Organocatalytic Enantioselective aza-Friedel-Crafts reaction of 2-Naphthols with benzoxathiazine 2,2-dioxides

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SUPPORTING INFORMATION

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General Experimental Methods

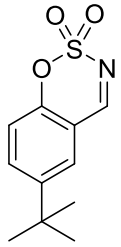
Reactions were carried out under nitrogen in test tubes or round bottom flasks oven-dried overnight at 120 ºC. Dicloromethane, 1,2-dichloroethane and toluene were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. Melting points were determined in capillary tubes. NMR spectra were run at 300 MHz for ^{1}H and at 75 MHz for ^{13}C NMR using residual nondeuterated solvent as internal standard ($CHCl_3$: δ 7.26 and 77.0 ppm, d^6-acetone: δ 2.05 and 29.4 ppm, d^6-dmso: δ 2.50 and 39.5 ppm,). Due to solubility reasons, NMR experiments for compounds **3** were run using $CHCl_3$ with ~5% of d^4-MeOH. Other solvents such as acetone, dmso or acetonitrile caused complicated spectrums possibly due to rotamers. Chemical shifts are given in ppm. The carbon type was determined by DEPT experiments. High resolution mass spectra (ESI) were recorded on a AB SCIEX Triple TOF^{TM} spectrometer equipped with an electrospray source with a capillary voltage of 4.5 kV(ESI). Specific optical rotations were measured using sodium light (D line 589 nm). Chiral HPLC analyses were performed in a chromatograph equipped with a UV diode-array detector using chiral stationary columns from Daicel. Slow addition was performed using a kdScientific (Model 100) apparatus, a 1mL Braun syringe and a 120 mm Braun needle. Commercially available naphthols and sesamol were used as received.

Catalysts **Ia**, **Ib**, **Id**, **Ie** and **If** were prepared from quinine using Deng's procedures.[1a] Catalysts **Ic** was prepared from quinine using the method described by Chen.[1b]

Typical procedures and characterization data for compounds 2

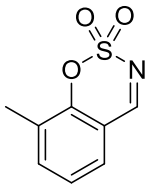
Benzoxathiazine 2,2-dioxides were prepared from the corresponding salicylaldehyde as described in the literature.[2] Products **2c**, **2f**, **2g** and **2h** were not described in the literature:

6-(*tert*-butyl)benzo-[*e*][1,2,3]oxathiazine 2,2-dioxide (2c)



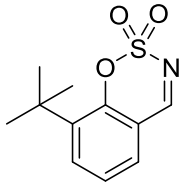
Yellow solid; mp 56.5-59.2 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.60 (d, *J* = 0.6 Hz, 1H), 7.71 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.19 – 7.07 (m, 1H), 1.28 (s, 9H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 168.7 (CH), 152.5 (C), 150.2 (C), 135.7 (CH), 127.8 (CH), 118.5 (CH), 115.3 (C), 35.2 (C), 31.5 (CH_3) ppm.

8-methylbenzo-[*e*][1,2,3]oxathiazine 2,2-dioxide (2f)



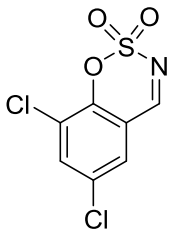
White solid; mp 89.5-90.9 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.56 (s, 1H), 7.58 – 7.36 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 2.25 (t, *J* = 0.8 Hz, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 168.2 (CH), 152.1 (C), 139.1 (CH), 128.6 (CH), 127.98 (C), 125.5 (CH), 114.9 (C), 14.2 (CH_3) ppm.

8-(*tert*-butyl)benzo-[*e*][1,2,3]oxathiazine 2,2-dioxide (2g)



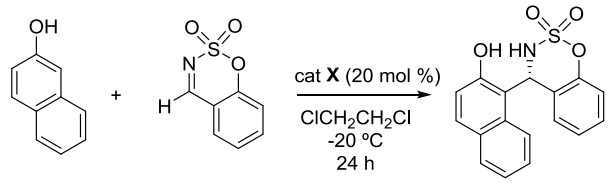
White solid; **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.56 (s, 1H), 7.65 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 1.35 (s, 9H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 169.3 (CH), 153.5 (C), 140.7 (C), 135.8 (CH), 129.7 (CH), 126.4 (CH), 116.6 (C), 35.4 (C), 30.1 (CH_3) ppm.

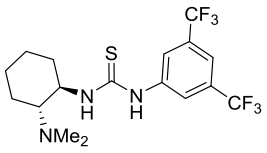
6,8-dichlorobenzo-[*e*][1,2,3]oxathiazine 2,2-dioxide (2h)



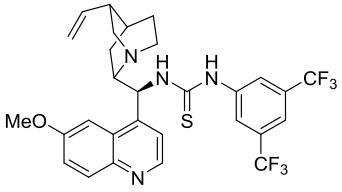
White solid; mp 136.0-137.3 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.62 (s, 1H), 7.82 – 7.74 (m, 1H), 7.59 (dd, *J* = 2.4, 0.8 Hz, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 165.9 (CH), 148.9 (C), 137.2 (CH), 131.6 (C), 128.3 (CH), 125.1 (C), 116.8 (C) ppm.

Other organocatalysts studied in the optimization process:

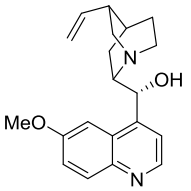




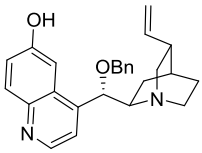
A, 86%, -2% ee



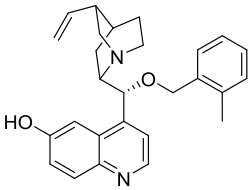
B, 92%, -5% ee



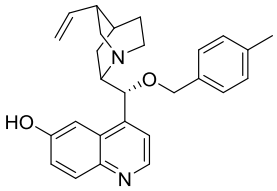
C, 68%, -14% ee



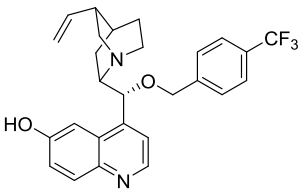
D, 84%, -57% ee



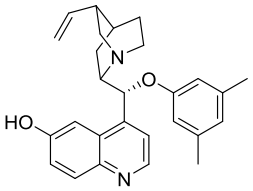
E, 70%, 81% ee



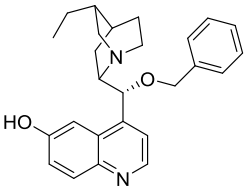
F, 72%, 80% ee



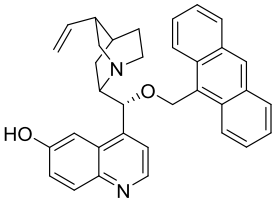
G, 76%, 80% ee



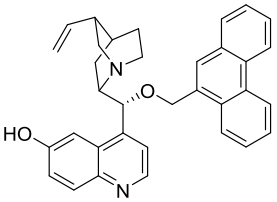
H, 91%, 59% ee



I, 79%, 72% ee



J, 93%, 76% ee



K, 68%, 77% ee

Typical procedures and characterization data for compounds 3, 6 and 7

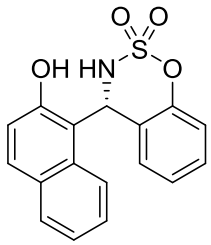
General procedure for the enantioselective Friedel-Crafts reaction

To a solution of naphthol **1** (0.1 mmol) and catalyst **Id** (0.01 mmol) in 1,2-dichloroethane (1 mL) at -20 °C under inert atmosphere, was added a solution of imine **2a** (0.1 mmol) in 1,2-dichloroethane (1 mL) during 12 hours using a syringe pump. Alternatively, naphthol **1a** can be added to a solution of imine **2** and catalyst **Id**. The reaction was followed by TLC using CH_2Cl_2 as eluent. Once the reaction was complete, the mixture was directly subjected to flash chromatography eluting with CH_2Cl_2 to CH_2Cl_2/EtOAc (95:5).

General procedure for the racemic Friedel-Crafts reaction

To a solution of naphthol **1** (0.1 mmol) and imine **2** (0.1 mmol) in 1mL of CH_2Cl_2, 10 μL of Et_3N were added. The solution was stirred at room temperature. The reaction was followed and purified as described above.

(+)-(*R*)-4-(2-hydroxynaphthalen-1-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (3aa)

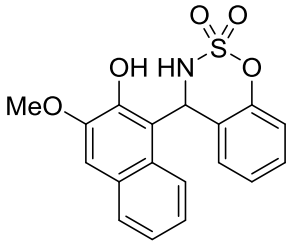


3aa

Enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 7.9 min, minor enantiomer t_r = 6.0 min.

White solid, mp 159-161 °C, **$[\alpha]_D^{20}$** + 102.1 (*c* 0.64, MeOH, 85% *ee*). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.7 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.53 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.25 – 7.14 (m, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 7.00 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.86 (td, *J* = 7.5, 1.5 Hz, 1H), 6.66 (s, 1H), 6.55 (dt, *J* = 7.5, 1.5 Hz, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 153.2 (C), 151.2 (C), 132.9 (C), 131.0 (CH), 128.85 (C), 128.8 (CH), 128.5 (C), 127.8 (CH), 126.7 (CH), 124.8 (CH), 123.5 (CH), 123.05 (C), 121.3 (CH), 117.9 (CH), 114.3 (C), 54.3 (CH) ppm; **HRMS (ESI)**: m/z: 326.0493 $[M-H]^-$, $C_{17}H_{13}NO_4S$ requires 326.0487.

(+)-(*R*)-4-(2-hydroxy-3-methoxynaphthalen-1-yl)-3,4-dihydrobenzo[e][1,2,3] oxathiazine 2,2-dioxide (3ba)



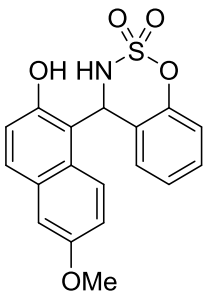
3ba

Enantiomeric excess (89%) was determined by chiral HPLC (Chiralpak OD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 17.8 min, minor enantiomer t_r = 13.0 min.

Brown solid, mp 160-170 °C, **$[\alpha]_D^{20}$** 119.6 (c 0.83, MeOH, 89% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.0, 1.5 Hz, 1H), 7.40 (ddd, *J* = 8.0, 7.0, 1.5 Hz, 1H), 7.28 – 7.20 (m, 3H),

7.05 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.91 (td, *J* = 7.5, 1.5 Hz, 1H), 6.72 (s, 1H), 6.58 (dt, *J* = 8.0, 1.3 Hz, 1H), 4.03 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 151.8 (C), 147.1 (C), 144.7 (C), 129.6 (CH), 129.4 (C), 128.1 (CH), 127.1 (CH), 126.3 (CH), 125.4 (CH), 125.2 (CH), 123.1 (C), 121.9 (CH), 118.6 (CH), 115.2 (C), 107.9 (CH), 56.5 (CH_3), 55.0 (CH) ppm; **HRMS** (ESI): *m/z*: 358.0748 $[M+H]^+$, $C_{18}H_{15}NO_5S$ requieres 358.0749.

