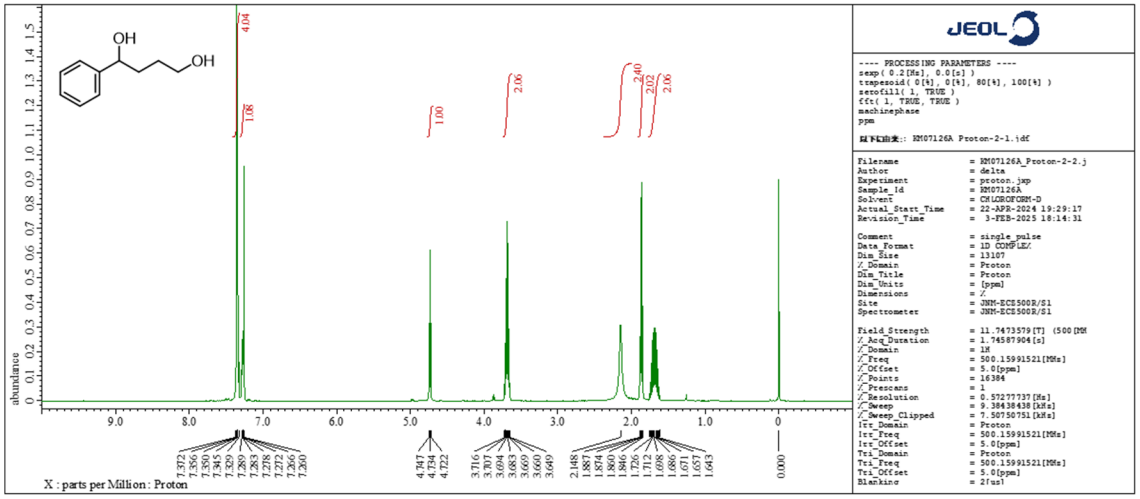

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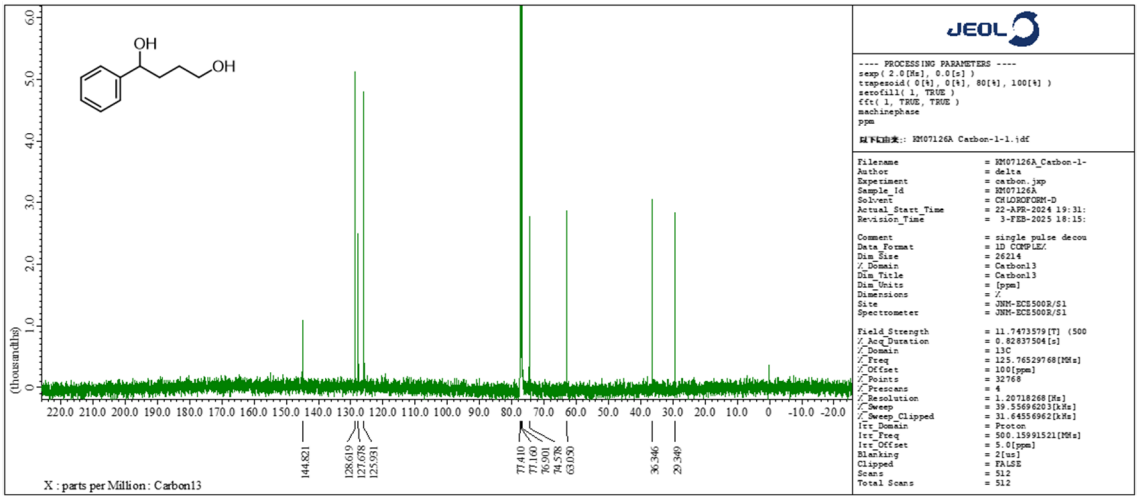

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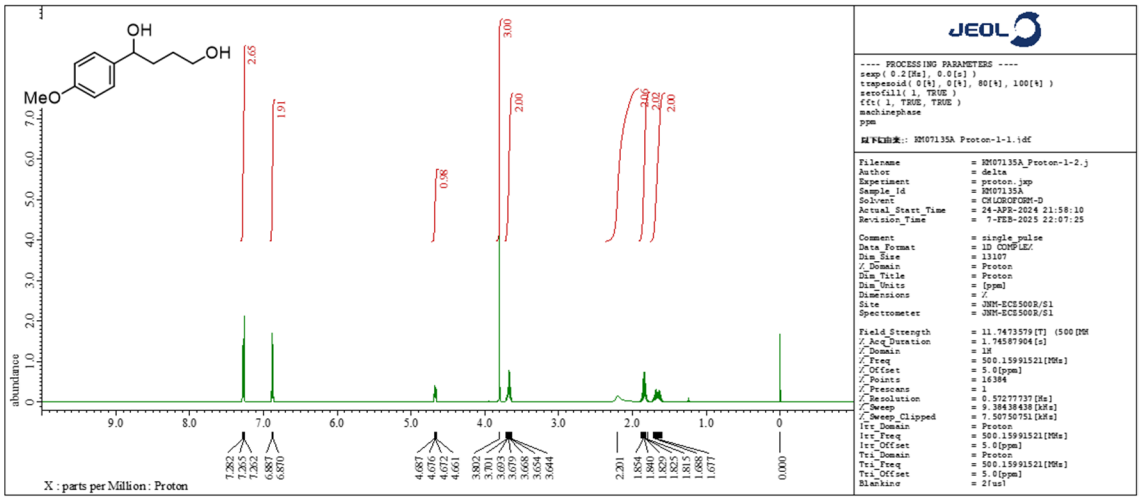

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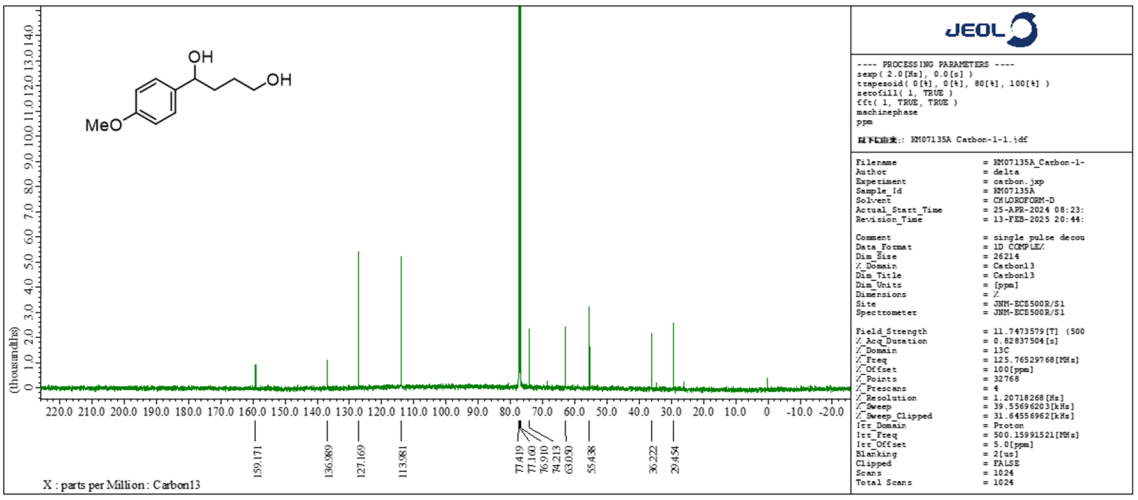


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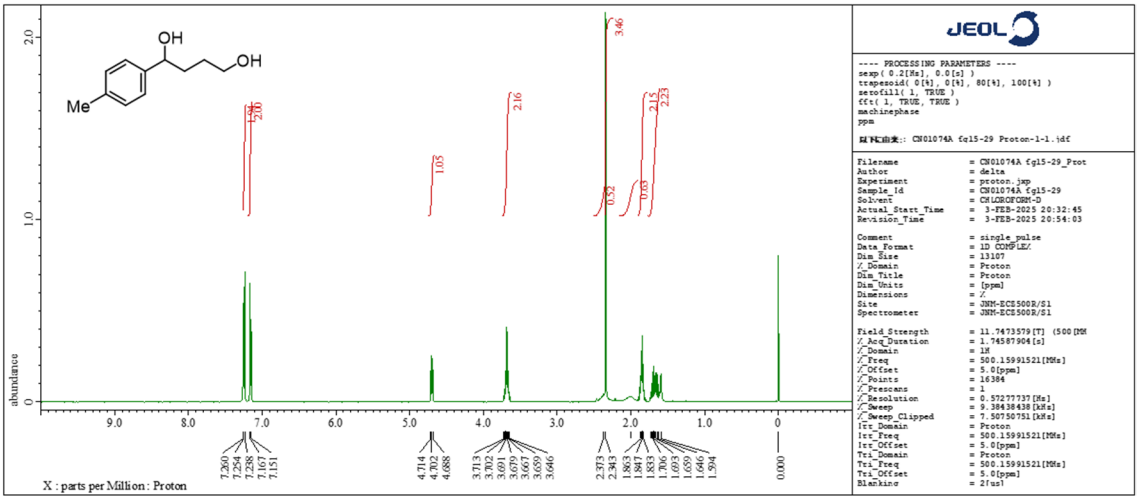


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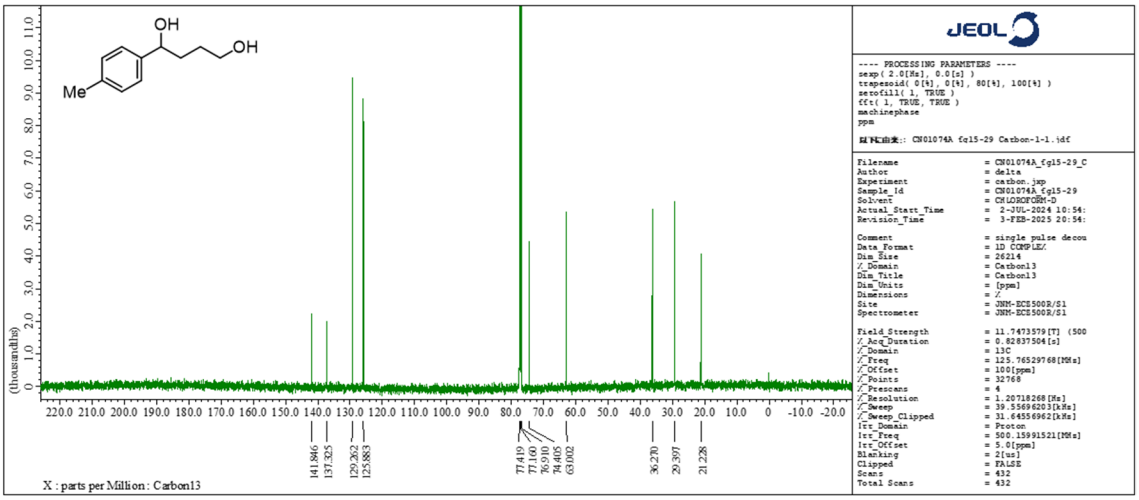

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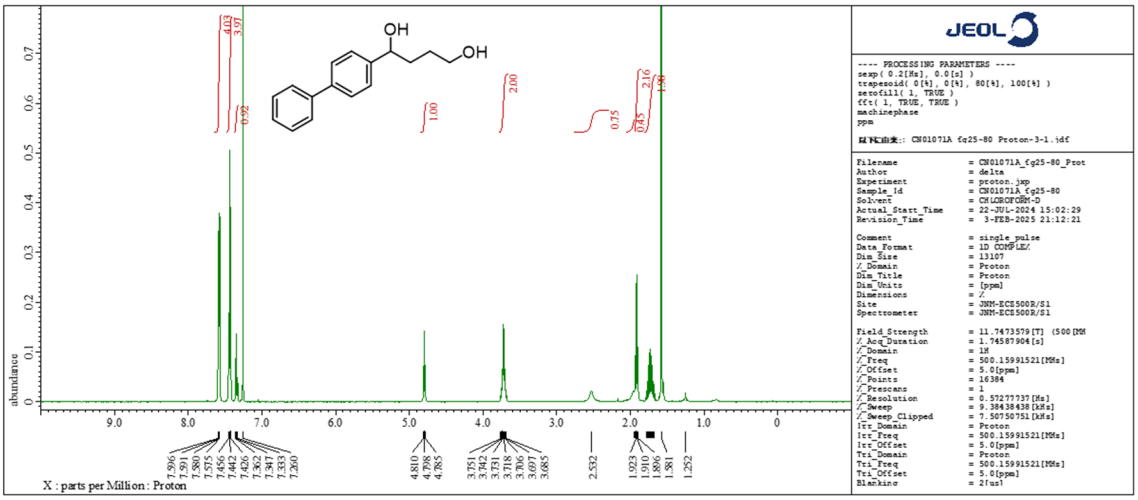

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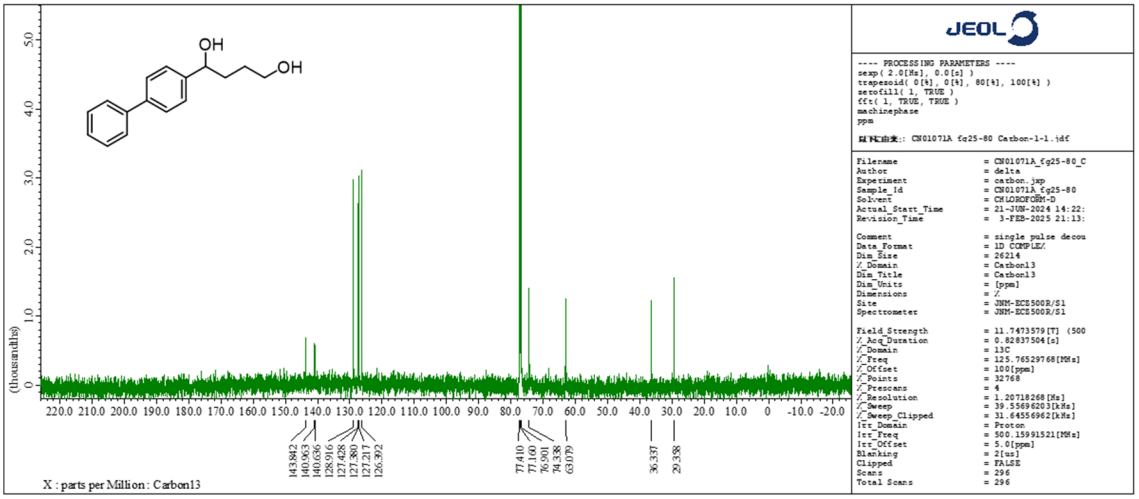

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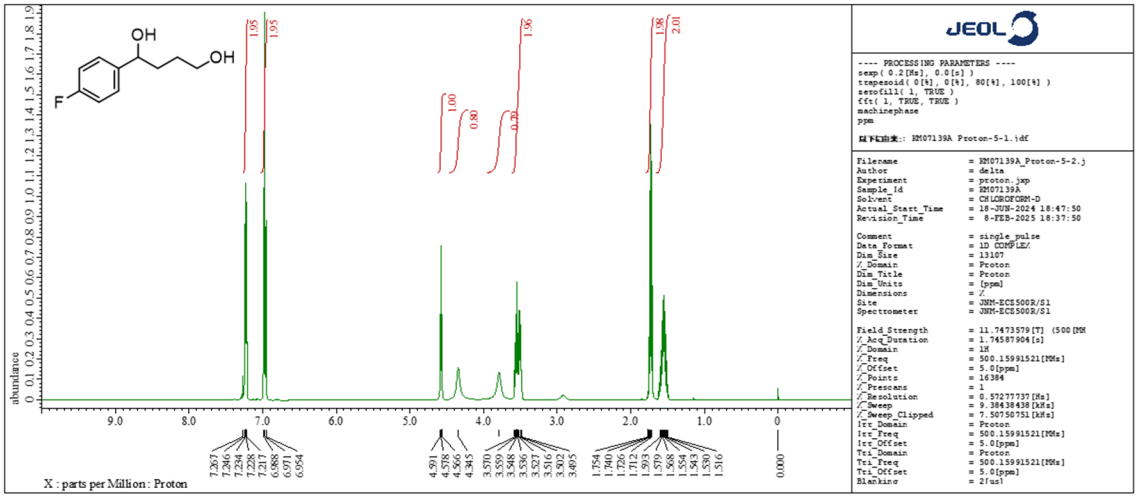

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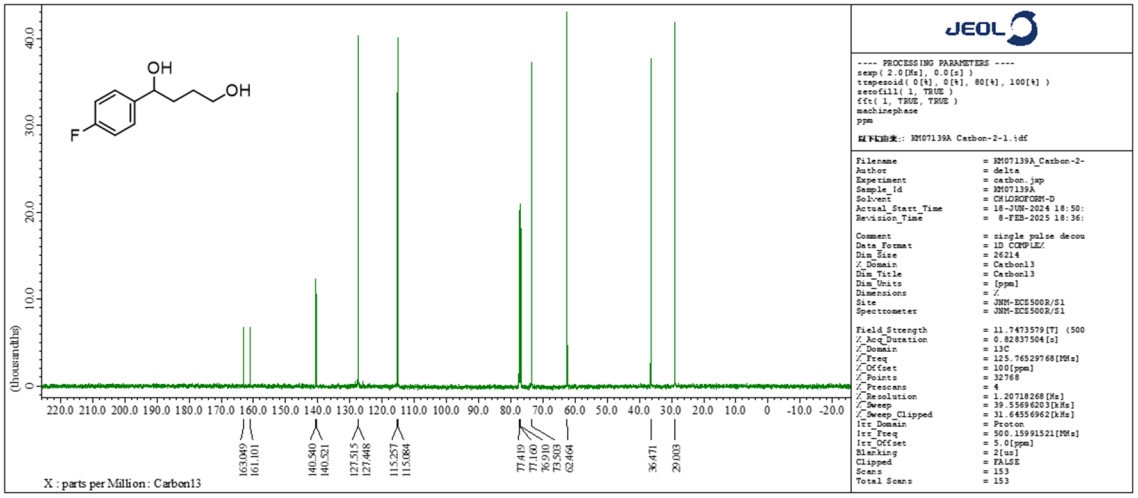


