

Supporting Information

Rapid Construction of Complex 2-Pyrrolines through Lewis Acid-Catalyzed, Sequential Three-Component Reactions via *in situ*-Generated 1-Azaallyl Cations

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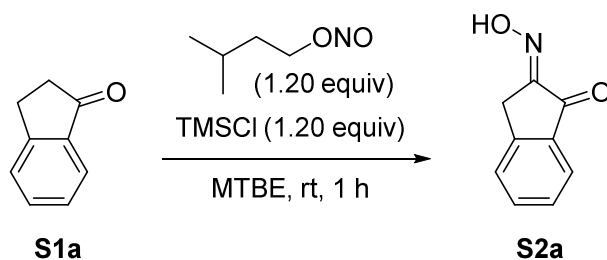
1 General Methods

Unless otherwise noted, all reactions were carried out in oven dried glassware and in dry solvents under an argon atmosphere. ^1H -, ^{13}C - and ^{19}F -NMR spectra were recorded in CDCl_3 or DMSO-d_6 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, ^1H ; 77.16 ppm, ^{13}C) or DMSO (2.50 ppm, ^1H ; 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 germinal, 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 and 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 *n*-hexane (KOH). Methanol was technical grade. Molecular Sieve (4 Å) was activated prior to use. 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/UV₂₅₄. Visualization of the spots was achieved by UV-light and treatment with a vanillin staining solution.

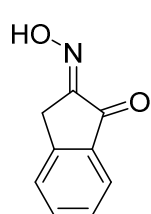
2 Starting Materials

2.1 Procedures of Indanone-Based 2-Hydroxy Oxime Ethers 1

1,2-Indandione-2-oxime **S2a**

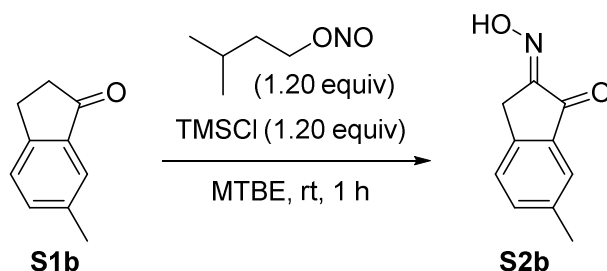


To a solution of 1-indanone **S1a** (6.61 g, 50.0 mmol, 1.00 equiv) in 50 mL MTBE, TMSCl (7.63 mL, 60.0 mmol, 1.20 equiv) was added dropwise at room temperature followed by *iso*-amyl nitrite (8.08 mL, 60.0 mmol, 1.00 eq.). Once the exothermic reaction started, it was cooled to 0 °C and then stirred at room temperature for 1 h. The resulting precipitate was filtered and washed twice with MTBE. The crude product was dried under reduced pressure. Compound **S2a** was obtained as a brown powder (6.37 g, 79%) and used without further purification for the subsequent reactions. The spectroscopic data are in agreement with literature.¹

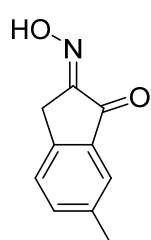


R_f: 0.11 (1.5% MeOH/CH₂Cl₂); **mp.**: 195 – 196 °C; **¹H-NMR** (400 MHz, DMSO-d₆): δ (ppm) = 12.63 (bs, 1H), 7.75 – 7.71 (m, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 3.78 (s, 2H); **¹³C-NMR** (100 MHz, DMSO-d₆): δ (ppm) = 189.3 (C=O), 154.2 (C=N), 147.1 (C_q), 137.5 (C_q), 135.8 (CH), 127.8 (CH), 127.3 (CH), 123.5 (CH), 28.3 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3184, 3143, 2922, 1725, 1655, 1609, 1468, 1324, 1297, 903, 739; **LR-MS** (ESI⁺): calcd. for C₉H₇NO₂Na ([M+Na]⁺): 184.0, found: 184.0; **M(C₉H₇NO₂)**: 161.16.

1,2-Indandione-2-oxime **S2b**

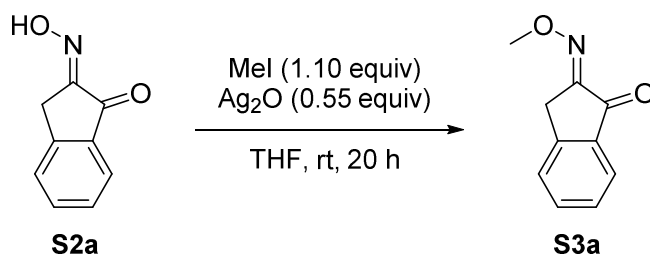


To a solution of 1-indanone **S1b** (3.65 g, 25.0 mmol, 1.00 equiv) in 25 mL MTBE, TMSCl (3.82 mL, 30.0 mmol, 1.20 equiv) was added dropwise at room temperature followed by *isoamyl*nitrite (4.04 mL, 30.0 mmol, 1.00 eq.). Once the exothermic reaction started, it was cooled to 0 °C and then stirred at room temperature for 1 h. The resulting precipitate was filtered and washed twice with MTBE. The crude product was dried under reduced pressure. Compound **S2b** was obtained as a colorless powder (3.12 g, 71%) and used without further purification for the subsequent reactions. The spectroscopic data are in agreement with literature.²

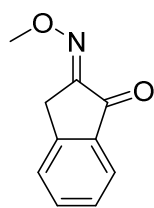


R_f: 0.12 (1.0% MeOH/CH₂Cl₂); **mp.**: 201 – 202 °C; **¹H-NMR** (400 MHz, DMSO-d₆): δ (ppm) = 12.60 (bs, 1H), 7.55 – 7.54 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 3.70 (s, 2H), 2.37 (s, 3H); **¹³C-NMR** (100 MHz, DMSO-d₆): δ (ppm) = 189.2 (C=O), 154.6 (C=N), 144.4 (C_q), 137.6 (C_q), 137.4 (C_q), 136.8 (CH), 126.9 (CH), 123.4 (CH), 27.9 (CH₂), 20.6 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3189, 2943, 2922, 2865, 1726, 1659, 1616, 1491, 1483, 1421, 1400, 1282, 1267, 1192, 1032, 943, 857, 826, 782, 769, 751, 509; **HR-MS** (ESI⁺): calcd. for C₁₀H₉NO₂Na ([M+Na]⁺): 198.0526, found: 198.0520; **M(C₁₀H₉NO₂)**: 175.19.

1,2-Indandione-2-oxime ether **S3a**

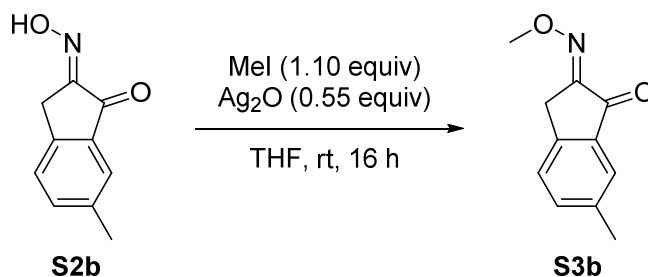


To a suspension of 1,2-indandione-2-oxime **S2a** (5.55 g, 34.4 mmol, 1.00 equiv) and Ag₂O (4.39 g, 18.9 mmol, 0.55 equiv) in 90 mL abs. THF, methyl iodide (2.36 mL, 37.9 mmol, 1.10 equiv) was added dropwise at room temperature. The reaction mixture was stirred overnight and then filtered over Celite. The filter cake was washed twice with EtOAc. The solvent of the filtrate was removed under reduced pressure and the crude product was recrystallized from EtOAc/hexane. Compound **S3a** was obtained as brown crystals (4.56 g, 76%). The mother solution was concentrated under reduced pressure and purified by flash column chromatography (5% → 15% EtOAc/hexane) to isolate 0.39 g of **S3a** (overall yield: 4.95 g, 82%) as brown crystals.

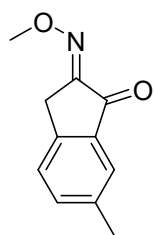


R_f: 0.39 (20% EtOAc/hexane); **mp.**: 126 – 127 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.87 (d, J = 7.5 Hz, 1H), 7.64 (td, J = 7.5, 1.0 Hz, 1H), 7.49 (dt, J = 7.5 Hz, 1.0 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 4.16 (s, 3H), 3.77 (s, 2H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 189.3 (C=O), 154.9 (C=N), 146.9 (C_q), 137.9 (C_q), 136.1 (CH), 128.2 (CH), 126.9 (CH), 124.7 (CH), 63.9 (CH₃), 28.9 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3070, 3051, 2984, 2941, 2833, 1719, 1627, 1609, 1596, 1577, 1467, 1456, 1434, 1327, 1302, 1267, 1206, 1194, 1151, 1035, 1017, 982, 886, 746, 675; **HR-MS** (ESI⁺): calcd. for C₁₀H₉NO₂Na ([M+Na]⁺): 198.0526, found: 198.0521; **M(C₁₀H₉NO₂)**: 175.19.

1,2-Indandione-2-oxime ether **S3b**

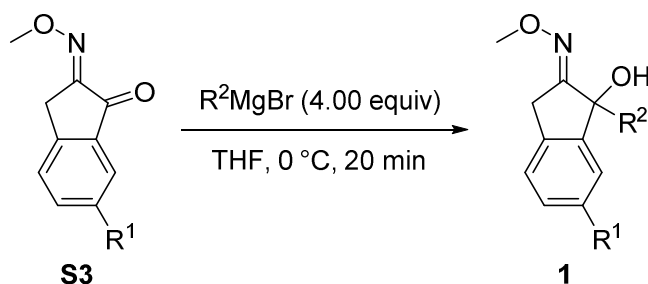


To a suspension of 6-methyl-1,2-indandione-2-oxime **S2b** (2.63 g, 15.0 mmol, 1.00 equiv) and Ag₂O (1.91 g, 8.30 mmol, 0.55 equiv) in 40 mL abs. THF, methyl iodide (1.03 mL, 16.5 mmol, 1.10 equiv) was added dropwise at room temperature. The reaction mixture was stirred overnight and then filtered over Celite. The filter cake was washed twice with EtOAc. The solvent of the filtrate was removed under reduced pressure and the crude product was recrystallized from EtOAc/hexane. Compound **S3b** was obtained as colorless crystals (1.87 g, 66%).



R_f: 0.30 (20% MTBE/hexane); **mp.**: 130 – 132 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.68 (s, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H, CH), 4.15 (s, 3H), 3.71 (s, 2H), 2.40 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 189.4 (C=O), 154.4 (C=N), 144.2 (C_q), 138.2 (C_q), 138.0 (C_q), 137.3 (CH), 126.5 (CH), 124.7 (CH), 63.8 (CH₃), 28.5 (CH₂), 21.3 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3033, 2977, 2942, 2908, 2827, 1708, 1623, 1615, 1576, 1488, 1466, 1429, 1405, 1289, 1274, 1192, 1137, 1036, 1014, 985, 901, 863, 830, 781, 772, 745, 669, 628, 514; **HR-MS** (ESI⁺): calcd. for C₁₁H₁₁NO₂Na ([M+Na]⁺): 212.0682, found: 212.0680; **M(C₁₁H₁₁NO₂)**: 189.21.

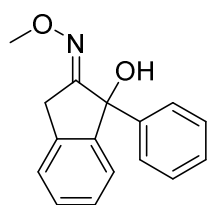
General procedure 1 for the addition of aryl-Grignards



Under an inert atmosphere, magnesium turnings (4.10 equiv) were suspended in abs. THF (0.25 M). Liquid arylbromides (4.00 equiv) were added dropwise at room temperature. Solid arylbromides (4.00 equiv) were first dissolved in minimal amounts of abs. THF before added dropwise. The formation of the Grignard reagents 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 2 hours and then cooled to 0 °C. The starting materials **S3** (1.00 equiv.) were dissolved in abs. THF (0.2 M) and added dropwise to the Grignard reagent. The reaction mixture was stirred at 0 °C for 20 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 products were purified by flash column chromatography (5% → 20% MTBE/hexane).

2-Hydroxy oxime ether **1a**

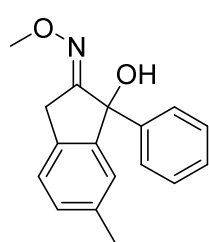
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (825 mg, 33.9 mmol, 4.10 equiv) and bromobenzene (3.49 mL, 33.1 mmol, 4.00 equiv) in 35 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (1.45 g, 8.28 mmol, 1.00 equiv) dissolved in 30 mL abs. THF. Compound **1a** was obtained as a colorless solid (1.82 g, 87%).



R_f: 0.56 (30% MTBE/hexane); **mp.**: 123 – 125 °C; **¹H-NMR** (400 MHz, CDCl_3): δ (ppm) = 7.38 – 7.22 (m, 9H), 4.03 (d, J = 22.0 Hz, 1H), 3.92 (s, 3H), 3.74 (d, J = 22.0 Hz, 1H), 2.95 (bs, 1H); **¹³C-NMR** (100 MHz, CDCl_3): δ (ppm) = 166.1 (C=N), 145.9 (C_q), 144.7 (C_q), 137.4 (C_q), 129.4 (CH), 128.3 (2x CH), 128.2 (CH), 127.5 (CH), 125.7 (2x CH), 125.2 (CH), 124.9 (CH), 82.9 (C_q), 62.4 (CH_3), 32.5 (CH_2); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3429, 3055, 2965, 2924, 2815, 1652, 1635, 1491, 1457, 1448, 1361, 1171, 1059, 1048, 862, 760, 738, 700, 646; **HR-MS** (ESI⁺): calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 276.0995, found: 276.0990; **M**($\text{C}_{16}\text{H}_{15}\text{NO}_2$): 253.30.

2-Hydroxy oxime ether 1b

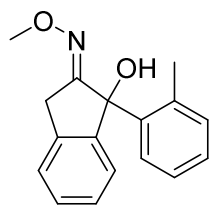
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and bromobenzene (2.11.0 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 6-methyl-1,2-indandione-2-oxime ether **S3b** (946 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1b** was obtained as a colorless solid (1.20 g, 90%).



R_f: 0.26 (20% MTBE/hexane); **mp.**: 73 – 75 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.40 – 7.22 (m, 6H), 7.16 – 7.13 (m, 1H), 7.08 (m, 1H), 3.99 (d, *J* = 22.0 Hz, 1H), 3.90 (s, 3H), 3.71 (d, *J* = 22.0 Hz, 1H), 3.03 (bs, 1H), 2.31 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.6 (C=N), 145.9 (C_q), 144.9 (C_q), 138.0 (C_q), 134.4 (C_q), 130.4 (CH), 128.3 (2x CH), 127.4 (CH), 125.6 (2x CH), 125.2 (CH), 124.9 (CH), 82.9 (C_q), 62.3 (CH₃), 32.2 (CH₂), 21.5 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3464, 3084, 3061, 3023, 3002, 2940, 2899, 2857, 2818, 1749, 1660, 1601, 1492, 1447, 1413, 1360, 1315, 1277, 1186, 1174, 1155, 1142, 1110, 1029, 983, 921, 910, 887, 874, 850, 814, 767, 736, 724, 694, 672, 650, 614, 562, 490, 457, 426; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₇NO₂Na ([M+Na]⁺): 290.1152, found: 290.1150; **M(C₁₇H₁₇NO₂)**: 267.33.

2-Hydroxy oxime ether 1c

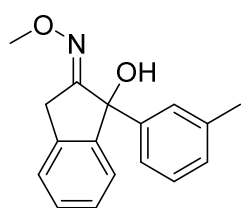
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 2-bromotoluene (2.41.0 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1c** was obtained as a colorless solid (1.20 g, 90%).



R_f: 0.45 (30% MTBE/hexane); **mp.**: 105 – 106 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 8.07 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.25 – 7.19 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.0 Hz, 1H), 4.03 (d, *J* = 22.0 Hz, 1H), 3.93 (d, *J* = 22.0 Hz, 1H), 3.87 (s, 3H), 2.59 – 2.56 (m, 1H), 1.73 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 165.7 (C=N), 145.0 (C_q), 141.7 (C_q), 138.3 (C_q), 135.2 (C_q), 131.6 (CH), 129.5 (CH), 128.1 (CH), 127.9 (CH), 125.7 (CH), 125.6 (CH), 125.2 (CH), 124.5 (CH), 82.6 (C_q), 62.4 (CH₃), 32.7 (CH₂), 20.6 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3434, 3066, 3029, 2938, 2899, 1653, 1605, 1485, 1478, 1459, 1413, 1176, 1163, 1022, 917, 871, 853, 773, 761, 742, 727, 642; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₇NO₂Na ([M+Na]⁺): 290.1152, found: 290.1148; **M(C₁₇H₁₇NO₂)**: 267.33.

2-Hydroxy oxime ether 1d

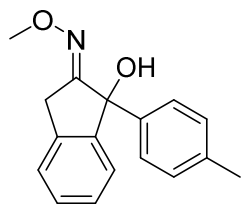
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 3-bromotoluene (2.43 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1d** was obtained as a colorless solid (1.29 g, 96%).



R_f: 0.32 (20% MTBE/hexane); **mp.**: 60 – 62 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.33 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.20 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.09 (m, 1H), 7.03 (m, 1H), 4.00 (d, *J* = 22.0 Hz, 1H), 3.89 (s, 3H), 3.72 (d, *J* = 22.0 Hz, 1H), 2.96 (bs, 1H), 2.30 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 166.2 (C=N), 146.0 (C_q), 144.6 (C_q), 138.0 (C_q), 137.4 (C_q), 129.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 126.2 (CH), 125.2 (CH), 124.9 (CH), 122.8 (CH), 82.9 (C_q), 62.4 (CH₃), 32.6 (CH₂), 21.7 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3420, 3030, 2964, 2923, 2886, 2815, 1653, 1605, 1587, 1480, 1457, 1441, 1427, 1352, 1237, 1156, 1147, 1062, 1047, 862, 781, 761, 739, 722, 700; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₇NO₂Na ([M+Na]⁺): 290.1152, found: 290.1147; **M(C₁₇H₁₇NO₂)**: 267.33.

2-Hydroxy oxime ether 1e

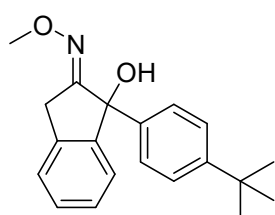
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 4-bromotoluene (3.42 g, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1e** was obtained as a colorless solid (1.08 g, 81%).



R_f: 0.19 (MTBE/hexane); **mp.**: 86 – 88 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.34 – 7.24 (m, 6H), 7.12 (d', *J* = 8.0 Hz, 2H), 4.02 (d, *J* = 22.0 Hz, 1H), 3.91 (s, 3H), 3.73 (d, *J* = 22.0 Hz, 1H), 2.90 (bs, 1H), 2.32 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 166.2 (C=N), 146.0 (C_q), 141.8 (C_q), 137.4 (C_q), 137.2 (C_q), 129.3 (CH), 129.0 (2x CH), 128.1 (CH), 125.6 (2x CH), 125.2 (CH), 124.9 (CH), 82.8 (C_q), 62.4 (CH₃), 32.5 (CH₂), 21.2 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3443, 3071, 3027, 2983, 2944, 2919, 2904, 2890, 2823, 1654, 1606, 1513, 1478, 1459, 1432, 1414, 1382, 1214, 1196, 1179, 1166, 1057, 1039, 1024, 914, 853, 838, 811, 766, 742, 726, 653, 622, 584, 537, 510, 485, 453; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₇NO₂Na ([M+Na]⁺): 290.1152, found: 290.1148. **M(C₁₇H₁₇NO₂)**: 267.33.

2-Hydroxy oxime ether 1f

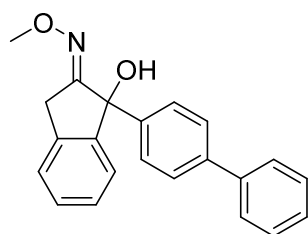
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-4-(*tert*-butyl)benzene (3.47 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1f** was obtained as a colorless solid (1.08 g, 70%).



R_f: 0.36 (20% MTBE/hexane); **mp.**: 125 – 127 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.36 – 7.26 (m, 8H), 4.03 (d, J = 22.0 Hz, 1H), 3.92 (s, 3H), 3.72 (d, J = 22.0 Hz, 1H), 3.17 (bs, 1H), 1.31 (s, 9H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.2 (C=N), 150.3 (C_q), 145.9 (C_q), 141.7 (C_q), 137.3 (C_q), 129.3 (CH), 128.0 (CH), 125.2 (2x CH), 125.1 (2x CH), 125.0 (CH), 124.8 (CH), 82.8 (C_q), 62.3 (CH₃), 34.6 (C_q), 32.5 (CH₂), 31.4 (3x CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3416, 3036, 2963, 2904, 2865, 1654, 1607, 1509, 1476, 1459, 1409, 1360, 1267, 1180, 1052, 1030, 916, 859, 827, 765, 728, 654, 559; **HR-MS** (ESI⁺): calcd. for C₂₀H₂₃NO₂Na ([M+Na]⁺): 332.1621, found: 332.1622; **M(C₂₀H₂₃NO₂)**: 309.41.

2-Hydroxy oxime ether 1g

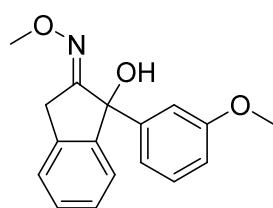
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-4-phenylbenzene (4.66 g, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1g** was obtained as a colorless solid (1.37 g, 83%).



R_f: 0.26 (20% MTBE/hexane), **mp.**: 119 – 121 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.59 – 7.54 (m, 4H), 7.46 – 7.41 (m, 4H), 7.37 – 7.31 (m, 5H), 4.06 (d, J = 22.0 Hz, 1H), 3.94 (s, 3H), 3.79 (d, J = 22.0 Hz, 1H), 3.11 (bs, 1H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 166.1 (C=N), 145.8 (C_q), 143.7 (C_q), 140.9 (C_q), 140.4 (C_q), 137.4 (C_q), 129.5 (CH), 128.9 (2x CH), 128.2 (CH), 127.4 (CH), 127.2 (2x CH), 127.1 (2x CH), 126.1 (2x CH), 125.3 (CH), 125.0 (CH), 82.8 (C_q), 62.4 (CH₃), 32.6 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3434, 3028, 2938, 2898, 1599, 1486, 1460, 1412, 1182, 1041, 1019, 1007, 918, 866, 855, 834, 769, 756, 739, 726, 698; **HR-MS** (ESI⁺): calcd. for C₂₂H₁₉NO₂Na ([M+Na]⁺): 352.1308, found: 352.1307; **M(C₂₂H₁₉NO₂)**: 329.40.

2-Hydroxy oxime ether 1h

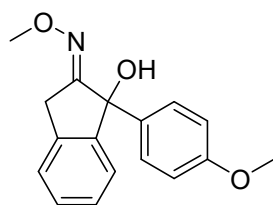
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-3-methoxybenzene (2.53 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1h** was obtained as a colorless solid (1.35 g, 95%).



R_f: 0.34 (30% MTBE/hexane); **mp.**: 100 – 102 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.34 – 7.26 (m, 4H), 7.21 (t, J = 8.0 Hz, 1H), 7.03 – 7.02 (m, 1H), 6.88 – 6.84 (m, 1H), 6.80 – 6.77 (m, 1H), 4.01 (d, J = 22.0 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 3.74 (d, J = 22.0 Hz, 1H), 3.16 – 3.15 (m, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.0 (C=N), 159.6 (C_q), 146.4 (C_q), 145.8 (C_q), 137.4 (C_q), 129.4 (CH), 129.3 (CH), 128.1 (CH), 125.2 (CH), 124.9 (CH), 118.2 (CH), 112.7 (CH), 111.7 (CH), 82.8 (C_q), 62.4 (CH₃), 55.4 (CH₃), 32.5 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3442, 2993, 2972, 2936, 2901, 2837, 2822, 1650, 1605, 1585, 1483, 1459, 1438, 1403, 1369, 1286, 1251, 1167, 1155, 1136, 1052, 1043, 1027, 950, 894, 852, 808, 780, 768, 742, 727, 699, 613, 585; **HR-MS** (ESI⁺): calc. for C₁₇H₁₇NO₃Na ([M+Na]⁺): 306.1101, found: 306.1096; **M(C₁₇H₁₇NO₃)**: 283.33.

2-Hydroxy oxime ether 1i

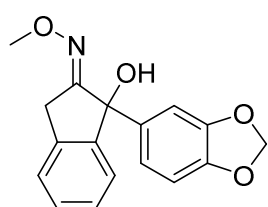
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-4-methoxybenzene (2.50 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1i** was obtained as a colorless solid (1.30 g, 91%).



R_f: 0.42 (40% MTBE/hexane); **mp.**: 99 – 101 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.31 – 7.26 (m, 6H), 6.83 (d', J = 9.0 Hz, 2H), 4.00 (d, J = 22.0 Hz, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 3.71 (d, J = 22.0 Hz, 1H), 3.04 (bs, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.2 (C=N), 159.0 (C_q), 146.0 (C_q), 137.3 (C_q), 136.9 (C_q), 129.3 (CH), 128.1 (CH), 127.0 (2x CH), 125.2 (CH), 124.9 (CH), 113.7 (2x CH), 82.6 (C_q), 62.3 (CH₃), 55.4 (CH₃), 32.4 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3442, 3068, 3011, 2948, 2839, 1608, 1582, 1509, 1477, 1461, 1419, 1295, 1252, 1175, 1059, 1034, 1024, 914, 852, 835, 807, 771, 745, 654, 591; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₇NO₃Na ([M+Na]⁺): 306.1101, found: 306.1098; **M(C₁₇H₁₇NO₃)**: 283.33.

2-Hydroxy oxime ether 1j

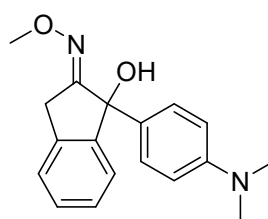
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-3,4-(methylenedioxy)benzene (2.42 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1j** was obtained as a colorless solid (1.42 g, 95%).



R_f: 0.35 (30% MTBE/hexane); **mp.**: 115 – 117 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.34 – 7.28 (m, 4H), 6.91 (d, J = 2.0 Hz, 1H), 6.79 (dd, J = 8.0, 2.0 Hz, 1H), 6.72 (dd, J = 8.0 Hz, 1H), 5.93 (d, J = 1.5 Hz, 1H), 5.92 (d, J = 1.5 Hz, 1H), 4.00 (d, J = 22.0 Hz, 1H), 3.92 (s, 3H), 3.71 (d, J = 22.0 Hz, 1H), 2.99 (bs, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.0 (C=N), 147.8 (C_q), 147.0 (C_q), 145.8 (C_q), 138.8 (C_q), 137.3 (C_q), 129.4 (CH), 128.1 (CH), 125.2 (CH), 124.8 (CH), 119.1 (CH), 107.9 (CH), 106.8 (CH), 101.2 (CH₂), 82.7 (C_q), 62.4 (CH₃), 32.4 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3406, 3010, 2946, 2884, 1654, 1614, 1504, 1489, 1436, 1410, 1241, 1063, 1039, 1027, 933, 857, 844, 821, 811, 770, 745, 658; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₅NO₄Na ([M+Na]⁺): 320.0893, found: 320.0888; **M**(C₁₇H₁₅NO₄): 297.31.

2-Hydroxy oxime ether 1k

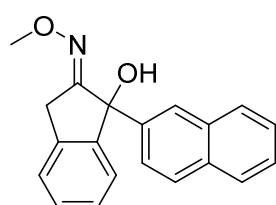
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 4-bromo-*N,N*-dimethylaniline (4.00 g, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1k** was obtained as a green solid (1.25 g, 85%).



R_f: 0.30 (40% MTBE/hexane); **mp.**: 99 – 101 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.36 – 7.23 (m, 6H), 6.67 (d', J = 8.5 Hz, 2H), 3.99 (d, J = 22.0 Hz, 1H), 3.93 (s, 3H), 3.68 (d, J = 22.0 Hz, 1H), 3.12 (bs, 1H), 2.92 (s, 6H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 166.3 (C=N), 149.9 (C_q), 146.1 (C_q), 137.3 (C_q), 132.4 (C_q), 129.1 (CH), 127.9 (CH), 126.6 (2x CH), 125.1 (CH), 124.9 (CH), 112.3 (2x CH), 82.7 (C_q), 62.2 (CH₃), 40.6 (2x CH₃), 32.3 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3463, 3069, 3001, 2984, 2941, 2894, 2803, 1613, 1590, 1522, 1479, 1459, 1444, 1375, 1351, 1213, 1182, 1167, 1128, 1051, 1023, 914, 850, 813, 769, 740, 651; **HR-MS** (ESI⁺): calcd. for C₁₈H₂₀N₂O₂Na ([M+Na]⁺): 319.1417, found: 319.1419; **M**(C₁₈H₂₀N₂O₂): 296.37.

2-Hydroxy oxime ether 1l

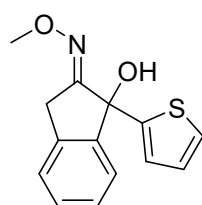
According to the [general procedure 1](#), the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 2-bromonaphthalene (4.14 g, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1l** was obtained as a colorless solid (1.36 g, 90%).



R_f: 0.27 (20% MTBE/hexane); **mp.**: 108 – 110 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.96 (m, 1H), 7.85 – 7.76 (m, 3H), 7.51 – 7.45 (m, 2H), 7.40 – 7.28 (m, 5H), 4.08 (d, J = 22.0 Hz, 1H), 3.91 (s, 3H), 3.85 (d, J = 22.0 Hz, 1H), 3.35 – 3.32 (m, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.1 (C=N), 145.8 (C_q), 142.0 (C_q), 137.5 (C_q), 133.1 (C_q), 132.7 (C_q), 129.5 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.6 (CH), 126.2 (CH), 126.1 (CH), 125.2 (CH), 125.1 (CH), 124.3 (CH), 123.9 (CH), 83.0 (C_q), 62.4 (CH₃), 32.6 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3455, 3045, 3024, 2977, 2940, 2899, 2820, 1654, 1634, 1600, 1508, 1479, 1460, 1433, 1411, 1375, 1249, 1166, 1123, 1048, 959, 924, 899, 863, 854, 835, 812, 765, 750, 739, 726, 669, 625, 570, 492, 475, 434; **HR-MS** (ESI⁺): calcd. for C₂₀H₁₇NO₂Na ([M+Na]⁺): 326.1152, found: 326.1150; **M(C₂₀H₁₇NO₂)**: 303.36.

2-Hydroxy oxime ether 1m

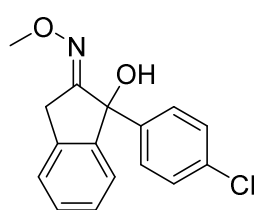
According to the [general procedure 1](#), the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 2-bromothiophene (1.92 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1m** was obtained as a colorless solid (1.26 g, 97%).



R_f: 0.45 (30% MTBE/hexane); **mp.**: 114 – 116 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.55 – 7.51 (m, 1H), 7.36 – 7.31 (m, 3H), 7.26 (dd, J = 5.0, 1.5 Hz, 1H), 6.90 (dd, J = 5.0, 3.5 Hz, 1H), 6.81 (dd, J = 3.5, 1.5 Hz, 1H), 3.99 (d, J = 22.0 Hz, 1H), 3.97 (s, 3H), 3.71 (d, J = 22.0 Hz, 1H), 3.25 (bs, 1H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 164.7 (C=N), 148.9 (C_q), 145.0 (C_q), 137.0 (C_q), 129.7 (CH), 128.0 (CH), 126.7 (CH), 125.9 (CH), 125.2 (CH), 125.0 (CH), 124.7 (CH), 80.9 (C_q), 62.5 (CH₃), 31.9 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3424, 3108, 3042, 2973, 2934, 2898, 2819, 1654, 1436, 1479, 1459, 1436, 1398, 1374, 1235, 1168, 1153, 1133, 1039, 1025, 858, 845, 829, 772, 748, 707, 651; **HR-MS** (ESI⁺): calcd. for C₁₄H₁₃NO₂SNa ([M+Na]⁺): 282.0559, found: 282.0555; **M(C₁₄H₁₃NO₂S)**: 259.32.

2-Hydroxy oxime ether 1n

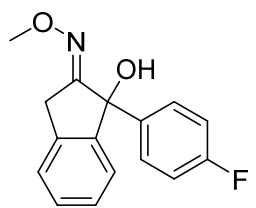
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-4-chlorobenzene (3.83 g, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1n** was obtained as a colorless solid (1.35 g, 94%).



R_f: 0.24 (20% MTBE/hexane); **mp.**: 108 – 110 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.36 – 7.21 (m, 8H), 4.01 (d, J = 22.0 Hz, 1H), 3.90 (s, 3H), 3.74 (d, J = 22.0 Hz, 1H), 3.10 (bs, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 165.8 (C=N), 145.5 (C_q), 143.2 (C_q), 137.4 (C_q), 133.4 (C_q), 129.7 (CH), 128.4 (2x CH), 128.3 (CH), 127.2 (2x CH), 125.3 (CH), 124.8 (CH), 82.5 (C_q), 62.4 (CH₃), 32.5 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3421, 3006, 2984, 2941, 2902, 2822, 1654, 1605, 1597, 1490, 1479, 1459, 1410, 1193, 1175, 1088, 1051, 1024, 915, 856, 831, 820, 766, 752, 727, 720, 647, 611, 507, 482, 444; **HR-MS** (ESI⁺): calcd. for C₁₆H₁₄³⁵ClNO₂Na ([M+Na]⁺): 310.0605, found: 310.0607; **M(C₁₆H₁₄ClNO₂)**: 287.74.

2-Hydroxy oxime ether 1o

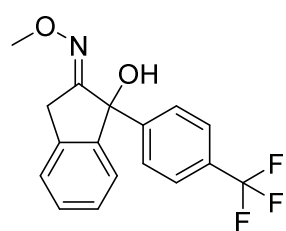
According to the general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-4-fluorobenzene (2.18 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1o** was obtained as a colorless solid (1.30 g, 96%).



R_f: 0.26 (20% MTBE/hexane); **mp.**: 99 – 101 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.37 – 7.24 (m, 6H, 6x CH), 7.02 – 6.94 (m, 2H), 4.01 (d, J = 22.0 Hz, 1H), 3.91 (s, 3H), 3.73 (d, J = 22.0 Hz, 1H), 3.01 (bs, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 165.9 (C=N), 162.2 (d, J = 246.0 Hz, C_q), 145.7 (C_q), 140.4 (d, J = 3.0 Hz, C_q), 137.4 (C_q), 129.6 (CH), 128.2 (CH), 127.6 (CH), 127.5 (CH), 125.0 (d, J = 34.0 Hz, 2x CH), 115.1 (d, J = 21.5 Hz, 2x CH), 82.5 (C_q), 62.4 (CH₃), 32.4 (CH₂); **¹⁹F-NMR** (375 MHz, CDCl₃): δ (ppm) = -115.5; **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3422, 3009, 2987, 2944, 2904, 2824, 1654, 1603, 1508, 1477, 1459, 1416, 1218, 1189, 1159, 1052, 1023, 917, 856, 831, 809, 768, 747, 725, 652, 583; **HR-MS** (ESI⁺): calcd. for C₁₆H₁₄FNO₂Na ([M+Na]⁺): 294.0901, found: 294.0897; **M(C₁₆H₁₄FNO₂)**: 271.29.

2-Hydroxy oxime ether 1p

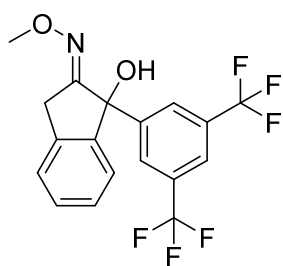
According to the [general procedure 1](#), the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and 1-bromo-4-(trifluoromethyl)-benzene (2.80 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. Compound **1p** was obtained as a colorless solid (1.60 g, >99%).



R_f: 0.33 (20% MTBE/hexane); **mp.**: 57 – 59 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.57 (d', *J* = 8.5 Hz, 2H), 7.48 (d', *J* = 8.5 Hz, 2H), 7.37 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 7.23 – 7.21 (m, 1H), 4.03 (d, *J* = 22.0 Hz, 1H), 3.90 (s, 3H), 3.78 (d, *J* = 22.0 Hz, 1H), 3.12 (bs, 1H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 165.6 (C=N), 148.6 (C_q), 145.3 (C_q), 137.5 (C_q), 129.8 (CH), 129.7 (q, *J* = 32.5 Hz, C_q), 128.4 (CH), 126.1 (2x CH), 125.4 (CH), 125.3 (q, *J* = 4.0 Hz, 2x CH), 124.9 (CH), 124.3 (q, *J* = 272.0 Hz, C_q), 82.7 (C_q), 62.5 (CH₃), 32.6 (CH₂); **¹⁹F-NMR** (375 MHz, CDCl₃): δ (ppm) = –62.5. **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3427, 3074, 2968, 2939, 2901, 2820, 1731, 715, 1659, 1617, 1480, 1462, 1412, 1325, 1196, 1165, 1126, 1068, 1040, 1017, 918, 872, 835, 767, 751, 733, 724, 650, 601, 438; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₄F₃NO₂Na ([M+Na]⁺): 344.0869, found: 344.0865; **M(C₁₇H₁₄F₃NO₂)**: 321.30.

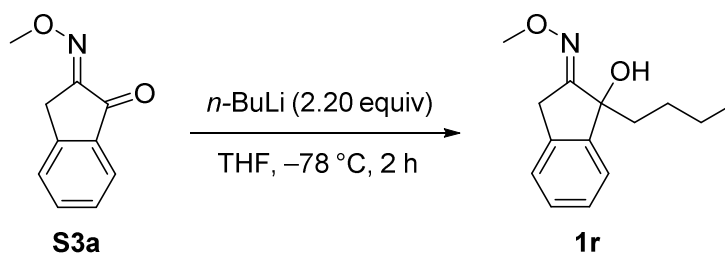
2-Hydroxy oxime ether 1q

According to the [general procedure 1](#), the Grignard reagent was synthesized from magnesium turnings (299 mg, 12.3 mmol, 4.10 equiv) and 1-bromo-3,5-bis(trifluoromethyl)-benzene (2.10 mL, 12.0 mmol, 4.00 equiv) in 15 mL abs. THF, and then treated with 1,2-indandione-2-oxime ether **S3a** (526 mg, 3.00 mmol, 1.00 equiv) dissolved in 20 mL abs. THF. Compound **1q** was obtained as a colorless solid (1.08 g, 93%).

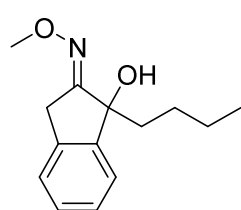


R_f: 0.16 (10% MTBE/hexane); **mp.**: 96 – 97 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.82 (s, 2H), 7.78 (s, 1H), 7.41 – 7.40 (m, 2H), 7.35 – 7.30 (m, 1H, CH), 7.20 (d, *J* = 7.5 Hz, 1H), 4.04 (d, *J* = 22.0 Hz, 1H), 3.92 (s, 3H), 3.83 (d, *J* = 22.0 Hz, 1H), 2.97 (bs, 1H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 164.8 (C=N), 147.2 (C_q), 144.5 (C_q), 137.7 (C_q), 131.6 (q, *J* = 33.0 Hz, C_q), 130.4 (CH), 128.7 (CH), 126.2 (2x CH), 125.7 (CH), 124.8 (CH), 123.4 (q, *J* = 273.0 Hz, C_q), 121.6 (m, CH), 82.3 (C_q), 62.7 (CH₃), 32.5 (CH₂); **¹⁹F-NMR** (375 MHz, CDCl₃): δ (ppm) = –62.7. **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3448, 2980, 2943, 1624, 1464, 1356, 1281, 1184, 1169, 1124, 1022, 859, 768, 682; **HR-MS** (ESI⁺): calcd. for C₁₈H₁₃F₆NO₂Na ([M+Na]⁺): 412.0743, found: 412.0731. **M(C₁₈H₁₃F₆NO₂)**: 389.30.

2-Hydroxy oxime ether 1r

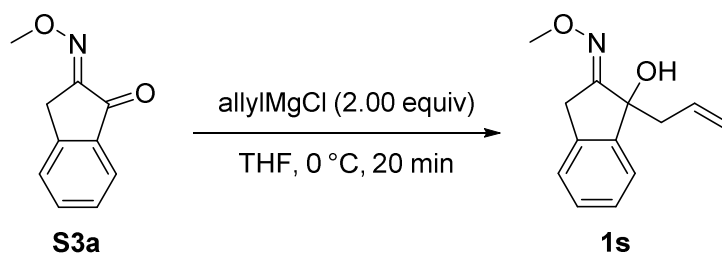


A solution of 1,2-indanedione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) in 25 mL abs. THF was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *n*-butyllithium* (4.40 mL, 2.5 M in *n*-hexane, 11.0 mmol, 2.20 equiv) dropwise. After complete addition, the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2 hours and then 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 (DCM \rightarrow 5% \rightarrow 15% MTBE/hexane). Compound **1r** was obtained as a colorless oil (368 mg, 32%, 47% based on recovered starting material).



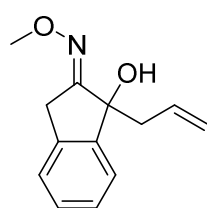
R_f: 0.33 (30% MTBE/hexane); **¹H-NMR** (400 MHz, CDCl_3): δ (ppm) = 7.44 – 7.40 (m, 1H), 7.33 – 7.25 (m, 3H), 3.96 (s, 3H), 3.87 (d, $J = 22.0\text{ Hz}$, 1H), 3.55 (d, $J = 22.0\text{ Hz}$, 1H), 2.49 (bs, 1H), 2.07 (ddd, $J = 13.0, 11.5, 4.5\text{ Hz}$, 1H), 1.98 (ddd, $J = 13.0, 11.5, 4.5\text{ Hz}$, 1H), 1.29 – 1.12 (m, 3H), 1.04 – 0.93 (m, 1H), 0.82 (t, $J = 7.0\text{ Hz}$, 3H); **¹³C-NMR** (100 MHz, CDCl_3): δ (ppm) = 165.2 (C=N), 144.9 (C_q), 137.5 (C_q), 129.2 (CH), 127.8 (CH), 125.1 (CH), 123.7 (CH), 81.8 (C_q), 62.3 (CH_3), 41.9 (CH_2), 32.5 (CH_2), 26.3 (CH_2), 23.0 (CH_2), 14.0 (CH_3); **IR** (film): $\tilde{\nu}$ (cm^{-1}) = 3432, 3028, 2955, 2935, 2903, 2871, 2859, 1608, 1479, 1462, 1409, 1047, 1028, 955, 893, 850, 770, 744, 729, 627; **HR-MS** (ESI⁺): calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 256.1308, found: 256.1305; **M**($\text{C}_{14}\text{H}_{19}\text{NO}_2$): 233.31.

2-Hydroxy oxime ether 1s



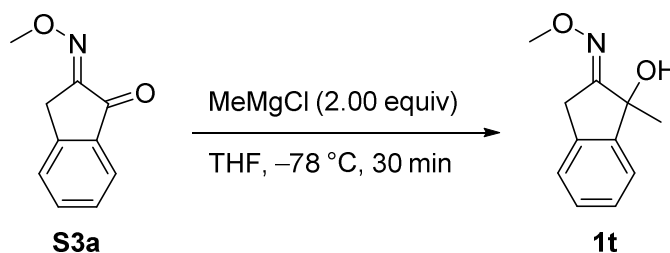
* Commercially available as well as self-made solutions of *n*-BuMgBr in THF were tried for this reaction but failed due to inseparable byproduct formation.

A solution of 1,2-indanedione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) in 25 mL abs. THF was cooled to 0 °C and treated with allylmagnesium chloride (5.88 mL, 1.7 M in THF, 10.0 mmol, 2.00 equiv) dropwise. After complete addition, the reaction mixture was stirred at 0 °C for 20 min and then quenched with sat. NH₄Cl-solution. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 15% MTBE/hexane). Compound **1s** was obtained as a colorless solid (490 mg, 45%).

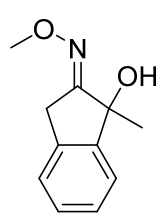


R_f: 0.19 (20% MTBE/hexane); **mp.**: 33 – 34 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.48 – 7.44 (m, 1H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 5.67 (dddd, *J* = 17.0, 10.0, 8.0, 7.0 Hz, 1H), 5.11 – 5.05 (m, 2H), 3.99 (s, 3H), 3.89 (d, *J* = 22.0 Hz, 1H), 3.54 (d, *J* = 22.0 Hz, 1H), 2.80 – 2.77 (m, 2H), 2.70 (bs, 1H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 164.7 (C=N), 144.4 (C_q), 137.4 (C_q), 132.1 (CH), 129.3 (CH), 127.7 (CH), 125.1 (CH), 124.0 (CH), 119.7 (CH₂), 80.8 (C_q), 62.3 (CH₃), 46.4 (CH₂), 32.3 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3425, 3071, 2978, 2939, 2819, 1641, 1607, 1481, 1463, 1434, 1410, 1375, 1049, 1023, 994, 927, 877, 834, 775, 746, 730, 686; **HR-MS** (ESI⁺): calcd. for C₁₃H₁₅NO₂Na ([M+Na]⁺): 240.0995, found: 240.0993; **M(C₁₃H₁₅NO₂)**: 217.27.

2-Hydroxy oxime ether **1t**

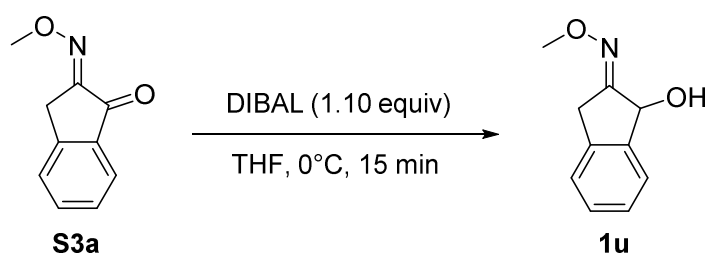


A solution of 1,2-indanedione-2-oxime ether **S3a** (876 mg, 5.00 mmol, 1.00 equiv) in 25 mL abs. THF was cooled to –78 °C and treated with methylmagnesium chloride (3.33 mL, 3.0 M in THF, 10.0 mmol, 2.00 equiv) dropwise. After complete addition, the reaction mixture was stirred at –78 °C for 30 min and then quenched with sat. NH₄Cl-solution. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 15% MTBE/hexane). Compound **1t** was obtained as a brown oil (405 mg, 42%).

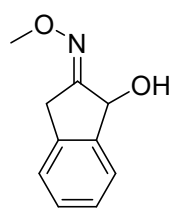


R_f: 0.41 (40% MTBE/hexane); **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.48 – 7.44 (m, 1H), 7.34 – 7.24 (m, 3H), 3.95 (s, 3H), 3.86 (d, *J* = 22.0 Hz, 1H), 3.64 (d, *J* = 22.0 Hz, 1H), 2.56 (bs, 1H), 1.70 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 165.6 (C=N), 146.0 (C_q), 136.9 (C_q), 129.3 (CH), 127.9 (CH), 125.2 (CH), 123.4 (CH), 78.8 (C_q), 62.2 (CH₃), 31.8 (CH₂), 28.3 (CH₃); **IR** (film): $\tilde{\nu}$ (cm⁻¹) = 3419, 2972, 2937, 2898, 2817, 1660, 1609, 1480, 1463, 1366, 1147, 1105, 1081, 1041, 930, 896, 843, 764, 743, 727, 628, 442; **HR-MS** (ESI⁺): calcd. for C₁₁H₁₃NO₂Na ([M+Na]⁺): 214.0839, found: 214.0836; **M(C₁₁H₁₃NO₂)**: 191.23.

2-Hydroxy oxime ether 1u



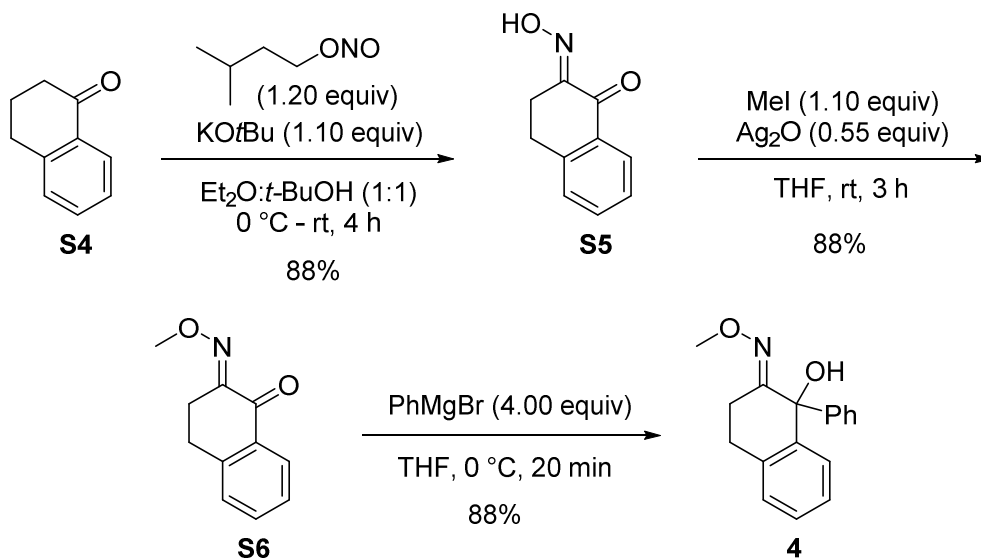
A solution of 1,2-indanedione-2-oxime ether **S3a** (526 mg, 3.00 mmol, 1.00 equiv) in 10 mL abs. THF was cooled to 0 °C and treated with DIBAL (2.75 mL, 1.2 M in toluene, 3.30 mmol, 1.10 equiv) dropwise. After complete addition, the reaction mixture was stirred at 0 °C for 15 min and then quenched with 0.1 M HCl-solution. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (30% → 40% MTBE/hexane). Compound **1u** was obtained as a colorless solid (461 mg, 87%).



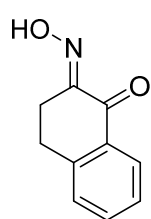
R_f: 0.46 (50% MTBE/hexane); **mp.**: 98 – 100 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.53 – 7.50 (m, 1H), 7.36 – 7.28 (m, 3H), 5.59 (m, 1H), 3.97 (s, 3H), 3.87 (d, *J* = 22.0 Hz, 1H), 3.64 (d, *J* = 22.0 Hz, 1H), 2.98 – 2.96 (m, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 163.2 (C=N), 141.5 (C_q), 138.3 (C_q), 129.6 (CH), 127.8 (CH), 125.5 (CH), 125.3 (CH), 73.9 (CH), 62.3 (CH₃), 32.3 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3316, 3040, 2996, 2961, 2937, 2899, 2821, 1667, 1588, 1482, 1463, 1406, 1281, 1236, 1167, 1043, 1023, 909, 858, 747, 727, 612; **HR-MS** (ESI⁺): calcd. for C₁₀H₁₁NO₂Na ([M+Na]⁺): 200.0682, found: 200.0680; **M(C₁₀H₁₁NO₂)**: 177.20.

2.2 Procedures of other 2-Hydroxy Oxime Ethers

2-Hydroxy oxime ether 4



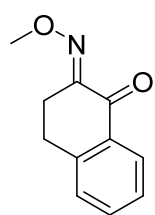
According to a modified procedure by Velasco *et al.*,³ a solution of potassium *tert*-butanolate (4.94 g, 44.0 mmol, 1.10 equiv) and *iso*-amyl nitrite (6.46 mL, 48.0 mmol, 1.20 equiv) in 100 mL of a 1:1-mixture of Et₂O and *tert*-butanol was treated with α -tetralone **S4** (5.32 mL, 40.0 mmol, 1.00 equiv) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 4 hours. The resulting precipitate was filtered and washed twice with MTBE. The filter cake was treated with 50 mL 1 N HCl-solution and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. Compound **S5** was obtained as a brown, crystalline solid (6.15 g, 88%) and used without further purification for the subsequent reactions.



R_f: 0.15 (1.0% MeOH/CH₂Cl₂); **mp.**: 119 – 121 °C; **¹H-NMR** (400 MHz, DMSO-d₆): δ (ppm) = 12.54 (bs, 1H), 7.93 – 7.90 (m, 1H), 7.59 (td, J = 7.0, 1.5 Hz, 1H), 7.43 – 7.38 (m, 2H), 3.01 (m, 4H); **¹³C-NMR** (100 MHz, DMSO-d₆): δ (ppm) = 182.6 (C=O), 152.8 (C=N), 143.5 (C_q), 133.8 (CH), 133.5 (C_q), 128.8 (CH), 127.2 (CH), 127.0 (CH), 26.1 (CH₂), 23.1 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3202, 2955, 2909, 1698, 1614, 1599, 1455, 1437, 1426, 1411, 1308, 1300, 1259, 1233, 1050, 1030, 1019, 907, 804, 735, 706, 658; **HR-MS** (ESI⁺): calcd. for C₁₀H₉NO₂Na ([M+Na]⁺): 198.0526, found: 198.0521; **M(C₁₀H₉NO₂)**: 175.19.

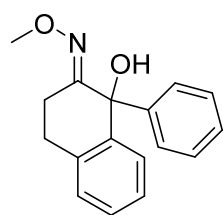
To a suspension of 2-(hydroxyimino)-1-tetralone **S5** (7.00 g, 40.0 mmol, 1.00 equiv) and Ag₂O (5.10 g, 22.0 mmol, 0.55 equiv) in 50 mL abs. THF, methyl iodide (2.74 mL, 44.0 mmol, 1.10 equiv) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 3 hours and then filtered over Celite. The filter cake was washed twice with EtOAc. The solvent of the filtrate was removed under reduced pressure and the crude

product was recrystallized from EtOAc/hexane. Compound **S6** was obtained as brown crystals (6.64 g, 88%).



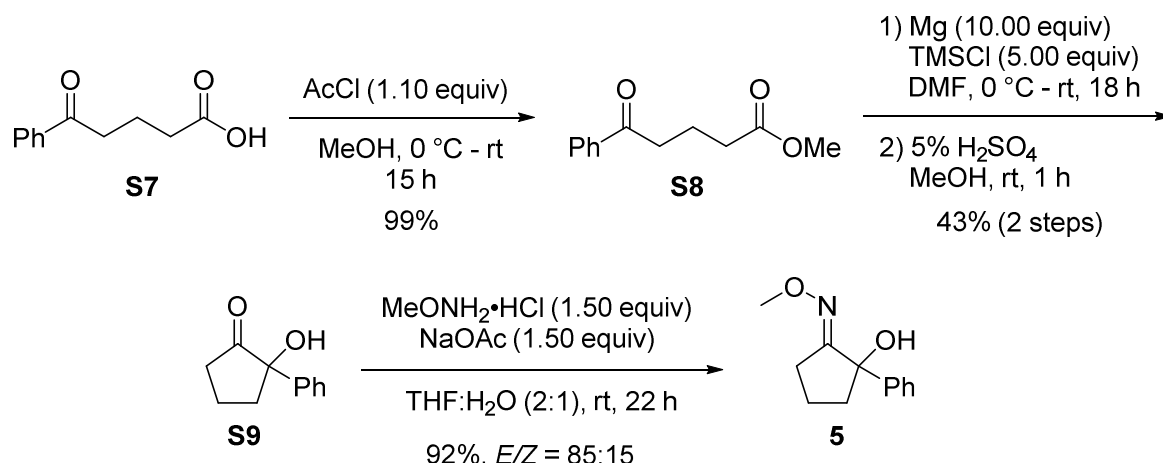
R_f: 0.79 (1.0% MeOH/CH₂Cl₂); **mp.**: 96 – 98 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 (td, J = 7.5, 1.5 Hz, 1H), 7.35 (td, J = 7.5, 1.0 Hz, 1H), 7.28 – 7.26 (m, 1H), 4.15 (s, 3H), 3.09 – 3.02 (m, 4H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 182.8 (C=O), 153.0 (C=N), 143.1 (C_q), 134.1 (CH), 133.7 (C_q), 128.5 (2x CH), 127.3 (CH), 63.6 (CH₃), 26.8 (CH₂), 24.1 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 2986, 2962, 2938, 2823, 1680, 1595, 1573, 1455, 1439, 1432, 1322, 1313, 1229, 1188, 1155, 1050, 1027, 1000, 893, 865, 798, 741, 731, 711, 645, 628; **HR-MS** (ESI⁺): calcd. for C₁₁H₁₁NO₂Na ([M+Na]⁺): 212.0682, found: 212.0678; **M(C₁₁H₁₁NO₂)**: 189.21.

