General and Versatile Synthesis of Highly Recyclable Chiral Phosphoric Acid Organocatalysts

Aitor Maestro*[a,b] Sándor B. Ötvös,[b,c] Gerald Auer,[d] C. Oliver Kappe[b,c]

[a] Department of Organic Chemistry I, University of the Basque Country, UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain; [b] Institute of Chemistry, University of Graz, NAWI Graz, A-8010 Graz, Austria; [c] Center for Continuous Flow Synthesis and Processing (CC FLOW), Research Center Pharmaceutical Engineering GmbH (RCPE), A-8010 Graz, Austria; [d] Department of Earth Sciences, University of Graz, NAWI Graz Geocenter, A-8010 Graz, Austria.

General Experimental Information

All solvents and chemicals were obtained from typical commercial vendors and were used as received, without any further purification.

When required, column chromatographic purification was performed by using a Biotage Isolera automated flash chromatography system with cartridges packed with KP-SIL, 60 Å (32–63 µm particle size). Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 GF254 plates. Compounds were visualized by means of UV or by using KMnO4.

^{1}H, ^{19}F, and ^{13}C-NMR spectra were recorded on a Bruker Avance III 300 MHz instrument at room temperature, in $CDCl_3$ or DMSO-d_6 as a solvent, at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak ($CDCl_3$, ^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm. DMSO-d_6, 2.50 ppm; ^{13}C: 39.52 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations.

GC analysis was performed on a Shimadzu GC FID 230 with a flame ionization detector (FID), using an RTX-5MS Cap. column (30 m × 0.25 mm ID × 0.25 µm) and helium as carrier gas (40 cm/sec-1 linear velocity). The injector temperature was set to 280 °C. After 1 min at 50 °C, the temperature was increased by 25 °C/min to 300 °C and kept constant at 300 °C for 4 min. FID was used for detection, and the detector gases used for flame ionization were hydrogen and synthetic air (5.0 quality).

Chiral HPLC analysis was performed on a Shimadzu HPLC system (DGU-403 degassing unit, CTO-40S column oven, CBM20 system controller, SPD-40 UV-VIS detector, LC-20AT pumps).

The absolute configuration was determined by comparison of chiral HPLC data with literature reports for compound **8a**, and the absolute configurations of other compounds were assigned by analogy.[S1]

High-resolution mass spectra were recorded in either negative or positive mode on an Agilent 6230 TOF LC/MS (G6230B) by flow injections on an Agilent 1260 Infinity Series HPLC (HiP Degasser G4225A, Binary Pump G1312B, ALS Autosampler G1329B, TCC Column thermostat G1316A, DAD Detector G4212B).

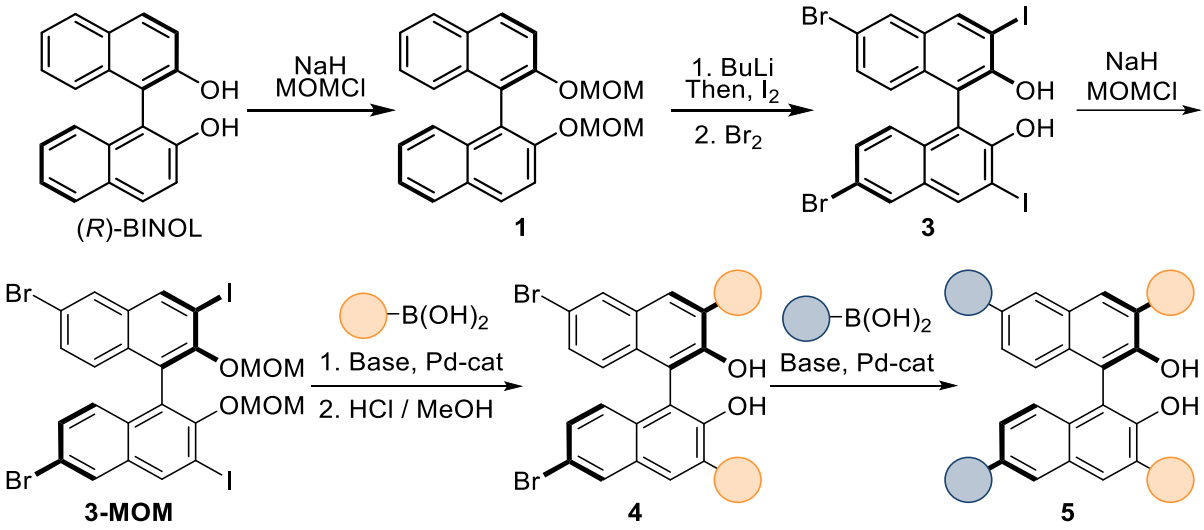
Equipment for the continuous flow reactions was assembled using commercially available components. Liquid streams were pumped by using Syrris® Asia syringe pumps. Reactor coils were made by using perfluoroalkoxy alkane (PFA) tubings (1/16” OD, 0.80 mm ID or 1/8” OD, 1.58 mm ID). Details of reaction setups as well as general procedures can be found in the following sections.

Infrared spectra (FTIR) were taken in a Bruker Alpha spectrometer with an ATR unit.

PS-Anth samples were imaged on a Zeiss Gemini DSM982 field-emission scanning electron microscope at the University of Graz, Department of Earth Sciences, NAWI Graz Geocenter.

For SEM imaging, aliquots of **PS-Anth** were transferred to a standard aluminum SEM stub using conductive graphite tape and coated with C/Pt (0.5 nm and 3 nm, respectively) using a Leica EM ACE600 Sputtercoater. Samples were imaged using combined external and in-lens secondary electron (SE) detectors. The detector signals were dynamically combined to increase structural resolution using the DISS5 SEM software (point electronic GmbH).

Synthesis and characterization of BINOL derivatives **1-5**



Procedure for the synthesis of BINOL derivative 3-MOM:

A suspension of NaH[1] (60 % dispersion in mineral oil, 5.00 g, 125.0 mmol, 2.5 equiv.) in anhydrous THF (50 mL) was cooled to 0°C in an ice bath and a solution of BINOL (14.32 g, 50.0 mmol, 1.0 equiv.) in THF (100 mL) was added dropwise over 10 min.[2] The reaction was stirred at room temperature for 1 h before the addition of MOMCl (9.50 mL, 125 mmol, 2.5 equiv.). The reaction mixture was stirred for 4 h at room temperature and quenched with water (30 mL). The organic layer was then separated and the aqueous phase was extracted with Et_2O (3 x 80 mL). The combined organic extracts were washed with brine (100 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the MOM-protected BINOL **1** as a white solid (18.72 g, quant.).

To a solution of **1** (18.72 g, 50 mmol, 1.0 equiv.) and TMEDA (18.74 mL, 125 mmol, 2.5 equiv.) in anhydrous THF (200 mL), n-BuLi (2.5M solution in hexanes, 48.00 mL, 120 mmol, 2.4 equiv.) was added dropwise at -78 °C under nitrogen atmosphere. The resulting solution was warmed up to 0 °C and stirred for 30 min. After cooling back to -78 °C, a solution of iodine (35.53 g, 140 mmol, 2.8 equiv.) in anhydrous THF was added dropwise and the mixture was slowly warmed up to room temperature and stirred overnight. The resulting mixture was opened to air and bromine (6.40 mL, 125 mmol, 2.5 equiv.) was added dropwise at 0 °C and the reaction was vigorously stirred at room temperature for 4 h. The excess of iodine and bromine was quenched with a saturated aqueous solution of Na_2SO_3 (100 mL). The organic layer was then separated and the aqueous phase was extracted with Et2O (3 x 40 mL). The combined organic extracts were washed with brine (50 mL) and dried over Na_2SO_4, filtered, and concentrated under vacuum to afford product **3** as a yellow solid, which was purified by column chromatography on silica gel (hexanes / EtOAc) (29.23 g, 84% over two steps).

A suspension of NaH[3] (60 % dispersion in mineral oil, 2.00 g, 50.0 mmol, 2.5 equiv.) in anhydrous THF (50 mL) was cooled to 0°C in an ice bath and a solution of **3** (13.92 g, 20.0 mmol, 1.0 equiv.) in THF (50 mL) was added dropwise over 10 min[4]. The reaction was stirred at room temperature for 1 h before the addition of MOMCl (3.80 mL, 50 mmol, 2.5 equiv.). The reaction mixture was stirred for 4 h at room temperature and quenched with water (10 mL). The organic layer was then separated and the aqueous

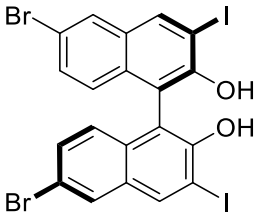
[1] NaH was washed with hexanes prior to use to remove mineral oils.
[2] Caution! Strong H_2 evolution.
[3] NaH was washed with hexanes prior to use to remove mineral oils.
[4] Caution! Strong H_2 evolution.

phase was extracted with Et2O (3 x 40 mL). The combined organic extracts were washed with brine (50 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the product **3-MOM** as a yellow solid (15.67 g, quant.).

General procedure for the synthesis of 4: Two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser was charged **3-MOM** (1.57 g, 2.0 mmol, 1.0 equiv.), Cs_2CO_3 (1.95 g, 6.0 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol, 0.05 equiv.) and the corresponding boronic acid (4.8 mmol, 2.5 equiv.). The flask was then purged with Ar in a Schlenk line. Then, degassed dimethoxyethane (9 mL) and water (3 mL) were added through a septum and the reaction was stirred at 85 °C for 16 h. After cooling down to room temperature and washing with saturated $NaHCO_3$ (3 x 10 mL), MeOH (30 mL) and aqueous HCl (37%, 3 mL) were added, and the reaction was heated at 50 °C overnight. Then, the reaction mixture was cooled down, diluted in CH_2Cl_2, and the organic phases were washed with saturated $NaHCO_3$ (2 x 30 mL) and brine (30 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to afford the crude 3,3´-diaryl BINOL **4**, which was purified by chromatography on silica gel (hexanes / CH_2Cl_2).

General procedure for the synthesis of 5: Two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser was charged **4a** (0.80 g, 1.0 mmol, 1.0 equiv.), Cs_2CO_3 (0.98 g, 3.0 mmol, 3.0 equiv.), Pd(PPh3)4 (57.8 mg, 0.05 mmol, 0.05 equiv.) and the corresponding boronic acid (2.6 mmol, 3.5 equiv.). The flask was then purged with Ar in a Schlenk line. Then, degassed toluene (10 mL) and water (5 mL) were added through a septum and the reaction was stirred at 110 °C for 16 h. After cooling down to room temperature, the reaction mixture was filtered off through a short pad of celite and washed with CH_2Cl_2 (2 x 30 mL). The resulting biphasic mixture was washed with saturated $NaHCO_3$ (30 mL) and brine (30 mL), and the organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum to afford the crude BINOL derivatives **5**, which was purified by chromatography on silica gel (hexanes / CH_2Cl_2).

(*R*)-6,6'-dibromo-3,3'-diiodo-[1,1'-binaphthalene]-2,2'-diol (3)



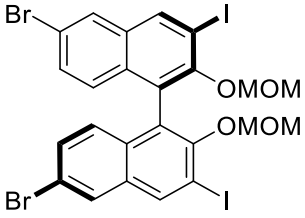
Spectroscopic data matches the literature.[S2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 2H), 7.94 (d, *J* = 2.0 Hz, 2H), 7.37 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.44 (s, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.5, 139.4, 131.9, 131.6, 131.4, 129.3, 126.3, 118.7, 112.9, 88.6.

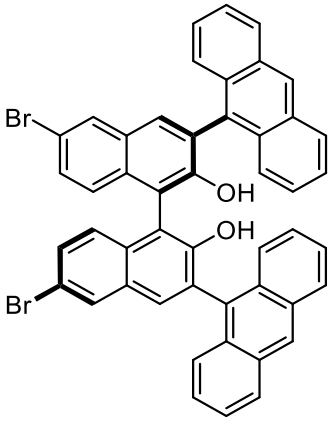
HRMS (TOF-, m/Z): calcd for $C_{20}H_{10}Br_2I_2O_2$-H $[M-H]^-$: 692.7064, found: 692.7056.

(*R*)-6,6'-dibromo-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (3-MOM)



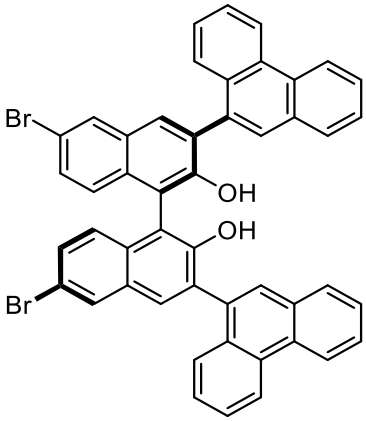
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 2H), 7.94 (d, *J* = 2.0 Hz, 2H), 7.37 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.80 (d, *J* = 5.9 Hz, 2H), 4.74 (d, *J* = 5.9 Hz, 2H), 2.57 (s, 6H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.0, 139.3, 133.1, 132.3, 130.7, 128.8, 128.3, 126.1, 120.1, 99.8, 94.1, 56.6, 27.0.
HRMS (TOF+, m/Z): calcd for $C_{24}H_{18}Br_2I_2O_4(C_2H_7OS)$ $[M+DMSO+H]^+$: 860.7873, found: 860.7848.

(*R*)- 6,6'-dibromo-3,3'-di(anthracen -9-yl)-[1,1'-binaphthalene]-2,2'-diol (4a)



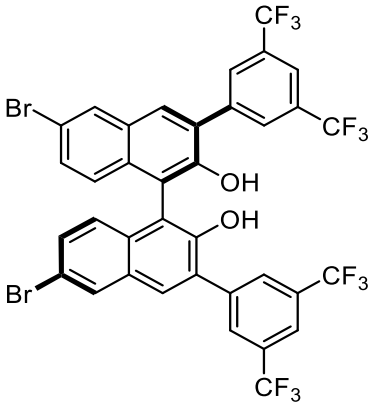
The general procedure was followed affording 1.18 g (74%) of the product as a pale yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 2H), 8.14 – 8.03 (m, 6H), 7.92 (s, 2H), 7.82 – 7.76 (m, 2H), 7.64 – 7.40 (m, 12H), 7.30 – 7.22 (m, 2H), 5.02 (s, 2H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.2, 132.6, 132.1, 131.6, 131.6, 131.0, 130.8, 130.8, 130.5, 130.5, 129.6, 128.9, 128.8, 128.5, 128.4, 126.7 (m), 125.9, 125.6 (m), 125.6, 118.2, 114.1.
HRMS (TOF-, m/Z): calcd for $C_{48}H_{28}Br_2O_2$-H $[M-H]^-$: 793.0383, found: 793.0378.

(*R*)- 6,6'-dibromo-3,3'-di(phenanthren-9-yl)-[1,1'-binaphthalene]-2,2'-diol (4b)



The general procedure was followed affording 1.13 g (71%) of the product as a pale yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 – 8.71 (m, 4H), 8.13 – 8.03 (m, 2H), 8.00 – 7.83 (m, 6H), 7.80 – 7.23 (m, 14H), 5.36 – 5.16 (m, 2H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.8, 133.1, 132.8, 132.4, 132.3, 131.5, 131.4, 131.1, 131.0, 130.8, 130.7, 130.5, 129.4, 129.3, 129.0, 127.5, 127.2, 126.7, 126.4, 123.3, 123.2, 122.8, 118.3, 118.2, 113.9, 113.5.
HRMS (TOF+, m/Z): calcd for $C_{48}H_{28}Br_2O_2Na$ $[M+Na]^+$: 817.0348, found: 817.0385.

(*R*)- 6,6'-dibromo-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (4c)



The general procedure was followed affording 0.97 g (56%) of the product as a pale yellow solid.

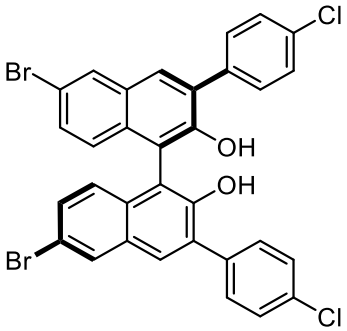
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 4H), 8.17 (d, *J* = 2.0 Hz, 2H), 8.03 (s, 2H), 7.94 (s, 2H), 7.49 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.06 (d, *J* = 9.1 Hz, 2H), 5.39 (s, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.3, 138.9, 132.2, 132.1, 131.8, 131.7, 131.6, 131.2, 131.0, 130.7, 130.0 (m), 129.1, 125.8, 125.3, 121.9 (m), 121.7, 119.3, 111.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8.

HRMS (TOF+, m/Z): calcd for 2($C_{36}H_{16}Br_2F_{12}O_2$)H $[2M+H]^+$: 1732.8723, found: 1732.8618.

(*R*)- 6,6'-dibromo-3,3'-bis(4-chlorophenyl)-[1,1'-binaphthalene]-2,2'-diol (4d)



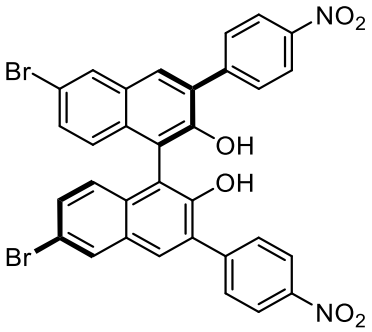
The general procedure was followed affording 0.89 g (67%) of the product as a pale yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.0 Hz, 2H), 7.90 (s, 2H), 7.64 (d, *J* = 8.6 Hz, 4H), 7.46 (d, *J* = 8.5 Hz, 4H), 7.39 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 5.31 (s, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.4, 135.3, 134.3, 131.5, 131.1, 130.9, 130.8, 130.7, 130.6, 130.6, 128.9, 125.9, 118.6, 112.2.

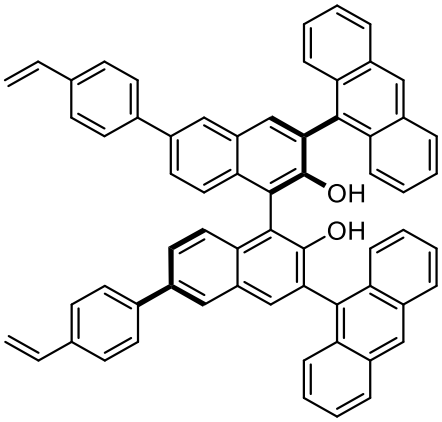
HRMS (TOF-, m/Z): calcd for 2($C_{32}H_{18}Br_2Cl_2O_2$)-H $[2M-H]^-$: 1322.8029, found: 1322.7996.

(*R*)- 6,6'-dibromo-3,3'-bis(4-nitrophenyl)-[1,1'-binaphthalene]-2,2'-diol (4e)



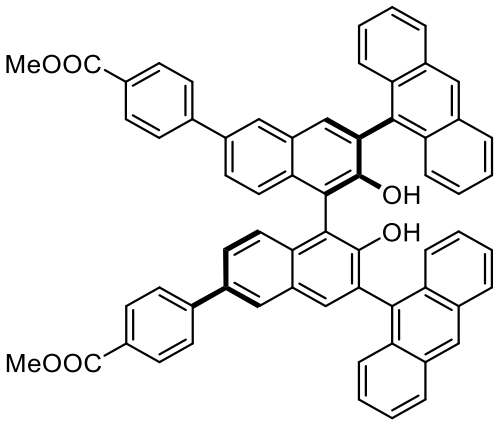
The general procedure was followed affording 0.81 g (59%) of the product as a pale yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.0 Hz, 4H), 8.11 (d, *J* = 2.4 Hz, 2H), 7.98 (s, 2H), 7.89 (d, *J* = 9.0 Hz, 4H), 7.44 (dd, *J* = 9.0, 2.4 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 5.53 (s, 2H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.4, 147.3, 143.7, 131.9, 131.8, 131.5, 130.9, 130.6, 130.5, 129.8, 125.8, 123.6, 119.0, 112.0.
HRMS (TOF-, m/Z): calcd for $C_{32}H_{18}Br_2N_2O_6$-H $[M-H]^-$: 682.9459, found: 682.9453.

(*R*)-3,3'-di(anthracen-9-yl)-6,6'-bis(4-vinylphenyl)-[1,1'-binaphthalene]-2,2'-diol (5aa)



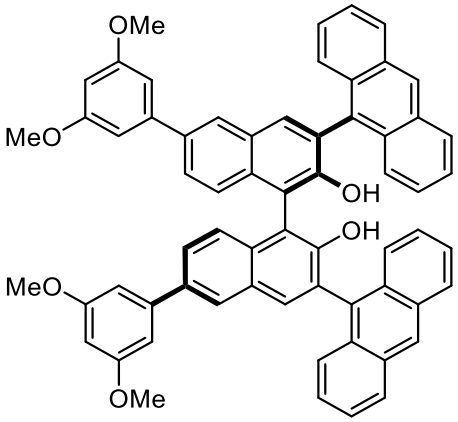
The general procedure was followed affording 767.2 mg (91%) of the product as a pale yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 2H), 8.25 – 8.03 (m, 8H), 8.02 – 7.93 (m, 2H), 7.85 – 7.71 (m, 8H), 7.62 – 7.41 (m, 12H), 7.35 – 7.29 (m, 2H), 6.81 (dd, *J* = 17.6, 11.0 Hz, 2H), 5.85 (d, *J* = 17.6 Hz, 2H), 5.32 (d, *J* = 11.0 Hz, 2H), 5.18 (s, 2H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.3, 140.4, 136.8, 136.7, 136.5, 133.4, 133.3, 131.7, 131.6, 131.0, 130.9, 130.6, 129.7, 128.9, 128.7, 128.1, 127.8, 127.5, 127.1, 126.9, 126.5, 126.3, 126.2, 125.6, 125.6, 114.1, 113.8.
HRMS (TOF+, m/Z): calcd for $C_{64}H_{42}O_2H$ $[M+H]^+$: 843.3258, found: 843.3260.

Dimethyl 4,4'-(*R*)-3,3'-di(anthracen-9-yl)-2,2'-dihydroxy-[1,1'-binaphthalene]-6,6'-diyl)dibenzoate (5ab)



The general procedure was followed affording 689.3 mg (76%) of the product as a pale yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 2H), 8.23 – 8.06 (m, 12H), 7.97 – 7.89 (m, 2H), 7.86 – 7.77 (m, 6H), 7.77 – 7.68 (m, 4H), 7.57 – 7.43 (m, 6H), 7.35 – 7.28 (m, 2H), 5.26 – 5.10 (m, 2H), 4.01 – 3.92 (m, 6H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 201.0, 167.0, 151.5, 145.4, 135.9, 133.6, 133.4, 131.6, 131.5, 130.9, 130.8, 130.3, 130.1, 129.5, 128.9, 128.8, 128.7, 128.1, 127.9, 127.1, 126.8, 126.4, 126.0, 125.7, 125.5, 123.9, 113.8, 52.2.
HRMS (TOF+, m/Z): calcd for $C_{64}H_{42}O_2H$ $[M+H]^+$: 907.3054, found: 907.3048.

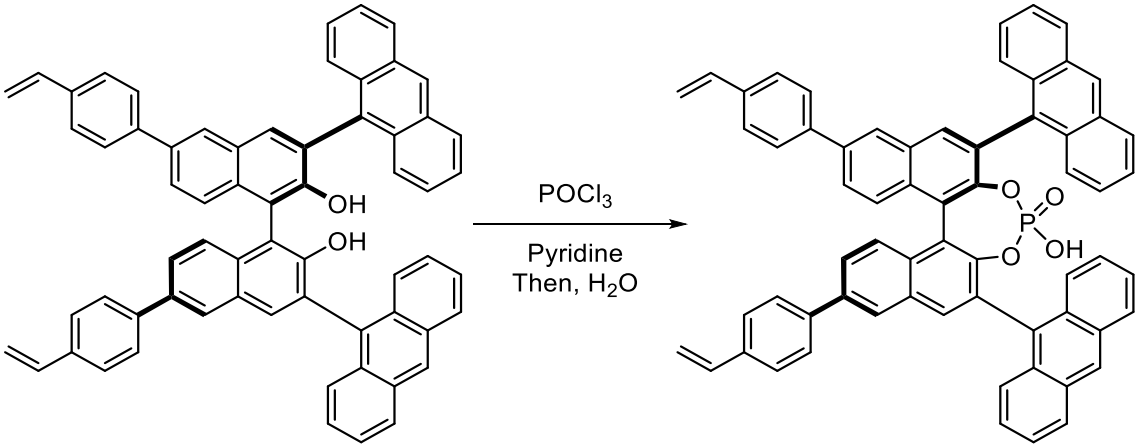
(*R*)-3,3'-di(anthracen-9-yl)-6,6'-bis(3,5-dimethoxyphenyl)-[1,1'-binaphthalene]-2,2'-diol (5ac)



The general procedure was followed affording 801.7 mg (88%) of the product as a pale yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 2H), 8.15 – 8.04 (m, 8H), 7.96 – 7.89 (m, 2H), 7.80 – 7.68 (m, 6H), 7.58 – 7.40 (m, 6H), 7.33 – 7.28 (m, 2H), 6.87 (d, *J* = 2.3 Hz, 4H), 6.50 (t, *J* = 2.2 Hz, 2H), 5.15 (s, 2H), 3.86 (s, 12H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.3, 151.3, 143.3, 137.3, 133.4, 131.7, 131.6, 131.0, 130.9, 130.6, 129.6, 128.9, 128.7, 128.1, 127.8, 127.3, 126.6, 126.5, 126.2, 125.5, 113.8, 105.7, 99.4, 55.6.
HRMS (TOF+, m/Z): calcd for $C_{64}H_{46}O_6H$ $[M+H]^+$: 911.3367, found: 911.3405.

Synthesis and characterization of PS-Anth catalyst

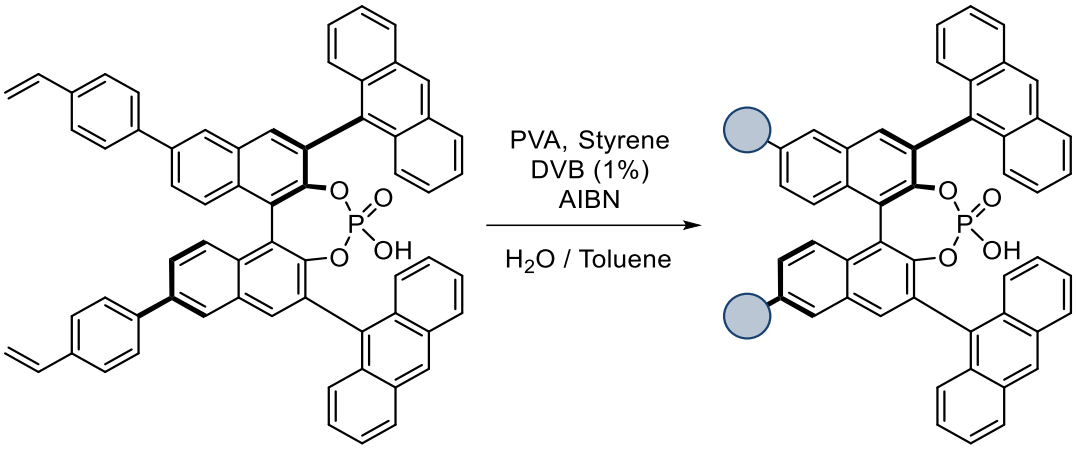
(*R*)-2,6-di(anthracen-9-yl)-4-hydroxy-9,14-bis(4-vinylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (6aa)



BINOL derivative **5aa** (843.0 mg, 1.0 mmol, 1.0 equiv.) was dissolved in anhydrous pyridine (5.0 mL) and $POCl_3$ (279.6 µL, 3.0 mmol, 3.0 equiv.) were added dropwise. Then, the reaction was heated at 95 °C for 8 h. The reaction was cold down to room temperature and H_2O (5.0 mL) was added dropwise. Then, the reaction mixture was heated at 95 °C for another 10 h. After completing the reaction, it was cold down to room temperature and acidified with 6 M HCl (40 mL). The reaction product was extracted from CH_2Cl_2 (50 mL) and the organic phase was sequentially washed with 6 M HCl (2x 30 mL) to fully acidify the phosphoric acid. The organic phase was then dried over $MgSO_4$ and filtered to afford 886.9 mg (98%) of the product as a pale yellow solid.

^{1}H NMR (300 MHz, , DMSO) δ 8.65 (s, 2H), 8.57 – 8.35 (m, 2H), 8.19 – 8.05 (m, 6H), 7.93 – 7.83 (m, 6H), 7.65 – 7.28 (m, 18H), 6.80 (dd, *J* = 17.6, 11.0 Hz, 2H), 5.91 (d, *J* = 17.7 Hz, 2H), 5.30 (d, *J* = 11.2 Hz, 2H). * The H from the phosphoric acid could not be observed.
^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 149.7, 139.0, 136.7 – 135.6 (m), 133.8 – 124.4 (m), 122.5, 118.8, 114.5.
^{31}P NMR (121 MHz, DMSO) δ 2.66.
HRMS (TOF+, m/Z): calcd for $C_{64}H_{41}O_4PH$ $[M+H]^+$: 905.2815, found: 905.2832.

Method for the copolymerization of 5 with styrene and divinylbencene



A round bottom flask was charged with a suspension of polyvinyl alcohol (PVA) (65 mg, 0.64 µmol, 0.001 equiv.) in 60 mL of deionized and degassed water at room temperature. After stirring at rt for 0.5 h, the solution was heated at 90 °C until PVA was dissolved (1.5-2 h) and then cooled down to room temperature.

On the other hand, the reaction mixture was prepared in a different flask. First, 1,4-divinylbenzene (DVB 85% purity, 88 µL, 0.5 mmol, 0.8 equiv.) and styrene (2.66 mL, 23.1 mmol, 35.0 equiv.) were filtered through a short pad of silica to remove the stabilizers, and the filter was further washed with 3.0 mL of toluene. Then, **6aa** (600 mg, 0.66 mmol, 1.0 equiv.) and AIBN (36 mg, 0.22 mmol, 0.33 equiv.) were dissolved in the DVB/Styrene/Toluene mixture and the resulting solution was degassed by bubbling Argon for 10 minutes.

The pre-made reaction mixture was added to the aqueous solution of PVA at room temperature. Additional 3.0 mL of degassed toluene was used to wash the flask containing the reaction mixture. Then, the reaction was stirred at 80 °C for 2 days. Then, the aqueous solution was decanted and the resin was washed with hot water (50 °C, 3x 100 mL), followed by MeOH (3x 50 mL) and CH_2Cl_2 (3x 50 mL). The resulting catalyst was dried overnight in a vacuum oven at 40 °C to afford 1.86 g of **PS-Anth** as brown beads.