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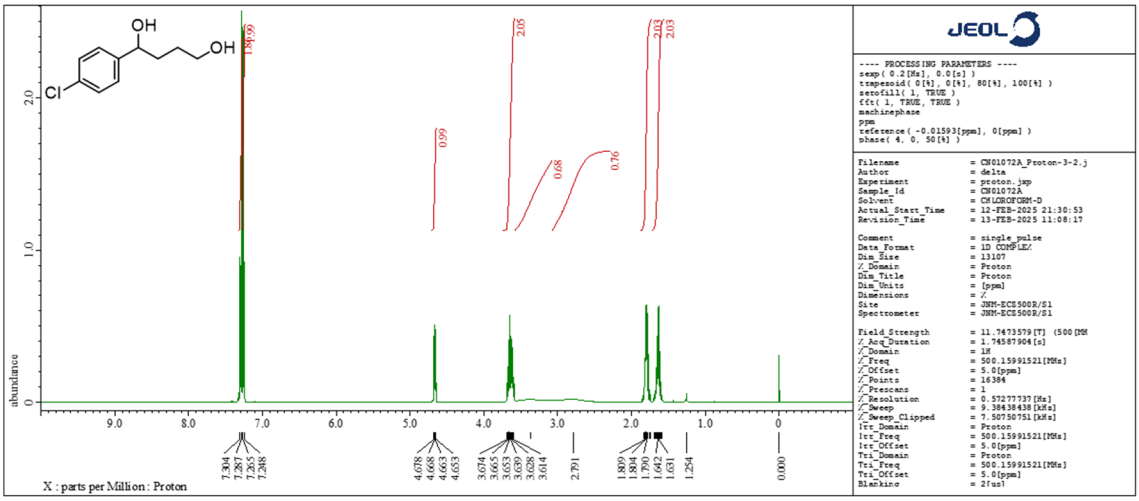


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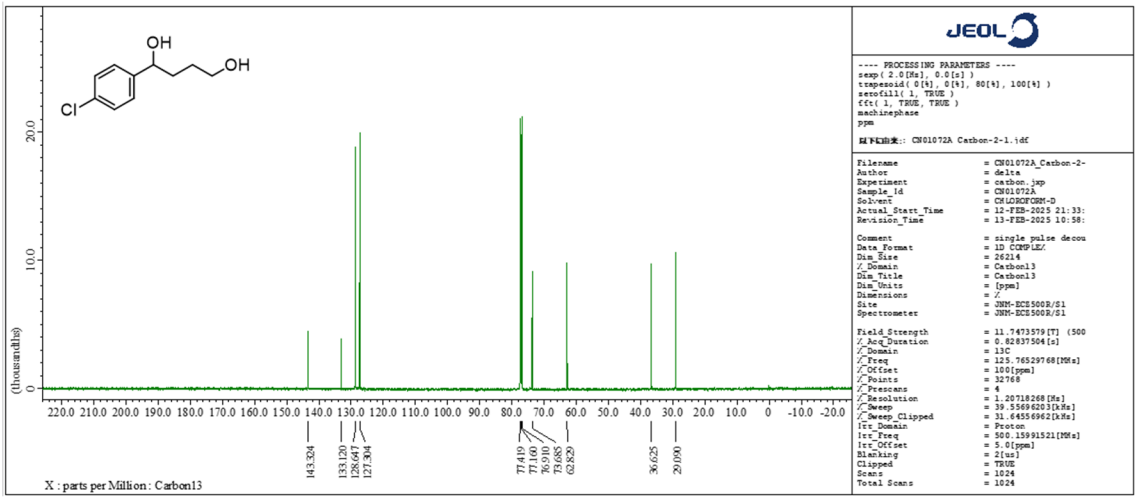

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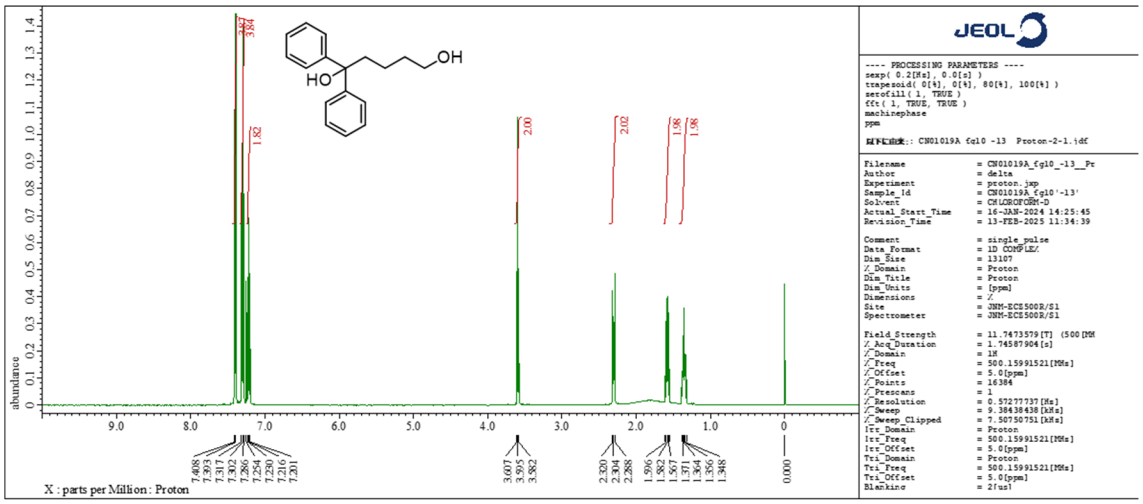


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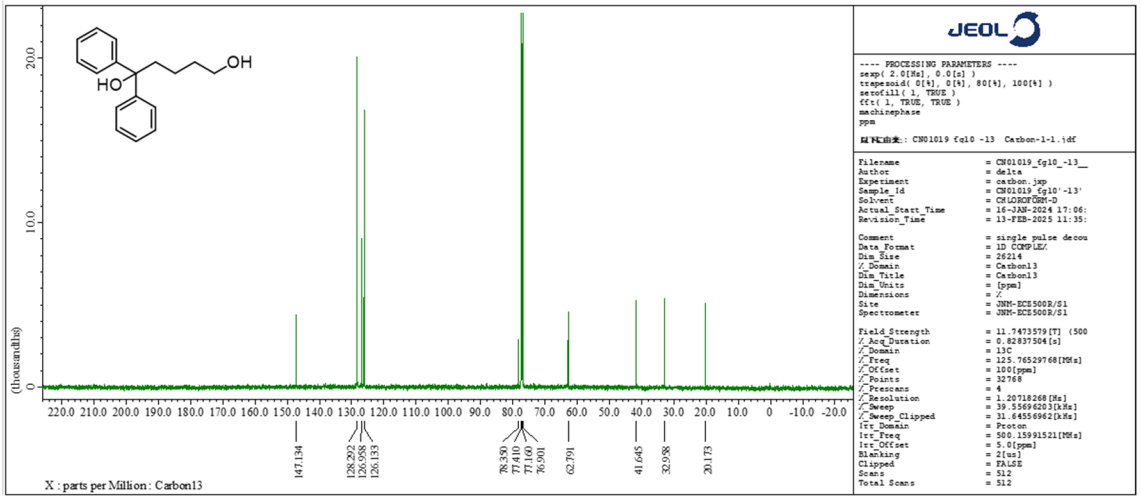


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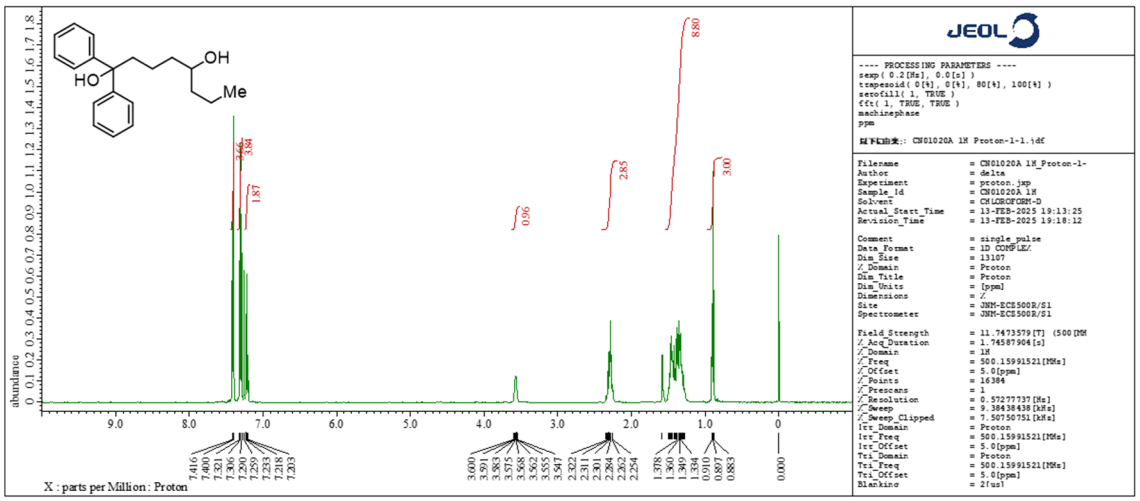
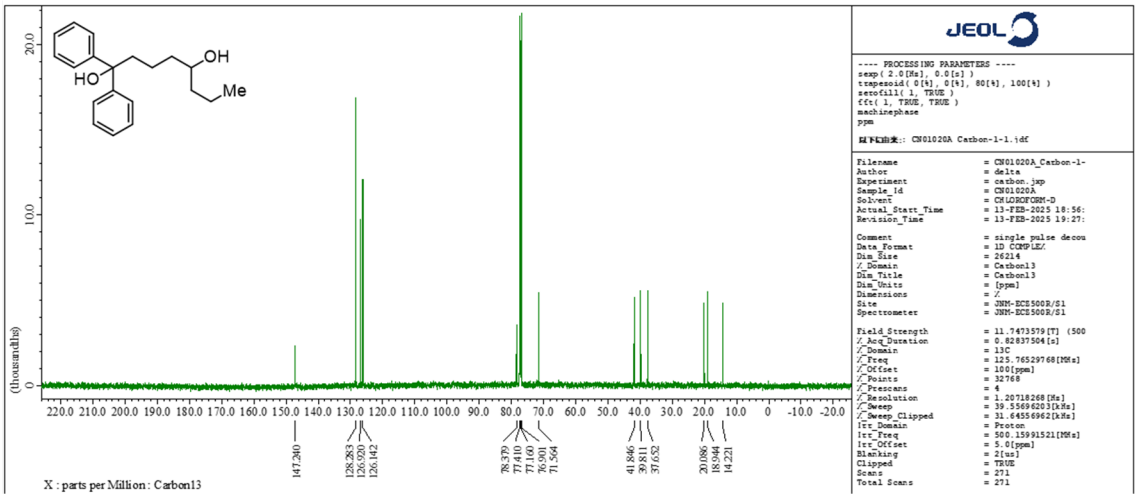
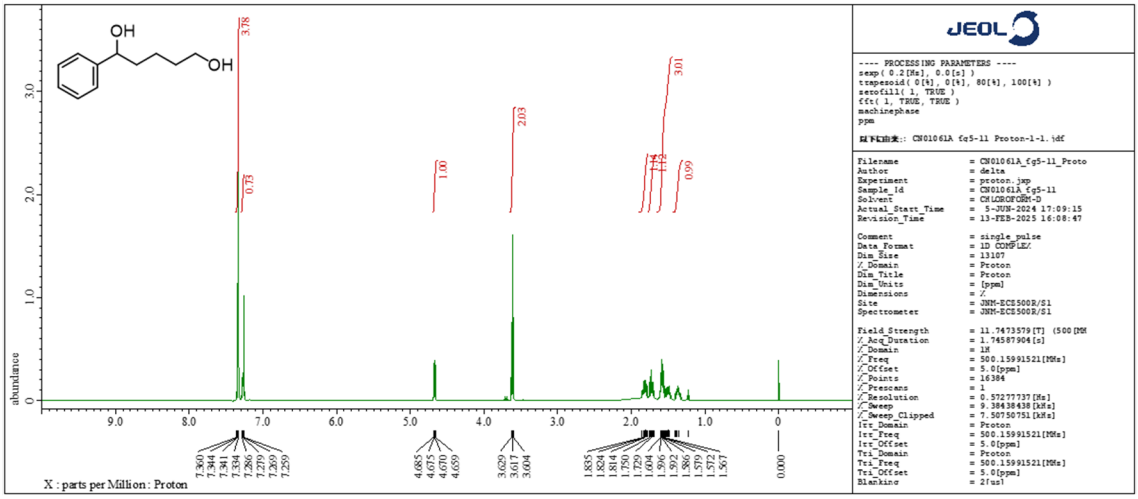


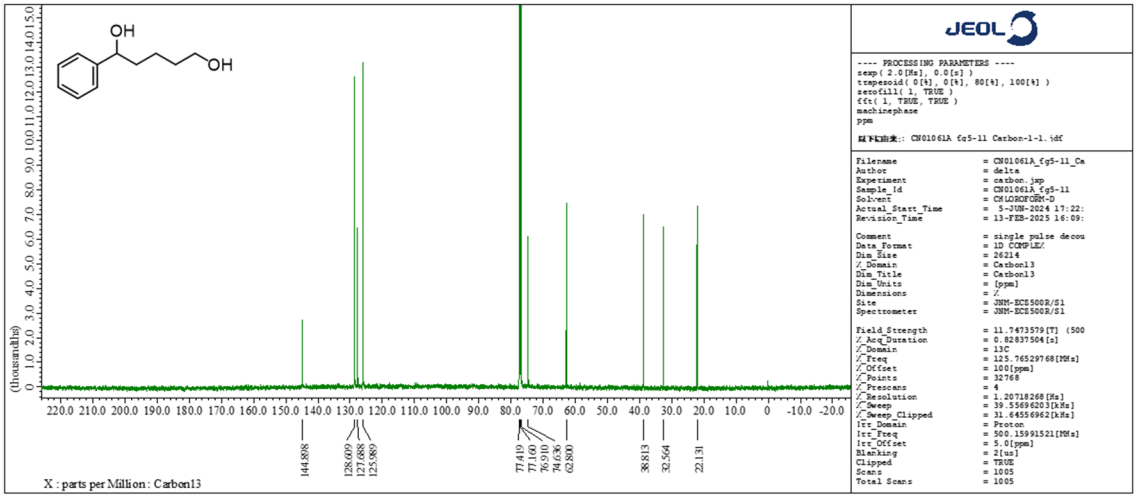
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **11n**



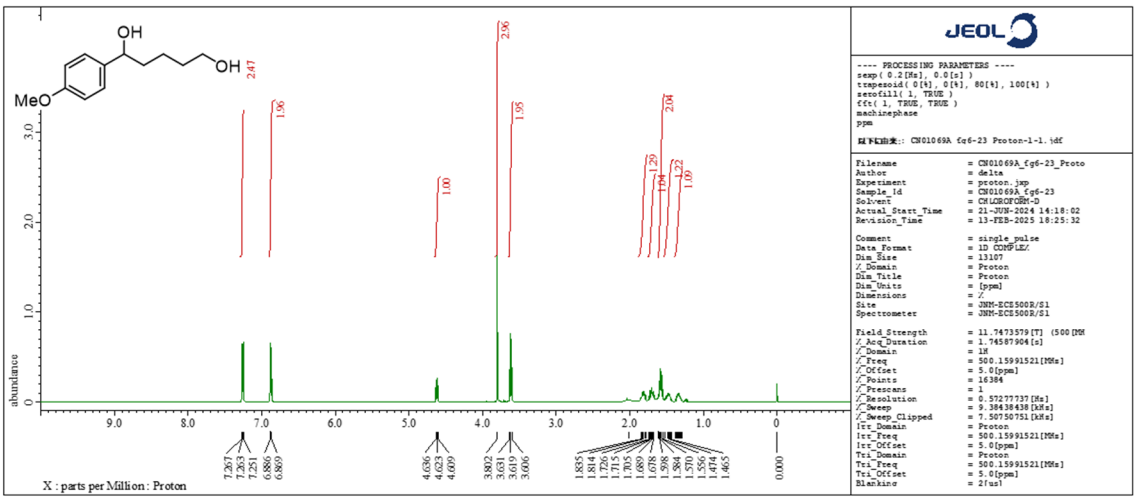

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **11o**



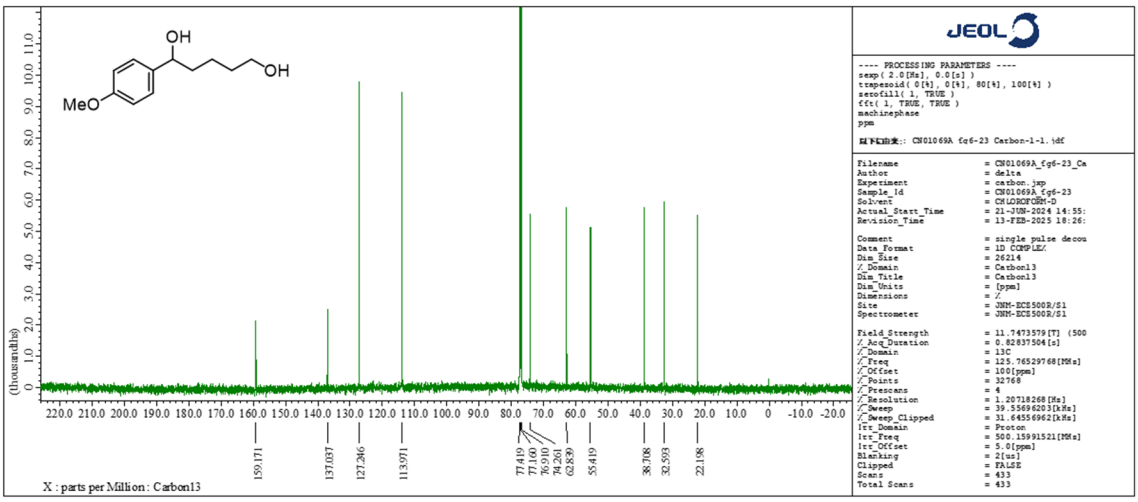

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **11o**



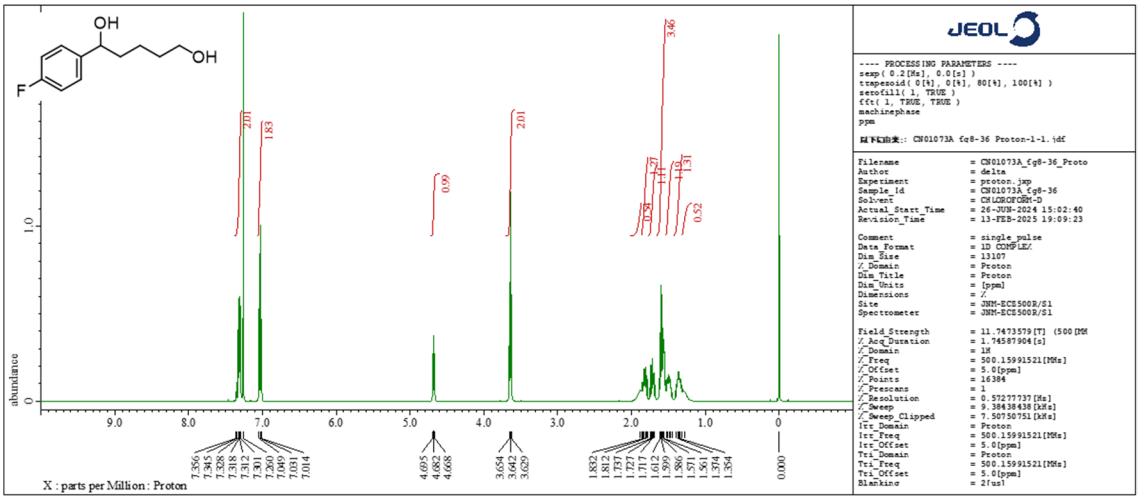
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **11p**



