Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Lewis Acid-Catalyzed Friedel-Crafts Reactions toward Highly Versatile, α-Quaternary Oxime Ethers

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Content

1 General Methods

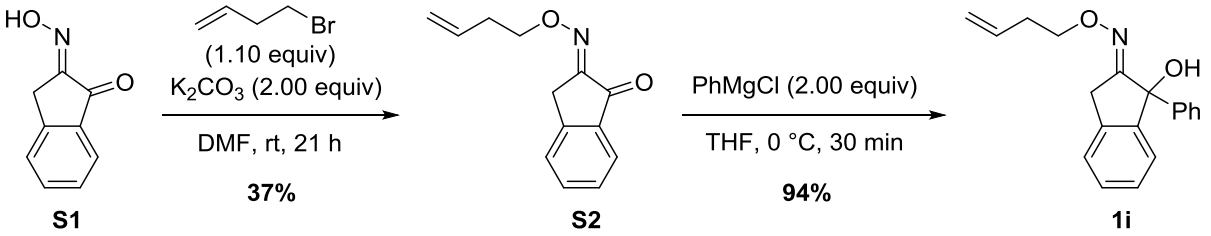
Unless otherwise noted, all reactions were carried out in oven dried glassware and in dry solvents. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded in $CDCl_3$ or DMSO-d6 at 26°C using a Mercury plus 300 MHz and a Bruker Avance DRX 400 MHz spectrometer. The spectra were referenced to residual $CHCl_3$ (7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C) or DMSO (2.50 ppm, ^{1}H; 39.52 ppm, ^{13}C), respectively. Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and related permutations. Coupling constants, *J*, are reported in Hertz and not further specified in geminal, vicinal or long-range couplings. All high-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics Apex II FT-ICR. IR spectra were obtained using a Jasco 4100 FTIR spectrometer. Melting points were determined uncorrected on a Boetius measurement device. The used solvents dichloromethane, tetrahydrofuran and toluene were dried using a MBraun Solvent Purification System (SPS) 800. Dry chloroform and methanol were purchased from Acros Organics and stored over molecular sieve. Solvents for column chromatography were of technical grade and distilled from the indicated drying reagents: dichloromethane (CaH_2), methyl-*tert*-butyl ether (KOH), ethyl acetate ($CaCl_2$) and hexane (KOH). Flash column chromatography was performed by using silica gel (Fluka, 60 Å, 230 – 400 mesh size). Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel pre-coated TLC-sheets AlugramXtra SIL G/UV_{254}. Visualization of the spots was achieved by UV-light and treatment with a vanillin staining solution.

2 Starting Materials

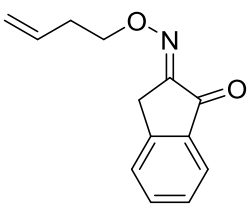
2.1 Synthesis of Cyclic 2-Hydroxy Ketoxime Ethers

Oxime **S1** as well as the 2-hydroxy ketoxime ethers **1a–h**, **2** and **3** were synthesized according to literature procedures.[1]

2-Hydroxy ketoxime ether 1i



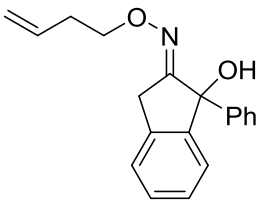
4-Bromo-1-butene (558 µL, 5.50 mmol, 1.10 equiv) was added dropwise to a suspension of oxime **S1** (806 mg, 5.00 mmol, 1.00 equiv) and K_2CO_3 (1.38 g, 10.0 mmol, 2.00 equiv) in 5.0 mL abs. DMF at room temperature. The reaction mixture was stirred for 21 hours and treated with EtOAc. It was extracted with water and sat. NaCl-solution. The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **S2** was obtained as a colorless solid (399 mg, 37%).



R_f: 0.44 (20% MTBE/hexane); **mp.:** 69-70 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.88 (d, J = 7.5 Hz, 1H), 7.64 (m, 1H), 7.49 (m, 1H), 7.42 (m, 1H), 5.83 (m, 1H), 5.12 (dt, J = 17.0, 1.5 Hz, 1H), 5.07 (dt, J = 10.5, 1.5 Hz, 1H), 4.42 (td, J = 6.5, 1.5 Hz, 2H), 3.78 (s, 2H), 2.53 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 189.4 (C=O), 154.1 (C=N), 146.9 (C_q), 137.9 (C_q), 136.0 (CH), 134.2 (CH), 128.1 (CH), 126.8 (CH), 127.7 (CH), 117.2 (CH_2), 75.3 (CH_2), 33.8 (CH_2), 29.0 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3410, 3073, 2979, 2942, 1709, 1622, 1610, 1578, 1467, 1389, 1327, 1301, 1273, 1196, 1061, 1061, 1042, 1025, 1014, 973, 922, 889, 745; **HR-MS** (ESI)**:** calcd. for $C_{13}H_{13}NO_2Na$ ([M+Na]$^+$): 238.0839, found: 238.0831; **M($C_{13}H_{13}NO_2$):** 215.25.

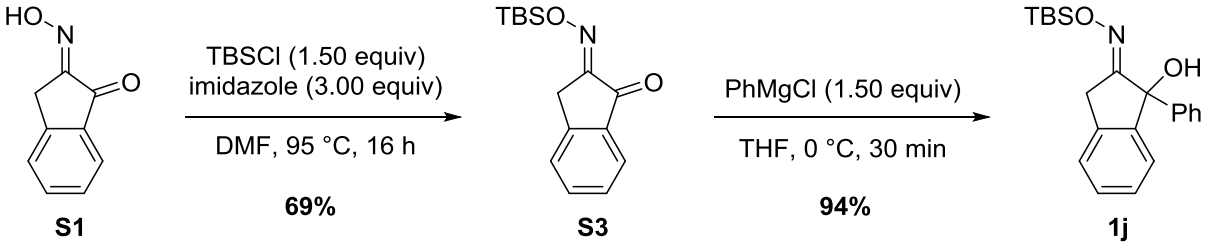
A solution of phenylmagnesiumchloride (2.0 M in THF, 1.50 mL, 3.00 mmol, 2.00 equiv) was added dropwise at 0 °C to oxime ether **S2** (323 mg, 1.50 mmol, 1.00 equiv), dissolved in 3.0 mL abs. THF. The reaction mixture was stirred at 0 °C for 30 min and quenched with sat. NH_4Cl-solution. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed

under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane) to obtain compound **1i** as a colorless solid (415 mg, 94%).

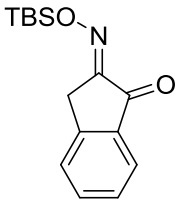


R_f: 0.35 (20% MTBE/hexane); **mp.:** 76-78 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.39-7.23 (m, 9H), 5.81 (ddt, *J* = 17.0, 10.5, 7.0 Hz, 1H), 5.10-5.03 (m, 2H), 4.16 (t, *J* = 6.5 Hz, 2H), 4.04 (d, *J* = 22.0 Hz, 1H), 3.77 (d, *J* = 22.0 Hz, 1H), 3.18 (bs, 1H), 2.41 (q, *J* = 6.5 Hz, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.2 (C=N), 145.9 (C_q), 144.8 (C_q), 137.4 (C_q), 134.9 (CH), 129.3 (CH), 128.3 (2x CH), 128.1 (CH), 127.4 (CH), 125.7 (2x CH), 125.2 (CH), 124.9 (CH), 116.8 (CH_2), 82.9 (C_q), 73.6 (CH_2), 33.9 (CH_2), 32.7 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 3064, 2950, 2886, 1644, 1477, 1450, 1408, 1375, 1196, 1176, 1046, 1018, 1001, 934, 922, 914, 868, 772, 760, 739, 727, 707, 647; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{19}NO_2Na$ ($[M+Na]^+$): 316.1308, found: 316.1306; **M($C_{19}H_{19}NO_2$):** 293.37.

2-Hydroxy ketoxime silyl ether 1j

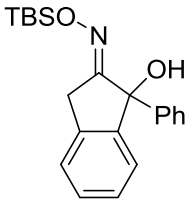


TBSCl (2.26 g, 15.0 mmol, 1.50 equiv) and imidazole (2.27 mL, 30.0 mmol, 3.00 equiv) were added to a solution of oxime **S1** (1.61 g, 10.0 mmol, 1.00 equiv) in 25 mL abs. DMF. The reaction mixture was stirred at 95 °C for 16 hours. After cooling to room temperature, the solvent was removed under reduced pressure. Water was added and it was extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 7% MTBE/hexane). Compound **S3** was obtained as a colorless solid (1.90 g, 69%).



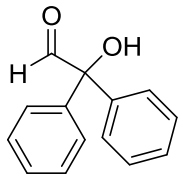
R_f: 0.50 (10% MTBE/hexane); **mp.:** 59-60 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.89 (d, *J* = 7.0 Hz, 1H), 7.64 (td, *J* = 7.5, 1.0 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 3.84 (s, 2H), 0.98 (s, 9H), 0.29 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 189.5 (C=O), 159.4 (C=N), 146.9 (CH), 138.4 (C_q), 136.0 (CH), 128.1 (CH), 126.9 (CH), 124.8 (CH), 29.2 (CH_2), 26.0 (3x CH_3), 18.2 (C_q), −5.0 (2x CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3423, 2928, 2856, 1719, 1617, 1581, 1471, 1322, 1300, 1246, 1000, 899, 866, 832, 733; **HR-MS** (ESI)**:** calcd. for ($[M+H]^+$): 276.1414, found: 276.1420; **M($C_{15}H_{21}NO_2Si$):** 275.42.

A solution of phenylmagnesiumchloride (2.0 M in THF, 3.75 mL, 7.50 mmol, 1.50 equiv) was added dropwise at 0 °C to oxime silyl ether **S3** (1.38 g, 5.00 mmol, 1.00 equiv), dissolved in 5.0 mL abs. THF. The reaction mixture was stirred at 0 °C for 30 min and quenched with sat. NH_4Cl-solution. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane) to obtain compound **1j** as a yellowish solid (1.65 g, 94%).

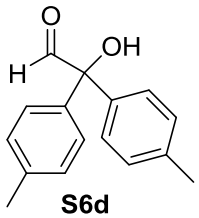


R_f: 0.37 (30% MTBE/hexane); **mp.:** 68-69 °C; **^{1}H-NMR:** (300 MHz, $CDCl_3$): δ (ppm) = 7.40-7.21 (m, 9H), 4.11 (d, J = 22.0 Hz, 2H), 3.77 (d, J = 22.0 Hz, 2H), 3.07 (bs, 1H), 0.91 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 170.8 (C=N), 145.7 (C_q), 144.7 (C_q), 137.7 (C_q), 129.3 (CH), 128.2 (2x CH), 128.0 (CH), 127.4 (CH), 125.8 (2x CH), 125.2 (CH), 125.1 (CH), 82.8 (C_q), 32.5 (CH_2), 26.2 (3x CH_3), 18.2 (C_q), −5.1 (2x CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3390, 2958, 2857, 1606, 1448, 1407, 1362, 1249, 1178, 1049, 969, 881, 847, 758, 700; **HR-MS** (ESI)**:** calcd. for ([M+Na]$^+$): 376.1703, found: 376.1700; **M($C_{21}H_{27}NO_2Si$):** 376.52.

2.2 Synthesis of 2-Hydroxy Aldehydes



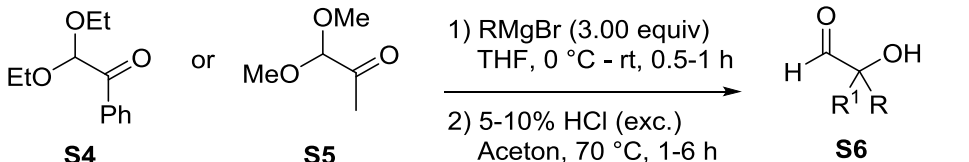
S6a



S6d

The aldehydes **S6a** and **S6d** were synthesized according to a procedure by Wulff *et al*. The spectroscopic data are in agreement with literature.[2]

General procedure 1



S4 **S5** **S6**

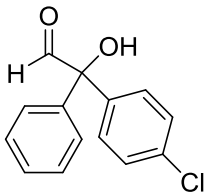
(R^1 = Ph, from **S4**)
(R^1 = Me, from **S5**)

Under an inert atmosphere, magnesium turnings (3.00 equiv) were suspended in abs. THF (0.67 M). Liquid arylbromides (3.00 equiv) were added dropwise at room temperature. Solid arylbromides (3.00 equiv) were first dissolved in minimal amounts of abs. THF before added

dropwise. The formation of the Grignard reagent started as soon as an exothermic reaction occurred and the colorless solution turned into grey/black. After complete addition, the reaction mixture was heated to reflux for 30 min and then cooled to 0 °C. The starting material **S4** or **S5**, respectively, was dissolved in abs. THF (1.0 M) and added dropwise to the Grignard reagent. The reaction mixture was stirred at room temperature for 0.5 to 1.0 hours and quenched with sat. NH_4Cl-solution at 0 °C. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude products were treated with aqueous HCl-solution (5–10%) and sufficient amounts of acetone to obtain a homogeneous solution. It was heated to 70 °C for 1–6 hours and then diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted twice with CH_2Cl_2 and the combined organic phases were washed once with sat. NaCl-solution, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude aldehyde **S6** was purified by flash column chromatography (MTBE/hexane).

2-Hydroxy aldehyde S6b

According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 1-bromo-4-chlorobenzene (5.74 g, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 2,2-diethoxy-1-phenylethanone **S4** (2.00 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 8 mL of 10% HCl-solution in 30 mL acetone at 70 °C for 1.5 hours. After flash column chromatography (5% → 10% MTBE/hexane) compound **S6b** was obtained as a yellowish oil (1.74 g, 71%).

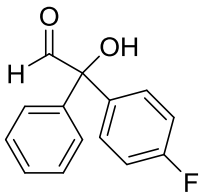


R_f: 0.27 (10% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 9.95 (s, 1H), 7.42-7.31 (m, 9H), 4.38 (bs, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 197.7 (HC=O), 139.2 (C_q), 137.9 (C_q), 134.8 (C_q), 129.2 (2x CH), 129.1 (2x CH), 129.0 (2x CH), 128.9 (CH), 127.5 (2x CH), 83.2 (C_q); **IR** (film): $\tilde{\nu}$ (cm^{-1}) = 3431, 3061, 1723, 1660, 1597, 1586, 1489, 1448, 1402, 1285, 1275, 1175, 1093, 1013, 965, 938, 924, 824, 792, 756, 731, 698, 550, 523; **HR-MS** (ESI)**:** calcd. for $C_{14}H_{10}{}^{35}ClO_2$ ($[M-H]^-$): 245.0375, found: 245.0364; **M($C_{14}H_{11}ClO_2$):** 246.69.

2-Hydroxy aldehyde S6c

According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 1-bromo-4-fluorobenzene (3.04 mL, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 2,2-diethoxy-1-

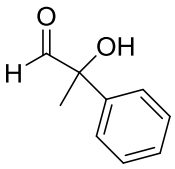
phenylethanone **S4** (2.00 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1.5 hour. The acetal was hydrolyzed with 8 mL of 10% HCl-solution in 25 mL acetone at 70 °C for 2 hours. After flash column chromatography (3% → 8% MTBE/hexane) compound **S6c** was obtained as a yellowish oil (1.92 g, 83%).



R_f: 0.24 (10% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 9.95 (s, 1H), 7.42-7.33 (m, 7H), 7.09 (t', J = 8.5 Hz, 2H), 4.38 (bs, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 197.8 (HC=O), 162.8 (d, J = 248.5 Hz, C_q), 139.3 (C_q), 135.3 (d, J = 3.0 Hz, C_q), 129.5 (d, J = 8.5 Hz, CH), 129.1 (2x CH), 128.8 (CH), 127.5 (2x CH), 116.0 (d, J = 21.7 Hz, 2x CH), 83.2 (C_q); **^{19}F-NMR** (282 MHz, $CDCl_3$)**:** δ (ppm) = −113.2; **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3469, 3063, 1724, 1660, 1599, 1506, 1448, 1279, 1229, 1159, 837, 739, 701, 601, 574; **HR-MS** (ESI)**:** calcd. for $C_{14}H_{11}FO_2Na$ ([M+Na]$^+$): 253.0635, found: 253.0634; **M($C_{14}H_{11}FO_2$):** 230.24.

2-Hydroxy aldehyde S6e

According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (2.19 g, 90.0 mmol, 3.00 equiv) and bromobenzene (9.42 mL, 90.0 mmol, 3.00 equiv) in 45 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (3.63 mL, 30.0 mmol, 1.00 equiv) dissolved in 30 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 30 mL of 7% HCl-solution in 60 mL acetone at 70 °C for 1 hour. After flash column chromatography (10% → 25% MTBE/hexane) compound **S6e** was obtained as a yellowish oil (2.36 g, 52%).

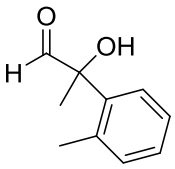


R_f: 0.50 (30% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.57 (s, 1H), 7.48-7.46 (m, 2H), 7.41 (t', J = 7.5 Hz, 2H), 7.35-7.32 (m, 1H), 3.81 (bs, 1H), 1.71 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 199.9 (HC=O), 139.3 (C_q), 129.0 (2x CH), 128.3 (CH), 125.9 (2x CH), 79.2 (C_q), 23.7 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3420, 3061, 2983, 1732, 1495, 1447, 1070, 760, 700; **HR-MS** (ESI)**:** calcd. for $C_9H_9O_2$ ([M-H]$^-$): 149.0608, found: 149.0603; **M($C_9H_{10}O_2$):** 150.18.

2-Hydroxy aldehyde S6f

According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 2-bromotoluene (3.61 mL, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 10 mL of 5% HCl-solution in 20 mL

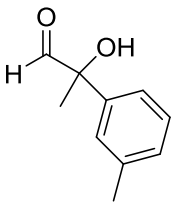
acetone at 70 °C for 2 hours. After flash column chromatography (5% → 15% MTBE/hexane) compound **S6f** was obtained as a colorless oil (1.15 g, 70%).



R_f: 0.43 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.55 (s, 1H), 7.50-7.48 (m, 1H), 7.32-7.26 (m, 2H), 7.22-7.20 (m, 1H), 3.79 (bs, 1H), 2.32 (s, 3H), 1.71 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 200.6 (HC═O), 137.6 (C_q), 136.3 (C_q), 132.3 (CH), 128.8 (CH), 126.9 (CH), 126.2 (CH), 79.8 (C_q), 23.1 (CH_3), 21.0 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2981, 1731, 1458, 759; **HR-MS** (ESI)**:** calcd. for $C_{10}H_{12}O_2Na$ ([M+Na]$^+$): 187.0730, found: 187.0722; **M($C_{10}H_{12}O_2$):** 164.20.

2-Hydroxy aldehyde S6g

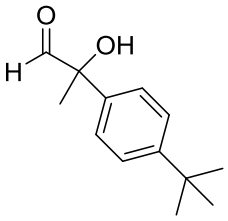
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 3-bromotoluene (3.64 mL, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 30 min. The acetal was hydrolyzed with 7 mL of 5% HCl-solution in 20 mL acetone at 70 °C for 3 hours. After flash column chromatography (5% → 15% MTBE/hexane) compound **S6g** was obtained as a colorless oil (958 mg, 58%).



R_f: 0.40 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.57 (s, 1H), 7.35-7.28 (m, 3H), 7.18 (d', J = 7.0 Hz, 1H), 3.96 (bs, 1H), 2.41 (s, 3H), 1.73 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 200.0 (HC═O), 139.2 (C_q), 138.7 (C_q), 129.0 (CH), 128.8 (CH), 126.5 (CH), 122.9 (CH), 79.2 (C_q), 23.6 (CH_3), 21.6 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2981, 2924, 1732, 1488, 1455, 1375, 1095, 1078, 831, 787, 703; **HR-MS** (ESI)**:** calcd. for: $C_{10}H_{12}O_2Na$ ([M+Na]$^+$): 187.0730, found: 187.0725; **M($C_{10}H_{12}O_2$):** 164.20.

2-Hydroxy aldehyde S6h

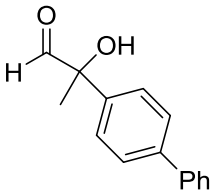
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 1-bromo-4-(*tert*-butyl)benzene (5.20 mL, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 7 mL of 5% HCl-solution in 20 mL acetone at 70 °C for 2 hours. After flash column chromatography (5% → 15% MTBE/hexane) compound **S6g** was obtained as a colorless oil (1.28 g, 62%).



R_f: 0.34 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.54 (s, 1H), 7.45 (d', *J* = 8.5 Hz, 2H), 7.41 (d', *J* = 8.5 Hz, 2H), 4.01 (bs, 1H), 1.70 (s, 3H), 1.35 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 200.0 (HC=O), 151.2 (C_q), 136.2 (C_q), 125.8 (2x CH), 125.6 (2x CH), 79.0 (C_q), 34.6 (C_q), 31.3 (3x CH_3), 23.5 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 2965, 2904, 2868, 2360, 1732, 1509, 1460, 1111, 1095, 865, 835, 590, 575; **HR-MS** (ESI)**:** calcd. for $C_{13}H_{18}O_2Na$ ([M+Na]$^+$): 229.1199, found: 229.1188; **M($C_{13}H_{18}O_2$):** 206.29.

2-Hydroxy aldehyde S6i

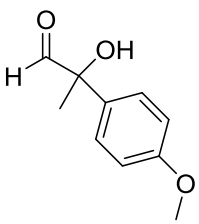
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 1-bromo-4-phenylbenzene (6.99 g, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 10 mL of 5% HCl-solution in 20 mL acetone at 70 °C for 4.5 hours. After flash column chromatography (10% → 20% MTBE/hexane) compound **S6i** was obtained as a colorless solid (1.40 g, 62%).



R_f: 0.21 (20% MTBE/hexane); **mp.:** 79-81 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 9.60 (s, 1H), 7.65-7.53 (m, 6H), 7.47-7.43 (m, 2H), 7.39-7.34 (m, 1H), 3.86 (bs, 1H), 1.75 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 199.8 (HC=O), 141.3 (C_q), 140.5 (C_q), 138.3 (C_q), 129.0 (2x CH), 127.74 (2x CH), 127.71 (CH), 127.3 (2x CH), 126.4 (2x CH), 79.2 (C_q), 23.8 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3464, 2993, 2822, 1723, 1486, 1314, 1094, 1076, 865, 767, 735, 694; **HR-MS** (ESI)**:** calcd. for $C_{15}H_{14}O_2Na$ ([M+Na]$^+$): 249.0886, found: 249.0884; **M($C_{15}H_{14}O_2$):** 226.28.

2-Hydroxy aldehyde S6j

According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 4-bromoanisole (3.77 mL, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 30 min. The acetal was hydrolyzed with 10 mL of 5% HCl-solution in 20 mL acetone at 70 °C for 2 hours. After flash column chromatography (10% → 20% MTBE/hexane) compound **S6j** was obtained as a colorless solid (982 mg, 55%).

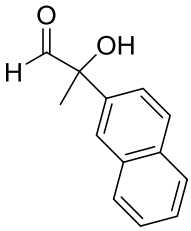


R_f: 0.32 (40% MTBE/hexane); **mp.:** 45-46 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.49 (s, 1H), 7.37 (d', *J* = 9.0 Hz, 2H), 6.93 (d', *J* = 9.0 Hz, 2H), 3.81 (s, 4H), 1.68 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 199.8

(HC═O), 159.7 (C_q), 131.1 (C_q), 127.3 (2x CH), 114.4 (2x CH), 78.8 (C_q), 55.6 (CH_3), 23.4 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3470, 3006, 2992, 2960, 2865, 2838, 1716, 1609, 1510, 1320, 1304, 1256, 1218, 1181, 1091, 1075, 1033, 861, 822, 808, 763, 546; **HR-MS** (ESI)**:** calcd. for $C_{10}H_{12}O_3Na$ ([M+Na]$^+$): 203.0679, found: 203.0681; **M($C_{10}H_{12}O_3$):** 180.20.

2-Hydroxy aldehyde S6k

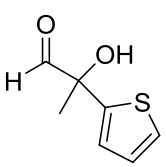
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 2-bromonaphthalene (6.21 g, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 10 mL of 5% HCl-solution in 20 mL acetone at 70 °C for 1.5 hours. After flash column chromatography (10% → 20% MTBE/hexane) compound **S6k** was obtained as a yellowish oil (1.23 g, 62%).



R_f: 0.27 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 9.64 (s, 1H), 7.97 (d, *J* = 1.5 Hz, 1H), 7.89-7.84 (m, 3H), 7.57-7.50 (m, 3H), 4.09 (bs, 1H), 1.81 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 199.9 (HC═O), 136.6 (C_q), 133.3 (C_q), 133.0 (C_q), 128.8 (CH), 128.3 (CH), 127.7 (CH), 126.6 (CH), 126.6 (CH), 125.2 (CH), 123.4 (CH), 79.4 (C_q), 23.7 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 3057, 2981, 2934, 1730, 1598, 1506, 1376, 1272, 1192, 1128, 1098, 1069, 951, 900, 858, 821, 751, 478; **HR-MS** (ESI)**:** calcd. for $C_{13}H_{12}O_2Na$ ([M+Na]$^+$): 223.0730, found: 223.0727; **M($C_{13}H_{12}O_2$):** 200.24.

2-Hydroxy aldehyde S6l

According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (729 mg, 30.0 mmol, 3.00 equiv) and 2-bromothiophene (2.88 mL, 30.0 mmol, 3.00 equiv) in 15 mL abs. THF, and then treated with 1,1-dimethoxypropan-2-one **S5** (1.21 mL, 10.0 mmol, 1.00 equiv) dissolved in 10 mL abs. THF. It was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 10 mL of 5% HCl-solution in 20 mL acetone at 70 °C for 3 hours. After flash column chromatography (5% → 15% MTBE/hexane) compound **S6l** was obtained as a yellow oil (506 mg, 32%).

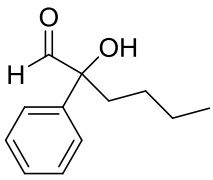


R_f: 0.24 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.48 (s, 1H), 7.33 (m, 1H), 7.05 (m, 1H), 7.02 (m, 1H), 4.05 (bs, 1H), 1.75 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 197.5 (HC═O), 143.9 (C_q), 127.9 (CH), 126.6 (CH), 124.9 (CH), 78.1 (C_q), 24.2 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 3104,

2984, 2935, 1731, 1450, 1434, 1239, 1121, 1099, 987, 850, 839, 702; **HR-MS** (ESI)**:** calcd. for $C_7H_8O_2SNa$ ([M+Na]$^+$): 179.0137, found: 179.0132; **M($C_7H_8O_2S$):** 156.20.

2-Hydroxy aldehyde S6m

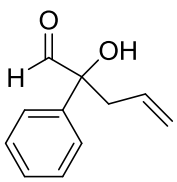
According to a modification of the general procedure 1, 2,2-diethoxy-1-phenylethanone **S4** (2.00 mL, 10.0 mmol, 1.00 equiv) was dissolved in 15 mL abs. THF and cooled to −78 °C. A solution of *n*-Butyllithium (2.5 M in hexane, 8.00 mL, 20.0 mmol, 2.00 equiv) was added dropwise and the reaction mixture was stirred at 0 °C for 2 hour. The acetal was hydrolyzed with 8 mL of 10% HCl-solution in 25 mL acetone at 70 °C for 1 hour. After flash column chromatography (5% → 10% MTBE/hexane) compound **S6m** was obtained as a yellowish oil (1.07 g, 56%).



R_f: 0.35 (10% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** *δ* (ppm) = 9.59 (s, 1H), 7.50 (d‘, *J* = 7.5 Hz, 2H), 7.41 (t‘, *J* = 7.5 Hz, 2H), 7.32 (t‘, *J* = 7.0 Hz, 1H), 3.81 (bs, 1H), 2.12-1.96 (m, 2H), 1.35-1.23 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** *δ* (ppm) = 200.5 (HC═O), 138.7 (C_q), 129.0 (2x CH), 128.0 (CH), 125.9 (2x CH), 82.0 (C_q), 36.7 (CH_2), 25.0 (CH_2), 23.0 (CH_2), 14.0 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3489, 3061, 2957, 2933, 2872, 1725, 1684, 1448, 756, 700; **HR-MS** (ESI)**:** calcd. for $C_{12}H_{16}O_2Na$ ([M+Na]$^+$): 215.1043, found: 215.1043; **M($C_{12}H_{16}O_2$):** 192.26.

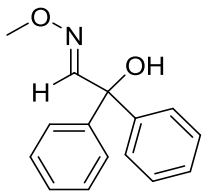
2-Hydroxy aldehyde S6n

According to a modification of the general procedure 1, 2,2-diethoxy-1-phenylethanone **S4** (2.00 mL, 10.0 mmol, 1.00 equiv) was dissolved in 15 mL abs. THF and cooled to 0 °C. A solution of allylmagnesiumchloride (1.7 M in THF, 11.8 mL, 20.0 mmol, 2.00 equiv) was added dropwise and the reaction mixture was stirred at room temperature for 1 hour. The acetal was hydrolyzed with 8 mL of 10% HCl-solution in 25 mL acetone at 70 °C for 2 hours. After flash column chromatography (5% MTBE/hexane) compound **S6n** was obtained as a yellowish oil (1.50 g, 85%).



R_f: 0.46 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** *δ* (ppm) = 9.61 (s, 1H), 7.50 (d‘, *J* = 7.5 Hz, 2H), 7.42 (t‘, *J* = 7.5 Hz, 2H), 7.33 (t‘, *J* = 7.5 Hz, 1H), 5.71 (ddt, *J* = 17.5, 10.0, 7.0 Hz, 1H), 5.23-5.16 (m, 2H), 3.70 (bs, 1H), 2.87-2.84 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** *δ* (ppm) = 200.0 (HC═O), 138.2 (C_q), 131.3 (CH), 129.0 (2x CH), 128.3 (CH), 125.9 (2x CH), 120.4 (C_q), 81.2 (C_q), 41.7 (CH_2); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3483, 3077, 1726, 1448, 996, 923, 759, 700; **HR-MS** (ESI)**:** calcd. for $C_{11}H_{12}O_2Na$ ([M+Na]$^+$): 199.0730, found: 199.0729; **M($C_{11}H_{12}O_2$):** 176.22.

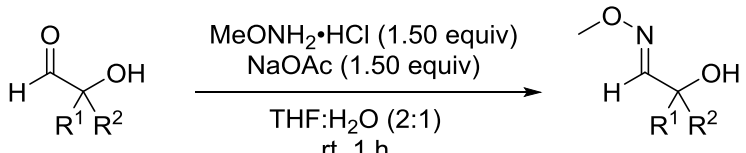
2.3 Synthesis of 2-Hydroxy Aldoxime Ethers



7a

2-Hydroxy aldoxime ether **7a** was synthesized according to a literature procedure. The spectroscopic data are in agreement.[1]

General procedure 2

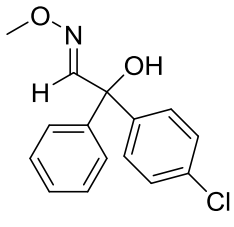


S6a-n **7a-o**

Methoxyamine hydrochloride (1.50 equiv) and sodium acetate (1.50 equiv) were added portionwise to a solution of aldehyde **S6** (1.00 equiv) in a 2:1-mixture (0.17 M) of THF and H_2O at room temperature. The reaction mixture was stirred at room temperature for 1 hour. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were washed once with sat. $NaHCO_3$-solution, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Compounds **7** were purified by flash column chromatography (MTBE/hexane).

2-Hydroxy aldoxime ether 7b

According to the general procedure 2, the aldehyde **S6b** (493 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (3% → 8% MTBE/hexane) compound **7b** was obtained as a colorless oil (463 mg, 84%, *E/Z* >95:5).

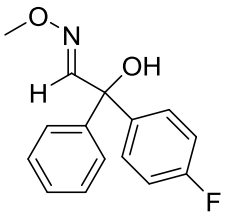


R_f: 0.18 (5% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.96 (s, 1H), 7.36-7.31 (m, 9H), 4.11 (bs, 1H), 3.92 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 152.0 (HC=N), 143.6 (C_q), 142.6 (C_q), 133.9 (C_q), 128.7 (4x CH), 128.5 (2x CH), 128.1 (CH), 126.9 (2x CH), 77.1 (C_q), 62.5 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3484, 3061, 2938, 1491, 1448,

1401, 1169, 1093, 1049, 1014, 915, 830, 755, 700, 648; **HR-MS** (ESI)**:** calcd. for $C_{15}H_{14}{}^{35}ClNO_2Na$ ([M+Na]$^+$): 298.0605, found: 298.0612; **M($C_{15}H_{14}ClNO_2$):** 275.73.

2-Hydroxy aldoxime ether 7c

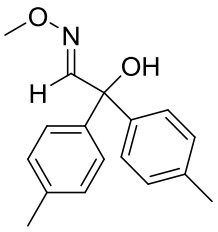
According to the general procedure 2, the aldehyde **S6c** (461 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (3% → 10% MTBE/hexane) compound **7c** was obtained as a colorless oil (451 mg, 87%, *E/Z* >95:5).



R_f: 0.13 (5% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.96 (s, 1H), 7.36-7.30 (m, 7H), 7.03 (t', *J* = 8.5 Hz, 2H), 4.11 (bs, 1H), 3.92 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 162.4 (d, *J* = 247.0 Hz, C_q), 152.2 (HC═N), 143.8 (C_q), 139.9 (C_q), 128.9 (d, *J* = 8.0 Hz, 2x CH), 128.6 (2x CH), 128.1 (CH), 126.9 (2x CH), 115.4 (d, *J* = 21.5 Hz, 2x CH), 62.5 (CH_3); **^{19}F-NMR** (282 MHz, $CDCl_3$)**:** δ (ppm) = −114.6; **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3482, 3062, 2940, 1603, 1448, 1227, 1161, 1049, 986, 838, 741, 700, 581; **HR-MS** (ESI)**:** calcd. for $C_{15}H_{14}FNO_2Na$ ([M+Na]$^+$): 282.0901, found: 282.0900; **M($C_{15}H_{14}FNO_2$):** 259.28.

2-Hydroxy aldoxime ether 7d

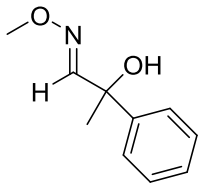
According to the general procedure 2, the aldehyde **S6d** (481 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (5% → 10% MTBE/hexane) compound **7d** was obtained as a colorless oil (144 mg, 27%, *E/Z* >95:5).



R_f: 0.34 (10% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.96 (s, 1H), 7.25 (d', *J* = 8.0 Hz, 4H), 7.15 (d', *J* = 8.0 Hz, 4H), 3.98 (bs, 1H), 3.91 (s, 3H), 2.35 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 152.8 (HC═N), 141.2 (2x C_q), 137.6 (2x C_q), 129.2 (4x CH), 126.9 (4x CH), 77.3 (C_q), 62.3 (CH_3), 21.2 (2x CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3502, 3025, 2938, 2921, 1611, 1509, 1184, 1165, 1049, 817, 754; **HR-MS** (ESI)**:** calcd. for $C_{17}H_{19}NO_2Na$ ([M+Na]$^+$): 292.1308, found: 292.1304; **M($C_{17}H_{19}NO_2$):** 269.34.

2-Hydroxy aldoxime ether 7e

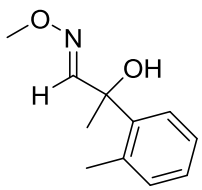
According to the general procedure 2, the aldehyde **S6e** (1.50 g, 10.0 mmol, 1.00 equiv), methoxyamine hydrochloride (1.25 g, 15.0 mmol, 1.50 equiv) and sodium acetate (1.23 g, 15.0 mmol, 1.50 equiv) in 20 mL THF and 10 mL H_2O were used. After flash column chromatography (5% → 15% MTBE/hexane) compound **7d** was obtained as a colorless oil (1.34 g, 75%, *E/Z* = 94:6).



R_f: 0.55 (30% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.59 (s, 1H), 7.48-7.45 (m, 2H), 7.37 (t', *J* = 7.5 Hz, 2H), 7.29 (m, 1H), 3.88 (s, 3H), 3.19 (bs, 1H), 1.71 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.5 (HC═N), 144.3 (C_q), 128.7 (2x CH), 127.6 (CH), 125.2 (2x CH), 73.4 (C_q), 62.1 (CH_3), 28.4 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 2937, 23259, 1492, 1447, 1372, 1218, 1052, 956, 885, 700, 595, 450; **HR-MS** (ESI)**:** calcd. for ($[M+Na]^+$): 202.0839, found: 202.0833; **M($C_{10}H_{13}NO_2$):** 179.22.

2-Hydroxy aldoxime ether 7f

According to the general procedure 2, the aldehyde **S6f** (328 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 15% MTBE/hexane) compound **7f** was obtained as a colorless oil (316 mg, 82%, *E/Z* = 91:9).

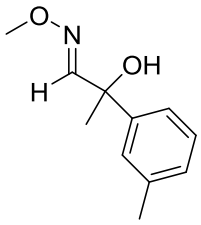


R_f: 0.46 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.59 (s, 1H), 7.50-7.47 (m, 1H), 7.21-7.15 (m, 3H), 3.88 (s, 3H), 2.98 (bs, 1H), 2.46 (s, 3H), 1.77 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.6 (HC═N), 141.2 (C_q), 136.5 (C_q), 132.6 (CH), 128.1 (CH), 126.0 (CH), 125.9 (CH), 74.2 (C_q), 62.1 (CH_3), 27.8 (CH_3), 21.7 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2938, 1732, 1458, 1372, 1052, 885, 764, 728; **HR-MS** (ESI)**:** calcd. for $C_{11}H_{15}NO_2Na$ ($[M+Na]^+$): 216.0995, found: 216.0986; **M($C_{11}H_{15}NO_2$):** 193.25.

2-Hydroxy aldoxime ether 7g

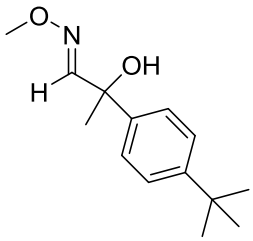
According to the general procedure 2, the aldehyde **S6g** (328 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 15% MTBE/hexane) compound **7g** was obtained as a colorless oil (337 mg, 87%, *E/Z* = 95:5).



R_f: 0.39 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.61 (s, 1H), 7.31-7.27 (m, 3H), 7.14-7.12 (m, 1H), 3.91 (s, 3H), 3.23 (bs, 1H), 2.40 (s, 3H), 1.73 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.6 (HC=N), 144.3 (C_q), 138.3 (C_q), 128.5 (CH), 128.48 (CH), 125.8 (CH), 122.2 (CH), 73.4 (C_q), 62.1 (CH_3), 28.4 (CH_3), 21.7 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2981, 2938, 1607, 1457, 1053, 887, 788, 705; **HR-MS** (ESI)**:** calcd. for $C_{11}H_{15}NO_2Na$ ([M+Na]$^+$): 216.0995, found: 216.0985; **M($C_{11}H_{15}NO_2$):** 193.25.

2-Hydroxy aldoxime ether 7h

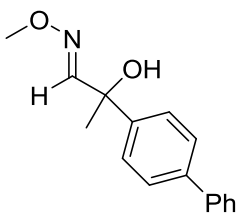
According to the general procedure 2, the aldehyde **S6h** (413 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 15% MTBE/hexane) compound **7h** was obtained as a colorless oil (390 mg, 83%, *E/Z* = 95:5).



R_f: 0.41 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.58 (s, 1H), 7.39 (s, 4H), 3.87 (s, 3H), 3.18 (bs, 1H), 1.71 (s, 3H), 1.32 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.7 (HC=N), 150.6 (C_q), 141.3 (C_q), 125.6 (2x CH), 124.9 (2x CH), 73.2 (C_q), 62.1 (CH_3), 34.6 (C_q), 31.5 (3x CH_3), 28.2 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2965, 2901, 2867, 2360, 1734, 1510, 1461, 1363, 1110, 1053, 886, 835, 595; **HR-MS** (ESI)**:** calcd. for $C_{14}H_{21}NO_2Na$ ([M+Na]$^+$): 258.1465, found: 258.1461; **M($C_{14}H_{21}NO_2$):** 235.33.

2-Hydroxy aldoxime ether 7i

According to the general procedure 2, the aldehyde **S6i** (453 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 20% MTBE/hexane) compound **7i** was obtained as a colorless oil (440 mg, 86%, *E/Z* = 95:5).

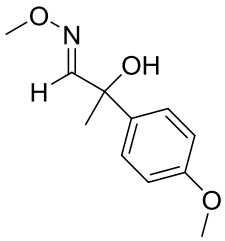


R_f: 0.31 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.64 (s, 1H), 7.62-7.58 (m, 4H), 7.55 (d‘, *J* = 8.5 Hz, 2H), 7.45 (t‘, *J* = 7.5 Hz, 2H), 7.38-7.35 (m, 1H), 3.90 (s, 3H), 3.32 (bs, 1H), 1.76 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.4 (HC=N), 143.3 (C_q), 140.8 (C_q), 140.6 (C_q), 128.9 (2x CH), 127.5 (CH), 127.4 (2x CH), 127.2

(2x CH), 125.7 (2x CH), 73.3 (C_q), 62.1 (CH_3), 28.4 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 2982, 2936, 1713, 1486, 1051, 766, 698; **HR-MS** (ESI)**:** calcd. for $C_{16}H_{17}NO_2Na$ ($[M+Na]^+$): 278.1152, found: 278.1142; **M($C_{16}H_{17}NO_2$):** 255.32.

2-Hydroxy aldoxime ether 7j

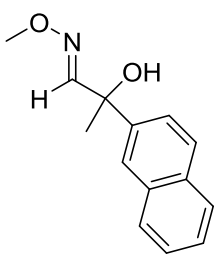
According to the general procedure 2, the aldehyde **S6j** (360 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 20% MTBE/hexane) compound **7j** was obtained as a colorless oil (383 mg, 92%, *E/Z* >95:5).



R_f: 0.24 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.55 (s, 1H), 7.37 (d', *J* = 9.0 Hz, 2H), 6.89 (d', *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.18 (bs, 1H), 1.69 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 159.1 (C_q), 153.7 (HC=N), 136.4 (C_q), 126.5 (2x CH), 114.0 (2x CH), 73.1 (C_q), 62.1 (CH_3), 55.4 (CH_3), 28.3 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2956, 2936, 2836, 1733, 1717, 1610, 1509, 1463, 1300, 1250, 1179, 1051, 1033, 885, 834; **HR-MS** (ESI)**:** calcd. for $C_{11}H_{15}NO_3Na$ ($[M+Na]^+$): 232.0944, found: 232.0944; **M($C_{11}H_{15}NO_3$):** 209.25.

2-Hydroxy aldoxime ether 7k

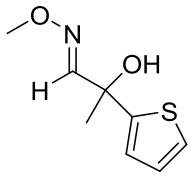
According to the general procedure 2, the aldehyde **S6k** (400 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 20% MTBE/hexane) compound **7k** was obtained as a colorless oil (355 mg, 78%, *E/Z* = 94:6).



R_f: 0.29 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.95 (s, 1H), 7.86-7.82 (m, 3H), 7.68 (s, 1H), 7.56 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.50-7.47 (m, 2H), 3.91 (s, 3H), 3.35 (bs, 1H), 1.81 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 153.4 (HC=N), 141.7 (C_q), 133.3 (C_q), 132.8 (C_q), 128.44 (CH), 128.35 (CH), 127.7 (CH), 126.4 (CH), 126.3 (CH), 123.8 (CH), 123.6 (CH), 73.6 (C_q), 62.2 (CH_3), 28.4 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 3057, 2982, 2937, 2898, 2817, 1599, 1507, 1463, 1373, 1189, 1127, 1051, 951, 889, 859, 819, 749, 477; **HR-MS** (ESI)**:** calcd. for $C_{14}H_{15}NO_2Na$ ($[M+Na]^+$): 252.0995, found: 252.0986; **M($C_{14}H_{15}NO_2$):** 229.28.

2-Hydroxy aldoxime ether 7l

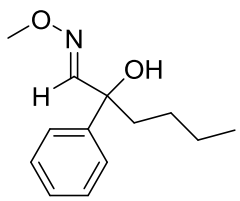
According to the general procedure 2, the aldehyde **S6l** (312 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (10% → 15% MTBE/hexane) compound **7k** was obtained as a yellowish oil (226 mg, 61%, *E/Z* >95:5).



R_f: 0.39 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.61 (s, 1H), 7.29-7.27 (m, 1H), 7.01-6.98 (m, 2H), 3.91 (s, 3H), 3.57 (bs, 1H), 1.81 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 152.4 (HC═N), 149.4 (C_q), 127.2 (CH), 125.2 (CH), 123.5 (CH), 72.1 (C_q), 62.2 (CH_3), 28.9 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2983, 2938, 1732, 1707, 1682, 1456, 1238, 1051, 703; **HR-MS** (ESI)**:** calcd. for $C_8H_{11}NO_2SNa$ ([M+Na]$^+$): 208.0403, found: 208.0403; **M($C_8H_{11}NO_2S$):** 185.24.

2-Hydroxy aldoxime ether 7m

According to the general procedure 2, the aldehyde **S6m** (385 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column chromatography (5% MTBE/hexane) compound **7m** was obtained as a colorless oil (406 mg, 92%, *E/Z* >95:5).

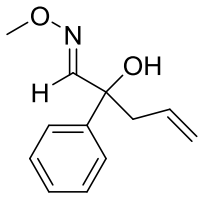


R_f: 0.59 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.62 (s, 1H), 7.45 (d‘, *J* = 7.5 Hz, 2H), 7.36 (t‘, *J* = 7.5 Hz, 2H), 7.28-7.25 (m, 1H), 3.86 (s, 3H), 3.36 (bs, 1H), 2.02-1.87 (m, 2H), 1.35-1.24 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.3 (HC═N), 143.8 (C_q), 128.6 (2x CH), 127.4 (CH), 125.3 (2x CH), 75.6 (C_q), 62.2 (CH_3), 41.0 (CH_2), 25.5 (CH_2), 23.0 (CH_2), 14.1 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3482, 3061, 2957, 2872, 1448, 1062, 1034, 702; **HR-MS** (ESI)**:** calcd. for $C_{13}H_{19}NO_2Na$ ([M+Na]$^+$): 244.1308, found: 244.1299; **M($C_{13}H_{19}NO_2$):** 221.30.

2-Hydroxy aldoxime ether 7n

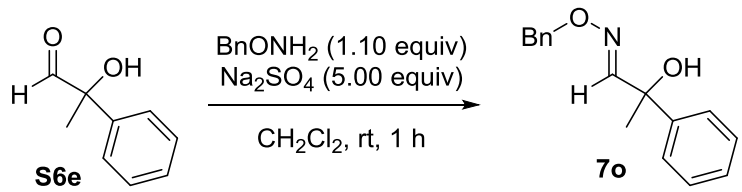
According to the general procedure 2, the aldehyde **S6n** (350 mg, 2.00 mmol, 1.00 equiv), methoxyamine hydrochloride (250 mg, 3.00 mmol, 1.50 equiv) and sodium acetate (246 mg, 3.00 mmol, 1.50 equiv) in 4.0 mL THF and 2.0 mL H_2O were used. After flash column

chromatography (3% → 5% MTBE/hexane) compound **7n** was obtained as a colorless oil (337 mg, 82%, *E/Z* >95:5).

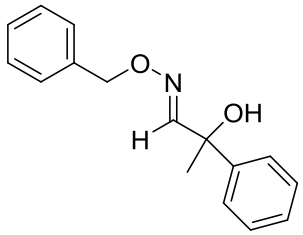


R_f: 0.50 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.58 (s, 1H), 7.48-7.44 (m, 2H), 7.40-7.34 (m, 2H), 7.30-7.27 (m, 1H), 5.75 (ddt, *J* = 17.5, 10.0, 7.0 Hz, 1H), 5.19-5.12 (m, 2H), 3.88 (s, 3H), 3.25 (bs, 1H), 2.84-2.69 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 152.7 (HC═N), 143.1 (C_q), 132.7 (CH), 128.6 (2x CH), 127.6 (CH), 125.4 (2x CH), 120.0 (CH_2), 74.8 (C_q), 62.2 (CH_3), 45.6 (CH_2); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3482, 3076, 2939, 1639, 1494, 1448, 1037, 1001, 917, 889, 763, 702; **HR-MS** (ESI)**:** calcd. for $C_{12}H_{15}NO_2Na$ ($[M+Na]^+$): 228.0995, found: 228.0994; **M($C_{12}H_{15}NO_2$):** 205.26.

2-Hydroxy aldoxime ether 7o

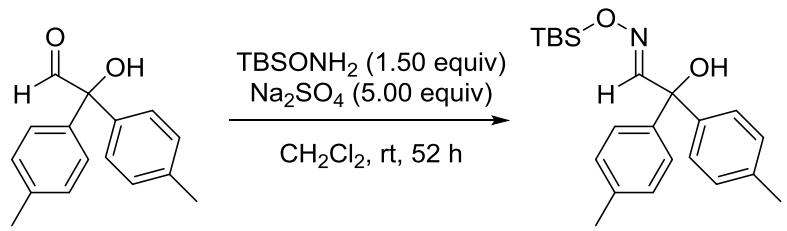


$BnONH_2$ (305 μL, 2.64 mmol, 1.10 equiv) and sodiumsulfate (1.70 g, 12.0 mmol, 5.00 equiv) were added portionwise to a solution of aldehyde **S6e** (360 mg, 2.40 mmol, 1.00 equiv) in 5.0 mL abs. CH_2Cl_2. The reaction mixture was stirred at room temperature for 1 hour and then filtered. The solvent was removed under reduced pressure. After flash column chromatography (3% → 7% EtOAc/hexane) compound **7o** was obtained as a colorless oil (480 mg, 78%, *E/Z* >95:5).



R_f: 0.33 (10% EtOAc/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.69 (s, 1H), 7.49-7.46 (m, 2H), 7.42-7.29 (m, 8H), 5.15 (s, 2H), 3.24 (bs, 1H), 1.74 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.1 (HC═N), 144.3 (C_q), 137.2 (C_q), 128.62 (2x CH), 128.58 (2x CH), 128.55 (2x CH), 128.2 (CH), 127.6 (CH), 125.2 (2x CH), 76.5 (C_q), 73.6 (CH_2), 28.4 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3434, 3030, 2982, 2930, 1601, 1495, 1453, 1369, 1026, 760, 739, 699; **HR-MS** (ESI)**:** calcd. for $C_{16}H_{17}NO_2Na$ ($[M+Na]^+$): 278.1152, found: 278.1146; **M($C_{16}H_{17}NO_2$):** 255.32.

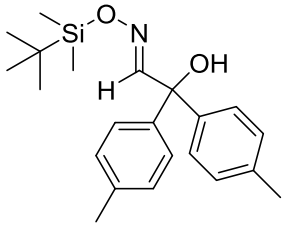
2-Hydroxy aldoxime silyl ether 7p



S6d **7p**

$TBSONH_2$ was synthesized according to a literature procedure.[3]

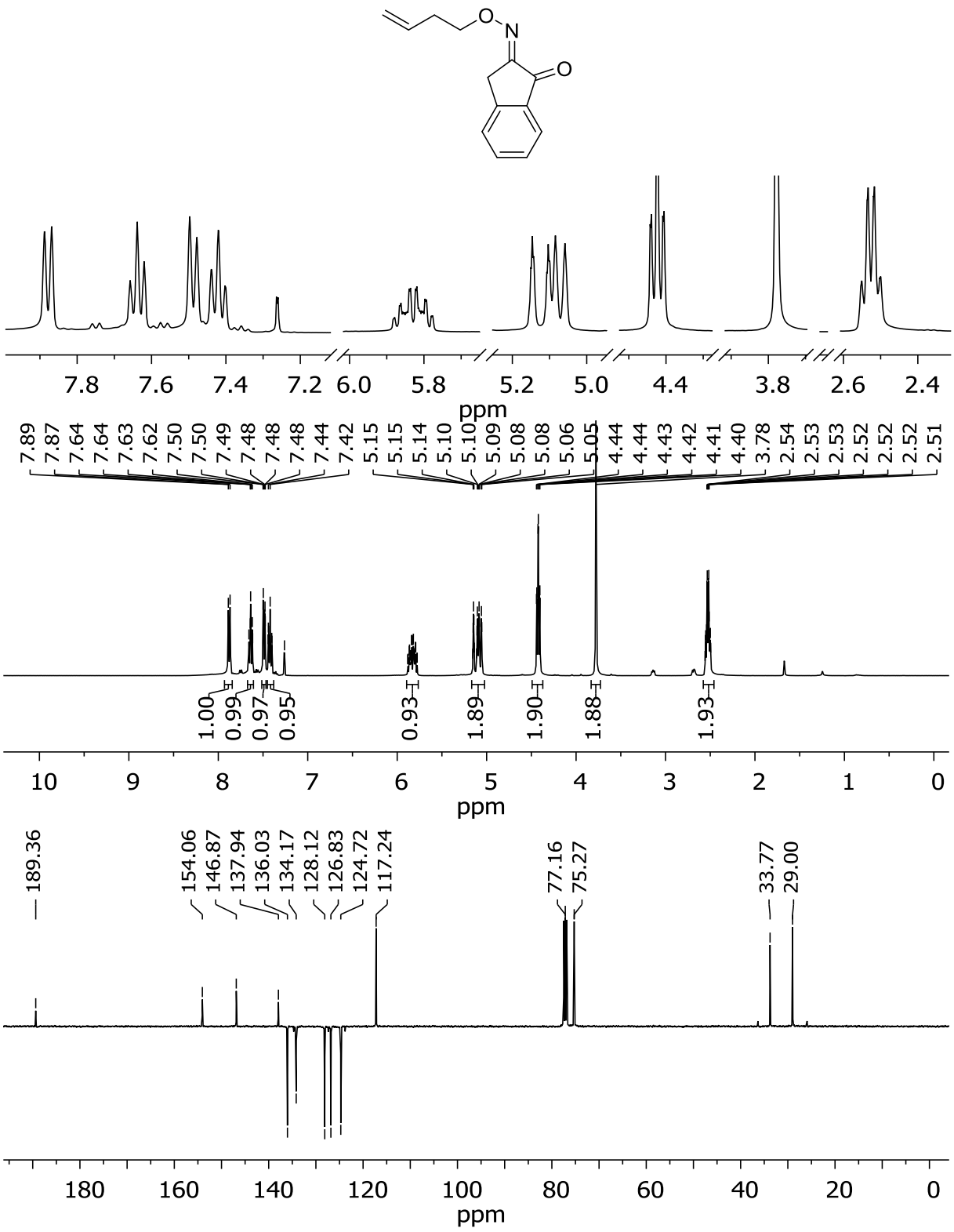
$TBSONH_2$ (221 mg, 1.50 mmol, 1.50 equiv) and sodiumsulfate (710 g, 5.00 mmol, 5.00 equiv) were added portionwise to a solution of aldehyde **S6d** (240 mg, 1.00 mmol, 1.00 equiv) in 3.0 mL abs. CH_2Cl_2. The reaction mixture was stirred at room temperature for 52 hours and then filtered. The solvent was removed under reduced pressure. After flash column chromatography (2% → 3% MTBE/hexane) compound **7p** was obtained as a colorless oil (247 mg, 67%, *E/Z* >95:5).