(+)-(*R*)-4-(2-hydroxy-6-methoxynaphthalen-1-yl)-3,4-dihydrobenzo[e][1,2,3] oxathiazine 2,2-dioxide (3ca)

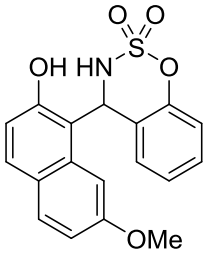


3ca

Enantiomeric excess (83%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 11.2 min, minor enantiomer t_r = 8.9 min.

Brown solid, mp 163-164 ^{o}C, **$[\alpha]^{20}_{D}$** + 106.0 (c 0.89, MeOH, 83% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 9.5 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.94 – 6.82 (m, 1H), 6.64 (s, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 3.91 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 155.9 (C), 151.3 (C), 151.1 (C), 129.7 (CH), 129.0 (CH), 128.2 (C), 126.7 (CH), 124.9 (CH), 123.05 (CH), 120.3 (CH), 118.5 (CH), 118.1 (CH), 114.9 (C), 107.2 (CH), 55.3 (CH_3), 54.9 (CH) ppm; **HRMS** (ESI): *m/z*: 358.0738 $[M+H]^+$, $C_{18}H_{15}NO_5S$ requieres 358.0749.

(+)-(*R*)-4-(2-hydroxy-7-methoxynaphthalen-1-yl)-3,4-dihydrobenzo[e][1,2,3] oxathiazine 2,2-dioxide (3da)

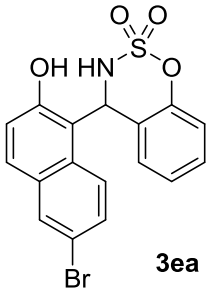


3da

Enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak OD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 13.6 min, minor enantiomer t_r = 18.6 min.

Brown solid, mp 167-168 ^{o}C, **$[\alpha]^{20}_{D}$** + 105.9 (c 0.81, MeOH, 88% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.78 – 7.67 (m, 2H), 7.32 – 7.20 (m, 2H), 7.12 – 7.02 (m, 2H), 6.99 – 6.86 (m, 2H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.61 (s, 1H), 3.92 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 159.5 (C), 153.5 (C), 151.3 (C), 134.4 (C), 130.9 (CH), 130.5 (CH), 123.0 (CH), 126.7 (CH), 124.9 (CH), 124.1 (C), 123.1 (C), 118.1 (CH), 116.0 (CH), 115.2 (CH), 113.8 (C), 100.4 (CH), 55.4 (CH_3), 55.0 (CH) ppm; **HRMS** (ESI): *m/z*: 358.0755 $[M+H]^+$, $C_{18}H_{15}NO_5S$ requieres 358.0749.

(+)-(*R*)-4-(6-bromo-2-hydroxynaphthalen-1-yl)-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ea)

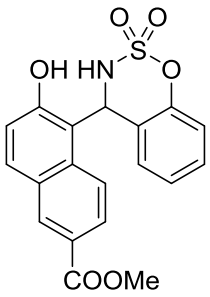


3ea

Enantiomeric excess (75%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 10.4 min, minor enantiomer t_r = 8.6 min.

Brown solid, mp 198-199 ^{o}C, **[α]$^{20}_{D}$** +86.0 (c 0.72, MeOH, 75% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.06 (dd, *J* = 16.0, 8.0 Hz, 2H), 6.90 (td, *J* = 7.5, 1.0 Hz, 1H), 6.61 (s, 1H), 6.51 (d, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 153.4 (C), 151.3 (C), 131.6 (C), 131.0 (CH), 130.7 (CH), 130.2 (CH), 129.7 (C), 129.1 (CH), 126.5 (CH), 125.0 (CH), 123.3 (CH), 122.8 (CH), 119.1 (CH), 118.1 (CH), 117.2 (C), 114.7 (C), 54.7 (CH) ppm; **HRMS**: m/z: 423.0008/424.9987 $[M+NH_4]^+$ (100/57.7), $C_{17}H_{17}N_2O_4S$ requires 423.0014/ 424.9994.

(+)-(*R*)-Methyl 5-(2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)-6-hydroxy-2-naphthoate (3fa)

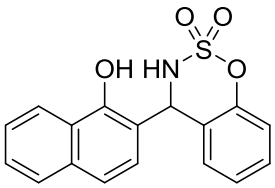


3fa

Enantiomeric excess (96%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 12.1 min, minor enantiomer t_r = 11.1 min.

White solid, mp 200-205 ^{o}C, **[α]$^{20}_{D}$** + 115.5 (c 0.23, MeOH,96% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 8.05 – 7.90 (m, 2H), 7.28 – 7.13 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 6.67 (s, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 3.97 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 171.7 (C), 160.1 (C), 155.7 (C), 139.9 (CH), 137.1 (CH), 136.4 (CH), 133.4 (CH), 131.9 (C), 131.5 (CH), 130.8 (CH), 129.3 (CH), 127.2(C), 126.0 (CH), 123.2 (CH), 122.4 (CH), 118.9(C), 59.1 (CH_3), 56.5 (CH) ppm; **HRMS (ESI):** *m/z*: 384.1273 $[M-H]^-$, $C_{19}H_{15}NO_6S$, requires 384.0542.

4-(1-hydroxynaphthalen-2-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (6)

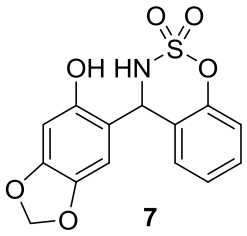


6

Enantiomeric excess (83%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 14.3 min, minor enantiomer t_r = 9.65 min.

Brown solid, $[\alpha]^{20}_{D}$ + 232.6 (c 0.6, MeOH, 83% *ee*), **^{1}H NMR (300 MHz, *d*^{6}-acetone)** δ 8.43 – 8.33 (m, 1H), 8.14 (s, 1H), 7.96 – 7.86 (m, 1H), 7.64 – 7.54 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.33 (m, 2H), 7.17 – 7.08 (m, 2H), 6.91 – 6.77 (m, 1H), 6.60 (s, 1H) ppm; **^{13}C NMR (75 MHz, *d*^{6}-acetone)** δ = 152.7 (C), 151.65 (C), 135.7 (C), 130.1 (CH), 129.1 (CH), 128.8 (CH), 127.7 (CH), 127.6 (CH), 126.6 (CH), 126.2 (C), 125.8 (CH), 124.2 (C), 122.6 (CH), 121.6 (CH), 120.0 (C), 119.0 (CH), 57.1 (CH) ppm; **HRMS (ESI)**: m/z: 328.0638 $[M+H]^+$, $C_{17}H_{14}NO_4S$ requires 328.0644.

4-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (7)

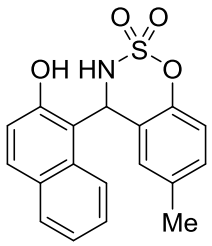


7

Enantiomeric excess (77%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 14.2 min, minor enantiomer t_r = 13.4 min.

White solid, mp 83-87 ^{o}C, $[\alpha]^{20}_{D}$ + 12.6 (c 0.7, MeOH, 77% *ee*), **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.34 – 7.26 (m, 1H), 7.05 (ddd, *J* = 15.7, 7.9, 1.1 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.72 (s, 1H), 6.41 (s, 1H), 5.97 (d, *J* = 0.9 Hz, 2H), 5.81 (d, *J* = 9.8 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 5.40 (s, 1H) ppm; **^{13}C NMR (75 MHz, CDCl$_3$)** δ = 151.05 (C), 149.1 (C), 148.6 (C), 142.0 (C), 129.45 (CH), 127.2 (CH), 125.1 (CH), 122.4 (C), 118.45 (CH), 114.9 (C), 110.0 (CH), 101.8 (CH_2), 99.25 (CH), 59.5 (CH) ppm; **HRMS** (ESI): m/z: 322.0386 $[M+H]^+$, $C_{14}H_{12}NO_6S$ requires 322.0385.

(+)-(*R*)-4-(2-hydroxynaphthalen-1-yl)-6-methyl-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ab)

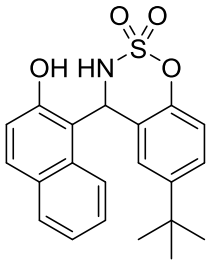


3ab

Enantiomeric excess (86%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 8.3 min, minor enantiomer t_r = 5.65 min.

Orange solid, mp 152-154 ^{o}C, **$[\alpha]_D^{20}$** + 132.8 (c 0.87, MeOH, 82% *ee*), **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.57 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.47 – 7.33 (m, 1H), 7.10 – 6.99 (m, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 5.0 Hz, 1H), 6.39 – 6.31 (m, 1H), 2.04 (s, 3H) ppm; **^{13}C NMR (75 MHz, CDCl$_3$)** δ = 152.8 (C), 149.2 (C), 134.7 (C), 133.0 (C), 131.2 (CH), 129.6 (CH), 128.8 (CH), 128.7 (C), 127.9 (CH), 126.7 (CH), 123.7 (CH), 122.6 (CH), 121.5 (CH), 117.9 (C), 117.85 (CH), 114.6 (C), 54.7 (CH), 20.6 (CH_3) ppm; **HRMS**: $[M+H]^+$ 342.0791, $C_{18}H_{16}NO_4S$ requires 342.0800.

(+)-(*R*)-6-(tert-butyl)-4-(2-hydroxynaphthalen-1-yl)-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ac)



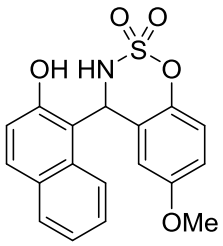
3ac

Enantiomeric excess (82%) was determined by chiral HPLC (Chiralpak IC), hexane-^{i}PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 10.5 min, minor enantiomer t_r = 9.1 min.

Browm solid, mp 154-159 ^{o}C, **$[\alpha]_D^{20}$** + 39.0 (c 0.88, MeOH, 82% *ee*), **NMR ^{1}H (300 MHz CDCl$_3$)** δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.53 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.26 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.60 (d, *J* = 11.5 Hz, 1H), 0.99 (s, 9H) ppm; **^{13}C NMR (75 MHz, CDCl$_3$)** δ = 152.4 (C), 149.0 (C), 148.1 (C), 133.0 (CH), 131.3 (CH), 128.9 (CH), 128.0 (CH), 126.1 (CH), 123.9 (CH), 123.3 (CH),

122.05 (CH), 121.5 (CH), 117.9 (CH), 117.8 (C), 117.6 (CH), 114.8 (C), 55.0 (CH), 34.2 (C), 31.0 (CH_3) ppm; **HRMS**: $[M+H]^+$ 384.1269, $C_{21}H_{22}NO_4S$ requires 384.1270.