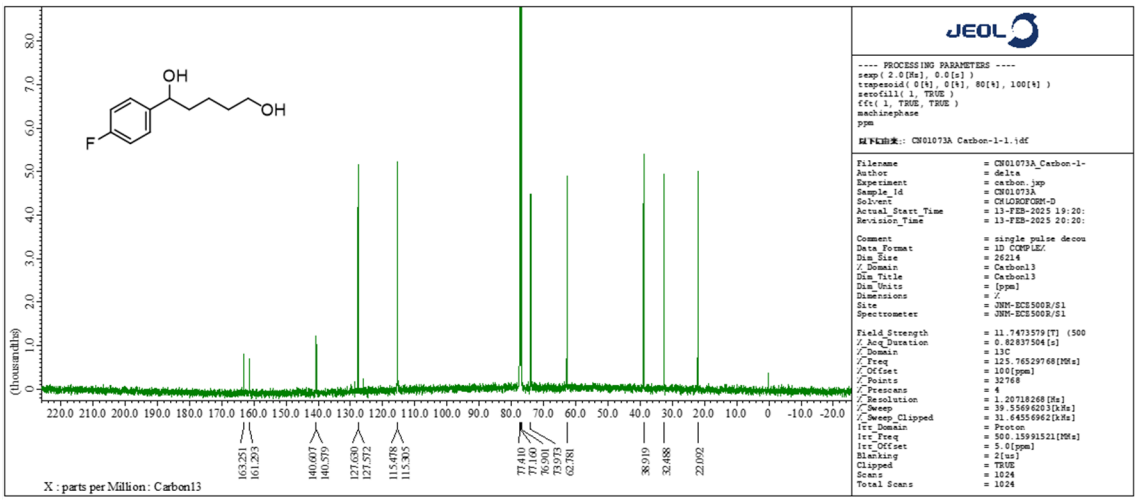

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **11p**



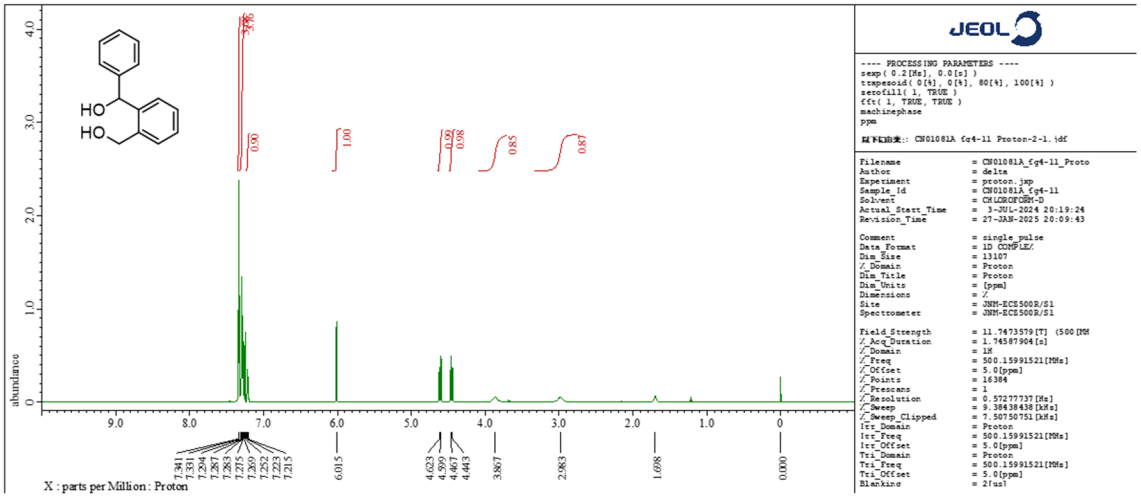

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **11q**



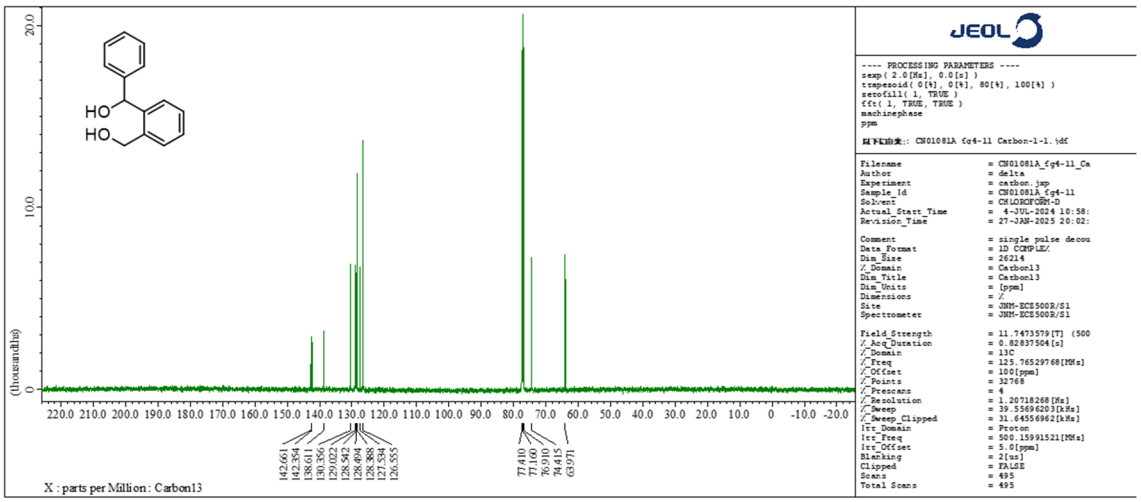
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **11q**



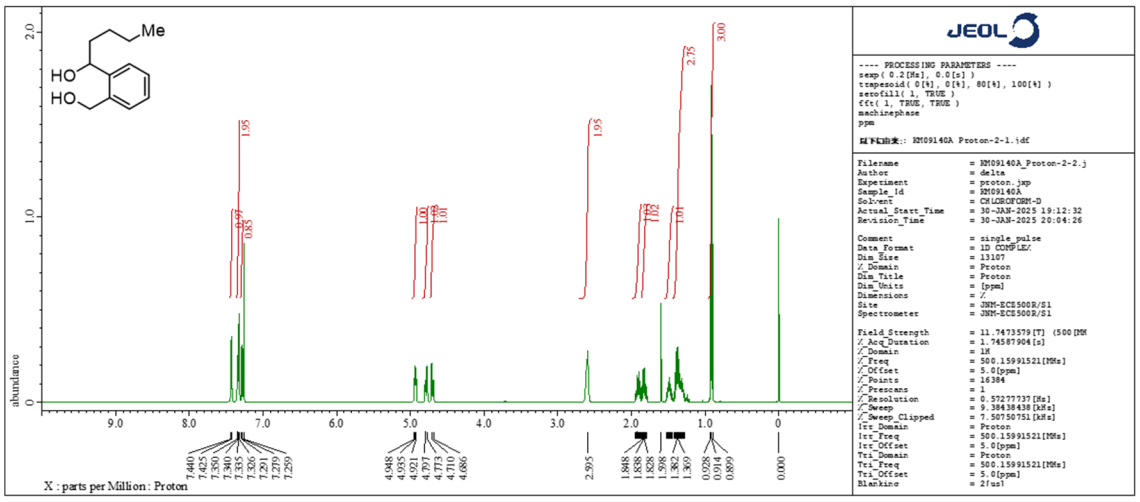

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **11r**



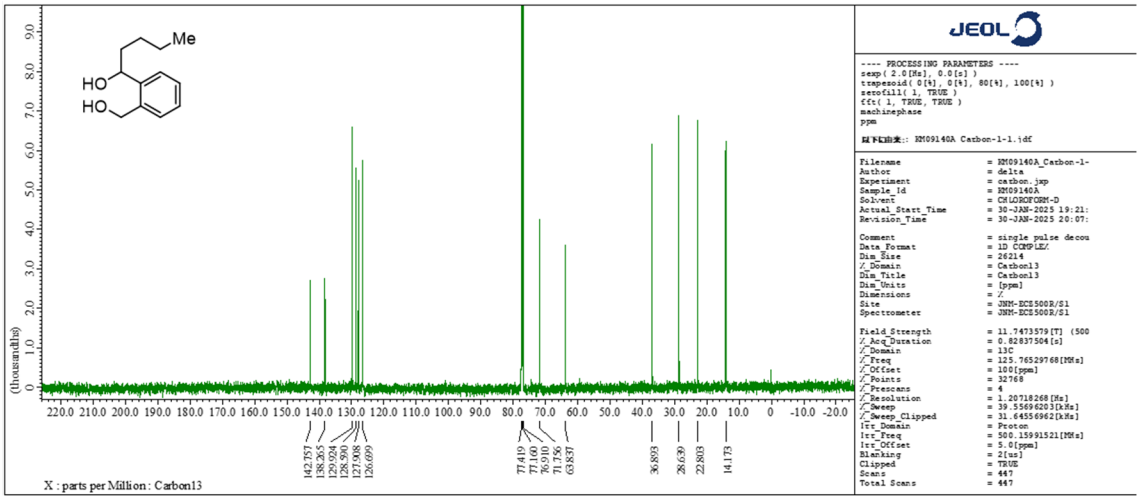

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **11r**



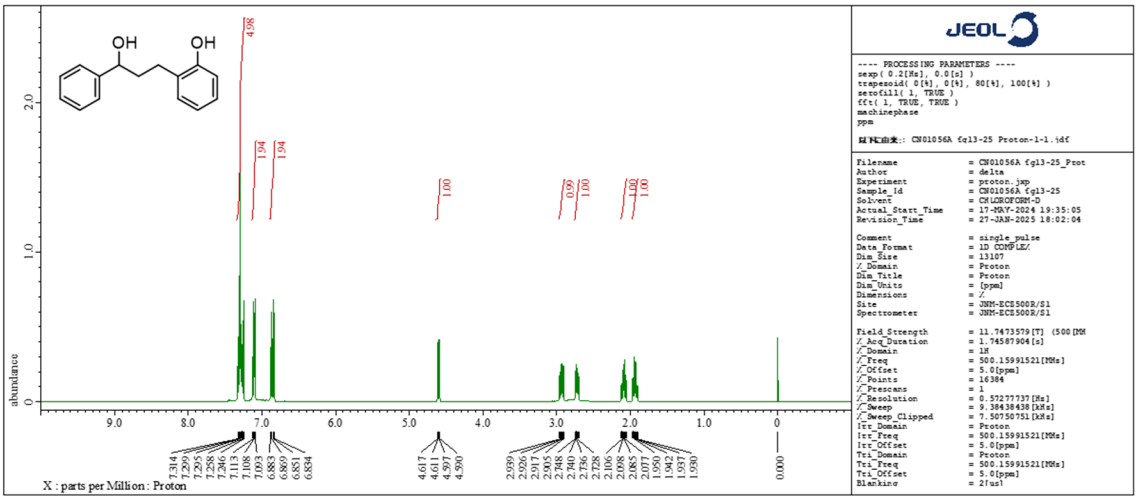
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **11s**



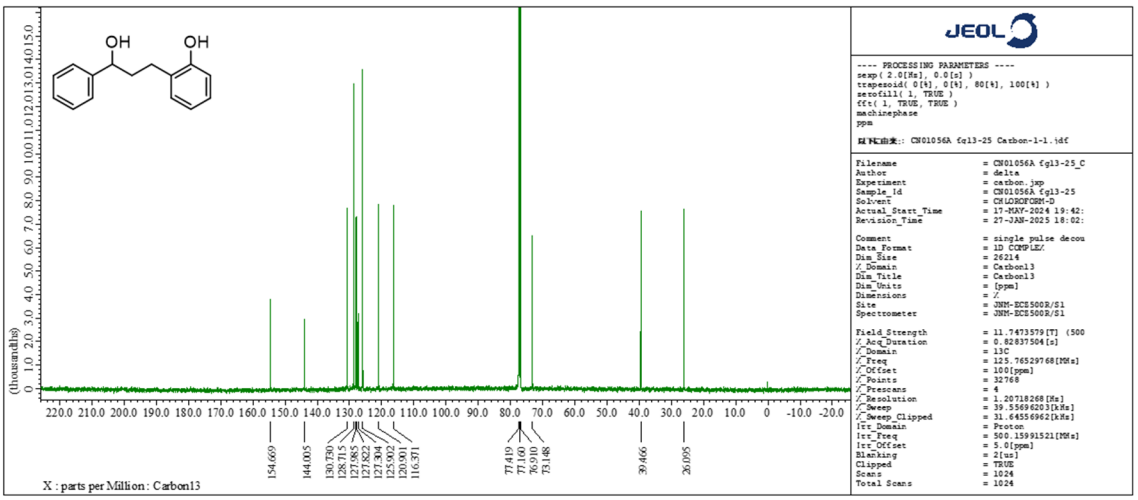

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **11s**



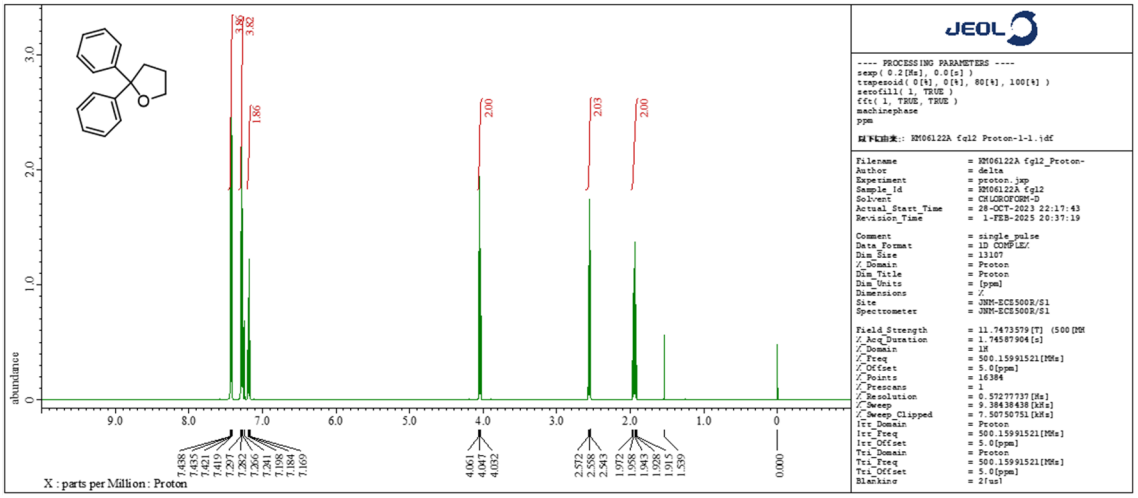

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **11t**



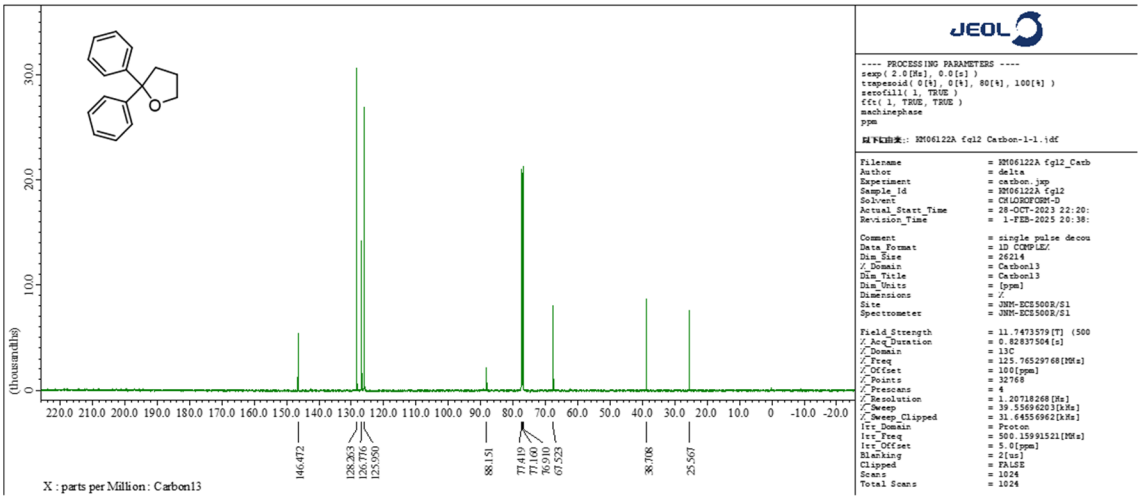
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **11t**