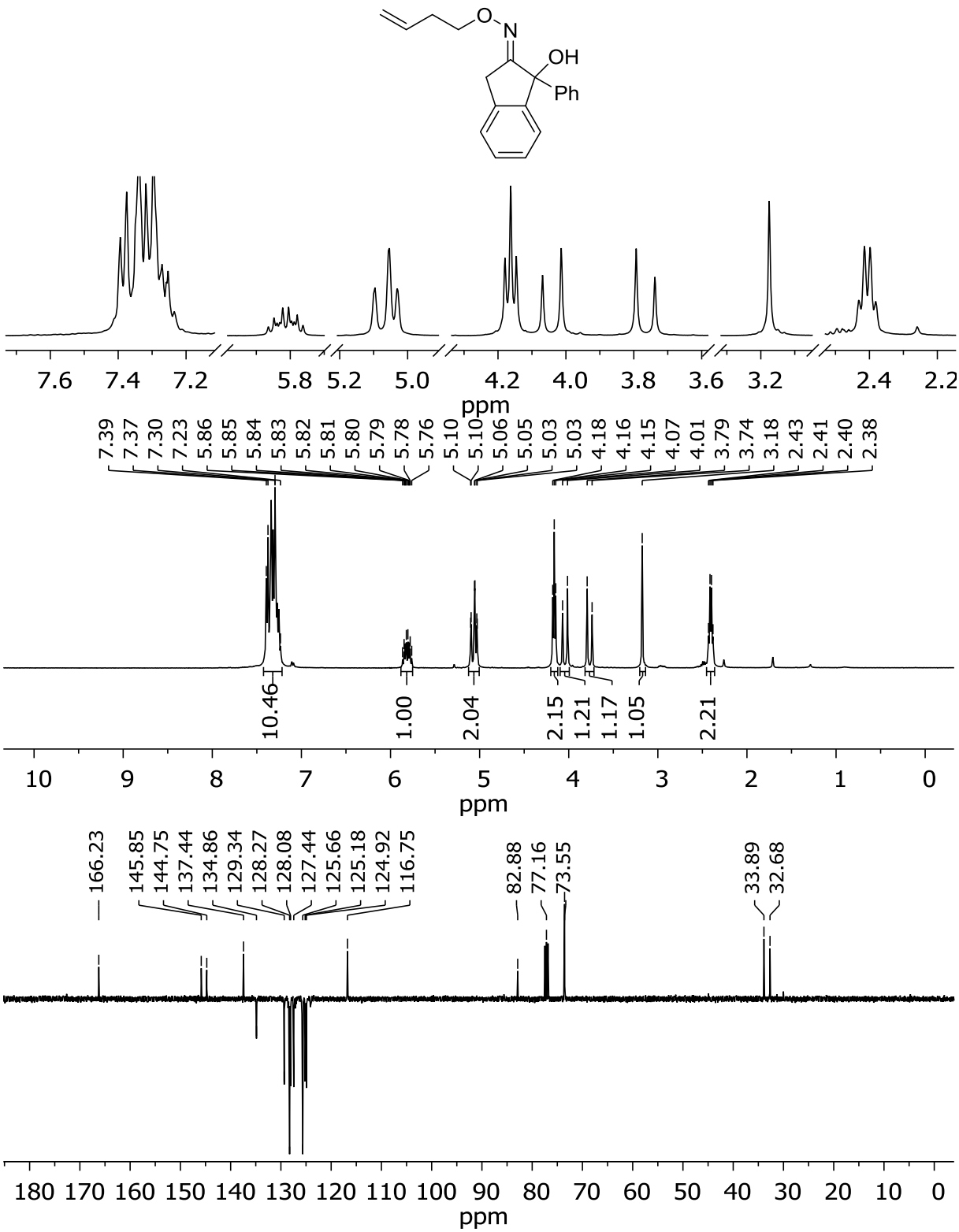
R_f: 0.31 (5% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.09 (bs, 1H), 7.24 (d‘, *J* = 8.0 Hz, 4H), 7.15 (d‘, *J* = 8.0 Hz, 4H), 4.22 (bs, 1H), 2.34 (s, 6H), 0.94 (s, 9H), −0.19 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 157.5 (HC═N), 141.3 (2x C_q), 137.5 (2x C_q), 129.1 (4x CH), 127.0 (4x CH), 26.2 (3x CH_3), 21.2 (2x CH_3), 18.4 (C_q), −5.1 (2x CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3511, 3025, 2956, 2929, 2857, 1615, 1509, 1471, 1461, 1362, 1252, 1165, 1022, 1002, 958, 947, 932, 877, 838, 824, 816, 783; **HR-MS** (ESI)**:** calcd. for $C_{22}H_{21}NO_2SiNa$ ([M+Na]$^+$): 392.2016, found: 392.2017; **M($C_{22}H_{21}NO_2Si$):** 369.58.

2.4 ^{1}H-NMR and ^{13}C-NMR Spectra

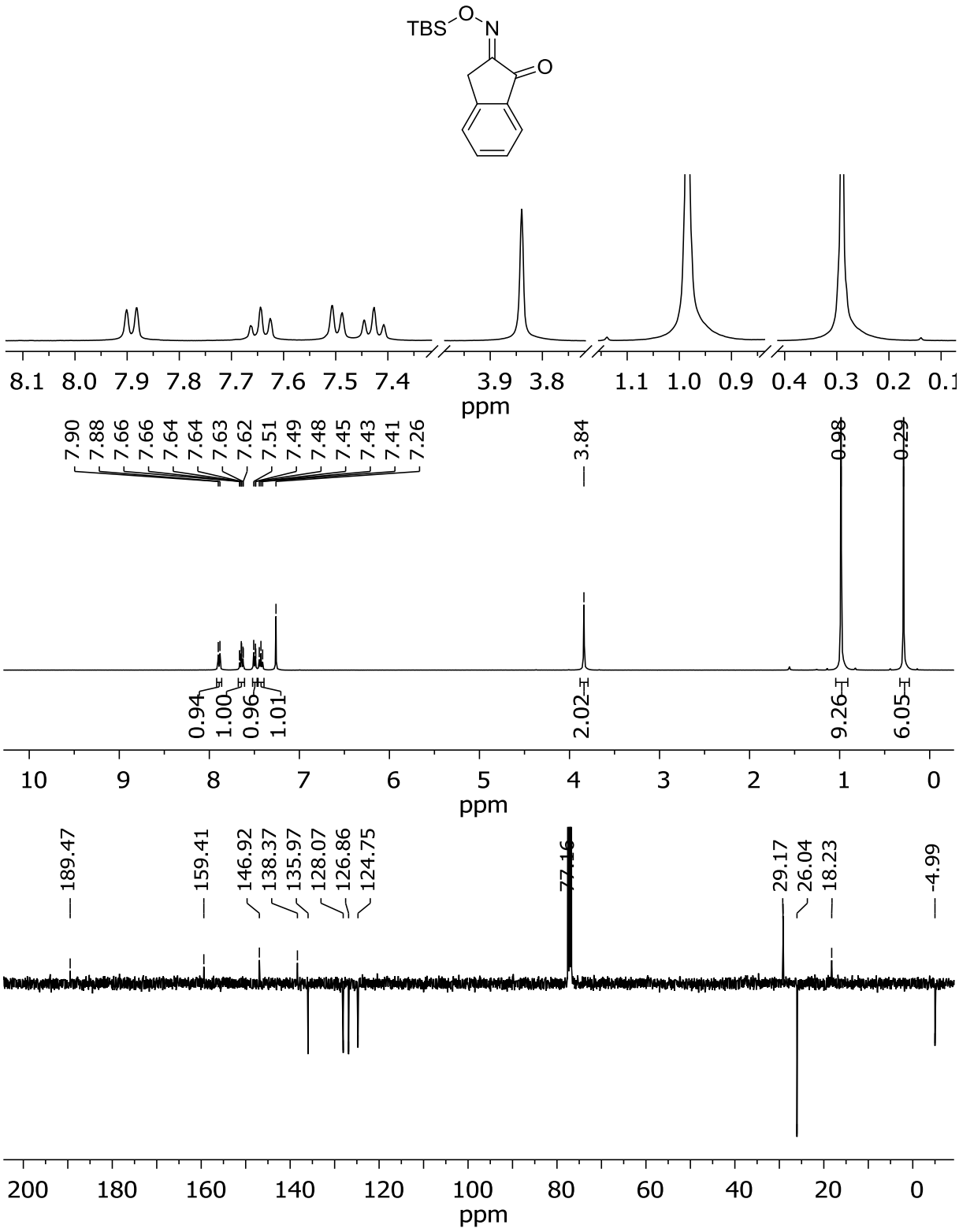
1,2-Indandione-2-oxime ether S2 ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



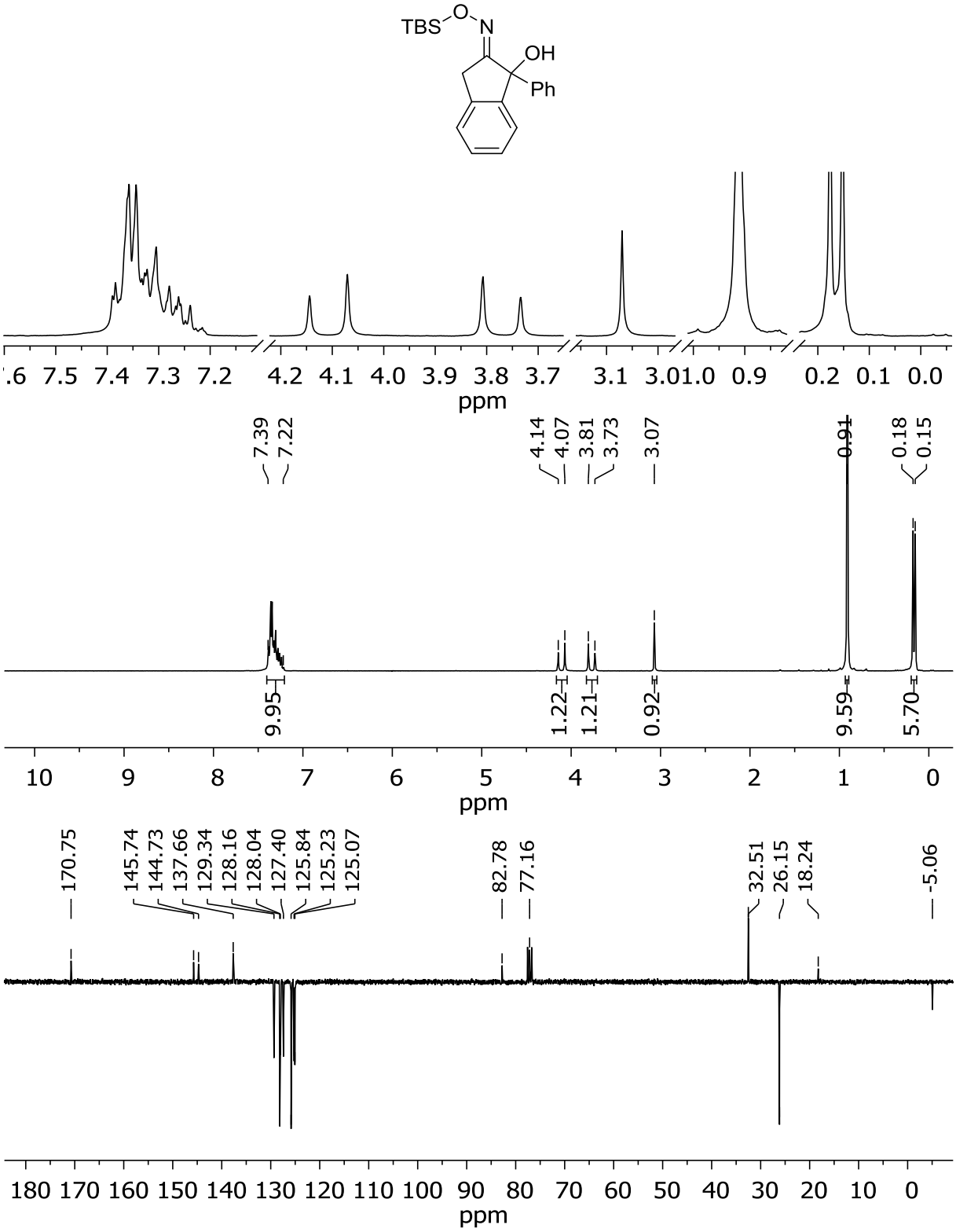
2-Hydroxy ketoxime ether 1i ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



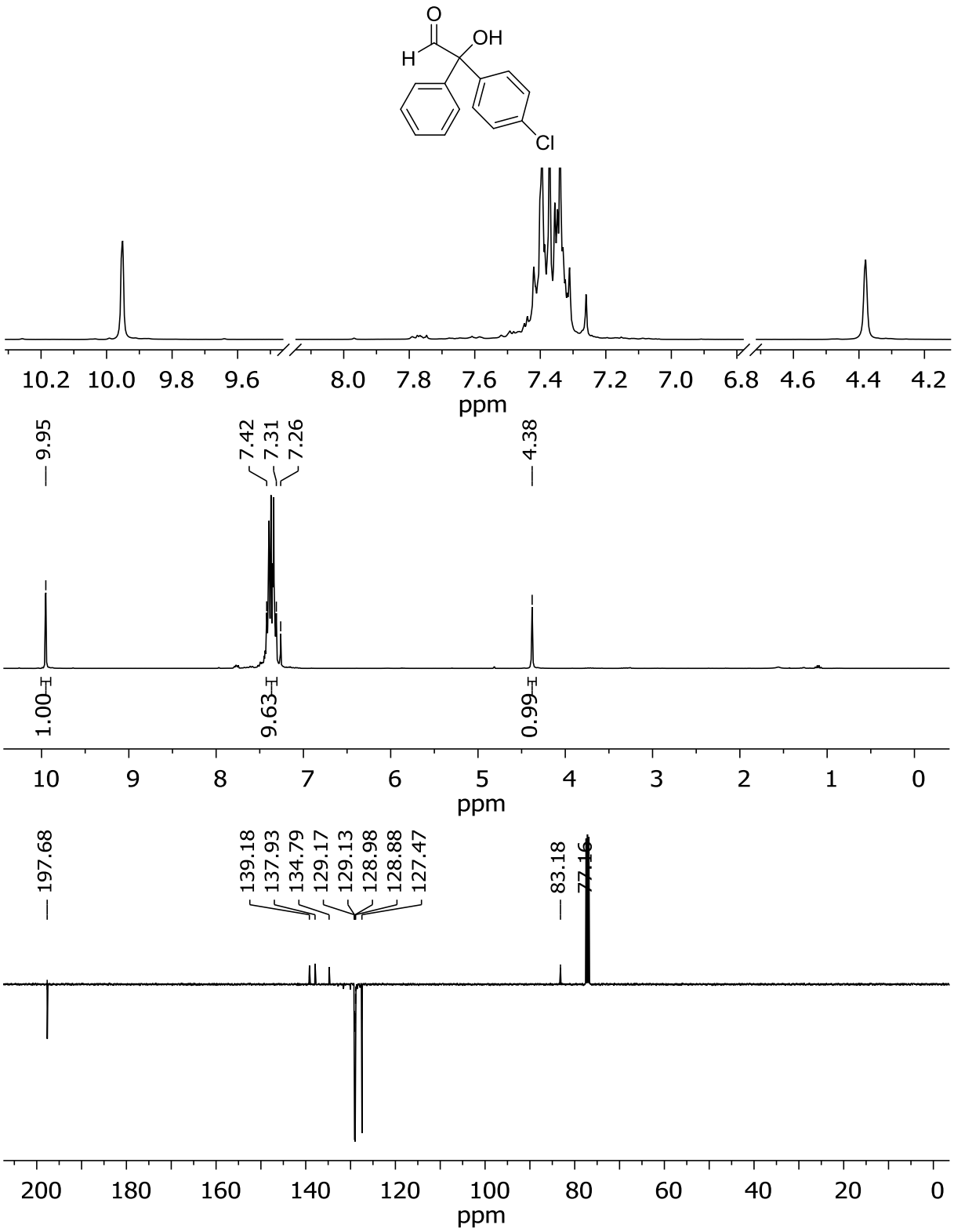
1,2-Indandione-2-oxime silyl ether S3 ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



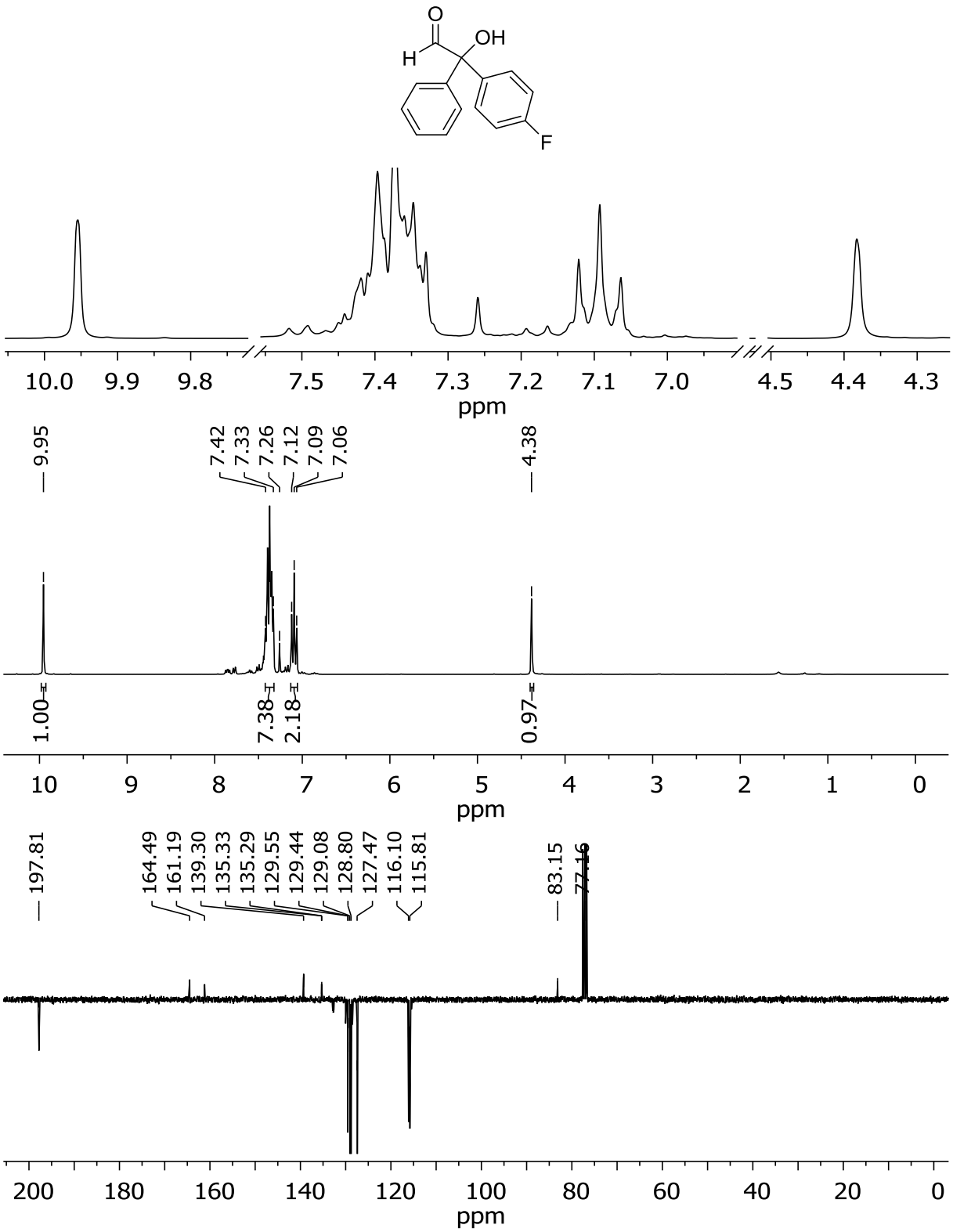
2-Hydroxy ketoxime silyl ether 1j ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



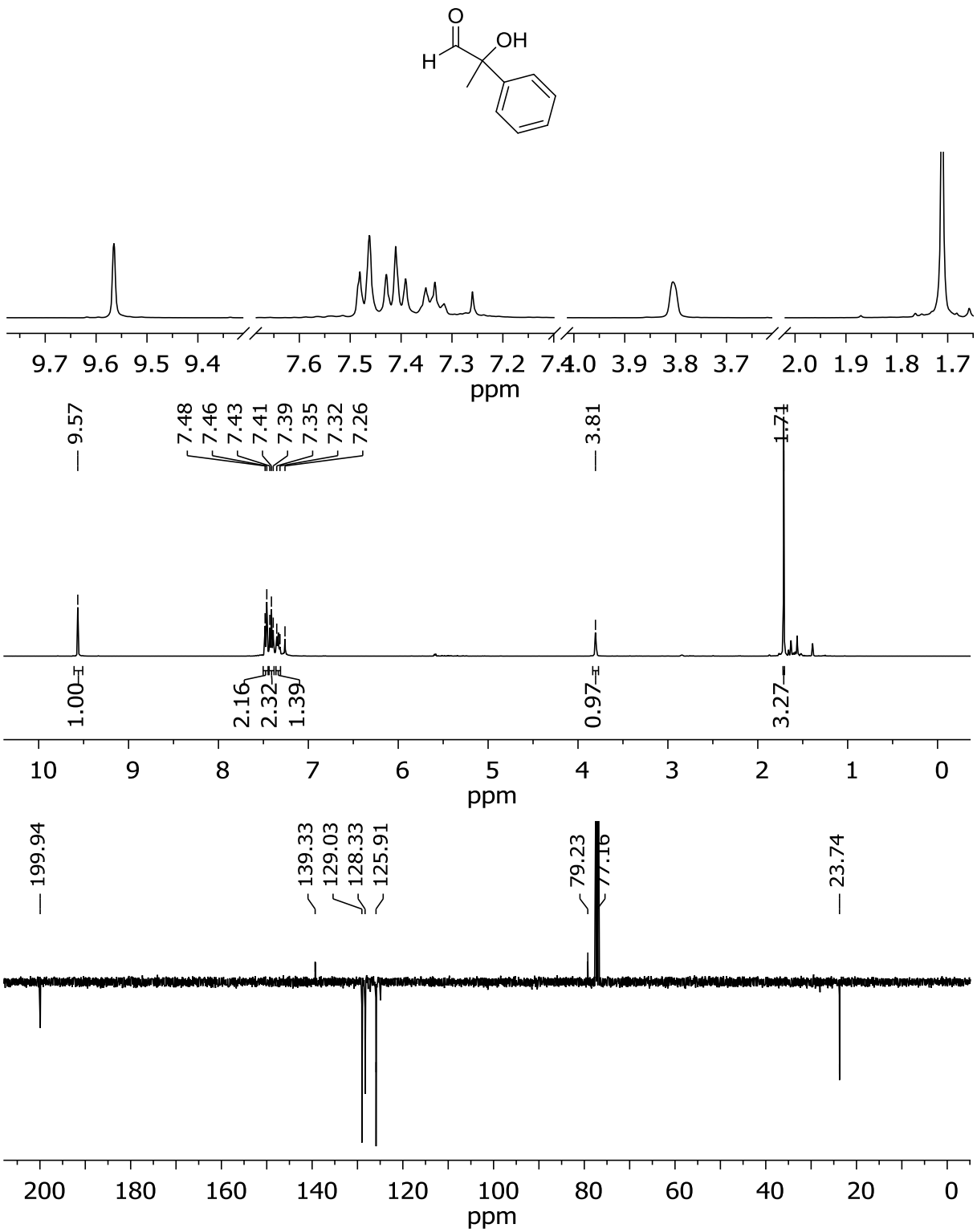
2-Hydroxy aldehyde S6b ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 100 MHz)



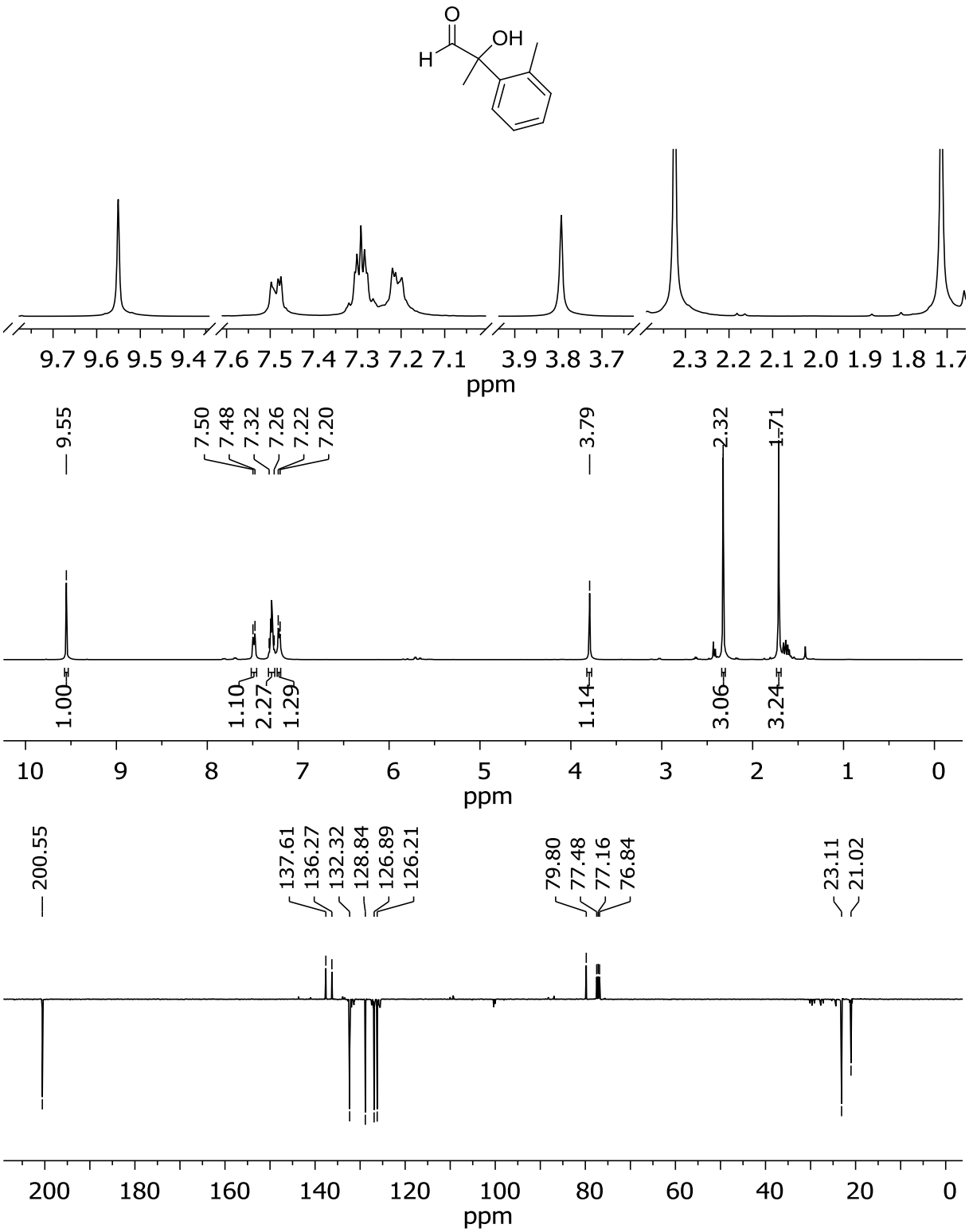
2-Hydroxy aldehyde S6c ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



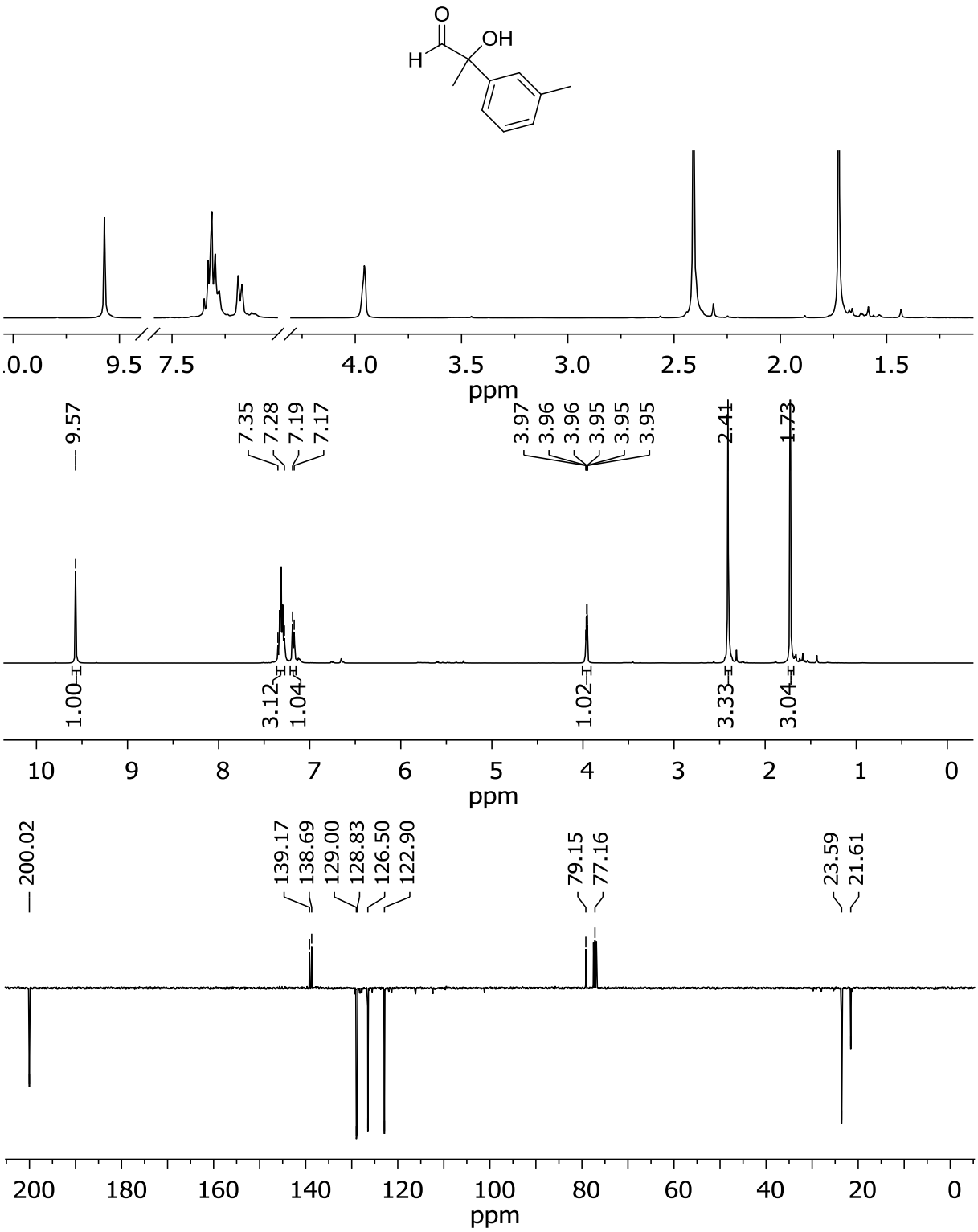
2-Hydroxy aldehyde S6e ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



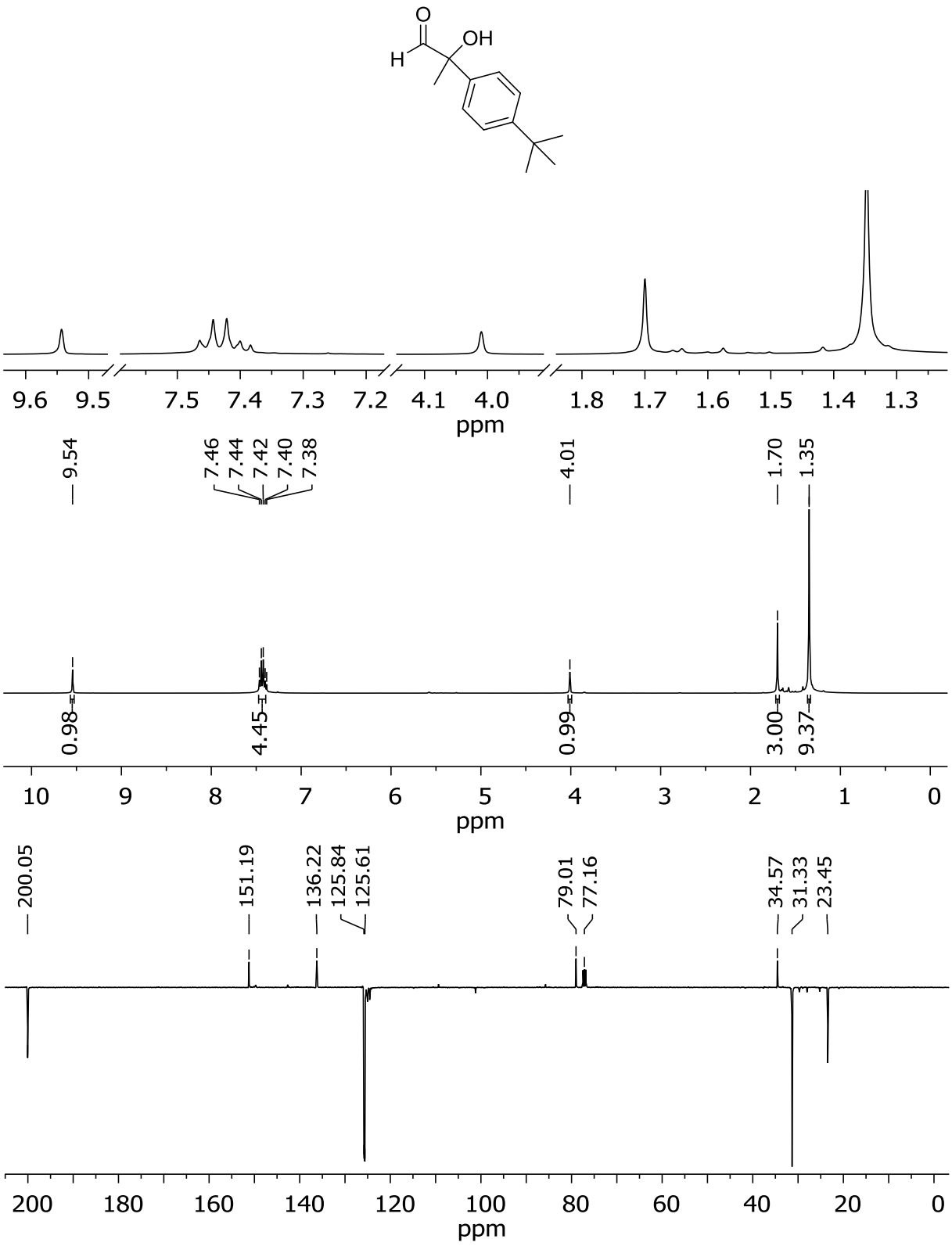
2-Hydroxy aldehyde S6f ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



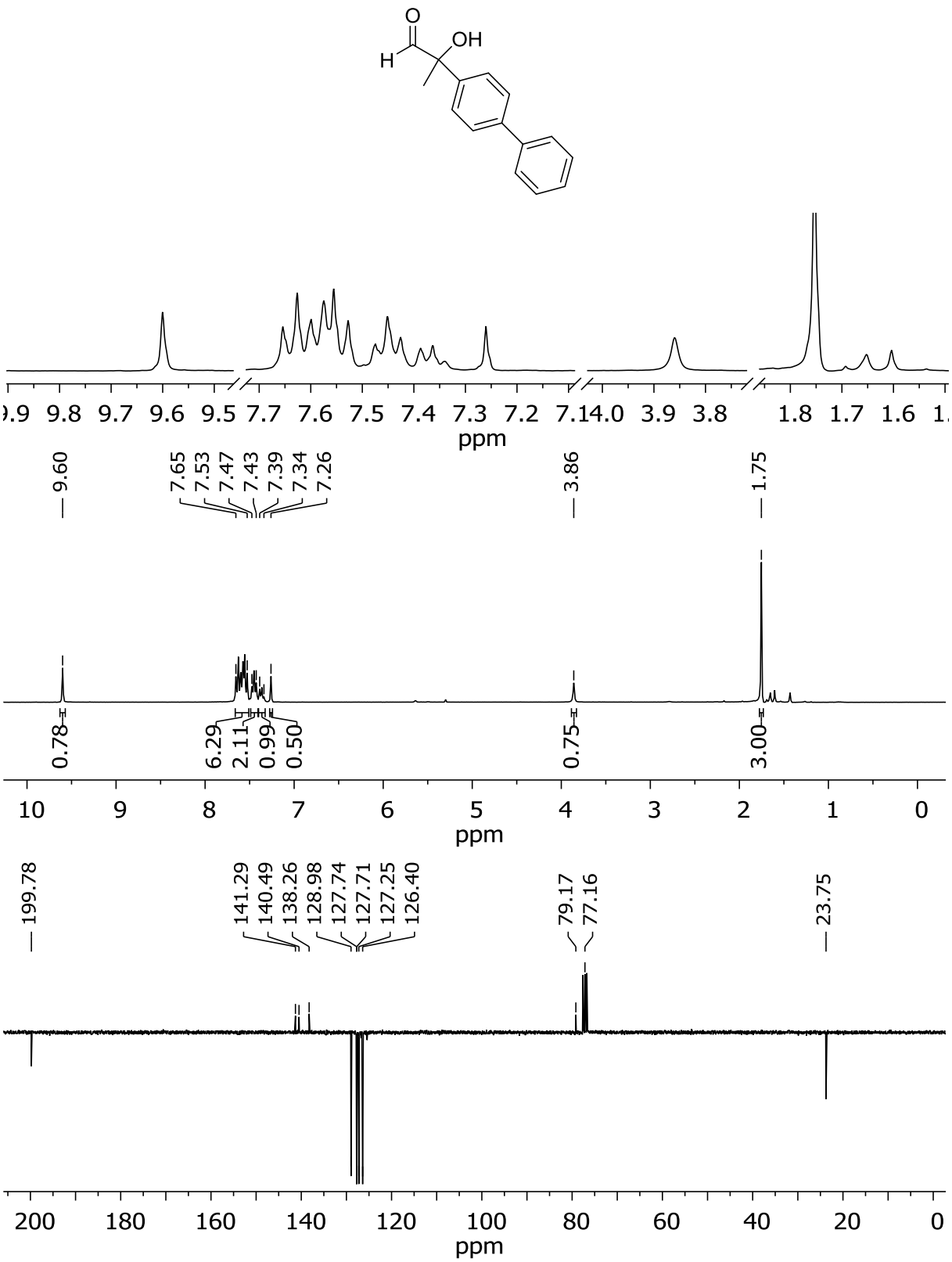
2-Hydroxy aldehyde S6g ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



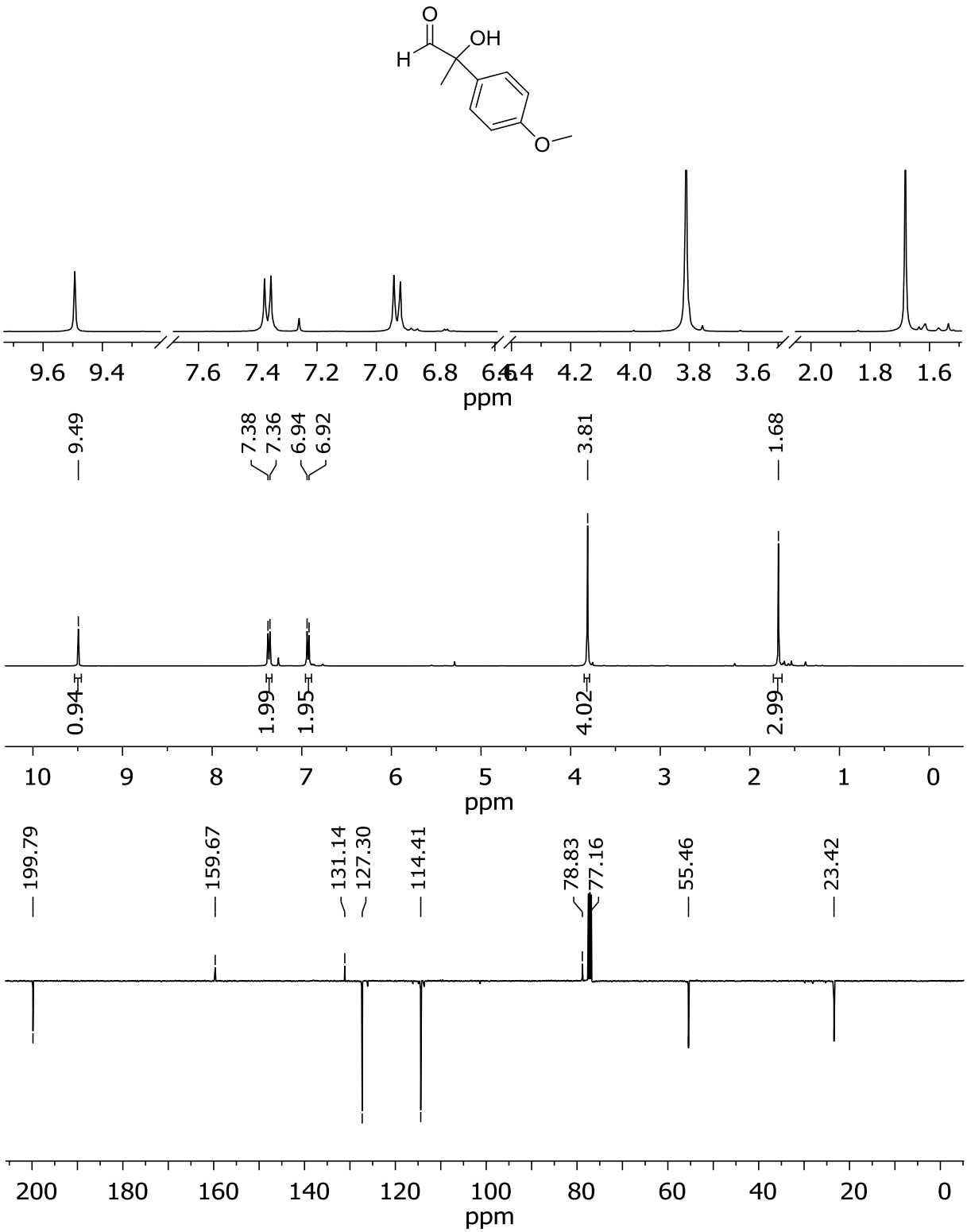
2-Hydroxy aldehyde S6h ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



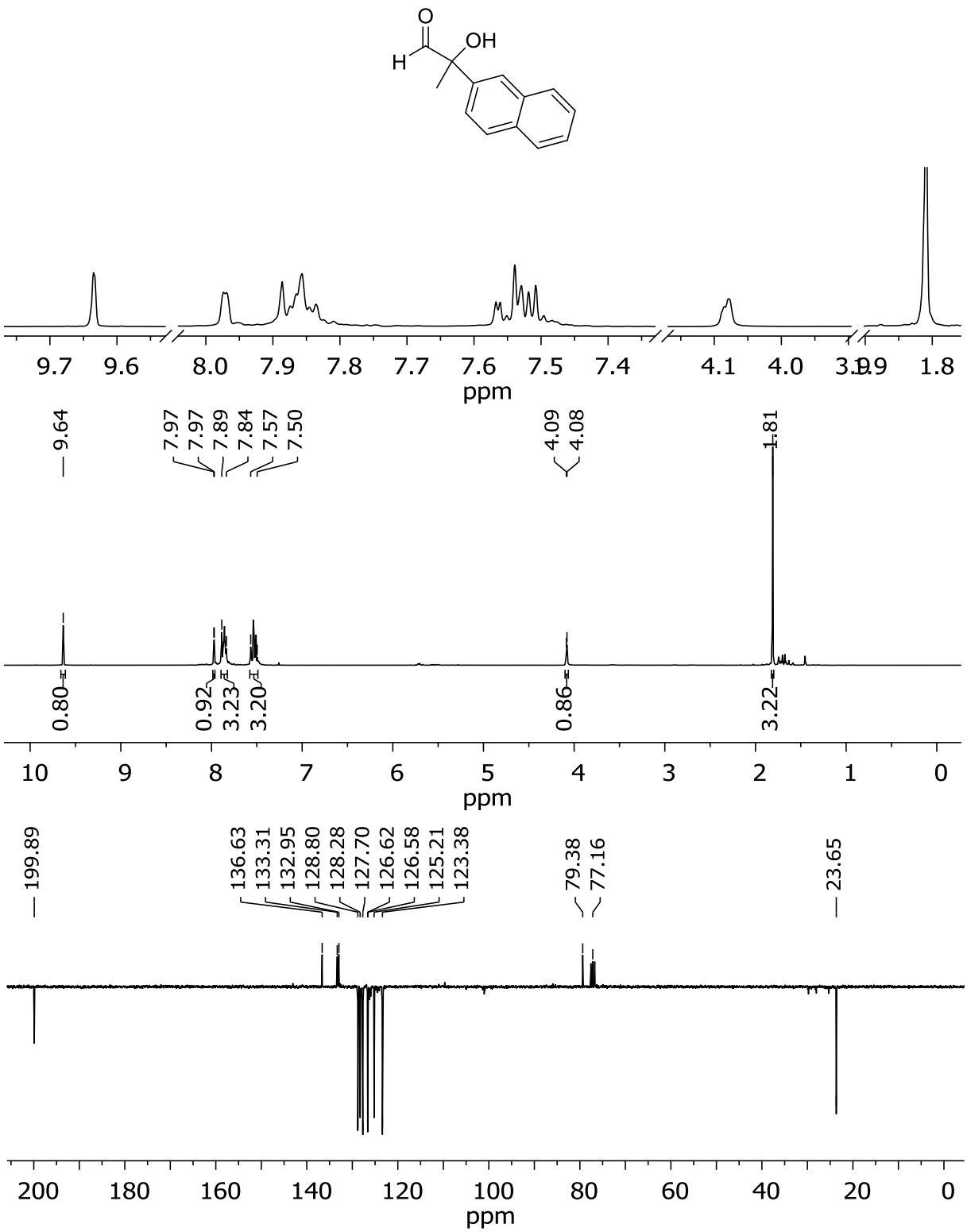
2-Hydroxy aldehyde S6i ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



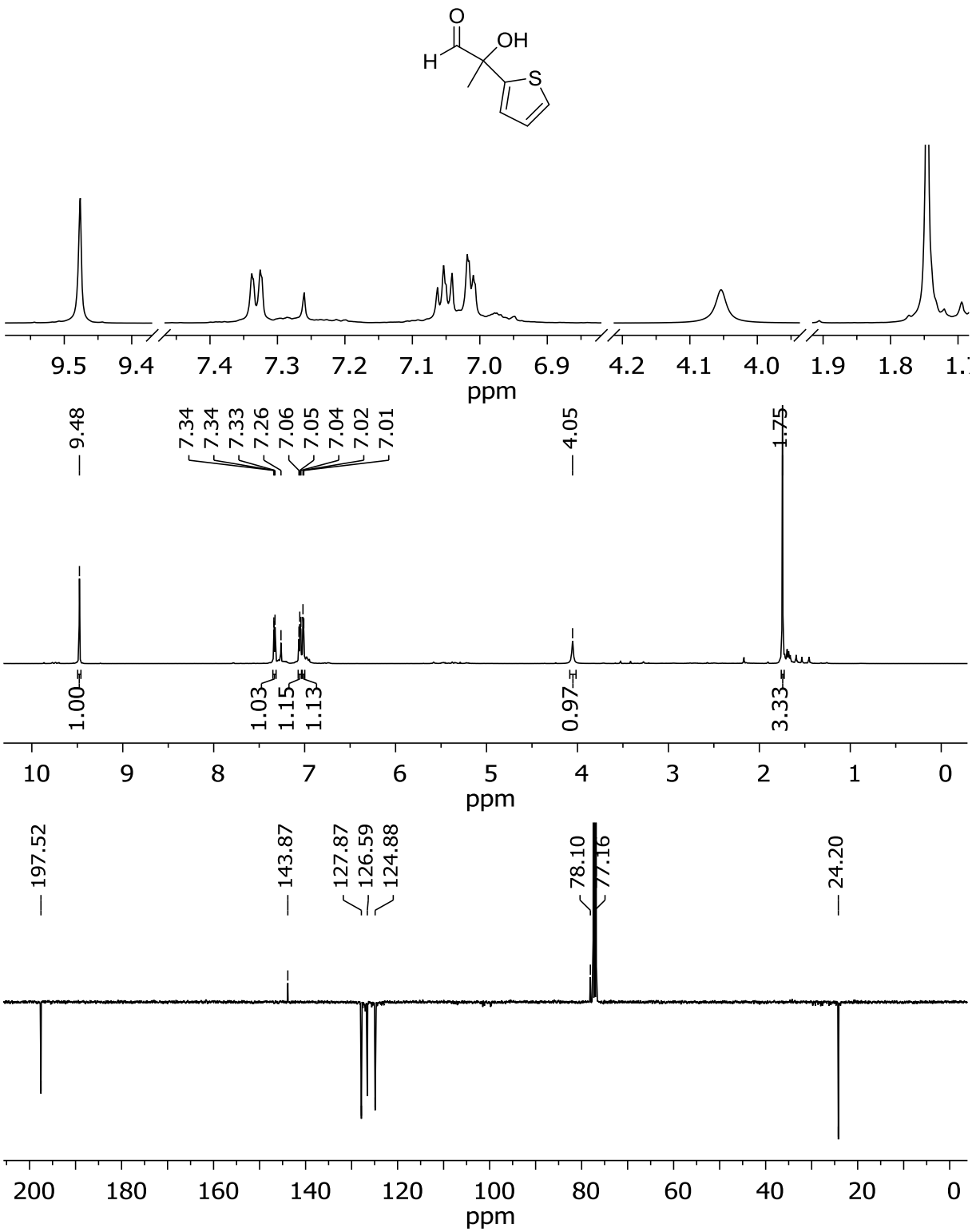
2-Hydroxy aldehyde S6j ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



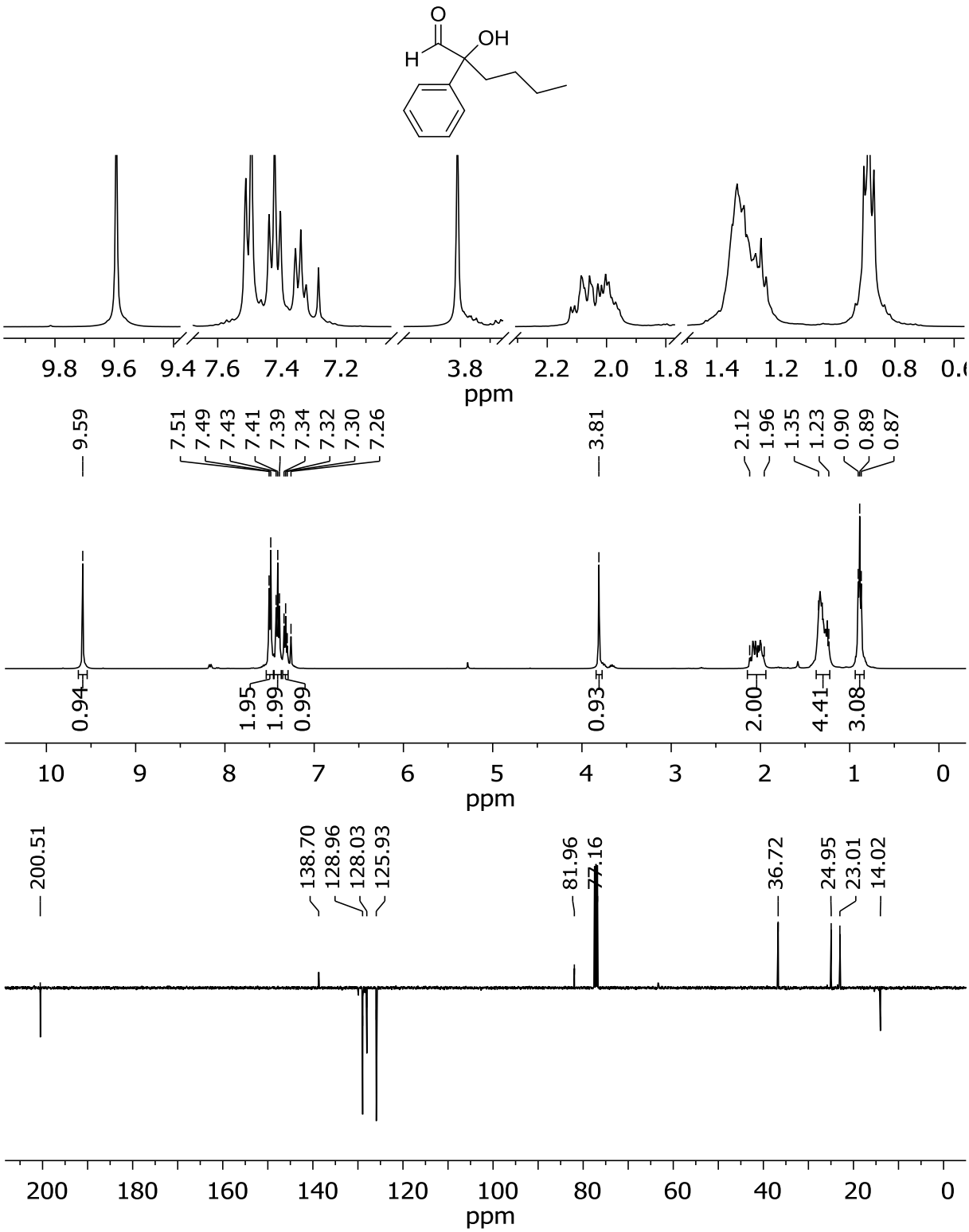
2-Hydroxy aldehyde S6k ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



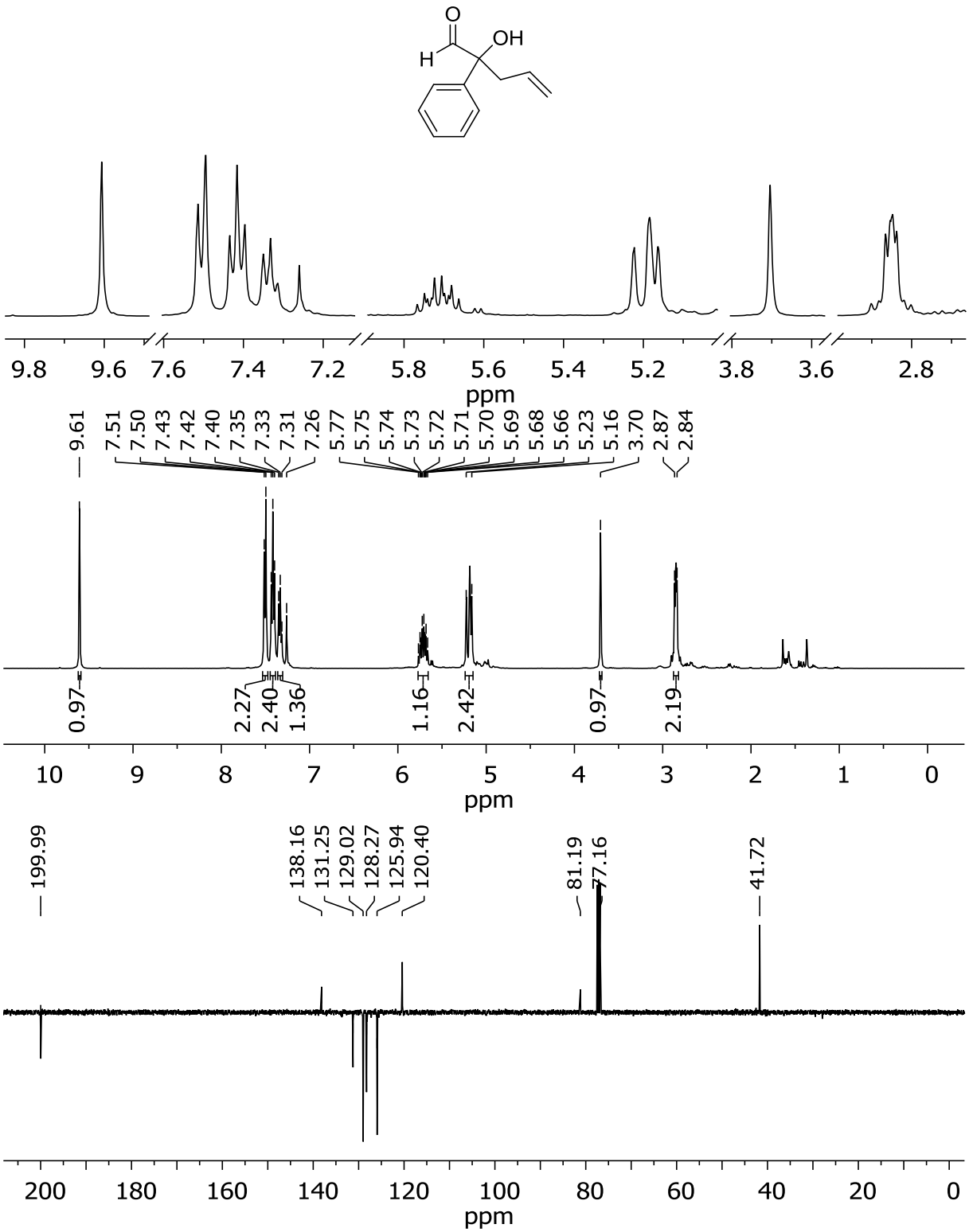
2-Hydroxy aldehyde S6l ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



