Electronic Supplementary Material (ESI) for ChemComm.

TMSBr/$InBr_3$-Promoted Prins Cyclization/Homobromination of Dienyl Alcohol with Aldehyde to Form *cis*-THP Containing An Exocyclic *E*-Alkene

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Supporting Information

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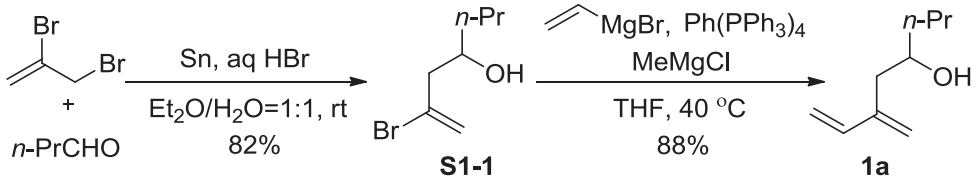
1. General Methods

TLC was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains, $H_3PO_4 \cdot 12MoO_3$/EtOH stains, H_2SO_4(conc.)/anisaldehyde/EtOH stains. Column chromatography was performed using silica gel (300-400 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 MHz (Varian) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed High-resolution massspectral analyses performed on Waters Q-TOF Premier. CH_2Cl_2, DMF, HMPA, TMEDA, CH_3CN, DMSO and NEt_3 were distilled from CaH_2. Et_2O and THF were distilled from sodium. All spectral data obtained for new compounds are reported here.

2. General Procedure and Spectral Data of Products

2.1. Preparation of Dienyl Alcohols

Preparation of 1a

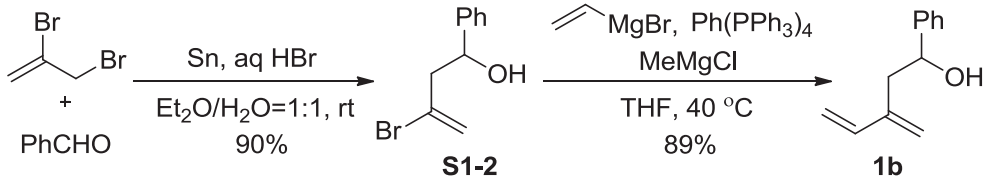


General Procedure: To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and *n*-butanal (86 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature and extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with sat aq NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-3% of EtOAc/petroleum ether) afforded **S1-1** (158 mg, 82% yield) as a colorless oil.

A solution of vinyl bromide **S1-1** (158 mg, 0.82 mmol) and MeMgCl (3.0 M in THF, 0.27 mL, 0.81 mmol) in anhyd. THF (5 mL) was stirred for 5 min at 0 °C before the addition of $Pd(PPh_3)_4$ (46 mg, 0.04 mmol). After stirring at room temperature for 5 min, vinylmagnesium bromide (1.0 M,

1.64 mL, 1.64 mmol) was added via syringe. The mixture was stirred for 15 min at room temperature and then heated at 40 °C for 7 h. After cooling to room temperature, the reaction was quenched with water and extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with sat aq NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-4% of EtOAc/petroleum ether) afforded **1a** (101 mg, 88% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, J_1 = 10.4 Hz, J_2 = 17.6 Hz, 1H), 5.33 (d, J = 17.2 Hz, 1H), 5.16 (s, 1H), 5.11 (d, J = 10.8 Hz, 1H), 5.10 (s, 1H), 3.76 (m, 1H), 2.51 (dd, J_1 = 2.8, J_2 = 13.6 Hz, 1H), 2.37 (dd, J_1 = 9.2, J_2 = 14.0 Hz, 1H), 1.68 (s, 1H), 1.37-1.55 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.1, 138.4, 118.3, 114.1, 69.2, 39.9, 39.2, 18.9, 14.0; IR (neat) cm^{-1} 3380brw, 3087m, 2960s, 2872s, 1594s, 1460s, 1419m, 1186w, 1123s, 1076s, 994s, 990s, 846w; HRMS (MALDI, m/z) calcd for $C_9H_{16}ONa$ $(M+Na)^+$: 163.1093, found 163.1091.

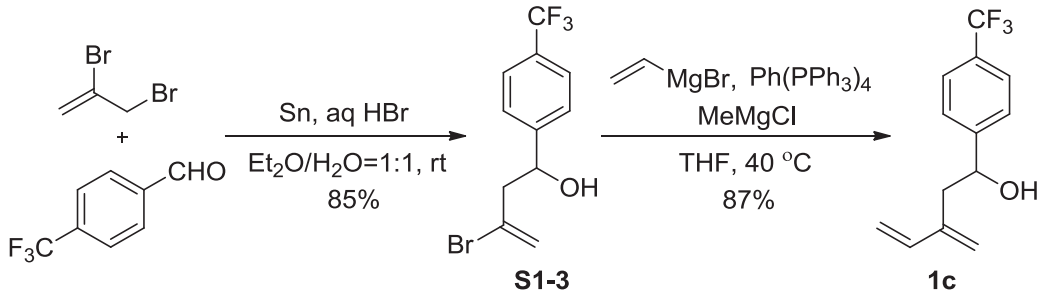
Preparation of 1b



1b: Using the same procedure as that used for **1a.** To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and benzaldehyde (127 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-2** (203 mg, 90% yield) as a colorless oil. To a solution of **S1-2** (271 mg, 1.09 mmol) in anhyd. THF (5.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.36 mL, 1.08 mmol), $Pd(PPh_3)_4$ (63 mg, 0.05 mmol) and vinylmagnesiumbromide (1.0 M, 2.18 mL, 2.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1b** (169 mg, 89% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.39 (m, 4H), 7.28 (m, 1H), 6.42 (dd, J_1 = 11.2 Hz, J_2 = 17.6 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 5.17 (s, 1H), 5.16 (d, J = 12.4 Hz, 1H), 5.10 (s, 1H), 4.84 (dd, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 1H), 2.70 (dd, J_1 = 4.0 Hz, J_2 = 14.4 Hz, 1H), 2.56 (dd, J_1 = 9.2 Hz, J_2 = 14.0 Hz, 1H), 2.11 (s, 1H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 142.6, 138.2, 128.4, 127.5, 125.7, 118.9, 114.3, 72.1, 42.1; IR (neat) cm^{-1} 3394brm, 2924s, 2855s, 1688m, 1599m,

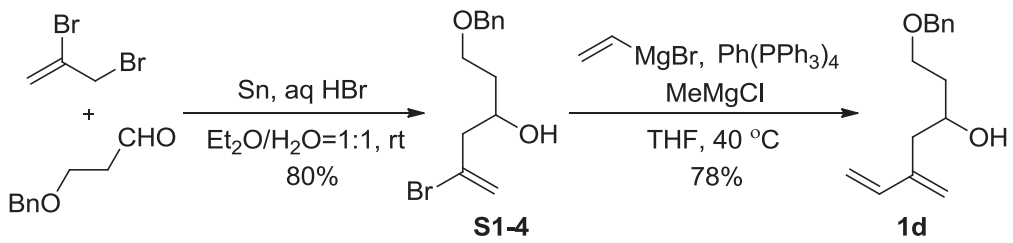
1493m, 1452s, 1418m, 1332m, 1202m, 1050s, 1004s, 912m; HRMS (MALDI, m/z) calcd for $C_{12}H_{14}ONa$ $(M+Na)^+$: 197.0937, found 197.0941.

Preparation of 1c



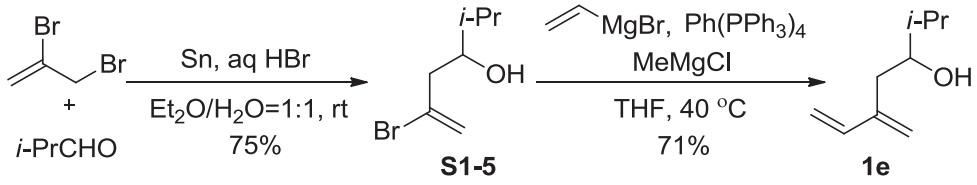
1c: Using the same procedure as that used for **1a**. To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and 4-(trifluoromethyl)benzaldehyde (209 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-3** (148 mg, 85% yield) as a colorless oil. To a solution of **S1-3** (320 mg, 1.09 mmol) in anhyd. THF (5.0 mL) were added sequentially methyl magnesium chloride (3.0 M, 0.36 mL, 1.08 mmol), $Pd(PPh_3)_4$ (63 mg, 0.05 mmol) and vinylmagnesiumbromide (1.0 M, 2.18 mL, 2.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1c** (230 mg, 87% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 6.42 (dd, J_1 = 10.8 Hz, J_2 = 17.6 Hz, 1H), 5.32 (d, J = 17.2 Hz, 1H), 5.19 (s, 1H), 5.18 (d, J = 12.0 Hz, 1H), 5.08 (s, 1H), 4.87 (m, 2H), 2.69 (dd, J_1 = 3.6 Hz, J_2 = 14.0 Hz, 1H), 2.53 (dd, J_1 = 9.2 Hz, J_2 = 14.4 Hz, 1H), 2.36 (s, 1H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.9, 142.1, 138.01, 138.02, 129.7 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 126.0, 125.3 (q, $^1J_{C\text{-}F}$ = 3.8 Hz), 119.3, 114.4, 71.5, 42.2; IR (neat) cm^{-1} 3388brm, 2928m, 1620m, 1595m, 1419m, 1327s, 1166s, 1128s, 1068s, 905m, 840m; HRMS (MALDI, m/z) calcd for $C_{13}H_{14}F_3O$ $(M+H)^+$: 243.0991, found 243.0991.

Preparation of 1d



1d: Using the same procedure as that used for **1a.** To a suspension of tin powder (178 mg, 1.50 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and 4-(benzyloxy)propanal (214 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-4** (142 mg, 80% yield) as a colorless oil. To a solution of **S1-4** (310 mg, 1.09 mmol) in anhyd. THF (5.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.36 mL, 1.08 mmol), $Pd(PPh_3)_4$ (63 mg, 0.05 mmol) and vinylmagnesiumbromide (1.0 M, 2.18 mL, 2.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1d** (197 mg, 78% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 5H), 6.39 (dd, J_1 = 10.8 Hz, J_2 = 17.6 Hz, 1H), 5.14 (s, 1H), 5.10 (d, J = 11.2 Hz, 1H), 5.09 (s, 1H), 4.53 (s, 2H), 4.00 (m, 1H), 3.71 (m, 1H), 3.65 (m, 1H), 2.90 (m, 1H), 2.42 (d, J = 6.0 Hz, 2H), 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.4, 137.9, 128.3, 127.6, 127.5, 118.2, 114.0, 73.1, 68.9, 68.7, 39.7, 36.1; IR (neat) cm^{-1} 3448brm, 2926s, 2861s, 1594m, 1544s, 1365s, 1180m, 1096s, 994s; HRMS (MALDI, m/z) calcd for $C_{15}H_{20}O_2Na$ $(M+Na)^+$: 255.1356, found 255.1357.

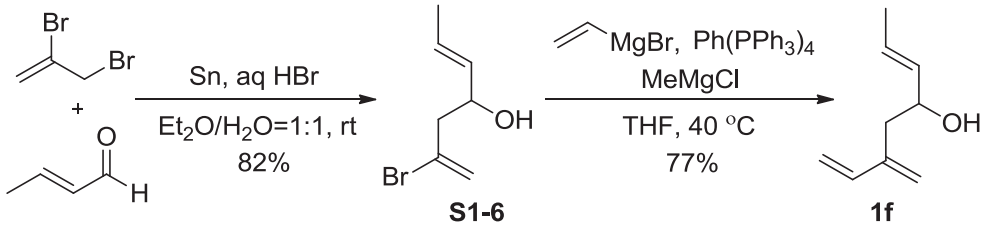
Preparation of 1e



1e: Using the same procedure as that used for **1a**. To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and isobutyraldehyde (86 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-5** (54 mg, 75% yield) as a colorless oil. To a solution of **S1-5** (209.3 mg, 1.09 mmol) in anhyd. THF (5.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.36 mL, 1.08 mmol), $Pd(PPh_3)_4$ (63 mg, 0.05 mmol) and vinylmagnesiumbromide (1.0 M, 2.18 mL, 2.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1e** (108.4 mg, 71% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, J_1 = 11.2 Hz, J_2 = 17.6 Hz, 1H), 5.24 (d, J = 18.0 Hz, 1H), 5.16 (s, 1H), 5.114 (d, J = 9.6 Hz, 1H), 5.109 (s, 1H), 3.51 (m, 1H), 2.58 (d, J = 14.0 Hz, 1H), 2.14 (dd, J_1 = 10.0 Hz, J_2 = 14.0 Hz, 1H), 1.74 (m, 1H), 1.64 (s, 2H), 0.99 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.3, 118.4, 114.2, 73.9, 36.6,

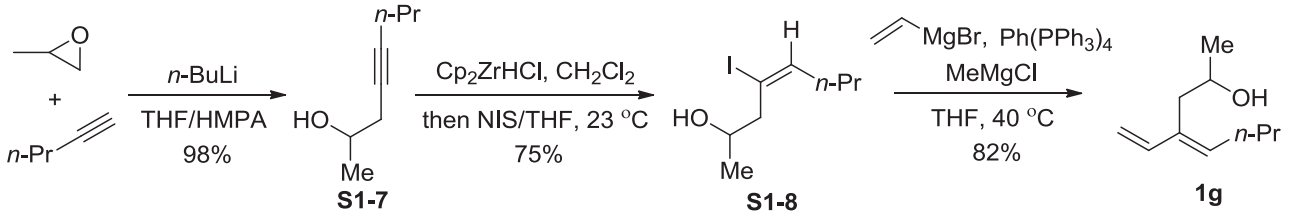
33.4, 18.6, 17.6; IR (neat) cm^{-1} 3448brm, 2926s, 2861s, 1594m, 1544s, 1365s, 1180m, 1096s, 994s; HRMS (MALDI, m/z) calcd for $C_9H_{16}OK$ $(M+K)^+$: 179.0833, found 179.0830.

Preparation of 1f



1f: Using the same procedure as that used for **1a**. To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) mixture was added aq HBr (1.0 M, 1.0 mL) and (*E*)-but-2-enal (84 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-6** (55 mg, 82% yield) as a colorless oil. To a solution of **S1-6** (207 mg, 1.09 mmol) in anhyd. THF (5.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.36 mL, 1.08 mmol), $Pd(PPh_3)_4$ (63 mg, 0.05 mmol) and vinylmagnesiumbromide (1.0 M, 2.18 mL, 2.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1f** (116 mg, 77% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, J_1 = 11.2 Hz, J_2 = 18.0 Hz, 1H), 5.69 (dq, J_1 = 6.8 Hz, J_2 = 15.6 Hz, 1H), 5.51 (dd, J_1 = 7.2, J_2 = 15.6 Hz, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.15 (s, 1H), 5.11 (d, J = 10.8 Hz, 2H), 5.10 (s, 1H), 4.22 (m, 1H), 2.49 (dd, J_1 = 4.4 Hz, J_2 = 14.0 Hz, 1H), 2.36 (dd, J_1 = 8.4 Hz, J_2 = 14.0 Hz, 1H), 1.86 (s, 1H), 1.70 (d, J = 6.4 Hz, 3H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.5, 138.4, 133.3, 126.8, 118.5, 114.1, 70.6, 39.9, 17.6; IR (neat) cm^{-1} 3377brm, 3087m, 2936s, 2858m, 1673w, 1594s, 1447s, 1381s, 1325m, 1258m, 1187w, 1117s, 1082m, 1024s, 992s, 966s, 899s; HRMS (MALDI, m/z) calcd for $C_9H_{14}ONa$ $(M+Na)^+$: 161.0937, found 161.0934.

Preparation of 1g



S1-7: To a solution of 1-pentyne (8.2 mL, 83 mmol) in dry THF (40 mL) was added *n*-BuLi (1.6 M in hexane, 27.5 mL, 44 mmol) at -40 °C under argon. The reaction mixture was warmed to 0 °C

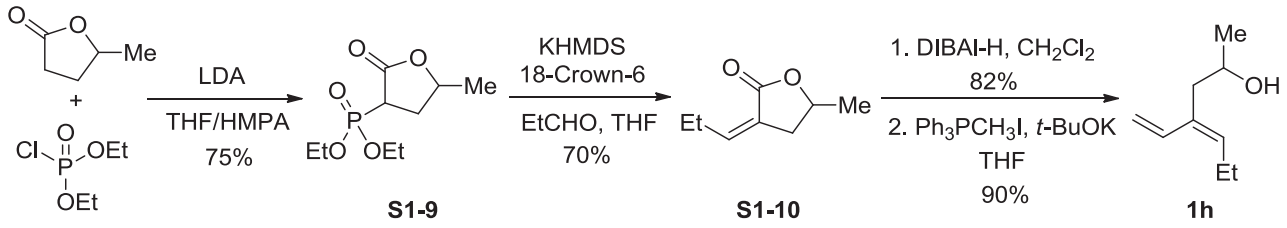
over 30 min before recooling to -20 °C. To the above mixture were added sequentially dry HMPA (15 mL) and a solution of 2-methyloxirane (2.61 g, 45 mmol) in dry HMPA (15 mL) at -20 °C over 15 min. The reaction was stirred at -20 °C for 30 min, then warmed to 20 °C over 4 h with stirring for another 12 h. The mixture was then poured into ice water (100 mL) and extracted with ether (4 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 10-20% of EtOAc/petroleum ether) afforded **S1-7** as a colorless oil (5.55 g, 98% yield).

S1-8[1]: To a stirred suspension of Cp_2ZrHCl (1.84 g, 7.14 mmol) in CH_2Cl_2 (15.0 mL) was added a solution of **S1-7** (300 mg, 2.38 mmol) in CH_2Cl_2 (6.0 mL) in one portion at room temperature. The mixture was stirred for 3 h before adding a solution of *N*-iodosuccinimide (1.84 g, 7.14 mmol) in THF (5.0 mL). After stirring for 0.5 h at room temperature, the reaction was quenched with a mixed solution of sat aq $Na_2S_2O_3$ (25 mL) and sat aq $NaHCO_3$ solution (25 mL). The mixture was then extracted with ether (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1% of EtOAc/petroleum ether) afforded **S1-8** as a colorless oil (453 mg, 75% yield).

1g: Using the same procedure as that used for **1a**. To a solution of **S1-8** (400 mg, 1.57 mmol) in anhyd. THF (25.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.52 mL, 1.57 mmol), $Pd(PPh_3)_4$ (91 mg, 0.05 mmol) and vinylmagnesiumbromide (1.0 M, 3.15 mL, 3.15 mmol). The reaction was heat at 40 °C for 7 h to produce **1g** (198 mg, 82% yield) as a colorless oil. ^{1}H NMR(400 MHz, $CDCl_3$) δ 6.32 (dd, J_1 = 12.8 Hz, J_2 = 17.6 Hz, 1H), 5.66 (t, J = 7.2 Hz, 1H), 5.13 (d, J = 17.6 Hz, 1H), 4.96 (d, J = 12.8 Hz, 1H), 3.95 (m, 1H), 2.36-2.49 (m, 2H), 2.17 (q, J_1= 7.6 Hz, J_2 = 15.2 Hz, 2H), 1.66 (s, 1H), 1.37-1.47 (m. 2H), 1.22 (d, J = 6.4 Hz, 3H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.4, 134.7, 111.2, 66.9, 35.9, 30.6, 23.0, 22.8, 13.9; IR (neat) cm^{-1} 3349brs, 2963s, 2930s, 2871s, 1636m, 1606m, 1461s, 1374m, 1308w, 1118m, 1077s, 992m, 939m, 894s, 845w; HRMS (MALDI, m/z) calcd for $C_{10}H_{18}ONa$ ($M+Na^+$): 177.1250, found 177.1254.

Preparation of 1h

1. X. F. Liu, J. M. Ready, *Tetrahedron*, **2008**, *64*, 6955-6960.



S1-9[2]**:** To a solution of LDA (5.5 mmol) in THF (15 mL) at -78 ^{o}C was added dropwise 5-methyldihydrofuran-2(3H)-one (500 mg, 5 mmol). After 30 min, a solution of diethyl chlorophosphate (0.83 mL, 5.7 mmol) in HMPA (1 mL) was added, and the resulting mixture was allowed to warm to room temperature over 30 min. After cooling of the reaction mixture to -78 °C, a solution of LDA (11 mmol) in THF (30 mL) was added, and the mixture was warmed to room temperature over 2 h. The reaction was quenched by slow addition of a solution of acetic acid in diethyl ether (1 M, 22 mL). The resulting mixture was filtered through a pad of silica gel, and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 50% of EtOAc/petroleum ether) afforded **S1-9** (885 mg, 75%).

S1-10[3]**:** To a solution of **S1-9** (264 mg, 1.2 mmol) in THF (30 mL) at room temperature was added 18-crown-6 (1.01g, 4.28 mmol). The reaction mixture was cooled to -78 °C and allowed to stir for an additional 5 min before adding KHMDS (1.0 M in THF, 4.6 mL, 4.6 mmol). After 30 min, propionaldehyde (290 mg, 5 mmol) was added dropwise over 2 min. Immediately after addition of the aldehyde, the reaction flask was placed in an 30 °C water bath and allowed to stir for an additional 3 h. The reaction mixture was quenched with sat aq NH_4Cl and extracted with ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-25% of EtOAc/petroleum ether) afforded **S1-10** as a colorless oil (419 mg, 70%).

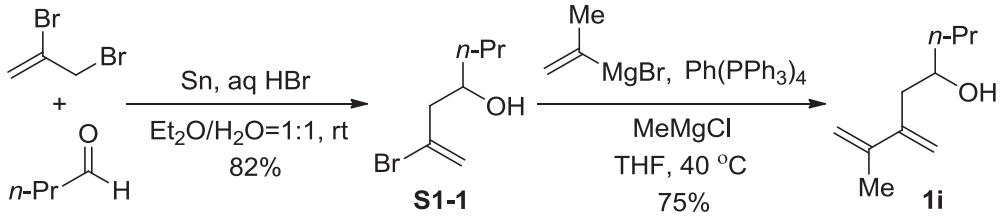
1h: To a solution of **S1-10** (248 mg, 1.77 mmol) in CH_2Cl_2 (17 mL) at -78 ^{o}C was added DIBAl-H (1.86 mL, 1.0 M in hexance, 1.86 mmol). After stirring for 30 min, the reaction was quenched with MeOH (5 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-30% of EtOAc/petroleum ether) afforded

2. J. A. Jackson, G. B. Hammond, D. F. Wiemer, *J. Org. Chem.* **1989**, *54*, 4750-4754.
3. J. S. Yu, D. F. Wiemer, *J. Org. Chem.* **2007**, *72*, 6263-6265.

hemiacetal (206 mg, 82%).

To a suspension of Ph_3PCH_3I (2.89 g) in THF (20 mL) at 0 ^oC was added *t*-BuOK (750 mg). After 30 min, a solution of hemiacetal (317 mg, 2.23 mmol) in THF (2 mL) at -78 ^oC was added slowly. The reaction was allowed to warm to room temperature and stir for 3 h before quenching with H_2O (20 mL) and extraction with Et_2O (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 30% of EtOAc/petroleum ether) afforded **1h** as a colorless oil (281 mg, 90%). ^1H NMR (600 MHz, $CDCl_3$) δ 6.64 (dd, J_1 = 10.8 Hz, J_2 = 17.4 Hz, 1H), 5.44 (t, J = 7.8 Hz, 1H), 5.20 (d, J = 17.4 Hz, 1H), 5.09 (d, J = 10.2 Hz, 1H), 3.88 (m, 1H), 2.41 (dd, J_1 = 4.2 Hz, J_2 = 13.8 Hz, 1H), 2.13-2.24 (m, 2H), 1.66 (s, 1H), 1.37-1.47(m. 3H), 1.83 (s, 1H), 1.16 (d, J = 6.0 Hz, 3H), 0.98 (t, J = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 132.6, 132.4, 114.0, 65.9, 43.5, 22.8, 20.7, 14.3; IR (neat) cm^{-1} 3360brs, 3089W, 2967s, 2875s, 1641w, 1595w, 1458s, 1420w, 1372m, 1264w, 1119s, 1078s, 991m, 939m, 904s; HRMS (MALDI, m/z) calcd for $C_9H_{16}OK$ ($M+K^+$):179.0833, found 179.0831.

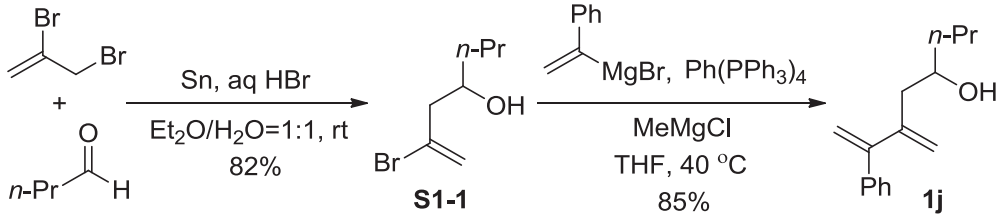
Preparation of 1i



1g: Using the same procedure as that used for **1a**. To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and *n*-butanal (86 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-1** (158 mg, 82% yield) as a colorless oil. To a solution of **S1-1** (400 mg, 2.07 mmol) in anhyd. THF (20.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.69 mL, 2.07 mmol), $Pd(PPh_3)_4$ (119 mg, 0.10 mmol) and prop-1-en-2-ylmagnesium bromide (1.0 M in THF, 4.14 mL, 4.14 mmol). The reaction was heat at 40 °C for 7 h to produce **1i** (239mg, 75% yield) as a colorless oil. ^1H NMR(400 MHz, $CDCl_3$) δ 5.21 (s, 1H), 5.08 (s, 1H), 5.05 (s, 1H), 5.02 (s, 1H), 3.72 (m, 1H), 2.59 (dd, J_1= 3.2 Hz, J_2 = 14.0 Hz, 1H), 2.23 (dd, J_1 = 8.8 Hz, J_2 = 14.0 Hz, 1H), 1.92

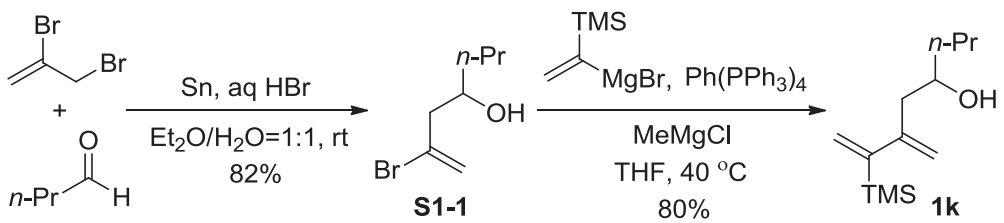
(s, 3H), 1.88 (s, 1H), 1.32-1.56 (m, 4H), 0.94 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.2, 114.8, 113.4, 69.4, 42.2, 39.2, 21.0, 18.8, 14.0; IR (neat) cm^{-1} 3359brs, 3094m, 2958s, 2872s, 1796w, 1597s, 1447s, 1377m, 1122m, 1073m, 1016m, 967m, 893s, 845w; HRMS (MALDI, m/z) calcd for $C_{10}H_{18}ONa$ ($M+Na^+$):177.1250, found 177.1245.

Preparation of 1j



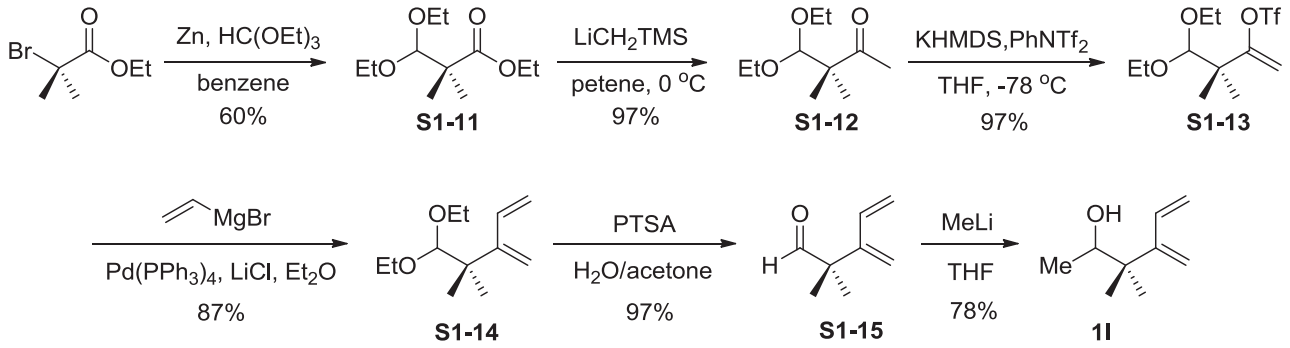
1j: Using the same procedure as that used for **1a.** To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and *n*-butanal (86 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-1** (158 mg, 82% yield) as a colorless oil. To a solution of **S1-1** (500 mg, 2.59 mmol) in anhyd. THF (25.0 mL) were added sequentially methylmagnesium chloride (3.0 M, 0.86 mL, 2.59 mmol), $Pd(PPh_3)_4$ (149 mg, 0.05 mmol) and (1-phenylvinyl)magnesium bromide (1.0 M in THF, 5.18 mL, 5.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1j** (475mg, 85% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.36 (m, 5H), 5.32 (s, 1H), 5.24 (s, 1H), 5.19 (s, 1H), 5.14 (d, J = 2.4 Hz, 1H), 3.74 (m, 1H), 2.52 (dd, J_1 = 3.6 Hz, J_2 = 13.8 Hz, 1H), 2.28 (dd, J_1 = 9.6 Hz, J_2 = 15.0 Hz, 1H), 1.67 (s, 1H), 1.40-1.50 (m, 3H), 1.31-1.39 (m, 1H), 0.91 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 145.9, 140.5, 128.1, 127.9, 127.4, 118.2, 114.2, 69.2, 42.8, 39.0, 18.8, 14.0; IR (neat) cm^{-1} 3378brs, 3083m, 2958s, 2871s, 1810w, 1591m, 1492m, 1447m, 1264m, 1122m, 1072m, 1022m, 901s, 778s; HRMS (MALDI, m/z) calcd for $C_{15}H_{20}ONa$ ($M+Na^+$): 239.1406, found 239.1410.

Preparation of 1k



1k: Using the same procedure as that used for **1a.** To a suspension of tin powder (178 mg, 1.5 mmol) and 2,3-dibromo-prop-1-ene (200 mg, 1.0 mmol) in Et_2O/H_2O (1:1, 10 mL) was added aq HBr (1.0 M, 1.0 mL) and *n*-butanal (86 mg, 1.2 mmol). The mixture was stirred for 4 h at room temperature to produce **S1-1** (158 mg, 82% yield) as a colorless oil. To a solution of **S1-1** (500 mg, 2.59 mmol) in anhyd. THF (25.0 mL) were added sequentially methylmagnesium chloride (3.0 M in THF, 0.86 mL, 2.59 mmol), $Pd(PPh_3)_4$ (149 mg, 0.05 mmol) and (1-(trimethylsilyl)vinyl)magnesium bromide (1.0 M in THF, 5.18 mL, 5.18 mmol). The reaction was heat at 40 °C for 7 h to produce **1k** (439 mg, 80% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (d, J = 2.8 Hz, 1H), 5.24 (d, J = 2.8 Hz, 1H), 4.95 (s, 1H), 4.94 (d, J = 2.4 Hz, 1H), 3.63 (m, 1H), 2.46 (dd, J_1 = 3.6 Hz, J_2 = 14 Hz, 1H), 2.18 (dd, J_1 = 9.2 Hz, J_2 = 13.6 Hz, 1H), 1.75 (s, 1H), 1.32.-1.42 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 148.8, 126.0, 114.4, 68.7, 44.0, 39.0, 18.9, 14.1, -0.71; IR (neat) cm^{-1} 3360brs, 2959s, 2873s, 1618m, 1460m, 1410m, 1251s, 1121m, 1018m, 866s, 838s, 758m; HRMS (MALDI, m/z) calcd for $C_{12}H_{25}OSi$ ($M+H^+$): 213.1669, found 213.1661.

Preparation of 1l



S1-11: To a solution of 2-bromoisobutyric acid ethyl ester (1.94 g, 10 mmol) and ethyl orthoformate (1.67 mL, 10 mmol) in dry benzene (15 ml) was added activated zinc (80 mmol, 5.12 g). After the initial reaction had subsided, the mixture was refluxed for 2 h before extraction with cool dilute AcOH followed by sat aq $NaHCO_3$. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-2% of EtOAc/petroleum ether) afforded **S1-11** (1.33 g, 60%).

S1-12: To a solution of **S1-11** (2.00 g, 9.16 mmol) in pentane (23 mL) at 0 °C was cooled (trimethylsilyl)methyllithium (1.0 M in pentane, 27.5 mL, 27.5 mmol). After 4 h, MeOH (8 mL)

was added drop-wise and the mixture was allowed to warm to room temperature and then stirred for 1 h. The mixture was quenched with sat aq $NaHCO_3$ (20 mL) and extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded **S1-12** (1.68 g, 97%).

S1-13[4]**:** To a solution of **S1-12** (3.25 g, 17.3 mmol) in THF (35 mL) at –78 °C was added potassium hexamethyldisilizide (1.0 M in THF, 20.7 mL, 20.7 mmol). After 1 h, a solution of *N*-phenyltrifluoromethanesulfonimide (7.40 g, 20.7 mmol) in THF (15 mL) was added dropwise. The reaction was stirred for 2 h before quenching with sat aq NaHCO3 and extraction with hexanes (2 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-3% of EtOAc/petroleum ether) afforded **S1-13** (5.36 g, 97%).

S1-14: A dry flask was charged with LiCl (1.06 g, 25.0 mmol) and the solid was flame-dried under reduced pressure and purged with argon. Et2O (25 mL) was added followed by a solution of **S1-13** (2.00 g, 6.24 mmol) in Et2O (15 mL). The suspension was cooled to 0 °C and $Pd(PPh_3)_4$ (361 mg, 0.312 mmol) was added followed by vinylmagnesium bromide (1.0 M in THF, 12.5 mL, 12.5 mmol). After 5 h, the suspension was filtered over a pad a silica gel and the filtration was eluted with Et_2O (40 mL). The resulting solution was poured over 50 mL of saturated aqueous NaHCO3 and extracted with Et_2O (2 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-2% of EtOAc/petroleum ether) afforded **S1-14** (1.40 g, 87%).

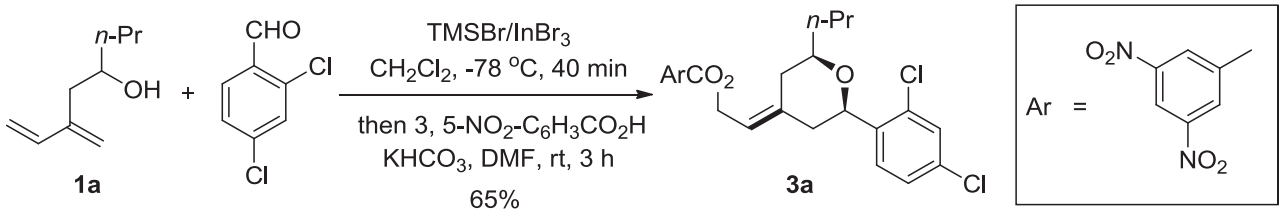
S1-15: To a solution of **S1-14** (1.72 g, 6.65 mmol) in a mixed solvent of acetone (35 mL) and H2O (35 mL) was added *p*-toluenesulfonic acid (253 mg, 1.33 mmol). After 17 h, the reaction was quenched with sat aq NaHCO3 (50 mL) and extracted with Et2O (100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded **S1-15** (1.18 g, 97%).

4. M. R. Gesinski, S. D. Rychnovsky, *J. Am. Chem. Soc*. **2011**, *133*, 9727-9729.

1l: To a solution of **S1-15** (163 mg, 1.31 mmol) in THF (13 mL) at -78 ^{o}C was added MeLi (1.6 M in Et_2O, 1.64 mL, 2.62 mmol). After 30 min, the reaction was quenched with sat aq NH_4Cl (10 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1% of EtOAc/petroleum ether) afforded **1l** (143 mg, 78%). ^{1}H NMR (400 MHz, CDCl3) δ 6.43 (dd, J_1 = 8.4 Hz, J_2 = 16.4 Hz, 1H), 5.41 (d, J = 16.4 Hz, 1H), 5.27 (s, 1H), 5.09 (d, J = 8.0, 1H), 3.73(m, 1H), 1.52 (s, 1H), 1.09 (d, J = 6.8, 6 H), 1.05(s, 3H); ^{13}C NMR (150 MHz, CDCl3)δ 153.9, 136.7, 115.7, 111.2, 72.1, 43.2, 22.9, 21.0, 16.9, 14.3; IR (neat) cm^{-1} 3385brw, 3082m, 2964s, 2875s, 1590s, 1462s, 1420m, 1185w, 1124s, 1078s, 994s, 990s, 845w; HRMS (MALDI, m/z) calcd for $C_9H_{16}ONa$ ($M+Na^+$):163.1093, found 163.1096.

2.2. Prins/Homobromination of Dienyl Alcohols with Aldehydes

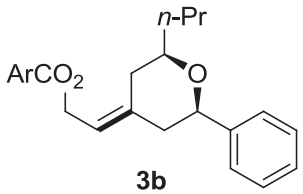
Preparation of 3a



General Procedure: To a solution of 2,4-dichlorobenzaldehyde (104 mg, 0.6 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.0 mL) was added TMSBr (110 mg, 0.72 mmol) at –78 °C. After stirring for 5 min, a solution of **1a** (100 mg, 0.71 mmol) in anhyd. CH_2Cl_2 (0.5 mL) was added over 5 min. The mixture was stirred for 40 min at –78 °C before quenching with sat aq $NaHCO_3$ (2 mL) and extraction with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. To a premixed solution of 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) was added the above crude residue with exclusion of direct light. The reaction was stirred for 3 h at room temperature before quenching with H_2O (5 mL) and extraction with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-2%

of EtOAc/petroleum ether) afforded **3a** (197 mg, 65% yield, mp = 128-129 °C, *E/Z* = 96:4) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.18 (s, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.33 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 5.63 (t, *J* = 7.2 Hz, 1H), 5.00 (m, 1H), 4.67 (d, *J* = 11.2, 1H), 3.50 (m, 1H), 2.75 (d, *J* = 13.6 Hz, 1H), 2.59 (d, *J* = 13.2 Hz, 1H), 2.07 (dd, $J_1 = J_2$ = 12.8 Hz, 1H), 1.95 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.70 (m, 1H), 1.42-1.66 (m, 3H), 0.94 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 148.6, 142.8, 138.6, 134.0, 133.5, 132.0, 129.5, 128.9, 128.1, 127.5, 122.3, 116.6, 77.9, 76.2, 62.4, 42.3, 38.5, 34.9, 18.6, 14.1; IR (neat) cm^{-1} 3475s, 3415s, 3105m, 2956m, 1731s, 1626m, 1548s, 1466m, 1394m, 1346s, 1260m, 1165m, 1077m; HRMS (MALDI, m/z) calcd for $C_{23}H_{22}Cl_2N_2O_7Na$ $(M+Na)^+$: 531.0696, found 531.0701.

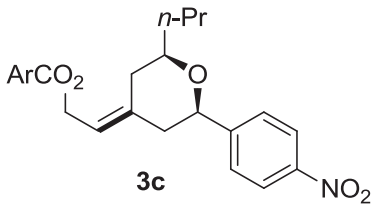
Preparation of 3b



3b

3b: Using the same general procedure as that used for **3a**. Benzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3b** (158 mg, 60% yield, mp = 74-75 °C, *E/Z* = 91:9) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.19 (s, 2H), 7.30-7.42 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 1H), 5.62 (t, *J* = 7.2 Hz, 1H), 5.03 (dd, J_1 = 7.2 Hz, J_2 = 12.0 Hz, 1H), 4.39 (d, *J* = 11.2, 1H), 3.48 (m, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.47 (d, *J* = 13.6 Hz, 1H), 2.35 (dd, $J_1 = J_2$ = 12.8 Hz,1H), 1.97 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.72 (m, 1H), 1.42-1.64 (m, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 143.7, 142.2, 134.0, 129.4, 128.3, 127.5, 125.7, 122.3, 116.1, 79.8, 77.7, 62.4, 44.0, 38.5, 34.9, 18.7, 14.1; IR (neat) cm^{-1} 3476s, 3415s, 3110m, 2964m, 1727s, 1627m, 1544s, 1458m, 1398m, 1346s, 1274s, 1165s, 1070m, 959m; HRMS (MALDI, m/z) calcd for $C_{23}H_{24}N_2O_7Na$ $(M+Na)^+$: 463.1476, found 463.1481.

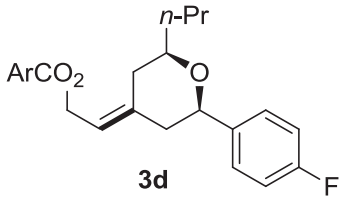
Preparation of 3c



3c

3c: Using the same general procedure as that used for **3a**. 4-Nitrobenzaldehyde (90 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3c** (195 mg, 67% yield, mp = 121-122 °C, *E/Z* = 92:8) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.18 (s, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 5.65 (t, *J* = 7.2 Hz, 1H), 5.03 (m, 2H), 4.50 (d, *J* = 11.2, 1H), 3.51 (m, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.50 (d, *J* = 13.2 Hz, 1H), 2.21 (dd, $J_1 = J_2$ = 12.0 Hz,1H), 1.97 (dd, $J_1 = J_2$ = 12.4 Hz, 1H) ,1.74 (m, 1H), 1.42-1.68 (m, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 149.5, 148.6, 147.2, 142.5, 133.9, 129.5, 126.4, 123.6, 122.4, 116.9, 78.7, 77.9, 62.3, 43.9, 38.4, 34.8, 29.7, 18.7, 14.1; IR (neat) cm^{-1} 3476s, 3415s, 3098m, 2926m, 2854m, 1731s, 1627m, 1548s, 1460m, 1348s, 1274s, 1166s, 1079m, 923m, 724m; HRMS (MALDI, m/z) calcd for $C_{23}H_{23}N_3O_9Na$ $(M+Na)^+$: 508.1327, found 508.1333.

Preparation of 3d

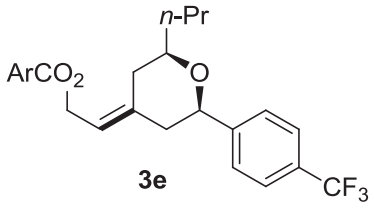


3d

3d: Using the same general procedure as that used for **3a**. 4-Fluorobenzaldehyde (74 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3d** (179 mg, 65% yield, mp = 88-89 °C, *E/Z* = 91:9) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.17 (s, 2H), 7.35 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.63 (t, *J* = 7.2 Hz, 1H), 5.03 (m, 2H), 4.37 (d, *J* = 10.0, 1H), 3.48 (m, 1H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.45 (d, *J* = 13.2 Hz, 1H), 2.31 (dd, $J_1 = J_2$ = 12.0 Hz,1H), 1.96 (dd, $J_1 = J_2$ = 12.4 Hz, 1H) ,1.70 (m, 1H), 1.44-1.66 (m, 3H), 0.97

(t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 162.0 (d, $^2J_{C\text{-}F}$ = 243.9 Hz), 148.7, 143,5, 138.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 134.0, 129.5, 127.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 122.4, 116.3, 115.1 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 79.1, 77.8, 62.4, 44.1, 38.5, 34.9, 18.7, 14.1; IR (neat) cm^{-1} 3476s, 3414s, 3085m, 2961m, 1719s, 1630m, 1549s, 1512m, 1351s, 1282s, 1171m, 1077m, 941m, 725s; HRMS (MALDI, m/z) calcd for $C_{23}H_{23}N_2O_7FNa$ $(M+Na)^+$: 481.1382, found 481.1386.

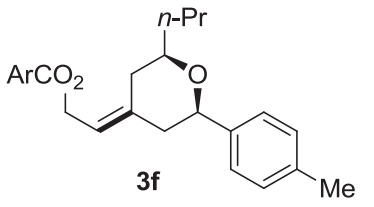
Preparation of 3e



3e

3e: Using the same general procedure as that used for **3a**. 4-(Trifluoromethyl)benzaldehyde (104 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3e** (219 mg, 72% yield, mp = 108-109 °C, *E*/Z= 92:8) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.18 (s, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 5.65 (t, J = 7.2 Hz, 1H), 5.05 (m, 2H), 4.46 (d, J = 10.4, 1H), 3.50 (m, 1H), 2.78 (d, J = 13.6 Hz, 1H), 2.48 (d, J = 13.2 Hz, 1H), 2.29 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.97 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.72 (m, 1H), 1.45-1.66 (m, 3H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 146.1, 143.0, 134.0, 129.5 (d, $^2J_{C\text{-}F}$ = 31.9 Hz), 129.4, 126.01 (d, $^3J_{C\text{-}F}$ = 11.8 Hz), 125.9, 125.2 (q, $^1J_{C\text{-}F}$ = 3.8 Hz), 122.3, 116.6, 79.1, 77.8, 62.3, 44.0, 38.4, 34.8, 18.7, 14.1; IR (neat) cm^{-1} 3476s, 3415s, 3103m, 2962m, 1722s, 1625m, 1547s, 1462m, 1343s, 1280s, 1168s, 1120s, 1069s, 925m; HRMS (MALDI, m/z) calcd for $C_{24}H_{23}F_3N_2O_7Na$ $(M+Na)^+$: 531.1350, found 531.1356.

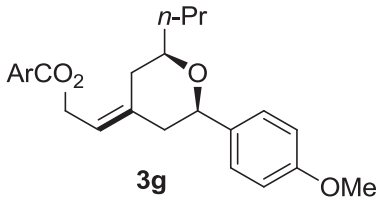
Preparation of 3f



3f

3f: Using the same general procedure as that used for **3a**. 4-Methylbenzaldehyde (71 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3f** (193 mg, 71% yield, mp = 66-67 °C, *E*/Z = 75:25) as a light yellow solid. ***E-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.16 (s, 2H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.61 (t, *J* = 7.2 Hz, 1H), 5.03 (m, 2H), 4.34 (d, *J* = 11.2, 1H), 3.46 (m, 1H), 2.75 (d, *J* = 13.6 Hz, 1H), 2.44 (d, *J* = 13.2 Hz, 1H), 2.26-2.36 (m, 4H), 1.95 (dd, *J* = 12.8 Hz, 1H), 1.42-1.74 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.5, 143.8, 139.20, 137.05, 134.0, 129.4, 128.92, 125.6, 122.3, 115.94, 79.7, 77.7, 62.4, 44.0, 38.5, 34.9, 21.0, 18.6, 14.1; ***Z-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.16 (s, 2H), 7.30 (d, *J* = 7.6 Hz 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.61 (t, *J* = 7.2 Hz, 1H), 5.00 (m, 2H), 4.29 (d, *J* = 10.4, 1H), 3.47 (m, 1H), 2.91 (d, *J* = 14.0 Hz, 1H), 2.34 (s, 3H), 2.28 (d, *J* = 14.4 Hz, 1H), 2.16 (dd, $J_1 = J_2$ = 10.0 Hz, 1H), 2.13 (dd, $J_1 = J_2$ = 10.0 Hz, 1H), 1.42-1.74 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 148.5, 143.9, 139.24, 137.16, 134.0, 129.4, 128.97, 125.7, 122.3, 115.88, 79.2, 78.3, 62.4, 41.7, 38.3, 37.2, 21.0, 18.5, 14.1; IR (neat) cm^{-1} 3103m, 2959m, 2871m, 1729s, 1629m, 1545s, 1460m, 1345s, 1273s, 1162s, 1075m, 918m; HRMS (MALDI, m/z) calcd for $C_{24}H_{26}N_2O_7Na$ $(M+Na)^+$: 477.1632, found 477.1634.

<u>Preparation of 3g</u>

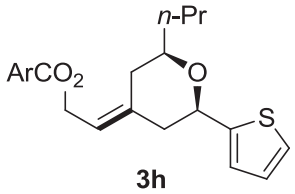


3g

3g: Using the same general procedure as that used for **3a**. 4-Methoxybenzaldehyde (81 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3g** (197 mg, 70% yield, mp = 120-122 °C, *E/Z* = 67:33] as a light yellow solid. ***E-isomer***: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.17 (s, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H),

5.61 (t, J = 7.2 Hz, 1H), 5.03 (m, 2H), 4.33 (d, J = 10.8, 1H), 3.77 (s, 3H), 3.46 (m, 1H), 2.75 (d, J = 13.6 Hz, 1H), 2.43 (d, J = 13.2 Hz, 1H), 2.34 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 1.95 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.42-1.74 (m, 4H), 0.95 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.94, 148.6, 143.8, 134.4, 134.0, 129.4, 127.0, 122.3, 116.1, 113.6, 79.4, 77.8, 62.5, 55.2, 43.9, 38.5, 34.9, 18.7, 14.1; ***Z-isomer***: δ 9.20 (s, 1H), 9.17 (s, 2H), 7.27 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.61 (t, J = 7.2 Hz, 1H), 5.00 (m, 2H), 4.28 (d, J = 10.8, 1H), 3.78 (s, 3H), 3.46 (m, 1H), 2.92 (d, J = 13.6 Hz, 1H), 2.29 (d, J = 13.2 Hz, 1H), 2.14-2.18 (m, 2H), 1.42-1.74 (m, 4H), 0.95 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.87, 148.6, 143.9, 134.5, 134.0, 129.4, 127.1, 122.3, 116.0, 113.7, 79.0, 78.3, 62.5, 55.2, 41.8, 38.3, 37.1, 18.6, 14.1; IR (neat) cm^{-1} 3072m, 2963m, 2863m, 1723s, 1629m, 1544s, 1512m, 1461m, 1347s, 1277s, 1244m, 1168s, 1071m, 1031m, 943m, 832m; HRMS (MALDI, m/z) calcd for $C_{24}H_{26}N_2O_8Na$ $(M+Na)^+$: 493.1581, found 493.1583.

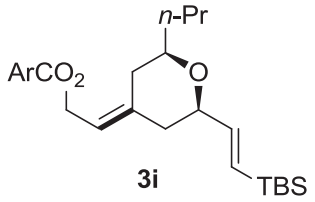
Preparation of 3h



3h

3h: Using the same general procedure as that used for **3a**. Thiophene-2-carbaldehyde (67 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3h** (193 mg, 72% yield, mp = 65-66 °C, E/Z = 91:9) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.17 (s, 2H), 7.24 (d, J = 4.8 Hz, 1H), 6.96 (m, 2H), 5.63 (t, J =6.8 Hz, 1H), 5.03 (m, 2H), 4.62 (d, J = 10.8, 1H), 3.49 (m, 1H), 2.75 (d, J = 13.6 Hz, 1H), 2.59 (d, J = 12.8 Hz, 1H), 2.50 (dd, $J_1 = J_2$ = 12.4 Hz,1H), 1.96 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.70 (m, 1H), 1.42-1.64 (m, 3H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 145.3, 142.8, 133.9, 129.4, 126.4, 124.6, 123.2, 122.3, 116.6, 77.9, 75.8, 62.3, 43.6, 38.3, 34.8, 18.7, 14.0; IR (neat) cm^{-1} 3476s, 3415s, 3108m, 2961m, 1729s, 1630s, 1547s, 1461m, 1347s , 1276s, 1169s, 1077m, 964m, 923m; HRMS (MALDI, m/z) calcd for $C_{21}H_{22}N_2O_7Na$ $(M+Na)^+$: 469.1040, found 469.1047.

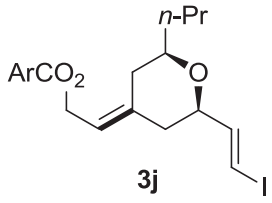
Preparation of 3i



3i

3i: Using the same general procedure as that used for **3a**. (*E*)-3-(tert-butyldimethylsilyl) -acrylaldehyde (101 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3i** (220 mg, 73% yield, mp = 94-96 °C, *E/Z* = 91:9) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.15 (s, 2H), 6.07 (dd, J_1 = 5.2 Hz, J_2 = 18.8 Hz, 1H), 5.86 (d, J = 18.8 Hz, 1H), 5.56 (t, J = 7.2 Hz, 1H), 4.98 (m, 2H), 3.83 (m, 1H), 3.31 (m, 1H), 2.67 (d, J = 13.6 Hz, 1H), 2.27 (d, J = 13.2 Hz, 1H), 2.12 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.83 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.66 (m, 1H), 1.39-1.52 (m, 3H), 0.93 (t, J = 7.2 Hz, 3H), 0.85 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 147.1, 143.6, 134.0, 129.4, 127.3, 122.3, 115.9, 80.4, 77.4, 62.4, 42.0, 38.5, 34.9, 26.4, 18.8, 16.4, 14.1, -6.2, -6.3; IR (neat) 3417s, 2953m, 1719s, 1629m, 1550s, 1344s, 1284s, 1171s, 940w, 829m; HRMS (MALDI, m/z) calcd for $C_{25}H_{36}N_2O_7SiNa$ $(M+Na)^+$: 527.2184, found 527.2188.

Preparation of 3j

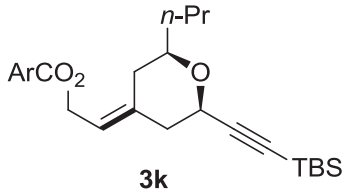


3j

3j: Using the same general procedure as that used for **3a**. (*Z*)-3-iodoacrylaldehyde (108 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3j** (194 mg, 63% yield, mp = 54-55 °C, *E/Z* = 86:14) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.15 (s, 2H), 6.56 (dd, J_1 = 5.2 Hz, J_2 = 14.4 Hz, 1H), 6.40 (d, J = 14.4 Hz, 1H), 5.55 (t, J = 7.2 Hz, 1H), 4.96 (m, 2H), 3.81 (m, 1H), 3.31 (m, 1H), 2.66 (d, J = 13.6 Hz, 1H), 2.25 (d, J = 13.6 Hz, 1H), 2.13 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.82 (dd, $J_1 = J_2$ = 12.8 Hz, 1H), 1.61 (m, 1H),

1.35-1.50 (m, 3H), 0.92 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 148.6, 145.5, 142.4, 133.9, 129.4, 122.3, 116.6, 79.6, 78.2, 77.4, 62.3, 41.4, 38.3, 34.8, 18.6, 14.0; IR (neat) 3100s, 2959s, 2871s, 1730s, 1674w, 1628s, 1547s, 1346s, 1274s, 1162s, 1075s; HRMS (MALDI, m/z) calcd for $C_{19}H_{21}IN_2O_7Na$ $(M+Na)^+$: 539.0286, found 539.0292.

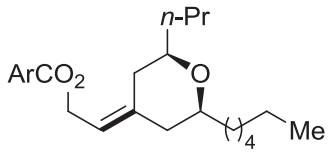
Preparation of 3k



3k

3k: Using the same general procedure as that used for **3a**. 3-(Tert-butyldimethylsilyl)-propiolaldehyde (100 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3k** (219 mg, 73% yield, mp = 92-93 °C, E/Z = 92:8) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.14 (s, 2H), 5.56 (t, J = 7.2 Hz, 1H), 4.95 (m, 2H), 4.10 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1H), 3.25 (m, 1H), 2.64 (d, J = 14.0 Hz, 1H), 2.41-2.48 (m, 2H), 1.85 (dd, J_1 = J_2 = 12.8 Hz, 1H), 1.66 (m, 1H), 1.38-1.55 (m, 3H), 0.91 (m, 12H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 148.6, 142.0, 133.9, 129.4, 122.3, 116.7, 104.4, 87.9, 77.8, 68.7 62.2, 42.8, 38.2, 34.5, 26.0, 18.7, 16.4, 14.0, -4.8; IR (neat) 3472s, 3415s, 2956m, 1718s, 1630m, 1549s, 1465m, 1343m, 1284m, 1170m, 940w; HRMS (MALDI, m/z) calcd for $C_{25}H_{34}N_2O_7SiNa$ $(M+Na)^+$: 525.2027, found 525.2021.

Preparation of 3l

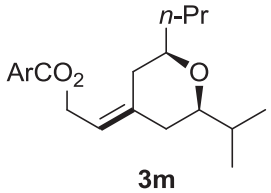


3l

3l: Using the same general procedure as that used for **3a**. *n*-Heptanal (68 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and

$KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3l** (180 mg, 67% yield, mp = 60-61 °C, *E/Z* = 87:13) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.15 (s, 2H), 5.50 (t, *J* = 7.6 Hz, 1H), 4.97 (m, 2H), 3.25-3.27 (m, 2H), 2.64 (d, *J* = 13.6 Hz, 1H), 2.18 (d, *J* = 13.2 Hz, 1H), 2.00 (dd, J_1 = J_2 = 12.8 Hz, 1H), 1.80 (dd, J_1 = J_2 = 12.4 Hz, 1H), 1.34-1.68 (m, 7H), 1.18-1.34 (m, 7H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 144.3, 134.1, 129.4, 122.3, 115.3, 78.2, 77.4, 62.5, 42.3, 38.5, 36.2, 35.4, 31.8, 29.2, 25.5, 22.6, 18.8, 14.03, 13.98; IR (neat) 3102m, 2957s, 2930s,2858s, 1732s, 1629m, 1549s, 1462s, 1346s, 1275s, 1162s, 1077m, 944m; HRMS (MALDI, m/z) calcd for $C_{23}H_{32}N_2O_7Na$ $(M+Na)^+$: 471.2102, found 471.2106.

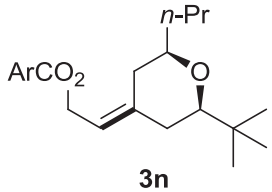
Preparation of 3m



3m

3m: Using the same general procedure as that used for **3a**. Isobutyraldehyde (43 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3m** (160 mg, 66% yield, mp = 59-60 °C; *E/Z* = 84:16) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.17 (s, 2H), 5.52 (t, *J* = 7.2 Hz, 1H), 4.98 (m, 2H), 3.23 (m, 1H), 2.95 (m, 1H), 2.64 (d, *J* = 13.6 Hz, 1H), 2.26 (d, *J* = 13.2 Hz, 1H), 2.00 (dd, J_1 = J_2 = 12.0 Hz, 1H), 1.80 (dd, J_1 = J_2 = 12.0 Hz, 1H), 1.69 (m, 1H), 1.36-1.62 (m, 4H), 0.97 (t, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 144.7, 134.1, 129.5, 122.3, 115.5, 83.3, 62.6, 39.4, 38.6, 35.4, 33.3, 18.9, 18.8, 18.5, 14.0; IR (neat) cm^{-1} 3476s, 3415s, 3105m, 2961m, 1724s, 1626m, 1543s, 1396m, 1351s, 1283s, 1165m, 948m, 725m; HRMS (MALDI, m/z) calcd for $C_{20}H_{26}N_2O_7Na$ $(M+Na)^+$: 429.1632, found 429.1635.

