
Supplementary information

Enantioselective synthesis of axially chiral 1,2'-binaphthyls via nickel-catalyzed asymmetric [2+4] annulation

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Table of Contents

I. General Information.....	S2
II. Preparation of Starting Materials.....	S3
III. Standard Procedures for Nickel-Catalyzed Asymmetric [2+4]Annulation.....	S28
IV. Procedure for Synthesis of 3aa on a 2-mmol Scale.....	S59
V. Derivatizations of the Axially Chiral Binaphthyl 3aa.....	S60
VI. Mechanistic Studies.....	S67
VII. Crystallographic Data.....	S74
VIII. References.....	S76
IX. NMR Spectra.....	S77
X. HPLC Chromatograms.....	S263

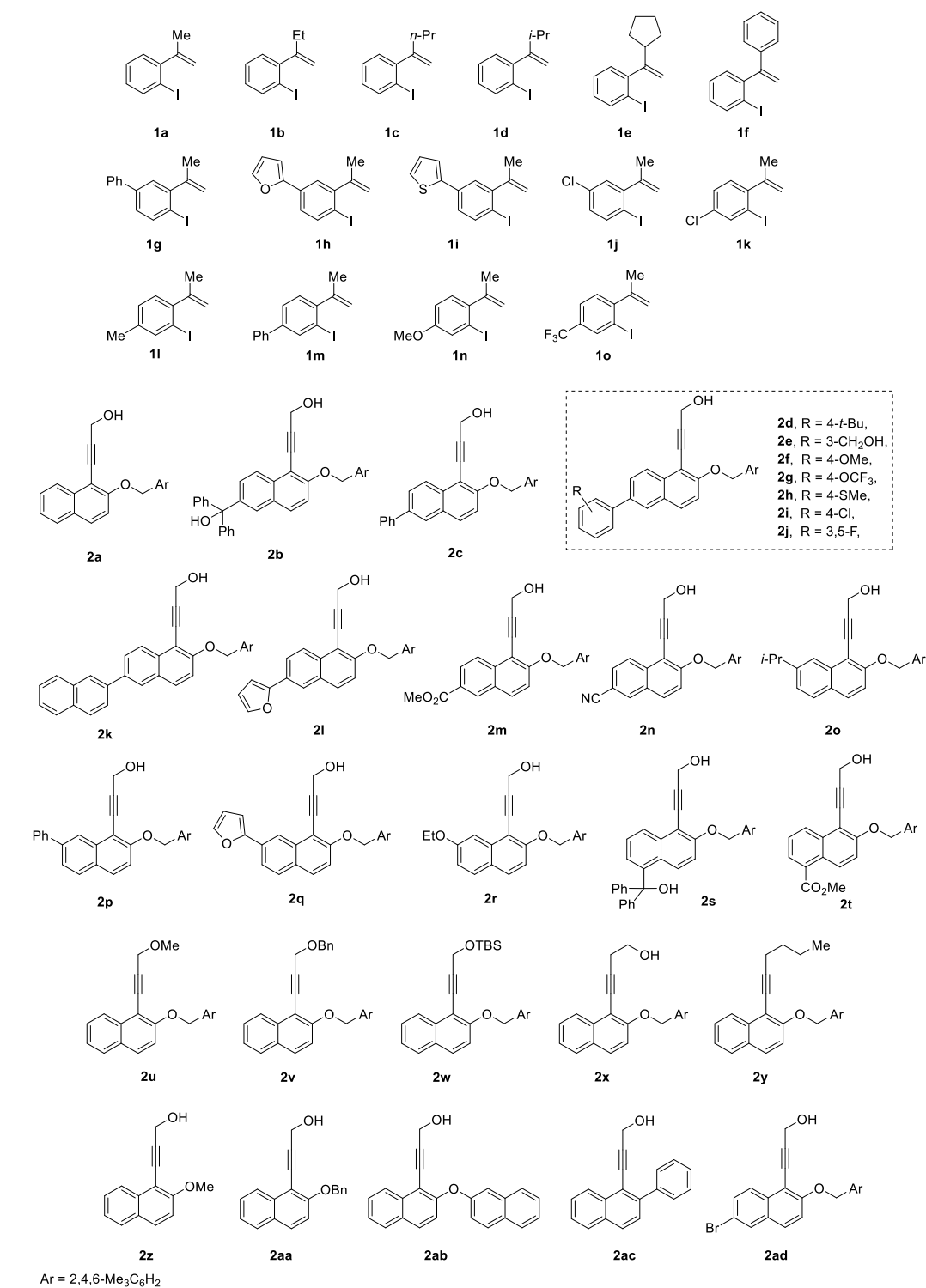
I. General Information

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR or 500M NMR spectrometers at ambient temperature in CDCl_3 at 400 and 101 MHz or 500 MHz and 126 MHz. ^{19}F NMR spectra were reported as ^{19}F exp. comp. pulse decoupling (F^{19}CPD) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [^1H : δ (SiMe_4) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^1H : δ (CDCl_3) = 7.26, ^{13}C : δ (CDCl_3) = 77.16 ppm]. Multiplicities are given as: s (singlet); d (doublet); t (triplet); q (quartet); quin (quintet), dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as J values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Enantiomer excesses were determined by HPLC analysis employing Daicel chiral column (chiralpak IA, chiralpak AD-H) or Guangzhou FLM Scientific Instrument chiral column (chiral MD) with *n*-hexane/*i*-PrOH as the eluents. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ZF-7 254 nm. Other visualization methods include staining with a basic solution of potassium permanganate or acidic solution of ceric ammonium molybdate, followed by heating.

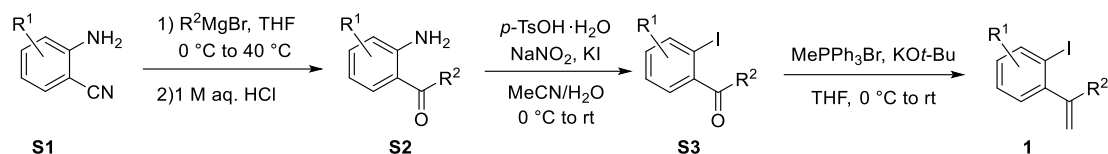
Unless otherwise noted, all reagents and starting materials were purchased from commercial vendors and used without further purification. All air- or moisture-sensitive reactions were protected with nitrogen atmosphere.

II. Preparation of Starting Materials



The compounds **1a**,¹ **1b**,¹ **1d**,¹ **1f**,¹ **1j**,¹ **1l**,¹ **1n**,¹ and **2z**² are known in the literature.

Procedure for Preparation of 1c, 1e, 1g-i, 1k, 1m, and 1o



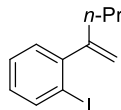
Step 1: To a stirred solution of **S1** (5 mmol, 1.0 equiv) in THF (20 mL) at $0\text{ }^{\circ}\text{C}$ was added an alkyl magnesium halide solution in THF (15 mmol, 3.0 equiv) dropwise. The reaction mixture was heated to $40\text{ }^{\circ}\text{C}$ and stirred overnight after which it was cooled to $0\text{ }^{\circ}\text{C}$. A 1 M aq. HCl solution (20 mL) was slowly added to quench the reaction. After stirring at room temperature for 15 min, the reaction was diluted with brine and extracted three times with EtOAc. The organic layers were combined, washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified through flash chromatography.

Step 2: To a stirred solution of $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (2.8 g, 15 mmol, 3.0 equiv) in MeCN (10 mL) was added the crude **S2**. The resulting suspension of the protonated aniline was cooled to $0\text{ }^{\circ}\text{C}$ and an aqueous solution of NaNO_2 (0.69 g, 10 mmol, 2.0 equiv) was slowly added, followed by an aqueous solution of KI (2.1 g, 12.5 mmol, 2.5 equiv). When the evolution of nitrogen gas ceased, the resulting solution was warmed to room temperature, and stirred for 1 h. A 1 M aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) followed by sat. aq. NaHCO_3 (10 mL) was added. The aqueous phase was extracted three times with EtOAc, and the organic phases were combined, washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified through flash chromatography.

Step 3: To a stirred suspension of methyltriphenylphosphonium bromide (1.5 equiv) in THF (0.3 M) at $0\text{ }^{\circ}\text{C}$ was added potassium *tert*-butoxide (1.8 equiv) portionwise. The resulting mixture was warmed to room temperature and stirred for 30 min before being cooled to $0\text{ }^{\circ}\text{C}$. A 1.0 M THF solution of **S3** (1.0 equiv) was added dropwise to the suspension, which was subsequently warmed to room temperature and stirred overnight. The mixture of pentanes and EtOAc (1:1) was added to the reaction mixture, which was filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure

and the crude mixture was purified by chromatography on silica gel using petroleum ether/ethyl acetate (99:1) as the eluent to afford **1c**, **1e**, **1g-i**, **1k**, **1m**, and **1o**.

1-Iodo-2-(pent-1-en-2-yl)benzene (1c)



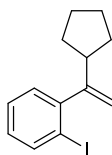
The title compound was isolated as a colorless oil (0.60 g, 44% over 3 steps).

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.85 (d, J = 7.9 Hz, 1H), 7.33–7.25 (m, 1H), 7.13 (dd, J = 7.6, 1.8 Hz, 1H), 6.96–6.90 (m, 1H), 5.24–5.20 (m, 1H), 4.94–4.91 (m, 1H), 2.37 (t, J = 7.9 Hz, 2H), 1.46 (h, J = 7.3 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 152.6, 148.3, 139.3, 129.2, 128.4, 127.9, 115.1, 97.8, 39.4, 20.9, 14.0 ppm.

HRMS (EI): Calcd for C₁₁H₁₃I, 272.0062; Found 272.0055

1-(1-Cyclopentylvinyl)-2-iodobenzene (1e)



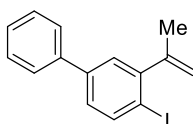
The title compound was isolated as a colorless oil (0.50 g, 34% over 3 steps).

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.86 (dd, J = 7.9, 1.3 Hz, 1H), 7.30 (td, J = 7.5, 1.3 Hz, 1H), 7.13 (dd, J = 7.6, 1.8 Hz, 1H), 6.94 (td, J = 7.6, 1.8 Hz, 1H), 5.27–5.24 (m, 1H), 4.92–4.90 (m, 1H), 2.85–2.75 (m, 1H), 1.86–1.44 (m, 8H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 155.8, 148.7, 139.2, 129.3, 128.3, 127.7, 113.1, 98.5, 46.6, 31.6 (2C), 24.7 (2C) ppm.

HRMS (EI): Calcd for C₁₃H₁₅I, 298.0218; Found 298.0211

4-Iodo-3-(prop-1-en-2-yl)-1,1'-biphenyl (1g)



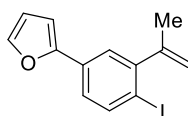
The title compound was isolated as a colorless oil (0.67 g, 42% over 3 steps).

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.91 (d, *J* = 8.2 Hz, 1H), 7.62–7.57 (m, 2H), 7.49–7.42 (m, 3H), 7.42–7.35 (m, 1H), 7.20 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.18–5.15 (m, 1H), 5.00–4.98 (m, 1H), 2.16–2.13 (m, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 149.0, 148.2, 141.1, 139.7, 139.4, 128.7 (2C), 127.5, 127.0, 126.9, 126.7 (2C), 116.0, 95.4, 23.8 ppm.

HRMS (EI): Calcd for C₁₅H₁₃I, 320.0062; Found 320.0052

2-(4-Iodo-3-(prop-1-en-2-yl)phenyl)furan (1h)



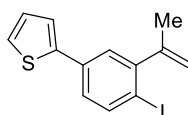
The title compound was isolated as a colorless oil (0.57 g, 37% over 3 steps).

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.44–7.42 (m, 1H), 7.20 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.65–6.62 (m, 1H), 6.43 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.25–5.21 (m, 1H), 4.93–4.91 (m, 1H), 2.09–2.06 (m, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 152.9, 149.2, 148.3, 142.5, 139.6, 130.9, 123.74, 123.66, 116.3, 111.9, 105.9, 95.2, 23.9 ppm.

HRMS (EI): Calcd for C₁₃H₁₁IO, 309.9855; Found 309.9844

2-(4-Iodo-3-(prop-1-en-2-yl)phenyl)thiophene (1i)



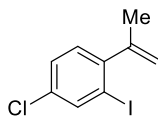
The title compound was isolated as a colorless oil (0.59 g, 36% over 3 steps).

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.78 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.28 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.25 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.15 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.26–5.21 (m, 1H), 4.95–4.91 (m, 1H), 2.08 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 149.4, 148.2, 143.1, 139.7, 134.5, 128.2, 125.84, 125.81, 125.4, 123.7, 116.4, 95.4, 24.0 ppm.

HRMS (EI): Calcd for C₁₃H₁₁IS, 325.9626; Found 325.9614

4-Chloro-2-iodo-1-(prop-1-en-2-yl)benzene (1k)



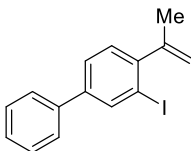
The title compound was isolated as a colorless oil (0.65 g, 47% over 3 steps).

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.83 (d, *J* = 2.1 Hz, 1H), 7.28 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 5.24–5.21 (m, 1H), 4.89–4.87 (m, 1H), 2.04 (t, *J* = 1.3 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 147.5, 147.4, 138.5, 133.1, 129.1, 128.4, 116.8, 97.0, 23.9 ppm.

HRMS (EI): Calcd for C₉H₈ICl, 277.9359; Found 277.9352

3-Iodo-4-(prop-1-en-2-yl)-1,1'-biphenyl (1m)



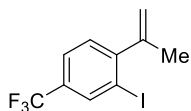
The title compound was isolated as a colorless oil (0.72 g, 45% over 3 steps).

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.94 (d, *J* = 1.9 Hz, 1H), 7.44–7.33 (m, 3H), 7.32–7.26 (m, 2H), 7.25–7.19 (m, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 5.14–5.11 (m, 1H), 4.84–4.80 (m, 1H), 1.97 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 148.1, 147.6, 141.6, 139.3, 137.8, 128.9 (2C), 128.7, 127.8, 127.1 (2C), 126.9, 116.4, 97.6, 24.0 ppm.

HRMS (EI): Calcd for C₁₅H₁₃I, 320.0062; Found 320.0054

2-Iodo-1-(prop-1-en-2-yl)-4-(trifluoromethyl)benzene (1o)



The title compound was isolated as a colorless oil (0.31 g, 20% over 3 steps).

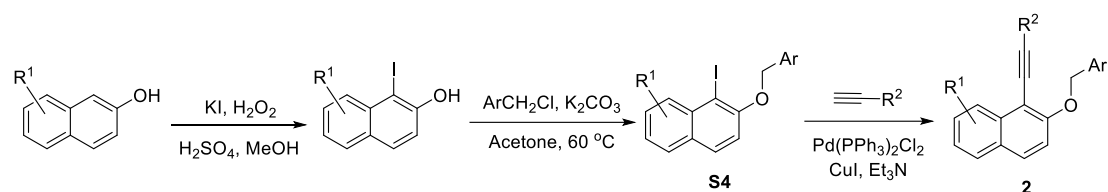
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.09–8.06 (m, 1H), 7.59–7.53 (m, 1H), 7.29–7.25 (m, 1H), 5.29–5.26 (m, 1H), 4.93–4.90 (m, 1H), 2.08–2.06 (m, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 152.7, 147.6, 136.2 (q, J = 4.0 Hz), 130.6 (q, J = 32.8 Hz), 128.7, 125.2 (q, J = 3.6 Hz), 123.0 (q, J = 272.6 Hz), 117.0, 96.7, 23.7 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -61.95 (s, 3F) ppm.

HRMS (EI): Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{I}$, 311.9623; Found 311.9607

Procedure for Preparation of 2a, 2m-r, 2t, 2x, 2y, 2aa, 2ab, and 2ad



Step 1: To MeOH (50 mL) being stirred at 0 °C in a round-bottom flask was added sulfuric acid (95.8%, 20.0 mmol, 2.0 equiv, 1.1 mL), *naphthalen-2-ol* or a derivative (10.0 mmol, 1.0 equiv), KI (2.0 g, 12.0 mmol, 1.2 equiv), and H_2O_2 (35%, 20.0 mmol, 2.0 equiv, 1.9 g). The dark mixture was kept stirring at 0 °C for 9 h. The mixture was quenched by adding excessive saturated aqueous Na_2SO_3 solution. The MeOH was evaporated, and the residue was extracted with EtOAc (3 $\times$ 30 mL). The combined organic phases were washed with brine, dried over sodium sulfate, and filtered. The solvent was evaporated to yield the product *1-iodonaphthalen-2-ol* or a derivative which was used directly for the next step.

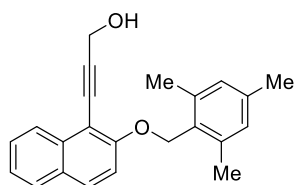
Step 2: To a solution of the crude *1-iodonaphthalen-2-ol* or a derivative obtained from Step 1 in acetone (30 mL) was added K_2CO_3 (2.8 g, 20.0 mmol, 2.0 equiv), 2-(chloromethyl)-1,3,5-trimethylbenzene or a derivative (11.0 mmol, 1.1 equiv). The solution was warmed to 60 °C and stirred overnight. The reaction mixture was cooled to room temperature and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the products **S4**.

Step 3: To a solution of **S4** (1.0 equiv) and propargyl alcohol (5.0 equiv)^a in Et_3N /THF (30 mL/5 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.04 equiv) and CuI (0.08 equiv). The flask

was flushed with nitrogen gas. The resulting mixture was stirred at room temperature while monitoring conversion by TLC. Upon complete conversion, the reaction mixture was filtered and washed with ethyl acetate three times. The combined filtrate was concentrated and the residue was purified by a silica gel column chromatography to afford **2a**, **2m-r**, **2t**, **2aa**, and **2ab**.

^a 3-Butyn-1-ol (2.0 equiv) for **2x** and 1-hexyne (2.0 equiv) for **2y**.

3-(2-((2,4,6-Trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2a)



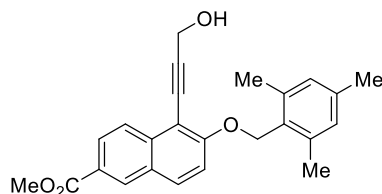
The title compound was isolated as a yellowish solid (2.0 g, 61% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1). Reaction time for step 3: 7 days.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.31 (d, *J* = 8.4 Hz, 1H), 7.8–7.82 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.43 (m, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 6.95 (s, 2H), 5.28 (s, 2H), 4.58 (s, 2H), 2.49 (s, 6H), 2.35 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 159.0, 138.4, 138.3 (2C), 134.6, 130.2, 129.9, 129.2 (2C), 129.0, 128.1, 127.4, 125.5, 124.6, 116.1, 107.8, 96.9, 80.1, 67.5, 52.0, 21.1, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₂₂O₂Na 353.1512; Found 353.1513

Methyl 5-(3-hydroxyprop-1-yn-1-yl)-6-((2,4,6-trimethylbenzyl)oxy)-2-naphthoate (2m)



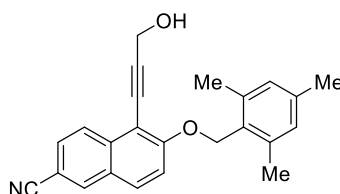
The title compound was isolated as a yellowish solid (2.4 g, 62% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1). Reaction time for step 3: 72 hours.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.49 (d, *J* = 1.7 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.01 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 6.89 (s, 2H), 5.23 (s, 2H), 4.53 (s, 2H), 3.96 (s, 3H), 2.42 (s, 6H), 2.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 167.3, 160.5, 138.5, 138.2 (2C), 137.0, 131.6, 131.3, 129.5, 129.2 (2C), 127.8, 126.6, 125.9, 125.6, 116.0, 107.5, 97.4, 79.4, 67.1, 52.3, 51.9, 21.1, 19.7 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₂₄O₄Na 411.1567; Found 411.1572

5-(3-Hydroxyprop-1-yn-1-yl)-6-((2,4,6-trimethylbenzyl)oxy)-2-naphthonitrile (2n)



The title compound was isolated as a yellowish solid (2.4 g, 68% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

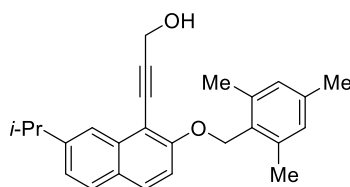
Reaction time for step 3: 48 hours.

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.29 (d, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.62 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 6.92 (s, 2H), 5.27 (s, 2H), 4.56 (d, *J* = 5.1 Hz, 2H), 2.43 (s, 6H), 2.30 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 161.1, 138.8, 138.3 (2C), 136.4, 134.3, 130.7, 129.33 (2C), 129.28, 127.8, 127.6, 126.8, 119.4, 116.8, 107.9, 107.8, 97.9, 79.1, 67.1, 52.0, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₁NO₂Na 378.1465; Found 378.1451

3-(7-Isopropyl-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2o)



The title compound was isolated as a yellowish solid (1.9 g, 51% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

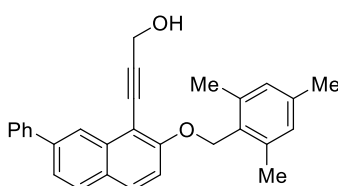
Reaction time for step 3: 7 days.

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.02 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.36–7.28 (m, 2H), 6.91 (s, 2H), 5.23 (s, 2H), 4.60 (s, 2H), 3.10–2.97 (m, 1H), 2.45 (s, 6H), 2.30 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.3, 148.3, 138.40, 138.36 (2C), 134.8, 130.1 (2C), 129.2 (2C), 128.3, 127.8, 124.2, 122.0, 115.3, 107.4, 96.7, 80.5, 67.6, 52.3, 34.7, 24.1 (2C), 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₉O₂ 373.2162; Found 373.2166

3-(7-Phenyl-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2p)



The title compound was isolated as a yellowish solid (1.7 g, 42% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

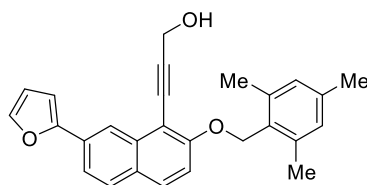
Reaction time for step 3: 7 days.

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.43 (s, 1H), 7.87–7.79 (m, 2H), 7.76–7.70 (m, 2H), 7.70–7.64 (m, 1H), 7.52–7.44 (m, 2H), 7.45–7.35 (m, 2H), 6.93 (s, 2H), 5.27 (s, 2H), 4.58 (d, *J* = 5.0 Hz, 2H), 2.46 (s, 6H), 2.31 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.5, 141.3, 140.2, 138.44, 138.35 (2C), 134.9, 130.0, 129.9, 129.2 (2C), 129.0 (2C), 128.7, 128.2, 127.7 (2C), 127.6, 124.5, 123.5, 116.0, 108.0, 97.1, 80.2, 67.5, 52.1, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₉H₂₇O₂ 407.2006; Found 407.2014

3-(7-(Furan-2-yl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2q)



The title compound was isolated as a yellowish solid (1.4 g, 36% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

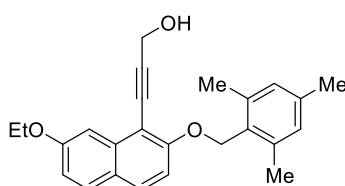
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.50 (s, 1H), 7.80–7.74 (m, 2H), 7.71–7.66

(m, 1H), 7.55 (d, $J = 1.8$ Hz, 1H), 7.32 (d, $J = 9.0$ Hz, 1H), 6.91 (s, 2H), 6.82 (d, $J = 3.4$ Hz, 1H), 6.52 (dd, $J = 3.5, 1.8$ Hz, 1H), 5.24 (s, 2H), 4.61 (s, 2H), 2.45 (s, 6H), 2.30 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 159.6, 154.1, 142.7, 138.4, 138.3$ (2C), 134.9, 130.0, 129.9, 129.6, 129.2 (2C), 128.7, 128.2, 121.1, 119.7, 115.8, 112.0, 107.9, 106.4, 97.2, 80.2, 67.4, 52.2, 21.2, 19.8 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_3\text{Na}$ 419.1618; Found 419.1621

3-(7-Ethoxy-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2r)



The title compound was isolated as a yellowish solid (1.6 g, 43% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

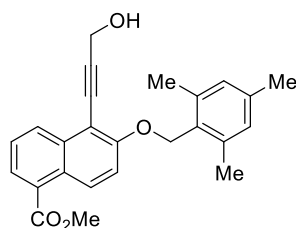
Reaction time for step 3: 7 days.

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.73$ (d, $J = 8.9$ Hz, 1H), 7.67 (d, $J = 8.9$ Hz, 1H), 7.51 (d, $J = 2.5$ Hz, 1H), 7.21 (d, $J = 8.9$ Hz, 1H), 7.05 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.90 (s, 2H), 5.22 (s, 2H), 4.58 (d, $J = 5.9$ Hz, 2H), 4.19 (q, $J = 7.0$ Hz, 2H), 2.44 (s, 6H), 2.30 (s, 3H), 1.49 (t, $J = 7.0$ Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform- d) $\delta = 159.8, 158.6, 138.36, 138.34$ (2C), 136.4, 130.10, 130.06, 129.8, 129.2 (2C), 124.4, 117.5, 113.2, 106.5, 104.7, 96.6, 80.7, 67.3, 63.7, 52.3, 21.2, 19.8 (2C), 14.9 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3\text{Na}$ 397.1774; Found 393.1783

Methyl 5-(3-hydroxyprop-1-yn-1-yl)-6-((2,4,6-trimethylbenzyl)oxy)-1-naphthoate (2t)



The title compound was isolated as a yellowish solid (2.2 g, 57% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

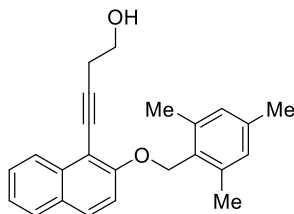
Reaction time for step 3: 7 days.

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.94 (d, *J* = 9.5 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.48–7.41 (m, 2H), 6.88 (s, 2H), 5.21 (s, 2H), 4.52 (d, *J* = 5.7 Hz, 2H), 3.99 (s, 3H), 2.42 (s, 6H), 2.28 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 167.9, 158.7, 138.3, 138.2 (2C), 135.2, 130.7, 129.6, 129.1 (2C), 128.8, 128.1, 127.0, 126.7, 125.9, 116.9, 107.8, 97.5, 79.6, 67.0, 52.2, 51.7, 21.0, 19.6 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₂₄O₄Na 411.1567; Found 411.1570

4-(2-((2,4,6-Trimethylbenzyl)oxy)naphthalen-1-yl)but-3-yn-1-ol (2x)



The title compound was isolated as a yellowish solid (2.4 g, 70% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

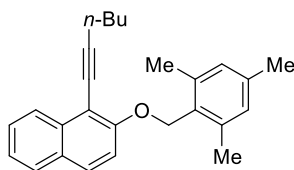
Reaction time for step 3: 48 hours.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.23 (d, *J* = 8.3 Hz, 1H), 7.81–7.76 (m, 2H), 7.55–7.50 (m, 1H), 7.43–7.35 (m, 2H), 6.92 (s, 2H), 5.24 (s, 2H), 3.76 (q, *J* = 6.0 Hz, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.44 (s, 6H), 2.31 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 158.9, 138.4, 138.2 (2C), 134.6 (2C), 129.9, 129.6, 129.2 (2C), 129.0, 128.2, 127.3, 125.5, 124.5, 115.7, 108.3, 96.2, 67.1, 61.4, 24.7, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₄O₂Na 367.1669; Found 367.1672

1-(Hex-1-yn-1-yl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalene (2y)



The title compound was isolated as a yellowish solid (2.2 g, 62% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99:1).

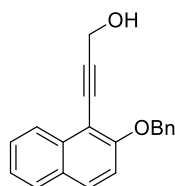
Reaction time for step 3: 48 hours.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.33 (d, J = 8.1 Hz, 1H), 7.82–7.76 (m, 2H), 7.58–7.53 (m, 1H), 7.49–7.39 (m, 1H), 7.36 (d, J = 9.0 Hz, 1H), 6.94 (s, 2H), 5.28 (s, 2H), 2.60 (t, J = 7.0 Hz, 2H), 2.49 (s, 6H), 2.33 (s, 3H), 1.72–1.64 (m, 2H), 1.58–1.49 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 158.6, 138.3 (2C), 138.1, 134.9, 130.3, 129.2, 129.1 (2C), 129.0, 128.1, 127.0, 125.7, 124.4, 116.7, 109.6, 100.2, 74.9, 67.5, 31.1, 22.1, 21.2, 19.9, 19.8 (2C), 13.8 ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₂₆H₂₈ONa 379.2032; Found 379.2036

3-(2-(Benzyloxy)naphthalen-1-yl)prop-2-yn-1-ol (2aa)



The title compound was isolated as a yellowish solid (1.6 g, 57% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

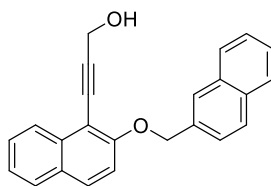
Reaction time for step 3: 72 hours.

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.24 (d, J = 8.5 Hz, 1H), 7.79–7.67 (m, 2H), 7.54–7.47 (m, 3H), 7.41–7.29 (m, 4H), 7.20 (d, J = 9.1 Hz, 1H), 5.30 (s, 2H), 4.67 (d, J = 4.1 Hz, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 158.5, 137.1, 134.6, 130.3, 128.9, 128.7 (2C), 128.2, 128.0, 127.5, 127.2 (2C), 125.4, 124.6, 115.0, 107.1, 97.1, 80.3, 71.6, 52.2 ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₂₀H₁₆O₂Na 311.1043; Found 311.1046

3-(2-(Naphthalen-2-ylmethoxy)naphthalen-1-yl)prop-2-yn-1-ol (2ab)



The title compound was isolated as a yellowish solid (1.9 g, 56% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

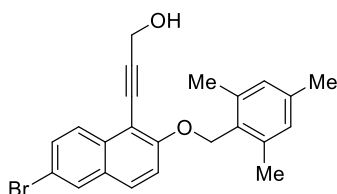
Reaction time for step 3: 72 hours.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.27 (dd, J = 8.4, 1.1 Hz, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.89–7.82 (m, 3H), 7.79–7.72 (m, 2H), 7.61 (dd, J = 8.4, 1.8 Hz, 1H), 7.58–7.51 (m, 1H), 7.52–7.45 (m, 2H), 7.42–7.36 (m, 1H), 7.29–7.23 (m, 1H), 5.48 (s, 2H), 4.71 (s, 2H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 158.5, 134.7, 134.6, 133.4, 133.2, 130.4, 128.9, 128.5, 128.2, 128.1, 127.9, 127.5, 126.4, 126.2, 126.1, 125.4, 125.0, 124.6, 115.0, 107.1, 97.2, 80.4, 71.8, 52.3 ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₂₄H₁₈O₂Na 361.1199; Found 361.1201

3-(6-Bromo-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2ad)



The title compound was isolated as a yellowish solid (3.1 g, 76% over 3 steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

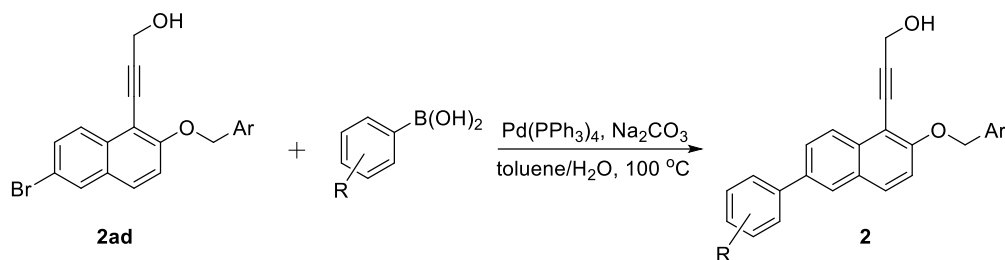
Reaction time for step 3: 72 hours.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.11–8.08 (m, 1H), 7.95–7.92 (m, 1H), 7.74–7.70 (m, 1H), 7.60–7.53 (m, 1H), 7.40–7.36 (m, 1H), 6.91 (s, 2H), 5.23 (s, 2H), 4.56 (s, 2H), 2.43 (s, 6H), 2.30 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 159.2, 138.5, 138.3 (2C), 133.2, 130.6, 130.1 (2C), 129.7, 129.27, 129.25 (2C), 127.4, 118.5, 117.0, 107.9, 97.2, 79.7, 67.5, 52.1, 21.2, 19.8 (2C) ppm.

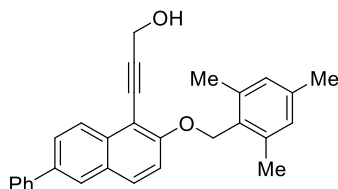
HRMS (ESI) m/z : $[M+H]^+$ Calcd for C₂₃H₂₂BrO₂ 409.0798; Found 409.0810

Procedure for Preparation of 2c-l



A mixture of **2ad** (816 mg, 2 mmol, 1.0 equiv), *phenylboronic acid* or a derivative (3 mmol, 1.5 equiv), Na_2CO_3 (424 mg, 3 mmol, 2.0 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 0.1 mmol, 0.05 equiv) in toluene/ H_2O (4 mL/2 mL) was stirred at 100 °C in an oil bath under N_2 for 16 h. The reaction mixture was cooled to room temperature and subsequently quenched with brine. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to afford **2c-l**.

3-(6-Phenyl-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (**2c**)



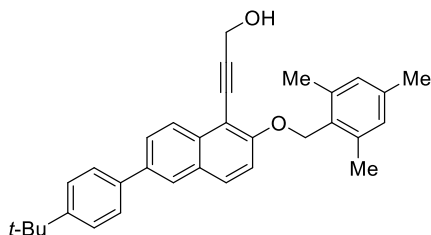
The title compound was isolated as a yellowish solid (447 mg, 55%).

^1H NMR (500 MHz, Chloroform-*d*) δ = 8.29 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 1.9 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.77 (dd, J = 8.7, 1.9 Hz, 1H), 7.70–7.68 (m, 2H), 7.50–7.44 (m, 2H), 7.41–7.37 (m, 2H), 6.90 (s, 2H), 5.24 (s, 2H), 4.57 (s, 2H), 2.44 (s, 6H), 2.29 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 159.1, 140.9, 138.44, 138.35 (2C), 137.4, 133.9, 130.6, 129.9, 129.3, 129.2 (2C), 129.0 (2C), 127.5, 127.4 (2C), 127.1, 126.1, 126.0, 116.6, 107.7, 96.8, 80.2, 67.6, 52.2, 21.2, 19.8 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{27}\text{O}_2$ 407.2006; Found 407.2019

3-(6-(4-(tert-Butyl)phenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2d)



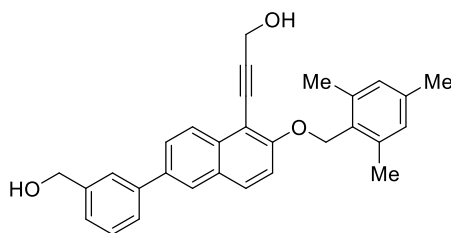
The title compound was isolated as a yellowish solid (480 mg, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.30 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.80 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.70–7.63 (m, 2H), 7.56–7.49 (m, 2H), 7.39 (d, *J* = 9.0 Hz, 1H), 6.93 (s, 2H), 5.26 (s, 2H), 4.59 (d, *J* = 5.2 Hz, 2H), 2.46 (s, 6H), 2.31 (s, 3H), 1.40 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.0, 150.5, 138.5, 138.4 (2C), 138.0, 137.2, 133.8, 130.5, 129.9, 129.4, 129.2 (2C), 127.1, 127.0 (2C), 126.03 (2C), 125.97, 125.7, 116.5, 107.7, 96.8, 80.3, 67.6, 52.1, 34.7, 31.5 (3C), 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₃H₃₅O₂ 463.2632; Found 463.2633

3-(6-(3-(Hydroxymethyl)phenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2e)



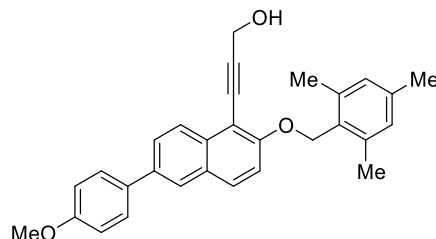
The title compound was isolated as a yellowish solid (340 mg, 39%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.27 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.77 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.70 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.49–7.43 (m, 1H), 7.39–7.35 (m, 2H), 6.92 (s, 2H), 5.24 (s, 2H), 4.77 (s, 2H), 4.58 (s, 2H), 2.44 (s, 6H), 2.30 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.1, 141.6, 141.2, 138.5, 138.4 (2C), 137.1, 133.9, 130.6, 129.9, 129.29, 129.25 (4C), 127.0, 126.7, 126.1, 126.0, 125.9, 116.5, 107.7, 96.9, 80.2, 67.5, 65.5, 52.1, 21.2, 19.8 (2C) ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{29}O_3$ 437.2111; Found 437.2112

3-(6-(4-Methoxyphenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2f)



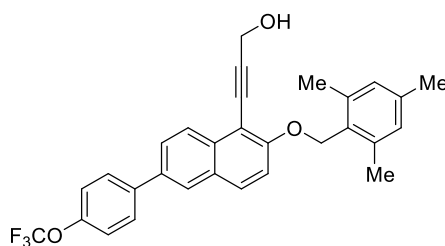
The title compound was isolated as a yellowish solid (419 mg, 48%).

1H NMR (500 MHz, Chloroform-*d*) δ = 8.28 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.77–7.75 (m, 1H), 7.69–7.61 (m, 2H), 7.38 (d, J = 9.0 Hz, 1H), 7.03–7.01 (m, 2H), 6.92 (s, 2H), 5.25 (s, 2H), 4.59 (s, 2H), 3.87 (s, 3H), 2.46 (s, 6H), 2.31 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 159.3, 158.9, 138.5, 138.4 (2C), 137.0, 133.5, 133.4, 130.4, 130.0, 129.4, 129.2 (2C), 128.4 (2C), 126.9, 126.1, 125.2, 116.5, 114.5 (2C), 107.7, 96.8, 80.3, 67.6, 55.5, 52.2, 21.2, 19.8 (2C) ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{29}O_3$ 437.2111; Found 437.2098

3-(6-(4-(Trifluoromethoxy)phenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2g)



The title compound was isolated as a yellowish solid (421 mg, 43%).

1H NMR (500 MHz, Chloroform-*d*) δ = 8.31 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 1.9 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.76–7.64 (m, 3H), 7.41 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 6.92 (s, 2H), 5.26 (s, 2H), 4.57 (d, J = 5.1 Hz, 2H), 2.46 (s, 6H), 2.31 (s, 3H) ppm.

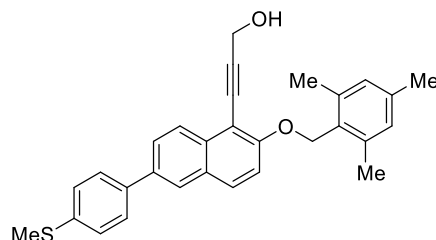
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 159.3, 148.8 (q, J = 1.7 Hz), 139.6, 138.5, 138.4 (2C), 135.9, 134.0, 130.5, 129.8, 129.3 (2C), 129.2, 128.6 (2C), 126.7, 126.3,

126.1, 121.5 (2C), 120.7 (q, $J = 257.0$ Hz), 116.6, 107.7, 97.0, 80.1, 67.5, 52.1, 21.2, 19.8 (2C) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) $\delta = -57.74$ (s, 3F) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{26}\text{F}_3\text{O}_3$ 491.1829; Found 491.1824

3-(6-(4-(Methylthio)phenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2h)



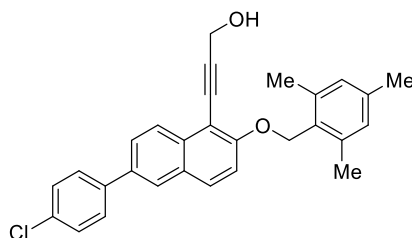
The title compound was isolated as a yellowish solid (280 mg, 31%).

^1H NMR (400 MHz, Chloroform-*d*) $\delta = 8.29$ (d, $J = 8.8$ Hz, 1H), 7.95 (d, $J = 1.9$ Hz, 1H), 7.85 (d, $J = 9.0$ Hz, 1H), 7.74 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.66–7.59 (m, 2H), 7.41–7.34 (m, 3H), 6.92 (s, 2H), 5.26 (s, 2H), 4.58 (d, $J = 5.2$ Hz, 2H), 2.54 (s, 3H), 2.46 (s, 6H), 2.31 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) $\delta = 159.1, 138.44, 138.35$ (2C), 137.8, 137.6, 136.6, 133.8, 130.5, 129.9, 129.3, 129.2 (2C), 127.6 (2C), 127.1 (2C), 126.7, 126.2, 125.5, 116.5, 107.7, 96.9, 80.2, 67.5, 52.1, 21.2, 19.8 (2C), 16.0 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{28}\text{SO}_2\text{Na}$ 475.1702; Found 475.1698.

3-(6-(4-Chlorophenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2i)



The title compound was isolated as a yellowish solid (458 mg, 52%).

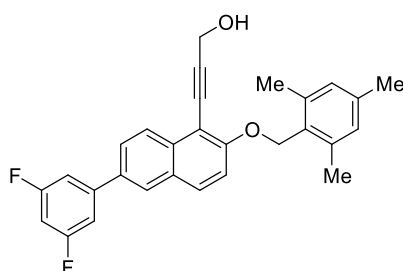
^1H NMR (500 MHz, Chloroform-*d*) $\delta = 8.30$ (d, $J = 8.7$ Hz, 1H), 7.94 (d, $J = 2.0$ Hz, 1H), 7.86 (d, $J = 9.0$ Hz, 1H), 7.73 (dd, $J = 8.8, 1.9$ Hz, 1H), 7.65–7.59 (m, 2H), 7.47–7.43 (m, 2H), 7.41 (d, $J = 9.0$ Hz, 1H), 6.92 (s, 2H), 5.26 (s, 2H), 4.59 (d, $J = 5.6$ Hz,

2H), 2.45 (s, 6H), 2.31 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 159.3, 139.3, 138.5, 138.4 (2C), 136.1, 134.0, 133.6, 130.6, 129.9, 129.3 (2C), 129.23, 129.15 (2C), 128.6 (2C), 126.7, 126.3, 125.9, 116.6, 107.7, 96.9, 80.1, 67.5, 52.2, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₅ClO₂Na 463.1435; Found 463.1436

3-(6-(3,5-Difluorophenyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2j)



The title compound was isolated as a yellowish solid (371 mg, 42%).

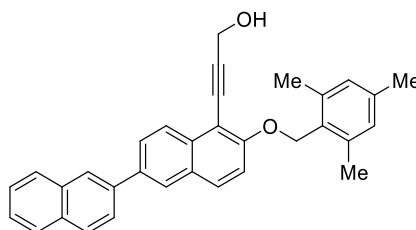
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.29 (d, *J* = 8.8 Hz, 1H), 7.92 (s, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.92 (s, 2H), 6.81 (t, *J* = 9.1 Hz, 1H), 5.26 (s, 2H), 4.56 (d, *J* = 4.2 Hz, 2H), 2.45 (s, 6H), 2.31 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 163.41 (dd, *J* = 247.9, 13.1 Hz, 2C), 159.4, 144.2 (t, *J* = 9.5 Hz), 138.5, 138.4 (2C), 134.9 (t, *J* = 2.5), 134.4, 130.6, 129.7, 129.3 (2C), 129.0, 126.5, 126.23, 126.19, 116.5, 110.0 (dd, *J* = 18.9, 5.0 Hz, 2C), 107.6, 102.6 (t, *J* = 25.4 Hz), 97.1, 79.9, 67.4, 52.0, 21.2, 19.8 (2C) ppm.

¹⁹F NMR (471 MHz, Chloroform-*d*) δ = -109.53 (s, 2F) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₄F₂O₂Na 465.1637; Found 465.1644

3-(6-((2,4,6-Trimethylbenzyl)oxy)-[2,2'-binaphthalen]-5-yl)prop-2-yn-1-ol (2k)



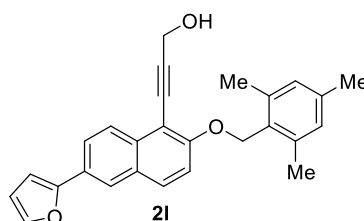
The title compound was isolated as a yellowish solid (419 mg, 46%).

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.36 (d, *J* = 8.7 Hz, 1H), 8.12–8.04 (m, 2H), 7.99–7.81 (m, 6H), 7.59–7.47 (m, 2H), 7.41 (d, *J* = 9.0 Hz, 1H), 6.94 (s, 2H), 5.27 (s, 2H), 4.59 (d, *J* = 4.8 Hz, 2H), 2.48 (s, 6H), 2.33 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 159.1, 138.44, 138.36 (2C), 138.1, 137.2, 133.9, 133.8, 132.7, 130.6, 129.9, 129.3, 129.2 (2C), 128.6, 128.3, 127.8, 127.1, 126.5, 126.3, 126.2, 126.1, 126.0, 125.7, 116.5, 107.7, 96.9, 80.1, 67.5, 52.1, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₃H₂₉O₂ 457.2162; Found 457.2164

3-(6-(Furan-2-yl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2l)



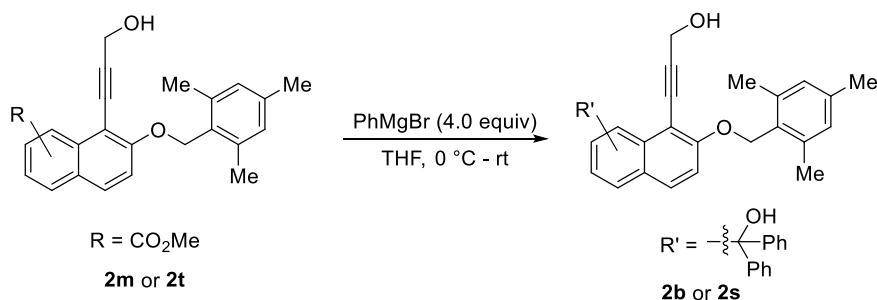
The title compound was isolated as a yellowish solid (317 mg, 40%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.23 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 1.8 Hz, 1H), 7.87–7.76 (m, 2H), 7.52 (d, *J* = 1.8 Hz, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 6.92 (s, 2H), 6.75 (d, *J* = 3.3 Hz, 1H), 6.54–6.50 (m, 1H), 5.24 (s, 2H), 4.57 (s, 2H), 2.45 (s, 6H), 2.31 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.1, 154.0, 142.3, 138.5, 138.4 (2C), 133.9, 130.5, 129.9, 129.2 (2C), 129.1, 127.2, 126.0, 123.9, 122.3, 116.5, 111.9, 107.8, 105.5, 96.8, 80.1, 67.4, 52.1, 21.2, 19.8 (2C) ppm.

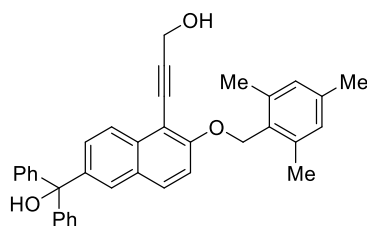
HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₇H₂₄O₃Na 419.1618; Found 419.1612

Procedure for Preparation of 2b and 2s



To a stirred solution of **2m** or **2t** (388 mg, 1 mmol, 1 equiv) in anhydrous THF (4 mL) was added PhMgBr (1.4 mL, 2.8 M in THF, 4 mmol, 4 equiv) dropwise at 0 °C. After stirring for 20 min, the reaction mixture was heated to 40 °C in an oil bath. The resulting mixture was stirred for 4 hours and then quenched by saturated aqueous NH₄Cl solution (5 mL). The organic phase was extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under vacuum to afford the crude products, which were further purified by chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to afford the corresponding products.

3-(6-(Hydroxydiphenylmethyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2b)



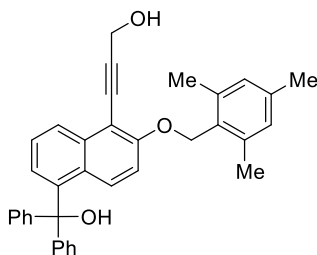
The title compound was isolated as a white solid (0.38 g, 75%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.17–8.15 (m, 1H), 7.74–7.67 (m, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.47 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.34–7.27 (m, 11H), 6.90 (s, 2H), 5.22 (s, 2H), 4.52 (s, 2H), 2.89 (s, 1H), 2.42 (s, 6H), 2.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 159.3, 146.8 (2C), 143.0, 138.5, 138.4 (2C), 133.8, 130.8, 129.9, 129.2 (2C), 128.4, 128.2 (4C), 128.1 (4C), 128.0, 127.5 (2C), 126.7, 125.3, 116.2, 107.6, 96.8, 82.2, 80.2, 67.5, 52.1, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₆H₃₂O₃Na 535.2244; Found 535.2247

3-(5-(Hydroxydiphenylmethyl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-ol (2s)



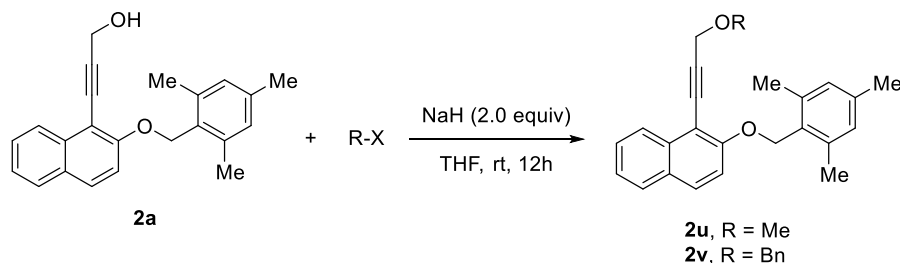
The title compound was isolated as a white solid (0.32 g, 63%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.29–8.25 (m, 1H), 8.19 (dd, J = 9.6, 0.8 Hz, 1H), 7.36–7.24 (m, 11H), 7.13 (d, J = 9.7 Hz, 1H), 6.89 (s, 2H), 6.74 (dd, J = 7.3, 1.2 Hz, 1H), 5.11 (s, 2H), 4.54 (s, 2H), 3.41 (s, 1H), 2.39 (s, 6H), 2.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 158.3, 147.0 (2C), 142.5, 138.4, 138.3 (2C), 136.4, 130.9, 129.8, 129.2 (2C), 128.2 (4C), 127.8 (4C), 127.4 (2C), 127.1, 126.9, 126.7, 125.8, 114.8, 107.7, 96.7, 83.4, 80.5, 67.0, 52.2, 21.2, 19.8 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₃₆H₃₂O₃Na 535.2244; Found 535.2247

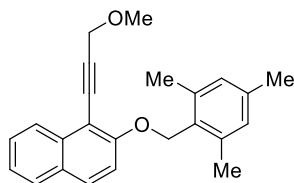
Procedure for Preparation of 2u and 2v



Compound **2a** (330 mg, 1 mmol, 1.0 equiv) was dissolved in 4 mL of anhydrous THF and treated with NaH (60% dispersion in mineral oil, 80 mg, 2.0 mmol, 2.0 equiv). After no more hydrogen evolved, methyl iodide or benzyl bromide (2.0 mmol, 2.0 equiv) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for 12 hours and subsequently quenched by adding saturated aqueous NH₄Cl solution (5 mL). The organic phase was extracted with ethyl acetate (20 mL $\times$ 3). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under vacuum to afford the crude products, which were purified by

chromatography on silica gel using petroleum ether/ethyl acetate (95:5) as the eluent to afford the corresponding products.

1-(3-Methoxyprop-1-yn-1-yl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalene (2u)



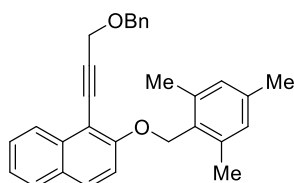
The title compound was isolated as a white solid (0.31 g, 90%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.29 (d, *J* = 8.5 Hz, 1H), 7.87–7.79 (m, 2H), 7.60–7.53 (m, 1H), 7.46–7.36 (m, 2H), 6.92 (s, 2H), 5.27 (s, 2H), 4.47 (s, 2H), 3.39 (s, 3H), 2.47 (s, 6H), 2.32 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.2, 138.26 (2C), 138.24, 134.7, 130.2, 130.0, 129.1 (2C), 129.0, 128.2, 127.4, 125.5, 124.5, 115.8, 107.7, 94.5, 81.2, 67.2, 60.8, 57.4, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₄O₂Na 367.1669; Found 367.1668

1-(3-(Benzyloxy)prop-1-yn-1-yl)-2-((2,4,6-trimethylbenzyl)oxy)naphthalene (2v)



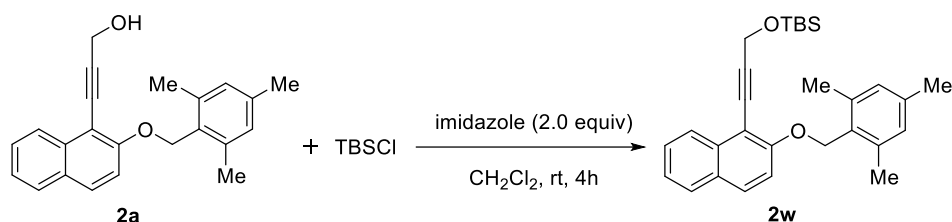
The title compound was isolated as a white solid (0.35 g, 84%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.19 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.49–7.43 (m, 1H), 7.36–7.29 (m, 2H), 7.27–7.15 (m, 5H), 6.75 (s, 2H), 5.17 (s, 2H), 4.50 (s, 2H), 4.42 (s, 2H), 2.35 (s, 6H), 2.14 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.3, 138.3, 138.2 (2C), 137.7, 134.7, 130.2, 129.9, 129.2 (2C), 128.9, 128.5 (2C), 128.4 (2C), 128.2, 127.8, 127.4, 125.5, 124.5, 115.4, 107.4, 94.6, 81.3, 71.0, 67.0, 58.0, 21.2, 19.8 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₀H₂₉O₂ 421.2162; Found 421.2160

Procedure for Preparation of 2w



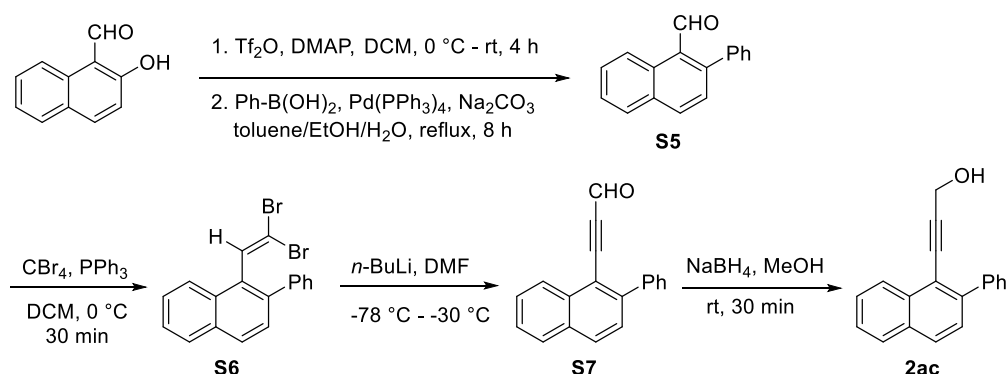
The alkyne **2a** (330 mg, 1.0 mmol, 1.0 equiv) in dry DCM (4 mL) followed by imidazole (136 mg, 2.0 mmol, 2.0 equiv) and tert-butyldimethylsilyl chloride (181 mg, 1.2 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 4 hours and then quenched by saturated aqueous NH₄Cl solution (5 mL). The organic phase was extracted with ethyl acetate (20 mL $\times$ 3). The combined organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated under vacuum to afford the crude products, which was further purified through column chromatography (petroleum ether/ethyl acetate 95:5) on silica gel, to afford *tert-butyldimethyl((3-(2-((2,4,6-trimethylbenzyl)oxy)naphthalen-1-yl)prop-2-yn-1-yl)oxy)silane* (**2w**) as a reddish oil (0.36 g, 82%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.31 (d, J = 9.2 Hz, 1H), 7.73–7.66 (m, 2H), 7.58–7.52 (m, 1H), 7.45–7.34 (m, 2H), 6.92 (s, 2H), 5.25 (s, 2H), 4.69 (s, 2H), 2.46 (s, 6H), 2.32 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.0, 138.4 (2C), 138.2, 134.9, 130.03, 130.00, 129.2 (2C), 129.0, 128.1, 127.2, 125.6, 124.5, 115.9, 107.8, 97.4, 79.3, 67.2, 52.8, 25.9 (3C), 21.2, 19.9 (2C), 18.4, –5.0 (2C) ppm.

HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₂₉H₃₆O₂SiNa 467.2377; Found 467.2373

Procedure for Preparation of 2ac



Step 1: A mixture of 2-hydroxy-1-naphthaldehyde (860 mg, 5.0 mmol, 1.0 equiv) and DMAP (1.22 g, 10.0 mmol, 2.0 equiv) in anhydrous DCM (30 mL) was cooled to $0\text{ }^\circ\text{C}$. Next, the solution of trifluoromethanesulfonic anhydride (1.83 g, 6.5 mmol, 1.3 equiv) in 10 mL anhydrous DCM was slowly added to the reaction mixture. After stirring for 30 min at $0\text{ }^\circ\text{C}$, the resulting mixture was allowed to warm to room temperature. After stirring for 8 h, the reaction was quenched with distilled water (50 mL) at $0\text{ }^\circ\text{C}$ followed by extraction with DCM (3×30 mL). The combined organic layers were washed with 1N HCl (3×30 mL), brine (3×30 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting crude yellow oil **S5** in 4.0 mL toluene was transferred to an 100 mL flask, phenylboronic acid (5.0 mmol, 1.0 equiv), $\text{Pd(PPh}_3)_4$ (173 mg, 0.15 mmol, 0.03 equiv), which was charged with Na_2CO_3 (1.06 g, 10 mmol, 2.0 equiv), toluene (21.0 mL), ethanol (14.0 mL), and H_2O (14.0 mL). The resultant mixture was vigorously stirred at $90\text{ }^\circ\text{C}$ for 8 h. Subsequently, the mixture was poured into brine (30 mL) and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (95:5) as the eluent to afford the corresponding product **S6** as a white solid (0.75 g, 72%).

Step 2: To a solution of **S6** (0.75 g, 3.2 mmol, 1.0 equiv) in DCM (50 mL) were added PPh_3 (4.2 g, 16 mmol, 5.0 equiv), and CBr_4 (2.6 g, 8 mmol, 2.5 equiv) at $0\text{ }^\circ\text{C}$ slowly. After stirring for 30 min, half of the solvent was evaporated. Next, petroleum ether : ethyl acetate (50 mL, 1:1) was added to the mixture, which was filtered through a pad of silica gel, and washed with petroleum ether : ethyl acetate (1:1). The filtrate was

evaporated and the residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (95:5) as the eluent to afford the corresponding product **S7** (1.1 g, 90%).

Step 3: To the solution of compound **S7** (1.1g, 2.8 mmol, 1.0 equiv) in THF (30 mL) was added *n*BuLi in hexane (2.5 mL, 6.2 mmol, 2.5 M, 2.2 equiv) at $-78\text{ }^{\circ}\text{C}$ under N_2 . Subsequently, the reaction was warmed to $-30\text{ }^{\circ}\text{C}$ and stirred for 1 h before the addition of DMF (0.41 g, 5.6 mmol, 2.0 equiv). The reaction was warmed to room temperature and stirred for another 2 h, before it was quenched by addition of saturated aqueous NH_4Cl . The reaction mixture was extracted with ethyl acetate (3×30 mL) and the combined organic layers were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated and the residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (95:5) as the eluent to afford the corresponding product **S8** (0.64 g, 89%).

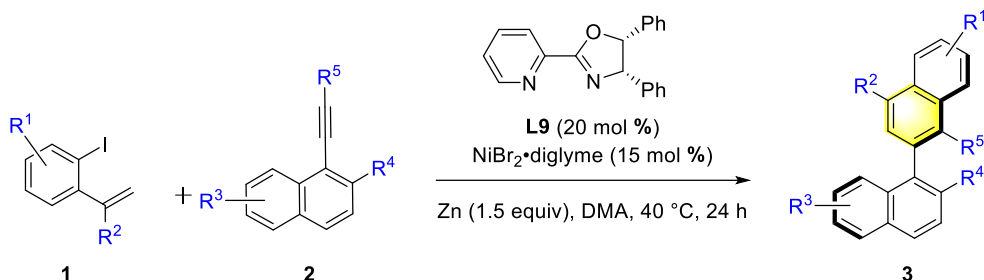
Step 4: To a stirred solution of **S8** (0.64 g, 2.5 mmol, 1.0 equiv) in methanol (10 mL), NaBH_4 (0.19 g, 5 mmol, 2.0 equiv) was added at room temperature and the resultant mixture was stirred for 30 min. After neutralization with 10% aqueous hydrochloric acid, the solution was extracted with CH_2Cl_2 for 2 times. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to afford the corresponding product 3-(2-phenylnaphthalen-1-yl)prop-2-yn-1-ol (**2ac**) as a white solid (0.62 g, 48% over 4 steps).

^1H NMR (400 MHz, Chloroform-*d*) δ = 8.48 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.74–7.67 (m, 2H), 7.65–7.59 (m, 1H), 7.58–7.45 (m, 4H), 7.45–7.37 (m, 1H), 4.49 (d, J = 4.6 Hz, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 142.8, 141.1, 133.8, 132.2, 129.8 (2C), 128.8, 128.2, 128.1 (2C), 127.7, 127.5, 127.3, 126.7, 126.5, 117.7, 95.5, 83.4, 51.9 ppm.

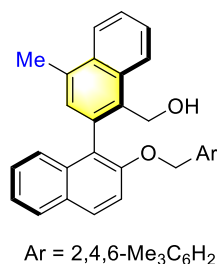
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{15}\text{O}$ 259.1117; Found 259.1130

III. Standard Procedures for Nickel-Catalyzed Asymmetric [2+4] Annulation



NiBr₂•diglyme (5.3 mg, 0.015 mmol, 15 mol%), (*4S,5R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (6.0 mg, 0.02 mmol, 20 mol%), Zn (9.7 mg, 0.15 mmol, 1.5 equiv), the olefin-tethered aryl iodides **1** (0.1 mmol, 1.0 equiv), and the alkynes **2** (0.2 mmol, 2.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, 0.5 mL anhydrous DMA was added subsequently under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 hours, before it was quenched by successive addition of water (3 mL) and saturated aqueous solution of NH₄Cl (3 mL). The aqueous phase was extracted with ethyl acetate (3 × 4 mL), and the combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the products **3**.

(*R*)-(4'-Methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3aa**)



The title compound was isolated as a white solid (39.9 mg, 90%, 91% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.42–8.35 (m, 1H), 8.16–8.09 (m, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.69–7.63 (m, 2H), 7.60 (d, *J* = 8.9 Hz,

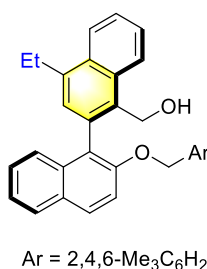
1H), 7.48–7.33 (m, 3H), 7.07 (s, 1H), 6.67 (s, 2H), 5.07 (d, $J = 10.7$ Hz, 1H), 4.94 (dd, $J = 12.0, 2.2$ Hz, 1H), 4.87 (d, $J = 10.6$ Hz, 1H), 4.49 (d, $J = 12.1$ Hz, 1H), 2.80–2.70 (m, 1H), 2.71 (s, 3H), 2.20 (s, 3H), 1.92 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 153.5, 138.20, 138.18$ (2C), 134.3, 134.1, 133.8, 132.9, 132.8, 132.7, 130.4, 129.63, 129.59, 129.3, 129.0 (2C), 128.2, 128.1, 126.6, 126.4, 126.1, 125.8, 125.6, 124.7, 124.5, 119.0, 69.0, 60.6, 21.1, 19.7, 19.0 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{30}\text{O}_2\text{Na}$ 469.2138; Found 469.2133

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R = 8.4$ (major), 12.0 (minor)

(R)-(4'-Ethyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ba**)



The title compound was isolated as a white solid (36 mg, 78%, 92% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

^1H NMR (400 MHz, Chloroform-*d*) $\delta = 8.39\text{--}8.32$ (m, 1H), 8.20–8.12 (m, 1H), 7.96 (d, $J = 8.9$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.63–7.58 (m, 2H), 7.56 (d, $J = 8.9$ Hz, 1H), 7.45–7.40 (m, 1H), 7.40–7.29 (m, 2H), 7.14 (s, 1H), 6.64 (s, 2H), 5.04 (d, $J = 10.5$ Hz, 1H), 4.90 (dd, $J = 12.0, 10.5$ Hz, 1H), 4.79 (d, $J = 10.4$ Hz, 1H), 4.46 (dd, $J = 12.2, 2.2$ Hz, 1H), 3.12 (q, $J = 7.5$ Hz, 2H), 2.78–2.72 (m, 1H), 2.16 (s, 3H), 1.90 (s, 6H), 1.35 (t, $J = 7.5$ Hz, 3H) ppm.

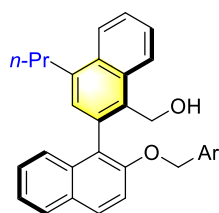
^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 153.5, 140.4, 138.3, 138.2$ (2C), 134.1, 133.9, 132.99, 132.96, 132.0, 130.5, 129.6, 129.3, 129.0 (2C), 128.2, 128.1, 128.0, 126.6, 126.3, 126.1, 125.8 (2C), 124.7, 124.1, 118.9, 68.9, 60.6, 26.1, 21.1, 19.1 (2C), 15.2 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{32}\text{O}_2\text{Na}$ 483.2295; Found 483.2306

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow

rate = 0.5 mL/min): t_R = 7.8 (major), 11.0 (minor)

(R)-(4'-Propyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ca**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (37 mg, 79%, 92% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

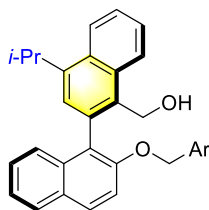
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.42–8.34 (m, 1H), 8.20–8.12 (m, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.65–7.59 (m, 2H), 7.56 (d, J = 9.0 Hz, 1H), 7.47–7.30 (m, 3H), 7.15 (s, 1H), 6.66 (s, 2H), 5.05 (d, J = 10.4 Hz, 1H), 4.92 (dd, J = 12.1, 10.5 Hz, 1H), 4.81 (d, J = 10.4 Hz, 1H), 4.48 (dd, J = 12.1, 2.1 Hz, 1H), 3.14–3.29 (m, 2H), 2.81–2.73 (m, 1H), 2.18 (s, 3H), 1.92 (s, 6H), 1.80 (h, J = 7.2 Hz, 2H), 1.03 (t, J = 7.3 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.5, 138.8, 138.3, 138.2 (2C), 134.2, 133.9, 133.1, 132.8, 132.2, 130.5, 129.6, 129.3, 129.14, 129.05 (2C), 128.1 (2C), 126.6, 126.3, 126.1, 125.8, 125.7, 124.7, 124.3, 118.8, 68.9, 60.7, 35.3, 24.0, 21.1, 19.1 (2C), 14.4 ppm.

HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₃₄H₃₄O₂Na 497.2451; Found 497.2458

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 7.7 (major), 9.6 (minor)

(R)-(4'-Isopropyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3da**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (24 mg, 52%, 91% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

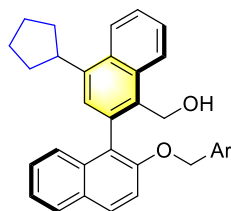
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.41–8.34 (m, 1H), 8.29–8.22 (m, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.64–7.59 (m, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.46–7.40 (m, 1H), 7.38–7.34 (m, 2H), 7.32 (s, 1H), 6.67 (s, 2H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.91 (t, *J* = 11.1 Hz, 1H), 4.74 (d, *J* = 10.2 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 3.92–3.79 (m, 1H), 2.74–2.66 (m, 1H), 2.16 (s, 3H), 1.94 (s, 6H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.35 (d, *J* = 6.8 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.6, 144.8, 138.4, 138.1 (2C), 134.0, 133.1, 132.9, 131.6, 130.5, 129.6, 129.3, 129.1 (3C), 128.2, 128.1, 126.7, 126.2, 126.1, 125.9, 125.8, 125.1, 124.7, 123.7, 118.6, 68.8, 60.7, 28.6, 23.9, 23.6, 21.1, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₄H₃₄O₂Na 497.2451; Found 497.2450

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 7.7 (major), 10.1 (minor)

(R)-(4'-Cyclopentyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol
(**3ea**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (21 mg, 42%, 87% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

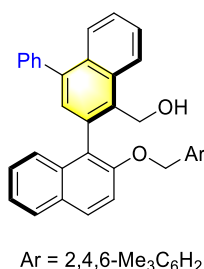
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.30–8.30 (m, 1H), 8.28–8.21 (m, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.60–7.55 (m, 2H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.42–7.37 (m, 1H), 7.35–7.29 (m, 2H), 7.23 (s, 1H), 6.63 (s, 2H), 5.00 (d, *J* = 10.2 Hz, 1H), 4.87 (t, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 10.3 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 3.84–3.72 (m, 1H), 2.72–2.65 (m, 1H), 2.34–2.07 (m, 4H), 2.08 (s, 3H), 1.89 (s, 6H), 1.82–1.67 (m, 4H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 152.4, 141.2, 137.2, 137.0 (2C), 132.8, 132.7, 131.9, 131.6, 131.3, 129.3, 128.4, 128.1, 127.9 (2C), 127.1, 127.0, 125.5, 125.0, 124.9, 124.6, 124.5, 124.2, 123.5, 123.2, 117.5, 67.7, 59.5, 40.0, 32.7, 32.5, 24.23, 24.21, 19.9, 17.9 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₃₆H₃₆O₂Na 523.2608; Found 523.2607

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 7.5 (major), 9.7 (minor)

(R)-(4'-Phenyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3fa**)



The title compound was isolated as a white solid (29 mg, 57%, 76% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

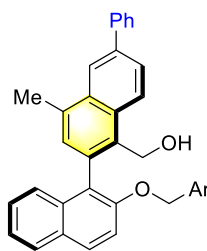
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.41 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.66–7.33 (m, 11H), 7.29 (s, 1H), 6.66 (s, 2H), 5.09 (d, J = 10.3 Hz, 1H), 4.97 (t, J = 11.2 Hz, 1H), 4.84 (d, J = 10.4 Hz, 1H), 4.54 (dd, J = 12.1, 2.1 Hz, 1H), 2.82–2.74 (m, 1H), 2.14 (s, 3H), 1.95 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.6, 140.6, 140.4, 138.4, 138.1 (2C), 135.5, 133.9, 133.1, 132.8, 131.8, 130.5, 130.3 (2C), 130.0, 129.8, 129.2, 129.1 (2C), 128.4 (2C), 128.2, 127.7, 127.5, 126.8, 126.7, 126.6, 126.1, 126.0, 125.4, 124.7, 118.7, 69.0, 60.7, 21.1, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₃₇H₃₂O₂Na 531.2295; Found 531.2297

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 8.0 (major), 11.3 (minor)

(*R*)-(4'-Methyl-6'-phenyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ga**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (49 mg, 98%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

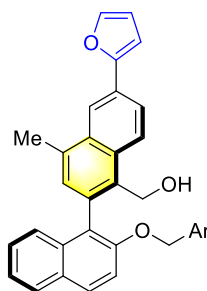
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.42 (d, *J* = 8.7 Hz, 1H), 8.28 (d, *J* = 1.8 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.92–7.87 (m, 2H), 7.85–7.80 (m, 2H), 7.61–7.48 (m, 3H), 7.46–7.40 (m, 2H), 7.38–7.31 (m, 2H), 7.07 (d, *J* = 1.1 Hz, 1H), 6.65 (s, 2H), 5.07 (d, *J* = 10.6 Hz, 1H), 4.92 (t, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 10.6 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 2.80–2.73 (m, 1H), 2.72 (s, 3H), 2.18 (s, 3H), 1.92 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.5, 141.6, 138.4, 138.3, 138.2 (2C), 134.6, 134.1, 133.9, 133.1, 133.0, 131.9, 130.5, 130.1, 129.7, 129.3, 129.1 (4C), 128.2, 128.1, 127.7 (2C), 127.5, 126.7, 126.2, 126.1, 126.0, 124.7, 122.6, 118.9, 69.0, 60.6, 21.1, 19.8, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₈H₃₄O₂Na 545.2451; Found 545.2444

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 9.50 (major), 12.6 (minor)

(*R*)-(6'-(Furan-2-yl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ha**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (44 mg, 86%, 91% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

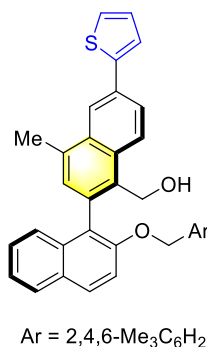
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.38 (d, *J* = 1.8 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.93–7.84 (m, 2H), 7.61–7.50 (m, 2H), 7.45–7.40 (m, 1H), 7.40–7.31 (m, 2H), 7.03 (s, 1H), 6.86 (d, *J* = 3.3 Hz, 1H), 6.63 (s, 2H), 6.58 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.04 (d, *J* = 10.7 Hz, 1H), 4.92–4.81 (m, 2H), 4.43 (dd, *J* = 12.2, 2.0 Hz, 1H), 2.80–2.75 (m, 1H), 2.72 (s, 3H), 2.17 (s, 3H), 1.88 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 154.5, 153.5, 142.5, 138.3, 138.2 (2C), 134.6, 134.2, 133.8, 132.99, 132.97, 132.0, 130.5, 130.2, 129.7, 129.3, 129.0 (2C), 128.3, 128.2, 128.0, 126.7, 126.17, 126.15, 124.8, 122.8, 119.2, 118.8, 112.1, 105.9, 69.1, 60.6, 21.1, 19.8, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₃O₃Na 513.2424; Found 513.2414

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 9.7 (major), 15.4 (minor)

(R)-(4'-Methyl-6'-(thiophen-2-yl)-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ia**)



The title compound was isolated as a white solid (48 mg, 92%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

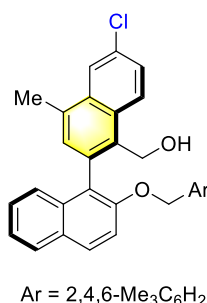
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.35 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.93–7.86 (m, 2H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 3.5 Hz, 1H), 7.45–7.33 (m, 4H), 7.19 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.05 (s, 1H), 6.65 (s, 2H), 5.06 (d, *J* = 10.7 Hz, 1H), 4.93–4.82 (m, 2H), 4.45 (dd, *J* = 12.2, 2.4 Hz, 1H), 2.80–2.74 (m, 1H), 2.72 (s, 3H), 2.18 (s, 3H), 1.91 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.5, 144.9, 138.3, 138.2 (2C), 134.4, 134.2, 133.8, 133.1, 133.0, 132.0, 131.7, 130.5, 130.3, 129.7, 129.2, 129.0 (2C), 128.4, 128.2, 128.0, 126.7, 126.4, 126.1, 125.3, 124.83, 124.75, 123.7, 121.0, 119.0, 69.0, 60.6, 21.1, 19.8, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₃₆H₃₂SO₂Na 551.2015; Found 551.2031

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 10.7 (major), 16.7 (minor)

(R)-(6'-Chloro-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ja**)



The title compound was isolated as a white solid (31 mg, 65%, 88% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

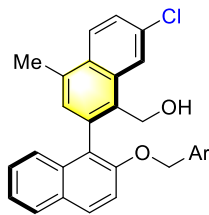
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.28 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 2.2 Hz, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.62–7.51 (m, 2H), 7.46–7.40 (m, 1H), 7.38–7.30 (m, 2H), 7.04 (s, 1H), 6.65 (s, 2H), 5.06 (d, J = 10.7 Hz, 1H), 4.88–4.79 (m, 2H), 4.43 (d, J = 13.0 Hz, 1H), 2.77–2.70 (m, 1H), 2.63 (s, 3H), 2.18 (s, 3H), 1.88 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.4, 138.3, 138.2 (2C), 134.3, 133.73, 133.70, 133.5, 133.2, 131.9, 131.1, 130.7, 130.4, 129.8, 129.2, 129.0 (2C), 128.2, 127.7, 127.5, 127.1, 126.7, 126.0, 124.8, 123.6, 118.9, 69.0, 60.5, 21.1, 19.6, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₃₂H₂₉ClO₂Na 503.1748; Found 503.1743

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 8.7 (major), 13.8 (minor)

(*R*)-(7'-Chloro-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ka**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (27 mg, 57%, 84% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

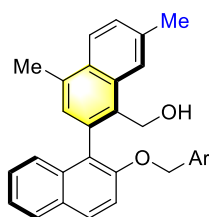
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.32 (d, *J* = 2.1 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.92–7.87 (m, 1H), 7.60–7.51 (m, 2H), 7.44–7.39 (m, 1H), 7.36–7.27 (m, 2H), 7.00 (d, *J* = 1.0 Hz, 1H), 6.64 (s, 2H), 5.06 (d, *J* = 10.7 Hz, 1H), 4.89–4.74 (m, 2H), 4.42 (dd, *J* = 12.3, 2.0 Hz, 1H), 2.70–2.62 (m, 4H), 2.18 (s, 3H), 1.89 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.4, 138.3, 138.2 (2C), 134.4, 134.2, 133.7, 133.6, 132.5, 131.1, 130.4, 129.93, 129.85, 129.2, 129.1 (3C), 128.2, 127.7, 126.8, 126.6, 126.2, 125.9, 124.78, 124.76, 118.9, 69.0, 60.5, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₂H₂₉ClO₂Na 503.1748; Found 503.1747

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t*_R = 8.3 (major), 13.2 (minor)

(*R*)-(4',7'-Dimethyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3la**)



Ar = 2,4,6-Me₃C₆H₂

The title compound was isolated as a white solid (32 mg, 70%, 83% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.14 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.49–7.39 (m, 2H), 7.38–7.30 (m, 2H), 6.99 (s, 1H), 6.66 (s, 2H), 5.05 (d, *J* = 10.6 Hz, 1H), 4.96–4.83

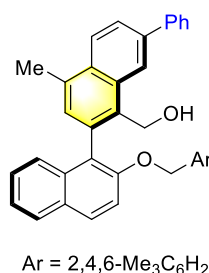
(m, 2H), 4.45 (dd, $J = 12.1, 2.0$ Hz, 1H), 2.79–2.73 (m, 1H), 2.67 (s, 3H), 2.61 (s, 3H), 2.19 (s, 3H), 1.92 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 153.5, 138.23$ (2C), 138.18, 136.0, 134.2, 133.9, 133.5, 133.1, 132.8, 131.0, 130.5, 129.5, 129.3, 129.0 (2C), 128.8, 128.5, 128.1, 128.0, 126.6, 126.2, 124.7, 124.6, 124.4, 119.1, 69.0, 60.6, 22.2, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{32}\text{O}_2\text{Na}$ 483.2295; Found 483.2304

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R = 8.2$ (major), 12.4 (minor)

(R)-(4'-Methyl-7'-phenyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ma**)



The title compound was isolated as a white solid (35 mg, 67%, 76% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

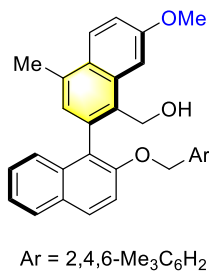
^1H NMR (400 MHz, Chloroform- d) $\delta = 8.55$ (d, $J = 1.8$ Hz, 1H), 8.17 (d, $J = 8.7$ Hz, 1H), 7.96 (d, $J = 8.9$ Hz, 1H), 7.93–7.86 (m, 2H), 7.83–7.77 (m, 2H), 7.57 (d, $J = 8.9$ Hz, 1H), 7.53–7.47 (m, 2H), 7.45–7.30 (m, 4H), 7.03 (s, 1H), 6.65 (s, 2H), 5.06 (d, $J = 10.7$ Hz, 1H), 5.01–4.92 (m, 1H), 4.88 (d, $J = 10.6$ Hz, 1H), 4.49 (dd, $J = 12.1, 2.2$ Hz, 1H), 2.74–2.67 (m, 1H), 2.70 (s, 3H), 2.18 (s, 3H), 1.92 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 153.5, 141.4, 138.9, 138.24$ (2C), 138.23, 134.4, 134.2, 133.8, 133.5, 133.0, 132.0, 130.4, 129.69, 129.66, 129.3, 129.0 (2C), 128.9 (2C), 128.13, 128.11, 127.8, 127.5 (2C), 126.7, 126.1, 125.4, 125.1, 124.7, 123.7, 118.9, 68.9, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{38}\text{H}_{34}\text{O}_2\text{Na}$ 545.2451; Found 545.2453

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R = 11.0$ (major), 13.7 (minor)

(*R*)-(7'-Methoxy-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3na**)



The title compound was isolated as a white solid (36 mg, 75%, 80% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

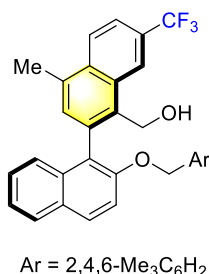
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 9.2 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 2.6 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.45–7.39 (m, 1H), 7.39–7.28 (m, 3H), 6.91 (s, 1H), 6.66 (s, 2H), 5.02 (d, *J* = 10.7 Hz, 1H), 4.88–4.78 (m, 2H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.98 (s, 3H), 2.69–2.65 (m, 1H), 2.65 (s, 3H), 2.19 (s, 3H), 1.91 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 158.0, 153.5, 138.3 (2C), 138.2, 134.3, 134.2, 133.9, 133.7, 133.1, 130.5, 129.5, 129.4, 129.0 (2C), 128.6, 128.2, 128.1, 127.6, 126.6, 126.2, 126.1, 124.7, 119.2, 118.1, 104.1, 69.1, 60.9, 55.5, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₃H₃₂O₃Na 513.2400; Found 513.2378

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 8.7 (major), 14.0 (minor)

(*R*)-(4'-Methyl-7'-(trifluoromethyl)-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3oa**)



The title compound was isolated as a white solid (17 mg, 30%, 72% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.79 (s, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.95–7.90 (m, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.61–7.55 (m, 1H), 7.52–7.46 (m, 1H), 7.43–7.41 (m, 2H), 6.79 (s, 2H), 5.23 (d, *J* = 10.8 Hz, 1H), 5.07–4.96 (m, 2H), 4.62 (d, *J* = 12.3 Hz, 1H), 2.86–2.78 (s, 1H), 2.84 (s, 3H), 2.33 (s, 3H), 2.03 (s, 6H) ppm.

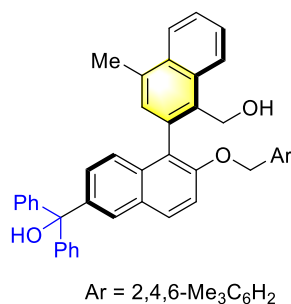
¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.5, 138.3, 138.2 (2C), 135.2, 134.5, 134.4, 134.1, 133.7, 131.9, 131.7, 130.4, 130.0, 129.2, 129.1 (2C), 128.3, 128.1 (q, *J* = 32 Hz), 127.3, 126.8, 125.8, 125.6, 124.8, 123.5 (q, *J* = 4.5 Hz), 124.7 (q, *J* = 274 Hz), 121.5 (q, *J* = 3.0 Hz), 118.7, 68.9, 60.3, 21.1, 19.7, 19.1 (2C) ppm.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ = –61.95 (s, 3F) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₃H₂₉F₃O₂Na 537.2012; Found 537.2016

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 7.5 (major), 10.7 (minor)

(*R*)-(1'-(Hydroxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-6-yl)diphenylmethanol (**3ab**)



The title compound was isolated as a white solid (56 mg, 90%, 92% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.36–8.30 (m, 1H), 8.11–8.05 (m, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.77–7.73 (m, 1H), 7.63–7.58 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.38–7.29 (m, 12H), 7.04 (s, 1H), 6.64 (s, 2H), 5.03 (d, *J* = 10.7 Hz, 1H), 4.90 (t, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 3.00 (s, 1H), 2.80–2.72 (m, 1H), 2.67 (s, 3H), 2.18 (s, 3H), 1.89 (s, 6H) ppm.

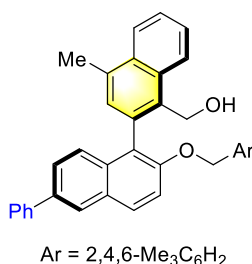
¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.8, 146.77, 146.74, 143.1, 138.24, 138.18 (2C), 134.3, 134.1, 132.9, 132.81, 132.78, 132.7, 130.1, 129.8, 129.6, 129.2, 129.0 (2C),

128.14 (4C), 128.10 (4C), 128.0, 127.5 (2C), 127.0, 126.7, 126.4, 126.0, 125.8, 125.6, 124.5, 119.1, 82.2, 69.0, 60.6, 21.1, 19.7, 19.0 (2C) ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{45}H_{40}O_3Na$ 651.2870; Found 651.2871

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 13.4 (major), 26.0 (minor)

(R)-(4'-Methyl-6-phenyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ac**)



The title compound was isolated as a white solid (49 mg, 95%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

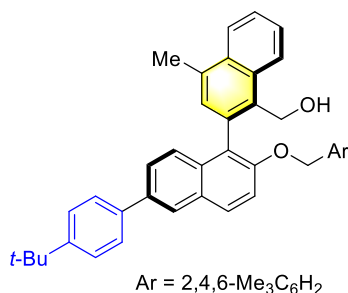
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.42–8.35 (m, 1H), 8.17–8.08 (m, 2H), 8.03 (d, J = 9.0 Hz, 1H), 7.74–7.69 (m, 2H), 7.67–7.59 (m, 4H), 7.52–7.47 (m, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.42–7.36 (m, 1H), 7.08 (s, 1H), 6.66 (s, 2H), 5.07 (d, J = 10.6 Hz, 1H), 4.95 (t, J = 11.0 Hz, 1H), 4.88 (d, J = 10.6 Hz, 1H), 4.51 (d, J = 12.1 Hz, 1H), 2.84–2.76 (m, 1H), 2.71 (s, 3H), 2.19 (s, 3H), 1.91 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.6, 140.9, 138.3, 138.2 (2C), 137.5, 134.4, 134.2, 133.0, 132.8 (2C), 132.7, 130.7, 129.9, 129.6, 129.2, 129.03 (2C), 129.0 (2C), 128.2, 127.5, 127.4 (2C), 126.7, 126.4, 126.3, 126.0, 125.9, 125.6, 124.5, 119.5, 69.0, 60.6, 21.1, 19.8, 19.1 (2C) ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{34}O_2Na$ 545.2451; Found 545.2462

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 10.1 (major), 13.2 (minor)

(*R*)-(6-(4-(*tert*-Butyl)phenyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ad**)



The title compound was isolated as a white solid (49 mg, 85%, 89% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

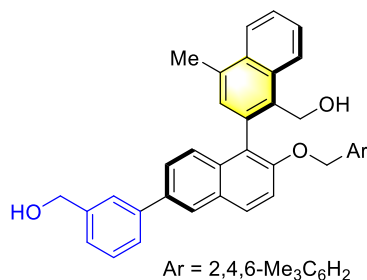
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.40–8.35 (m, 1H), 8.14–8.07 (m, 2H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.68–7.57 (m, 6H), 7.55–7.49 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.08 (s, 1H), 6.65 (s, 2H), 5.05 (d, *J* = 10.7 Hz, 1H), 4.94 (t, *J* = 10.5 Hz, 1H), 4.87 (d, *J* = 10.7 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 2.81–2.74 (m, 1H), 2.70 (s, 3H), 2.19 (s, 3H), 1.91 (s, 6H), 1.39 (s, 9H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.5, 150.5, 138.24, 138.22 (2C), 138.0, 137.4, 134.4, 134.2, 132.90, 132.88, 132.85, 132.7, 130.8, 129.9, 129.6, 129.3, 129.0 (2C), 128.2, 127.1 (2C), 126.6, 126.4, 126.3, 126.0 (2C), 125.8, 125.7, 125.6, 124.5, 119.4, 69.1, 60.6, 34.7, 31.5 (3C), 21.1, 19.8, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₄₂H₄₂O₂Na 601.3077; Found 601.3073

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t*_R = 8.8 (major), 11.9 (minor)

(*R*)-(3-(1'-(Hydroxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-6-yl)phenyl)methanol (**3ae**)



The title compound was isolated as a white solid (39 mg, 75%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1).

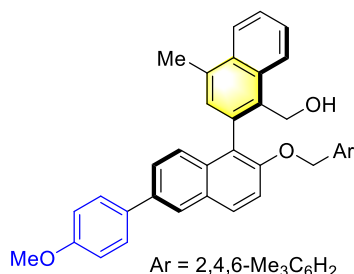
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.41–8.32 (m, 1H), 8.13–8.08 (m, 2H), 8.04–7.97 (m, 1H), 7.72–7.70 (m, 1H), 7.65–7.57 (m, 5H), 7.51–7.34 (m, 3H), 7.06 (d, *J* = 1.0 Hz, 1H), 6.65 (s, 2H), 5.06 (d, *J* = 10.7 Hz, 1H), 4.92 (t, *J* = 10.4 Hz, 1H), 4.86 (d, *J* = 10.6 Hz, 1H), 4.78 (s, 2H), 4.49 (d, *J* = 12.1 Hz, 1H), 2.80–2.72 (m, 1H), 2.69 (d, *J* = 1.0 Hz, 3H), 2.18 (s, 3H), 1.90 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.7, 141.7, 141.3, 138.3, 138.2 (2C), 137.2, 134.5, 134.2, 133.1, 132.87, 132.85, 132.7, 130.7, 129.9, 129.6, 129.3 (2C), 129.1 (2C), 128.2, 126.74, 126.71, 126.5, 126.2, 126.05 (2C), 126.00, 125.9, 125.6, 124.5, 119.5, 69.0, 65.5, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₉H₃₆O₃Na 575.2557; Found 575.2552

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 60/40, flow rate = 0.5 mL/min): *t_R* = 12.9 (major), 34.7 (minor)

(R)-(6-(4-Methoxyphenyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3af**)



The title compound was isolated as a white solid (44 mg, 85%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.42–8.35 (m, 1H), 8.16–8.09 (m, 1H), 8.06 (d, *J* = 1.9 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.70–7.55 (m, 6H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.08 (s, 1H), 7.05–7.00 (m, 2H), 6.66 (s, 2H), 5.06 (d, *J* = 10.7 Hz, 1H), 5.00–4.90 (m, 1H), 4.87 (d, *J* = 10.6 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 3.88 (s, 3H), 2.90–2.77 (m, 1H), 2.71 (s, 3H), 2.19 (s, 3H), 1.91 (s, 6H) ppm.

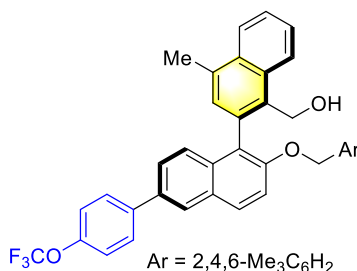
¹³C NMR (101 MHz, Chloroform-*d*) δ = 159.3, 153.4, 138.22, 138.20 (2C), 137.1, 134.4, 134.1, 133.4, 132.88, 132.82, 132.68, 132.62, 130.8, 129.8, 129.6, 129.3, 129.0

(2C), 128.4 (2C), 128.2, 126.7, 126.4, 126.1, 125.8, 125.6, 125.2, 124.5, 119.5, 114.4 (2C), 69.1, 60.6, 55.5, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{39}H_{36}O_3Na$ 575.2557; Found 575.2558

HPLC-Data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 11.4 (major), 14.6 (minor)

(R)-(4'-Methyl-6-(4-(trifluoromethoxy)phenyl)-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ag**)



The title compound was isolated as a white solid (49 mg, 81%, 89% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.40–8.33 (m, 1H), 8.15–8.09 (m, 1H), 8.06 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.73–7.67 (m, 2H), 7.66–7.59 (m, 3H), 7.54 (dd, J = 8.8, 1.9 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.05 (s, 1H), 6.65 (s, 2H), 5.07 (d, J = 10.6 Hz, 1H), 4.98–4.83 (m, 2H), 4.48 (dd, J = 12.0, 2.1 Hz, 1H), 2.75–2.69 (m, 1H), 2.69 (s, 3H), 2.18 (s, 3H), 1.90 (s, 6H) ppm.

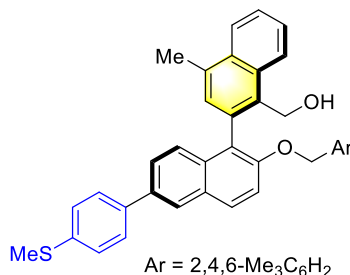
¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.8, 148.8 (q, J = 2.0 Hz), 139.7, 138.3, 138.2 (2C), 136.1, 134.5, 134.2, 133.2, 132.9, 132.72, 132.69, 130.6, 129.9, 129.5, 129.2, 129.1 (2C), 128.7 (2C), 128.2, 126.9, 126.5, 126.1, 126.0, 125.9, 125.6, 124.5, 121.5 (2C), 120.7 (q, J = 257.6 Hz), 119.6, 69.0, 60.6, 21.1, 19.8, 19.1 (2C) ppm.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ = –57.74 (s, 3F) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{39}H_{33}F_3O_3Na$ 629.2274; Found 629.2272

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 10.6 (major), 12.5 (minor)

(*R*)-(4'-Methyl-6-(4-(methylthio)phenyl)-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ah**)



The title compound was isolated as a white solid (26 mg, 46%, 89% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

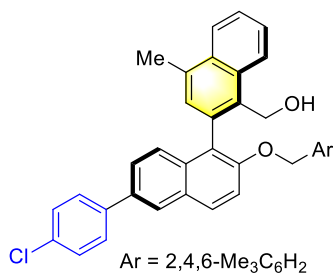
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.38–8.34 (m, 1H), 8.13–8.08 (m, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.68–7.52 (m, 6H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.38–7.33 (m, 2H), 7.05 (s, 1H), 6.64 (s, 2H), 5.05 (d, *J* = 10.7 Hz, 1H), 4.92 (t, *J* = 10.3 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 2.78–2.71 (m, 1H), 2.69 (s, 3H), 2.54 (s, 3H), 2.18 (s, 3H), 1.90 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.6, 138.3, 138.2 (2C), 137.9, 137.7, 136.8, 134.4, 134.2, 133.0, 132.9, 132.8, 132.7, 130.7, 129.9, 129.6, 129.3, 129.0 (2C), 128.2, 127.7 (2C), 127.1 (2C), 126.8, 126.5, 126.0, 125.9, 125.61 125.56, 124.5, 119.5, 69.0, 60.6, 21.1, 19.7, 19.1 (2C), 16.0 ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₉H₃₆SO₂Na 591.2328; Found 591.2335

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 65/35, flow rate = 0.75 mL/min): *t_R* = 10.1 (minor), 14.6 (major)

(*R*)-(6-(4-Chlorophenyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ai**)



The title compound was isolated as a white solid (44 mg, 80%, 88% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

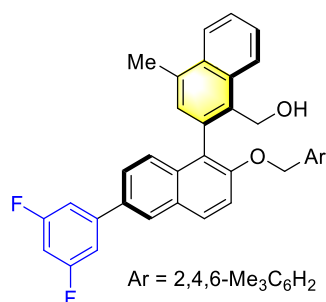
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.40–8.34 (m, 1H), 8.15–8.08 (m, 1H), 8.06 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.70–7.58 (m, 5H), 7.54 (dd, J = 8.8, 2.0 Hz, 1H), 7.50–7.39 (m, 3H), 7.05 (d, J = 1.0 Hz, 1H), 6.65 (s, 2H), 5.07 (d, J = 10.7 Hz, 1H), 4.93 (t, J = 10.9 Hz, 1H), 4.87 (d, J = 10.7 Hz, 1H), 4.49 (d, J = 12.1 Hz, 1H), 2.75–2.69 (m, 1H), 2.69 (d, J = 1.0 Hz, 3H), 2.18 (s, 3H), 1.91 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.8, 139.4, 138.3, 138.2 (2C), 136.2, 134.5, 134.2, 133.6, 133.1, 132.9, 132.74, 132.69, 130.6, 129.9, 129.5, 129.21, 129.16 (2C), 129.1 (2C), 128.6 (2C), 128.2, 126.9, 126.5, 125.91 (2C), 125.89, 125.6, 124.5, 119.6, 69.0, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for C₃₈H₃₃ClO₂Na 579.2061; Found 579.2077

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 13.1 (major), 16.1 (minor)

(R)-(6-(3,5-Difluorophenyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3aj**)



The title compound was isolated as a white solid (48 mg, 86%, 88% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.4–8.3 (m, 1H), 8.14–8.09 (m, 1H), 8.07 (d, J = 2.0 Hz, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.72–7.58 (m, 3H), 7.51 (dd, J = 8.8, 2.0 Hz, 1H), 7.43 (d, J = 8.7 Hz, 1H), 7.25–7.17 (m, 2H), 7.05 (s, 1H), 6.85–6.77 (m, 1H), 6.66 (s, 2H), 5.08 (d, J = 10.7 Hz, 1H), 4.96–4.86 (m, 2H), 4.48 (d, J = 12.1 Hz, 1H), 2.73–2.64 (m, 1H), 2.70 (s, 3H), 2.18 (s, 3H), 1.92 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 163.5 (dd, J = 248.0, 13.1 Hz, 2C), 154.1, 144.3 (t, J = 9.6 Hz), 138.3, 138.2 (2C), 135.0 (t, J = 2.5 Hz), 134.6, 134.2, 133.6, 132.9,

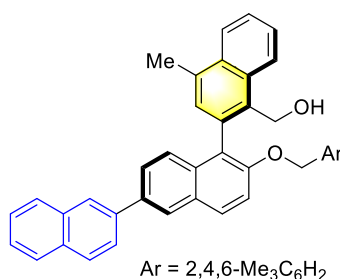
132.7, 132.6, 130.4, 130.1, 129.5, 129.2, 129.1 (2C), 128.1, 127.1, 126.5, 126.3, 125.9, 125.6, 125.5, 124.5, 119.6, 110.1 (dd, $J = 26.5, 13.9$ Hz, 2C), 102.7 (t, $J = 25.4$ Hz), 68.9, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) $\delta = -109.54$ (s, 2F) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{38}\text{H}_{32}\text{F}_2\text{O}_2\text{Na}$ 581.2263; Found 581.2278

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R = 11.9$ (major), 14.7 (minor)

(R)-(4-Methyl-2'-((2,4,6-trimethylbenzyl)oxy)-[2,1':6',2''-ternaphthalen]-1-yl)methanol (**3ak**)



The title compound was isolated as a white solid (42 mg, 74%, 89% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

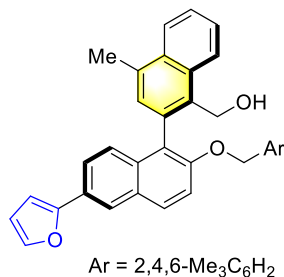
^1H NMR (400 MHz, Chloroform-*d*) $\delta = 8.43\text{--}8.36$ (m, 1H), 8.24 (d, $J = 1.9$ Hz, 1H), 8.18–8.10 (m, 2H), 8.06 (d, $J = 8.9$ Hz, 1H), 8.00–7.82 (m, 4H), 7.74 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.69–7.59 (m, 3H), 7.58–7.44 (m, 3H), 7.10 (d, $J = 1.1$ Hz, 1H), 6.66 (s, 2H), 5.08 (d, $J = 10.7$ Hz, 1H), 4.96 (t, $J = 10.6$ Hz, 1H), 4.89 (d, $J = 10.6$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 2.82–2.74 (m, 1H), 2.71 (d, $J = 1.0$ Hz, 3H), 2.19 (s, 3H), 1.92 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 153.7, 138.3, 138.2$ (3C), 137.3, 134.5, 134.2, 133.9, 133.1, 132.9 (2C), 132.8, 132.7, 130.8, 123.0, 129.6, 129.3, 129.1 (2C), 128.7, 128.3, 128.2, 127.8, 126.8, 126.50, 126.46, 126.4, 126.3, 126.14, 126.09, 125.9, 125.7, 125.6, 124.5, 119.5, 69.0, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{42}\text{H}_{36}\text{O}_2\text{Na}$ 595.2608; Found 595.2625

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R = 13.1$ (major), 21.0 (minor)

(*R*)-(6-(Furan-2-yl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3al**)



The title compound was isolated as a white solid (38 mg, 75%, 89% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

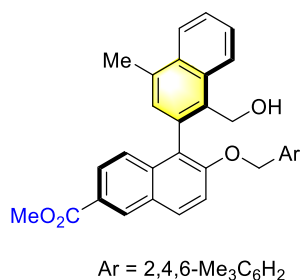
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.39–8.32 (m, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 8.14–8.06 (m, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.65–7.59 (m, 3H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.52 (d, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.05 (s, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.65 (s, 2H), 6.53–6.50 (m, 1H), 5.05 (d, *J* = 10.6 Hz, 1H), 4.91 (t, *J* = 11.1 Hz, 1H), 4.84 (d, *J* = 10.6 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 2.73–2.67 (m, 1H), 2.69 (s, 3H), 2.18 (s, 3H), 1.90 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 154.0, 153.7, 142.4, 138.3, 138.2 (2C), 134.4, 134.2, 133.0, 132.9, 132.8, 132.7, 130.5, 129.9, 129.6, 129.2, 129.0 (2C), 128.3, 127.2, 126.6, 126.4, 125.9, 125.6, 124.5, 123.1, 122.3, 119.5, 111.9, 105.6, 69.0, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₆H₃₂O₃Na 535.2244; Found 535.2252

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 11.1 (major), 14.8 (minor)

(*R*)-Methyl 1'-(hydroxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalene]-6-carboxylate (**3am**)



The title compound was isolated as a white solid (38 mg, 76%, 86% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

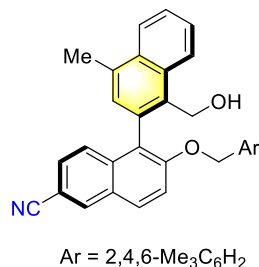
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.66 (d, *J* = 1.7 Hz, 1H), 8.38–8.31 (m, 1H), 8.15–8.05 (m, 2H), 7.89 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.68–7.58 (m, 3H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.02 (s, 1H), 6.66 (s, 2H), 5.13 (d, *J* = 10.6 Hz, 1H), 4.95–4.85 (m, 2H), 4.45 (d, *J* = 12.1 Hz, 1H), 3.97 (s, 3H), 2.69 (s, 3H), 2.54–2.45 (m, 1H), 2.18 (s, 3H), 1.94 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 167.3, 155.4, 138.4, 138.1 (2C), 136.2, 134.7, 134.1, 132.9, 132.6, 132.4, 131.3, 131.1, 129.4, 129.2, 129.1 (2C), 128.9, 127.7, 126.5, 126.3, 126.1, 126.0, 125.9, 125.6, 124.5, 118.8, 68.5, 60.5, 52.4, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₄H₃₂O₄Na 527.2193; Found 527.2200

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 11.9 (major), 22.1 (minor)

(R)-1'-(Hydroxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalene]-6-carbonitrile (**3an**)



The title compound was isolated as a white solid (39 mg, 83%, 85% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

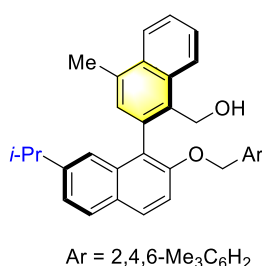
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.37–8.29 (m, 1H), 8.27 (d, *J* = 1.6 Hz, 1H), 8.13–8.06 (m, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.68–7.57 (m, 2H), 7.47–7.35 (m, 2H), 6.97 (d, *J* = 1.1 Hz, 1H), 6.67 (s, 2H), 5.17 (d, *J* = 10.6 Hz, 1H), 4.93 (d, *J* = 10.6 Hz, 1H), 4.87 (t, *J* = 10.2 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 2.68 (d, *J* = 0.9 Hz, 3H), 2.26–2.21 (m, 1H), 2.18 (s, 3H), 1.96 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.9, 138.6, 138.1 (2C), 135.5, 134.9, 134.2, 134.1, 133.0, 132.6, 131.7, 130.2, 129.2 (2C), 129.1, 128.8, 128.7, 127.8, 127.3, 127.1, 126.6, 126.1, 125.6, 124.6, 119.42, 119.35, 107.9, 68.4, 60.5, 21.1, 19.7, 19.2 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{29}\text{NO}_2\text{Na}$ 494.2091; Found 494.2089

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 12.2 (major), 22.3 (minor)

(*R*)-(7-Isopropyl-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ao**)



The title compound was isolated as a white solid (35 mg, 73%, 85% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

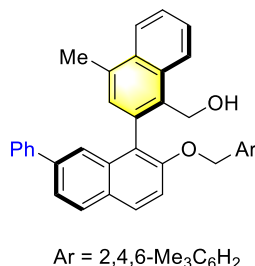
^1H NMR (400 MHz, Chloroform-*d*) δ = 8.33–8.24 (m, 1H), 8.07–7.99 (m, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.59–7.50 (m, 2H), 7.41 (d, J = 8.9 Hz, 1H), 7.27 (dd, J = 8.5, 1.7 Hz, 1H), 7.06 (dd, J = 1.7, 0.8 Hz, 1H), 6.97 (d, J = 1.1 Hz, 1H), 6.54 (s, 2H), 4.91 (d, J = 10.7 Hz, 1H), 4.88–4.78 (m, 2H), 4.72 (d, J = 10.7 Hz, 1H), 4.38 (dd, J = 12.2, 2.1 Hz, 1H), 2.83–2.71 (m, 1H), 2.60 (d, J = 1.0 Hz, 3H), 2.09 (s, 3H), 1.77 (s, 6H), 1.08 (dd, J = 9.7, 6.9 Hz, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 153.6, 147.3, 138.21 (2C), 138.16, 134.22, 134.15, 133.9, 133.1, 132.79, 132.75, 129.7, 129.34, 129.32, 129.2, 129.0 (2C), 128.2, 128.1, 126.3, 125.72, 125.66, 124.5, 124.1, 122.9, 118.4, 69.1, 60.7, 34.5, 24.1, 23.9, 21.1, 19.7, 19.0 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{36}\text{O}_2\text{Na}$ 511.2608; Found 511.2602

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 7.2 (major), 9.0 (minor)

(*R*)-(4'-Methyl-7-phenyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)-methanol (**3ap**)



The title compound was isolated as a white solid (42 mg, 80%, 89% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

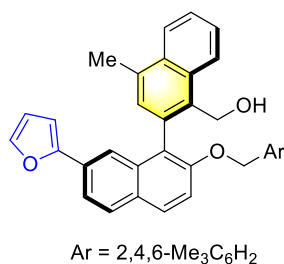
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.44–8.36 (m, 1H), 8.17–8.08 (m, 1H), 8.03–7.96 (m, 2H), 7.71 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.70–7.61 (m, 2H), 7.63–7.56 (m, 2H), 7.54–7.47 (m, 2H), 7.41–7.33 (m, 2H), 7.34–7.24 (m, 1H), 7.10 (s, 1H), 6.66 (s, 2H), 5.07 (d, *J* = 10.7 Hz, 1H), 4.98 (t, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 10.7 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 2.90–2.84 (m, 1H), 2.70 (s, 3H), 2.20 (s, 3H), 1.91 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.9, 141.1, 139.4, 138.23, 138.20 (2C), 134.4, 134.2, 134.1, 132.9, 132.8, 132.7, 129.7, 129.6, 129.4, 129.2, 129.0 (2C), 128.9 (2C), 128.7, 128.6, 127.6 (2C), 127.5, 126.4, 125.8, 125.64, 124.58, 124.5, 124.0, 119.2, 69.1, 60.7, 21.1, 19.8, 19.0 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₈H₃₄O₂Na 545.2451; Found 545.2458

HPLC-Data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): *t_R* = 16.4 (minor), 19.2 (major)

(*R*)-(7-(Furan-2-yl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3aq**)



The title compound was isolated as a white solid (45 mg, 88%, 91% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

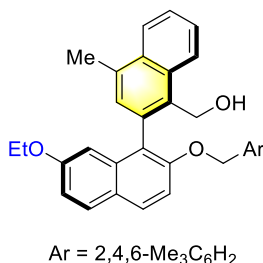
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.40–8.35 (m, 1H), 8.16–8.10 (m, 1H), 7.94–7.87 (m, 2H), 7.71 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.67–7.61 (m, 3H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 7.07 (s, 1H), 6.64 (s, 2H), 6.58 (d, *J* = 3.4 Hz, 1H), 6.41–6.38 (m, 1H), 5.03 (d, *J* = 10.6 Hz, 1H), 4.94 (t, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 10.6 Hz, 1H), 4.48 (d, *J* = 12.8 Hz, 1H), 2.84–2.76 (m, 1H), 2.69 (s, 3H), 2.17 (s, 3H), 1.88 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 154.1, 153.9, 142.5, 138.3, 138.2 (2C), 134.5, 134.3, 134.0, 132.9, 132.77, 132.75, 129.7, 129.6, 129.5, 129.2, 129.0 (2C), 128.9, 128.7, 128.6, 126.4, 125.8, 125.7, 124.5, 121.3, 120.3, 118.9, 111.8, 106.1, 69.0, 60.7, 21.1, 19.8, 19.0 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₆H₃₂O₃Na 535.2244; Found 535.2244

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 9.6 (major), 13.0 (minor)

(R)-(7-Ethoxy-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3ar**)



The title compound was isolated as a white solid (41 mg, 84%, 88% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.41–8.34 (m, 1H), 8.14–8.08 (m, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.72–7.58 (m, 2H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.12–7.06 (m, 2H), 6.66–6.62 (m, 3H), 5.03 (d, *J* = 10.7 Hz, 1H), 4.93 (t, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 10.6 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 3.86–3.73 (m, 2H), 2.83–2.77 (m, 1H), 2.69 (d, *J* = 1.0 Hz, 3H), 2.18 (s, 3H), 1.89 (s, 6H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm.

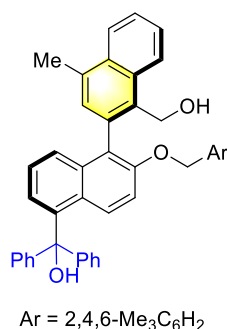
¹³C NMR (126 MHz, Chloroform-*d*) δ = 157.6, 154.1, 138.19 (2C), 138.17, 135.2, 134.4, 134.2, 133.2, 132.8 (2C), 129.7, 129.5, 129.3 (2C), 129.0 (2C), 127.0, 126.3,

125.9, 125.72, 125.68, 124.5, 117.3, 116.3, 105.6, 68.9, 63.5, 60.6, 21.1, 19.7, 19.0 (2C), 14.6 ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{34}H_{34}O_3Na$ 513.2400; Found 513.2407

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 9.4 (major), 11.5 (minor)

(R)-(1'-(Hydroxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-bina-phthalen]-5-yl)diphenylmethanol (**3as**)



The title compound was isolated as a white solid (44 mg, 70%, 91% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

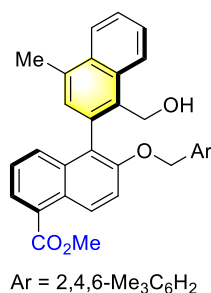
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.35–8.26 (m, 2H), 8.11–8.05 (m, 1H), 7.64–7.55 (m, 2H), 7.40–7.32 (m, 12H), 7.09 (dd, J = 8.6, 7.2 Hz, 1H), 7.04 (d, J = 1.1 Hz, 1H), 6.78 (dd, J = 7.3, 1.2 Hz, 1H), 6.63 (s, 2H), 4.99 (d, J = 10.5 Hz, 1H), 4.82–4.73 (m, 2H), 4.40 (d, J = 12.0 Hz, 1H), 3.58 (s, 1H), 2.67 (d, J = 1.0 Hz, 3H), 2.64–2.57 (m, 1H), 2.16 (s, 3H), 1.86 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 152.8, 147.3, 147.1, 142.5, 138.21, 138.17 (2C), 135.6, 134.3, 134.1, 133.3, 132.8, 132.6, 130.1, 129.8, 129.2, 129.0 (2C), 128.3 (2C), 128.20 (2C), 128.16, 128.1, 128.0 (2C), 127.9 (2C), 127.39, 127.37, 127.3, 127.1, 126.4, 125.8, 125.6, 124.9, 124.5, 117.6, 83.6, 68.4, 60.5, 21.1, 19.7, 19.0 (2C) ppm.

HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{45}H_{40}O_3Na$ 651.2870; Found 651.2853

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 60/40, flow rate = 0.5 mL/min): t_R = 10.4 (minor), 12.5 (major)

(R)-Methyl 1'-(hydroxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalene]-5-carboxylate (**3at**)



The title compound was isolated as a white solid (43 mg, 85%, 87% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

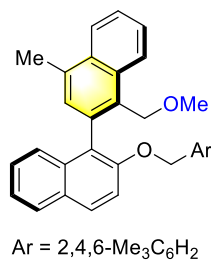
¹H NMR (400 MHz, Chloroform-*d*) δ = 9.06 (dd, *J* = 9.4, 0.8 Hz, 1H), 8.39–8.30 (m, 1H), 8.14–8.06 (m, 2H), 7.70 (d, *J* = 9.5 Hz, 1H), 7.67–7.58 (m, 2H), 7.56–7.52 (m, 1H), 7.33 (dd, *J* = 8.6, 7.2 Hz, 1H), 6.99 (d, *J* = 1.1 Hz, 1H), 6.65 (s, 2H), 5.11 (d, *J* = 10.6 Hz, 1H), 4.93–4.85 (m, 2H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.05 (s, 3H), 2.68 (d, *J* = 0.9 Hz, 3H), 2.62–2.54 (m, 1H), 2.18 (s, 3H), 1.92 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 168.3, 153.6, 138.3, 138.2 (2C), 134.6, 134.5, 134.2, 132.9, 132.7, 132.6, 131.2, 129.5, 129.2, 129.1 (2C), 128.8, 128.13, 128.08, 127.6, 127.4, 126.5, 125.9, 125.6, 125.3, 124.5, 119.9, 68.6, 60.5, 52.4, 21.1, 19.7, 19.1 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₄H₃₂O₄Na 527.2193; Found 527.2198

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t*_R = 12.2 (major), 14.8 (minor)

(R)-1'-(Methoxymethyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-1,2'-binaphthalene (**3au**)



The title compound was isolated as a white solid (30 mg, 65%, 86% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5).

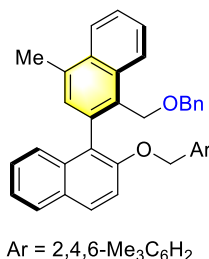
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.33–8.25 (m, 1H), 8.10–8.02 (m, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.61–7.54 (m, 2H), 7.41–7.28 (m, 3H), 7.08 (d, *J* = 1.1 Hz, 1H), 6.68 (s, 2H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.92 (d, *J* = 10.5 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 2.98 (s, 3H), 2.65 (d, *J* = 1.0 Hz, 3H), 2.19 (s, 3H), 2.00 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.9, 138.1 (2C), 137.9, 134.4, 134.3, 134.1, 133.0, 132.8, 131.0, 130.2, 129.9, 129.7, 129.5, 128.9 (2C), 127.9, 127.3, 126.5, 126.1, 126.03, 126.00, 125.6, 124.5, 124.3, 118.2, 69.7, 68.0, 57.8, 21.1, 19.6, 19.2 (2C) ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₃H₃₂O₂Na 483.2295; Found 483.2297

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 6.8 (major), 10.0 (minor)

(R)-1'-((Benzyloxy)methyl)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-1,2'-bina-phthalene (**3av**)



The title compound was isolated as a white solid (36 mg, 67%, 84% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.39–8.30 (m, 1H), 8.13–8.04 (m, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.92–7.89 (m, 1H), 7.64–7.55 (m, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.46–7.36 (m, 2H), 7.36–7.28 (m, 1H), 7.16–7.06 (m, 4H), 6.93–6.84 (m, 2H), 6.66 (s, 2H), 5.02 (d, *J* = 10.6 Hz, 1H), 4.92 (d, *J* = 10.6 Hz, 1H), 4.65 (d, *J* = 11.3 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 4.22–4.10 (m, 2H), 2.68 (d, *J* = 1.0 Hz, 3H), 2.19 (s, 3H), 1.97 (s, 6H) ppm.

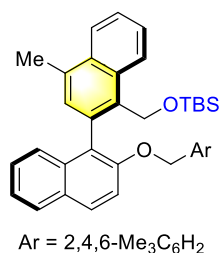
¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.8, 138.6, 138.1 (2C), 137.9, 134.42, 134.41, 134.2, 133.1, 132.8, 131.2, 130.2, 129.89, 129.86, 129.5, 128.9 (2C), 128.1

(2C), 127.9, 127.6 (2C), 127.4, 127.2, 126.5, 126.3, 126.1, 126.0, 125.6, 124.4, 124.3, 118.3, 72.1, 68.1, 67.5, 21.1, 19.6, 19.2 (2C) ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{36}O_2Na$ 559.2608; Found 559.2617

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 96/4, flow rate = 0.5 mL/min): t_R = 10.0 (major), 13.0 (minor)

(R)-tert-Butyldimethyl((4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methoxy)silane (**3aw**)



The title compound was isolated as a white solid (37 mg, 67%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5).

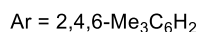
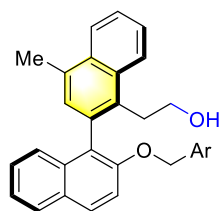
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.23–8.17 (m, 1H), 8.01–7.95 (m, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.52–7.45 (m, 3H), 7.31–7.23 (m, 2H), 7.23–7.15 (m, 1H), 7.01 (s, 1H), 6.57 (s, 2H), 4.93 (d, J = 10.7 Hz, 1H), 4.82 (d, J = 10.7 Hz, 1H), 4.60 (d, J = 11.1 Hz, 1H), 4.37 (d, J = 11.2 Hz, 1H), 2.57 (s, 3H), 2.10 (s, 3H), 1.85 (s, 90 6H), 0.57 (s, 9H), –0.47 (s, 3H), –0.59 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.7, 138.2 (2C), 137.9, 134.2, 133.9, 133.5, 133.2, 133.0, 132.8, 130.4, 129.9, 129.8, 129.3, 128.9 (2C), 128.1, 127.7, 126.7, 126.4, 126.2, 125.7, 125.4, 124.4, 124.3, 118.9, 68.5, 60.3, 25.9 (3C), 21.1, 19.6, 19.2 (2C), 18.3, –6.0, –6.1 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{44}SiO_2Na$ 583.3003; Found 583.3006

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min): t_R = 10.8 (major), 11.4 (minor)

(R)-2-(4'-Methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)ethan-1-ol
(**3ax**)



The title compound was isolated as a white solid (31 mg, 67%, 86% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

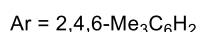
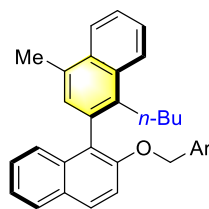
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.16–8.07 (m, 2H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.63–7.56 (m, 3H), 7.39–7.34 (m, 1H), 7.31–7.25 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.02 (s, 1H), 6.73 (s, 2H), 5.17 (d, *J* = 10.5 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 3.83–3.75 (m, 1H), 3.69–3.61 (m, 1H), 3.28–3.20 (m, 1H), 2.88–2.78 (m, 1H), 2.64 (s, 3H), 2.21 (s, 3H), 2.12 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.5, 138.2 (2C), 138.1, 134.1, 133.6, 132.9, 132.8, 132.6, 132.0, 130.1, 129.8, 129.7, 129.5, 129.0 (2C), 128.1, 127.4, 126.6, 125.8, 125.5, 125.4, 125.00, 124.98, 124.2, 117.0, 67.4, 63.0, 33.3, 21.1, 19.5, 19.3 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₃H₃₃O₂ 461.2475; Found 461.2482

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 8.5 (major), 10.5 (minor)

(R)-1'-Butyl-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-1,2'-binaphthalene (**3ay**)



The title compound was isolated as a white solid (16 mg, 34%, 78% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.12–8.01 (m, 2H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.61–7.50 (m, 3H), 7.39–7.28 (m, 1H), 7.26–7.24 (m, 2H),

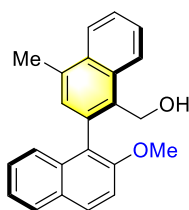
7.01 (s, 1H), 6.68 (s, 2H), 5.00 (d, $J = 10.5$ Hz, 1H), 4.92 (d, $J = 10.4$ Hz, 1H), 2.79–2.62 (m, 2H), 2.61 (s, 3H), 2.18 (s, 3H), 2.01 (s, 6H), 1.13–0.82 (m, 4H), 0.56 (t, $J = 7.3$ Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 153.7, 138.2$ (2C), 137.8, 136.6, 134.0, 132.8, 132.6, 132.5, 131.5, 130.4, 130.3, 129.8, 129.1, 128.9 (2C), 128.2, 127.9, 126.2, 126.0, 125.4, 125.3, 125.0, 124.8, 124.1, 118.1, 67.8, 32.7, 29.8, 23.1, 21.1, 19.5, 19.3 (2C), 13.7 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{36}\text{ONa}$ 495.2658; Found 495.2672

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.5 mL/min): $t_R = 8.0$ (major), 8.3 (minor)

(R)-(2-Methoxy-4'-methyl-[1,2'-binaphthalen]-1'-yl)methanol (**3az**)



The title compound was isolated as a white solid (20 mg, 60%, 54% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

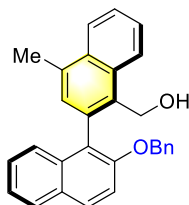
^1H NMR (400 MHz, Chloroform-*d*) $\delta = 8.43$ (dd, $J = 7.7, 1.9$ Hz, 1H), 8.13 (dd, $J = 7.8, 1.9$ Hz, 1H), 7.96 (d, $J = 9.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.70–7.59 (m, 2H), 7.43 (d, $J = 9.1$ Hz, 1H), 7.41–7.29 (m, 3H), 7.19 (s, 1H), 4.95 (dd, $J = 11.9, 8.8$ Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 3.83 (s, 3H), 2.74 (s, 3H), 2.32–2.44 (m, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 153.9, 134.9, 133.9, 133.8, 133.3, 132.9, 132.6, 129.7$ (2C), 129.5, 128.1, 126.8, 126.6, 125.9, 125.6, 125.5, 124.8, 124.6, 124.1, 113.9, 60.7, 57.1, 19.9 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{Na}$ 351.1356; Found 351.1349

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R = 11.2$ (major), 14.5 (minor)

(R)-(2-(Benzyloxy)-4'-methyl-[1,2'-binaphthalen]-1'-yl)methanol (**3aaa**)



The title compound was isolated as a white solid (27 mg, 66%, 82% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

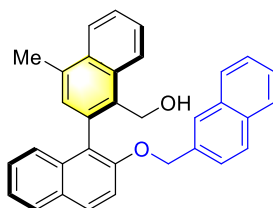
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.46–8.39 (m, 1H), 8.18–8.11 (m, 1H), 7.93–7.85 (m, 2H), 7.70–7.60 (m, 2H), 7.47–7.31 (m, 4H), 7.23–7.08 (m, 4H), 7.04–7.00 (m, 2H), 5.12–5.00 (m, 2H), 4.94 (dd, *J* = 12.0, 9.6 Hz, 1H), 4.59 (dd, *J* = 12.1, 2.8 Hz, 1H), 2.74 (s, 3H), 2.52–2.46 (m, 1H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 153.0, 136.5, 134.6, 134.0, 133.9, 133.2, 132.9, 132.7, 130.0, 129.6, 129.5, 128.5 (2C), 128.11, 128.08 (2C), 127.6 (2C), 126.7, 126.5, 125.9, 125.8, 125.6, 124.7, 124.5, 117.0, 72.9, 60.7, 19.8 ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₉H₂₄O₂Na 427.1669; Found 427.1684

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 13.5 (major), 40.4 (minor)

(R)-(4'-Methyl-2-(naphthalen-2-ylmethoxy)-[1,2'-binaphthalen]-1'-yl)methanol (**3aab**)



The title compound was isolated as a white solid (33 mg, 72%, 83% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

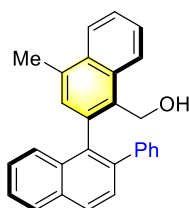
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.49–8.40 (m, 1H), 8.20–8.12 (m, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.72–7.63 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.46–7.31 (m, 7H), 7.13–7.06 (m, 2H), 5.26 (d, *J* = 12.3 Hz, 1H), 5.17 (d, *J* = 12.3 Hz, 1H), 4.97 (dd, *J* = 12.0, 9.2 Hz, 1H), 4.62 (dd, *J* = 11.9, 1.7 Hz, 1H), 2.67 (s, 3H), 2.64–2.58 (m, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 153.0, 134.7, 134.1, 134.0, 133.9, 133.3, 133.2, 133.0, 132.9, 132.8, 130.0, 129.6 (2C), 128.2, 128.1, 128.0, 127.7, 126.9, 126.7, 126.6, 126.5, 126.2, 126.1, 125.93, 125.88, 125.7, 125.2, 124.7, 124.5, 117.1, 73.1, 60.8, 19.7 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{26}\text{O}_2\text{Na}$ 477.1825; Found 477.1822

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 17.5 (major), 38.0 (minor)

(R)-(4'-Methyl-2-phenyl-[1,2'-binaphthalen]-1'-yl)methanol (**3aac**)



The title compound was isolated as a white solid (12 mg, 32%, 76% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

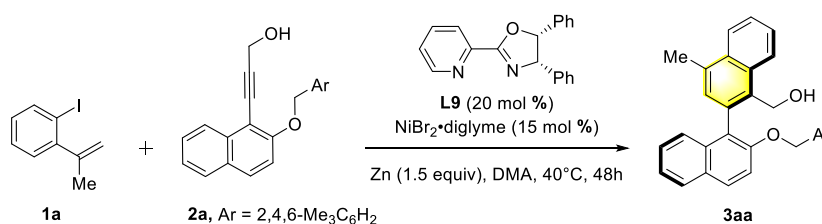
^1H NMR (500 MHz, Chloroform-*d*) δ = 8.25–8.19 (m, 1H), 8.12–8.02 (m, 1H), 8.01–7.95 (m, 1H), 7.97–7.91 (m, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.60–7.51 (m, 2H), 7.53–7.45 (m, 1H), 7.34–7.32 (m, 1H), 7.29 (s, 1H), 7.28–7.23 (m, 3H), 7.19–7.07 (m, 3H), 4.72–4.62 (m, 1H), 4.50–4.44 (m, 1H), 2.71 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 141.6, 138.3, 136.5, 135.8, 134.3, 133.3, 132.9, 132.8, 132.7, 132.5, 130.7, 130.0 (2C), 128.21 (3C), 128.15, 128.1, 127.04, 126.96, 126.6, 126.4, 126.1, 125.9, 125.8, 124.7, 60.4, 19.7 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{22}\text{ONa}$ 397.1563; Found 397.1573

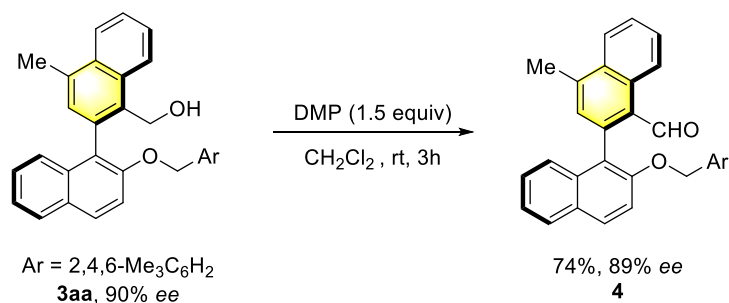
HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 11.3 (major), 13.6 (minor)

IV. Procedure for Synthesis of 3aa on a 2-mmol Scale



NiBr₂•diglyme (105.8 mg, 0.3 mmol, 15 mol %), (4*S*,5*R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (120 mg, 0.4 mmol, 20 mol %), Zn (195 mg, 3 mmol, 1.5 equiv), 1-iodo-2-(prop-1-en-2-yl)benzene (**1a**) (488 mg, 2 mmol, 1.0 equiv), and the alkyne **2a** (1.32 g, 4 mmol, 2.0 equiv) were placed in a round-bottomed flask (25 mL) equipped with a stir bar. Subsequently, the flask was evacuated and filled with nitrogen (three cycles). To these solids, 10 mL anhydrous DMA was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 48 hours, before it was quenched by addition of water (20 mL) and saturated aqueous solution of NH₄Cl (20 mL). The aqueous phase was extracted with ethyl acetate (3×20 mL), and the combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was then purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give (*R*)- (2-((2,6-dimethylbenzyl)oxy)-4'-methyl-[1,2'-binaphthalen]-1'-yl)methanol (**3aa**) (734 mg, 85% yield, 90% *ee*) as a white solid.

V. Derivatizations of the Axially Chiral Binaphthyl **3aa**.



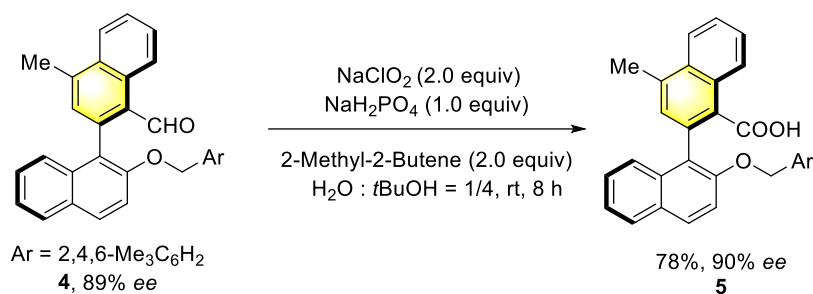
To a stirred suspension of Dess-Martin periodinane (127 mg, 0.3 mmol, 1.5 equiv) in DCM (1.0 mL) was added **3aa** (86 mg, 0.2 mmol, 1.0 equiv) in DCM (0.5 mL). After stirring for 3 h at room temperature, the mixture was quenched with brine. The organic layer was separated and the aqueous layer was extracted with DCM (3×4 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give (*R*)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalene]-1'-carbaldehyde (**4**) (65 mg, 74% yield, 89% *ee*) as a white solid.

¹H NMR (400 MHz, Chloroform-*d*) δ = 9.82 (s, 1H), 9.41 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.75–7.55 (m, 3H), 7.43–7.35 (m, 1H), 7.36–7.28 (m, 1H), 7.23–7.19 (m, 1H), 7.14 (s, 1H), 6.63 (s, 2H), 5.12–5.04 (m, 2H), 2.71 (s, 3H), 2.18 (s, 3H), 2.00 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 194.6, 154.0, 144.0, 141.6, 138.13, 138.06 (2C), 134.2, 132.6, 130.9, 130.8, 130.3, 129.8, 129.5, 129.0 (2C), 128.7, 128.4, 128.1, 127.1, 126.7, 126.6, 125.6, 124.5, 124.3, 124.2, 117.6, 67.9, 21.1, 20.4, 19.4 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₂H₂₉O₂ 445.2162; Found 445.2169

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): *t_R* = 11.4 (major), 13.3 (minor)



To a solution of compound **4** (44.4 mg, 0.1 mmol, 1.0 equiv), NaClO₂ (18 mg, 0.2 mmol, 2.0 equiv), and NaH₂PO₄ (12 mg, 0.1 mmol, 1.0 equiv) in H₂O/*t*BuOH (0.25 mL/1.0 mL) was added 2-methyl-2-butene (14.0 mg, 0.2 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 8 hours. Subsequently, hydrochloric acid (1.0 M, 1.0 mL) was added into the reaction solution and the mixture continued to stir for 5 minutes, before it was quenched by addition of water (4 mL). The aqueous phase was extracted with ethyl acetate (3×4 mL), and the combined organic phases were dried over Na₂SO₄, filtered and concentrated in vacuo. The crude material was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to afford (*R*)-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalene]-1'-carboxylic acid (**5**) (36 mg, 78% yield, 90% ee) as a white solid.

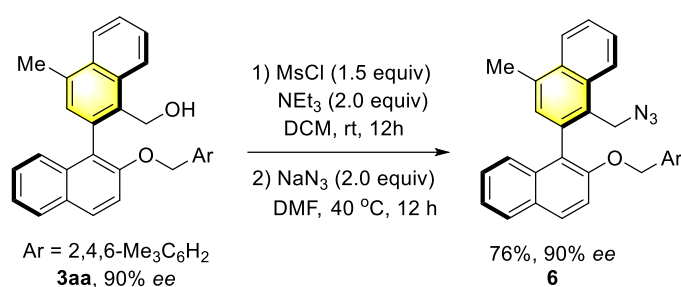
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.16–8.10 (m, 1H), 8.12–8.06 (m, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.67–7.57 (m, 2H), 7.52 (d, *J* = 9.0 Hz,

1H), 7.42–7.35 (m, 1H), 7.35–7.27 (m, 2H), 7.05 (s, 1H), 6.67 (s, 2H), 5.07–4.98 (m, 2H), 2.67 (s, 3H), 2.20 (s, 3H), 1.96 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 171.3, 153.0, 138.3 (2C), 138.1, 137.0, 133.6, 132.7, 132.0, 130.2, 130.08, 130.05, 129.9, 129.74, 129.67, 129.0 (2C), 127.9, 127.1, 126.9, 126.7, 126.5, 126.2, 125.8, 124.6, 124.3, 118.3, 68.6, 21.1, 19.8, 19.2 (2C) ppm.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₂H₂₉O₂ 461.2111; Found 461.2120

HPLC-Data: (Chiralpak IA column, λ = 225 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): *t_R* = 6.3 (major), 15.6 (minor)



A solution of the **3aa** (89.2 mg, 0.2 mmol, 1.0 equiv) in DCM (1 mL) was cooled in an ice water bath and treated with Et₃N (40.5 mg, 56 μ L, 0.4 mmol, 2.0 equiv) and mesyl chloride (34.4 mg, 23 μ L, 0.3 mmol, 1.5 equiv). After the resulting solution was stirred at room temperature for 12 hours, the reaction was diluted with ethyl acetate and washed with saturated aqueous NaHCO₃ and brine, successively. The organic phase was dried over anhydrous MgSO₄, filtered, and concentrated. Next, NaN₃ (26.0 mg, 0.4 mmol, 2 equiv) was added to the residue dissolved in DMF (1 mL) and the resulting mixture was stirred at 40°C in an oil bath for 12 hours. Next, the mixture was diluted with ethyl acetate, and the organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated. The residue was purified through column chromatography (petroleum ether/ethyl acetate 20:1) on silica gel, to afford (*R*)-1'-*(azidomethyl)*-4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-1,2'-binaphthalene (**6**) (71.6 mg, 76%, 90% *ee*) as a white solid.

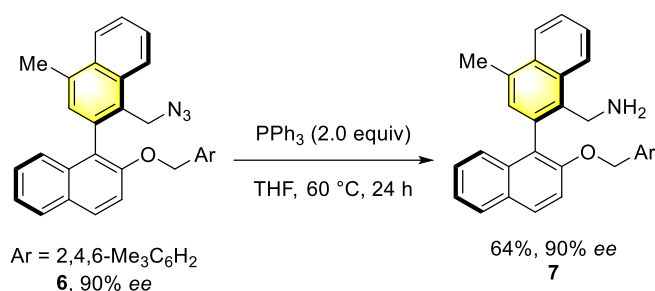
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.17–8.07 (m, 2H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.66–7.57 (m, 3H), 7.44–7.37 (m, 1H), 7.38–7.31 (m, 1H),

7.30–7.24 (m, 1H), 7.08 (s, 1H), 6.69 (s, 2H), 5.09 (d, $J = 10.8$ Hz, 1H), 4.98 (d, $J = 10.8$ Hz, 1H), 4.45–4.35 (m, 2H), 2.68 (s, 3H), 2.21 (s, 3H), 2.02 (s, 6H) ppm.

^{13}C NMR (126 MHz, Chloroform- d) $\delta = 153.8, 138.2$ (2C), 137.9, 135.0, 134.9, 133.9, 132.7, 132.3, 130.1, 129.9 (2C), 129.7, 128.9 (2C), 128.8, 128.0, 126.7, 126.5, 126.1, 125.9, 125.7, 125.0, 124.9, 124.4, 117.8, 67.8, 49.6, 21.1, 19.7, 19.3 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{29}\text{N}_3\text{ONa}$ 494.2203; Found 494.2206

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 7.3$ (major), 8.1 (minor)



A mixture of the azide **6** (47.1 mg, 0.1 mmol, 1.0 equiv) and PPh_3 (52.5 mg, 0.2 mmol, 2.0 equiv) in THF (1 mL) was stirred at 60 °C in an oil bath for 24 hours. Next, the mixture was diluted with EtOAc, washed with H_2O and brine, dried over MgSO_4 , filtered and concentrated. The residue was purified through column chromatography (ethyl acetate) over silica gel, to afford (*R*)-(*4'*-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methanamine (**7**) (28.5 mg, 64%, 90% ee) as a white solid.

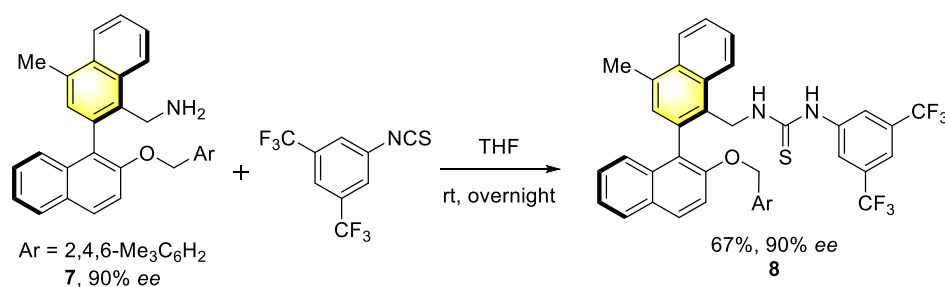
^1H NMR (400 MHz, Chloroform- d) $\delta = 8.23\text{--}8.14$ (m, 1H), 8.15–8.06 (m, 1H), 7.96 (d, $J = 8.9$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.64–7.55 (m, 3H), 7.42–7.34 (m, 1H), 7.33–7.18 (m, 2H), 7.02 (s, 1H), 6.66 (s, 2H), 5.07 (d, $J = 10.5$ Hz, 1H), 4.92 (d, $J = 10.5$ Hz, 1H), 4.00 (d, $J = 13.7$ Hz, 1H), 3.71 (d, $J = 13.7$ Hz, 1H), 2.65 (s, 3H), 2.17 (s, 3H), 1.98 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 153.7, 138.2$ (2C), 138.0, 134.0, 133.2, 133.0, 132.7, 131.9, 130.0, 129.93, 129.89, 129.5, 129.0 (3C), 128.1, 127.7, 126.5, 126.3, 125.8, 125.5, 125.0, 124.6, 124.4, 118.3, 68.2, 41.1, 21.1, 19.6, 19.2 (2C) ppm.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{32}\text{NO}$ 446.2478; Found 446.2486

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 65/35, flow

rate = 0.5 mL/min): t_R = 7.8 (major), 10.1 (minor)



To a well stirred solution of compound **7** (44.5 mg, 0.1 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (1 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate (40.7 mg, 0.15 mmol, 1.5 equiv) under N₂. The reaction mixture was stirred at room temperature overnight. After evaporation of the solvent, the residue was purified through column chromatography (petroleum ether/ethyl acetate = 5:1) on silica gel, to afford (*R*)-1-(3,5-bis(trifluoromethyl)phenyl)-3-((4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methyl)thiourea (**8**) (47.9 mg, 67%, 90% ee) as a white solid.

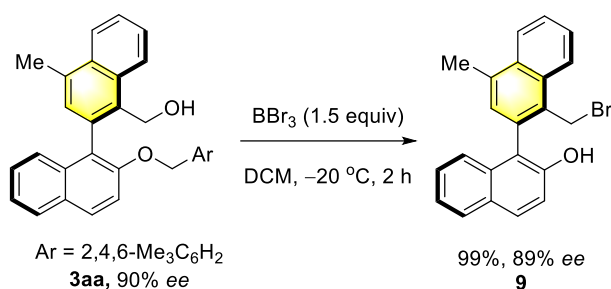
¹H NMR (400 MHz, Chloroform-*d*) δ = 8.33–8.24 (m, 1H), 8.18–8.09 (m, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.71 (s, 2H), 7.70–7.61 (m, 2H), 7.63–7.56 (m, 2H), 7.50–7.40 (m, 1H), 7.38–7.35 (m, 2H), 7.19 (s, 1H), 6.92 (d, J = 8.6 Hz, 1H), 6.67 (s, 2H), 5.94–5.80 (m, 1H), 5.70 (s, 1H), 5.17 (d, J = 9.8 Hz, 1H), 4.69 (d, J = 9.9 Hz, 1H), 4.05 (d, J = 13.9 Hz, 1H), 2.74 (s, 3H), 2.03 (s, 3H), 1.85 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 179.5, 152.3, 140.2, 139.2, 138.5 (2C), 134.9, 133.9, 133.8, 132.8, 132.5, 132.2, 131.9, 131.5, 130.8, 130.2, 129.63, 129.60, 129.5 (2C), 128.2, 127.9, 127.2, 127.0, 126.28, 126.25, 125.6, 125.1, 124.7, 124.6–123.9 (m, 2C), 123.2 (q, J = 273.7 Hz, 2C), 118.4–118.1 (m, 2C), 68.4, 44.6, 20.8, 19.7, 18.6 (2C) ppm.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ = –62.81 (s, 6F) ppm.

HRMS (ESI) m/z : [M+Na]⁺ Calcd for C₄₁H₃₄F₆N₂SONa 739.2188; Found 739.2199

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): t_R = 12.9 (minor), 15.1 (major)



To a stirred solution of compound **3aa** (43 mg, 0.1 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (0.1 M, 1.0 mL) was added BBr₃ 1.0 mol/L (17%) in DCM (150 μL, 0.15 mmol, 1.5 equiv) at −20 °C. After stirring for 2 hours, the mixture was quenched with brine (4 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×4 mL). The combined organic layer was dried over anhydrous Na₂SO₄,

filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give (*R*)- 1'-(*bromomethyl*)-4'-methyl-[1,2'-binaphthalen]-2-ol (**9**) (37 mg, 99%, 89% ee) as a white solid.

¹H NMR (500 MHz, Chloroform-*d*) δ = 8.30 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 15.7, 8.5 Hz, 2H), 7.78–7.66 (m, 2H), 7.39–7.28 (m, 3H), 7.21 (s, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 4.93 (s, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.62 (d, *J* = 10.4 Hz, 1H), 2.74 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 150.8, 137.7, 133.5, 133.2, 132.4, 131.9, 131.7, 130.3, 129.8, 129.1, 128.3, 127.1, 126.91, 126.88, 125.2, 125.0, 124.8, 123.7, 119.3, 118.0, 28.8, 19.8 ppm.

HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₂H₁₇BrONa 399.0355; Found 399.0373

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 9.2 (major), 11.7 (minor)



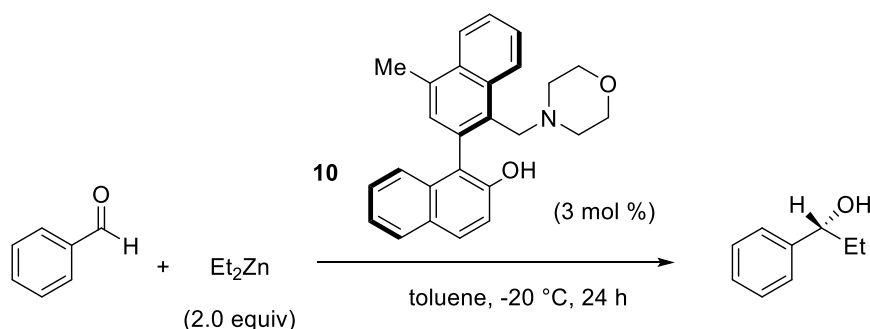
To a stirred suspension of K_2CO_3 (27 mg, 0.2 mmol, 2.0 equiv) and morpholine (13 mg, 0.15 mmol, 1.5 equiv) in DMF (0.2 M, 0.5 mL) was added the aryl bromide **9** in 0.5 mL DMF. After stirring 8 hours at room temperature, the mixture was quenched with brine (4 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×4 mL). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give (*R*)-4-((4'-methyl-2-((2,4,6-trimethylbenzyl)oxy)-[1,2'-binaphthalen]-1'-yl)methyl)morpholine (**10**) (24 mg, 48%, 89% *ee*) as a white solid.