According to general procedure 1, the Grignard reagent was synthesized from magnesium turnings (498 mg, 20.5 mmol, 4.10 equiv) and bromobenzene (2.11.0 mL, 20.0 mmol, 4.00 equiv) in 20 mL abs. THF, and then treated with 2-(methoxyimino)-1-tetralone **S6** (946 mg, 5.00 mmol, 1.00 equiv) dissolved in 25 mL abs. THF. After flash column chromatography (2% → 4% MTBE/hexane), compound **4** was obtained as an orange solid (1.18 g, 88%).



R_f: 0.20 (5% MTBE/hexane); **mp.**: 111 – 112 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.91 (dd, J = 7.5, 1.5 Hz, 1H), 7.39 (tdd, J = 7.5, 1.5, 1.0 Hz, 1H), 7.29 (td, J = 7.5, 1.5 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.15 – 7.11 (m, 3H), 4.61 (bs, 1H), 3.97 (s, 3H), 2.82 – 2.53 (m, 3H), 2.43 – 2.30 (m, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 160.1 (C=N), 142.6 (C_q), 140.4 (C_q), 136.7 (C_q), 128.6 (2x CH), 128.0 (CH), 127.8 (CH), 127.4 (CH), 127.0 (3x CH), 125.5 (CH), 76.2 (C_q), 62.5 (CH₃), 26.4 (CH₂), 23.1 (CH₂); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3383, 3031, 2965, 2938, 2902, 2822, 1632, 1487, 1478, 1458, 1449, 1355, 1341, 1207, 1186, 1119, 1049, 983, 867, 839, 785, 774, 754, 700, 645, 624; **HR-MS** (ESI⁺): calcd. for C₁₇H₁₇NO₂Na ([M+Na]⁺): 290.1152, found: 290.1153; **M(C₁₇H₁₇NO₂)**: 267.33.

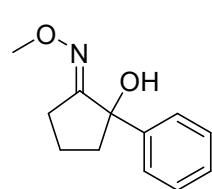
2-Hydroxy oxime ether 5



Methyl 5-oxo-5-phenylpentanoate **S8** was synthesized from carboxylic acid **S7** with 99% yield according to a procedure by Bergmeier *et al.* The spectroscopic data are in agreement with literature.⁴

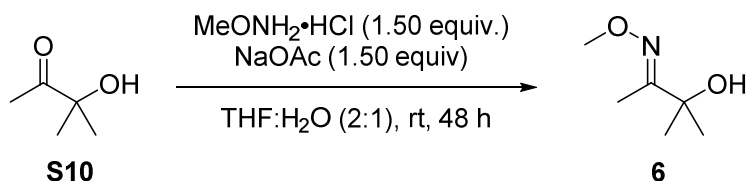
2-Hydroxy-2-phenylcyclopentanone **S9** was synthesized from **S8** with 43% yield according to a procedure by Nishiguchi *et al.* The spectroscopic data are in agreement with literature.⁵

To a solution of **S9** (682 mg, 3.87 mmol, 1.00 equiv) in 9 mL of a 2:1-mixture of THF and H₂O, methoxyamine hydrochloride (485 mg, 5.81 mmol, 1.50 equiv) was added portionwise followed by sodium acetate (476 mg, 5.81 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature overnight. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were washed once with sat. NaHCO₃-solution and brine. It was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 20% MTBE/hexane). Compound **5** was obtained as a yellowish oil (730 mg, 92%, *E/Z* = 85:15). The spectroscopic data are displayed for (*E*)-**5**.



R_f: 0.27 (20% MTBE/hexane); **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.47 – 7.44 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.28 (m, 1H), 3.90 (s, 3H), 2.86 – 2.78 (m, 2H), 2.57 – 2.49 (m, 1H), 2.22 – 2.11 (m, 2H), 2.01 – 1.91 (m, 1H), 1.76 – 1.65 (m, 1H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.6 (C=N), 144.5 (C_q), 128.2 (2x CH), 127.5 (CH), 126.1 (2x CH), 81.6 (C_q), 62.1 (CH₃), 42.8 (CH₂), 27.5 (CH₂), 20.4 (CH₂); **IR** (film): $\tilde{\nu}$ (cm⁻¹) = 3433, 3059, 2965, 2938, 1652, 1147, 1045, 874, 842, 760, 700; **HR-MS** (ESI⁺): calcd. for C₁₂H₁₅NO₂Na ([M+Na]⁺): 228.0995, found: 228.0992; **M(C₁₂H₁₅NO₂)**: 205.26.

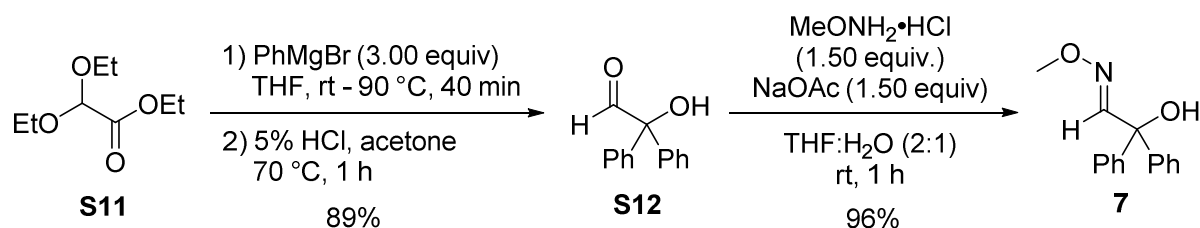
2-Hydroxy oxime ether 6



To a solution of **S10** (319 μL , 3.00 mmol, 1.00 equiv) in 9 mL of a 2:1-mixture of THF and H_2O , methoxyamine hydrochloride (376 mg, 4.50 mmol, 1.50 equiv) was added portionwise followed by sodium acetate (369 mg, 4.50 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 48 h. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were washed once with sat. NaHCO_3 -solution and brine. It was dried over Na_2SO_4 , filtered and the solvent was removed under reduced pressure (>150 mbar at 40°C since **6** is volatile). The crude product was purified by flash column chromatography (10% \rightarrow 20% MTBE/hexane). Compound **6** was obtained as a colorless oil (327 mg, 83%).

R_f: 0.30 (20% MTBE/hexane); **¹H-NMR** (300 MHz, CDCl_3): δ (ppm) = 3.83 (s, 3H), 3.62 (bs, 1H), 1.82 (s, 3H), 1.32 (s, 6H); **¹³C-NMR** (100 MHz, CDCl_3): δ (ppm) = 160.8 (C=N), 72.4 (C_q), 61.8 (CH_3), 28.0 (2x CH_3), 10.5 (CH_3); **IR** (film): $\tilde{\nu}$ (cm^{-1}) = 3420, 2981, 2938, 818, 1636, 1464, 1367, 1173, 1143, 1053, 950, 893, 856; **HR-MS** (ESI⁺): calcd. for $\text{C}_6\text{H}_{13}\text{NO}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 154.0839, found: 154.0836; **M**($\text{C}_6\text{H}_{13}\text{NO}_2$): 131.18.

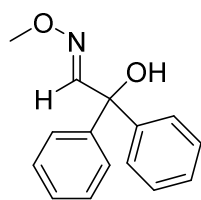
2-Hydroxy oxime ether 7



2-Hydroxy-2,2-diphenylacetaldehyde **S12** was synthesized from ester **S11** with 89% yield according to a slightly modified procedure by Wulff *et al.* The spectroscopic data are in agreement with literature.⁶

To a solution of **S12** (849 mg, 2.00 mmol, 1.00 equiv) in 12 mL of a 2:1-mixture of THF and H_2O , methoxyamine hydrochloride (501 mg, 3.00 mmol, 1.50 equiv) was added portionwise followed by sodium acetate (492 mg, 3.00 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 1 h. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were washed once with sat. NaHCO_3 -solution

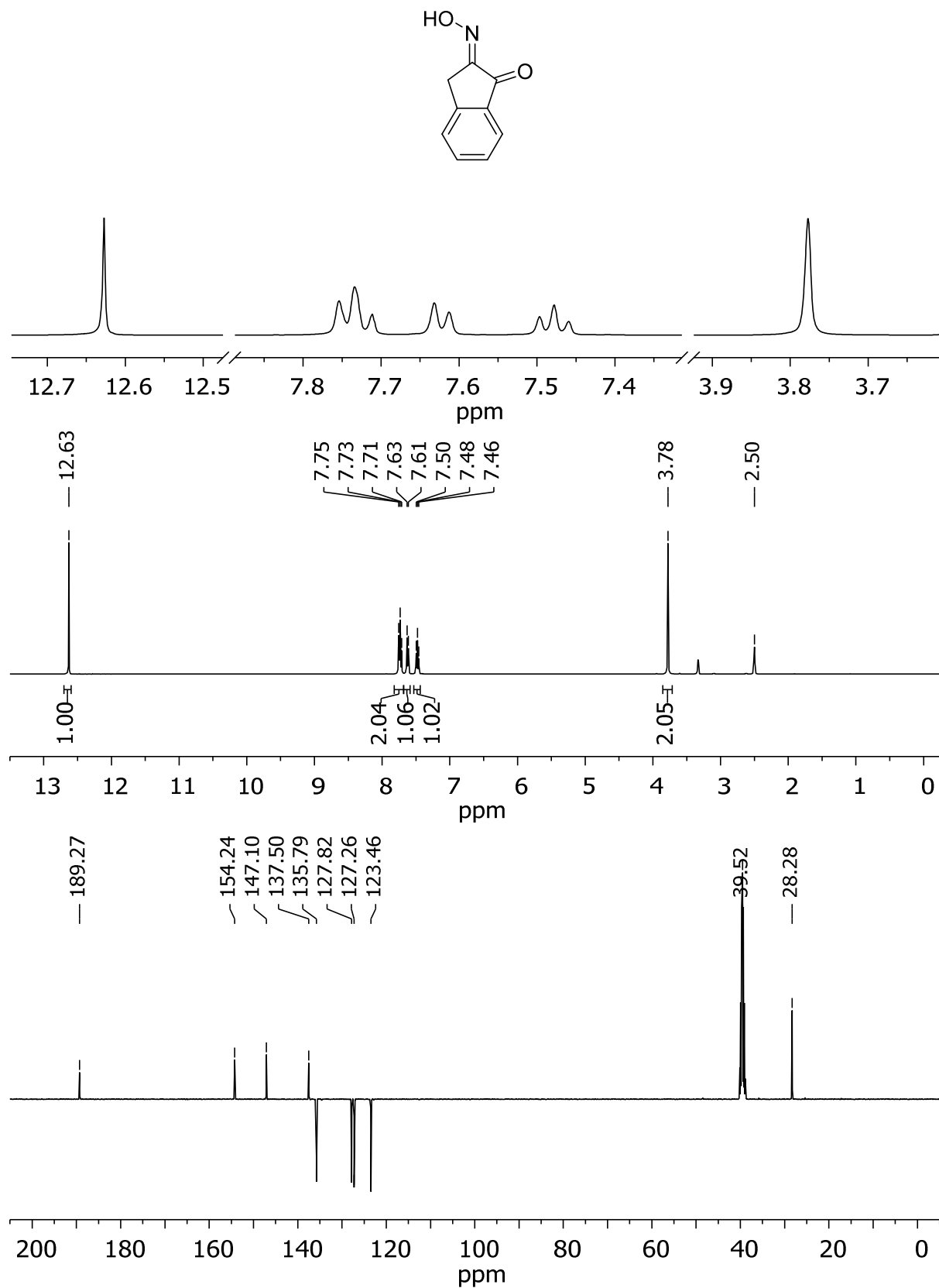
and brine. It was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (2% → 5% MTBE/hexane). Compound **7** was obtained as a white solid (925 mg, 96%).



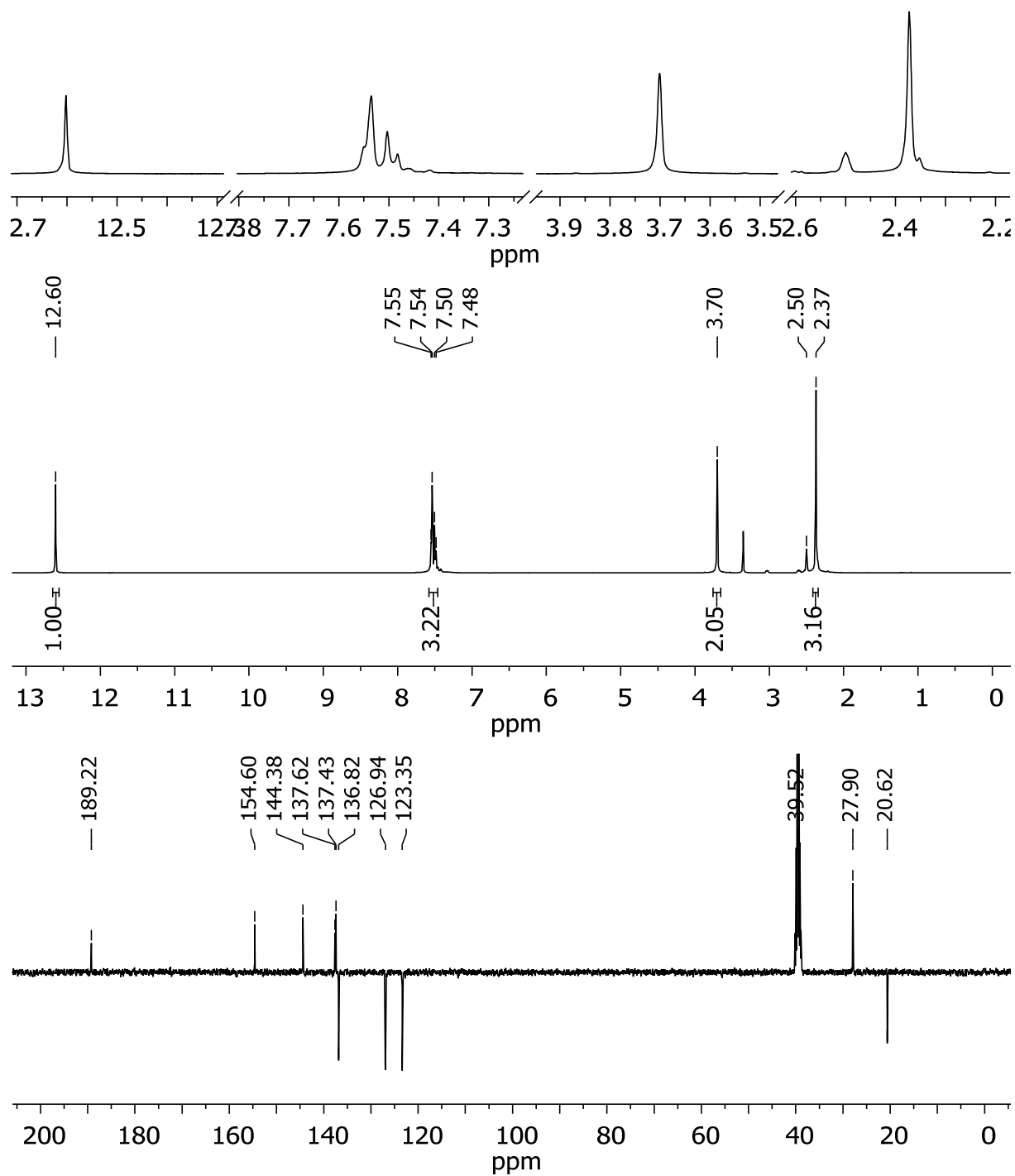
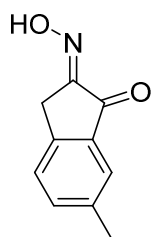
R_f: 0.27 (10% MTBE/hexane); **mp.**: 62 – 64 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 8.05 (s, 1H), 7.44 – 7.33 (m, 10H), 4.16 (bs, 1H), 3.96 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 152.5 (HC=N), 144.0 (2x C_q), 128.5 (4x CH), 127.9 (2x CH), 127.0 (4x CH), 77.5 (C_q), 62.4 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 3088, 3057, 3028, 2972, 2938, 2898, 2817, 1598, 1491, 1462, 1449, 1337, 1187, 1168, 1141, 1070, 1046, 1002, 992, 962, 901, 877, 785, 769, 760, 749, 699, 663, 636, 488; **HR-MS** (ESI⁺): calcd. for C₁₅H₁₅NO₂Na ([M+Na]⁺): 264.0995, found: 264.0995; **M(C₁₅H₁₅NO₂)**: 241.29.

2.3 ^1H -NMR and ^{13}C -NMR Spectra

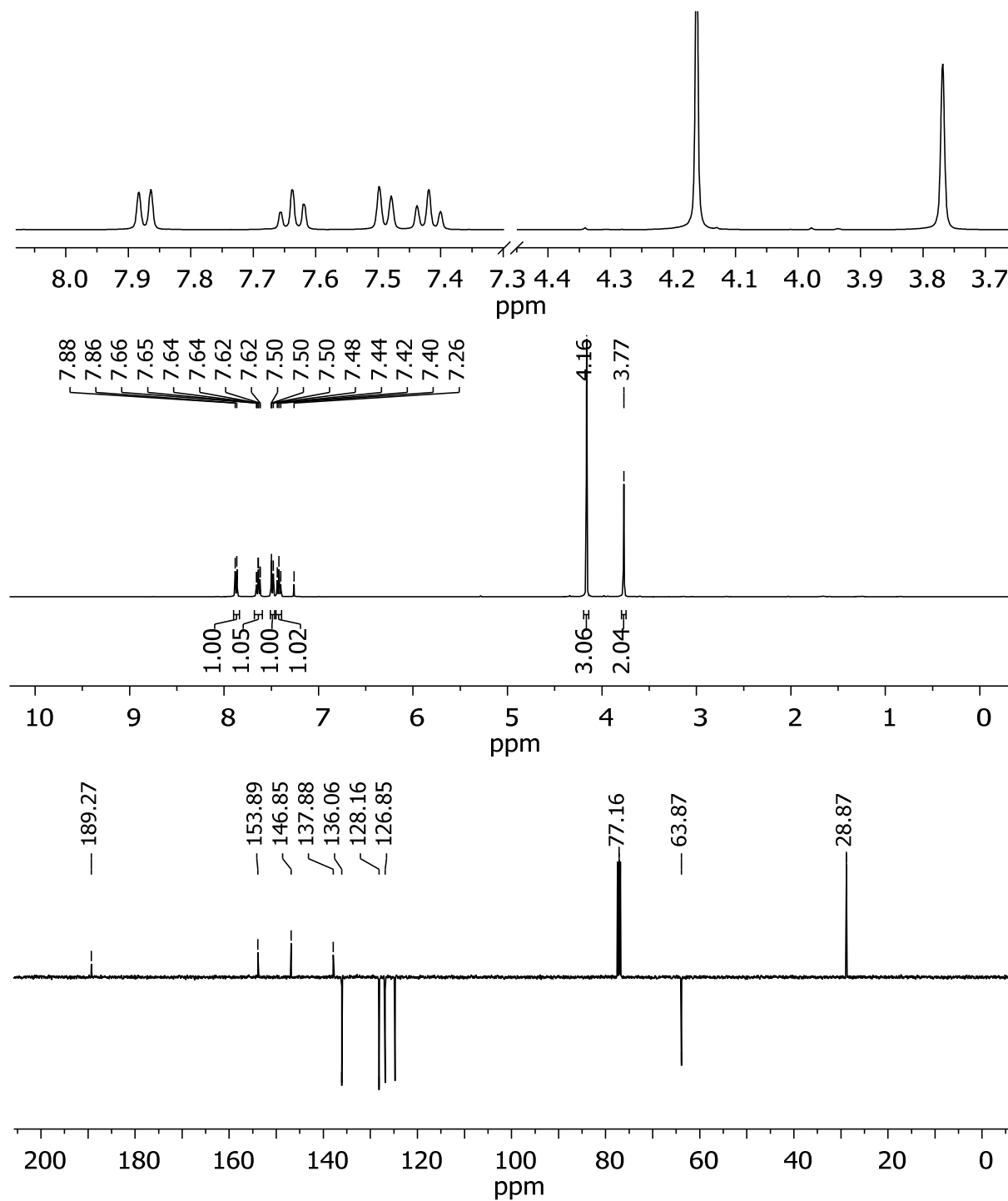
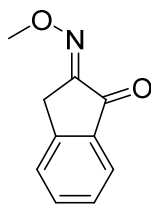
1,2-Indandione-2-oxime S2a (DMSO- d_6 , ^1H -NMR: 400 MHz, APT: 100 MHz)



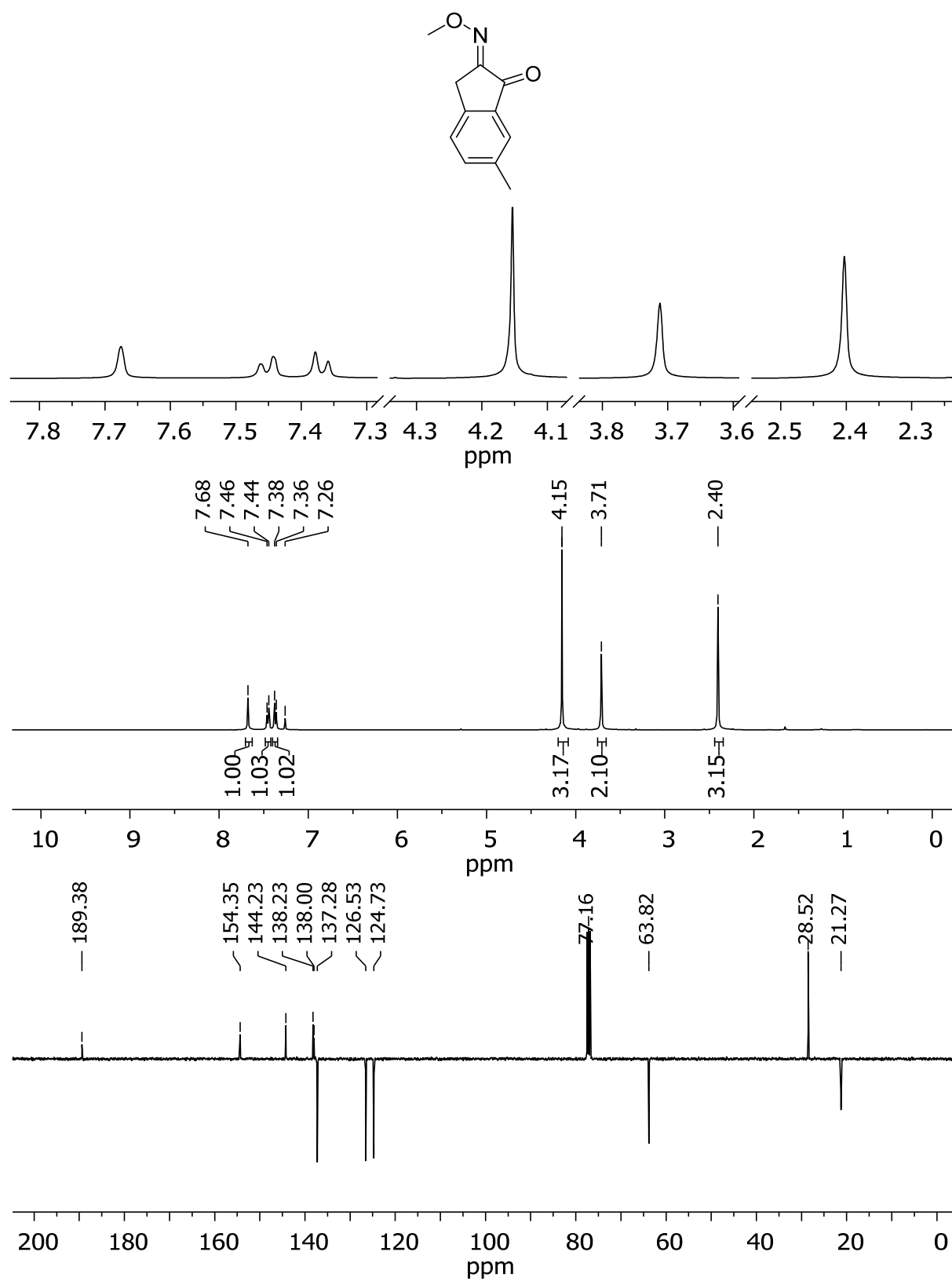
1,2-Indandione-2-oxime S2b (DMSO-d₆, ¹H-NMR: 400 MHz, APT: 100 MHz)



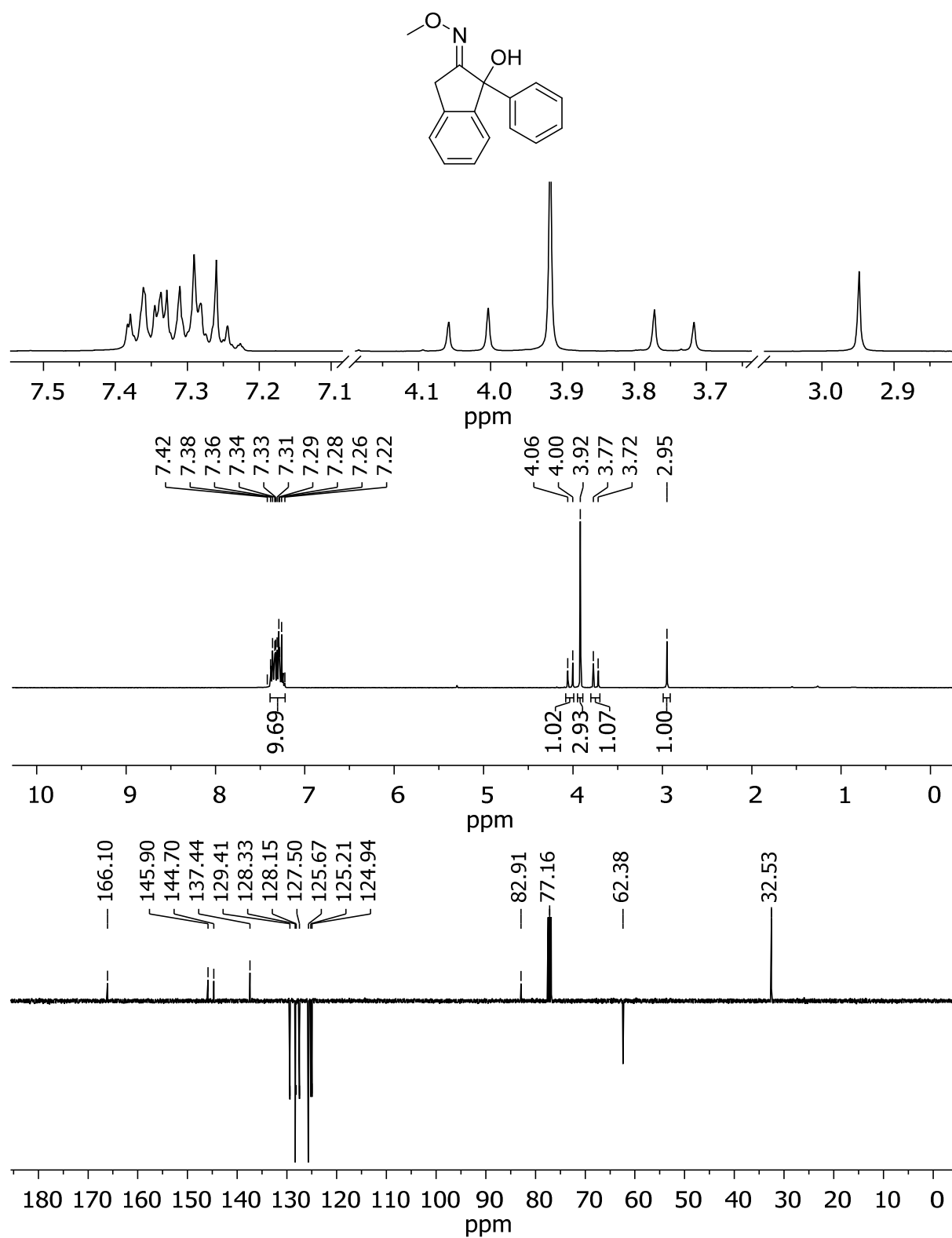
1,2-Indandione-2-oxime S3a (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



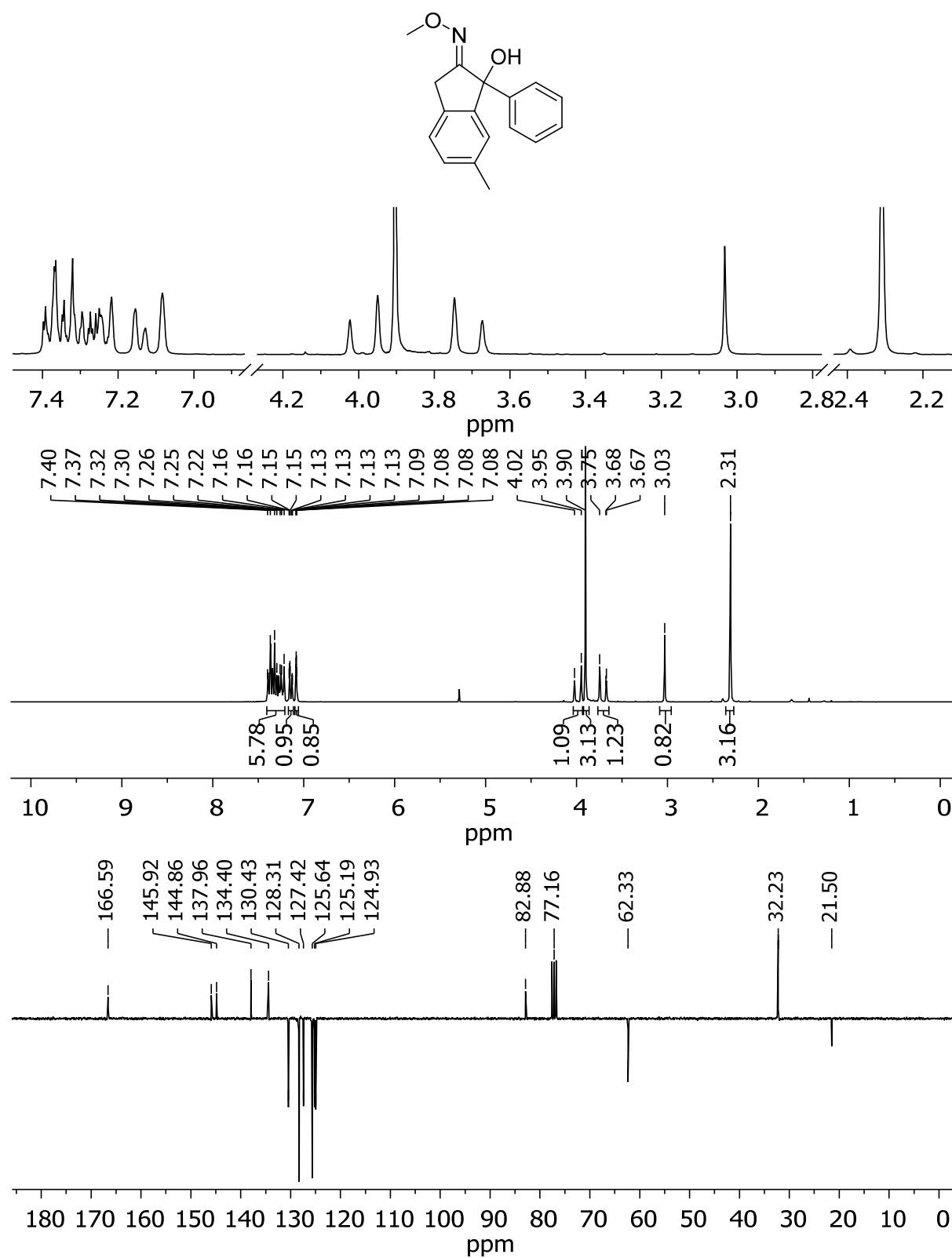
1,2-Indandione-2-oxime S3b (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



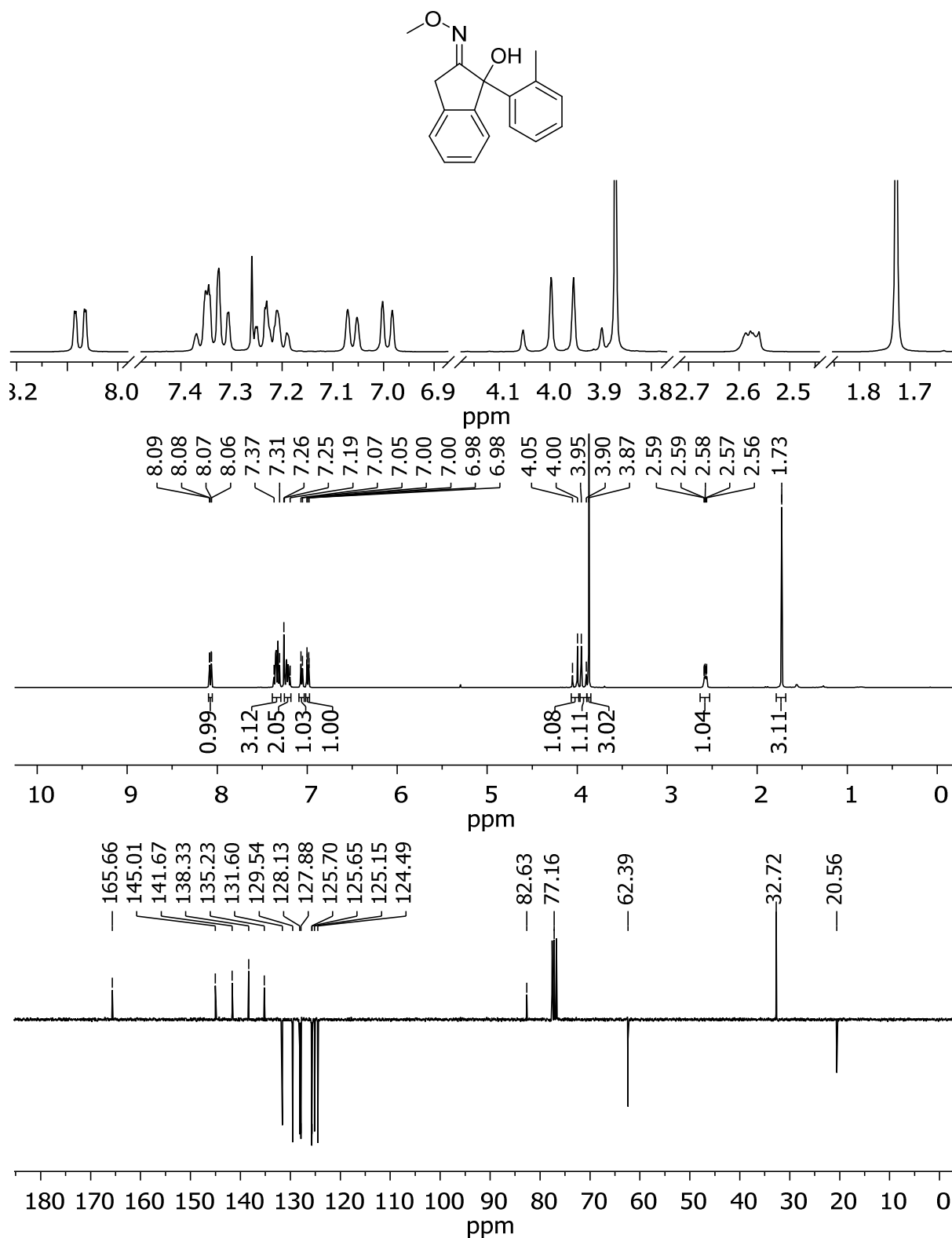
2-Hydroxy oxime ether 1a (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



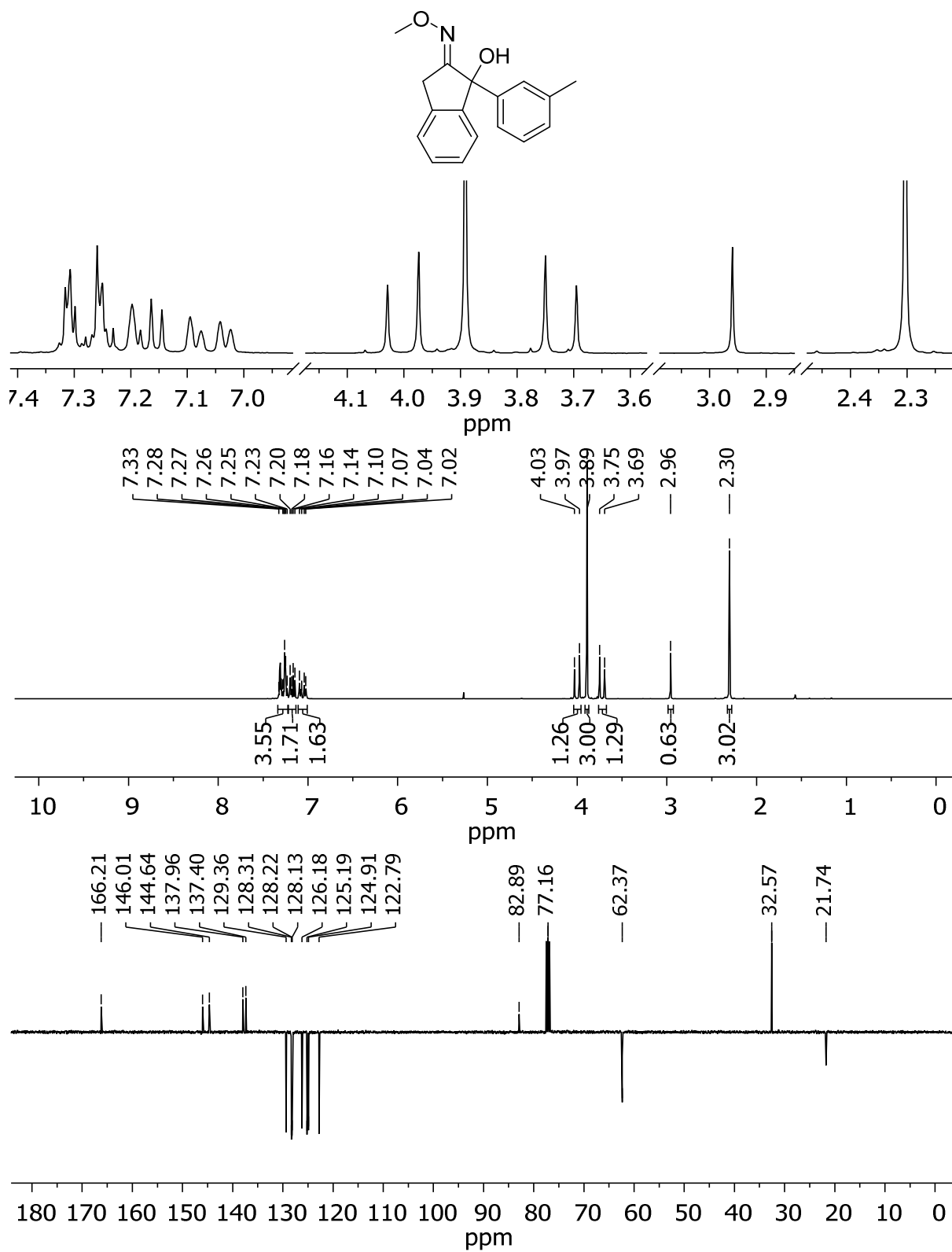
2-Hydroxy oxime ether 1b (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



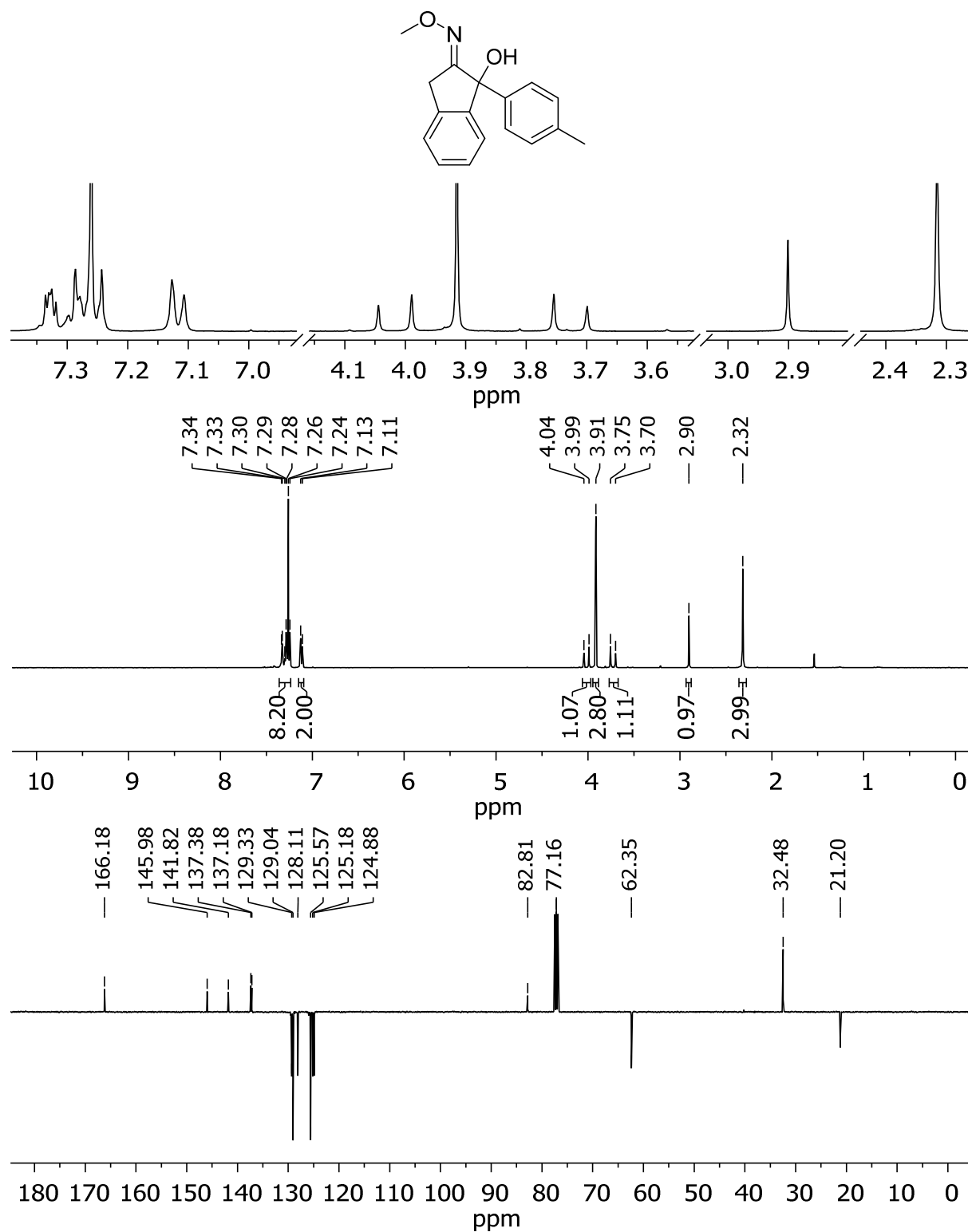
2-Hydroxy oxime ether 1c (CDCl₃, ¹H-NMR: 400 MHz, APT: 75 MHz)



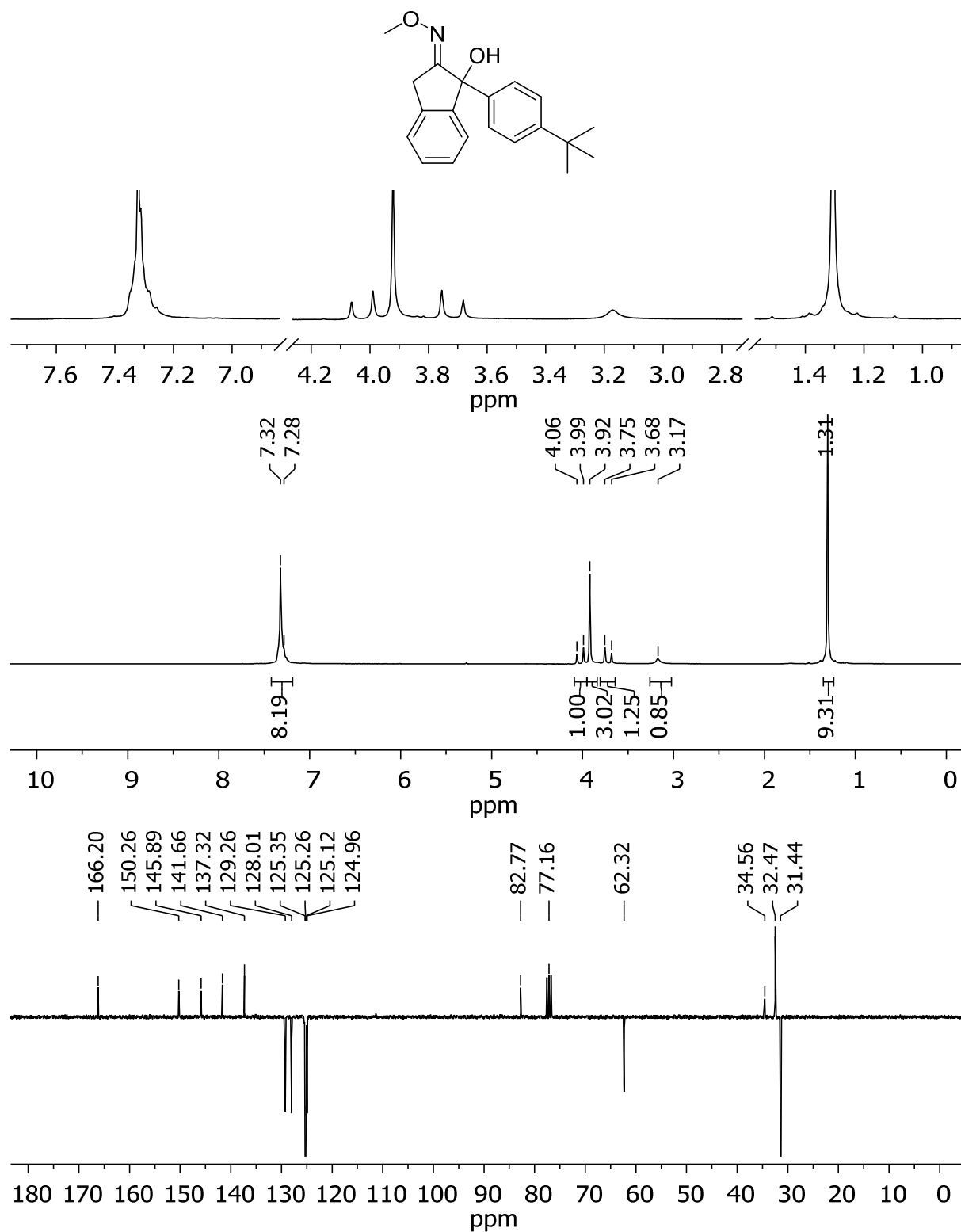
2-Hydroxy oxime ether 1d (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



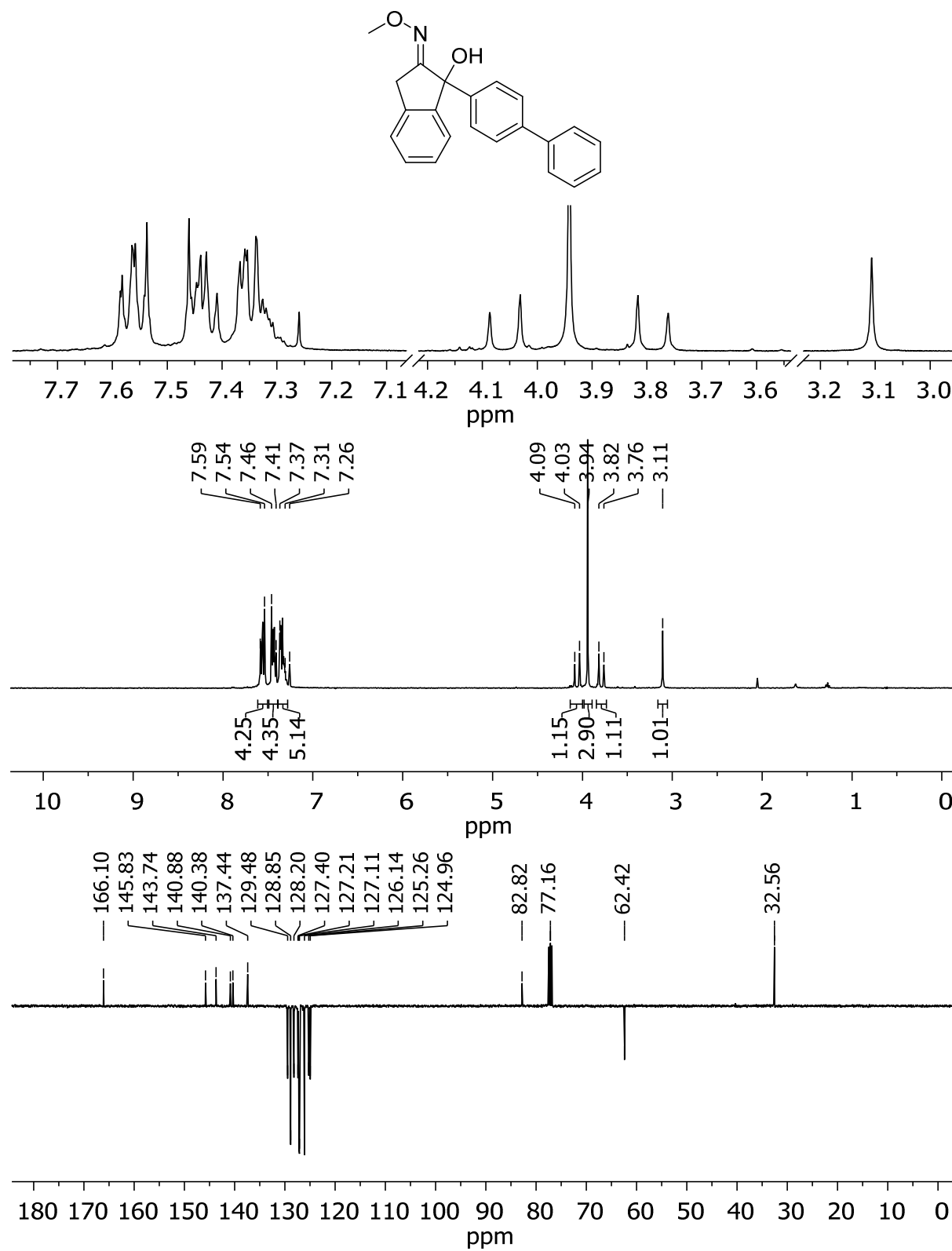
2-Hydroxy oxime ether 1e (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



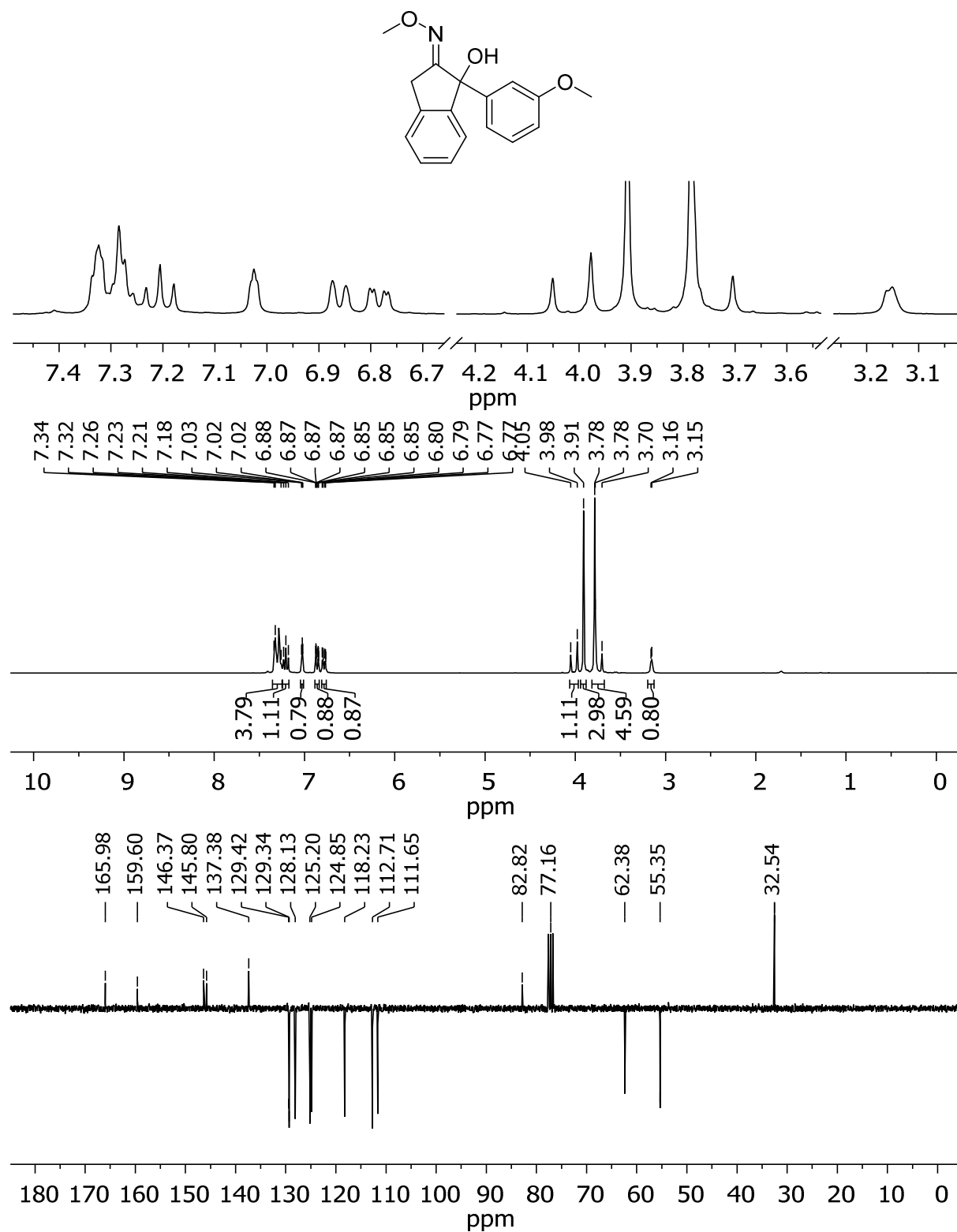
2-Hydroxy oxime ether 1f (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