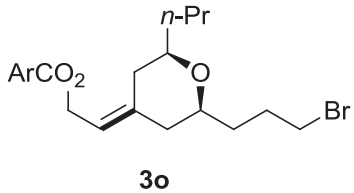
Preparation of 3n



3n

3n: Using the same general procedure as that used for **3a**. Pivalaldehyde (51 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3n** (176 mg, 70% yield, mp = 56-57 °C, *E/Z* = 67:33) as a white powder. ***E-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.16 (s, 2H), 5.51 (t, J = 7.2 Hz, 1H), 4.97 (m, 2H), 3.24 (m, 1H), 2.91 (d, J = 11.6 Hz, 1H), 2.61 (d, J = 13.6 Hz, 1H), 2.16 (d, J = 12.4 Hz, 1H), 2.04 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 1.76 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.33-1.64 (m, 4H), 0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 145.37, 134.2, 129.5, 122.3, 115.26, 85.6, 77.3, 62.7, 42,5, 38.6, 36.5, 35.5, 34.2, 29.5, 25.87, 18.8, 14.0; ***Z-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.16 (s, 2H), 5.51 (t, J = 7.2 Hz, 1H), 4.97 (m, 2H), 3.21 (m, 1H), 2.85 (d, J = 11.6 Hz 1H), 2.63 (d, J = 13.6 Hz, 1H), 2.13 (d, J = 12.4 Hz, 1H), 2.00 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 1.80 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.33-1.64 (m, 4H), 0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 145.44, 134.2, 129.5, 122.3, 115.31, 85.1, 77.9, 62.5, 42.5, 38.4, 36.5, 35.5, 34.4, 29.5, 25.94, 18.7, 14.0; IR (neat) cm^{-1} 3423s, 2958m, 1719s, 1630m, 1549s, 1462w, 1398m, 1351s, 1282s, 1173m, 1085m, 934m; HRMS (MALDI, m/z) calcd for $C_{21}H_{28}N_2O_7Na$ $(M+Na)^+$: 443.1789, found 443.1790.

Preparation of 3o

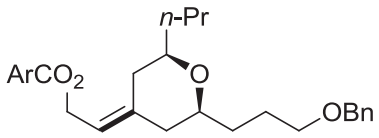


3o

3o: Using the same general procedure as that used for **3a**. 4-Bromobutanal (89 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3o** (182 mg, 67% yield, mp = 60-61 °C, *E/Z* = 93:7) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s,

1H), 9.16 (s, 2H), 5.51 (t, J = 7.6 Hz, 1H), 4.98 (m, 2H), 3.46 (m, 2H), 3.22-3.35 (m, 2H), 2.66 (d, J = 13.6 Hz, 1H), 2.19 (d, J = 13.6 Hz, 1H), 2.08 (m, 2H), 1.86 (m, 2H), 1.82 (dd, $J_1 = J_2$ = 12.8 Hz, 1H), 1.37-1.73 (m, 6H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 143.7, 134.0, 129.4, 122.3, 115.8, 77.5, 77.2, 62.4, 42.2, 38.5, 35.3, 34.6, 33.9, 29.0, 18.8, 14.0; IR (neat) 3474s, 3415s, 3086m, 2956m, 1719s, 1630m, 1550s, 1461m, 1351s, 1285s, 1174s, 947m; HRMS (MALDI, m/z) calcd for $C_{20}H_{25}BrN_2O_7Na$ $(M+Na)^+$: 507.0737, found 507.0732.

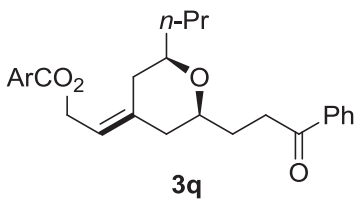
Preparation of 3p



3p

3p: Using the same general procedure as that used for **3a**. 4-(Benzyloxy)butanal (106 mg, 0.6 mmol) and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3p** (214 mg, 70% yield, $E/Z \geq$ 95:5) as an colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.16 (s, 2H), 7.33 (m, 4H), 7.28 (m, 1H), 5.51 (t, J = 7.2 Hz, 1H), 4.98 (m, 2H), 4.50 (s, 2H), 3.49 (m, 2H), 3.24-3.30 (m, 2H), 2.65 (d, J = 13.2 Hz, 1H), 2.19 (d, J = 13.2 Hz, 1H), 2.04 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 1.81 (dd, $J_1 = J_2$ = 12.0 Hz, 2H), 1.36-1.72 (m, 7H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 144.1, 138.5, 134.0, 129.4 128.3, 127.5, 127.4, 122.2, 115.5, 77.9, 77.3, 72.8, 70.1, 62.4, 42.3, 38.5, 35.3, 32.8, 25.8, 18.8, 14.0; IR (neat), 3102m, 2956s, 2865s, 1731s, 1629m, 1547s, 1458s, 1347s, 1274s, 1162s, 1102s, 1075s, 944m; HRMS (MALDI, m/z) calcd for $C_{27}H_{32}N_2O_8Na$ $(M+Na)^+$: 535.2051, found 535.2051.

Preparation of 3q

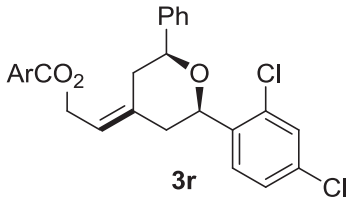


3q

3q: Using the same general procedure as that used for **3a**. 4-Oxo-4-phenylbutanal (96 mg, 0.6 mmol)

and dienyl alcohol **1a** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3q** (193 mg, 67% yield, mp = 93-95 °C, *E/Z* = 93:7] as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.15 (s, 2H), 7.96 (d, *J* = 6.8 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.45 (t, *J* = 6.8 Hz, 2H), 5.52 (t, *J* = 7.6 Hz, 1H), 4.97 (m, 2H), 3.37 (t, *J* = 10.0 Hz, 1H), 3.23 (m, 1H), 3.13 (dd, $J_1 = J_2$ = 7.2 Hz, 2H), 2.66 (d, *J* = 13.6 Hz, 1H), 2.25 (d, *J* = 13.6 Hz, 1H), 2.09 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 2.01 (m, 1H), 1.90 (m, 1H), 1.81 (dd, *J* = 12.4 Hz, 2H), 1.32-1.61 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 162.4, 148.6, 143.8, 137.0, 134.1, 133.0, 129.4, 128.5, 128.0, 122.3, 115.8, 77.3, 76.7, 62.4, 42.3, 38.5, 35.2, 34.3, 30.4, 18.8, 14.0; IR (neat), 2960m, 2927m, 2851w, 1723s, 1678s, 1631w, 1544s, 1458m, 1346s, 1273s,1073w, 951w; HRMS (MALDI, m/z) calcd for $C_{26}H_{28}N_2O_8Na(M+Na)^+$: 519.1738, found 519.1744.

Preparation of 3r

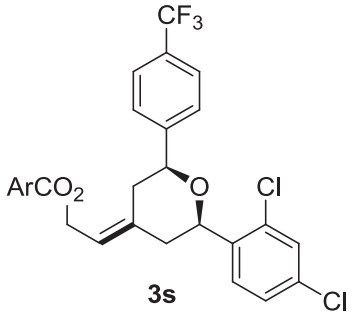


3r

3r: Using the same general procedure as that used for **3a**. 2,4-Dichlorobenzaldehyde (104 mg, 0.6 mmol) and dienyl alcohol **1b** (124 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3r** (217 mg, 67% yield, mp = 182-184 °C, *E/Z* = 92:8) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.18 (s, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.27-7.36 (m, 3H), 5.73 (t, *J* = 7.2 Hz, 1H), 5.10 (dd, J_1 = 7.6 Hz, J_2 = 12.0 Hz, 1H), 5.00 (dd, J_1 = 7.2 Hz, J_2 = 12.0 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H), 2.69 (d, *J* = 13.2 Hz, 1H), 2.29 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 2.23 (dd, $J_1 = J_2$ = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 142.1, 141.6, 138.3, 133.9, 133.6, 131.9, 129.5, 128.9, 128.5, 128.2, 127.9, 127.6, 125.8, 122.4, 117.3, 80.1, 76.7, 62.3, 42.2, 37.3; IR (neat) cm^{-1} 3424s, 3099m, 1732s, 1627m, 1544s, 1469m, 1344s, 1276s, 1166s, 1076s; HRMS (MALDI, m/z)

calcd for $C_{26}H_{20}N_2O_7Cl_2Na$ $(M+Na)^+$: 565.0540, found 565.0542.

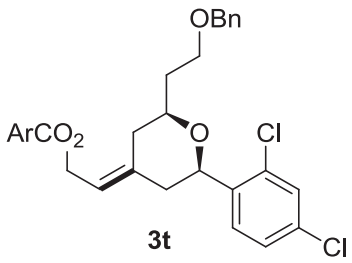
Preparation of 3s



3s

3s: Using the same general procedure as that used for **3a**. 2,4-Dichlorobenzaldehyde (104 mg, 0.6 mmol) and dienyl alcohol **1c** (173 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3s** (255 mg, 70% yield, mp = 195-197°C, *E/Z* = 90:10) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 9.20 (s, 2H), 7.63-7.69 (m, 5H), 7.37 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 5.75 (t, J = 6.8 Hz, 1H), 5.15 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H), 4.97 (dd, J_1 = 6.8 Hz, J_2 = 12.0 Hz, 1H), 4.92 (d, J = 10.0 Hz, 1H), 4.66 (d, J = 10.8 Hz, 1H), 3.10 (d, J = 14.0, 1H), 2.71 (d, J = 13.2 Hz, 1H), 2.25 (dd, $J_1 = J_2$ = 12.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 148.7, 145.5, 141.5, 137.9, 133.9, 133.8, 131.9, 130.1 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 129.5, 129.1, 128.1, 127.6, 126.1, 125.5, 122.4, 117.8, 79.4, 76.8, 62.2, 42.1, 37.2; IR (neat) cm^{-1} 3447m, 3103m, 1732s, 1627m, 1546s, 1472m, 1347s, 1323s, 1276s, 1165s, 1073s, 834m; HRMS (MALDI, m/z) calcd for $C_{27}H_{19}N_2O_7Cl_2F_3Na$ $(M+H)^+$: 633.0414, found 633.0422.

Preparation of 3t

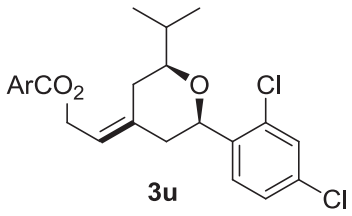


3t

3t: Using the same general procedure as that used for **3a**. 2,4-Dichlorobenzaldehyde (104 mg, 0.6 mmol) and dienyl alcohol **1d** (176 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42

mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3t** (260 mg, 71% yield, mp = 97-99 °C, *E/Z* = 95:5) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 9.16 (s, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.22-7.29 (m, 6H), 5.65 (t, *J* = 7.2 Hz, 1H), 5.01 (d, *J* = 6.4, 2H), 4.67 (d, *J* = 10.4, 1H), 4.49 (dd, J_1 = 12.0 Hz, J_2 = 14.0 Hz, 1H), 3.64-3.73 (m, 3H), 2.78 (d, *J* = 13.6, 1H), 2.60 (d, *J* = 13.2 Hz, 1H), 2.09 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.96 -2.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 142.4, 138.4, 138.3, 134.0, 133.4, 132.0, 129.4, 128.9, 128.3, 128.1, 127.5, 127.5, 127.4, 122.3, 116.9, 76.1, 75.1, 72.9, 66.4, 62.3, 42.2, 36.5, 35.1; IR (neat) cm^{-1} 3448s, 3106m, 1729s, 1629s, 1546s, 1399m, 1346s, 1271s, 1162m, 1076m; HRMS (MALDI, m/z) calcd for $C_{29}H_{26}N_2O_8Cl_2Na$ $(M+Na)^+$: 623.0958, found 623.0963.

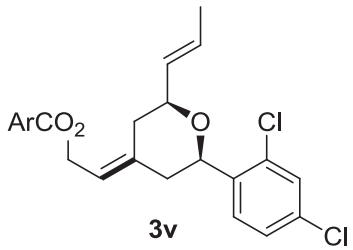
Preparation of 3u



3u

3u: Using the same general procedure as that used for **3a**. 2,4-Dichlorobenzaldehyde (104 mg, 0.6 mmol) and dienyl alcohol **1e** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3u** (222 mg, 73% yield, mp = 182-184 °C; *E/Z* = 92:8) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.18 (s, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 5.65 (t, *J* = 7.2 Hz, 1H), 5.03 (m, 2H), 4.65 (d, *J* = 11.2 Hz, 1H), 3.26 (m, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.61 (d, *J* = 13.2 Hz, 1H), 2.05 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.98 (dd, $J_1 = J_2$ = 12.4 Hz, 1H), 1.87 (m, 1H), 1.04 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 143.0, 138.8, 134.0, 133.4, 131.9, 129.5, 128.9, 128.1, 127.4, 122.4, 116.7, 82.7, 76.2, 62.6, 42.5, 33.3, 31.5, 35.4, 33.3, 18.4, 18.2; IR (neat) cm^{-1} 3108m, 2965m, 2934m, 2878m, 1727s, 1628m, 1592w, 1545s, 1467s, 1388m, 1345s, 1276s, 1165s, 1078s, 1030w, 961m, 824m; HRMS (MALDI, m/z) calcd for $C_{23}H_{22}N_2O_7Cl_2Na$ $(M+Na)^+$: 531.0696, found 531.0696.

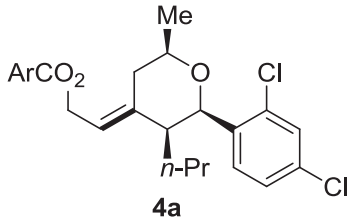
Preparation of 3v



3v

3v: Using the same general procedure as that used for **3a**. 2,4-Dichlorobenzaldehyde (104 mg, 0.6 mmol) and dienyl alcohol **1f** (99 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **3v** (206 mg, 68% yield, mp = 134-135 °C, *E/Z* = 88:12) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.16 (s, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 5.79 (m, 1H), 5.67 (t, J = 7.2 Hz, 1H), 5.60 (dd, J_1 = 6.4 Hz, J_2 = 15.6 Hz, 1H), 5.01 (d, J = 7.2 Hz, 1H), 4.70 (d, J = 10.8 Hz, 1H), 4.02 (m, 1H), 3.03 (d, J = 13.6 Hz, 1H), 2.34 (d, J = 12.8 Hz, 1H), 2.28 (dd, J_1 = J_2 = 12.8 Hz, 1H), 1.91 (dd, J_1 = J_2 = 12.4 Hz, 1H), 1.73 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 142.5, 138.3, 133.9, 133.6, 131.8, 130.9, 129.5, 128.9, 128.2, 128.2, 127.6, 122.3, 117.0, 79.4, 75.7, 62.2, 41.9, 35.6, 17.8; IR (neat) cm^{-1} 3424s, 3095m, 1728s, 1627m, 1547s, 1471m, 1386m, 1349s, 1276s, 1167m, 1086m; HRMS (MALDI, m/z) calcd for $C_{23}H_{21}N_2O_7Cl_2$ $(M+H)^+$: 507.0720, found 507.0721.

Preparation of 4a

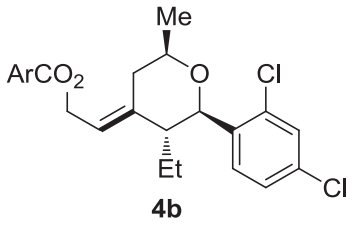


4a

4a: Using the same general procedure as that used for **3a**. 2,4-dichlorobenzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1g** (109 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **4a** (222 mg, 71% yield, *E/Z* = 91:9, mp = 144-145 °C) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 9.21 (t, J = 2.0 Hz, 1H), 9.16 (d, J = 2 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.24 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 5.68 (t, J = 7.2 Hz, 1H), 5.05 (ddd, J_1 = 7.6 Hz, J_2 = 12 Hz, J_2 = 22.0 Hz, 2H), 4.81 (d, J = 2 Hz, 1H), 3.66 (m, 1H), 2.63 (d, J = 13.6 Hz, 1H), 2.60 (d, J = 11.2 Hz, 1H), 2.03 (t, J = 12.8 Hz, 1H), 1.42~1.52 (m, 1H), 1.40 (d, J = 6 Hz, 3H), 1.05~1.15 (m, 1H), 0.78~0.95 (m, 1H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.5, 145.6, 136.5, 134.0, 133.0, 131.3, 129.7, 129.4, 128.7, 126.7, 122.2, 117.1, 78.9, 74.8, 62.4, 46.2, 32.8, 27.6, 22.0, 20.2, 13.8; IR (neat) cm^{-1} 3456s, 3421s, 3099m, 2970m, 1722s, 1629s, 1549s, 1461m, 1387m, 1346s, 1276s, 1166m, 1105w, 1068m, 950m; HRMS (MALDI, m/z) calcd for $C_{24}H_{24}N_2O_7Cl_2Na$ $(M+Na)^+$: 545.0853, found 545.0851.

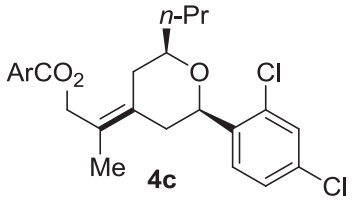
Preparation of 4b



4b

4b: Using the same general procedure as that used for **3a**. 2,4-dichlorobenzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1h** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **4b** (223 mg, 73% yield, $E/Z \geq$ 95:5, mp = 128-129 °C) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.18 (s, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.35 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 5.60 (t, J = 6.4 Hz, 1H), 5.10 (d, J = 6.8 Hz, 2H), 4.60 (d, J = 9.6 Hz, 1H), 3.63 (m, 1H), 2.85 (d, J = 13.2 Hz, 1H), 2.15 (t, J = 9.2 Hz, 1H), 2.00 (t, J = 12.4 Hz, 1H), 1.48~1.58 (m, 1H), 1.31 (d, J = 6 Hz, 3H), 1.08~1.20 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 148.7, 144.6, 137.6, 134.2, 134.0, 133.9, 129.5, 128.9, 127.7, 122.3, 114.5, 80.3, 74.9, 62.9, 51.4, 38.3, 22.0, 18.6, 12.1; IR (neat) cm^{-1} 3425s, 3108m, 2969m, 2888m, 1724s, 1627m, 1545s, 1469m, 1384m, 1348s, 1280s, 1172s, 1144m, 1105w, 1068m, 954m, 924m, 723s; HRMS (MALDI, m/z) calcd for $C_{23}H_{22}N_2O_7Cl_2Na$ $(M+Na)^+$: 531.0609, found 531.0609.

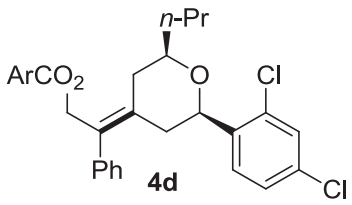
Preparation of 4c



4c

4c: Using the same general procedure as that used for **3a**. 2,4-dichlorobenzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1i** (109 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **4c** (241 mg, 77% yield, *E/Z* = 86:14, mp = 145-146 °C) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.0 Hz, 1H), 9.16 (d, *J* = 2.4 Hz, 2H), 7.57 (d, *J* = 9.6 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.27 (dd, J_1 = 2.4 Hz, J_2 = 9.2 Hz, 1H), 5.08 (d, *J*= 12.0 Hz, 1H), 5.02 (d, *J*= 12.0 Hz, 1H), 4.61 (d, *J*= 11.2 Hz, 1H), 3.5 (m, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.82 (d, *J* = 14 Hz, 1H), 1.88~2.0 (m, 4H), 1.78 (t, *J* = 12.4 Hz, 1H), 1.40~1.74(m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 148.6, 138.9, 136.2, 134.0, 133.3, 131.9, 129.4, 128.8, 128.1, 127.4, 122.3, 121.6, 78.1, 75.7, 67.1, 38.5, 37.1, 36.0, 18.6, 16.5, 14.1; IR (neat) cm^{-1} 3448s, 3102s, 2965w, 1724s, 1630s, 1548s, 1462w, 1400m, 1344s, 1289m, 1170m, 1078m, 723m; HRMS (MALDI, m/z) calcd for $C_{24}H_{24}Cl_2N_2O_7Na$ $(M+Na)^+$: 545.0853, found 545.0853.

Preparation of 4d

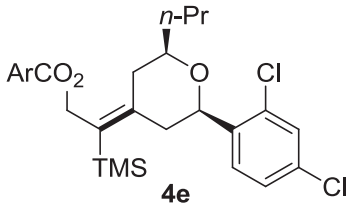


4d

4d: Using the same general procedure as that used for **3a**. 2,4-dichlorobenzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1j** (153 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **4d** (252 mg, 72% yield, *E/Z* = 75:25, mp = 146-147 °C) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 9.0 (s, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J*= 8.4 Hz, 1H), 7.21 (d, *J*= 5.2 Hz, 1H), 5.34 (d, *J*= 12.4 Hz, 1H), 5.26 (d, *J*= 12.0 Hz, 1H), 4.64 (d, *J*= 9.6 Hz, 1H), 3.63 (m, 1H), 2.93 (d, *J* = 13.6 Hz, 1H), 2.82 (d, *J* = 13.6 Hz, 1H), 2.12 (t, *J* = 13.6 Hz, 1H),

1.65~1.79 (m, 2H), 1.47~1.68 (m, 3H), 1.78 (t, J = 18.6 Hz, 1H), 1.40~1.74 (m, 4H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 148.5, 139.3, 138.8, 138.5, 133.9, 133.3, 132.0, 129.3, 129.04, 128.99, 128.8, 128.5, 128.0, 127.34, 127.27, 122.3, 78.2, 76.1, 66.2, 38.6, 36.2, 18.6, 14.1; IR (neat) cm^{-1} 3457s, 3422s, 2966w, 1722s, 1634s, 1542m, 1469w, 1400s, 1347s, 1289m, 1176m, 1078m, 719m; HRMS (MALDI, m/z) calcd for $C_{29}H_{26}N_2O_7Cl_2Na$ $(M+Na)^+$: 607.1009, found 607.1008.

Preparation of 4e

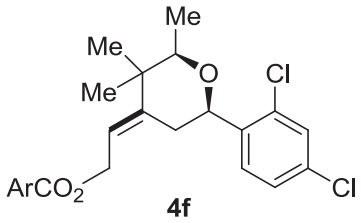


4e

4e: Using the same general procedure as that used for **3a**. 2,4-dichlorobenzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1k** (151 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **4e**, (219 mg, 63% yield, E/Z = 50:50, mp = 140-141°C) as a white powder. ***E-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.12 (s, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.33 (s, 1H), 7.26 (d, J = 8.4 Hz, 1H), 5.13 (d, J = 11.6 Hz, 1H), 5.05 (d, J = 11.6 Hz, 1H), 4.70 (d, J = 10.8 Hz, 1H), 3.49 (m, 1H), 2.95 (d, J = 13.2 Hz, 1H), 2.86 (d, J = 13.2 Hz, 1H), 2.05 (t, J = 12.8 Hz, 1H), 1.93 (t, J = 12.4 Hz, 1H), 1.35~1.72 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 154.1, 148.7, 138.8, 134.1, 133.6, 131.9, 129.3, 129.3, 128.9, 128.6, 127.6, 127.1, 122.3, 77.8, 75.6, 65.5, 42.0, 38.6, 37.0, 18.6, 14.1, 0.8; ***Z-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 9.11 (s, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 5.12 (d, J = 11.6, 1H), 5.04 (d, J = 11.6 Hz, 1H), 4.64 (d, J = 10.8 Hz, 1H), 3.56 (m, 1H), 3.20 (d, J = 13.2 Hz, 1H), 2.70 (d, J = 13.2 Hz, 1H), 2.13 (t, J = 12.4 Hz, 1H), 1.88 (t, J = 12.8 Hz, 1H), 1.40~1.63 (m, 3H), 1.65~1.75 (m, 1H), 0.97 (t, J = 7.2 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (150 Hz, $CDCl_3$) δ 162.3, 154.8, 148.6, 138.5, 134.1, 133.5, 131.8, 129.3, 129.3, 128.9, 128.2, 127.5, 126.5, 122.3, 78.4, 76.2, 65.4, 41.3, 38.5, 38.0, 18.6, 14.1, 0.7; IR (neat) cm^{-1} 3109m, 2964m, 2835w3421s, 3099m, 2970m, 1722s, 1629s, 1549s, 1461m, 1387m, 1346s, 1276s, 1731s, 1625m, 1546s, 1468m, 1346s, 1281m, 1249m, 1164,

1085m, 919m, 840m; HRMS (MALDI, m/z) calcd for $C_{26}H_{30}N_2O_7Cl_2SiNa$ $(M+Na)^+$: 603.1092, found 603.1099.

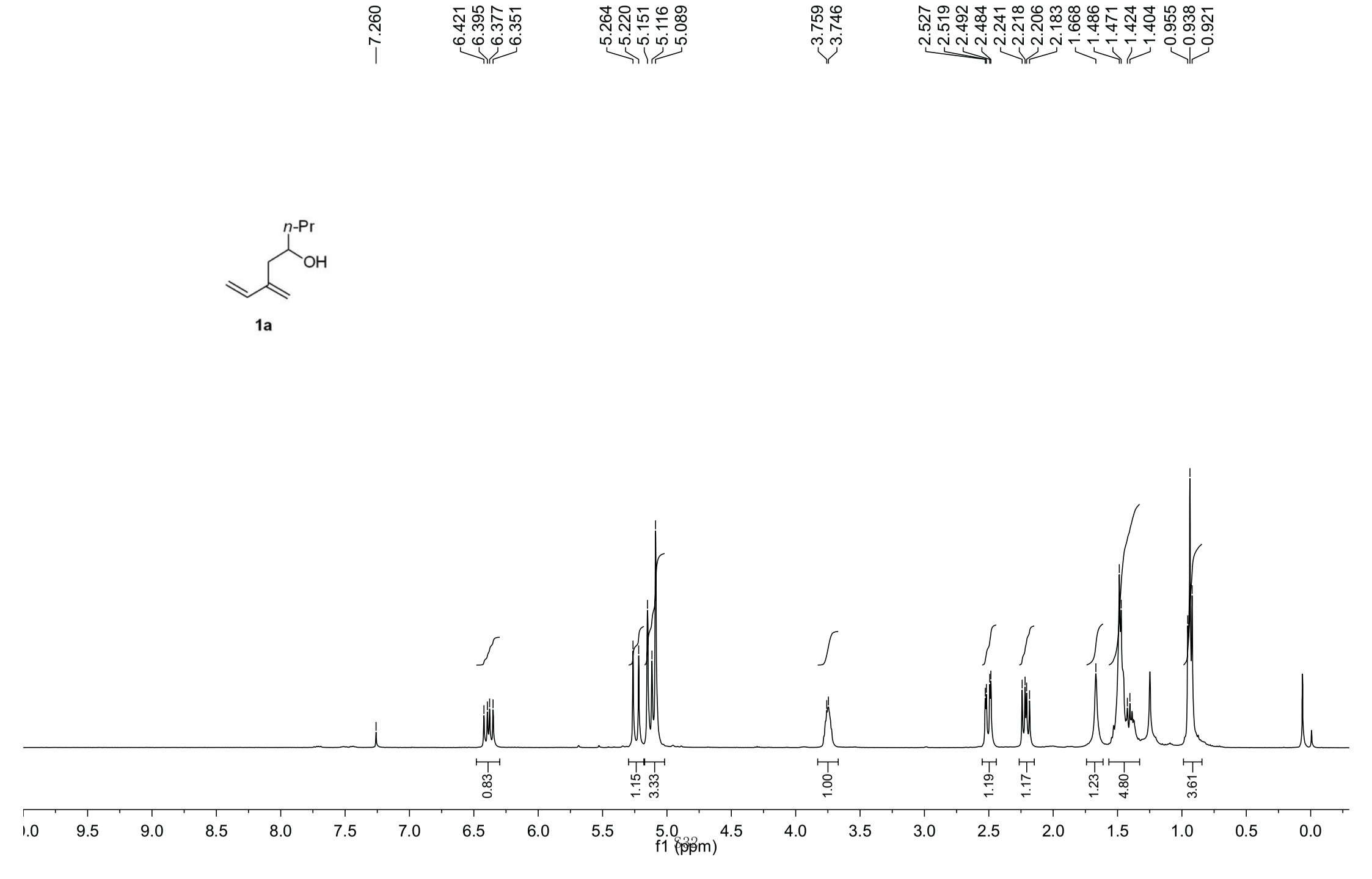
Preparation of 4f



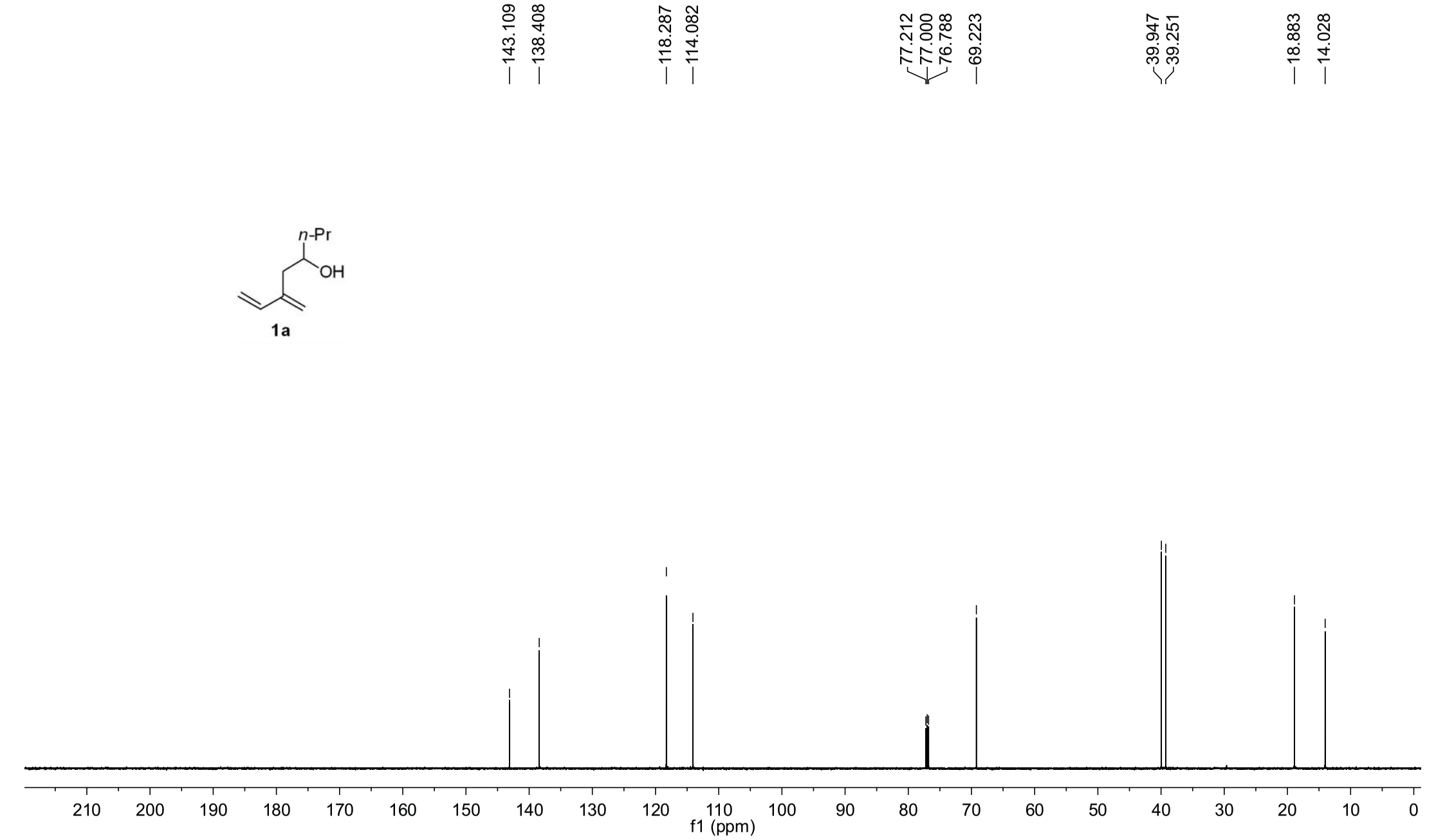
4f

4f: Using the same general procedure as that used for **3a**. 2,4-dichlorobenzaldehyde (63 mg, 0.6 mmol) and dienyl alcohol **1l** (100 mg, 0.71 mmol) with TMSBr (110 mg, 0.72 mmol) and $InBr_3$ (42 mg, 0.12 mmol) in anhyd. CH_2Cl_2 (3.5 mL) at –78 °C for 40 min, 3,5-$NO_2C_6H_3CO_2H$ (757 mg, 3.6 mmol) and $KHCO_3$ (369 mg, 3.7 mmol) in DMF (5 mL) at room temperature for 3 h produced **4f** (229 mg, 75% yield, *Z/E* ≥ 95:5, 128-129 °C) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 2.0 Hz, 1H), 9.17 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 5.65 (t, *J* = 6.8 Hz, 1H), 5.04 (d, *J* = 7.2 Hz, 2H), 4.66 (d, *J* = 9.2 Hz, 1H), 3.46 (dd, J_1 = 6.4 Hz, J_2 = 12.8 Hz, 1H), 2.93 (dd, J_1 = 2.0 Hz, J_2 = 13.6 Hz, 1H), 2.16 (t, *J* = 12.8 Hz, 1H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.16 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 150.9, 148.6, 138.6, 134.0, 133.6, 131.8, 129.5, 128.9, 128.1, 127.6, 122.3, 81.3, 76.4, 63.1, 40.1, 32.7, 22.7, 20.1, 15.8; IR (neat) 3105m, 2975m, 2853w, 1727s, 1628m, 1547s, 1470m, 1383m, 1346s, 1295m, 1264s, 1165s, 1094s, 947m, 777m; HRMS (MALDI, m/z) calcd for $C_{23}H_{22}Cl_2N_2O_7Na$ $(M+Na)^+$: 531.0696, found 531.0697.