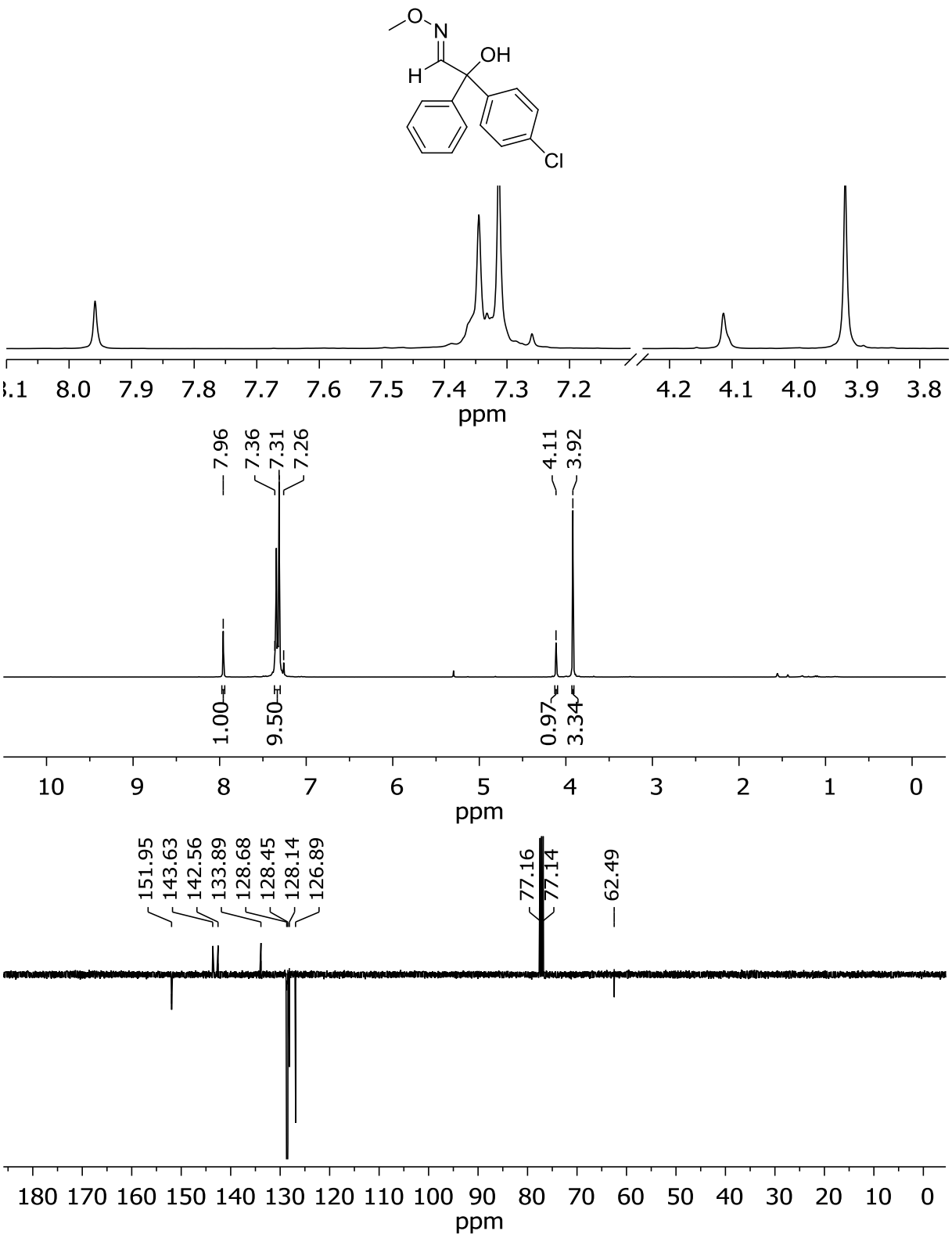
2-Hydroxy aldehyde S6m ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



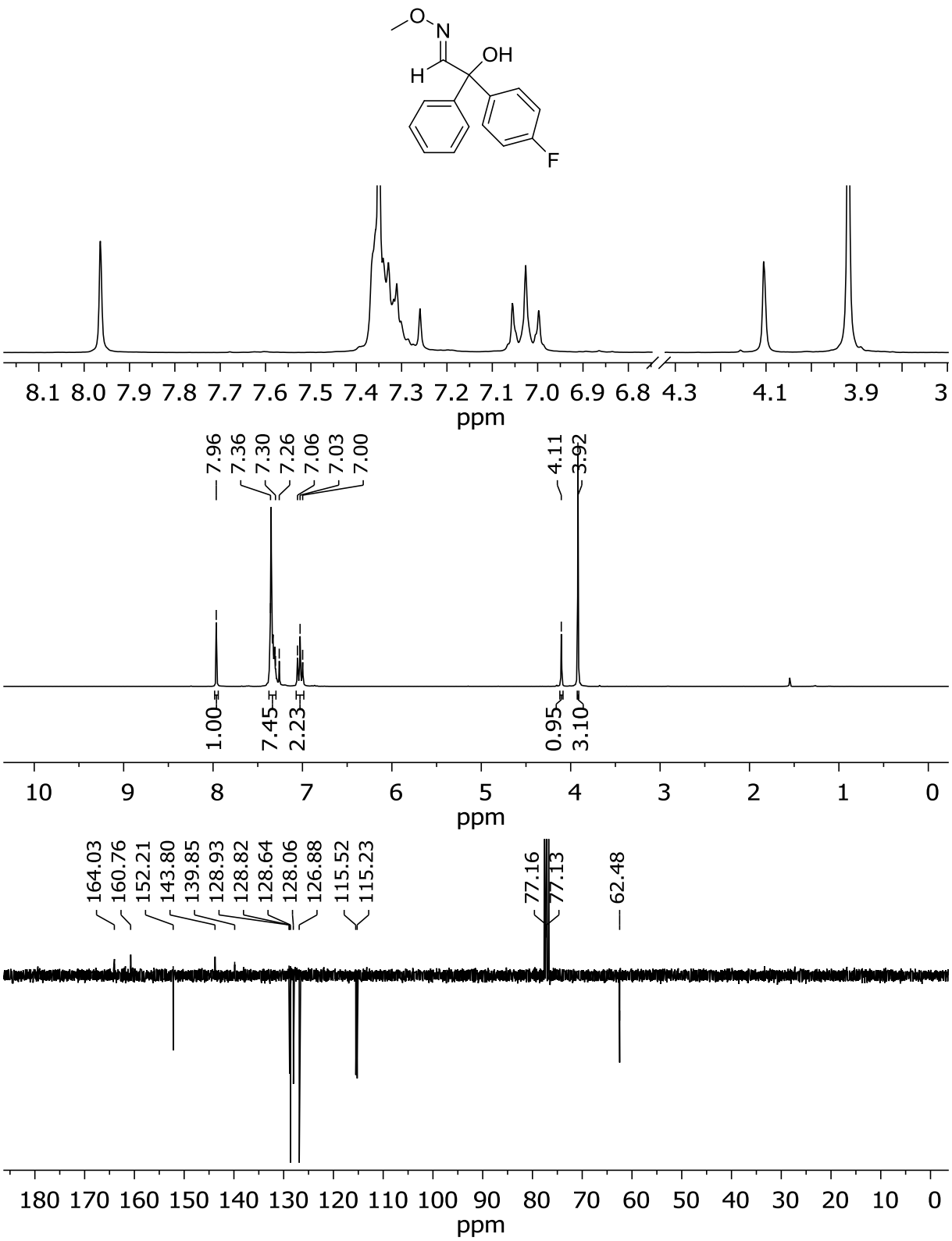
2-Hydroxy aldehyde S6n ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



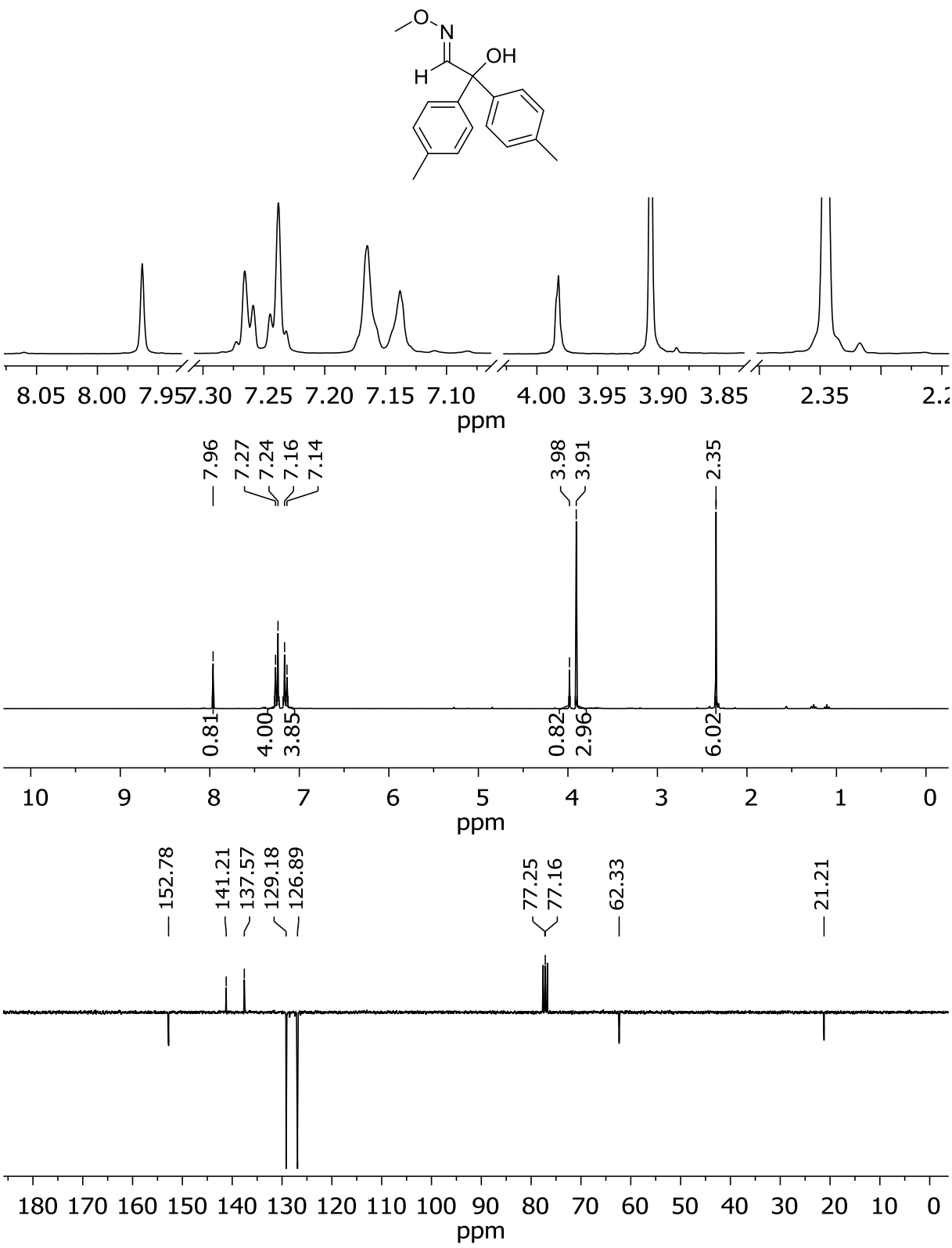
2-Hydroxy aldoxime ether 7b ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 100 MHz)



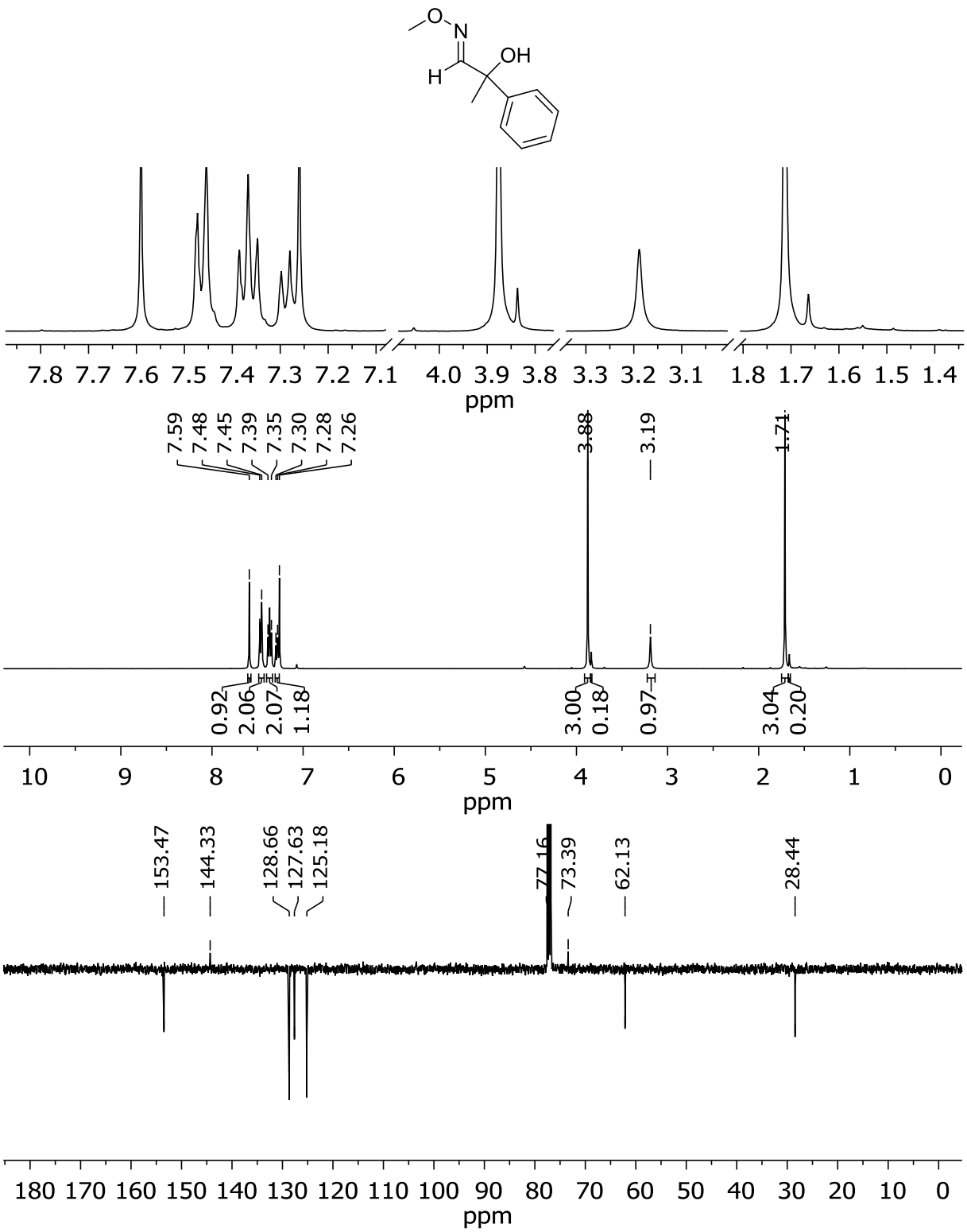
2-Hydroxy aldoxime ether 7c ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



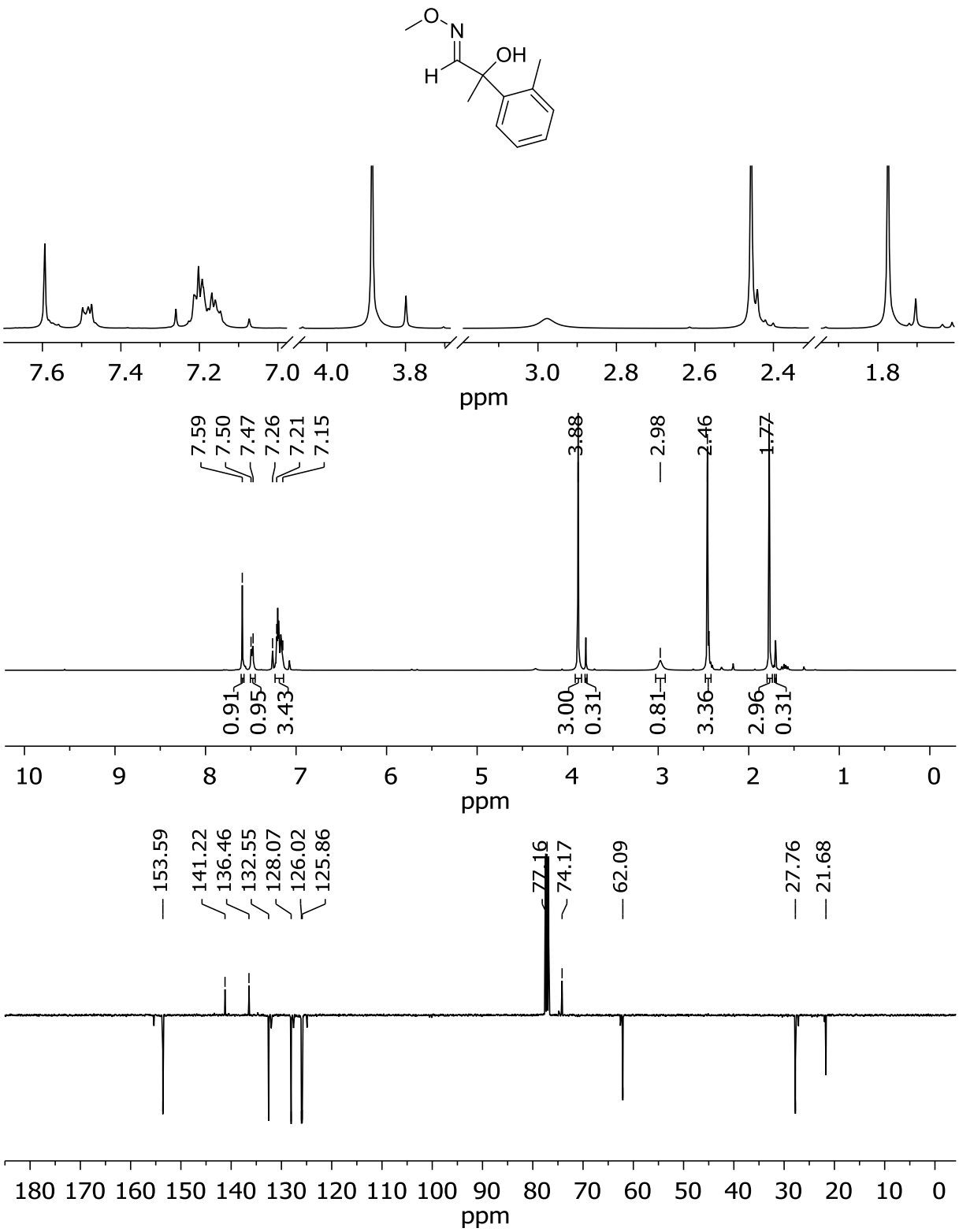
2-Hydroxy aldoxime ether 7d ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



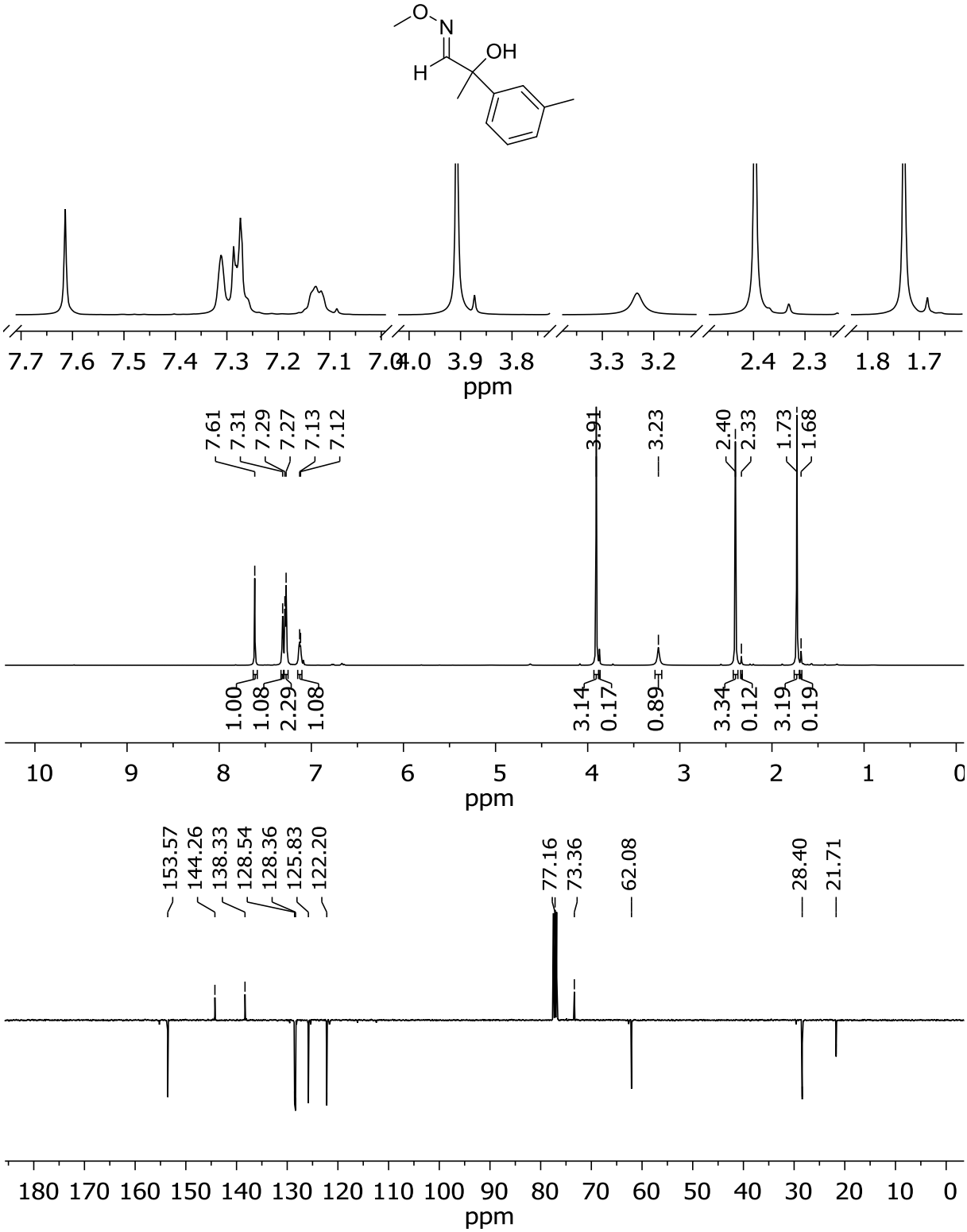
2-Hydroxy aldoxime ether 7e ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



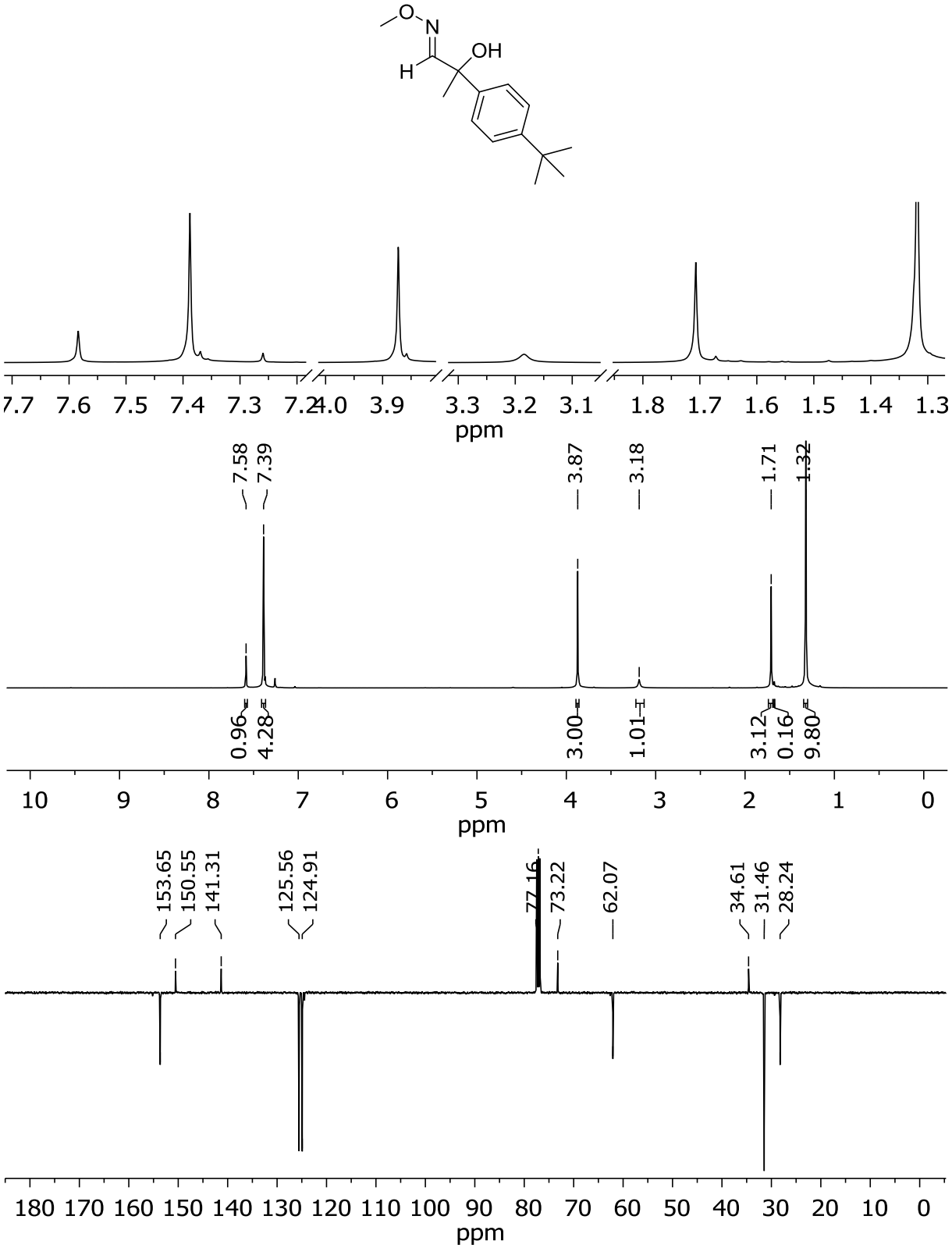
2-Hydroxy aldoxime ether 7f ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



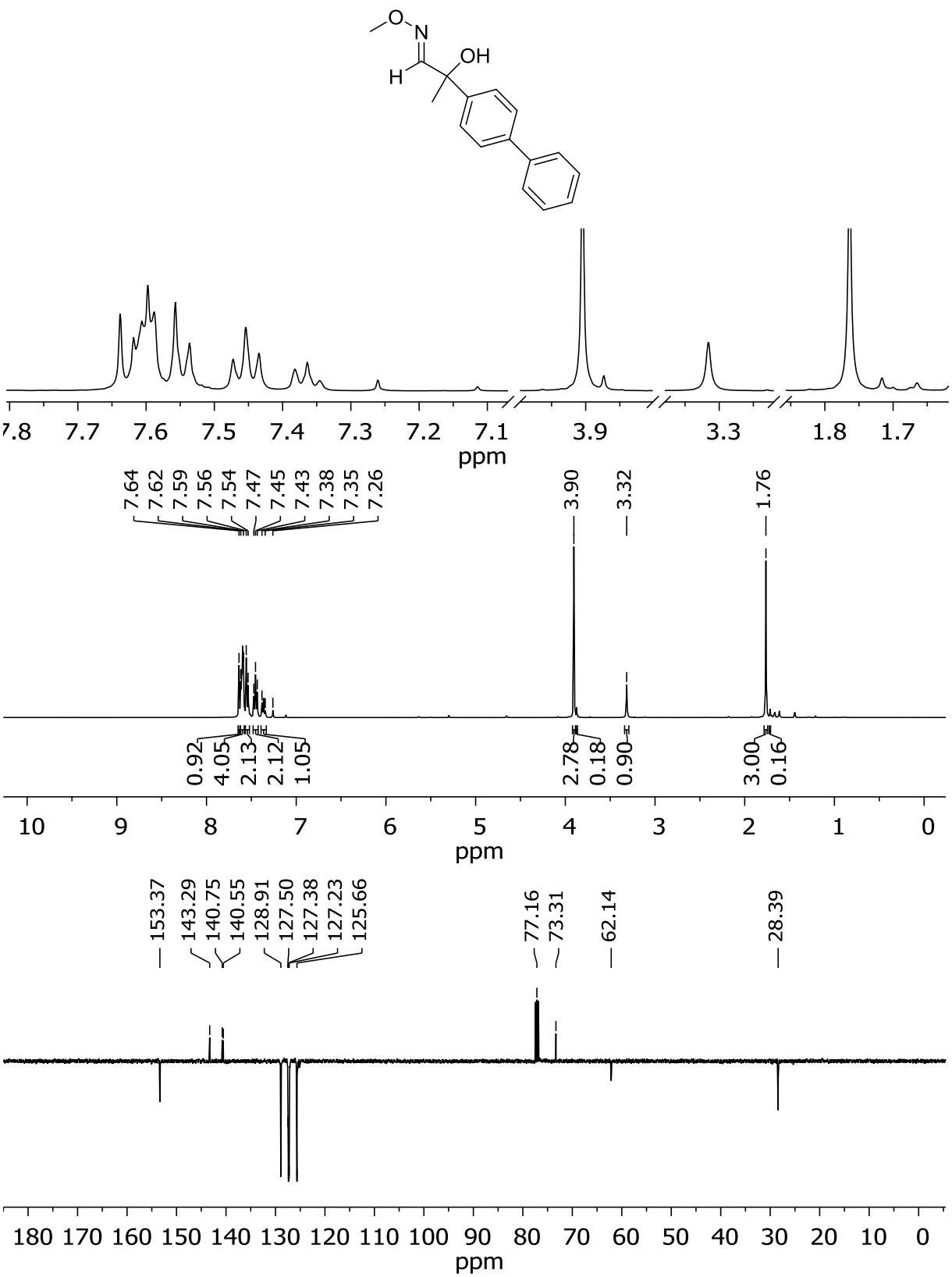
2-Hydroxy aldoxime ether 7g ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



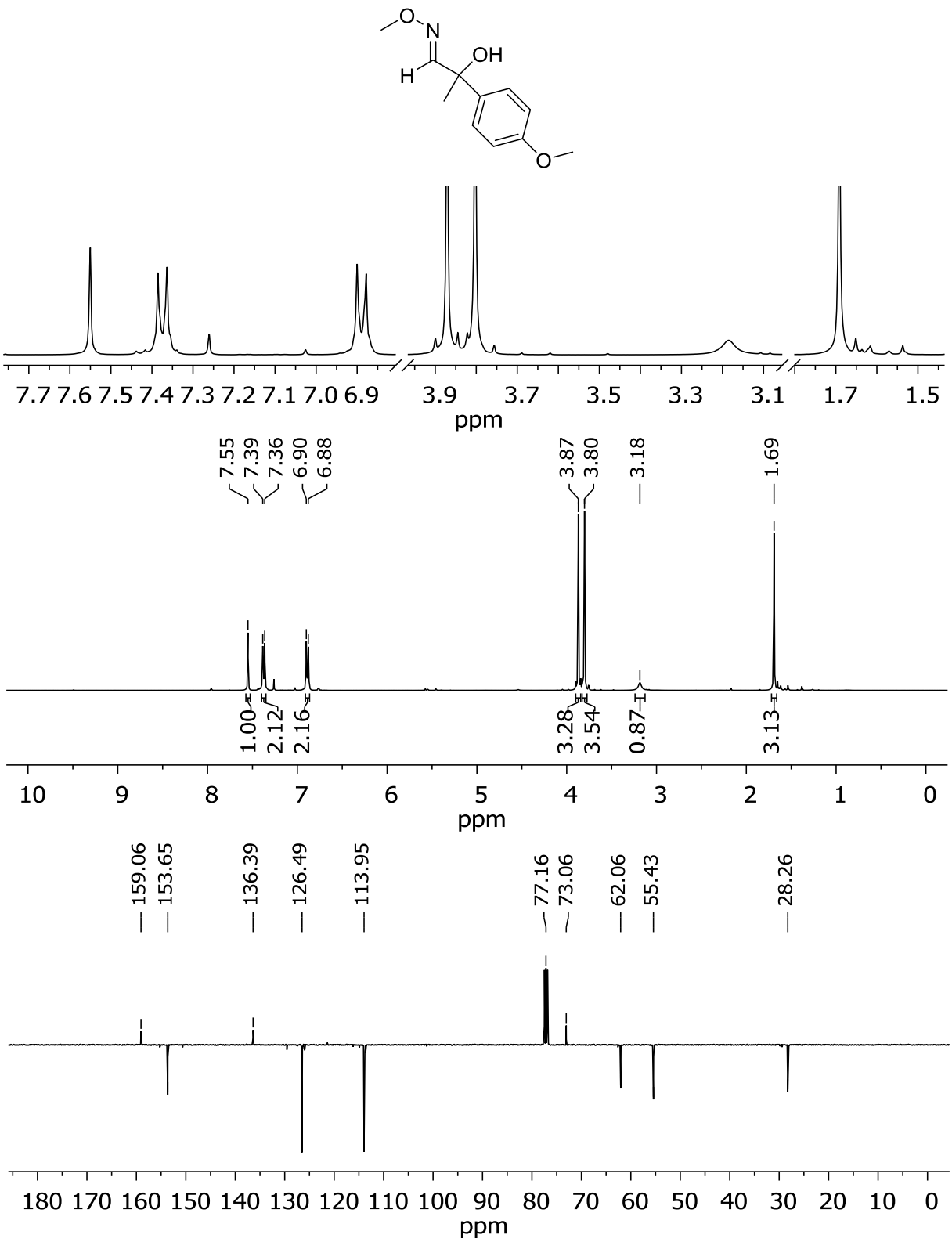
2-Hydroxy aldoxime ether 7h ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



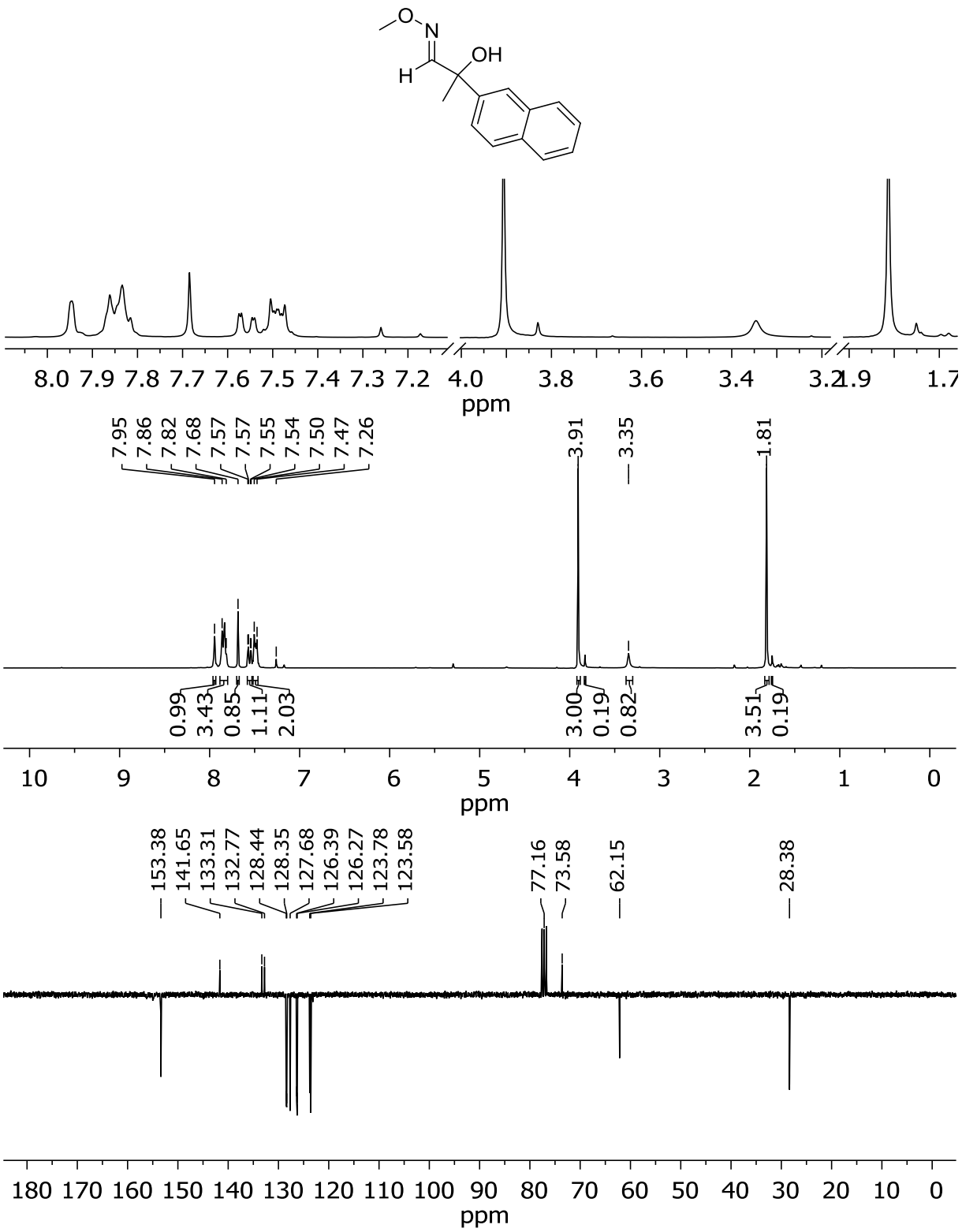
2-Hydroxy aldoxime ether 7i ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



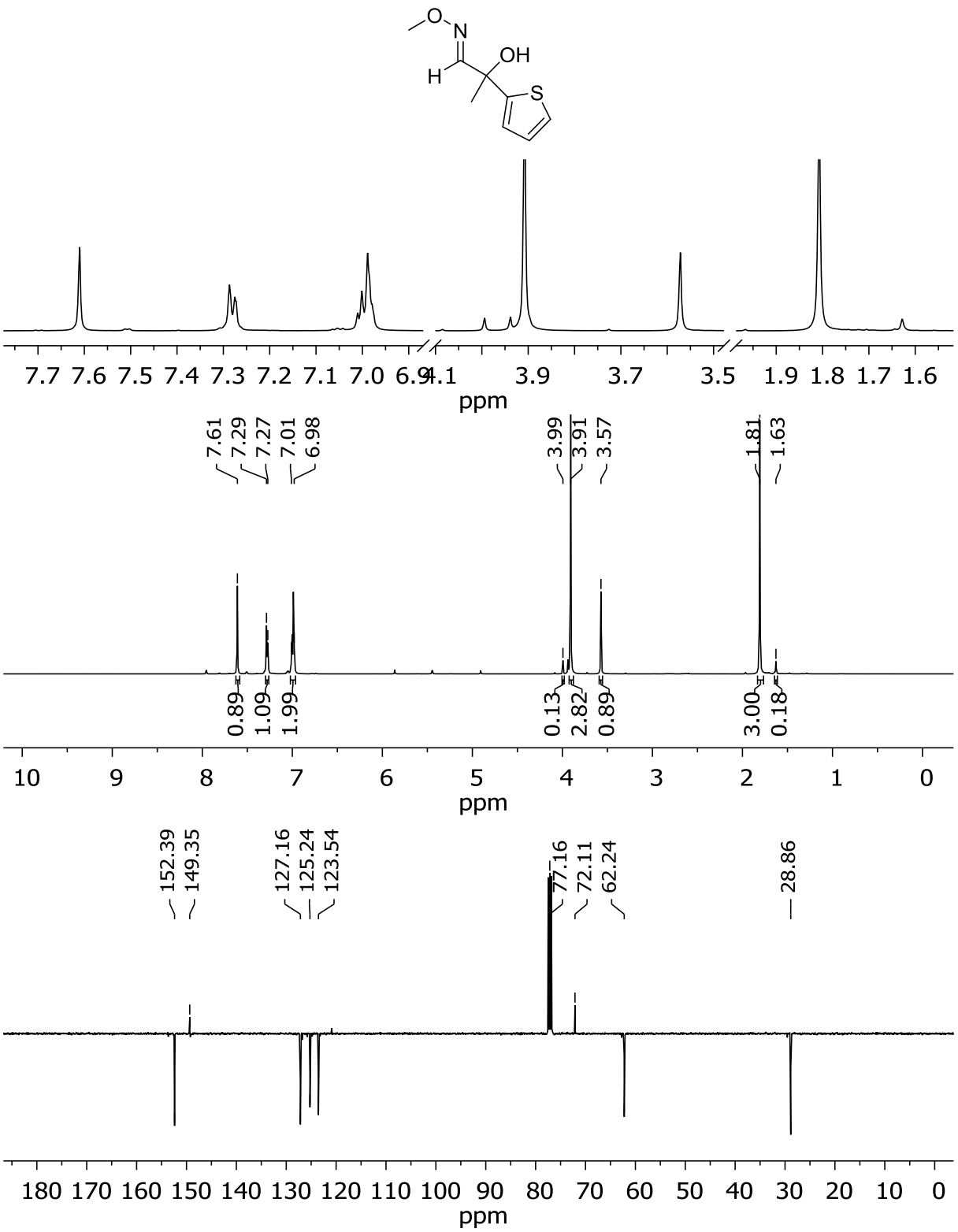
2-Hydroxy aldoxime ether 7j ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



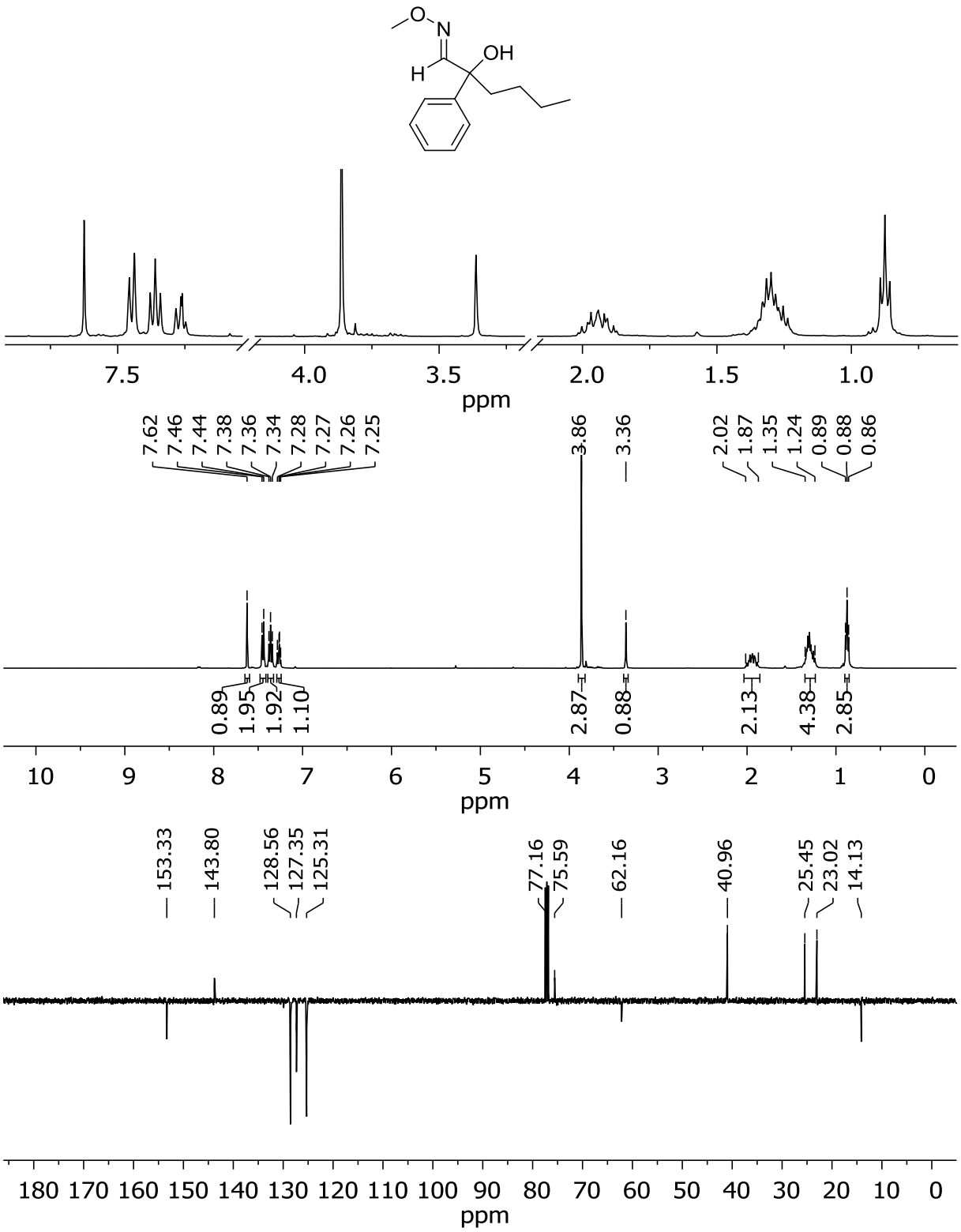
2-Hydroxy aldoxime ether 7k ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



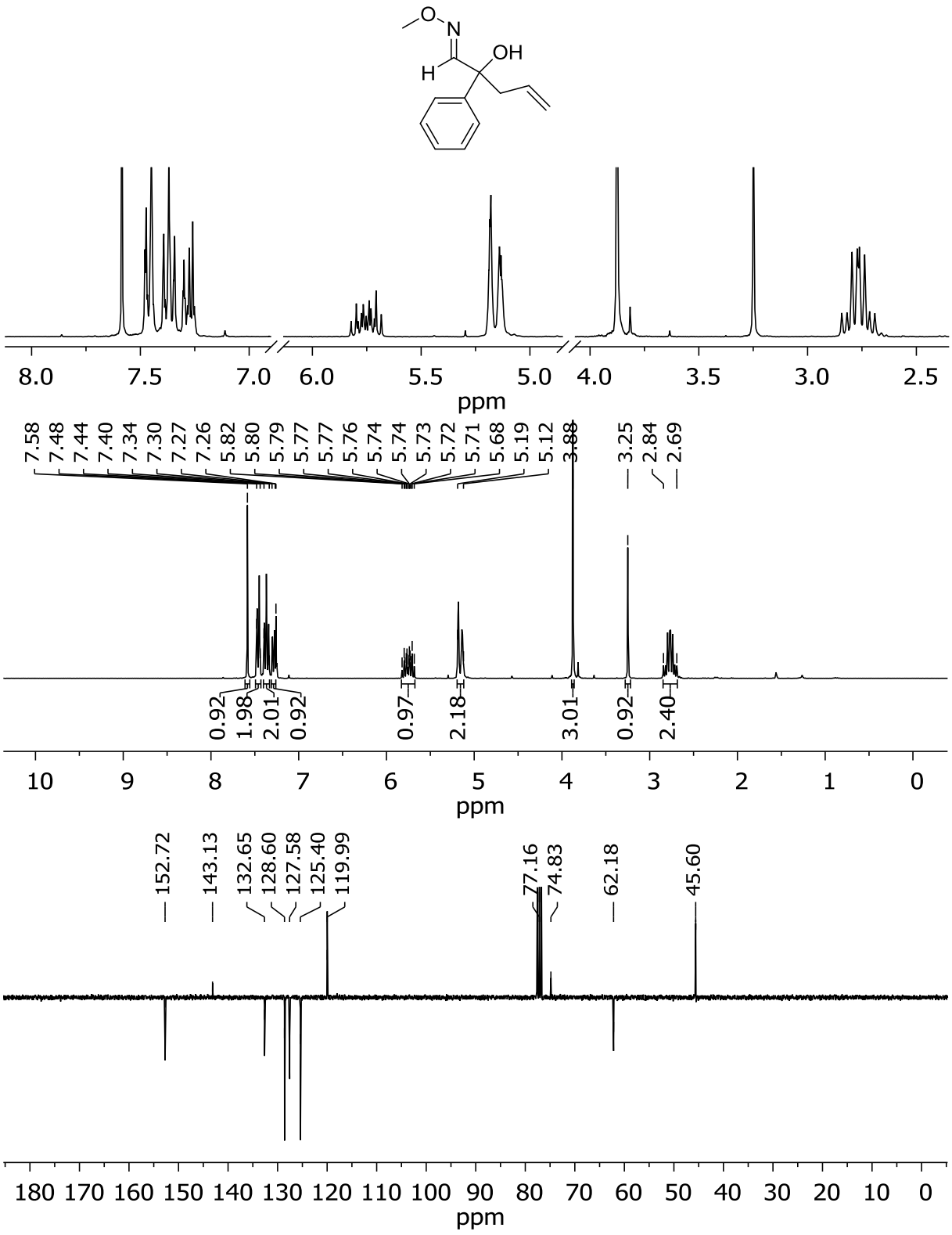
2-Hydroxy aldoxime ether 7l ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



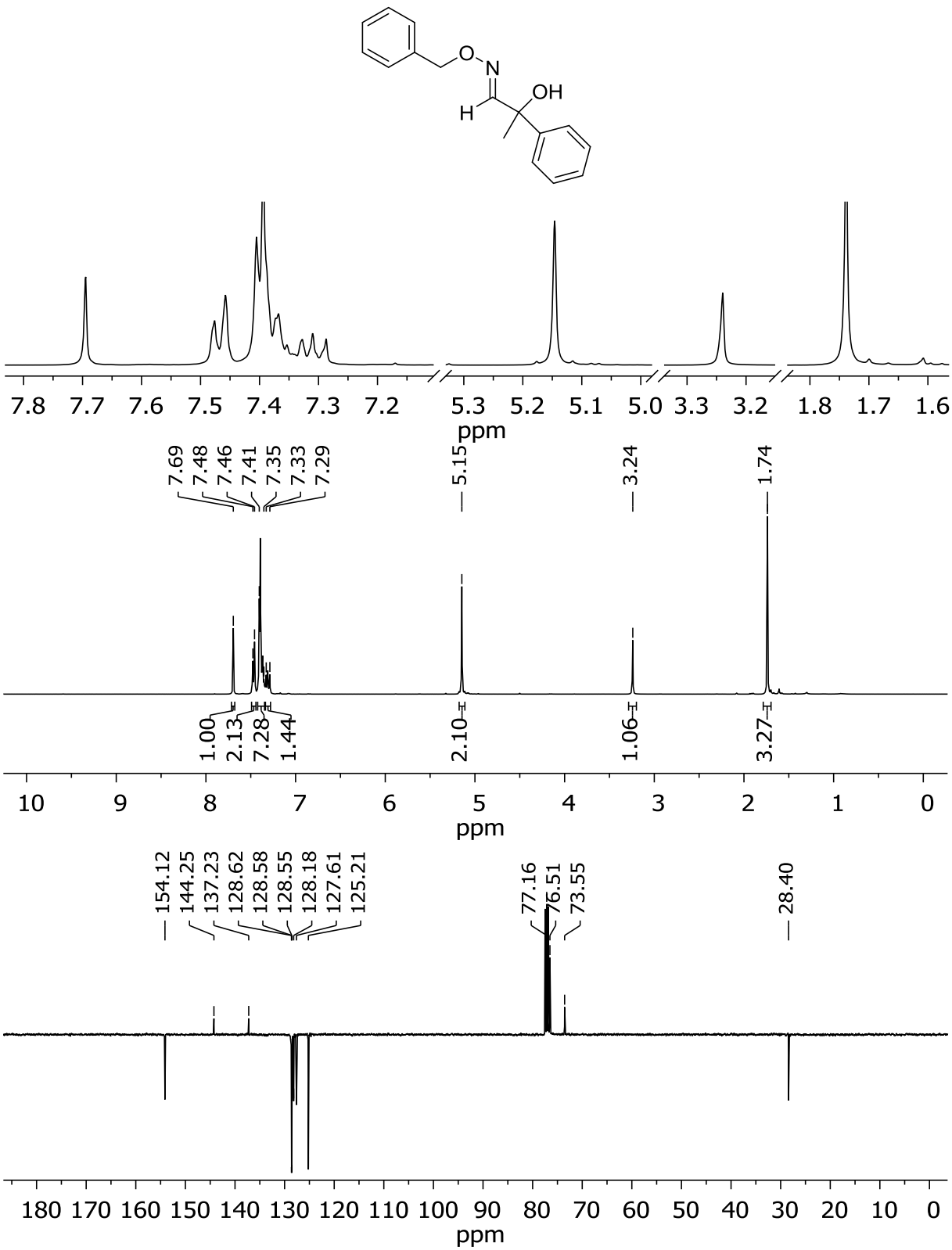
2-Hydroxy aldoxime ether 7m ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



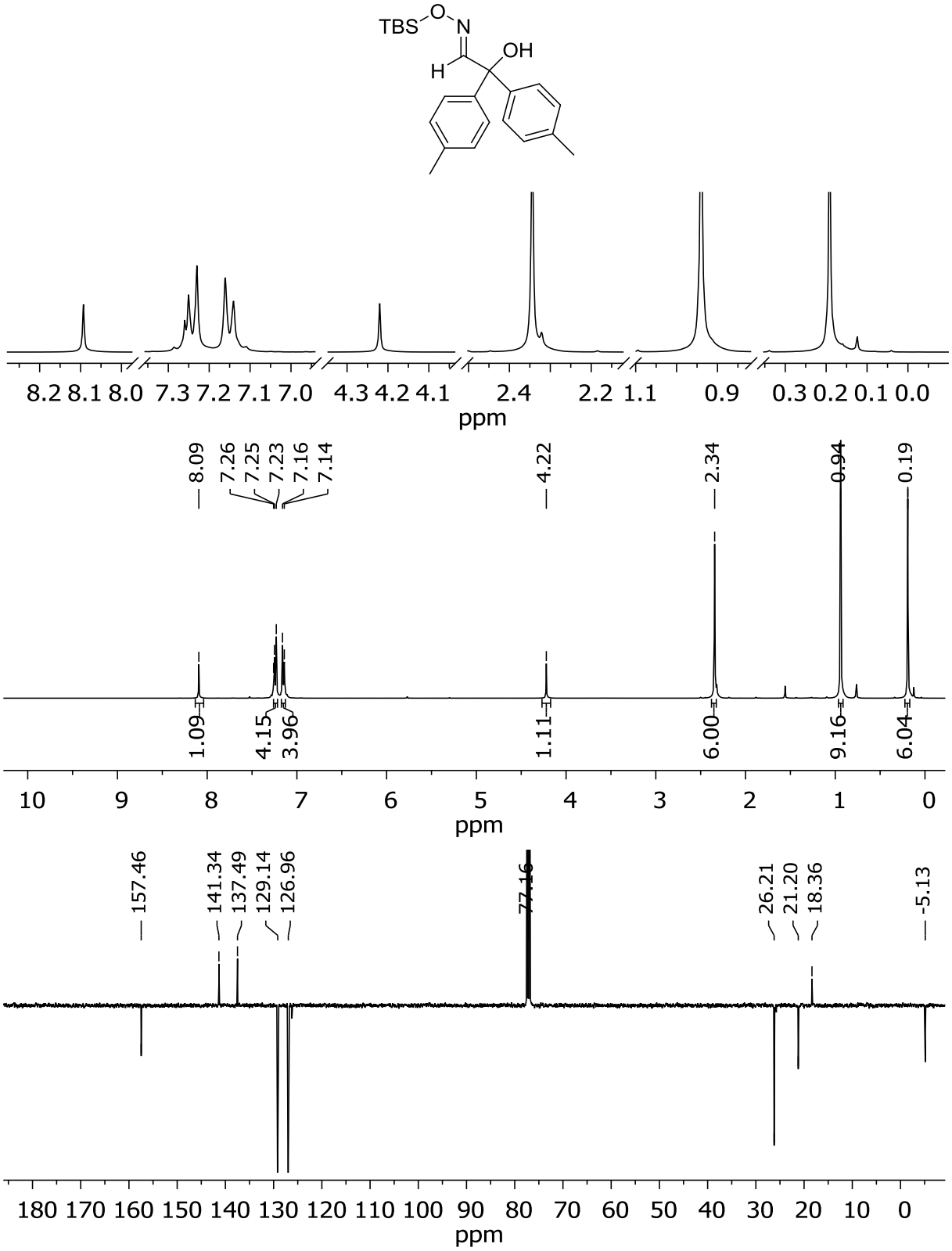
2-Hydroxy aldoxime ether 7n ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



2-Hydroxy aldoxime ether 7o ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)

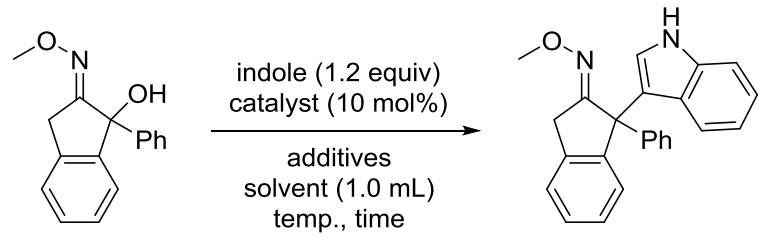


2-Hydroxy aldoxime silyl ether 7p ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



3 The FCR of Cyclic 2-Hydroxy Ketoxime Ethers

3.1 Optimization Studies of Compound 4a



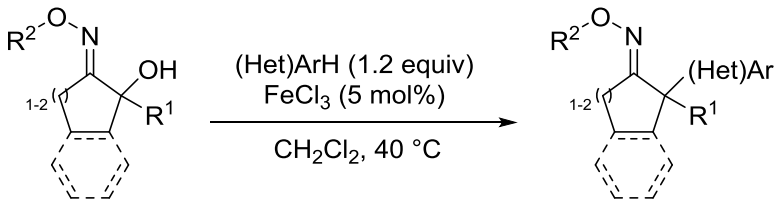
1a (0.20 mmol) **4a**

entry	catalyst	additive	solvent	temp. [°C]	time	yield 4a [%]
1	$Sc(OTf)_3$	4 Å MS (50 mg)	CH_2Cl_2	40	2 d	traces
2	$Sc(OTf)_3$	---	CH_2Cl_2	40	1 h	88
3	$Sc(OTf)_3$	---	$CHCl_3$	RT	4 h	92
4	$Sc(OTf)_3$	---	$CHCl_3$	60	1 h	87
5	$Sc(OTf)_3$	---	CH_3CN	60	0.5 h	87
6	$Sc(OTf)_3$	---	CH_3NO_2	60	0.5 h	81
7	$Ca(NTf_2)_2$	Bu_4NPF_6 (10 mol%)	$CHCl_3$	60	1 h	76
8	$LiNTf_2$	Bu_4NPF_6 (10 mol%)	$CHCl_3$	60	1 h	86
9	$Al(OTf)_3$	---	CH_2Cl_2	40	0.5 h	84
10	$Bi(OTf)_3$	---	CH_2Cl_2	40	0.5 h	89
11	$FeCl_3$	---	CH_2Cl_2	40	0.5 h	87
12[a]	$FeCl_3$	---	CH_2Cl_2	40	1 h	92

[a] catalyst (5 mol%), solvent (0.6 mL).