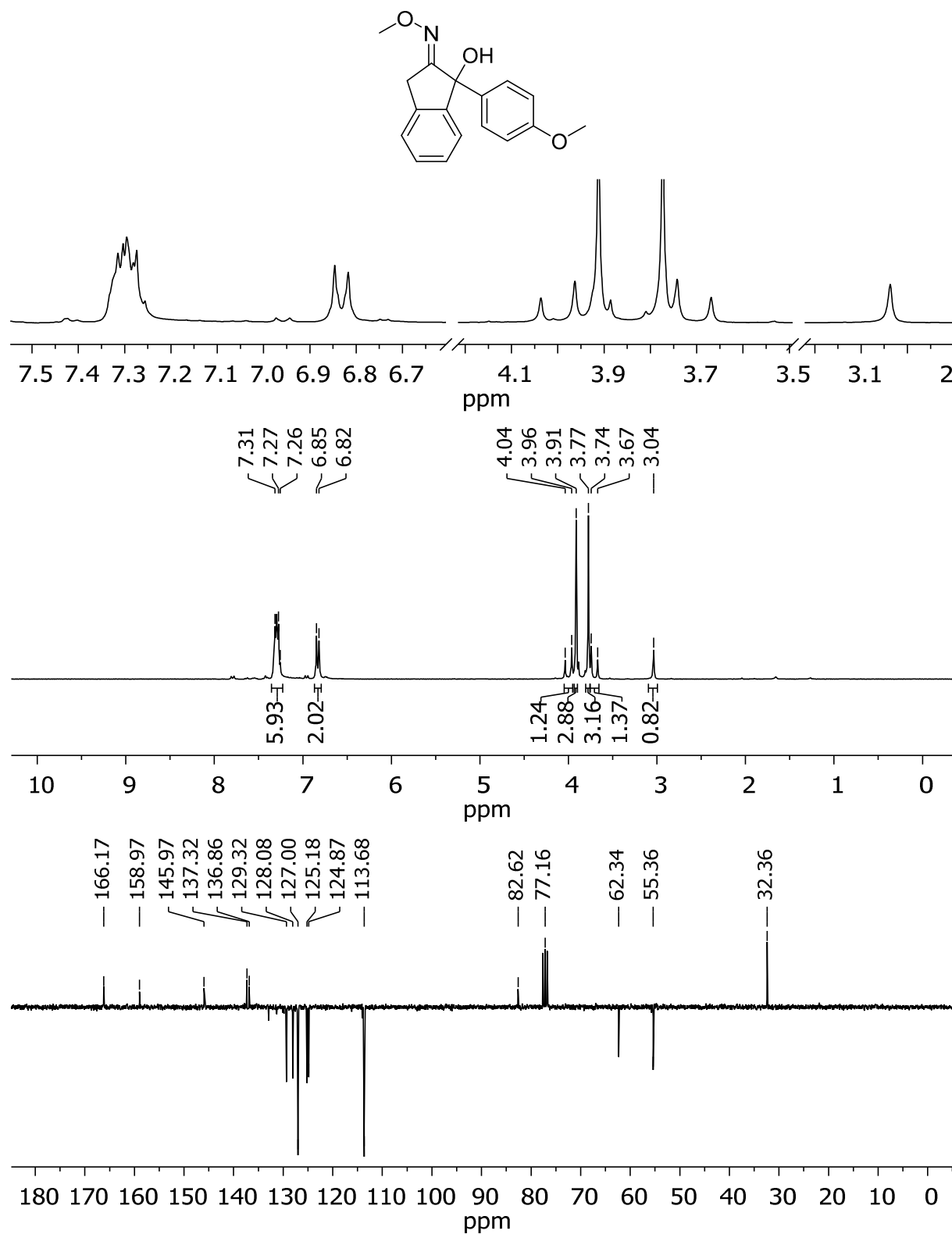
2-Hydroxy oxime ether 1g (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



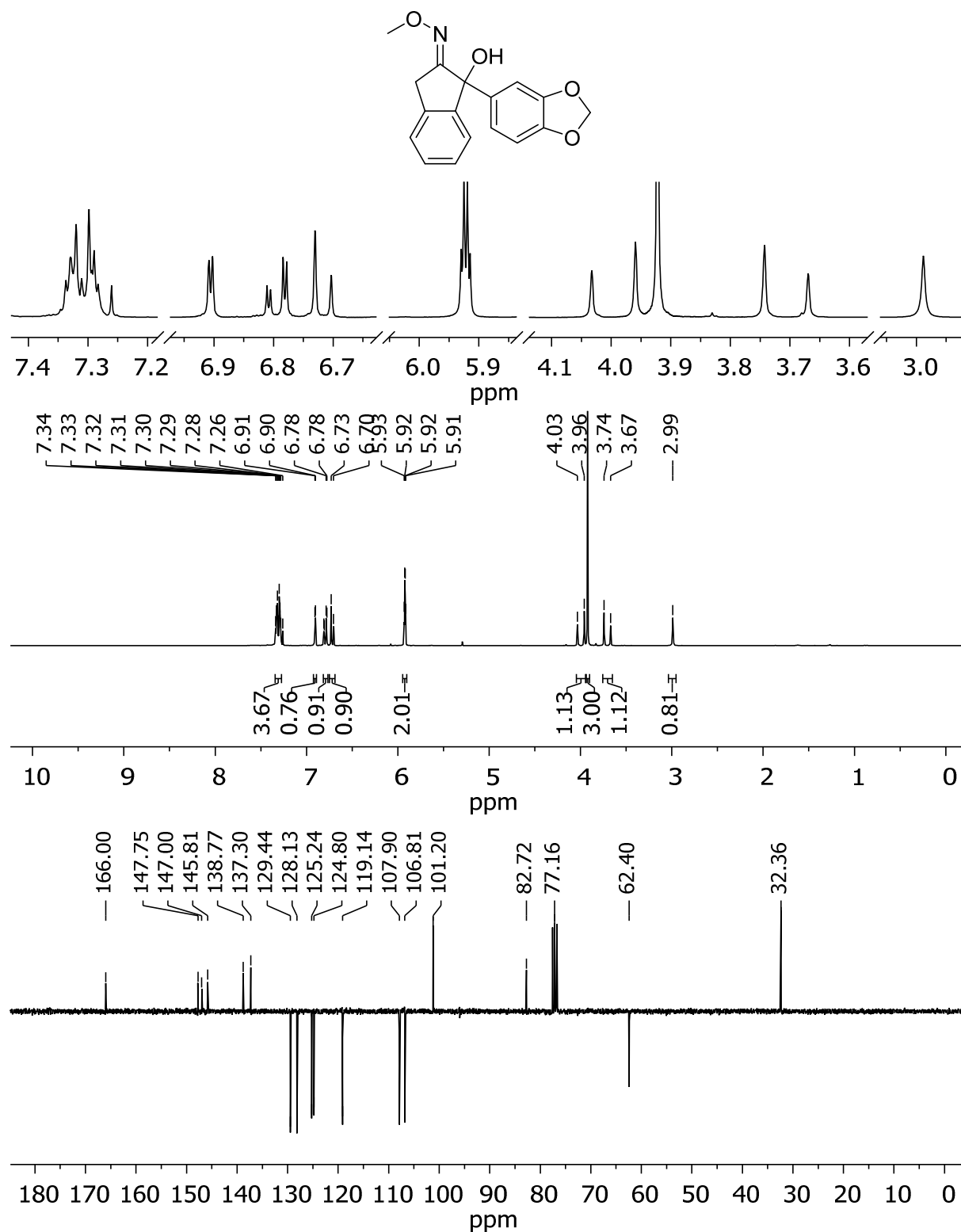
2-Hydroxy oxime ether 1h (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



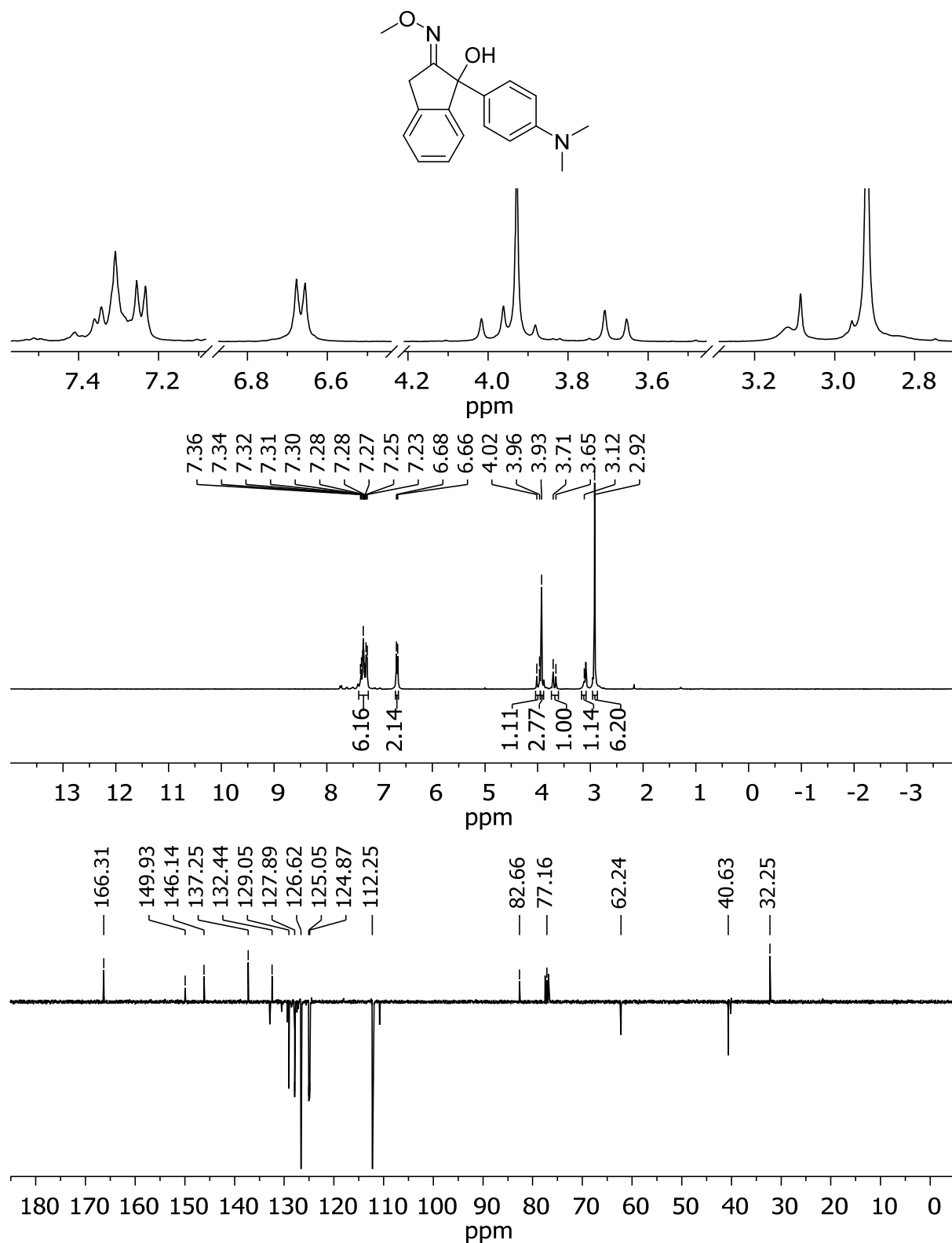
2-Hydroxy oxime ether 1i (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



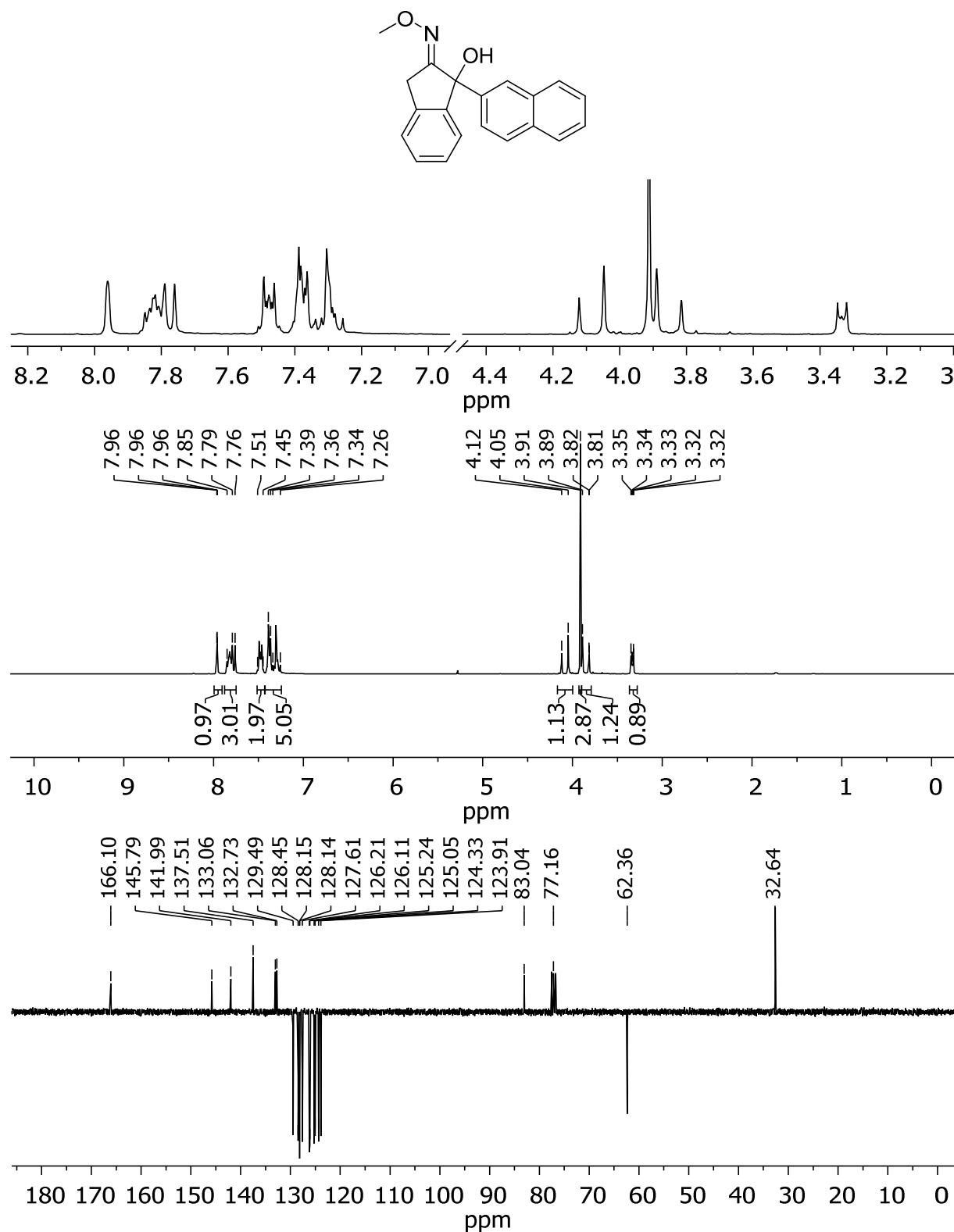
2-Hydroxy oxime ether 1j (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



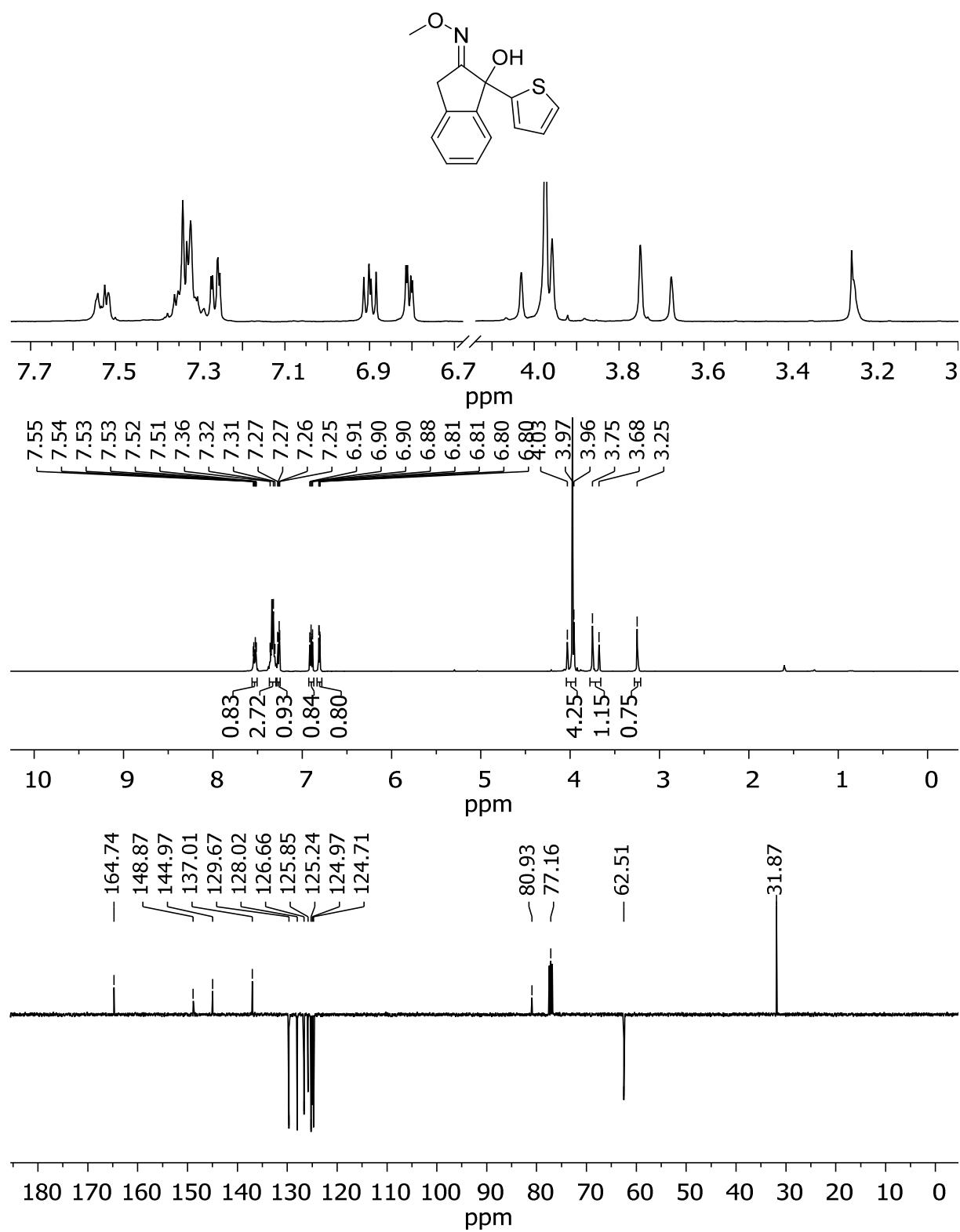
2-Hydroxy oxime ether 1k (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



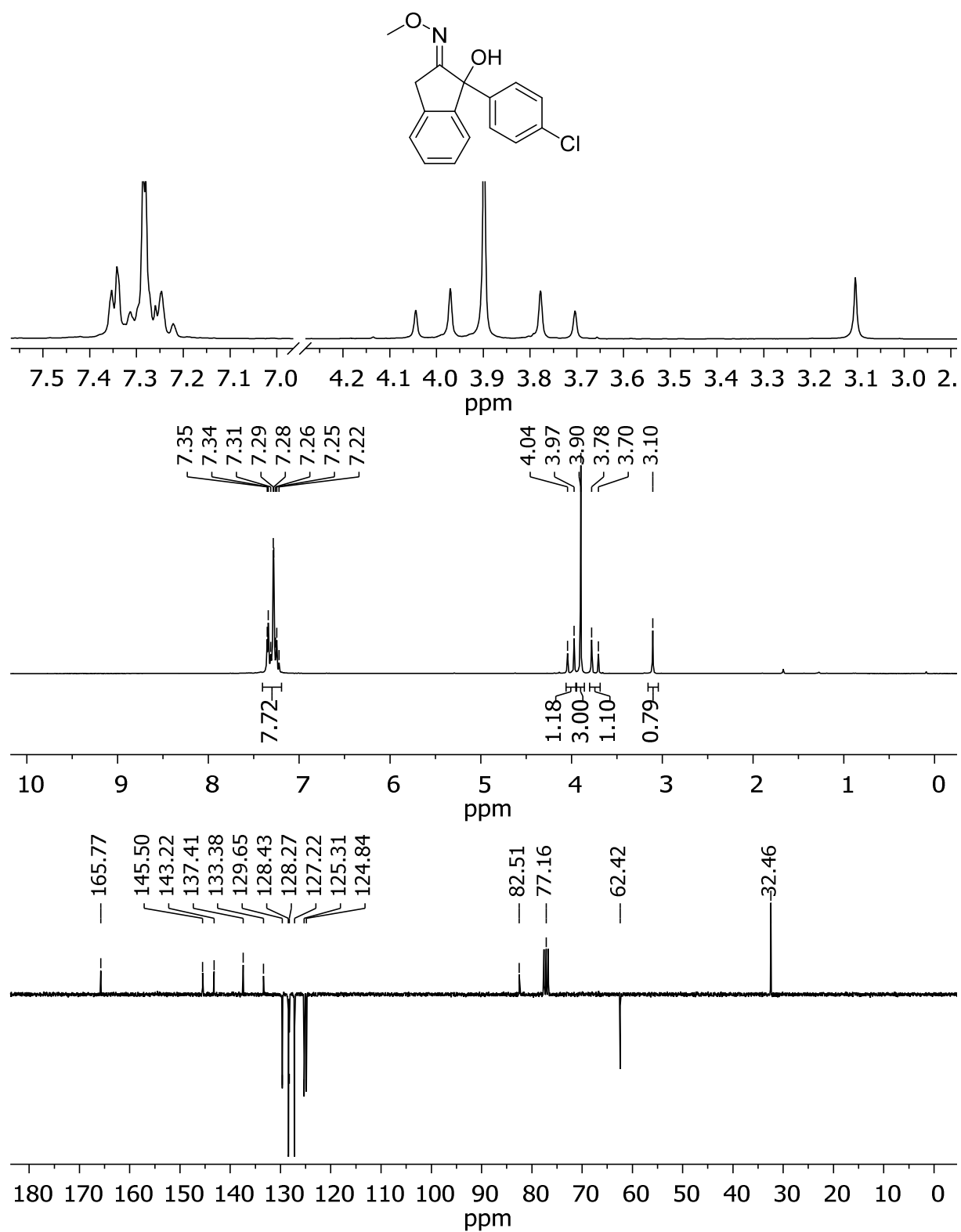
2-Hydroxy oxime ether 11 (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



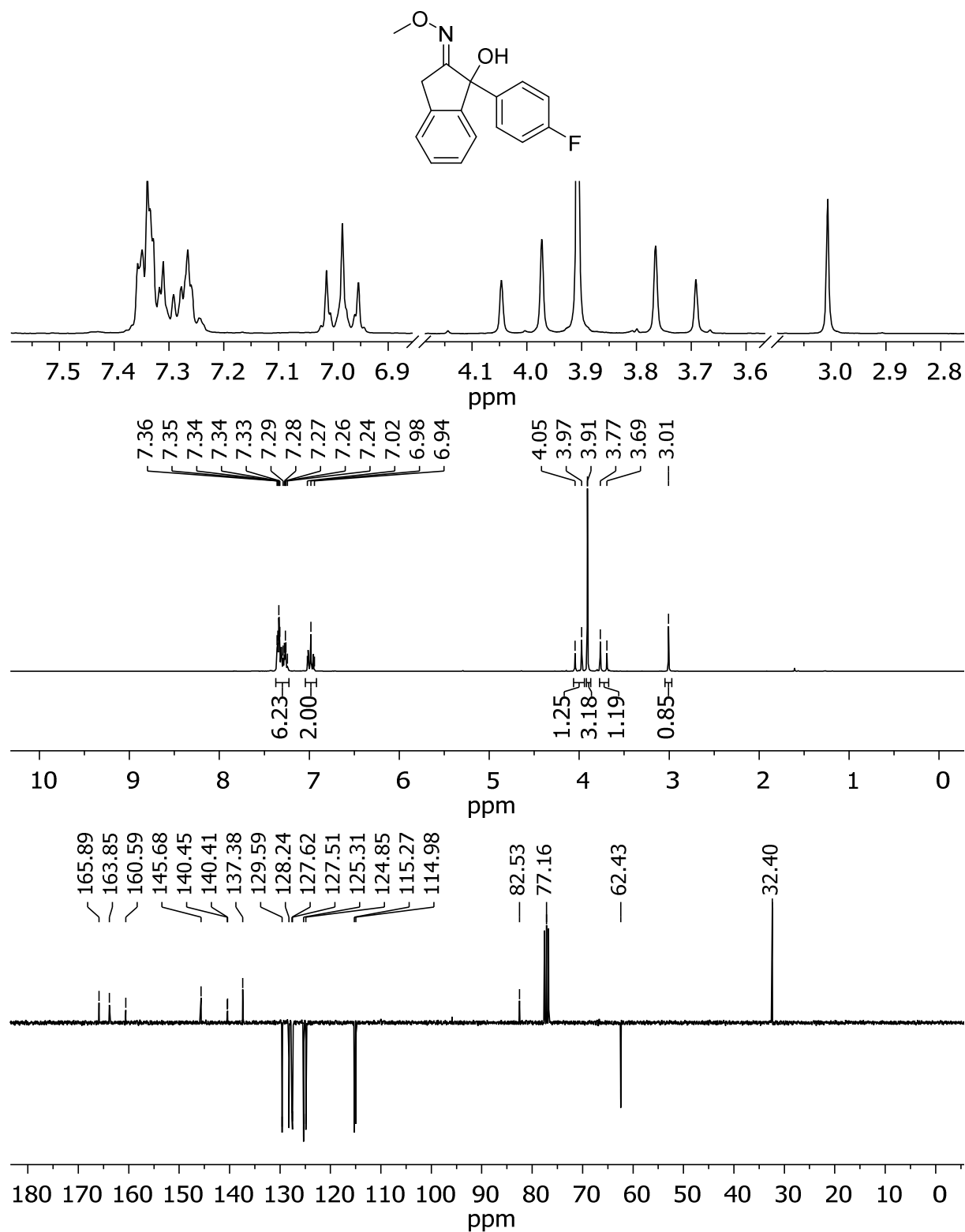
2-Hydroxy oxime ether 1m (CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)



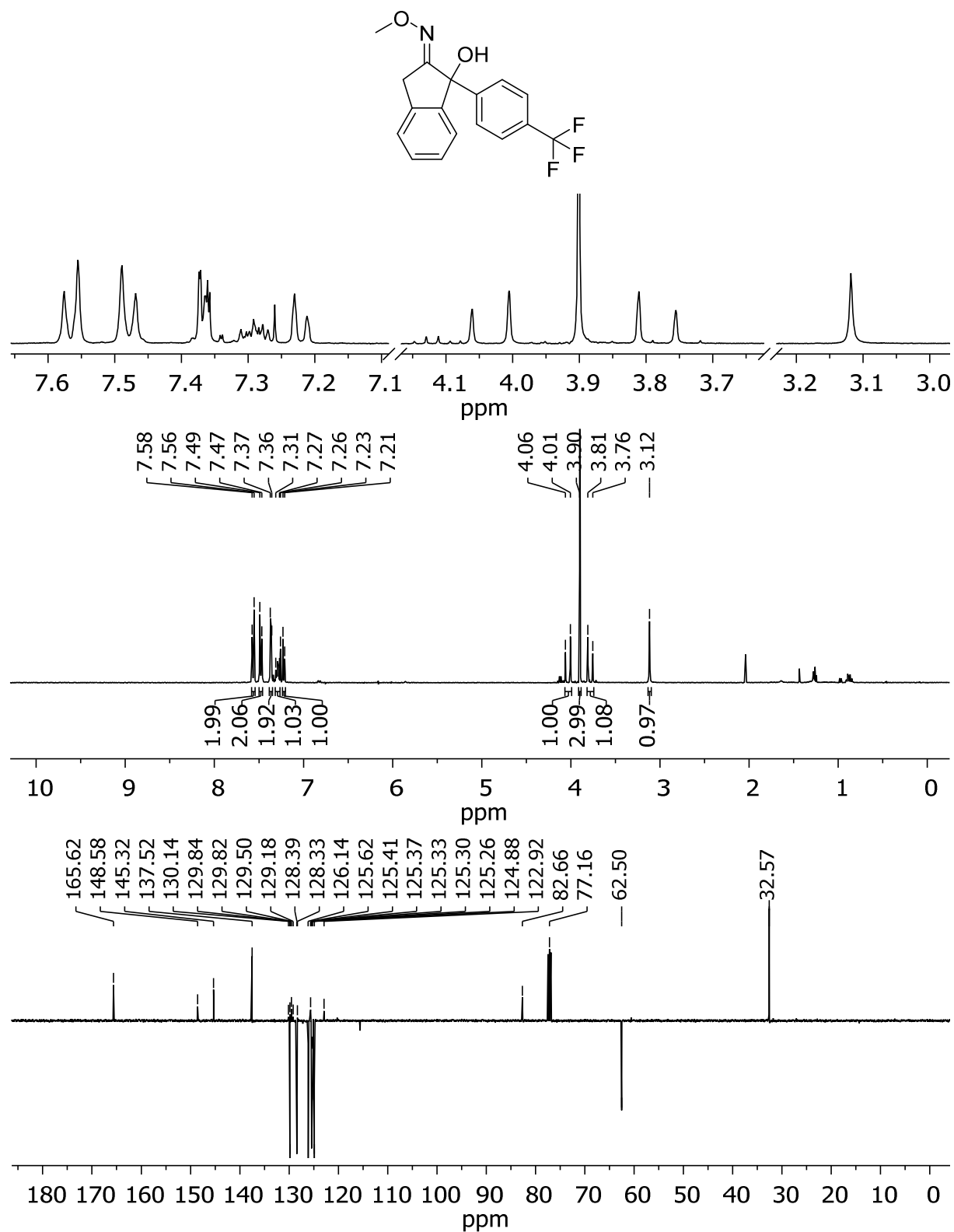
2-Hydroxy oxime ether 1n (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



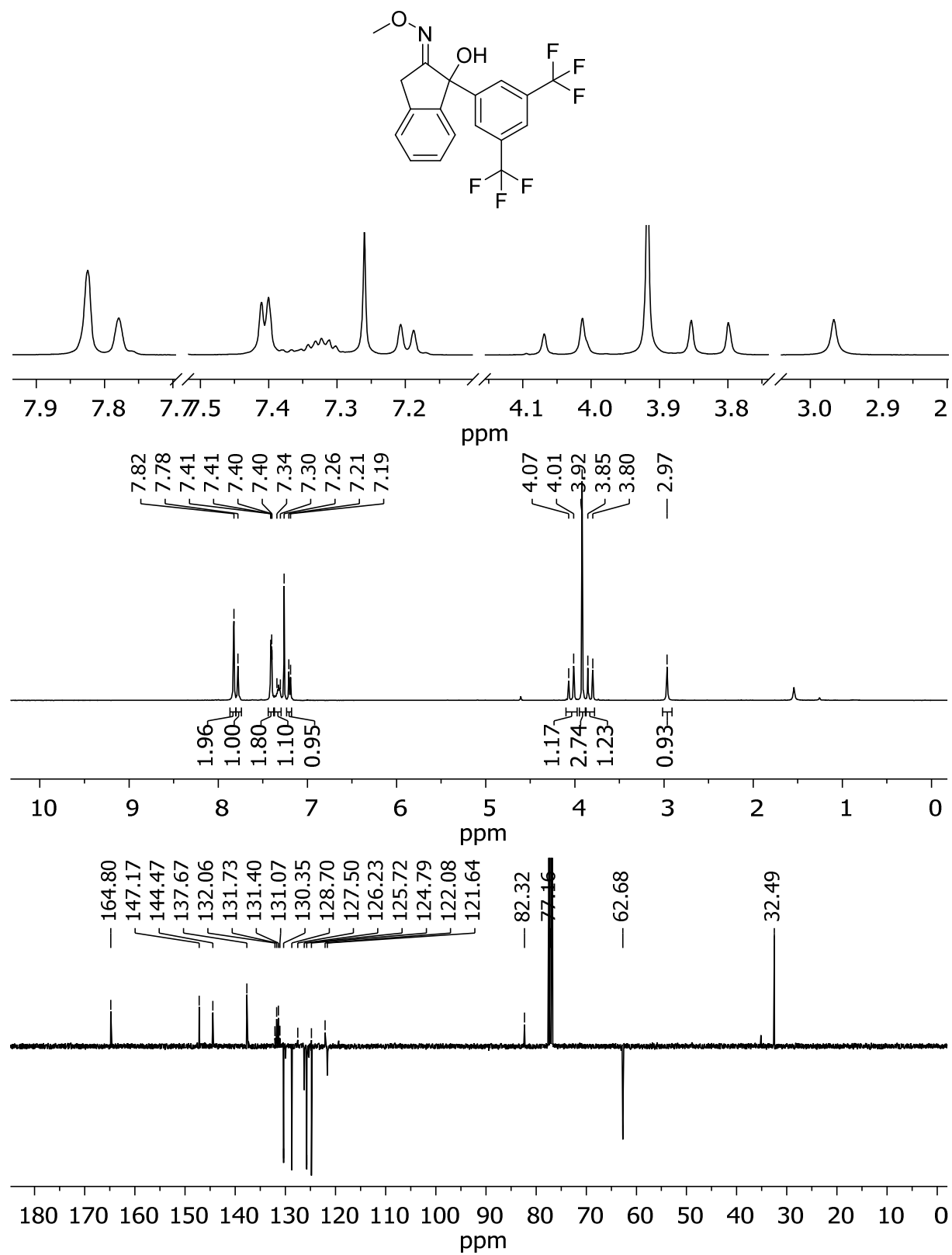
2-Hydroxy oxime ether 1o (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



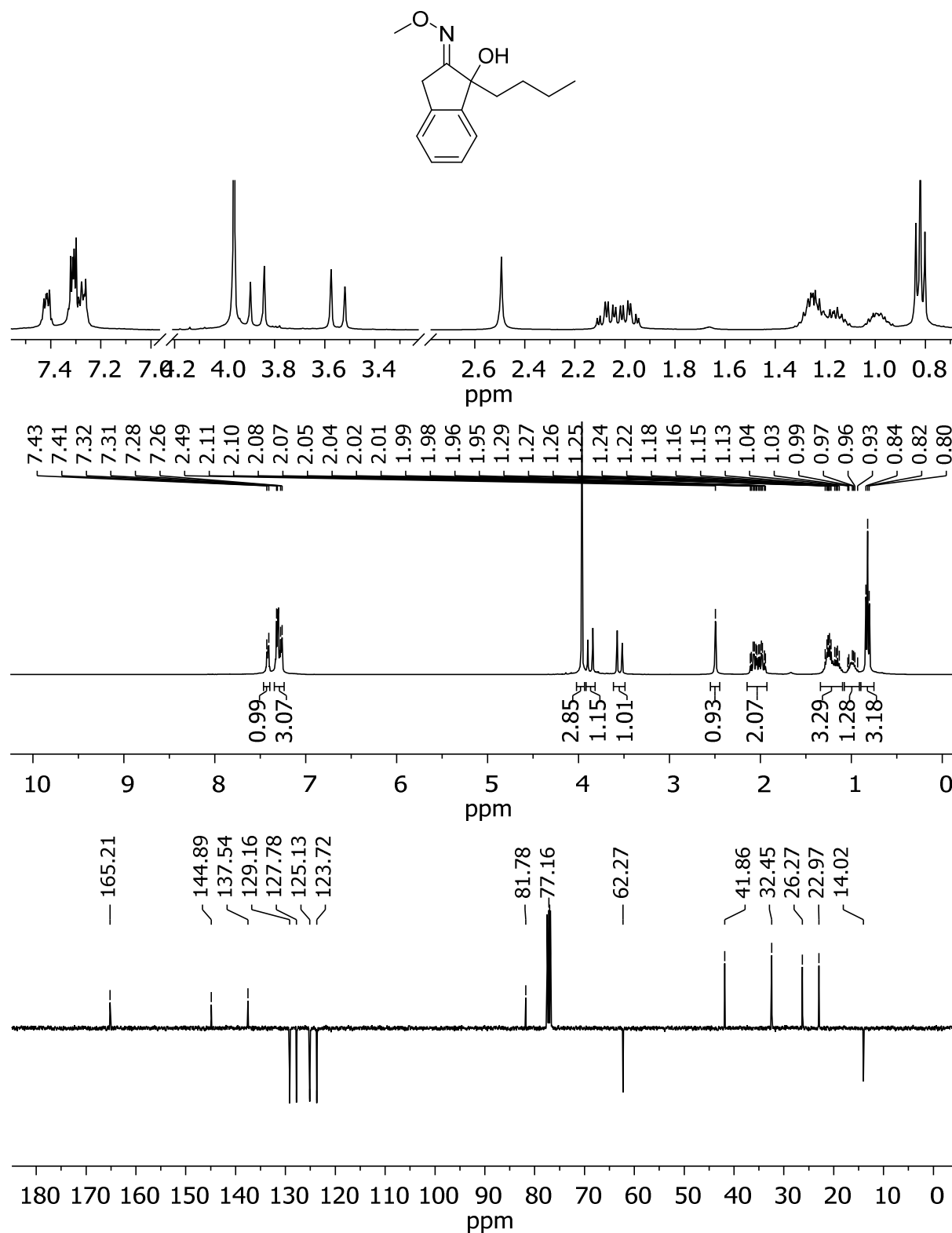
2-Hydroxy oxime ether 1p (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



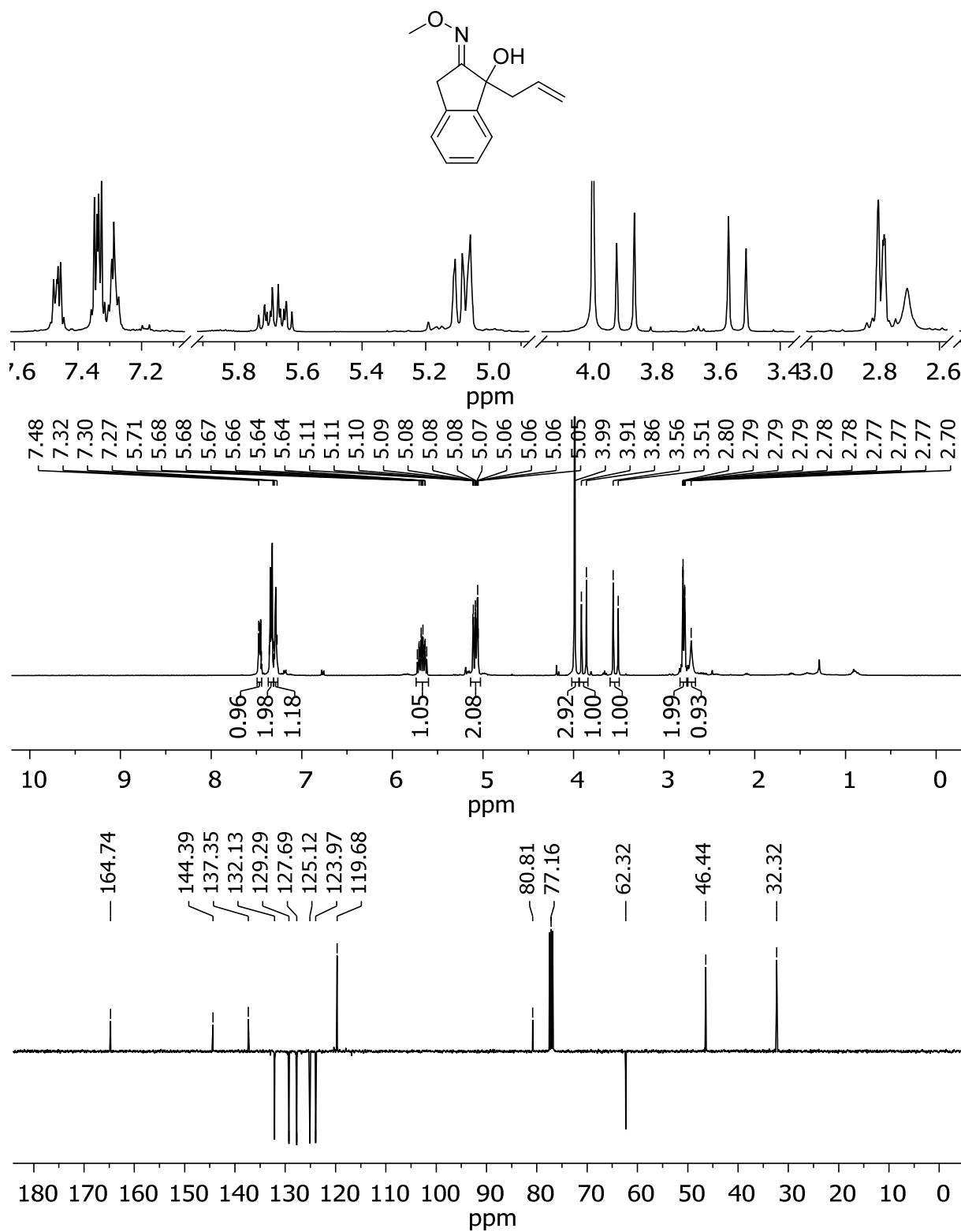
2-Hydroxy oxime ether 1q (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



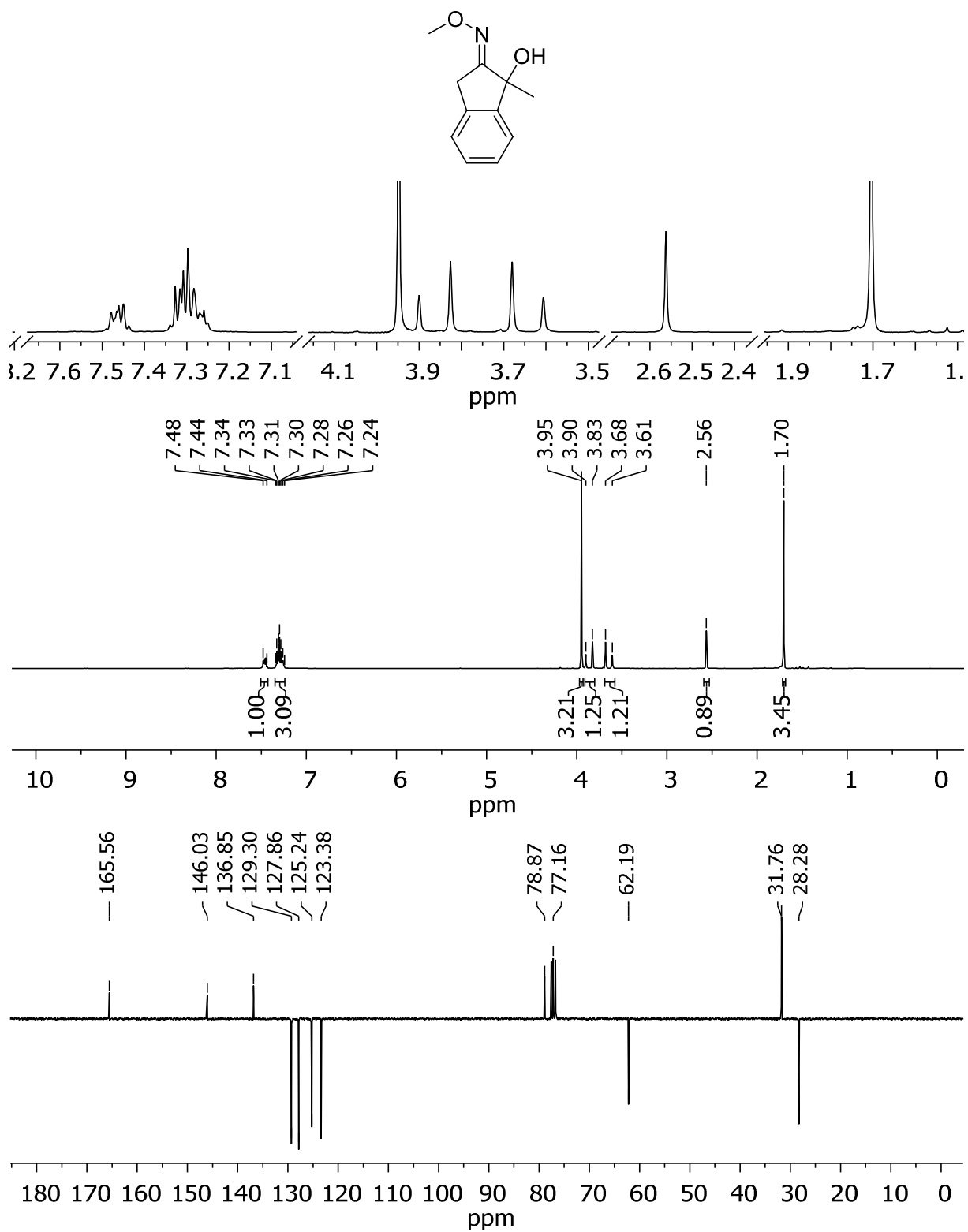
2-Hydroxy oxime ether 1r (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



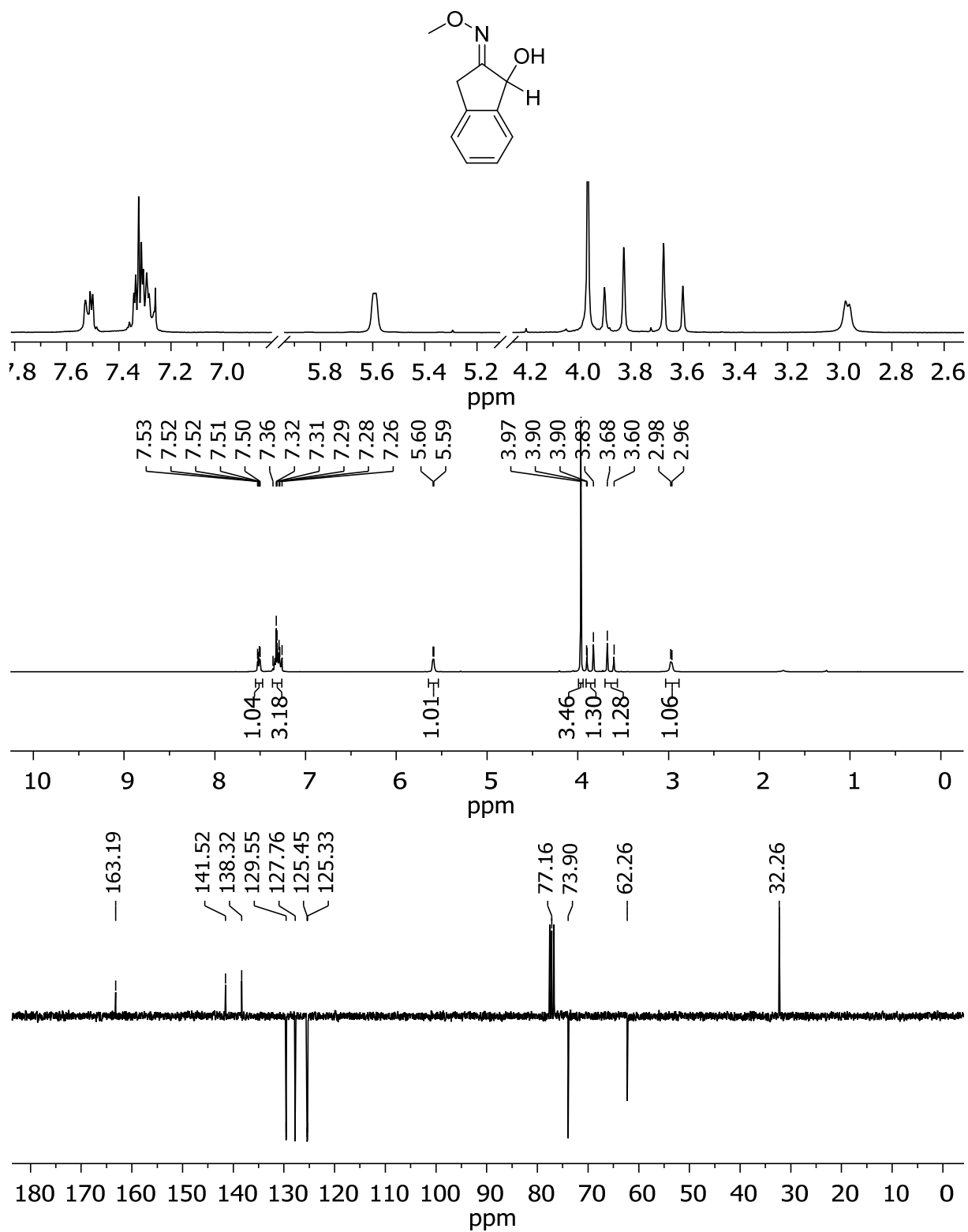
2-Hydroxy oxime ether 1s (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



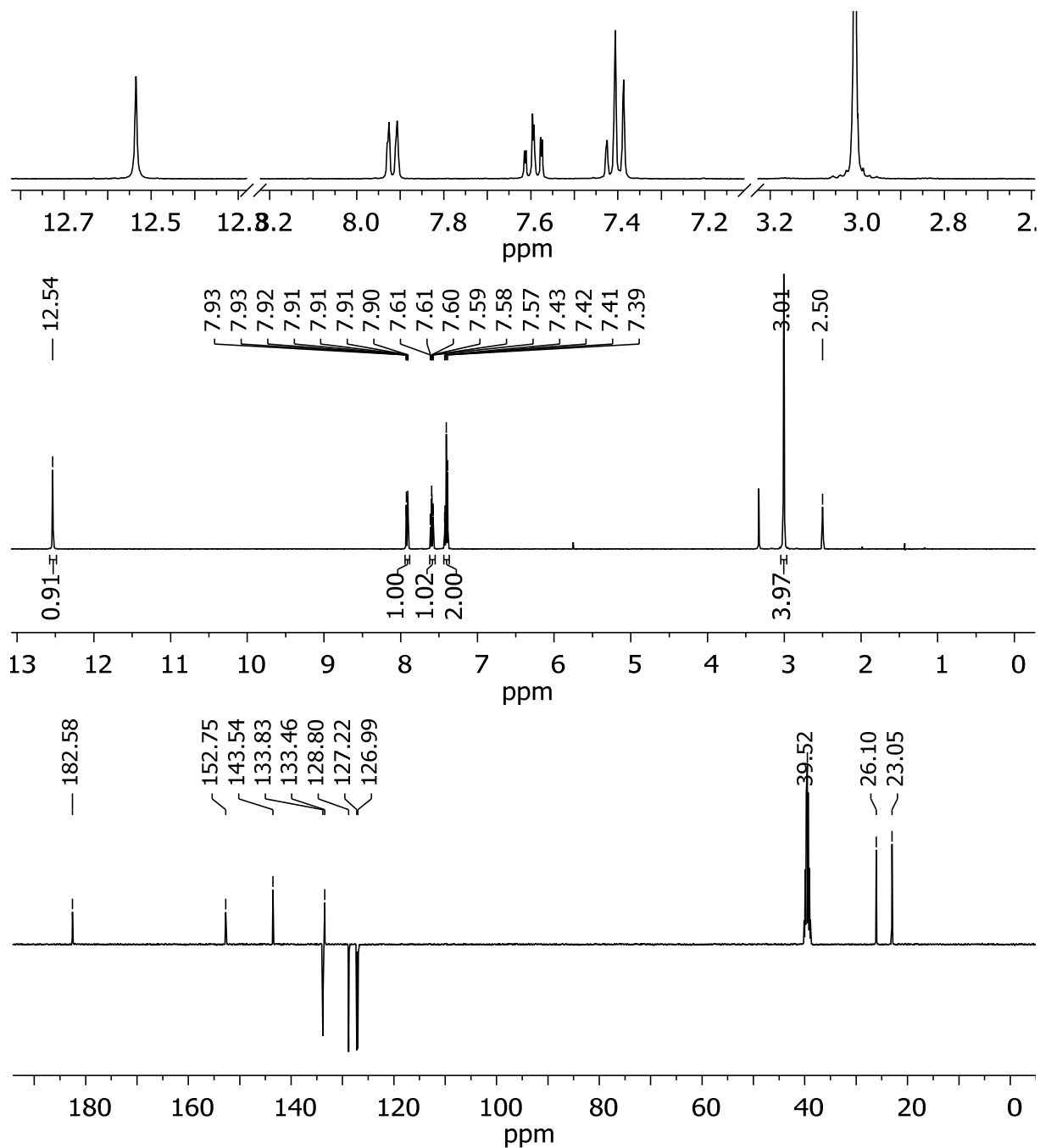
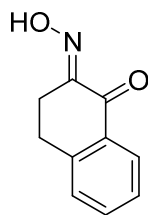
2-Hydroxy oxime ether 1t (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



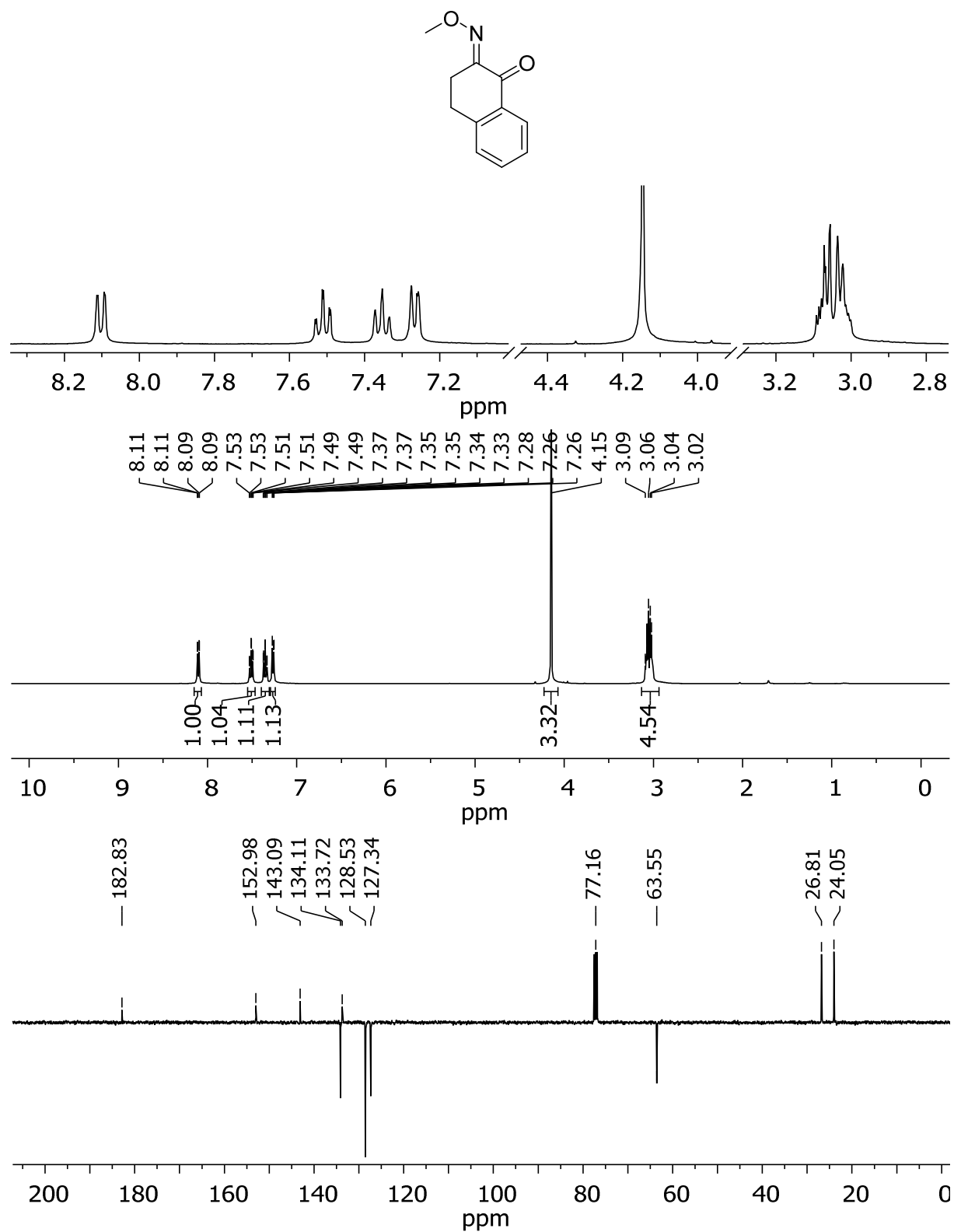
2-Hydroxy oxime ether 1u (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