(+)-(*R*)-4-(2-hydroxynaphthalen-1-yl)-6-methoxy-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ad)

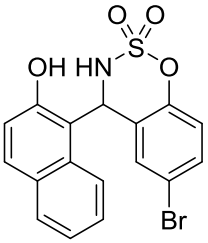


3ad

Enantiomeric excess (84%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 13.2 min, minor enantiomer t_r = 7.6 min.

White solid, mp 163-164 ^{o}C, **$[\alpha]_D^{20}$** + 70.2 (c 0.88, MeOH, 84% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.38 – 7.27 (m, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 6.45 (d, *J* = 10.2 Hz, 1H), 6.07 – 5.99 (m, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 156.2 (C), 153.2 (C), 145.1 (C), 132.8 (C), 131.0 (CH), 128.7 (CH), 128.4 (C), 127.7 (CH), 124.1 (C), 123.3 (CH), 121.0 (CH), 118.6 (CH), 117.8 (CH), 114.0 (C), 113.4 (CH), 112.0 (CH), 55.2 (CH_3), 54.71 (CH) ppm; **HRMS (ESI):** *m/z*: 358.0747 $[M+H]^+$,$C_{17}H_{13}NO_4S$ requires 358.0749.

(+)-(*R*)-6-bromo-4-(2-hydroxynaphthalen-1-yl)-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ae)

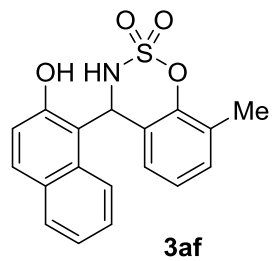


3ae

Enantiomeric excess (86%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 8.2 min, minor enantiomer t_r = 5.9 min.

White solid, mp 198-199 ^{o}C, **$[\alpha]_D^{20}$** + 38.7 (c 0.84, MeOH, 82% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.76 (m, 2H), 7.59 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.42 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 152.9 (C), 150.4 (C), 132.75 (C), 132.0 (CH), 131.6 (CH), 129.2 (CH), 129.0 (CH), 128.7 (CH), 128.2 (CH), 125.3 (CH), 123.8 (C), 121.1 (CH), 119.9 (CH), 117.9 (C), 117.8 (C), 117.6 (CH), 113.8 (C), 54.4 (CH) ppm; **HRMS**:. $[M+H]^+$, requires.

(+)-(*R*)-4-(2-hydroxynaphthalen-1-yl)-8-methyl-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3af)



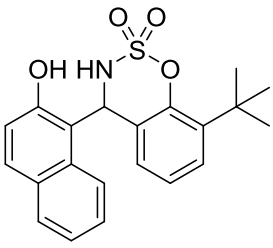
3af

Enantiomeric excess (83%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 7.25 min, minor enantiomer t_r = 5.6 min.

Brown solid, mp 177-179 ^{o}C, **$[\alpha]_D^{20}$** + 132.8 (c 0.74, MeOH, 83% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.80 (dd, *J* = 12.5, 8.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H),

7.38 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.68 (s, 1H), 6.40 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 152.95 (C), 149.9 (C), 133.0 (C), 131.05 (C), 130.5 (CH), 128.8 (CH), 128.6 (C), 127.85 (CH), 127.3 (C), 124.2 (CH), 124.1 (CH), 123.6 (CH), 122.8 (CH), 121.5 (CH), 117.9 (CH), 114.65 (C), 54.7 (CH), 15.5 (CH_3) ppm; **HRMS** (ESI): m/z: 342.0805 $[M+H]^+$, $C_{18}H_{15}NO_4S$, requires 342.0800.

(+)-(*R*)-8-(tert-butyl)-4-(2-hydroxynaphthalen-1-yl)-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ag)

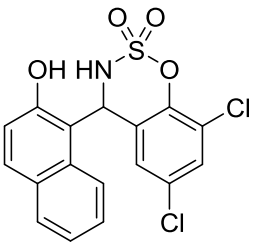


3ag

Enantiomeric excess (80%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 90:10, 1.0 mL/min, major enantiomer t_r = 10.7 min, minor enantiomer t_r = 8.65 min.

Brown solid, mp 90 ^{o}C (decompose), **$[\alpha]^{20}_{D}$** +132.8 (c 0.74, MeOH, 80% *ee*), **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.80 (dd, *J* = 11.5, 8.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.35 (m, 1H), 7.30 – 7.22 (m, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 5.5 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 1H), 1.47 (s, 9H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 152.9 (C), 150.7 (C), 139.3 (C), 132.9 (C), 131.2 (C), 131.1 (CH), 128.8 (CH), 128.7 (C), 127.9 (CH), 126.7 (CH), 124.7 (CH), 124.3 (CH), 121.5 (CH), 118.0 (CH), 114.65 (C), 54.5 (CH), 34.9 (C), 30.0 (CH_3) ppm; **HRMS (ESI)**: *m/z*: 384.1266 $[M+H]^+$, $C_{21}H_{21}NO_4S$, requieres 384.1270.

(+)-(*R*)-6,8-dichloro-4-(2-hydroxynaphthalen-1-yl)-3,4-dihydrobenzo[*e*][1,2,3] oxathiazine 2,2-dioxide (3ah)



3ah

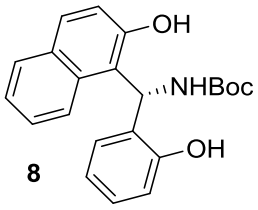
Enantiomeric excess (77%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 85:15, 1.0 mL/min, major enantiomer t_r = 7.85 min, minor enantiomer t_r = 6.3 min.

White solid, mp 184-186 ^{o}C, **$[\alpha]^{20}_{D}$** + 70.0 (c 0.90, MeOH, 77% *ee*). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.07 – 7.90 (m, 1H), 7.89 – 7.77 (m, 2H), 7.60 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.43 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.32 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.64 (d, *J* = 1.0 Hz, 1H), 6.46 (dd, *J* = 2.5, 1.0 Hz, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.0 (C), 146.05 (C), 132.7 (C), 131.8 (CH), 129.7 (C), 129.5 (CH), 129.0 (CH), 128.71 (C), 128.3 (CH), 126.4 (C), 124.9 (CH), 124.0 (C), 123.9 (CH), 121.0 (CH), 117.8 (CH), 113.5 (C), 54.65 (CH) ppm; **HRMS (ESI)** *m/z:* 393.9694/395.9666/397.9639 $[M-H]^-$ (100.0/70.8/15.5) $C_{17}H_{13}NO_4S$ requires 393.9708/395.2300/397.9649.

Procedures and characterization data for compounds 8 and 9

***tert*-butyl (*R*)-((2-hydroxynaphthalen-1-yl)(2-hydroxyphenyl)methyl)**

carbamate (8)

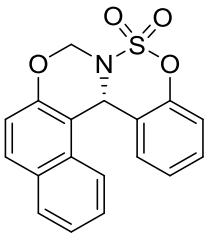


8

Enantiomeric excess (89%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 7.6 min, minor enantiomer t_r = 5.2 min.

White solid, mp 171-173 ^{o}C, **[α]$^{20}_{D}$** – 228.3 (c 0.45, MeOH, 89% *ee*). **^{1}H NMR (300 MHz, *d*^{6}-dmso)** δ 10.02 (s, 1H), 9.46 (s, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.97 (dt, *J* = 18.1, 8.1 Hz, 3H), 6.69 (dd, *J* = 13.4, 7.2 Hz, 2H), 1.56 – 1.16 (m, 10H) ppm; **^{13}C NMR (75 MHz, *d*^{6}-dmso)** δ 154.67 (C), 154.3 (C), 152.8 (C), 132.3 (C), 128.6 (C), 128.5 (CH), 128.4 (C), 128.1 (CH), 127.6 (CH), 127.5 (C), 125.9 (CH), 123.4 (CH), 122.4 (CH), 119.5 (C), 118.7 (CH), 118.4 (CH), 114.95 (CH), 78.0 (C), 39.7 (CH), 28.1 (CH_3) ppm; **HRMS (ESI)** *m/z:* 364.1542 $[M-H]^-$ $C_{22}H_{22}NO_4$ requires 364.1549.

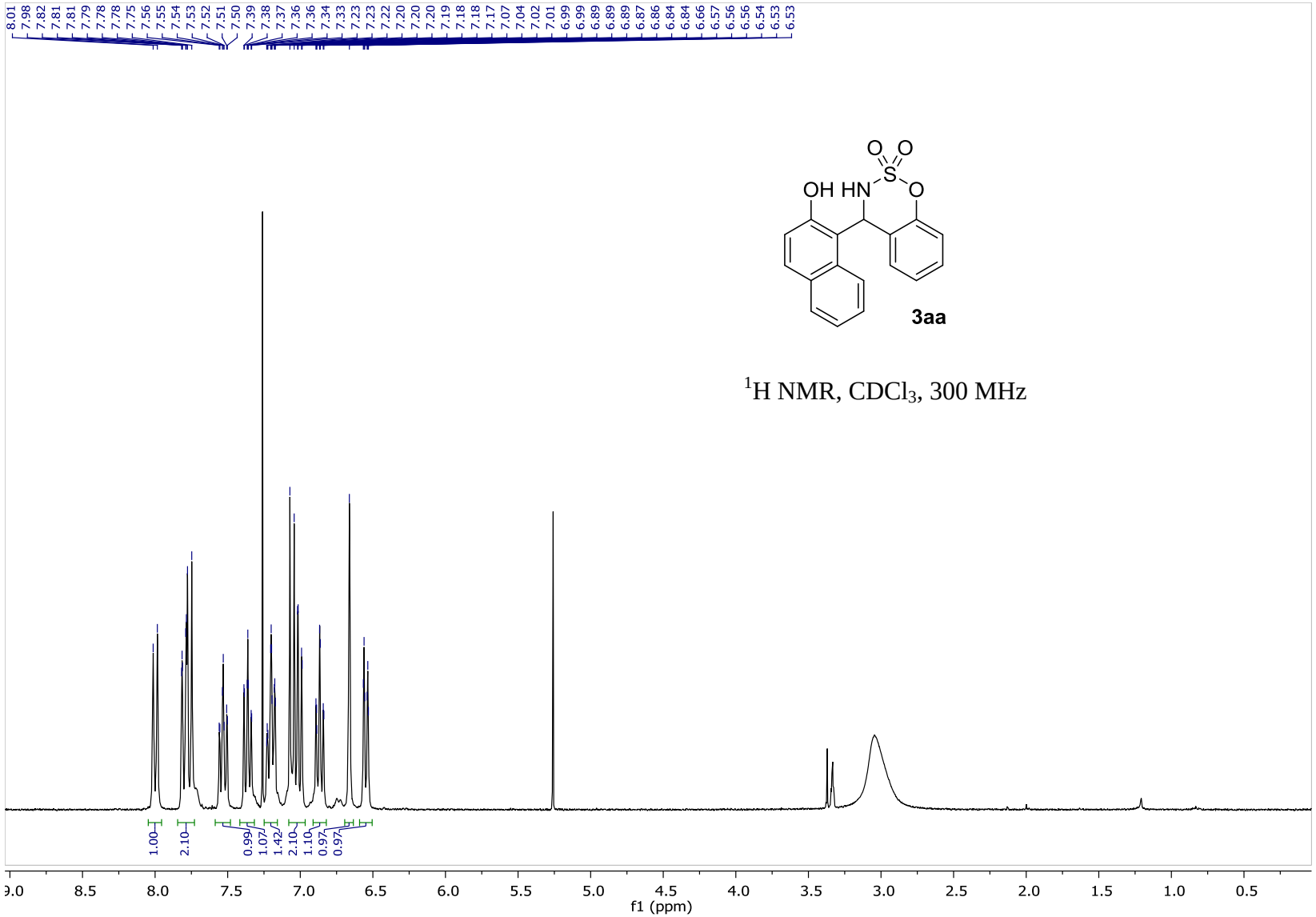
(*R*)-4H,11*c*H-benzo[*e*]naphtho[1',2':5,6][1,3]oxazino[3,4-*c*][1,2,3]oxathiazine 2,2-dioxide (9)