3.2 Substrate Scope

General procedure 3 of the FCR

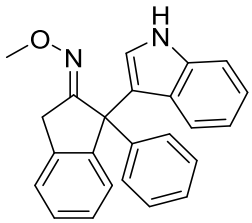


1a-j, **2**, **3** **4a-p**, **5**, **6**

2-Hydroxy ketoxime ether **1** (or **2**, **3**) (1.0 equiv), a (hetero)arene (1.2 equiv) and $FeCl_3$ (0.05 equiv) were placed in an oven dried and sealable DURAN® test tube. Abs. CH_2Cl_2 (0.33 M) was added and the reaction mixture was heated to 40 °C while stirring. After complete reaction it was quenched with sat. $NaHCO_3$-solution and extracted twice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 20% MTBE/hexane). The products **4** (or **5**, **6**) were dried in vacuo (~0.1 mbar) at 60 °C overnight.

2-Indolyl ketoxime ether 4a

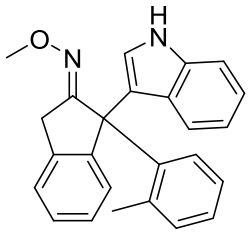
According to the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4a** was obtained as a colorless solid (65 mg, 92%).



R_f: 0.23 (20% MTBE/hexane); **mp.:** 163-165 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.90 (bs, 1H), 7.40-7.36 (m, 3H), 7.31-7.24 (m, 5H), 7.21-7.18 (m, 2H), 7.14-7.10 (m, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.54 (d, J = 2.5 Hz, 1H), 4.02 (d, J = 21.5 Hz, 1H), 3.88 (d, J = 21.5 Hz, 1H), 3.86 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.5 (C=N), 147.4 (C_q), 144.1 (C_q), 137.5 (C_q), 137.3 (C_q), 128.6 (2x CH), 128.1 (2x CH), 127.7 (CH), 127.2 (CH), 126.7 (CH), 126.2 (CH), 126.0 (C_q), 125.1 (CH), 124.8 (CH), 122.3 (CH), 122.0 (CH), 121.0 (C_q), 119.2 (CH), 111.1 (CH), 62.1 (CH_3), 59.8 (C_q), 33.2 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 2933, 1621, 1457, 1042, 862, 751, 700; **HR-MS** (ESI)**:** calcd. for $C_{24}H_{20}N_2ONa$ ($[M+Na]^+$): 375.1468, found: 375.1468; **M($C_{24}H_{20}N_2O$):** 352.44.

2-Indolyl ketoxime ether 4b

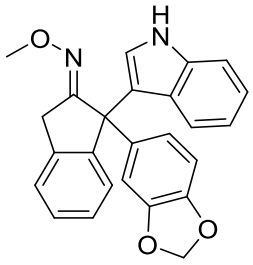
According to the general procedure 3, 2-hydroxy ketoxime ether **1b** (54 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4b** was obtained as a colorless solid (70 mg, 96%).



R_f: 0.37 (20% MTBE/hexane); **mp.:** 197-199 °C; **^{1}H-NMR** (300 MHz, DMSO-d6)**:** δ (ppm) = 10.93 (bs, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.42-7.36 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.16-7.05 (m, 4H), 6.99 (ddd, J = 8.5, 6.5, 2.0 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.76 (bs, 1H), 6.20 (bs, 1H), 3.98 (d, J = 22.0 Hz, 1H), 3.74 (s, 3H), 3.61 (d, J = 22.0 Hz, 1H), 1.77 (s, 3H); **^{13}C-NMR** (75 MHz, DMSO-d6)**:** δ (ppm) = 165.2 (C=N), 146.3 (C_q), 141.6 (C_q), 137.6 (C_q), 137.5 (C_q), 136.4 (C_q), 131.8 (CH), 129.3 (CH), 127.5 (CH), 127.1 (CH), 126.8 (CH), 125.5 (C_q), 125.5 (CH), 124.9 (CH), 124.8 (CH), 124.5 (CH), 122.6 (CH), 121.1 (CH), 118.1 (CH), 117.3 (C_q), 111.6 (CH), 61.6 (CH_3), 59.6 (C_q), 32.6 (CH_2), 20.0 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3415, 3055, 2934, 1617, 1475, 1457, 1412, 1040, 856, 748; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{22}N_2ONa$ ($[M+Na]^+$): 389.1624, found: 389.1607; **M($C_{25}H_{22}N_2O$):** 366.46.

2-Indolyl ketoxime ether 4c

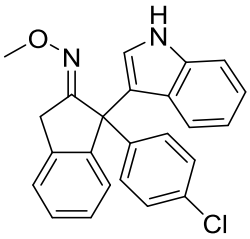
According to the general procedure 3, 2-hydroxy ketoxime ether **1c** (60 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4c** was obtained as a colorless solid (79 mg, >99%).



R_f: 0.20 (20% MTBE/hexane); **mp.:** 109-111 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.95 (bs, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.32-7.26 (m, 3H), 7.22 (t, J = 7.5 Hz, 1H), 7.17-7.13 (m, 2H), 6.99-6.95 (m, 2H), 6.82 (dd, J = 8.0, 2.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 2.5 Hz, 1H), 5.95 (m, 2H), 4.00 (d, J = 22.0 Hz, 1H), 3.90 (d, J = 22.0 Hz, 1H), 3.89 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.5 (C=N), 147.5 (C_q), 147.4 (C_q), 146.3 (C_q), 138.1 (C_q), 137.4 (C_q), 137.3 (C_q), 127.8 (CH), 127.3 (CH), 126.1 (CH), 125.9 (C_q), 125.1 (CH), 124.8 (CH), 122.3 (CH), 122.0 (CH), 121.8 (CH), 121.0 (C_q), 119.2 (CH), 111.2 (CH), 109.6 (CH), 107.5 (CH), 101.1 (CH_2), 62.1 (CH_3), 59.5 (C_q), 33.0 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3419, 2894, 1617, 1502, 1484, 1240, 1040, 745; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{20}N_2O_3Na$ ($[M+Na]^+$): 419.1366, found: 419.1355; **M($C_{25}H_{20}N_2O_3$):** 396.45.

2-Indolyl ketoxime ether 4d

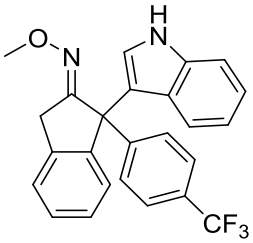
According to the general procedure 3, 2-hydroxy ketoxime ether **1d** (58 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4d** was obtained as a colorless solid (77 mg, 99%).



R_f: 0.30 (20% MTBE/hexane); **mp.:** 88-90 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.92 (bs, 1H), 7.39-7.36 (m, 1H), 7.31-7.18 (m, 8H), 7.14 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.09 (m, 1H), 6.93 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.53 (d, J = 2.5 Hz, 1H), 3.97 (d, J = 22.0 Hz, 1H), 3.89 (d, J = 21.5 Hz, 1H), 3.85 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 166.2 (C=N), 147.0 (C_q), 142.8 (C_q), 137.5 (C_q), 137.3 (C_q), 132.6 (C_q), 130.1 (2x CH), 128.2 (2x CH), 128.0 (CH), 127.4 (CH), 126.0 (CH), 125.8 (C_q), 125.2 (CH), 124.7 (CH), 122.3 (CH), 122.2 (CH), 120.6 (C_q), 119.4 (CH), 111.2 (CH), 62.2 (CH_3), 59.4 (C_q), 33.1 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3415, 2935, 1617, 1488, 1457, 1094, 1042, 1014, 815, 754, 743; **HR-MS** (ESI)**:** calcd. for $C_{24}H_{19}{}^{35}ClN_2ONa$ ($[M+Na]^+$): 409.1078, found: 409.1076; **M($C_{24}H_{19}ClN_2O$):** 386.88.

2-Indolyl ketoxime ether 4e

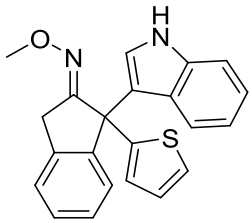
According to the general procedure 3, 2-hydroxy ketoxime ether **1e** (64 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 4.5 hours. Compound **4e** was obtained as a colorless solid (78 mg, 93%).



R_f: 0.30 (20% MTBE/hexane); **mp.:** 104-106 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.95 (bs, 1H), 7.52 (d', J = 8.5 Hz, 2H), 7.47 (d', J = 8.5 Hz, 2H), 7.40-7.38 (m, 1H), 7.32-7.13 (m, 5H), 7.08 (m, 1H), 6.96 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.55 (d, J = 2.5 Hz, 1H), 3.94 (s, 2H), 3.86 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 165.9 (C=N), 148.4 (C_q), 146.8 (C_q), 137.6 (C_q), 137.3 (C_q), 129.0 (2x CH), 128.8 (q, J = 32.5 Hz, C_q), 128.1 (CH), 127.5 (CH), 126.0 (CH), 125.8 (C_q), 125.3 (CH), 125.0 (q, J = 3.5 Hz, 2x CH), 124.8 (CH), 124.6 (q, J = 272.5 Hz, C_q), 122.4 (CH), 122.3 (CH), 120.3 (C_q), 119.5 (CH), 111.3 (CH), 62.2 (CH_3), 59.8 (C_q), 33.2 (CH_2); **^{19}F-NMR** (282 MHz, $CDCl_3$)**:** δ (ppm) = −62.3; **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3411, 2938, 1617, 1457, 1411, 1326, 1165, 1123, 1115, 1068, 1042, 1018, 824, 745; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{19}F_3N_2ONa$ ($[M+Na]^+$): 443.1342, found: 443.1338; **M($C_{25}H_{19}F_3N_2O$):** 420.44.

2-Indolyl ketoxime ether 4f

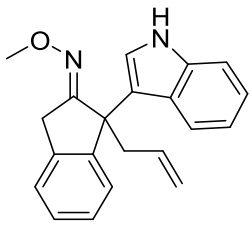
According to the general procedure 3, 2-hydroxy ketoxime ether **1f** (52 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 2 hours. Compound **4f** was obtained as a colorless solid (69 mg, 97%).



R_f: 0.19 (20% MTBE/hexane); **mp.:** 164-165 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.97 (bs, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.31-7.19 (m, 5H), 7.11-7.06 (m, 2H), 6.98-6.89 (m, 3H), 6.73 (d, J = 2.5 Hz, 1H), 4.04 (d, J = 22.0 Hz, 1H), 3.93 (d, J = 22.0 Hz, 1H), 3.87 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.2 (C=N), 148.9 (C_q), 147.2 (C_q), 137.22 (C_q), 137.20 (C_q), 128.2 (CH), 127.4 (CH), 126.43 (CH), 126.40 (CH), 125.8 (C_q), 125.7 (CH), 125.2 (CH), 125.1 (CH), 124.5 (CH), 122.1 (CH), 121.4 (CH), 121.1 (C_q), 119.4 (CH), 111.2 (CH), 62.3 (CH_3), 56.9 (C_q), 33.0 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3412, 2934, 1618, 1457, 1041, 865, 743, 702; **HR-MS** (ESI)**:** calcd. for $C_{22}H_{18}N_2OSNa$ ([M+Na]$^+$): 381.1032, found: 381.1031; **M($C_{22}H_{18}N_2OS$):** 358.46.

2-Indolyl ketoxime ether 4g

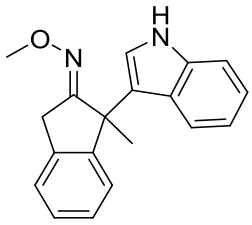
According to the general procedure 3, 2-hydroxy ketoxime ether **1g** (44 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 6 hours. Compound **4g** was obtained as a colorless solid (55 mg, 87%).



R_f: 0.27 (20% MTBE/hexane); **mp.:** 185-187 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.23 (bs, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.31-7.24 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.12-7.07 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.94-6.88 (m, 2H), 5.56 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 5.04 (d, J = 17.0 Hz, 1H), 4.95 (d, J = 10.0 Hz, 1H), 3.98 (d, J = 22.5 Hz, 1H), 3.86 (s, 3H), 3.80 (d, J = 22.5 Hz, 1H), 3.28 (dd, J = 13.0, 8.0 Hz, 1H), 3.06 (dd, J = 13.0, 7.0 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.8 (C=N), 146.6 (C_q), 138.0 (C_q), 137.1 (C_q), 133.8 (CH), 127.6 (CH), 127.4 (CH), 125.9 (C_q), 124.8 (CH), 124.7 (CH), 122.0 (CH), 121.9 (CH), 120.9 (C_q), 120.7 (CH), 119.3 (CH), 118.5 (CH_2), 111.2 (CH), 62.0 (CH_3), 54.4 (C_q), 45.0 (CH_2), 34.4 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3259, 2931, 1640, 1457, 1045, 887, 746, 739; **HR-MS** (ESI)**:** calcd. for $C_{21}H_{20}N_2ONa$ ([M+Na]$^+$): 339.1468, found: 339.1464; **M($C_{21}H_{20}N_2O$):** 316.40.

2-Indolyl ketoxime ether 4h

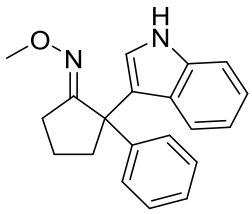
According to the general procedure 3, 2-hydroxy ketoxime ether **1h** (38 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4h** was obtained as a colorless solid (56 mg, 96%).



R_f: 0.18 (20% MTBE/hexane); **mp.:** 165-166 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.30 (bs, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.31-7.25 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.12-7.05 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.90 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.87-6.85 (m, 2H), 4.07 (d, J = 23.0 Hz, 1H), 3.98 (d, J = 23.0 Hz, 1H), 3.86 (s, 3H), 1.92 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 168.4 (C=N), 149.1 (C_q), 137.1 (C_q), 137.0 (C_q), 127.58 (CH), 127.56 (CH), 125.8 (C_q), 124.9 (CH), 124.1 (CH), 122.1 (CH), 121.8 (CH), 121.2 (C_q), 120.5 (CH), 119.2 (CH), 111.3 (CH), 61.9 (CH_3), 50.3 (C_q), 33.4 (CH_2), 28.0 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3285, 3020, 2969, 1654, 1478, 1459, 1336, 1245, 1043, 899, 853, 754, 739, 730; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{18}N_2ONa$ ([M+Na]$^+$): 313.1311, found: 313.1307; **M($C_{19}H_{18}N_2O$):** 290.37.

2-Indolyl ketoxime ether 5

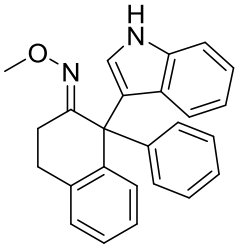
According to the general procedure 3, 2-hydroxy ketoxime ether **2** (*E/Z* = 85:15, 41 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **5** was obtained as a colorless solid (48 mg, 79%, *E/Z* >95:5).



R_f: 0.25 (20% MTBE/hexane); **mp.:** 114-116 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.97 (bs, 1H), 7.45-7.40 (m, 3H), 7.32-7.23 (m, 4H), 7.13 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.00 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H), 3.84 (s, 3H), 2.83-2.52 (m, 4H), 1.75 (p, J = 7.0 Hz, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 168.4 (C=N), 143.8 (C_q), 137.4 (C_q), 128.2 (2x CH), 128.1 (2x CH), 126.4 (CH), 125.9 (C_q), 124.0 (CH), 121.9 (CH), 121.7 (CH), 120.0 (C_q), 119.1 (CH), 111.4 (CH), 61.9 (CH_3), 54.6 (C_q), 40.2 (CH_2), 27.9 (CH_2), 21.4 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3410, 3314, 3054, 2952, 2936, 2895, 1617, 1491, 1458, 1446, 1417, 1340, 1246, 1043, 862, 745, 699; **HR-MS** (ESI)**:** calcd. for $C_{20}H_{20}N_2ONa$ ([M+Na]$^+$): 327.1468, found: 327.1465; **M($C_{20}H_{20}N_2O$):** 304.39.

2-Indolyl ketoxime ether 6

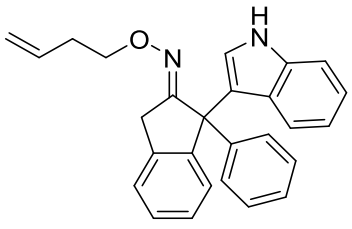
According to the general procedure 3, 2-hydroxy ketoxime ether **3** (54 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 68 hours. Compound **6** was obtained as a colorless solid (64 mg, 87%).



R_f: 0.20 (20% MTBE/hexane); **mp.:** 204-206 °C; **^{1}H-NMR** (300 MHz, DMSO-d6)**:** δ (ppm) = 10.79 (bs, 1H), 7.36-7.17 (m, 6H), 7.08-6.99 (m, 4H), 6.85-6.75 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 2.5 Hz, 1H), 3.59 3.86 (s, 3H), 2.88-2.78 (m, 1H), 2.72-2.60 (m, 2H), 2.32-2.21 (m, 1H); **^{13}C-NMR** (75 MHz, DMSO-d6)**:** δ (ppm) = 160.3 (C=N), 142.7 (C_q), 140.8 (C_q), 138.2 (C_q), 137.1 (C_q), 128.7 (CH), 128.4 (2x CH), 127.9 (2x CH), 127.8 (CH), 126.8 (CH), 126.6 (CH), 126.3 (C_q), 126.1 (CH), 125.9 (CH), 121.6 (CH), 120.7 (CH), 118.6 (C_q), 117.9 (CH), 111.5 (CH), 61.3 (CH_3), 54.7 (C_q), 26.1 (CH_2), 24.4 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 3055, 2934, 1617, 1486, 1457, 1445, 1044, 859, 766, 744, 700; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{23}N_2O$ ($[M+H]^+$): 367.1805, found: 3671798; **M($C_{25}H_{22}N_2O$):** 366.46.

2-Indolyl ketoxime ether 4i

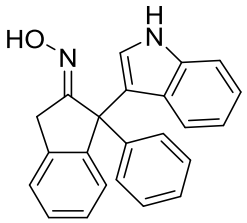
According to the general procedure 3, 2-hydroxy ketoxime ether **1i** (59 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4i** was obtained as a colorless solid (72 mg, 92%).



R_f: 0.72 (40% MTBE/hexane); **mp.:** 74-76 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.89 (bs, 1H), 7.46-7.42 (m, 3H), 7.35-7.29 (m, 4H), 7.26-7.22 (m, 3H), 7.17-7.14 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 2.5 Hz, 1H), 5.81 (m, 1H), 5.06-5.02 (m, 2H), 4.15 (tt, *J* = 6.5, 3.5 Hz, 2H), 4.07 (d, *J* = 22.0 Hz, 1H), 3.94 (d, *J* = 22.0 Hz, 1H), 2.37 (q, *J* = 7.0 Hz, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.8 (C=N), 147.3 (C_q), 144.0 (C_q), 137.6 (C_q), 137.3 (C_q), 135.2 (CH), 128.6 (2x CH), 128.0 (2x CH), 127.7 (CH), 127.2 (CH), 126.2 (CH), 126.2 (CH), 125.9 (C_q), 125.0 (CH), 124.9 (CH), 122.2 (CH), 121.9 (CH), 121.0 (C_q), 119.1 (CH), 116.5 (CH_2), 111.1 (CH), 73.2 (CH_2), 59.8 (C_q), 34.1 (CH_2), 33.3 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3412, 3057, 2928, 1639, 1491, 1457, 1414, 1043, 1032, 750, 744, 699; **HR-MS** (ESI)**:** calcd. for $C_{27}H_{24}N_2ONa$ ($[M+Na]^+$): 415.1781, found: 415.1778; **M($C_{27}H_{24}N_2O$):** 392.50.

2-Indolyl ketoxime 4j'

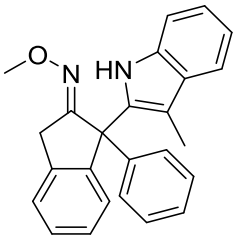
According to a modificiation of the general procedure 3, 2-hydroxy ketoxime silyl ether **1j** (R^2 = TBS, 71 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Then, TBAF•$3H_2O$ (0.13 g, 0.40 mmol, 2.0 equiv) was added and it was stirred at room temperature for 20 min. Compound **4j'** was obtained as a colorless solid (59 mg, 87%).



R_f: 0.44 (50% MTBE/hexane); **mp.:** 151-153 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.93 (bs, 1H), 7.64 (bs, 1H), 7.41-7.39 (m, 3H), 7.32-7.19 (m, 7H), 7.14 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 4.08 (d, J = 22.0 Hz, 1H), 3.91 (d, J = 22.0 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 168.3 (C=N), 147.2 (C_q), 143.6 (C_q), 137.4 (C_q), 137.2 (C_q), 128.5 (2x CH), 128.2 (2x CH), 127.9 (CH), 127.3 (CH), 126.8 (CH), 126.2 (CH), 125.9 (C_q), 125.2 (CH), 124.9 (CH), 122.1 (CH), 121.8 (CH), 121.0 (C_q), 119.4 (CH), 111.3 (CH), 59.8 (C_q), 32.6 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3420, 1629, 749; **HR-MS** (ESI)**:** calcd. for $C_{23}H_{18}N_2ONa$ ($[M+Na]^+$): 361.1311, found: 361.1310; **M($C_{23}H_{18}N_2O$):** 338.41.

2-Indolyl ketoxime ether 4k

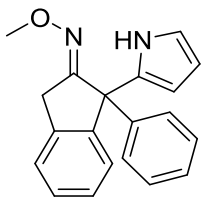
According to a modificiation of the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 3-methylindole (26 mg, 0.20 mmol, 1.0 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 2 hours. Compound **4k** was obtained as a colorless solid (65 mg, 88%).



R_f: 0.46 (10% MTBE/hexane); **mp.:** 163-164 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.79 (bs, 1H), 7.52 (m, 1H), 7.42-7.07 (m, 12H), 4.02 (d, J = 22.0 Hz, 1H), 3.93 (s, 3H), 3.82 (d, J = 22.0 Hz, 1H), 1.83 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 165.8 (C=N), 145.3 (C_q), 143.2 (C_q), 137.8 (C_q), 135.9 (C_q), 134.6 (C_q), 130.3 (C_q), 128.5 (4x CH), 128.3 (CH), 127.6 (CH), 127.3 (CH), 126.5 (CH), 125.3 (CH), 121.7 (CH), 119.2 (CH), 118.5 (CH), 110.7 (CH), 109.5 (C_q), 62.4 (CH_3), 60.8 (C_q), 33.3 (CH_2), 9.8 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3397, 3053, 2936, 1596, 1491, 1458, 1332, 1240, 1034, 855, 745, 732, 700; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{22}N_2ONa$ ($[M+Na]^+$): 389.1624, found: 389.1623; **M($C_{25}H_{22}N_2O$):** 366.46.

2-Pyrrolyl ketoxime ether 4l

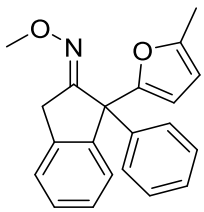
According to a modificiation of the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), pyrrole (42 μL, 0.60 mmol, 3.0 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4l** was obtained as a colorless solid (58 mg, 96%). Small amounts (ca. 10%) of twice alkylated pyrrole was included which could not be separated by column chromatography.



R_f: 0.27 (5% MTBE/hexane); **mp.:** 158-159 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.77 (bs, 1H), 7.37-7.20 (m, 7H), 7.06 (m, 2H), 6.87 (td, *J* = 2.5, 1.5 Hz, 1H), 6.18 (dt, *J* = 3.5, 2.5 Hz, 1H), 5.96 (ddd, *J* = 3.5, 2.5, 1.5 Hz, 1H), 4.06 (d, *J* = 22.5 Hz, 1H), 3.97 (s, 3H), 3.94 (d, *J* = 22.5 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 168.0 (C=N), 146.9 (C_q), 146.3 (C_q), 137.3 (C_q), 132.3 (C_q), 128.2 (2x CH), 128.0 (CH), 127.8 (2x CH), 127.4 (CH), 126.7 (CH), 126.1 (CH), 125.1 (CH), 118.5 (CH), 109.0 (CH), 107.8 (CH), 62.3 (CH_3), 60.0 (C_q), 34.1 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3429, 3055, 2935, 1654, 1491, 1476, 1457, 1445, 1414, 1116, 1091, 1035, 862, 794, 757, 730, 719, 698, 555; **HR-MS** (ESI)**:** calcd. for $C_{20}H_{18}N_2ONa$ ($[M+Na]^+$): 325.1311, found: 325.1311; **M($C_{20}H_{18}N_2O$):** 302.38.

2-Furanyl ketoxime ether 4m

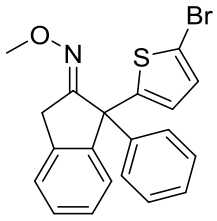
According to the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 2-methylfuran (21 μL, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4m** was obtained as a colorless oil (52 mg, 83%).



R_f: 0.54 (5% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.37-7.23 (m, 7H), 7.17-7.15 (m, 2H), 6.08 (d, *J* = 3.0 Hz, 1H), 5.93-5.92 (m, 1H), 3.97 (s, 3H), 3.95 (s, 2H), 2.29 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 164.7 (C=N), 153.5 (C_q), 152.7 (C_q), 145.3 (C_q), 144.1 (C_q), 137.9 (C_q), 128.2 (2x CH), 128.1 (3x CH), 127.4 (CH), 126.9 (CH), 126.6 (CH), 125.0 (CH), 110.1 (CH), 106.0 (CH), 62.2 (CH_3), 60.5 (C_q), 33.5 (CH_2), 13.9 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3449, 3025, 2937, 2916, 1602, 1554, 1491, 1478, 1459, 1446, 1217, 1204, 1164, 1044, 1025, 1009, 909, 863, 787, 755, 729, 720, 698; **HR-MS** (ESI)**:** calcd. for $C_{21}H_{19}NO_2Na$ ($[M+Na]^+$): 340.1308, found: 340.1315; **M($C_{21}H_{19}NO_2$):** 317.39.

2-Thiophenyl ketoxime ether 4n

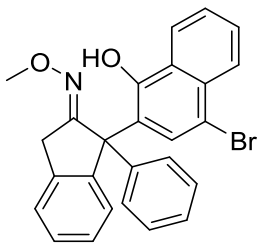
According to the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 2-bromothiophene (23 μL, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 2 hours. Compound **4n** was obtained as a colorless oil (61 mg, 77%).



R_f: 0.59 (5% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.38-7.22 (m, 9H), 6.92 (d, J = 4.0 Hz, 1H), 6.66 (d, J = 4.0 Hz, 1H), 3.98-3.96 (m, 4H), 3.89 (d, J = 22.0 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 166.3 (C=N), 150.8 (C_q), 146.4 (C_q), 144.6 (C_q), 137.6 (C_q), 129.2 (CH), 128.5 (CH), 128.3 (2x CH), 128.2 (2x CH), 127.5 (2x CH), 127.2 (CH), 126.1 (CH), 125.3 (CH), 112.0 (C_q), 62.4 (CH_3), 62.0 (C_q), 33.2 (CH_2); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 2935, 1597, 1491, 1477, 1459, 1445, 1436, 1043, 970, 862, 796, 754, 732, 697; **HR-MS** (ESI)**:** calcd. for $C_{20}H_{16}{}^{79}BrNOSNa$ ($[M+Na]^+$): 420.0028, found: 420.0032; **M($C_{20}H_{16}BrNOS$):** 398.32.

2-Naphthyl ketoxime ether 4o

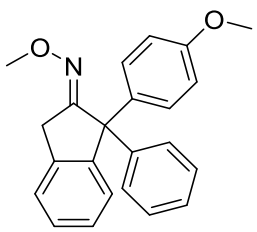
According to the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 4-bromo-1-naphthol (54 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Compound **4o** was obtained as a colorless solid (87 mg, 95%).



R_f: 0.72 (10% MTBE/hexane); **mp.:** 164-166 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 9.41 (bs, 1H), 8.43 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.62 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.53 (ddd, J = 8.0, 7.0, 1.5 Hz, 1H), 7.44-7.42 (m, 1H), 7.38-7.22 (m, 5H), 7.18 (s, 1H), 7.15-7.12 (m, 2H), 7.01-6.98 (m, 1H), 4.16 (d, J = 23.0 Hz, 1H), 3.98 (s, 3H), 3.91 (d, J = 23.0 Hz, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 170.8 (C=N), 152.0 (C_q), 145.7 (C_q), 144.2 (C_q), 136.6 (C_q), 132.6 (C_q), 130.1 (CH), 128.5 (C_q), 128.54 (2x CH), 128.45 (2x CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.1 (CH), 126.7 (CH), 125.9 (CH), 125.6 (CH), 123.9 (CH), 123.2 (C_q), 112.4 (C_q), 63.8 (C_q), 62.8 (CH_3), 34.0 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3481, 3069, 2933, 1586, 1494, 1458, 1445, 1369, 1276, 1258, 1044, 880, 758, 698, 690, 629; **HR-MS** (ESI)**:** calcd. for $C_{26}H_{20}{}^{79}BrNO_2Na$ ($[M+Na]^+$): 480.0570, found: 480.0570; **M($C_{26}H_{20}BrNO_2$):** 458.36.

2-Phenyl ketoxime ether 4p

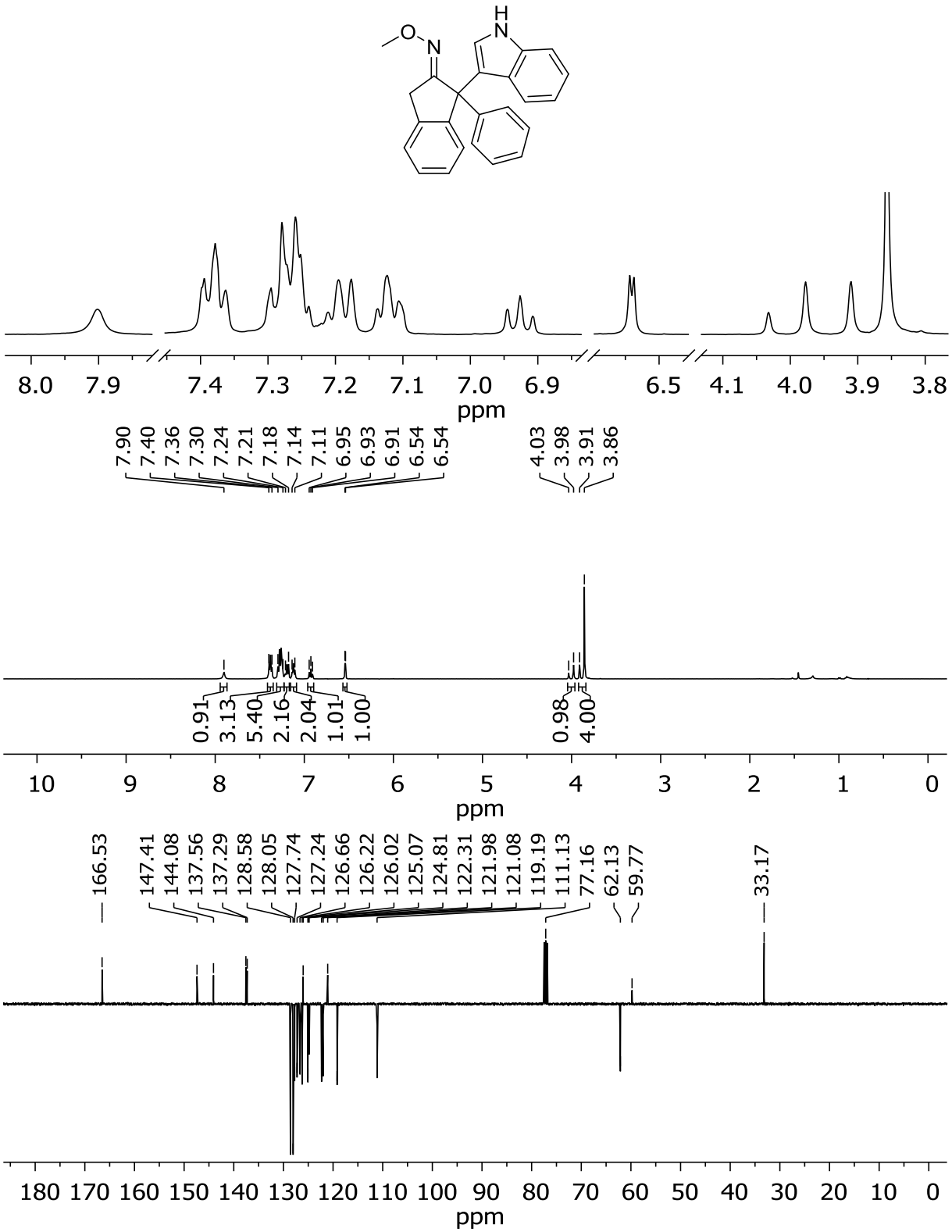
According to the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), anisole (26 μL, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 24 hours. Compound **4p** was obtained as a colorless oil (38 mg, 56%).



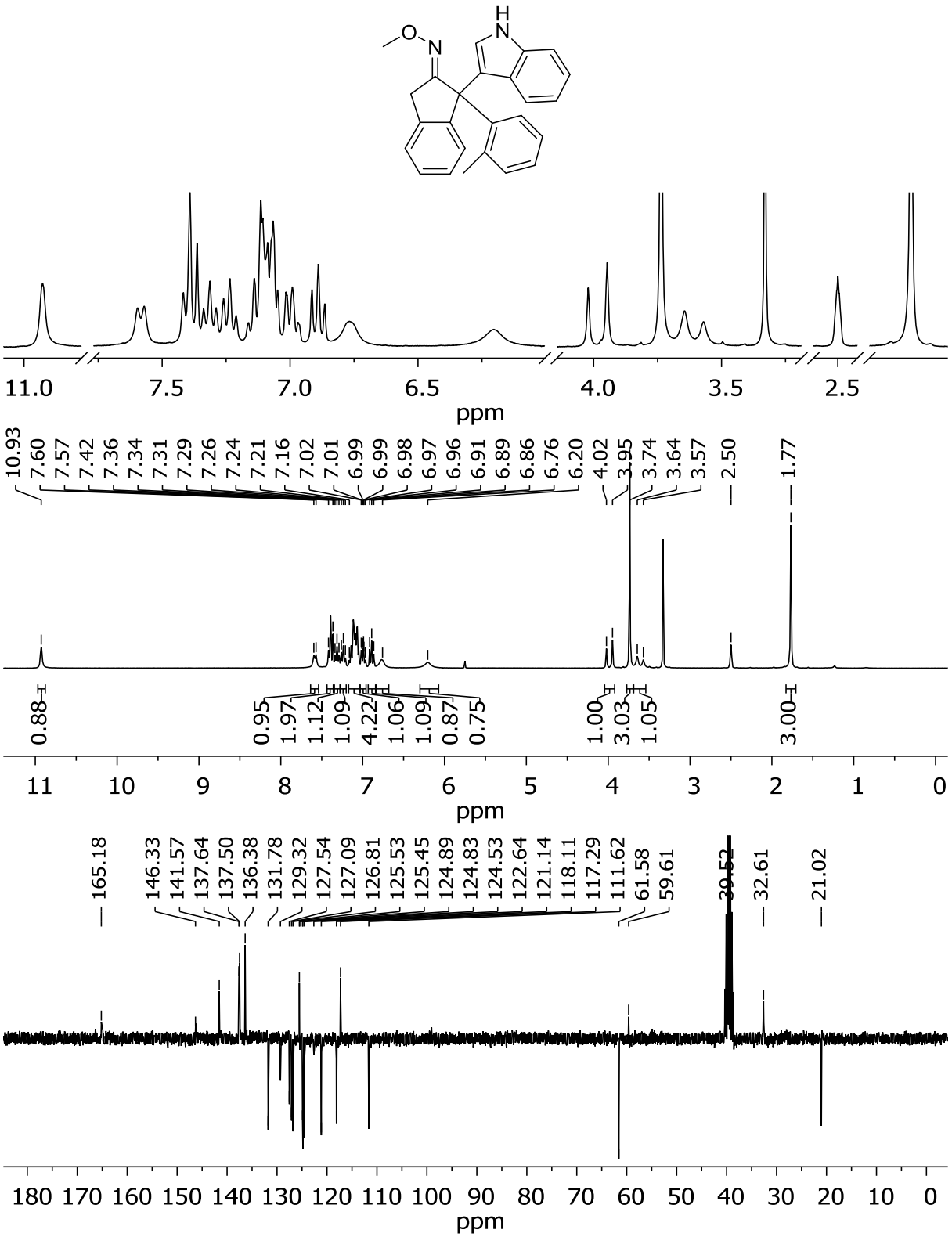
R_f: 0.53 (10% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.38-7.36 (m, 1H), 7.32-7.25 (m, 7H), 7.18 (d‘, *J* = 9.0 Hz, 2H), 7.11-7.10 (m, 1H), 6.84 (d‘, *J* = 9.0 Hz, 2H), 3.95 (s, 3H), 3.91 (s, 3H), 3.82 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 167.5 (C=N), 158.3 (C_q), 147.4 (C_q), 145.8 (C_q), 137.7 (C_q), 137.6 (C_q), 130.2 (2x CH), 129.0 (2x CH), 128.0 (2x CH), 127.7 (CH), 127.3 (CH), 126.7 (CH), 126.6 (CH), 125.2 (CH), 113.4 (2x CH), 64.3 (C_q), 61.1 (CH_3), 55.3 (CH_3), 33.5 (CH_2); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3021, 3007, 2936, 2898, 1607, 1509, 1460, 1444, 1297, 1250, 1216, 1181, 1043, 862, 826, 755, 724, 699, 589; **HR-MS** (ESI)**:** calcd. for $C_{23}H_{21}NO_2Na$ ($[M+Na]^+$): 366.1465, found: 366.1465; **M($C_{23}H_{21}NO_2$):** 343.43.

3.3 ^{1}H-NMR and ^{13}C-NMR Spectra

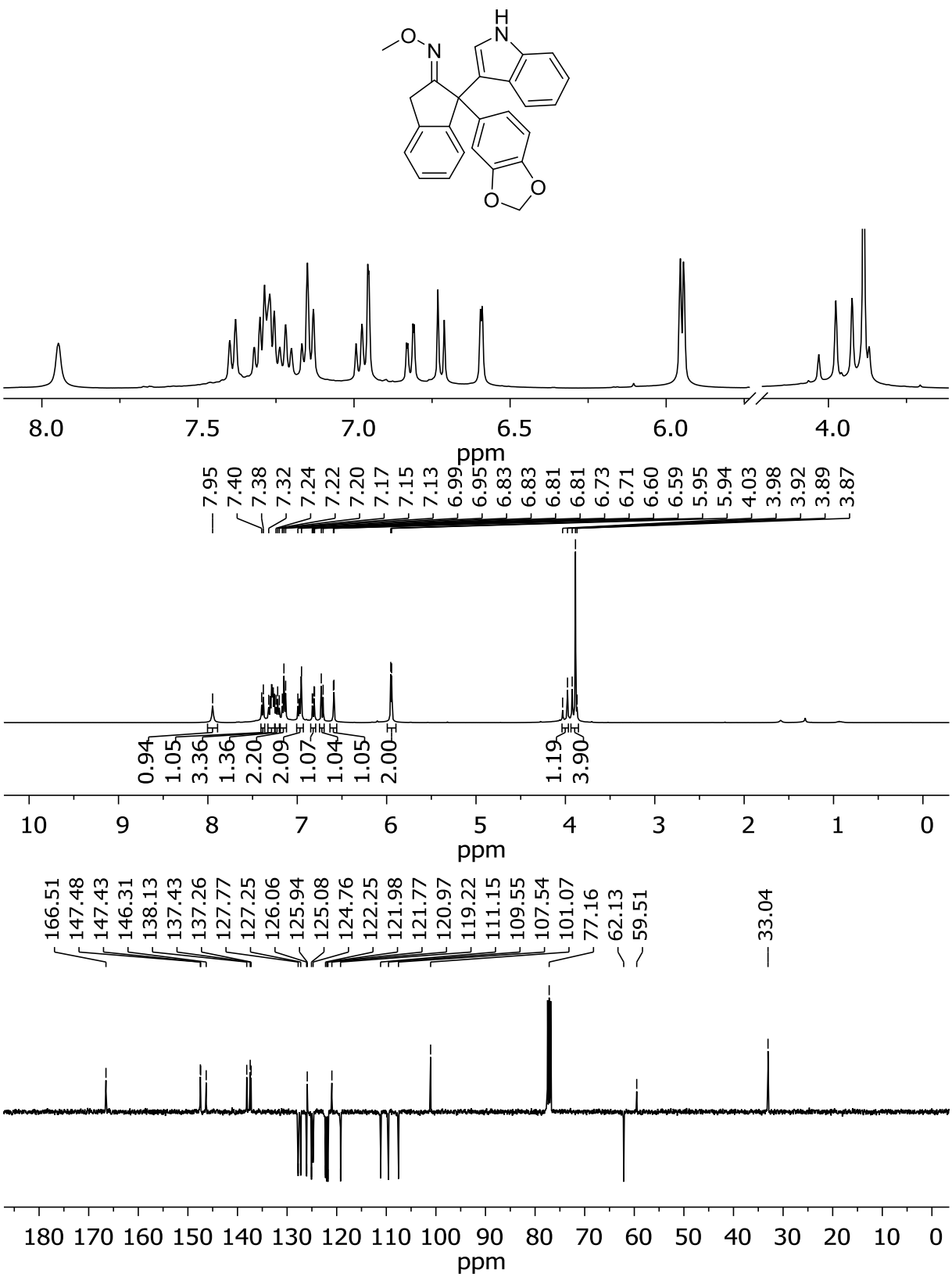
2-Indolyl ketoxime ether 4a ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



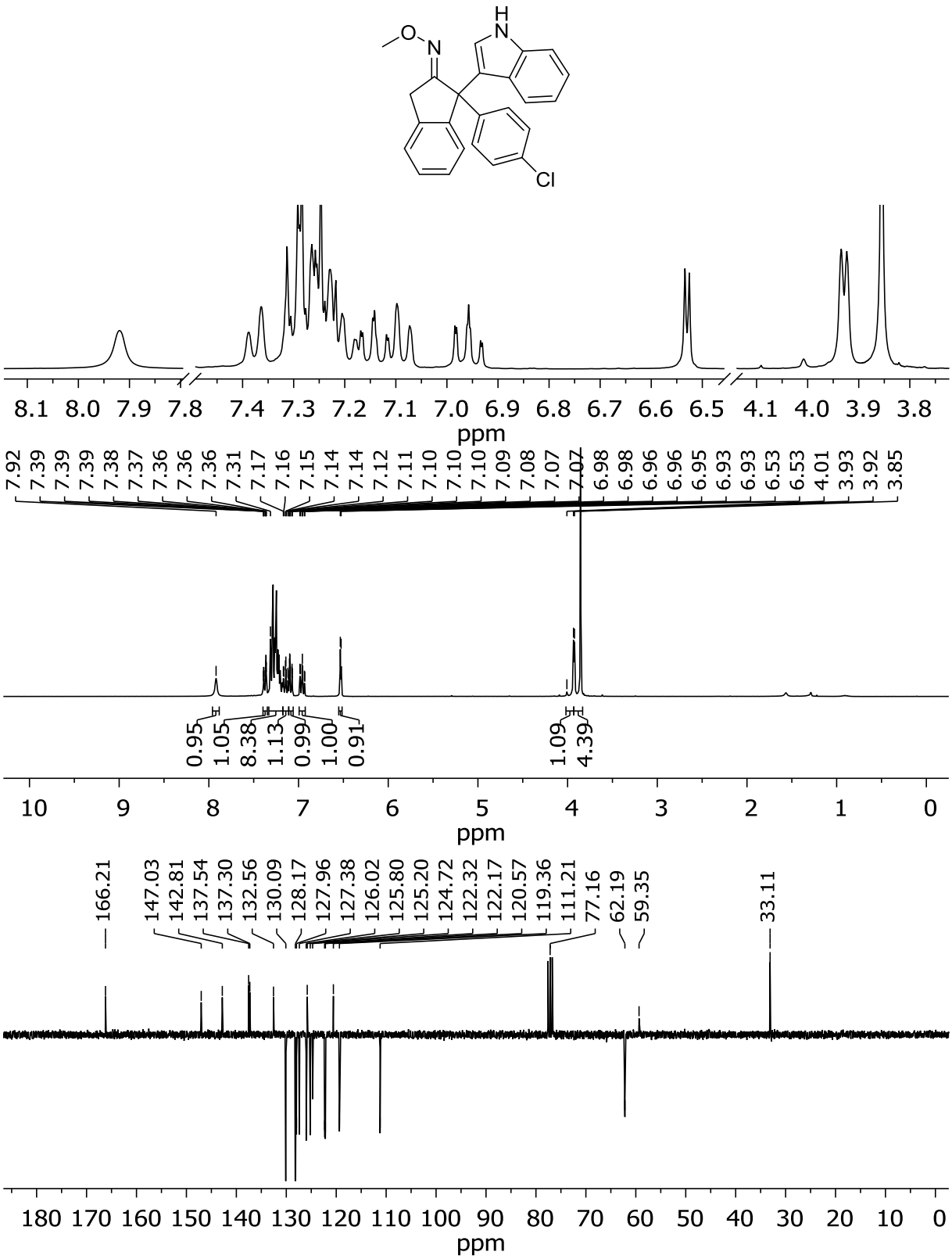
2-Indolyl ketoxime ether 4b (DMSO-d6; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



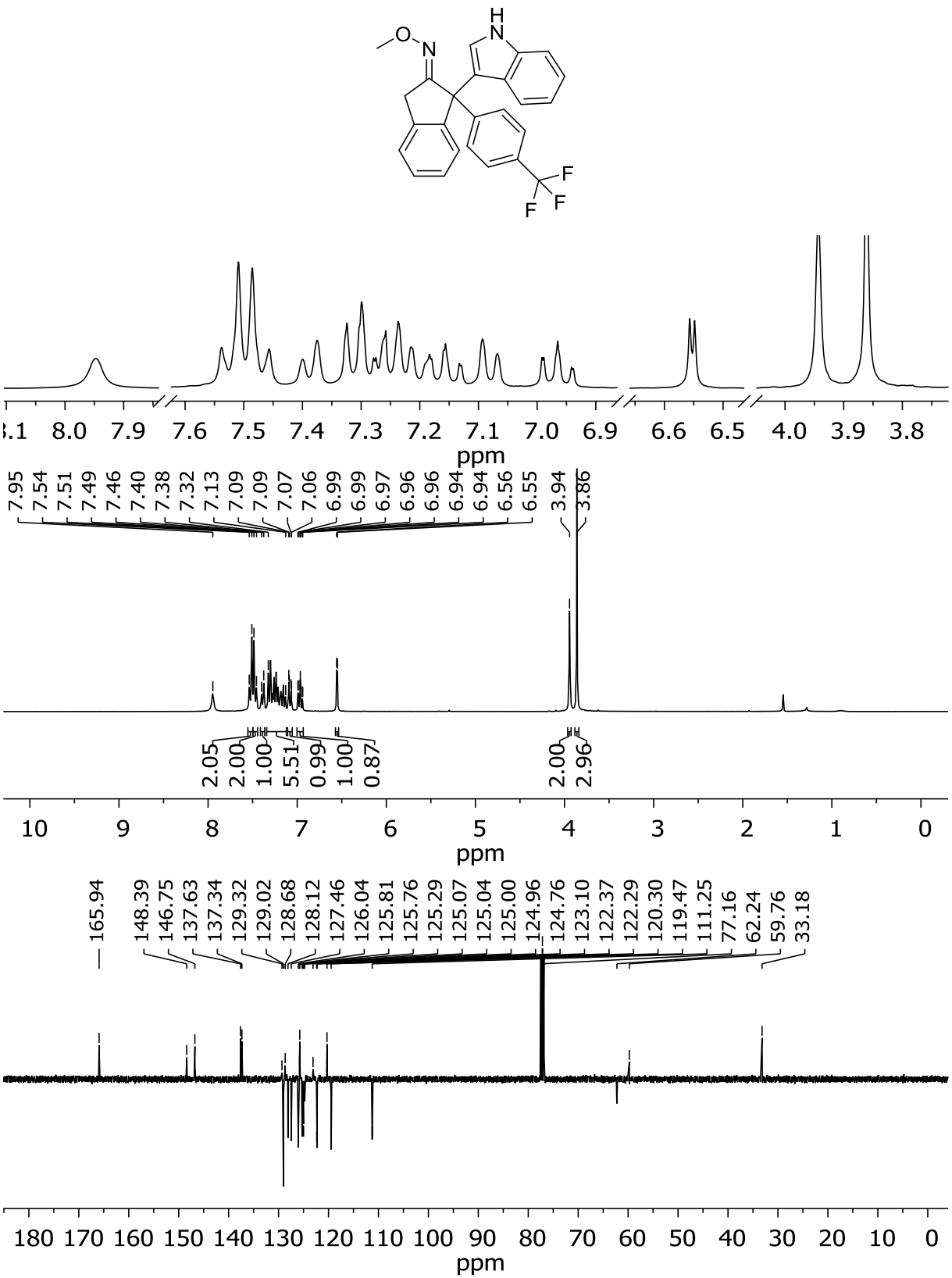
2-Indolyl ketoxime ether 4c ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



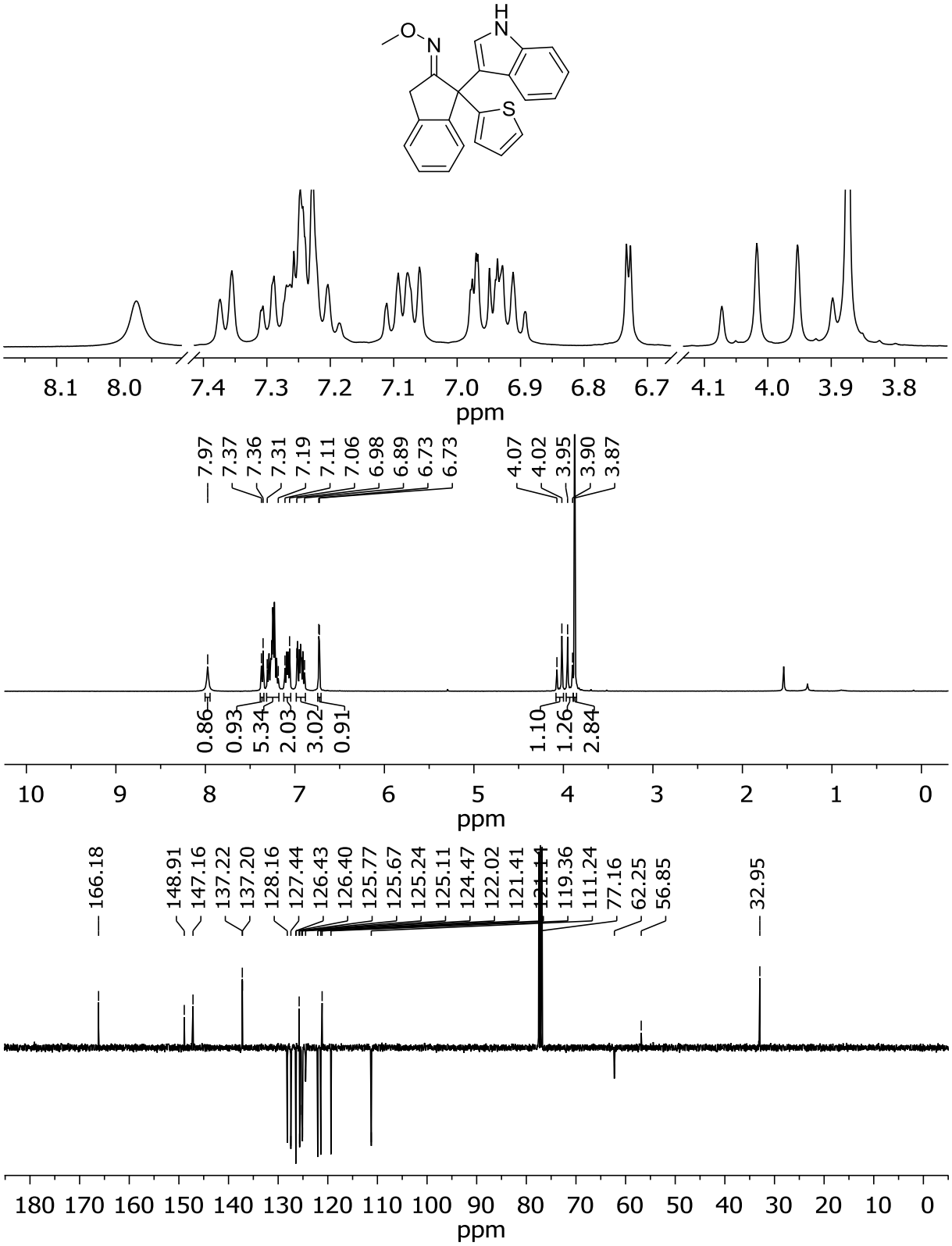
2-Indolyl ketoxime ether 4d ($CDCl_3$; ^{1}H-NMR: 300 MHz, ^{13}C-NMR: 75 MHz)



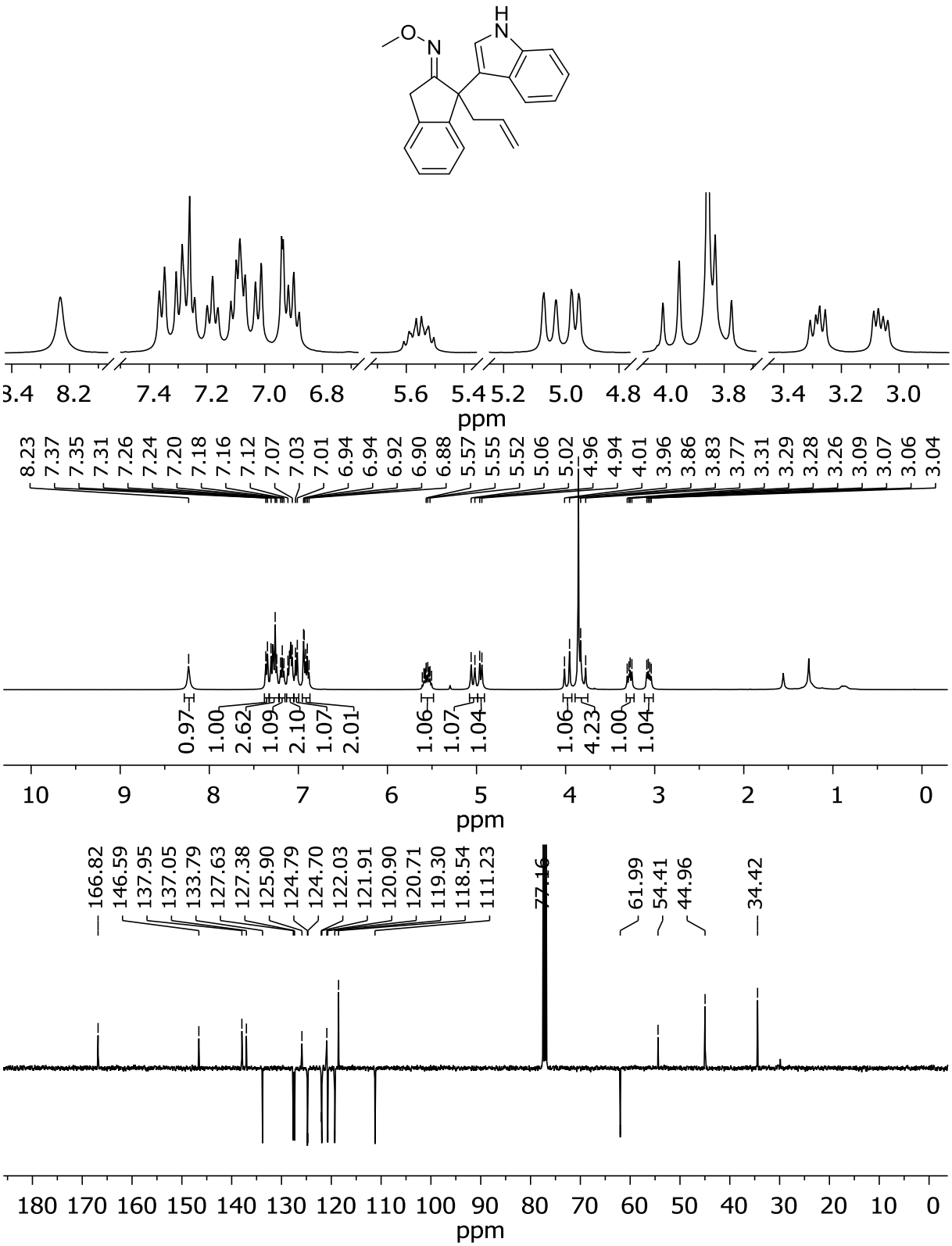
2-Indolyl ketoxime ether 4e ($CDCl_3$; ^{1}H-NMR: 300 MHz, ^{13}C-NMR: 100 MHz)