The catalyst loading of the resin was calculated based on the P elemental analysis by using the following formula:

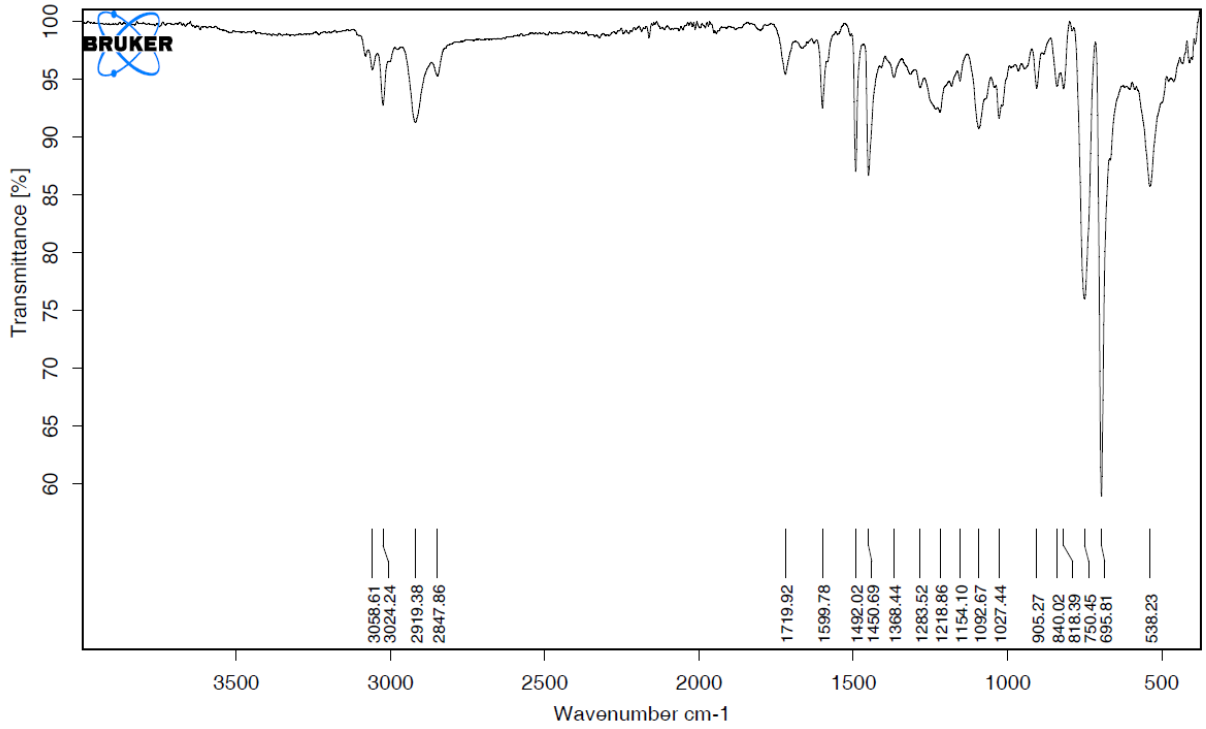
$$f\left(\frac{mmol}{g}\right) = \frac{\%P\ x\ 1000}{number\ of\ P\ atoms\ x\ MW(P) x\ 100}$$

Elem. Anal. P: 0.21%.

f = 0.07 mmol/g

FTIR

As prepared catalyst



Used catalyst

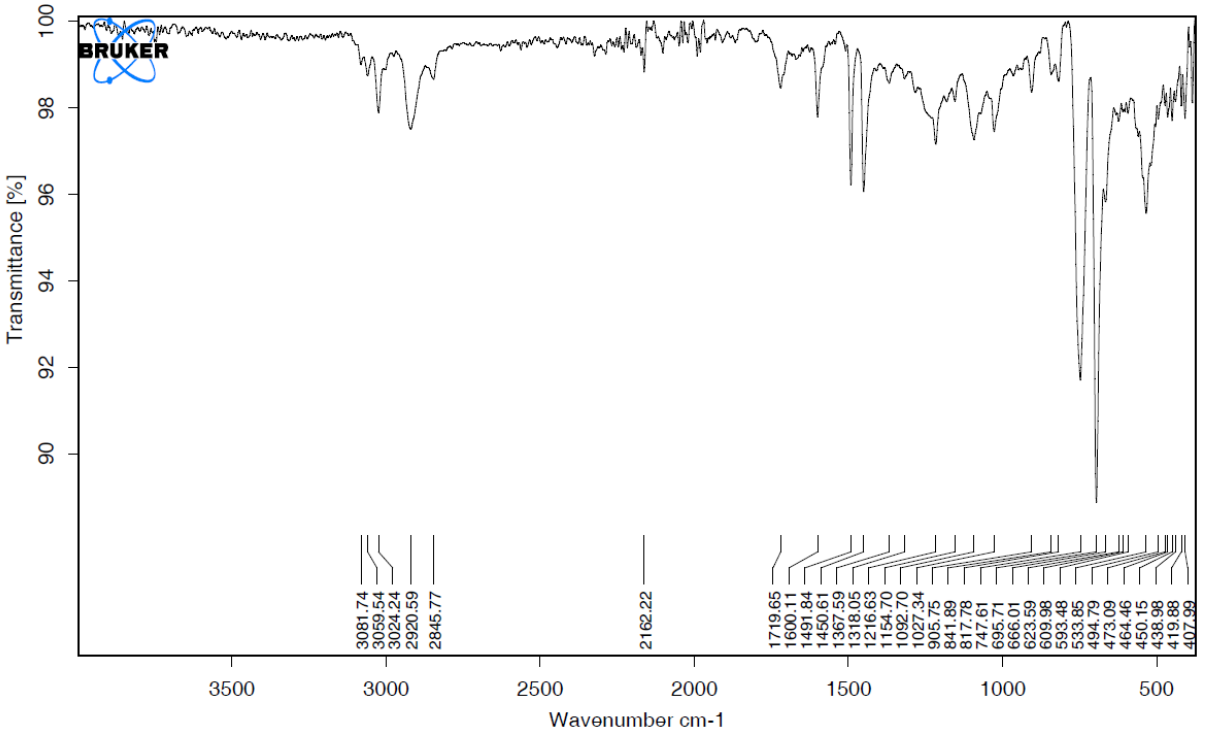
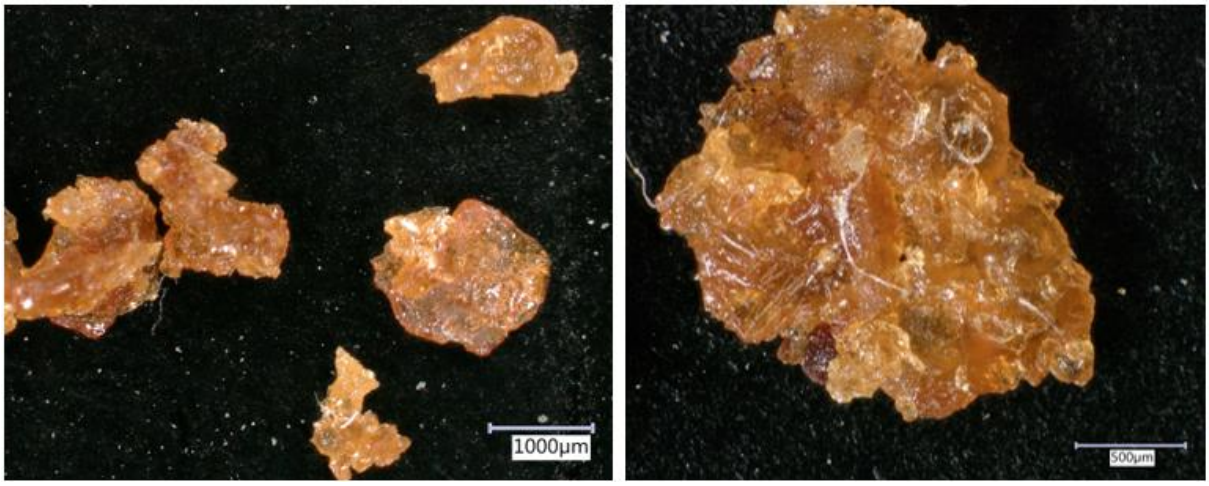


Figure S1. *FTIR of as prepared and used* ***PS-Anth*** *catalyst.*

Optical microscopy

As prepared catalyst



Used catalyst

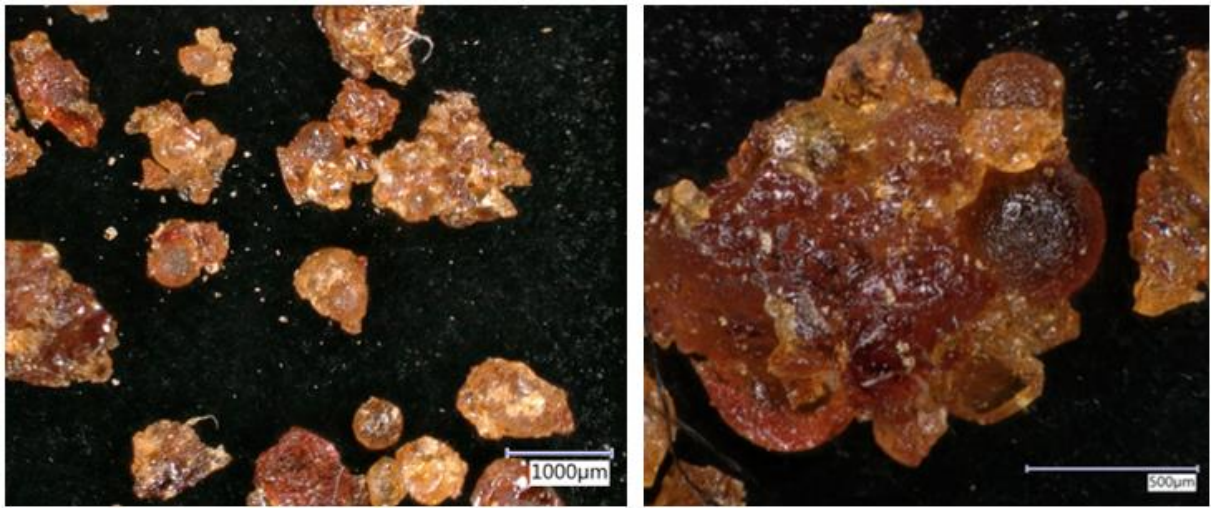


Figure S2. *Optical microscopy of as prepared and used* ***PS-Anth*** *catalyst.*

SEM

As prepared catalyst

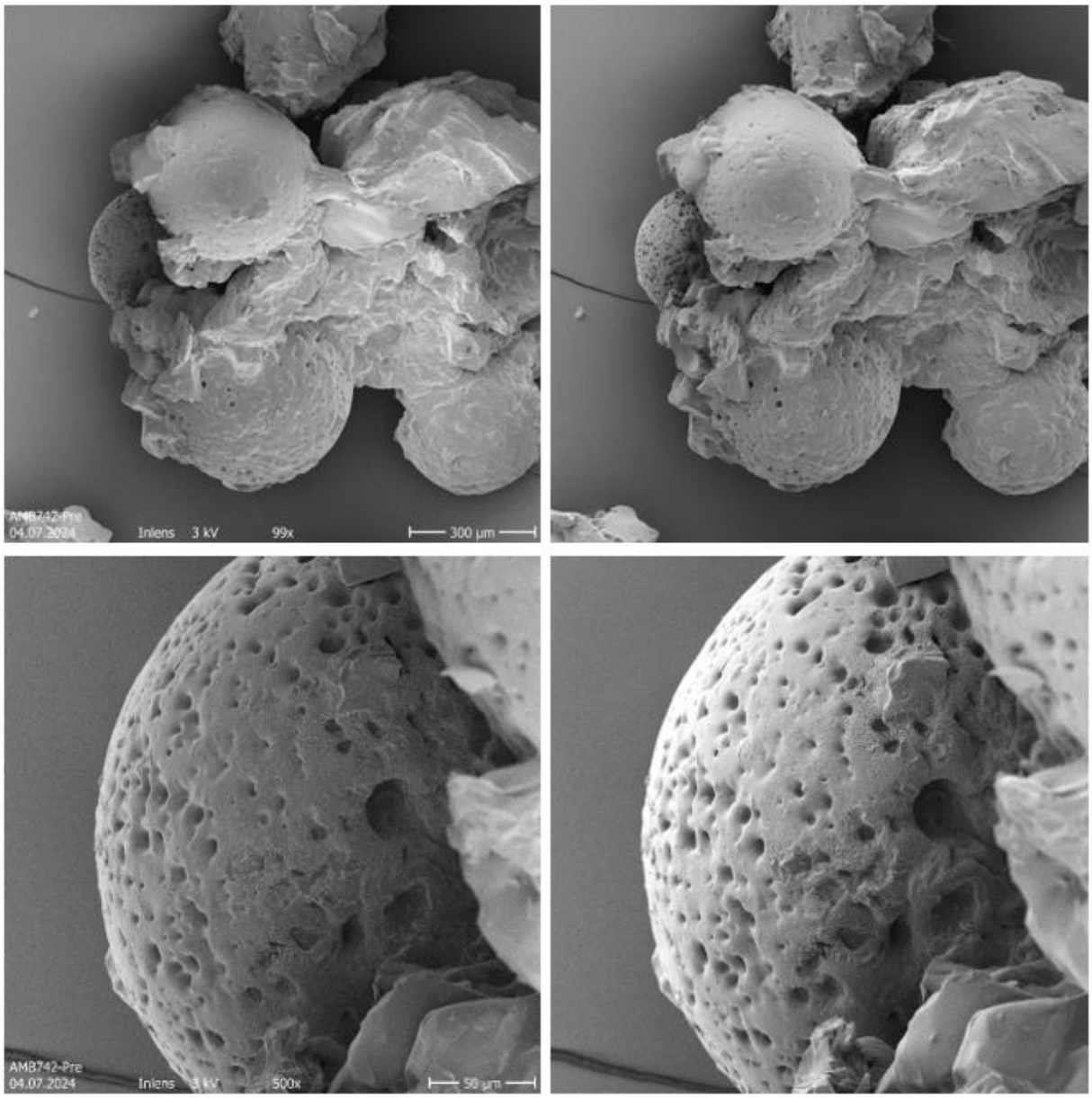


Figure S3.1 *SEM of as prepared* ***PS-Anth*** *catalyst.*

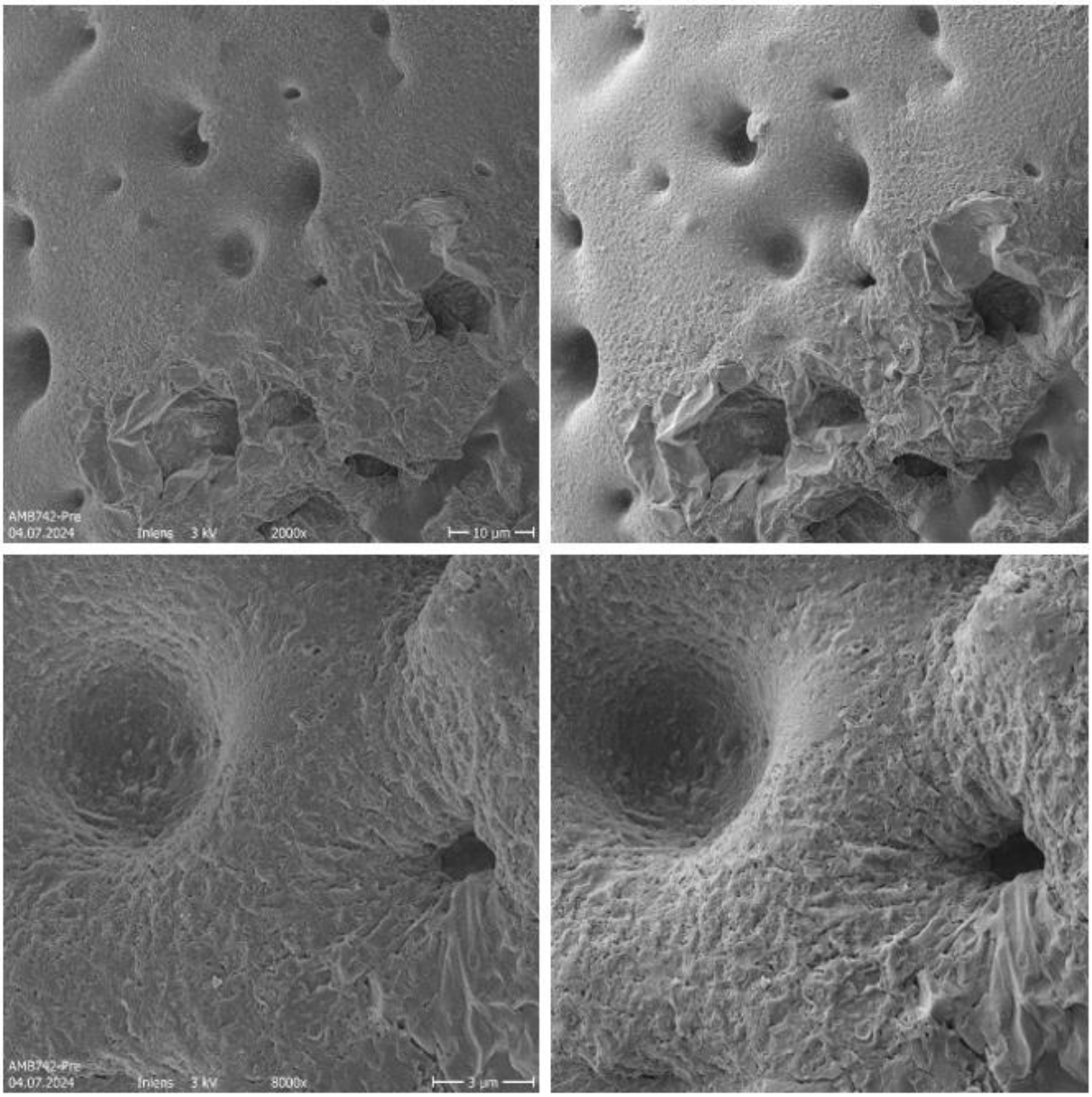


Figure S3.2 *SEM of as prepared* ***PS-Anth*** *catalyst.*

Used catalyst

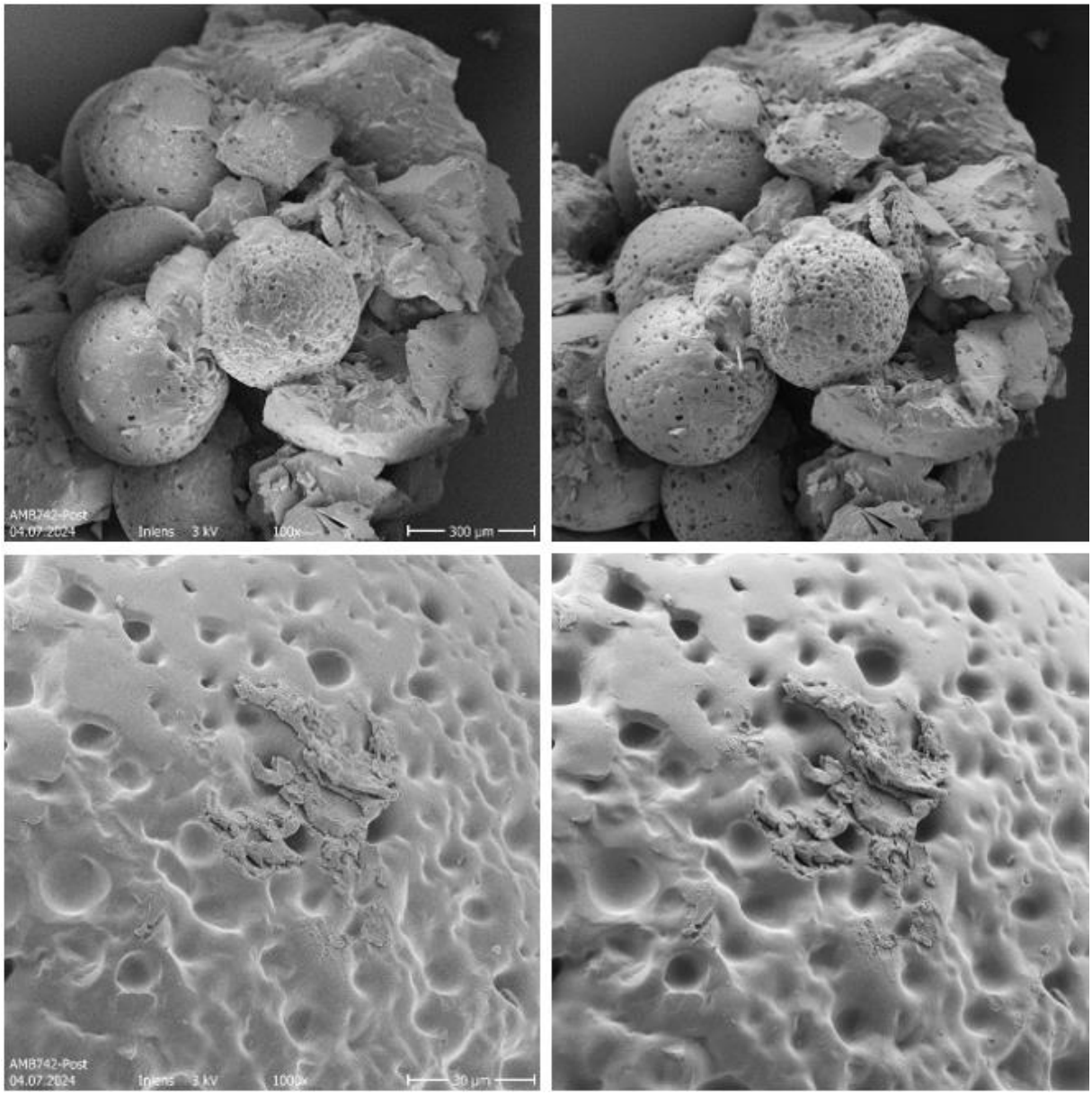


Figure S4.1 *SEM of used* ***PS-Anth*** *catalyst.*

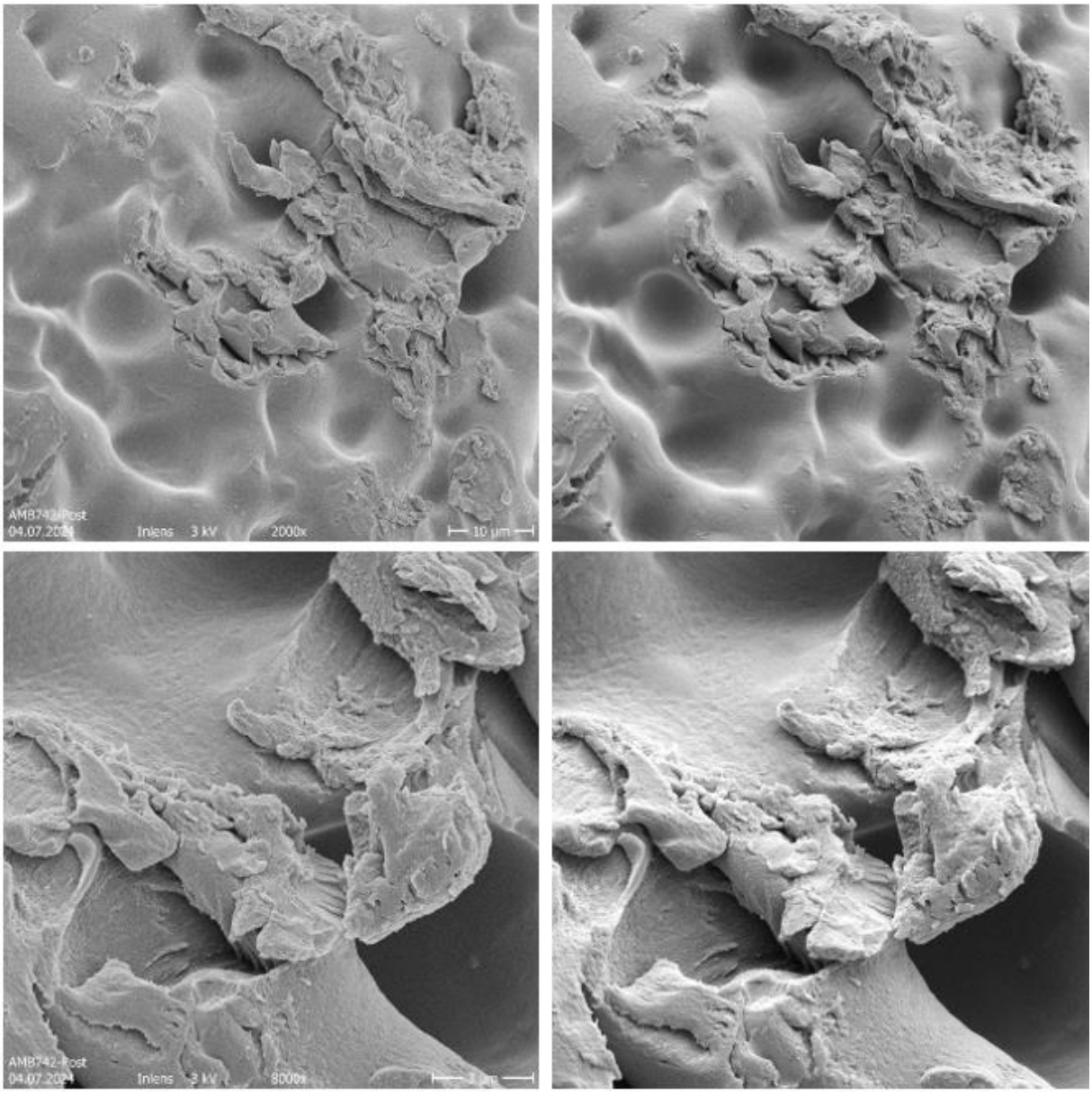
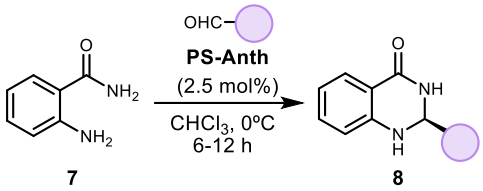


Figure S4.2 *SEM of used* ***PS-Anth*** *catalyst.*

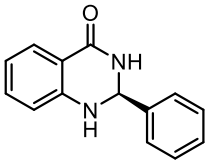
Synthesis and characterization of **8**



To a solution of **7** (13.6 mg, 0.1 mmol, 1.0 equiv.) in $CHCl_3$ (1.0 mL) was added **PS-Anth** (0.07 mmol/g, 36 mg, 0.0025 mmol, 0.05 equiv.) the corresponding aldehyde (0.102 mmol, 1.02 equiv.) at 0 °C. The reaction was stirred at 300 rpm for 6-12 h and monitored by GC-FID area %. The reaction mixture was then filtered and washed with CH_2Cl_2 (20 mL) to recover the catalyst and the solution was concentrated under reduced pressure to afford pure **8**.

Note: The racemic products were prepared using TFA (5 mol%) as the catalyst.

(S)-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (8a)



The general procedure was followed affording 20.4 mg (91%) of the product as a white solid. The reported data match the literature.[S1,3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.3 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.44 – 7.31 (m, 3H), 7.24 (ddd, *J* = 8.1, 7.1, 1.6 Hz, 1H), 7.14 (d, *J* = 16.8 Hz, 1H), 6.75 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.67 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 5.75 (d, *J* = 2.3 Hz, 1H).

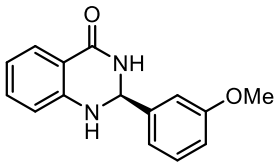
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.6, 147.9, 141.6, 133.3, 128.5, 128.3, 127.4, 126.9, 117.1, 115.0, 114.4, 66.6.

HRMS (TOF+, m/Z): calcd for $C_{14}H_{12}N_2OH$ $[M+H]^+$: 225.1023, found: 225.1025.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 11.3 min (major), 14.2 (minor). 91:9 er.

Lit. HPLC (chiral): Chiralpak-AD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, detection at 254 nm. Residence time: 11.7 min (major), 14.7 min (minor). *S* isomer.[S1]

(S)-2-(3-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (8b)



The general procedure was followed affording 24.9 mg (98%) of the product as a white solid. The reported data match the literature.[S1]

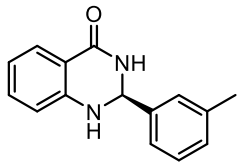
^{1}H NMR (300 MHz, DMSO) δ 8.32 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.34 – 7.08 (m, 3H), 7.08 – 7.04 (m, 2H), 6.91 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.76 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.67 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 5.73 (d, *J* = 2.3 Hz, 1H), 3.74 (s, 3H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.6, 159.3, 147.8, 143.4, 133.4, 129.5, 127.4, 119.0, 117.2, 115.0, 114.5, 113.7, 112.6, 66.3, 55.1.

HRMS (TOF+, m/Z): calcd for $C_{15}H_{14}N_2O_2H$ $[M+H]^+$: 255.1128, found: 255.1133.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 16.5 min (major), 18.5 (minor). 91:9 er.

(S)-2-(m-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8c)



The general procedure was followed affording 21.9 mg (92%) of the product as a white solid. The reported data match the literature.[S3]

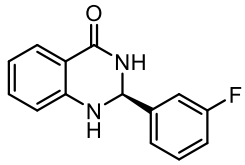
^{1}H NMR (300 MHz, DMSO) δ 8.24 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32 (s, 1H), 7.24 – 7.23 (m, 0H), 7.07 (s, 1H), 6.75 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.67 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 5.72 (d, *J* = 2.1 Hz, 1H), 2.31 (s, 3H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.6, 147.9, 141.5, 137.5, 133.3, 129.1, 128.3, 127.5, 127.4, 124.1, 117.1, 114.9, 114.4, 66.7, 21.1.

HRMS (TOF+, m/Z): calcd for $C_{15}H_{14}N_2OH$ $[M+H]^+$: 239.1179, found: 239.1183.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 11.3 min (major), 13.0 (minor). 94:6 er.

(S)-2-(3-fluorophenyl)-2,3-dihydroquinazolin-4(1H)-one (8d)



The general procedure was followed affording 23.3 mg (96%) of the product as a white solid. The reported data match the literature.[S3]

^{1}H NMR (300 MHz, DMSO) δ 8.42 (d, *J* = 2.7 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.43 (td, *J* = 7.9, 5.9 Hz, 1H), 7.27 – 7.25 (m, 5H), 6.78 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.69 (td, *J* = 7.5, 1.1 Hz, 1H), 5.80 (d, *J* = 2.5 Hz, 1H).

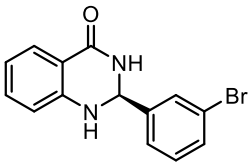
^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.5, 162.1 (d, *J* = 243.9 Hz), 147.6, 144.9 (d, *J* = 6.3 Hz), 133.5, 130.4 (d, *J* = 8.1 Hz), 127.4, 122.8 (d, *J* = 2.7 Hz), 117.4, 115.2 (d, *J* = 21.0 Hz), 115.0, 114.5, 113.7 (d, *J* = 22.0 Hz), 65.7 (d, *J* = 2.2 Hz).

^{19}F NMR (282 MHz, DMSO) δ -112.98.

HRMS (TOF+, m/Z): calcd for $C_{14}H_{11}FN_2OH$ $[M+H]^+$: 243.0928, found: 243.0934.

HPLC (chiral): Chiralpak-IE, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 11.1 min (major), 13.5 (minor). 86:14 er.

(S)-2-(3-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (8e)



The general procedure was followed affording 28.5 mg (94%) of the product as a white solid. The reported data match the literature.[S3]

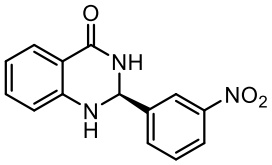
^{1}H NMR (300 MHz, DMSO) δ 8.54 (s, 1H), 8.36 (s, 1H), 8.20 (ddd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (s, 1H), 7.27 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 6.79 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.70 (td, *J* = 7.4, 1.1 Hz, 1H), 5.95 (s, 1H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.4, 147.7, 147.3, 144.3, 133.6, 133.4, 130.1, 127.4, 123.3, 121.6, 117.6, 115.0, 114.6, 65.2.

HRMS (TOF+, m/Z): calcd for $(C_{14}H_{11}BrN_2O)_2H$ $[2M+H]^+$: 605.0183, found: 605.0164.

HPLC (chiral): Chiralpak-IE, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 11.3 min (major), 15.1 (minor). 84:16 er.

(S)-2-(3-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (8f)



The general procedure was followed affording 19.7 mg (73%) of the product as a pale yellow solid. The reported data match the literature.[S4]

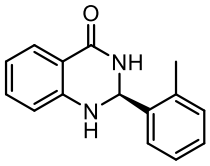
^{1}H NMR (300 MHz, DMSO) δ 8.41 (s, 1H), 7.68 (s, 1H), 7.61 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.52 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.25 (m, 2H), 6.76 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.69 (td, *J* = 7.5, 1.1 Hz, 1H), 5.78 (s, 1H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.4, 147.5, 144.6, 133.5, 131.2, 130.6, 129.7, 127.4, 125.8, 121.6, 117.4, 114.9, 114.5, 65.5.

HRMS (TOF+, m/Z): calcd for $C_{14}H_{11}N_3O_3H$ $[M+H]^+$: 270.0887, found: 270.0872.

HPLC (chiral): Chiralpak-IE, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 18.8 min (major), 23.3 (minor). 76:24 er.

(S)-2-(o-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8g)



The general procedure was followed affording 21.2 mg (89%) of the product as a white solid. The reported data match the literature.[S5]

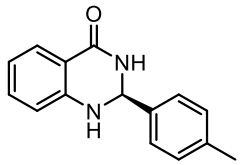
^{1}H NMR (300 MHz, DMSO) δ 8.07 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 6.6 Hz, 1H), 7.38 – 7.11 (m, 4H), 6.87 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.01 (s, 1H), 2.43 (s, 3H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 164.1, 148.6, 138.1, 136.1, 133.2, 130.7, 128.5, 127.5, 125.9, 117.2, 114.9, 114.5, 64.7, 18.8.

HRMS (TOF+, m/Z): calcd for $C_{15}H_{14}N_2OH$ $[M+H]^+$: 239.1179, found: 239.1181.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 10.9 min (major), 16.8 (minor). 88:12 er.