^1H NMR (400 MHz, Chloroform-*d*) δ = 8.32–8.23 (m, 1H), 8.17–8.09 (m, 1H), 7.86–7.79 (m, 2H), 7.67–7.56 (m, 2H), 7.36 (d, J = 8.8 Hz, 1H), 7.35–7.26 (m, 1H), 7.25 (s, 1H), 7.25–7.19 (m, 1H), 7.03 (d, J = 8.1 Hz, 1H), 4.19 (d, J = 12.8 Hz, 1H), 3.82–3.73 (m, 2H), 3.68–3.58 (m, 3H), 2.69 (s, 3H), 2.69–2.60 (m, 2H), 2.54–2.44 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 153.1, 136.6, 134.9, 134.1, 133.3, 132.5, 131.5, 130.0, 129.6, 129.5, 128.0, 126.3, 126.1, 125.7, 125.5, 125.1, 124.9, 124.4, 123.3, 122.0, 66.3 (2C), 56.1 (2C), 53.4, 19.8 ppm.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_2$ 384.1958; Found 384.1965

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 9.3 (major), 10.5 (minor)



To a solution of chiral ligand **10** (2.3 mg, 0.006 mmol, 3 mol%) in toluene (1 mL) at $-20\text{ }^\circ\text{C}$ was added dropwise a solution of diethylzinc (0.2 mL, 2.0 M solution in toluene, 0.4 mmol, 2.0 equiv). After the resulting solution was stirred for 15 min, benzaldehyde (21.2 mg, 0.2 mmol, 1.0 equiv) was added in one portion. After stirring for 24h at $-$

20 °C, the reaction was quenched by the addition of 1M HCl solution (5 mL), and the mixture was extracted with ethyl acetate (4 mL × 3). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexanes (1:7) to give the product (*R*)-1-phenyl-1-propanol (**11**) (21 mg, 77%, 95% *ee*).

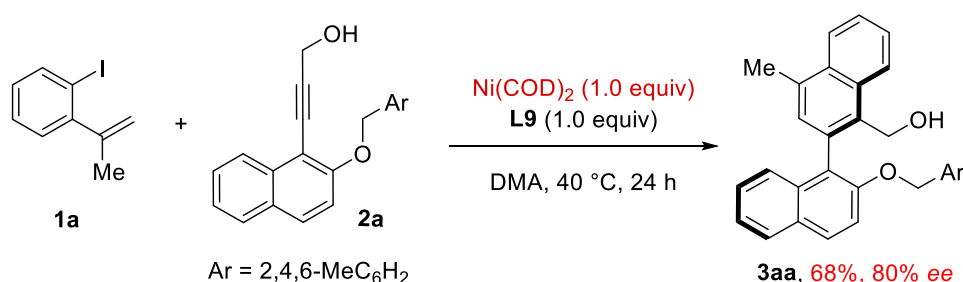
¹H NMR (400 MHz, Chloroform-*d*) δ = 7.39 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 4.60 (t, *J* = 6.6 Hz, 1H), 1.91 – 1.68 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 144.7, 128.5 (2C), 127.6, 126.1 (2C), 76.2, 32.0, 10.3 ppm.

HPLC-Data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R = 16.1 (major), 17.7 (minor)

VI. Mechanistic Studies

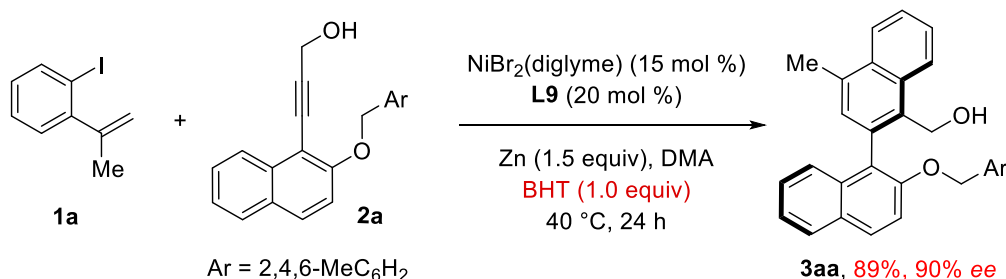
Stoichiometric Reaction Using Ni(cod)₂



Ni(COD)₂ (27.5 mg, 0.1 mmol, 1.0 equiv), (*4S,5R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (30.0 mg, 0.02 mmol, 1.0 equiv), the olefin-tethered aryl iodide **1a** (24.4 mg, 0.1 mmol, 1.0 equiv), and the alkyne **2a** (66.0 mg, 0.2 mmol, 2.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, 0.5 mL anhydrous DMA was added subsequently under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 hours, before it was quenched by successive addition of water (3 mL) and saturated aqueous solution of NH₄Cl (3 mL). The aqueous phase was extracted with ethyl acetate (3 × 4 mL), and the combined organic phase was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified

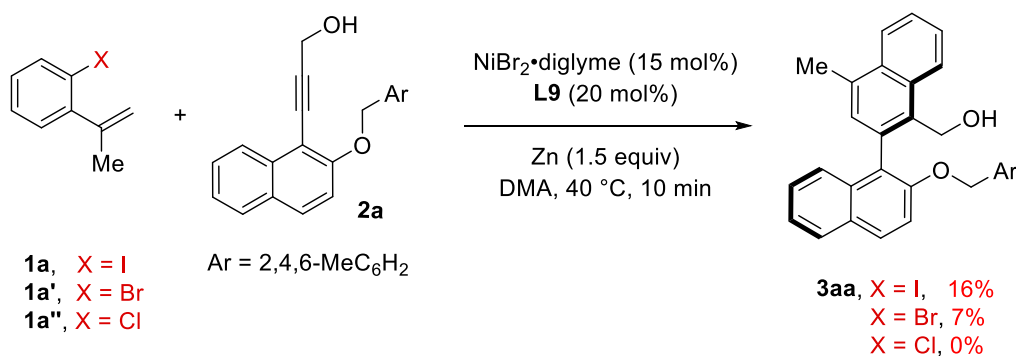
through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **3aa** (31.0 mg, 69%, 80% *ee*).

Radical Trapping Reaction Using BHT



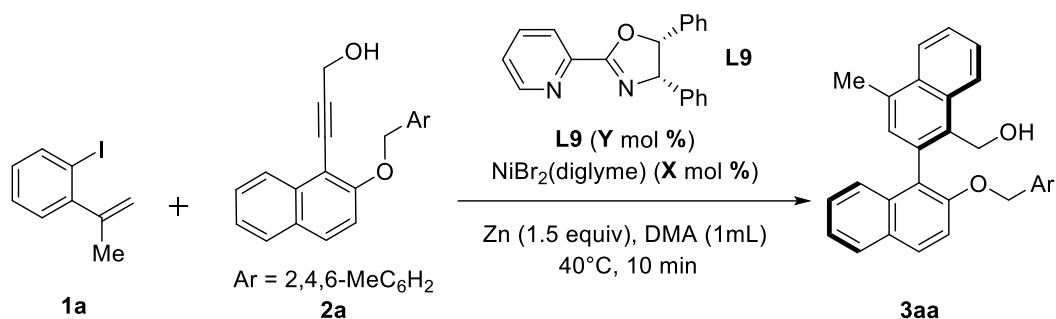
NiBr₂(diglyme) (5.3 mg, 0.015 mmol, 15 mol%), (4*S*,5*R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (6.0 mg, 0.02 mmol, 20 mol%), zinc (9.7 mg, 0.15 mmol, 1.5 equiv), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 22.0 mg, 0.1 mmol, 1.0 equiv), the olefin-tethered aryl iodide **1a** (24.4 mg, 0.1 mmol, 1.0 equiv), and the alkyne **2a** (66.0 mg, 0.2 mmol, 2.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, 0.5 mL anhydrous DMA was added subsequently under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 hours before it was quenched by successive addition of water (3 mL) and saturated aqueous solution of NH₄Cl (3 mL). The aqueous phase was extracted with ethyl acetate (3 × 4 mL), and the combined organic phase was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **3aa** (39.4 mg, 89%, 90% *ee*).

Comparison of Initial Rates for Various Olefin-Tethered Aryl Halides



NiBr₂(diglyme) (5.3 mg, 0.015 mmol, 15 mol%), (4*S*,5*R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (6.0 mg, 0.02 mmol, 20 mol%), zinc (9.7 mg, 0.15 mmol, 1.5 equiv), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 22.0 mg, 0.1 mmol, 1.0 equiv), the olefin-tethered aryl halides **1a**, **1a'**, or **1a''** (0.1 mmol, 1.0 equiv), and the alkyne **2a** (66.0 mg, 0.2 mmol, 2.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, 0.5 mL anhydrous DMA was added subsequently under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 10 min before it was quenched by successive addition of water (3 mL) and saturated aqueous solution of NH₄Cl (3 mL). The aqueous phase was extracted with ethyl acetate (3 × 4 mL), and the combined organic phase was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **3aa**.

Kinetic Studies



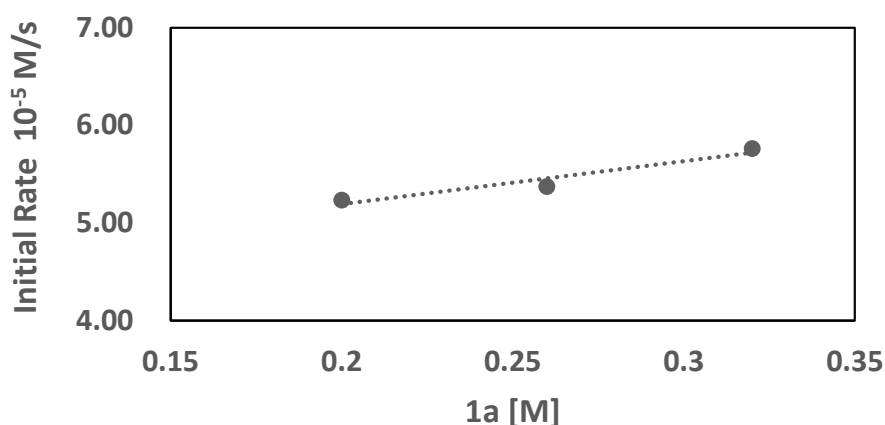
NiBr₂(diglyme), (4*S*,5*R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**), Zn, 1-iodo-2-(prop-1-en-2-yl)benzene (**1a**) and the alkyne (**2a**) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, 1.0 mL anhydrous DMA was added under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 10 minutes before it was quenched by addition of water (1 mL) and saturated aqueous solution of NH₄Cl (1 mL). The aqueous phase was extracted with ethyl acetate (3×5 mL), and the combined organic phases were dried over Na₂SO₄, filtered, and concentrated in vacuo.

The crude material was then purified through column chromatography on silica gel. The reaction mixture was analyzed by the molar concentration of **3aa**. The initial rates were calculated and plotted against the reactant or catalyst concentration to determine the reaction orders.

Determination of the Reaction Order in the Alkene (**1a**)

The reaction was performed with the alkyne **2a** (132 mg, 0.4 mmol, 1.0 equiv), NiBr₂•diglyme (10.6 mg, 0.03 mmol, 7.5 mol %), the ligand (*4S,5R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (12.0 mg, 0.04 mmol, 10 mol %), and Zn (19.5 mg, 0.3 mmol, 0.75 equiv) in DMA (1.0 mL) in the presence of 0.20 M, 0.26 M, and 0.32 M *1-Iodo-2-(prop-1-en-2-yl)benzene* (**1a**). The initial rates at various [**1a**] are similar, showing the reaction exhibits zero-order rate dependence on the concentration of **1a**.

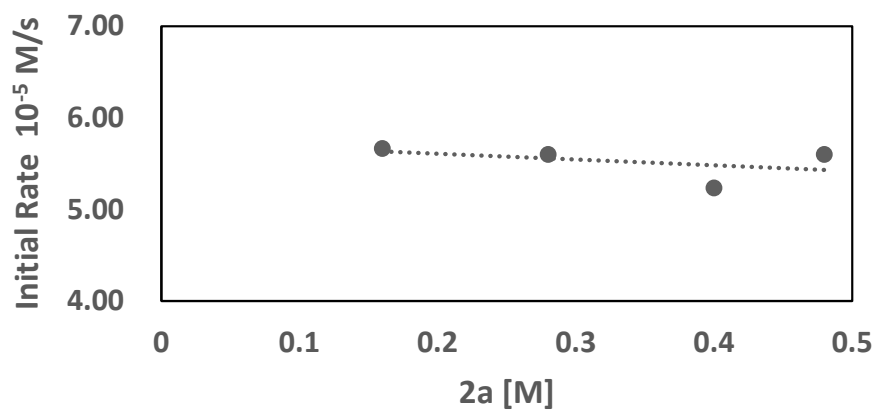
[1a] (M)	Conversion of 1a (%)	[3aa] (10 ⁻² M)	Initial Rate (10 ⁻⁵ M/s)
0.20	15.7	3.14	5.23
0.26	12.4	3.22	5.36
0.32	10.8	3.46	5.78



Determination of the Reaction Order in Alkyne **2a**

The reaction was performed with *1-iodo-2-(prop-1-en-2-yl)benzene* (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), NiBr₂•diglyme (10.6 mg, 0.02 mmol, 15 mol %), the ligand (*4S,5R*)-*4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole* (**L9**) (12.0 mg, 0.04 mmol, 20 mol %), and Zn (19.5 mg, 0.3 mmol, 1.5 equiv) in DMA (1.0 mL) in the presence of 0.16 M, 0.28 M, 0.40 M and 0.48 M the alkyne **2a**. The initial rates at various [**2a**] are similar, showing the reaction exhibits zero-order rate dependence on the concentration of **2a**.

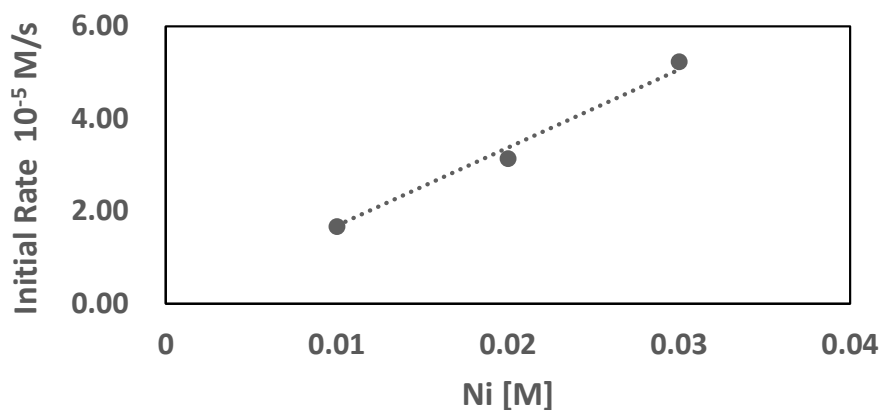
[2a] (M)	Conversion of 1a (%)	[3aa] (10 ⁻² M)	Initial Rate (10 ⁻⁵ M/s)
0.16	17.0	3.43	5.72
0.28	16.8	3.36	5.60
0.40	15.7	3.14	5.23
0.48	16.8	3.36	5.60



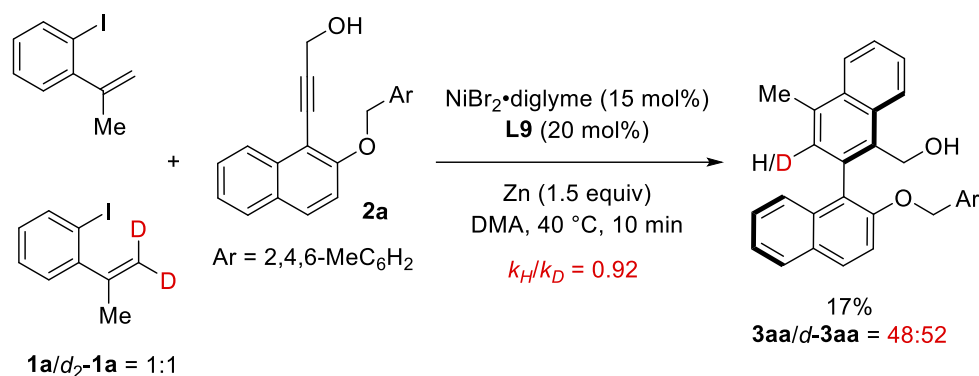
Determination of the Reaction Order in Ni-Catalyst

The reaction was performed with *1-iodo-2-(prop-1-en-2-yl)benzene* **1a** (48.8 mg, 0.2 mmol, 1.0 equiv), the alkyne **2a** (132 mg, 0.4 mmol, 2.0 equiv), the ligand (*4S,5R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (12.0 mg, 0.04 mmol, 20 mol %), and Zn (19.5 mg, 0.3 mmol, 1.5 equiv) in DMA (1.0 mL) in the presence of 0.01 M, 0.02 M and 0.03 M NiBr₂•diglyme. The relationship between the initial rates and [Ni] is linear, showing the reaction exhibits first-order rate dependence on the concentration of NiBr₂•diglyme.

[Ni] (M)	Conversion of 1a (%)	[3aa] (10 ⁻² M)	Initial Rate (10 ⁻⁵ M/s)
0.01	5.0	1.01	1.73
0.02	9.4	1.88	3.13
0.03	15.7	3.14	5.23



Competition Reaction between **1a** and Its Dideuterated Analog **d₂-1a**



$\text{NiBr}_2 \cdot \text{diglyme}$ (10.6 mg, 0.02 mmol, 15 mol %), (4*S*,5*R*)-4,5-diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (**L9**) (12.0 mg, 0.04 mmol, 20 mol %), the mixture of olefins (**1a/d₂-1a** = 1:1) (48.8 mg, 0.2 mmol, 1.0 equiv), and the alkyne **2a** (132 mg, 0.4 mmol, 2.0 equiv) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To this mixture, 1.0 mL anhydrous DMA was added subsequently under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 10 minutes, before it was quenched by successive addition of water (3 mL) and saturated aqueous solution of NH_4Cl (3 mL). The aqueous phase was extracted with ethyl acetate (3×4 mL), and the combined organic phases were dried over Na_2SO_4 , filtered, and concentrated in vacuo. The crude material was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the products **3aa/d-3aa** = 48:52^a (15 mg, 17%).

^a For the NMR spectra, see Page S154 (for **3aa**), S260 (for *d*-**3aa**), and S262 (for the mixture of **3aa** and *d*-**3aa**).

Characterization Data of *d*-**3aa** (D% > 98%^a)

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.40–8.31 (m, 1H), 8.14–8.07 (m, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.66–7.59 (m, 2H), 7.57 (d, J = 8.9 Hz, 1H), 7.47–7.39 (m, 2H), 7.39–7.31 (m, 1H), 6.64 (s, 2H), 5.04 (d, J = 10.6 Hz, 1H), 4.96–4.87 (m, 1H), 4.85 (d, J = 10.6 Hz, 1H), 4.46 (d, J = 12.1 Hz, 1H), 2.86–2.70 (m, 1H), 2.68 (s, 3H), 2.18 (s, 3H), 1.89 (s, 6H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 153.5, 138.22, 138.21 (2C), 134.3, 134.1, 133.9, 132.9, 132.8, 132.7, 130.5, 129.6 (2C), 129.3, 129.0 (2C), 128.2, 128.1, 126.6, 126.4, 126.1, 125.8, 125.6, 124.7, 124.5, 119.1, 69.0, 60.6, 21.1, 19.7, 19.1 (2C) ppm.

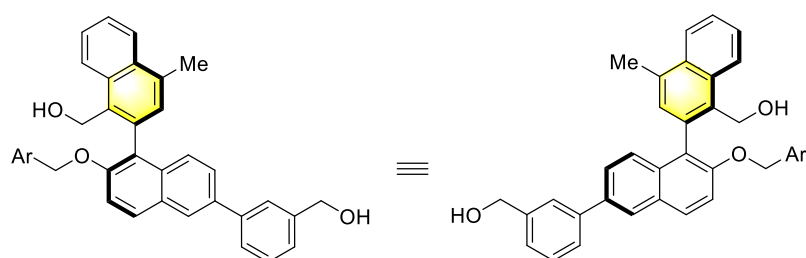
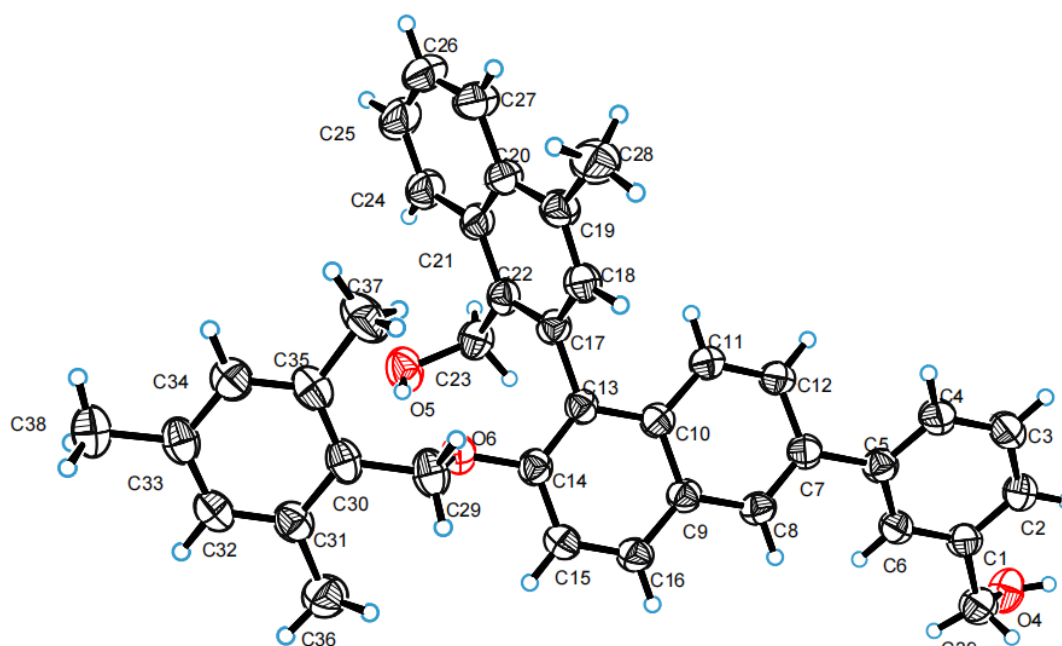
HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{29}\text{DO}_2\text{Na}$ 470.2201; Found 470.2210

HPLC-Data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): t_R = 8.4 (major), 12.1 (minor)

^a Determined by ^1H -NMR spectroscopy.

VII. Crystallographic Data

CCDC 2247891 contains the supplementary crystallographic data for **3ae**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.



Ar = 2,4,6-Me₃C₆H₂
3ae

Identification code

3ae

S74

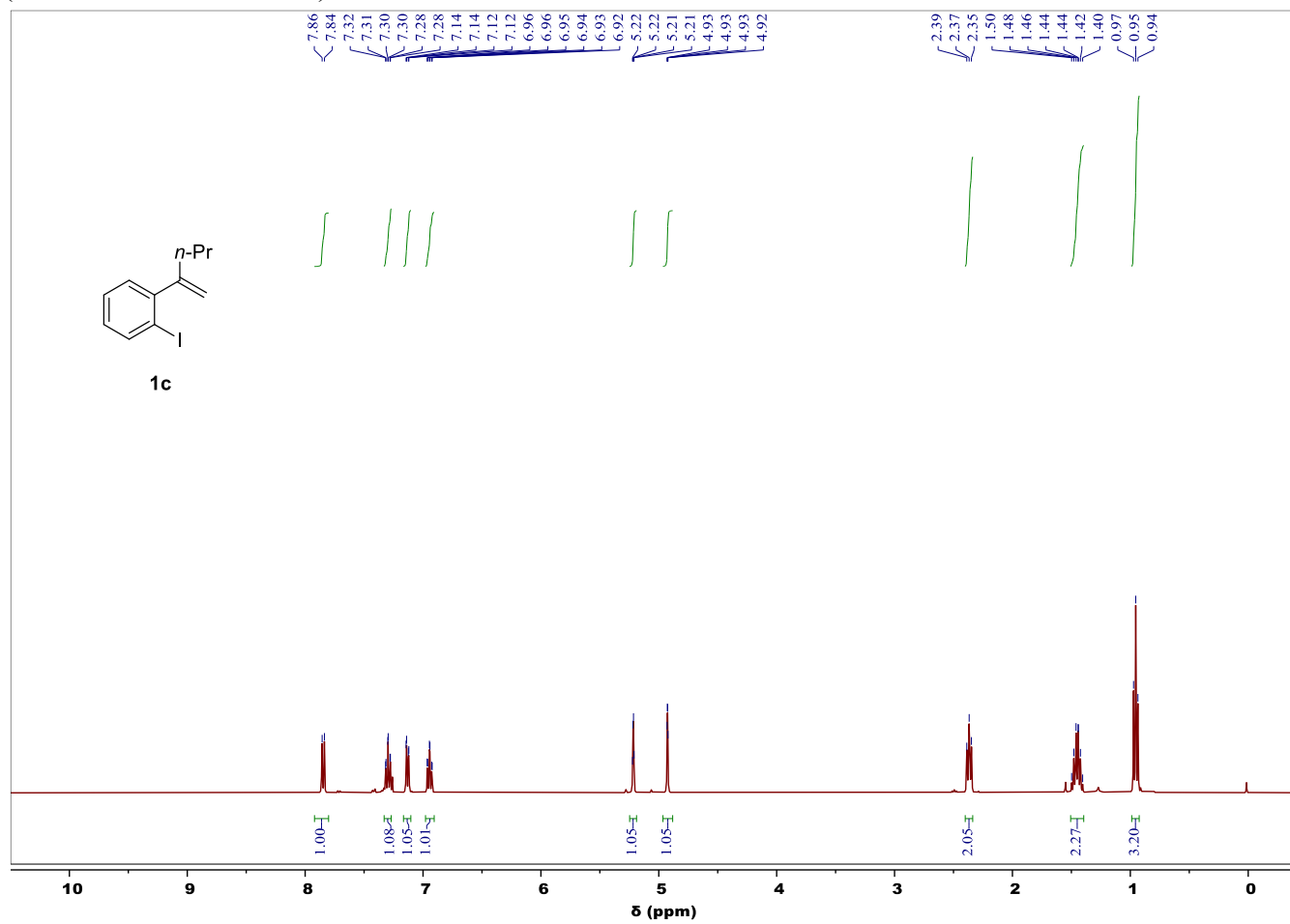
Empirical formula	C ₃₉ H ₃₆ O ₃
Formula weight	552.68
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	8.81447(12)
b/Å	33.2257(4)
c/Å	11.84777(14)
α/°	90
β/°	90.9522(11)
γ/°	90
Volume/Å ³	3469.34(7)
Z	4
ρ _{calc} /cm ³	1.058
μ/mm ⁻¹	0.512
F(000)	1176.0
Crystal size/mm ³	0.22 × 0.2 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.462 to 146.182
Index ranges	-10 ≤ h ≤ 10, -41 ≤ k ≤ 40, -13 ≤ l ≤ 14
Reflections collected	22869
Independent reflections	12184 [R _{int} = 0.0188, R _{sigma} = 0.0246]
Data/restraints/parameters	12184/1/770
Goodness-of-fit on F ²	1.054
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0370, wR ₂ = 0.0998
Final R indexes [all data]	R ₁ = 0.0401, wR ₂ = 0.1033
Largest diff. peak/hole / e Å ⁻³	0.15/-0.17
Abs Structure Flack	0.11(7)

VIII. References

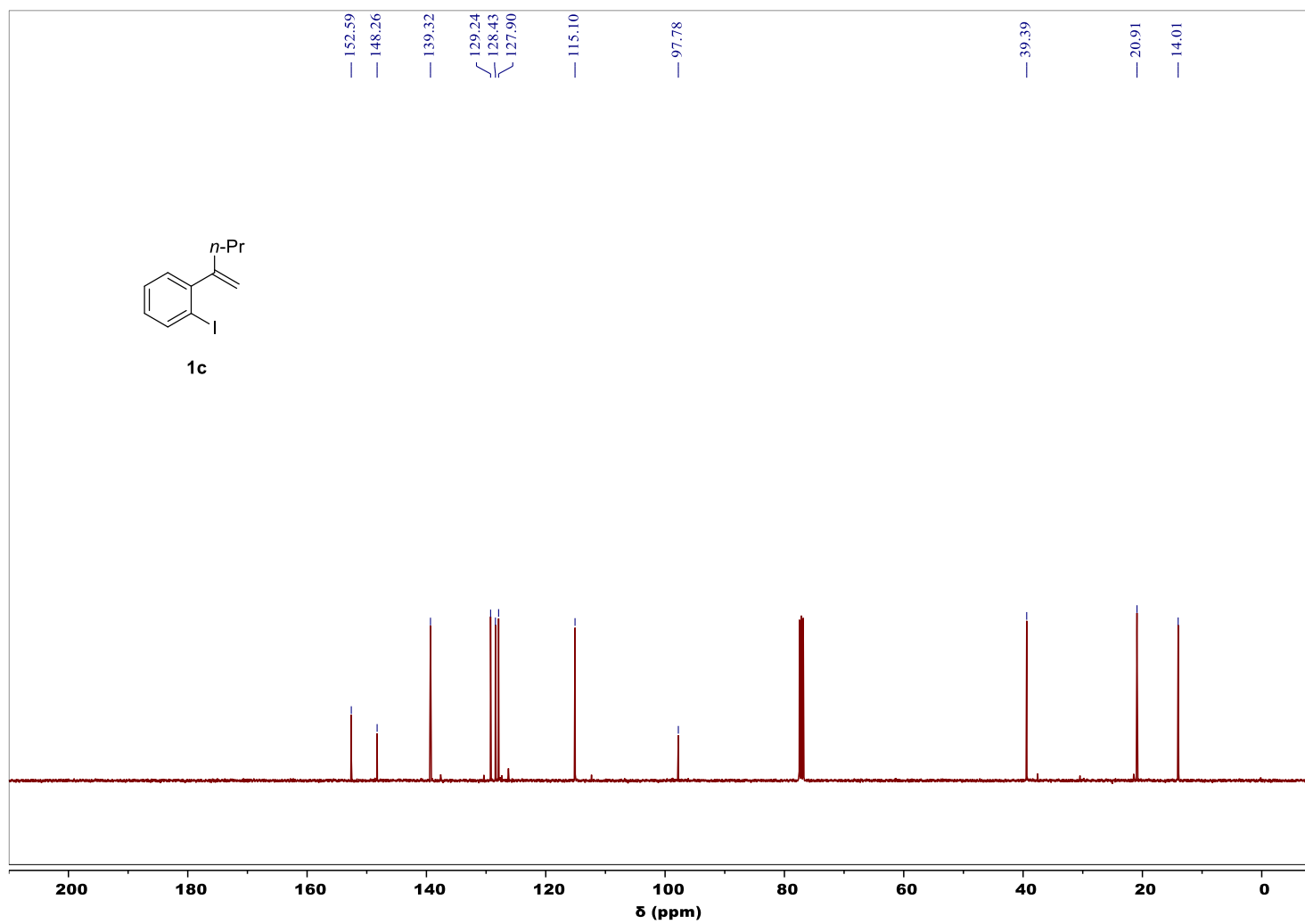
1. Abel-Snape, X.; Wycich, G.; Lautens, M. Synthesis of Indenes and Benzofulvenes via a Palladium-Catalyzed Three-Component Reaction. *ACS Catal.* **2022**, *12*, 3291-3301.
2. Zhao, C.; Guo, D.; Munkrup, K.; Huang, K.; Li, F.; Wang, J. Enantioselective [3+3] Atroposelective Annulation Catalyzed by N-Heterocyclic Carbenes. *Nat. Commun.* **2018**, *9*, 611.

IX. NMR Spectra

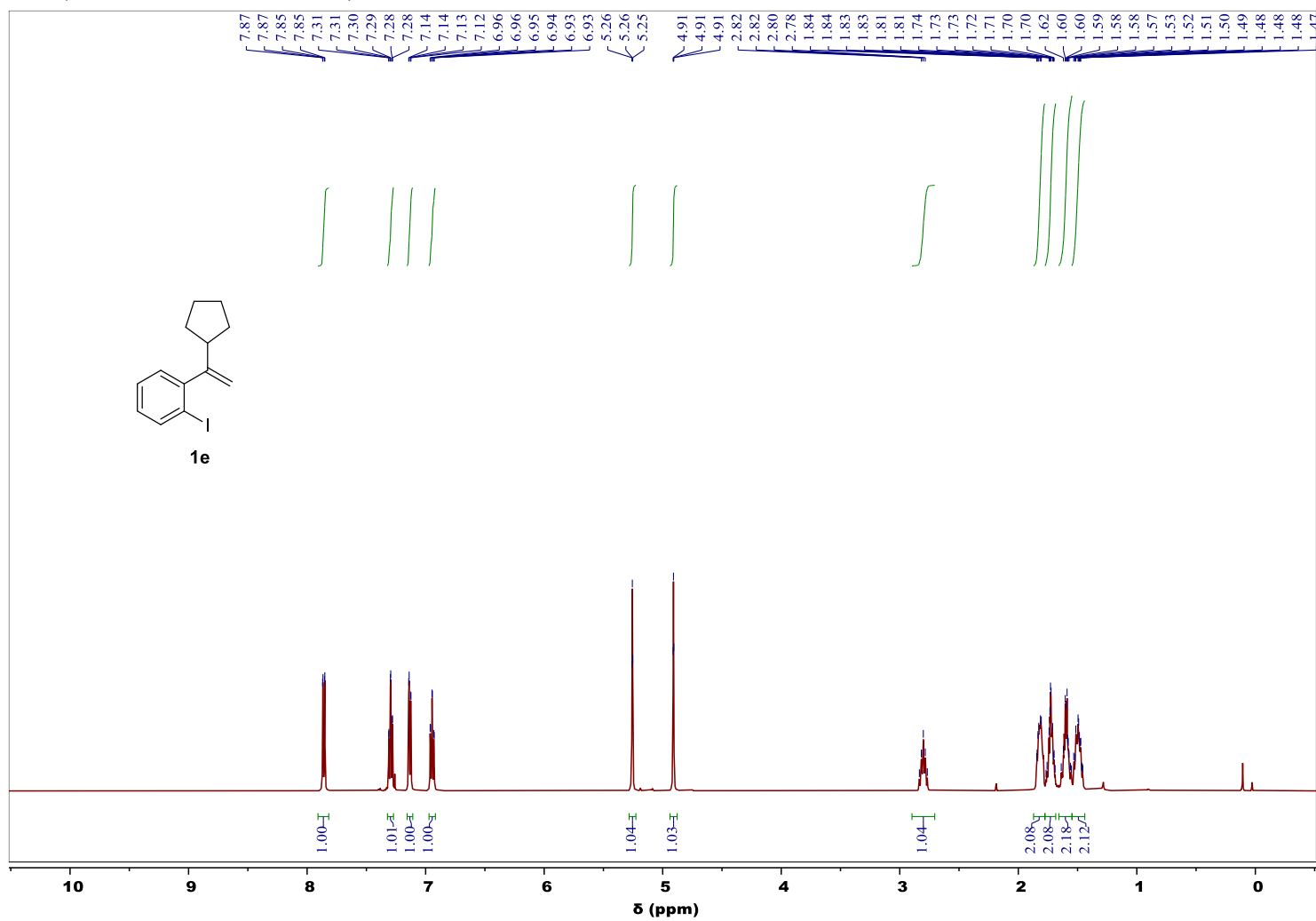
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **1c**



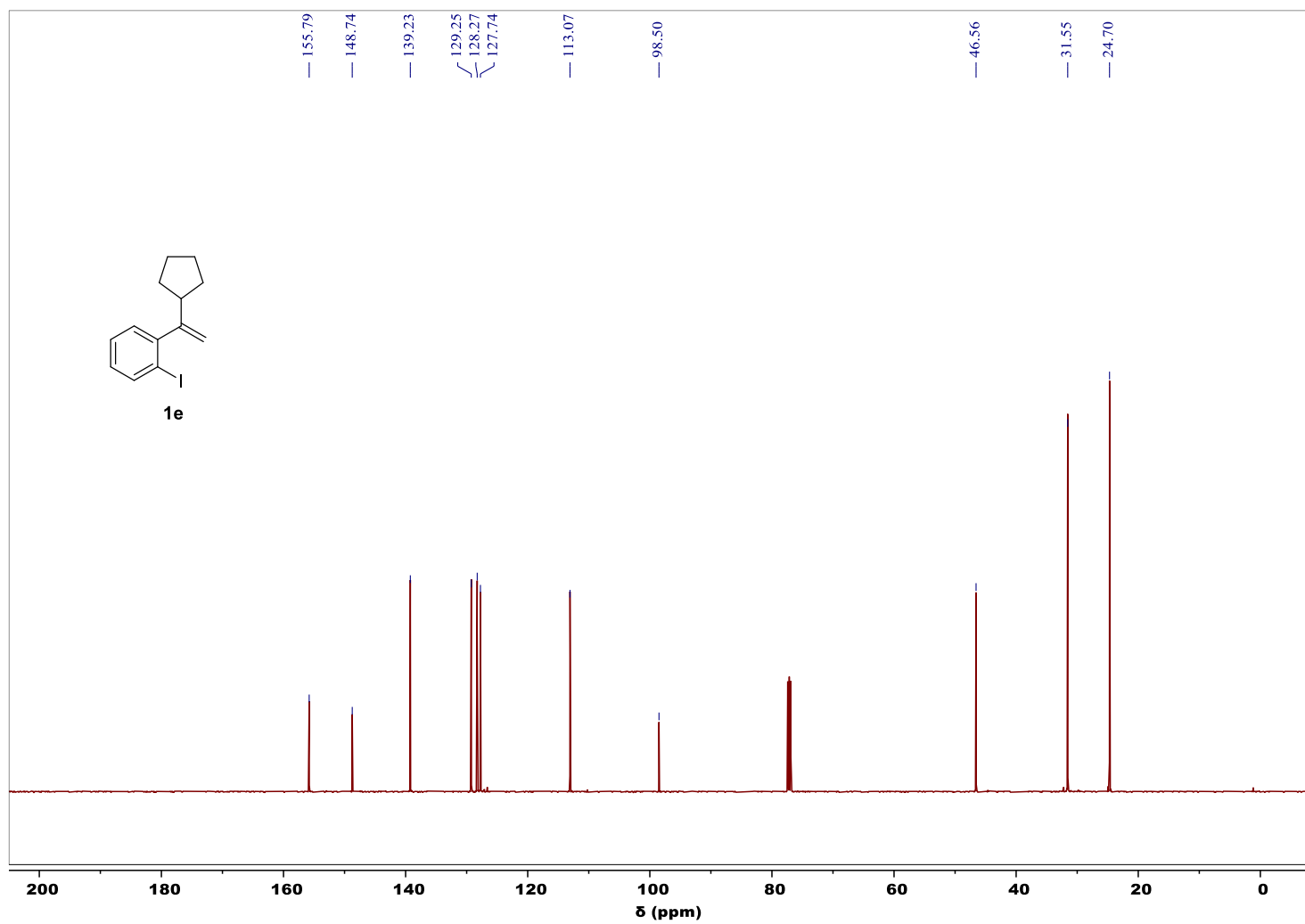
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **1c**



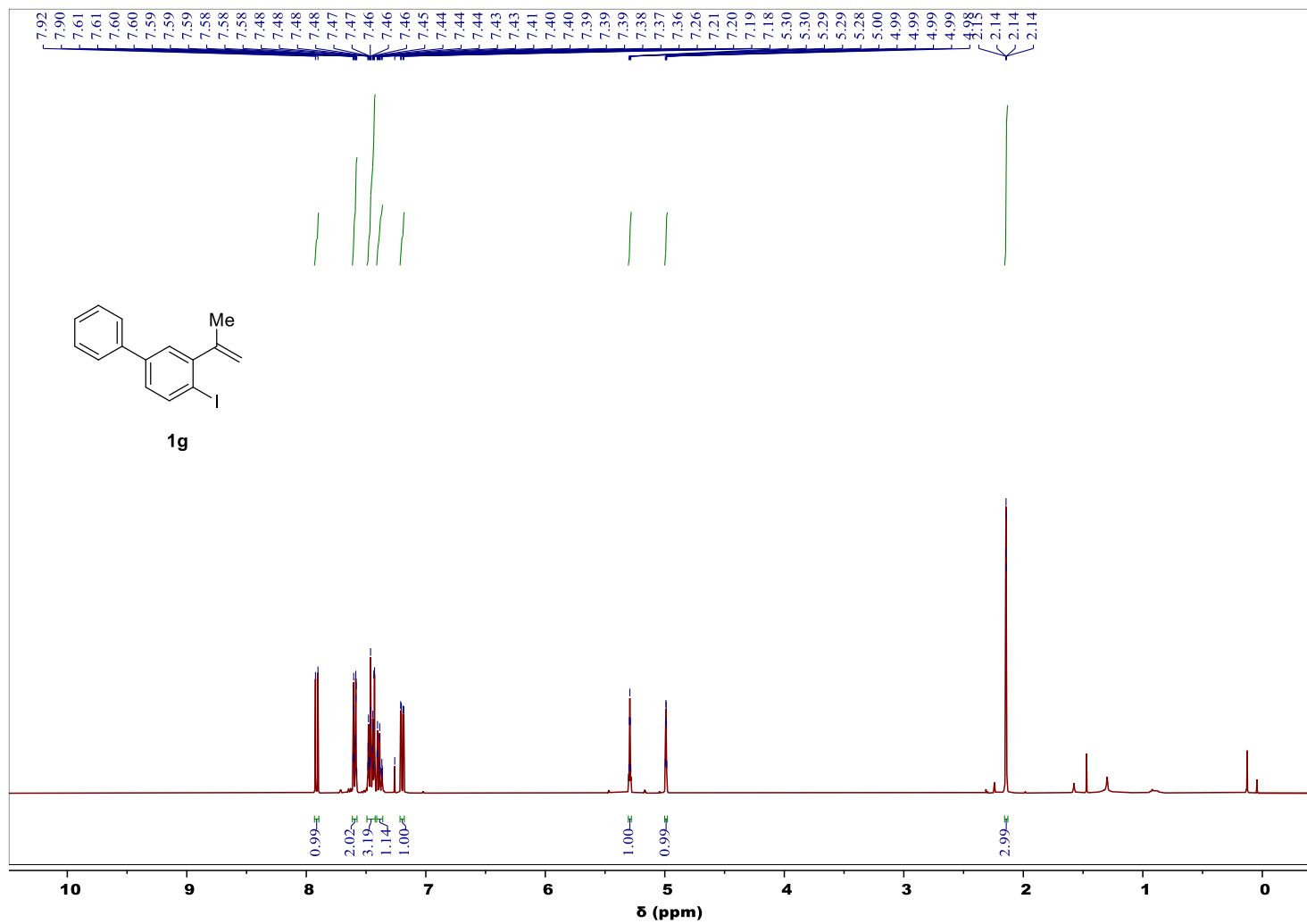
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **1e**



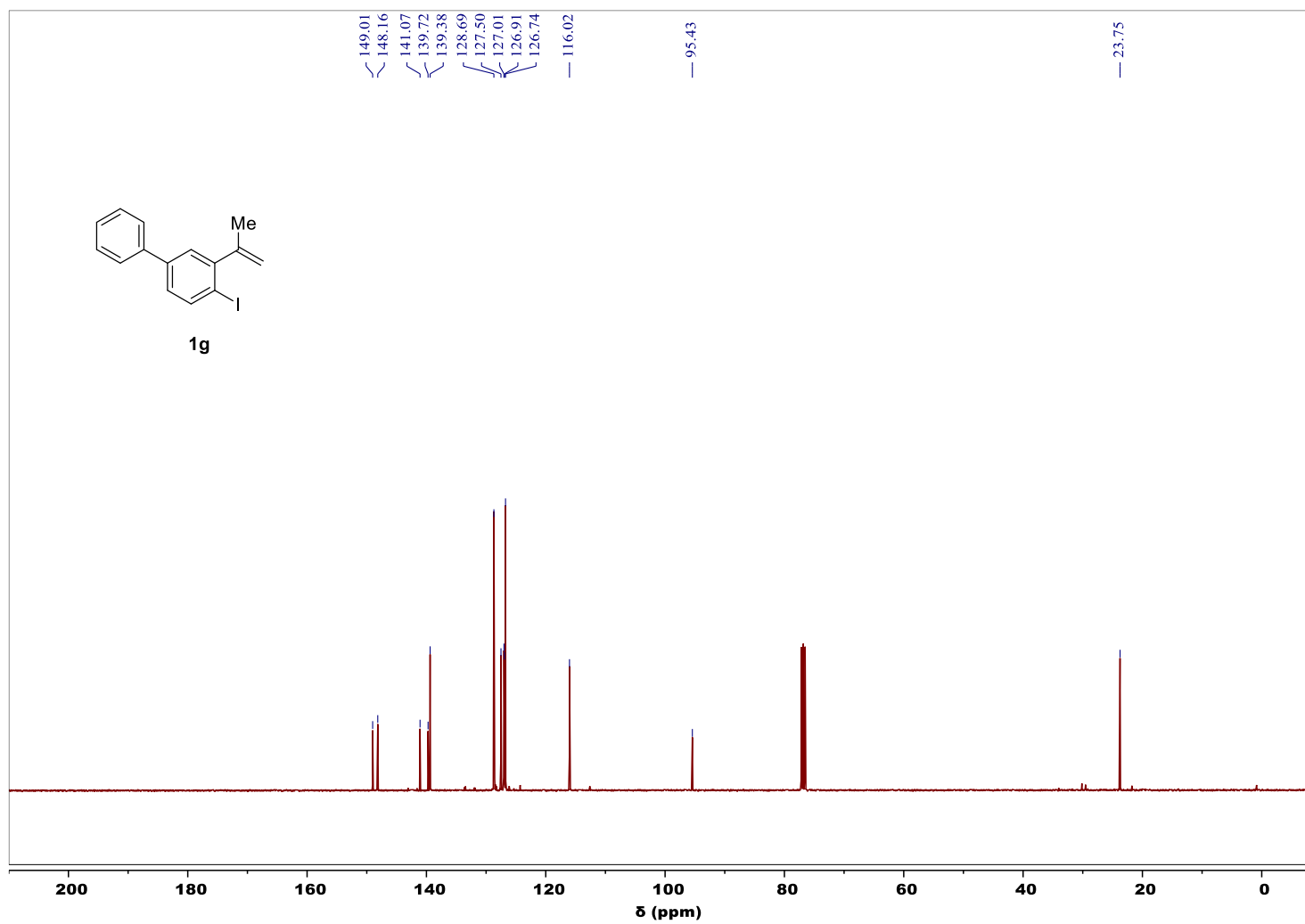
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **1e**



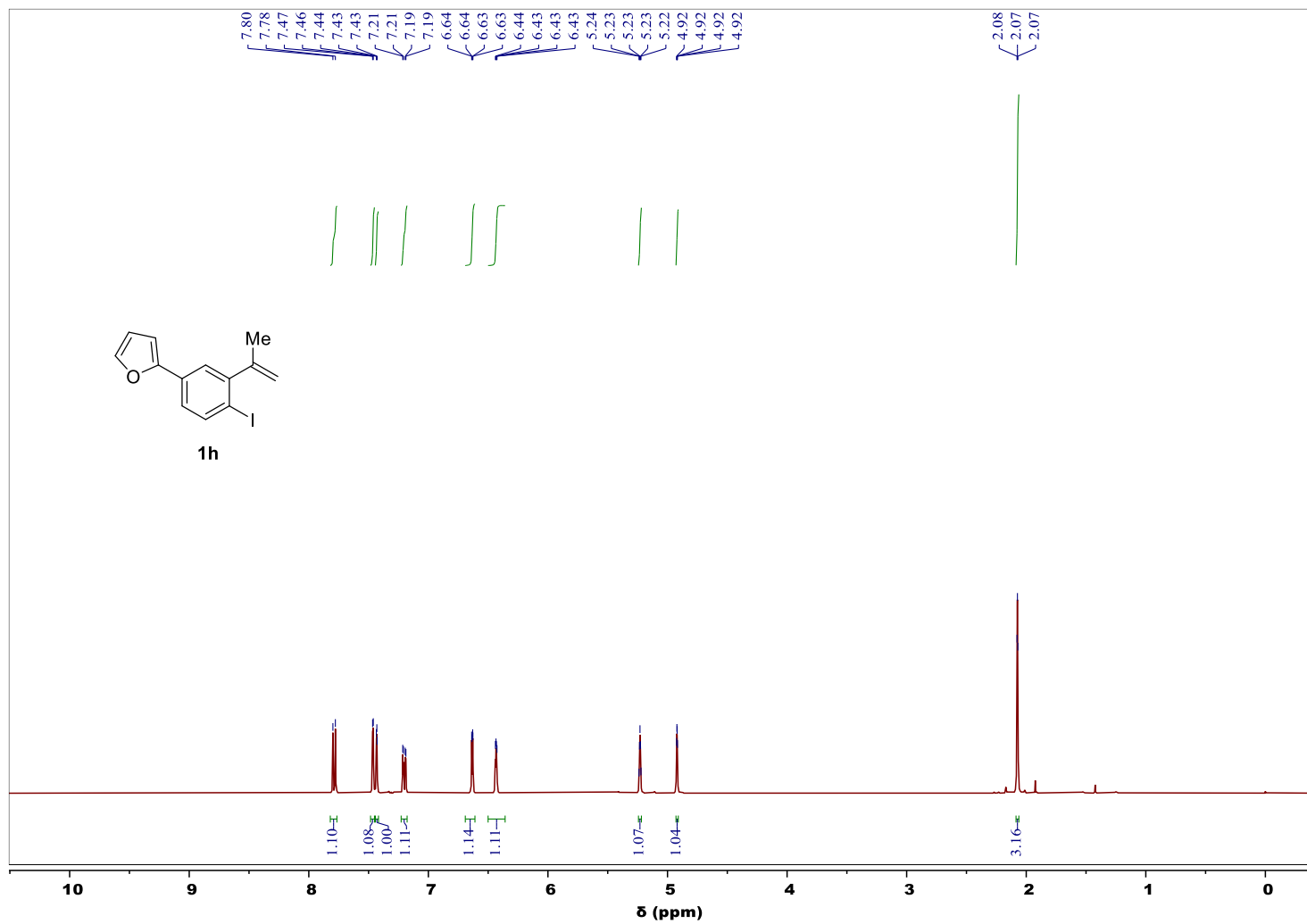
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **1g**



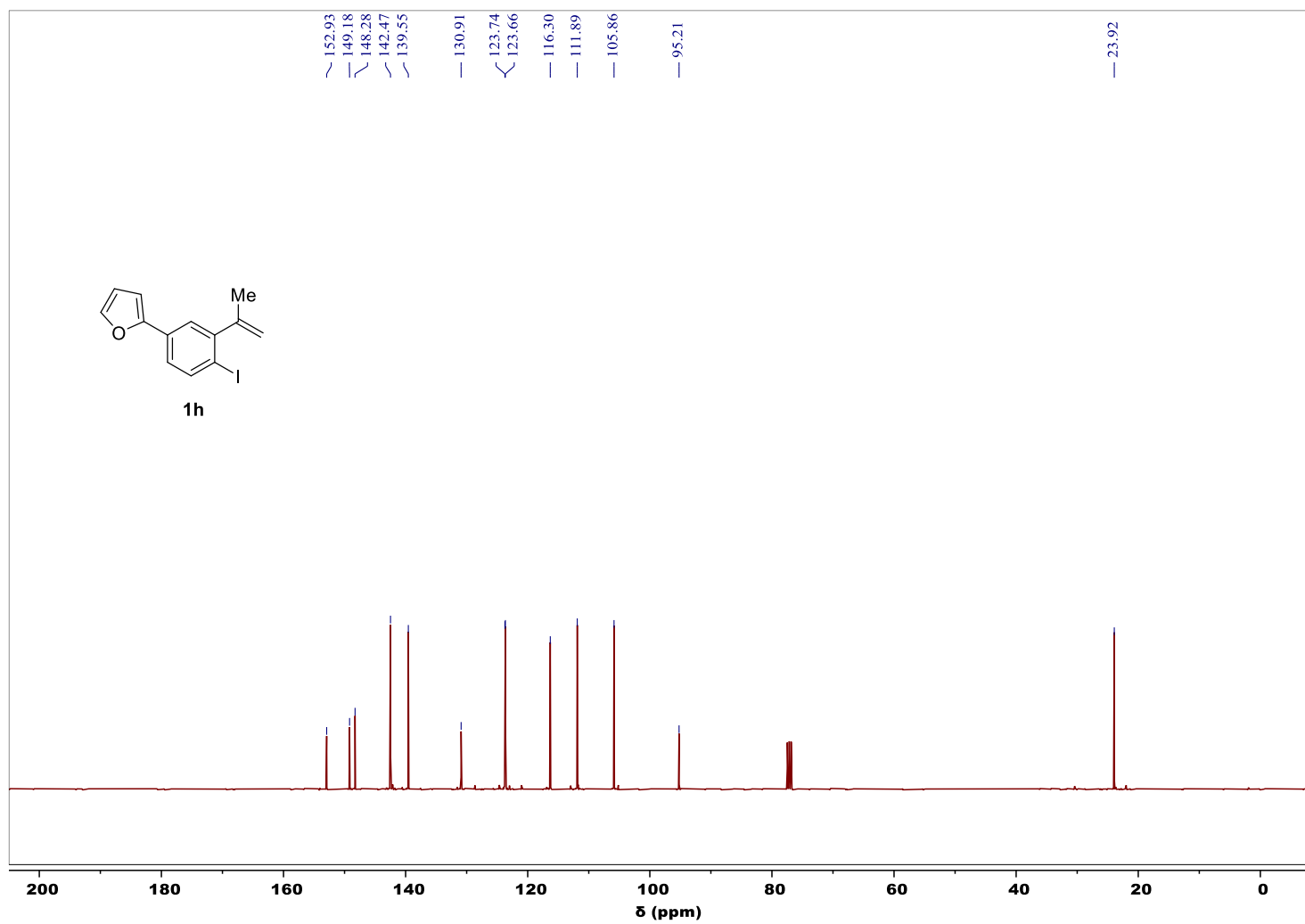
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **1g**



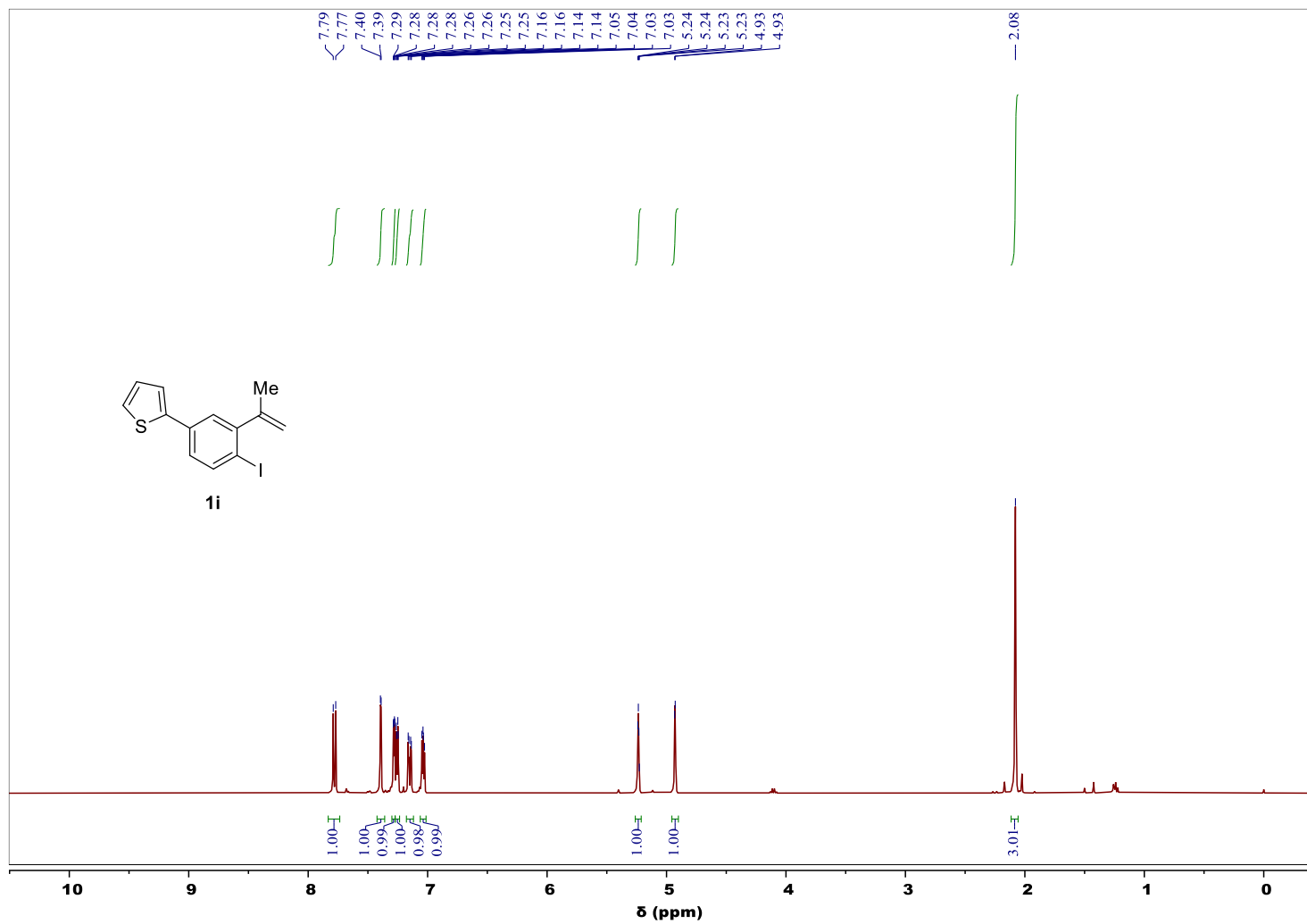
^1H NMR-spectrum (400 MHz, Chloroform- d) of **1h**



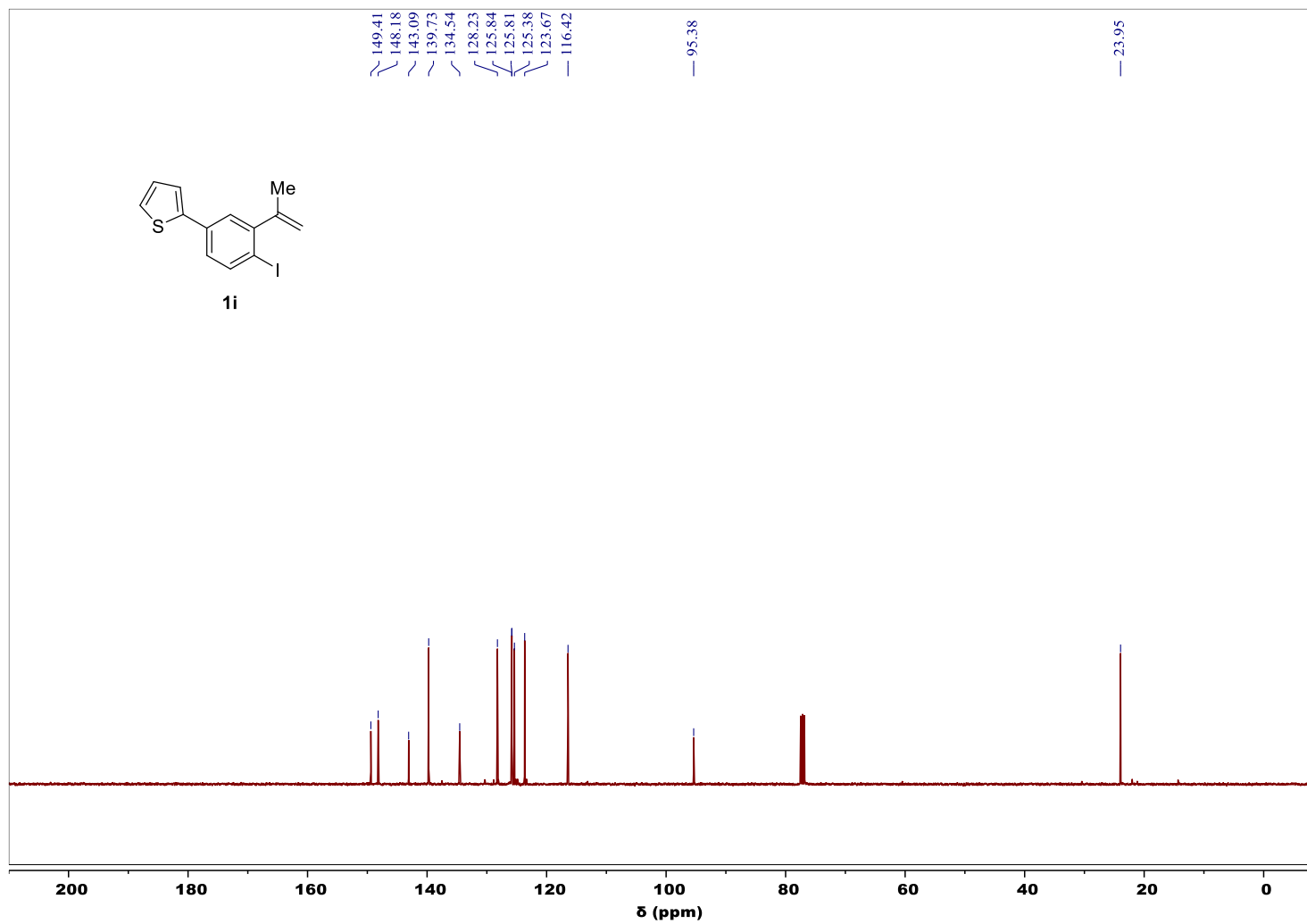
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **1h**



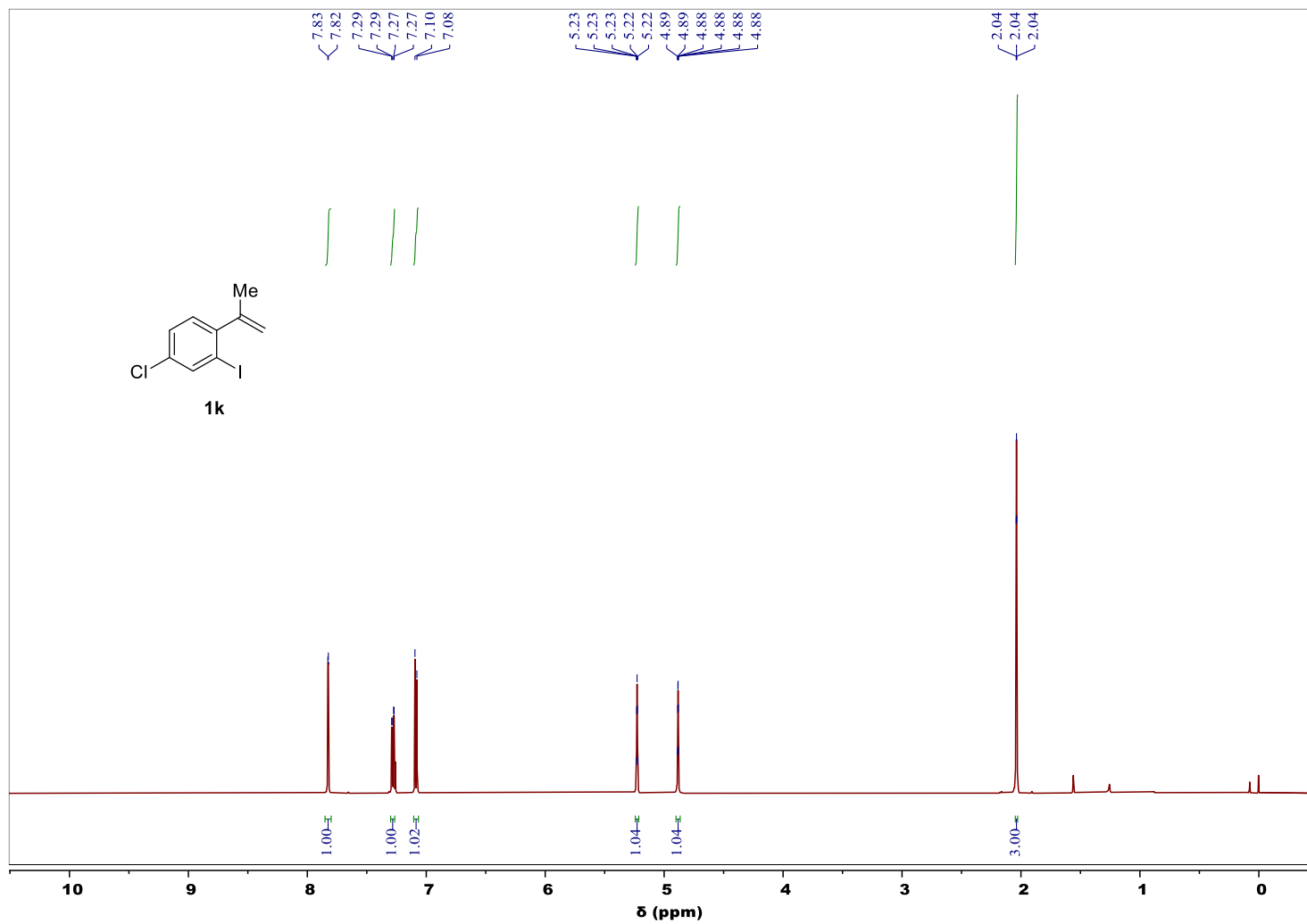
^1H NMR-spectrum (400 MHz, Chloroform- d) of **1i**



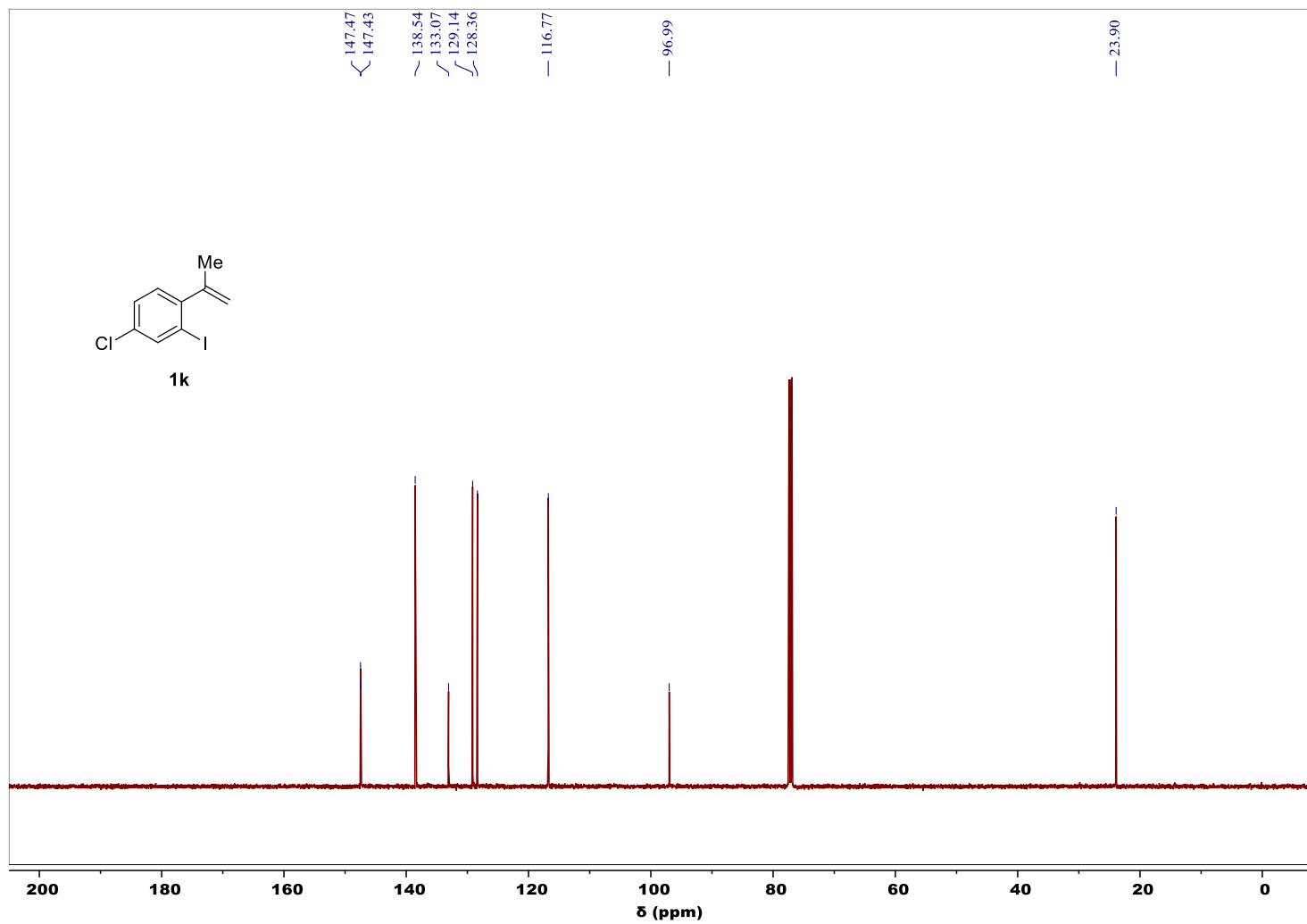
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **1i**



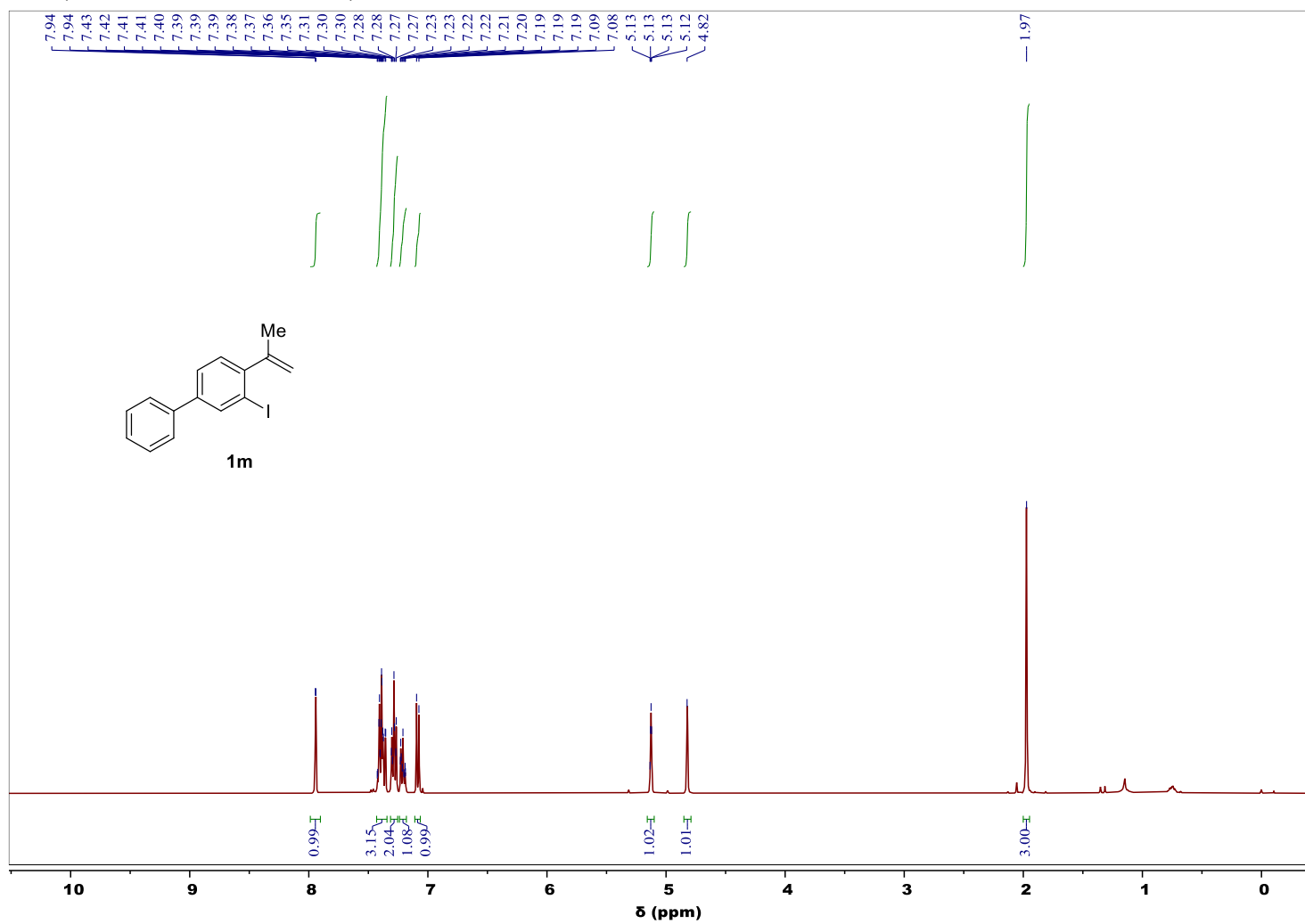
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **1k**



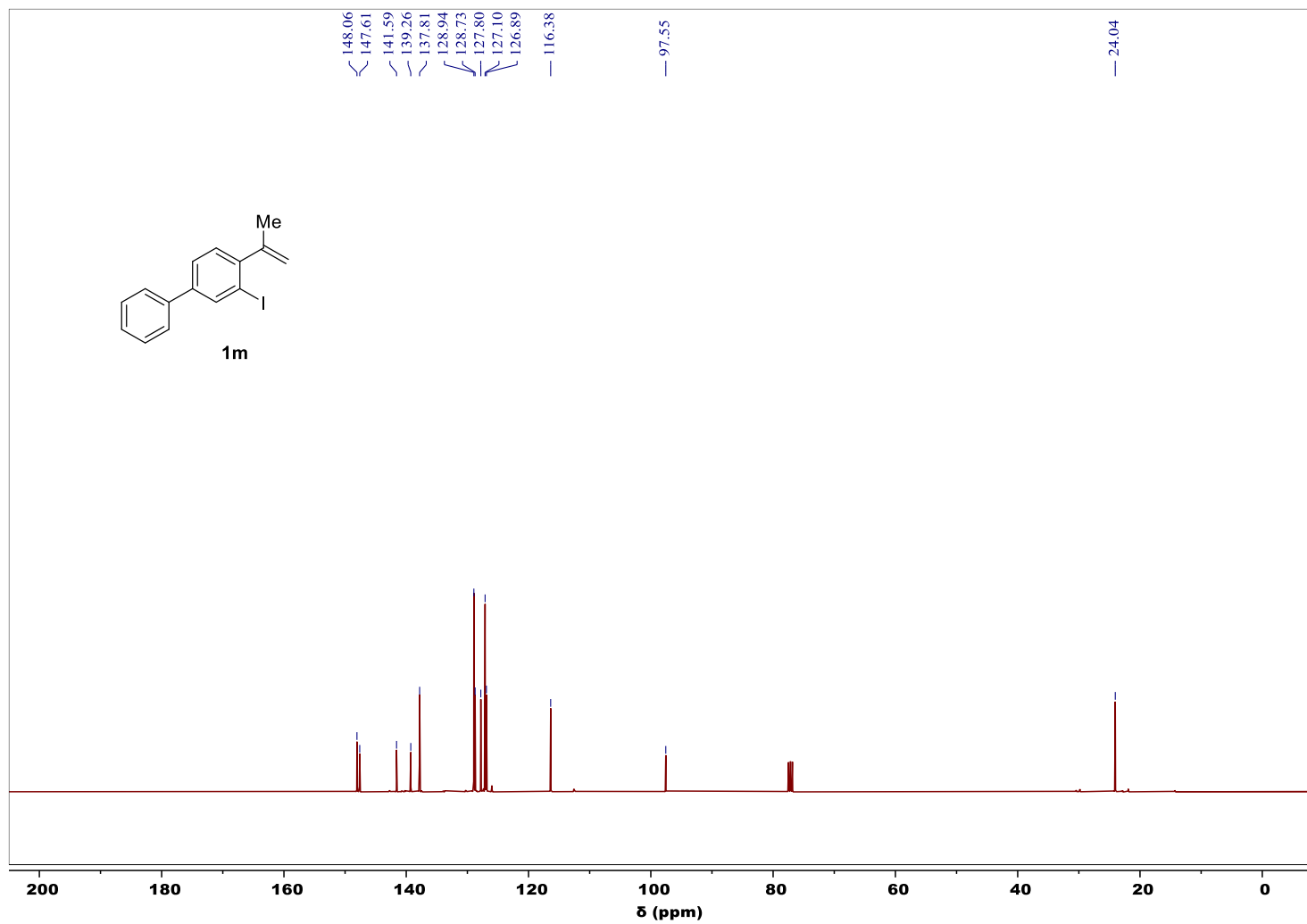
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **1k**



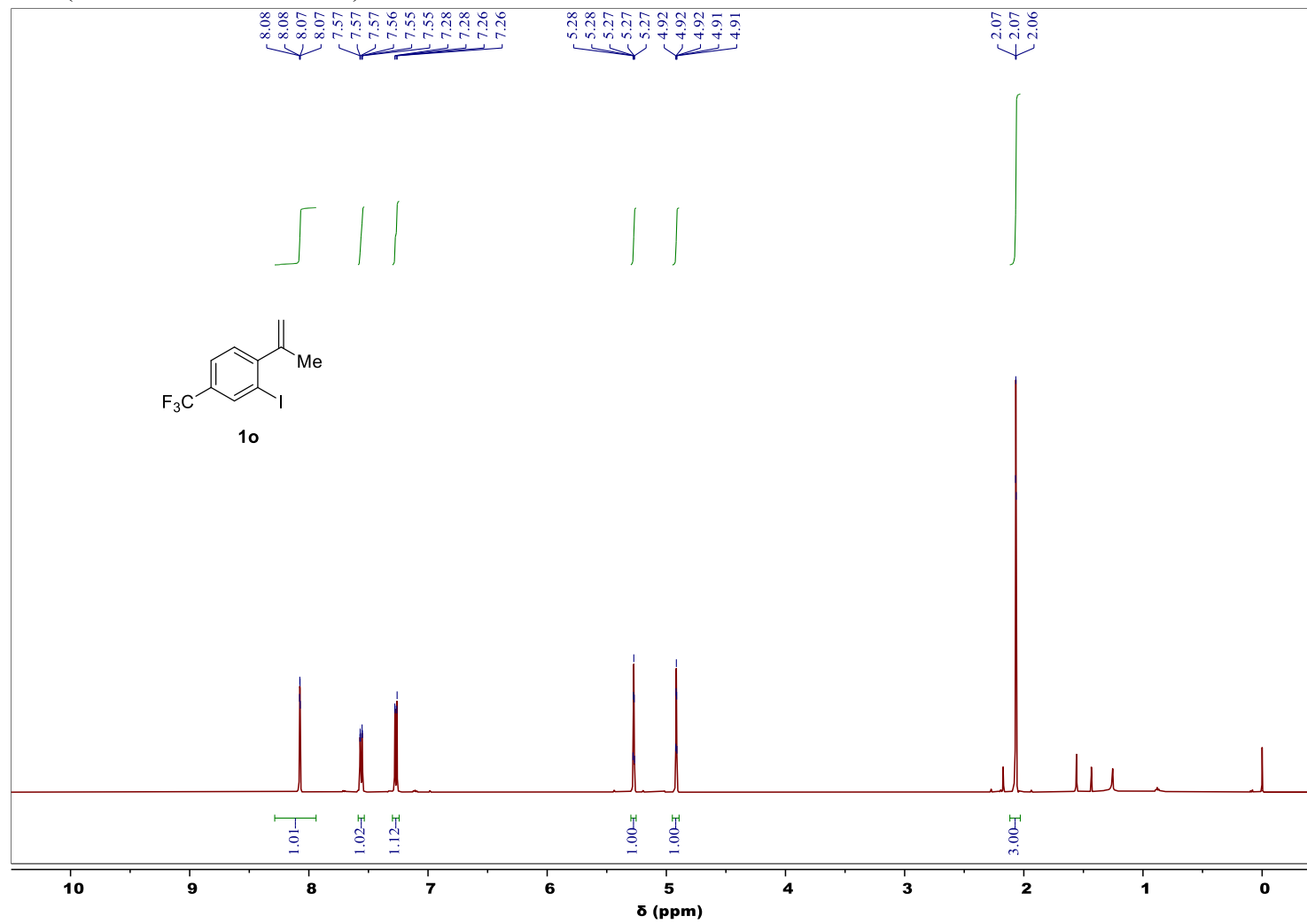
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **1m**



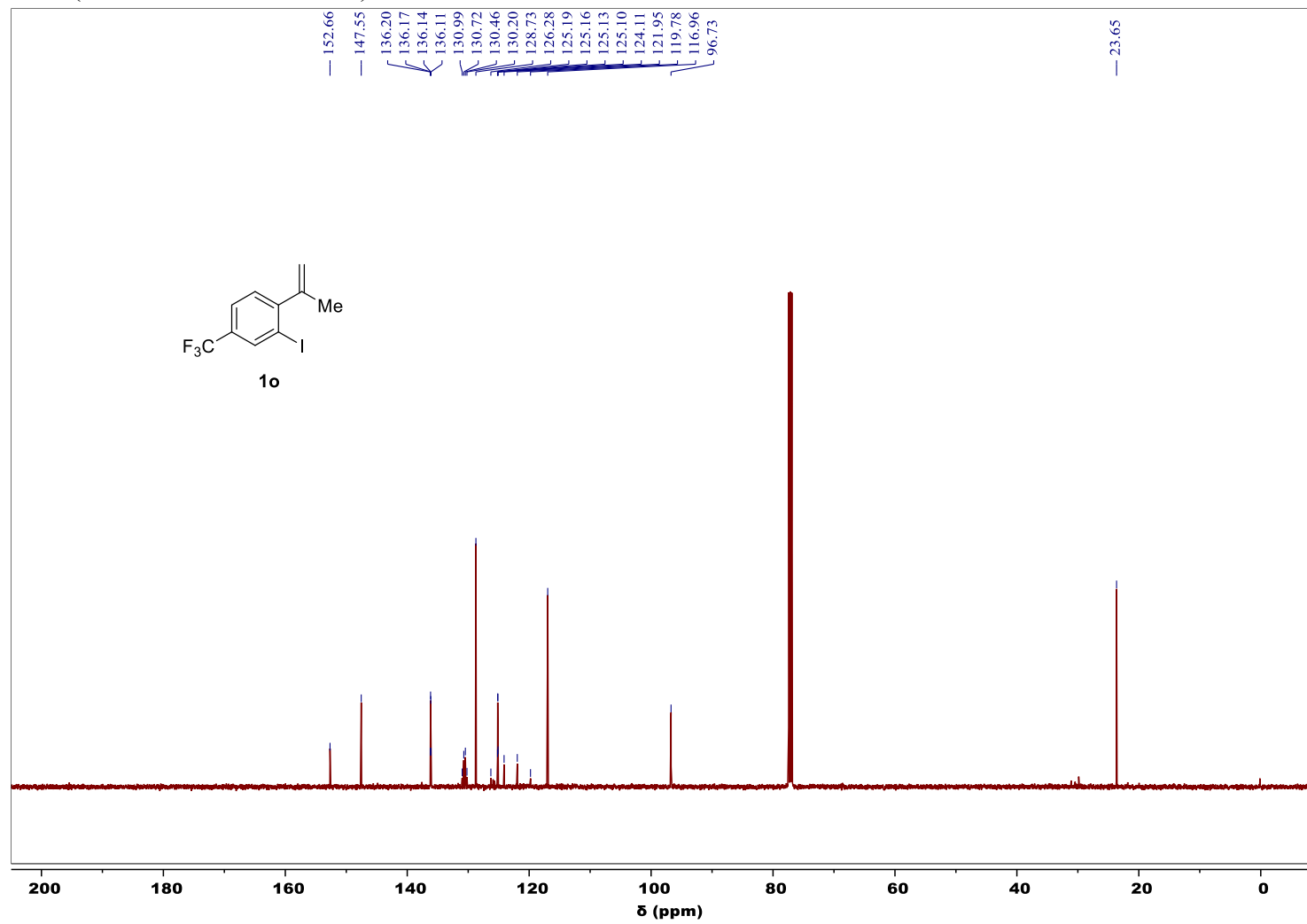
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **1m**



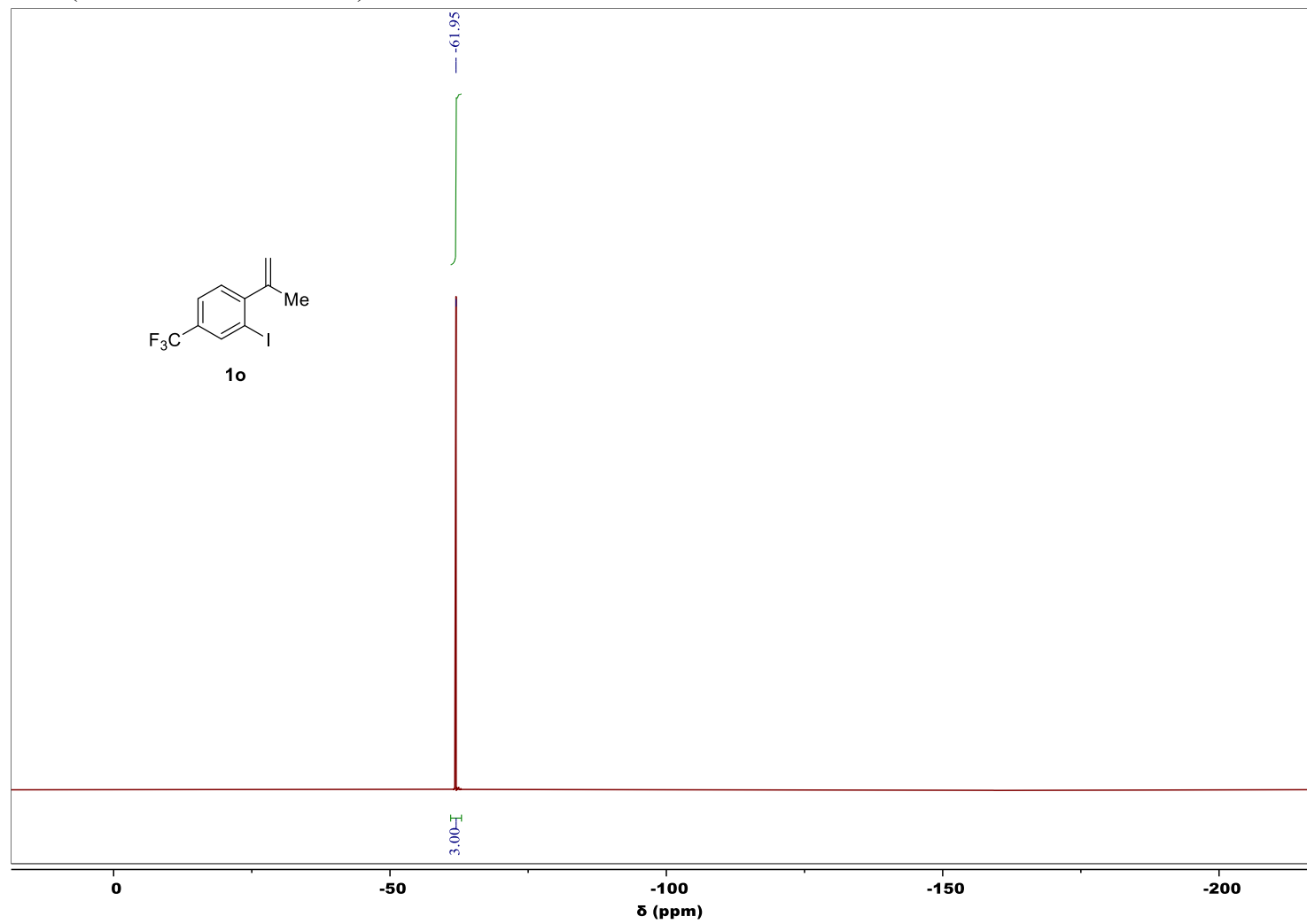
^1H NMR-spectrum (500 MHz, Chloroform- d) of **1o**



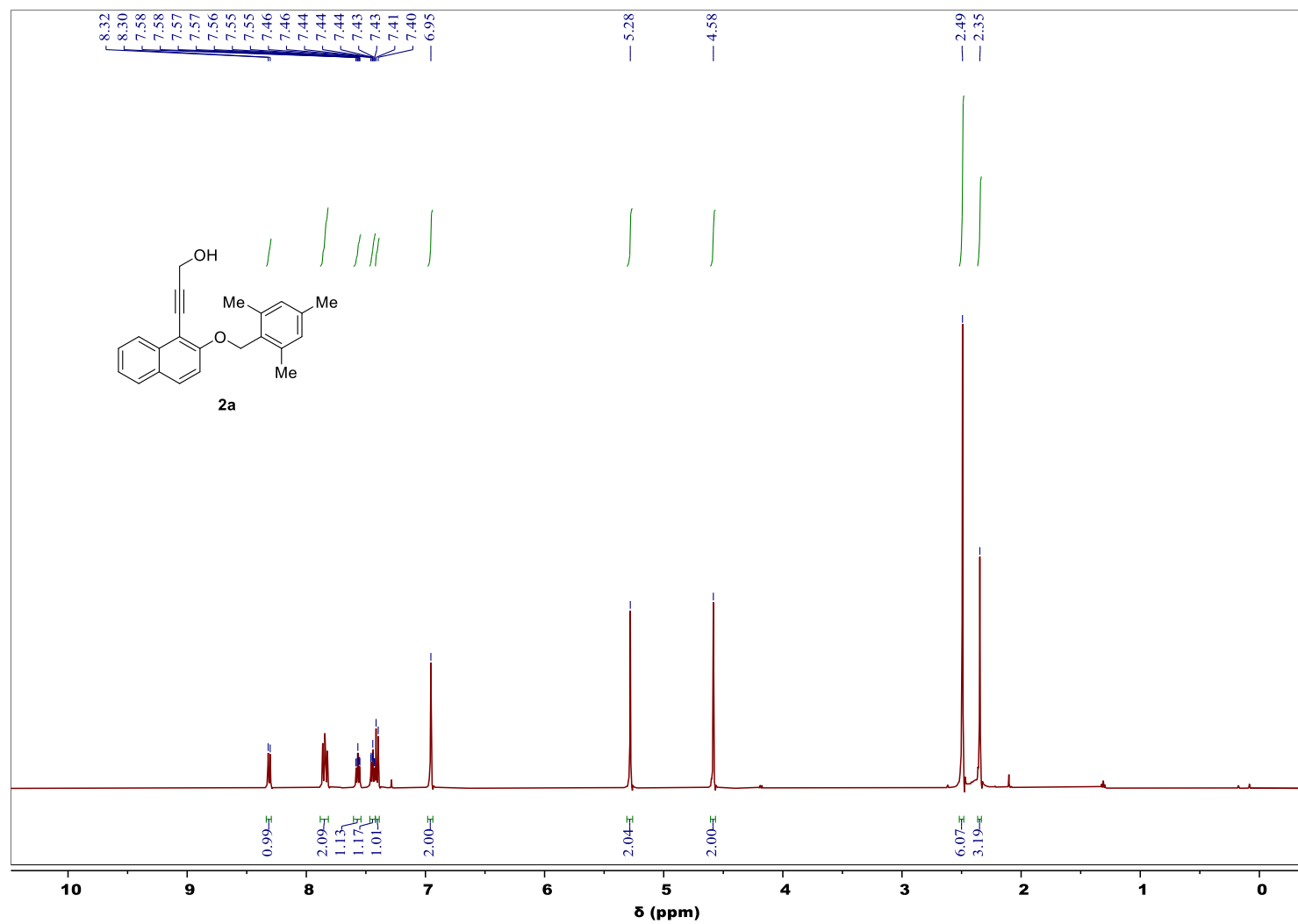
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **1o**



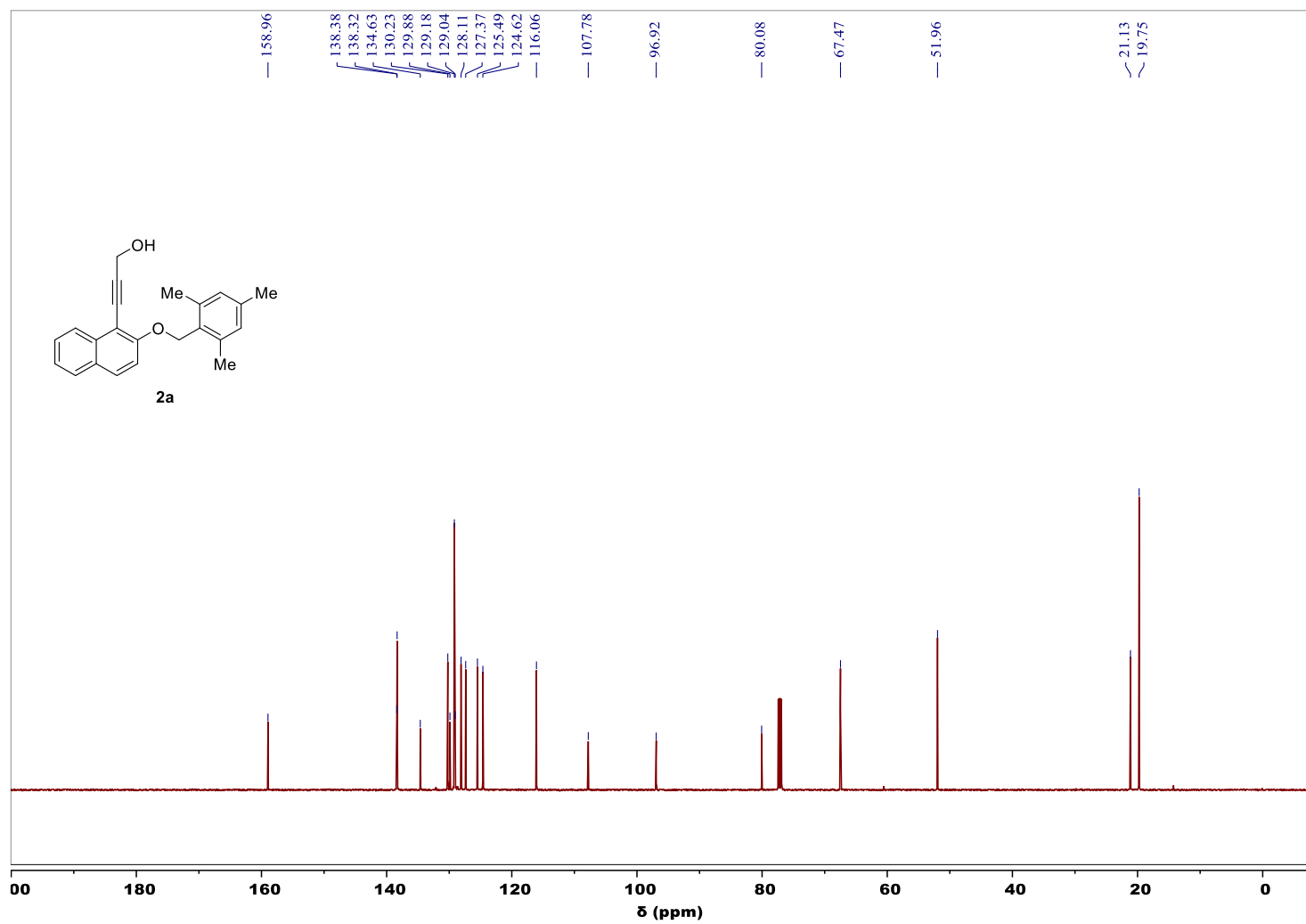
^{19}F NMR-spectrum (376 MHz, Chloroform-*d*) of **1o**



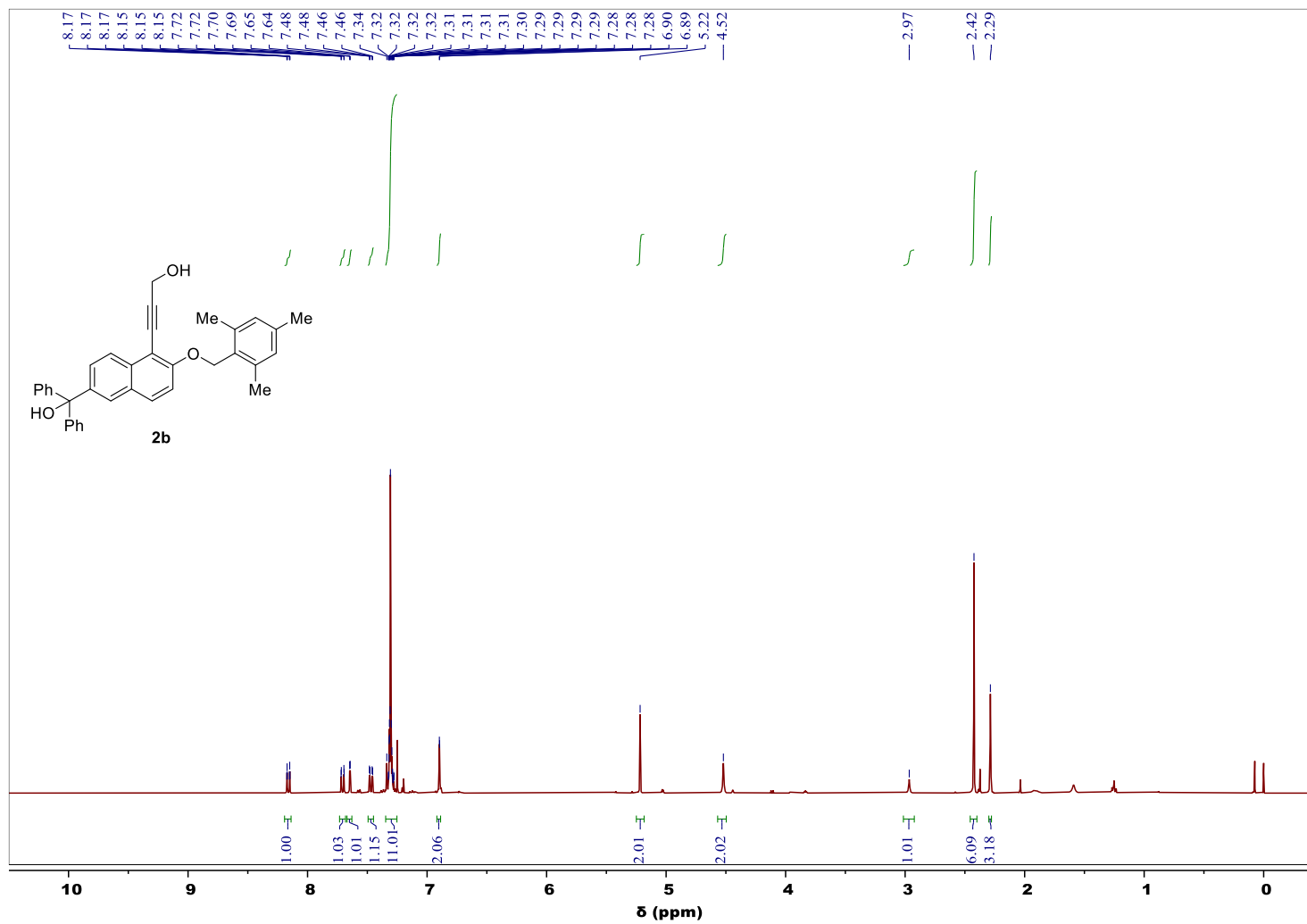
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2a**



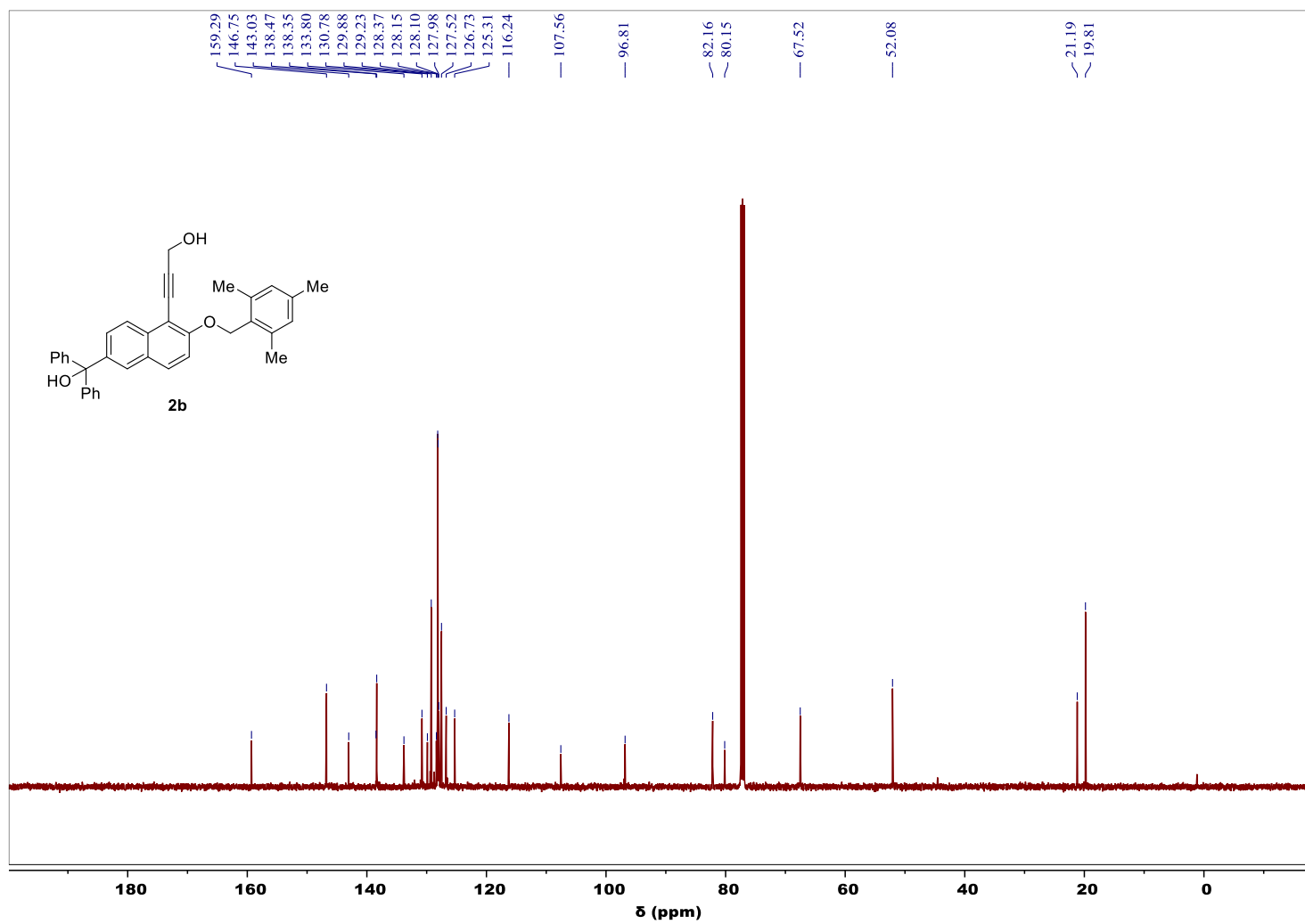
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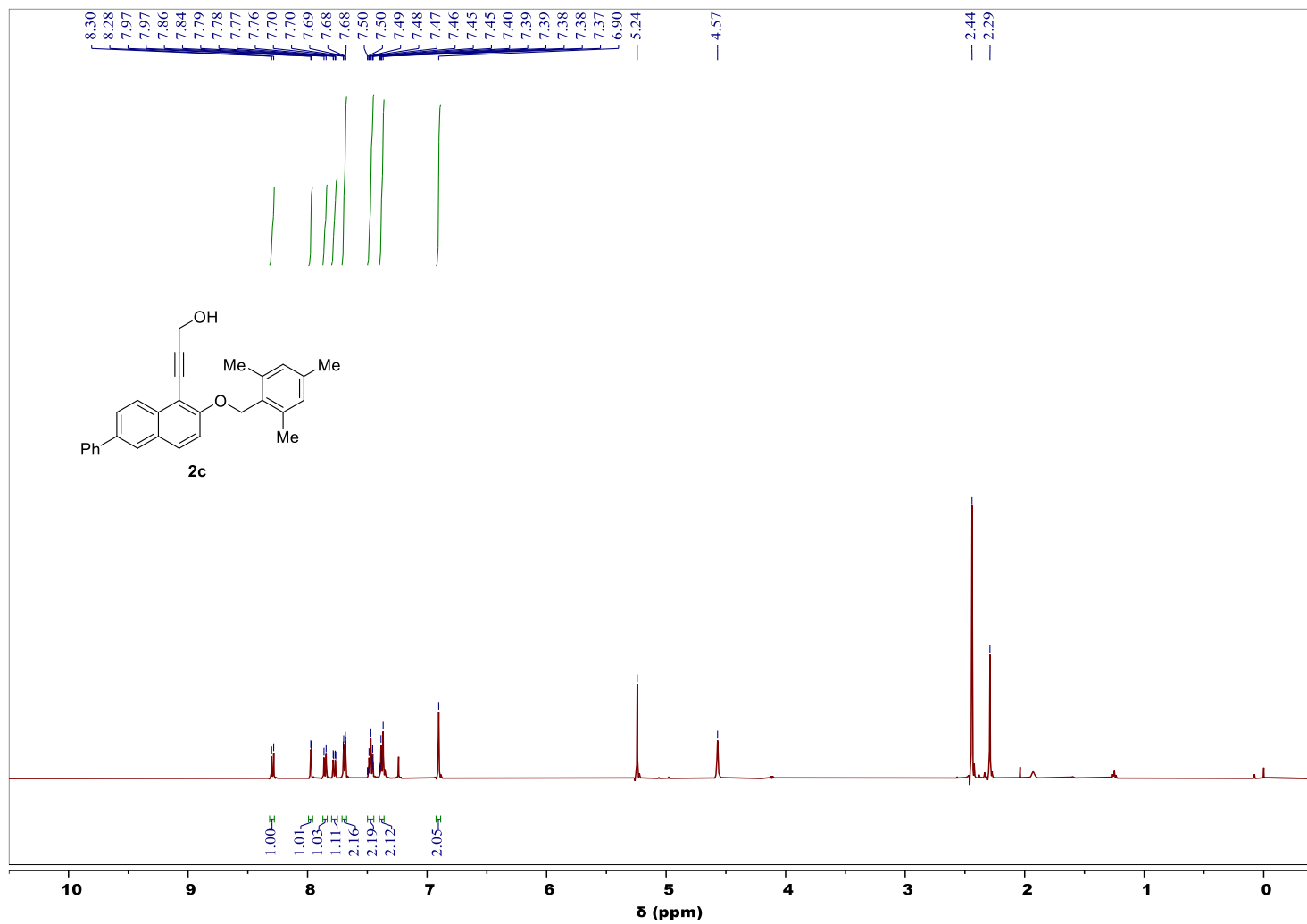
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2b**



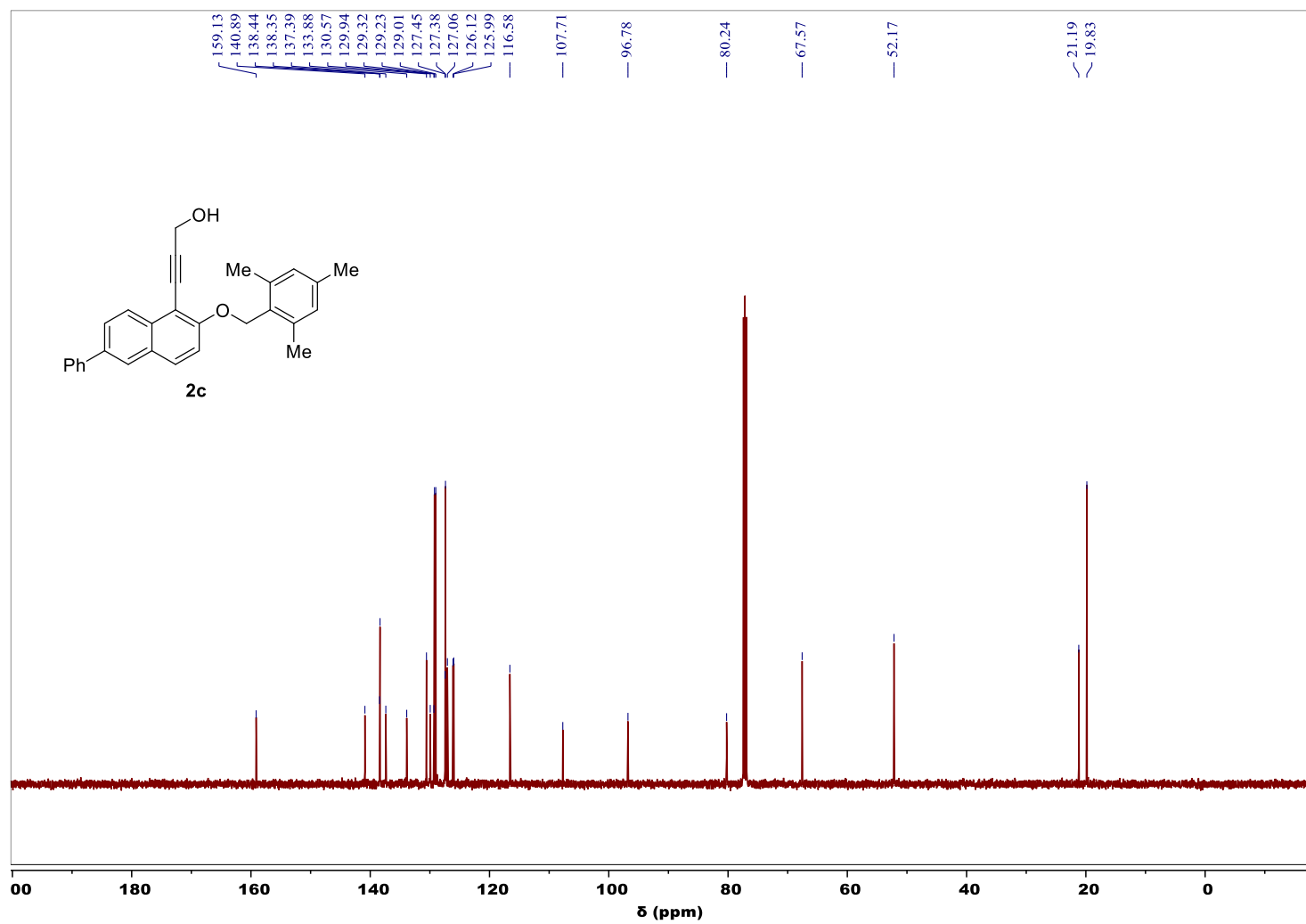
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2b**



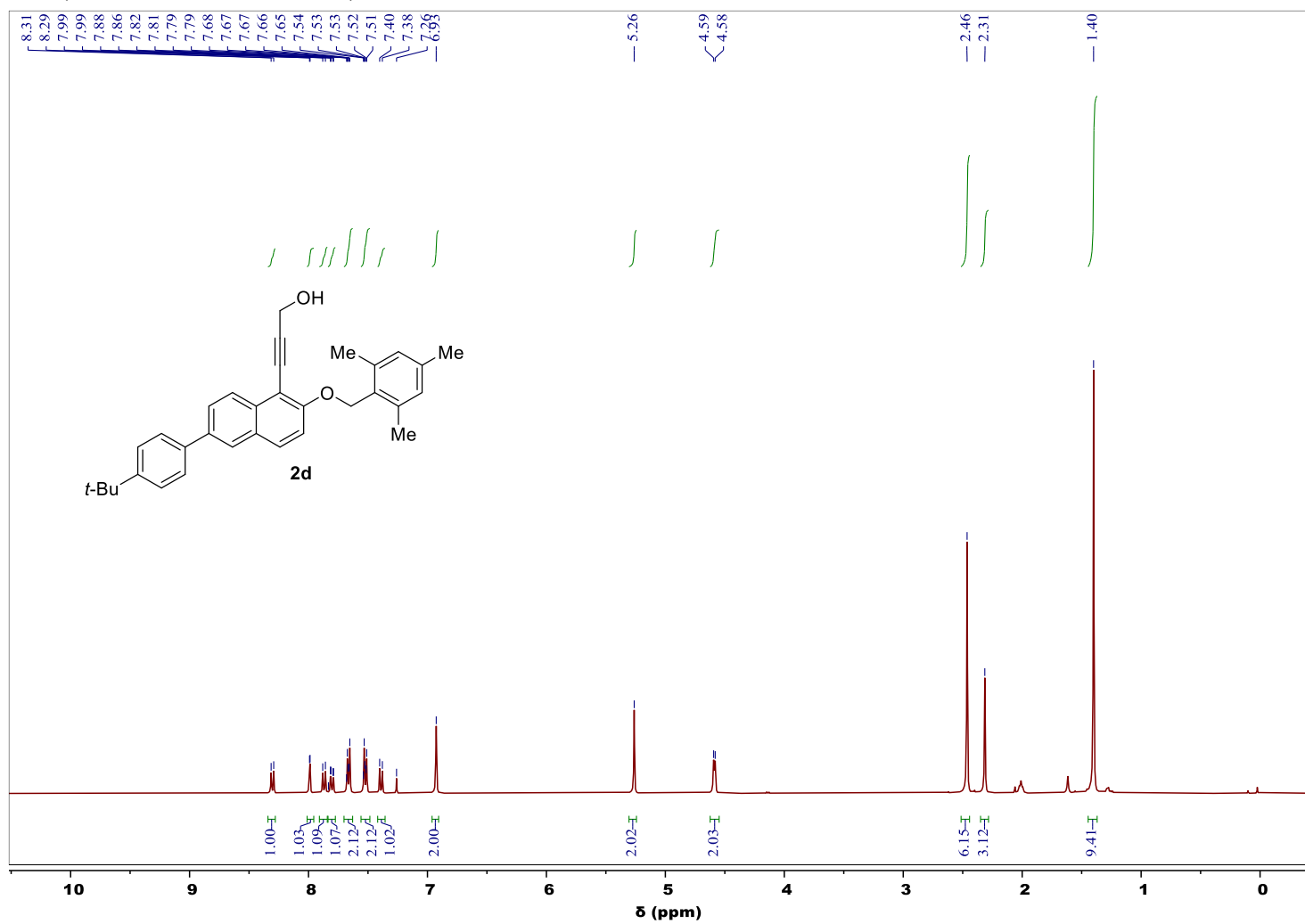
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2c**



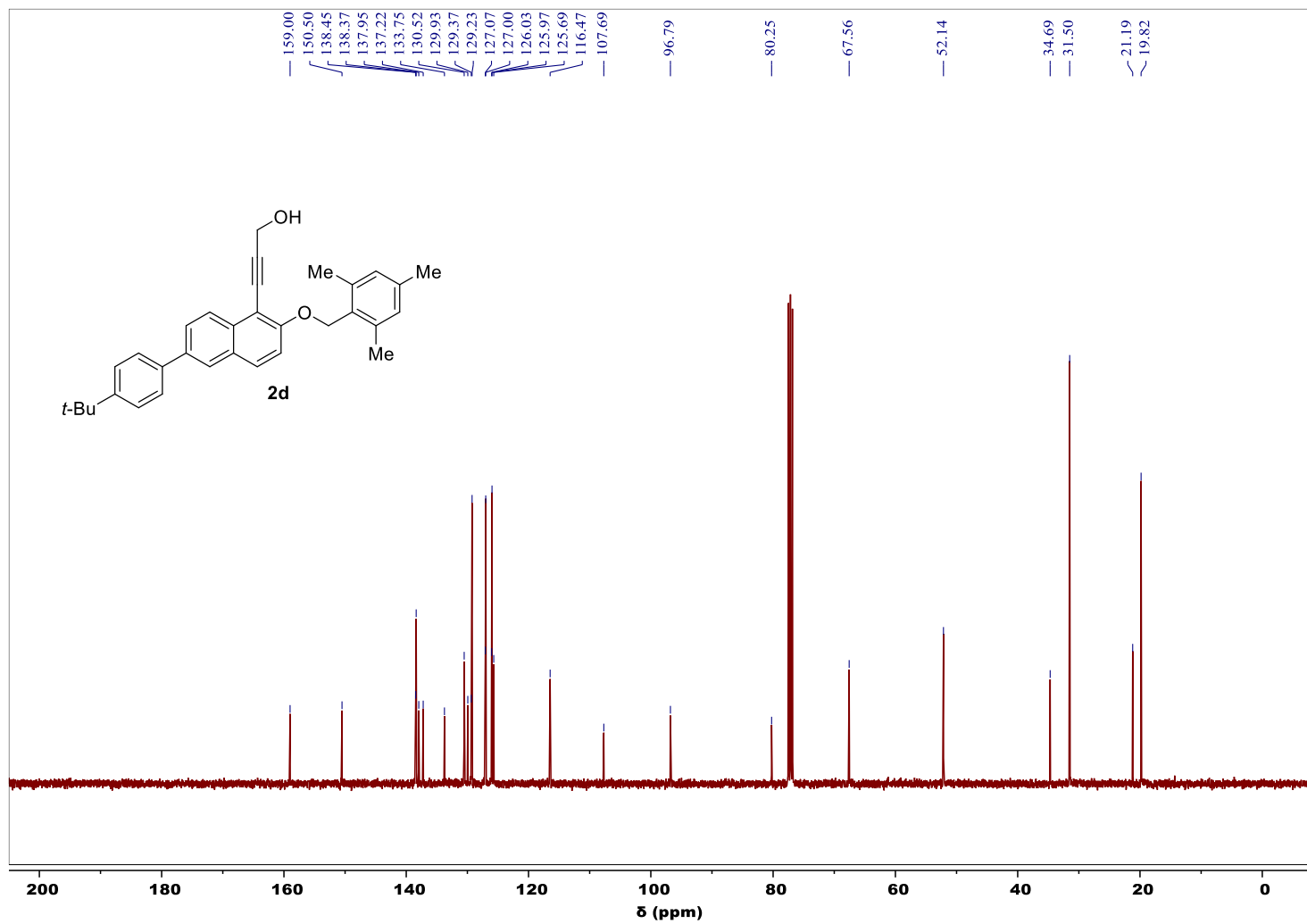
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2c**



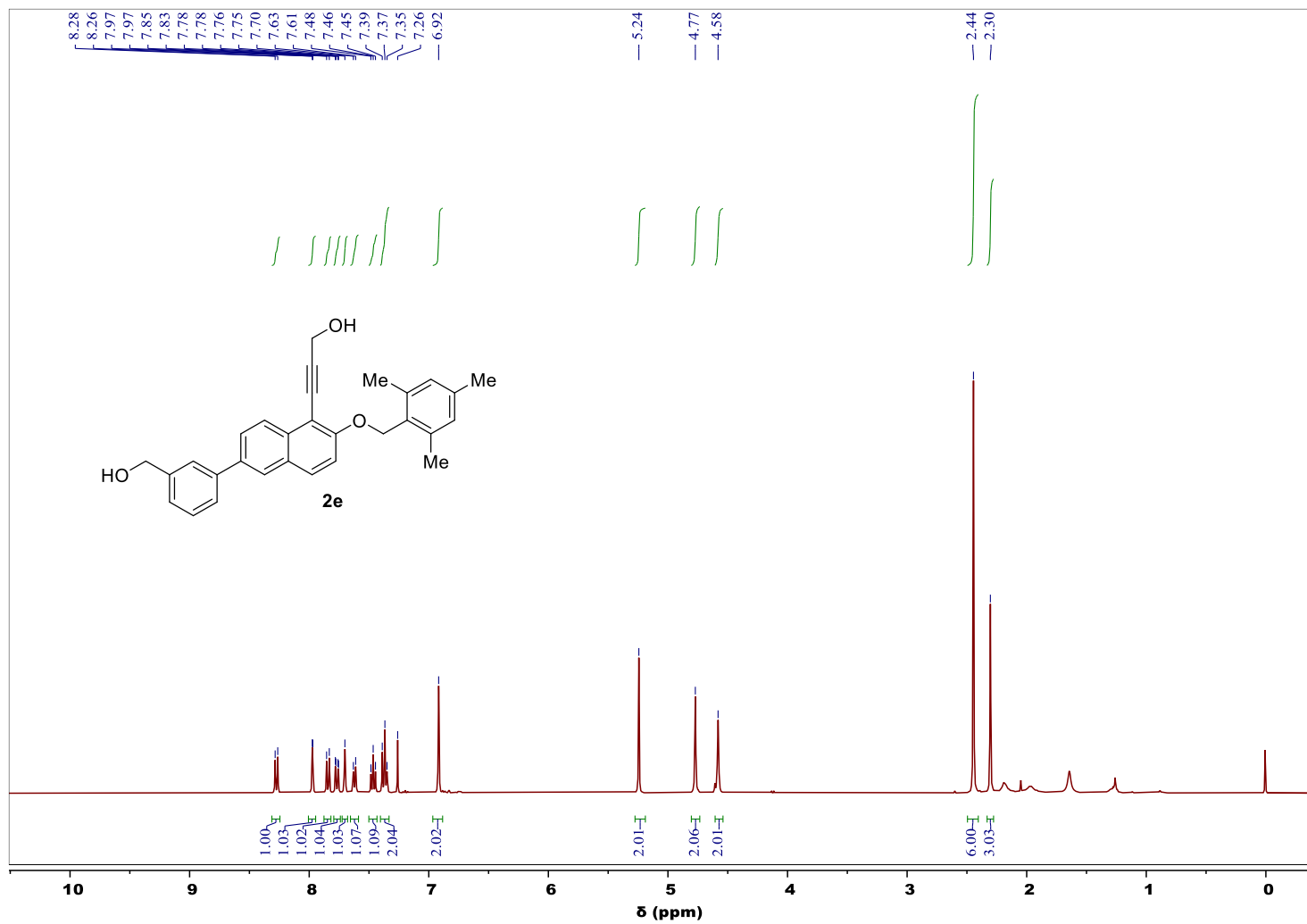
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2d**



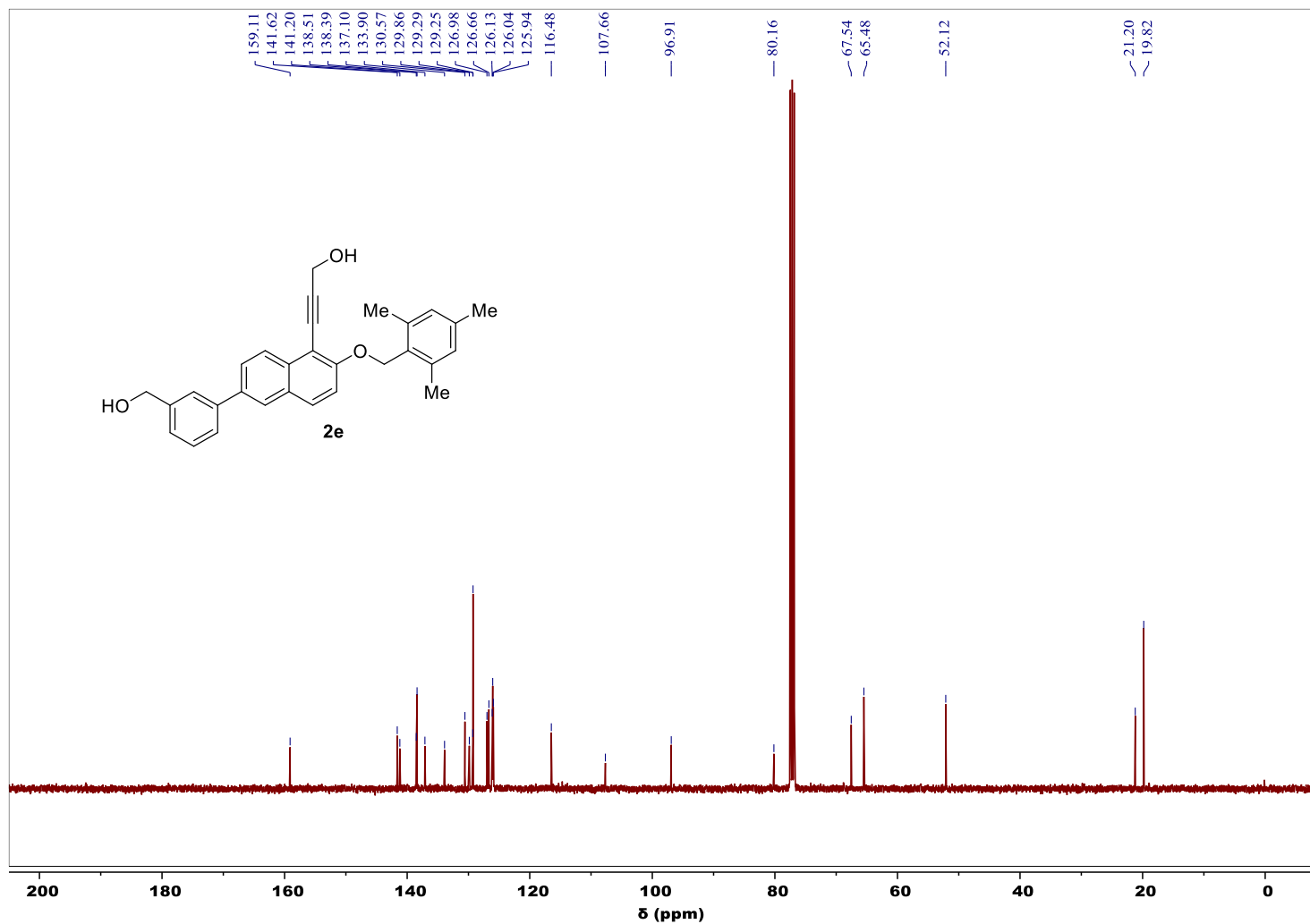
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2d**



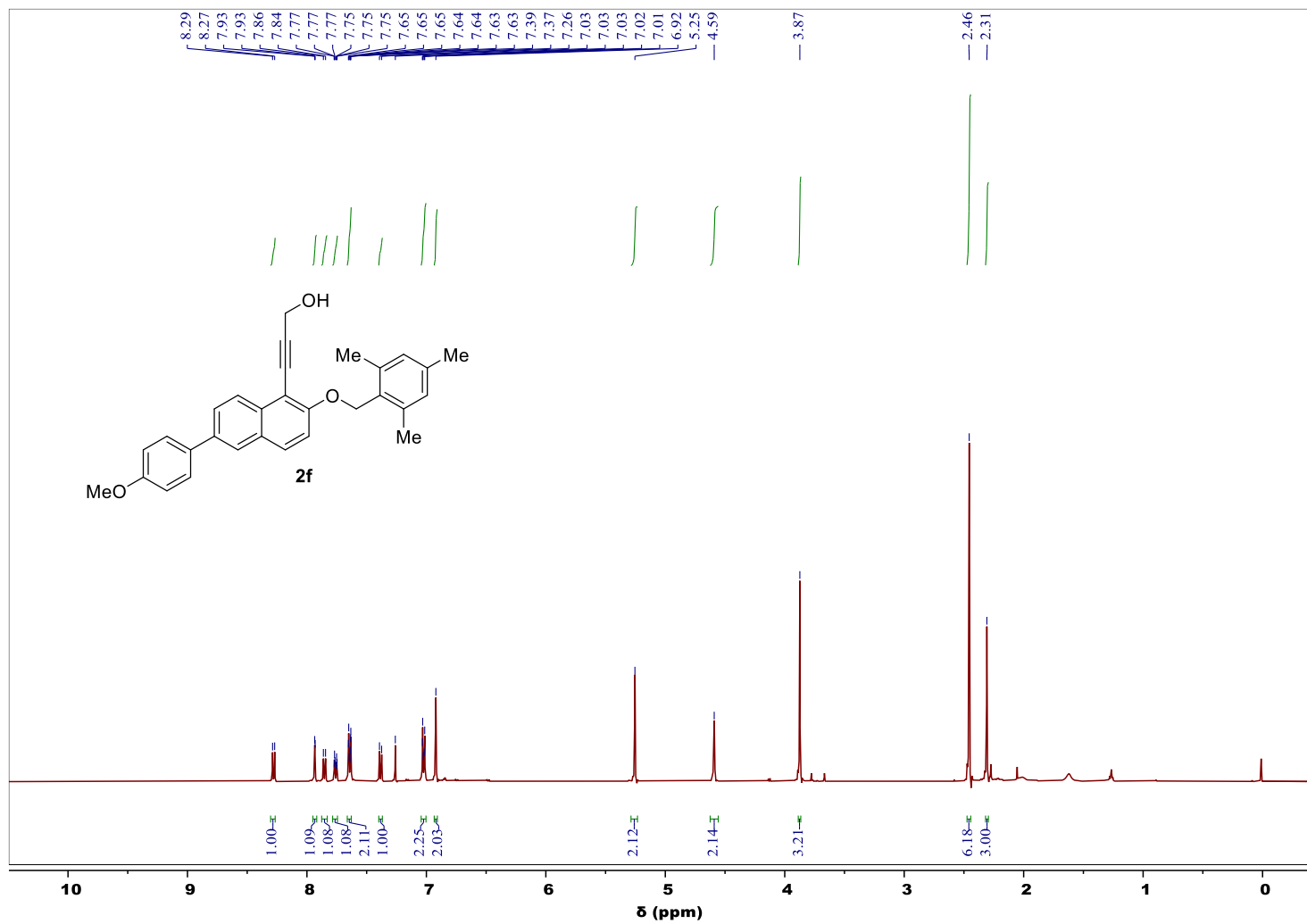
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2d**



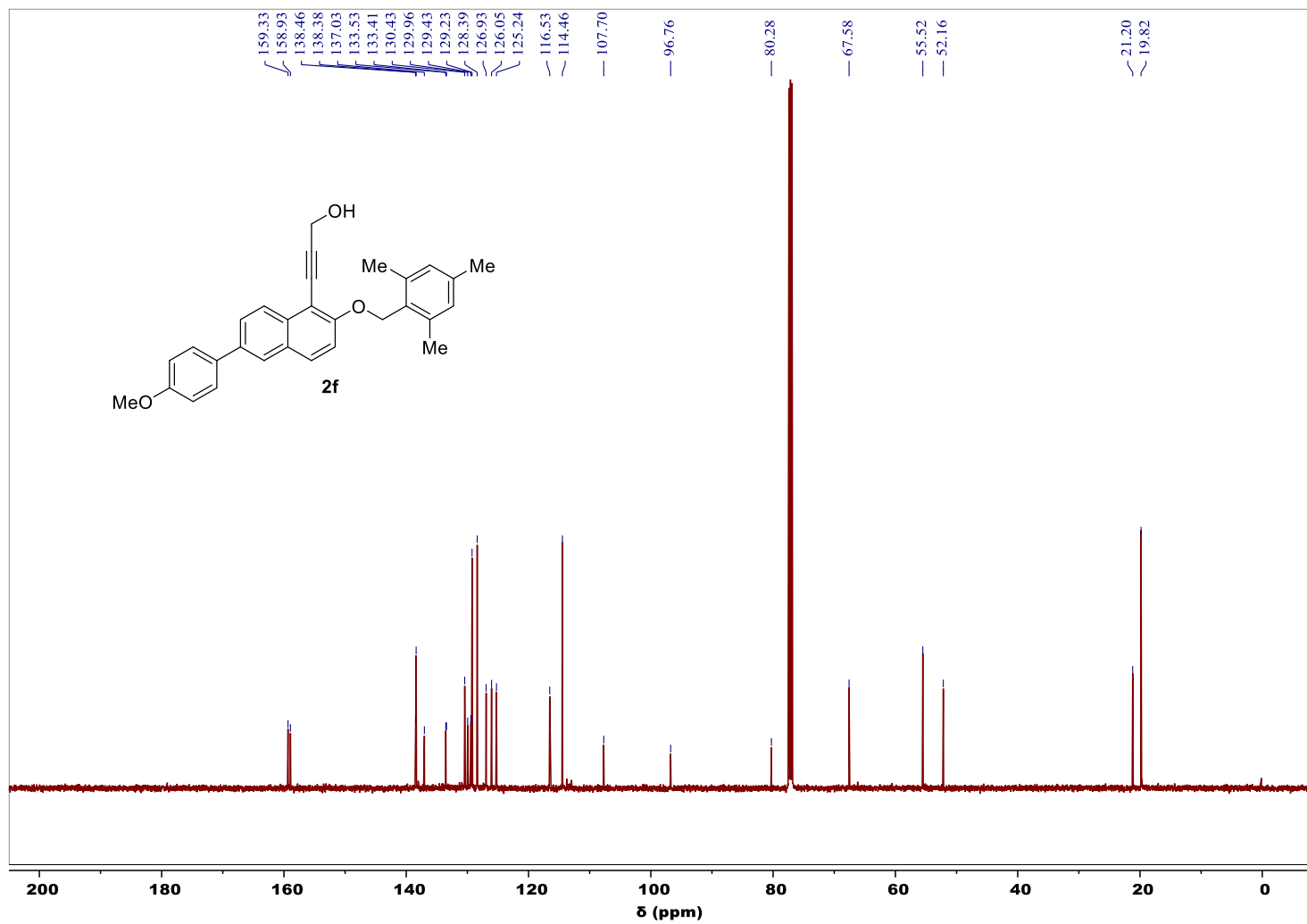
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2e**



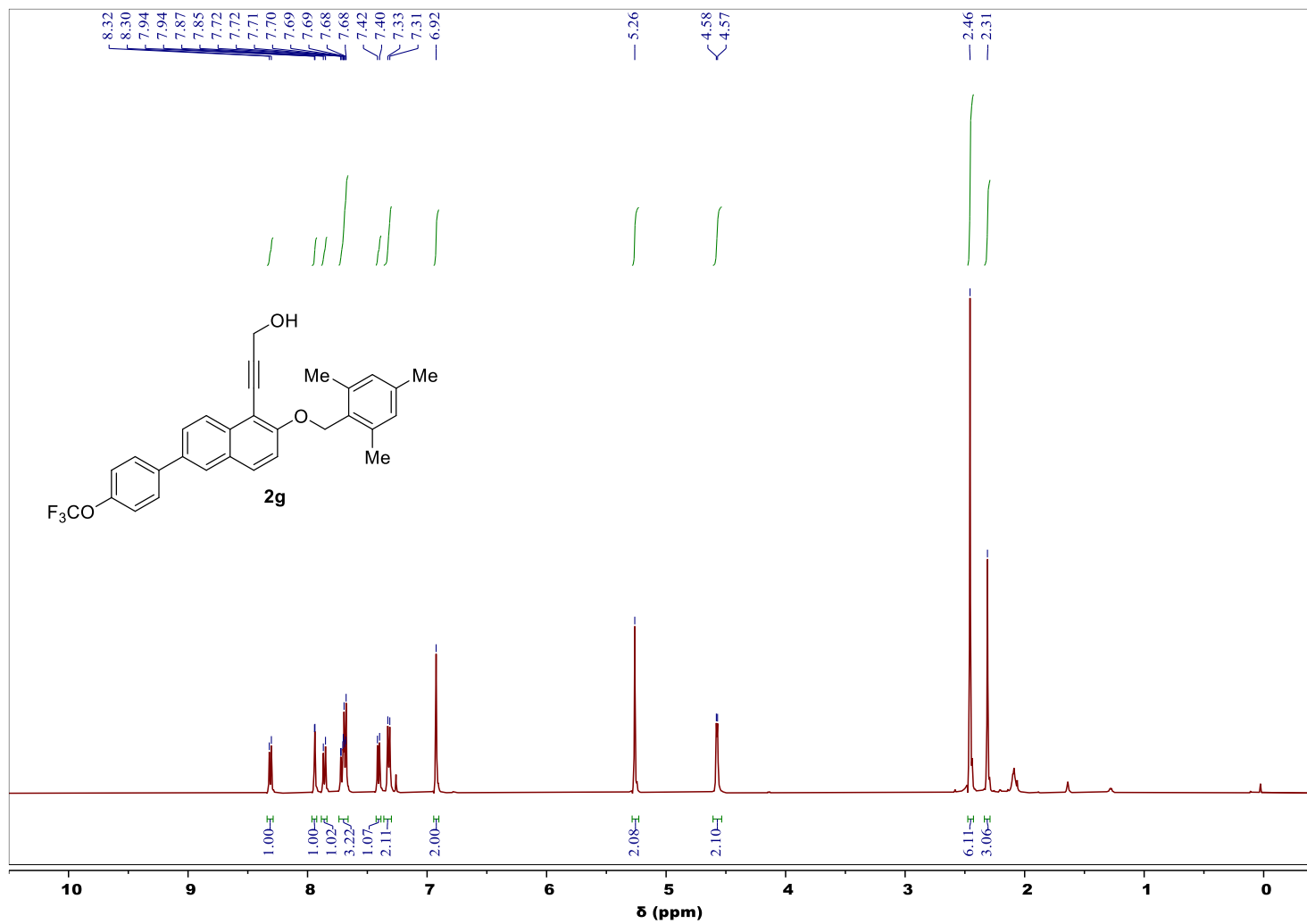
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2f**



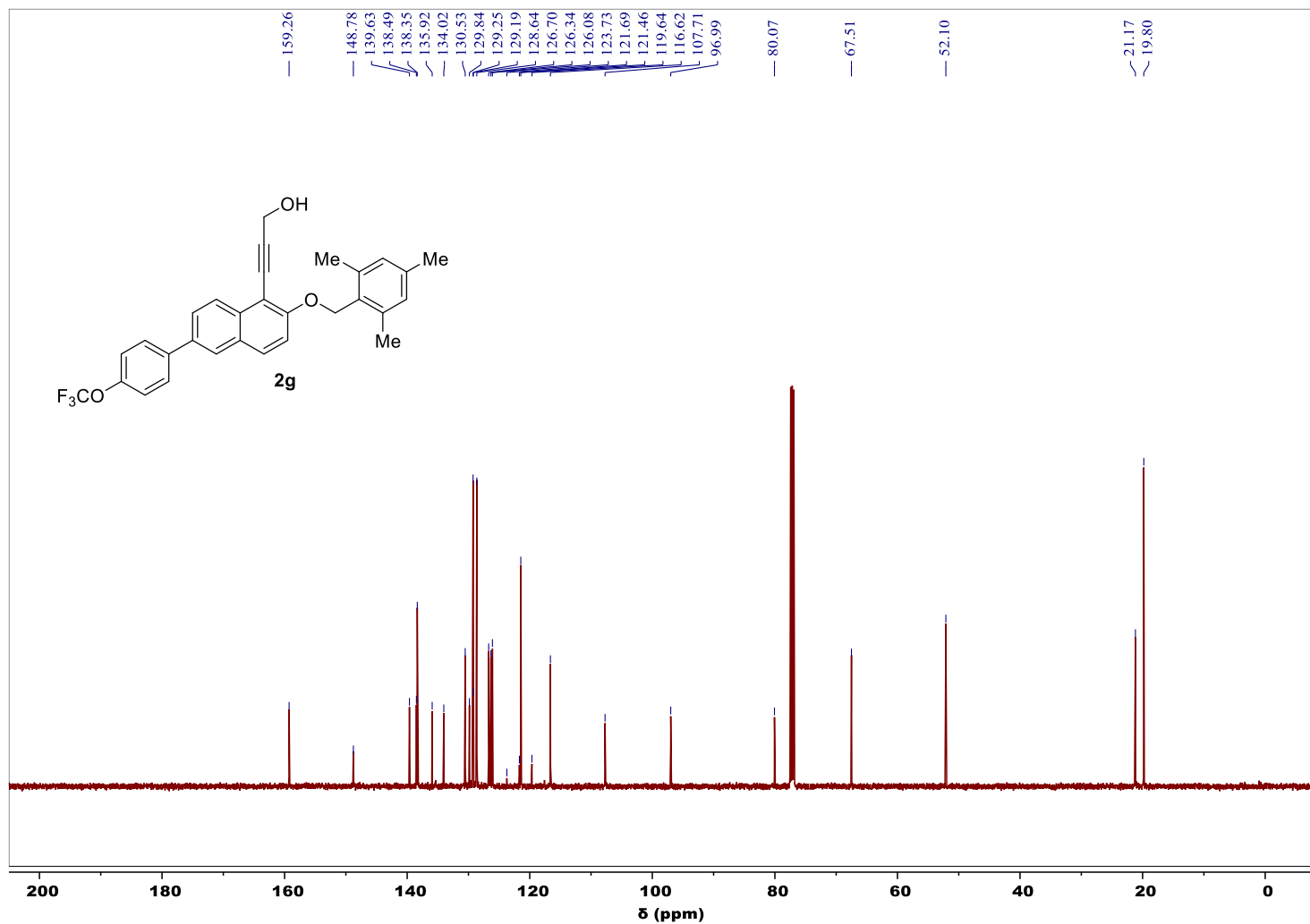
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2f**



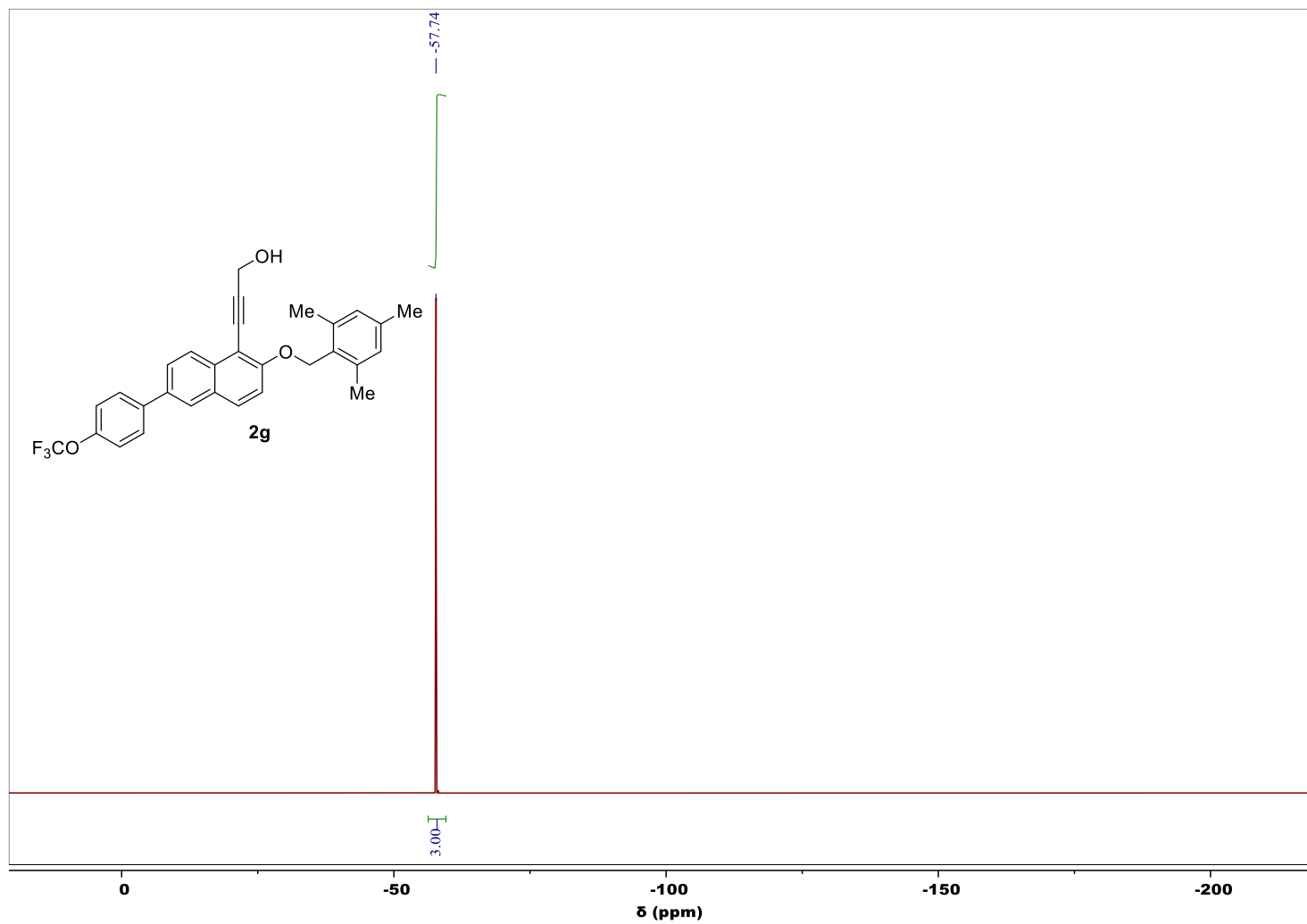
^1H NMR-spectrum (500 MHz, Chloroform- d) of **2g**