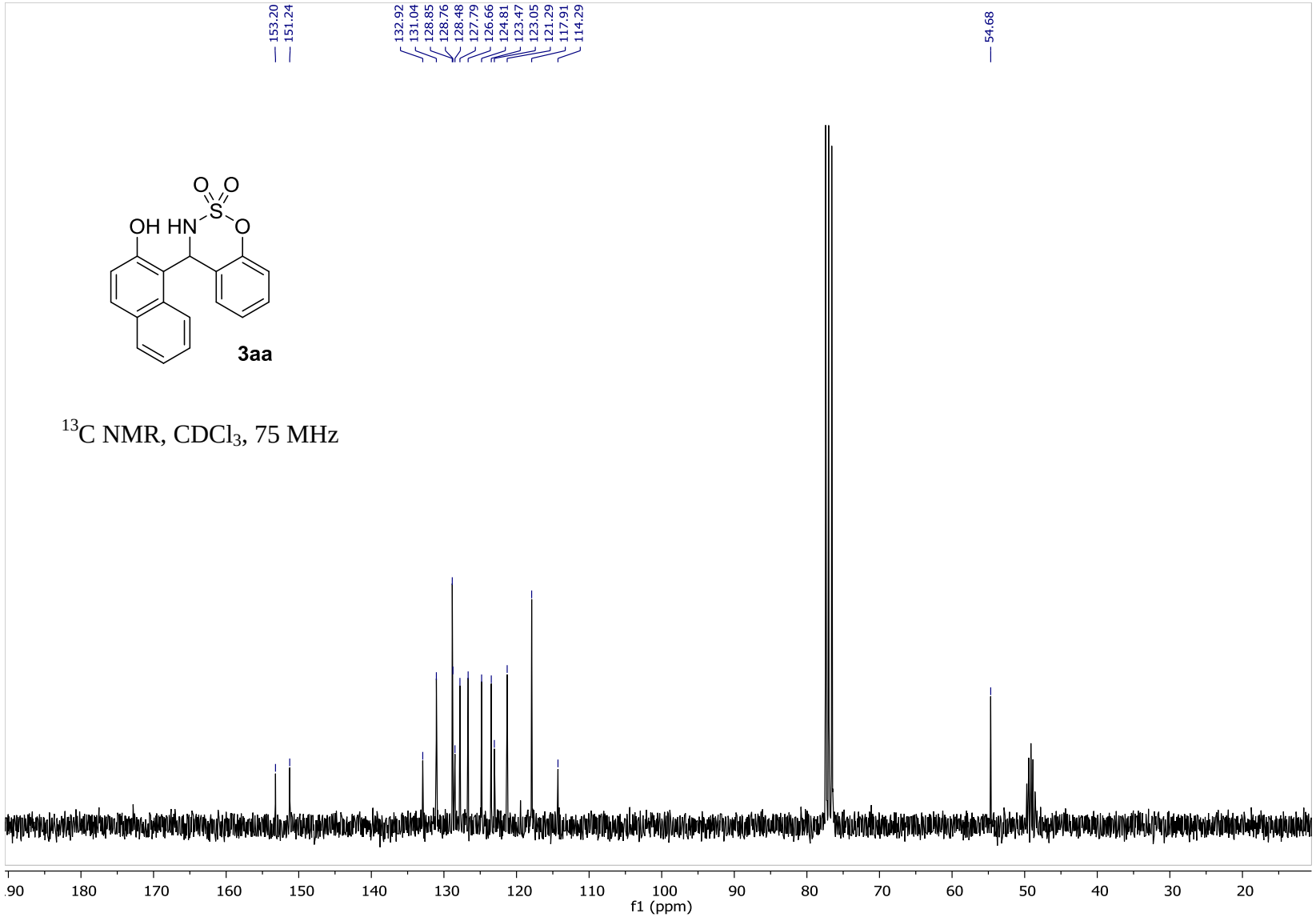
9

Enantiomeric excess (85%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 9.7 min, minor enantiomer t_r = 10.65 min.

White solid, mp 203-206 ^{o}C, **[α]$^{20}_{D}$** + 343.4 (c 0.90, $CHCl_3$, 85% *ee*). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.93 – 7.82 (m, 2H), 7.77 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.58 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.36 (dddd, *J* = 8.3, 5.9, 3.1, 0.8 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.07 – 6.99 (m, 2H), 6.68 (s, 1H), 5.47 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.83 (d, *J* = 7.9 Hz, 1H) ppm **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.2 (C), 150.0 (C), 131.8 (C), 131.0 (CH), 130.3 (CH), 129.6 (CH), 129.5 (C), 128.9 (CH), 127.8 (CH), 125.5 (CH), 124.6 (CH), 122.3 (CH), 121.4 (C), 118.51 (CH), 118.46 (CH), 110.25 (C), 73.35 (CH_2), 54.9 (CH) ppm; **HRMS (ESI)** *m/z:* 340.0636 $[M+H]^+$, $C_{18}H_{14}NO_4S$ requires 340.0644.



^{1}H NMR, $CDCl_3$, 300 MHz


153.20
151.24
132.92
131.04
128.85
128.76
128.48
127.79
126.66
124.81
123.47
123.05
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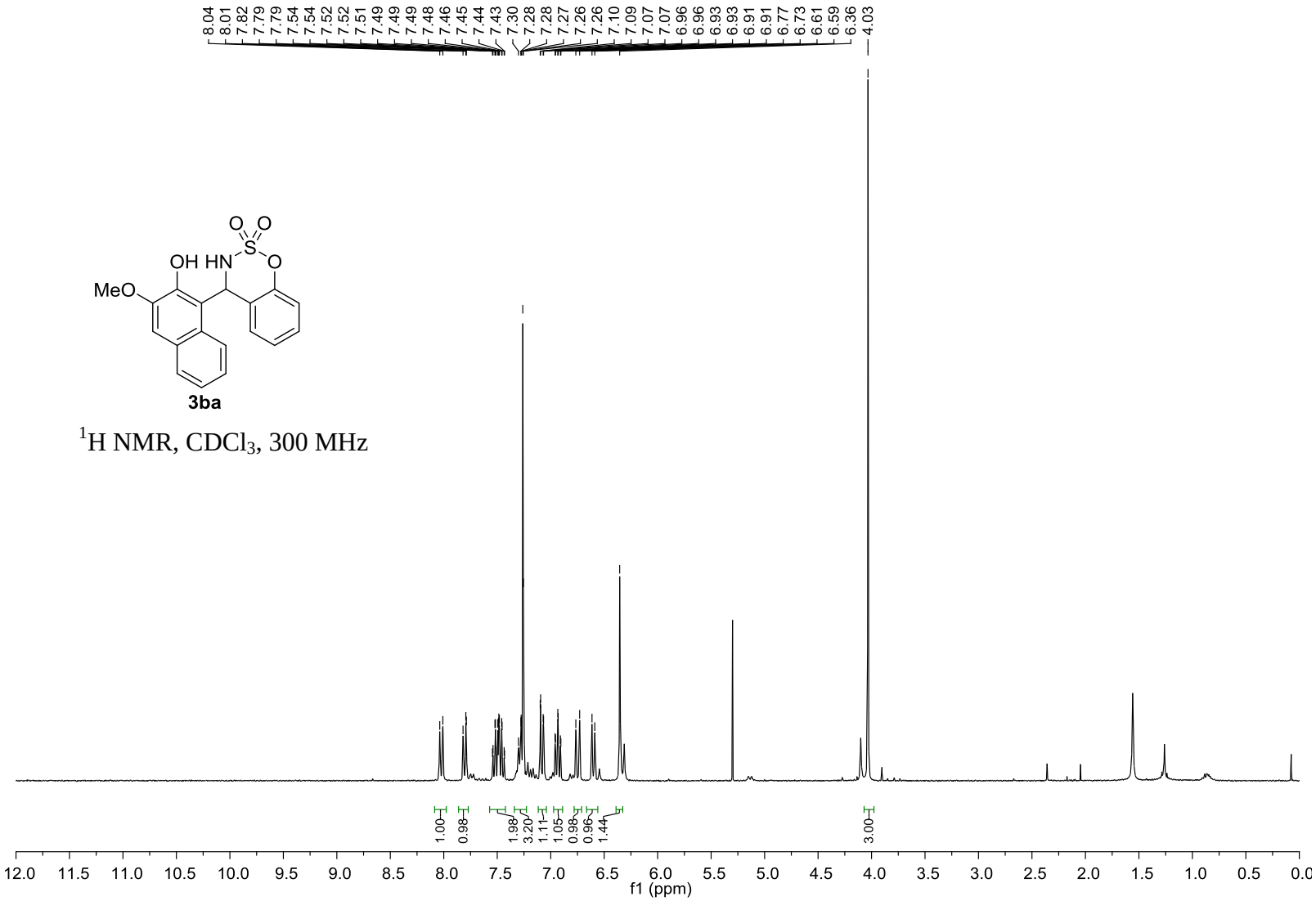
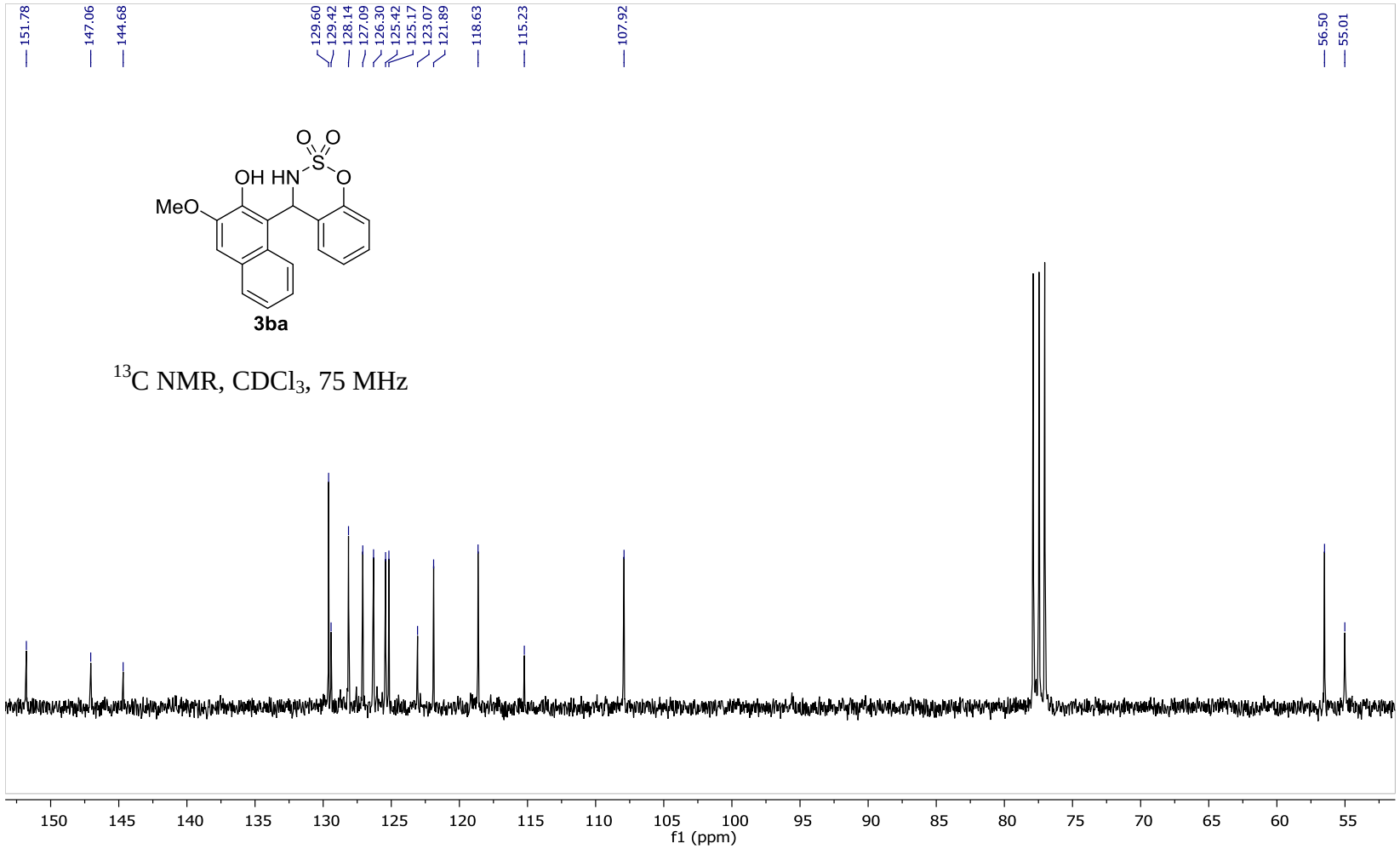
OH HN
O
3aa
13C NMR, CDCl3, 75 MHz
f1 (ppm)