(S)-2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8h)



The general procedure was followed affording 20.2 mg (85%) of the product as a white solid. The reported data match the literature.[S5]

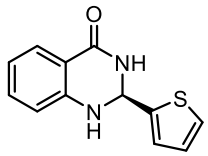
^{1}H NMR (300 MHz, DMSO) δ 8.23 (d, *J* = 2.2 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.15 (m, 3H), 7.05 (s, 1H), 6.73 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.66 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 5.70 (d, *J* = 2.2 Hz, 1H), 2.29 (s, 3H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.7, 147.9, 138.7, 137.7, 133.3, 128.8, 127.3, 126.8, 117.1, 115.0, 114.4, 66.4, 20.7.

HRMS (TOF+, m/Z): calcd for $C_{15}H_{14}N_2OH$ $[M+H]^+$: 239.1179, found: 239.1193.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 13.7 min (major), 16.9 (minor). 80:20 er.

(S)-2-(thiophen-2-yl)-2,3-dihydroquinazolin-4(1H)-one (8i)



The general procedure was followed affording 21.4 mg (93%) of the product as a white solid. The reported data match the literature.[S4]

^{1}H NMR (300 MHz, DMSO) δ 8.45 (d, *J* = 2.7 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.32 – 7.20 (m, 2H), 7.15 – 7.09 (m, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.76 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.70 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 6.02 (d, *J* = 2.7 Hz, 1H).

^{13}C {^{1}H} NMR (75 MHz, DMSO) δ 163.1, 147.3, 146.4, 133.4, 127.3, 126.5, 125.9, 125.7, 117.5, 115.1, 114.7, 62.6.

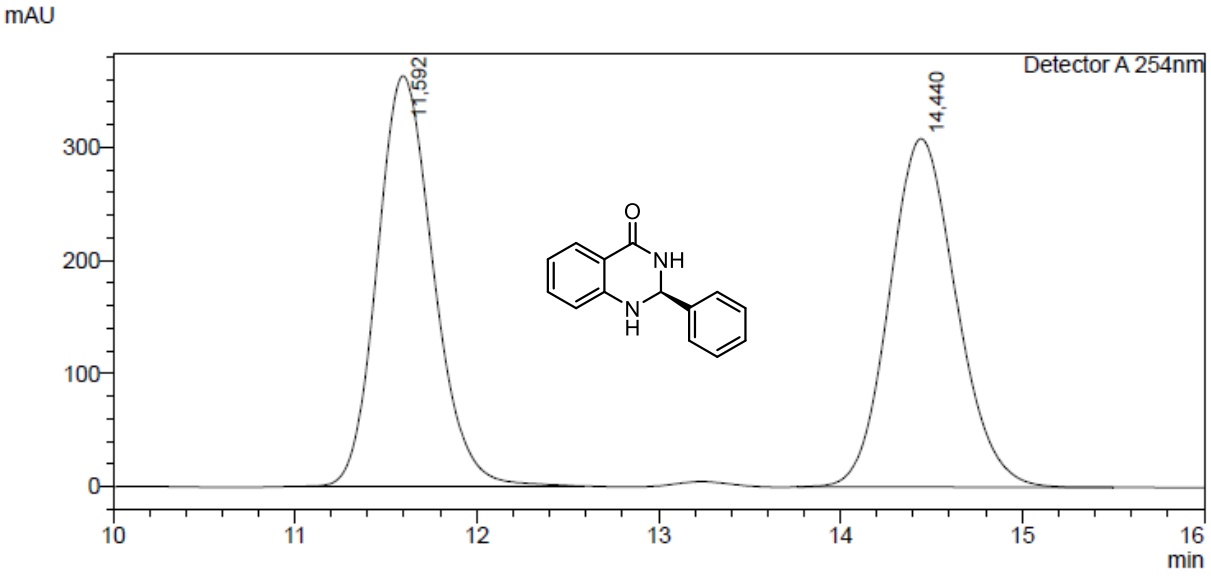
HRMS (TOF+, m/Z): calcd for $C_{12}H_{10}N_2OSH$ $[M+H]^+$: 231.0587, found: 231.0583.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 80:20, 1.0 mL/min, 25 °C, detection at 254 nm. Residence time: 8.4 min (minor), 11.1 (major). 1:99 er.

Chiral HPLC chromatograms of **8**

(S)-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (8a)

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
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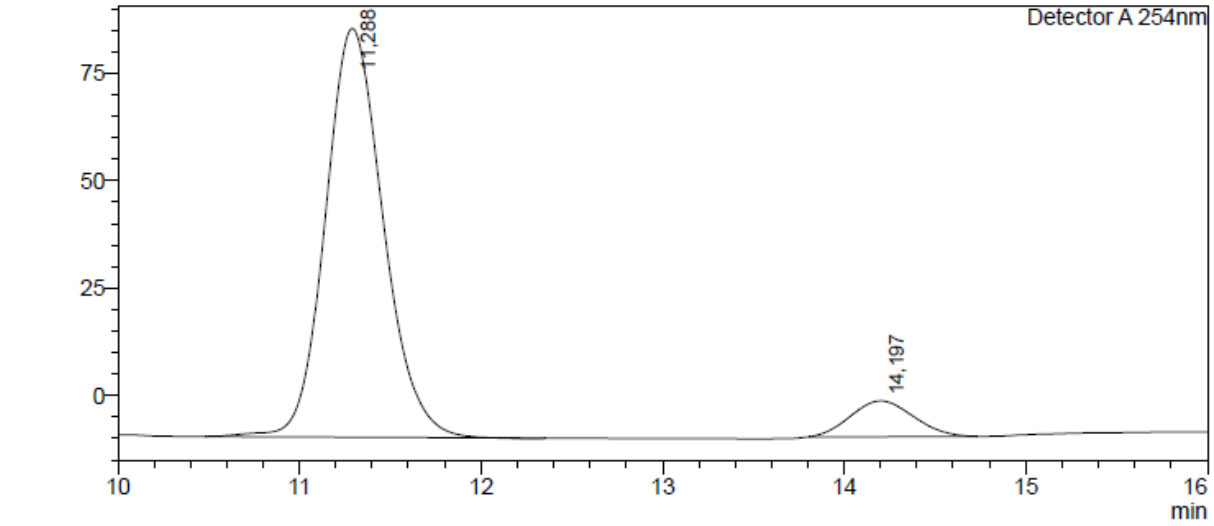
2	14,440	7899313	308176	50,374
Total		15681269	670944	100,000

<Chromatogram>



<Peak Table>

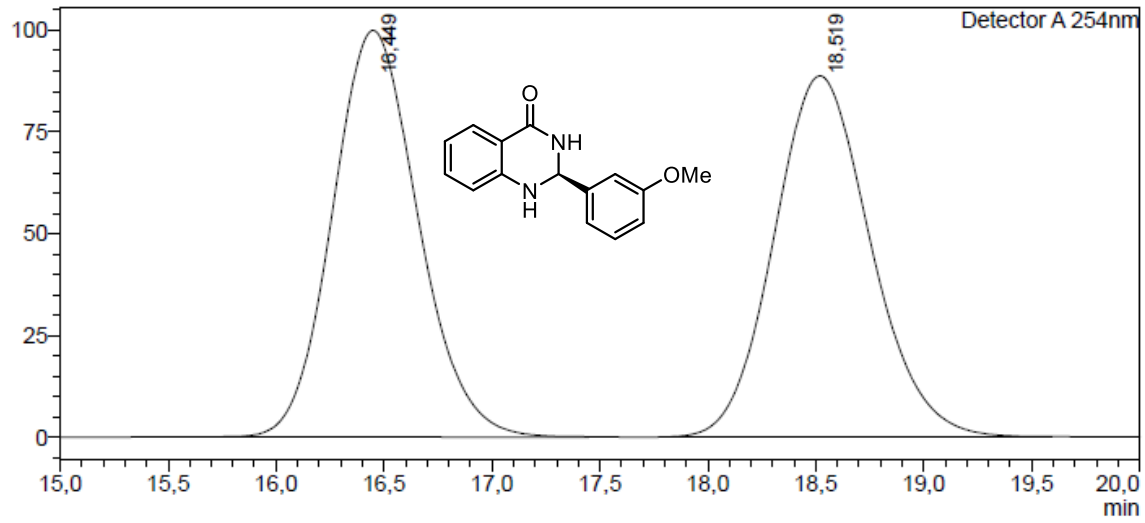
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11,288	2108847	95208	91,325
2	14,197	200313	8326	8,675
Total		2309160	103534	100,000

(S)-2-(3-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (8b)

<Chromatogram>

mV



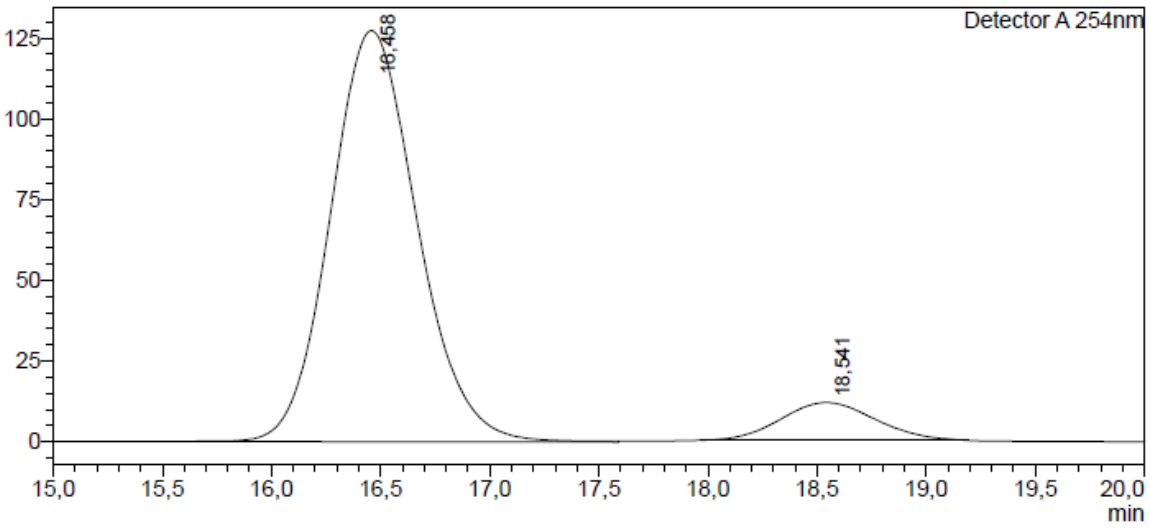
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16,449	2765002	99892	49,999
2	18,519	2765140	88725	50,001
Total		5530142	188617	100,000

<Chromatogram>

mV



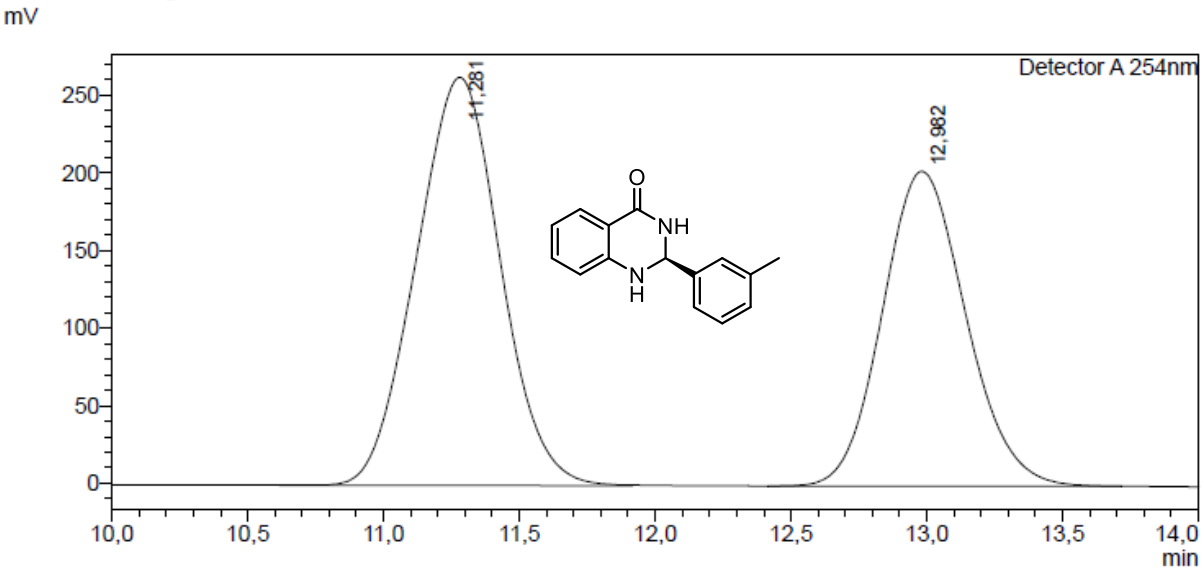
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16,458	3525348	127293	90,906
2	18,541	352684	11697	9,094
Total		3878032	138990	100,000

(S)-2-(m-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8c)

<Chromatogram>

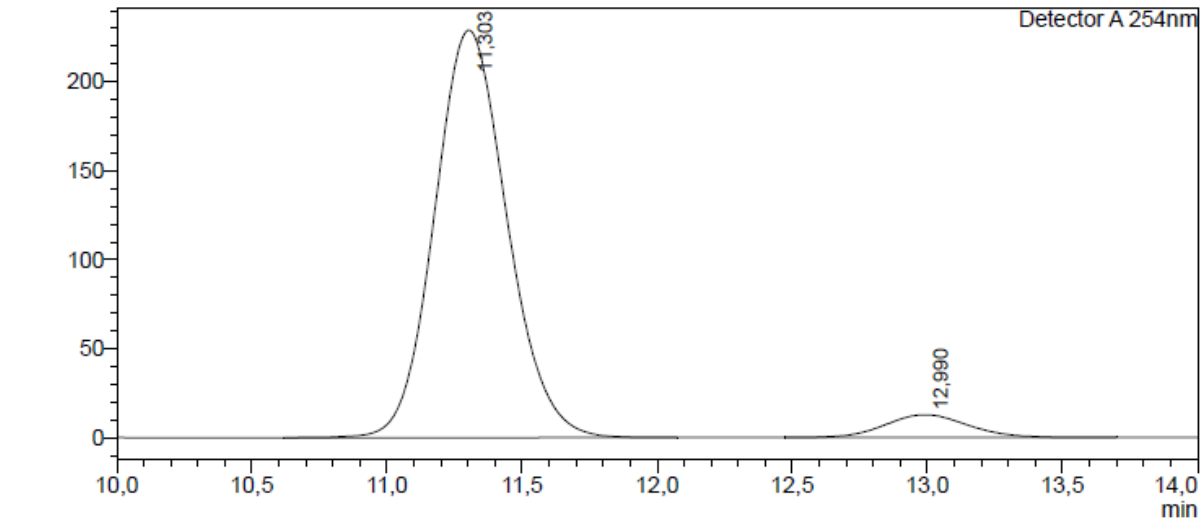


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11,281	5671328	263002	56,649
2	12,982	4339932	202878	43,351
Total		10011260	465880	100,000

<Chromatogram>



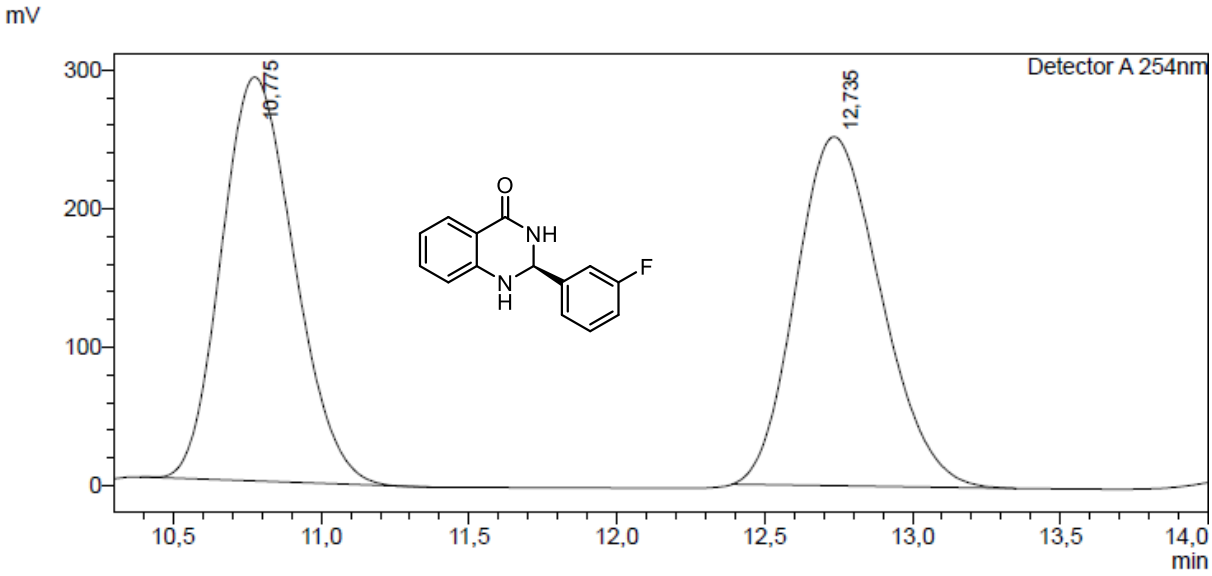
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11,303	4276590	228848	94,118
2	12,990	267272	12711	5,882
Total		4543863	241559	100,000

(S)-2-(3-fluorophenyl)-2,3-dihydroquinazolin-4(1H)-one (8d)

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10,775	4991117	291335	49,676
2	12,735	5056288	251585	50,324
Total		10047405	542920	100,000

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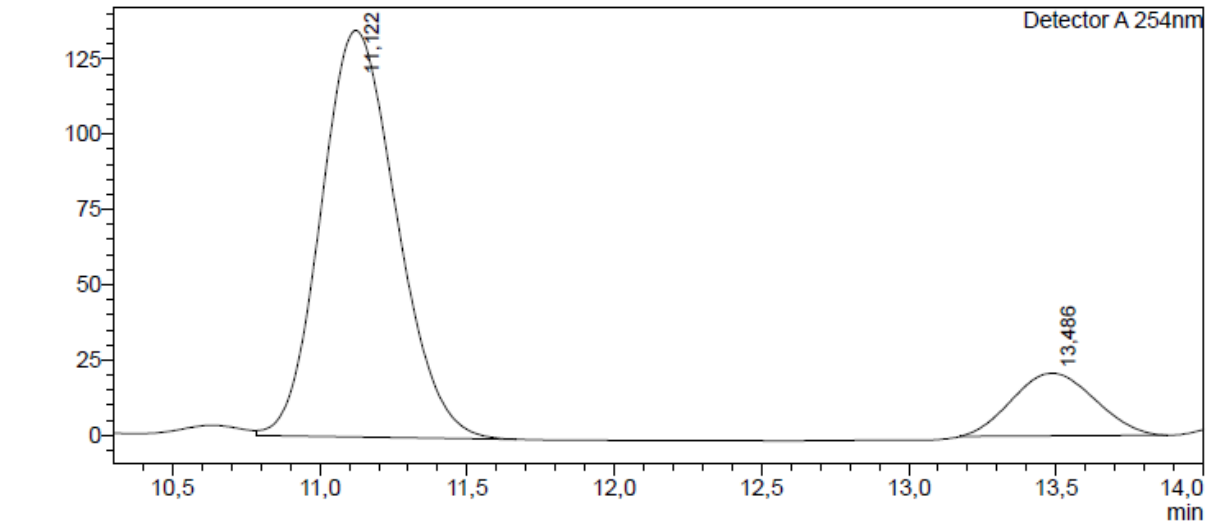


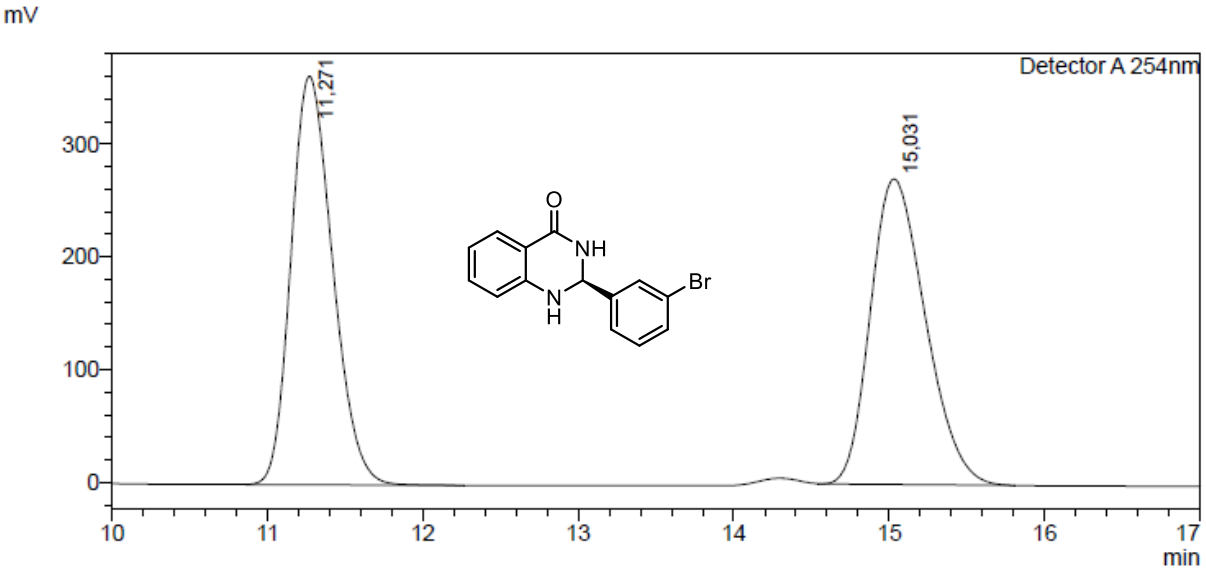
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11,122	2409309	135003	85,549
2	13,486	406984	20807	14,451
Total		2816293	155810	100,000

(S)-2-(3-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (8e)

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11,271	6750893	362408	50,263
2	15,031	6680201	271023	49,737
Total		13431094	633431	100,000

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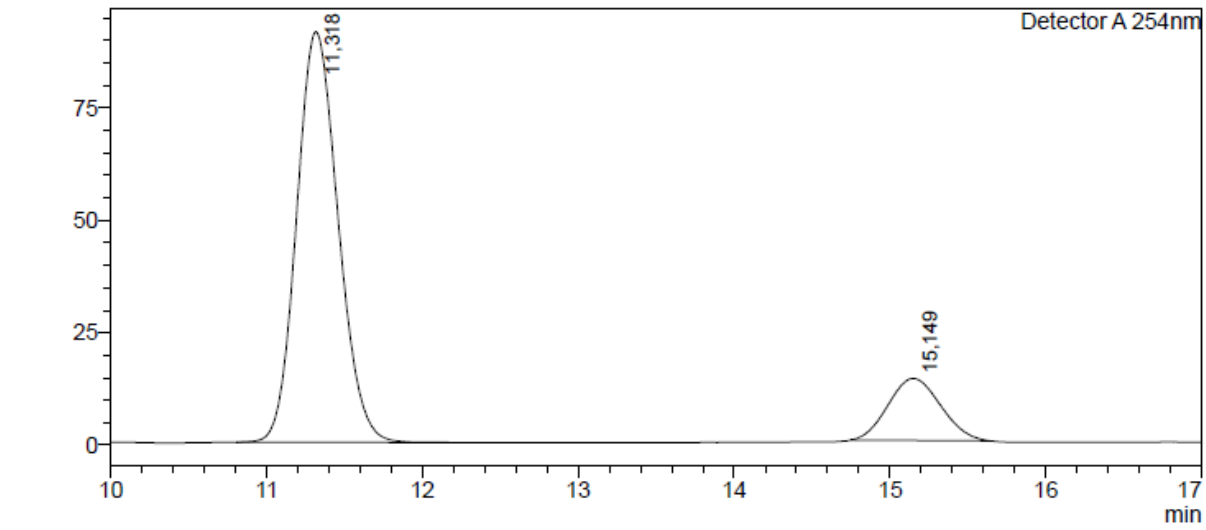

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11,318	1689162	91250	83,964
2	15,149	322607	13768	16,036
Total		2011769	105019	100,000

(S)-2-(3-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (8f)

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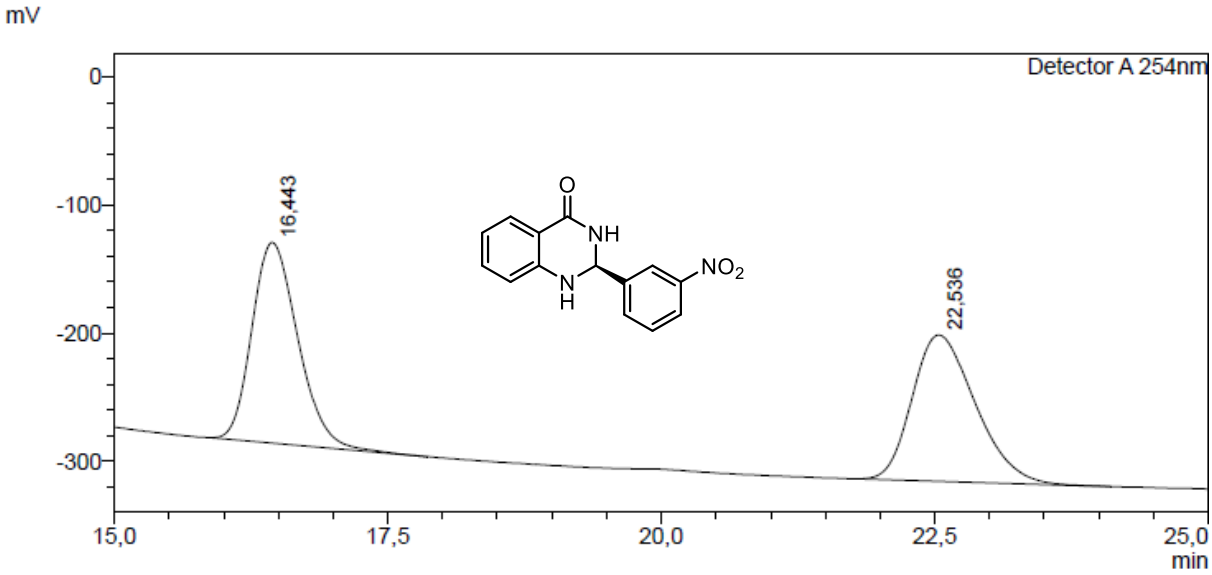
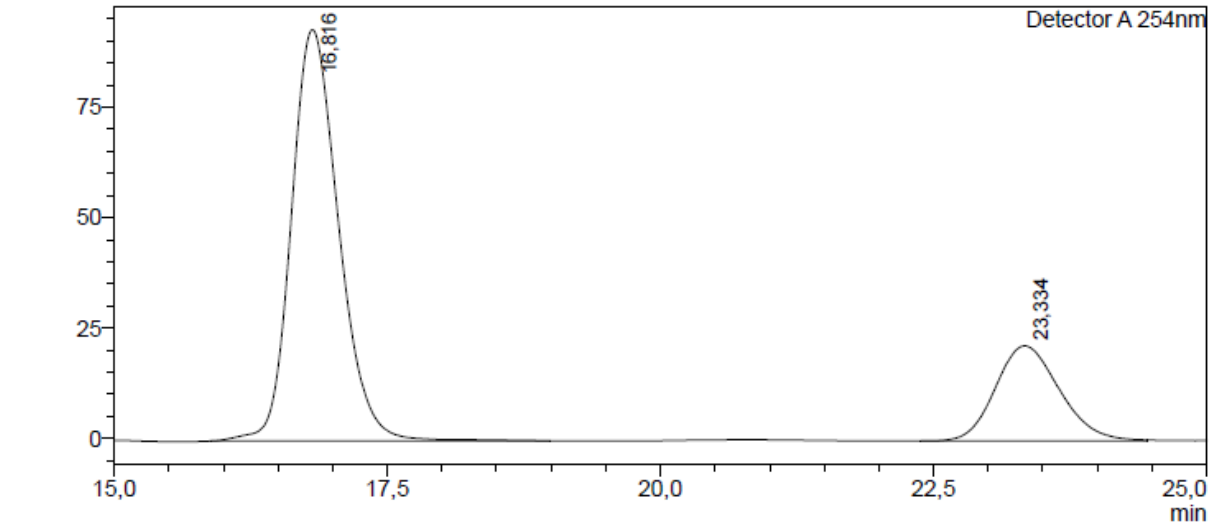


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16,443	4570293	156519	49,934
2	22,536	4582308	114113	50,066
Total		9152600	270632	100,000

<Chromatogram>



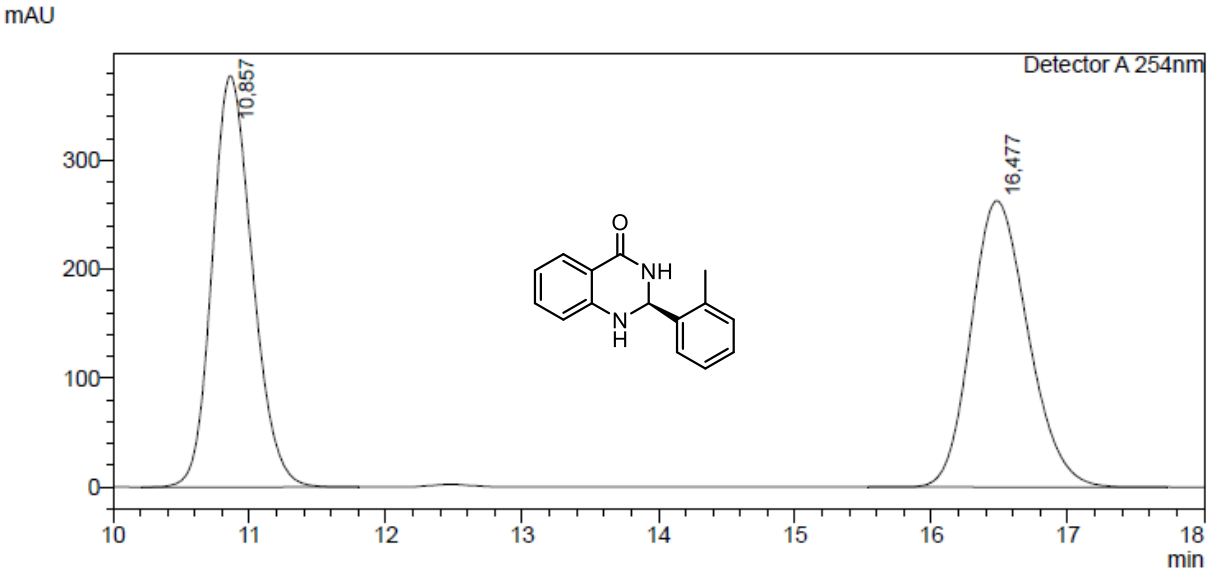
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16,816	2804202	93078	76,239
2	23,334	873946	21480	23,761
Total		3678148	114558	100,000

(S)-2-(o-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8g)

<Chromatogram>

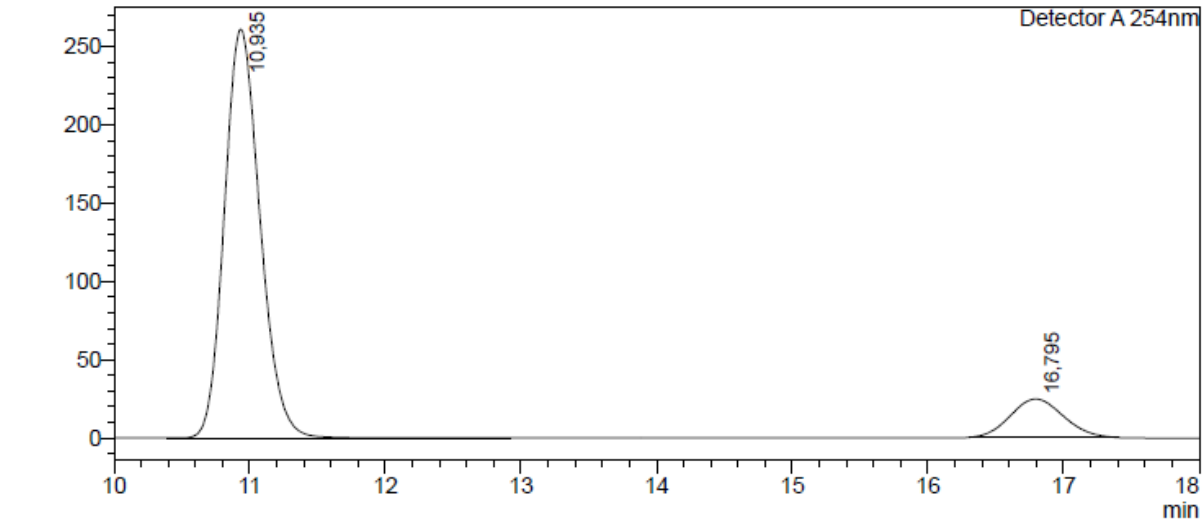


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10,857	7749965	377275	50,354
2	16,477	7641029	262646	49,646
Total		15390993	639921	100,000