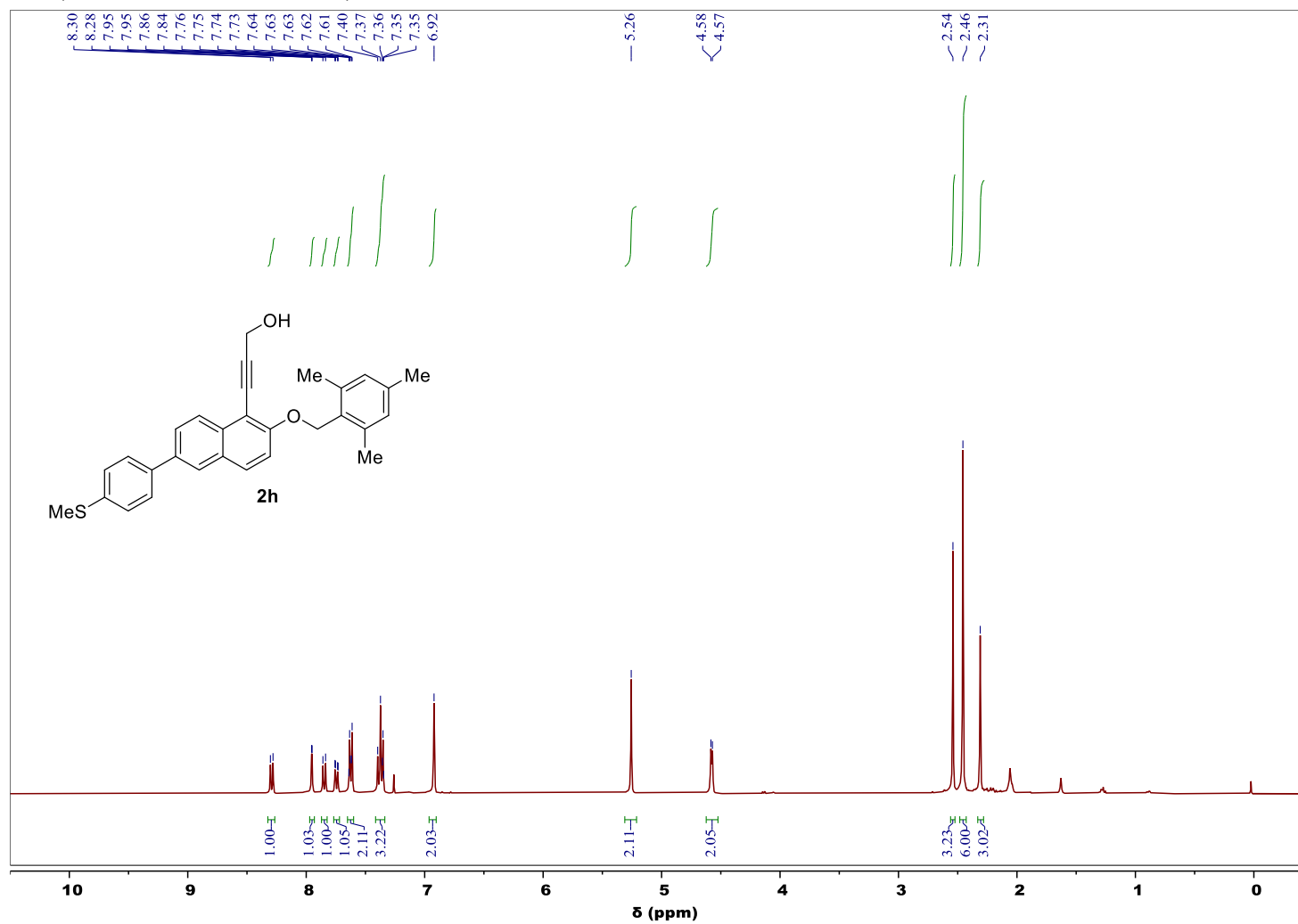
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2g**



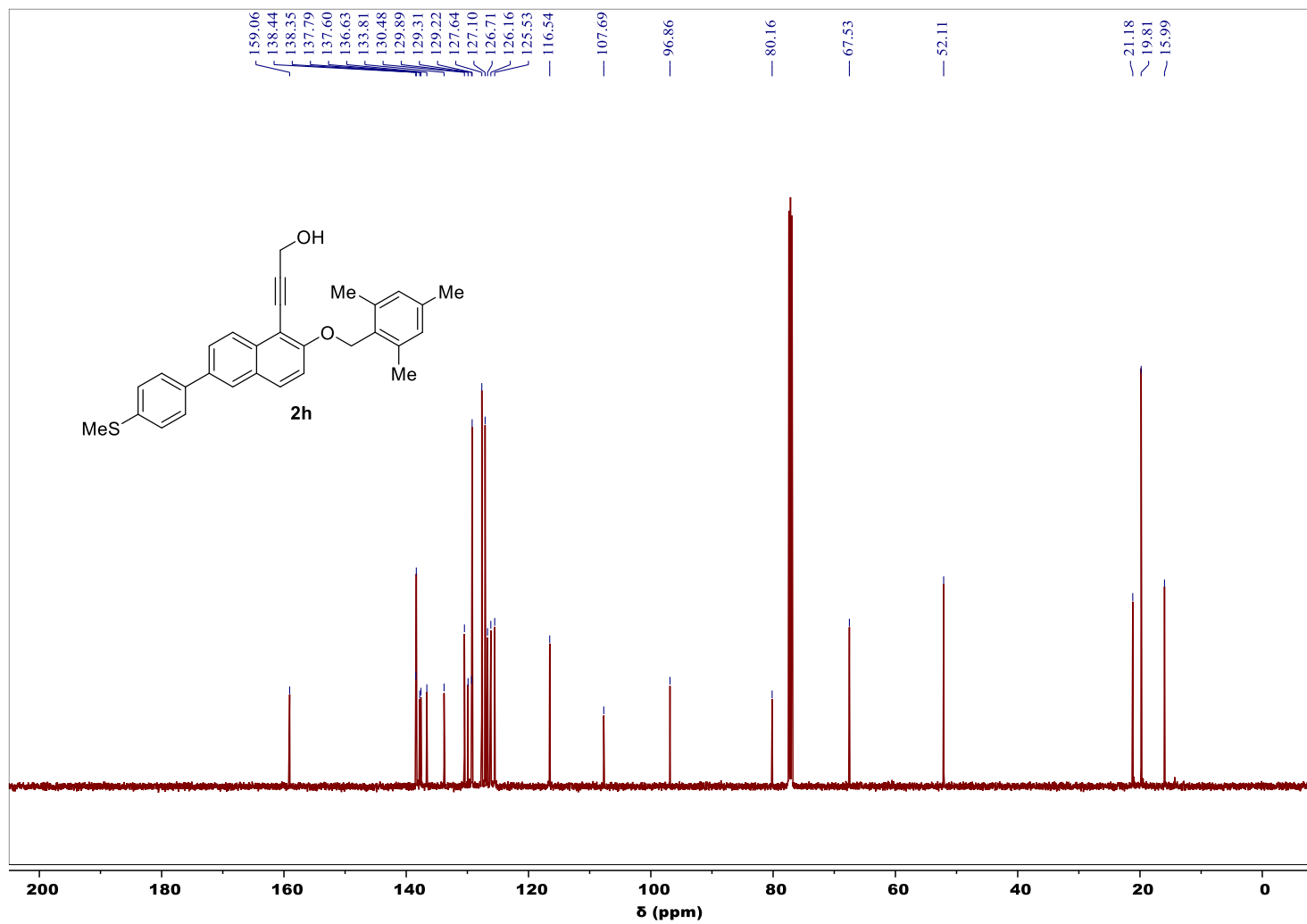
^{19}F NMR-spectrum (471 MHz, Chloroform-*d*) of **2g**



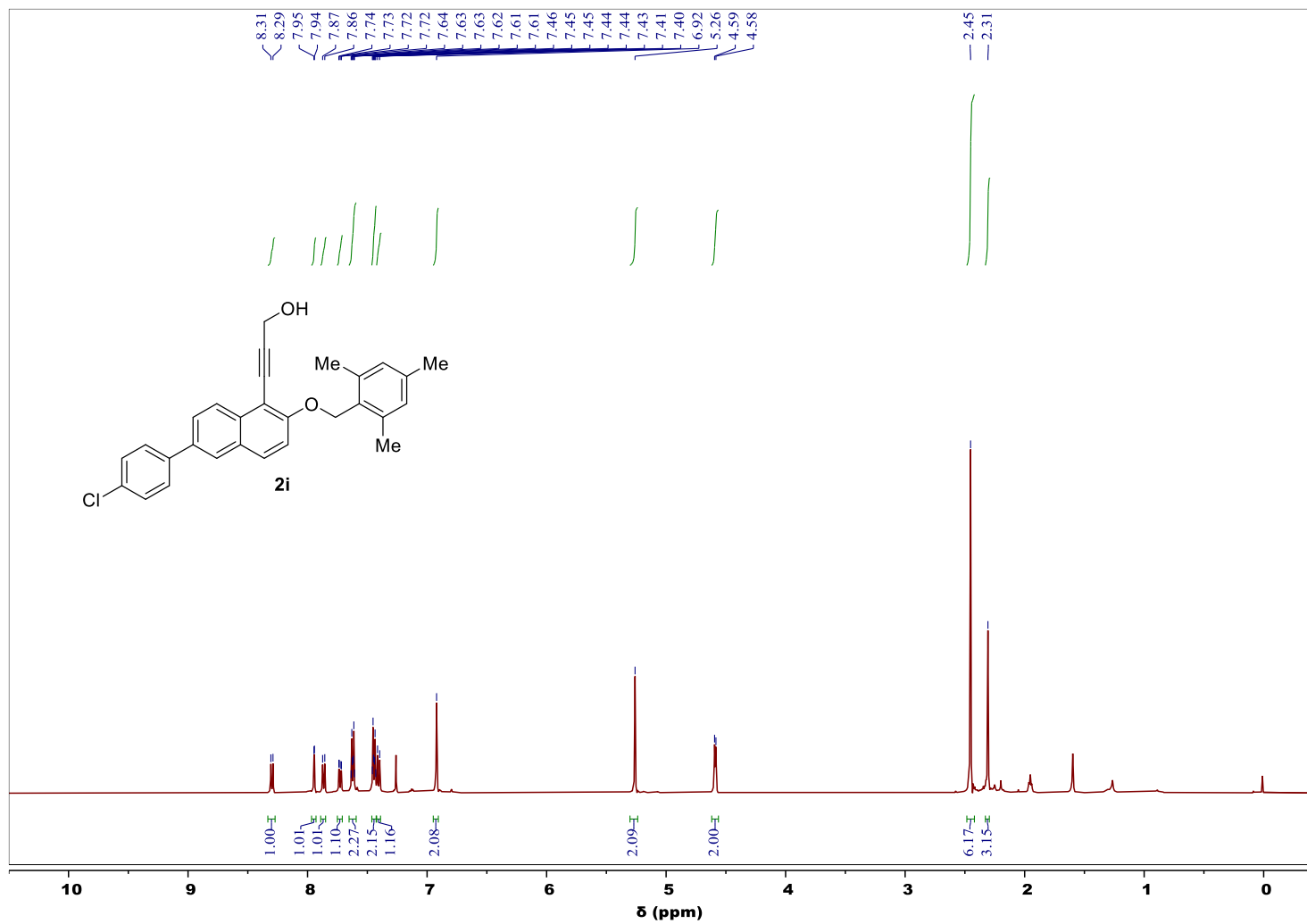
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2h**



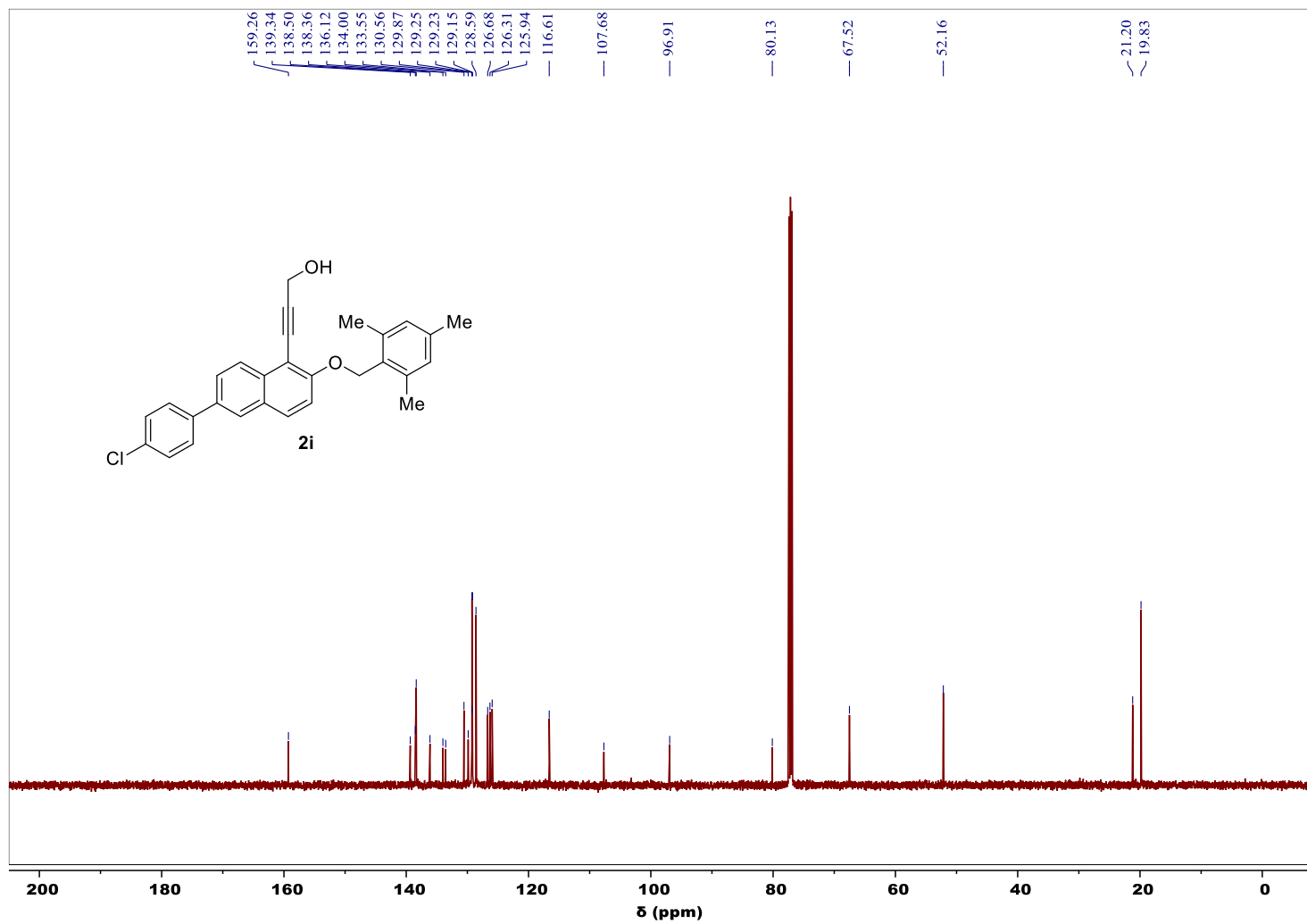
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2h**



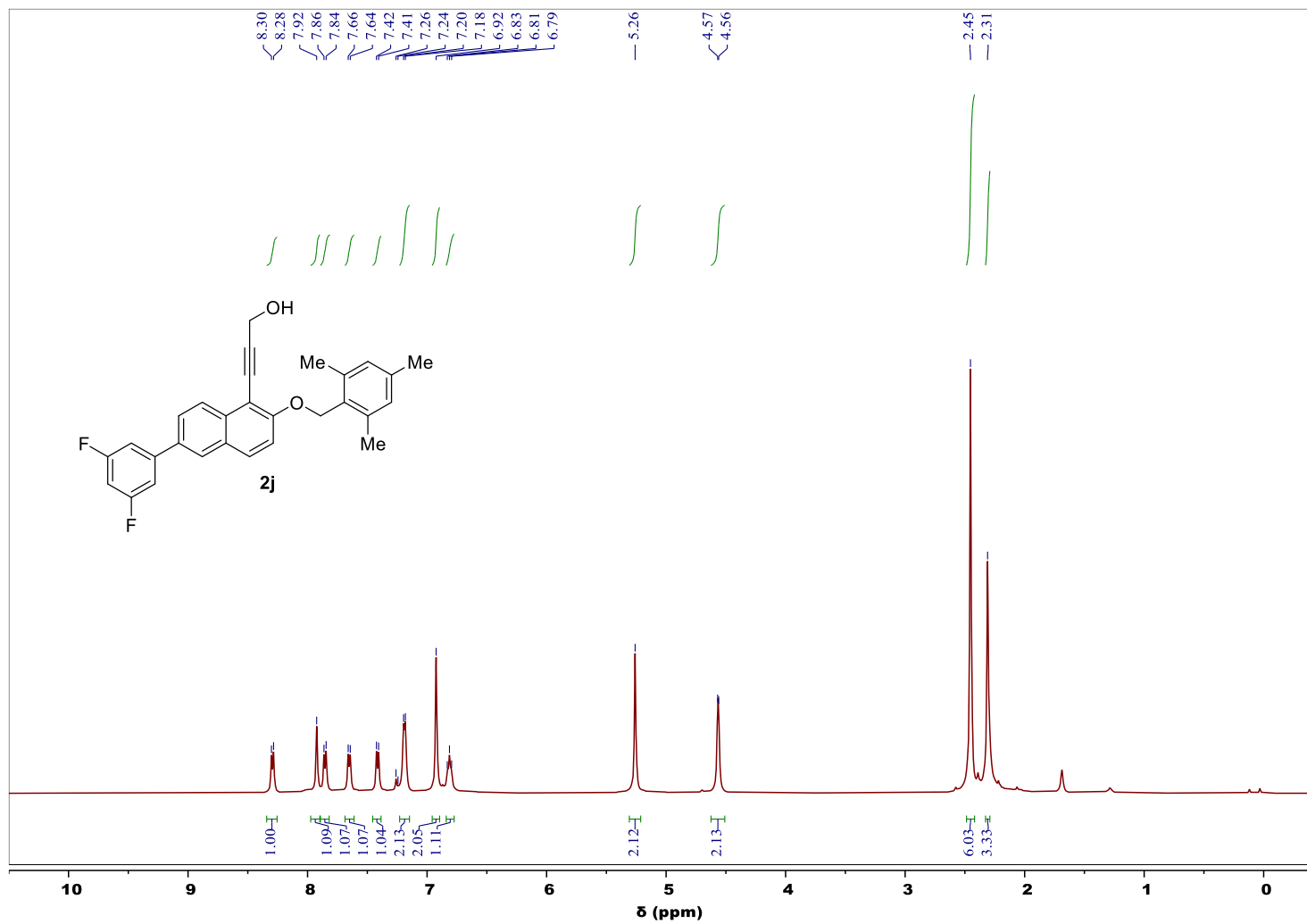
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2i**



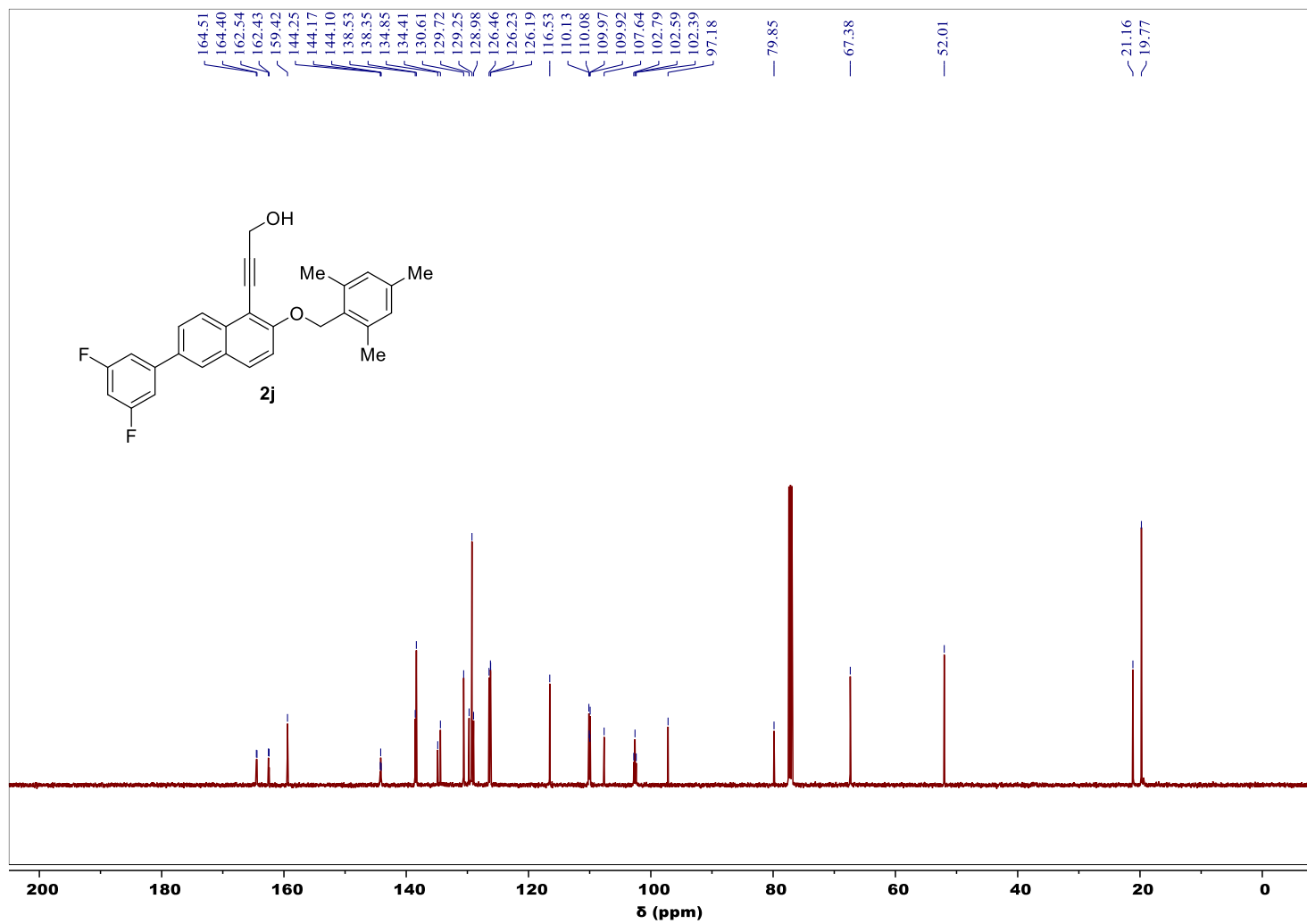
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2i**



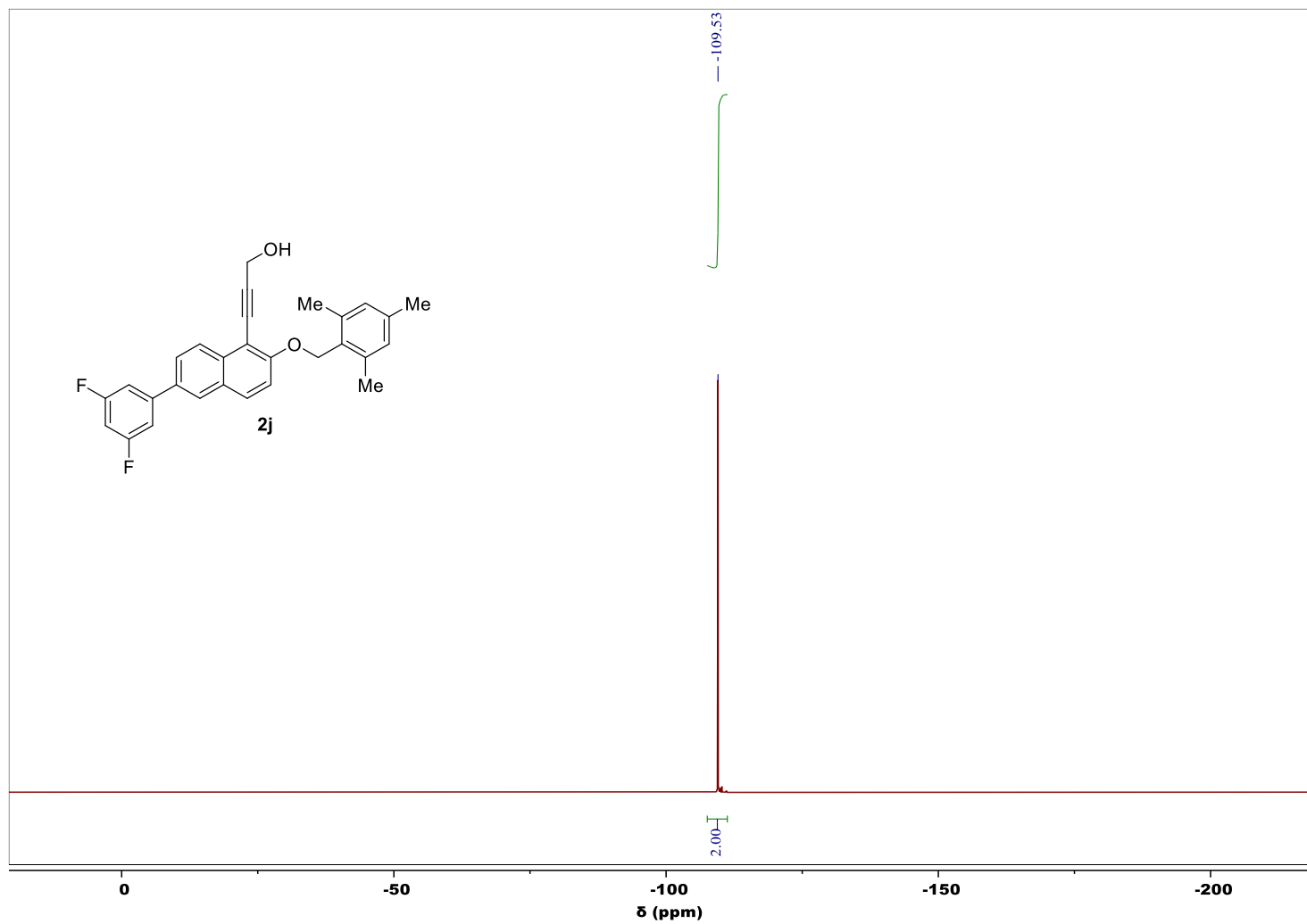
^1H NMR-spectrum (500 MHz, Chloroform- d) of **2j**



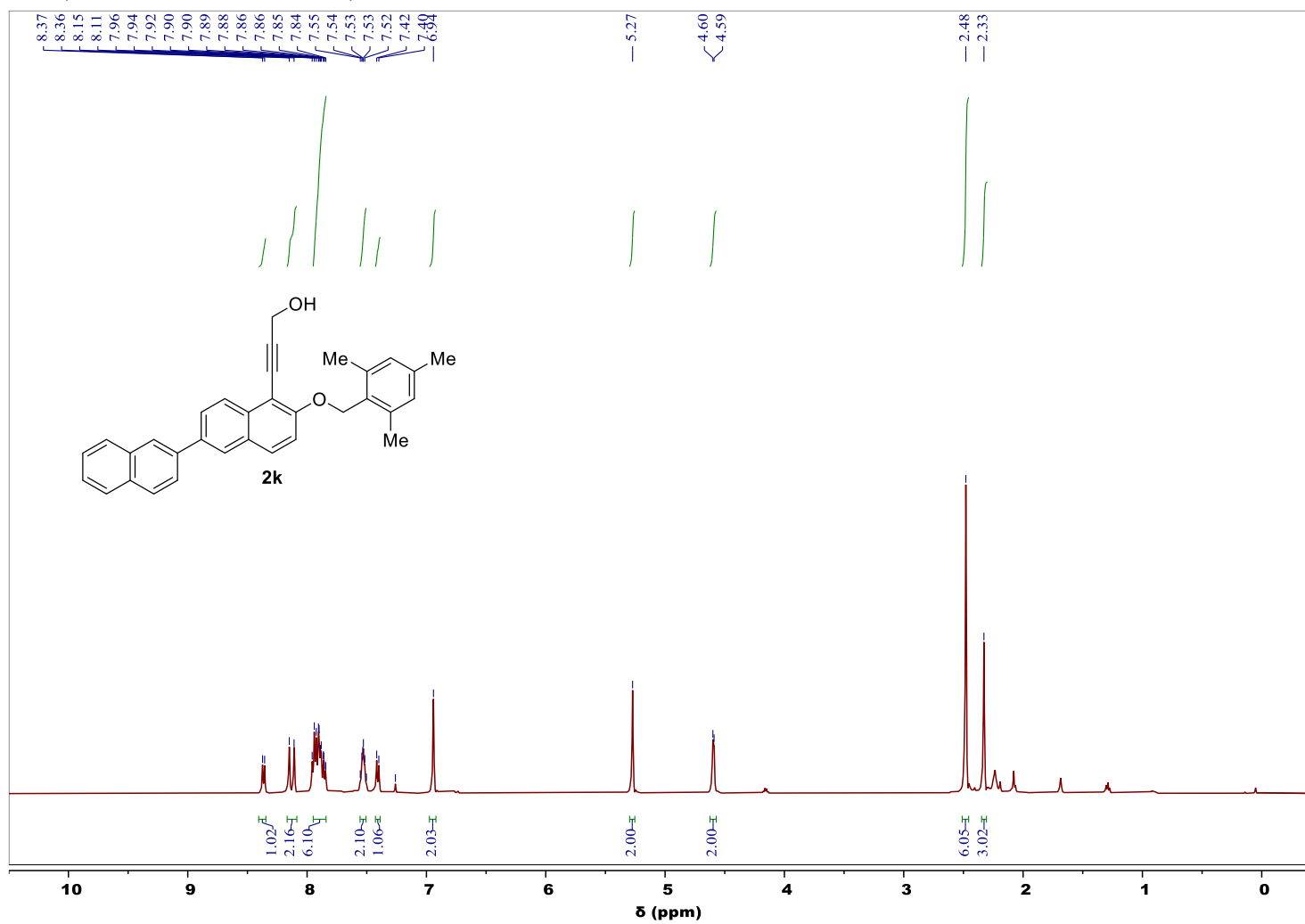
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2j**



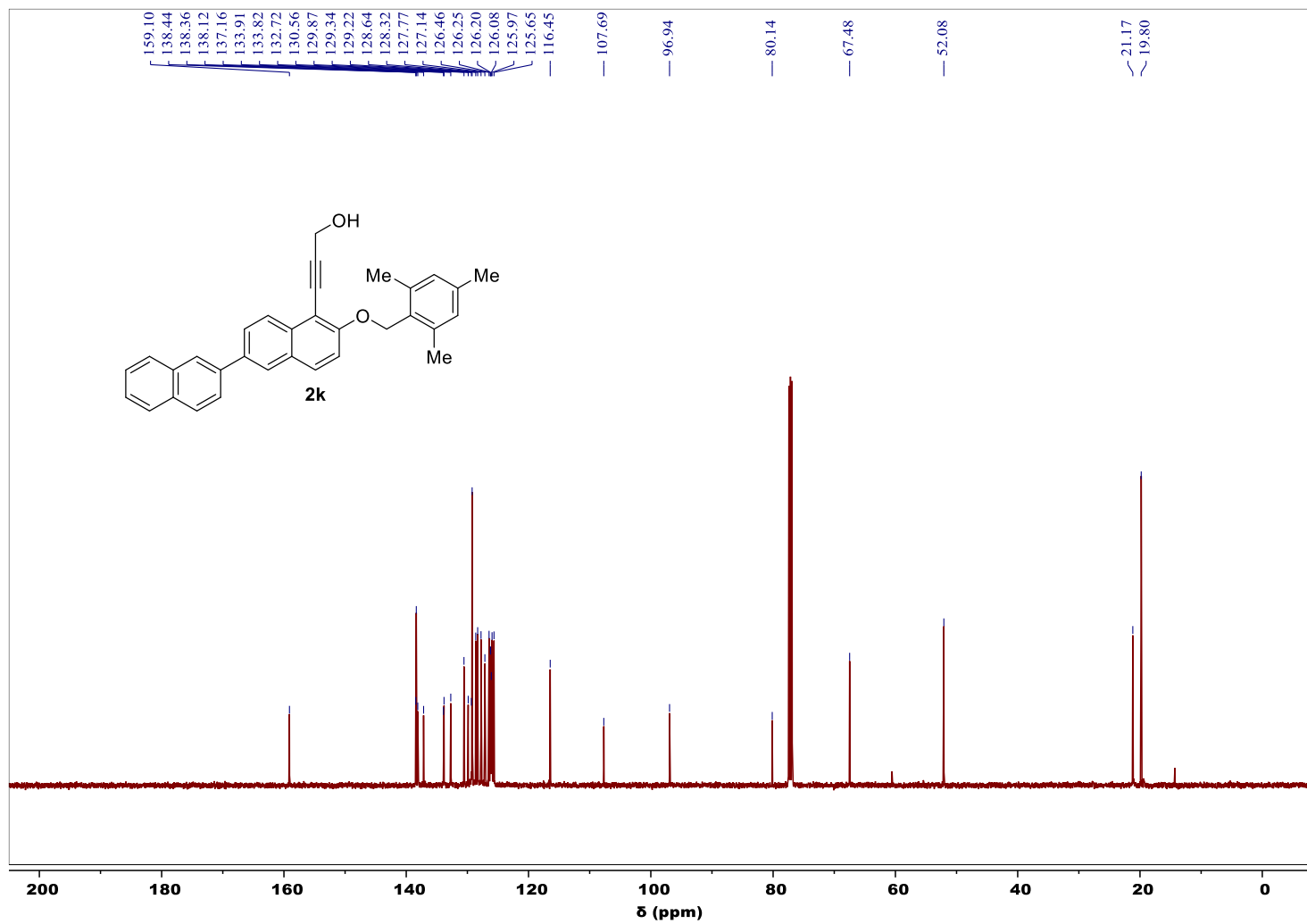
^{19}F NMR-spectrum (471 MHz, Chloroform-*d*) of **2j**



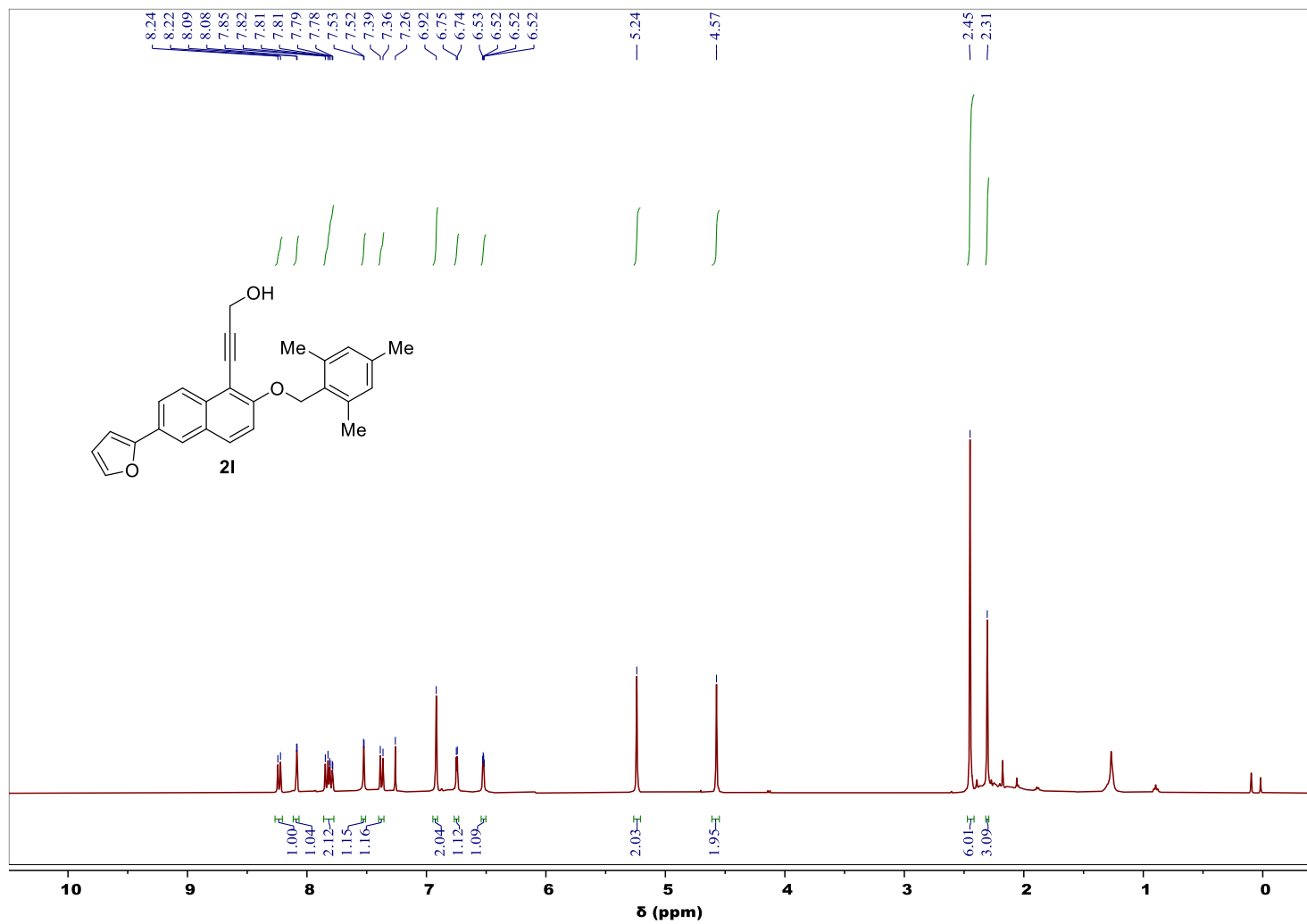
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2k**



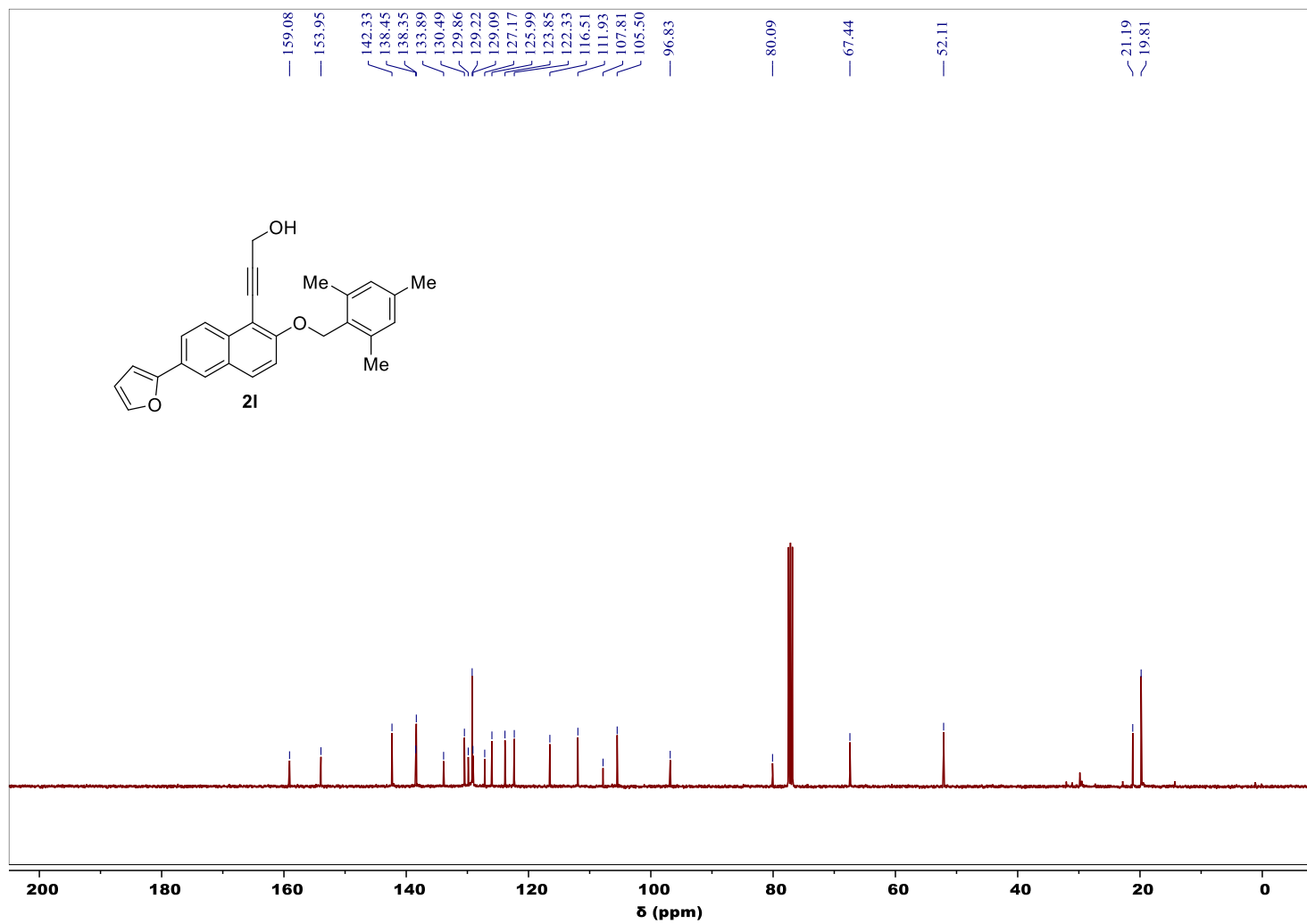
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2k**



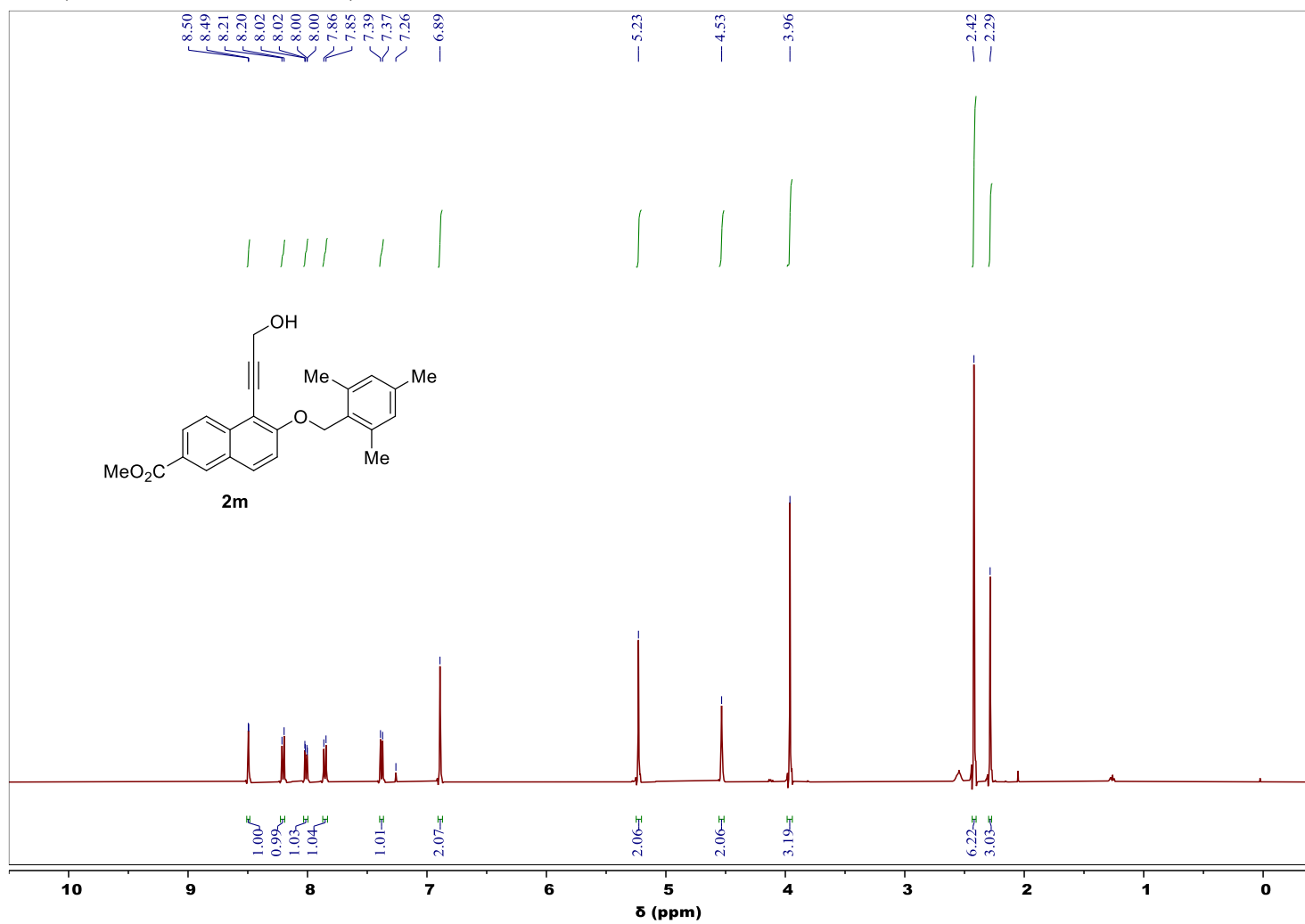
^1H NMR-spectrum (400 MHz, Chloroform- d) of **21**



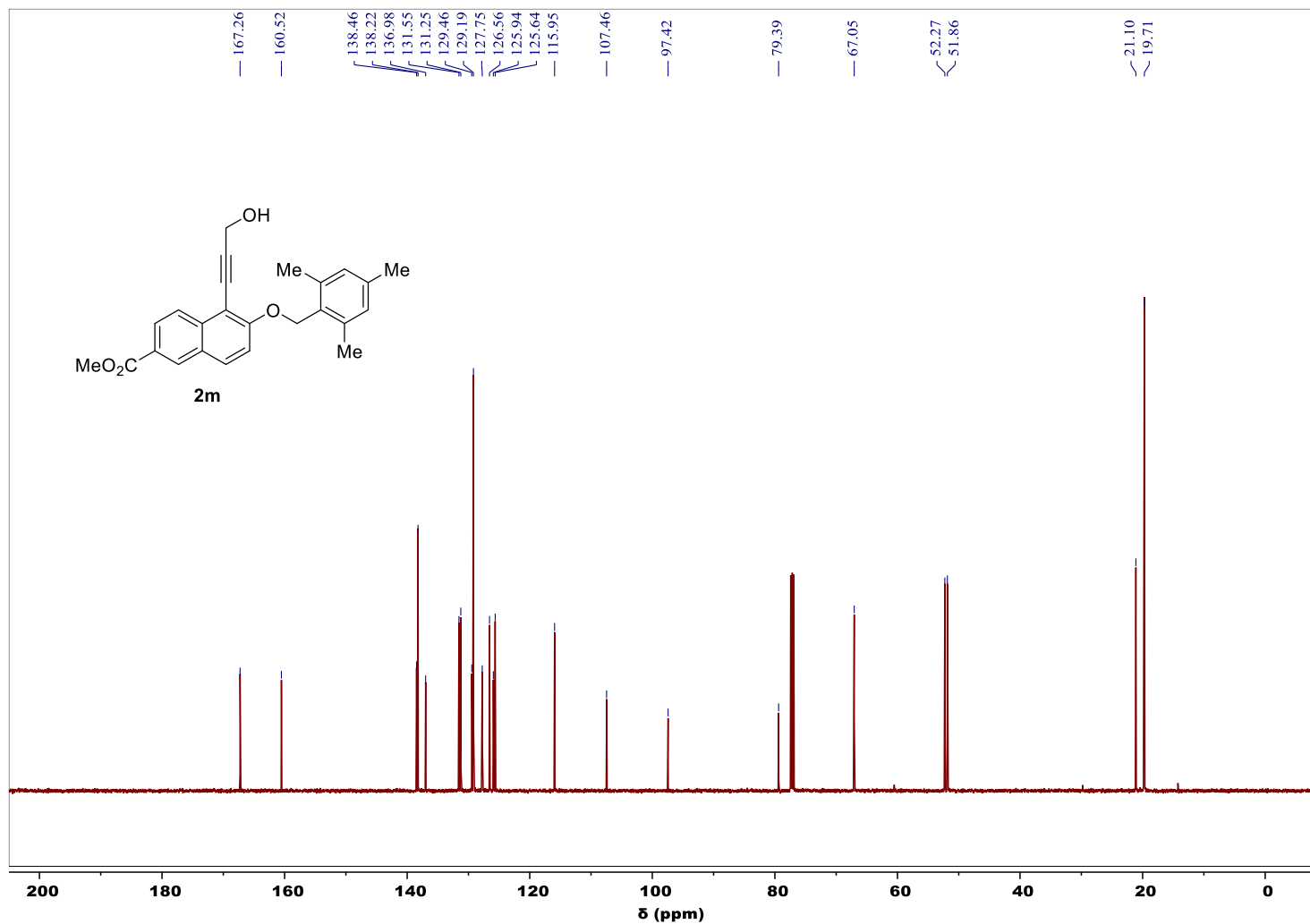
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **21**



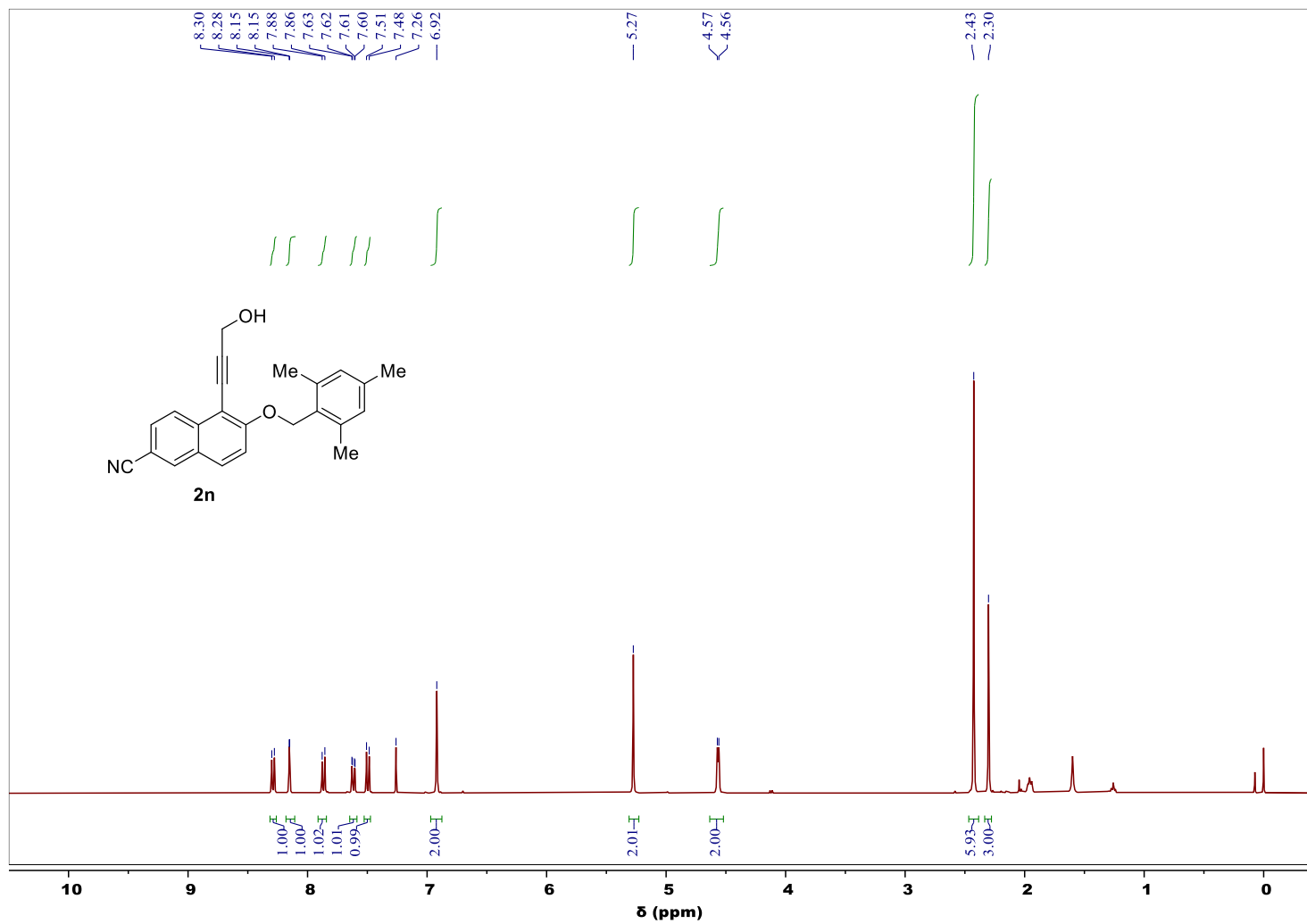
¹H NMR-spectrum (500 MHz, Chloroform-*d*) of **2m**



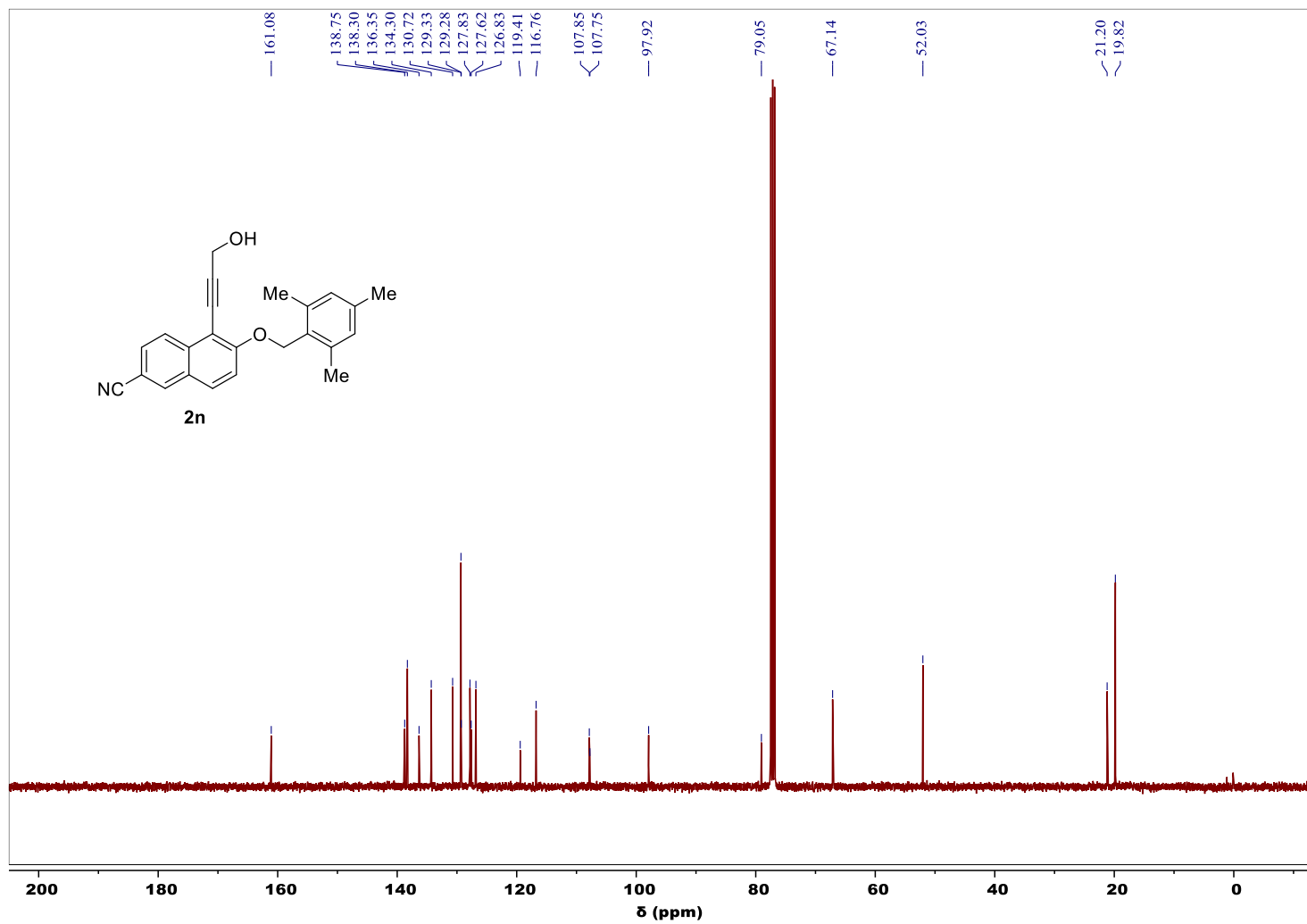
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2m**



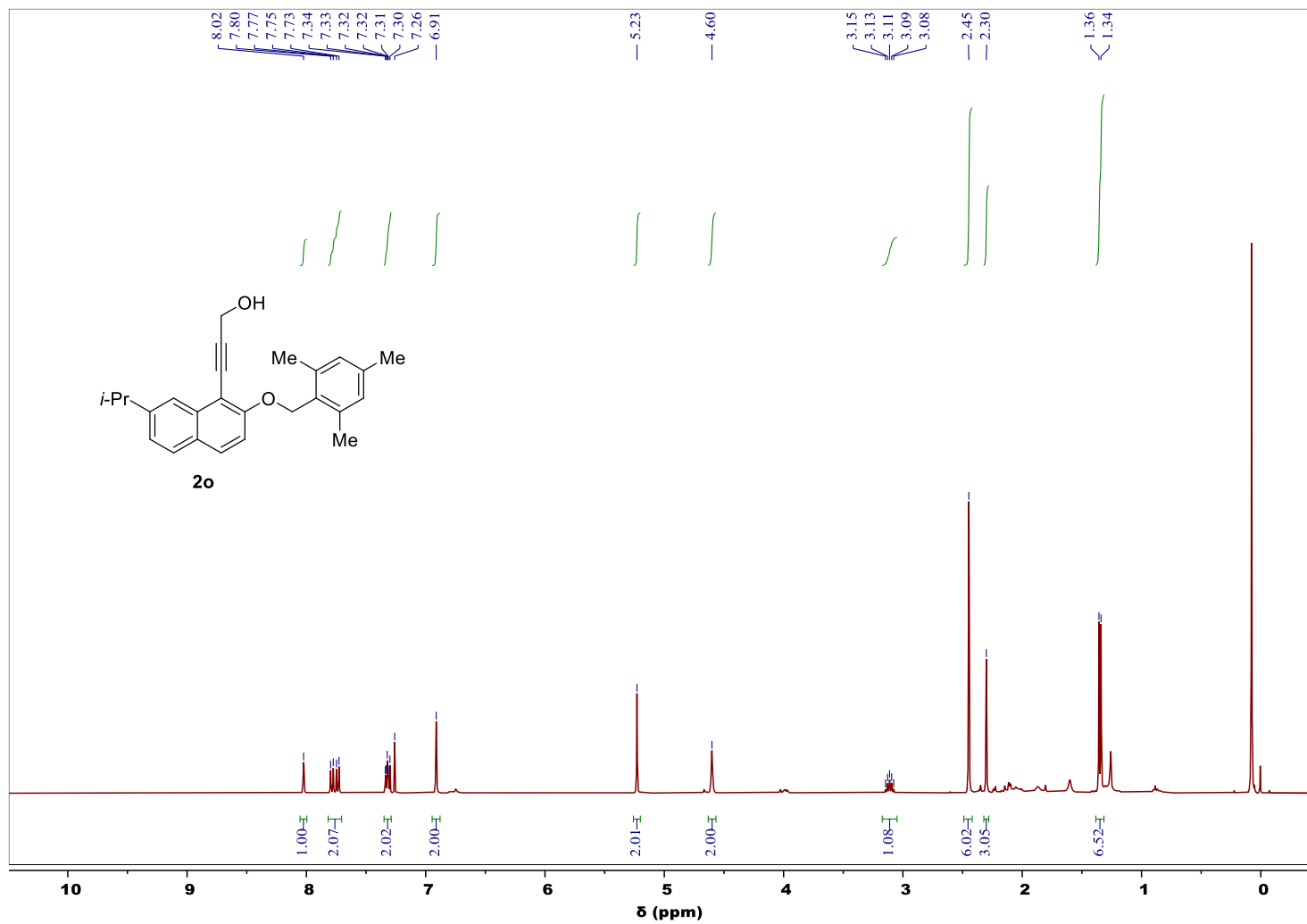
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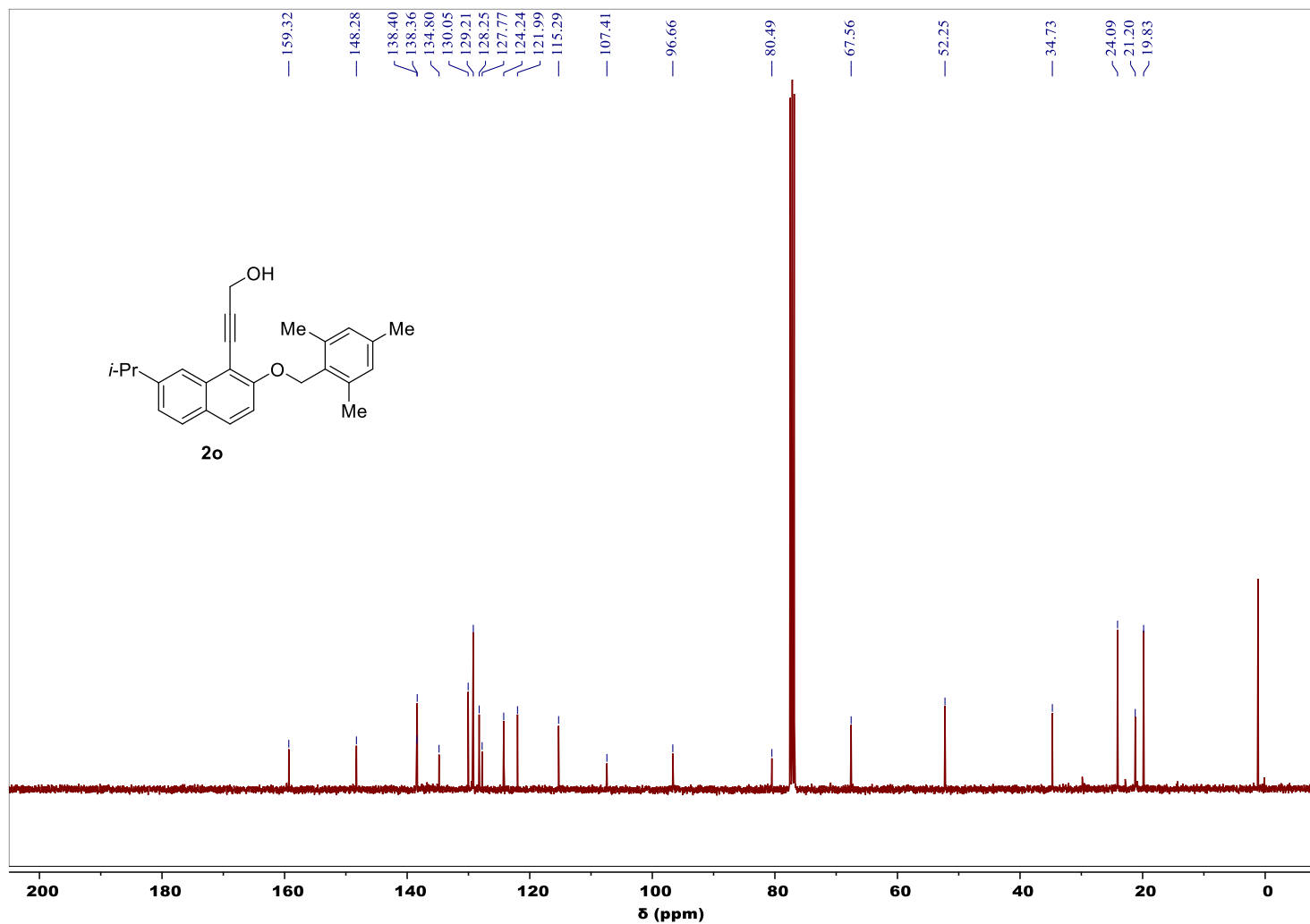
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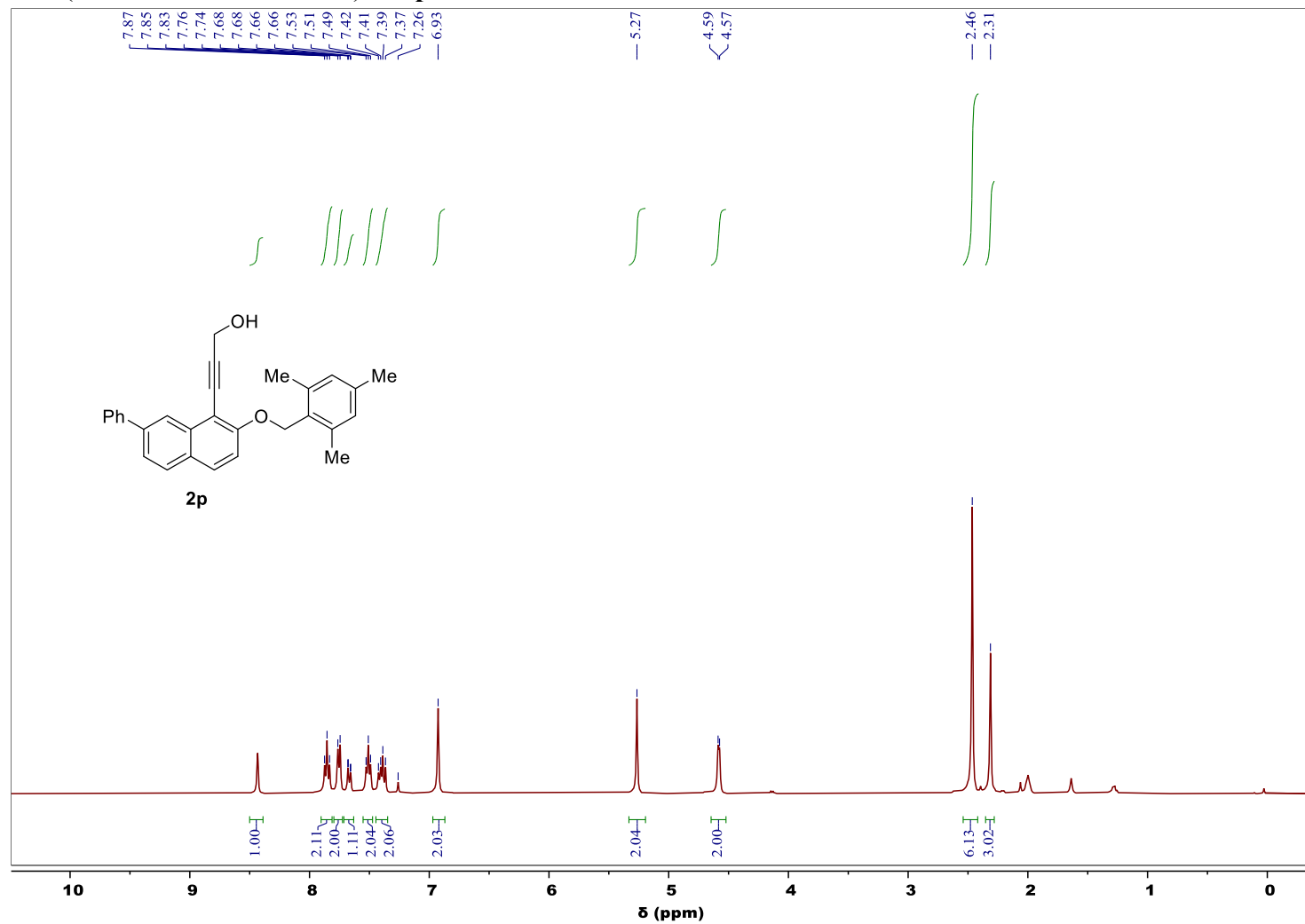
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2o**



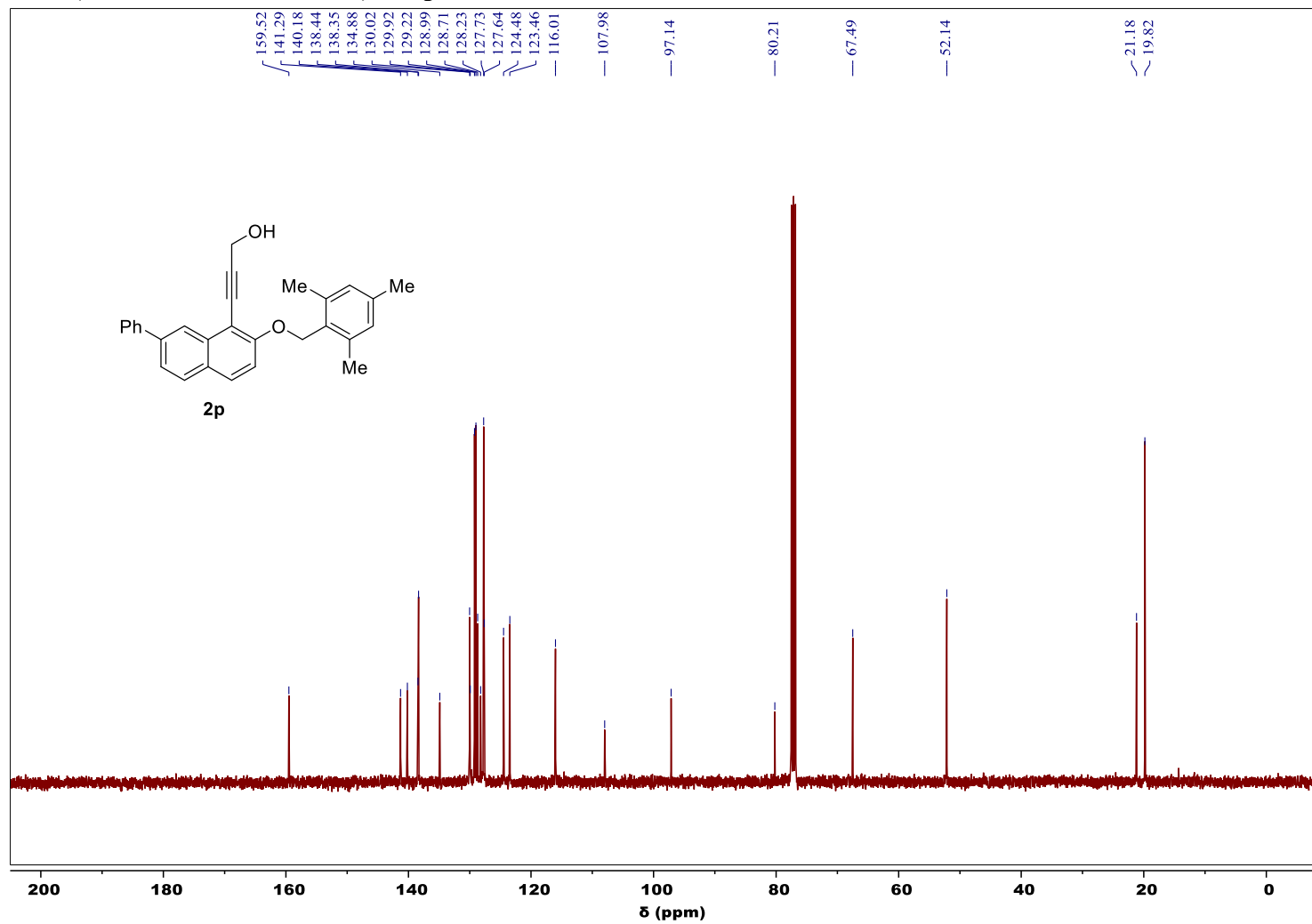
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2o**



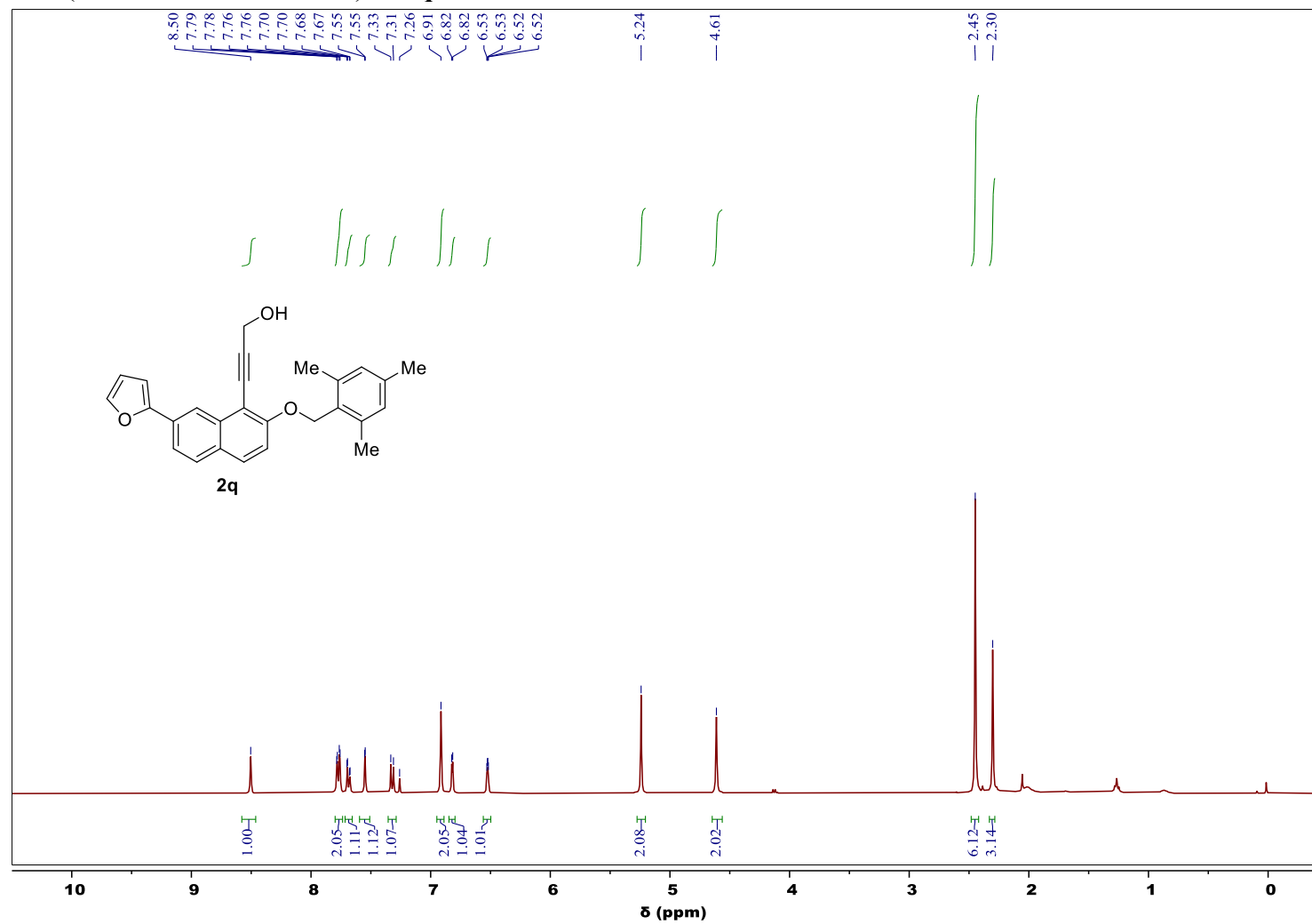
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2p**



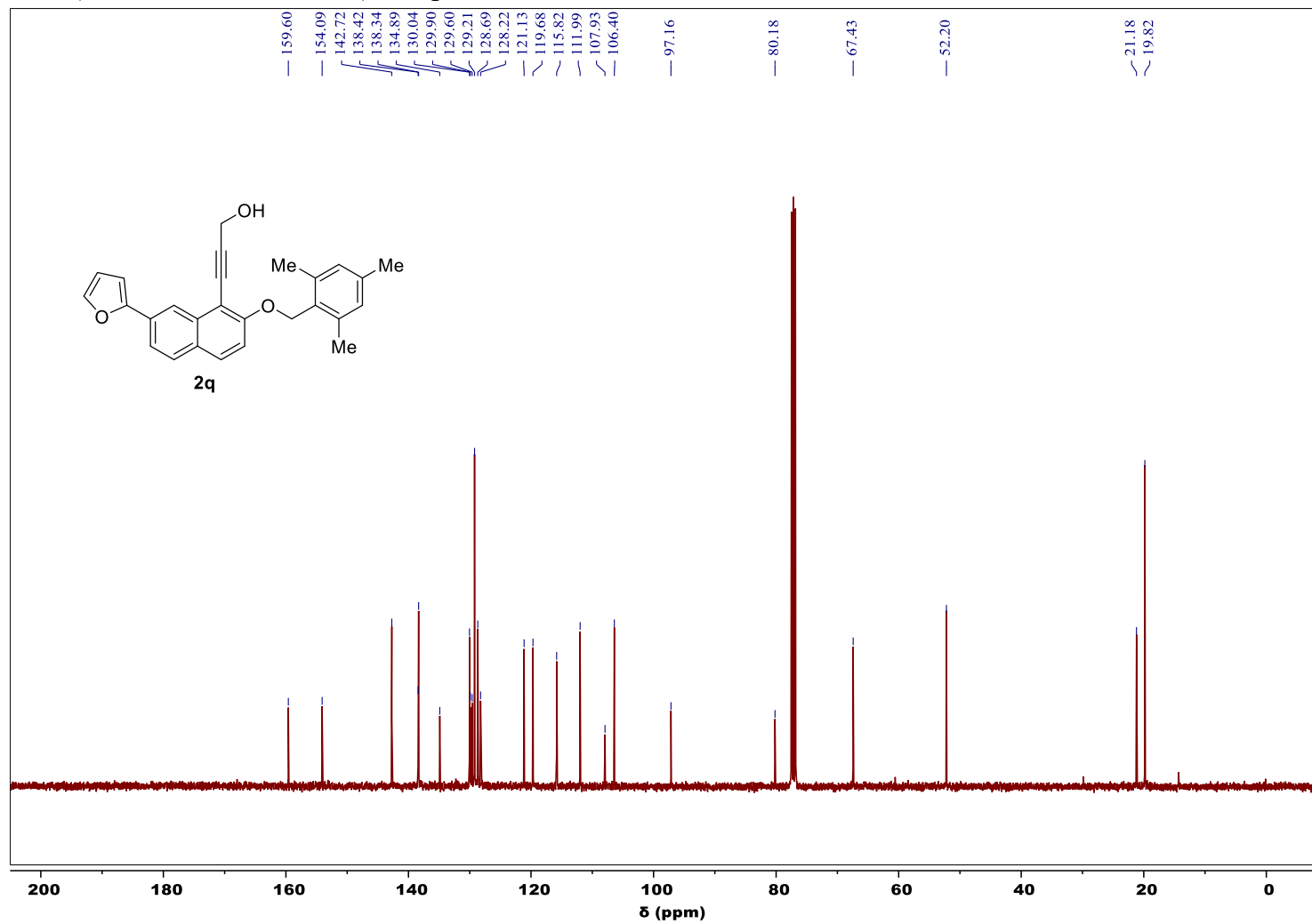
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2p**



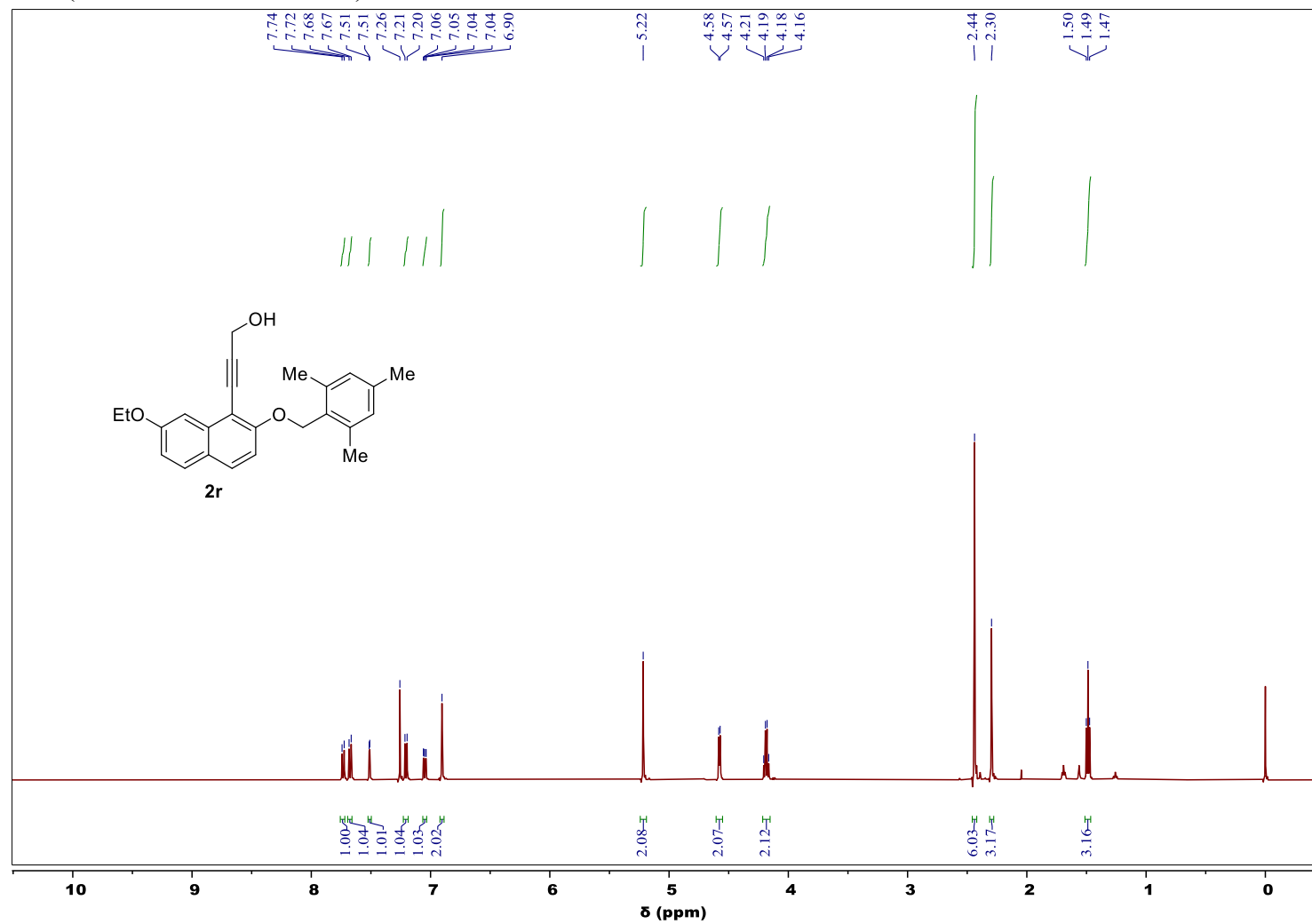
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2q**



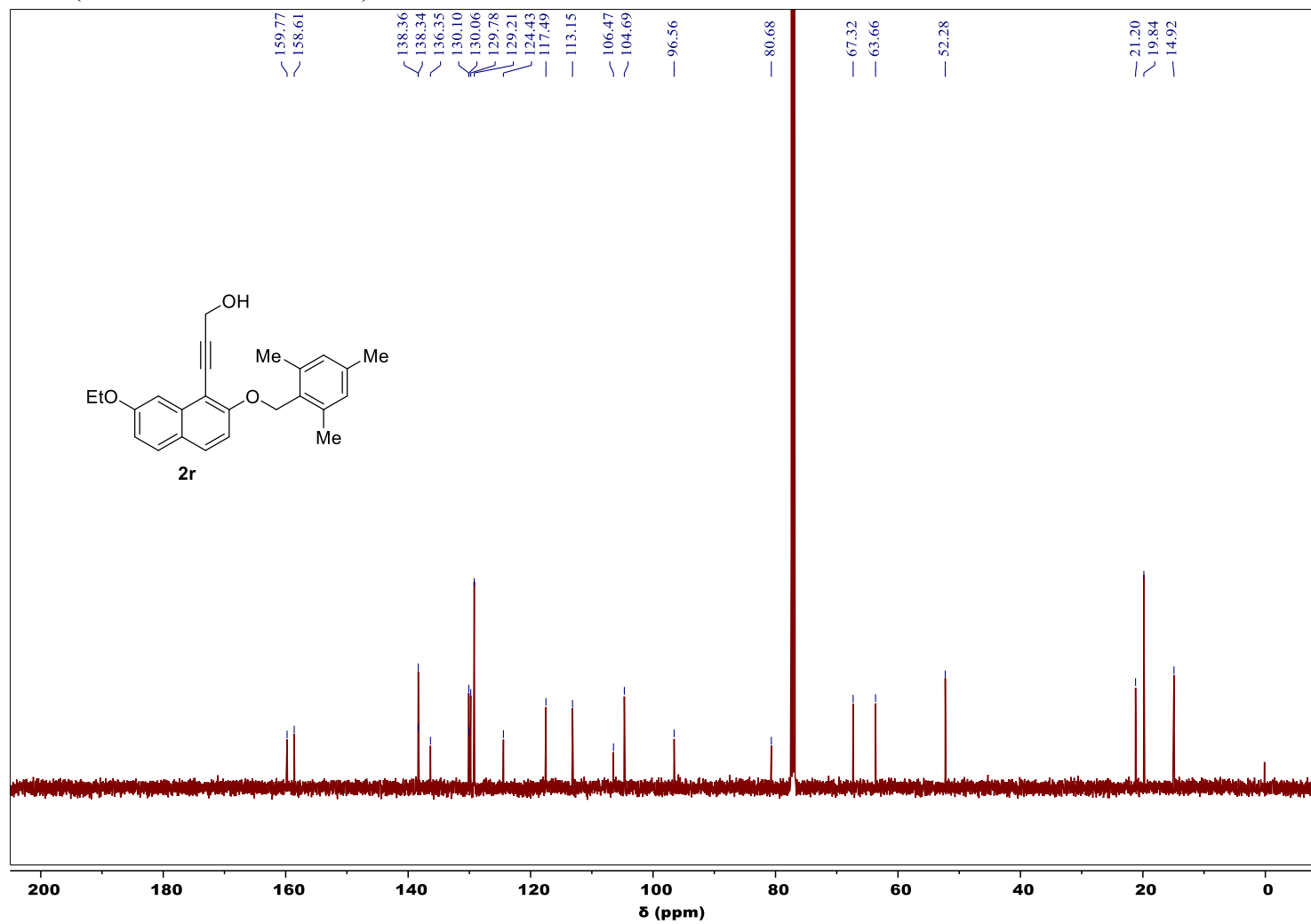
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2q**



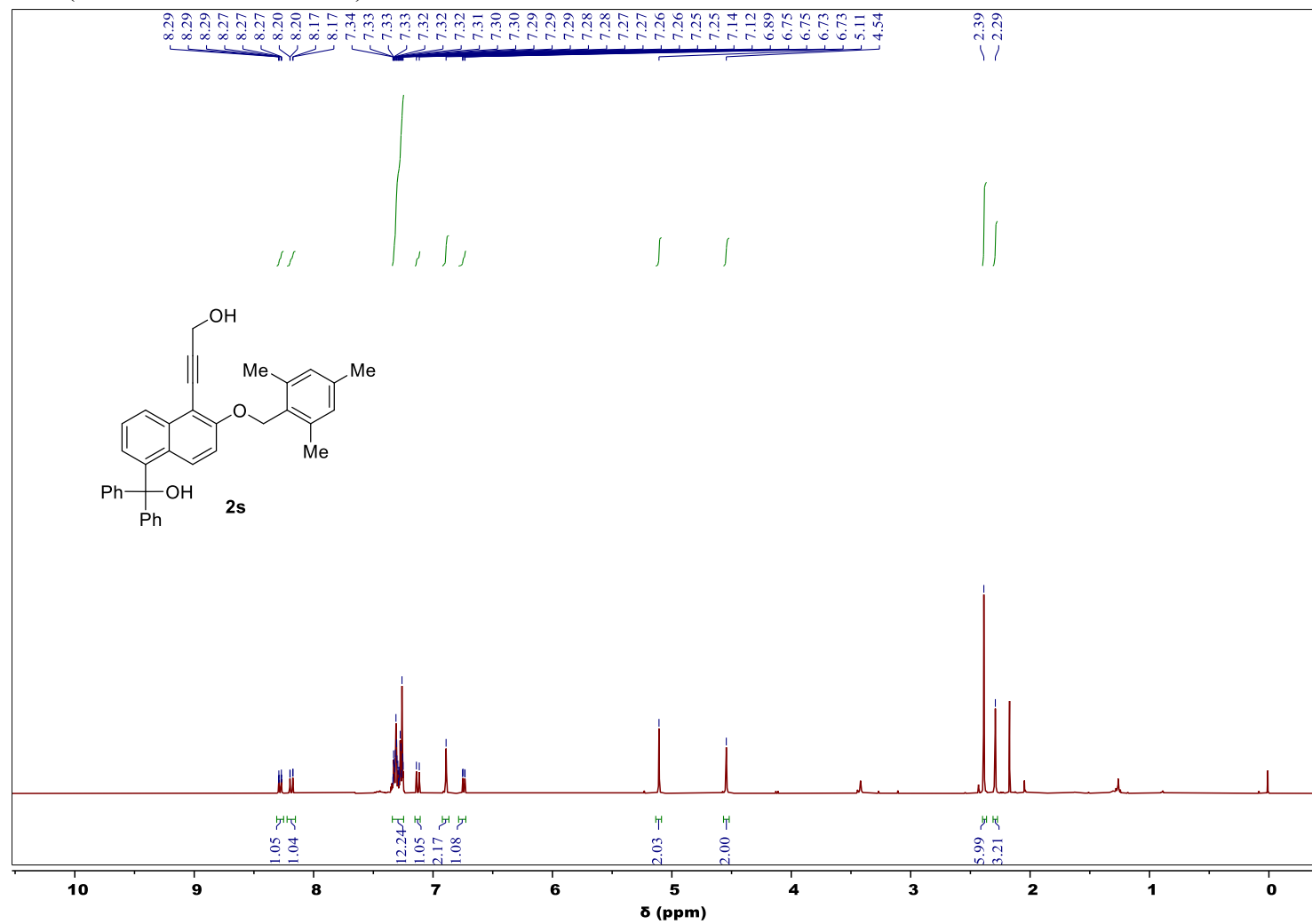
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2r**



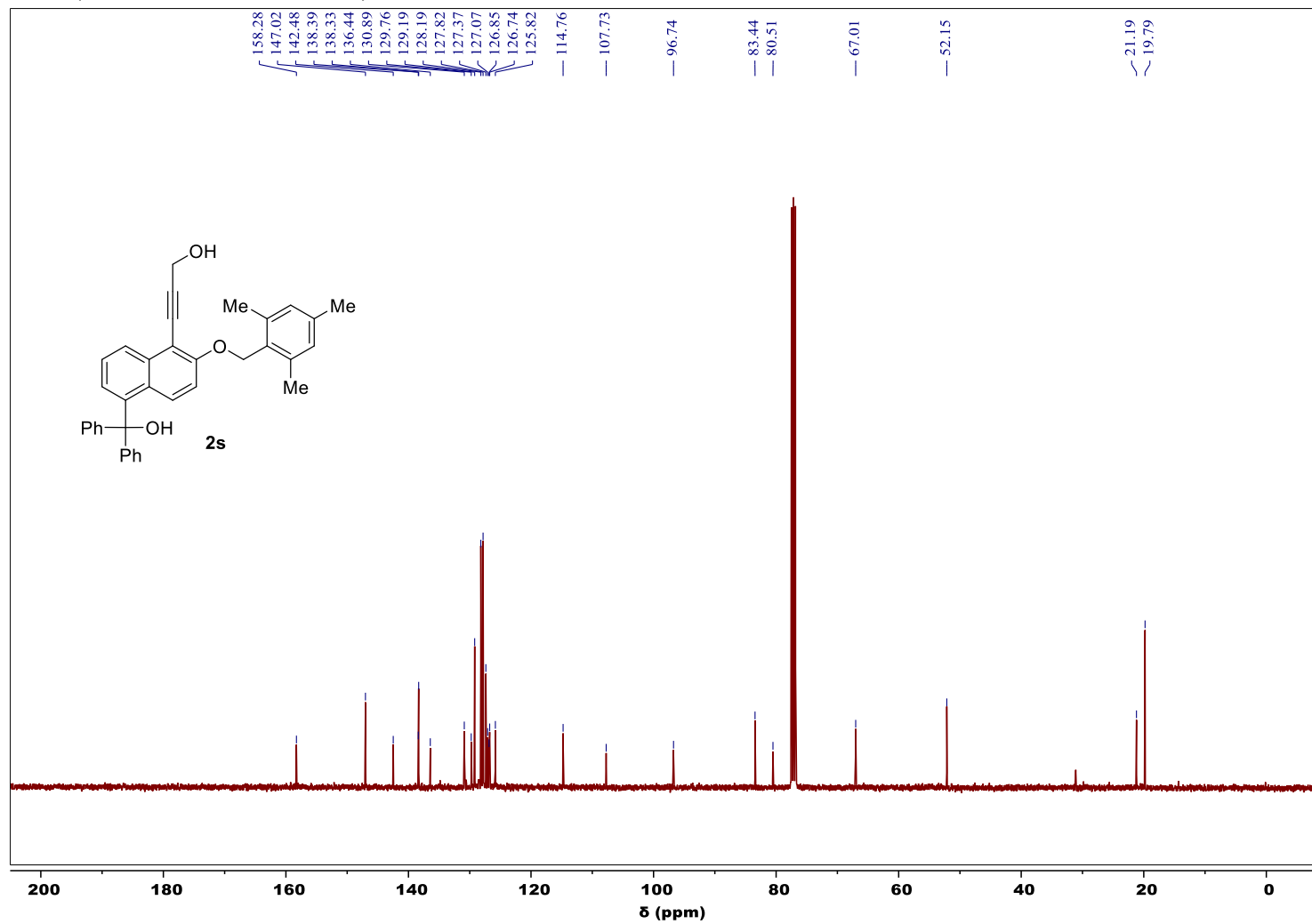
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2r**



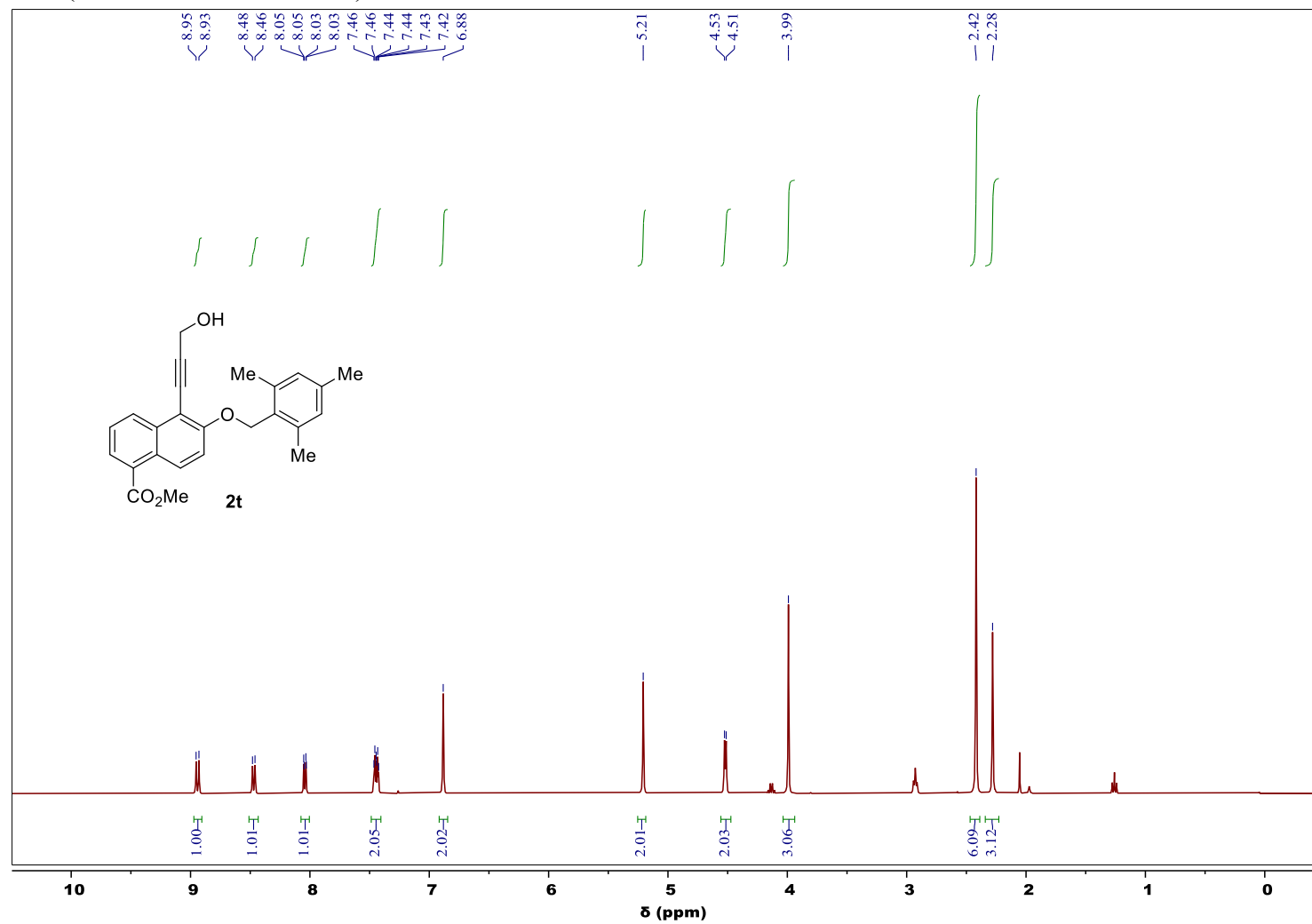
^1H NMR-spectrum (400 MHz, Chloroform- d) of **2s**



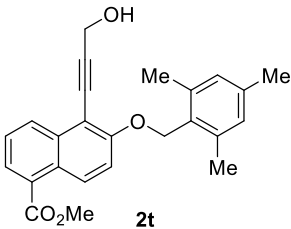
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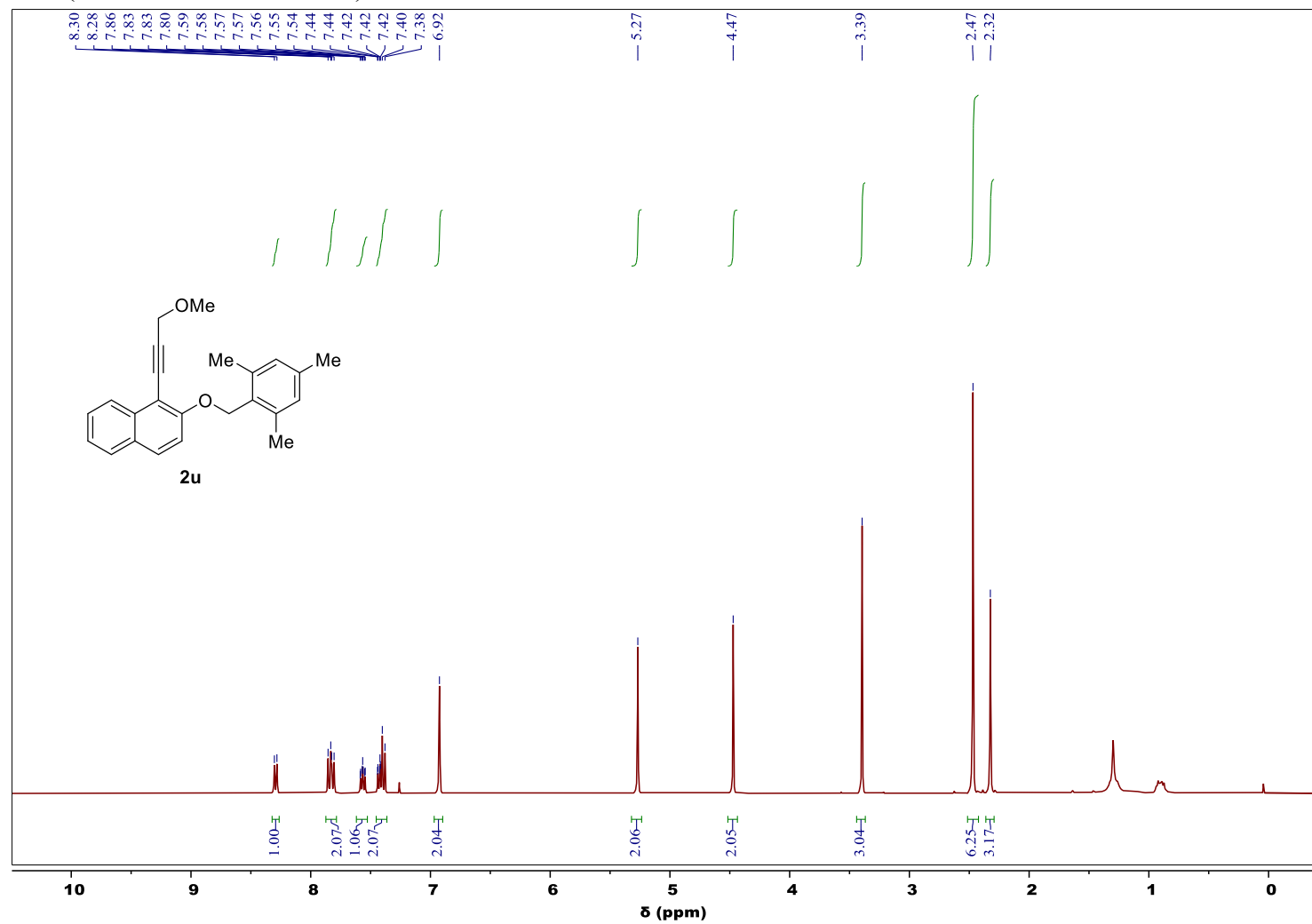
^1H NMR-spectrum (400 MHz, Chloroform- d) of **2t**



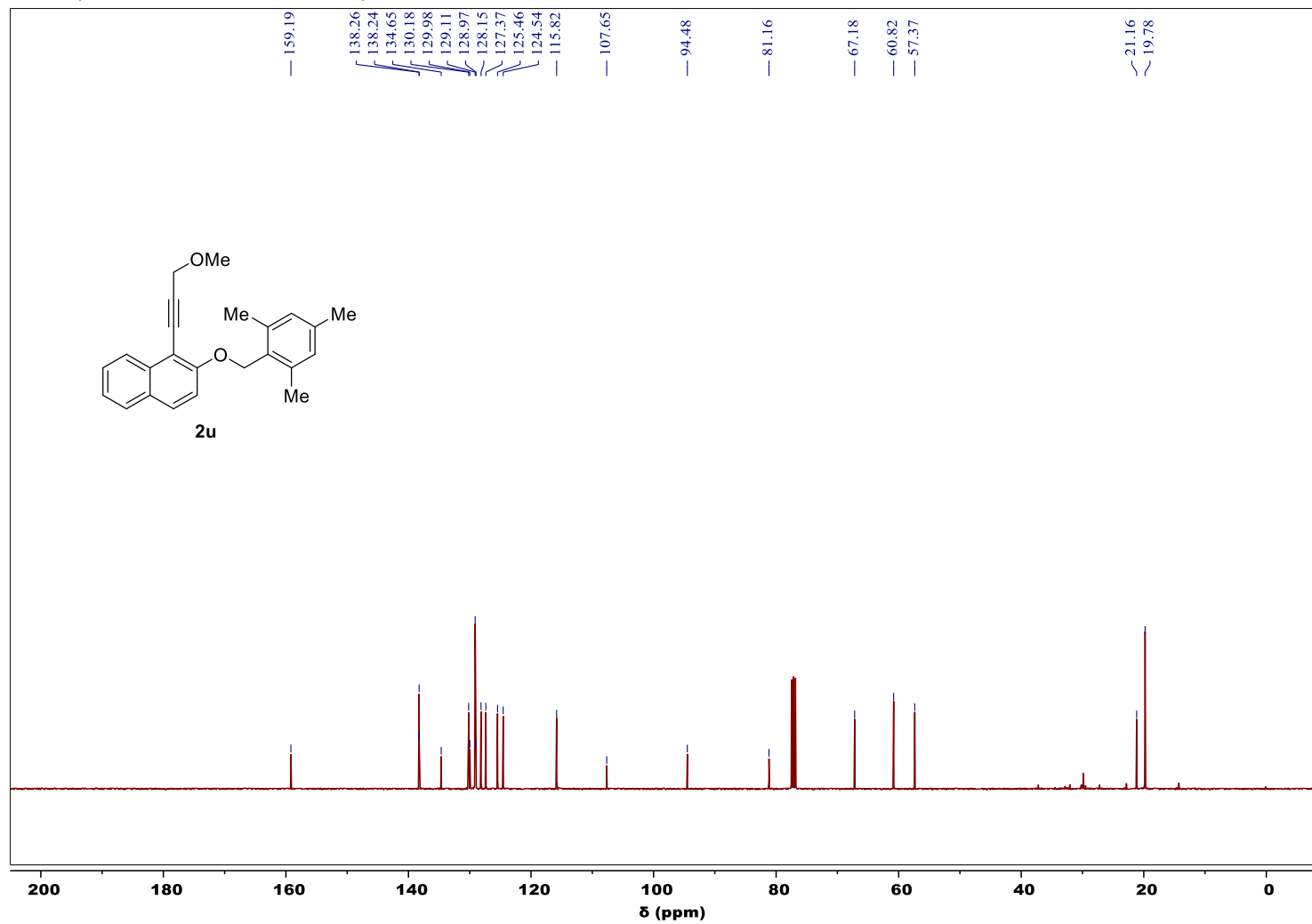
¹³C NMR-spectrum (101 MHz, Chloroform-*d*) of **2t**



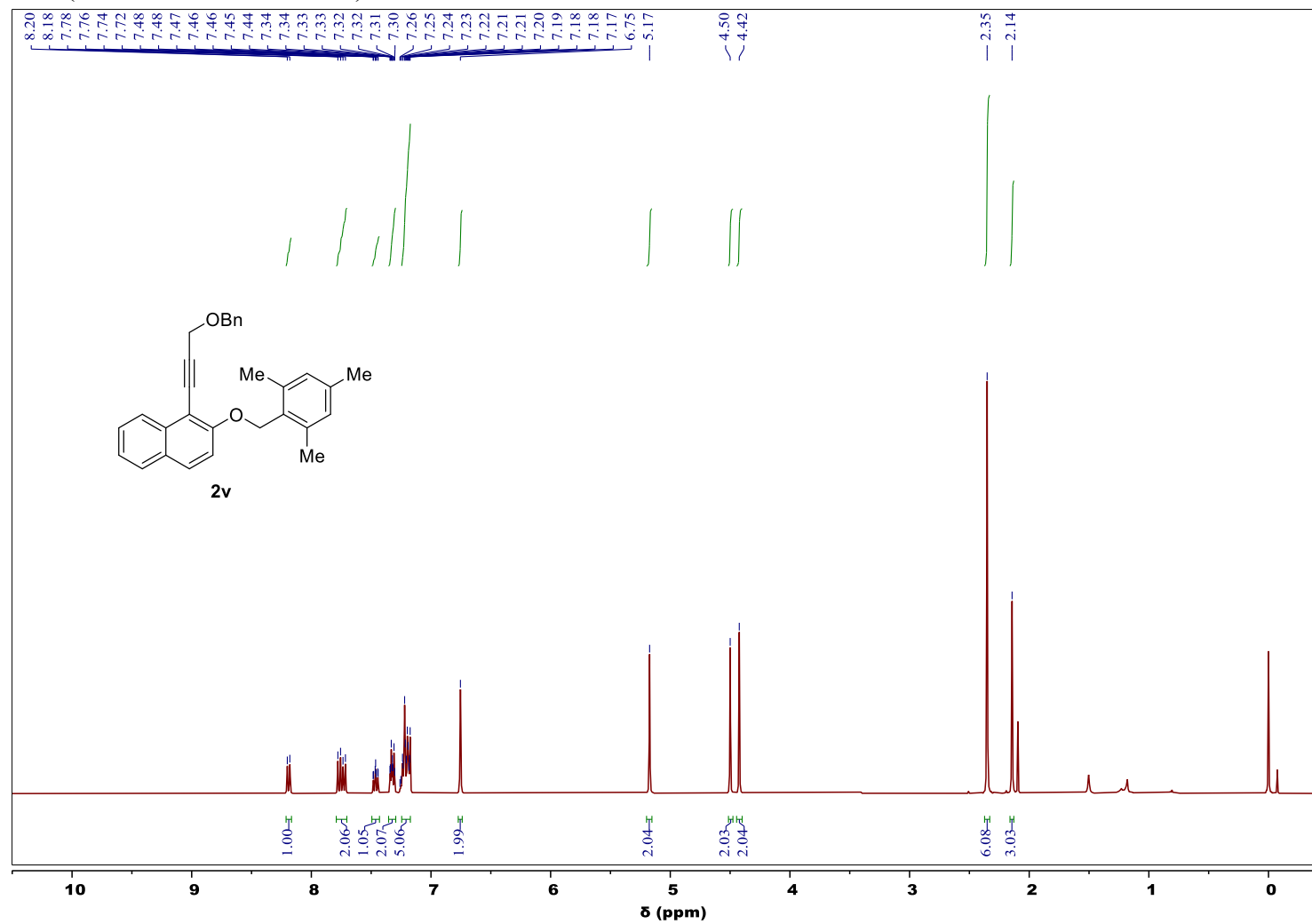
^1H NMR-spectrum (400 MHz, Chloroform- d) of **2u**



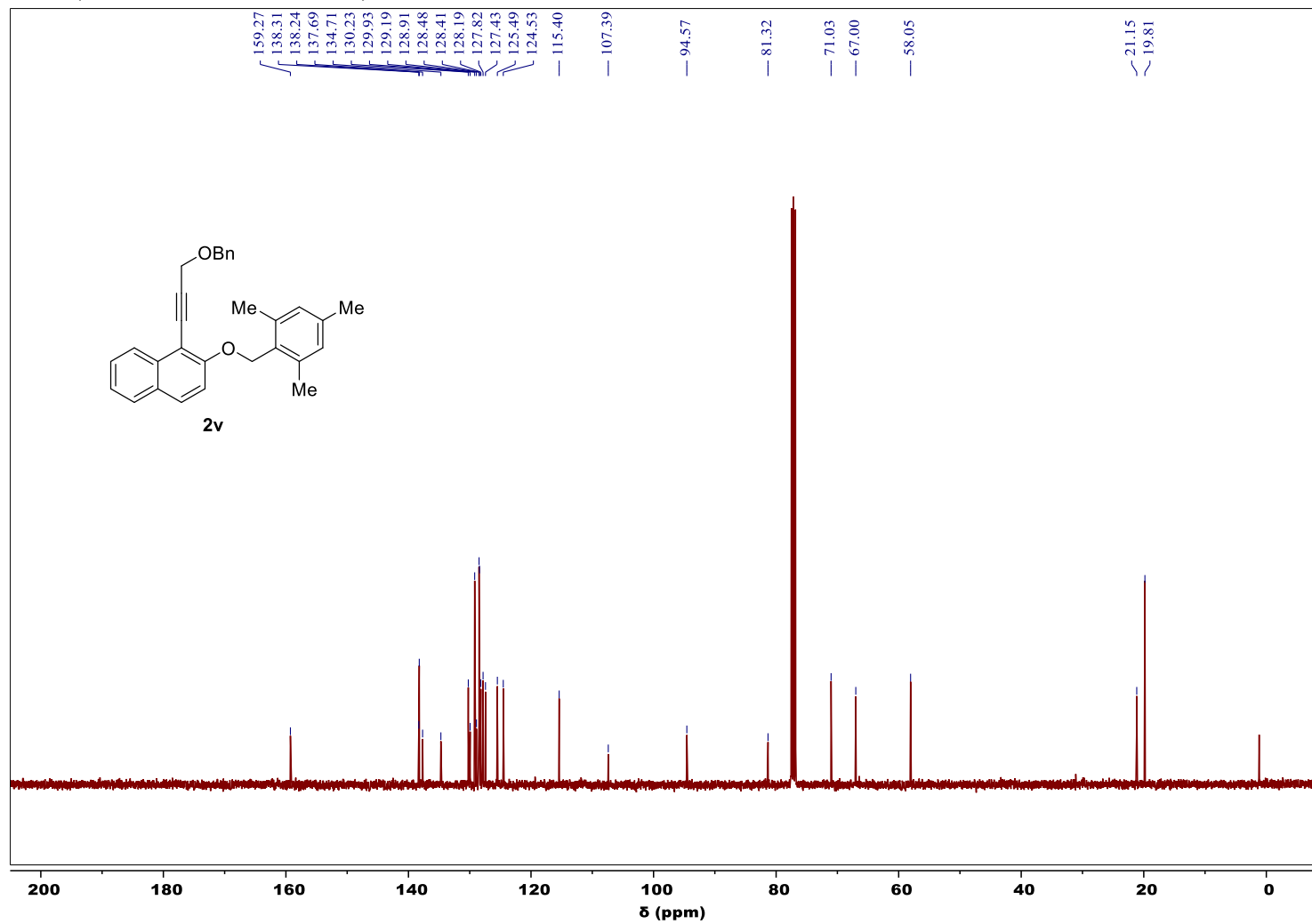
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2u**



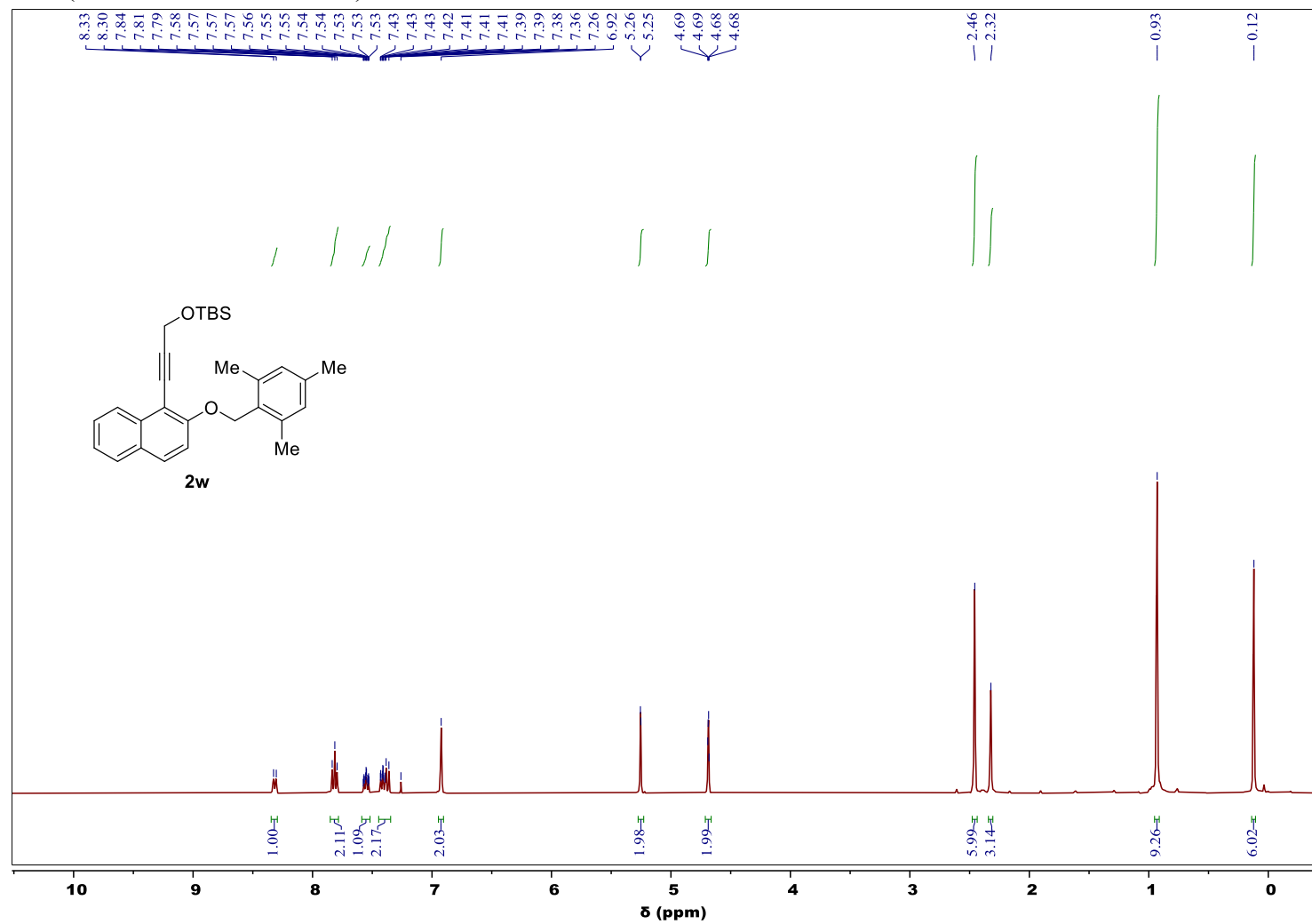
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2v**



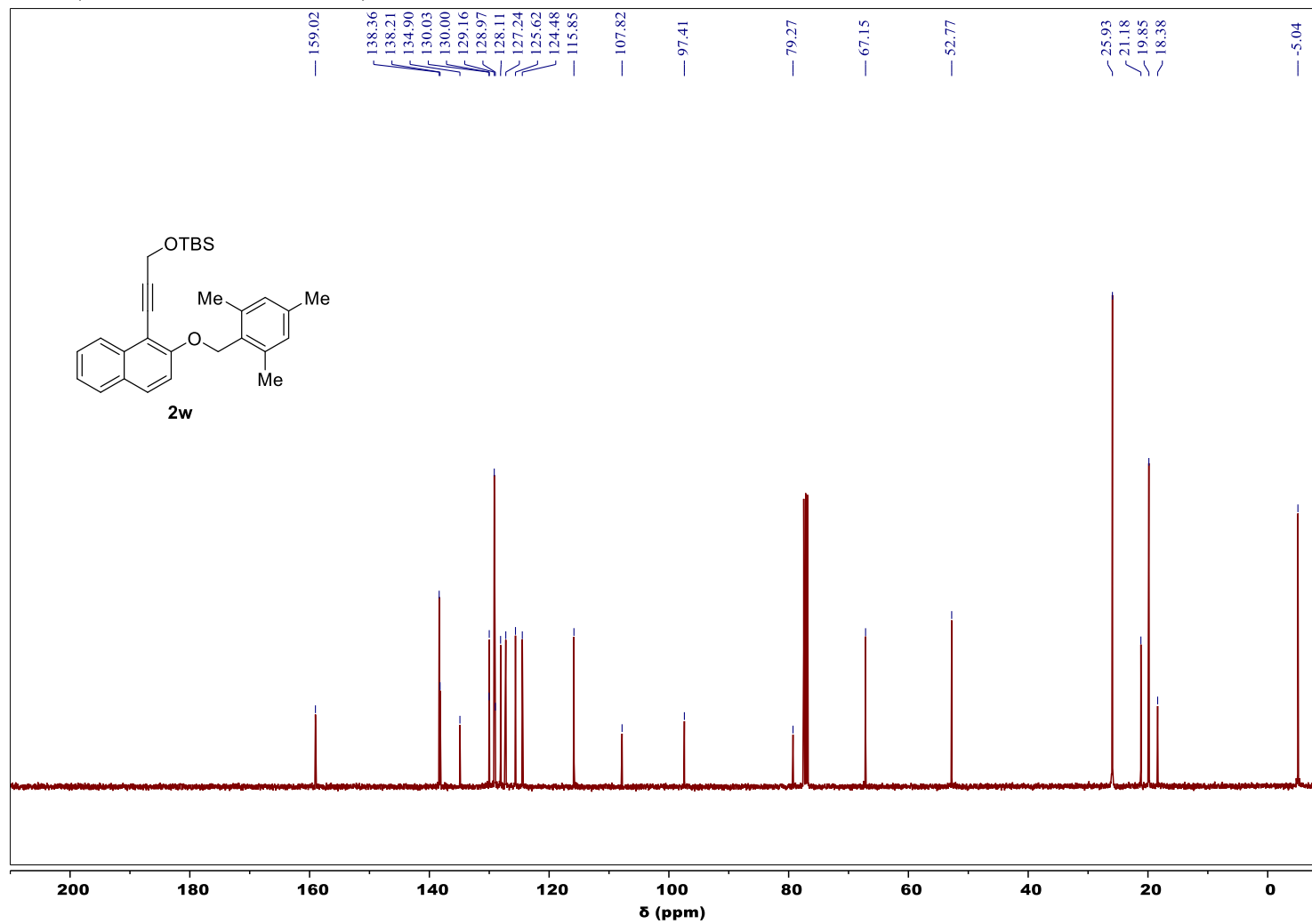
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2v**



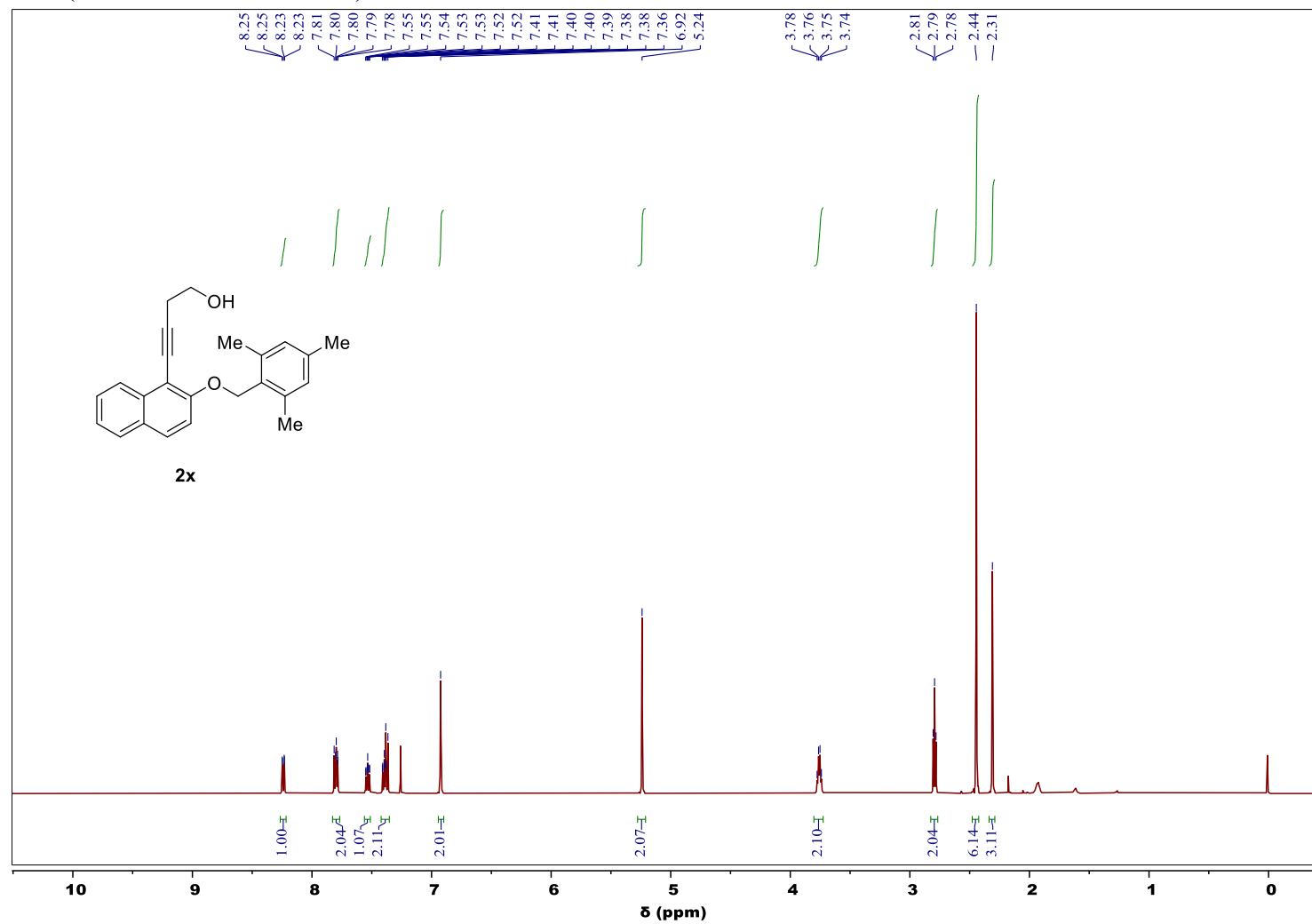
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2w**



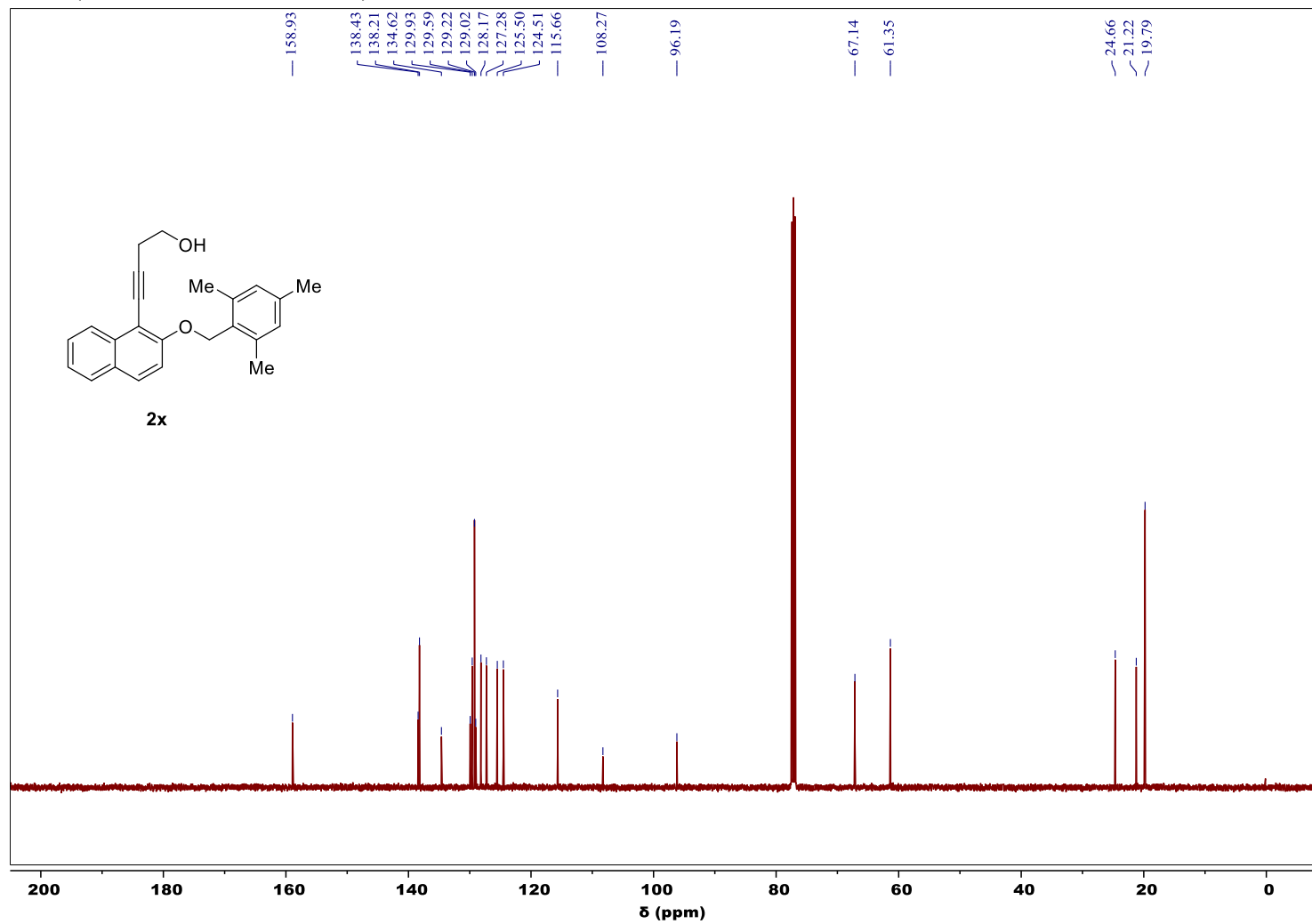
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2w**



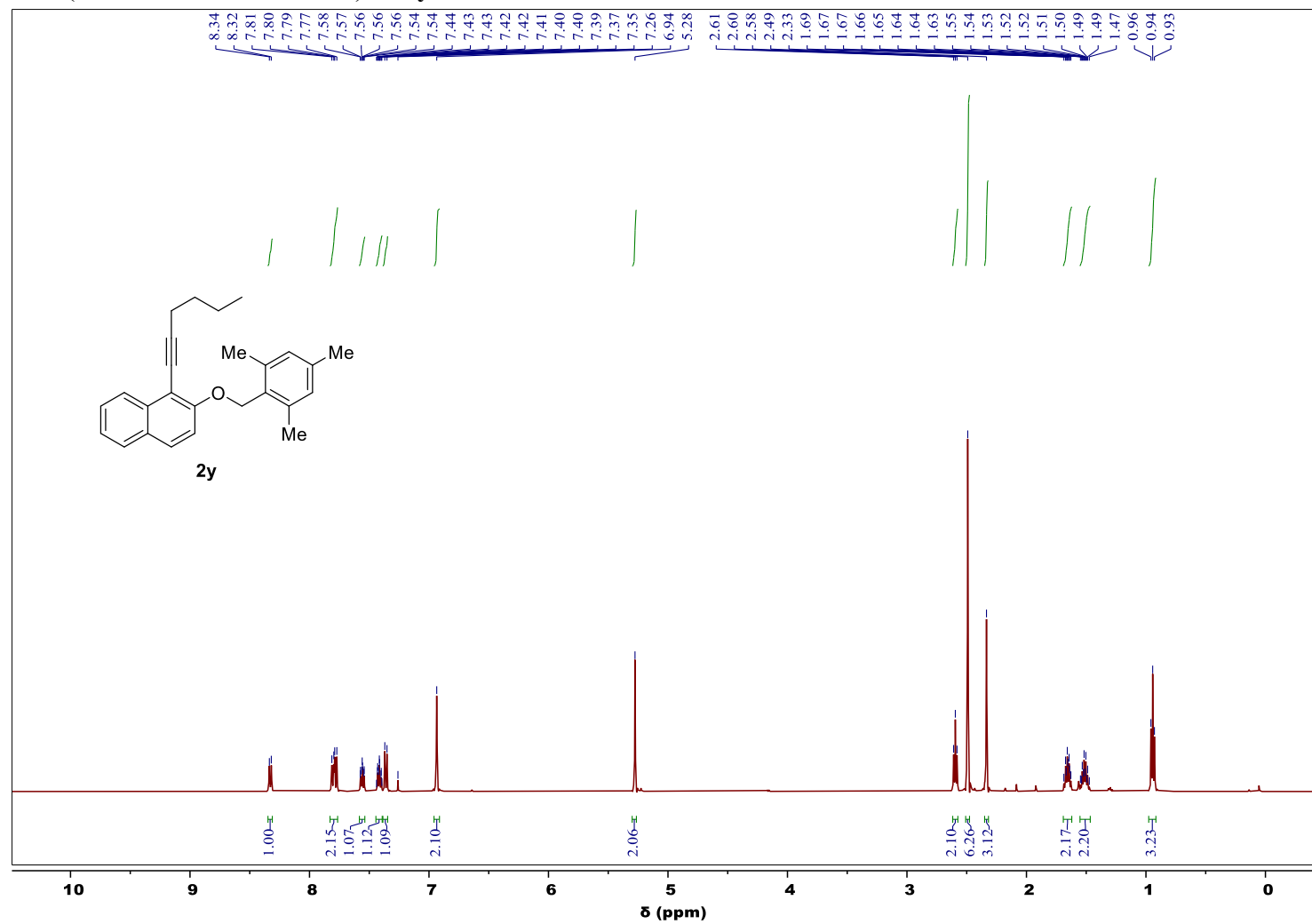
^1H NMR-spectrum (500 MHz, Chloroform- d) of **2x**



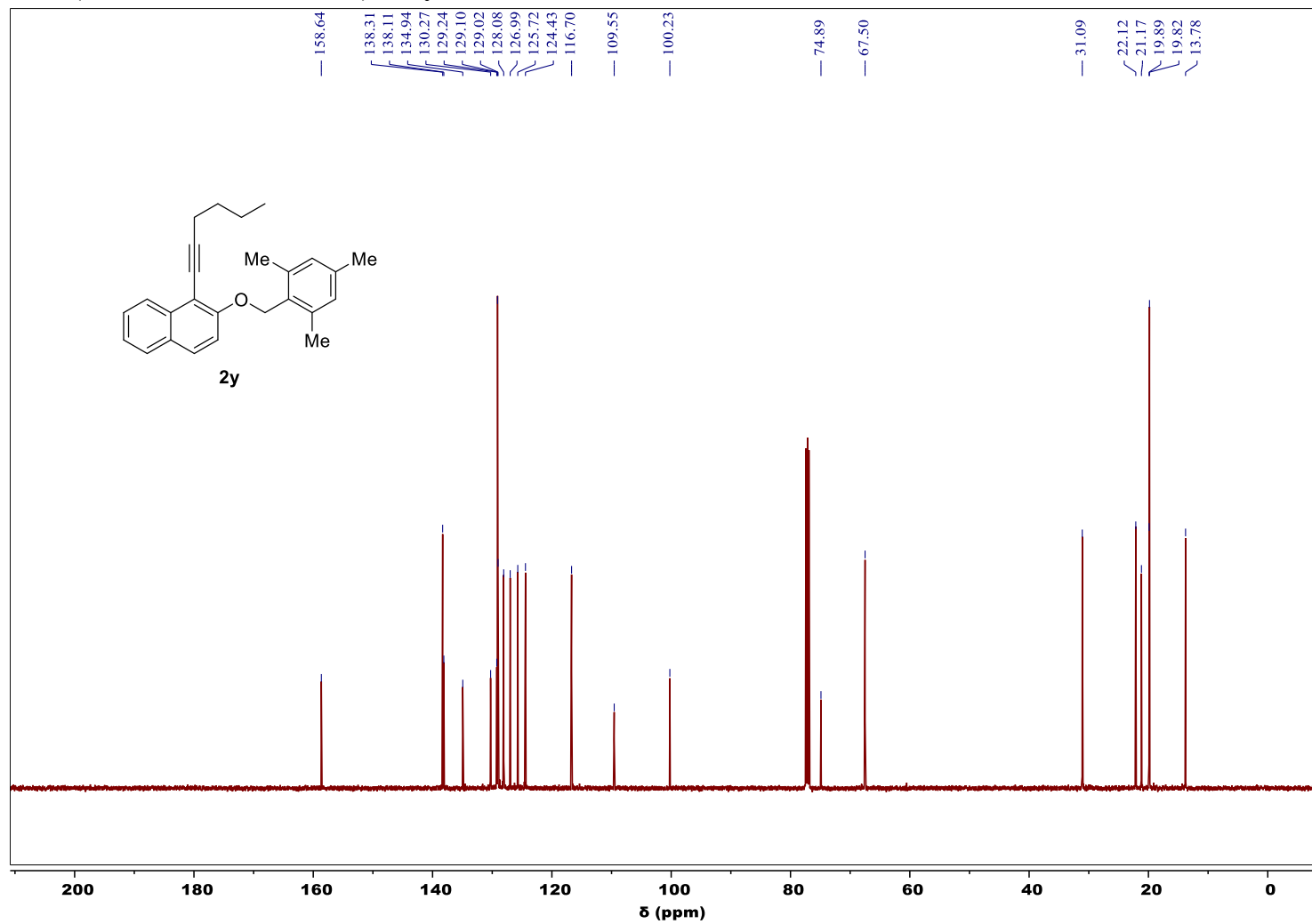
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2x**



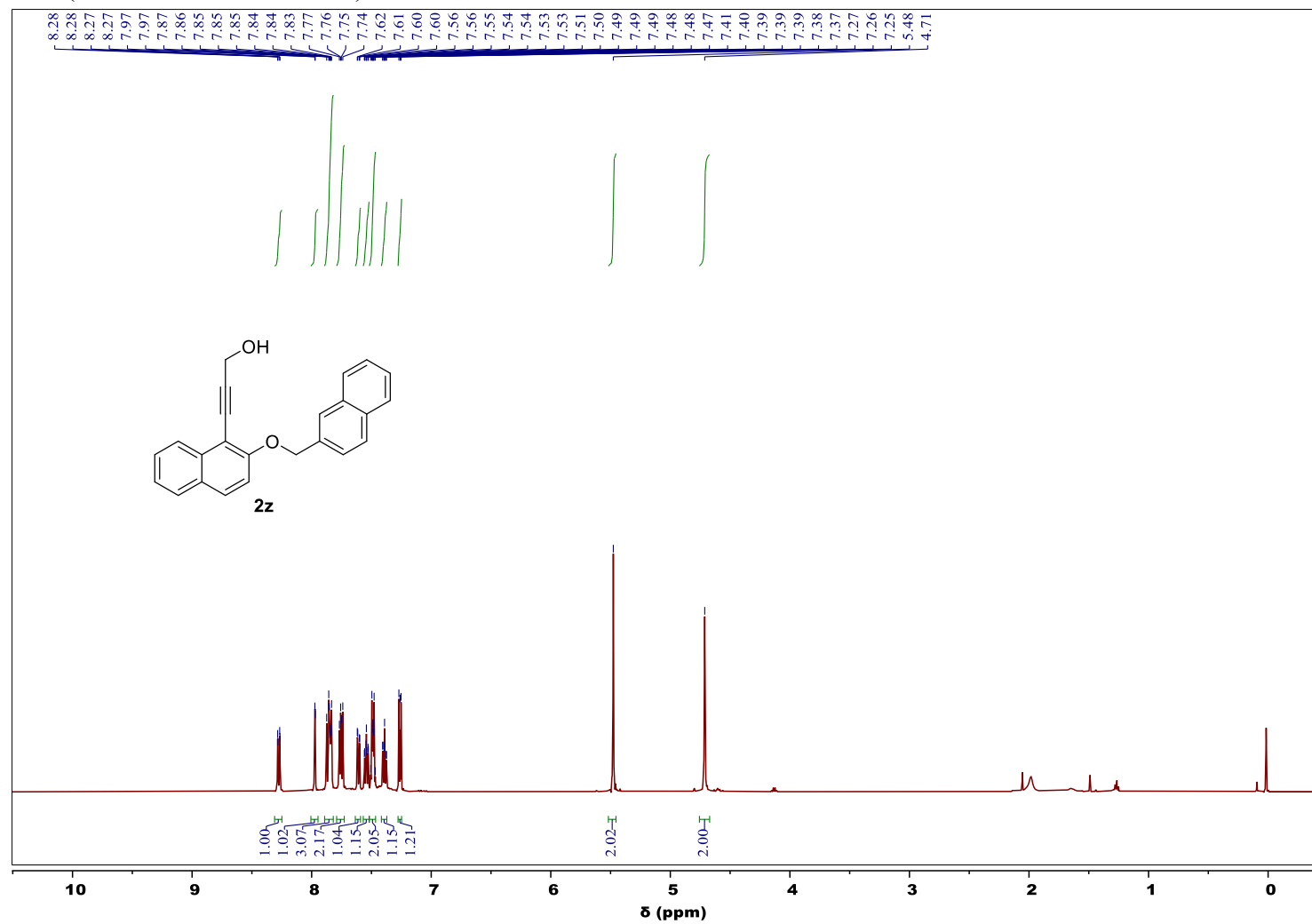
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2y**



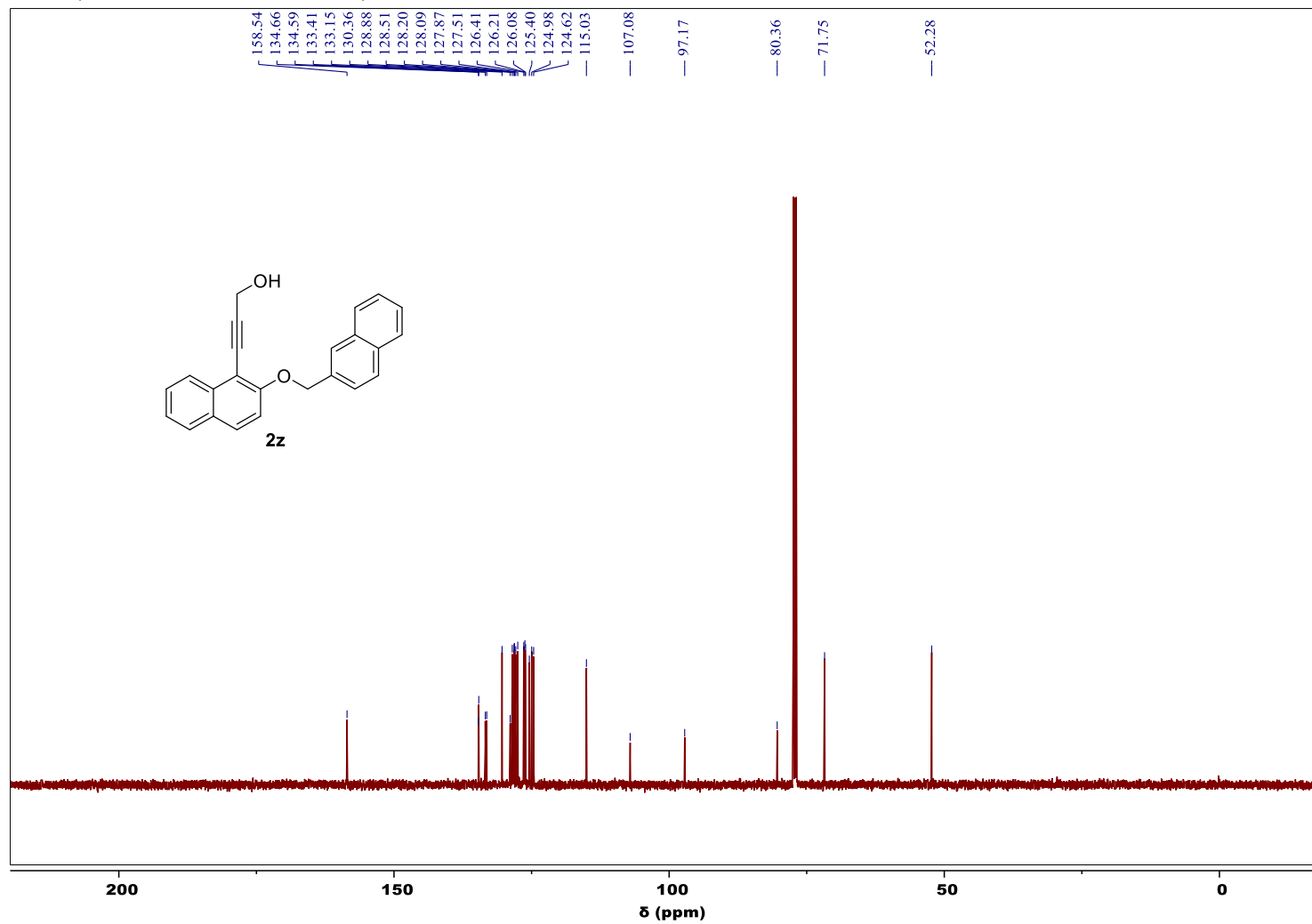
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2y**