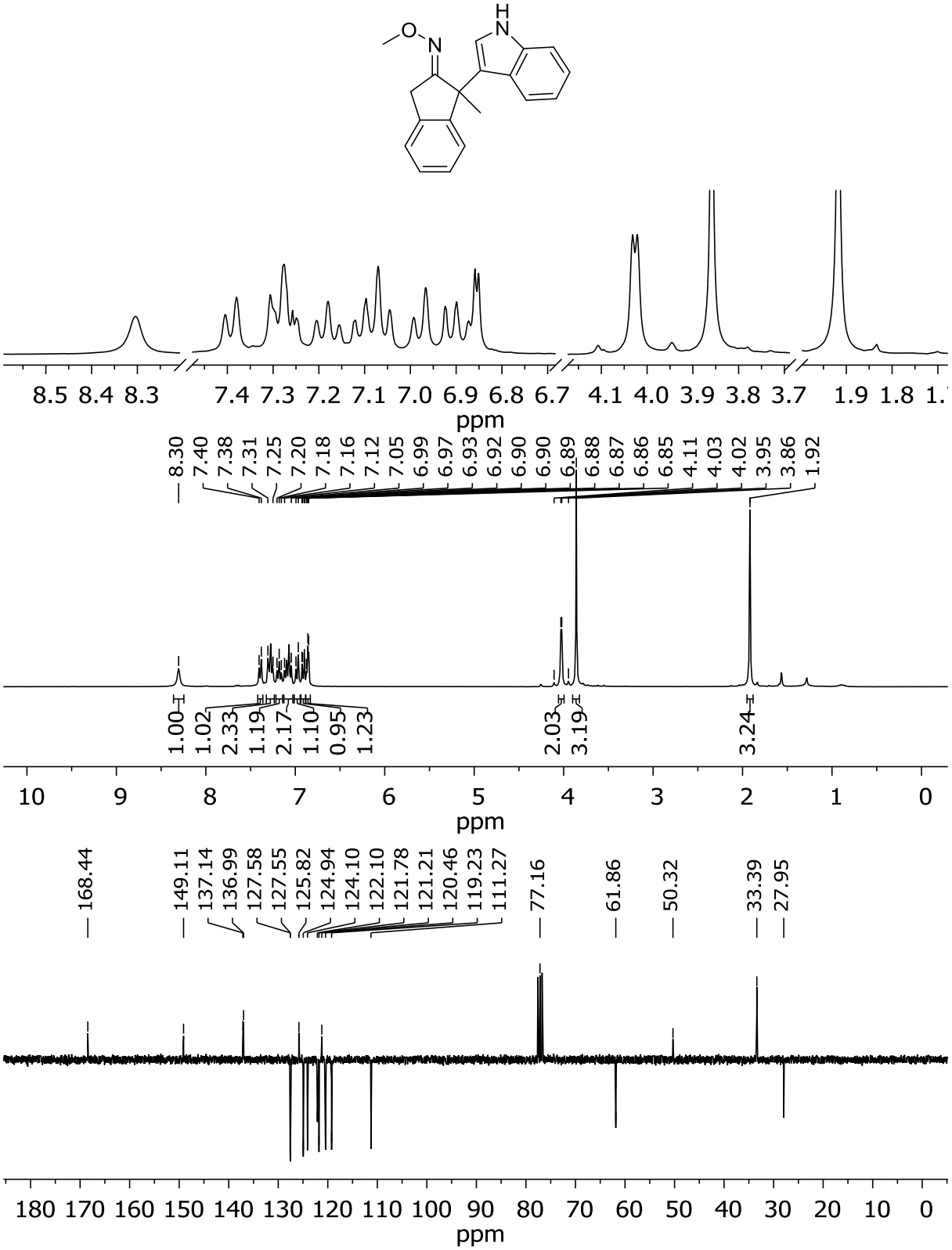
2-Indolyl ketoxime ether 4f ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



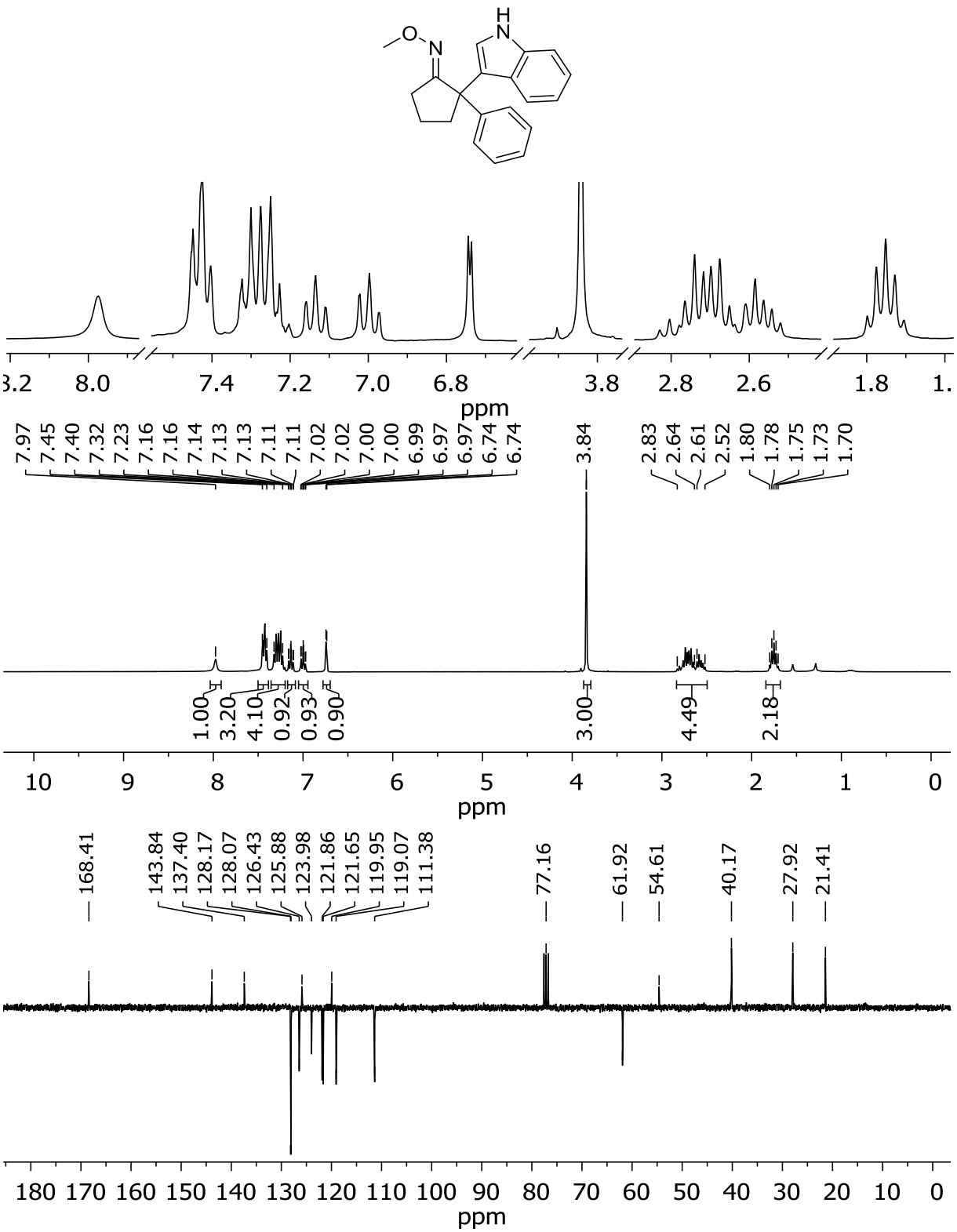
2-Indolyl ketoxime ether 4g ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



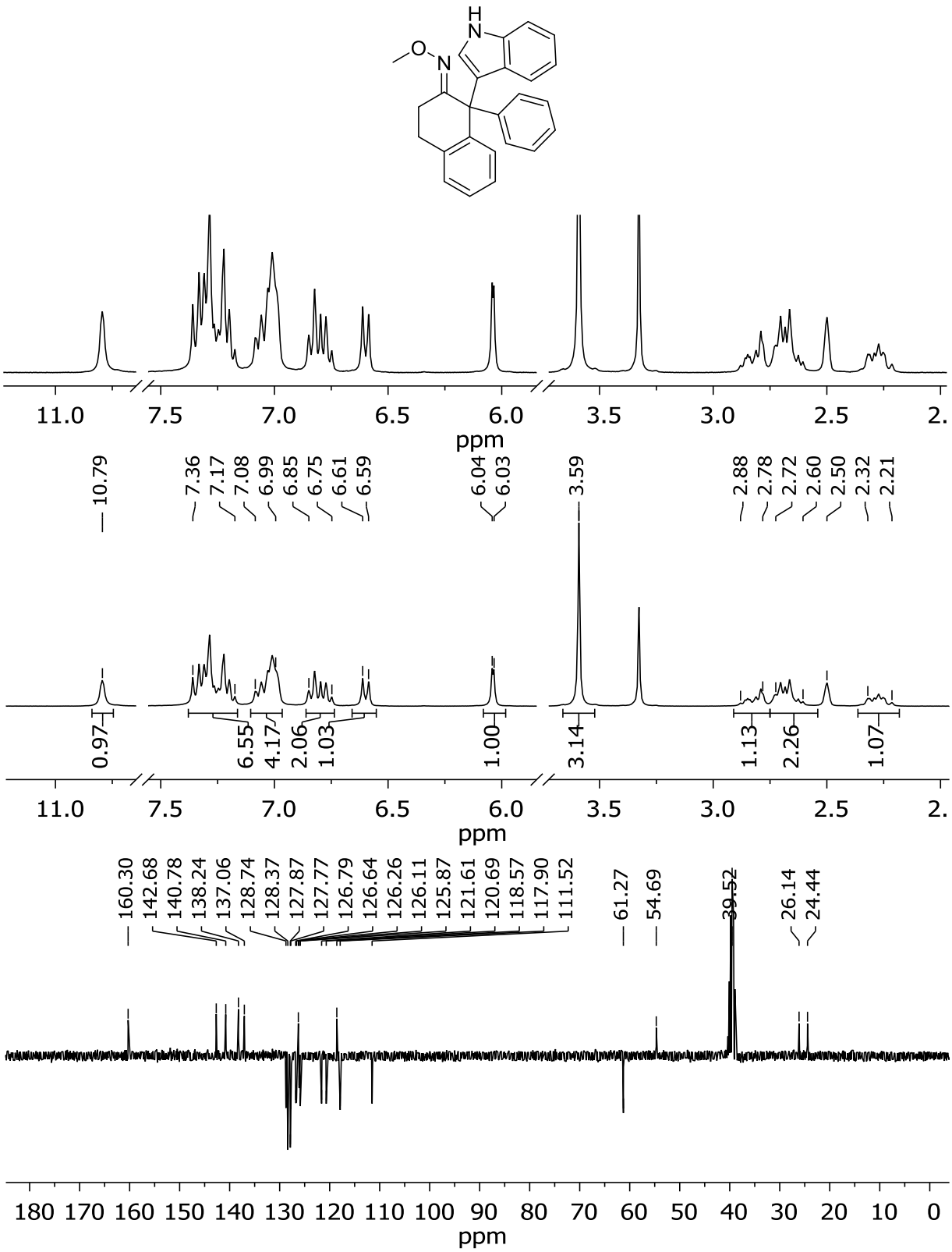
2-Indolyl ketoxime ether 4h ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



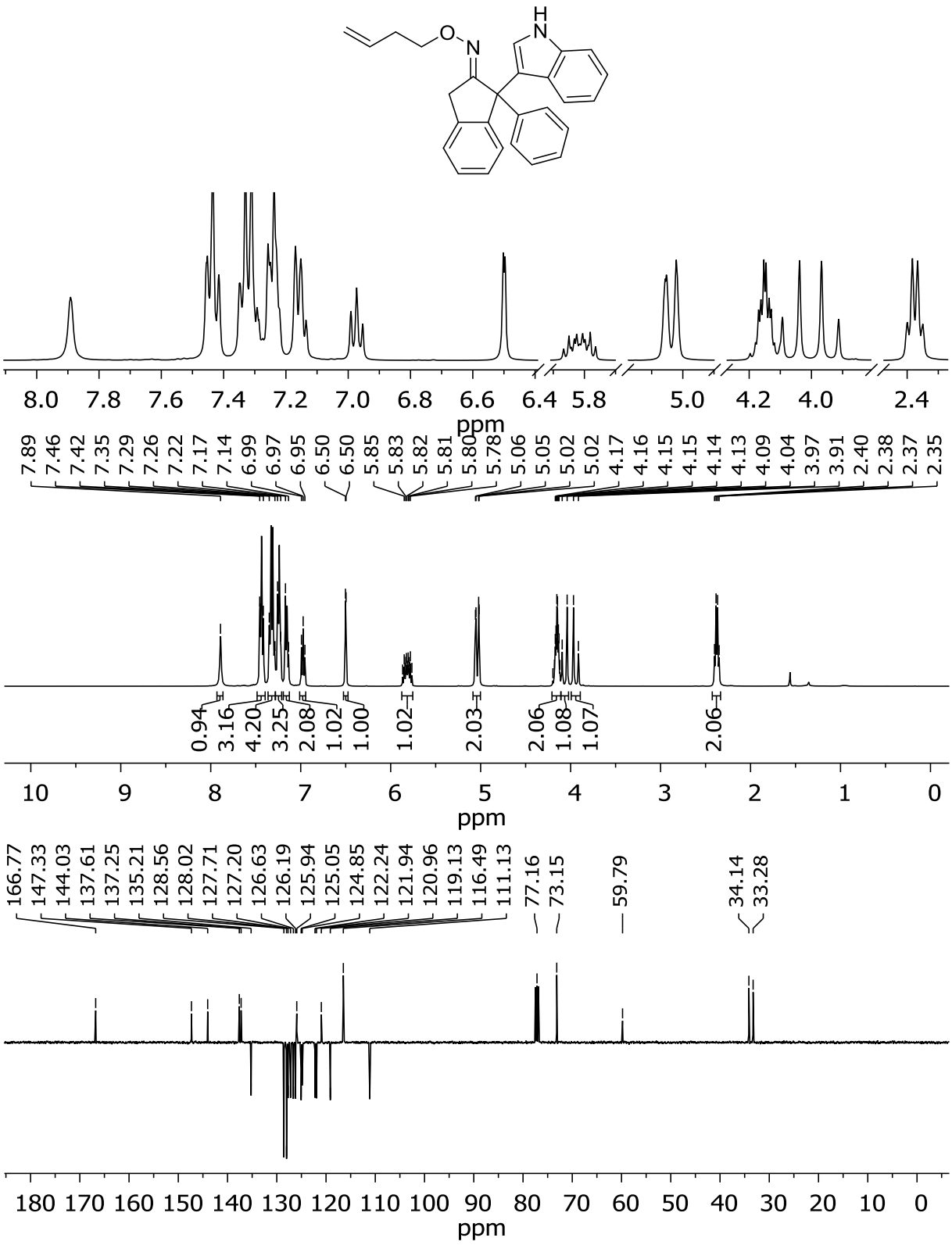
2-Indolyl ketoxime ether 5 ($CDCl_3$; ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz)



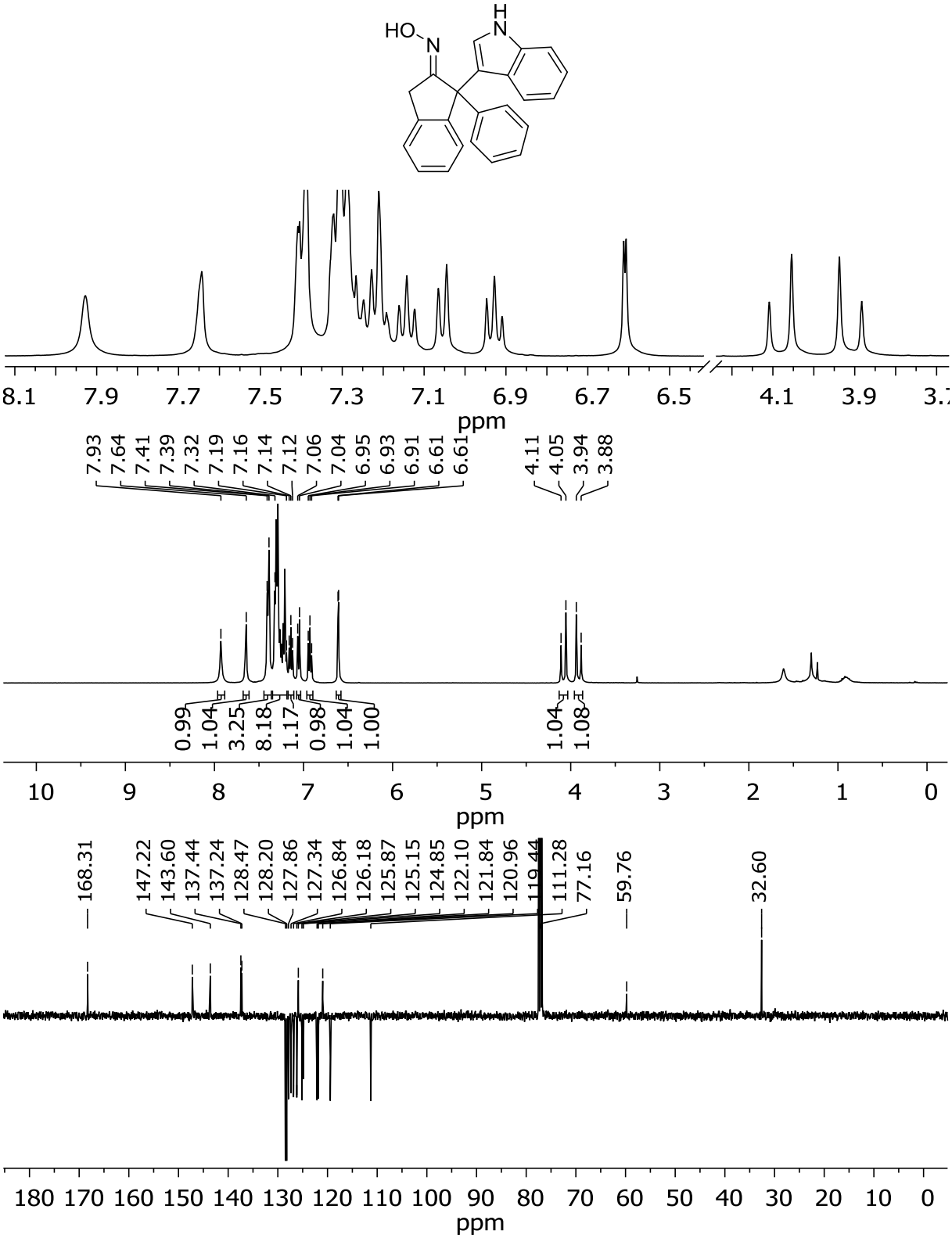
2-Indolyl ketoxime ether 6 (DMSO-d6; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



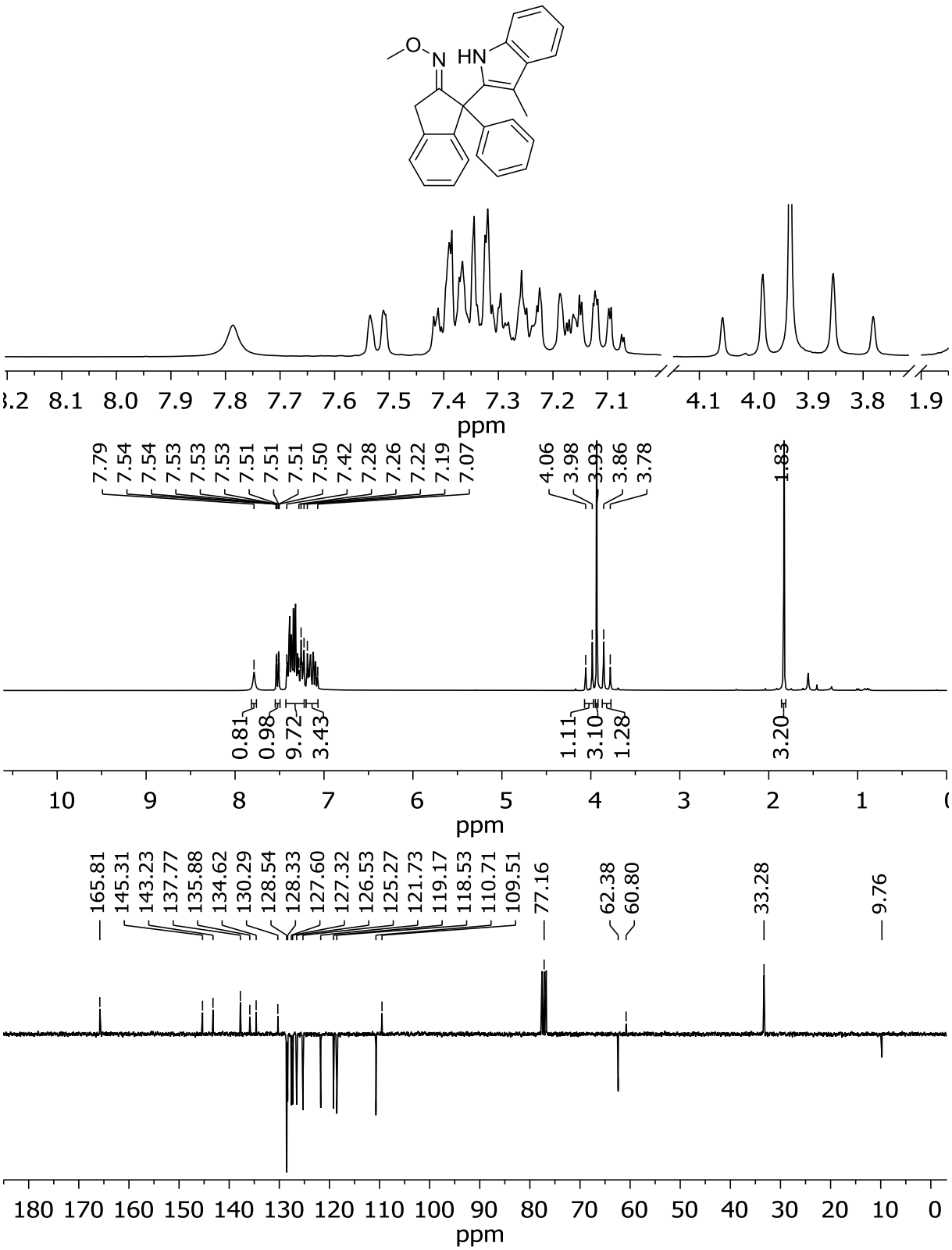
2-Indolyl ketoxime ether 4i ($CDCl_3$; ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz)



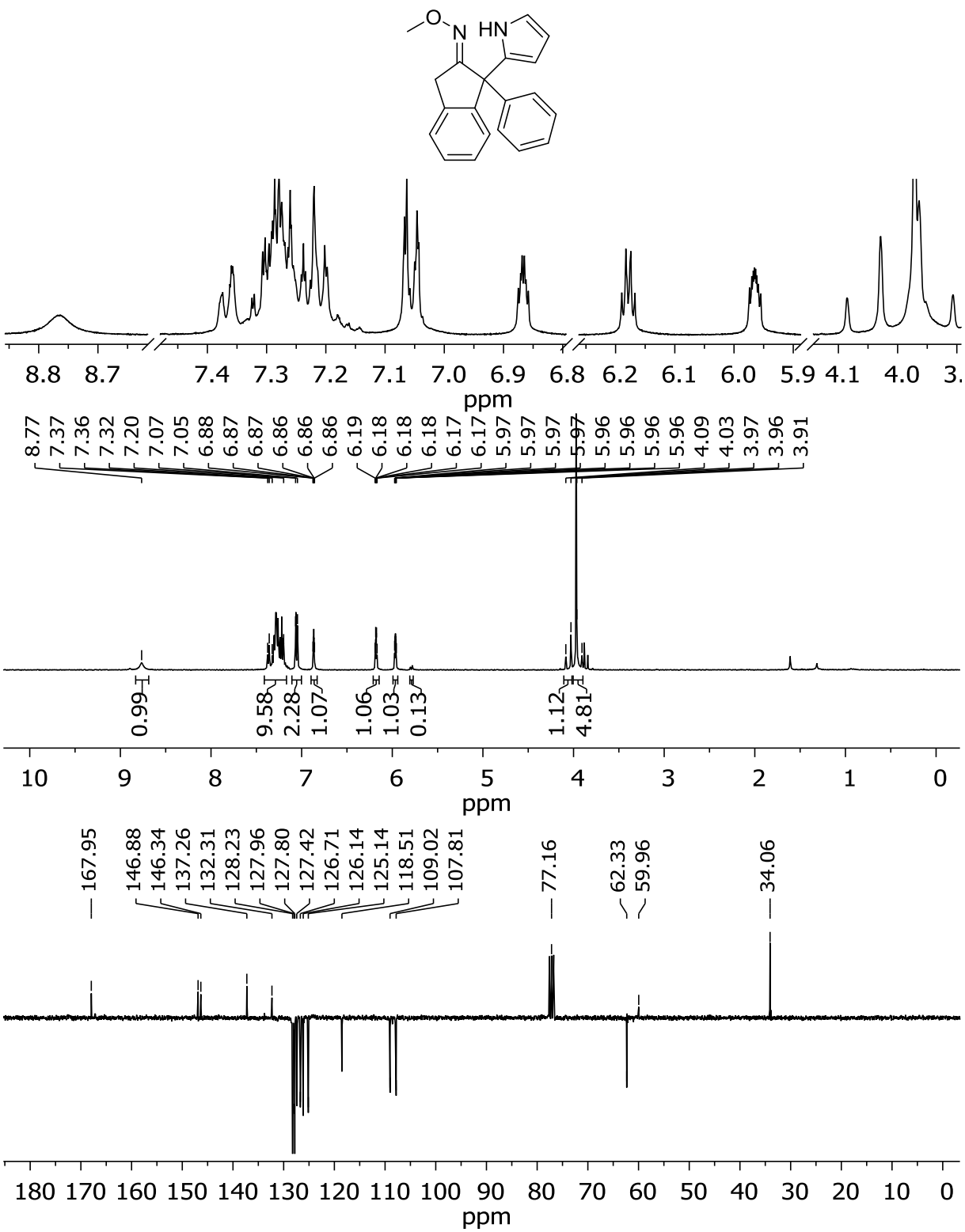
2-Indolyl ketoxime 4j' ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



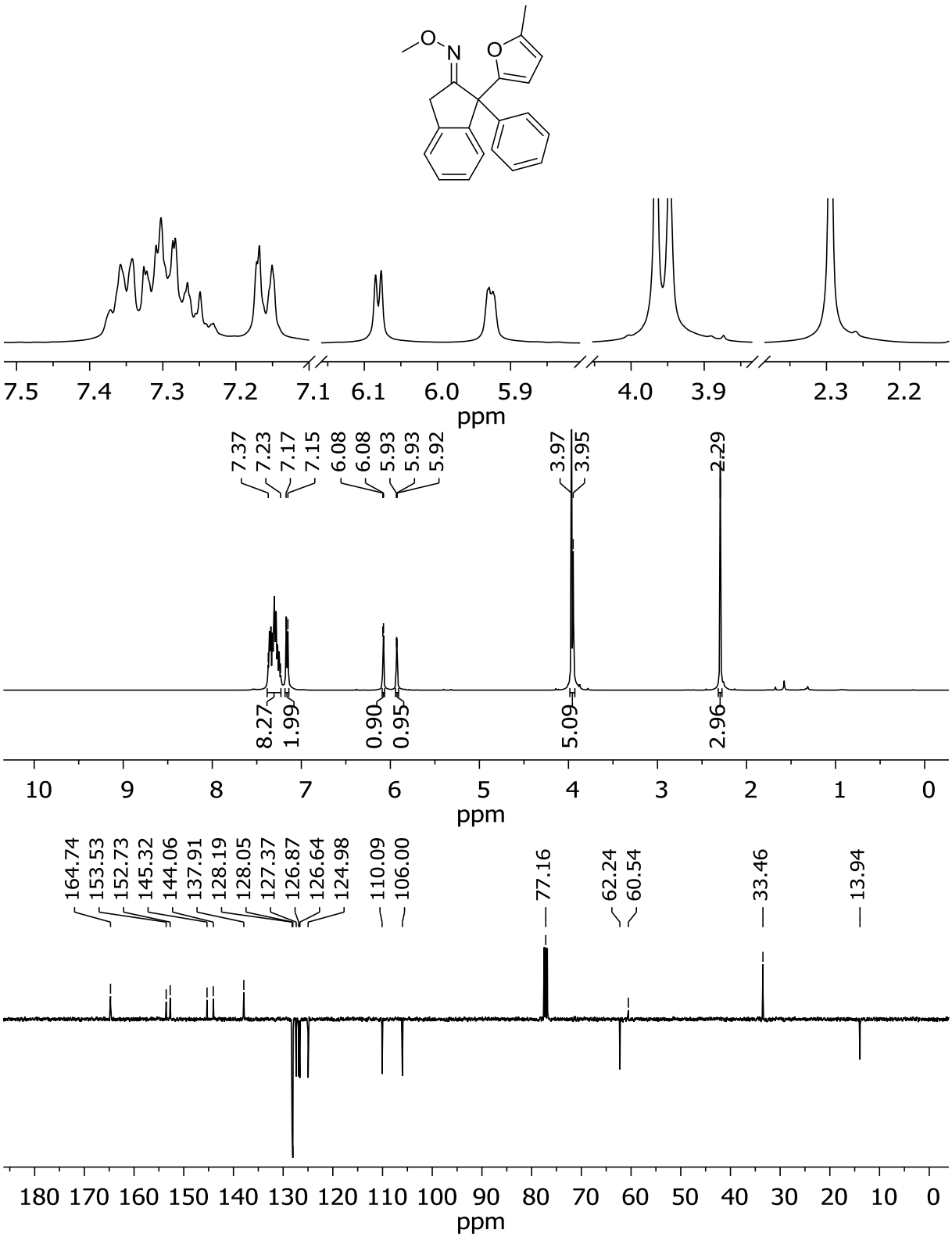
2-Indolyl ketoxime ether 4k ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



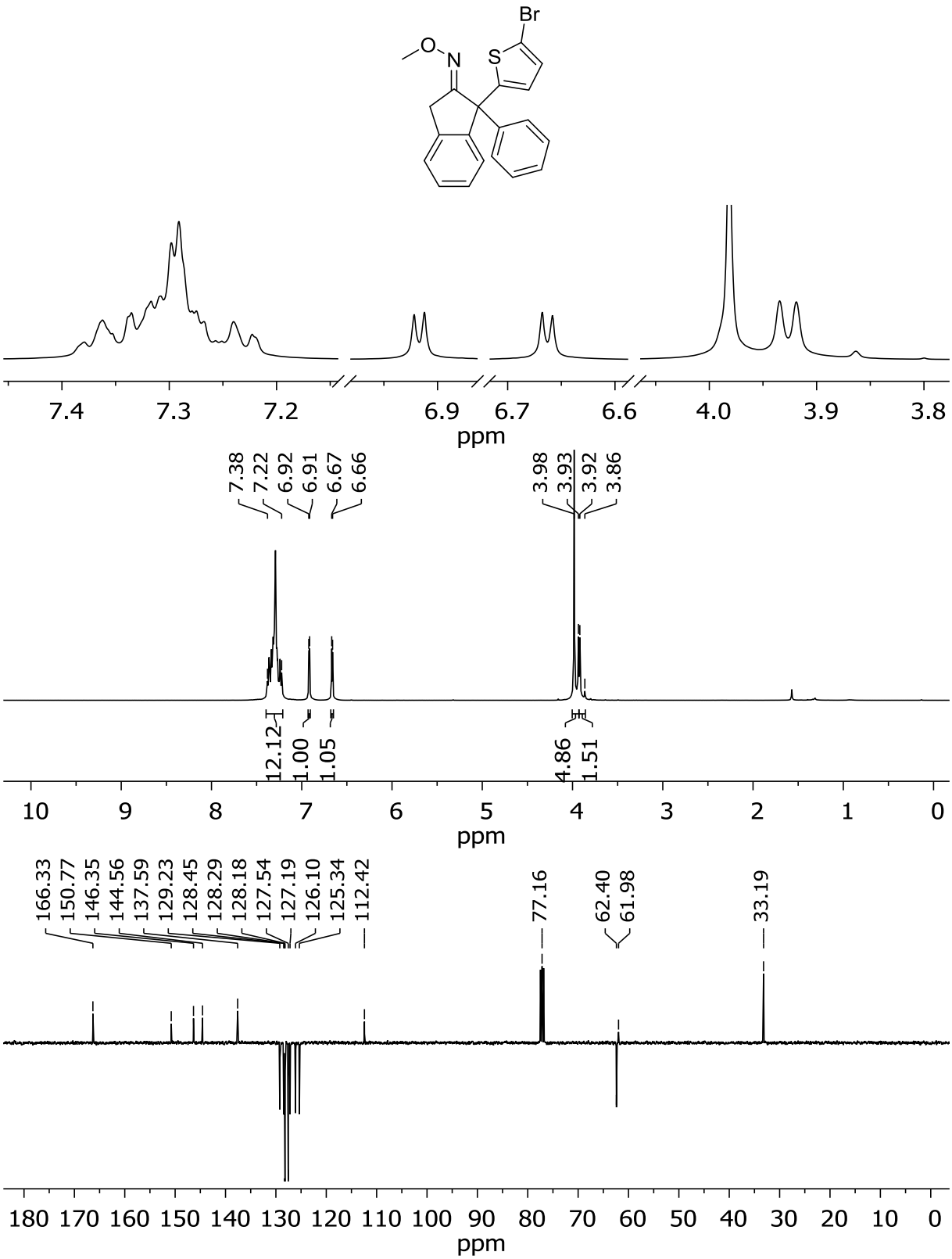
2-Pyrrolyl ketoxime ether 4l ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 75 MHz)



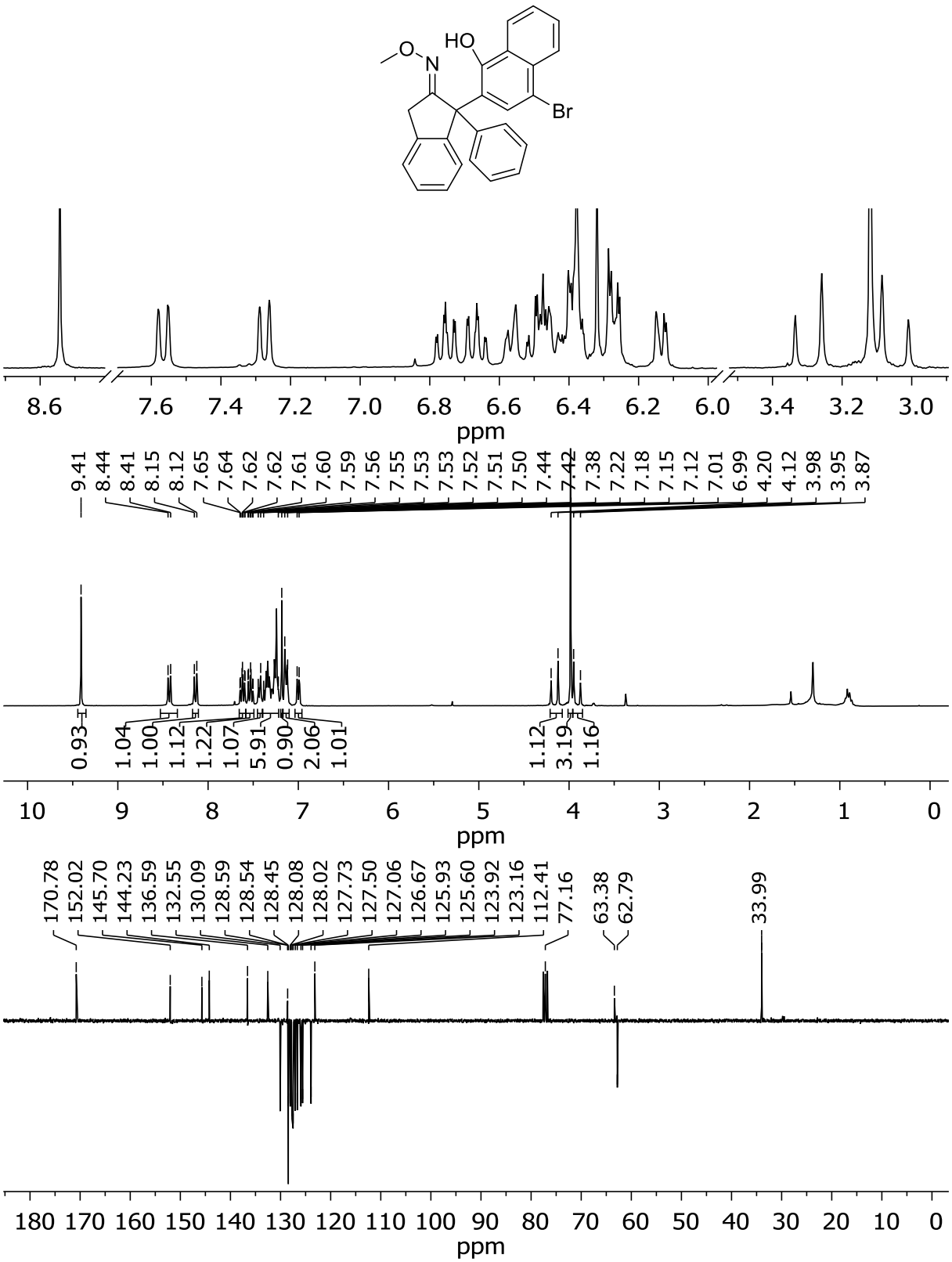
2-Furanyl ketoxime ether 4m ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



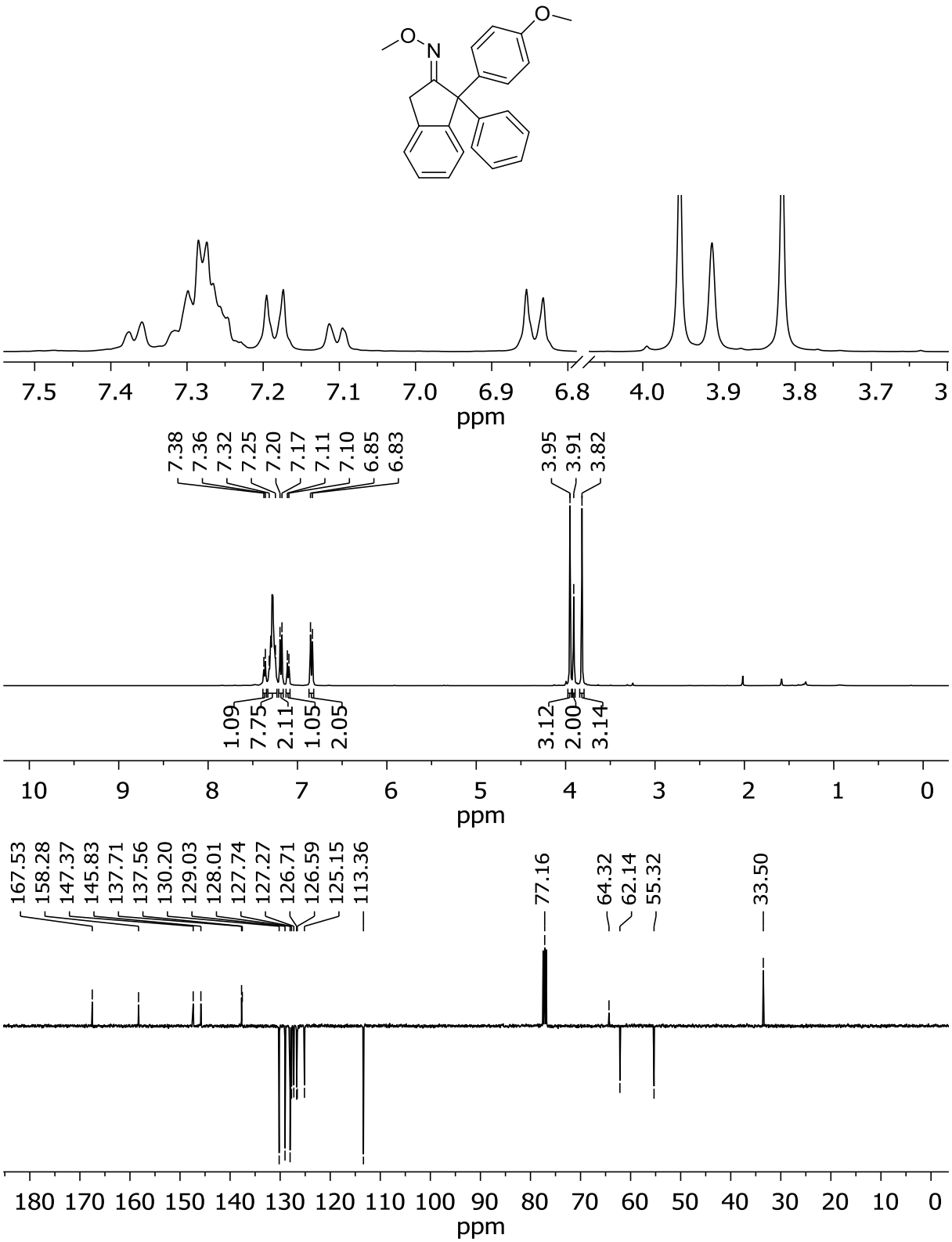
2-Thiophenyl ketoxime ether 4n ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



2-Naphthyl ketoxime ether 4o ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



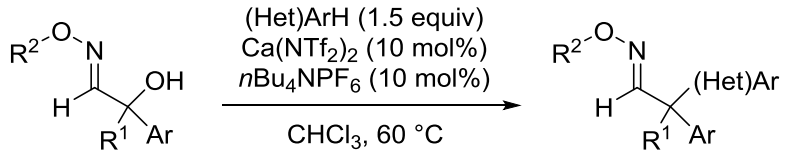
2-Phenyl ketoxime ether 4p ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



4 The FCR of 2-Hydroxy Aldoxime Ethers

4.1 Substrate Scope

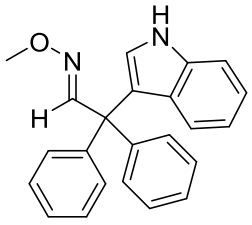
General procedure 4 of the FCR



2-Hydroxy aldoxime ether **7** (1.0 equiv), a (hetero)arene (1.5 equiv), $Ca(NTf_2)_2$ (0.10 equiv) and $n$$Bu_4NPF_6$ (0.10 equiv) were placed in an oven dried and sealable DURAN® test tube. Abs. $CHCl_3$ (0.2 M) was added and the reaction mixture was heated to 60 °C while stirring. After complete reaction it was quenched with sat. $NaHCO_3$-solution and extracted twice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 20% MTBE/hexane).

2-Indolyl aldoxime ether 8a

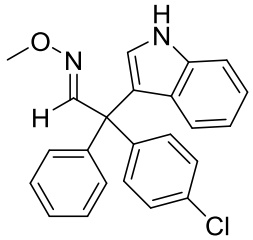
According to the general procedure 4, 2-hydroxy aldoxime ether **7a** (48 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and $n$$Bu_4NPF_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 3 hours. Compound **8a** was obtained as a colorless solid (57 mg, 84%).



R_f: 0.32 (20% MTBE/hexane); **mp.:** 120-121 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.34 (s, 1H), 7.98 (bs, 1H), 7.33-7.24 (m, 11H), 7.20-7.14 (m, 2H), 6.99 (t, J = 7.5 Hz, 1H), 6.41 (d, J = 2.5 Hz, 1H), 3.83 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.5 (HC=N), 143.6 (2x C_q), 137.1 (C_q), 129.8 (4x CH), 128.0 (4x CH), 126.9 (2x CH), 126.6 (C_q), 125.7 (CH), 122.5 (CH), 122.1 (CH), 119.9 (C_q), 119.4 (CH), 111.4 (CH), 61.8 (CH_3), 55.1 (C_q); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 3056, 2935, 1617, 1457, 1020, 748, 702; **HR-MS** (ESI)**:** calcd. for $C_{23}H_{20}N_2ONa$ ([M+Na]$^+$): 363.1468, found: 363.1465; **M($C_{23}H_{20}N_2O$):** 340.43.

2-Indolyl aldoxime ether 8b

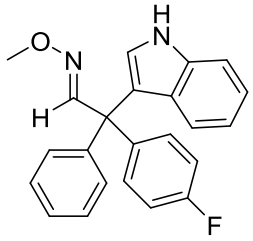
According to the general procedure 4, 2-hydroxy aldoxime ether **7b** (55 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 5 hours. Compound **8b** was obtained as a colorless solid (67 mg, 89%).



R_f: 0.32 (20% MTBE/hexane); **mp.:** 81-82 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.24 (s, 1H), 8.01 (bs, 1H), 7.34-7.27 (m, 4H), 7.26-7.23 (m, 2H), 7.21-7.13 (m, 5H), 7.10 (d, J = 8.5 Hz, 1H), 6.97 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.44 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.0 (HC=N), 143.3 (C_q), 142.0 (C_q), 137.1 (C_q), 132.8 (C_q), 131.4 (2x CH), 129.6 (2x CH), 128.2 (2x CH), 128.1 (2x CH), 127.1 (CH), 126.3 (C_q), 125.5 (CH), 122.3 (2x CH), 119.6 (CH), 119.6 (C_q), 111.4 (CH), 61.9 (CH_3), 54.8 (C_q); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3412, 3056, 2936, 1617, 1489, 1457, 1095, 1057, 1035, 1022, 1014, 816, 764, 744, 703; **HR-MS** (ESI)**:** calcd. for $C_{23}H_{19}{}^{35}ClN_2ONa$ ([M+Na]$^+$): 397.1078, found: 397.1083; **M($C_{23}H_{19}ClN_2O$):** 374.87.

2-Indolyl aldoxime ether 8c

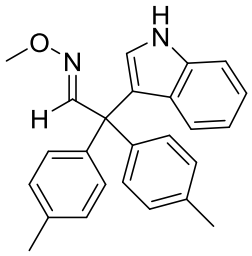
According to the general procedure 4, 2-hydroxy aldoxime ether **7c** (52 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8c** was obtained as a colorless solid (70 mg, 97%).



R_f: 0.23 (20% MTBE/hexane); **mp.:** 77-78 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.27 (s, 1H), 8.00 (bs, 1H), 7.33-7.27 (m, 4H), 7.22-7.09 (m, 6H), 6.99-6.93 (m, 3H), 6.42 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 161.7 (d, J = 246.0 Hz, C_q), 154.3 (HC=N), 143.5 (C_q), 139.1 (d, J = 3.5 Hz, C_q), 137.1 (C_q), 131.5 (d, J = 8.0 Hz, 2x CH), 129.6 (2x CH), 128.2 (2x CH), 127.1 (CH), 126.4 (C_q), 125.5 (CH), 122.3 (CH), 122.2 (CH), 119.9 (C_q), 119.6 (CH), 114.7 (d, J = 21.0 Hz, 2x CH), 111.4 (CH), 61.9 (CH_3), 54.7 (C_q); **^{19}F-NMR** (282 MHz, $CDCl_3$)**:** δ (ppm) = −116.2; **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3411, 3057, 2937, 1602, 1506, 1457, 1445, 1228, 1161, 1105, 1057, 1035, 1022, 854, 827, 808, 763, 744, 704, 585; **HR-MS** (ESI)**:** calcd. for $C_{23}H_{19}FN_2ONa$ ([M+Na]$^+$): 381.1374, found: 381.1379; **M($C_{23}H_{19}FN_2O$):** 358.42.

2-Indolyl aldoxime ether 8d

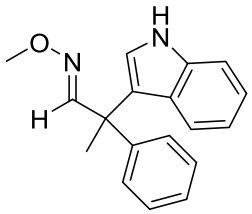
According to the general procedure 4, 2-hydroxy aldoxime ether **7d** (54 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 3 hours. Compound **8d** was obtained as a colorless solid (69 mg, 93%).



R_f: 0.29 (20% MTBE/hexane); **mp.:** 85-86 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.26 (s, 1H), 7.96 (bs, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.17-7.09 (m, 10H), 6.95 (t, J = 7.5 Hz, 1H), 6.42 (d, J = 2.5 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.7 (HC═N), 140.8 (2x C_q), 137.1 (C_q), 136.3 (2x C_q), 129.6 (4x CH), 128.7 (4x CH), 126.7 (C_q), 125.6 (CH), 122.6 (CH), 122.0 (CH), 120.3 (C_q), 119.4 (CH), 111.3 (CH), 61.8 (CH_3), 54.5 (C_q), 21.1 (2x CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3415, 3054, 2935, 1617, 1509, 1457, 1057, 1029, 1019, 810, 786, 742; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{24}N_2ONa$ ([M+Na]$^+$): 391.1781, found: 391.1782; **M($C_{25}H_{24}N_2O$):** 368.48.

2-Indolyl aldoxime ether 8e

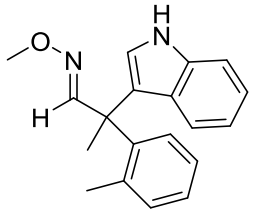
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 7 hours. Compound **8e** was obtained as a colorless solid (49 mg, 89%).



R_f: 0.29 (20% MTBE/hexane); **mp.:** 103-105 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.08 (bs, 1H), 8.02 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.30-7.23 (m, 5H), 7.15 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.93 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.88 (s, 3H), 1.94 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.8 (HC═N), 145.5 (C_q), 137.1 (C_q), 128.5 (2x CH), 127.3 (2x CH), 126.7 (CH), 125.6 (C_q), 122.4 (CH), 122.2 (CH), 121.2 (CH), 120.5 (C_q), 119.5 (CH), 111.4 (CH), 61.6 (CH_3), 45.7 (C_q), 26.0 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 3056, 2976, 2935, 1617, 1490, 1457, 1447, 1338, 1054, 881, 764, 744, 703; **HR-MS** (ESI)**:** calcd. for $C_{18}H_{18}N_2ONa$ ([M+Na]$^+$): 301.1311, found: 301.1301; **M($C_{18}H_{18}N_2O$):** 278.36.

2-Indolyl aldoxime ether 8f

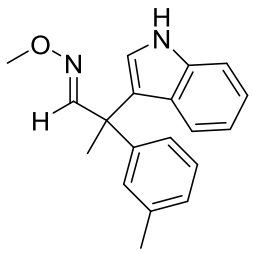
According to the general procedure 4, 2-hydroxy aldoxime ether **7f** (39 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 27 hours. Compound **8f** was obtained as a colorless solid (50 mg, 85%).



R_f: 0.28 (20% MTBE/hexane); **mp.:** 83-85 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.12 (s, 1H), 8.08 (bs, 1H), 7.39 (dd, J = 5.5, 3.5 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 2H), 7.15 (ddd, J = 8.0, 6.5, 2.0 Hz, 1H), 7.11-7.08 (m, 2H), 6.94-6.88 (m, 2H), 3.89 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 155.6 (HC=N), 142.9 (C_q), 137.1 (C_q), 136.9 (C_q), 132.7 (CH), 127.7 (CH), 127.1 (CH), 126.2 (CH), 125.8 (C_q), 122.1 (CH), 121.6 (CH), 120.7 (C_q), 120.5 (CH), 119.5 (CH), 111.4 (CH), 61.5 (CH_3), 46.0 (C_q), 24.3 (CH_3), 21.6 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 3058, 2979, 2937, 1618, 1486, 1456, 1417, 1336, 1244, 1101, 1049, 1013, 878, 765, 744, 728, 623, 588; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{21}N_2O$ ([M+H]$^+$): 293.1648, found: 293.1644; **M($C_{19}H_{20}N_2O$):** 292.38.

2-Indolyl aldoxime ether 8g

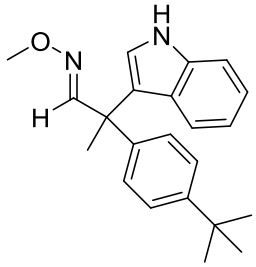
According to the general procedure 4, 2-hydroxy aldoxime ether **7g** (39 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8g** was obtained as a colorless solid (50 mg, 86%).



R_f: 0.26 (20% MTBE/hexane); **mp.:** 81-83 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.07-8.04 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.22-7.13 (m, 3H), 7.10-7.06 (m, 4H), 6.95 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.91 (s, 3H), 2.32 (s, 3H), 1.95 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 155.1 (HC=N), 145.5 (C_q), 138.0 (C_q), 137.1 (C_q), 128.4 (CH), 127.8 (CH), 127.5 (CH), 125.7 (C_q), 124.4 (CH), 122.3 (CH), 122.1 (CH), 121.3 (CH), 120.6 (C_q), 119.4 (CH), 111.4 (CH), 61.6 (CH_3), 45.6 (C_q), 26.0 (CH_3), 21.7 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3417, 3056, 2981, 2937, 2816, 1700, 1604, 1485, 1457, 1417, 1050, 908, 880, 744, 710; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{20}N_2ONa$ ([M+Na]$^+$): 315.1468, found: 315.1460; **M($C_{19}H_{20}N_2O$):** 292.38.

2-Indolyl aldoxime ether 8h

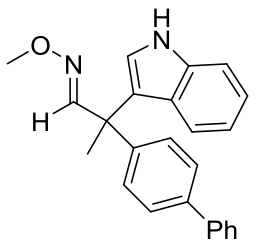
According to the general procedure 4, 2-hydroxy aldoxime ether **7h** (47 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8h** was obtained as a colorless solid (64 mg, 96%).



R_f: 0.32 (20% MTBE/hexane); **mp.:** 75-77 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.07 (bs, 1H), 8.02 (s, 1H), 7.37-7.30 (m, 3H), 7.25-7.11 (m, 4H), 7.04 (d, J = 2.5 Hz, 1H), 6.96 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.90 (s, 3H), 1.95 (s, 3H), 1.33 (s, 9H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 155.2 (HC=N), 149.4 (C_q), 142.4 (C_q), 137.1 (C_q), 126.9 (2x CH), 125.8 (C_q), 125.4 (2x CH), 122.4 (CH), 122.1 (CH), 121.4 (CH), 120.7 (C_q), 119.4 (CH), 111.4 (CH), 61.6 (CH_3), 45.3 (C_q), 34.5 (C_q), 31.5 (3x CH_3), 25.9 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3417, 2962, 2938, 1618, 1458, 1053, 743; **HR-MS** (ESI)**:** calcd. for $C_{22}H_{26}N_2ONa$ ([M+Na]$^+$): 357.1937, found: 357.1931; **M($C_{22}H_{26}N_2O$):** 334.46.

2-Indolyl aldoxime ether 8i

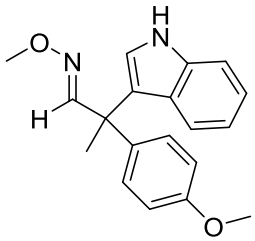
According to the general procedure 4, 2-hydroxy aldoxime ether **7i** (51 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8i** was obtained as a colorless solid (64 mg, 90%).



R_f: 0.21 (20% MTBE/hexane); **mp.:** 147-148 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.09 (bs, 1H), 8.03 (s, 1H), 7.58 (m, 2H), 7.53 (d‘, J = 8.5 Hz, 2H), 7.45-7.31 (m, 6H), 7.19-7.09 (m, 3H), 6.95 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.89 (s, 3H), 1.97 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 154.8 (HC=N), 144.6 (C_q), 140.9 (C_q), 139.5 (C_q), 137.2 (C_q), 128.9 (2x CH), 127.7 (2x CH), 127.3 (CH), 127.18 (2x CH), 127.15 (2x CH), 125.7 (C_q), 122.4 (CH), 122.2 (CH), 121.3 (CH), 120.5 (C_q), 119.6 (CH), 111.4 (CH), 61.7 (CH_3), 45.5 (C_q), 26.1 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3419, 3028, 2979, 2934, 2897, 1617, 1485, 1457, 1416, 1336, 1244, 1105, 1049, 1007, 882, 839, 765, 743, 699; **HR-MS** (ESI)**:** calcd. for $C_{24}H_{23}N_2O$ ([M+H]$^+$): 355.1805, found: 355.1802; **M($C_{24}H_{22}N_2O$):** 354.45.