^{1}H NMR, $CDCl_3$, 300 MHz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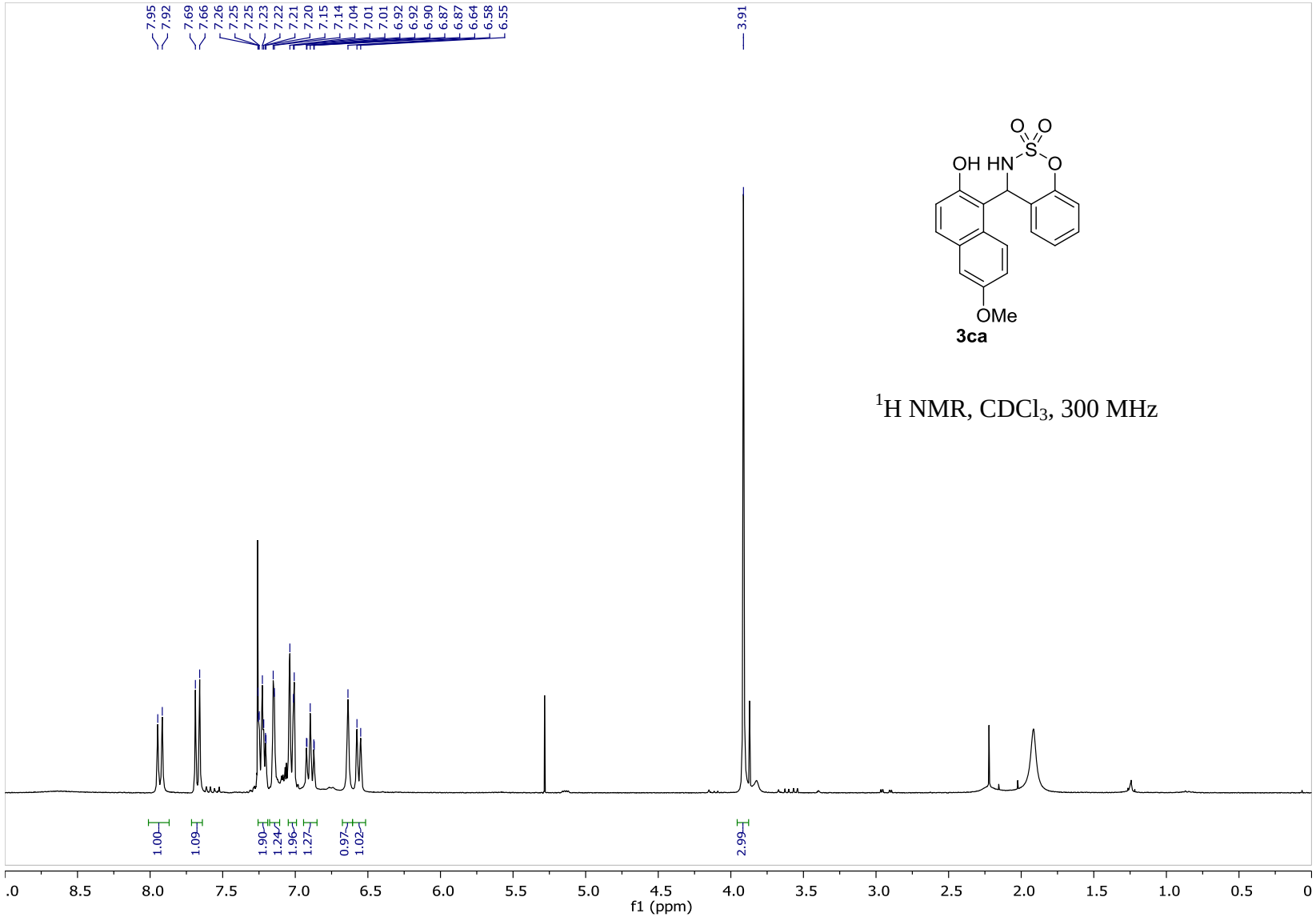
128.14
127.09
126.30
125.42
125.17
123.07
121.89
118.63
115.23
107.92
56.50
55.01
OH HN
MeO
3ba
13C NMR, CDCl3, 75 MHz
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
f1 (ppm)