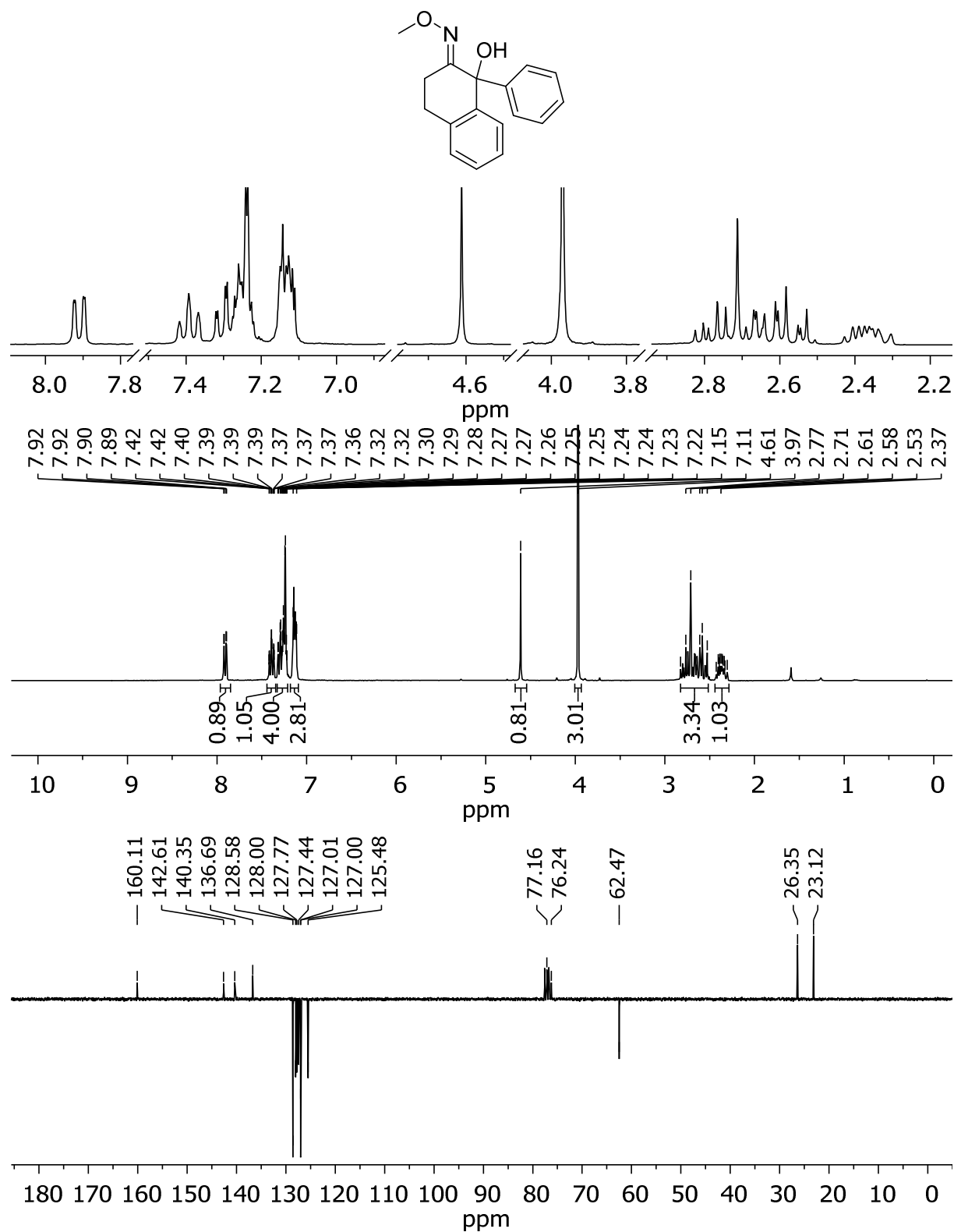
2-(Hydroxyimino)-1-tetralone S5 (DMSO-d₆, ¹H-NMR: 400 MHz, APT: 100 MHz)



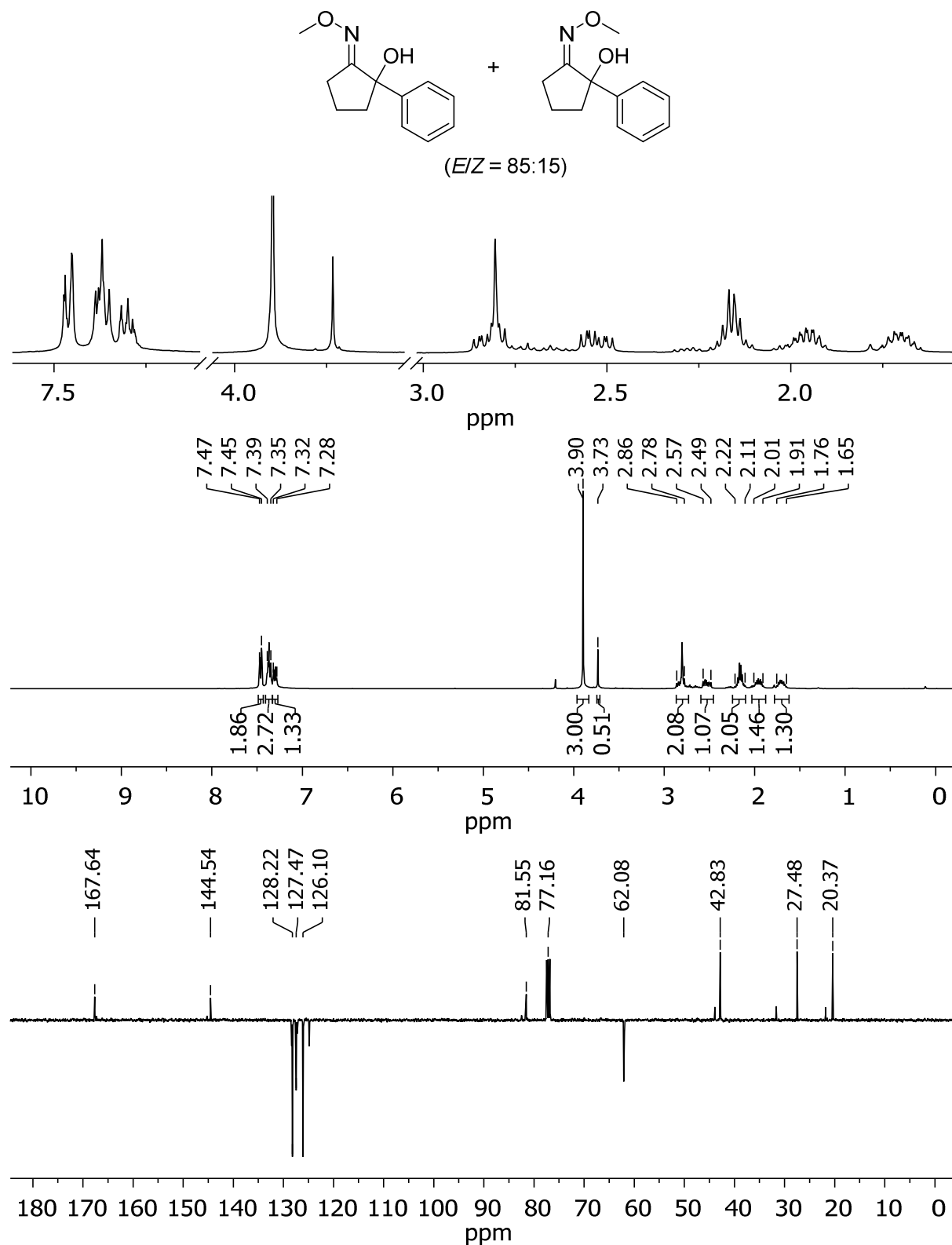
2-(Methoxyimino)-1-tetralone S6 (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



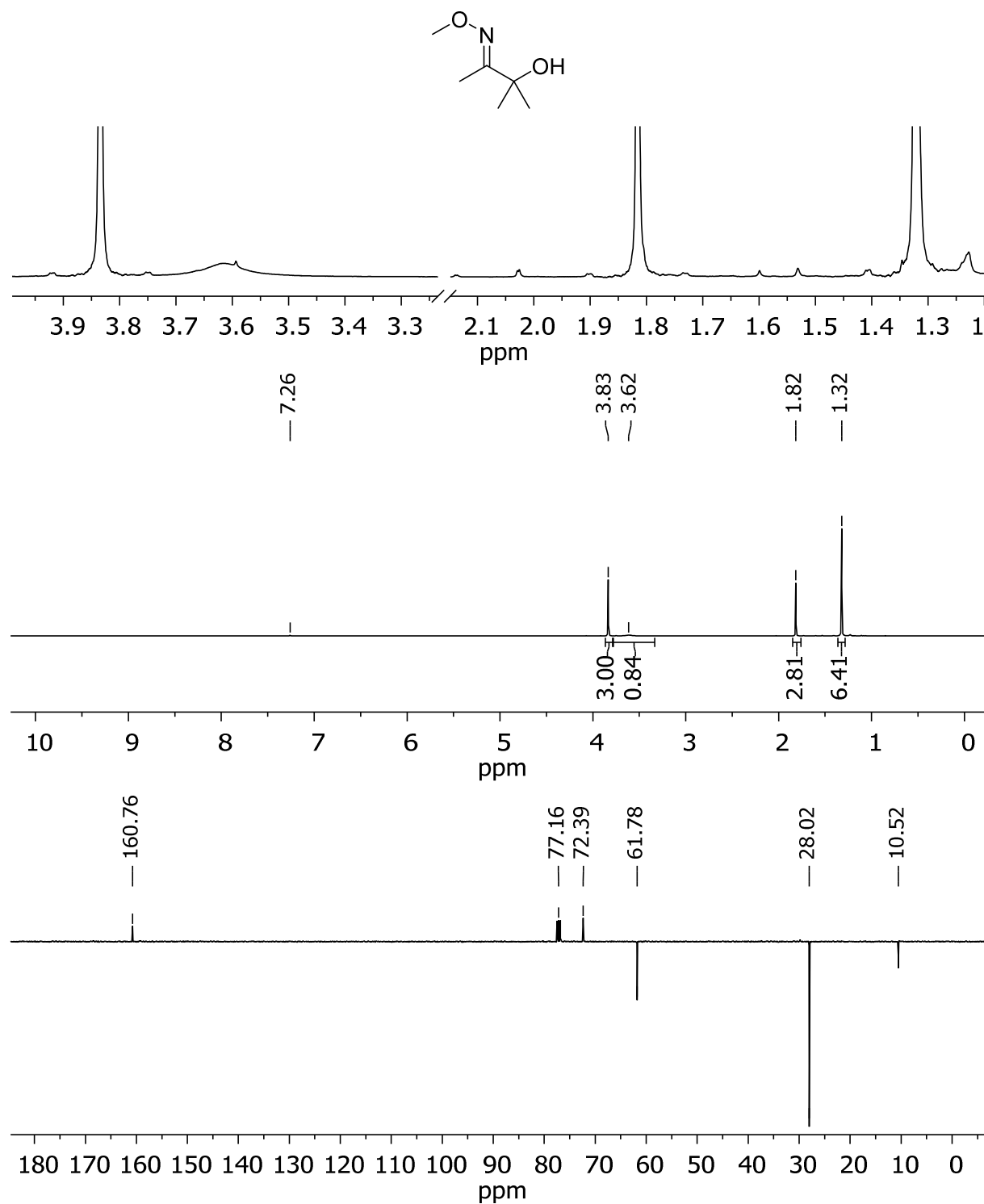
2-Hydroxy oxime ether 4 (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



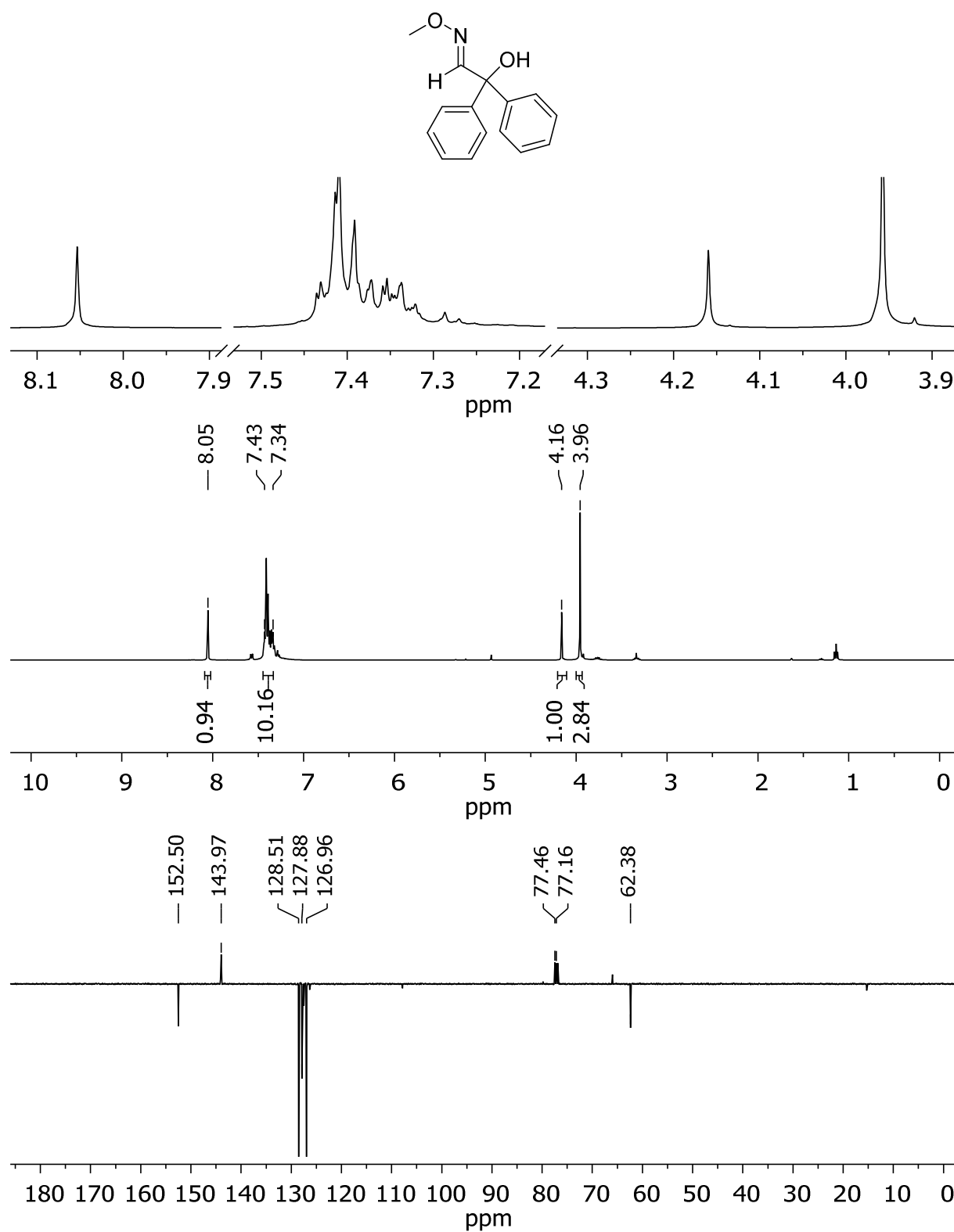
2-Hydroxy oxime ether 5 (CDCl_3 , $^1\text{H-NMR}$: 400 MHz, APT: 100 MHz)



2-Hydroxy oxime ether 6 (CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)

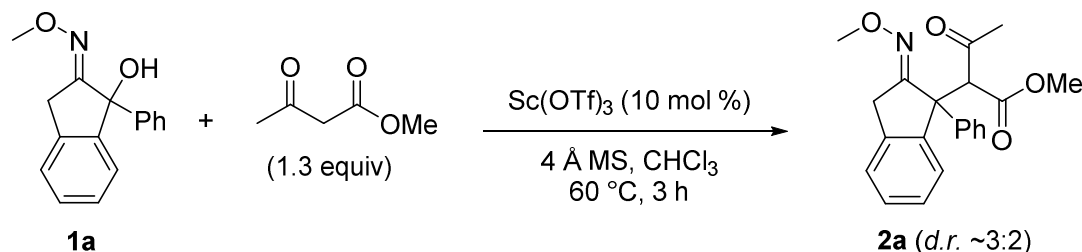


2-Hydroxy oxime ether 7 (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)

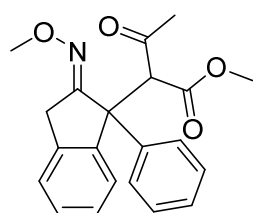


3 The Three-Component Reaction (3CR)

Intermediate 2a



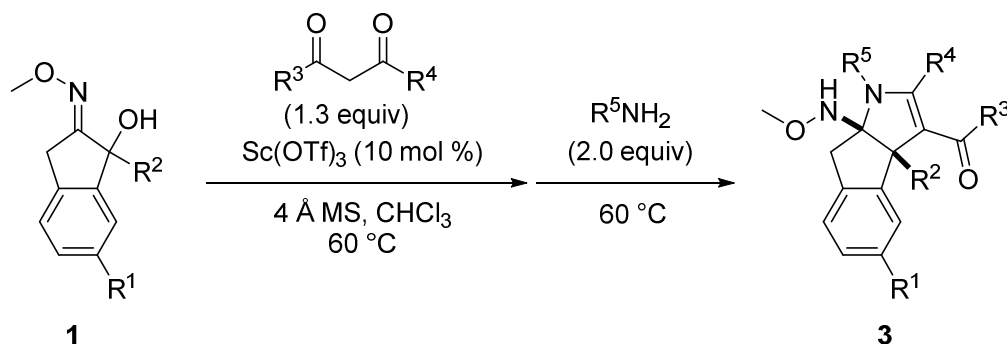
2-Hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), Sc(OTf)_3 (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were placed in an oven dried and sealable DURAN® test tube. Abs. CHCl_3 (1.0 mL) was added and the reaction mixture was heated to 60 °C for 3 h while stirring. After the reaction was completed, 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 (50% CH_2Cl_2 /hexane \rightarrow CH_2Cl_2 \rightarrow 30% MTBE/hexane). Compound **2a** was obtained as a colorless oil (68 mg, 97%, *d.r.* ~3:2) that crystallized slowly upon standing at 5 °C. The spectroscopic data are displayed for the inseparable diastereomeric mixture.



R_f: 0.73 (DCM); **mp.**: 71 – 74 °C; **¹H-NMR** (300 MHz, CDCl_3): δ (ppm) = 7.92 – 7.88 (m, 1H), 7.77 – 7.74 (m, 1H), 7.33 – 7.15 (m, 16H), 5.22 (s, 1H), 5.14 (s, 1H), 3.95 (s, 3H), 3.94 (d, J = 22.0 Hz, 1H), 3.94 (s, 3H), 3.91 (d, J = 22.0 Hz, 1H), 3.50 (d, J = 22.0 Hz, 1H), 3.50 (s, 3H), 3.47 (d, J = 22.0 Hz, 1H), 3.44 (s, 3H), 2.06 (s, 3H), 1.94 (s, 3H); **¹³C-NMR** (75 MHz, CDCl_3): δ (ppm) = 202.8 (C=O), 201.5 (C=O), 169.5 (C=O), 168.5 (C=O), 165.5 (C=N), 164.7 (C=N), 142.3 (C_q), 142.1 (C_q), 142.0 (C_q), 141.8 (C_q), 139.2 (C_q), 138.7 (C_q), 128.43 (CH), 128.39 (CH), 128.3 (3x CH), 128.2 (CH), 127.6 (CH), 127.4 (CH), 127.33 (2x CH), 127.31 (CH), 127.2 (2x CH), 127.10 (2x CH), 127.07 (CH), 125.2 (CH), 125.0 (CH), 68.4 (CH), 66.9 (CH), 62.3 (CH_3), 62.2 (CH_3), 59.3 (C_q), 58.9 (C_q), 52.14 (CH_3), 52.10 (CH_3), 32.9 (2x CH_2), 32.8 (CH_3), 30.5 (CH_3); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3447, 3066, 2952, 2934, 2893, 2813, 1743, 1717, 1596, 1493, 1481, 1459, 1445, 1433, 1356, 1327, 1241, 1203, 1191, 1166, 1152, 1048, 866, 763, 738, 725, 700, 560; **HR-MS** (ESI⁺): calcd. for $\text{C}_{21}\text{H}_{21}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 374.1363, found: 374.1360; **M**($\text{C}_{21}\text{H}_{21}\text{NO}_4$): 351.40.

3.1 Substrate Scope of the 3CR to Tetrahydroindeno[2,1-*b*]pyrroles 3

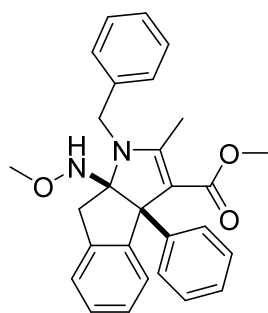
General procedure 2 of the 3CR



2-Hydroxy oxime ether **1** (1.0 equiv), a 1,3-dicarbonyl compound (1.3 equiv), Sc(OTf)₃ (0.10 equiv) and 4 Å molecular sieve (25 mg per 0.10 mmol **2**) were placed in an oven dried and sealable DURAN® test tube. Abs. CHCl₃ (1.0 mL) was added and the reaction mixture was heated to 60 °C while stirring. After complete formation of the intermediate, an amine (2.0 equiv) was added and it was stirred for the indicated time at 60 °C. The reaction mixture was quenched with sat. NaHCO₃-solution and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% → 40% MTBE/hexane). The products **3** were dried in vacuo (~0.1 mbar) at 60 °C overnight.

Tetrahydroindeno[2,1-*b*]pyrrole 3a

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 µL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 µmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 µL, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2.5 days. Compound **3a** was obtained as a colorless solid (84 mg, 95%).



R_f: 0.35 (30% MTBE/hexane); **mp.**: 176 – 178 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.64 – 7.62 (m, 1H), 7.27 – 7.17 (m, 10H), 7.09 – 7.07 (m, 1H), 6.96 – 6.93 (m, 2H), 5.14 (bs, 1H), 4.80 (d, *J* = 17.5 Hz, 1H), 4.64 (d, *J* = 17.5 Hz, 1H), 3.59 (s, 3H), 3.26 (s, 3H), 3.04 (d, *J* = 16.5 Hz, 1H), 2.95 (d, *J* = 16.5 Hz, 1H), 2.25 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.2 (C=O), 162.7 (C_q), 148.2 (C_q), 139.7 (C_q), 139.3 (C_q), 138.7 (C_q), 128.7 (2x CH), 128.1 (CH), 127.4 (3x CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 125.7 (2x CH), 123.8 (CH), 102.1 (C_q), 96.6

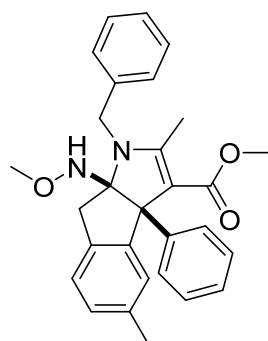
(C_q), 68.4 (C_q), 62.0 (CH₃), 49.9 (CH₃), 45.8 (CH₂), 38.8 (CH₂), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3446, 2945, 1660, 1586, 1559, 1418, 1402, 1332, 1201, 1179, 1166, 1129, 1106, 947, 759, 745, 734, 698; **HR-MS** (ESI+): calcd. for C₂₈H₂₈N₂O₃Na ([M+Na]⁺): 463.1992, found: 463.1993; **M**(C₂₈H₂₈N₂O₃): 440.54.

Gram-scale procedure for **3a**:

According to general procedure 2, 2-hydroxy oxime ether **1a** (1.01 g, 4.00 mmol, 1.00 equiv), methyl acetoacetate (559 μ L, 5.20 mmol, 1.3 equiv), Sc(OTf)₃ (197 mg, 400 μ mol, 0.10 equiv) and 4 Å molecular sieve (1.0 g) were dissolved in abs. CHCl₃ (20 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (874 μ L, 8.00 mmol, 2.00 equiv) was added and it was stirred at 60 °C for 2.5 days. Compound **3a** was obtained as a colorless solid (1.71 g, 95%). The spectroscopic data are in agreement with those listed above.

Tetrahydroindeno[2,1-*b*]pyrrole **3b**

According to general procedure 2, 2-hydroxy oxime ether **1b** (54 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3b** was obtained as a colorless solid (82 mg, 91%).

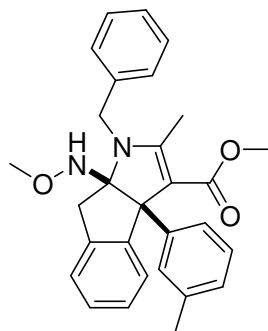


R_f: 0.18 (20% MTBE/hexane); **mp.**: 85 – 87 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.44 (s, 1H), 7.27 – 7.17 (m, 8H), 7.08 – 7.05 (m, 1H), 7.00 – 6.95 (m, 3H), 5.14 (bs, 1H), 4.82 (d, *J* = 18.0 Hz, 1H), 4.64 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 3.27 (s, 3H), 3.00 (d, *J* = 16.5 Hz, 1H), 2.88 (d, *J* = 16.5 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.2 (C=O), 162.8 (C_q), 148.3 (C_q), 139.8 (C_q), 139.3 (C_q), 137.6 (C_q), 135.5 (C_q), 128.7 (2x CH), 128.4 (CH), 127.3 (2x CH), 127.2 (CH), 126.9 (CH), 126.6 (CH), 125.7 (2x CH), 123.5 (CH), 102.0 (C_q), 96.9 (C_q), 68.3 (C_q), 61.9 (CH₃), 49.8 (CH₃), 45.7 (CH₂), 38.4 (CH₂), 21.8 (CH₃), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3455, 3023, 2942, 2893, 1664, 1586, 1564, 1494, 1465, 1446, 1431, 1421, 1403, 1335, 1296, 1213, 1183, 1169, 1076, 1131, 1106, 1076, 1065, 1041, 946, 926, 771, 744, 732, 723, 698; **HR-MS** (ESI+): calcd. for C₂₉H₃₀N₂O₃Na ([M+Na]⁺): 477.2149, found: 477.2147; **M**(C₂₉H₃₀N₂O₃): 454.57.

* One ¹³C-signal is very broad and could not be clearly detected.

Tetrahydroindeno[2,1-*b*]pyrrole 3d

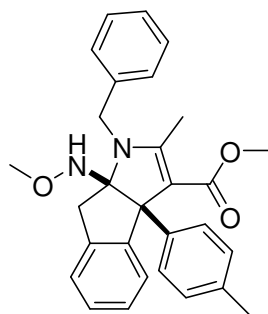
According to general procedure 2, 2-hydroxy oxime ether **1d** (54 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3d** was obtained as a colorless solid (86 mg, 95%).



R_f: 0.23 (20% MTBE/hexane); **mp.**: 185 – 187 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.65 – 7.62 (m, 1H), 7.29 – 7.17 (m, 6H), 7.13 – 7.07 (m, 3H), 7.04 – 7.02 (m, 1H), 6.96 – 6.93 (m, 2H), 5.14 (bs, 1H), 4.79 (d, J = 17.5 Hz, 1H), 4.64 (d, J = 17.5 Hz, 1H), 3.59 (s, 3H), 3.27 (s, 3H), 3.03 (d, J = 16.5 Hz, 1H), 2.95 (d, J = 16.5 Hz, 1H), 2.28 (bs, 3H), 2.25 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.2 (C=O), 162.6 (C_q), 148.2 (C_q), 139.5 (C_q), 139.4 (C_q), 138.7 (C_q), 136.7 (C_q), 128.7 (2x CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 127.0 (2x CH), 125.7 (2x CH), 123.7 (CH), 102.3 (C_q), 96.5 (C_q), 68.4 (C_q), 61.9 (CH₃), 49.9 (CH₃), 45.8 (CH₂), 38.9 (CH₂), 21.7 (CH₃), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 3023, 2943, 1661, 1601, 1586, 1566, 1477, 1459, 1424, 1402, 1328, 1294, 1193, 1186, 1166, 1127, 1064, 1049, 934, 785, 751, 736, 696; **HR-MS** (ESI⁺): calcd. for C₂₉H₃₀N₂O₃Na ([M+Na]⁺): 477.2149, found: 477.2150; **M(C₂₉H₃₀N₂O₃)**: 454.57.

Tetrahydroindeno[2,1-*b*]pyrrole 3e

According to general procedure 2, 2-hydroxy oxime ether **1e** (54 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3e** was obtained as a colorless solid (88 mg, 97%).



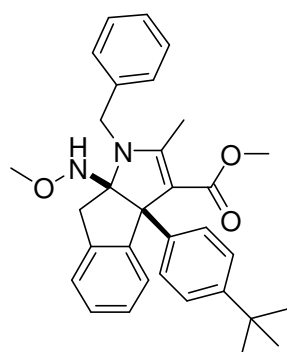
R_f: 0.29 (20% MTBE/hexane); **mp.**: 185 – 186 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.67 – 7.64 (m, 1H), 7.31 – 7.20 (m, 7H), 7.12 – 7.05 (m, 3H), 6.98 – 6.96 (m, 2H), 5.20 (bs, 1H), 4.83 (d, J = 17.5 Hz, 1H), 4.67 (d, J = 17.5 Hz, 1H), 3.63 (s, 3H), 3.32 (s, 3H), 3.06 (d, J = 16.5 Hz, 1H), 2.96 (d, J = 16.5 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.2 (C=O), 162.6 (C_q), 148.4

* Two ¹³C-signals are very broad and could not be clearly detected.

(C_q), 139.4 (C_q), 138.7 (C_q), 136.5 (C_q), 136.1 (C_q), 128.7 (2x CH), 128.2 (2x CH), 128.0 (CH), 127.3 (CH), 126.95 (CH), 126.93 (CH), 125.7 (2x CH), 123.7 (CH), 102.3 (C_q), 96.5 (C_q), 68.1 (C_q), 62.0 (CH₃), 49.9 (CH₂), 38.9 (CH₂), 21.2 (CH₃), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3501, 3024, 2941, 2894, 1663, 1644, 1558, 1475, 1421, 1402, 1330, 1297, 1200, 1186, 1165, 1129, 1107, 1063, 1040, 945, 930, 804, 750, 734, 726, 698; **HR-MS** (ESI⁺): calcd. for C₂₉H₃₀N₂O₃Na ([M+Na]⁺): 477.2149, found: 477.2152; **M**(C₂₉H₃₀N₂O₃): 454.57.

Tetrahydroindeno[2,1-*b*]pyrrole 3f

According to general procedure 2, 2-hydroxy oxime ether **1f** (62 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 4 days. Compound **3f** was obtained as a colorless solid (89 mg, 89%).



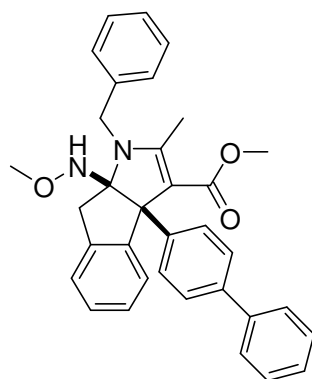
R_f: 0.32 (20% MTBE/hexane); **mp.**: 142 – 144 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.66 – 7.63 (m, 1H), 7.29 – 7.17 (m, 9H), 7.09 – 7.06 (m, 1H), 6.96 – 6.93 (m, 2H), 5.12 (bs, 1H), 4.81 (d, *J* = 17.5 Hz, 1H), 4.64 (d, *J* = 17.5 Hz, 1H), 3.60 (s, 3H), 3.26 (s, 3H), 3.03 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 2.24 (s, 3H), 1.31 (s, 9H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.3 (C=O), 162.6 (C_q), 149.2 (C_q), 148.4 (C_q), 139.4 (C_q), 138.6 (C_q), 136.4 (C_q), 128.7 (2x CH), 128.0 (CH), 127.3 (CH), 126.9 (2x CH), 125.7 (2x CH), 124.2 (2x CH), 123.7 (CH), 102.2 (C_q), 96.5 (C_q), 68.1 (C_q), 61.8 (CH₃), 49.9 (CH₃), 45.8 (CH₂), 38.9 (CH₂), 34.5 (C_q), 31.5 (3x CH₃), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3459, 3028, 2960, 2900, 2866, 1673, 1589, 1577, 1473, 1463, 1418, 1400, 1338, 1326, 1201, 1165, 1132, 754, 732; **HR-MS** (ESI⁺): calcd. for C₃₂H₃₆N₂O₃Na ([M+Na]⁺): 519.2618, found: 519.2619; **M**(C₃₂H₃₆N₂O₃): 496.65.

Tetrahydroindeno[2,1-*b*]pyrrole 3g

According to general procedure 2, 2-hydroxy oxime ether **1g** (66 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added

* One ¹³C-signal is very broad and could not be clearly detected.

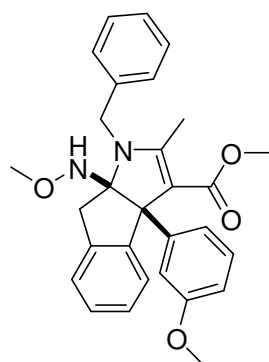
and it was stirred at 60 °C for 3 days. Compound **3g** was obtained as a colorless solid (95 mg, 92%).



R_f: 0.26 (20% MTBE/hexane); **mp.**: 109 – 111 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.69 – 7.67 (m, 1H), 7.64 – 7.62 (m, 2H), 7.52 – 7.46 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.19 (m, 8H), 7.13 – 7.10 (m, 1H), 6.98 – 6.96 (m, 2H), 5.23 (bs, 1H), 4.83 (d, *J* = 17.5 Hz, 1H), 4.67 (d, *J* = 17.5 Hz, 1H), 3.63 (s, 3H), 3.30 (s, 3H), 3.07 (d, *J* = 16.5 Hz, 1H), 2.98 (d, *J* = 16.5 Hz, 1H), 2.28 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.2 (C=O), 162.8 (C_q), 148.2 (C_q), 141.1 (C_q), 139.3 (C_q), 139.2 (C_q), 138.9 (C_q), 138.6 (C_q), 128.8 (2x CH), 128.7 (2x CH), 128.2 (CH), 127.4 (CH), 127.2 (CH), 127.1 (2x CH), 127.0 (CH), 126.9 (CH), 126.0 (2x CH), 125.7 (2x CH), 123.8 (CH), 102.1 (C_q), 96.6 (C_q), 68.2 (C_q), 62.0 (CH₃), 50.0 (CH₃), 45.8 (CH₂), 38.9 (CH₂), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3446, 3027, 2942, 1715, 1670, 1586, 1574, 1487, 1418, 1402, 1339, 1326, 1202, 1130, 1038, 758, 743, 698; **HR-MS** (ESI⁺): calcd. for C₃₄H₃₂N₂O₃Na ([M+Na]⁺): 539.2305, found: 539.2310; **M**(C₃₄H₃₂N₂O₃): 516.64.

Tetrahydroindeno[2,1-*b*]pyrrole **3h**

According to general procedure 2, 2-hydroxy oxime ether **1h** (57 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μL, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2.5 days. Compound **3h** was obtained as a colorless solid (84 mg, 89%).



R_f: 0.30 (40% MTBE/hexane); **mp.**: 169 – 171 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.65 – 7.62 (m, 1H), 7.28 – 7.17 (m, 8H), 7.08 – 7.06 (m, 1H), 6.95 – 6.93 (m, 2H), 6.77 (ddd, *J* = 8.0, 2.5, 1.0 Hz, 1H), 5.20 (bs, 1H), 4.80 (d, *J* = 17.5 Hz, 1H), 4.64 (d, *J* = 17.5 Hz, 1H), 3.73 (bs, 3H), 3.60 (s, 3H), 3.30 (s, 3H), 3.03 (d, *J* = 16.5 Hz, 1H), 2.94 (d, *J* = 16.5 Hz, 1H), 2.24 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.2 (C=O), 162.8 (C_q), 159.0 (C_q), 148.0 (C_q), 141.5 (C_q), 139.3 (C_q), 138.6 (C_q), 128.7 (2x CH), 128.2 (CH), 128.1 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 125.7 (2x CH), 123.8 (CH), 115.3 (CH), 102.2 (C_q), 96.6 (C_q), 68.4 (C_q), 62.0 (CH₃), 55.3 (CH₃), 49.9 (CH₃), 45.8 (CH₂), 38.8 (CH₂), 13.5 (CH₃);** **IR** (KBr): $\tilde{\nu}$

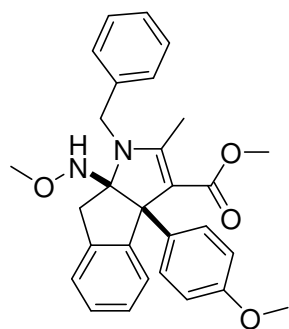
* One ¹³C-signal is very broad and could not be clearly detected.

** Two ¹³C-signals are very broad and could not be clearly detected.

(cm^{-1}) = 3433, 3025, 2981, 2939, 2896, 2835, 1664, 1607, 1584, 1572, 1487, 1478, 1461, 1450, 1426, 1402, 1360, 1328, 1287, 1264, 1201, 1167, 1127, 1108, 1076, 1055, 1043, 955, 933, 779, 767, 751, 739, 725, 696, 457; **HR-MS** (ESI⁺): calcd. for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 493.2098, found: 493.2095; **M**($\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4$): 470.57.

Tetrahydroindeno[2,1-*b*]pyrrole 3i

According to general procedure 2, 2-hydroxy oxime ether **1i** (57 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3i** was obtained as a colorless solid (92 mg, 98%).

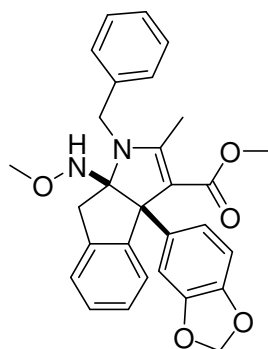


R_f: 0.26 (30% MTBE/hexane); **mp.**: 146 – 148 °C; **¹H-NMR** (400 MHz, CDCl_3): δ (ppm) = 7.63 – 7.61 (m, 1H), 7.27 – 7.17 (m, 7H), 7.08 – 7.06 (m, 1H), 6.95 – 6.93 (m, 2H), 6.80 – 6.74 (m, 2H), 5.15 (bs, 1H), 4.79 (d, J = 17.5 Hz, 1H), 4.64 (d, J = 17.5 Hz, 1H), 3.79 (s, 3H), 3.60 (s, 3H), 3.29 (s, 3H), 3.02 (d, J = 16.5 Hz, 1H), 2.92 (d, J = 16.5 Hz, 1H), 2.23 (s, 3H); **¹³C-NMR** (100 MHz, CDCl_3): δ (ppm) = 167.2 (C=O), 162.6 (C_q), 158.3 (C_q), 148.4 (C_q), 139.4 (C_q), 138.6 (C_q), 131.7 (C_q), 128.7 (2x CH), 128.0 (CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 125.7 (2x CH), 123.7 (CH), 112.8 (2x CH), 102.3 (C_q), 96.4 (C_q), 67.8 (C_q), 62.0 (CH_3), 55.2 (CH_3), 49.9 (CH_3), 45.8 (CH_2), 38.8 (CH_2), 13.5 (CH_3);* **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3464, 3064, 2943, 2895, 1670, 1604, 1586, 1567, 1509, 1473, 1462, 1402, 1339, 1327, 1294, 1248, 1201, 1178, 1165, 1130, 1107, 1064, 1036, 948, 768, 751, 726, 698; **HR-MS** (ESI⁺): calcd. for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 493.2098, found: 493.2097; **M**($\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4$): 470.57.

Tetrahydroindeno[2,1-*b*]pyrrole 3j

According to general procedure 2, 2-hydroxy oxime ether **1j** (60 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 5 h. Benzylamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3j** was obtained as a colorless solid (93 mg, 96%).

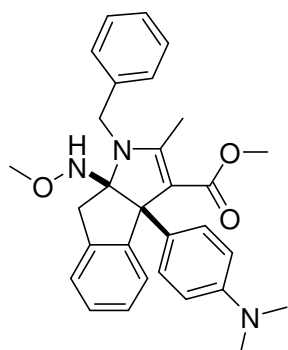
* One ^{13}C -signal is very broad and could not be clearly detected.



R_f: 0.28 (30% MTBE/hexane); **mp.**: 164 – 166 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.65 – 7.62 (m, 1H), 7.28 – 7.16 (m, 7H), 7.07 – 7.05 (m, 1H), 6.95 – 6.91 (m, 2H), 6.69 – 6.64 (m, 1H), 5.92 (s, 2H), 5.24 (bs, 1H), 4.79 (d, *J* = 17.5 Hz, 1H), 4.63 (d, *J* = 17.5 Hz, 1H), 3.62 (s, 3H), 3.33 (s, 3H), 3.01 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 2.22 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.1 (C=O), 162.5 (C_q), 148.1 (C_q), 147.1 (C_q), 146.3 (C_q), 139.3 (C_q), 138.6 (C_q), 133.8 (C_q), 128.7 (2x CH), 128.1 (CH), 127.4 (CH), 127.0 (2x CH), 125.7 (2x CH), 123.8 (CH), 107.2 (CH), 102.4 (C_q), 100.9 (C_q), 98.4 (C_q), 68.2 (C_q), 62.1 (CH₃), 50.0 (CH₃), 45.9 (CH₂), 38.8 (CH₂), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3443, 3028, 2943, 2895, 1667, 1587, 1568, 1502, 1487, 1434, 1402, 1336, 1326, 1245, 1165, 1122, 1086, 1038, 937, 808, 752, 735; **HR-MS** (ESI⁺): calcd. for C₂₉H₂₈N₂O₅Na ([M+Na]⁺): 507.1890, found: 507.1894; **M**(C₂₉H₂₈N₂O₅): 484.55.

Tetrahydroindeno[2,1-*b*]pyrrole 3k

According to general procedure 2, 2-hydroxy oxime ether **1k** (59 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μL, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 3 days. Compound **3k** was obtained as a brown solid (45 mg, 46%).



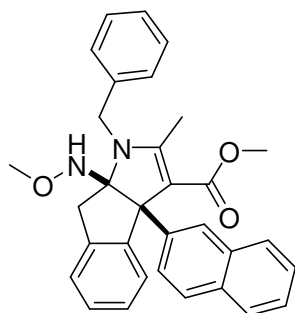
R_f: 0.41 (50% MTBE/hexane); **mp.**: 171 – 173 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.64 – 7.62 (m, 1H), 7.27 – 7.17 (m, 7H), 7.08 – 7.06 (m, 1H), 6.97 – 6.94 (m, 2H), 6.64 – 6.60 (m, 2H), 5.20 (bs, 1H), 4.79 (d, *J* = 17.5 Hz, 1H), 4.65 (d, *J* = 17.5 Hz, 1H), 3.60 (s, 3H), 3.31 (s, 3H), 3.03 (d, *J* = 16.5 Hz, 1H), 2.94 (d, *J* = 16.5 Hz, 1H), 2.93 (s, 6H), 2.24 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.4 (C=O), 162.5 (C_q), 149.3 (C_q), 148.6 (C_q), 139.5 (C_q), 138.8 (C_q), 128.6 (2x CH), 127.9 (CH), 127.3 (C_q), 127.1 (CH), 127.0 (CH), 126.9 (CH), 125.8 (2x CH), 123.6 (CH), 111.7 (2x CH), 102.4 (C_q), 96.4 (C_q), 67.8 (C_q), 62.0 (CH₃), 50.0 (CH₃), 46.0 (CH₂), 40.7 (2x CH₃), 39.0 (CH₂), 13.5 (CH₃);** **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3444, 3064, 2943, 2803, 1670, 1613, 1587, 1574, 1519, 1401, 1354, 1339, 1200, 1165, 1121, 948, 809, 758, 743; **HR-MS** (ESI⁺): calcd. for C₃₀H₃₃N₃O₃Na ([M+Na]⁺): 506.2414, found: 506.2410; **M**(C₃₀H₃₃N₃O₃): 483.61.

* Two ¹³C-signals are very broad and could not be clearly detected.

** One ¹³C-signal is very broad and could not be clearly detected.

Tetrahydroindeno[2,1-*b*]pyrrole 3l

According to [general procedure 2](#), 2-hydroxy oxime ether **1l** (61 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3l** was obtained as a colorless solid (92 mg, 94%).

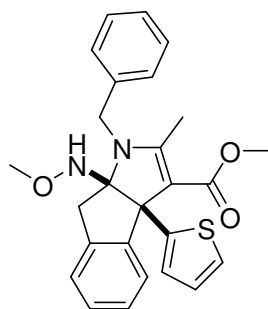


R_f: 0.21 (20% MTBE/hexane); **mp.**: 182 – 184 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.83 – 7.81 (m, 1H), 7.75 – 7.72 (m, 2H), 7.68 – 7.65 (m, 2H), 7.45 – 7.38 (m, 3H), 7.33 – 7.28 (m, 2H), 7.23 – 7.19 (m, 3H), 7.16 – 7.12 (m, 1H), 6.98 – 6.95 (m, 2H), 5.15 (bs, 1H), 4.84 (d, J = 18.0 Hz, 1H), 4.68 (d, J = 18.0 Hz, 1H), 3.57 (s, 3H), 3.25 (bs, 3H), 3.08 (d, J = 16.5 Hz, 1H), 2.99 (d, J = 16.5 Hz, 1H), 2.31 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.3 (C=O), 163.0 (C_q), 148.3 (C_q), 139.3 (C_q), 133.1 (C_q), 132.7 (C_q), 128.7 (2x CH), 128.2 (CH), 127.5 (2x CH), 127.0 (2x CH), 126.4 (CH), 125.7 (2x CH), 125.6 (CH), 125.5 (CH), 123.9 (CH), 102.2 (C_q), 96.8 (C_q), 68.5 (C_q), 62.0 (CH₃), 49.9 (CH₃), 45.8 (CH₂), 38.9 (CH₂), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3443, 3059, 2943, 1671, 1588, 1570, 1418, 1403, 1336, 1325, 1191, 1165, 1134, 1103, 748; **HR-MS** (ESI⁺): calcd. for C₃₂H₃₀N₂O₃Na ([M+Na]⁺): 513.2149, found: 513.2148.

M(C₃₂H₃₀N₂O₃): 490.60.

Tetrahydroindeno[2,1-*b*]pyrrole 3m

According to [general procedure 2](#), 2-hydroxy oxime ether **1m** (52 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 3 days. Compound **3m** was obtained as a dark violet solid (59 mg, 66%).



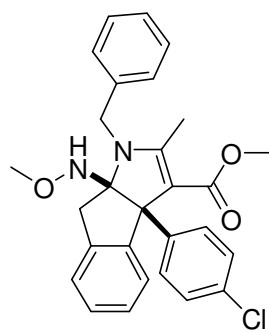
R_f: 0.29 (30% MTBE/hexane); **mp.**: 155 – 157 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.76 – 7.73 (m, 1H), 7.28 – 7.18 (m, 6H), 7.10 – 7.07 (m, 1H), 7.01 – 6.94 (m, 3H), 6.78 – 6.75 (m, 1H), 5.46 (bs, 1H), 4.77 (d, J = 17.5 Hz, 1H), 4.67 (d, J = 17.5 Hz, 1H), 3.61 (s, 3H), 3.36

* Five ¹³C-signals are very broad and could not be clearly detected.

(s, 3H), 3.15 (d, $J = 16.5$ Hz, 1H), 3.05 (d, $J = 16.5$ Hz, 1H), 2.23 (s, 3H); **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ (ppm) = 166.8 (C=O), 162.1 (C_q), 147.4 (C_q), 145.3 (C_q), 139.2 (C_q), 138.7 (C_q), 128.7 (2x CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.01 (CH), 126.96 (CH), 126.6 (CH), 125.8 (2x CH), 124.6 (CH), 123.7 (CH), 103.3 (C_q), 96.4 (C_q), 65.4 (C_q), 62.4 (CH_3), 50.0 (CH_3), 46.2 (CH_2), 39.0 (CH_2), 13.4 (CH_3); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3446, 3268, 3024, 2986, 2949, 2934, 2895, 1660, 1585, 1563, 1494, 1478, 1459, 1446, 1433, 1419, 1402, 1360, 1330, 1294, 1239, 1200, 1181, 1166, 1122, 1100, 1080, 1065, 1044, 1029, 933, 814, 765, 753, 735, 720, 699, 474; **HR-MS** (ESI⁺): calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 469.1556, found: 469.1553; **M**($\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$): 446.57.

Tetrahydroindeno[2,1-*b*]pyrrole 3n

According to [general procedure 2](#), 2-hydroxy oxime ether **1n** (58 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 20 h. Benzylamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3n** was obtained as a colorless solid (95 mg, >99%).



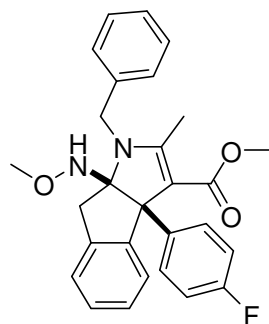
R_f: 0.24 (20% MTBE/hexane); **mp.**: 61 – 63 °C; **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ (ppm) = 7.62 – 7.59 (m, 1H), 7.33 – 7.16 (m, 9H), 7.09 – 7.07 (m, 1H), 6.94 – 6.91 (m, 2H), 5.16 (bs, 1H), 4.80 (d, $J = 18.0$ Hz, 1H), 4.63 (d, $J = 18.0$ Hz, 1H), 3.60 (s, 3H), 3.28 (s, 3H), 3.03 (d, $J = 16.5$ Hz, 1H), 2.90 (d, $J = 16.5$ Hz, 1H), 2.25 (s, 3H); **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ (ppm) = 167.0 (C=O), 162.9 (C_q), 147.9 (C_q), 139.1 (C_q), 138.5 (C_q), 138.4 (C_q), 132.4 (C_q), 128.7 (2x CH), 128.2 (CH), 127.6 (CH), 127.5 (2x CH), 127.0 (CH), 126.8 (CH), 125.7 (2x CH), 123.9 (CH), 101.8 (C_q), 96.6 (C_q), 67.9 (C_q), 62.0 (CH_3), 49.9 (CH_3), 45.7 (CH_2), 38.7 (CH_2), 13.5 (CH_3);* **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3441, 3220, 3064, 3028, 2943, 2897, 1665, 1577, 1490, 1475, 1419, 1401, 1361, 1340, 1326, 1295, 1270, 1201, 1184, 1166, 1130, 1104, 1092, 1063, 1038, 1028, 1015, 950, 943, 930, 908, 811, 754, 733, 710, 696, 456; **HR-MS** (ESI⁺): calcd. for $\text{C}_{28}\text{H}_{27}^{35}\text{ClN}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 497.1602, found: 497.1600; **M**($\text{C}_{28}\text{H}_{27}\text{ClN}_2\text{O}_3$): 474.99.

Tetrahydroindeno[2,1-*b*]pyrrole 3o

According to [general procedure 2](#), 2-hydroxy oxime ether **1o** (54 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv)

* One ^{13}C -signal is very broad and could not be clearly detected.

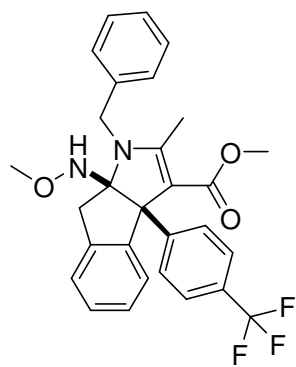
and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 5 h. Benzylamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3o** was obtained as a colorless solid (85 mg, 93%).



R_f: 0.28 (20% MTBE/hexane); **mp.**: 119 – 121 °C; **¹H-NMR** (400 MHz, CDCl_3): δ (ppm) = 7.64 – 7.62 (m, 1H), 7.31 – 7.19 (m, 7H), 7.11 – 7.09 (m, 1H), 6.98 – 6.93 (m, 4H), 5.17 (bs, 1H), 4.82 (d, J = 17.5 Hz, 1H), 4.66 (d, J = 17.5 Hz, 1H), 3.62 (s, 3H), 3.31 (s, 3H), 3.05 (d, J = 16.5 Hz, 1H), 2.93 (d, J = 16.5 Hz, 1H), 2.27 (s, 3H); **¹³C-NMR** (100 MHz, CDCl_3): δ (ppm) = 167.1 (C=O), 162.8 (C_q), 161.8 (d, J = 245.0 Hz, C_q), 148.1 (C_q), 139.2 (C_q), 138.4 (C_q), 135.5 (d, J = 3.0 Hz, C_q), 128.7 (2x CH), 128.2 (CH), 127.5 (CH), 127.0 (CH), 126.8 (CH), 125.7 (2x CH), 123.8 (CH), 114.1 (d, J = 21.0 Hz, 2x CH), 102.1 (C_q), 96.5 (C_q), 67.8 (C_q), 62.0 (CH_3), 49.9 (CH_3), 45.7 (CH_2), 38.7 (CH_2), 13.5 (CH_3);* **¹⁹F-NMR** (375 MHz, CDCl_3): δ (ppm) = –116.9; **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3446, 3194, 3062, 2945, 2899, 1670, 1643, 1601, 1587, 1568, 1507, 1471, 1454, 1403, 1342, 1326, 1223, 1214, 1202, 1186, 1160, 1129, 1092, 1039, 1017, 952, 828, 815, 768, 748, 734, 698; **HR-MS** (ESI⁺): calcd. for $\text{C}_{28}\text{H}_{27}\text{FN}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 481.1898, found: 481.1899; **M**($\text{C}_{28}\text{H}_{27}\text{FN}_2\text{O}_3$): 458.53.

Tetrahydroindeno[2,1-*b*]pyrrole **3p**

According to general procedure 2, 2-hydroxy oxime ether **1p** (64 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 51 h. Benzylamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 5 days. Compound **3p** was obtained as a colorless solid (96 mg, 94%).



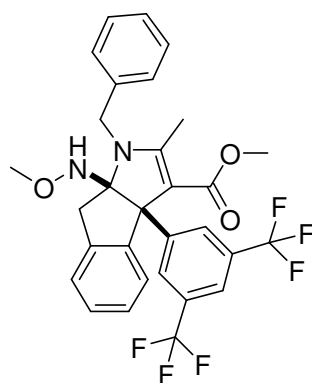
R_f: 0.27 (20% MTBE/hexane); **mp.**: 50 – 52 °C; **¹H-NMR** (400 MHz, CDCl_3): δ (ppm) = 7.64 – 7.62 (m, 1H), 7.52 – 7.49 (m, 2H), 7.33 – 7.21 (m, 7H), 7.14 – 7.10 (m, 1H), 6.97 – 6.95 (m, 2H), 5.16 (bs, 1H), 4.83 (d, J = 18.0 Hz, 1H), 4.67 (d, J = 18.0 Hz, 1H), 3.63 (s, 3H), 3.29 (s, 3H), 3.07 (d, J = 17.0 Hz, 1H), 2.94 (d, J = 17.0 Hz, 1H), 2.29 (s, 3H); **¹³C-NMR** (100 MHz, CDCl_3): δ (ppm) = 166.9 (C=O), 163.0 (C_q), 147.7 (C_q), 144.3 (C_q), 139.0 (C_q), 138.4 (C_q), 128.8 (2x CH), 128.7 (q, J = 32.5 Hz, C_q), 128.4 (CH), 127.8 (CH), 127.1 (CH), 126.8 (CH), 125.6 (2x CH), 124.6 (q, J = 271.5 Hz, C_q), 124.2 (2x CH), 124.0

* One ¹³C-signal is very broad and could not be clearly detected.

(CH), 101.7 (C_q), 96.8 (C_q), 68.2 (C_q), 62.0 (CH₃), 50.0 (CH₃), 45.6 (CH₂), 38.7 (CH₂), 13.5 (CH₃);* **¹⁹F-NMR** (375 MHz, CDCl₃): δ (ppm) = −62.2; **IR** (KBr): $\tilde{\nu}$ (cm^{−1}) = 3434, 3206, 3066, 2944, 1670, 1587, 1569, 1475, 1409, 1326, 1298, 1291, 1203, 1164, 1129, 1068, 1038, 1019, 946, 930, 831, 766, 752, 733, 698; **HR-MS** (ESI⁺): calcd. for C₂₉H₂₇F₃N₂O₃Na ([M+Na]⁺): 531.1866, found: 531.1868; **M**(C₂₉H₂₇F₃N₂O₃): 508.54.

Tetrahydroindeno[2,1-*b*]pyrrole 3q

According to general procedure 2, 2-hydroxy oxime ether **1q** (78 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 18 h. Benzylamine (44 μL, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 6 days. Compound **3q** was obtained as a colorless solid (111 mg, 96%).



R_f: 0.23 (20% MTBE/hexane); **mp.**: 186 – 187 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.73 (s, 1H), 7.56 – 7.53 (m, 1H), 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 7.12 – 7.10 (m, 1H), 6.94 – 6.92 (m, 2H), 5.07 (bs, 1H), 4.78 (d, *J* = 18.0 Hz, 1H), 4.63 (d, *J* = 18.0 Hz, 1H), 3.58 (s, 3H), 3.20 (s, 3H), 3.04 (d, *J* = 17.0 Hz, 1H), 2.88 (d, *J* = 17.0 Hz, 1H), 2.29 (s, 3H);** **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 166.6 (C=O), 163.6 (C_q), 146.8 (C_q), 143.5 (C_q), 138.7 (C_q), 138.1 (C_q), 130.4 (q, *J* = 33.0 Hz, C_q), 128.84 (2x CH), 128.8 (CH), 128.3 (CH), 127.2 (CH), 126.5 (CH), 125.6 (2x CH), 124.2 (CH), 123.8 (q, *J* = 272.5 Hz, C_q), 120.5 (m, CH), 101.0 (C_q), 96.9 (C_q), 68.2 (C_q), 61.8 (CH₃), 50.0 (CH₃), 45.4 (CH₂), 38.6 (CH₂), 13.6 (CH₃);* **¹⁹F-NMR** (375 MHz, CDCl₃): δ (ppm) = −62.6; **IR** (KBr): $\tilde{\nu}$ (cm^{−1}) = 3443, 3214, 3030, 2946, 2903, 1665, 1637, 1587, 1567, 1471, 1410, 1372, 1340, 1278, 1202, 1176, 1133, 1107, 1038, 744, 681; **HR-MS** (ESI⁺): calcd. for C₃₀H₂₇F₆N₂O₃ ([M+H]⁺): 577.1920, found: 577.1920; **M**(C₃₀H₂₆F₆N₂O₃): 576.54.