<Chromatogram>



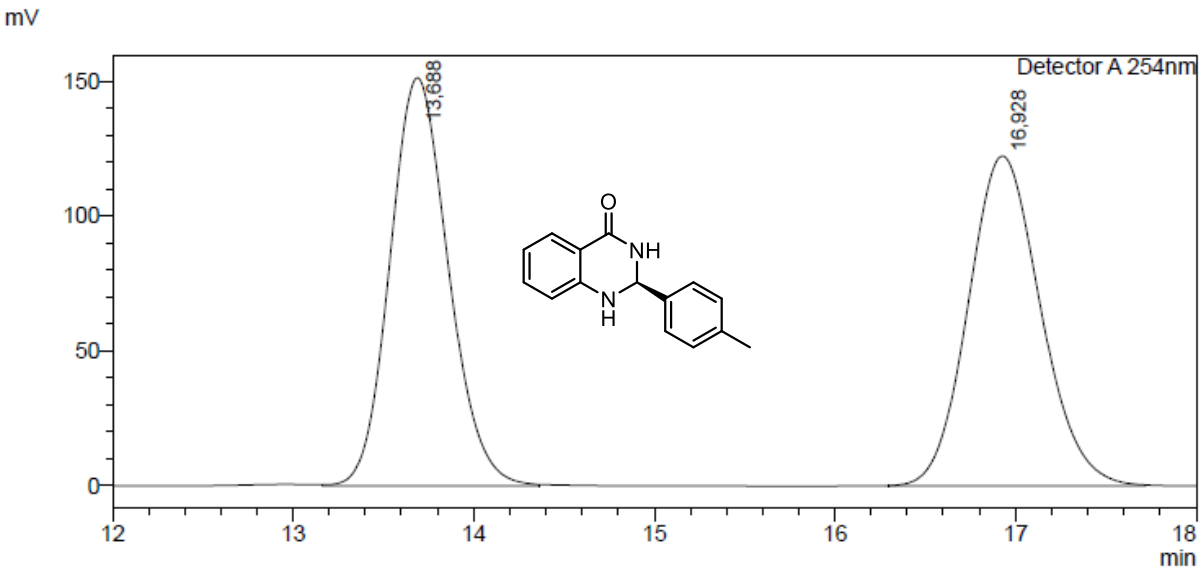
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10,935	4767445	260816	87,782
2	16,795	663530	24491	12,218
Total		5430975	285308	100,000

(S)-2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8h)

<Chromatogram>

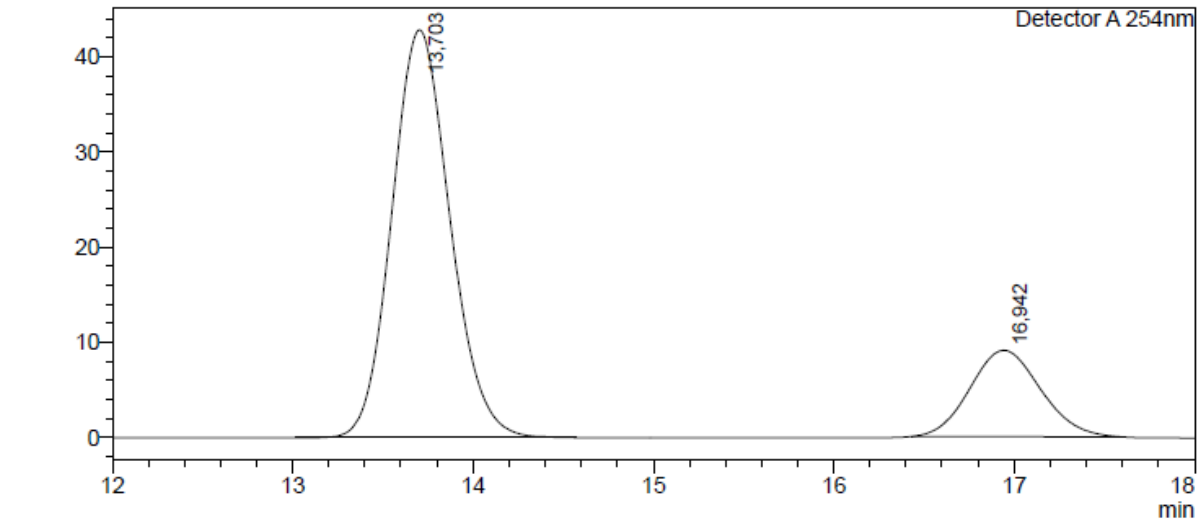


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13,688	3406565	151379	49,969
2	16,928	3410788	122349	50,031
Total		6817354	273729	100,000

<Chromatogram>



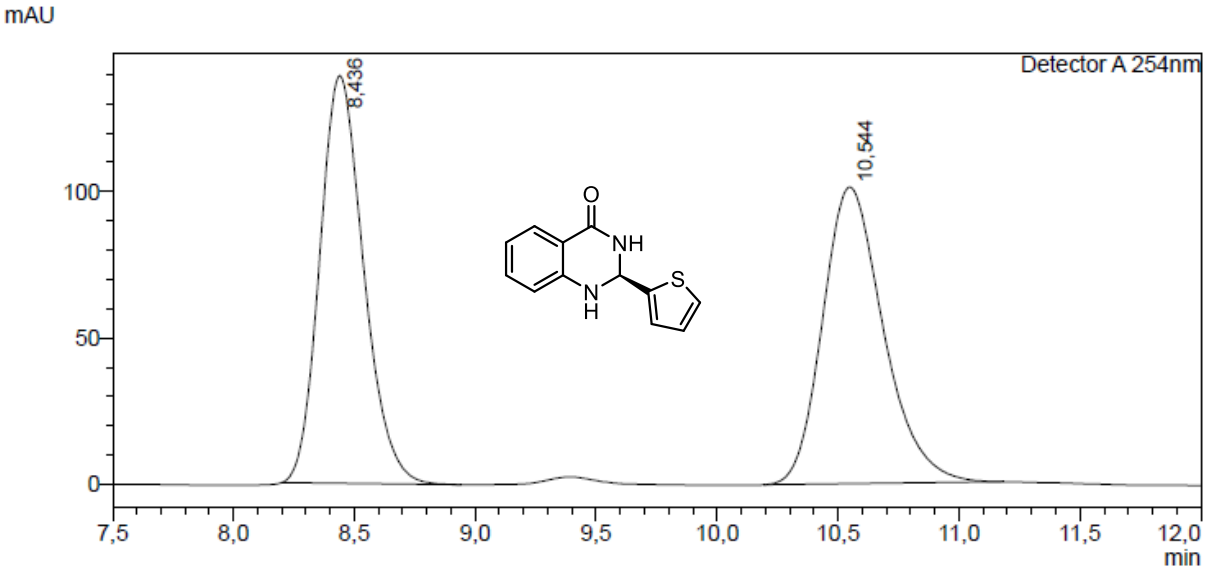
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13,703	959813	42833	79,538
2	16,942	246917	9068	20,462
Total		1206730	51901	100,000

(S)-2-(thiophen-2-yl)-2,3-dihydroquinazolin-4(1H)-one (8i)

<Chromatogram>

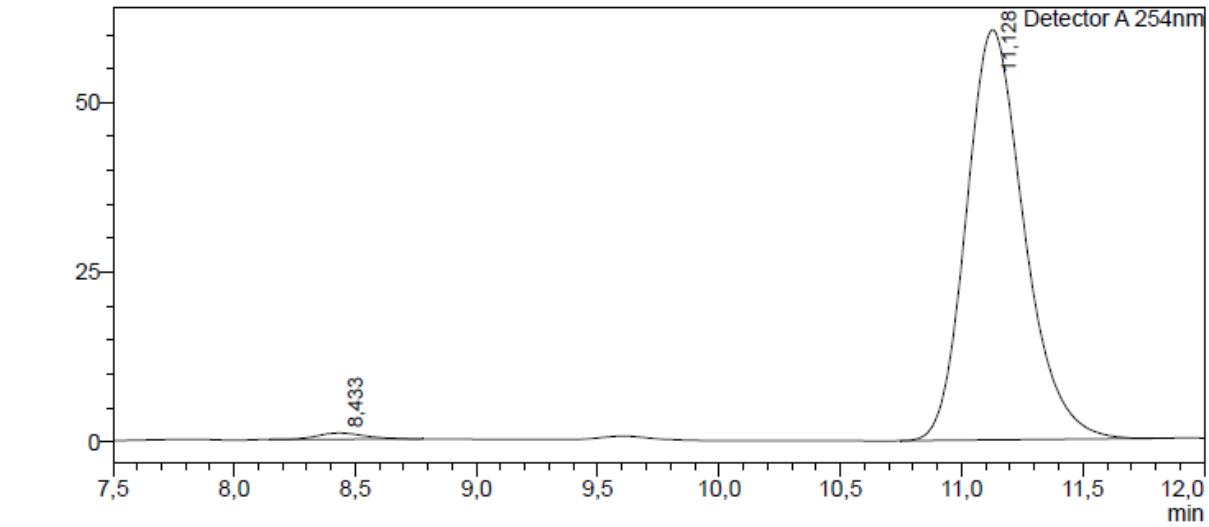


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8,436	1758330	139246	49,758
2	10,544	1775419	101349	50,242
Total		3533749	240595	100,000

<Chromatogram>



<Peak Table>

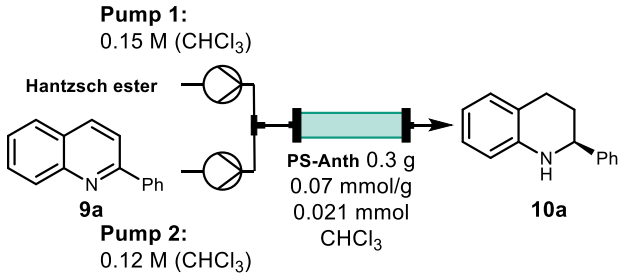
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8,433	12445	918	1,225
2	11,128	1003078	60435	98,775
Total		1015523	61353	100,000

Synthesis and characterization of **10**

Optimization in flow

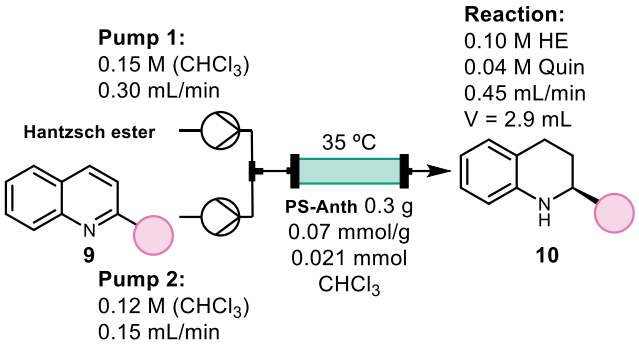
Table S1. *Optimization of the asymmetric transfer hydrogenation in flow.*



#	Flow rate P1 (mL/min)	Flow rate P2 (mL/min)	Equiv. HE	T (°C)	Conv. (%)[a]	er[b]
1	0.28	0.15	2.3	20	80	5:95
2	0.30	0.15	2.5	20	88	5:95
3	0.33	0.15	2.7	20	94	5:95
4	0.33	0.15	2.7	30	97	5:95
5	0.33	0.15	2.7	40	>98	7:93
6	0.30	0.15	2.7	35	>98	5:95
7	0.30	0.15	2.5	35	>98	5:95
8	0.28	0.15	2.3	35	87	6:94

a) Conversion was determined by GC-FID Area %.
b) ee was determined by chiral HPLC.

Preparative run



The packed bed reactor was filled with a mixture of glass beads (2.3 g, 2 mm ø) and 0.3 g of **PS-Anth** (0.07 mmol/g, 0.021 mmol, dried overnight at 40°C in a vacuum oven). The adjustable end of the Omnifit® glass column (10 mm ID) was opened. The reactor was then filled with chloroform to swell the resin, closed and adjusted as required. Both ends were closed with a frit to prevent the catalyst particles from clogging the system (See Figure S5). Before each reaction, the catalyst bed was swollen by pumping $CHCl_3$ at 0.5 mL/min for 5-10 min and the catalyst bed was pre-heated to 35 °C. The stock solutions (in $CHCl_3$) of quinoline **9** (0.12 M, 0.15 mL/min, 1.0 equiv.) and **Hantzsch ester** (0.15 M, 0.30 mL/min, 2.5 equiv.) were pumped independently and pre-mixed right before entering the Omnifit column containing the **PS-Anth** catalyst by using a Syrris® Asia syringe pump (0.45 mL/min overall flow rate). The pressure of the system generated by the packed bed reactor during the long run was around 1.0 bar. Between runs, the quinolone stream was washed by pumping $CHCl_3$ at 0.5 mL/min for 5 min.

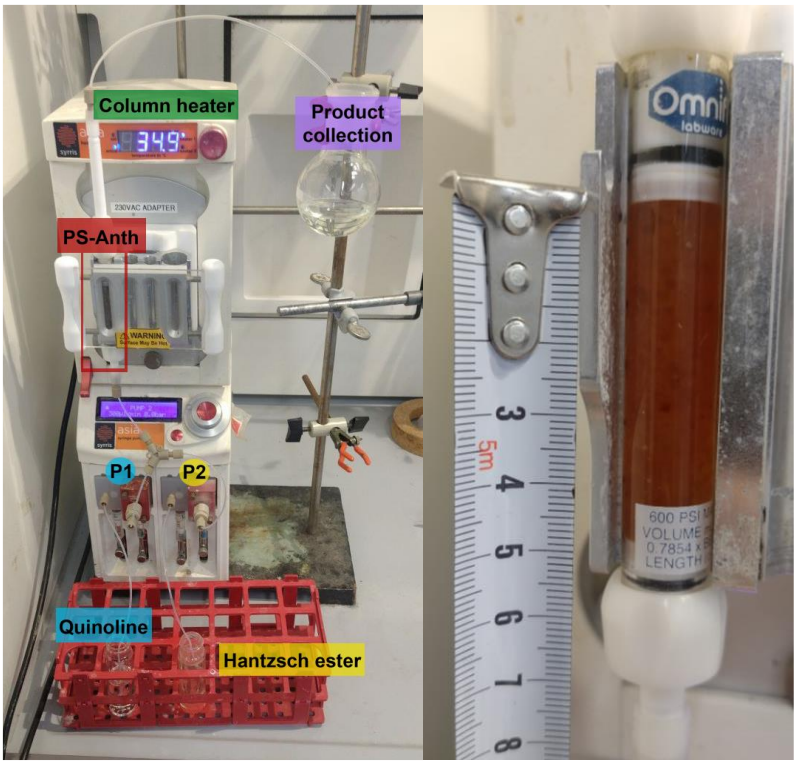


Figure S5. *Optimal flow set up.*

The reactor volume was calculated using the packed bed reactor volume. It was calculated according to the indications from the vendor and the volume corresponding to 2.3 g of glass beads (1.4 mL) was subtracted.

$$\text{Bed volume (mL)} = 0.7854 \times \text{bed height (cm)} - \textit{spiral volume}\ (mL) = 0.7854 \times 5.5 - 1.4$$
$$= 2.9197\ mL$$

Catalyst metrics for the preparative run (Tetrahydroquinoline 9a)

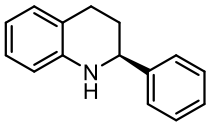
Turnover number (TON) and space time yield (STY) were calculated for the 5 h run following the literature formulas.[S6]

$$\text{TON} = \frac{mmoles\ limiting\ reactant}{mmoles\ catalyst} \times yield = \frac{5.4}{0.021} \times 0.93 = 239.1$$

$$\text{STY} = \frac{mass\ of\ product}{volume\ of\ reactor\ \times reaction\ time} = \frac{1.051\ e^{-3} kg}{2.9197 e^{-6}\ m^3\ \times 5\ h} = 71.99\ kg\ m^{-3}\ h^{-1}$$

$$\text{Productivity} = \frac{mmol\ of\ product}{reaction\ time \times g_{resin}} = \frac{5.02\ mmol}{5\ h\ \times 0.3\ g_{PS-Anth}} = 3.35\ mmol\ h^{-1}\ {g_{resin}}^{-1}$$

(S)-2-phenyl-1,2,3,4-tetrahydroquinoline (10a)



The general procedure was followed, collecting the reaction product for 5h in steady state to afford 1.051 g (93%) of the product as a colorless liquid. The reported data match the literature.[S7]

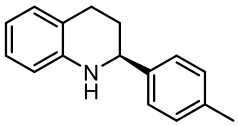
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.41 (m, 5H), 7.23 – 7.12 (m, 2H), 6.87 – 6.80 (m, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 4.56 (dd, *J* = 9.2, 3.4 Hz, 1H), 4.13 (s, 1H), 3.08 (ddd, *J* = 16.1, 10.5, 5.5 Hz, 1H), 2.89 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.34 – 2.07 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.9, 144.8, 129.3, 128.6, 127.4, 126.9, 126.6, 120.8, 117.2, 114.0, 56.2, 31.0, 26.4.

HRMS (TOF+, m/Z): calcd for $C_{15}H_{15}NH$ $[M+H]^+$: 210.1277, found: 210.1274.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 95:5, 0.6 mL/min, 40 °C, detection at 254 nm. Residence time: 9.1 min (minor), 10.6 (major). 5:95 er.

(S)-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline (10b)



The general procedure was followed, collecting the reaction product for 1h in steady state to afford 214.7 mg (89%) of the product as a colorless liquid. The reported data match the literature.[S7]

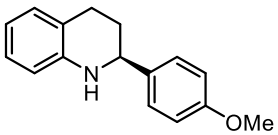
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.01 (s, 2H), 6.65 (td, *J* = 7.4, 1.1 Hz, 1H), 6.54 (dd, *J* = 8.4, 1.1 Hz, 1H), 4.41 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.03 (bs, 1H), 2.93 (ddd, *J* = 16.3, 10.7, 5.5 Hz, 1H), 2.75 (dt, *J* = 16.4, 4.7 Hz, 1H), 2.36 (s, 3H), 2.18 – 1.91 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.9, 141.9, 137.2, 129.4, 129.4, 127.0, 126.6, 121.0, 117.2, 114.1, 56.1, 31.1, 26.6, 21.2.

HRMS (TOF+, m/Z): calcd for $C_{16}H_{17}NH$ $[M+H]^+$: 224.1434, found: 224.1435.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 95:5, 0.6 mL/min, 40 °C, detection at 254 nm. Residence time: 8.8 min (minor), 12.6 (major). 1:99 er.

(S)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (10c)



The general procedure was followed, collecting the reaction product for 1h in steady state to afford 222.3 mg (86%) of the product as a colorless liquid. The reported data match the literature.[S7]

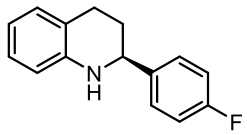
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.66 (td, *J* = 7.4, 1.1 Hz, 1H), 6.53 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.39 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.00 (bs, 1H), 3.82 (s, 3H), 2.94 (ddd, *J* = 16.4, 10.8, 5.6 Hz, 1H), 2.75 (dt, *J* = 16.4, 4.6 Hz, 1H), 2.16 – 1.89 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.1, 144.9, 137,0, 129.4, 127.8, 127.0, 121.0, 117.3, 114.1, 114.0, 55.9, 55.4, 31.2, 26.7.

HRMS (TOF+, m/Z): calcd for $C_{16}H_{17}NOH$ $[M+H]^+$: 239.1383, found: 239.1377.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 90:10, 0.6 mL/min, 40 °C, detection at 254 nm. Residence time: 10.8 min (minor), 15.4 (major). 2:98 er.

(S)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline (10d)



The general procedure was followed, collecting the reaction product for 1h in steady state to afford 223.4 mg (91%) of the product as a colorless liquid. The reported data match the literature.[S7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.09 – 6.97 (m, 4H), 6.67 (td, *J* = 7.4, 1.1 Hz, 1H), 6.55 (dd, *J* = 8.4, 1.1 Hz, 1H), 4.43 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.04 (bs, 1H), 2.93 (ddd, *J* = 16.2, 10.6, 5.5 Hz, 1H), 2.74 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.18 – 1.87 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz), 144.6, 140.6 (d, *J* = 3.1 Hz), 129.5, 128.2 (d, *J* = 8.0 Hz), 127.1, 121.0, 117.5, 115.5 (d, *J* = 21.3 Hz), 114.2, 55.7, 31.2, 26.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ -115.32.

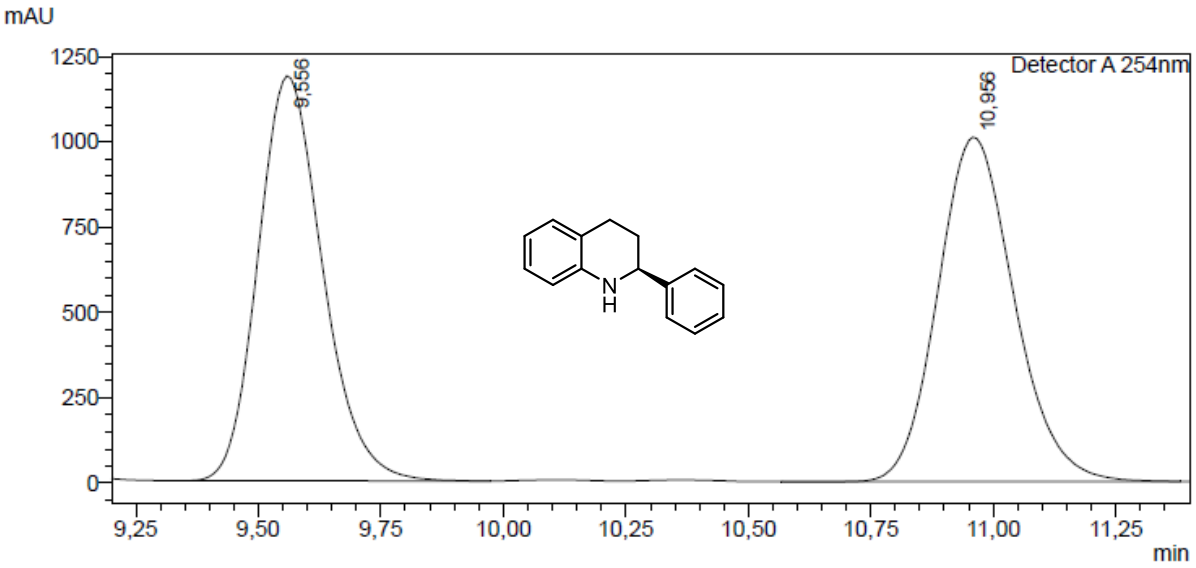
HRMS (TOF+, m/Z): calcd for $C_{15}H_{14}FNH$ $[M+H]^+$: 228.1183, found: 228.1178.

HPLC (chiral): Chiralpak-AD-H, n-heptane/i-PrOH 95:5, 0.6 mL/min, 40 °C, detection at 254 nm. Residence time: 9.8 min (minor), 12.7 (major). 2:98 er.

Chiral HPLC chromatograms of **10**

(S)-2-phenyl-1,2,3,4-tetrahydroquinoline (10a)

<Chromatogram>

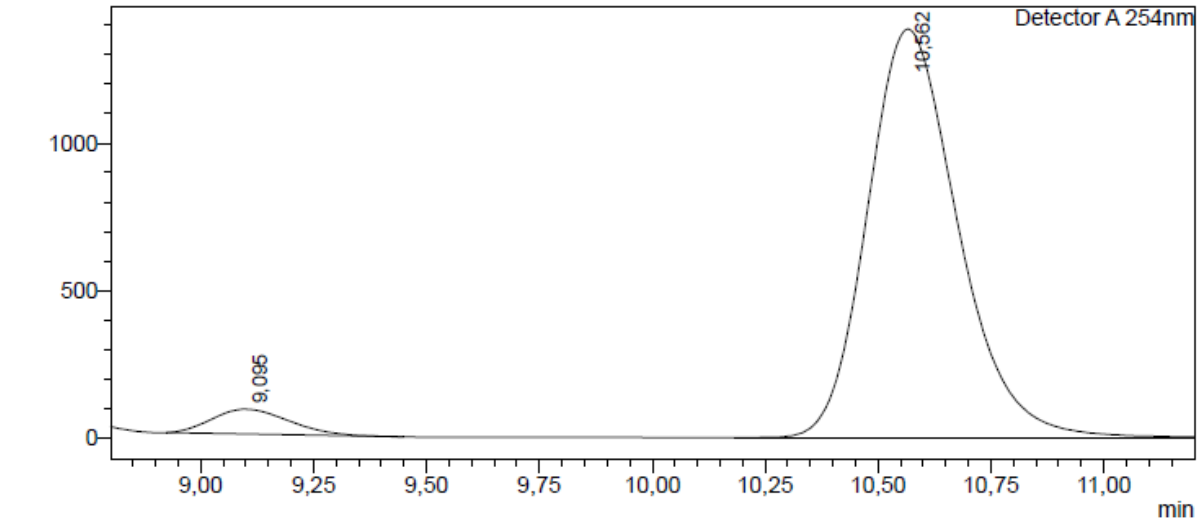


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9,556	10887794	1185958	49,883
2	10,956	10938747	1008829	50,117
Total		21826541	2194787	100,000

<Chromatogram>



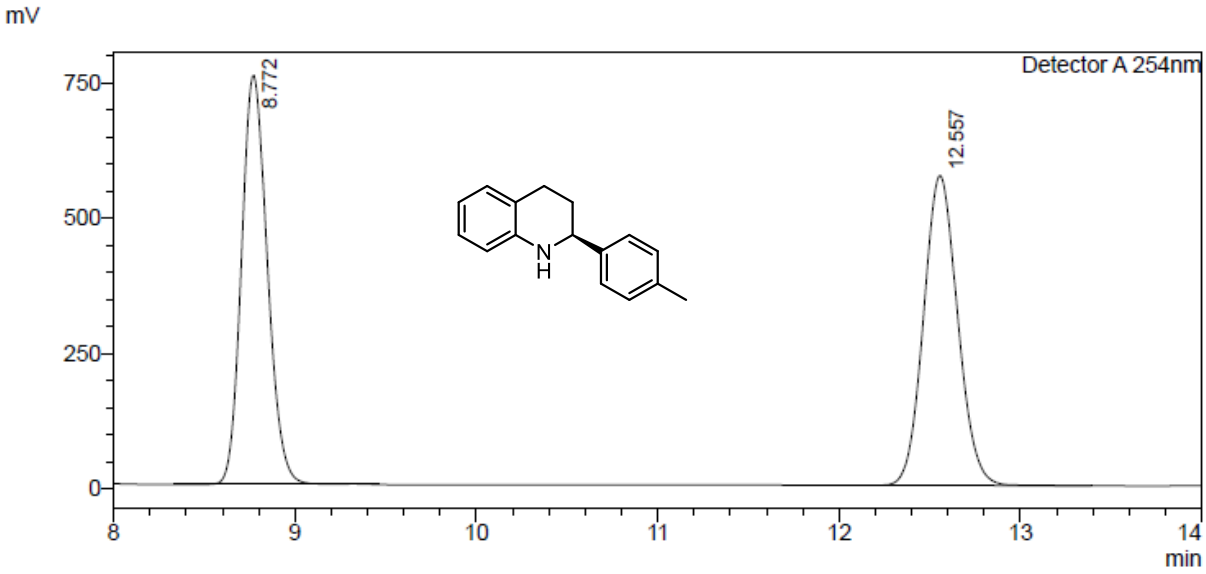
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9,095	992923	83724	4,877
2	10,562	19367563	1387417	95,123
Total		20360486	1471141	100,000

(S)-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline (10b)

<Chromatogram>

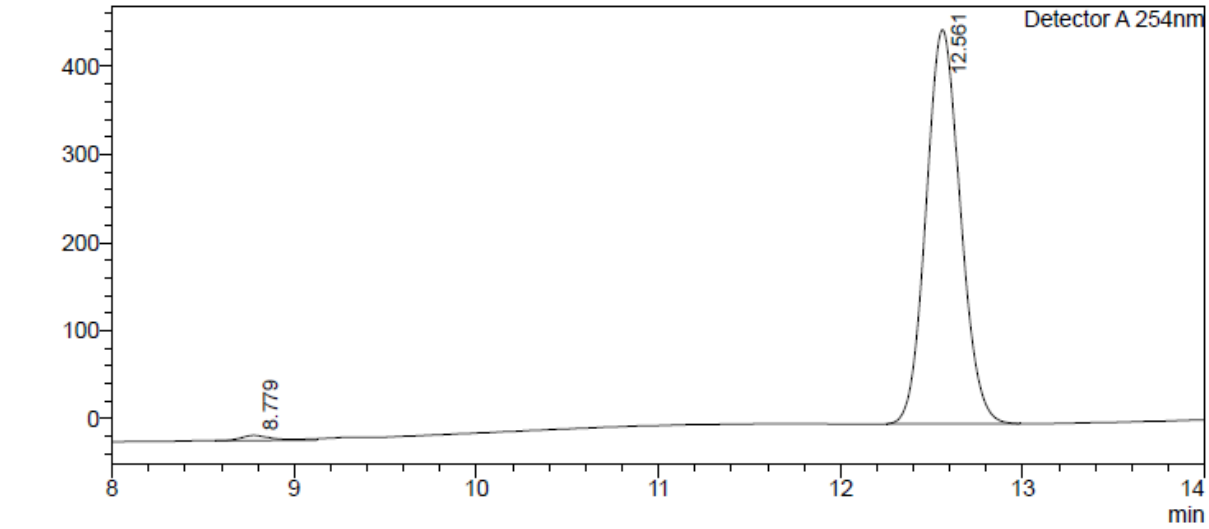


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.772	7504278	756995	50.019
2	12.557	7498434	573402	49.981
Total		15002712	1330397	100.000

<Chromatogram>



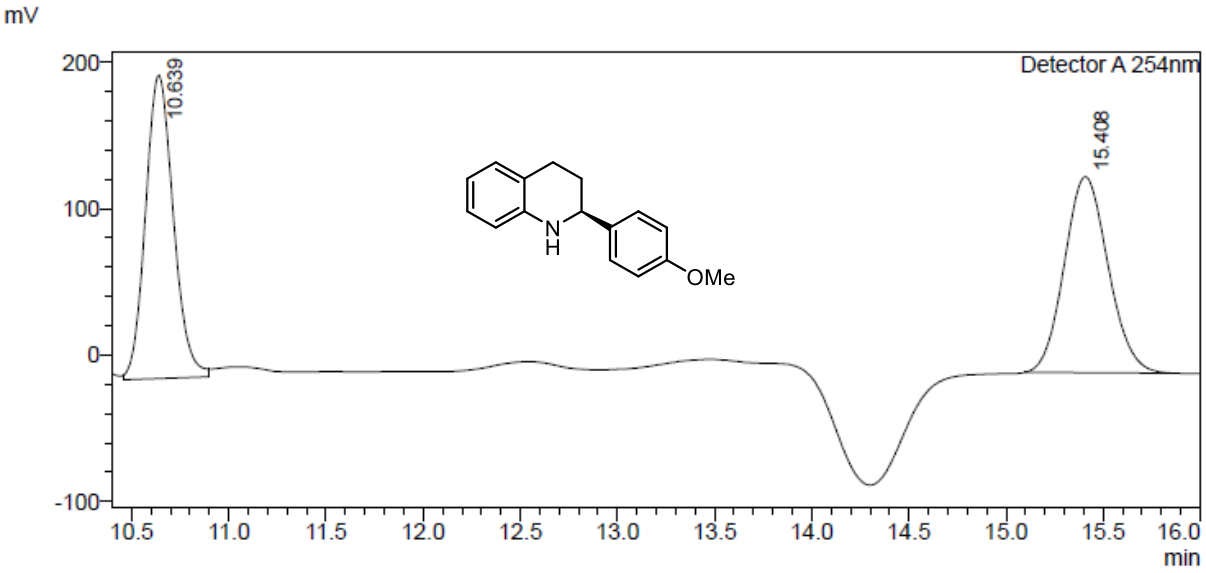
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.779	71174	5651	1.200
2	12.561	5857822	447241	98.800
Total		5928996	452891	100.000