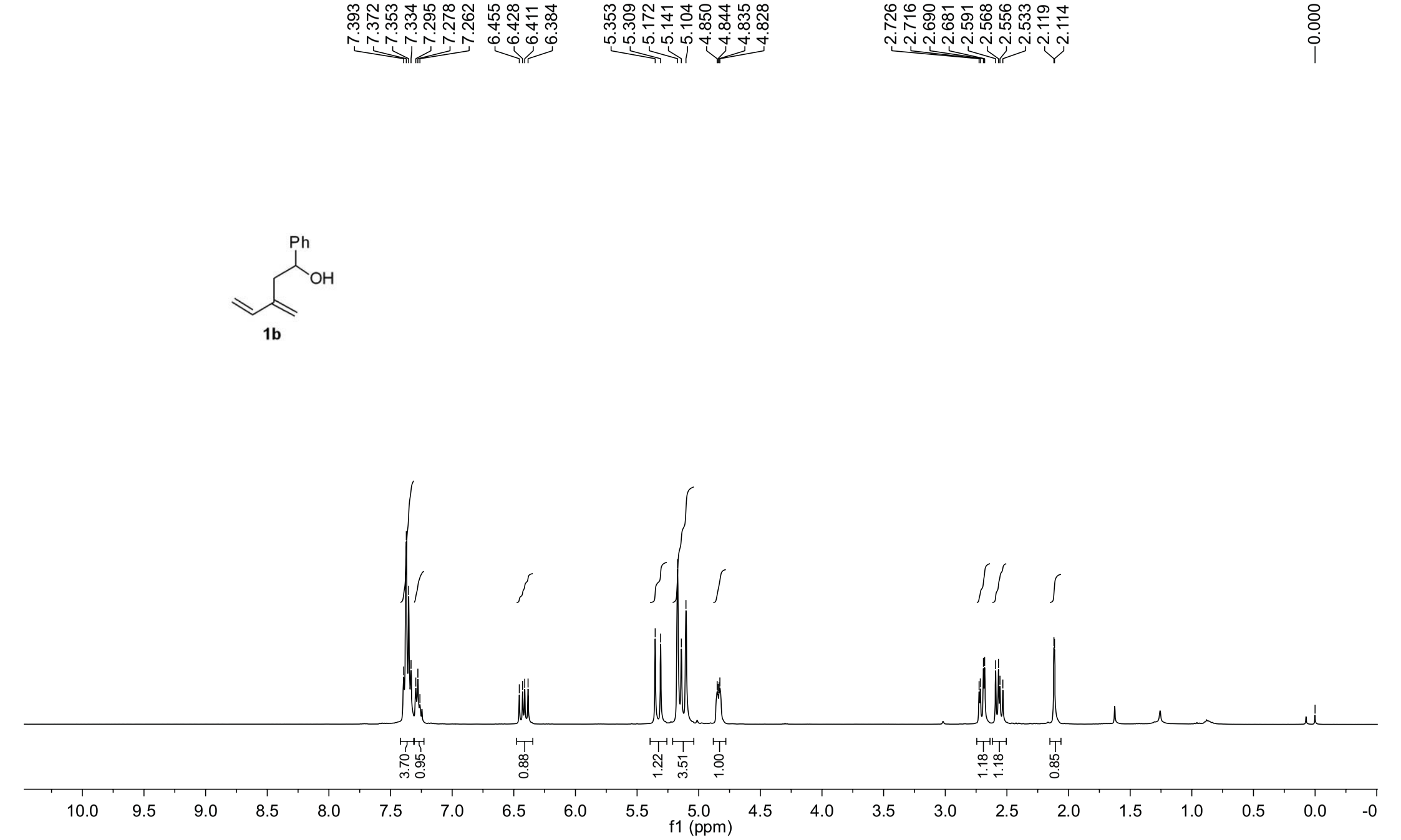
YZP-II-30 H1 CDCl3 400 MHz



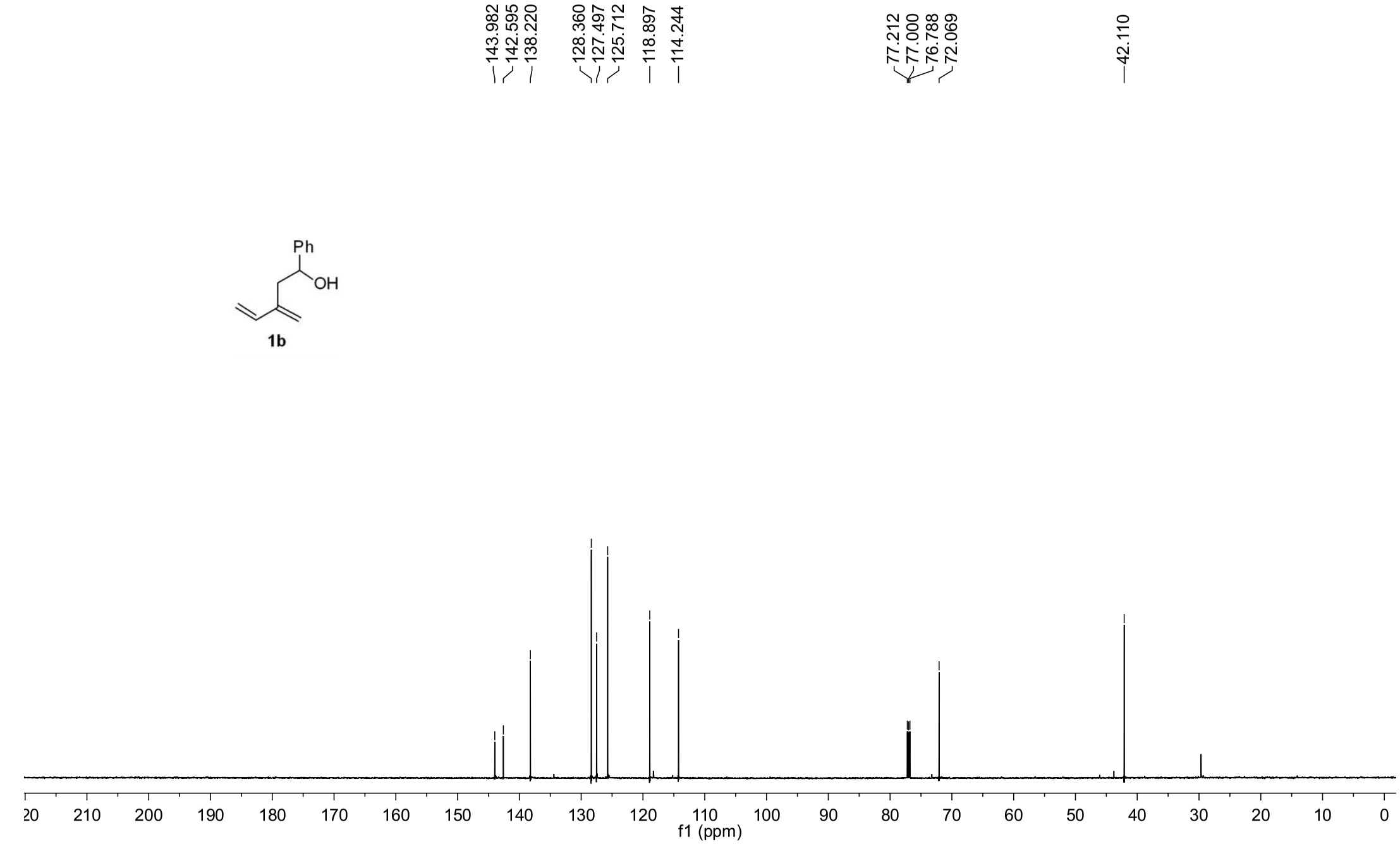
HYY-I-90 C13 CDCl3 150 MHz



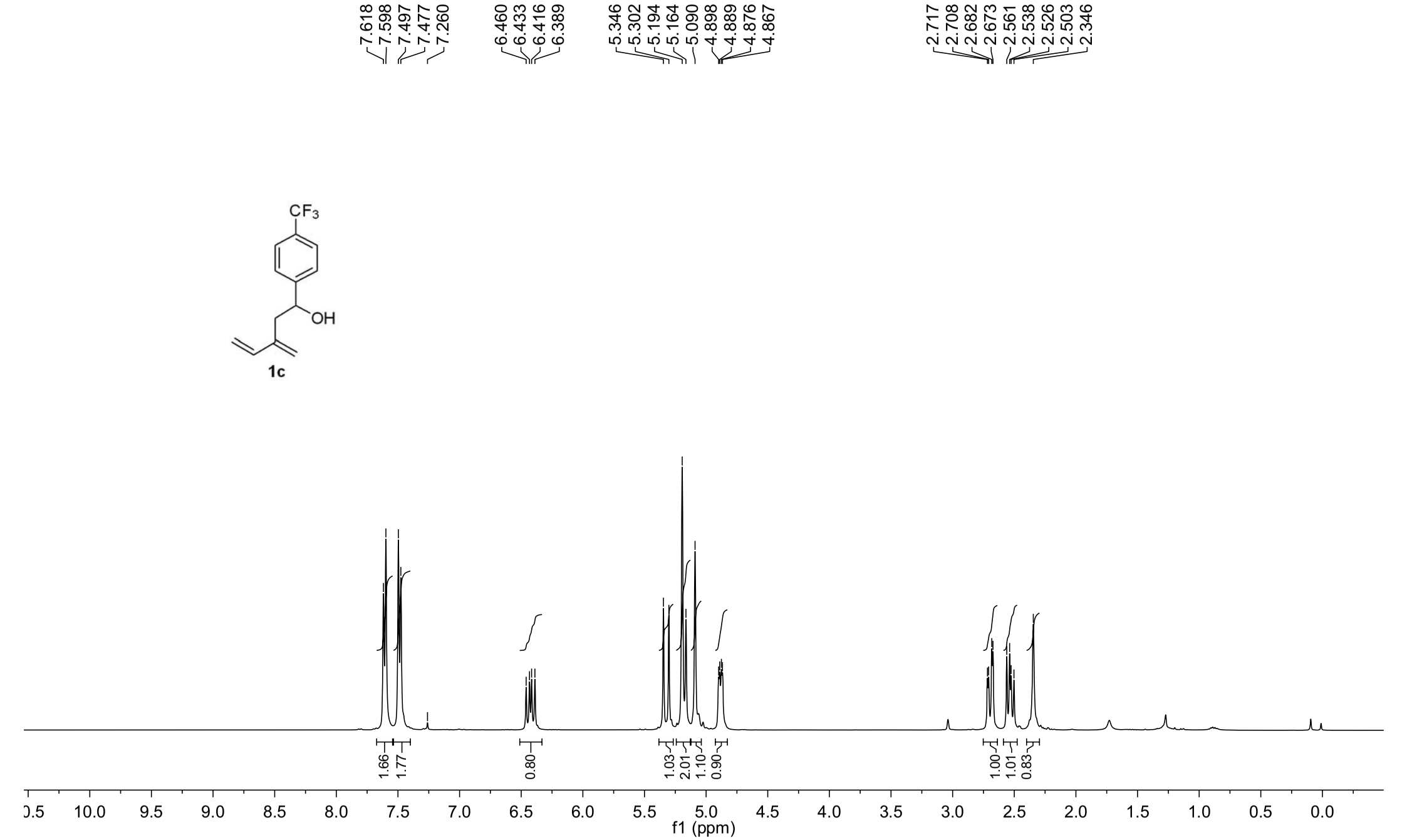
XYJ-4-46 H1 CDCl3 400 MHz



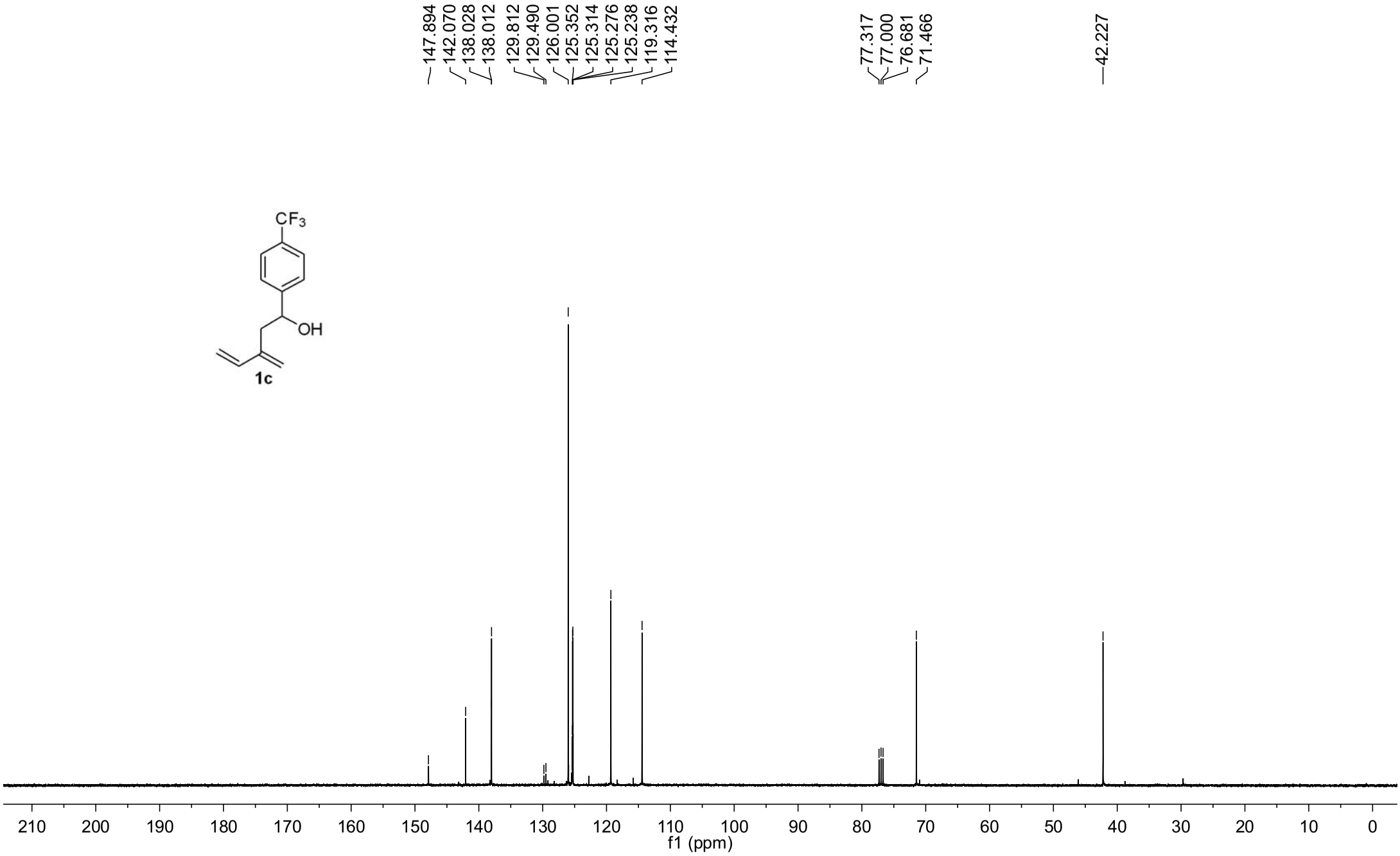
XYJ-ph C13 CDCl3 150 MHz



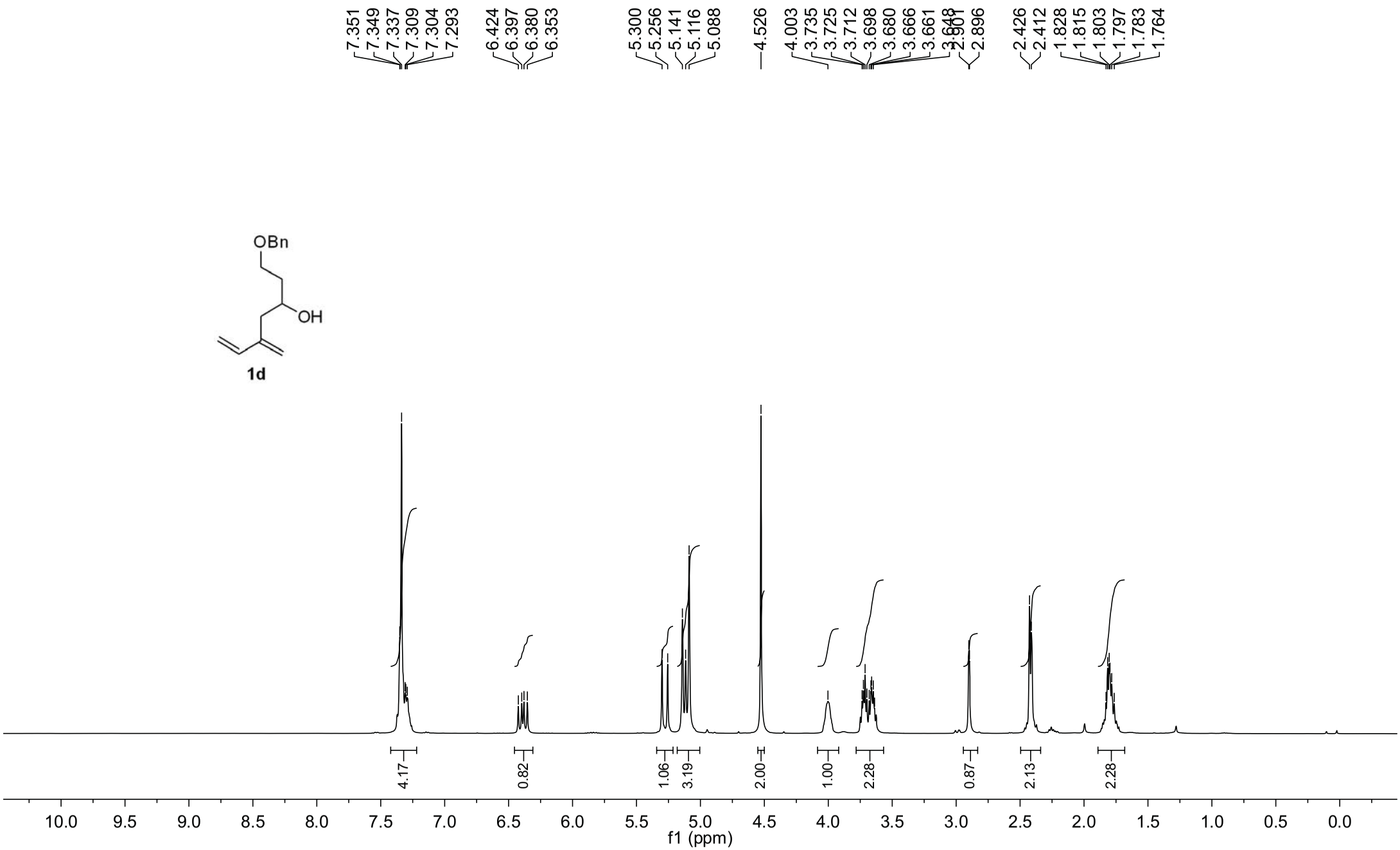
HYY-I-60 H1 CDCl3 400 MHz



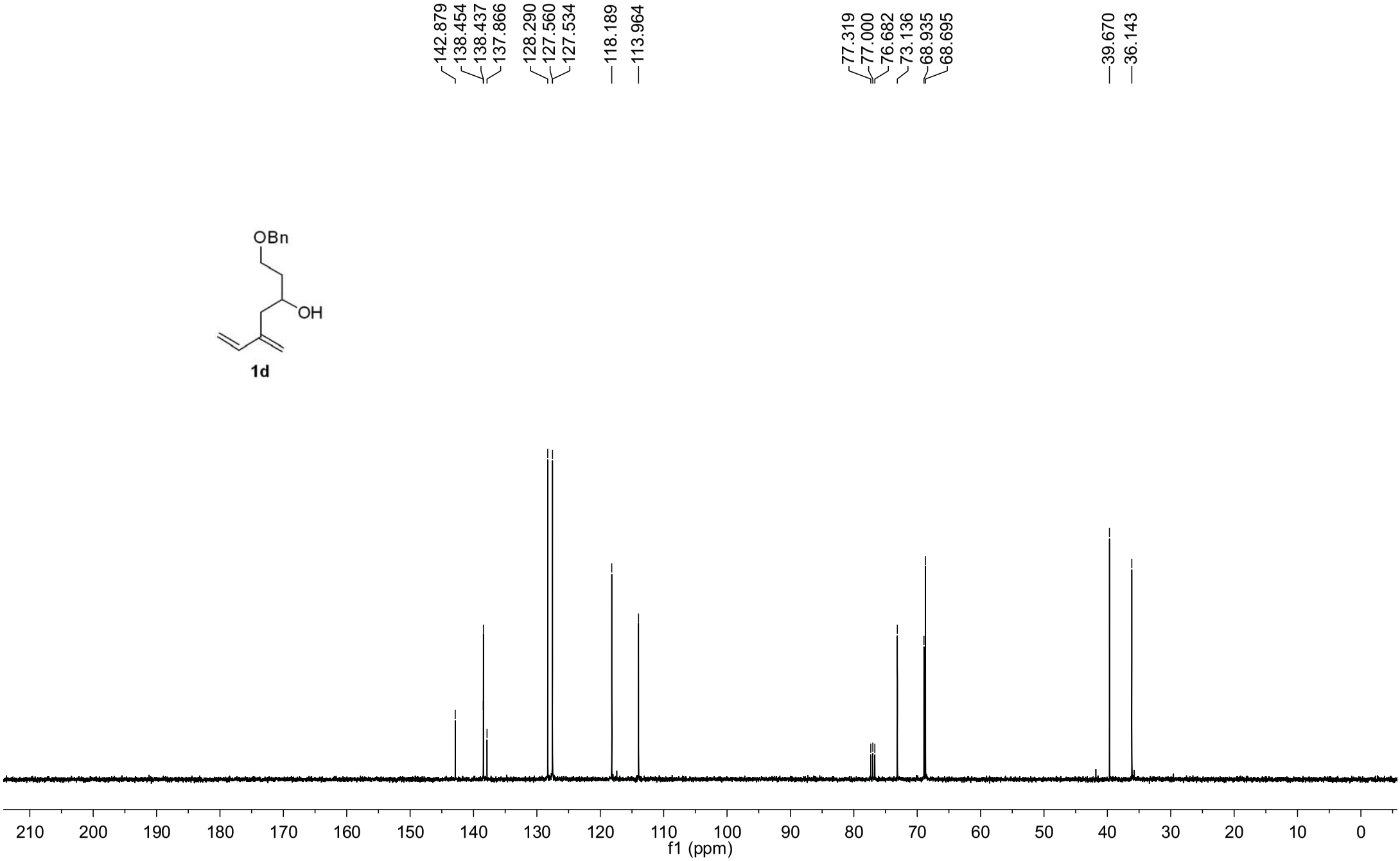
HYY-I-60a C13 CDCl3 100 MHz



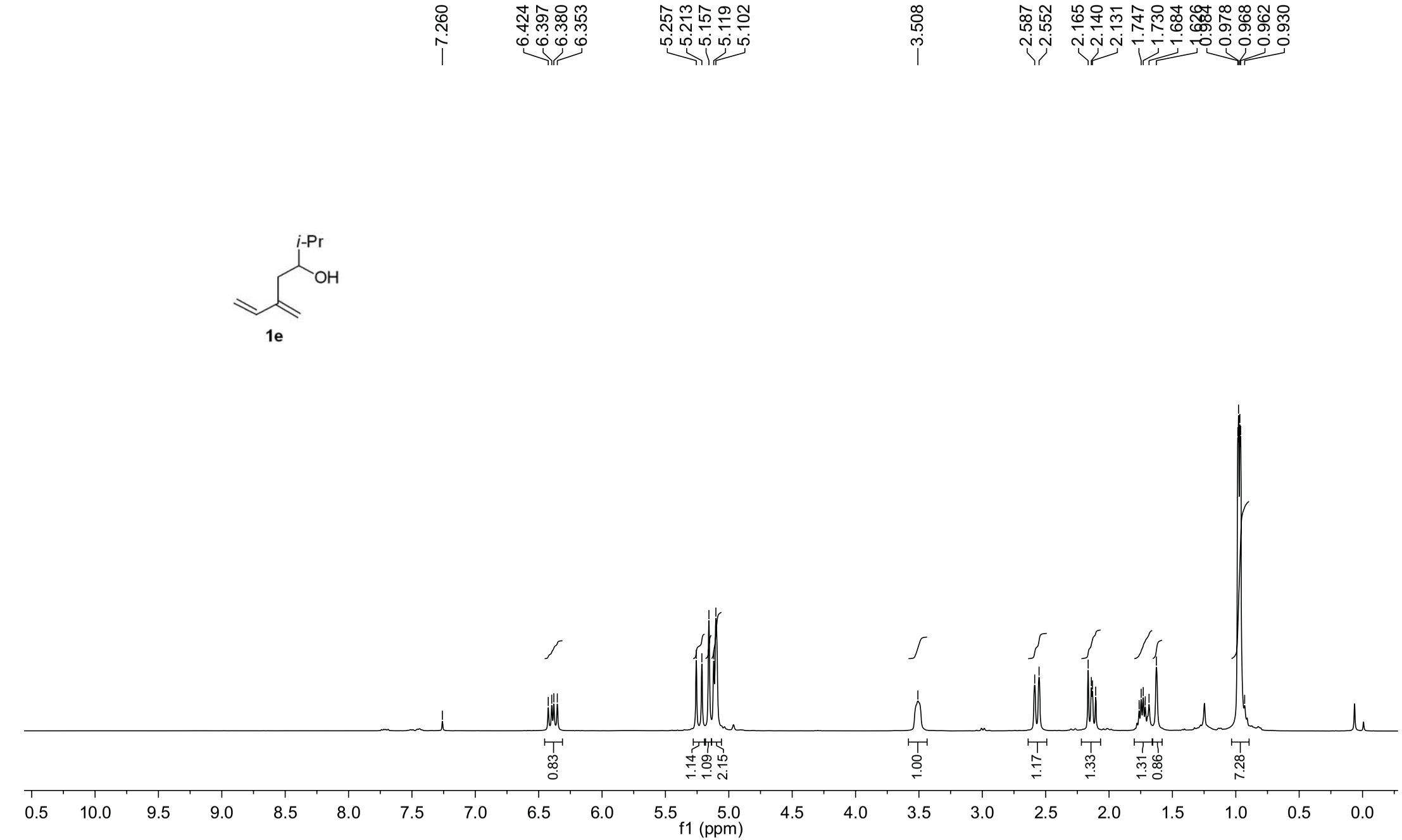
HYY-I-21-P H1 CDCl3 400 MHz



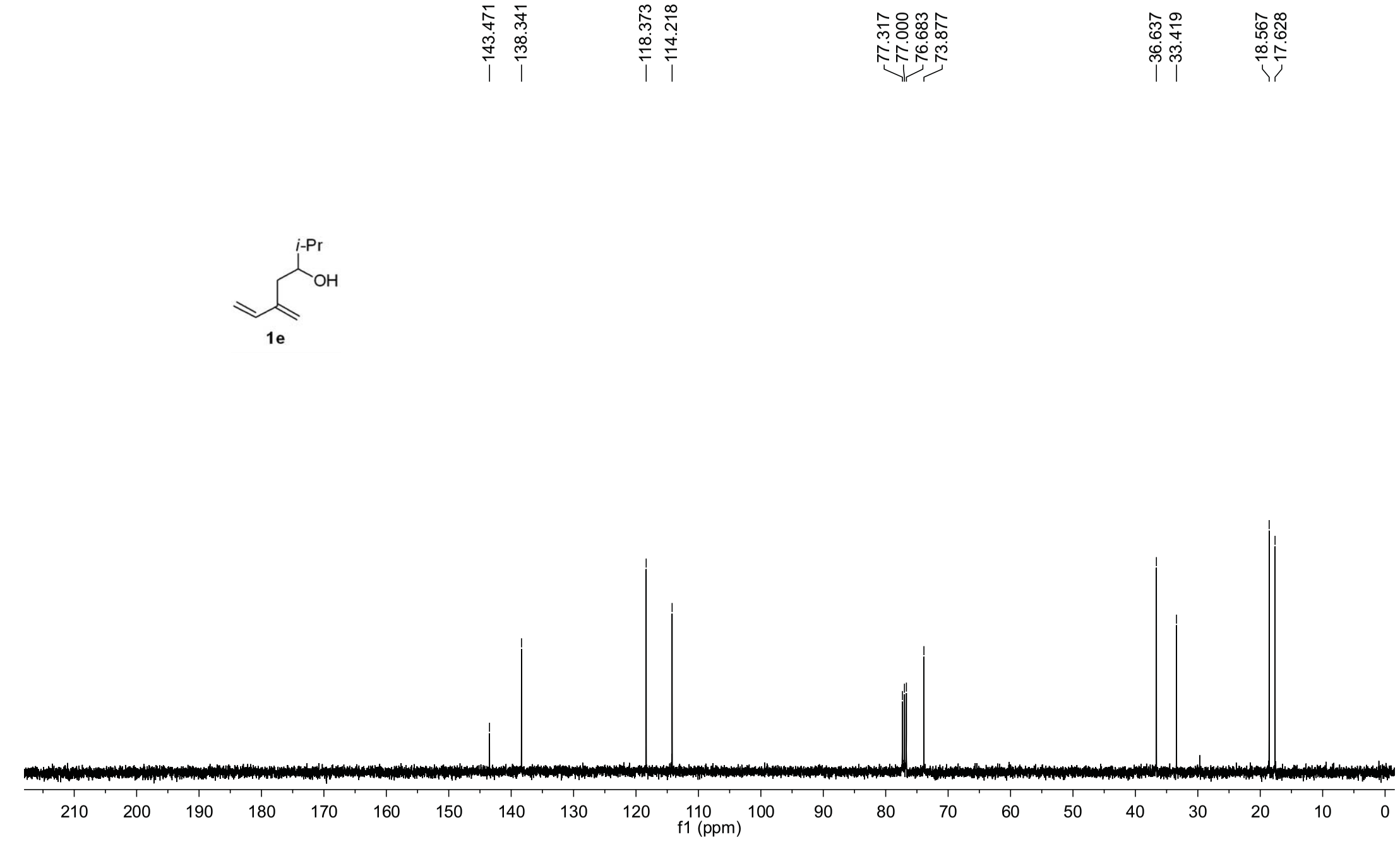
HYY-I-21-P C13 CDCl3 100 MHz



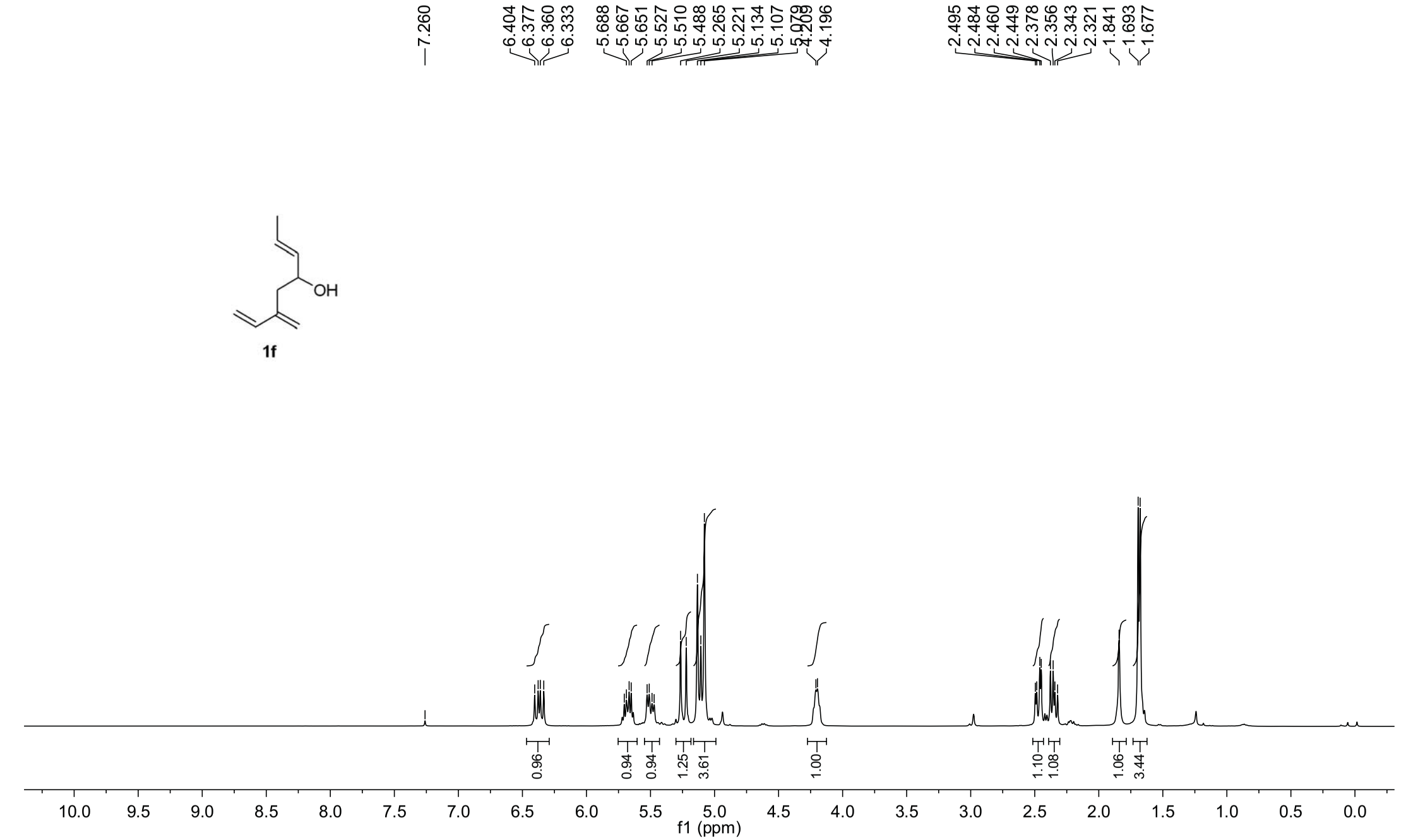
SCZ-7-73 H1 CDCl3 400 MHz



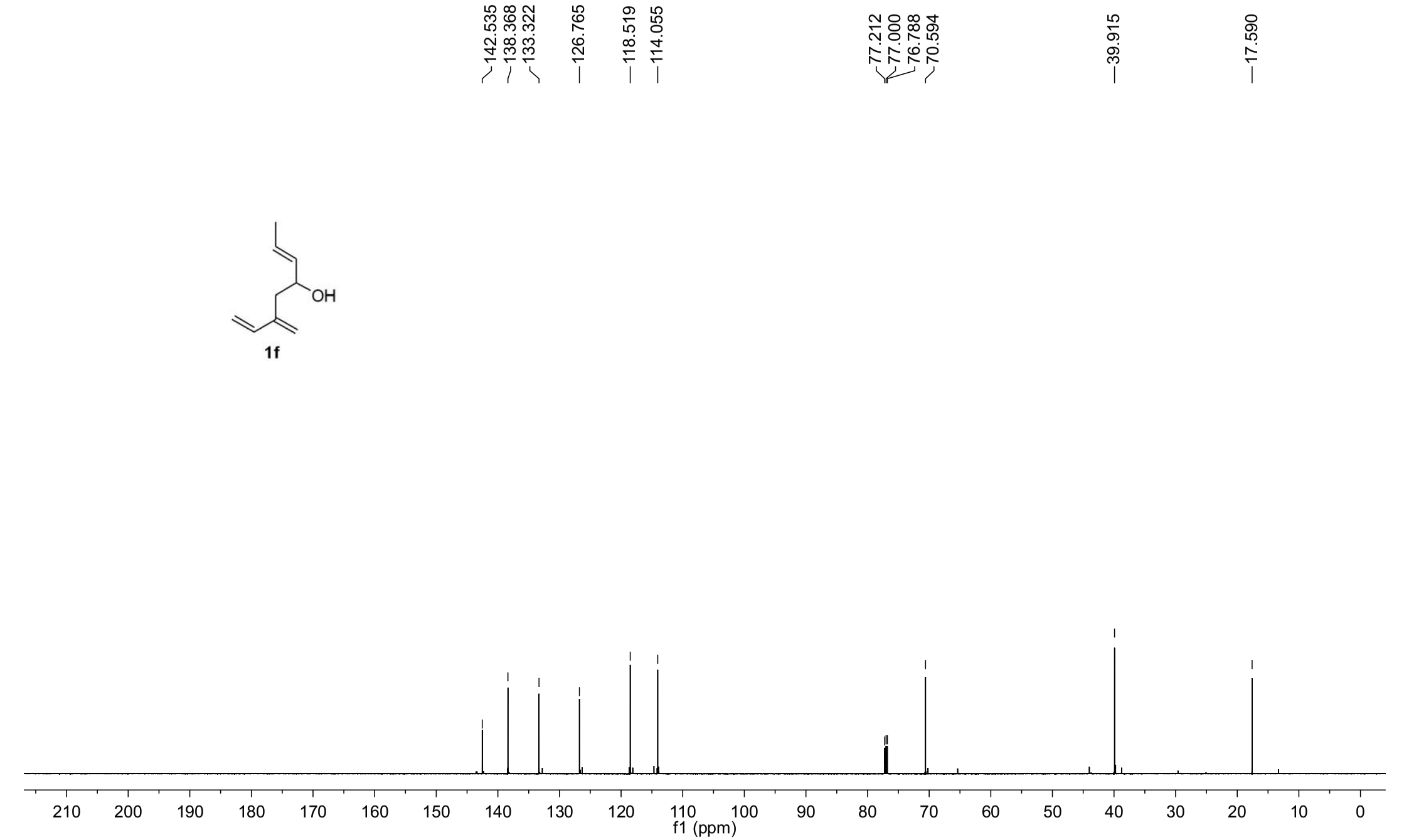
SCZ-7-73 C13 CDCL3 100MHz



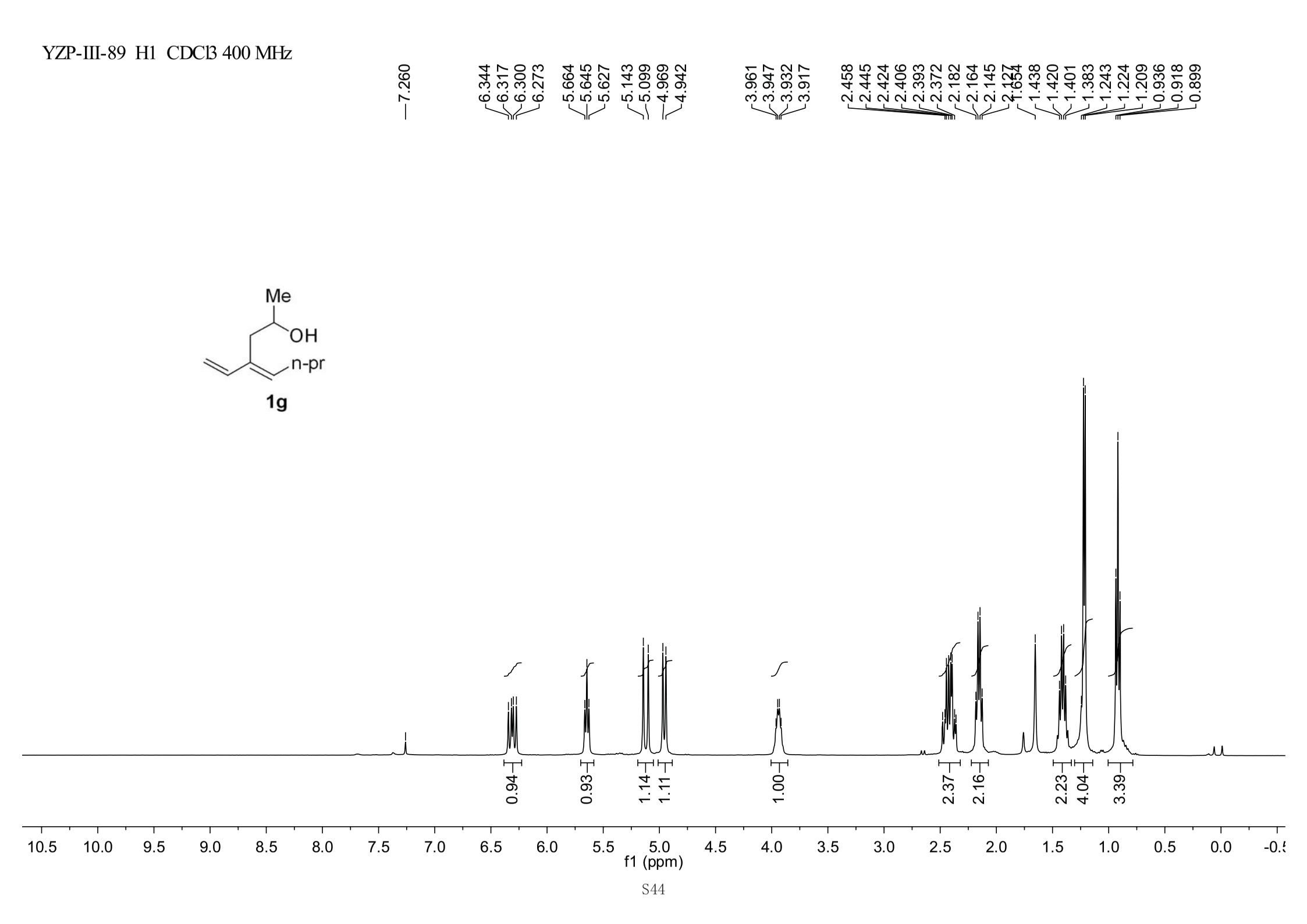
YZP-V-73 H1 CDCl3 400 MHz



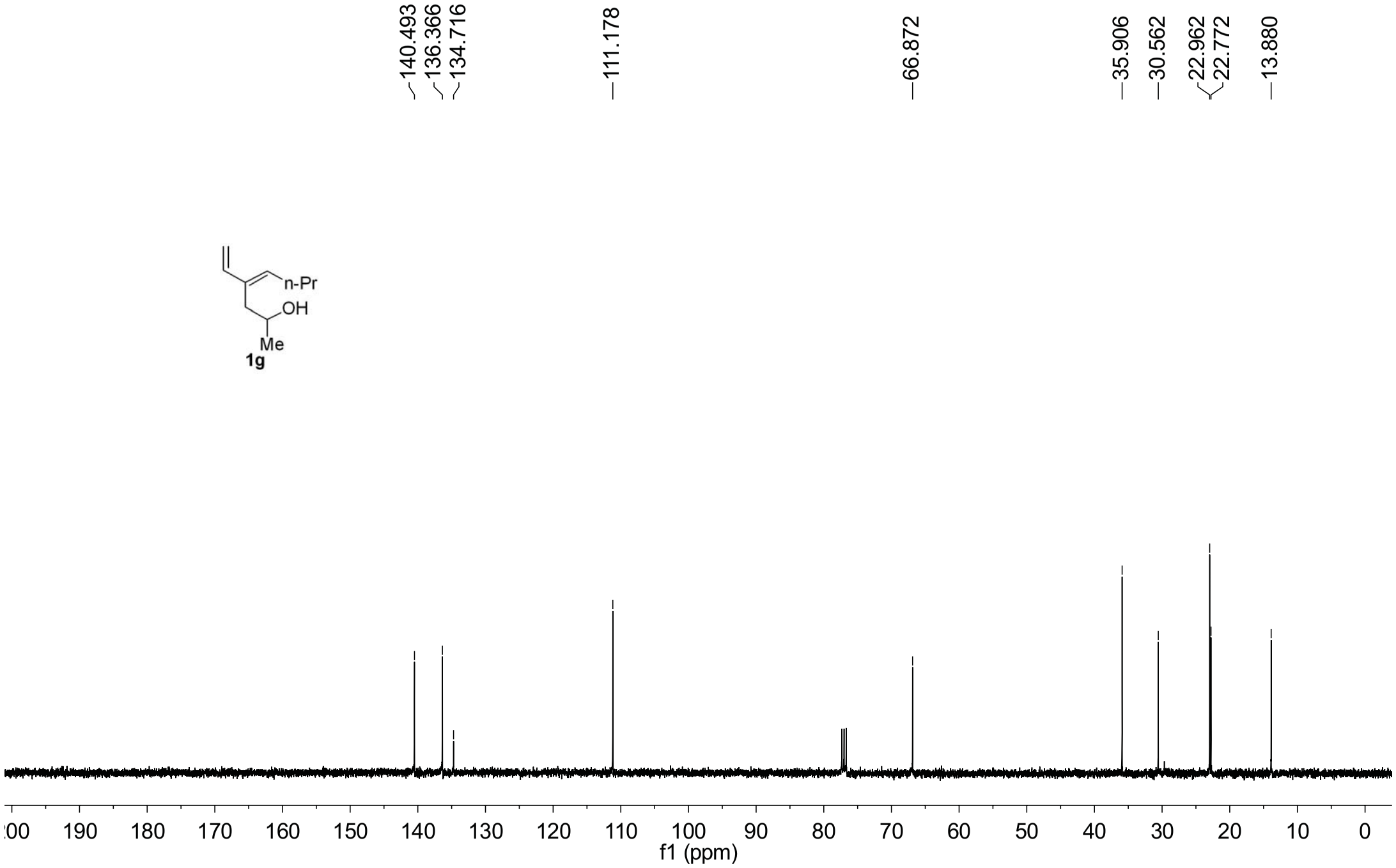
YZP-V-73 C13 CDCl3 150 MHz



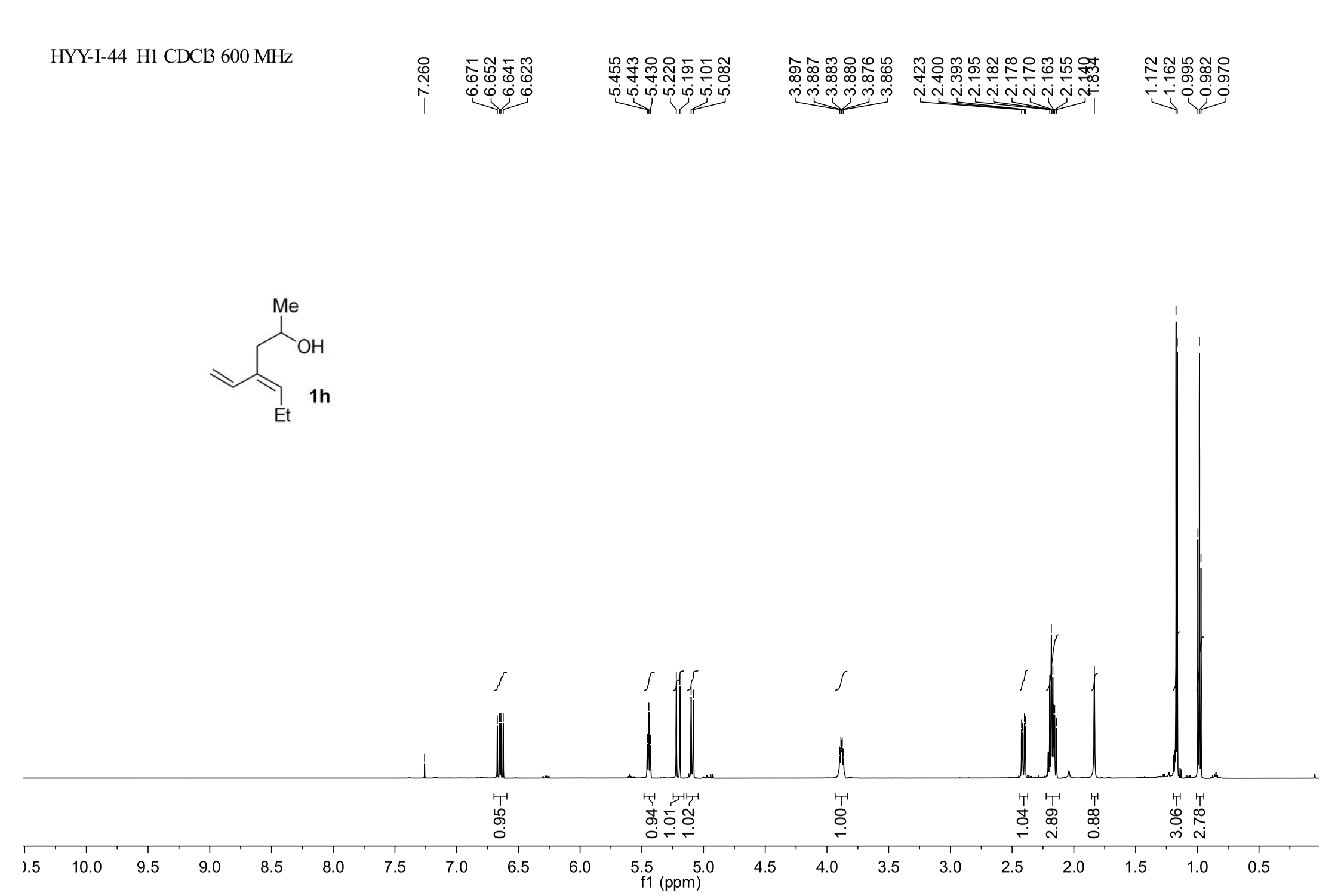
YZP-III-89 H1 CDCl3 400 MHz



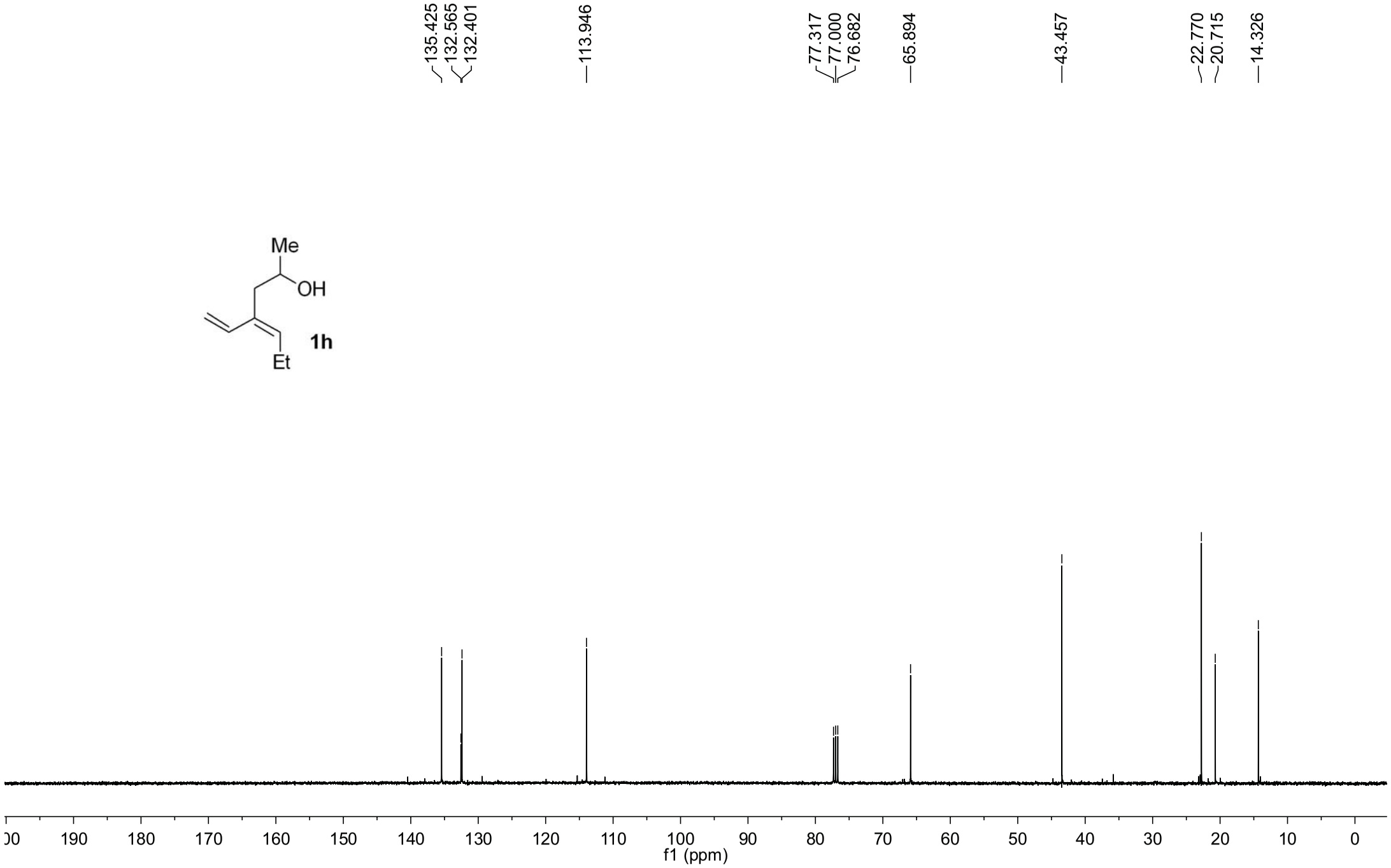
YZP-III-89 C13 CDCl3 100 MHz



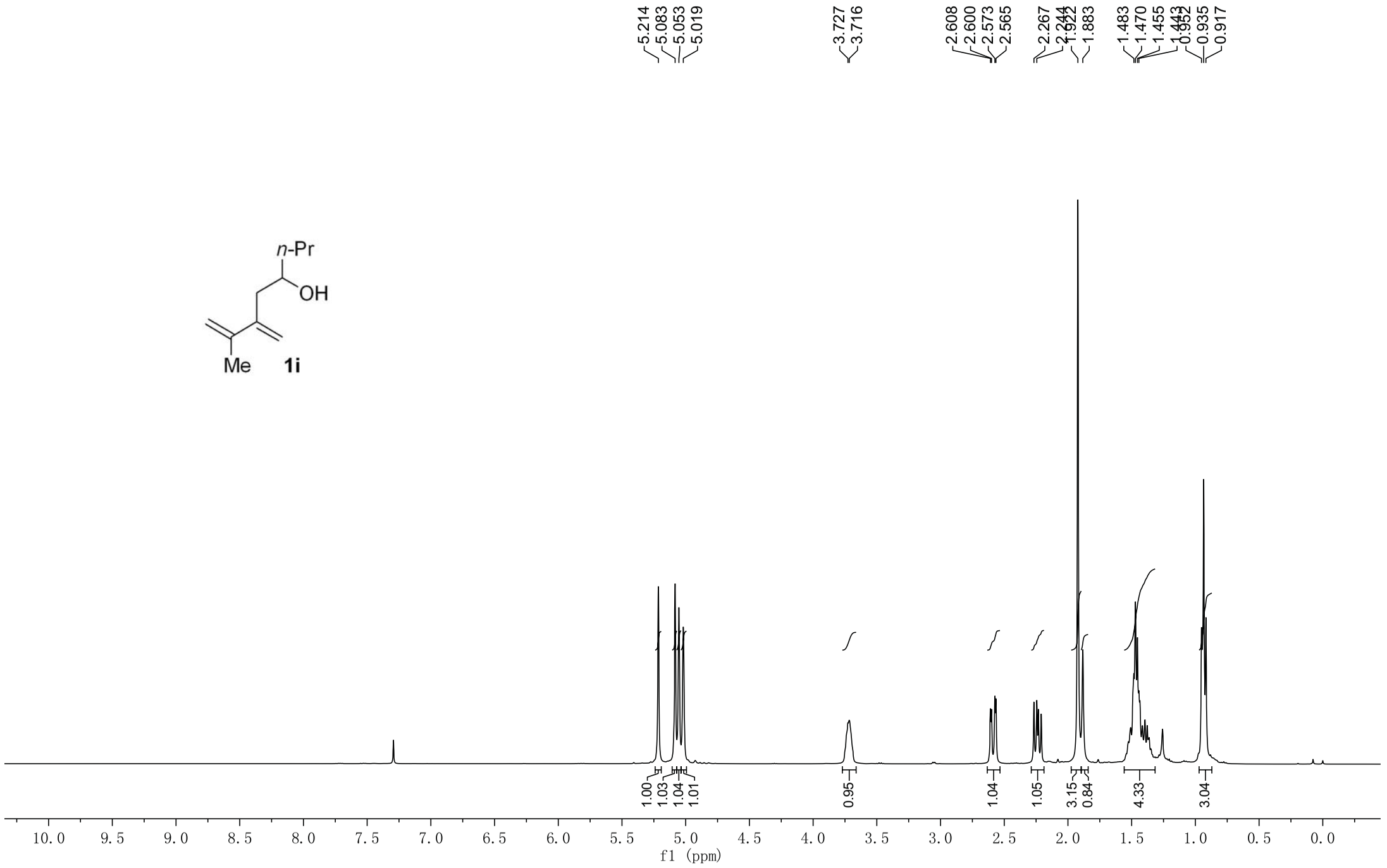
HYY-I-44 H1 CDCl3 600 MHz



HYY-I-44 C13 CDCl3 100 MHz

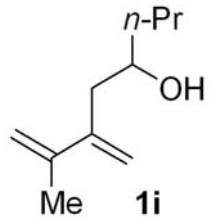


YZP-III-90 H1 CDCl3 400M Hz

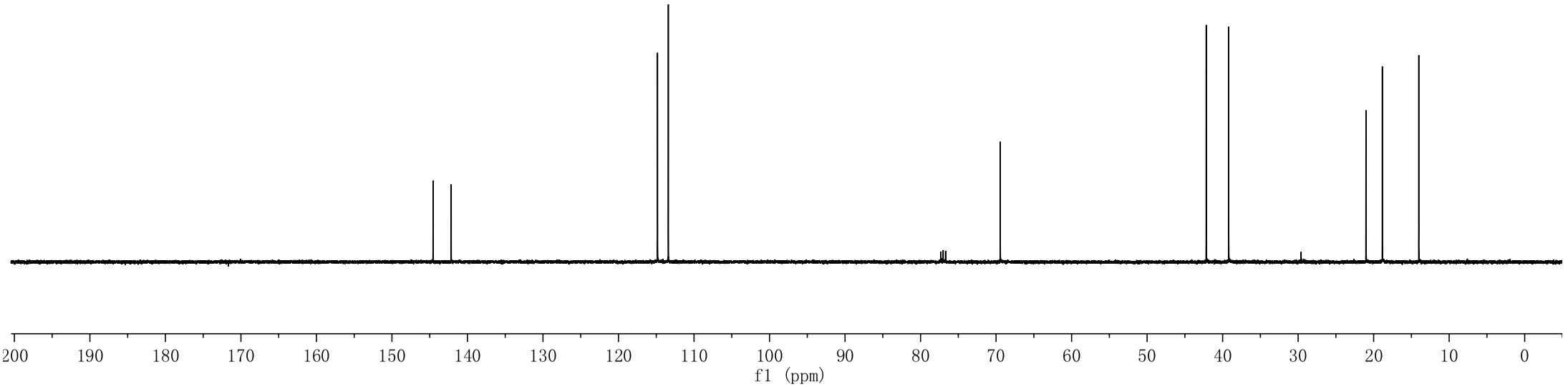


YZP-III-90 C13 CDCl3 100M Hz

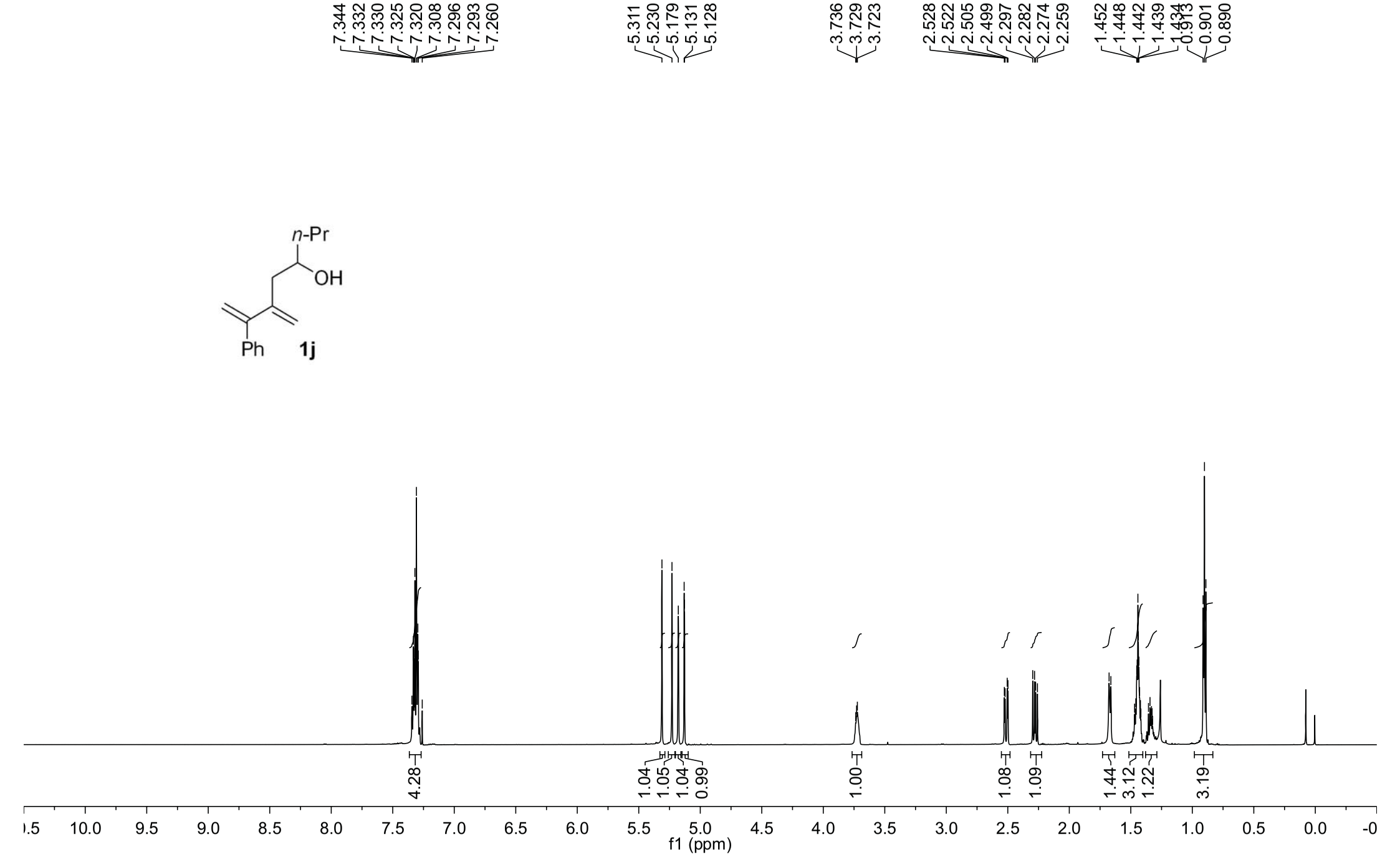
144.556
142.151
114.836
113.403
77.322
77.000
76.684
69.449
42.175
39.197
21.018
18.853
14.021



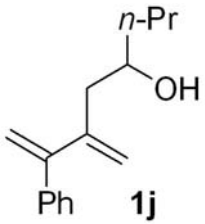
1i



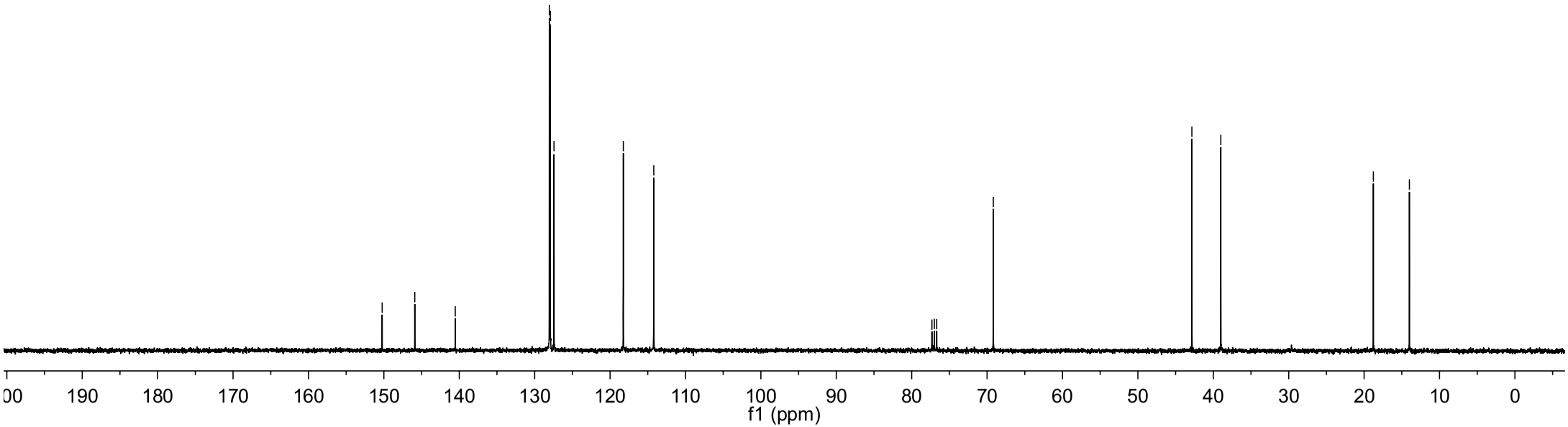
HYY-I-74-1 H1 CDCl3 600 MHz



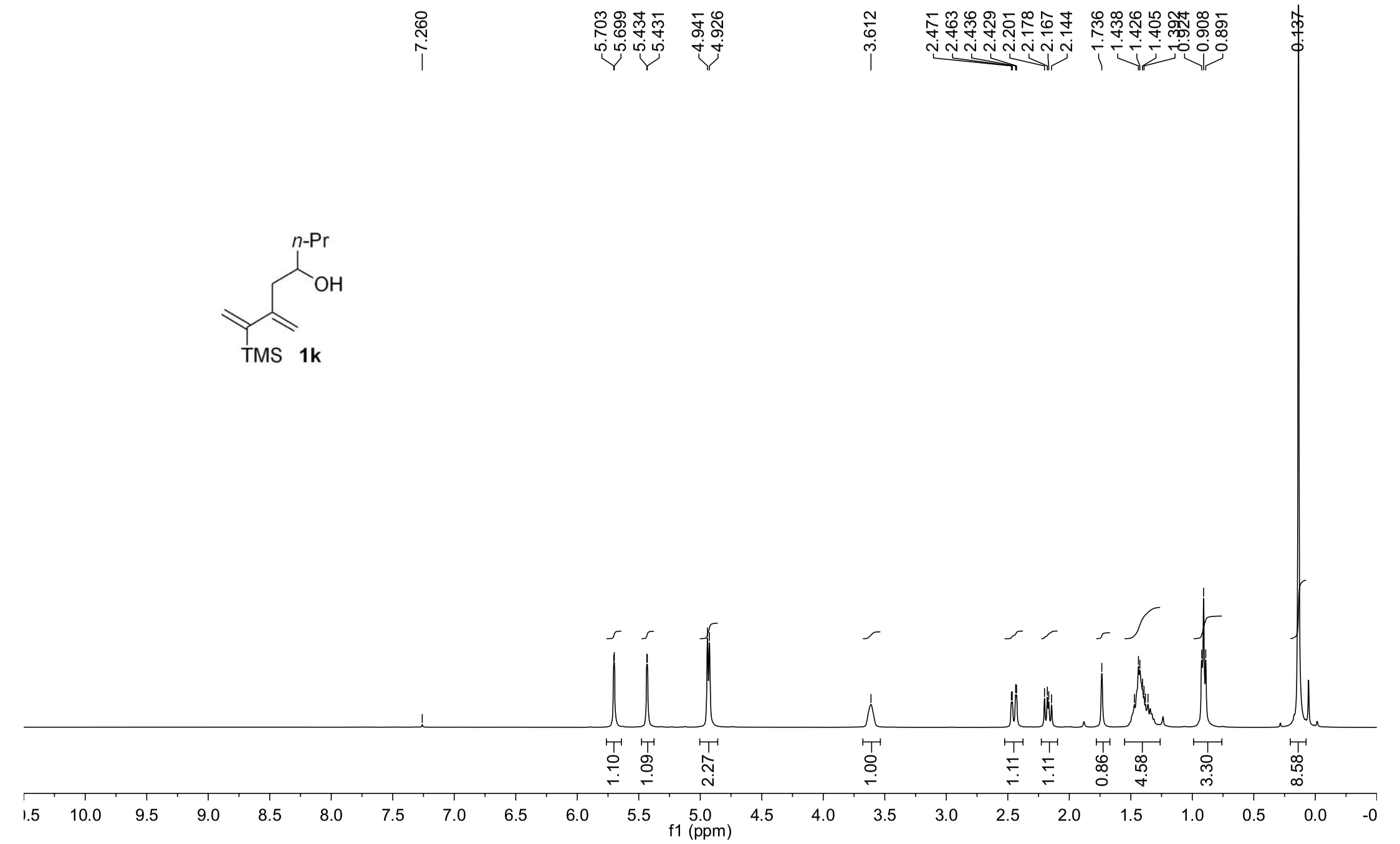
YZP-III-86 C13 CDCl3 100 MHz



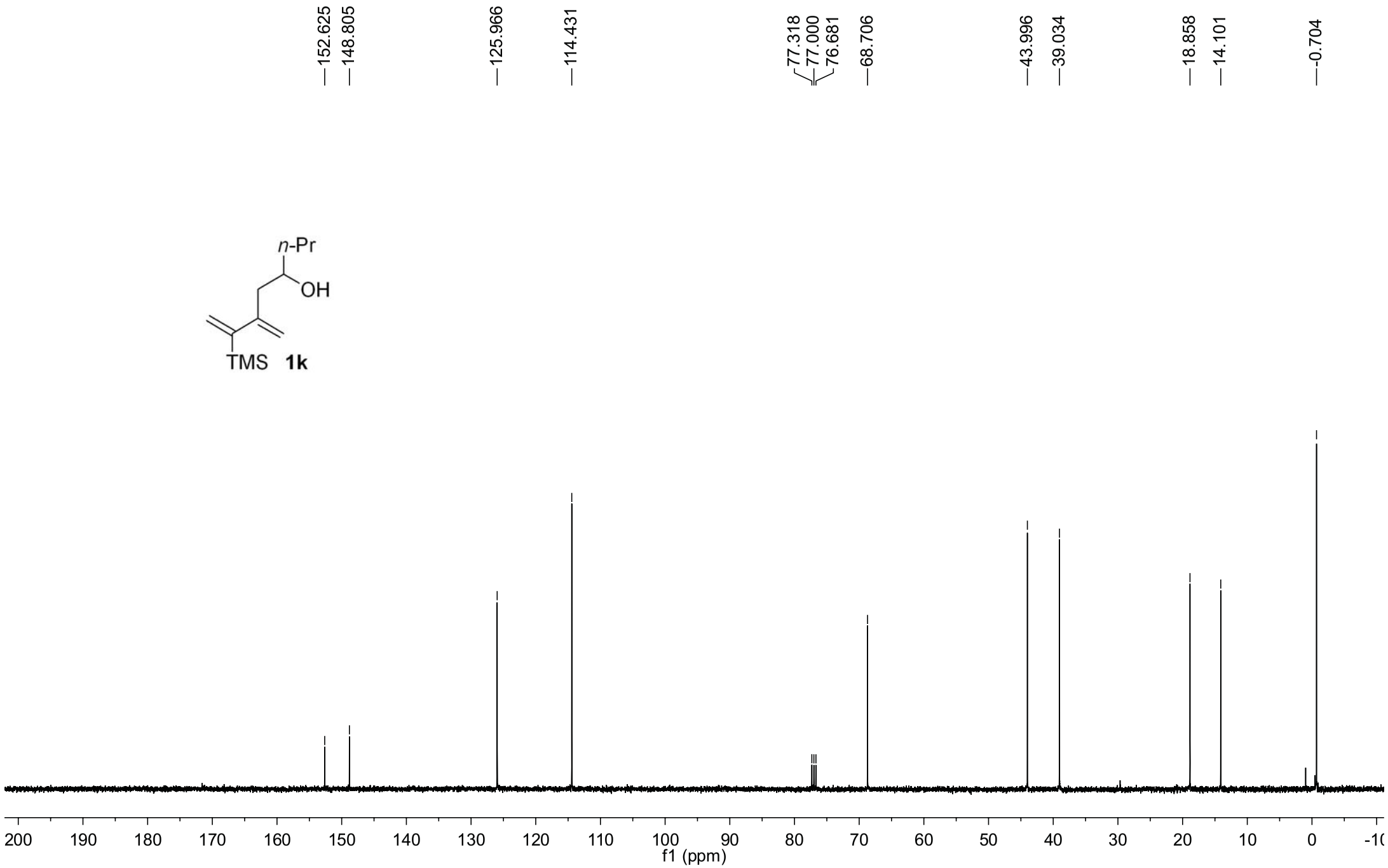
1j



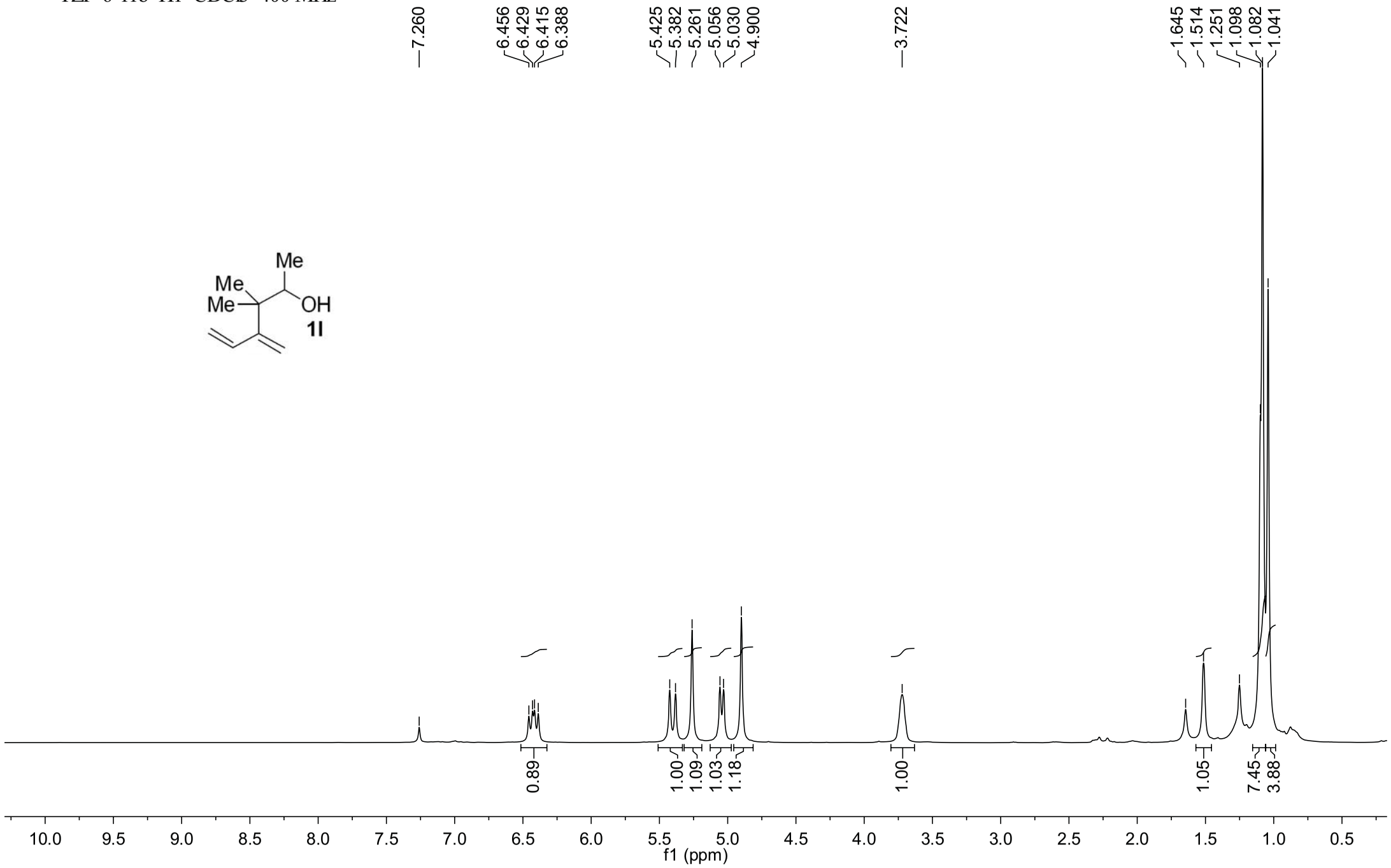
YZP-III-82 H1 CDCl3 400MHz



YZP-III-82 C13 CDCl3 100MHz

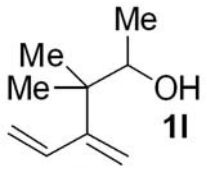


YZP-6-11b H1 CDCl3 400 MHz

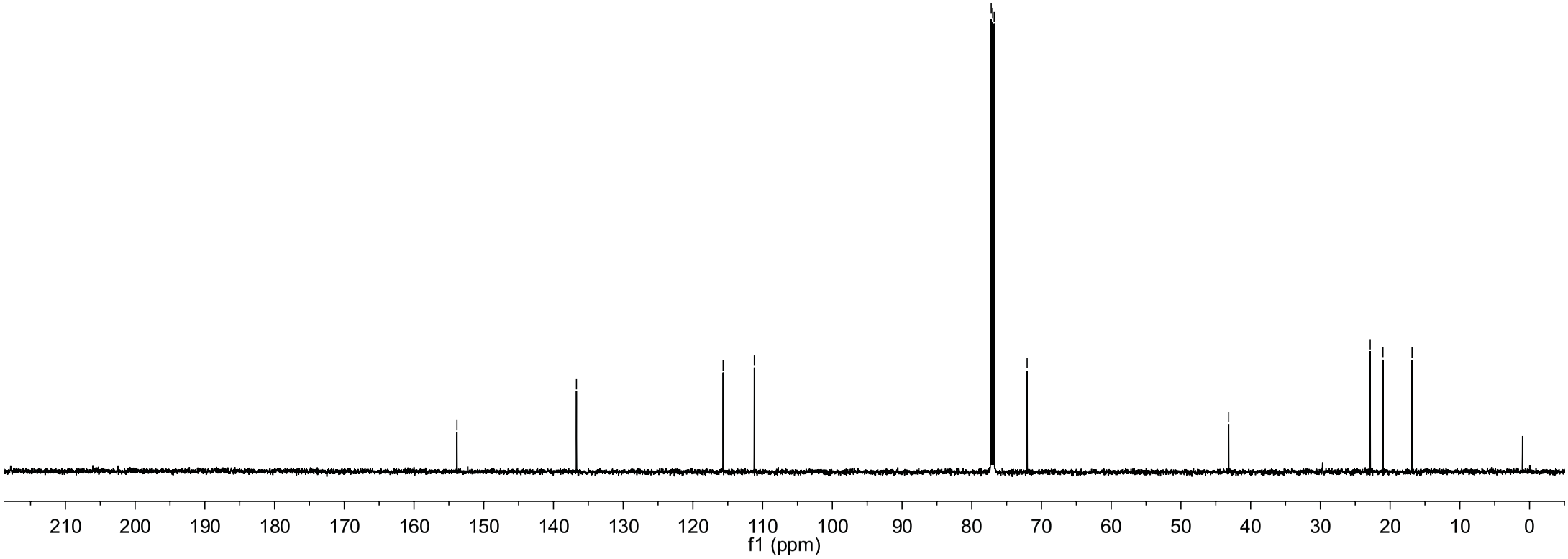


YZP-6-11b C13 CDCl3 150 MHz

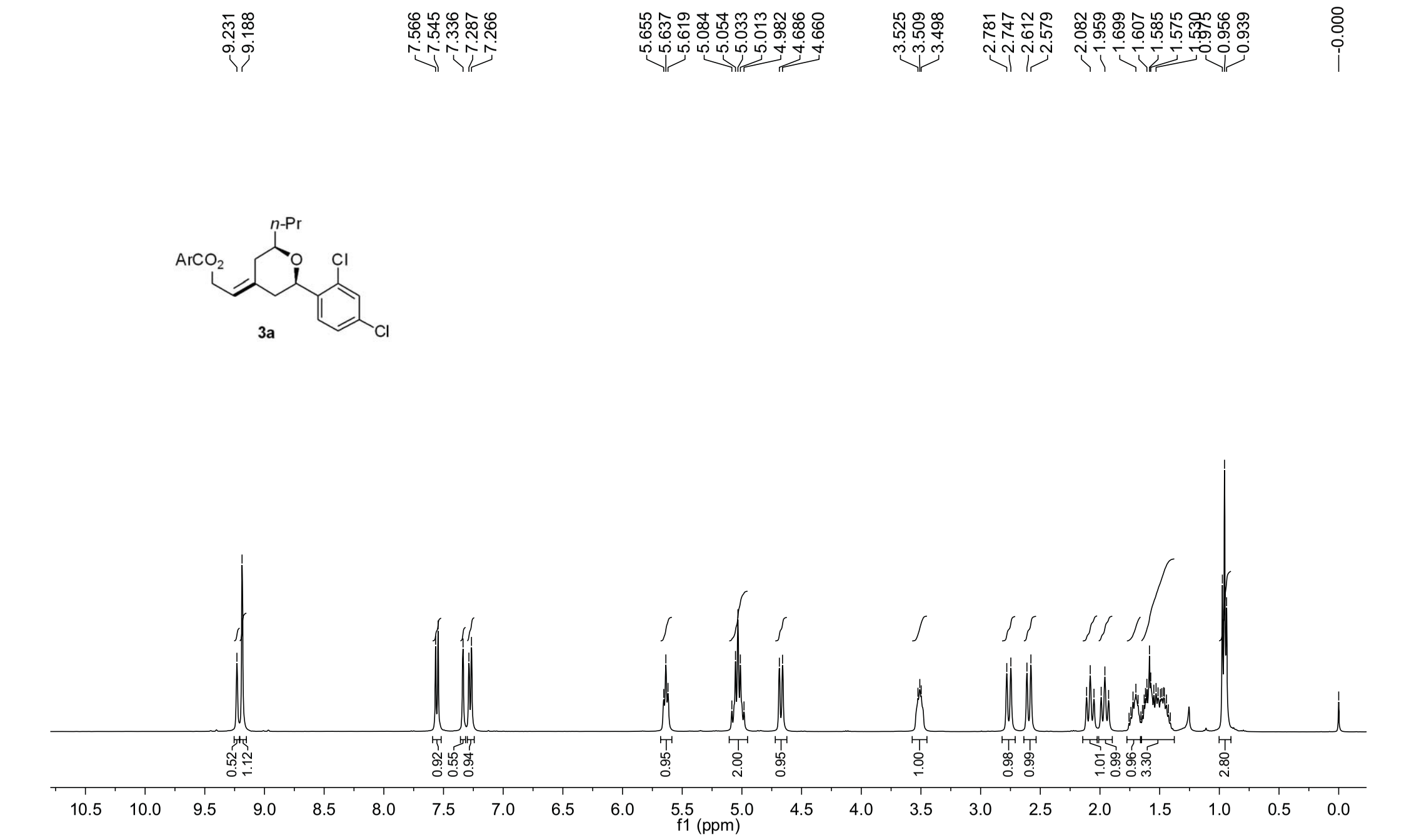
153.840
136.704
115.666
111.193
77.211
77.000
76.788
72.059
43.151
22.853
21.025
16.852