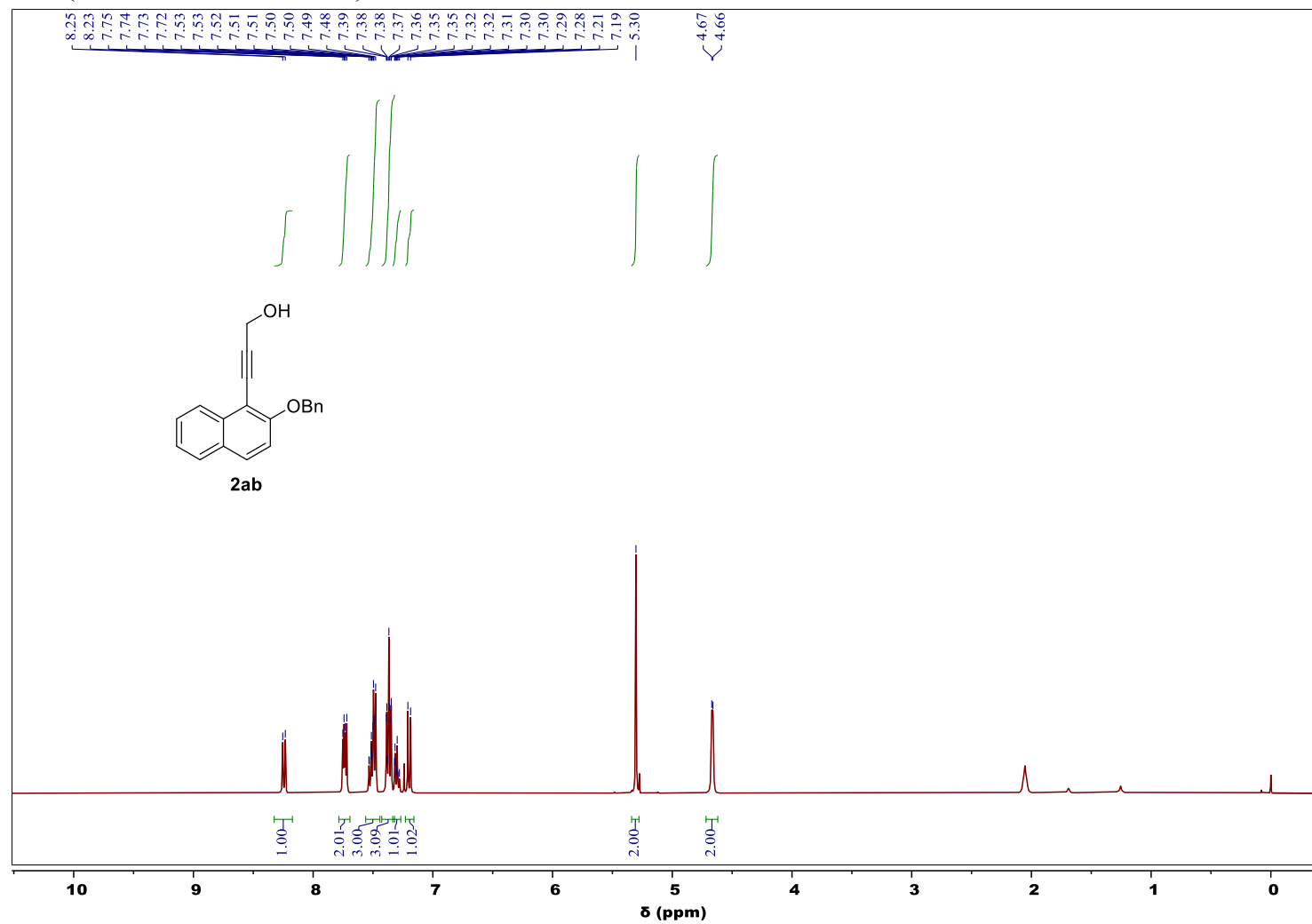
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **2z**



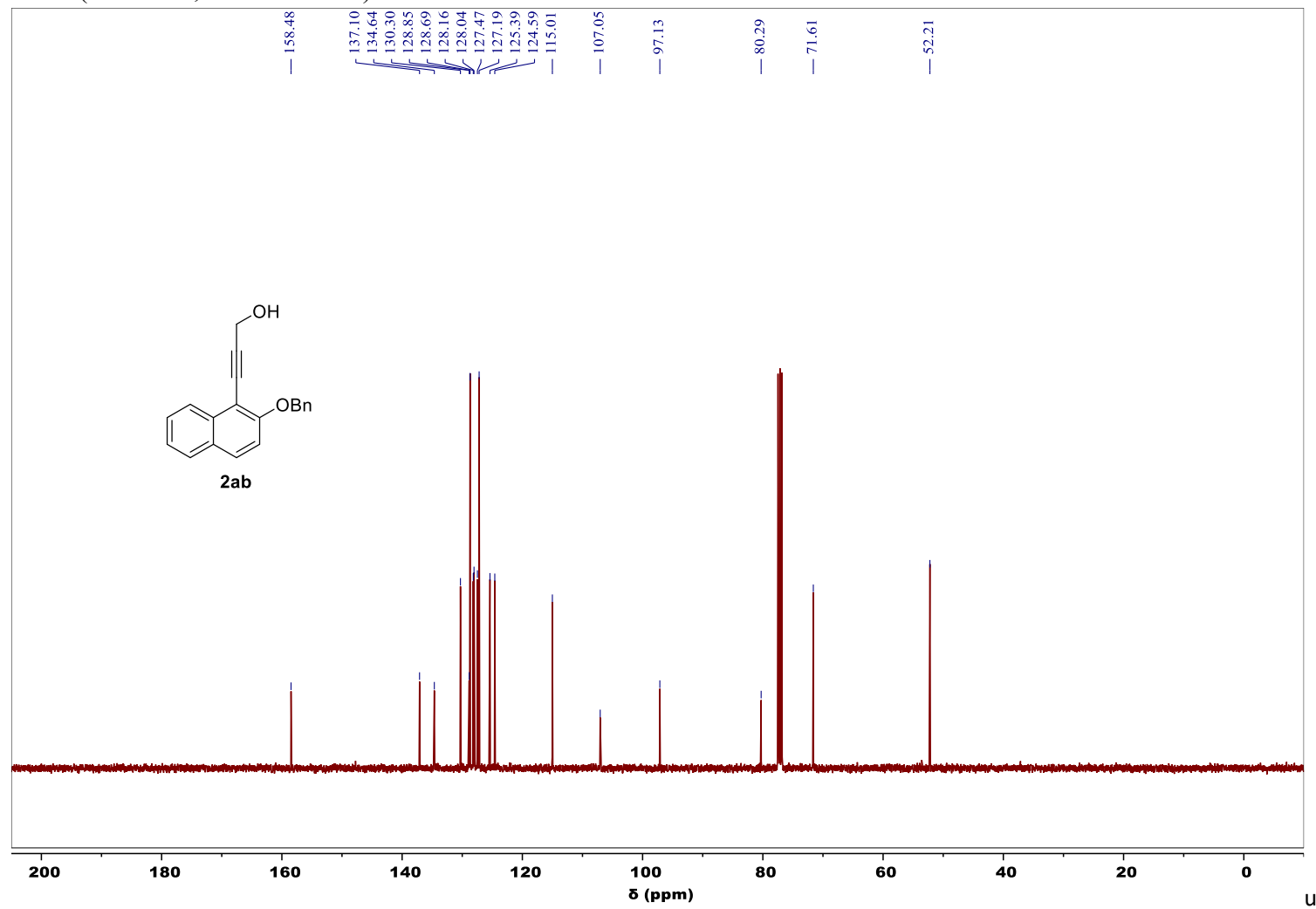
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2z**



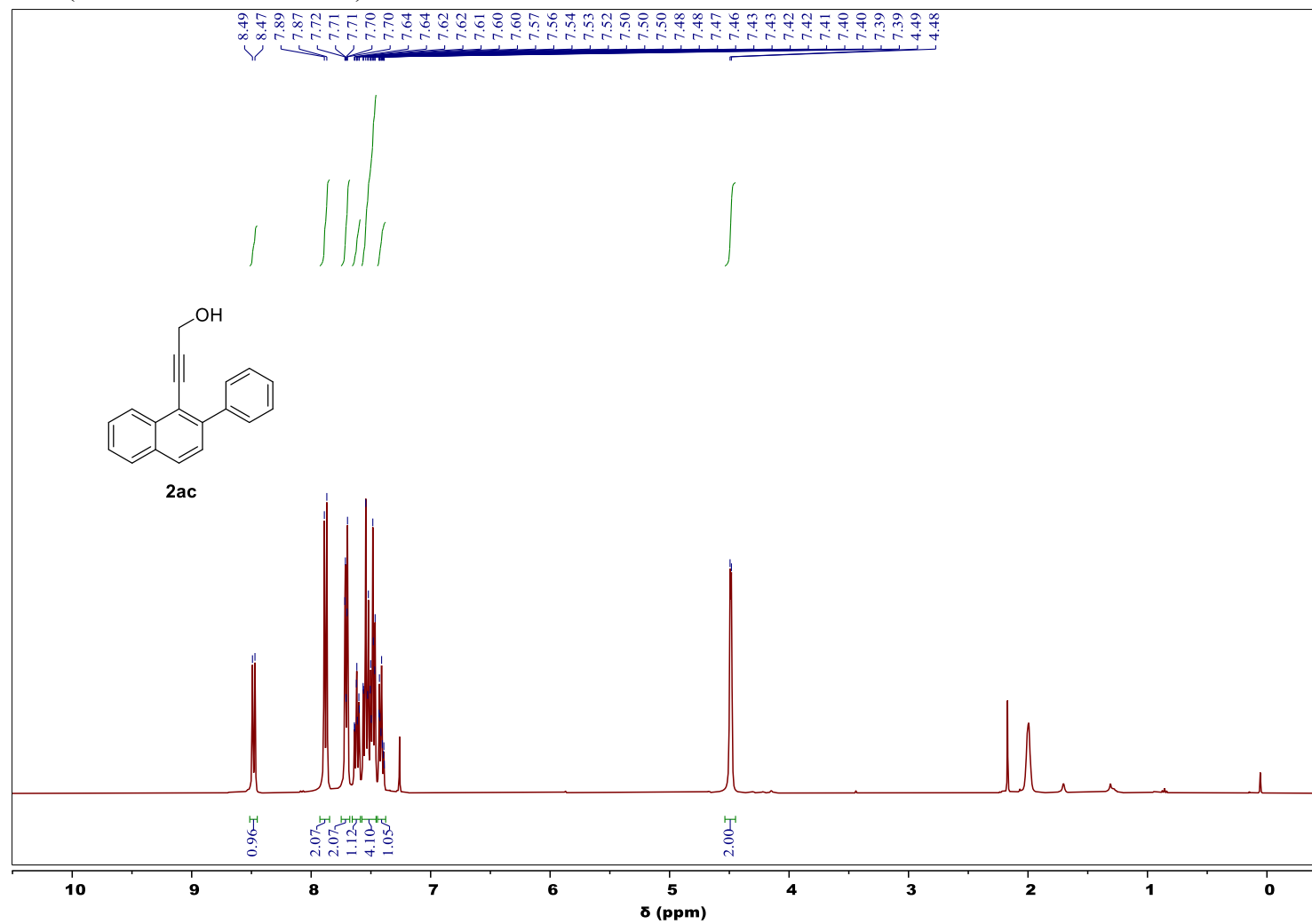
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2ab**



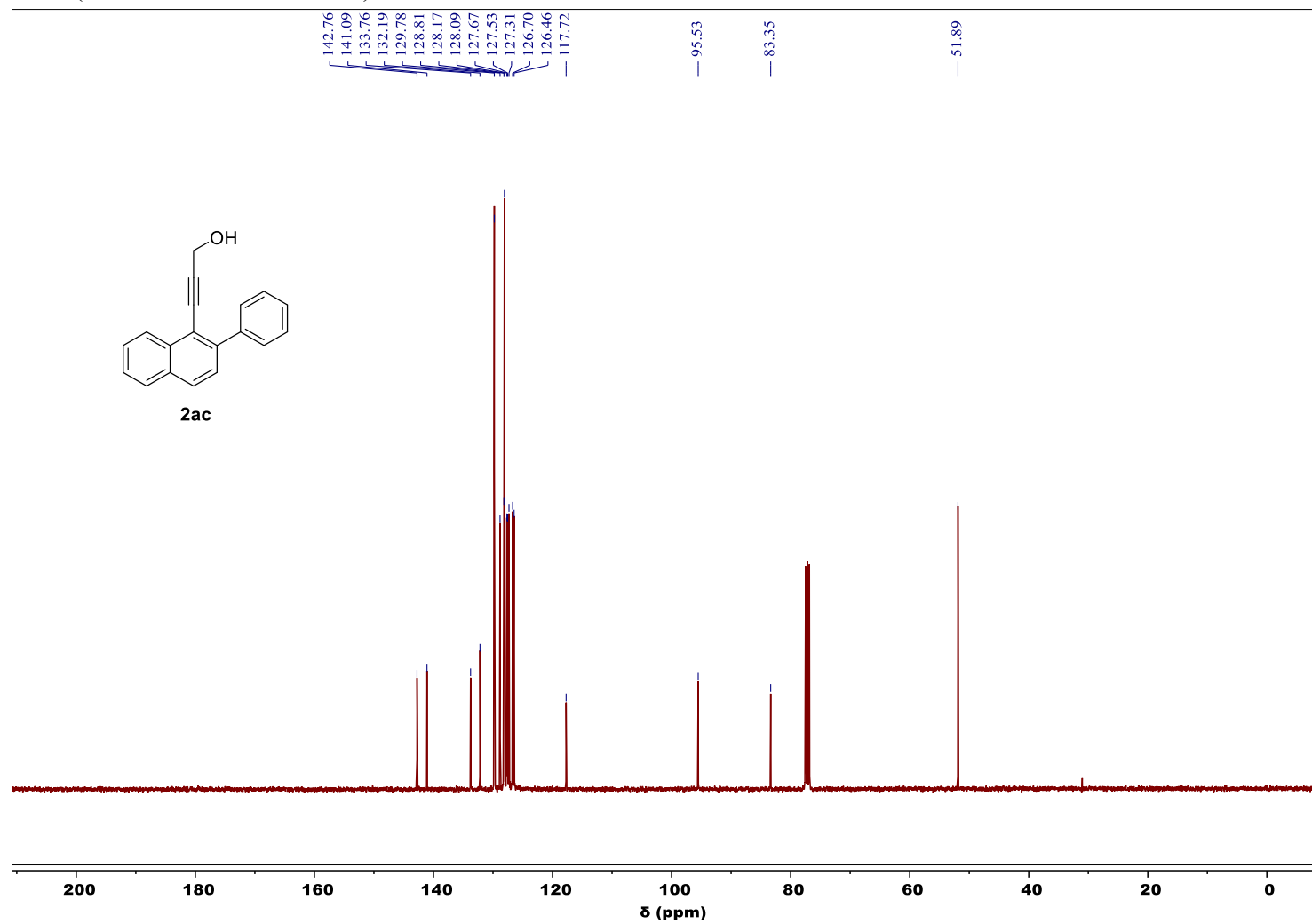
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2ab**



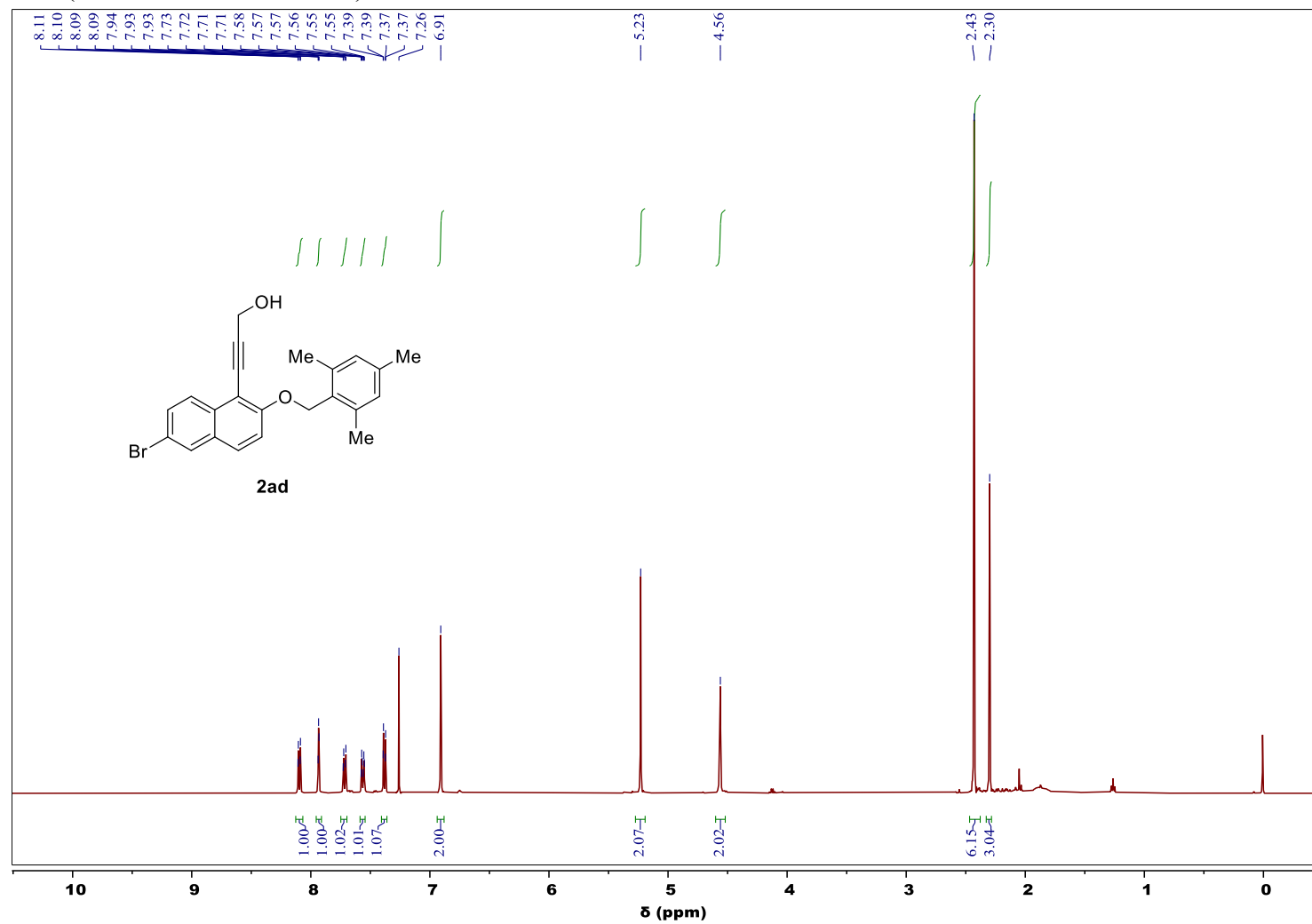
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **2ac**



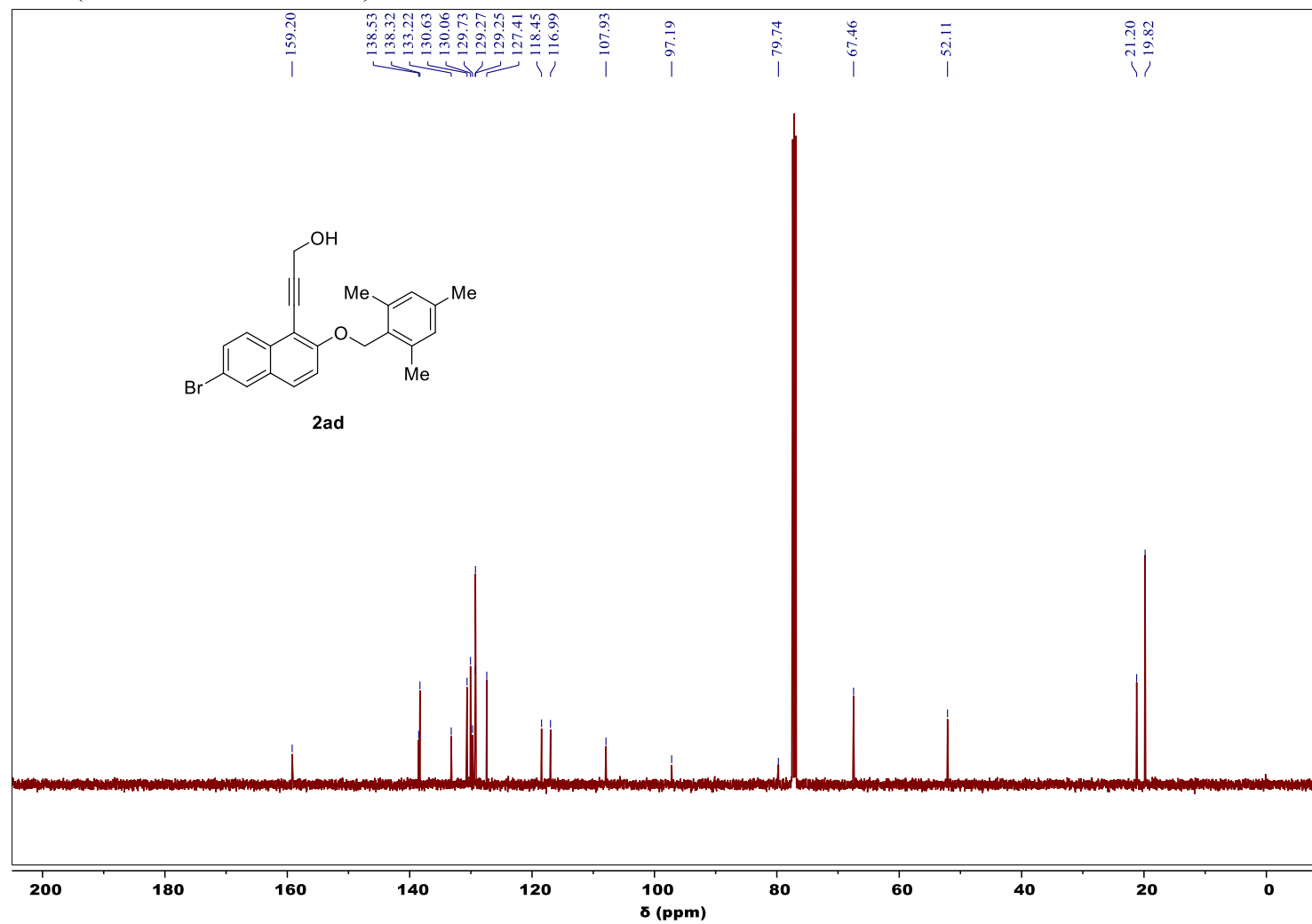
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **2ac**



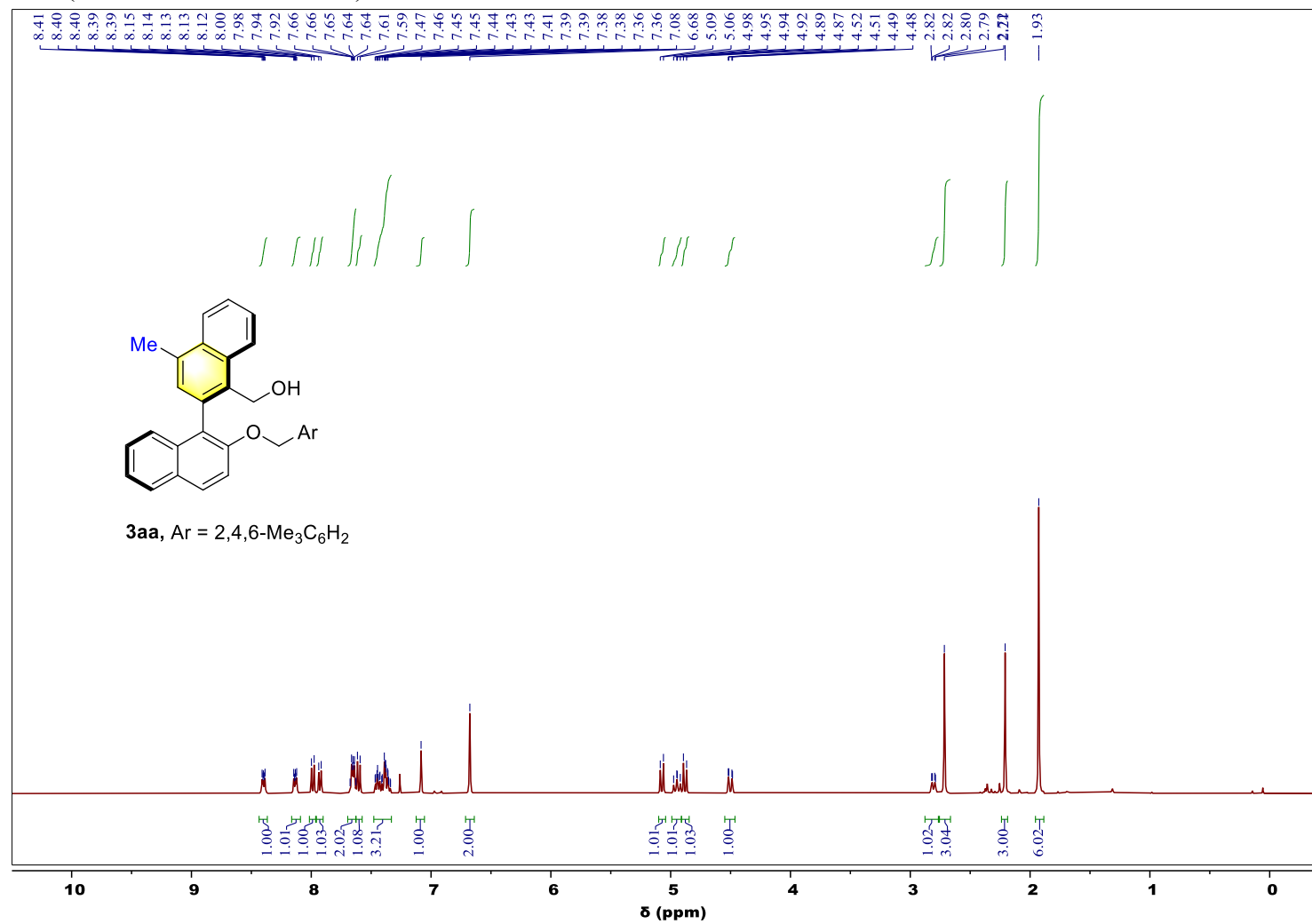
^1H NMR-spectrum (500 MHz, Chloroform- d) of **2ad**



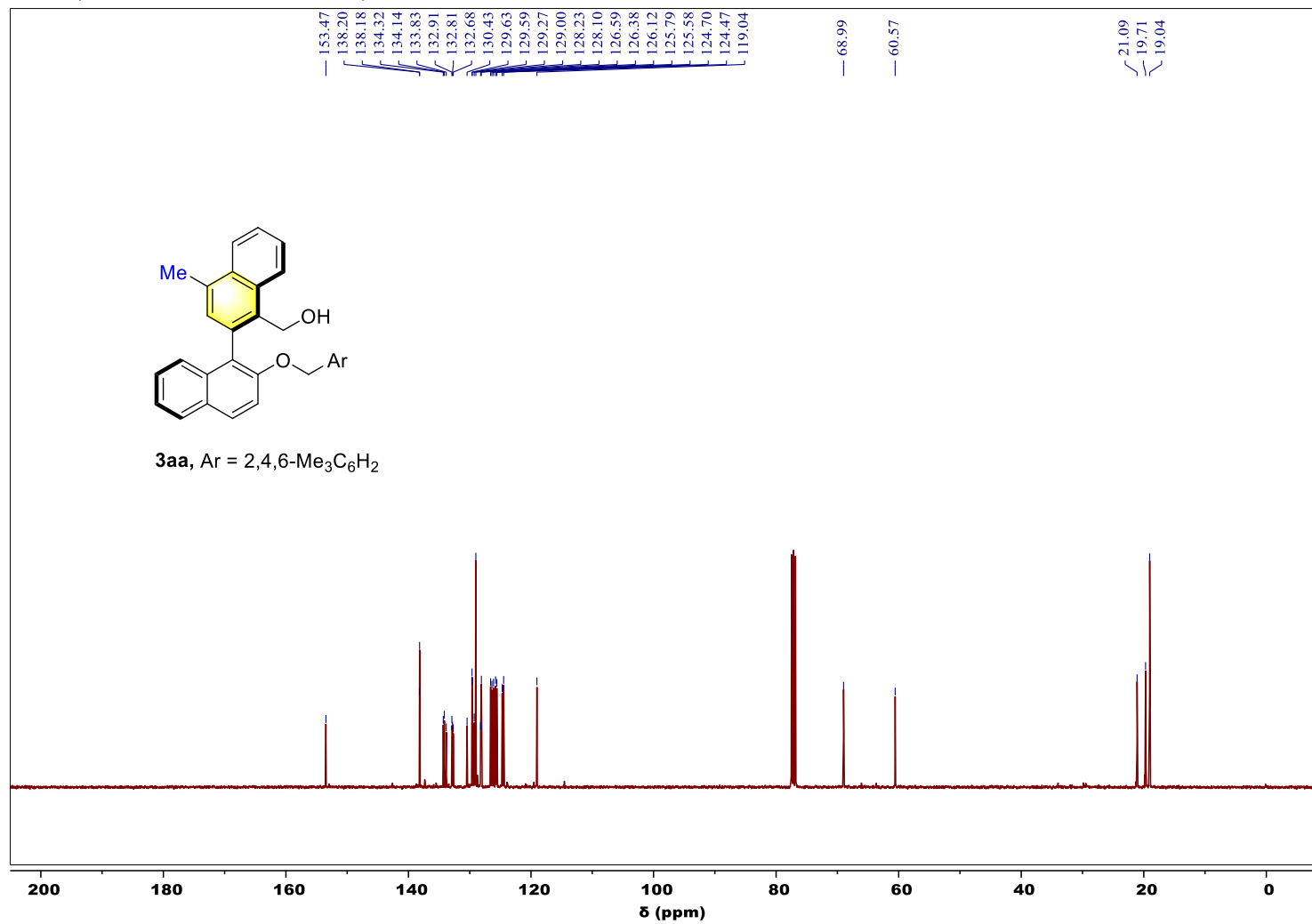
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **2ad**



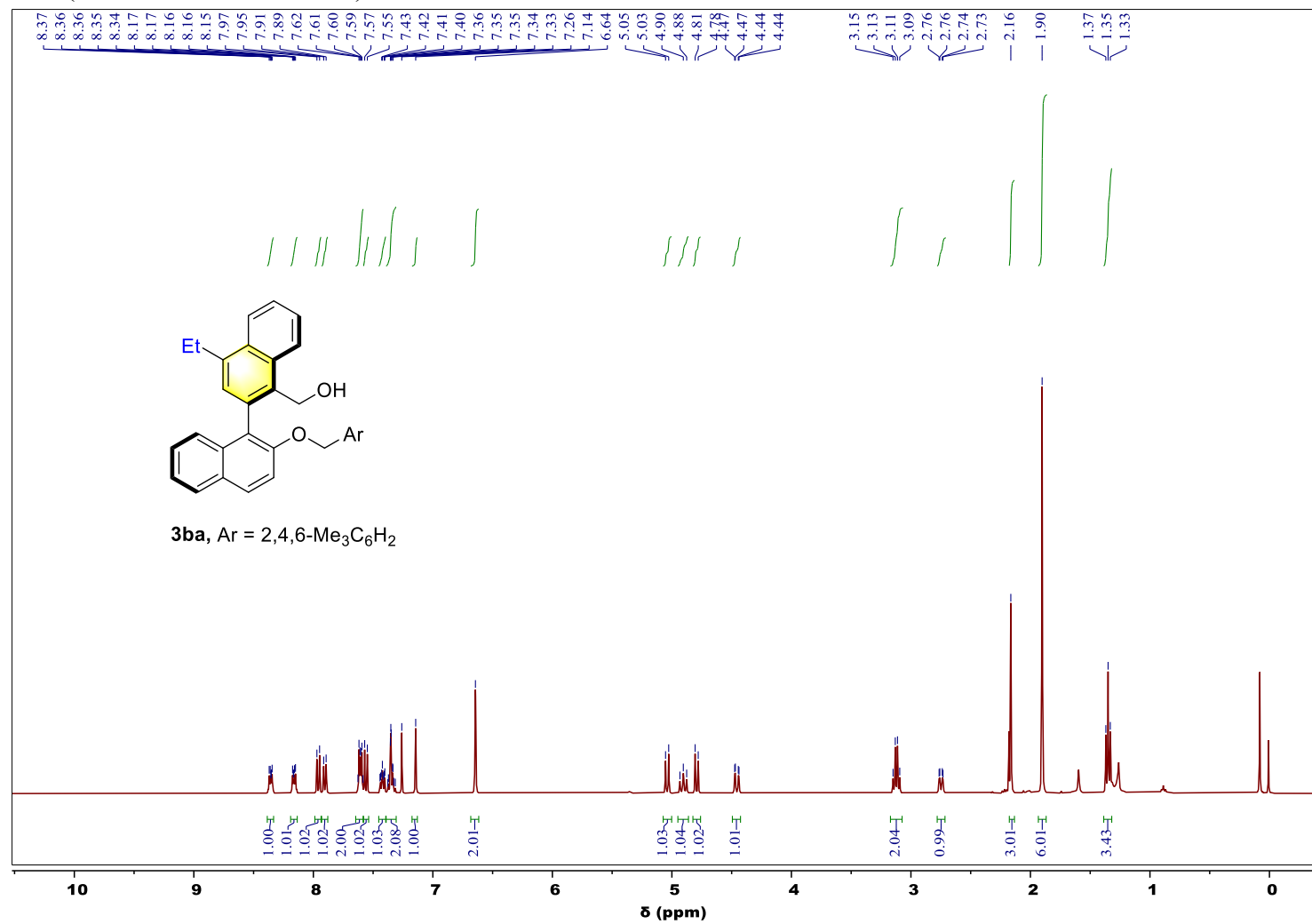
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3aa**



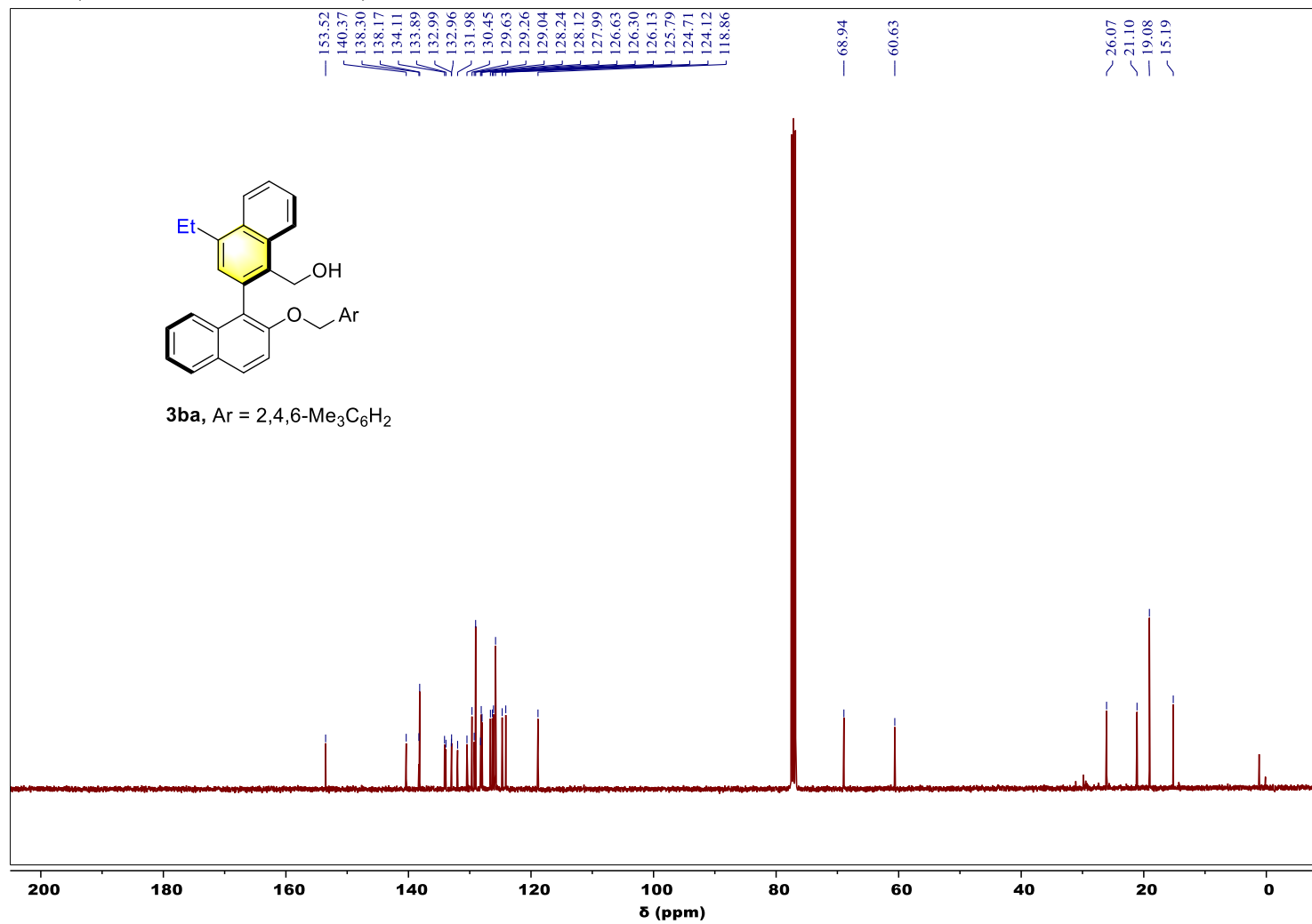
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3aa**



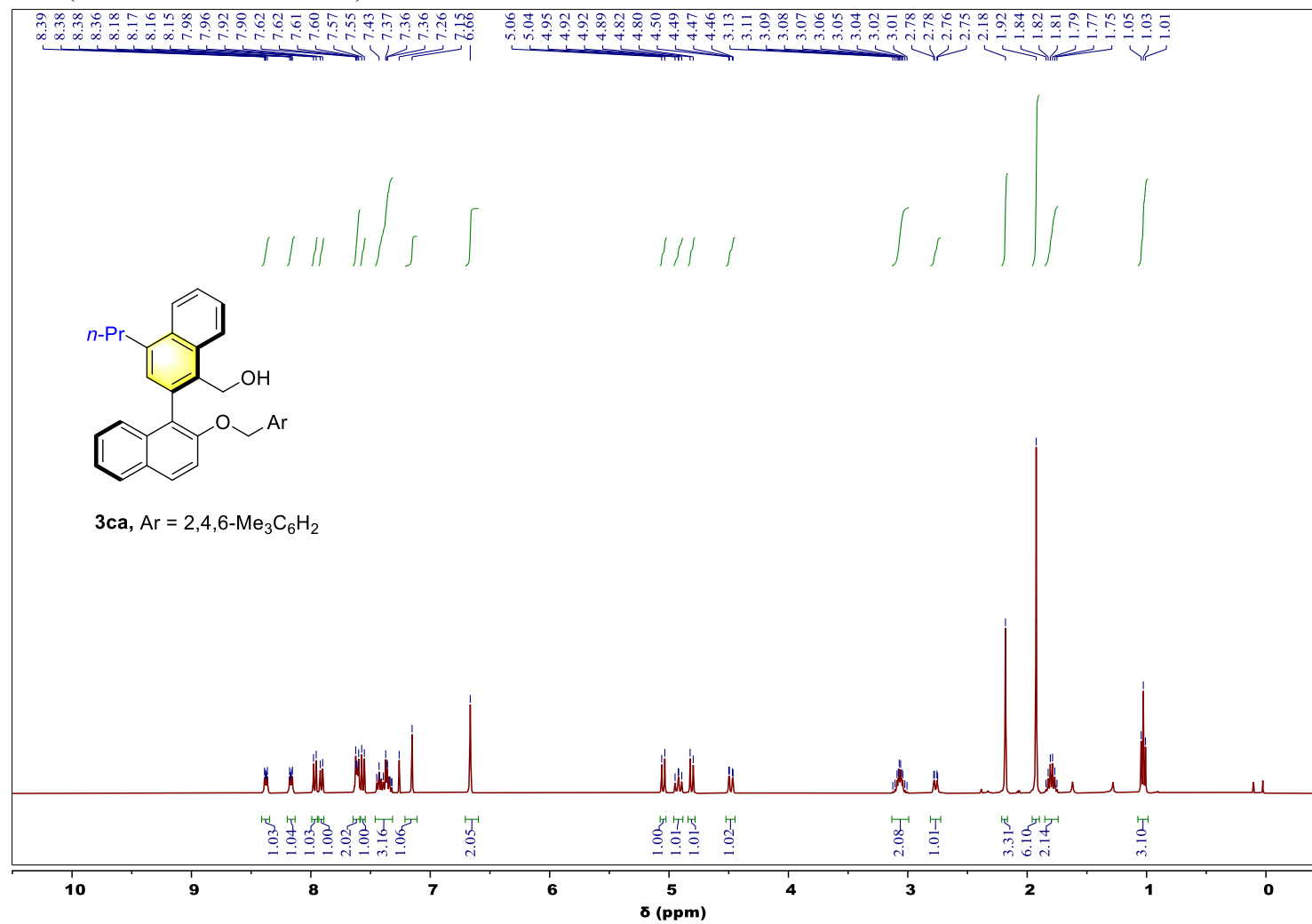
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ba**



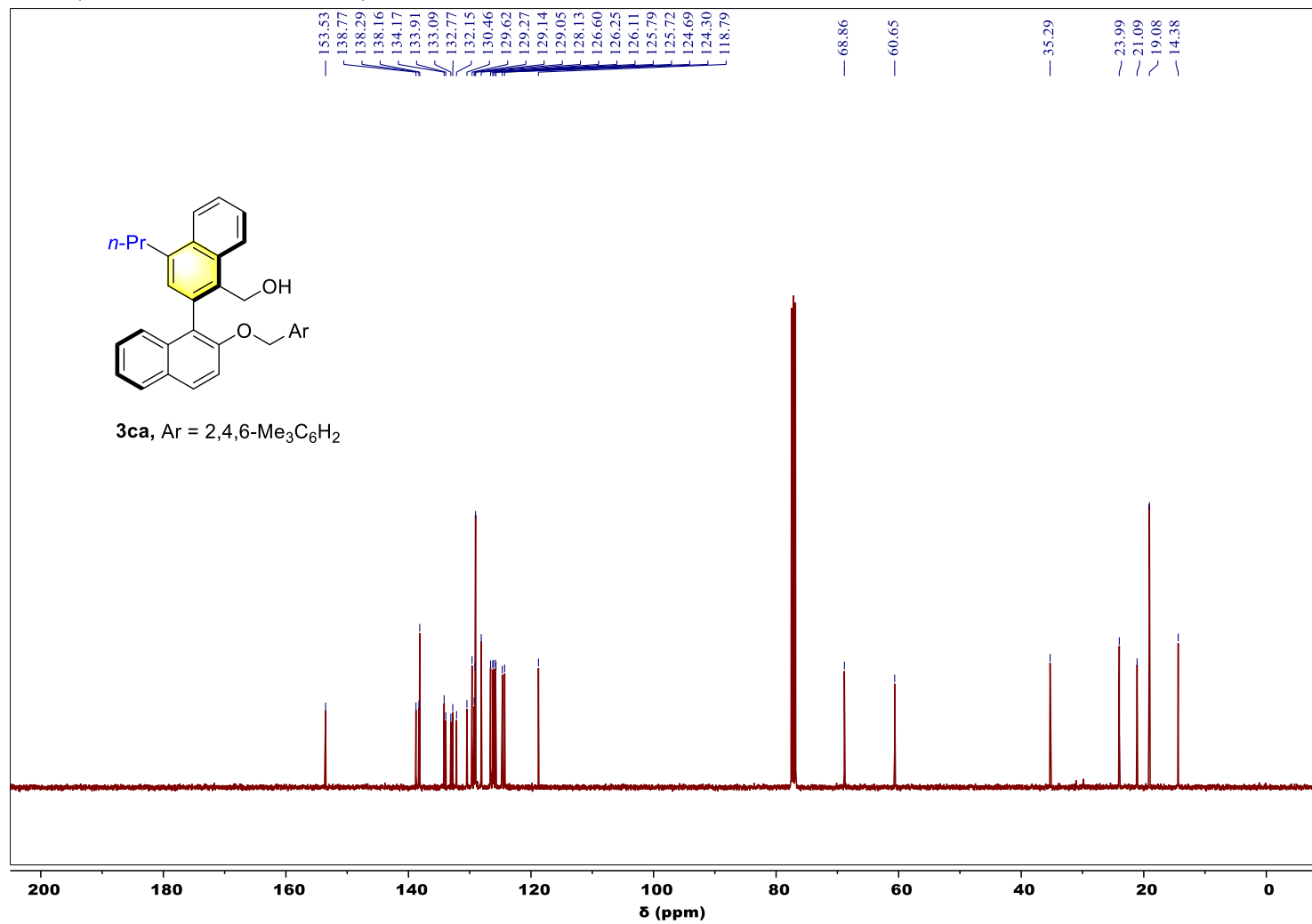
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ba**



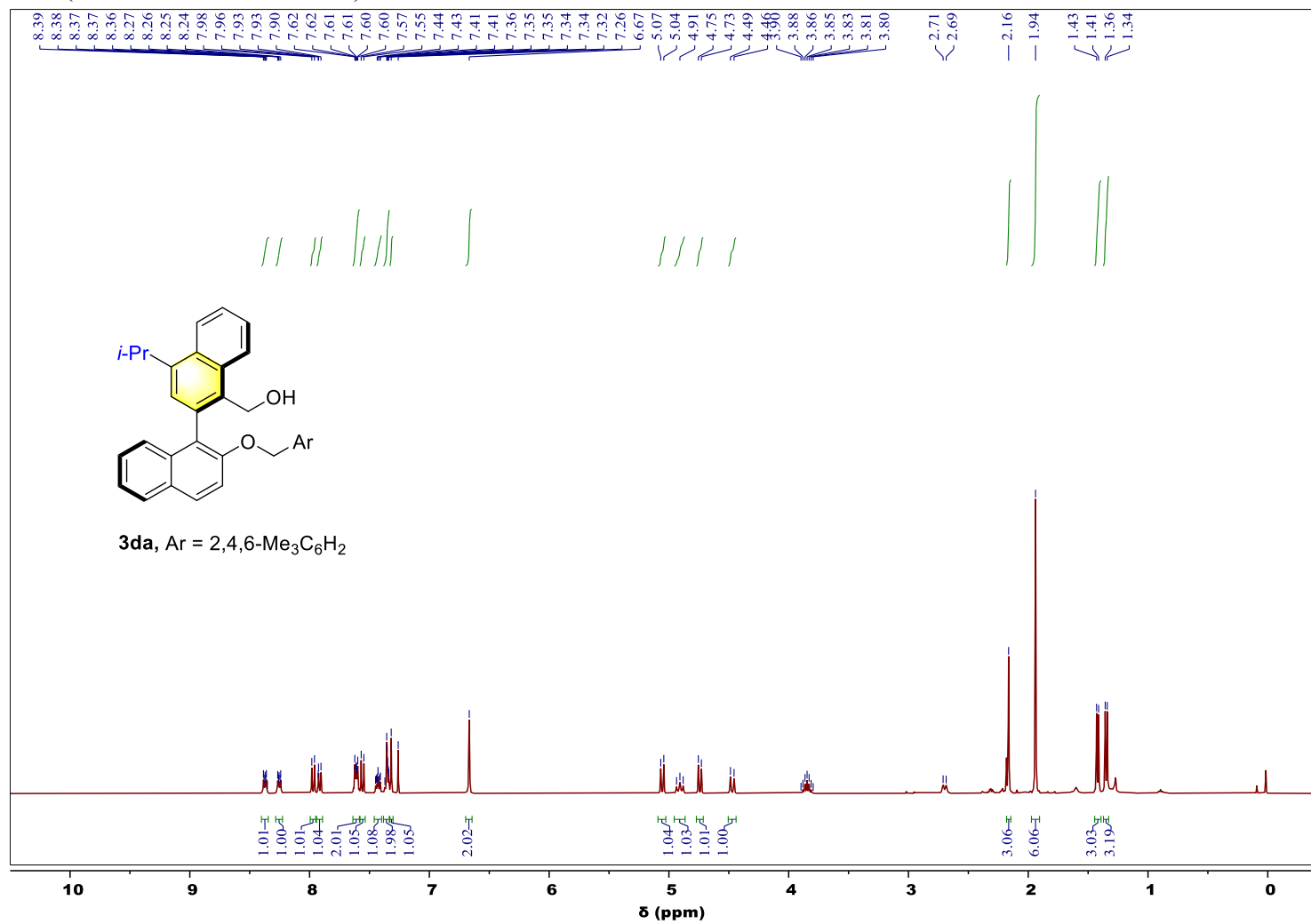
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ca**



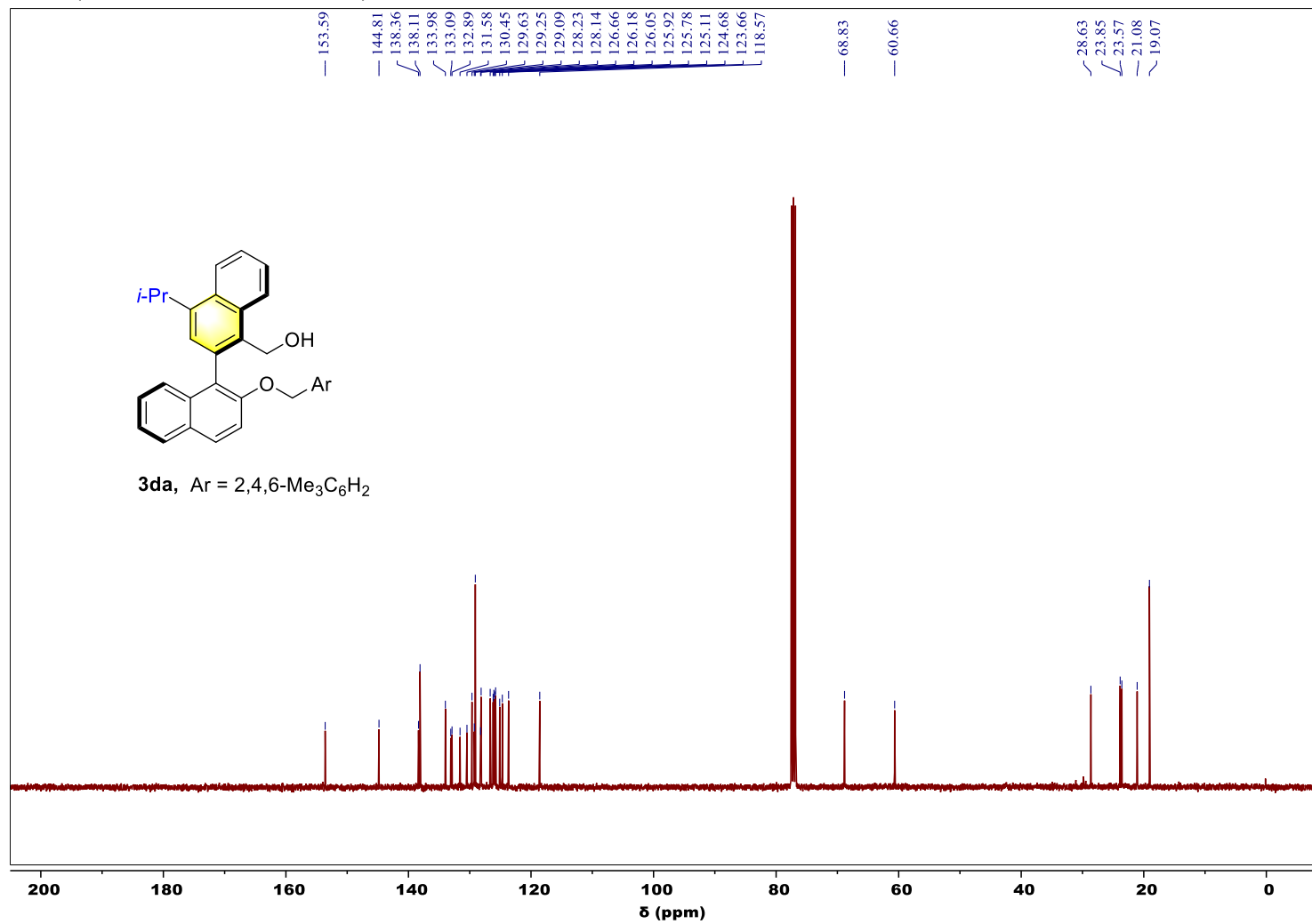
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ca**



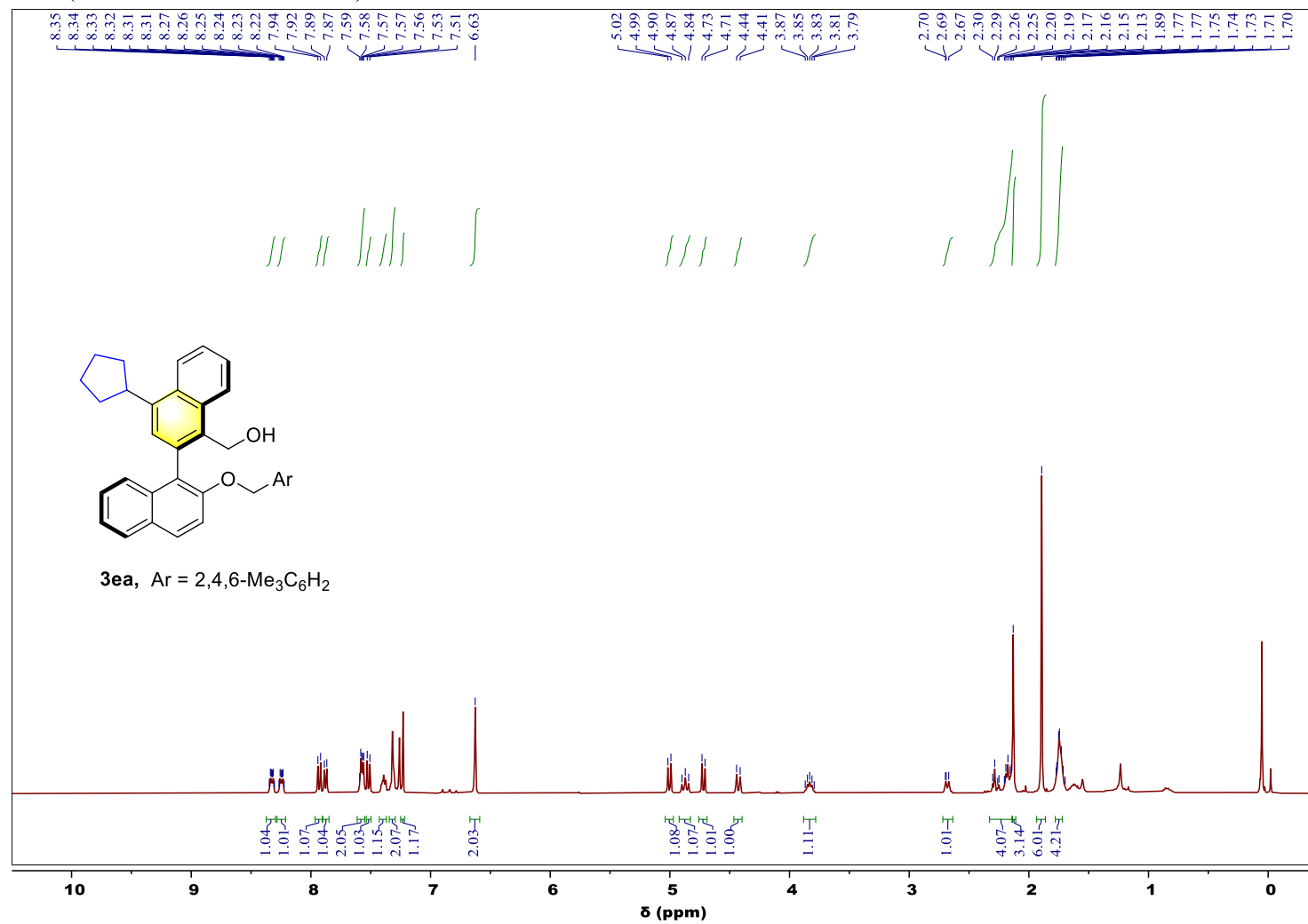
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3da**



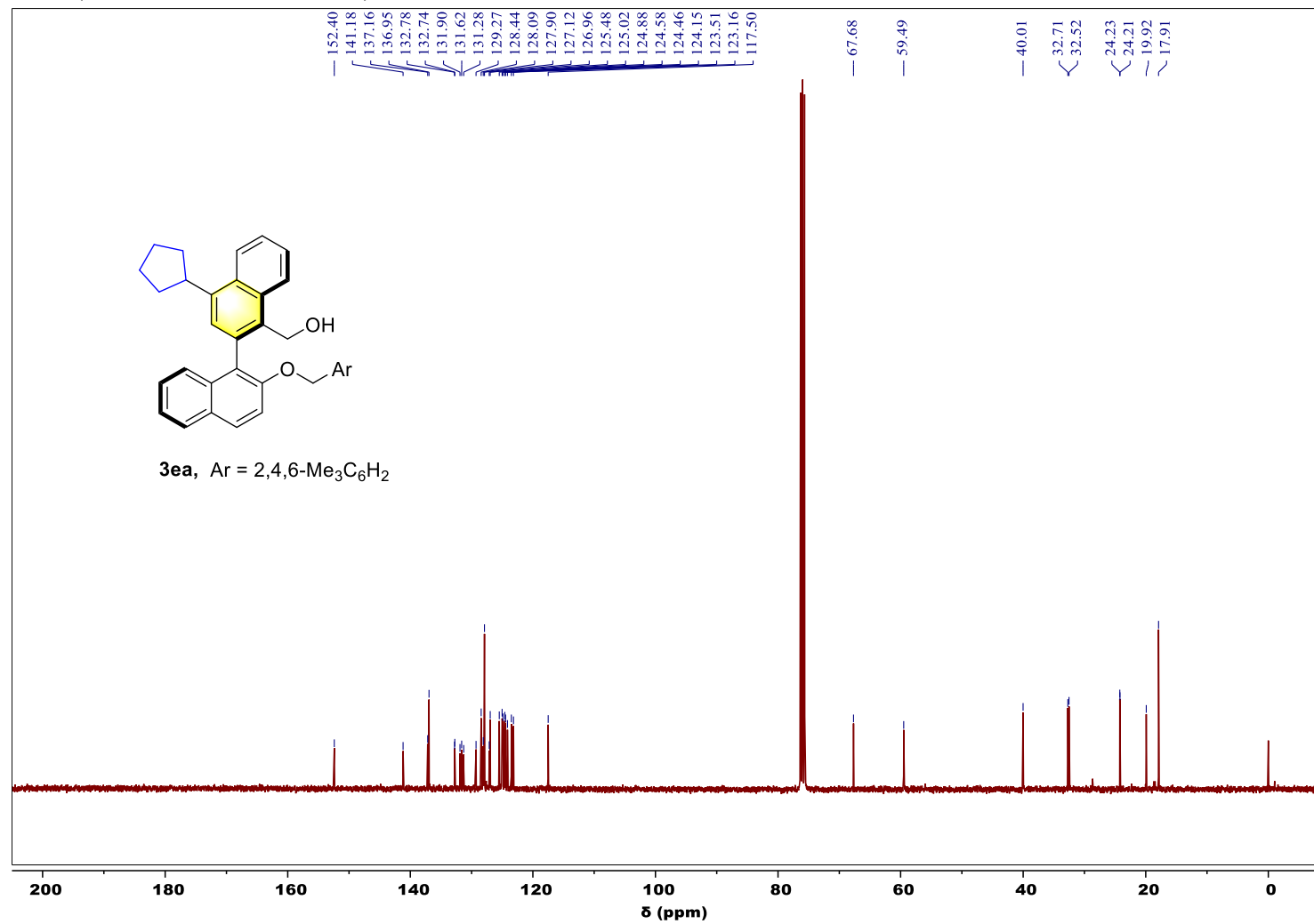
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3da**



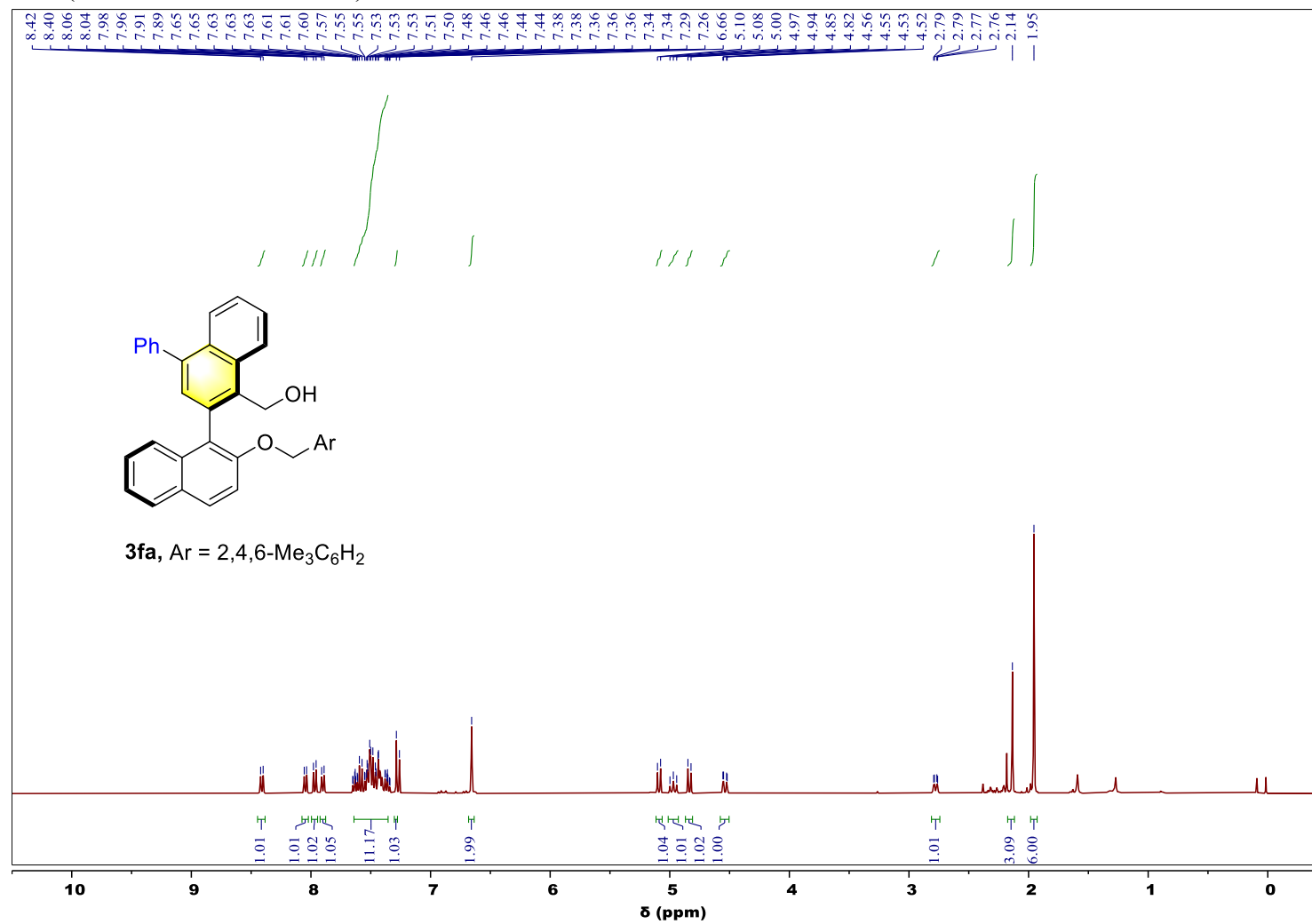
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3ea**



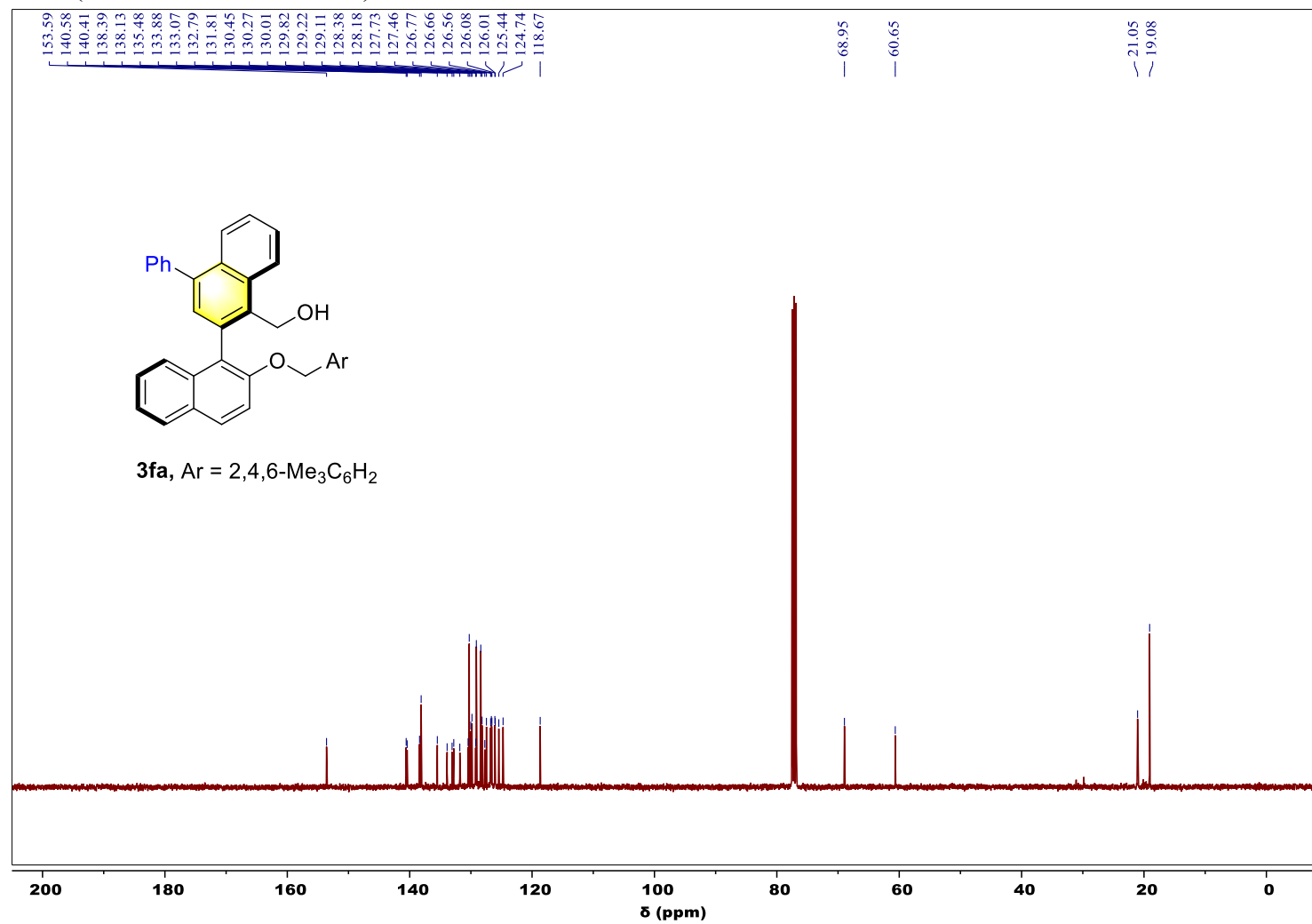
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ea**



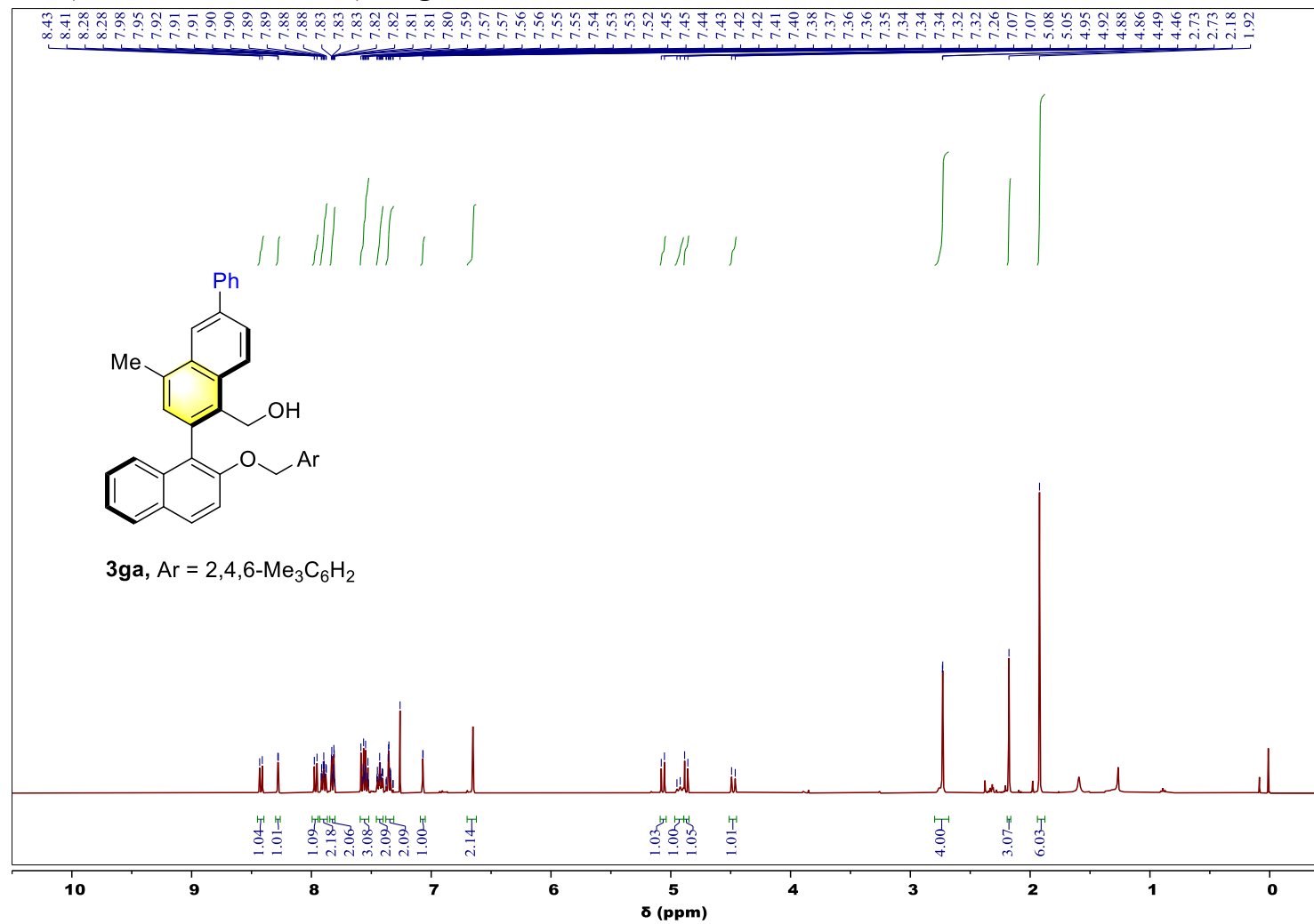
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3fa**



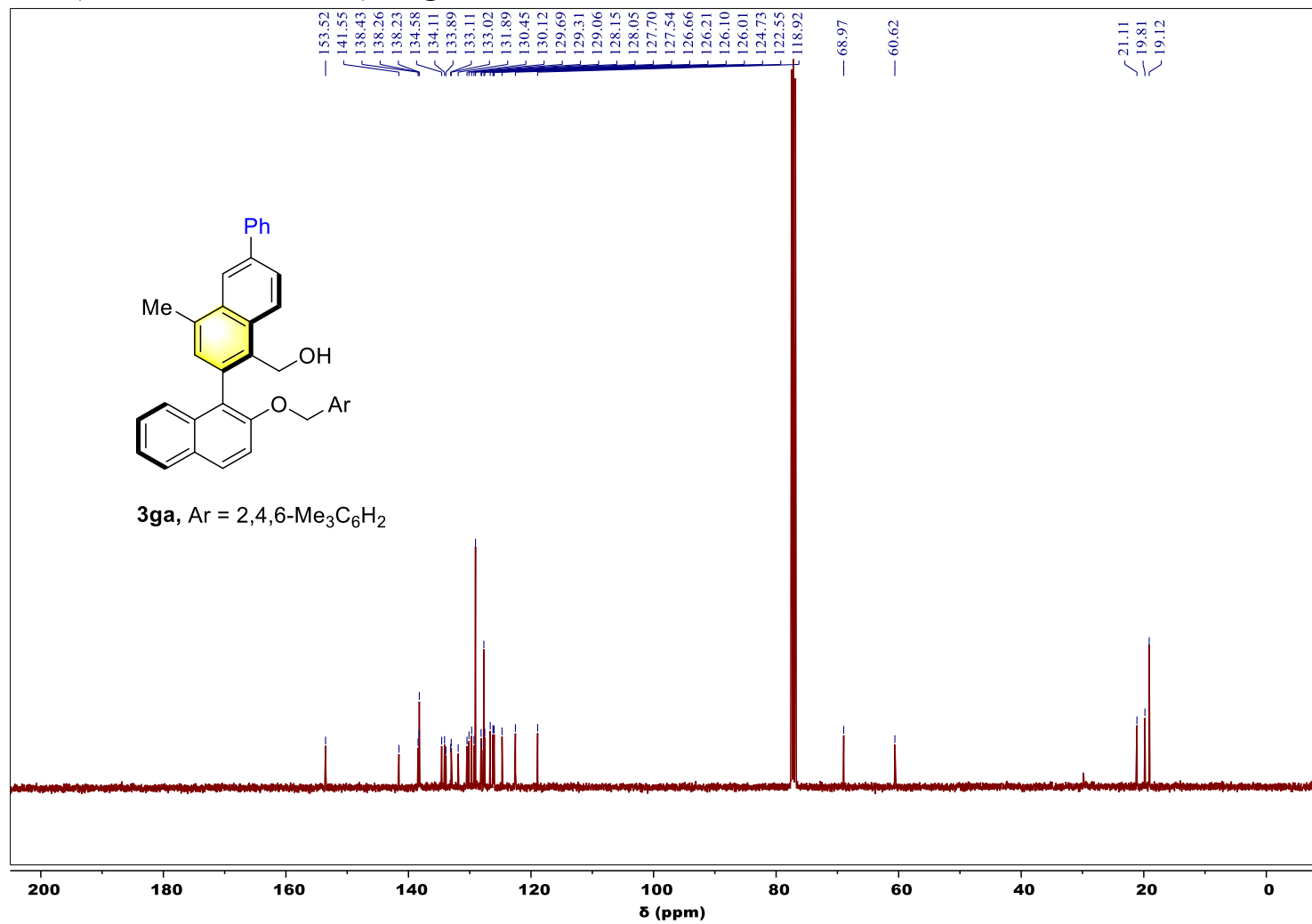
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3fa**



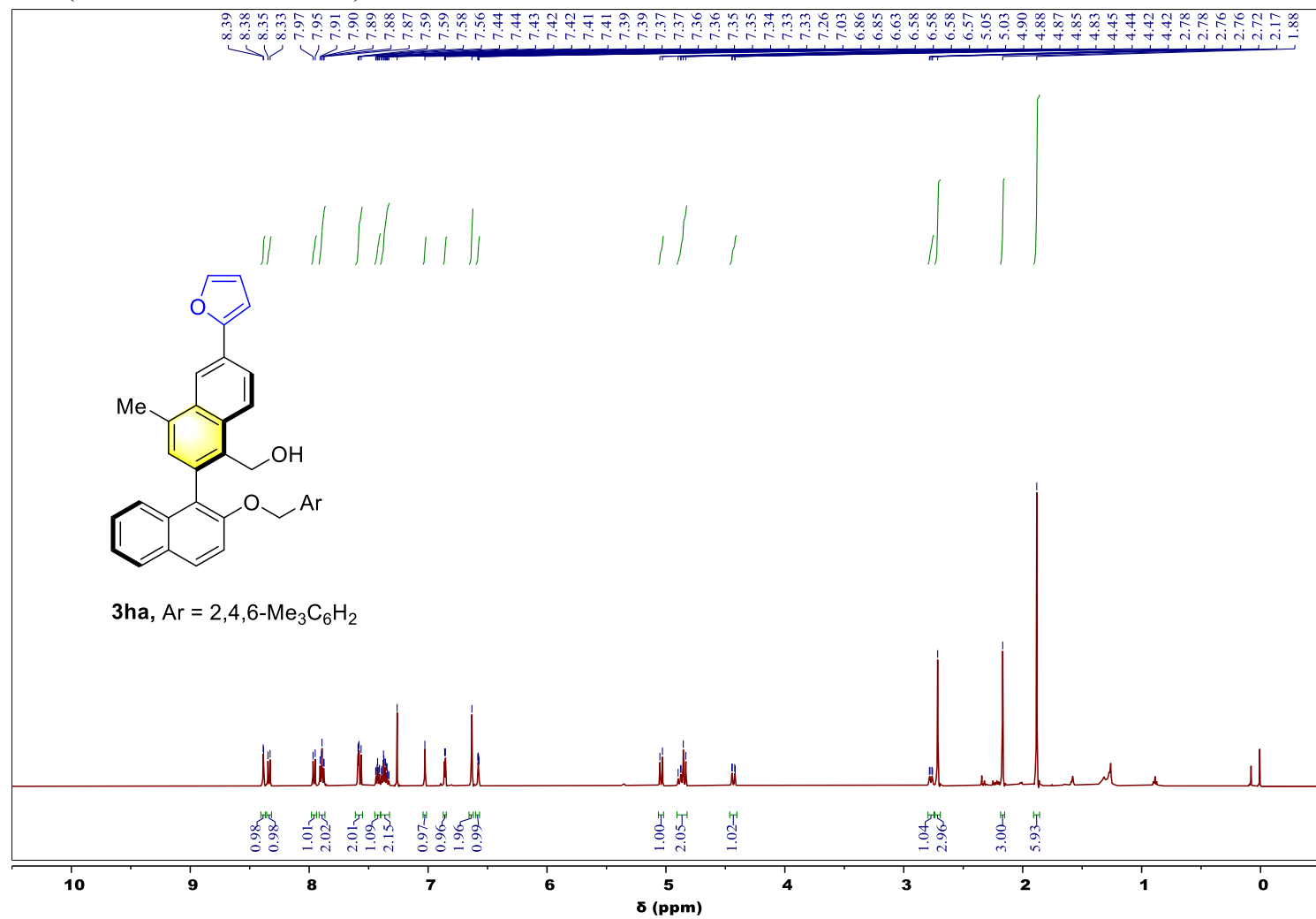
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ga**



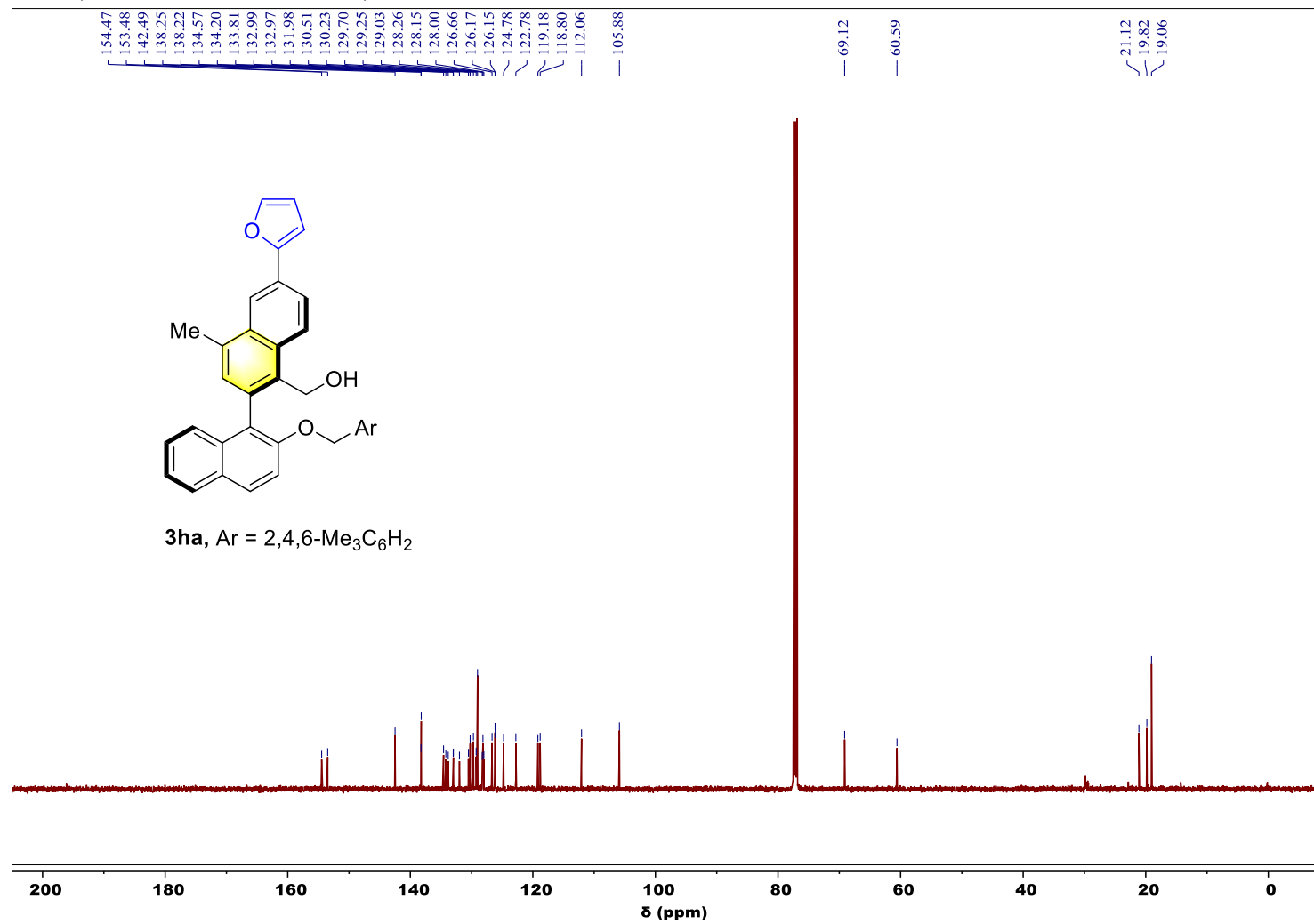
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ga**



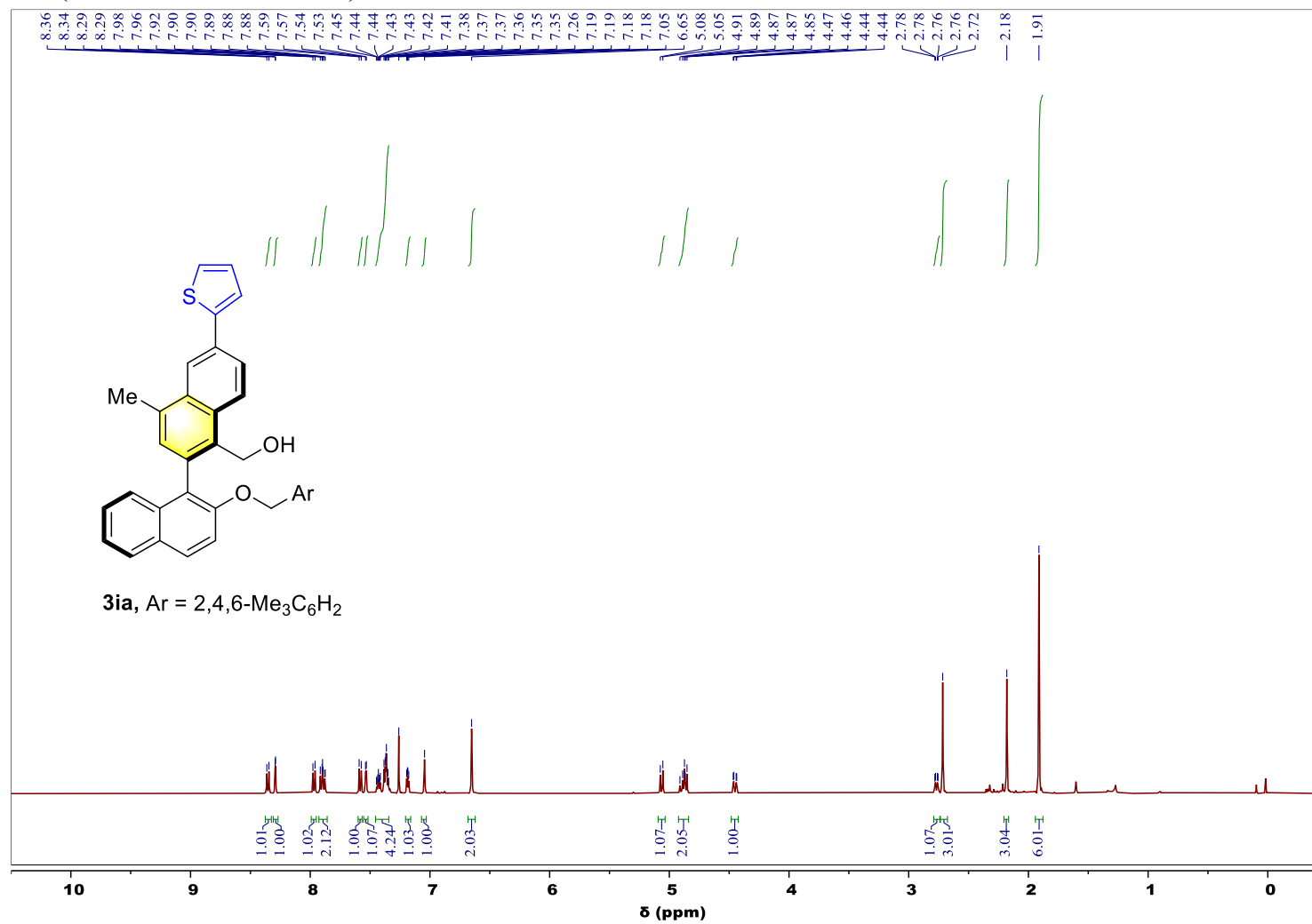
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3ha**



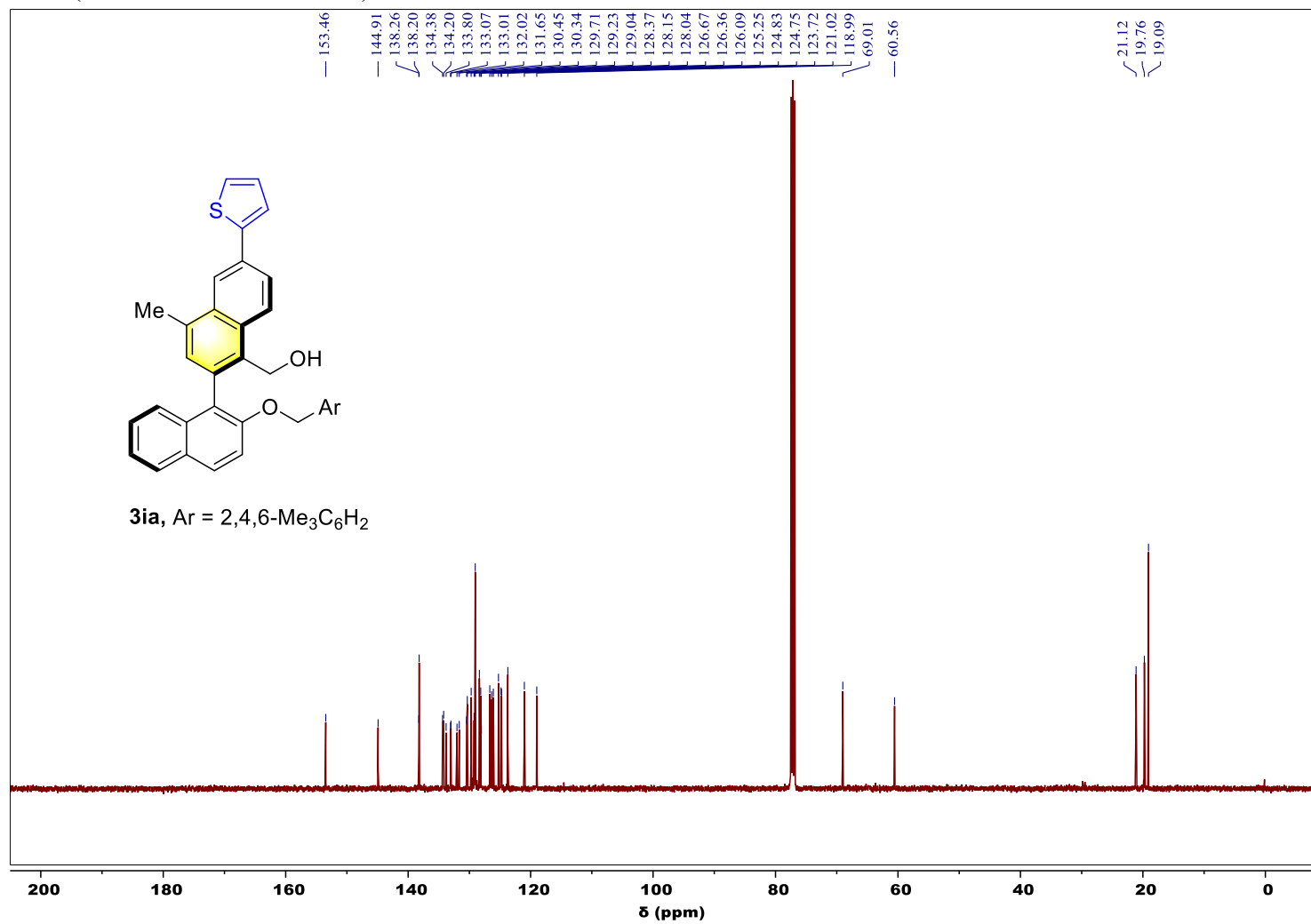
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ha**



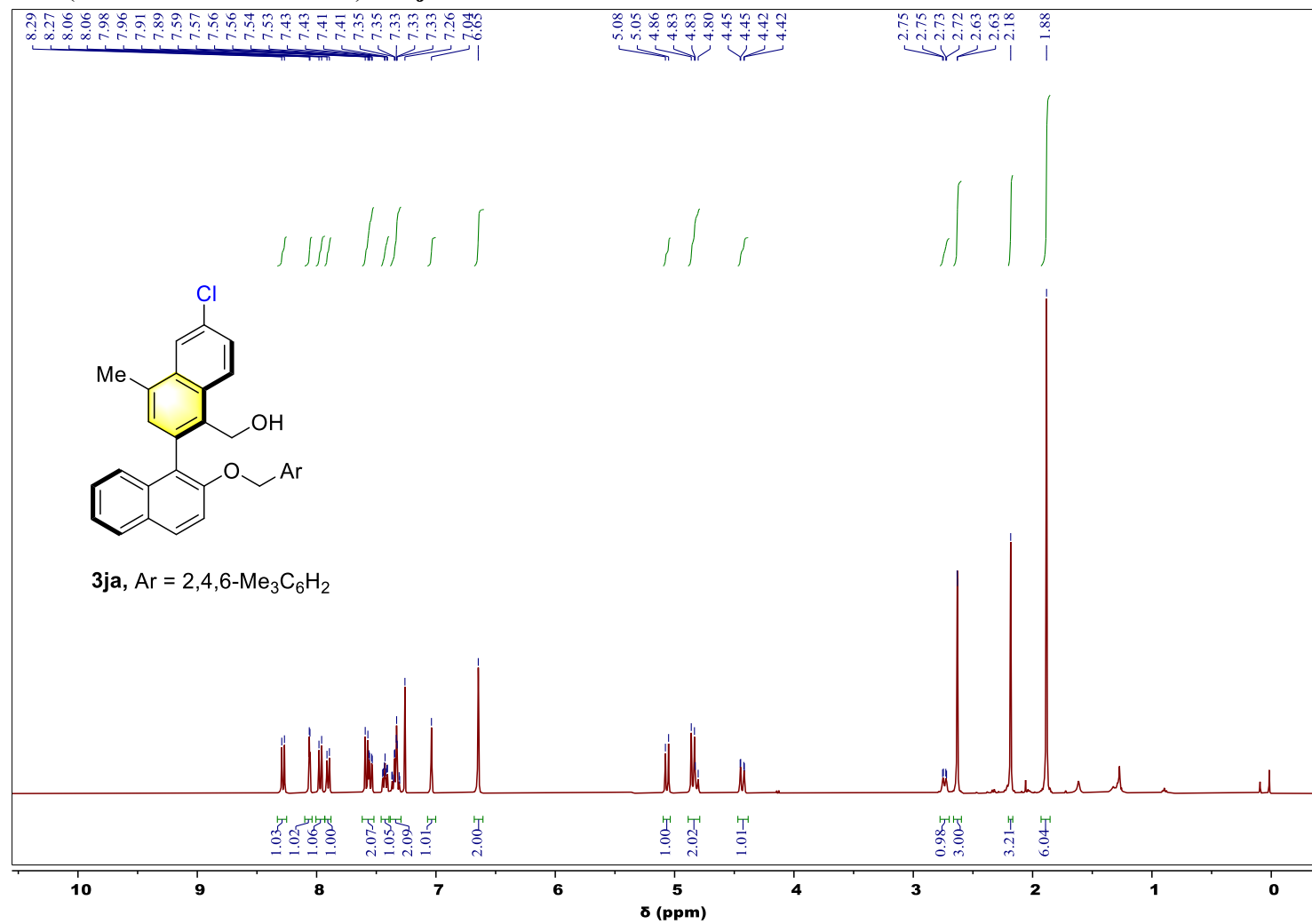
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3ia**



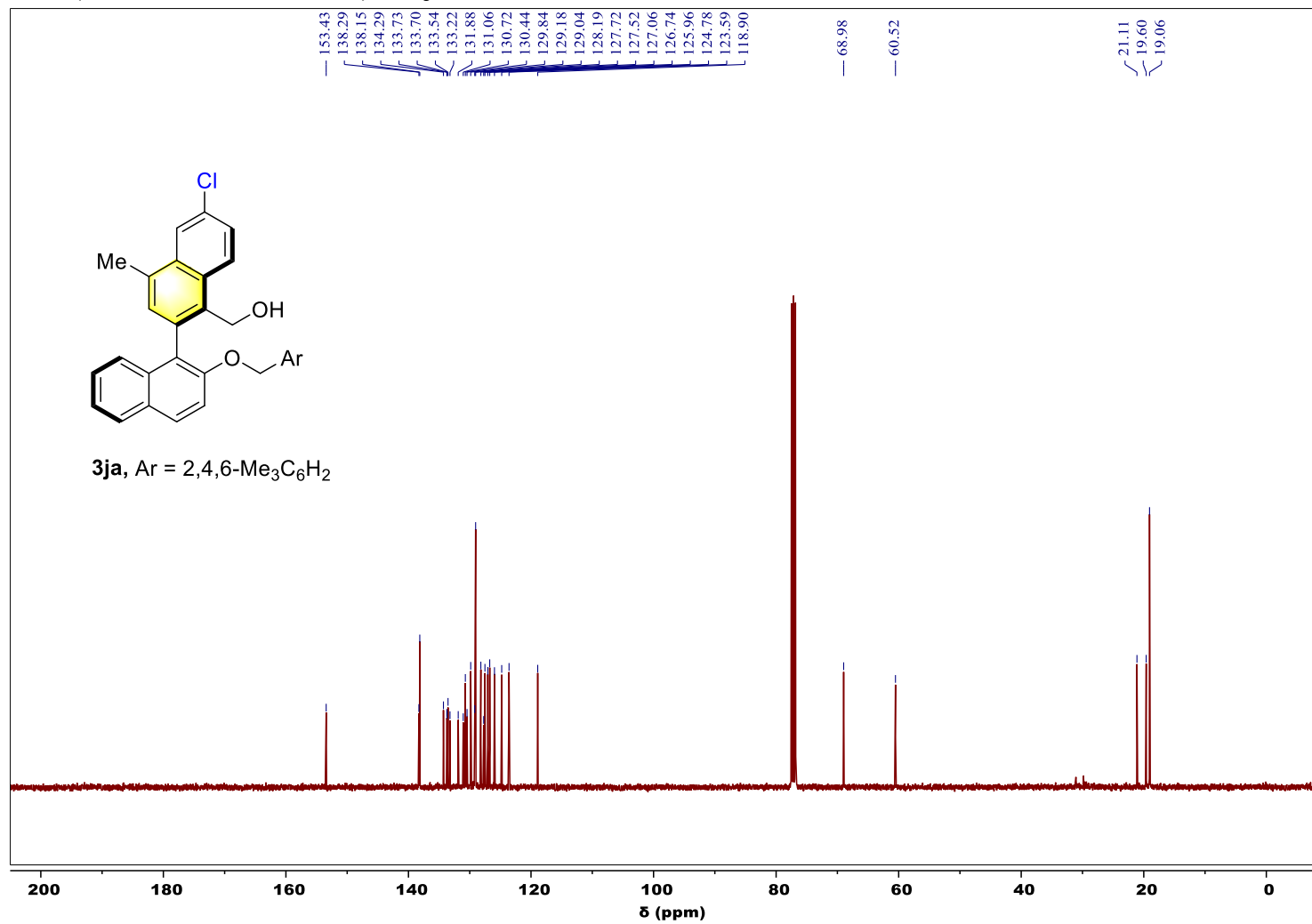
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ia**



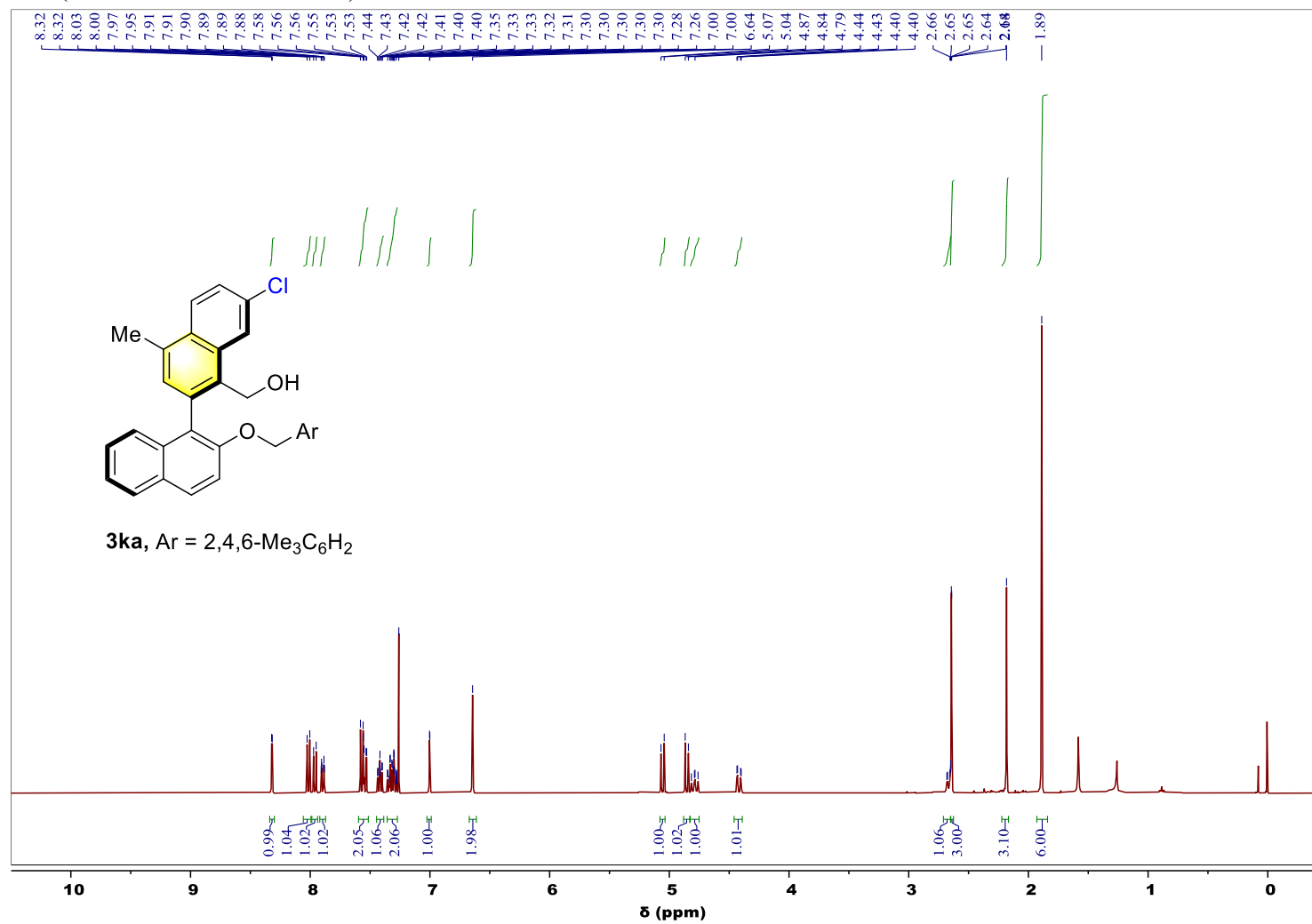
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3ja**



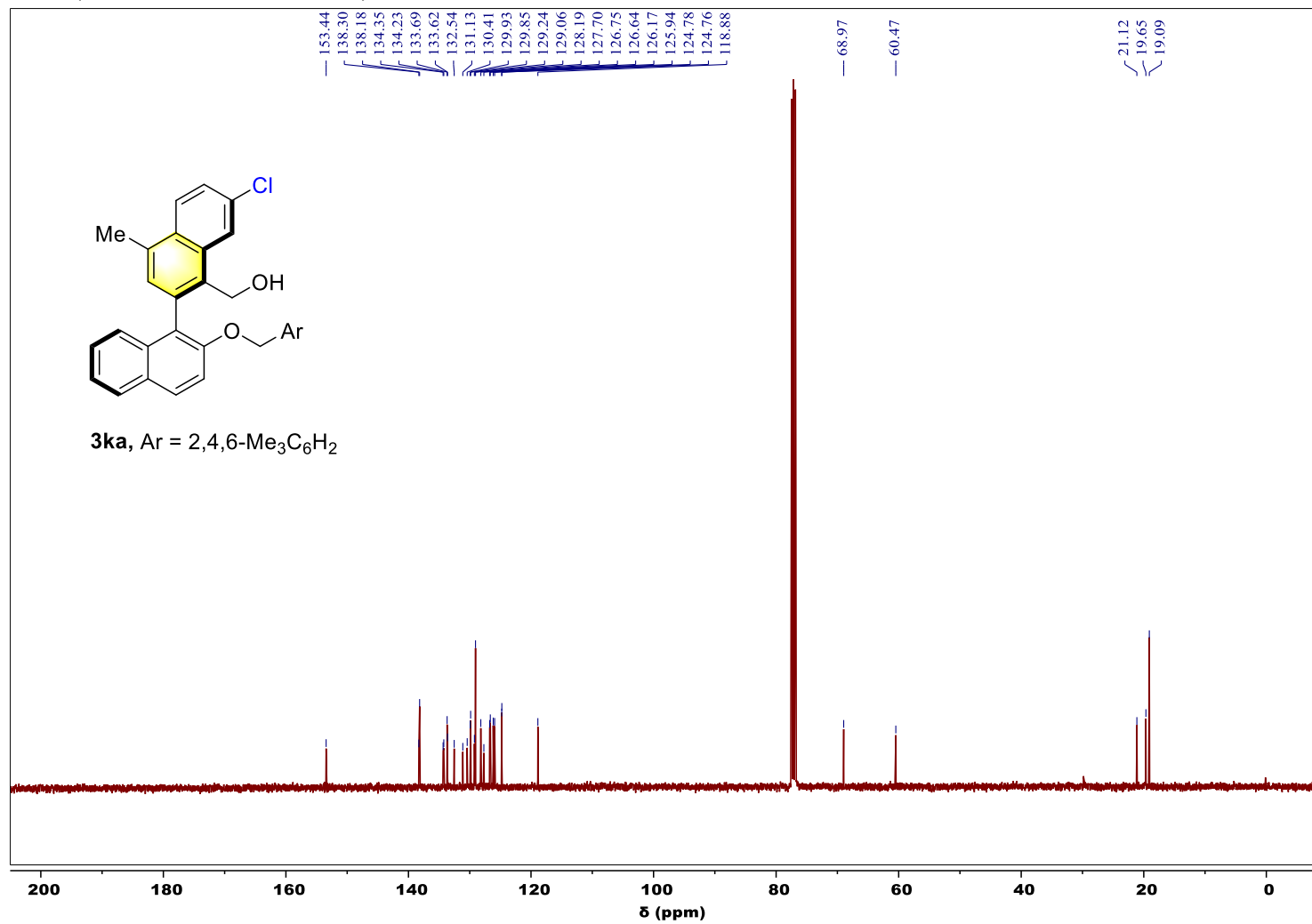
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ja**



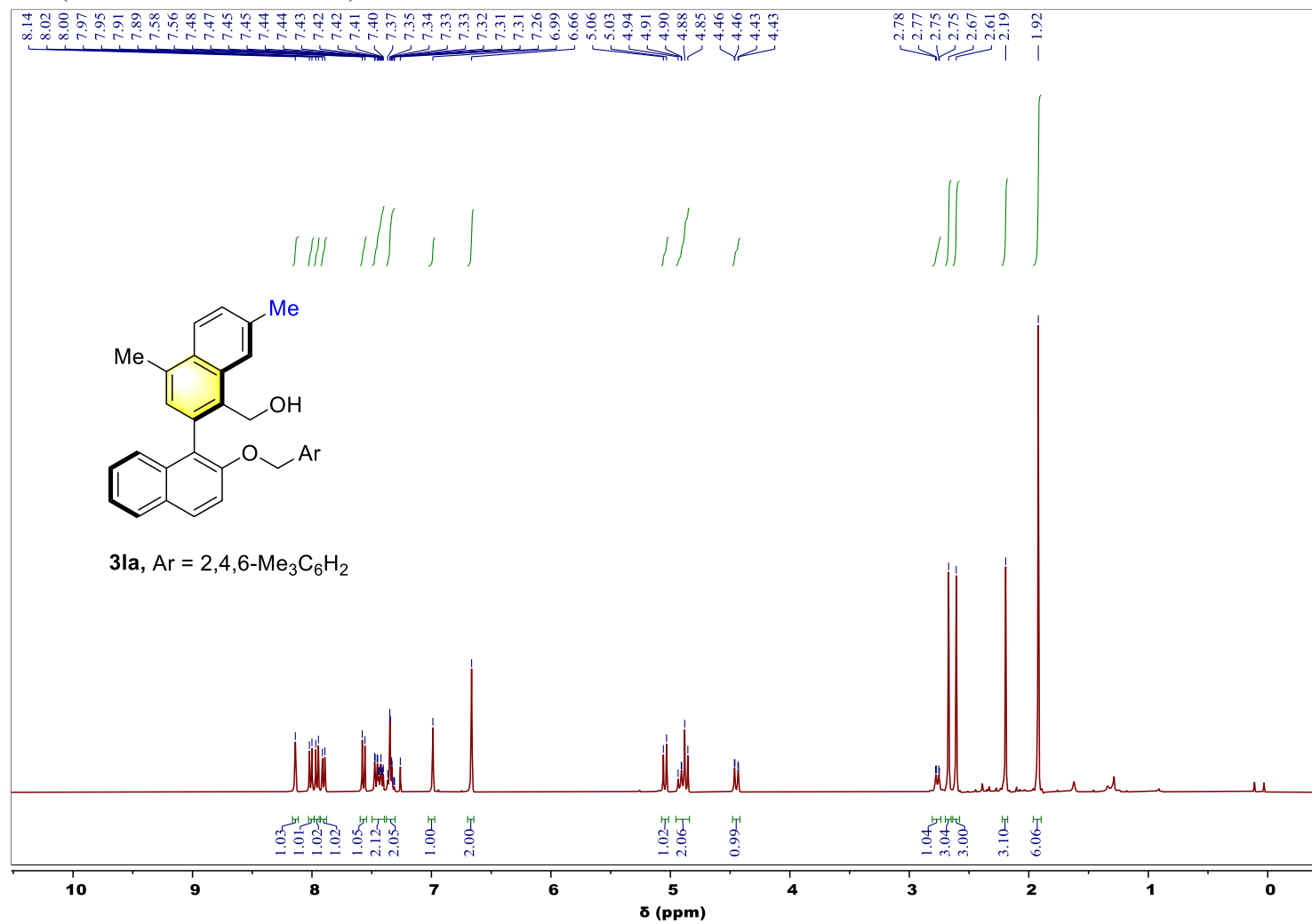
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ka**



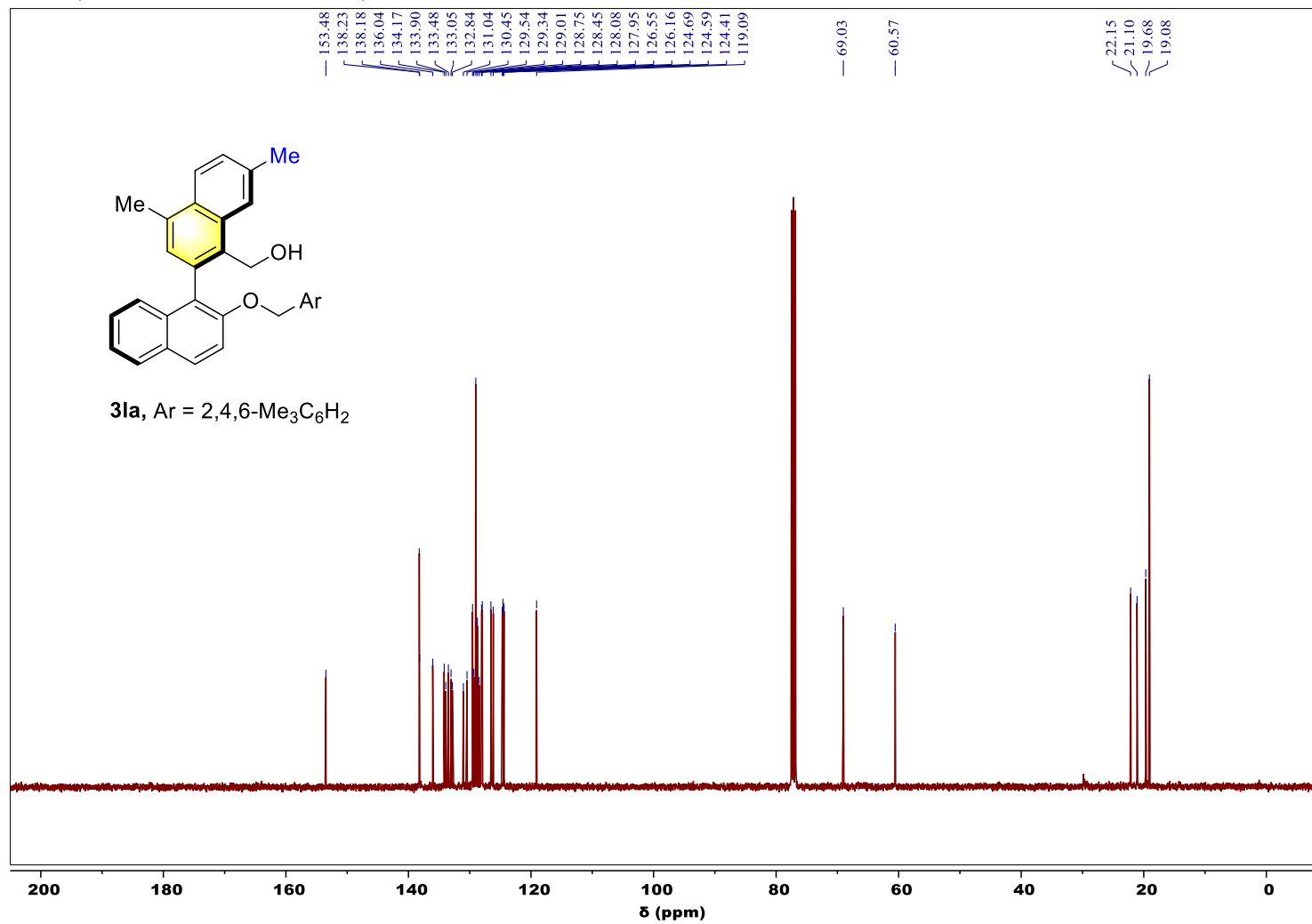
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ka**



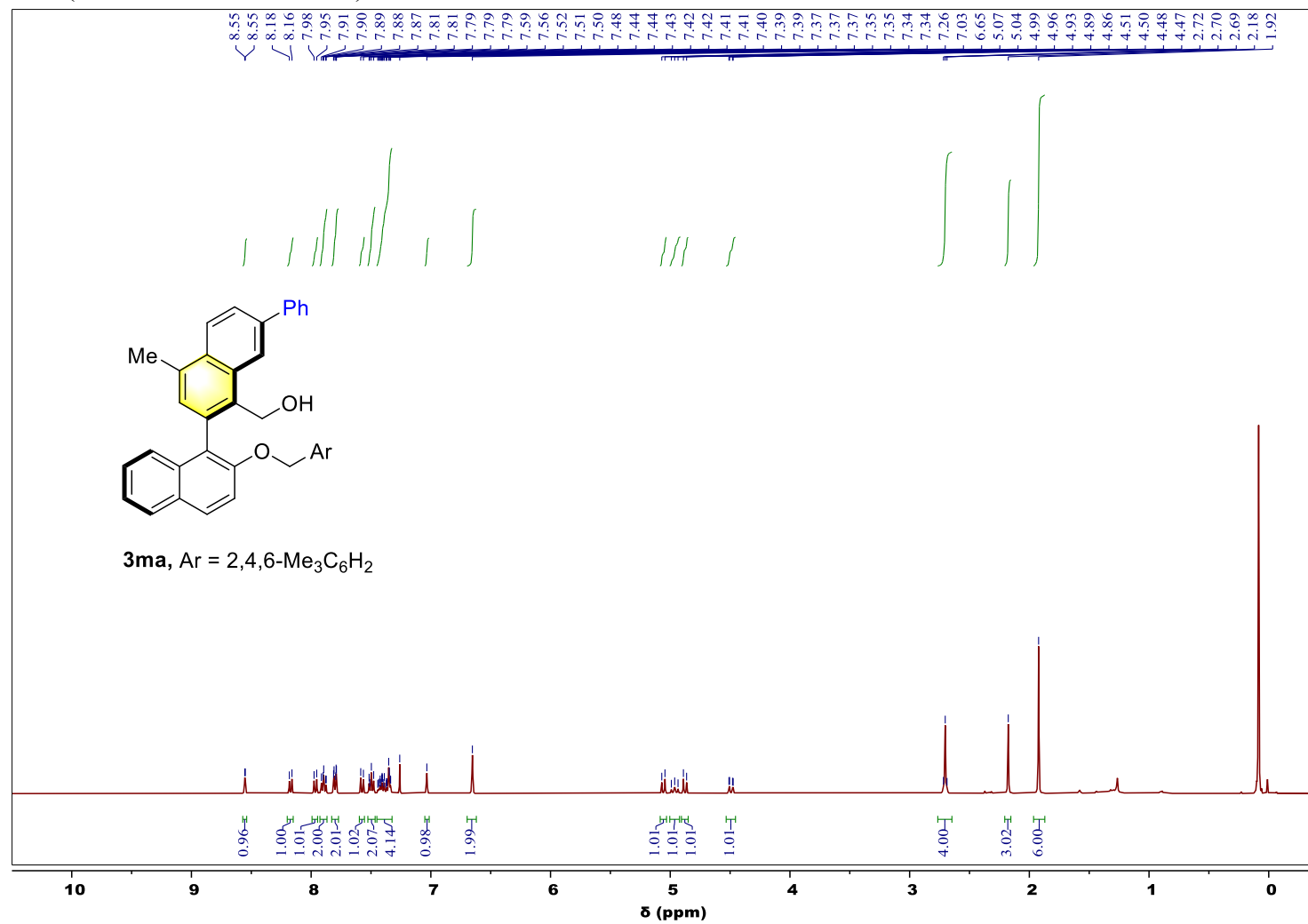
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3la**



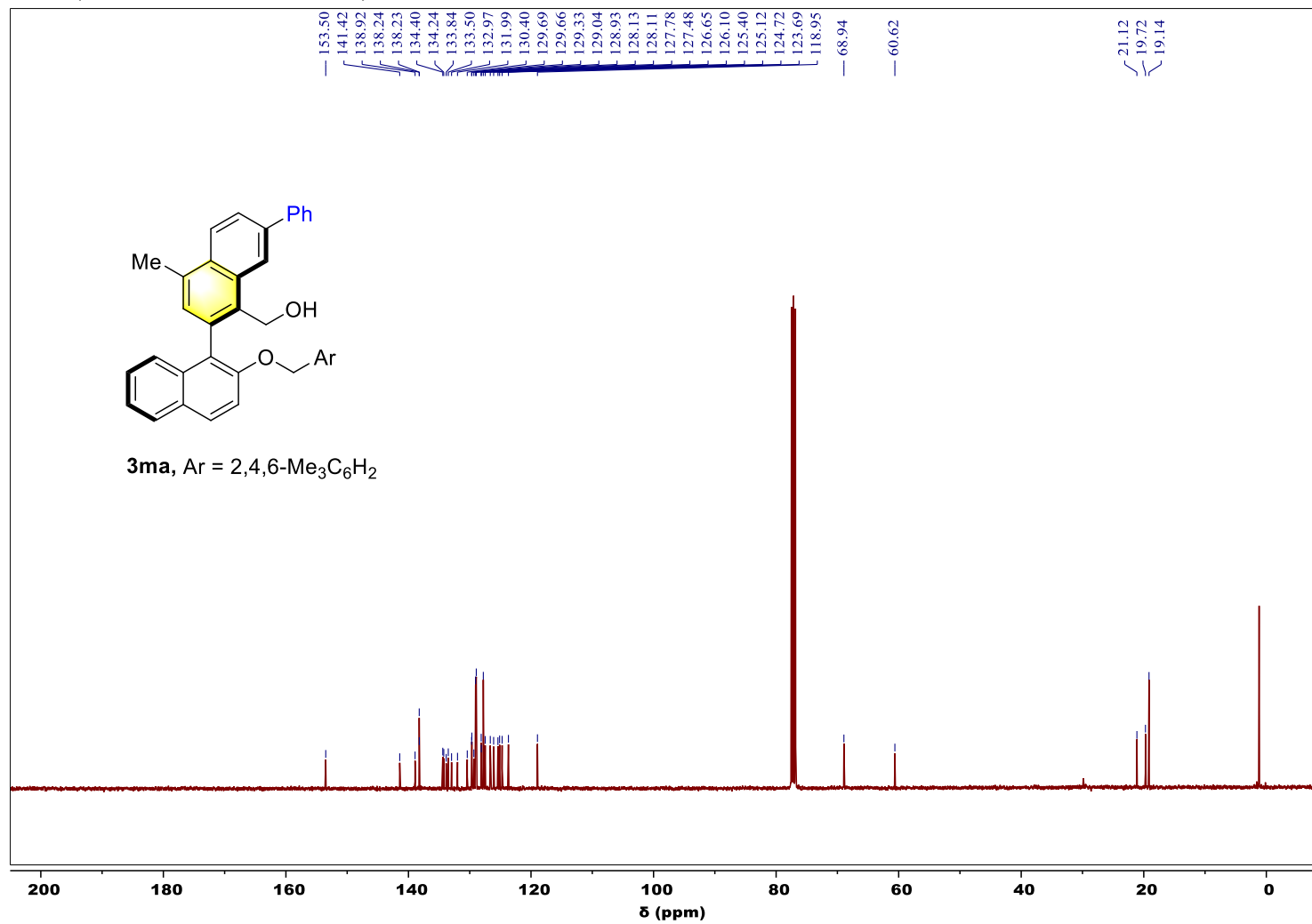
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3la**



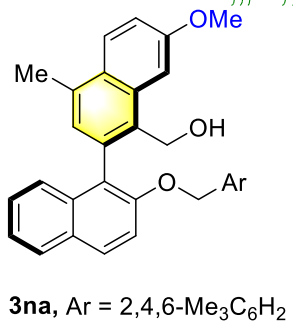
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ma**



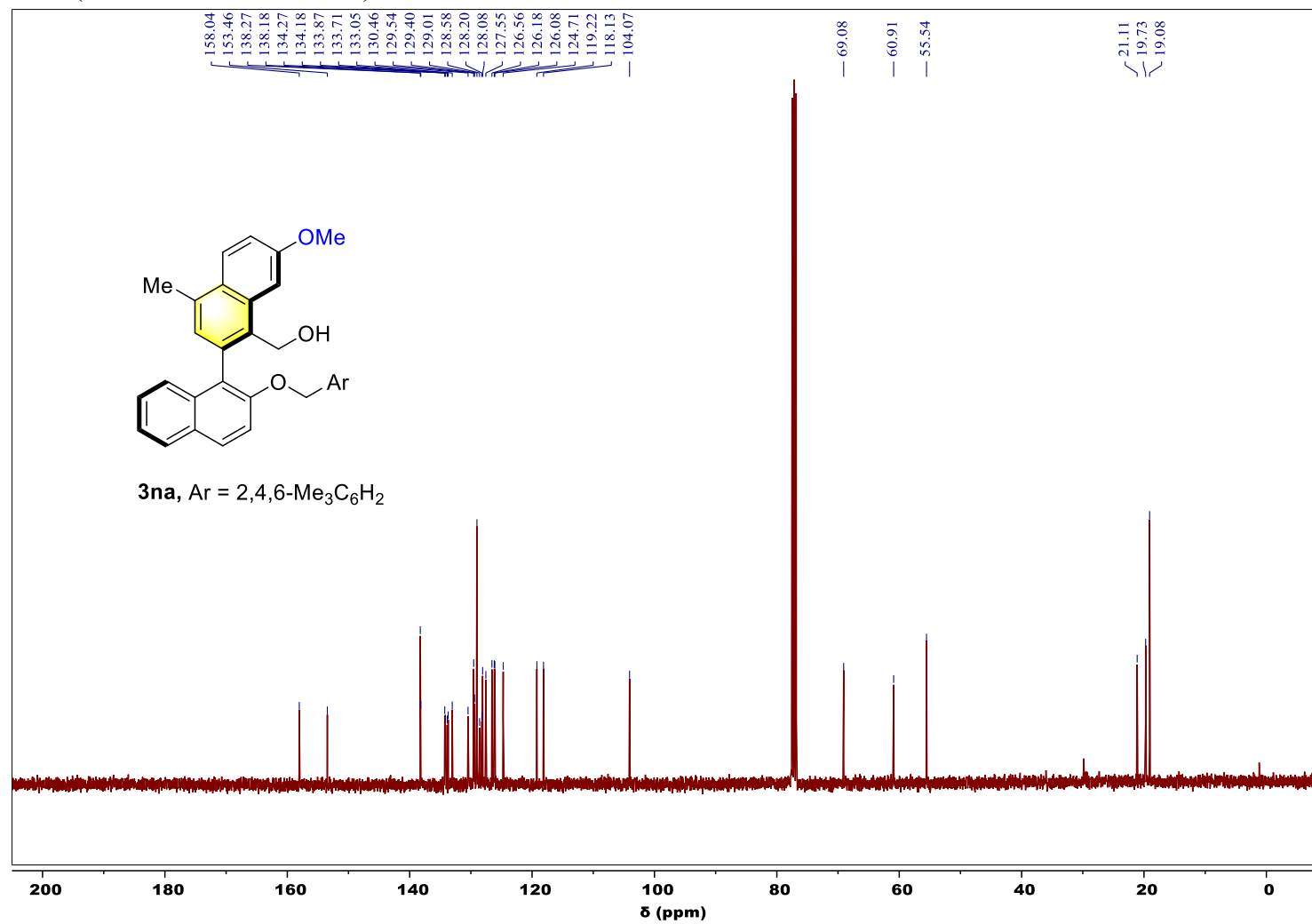
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ma**



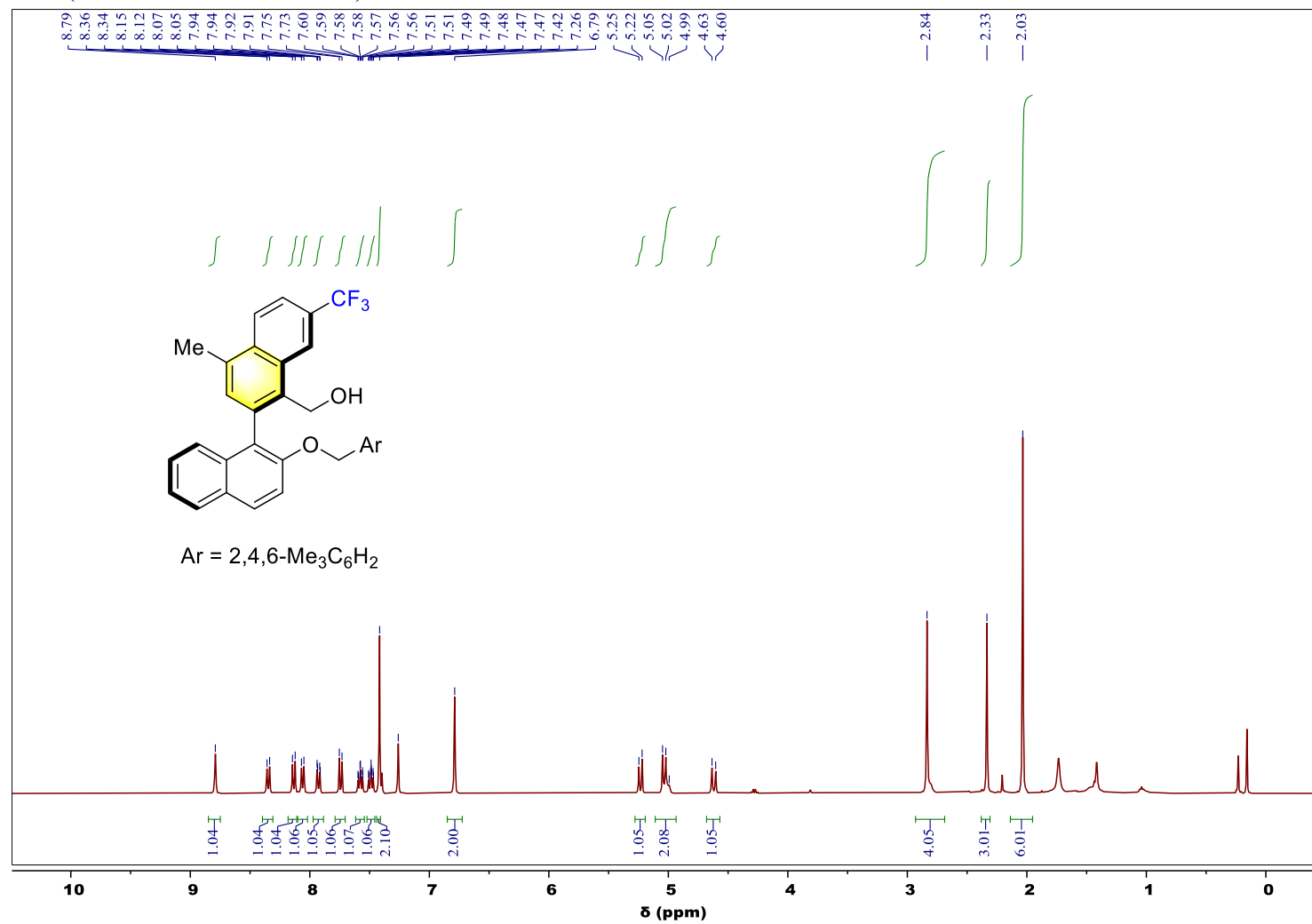
¹H NMR-spectrum (400 MHz, Chloroform-*d*) of **3na**



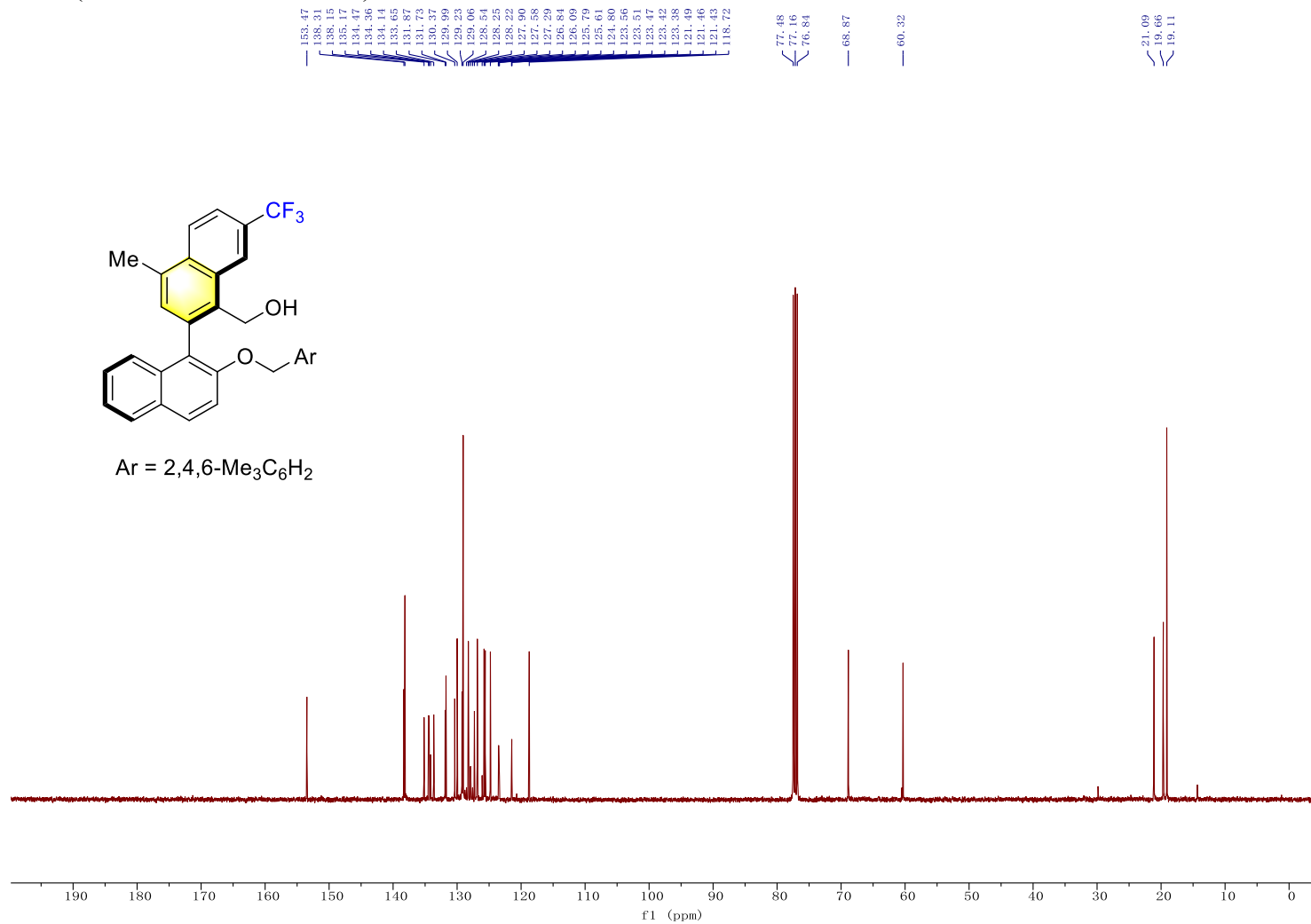
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3na**



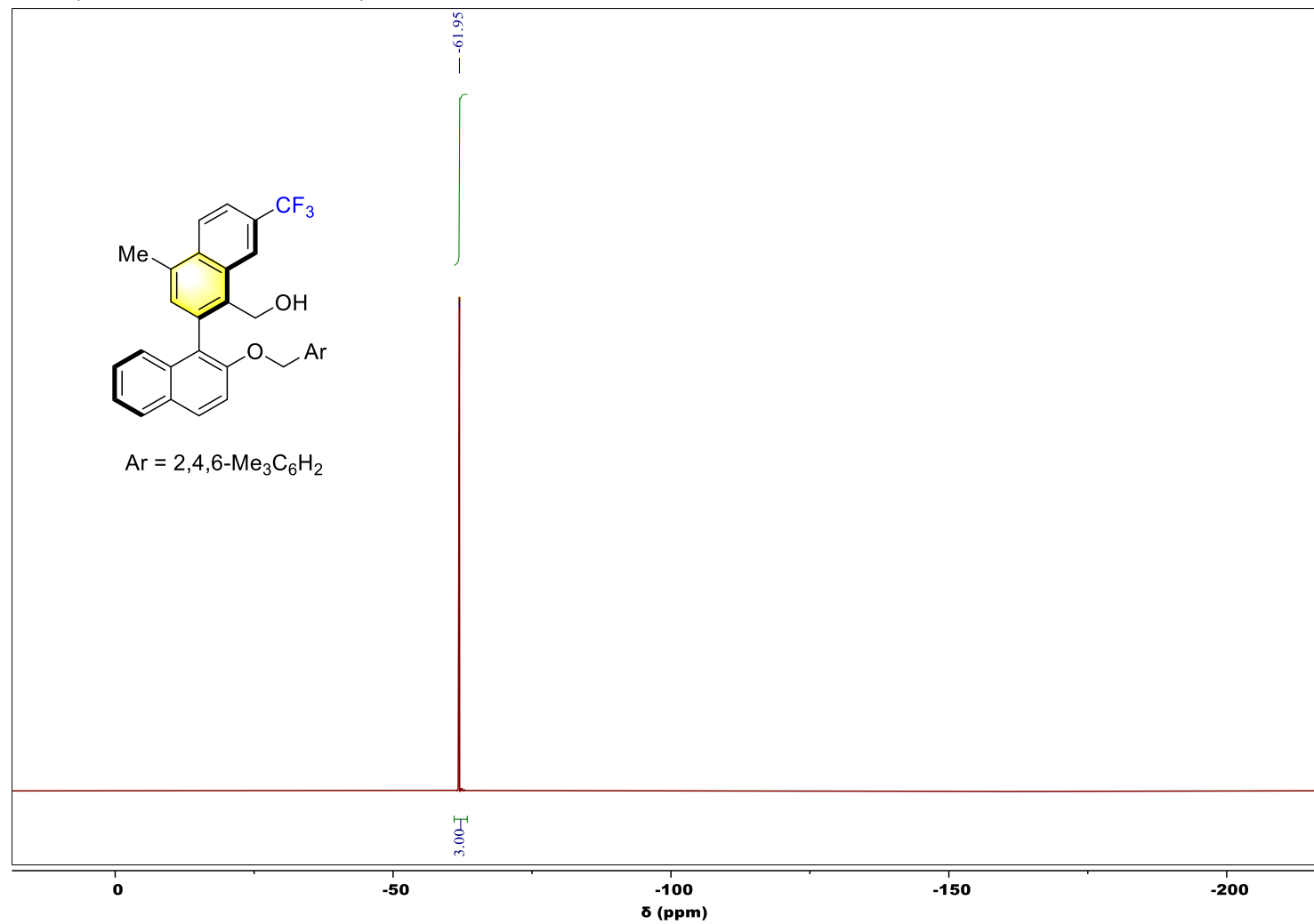
^1H NMR-spectrum (400 MHz, Chloroform- d) of **30a**



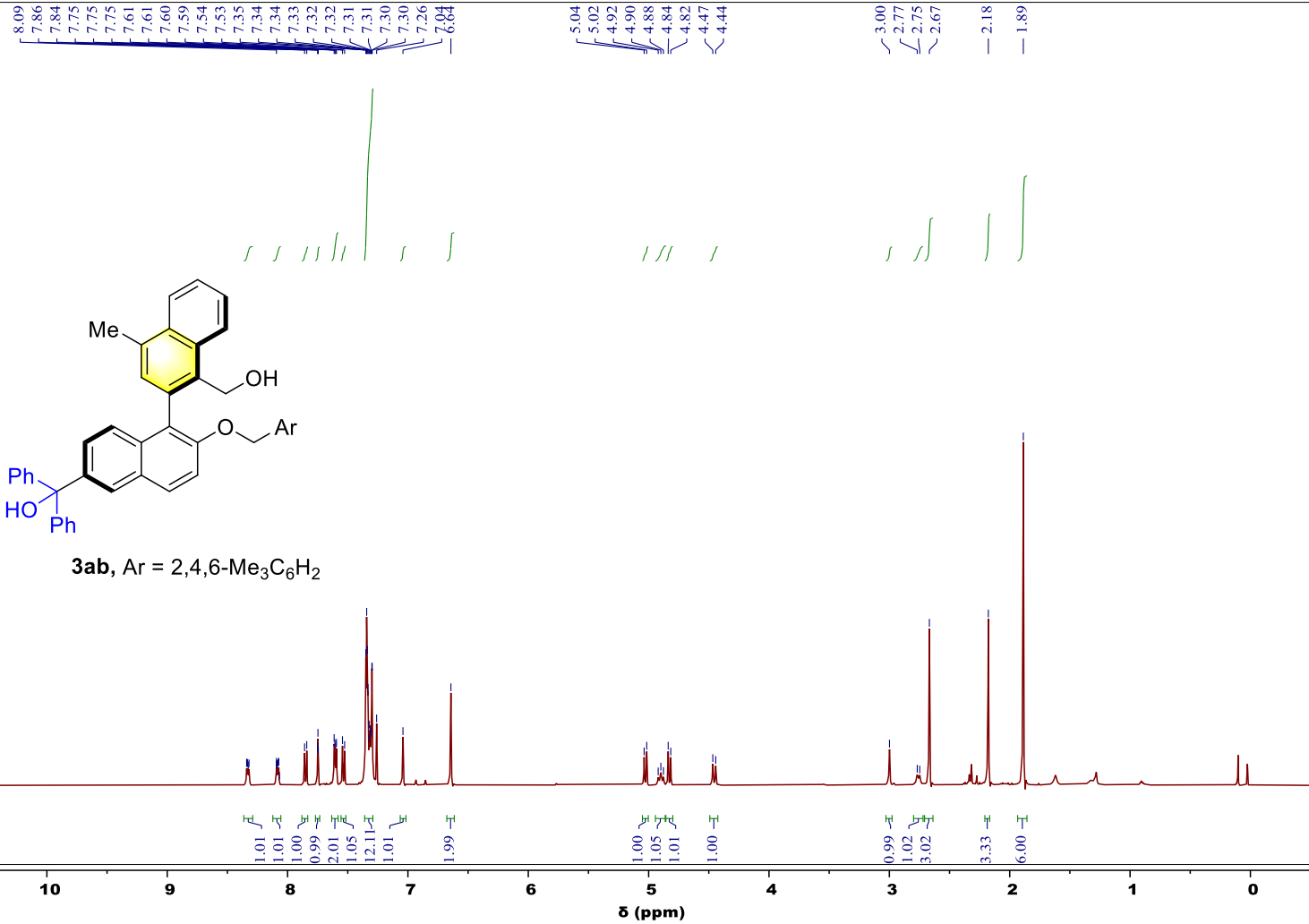
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **30a**



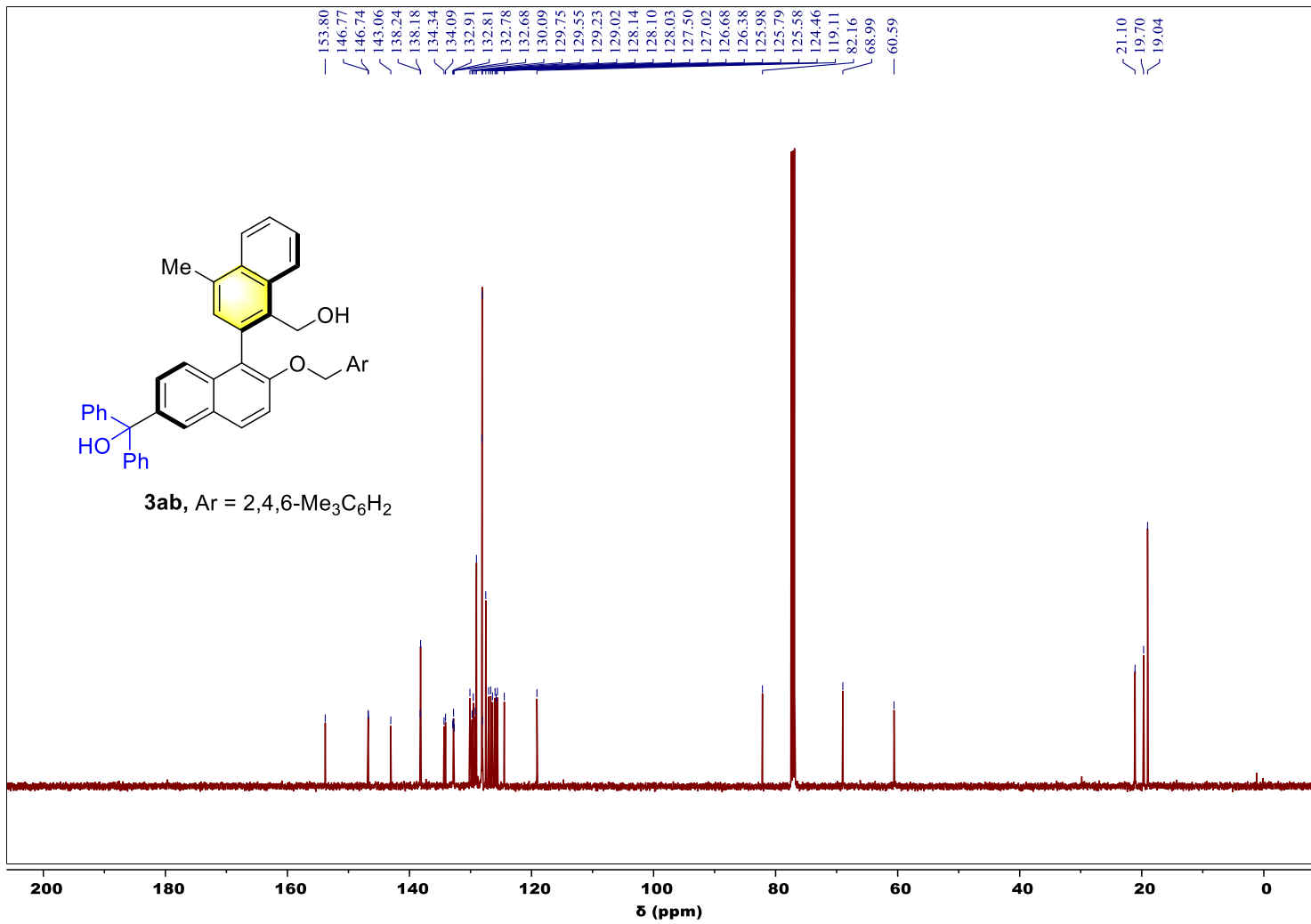
^{19}F NMR-spectrum (376 MHz, Chloroform-*d*) of **30a**