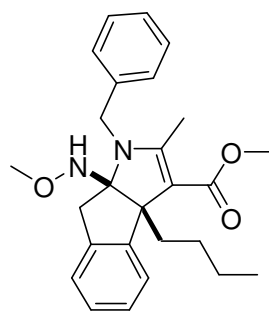
Tetrahydroindeno[2,1-*b*]pyrrole 3r

According to general procedure 2, 2-hydroxy oxime ether **1r** (47 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 23 h. Benzylamine (44 μL, 0.40 mmol, 2.0 equiv) was added

* One ¹³C-signal is very broad and could not be clearly detected.

** One ¹H-signal is very broad and could not be clearly detected.

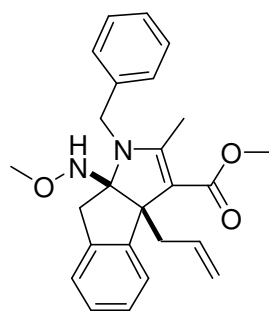
and it was stirred at 60 °C for 2.5 days. Compound **3r** was obtained as a colorless oil (24 mg, 29%).



R_f: 0.35 (20% MTBE/hexane); **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.75 (d', *J* = 7.5 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.19 – 7.17 (m, 3H), 6.99 (d', *J* = 7.5 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.10 (bs, 1H), 4.88 (d, *J* = 18.0 Hz, 1H), 4.61 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 3.05 (s, 2H), 2.69 – 2.61 (m, 1H), 2.14 – 2.02 (m, 4H), 1.34 – 1.25 (m, 3H), 1.01 – 0.88 (m, 1H), 0.86 (t, *J* = 7.0 Hz, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.5 (C=O), 160.6 (C_q), 148.8 (C_q), 139.4 (C_q), 137.8 (C_q), 128.6 (2x CH), 127.7 (CH), 126.9 (CH), 126.8 (CH), 125.6 (2x CH), 125.5 (CH), 123.7 (CH), 102.3 (C_q), 95.2 (C_q), 62.9 (C_q), 62.8 (CH₃), 50.0 (CH₃), 45.7 (CH₂), 39.7 (CH₂), 32.5 (CH₂), 27.9 (CH₂), 23.7 (CH₂), 14.2 (CH₃), 13.7 (CH₃); **IR** (film): $\tilde{\nu}$ (cm⁻¹) = 3065, 3009, 2953, 2869, 2859, 1739, 1723, 1655, 1587, 1568, 1495, 1464, 1434, 1407, 1361, 1341, 1295, 1184, 1172, 1152, 1072, 1045, 1028, 755, 735, 697; **HR-MS** (ESI⁺): calcd. for C₂₆H₃₂N₂O₃Na ([M+Na]⁺): 443.2305, found: 443.2306; **M**(C₂₆H₃₂N₂O₃): 420.55.

Tetrahydroindeno[2,1-*b*]pyrrole **3s**

According to general procedure 2, 2-hydroxy oxime ether **1s** (44 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture stirred at room temperature for 40 h as well as at 60 °C for 25 h. Benzylamine (44 μL, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 3 days. Compound **3s** was obtained as a colorless solid (24 mg, 29%).

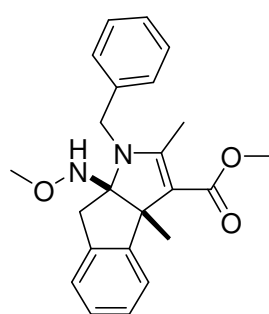


R_f: 0.38 (20% MTBE/hexane); **mp.**: 78 – 80 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.75 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.19 – 7.14 (m, 4H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.54 (bs, 1H), 5.58 (dtd, *J* = 17.0, 10.0, 5.0 Hz, 1H), 5.26 (dt, *J* = 17.0, 2.5 Hz, 1H), 4.96 (dt, *J* = 10.0, 2.0 Hz, 1H), 4.86 (d, *J* = 18.0 Hz, 1H), 4.55 (d, *J* = 18.0 Hz, 1H), 3.75 (s, 3H), 3.61 – 3.55 (m, 4H), 3.06 (dd, *J* = 15.0, 9.5 Hz, 1H), 2.95 (d, *J* = 16.5 Hz, 1H), 2.78 (d, *J* = 16.5 Hz, 1H), 2.12 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.4 (C=O), 161.4 (C_q), 148.3 (C_q), 139.4 (C_q), 138.0 (CH), 137.5 (C_q), 128.7 (2x CH), 127.9 (CH), 127.2 (CH), 126.9 (CH), 125.6 (2x CH), 125.4 (CH), 123.8 (CH), 116.4 (CH₂), 102.3 (C_q), 95.7 (C_q), 62.8 (CH₃), 61.5 (C_q), 50.0 (CH₃), 45.1 (CH₂), 39.8 (CH₂), 38.3 (CH₂), 13.6 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3434, 3065, 2946, 2900, 1727, 1664, 1586, 1571, 1495, 1477, 1455, 1436, 1409, 1342, 1184, 1170, 1068,

1043, 758, 736, 699; **HR-MS** (ESI⁺): calcd. for C₂₅H₂₉N₂O₃ ([M+H]⁺): 405.2173, found: 405.2175; **M**(C₂₅H₂₈N₂O₃): 404.51.

Tetrahydroindeno[2,1-*b*]pyrrole 3t

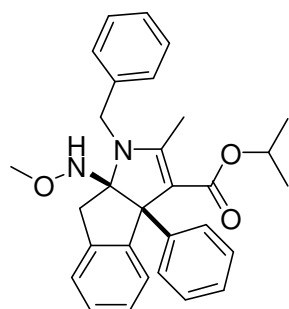
According to general procedure 2, 2-hydroxy oxime ether **1t** (38 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture stirred at room temperature for 40 h as well as at 60 °C for 25 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 3 days. Compound **3t** was obtained as a colorless solid (38 mg, 50%).



R_f: 0.13 (30% MTBE/hexane); **mp.**: 68 – 70 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.71 (d', *J* = 7.5 Hz, 1H), 7.27 – 7.12 (m, 5H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.89 – 6.87 (m, 2H), 6.03 (bs, 1H), 4.83 (d, *J* = 18.0 Hz, 1H), 4.58 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 3.55 (s, 3H), 2.99 (d, *J* = 16.5 Hz, 1H), 2.89 (d, *J* = 16.5 Hz, 1H), 2.14 (s, 3H), 1.71 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.5 (C=O), 161.0 (C_q), 150.5 (C_q), 139.4 (C_q), 136.4 (C_q), 128.7 (2x CH), 127.8 (CH), 127.0 (CH), 126.9 (CH), 125.6 (2x CH), 125.1 (CH), 123.9 (CH), 103.3 (C_q), 95.5 (C_q), 62.7 (CH₃), 58.8 (C_q), 50.0 (CH₃), 45.3 (CH₂), 38.2 (CH₂), 19.9 (CH₃), 13.4 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3465, 3025, 2976, 2943, 2901, 1660, 1587, 1572, 1476, 1460, 1433, 1404, 1341, 1331, 1196, 1177, 1157, 1087, 1059, 1024, 935, 761, 748, 734, 697; **HR-MS** (ESI⁺): calcd. for C₂₃H₂₆N₂O₃Na ([M+Na]⁺): 401.1836, found: 401.1831; **M**(C₂₃H₂₆N₂O₃): 378.47.

Tetrahydroindeno[2,1-*b*]pyrrole 3u

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), *iso*-propyl acetoacetate (38 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3u** was obtained as a colorless solid (89 mg, 95%).

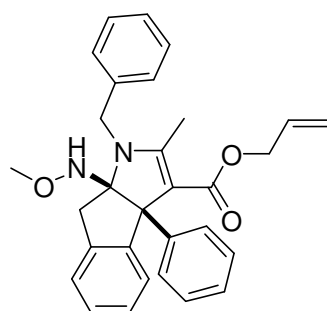


R_f: 0.50 (30% MTBE/hexane); **mp.**: 46 – 48 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.76 – 7.73 (m, 1H), 7.31 – 7.20 (m, 10H), 7.12 – 7.11 (m, 1H), 6.98 – 6.97 (m, 2H), 5.24 (bs, 1H), 5.04 (h, *J* = 6.5 Hz, 1H), 4.84 (d, *J* = 17.5 Hz, 1H), 4.68 (d, *J* = 17.5 Hz, 1H), 3.33 (s, 3H), 3.07 (d, *J* = 16.5 Hz, 1H), 2.96 (d, *J* = 16.5 Hz, 1H), 2.29 (s,

3H), 1.20 (d, $J = 6.5$ Hz, 1H), 0.94 (d, $J = 6.5$ Hz, 1H); **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ (ppm) = 166.4 (C=O), 162.7 (C_q), 148.1 (C_q), 140.0 (C_q), 139.4 (C_q), 138.7 (C_q), 128.6 (2x CH), 127.9 (CH), 127.3 (CH), 127.2 (2x CH), 127.0 (CH), 126.9 (CH), 126.5 (CH), 125.7 (2x CH), 123.8 (CH), 102.8 (C_q), 96.5 (C_q), 68.5 (C_q), 65.6 (CH), 62.0 (CH_3), 45.7 (CH_2), 38.7 (CH_2), 22.4 (CH_3), 21.9 (CH_3), 13.3 (CH_3);* **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3446, 3061, 3026, 2973, 2933, 2897, 1664, 1589, 1573, 1494, 1466, 1452, 1417, 1403, 1374, 1347, 1313, 1294, 1203, 1166, 1132, 1105, 1076, 1051, 1039, 953, 770, 754, 747, 733, 698; **HR-MS** (ESI⁺): calcd. for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 491.2305, found: 491.2305; **$\text{M}(\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_3)$** : 468.60.

Tetrahydroindeno[2,1-*b*]pyrrole **3v**

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), allyl acetoacetate (36 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3v** was obtained as a colorless solid (88 mg, 94%).



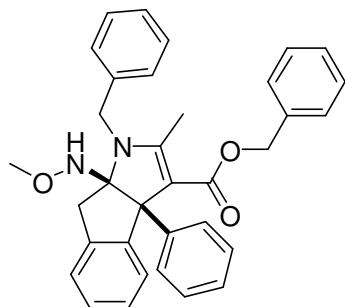
R_f: 0.33 (20% MTBE/hexane); **mp.**: 79 – 82 °C; **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ (ppm) = 7.65 – 7.62 (m, 1H), 7.26 – 7.15 (m, 10H), 7.07 – 7.04 (m, 1H), 6.93 – 6.91 (m, 2H), 5.71 (ddt, $J = 17.5, 10.5, 5.0$ Hz, 1H), 5.15 (bs, 1H), 4.95 (dq, $J = 10.5, 1.5$ Hz, 1H), 4.87 (dq, $J = 17.5, 1.5$ Hz, 1H), 4.79 (d, $J = 17.5$ Hz, 1H), 4.62 (d, $J = 17.5$ Hz, 1H), 4.57 (ddt, $J = 14.0, 5.0, 1.5$ Hz, 1H), 4.46 (ddt, $J = 14.0, 5.0, 1.5$ Hz, 1H), 3.26 (s, 3H), 3.02 (d,

$J = 16.5$ Hz, 1H), 2.92 (d, $J = 16.5$ Hz, 1H), 2.24 (s, 3H); **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ (ppm) = 166.4 (C=O), 163.2 (C_q), 148.2 (C_q), 139.7 (C_q), 139.2 (C_q), 138.6 (C_q), 133.3 (CH), 128.7 (2x CH), 128.1 (CH), 127.4 (3x CH), 127.0 (2x CH), 126.7 (CH), 125.7 (2x CH), 123.8 (CH), 116.4 (CH_2), 102.1 (C_q), 96.6 (C_q), 68.4 (C_q), 63.5 (CH_2), 62.0 (CH_3), 45.8 (CH_2), 38.8 (CH_2), 13.5 (CH_3);* **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3446, 3061, 3026, 2934, 2895, 1671, 1645, 1587, 1569, 1494, 1472, 1447, 1401, 1350, 1322, 1294, 1200, 1164, 1129, 1039, 948, 933, 755, 746, 734, 698; **HR-MS** (ESI⁺): calcd. for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 489.2149, found: 489.2148; **$\text{M}(\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_3)$** : 466.58.

* One ^{13}C -signal is very broad and could not be clearly detected.

Tetrahydroindeno[2,1-*b*]pyrrole 3w

According to [general procedure 2](#), 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), benzyl acetoacetate (45 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3w** was obtained as a colorless solid (93 mg, 93%).

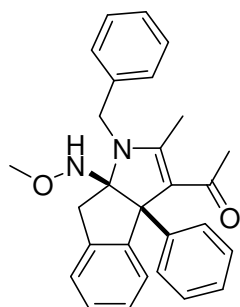


R_f: 0.28 (20% MTBE/hexane); **mp.**: 123 – 125 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.57 – 7.54 (m, 1H), 7.26 – 7.13 (m, 13H), 7.09 – 7.06 (m, 1H), 6.96 – 6.88 (m, 4H), 5.20 (bs, 1H), 5.16 (d, J = 13.0 Hz, 1H), 5.04 (d, J = 13.0 Hz, 1H), 4.82 (d, J = 18.0 Hz, 1H), 4.65 (d, J = 18.0 Hz, 1H), 3.29 (s, 3H), 3.05 (d, J = 16.5 Hz, 1H), 2.95 (d, J = 16.5 Hz, 1H), 2.28 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.6 (C=O), 163.5 (C_q),

148.0 (C_q), 139.9 (C_q), 139.2 (C_q), 138.6 (C_q), 137.2 (C_q), 128.7 (2x CH), 128.2 (2x CH), 128.1 (CH), 127.5 (4x CH), 127.4 (CH), 127.3 (CH), 127.0 (2x CH), 126.7 (CH), 125.7 (2x CH), 123.8 (CH), 102.1 (C_q), 96.6 (C_q), 68.5 (C_q), 64.6 (CH₂), 62.0 (CH₃), 45.8 (CH₂), 38.8 (CH₂), 13.5 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 3061, 3029, 2936, 2894, 1666, 1586, 1570, 1494, 1473, 1418, 1399, 1324, 1295, 1199, 1162, 1129, 948, 754, 745, 733, 698; **HR-MS** (ESI⁺): calcd. for C₃₄H₃₂N₂O₃Na ([M+Na]⁺): 539.2305, found: 539.2307; **M(C₃₄H₃₂N₂O₃)**: 516.64.

Tetrahydroindeno[2,1-*b*]pyrrole 3x

According to [general procedure 2](#), 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), acetylacetone (27 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3x** was obtained as a colorless solid (75 mg, 88%).



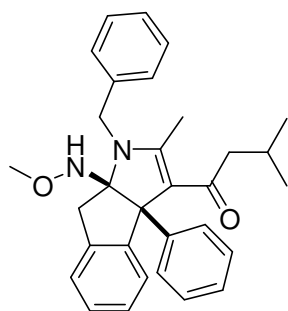
R_f: 0.22 (50% MTBE/hexane); **mp.**: 173 – 175 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.60 – 7.57 (m, 1H), 7.31 – 7.16 (m, 10H), 7.07 – 7.05 (m, 1H), 6.89 – 6.87 (m, 2H), 5.15 (bs, 1H), 4.87 (d, J = 18.0 Hz, 1H), 4.66 (d, J = 18.0 Hz, 1H), 3.32 (s, 3H), 3.01 (d, J = 16.5 Hz, 1H), 2.90 (d, J = 16.5 Hz, 1H), 2.26 (s, 3H), 2.15 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 191.5 (C=O), 163.0 (C_q), 148.0 (C_q), 139.4 (C_q), 138.7 (C_q),

* One ¹³C-signal is very broad and could not be clearly detected.

138.5 (C_q), 128.7 (2x CH), 128.2 (CH), 127.8 (2x CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 126.7 (CH), 125.6 (2x CH), 123.8 (CH), 115.8 (C_q), 96.7 (C_q), 68.8 (C_q), 62.0 (CH₃), 45.8 (CH₂), 38.4 (CH₂), 31.1 (CH₃), 14.7 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3441, 3156, 3059, 3028, 2940, 2889, 2804, 1601, 1585, 1572, 1535, 1494, 1474, 1447, 1397, 1350, 1340, 1298, 1162, 1033, 1016, 973, 949, 930, 755, 735, 699; **HR-MS** (ESI⁺): calcd. for C₂₈H₂₈N₂O₂Na ([M+Na]⁺): 447.2043, found: 447.2046; **M**(C₂₈H₂₈N₂O₂): 424.54.

Tetrahydroindeno[2,1-*b*]pyrrole 3y

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 6-methylheptane-2,4-dione (40 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 3 days. Compound **3y** was obtained as a colorless solid (43 mg, 46%).



R_f: 0.29 (30% MTBE/hexane); **mp.**: 59 – 61 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.68 – 7.66 (m, 1H), 7.29 – 7.18 (m, 10H), 7.08 – 7.06 (m, 1H), 6.92 – 6.90 (m, 2H), 5.13 (bs, 1H), 4.87 (d, *J* = 18.0 Hz, 1H), 4.66 (d, *J* = 18.0 Hz, 1H), 3.32 (s, 3H), 3.02 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 2.41 – 2.29 (m, 2H), 2.27 – 2.20 (m, 4H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H);

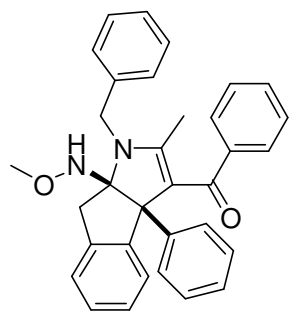
¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 193.5 (C=O), 160.9 (C_q), 148.0 (C_q), 139.4 (C_q), 139.0 (C_q), 138.7 (C_q), 128.7 (2x CH), 128.1 (CH), 127.6 (2x CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 126.8 (CH), 125.7 (2x CH), 123.7 (CH), 116.6 (C_q), 96.1 (C_q), 69.3 (C_q), 62.0 (CH₃), 51.0 (CH₂), 46.0 (CH₂), 38.6 (CH₂), 25.2 (CH), 23.2 (CH₃), 23.0 (CH₃), 14.9 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 3061, 3027, 2952, 2866, 1614, 1606, 1556, 1466, 1398, 1347, 1026, 949, 757, 734, 698; **HR-MS** (ESI⁺): calcd. for C₃₁H₃₅N₂O₂ ([M+H]⁺): 467.2693, found: 467.2694; **M**(C₃₁H₃₄N₂O₂): 466.63.

Tetrahydroindeno[2,1-*b*]pyrrole 3z

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 1-phenyl-1,3-butanedione (42 mg, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 5 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was

* One ¹³C-signal is very broad and could not be clearly detected.

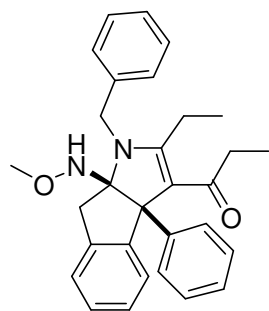
added and it was stirred at 60 °C for 2 days. Compound **3z** was obtained as a colorless solid (50 mg, 52%).



R_f: 0.50 (40% MTBE/hexane); **mp.**: 224 – 226 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 8.06 – 8.04 (m, 1H), 7.69 – 7.64 (m, 2H), 7.42 – 7.31 (m, 4H), 7.28 – 7.01 (m, 10H), 6.86 – 6.83 (m, 2H), 5.29 (bs, 1H), 4.92 (d, *J* = 18.0 Hz, 1H), 4.63 (d, *J* = 18.0 Hz, 1H), 3.45 (s, 3H), 3.00 (d, *J* = 16.5 Hz, 1H), 2.90 (d, *J* = 16.5 Hz, 1H), 1.51 (s, 3H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 190.4 (C=O), 162.0 (C_q), 148.8 (C_q), 144.1 (C_q), 138.59 (C_q), 138.57 (C_q), 138.0 (C_q), 130.2 (CH), 129.0 (2x CH), 128.70 (2x CH), 128.65 (CH), 128.56 (2x CH), 128.4 (CH), 128.3 (2x CH), 127.7 (2x CH), 127.4 (CH), 127.1 (CH), 126.8 (CH), 125.6 (2x CH), 123.5 (CH), 115.8 (C_q), 96.3 (C_q), 70.0 (C_q), 62.2 (CH₃), 45.7 (CH₂), 38.1 (CH₂), 15.7 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 3161, 3026, 2950, 2929, 1601, 1583, 1541, 1524, 1473, 1446, 1405, 1348, 1014, 951, 738, 699; **HR-MS** (ESI⁺): calcd. for C₃₃H₃₀N₂O₂Na ([M+Na]⁺): 509.2200, found: 509.2202; **M(C₃₃H₃₀N₂O₂)**: 486.62.

Tetrahydroindeno[2,1-*b*]pyrrole **3aa**

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), 3,5-heptanedione (35 μL, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μmol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μL, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 8 days. Compound **3aa** was obtained as a colorless solid (39 mg, 43%).



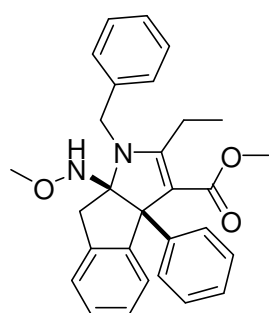
R_f: 0.31 (30% MTBE/hexane); **mp.**: 115 – 117 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.53 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.16 (m, 10H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.86 – 6.84 (m, 2H), 5.20 (bs, 1H), 4.87 (d, *J* = 18.0 Hz, 1H), 4.70 (d, *J* = 18.0 Hz, 1H), 3.38 (s, 3H), 3.06 (dq, *J* = 13.0, 7.5 Hz, 1H), 2.96 (d, *J* = 16.5 Hz, 1H), 2.84 (d, *J* = 16.5 Hz, 1H), 2.43 (dq, *J* = 14.5, 7.5 Hz, 1H), 2.34 – 2.21 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 195.1 (C=O), 168.4 (C_q), 147.9 (C_q), 139.7 (C_q), 139.1 (C_q), 138.7 (C_q), 128.6 (2x CH), 128.2 (CH), 127.8 (2x CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 126.2 (CH), 125.6 (2x CH), 123.9 (CH), 114.4 (C_q), 97.3 (C_q), 68.6 (C_q), 62.2 (CH₃), 45.2 (CH₂), 38.0 (CH₂), 34.8 (CH₂), 21.0 (CH₂), 12.5 (CH₃), 9.7 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3436, 3061, 3027, 2962, 2934, 2897, 2873, 1720, 1637, 1608, 1547, 1518, 1495, 1473, 1461, 1442, 1422, 1402, 1373,

* One ¹³C-signal is very broad and could not be clearly detected.

1348, 1249, 1123, 1106, 1024, 946, 753, 732, 699; **HR-MS** (ESI⁺): calcd. for C₃₀H₃₂N₂O₂Na ([M+Na]⁺): 475.2356, found: 475.2352; **M**(C₃₀H₃₂N₂O₂): 452.60.

Tetrahydroindeno[2,1-*b*]pyrrole **3ab**

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl 3-oxopentanoate (33 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Benzylamine (44 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 9 days. Compound **3ab** was obtained as a colorless solid (25 mg, 26%).



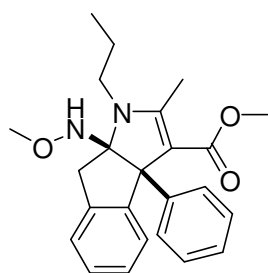
R_f: 0.34 (20% MTBE/hexane); **mp.**: 132 – 135 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.67 – 7.65 (m, 1H), 7.32 – 7.19 (m, 10H), 7.07 – 7.05 (m, 1H), 6.97 – 6.93 (m, 2H), 5.19 (bs, 1H), 4.84 (d, *J* = 18.0 Hz, 1H), 4.67 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 3.32 (s, 3H), 3.06 – 2.98 (m, 2H), 2.91 (d, *J* = 16.5 Hz, 1H), 2.22 (dq, *J* = 12.5, 7.5 Hz, 1H), 1.22 (t, *J* = 7.5 Hz, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 168.1 (C=O), 166.7 (C_q), 148.3 (C_q), 139.7 (C_q), 139.6 (C_q), 138.7 (C_q), 128.6 (2x CH), 128.1 (CH), 127.4 (2x CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 125.7 (2x CH), 123.7 (CH), 101.3 (C_q), 96.9 (C_q), 68.2 (C_q), 62.1 (CH₃), 49.9 (CH₃), 45.4 (CH₂), 38.6 (CH₂), 20.4 (CH₂), 12.8 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3443, 3061, 3028, 2938, 2895, 1668, 1585, 1566, 1494, 1464, 1446, 1433, 1421, 1405, 1340, 1252, 1198, 1182, 1165, 1129, 1107, 1077, 1040, 948, 927, 775, 754, 745, 732, 698; **HR-MS** (ESI⁺): calcd. for C₂₉H₃₀N₂O₃Na ([M+Na]⁺): 477.2149, found: 477.2150; **M**(C₂₉H₃₀N₂O₃): 454.57.

Tetrahydroindeno[2,1-*b*]pyrrole **3ad**

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. *n*-Propylamine (33 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3ad** was obtained as a colorless solid (73 mg, 93%).

R_f: 0.23 (20% MTBE/hexane); **mp.**: 94 – 95 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.56 – 7.53 (m, 1H), 7.25 – 7.18 (m, 8H), 5.00 (bs, 1H), 3.54 (s, 3H), 3.32 (m, 2H), 3.20 (s, 3H), 3.17 (d, *J* = 16.5 Hz, 1H), 3.10 (d, *J* = 16.5 Hz, 1H), 2.40 (s, 3H), 1.58 – 1.45 (m, 2H), 0.89 (t,

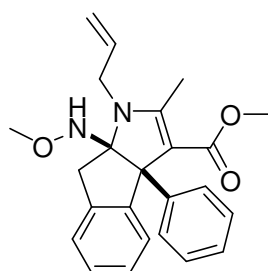
* One ¹³C-signal is very broad and could not be clearly detected.



$J = 7.5$ Hz, 3H); **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ (ppm) = 167.2 (C=O), 162.1 (C_q), 147.8 (C_q), 139.6 (C_q), 139.1 (C_q), 129.1 (2x CH), 127.6 (CH), 127.3 (2x CH), 127.2 (CH), 127.0 (CH), 126.6 (CH), 123.5 (CH), 101.1 (C_q), 96.4 (C_q), 68.3 (C_q), 62.1 (CH_3), 49.7 (CH_3), 44.7 (CH_2), 39.6 (CH_2), 24.8 (CH_2), 13.2 (CH_3), 11.5 (CH_3); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3495, 3056, 3021, 2959, 2941, 2893, 2874, 1665, 1583, 1563, 1493, 1475, 1463, 1445, 1429, 1406, 1376, 1365, 1332, 1293, 1197, 1182, 1166, 1134, 1103, 1066, 956, 932, 922, 892, 854, 768, 756, 749, 648, 485; **HR-MS** (ESI+): calcd. for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 415.1992, found: 415.1991; **$\text{M}(\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_3)$** : 392.50.

Tetrahydroindeno[2,1-*b*]pyrrole 3ae

According to [general procedure 2](#), 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Allylamine (30 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 4 days. Compound **3ae** was obtained as a colorless solid (67 mg, 86%).



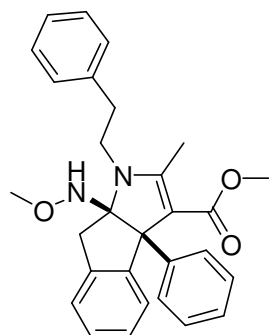
R_f : 0.35 (30% MTBE/hexane); **mp.**: 97 – 99 °C; **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ (ppm) = 7.60 – 7.55 (m, 1H), 7.25 – 7.15 (m, 8H), 5.82 (ddt, $J = 17.0, 10.5, 4.0$ Hz, 1H), 5.07 (bs, 1H), 4.99 (dq, $J = 10.5, 2.0$ Hz, 1H), 4.81 (dq, $J = 17.0, 2.0$ Hz, 1H), 4.15 (ddt, $J = 18.0, 4.0, 2.0$ Hz, 1H), 3.99 (ddt, $J = 18.0, 4.0, 2.0$ Hz, 1H), 3.57 (s, 3H), 3.20 (s, 3H), 3.14 (d, $J = 16.5$ Hz, 1H), 2.98 (d, $J = 16.5$ Hz, 1H), 2.34 (s, 3H); **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3): δ (ppm) = 167.2 (C=O), 162.6 (C_q), 148.2 (C_q), 139.8 (C_q), 138.8 (C_q), 135.5 (CH), 127.9 (CH), 127.3 (2x CH), 127.2 (CH), 126.9 (CH), 126.6 (CH), 123.7 (CH), 115.4 (CH_2), 101.5 (C_q), 96.3 (C_q), 68.4 (C_q), 62.0 (CH_3), 49.8 (CH_3), 44.5 (CH_2), 39.0 (CH_2), 13.2 (CH_3);* **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3462, 3254, 3060, 2976, 2941, 2892, 1666, 1584, 1562, 1495, 1475, 1445, 1428, 1403, 1326, 1292, 1212, 1199, 1183, 1170, 1129, 1106, 1076, 1068, 1043, 945, 928, 755, 745, 698; **HR-MS** (ESI+): calcd. for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 413.1836, found: 413.1834; **$\text{M}(\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_3)$** : 390.48.

Tetrahydroindeno[2,1-*b*]pyrrole 3af

According to [general procedure 2](#), 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv)

* One ^{13}C -signal is very broad and could not be clearly detected.

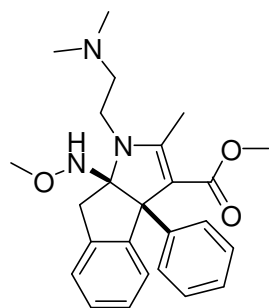
and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. 2-Phenylethylamine (50 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 2 days. Compound **3af** was obtained as a colorless solid (87 mg, 95%).



R_f: 0.50 (30% MTBE/hexane); **mp.**: 111 – 114 °C; **¹H-NMR** (300 MHz, CDCl_3): δ (ppm) = 7.55 – 7.51 (m, 1H), 7.30 – 7.20 (m, 11H), 7.10 – 7.07 (m, 2H), 4.96 (bs, 1H), 3.72 – 3.51 (m, 5H), 3.21 (s, 3H), 3.20 (d, J = 16.5 Hz, 1H), 3.12 (d, J = 16.5 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.33 (s, 3H); **¹³C-NMR** (75 MHz, CDCl_3): δ (ppm) = 167.1 (C=O), 161.7 (C_q), 147.6 (C_q), 139.4 (C_q), 139.3 (C_q), 139.0 (C_q), 129.1 (2x CH), 128.9 (2x CH), 128.7 (2x CH), 127.5 (CH), 127.4 (2x CH), 127.3 (CH), 127.1 (CH), 126.7 (CH), 126.7 (CH), 123.6 (CH), 101.6 (C_q), 96.5 (C_q), 68.4 (C_q), 62.2 (CH_3), 49.8 (CH_3), 44.9 (CH_2), 39.8 (CH_2), 38.2 (CH_2), 13.1 (CH_3); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3445, 3059, 3024, 2946, 2885, 1671, 1586, 1571, 1494, 1475, 1457, 1445, 1399, 1359, 1327, 1314, 1194, 1156, 1128, 1105, 1063, 989, 960, 949, 929, 770, 753, 720, 699, 496; **HR-MS** (ESI⁺): calcd. for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 477.2149, found: 477.2152; **M**($\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_3$): 454.57.

Tetrahydroindeno[2,1-*b*]pyrrole **3ag**

According to [general procedure 2](#), 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μL , 0.26 mmol, 1.3 equiv), $\text{Sc}(\text{OTf})_3$ (9.8 mg, 20 μmol , 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl_3 (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. *N,N*-Dimethylethylenediamine (44 μL , 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 1 day. After flash column chromatography (1% → 5% MeOH/ CH_2Cl_2), Compound **3ag** was obtained as a colorless solid (80 mg, 95%).



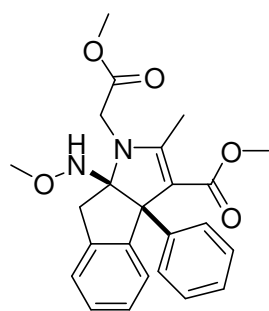
R_f: 0.15 (4% MeOH/ CH_2Cl_2); **mp.**: 122 – 124 °C; **¹H-NMR** (300 MHz, CDCl_3): δ (ppm) = 7.53 – 7.51 (m, 1H), 7.23 – 7.18 (m, 8H), 5.21 (bs, 1H), 3.63 – 3.47 (m, 4H), 3.42 (ddd, J = 15.0, 9.5, 6.0 Hz, 1H), 3.16 (m, 5H), 2.47 – 2.37 (m, 4H), 2.34 – 2.24 (m, 7H); **¹³C-NMR** (75 MHz, CDCl_3): δ (ppm) = 167.1 (C=O), 161.7 (C_q), 147.7 (C_q), 139.6 (C_q), 139.3 (C_q), 129.1 (2x CH), 127.6 (CH), 127.33 (2x CH), 127.30 (CH), 127.1 (CH), 126.6 (CH), 123.6 CH), 101.6 (C_q), 96.3 (C_q), 68.4 (C_q), 62.0 (CH_3), 60.3 (CH_2), 49.8 (CH_3), 46.0 (2x CH_3), 41.3 (CH_2), 39.7 (CH_2), 13.3 (CH_3); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3446, 3064, 2944, 2904, 2822, 2770, 1661, 1584, 1566, 1493, 1474, 1459, 1445, 1408, 1353, 1336, 1322, 1310, 1197, 1183, 1166, 1143, 1128, 1107, 1065, 993, 950,

932, 771, 753, 743, 699; **HR-MS** (ESI⁺): calcd. for C₂₅H₃₁N₃O₃Na ([M+Na]⁺): 444.2258, found: 444.2255; **M**(C₂₅H₃₁N₃O₃): 421.54.

Tetrahydroindeno[2,1-*b*]pyrrole **3ah**

Glycine methyl ester hydrochloride was treated with sat. NaHCO₃-solution and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. Glycine methyl ester was used without further purification.

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Glycine methyl ester (71 mg, 0.80 mmol, 4.0 equiv) was added and it was stirred at 60 °C for 6 days. Compound **3ah** was obtained as a colorless solid (68 mg, 81%).

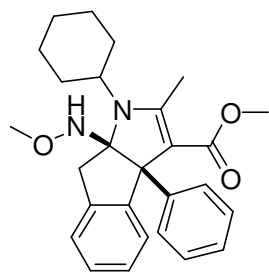


R_f: 0.28 (40% MTBE/hexane); **mp.**: 136 – 138 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.60 – 7.56 (m, 1H), 7.25 – 7.18 (m, 8H), 5.22 (bs, 1H), 4.16 (s, 2H), 3.70 (s, 3H), 3.55 (s, 3H), 3.32 (d, *J* = 16.5 Hz, 1H), 3.21 (d, *J* = 16.5 Hz, 1H), 3.16 (s, 3H), 2.31 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 171.3 (C=O), 166.9 (C=O), 160.0 (C_q), 146.9 (C_q), 139.9 (C_q), 139.8 (C_q), 128.6 (2x CH), 127.5 (2x CH), 127.4 (2x CH), 127.3 (CH), 126.6 (CH), 123.9 (CH), 102.7 (C_q), 95.1 (C_q), 69.0 (C_q), 62.4 (CH₃), 52.3 (CH₃), 49.9 (CH₃), 45.0 (CH₂), 40.1 (CH₂), 13.1 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3450, 3026, 2950, 2935, 1750, 1666, 1590, 1576, 1433, 1393, 1365, 1345, 1201, 1171, 1129, 1093, 1013, 916, 753, 700; **HR-MS** (ESI⁺): calcd. for C₂₄H₂₆N₂O₅Na ([M+Na]⁺): 445.1734, found: 445.1735; **M**(C₂₄H₂₆N₂O₅): 422.48.

Tetrahydroindeno[2,1-*b*]pyrrole **3ai**

According to general procedure 2, 2-hydroxy oxime ether **1a** (51 mg, 0.20 mmol, 1.0 equiv), methyl acetoacetate (28 μ L, 0.26 mmol, 1.3 equiv), Sc(OTf)₃ (9.8 mg, 20 μ mol, 0.10 equiv) and 4 Å molecular sieve (50 mg) were dissolved in abs. CHCl₃ (1.0 mL) and the reaction mixture was heated to 60 °C for 3 h. Cyclohexylamine (46 μ L, 0.40 mmol, 2.0 equiv) was added and it was stirred at 60 °C for 4.5 days followed by 90 °C for 1 day. Compound **3ai** was obtained as a colorless solid (55 mg, 60%).

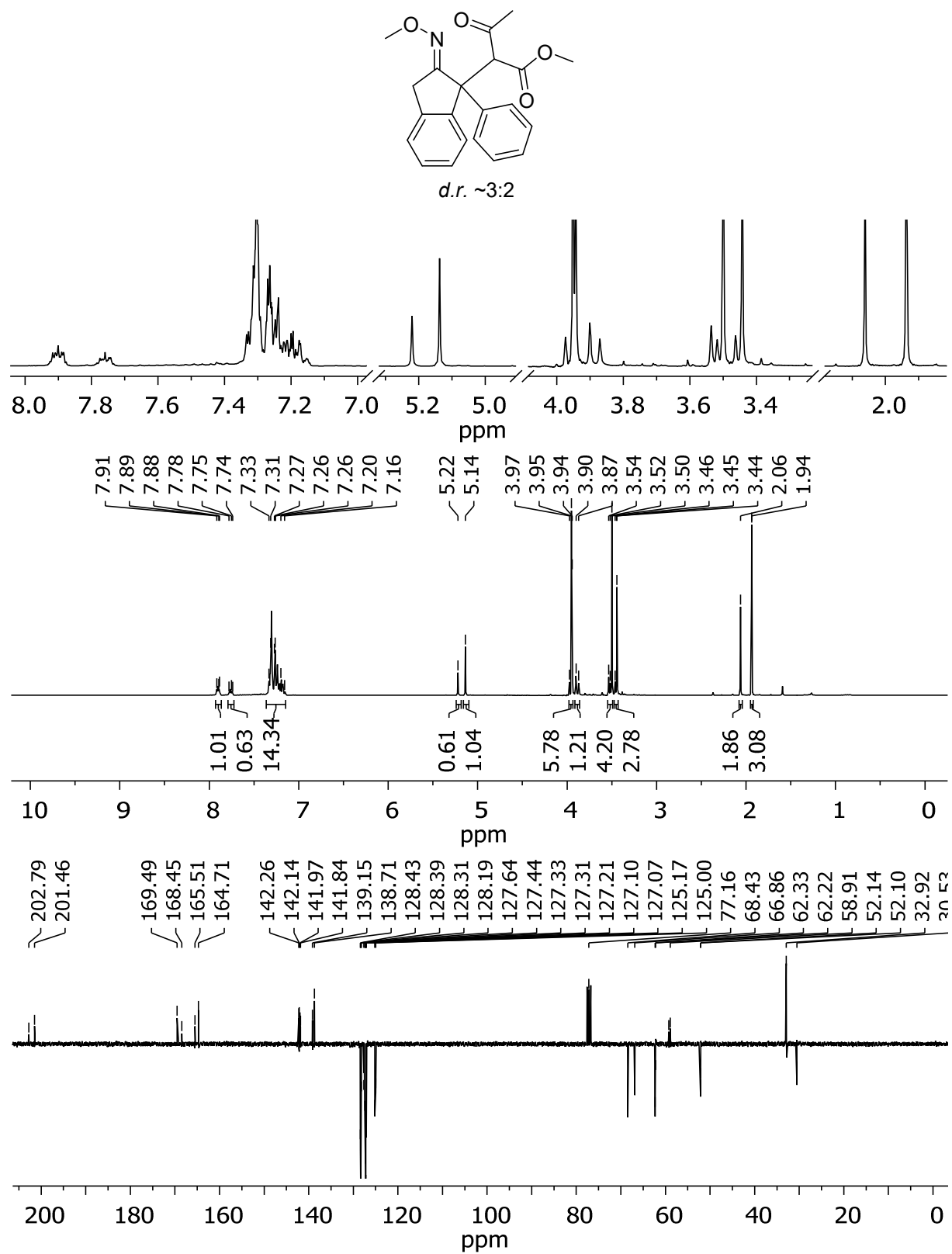
R_f: 0.31 (30% MTBE/hexane); **mp.**: 106 – 109 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.57 – 7.54 (m, 1H), 7.25 – 7.18 (m, 8H), 4.90 (bs, 1H), 3.52 – 3.49 (m, 4H), 3.24 (s, 2H),



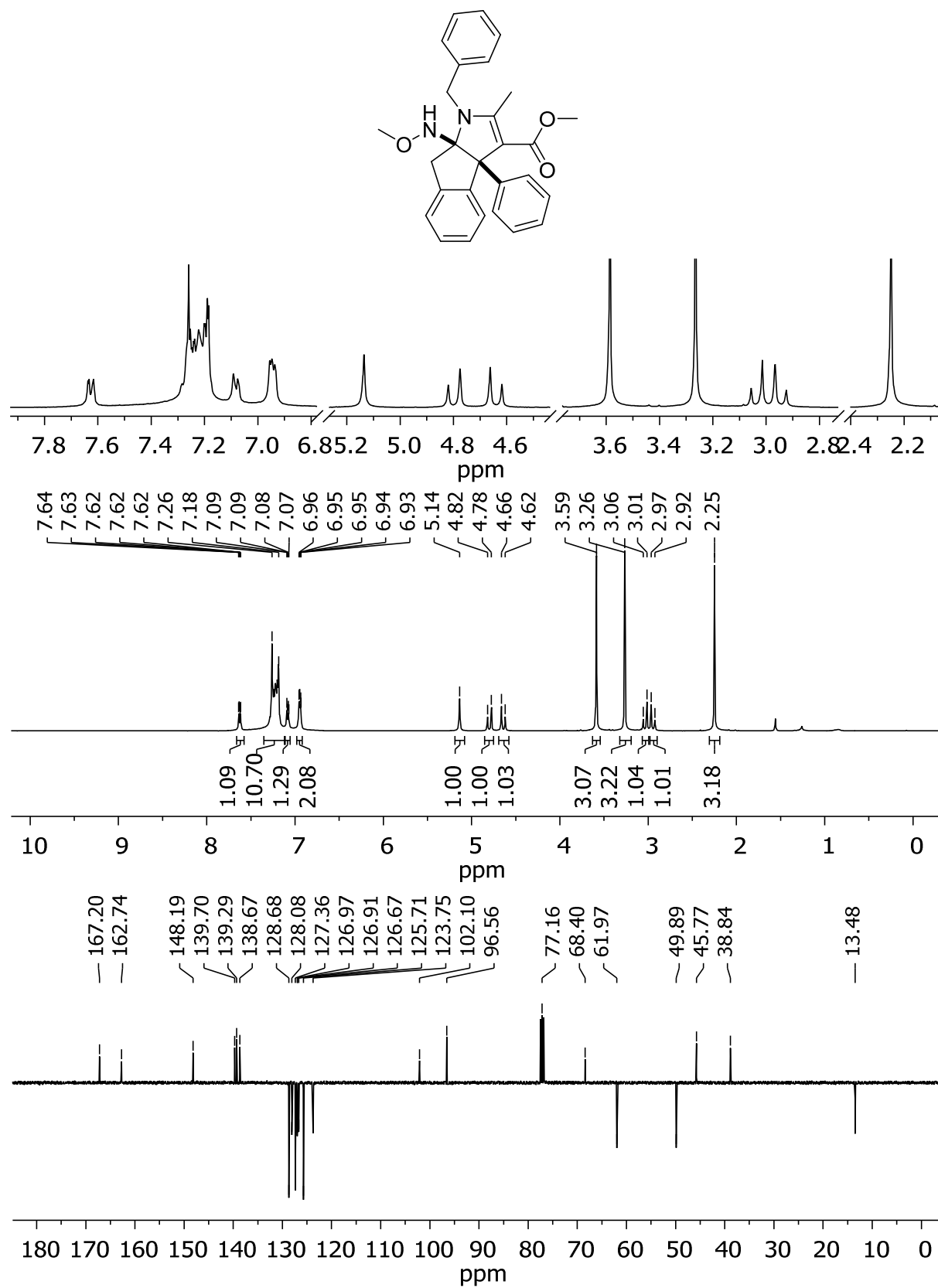
3.08 (s, 3H), 2.49 (s, 3H), 1.93 – 1.66 (m, 7H), 1.38 – 1.08 (m, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.3 (C=O), 161.7 (C_q), 147.7 (C_q), 140.0 (C_q), 139.7 (C_q), 129.0 (2x CH), 127.4 (CH), 127.32 (CH), 127.27 (2x CH), 126.9 (CH), 126.5 (CH), 123.4 (CH), 101.2 (C_q), 97.1 (C_q), 68.7 (C_q), 61.5 (CH₃), 55.7 (CH), 49.6 (CH₃), 40.7 (CH₂), 34.0 (CH₂), 32.8 (CH₂), 27.1 (CH₂), 27.0 (CH₂), 25.8 (CH₂), 15.2 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3444, 3063, 2934, 2852, 1668, 1584, 1561, 1509, 1445, 1433, 1413, 1374, 1349, 1334, 1240, 1185, 1129, 754, 739, 700; **HR-MS** (ESI⁺): calcd. for C₂₇H₃₂N₂O₃Na ([M+Na]⁺): 455.2305, found: 455.2309; **M(C₂₇H₃₂N₂O₃)**: 432.56.

3.2 ^1H -NMR and ^{13}C -NMR Spectra

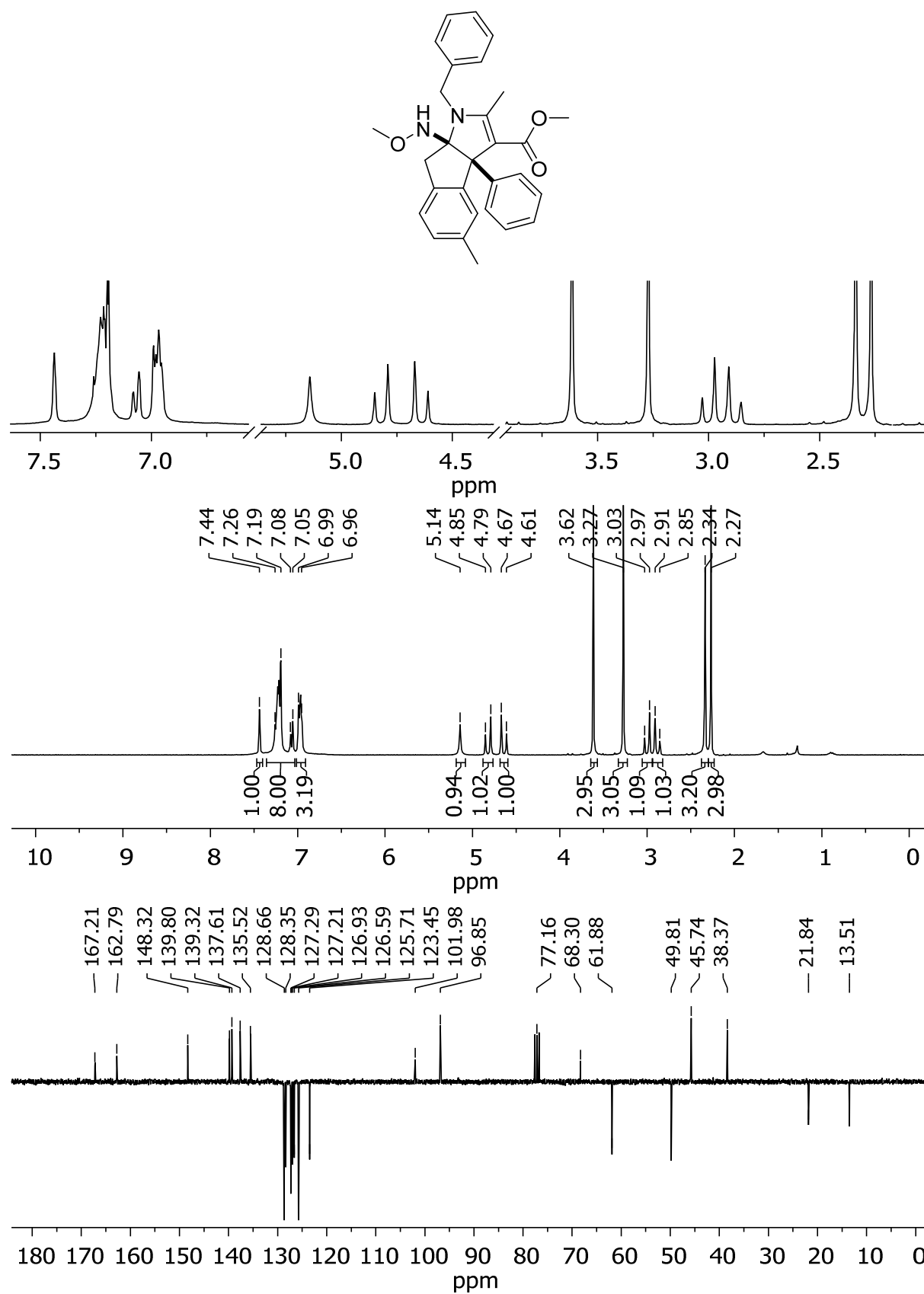
Intermediate 2a (CDCl_3 , ^1H -NMR: 300 MHz, APT: 75 MHz)



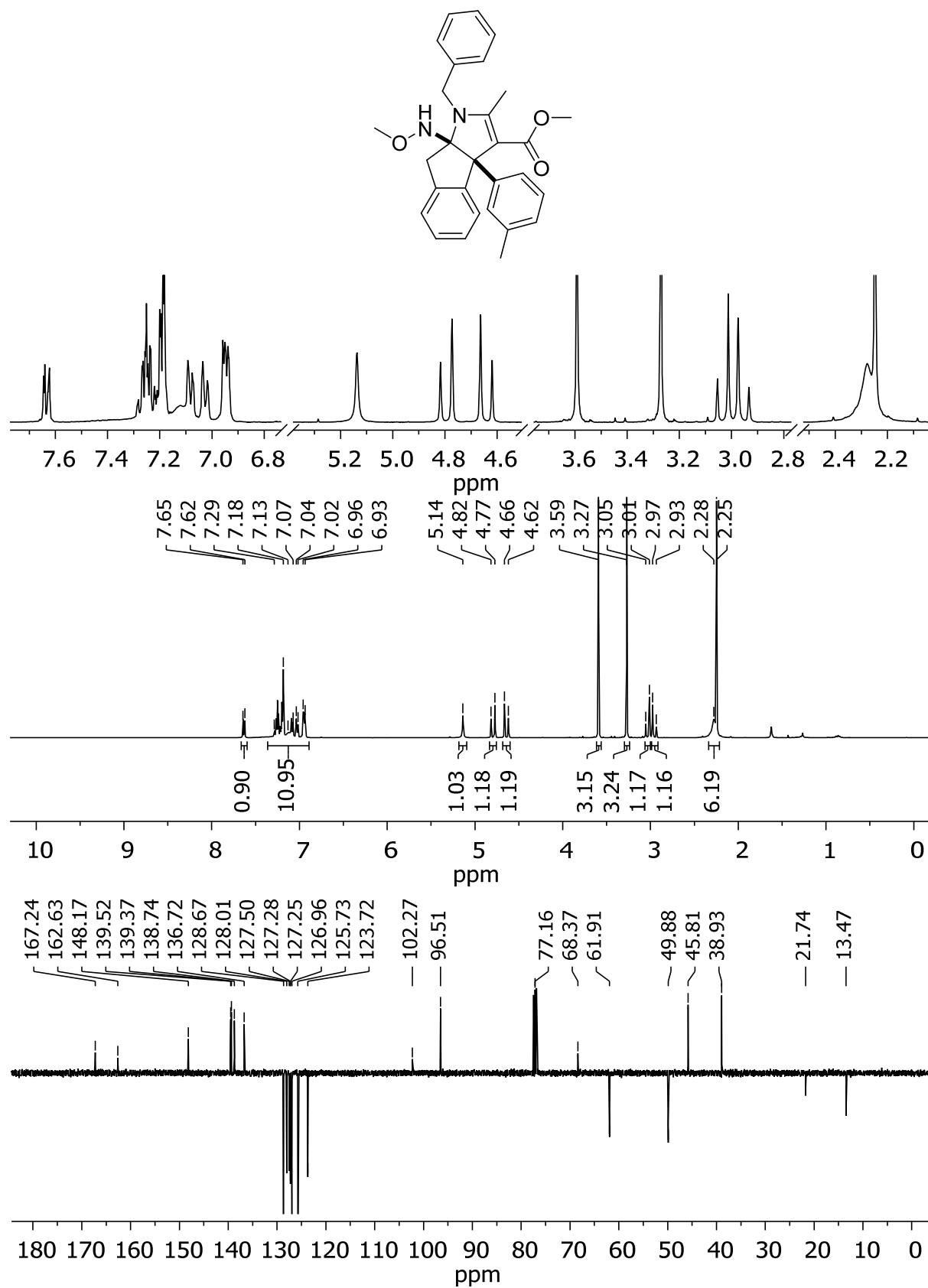
Tetrahydroindeno[2,1-*b*]pyrrole 3a (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



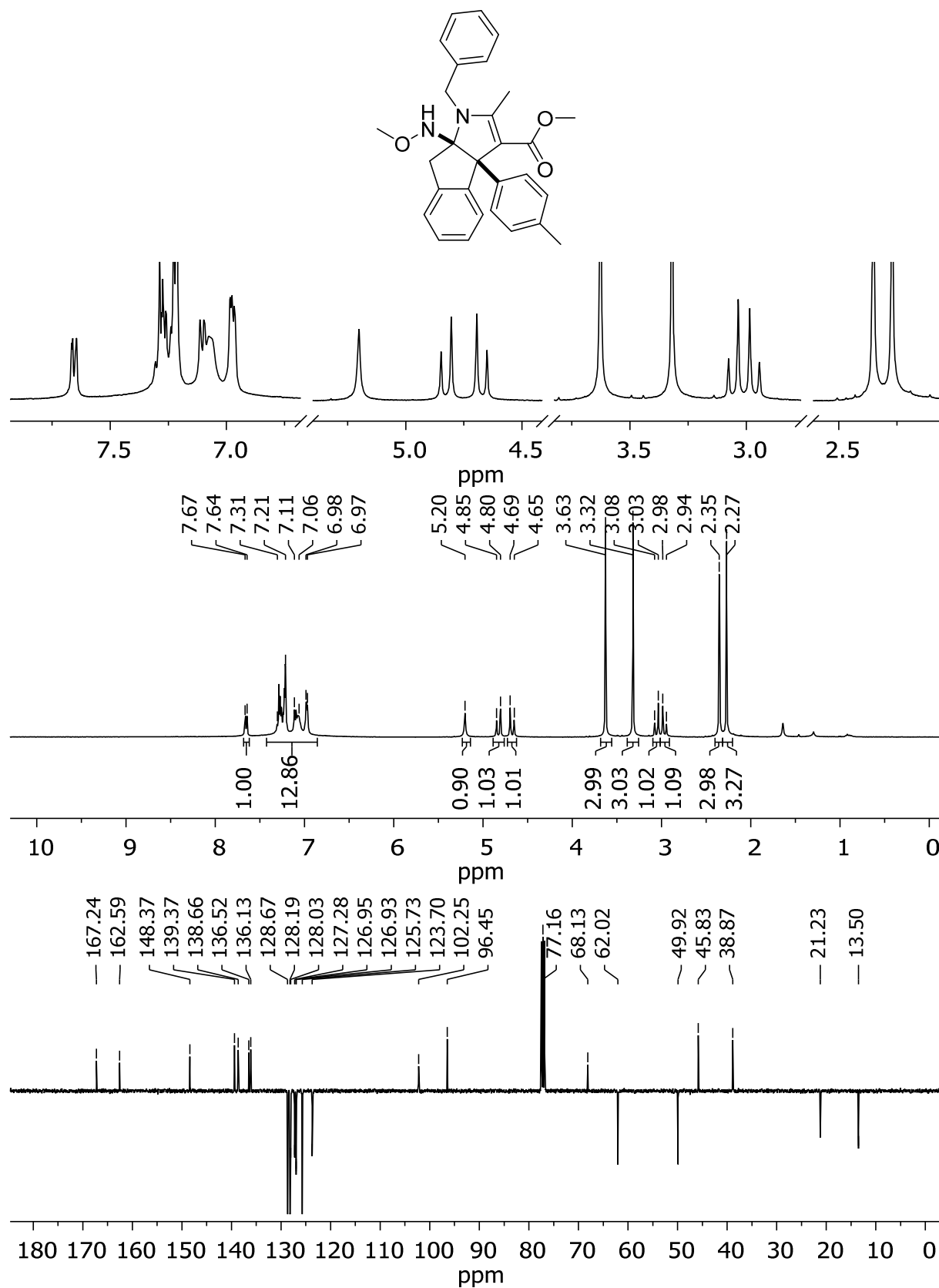
Tetrahydroindeno[2,1-*b*]pyrrole 3b (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