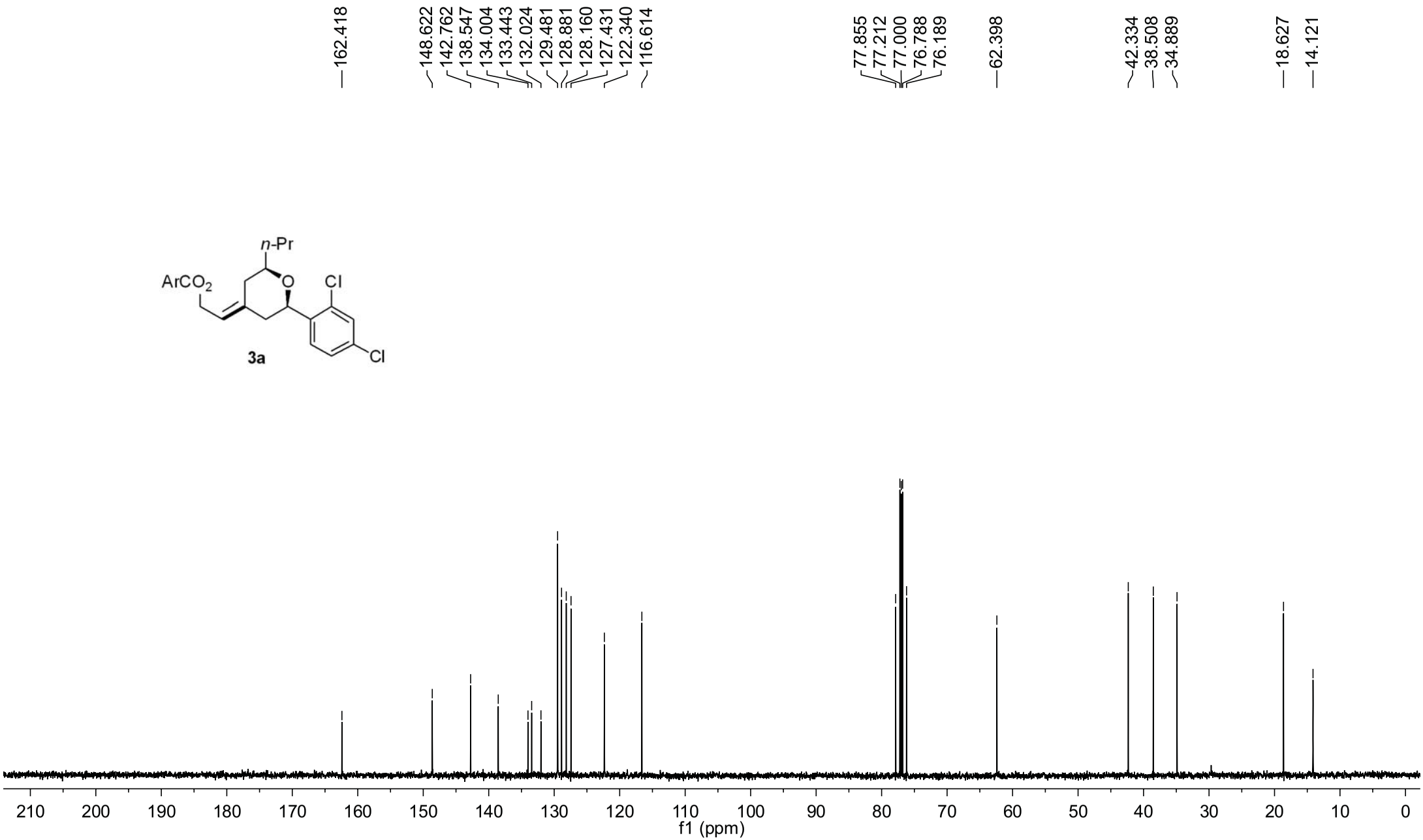
1l



YZP-V-68-3 H1 CDCl3 400 MHz



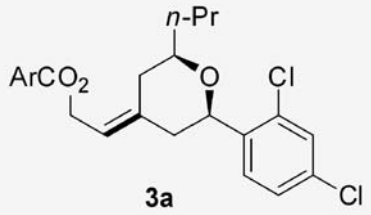
YZP-V-68-3 C13 CDCl3 150 MHz



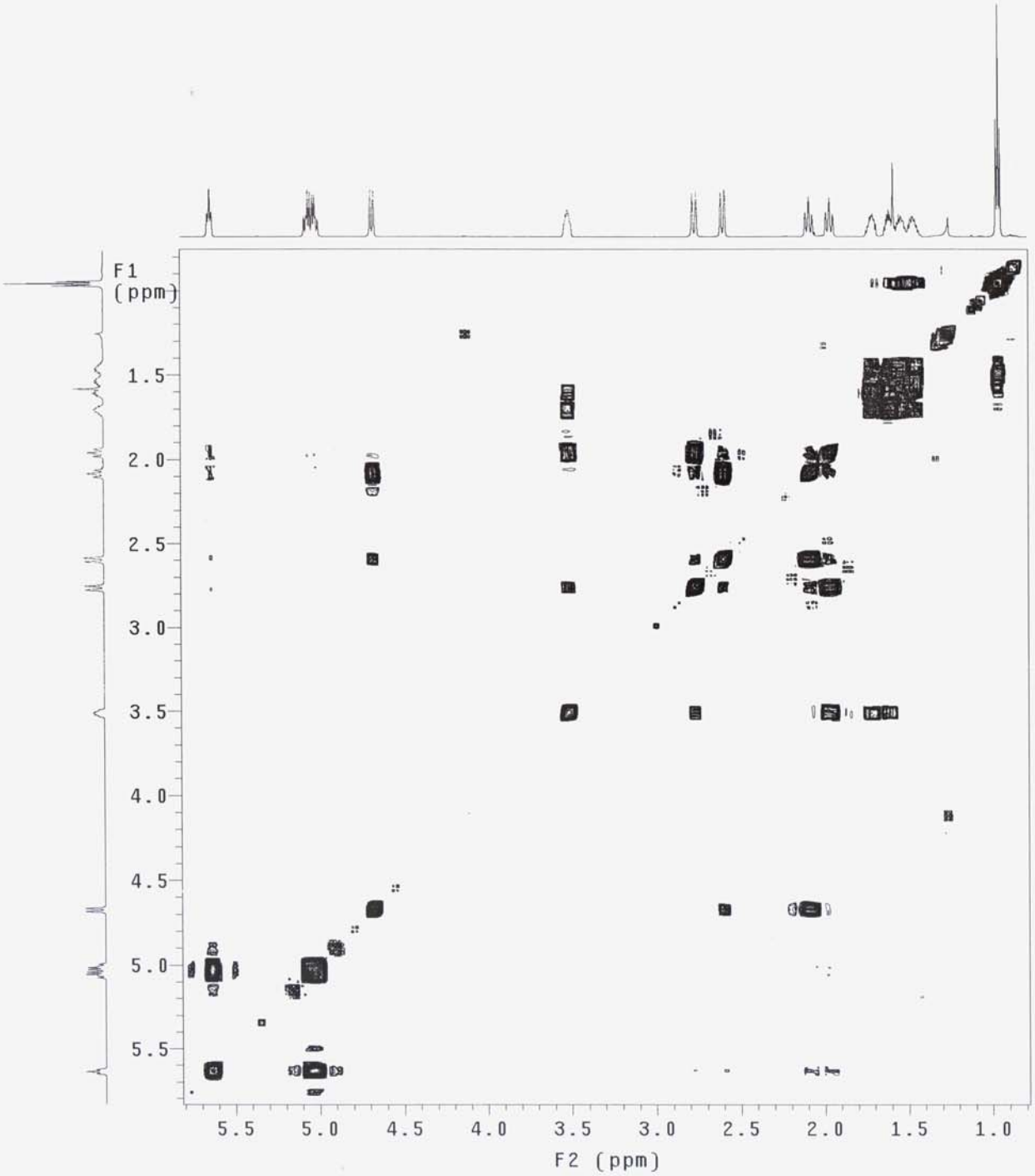
YZP-V-68-3 gCOSY CDCl3 2014-10-12

Archive directory:
Sample directory:

Pulse Sequence: gCOSY



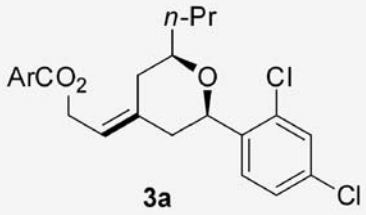
3a



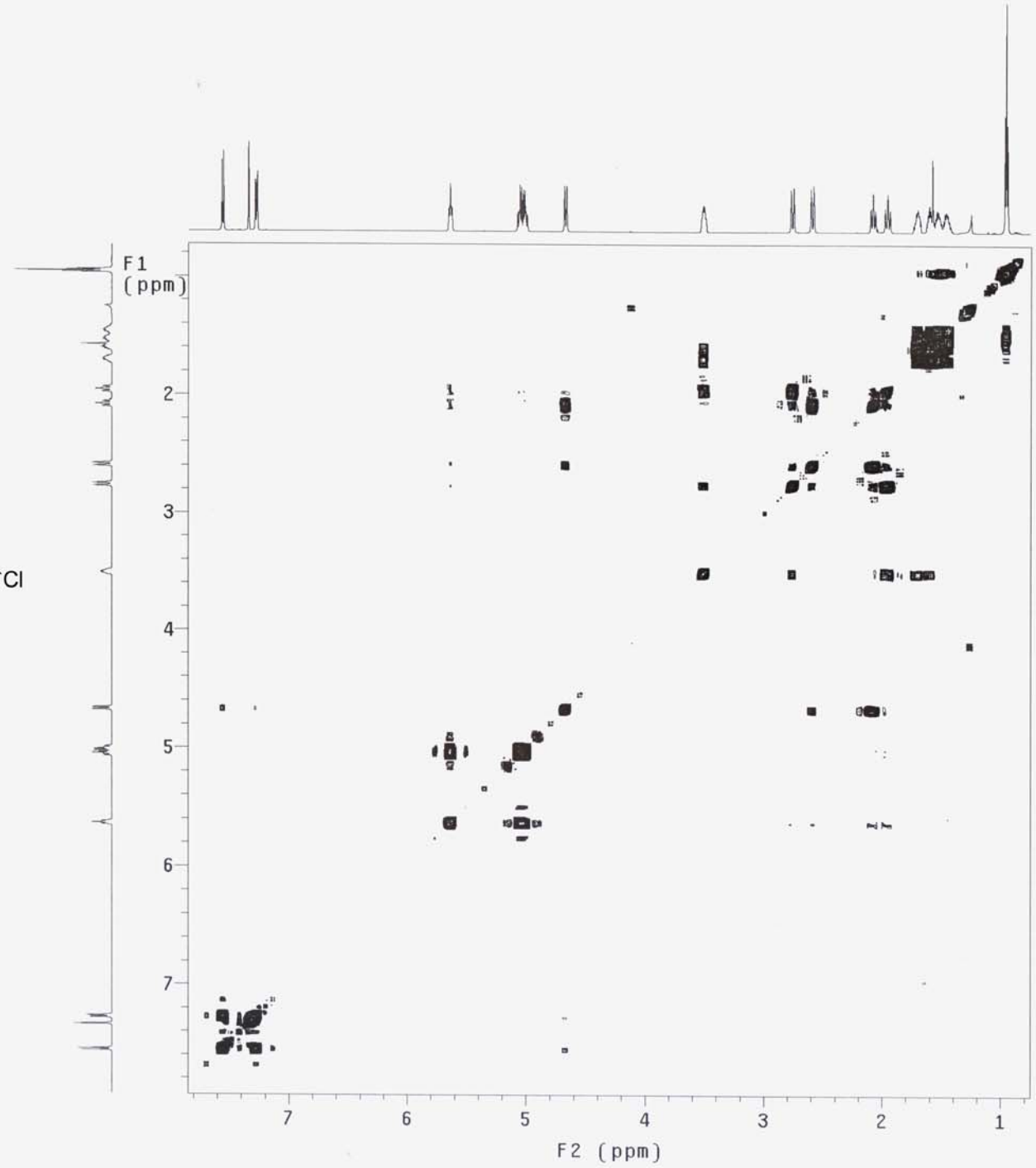
YZP-V-68-3 gCOSY CDCl3 2014-10-12

Archive directory:
Sample directory:

Pulse Sequence: gCOSY



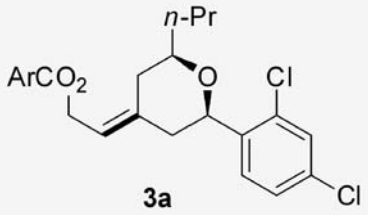
3a



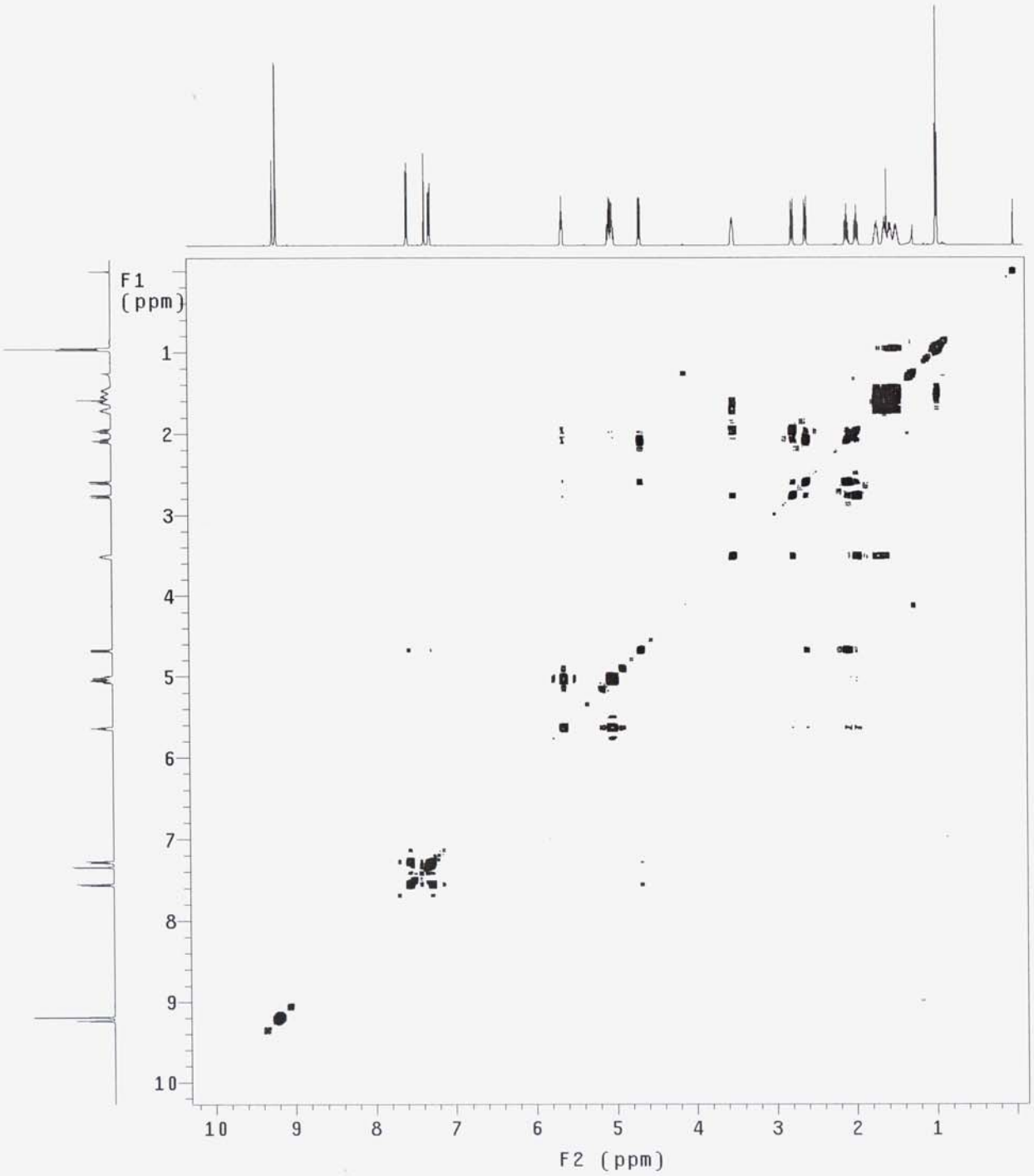
YZP-V-68-3 gCOSY CDCl3 2014-10-12

Archive directory:
Sample directory:

Pulse Sequence: gCOSY

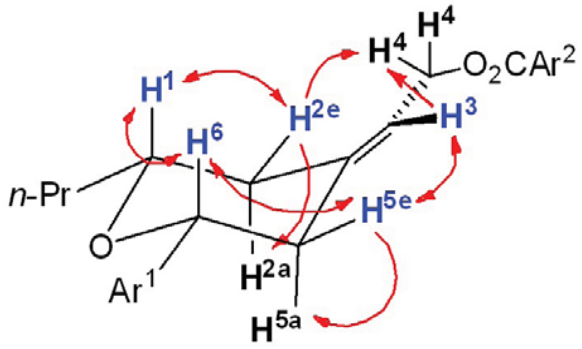


3a

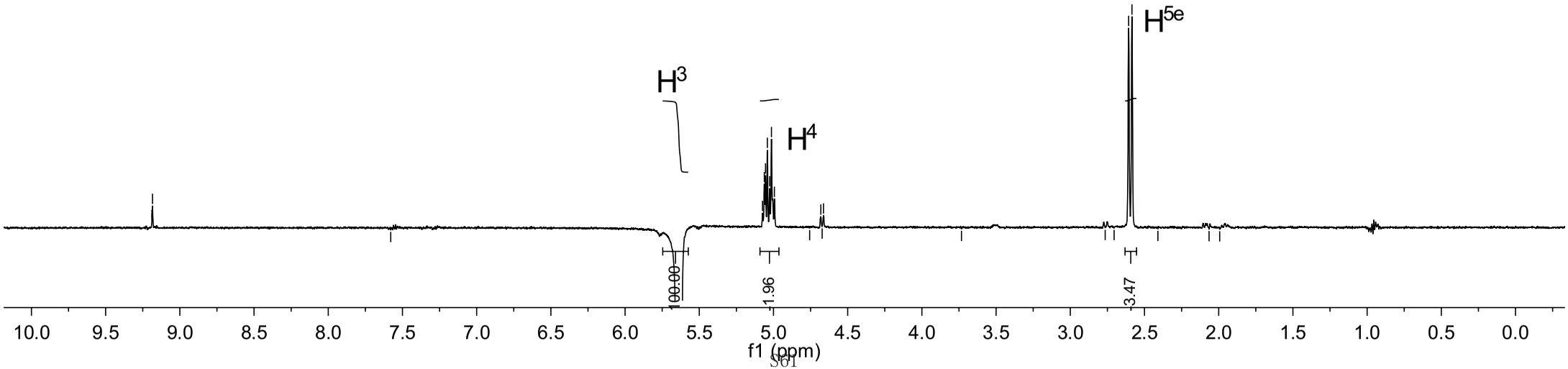


YZP-V-68-3 NOEDS CDCl3 5.64 600 MHz

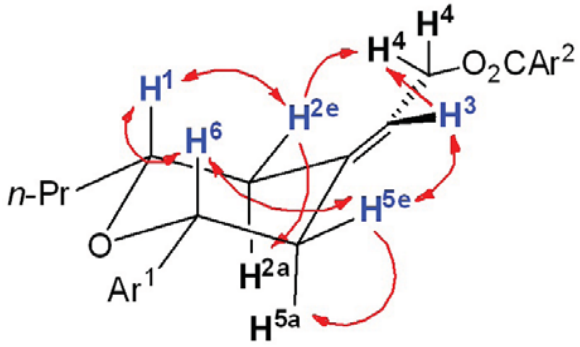
9.184 7.579 5.649 5.637 5.625 5.074 5.062 5.054 5.041 5.026 5.014 4.994 4.756 4.681 4.663 3.733 2.765 2.705 2.607 2.585 2.410 2.065 1.993



NOE of 3a

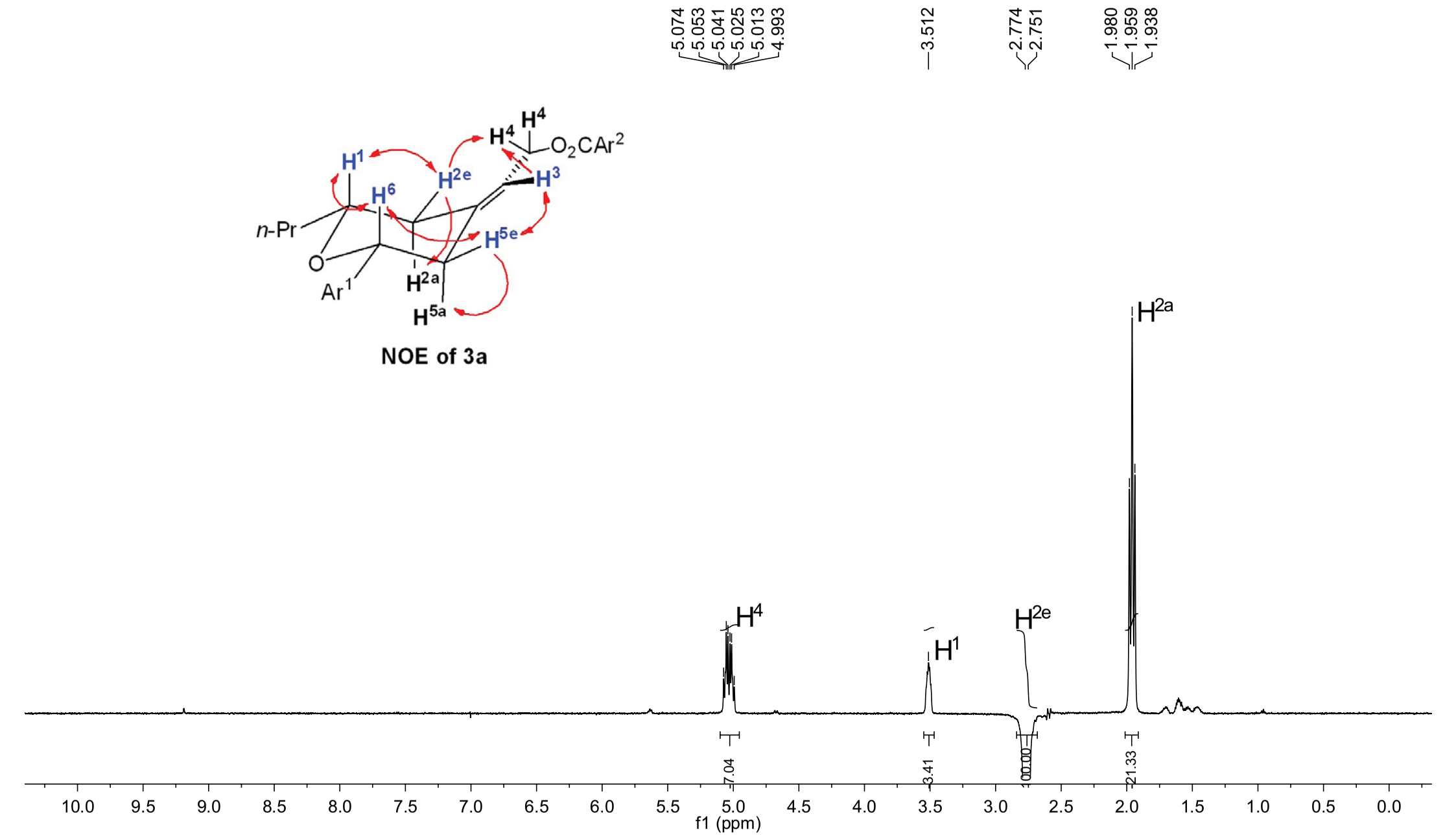


YZP-V-68-3 NOEDS CDCl3 2.59 600 MHz

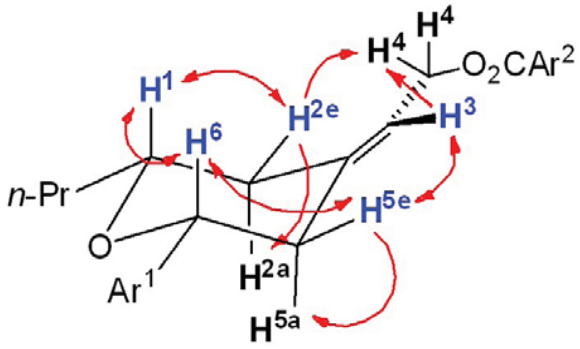


NOE of 3a

YZP-V-68-3 NOEDS CDCl3 2.76 600 MHz

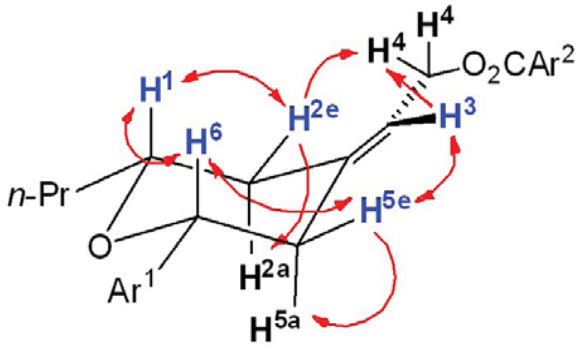


YZP-V-68-3 NOEDS CDCl3 3.51 600 MHz



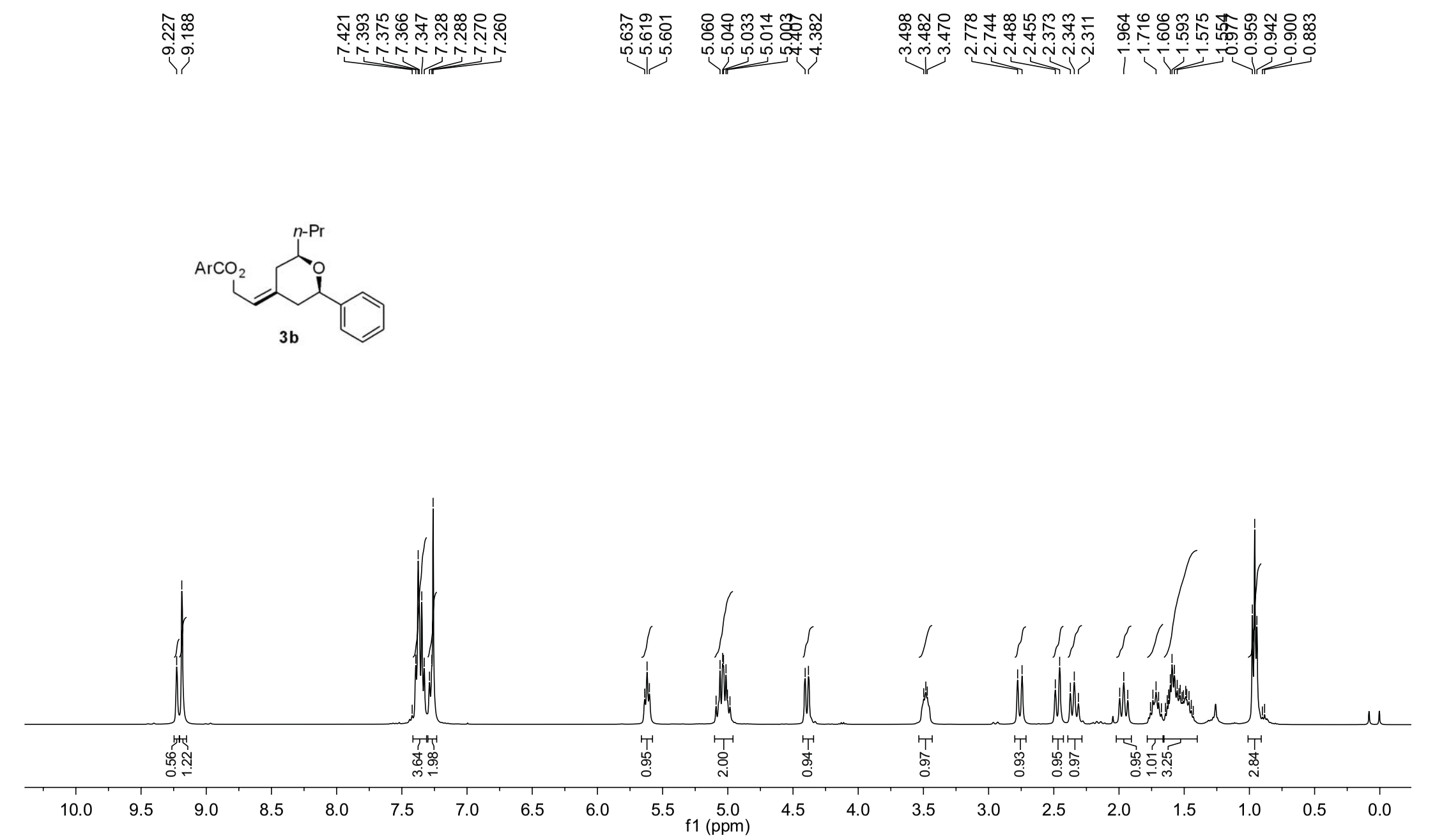
NOE of 3a

YZP-V-68-3 NOEDS CDCl3 4.67 600 MHz

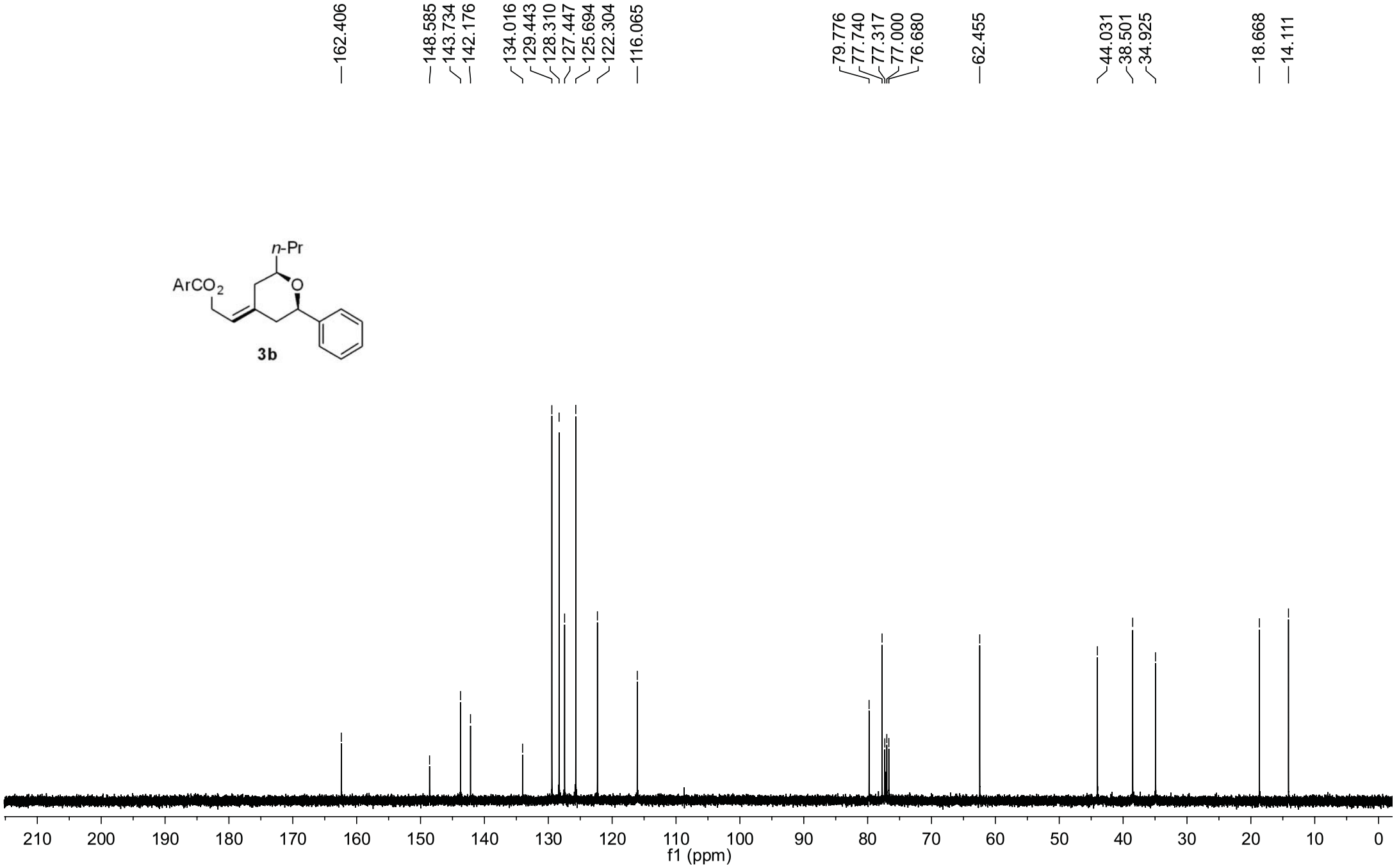


NOE of 3a

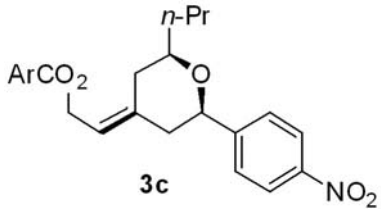
YZP-III-21-A H1 CDCl3 400 MHz



YZP-III-21-A C13 CDCl3 100 MHz

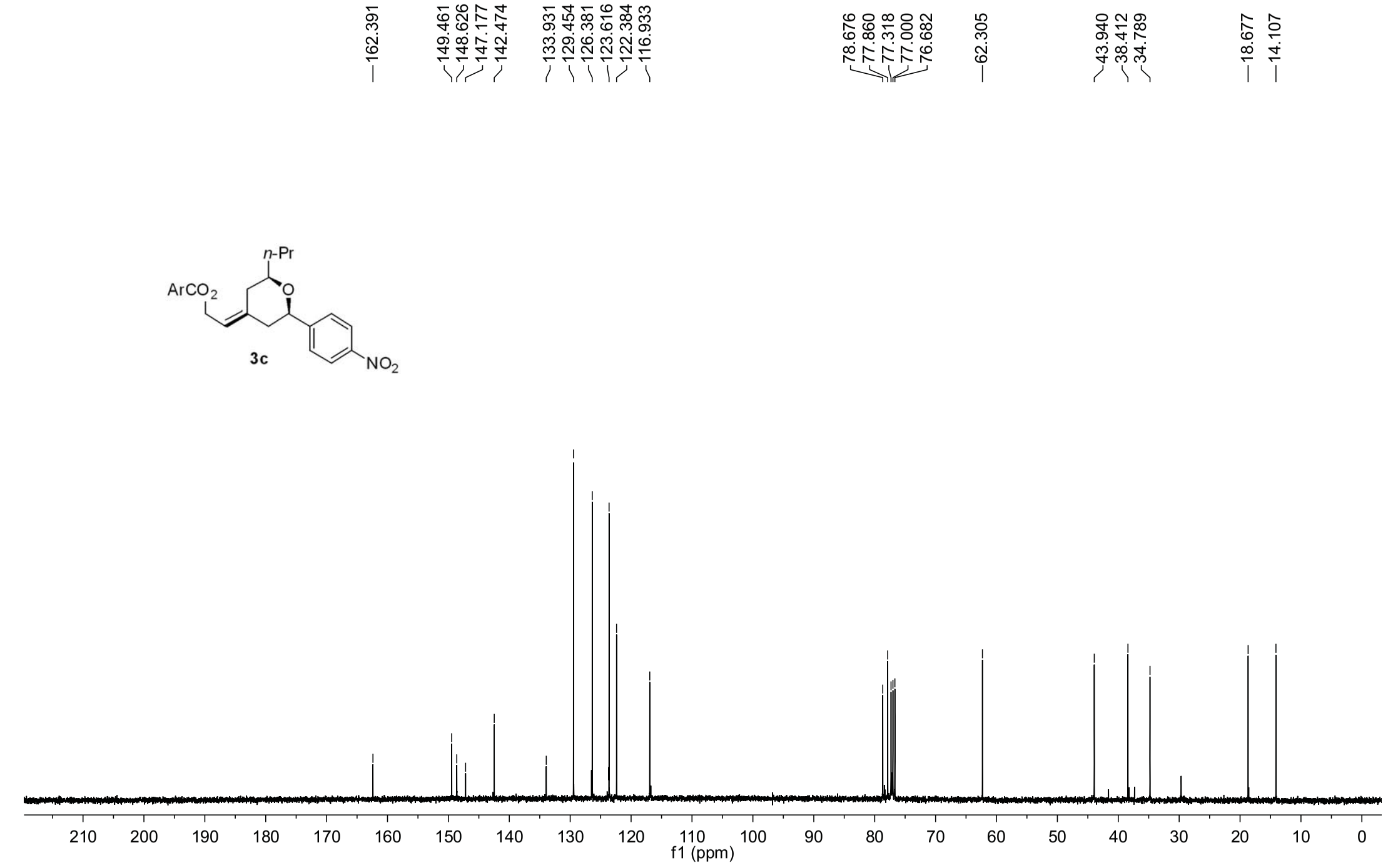


YZP-III-23-C H1 CDCl3 400 MHz



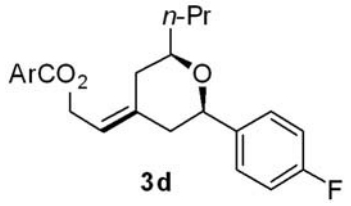
3c

YZP-III-23-C C13 CDCl3 100 MHz

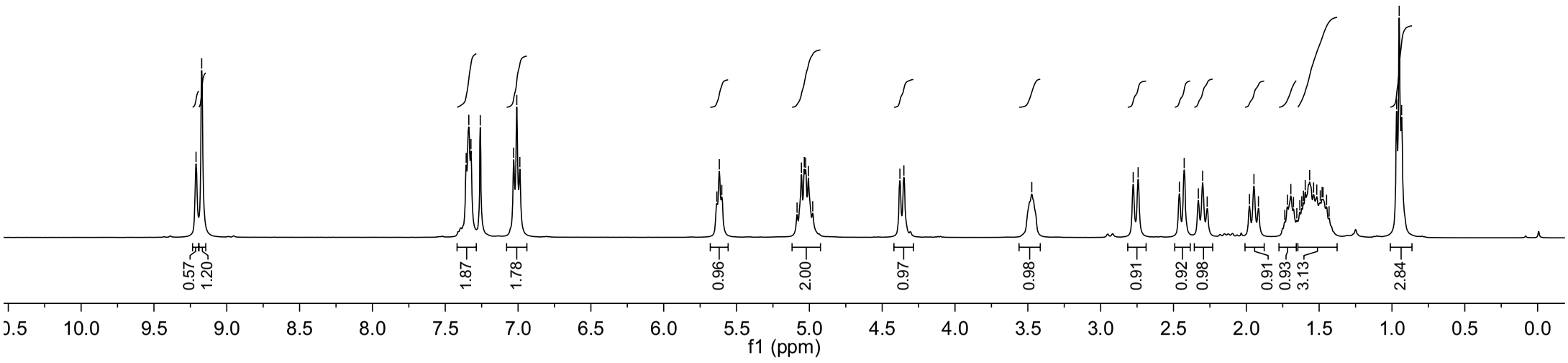


YZP-III-47 H1 CDCl3 400 MHz

9.211
9.172
7.356
7.338
7.324
7.260
7.030
7.009
6.988
5.635
5.618
5.601
5.054
5.035
5.025
5.007
4.977
4.378
4.351
3.473
2.777
2.743
2.460
2.427
2.329
2.300
1.948
1.694
1.596
1.565
1.538
1.516
1.480
1.473
0.968
0.950
0.934

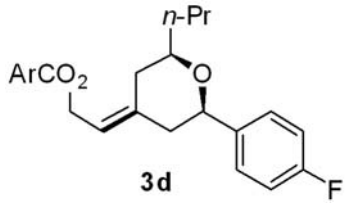


3d

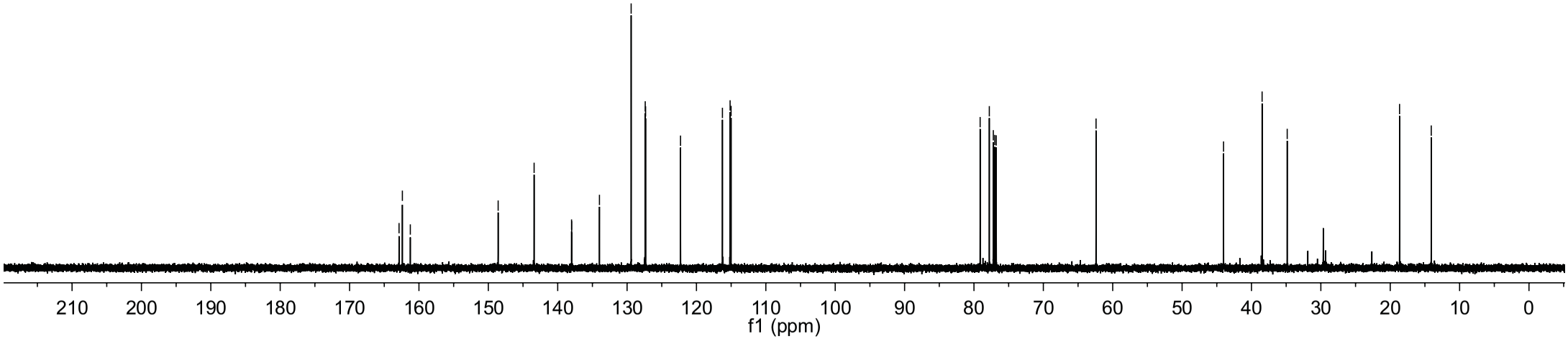


YZP-V-49-1 C13 CDCl3 150MHz

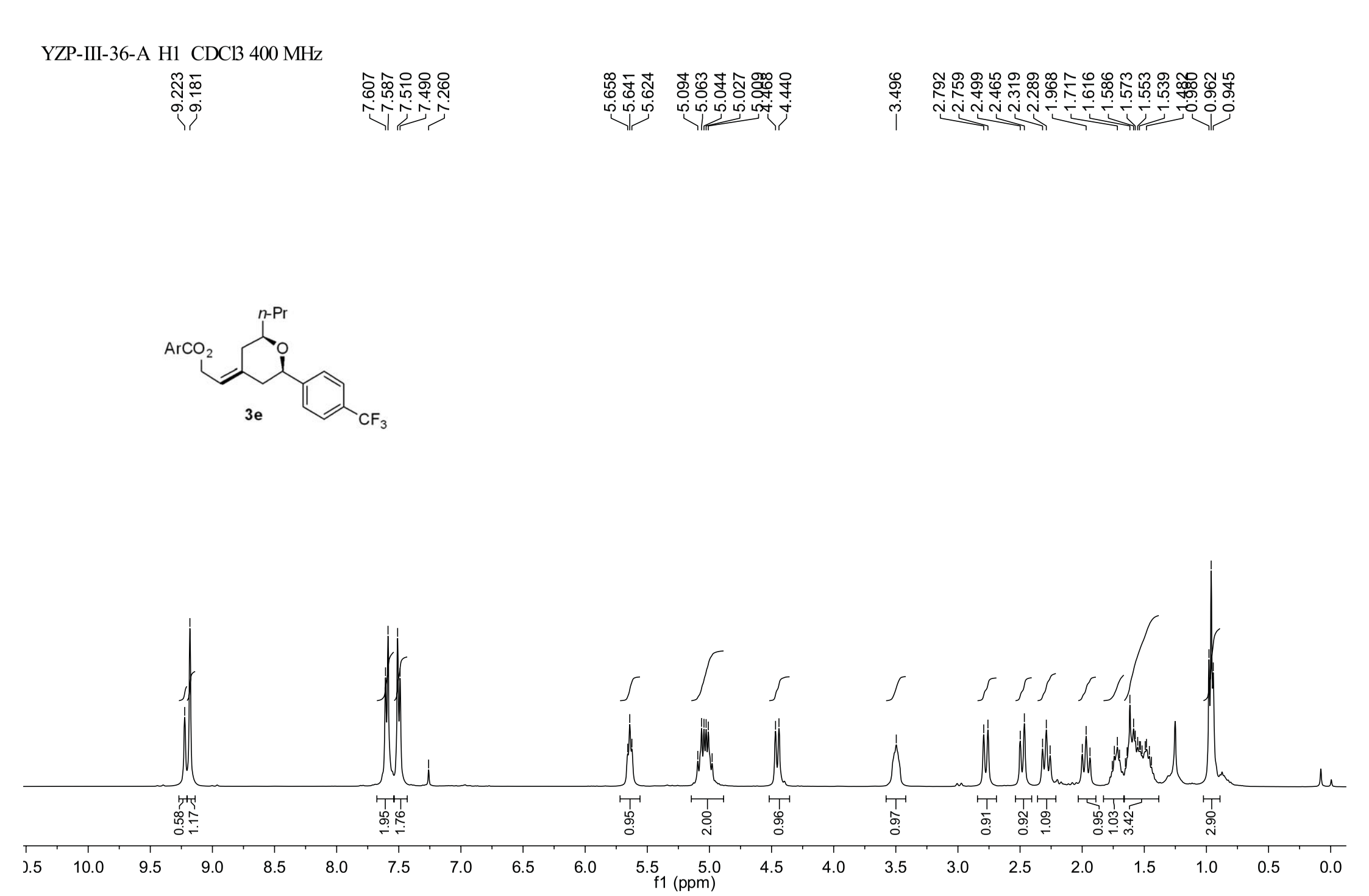
162.870
162.389
161.244
148.584
143.401
138.004
137.984
133.983
129.413
127.384
127.331
122.296
116.256
115.151
115.009
79.110
77.787
77.212
77.000
76.788
62.402
44.025
38.467
34.849
18.655
14.086