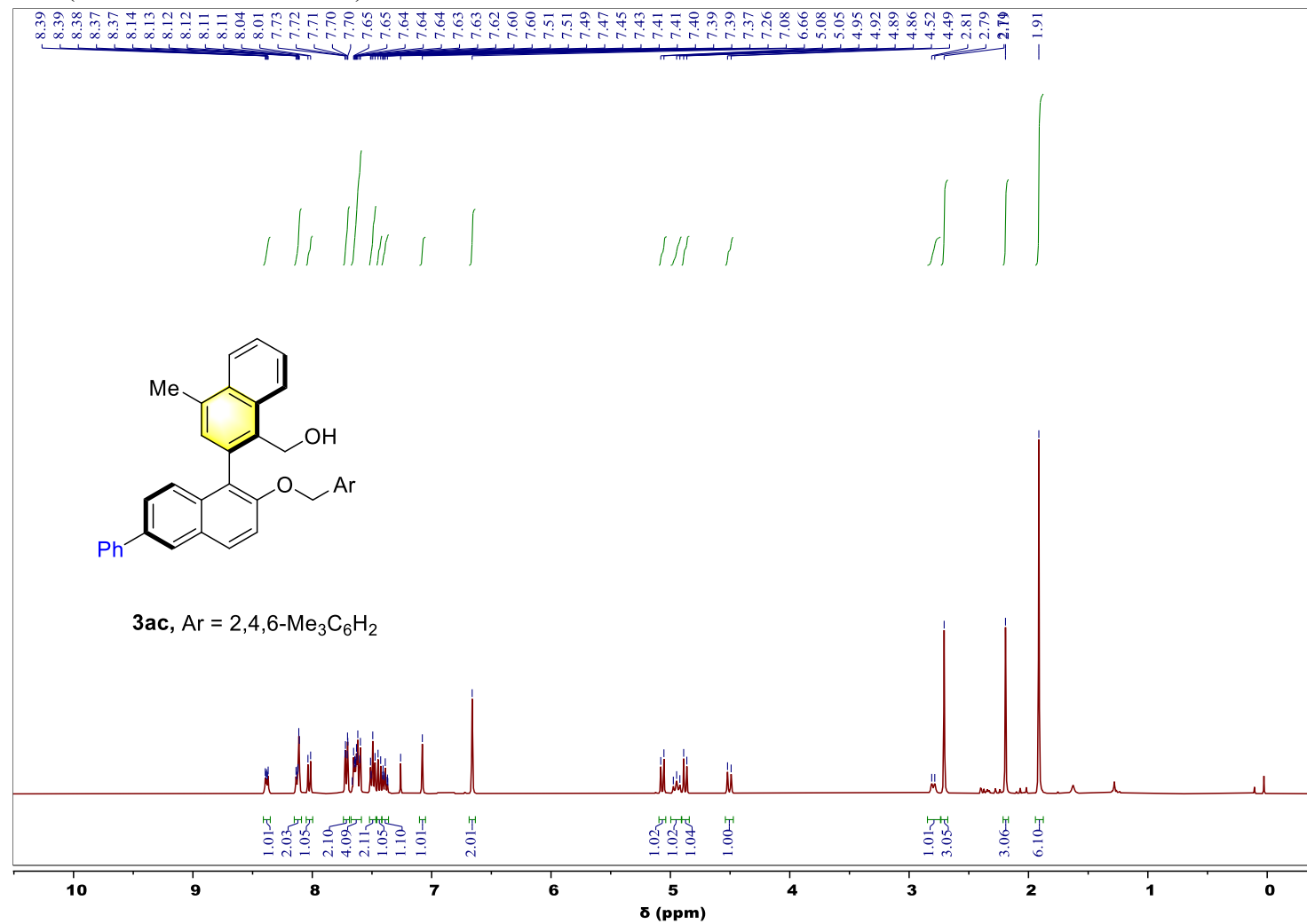
¹H NMR-spectrum (500 MHz, Chloroform-*d*) of **3ab**



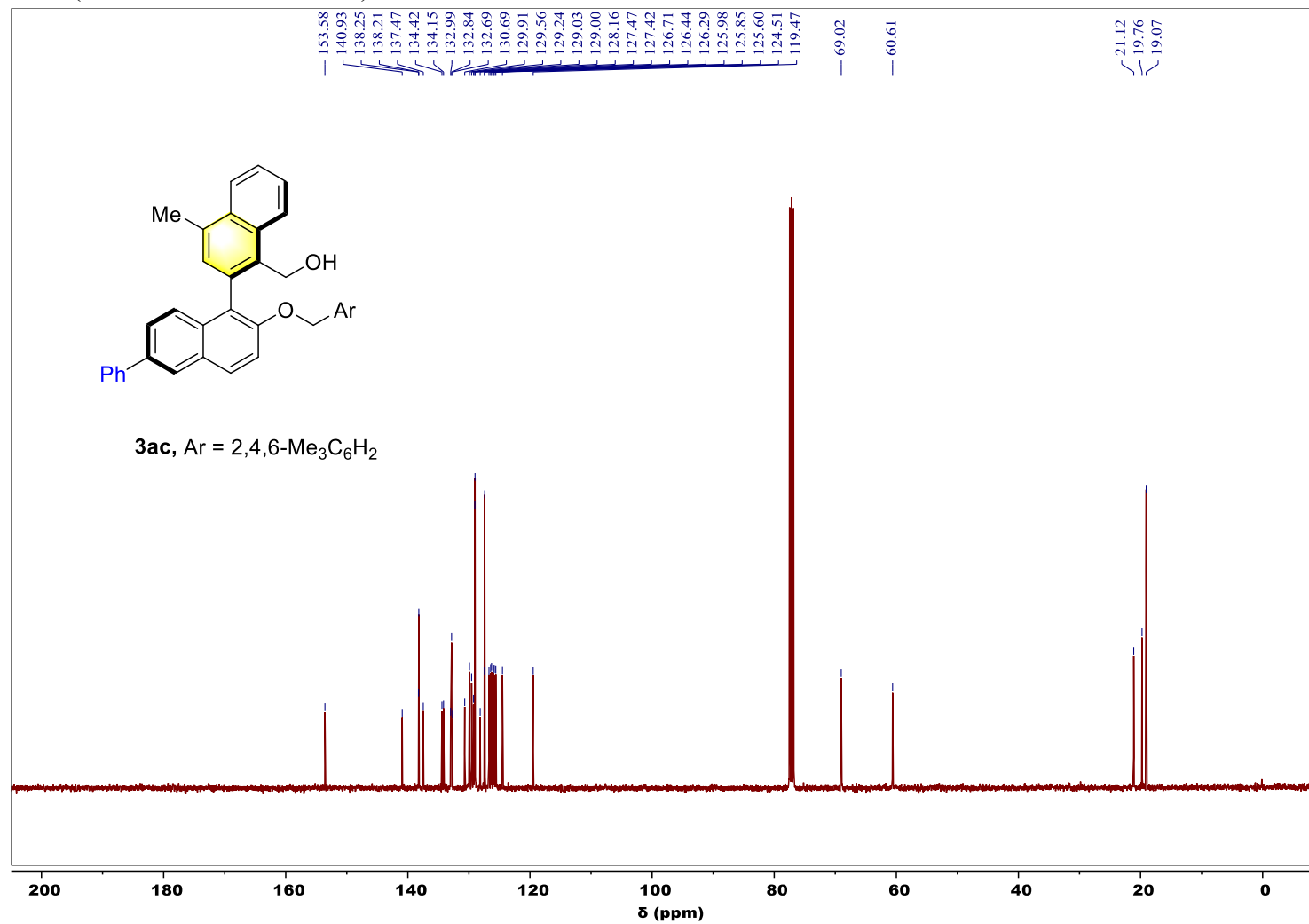
¹³C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ab**



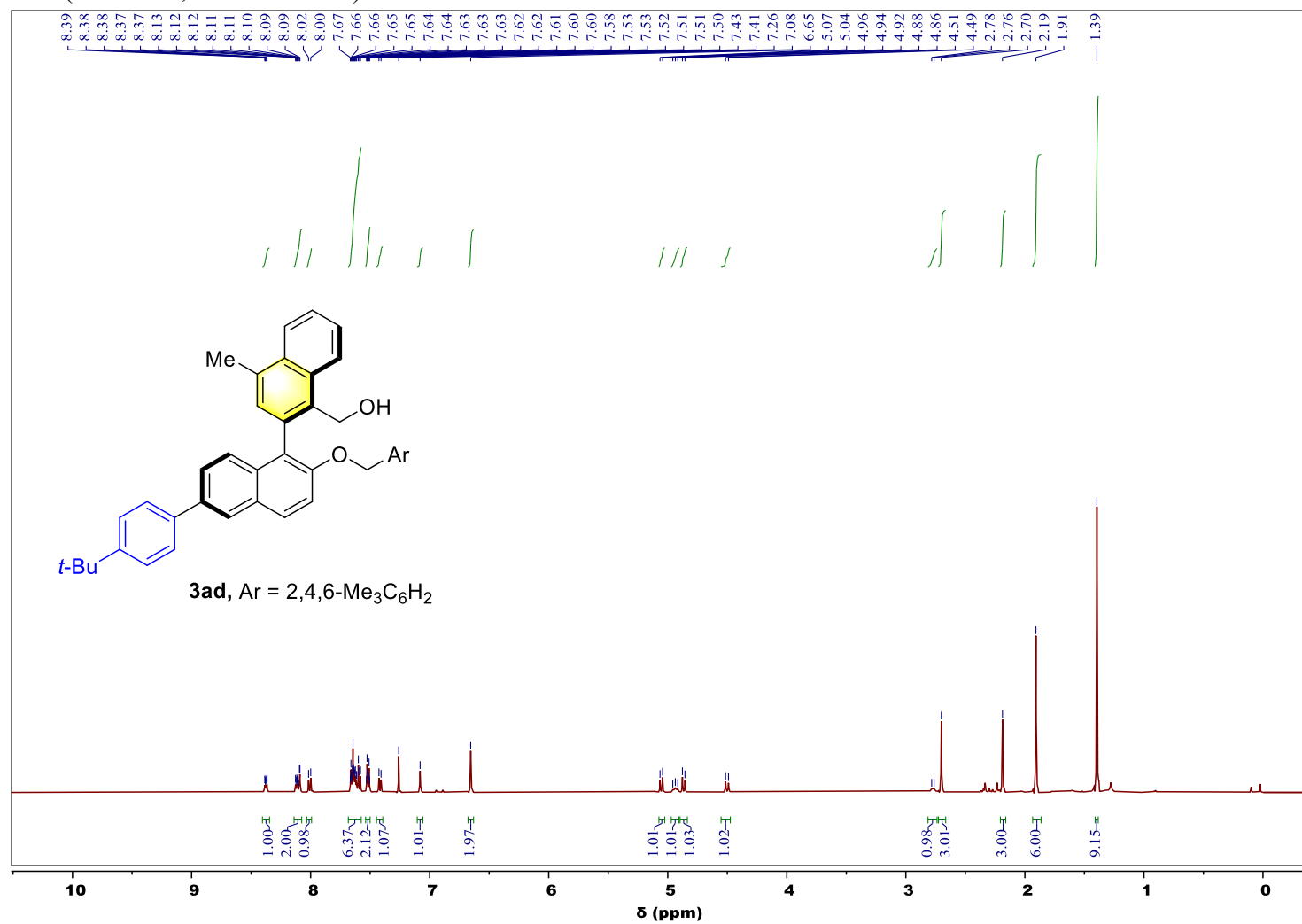
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3ac**



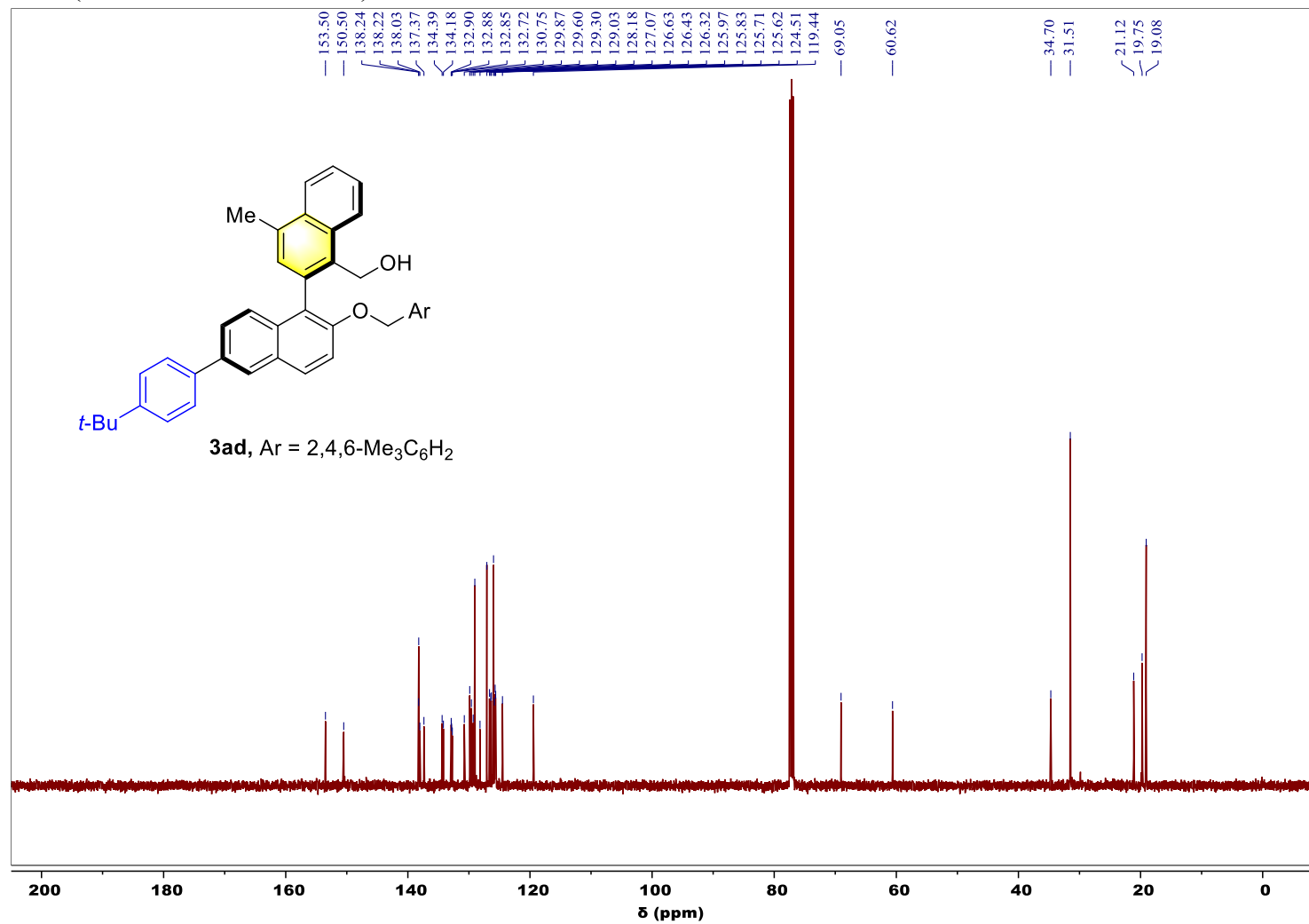
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ac**



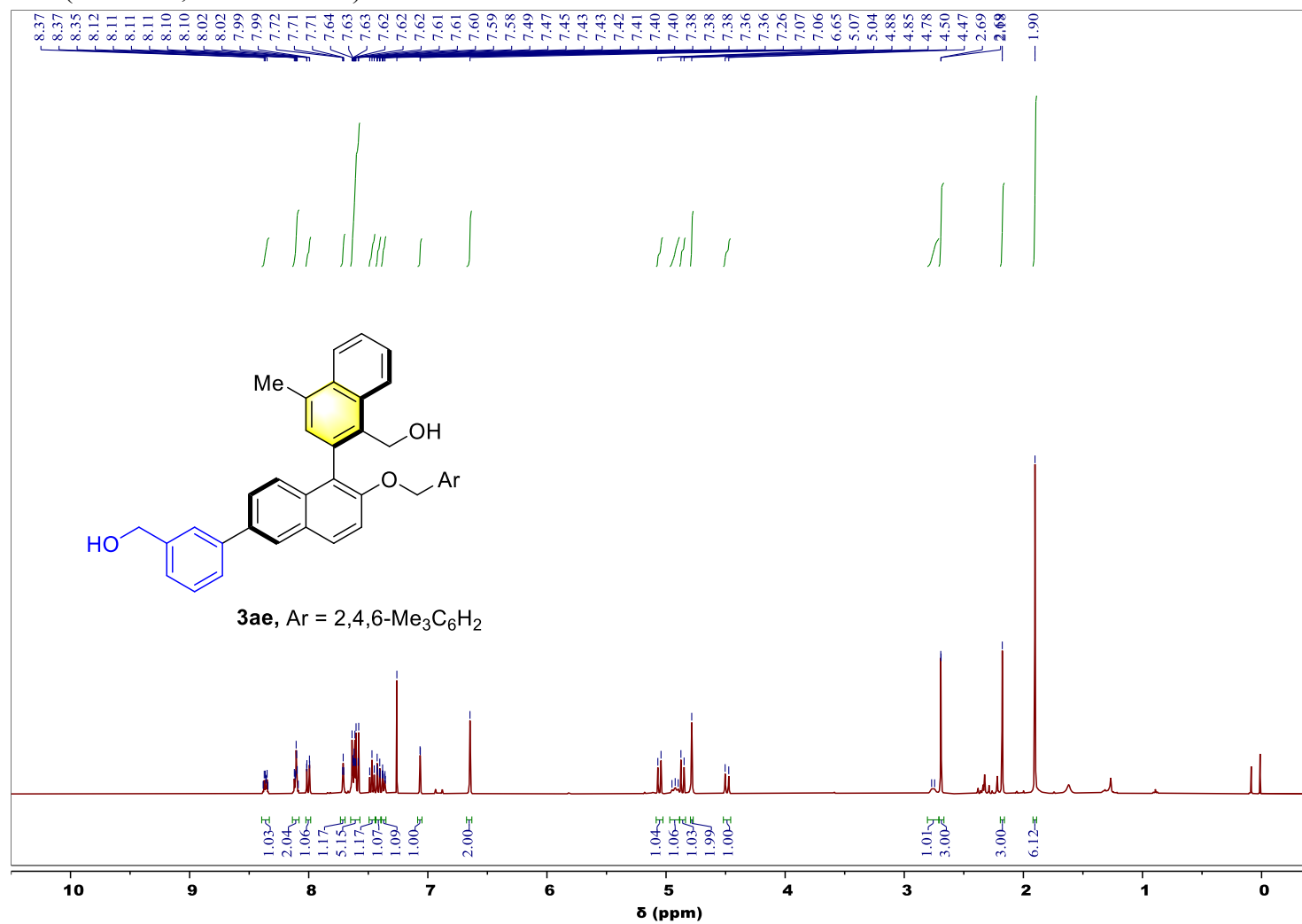
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3ad**

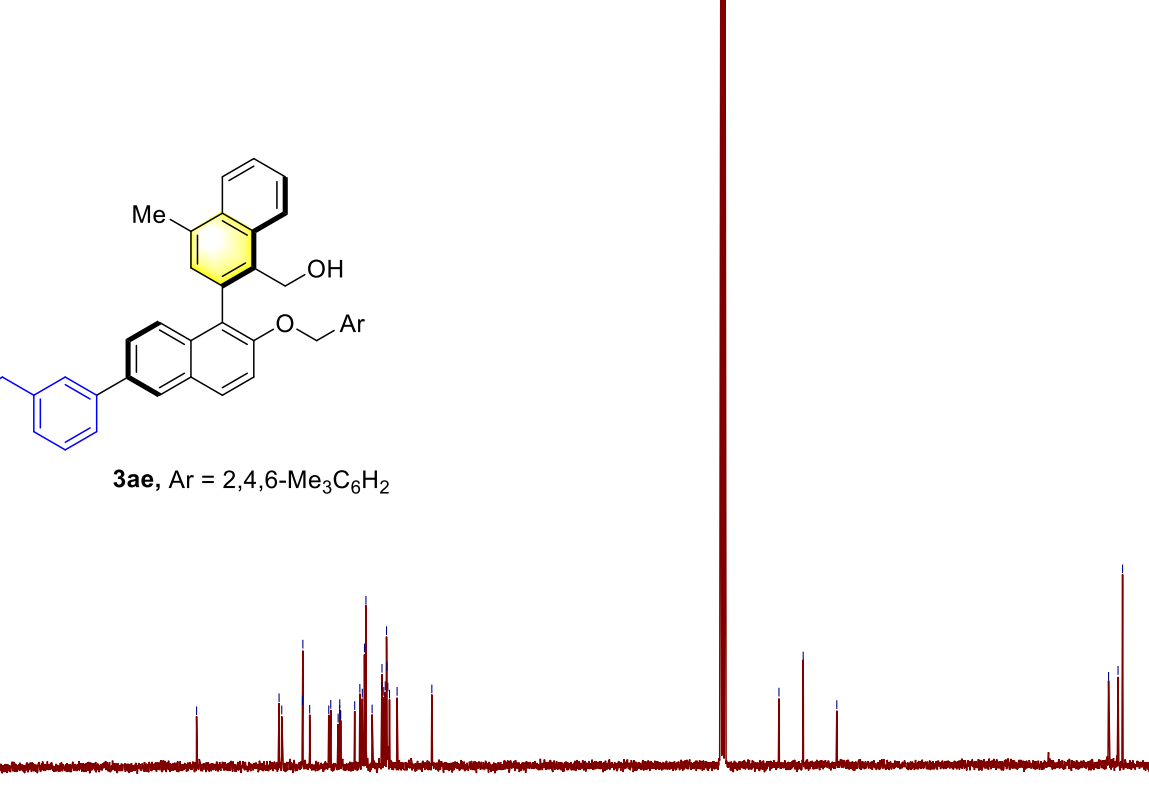


^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ad**



^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ae**

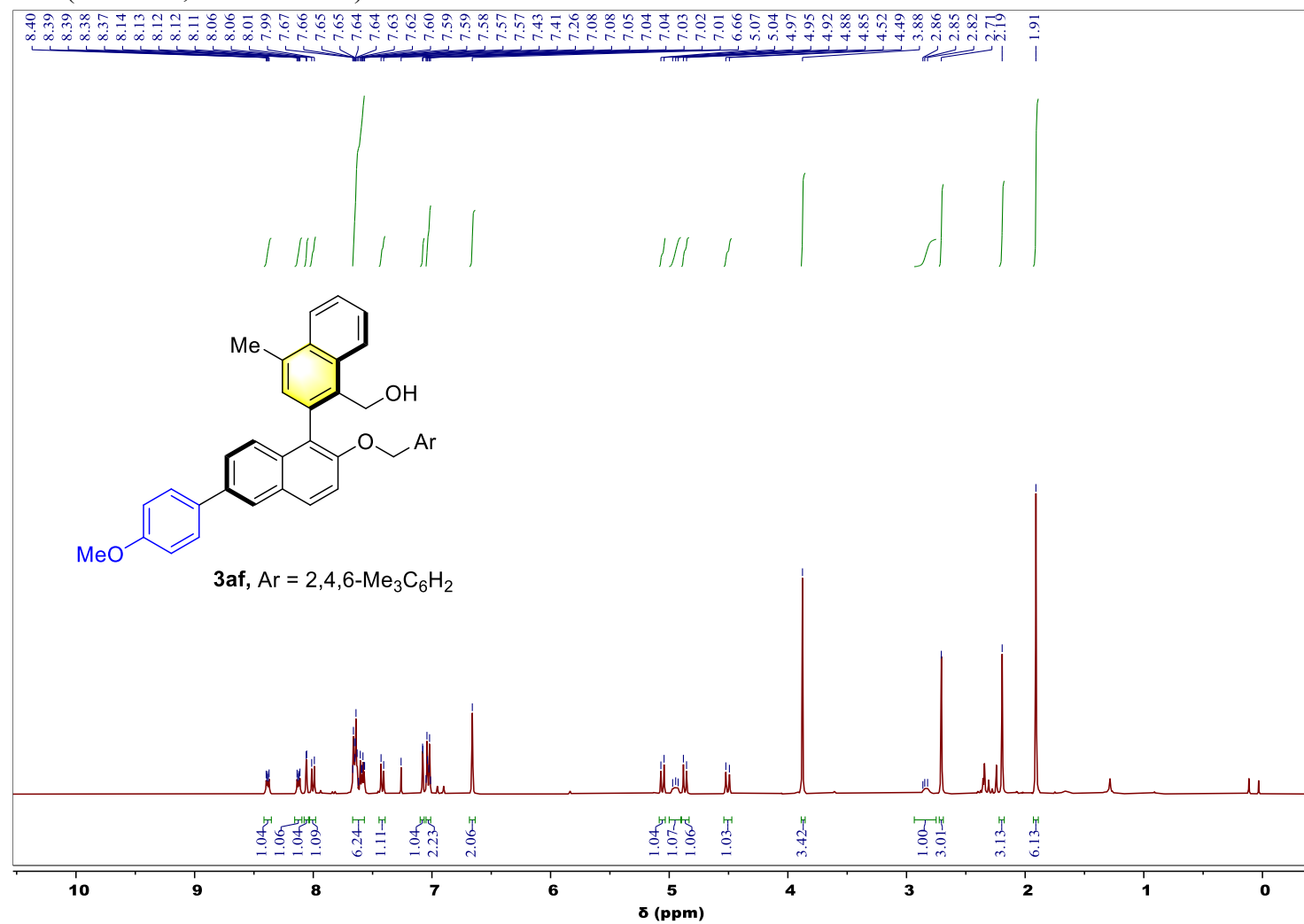




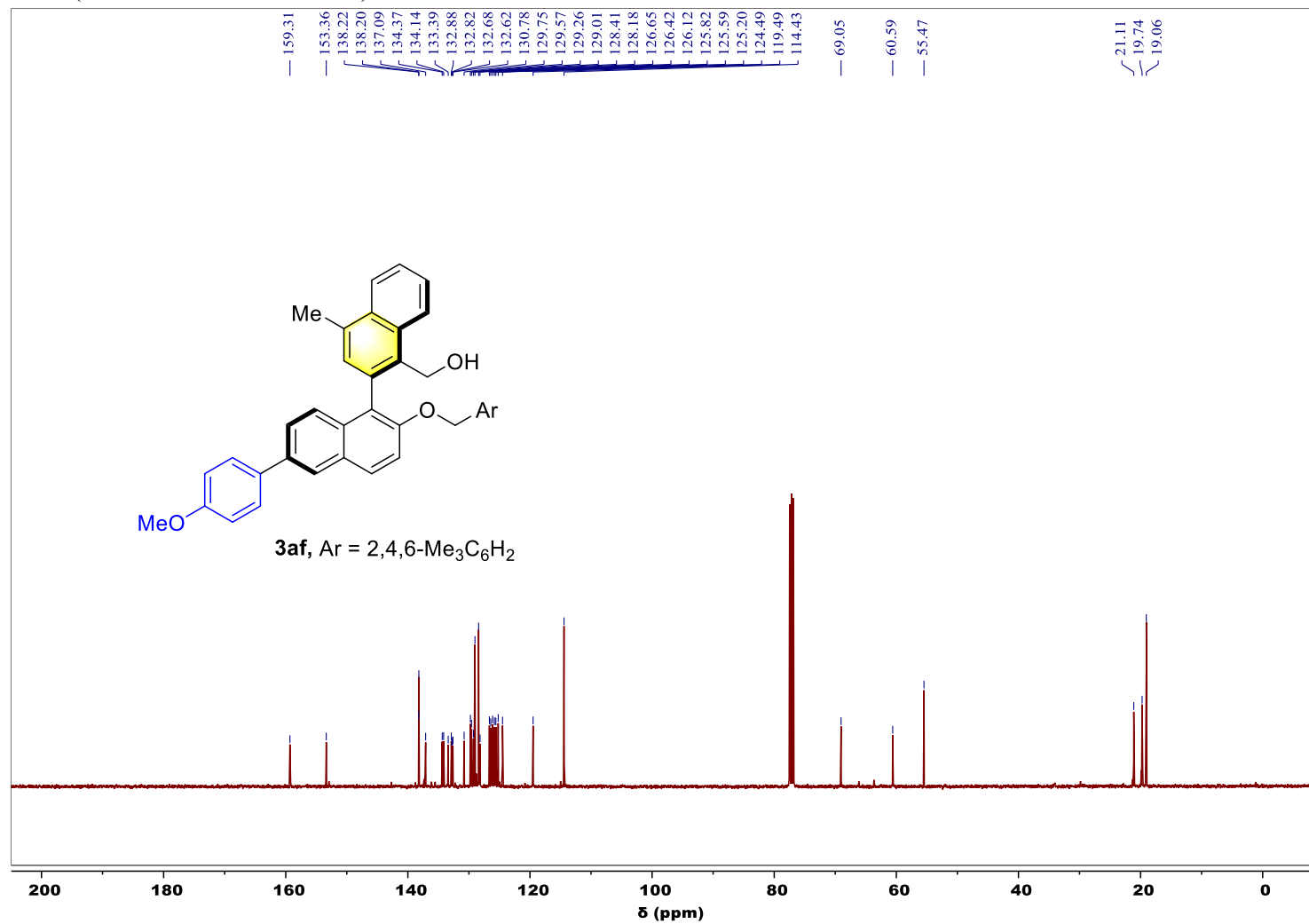
CC1=CC=C(C=C1C2=CC=CC=C2C3=CC=CC=C3OC3C4=CC=CC=C4C5=CC=C(C=C5)CO)OC6=CC=C(C=C6)CO

3ae, Ar = 2,4,6-Me₃C₆H₂

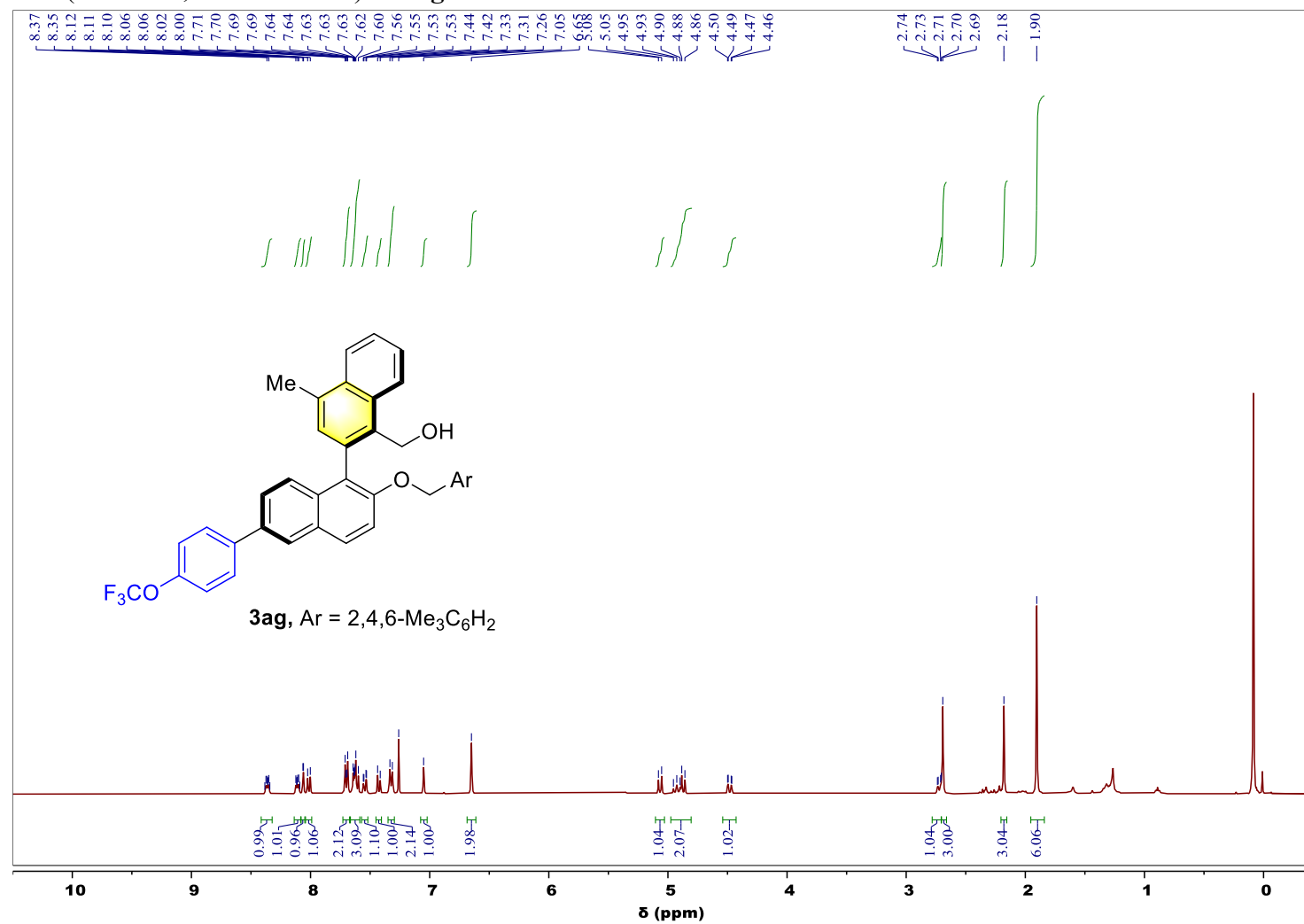
¹H NMR-spectrum (400 MHz, Chloroform-*d*) of **3af**



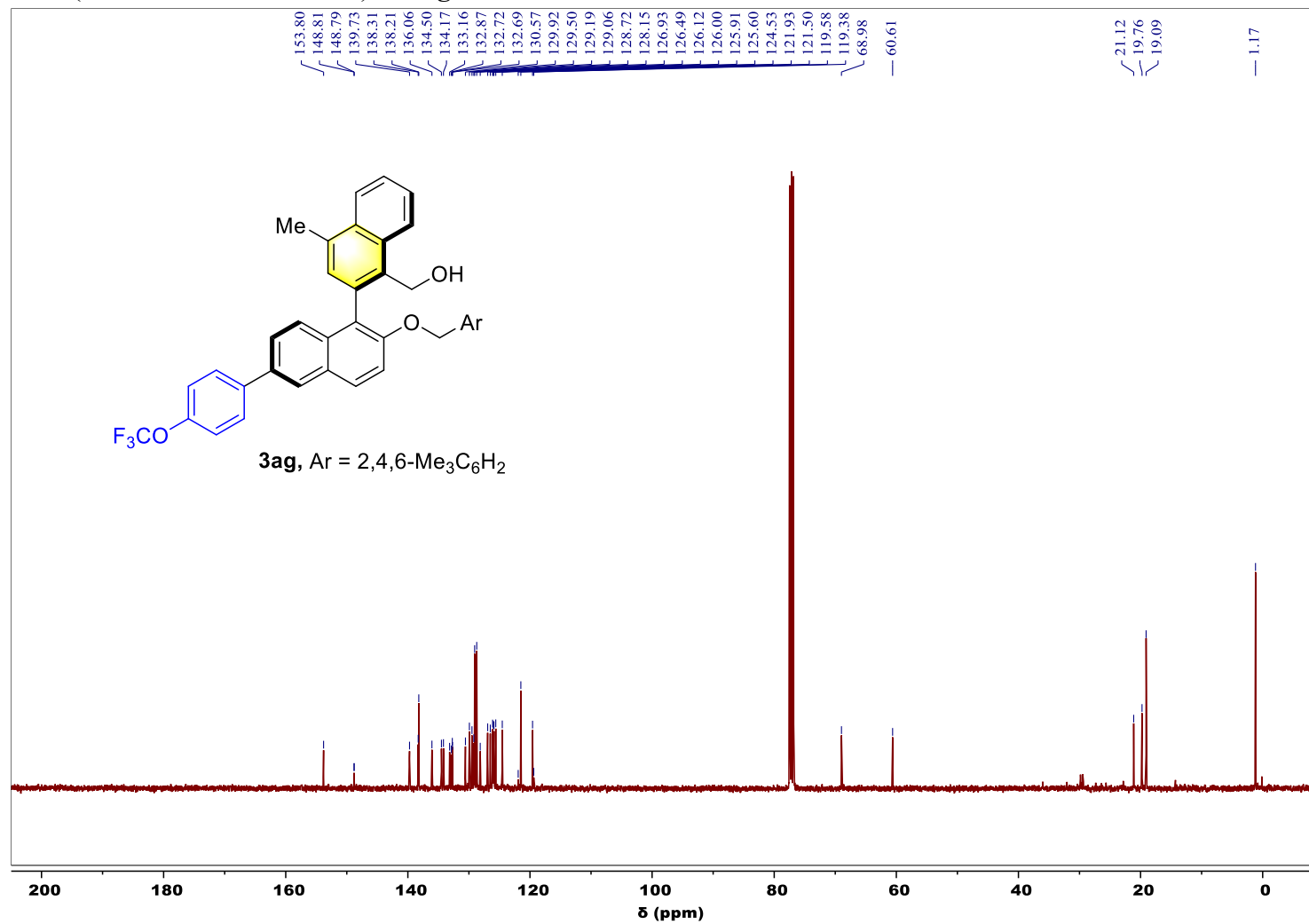
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3af**



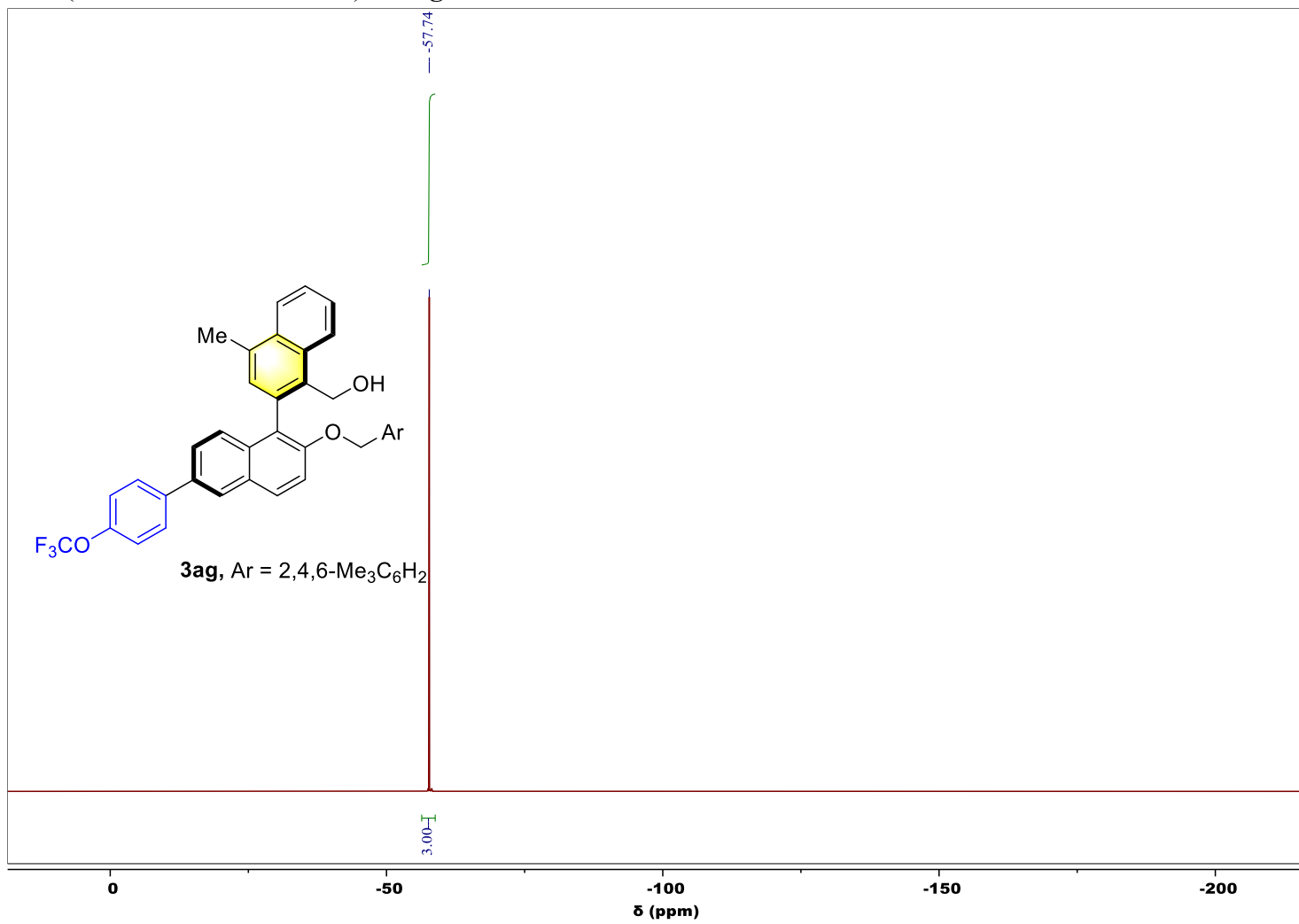
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ag**



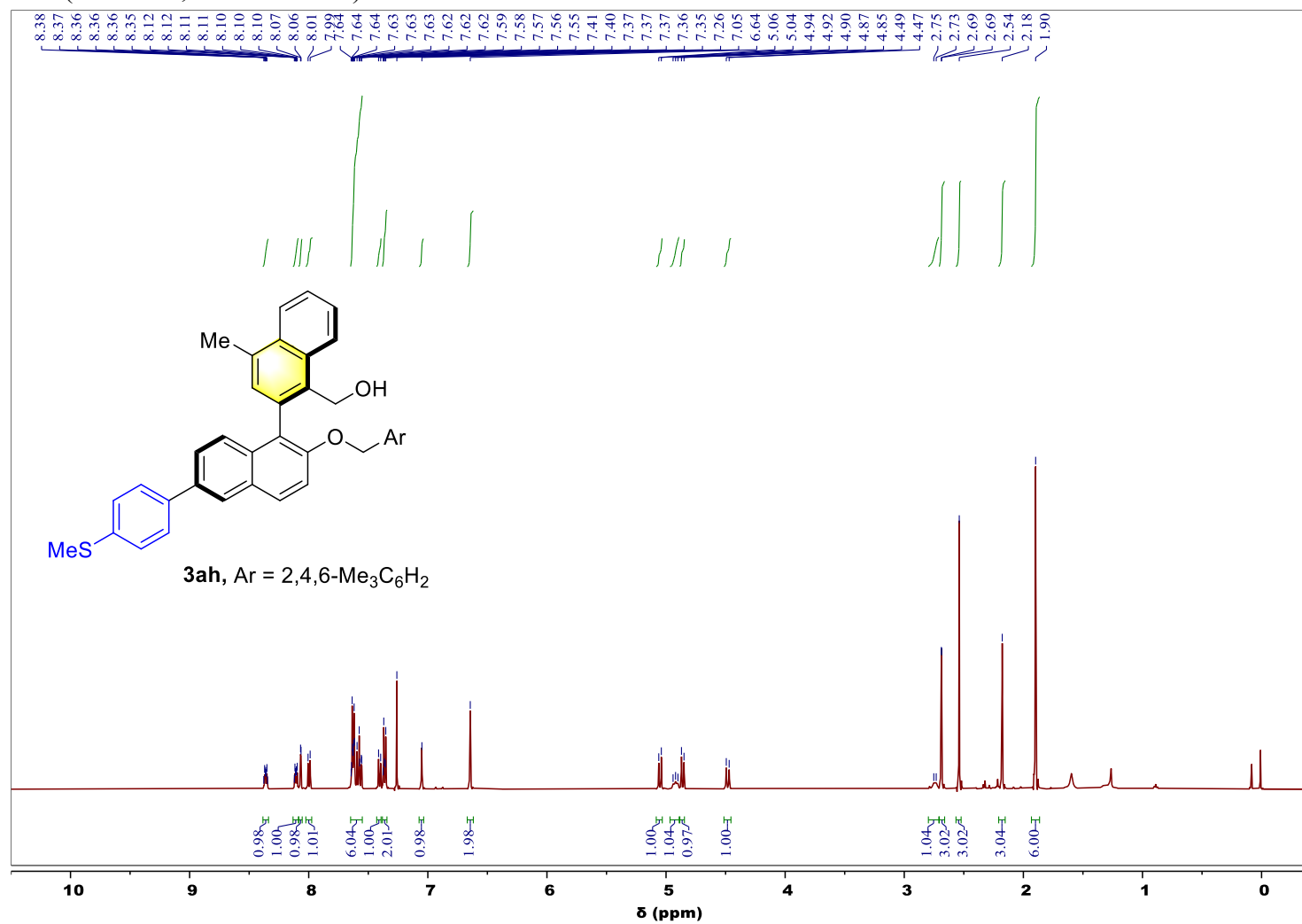
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ag**



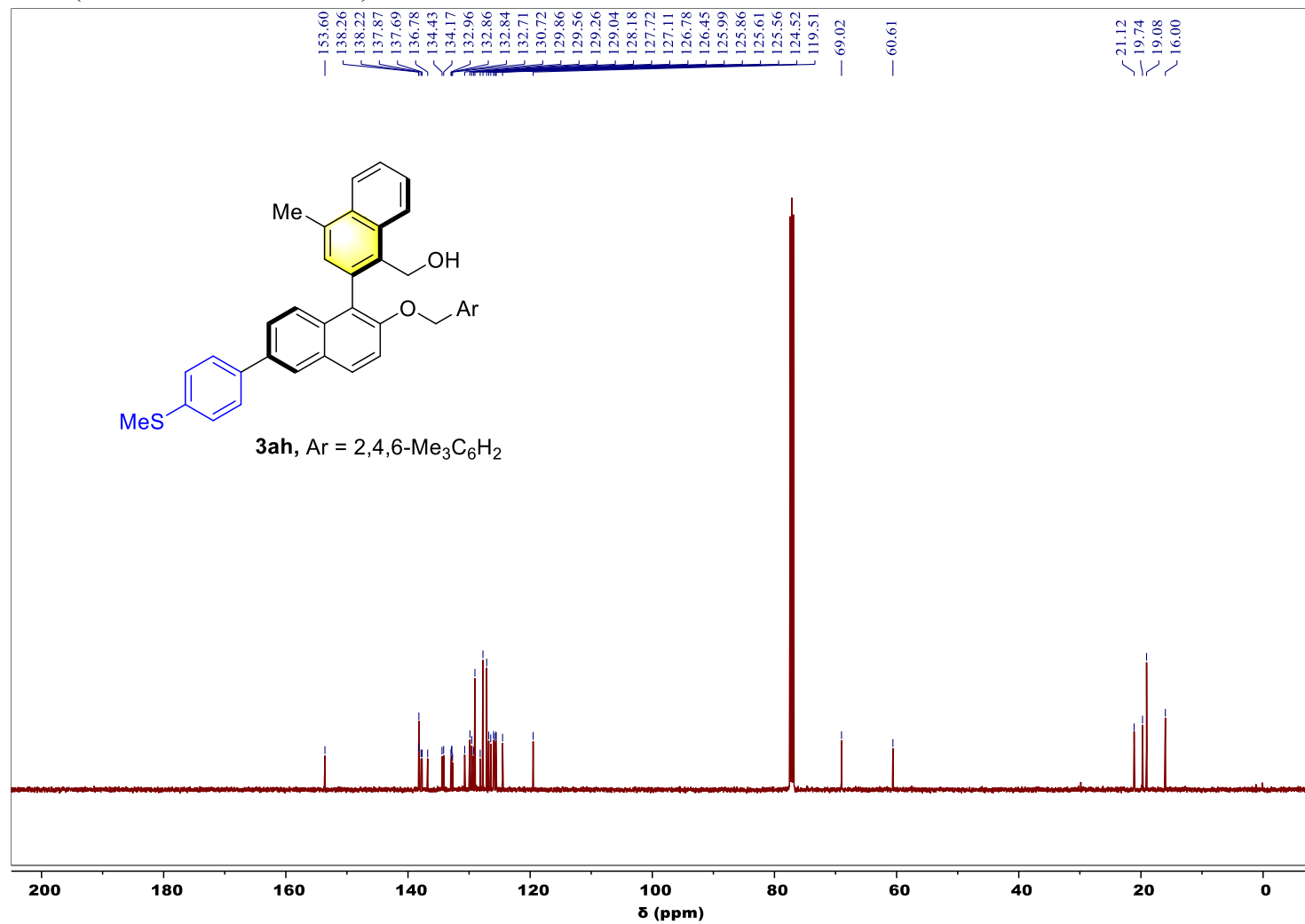
^{19}F NMR-spectrum (376 MHz, Chloroform-*d*) of **3ag**



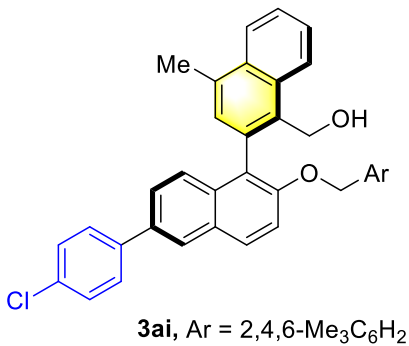
^1H NMR-spectrum (500 MHz, Chloroform- d) of **3ah**



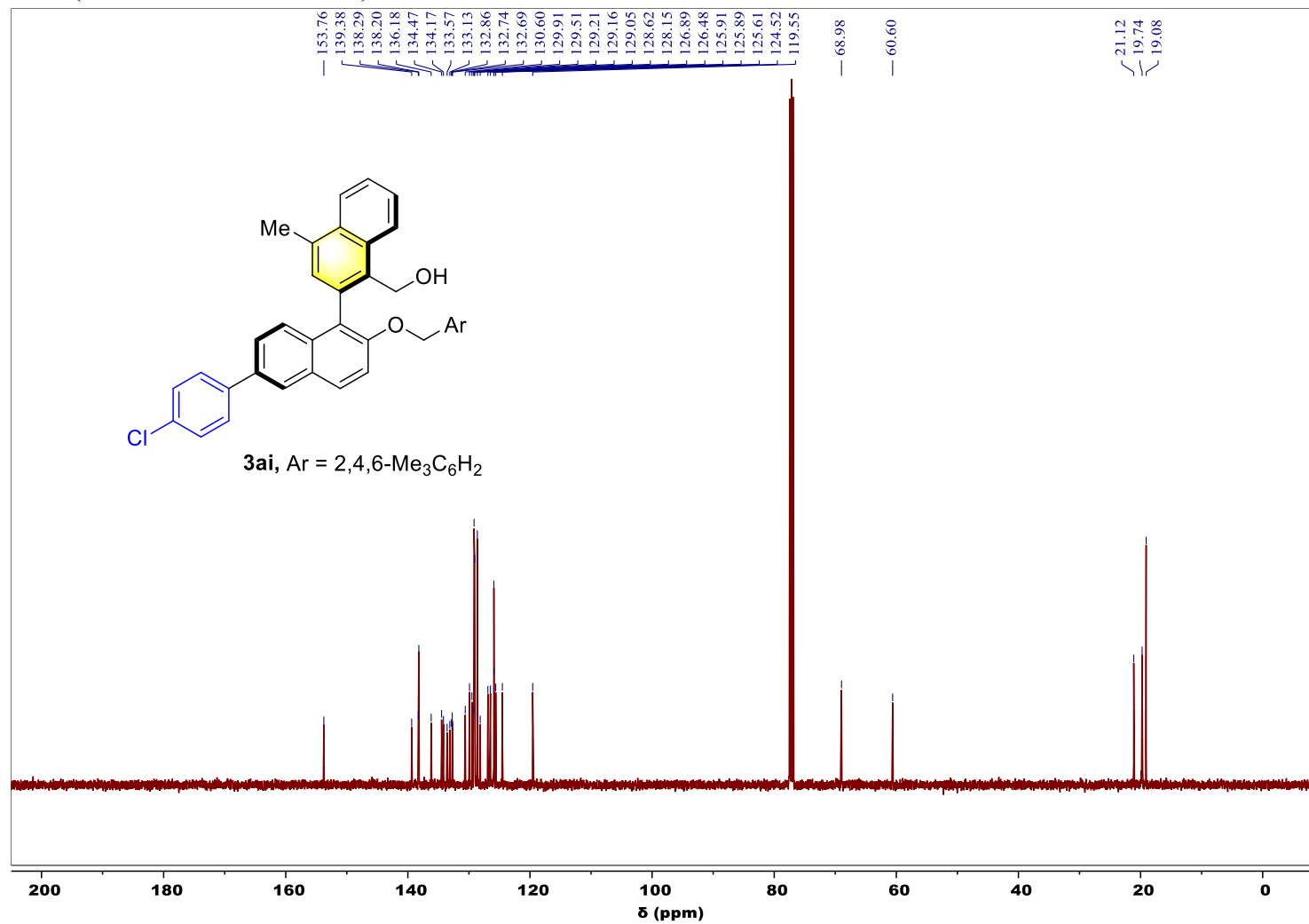
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ah**



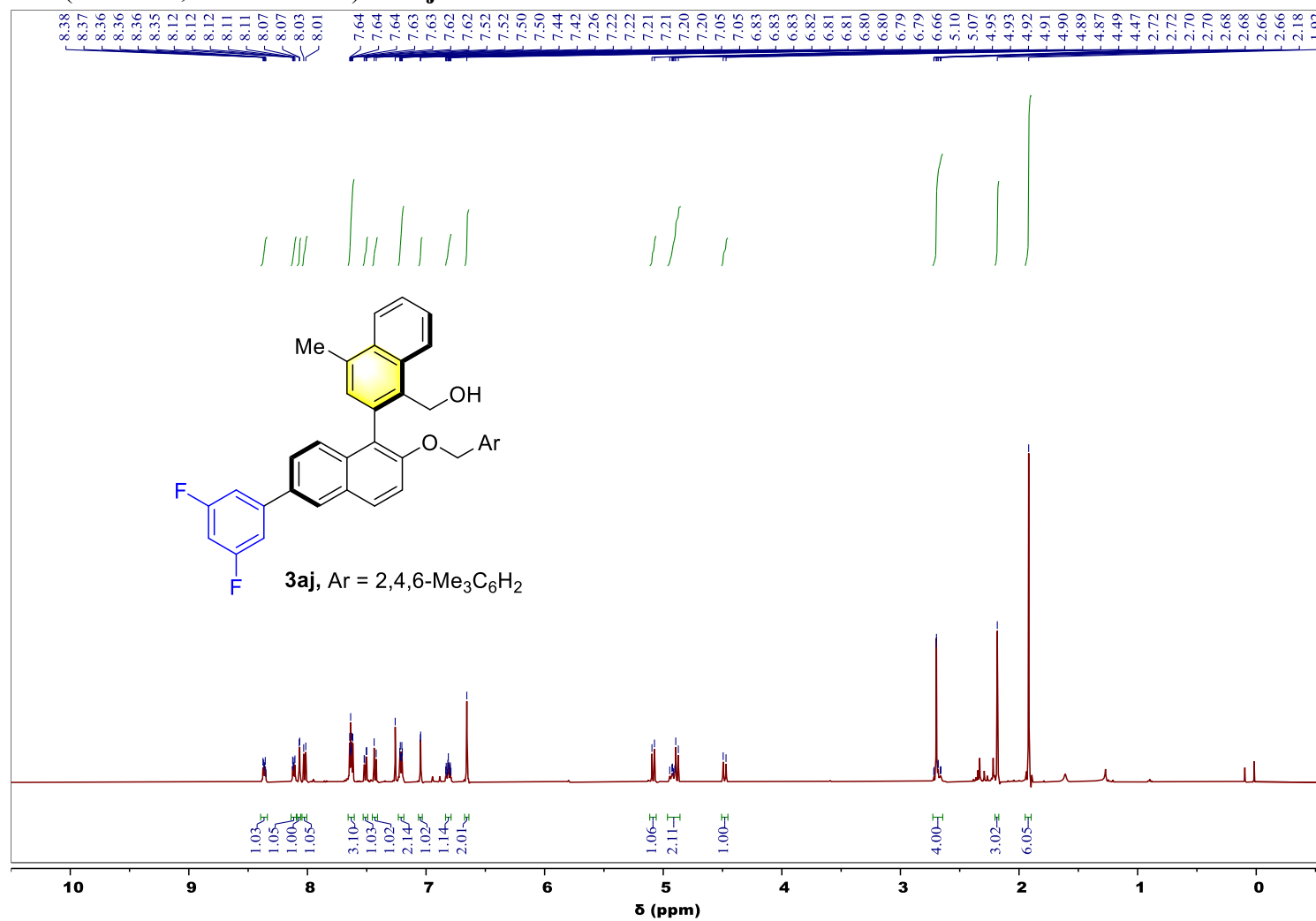
¹H NMR-spectrum (500 MHz, Chloroform-*d*) of **3ai**



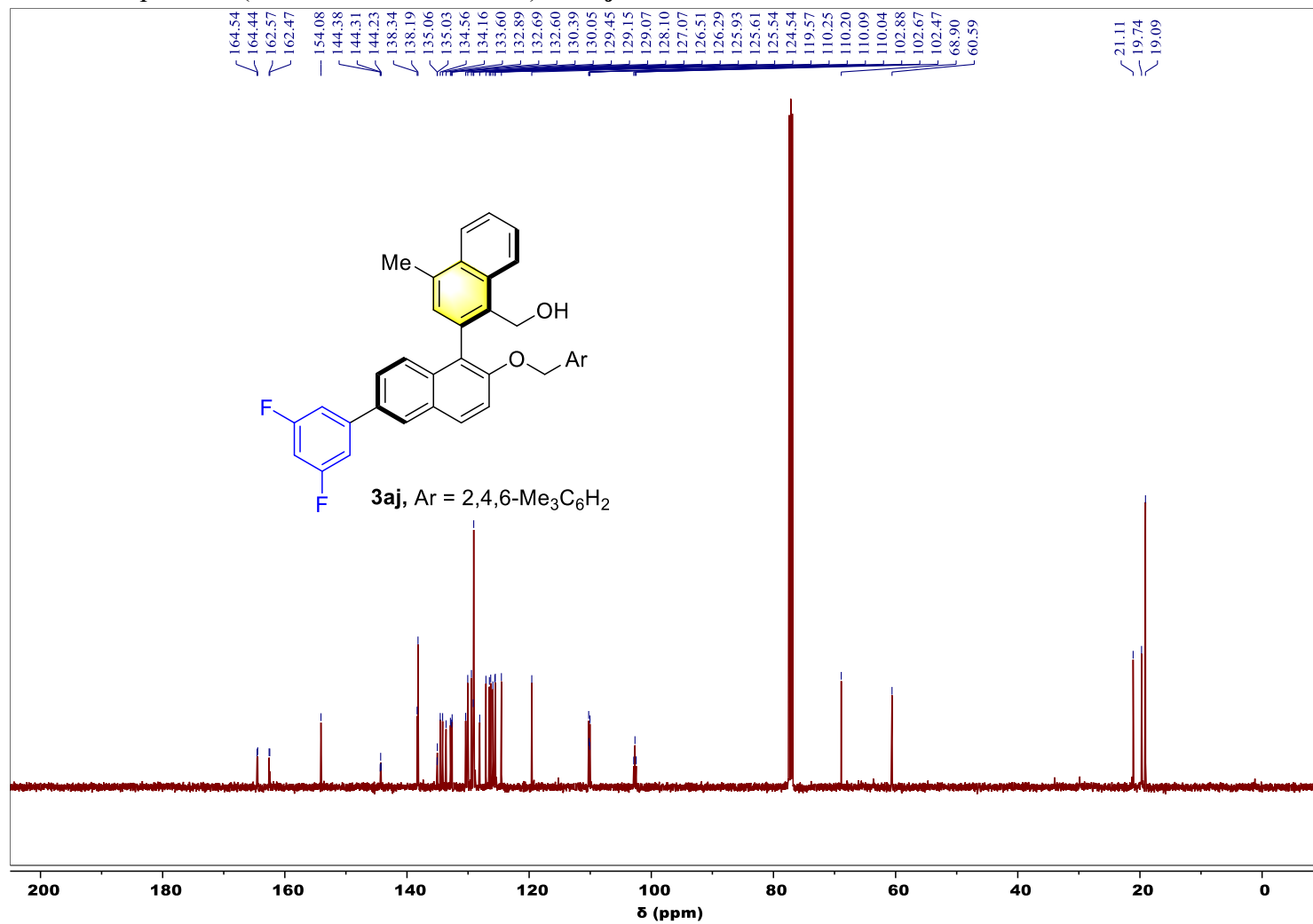
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ai**



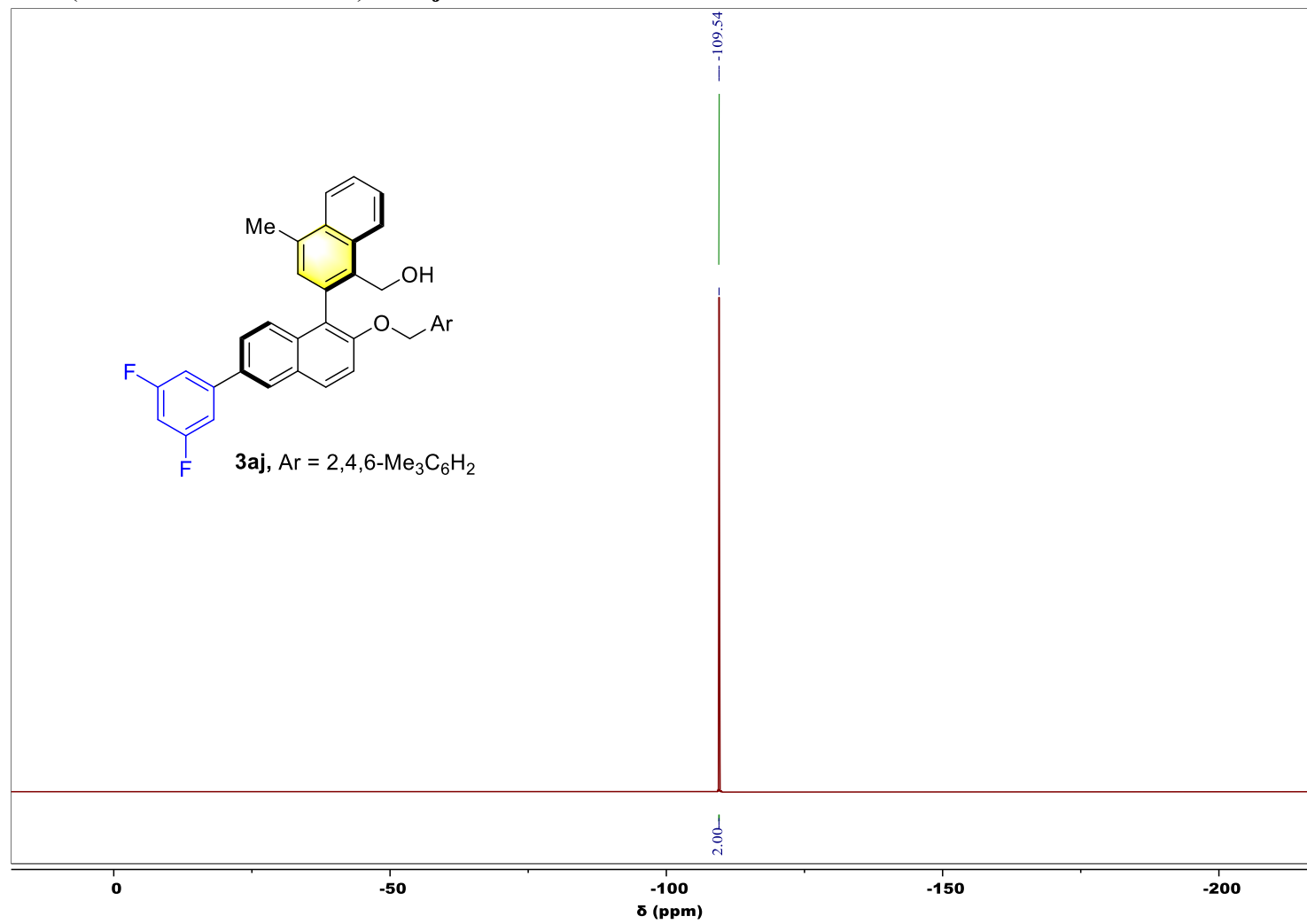
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3aj**



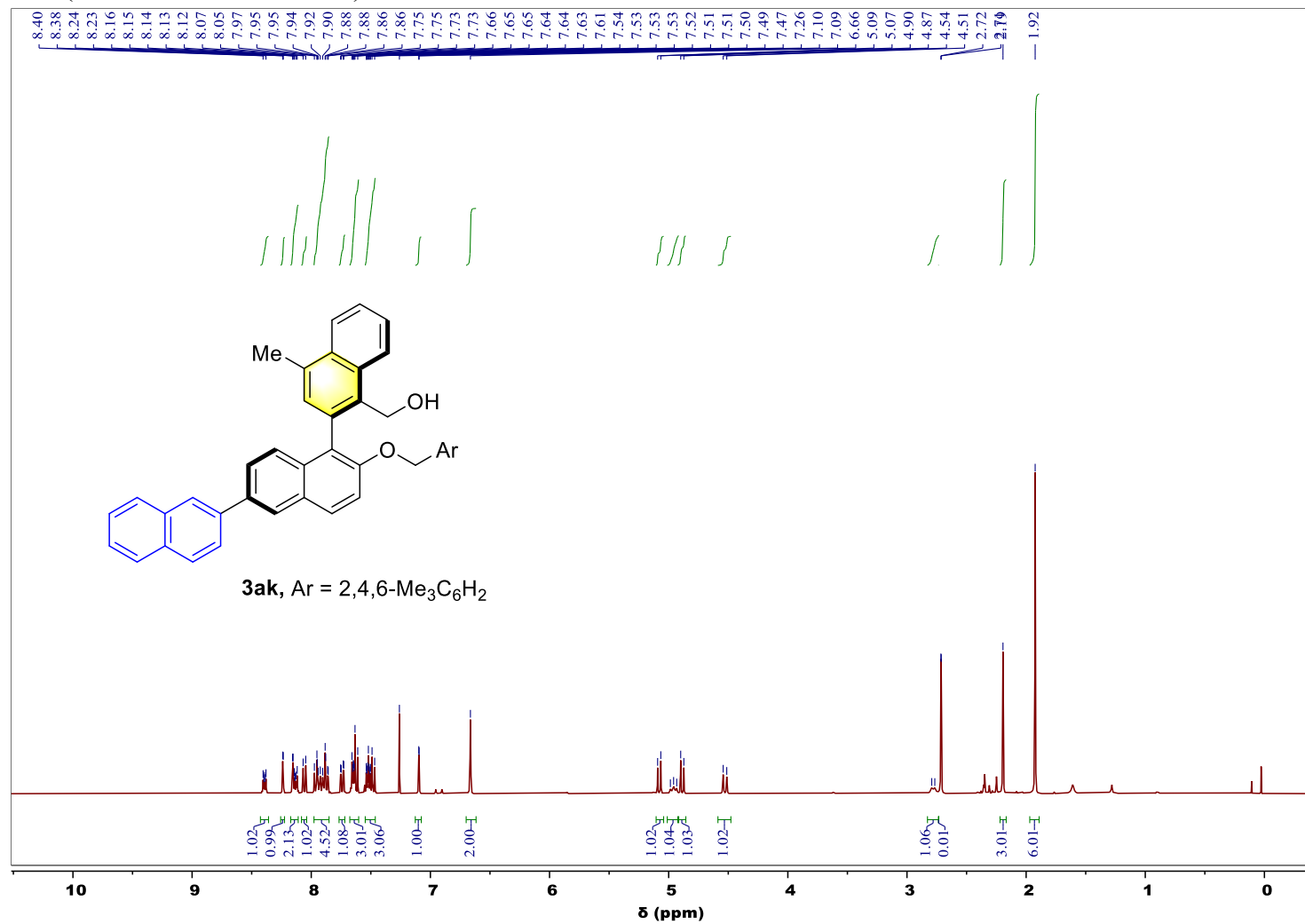
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3aj**



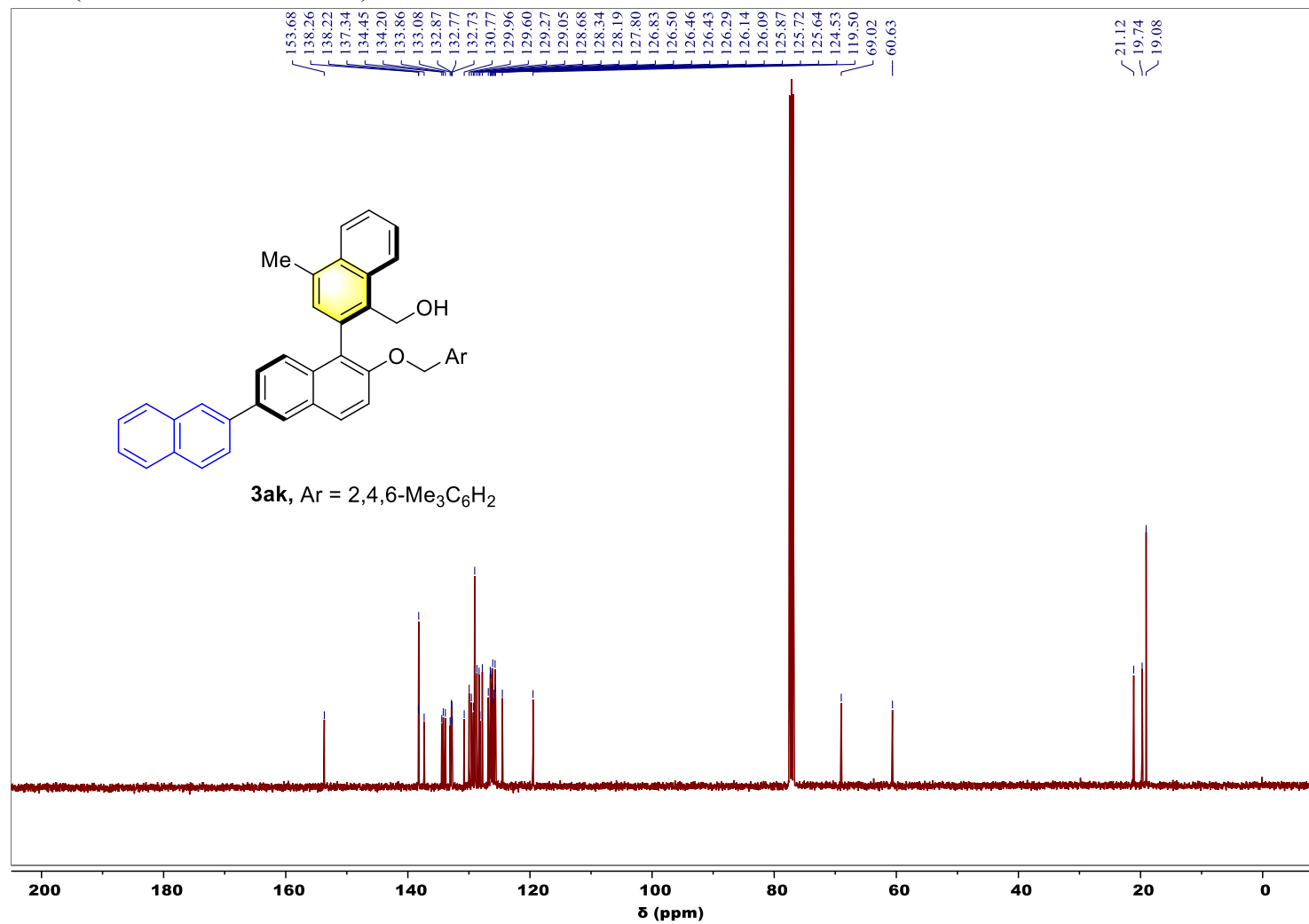
^{19}F NMR-spectrum (376 MHz, Chloroform-*d*) of **3aj**



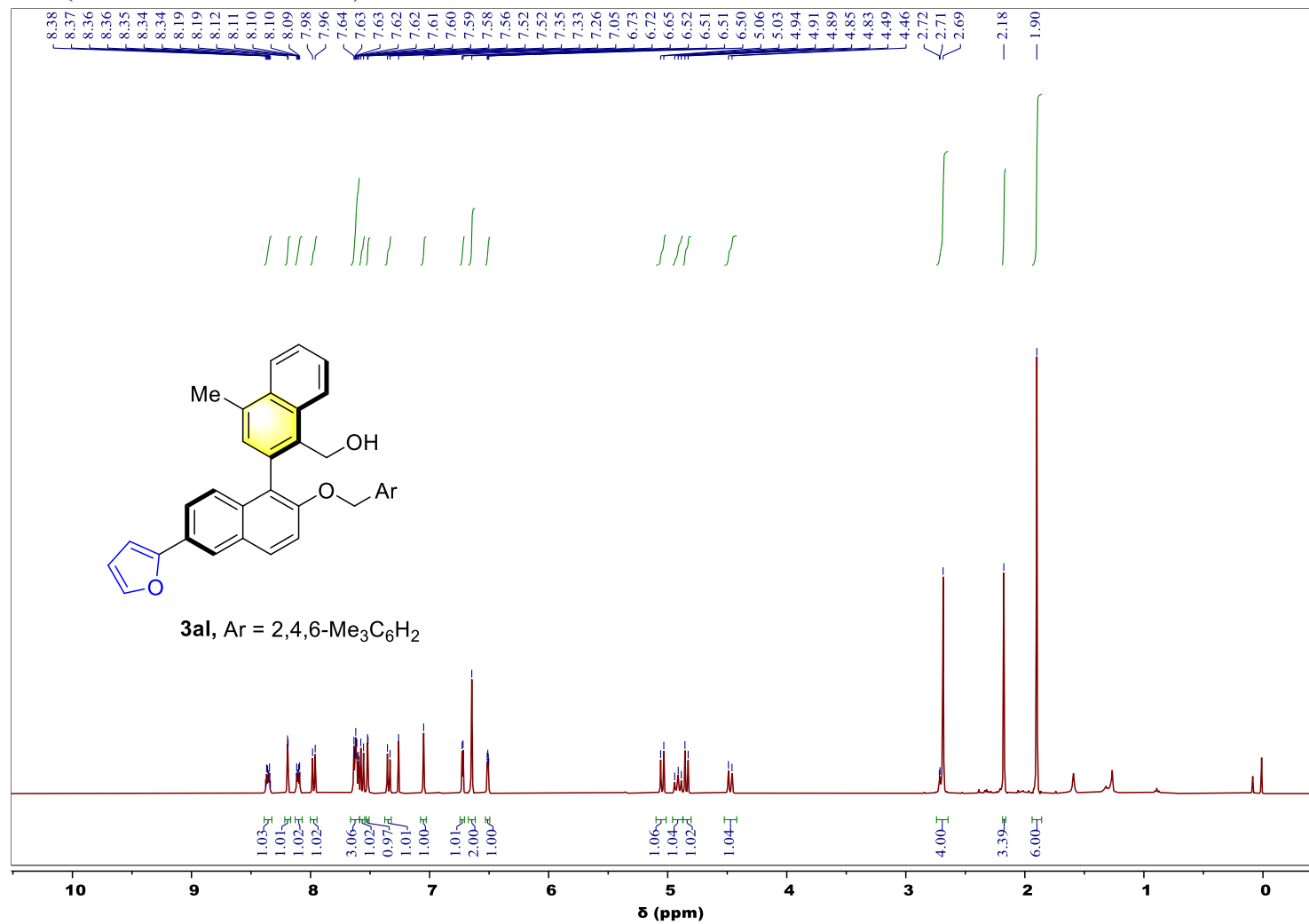
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ak**



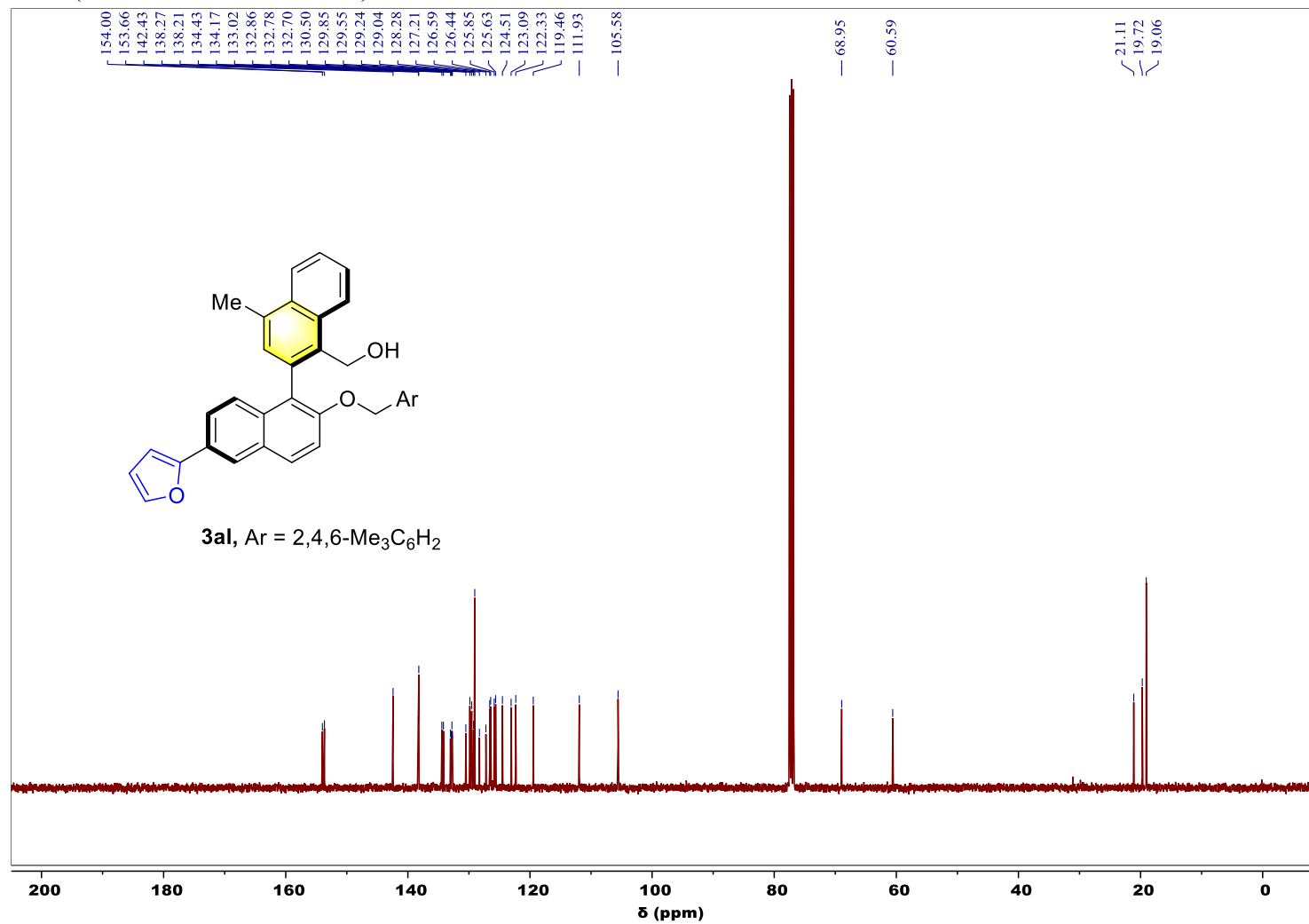
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ak**



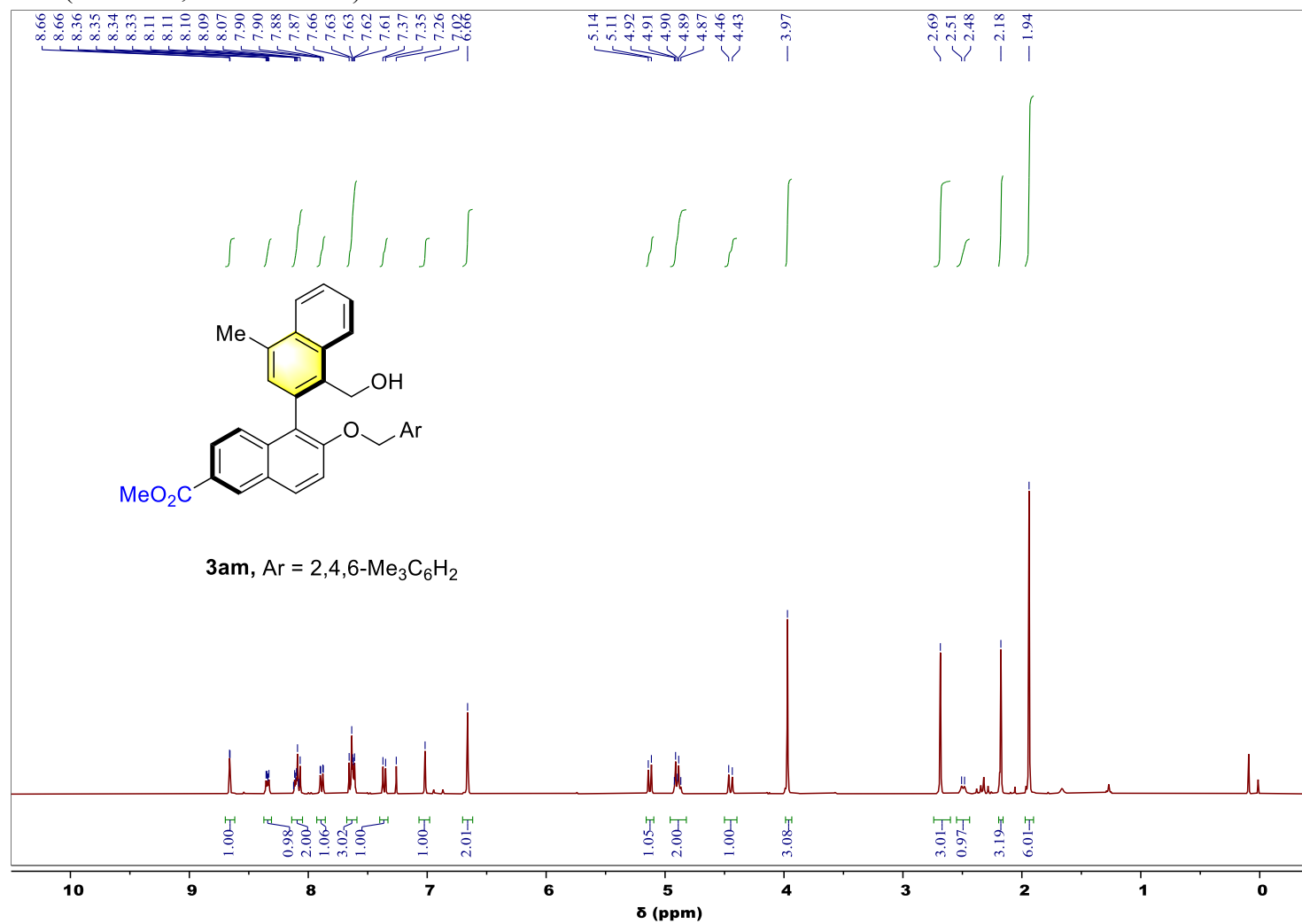
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3al**



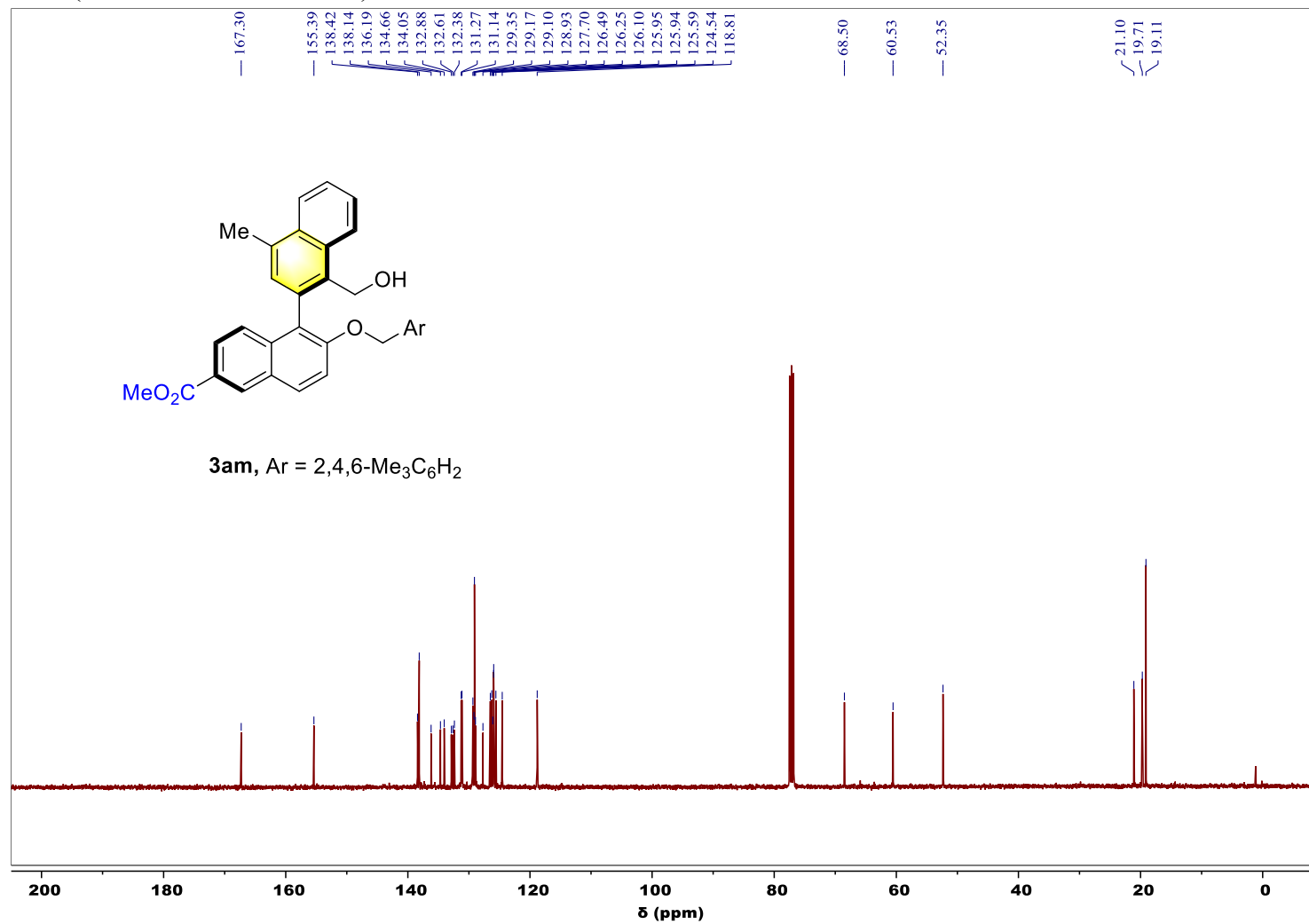
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3al**



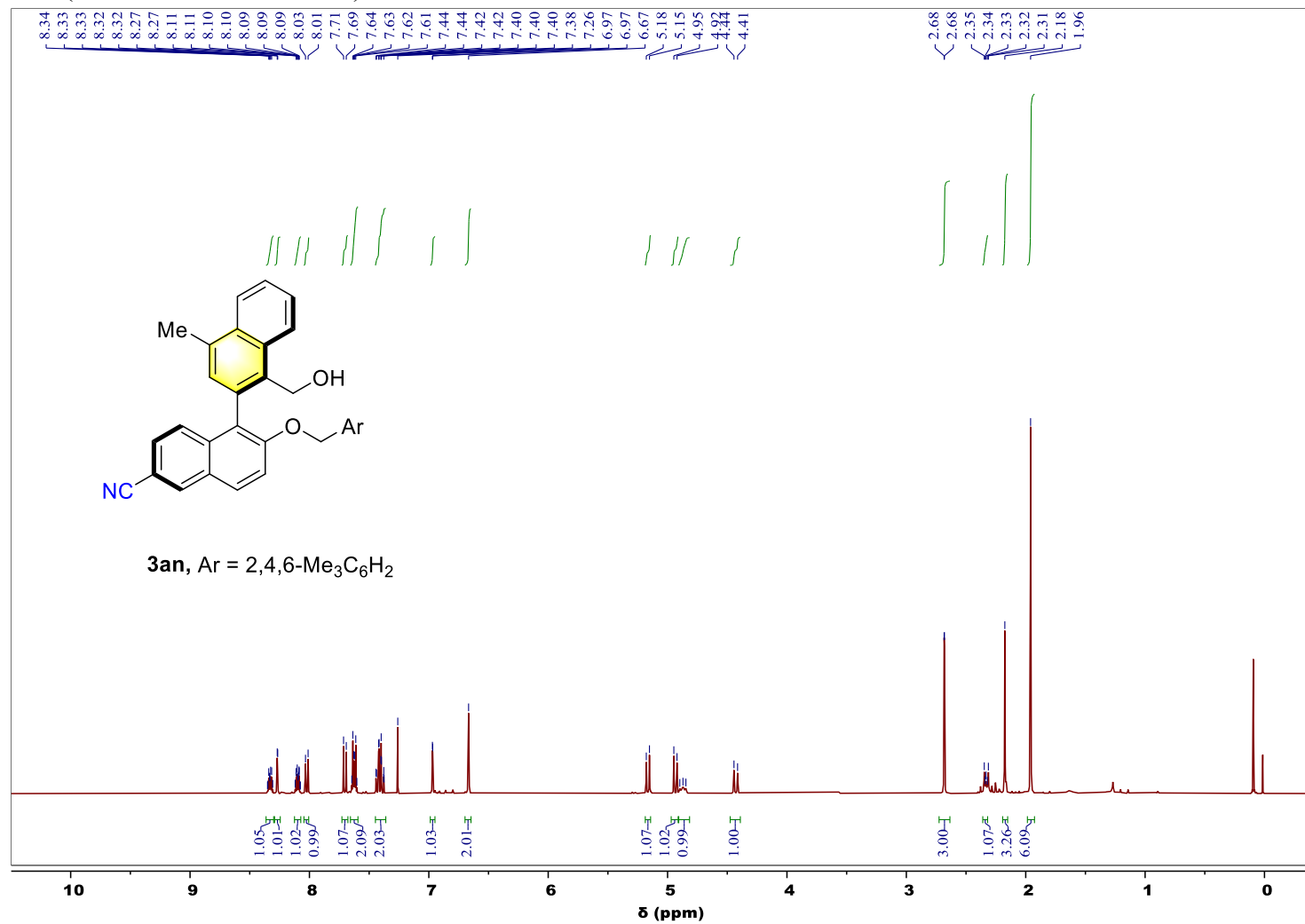
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3am**



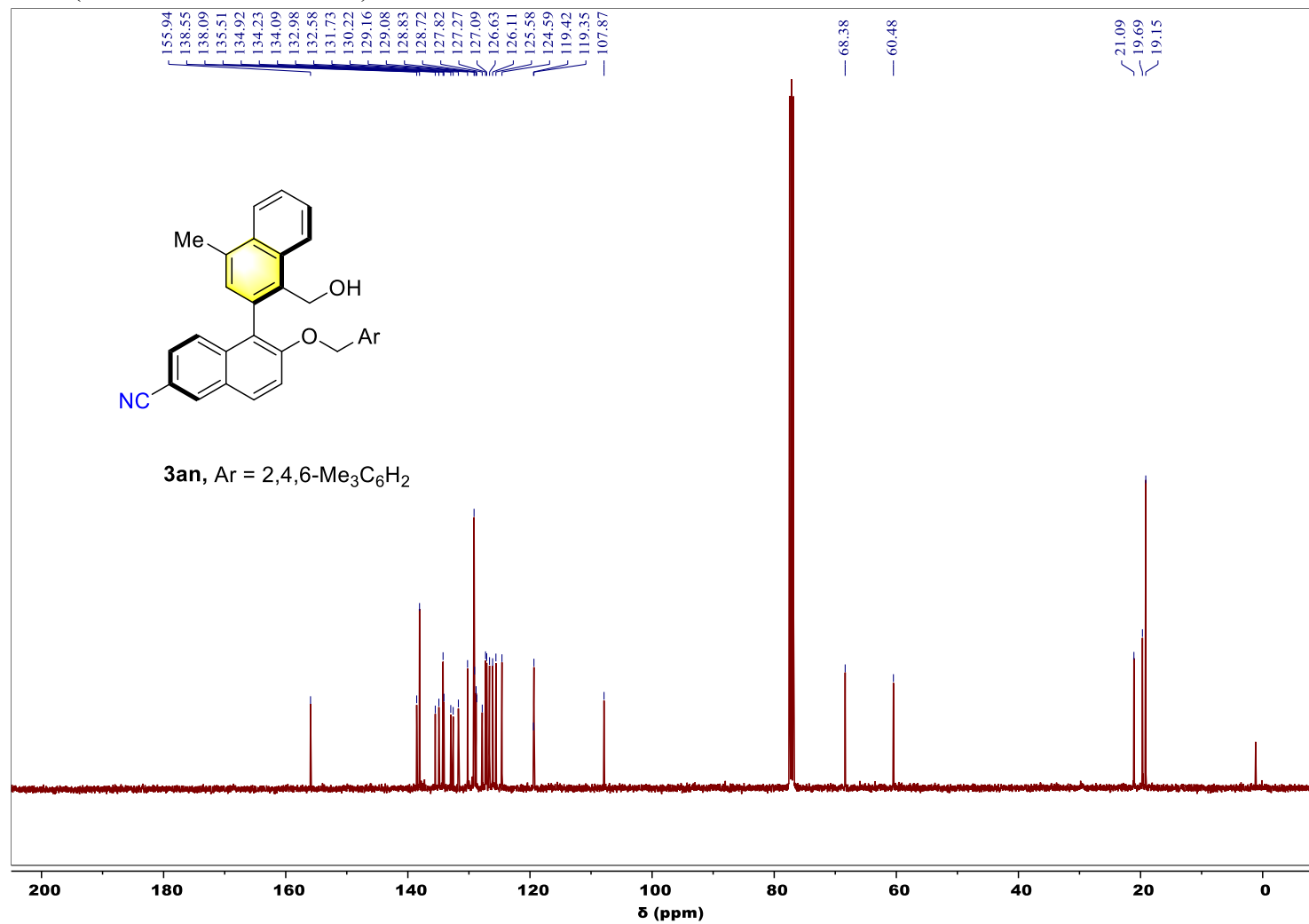
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3am**



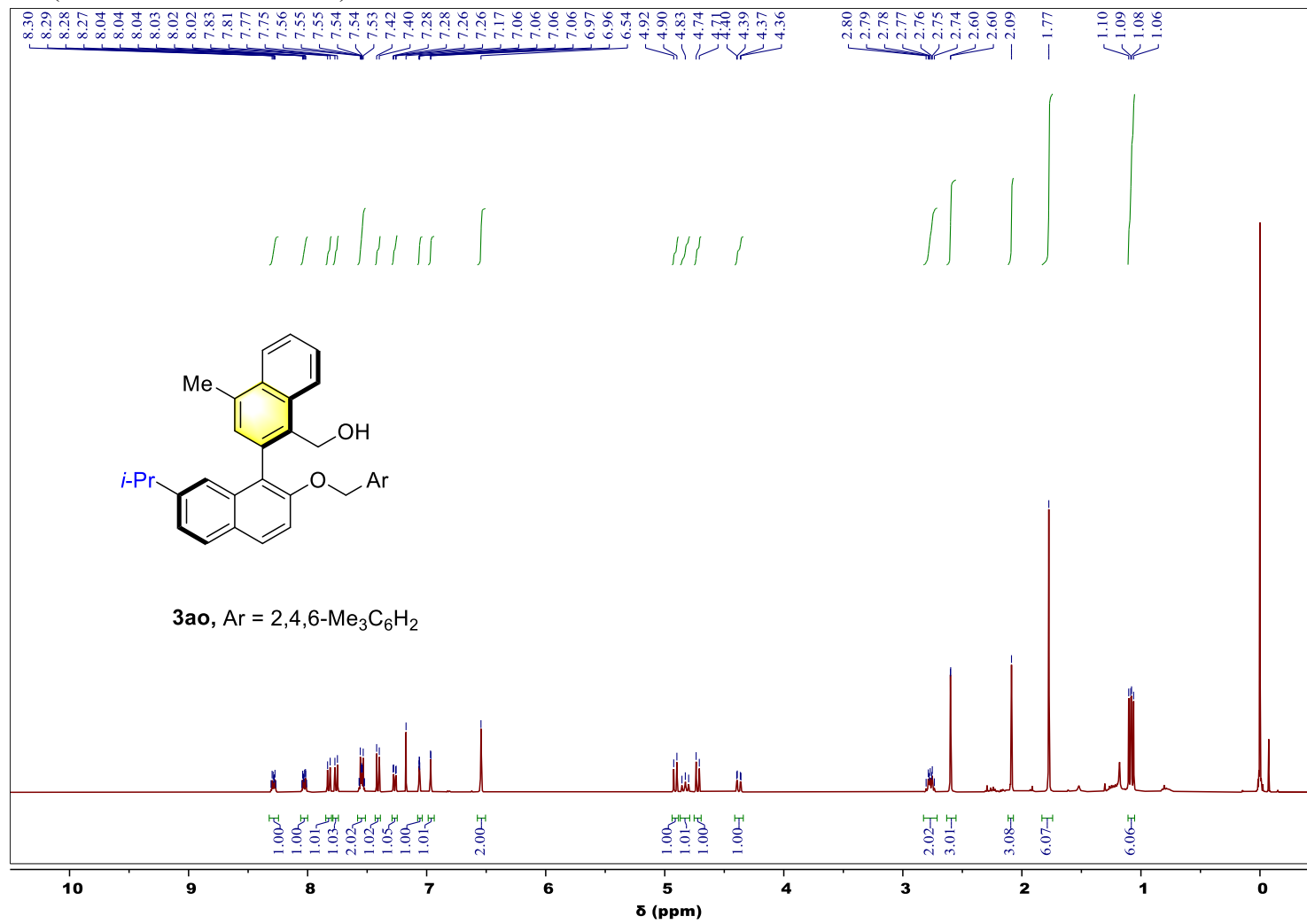
¹H NMR-spectrum (400 MHz, Chloroform-*d*) of **3an**



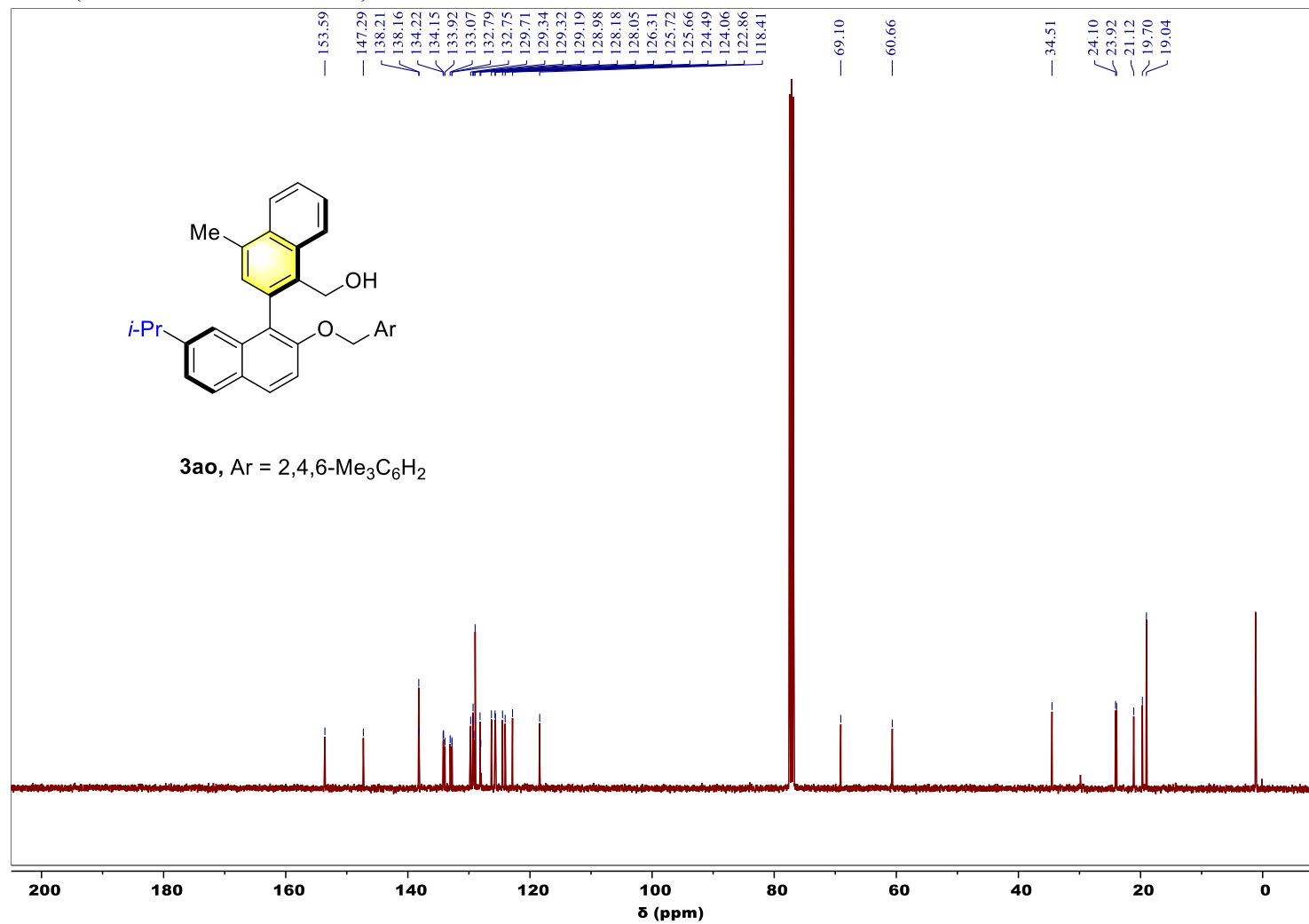
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3an**



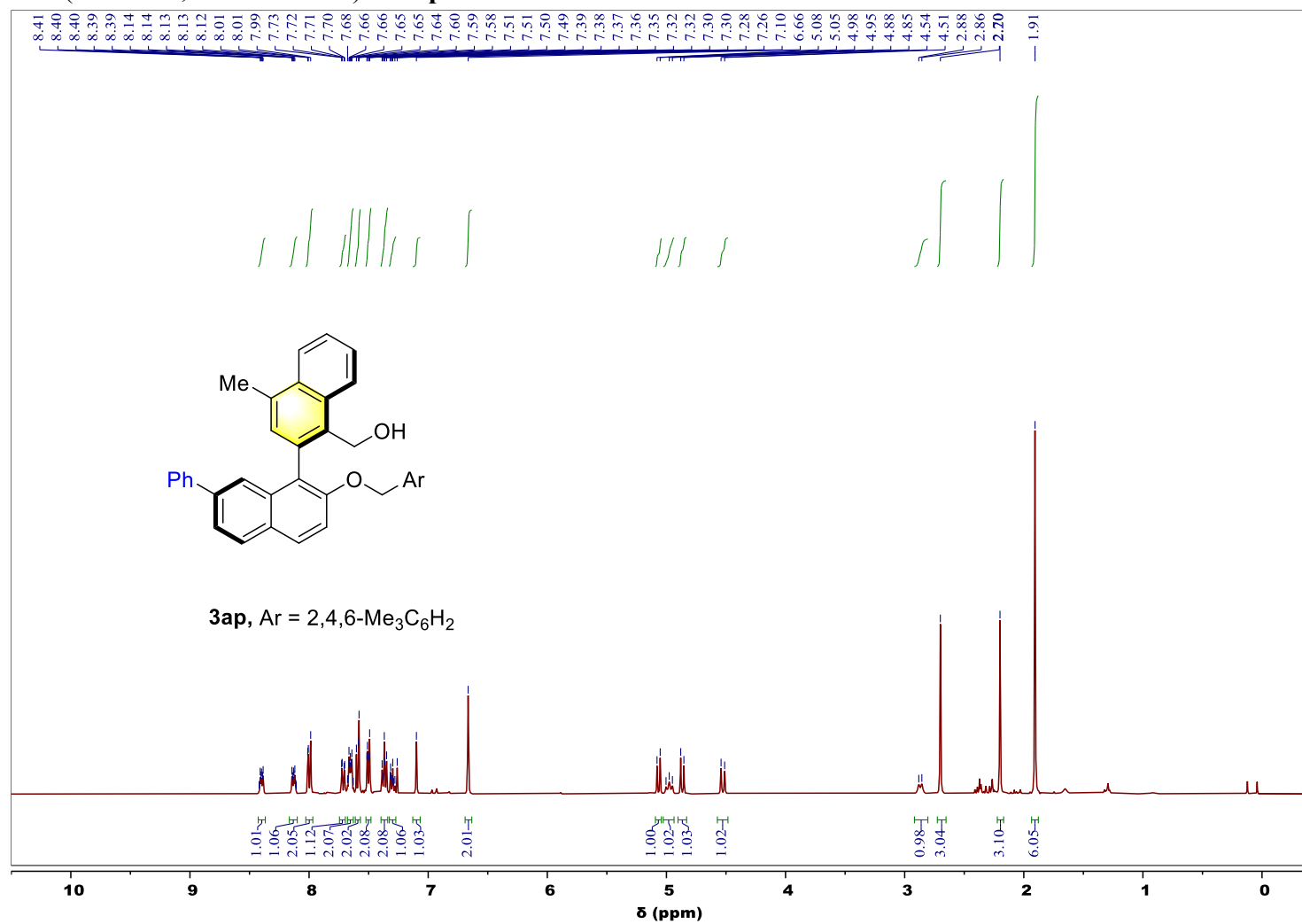
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ao**



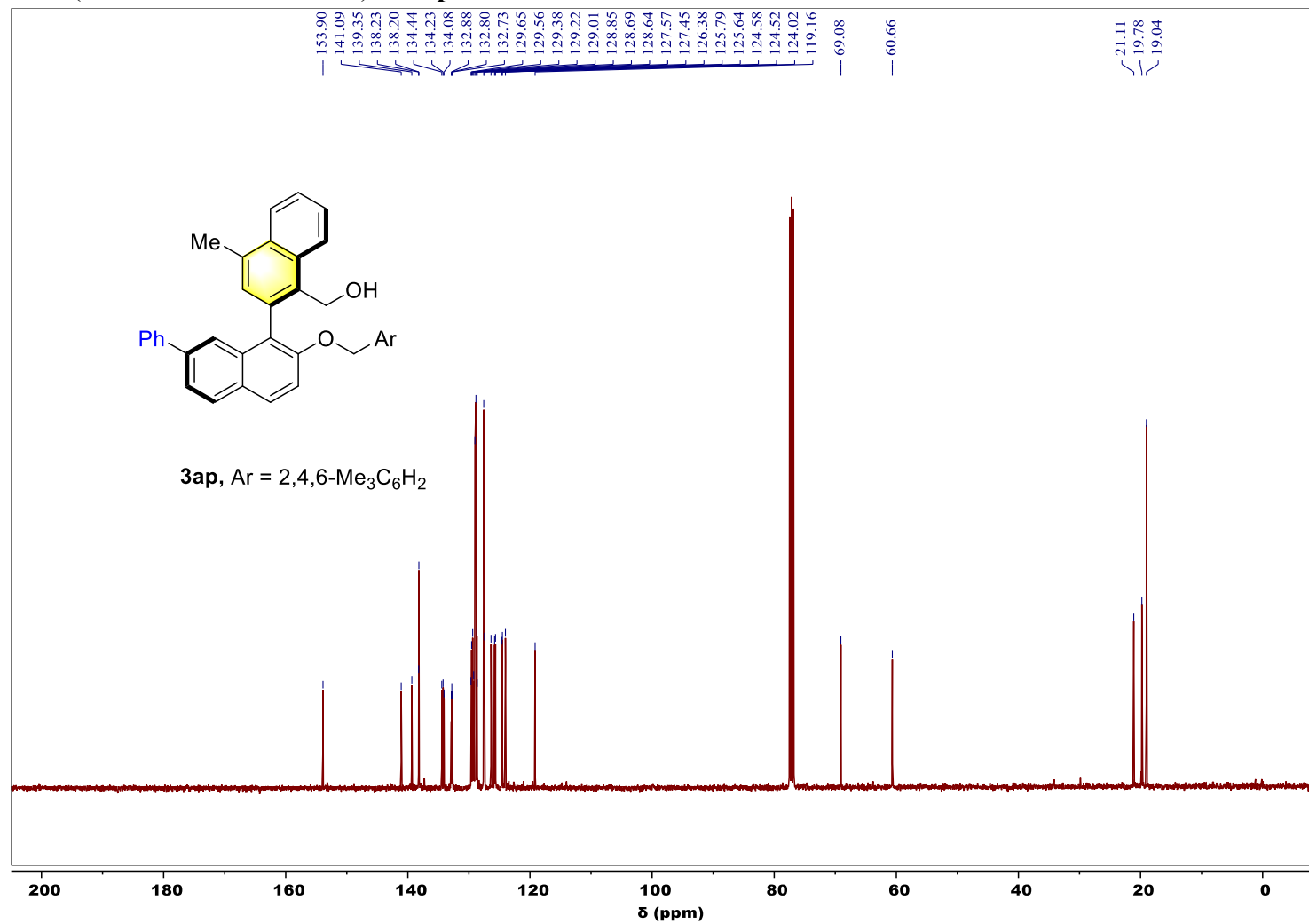
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ao**



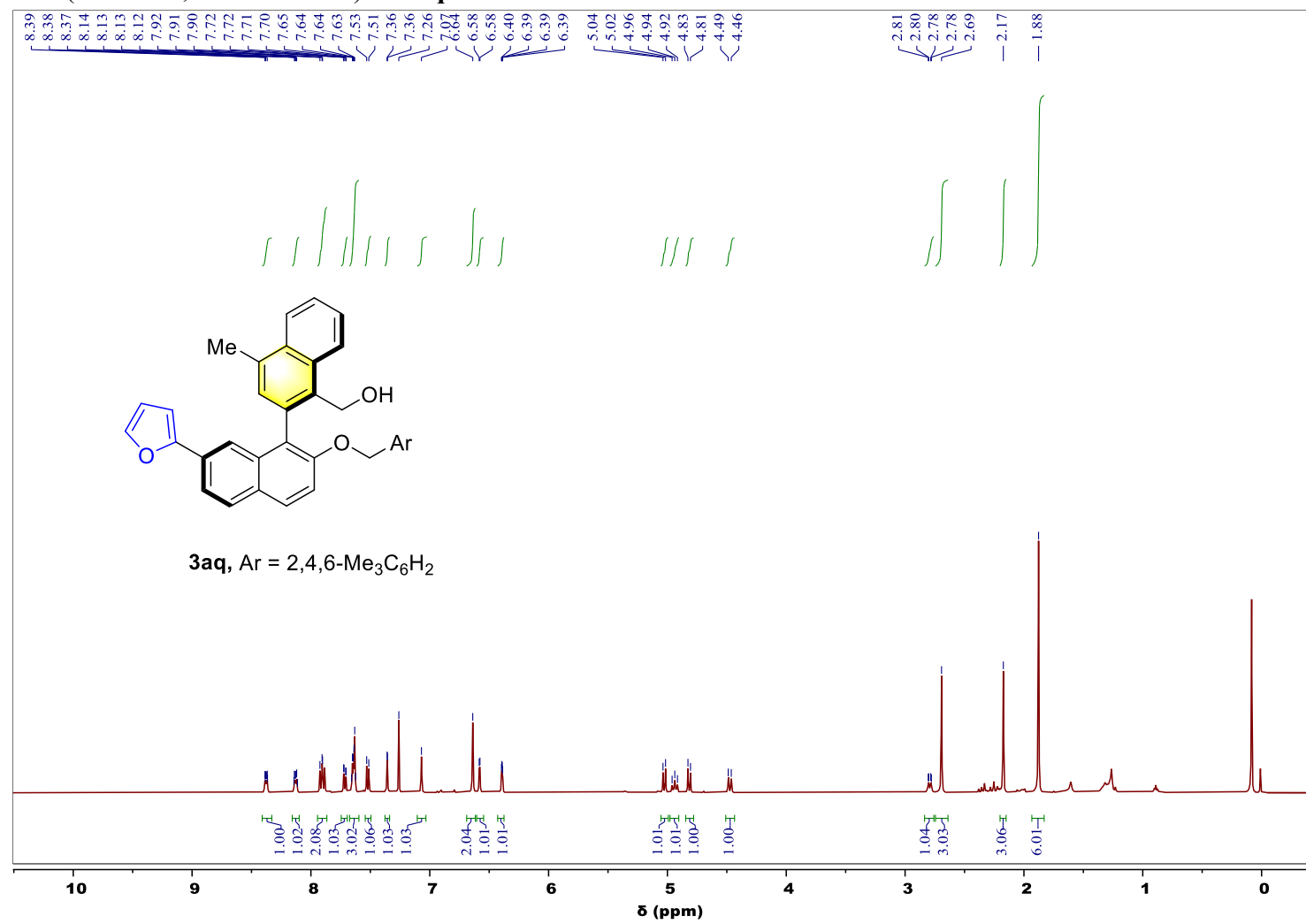
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3ap**



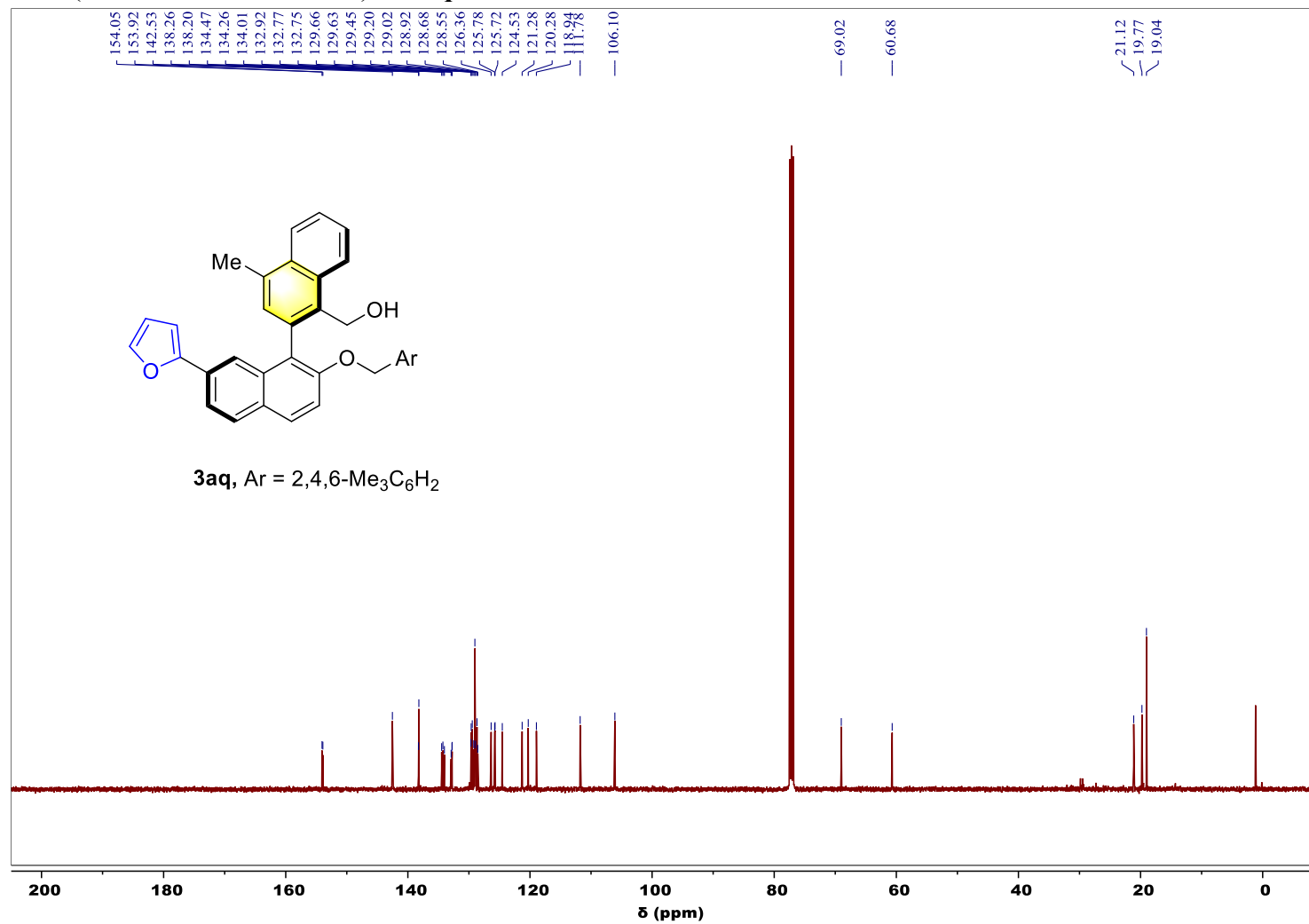
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3ap**



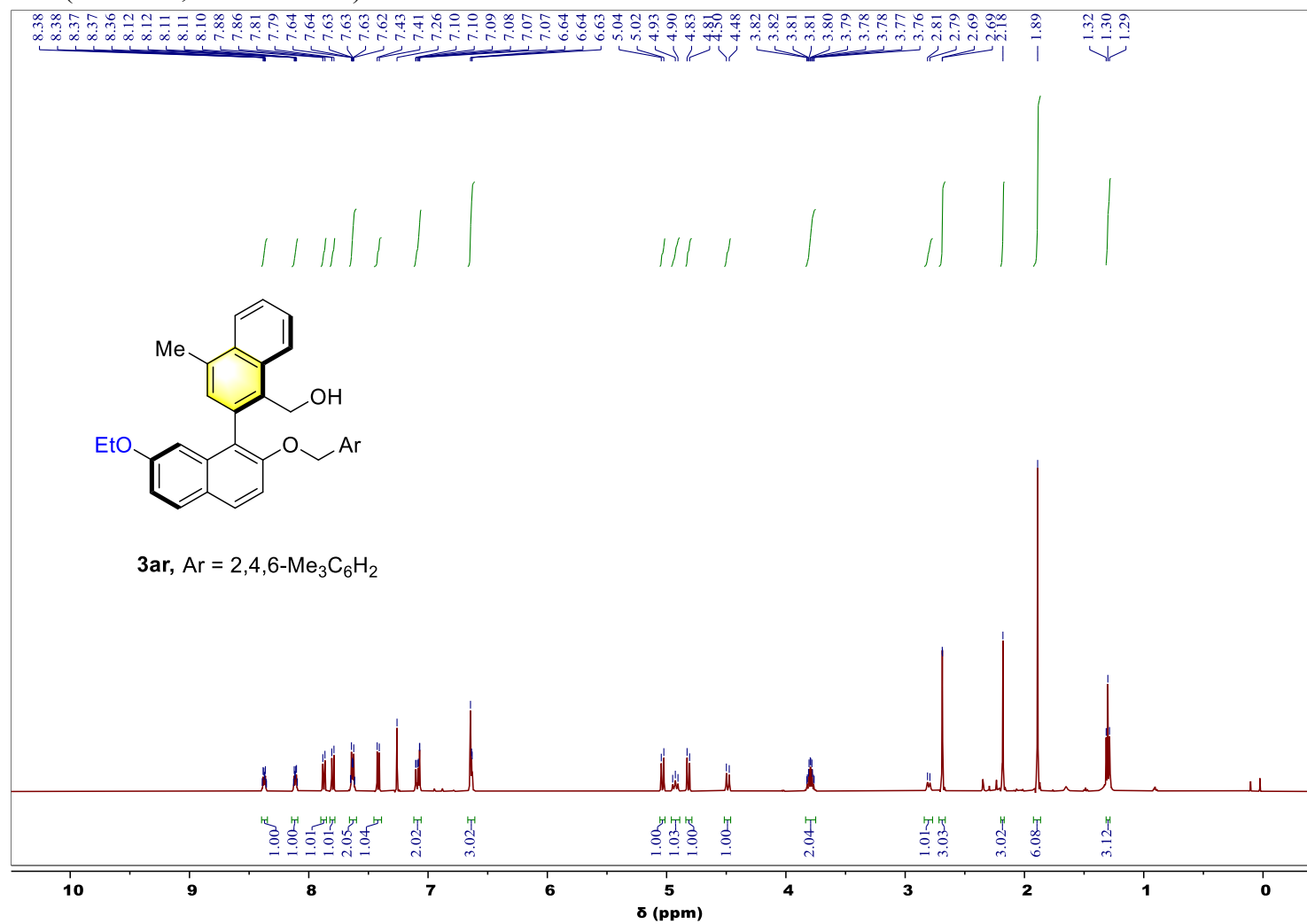
^1H NMR-spectrum (500 MHz, Chloroform- d) of **3aq**



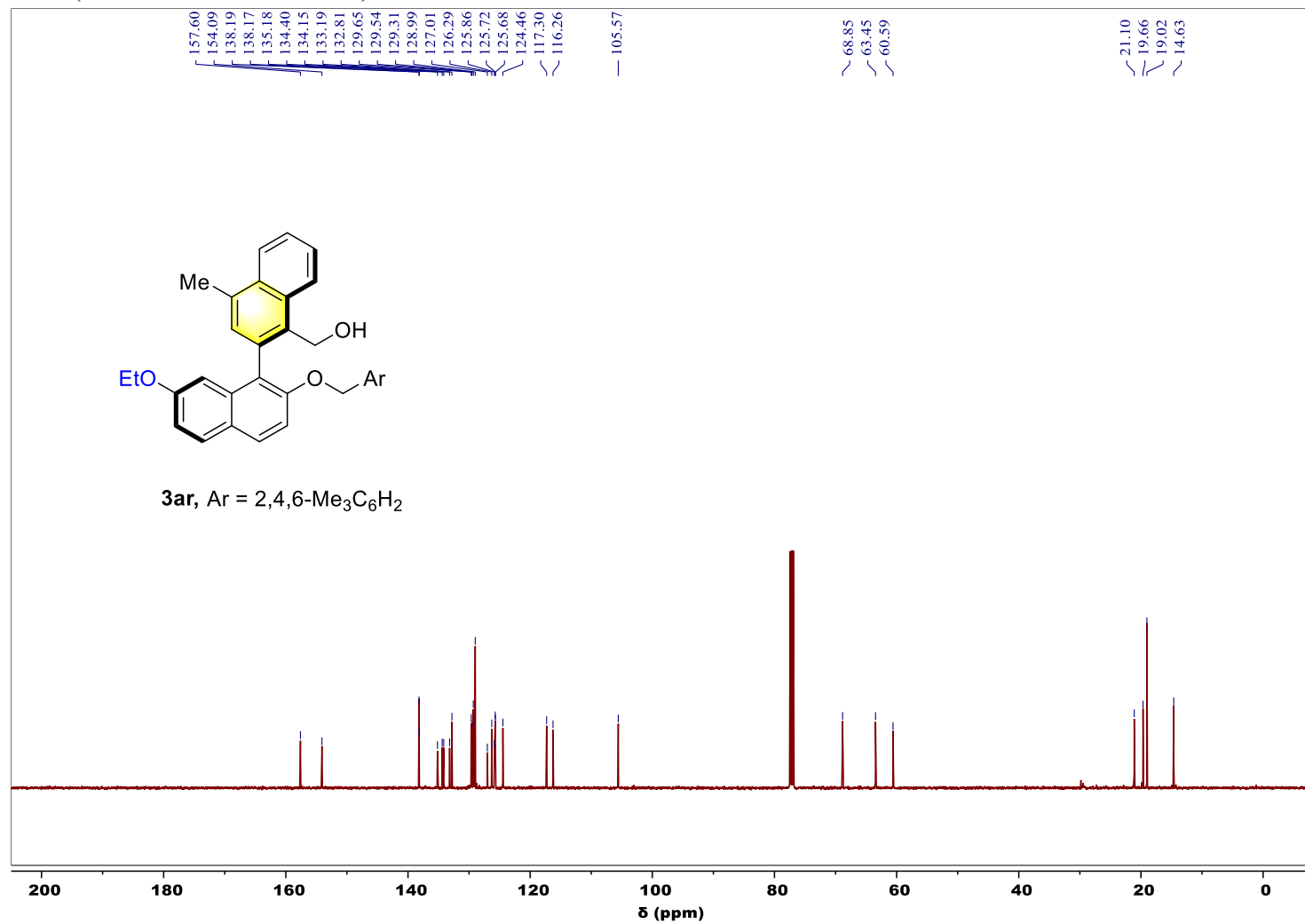
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3aq**



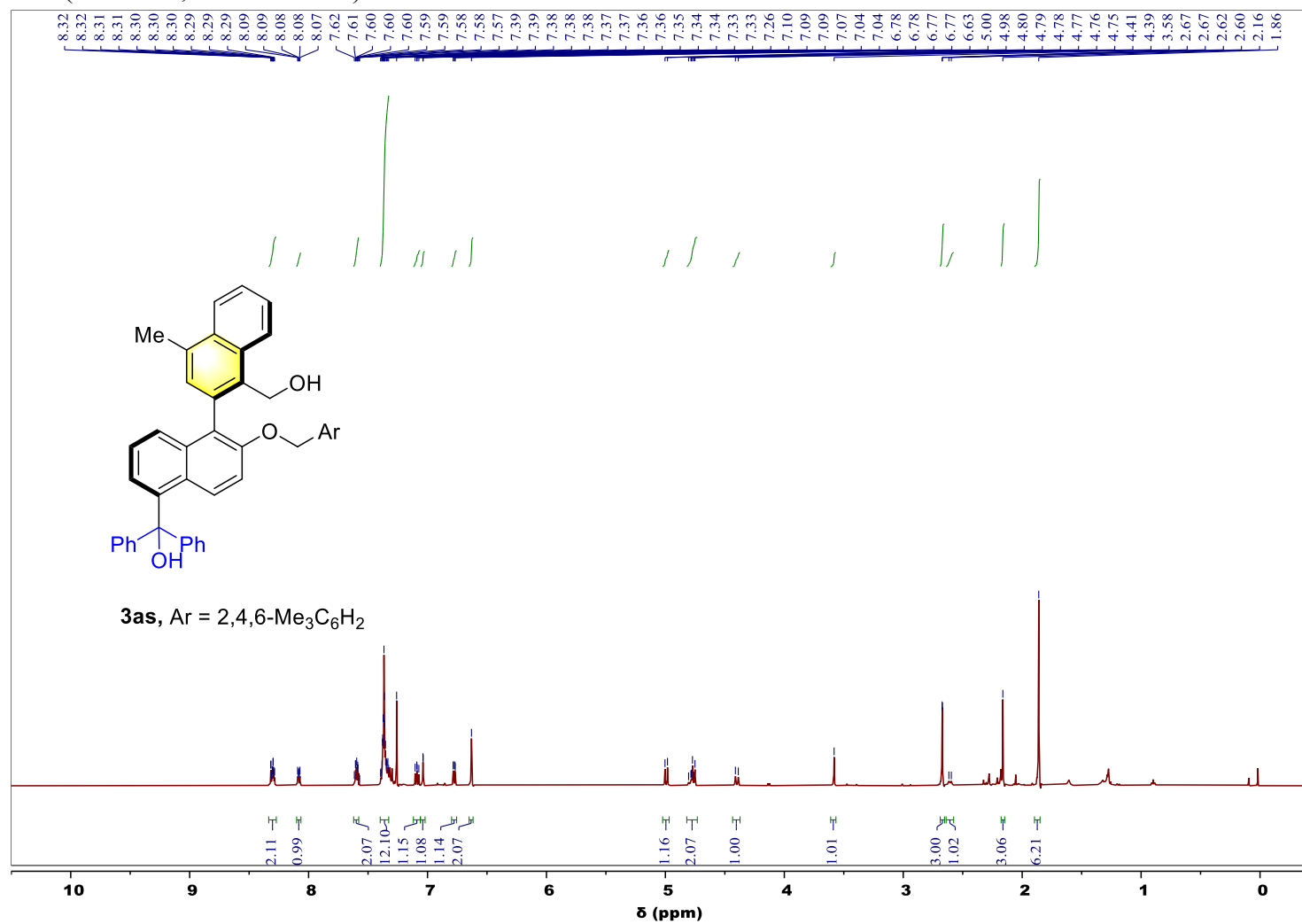
^1H NMR-spectrum (500 MHz, Chloroform- d) of **3ar**



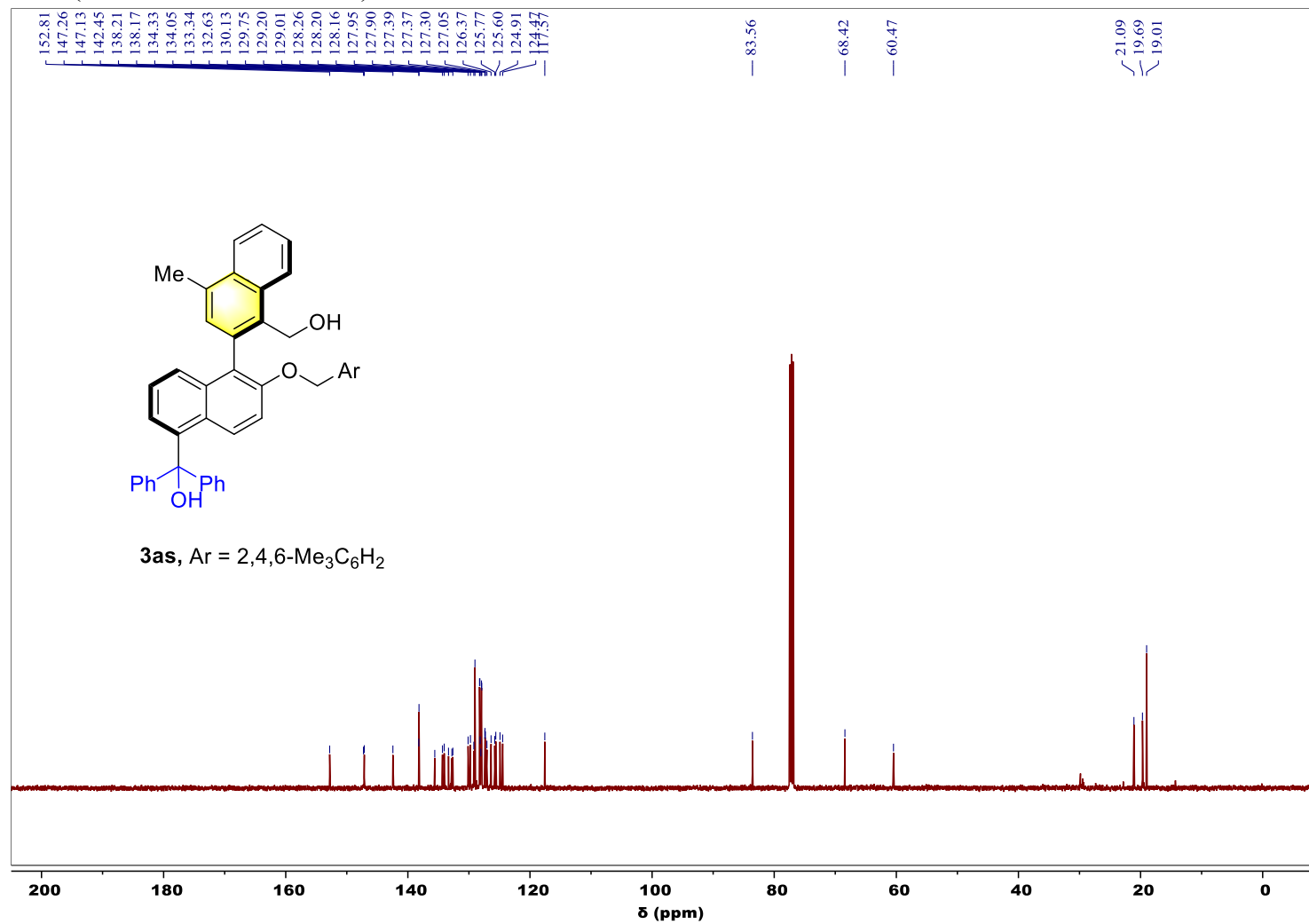
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ar**



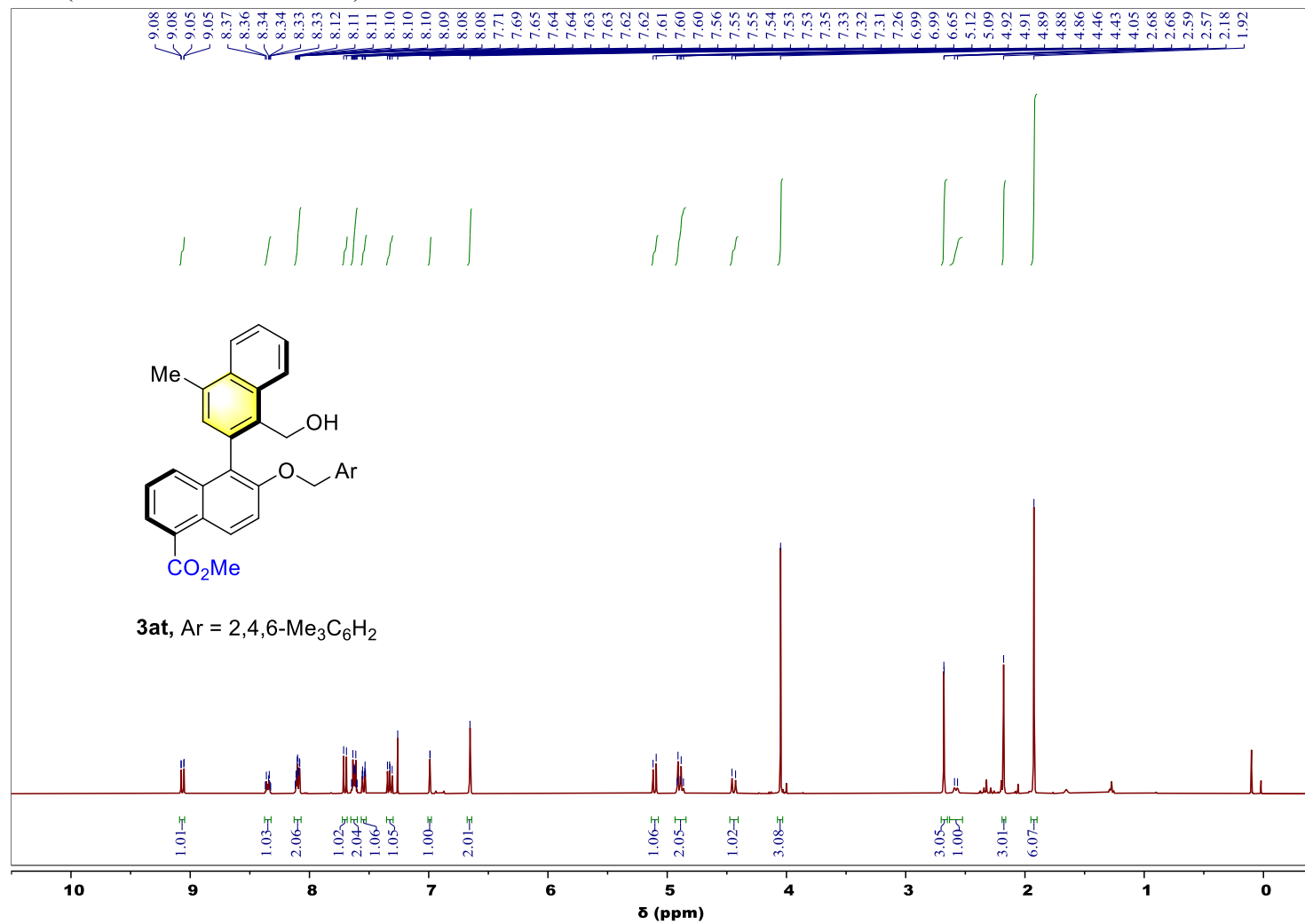
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3as**



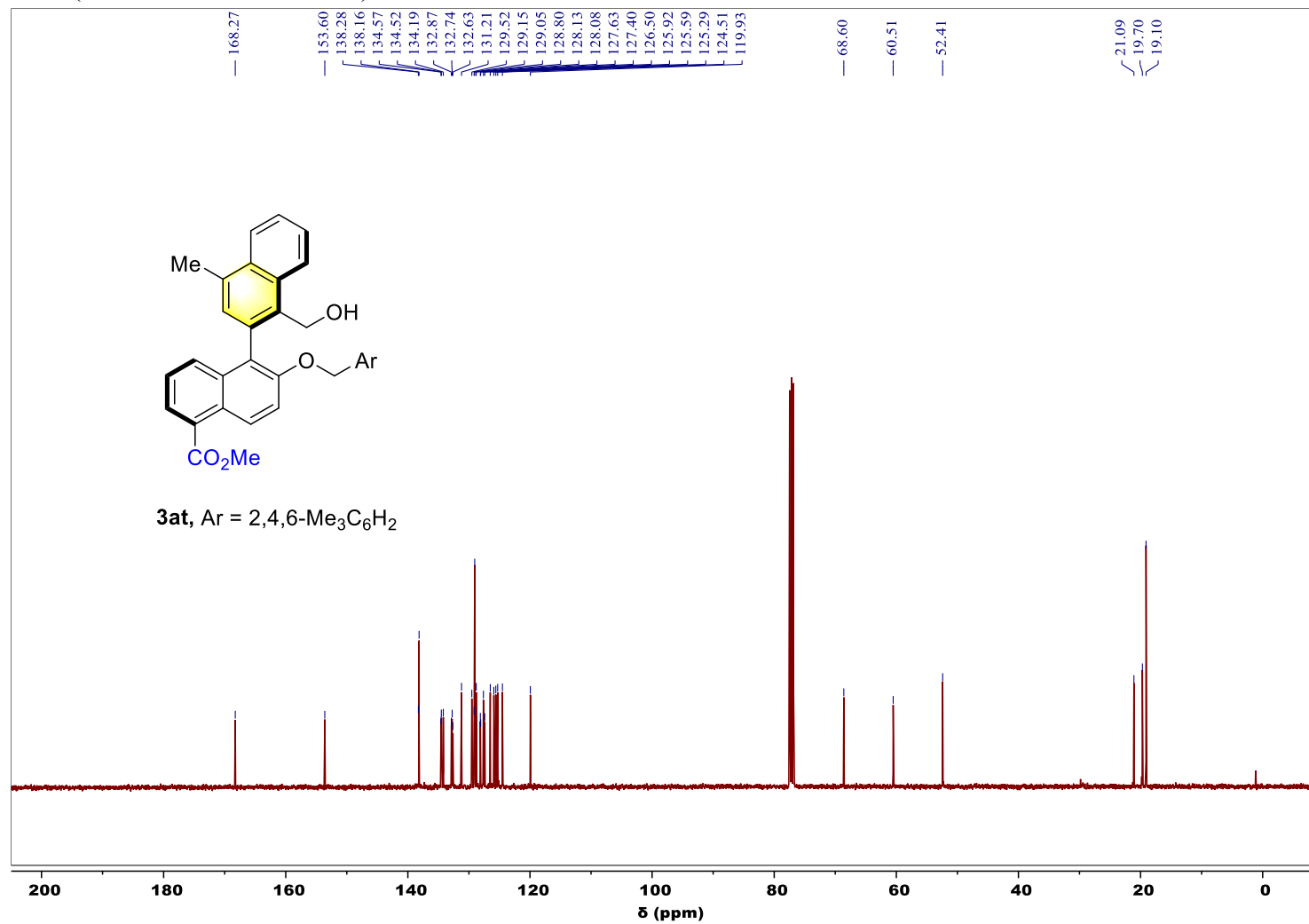
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3as**



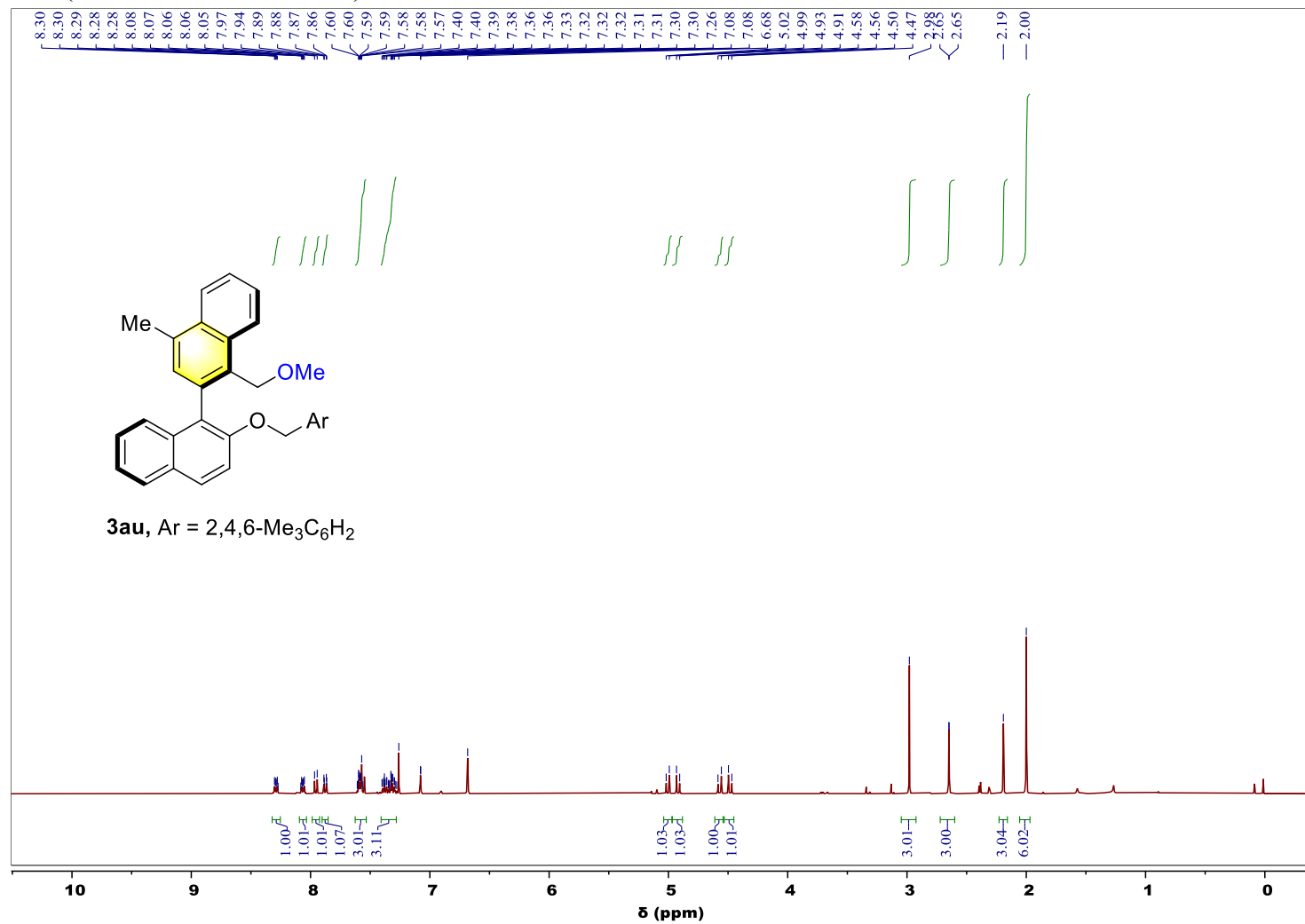
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3at**