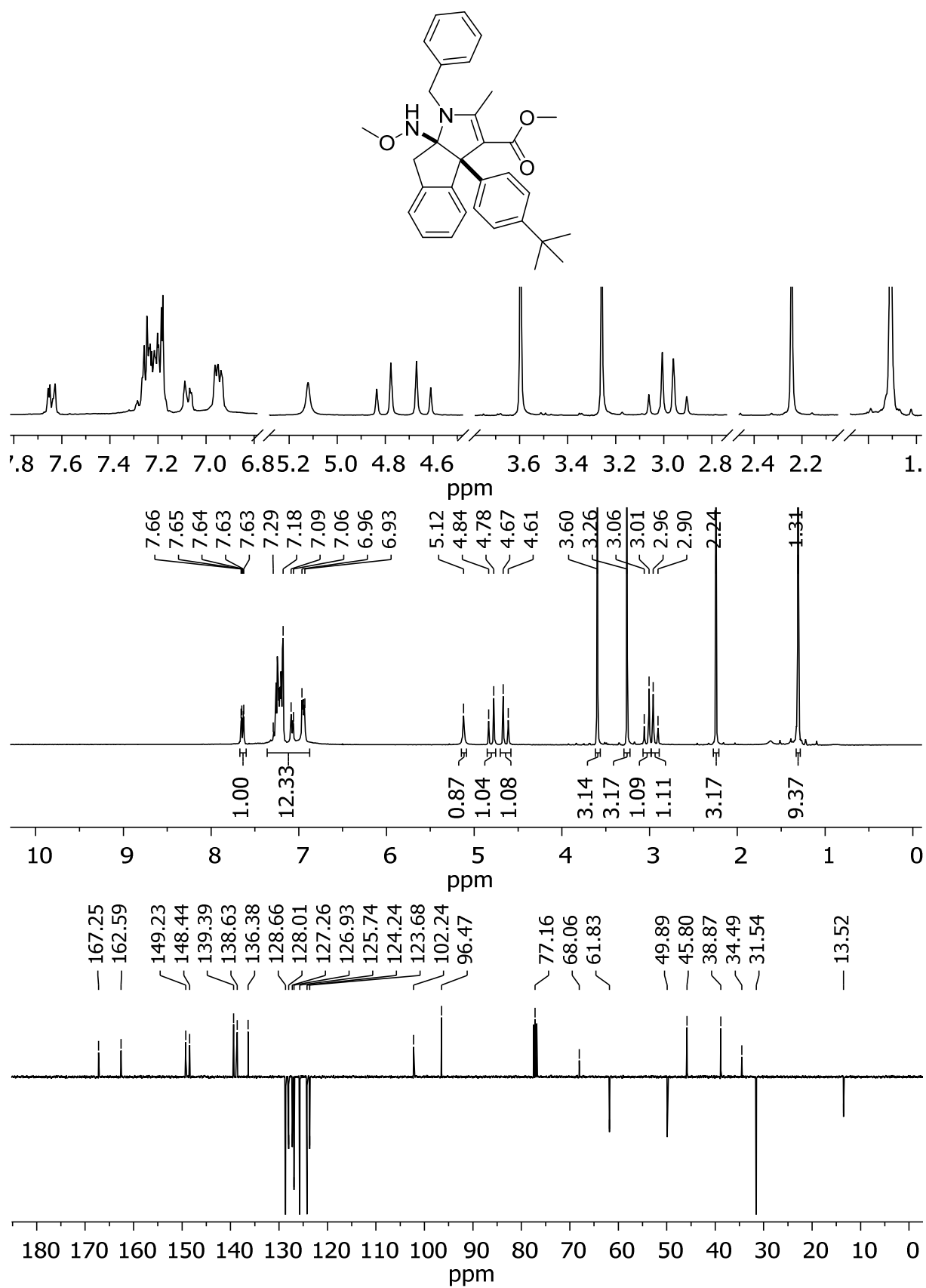
Tetrahydroindeno[2,1-*b*]pyrrole 3d (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



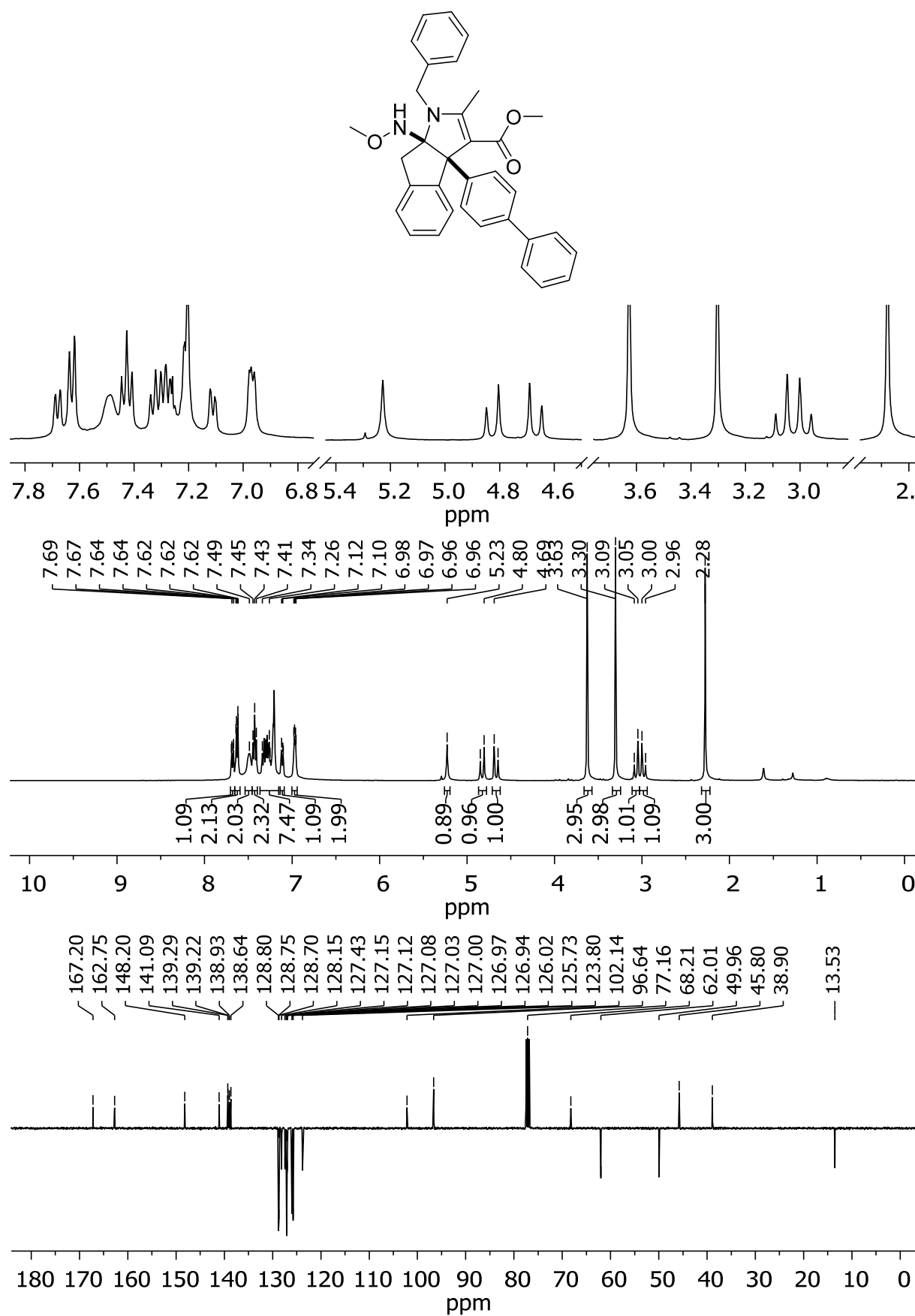
Tetrahydroindeno[2,1-*b*]pyrrole 3e (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



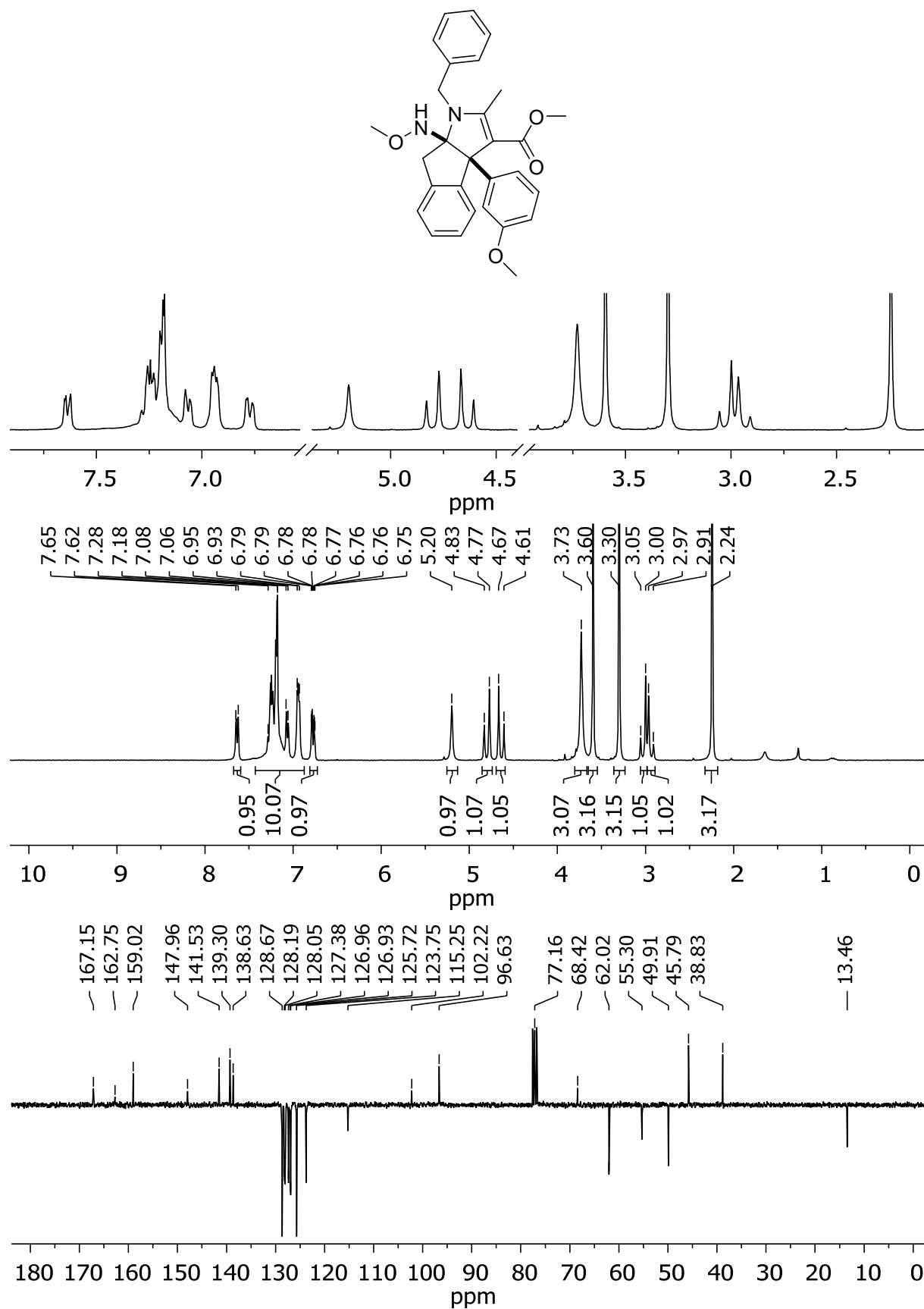
Tetrahydroindeno[2,1-*b*]pyrrole 3f (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



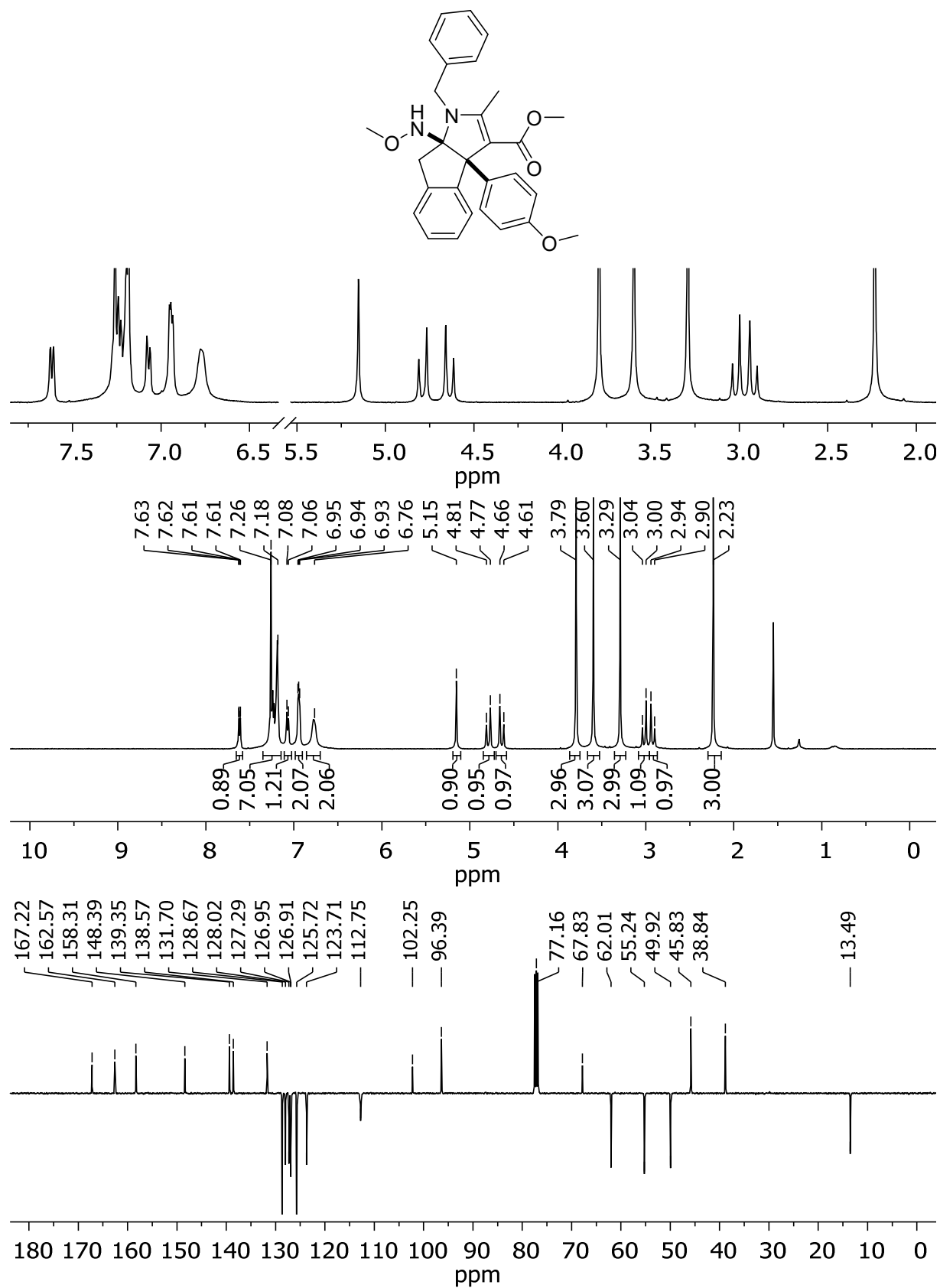
Tetrahydroindeno[2,1-*b*]pyrrole 3g (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



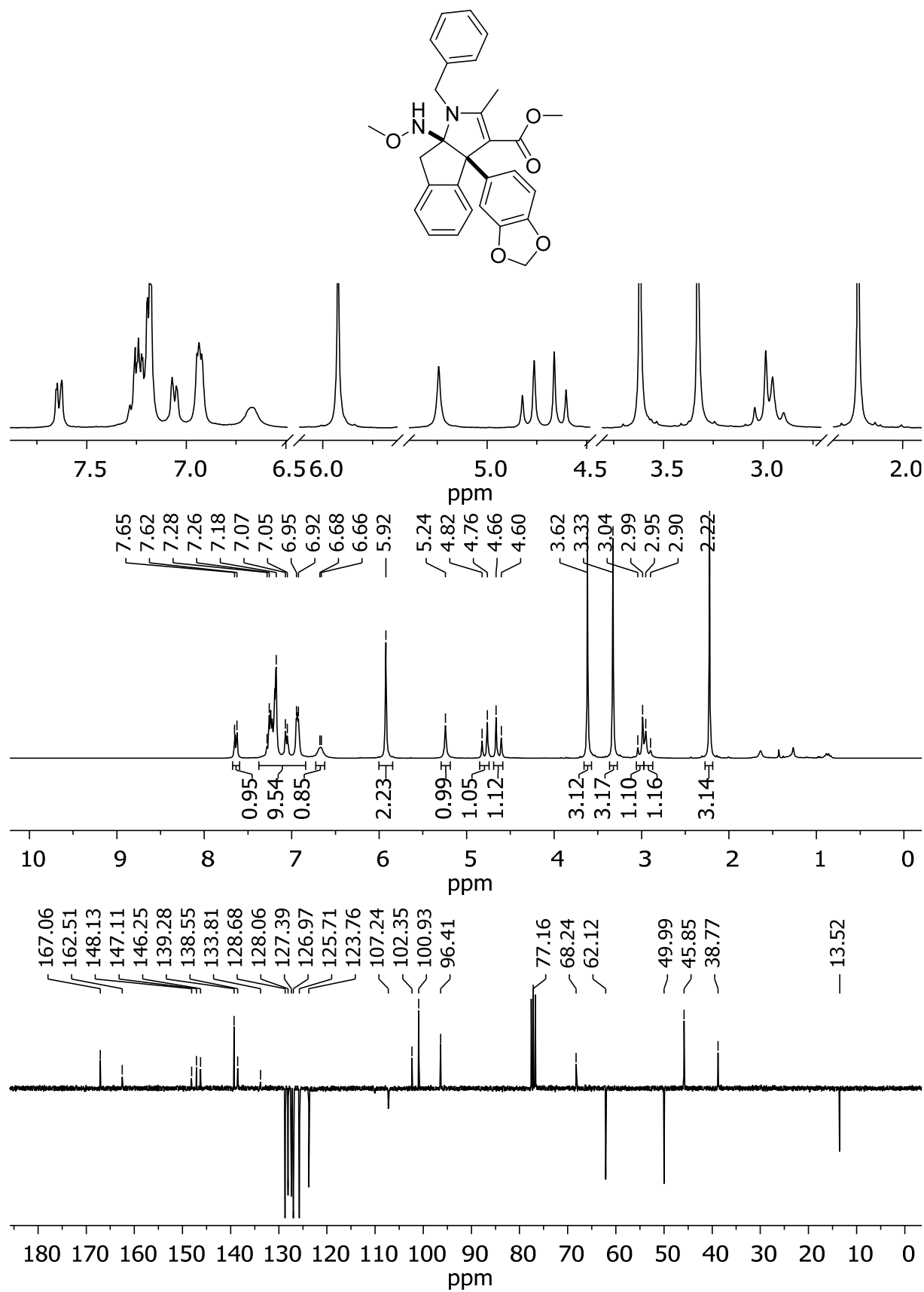
Tetrahydroindeno[2,1-*b*]pyrrole 3h (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



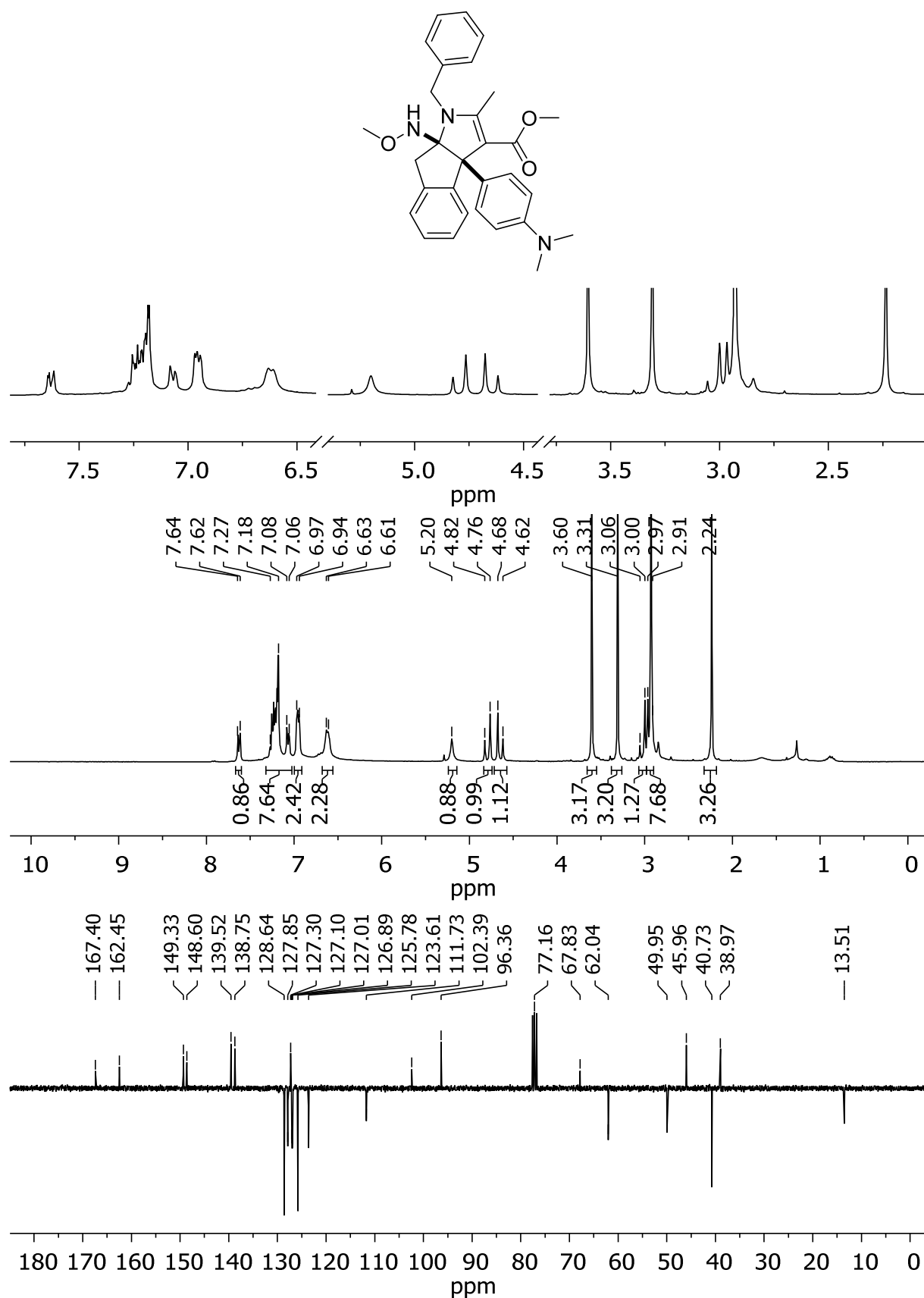
Tetrahydroindeno[2,1-*b*]pyrrole 3i (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



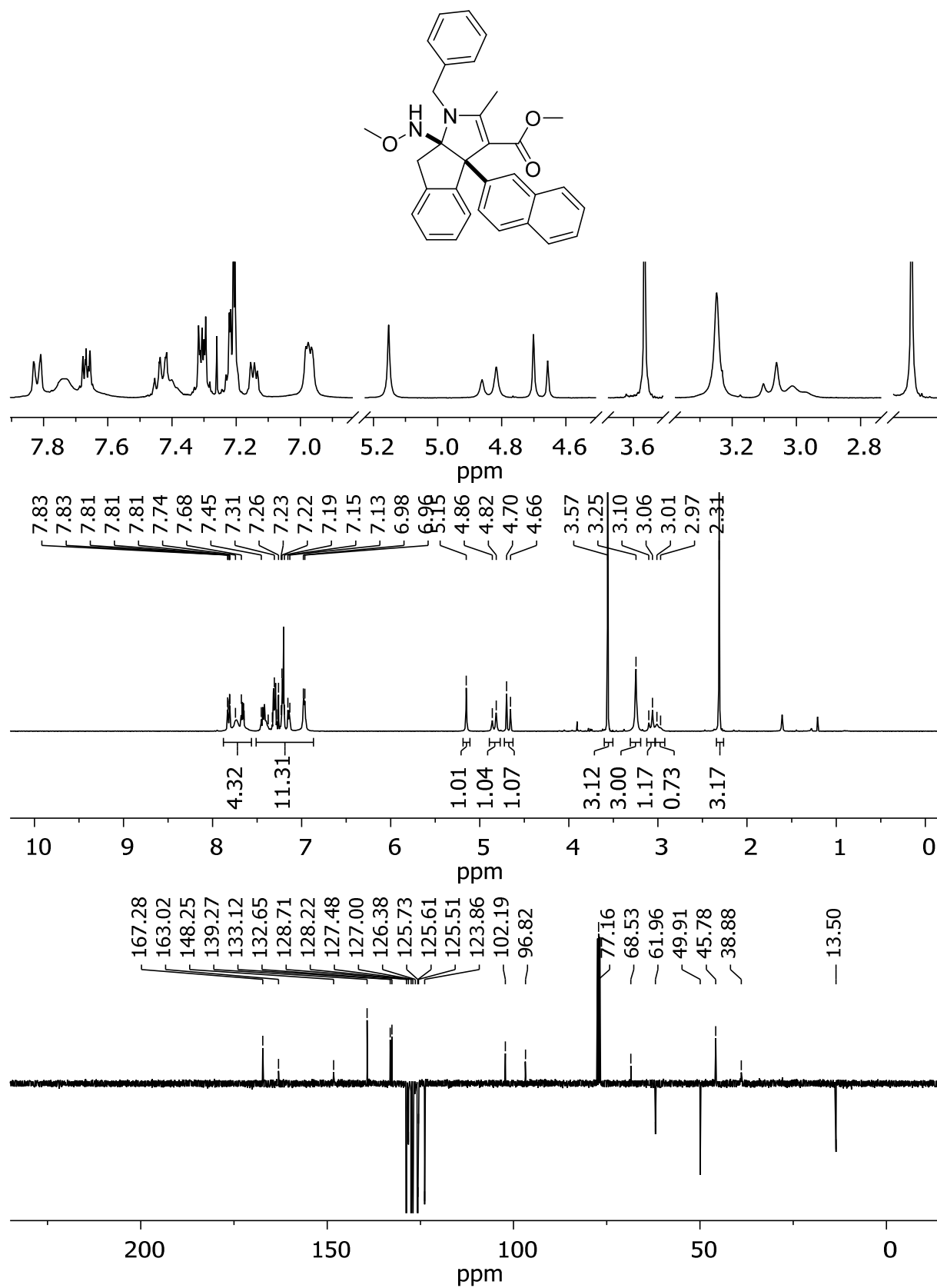
Tetrahydroindeno[2,1-*b*]pyrrole 3j (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



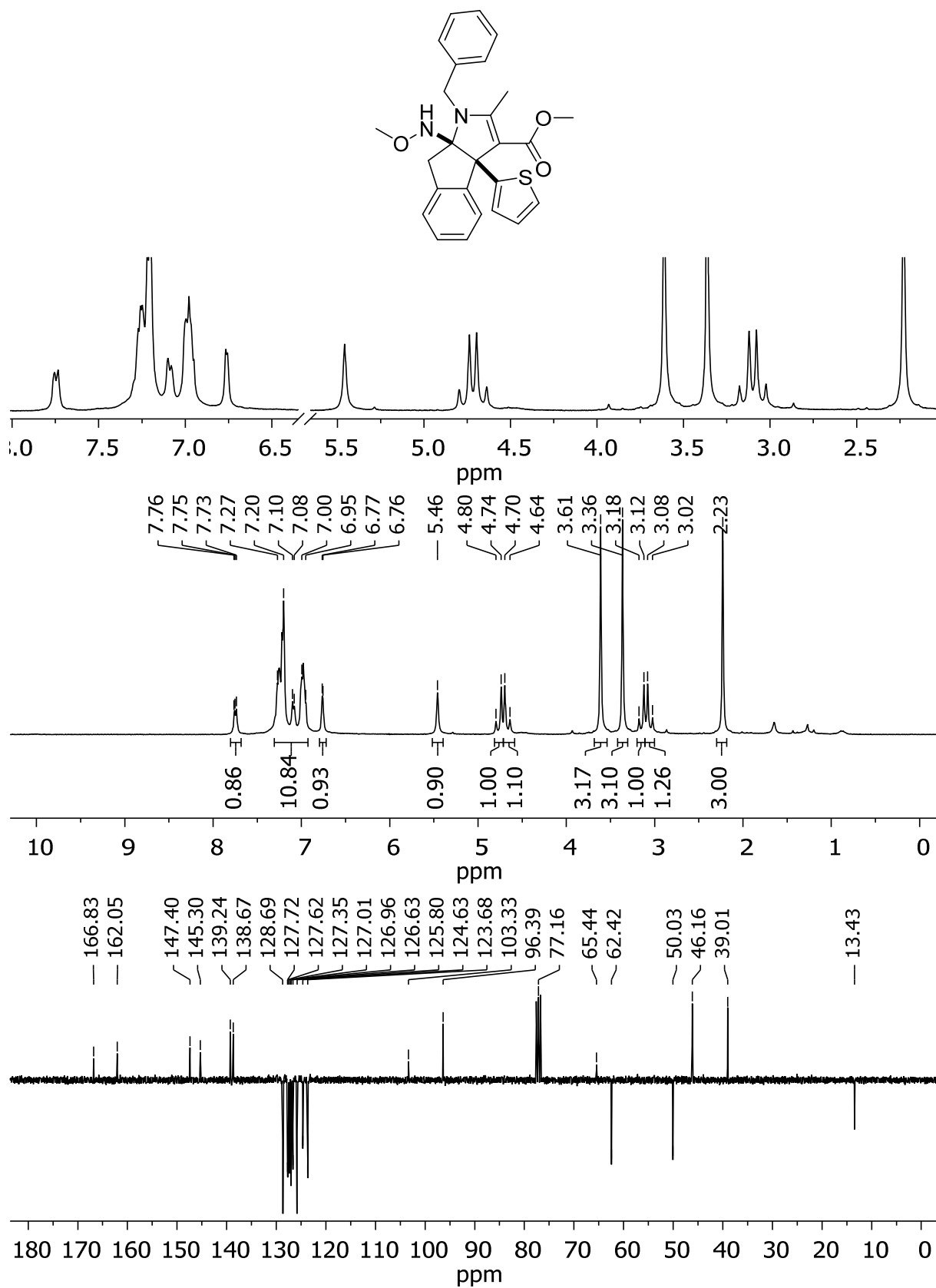
Tetrahydroindeno[2,1-*b*]pyrrole 3k (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



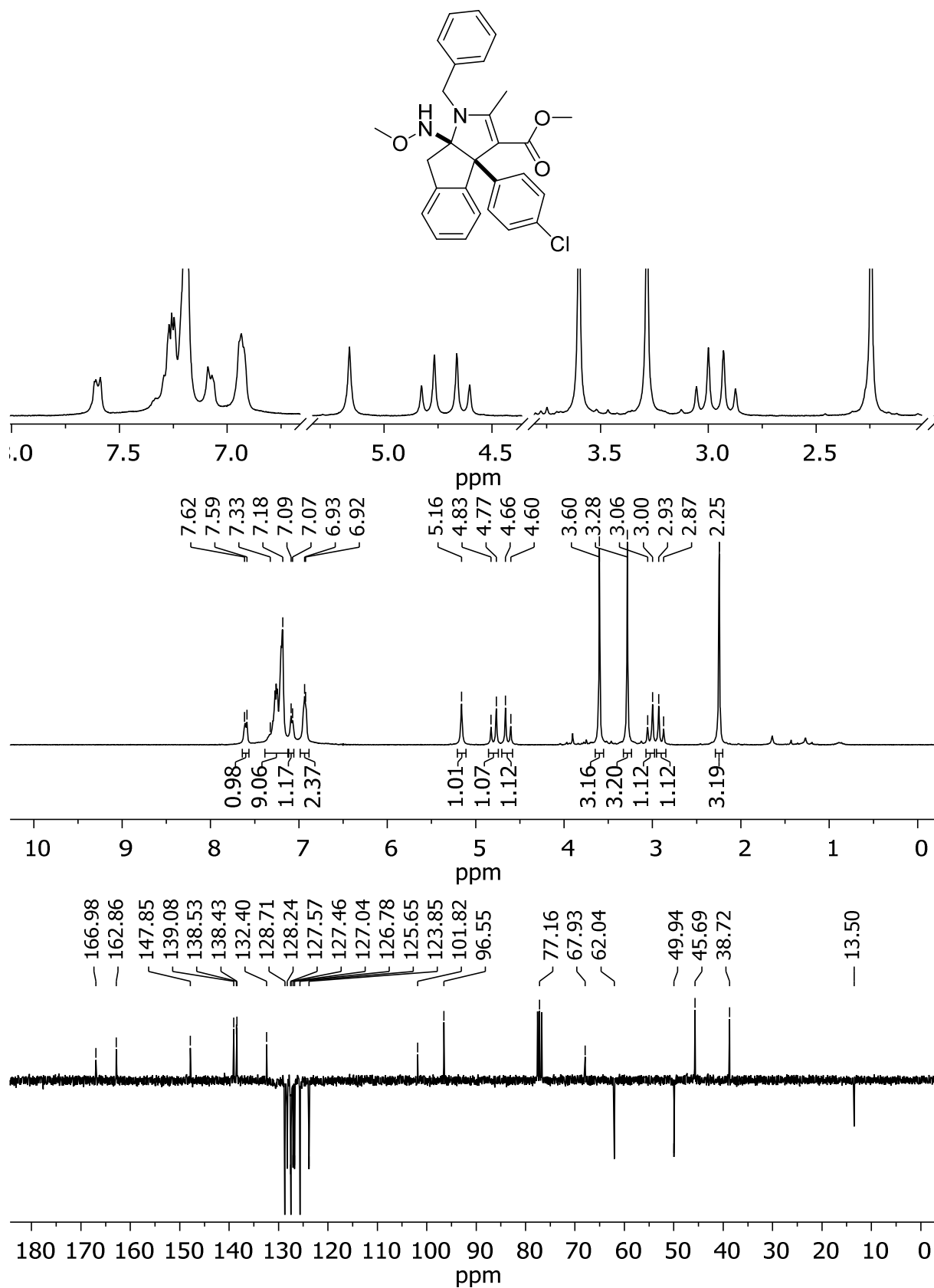
Tetrahydroindeno[2,1-*b*]pyrrole 3l (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



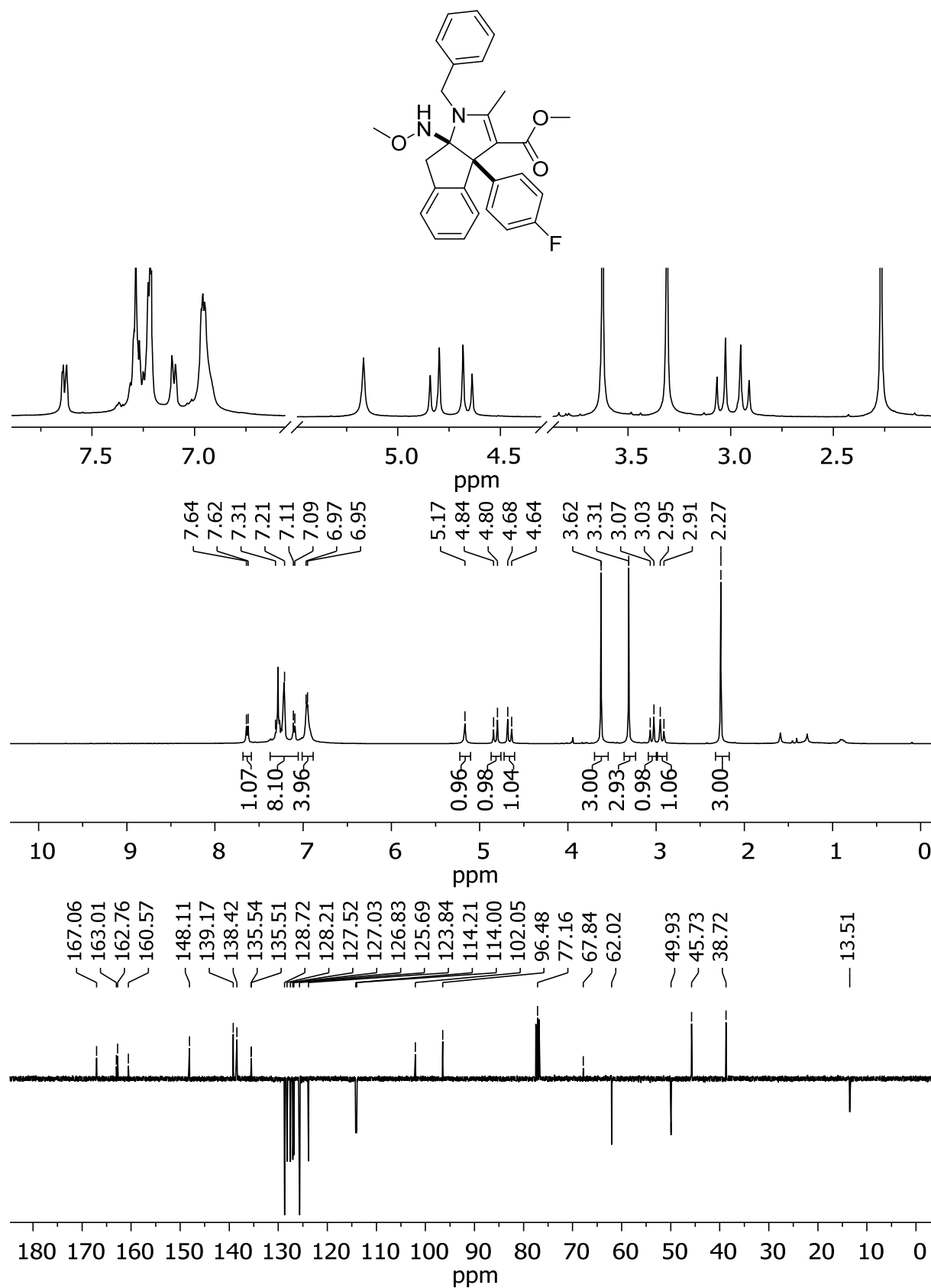
Tetrahydroindeno[2,1-*b*]pyrrole 3m (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



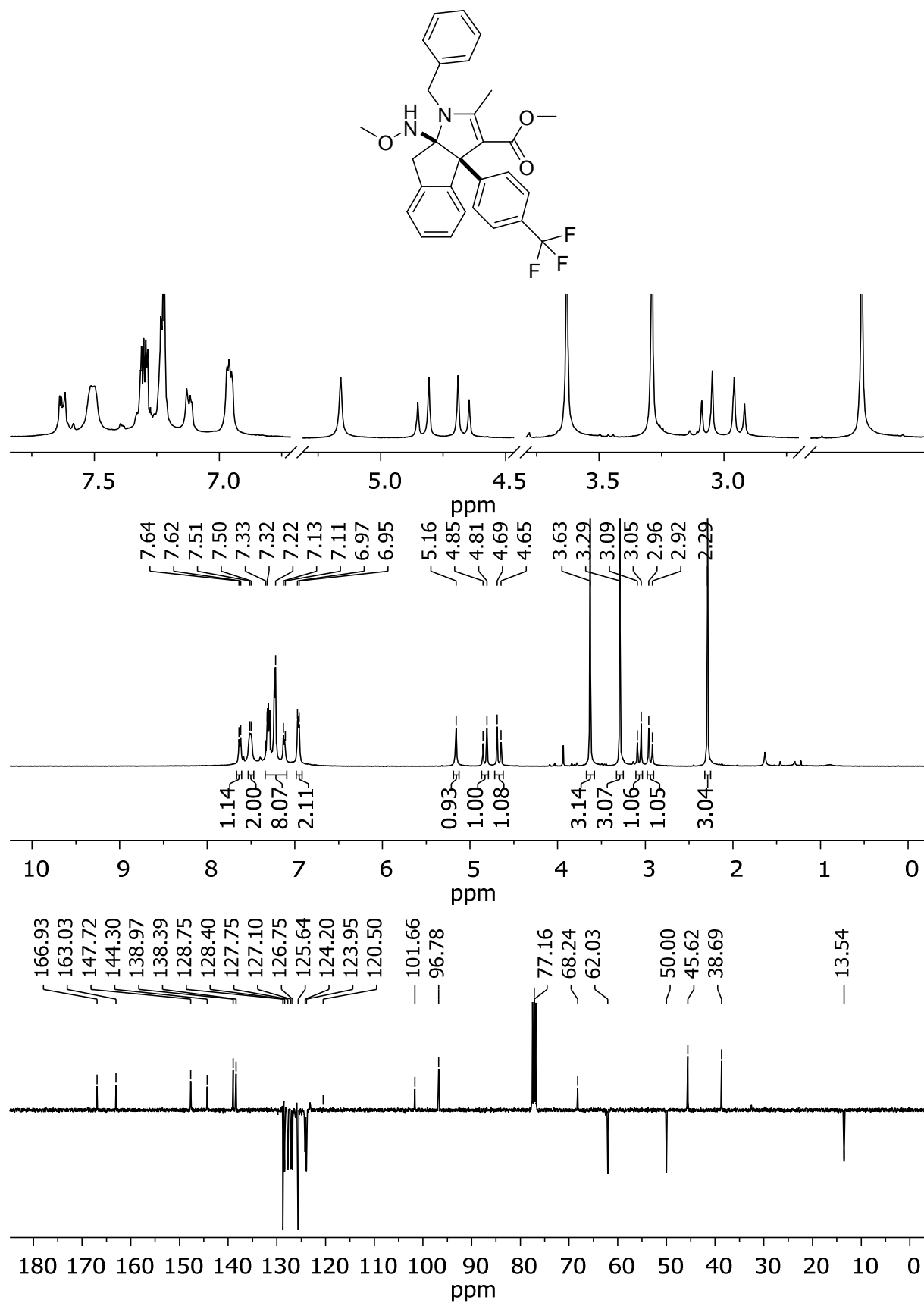
Tetrahydroindeno[2,1-*b*]pyrrole 3n (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



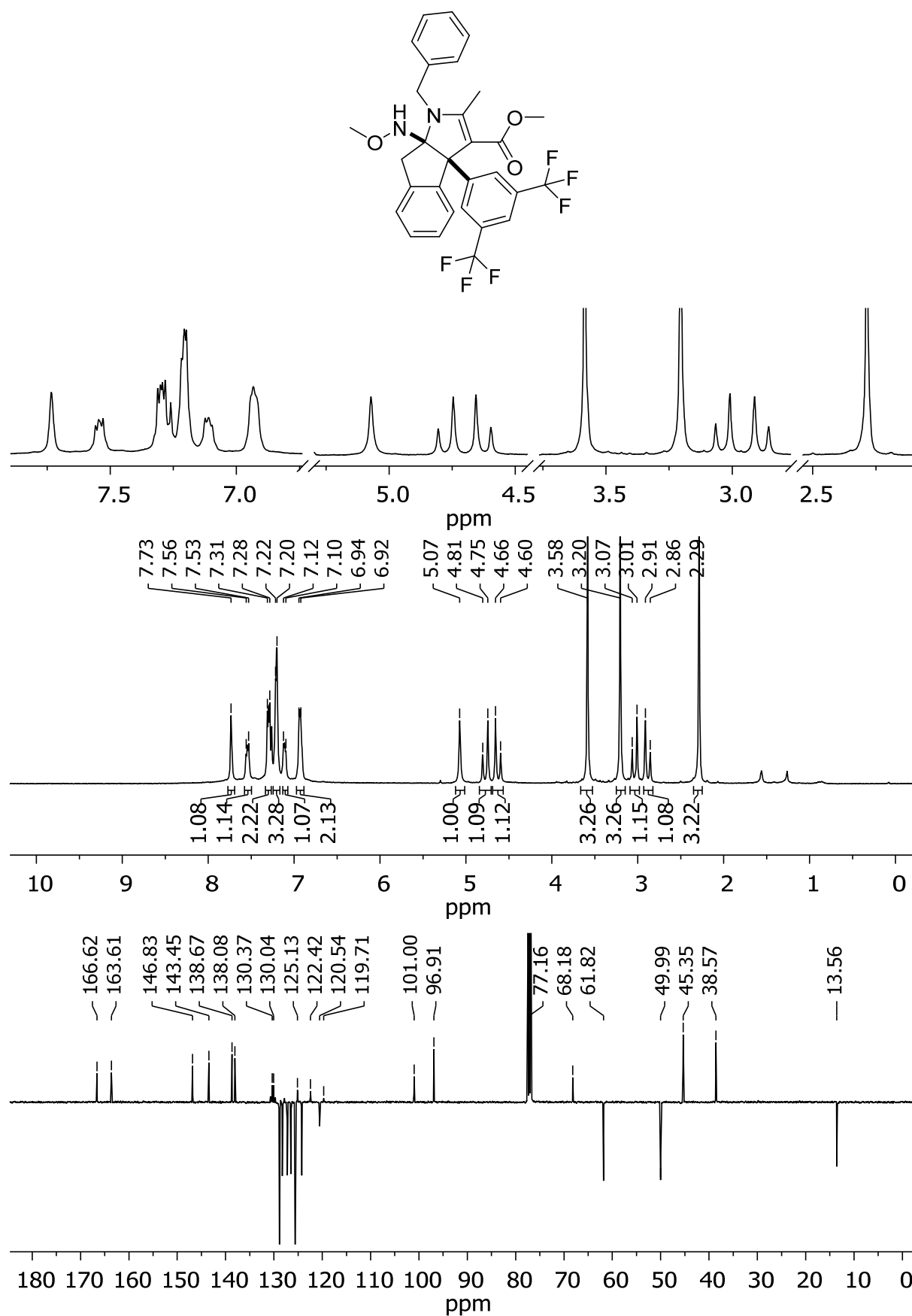
Tetrahydroindeno[2,1-*b*]pyrrole 3o (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



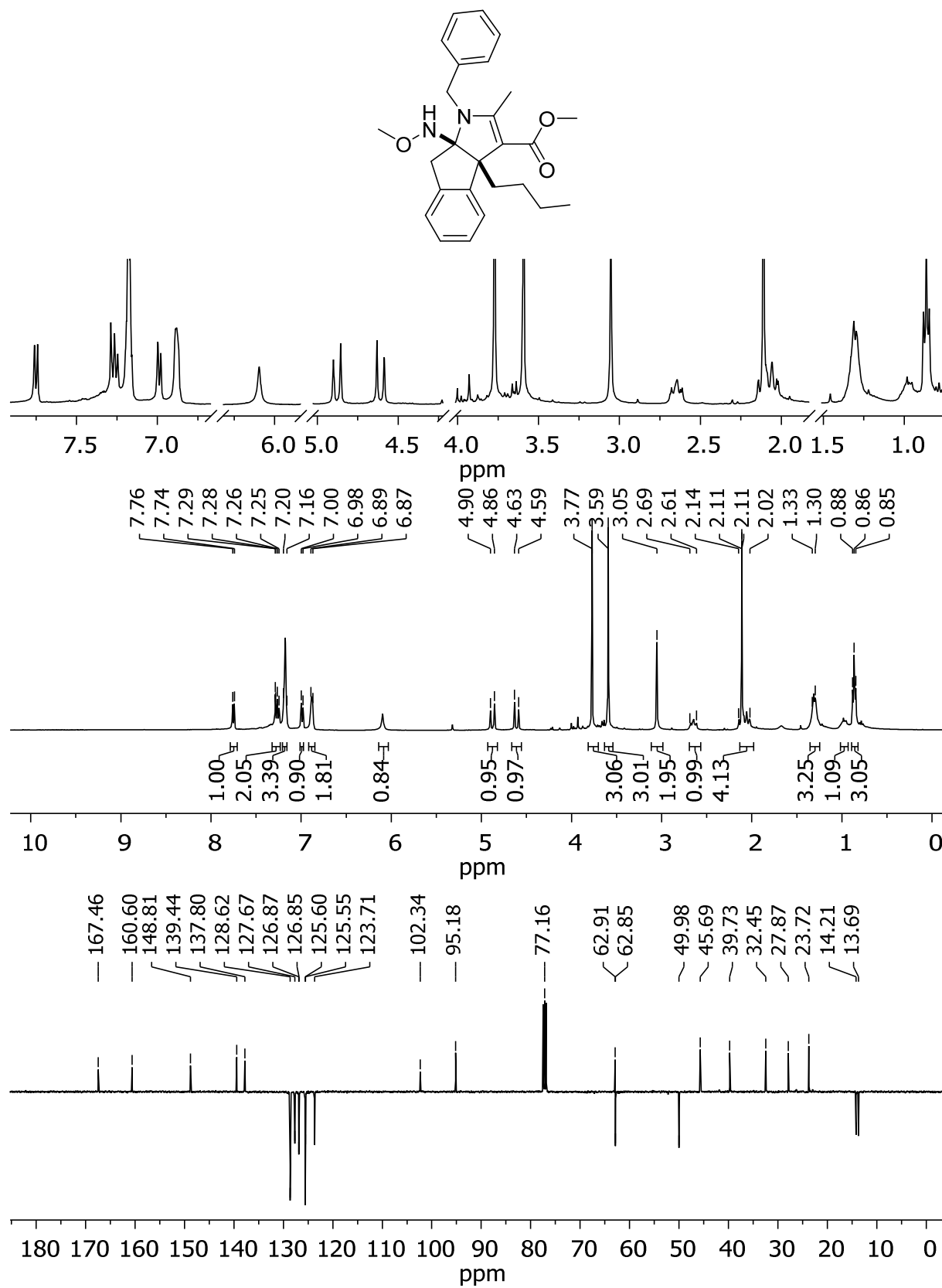
Tetrahydroindeno[2,1-*b*]pyrrole 3p (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



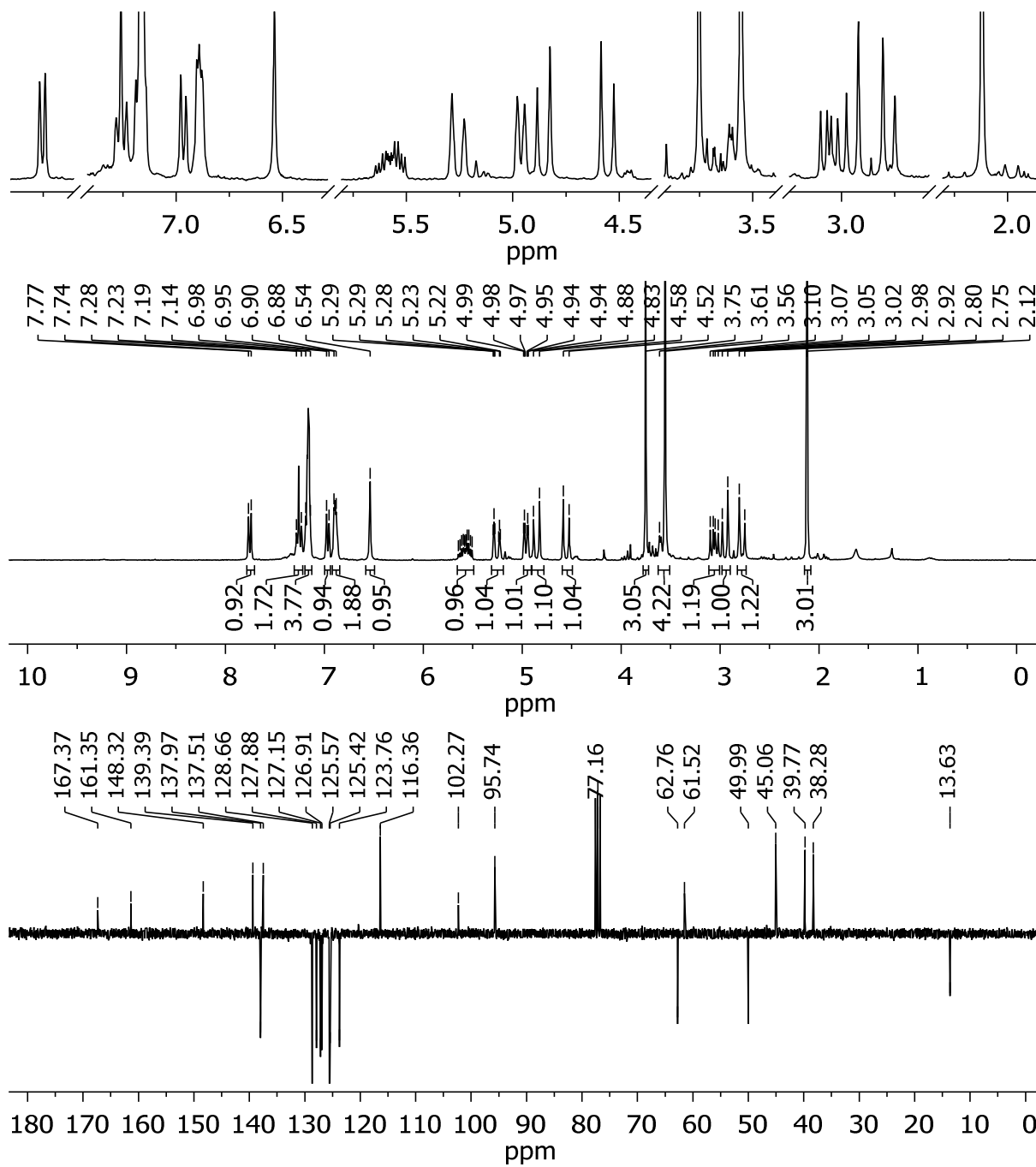
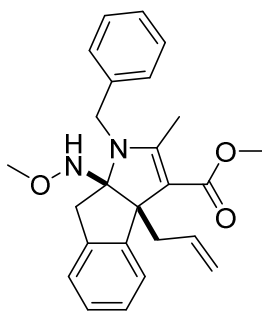
Tetrahydroindeno[2,1-*b*]pyrrole 3q (CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)