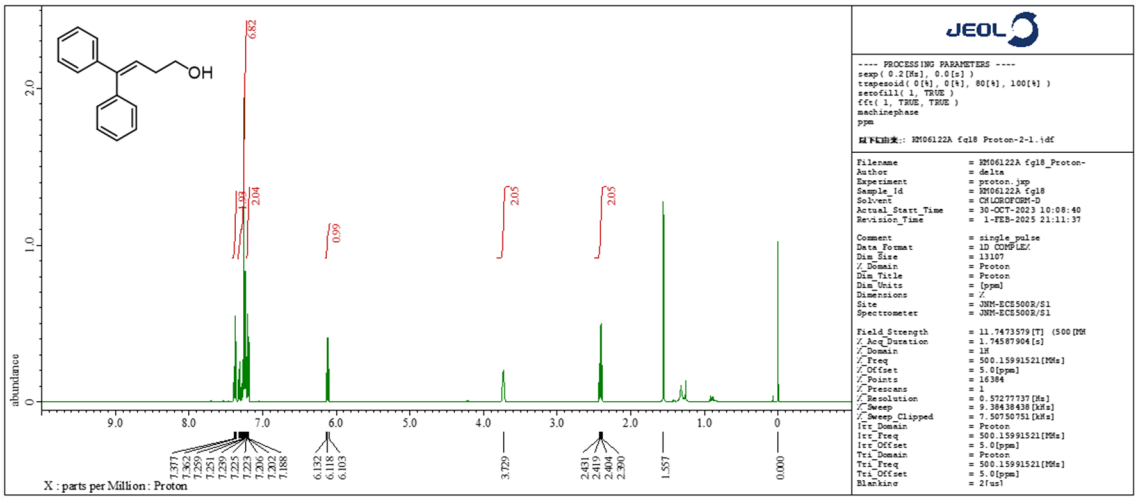

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12a**



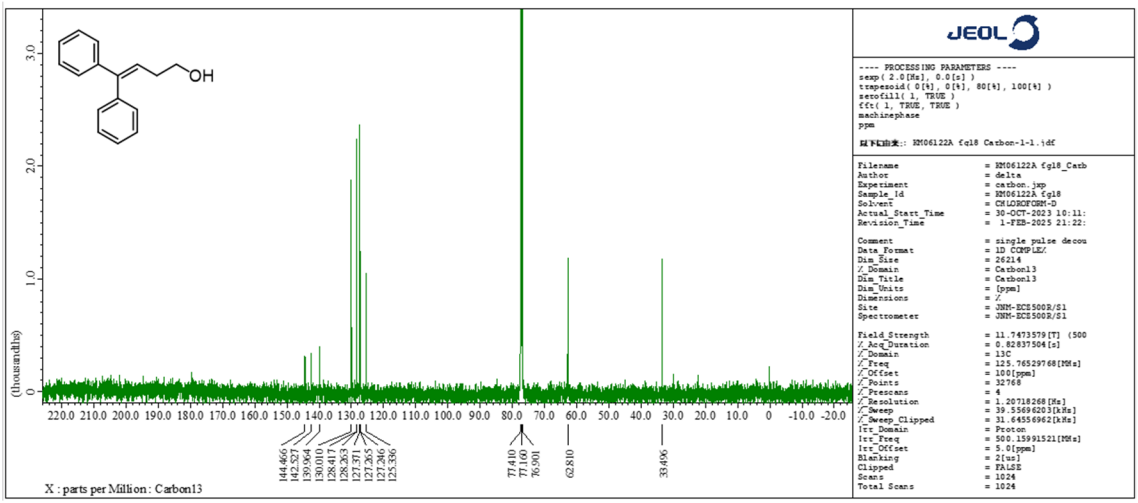

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12a**



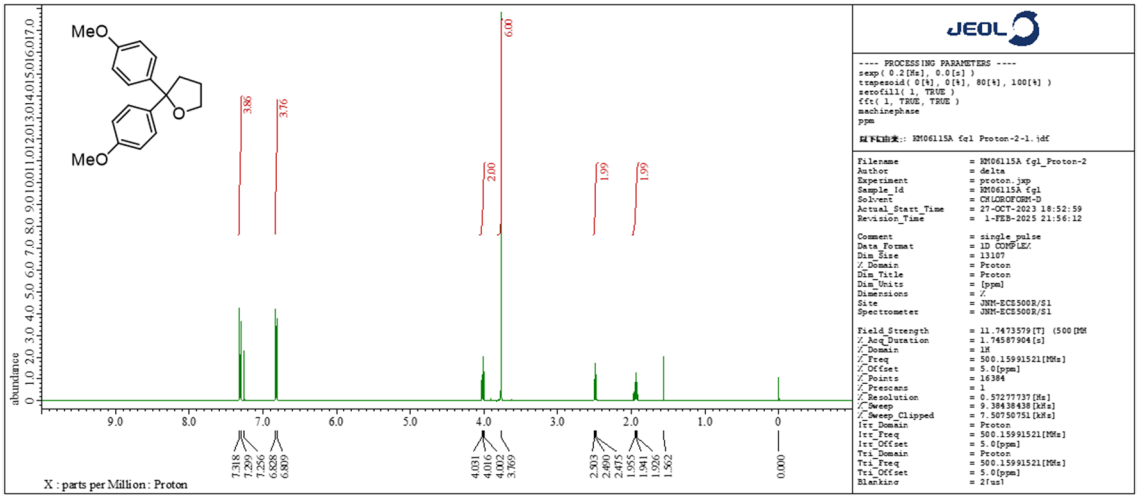
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **13a**



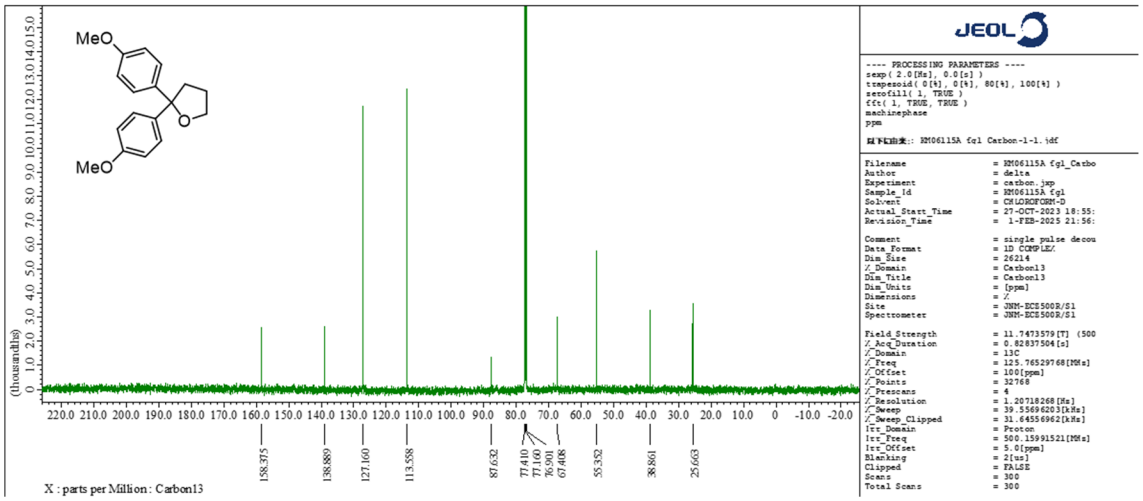

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **13a**



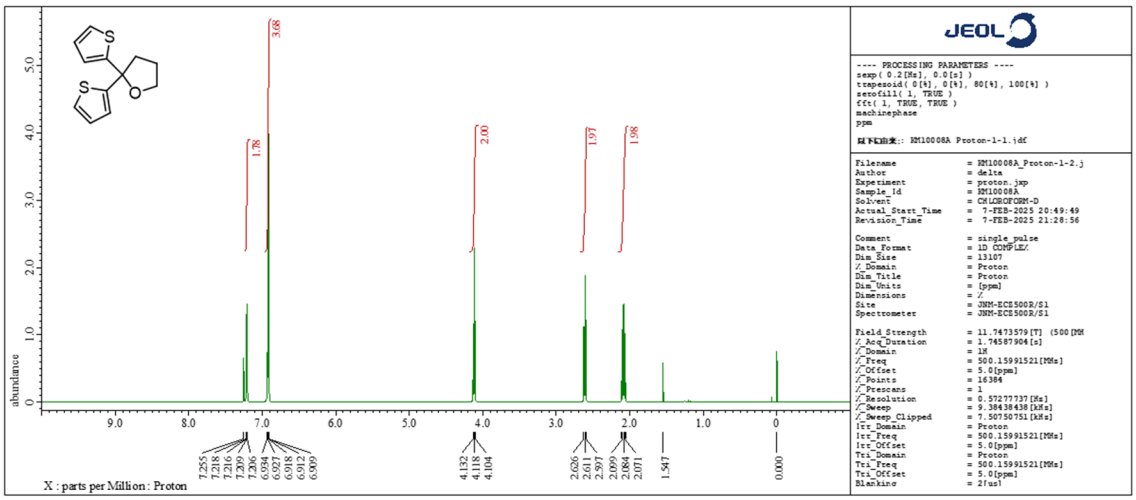

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12b**



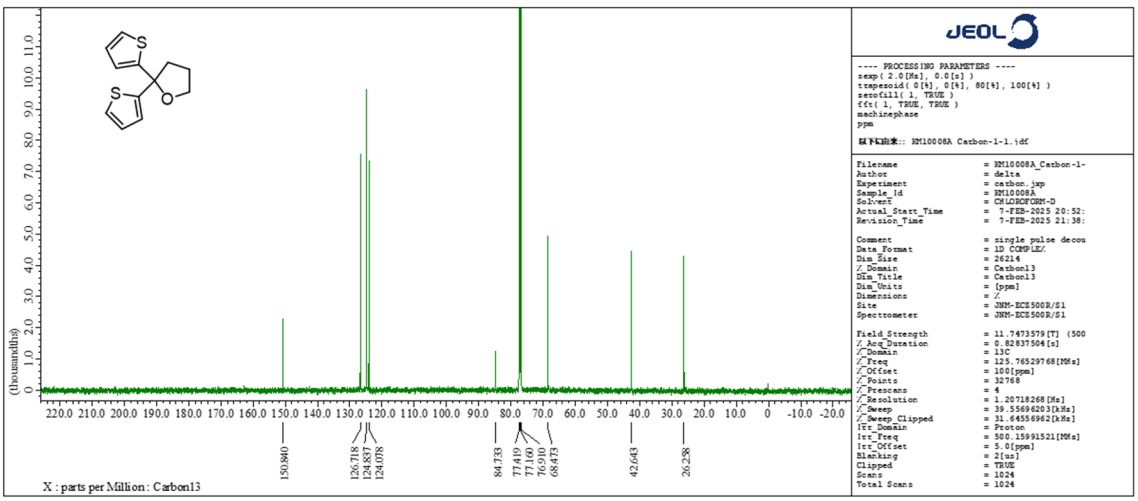
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12b**



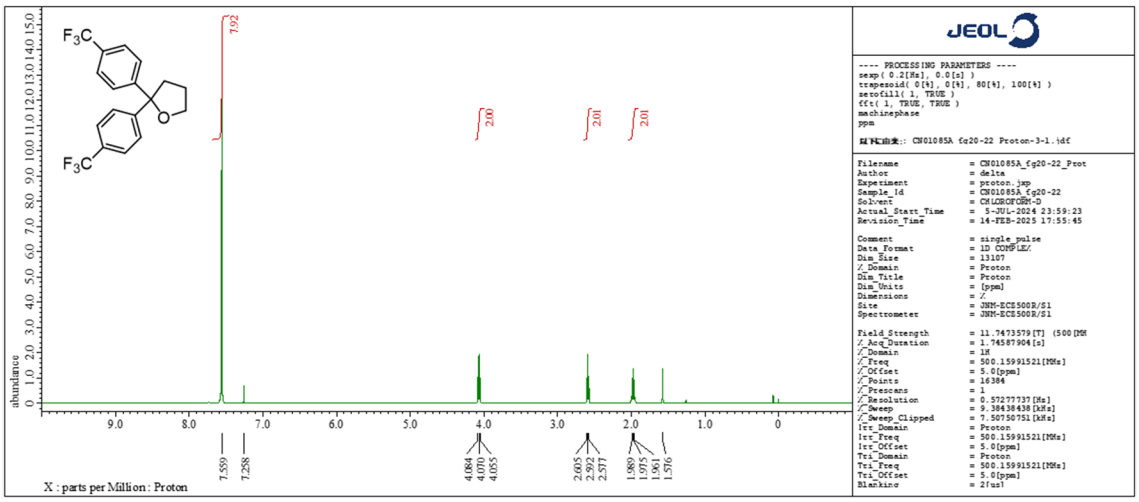

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12c**



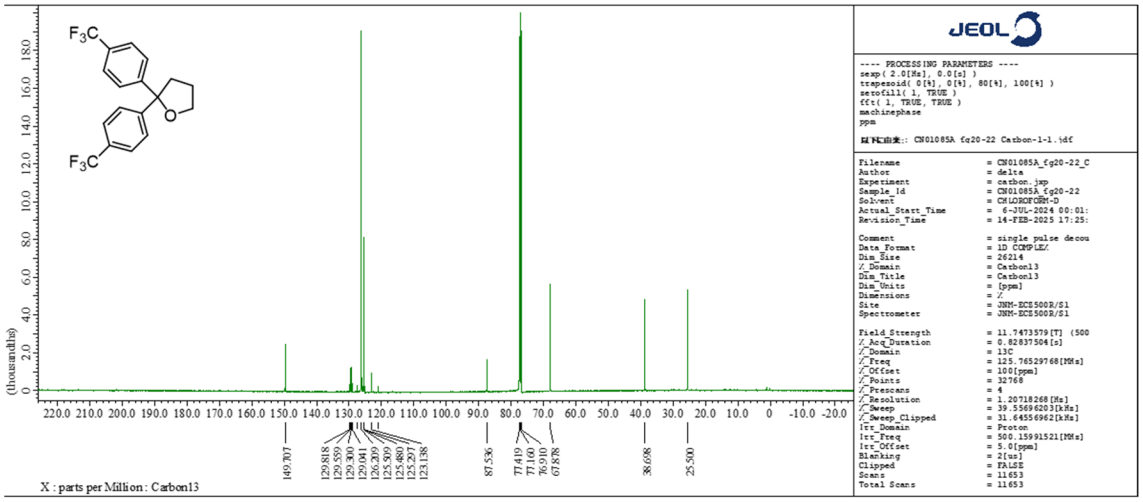

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12c**



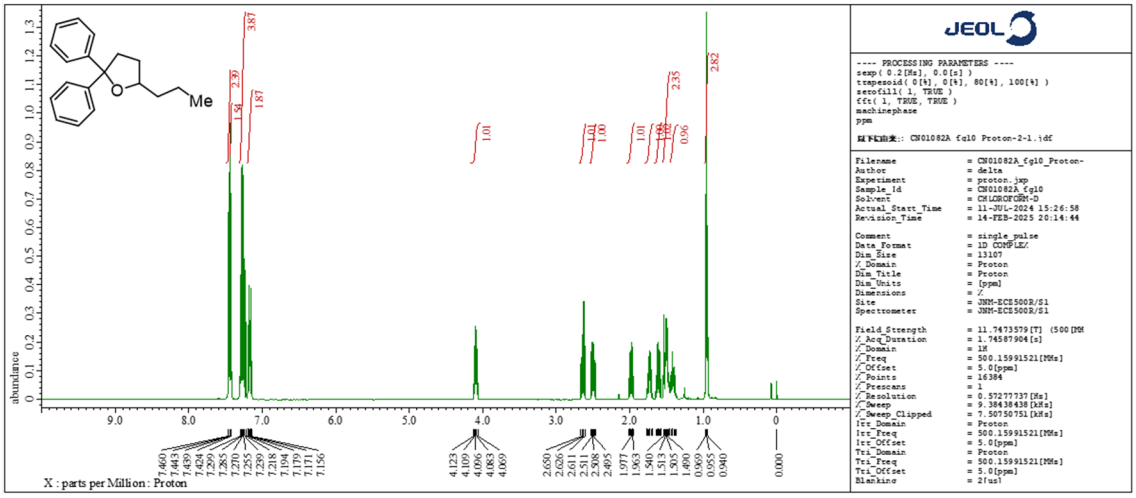
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12d**



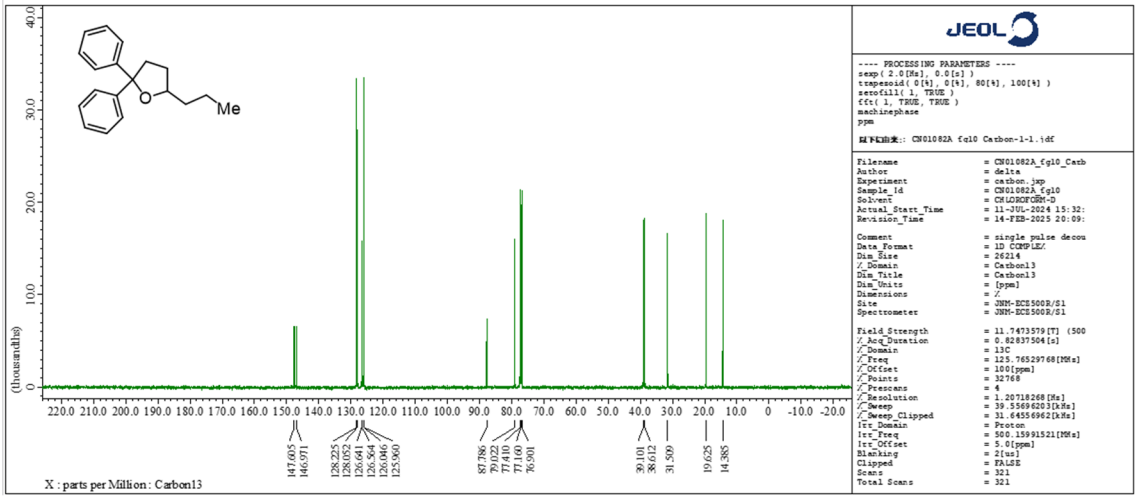

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **12d**



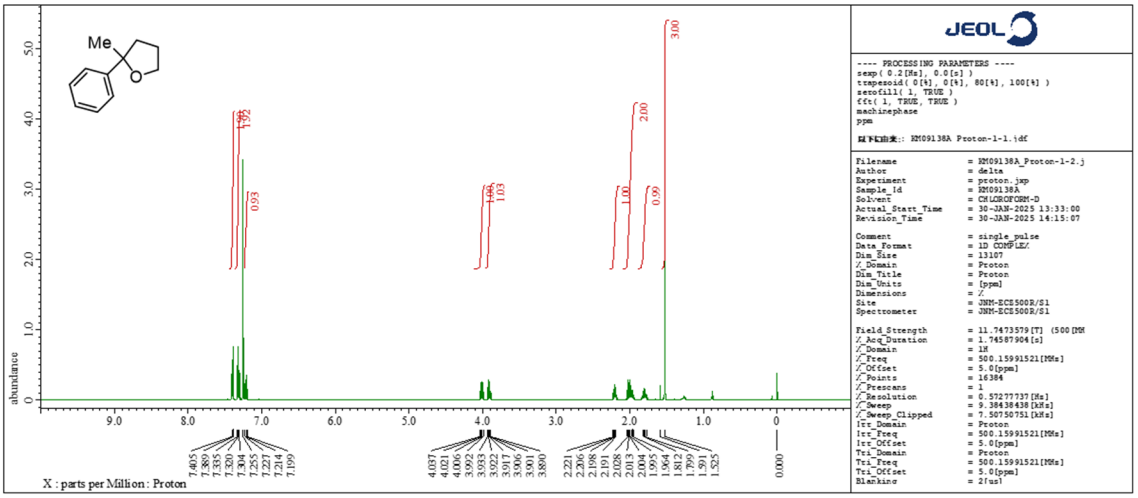

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12e**



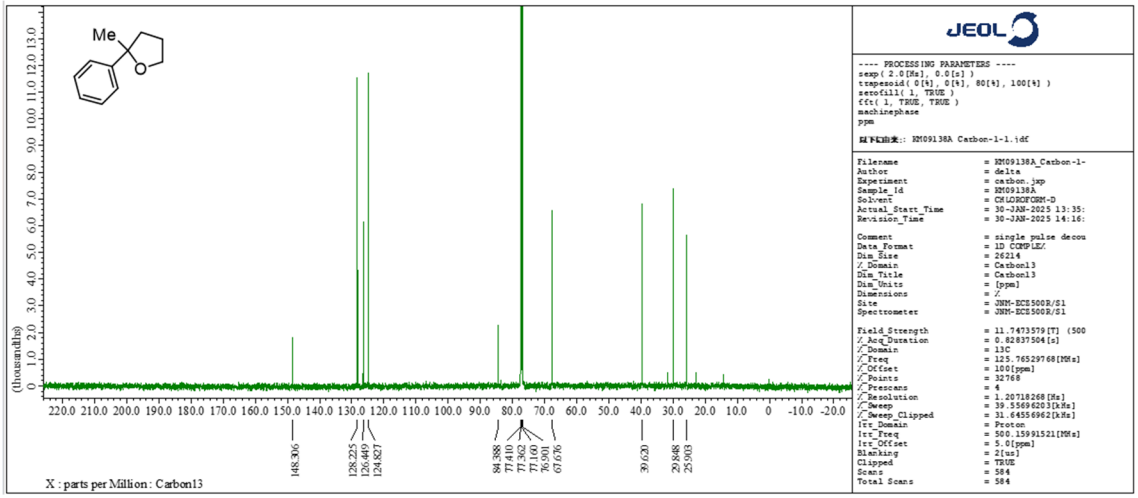
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12e**