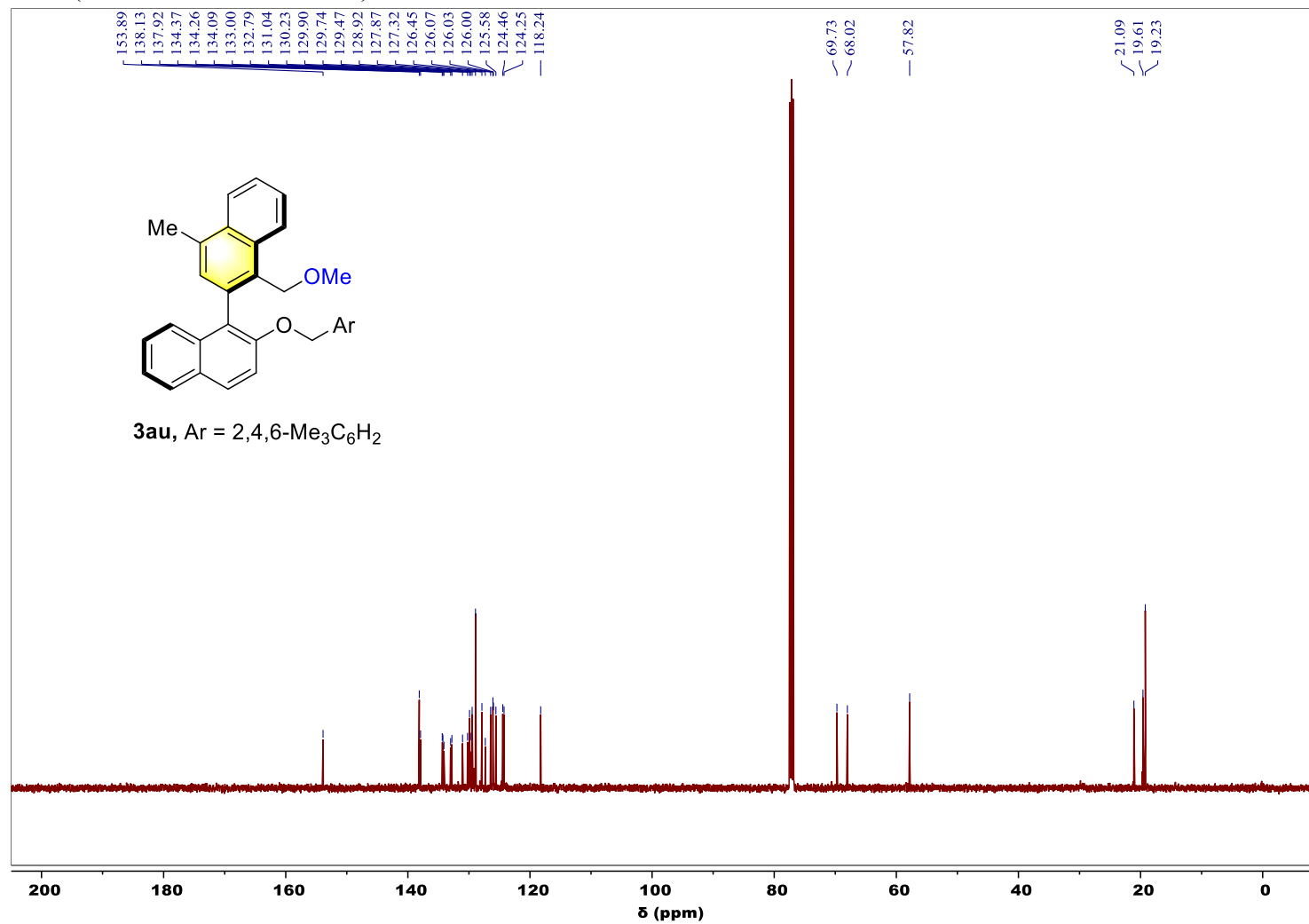
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3at**



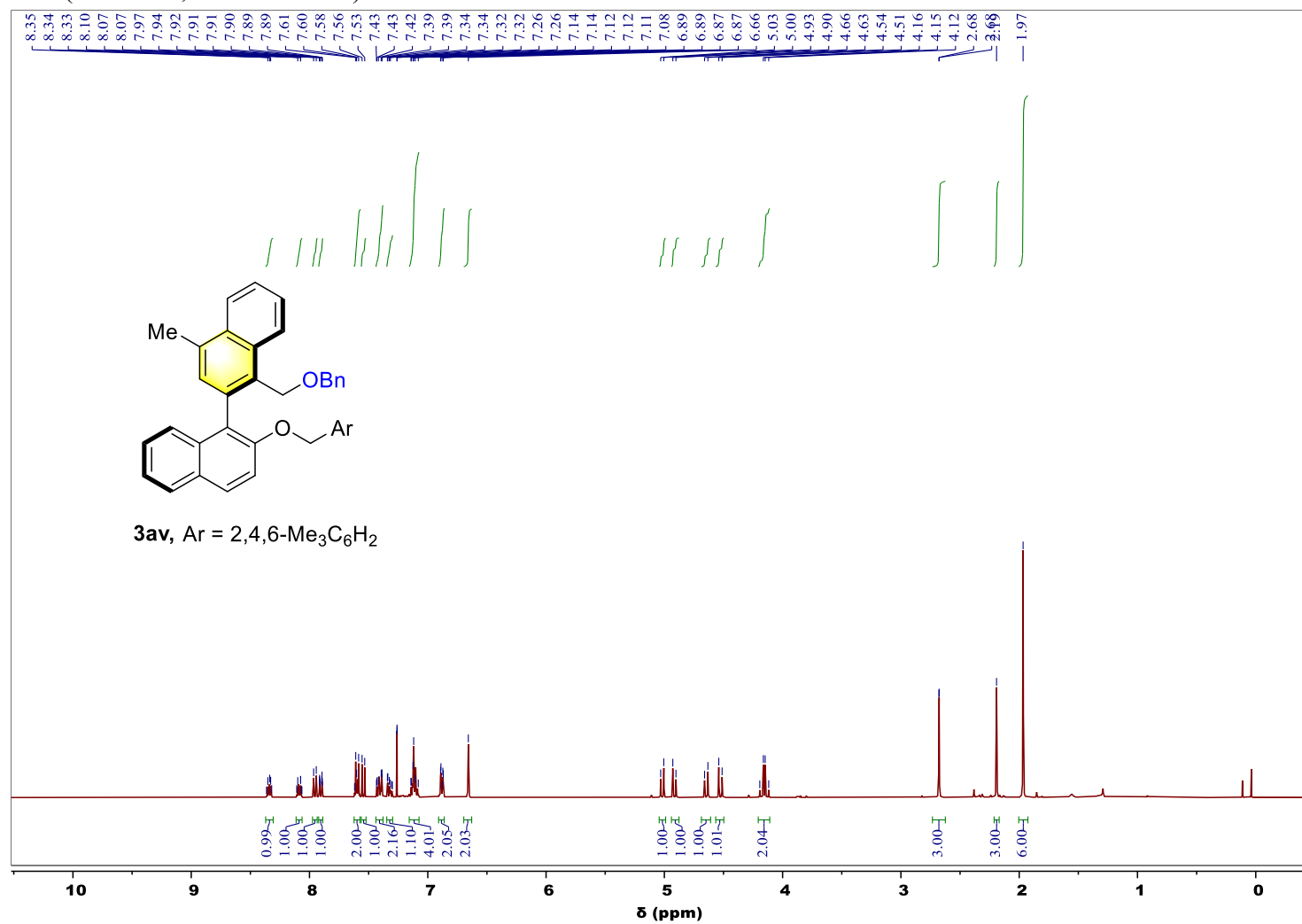
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3au**



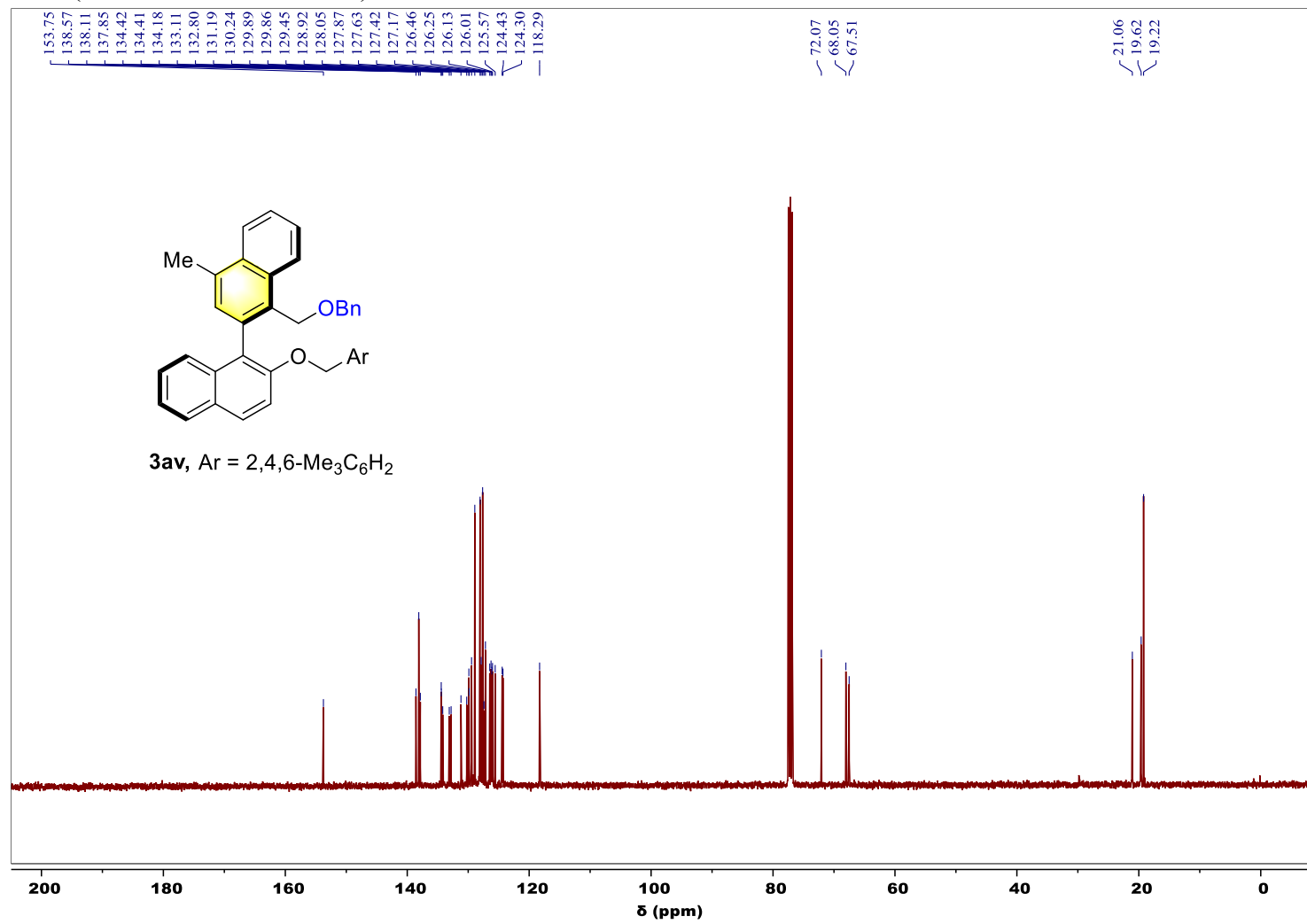
^{13}C NMR-spectrum (126 MHz, Chloroform- d) of **3au**



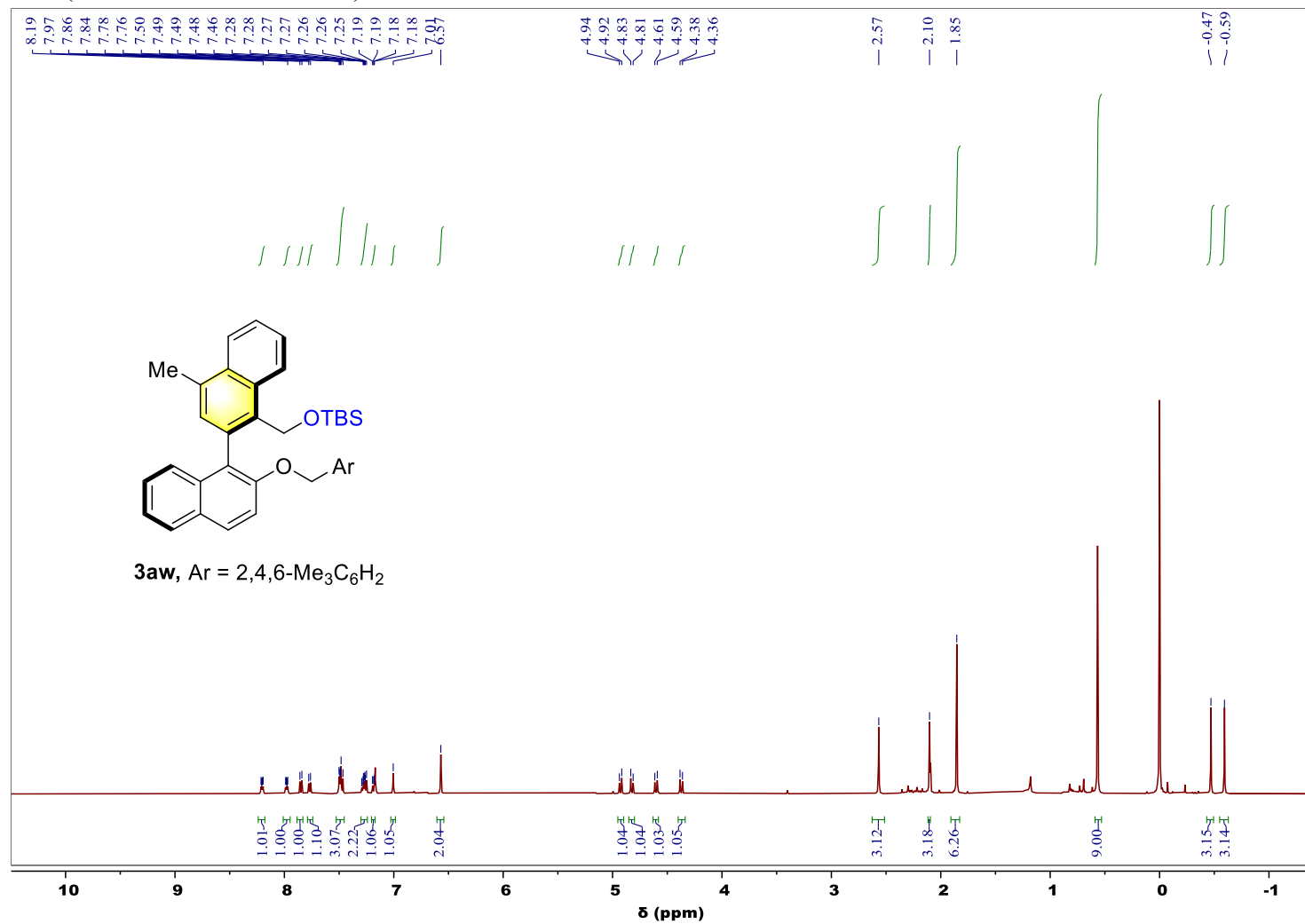
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3av**



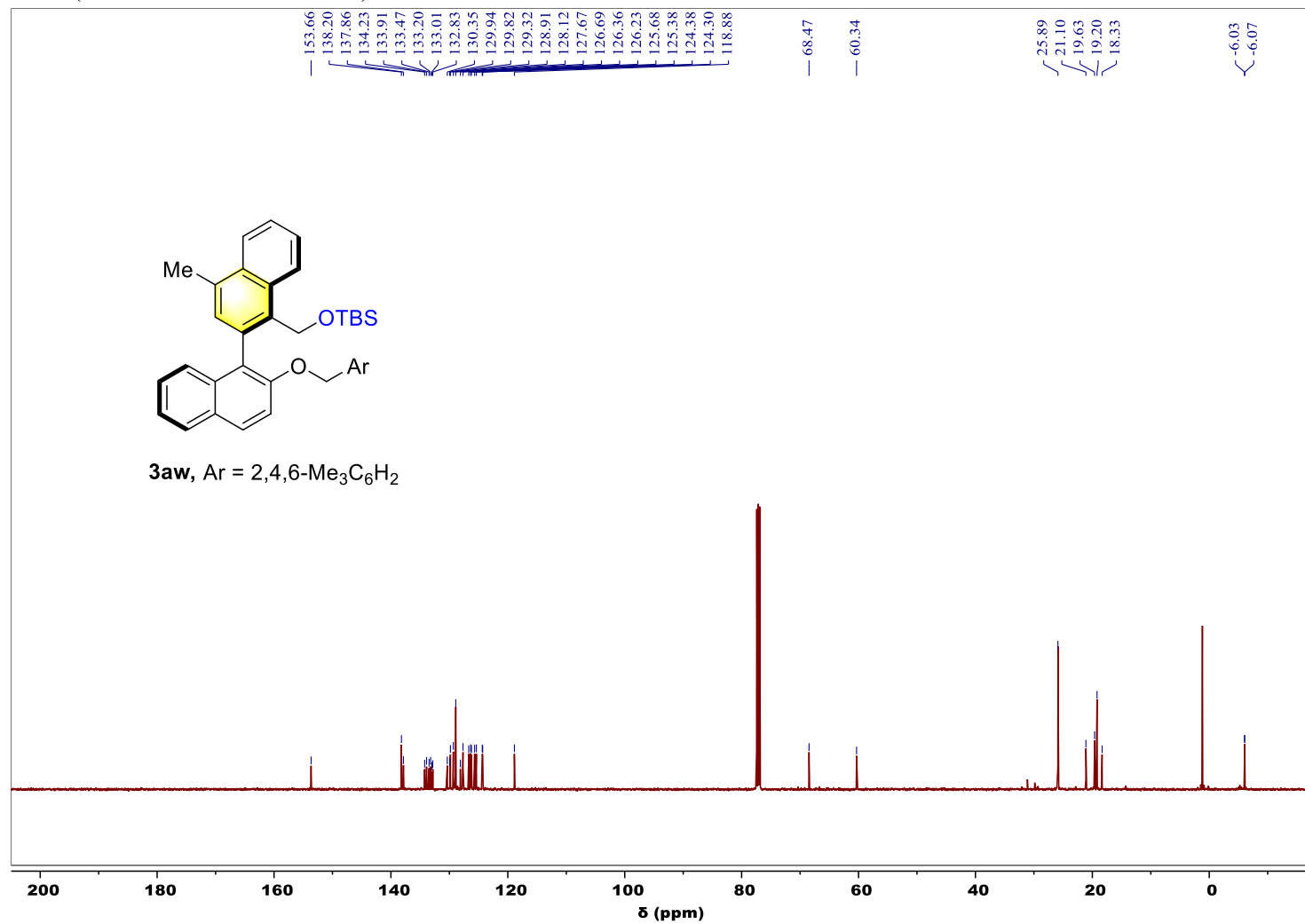
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3av**



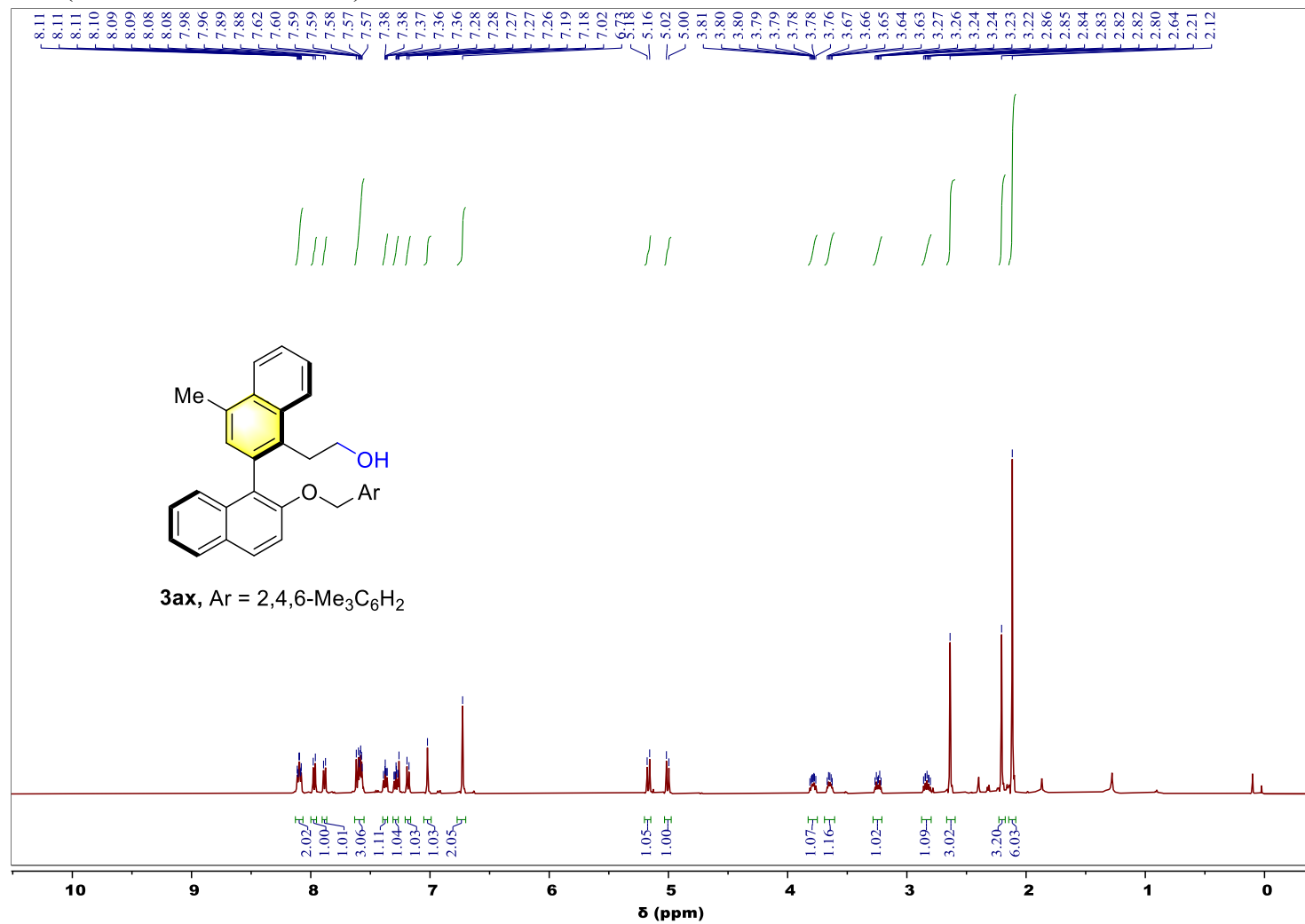
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3aw**



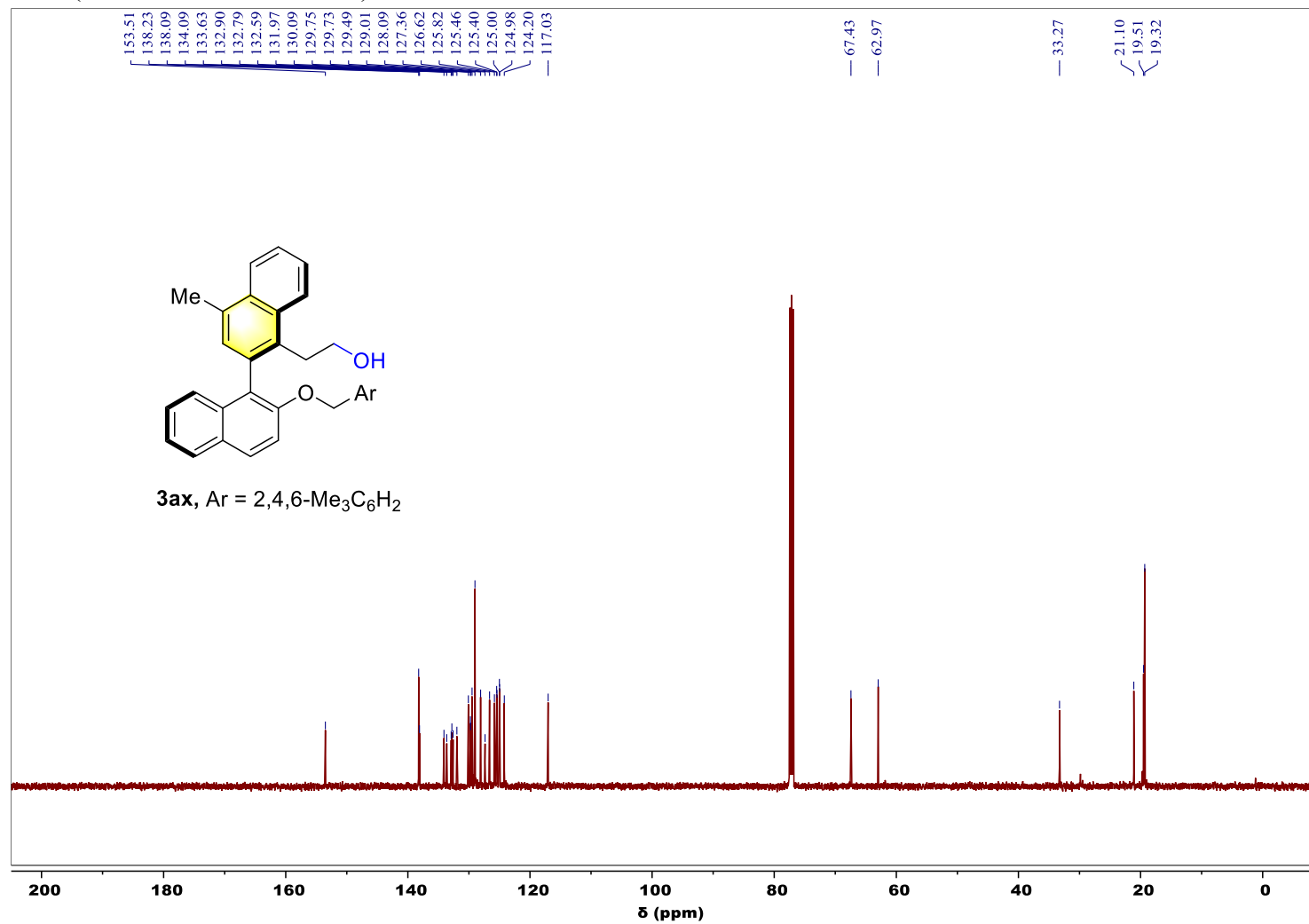
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3aw**



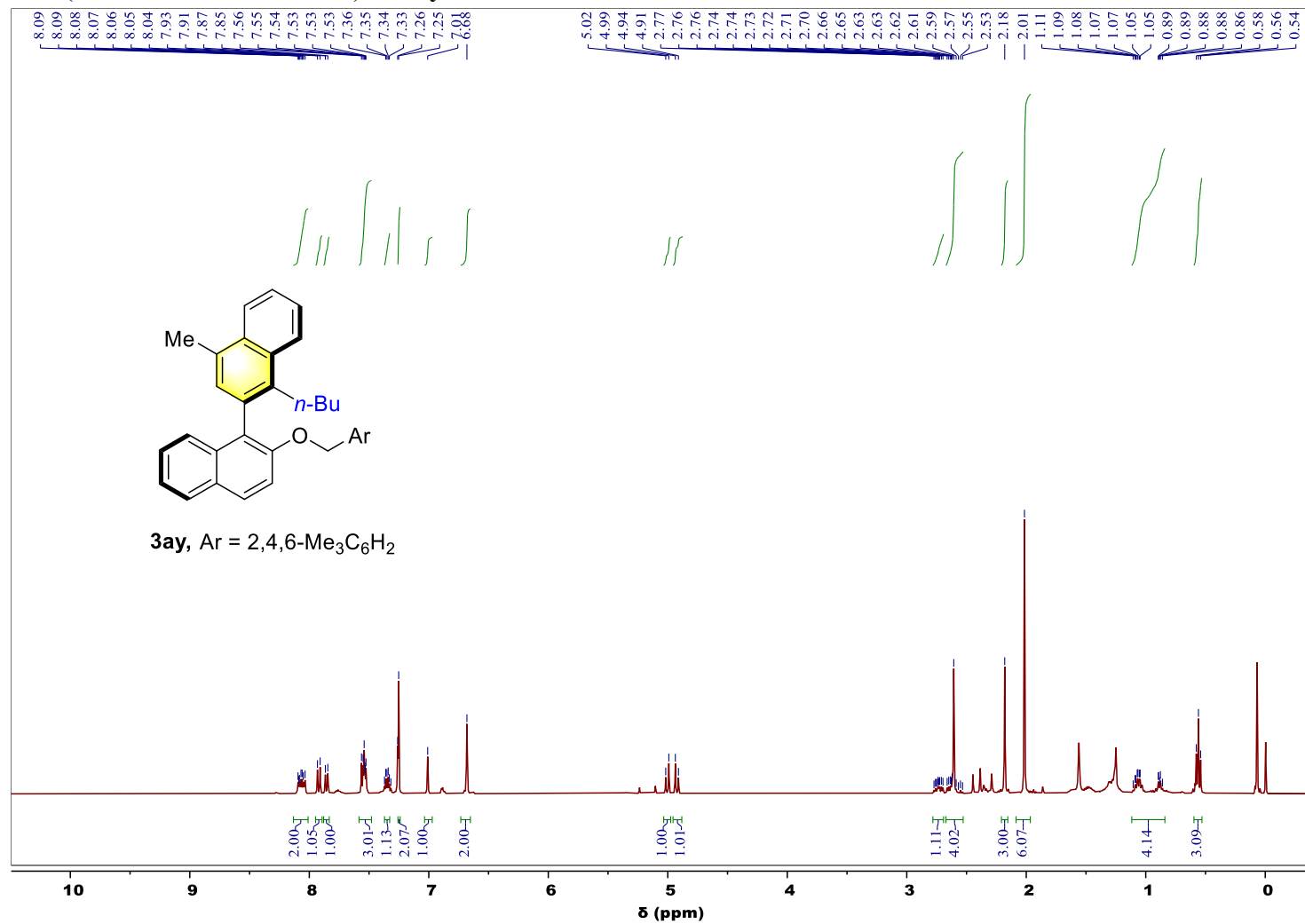
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3ax**



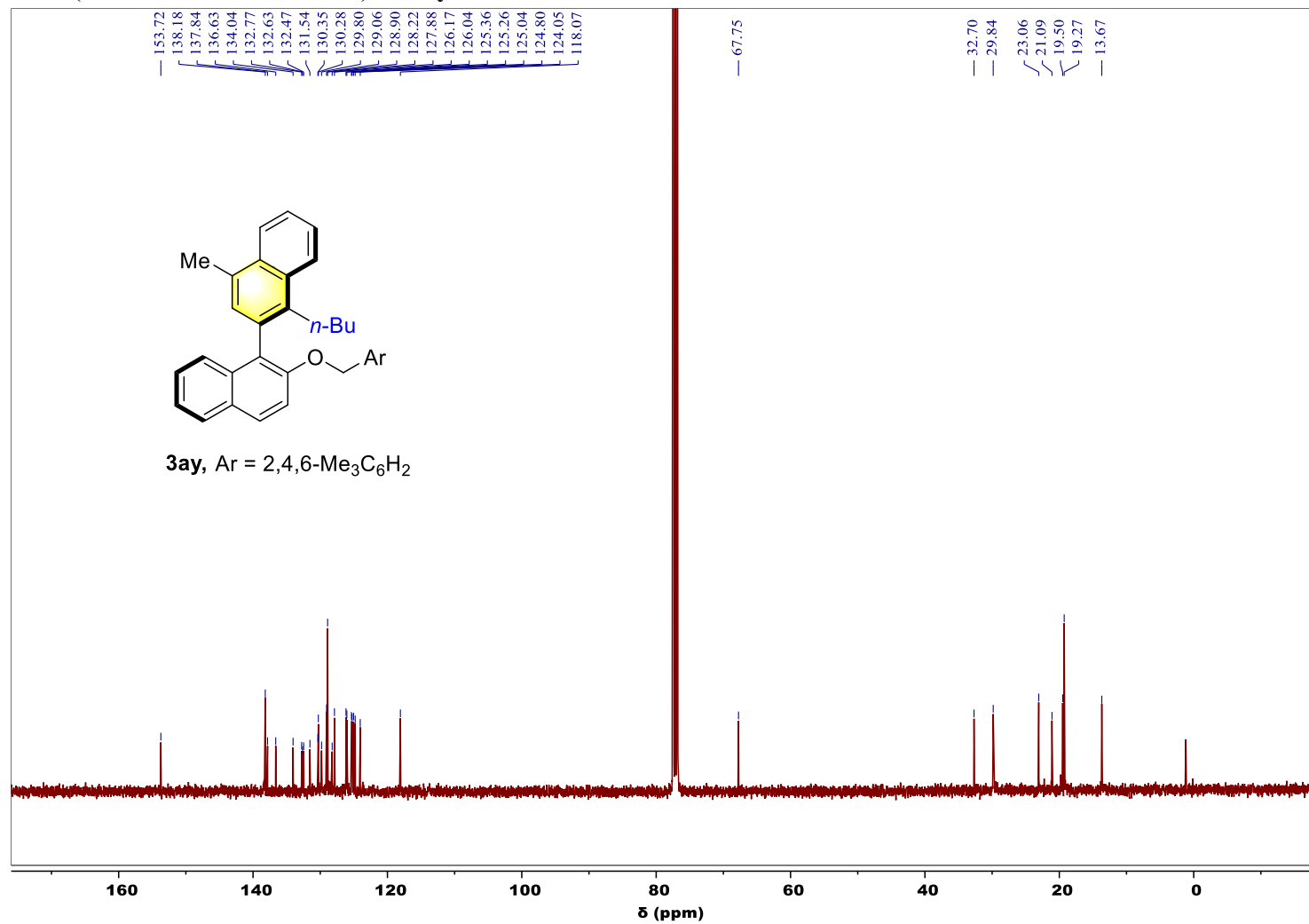
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3ax**



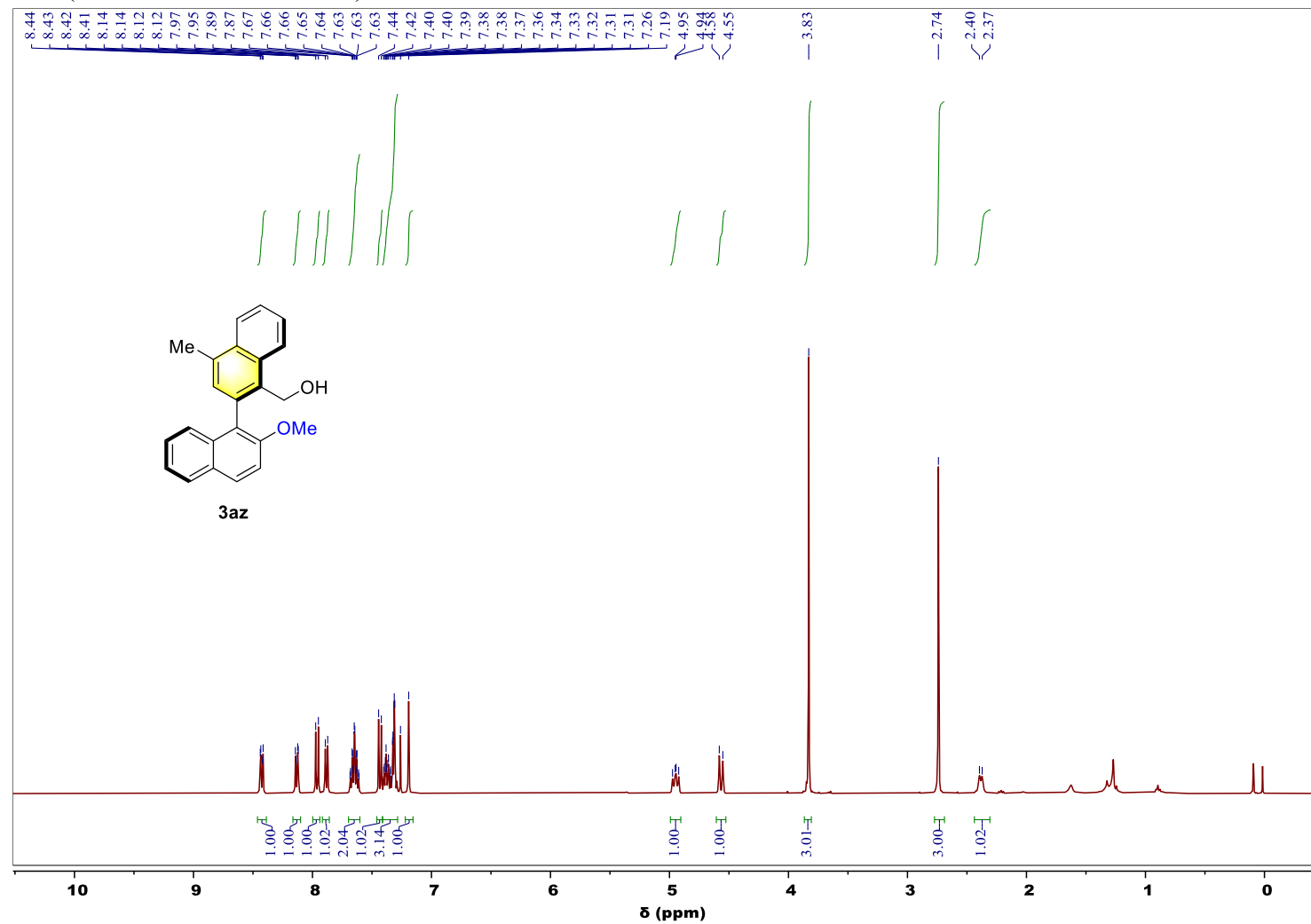
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3ay**



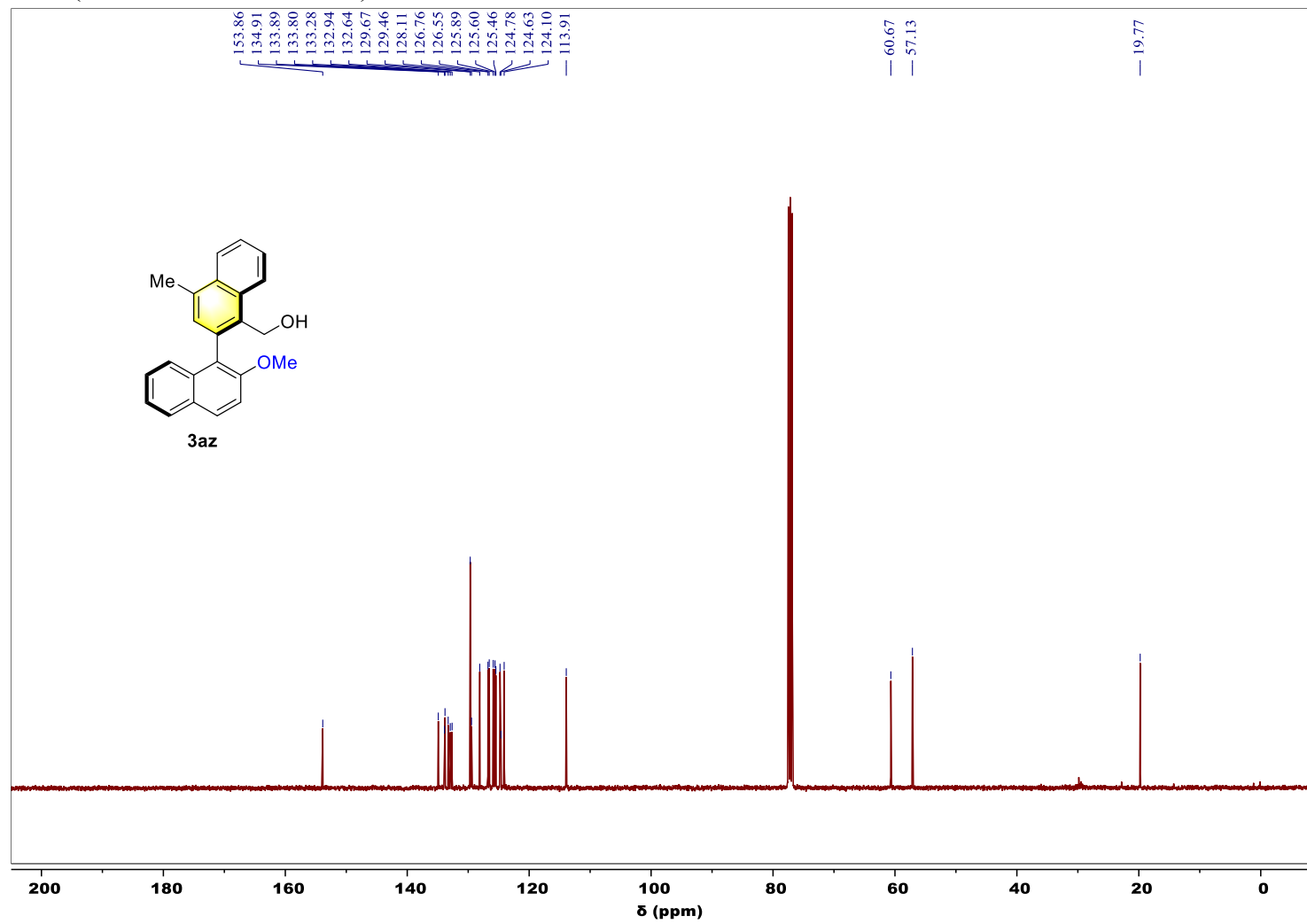
^{13}C NMR-spectrum (101 MHz, Chloroform- d) of **3ay**



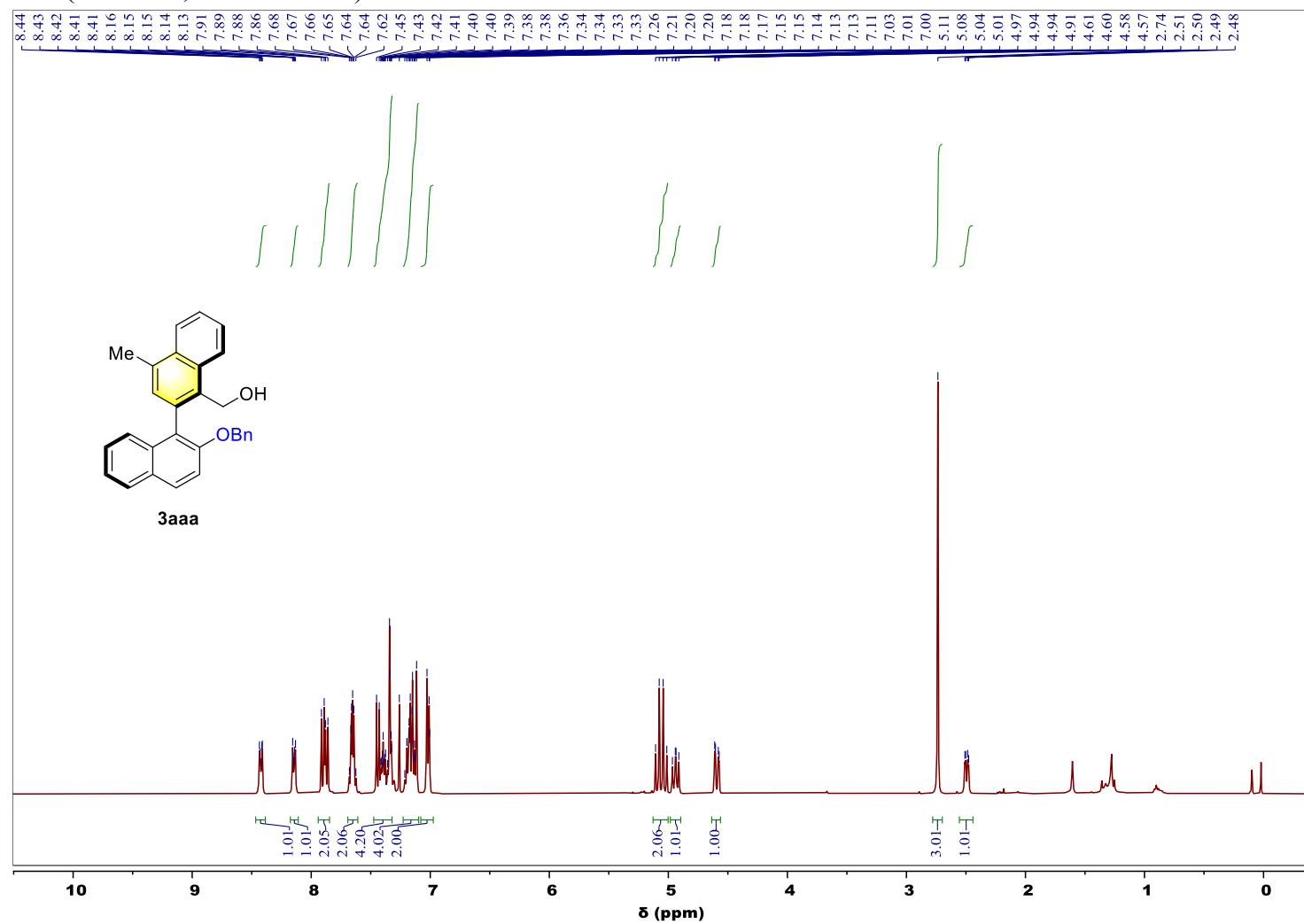
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3az**



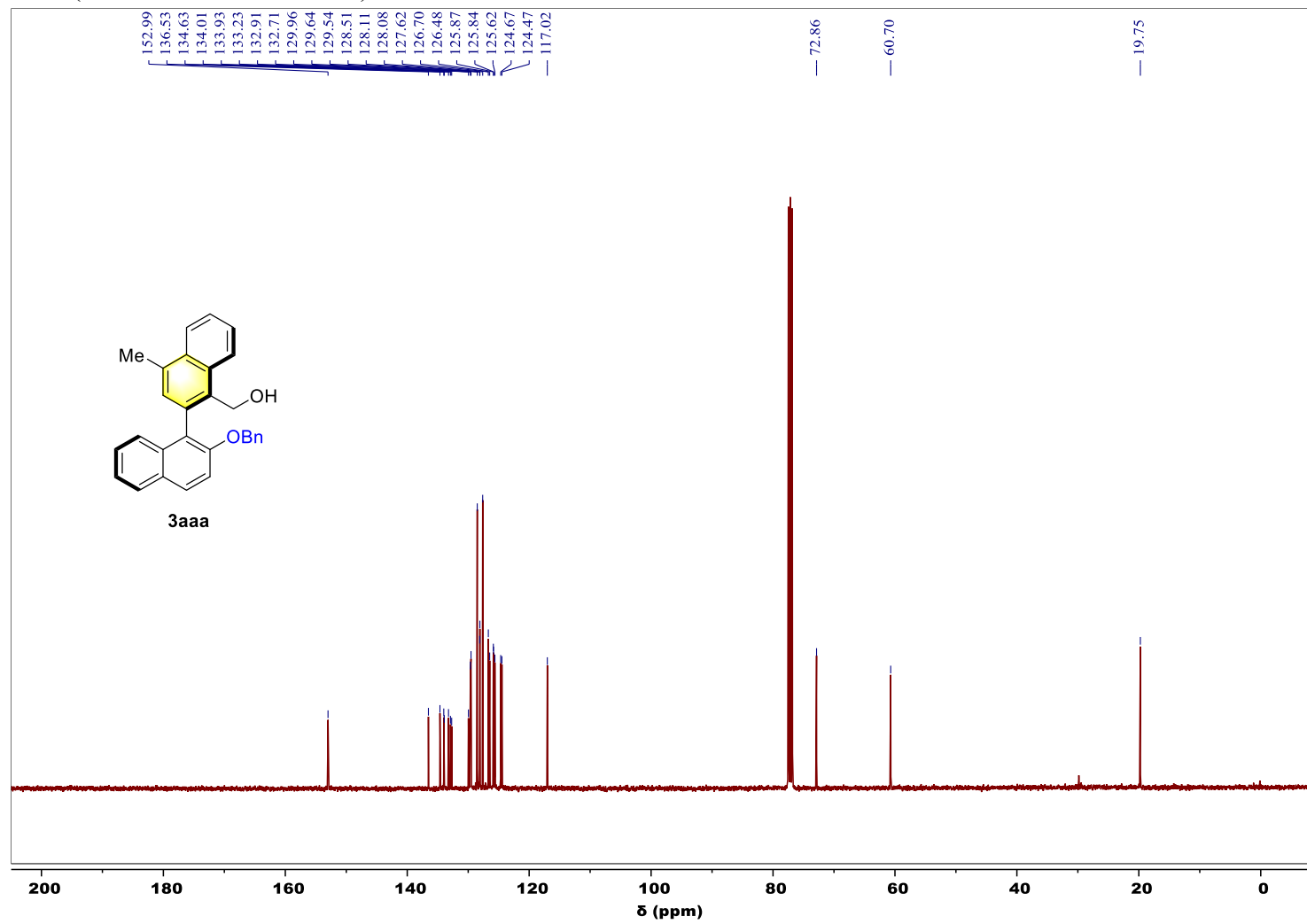
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3az**



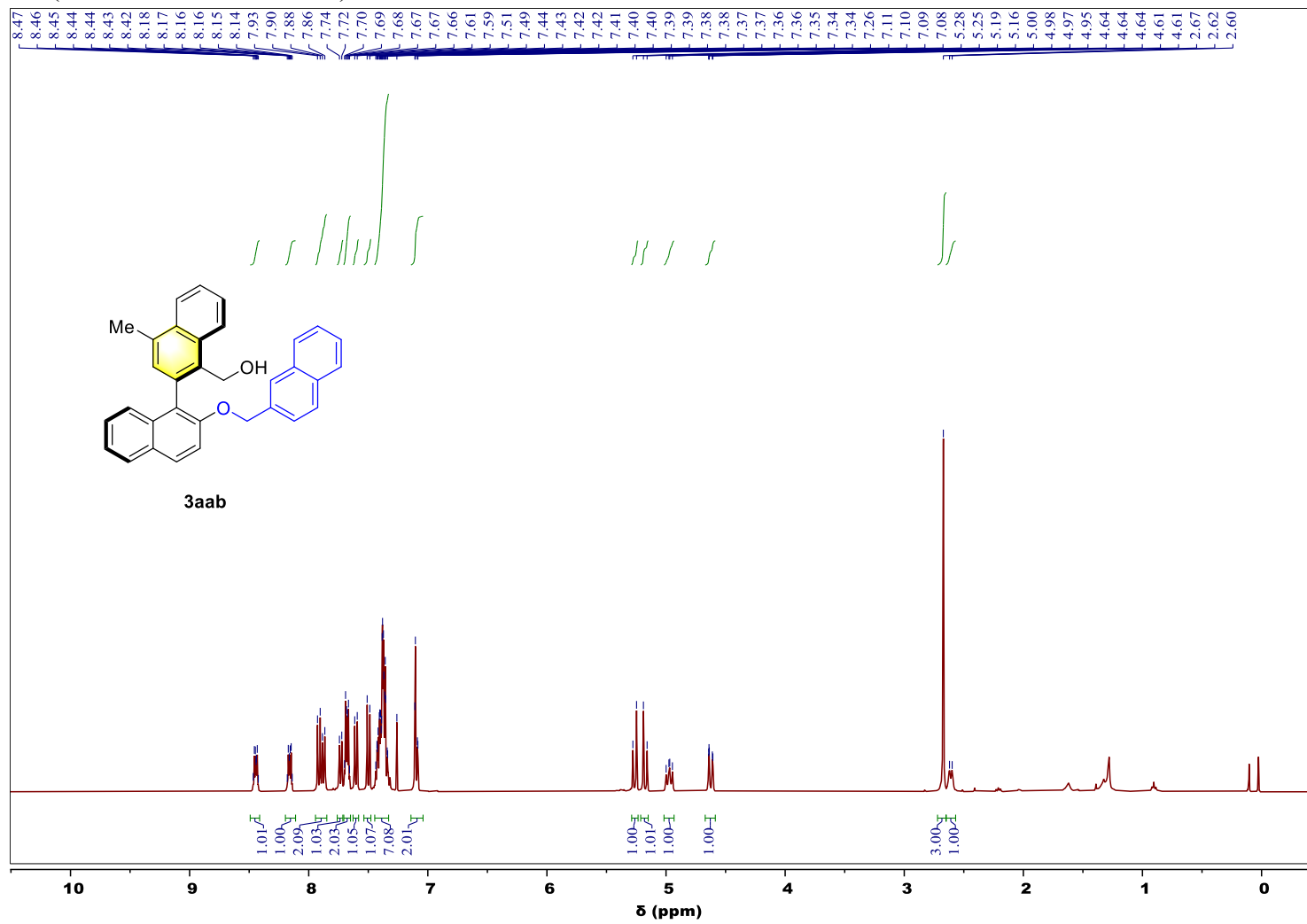
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **3aaa**



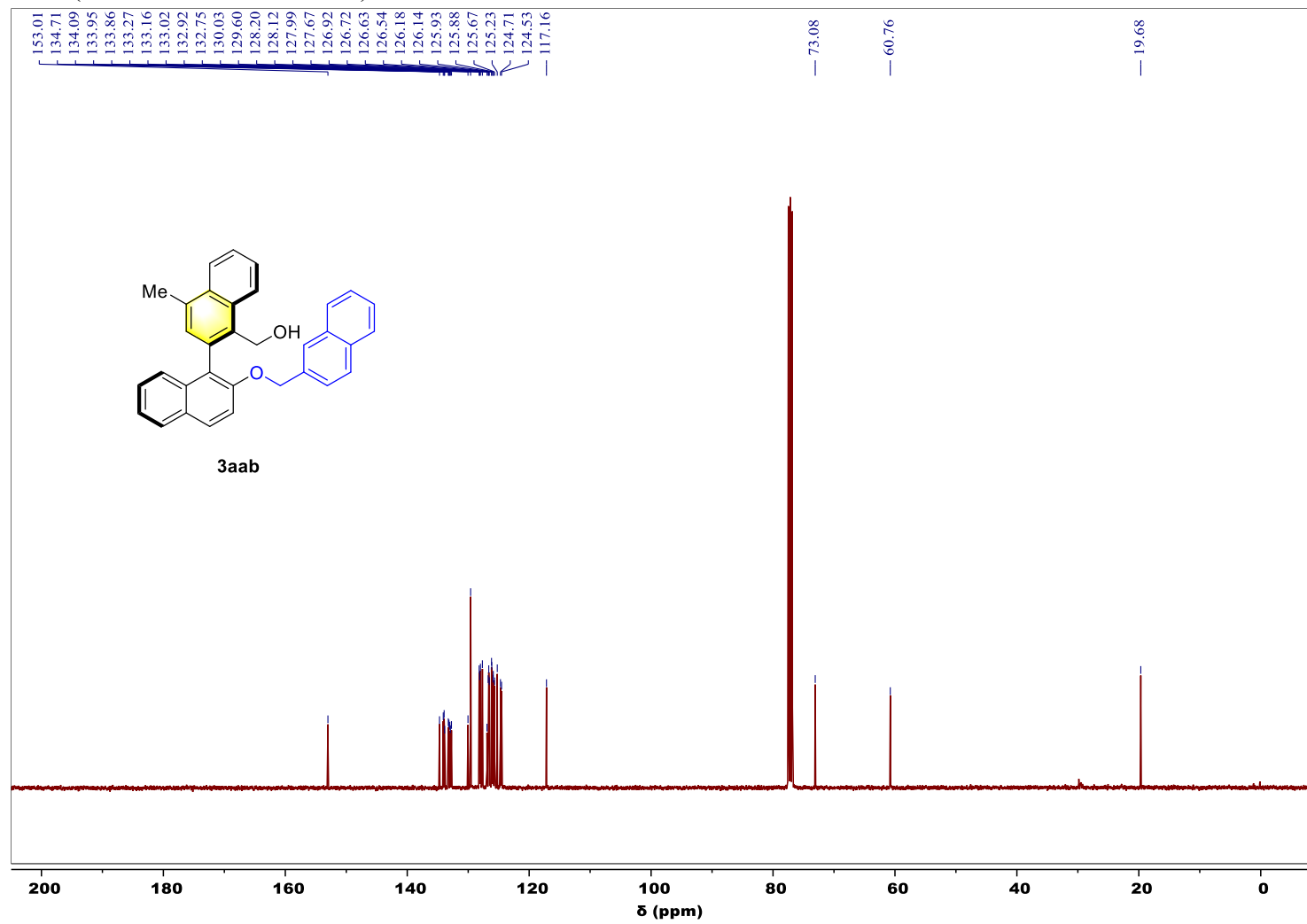
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3aaa**



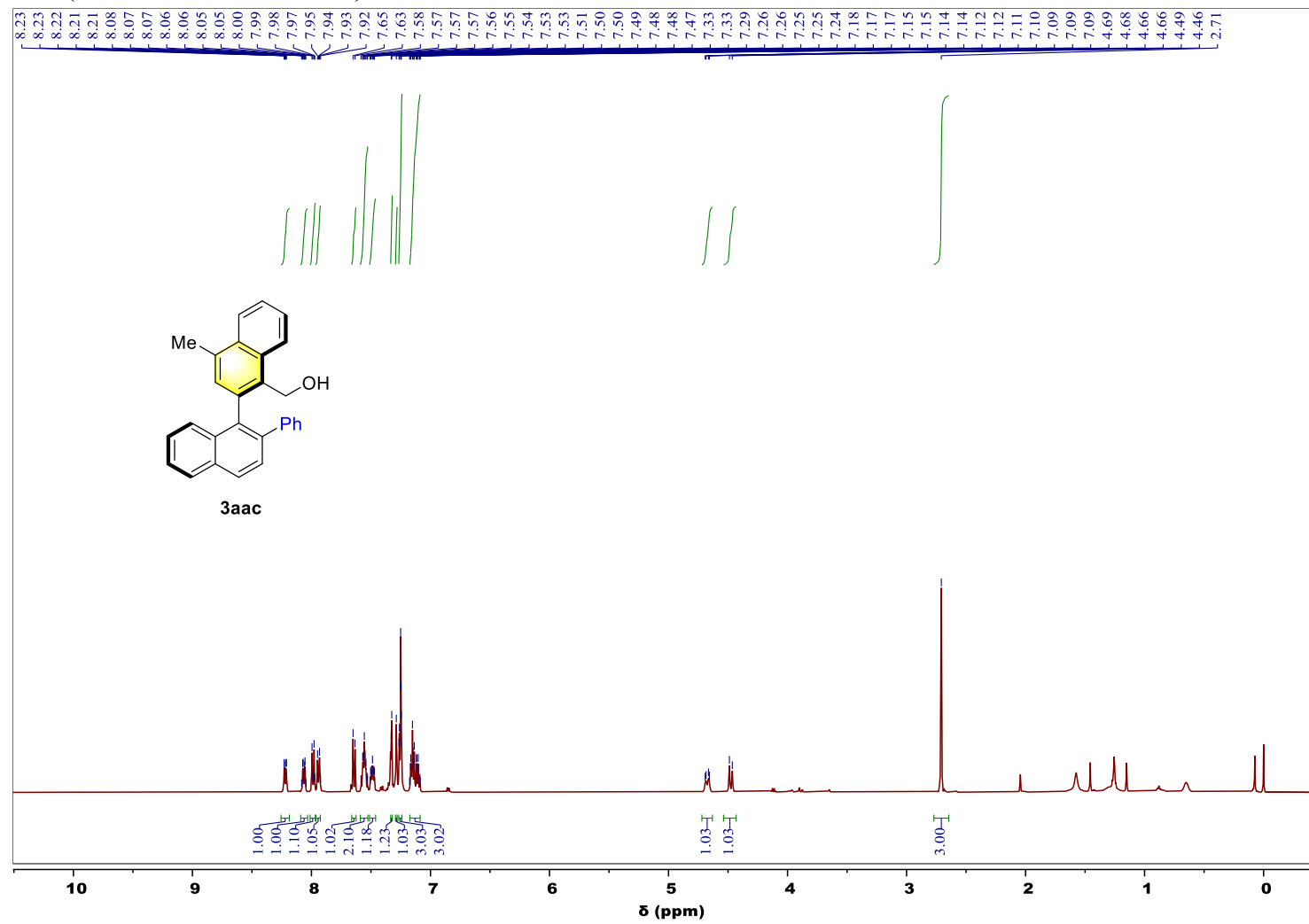
^1H NMR-spectrum (400 MHz, Chloroform- d) of **3aab**



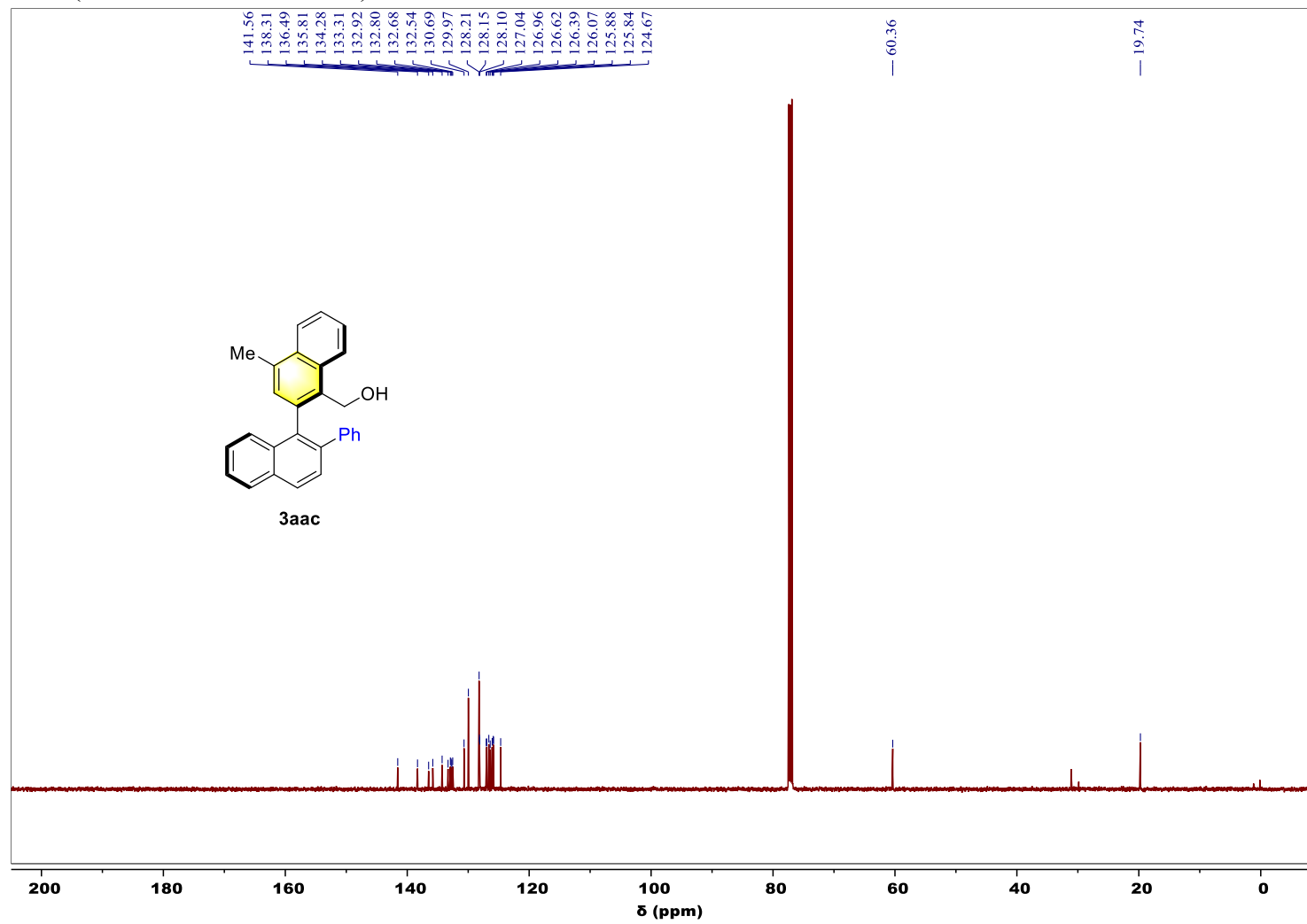
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **3aab**



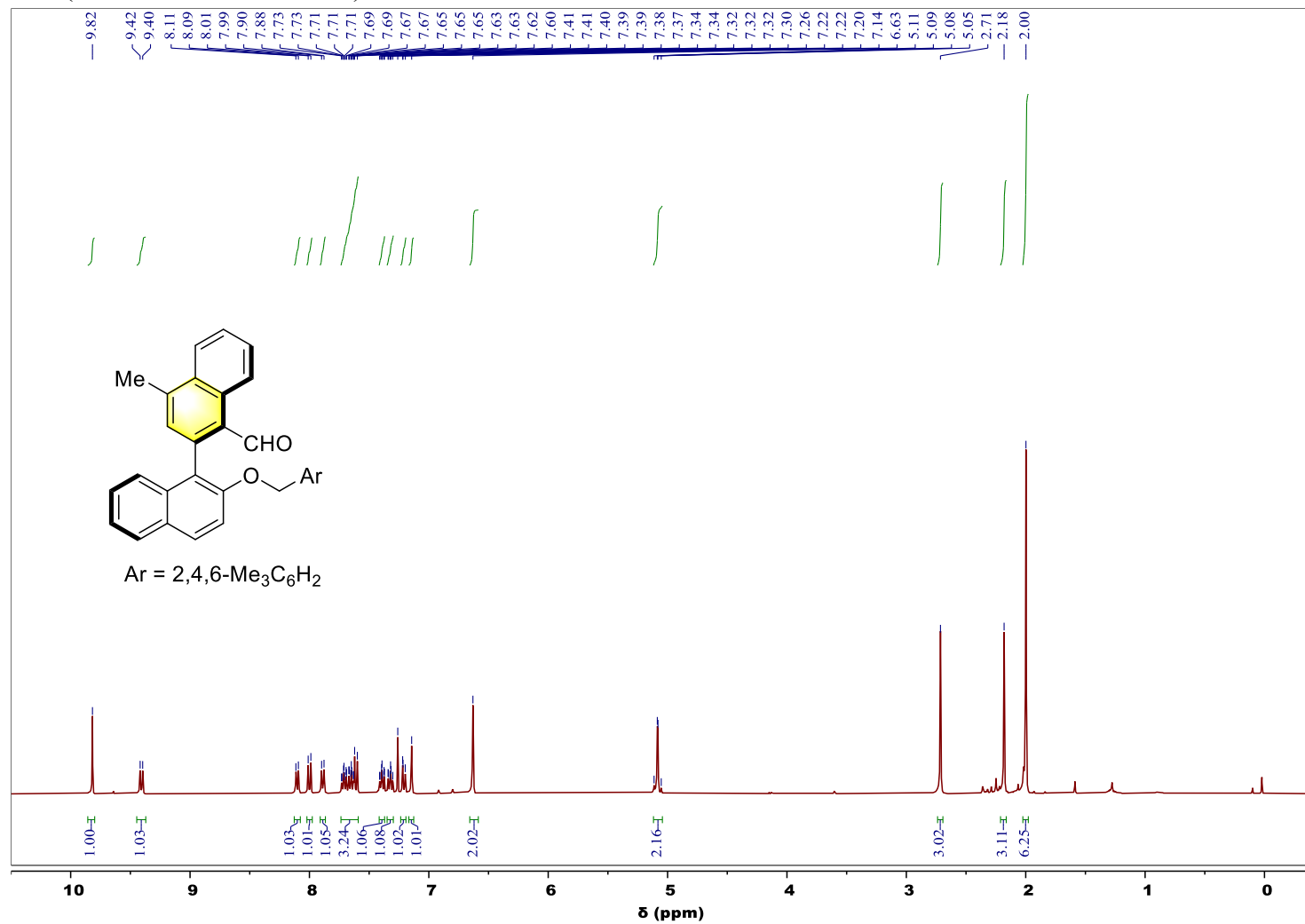
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **3aac**



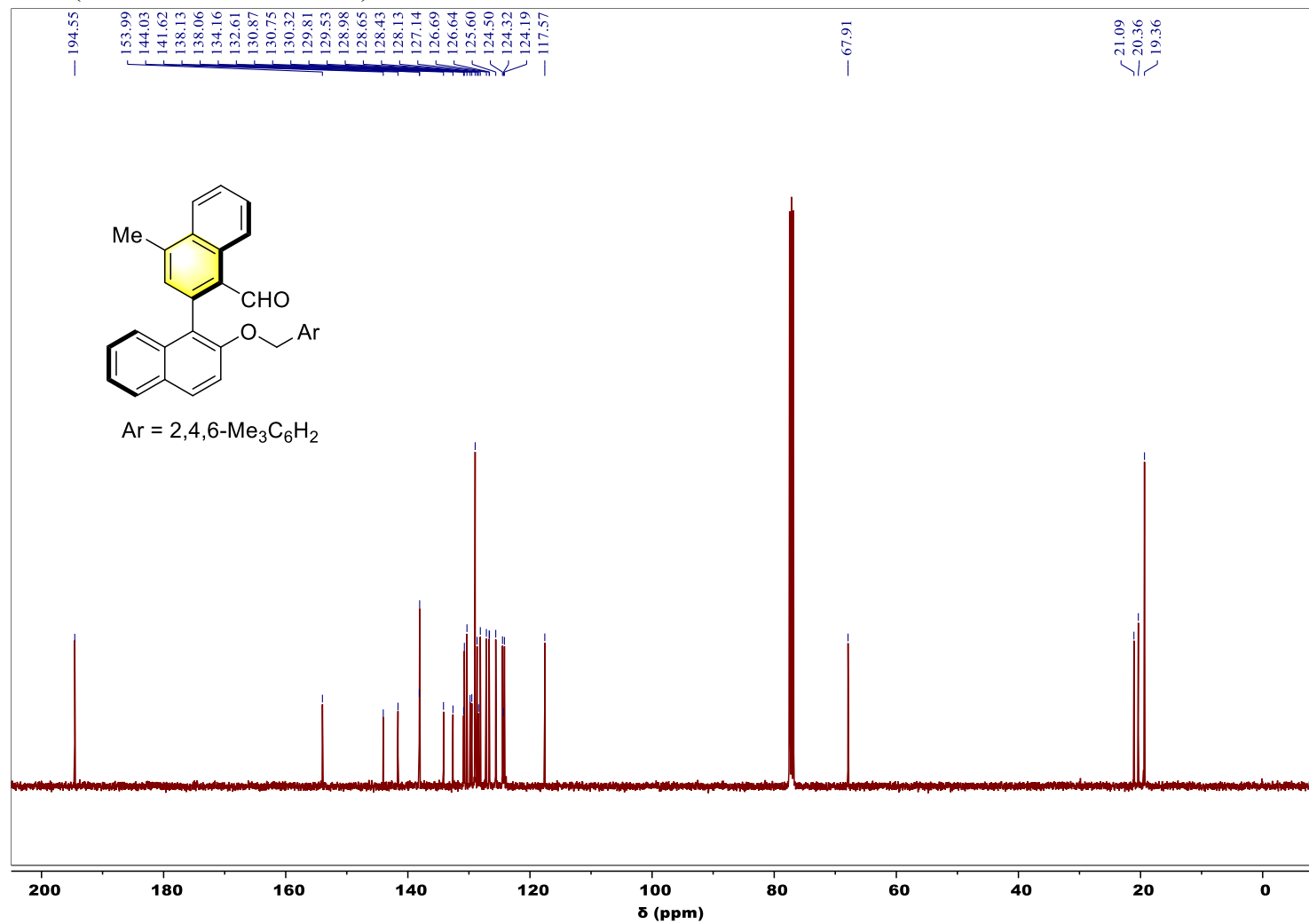
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **3aac**



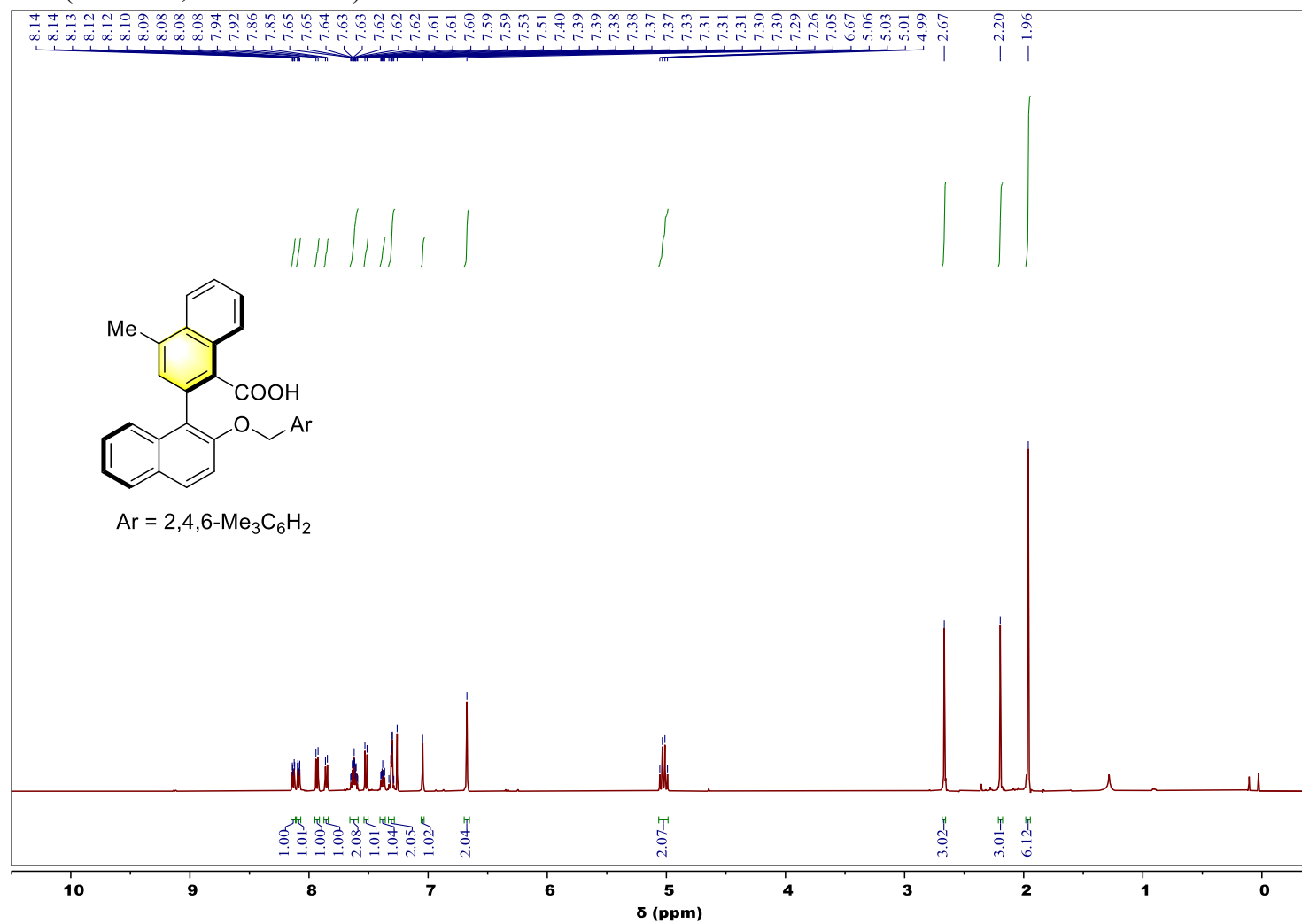
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **4**



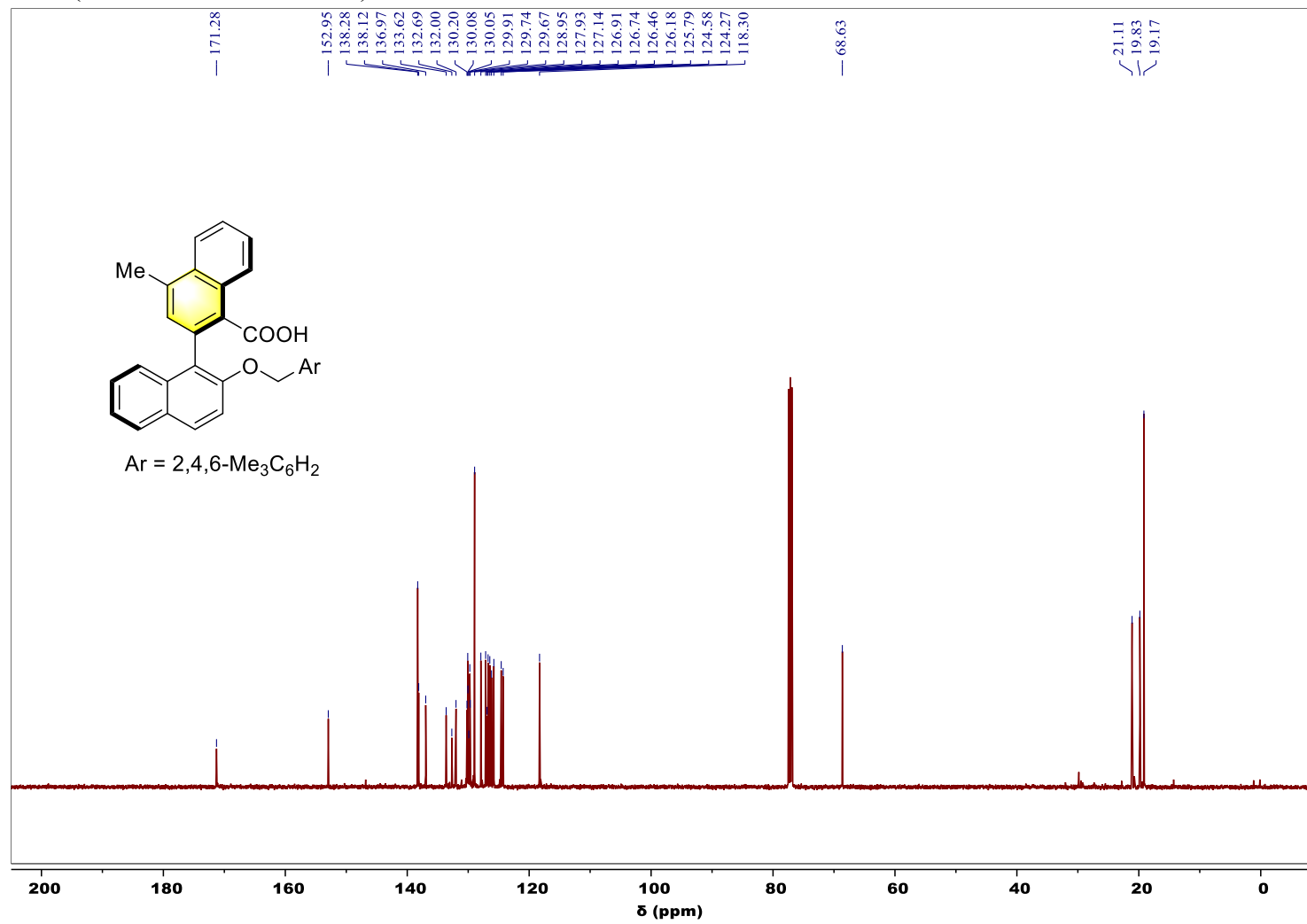
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of 4



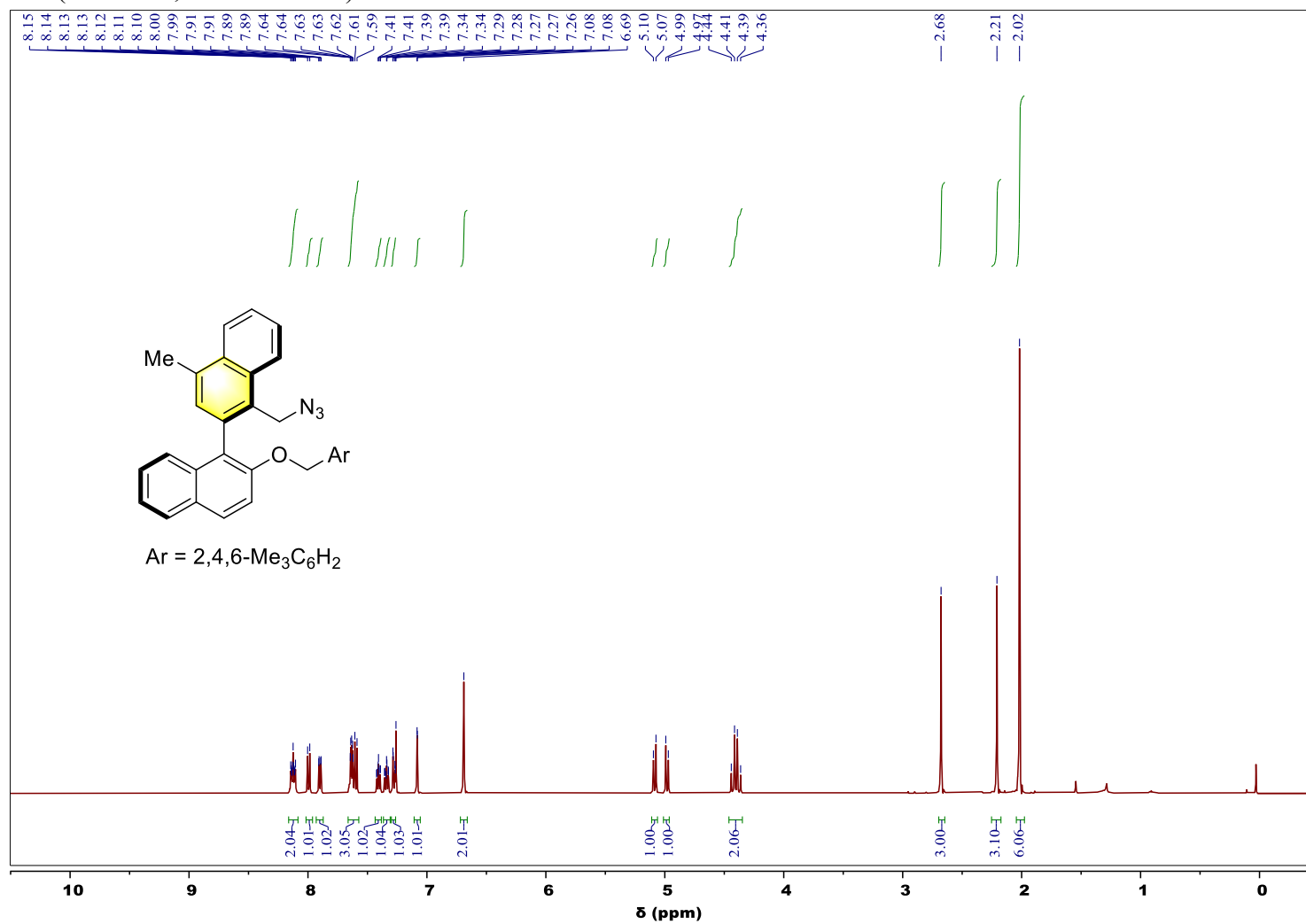
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **5**



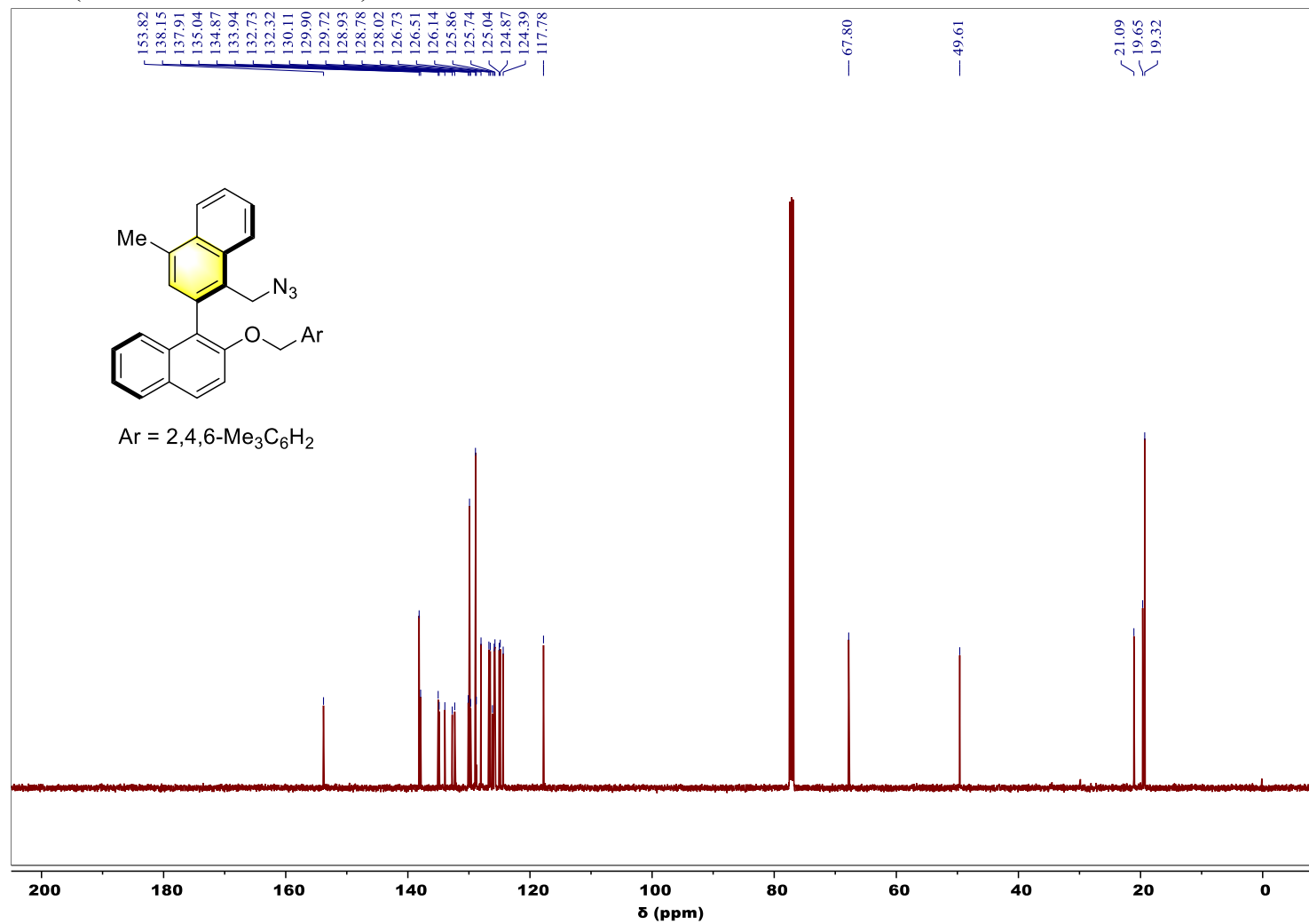
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **5**



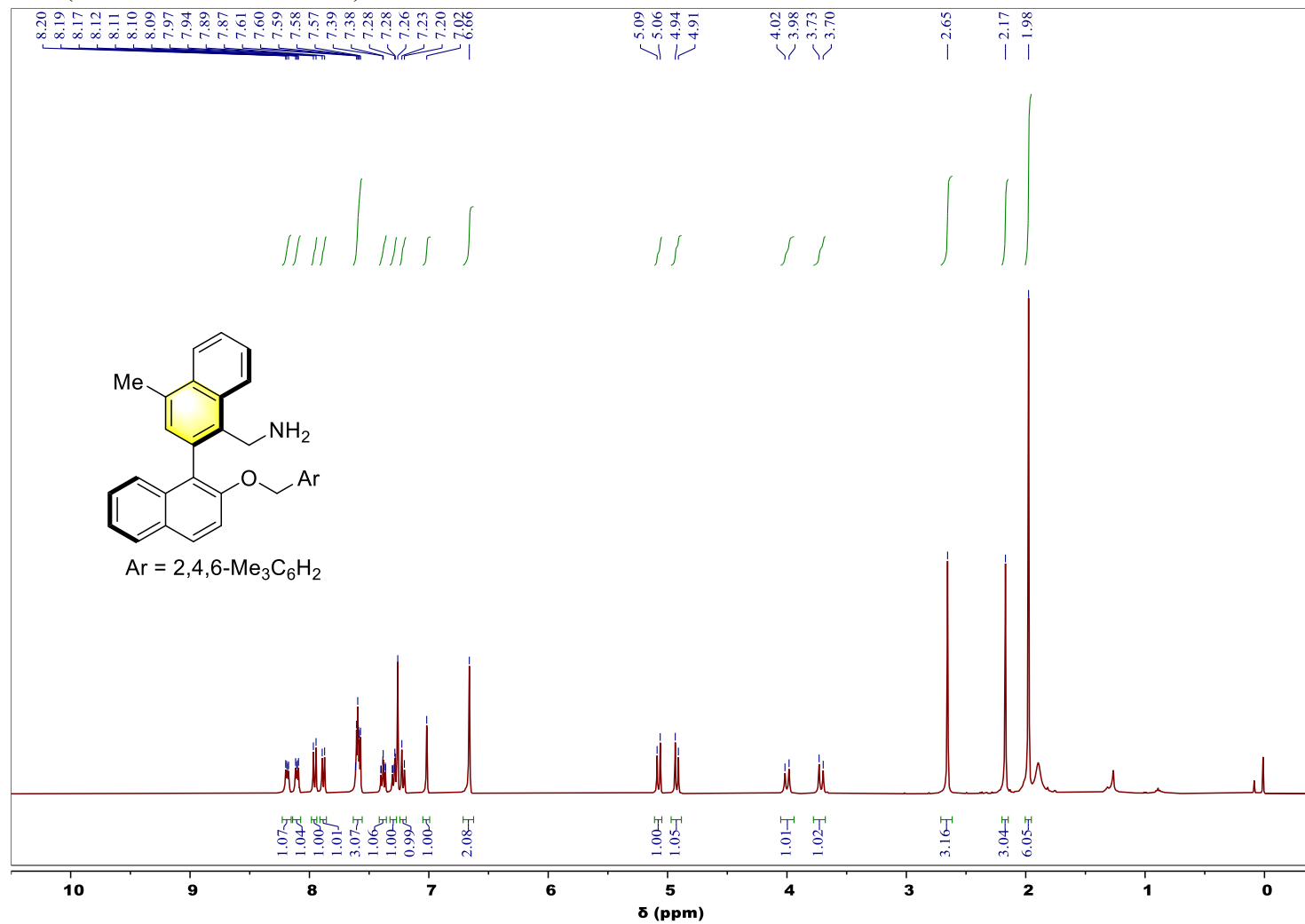
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **6**



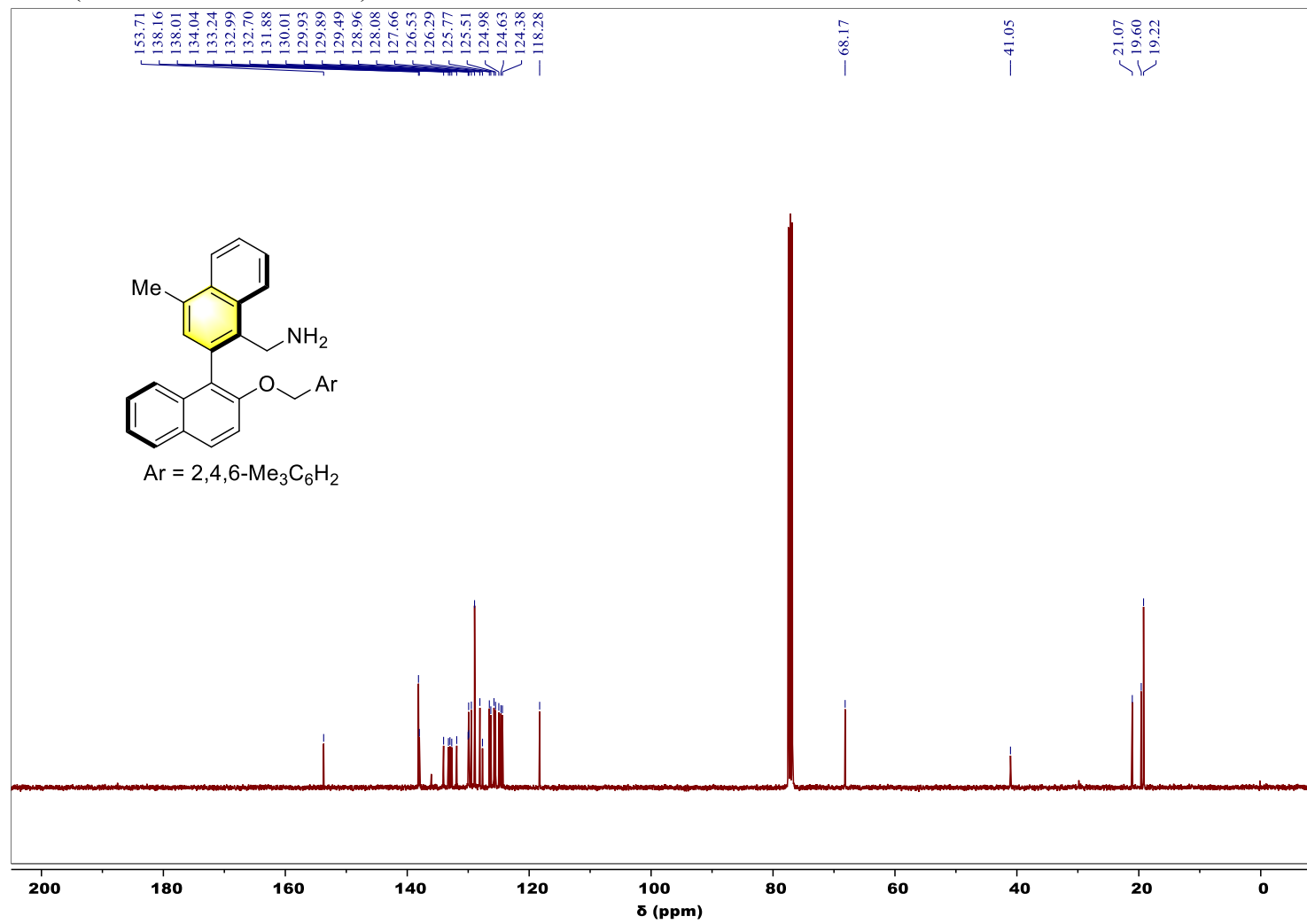
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **6**



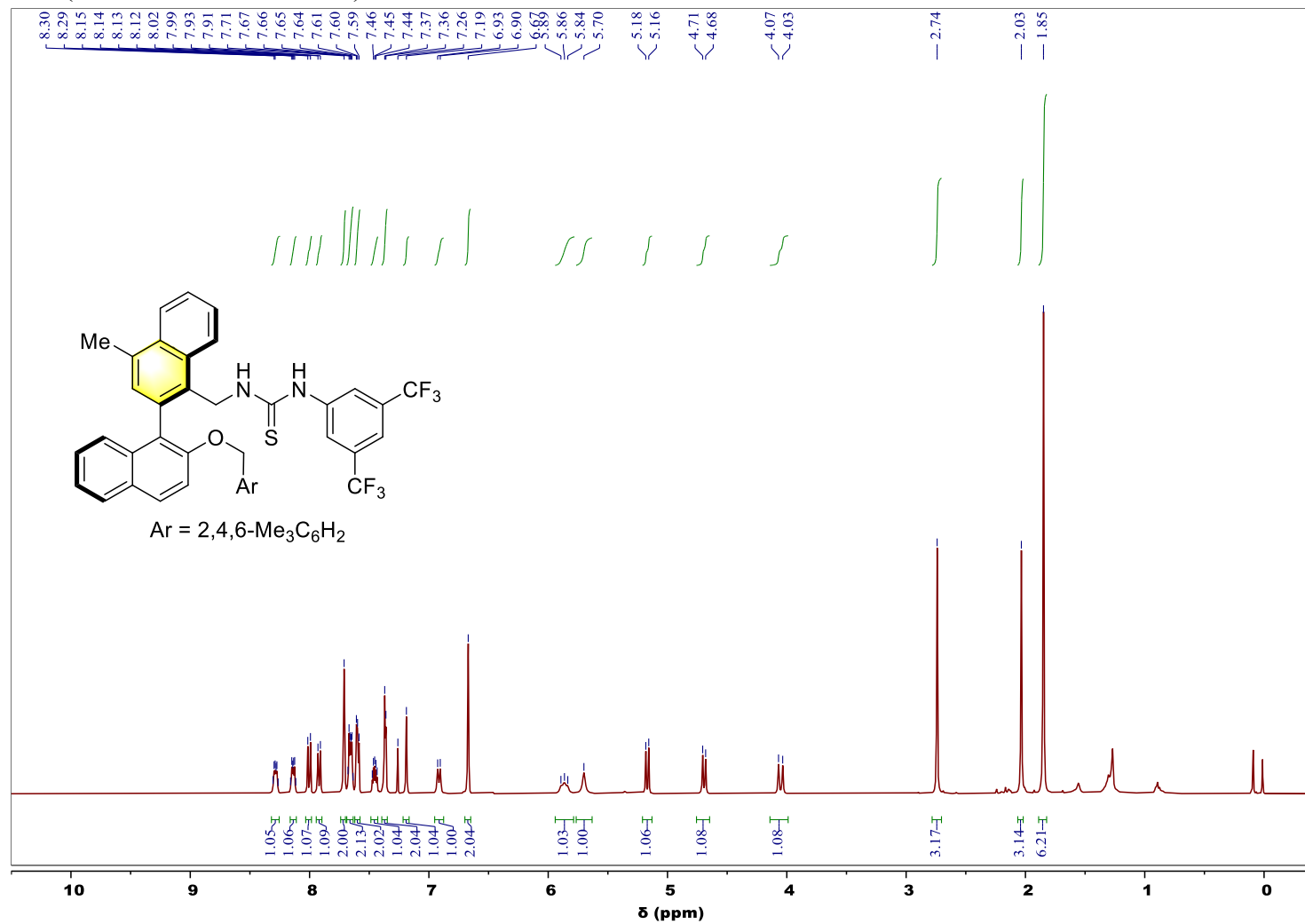
^1H NMR-spectrum (400 MHz, Chloroform- d) of **7**



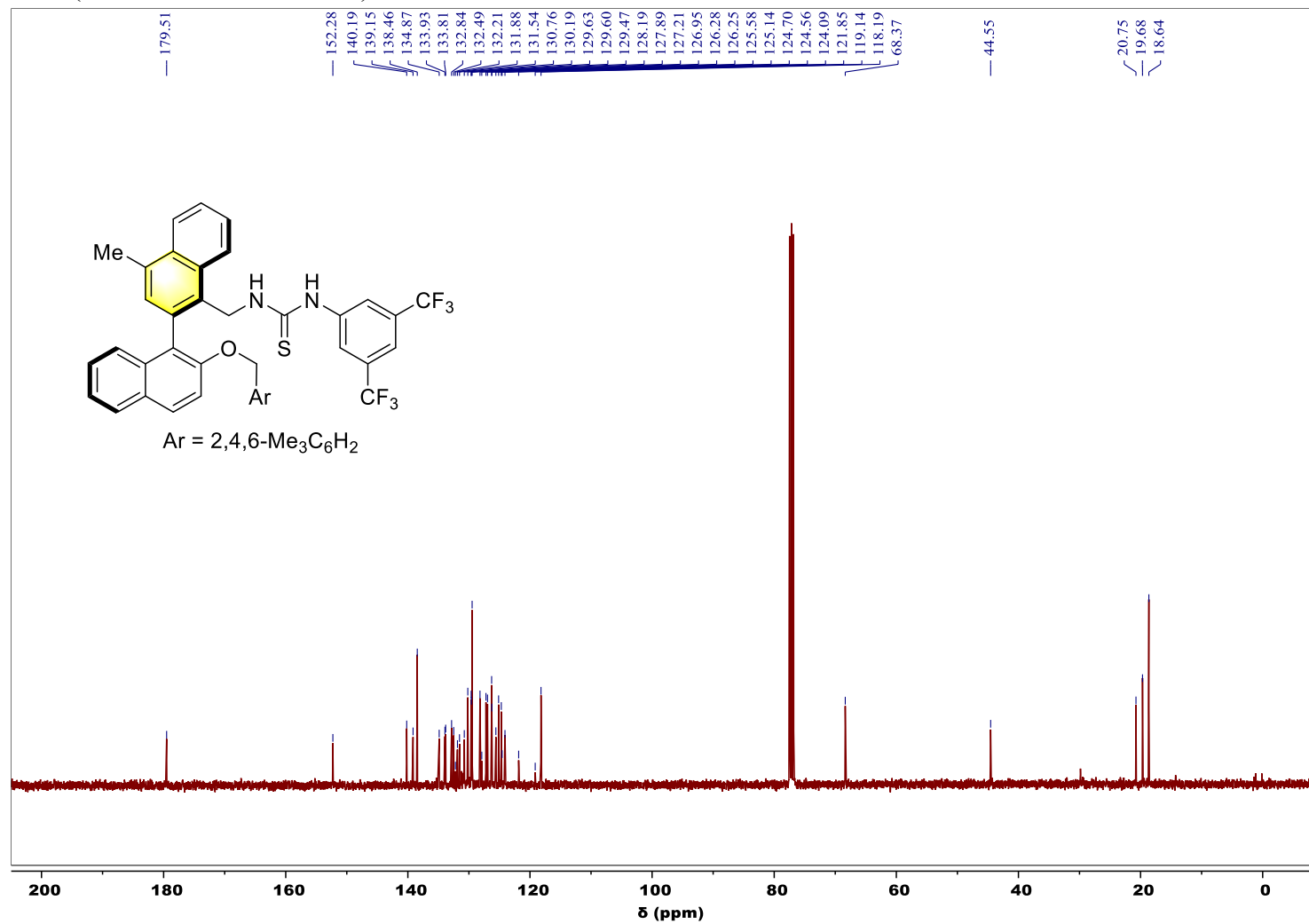
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of 7



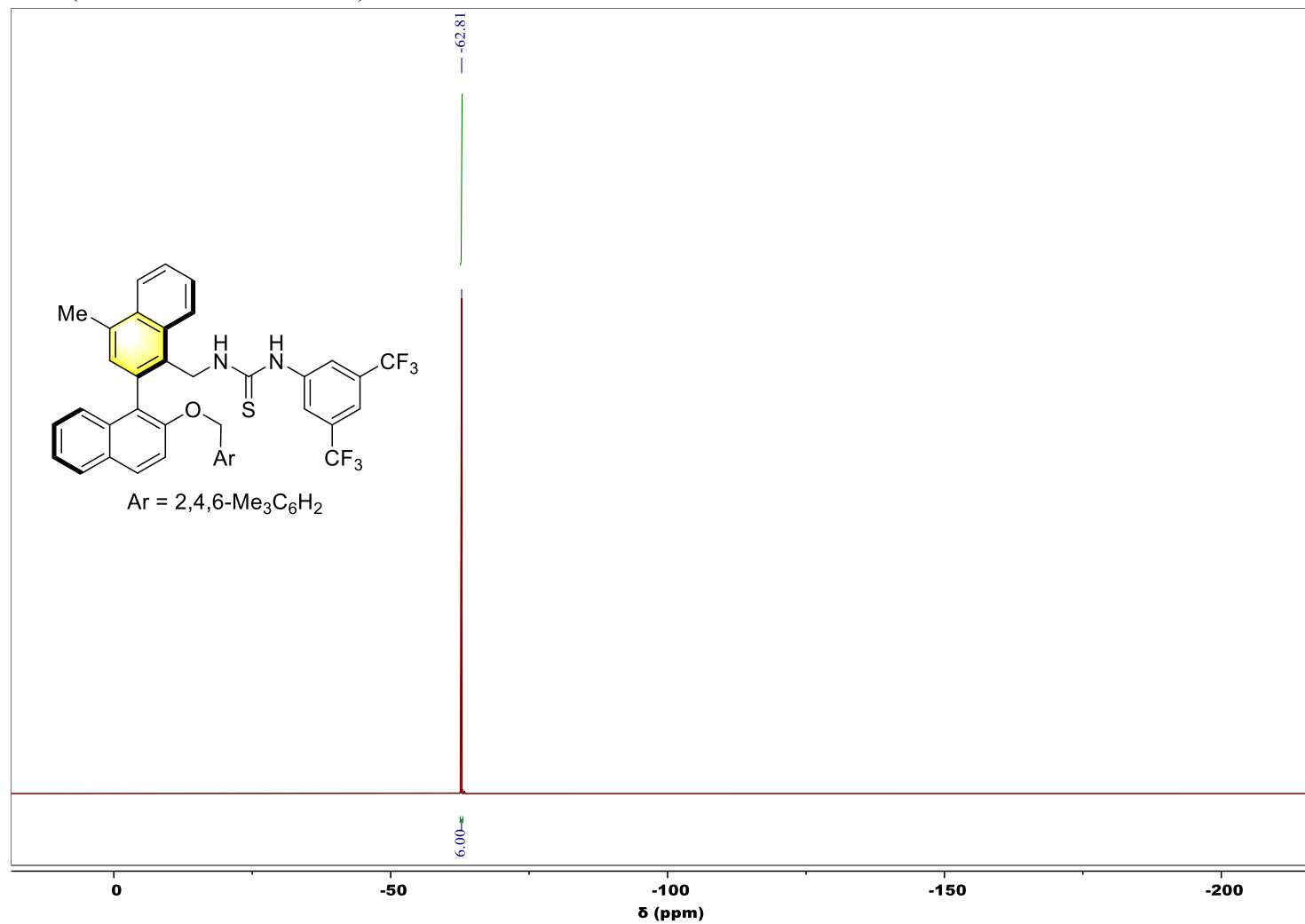
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **8**



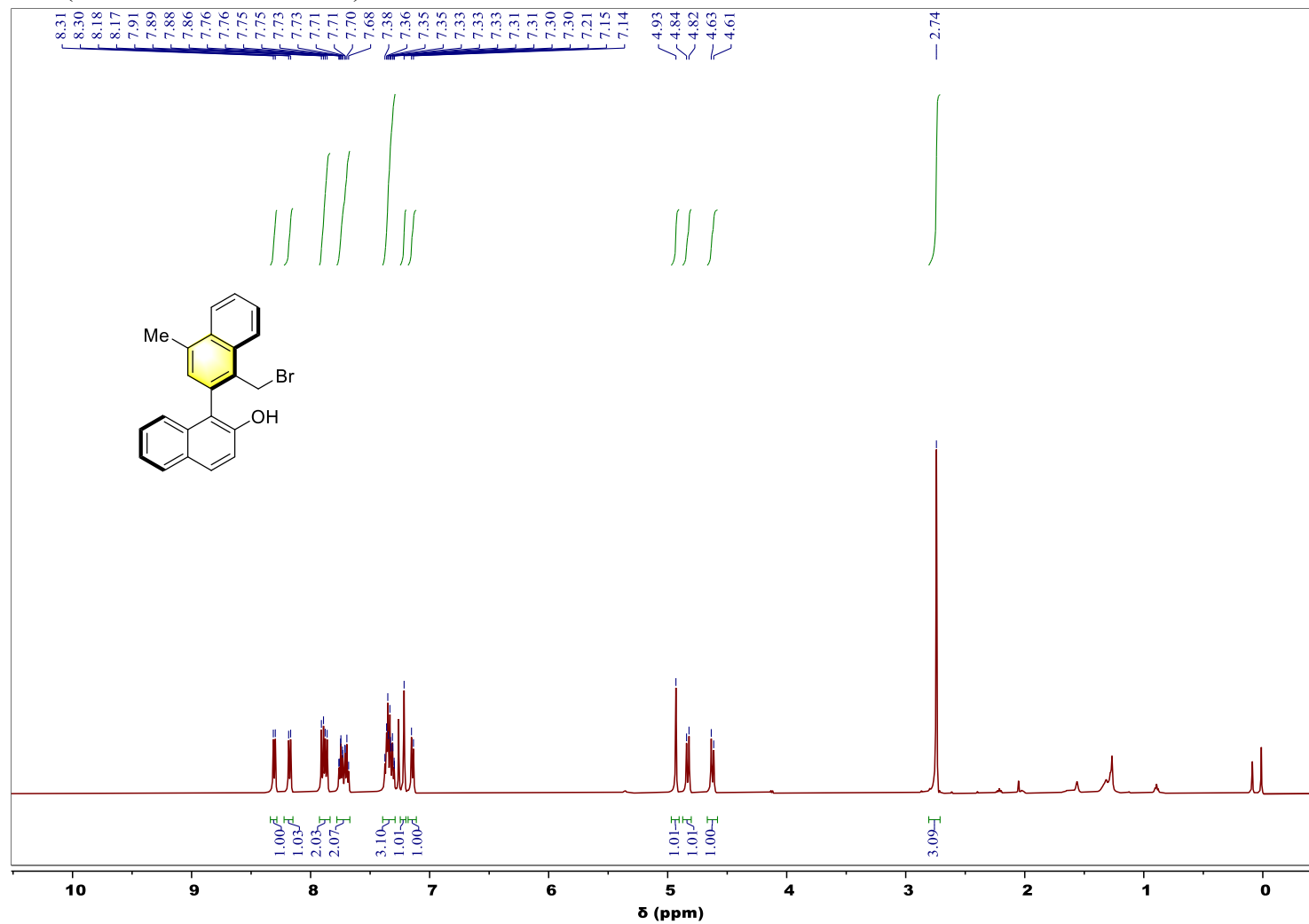
^{13}C NMR-spectrum (101 MHz, Chloroform- d) of **8**



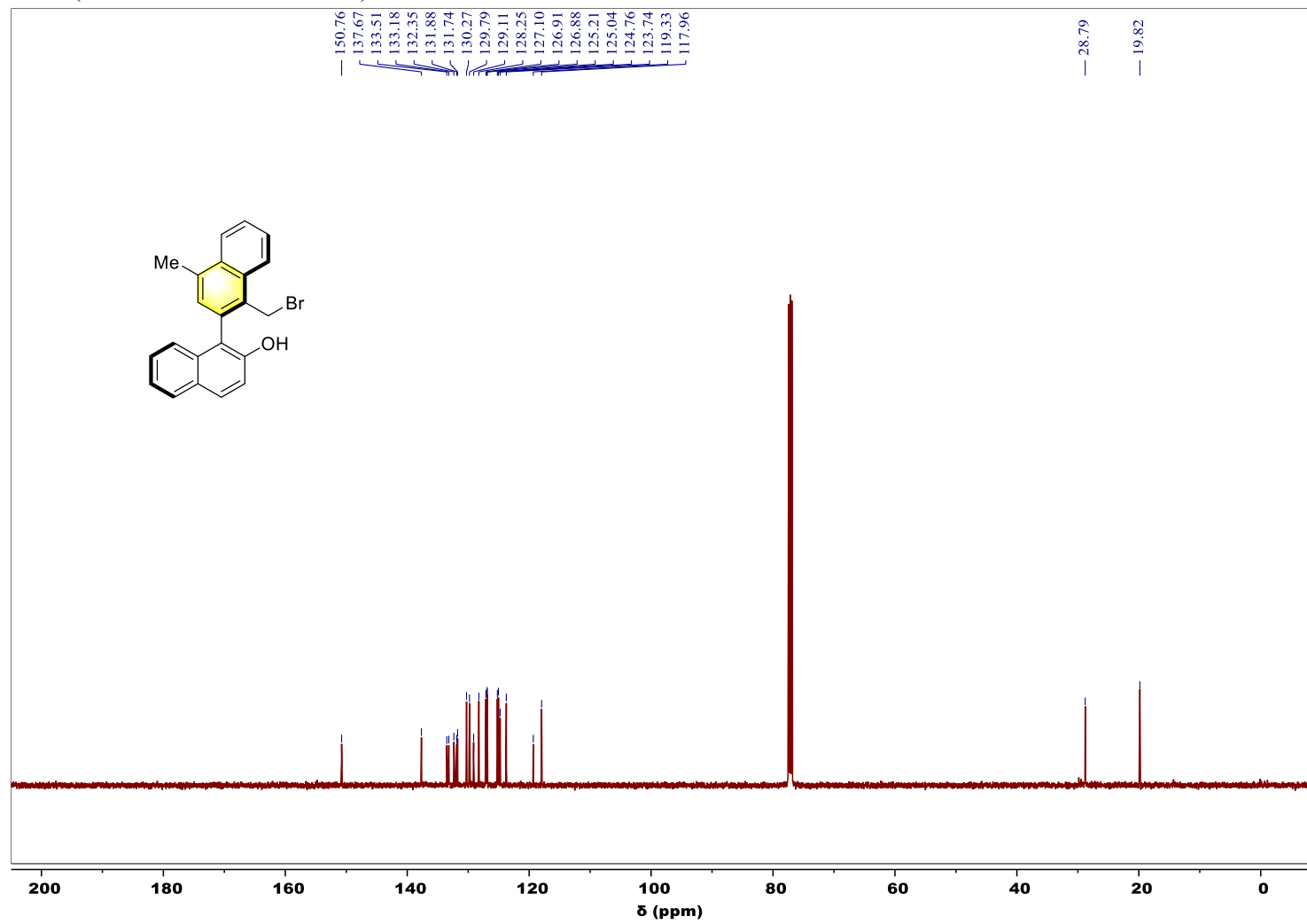
^{19}F NMR-spectrum (376 MHz, Chloroform-*d*) of **8**



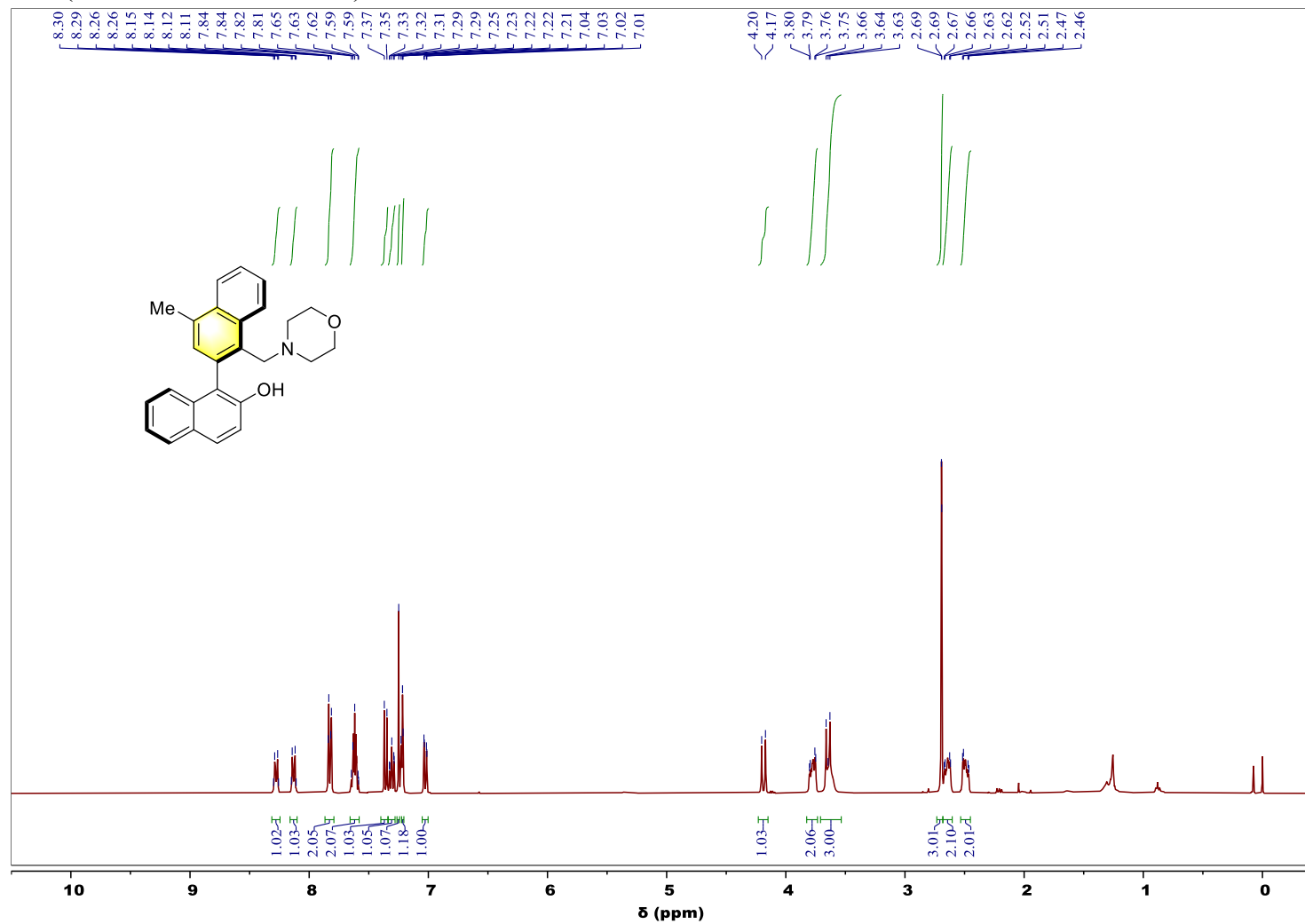
^1H NMR-spectrum (500 MHz, Chloroform- d) of **9**



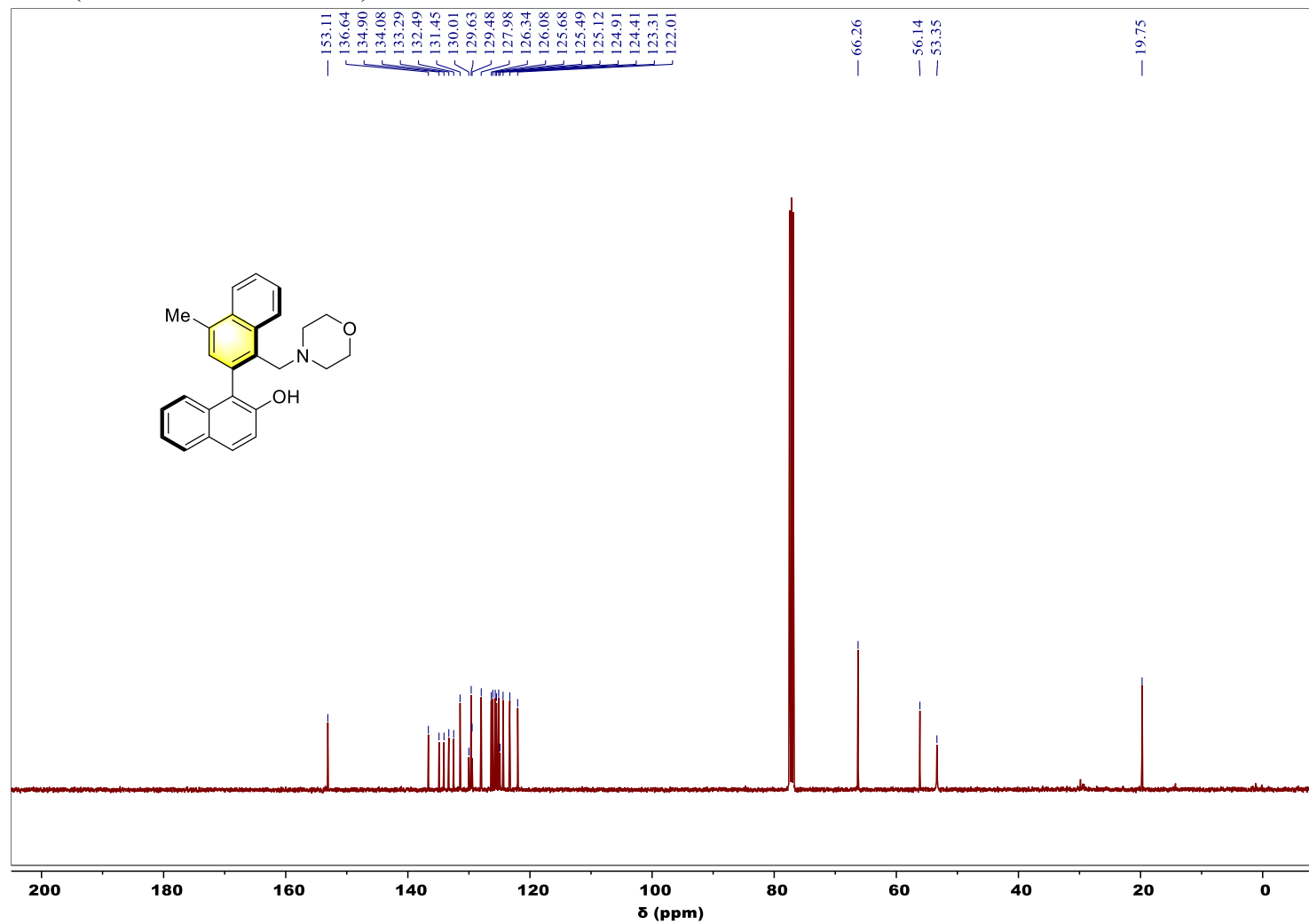
^{13}C NMR-spectrum (126 MHz, Chloroform-*d*) of **9**



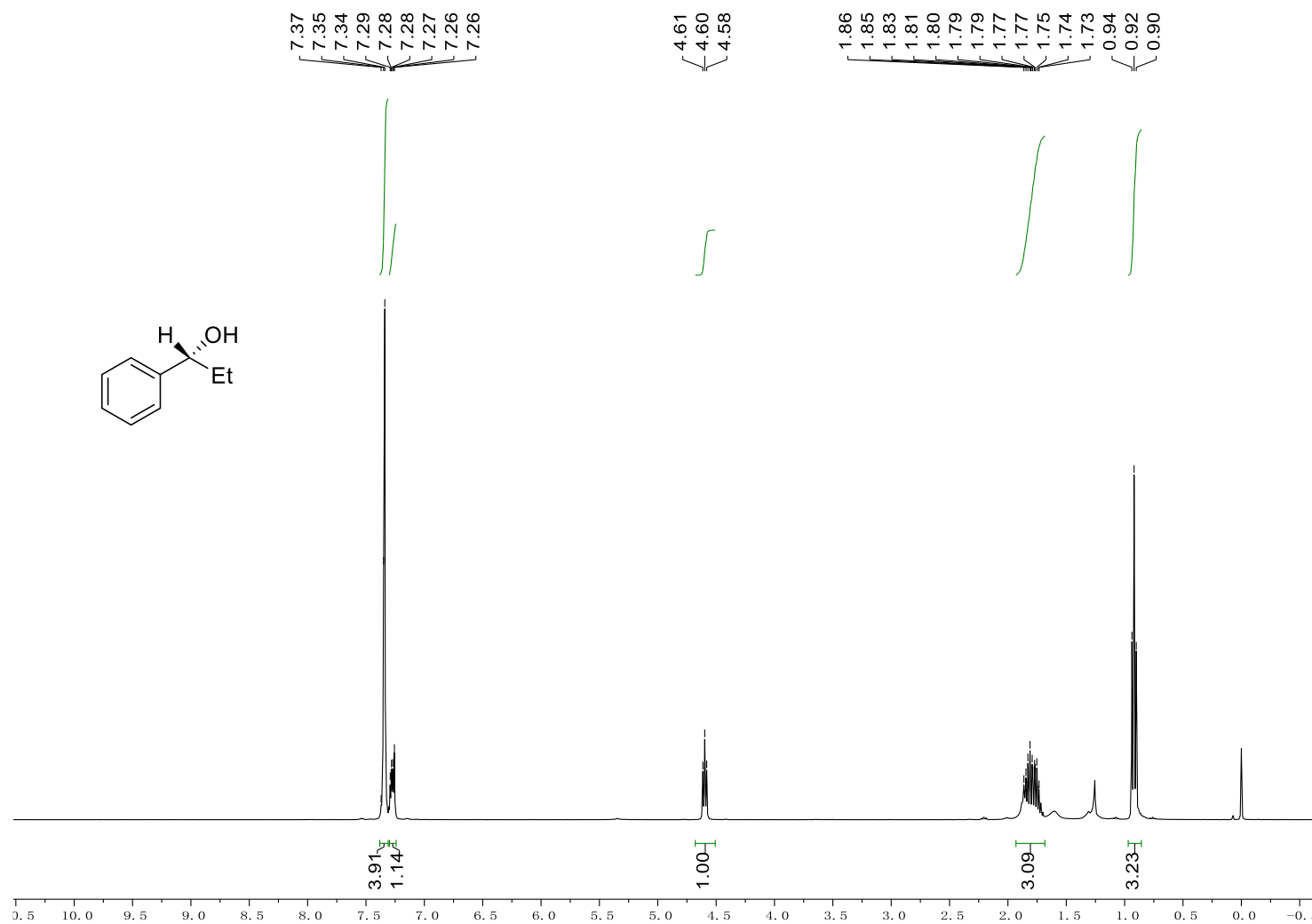
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **10**



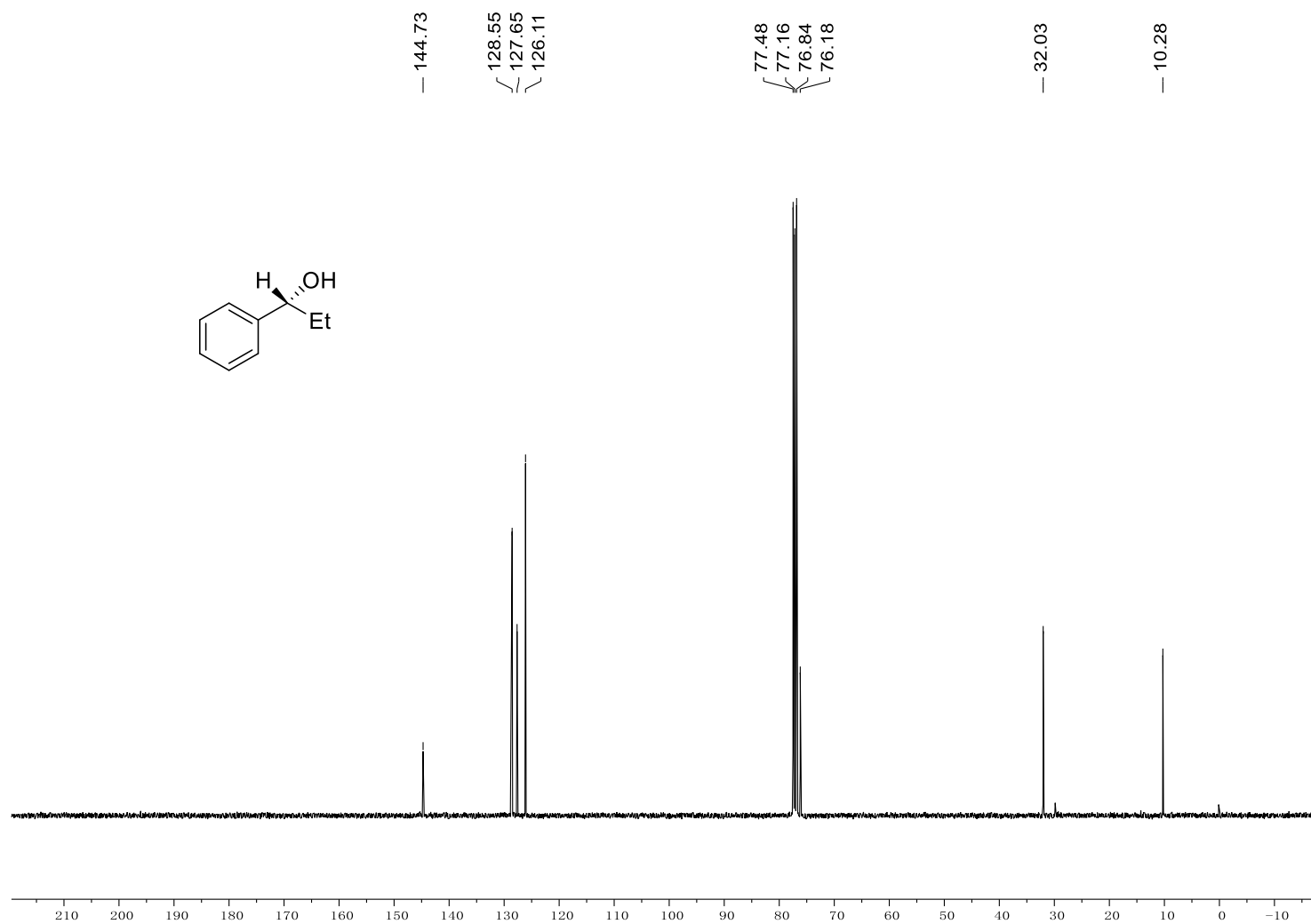
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **10**



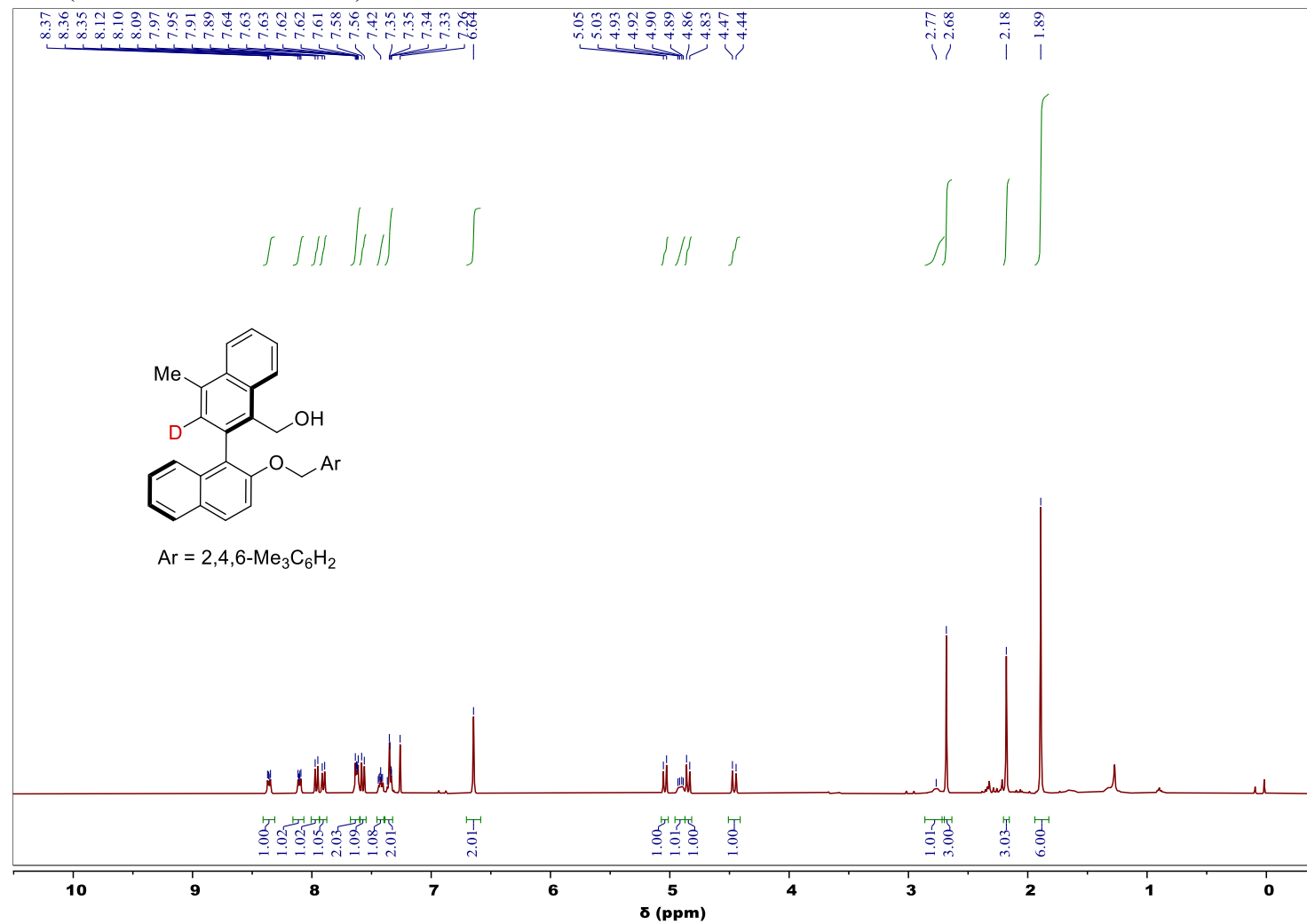
^1H NMR-spectrum (400 MHz, Chloroform-*d*) of **11**



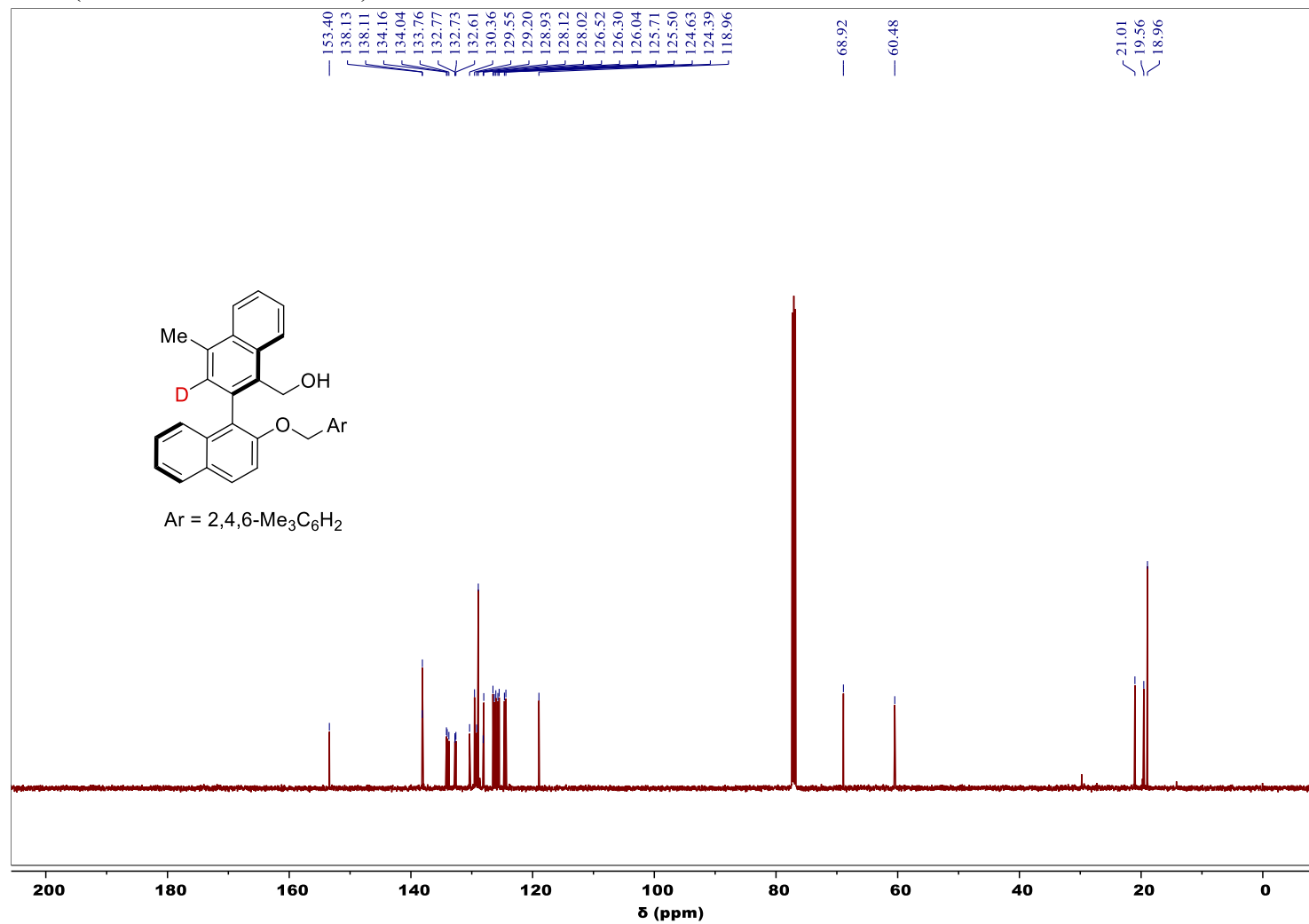
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of **11**



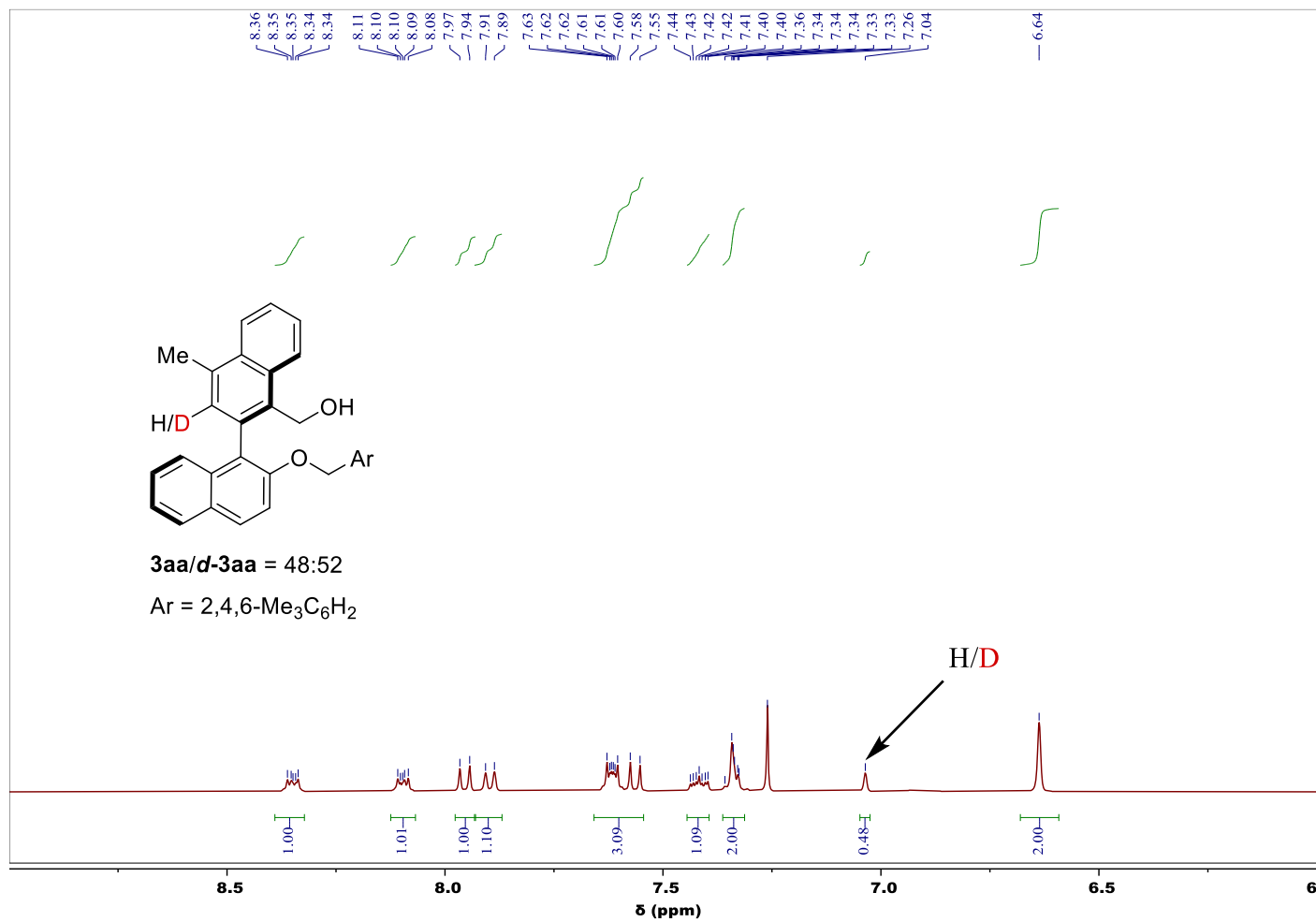
^1H NMR-spectrum (500 MHz, Chloroform-*d*) of **d-3aa**



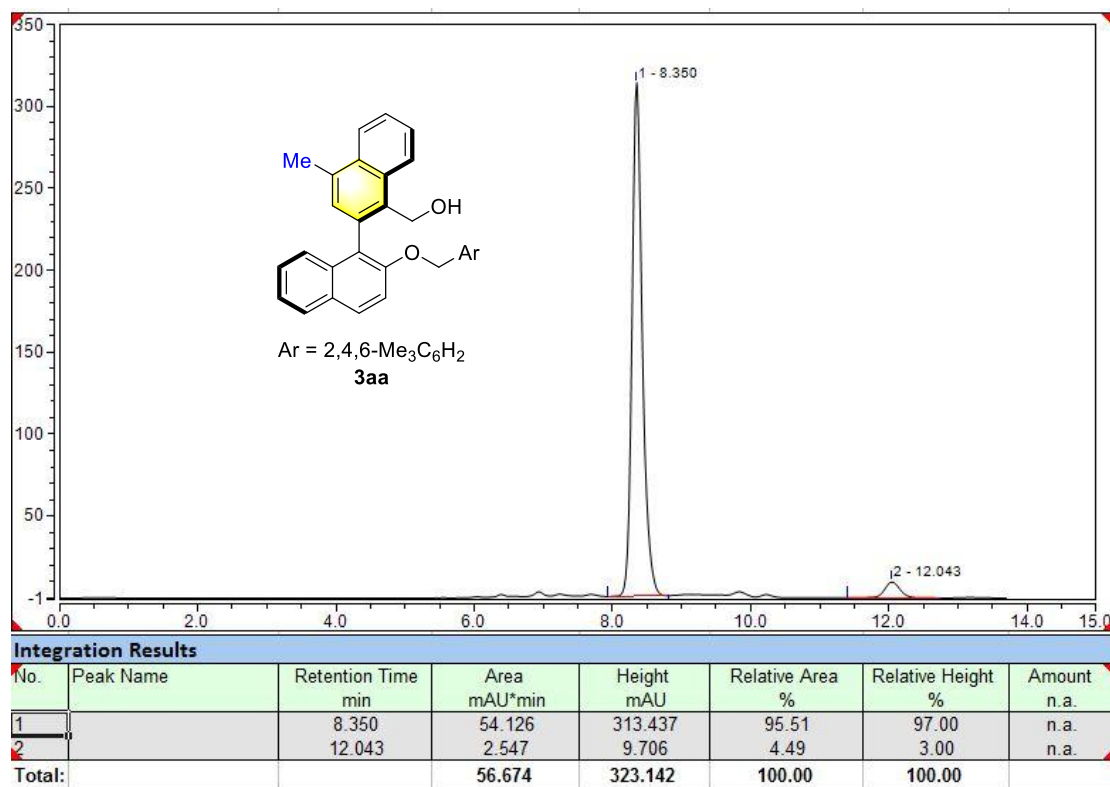
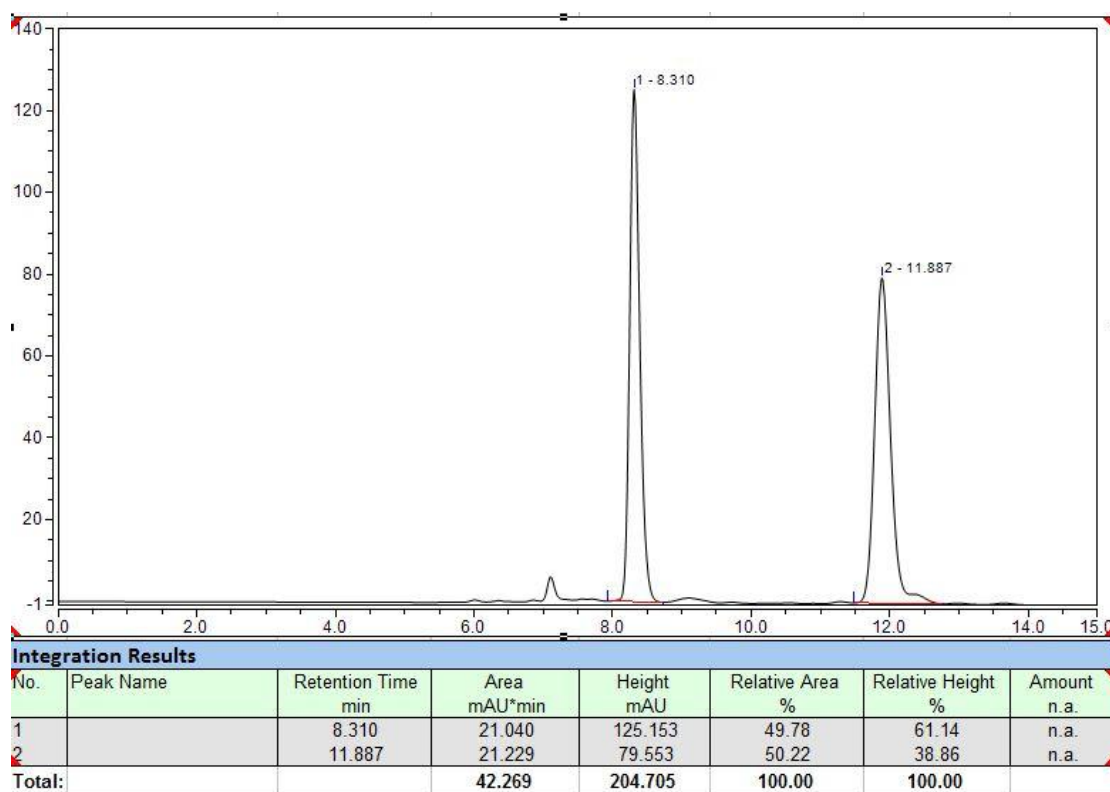
^{13}C NMR-spectrum (101 MHz, Chloroform-*d*) of ***d*-3aa**