(S)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (10c)

<Chromatogram>

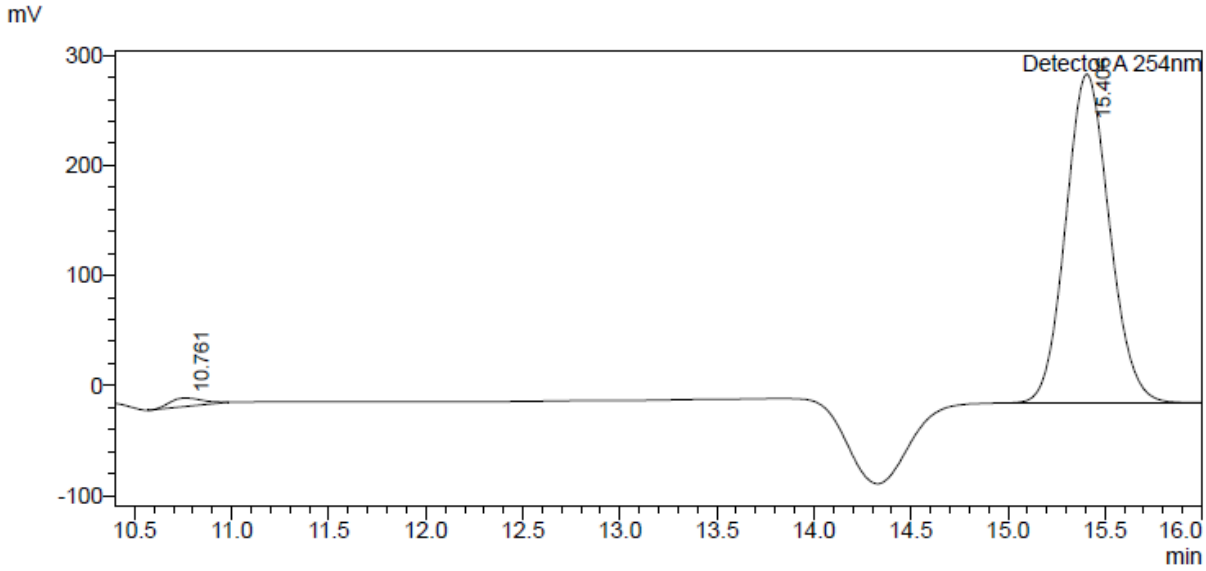


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.639	2070633	207293	49.667
2	15.408	2098379	133883	50.333
Total		4169012	341177	100.000

<Chromatogram>



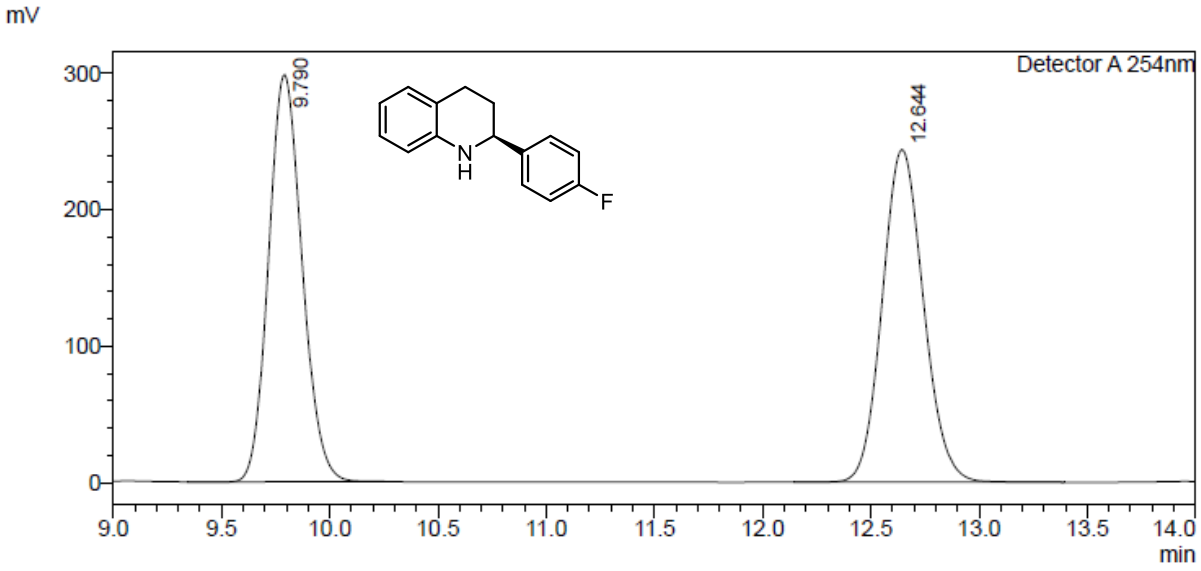
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.761	92101	7818	1.922
2	15.406	4698770	298735	98.078
Total		4790872	306553	100.000

(S)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline (10d)

<Chromatogram>

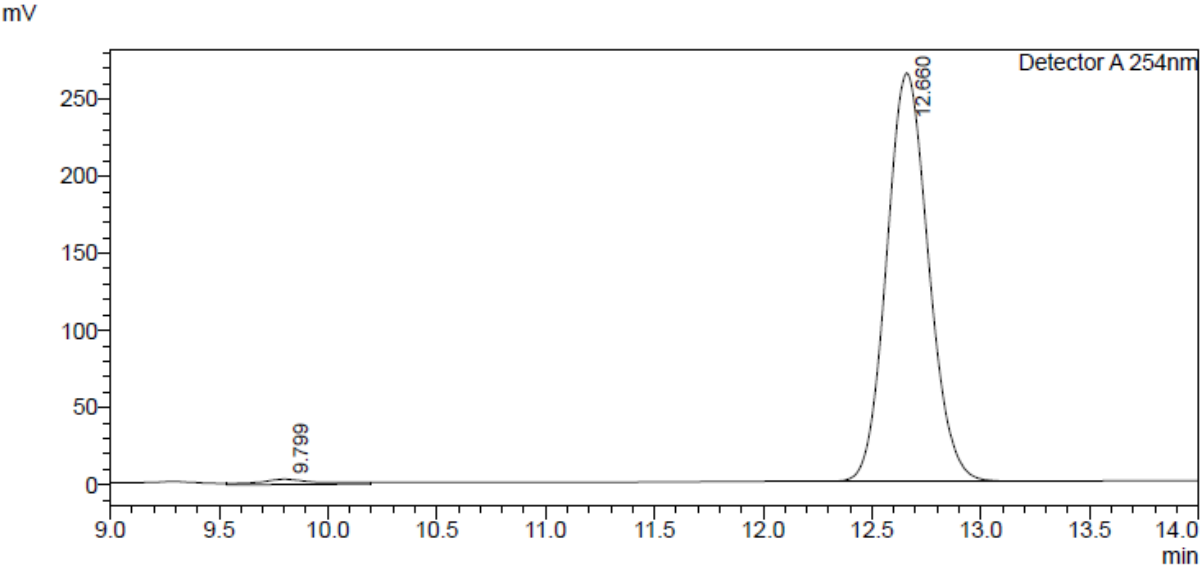


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.790	3226029	298513	49.994
2	12.644	3226826	243738	50.006
Total		6452855	542251	100.000

<Chromatogram>



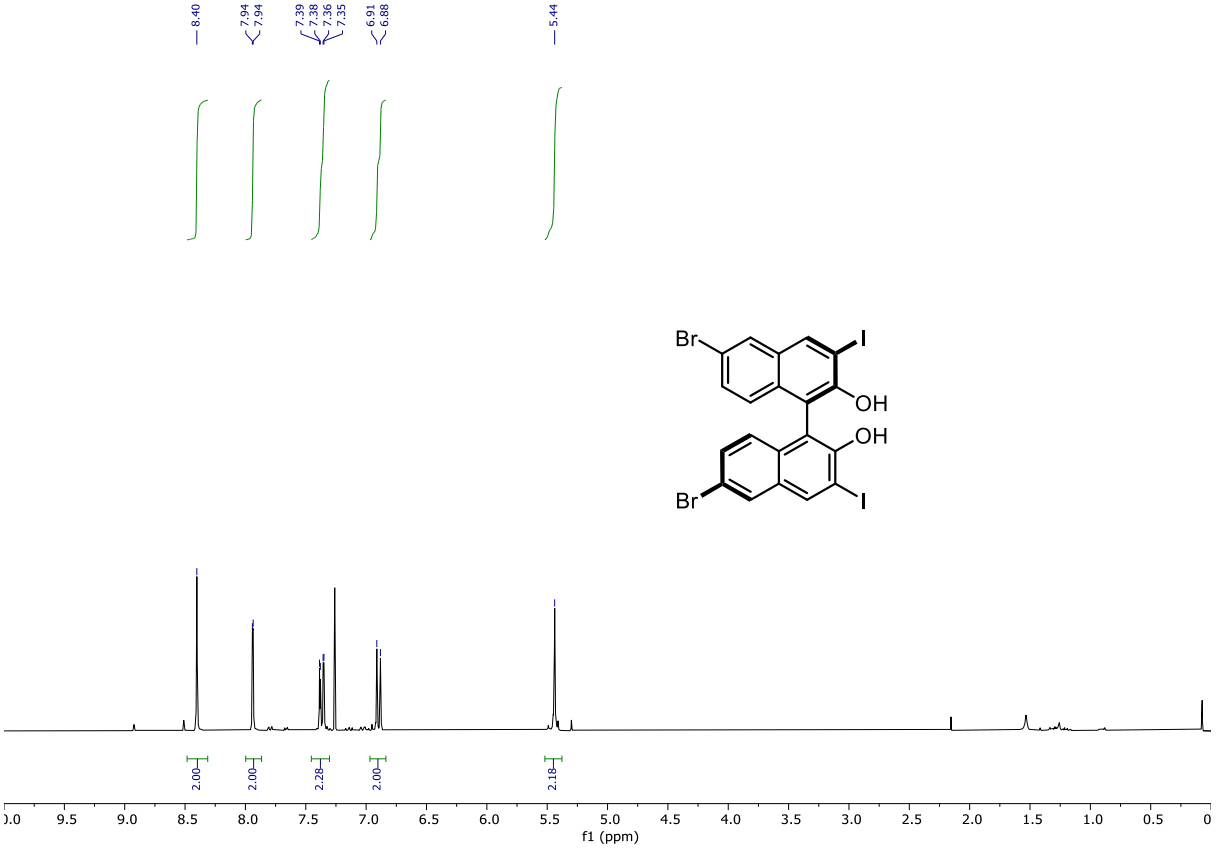
<Peak Table>

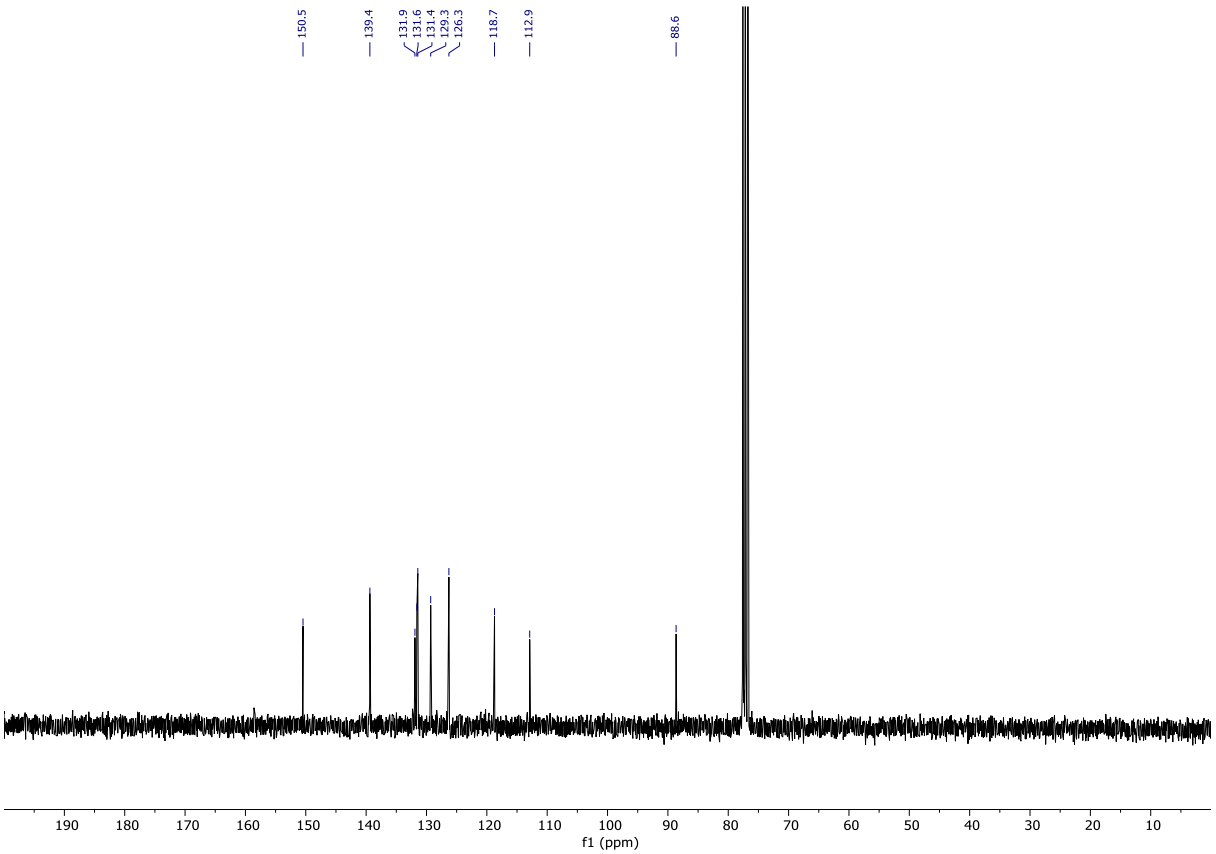
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.799	67529	3389	1.878
2	12.660	3529107	264377	98.122
Total		3596635	267766	100.000

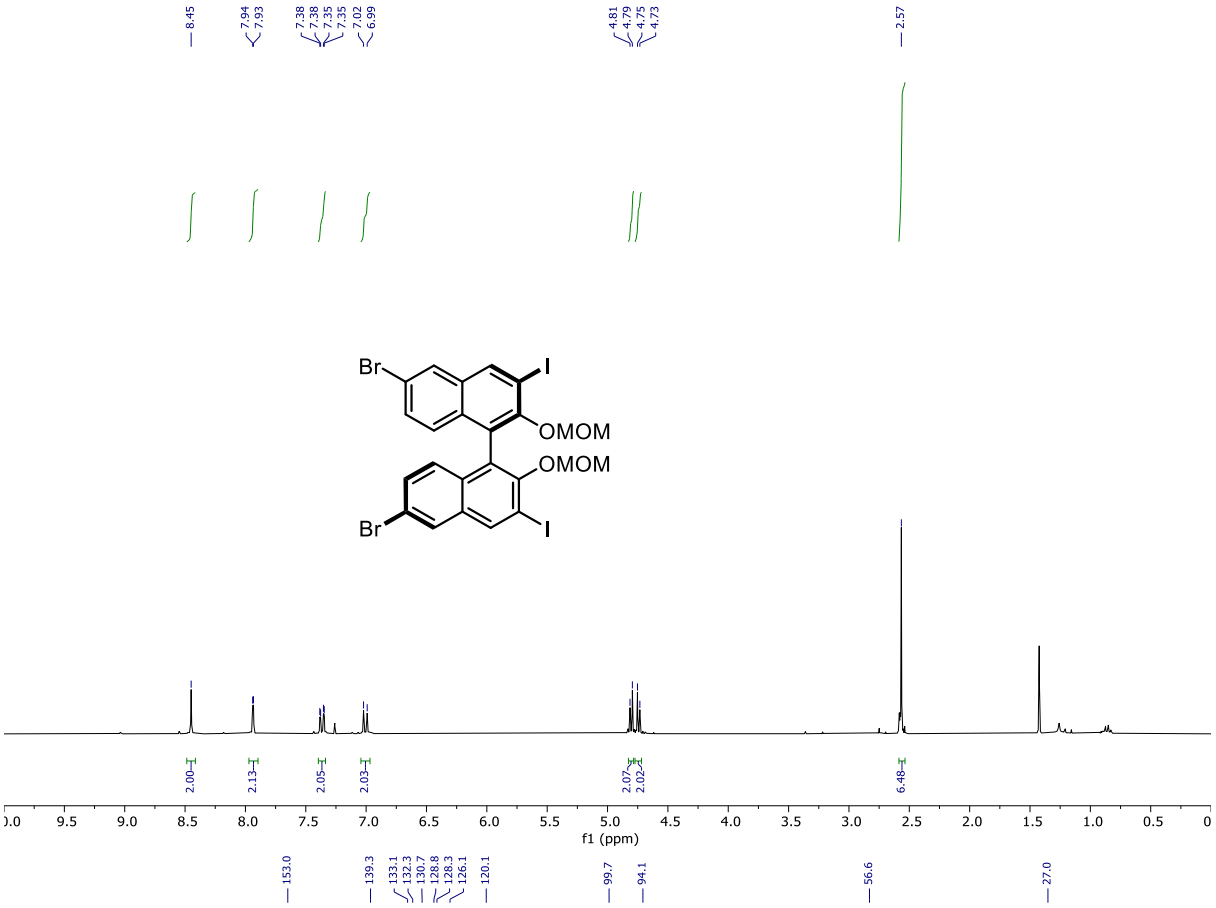
NMR spectra of BINOL derivartives **3-6**

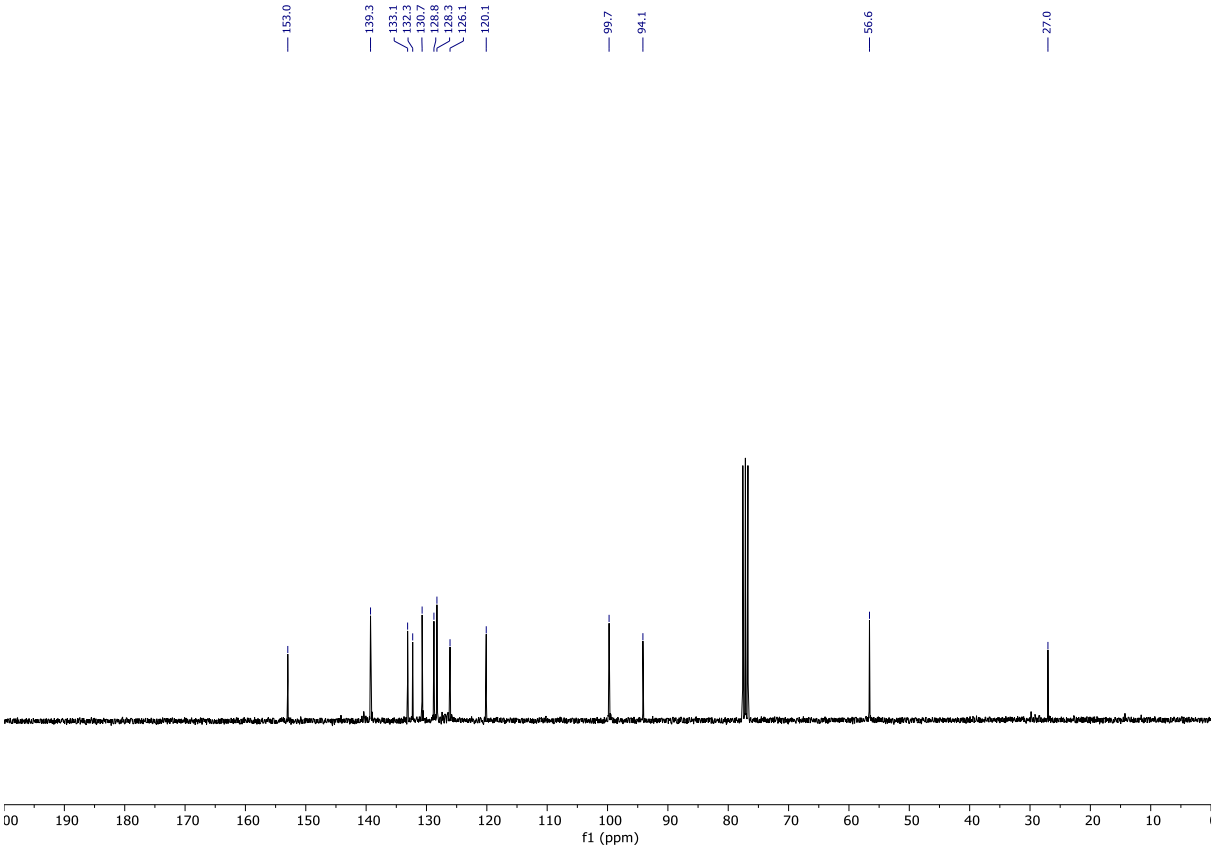
(*R*)-6,6'-dibromo-3,3'-diiodo-[1,1'-binaphthalene]-2,2'-diol (3) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)





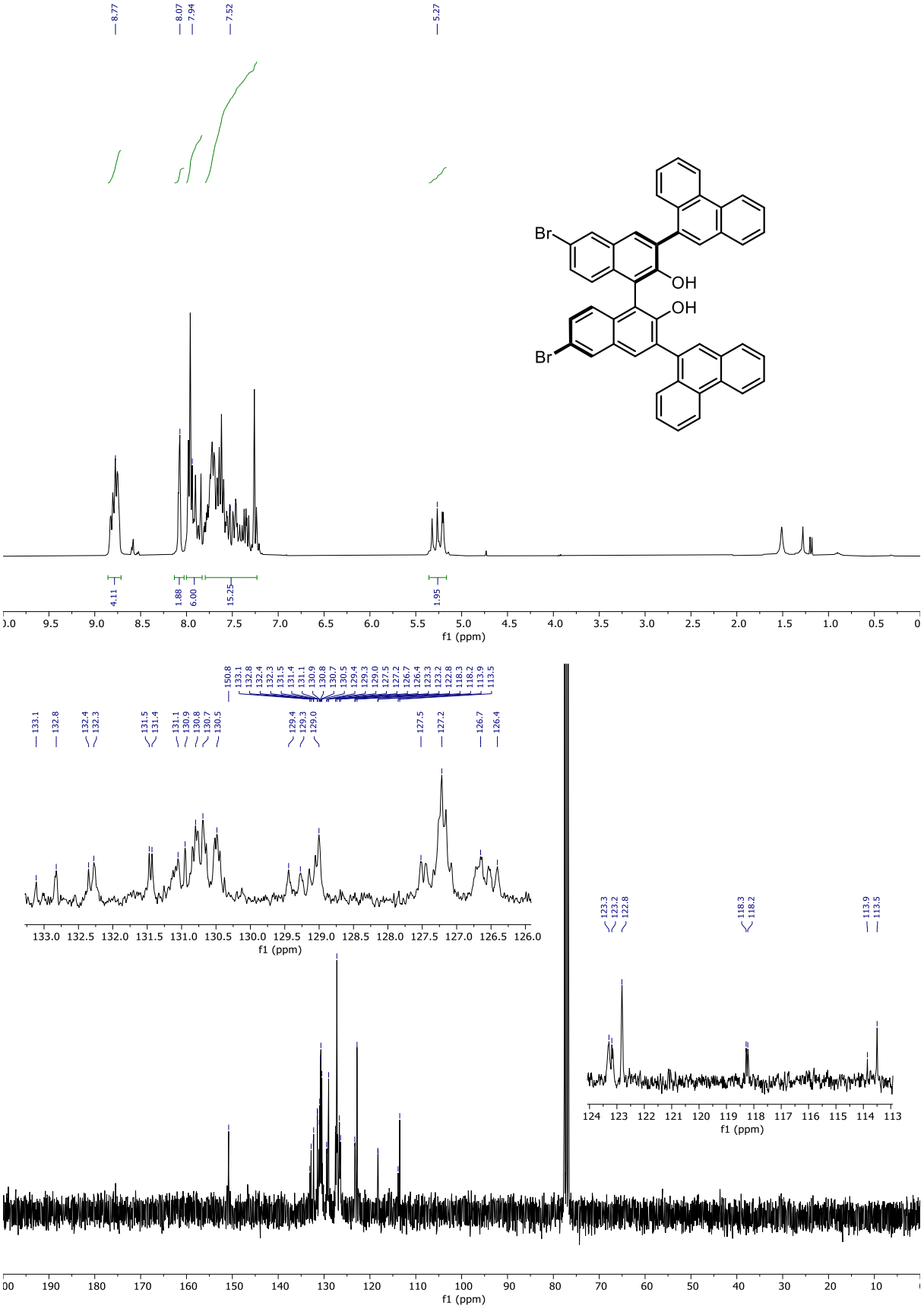
(*R*)-6,6'-dibromo-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (3-MOM) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)



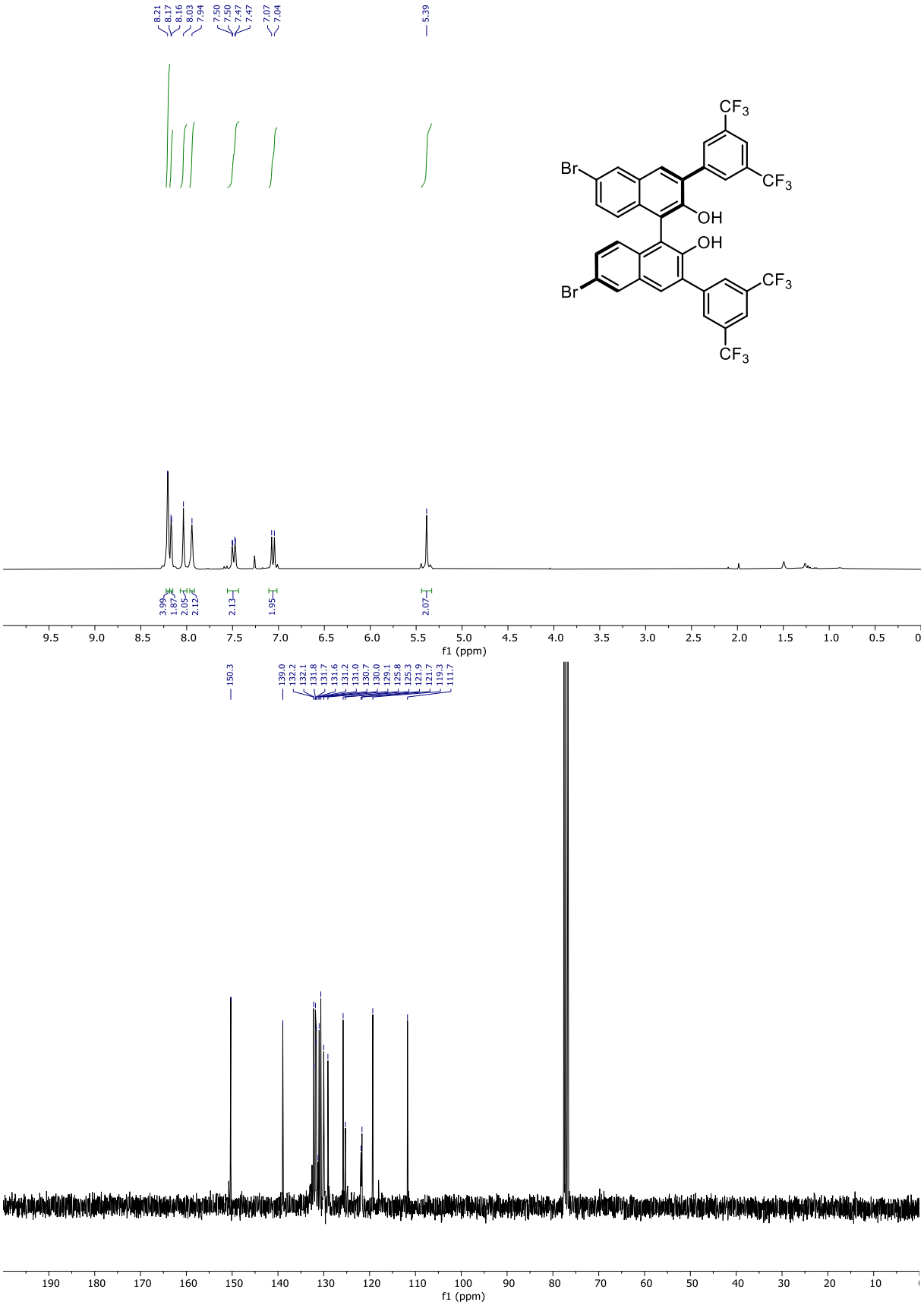


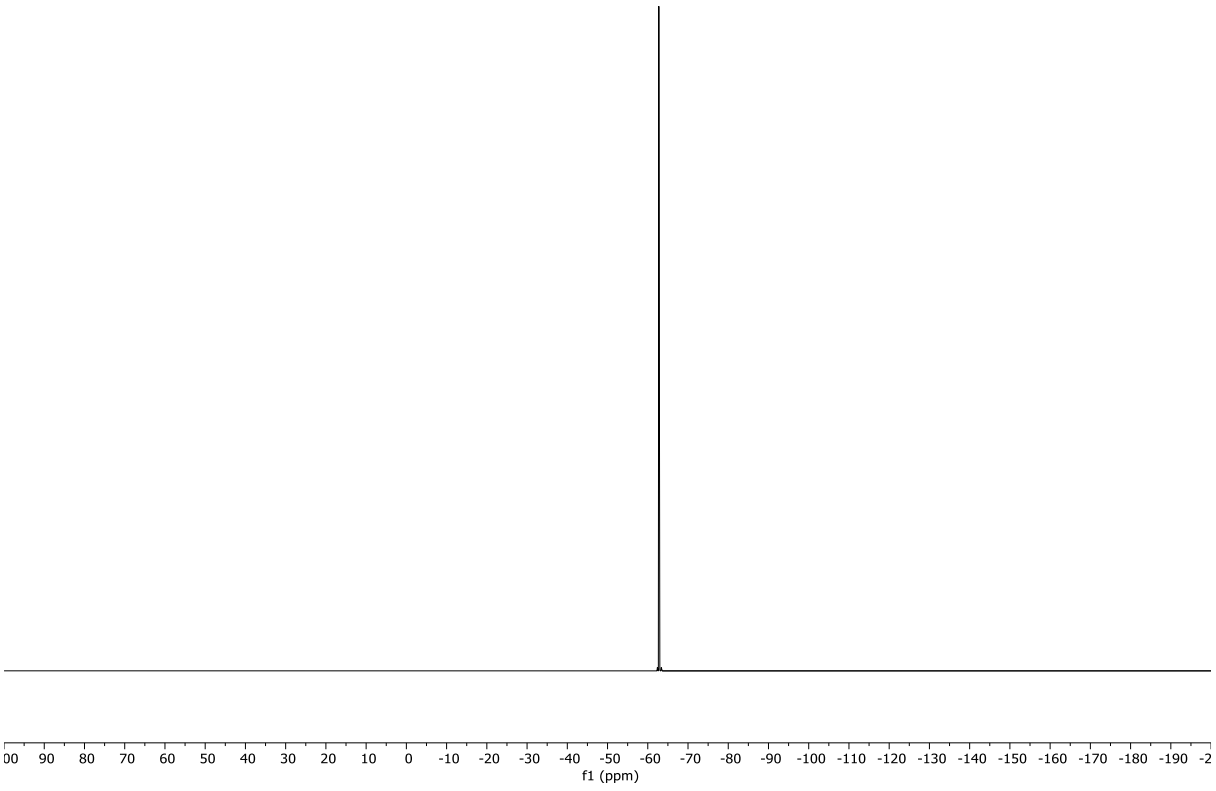
(*R*)- 6,6'-dibromo-3,3'-di(anthracen -9-yl)-[1,1'-binaphthalene]-2,2'-diol (4a) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)

(*R*)- 6,6'-dibromo-3,3'-di(phenanthren-9-yl)-[1,1'-binaphthalene]-2,2'-diol (4b) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)