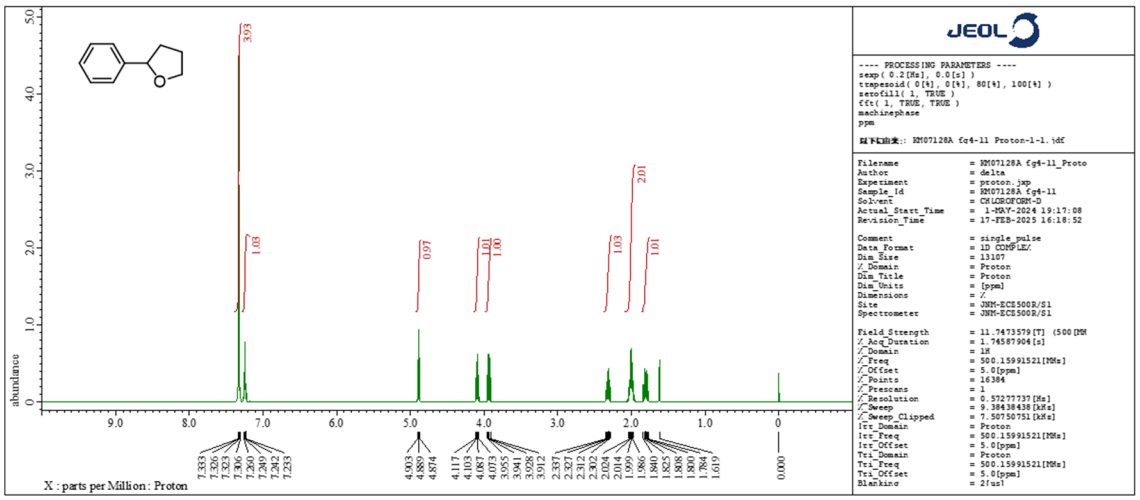

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12f**



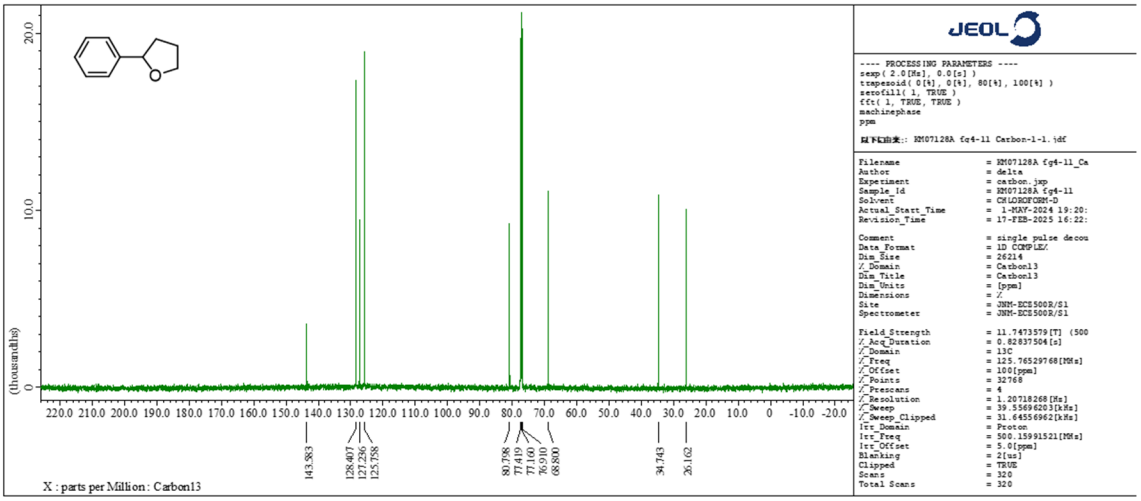

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12f**



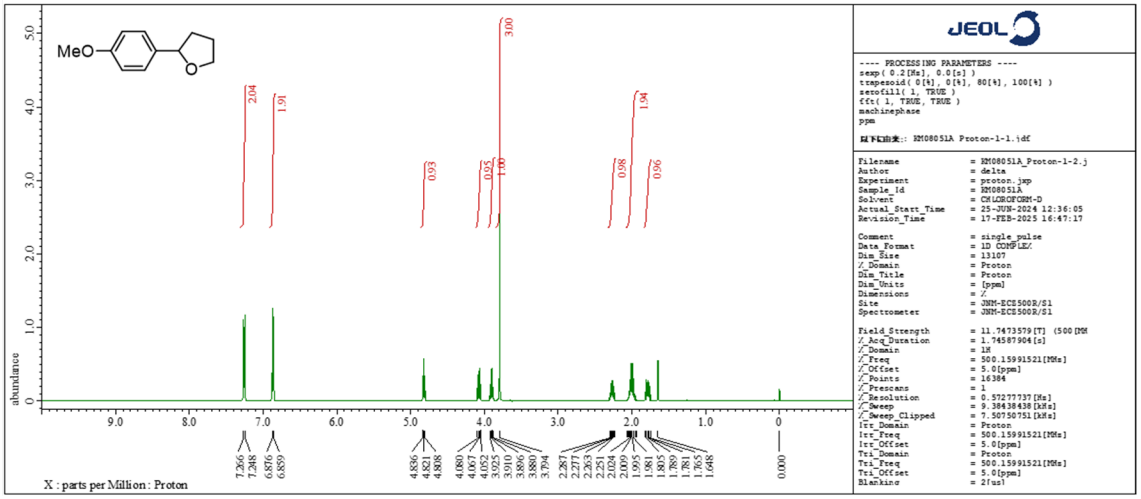
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12g**



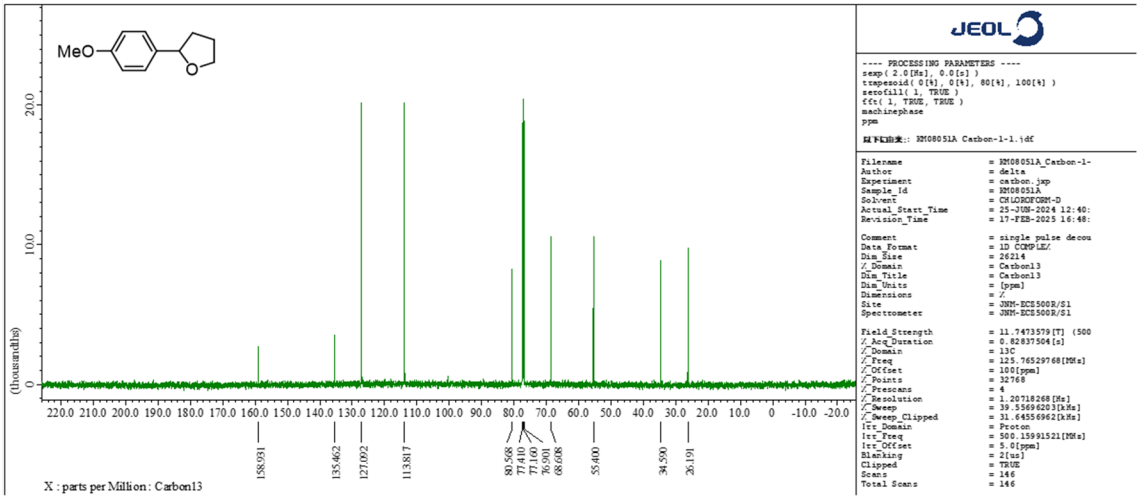

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **12g**



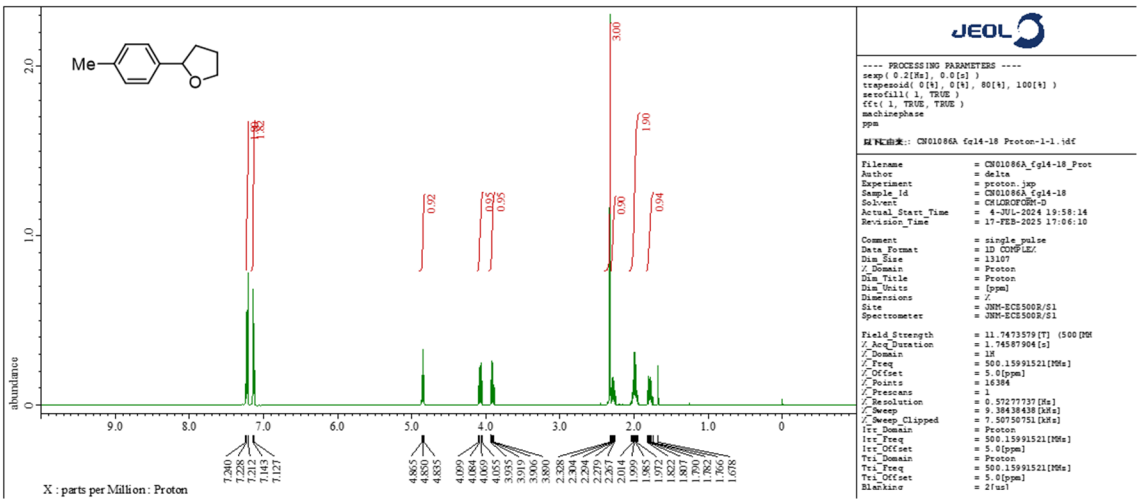

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12h**



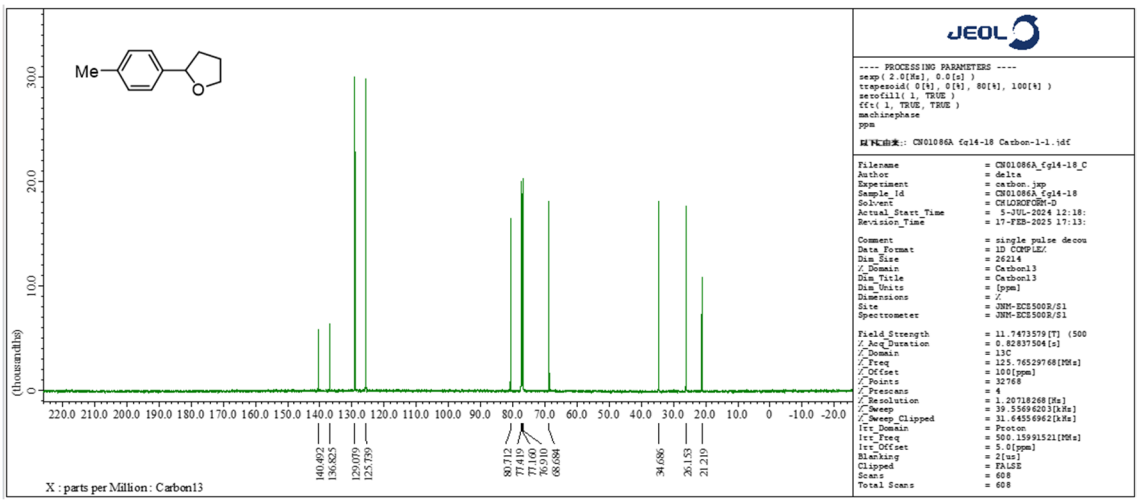
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12h**



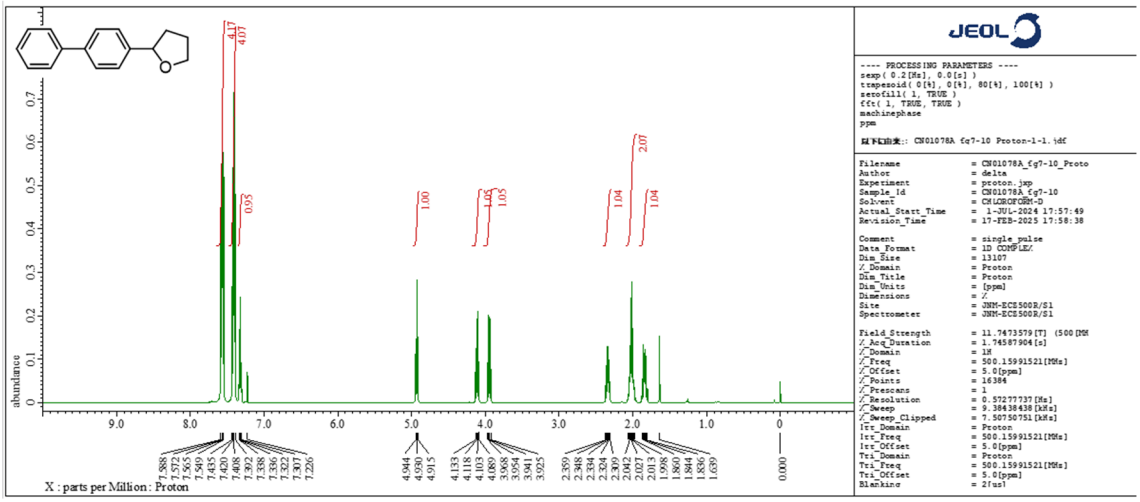

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12i**



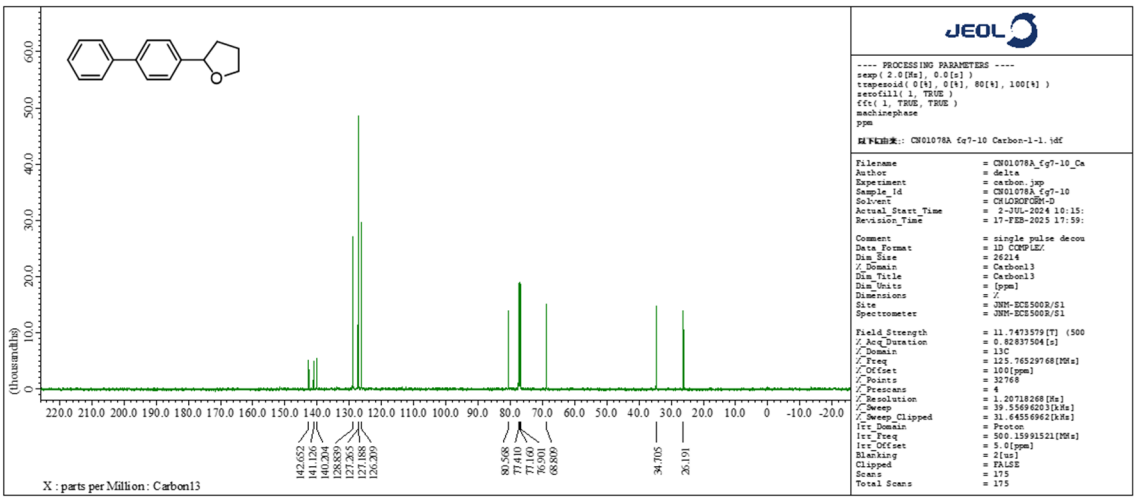

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12i**



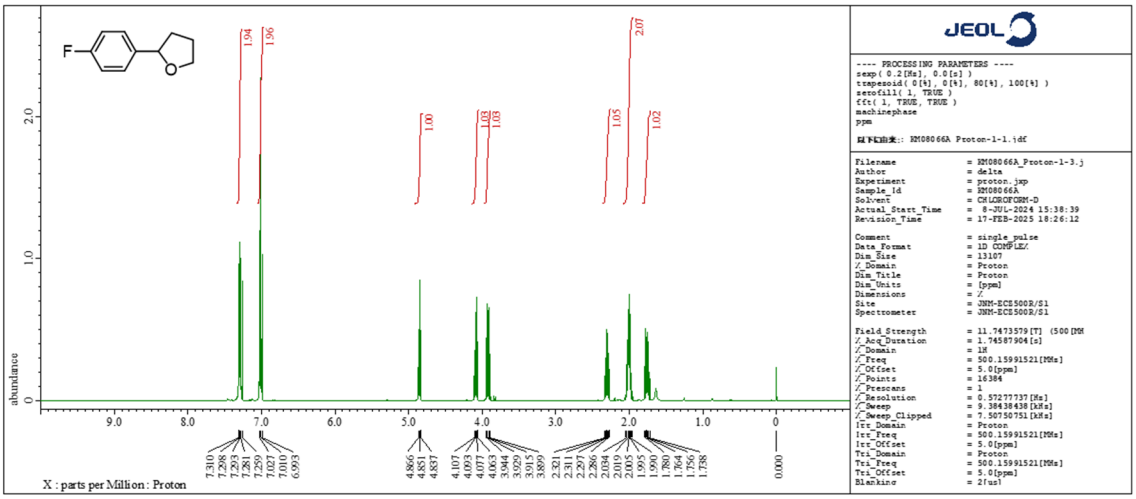
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12j**