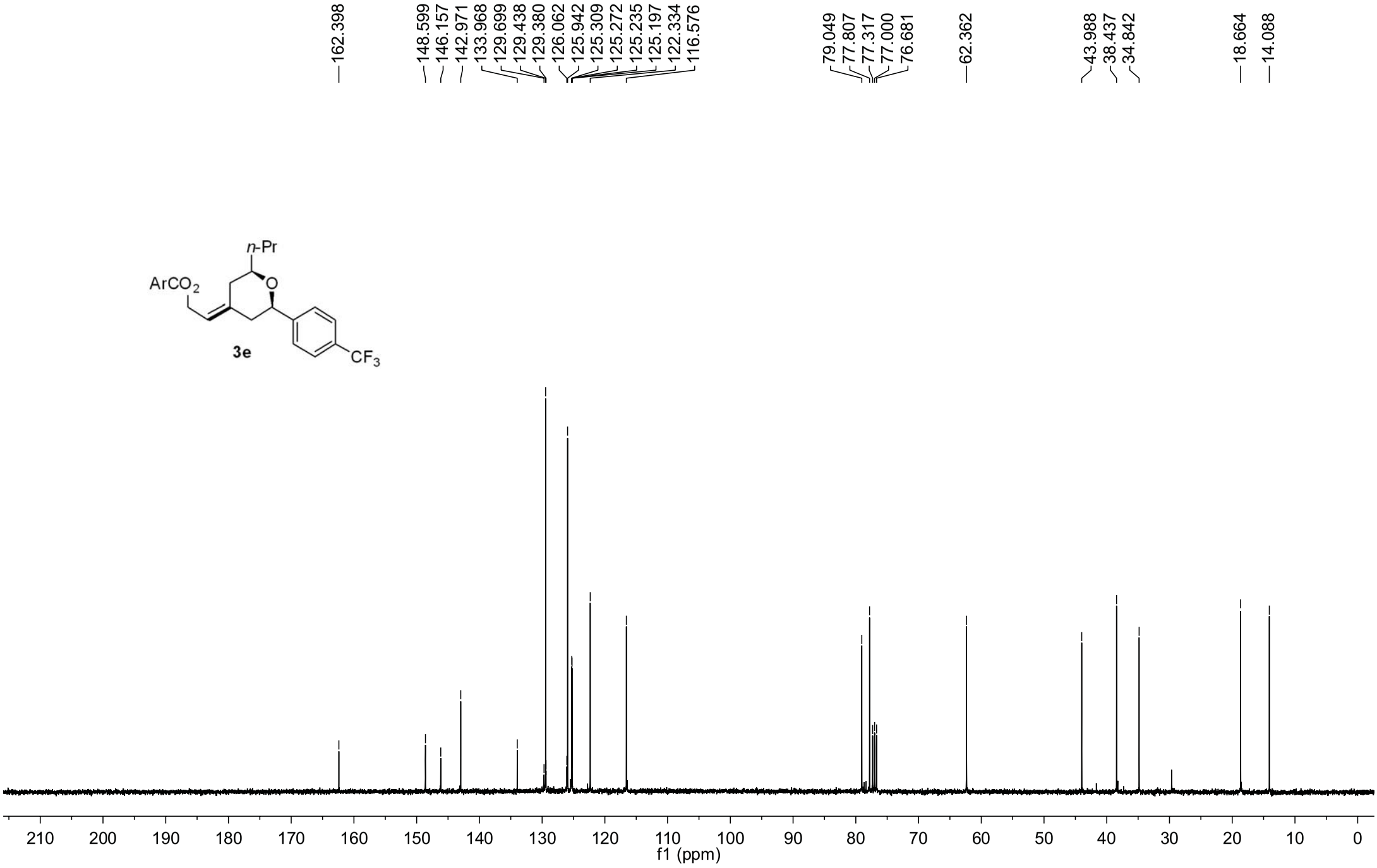
3d



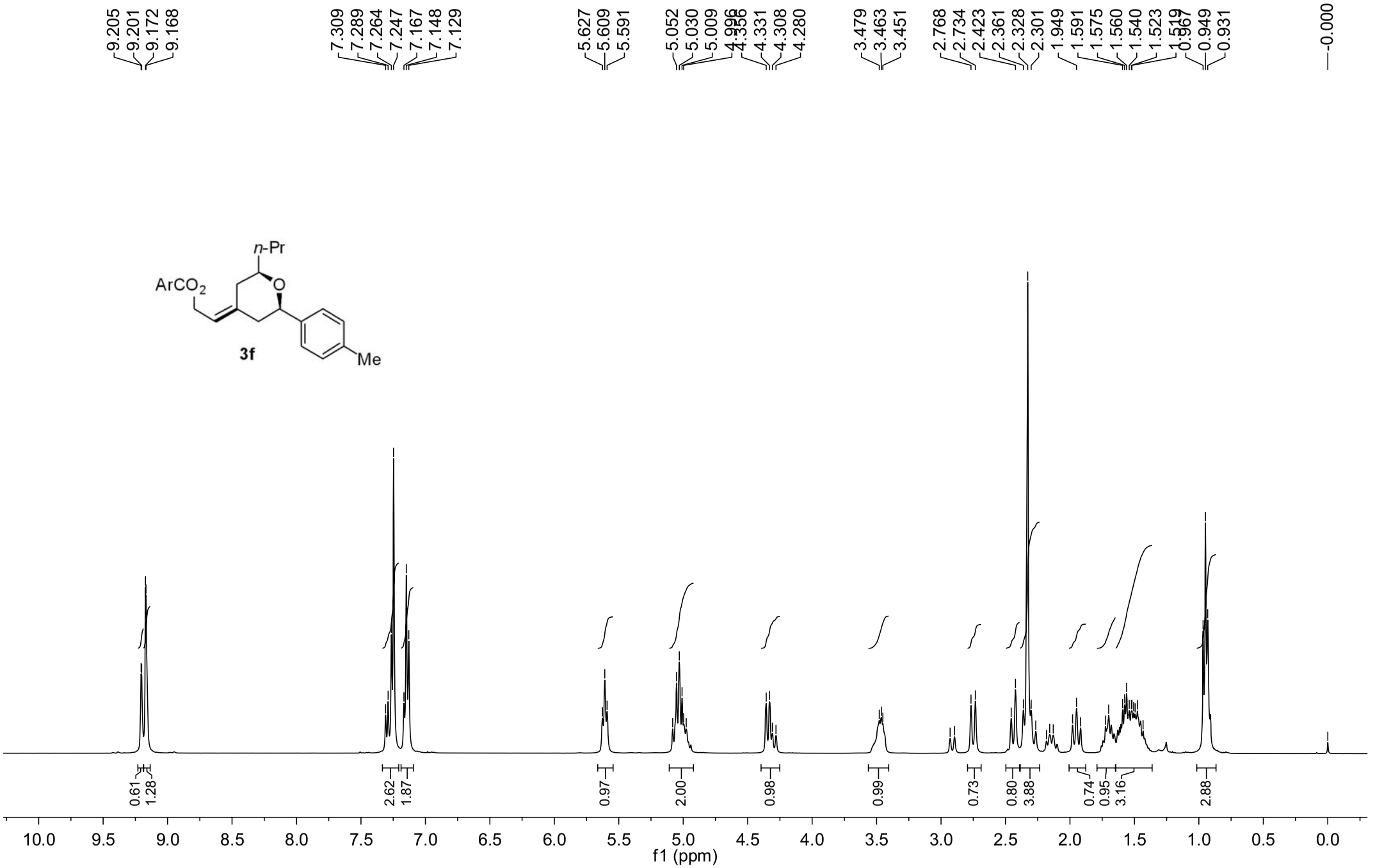
YZP-III-36-A H1 CDCl3 400 MHz



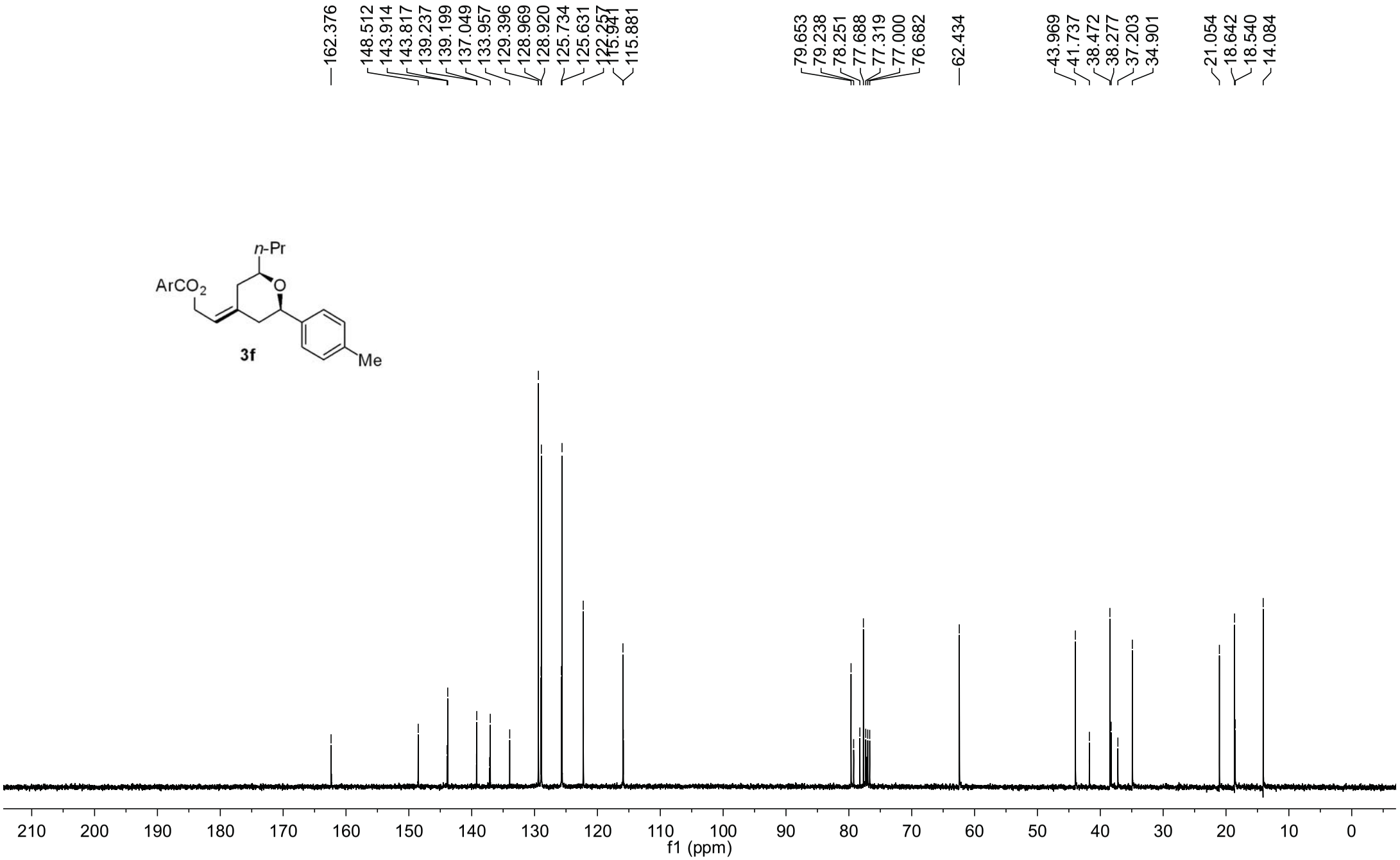
YZP-III-36-A C13 CDCl3 100 MHz



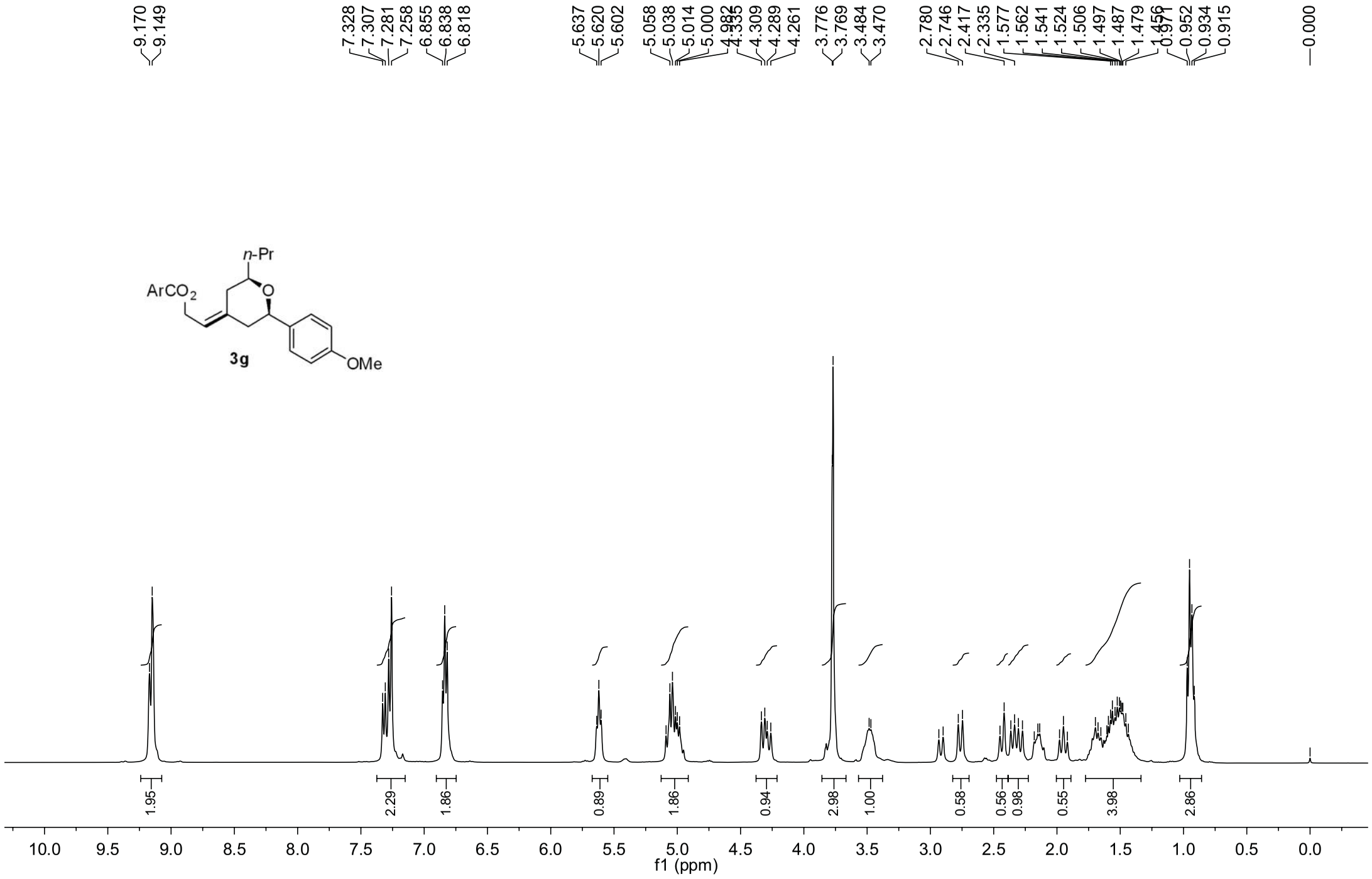
YZP-III-65-A H1 CDCl3 400 MHz



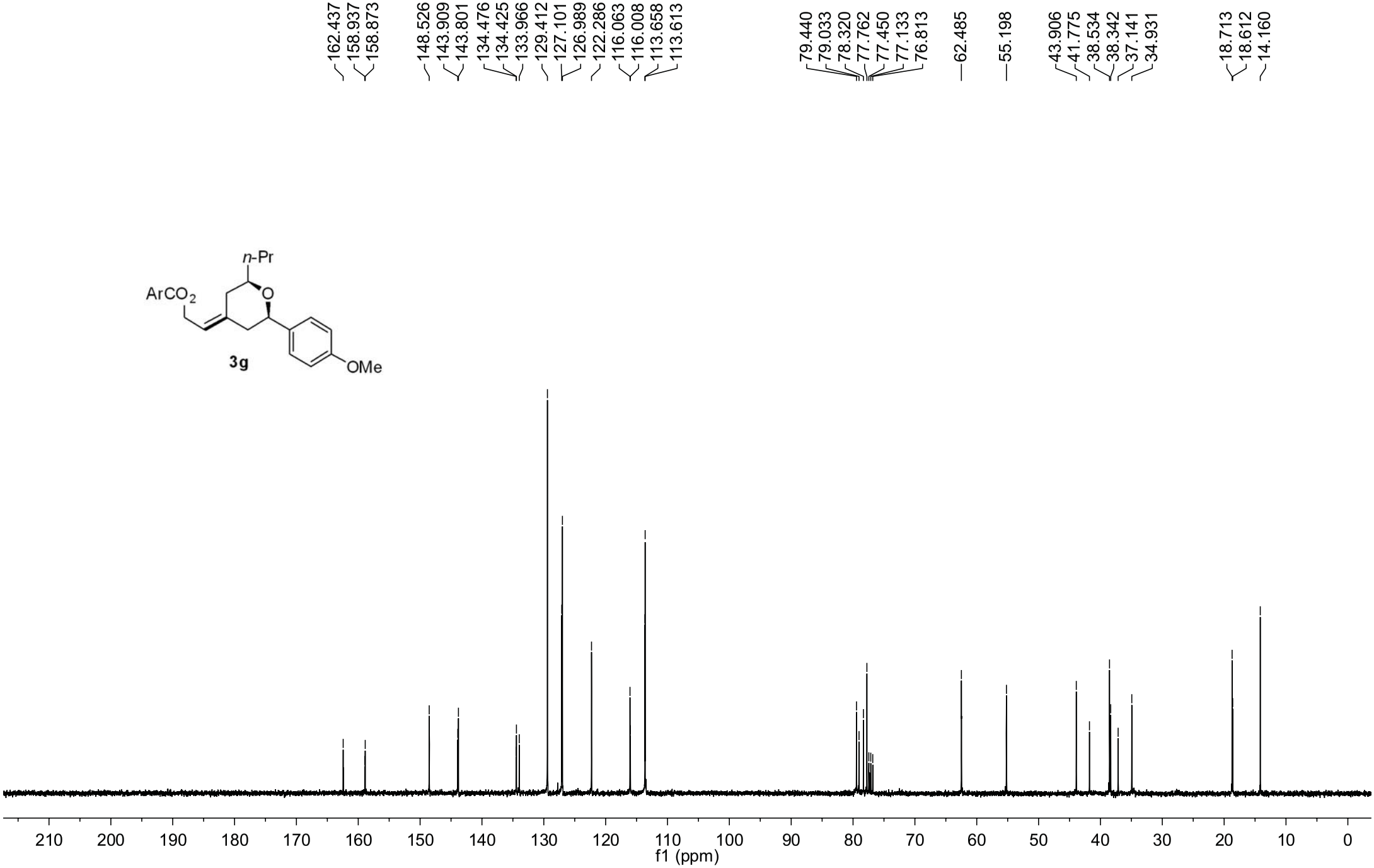
YZP-III-65-A C13 CDCl3 100 MHz



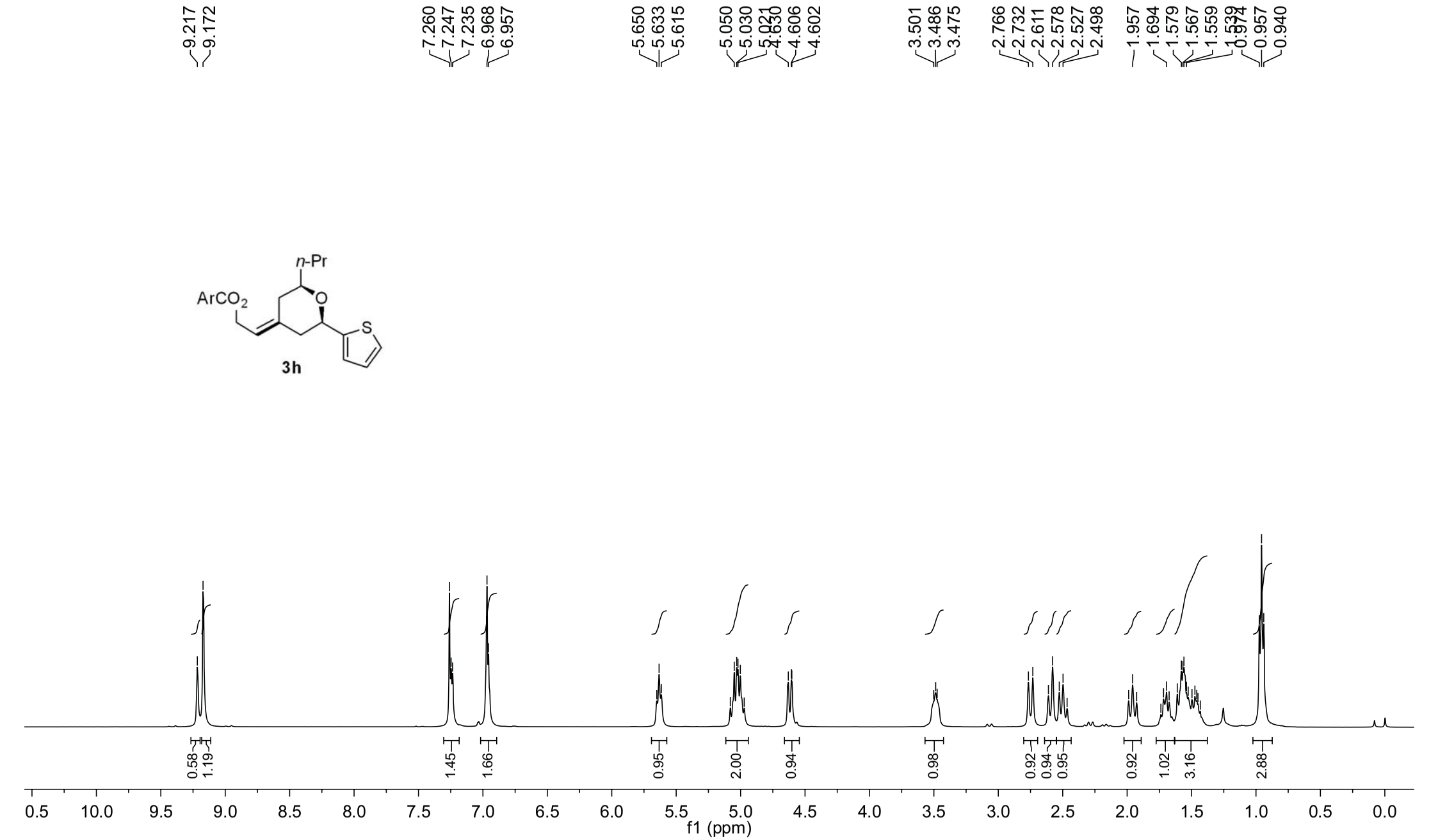
YZP-II-85-1 H1 CDCl3 400 MHz



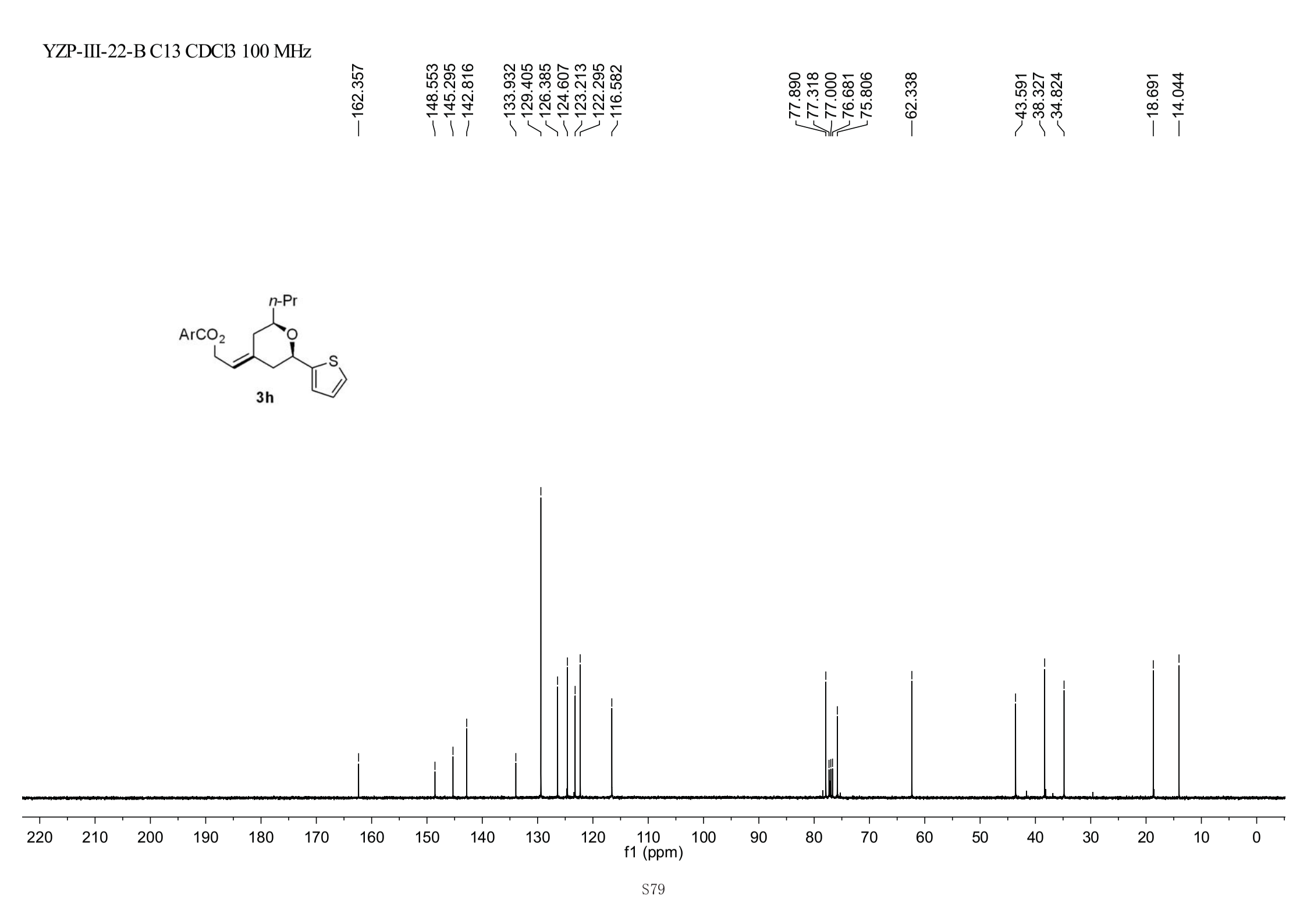
YZP-III-85-1 C13 CDCl3 100 MHz



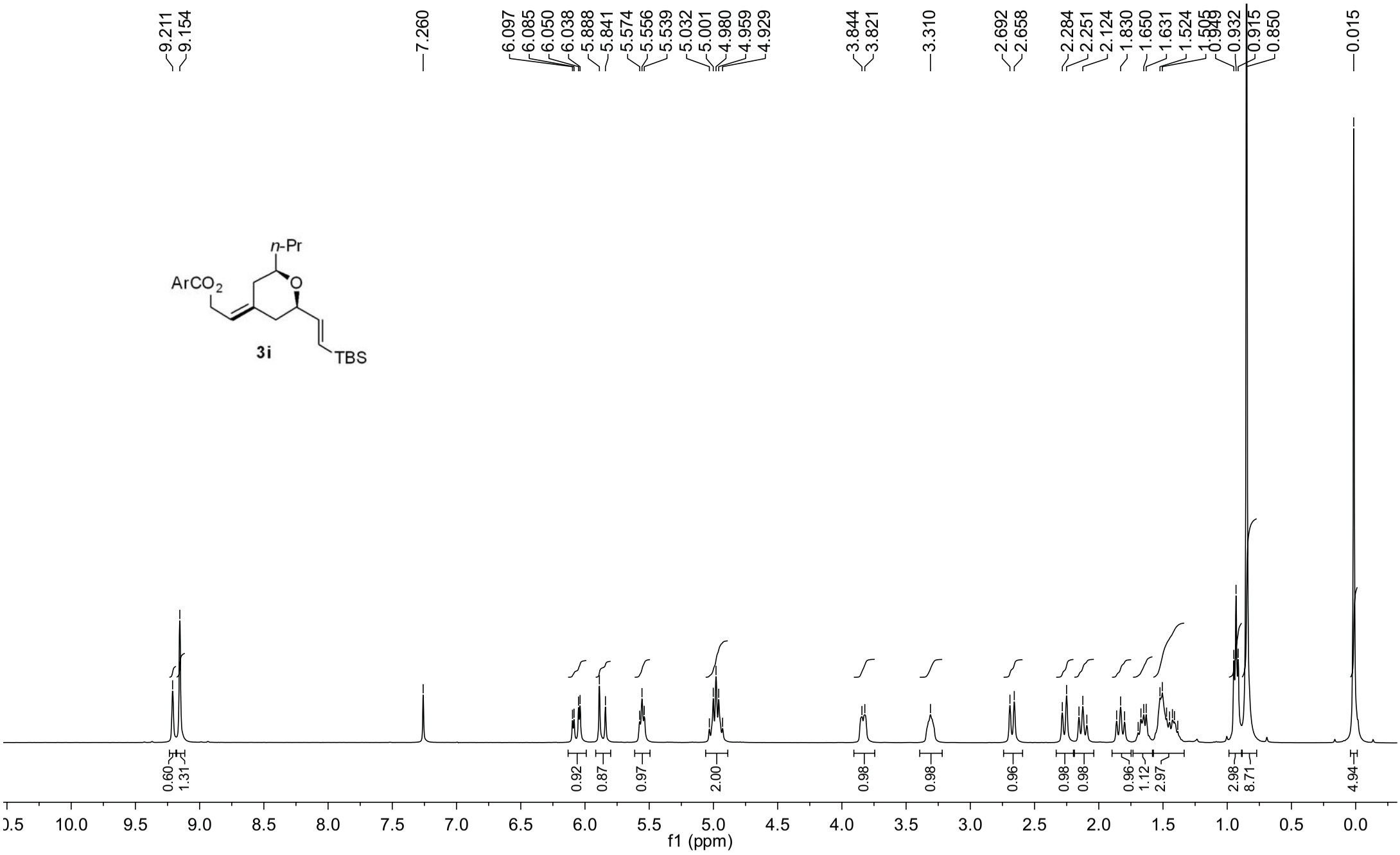
YZP-III-22-B H1 CDCl3 400 MHz



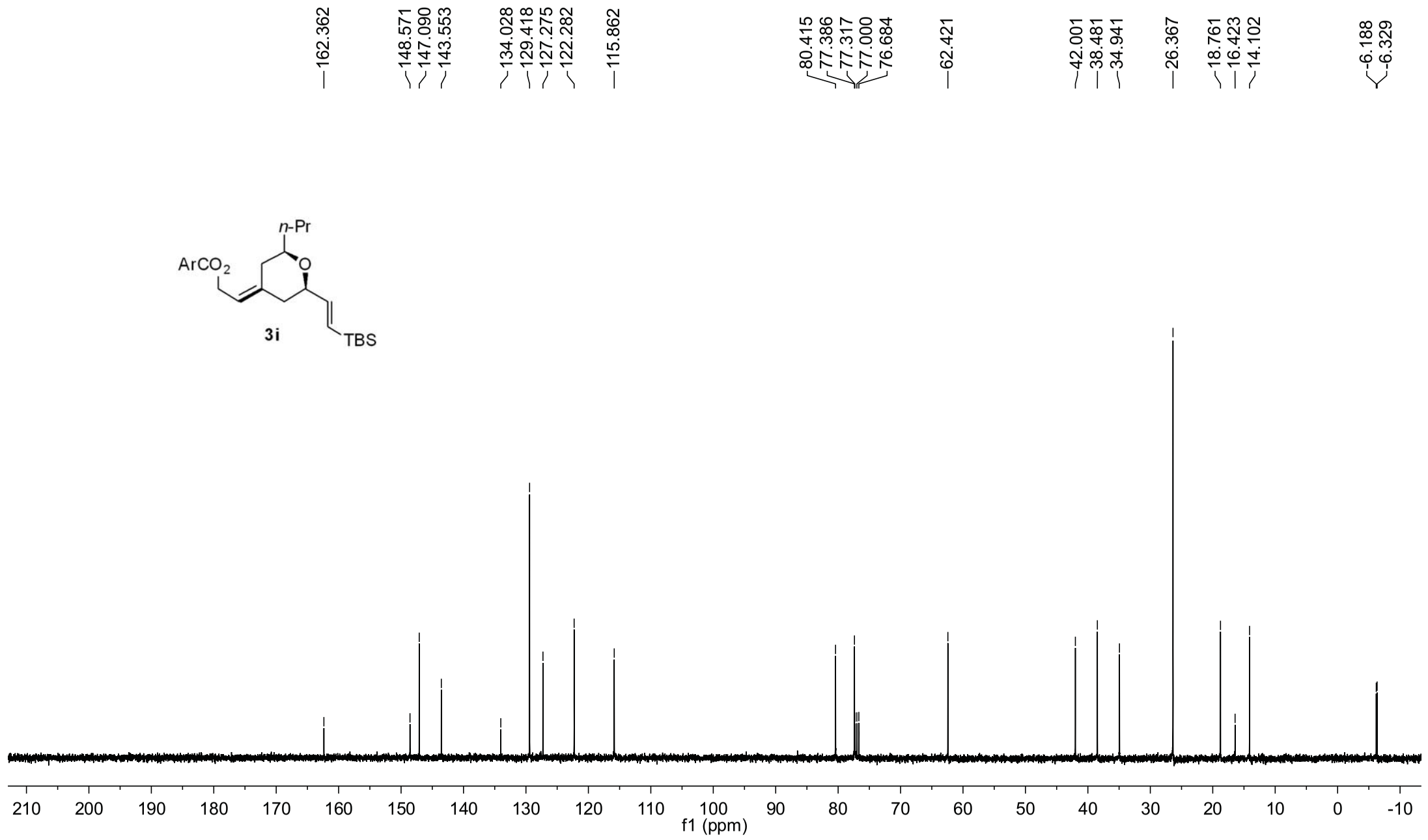
YZP-III-22-B C13 CDCl3 100 MHz



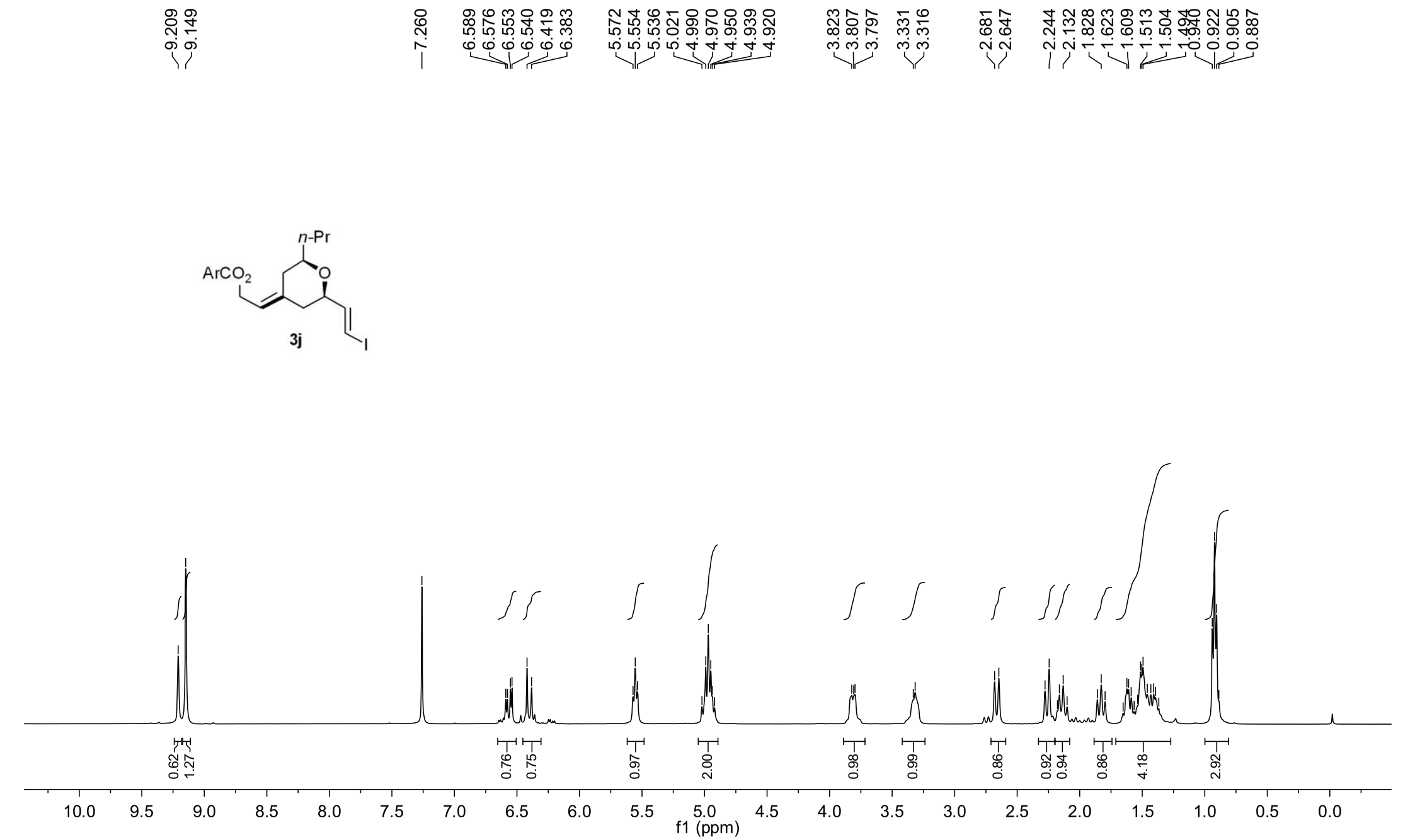
YZP-III-56-B H1 CDCl3 400 MHz



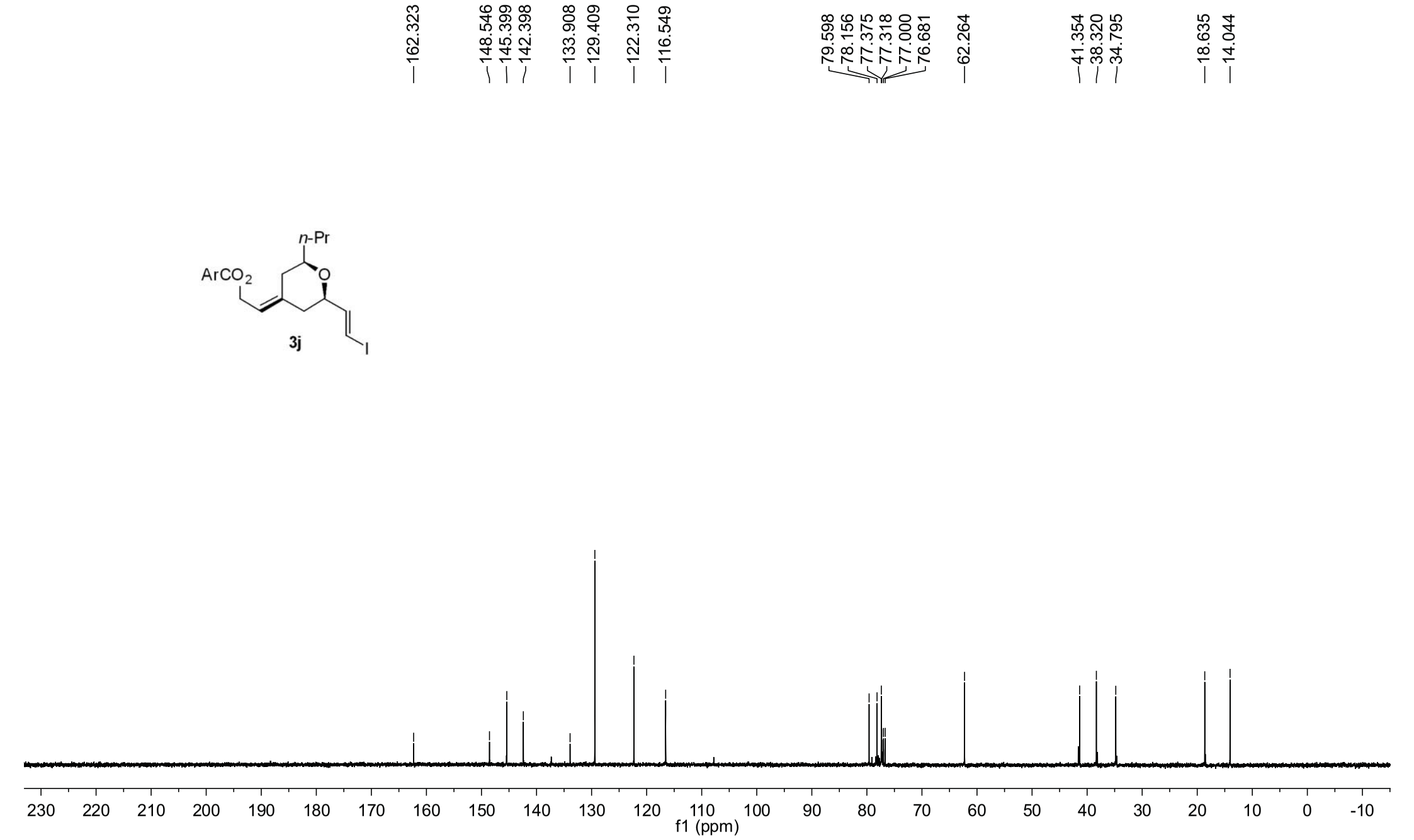
YZP-III-56-B C13 CDCl3 100 MHz



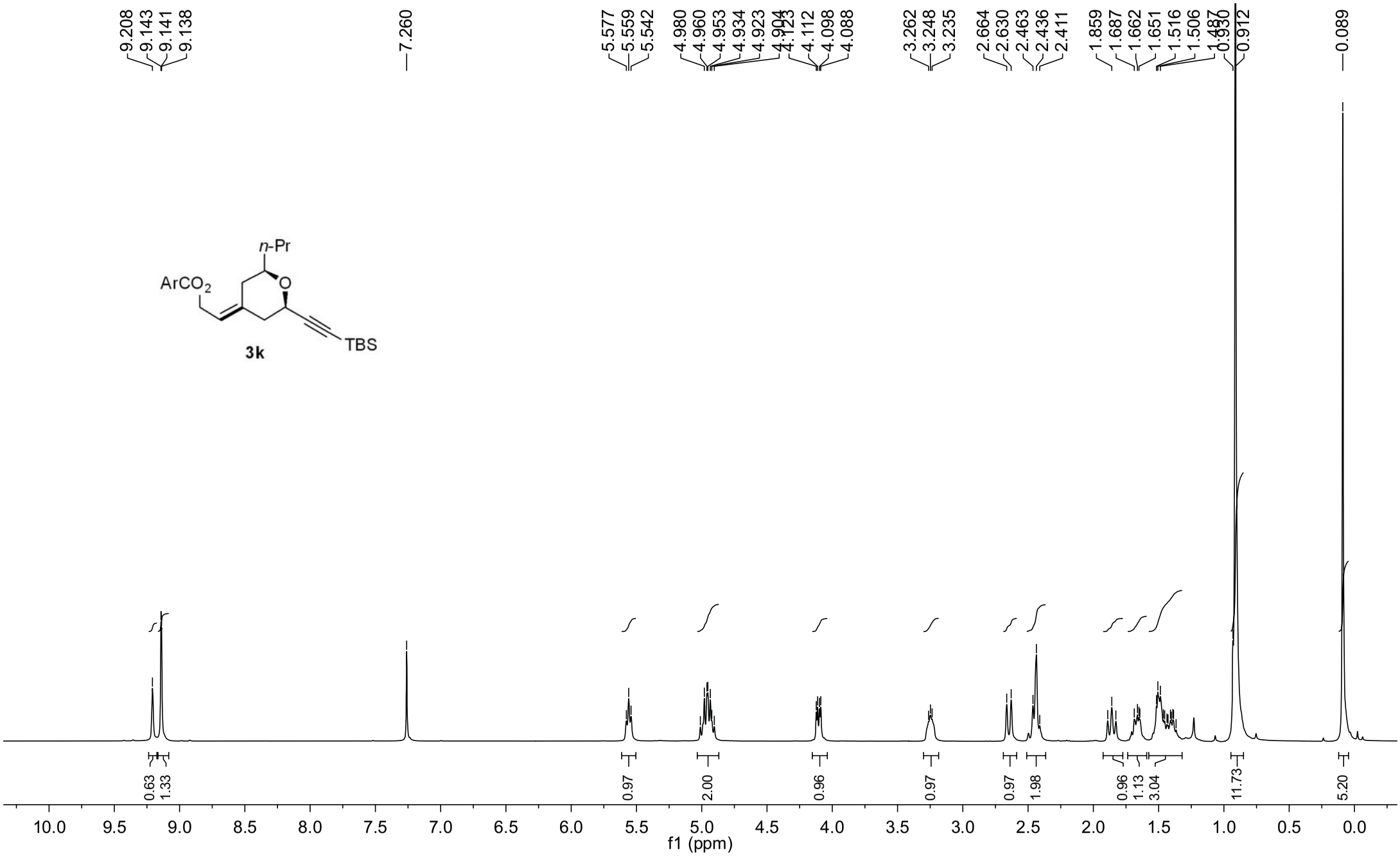
YZP-III-56-A H1 CDCl3 400 MHz



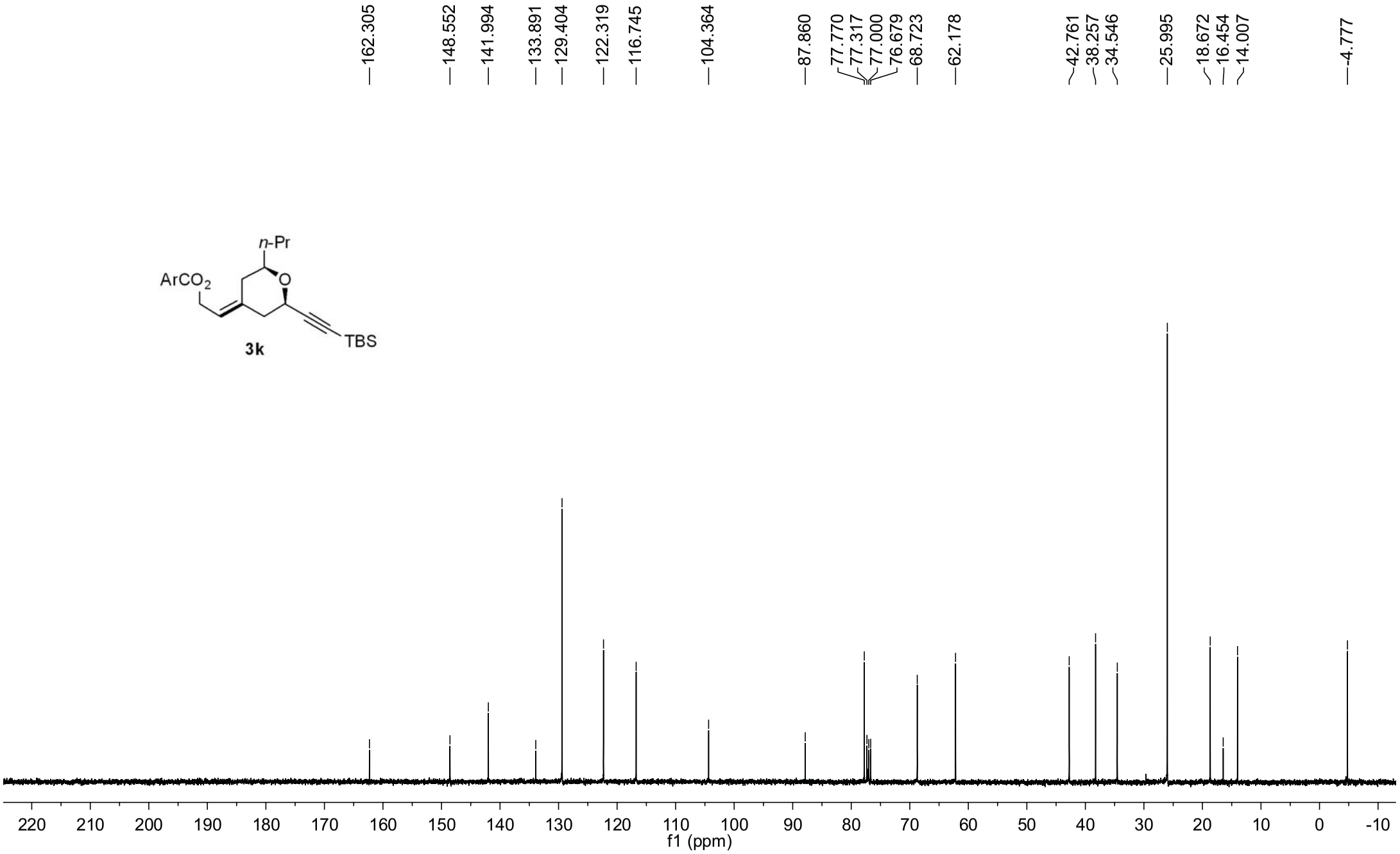
YZP-III-56-A C13 CDCl3 100 MHz



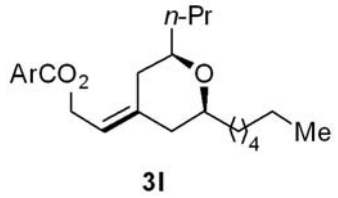
YZP-III-60 H1 CDCl3 400 MHz



YZP-III-60 C13 CDCl3 100 MHz

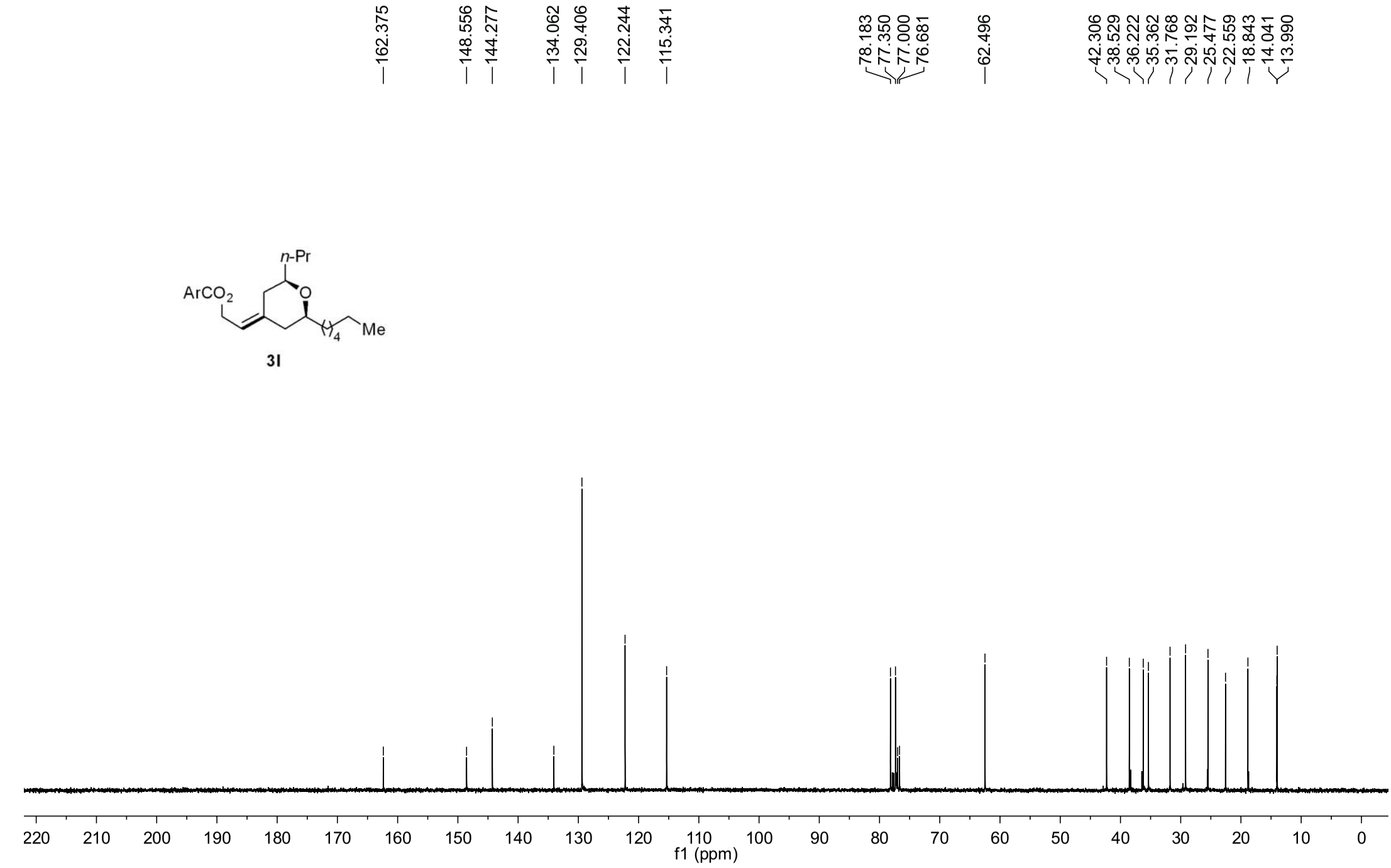


YZP-III-32-B H1 CDCl3 400 MHz



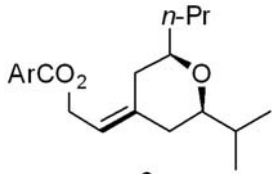
3l

YZP-III-32-B C13 CDCl3 100 MHz

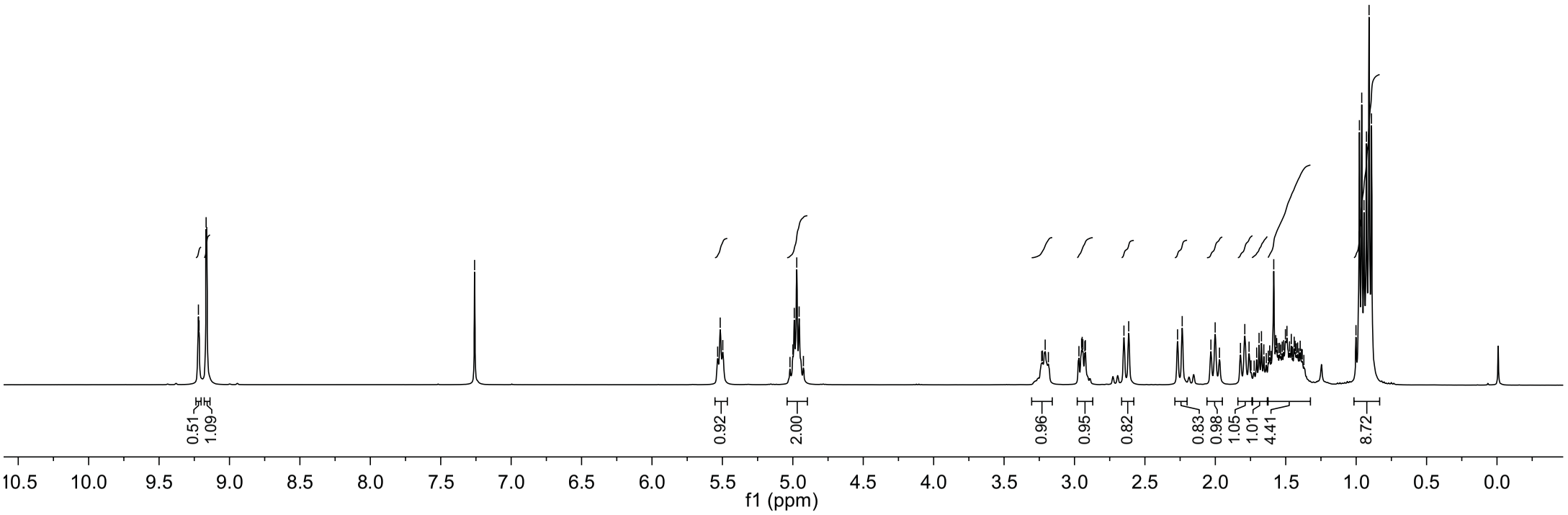


YZP-III-28 H1 CDCl3 400 MHz

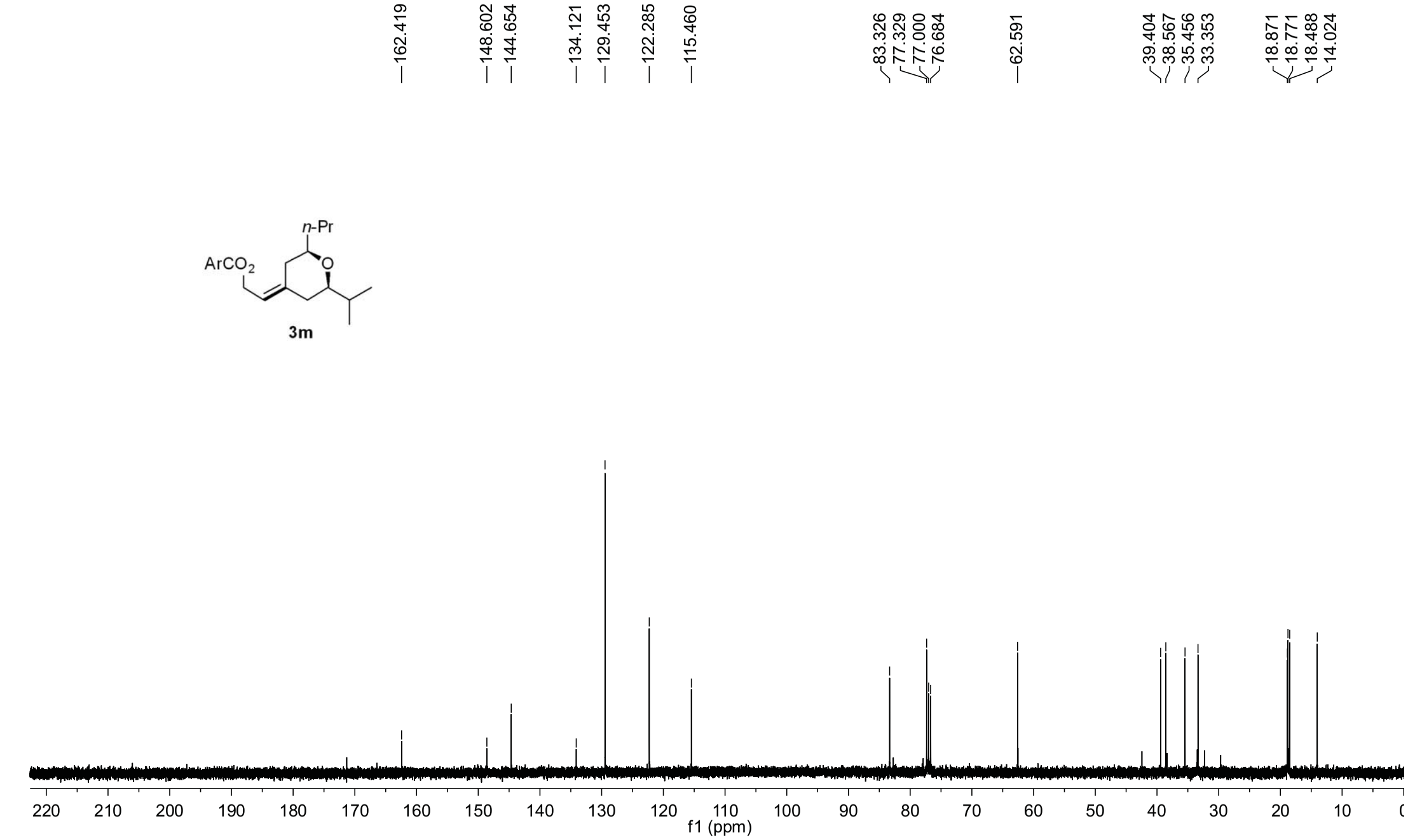
9.221 9.216 9.166 9.161 7.260 5.534 5.516 5.497 4.999 4.990 4.972 4.955 4.925 3.233 3.228 3.208 3.185 2.968 2.950 2.945 2.940 2.927 2.923 2.649 2.615 2.268 2.235 2.031 2.001 1.971 1.822 1.791 1.760 1.707 1.690 1.673 1.656 1.638 1.624 1.614 1.604 1.585 1.571 1.564 1.555 1.544 1.536 1.525 1.515 1.502 1.492 1.473 1.461 1.450 1.440 1.433 1.424 1.416 1.407 1.397 1.389 1.383 1.371 1.001 0.977 0.960 0.945 0.927 0.908 0.891



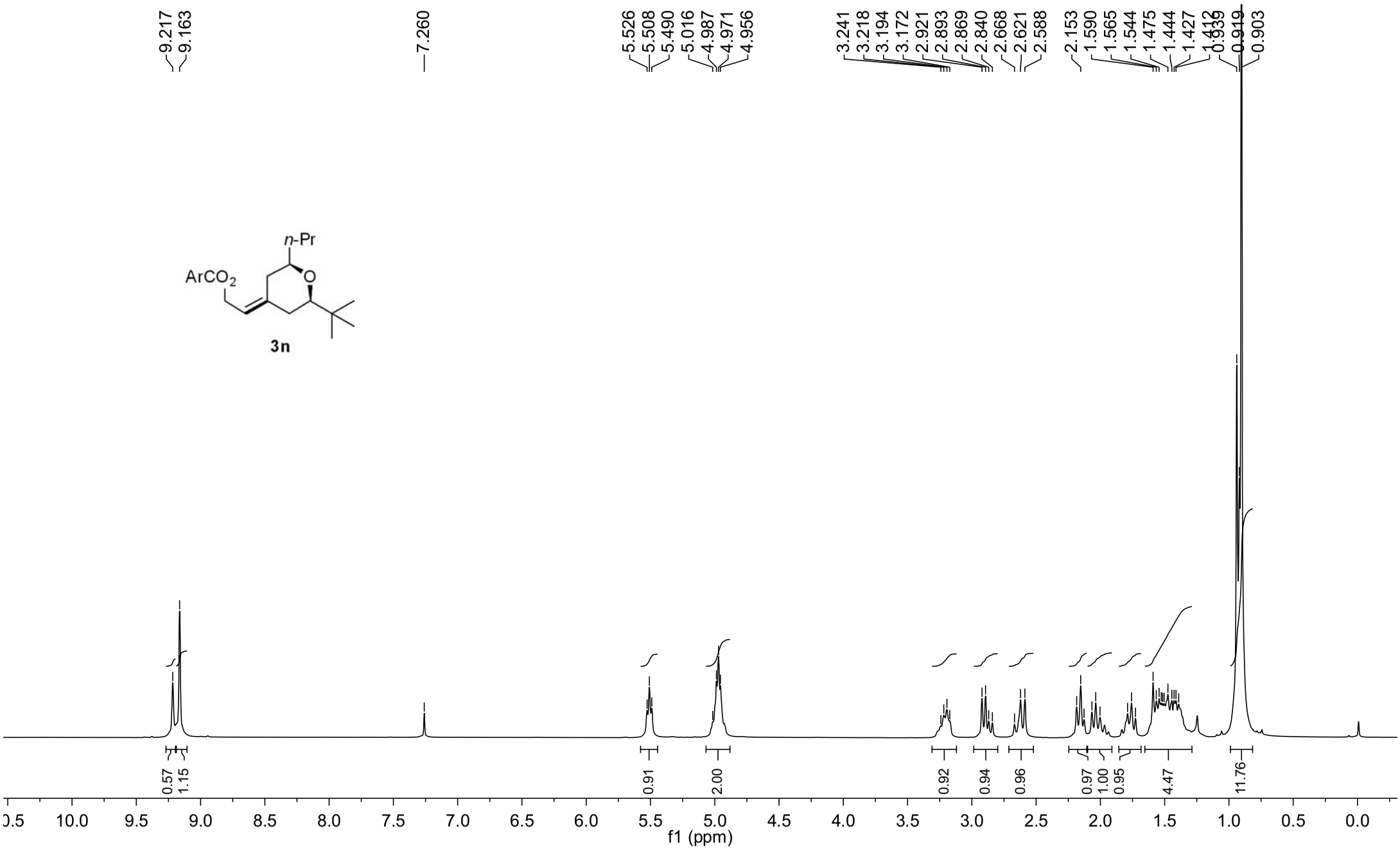
3m



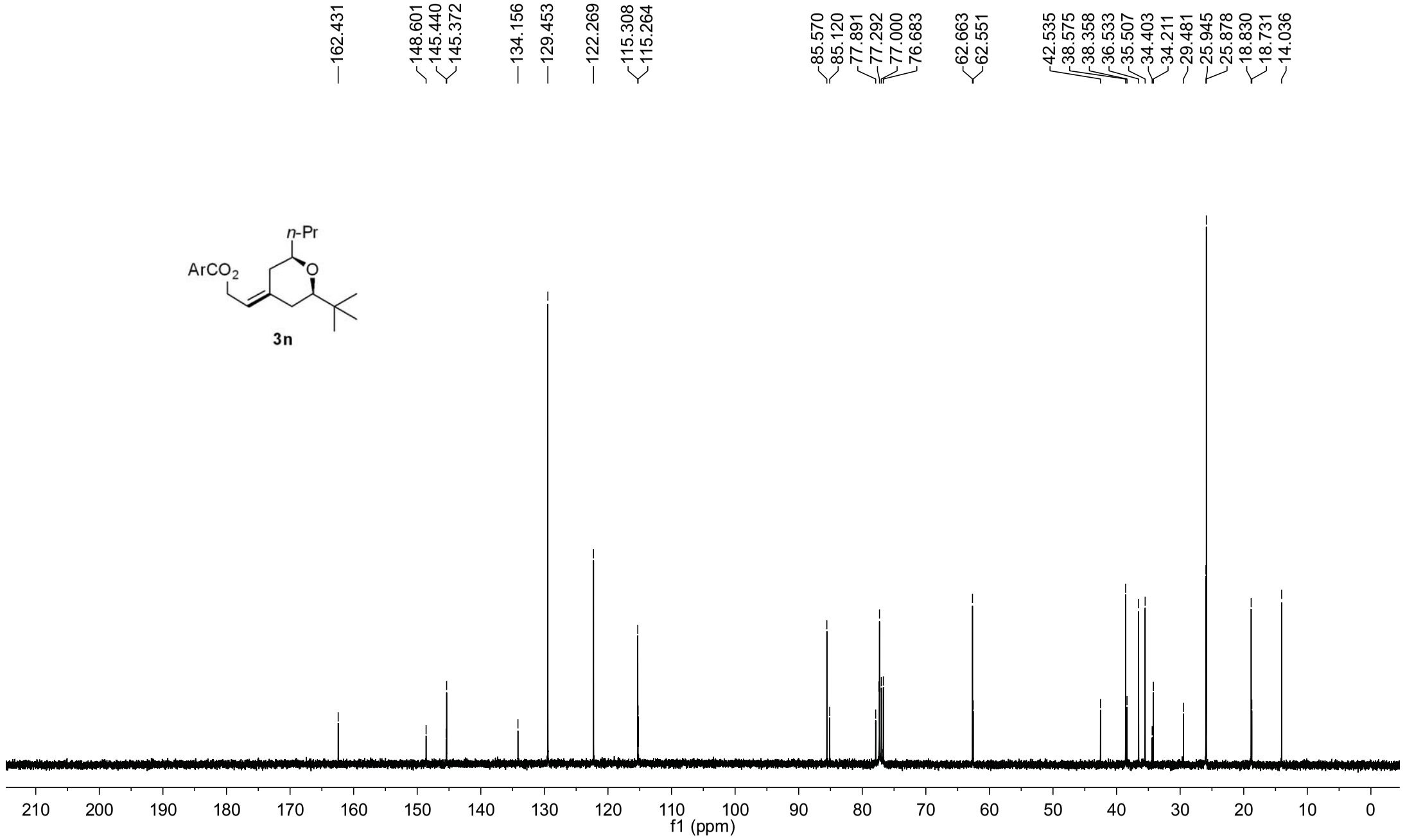
YZP-III-19-C CDCl3 C13 100 MHz



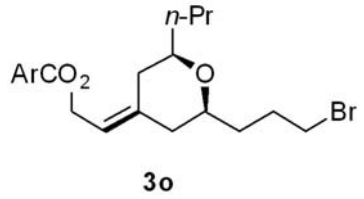
YZP-IV-23-a H1 CDCl3 400 MHz



YZP-IV-23-a C13 CDCl3 100 MHz

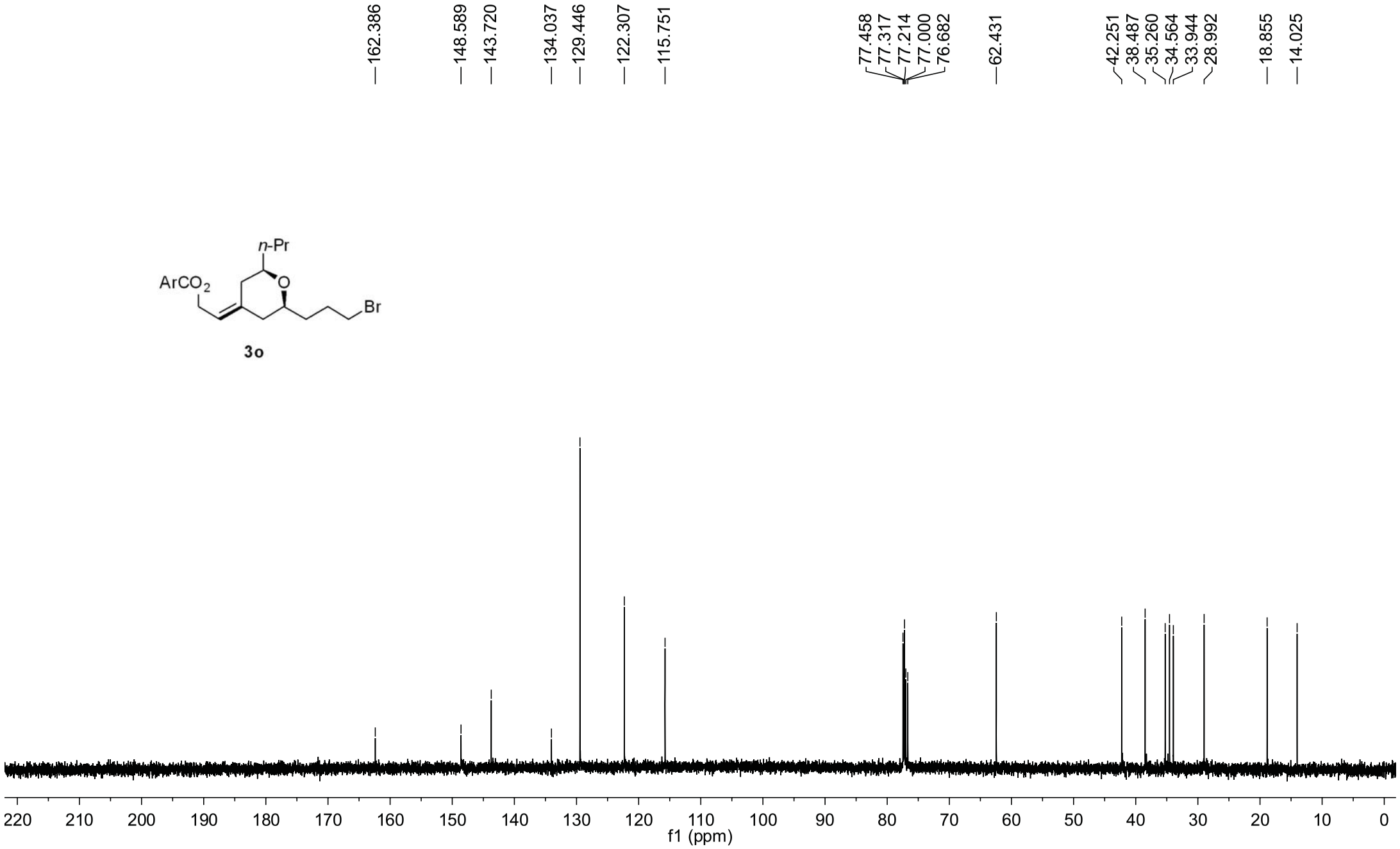


YZP-III-50 H1 CDCl3 400 MHz

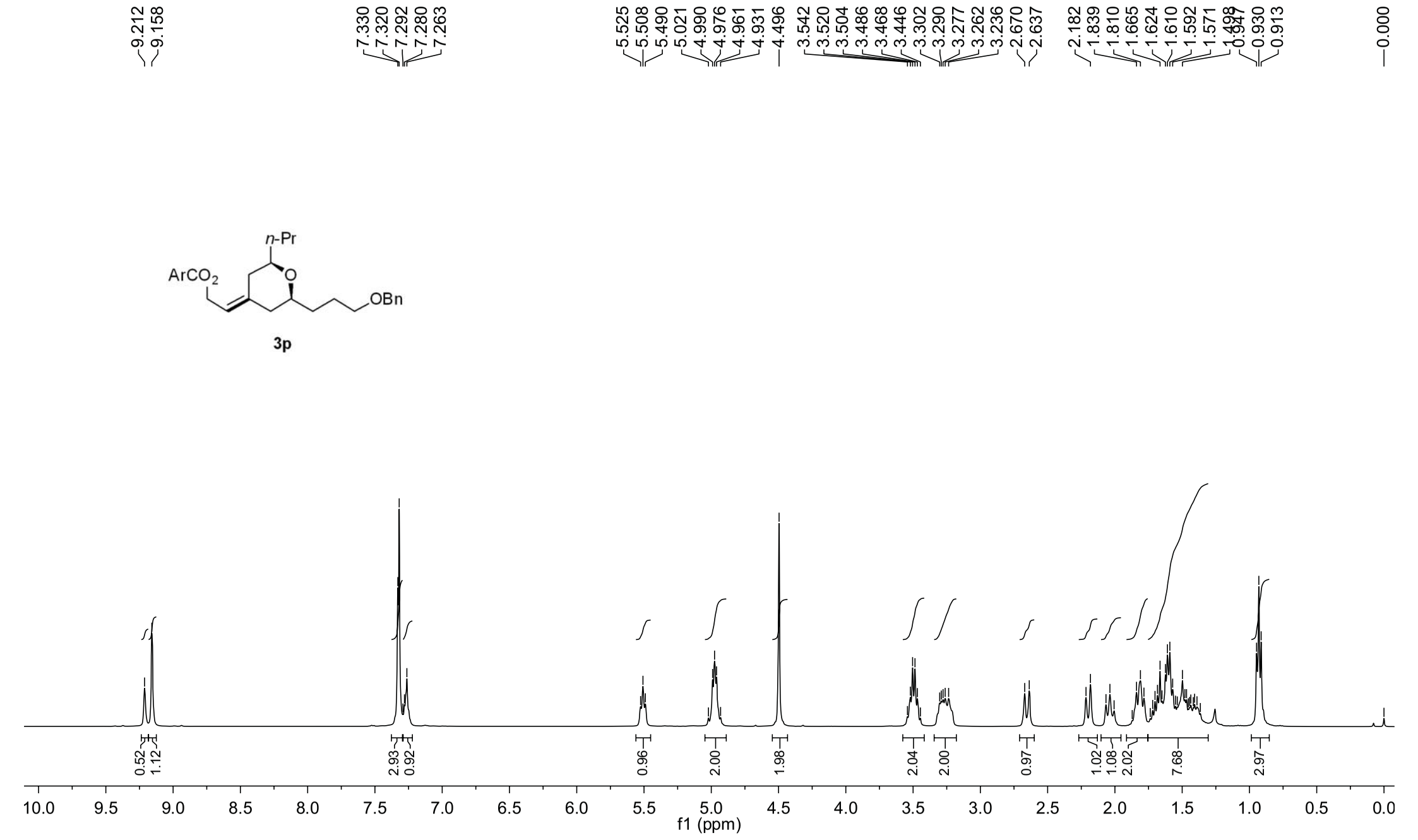


3o

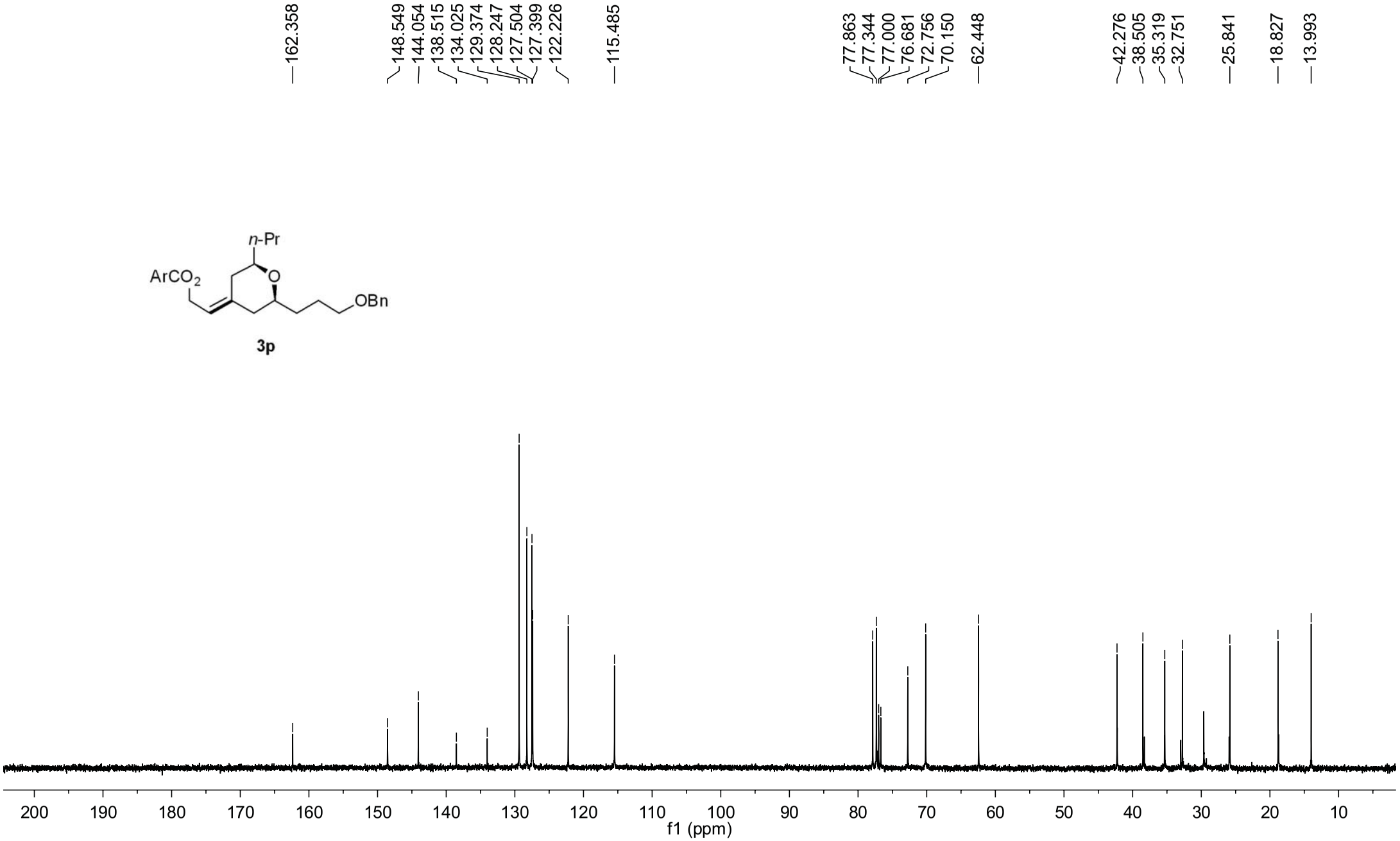
YZP-III-50 C13 CDCl3 100 MHz



HYY-I-87 H1 CDCl3 400 MHz

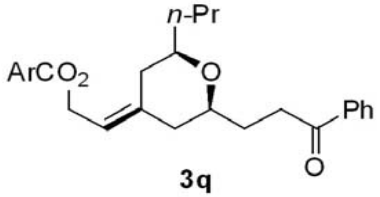


HYY-I-57-1 C13 CDCl3 100 MHz

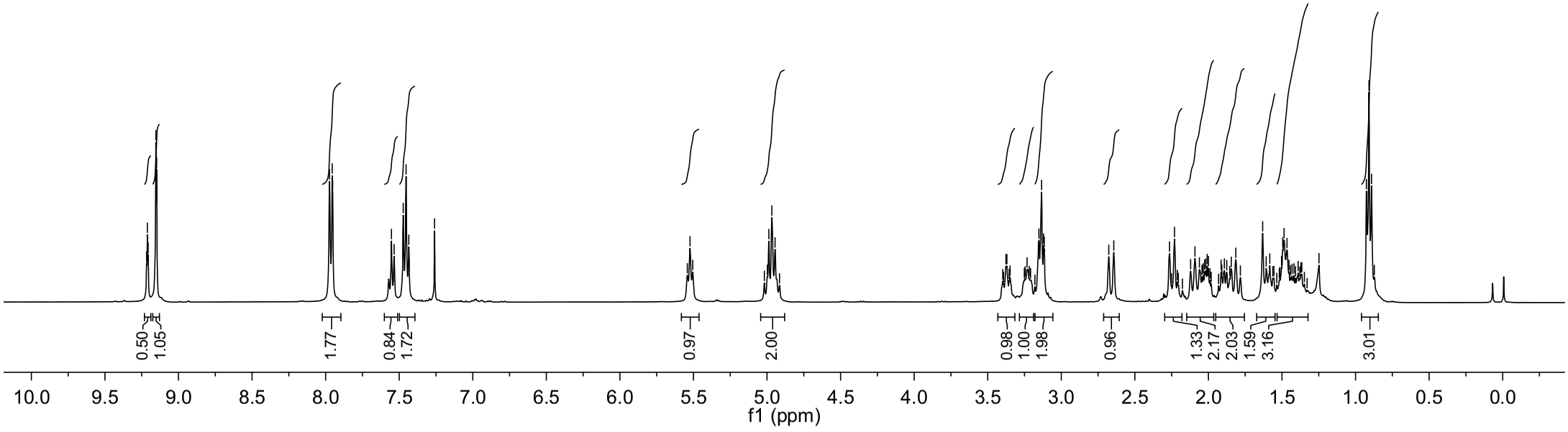


HYY-I-57-2 H1 CDCl3 400 MHz

9.217 9.212 9.206 9.154 9.149 7.973 7.955 7.952 7.553 7.535 7.473 7.453 7.435 7.260 5.542 5.523 5.505 4.998 4.988 4.967 4.945 3.376 3.370 3.348 3.233 3.152 3.134 3.120 3.116 2.677 2.643 2.264 2.230 2.121 2.091 2.061 2.044 2.035 2.026 2.018 2.008 2.000 1.914 1.909 1.892 1.875 1.855 1.845 1.814 1.783 1.631 1.607 1.583 1.555 1.503 1.495 1.486 1.466 1.452 1.442 1.431 1.418 1.390 1.371 1.365 1.248 0.926 0.909 0.891 0.872