7.95
7.92
7.69
7.66
7.26
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7.23
7.22
7.21
7.20
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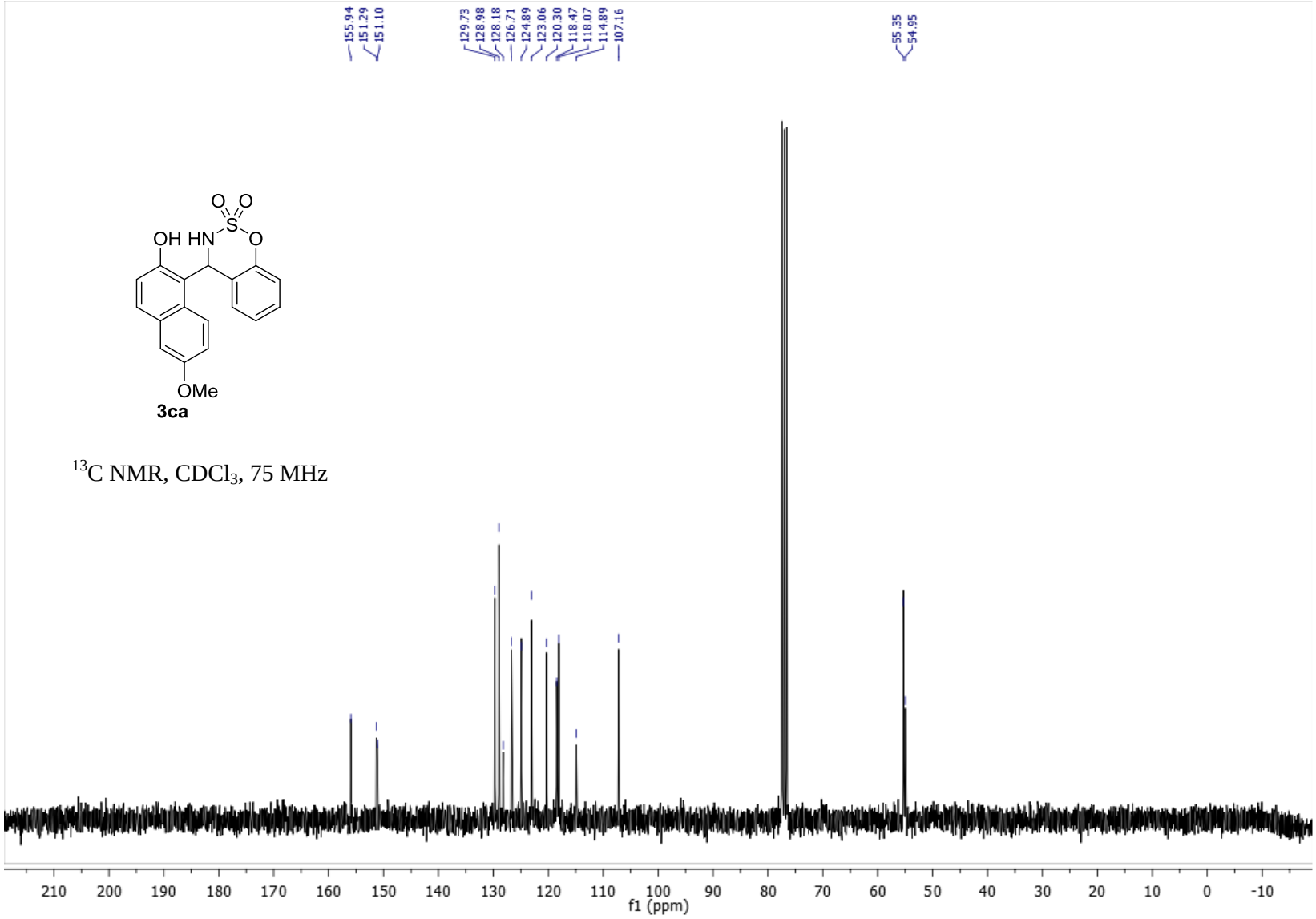
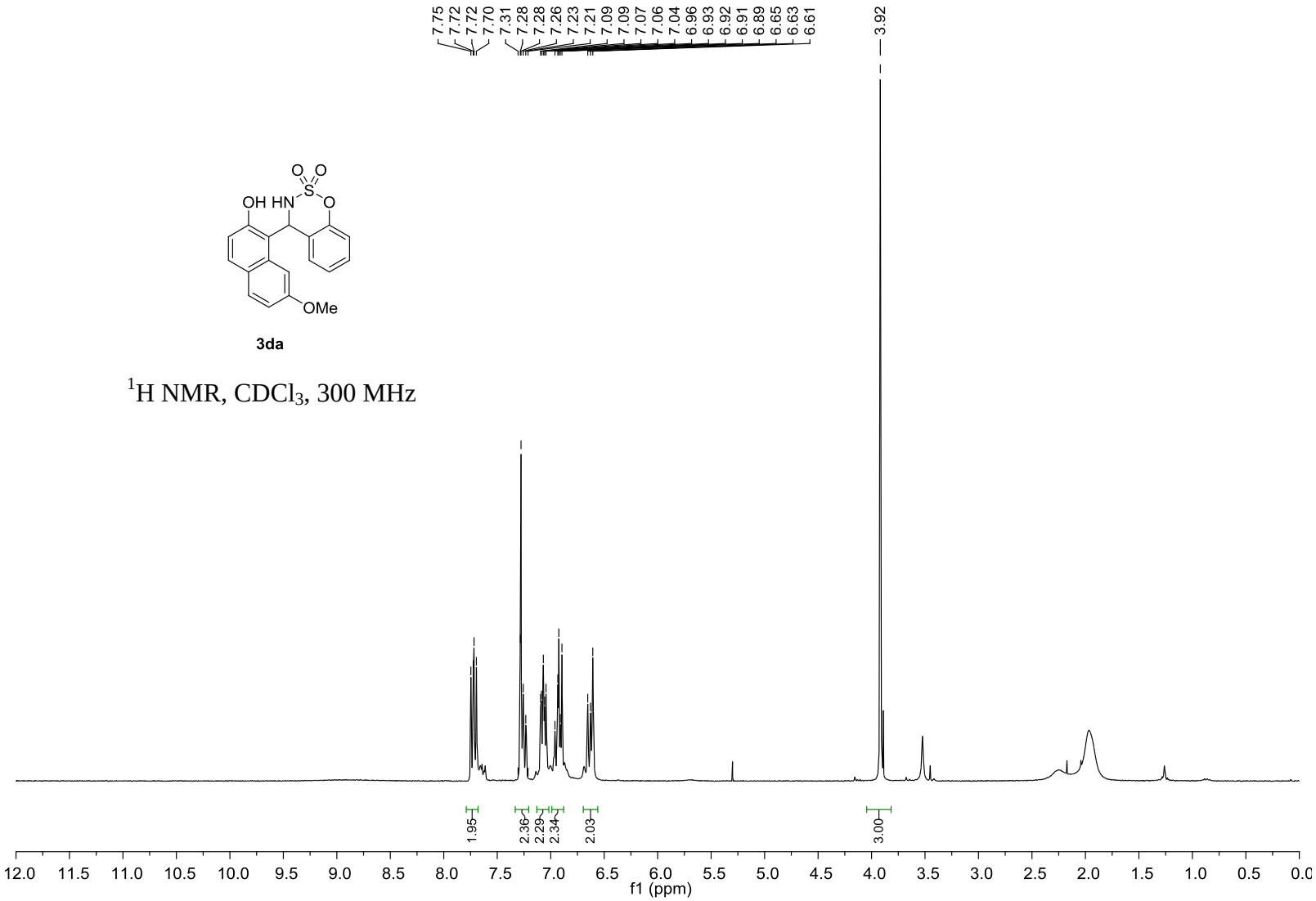
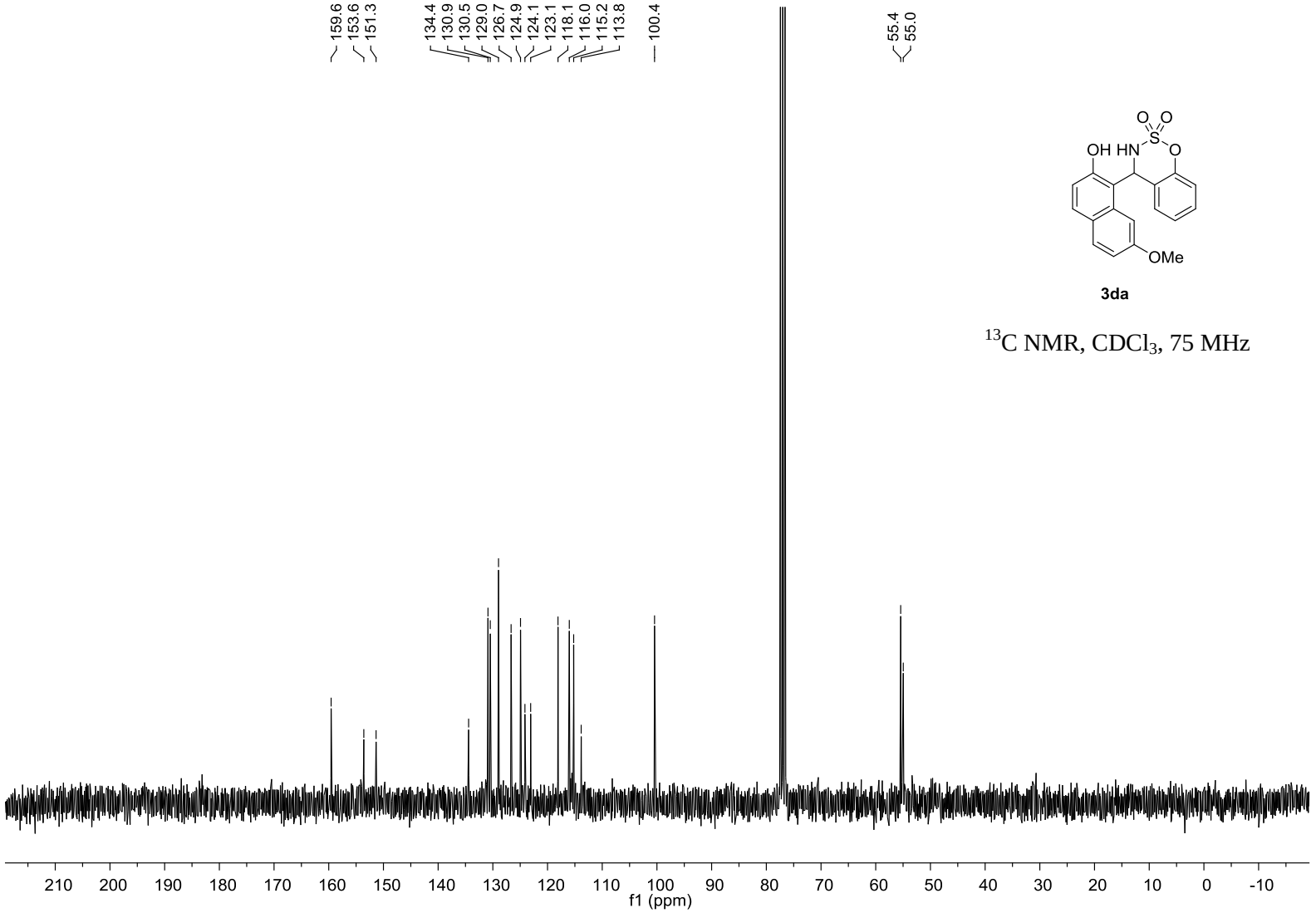
7.04
7.01
7.01
6.92
6.90
6.87
6.64
6.58
6.55
3.91
O
O
S
OH HN
O
OMe
3ca
1H NMR, CDCl3, 300 MHz
1.00
1.09
1.90
1.24
1.96
1.27
0.97
1.02
2.99
f1 (ppm)


155.94
151.29
151.10
129.73
128.98
128.18
126.71
124.89
123.06
120.30
118.47
118.07
114.89
107.16
55.35
54.95
OH HN
O
S
O
O
OMe
3ca
13C NMR, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