2-Indolyl aldoxime ether 8j

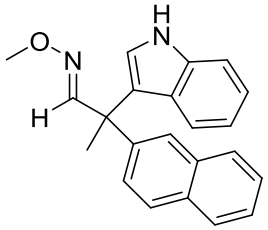
According to the general procedure 4, 2-hydroxy aldoxime ether **7j** (42 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8j** was obtained as a colorless solid (54 mg, 88%).



R_f: 0.23 (20% MTBE/hexane); **mp.:** 102-103 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.08 (bs, 1H), 7.99 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.21 (d‘, J = 9.0 Hz, 2H), 7.18-7.13 (m, 1H), 7.09-7.06 (m, 2H), 6.95 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.83 (d‘, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 1.92 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 158.3 (C_q), 155.1 (HC=N), 137.5 (C_q), 137.2 (C_q), 128.4 (2x CH), 125.7 (C_q), 122.3 (CH), 122.1 (CH), 121.3 (CH), 120.7 (C_q), 119.4 (CH), 113.8 (2x CH), 111.4 (CH), 61.6 (CH_3), 55.3 (CH_3), 45.0 (C_q), 26.1 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3416, 3329, 2985, 2975, 2936, 2900, 1608, 1509, 1457, 1338, 1296, 1247, 1179, 1105, 1051, 1013, 882, 833, 763, 747; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{20}N_2O_2Na$ ([M+Na]$^+$): 331.1417, found: 331.1416; **M($C_{19}H_{20}N_2O_2$):** 308.38.

2-Indolyl aldoxime ether 8k

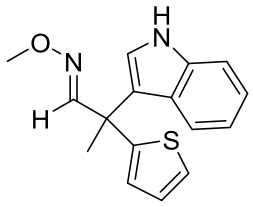
According to the general procedure 4, 2-hydroxy aldoxime ether **7k** (46 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8k** was obtained as a colorless solid (95 mg, 62%).



R_f: 0.29 (20% MTBE/hexane); **mp.:** 143-145 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.15 (s, 1H), 8.08 (bs, 1H), 7.85-7.79 (m, 3H), 7.75 (d, J = 8.5 Hz, 1H), 7.51-7.46 (m, 2H), 7.42-7.35 (m, 2H), 7.18-7.12 (m, 2H), 7.06 (dd, J = 8.0, 1.0 Hz, 1H), 6.89 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.95 (s, 3H), 2.05 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 154.8 (HC=N), 143.1 (C_q), 137.1 (C_q), 133.5 (C_q), 132.4 (C_q), 128.24 (CH), 128.23 (CH), 127.6 (CH), 126.1 (CH), 126.0 (CH), 125.9 (CH), 125.7 (C_q), 125.4 (CH), 122.5 (CH), 122.2 (CH), 121.1 (CH), 120.3 (C_q), 119.6 (CH), 111.4 (CH), 61.7 (CH_3), 45.8 (C_q), 26.0 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3417, 3338, 3051, 2986, 2973, 2933, 2896, 1630, 1617, 1596, 1505, 1456, 1443, 1420, 1369, 1337, 1244, 1111, 1106, 1050, 1014, 945, 891, 882, 863, 824, 767, 750, 477; **HR-MS** (ESI)**:** calcd. for $C_{22}H_{20}N_2ONa$ ([M+Na]$^+$): 351.1468, found: 351.1467; **M($C_{22}H_{20}N_2O$):** 308.38.

2-Indolyl aldoxime ether 8l

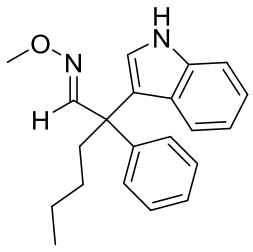
According to the general procedure 4, 2-hydroxy aldoxime ether **7l** (37 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8l** was obtained as a colorless oil (48 mg, 85%).



R_f: 0.18 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.03 (bs, 1H), 8.00 (s, 1H), 7.36-7.33 (m, 2H), 7.24-7.17 (m, 2H), 7.04 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.99.6.96 (m, 2H), 6.94 (ddd, J = 3.5, 1.5 Hz, 1H), 3.92 (s, 3H), 2.08 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 154.4 (HC=N), 150.5 (C_q), 137.0 (C_q), 126.8 (CH), 125.5 (C_q), 124.8 (CH), 124.5 (CH), 122.2 (CH), 121.9 (CH), 121.0 (CH), 120.9 (C_q), 119.6 (CH), 111.5 (CH), 61.8 (CH), 43.4 (C_q), 26.9 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3413, 2982, 2935, 2897, 1617, 1457, 1416, 1336, 1245, 1233, 1105, 1050, 1013, 885, 851, 747, 700; **HR-MS** (ESI)**:** calcd. for $C_{16}H_{16}N_2OSNa$ ([M+Na]$^+$): 307.0876, found: 307.0871; **M($C_{16}H_{16}N_2OS$):** 284.38.

2-Indolyl aldoxime ether 8m

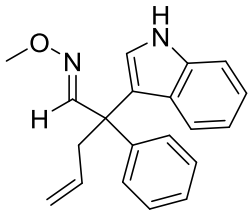
According to the general procedure 4, 2-hydroxy aldoxime ether **7m** (44 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Compound **8m** was obtained as a colorless oil (48 mg, 75%).



R_f: 0.34 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.09 (bs, 1H), 7.92 (s, 1H), 7.34 (dt, J = 8.0, 1.0 Hz, 1H), 7.33-7.26 (m, 5H), 7.17-7.11 (m, 2H), 6.99 (d, J = 8.0, 1.5, 1.0 Hz, 1H), 6.91 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.87 (s, 3H), 2.50 (ddd, J = 13.5, 11.0, 5.0 Hz, 1H), 2.35 (ddd, J = 13.5, 11.0, 5.0 Hz, 1H), 1.37-1.11 (m, 4H), 7.15 (t, J = 7.0 Hz, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 154.5 (HC=N), 143.6 (C_q), 137.0 (C_q), 128.2 (4x CH), 126.6 (CH), 126.0 (C_q), 123.0 (CH), 122.0 (CH), 121.5 (CH), 119.3 (CH), 119.2 (C_q), 111.3 (CH), 61.6 (CH_3), 49.4 (C_q), 37.1 (CH_2), 27.2 (CH_2), 23.4 (CH_2), 14.2 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3417, 3057, 2955, 2936, 2869, 1599, 1490, 1457, 1446, 1416, 1338, 1243, 1216, 1104, 1063, 1041, 1014, 881, 759, 744, 701; **HR-MS** (ESI)**:** calcd. for $C_{21}H_{24}N_2ONa$ ([M+Na]$^+$): 343.1781, found: 343.1786; **M($C_{21}H_{24}N_2O$):** 320.44.

2-Indolyl aldoxime ether 8n

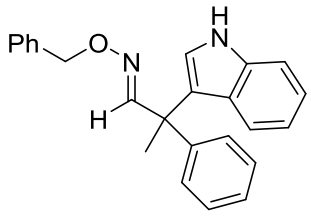
According to the general procedure 4, 2-hydroxy aldoxime ether **7n** (41 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 120 hours. Compound **8n** was obtained as a yellowish oil (21 mg, 34%).



R_f: 0.36 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.07 (bs, 1H), 7.94 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.31-7.24 (m, 5H), 7.18 (d, J = 2.5 Hz, 1H), 7.14 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.91 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 5.75 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 4.98-4.90 (m, 2H), 3.86 (s, 3H), 3.26 (ddt, J = 14.0, 7.0, 1.5 Hz, 1H), 3.19 (ddt, J = 14.0, 7.0, 1.5 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.0 (HC=N), 142.9 (C_q), 136.9 (C_q), 135.2 (CH), 128.3 (2x CH), 128.2 (2x CH), 126.8 (CH), 126.0 (C_q), 123.3 (CH), 122.1 (CH), 121.5 (CH), 119.6 (CH), 118.6 (C_q), 117.4 (CH_2), 111.4 (CH), 61.7 (CH_3), 49.1 (C_q), 42.1 (CH_2); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 3075, 3061, 2937, 2898, 2816, 1638, 1617, 1598, 1490, 1458, 1417, 1337, 1243, 763; **HR-MS** (ESI)**:** calcd. for $C_{20}H_{20}N_2ONa$ ([M+Na]$^+$): 327.1468, found: 327.1464; **M($C_{20}H_{20}N_2O$):** 304.39.

2-Indolyl aldoxime ether 8o

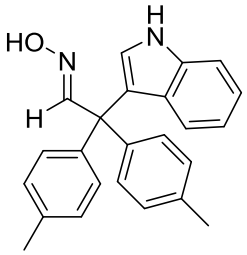
According to the general procedure 4, 2-hydroxy aldoxime ether **7o** (51 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 24 hours. Compound **8o** was obtained as a colorless oil (48 mg, 67%).



R_f: 0.28 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.08 (s, 1H), 8.00 (bs, 1H), 7.42-7.23 (m, 11H), 7.14 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.01-6.98 (m, 2H), 6.90 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 5.16 (d, J = 12.0 Hz, 1H), 5.13 (d, J = 12.0 Hz, 1H), 1.93 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 155.6 (HC=N), 145.4 (C_q), 137.8 (C_q), 137.1 (C_q), 128.6 (2x CH), 128.49 (2x CH), 128.46 (2x CH), 128.0 (CH), 127.3 (2x CH), 126.7 (CH), 125.6 (C_q), 122.5 (CH), 122.1 (CH), 121.2 (CH), 120.4 (C_q), 119.5 (CH), 111.4 (CH), 76.0 (CH_2), 45.9 (C_q), 26.1 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3421, 3060, 3029, 2980, 2931, 1598, 1492, 1455, 1416, 1370, 1336, 1245, 1105, 1029, 1014, 909, 763, 700, 584; **HR-MS** (ESI)**:** calcd. for $C_{24}H_{22}N_2ONa$ ([M+Na]$^+$): 377.1624, found: 377.1637; **M($C_{24}H_{22}N_2O$):** 354.45.

2-Indolyl aldoxime 8p'

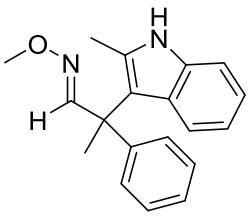
According to a modification of the general procedure 4, 2-hydroxy aldoxime silyl ether **7p** (74 mg, 0.20 mmol, 1.0 equiv), indole (35 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 4 hours. Then, TBAF•3H$_2$O (126 mg, 0.40 mmol, 2.0 equiv) was added and it was stirred at room temperature for 20 min. Compound **8p'** was obtained as a yellow solid (63 mg, 89%).



R_f: 0.22 (30% MTBE/hexane); **mp.:** 217-218 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.28 (s, 1H), 7.99 (bs, 1H), 7.35-7.33 (m, 2H), 7.15 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.10-7.05 (m, 9H), 6.95 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H), 2.34 (s, 6H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 156.0 (HC=N), 140.5 (2x C_q), 137.1 (C_q), 136.5 (2x C_q), 129.5 (4x CH), 128.8 (4x CH), 126.6 (C_q), 125.5 (CH), 122.5 (CH), 122.2 (CH), 120.1 (C_q), 119.6 (CH), 111.4 (CH), 54.5 (C_q), 21.2 (2x CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3409, 3053, 3024, 2919, 1617, 1509, 1456, 1416, 1243, 1105, 962, 946, 888, 809, 794, 767, 741; **HR-MS** (ESI)**:** calcd. for $C_{24}H_{21}N_2O$ ([M-H]$^-$): 353.1659, found: 353.1669; **M($C_{24}H_{22}N_2O$):** 354.45.

2-Indolyl aldoxime ether 8q

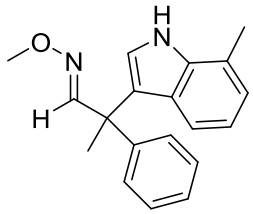
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 2-methylindole (39 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 28 hours. Compound **8q** was obtained as a colorless oil (38 mg, 66%).



R_f: 0.33 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.98 (s, 1H), 7.75 (bs, 1H), 7.40-7.23 (m, 6H), 7.07 (ddd, J = 8.0, 7.0, 1.5 Hz, 1H), 6.96 (dd, J = 8.0, 1.5 Hz, 1H), 6.89 (ddd, J = 8.0, 7.0, 1.5 Hz, 1H), 3.91 (s, 3H), 2.22 (s, 3H), 2.03 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 156.6 (HC=N), 145.9 (C_q), 135.2 (C_q), 131.7 (C_q), 128.6 (2x CH), 127.6 (C_q), 127.3 (2x CH), 126.6 (CH), 121.0 (CH), 120.7 (CH), 119.2 (CH), 115.3 (C_q), 110.3 (CH), 61.6 (CH_3), 46.5 (C_q), 24.6 (CH_3), 14.6 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3403, 3057, 2984, 2936, 2899, 1618, 1490, 1458, 1422, 1298, 1053, 881, 747, 704; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{20}N_2ONa$ ([M+Na]$^+$): 315.1468, found: 315.1466; **M($C_{19}H_{20}N_2O$):** 292.38.

2-Indolyl aldoxime ether 8r

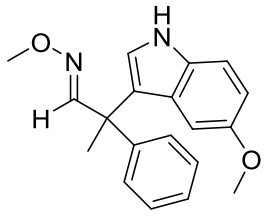
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 7-methylindole (39 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 5 hours. Compound **8r** was obtained as a colorless solid (36 mg, 62%).



R_f: 0.21 (20% MTBE/hexane); **mp.:** 106-107°C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.05 (bs, 2H), 7.33-7.26 (m, 5H), 7.15 (d, J = 2.5 Hz, 1H), 7.00-6.99 (m, 1H), 6.91-6.87 (m, 2H), 3.91 (s, 3H), 2.52 (s, 3H), 1.97 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.9 (HC=N), 145.5 (C_q), 136.7 (C_q), 128.5 (2x CH), 127.3 (2x CH), 126.7 (CH), 125.2 (C_q), 122.7 (CH), 122.1 (CH), 121.1 (C_q), 120.5 (C_q), 119.7 (CH), 119.0 (CH), 61.6 (CH_3), 45.7 (C_q), 26.0 (CH_3), 16.7 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3320, 3052, 2973, 2936, 1616, 1598, 1491, 1455, 1445, 1438, 1372, 1343, 1324, 1168, 1115, 1069, 1057, 1044, 955, 870, 785, 762, 755, 716, 698, 645, 559; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{20}N_2ONa$ ([M+Na]$^+$): 315.1468, found: 315.1465; **M($C_{19}H_{20}N_2O$):** 292.38.

2-Indolyl aldoxime ether 8s

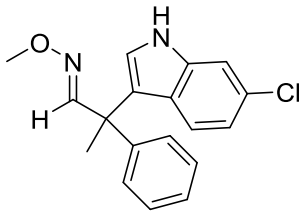
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 5-methoxyindole (44 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 25 hours. Compound **8s** was obtained as a colorless oil (22 mg, 35%).



R_f: 0.22 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.00 (bs, 1H), 7.97 (s, 1H), 7.30-7.22 (m, 6H), 7.07 (d, J = 2.5 Hz, 1H), 6.81 (dd, J = 9.0, 2.5 Hz, 1H), 6.41 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H), 3.59 (s, 3H), 1.92 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.8 (HC=N), 153.6 (C_q), 145.3 (C_q), 137.3 (C_q), 128.5 (2x CH), 127.3 (2x CH), 126.7 (CH), 126.1 (C_q), 123.1 (CH), 120.2 (C_q), 112.2 (CH), 112.0 (CH), 103.2 (CH), 61.7 (CH_3), 55.8 (CH_3), 45.6 (C_q), 25.9 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3418, 2935, 1579, 1484, 1455, 1442, 1215, 1051, 702; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{20}N_2O_2Na$ ([M+Na]$^+$): 331.1417, found: 331.1415; **M($C_{19}H_{20}N_2O_2$):** 308.38.

2-Indolyl aldoxime ether 8t

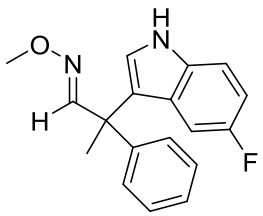
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 6-chloroindole (46 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 3 hours. Compound **8t** was obtained as a colorless oil (63 mg, >99%).



R_f: 0.23 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.09 (bs, 1H), 7.95 (s, 1H), 7.33-7.24 (m, 6H), 7.07 (d, J = 2.5 Hz, 1H), 6.89 (m, 2H), 3.88 (s, 3H), 1.91 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 154.6 (HC=N), 145.2 (C_q), 137.5 (C_q), 128.6 (2x CH), 128.2 (C_q), 127.2 (2x CH), 126.9 (CH), 124.3 (C_q), 123.0 (CH), 122.0 (CH), 120.8 (C_q), 120.3 (CH), 111.3 (CH), 61.7 (CH_3), 45.6 (C_q), 26.0 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3423, 2934, 1617, 1455, 1051, 883, 805, 700; **HR-MS** (ESI)**:** calcd. for $C_{18}H_{17}{}^{35}ClN_2ONa$ ([M+Na]$^+$): 335.0922, found: 335.0922; **M($C_{18}H_{17}ClN_2O$):** 312.80.

2-Indolyl aldoxime ether 8u

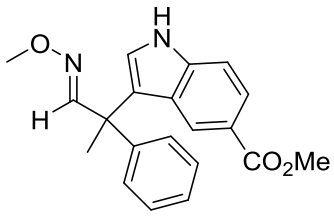
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 5-fluoroindole (41 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 3 hours. Compound **8u** was obtained as a colorless oil (57 mg, 96%).



R_f: 0.17 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 8.09 (bs, 1H), 7.95 (s, 1H), 7.33-7.23 (m, 6H), 7.12 (d, J = 2.5 Hz, 1H), 6.89 (dt, J = 9.0, 2.5 Hz, 1H), 6.66 (dd, J = 10.0, 2.5 Hz, 1H), 3.88 (s, 3H), 1.91 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 157.4 (d, J = 234.5 Hz, CF), 154.5 (HC=N), 145.0 (C_q), 133.6 (C_q), 128.6 (2x CH), 127.2 (2x CH), 126.9 (CH), 126.1 (d, J = 10.0 Hz, C_q), 124.1 (CH), 120.8 (d, J = 5.0 Hz, C_q), 112.0 (d, J = 9.5 Hz, CH), 110.7 (d, J = 26.5 Hz, CH), 106.1 (d, J = 24.0 Hz, CH), 61.7 (CH_3), 45.6 (C_q), 25.9 (CH_3); **^{19}F-NMR** (282 MHz, $CDCl_3$)**:** δ (ppm) = −282.3; **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3426, 3358, 2981, 2936, 2899, 1629, 1580, 1485, 1455, 1448, 1419, 1344, 1288, 1239, 1191, 1182, 1161, 1109, 1051, 1029, 936, 883, 855, 799, 766, 751, 733, 702; **HR-MS** (ESI)**:** calcd. for $C_{18}H_{17}FN_2ONa$ ([M+Na]$^+$): 319.1217, found: 319.1215; **M($C_{18}H_{17}FN_2O$):** 296.35.

2-Indolyl aldoxime ether 8v

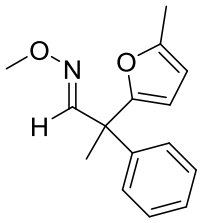
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), methyl indole-5-carboxylate (53 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 3 hours. Compound **8v** was obtained as a colorless solid (66 mg, 98%).



R_f: 0.34 (40% MTBE/hexane); **mp.:** 155-156 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.49 (bs, 1H), 8.01 (s, 1H), 7.86-7.84 (m, 2H), 7.33 (d, J = 9.0 Hz, 1H), 7.29-7.22 (m, 5H), 7.09 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 1.95 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 168.2 (C=O), 154.7 (HC=N), 145.0 (C_q), 139.8 (C_q), 128.6 (2x CH), 127.2 (2x CH), 126.9 (CH), 125.3 (C_q), 124.1 (CH), 123.8 (CH), 123.6 (CH), 122.1 (C_q), 121.6 (C_q), 111.2 (CH), 61.7 (CH_3), 51.9 (CH_3), 45.6 (C_q), 26.1 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3307, 2937, 1692, 1617, 1436, 1355, 1317, 1300, 1252, 1117, 1051, 884, 764, 753, 701; **HR-MS** (ESI)**:** calcd. for $C_{20}H_{20}N_2O_3Na$ ([M+Na]$^+$): 359.1366, found: 359.1370; **M($C_{20}H_{20}N_2O_3$):** 336.39.

2-Furanyl aldoxime ether 8w

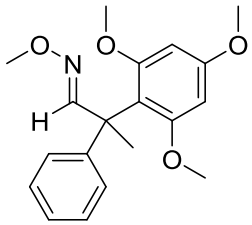
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 2-methylfuran (27 μL, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 3 hours. Compound **8w** was obtained as a colorless oil (41 mg, 85%).



R_f: 0.63 (5% MBTE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.85 (s, 1H), 7.34-7.21 (m, 3H), 7.15-7.12 (m, 2H), 6.13 (d, J = 3.0 Hz, 1H), 5.95 (dq, J = 3.0, 1.0 Hz, 1H), 3.91 (s, 3H), 2.26 (s, 3H), 1.78 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 155.1 (C_q), 153.0 (HC=N), 152.1 (C_q), 144.7 (C_q), 128.6 (2x CH), 127.0 (CH), 126.9 (2x CH), 107.8 (CH), 106.0 (CH), 61.8 (CH_3), 46.9 (C_q), 24.2 (CH_3), 13.8 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 2989, 2937, 1446, 1054, 1218, 1054, 1023, 888, 783, 700; **HR-MS** (ESI)**:** calcd. for $C_{15}H_{17}NO_2Na$ ([M+Na]$^+$): 266.1152, found: 266.1155; **M($C_{15}H_{17}NO_2$):** 243.31.

2-Phenyl aldoxime ether 8x

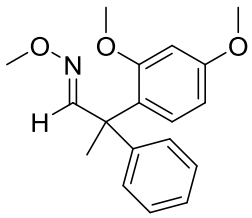
According to a modification of the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (101 mg, 0.60 mmol, 3.0 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 2 hours. Compound **8x** was obtained as a colorless solid (54 mg, 82%).



R_f: 0.43 (20% MTBE/hexane); **mp.:** 112-113 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** δ (ppm) = 7.83 (s, 1H), 7.26-7.15 (m, 4H), 7.14-7.09 (m, 1H), 6.12 (s, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.48 (s, 6H), 1.92 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** δ (ppm) = 160.1 (C_q), 159.5 (2x C_q), 158.5 (HC=N), 147.9 (C_q), 128.1 (2x CH), 125.7 (2x CH), 125.3 (CH), 116.6 (C_q), 93.2 (2x CH), 61.2 (CH_3), 56.1 (2x CH_3), 55.3 (CH_3), 47.5 (C_q), 21.4 (3-CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3455, 2998, 2939, 1605, 1585, 1490, 1474, 1457, 1439, 1416, 1338, 1231, 1206, 1190, 1157, 1122, 1053, 1042, 948, 878, 817, 717, 701; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{23}NO_4Na$ ([M+Na]$^+$): 352.1519, found: 352.1521; **M($C_{19}H_{23}NO_4$):** 329.40.

2-Phenyl aldoxime ether 8y

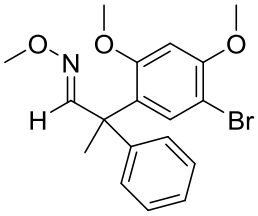
According to a modification of the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 1,3-dimethoxybenzene (79 μL, 0.60 mmol, 3.0 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 2 hours. Compound **8y** was obtained as a colorless solid (49 mg, 81%).



R_f: 0.28 (5% MTBE/hexane); **mp.:** 45-46 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.14 (s, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.29-7.24 (m, 2H), 7.20-7.17 (m, 1H), 7.11-7.09 (m, 2H), 6.55 (dd, J = 8.5, 2.5 Hz, 1H), 6.45 (d, J = 2.5 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.45 (s, 3H), 1.82 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 160.3 (C_q), 158.5 (C_q), 155.8 (HC=N), 148.0 (C_q), 128.4 (CH), 128.1 (2x CH), 125.7 (2x CH), 125.8 (CH), 125.7 (C_q), 104.1 (CH), 100.3 (CH), 61.5 (CH_3), 55.5 (CH_3), 55.3 (CH_3), 48.0 (C_q), 26.1 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 3011, 2975, 2934, 1606, 1586, 1503, 1490, 1463, 1440, 1407, 1373, 1320, 1308, 1291, 1275, 1209, 1181, 1165, 1153, 1121, 1064, 1046, 1036, 962, 943, 882, 824, 769, 705, 638, 573, 527; **HR-MS** (ESI)**:** calcd. for $C_{18}H_{21}NO_3Na$ ([M+Na]$^+$): 322.1414, found: 322.1419; **M($C_{18}H_{21}NO_3$):** 299.37.

2-Phenyl aldoxime ether 8z

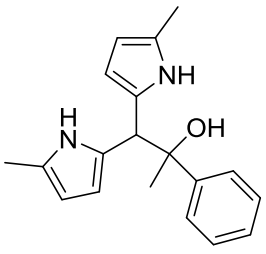
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 1-bromo-2,4-dimethoxybenzene (43 μL, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 2 hours. Compound **8z** was obtained as a colorless solid (27 mg, 36%).



R_f: 0.34 (20% MTBE/hexane); **mp.:** 110-111 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.07 (s, 1H), 7.31 (s, 1H), 7.22-7.22 (m, 2H), 7.18-7.14 (m, 1H), 7.06-7.04 (m, 2H), 6.43 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.43 (s, 3H), 1.77 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 157.8 (C_q), 156.1 (C_q), 155.0 (HC=N), 147.5 (C_q), 132.0 (CH), 128.3 (2x CH), 127.1 (C_q), 126.0 (CH), 125.8 (2x CH), 102.1 (C_q), 98.3 (CH), 61.6 (CH_3), 56.5 (CH_3), 55.7 (CH_3), 47.9 (C_q), 26.2 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3445, 2983, 2961, 2938, 1597, 1500, 1490, 1464, 1445, 1438, 1379, 1294, 1210, 1167, 1049, 1029, 890, 884, 818, 768, 703; **HR-MS** (ESI)**:** calcd. for $C_{18}H_{20}{}^{79}BrNO_3Na$ ([M+Na]$^+$): 400.0519, found: 400.0504; **M($C_{18}H_{20}BrNO_3$):** 378.27.

Bis(pyrrol-2-yl)ethyl alcohol 9

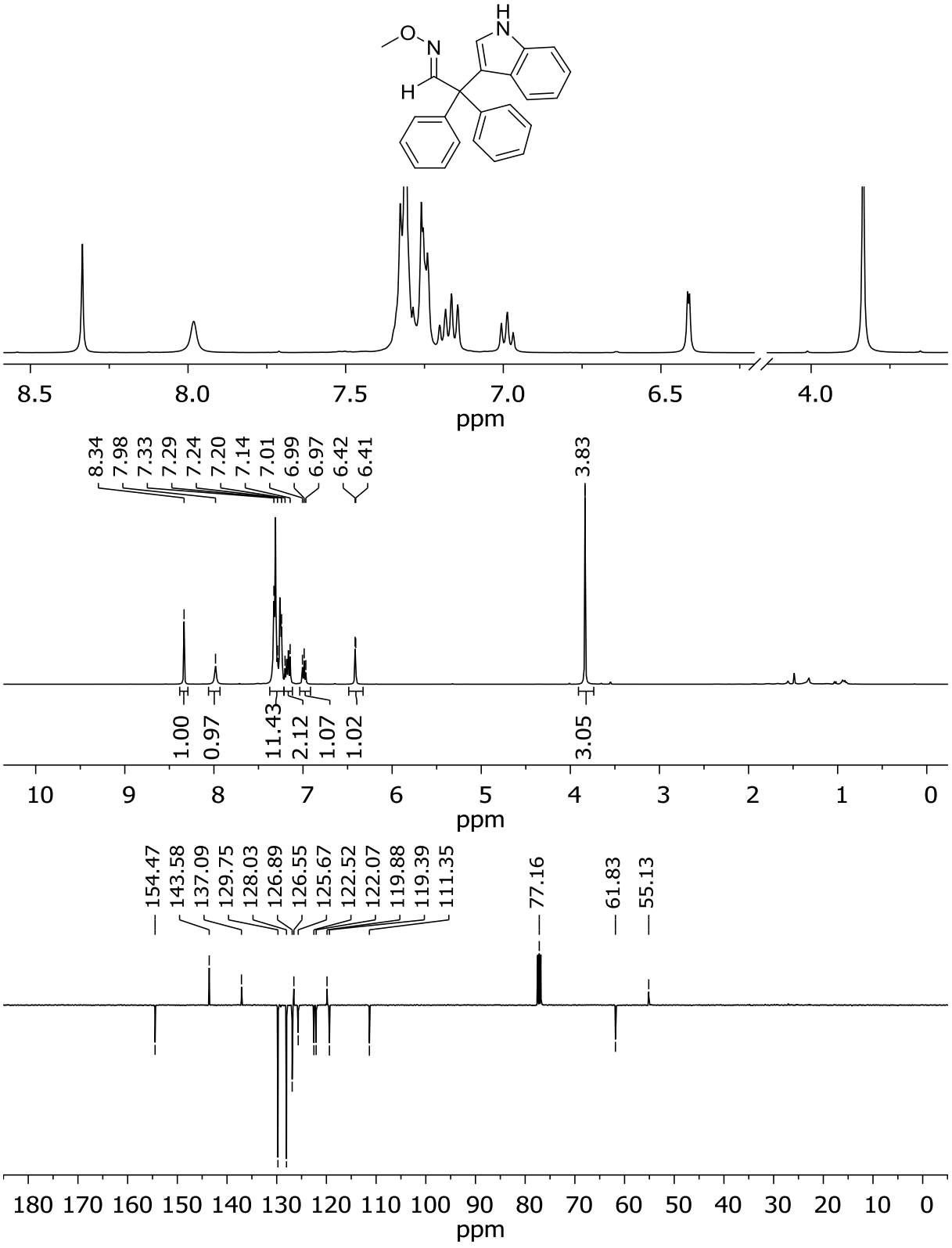
According to the general procedure 4, 2-hydroxy aldoxime ether **7e** (36 mg, 0.20 mmol, 1.0 equiv), 2-methylpyrrole (24 mg, 0.30 mmol, 1.5 equiv), $Ca(NTf_2)_2$ (12 mg, 20 μmol, 0.10 equiv) and nBu$_4$NPF$_6$ (7.7 mg, 20 μmol, 0.10 equiv) in 1.0 mL abs. $CHCl_3$ were used. The reaction mixture was stirred at 60 °C for 72 hours. Compound **9** was obtained as a brown oil (13 mg, 22%).



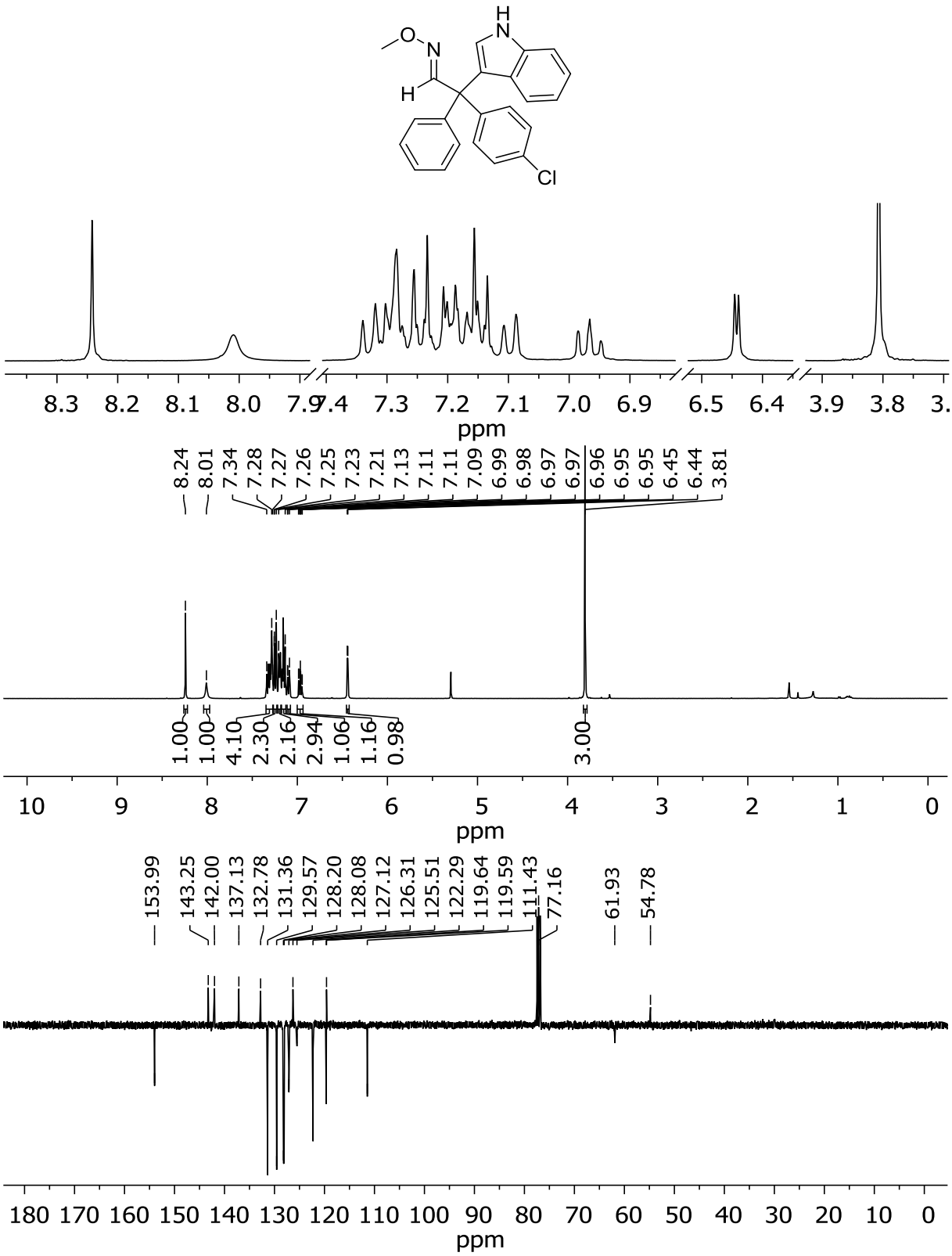
R_f: 0.15 (20% MTBE/hexane); **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.43 (bs, 1H), 7.44-7.42 (m, 2H), 7.36 (t', J = 7.5 Hz, 2H), 7.30-7.26 (m, 2H), 5.99 (t, J = 3.0 Hz, 1H), 5.82 (t, J = 3.0 Hz, 1H), 5.59 (t, J = 3.0 Hz, 1H), 5.35 (t, J = 3.0 Hz, 1H), 4.53 (s, 1H), 2.60 (bs, 1H), 2.27 (s, 3H), 2.04 (s, 3H), 1.45 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 148.0 (C_q), 128.4 (2x CH), 128.4 (2x C_q), 127.4 (C_q), 127.0 (CH), 126.8 (C_q), 124.9 (2x CH), 108.7 (CH), 107.8 (CH), 105.9 (CH), 105.4 (CH), 77.8 (C_q), 49.1 (CH), 29.2 (CH_3), 13.4 (CH_3), 13.0 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3439, 2976, 2925, 2854, 1682, 1586, 1445, 1053, 1039, 770, 700; **HR-MS** (ESI)**:** calcd. for $C_{19}H_{22}N_2ONa$ ([M+Na]$^+$): 317.1624, found: 317.1624; **M($C_{19}H_{22}N_2O$):** 294.40.

4.2 ^{1}H-NMR and ^{13}C-NMR Spectra

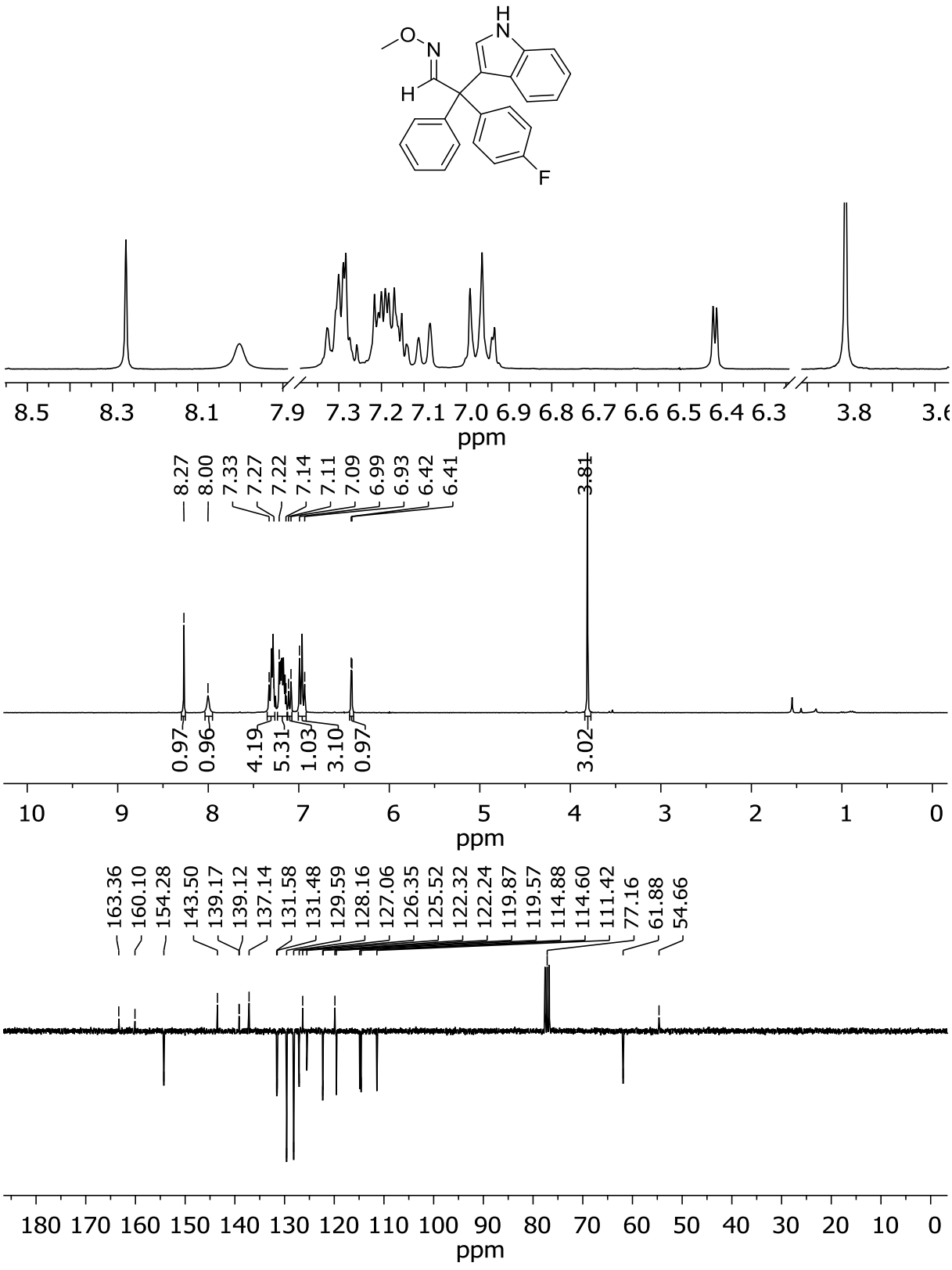
2-Indolyl aldoxime ether 8a ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



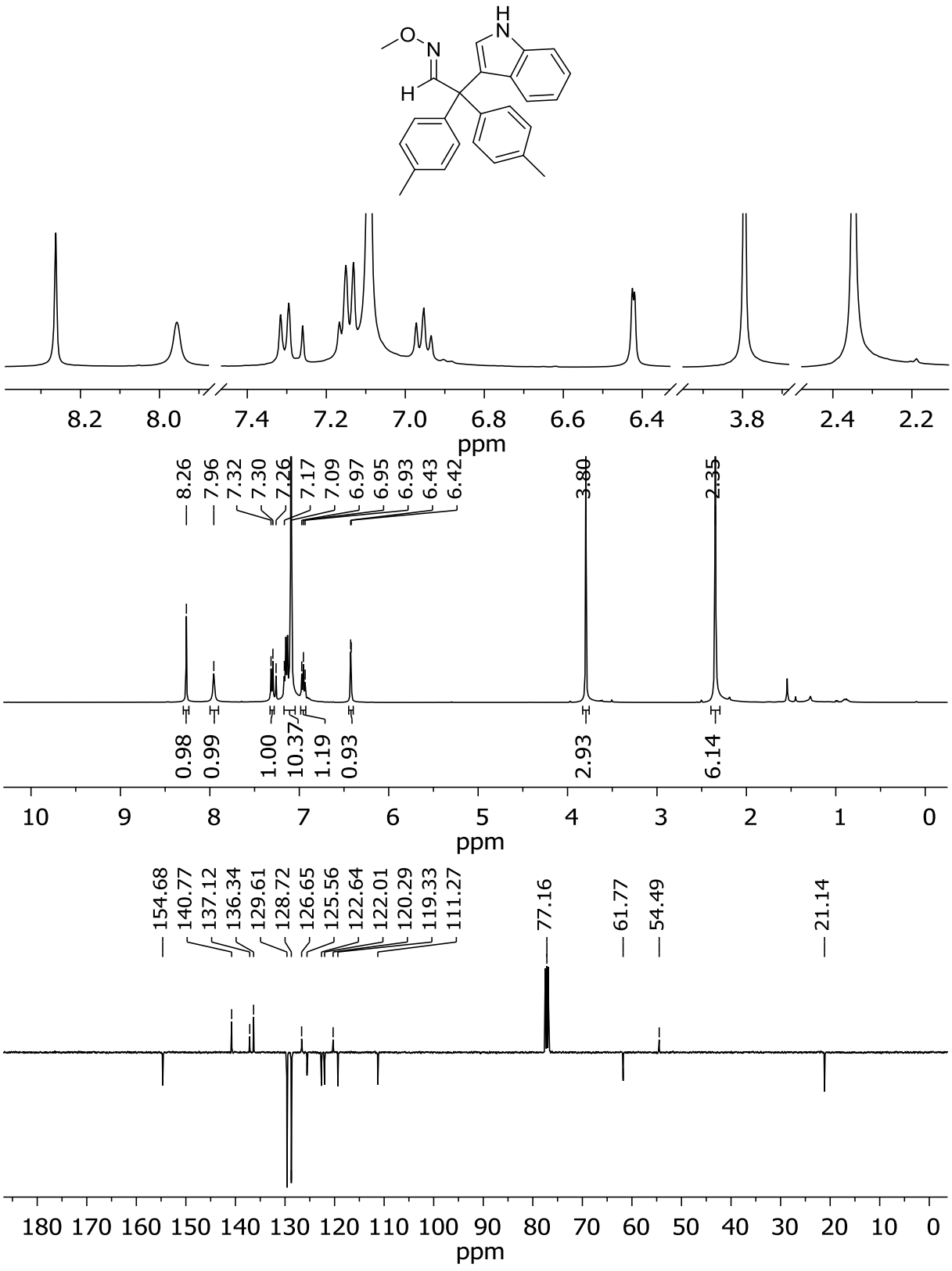
2-Indolyl aldoxime ether 8b ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



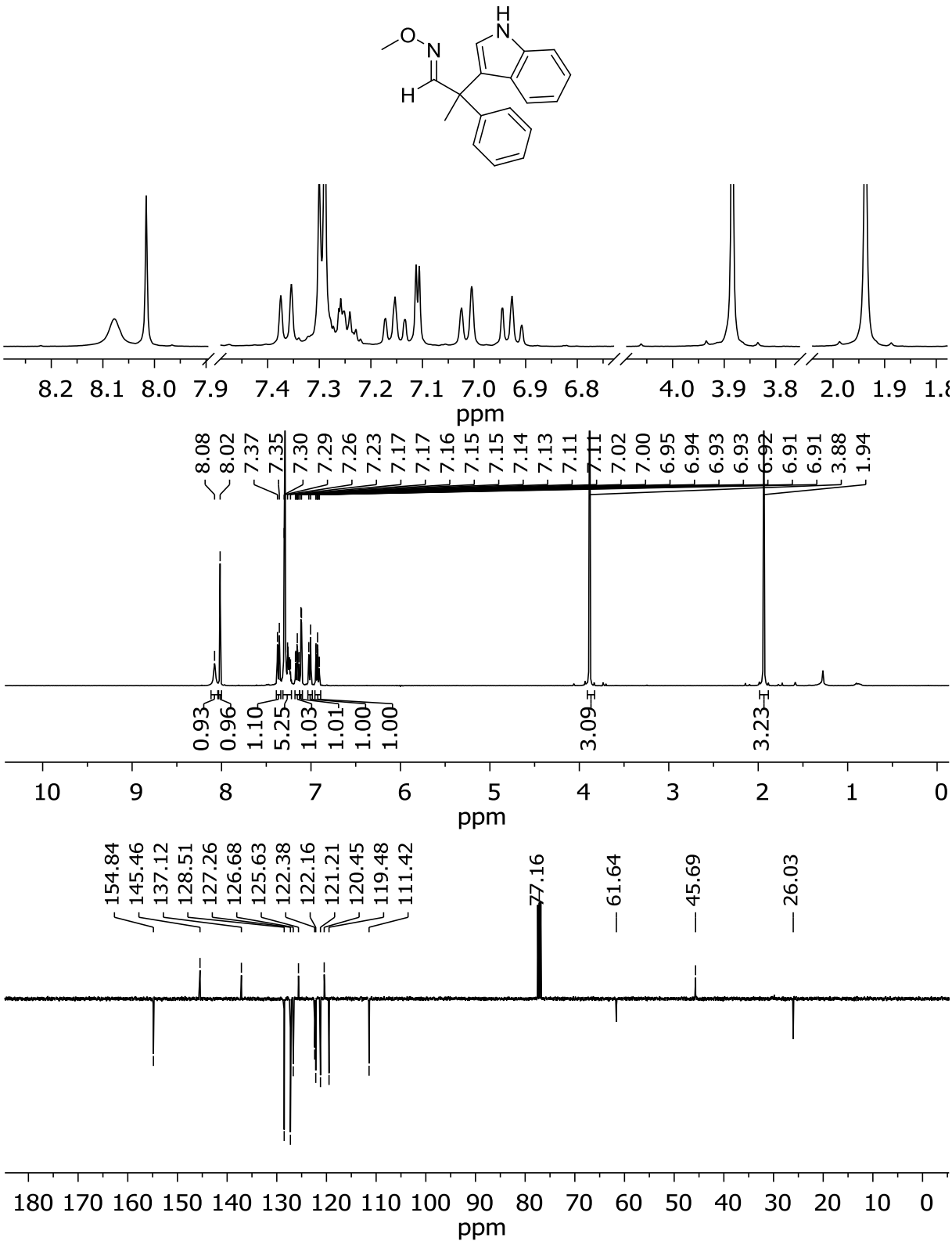
2-Indolyl aldoxime ether 8c ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



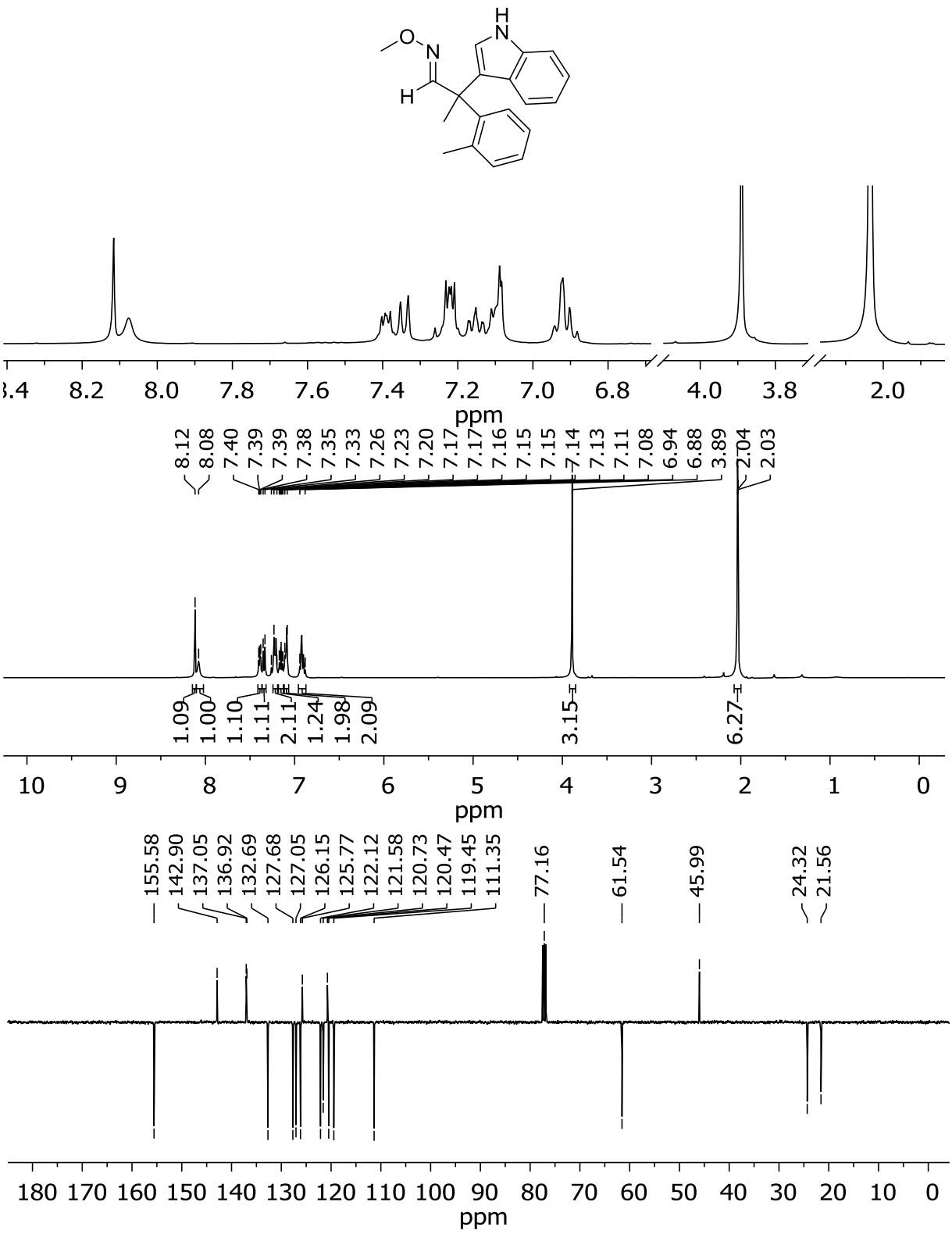
2-Indolyl aldoxime ether 8d ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



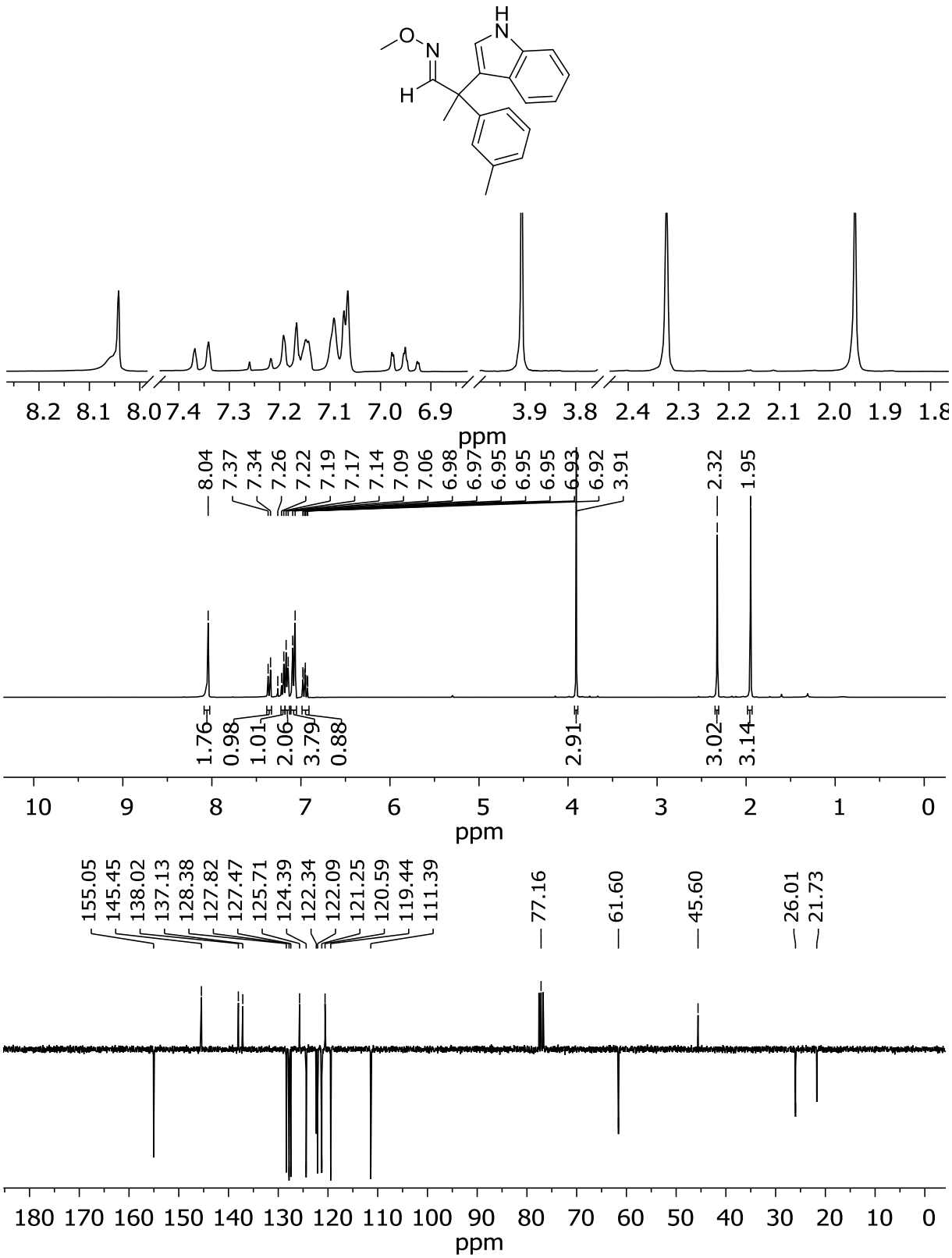
2-Indolyl aldoxime ether 8e ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



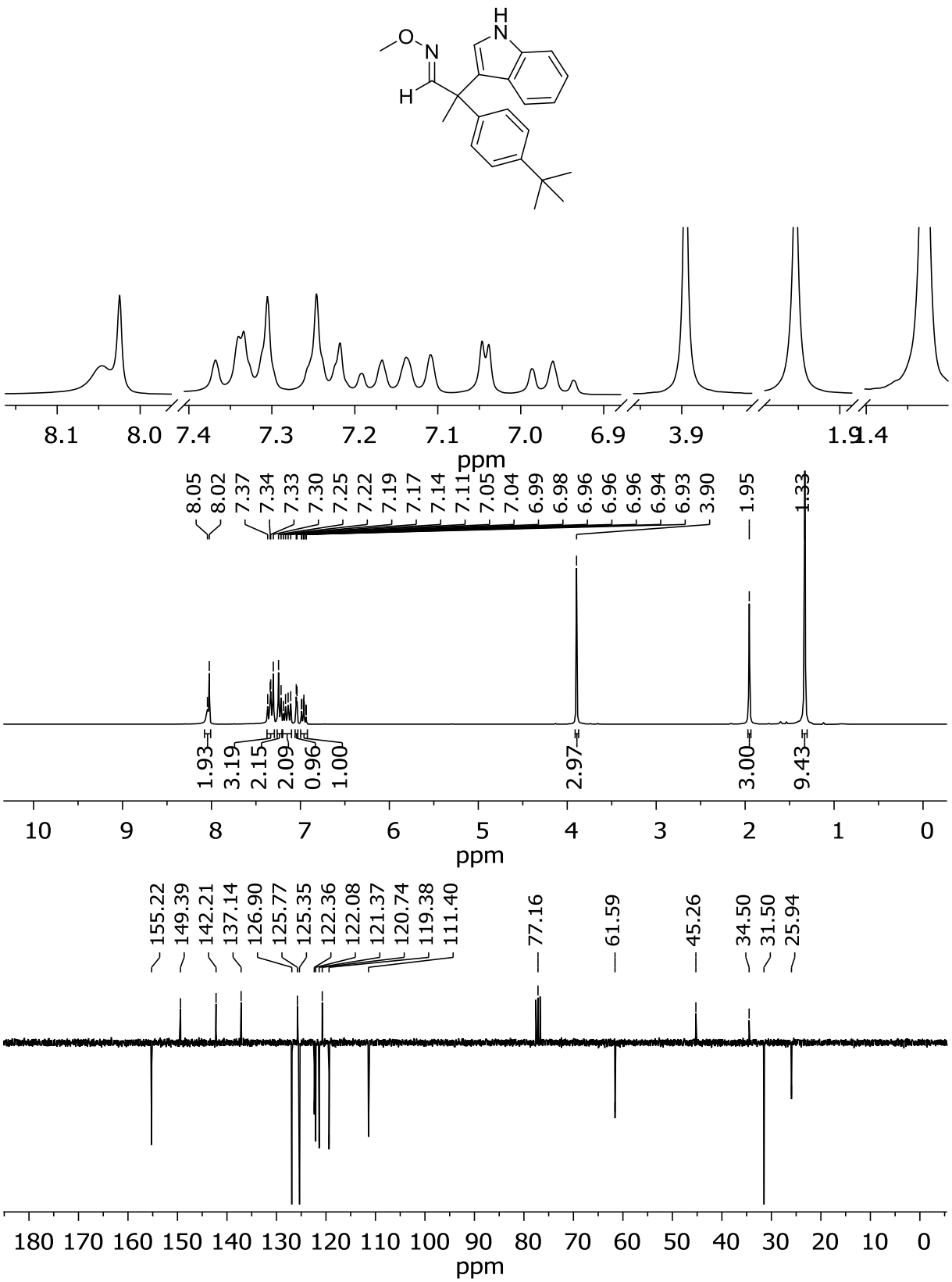
2-Indolyl aldoxime ether 8f ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