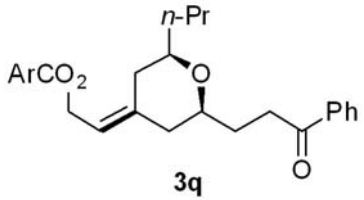


3q

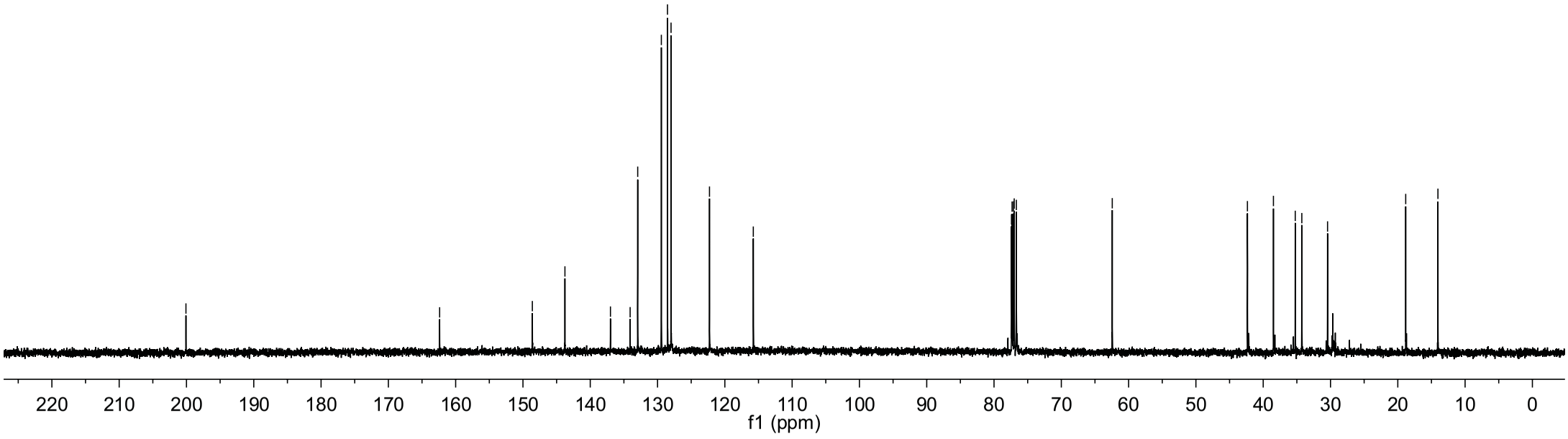


HYY-I-57-2 C13 CDCl3 100 MHz

200.078
162.381
148.605
143.762
136.998
134.074
132.947
129.435
128.522
127.994
122.280
115.771
77.410
77.318
77.107
77.000
76.682
62.431
42.346
38.481
35.240
34.262
30.437
18.824
14.036

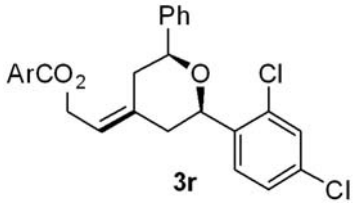


3q

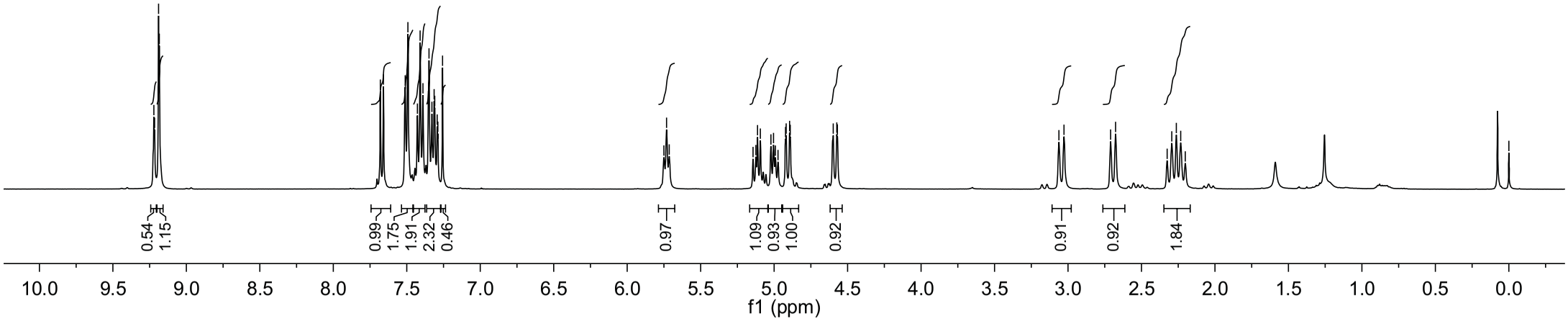


SCZ-7-66III H1 CDCl3 400 MHz

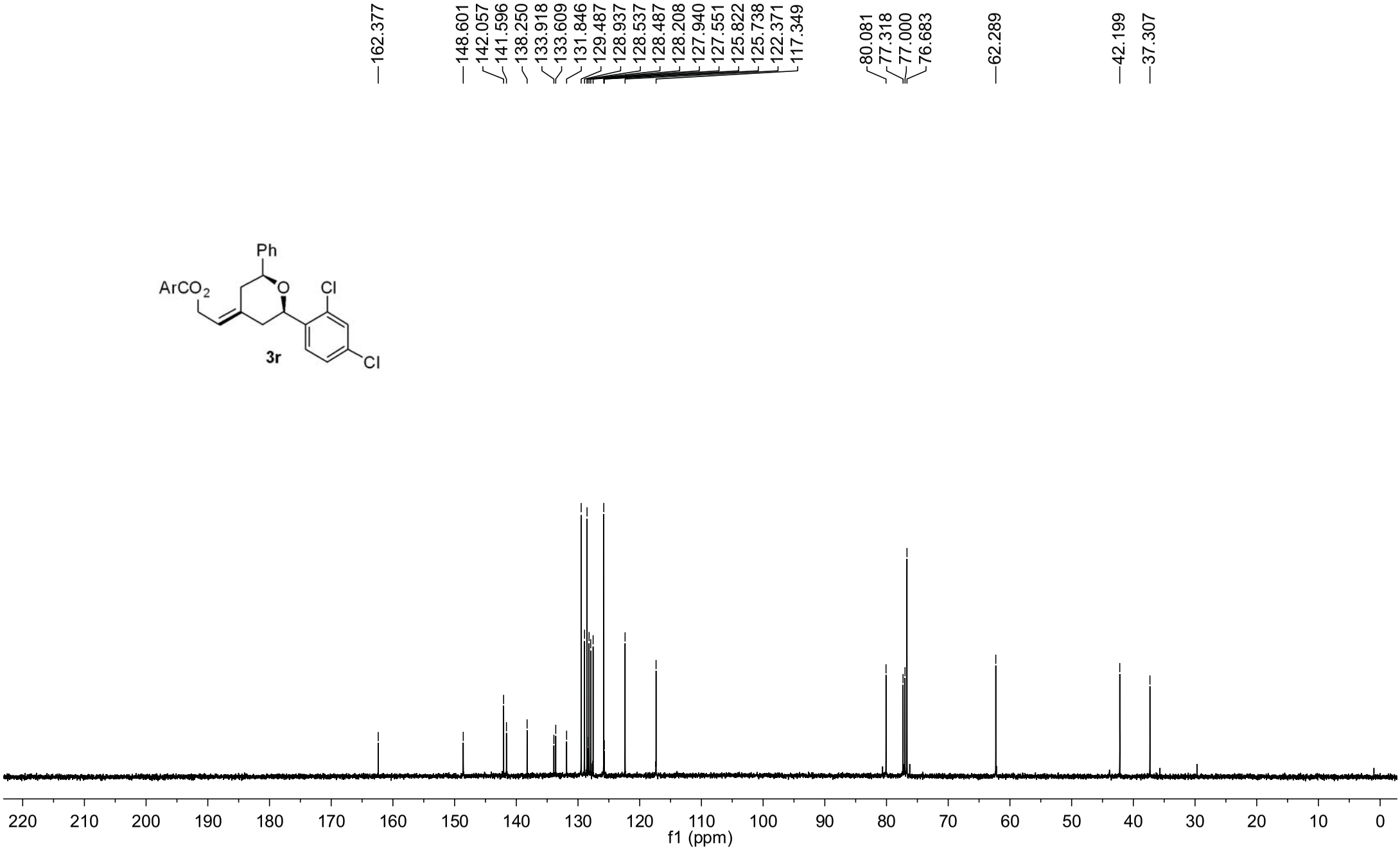
9.221 9.216 9.189 9.184 7.680 7.659 7.511 7.492 7.428 7.409 7.390 7.353 7.349 7.329 7.314 7.310 7.293 7.288 7.256 5.750 5.732 5.714 5.144 5.124 5.113 5.094 5.022 5.004 4.992 4.974 4.922 4.918 4.895 4.890 4.598 4.574 4.569 3.062 3.027 2.710 2.676 2.325 2.294 2.263 2.233 2.202 -0.000



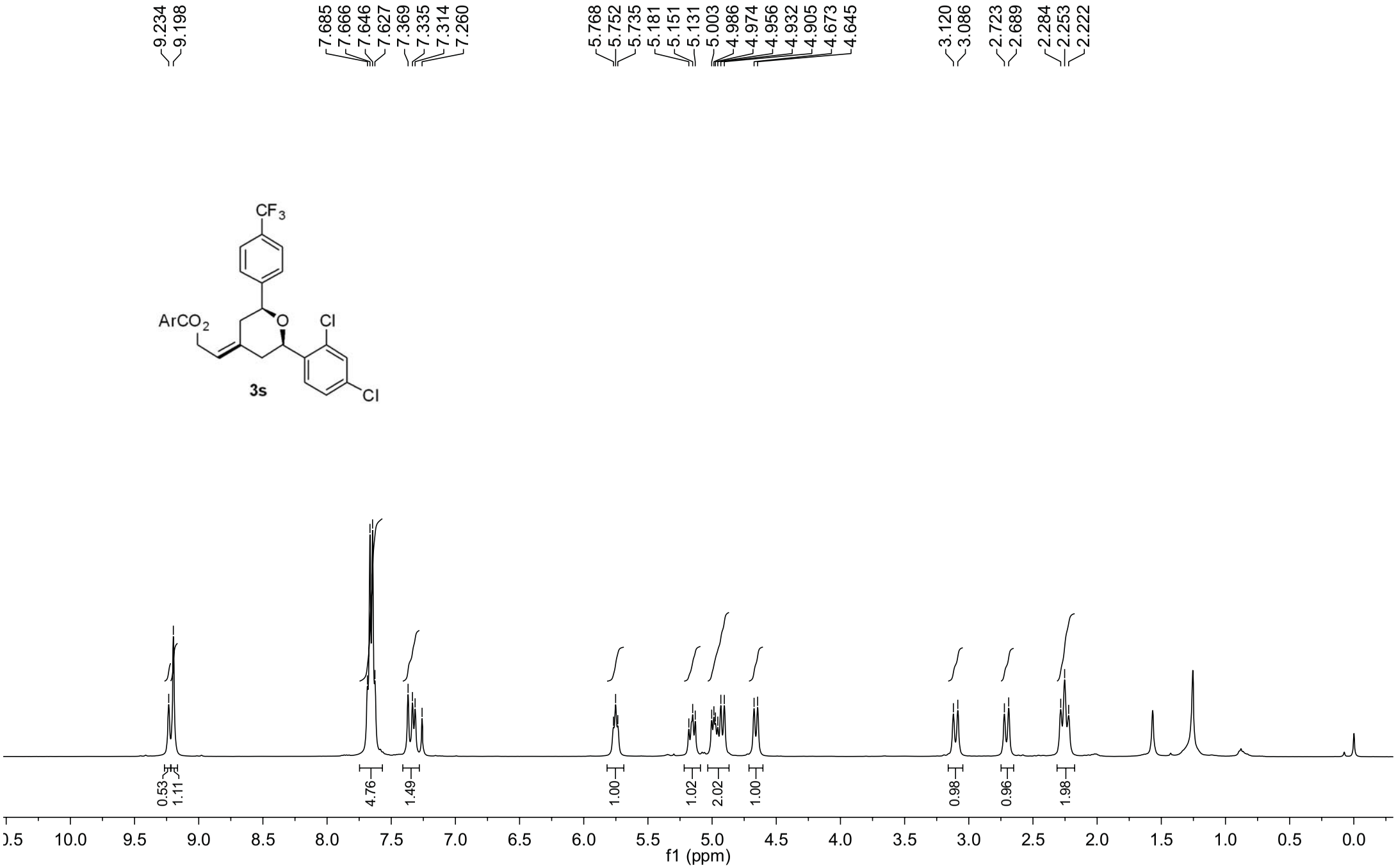
3r



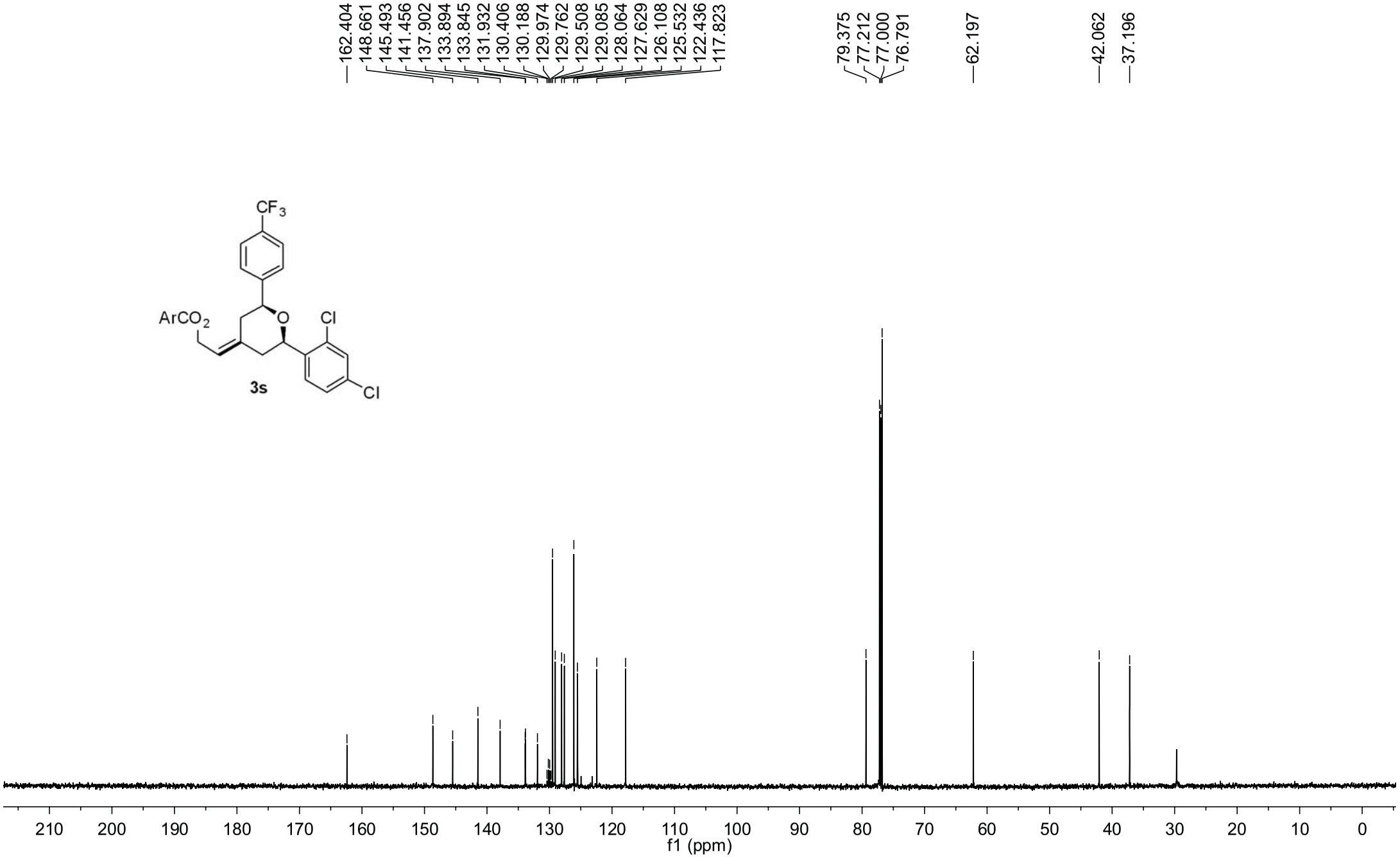
SCZ-7-66III C13 CDCl3 100MHz



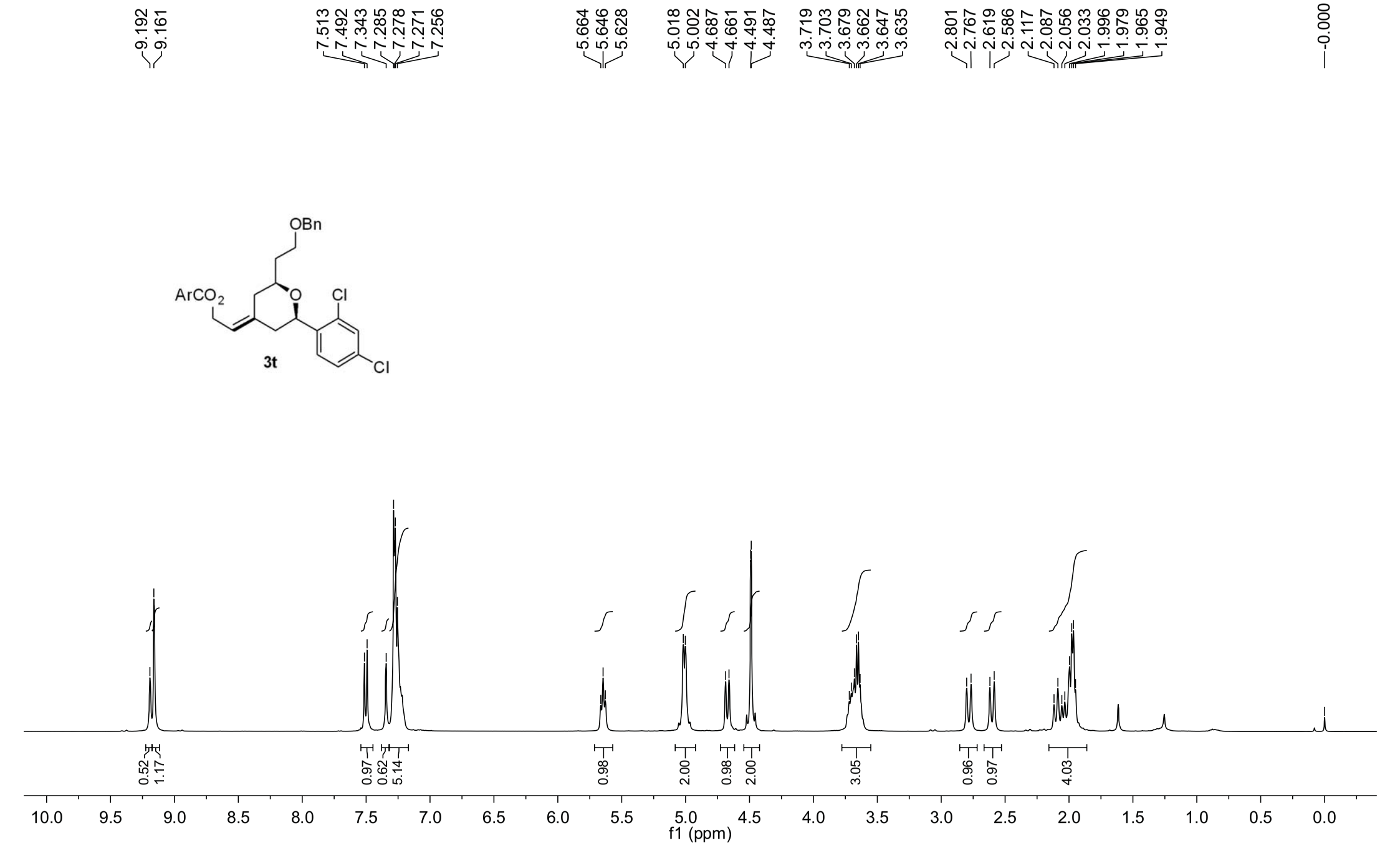
YZP-V-64-5 H1 CDCl3 400 MHz



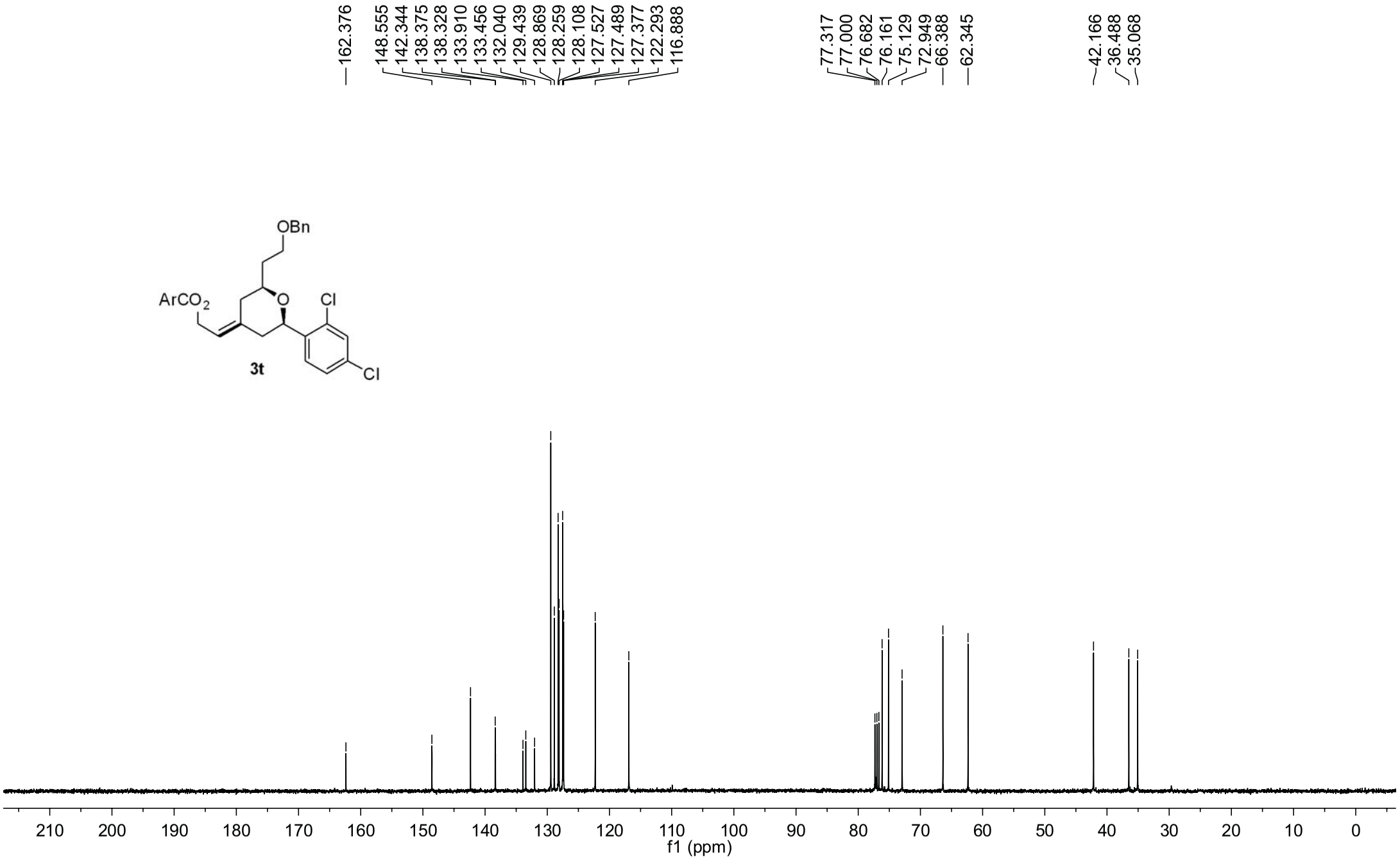
YZP-V-64-5 C13 CDCl3 150 MHz



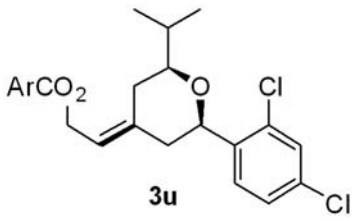
YZP-IV-82-2 H1 CDCl3 400 MHz



YZP-IV-82-2 C13 CDCl3 100 MHz

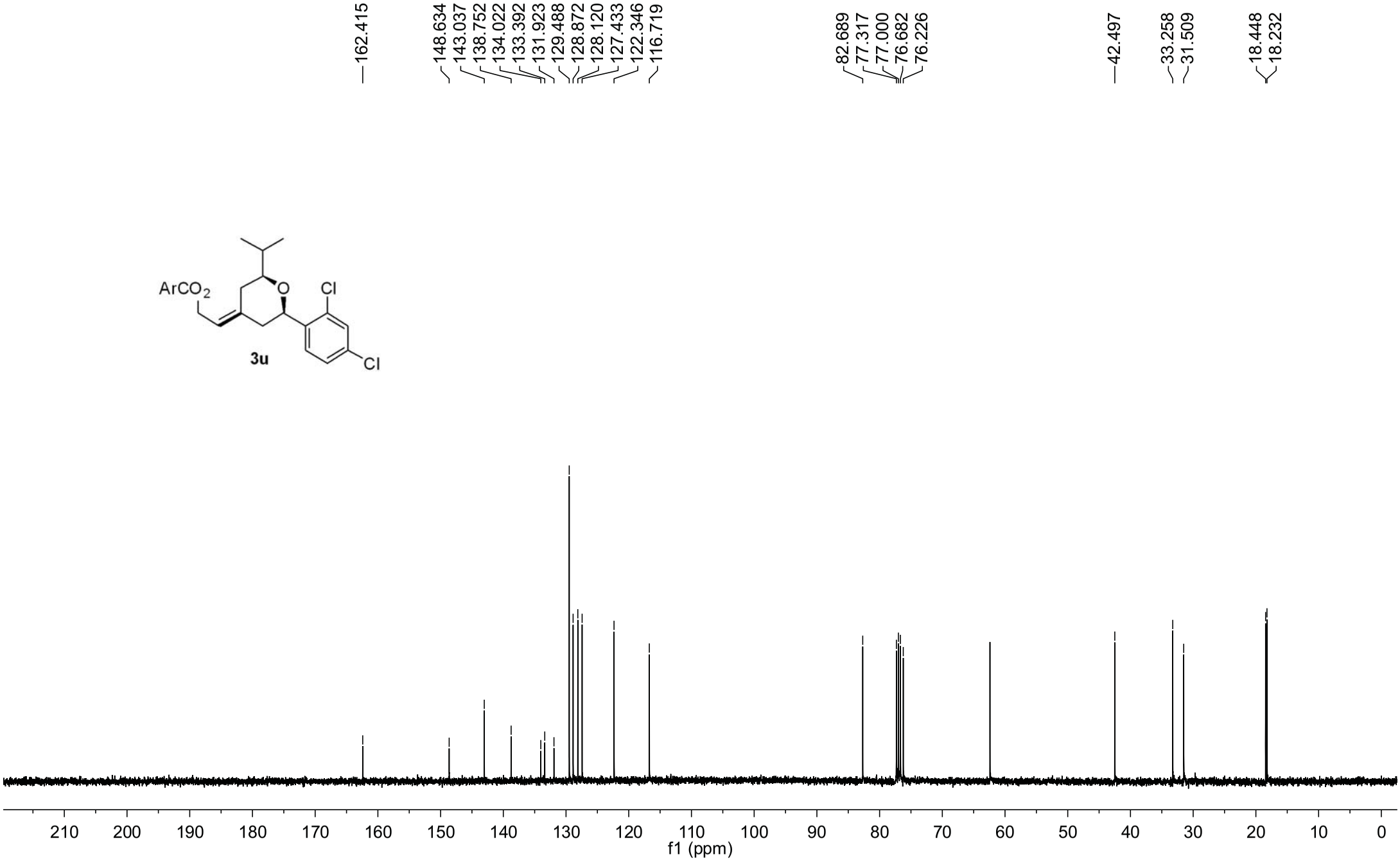


YZP-IV-75-b H1 CDCl3 400 MHz



3u

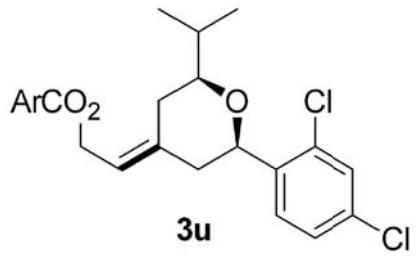
YZP-IV-75-6 C13 CDCl3 100 MHz



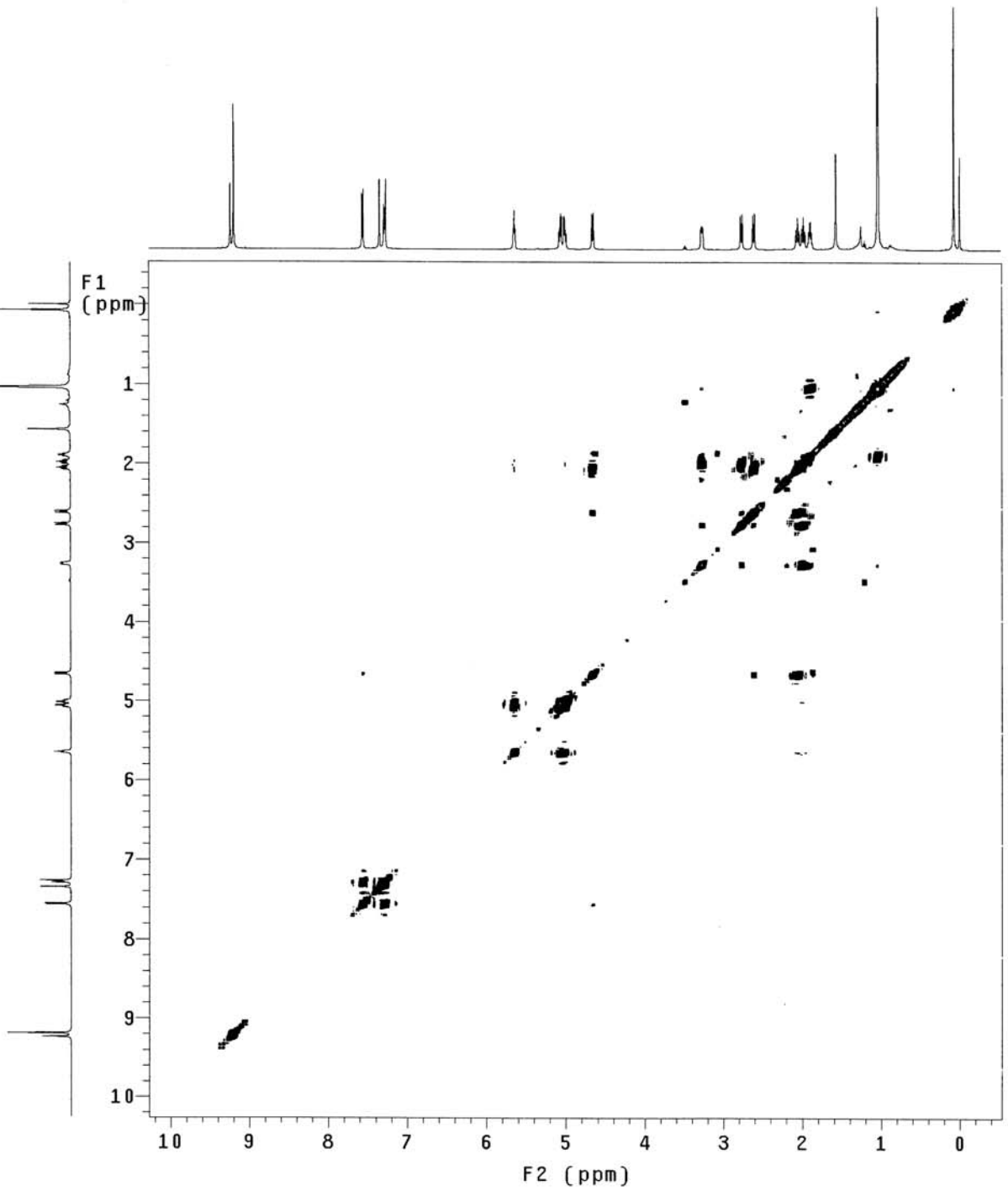
YZP-IV-75-b gCOSY CDCl3 2015-6-30

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20140603_05

Pulse Sequence: gCOSY



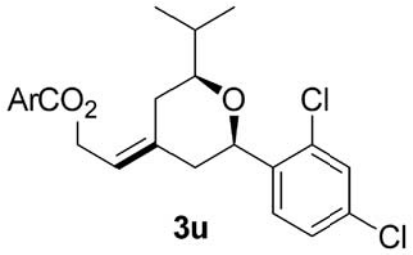
3u



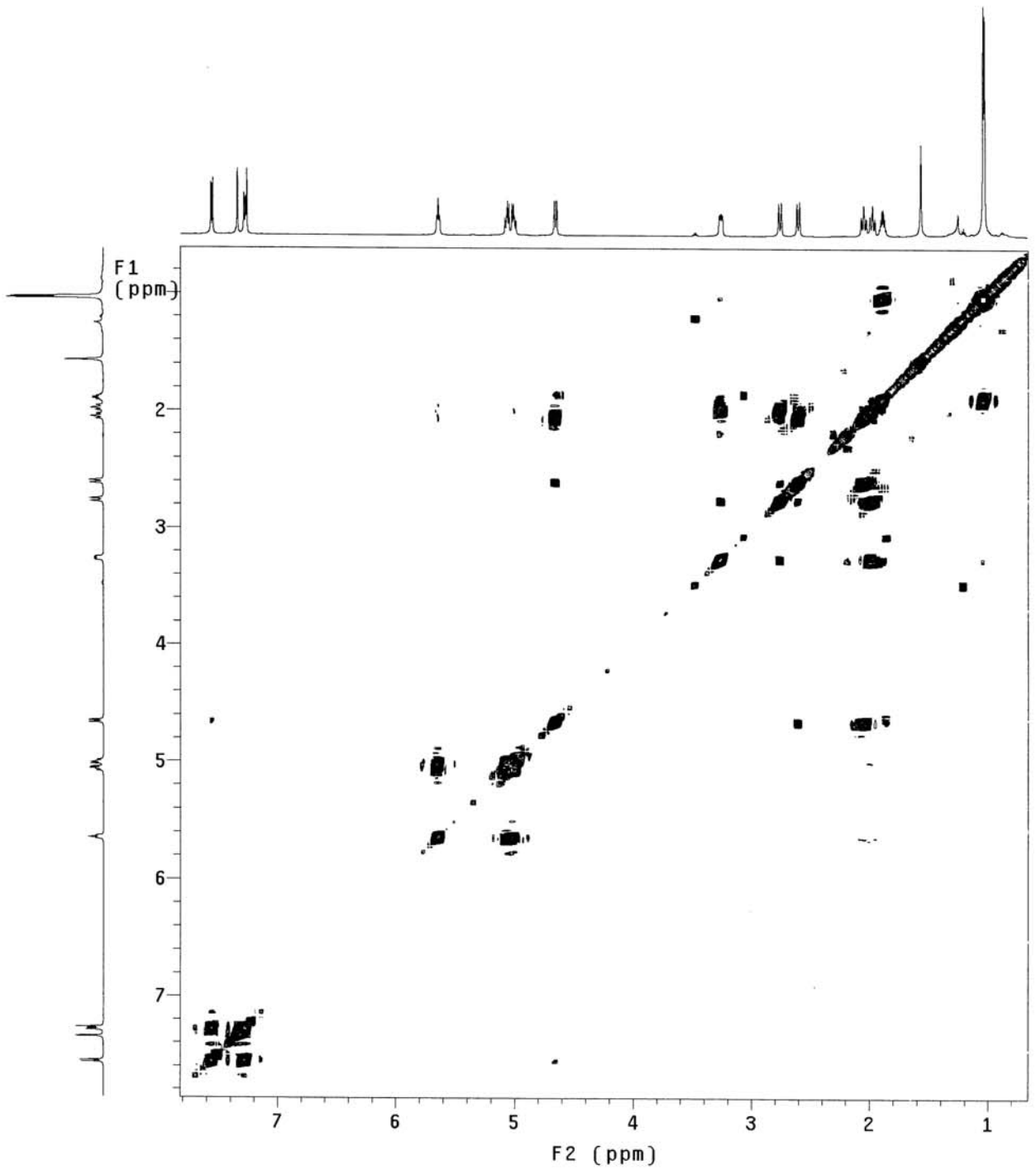
YZP-IV-75-b gCOSY CDCl3 2015-6-30

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20140603_05

Pulse Sequence: gCOSY



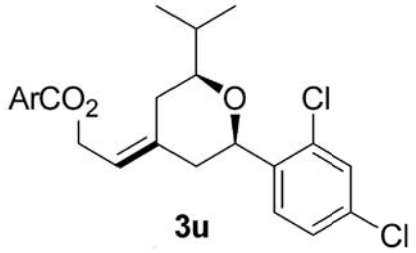
3u



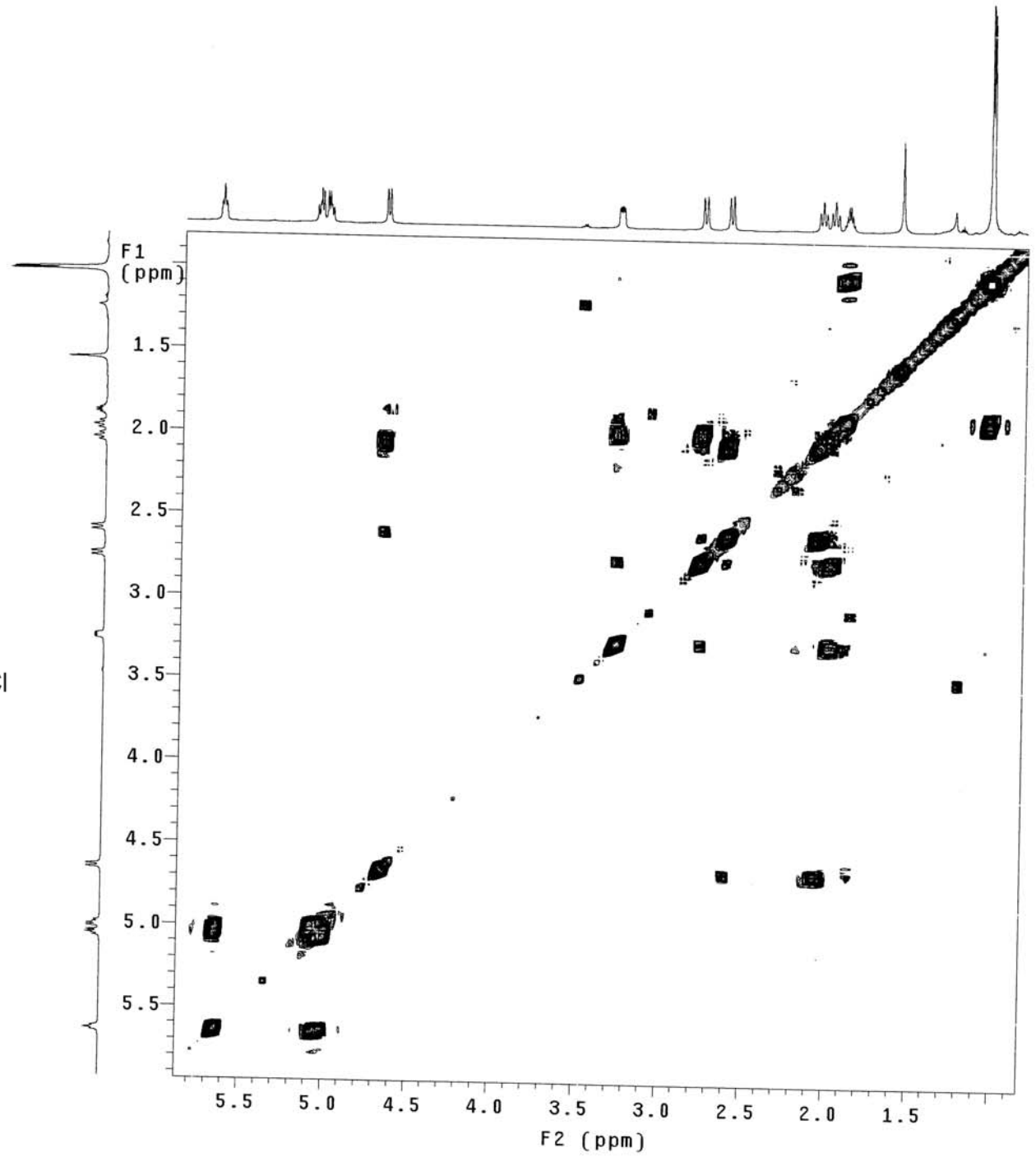
YZP-IV-75-b gCOSY CDCl3 2015-6-30

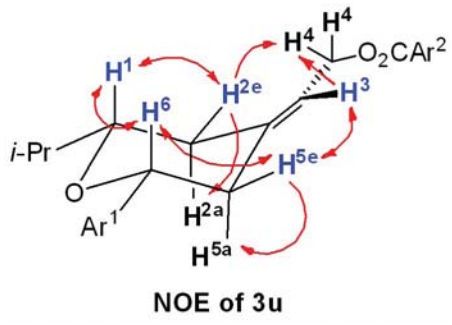
Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20140603_05

Pulse Sequence: gCOSY



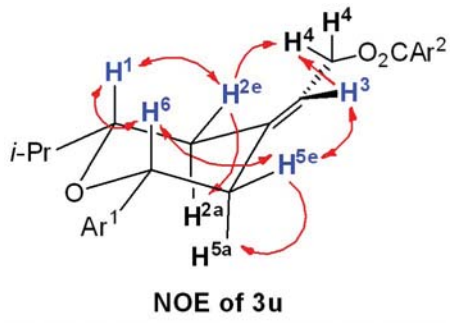
3u




H4
H4
O2CAr2
H1
H2e
H3
H6
i-Pr
H5e
O
Ar1
H2a
H5a

NOE of 3u

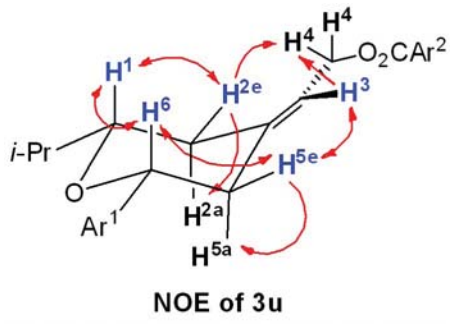
5.645
5.633
4.665
4.650
2.072
2.053
2.032
H3
H6
H5e
H5a
4.95
2.39
100.00
15.64
f1 (ppm)


H4
H4
O2CAr2
H1
H2e
H3
H6
i-Pr
H5e
O
Ar1
H2a
H5a

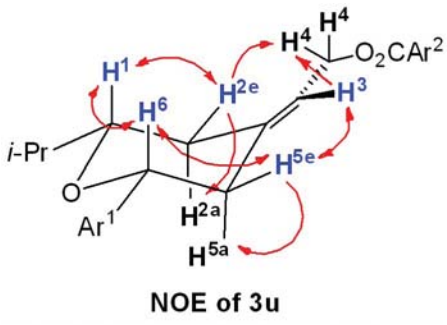
NOE of 3u

5.082
5.069
5.061
5.049
5.022
5.010
4.989
3.277
3.268
3.262
3.252
2.000
1.979
1.959
1.041
1.029
H4
H1
H2e
H2a
6.62
3.16
100.00
19.92
2.50
f1 (ppm)

90%con

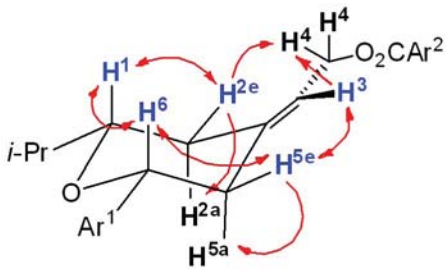


NOE of 3u

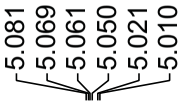

H4
H4
O2CAr2
H1
H2e
H3
H6
i-Pr
H5e
O
Ar1
H2a
H5a

NOE of 3u

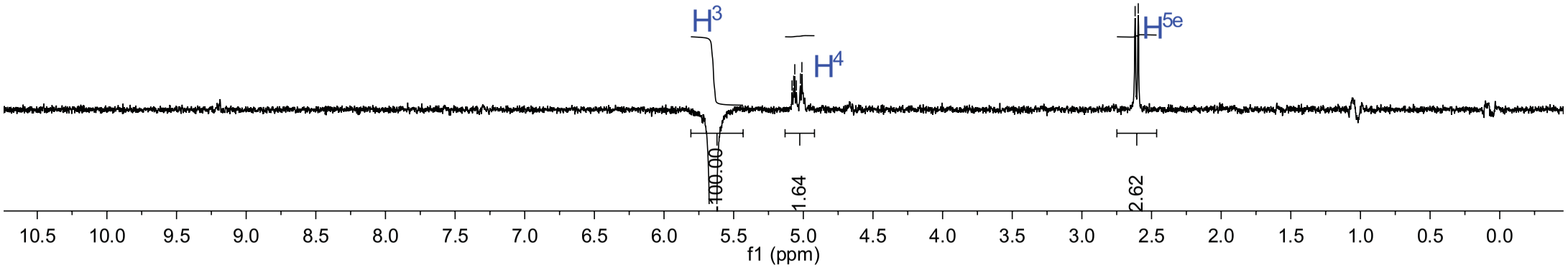
3.277
3.268
3.261
3.252
2.617
2.595
H6
H1
H5e
100.00
3.29
1.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H4
H4
O2CAr2
H1
H2e
H3
H6
i-Pr
H5e
O
Ar1
H2a
H5a