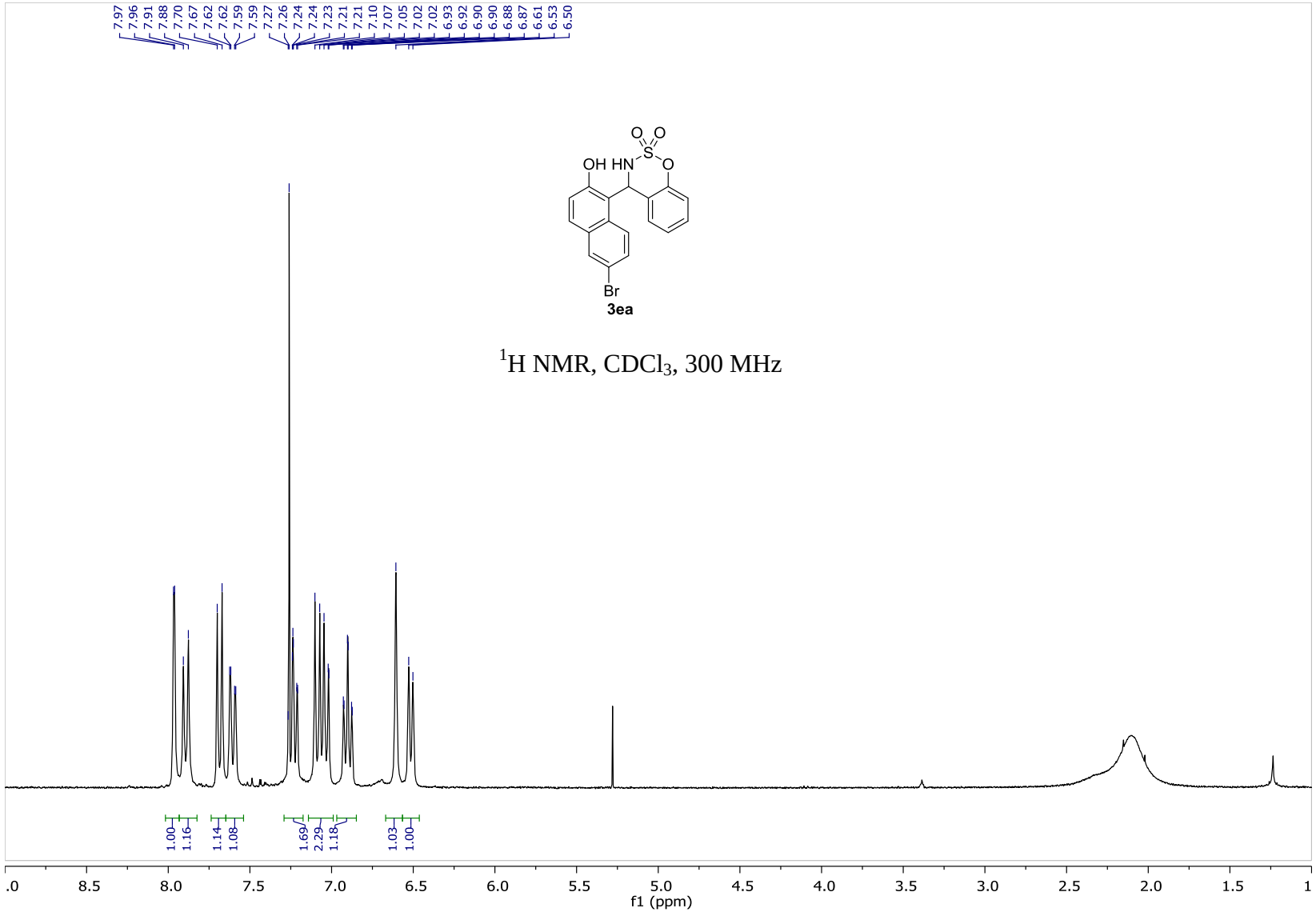
3da

^{1}H NMR, $CDCl_3$, 300 MHz

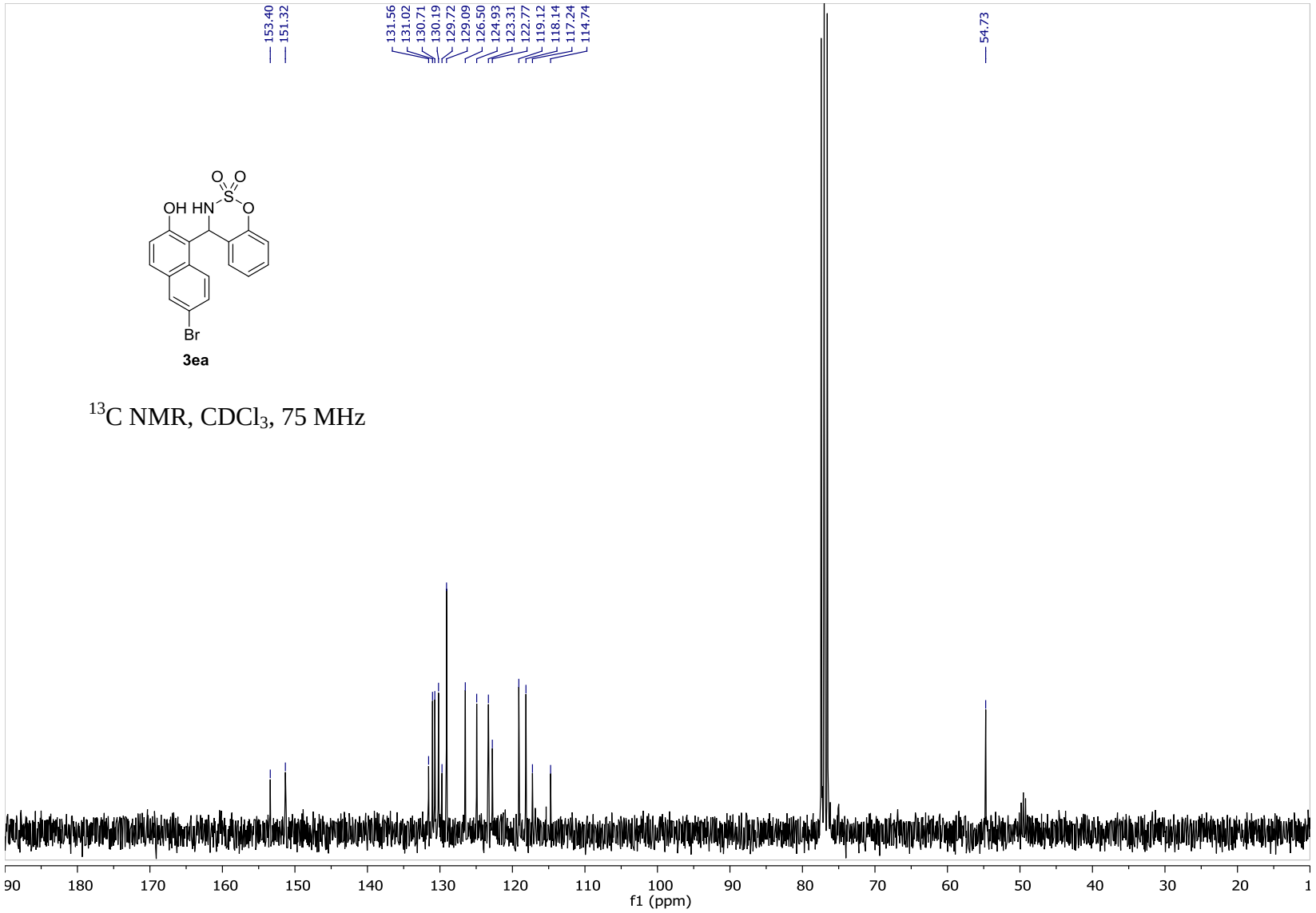


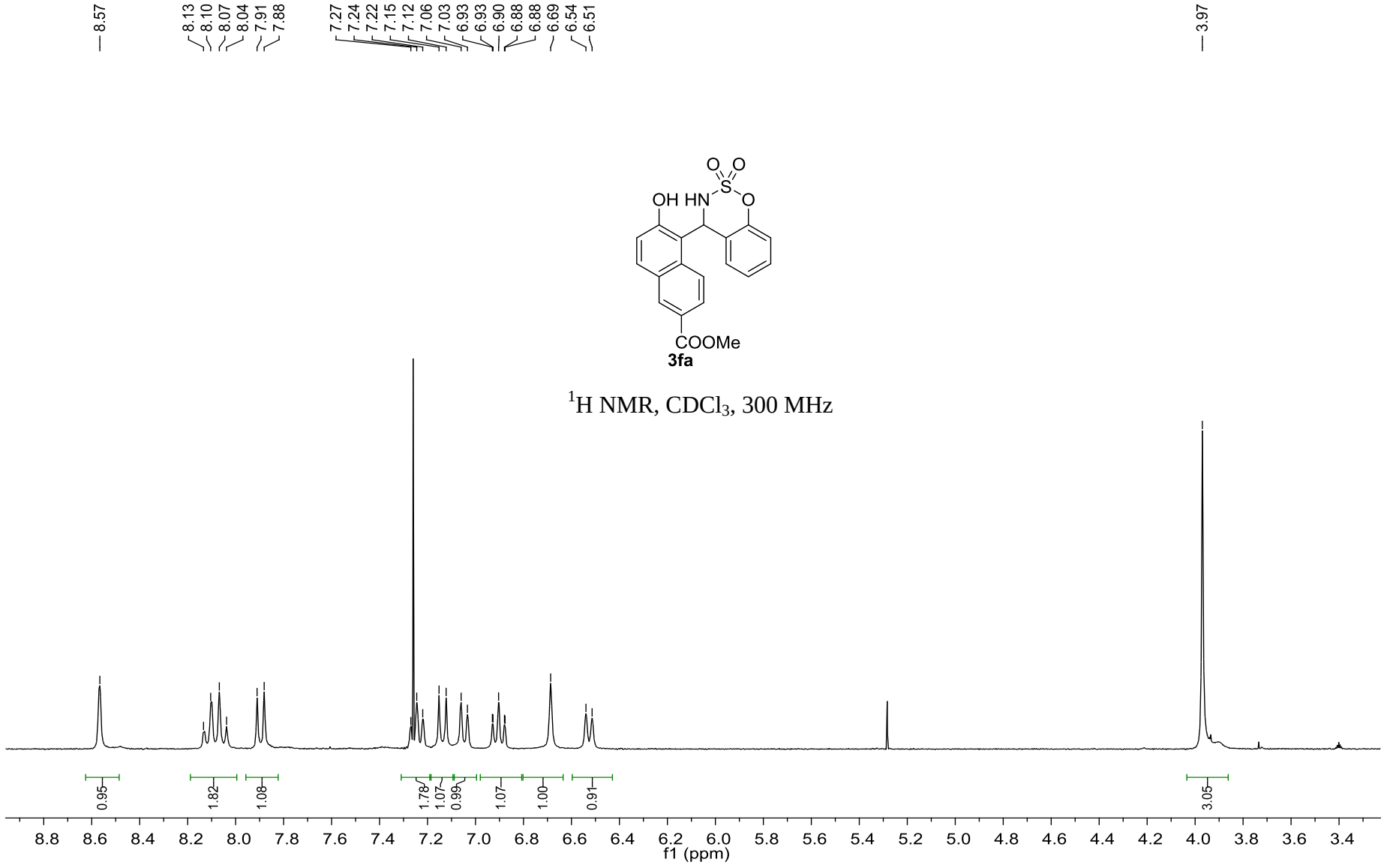
3da

^{13}C NMR, $CDCl_3$, 75 MHz

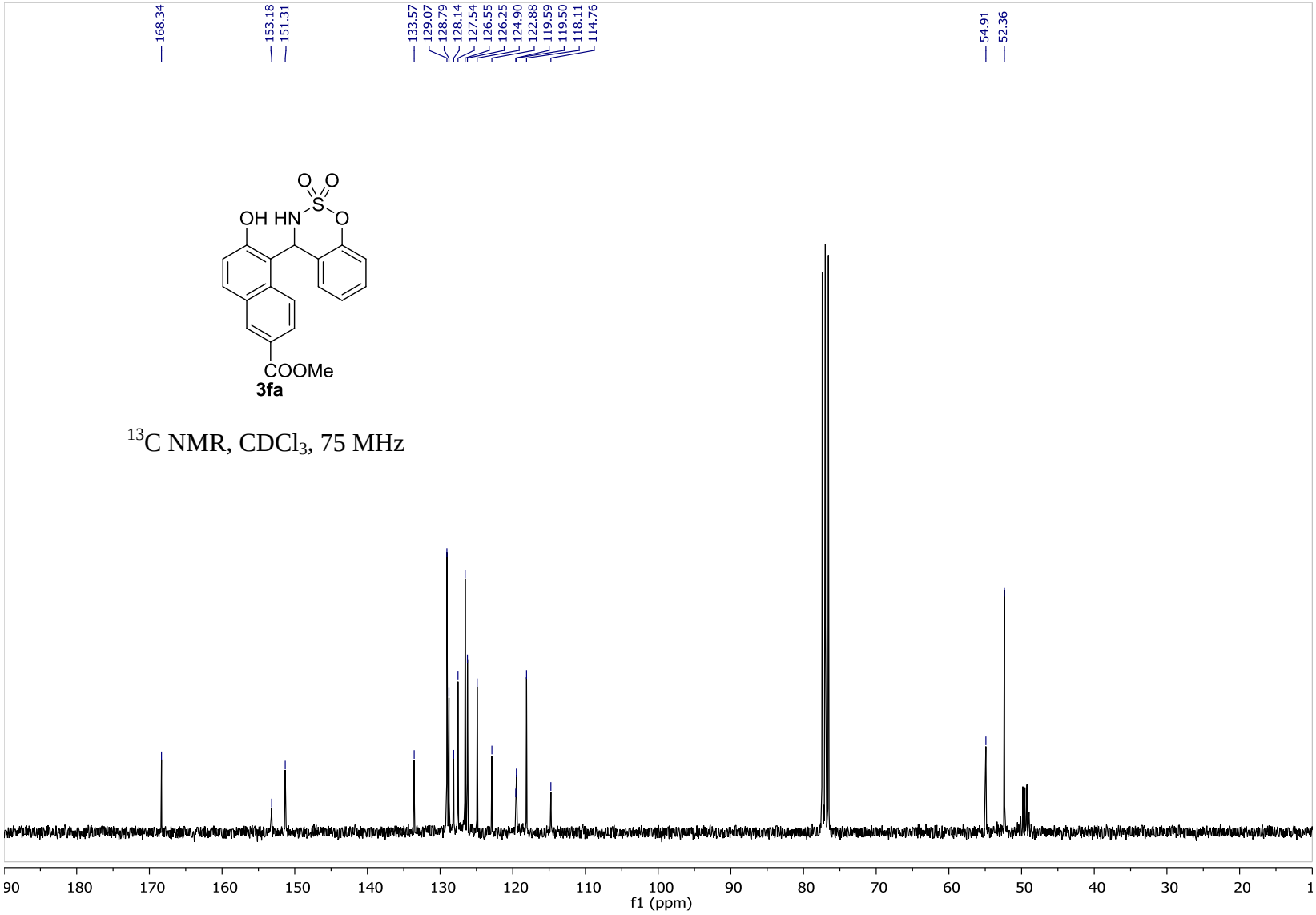


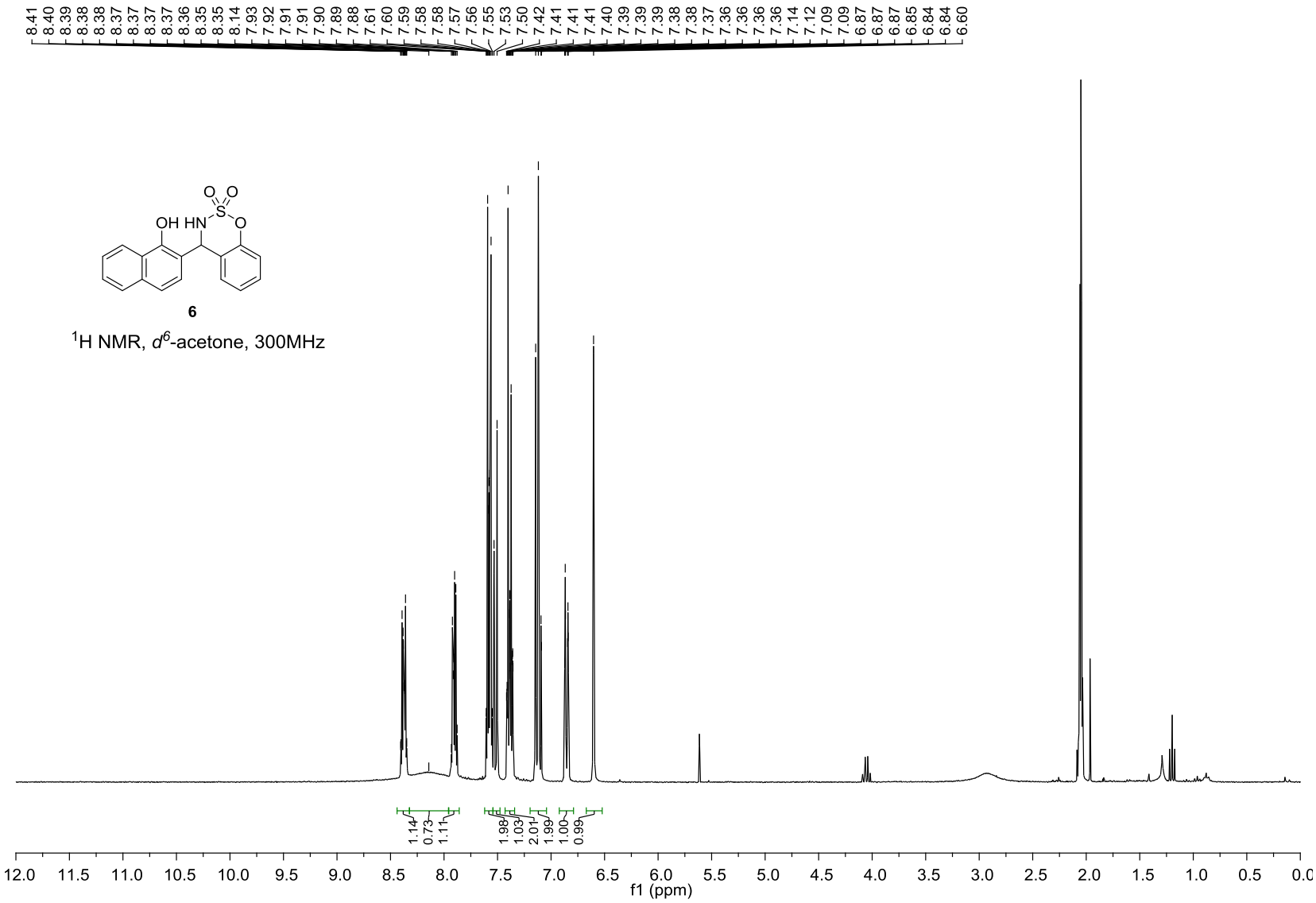