^1H NMR-spectrum (400 MHz, Chloroform-*d*) of the mixture of **3aa**/*d*-**3aa**

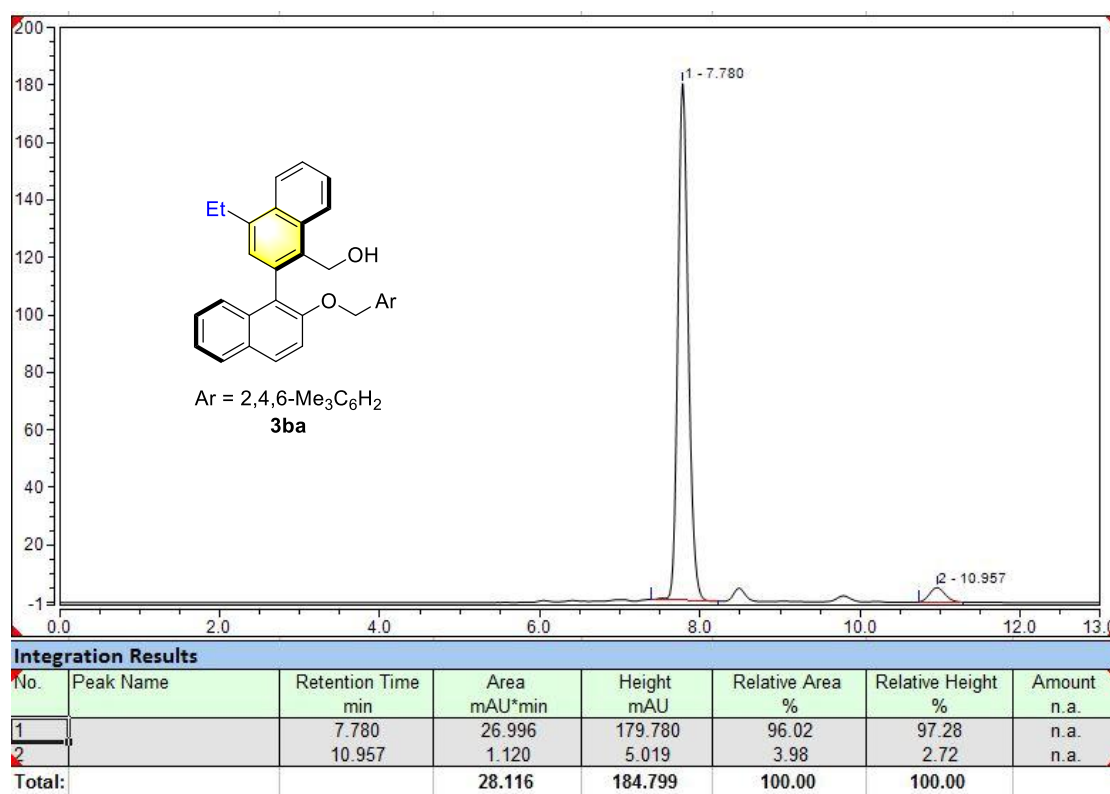
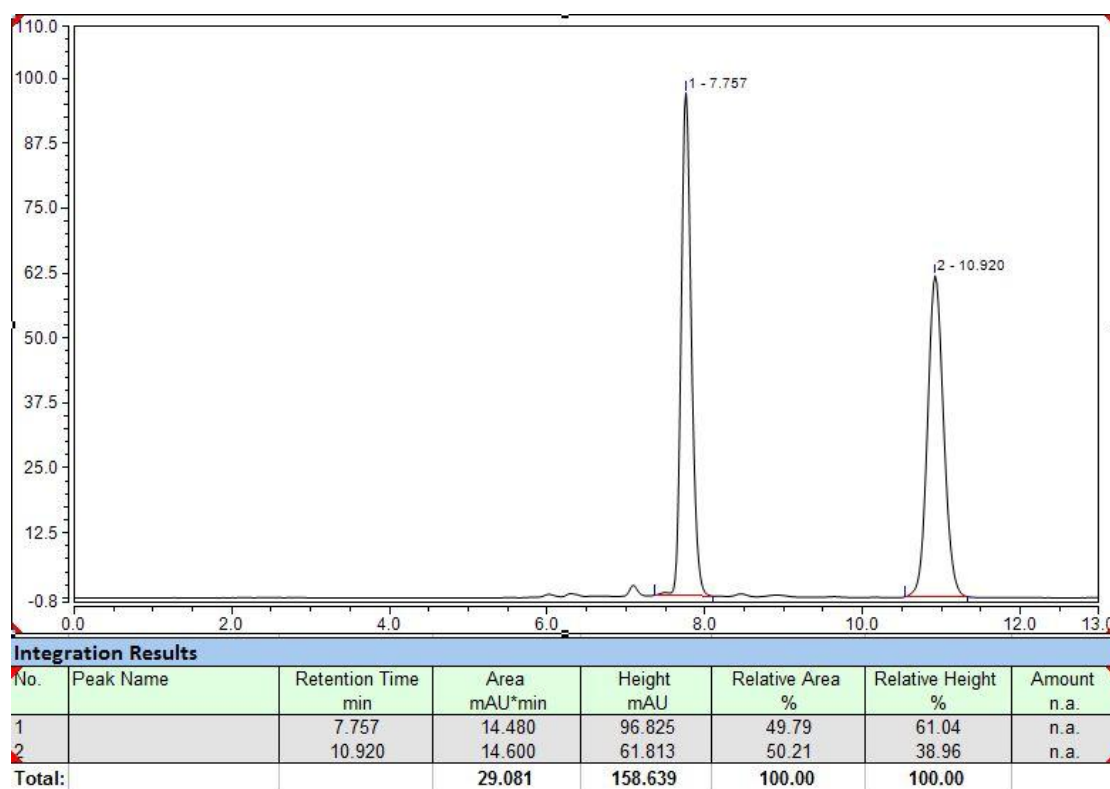


X. HPLC Chromatograms



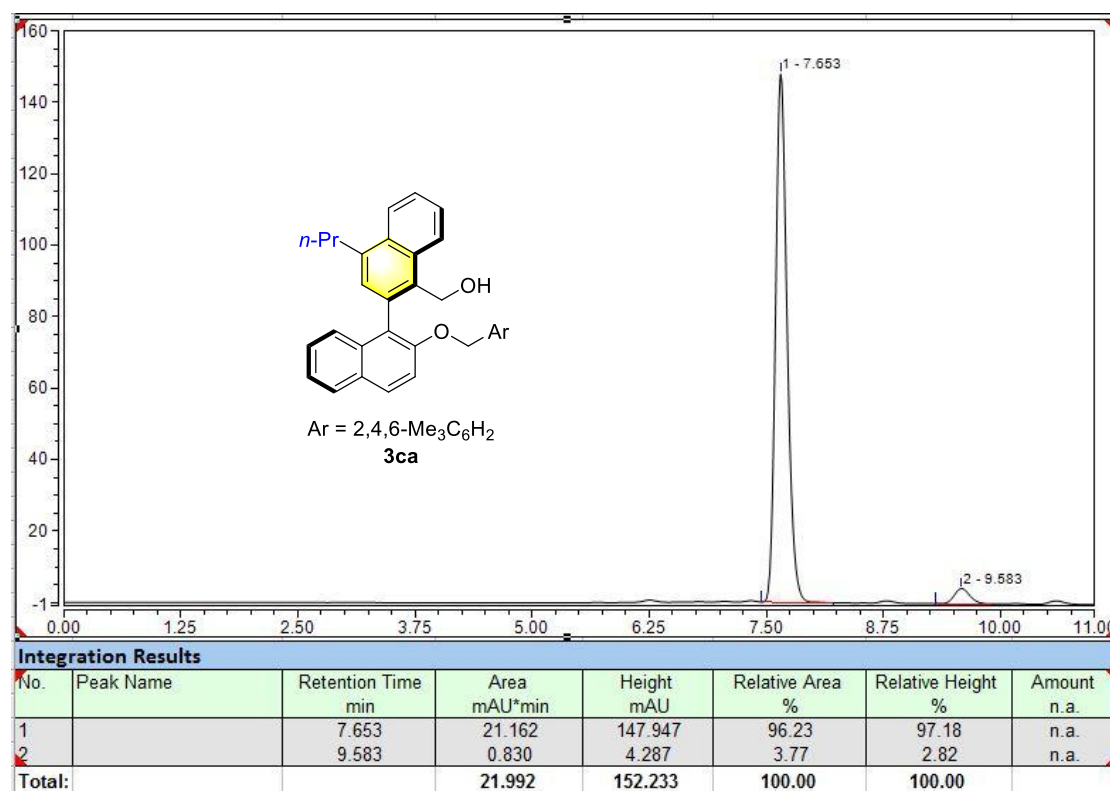
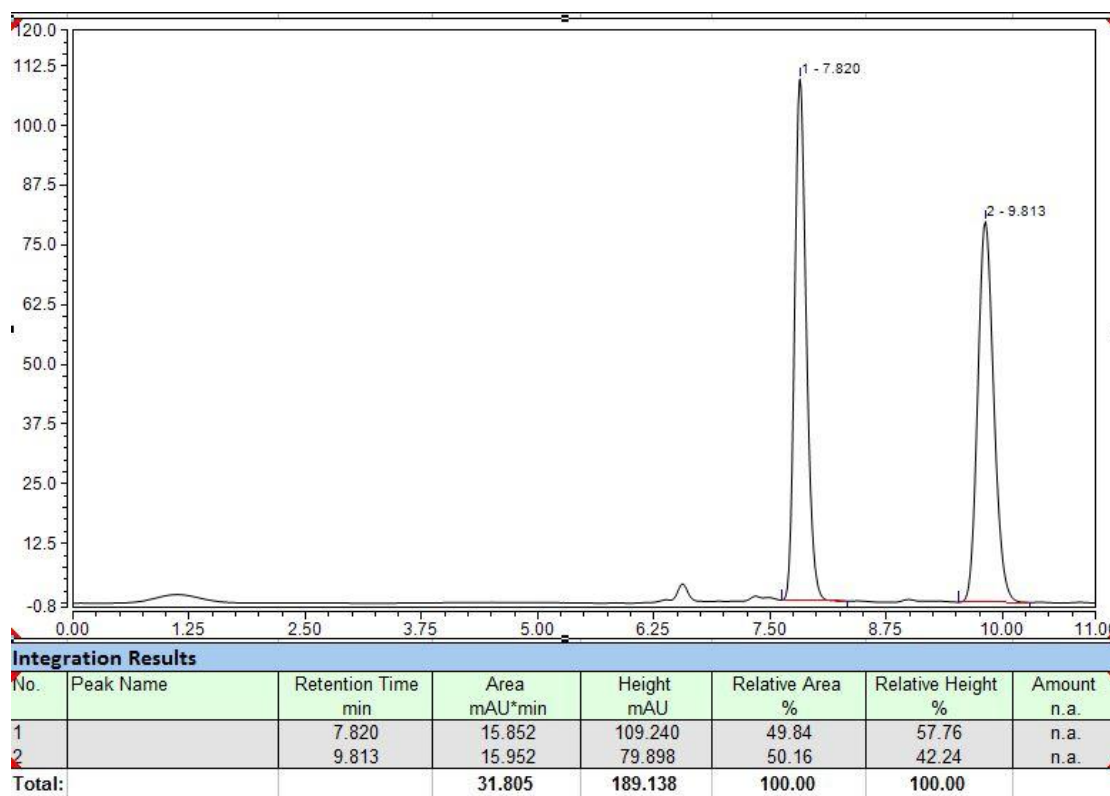
HPLC (Chiralpak AD-H): t_R = 8.4 (major), 12.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



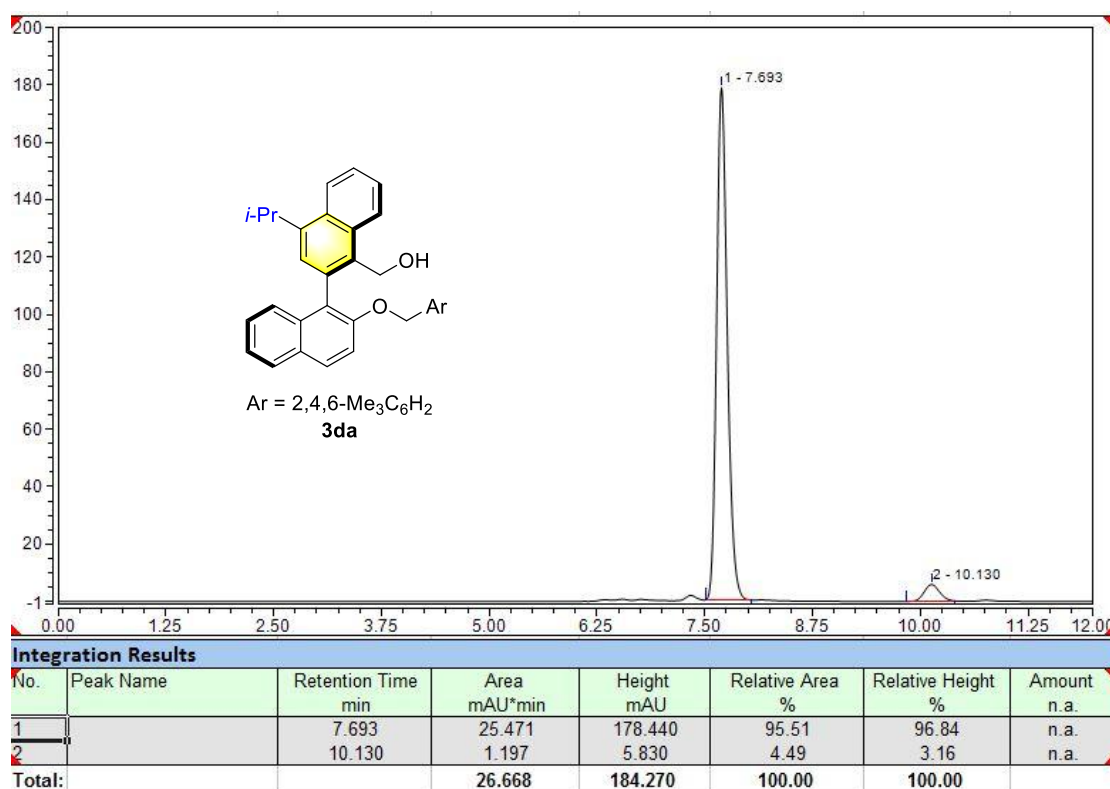
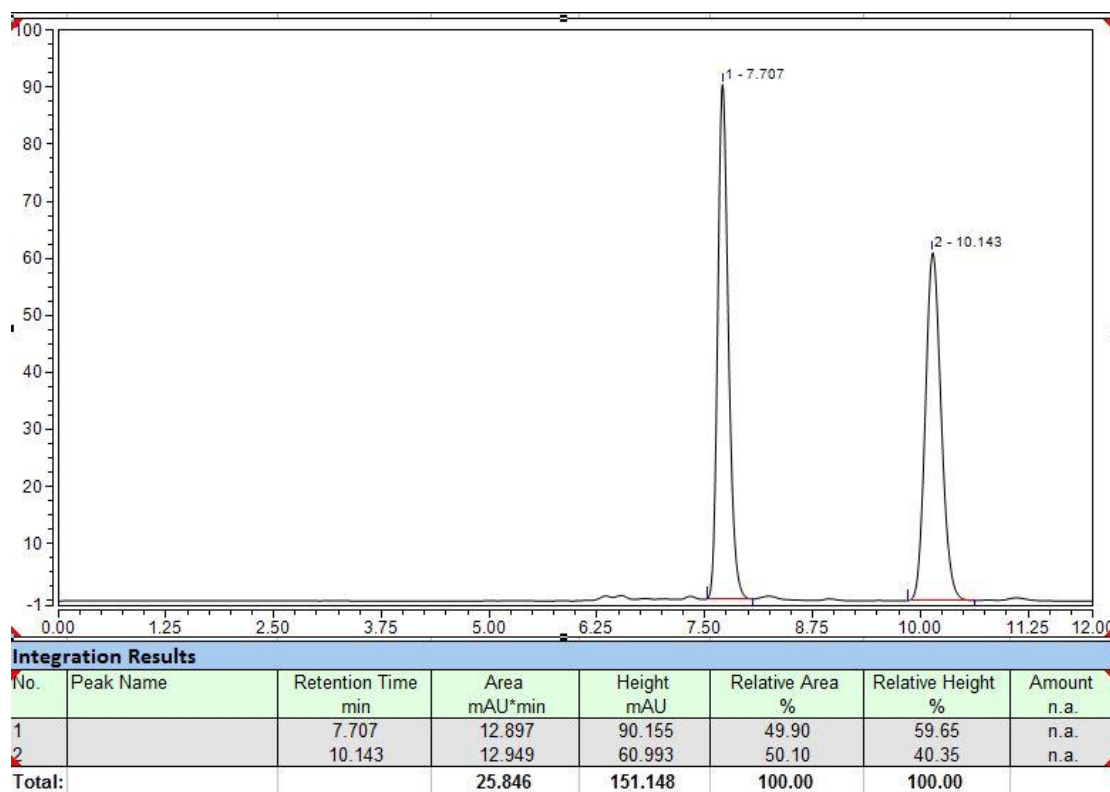
HPLC (Chiralpak AD-H): t_R = 7.8 (major), 11.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



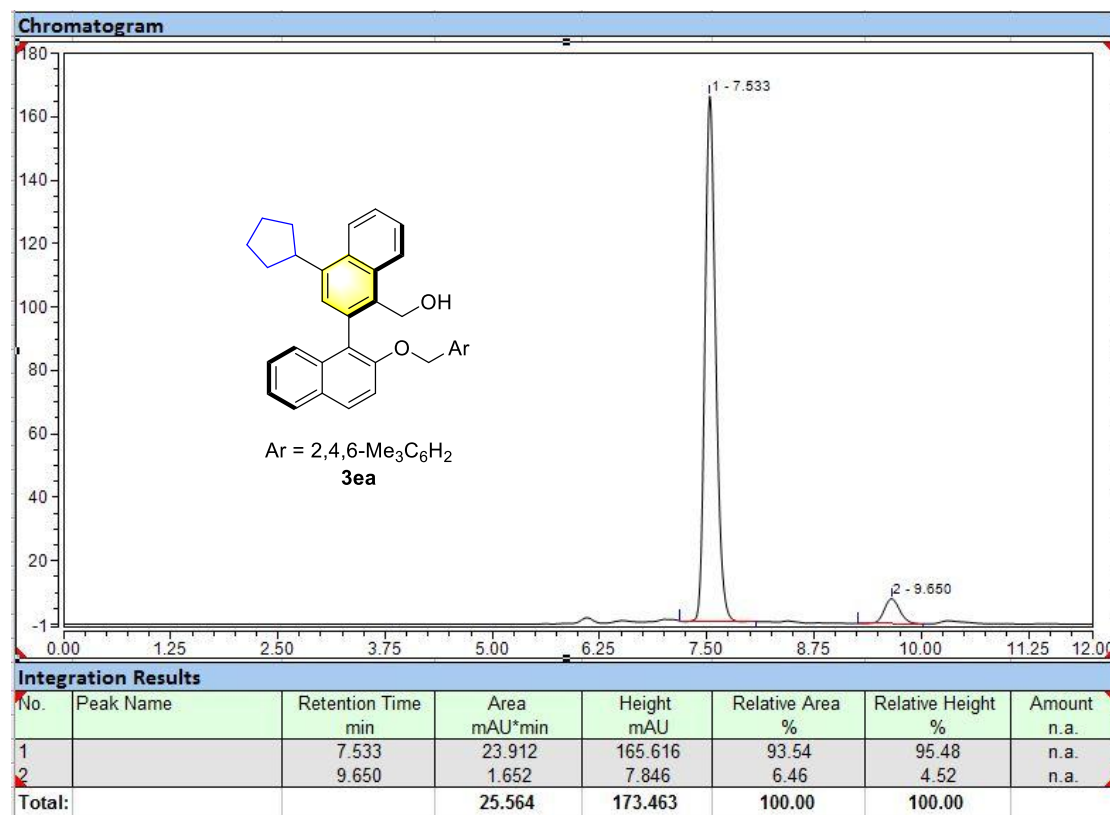
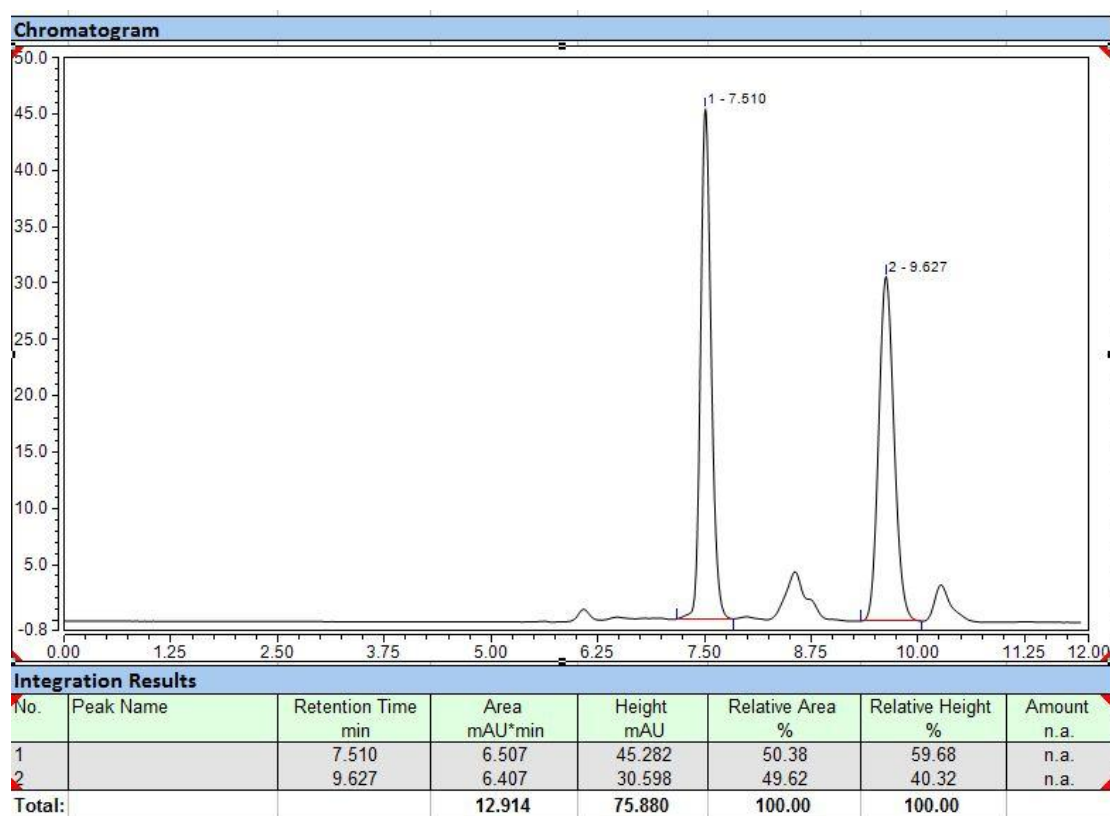
HPLC (Chiralpak AD-H): t_R = 7.7 (major), 9.6 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



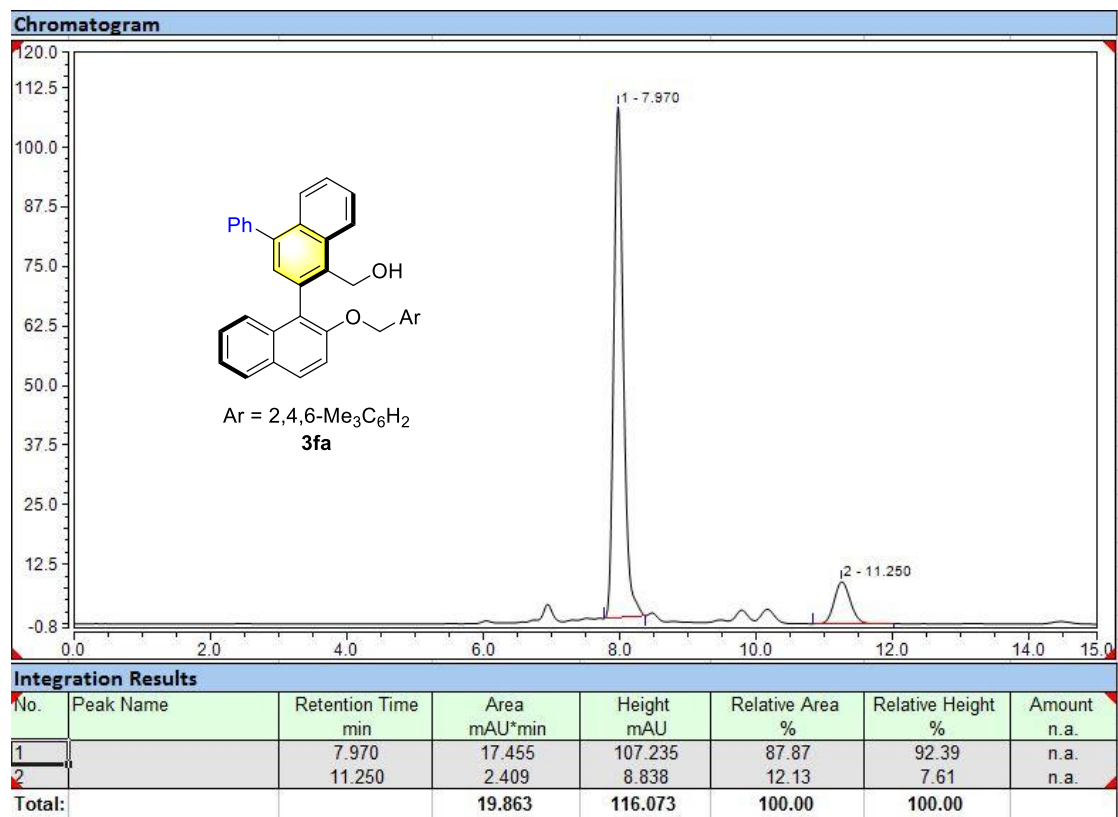
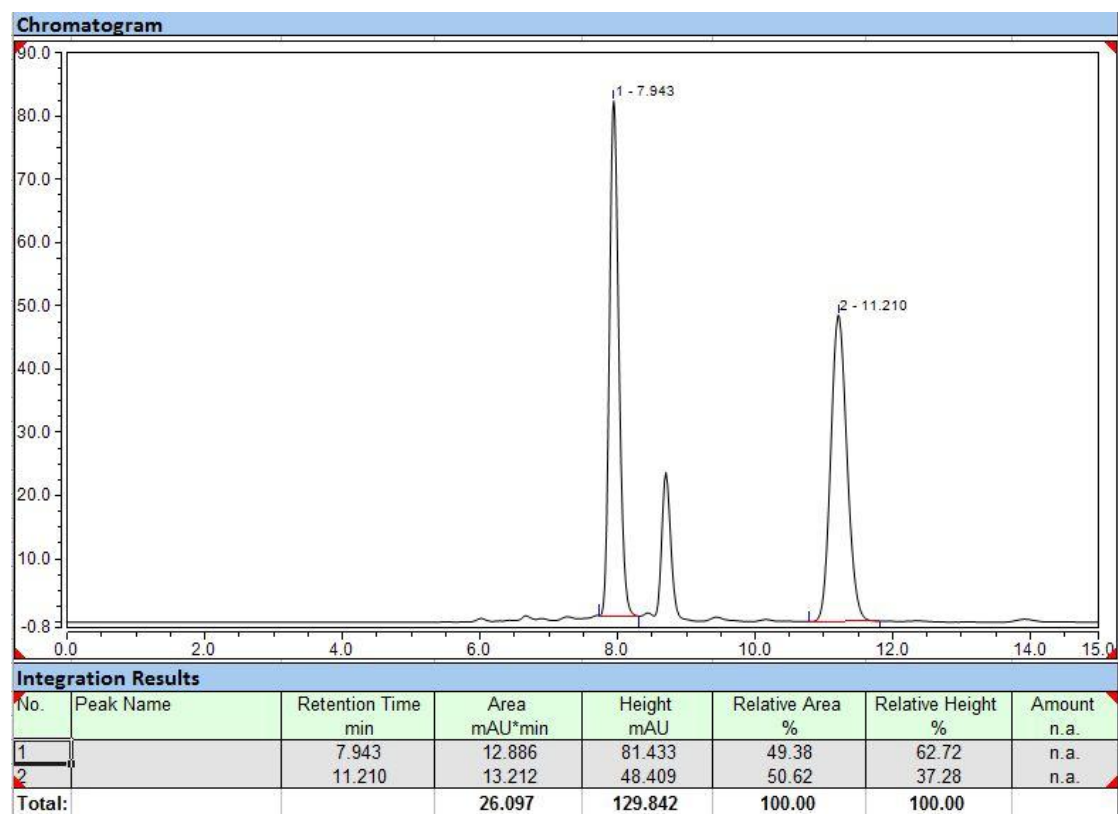
HPLC (Chiralpak AD-H): t_R = 7.7 (major), 10.1 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



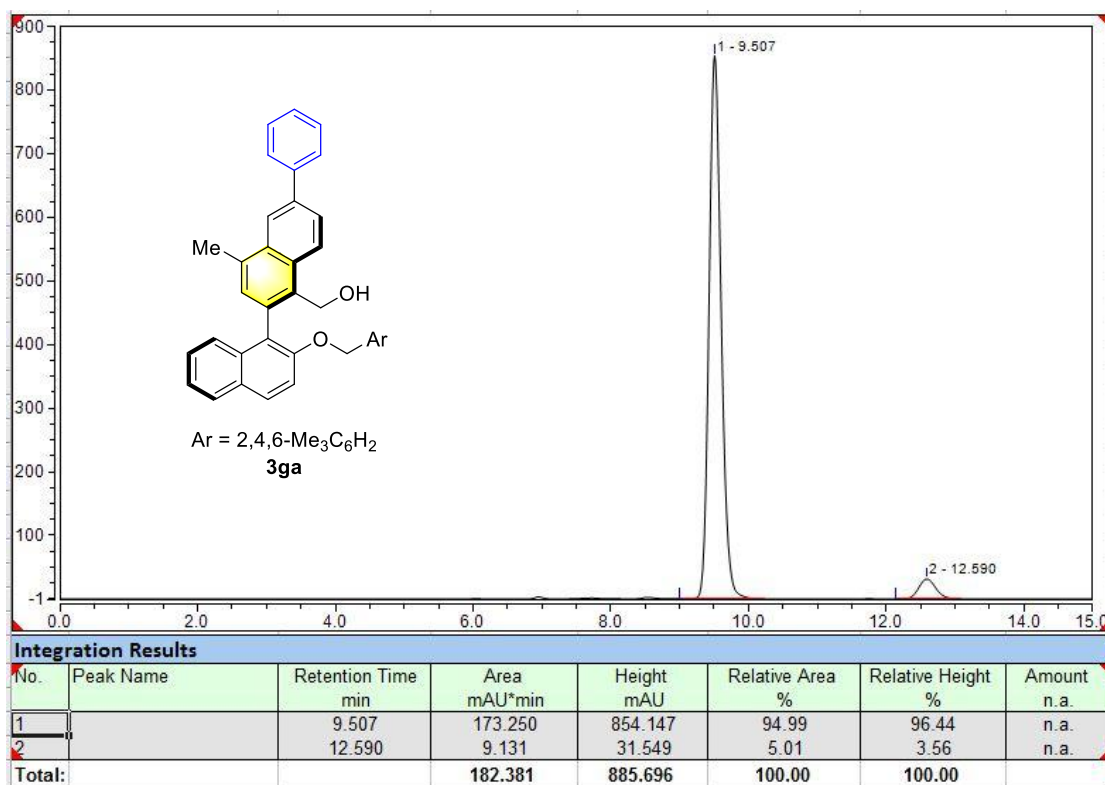
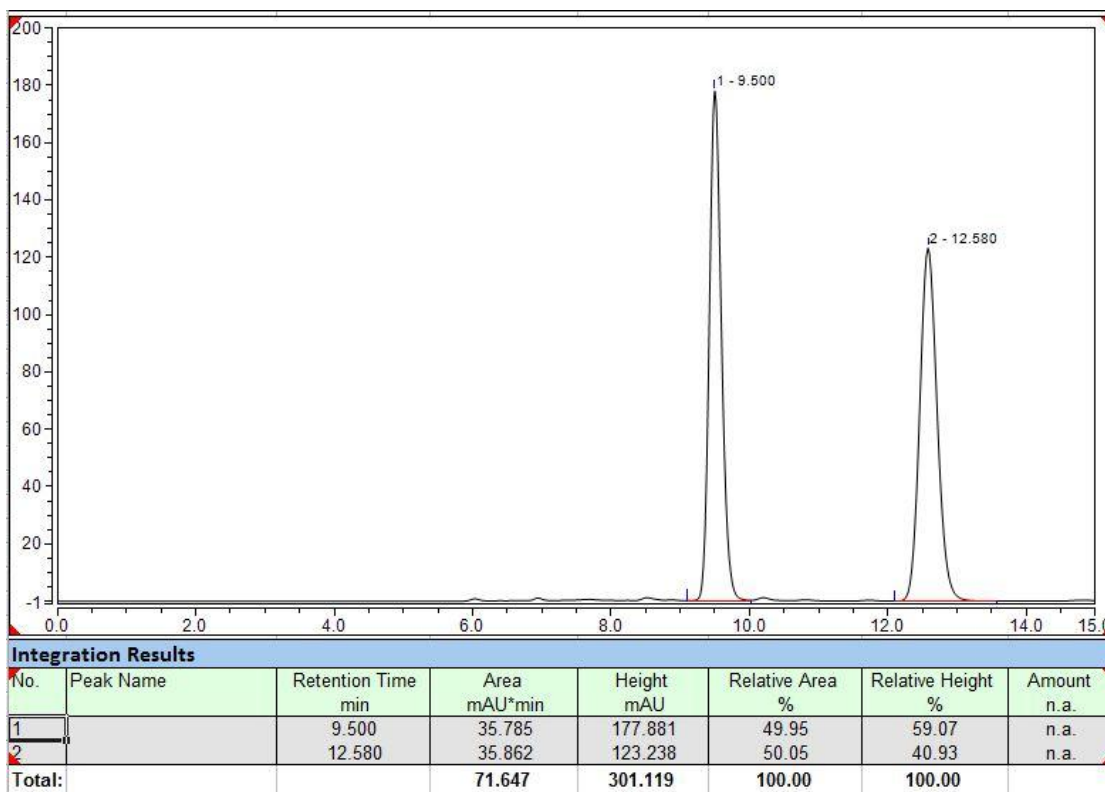
HPLC (Chiralpak AD-H): t_R = 7.5 (major), 9.7 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



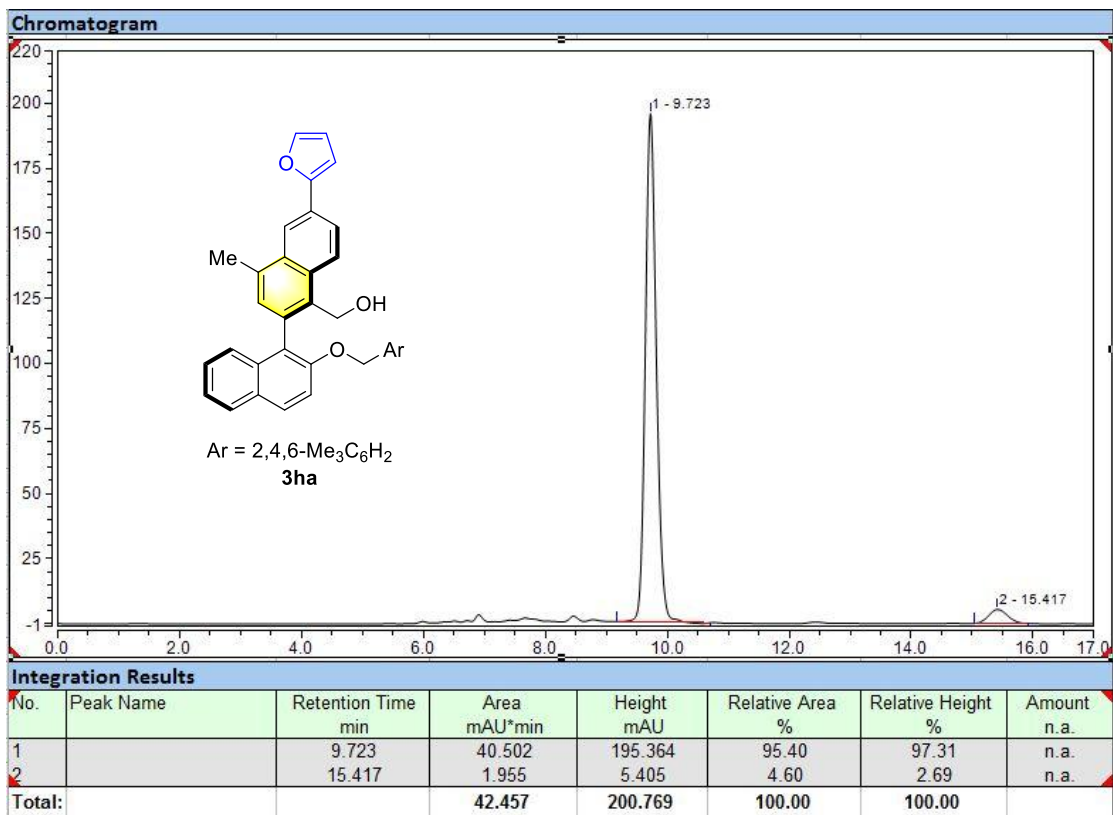
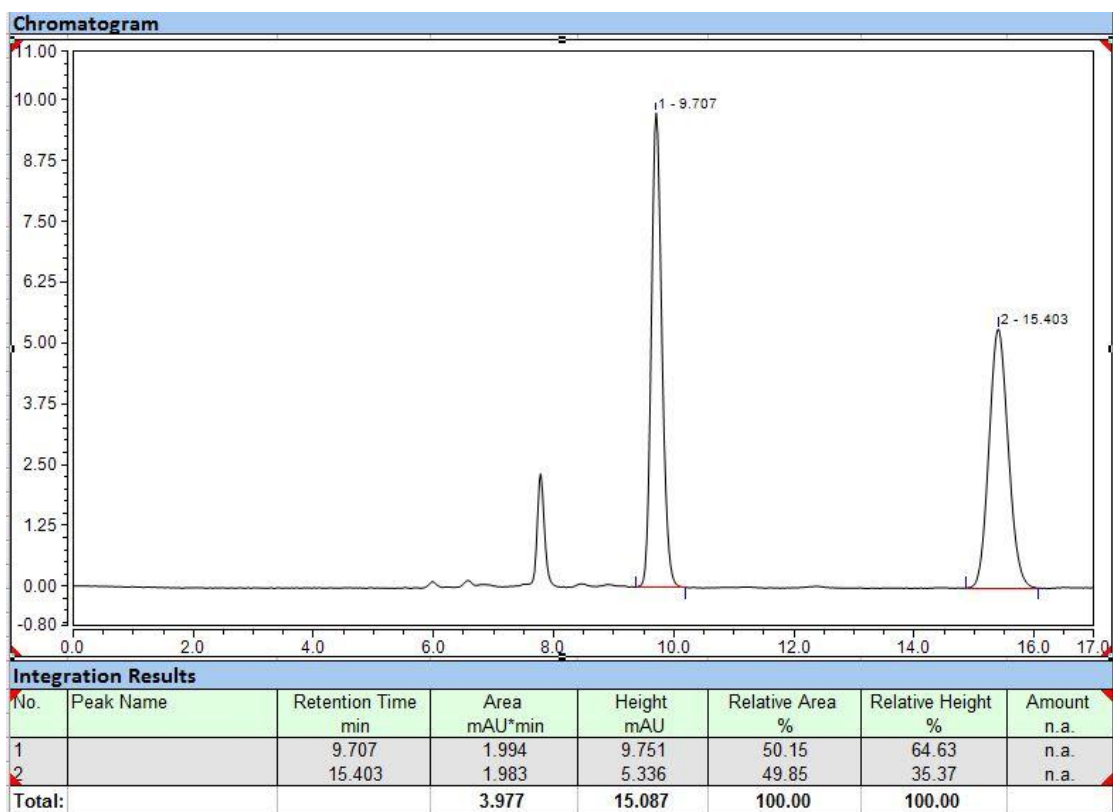
HPLC (Chiralpak AD-H): t_R = 8.0 (major), 11.3 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



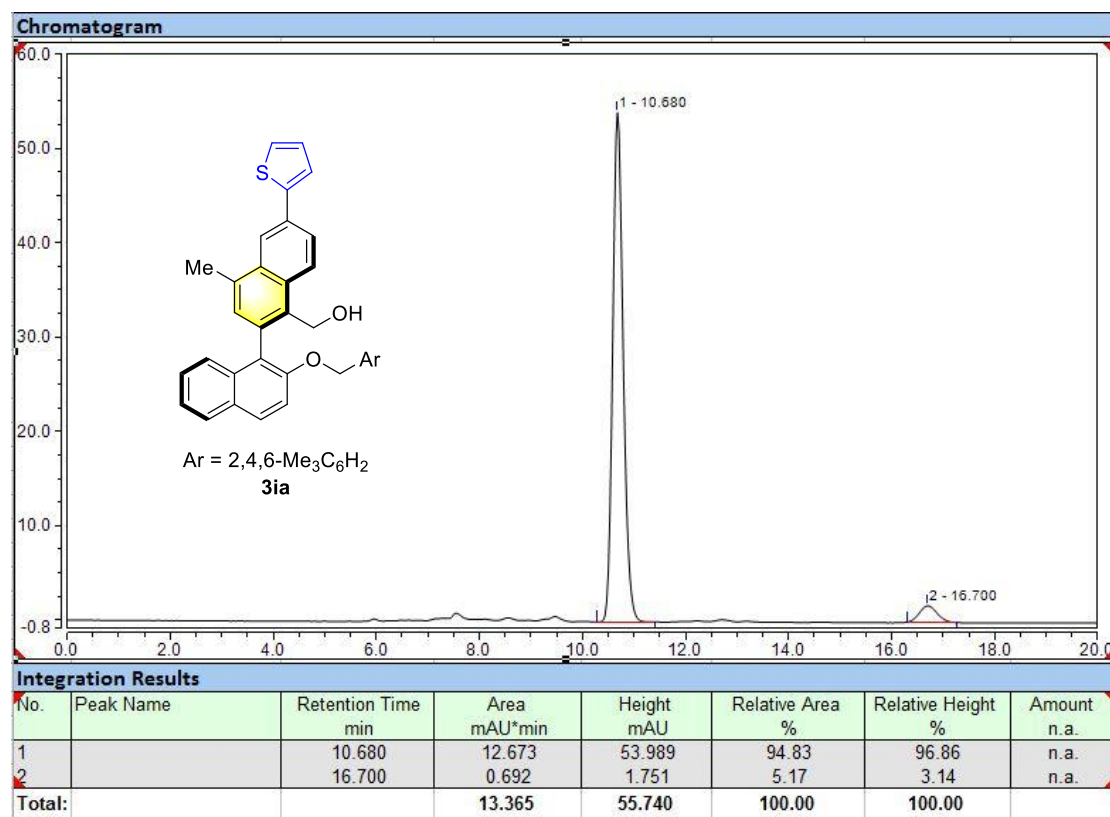
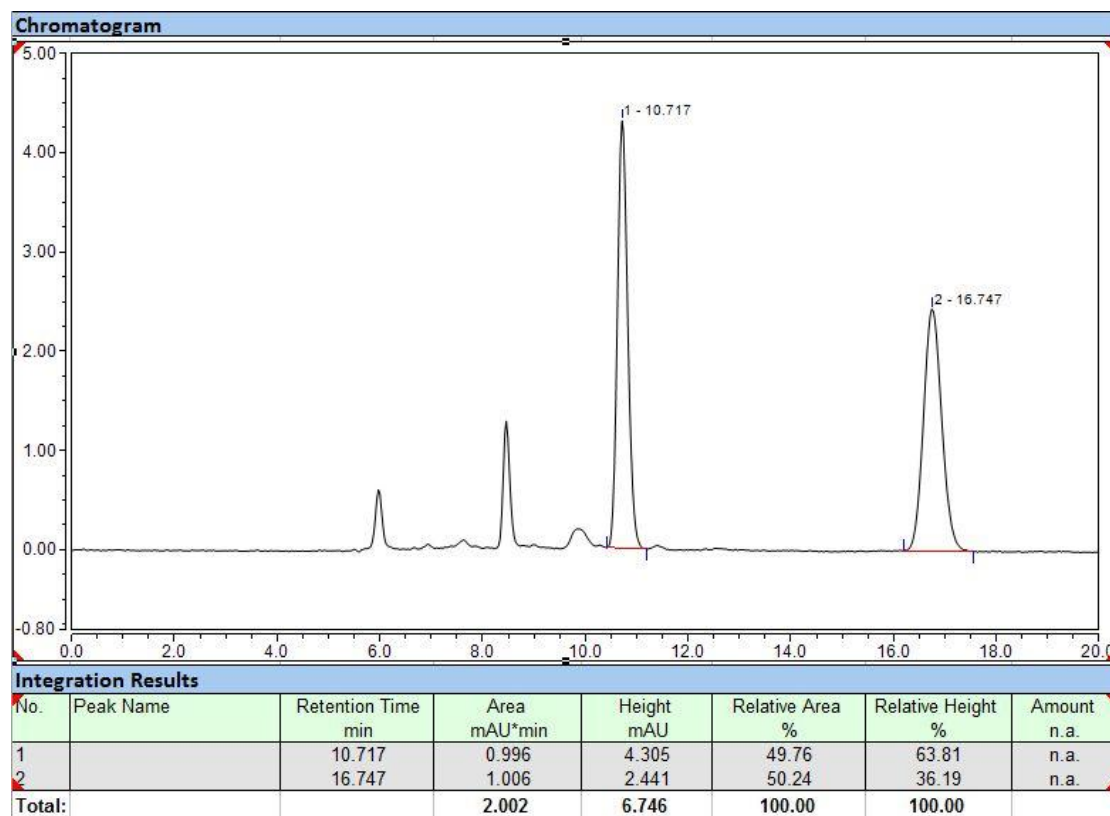
HPLC (Chiralpak AD-H): t_R = 9.5 (major), 12.6 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



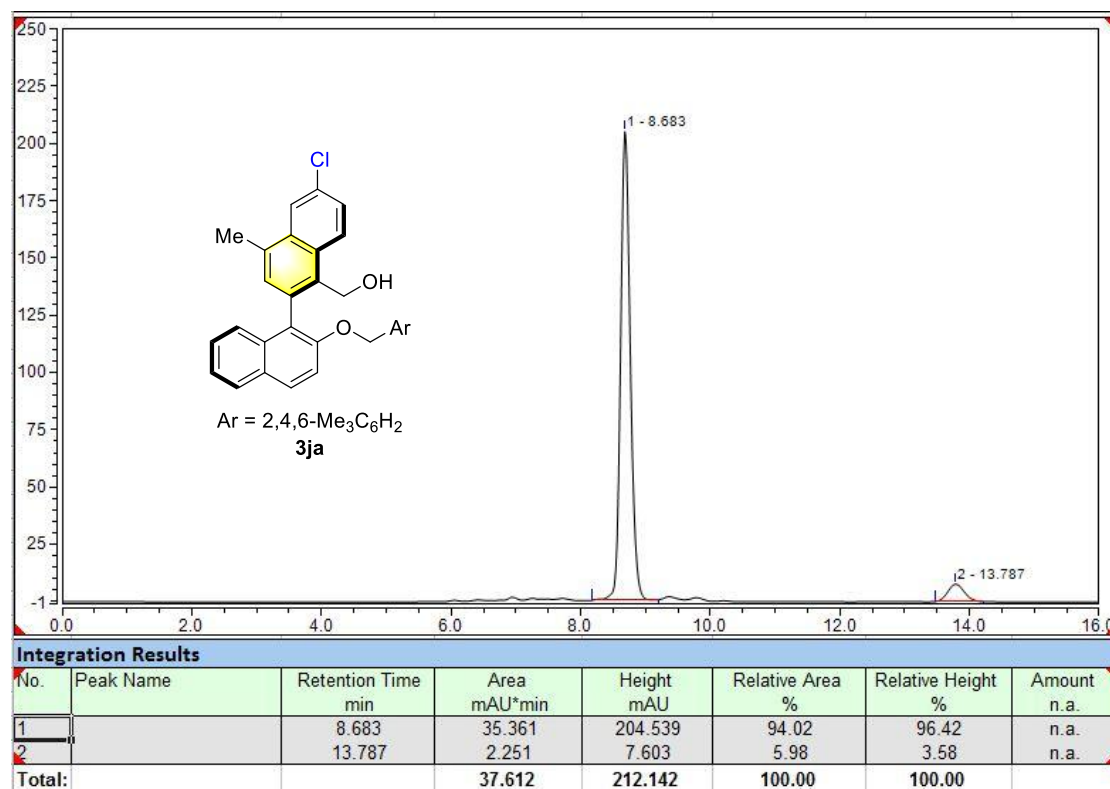
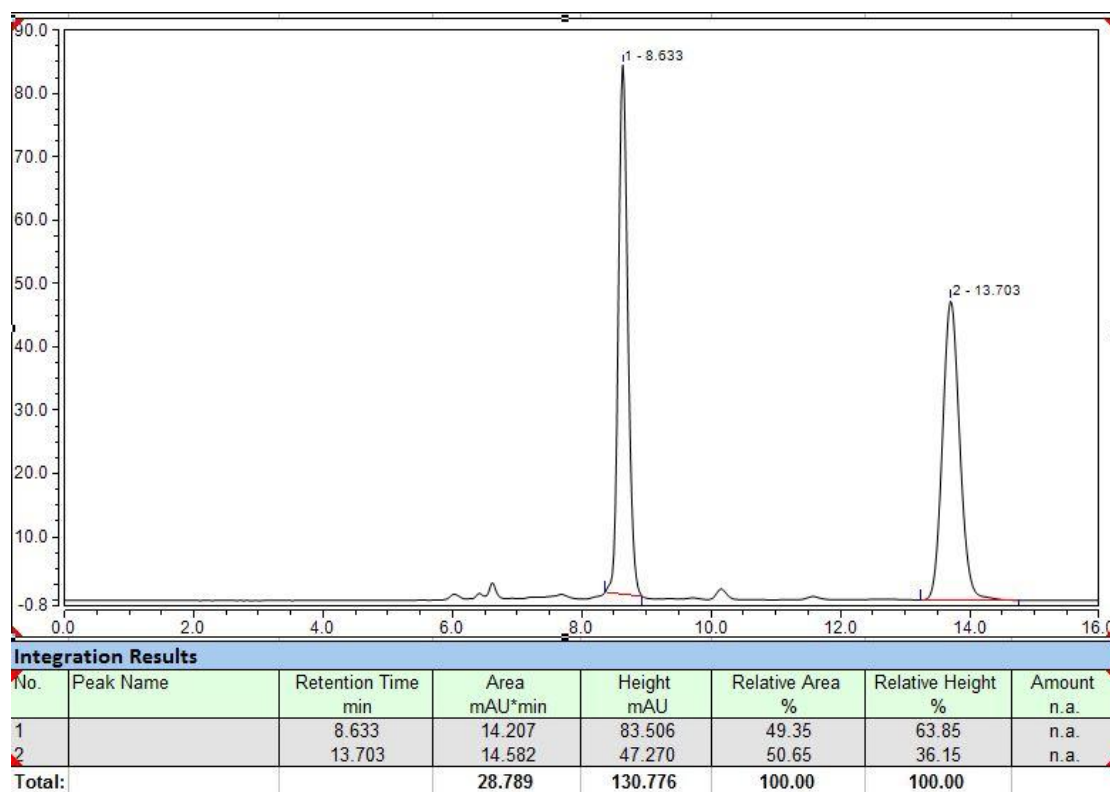
HPLC (Chiralpak AD-H): t_R = 9.7 (major), 15.4 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



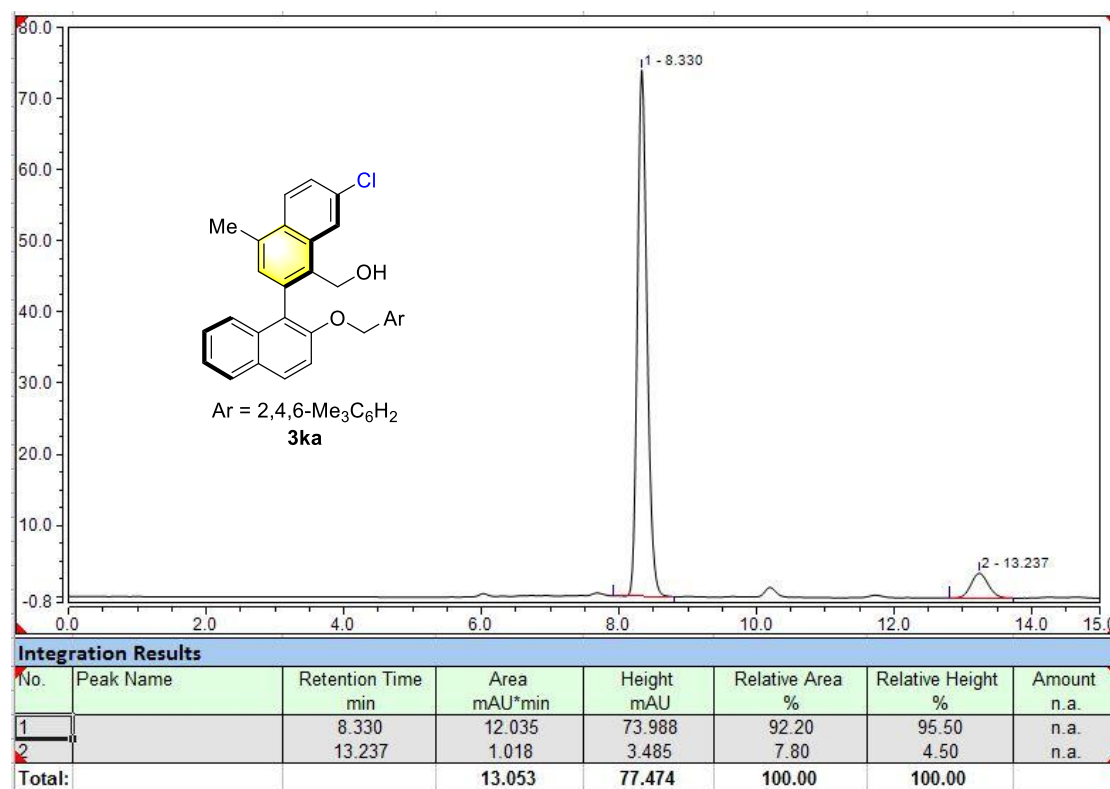
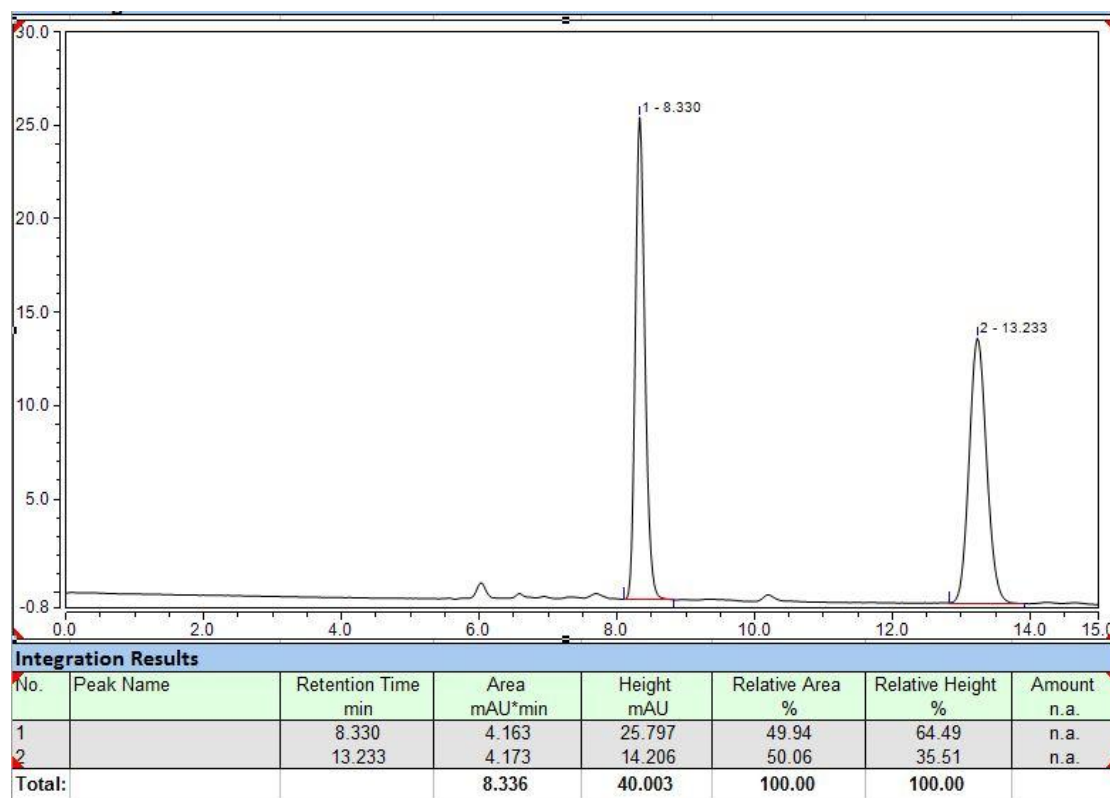
HPLC (Chiralpak AD-H): t_R = 10.7 (major), 16.7 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



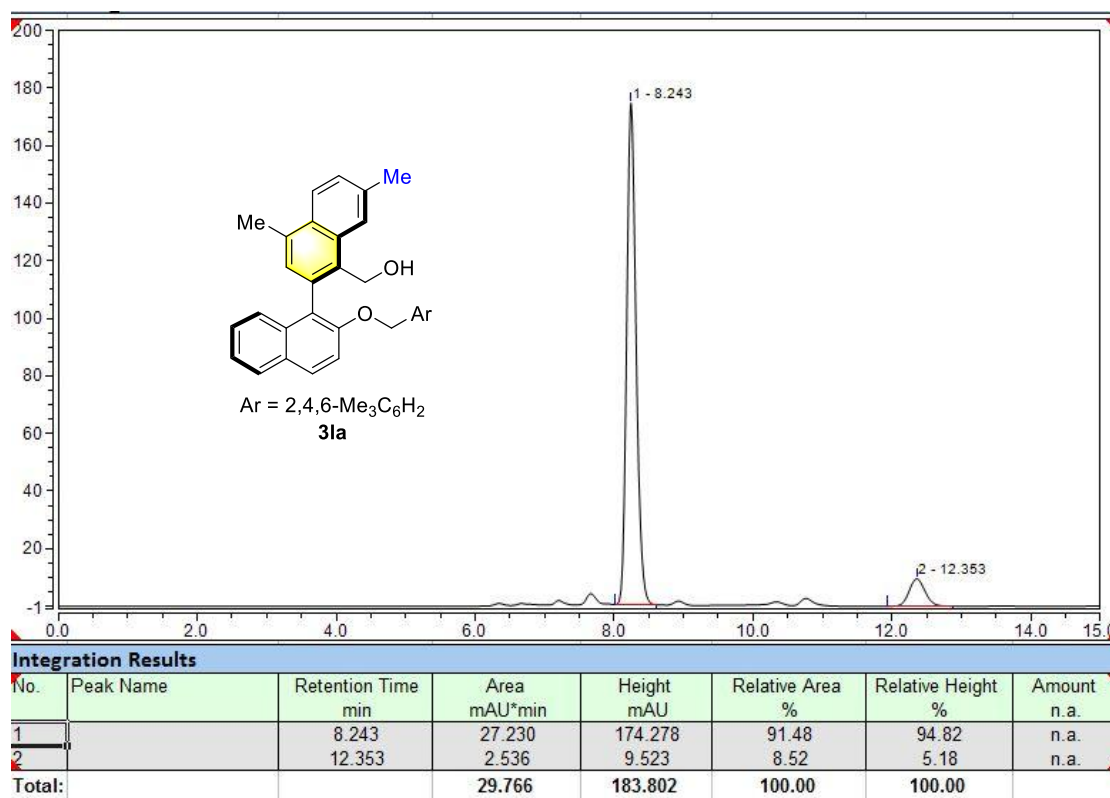
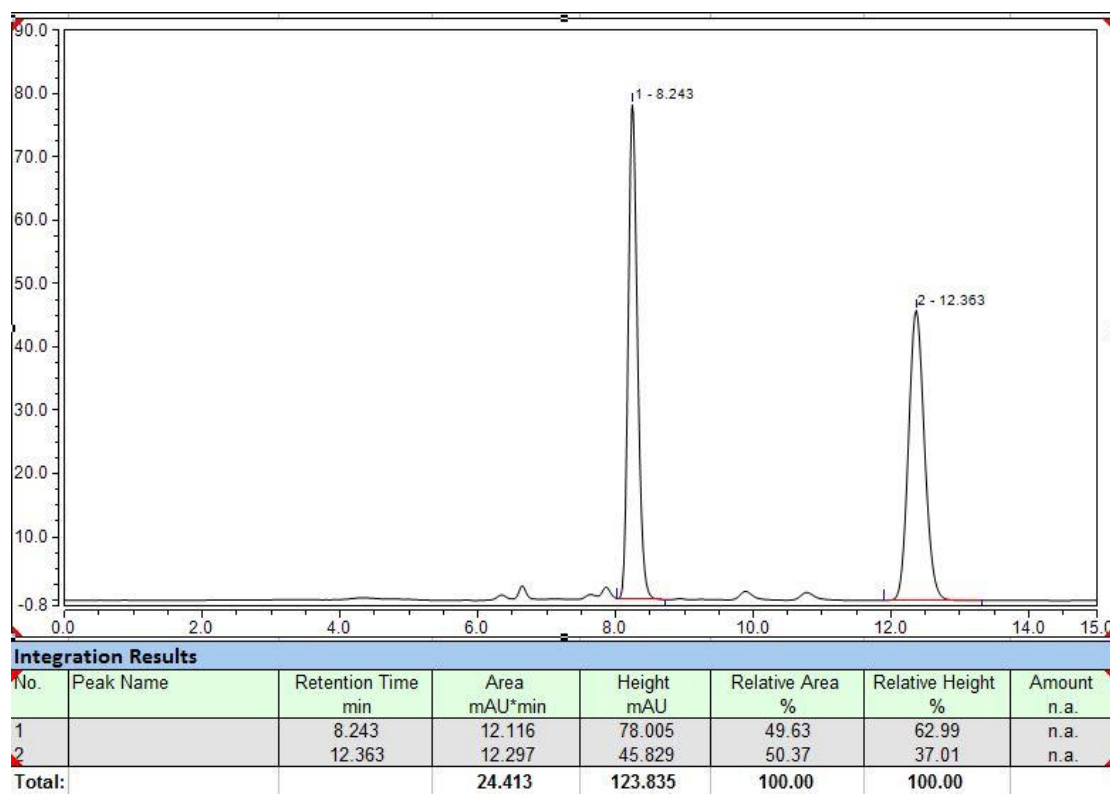
HPLC (Chiralpak AD-H): t_R = 8.7 (major), 13.8 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



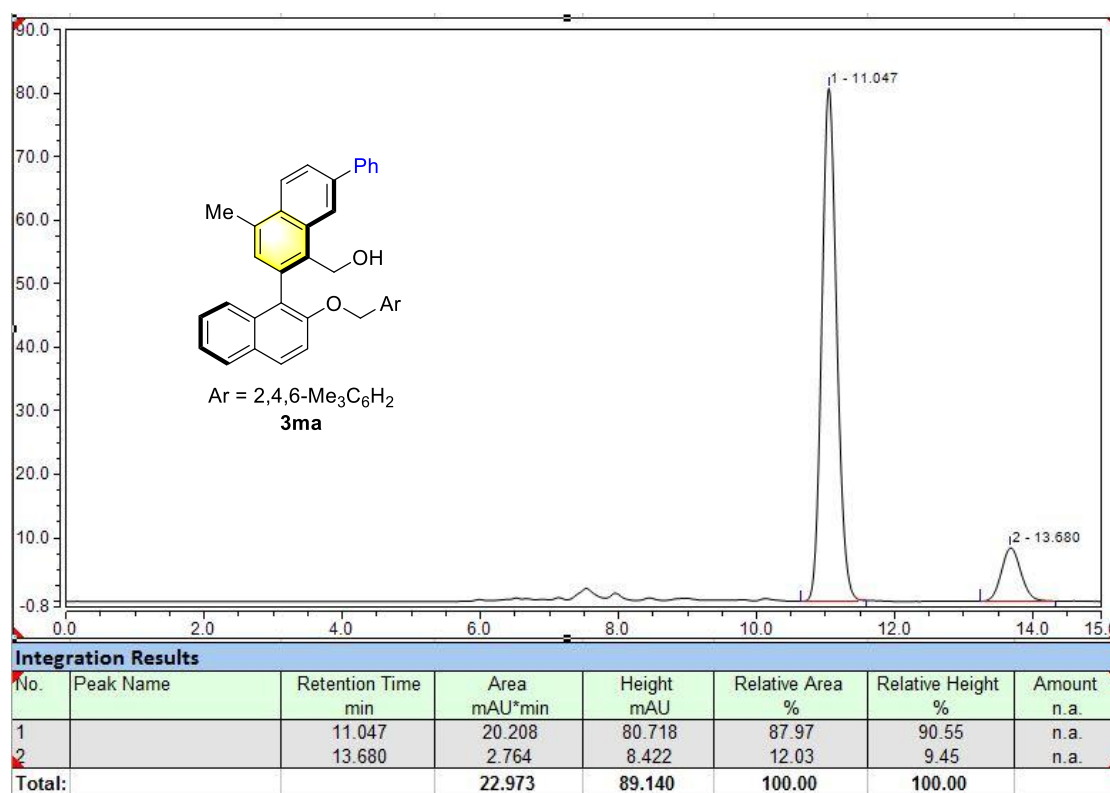
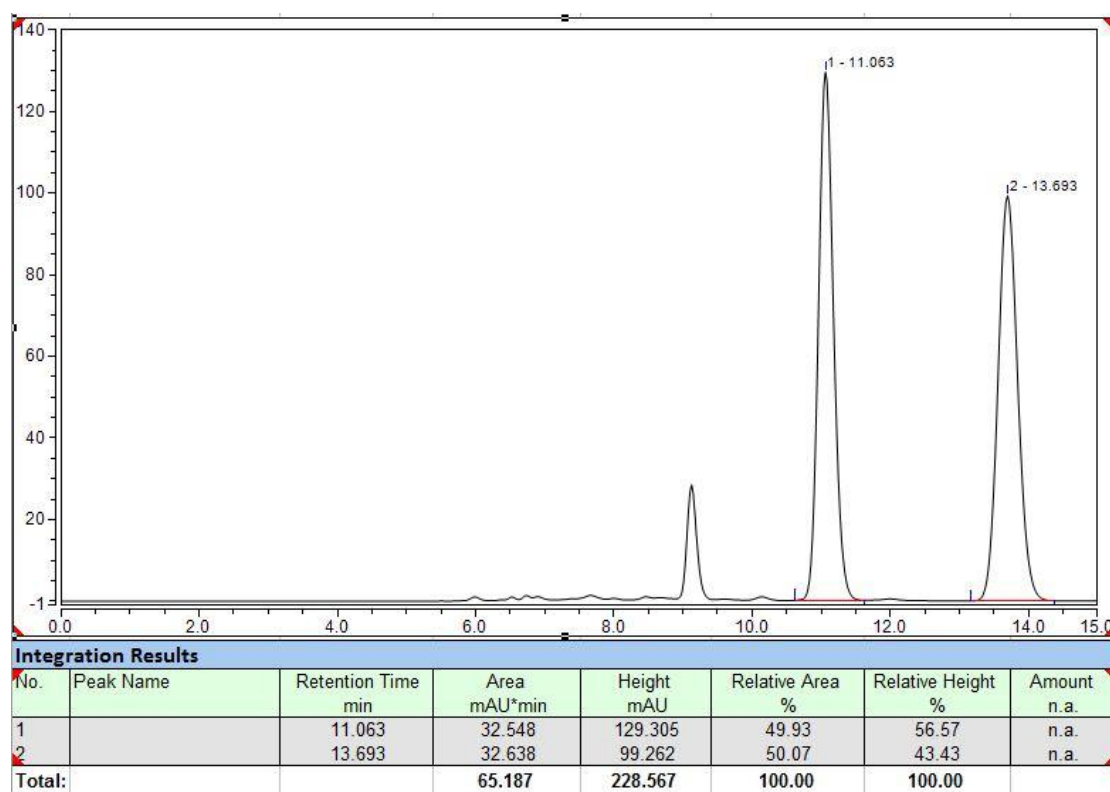
HPLC (Chiralpak AD-H): t_R = 8.3 (major), 13.2 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



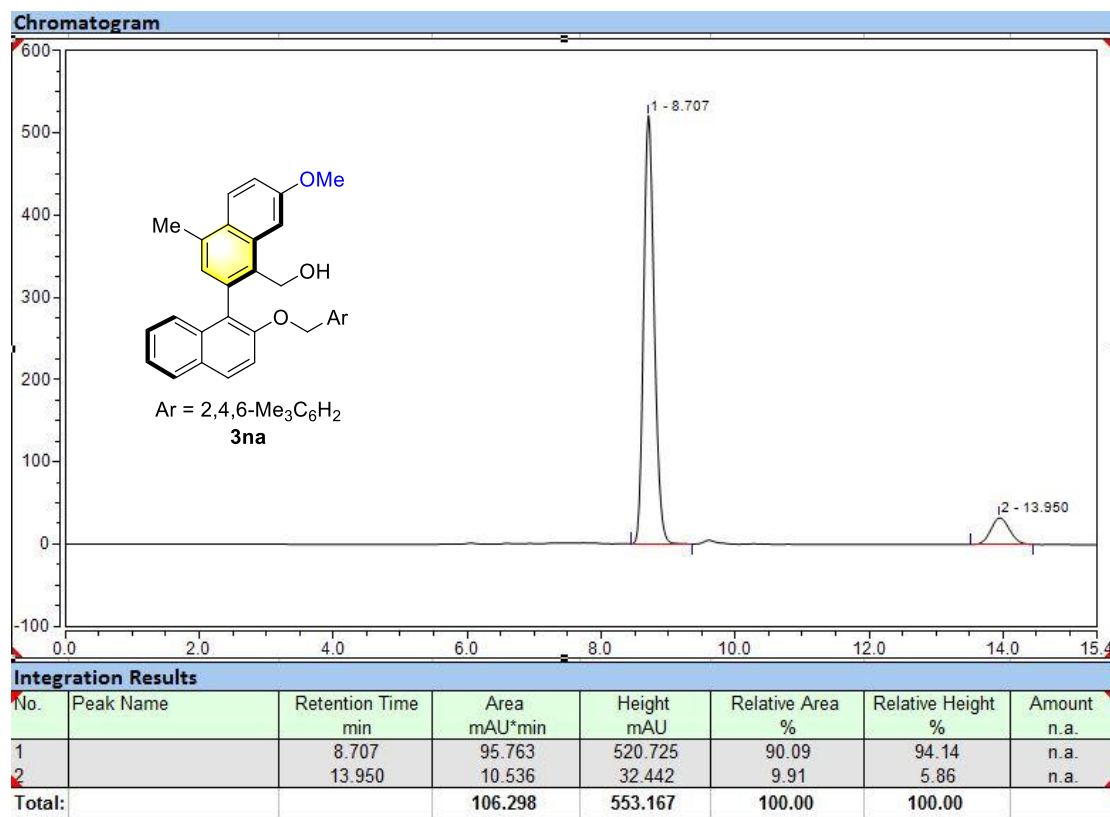
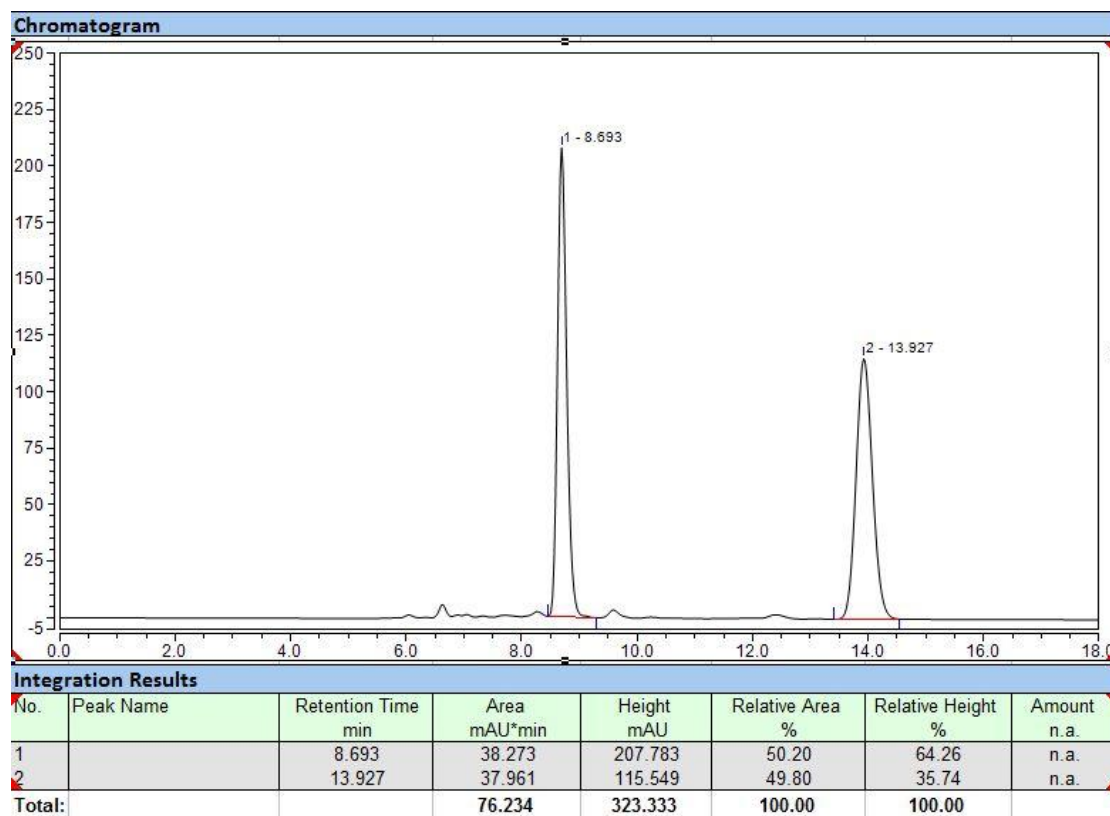
HPLC (Chiralpak AD-H): t_R = 8.2 (major), 12.4 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



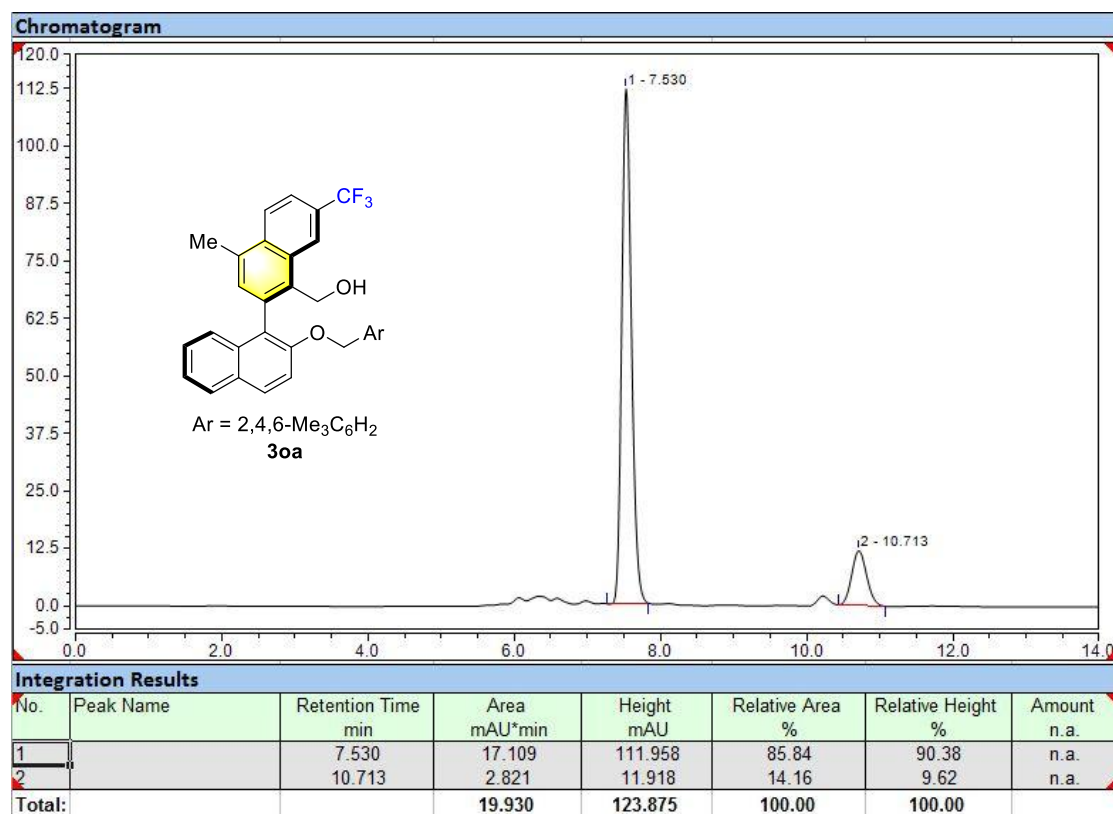
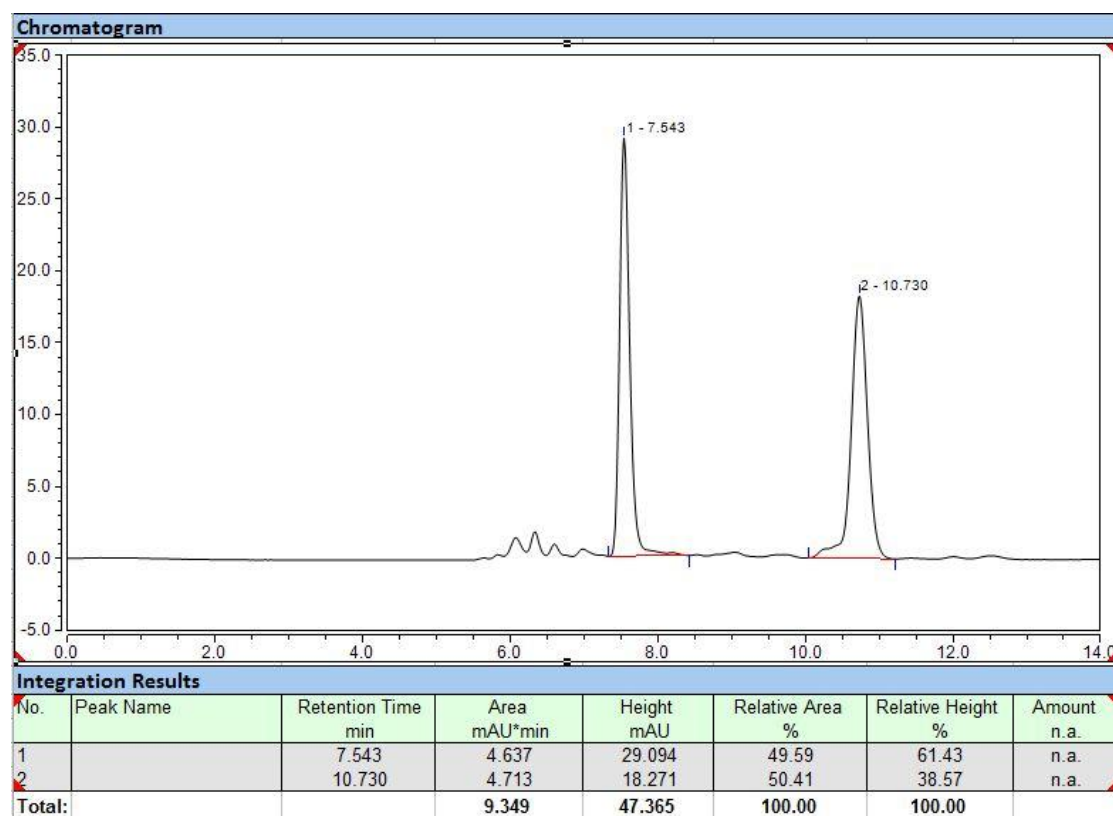
HPLC (Chiralpak AD-H): t_R = 11.0 (major), 13.7 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



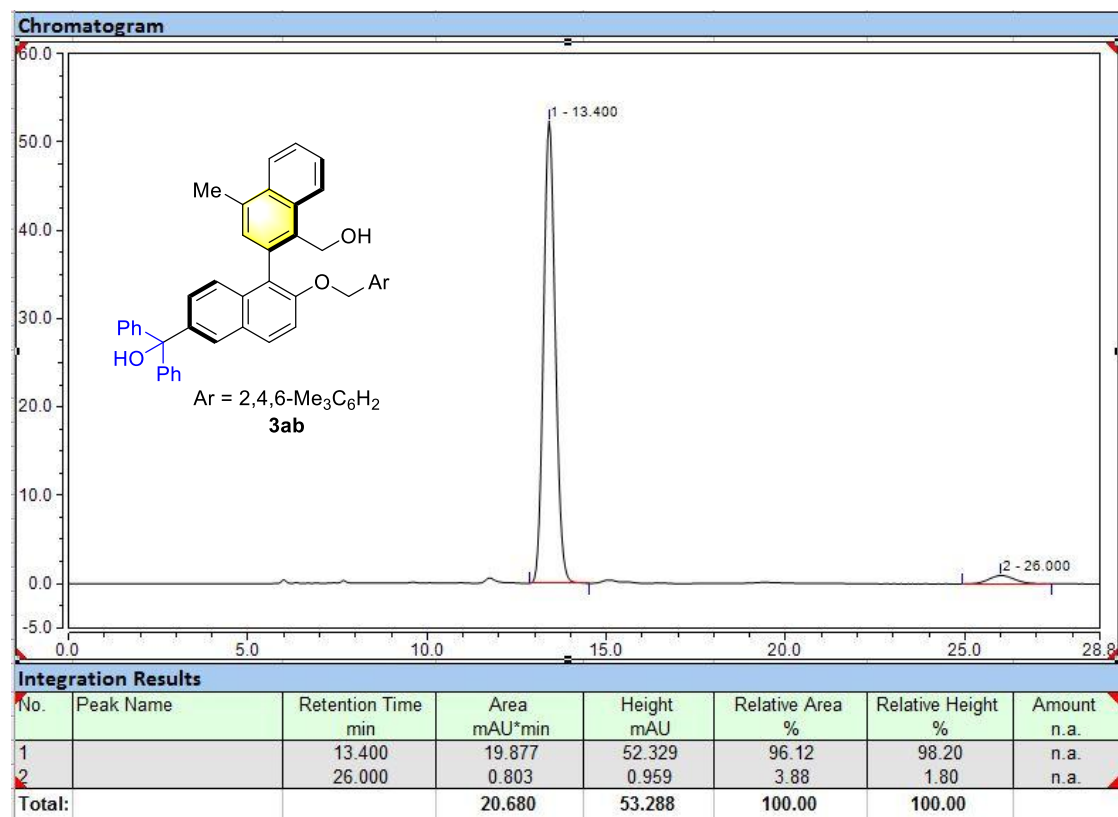
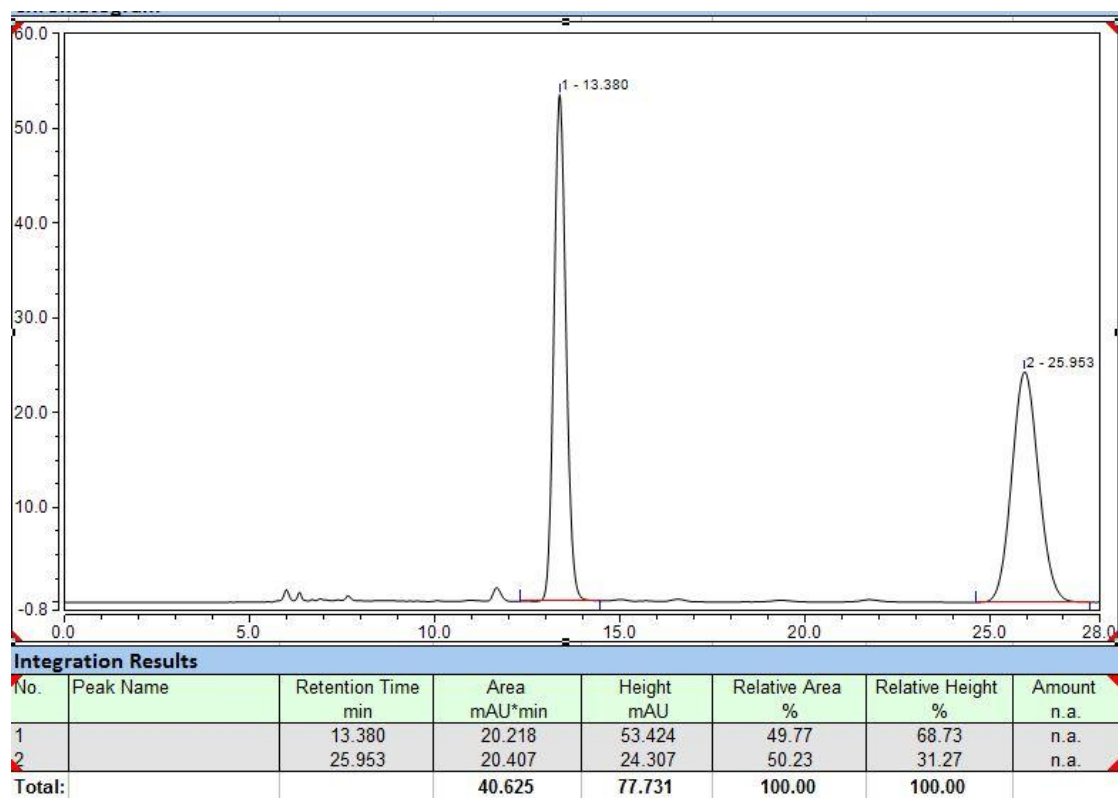
HPLC (Chiralpak AD-H): t_R = 8.7 (major), 14.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



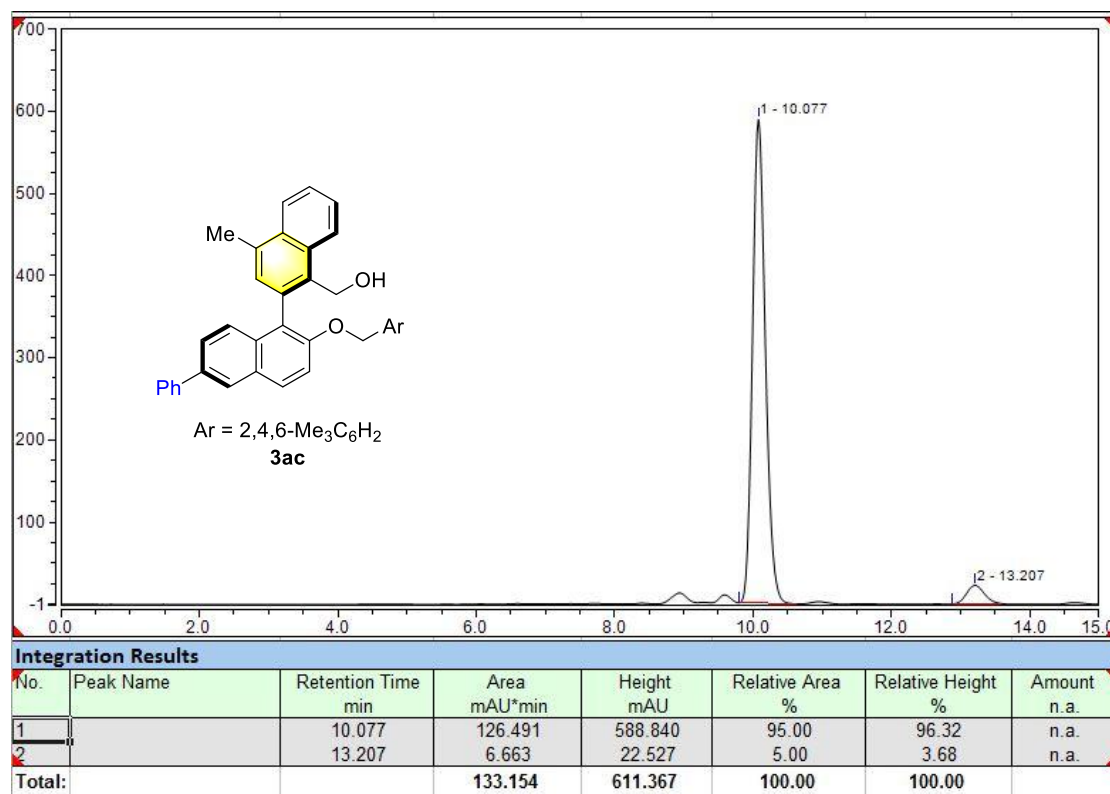
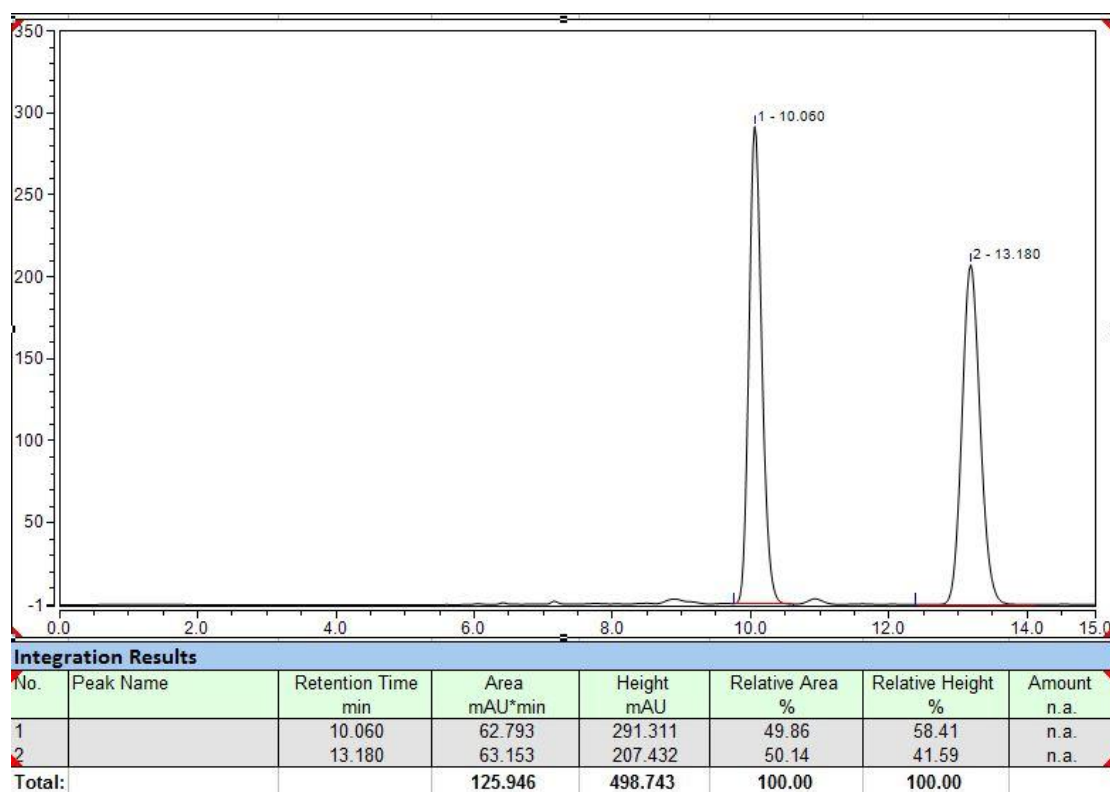
HPLC (Chiralpak AD-H): t_R = 7.5 (major), 10.7 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



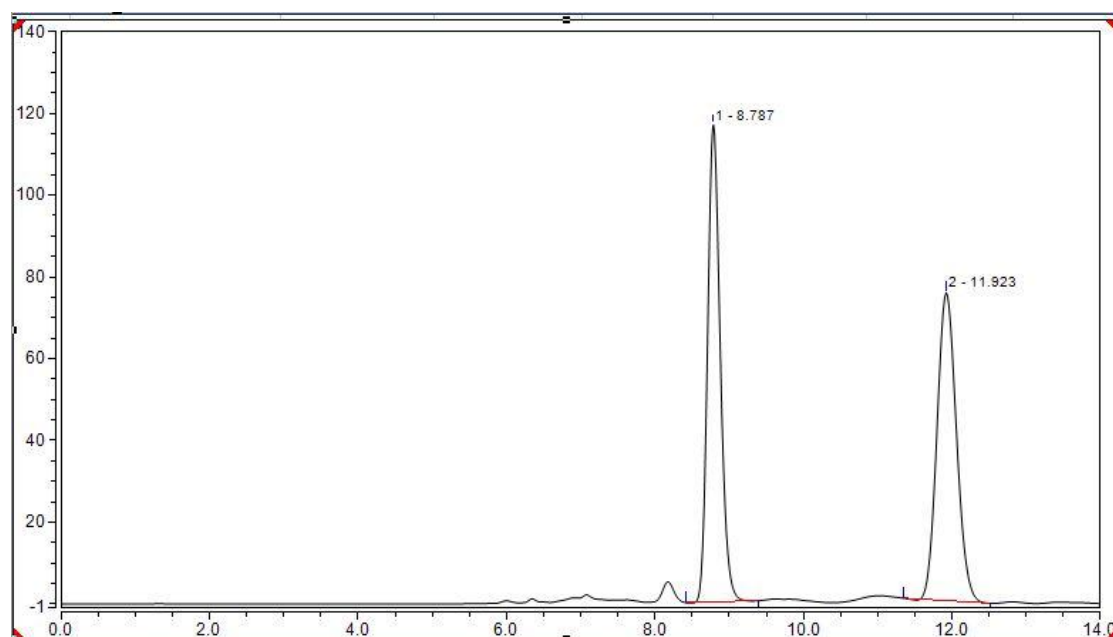
HPLC (Chiralpak AD-H): t_R = 13.4 (major), 26.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.

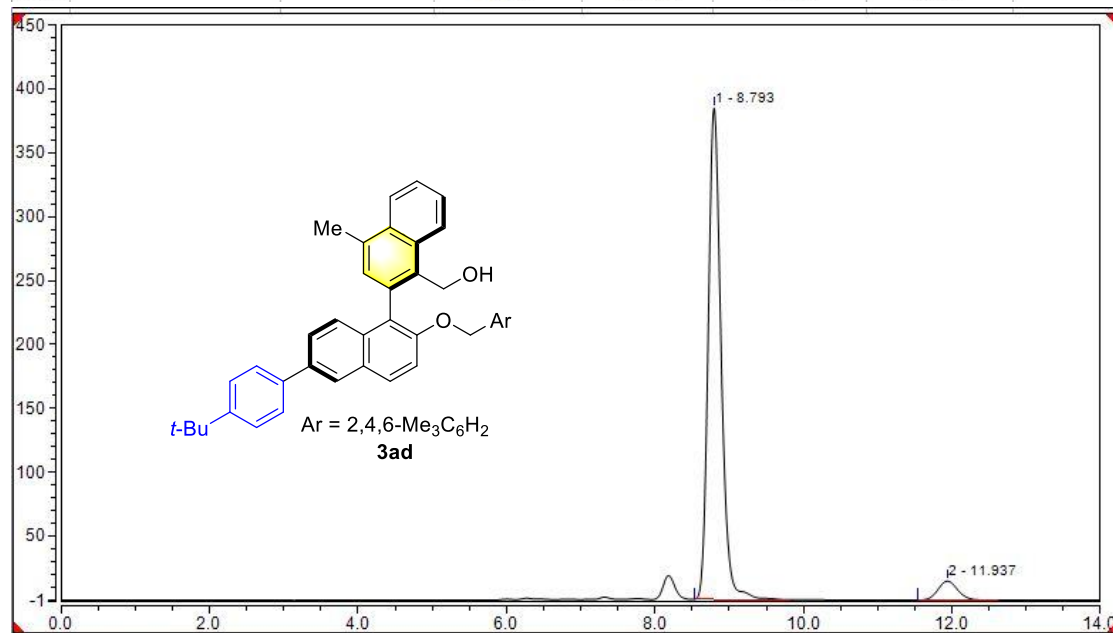


HPLC (Chiralpak AD-H): t_R = 10.1 (major), 13.2 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



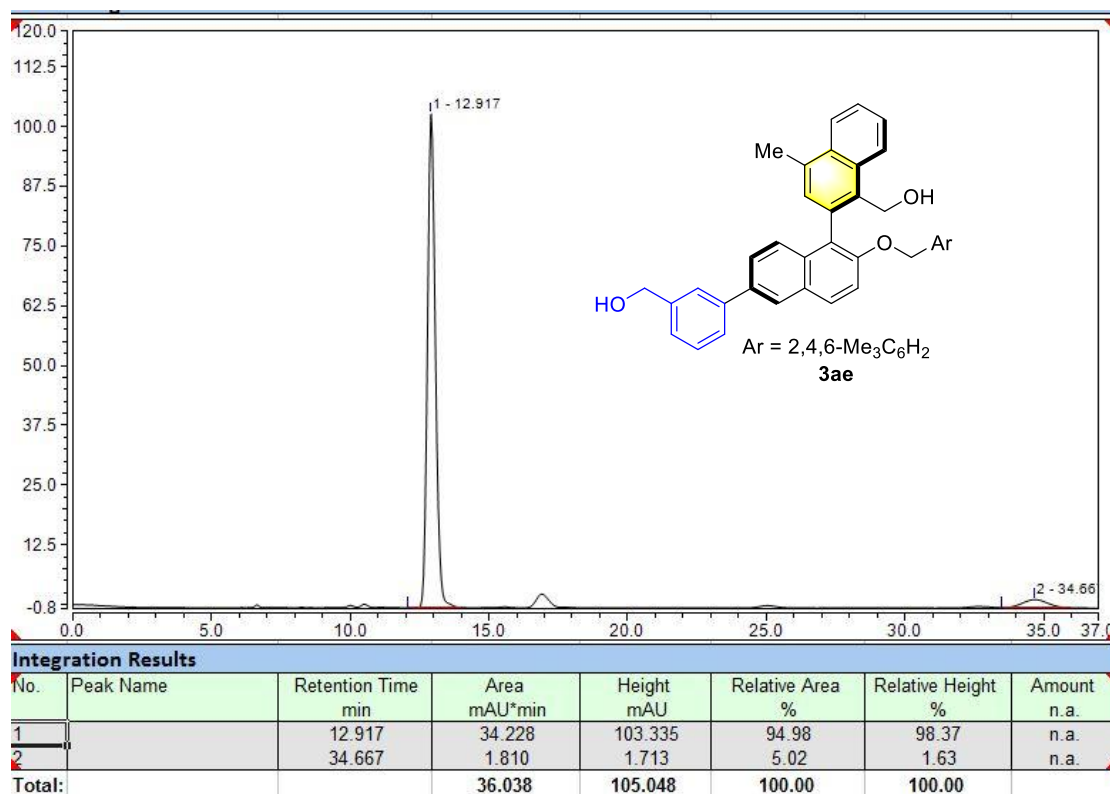
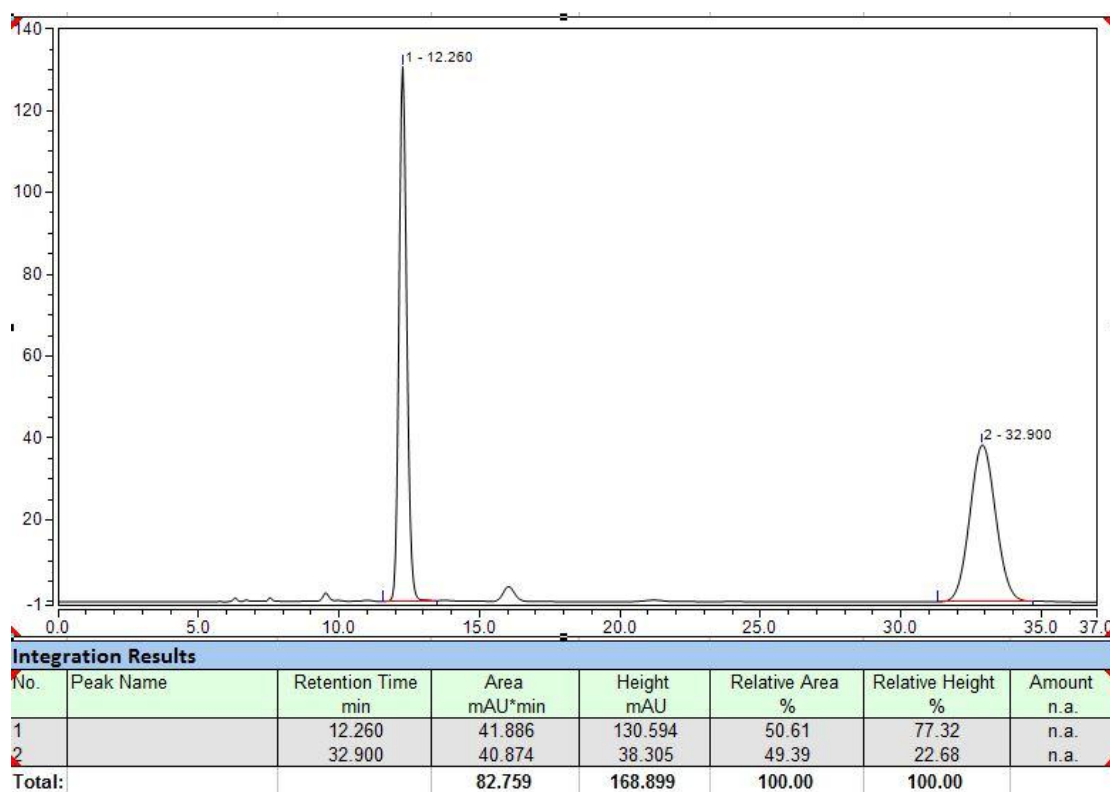
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.787	22.958	116.683	50.22	60.76	n.a.
2		11.923	22.753	75.367	49.78	39.24	n.a.
Total:			45.712	192.050	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.793	76.969	384.757	94.40	96.27	n.a.
2		11.937	4.565	14.924	5.60	3.73	n.a.
Total:			81.535	399.682	100.00	100.00	

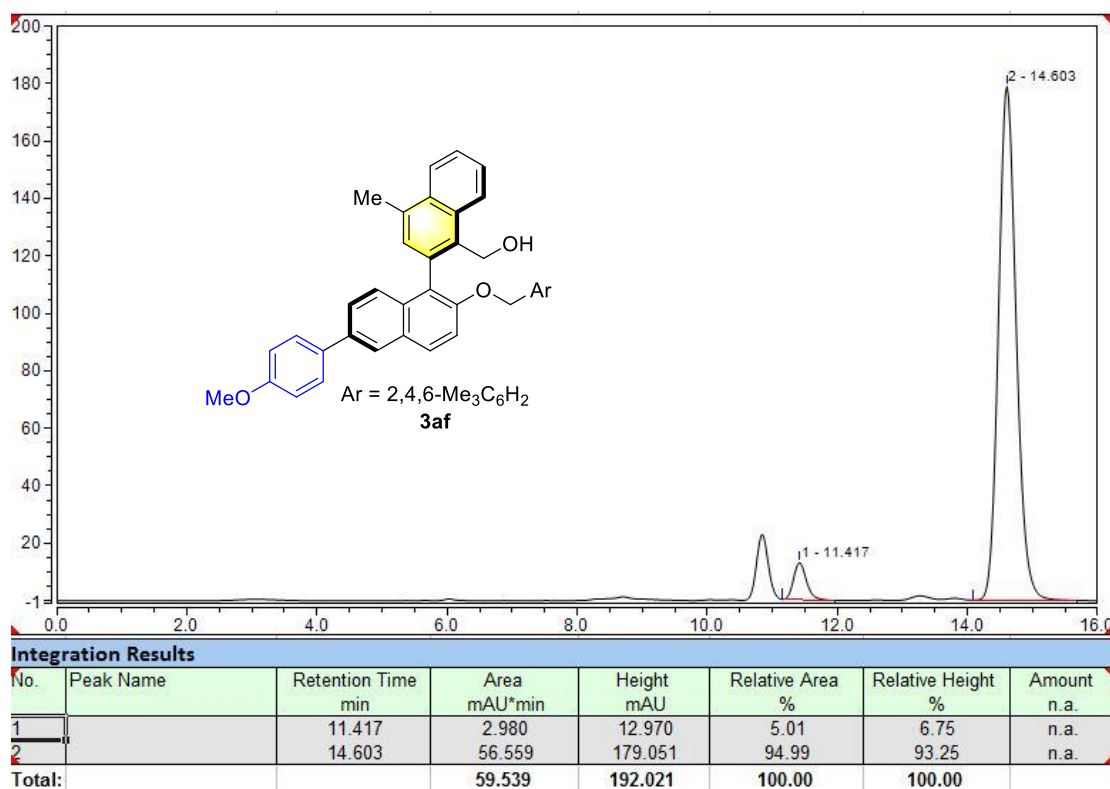
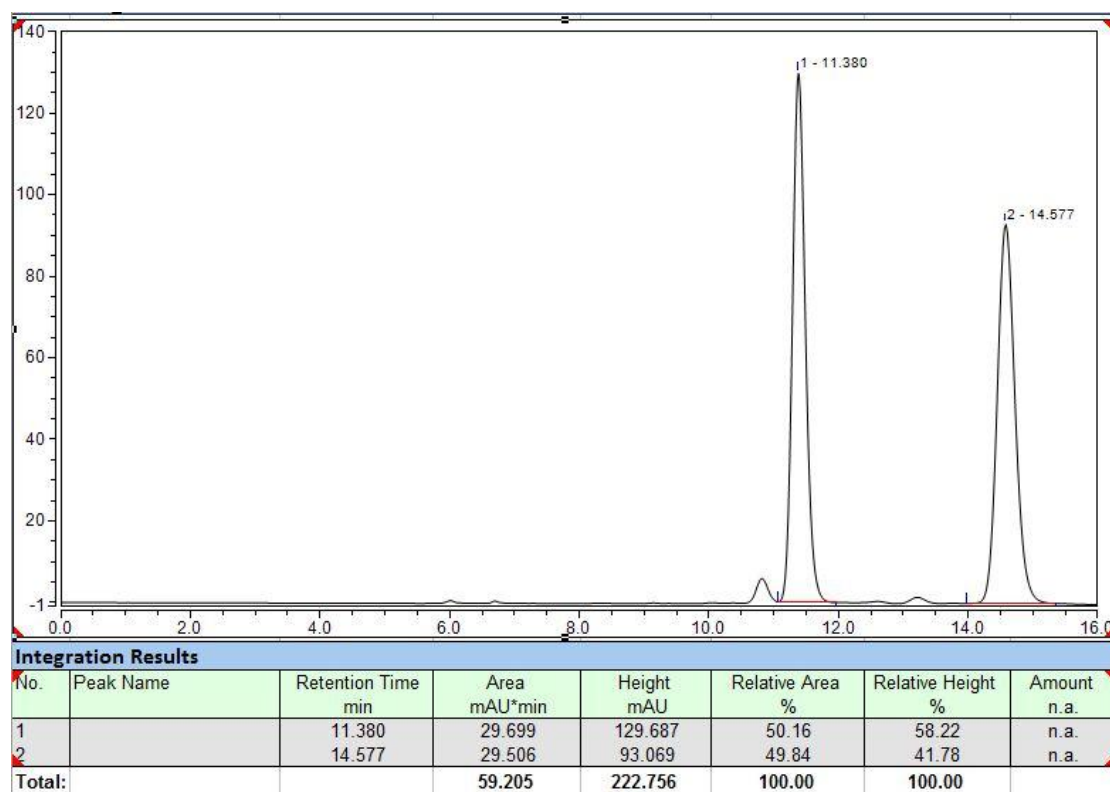
HPLC (Chiralpak AD-H): t_R = 8.8 (major), 11.9 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



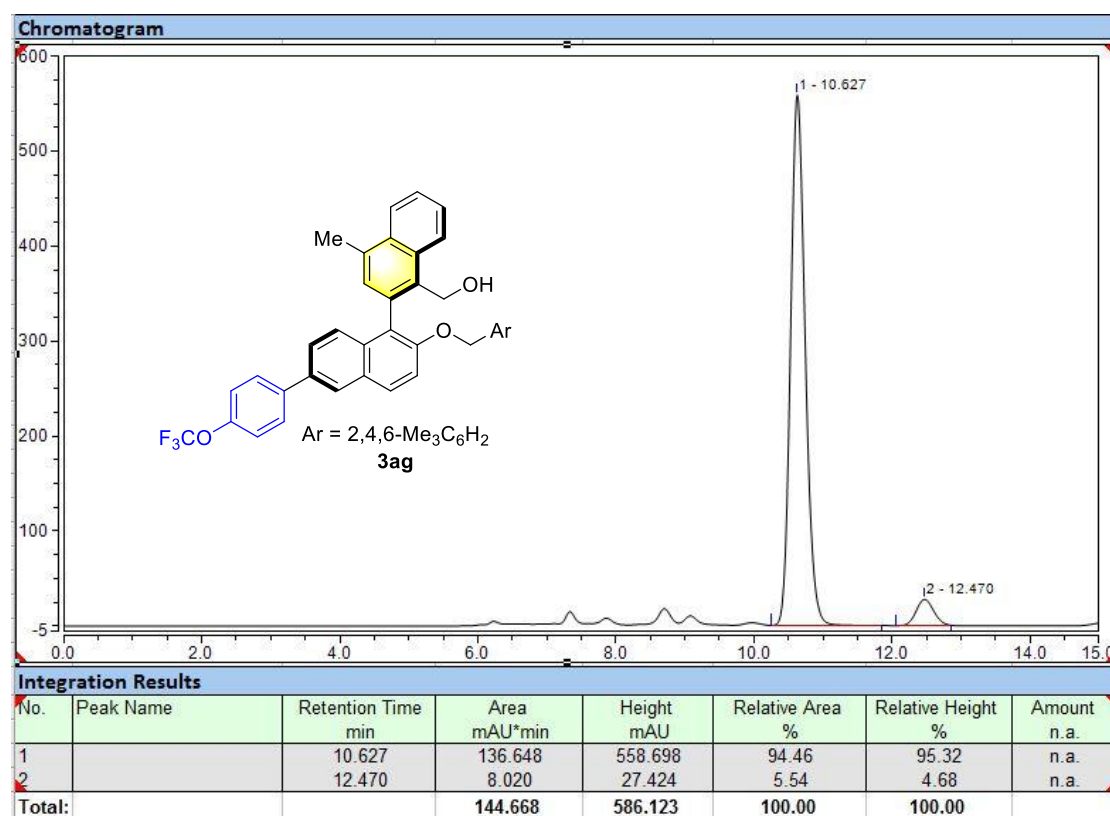
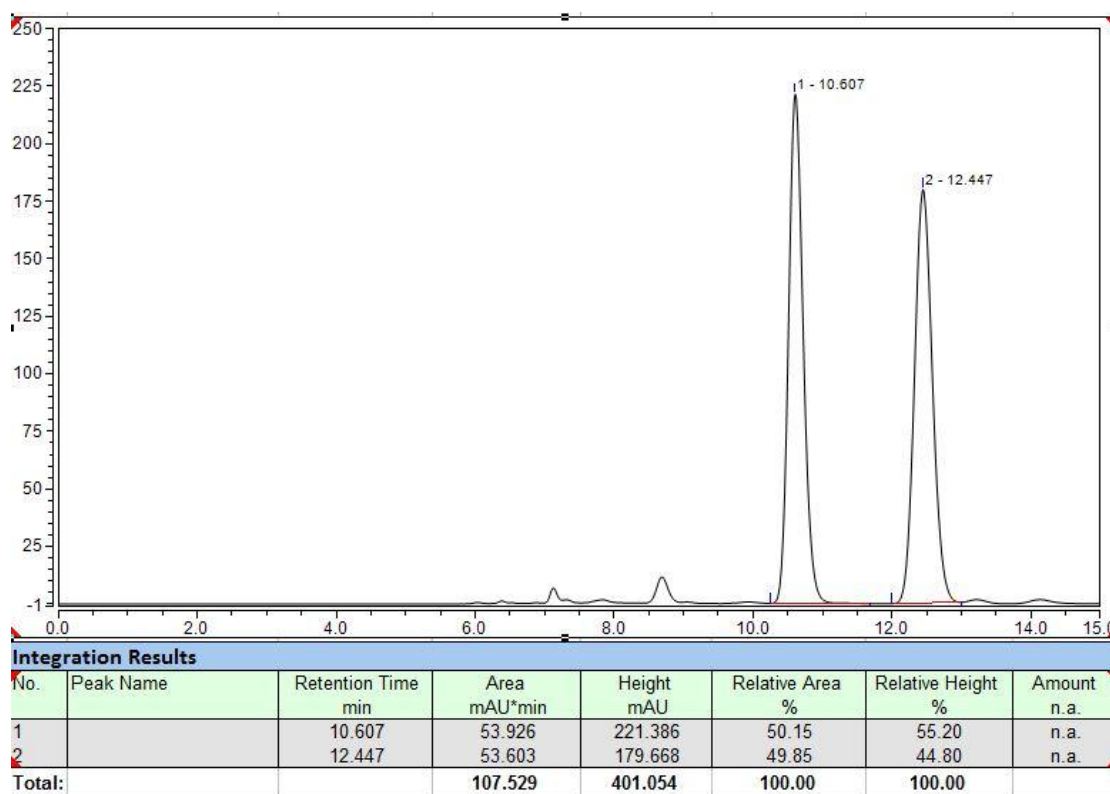
HPLC (Chiralpak AD-H): t_R = 12.9 (major), 34.7 (minor)

Condition: hexane/isopropanol = 60/40, flow rate 0.5 mL/min, 25°C.



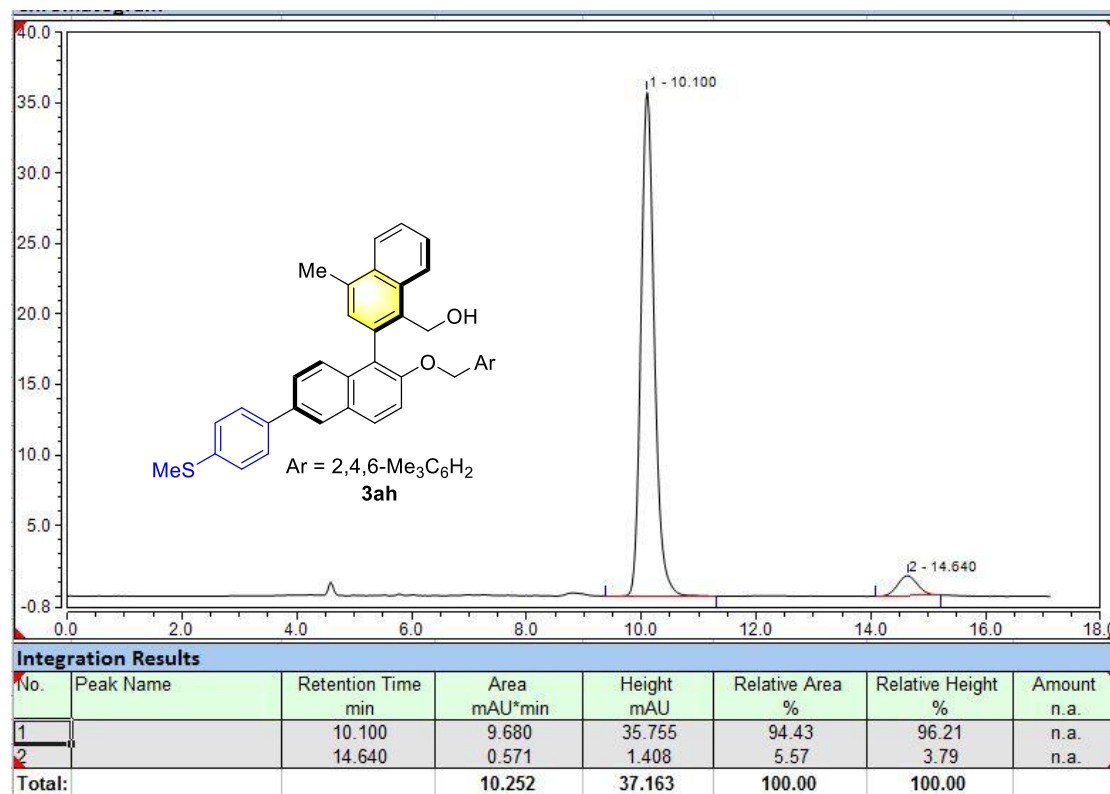
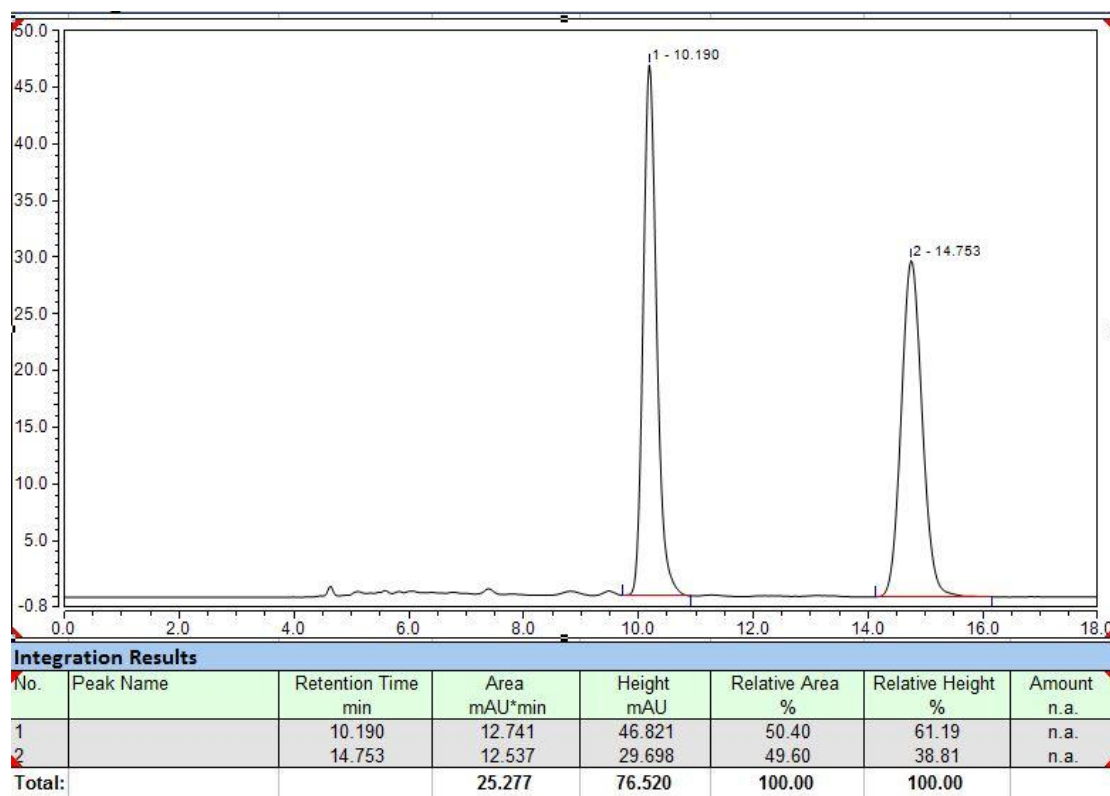
HPLC (Chiral MD): t_R = 11.4 (minor), 14.6 (major)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



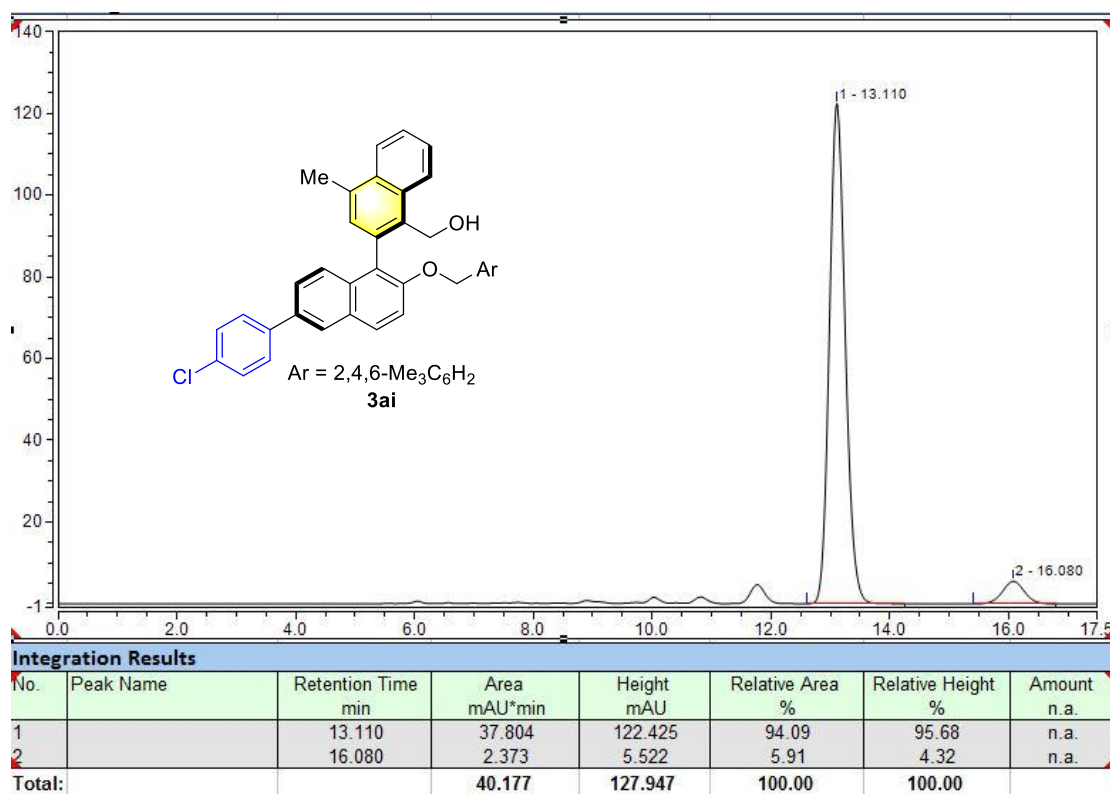
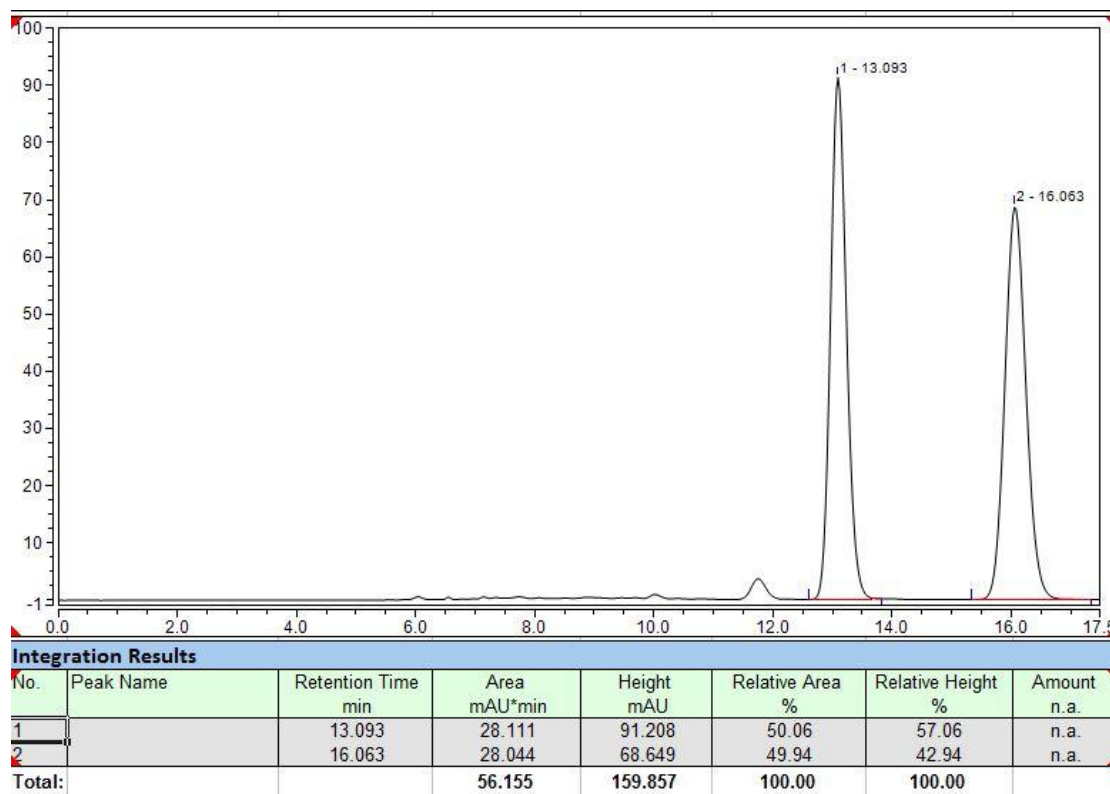
HPLC (Chiralpak AD-H): t_R = 10.6 (major), 12.5 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



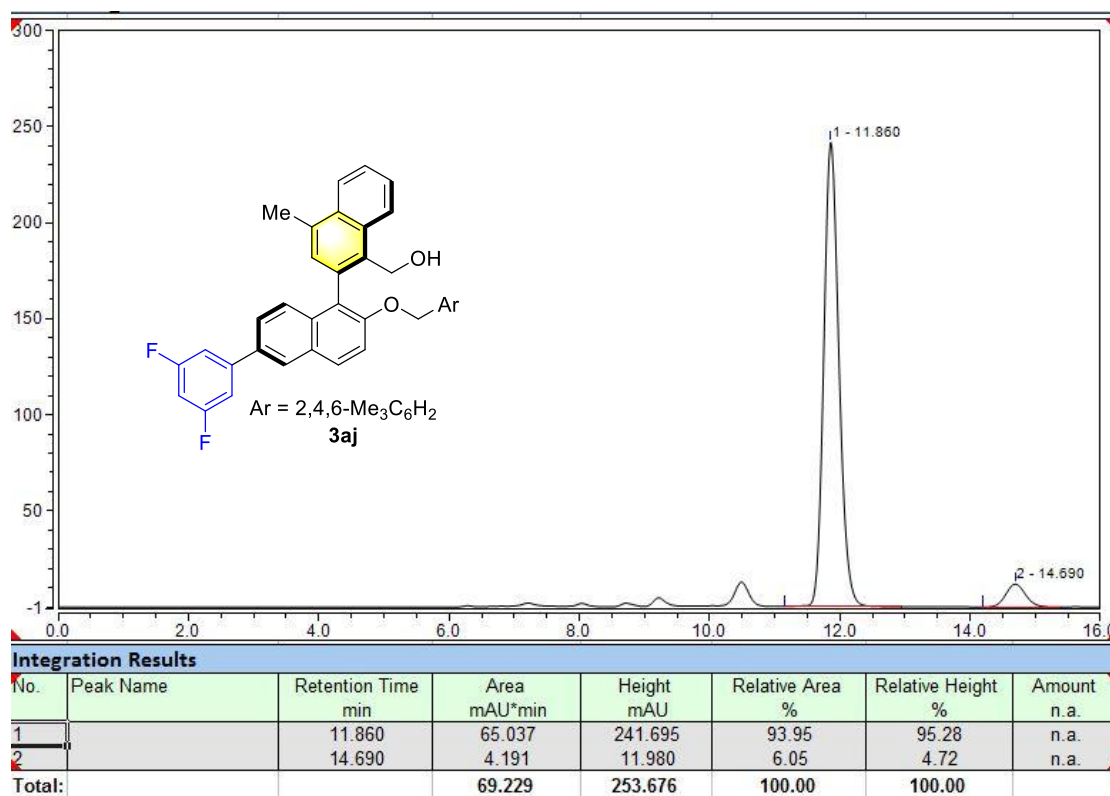
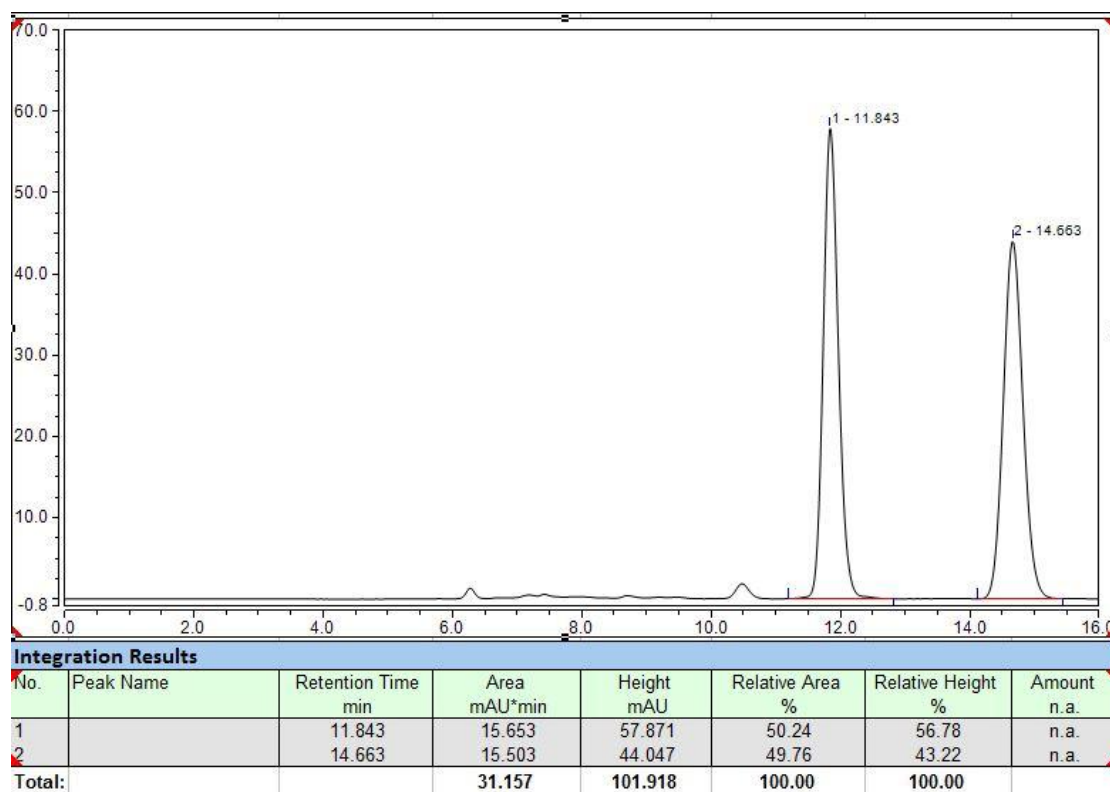
HPLC (Chiralpak AD-H): t_R = 10.1 (major), 14.6 (minor)

Condition: hexane/isopropanol = 65/35, flow rate 0.75 mL/min, 25°C.