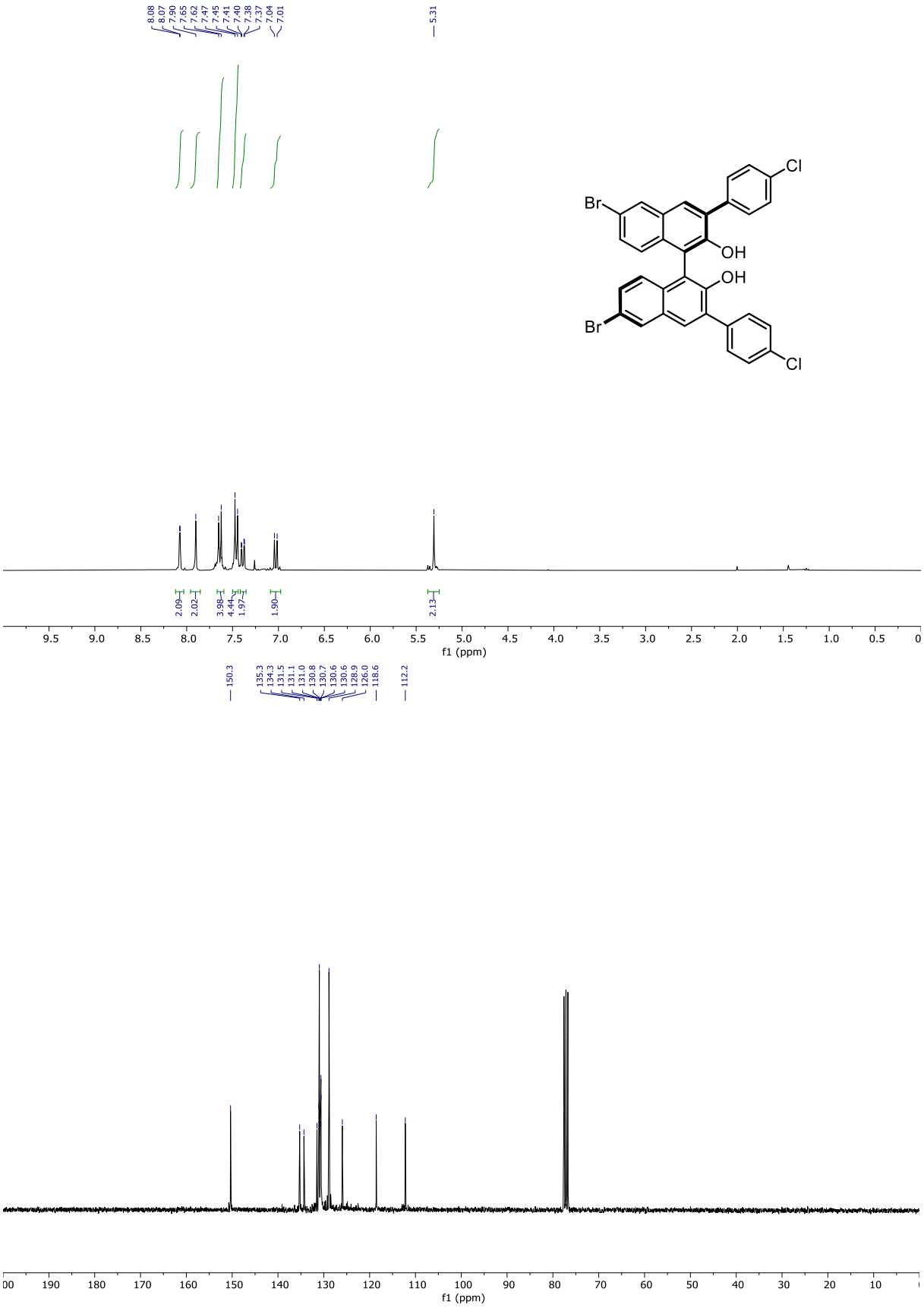


(*R*)- 6,6'-dibromo-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (4c) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz)

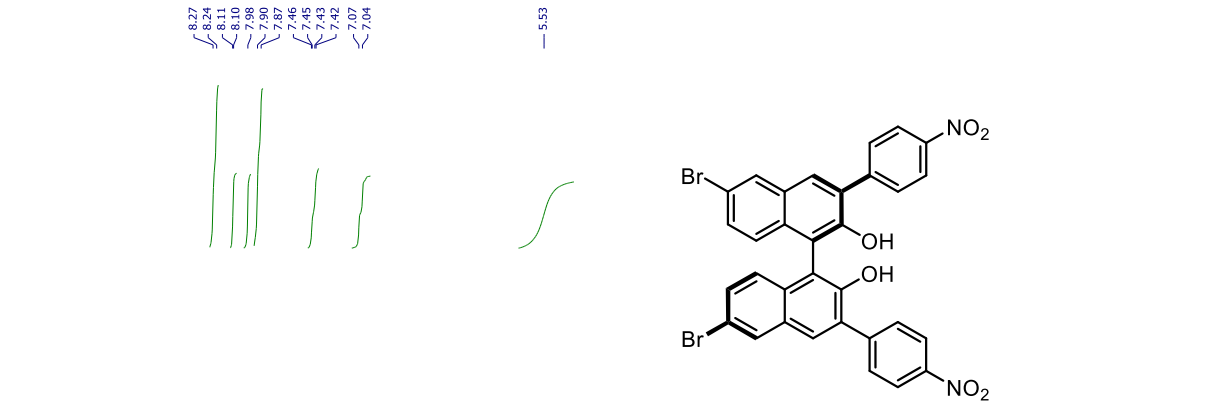


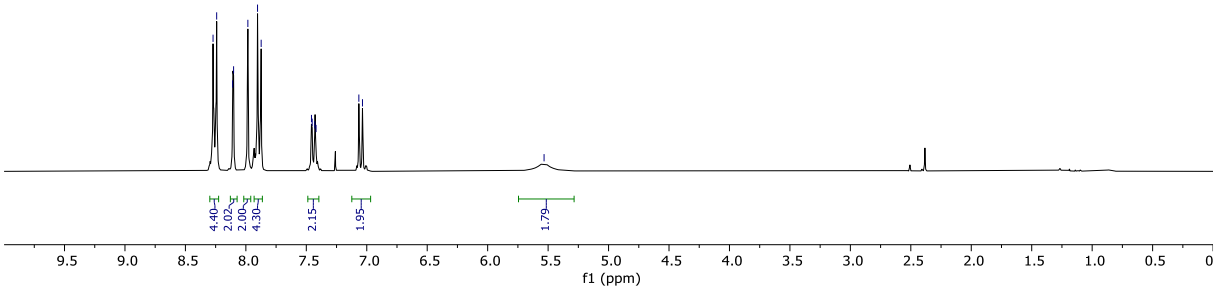

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

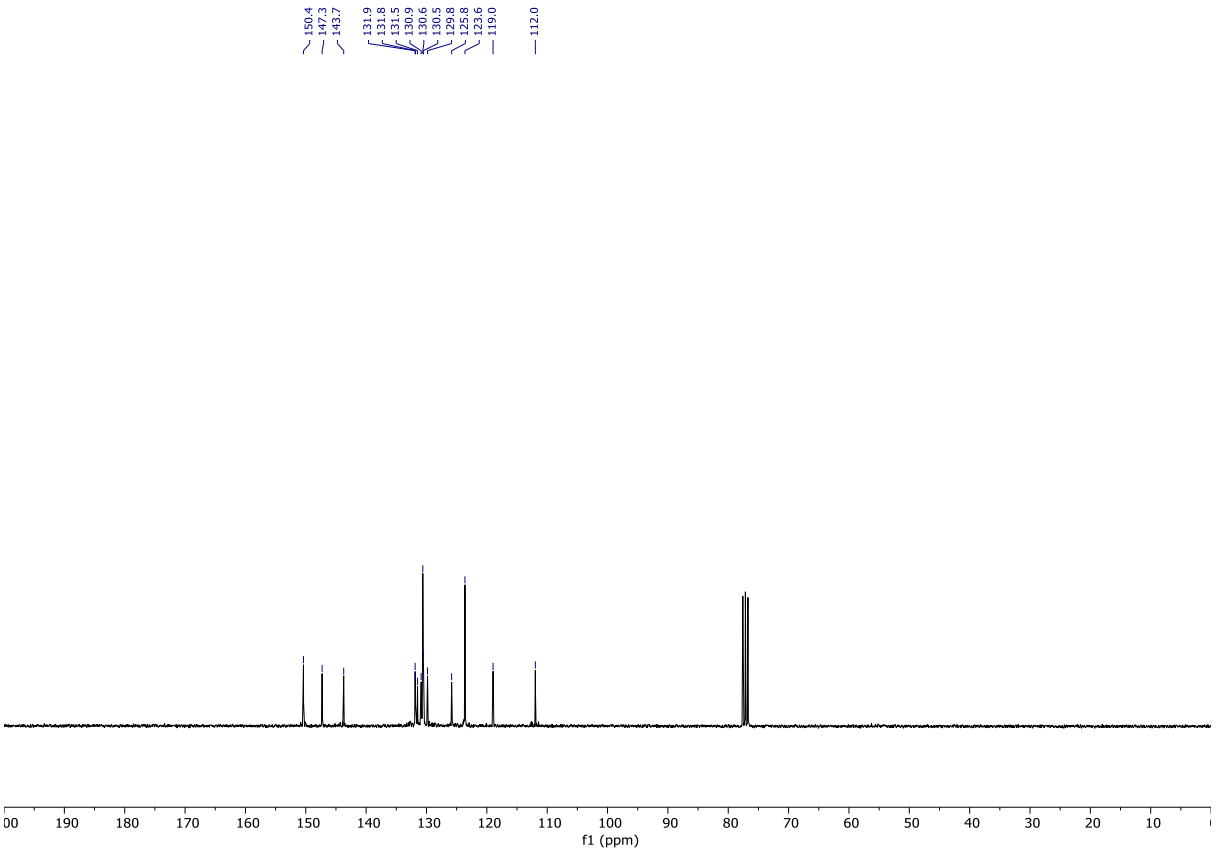
(*R*)- 6,6'-dibromo-3,3'-bis(4-chlorophenyl)-[1,1'-binaphthalene]-2,2'-diol (4d) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)



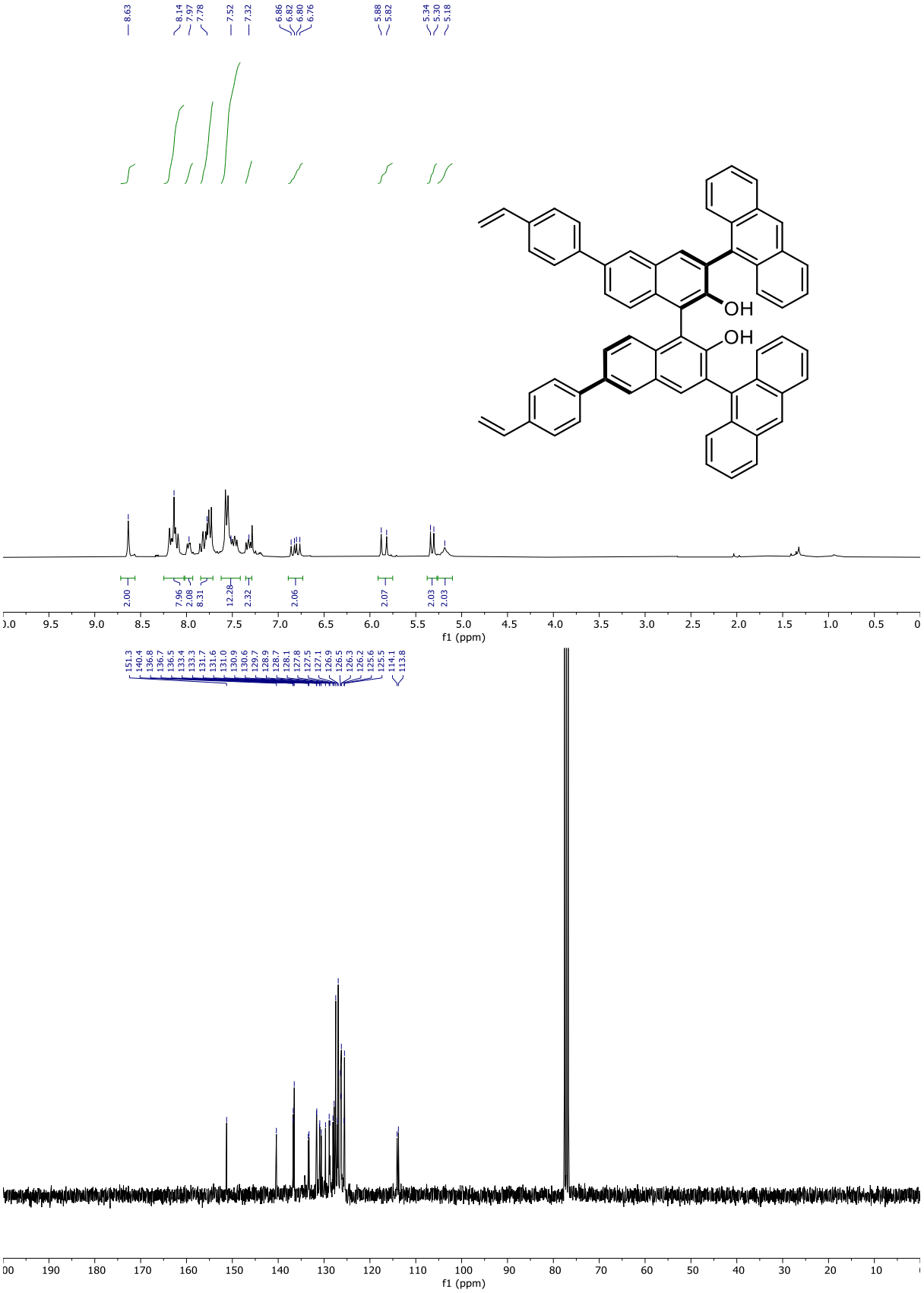
(*R*)- 6,6'-dibromo-3,3'-bis(4-nitrophenyl)-[1,1'-binaphthalene]-2,2'-diol (4e) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)



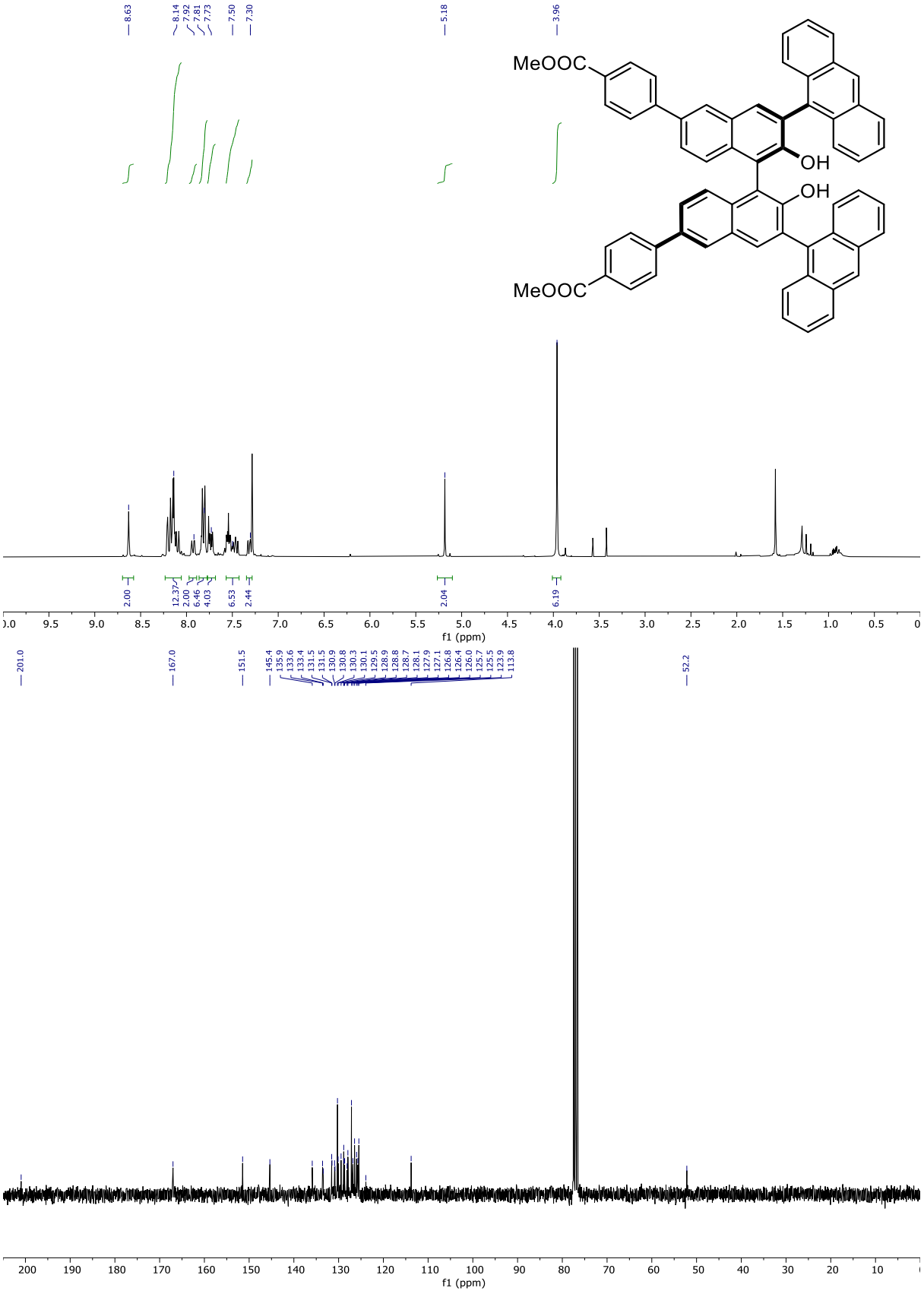




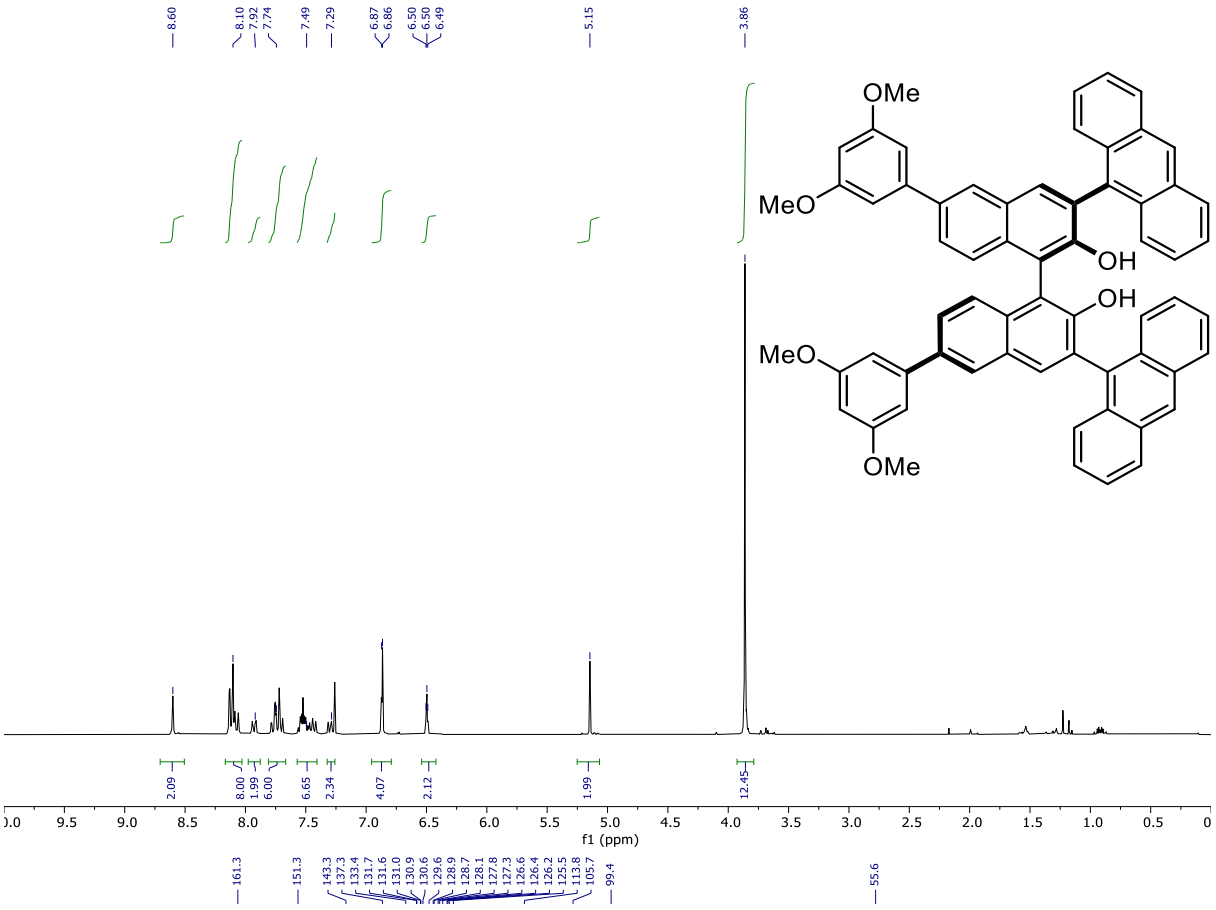
(*R*)-3,3'-di(anthracen-9-yl)-6,6'-bis(4-vinylphenyl)-[1,1'-binaphthalene]-2,2'-diol (5aa) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)

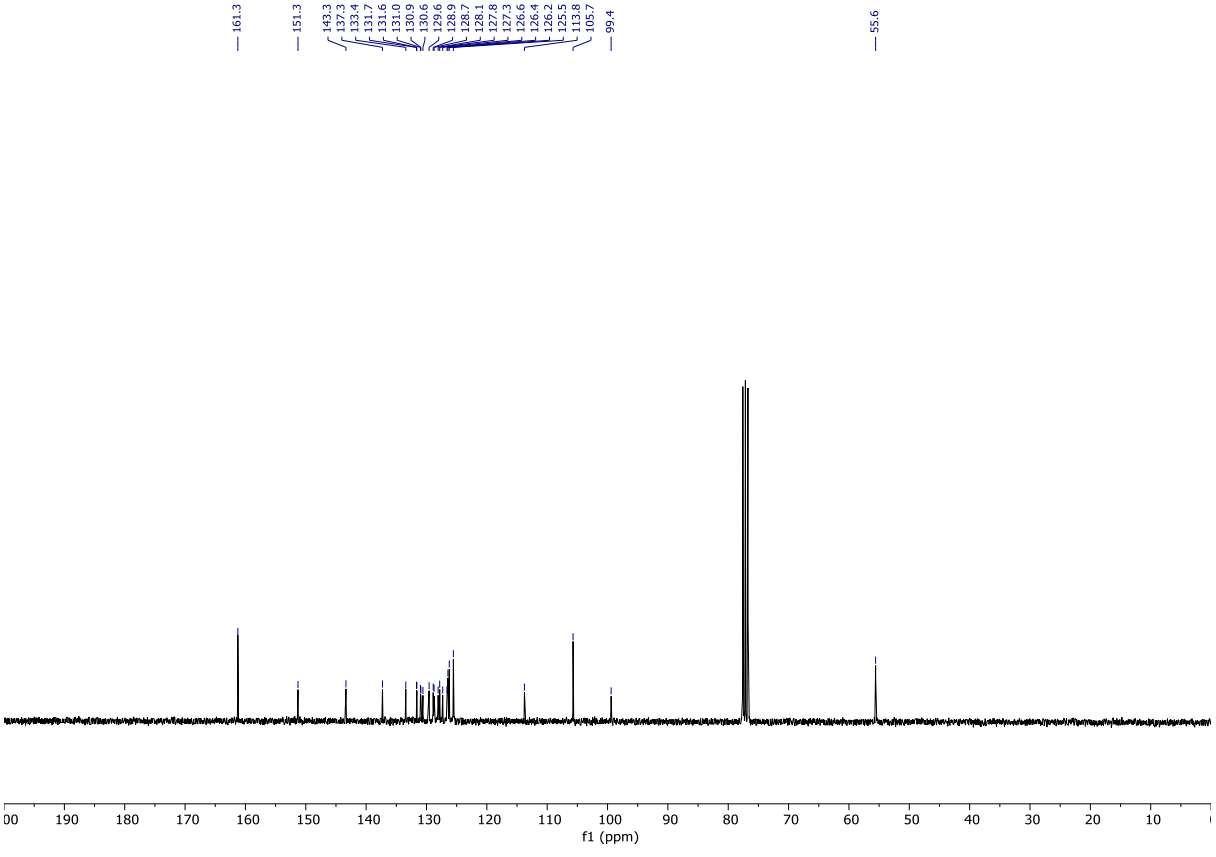


Dimethyl 4,4'-(*R*)-3,3'-di(anthracen-9-yl)-2,2'-dihydroxy-[1,1'-binaphthalene]-6,6'-diyl)dibenzoate (5ab) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)

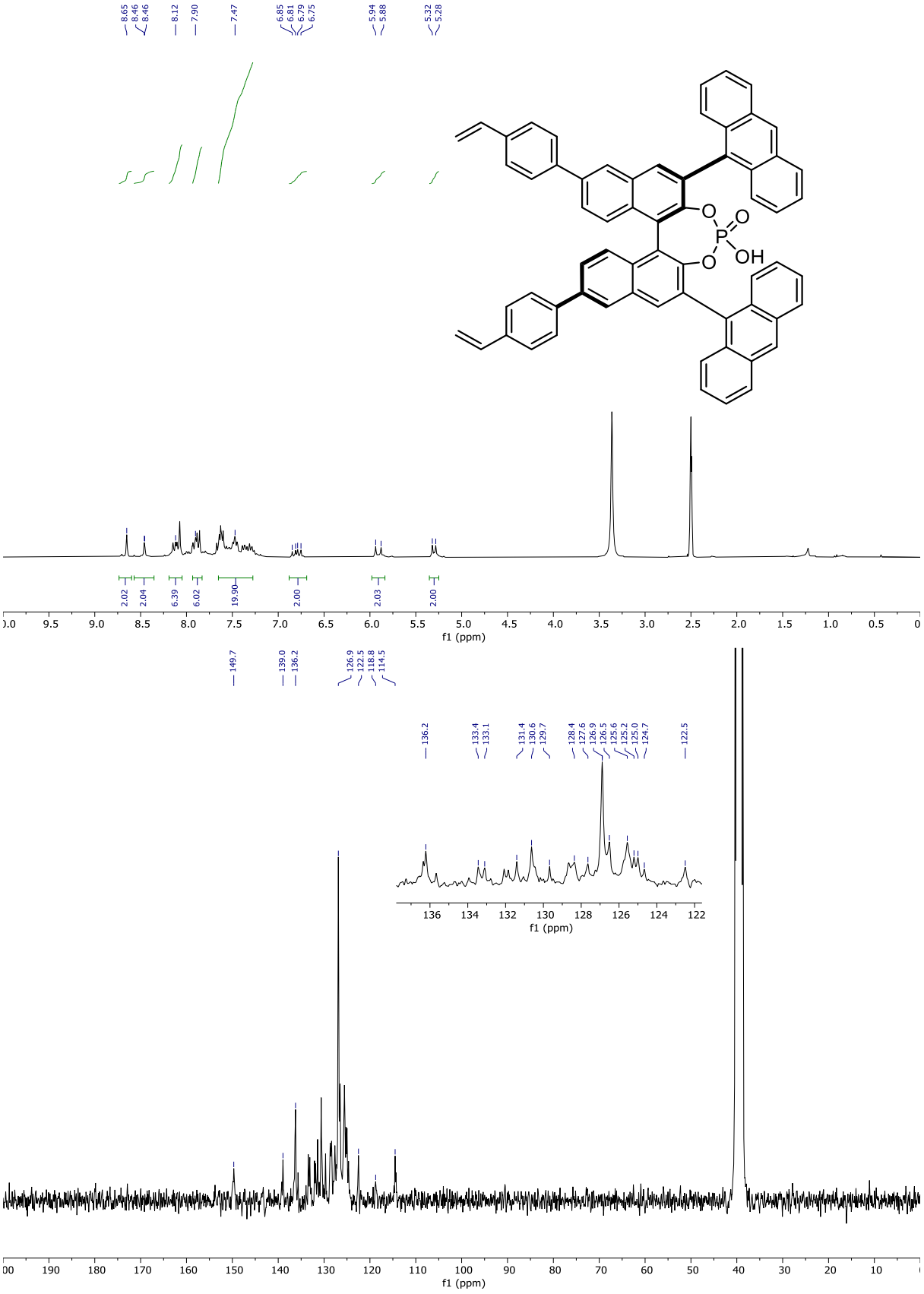


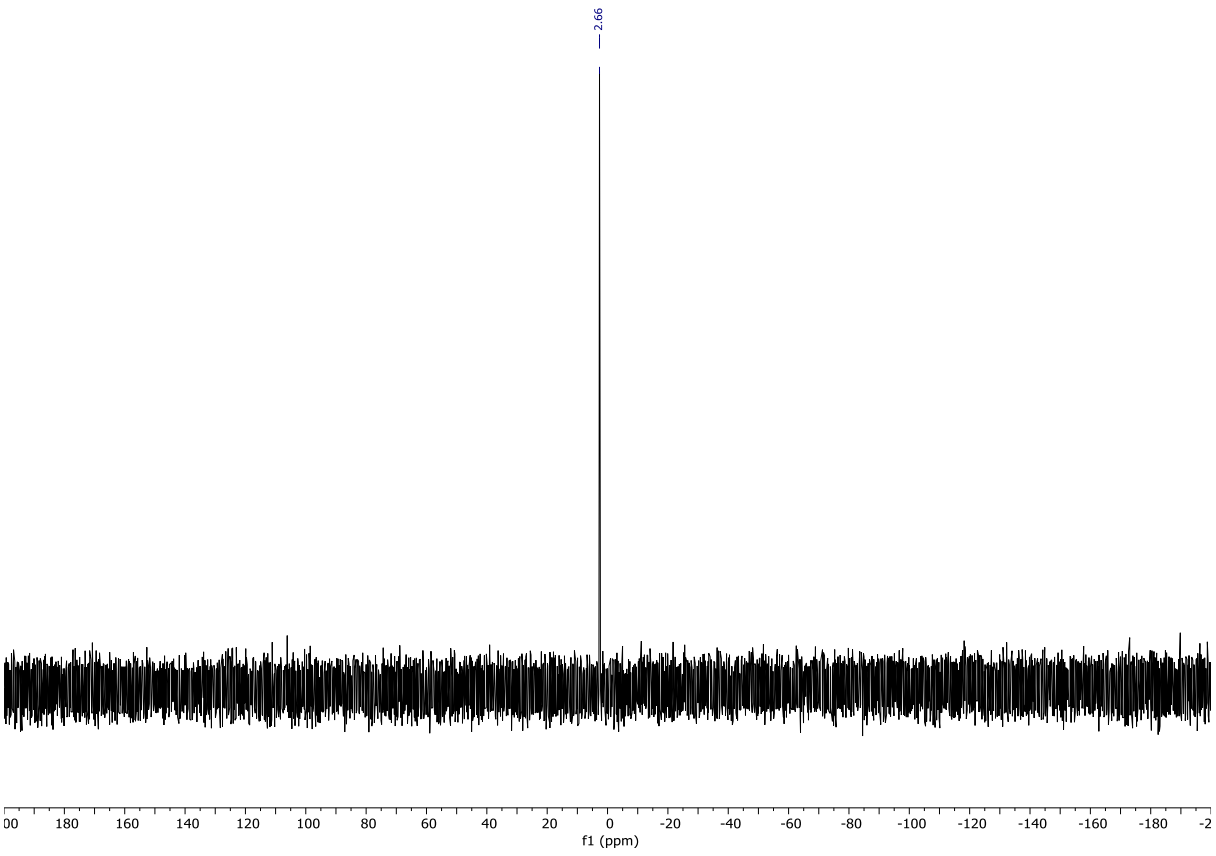
(*R*)-3,3'-di(anthracen-9-yl)-6,6'-bis(3,5-dimethoxyphenyl)-[1,1'-binaphthalene]-2,2'-diol (5ac)
($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)