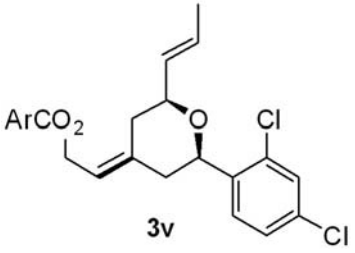
NOE of 3u


5.081
5.069
5.061
5.050
5.021
5.010


2.618
2.595

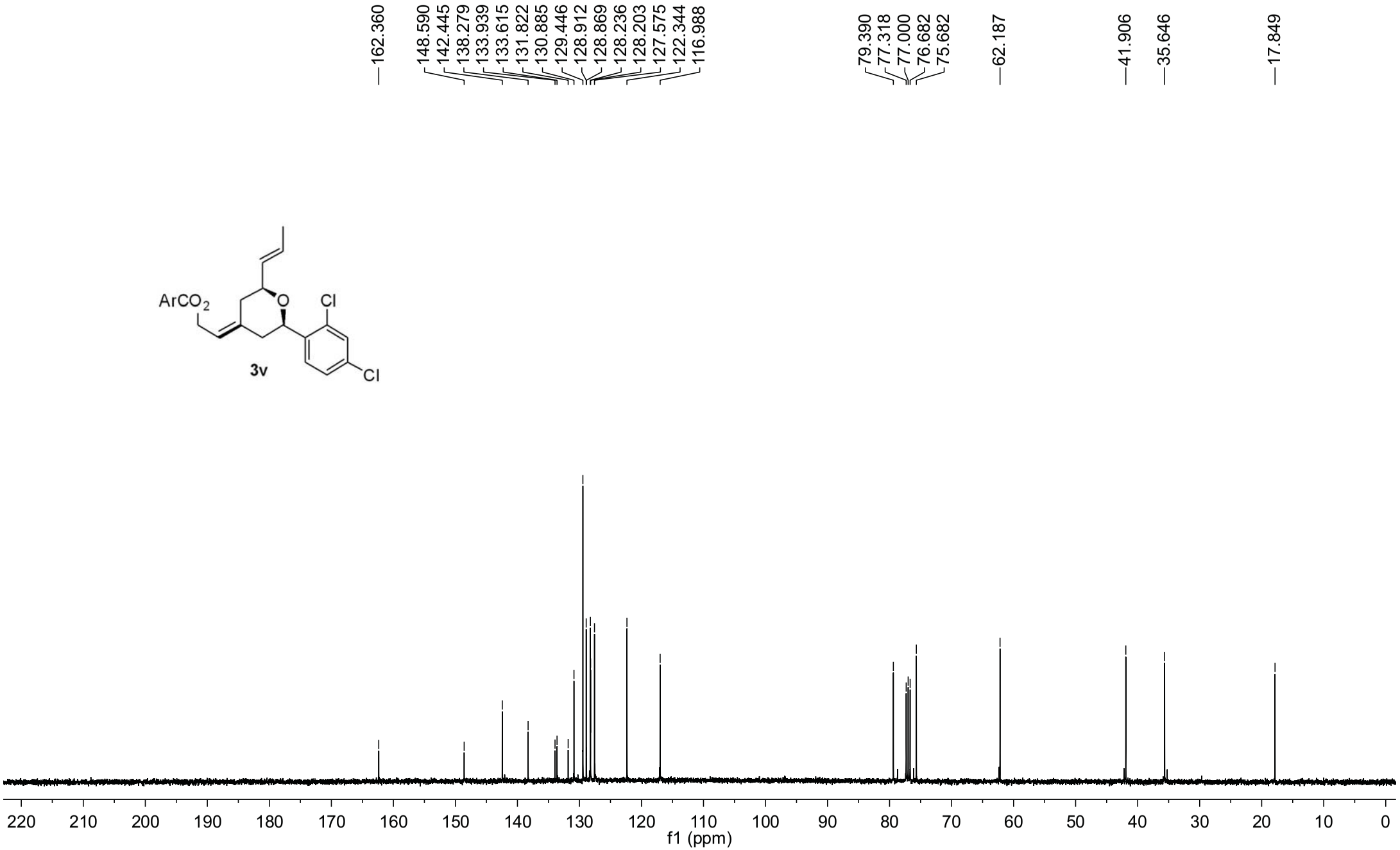

H3
H4
H5e
100.00
1.64
2.62
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

YZP-IV-82-4 H1 CDCl3 400 MHz

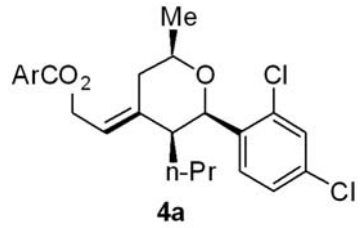


3v

YZP-IV-82-4 C13 CDCl3 100 MHz

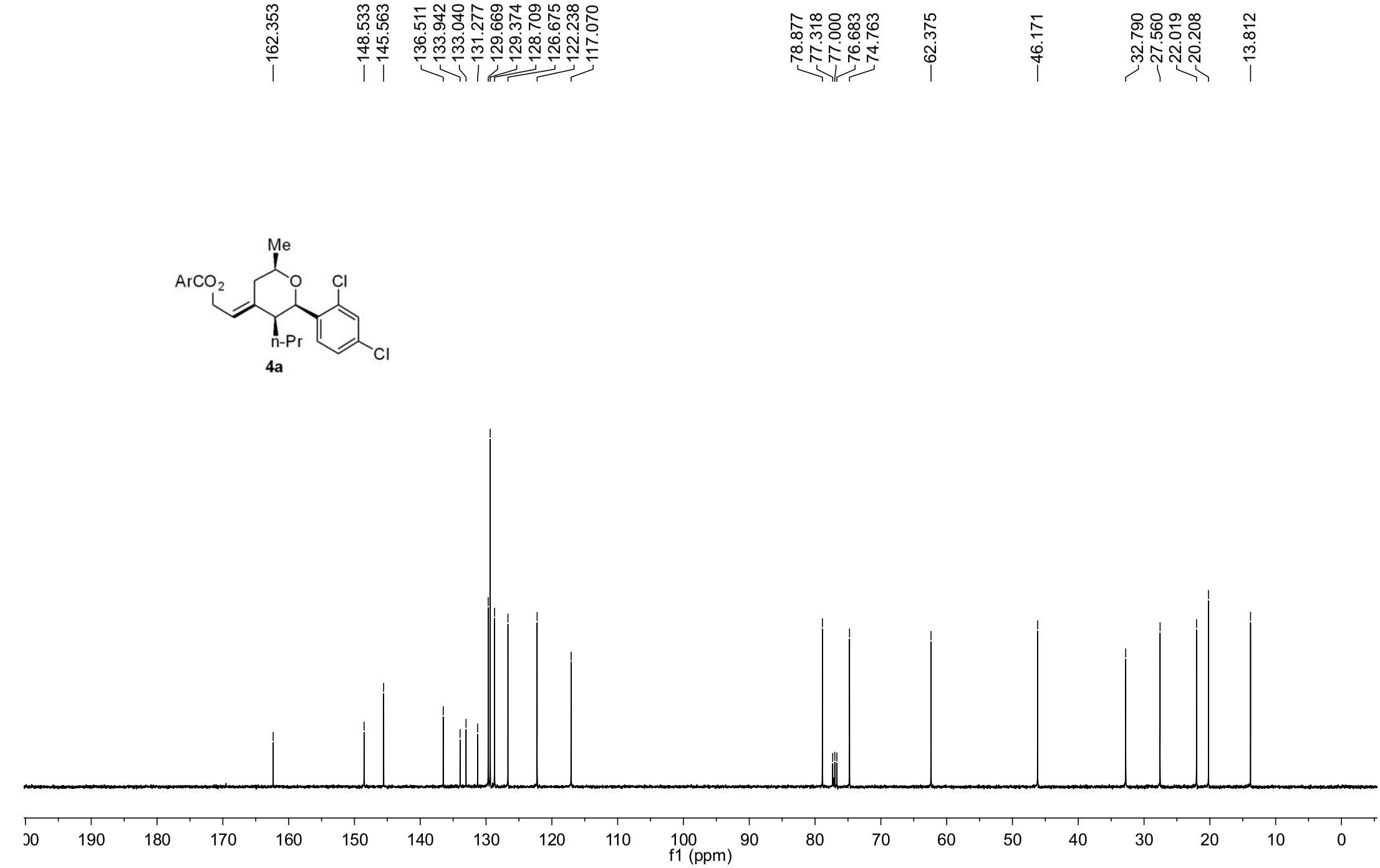


YZP-IV-47-II H1 CDCl3 400 MHz

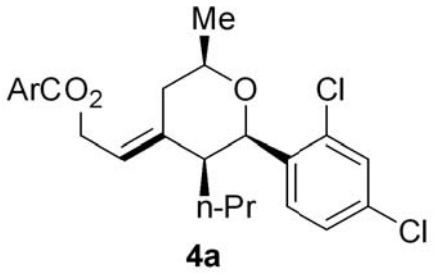


4a

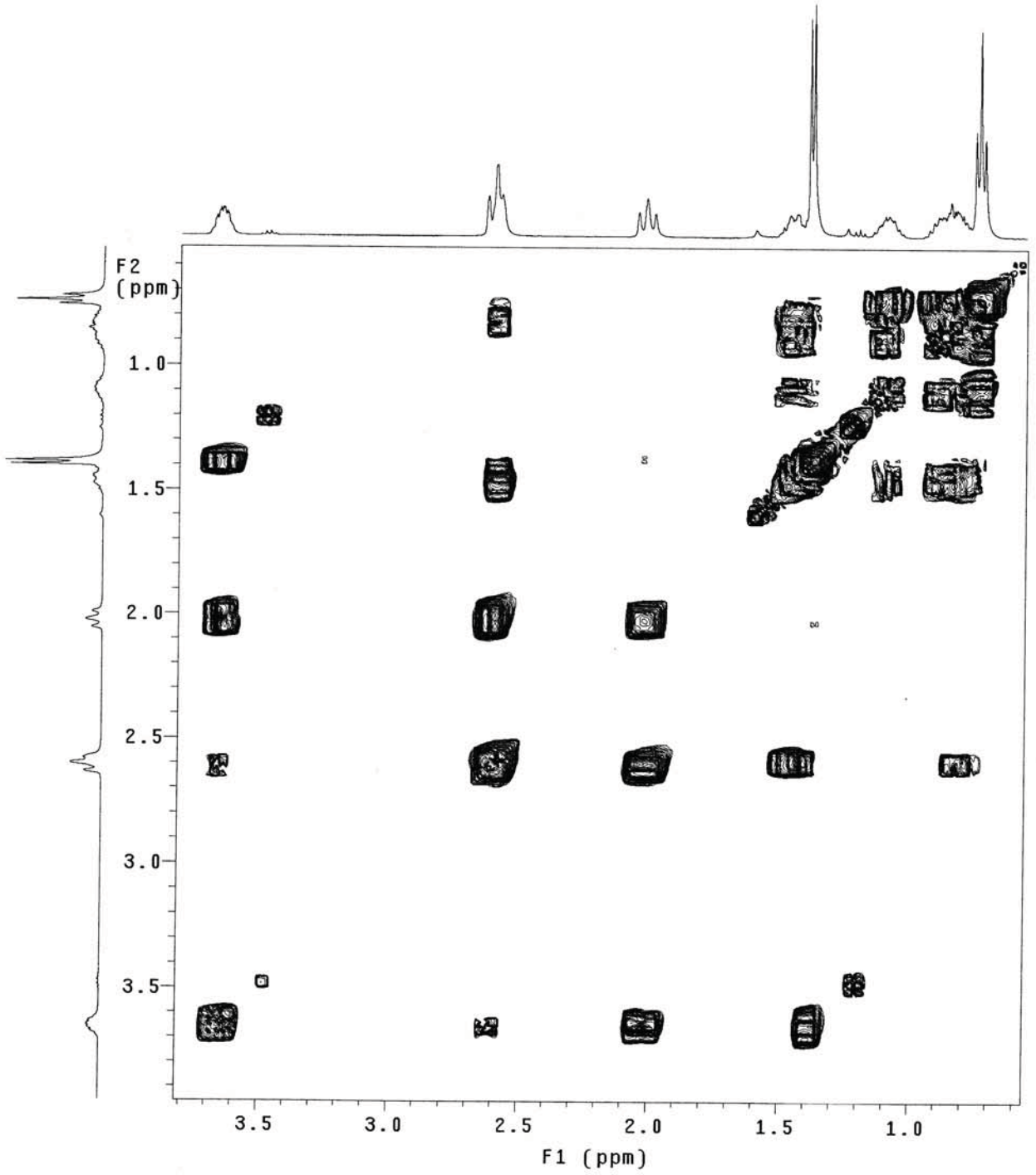
YZP-IV-47-II C13 CDCl3 100 MHz



CDCl3 2015-3-6

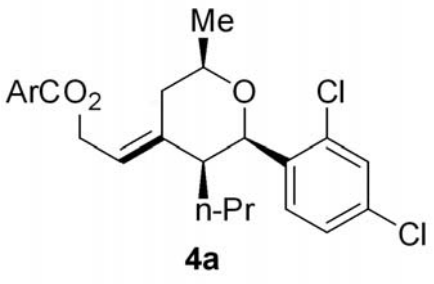


4a

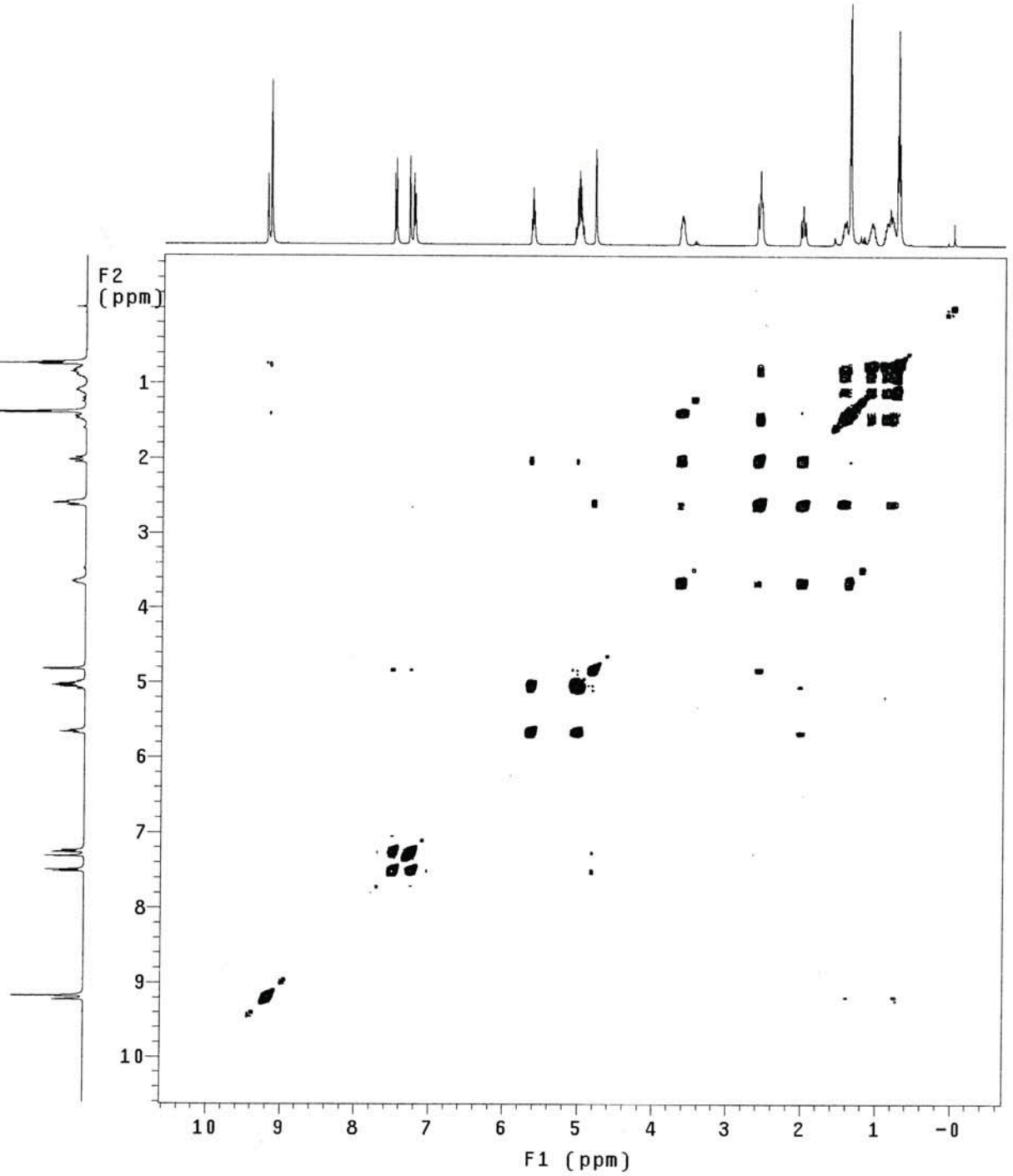


YZP-IV-47-II gCOSY CDCl3 2015-3-6

Pulse Sequence: gCOSY

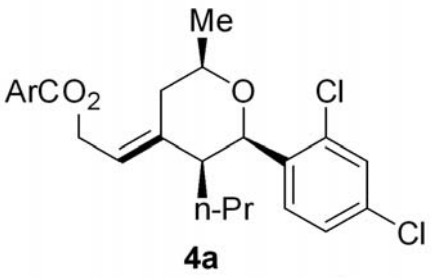


4a

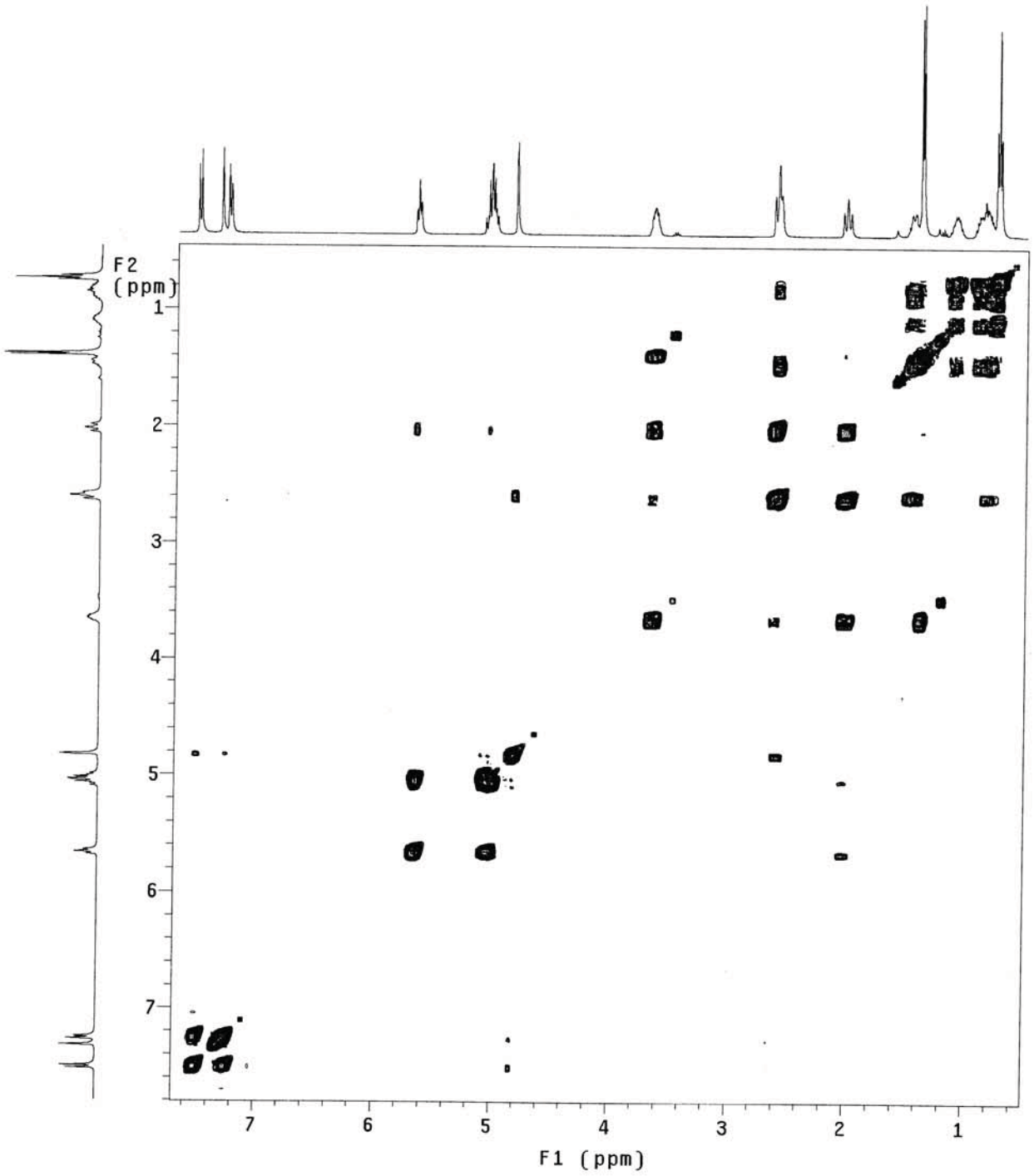


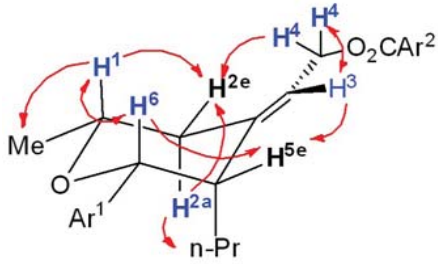
YZP-IV-47-II gCOSY CDCl3 2015-3-6

Pulse Sequence: gCOSY



4a

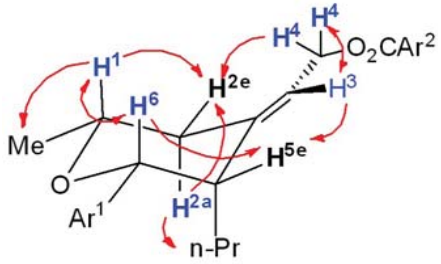



H4
H4
O2CAr2
H1
H2e
H3
H6
Me
H5e
O
Ar1
H2a
n-Pr

NOE of 4a

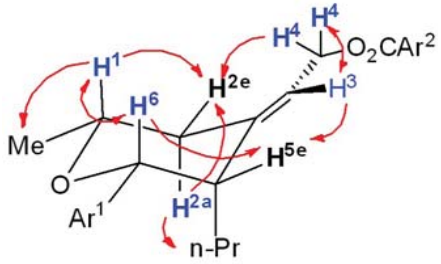
2.632
2.611
2.592
1.498
1.490
1.473
1.457
1.451
1.441
1.432
1.399
1.389
H2e
H2a
Hn-Pr
-18.69
100.00
-3.90
-2.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

YZP-IV-47-II NOEDS3.66 CDCl3 600 MHz

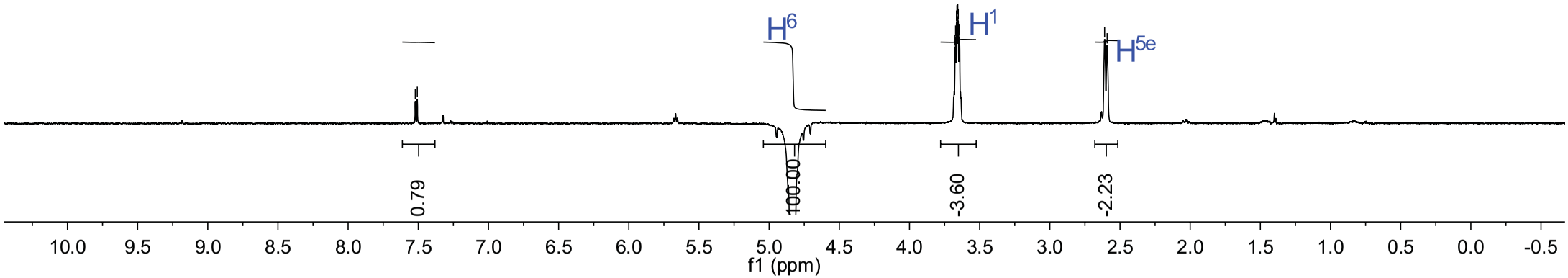


NOE of 4a

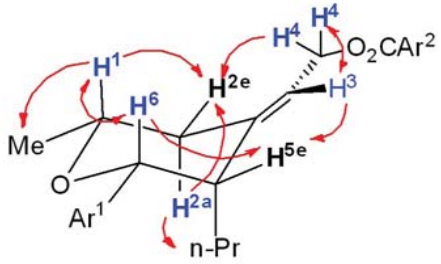
YZP-IV-47-II NOEDS4.82 CDCl3 600 MHz



NOE of 4a

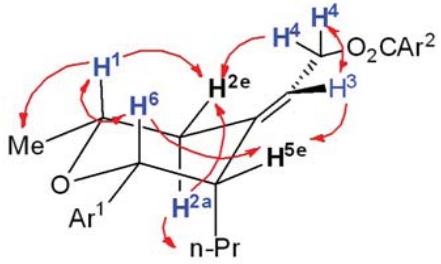


YZP-IV-47-II NOEDS5.05 CDCl3 600 MHz

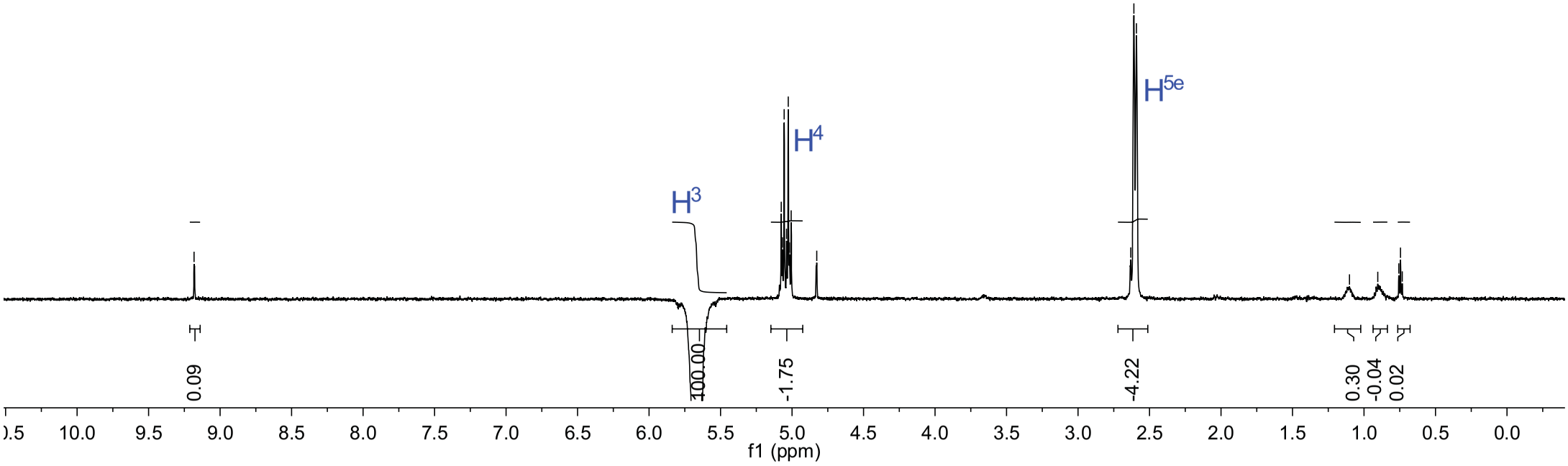


NOE of 4a

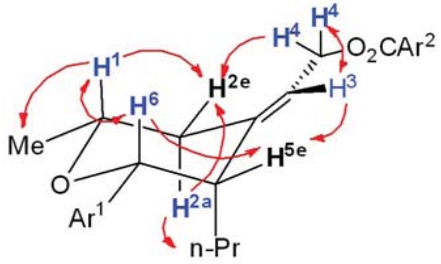
YZP-IV-47-II NOEDS5.67 CDCl3 600 MHz



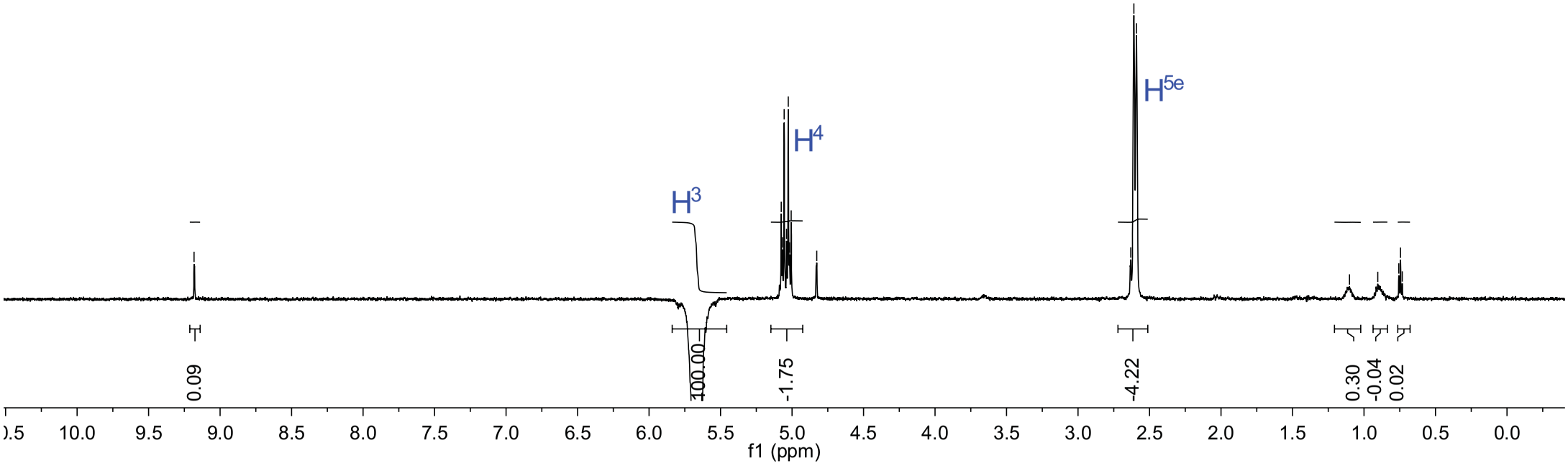
NOE of 4a



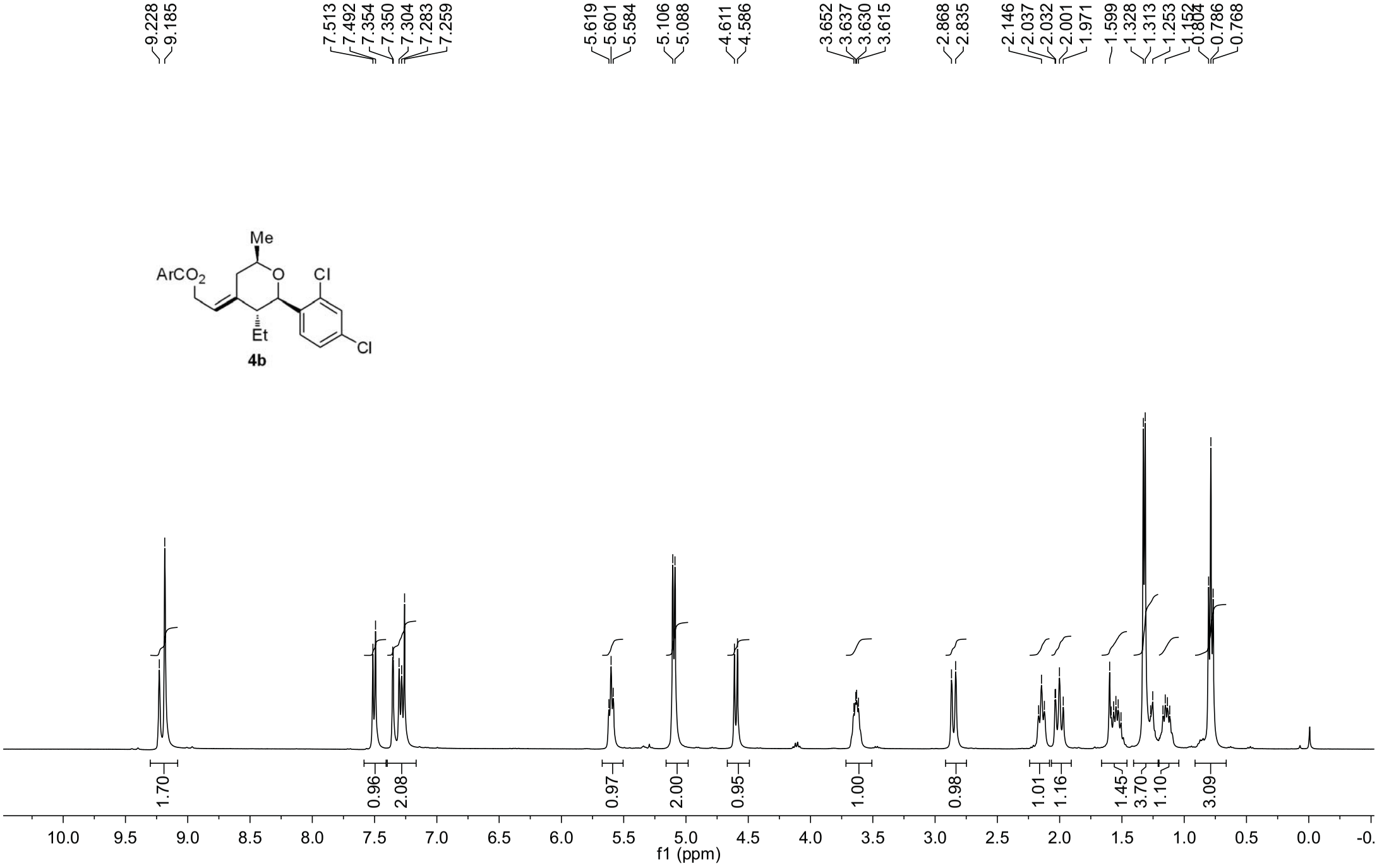
YZP-IV-47-II NOEDS5.67 CDCl3 600 MHz



NOE of 4a

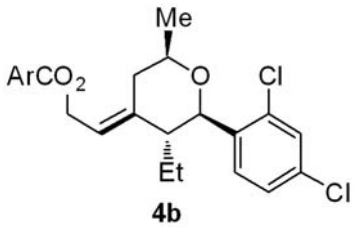


HYY-I-51a H1 CDCl3 400 MHz

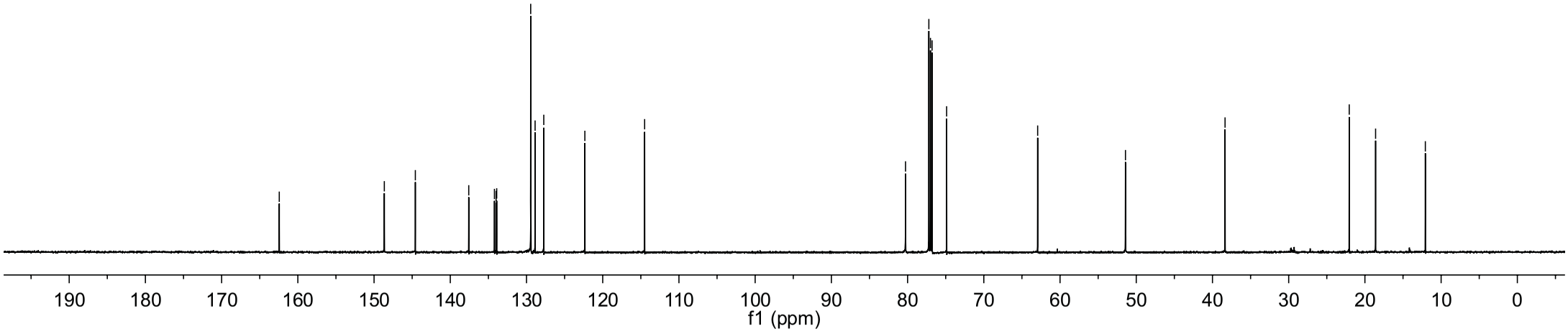


HYY-I-51a C13 CDCl3 150 MHz

162.437
148.654
144.584
137.577
134.206
133.987
133.909
129.449
128.872
127.733
122.344
114.501
80.271
77.211
77.000
76.788
74.878
62.936
51.415
38.349
22.057
18.599
12.072



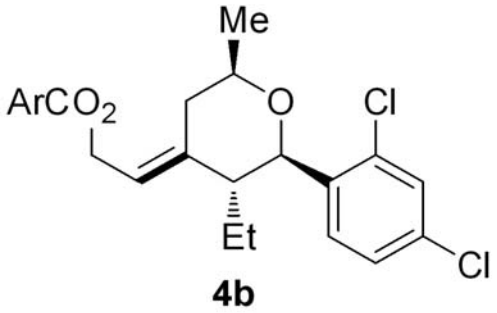
4b



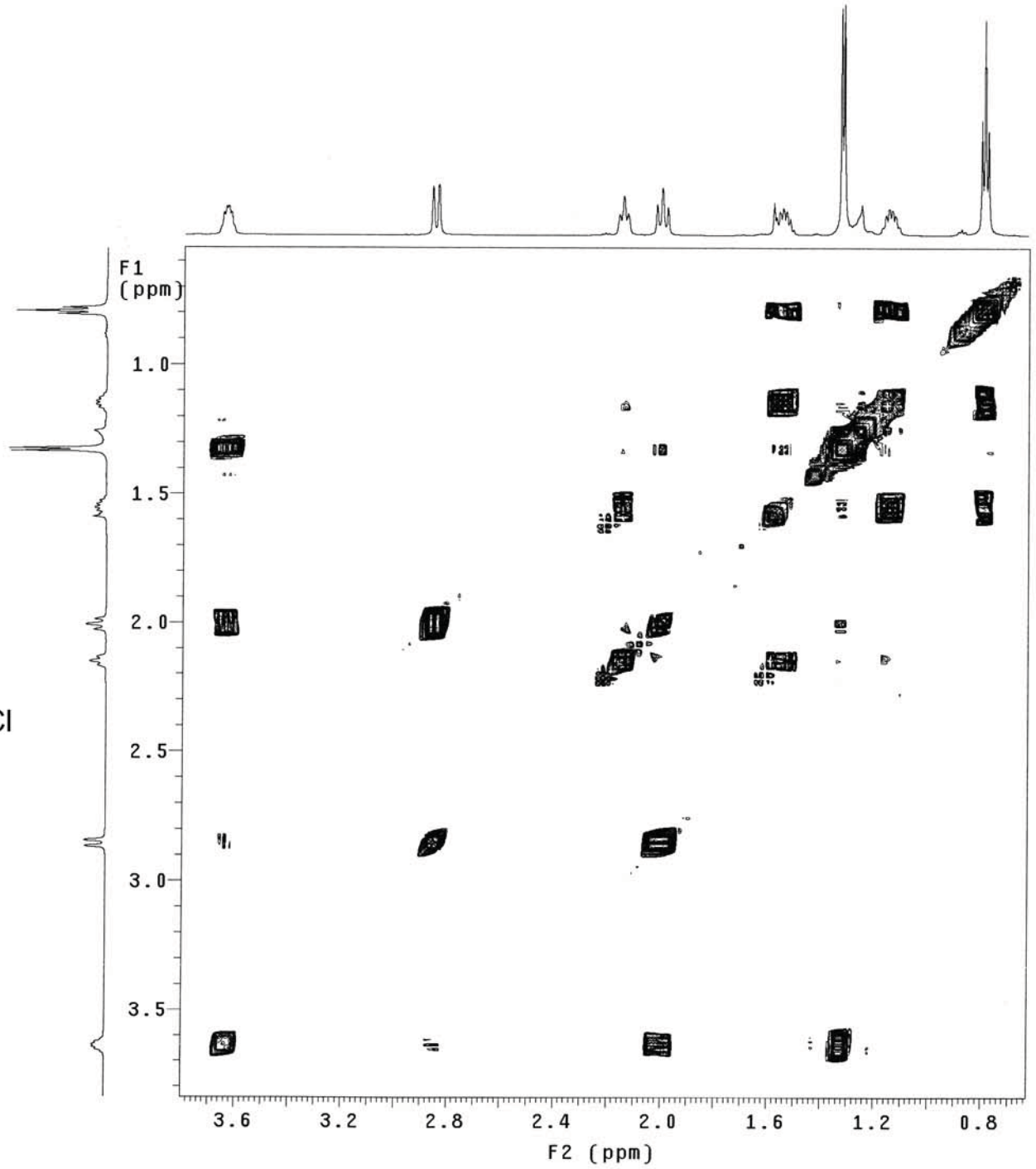
HYY-I-51a gCOSY CDCl3 2015-3-6

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20140603_05

Pulse Sequence: gCOSY



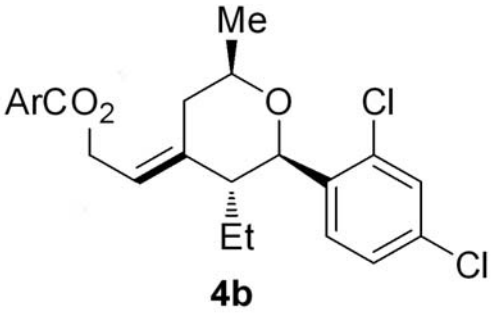
4b



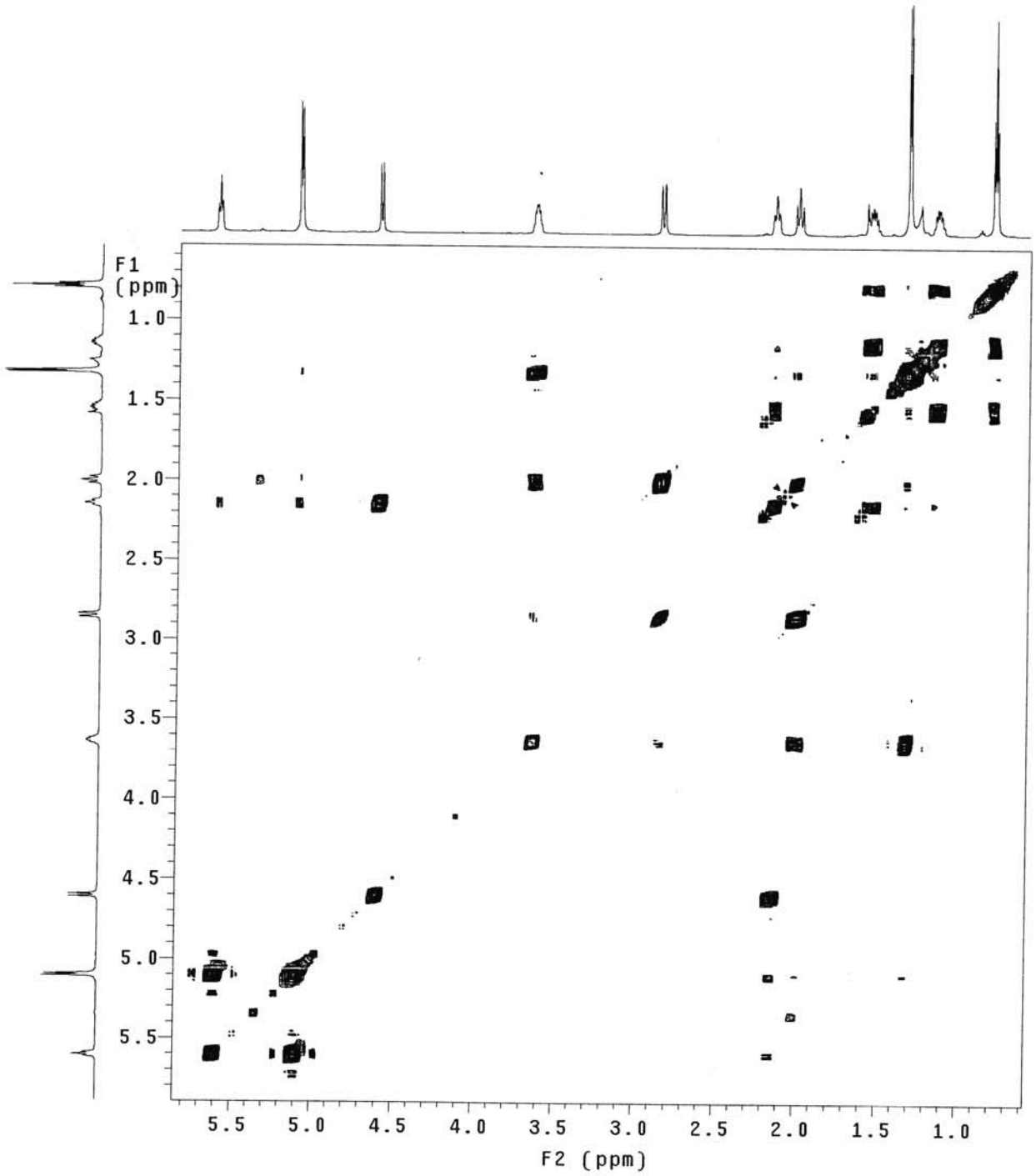
HYY-I-51a gCOSY CDCl3 2015-3-6

Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20140603_05

Pulse Sequence: gCOSY



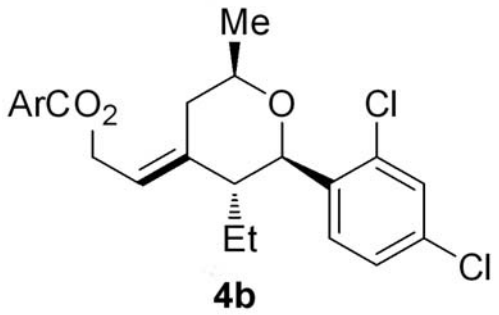
4b



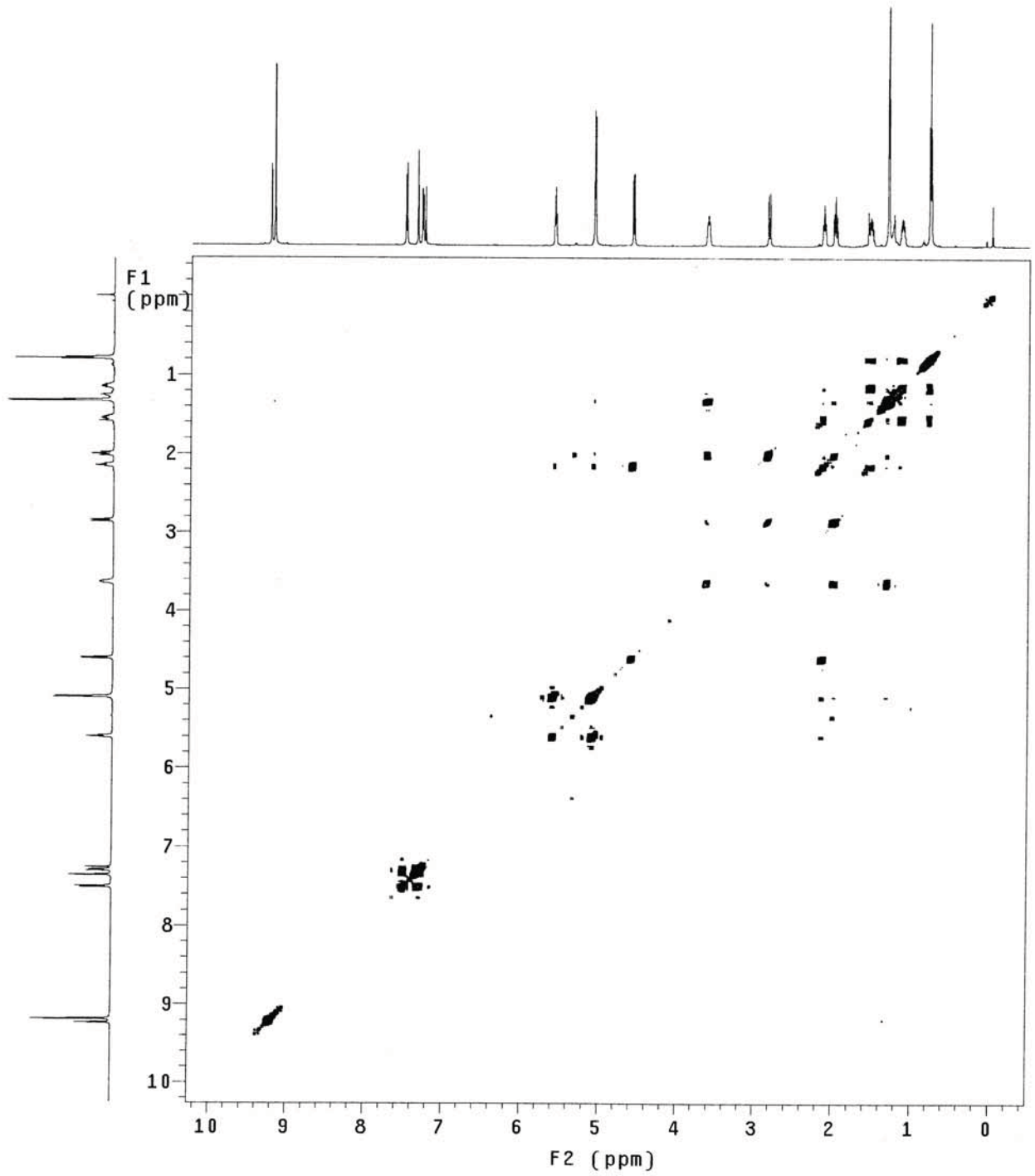
HYY-I-51a gCOSY CDCl3 2015-3-6

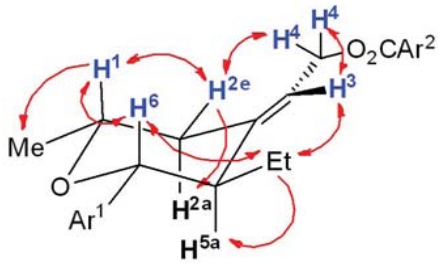
Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20140603_05

Pulse Sequence: gCOSY



4b

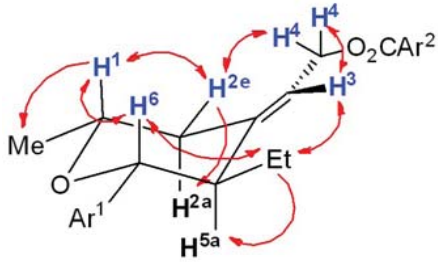



H4
H4
O2CAr2
H1
H2e
H3
H6
Me
Et
O
Ar1
H2a
H5a

NOE of 4b

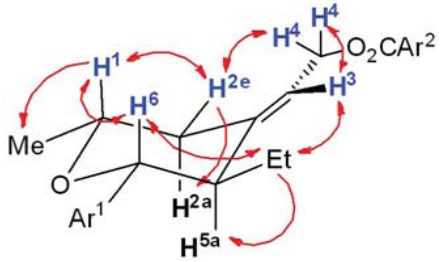
9.192
5.098
1.580
1.568
1.552
1.540
1.528
0.807
0.795
0.783
H3
H4
HEt
HEt
100.00
-2.25
-4.39
-2.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

HYY-I-51a NOEDS4.61 CDCl3 600 MHz

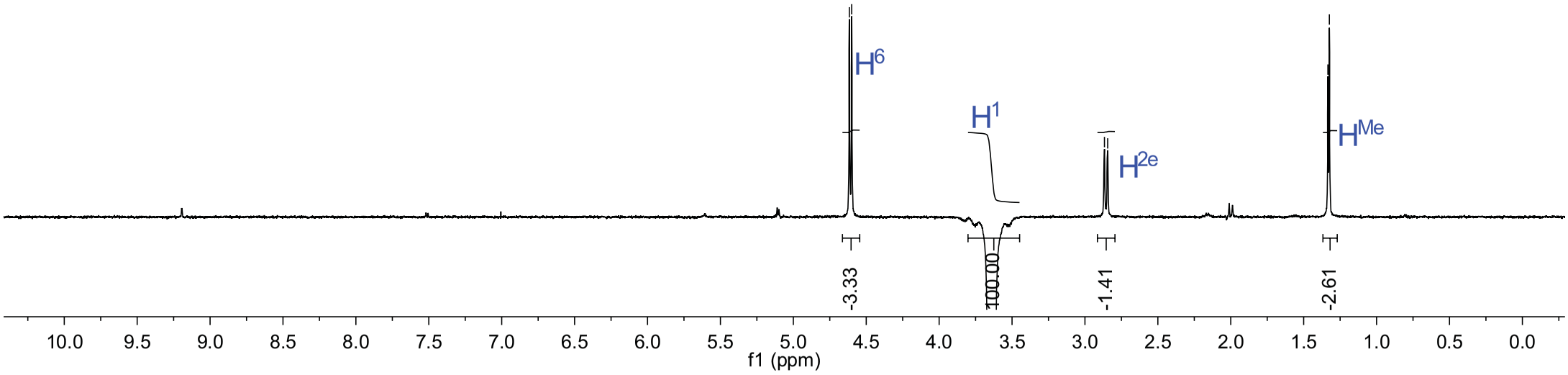


NOE of 4b

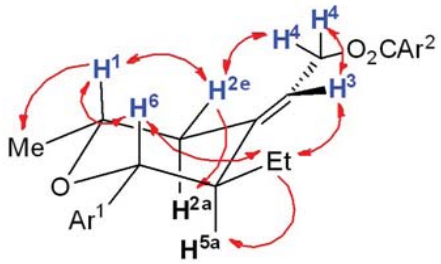
HYY-I-51a NOEDS3.64 CDCl3 600 MHz



NOE of 4b

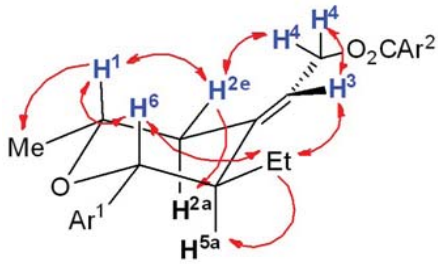


HYY-I-51a NOEDS2.86 CDCl3 600 MHz

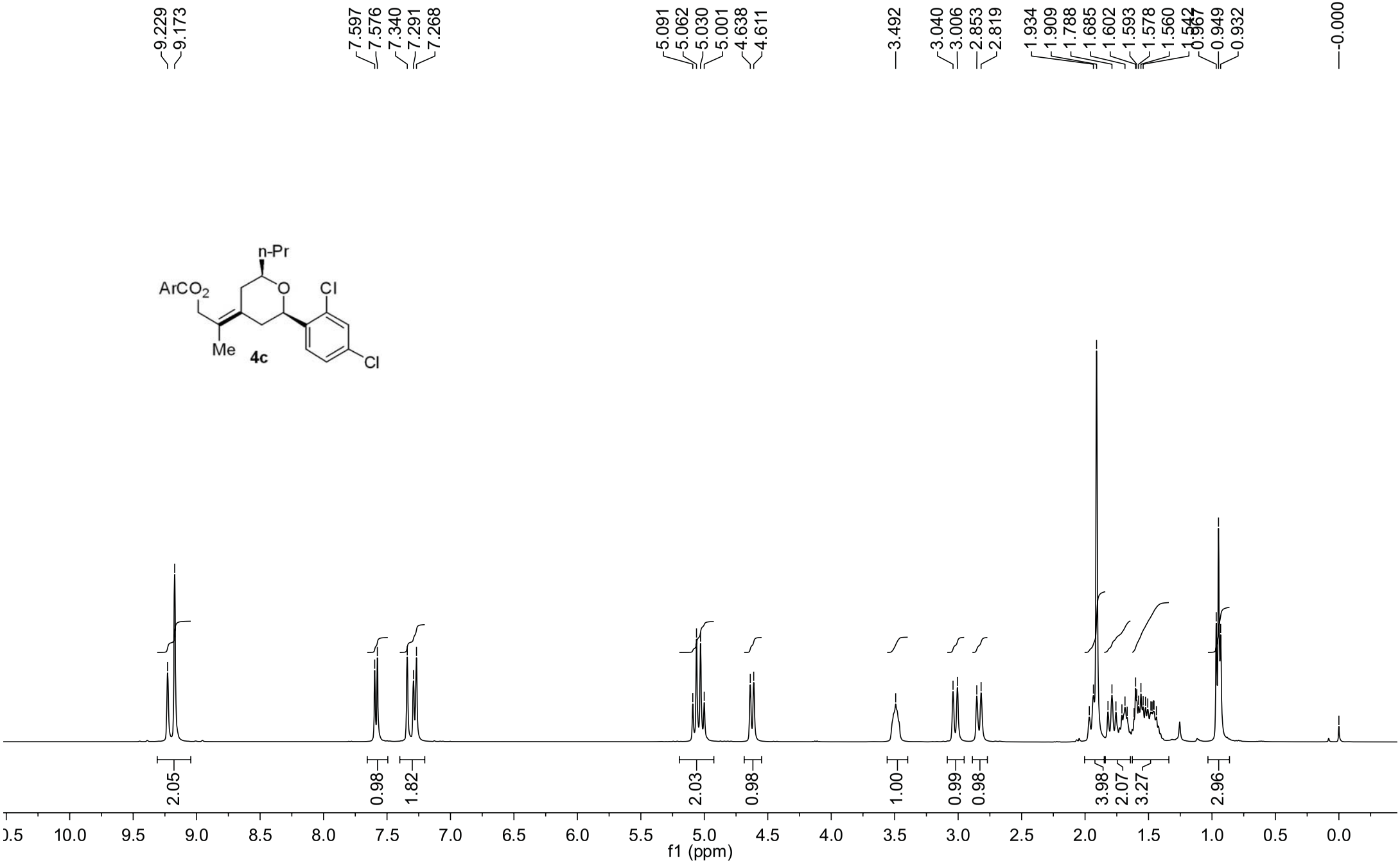


NOE of 4b

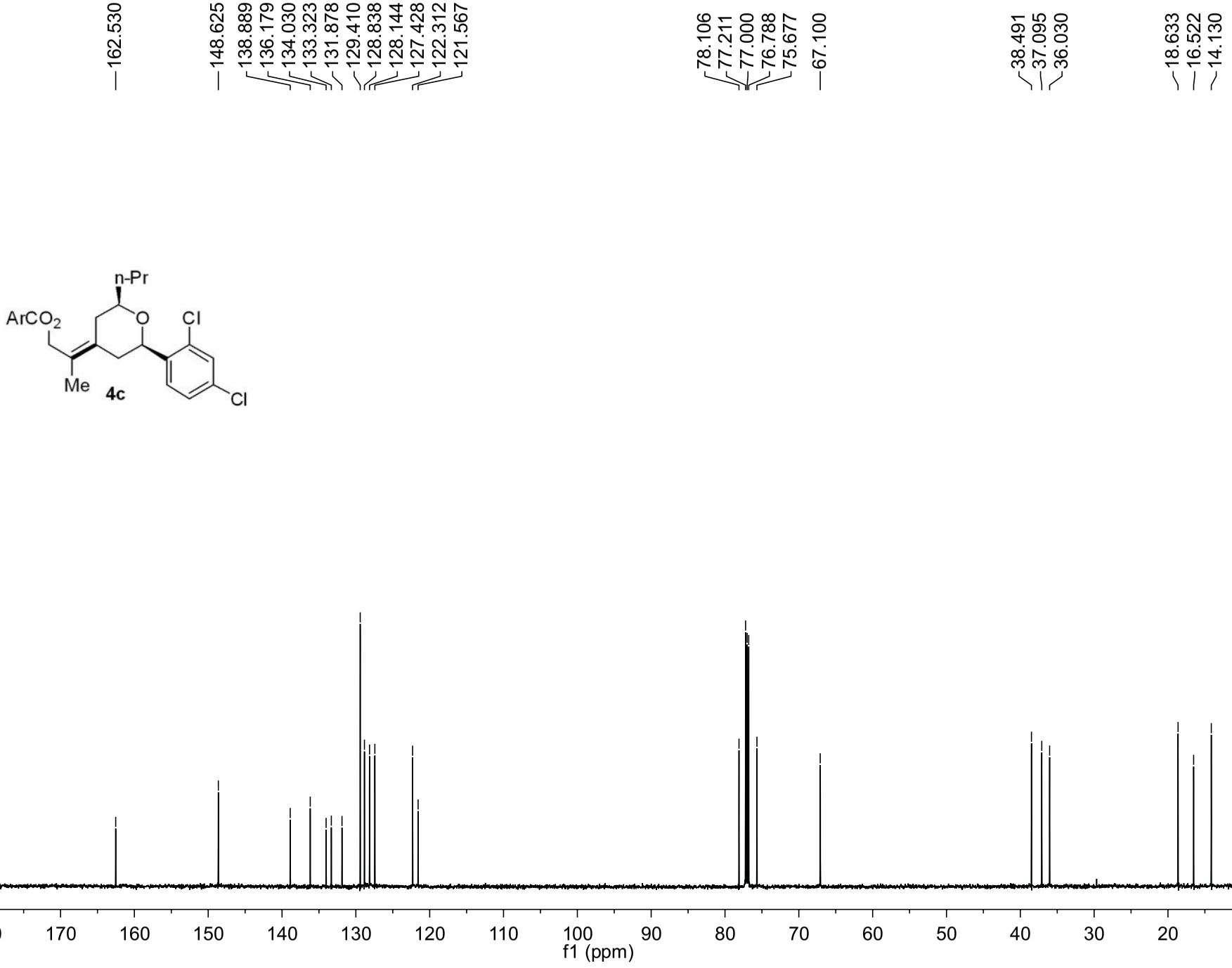
HYY-I-51a NOEDS CDCl3 5.10 600 MHz



NOE of 4b

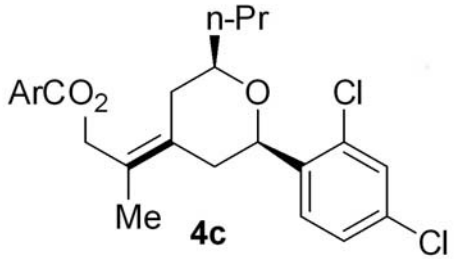

9.229
9.173
7.597
7.576
7.340
7.291
7.268
5.091
5.062
5.030
5.001
4.638
4.611
3.492
3.040
3.006
2.853
2.819
1.934
1.909
1.788
1.685
1.602
1.593
1.578
1.560
1.542
0.967
0.949
0.932
-0.000
n-Pr
ArCO2
O
Cl
Cl
Me
4c
2.05
0.98
1.82
2.03
0.98
1.00
0.99
0.98
3.98
2.07
3.27
2.96
f1 (ppm)