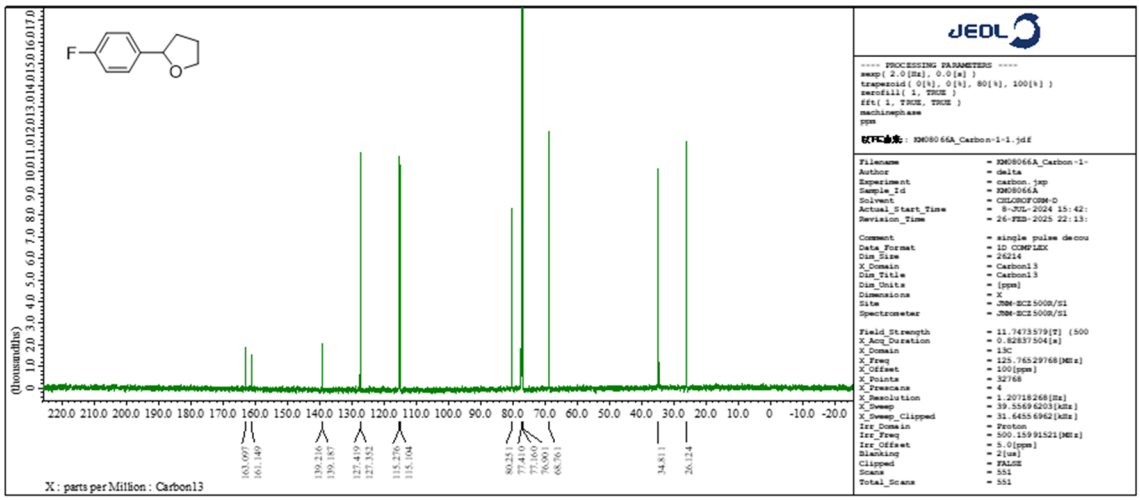
$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **12j**



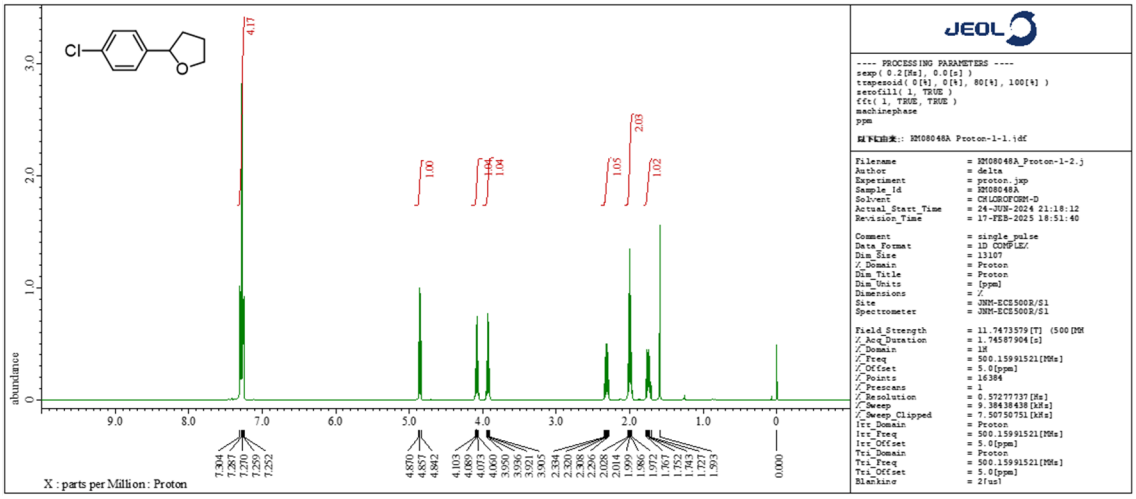
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12k**



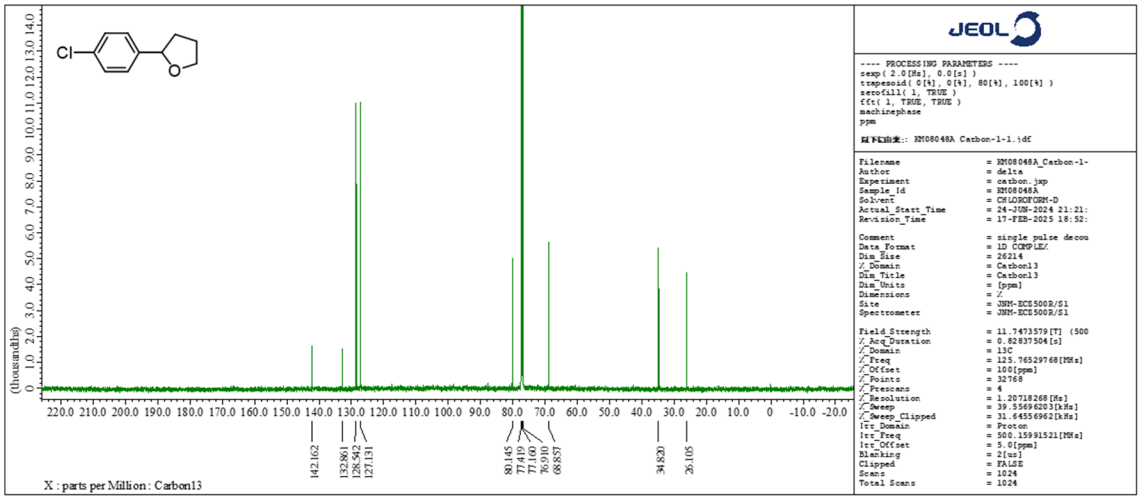
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12k**



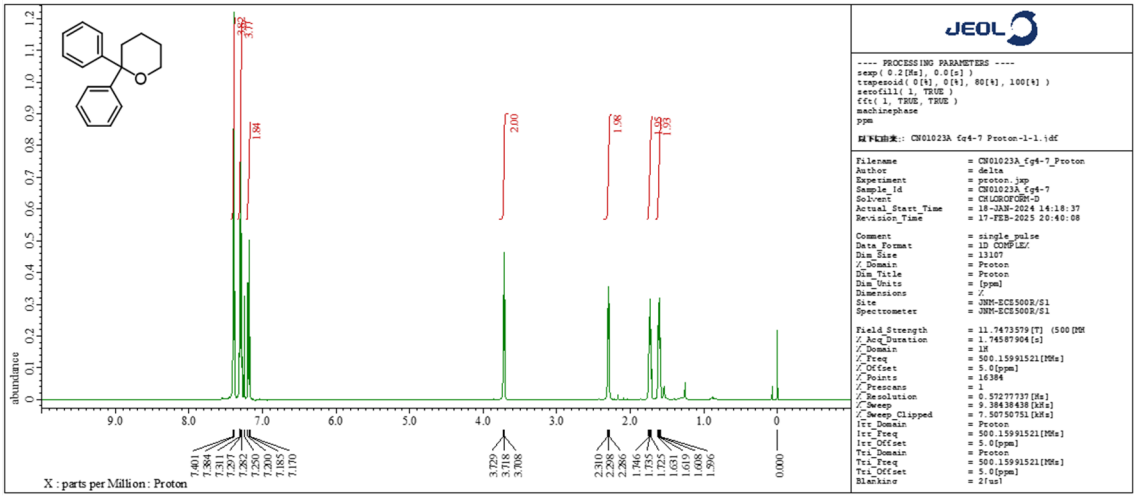
$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12l**



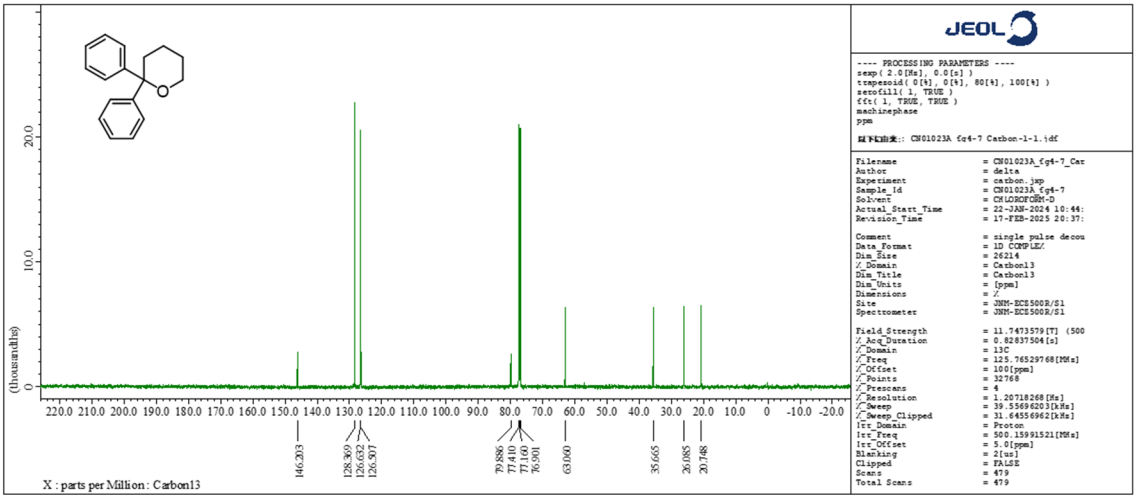
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12l**



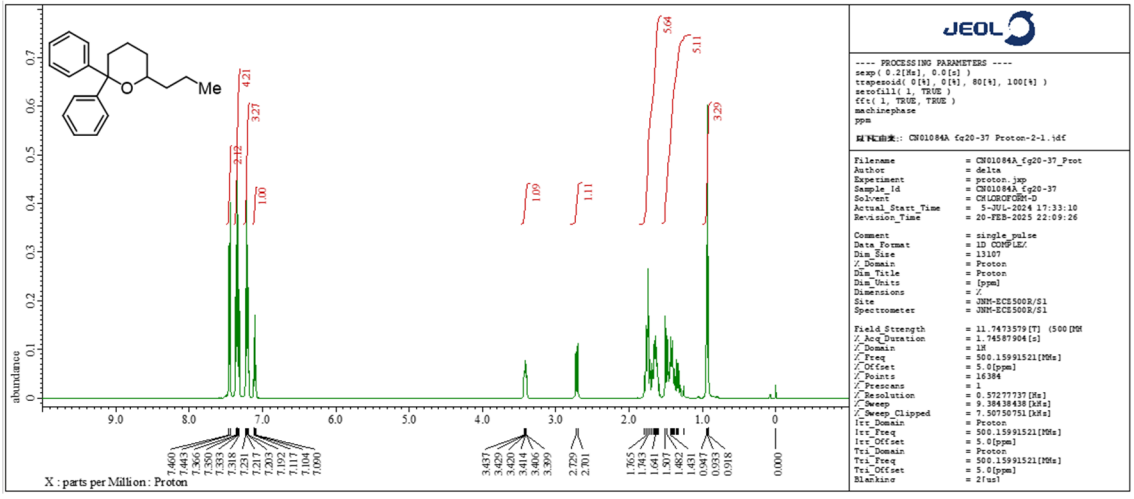
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12m**



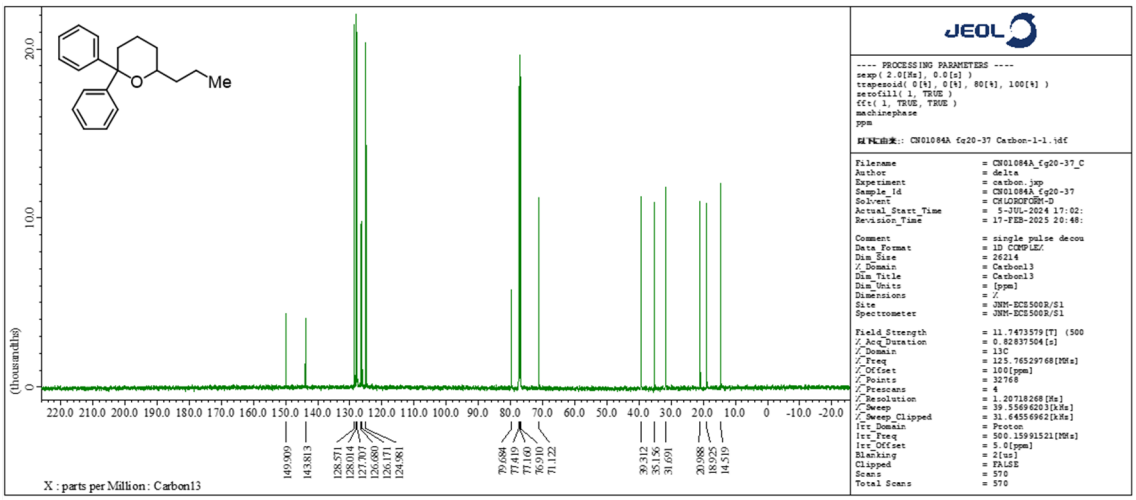
$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **12m**



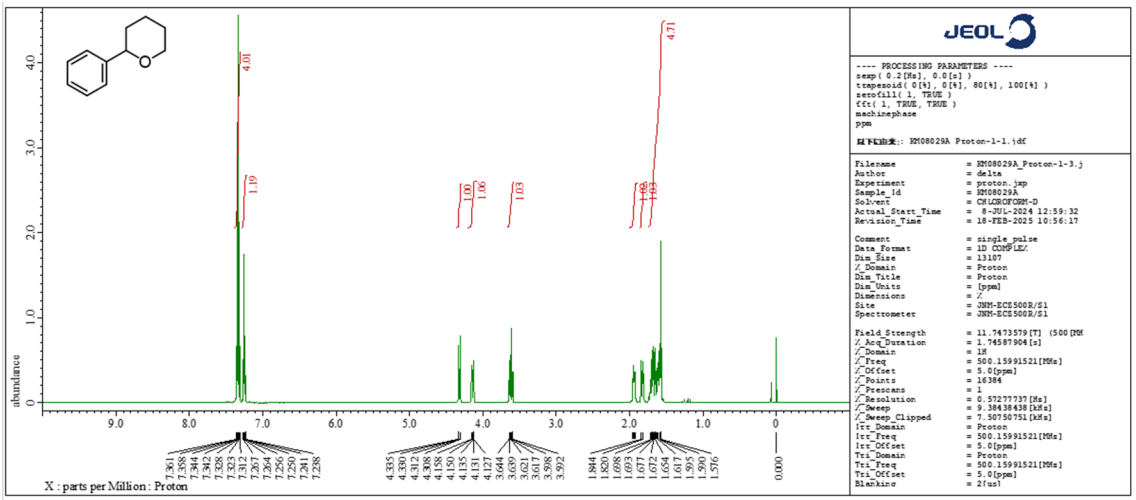
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12n**



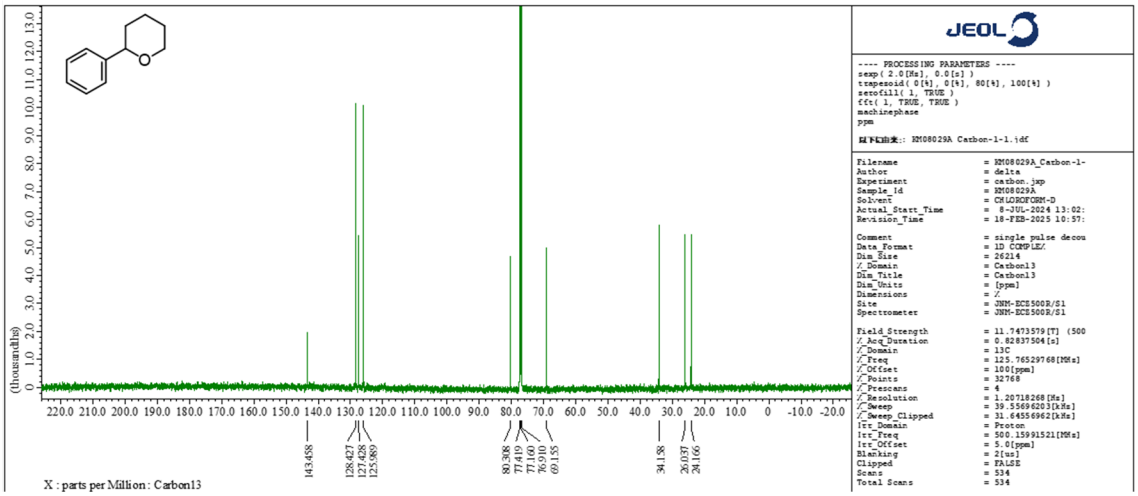
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12n**