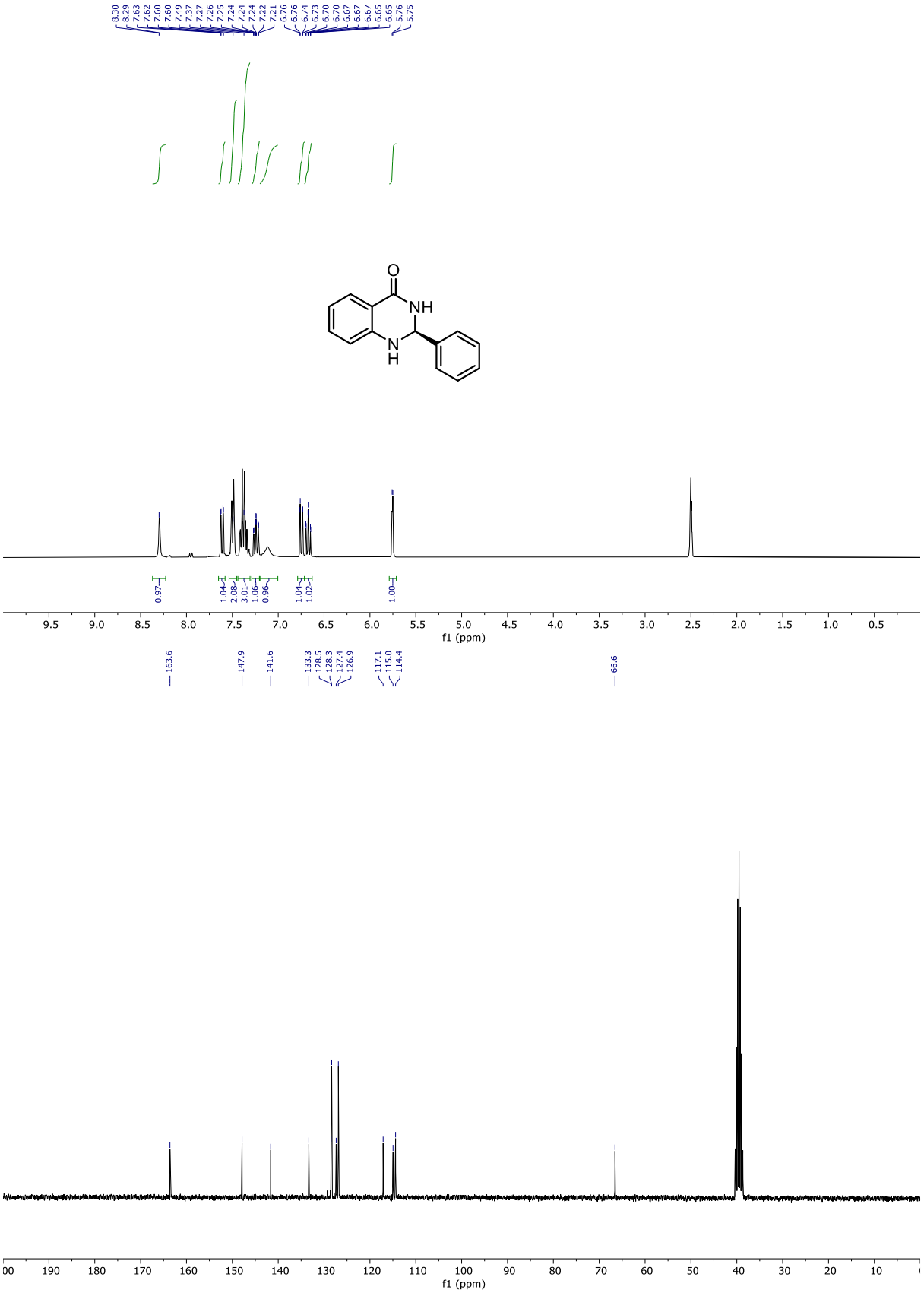
(*R*)-2,6-di(anthracen-9-yl)-4-hydroxy-9,14-bis(4-vinylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (6aa) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz, ^{31}P 121 MHz)



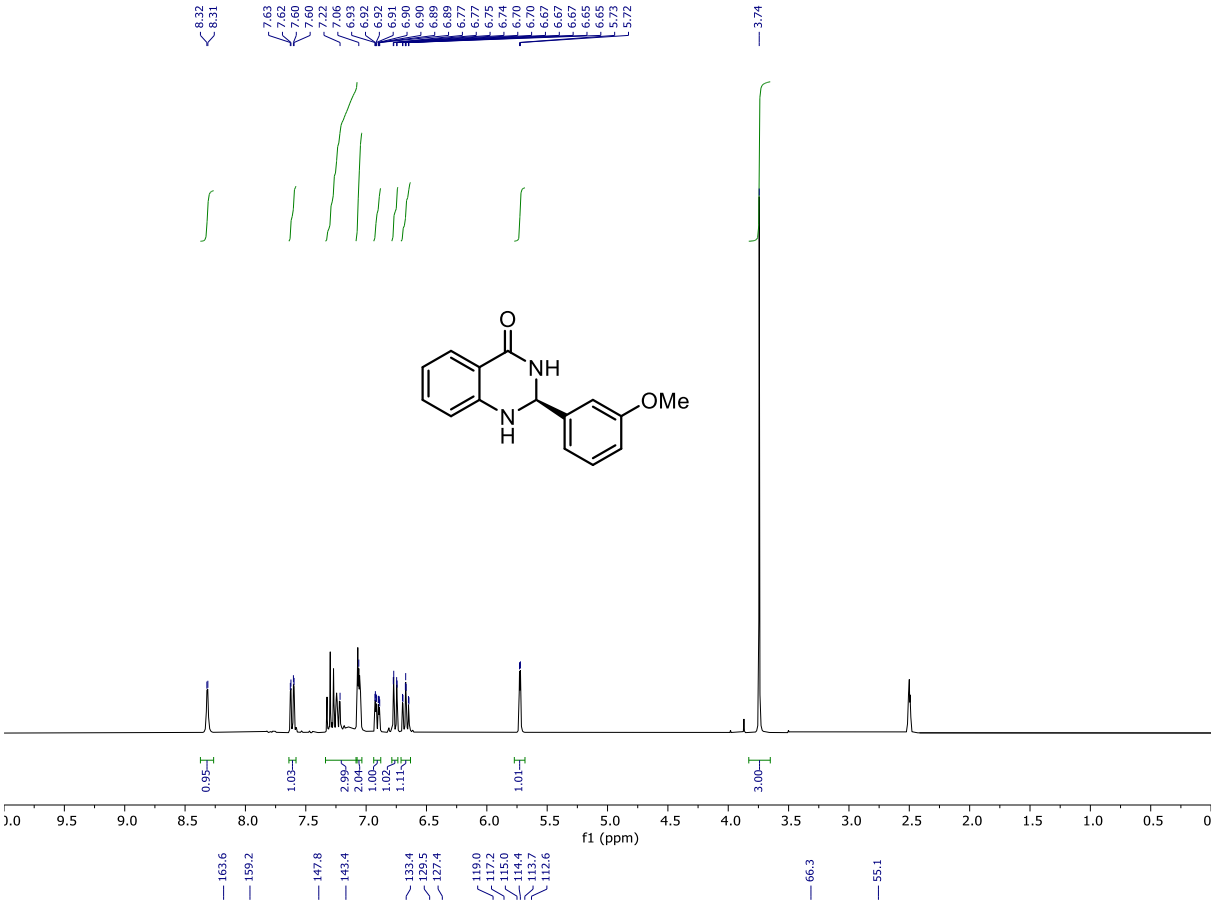

2.66
00
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

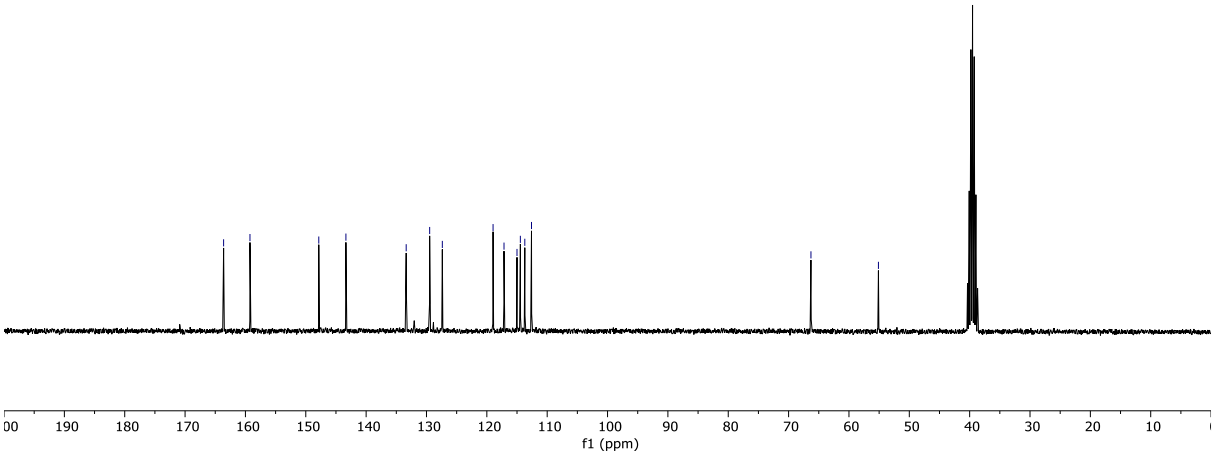
NMR spectra of **8**

(S)-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (8a) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)

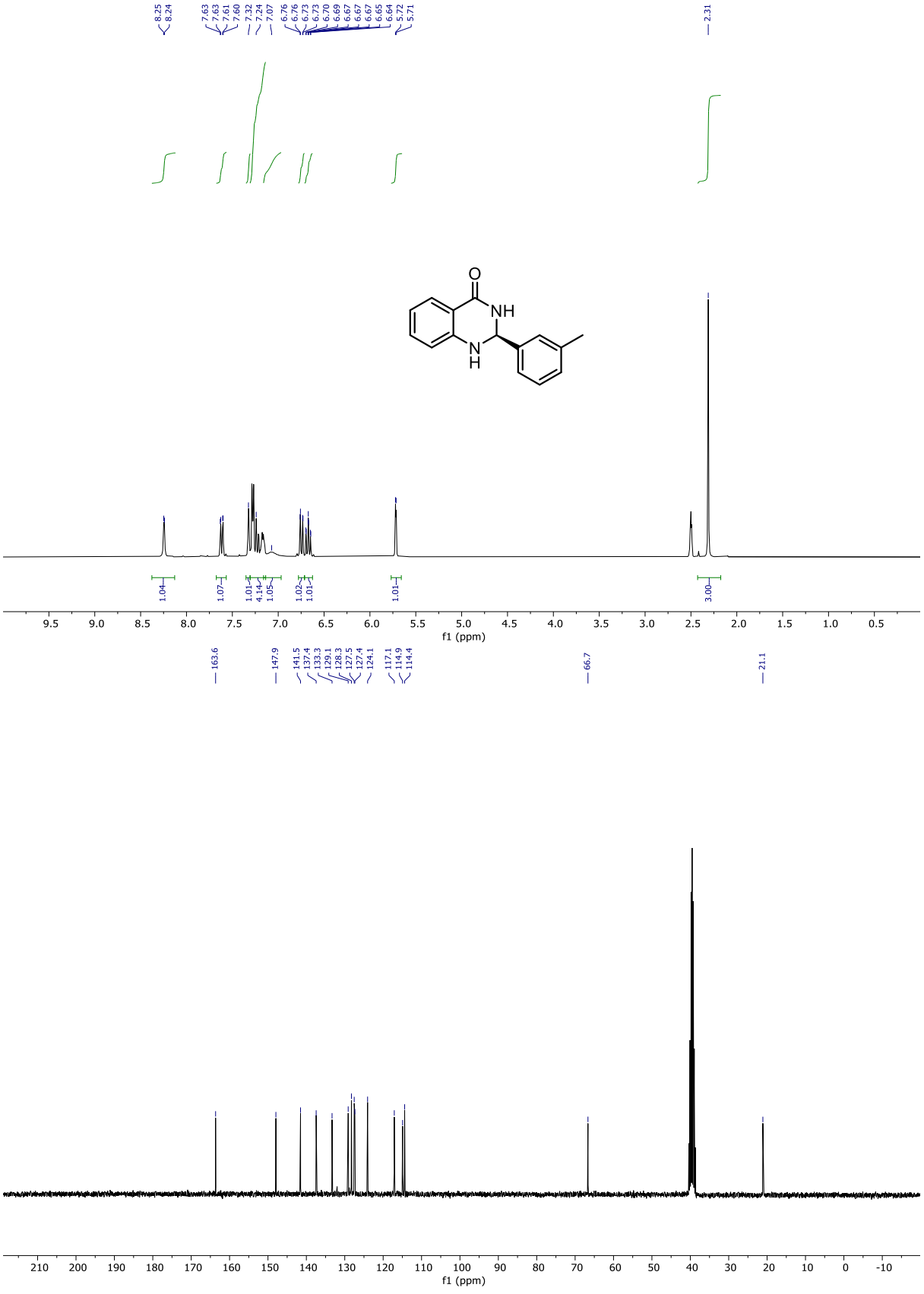


(S)-2-(3-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (8b) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)

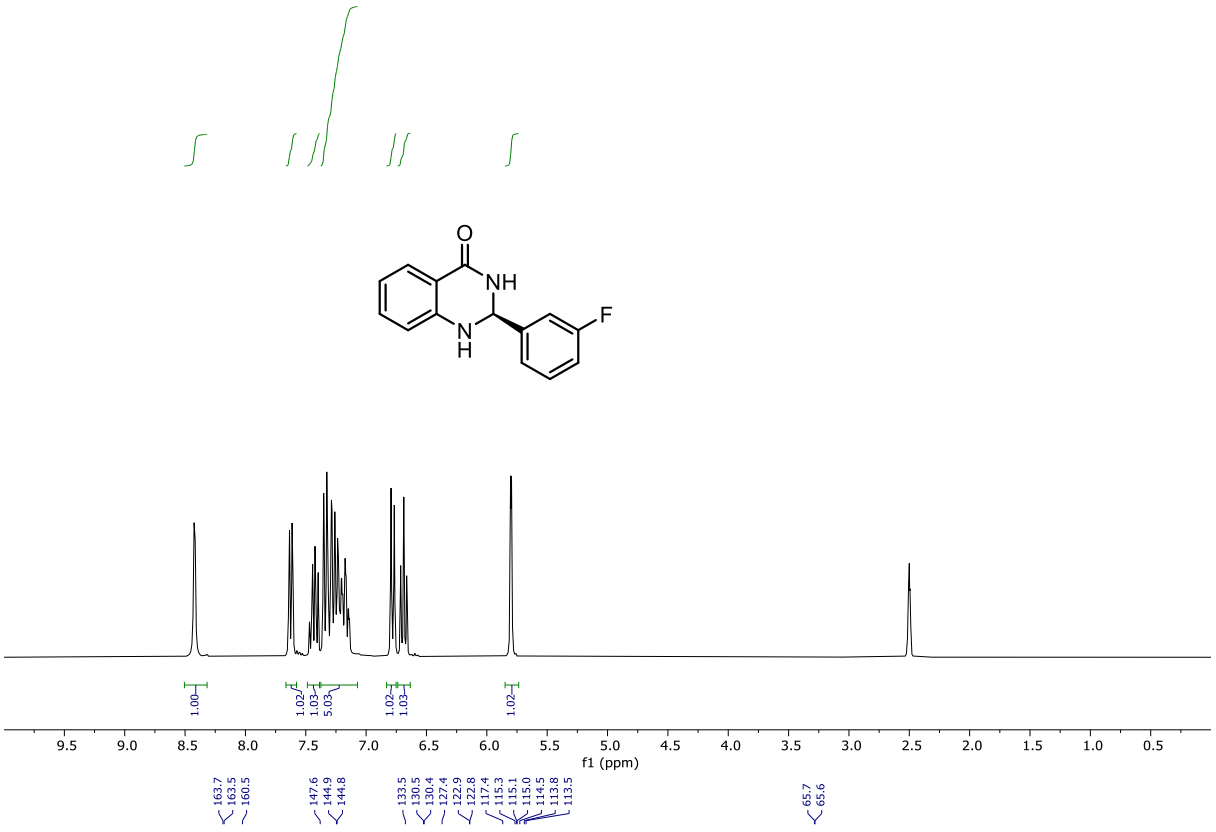


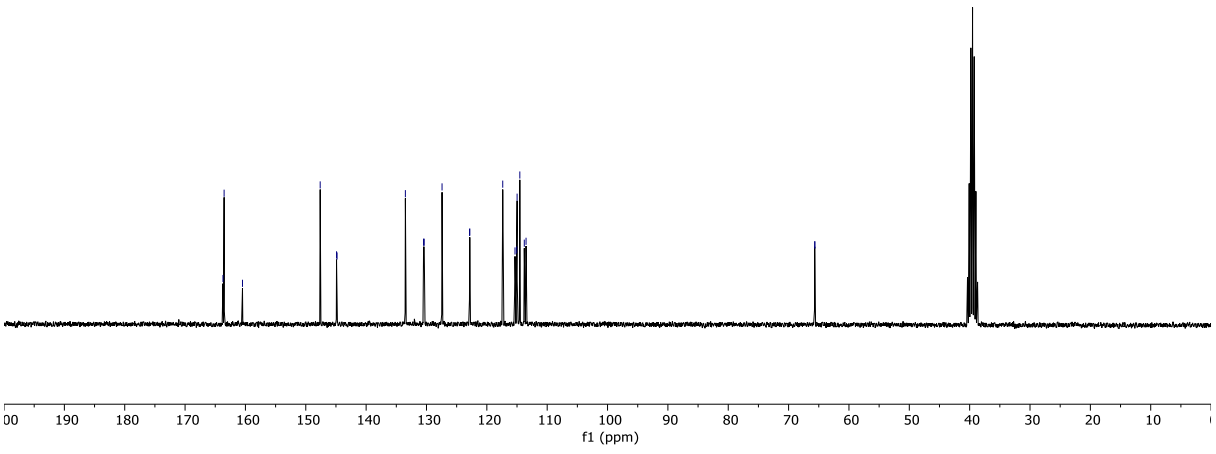


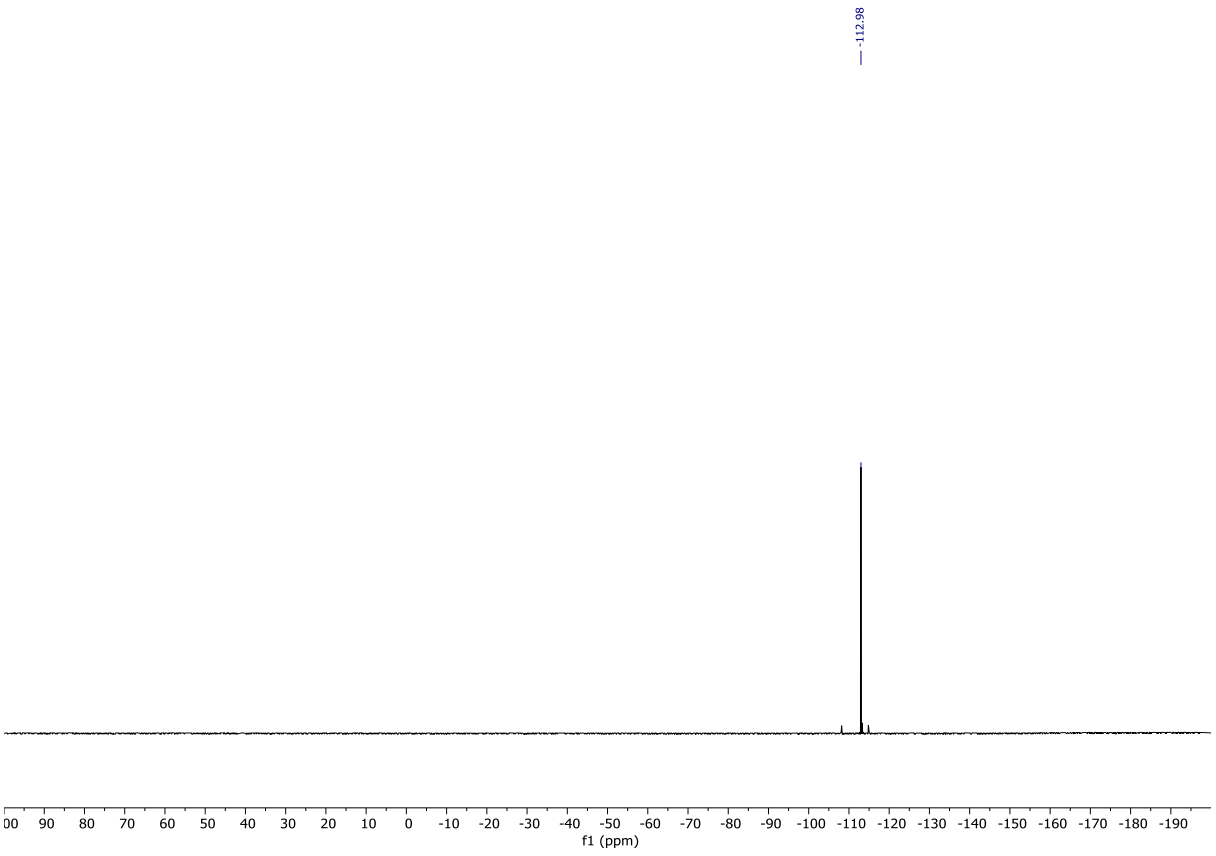
(S)-2-(m-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8c) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)



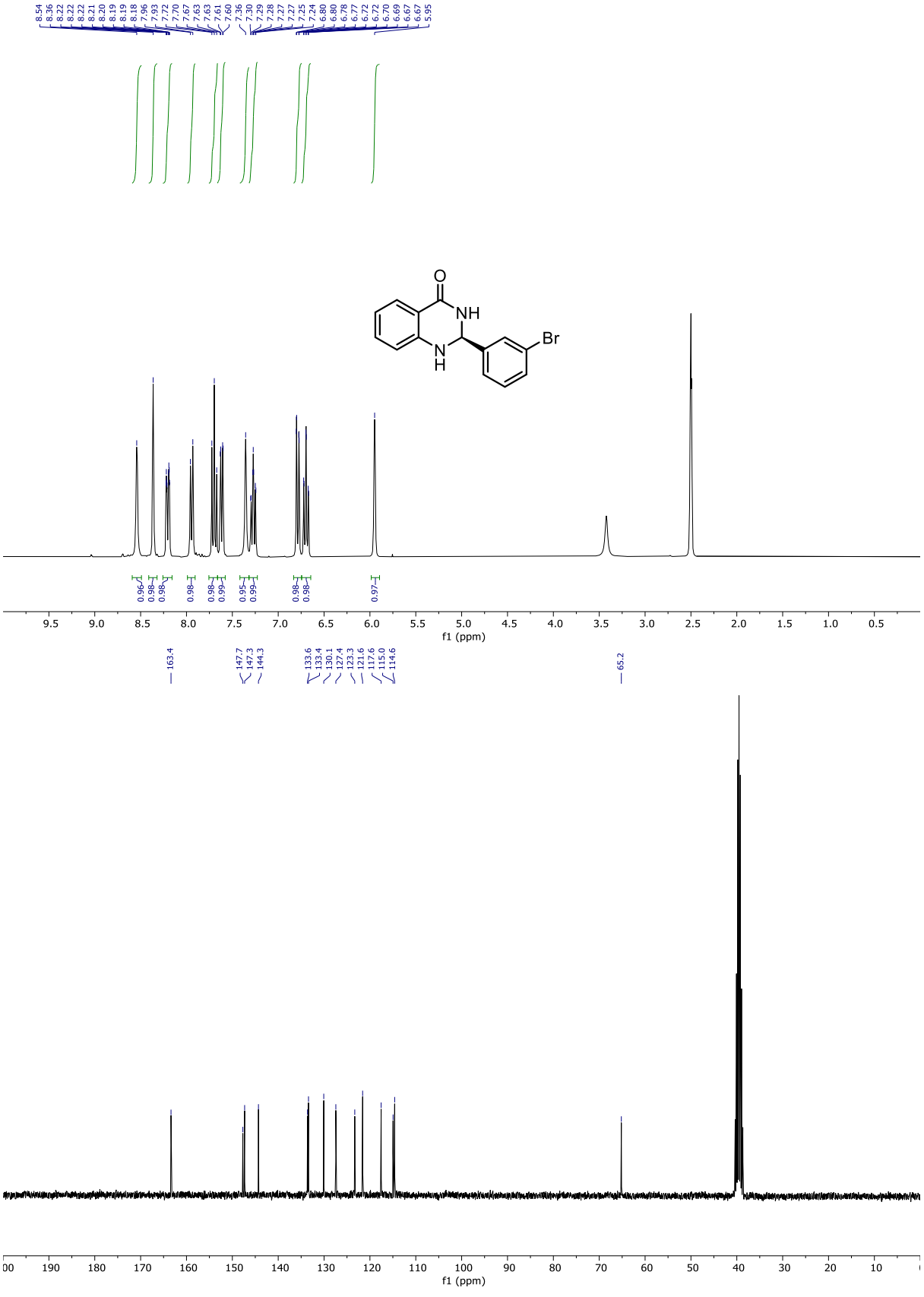
(S)-2-(3-fluorophenyl)-2,3-dihydroquinazolin-4(1H)-one (8d) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz)



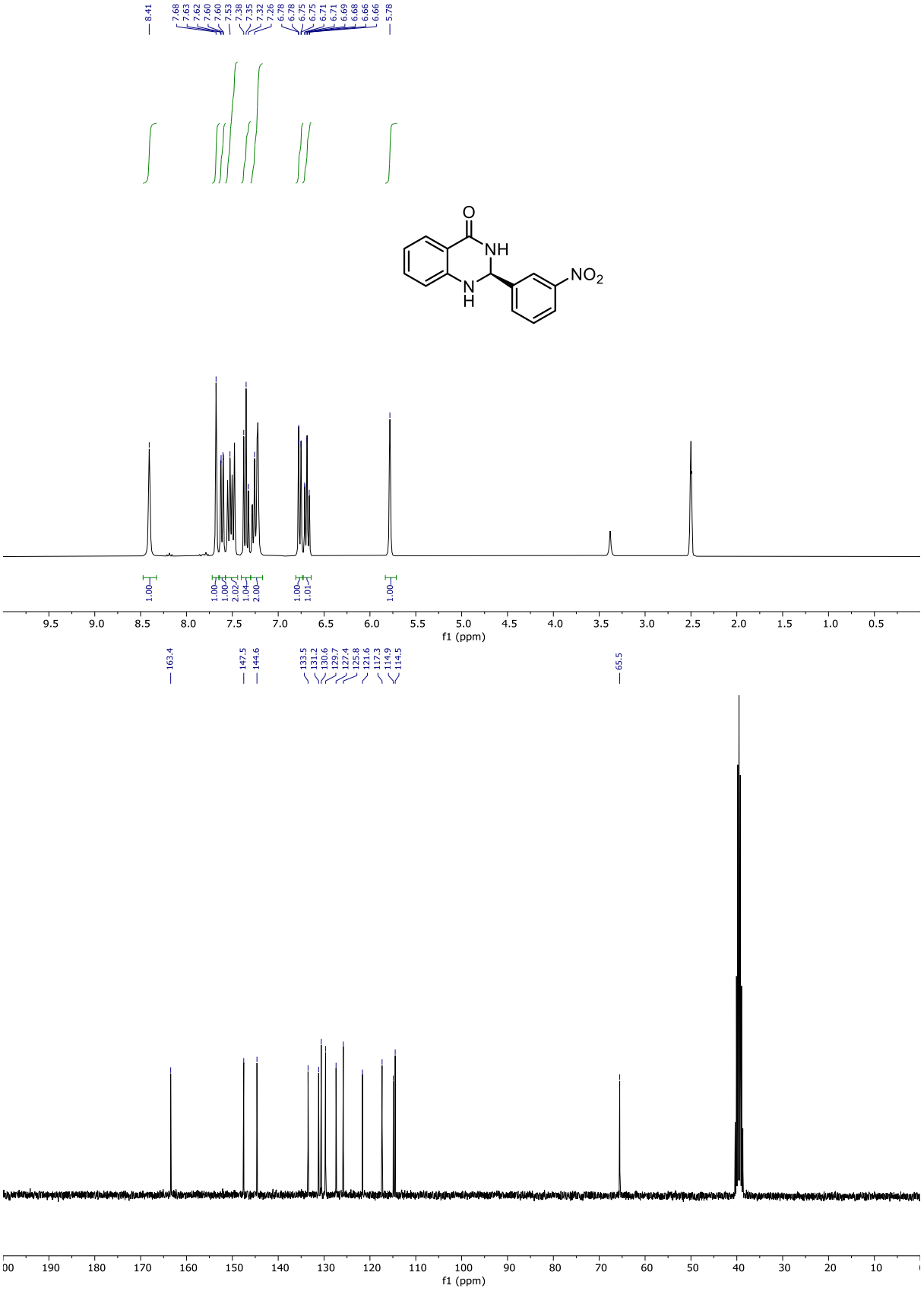



-112.98
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

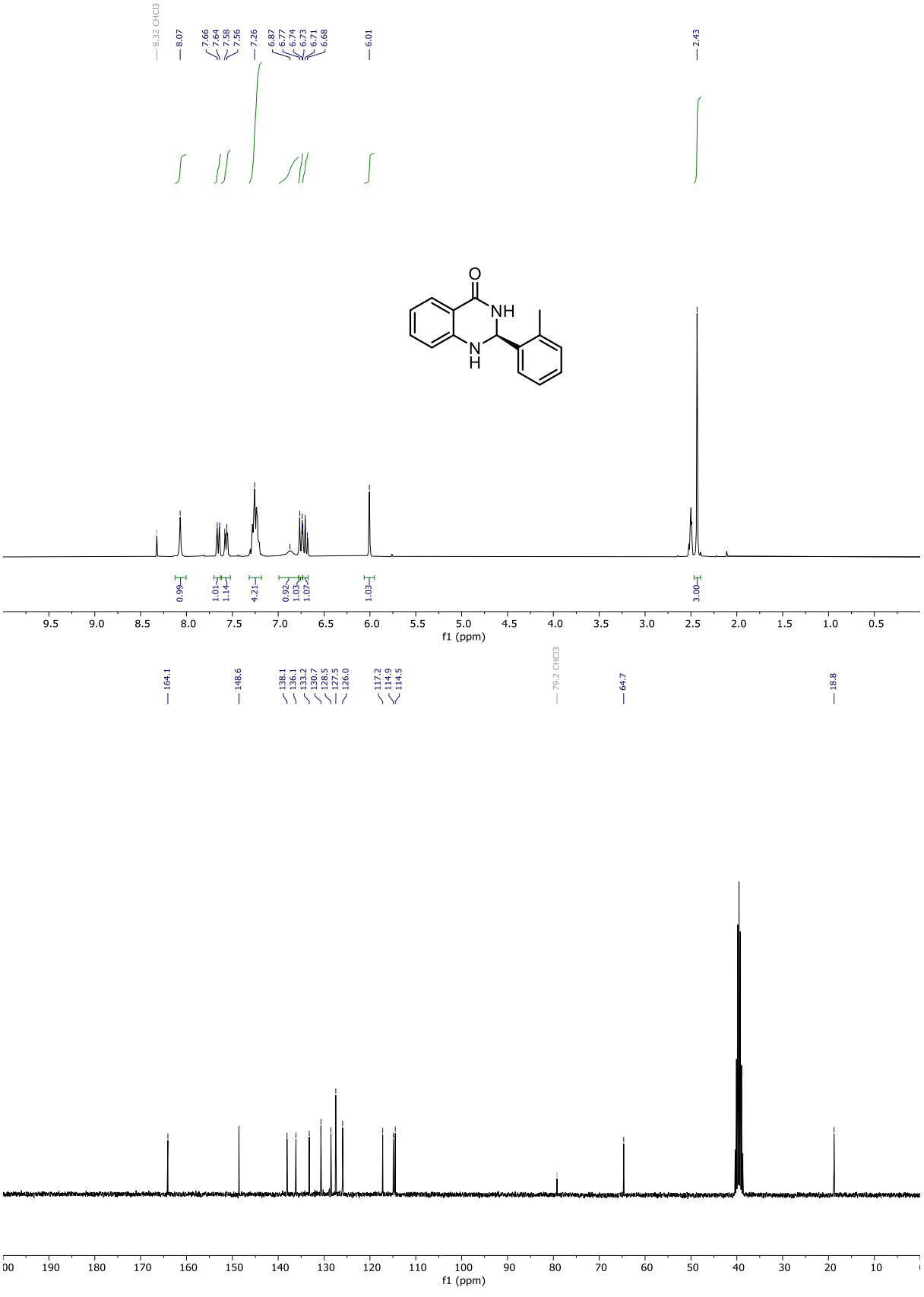
(S)-2-(3-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (8e) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)