YZP-IV-47-I C13 CDCl3 150 MHz

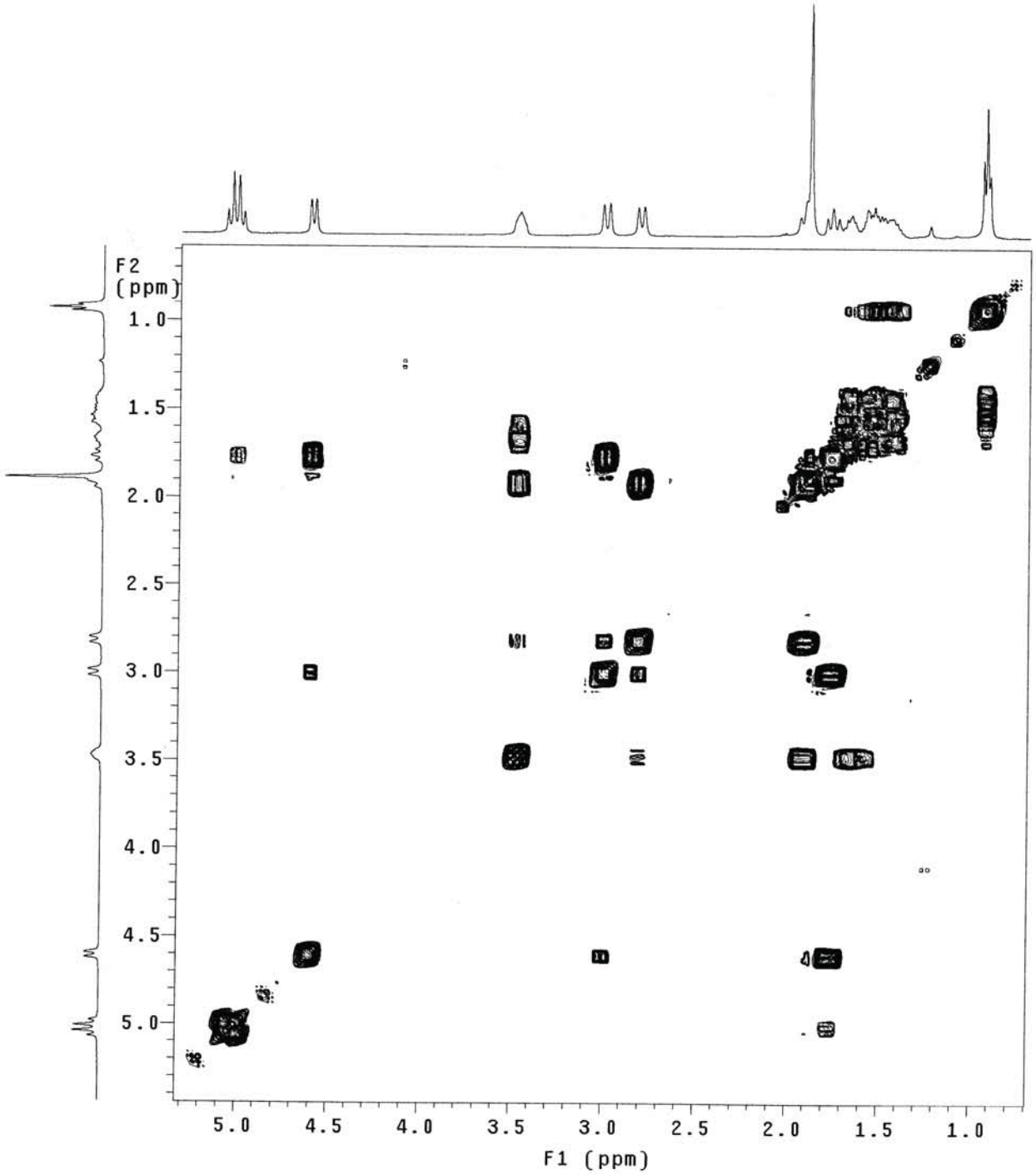


YZP-IV-47-I-CDCL3-H1-2015-3-7

Pulse Sequence: gCOSY

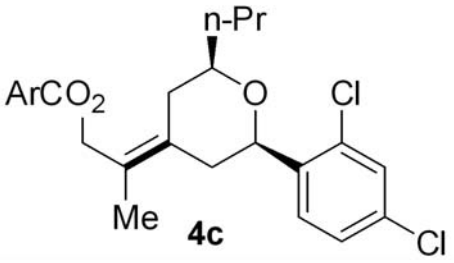


4c

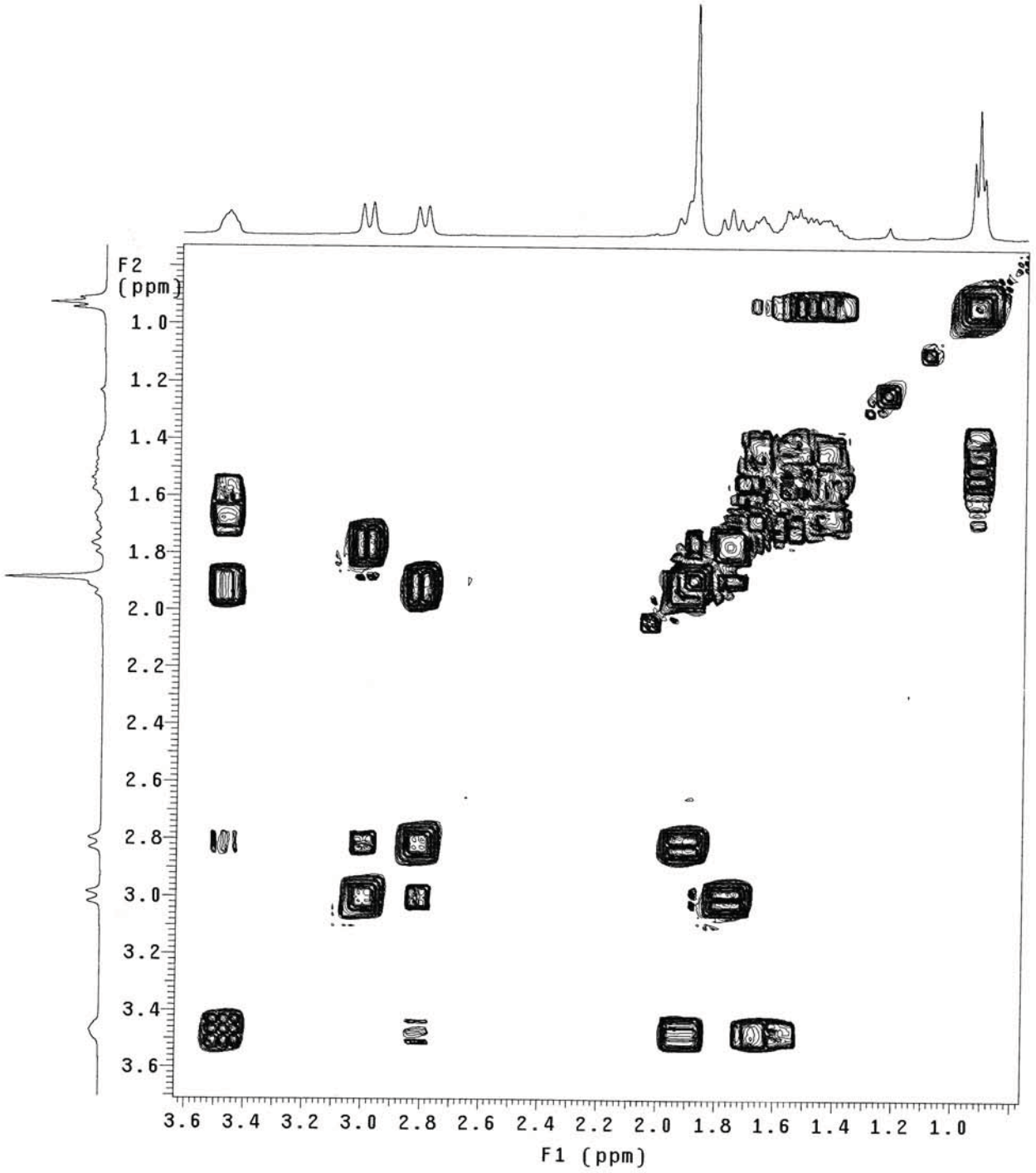


YZP-IV-47-I-CDCL3-H1-2015-3-7

Pulse Sequence: gCOSY

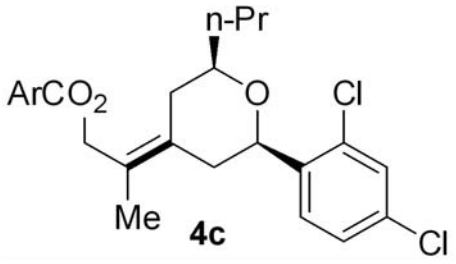


4c

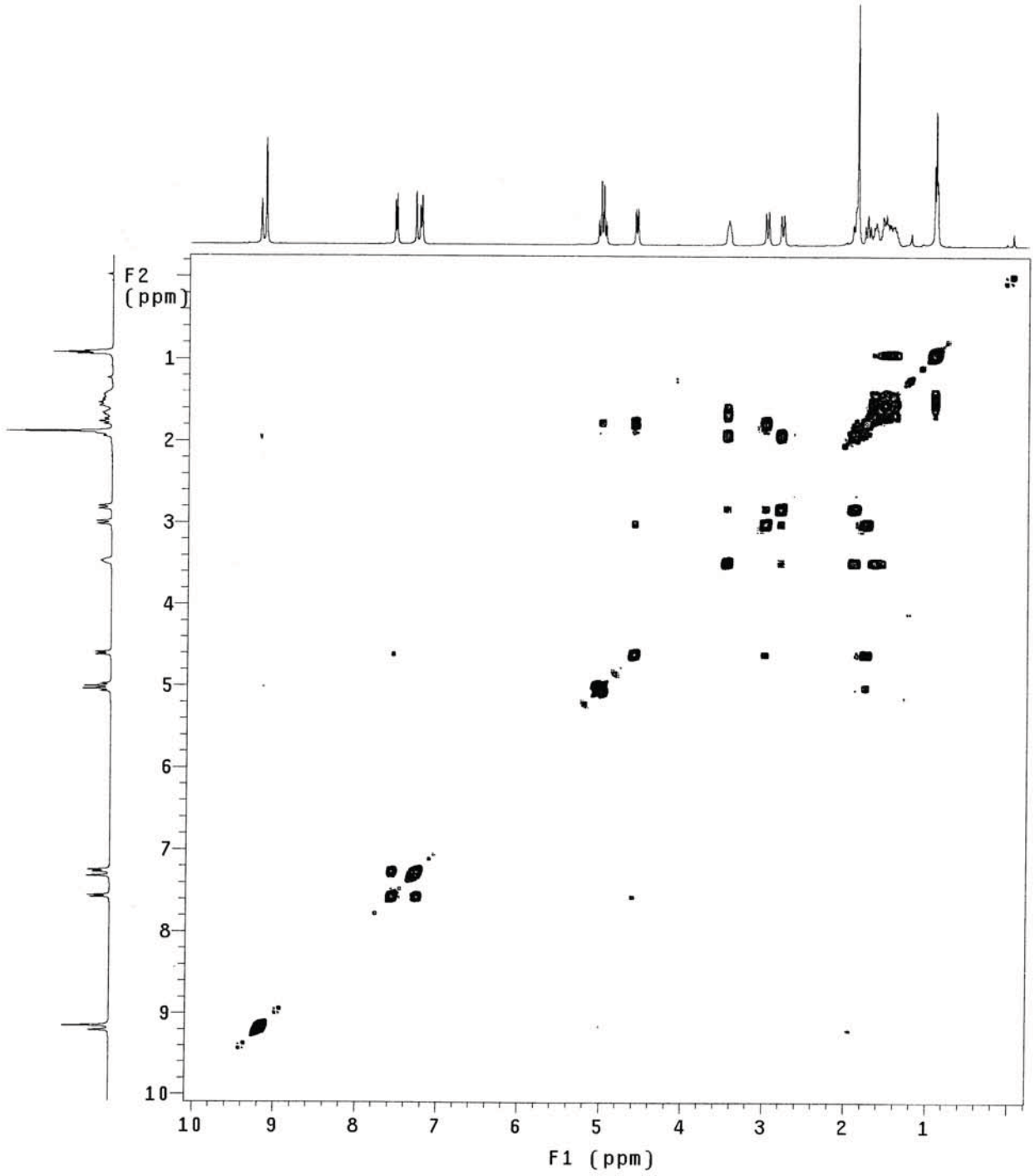


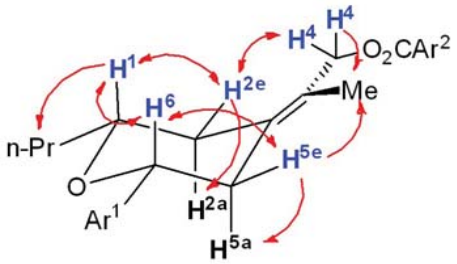
YZP-IV-47-I-CDCL3-H1-2015-3-7

Pulse Sequence: gCOSY



4c

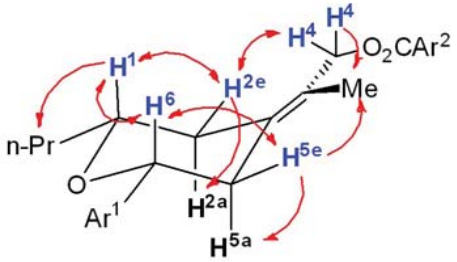



H4
H4
O2CAr2
H1
H2e
Me
H6
n-Pr
H5e
O
Ar1
H2a
H5a

NOE of 4c

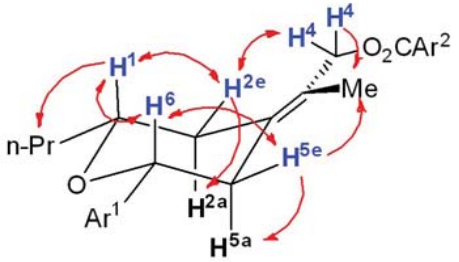
5.085
5.066
5.028
5.009
3.494
1.959
1.938
1.912
1.591
1.569
H4
H1
H2e
H2a
-11.35
-3.89
100.00
-24.76
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

YZP-IV-47-I NOEDS3.03 CDCl3 600 MHz



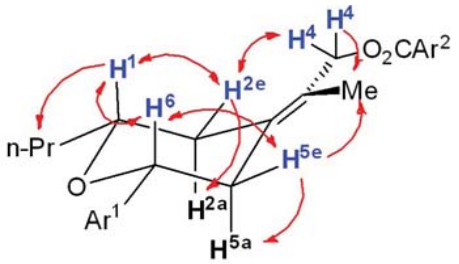
NOE of 4c

YZP-IV-47-I NOEDS3.50 CDCl3 600 MHz



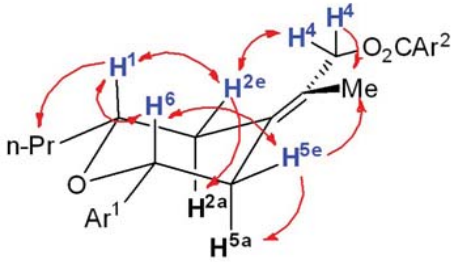
NOE of 4c

YZP-IV-47-I NOEDS4.63 CDCl3 600 MHz

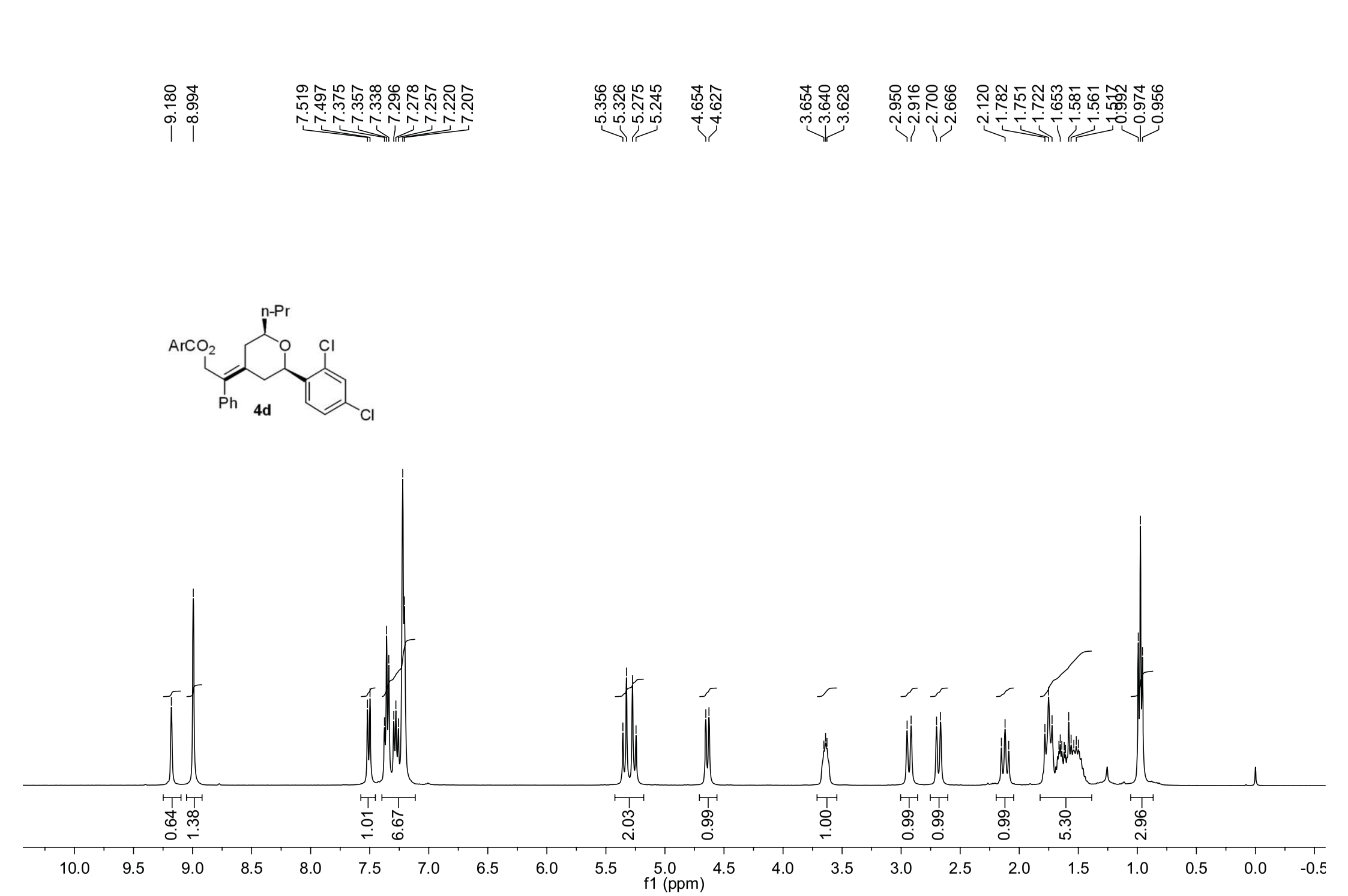


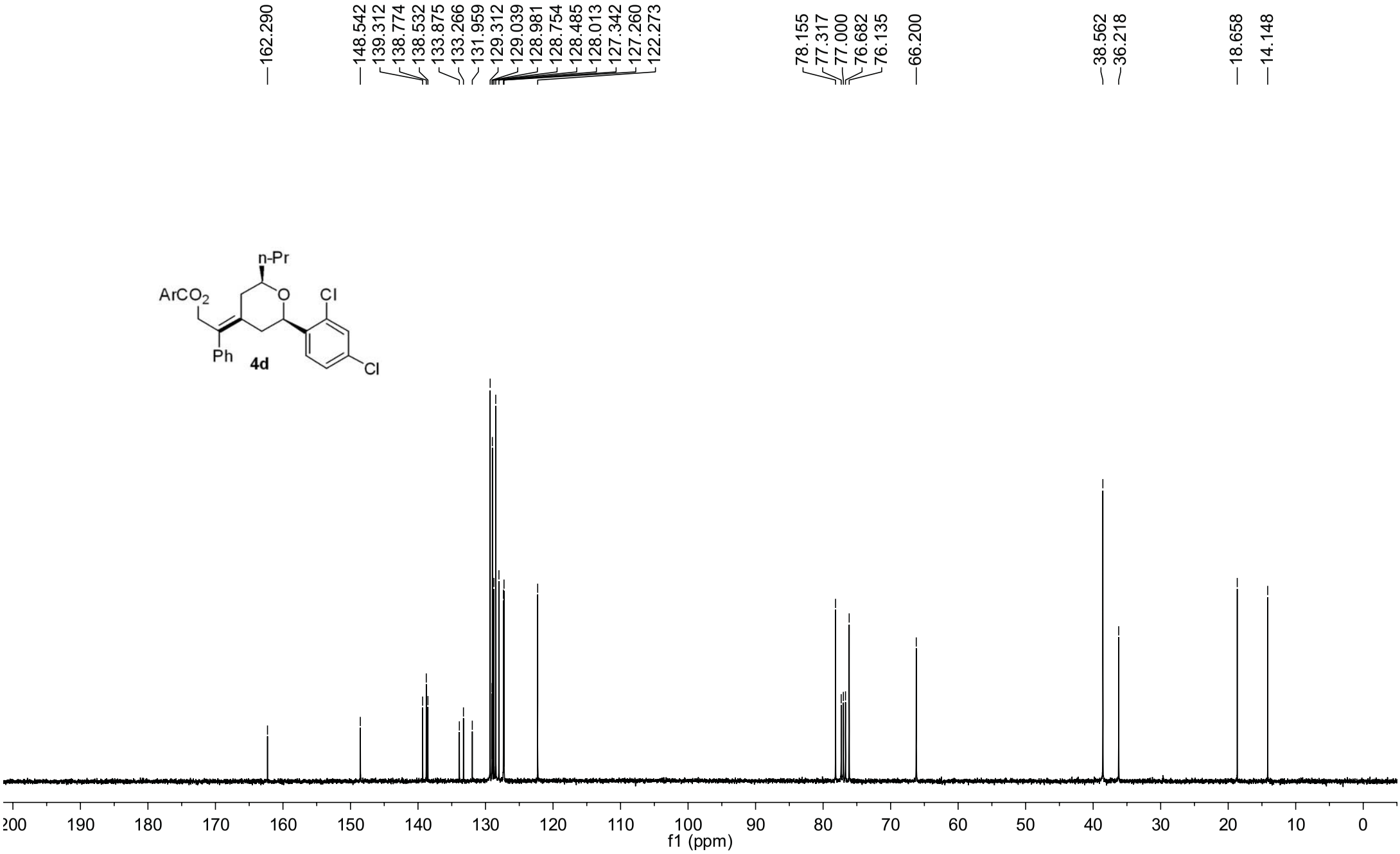
NOE of 4c

YZP-IV-47-I NOEDS5.05 CDCl3 600 MHz



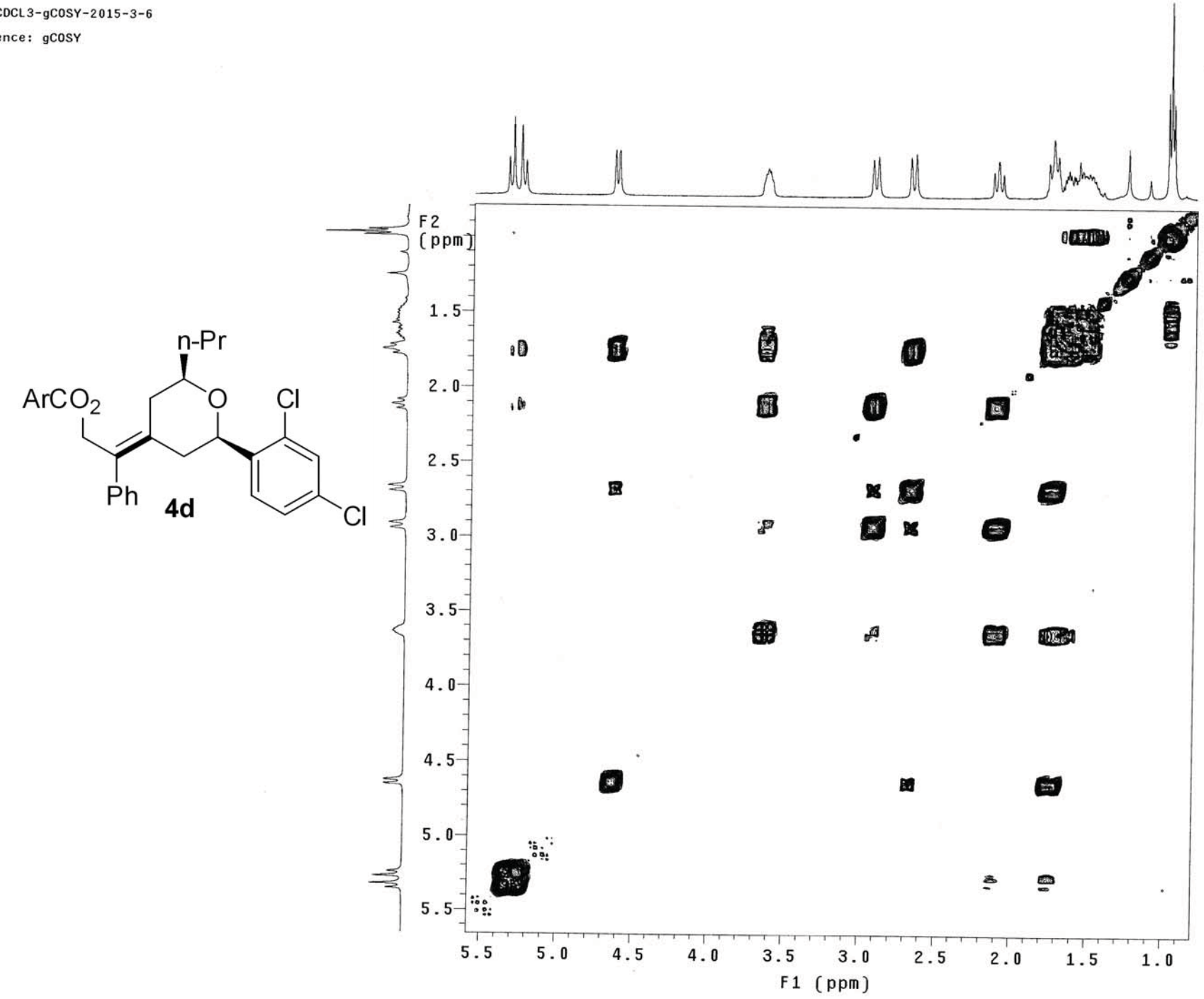
NOE of 4c


9.180
8.994
7.519
7.497
7.375
7.357
7.338
7.296
7.278
7.257
7.220
7.207
5.356
5.326
5.275
5.245
4.654
4.627
3.654
3.640
3.628
2.950
2.916
2.700
2.666
2.120
1.782
1.751
1.722
1.653
1.581
1.561
1.517
0.992
0.974
0.956
n-Pr
ArCO2
O
Cl
Ph
Cl
4d
0.64
1.38
1.01
6.67
2.03
0.99
1.00
0.99
0.99
0.99
5.30
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


162.290
148.542
139.312
138.774
138.532
133.875
133.266
131.959
129.312
129.039
128.981
128.754
128.485
128.013
127.342
127.260
122.273
78.155
77.317
77.000
76.682
76.135
66.200
38.562
36.218
18.658
14.148
n-Pr
ArCO2
O
Cl
Ph
4d
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

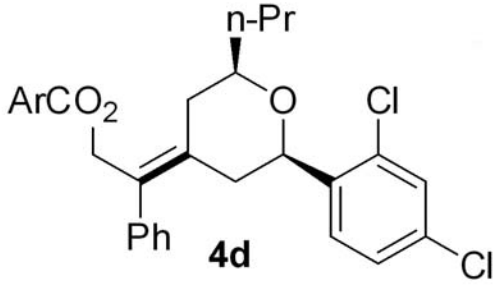
YZP-IV-48-CDCL3-gCOSY-2015-3-6

Pulse Sequence: gCOSY

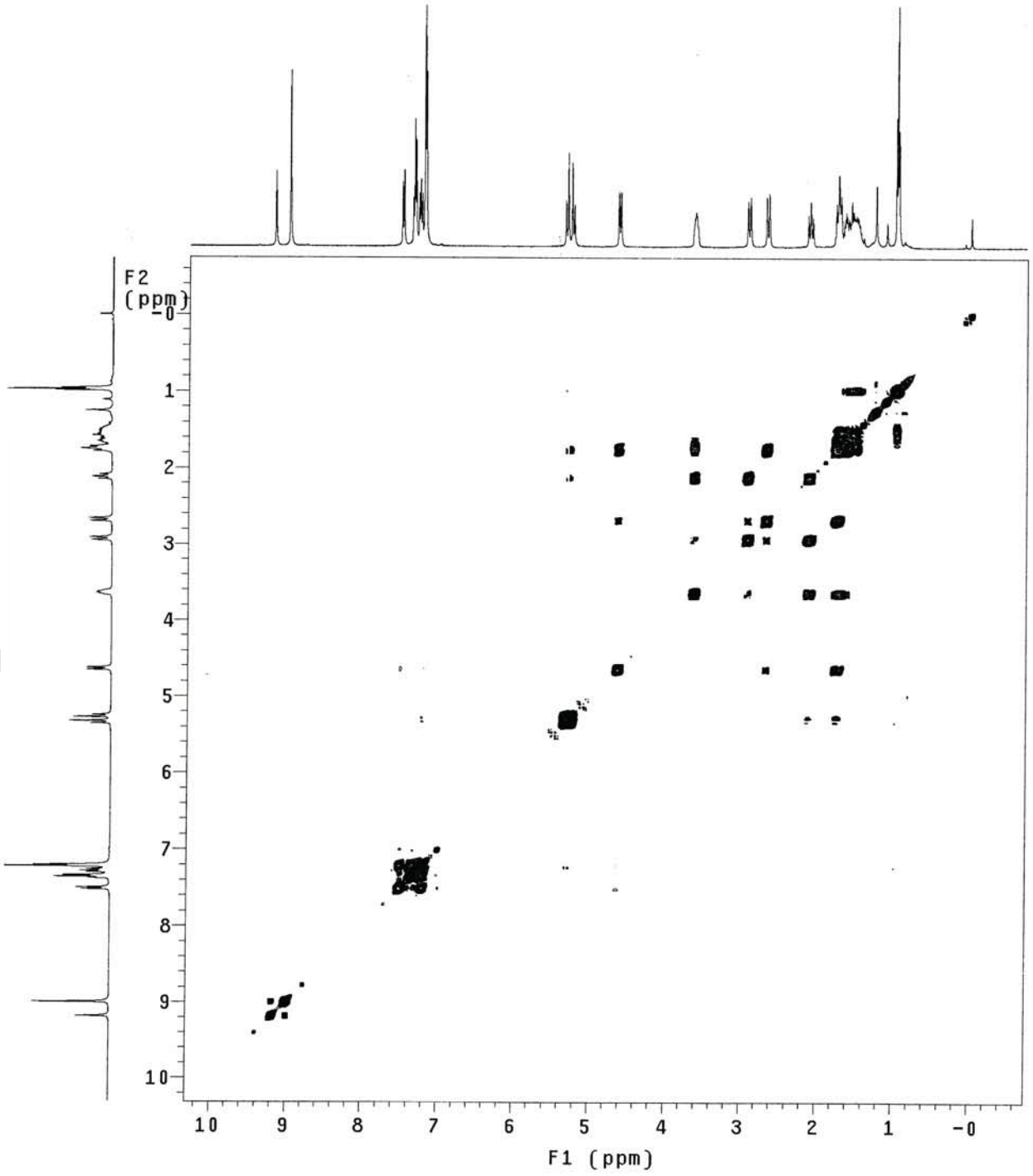


YZP-IV-48-CDCL3-gCOSY-2015-3-6

Pulse Sequence: gCOSY

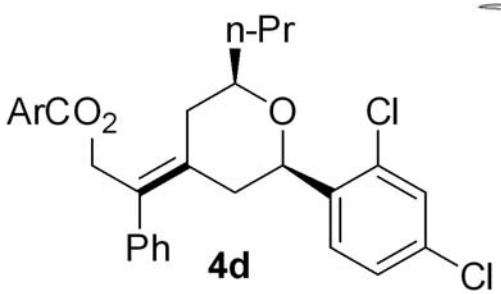


4d

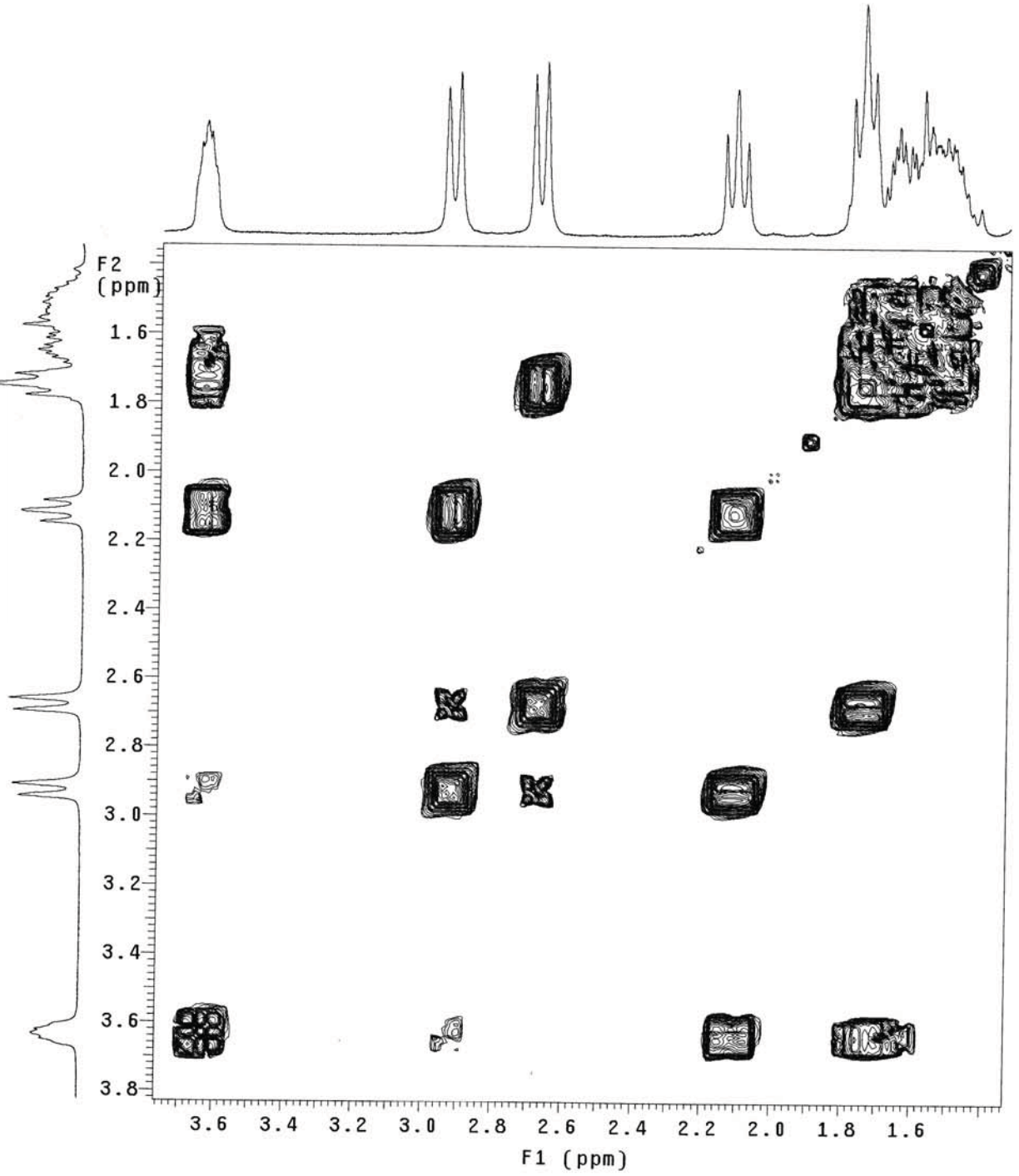


YZP-IV-48-CDCL3-gCOSY-2015-3-6

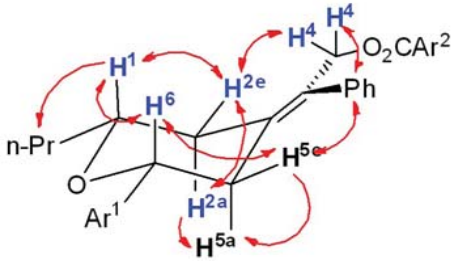
Pulse Sequence: gCOSY



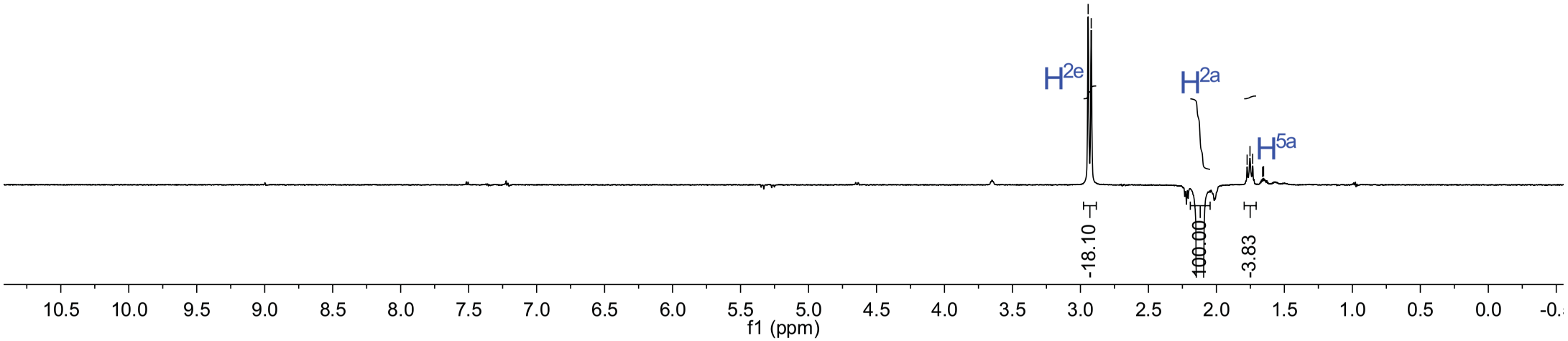
4d



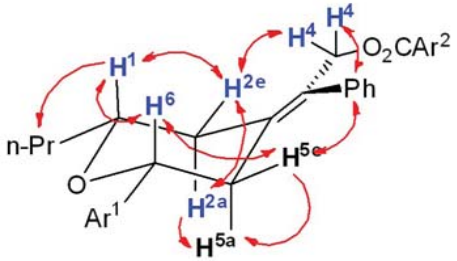
YZP-IV-48 NOEDS2.12 CDCl3 600 MHz



NOE of 4d

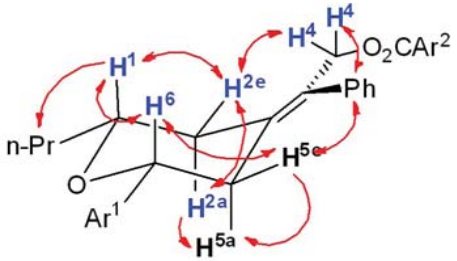


YZP-IV-48 NOEDS2.68 CDCl3 600 MHz



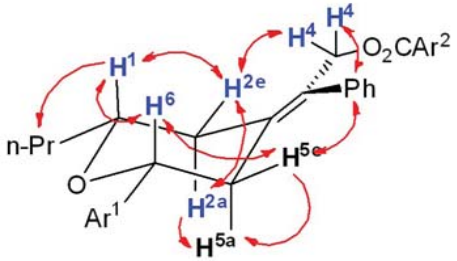
NOE of 4d

YZP-IV-48 NOEDS2.93 CDCl3 600 MHz



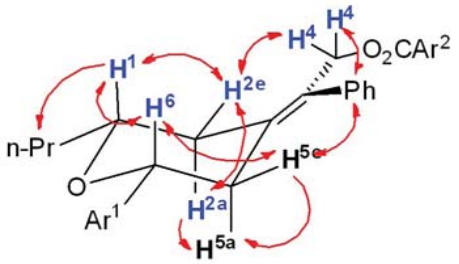
NOE of 4d

YZP-IV-48 NOEDS3.64 CDCl3 600 MHz



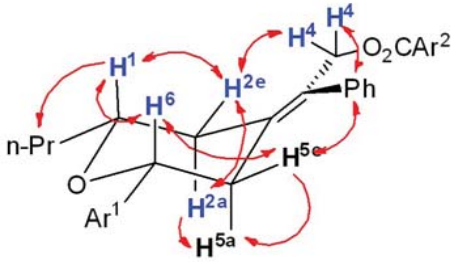
NOE of 4d

YZP-IV-48 NOEDS4.64 CDCl3 600 MHz

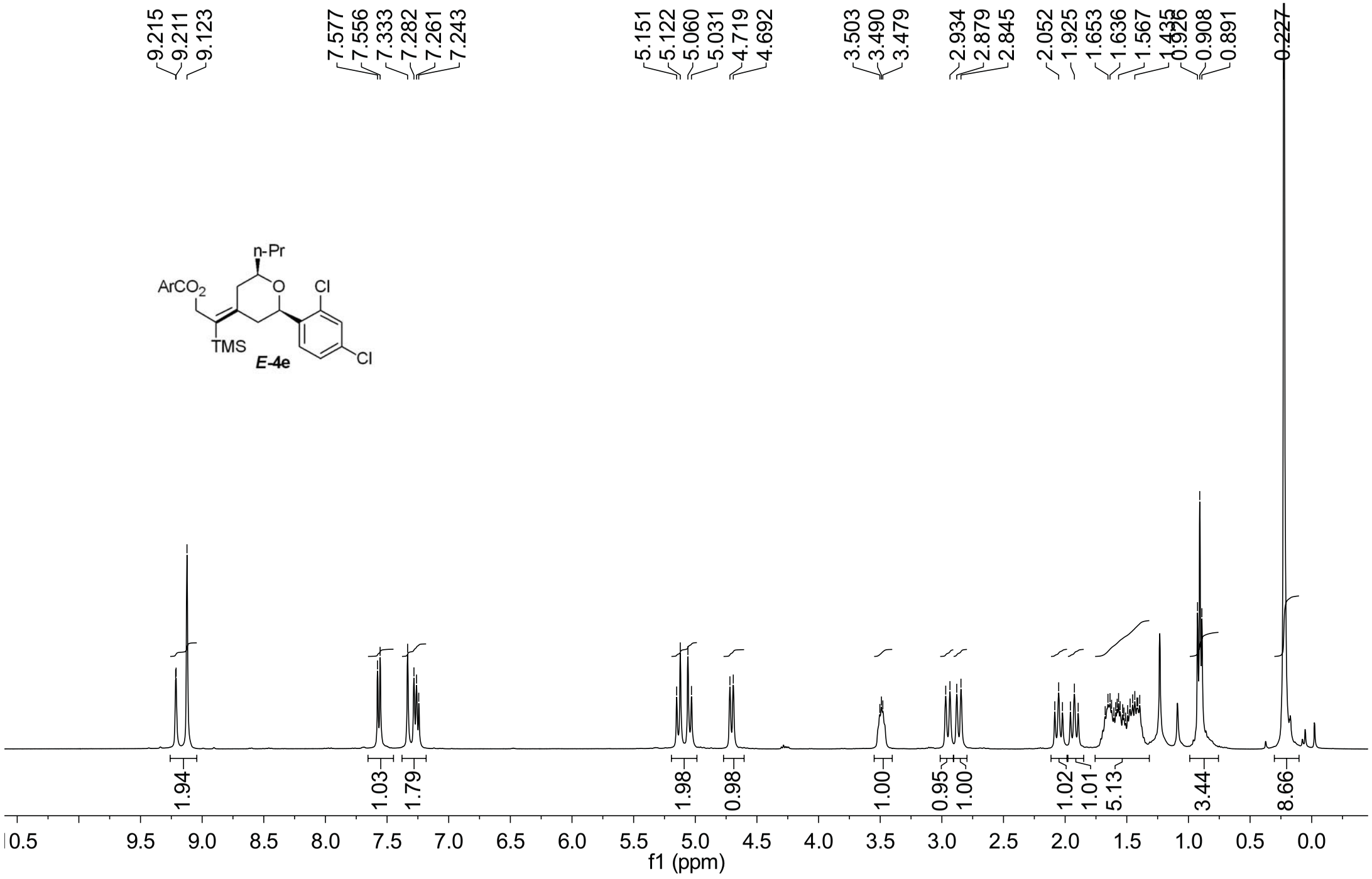


NOE of 4d

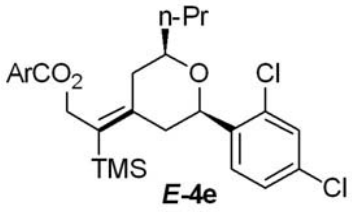
YZP-IV-48 NOEDS5.30 CDCl3 600 MHz



NOE of 4d

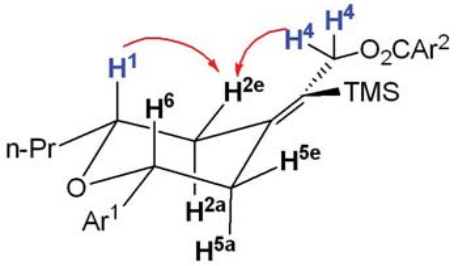

9.215
9.211
9.123
7.577
7.556
7.333
7.282
7.261
7.243
5.151
5.122
5.060
5.031
4.719
4.692
3.503
3.490
3.479
2.934
2.879
2.845
2.052
1.925
1.653
1.636
1.567
1.435
0.926
0.908
0.891
0.227
n-Pr
ArCO2
O
Cl
TMS
Cl
E-4e
1.94
1.03
1.79
1.98
0.98
1.00
0.95
1.00
1.02
1.01
5.13
3.44
8.66
f1 (ppm)

YZP-6-4a C13 CDCl3 150MHz



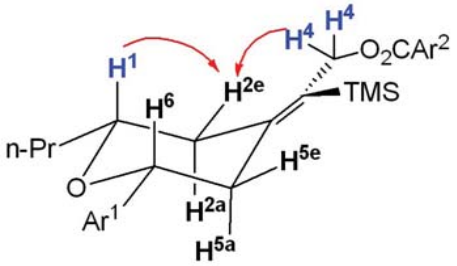
E-4e

YZP-6-4a NOEDS3.52 CDCl3 600 MHz



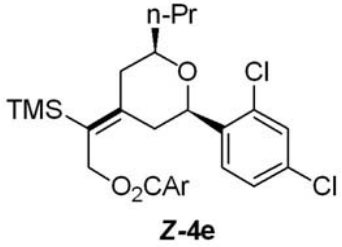
NOE of *E*-4e

YZP-6-4a NOEDS5.12 CDCl3 600 MHz



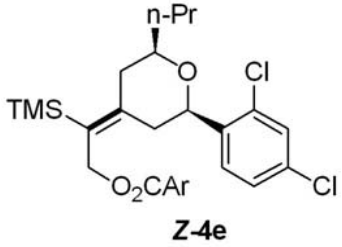
NOE of *E*-4e

YZP-6-4 1H CDCl3 400MHz

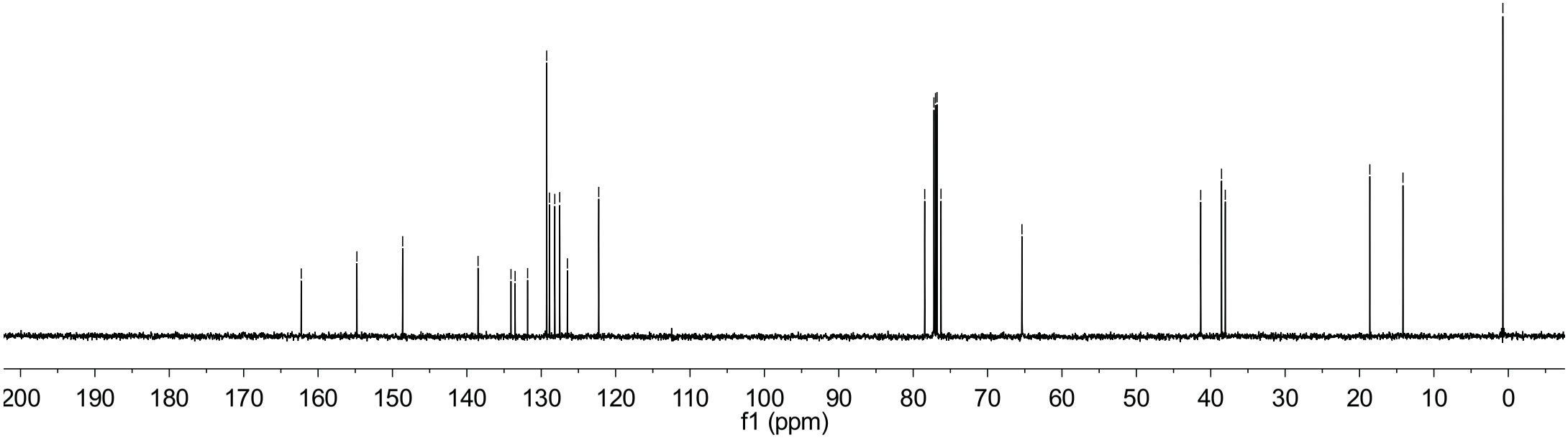


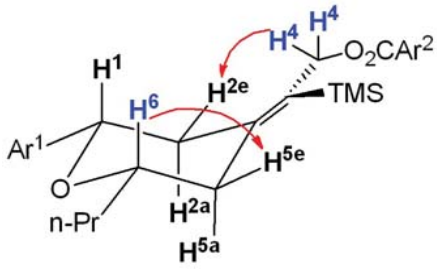
Z-4e

YZP-V-6-4 C13 CDCl3 150MHz



Z-4e

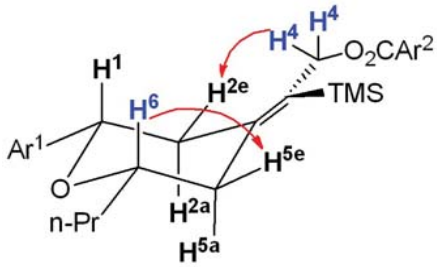



H4
H4
O2CAr2
H1
H6
H2e
TMS
Ar1
H5e
O
n-Pr
H2a
H5a

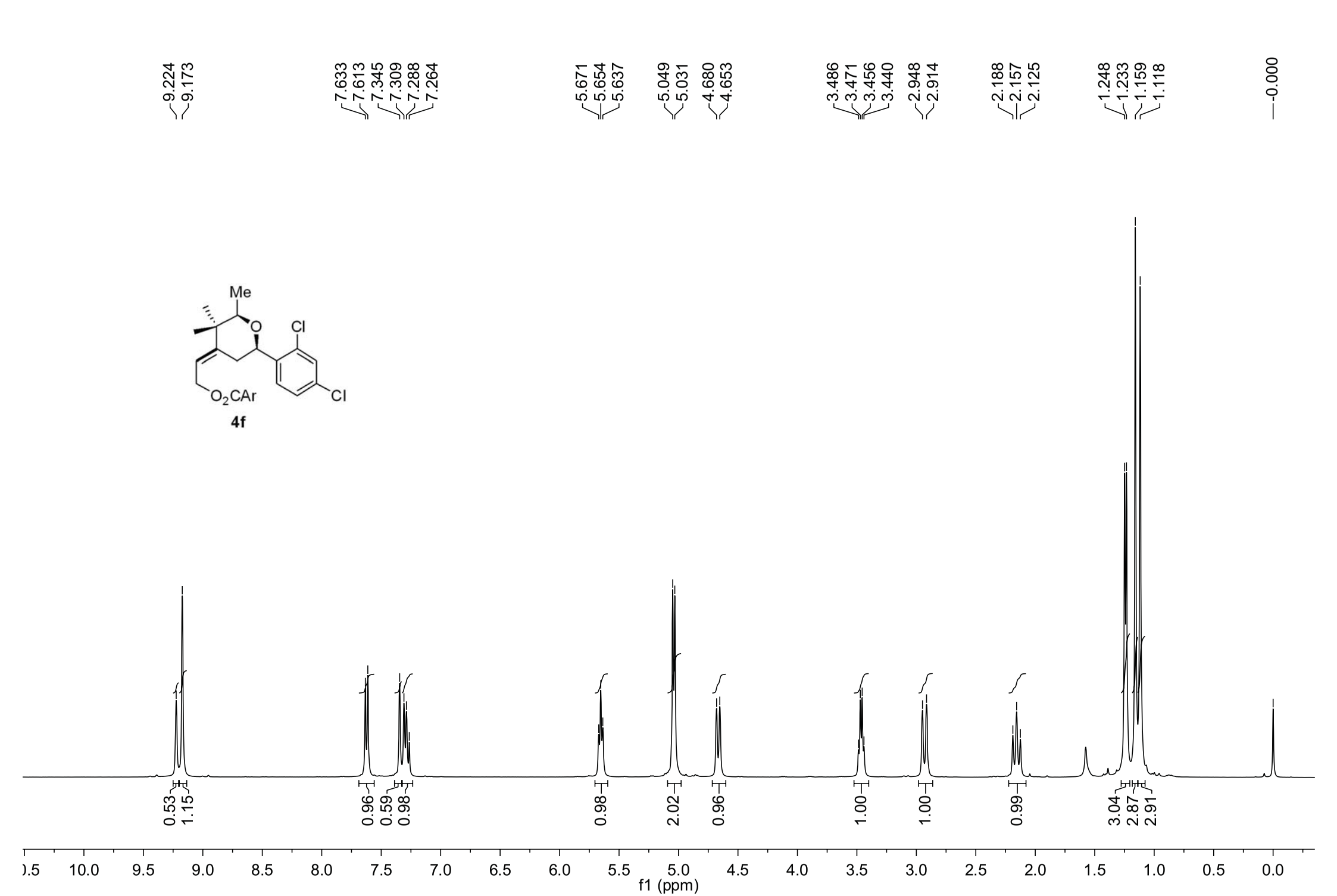
NOE of *Z*-4e

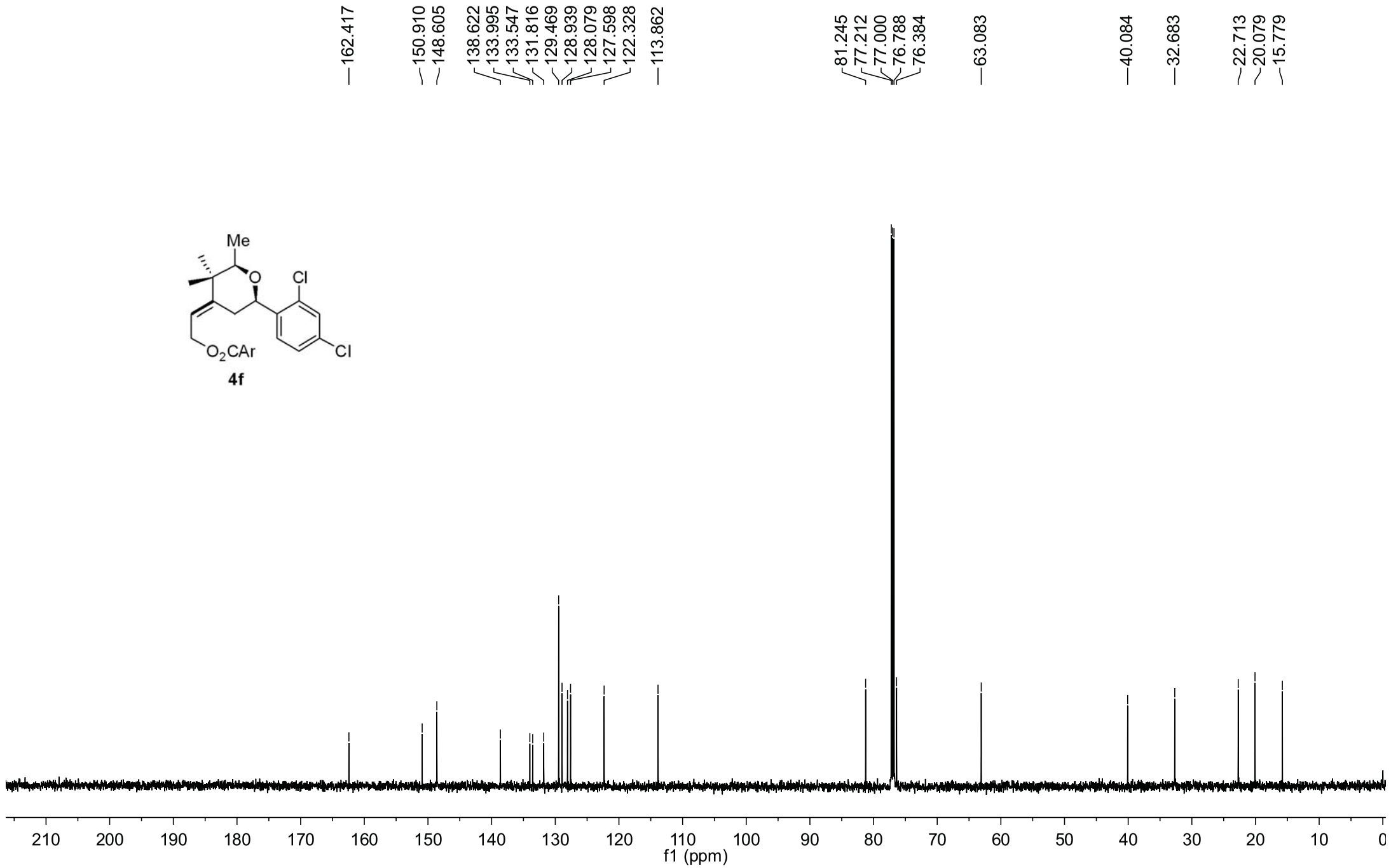
4.653
4.636
2.712
2.689
1.713
1.697
1.599
1.583
1.573
1.561
0.981
0.969
0.957
0.271
H1
H6
H5e
4.77
-100.00
1.88
0.06
0.93
2.23
0.17
0.73
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

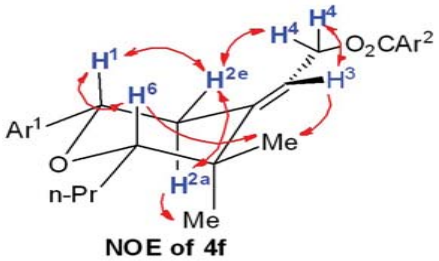
YZP-6-4 NOEDS5.09 CDCl3 600 MHz



NOE of *Z*-4e

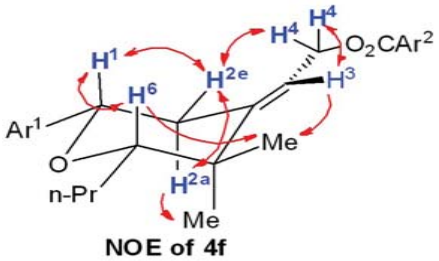

9.224
9.173
7.633
7.613
7.345
7.309
7.288
7.264
5.671
5.654
5.637
5.049
5.031
4.680
4.653
3.486
3.471
3.456
3.440
2.948
2.914
2.188
2.157
2.125
1.248
1.233
1.159
1.118
-0.000
Me
O
Cl
Cl
O2CAr
4f
0.53
1.15
0.96
0.59
0.98
0.98
2.02
0.96
1.00
1.00
0.99
3.04
2.87
2.91
f1 (ppm)


162.417
150.910
148.605
138.622
133.995
133.547
131.816
129.469
128.939
128.079
127.598
122.328
113.862
81.245
77.212
77.000
76.788
76.384
63.083
40.084
32.683
22.713
20.079
15.779
Me
O
Cl
Cl
O2CAr
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H1
H4
H4
O2CAr2
H2e
H3
H6
Ar1
O
n-Pr
H2a
Me
Me

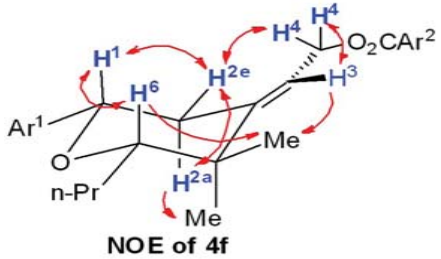
NOE of 4f

7.630
7.617
4.676
2.943
2.920
1.159
H2e
H2a
HMe
1.11
17.44
-100.00
3.66
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

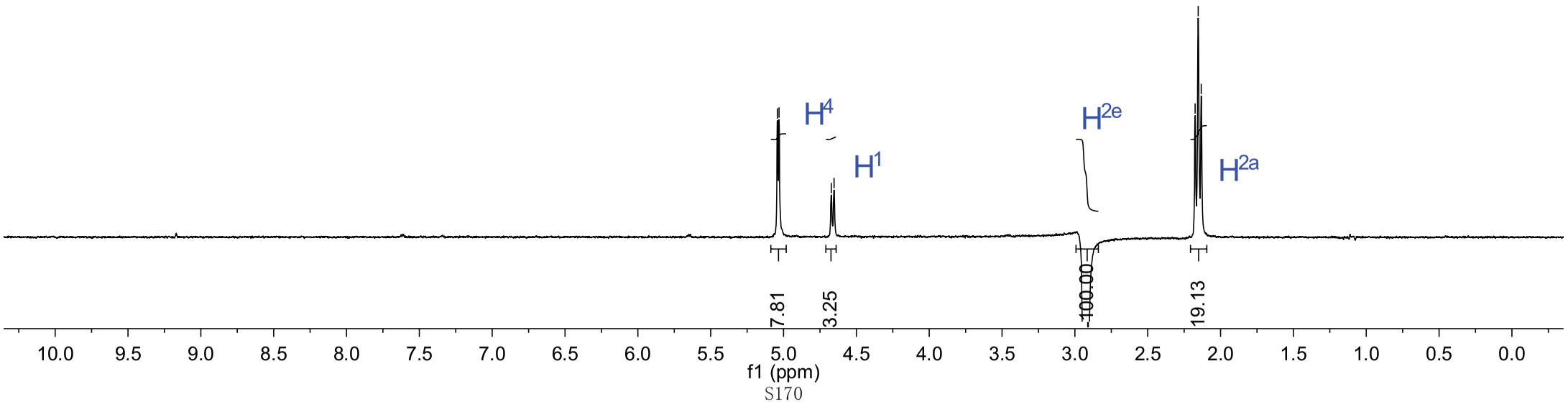

H1
H4
H4
O2CAr2
H2e
H3
H6
Ar1
Me
O
n-Pr
H2a
Me

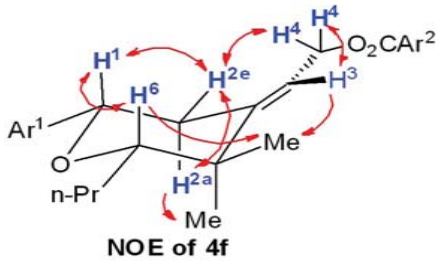
NOE of 4f

5.666
5.655
5.643
2.943
2.920
H2
H4
H2e
1.24
100.00
3.43
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H4
H4
O2CAr2
H1
H2e
H3
H6
Ar1
Me
O
H2a
n-Pr
Me

NOE of 4f


5.042
5.031
4.672
4.653
2.175
2.153
2.133
H4
H1
H2e
H2a
7.81
3.25
-100.00
19.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H1
H4
H4
O2CAr2
H2e
H3
H6
Ar1
O
n-Pr
Me
H2a
Me

NOE of 4f

4.672
4.653
1.243
1.232
1.115
H1
H6
HMe
4.32
100.00
2.91
1.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)