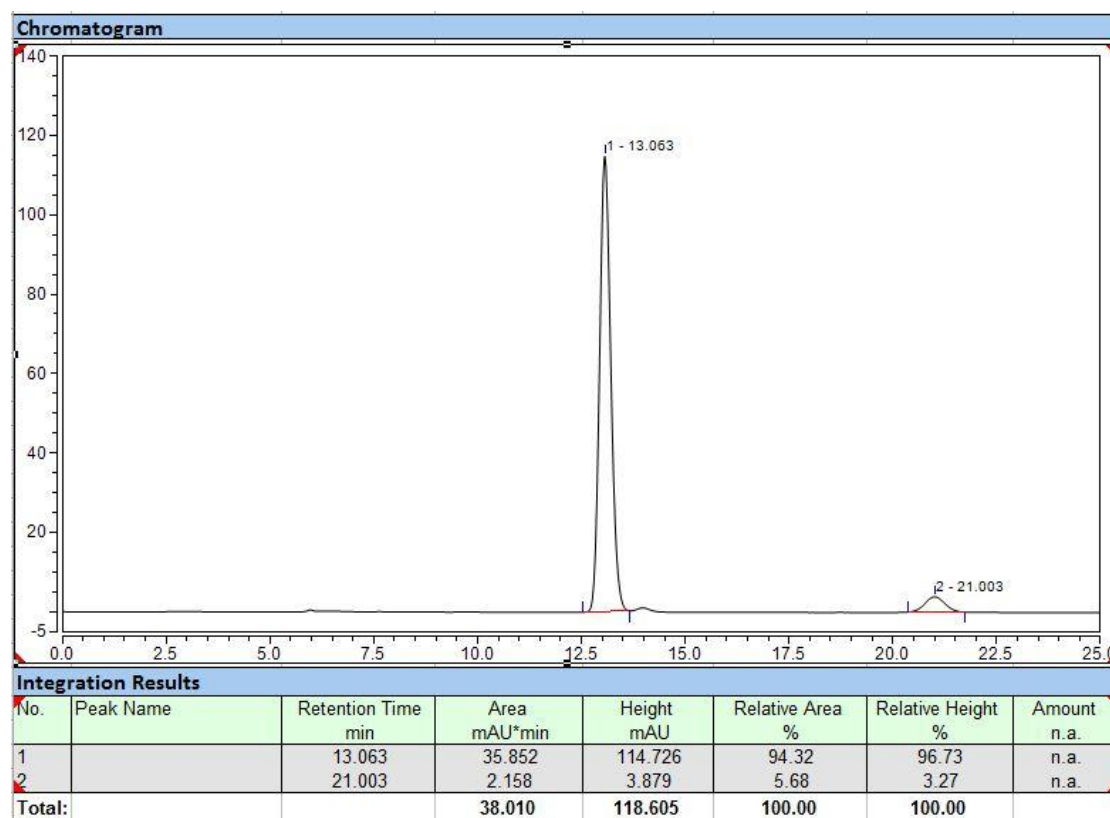
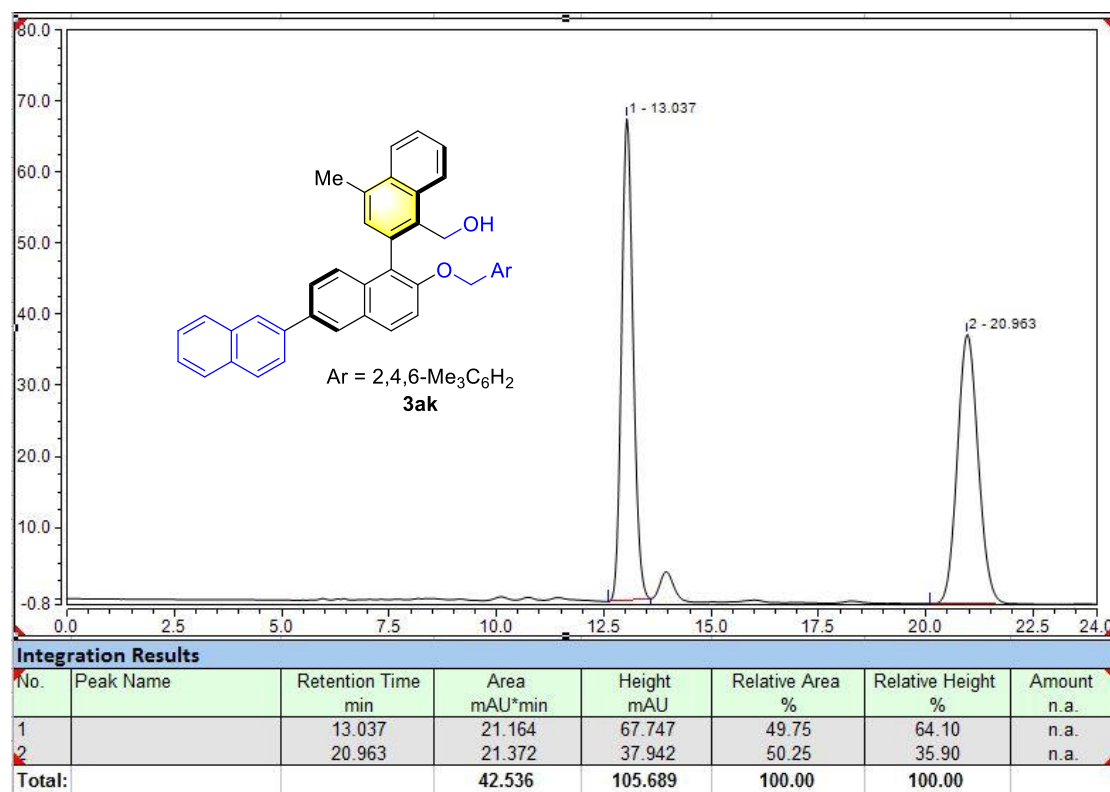
HPLC (Chiralpak AD-H): t_R = 13.1 (major), 16.1 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



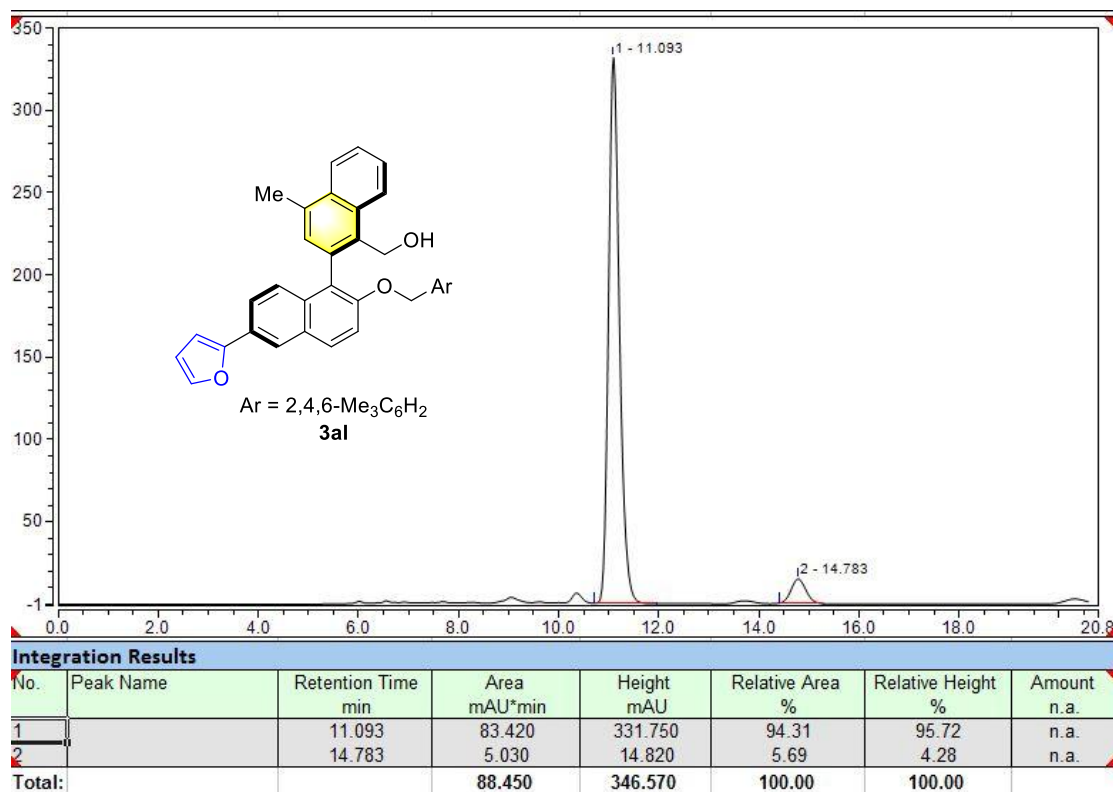
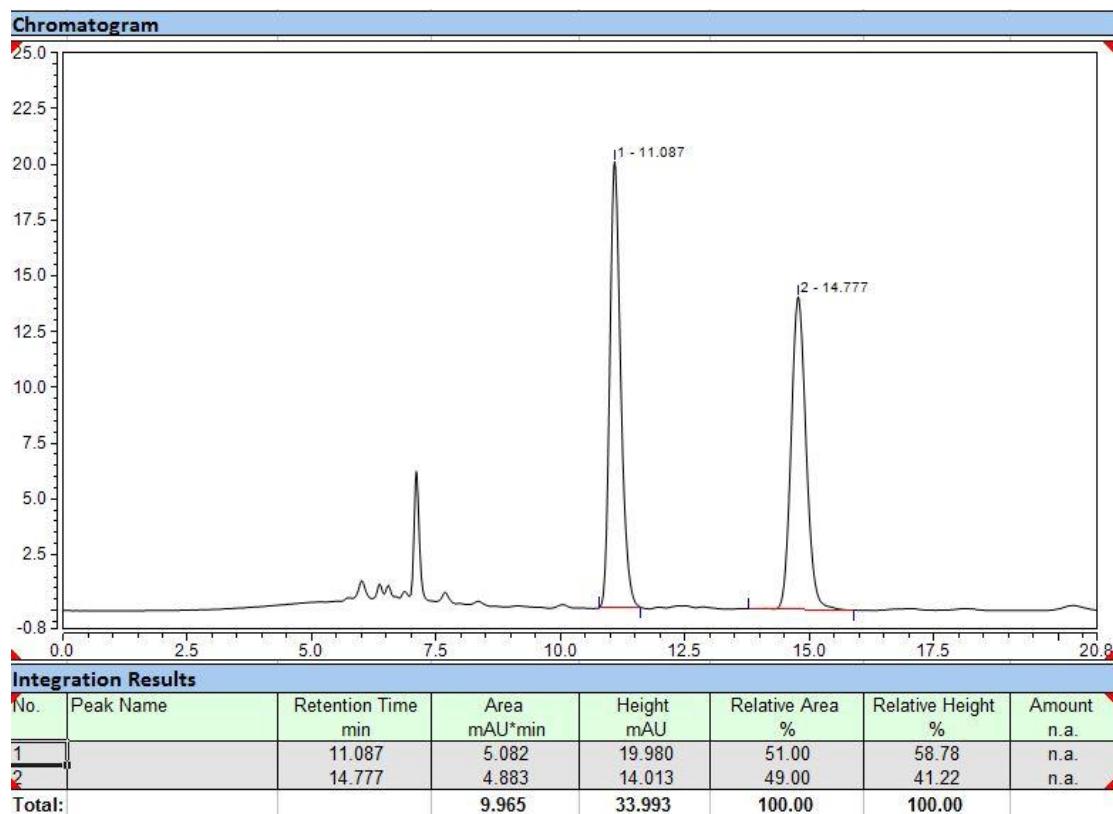
HPLC (Chiralpak AD-H): t_R = 11.9 (major), 14.7 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



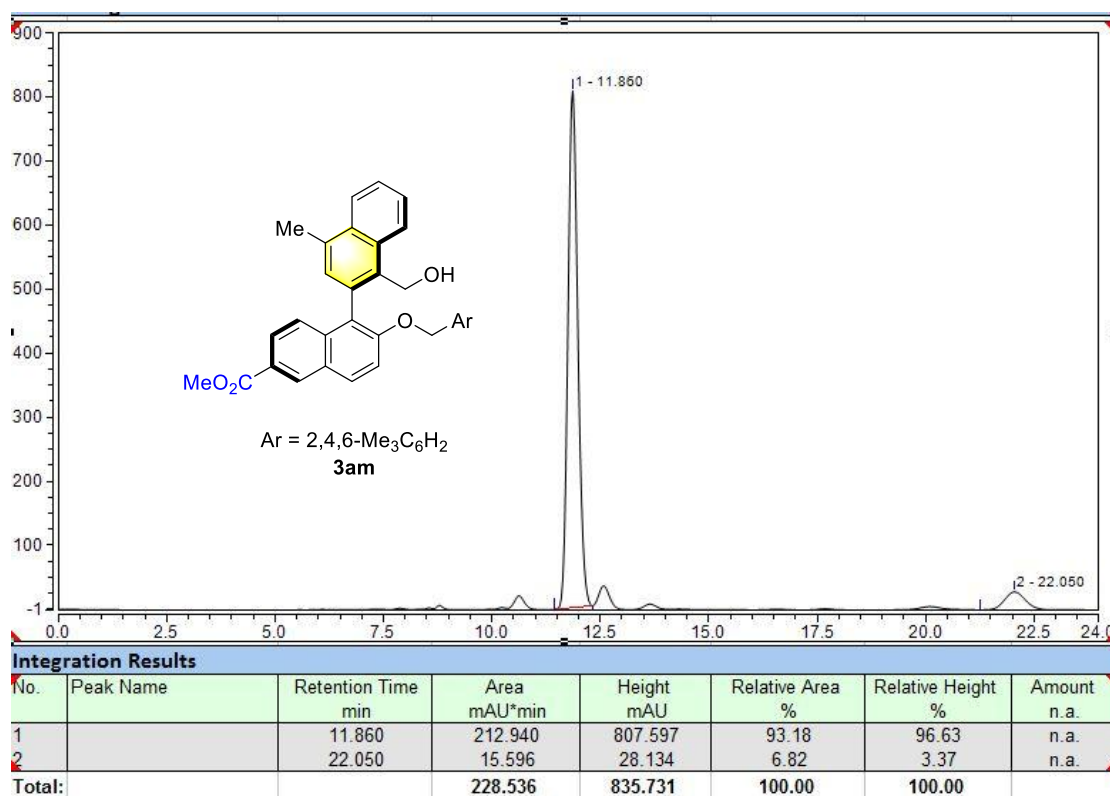
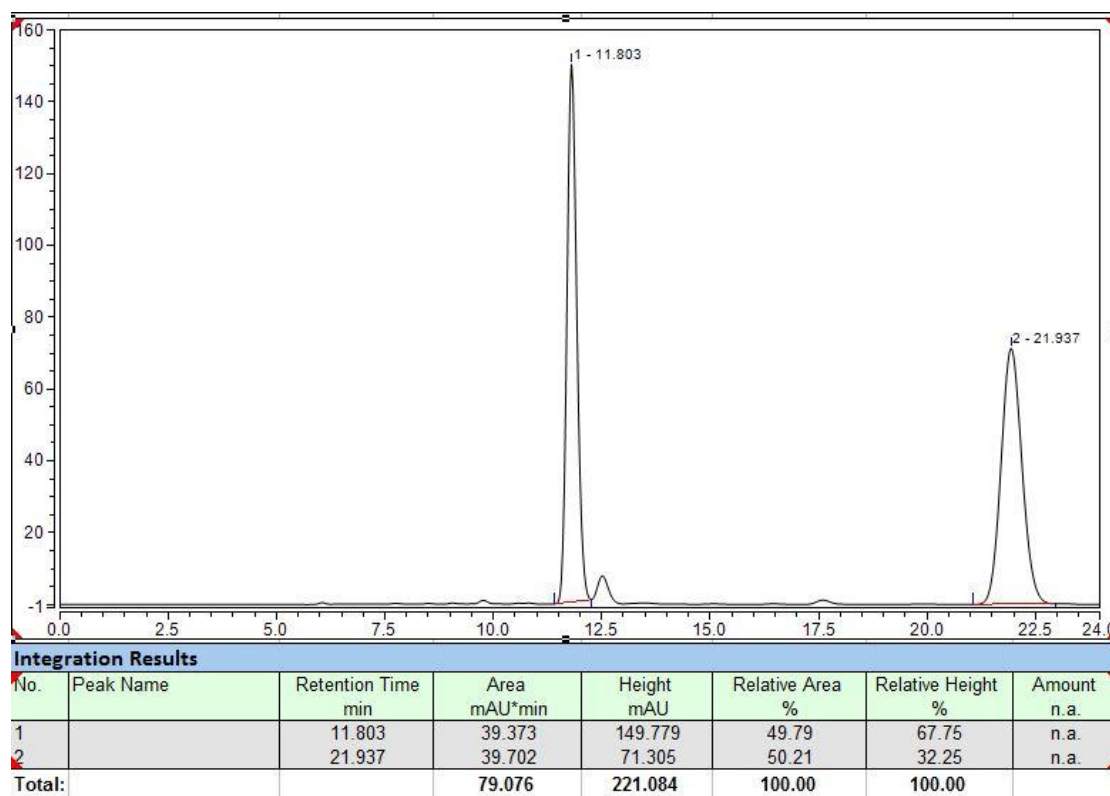
HPLC (Chiralpak AD-H): t_R = 13.1 (major), 21.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



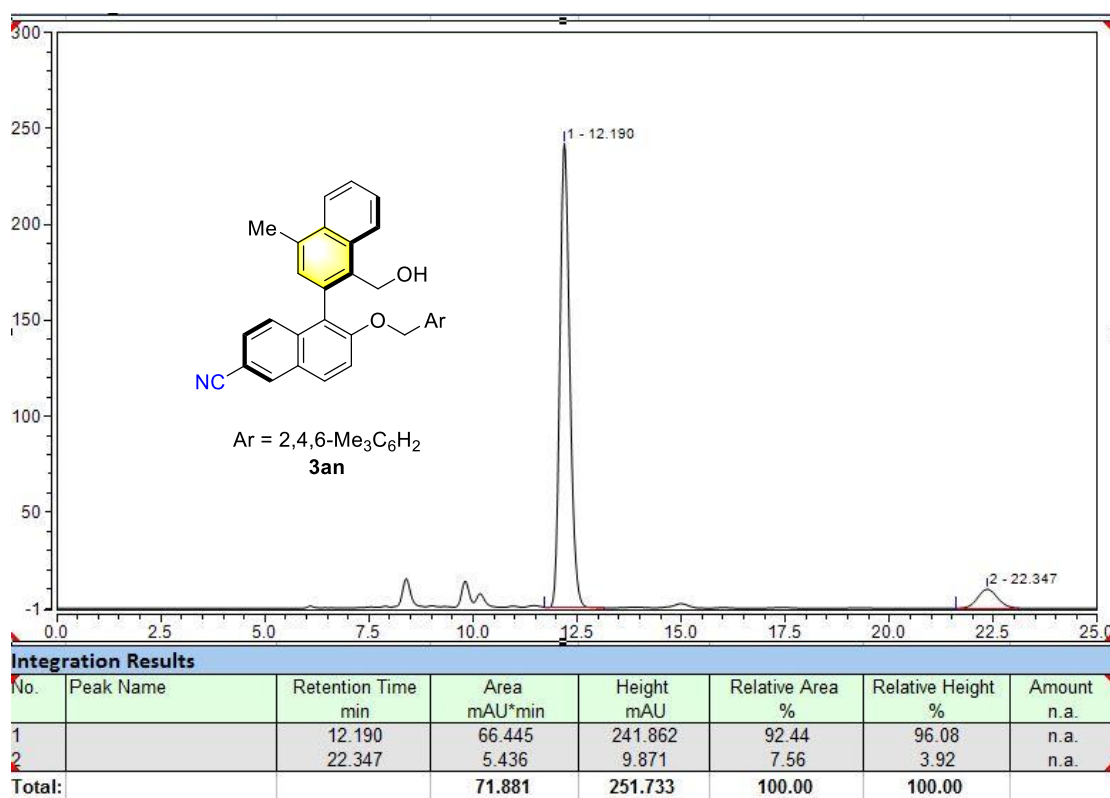
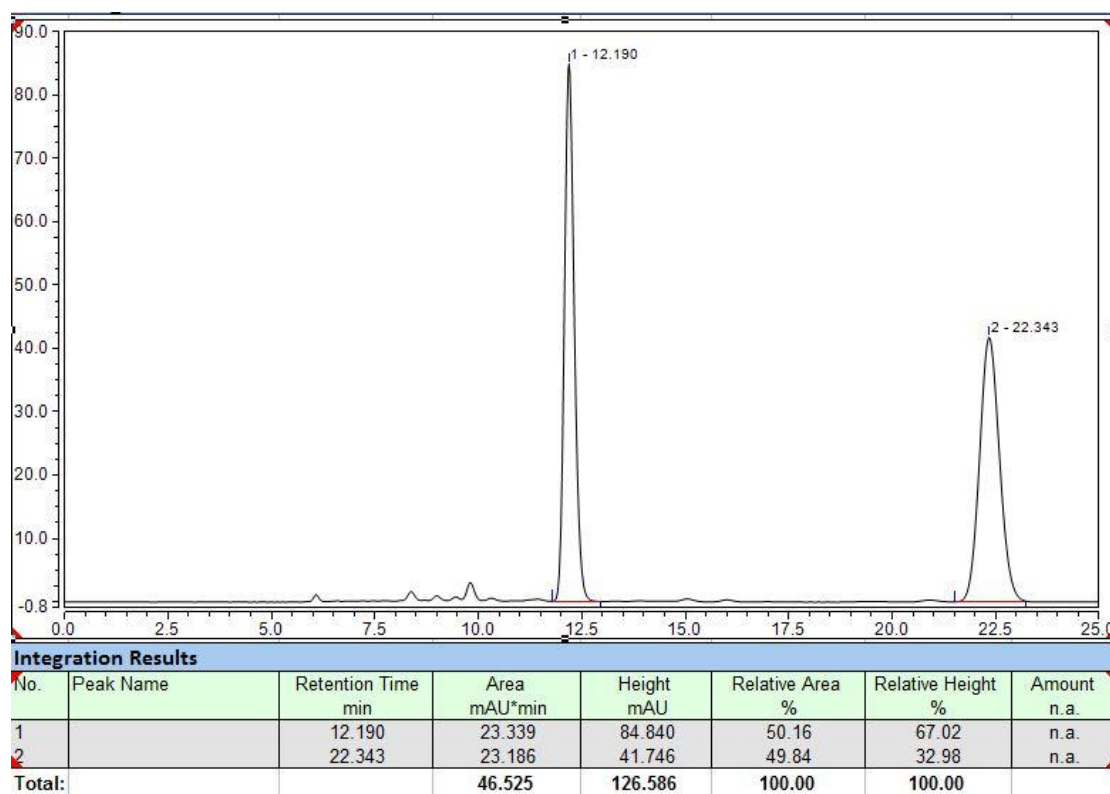
HPLC (Chiralpak AD-H): t_R = 11.1 (major), 14.8 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



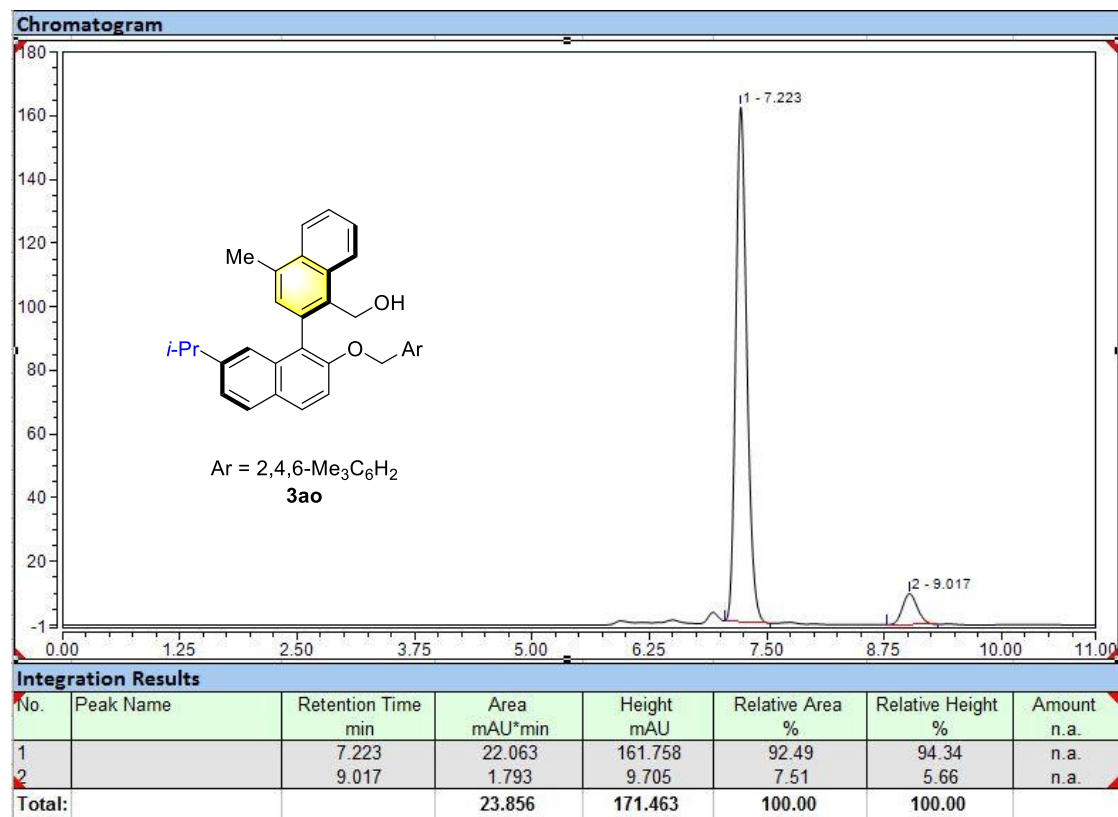
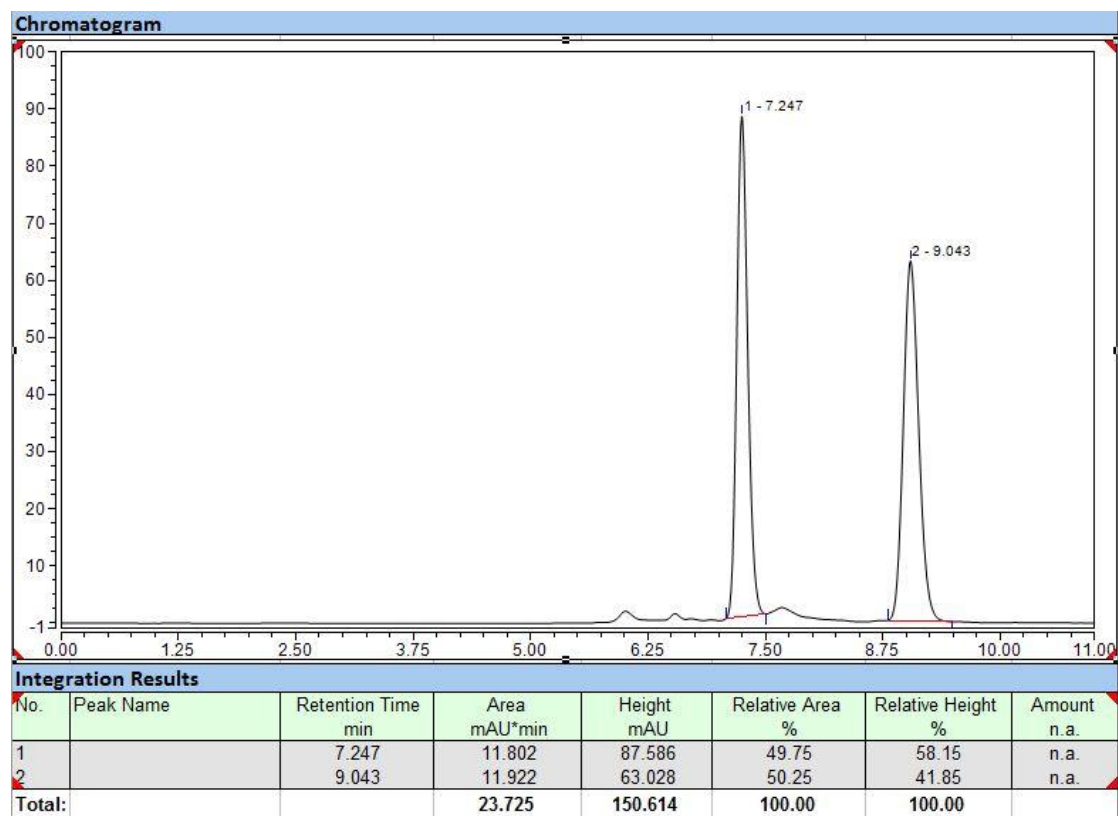
HPLC (Chiralpak AD-H): t_R = 11.9 (major), 22.1 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



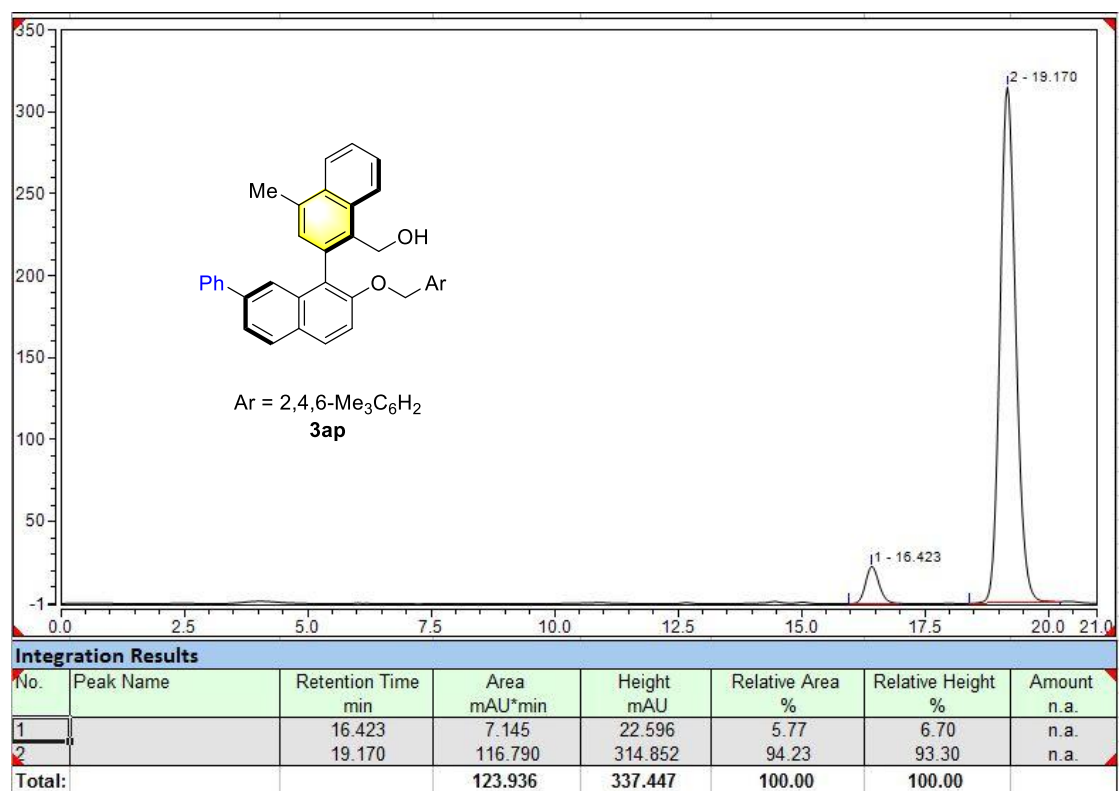
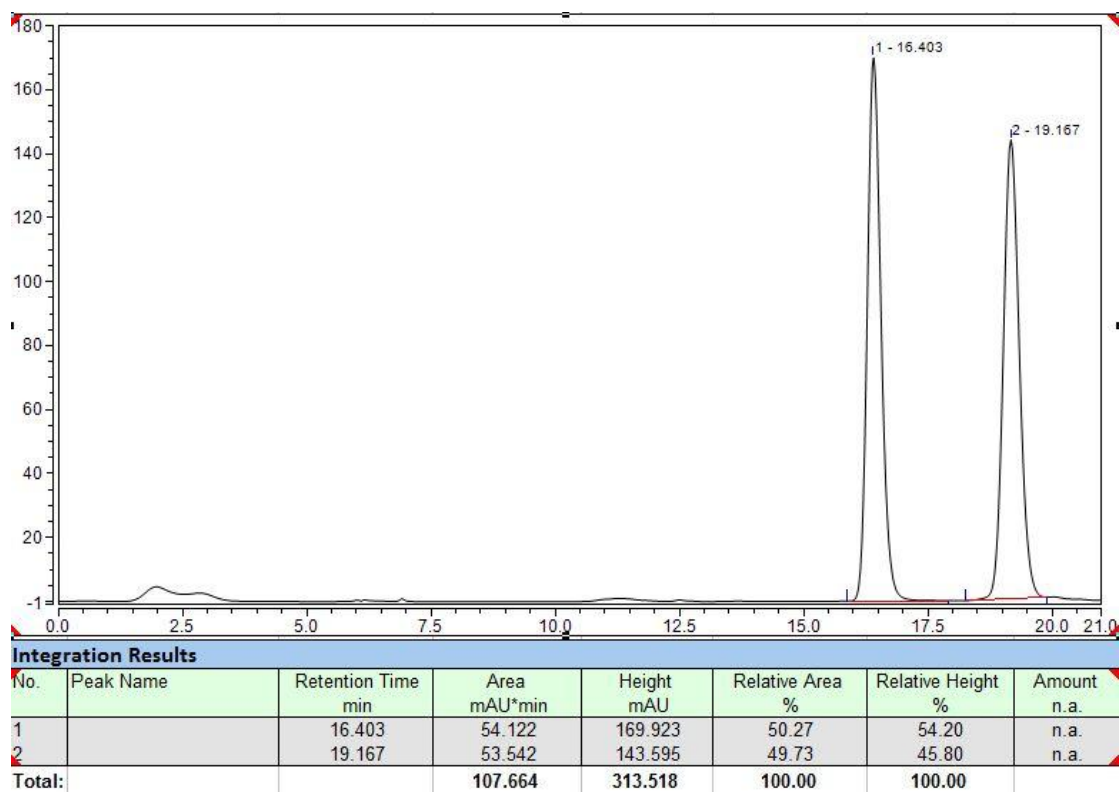
HPLC (Chiralpak AD-H): t_R = 12.2 (major), 22.3 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



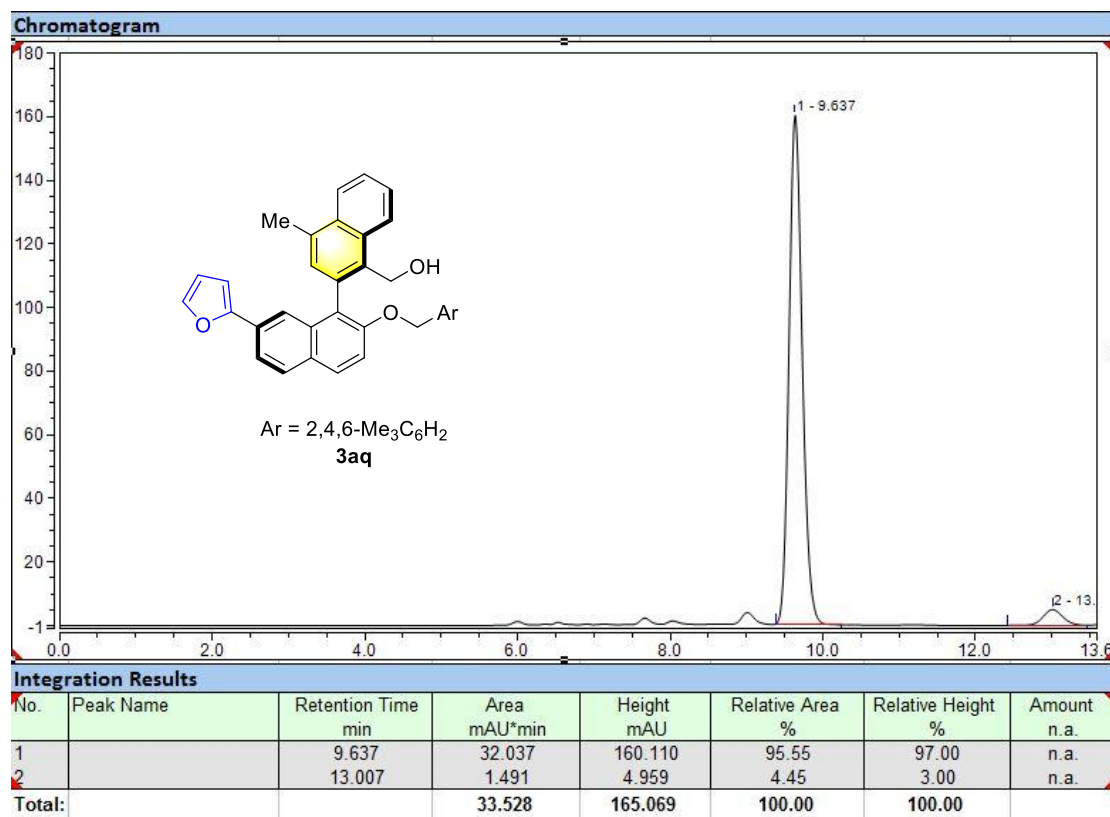
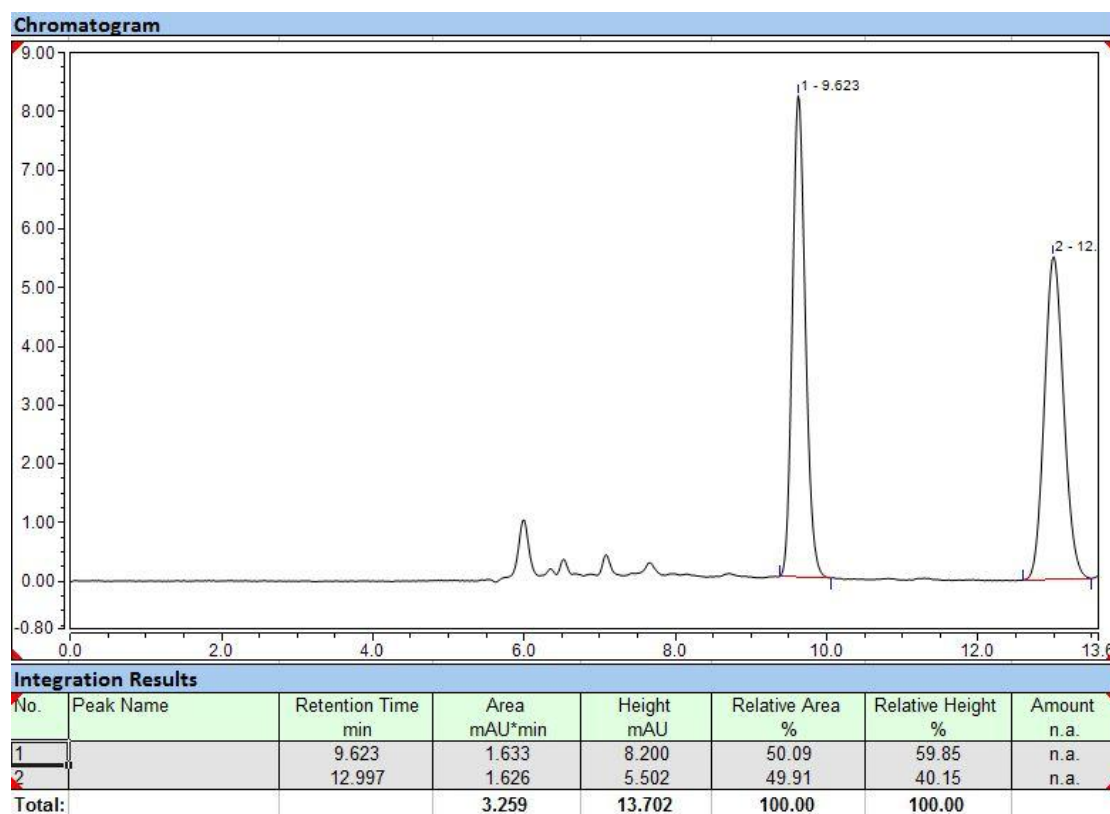
HPLC (Chiralpak AD-H): t_R = 7.2 (major), 9.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



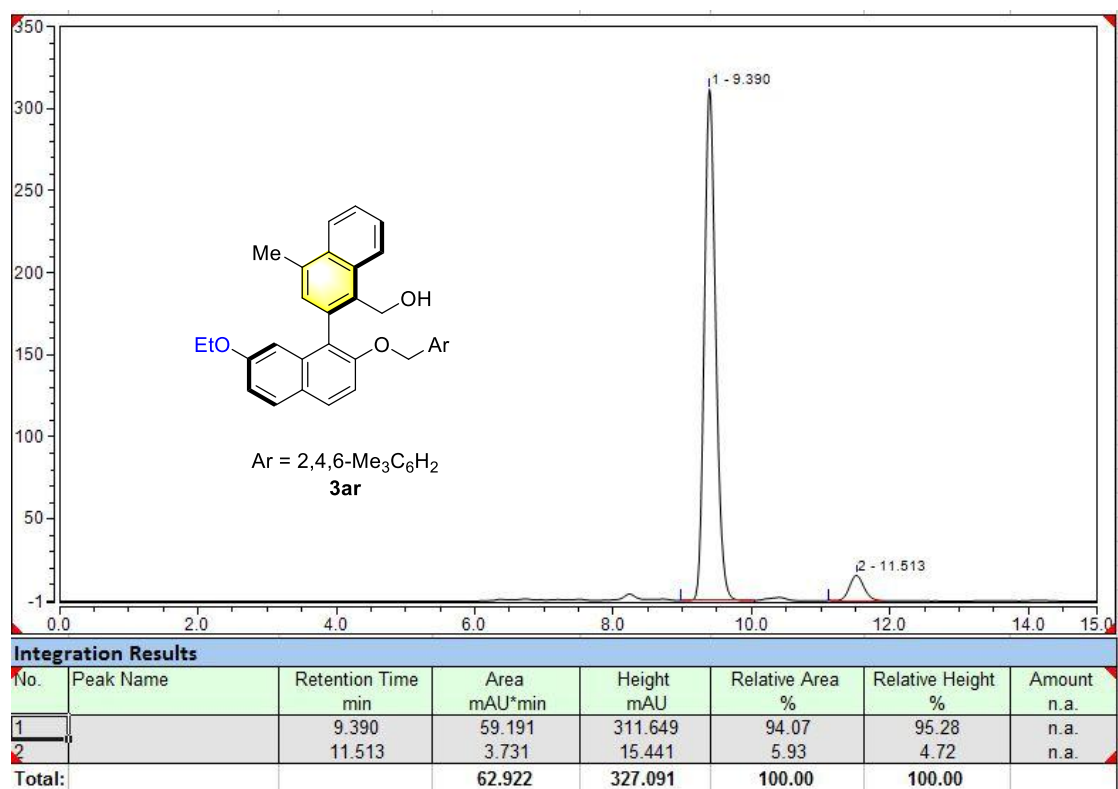
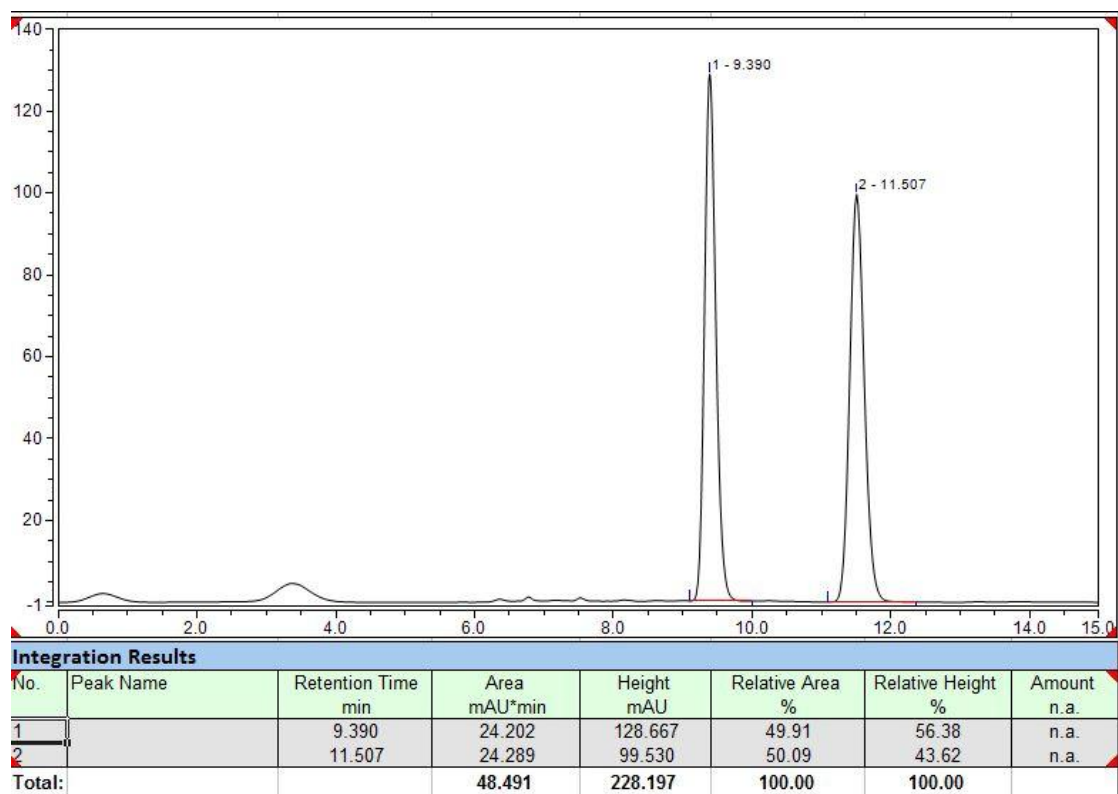
HPLC (Chiral MD): t_R = 16.4 (minor), 19.2 (major)

Condition: hexane/isopropanol = 95/5, flow rate 0.5 mL/min, 25°C.



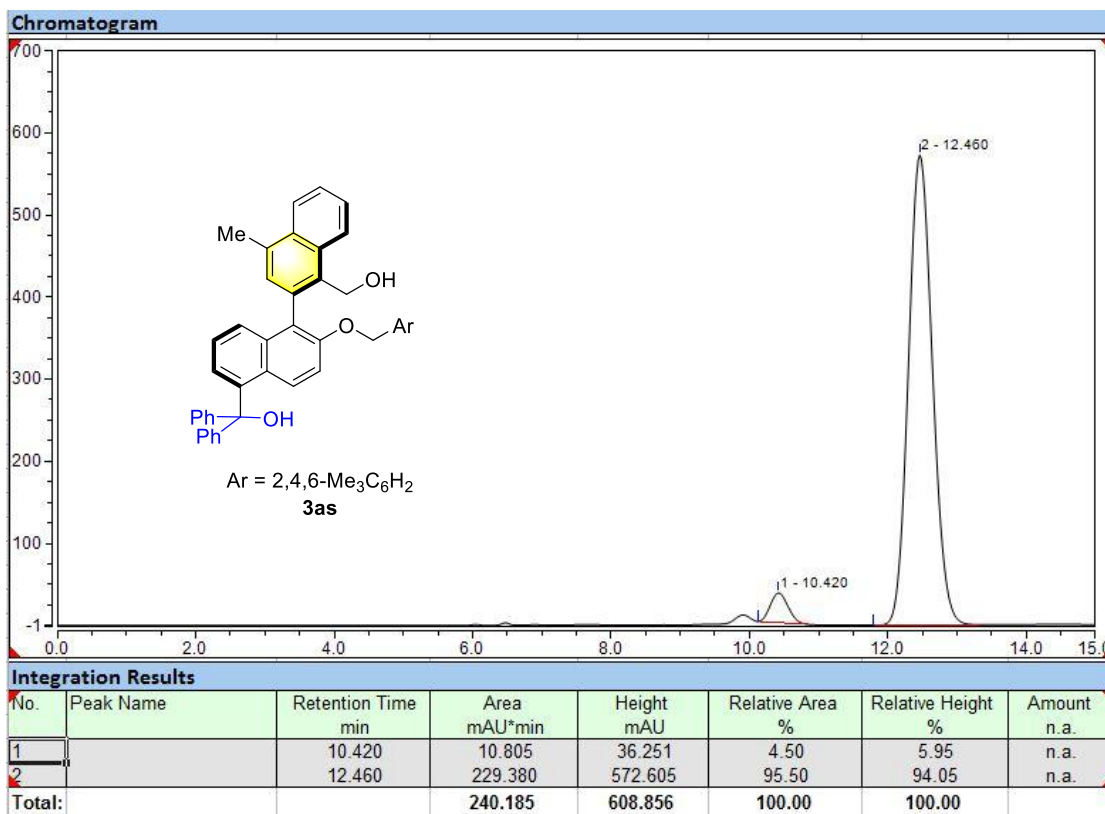
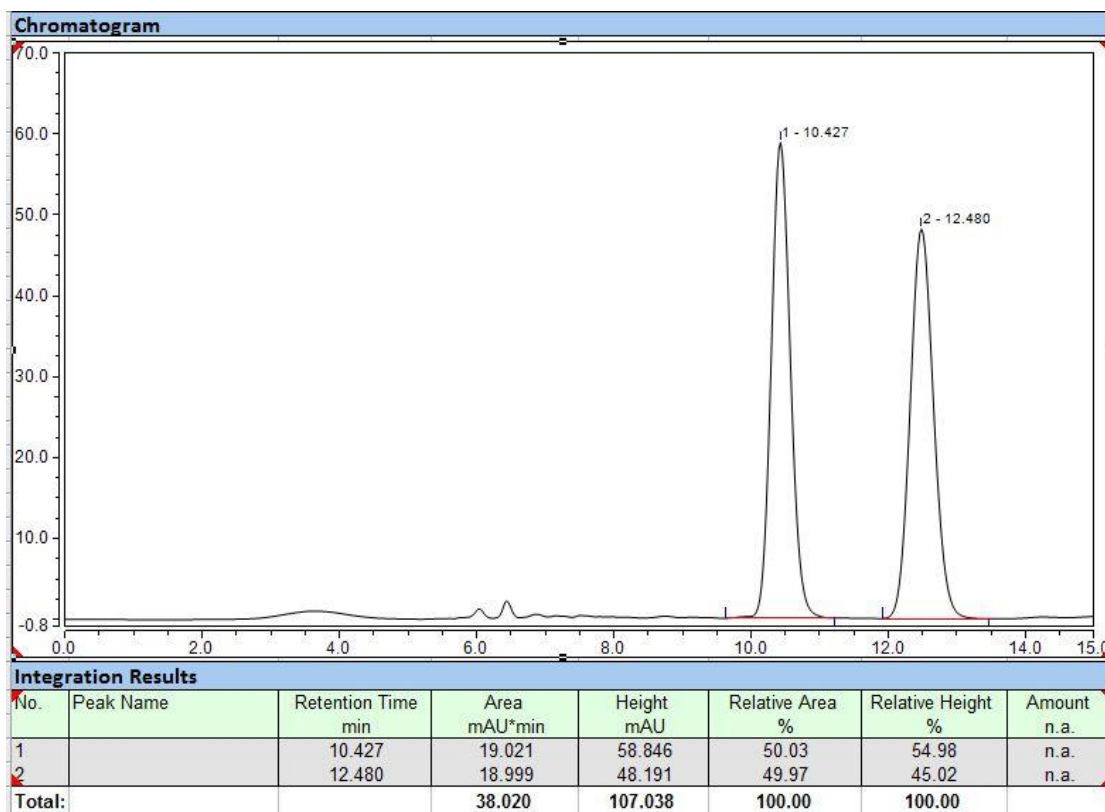
HPLC (Chiralpak AD-H): t_R = 9.6 (major), 13.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



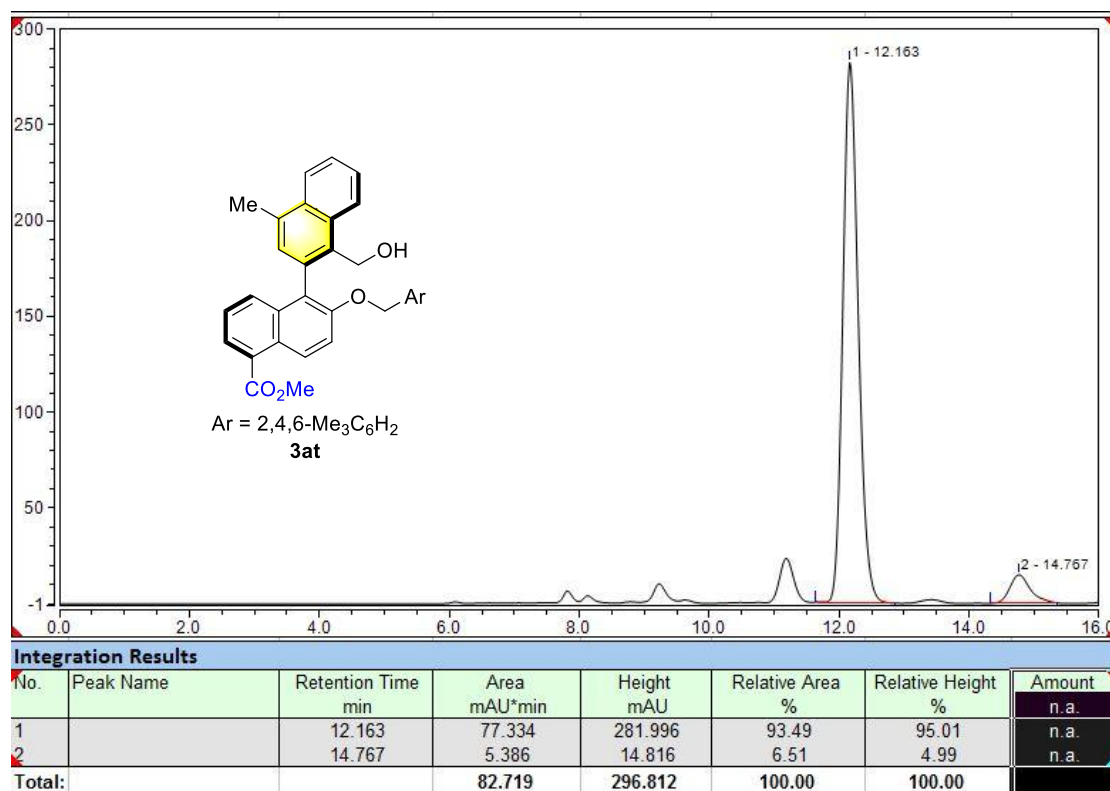
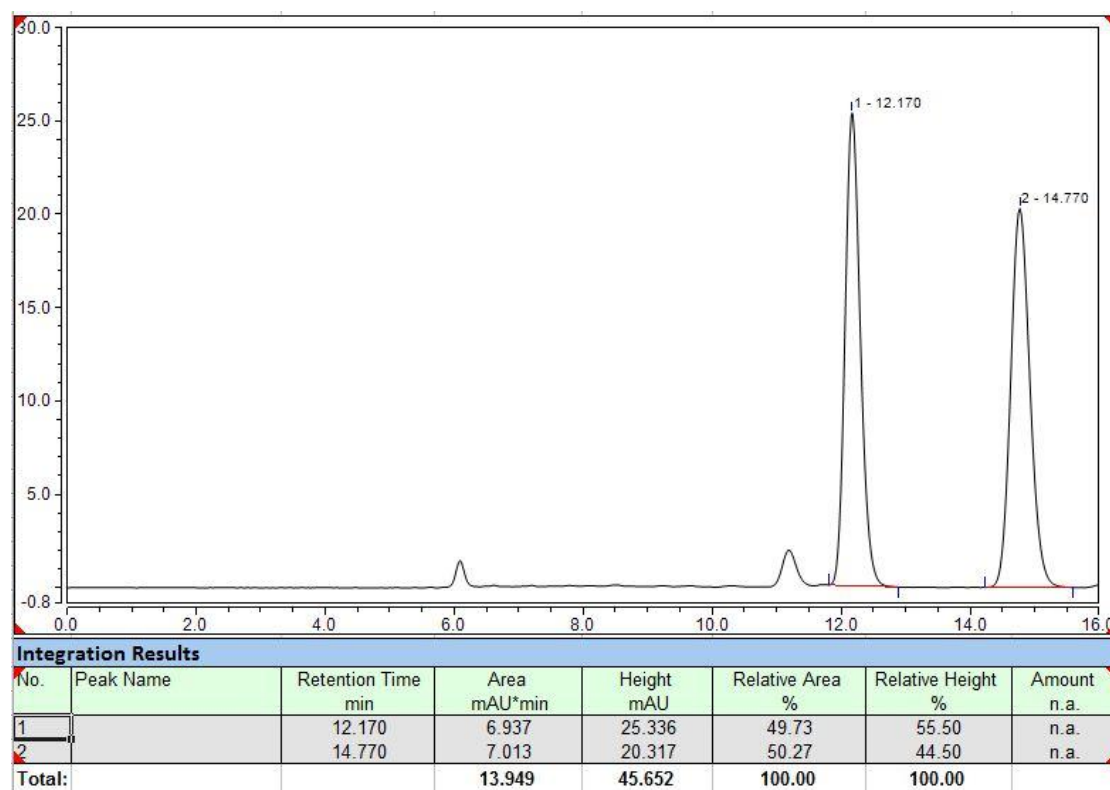
HPLC (Chiralpak AD-H): t_R = 9.4 (major), 11.5 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



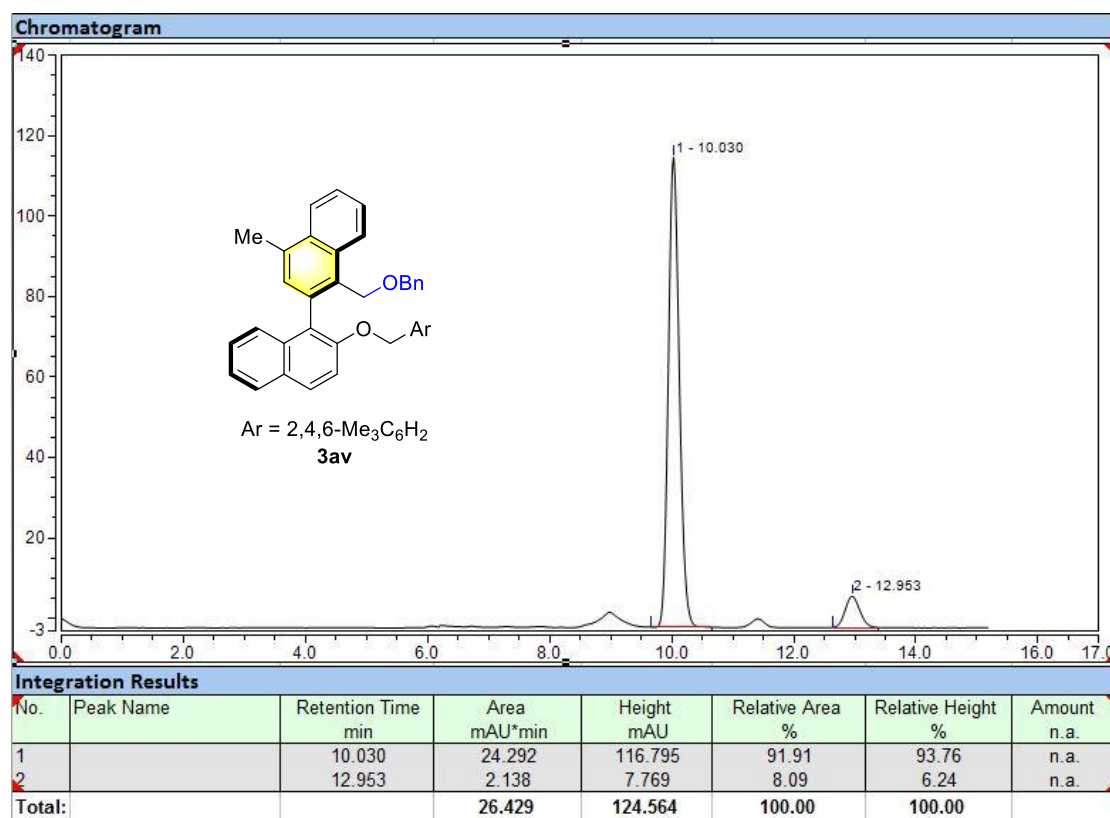
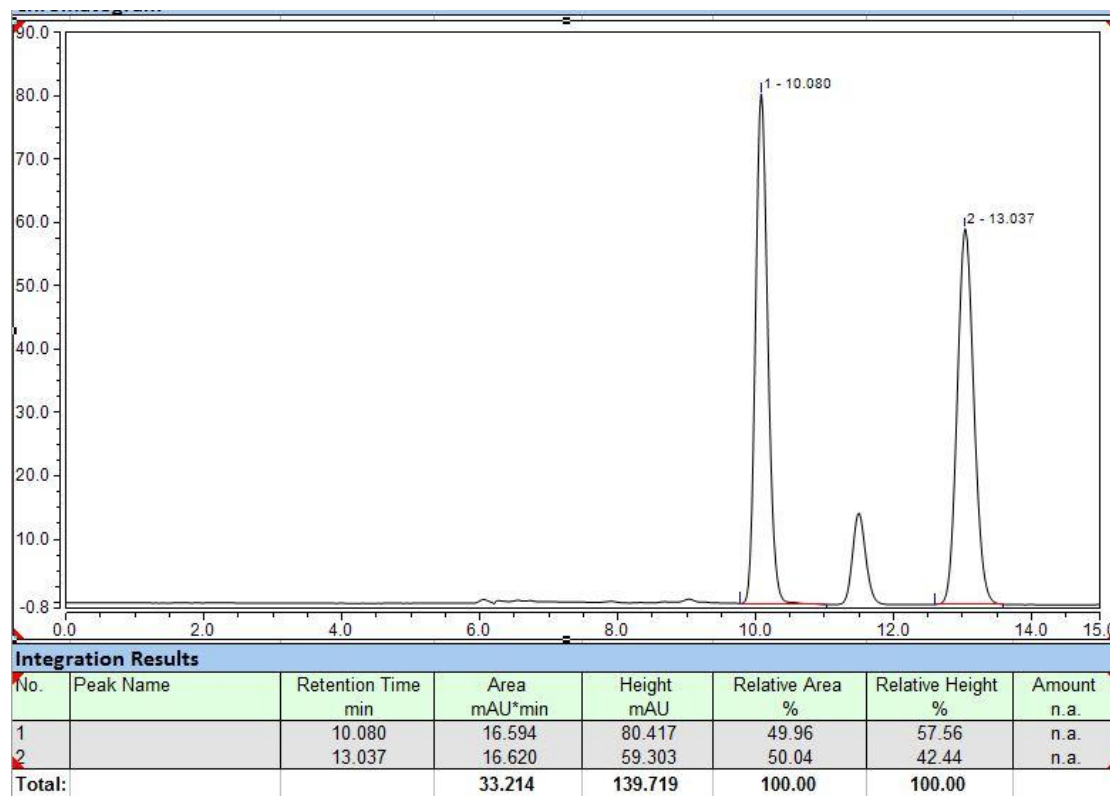
HPLC (Chiralpak AD-H): t_R = 10.4 (minor), 12.5 (major)

Condition: hexane/isopropanol = 60/40, flow rate 0.5 mL/min, 25°C.



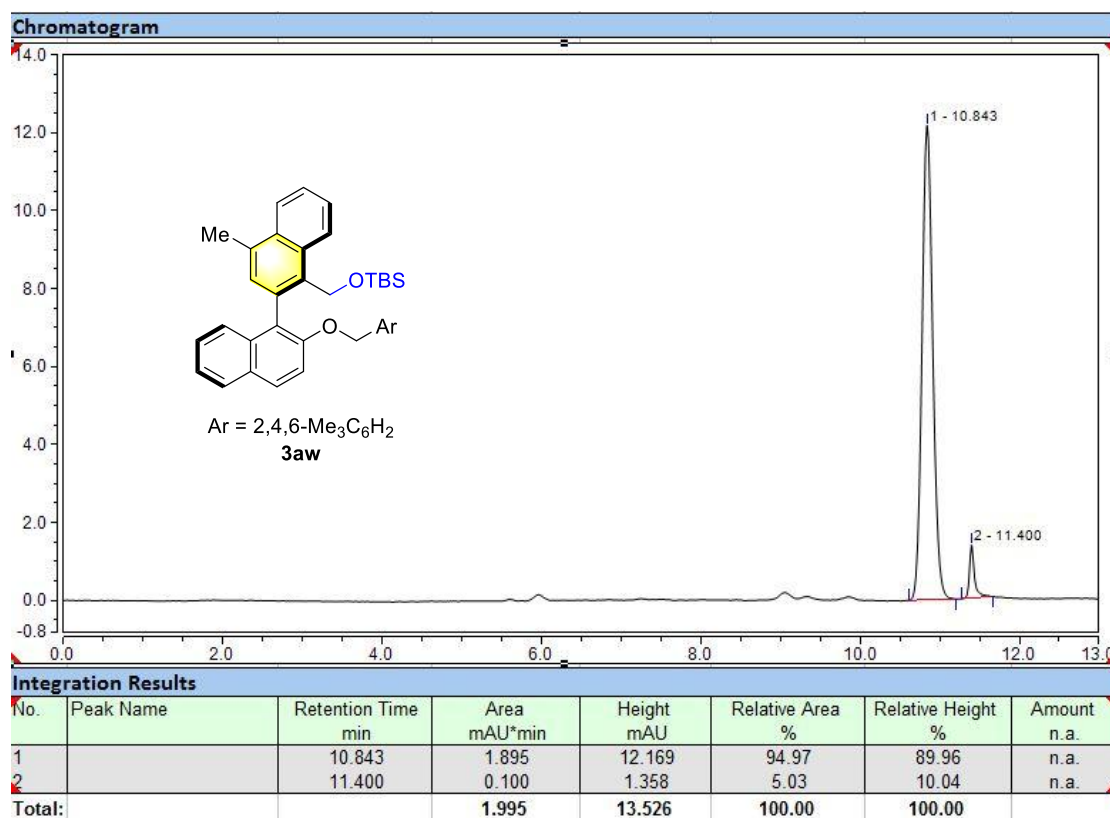
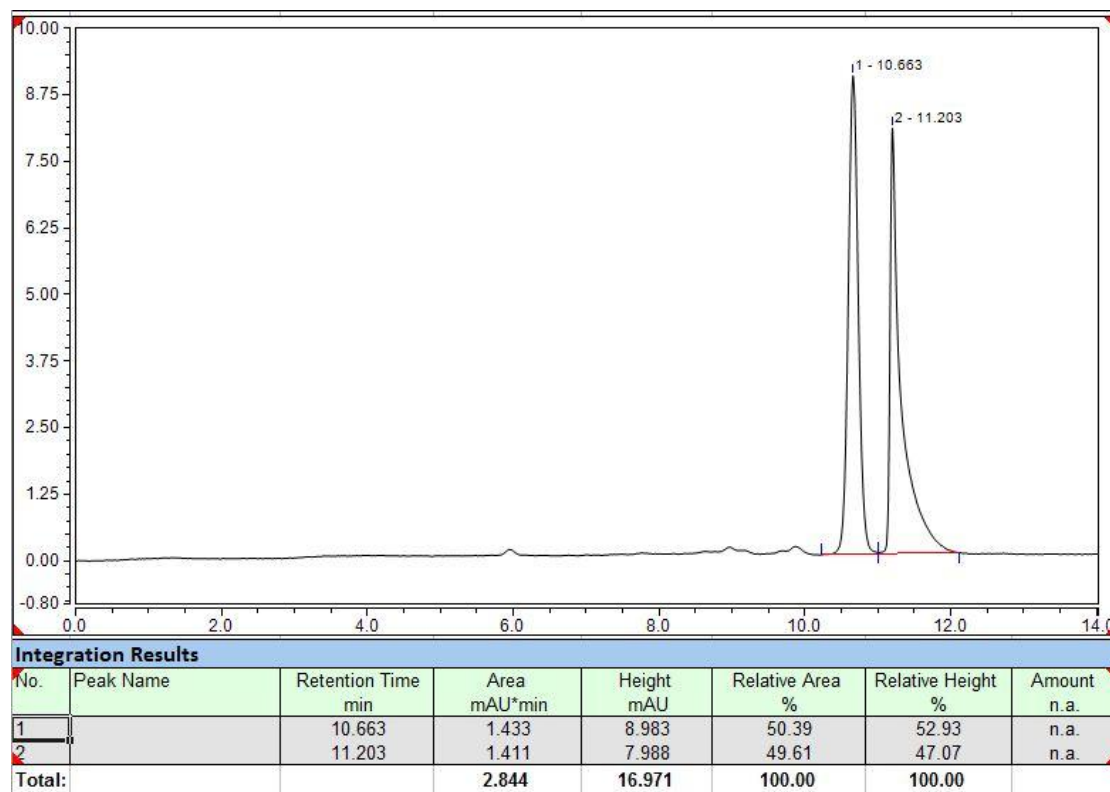
HPLC (Chiralpak AD-H): t_R = 12.2 (major), 14.8 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



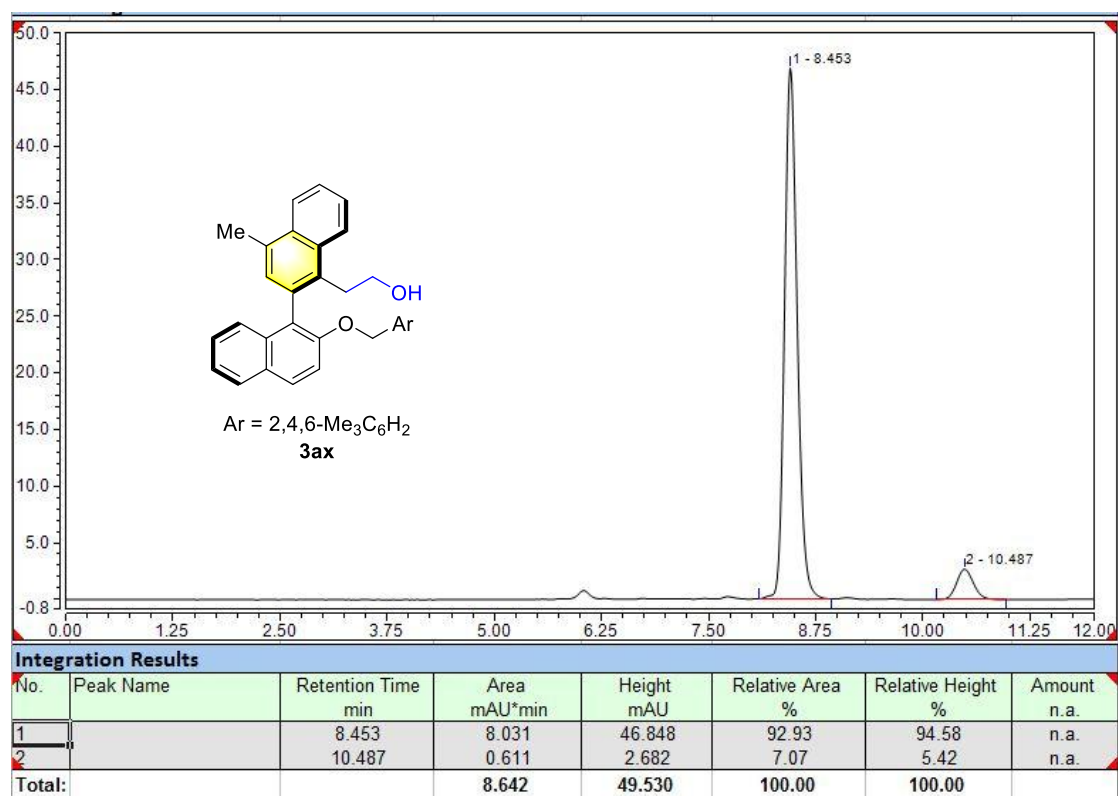
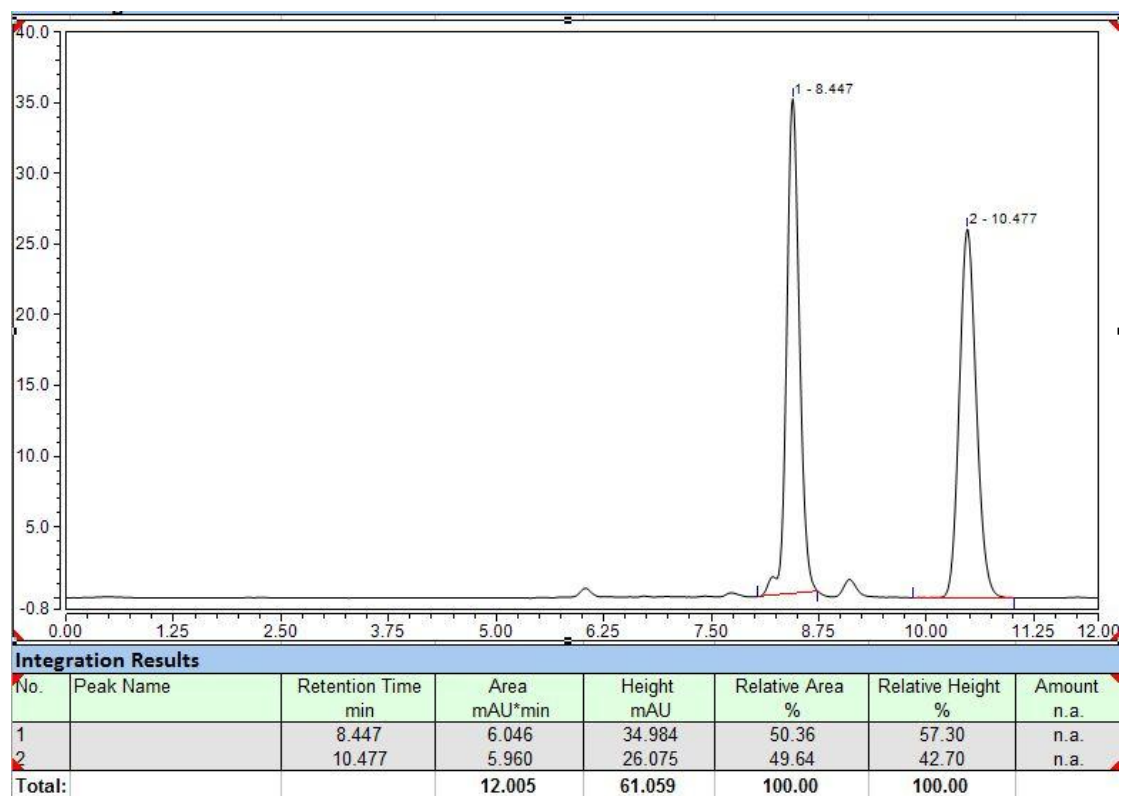
HPLC (Chiralpak AD-H): t_R = 10.0 (major), 13.0 (minor)

Condition: hexane/isopropanol = 96/4, flow rate 0.5 mL/min, 25°C.



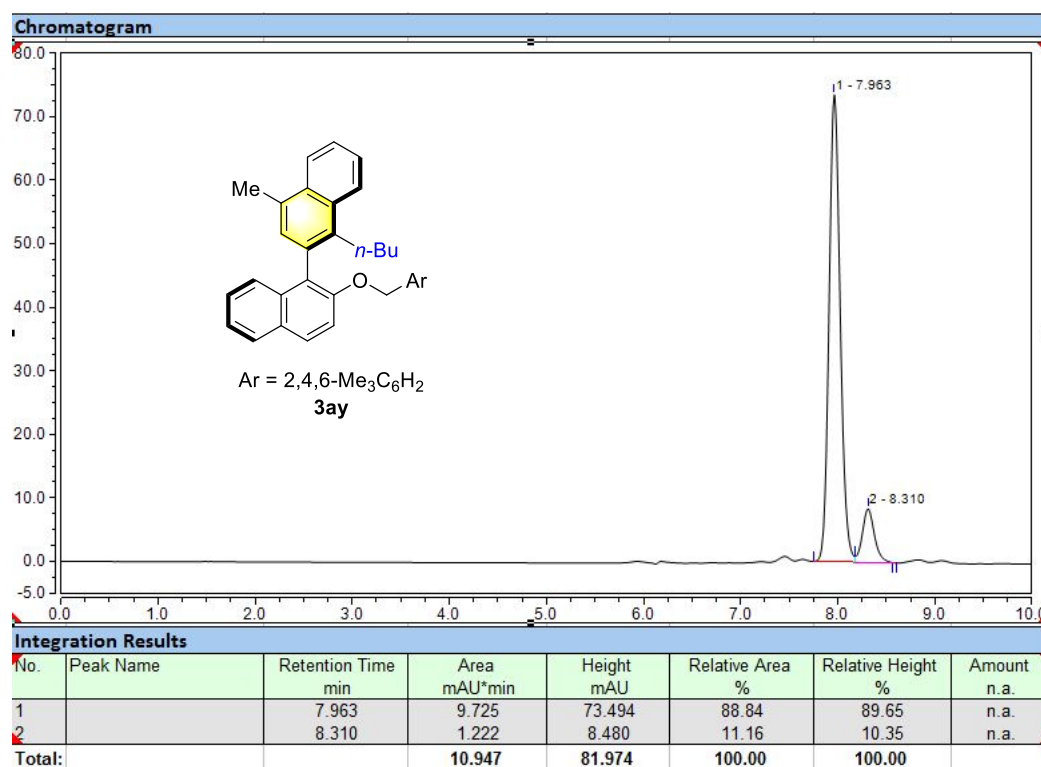
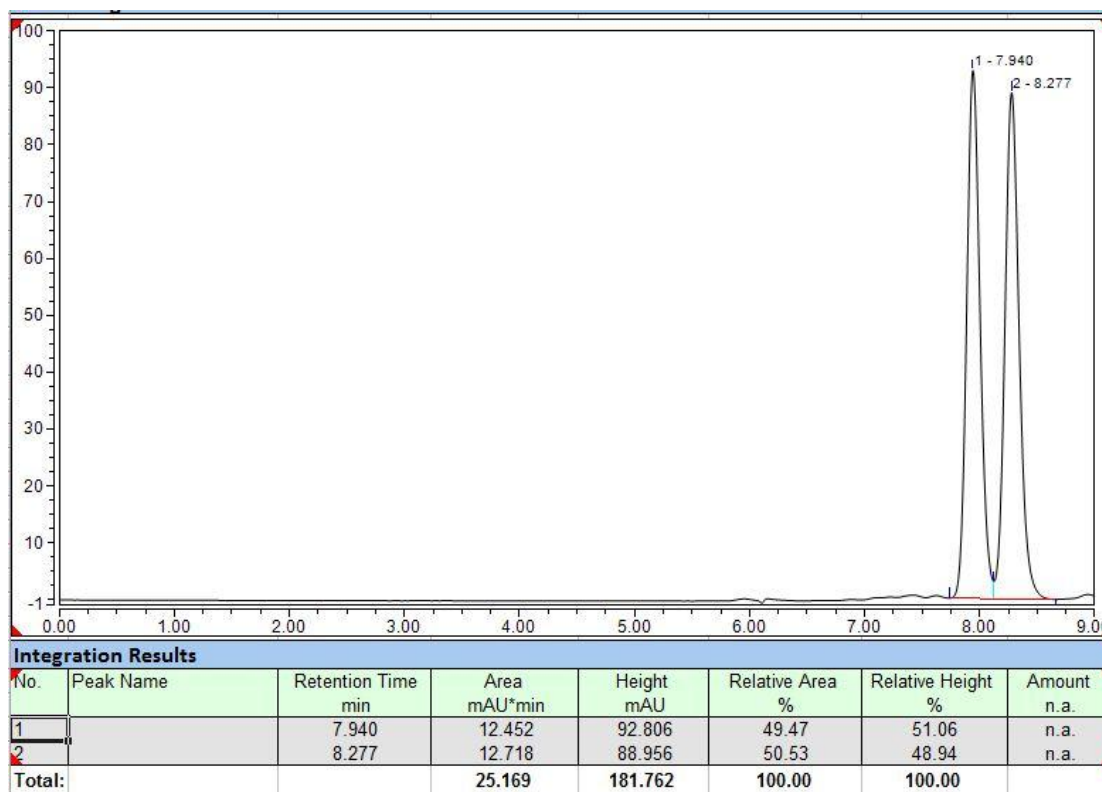
HPLC (Chiralpak AD-H): t_R = 10.8 (major), 11.4 (minor)

Condition: hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 25°C.



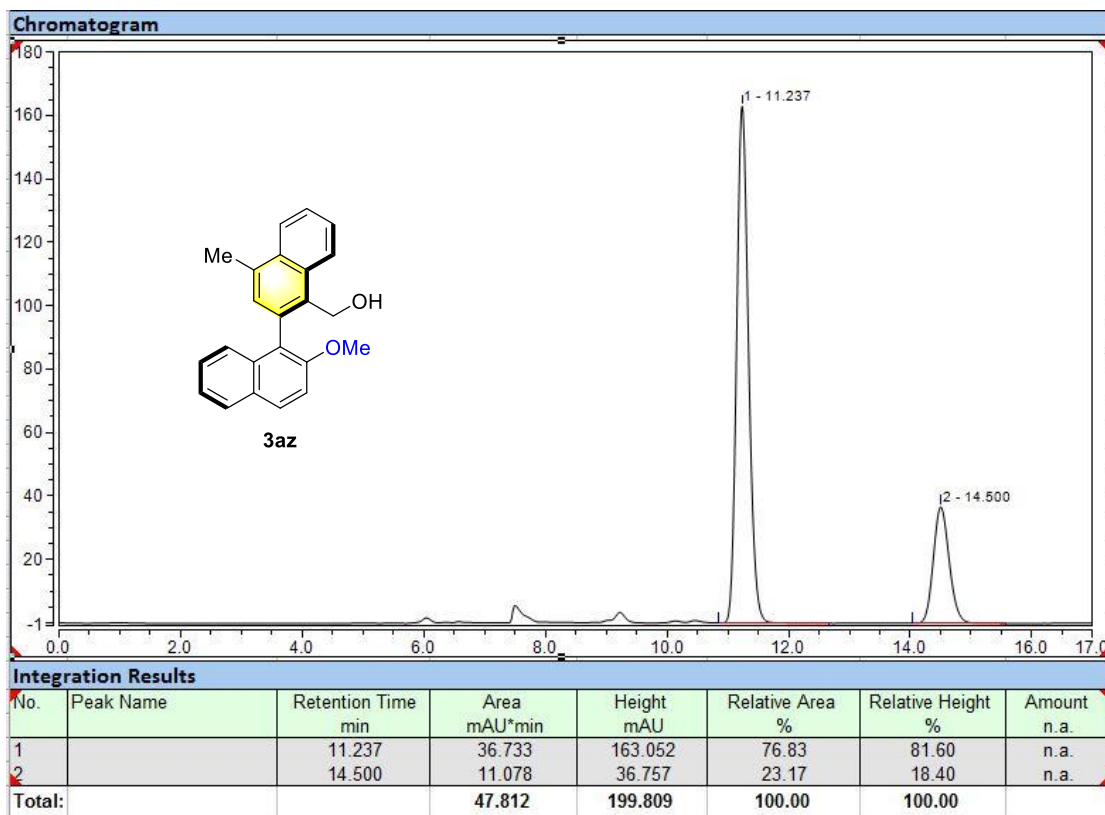
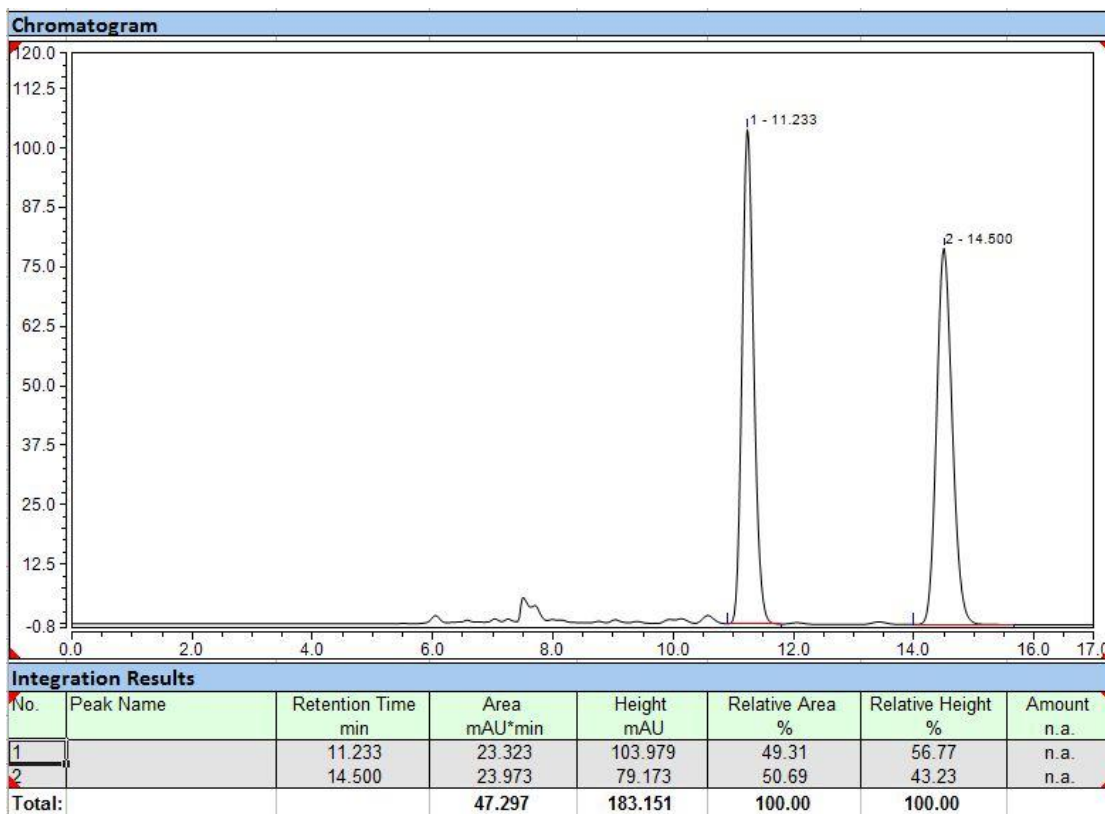
HPLC (Chiralpak AD-H): t_R = 8.5 (major), 10.5 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



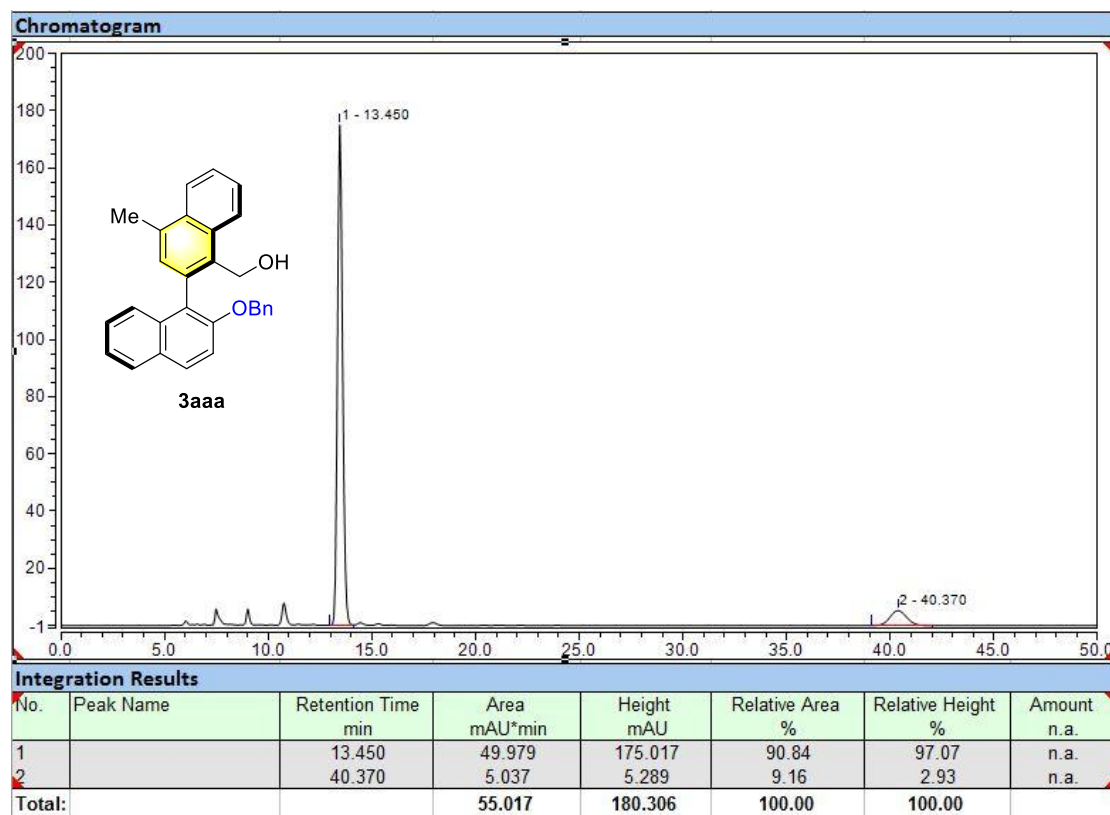
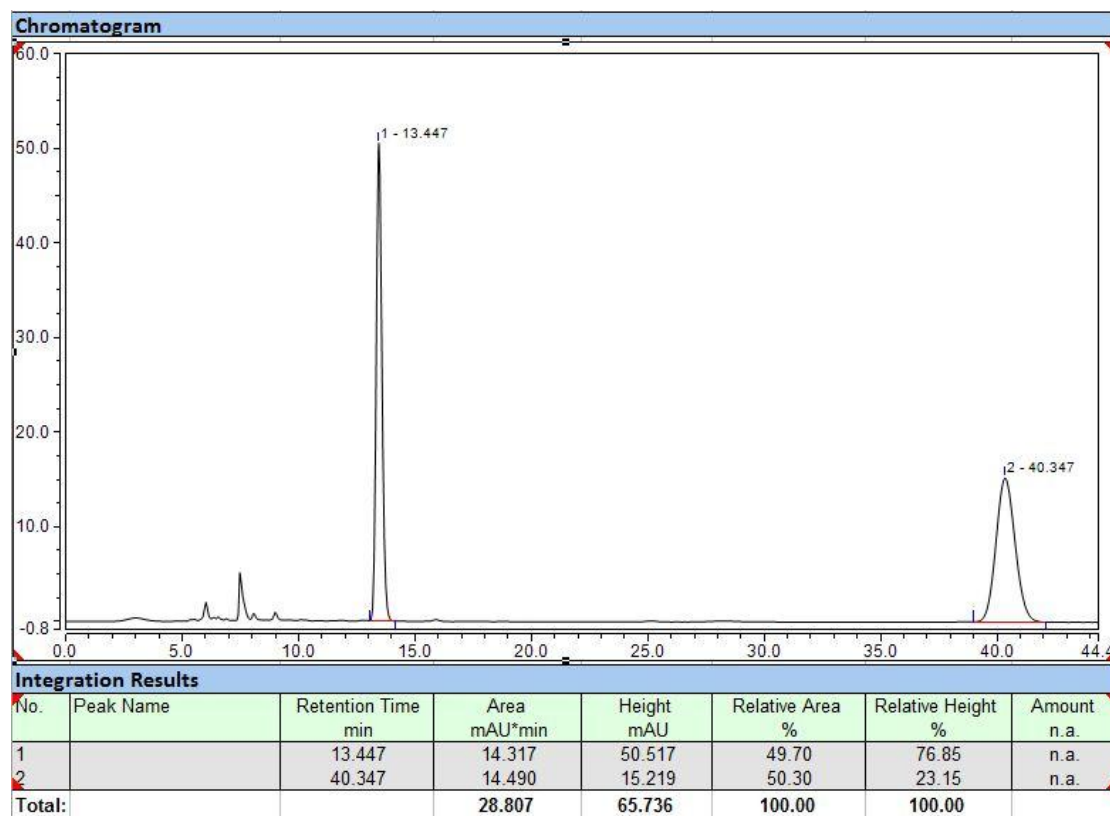
HPLC (Chiral MD): t_R = 8.0 (major), 8.3 (minor)

Condition: hexane/isopropanol = 96/4, flow rate 0.5 mL/min, 25°C.



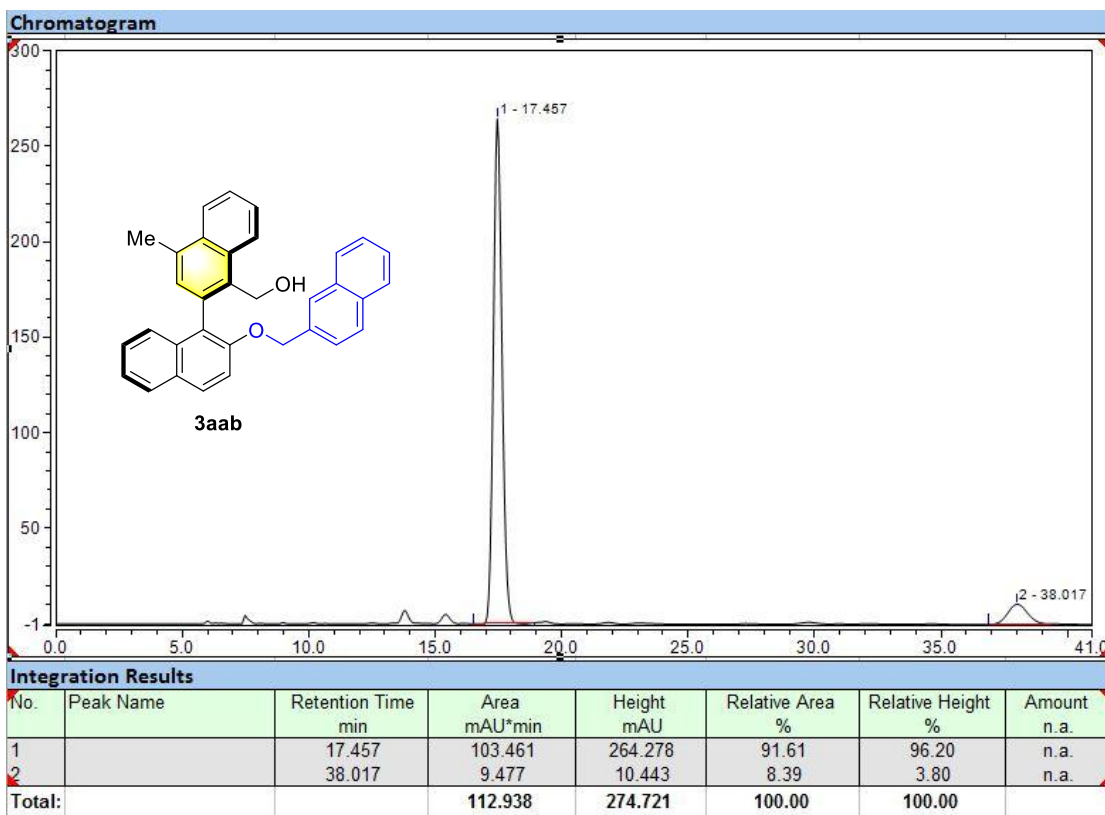
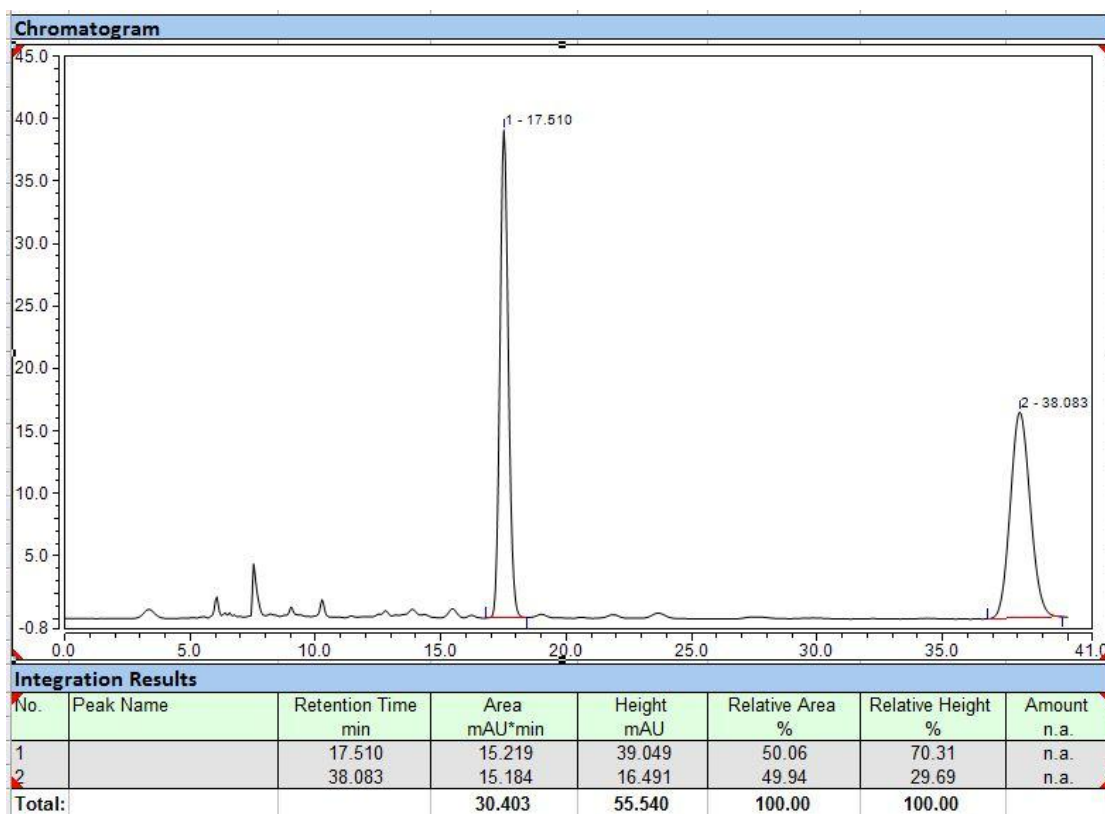
HPLC (Chiralpak AD-H): t_R = 11.2 (major), 14.5 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



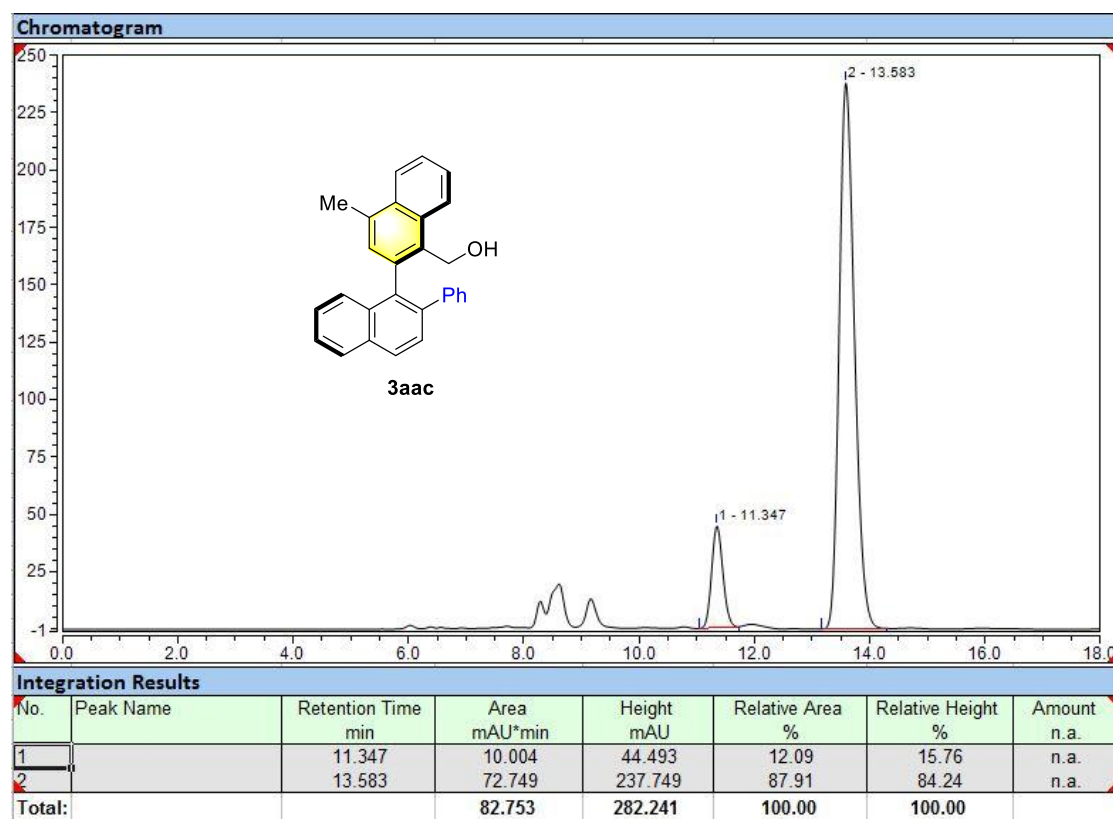
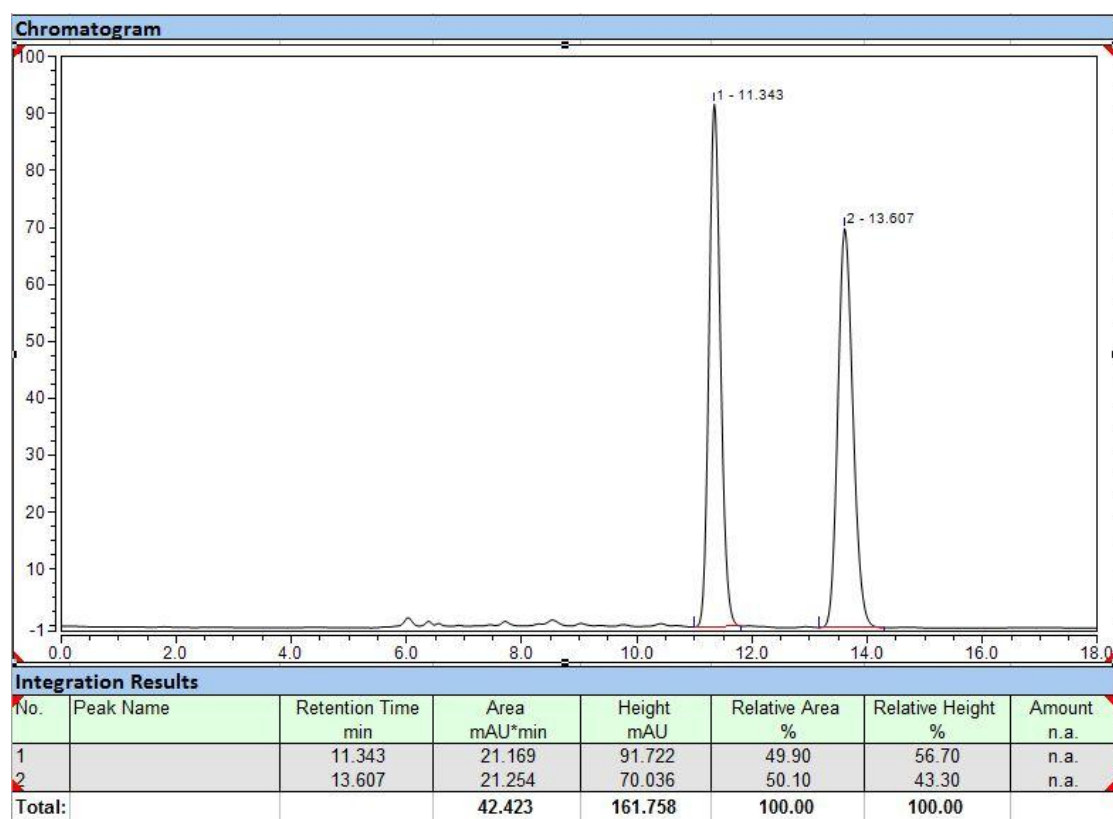
HPLC (Chiralpak AD-H): t_R = 13.5 (major), 40.4 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



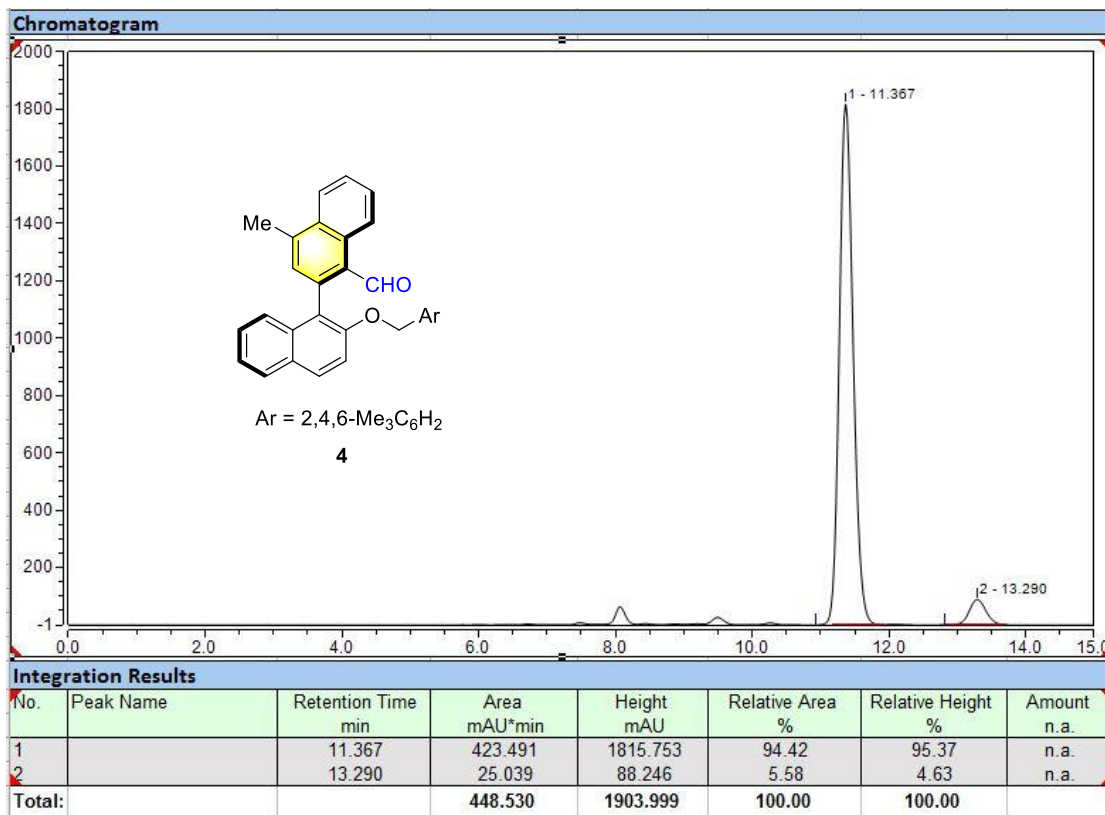
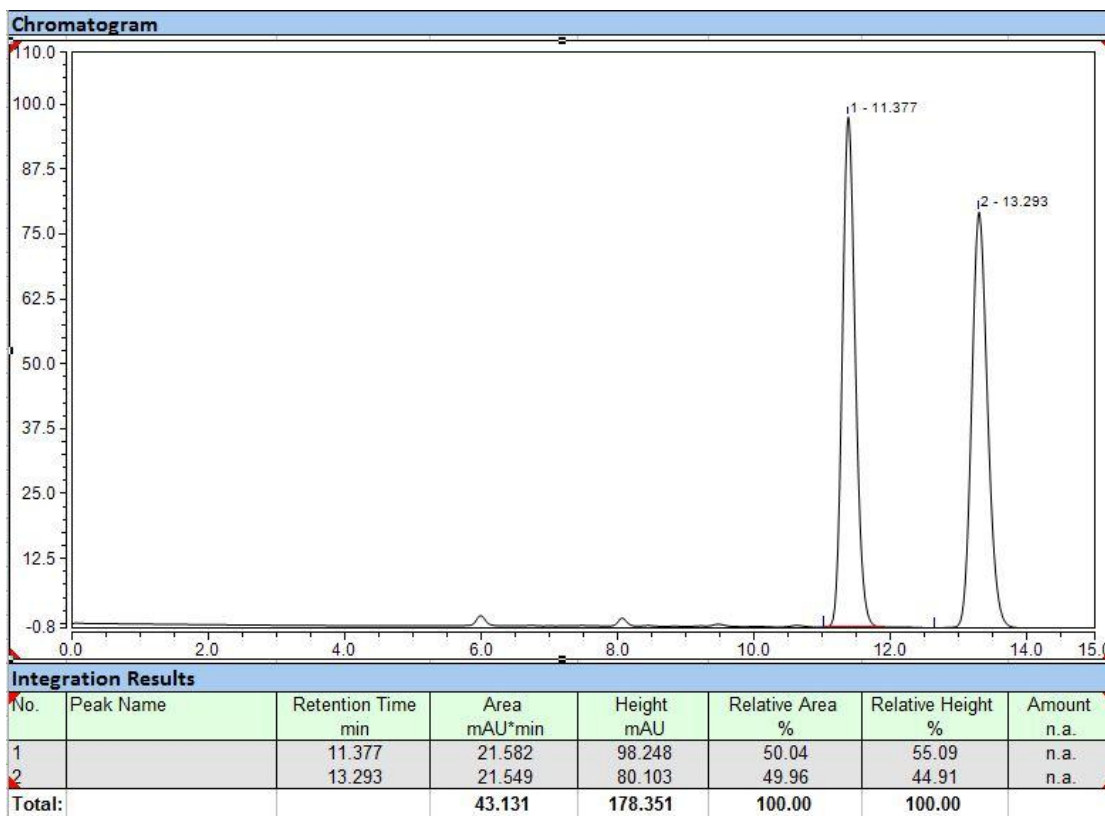
HPLC (Chiral MD): t_R = 17.5 (major), 38.0 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



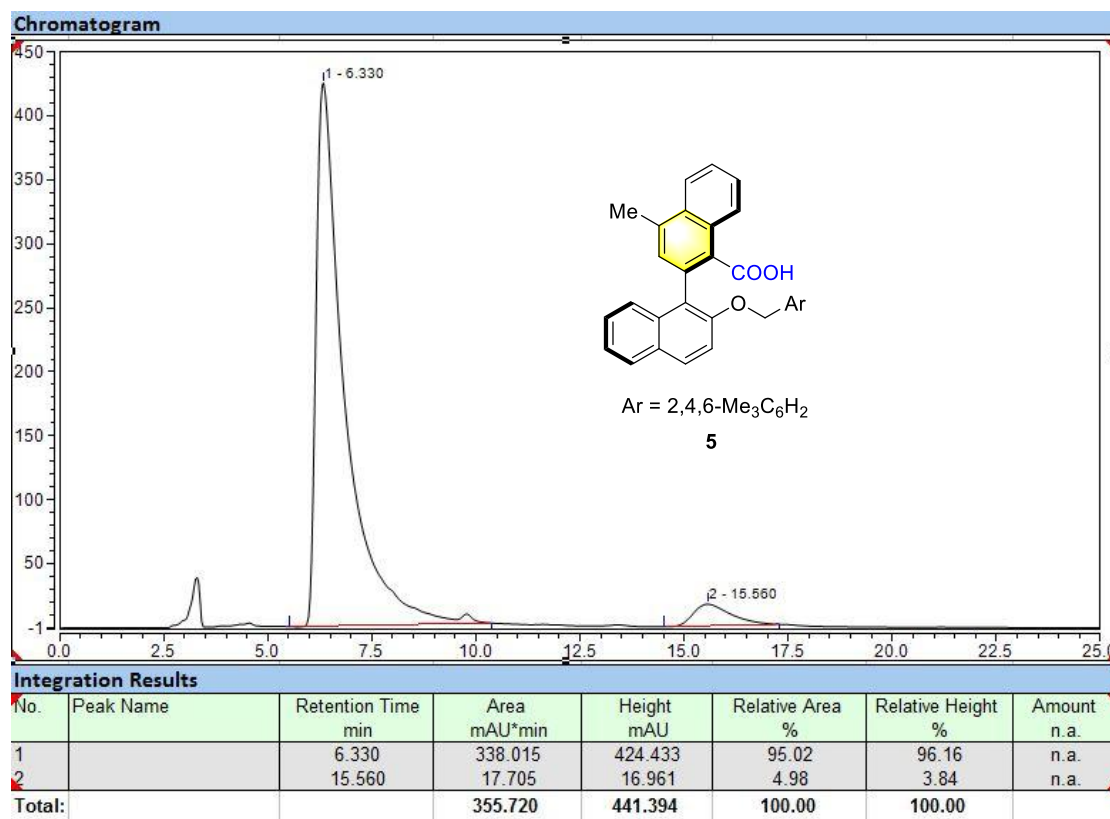
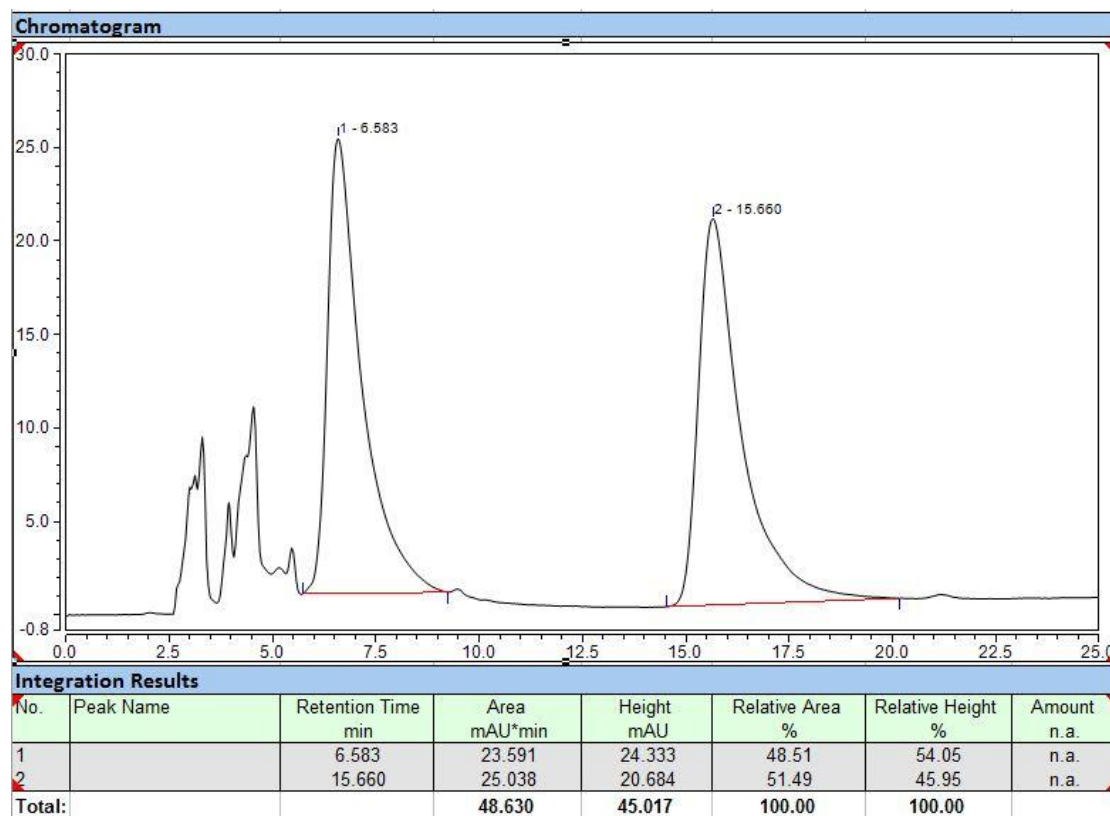
HPLC (Chiralpak AD-H): t_R = 11.3 (minor), 13.6 (major)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



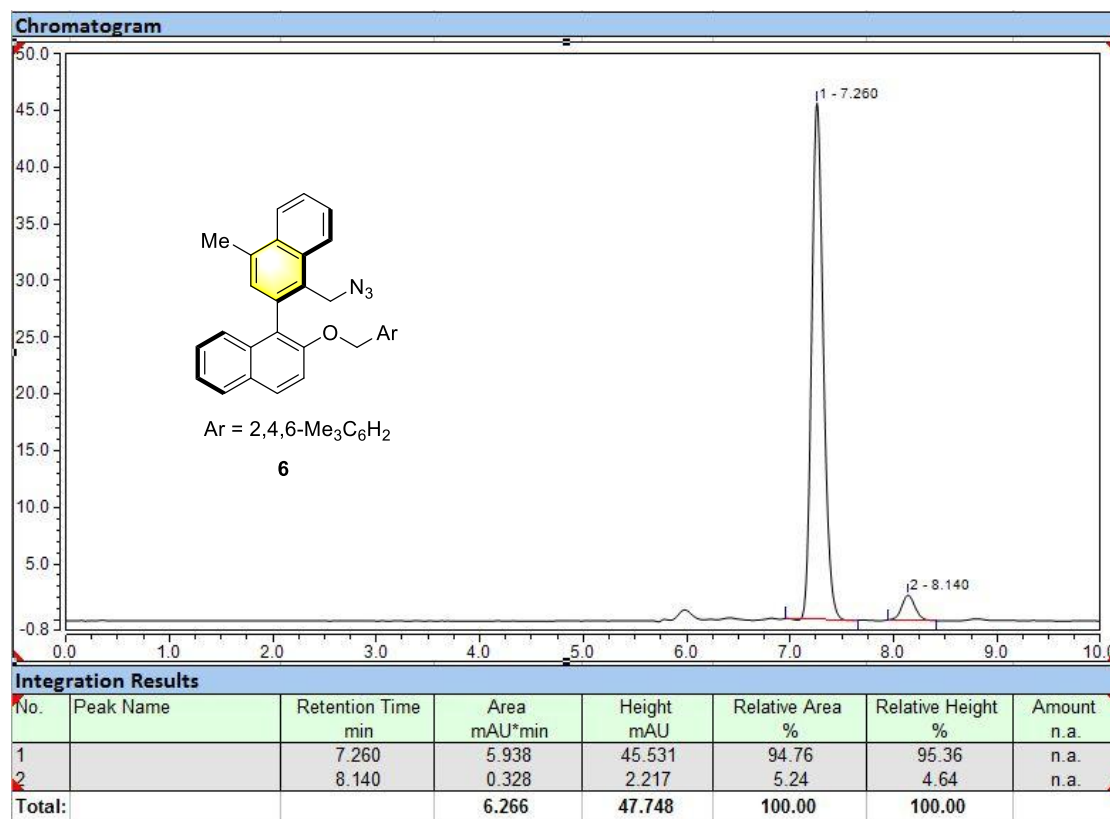
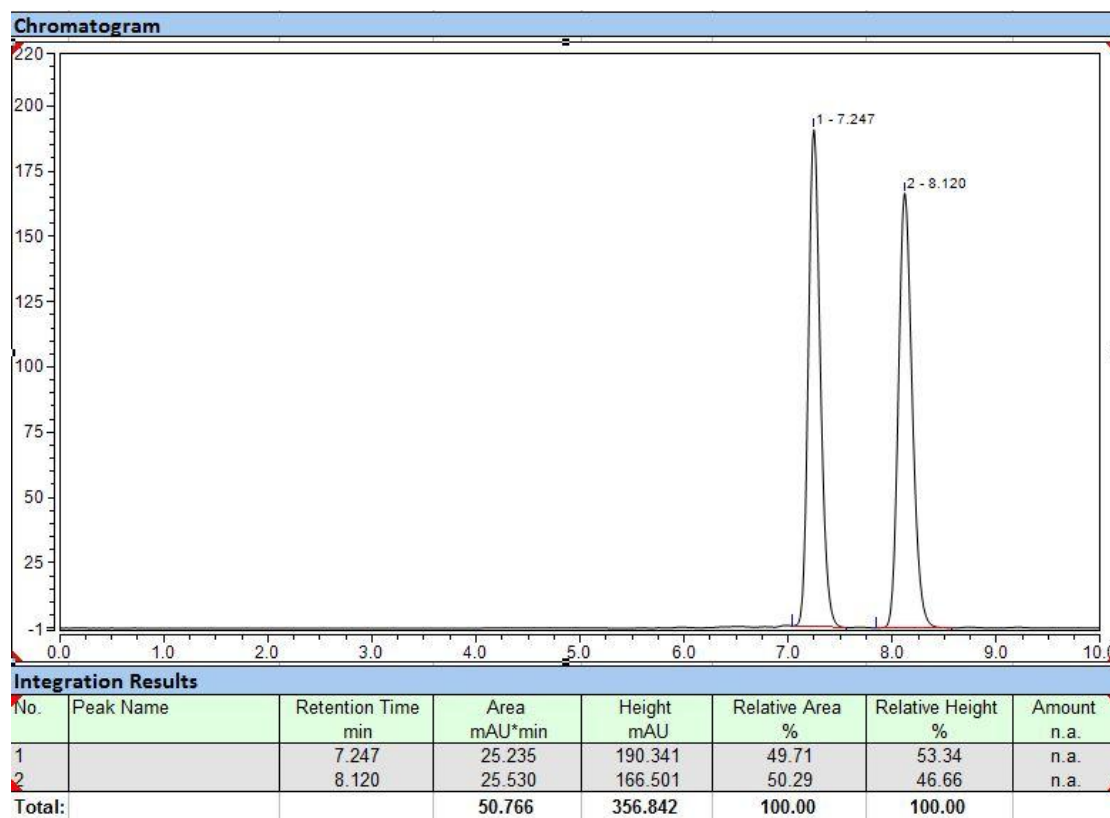
HPLC (Chiralpak AD-H): t_R = 11.4 (major), 13.3 (minor)

Condition: hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 25°C.



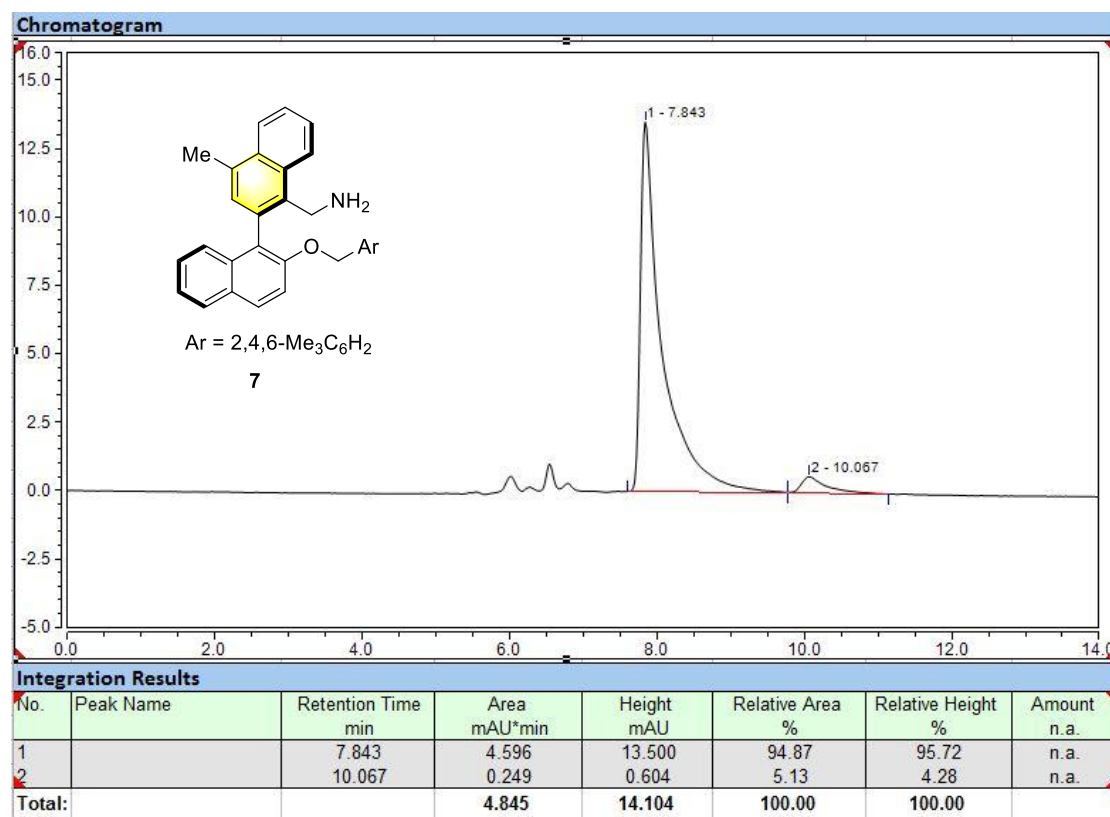
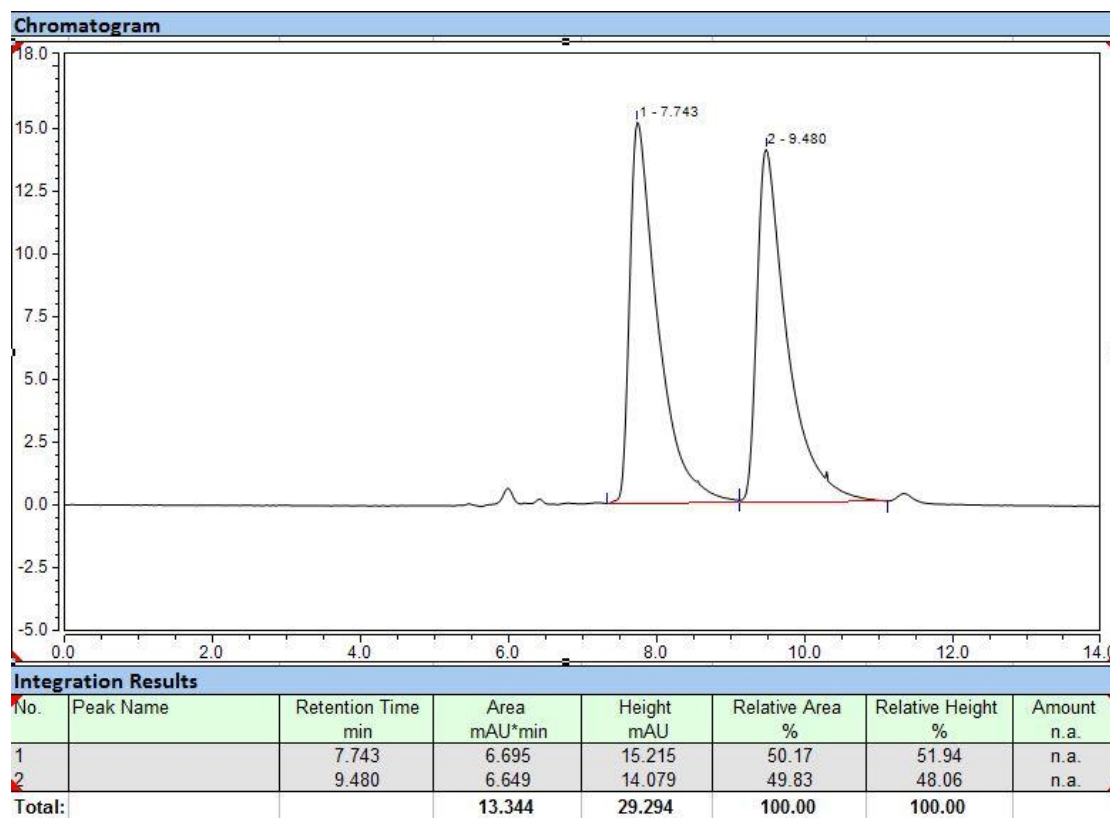
HPLC (Chiralpak IA): t_R = 6.3 (major), 15.6 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



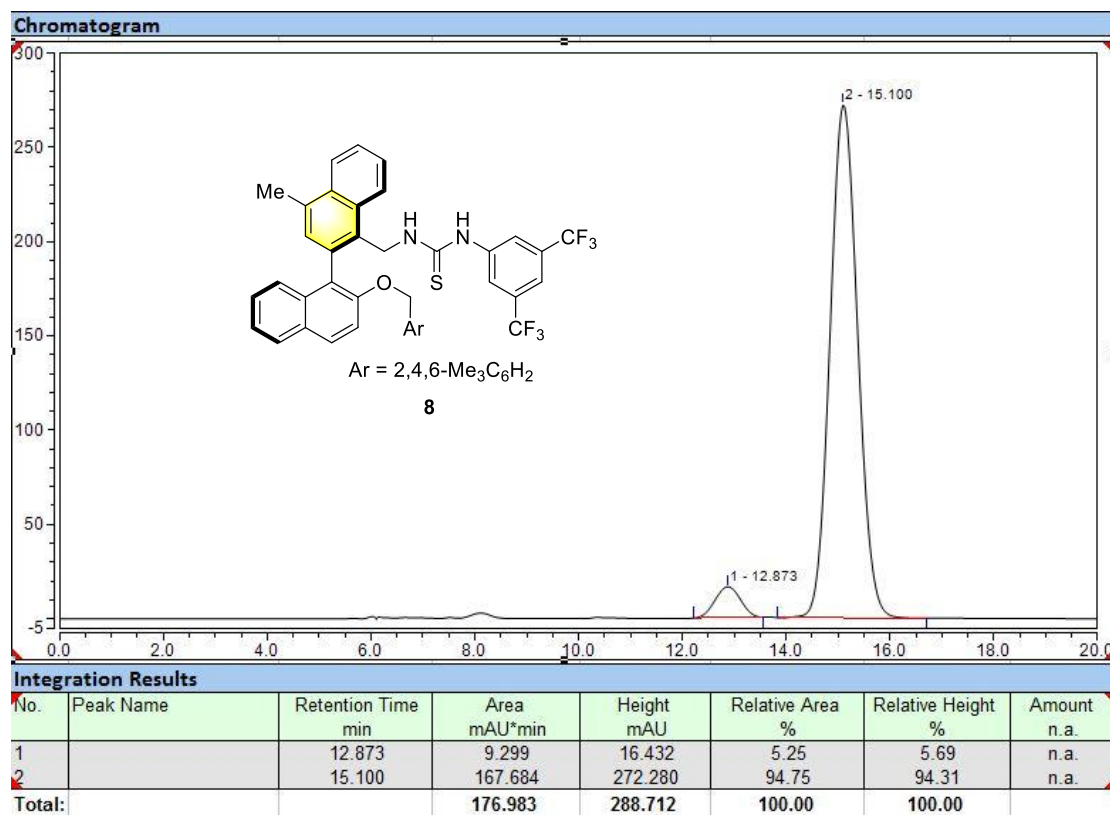
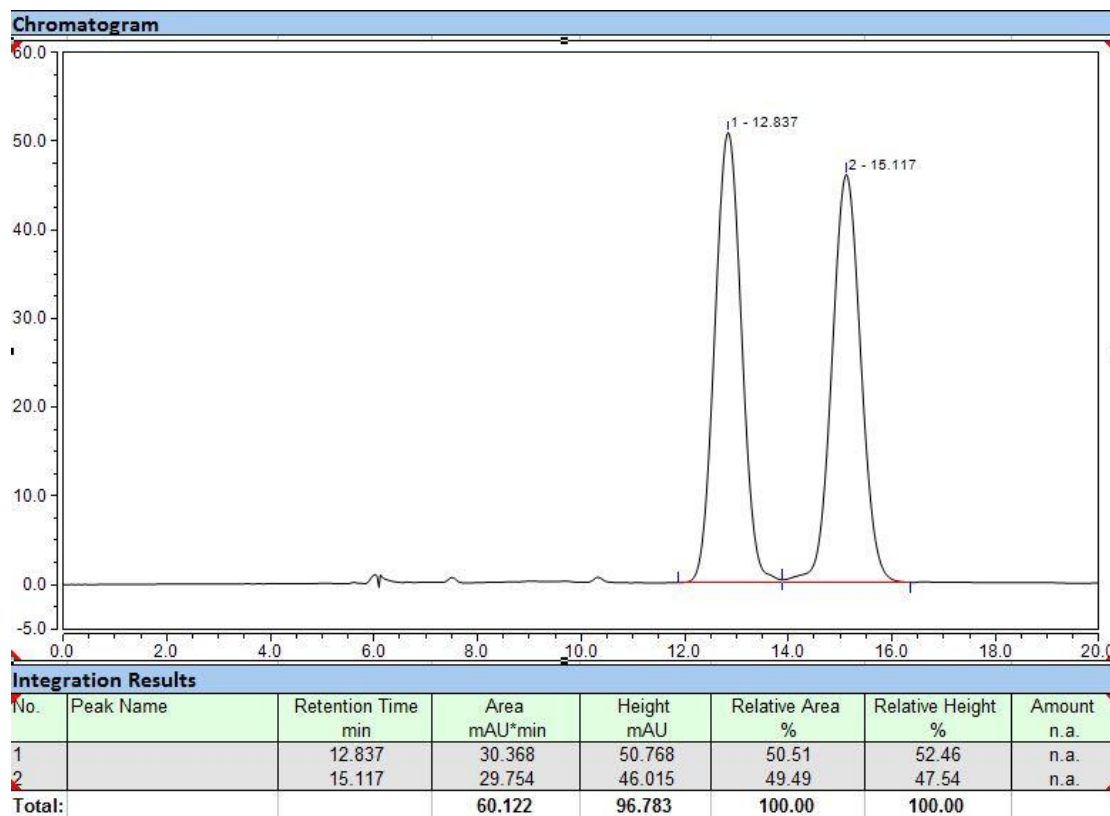
HPLC (Chiralpak AD-H): t_R = 7.3 (major), 8.1 (minor)

Condition: hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 25°C.



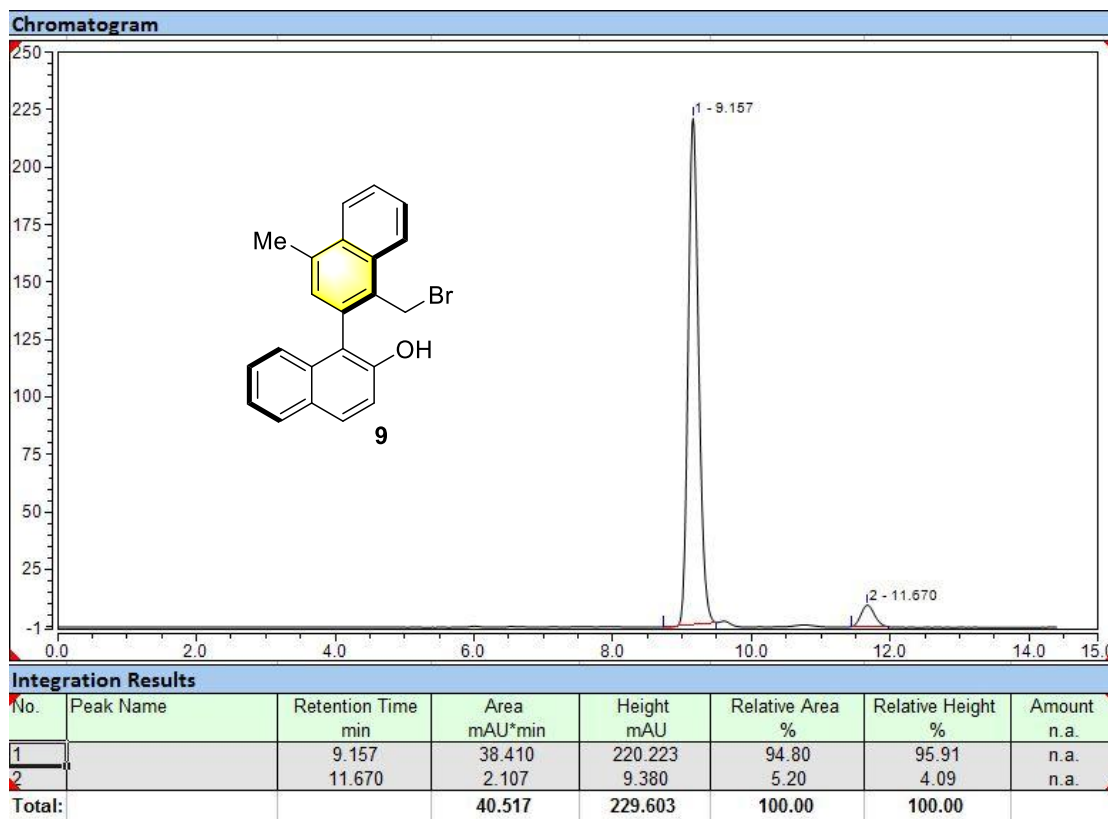
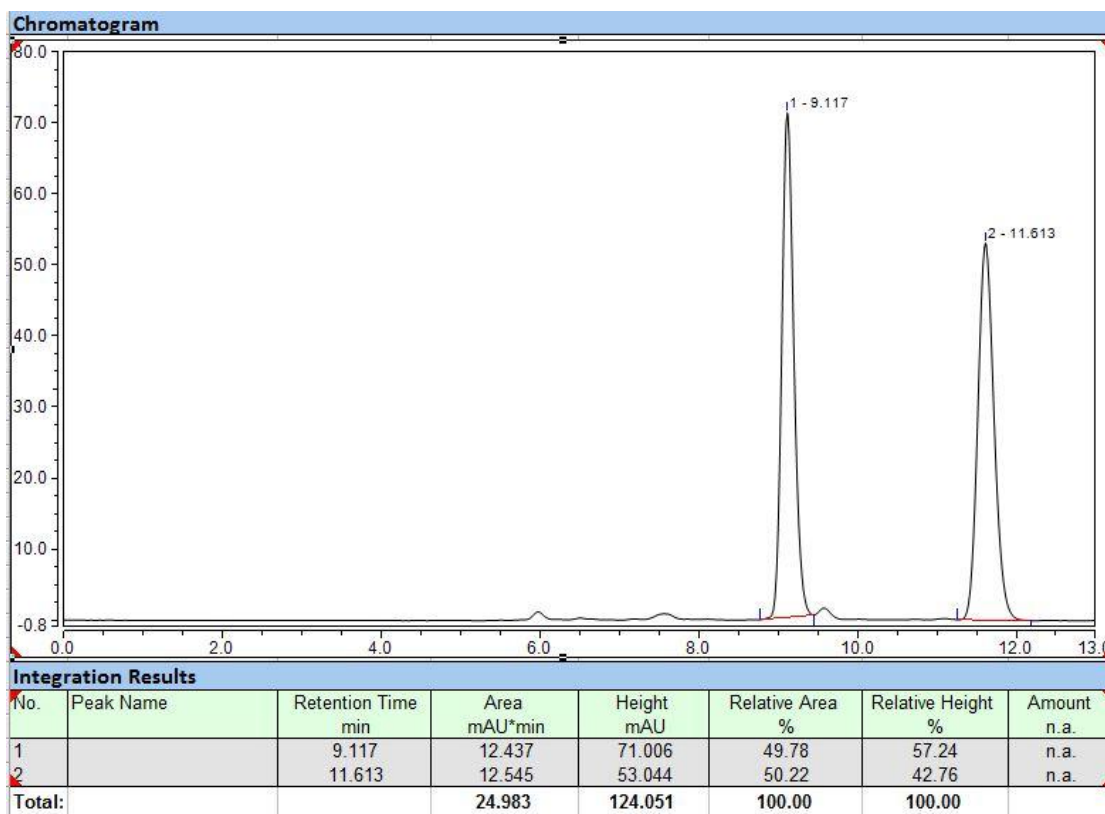
HPLC (Chiralpak AD-H): t_R = 7.8 (major), 10.1 (minor)

Condition: hexane/isopropanol = 65/35, flow rate 0.5 mL/min, 25°C.



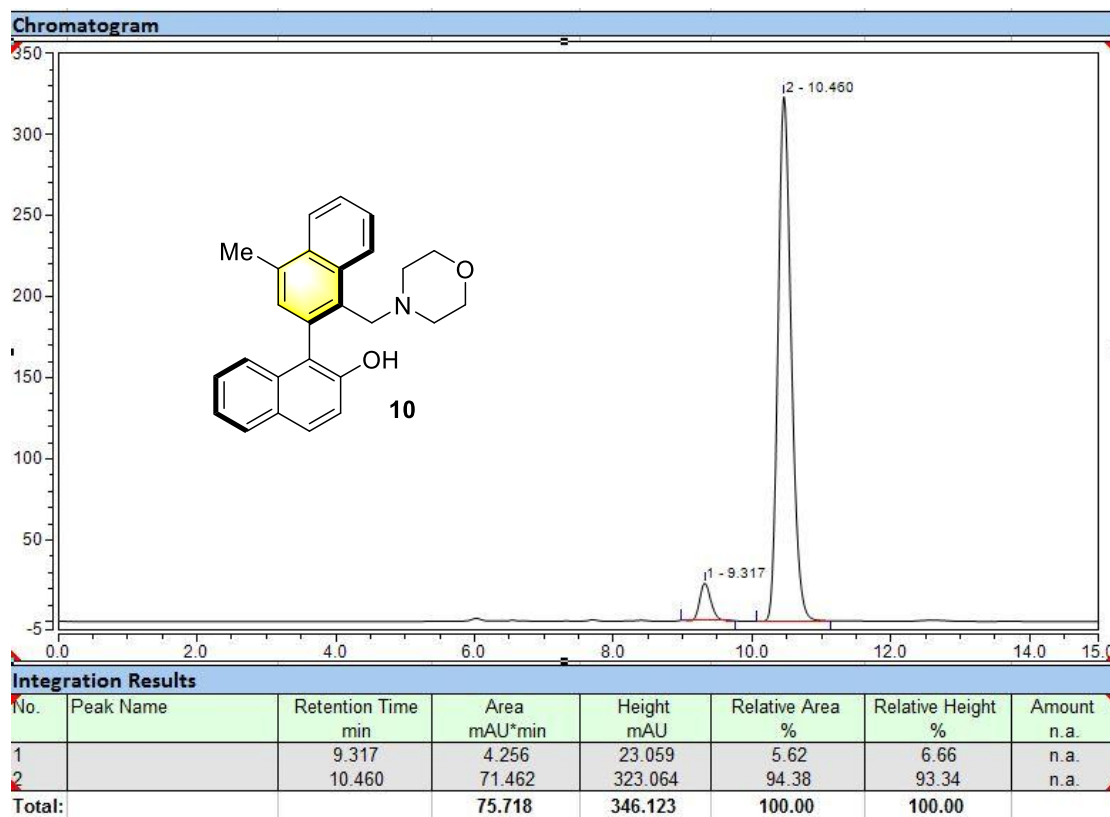
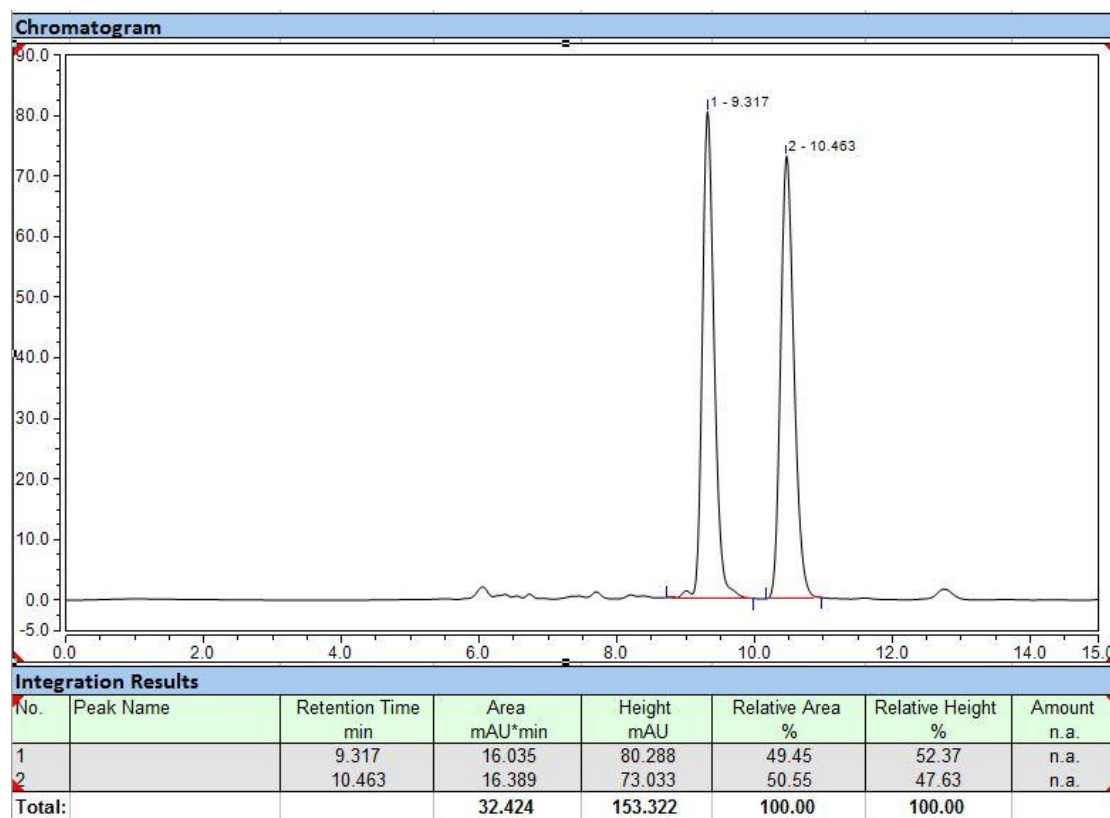
HPLC (Chiralpak AD-H): t_R = 12.9 (minor), 15.1 (major)

Condition: hexane/isopropanol = 97/3, flow rate 0.5 mL/min, 25°C.



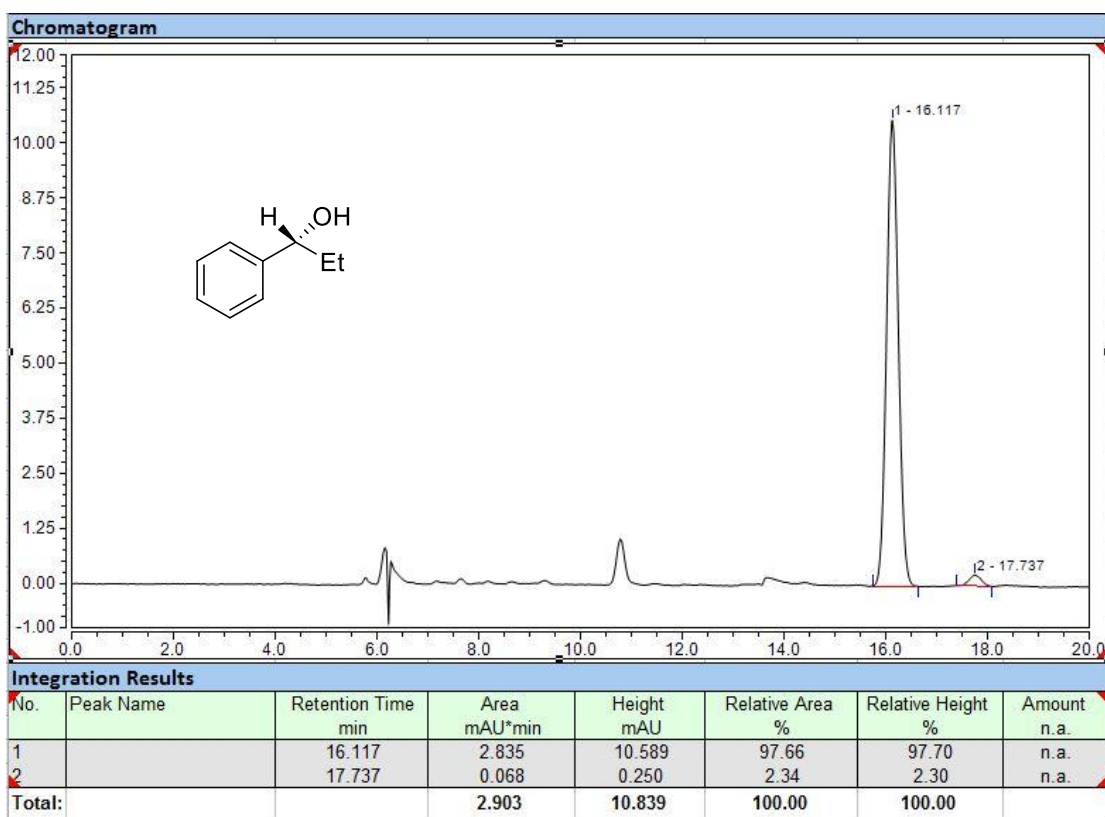
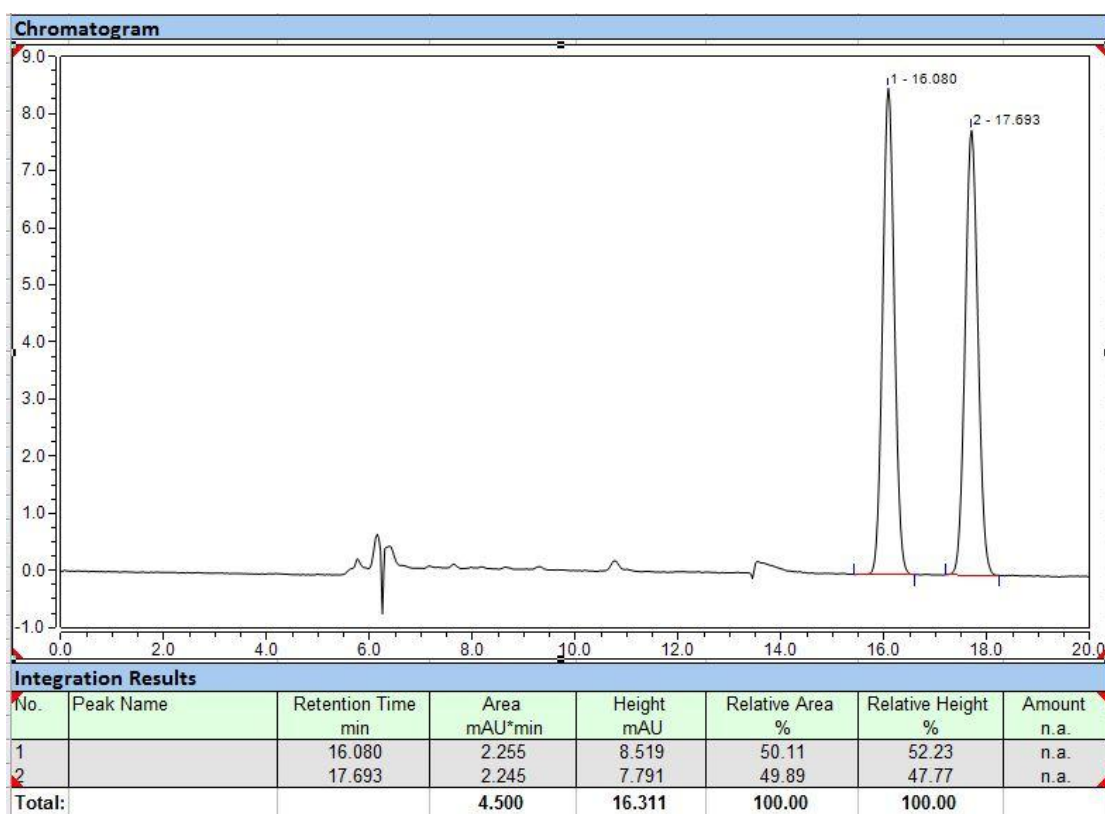
HPLC (Chiralpak AD-H): t_R = 9.2 (major), 11.7 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



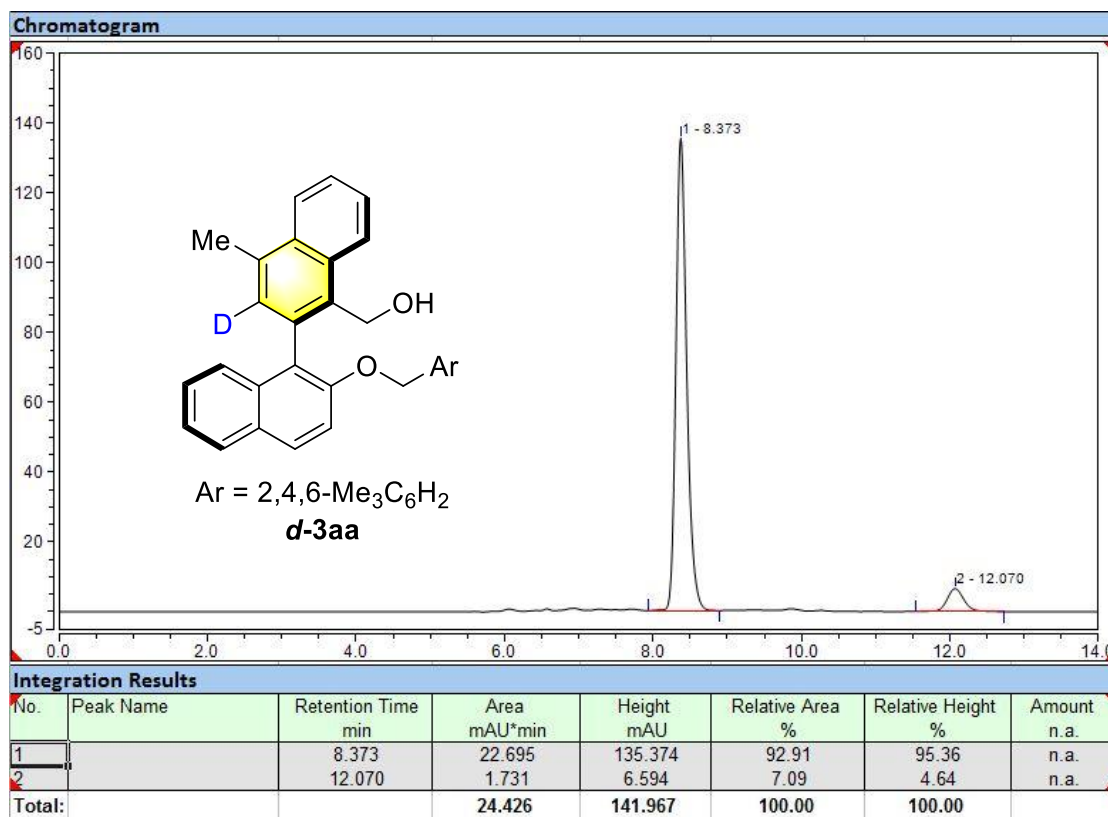
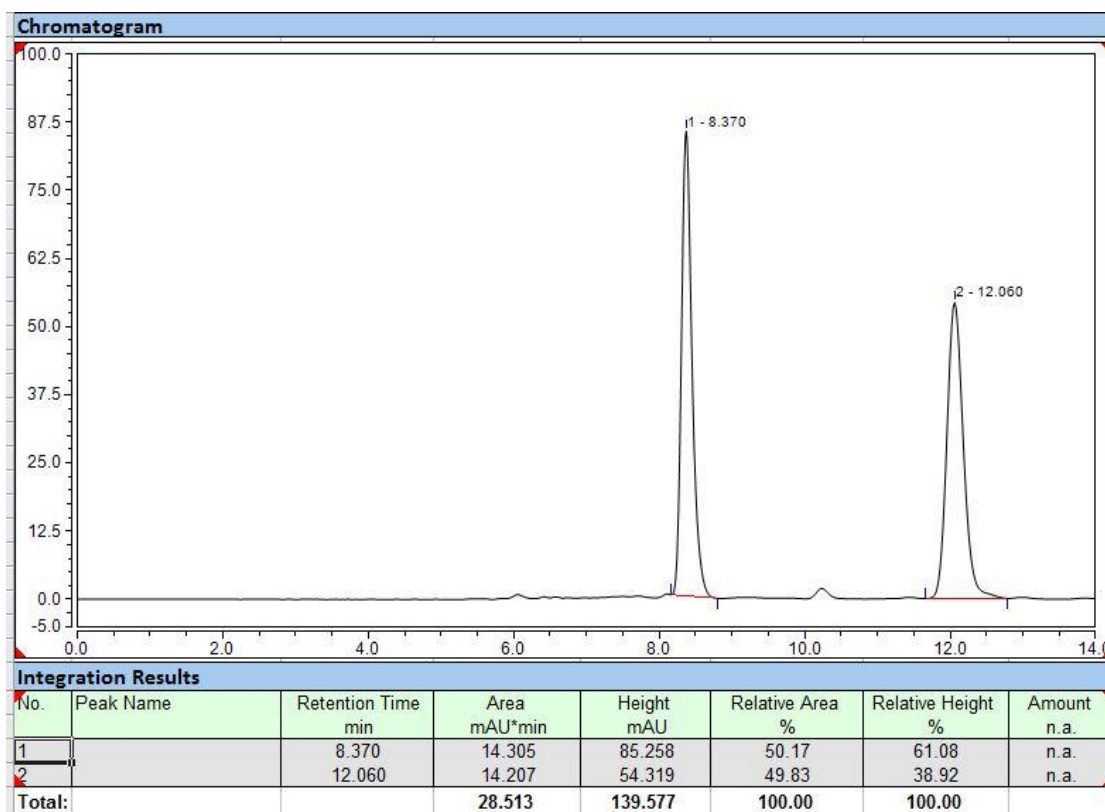
HPLC (Chiralpak AD-H): t_R = 9.3 (minor), 10.5 (major)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.



HPLC (Chiral MD): t_R = 16.1 (major), 17.7 (minor)

Condition: hexane/isopropanol = 95/5, flow rate = 0.5 mL/min, 25°C.



HPLC (Chiralpak AD-H): t_R = 8.4 (major), 12.1 (minor)

Condition: hexane/isopropanol = 70/30, flow rate 0.5 mL/min, 25°C.