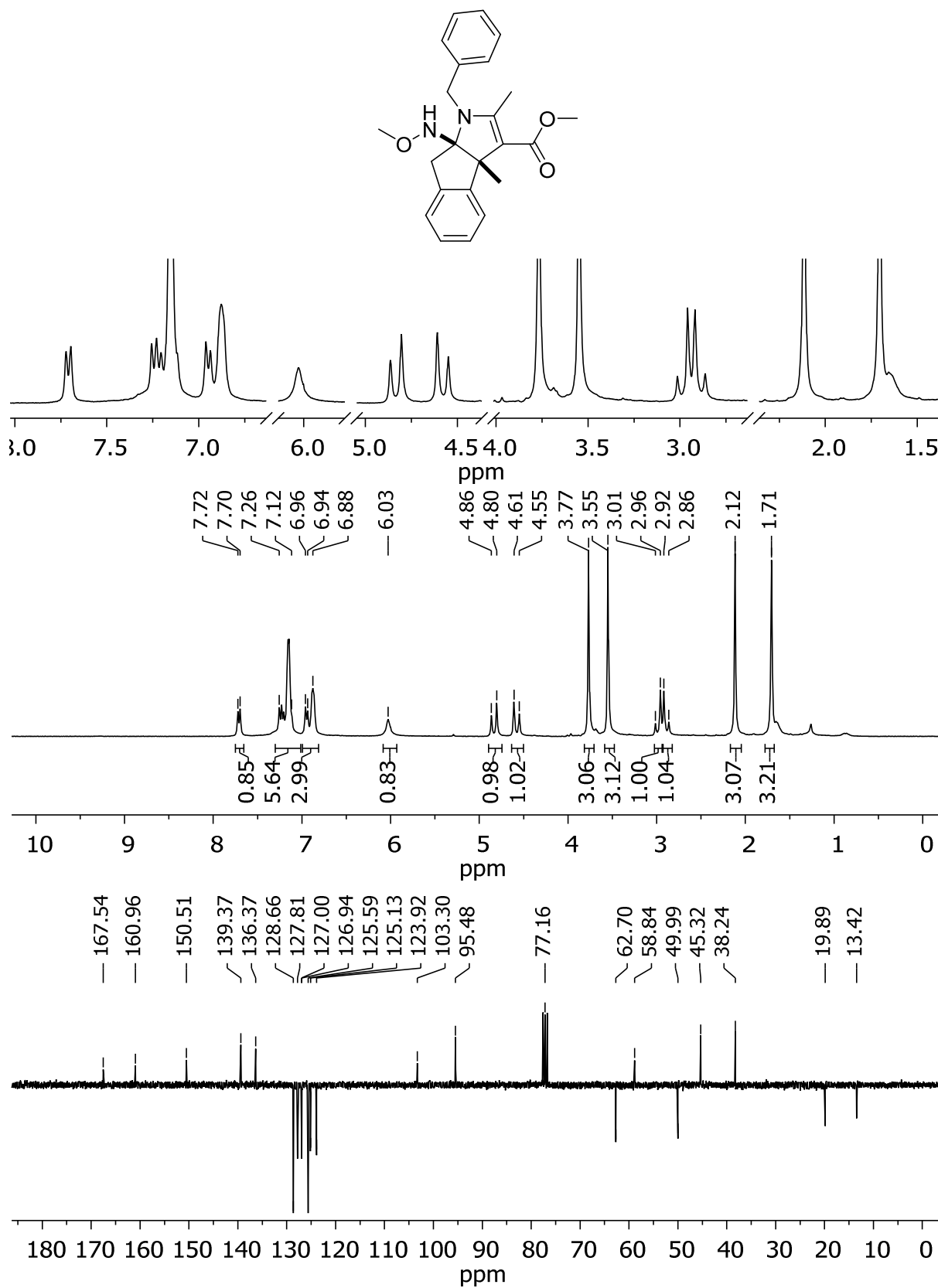
Tetrahydroindeno[2,1-*b*]pyrrole 3r (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



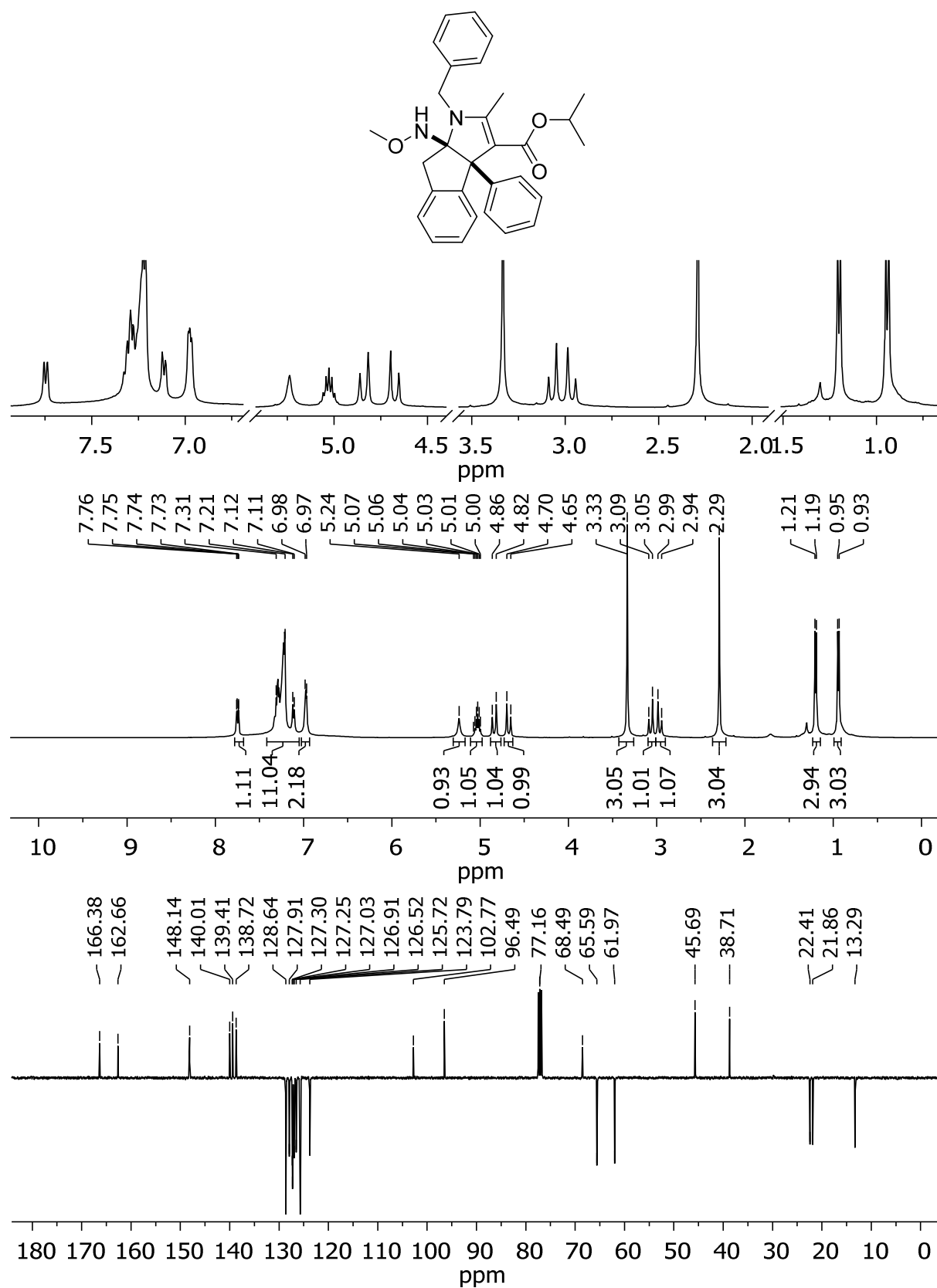
Tetrahydroindeno[2,1-*b*]pyrrole 3s (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



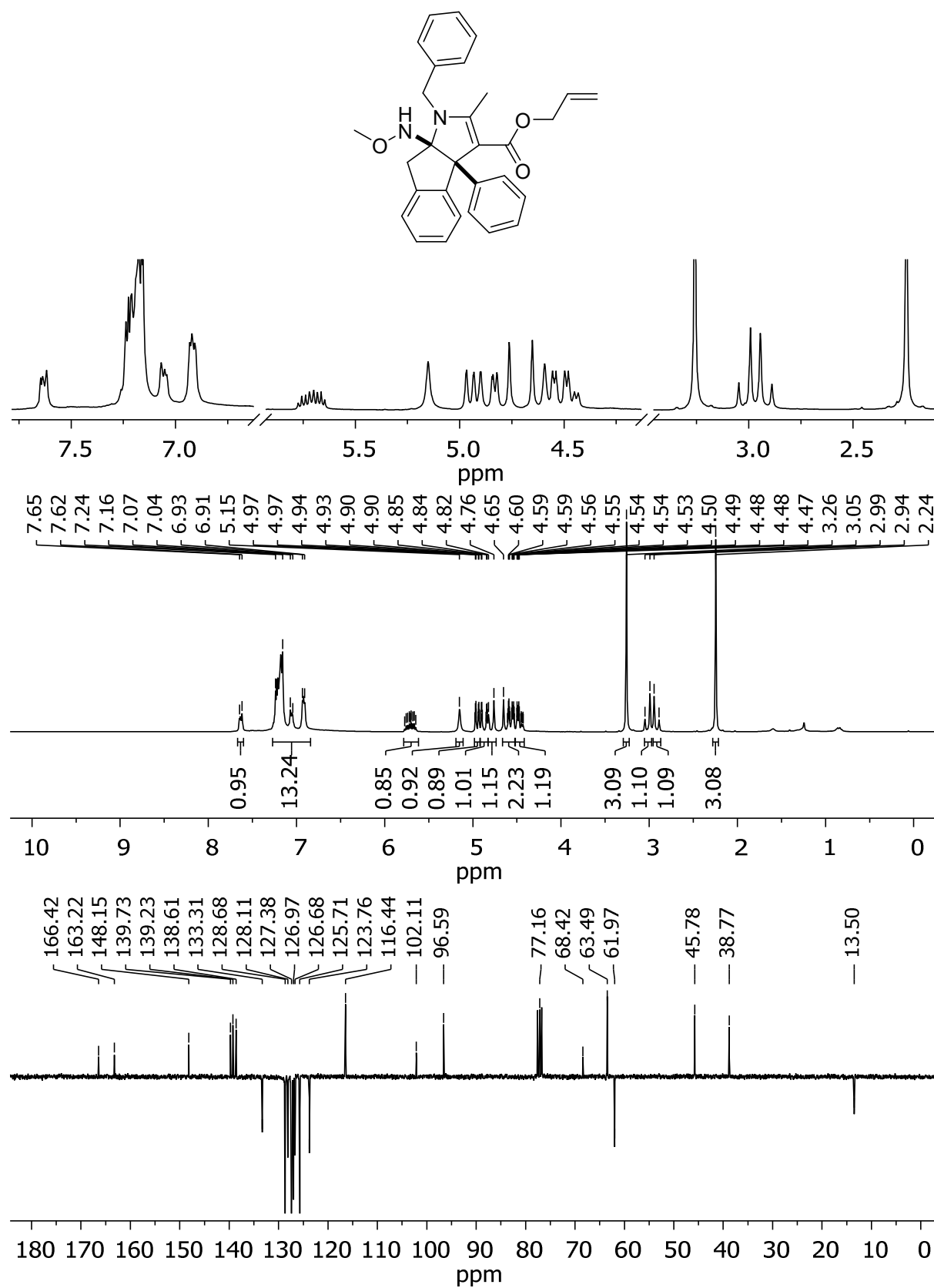
Tetrahydroindeno[2,1-*b*]pyrrole 3t (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



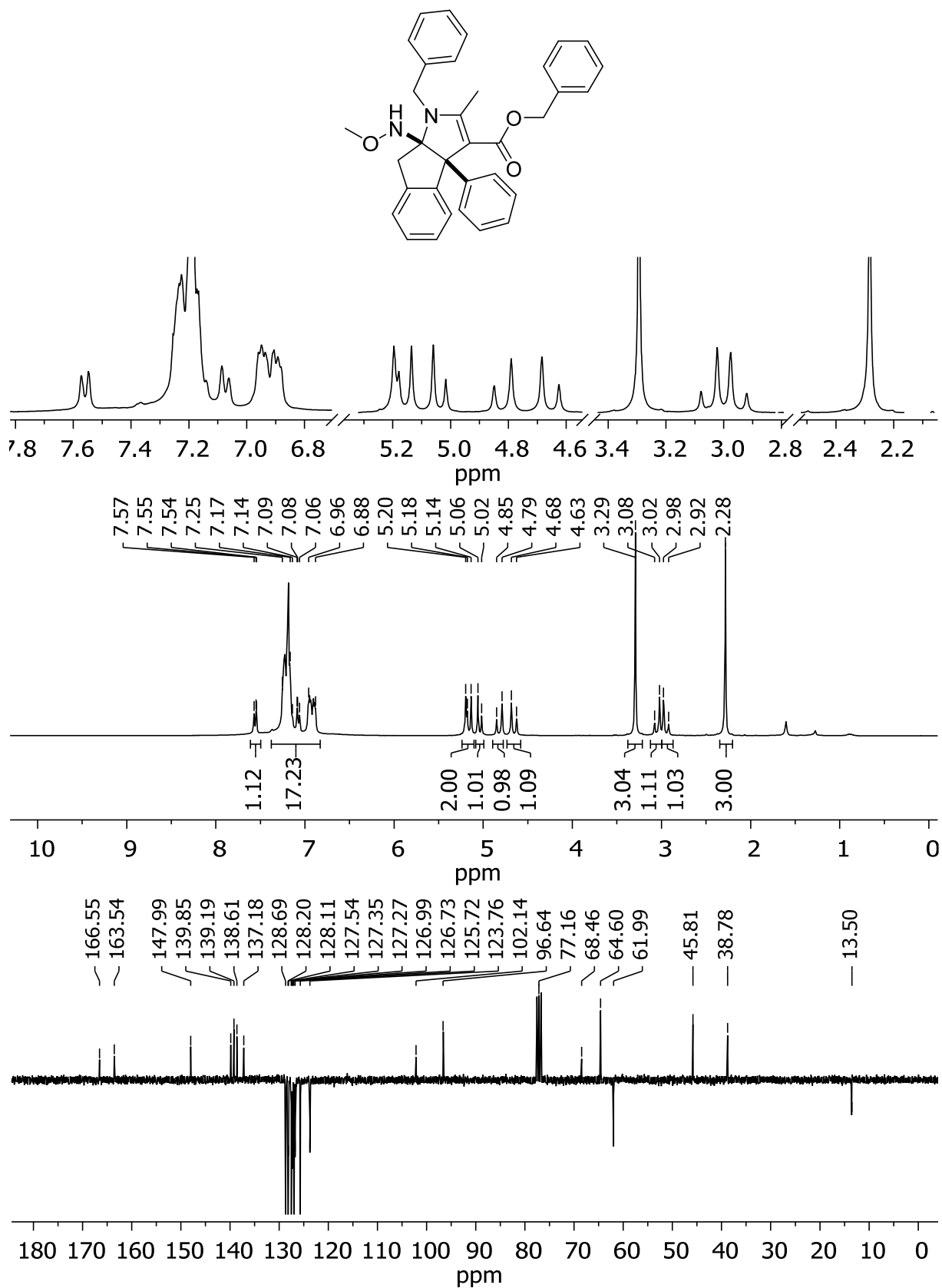
Tetrahydroindeno[2,1-*b*]pyrrole 3u (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



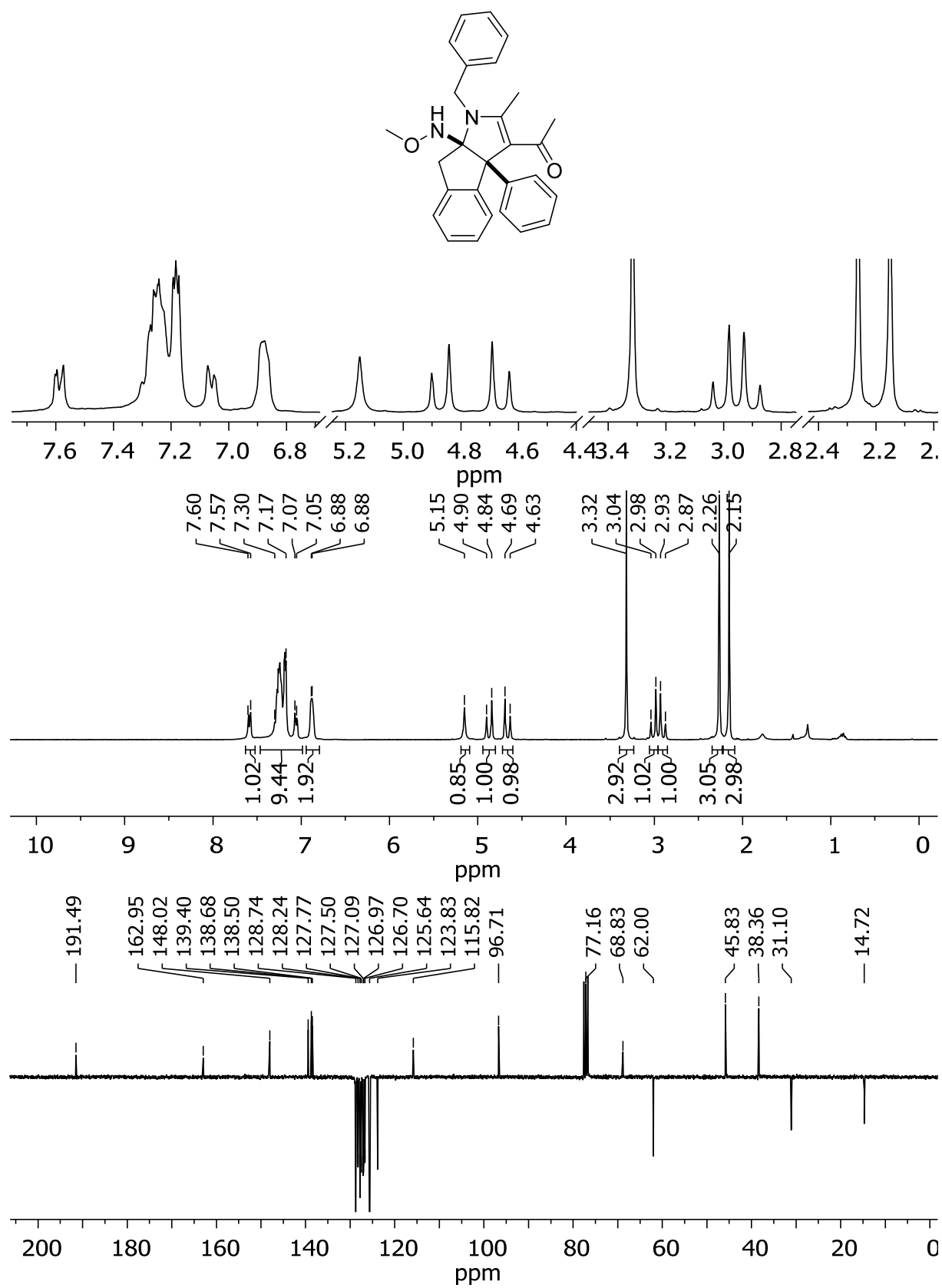
Tetrahydroindeno[2,1-*b*]pyrrole 3v (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



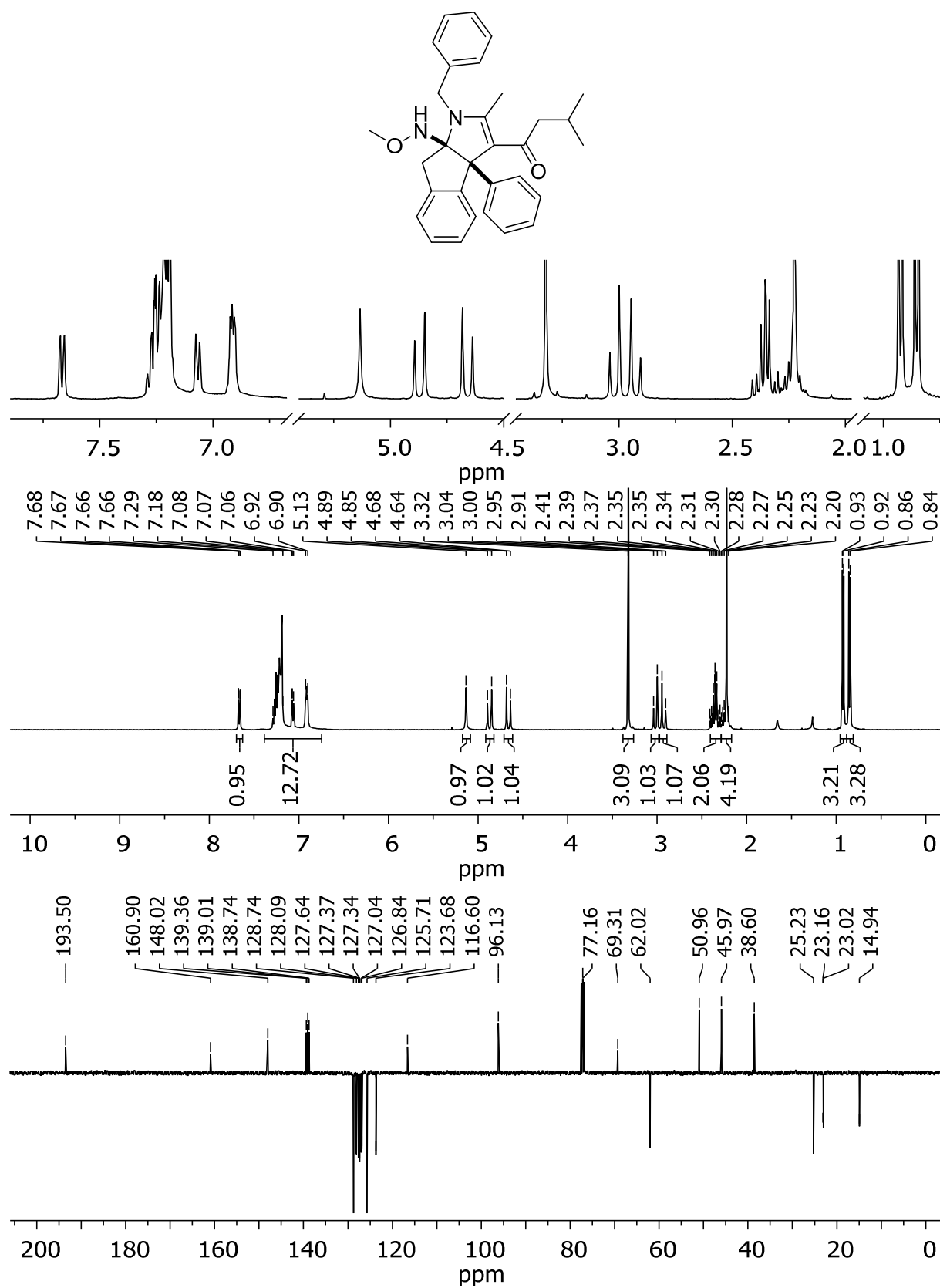
Tetrahydroindeno[2,1-*b*]pyrrole 3w (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



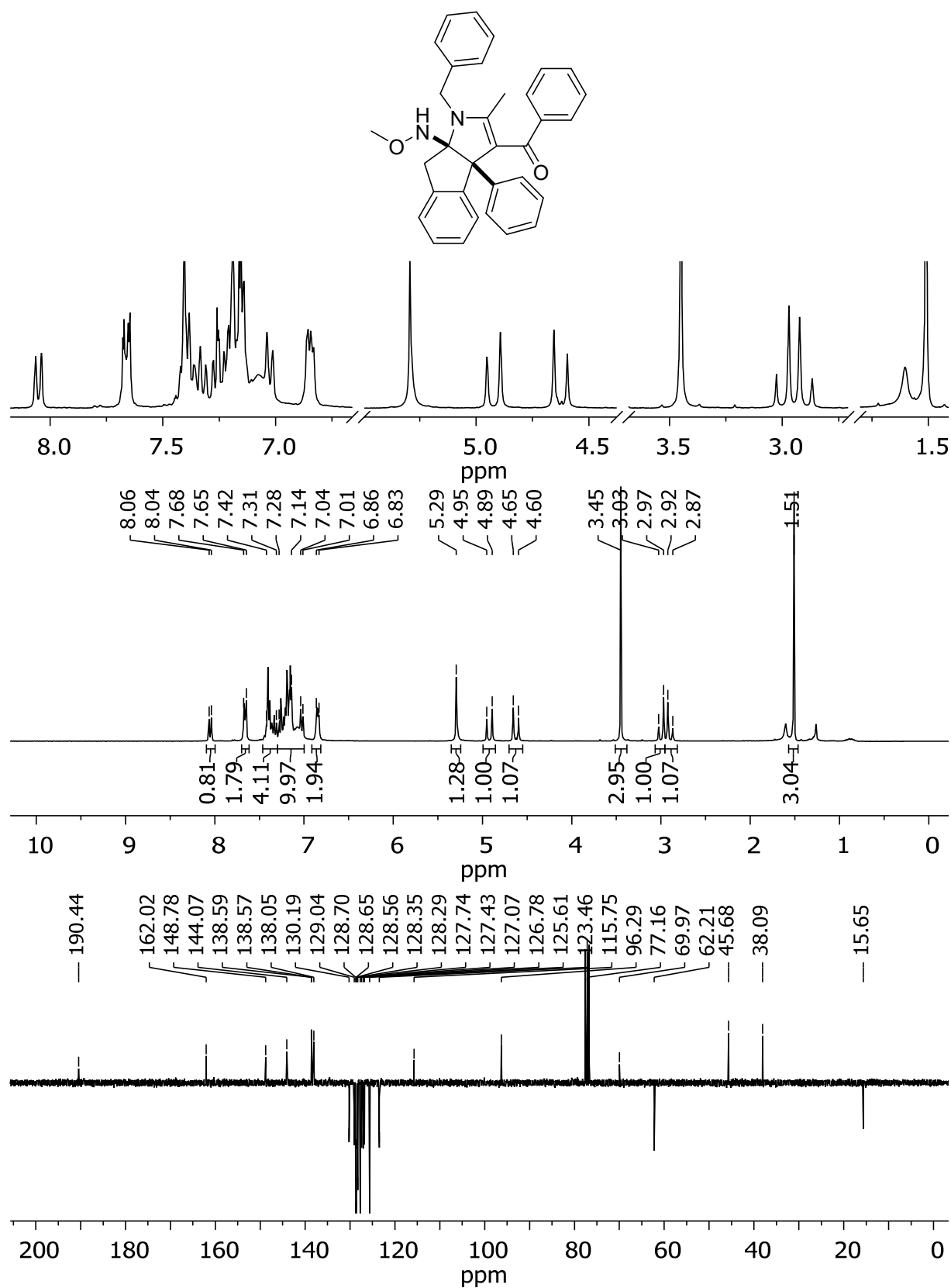
Tetrahydroindeno[2,1-*b*]pyrrole 3x (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



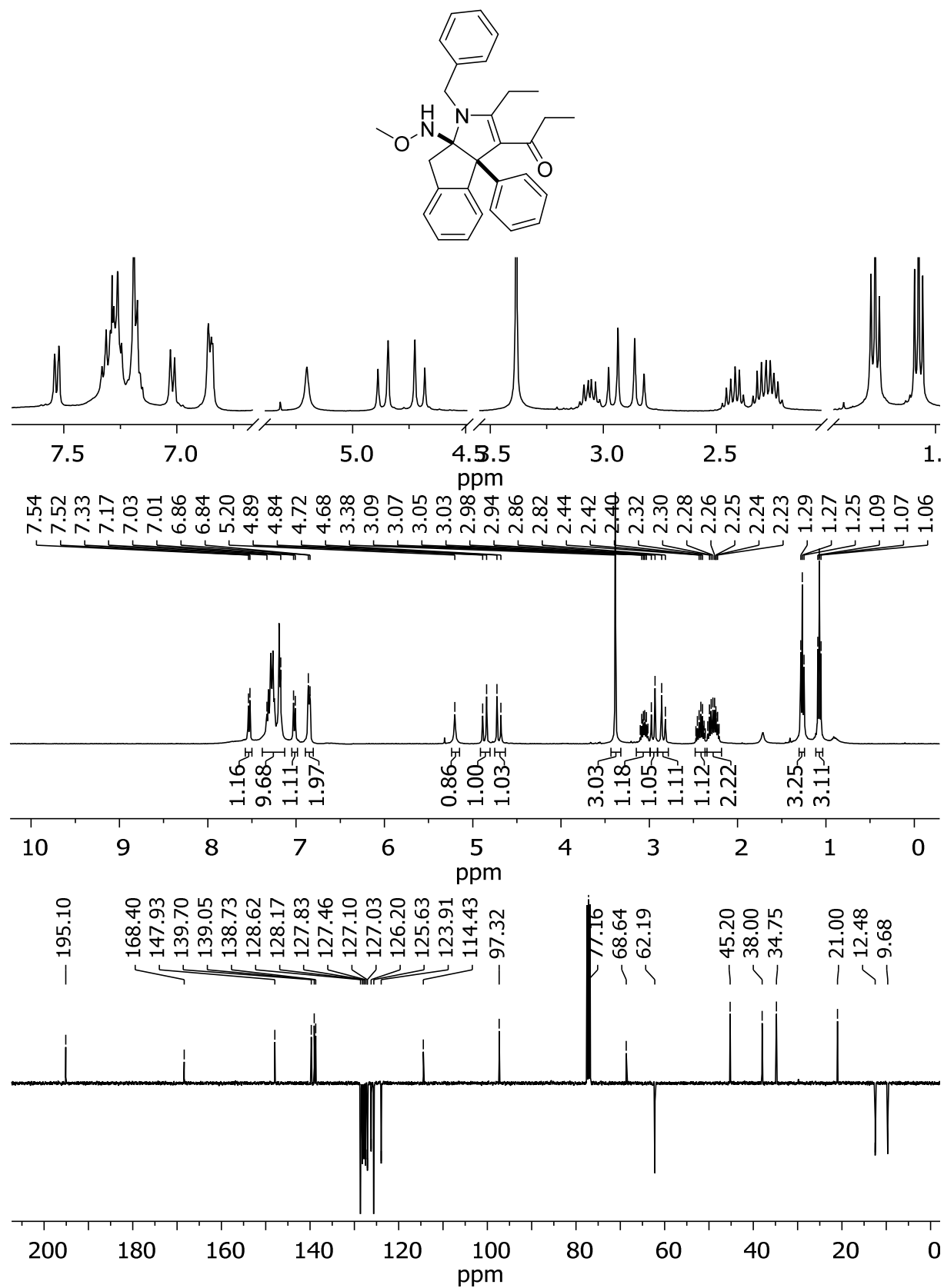
Tetrahydroindeno[2,1-*b*]pyrrole 3y (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



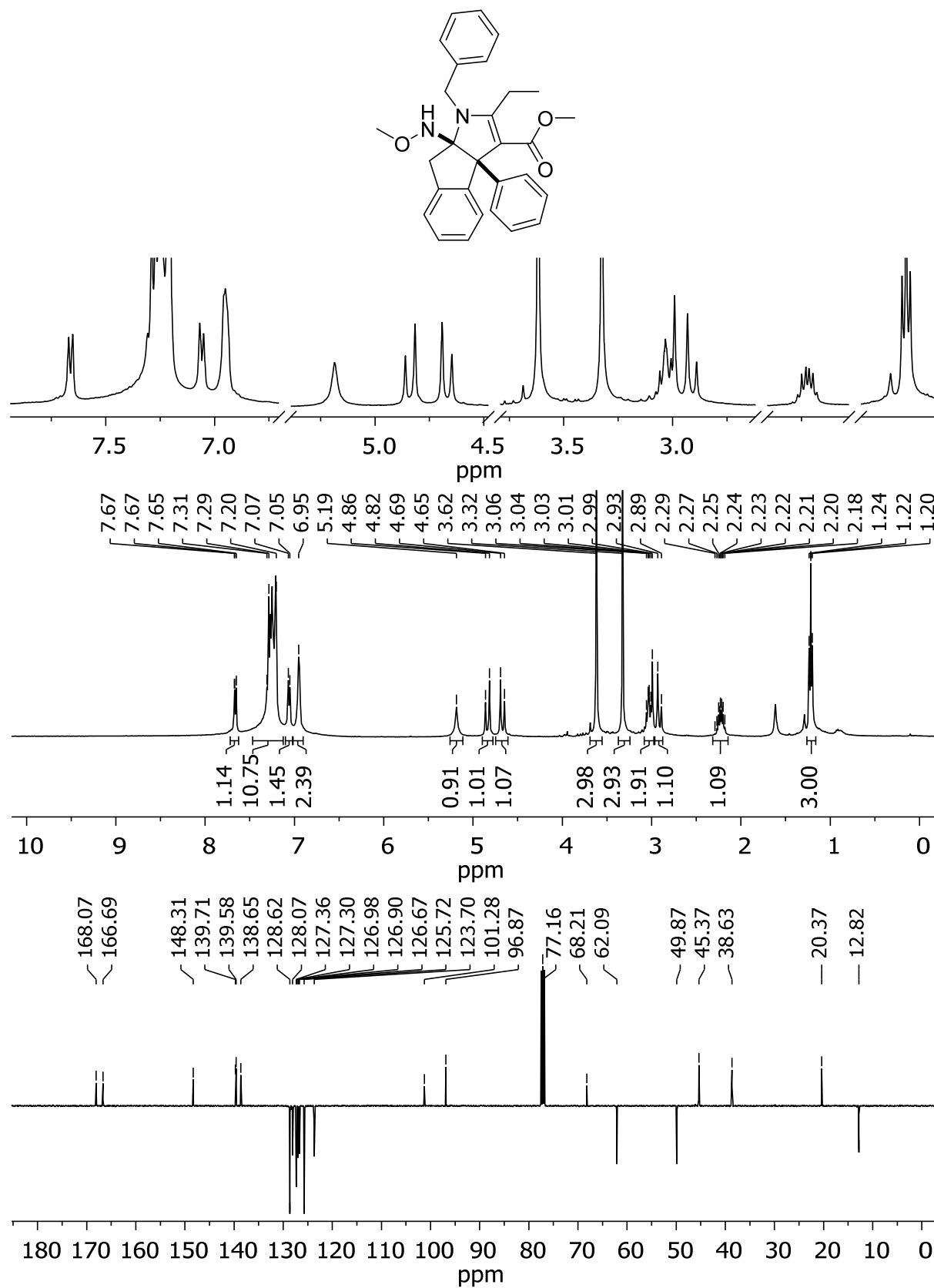
Tetrahydroindeno[2,1-*b*]pyrrole 3z (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



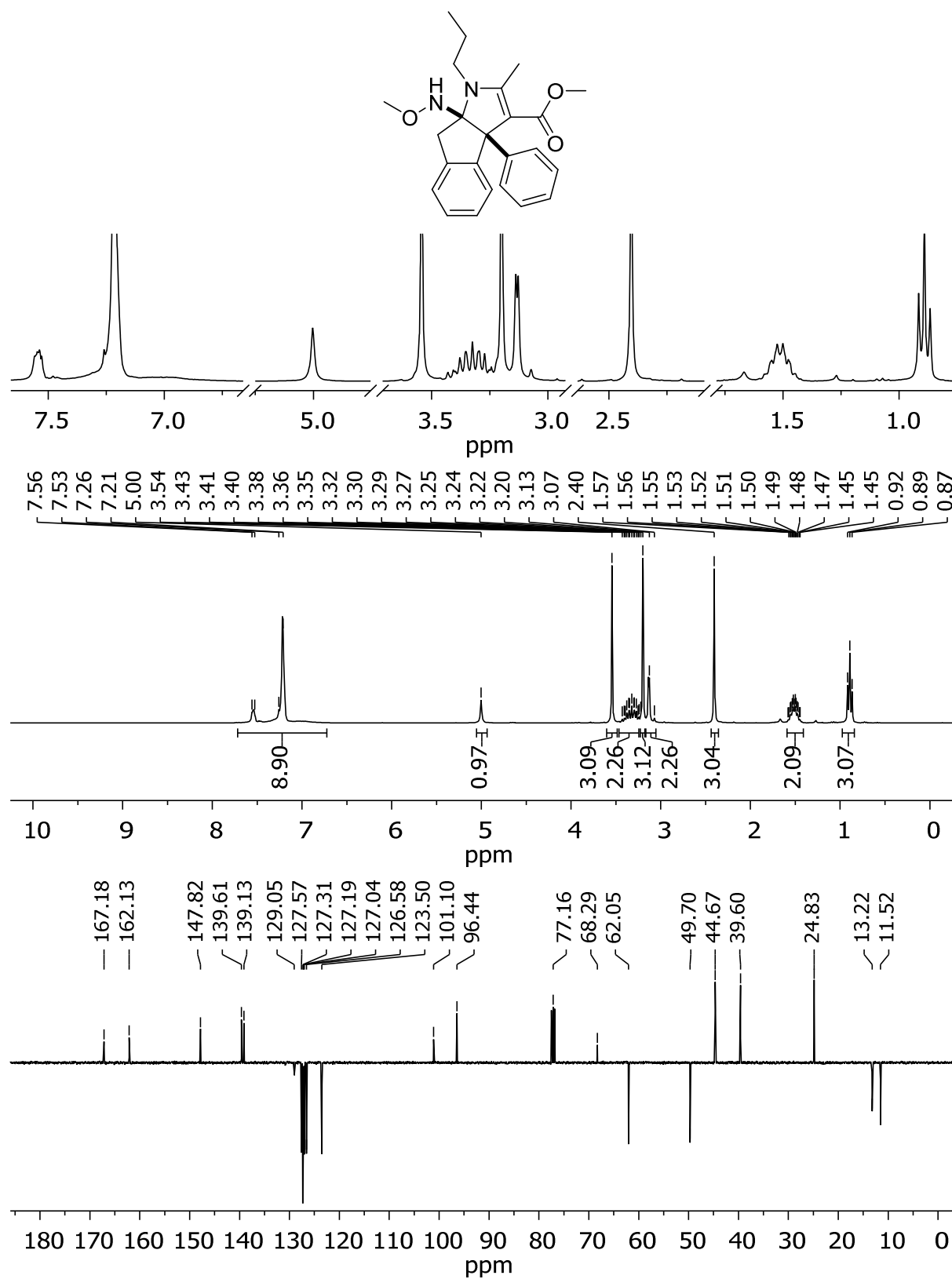
Tetrahydroindeno[2,1-*b*]pyrrole 3aa (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



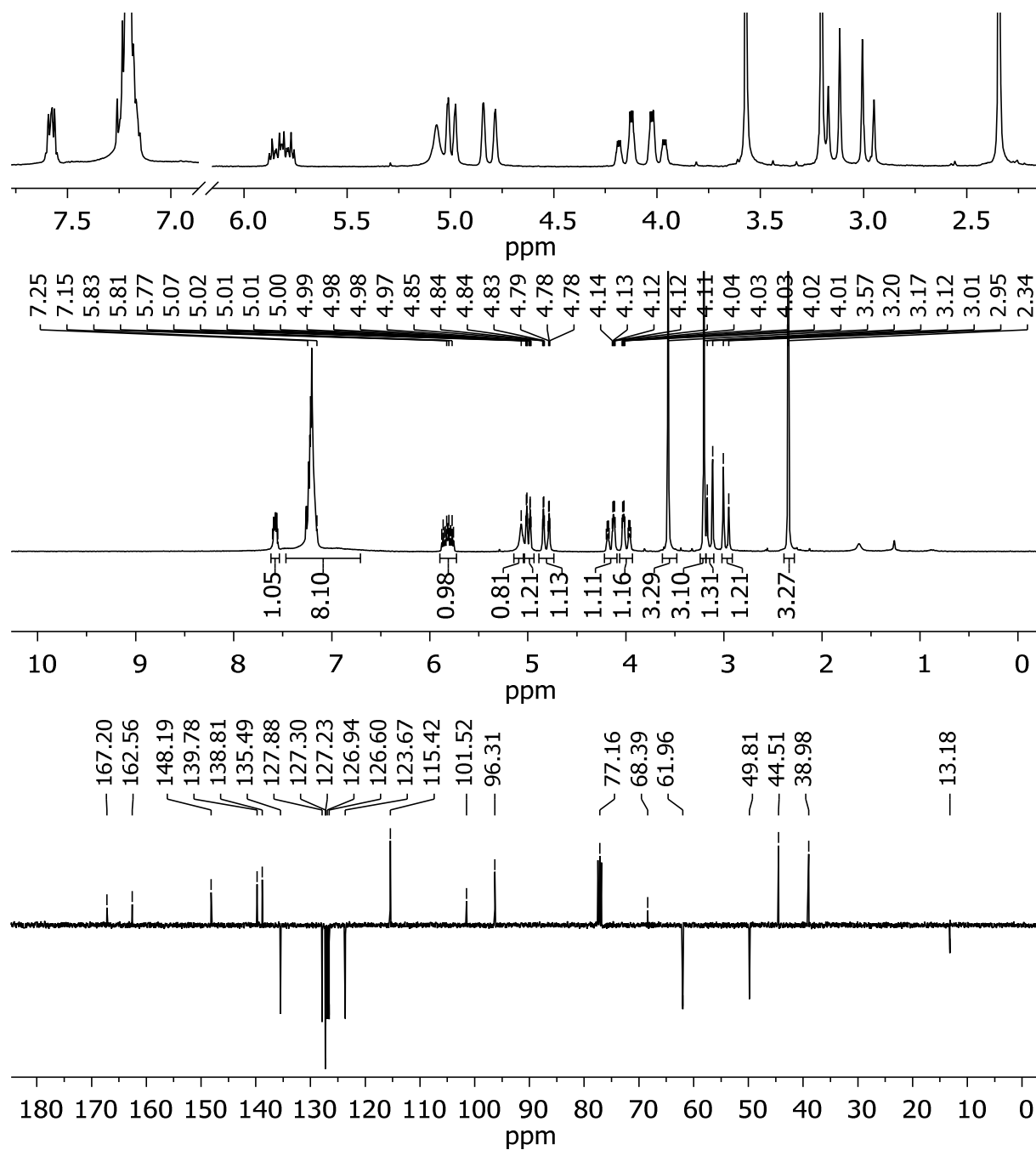
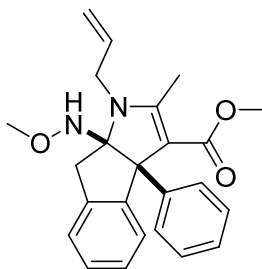
Tetrahydroindeno[2,1-*b*]pyrrole 3ab (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



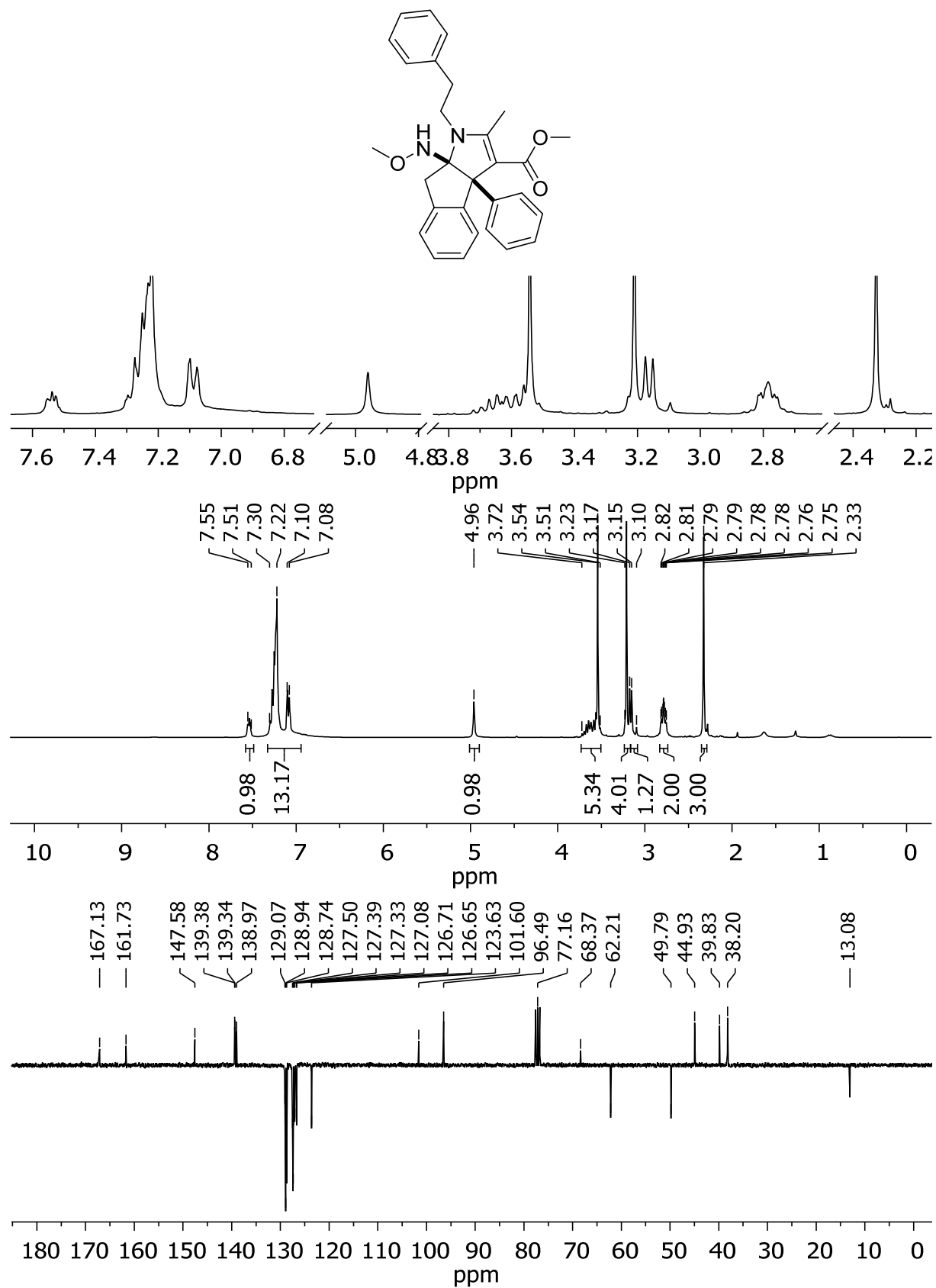
Tetrahydroindeno[2,1-*b*]pyrrole 3ad (CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)



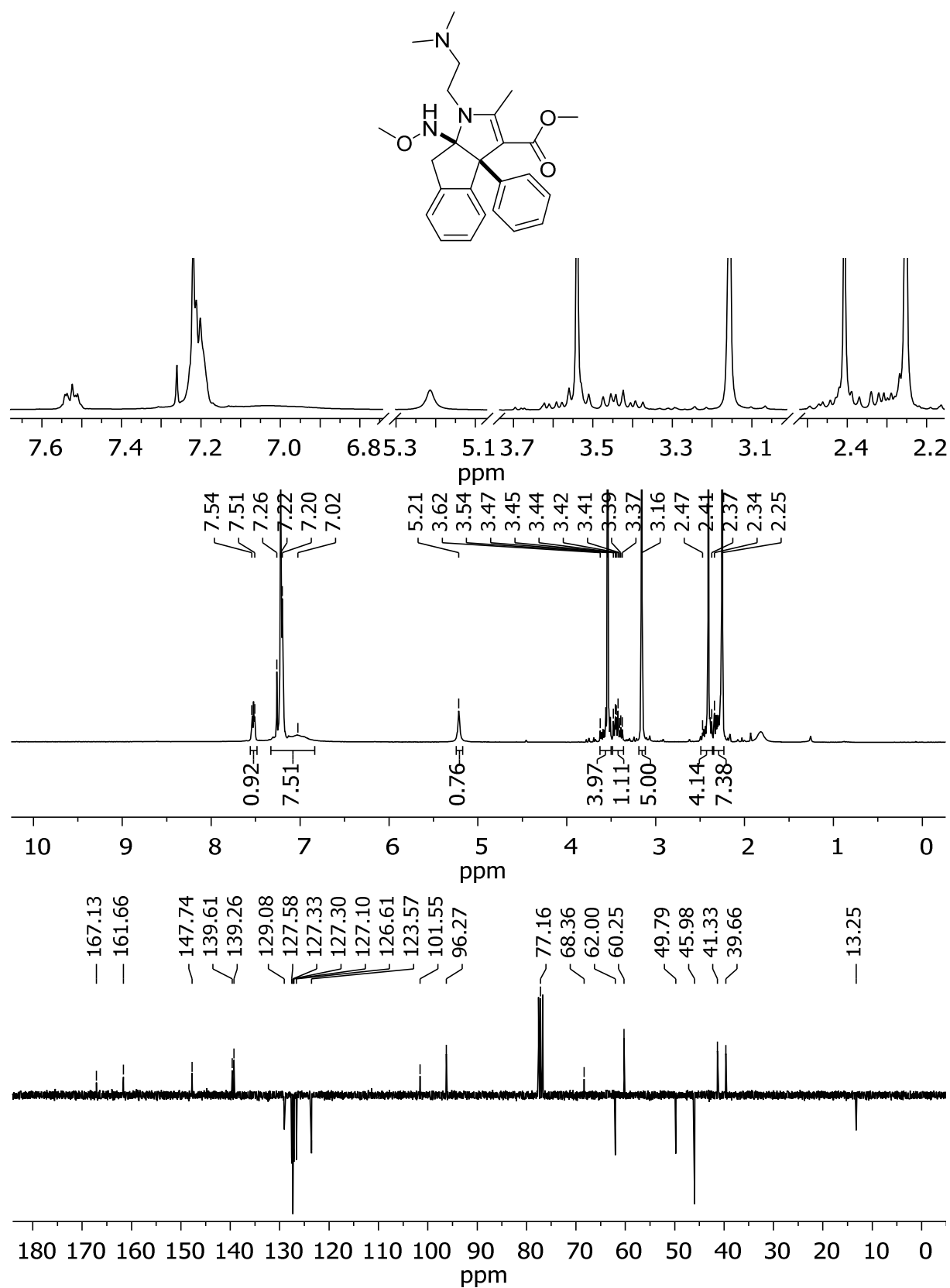
Tetrahydroindeno[2,1-*b*]pyrrole 3ae (CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)



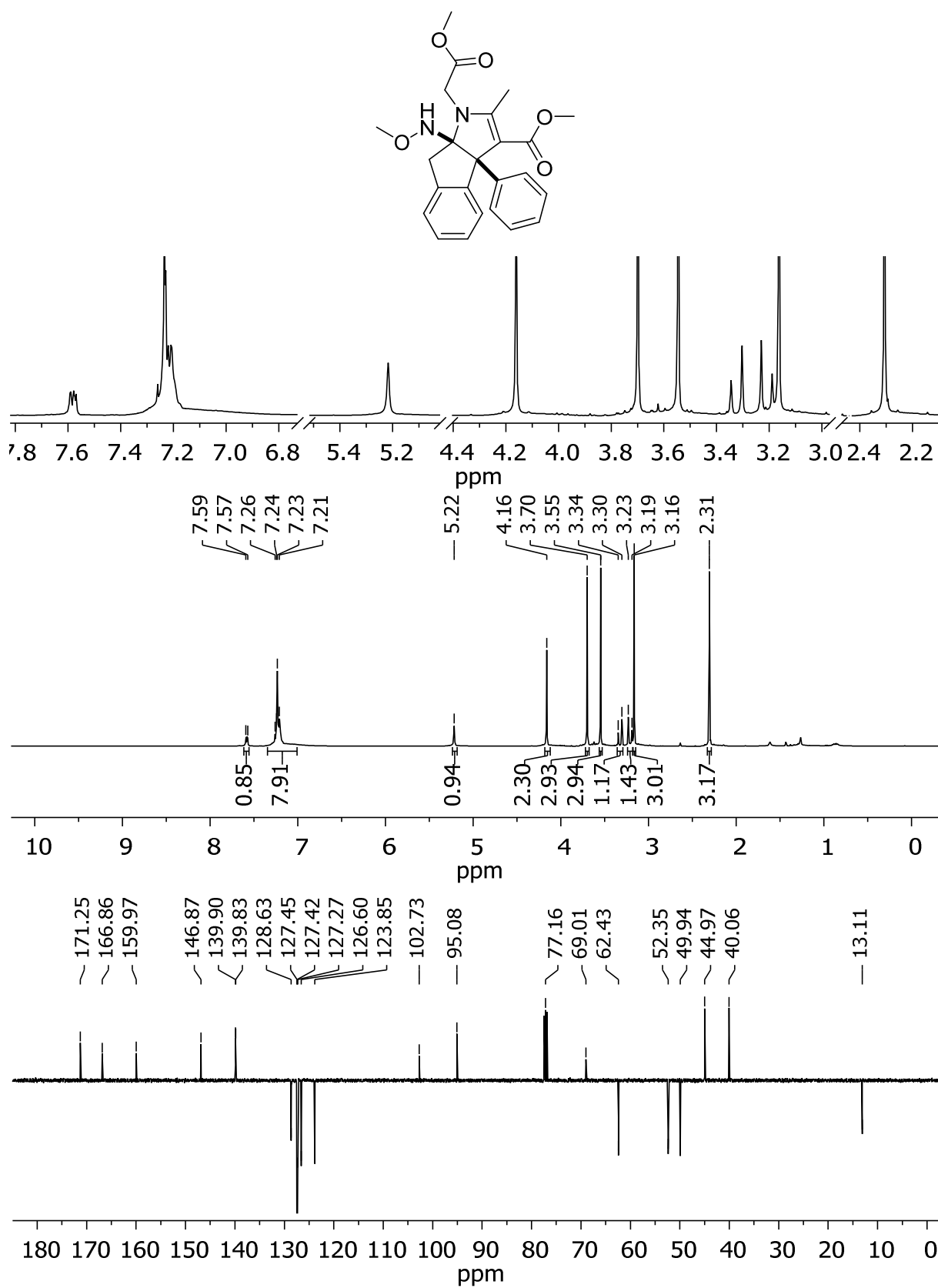
Tetrahydroindeno[2,1-*b*]pyrrole 3af (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



Tetrahydroindeno[2,1-*b*]pyrrole 3ag (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)



Tetrahydroindeno[2,1-*b*]pyrrole 3ah (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



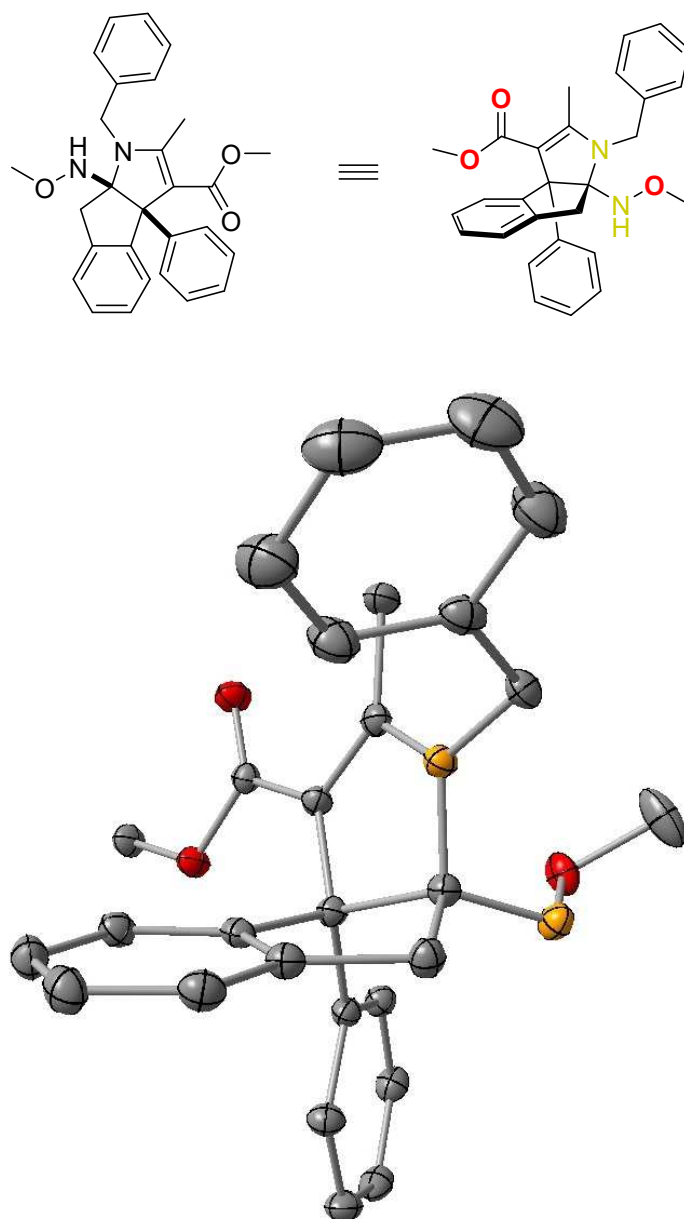
Chemical structure of compound 10 is shown above the spectra. The ¹H NMR spectrum (top) shows peaks at 7.56, 7.54, 7.26, 7.21, 7.20, 7.20, 7.19, 4.90, 3.51, 3.24, 3.08, 2.49, 1.93, 1.78, 1.72, 1.66, 1.38, and 1.08 ppm. The ¹³C NMR spectrum (middle) shows peaks at 167.30, 161.65, 147.65, 140.07, 139.70, 129.01, 128.32, 127.38, 127.32, 127.27, 126.93, 126.49, 123.36, 101.18, 97.13, 77.16, 68.66, 68.45, 61.54, 55.65, 49.64, 40.70, 33.98, 32.75, 27.12, 27.05, 25.84, and 15.19 ppm.