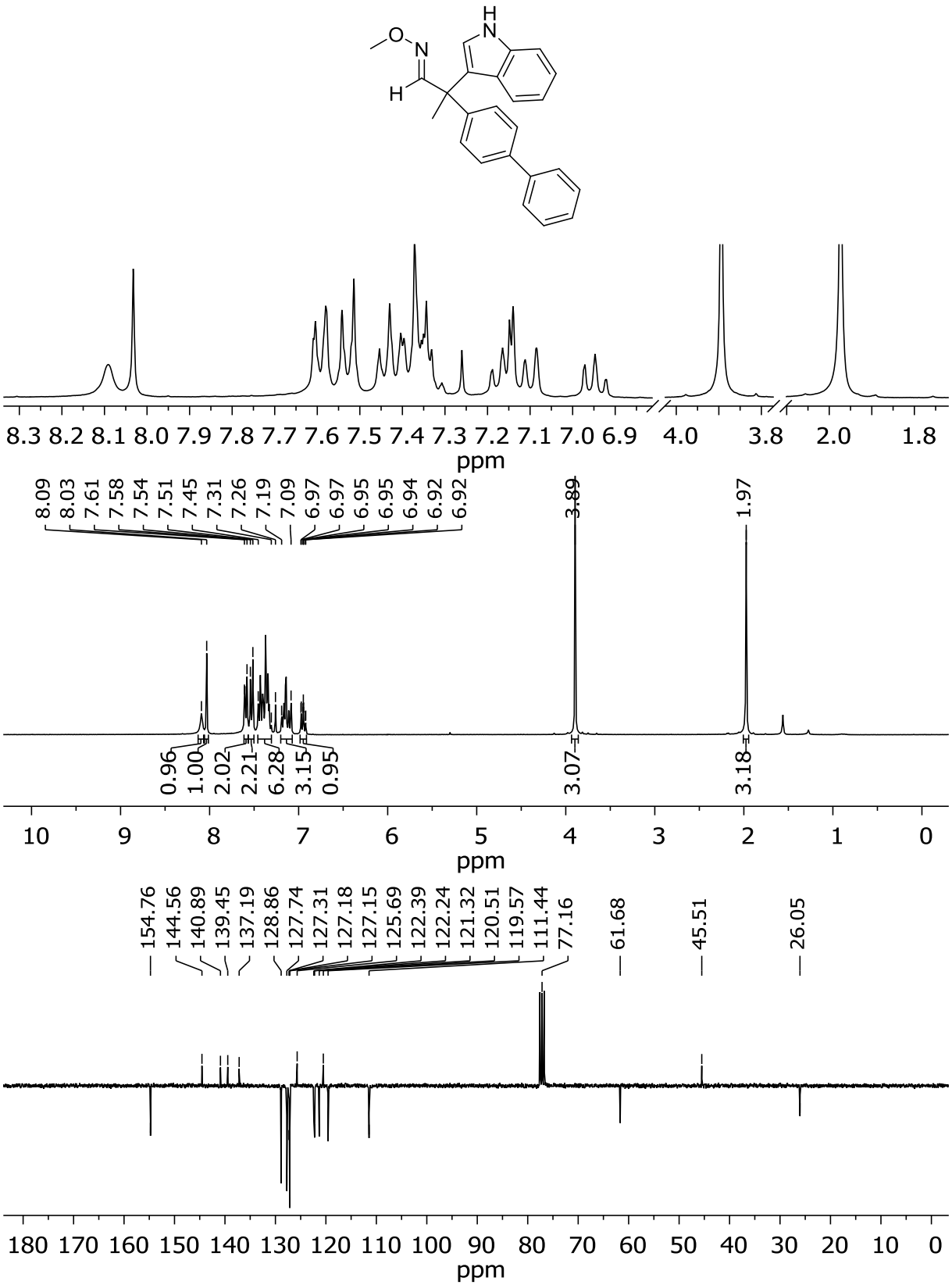
2-Indolyl aldoxime ether 8g ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



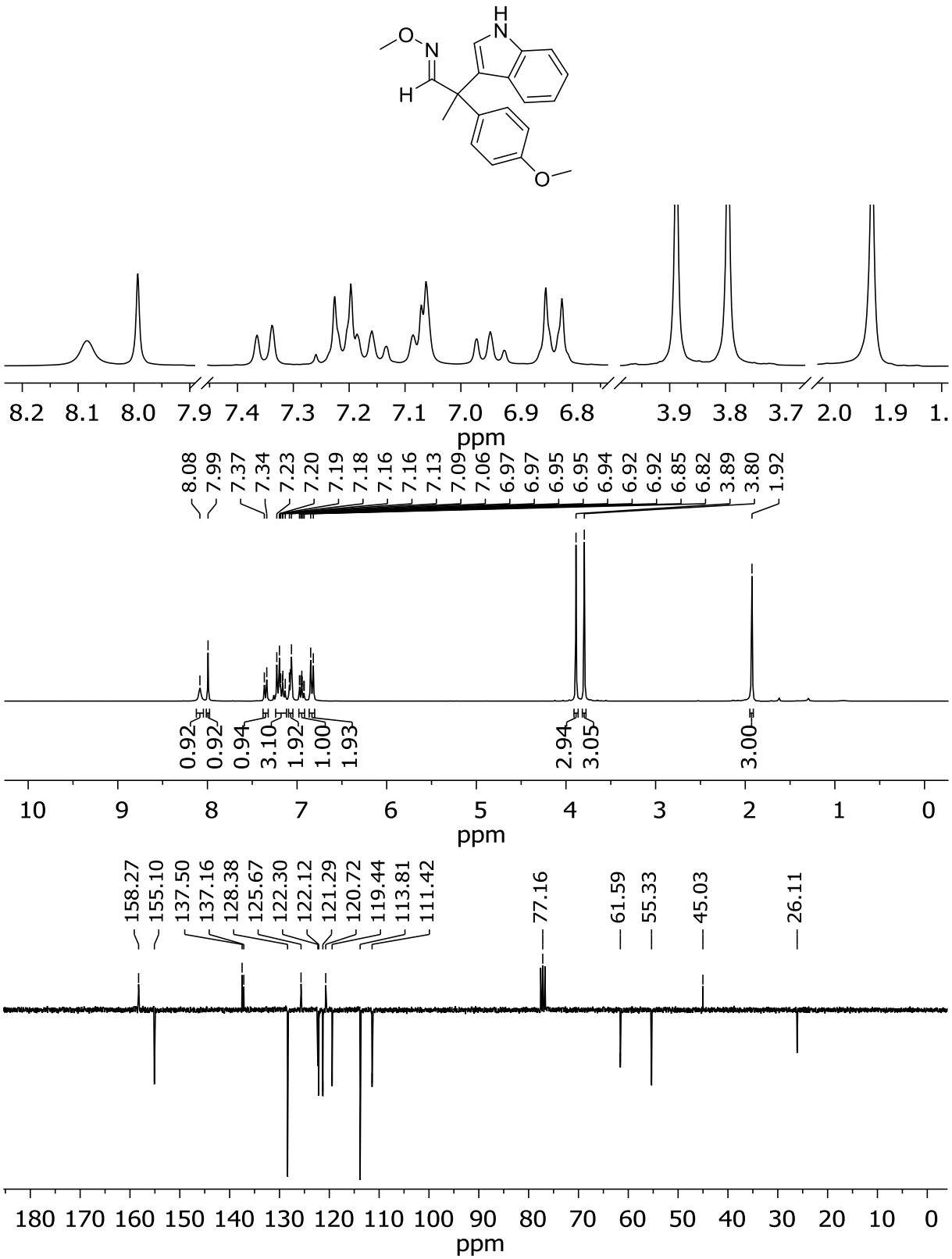
2-Indolyl aldoxime ether 8h ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



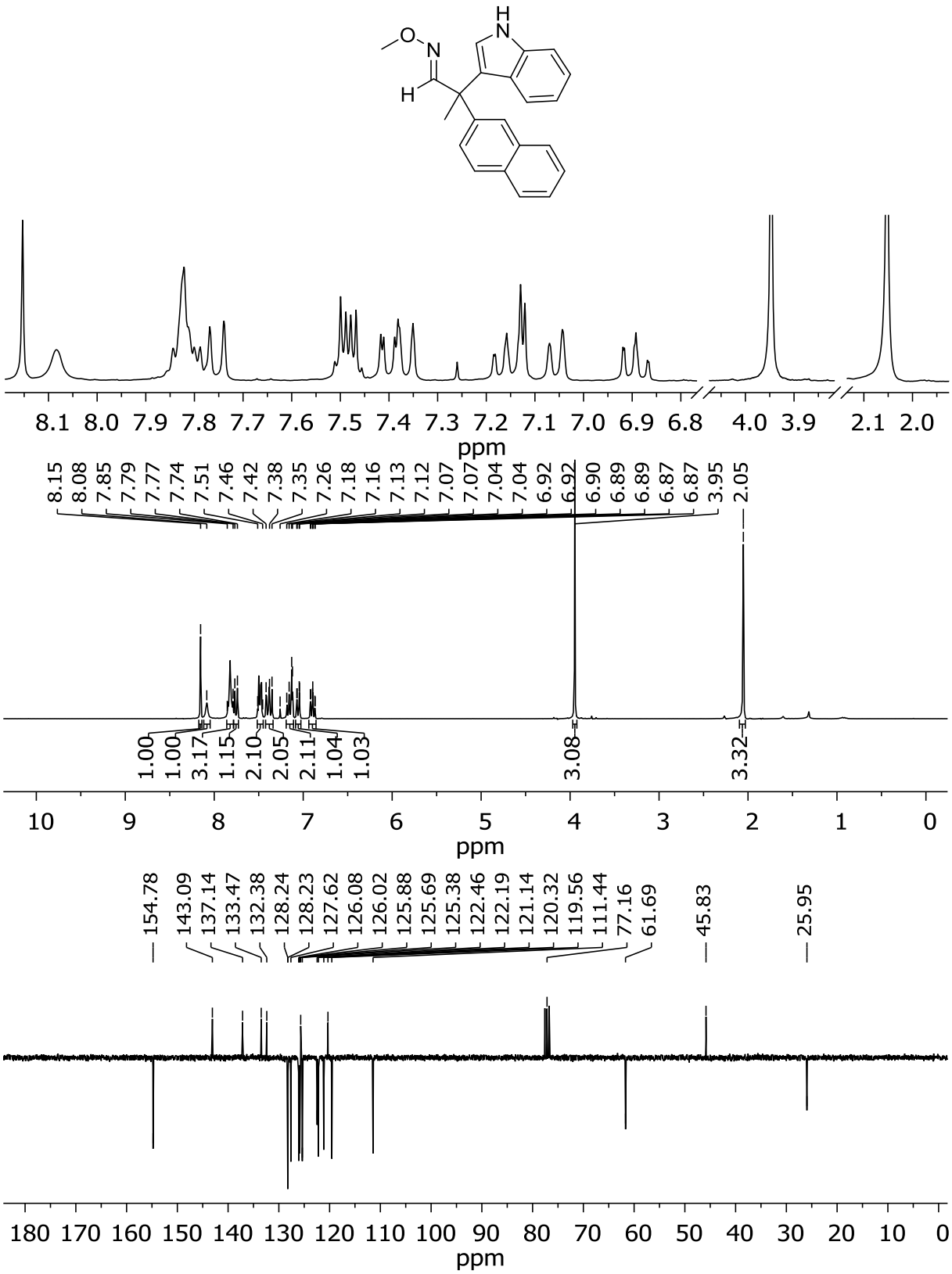
2-Indolyl aldoxime ether 8i ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



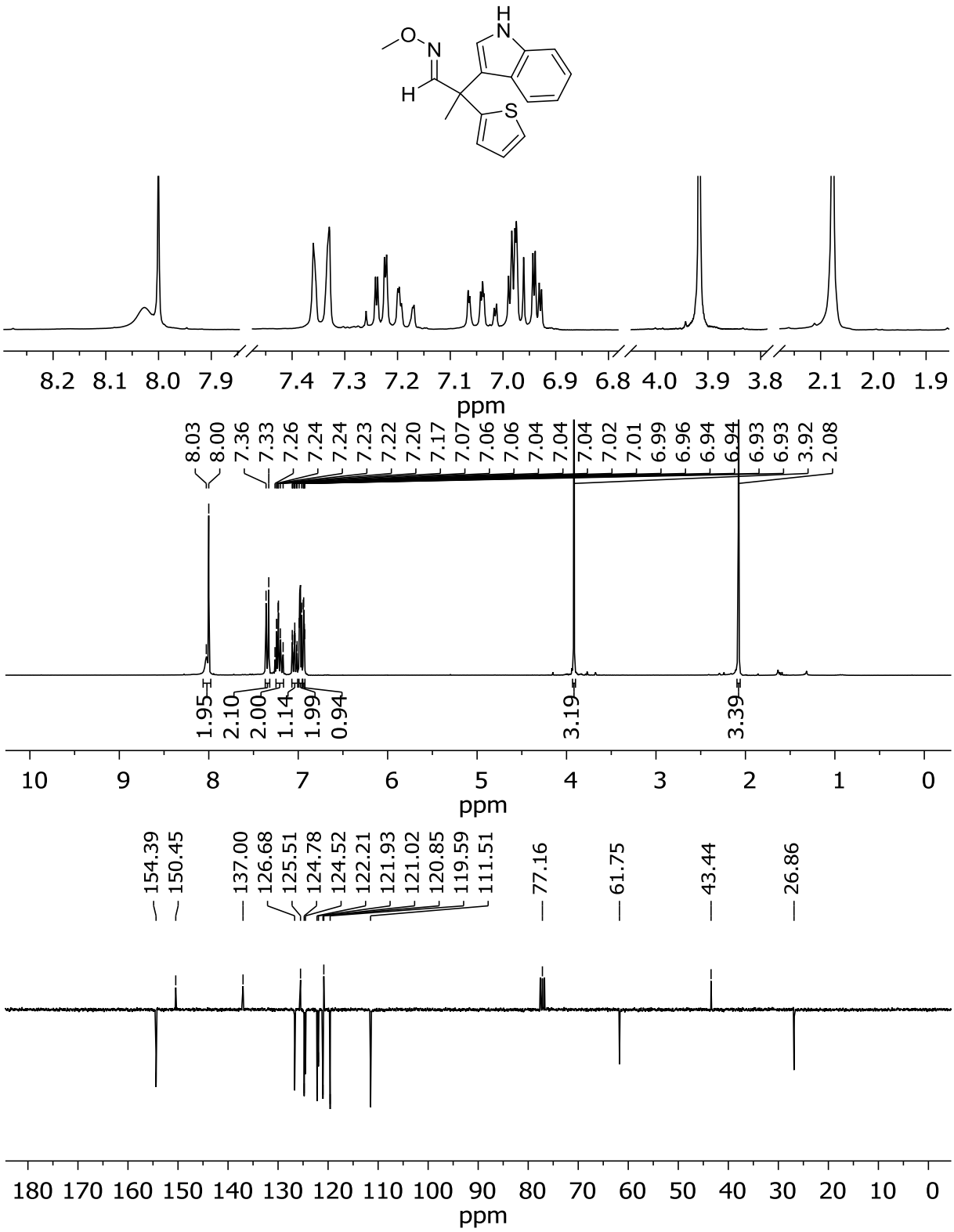
2-Indolyl aldoxime ether 8j ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



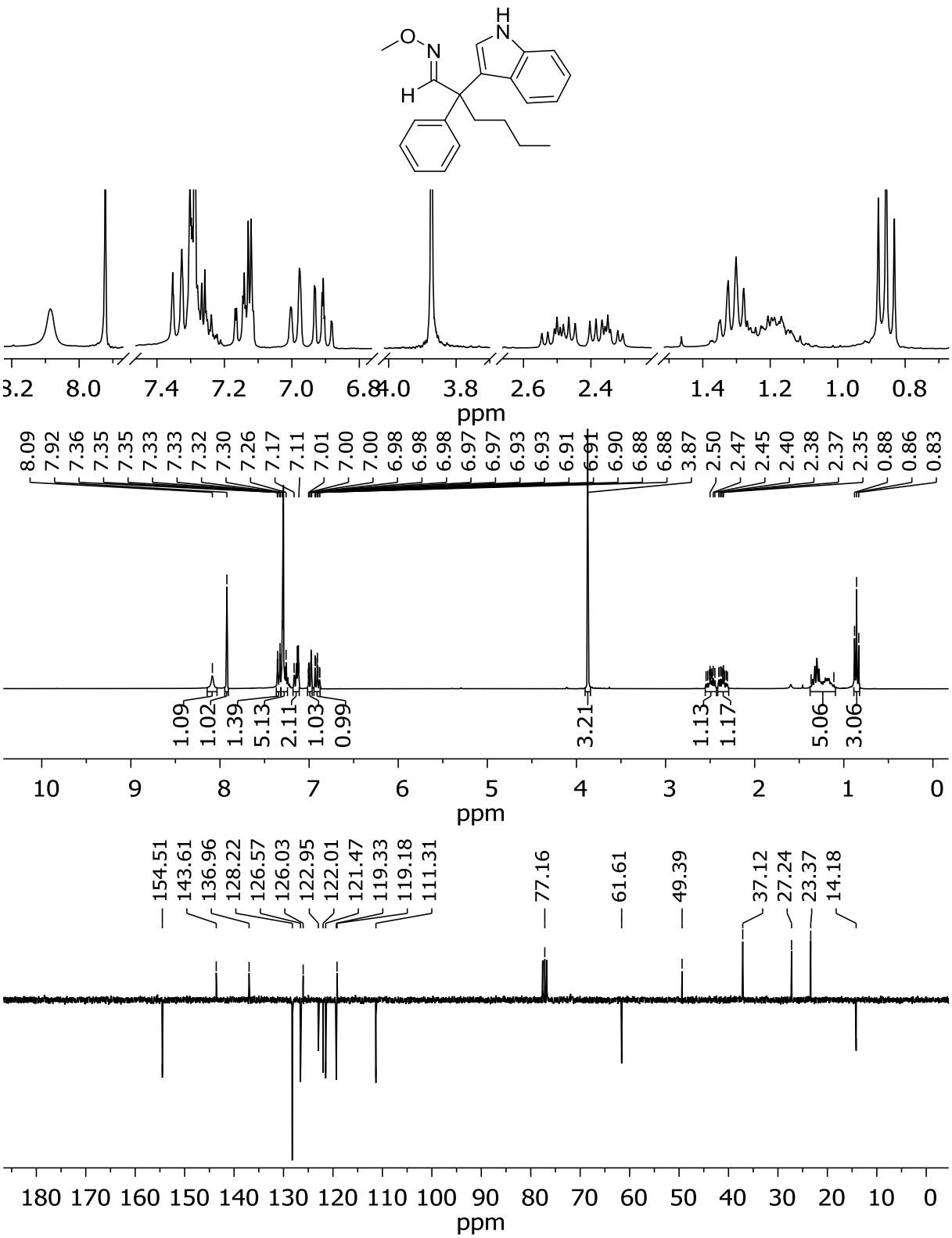
2-Indolyl aldoxime ether 8k ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



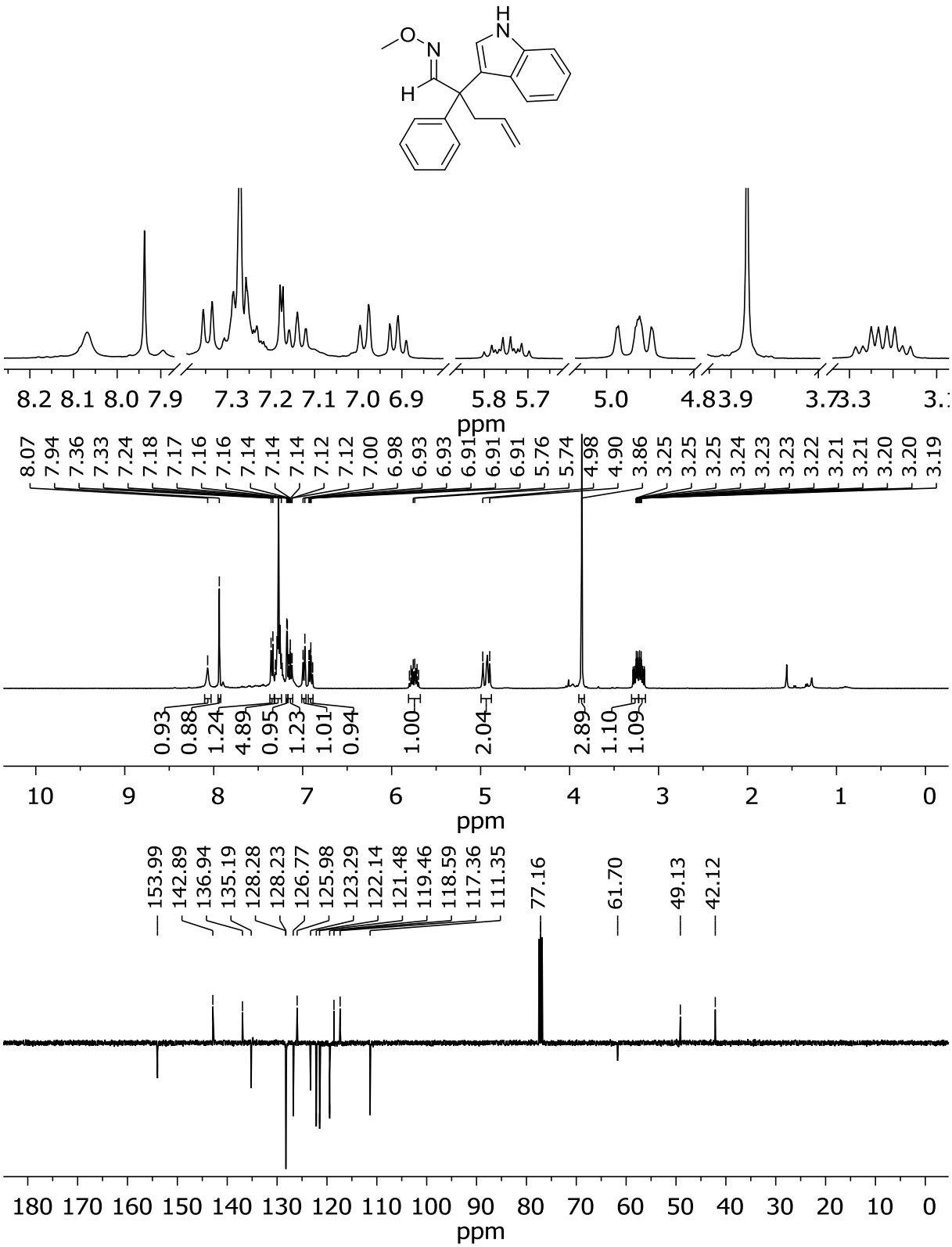
2-Indolyl aldoxime ether 8l ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



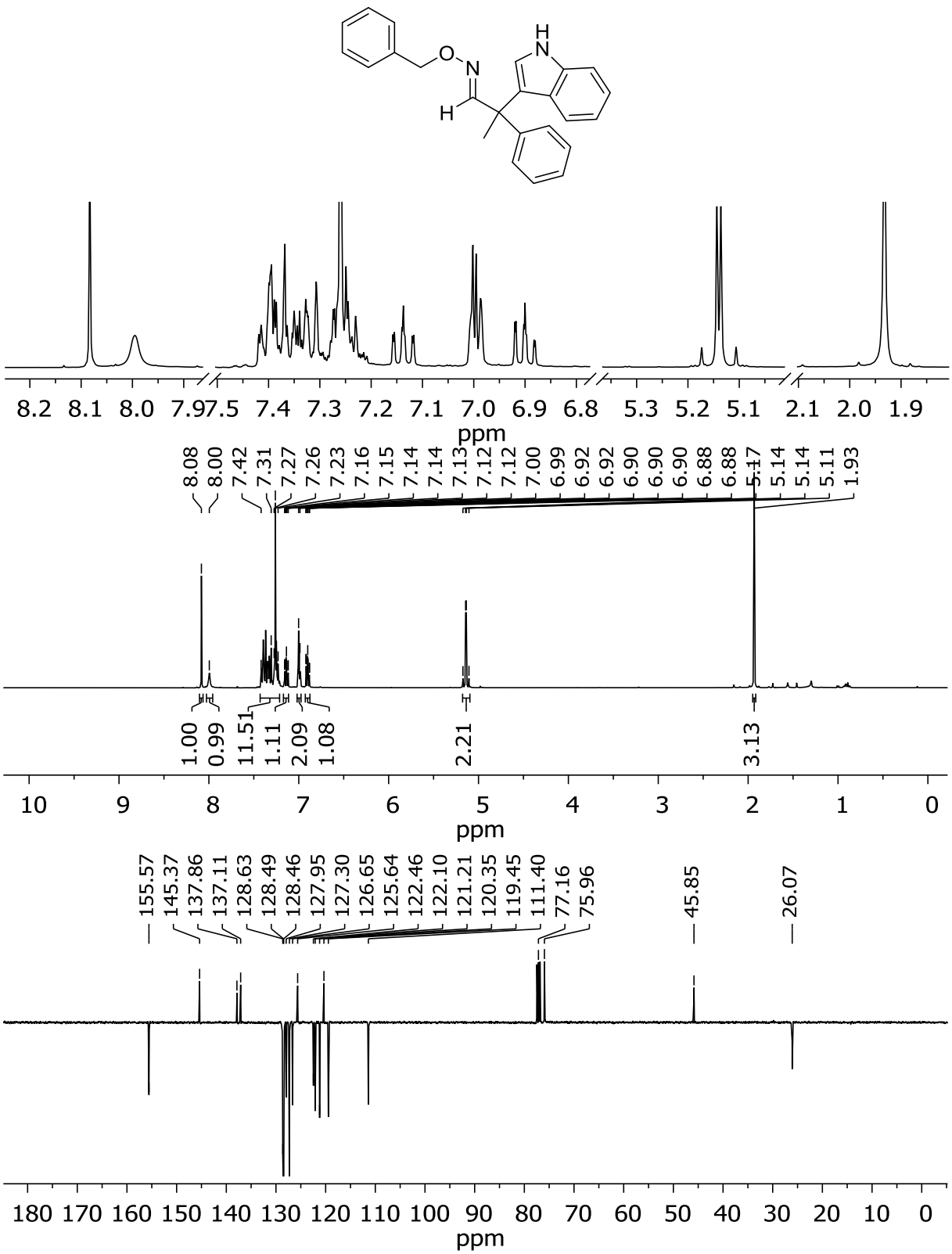
2-Indolyl aldoxime ether 8m ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



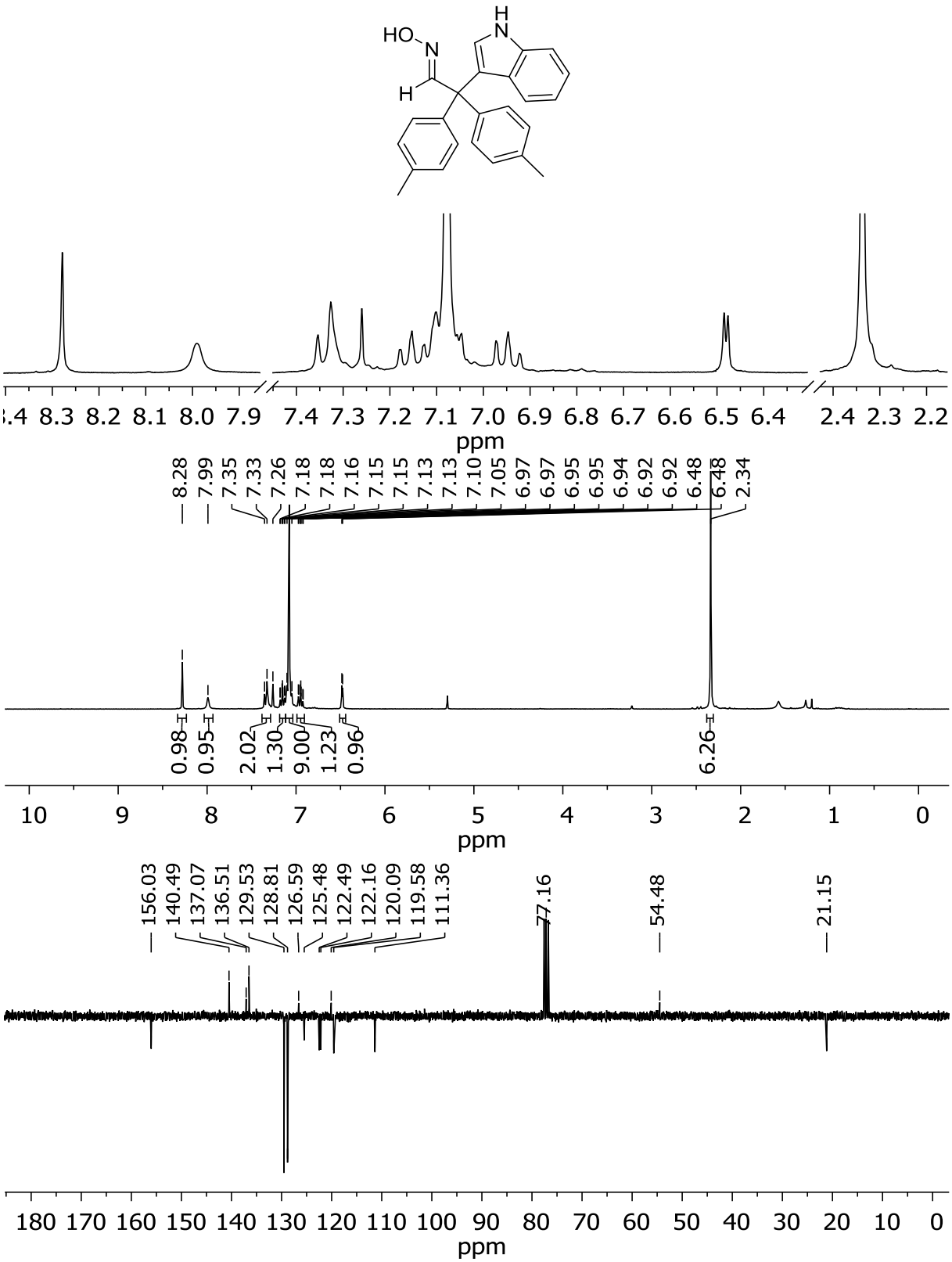
2-Indolyl aldoxime ether 8n ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



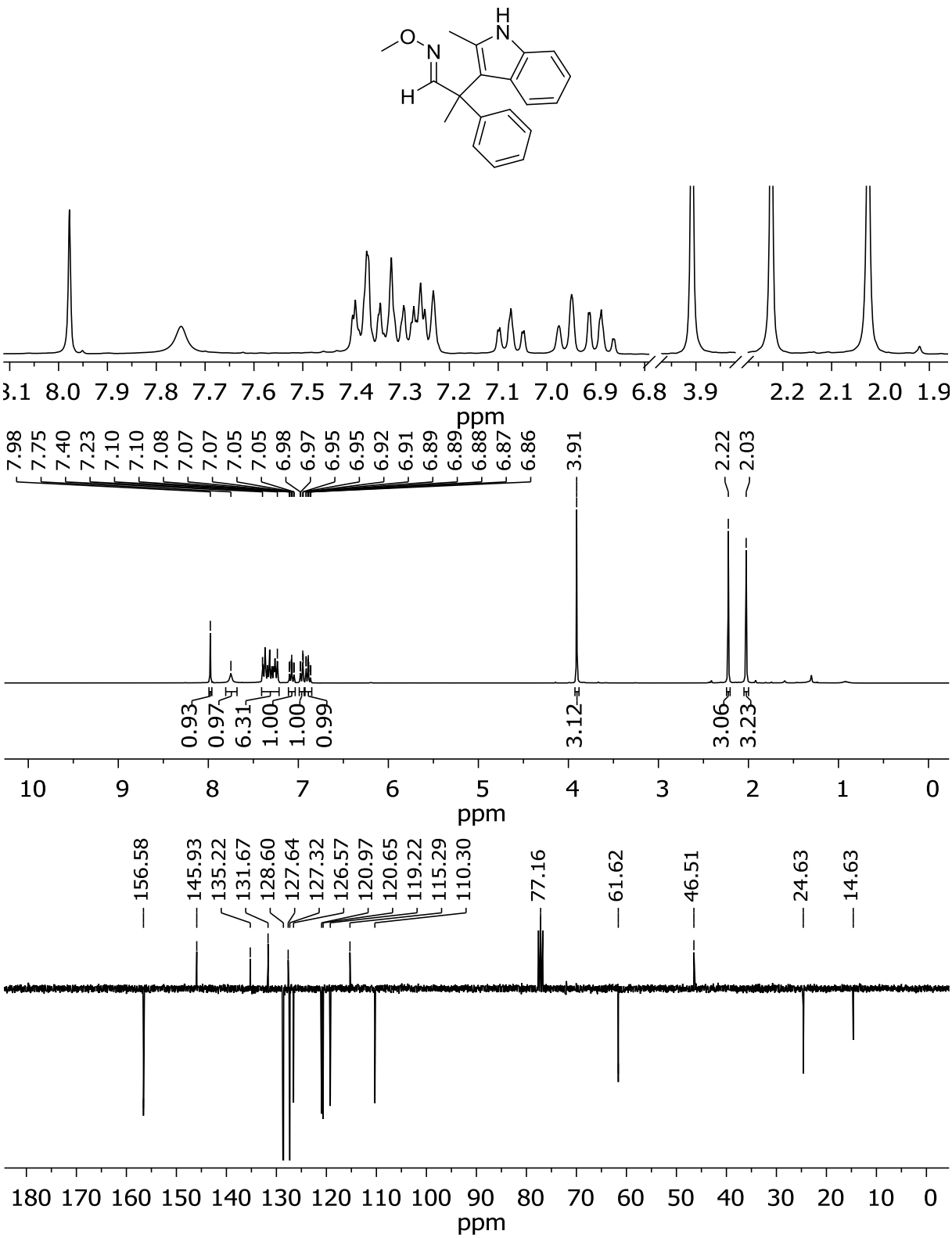
2-Indolyl aldoxime ether 8o ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



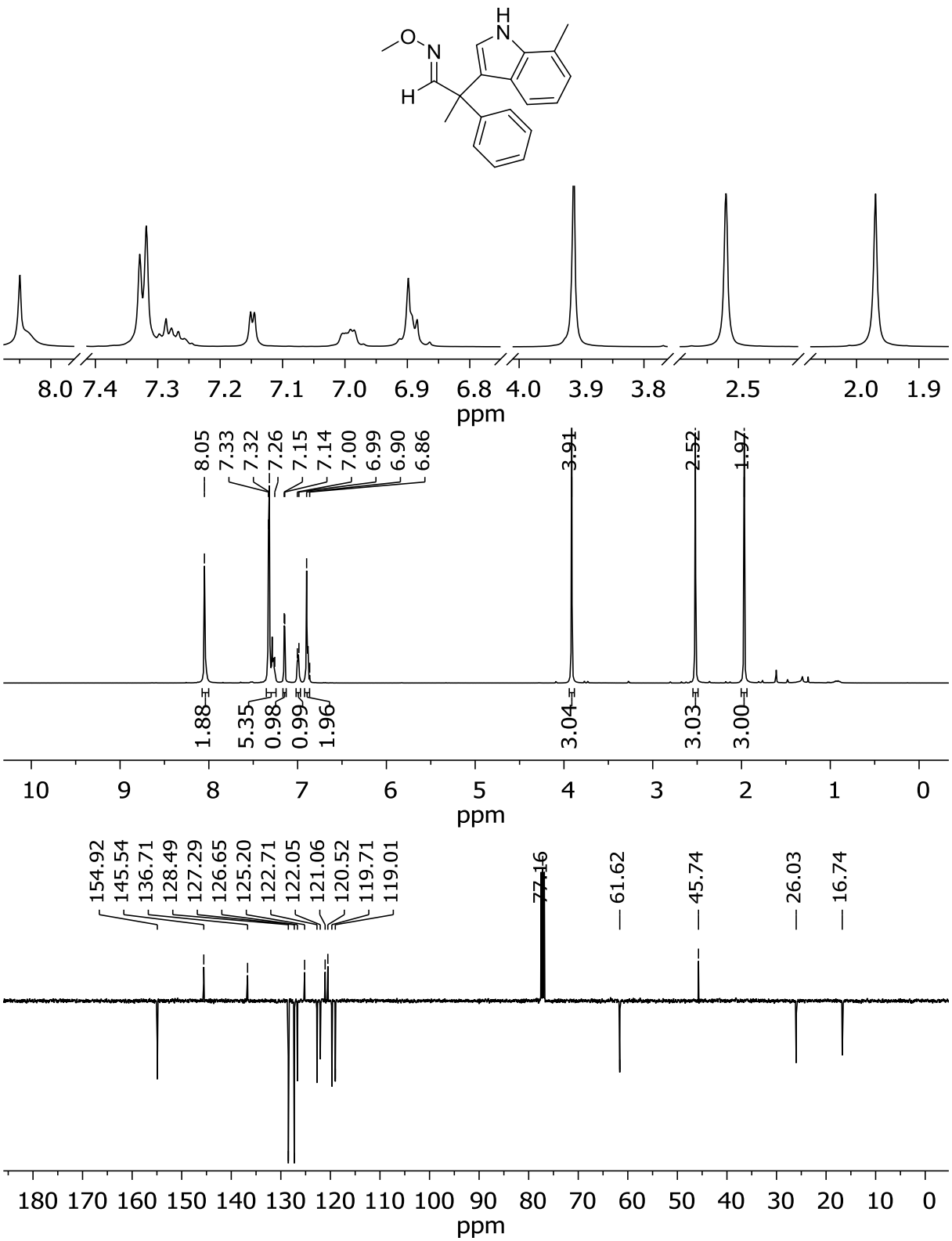
2-Indolyl aldoxime 8p' ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



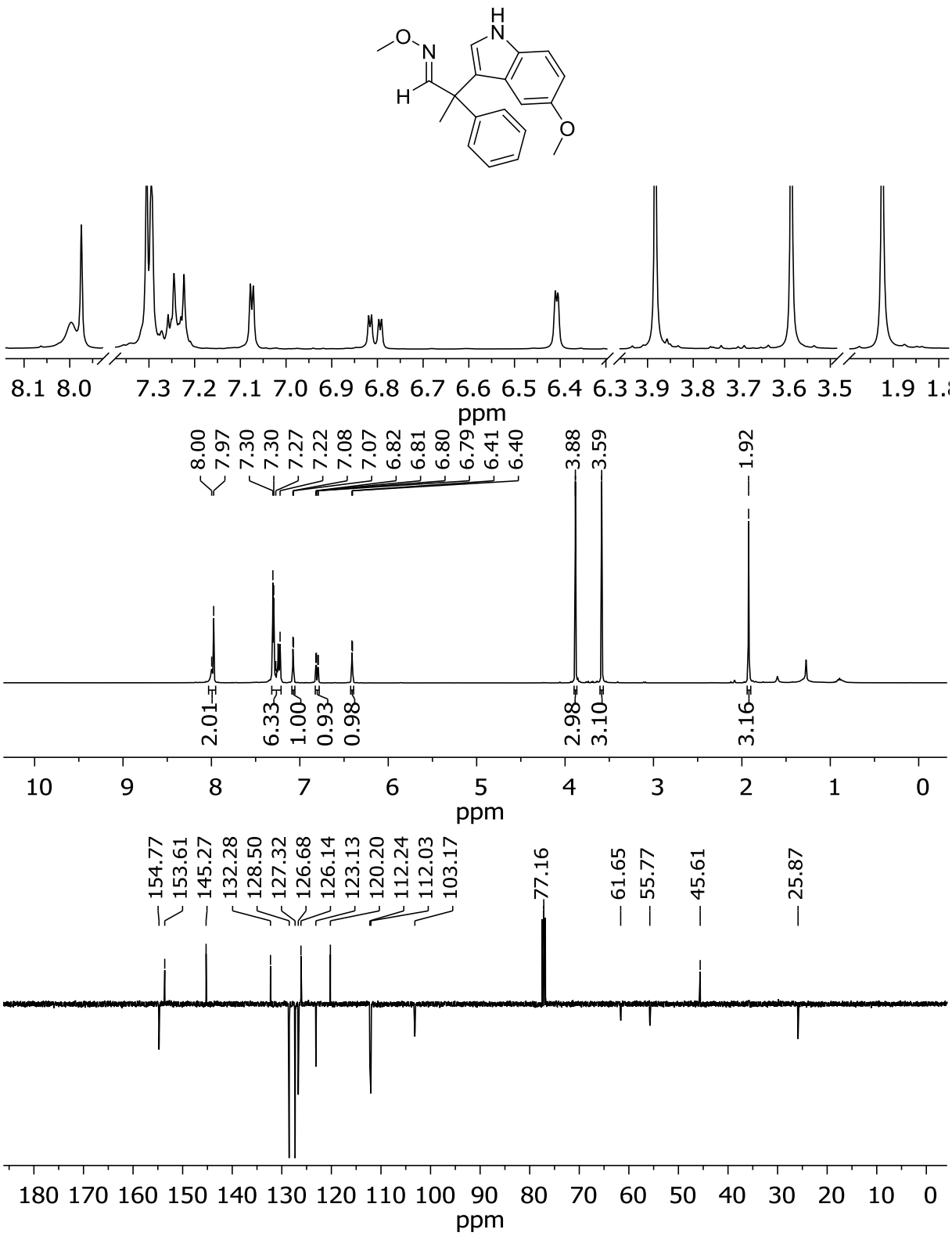
2-Indolyl aldoxime ether 8q ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



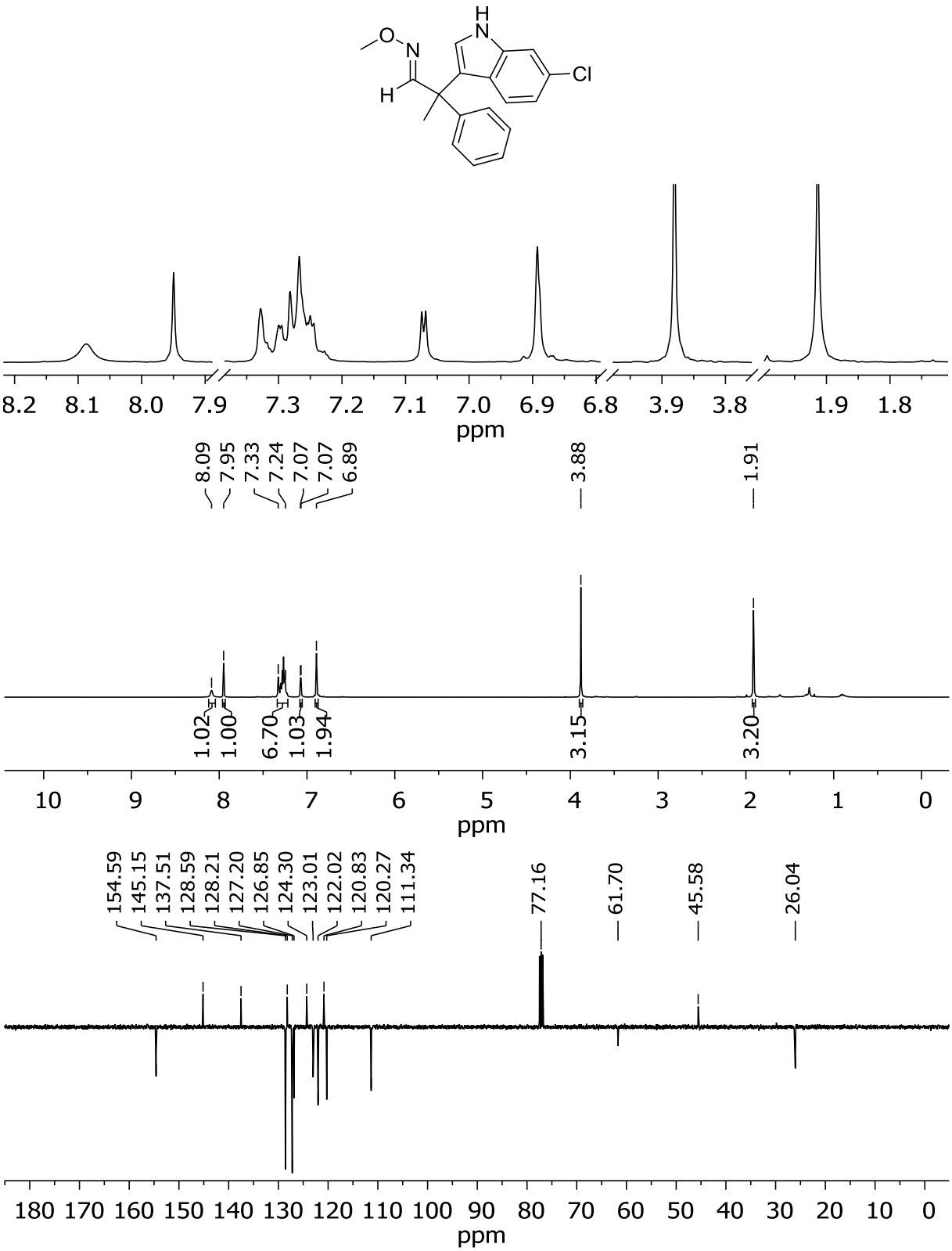
2-Indolyl aldoxime ether 8r ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



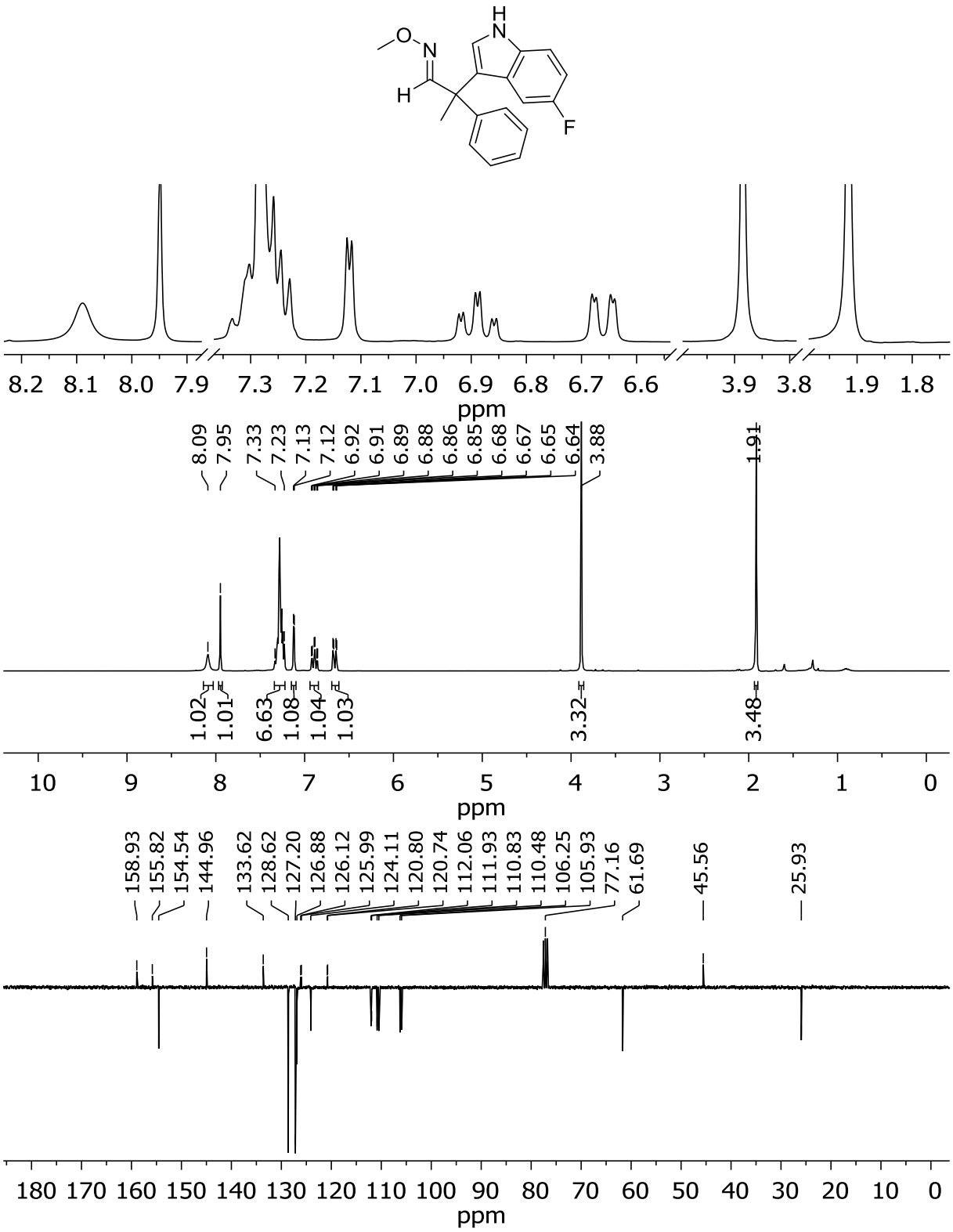
2-Indolyl aldoxime ether 8s ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



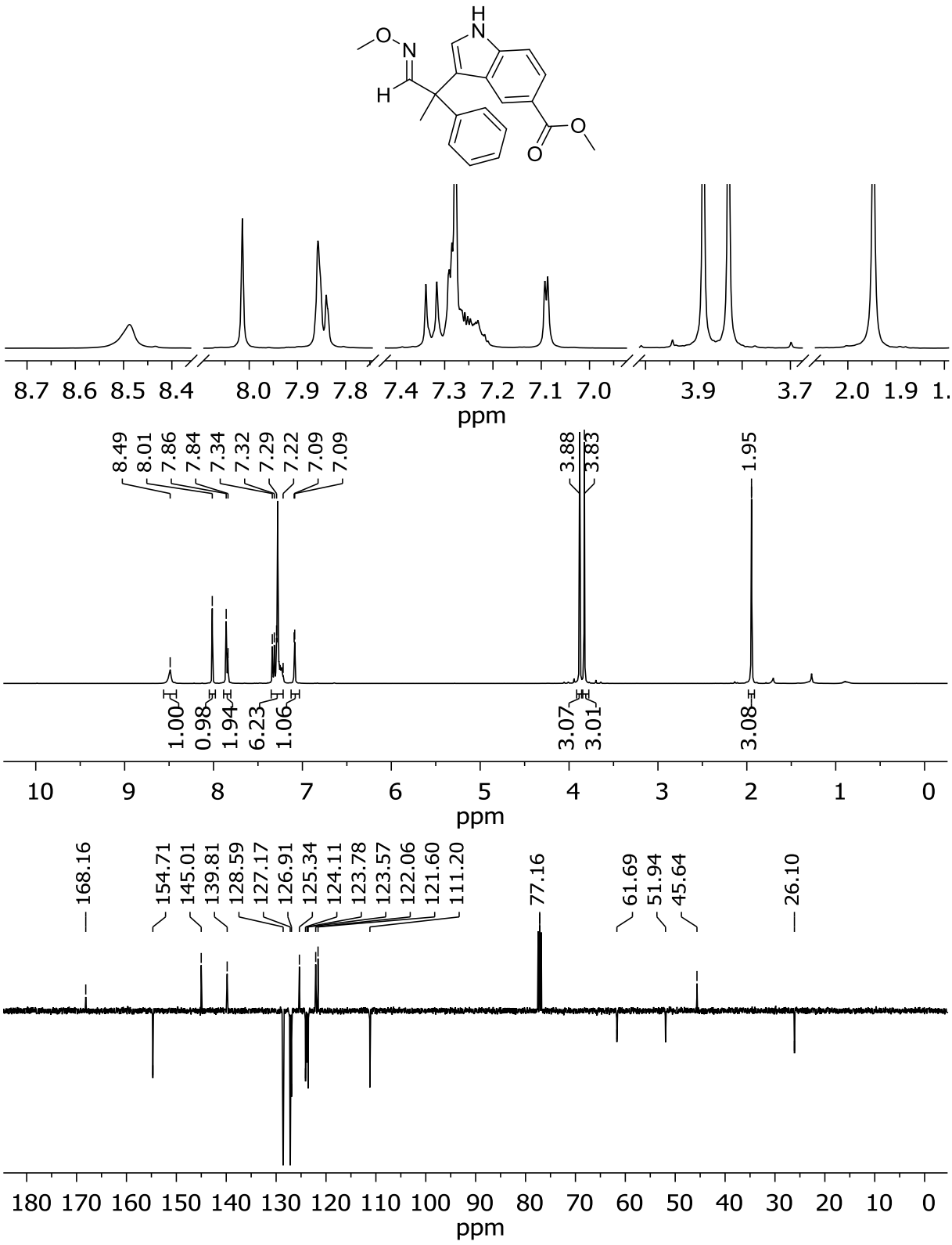
2-Indolyl aldoxime ether 8t ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



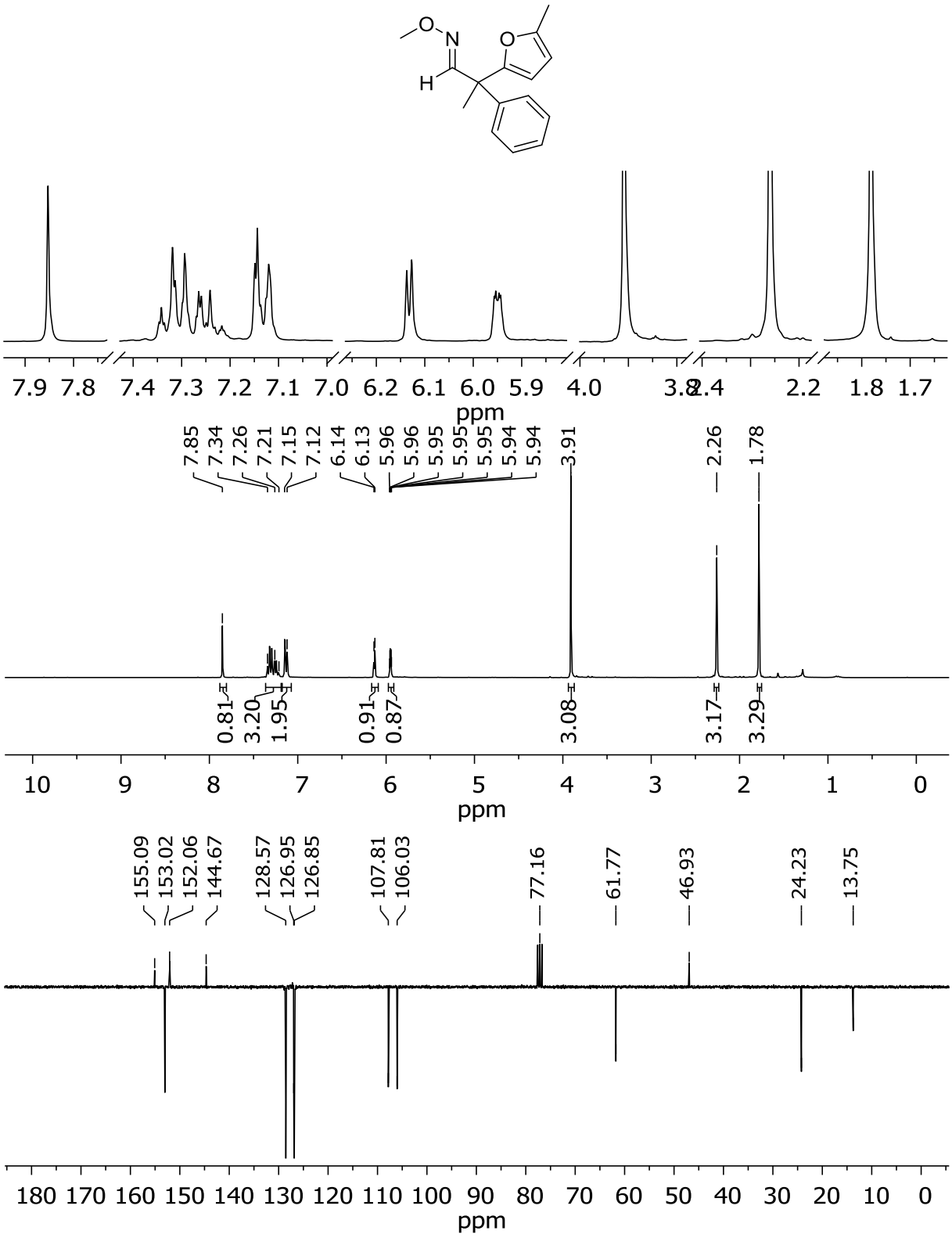
2-Indolyl aldoxime ether 8u ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