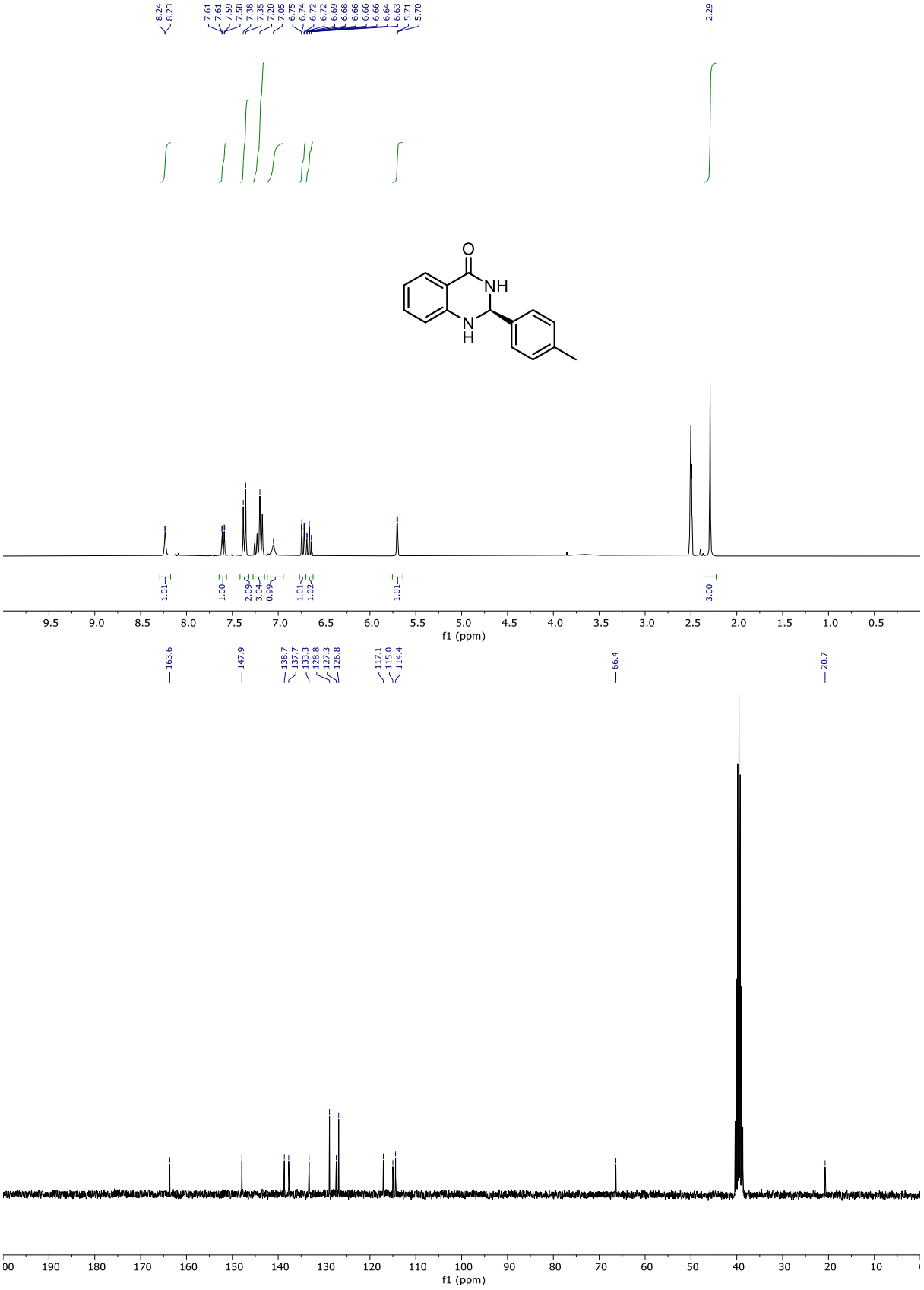
(S)-2-(3-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (8f) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)



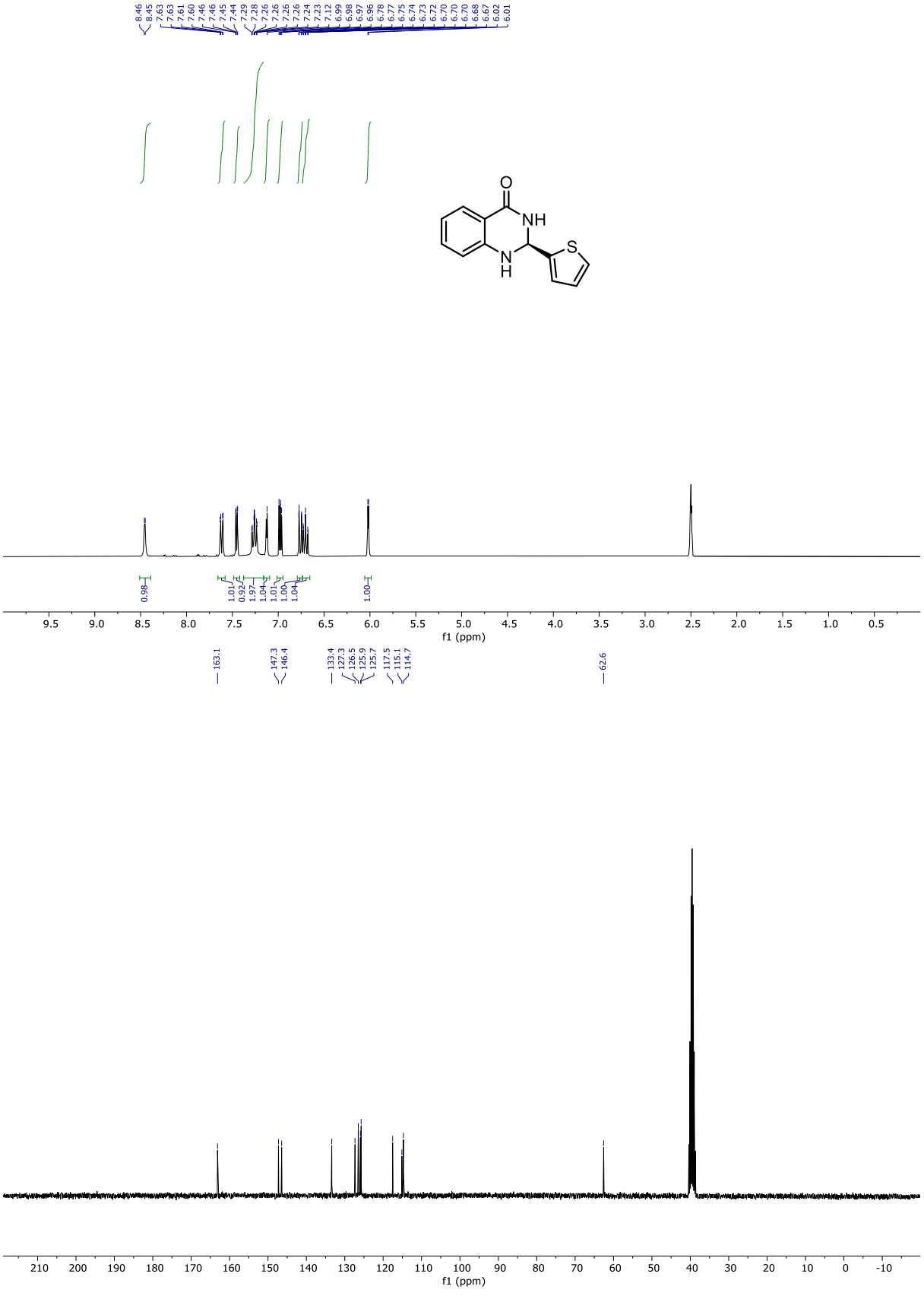
(S)-2-(o-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8g) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)



(S)-2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-one (8h) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)

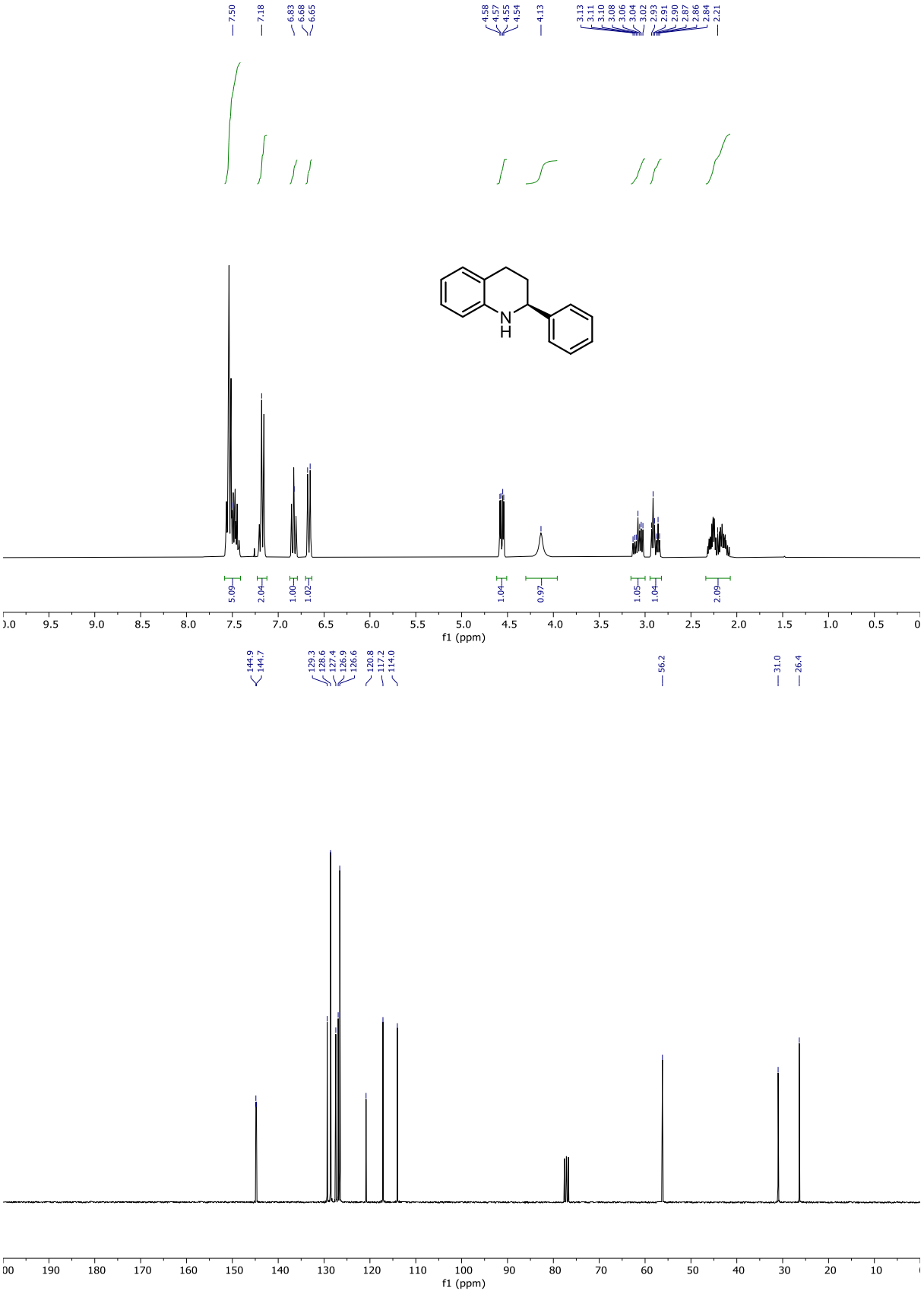


(S)-2-(thiophen-2-yl)-2,3-dihydroquinazolin-4(1H)-one (8i) (DMSO, ^{1}H 300 MHz, ^{13}C 75 MHz)

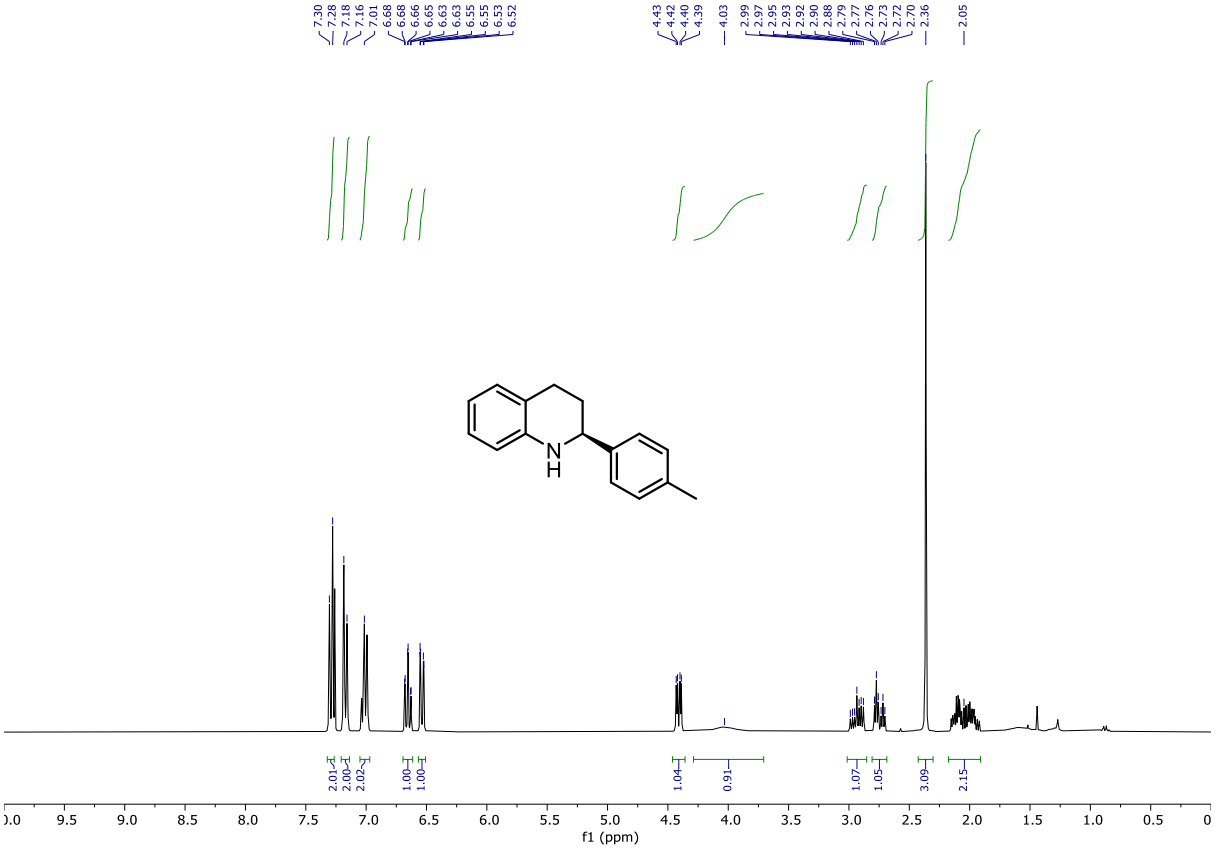


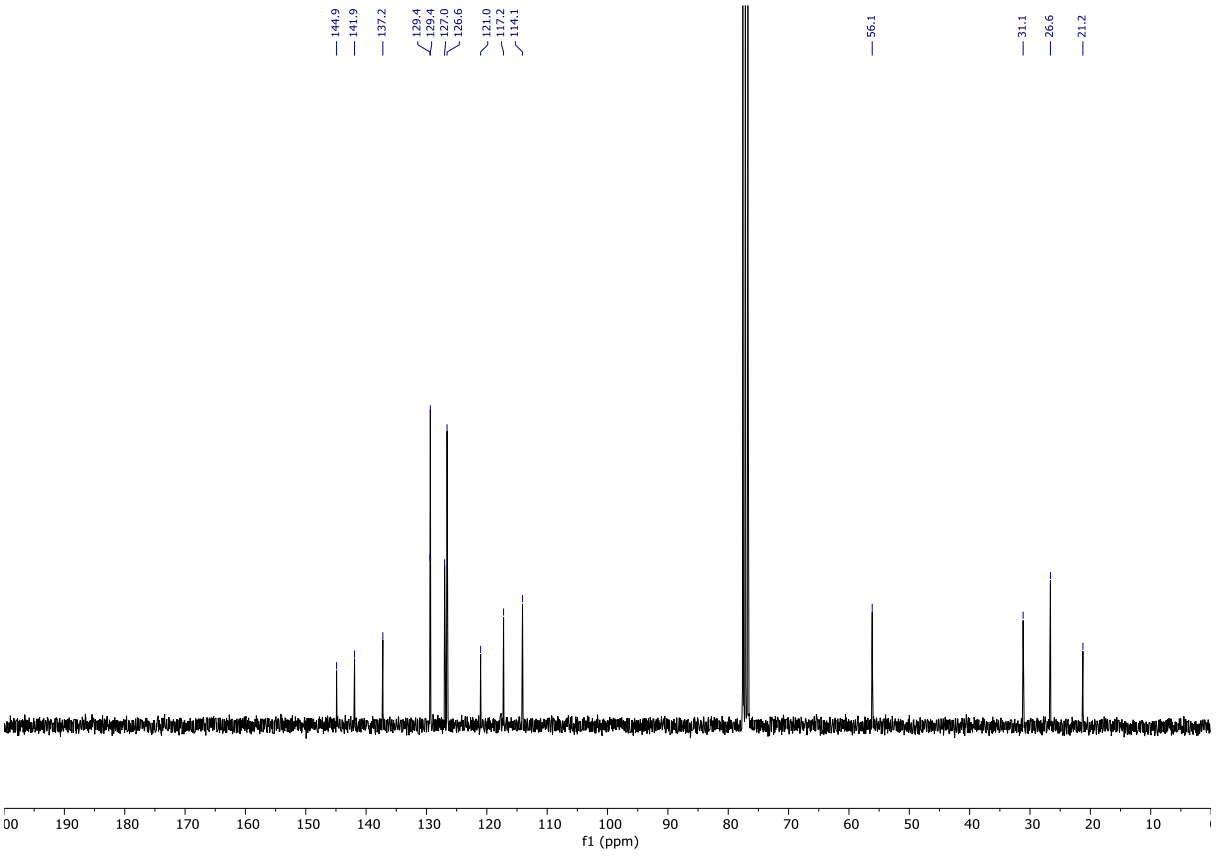
NMR spectra of **10**

(S)-2-phenyl-1,2,3,4-tetrahydroquinoline (10a) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)

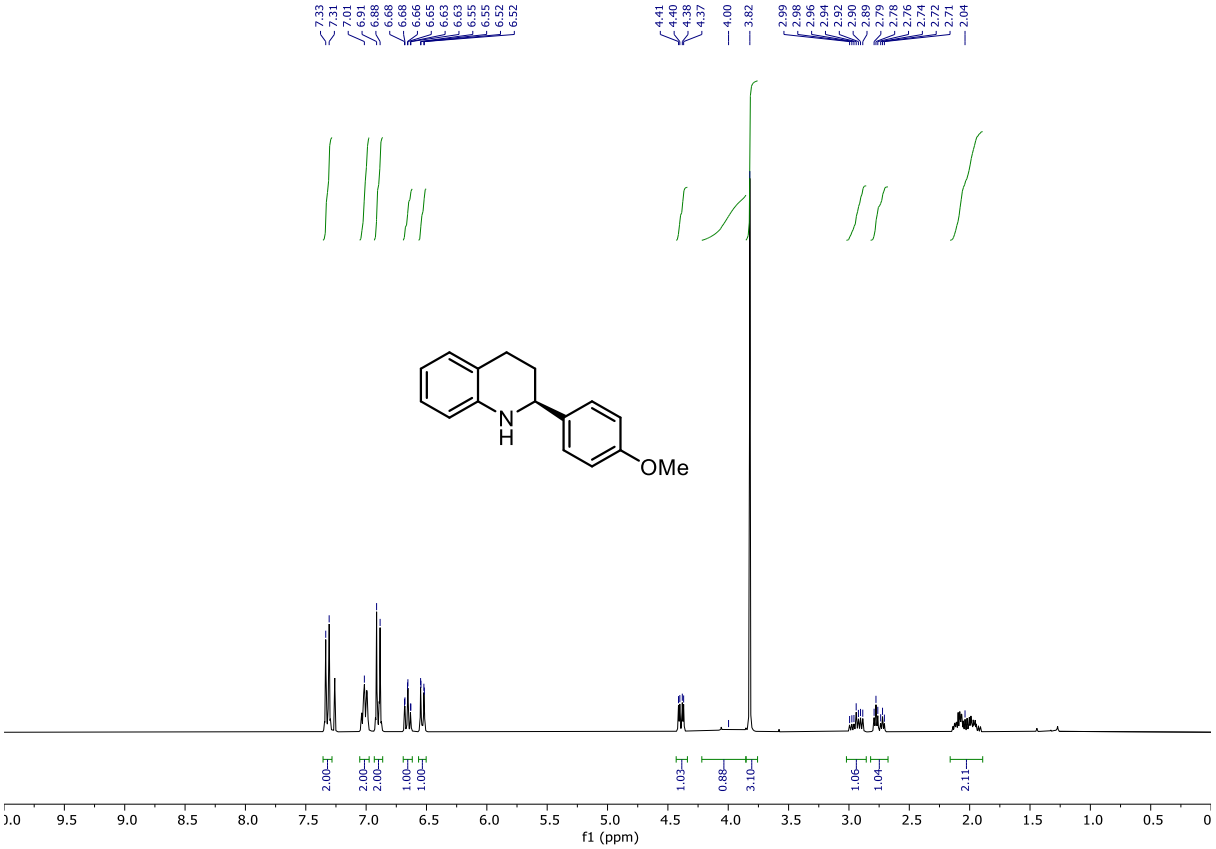


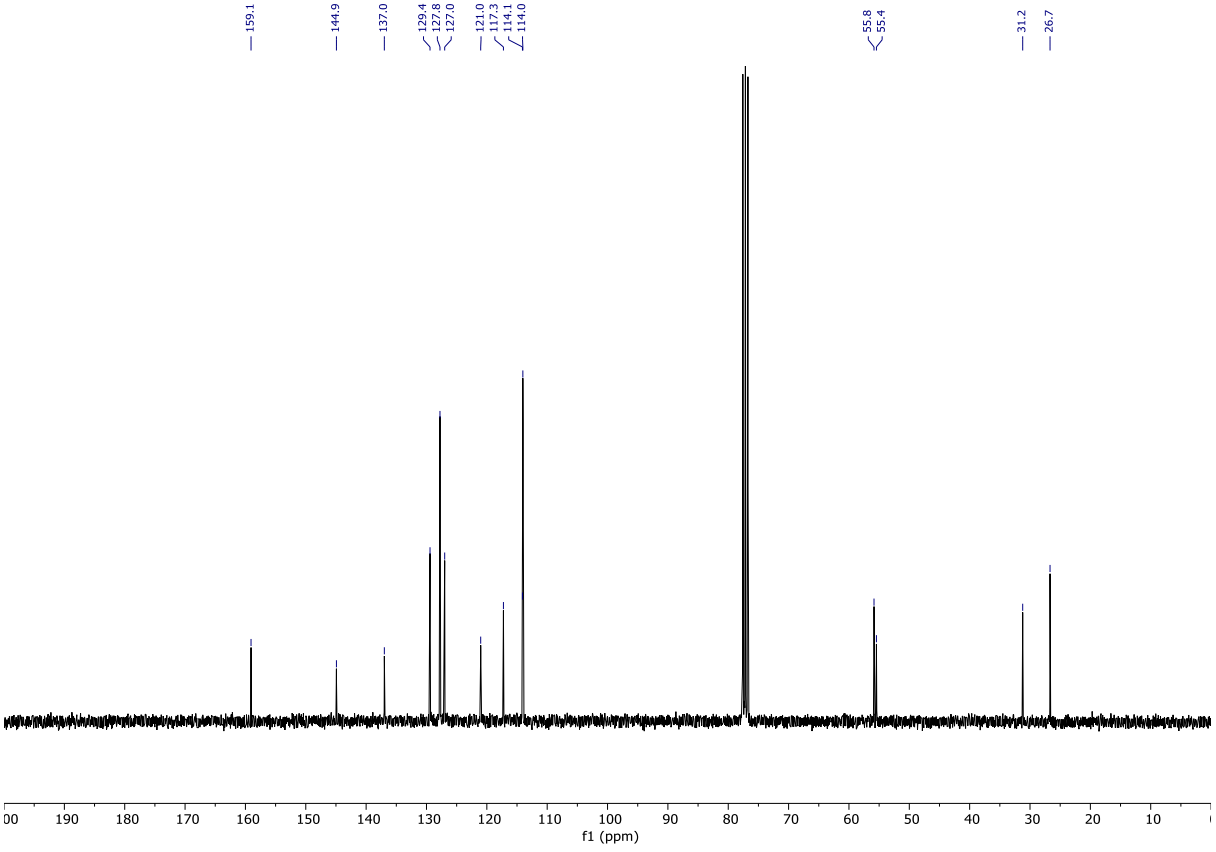
(S)-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline (10b) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)



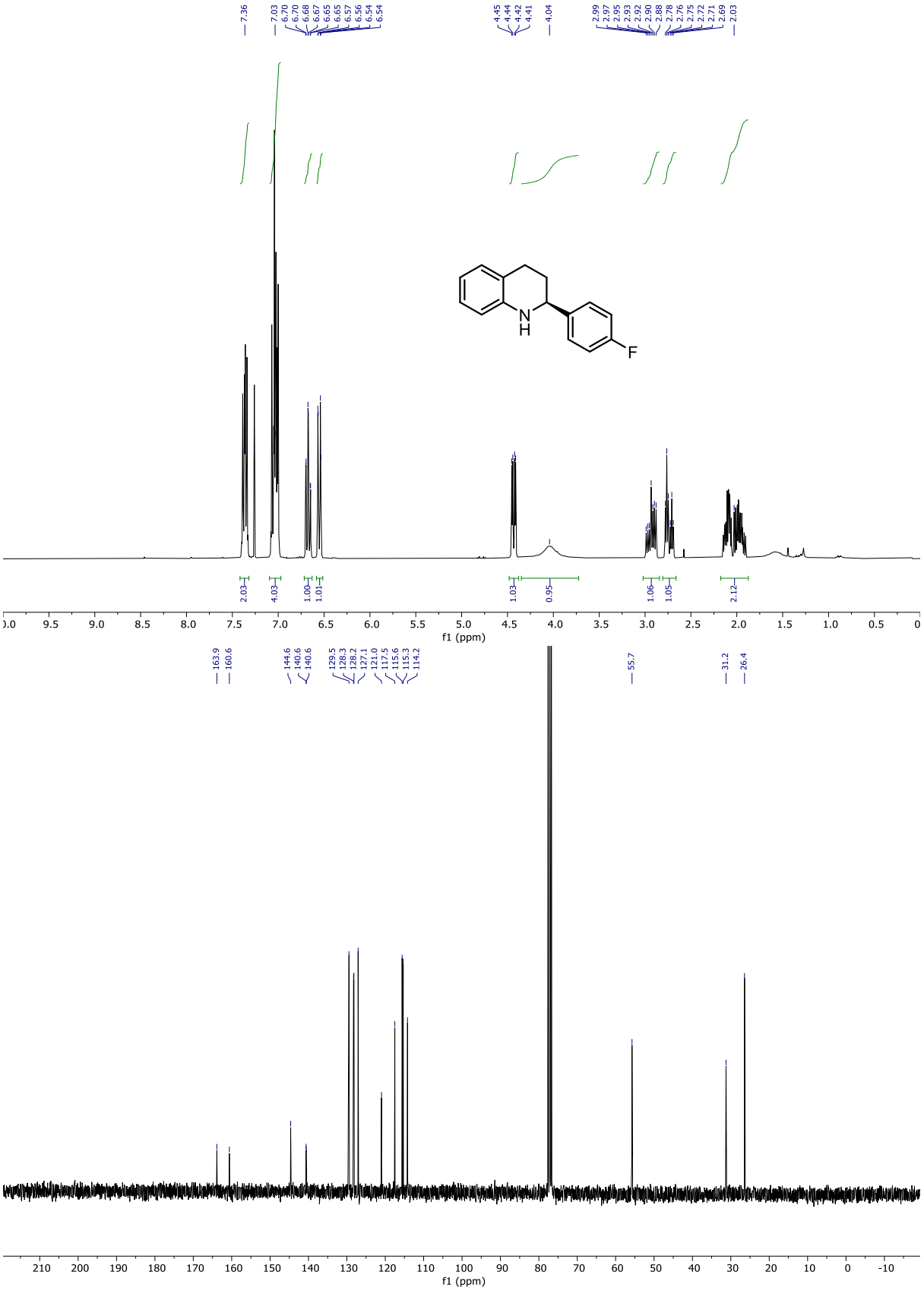


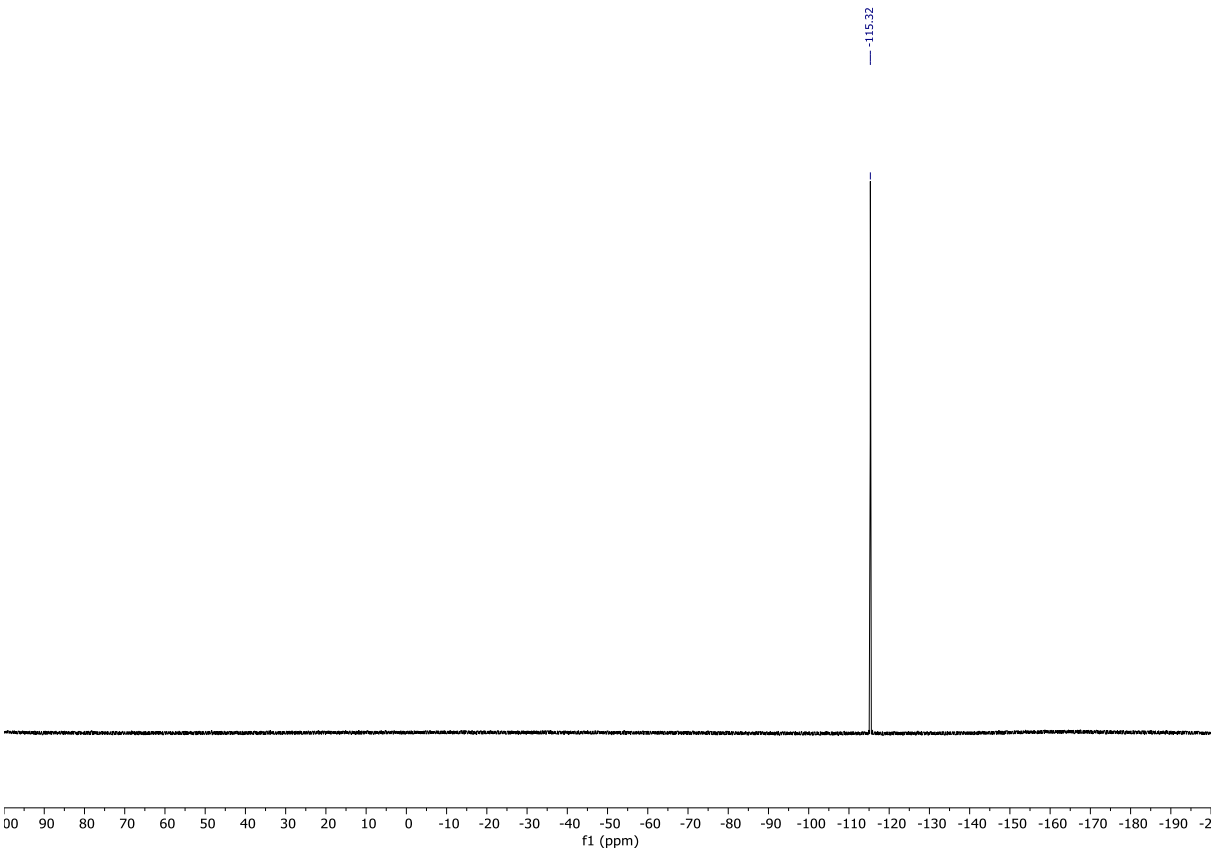
(S)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (10c) ($CDCl_3$, ^1H 300 MHz, ^{13}C 75 MHz)





(S)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline (10d) ($CDCl_3$, ^{1}H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz)





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S1 D. Huang, X. Li, F. Xu, L. Li and X. Lin, Highly enantioselective synthesis of dihydroquinazolinones catalyzed by SPINOL-phosphoric acids, *ACS Catal.*, 2013, **3**, 2244–2247.

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