3.3 X-Ray Crystal Structure of 3a

Crystal Data and Structure Refinement for Tetrahydroindeno[2,1-*b*]pyrrole 3a

Identification code	try1	
Empirical formula	C ₂₈ H ₂₈ N ₂ O ₃	
Formula weight	440.52	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.1041(2) Å	α = 90°.
	b = 17.9552(4) Å	β = 90°.
	c = 22.3185(5) Å	γ = 90°.
Volume	4449.78(16) Å ³	
Z	8	
Density (calculated)	1.315 Mg/m ³	
Absorption coefficient	0.086 mm ⁻¹	
F(000)	1872	
Crystal size	0.3000 x 0.3000 x 0.2000 mm ³	
Theta range for data collection	2.342 to 30.390°.	
Index ranges	-14 ≤ h ≤ 15, -24 ≤ k ≤ 24, -30 ≤ l ≤ 30	
Reflections collected	43124	
Independent reflections	6306 [R(int) = 0.0504]	
Completeness to theta = 30.390°	93.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.99762	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6306 / 0 / 305	
Goodness-of-fit on F ²	1.017	
Final R indices [I > 2σ(I)]	R1 = 0.0481, wR2 = 0.0982	
R indices (all data)	R1 = 0.0712, wR2 = 0.1072	
Largest diff. peak and hole	0.300 and -0.224 e.Å ⁻³	

Crystal Structure of Tetrahydroindeno[2,1-*b*]pyrrole **3a**

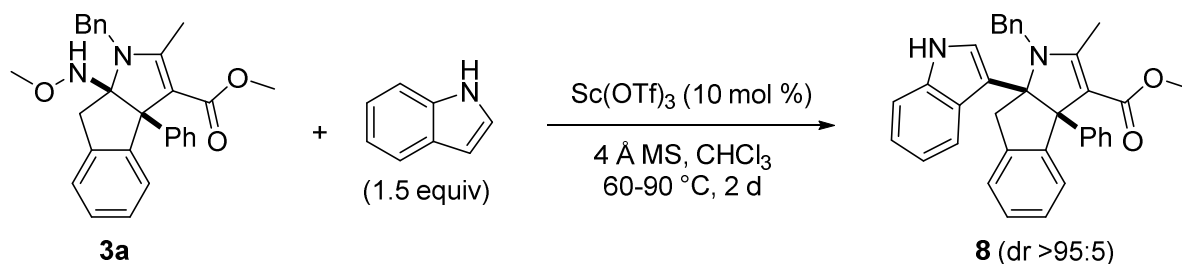


DIAMOND representation of tetrahydroindeno[2,1-*b*]pyrrole **3a** with thermal ellipsoids shown at 50% probability level. Hydrogen atoms are omitted for clarity. CCDC 1817406 contains the supplementary crystallographic data of **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

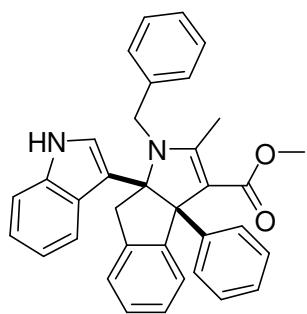
4 Derivatization of Tetrahydroindeno[2,1-*b*]pyrrole 3a

4.1 Procedures

Aza-Friedel-Crafts reaction of 3a with indole

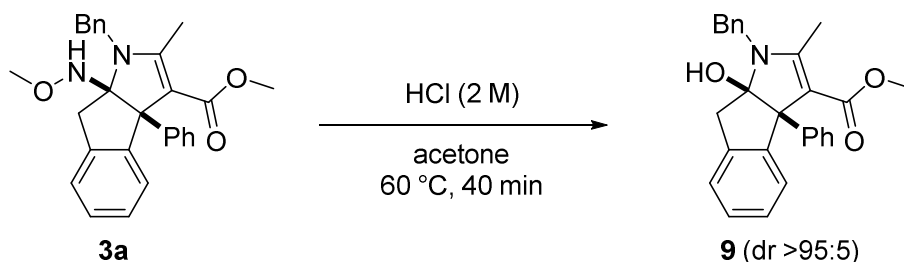


A mixture of amina **3a** (44 mg, 0.10 mmol, 1.0 equiv), indole (18 mg, 0.15 mmol, 1.5 equiv), Sc(OTf)₃ (4.9 mg, 10 μmol, 0.10 equiv) and 4 Å molecular sieve (25 mg) were dissolved in 0.5 mL abs. CHCl₃. The reaction mixture was stirred at 60 °C for 24 h followed by 90 °C for another 24 h. It was quenched with sat. NaHCO₃-solution and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (15% → 50% MTBE/hexane). Compound **8** was obtained as a colorless solid (48 mg, 94%, dr >95:5). The NMR-spectrum of **8** shows two rotamers at room temperature in the ratio of 85:15. The spectroscopic data are displayed for the major rotamer.

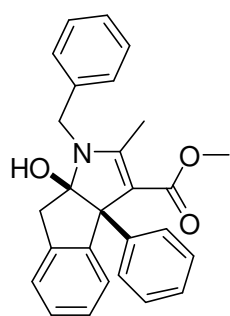


R_f: 0.30 (40% MTBE/hexane); **mp.**: 134 – 136 °C; **¹H-NMR** (400 MHz, DMSO-d₆): δ (ppm) = 10.76 (bs, 1H), 7.56 (d, *J* = 7.0 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.16 (m, 5H), 7.05 – 7.02 (m, 2H), 6.92 – 6.88 (m, 3H), 6.75 – 6.70 (m, 1H), 6.69 – 6.64 (m, 2H), 6.49 (m, 2H), 4.53 (d, *J* = 18.0 Hz, 1H), 4.10 (d, *J* = 18.0 Hz, 1H), 3.79 (d, *J* = 17.0 Hz, 1H), 3.47 (s, 3H), 3.15 (d, *J* = 17.0 Hz, 1H), 2.30 (s, 3H); **¹³C-NMR** (100 MHz, DMSO-d₆): δ (ppm) = 166.2 (C=O), 161.9 (C_q), 148.9 (C_q), 142.6 (C_q), 139.8 (C_q), 139.2 (C_q), 136.8 (C_q), 128.3 (2x CH), 127.6 (2x CH), 126.9 (CH), 126.7 (CH), 126.1 (3x CH), 126.0 (CH), 125.6 (3x CH), 125.5 (C_q), 125.0 (CH), 123.6 (CH), 120.7 (CH), 120.2 (CH), 119.1 (CH), 113.8 (C_q), 111.5 (CH), 100.8 (C_q), 84.6 (C_q), 70.1 (C_q), 49.4 (CH₃), 46.4 (CH₂), 41.2 (CH₂), 13.5 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3419, 3059, 3028, 2943, 1649, 1560, 1494, 1474, 1457, 1415, 1340, 1329, 1202, 1188, 1162, 1127, 753, 736, 699; **HR-MS** (ESI⁺): calcd. for C₃₅H₃₀N₂O₂Na ([M+Na]⁺): 533.2200, found: 533.2203; **M**(C₃₅H₃₀N₂O₂): 510.64.

Hydrolysis of 3a

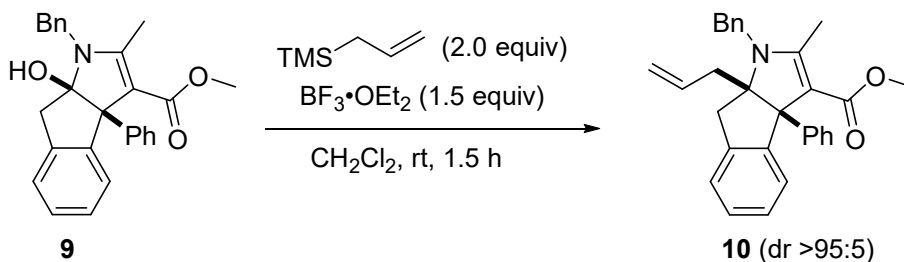


To a solution of **3a** (441 mg, 1.00 mmol, 1.00 equiv) in 10.0 mL acetone, 2.0 mL of a 2.0 M HCl-solution was added dropwise. The reaction mixture was stirred at 60 °C for 40 min and then cooled to room temperature. It was treated with sat. NaHCO_3 -solution and EtOAc. The aqueous phase was separated 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 (30% \rightarrow 50% MTBE/hexane). Compound **9** was obtained as a colorless solid (345 mg, 84%, dr >95:5).



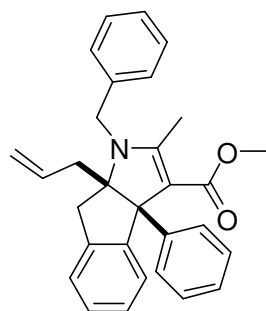
R_f: 0.40 (50% MTBE/hexane); **mp.**: 52 – 54 °C; **¹H-NMR** (400 MHz, CDCl_3): δ (ppm) = 7.68 – 7.66 (m, 1H), 7.37 – 7.25 (m, 8H), 7.19 – 7.06 (m, 5H), 4.68 (d, J = 17.5 Hz, 1H), 4.60 (d, J = 17.5 Hz, 1H), 3.60 (s, 3H), 3.32 (d, J = 16.5 Hz, 1H), 3.19 (d, J = 16.5 Hz, 1H), 2.29 (s, 3H), 1.97 (bs, 1H); **¹³C-NMR** (75 MHz, CDCl_3): δ (ppm) = 167.0 (C=O), 160.8 (C_q), 146.0 (C_q), 139.8 (C_q), 139.5 (C_q), 139.0 (C_q), 128.9 (2x CH), 128.5 (2x CH), 128.2 (2x CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.0 (2x CH), 124.0 (CH), 103.7 (C_q), 101.6 (C_q), 68.6 (C_q), 50.0 (CH_3), 45.3 (CH_2), 43.5 (CH_2), 13.5 (CH_3); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3420, 3062, 3027, 2946, 2924, 1731, 1716, 1651, 1671, 1651, 1586, 1569, 1495, 1473, 1448, 1435, 1413, 1339, 1204, 1160, 1132, 1093, 1078, 1063, 754, 747, 733, 698; **HR-MS** (ESI⁺): calcd. for $\text{C}_{27}\text{H}_{25}\text{NO}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 434.1727, found: 434.1730; **M**($\text{C}_{27}\text{H}_{25}\text{NO}_3$): 411.50.

Hosomi-Sakurai reaction of 9



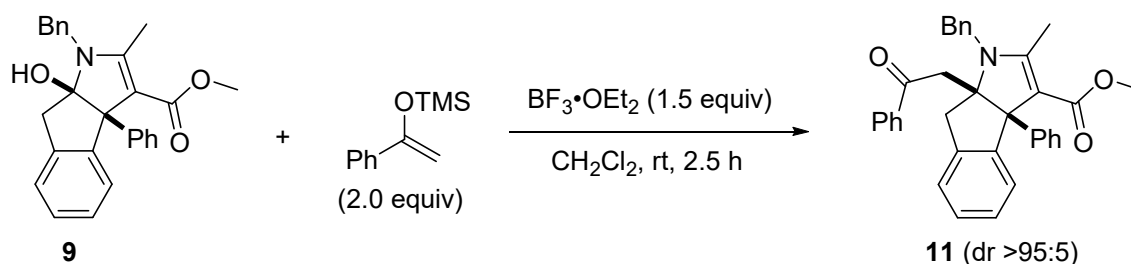
To a solution of **9** (41 mg, 0.10 mmol, 1.0 equiv) in 0.5 mL abs. CH_2Cl_2 , allyltrimethylsilane (32 μL , 0.20 mmol, 1.0 equiv) followed by $\text{BF}_3\cdot\text{OEt}_2$ (19 μL , 0.15 mmol, 1.5 equiv) were

added dropwise. The reaction mixture was stirred at room temperature for 1.5 h and quenched with water. The aqueous phase was separated and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, 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 (33 mg, 77%, dr >95:5).



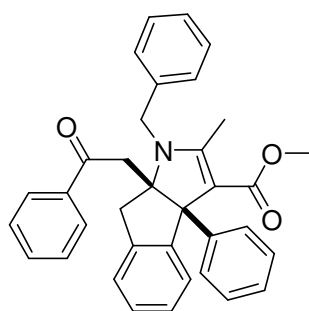
R_f: 0.30 (15% MTBE/hexane); **mp.**: 130 – 132 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.67 (d', *J* = 7.0 Hz, 1H), 7.49 – 7.14 (m, 9H), 7.05 (d', *J* = 7.0 Hz, 1H), 6.83 – 6.81 (m, 2H), 6.54 (m, 1H), 5.60 (ddt, *J* = 17.5, 10.5, 7.0 Hz, 1H), 4.95 – 4.88 (m, 2H), 4.57 (d, *J* = 18.0 Hz, 1H), 4.48 (d, *J* = 18.0 Hz, 1H), 3.60 (s, 3H), 3.03 (s, 2H), 2.18 (s, 3H), 1.97 (bs, 1H), 2.07 (dd, *J* = 15.0, 7.5 Hz, 1H), 1.94 (dd, *J* = 15.0, 6.5 Hz, 1H); **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 167.7 (C=O), 162.6 (C_q), 149.0 (C_q), 141.6 (C_q), 140.2 (C_q), 138.9 (C_q), 134.3 (CH), 128.6 (2x CH), 128.1 (CH), 127.7 (2x CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 125.7 (2x CH), 123.6 (CH), 118.1 (CH₂), 101.3 (C_q), 83.3 (C_q), 69.5 (C_q), 49.8 (CH₃), 46.8 (CH₂), 41.1 (CH₂), 40.6 (CH₂), 13.4 (CH₃);* **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3433, 3063, 2942, 2902, 1662, 1585, 1562, 1413, 1328, 1198, 1162, 1124, 755, 743, 733, 701; **HR-MS** (ESI⁺): calcd. for C₃₀H₃₀NO₂ ([M+H]⁺): 436.2271, found: 436.2271; **M**(C₃₀H₂₉NO₂): 435.57.

Mukaiyama-Mannich reaction of **9**



To a solution of **9** (41 mg, 0.10 mmol, 1.0 equiv) in 1.0 mL abs. CH₂Cl₂, 1-phenyl-1-trimethylsiloxyethylene (41 μ L, 0.20 mmol, 1.0 equiv) followed by BF₃·OEt₂ (19 μ L, 0.15 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at room temperature for 2.5 h and quenched with water. The aqueous phase was separated and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (10% → 50% MTBE/hexane). Compound **11** was obtained as a colorless solid (41 mg, 79%, dr >95:5).

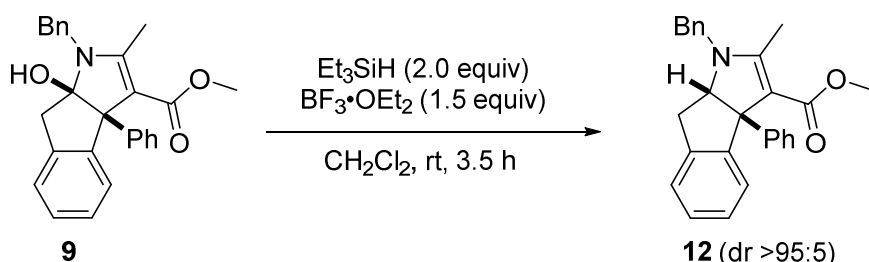
* One ¹³C-signal is very broad and could not be clearly detected.



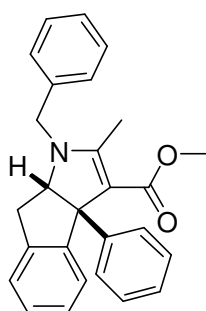
R_f: 0.27 (20% MTBE/hexane); **mp.**: 129 – 131 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.70 – 7.68 (m, 1H), 7.59 – 7.57 (m, 2H), 7.53 – 7.49 (m, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.19 (m, 3H), 7.15 – 7.12 (m, 2H), 7.09 – 7.04 (m, 4H), 6.72 – 6.70 (m, 2H), 6.50 – 6.47 (m, 1H), 4.54 (d, *J* = 18.0 Hz, 1H), 4.45 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 3.44 (d, *J* = 17.0 Hz, 1H), 3.30 (d, *J* = 17.0 Hz, 1H), 3.28 (d, *J* = 16.5 Hz, 1H), 2.22 (s, 3H), 2.20 (d, *J* = 16.5 Hz, 1H);

¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 198.9 (C=O), 167.7 (C=O), 162.5 (C_q), 147.7 (C_q), 141.7 (C_q), 140.8 (C_q), 138.8 (C_q), 137.7 (C_q), 133.2 (CH), 128.9 (2x CH), 128.6 (2x CH), 128.5 (2x CH), 128.1 (CH), 128.0 (2x CH), 127.7 (2x CH), 127.4 (CH), 126.8 (CH), 127.7 (CH), 126.5 (CH), 125.7 (2x CH), 123.8 (CH), 101.6 (C_q), 81.8 (C_q), 71.1 (C_q), 49.9 (CH₃), 47.1 (CH₂), 43.9 (CH₂), 40.9 (CH₂), 13.7 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3444, 3061, 3025, 2941, 2924, 1669, 1586, 1567, 1448, 1415, 1361, 1340, 1199, 1158, 1124, 754, 744, 730, 700; **HR-MS** (ESI⁺): calcd. for C₃₅H₃₁NO₃Na ([M+Na]⁺): 536.2196, found: 536.2191; **M(C₃₅H₃₁NO₃)**: 513.64.

Reduction of 9



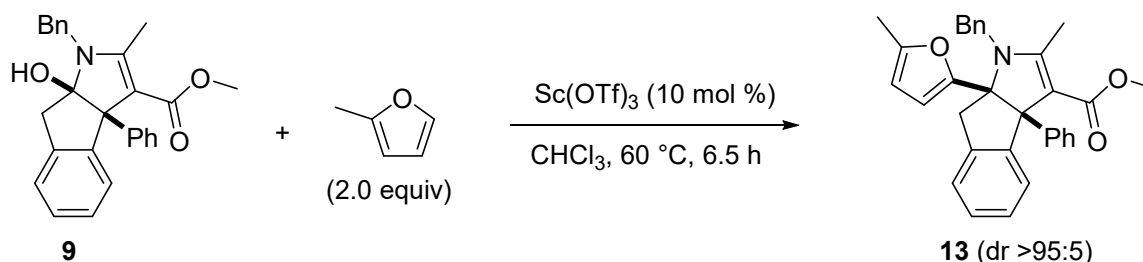
To a solution of **9** (41 mg, 0.10 mmol, 1.0 equiv) in 0.5 mL abs. CH₂Cl₂, triethylsilane (32 μL, 0.20 mmol, 1.0 equiv) followed by BF₃·OEt₂ (19 μL, 0.15 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at room temperature for 3.5 h and quenched with water. The aqueous phase was separated and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, 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 (21 mg, 52%, dr >95:5).



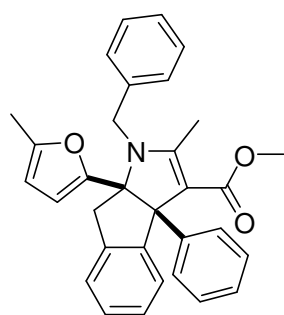
R_f: 0.31 (20% MTBE/hexane); **mp.**: 47 – 49 °C; **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 7.72 – 7.70 (m, 1H), 7.33 – 7.26 (m, 6H), 7.23 – 7.19 (m, 2H), 7.16 – 7.12 (m, 3H), 7.06 (d', *J* = 7.5 Hz, 2H), 4.57 (d, *J* = 16.5 Hz, 1H), 4.34 (d, *J* = 16.5 Hz, 1H), 4.13 (d, *J* = 6.0 Hz, 1H), 3.56 (s, 3H), 3.12 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.03 (d, *J* = 16.5 Hz, 1H), 2.39 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.4 (C=O), 161.8 (C_q), 147.0 (C_q), 146.7

(C_q), 141.4 (C_q), 137.1 (C_q), 129.0 (2x CH), 128.0 (2x CH), 127.61 (CH), 127.56 (CH), 127.44 (CH), 127.36 (CH), 127.0 (2x CH), 126.8 (2x CH), 125.9 (CH), 124.5 (CH), 103.1 (C_q), 77.5 (CH), 66.7 (C_q), 49.9 (CH₃), 48.0 (CH₂), 36.2 (CH₂), 13.4 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3444, 3025, 2942, 2922, 1668, 1566, 1560, 1420, 1202, 1157, 1127, 756, 732, 699; **HR-MS** (ESI⁺): calcd. for C₂₇H₂₅NO₂Na ([M+Na]⁺): 418.1778, found: 418.1776; **M**(C₂₇H₂₅NO₂): 395.50.

Aza-Friedel-Crafts reaction of **9** with 2-methylfuran



Compound **9** (41 mg, 0.10 mmol, 1.0 equiv), 2-methylfuran (18 μ L, 0.20 mmol, 2.0 equiv) and Sc(OTf)₃ (4.9 mg, 10 μ mol, 0.10 equiv) were placed in an oven dried and sealable DURAN® test tube. Abs. CHCl₃ (1.0 mL) was added and the reaction mixture was stirred at 60 °C for 6.5 h. It was quenched with sat. NaHCO₃-solution and extracted twice with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄, 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 solid (40 mg, 84%, dr >95:5).

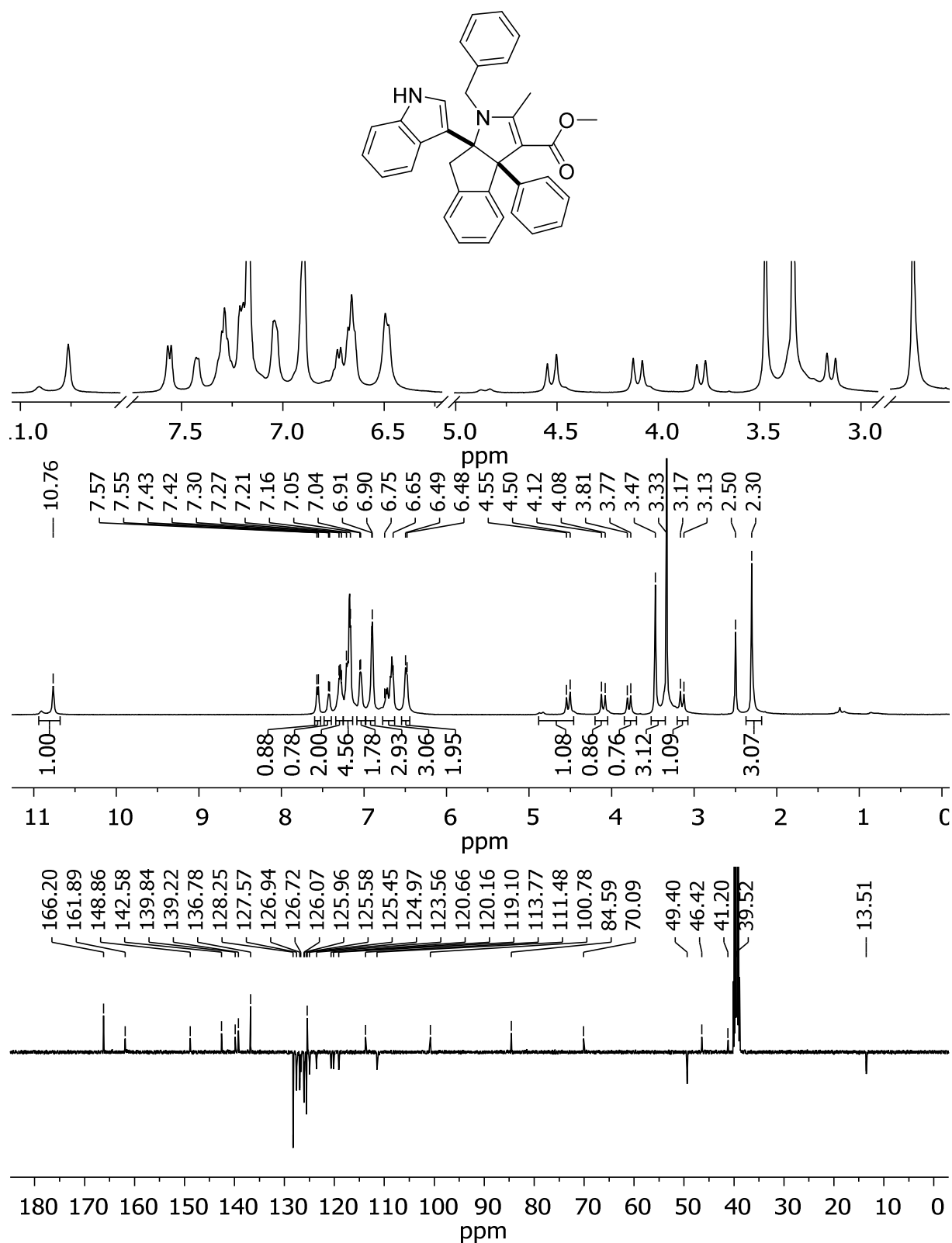


R_f: 0.37 (20% MTBE/hexane); **mp.**: 182 – 184 °C; **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.68 – 7.65 (m, 1H), 7.34 – 7.26 (m, 2H), 7.19 – 7.15 (m, 4H), 7.00 – 6.92 (m, 5H), 6.74 (m, 2H), 5.79 (d, J = 3.0 Hz, 1H), 5.63 (m, 1H), 4.62 (d, J = 17.5 Hz, 1H), 4.22 (d, J = 17.5 Hz, 1H), 3.60 – 3.55 (m, 4H), 3.09 (d, J = 16.5 Hz, 1H), 2.32 (s, 3H), 1.95 (s, 3H); **¹³C-NMR** (100 MHz, CDCl₃): δ (ppm) = 167.6 (C=O), 162.9 (C_q), 152.4 (C_q), 150.1 (C_q), 147.2 (C_q), 142.2 (C_q), 140.1 (C_q), 139.0 (C_q), 128.6 (2x CH), 128.0 (CH), 127.8 (2x CH), 127.3 (CH), 127.12 (CH), 127.08 (CH), 126.8 (2x CH), 125.9 (2x CH), 125.7 (CH), 123.8 (CH), 110.1 (CH), 105.9 (CH), 101.4 (C_q), 84.4 (C_q), 71.3 (C_q), 49.9 (CH₃), 47.6 (CH₂), 39.6 (CH₂), 13.6 (CH₃), 13.4 (CH₃); **IR** (KBr): $\tilde{\nu}$ (cm⁻¹) = 3445, 3061, 3028, 2944, 2918, 1670, 1587, 1572, 1449, 1411, 1339, 1326, 1296, 1203, 1188, 1160, 1132, 1025, 754, 736, 698; **HR-MS** (ESI⁺): calcd. for C₃₂H₂₉NO₃Na ([M+Na]⁺): 498.2040, found: 498.2045; **M**(C₃₂H₂₉NO₃): 475.59.

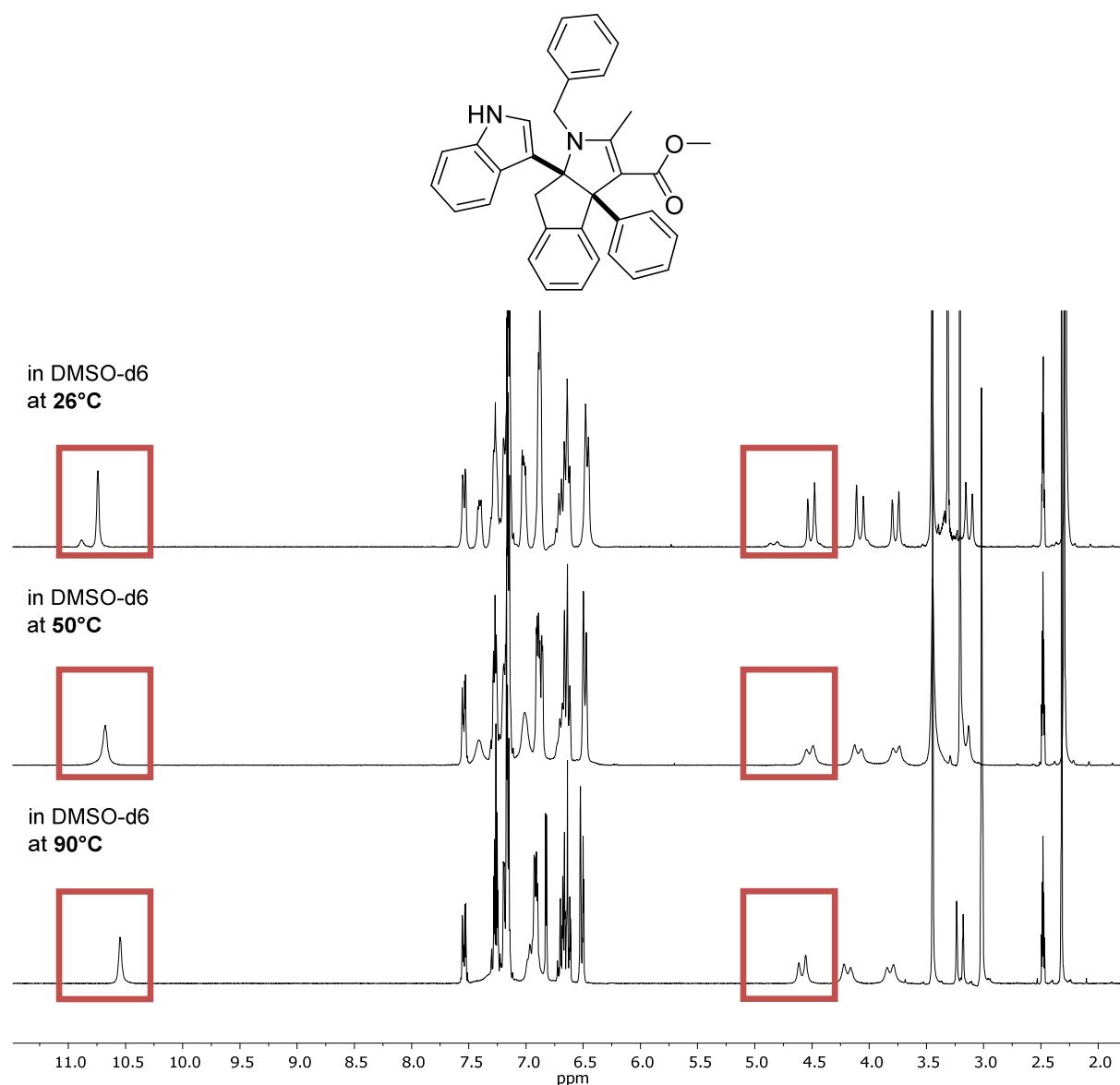
4.2 ^1H -NMR and ^{13}C -NMR Spectra

8a-(Indolyl)tetrahydroindeno[2,1-b]pyrrole 8

(DMSO- d_6 , ^1H -NMR: 400 MHz, APT: 100 MHz)

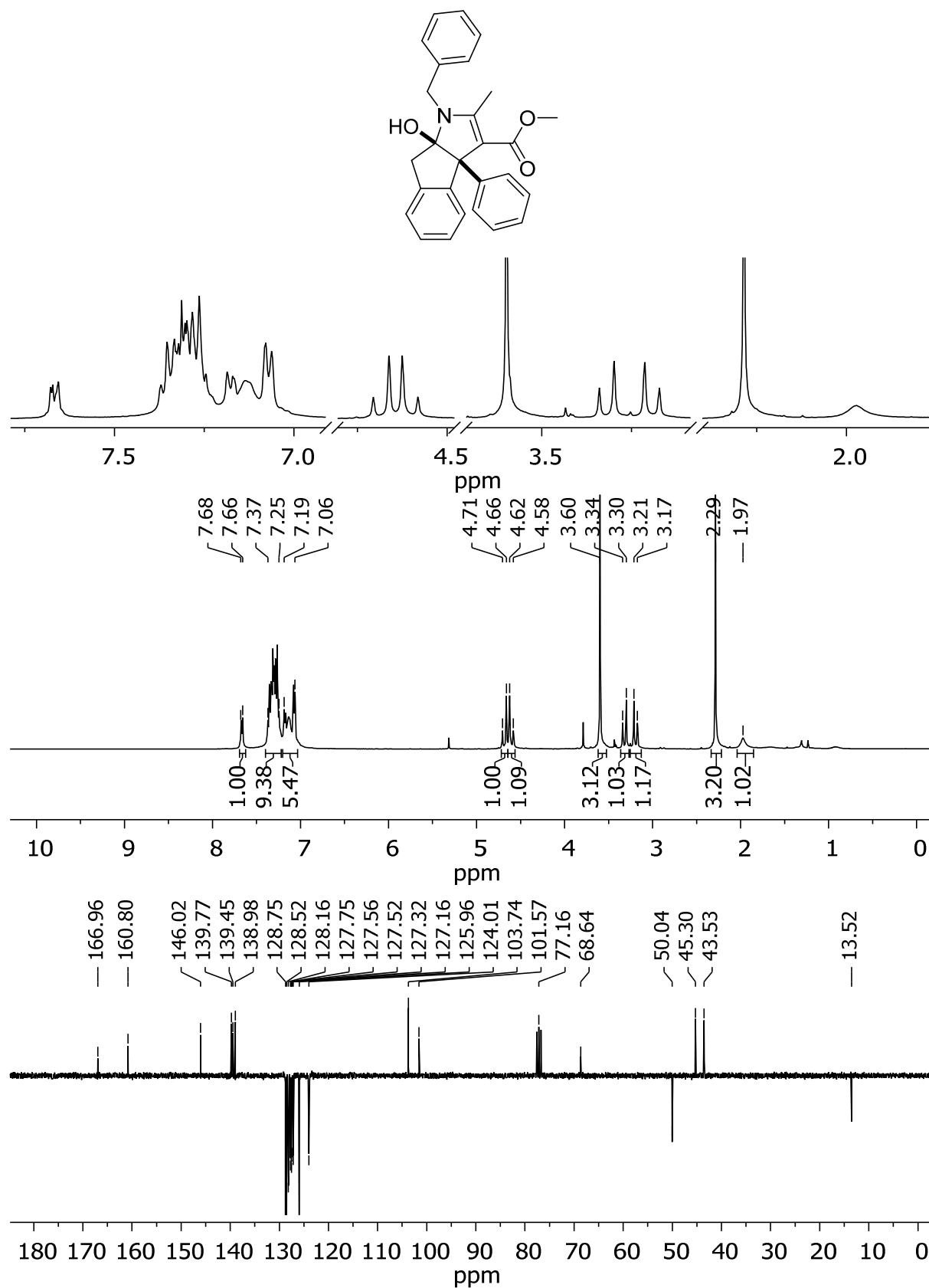


High-Temperature- ^1H -NMR Experiments of **8**

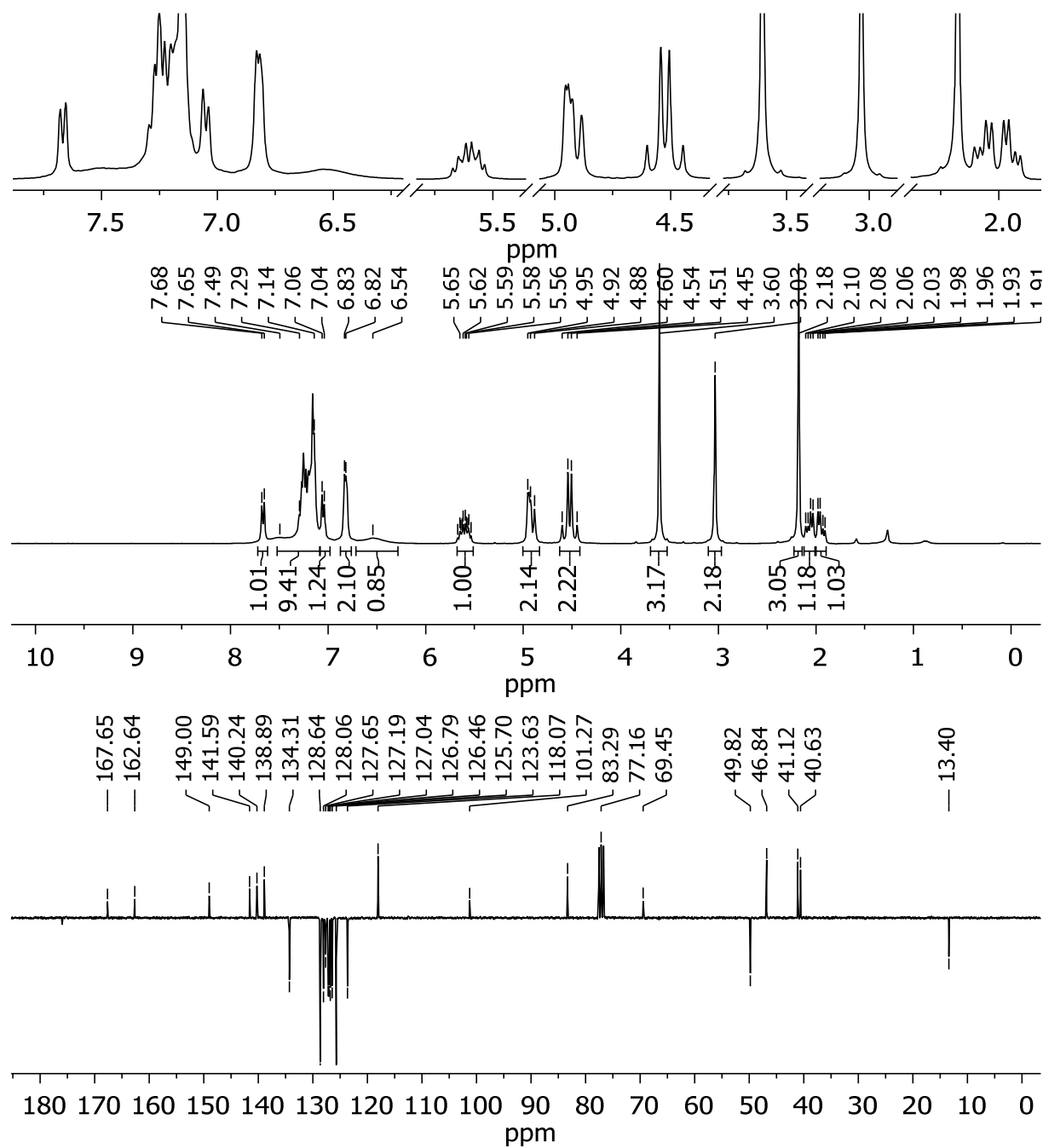
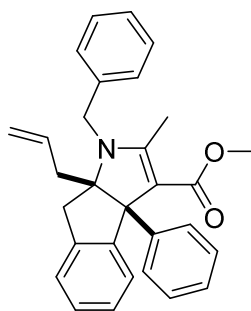


The ^1H -NMR spectra of compound **8** were measured in DMSO-d_6 (400 MHz) at 26 °C, 50 °C and 90 °C. Coalescence was observed at 90 °C to give rise to one final set of signals. Consequently, compound **8** consists of two rotamers in DMSO-d_6 at room temperature.

Hemiaminal 9 (CDCl₃, ¹H-NMR: 400 MHz, APT: 75 MHz)

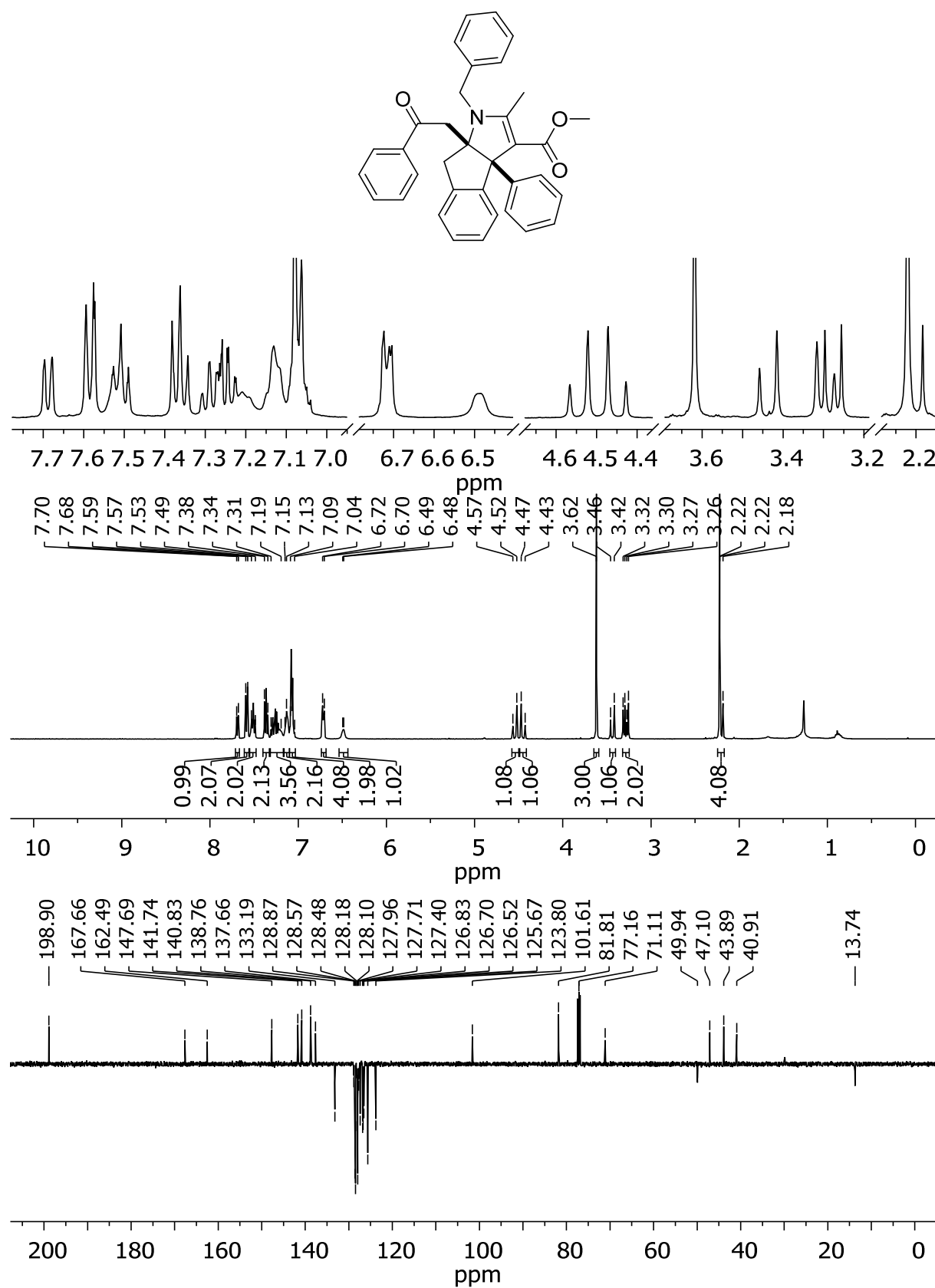


8a-(Allyl)tetrahydroindeno[2,1-b]pyrrole 10 (CDCl₃, ¹H-NMR: 300 MHz, APT: 75 MHz)

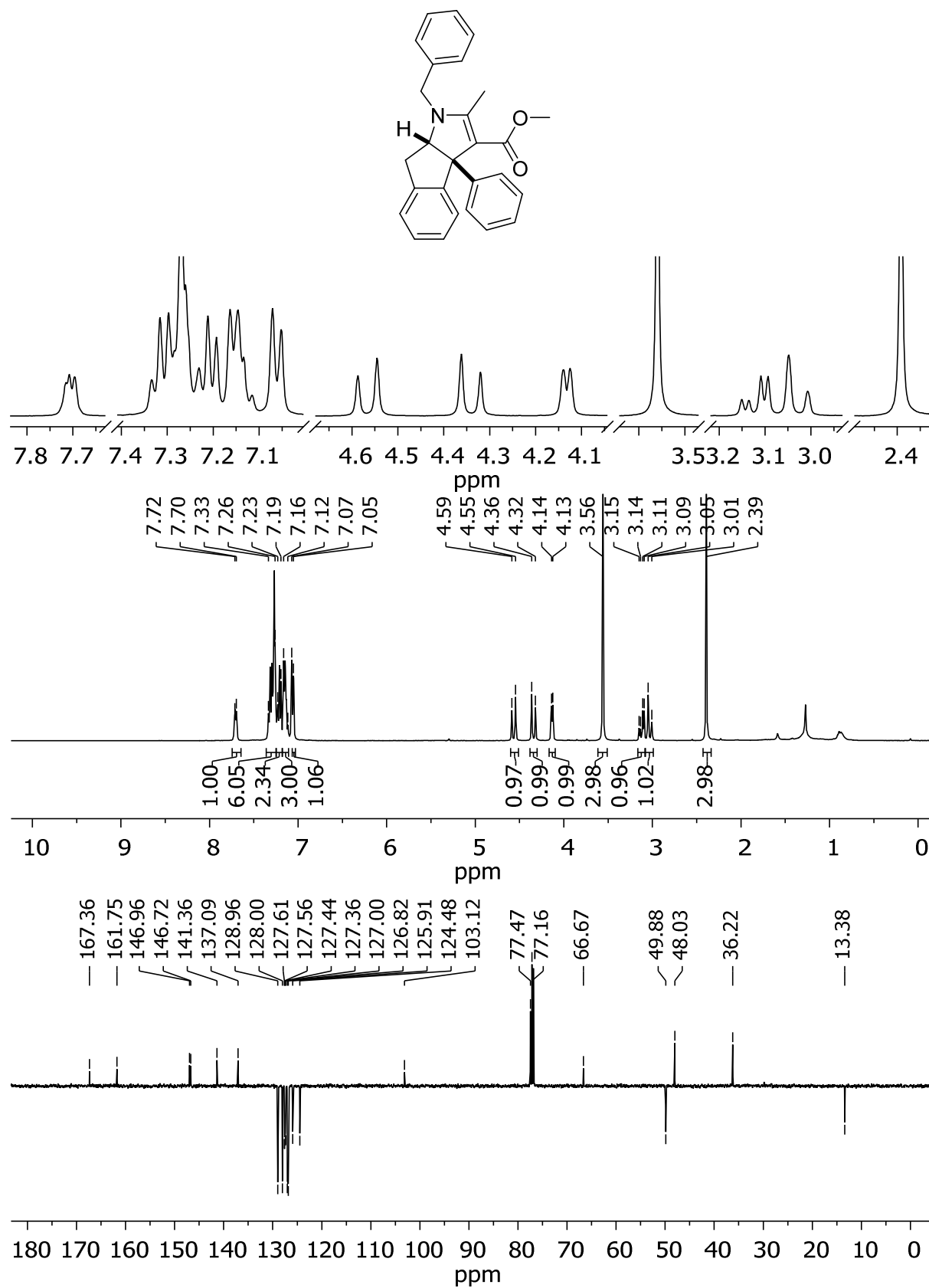


8a-(2-Oxo-2-phenylethyl)tetrahydroindeno[2,1-b]pyrrole 11

(CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)

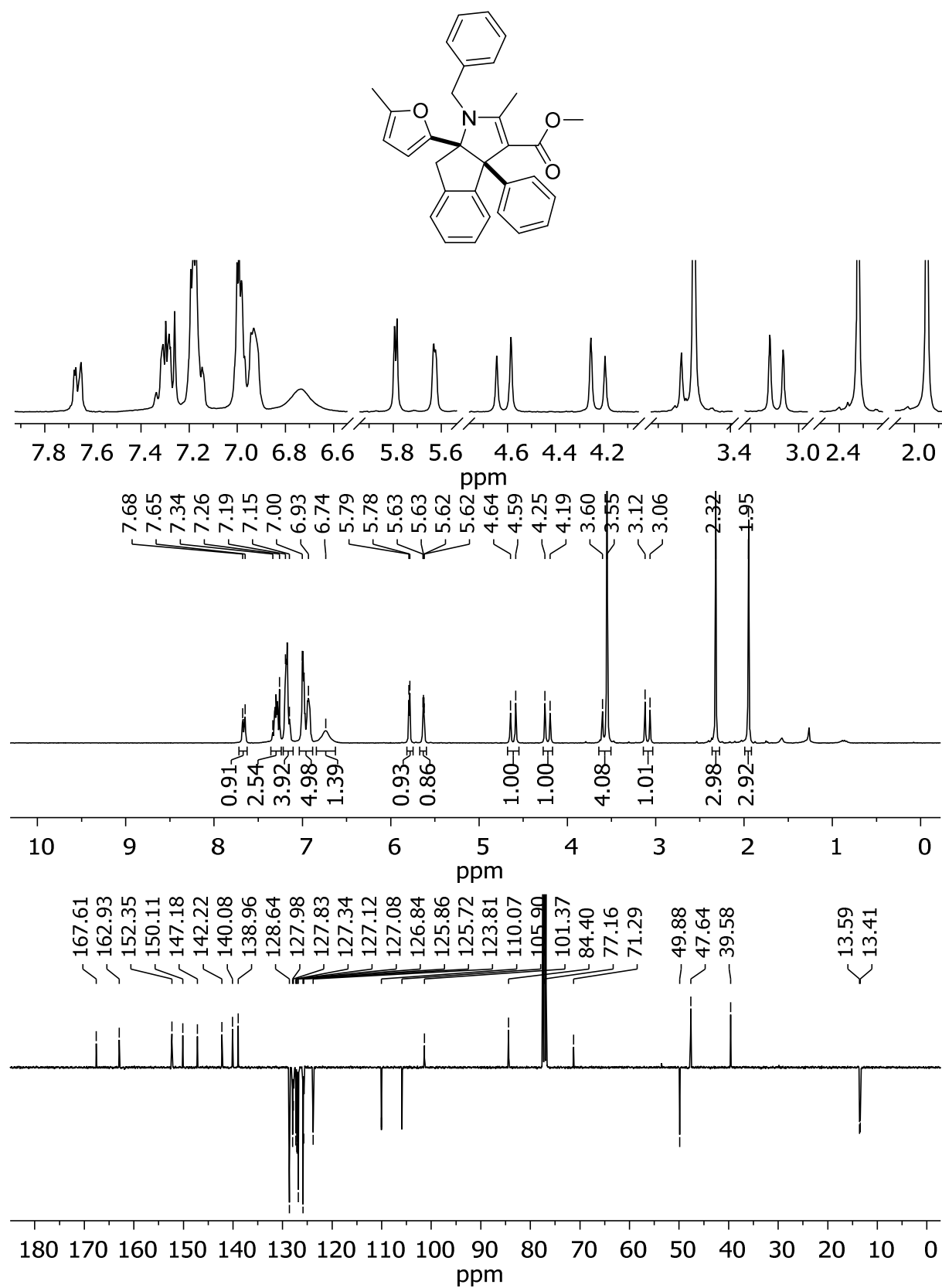


Tetrahydroindeno[2,1-*b*]pyrrole 12 (CDCl₃, ¹H-NMR: 400 MHz, APT: 100 MHz)



8a-(Furanyl)tetrahydroindeno[2,1-*b*]pyrrole 13

(CDCl₃, ¹H-NMR: 300 MHz, APT: 100 MHz)



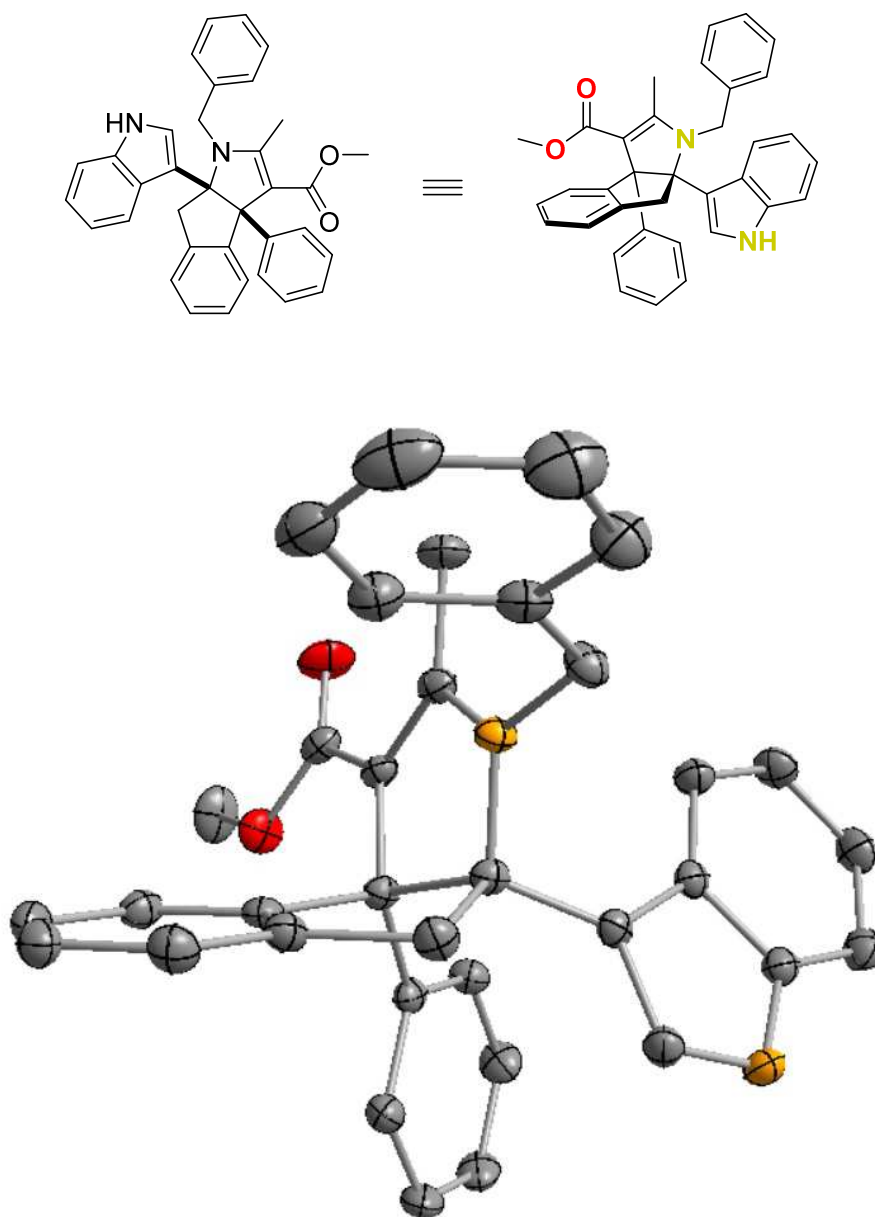
4.3 X-Ray Crystal Structure of **8**

Crystal Data and Structure Refinement for 8a-(Indolyl)tetrahydroindeno[2,1-*b*]pyrrole **8**

Note: The single-crystal of **8** was obtained from a solution in CH₂Cl₂. The unit cell contains one molecule of CH₂Cl₂ per molecule of **8**.

Identification code	P21n	
Empirical formula	C ₃₆ H ₃₂ Cl ₂ N ₂ O ₂	
Formula weight	595.53	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 9.9933(2) Å	α = 90°.
	b = 25.3761(5) Å	β = 96.046(2)°.
	c = 11.9005(2) Å	γ = 90°.
Volume	3001.07(10) Å ³	
Z	4	
Density (calculated)	1.318 Mg/m ³	
Absorption coefficient	0.252 mm ⁻¹	
F(000)	1248	
Crystal size	0.5500 x 0.4000 x 0.0300 mm ³	
Theta range for data collection	2.201 to 26.372°.	
Index ranges	-12 ≤ h ≤ 12, -31 ≤ k ≤ 31, -14 ≤ l ≤ 14	
Reflections collected	32405	
Independent reflections	6144 [R(int) = 0.0281]	
Completeness to theta = 26.372°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.96903	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6144 / 0 / 381	
Goodness-of-fit on F ²	1.031	
Final R indices [I > 2σ(I)]	R1 = 0.0373, wR2 = 0.0856	
R indices (all data)	R1 = 0.0461, wR2 = 0.0900	
Largest diff. peak and hole	0.285 and -0.425 e.Å ³	

Crystal Structure of 8a-(Indolyl)tetrahydroindeno[2,1-*b*]pyrrole **8**



DIAMOND representation of 8a-(indolyl)tetrahydroindeno[2,1-*b*]pyrrole **8** with thermal ellipsoids shown at 50% probability level. Hydrogen atoms are omitted for clarity. CCDC 1817407 contains the supplementary crystallographic data of **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

5 References

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