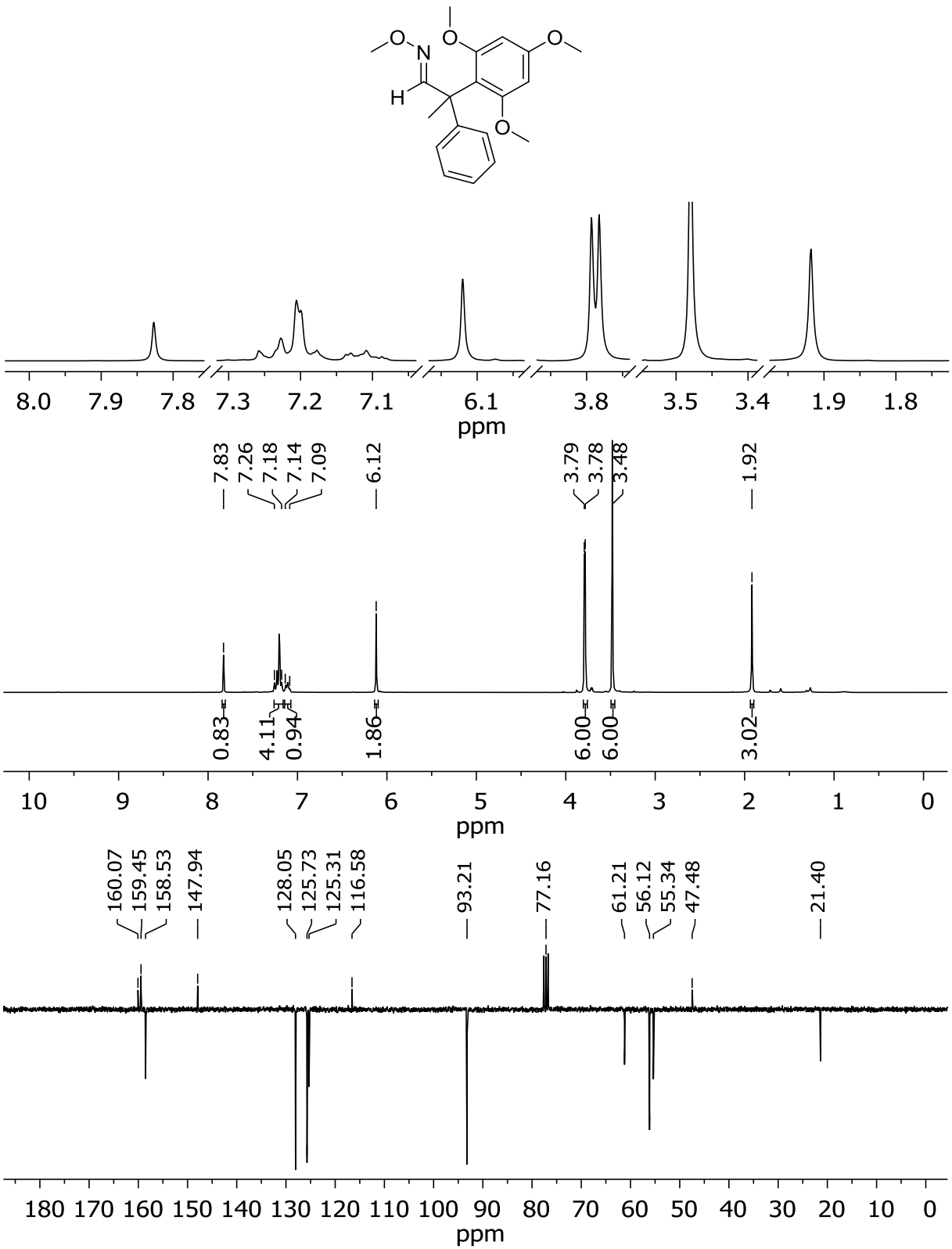
2-Indolyl aldoxime ether 8v ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



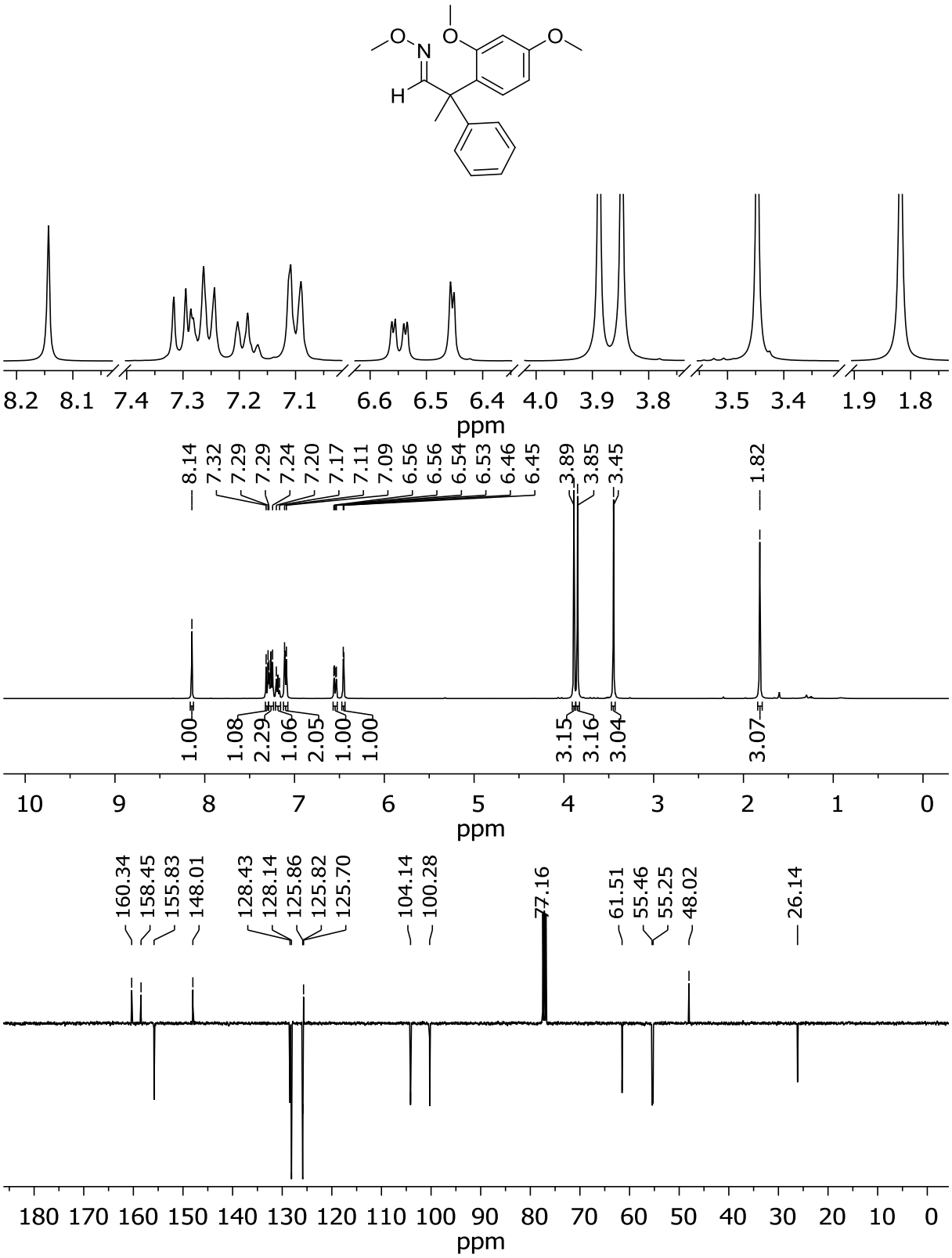
2-Furanyl aldoxime ether 8w ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



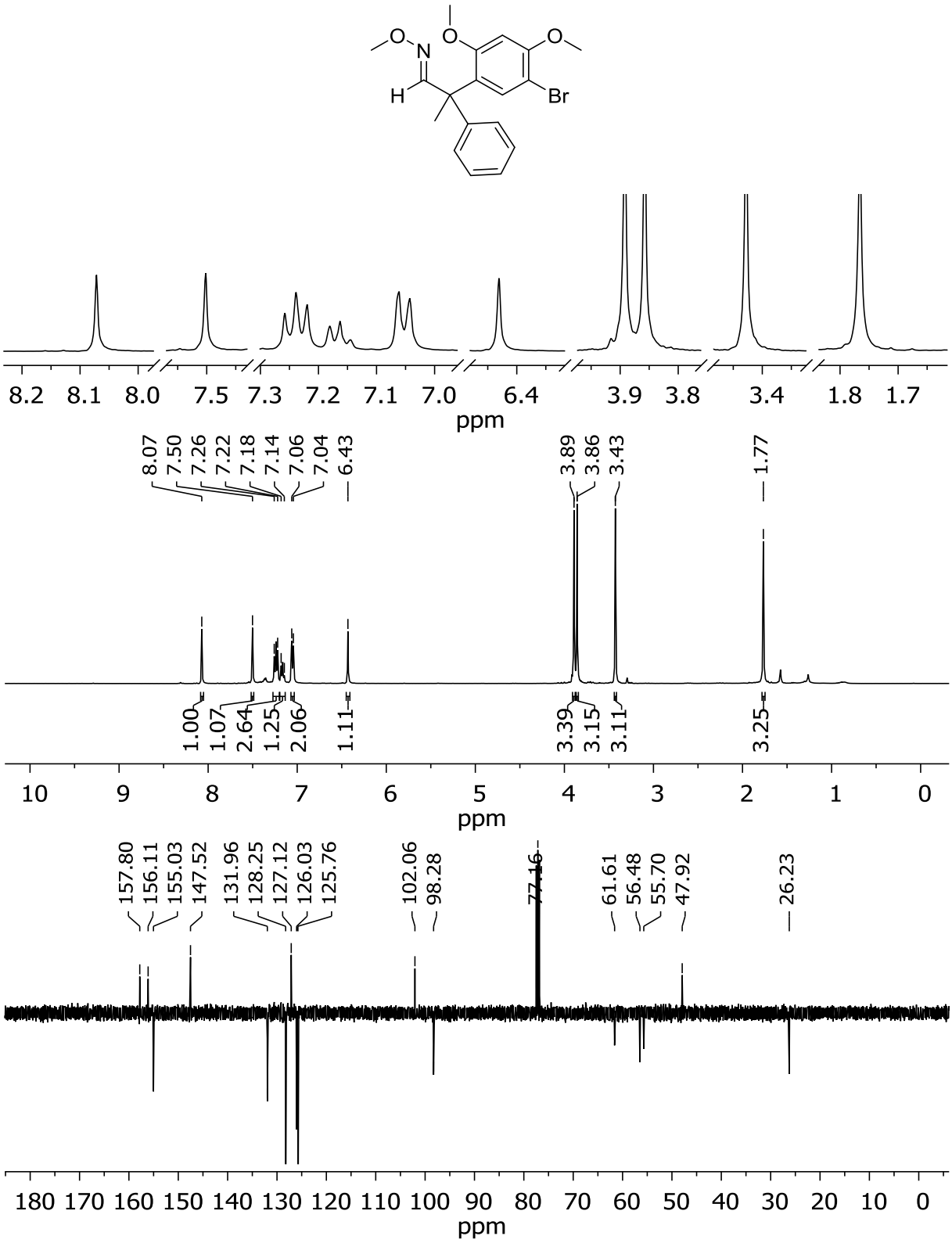
2-Phenyl aldoxime ether 8x ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



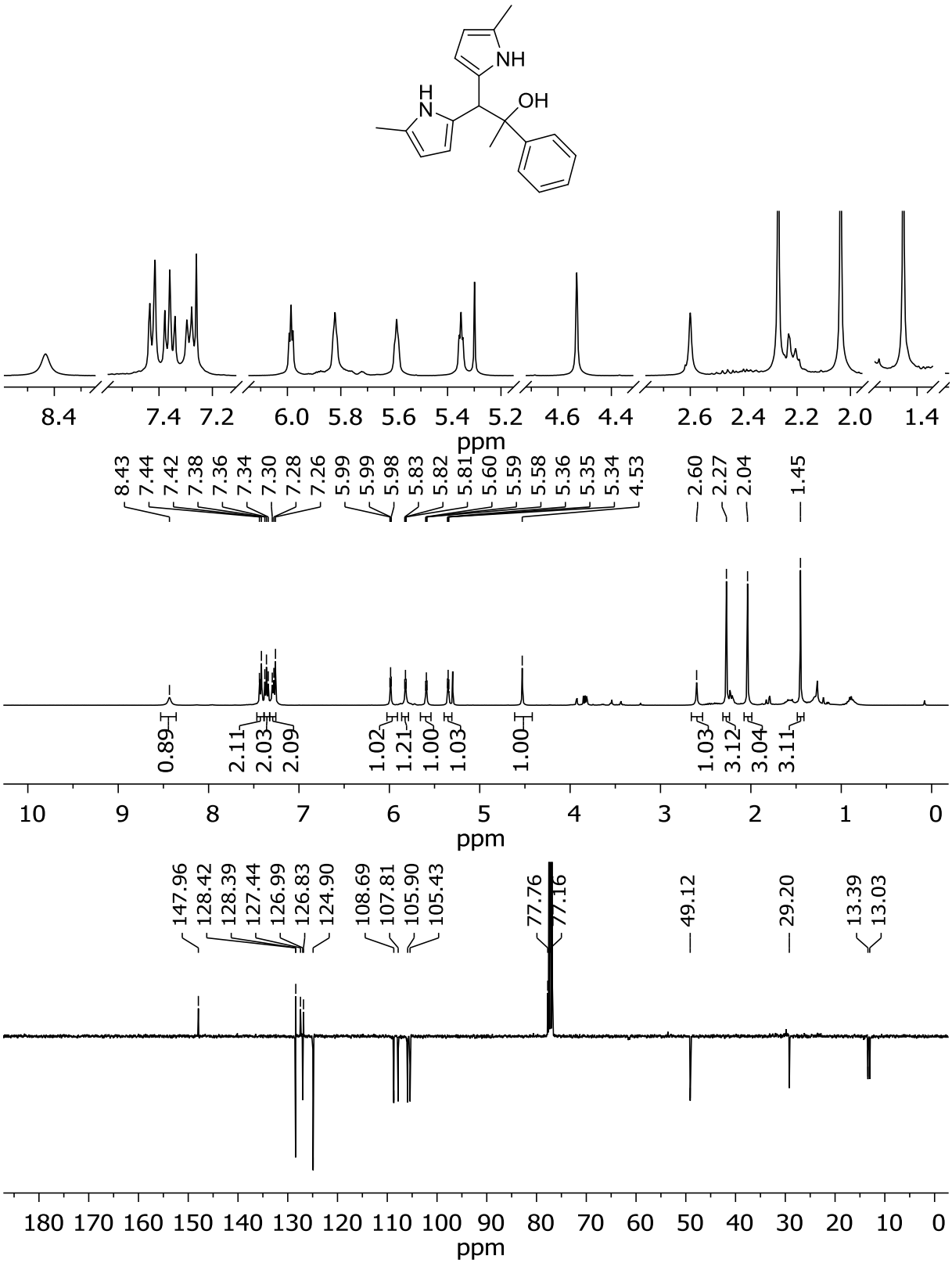
2-Phenyl aldoxime ether 8y ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



2-Phenyl aldoxime ether 8z ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



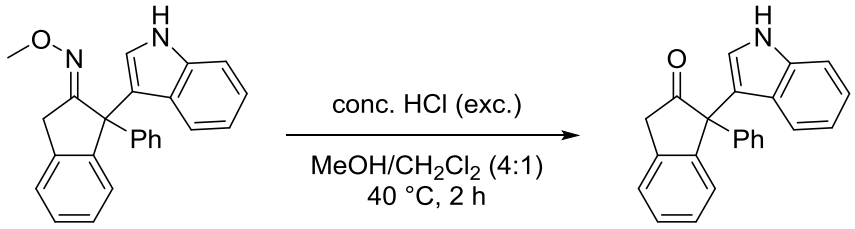
Bis(pyrrol-2-yl)ethyl alcohol 9 ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



5 Derivatization of the FCR-Products

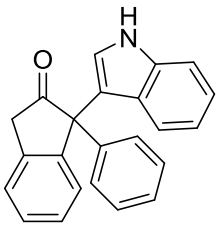
5.1 Procedures

2-Indolyl ketone 10



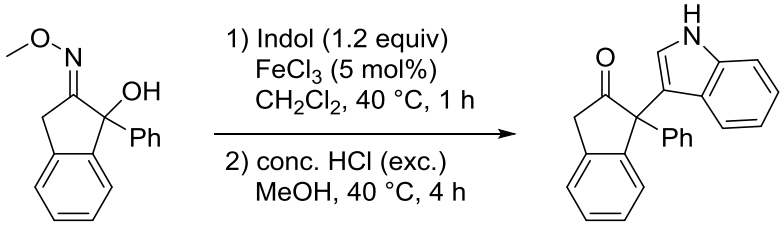
4a **10**

Concentrated HCl (0.20 mL) was added to a solution of **4a** (35 mg, 0.10 mmol, 1.0 equiv) dissolved in 0.80 mL MeOH and 0.20 mL CH_2Cl_2 at room temperature. The reaction mixture was stirred at 40 °C for 2 hours and then treated with 2.0 mL H_2O. The aqueous phase was separated and extracted twice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **10** was obtained as a colorless solid (26 mg, 80%).



R_f: 0.19 (20% MTBE/hexane); **mp.:** 153-154 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 8.05 (bs, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.35-7.22 (m, 8H), 7.17-7.12 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 2.5 Hz, 1H), 3.78 (d, J = 22.0 Hz, 1H), 3.69 (d, J = 22.0 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 213.8 (C=O), 145.9 (C_q), 140.9 (C_q), 137.1 (C_q), 135.7 (C_q), 128.7 (2x CH), 128.4 (2x CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.7 (CH), 125.9 (C_q), 125.5 (CH), 124.9 (CH), 122.4 (CH), 121.7 (CH), 119.9 (CH), 117.8 (C_q), 111.3 (CH), 64.2 (C_q), 42.1 (CH_2); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3411, 1747, 1617, 1457, 764, 746, 700; **HR-MS** (ESI)**:** calcd. for $C_{23}H_{17}NONa$ ([M+Na]$^+$): 346.1202, found: 346.1208; **M($C_{23}H_{17}NO$):** 323.40.

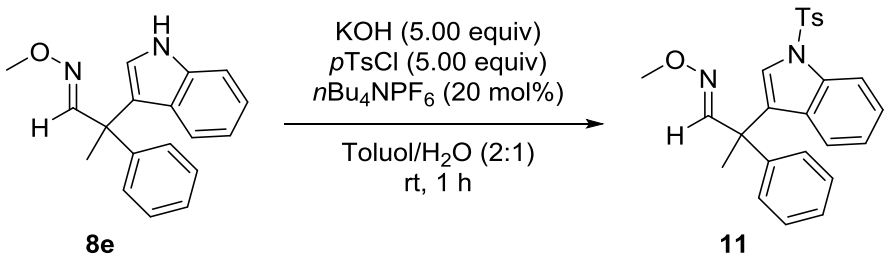
sequential two-steps-reaction:



1a **10**

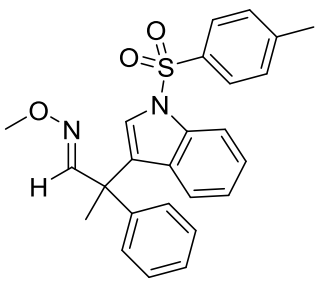
According to the general procedure 3, 2-hydroxy ketoxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), indole (28 mg, 0.24 mmol, 1.2 equiv) and $FeCl_3$ (1.6 mg, 10 μmol, 0.05 equiv) in 0.6 mL abs. CH_2Cl_2 were used. The reaction mixture was stirred at 40 °C for 1 hour. Notwithstanding the general procedure 3, 1.6 mL MeOH and 0.40 mL concentrated HCl were added and the mixture was stirred at 40 °C for another 4 hours. After complete hydrolysis 3.0 mL H_2O were added. The aqueous phase was separated and extracted twice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **10** was obtained as a colorless solid (56 mg, 86%). The spectroscopic data are in agreement with those listed above.

p-Tosyl-protected 2-indolyl aldoxime ether 11



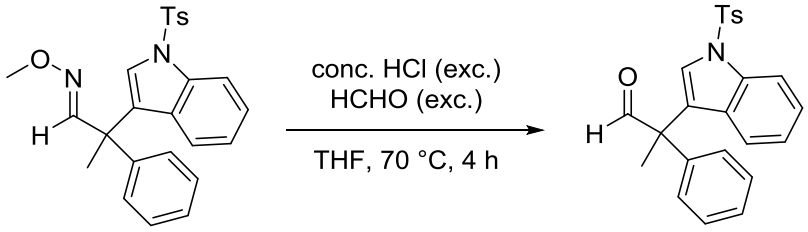
8e **11**

*p*TsCl (1.37 g, 7.18 mmol, 5.00 equiv) was added portionwise to a solution of **8e** (400 mg, 1.44 mmol, 1.00 equiv), KOH (403 mg, 7.18 mmol, 5.00 equiv) and nBu$_4$NPF$_6$ (97.6 mg, 290 μmol, 0.20 equiv) in a mixture of 5.0 mL toluene and 2.5 mL H_2O at room temperature. The reaction mixture was stirred for 1 hour and then treated with 4.0 mL H_2O. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (4% → 8% MTBE/hexane). Compound **11** was obtained as a colorless solid (617 mg, 99%).



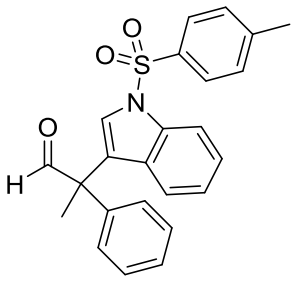
R_f: 0.42 (20% MTBE/hexane); **mp.:** 44-46 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.97 (d, J = 8.5 Hz, 1H), 7.88 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.53 (s, 1H), 7.27-7.21 (m, 6H), 7.16-7.14 (m, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.87 (s, 3H), 2.37 (s, 3H), 1.90 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 153.4 (HC=N), 145.1 (C_q), 144.0 (C_q), 136.0 (C_q), 135.3 (C_q), 130.1 (2x CH), 129.0 (C_q), 128.7 (2x CH), 127.1 (CH), 127.01 (4x CH), 126.99 (C_q), 124.7 (CH), 124.1 (CH), 123.0 (CH), 121.9 (CH), 113.9 (CH), 61.8 (CH_3), 45.6 (C_q), 25.7 (CH_3), 21.7 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3446, 2936, 1597, 1447, 1372, 1187, 1175, 1134, 1090, 1053, 748, 701, 677, 577, 538; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{24}N_2O_3SNa$ ([M+Na]$^+$): 455.1400, found: 455.1396; **M($C_{25}H_{24}N_2O_3S$):** 432.54.

***p*-Tosyl-protected 2-indolyl aldehyde S7**



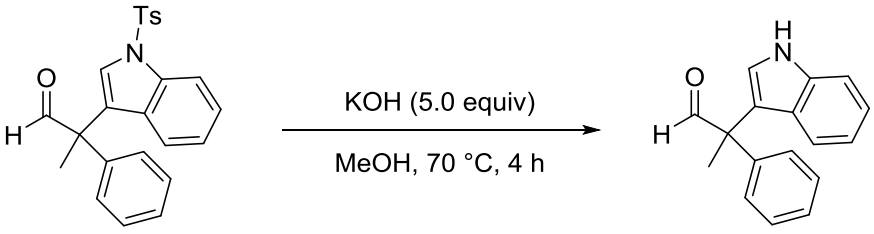
11 **S7**

Concentrated HCl (0.10 mL) was added to a solution of **11** (87 mg, 0.20 mmol, 1.0 equiv) dissolved in 1.0 mL THF and 1.0 mL of 37% aqueous HCHO-solution at room temperature. The reaction mixture was stirred at 70 °C for 4 hours and then treated with 2.0 mL H_2O. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 10% MTBE/hexane). Compound **S7** was obtained as a colorless solid (79 mg, 98%).



R_f: 0.30 (20% MTBE/hexane); **mp.:** 143-144 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 9.87 (s, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.34-7.25 (m, 6H), 7.15-7.13 (m, 2H), 7.03 (m, 1H), 6.90 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H), 1.83 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 198.3 (HC═O), 145.3 (C_q), 139.7 (C_q), 135.9 (C_q), 135.2 (C_q), 130.1 (2x CH), 129.1 (2x CH), 128.9 (C_q), 127.8 (CH), 127.7 (3x CH), 127.0 (2x CH), 125.0 (CH), 123.2 (CH), 122.8 (C_q), 121.9 (CH), 114.0 (CH), 55.6 (C_q), 22.6 (CH_3), 21.8 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3427, 2988, 1723, 1447, 1373, 1178, 1130, 1090, 1040, 765, 755, 727, 674, 578, 539; **HR-MS** (ESI)**:** calcd. for $C_{24}H_{21}NO_3SNa$ ([M+Na]$^+$): 426.1134, found: 426.1127; **M($C_{24}H_{21}NO_3S$):** 403.50.

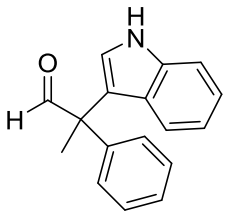
2-Indolyl aldehyde 12



S7 **12**

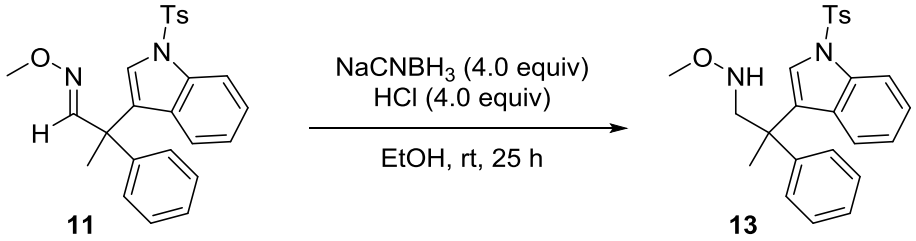
KOH (28 mg, 0.50 mmol, 5.0 equiv) was added to a solution of **S7** (40 mg, 0.10 mmol, 1.0 equiv) in 0.50 mL MeOH. The reaction mixture was stirred at 70 °C for 4 hours and then treated with 2.0 mL H_2O and 2.0 mL EtOAc. The aqueous phase was separated and

extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **12** was obtained as a colorless solid (25 mg, 99%).

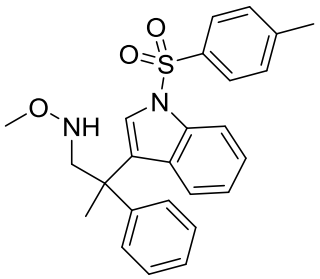


R_f: 0.20 (20% MTBE/hexane); **mp.:** 60-61 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** *δ* (ppm) = 9.98 (s, 1H), 8.30 (bs, 1H), 7.42-7.31 (m, 4H), 7.27-7.24 (m, 2H), 7.22-7.15 (m, 2H), 7.05 (ddt, *J* = 8.0, 1.5, 1.0 Hz, 1H), 6.96 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 1.83 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** *δ* (ppm) = 199.2 (HC=O), 141.4 (C_q), 137.1 (C_q), 128.8 (2x CH), 127.9 (2x CH), 127.3 (CH), 125.8 (C_q), 123.5 (CH), 122.5 (CH), 121.2 (CH), 119.8 (CH), 115.8 (C_q), 111.6 (CH), 55.8 (C_q), 23.1 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3390, 2983, 2934, 2824, 2719, 1719, 1537, 1490, 1454, 1415, 1365, 1333, 1242, 1115, 1106, 1025, 1010, 897, 837, 760, 747, 713, 700, 584, 572, 533, 428; **HR-MS** (ESI)**:** calcd. for $C_{17}H_{15}NONa$ ($[M+Na]^+$): 272.1046, found: 272.1044; **M($C_{17}H_{15}NO$):** 249.31.

3-(Methoxyaminoethyl)indole 13



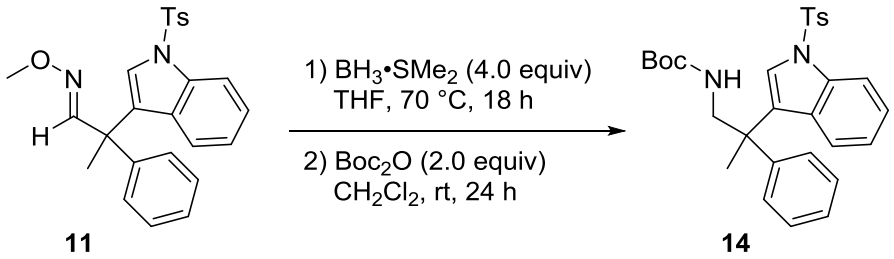
$NaCNBH_3$ (50 mg, 0.80 mmol, 4.0 equiv) followed by an ethanolic solution of HCl (1.25 M in EtOH, 0.64 mL, 0.80 mmol, 4.0 equiv) were added to a solution of **11** (87 mg, 0.20 mmol, 1.0 equiv) in 1.0 mL abs. EtOH at room temperature. The reaction mixture was stirred at room temperature for 25 hours and then quenched with sat. Na_2CO_3-solution. It was extracted twice with CH_2Cl_2 and the combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **13** was obtained as a colorless oil (81 mg, 93%).



R_f: 0.32 (20% MTBE/hexane); **^{1}H-NMR** (300 MHz, $CDCl_3$)**:** *δ* (ppm) = 7.98 (d, *J* = 8.5 Hz, 1H), 7.79 (d', *J* = 8.5 Hz, 2H), 7.63 (s, 1H), 7.26-7.14 (m, 8H), 6.95 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.80 (ddd, *J* = 8.0, 1.0, 0.5 Hz, 1H), 5.12 (bs, 1H), 3.65 (d, *J* = 11.0 Hz, 1H), 3.60 (d, *J* = 11.0 Hz, 1H), 3.45 (s, 3H), 2.37 (s, 3H), 1.80 (s, 3H); **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** *δ* (ppm) = 145.1 (C_q), 145.0 (C_q), 136.1 (C_q), 135.2 (C_q), 129.9 (2x CH), 129.4 (C_q), 128.7 (C_q), 128.3 (2x CH), 126.9 (2x CH),

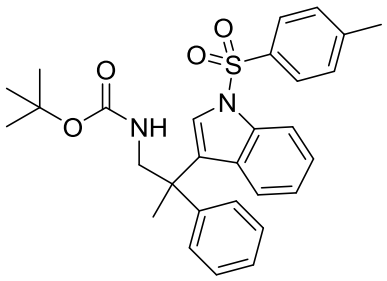
126.69 (2x CH), 126.66 (CH), 124.5 (CH), 124.0 (CH), 123.0 (CH), 121.9 (CH), 114.0 (CH), 61.5 (CH_3), 60.0 (CH_2), 42.5 (C_q), 27.0 (CH_3), 21.7 (CH_3); **IR** (film)**:** $\tilde{\nu}$ (cm^{-1}) = 3446, 2934, 1598, 1447, 1370, 1187, 1175, 1134, 759, 750, 711, 701, 669, 575, 538; **HR-MS** (ESI)**:** calcd. for $C_{25}H_{27}N_2O_3SNa$ ([M+H]$^+$): 435.1737, found: 435.1736; **M($C_{25}H_{26}N_2O_3S$):** 434.55.

***N*-(Indol-3-ylethyl)carbamate 14**



11 **14**

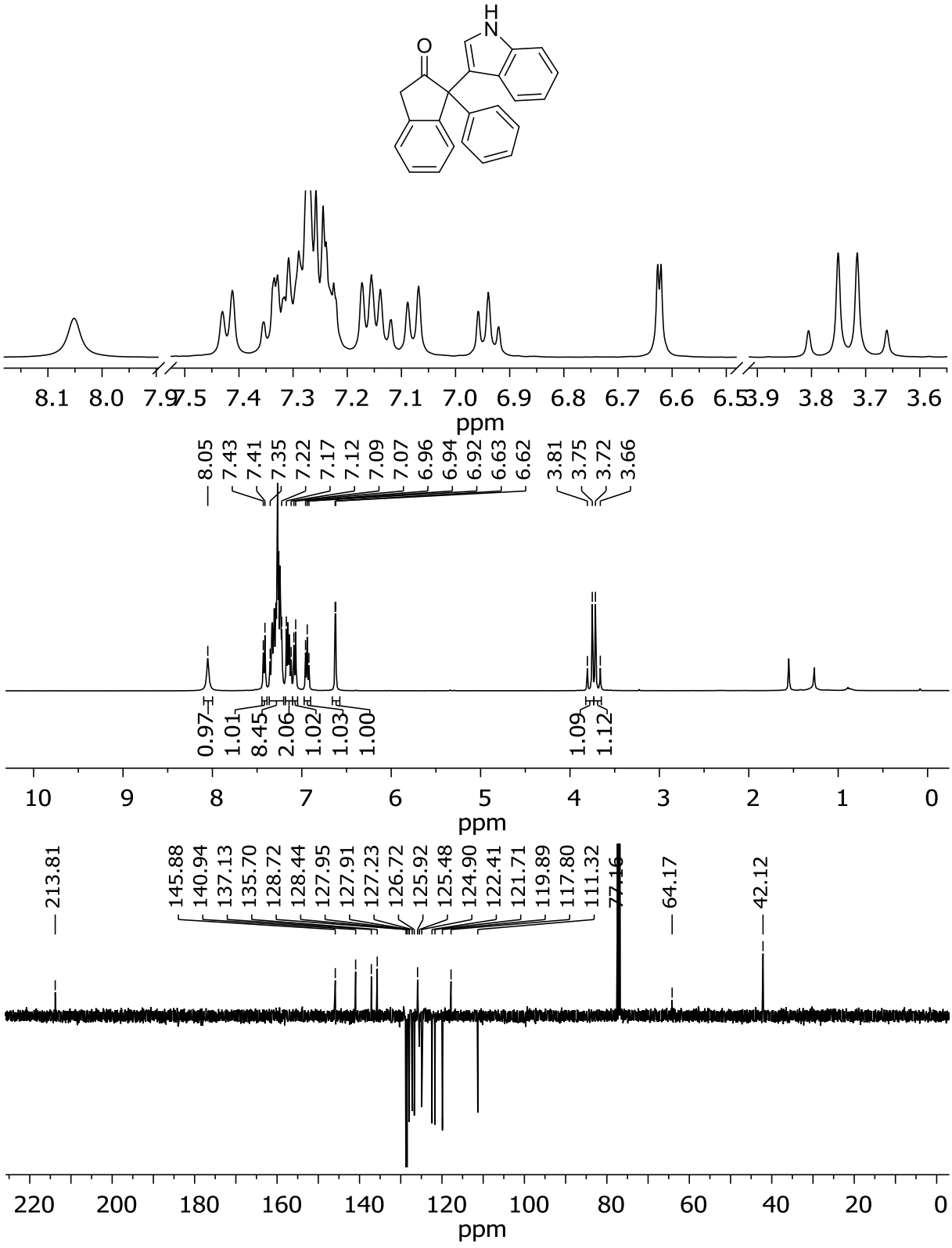
BH_3•SMe_2 (2.0 M in THF, 200 μL, 0.40 mmol, 4.0 equiv) was added dropwise to a solution of **11** (43 mg, 0.10 mmol, 1.0 equiv) in 0.5 mL abs. THF at room temperature. The reaction mixture was stirred at 70 °C for 18 hours and then treated with 2.0 mL H_2O and 2.0 mL EtOAc. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was dissolved in 0.5 mL abs. CH_2Cl_2 and Boc_2O (46 μL, 0.20 mmol, 2.0 equiv) was added. It was stirred at room temperature for 24 hours and then quenched with 1.0 mL of 1 M HCl-solution. The aqueous phase was separated and extracted twice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **14** was obtained as a colorless solid (43 mg, 84%).



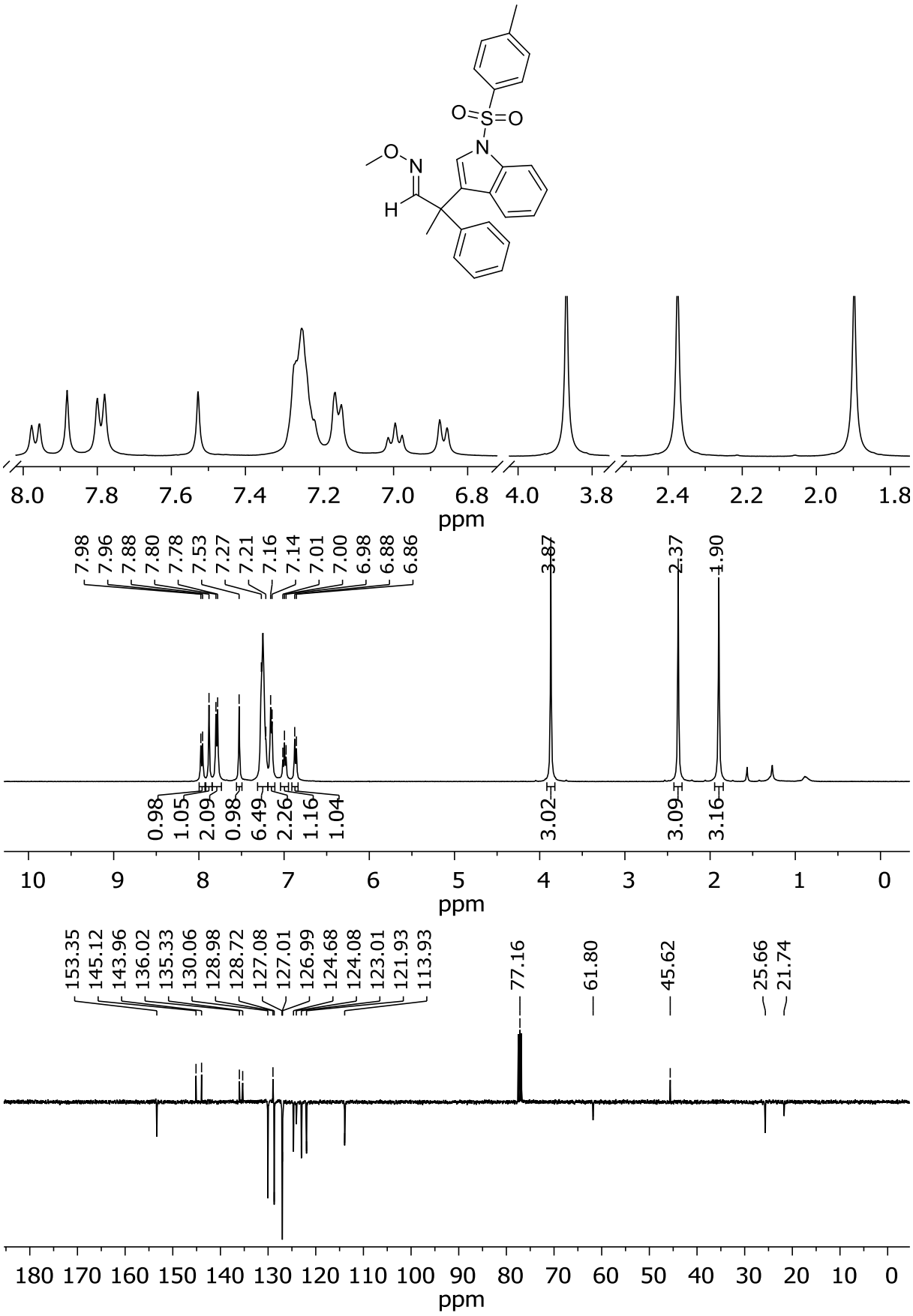
R_f: 0.26 (20% MTBE/hexane); **mp.:** 95-96 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$)**:** δ (ppm) = 7.96 (d, J = 8.5 Hz, 1H), 7.78 (d‘, J = 8.0 Hz, 2H), 7.59 (s, 1H), 7.26-7.14 (m, 8H), 6.95 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.22 (t, J = 6.5 Hz, 1H), 3.93 (dd, J = 13.0, 7.0 Hz, 1H), 3.80 (dd, J = 13.0, 5.5 Hz, 1H), 2.37 (s, 3H), 1.68 (s, 3H), 1.42 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$)**:** δ (ppm) = 156.2 (C=O), 145.1 (C_q), 144.5 (C_q), 136.1 (C_q), 135.2 (C_q), 130.0 (2x CH), 129.3 (C_q), 128.7 (2x CH), 128.2 (C_q), 126.94 (2x CH), 126.89 (2x CH), 126.8 (CH), 124.7 (CH), 123.7 (CH), 123.0 (CH), 122.0 (CH), 114.0 (CH), 79.7 (C_q), 49.2 (CH_2), 43.8 (C_q), 28.5 (3x CH_3), 25.7 (CH_3), 21.7 (CH_3); **IR** (KBr)**:** $\tilde{\nu}$ (cm^{-1}) = 3444, 2978, 1715, 1505, 1447, 1368, 1175, 576; **HR-MS** (ESI)**:** calcd. for $C_{29}H_{32}N_2O_4SNa$ ([M+Na]$^+$): 527.1975, found: 527.1973; **M($C_{29}H_{32}N_2O_4S$):** 504.65.

5.2 ^{1}H-NMR and ^{13}C-NMR Spectra

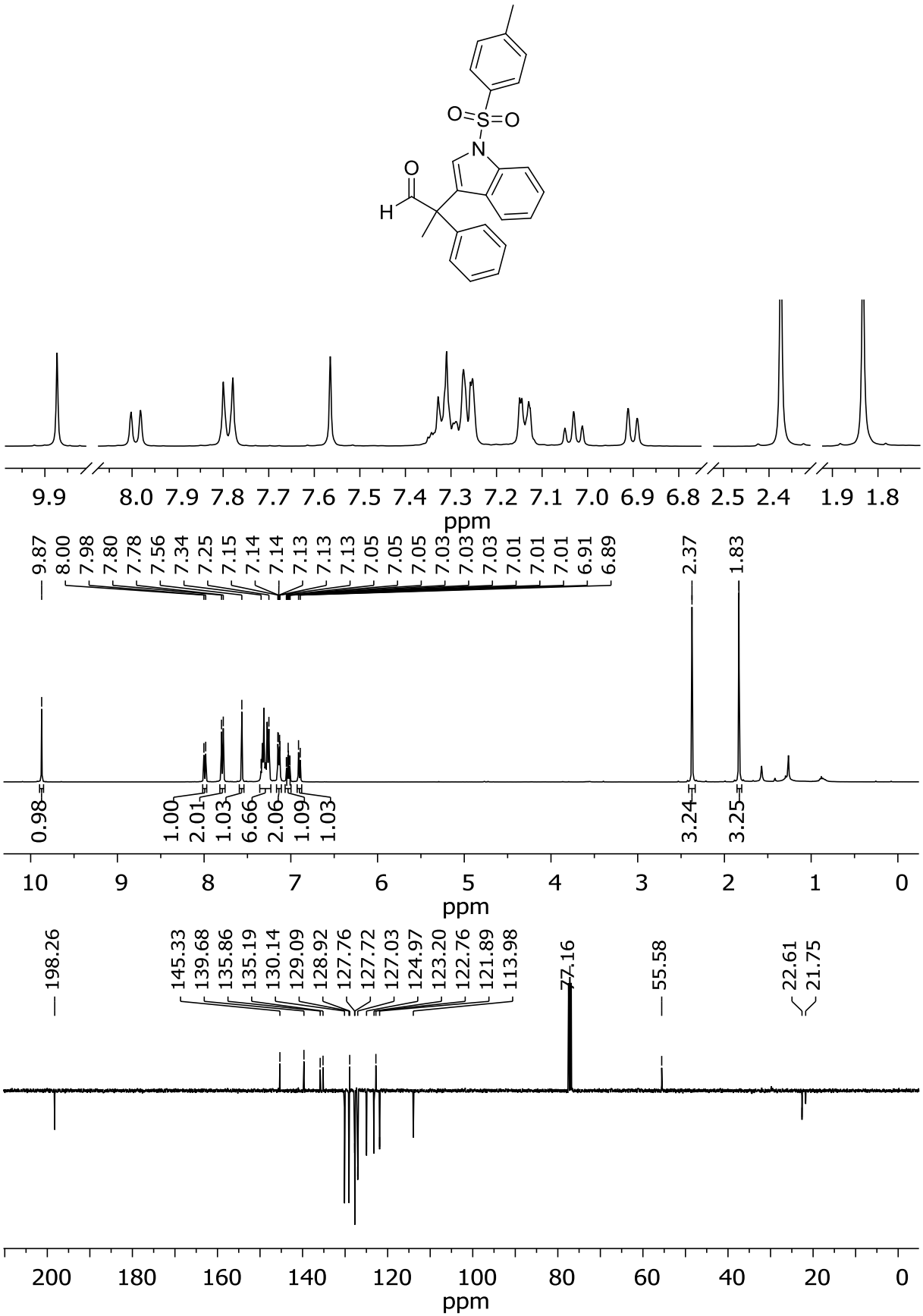
2-Indolyl ketone 10 ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



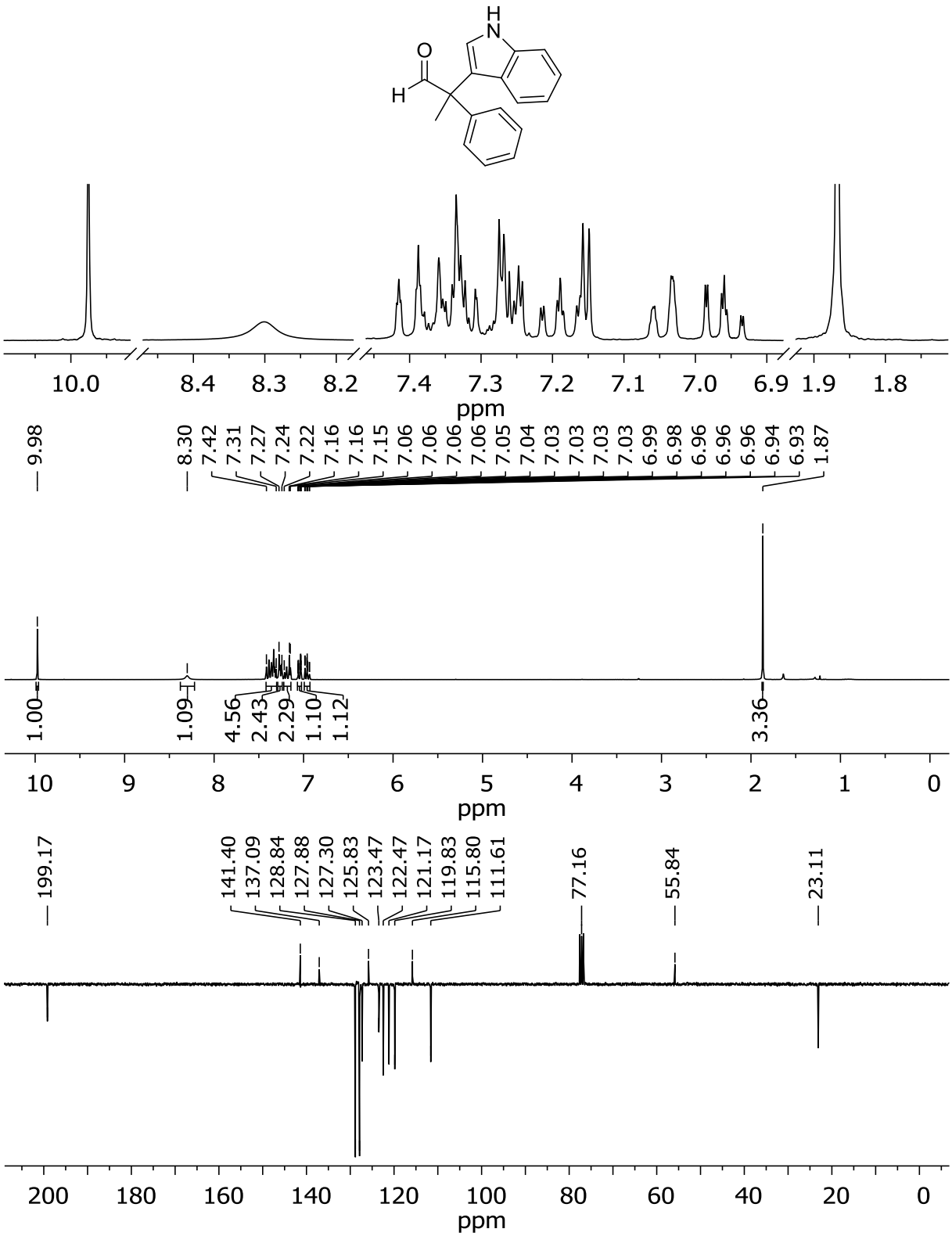
***p*-Tosyl-protected 2-indolyl aldoxime ether 11** ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



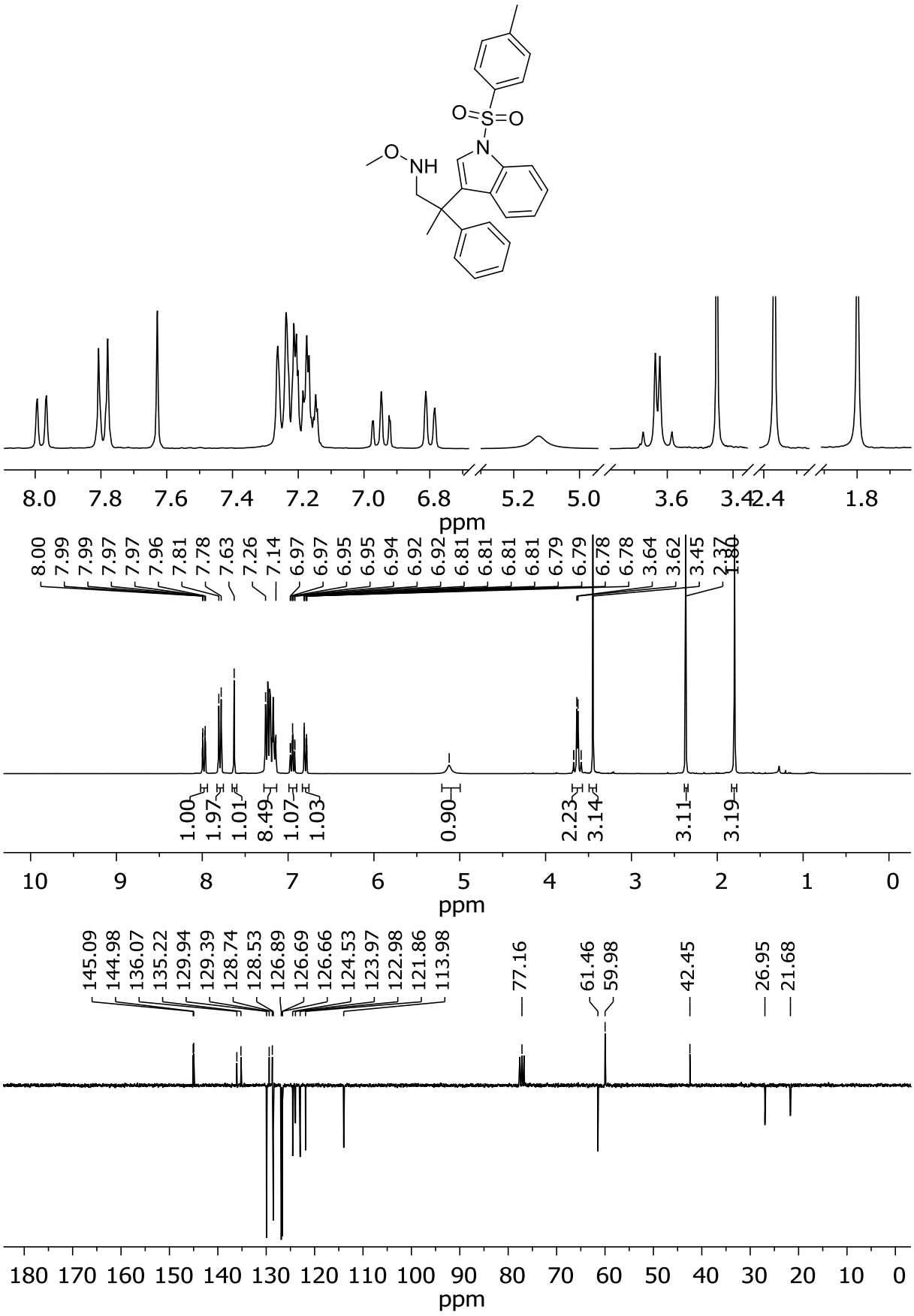
***p*-Tosyl-protected 2-indolyl aldehyde S7** ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



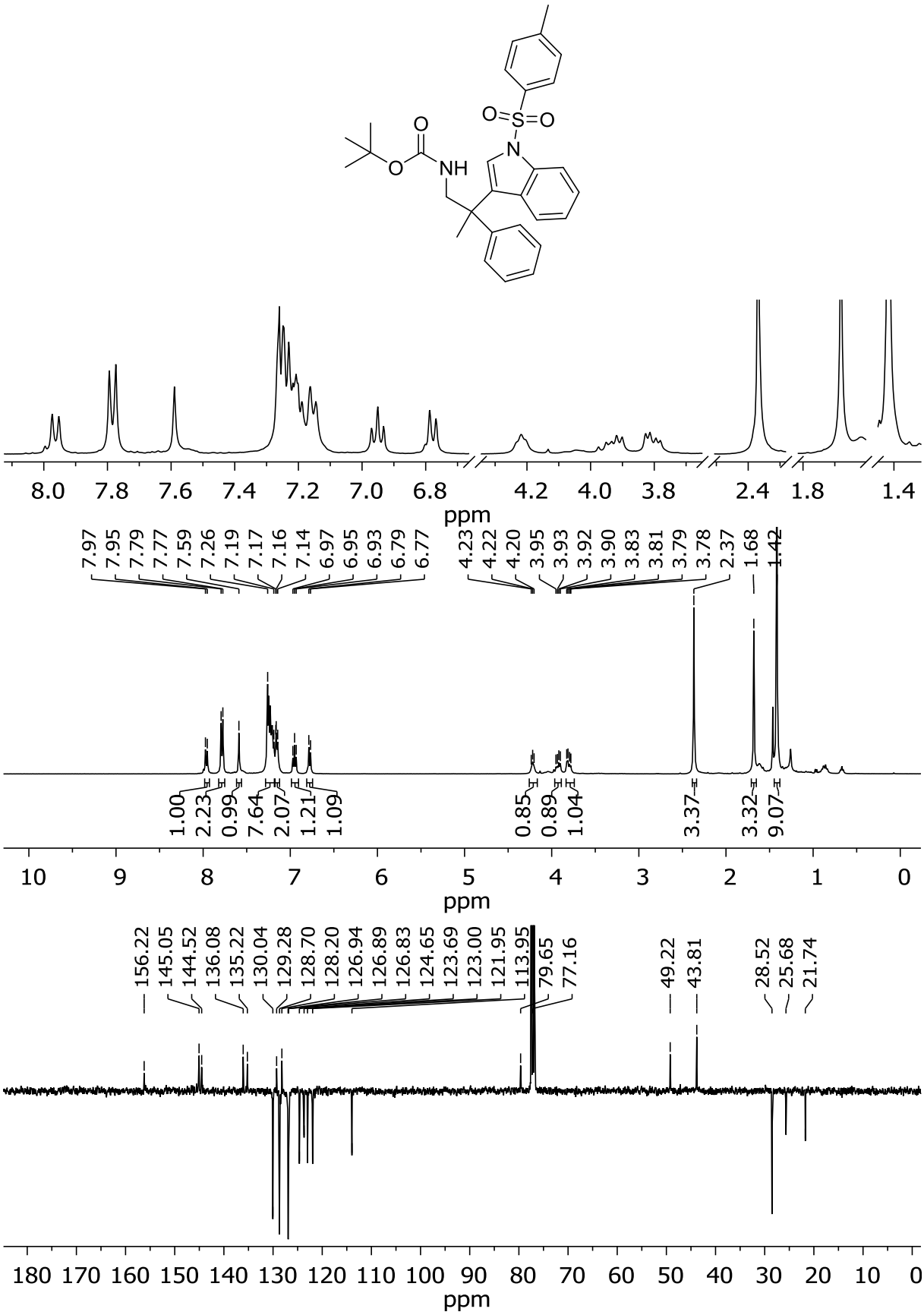
2-Indolyl aldehyde 12 ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



3-(Methoxyaminoethyl)indole 13 ($CDCl_3$; ^{1}H-NMR: 300 MHz, APT: 75 MHz)



***N*-(Indol-3-ylethyl)carbamate 14** ($CDCl_3$; ^{1}H-NMR: 400 MHz, APT: 100 MHz)



6 Reference

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