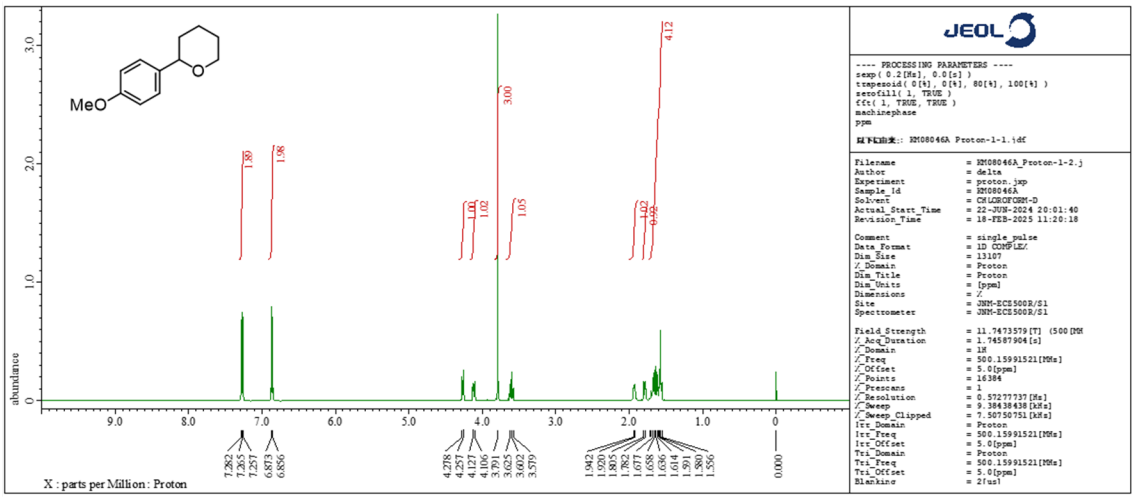

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12o**



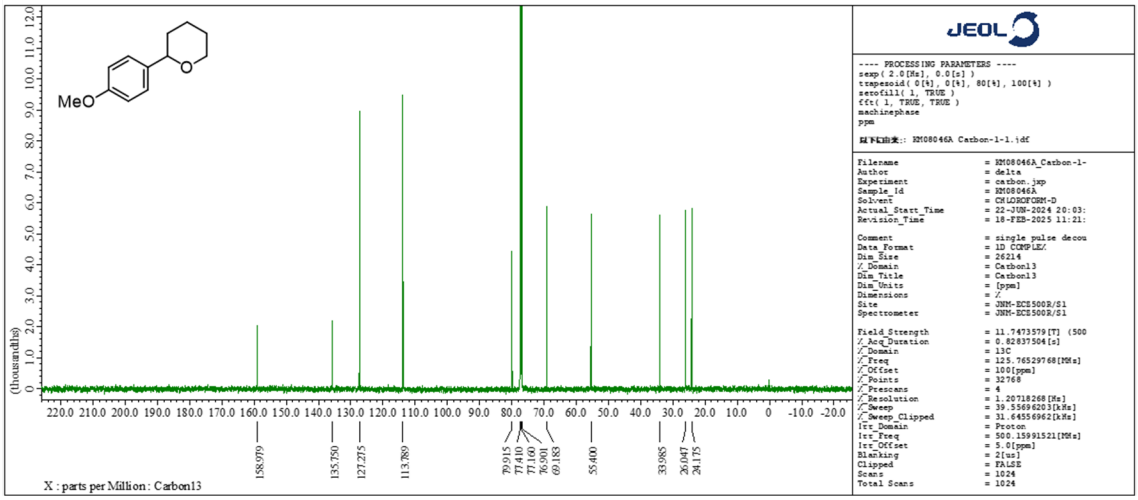

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12o**



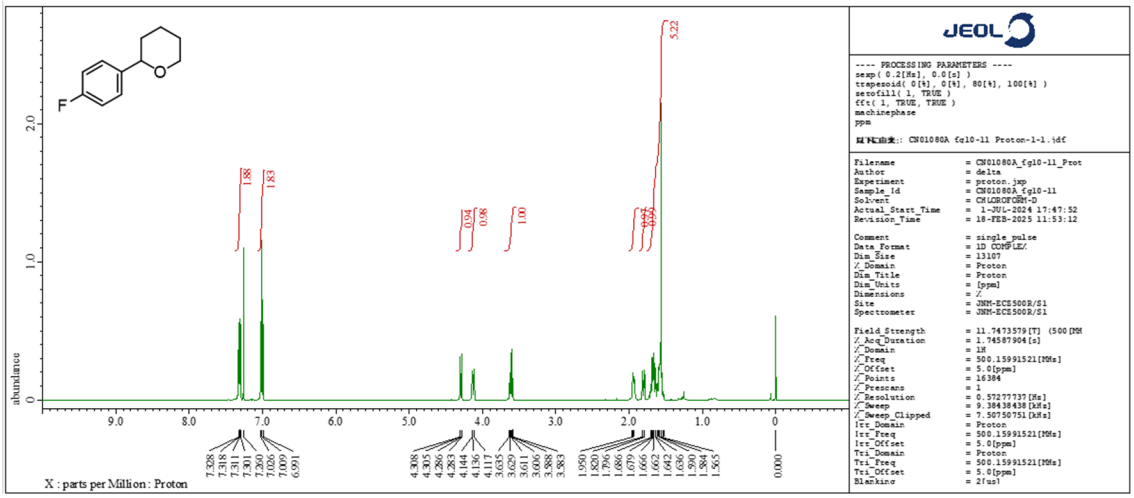
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12p**



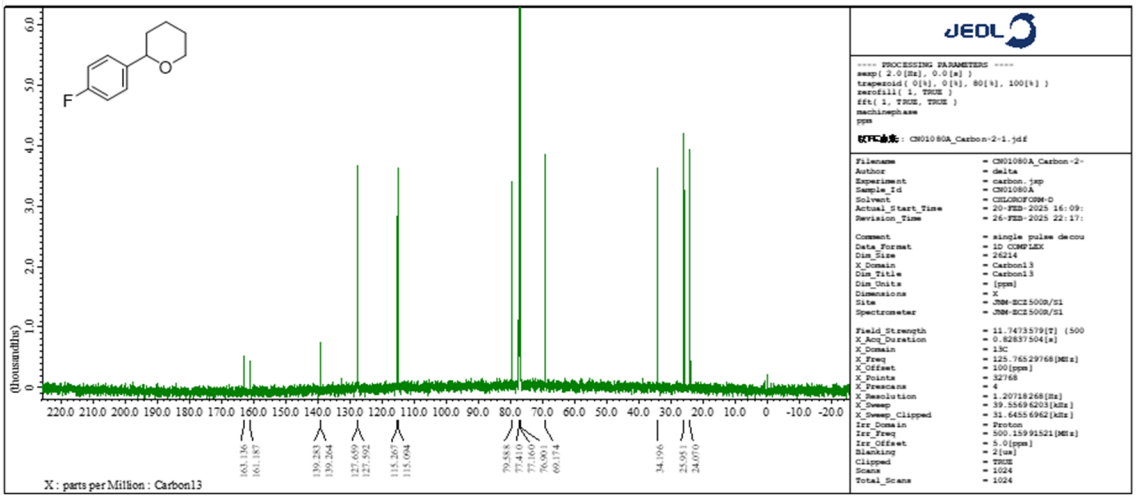

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **12p**



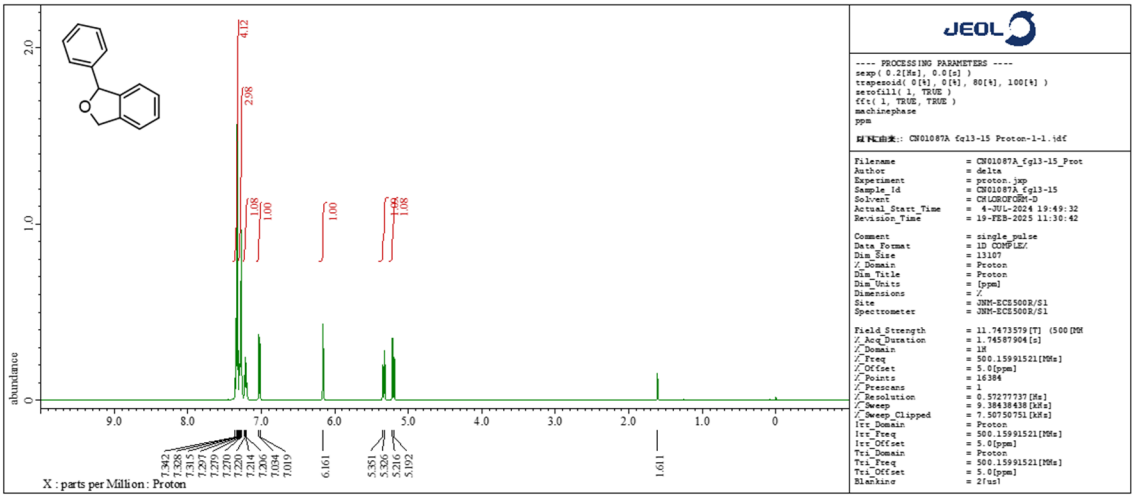

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12q**



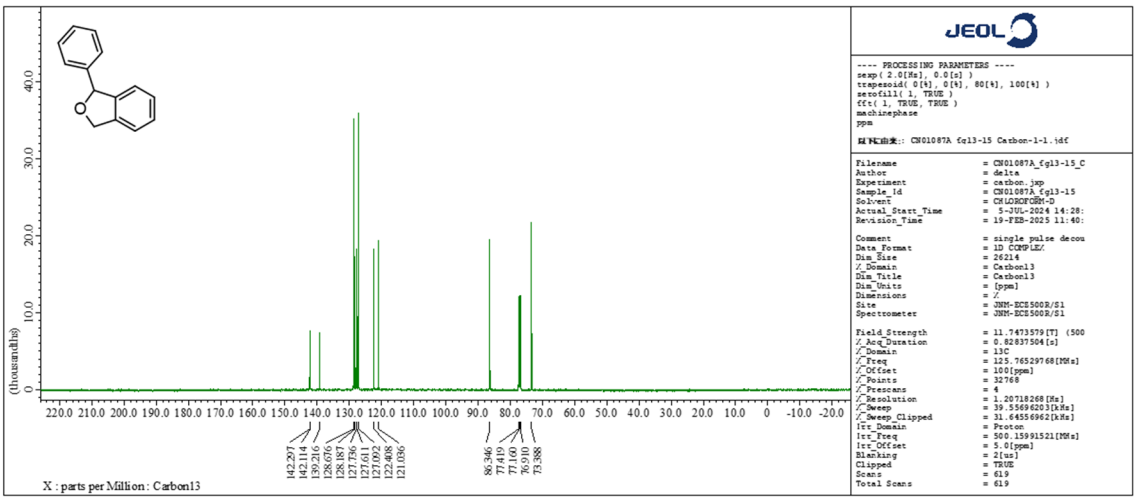
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12q**



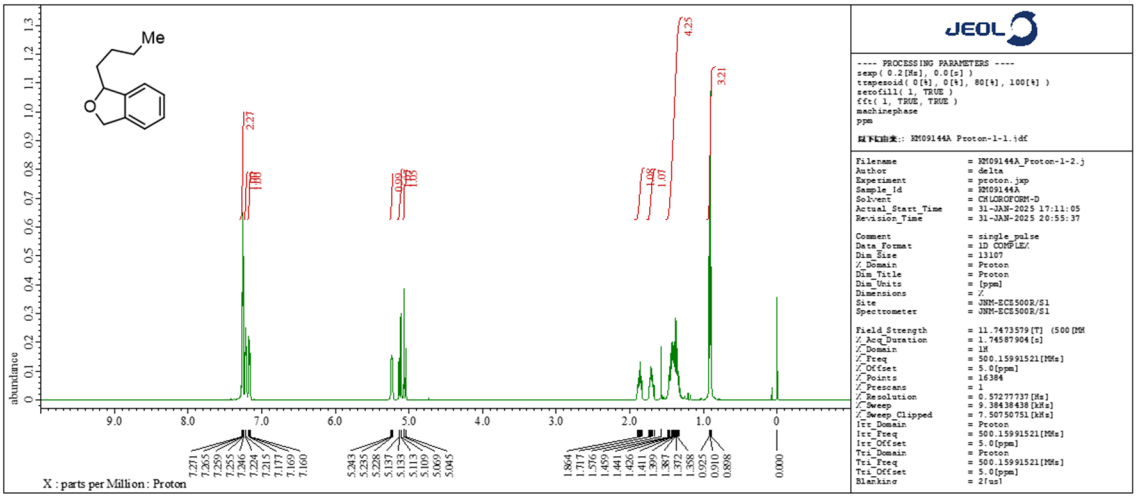

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **12r**



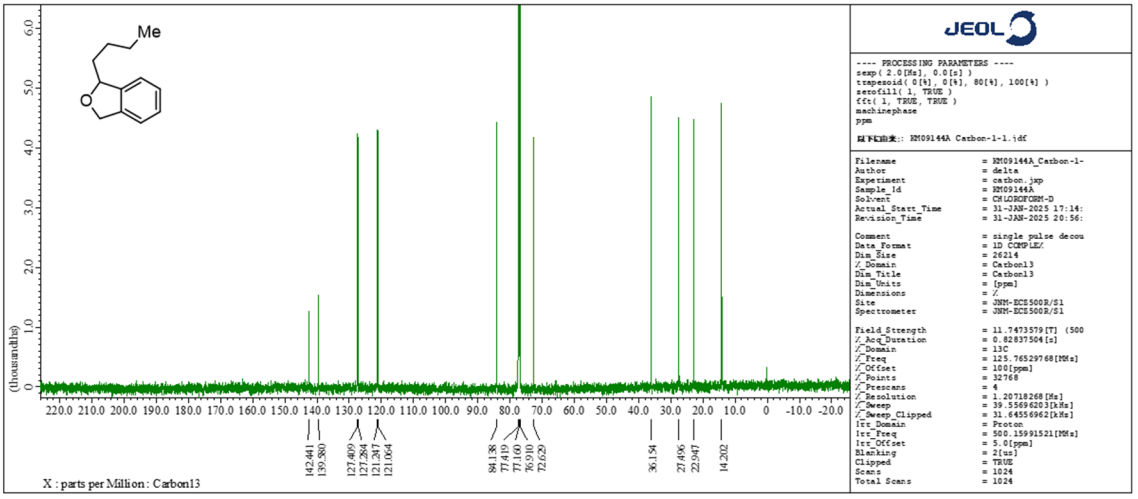

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12r**



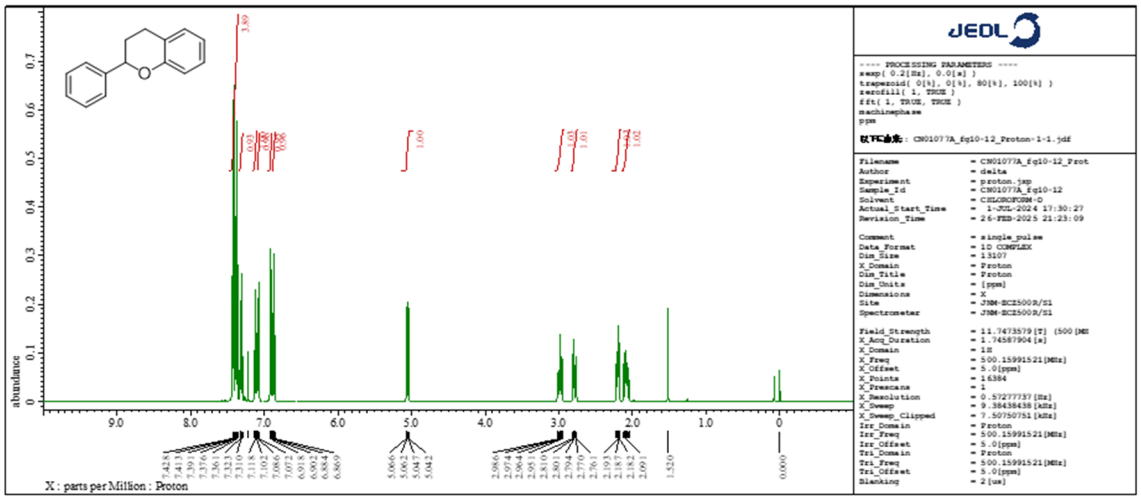
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12s**



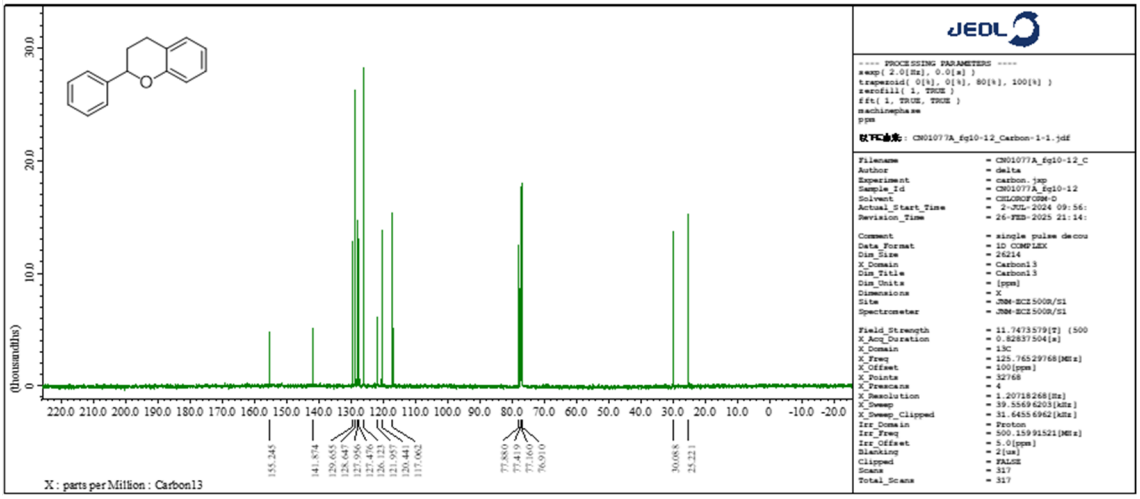

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12s**



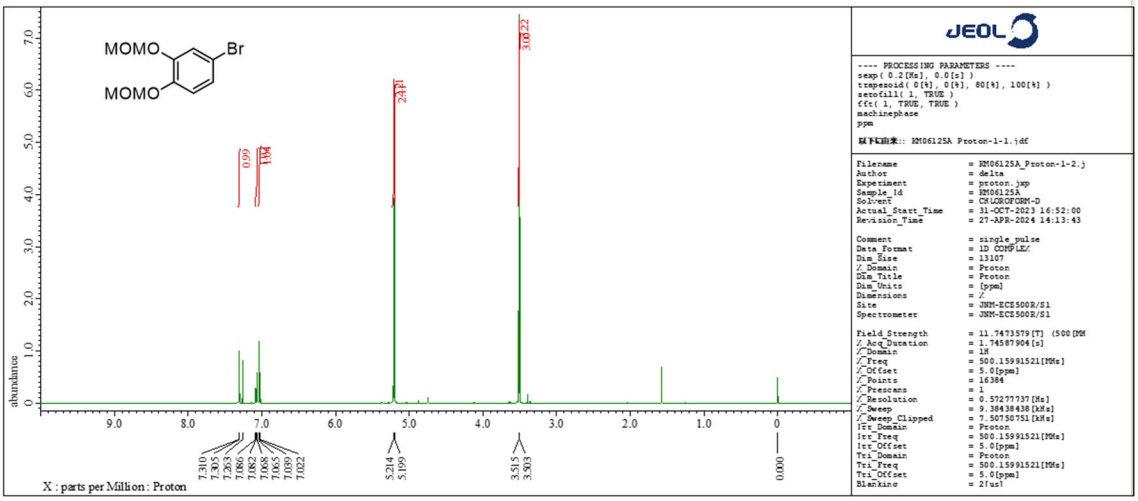

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **12t**



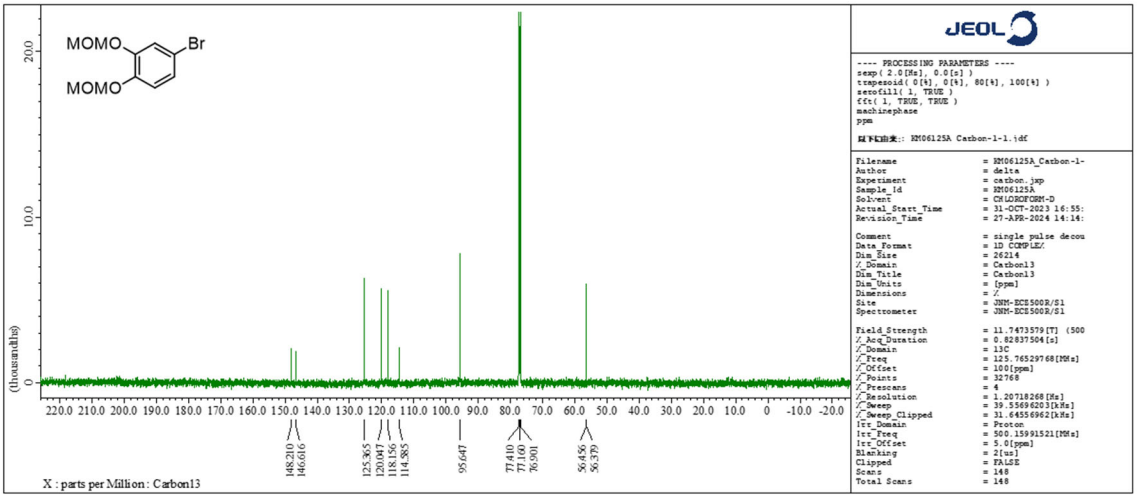
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12t**



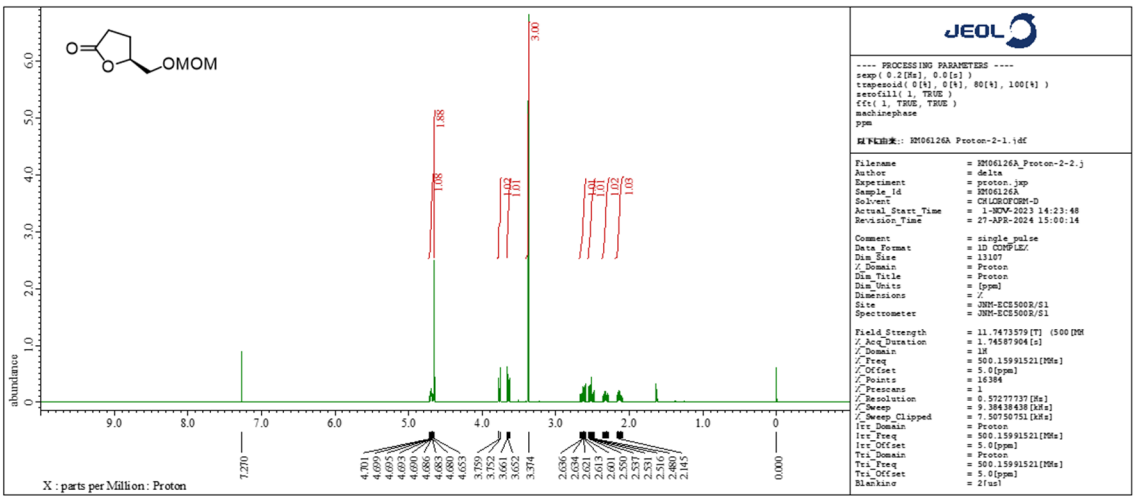
$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **5**



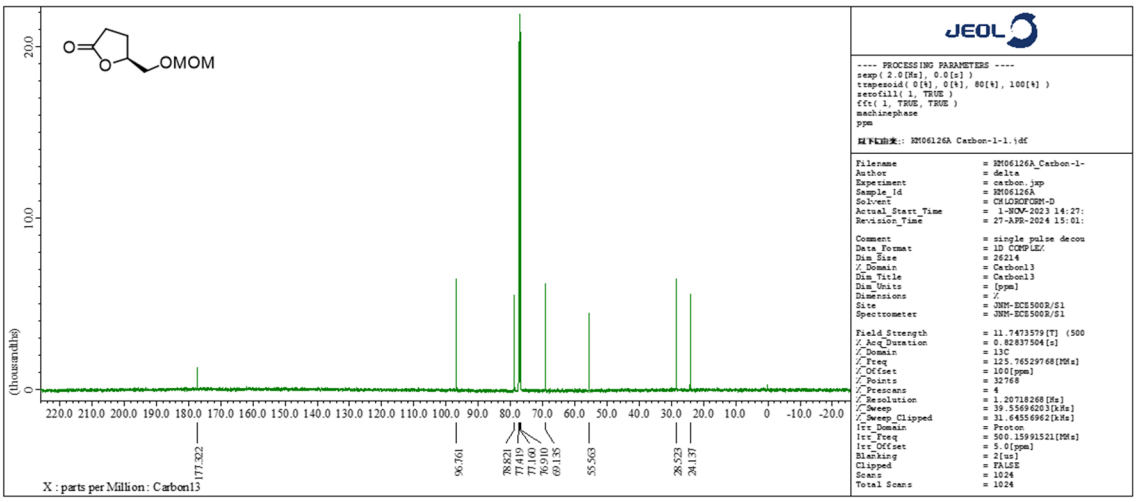

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **5**



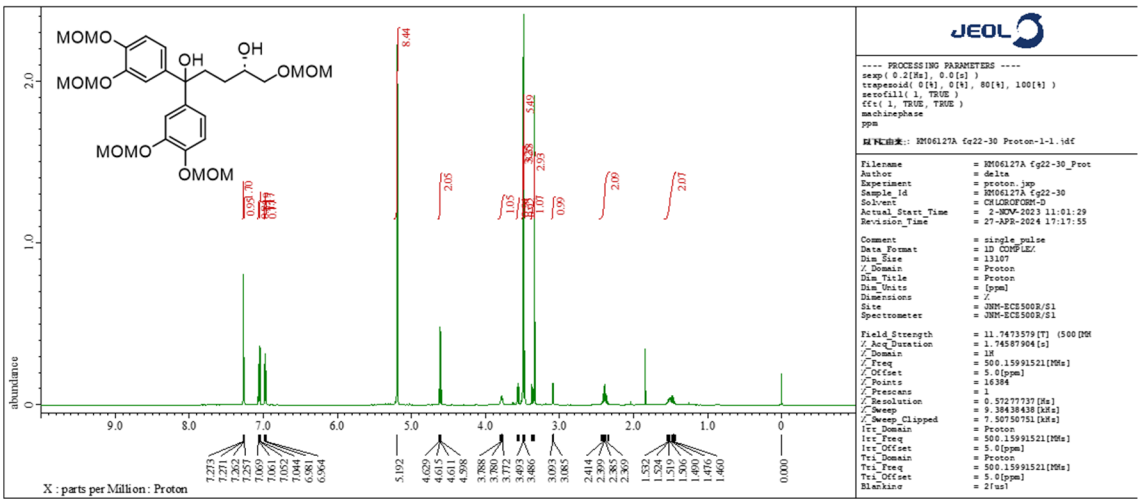
$^{1}$H NMR ($CDCl_3$, 500 MHz) of **6**



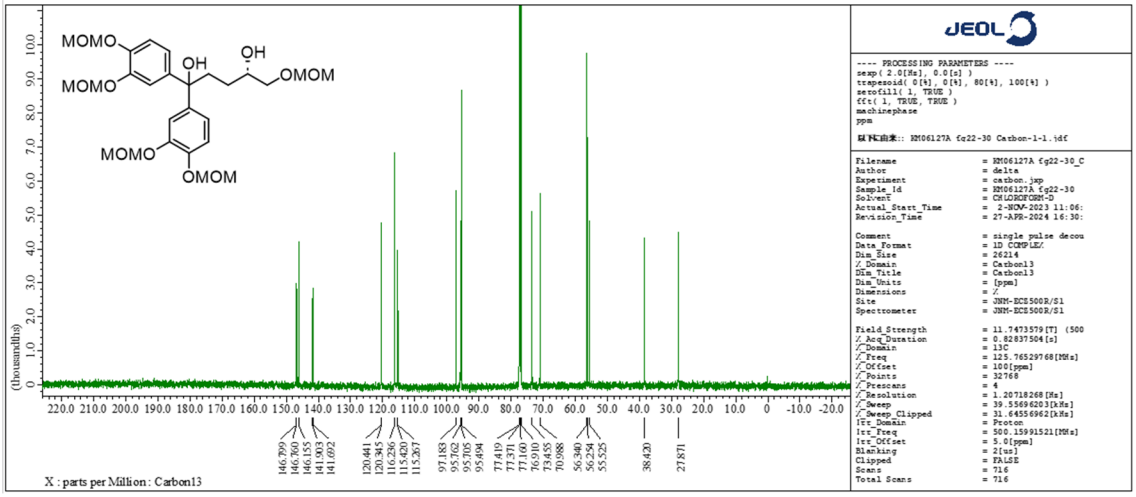

$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) of **6**



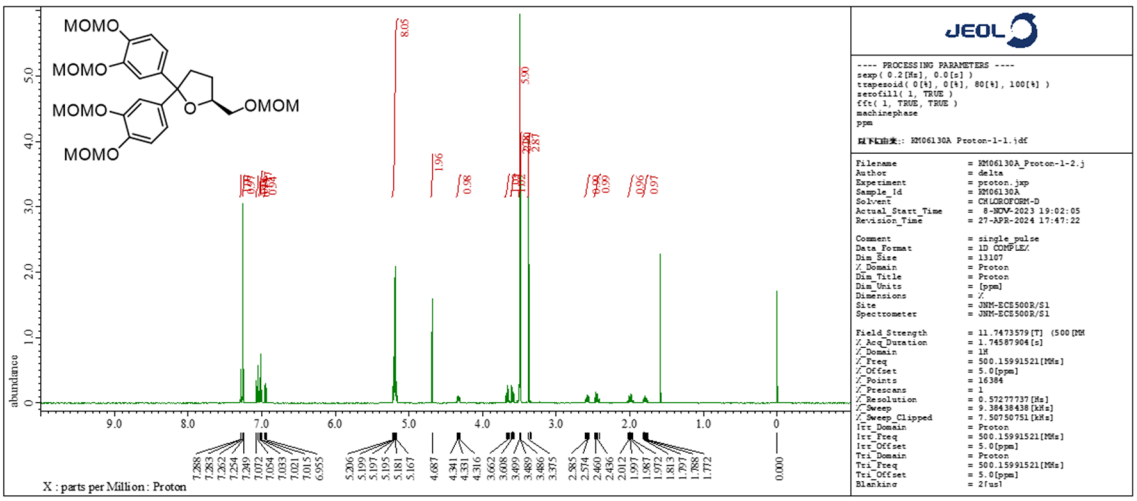

$^{1}$H NMR ($CDCl_3$, 500 MHz) of **4**



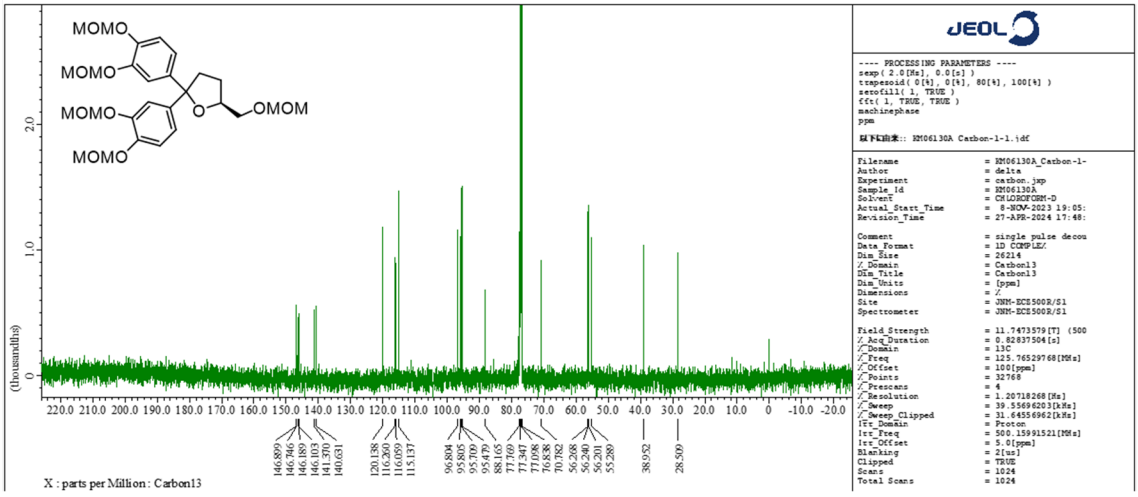
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **4**



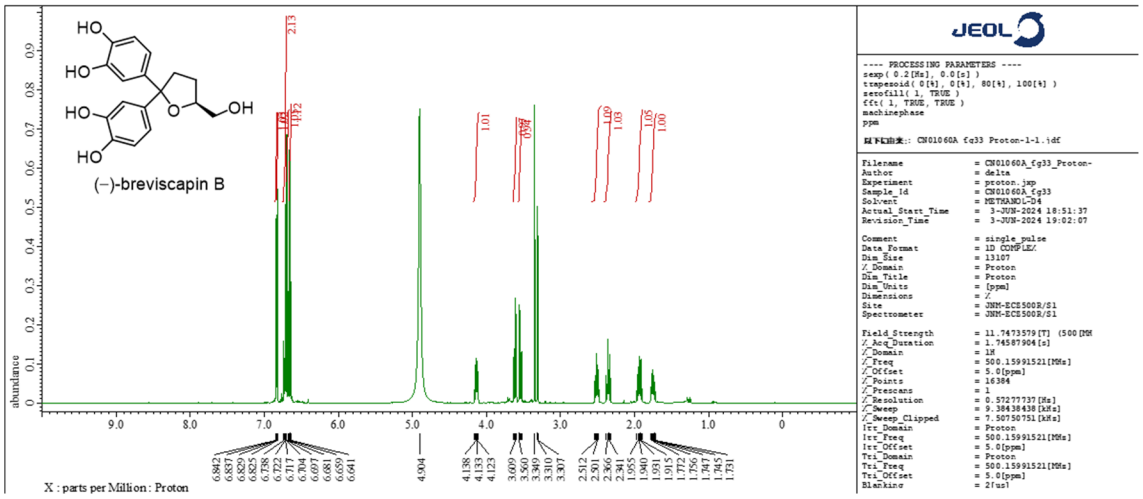

$^{1}H$ NMR ($CDCl_3$, 500 MHz) of **14**



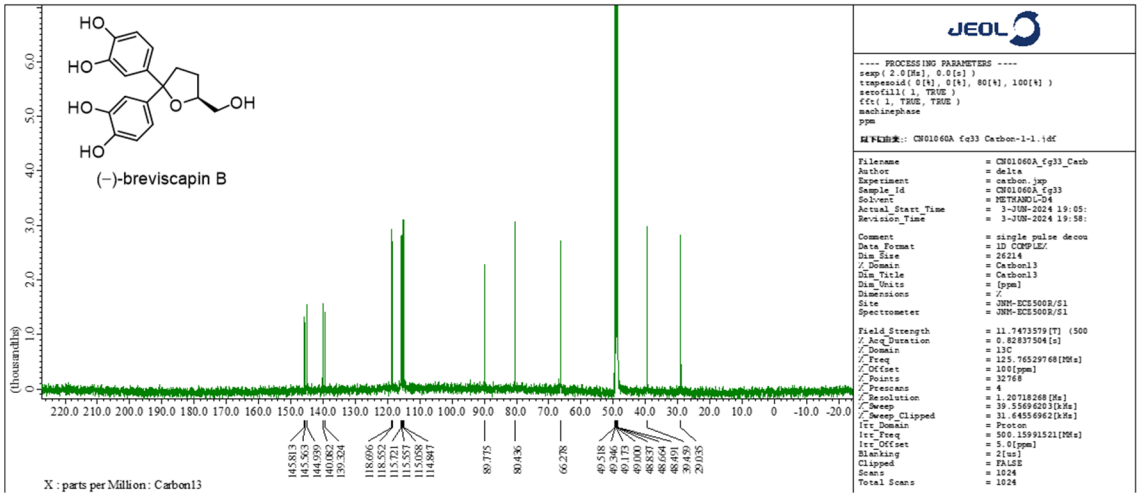

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **14**

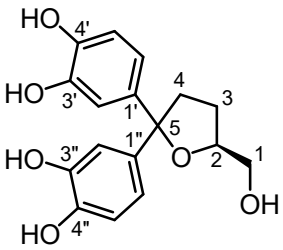


$^{1}$H NMR ($CD_3OD$, 500 MHz) of **(−)-Breviscapin B (1)**




$^{13}$C{$^{1}$H} NMR ($CD_3OD$, 125 MHz) of **(−)-Breviscapin B (1)**






breviscapin B (**1**)

**Comparison of $^{1}H$ and $^{13}C$ NMR between synthetic and natural Breviscapin B**

| | Synthetic Breviscapin B | | Natural Breviscapin B | |
|---|---|---|---|---|
| position | $\delta_C$ | $\delta_H$ ($J$ in Hz) | $\delta_C$ | $\delta_H$ ($J$ in Hz) |
| 1 | 66.3 | 3.54 (dd, 11.5, 5.2)<br>3.62 (dd, 11.5, 5.7) | 66.3 | 3.52 (dd, 11.2, 5.1)<br>3.58 (dd, 11.2, 5.9) |
| 2 | 80.4 | 4.16-4.11 (m) | 80.4 | 4.11 (m) |
| 3 | 29.0 | 1.78-1.72 (m)<br>1.97-1.90 (m) | 29.0 | 1.74 (m), 1.90 (m) |
| 4 | 39.5 | 2.38-2.33 (m)<br>2.54-2.49 (m) | 39.4 | 2.32 (m), 2.48 (m) |
| 5 | 89.8 | | 89.8 | |
| 1' | 140.1 | | 140.1 | |
| 2' | 114.8 | 6.84 (d, 2.3) | 114.8 | 6.81 (d, 2.1) |
| 3' | 145.6 | | 145.5 | |
| 4' | 145.8 | | 145.8 | |
| 5' | 115.6 | 6.65 (d, 8.6) | 115.6 | 6.61 (d, 8.3) |
| 6' | 118.7 | 6.71 (dd, 8.6, 2.3) | 118.7 | 6.67 (overlap) |
| 1'' | 139.3 | | 139.3 | |
| 2'' | 115.1 | 6.83 (d, 2.3) | 115.1 | 6.79 (d, 2.1) |
| 3'' | 144.9 | | 144.88 | |
| 4'' | 144.9 | | 144.90 | |
| 5'' | 115.7 | 6.69 (d, 8.0) | 115.7 | 6.66 (d, 8.3) |
| 6'' | 118.6 | 6.73 (dd, 8.0, 2.3) | 118.5 | 6.68 (overlap) |
| Optical rotation | -7.07 (*c* 0.52, MeOH) | | −7.1 (*c* 0.22, MeOH). | |

N. Li, C.-C. Zhu, K.-J. Wang, J.-M. Hu, *Z. Naturforsch.*, 2010, **65b**, 79–82.