^{1}H NMR, $CDCl_3$, 300 MHz

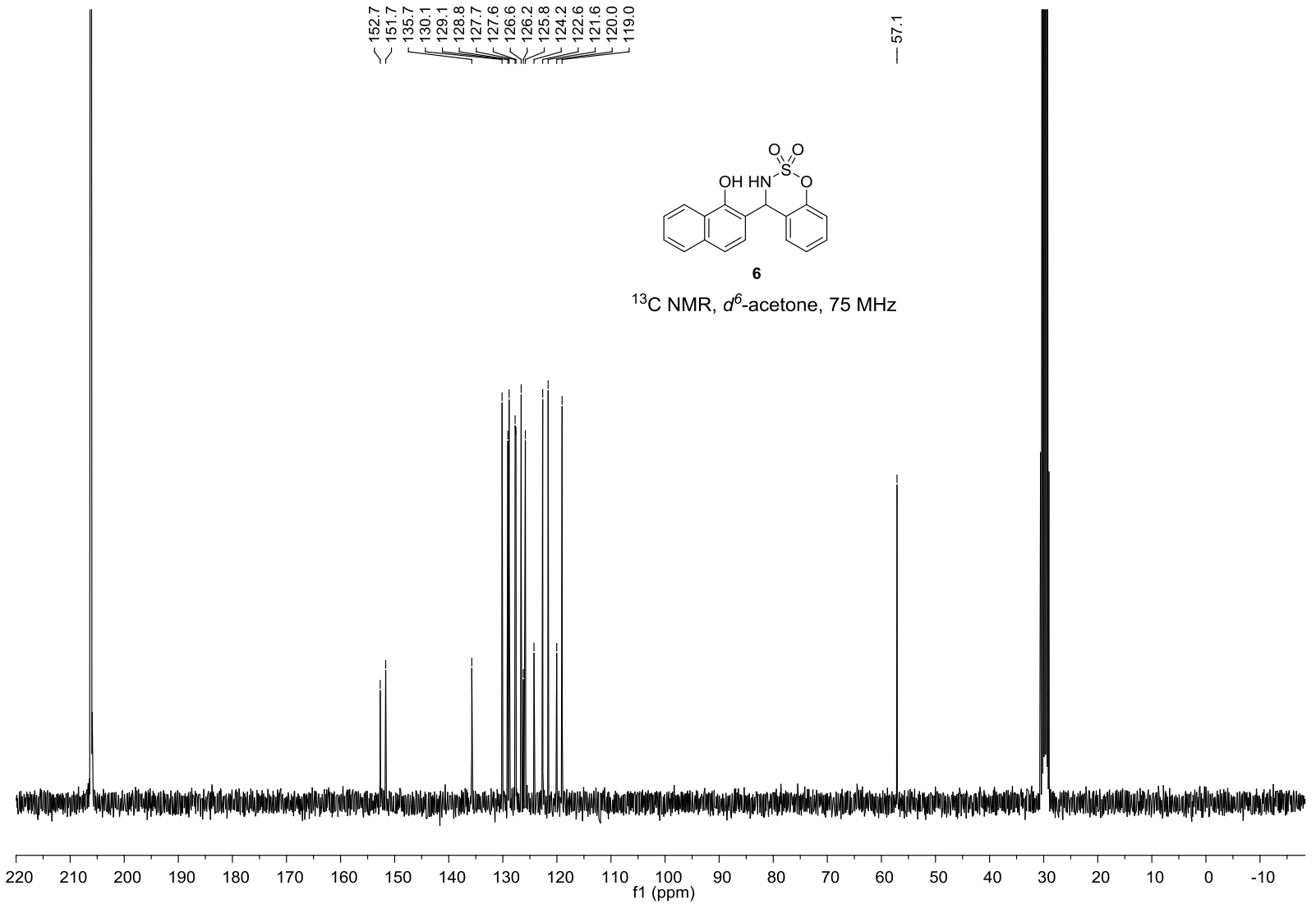

153.40
151.32
131.56
131.02
130.71
130.19
129.72
129.09
126.50
124.93
123.31
122.77
119.12
118.14
117.24
114.74
54.73
OH HN
O
O
S
O
Br
3ea
^{13}C NMR, $CDCl_3$, 75 MHz
f1 (ppm)

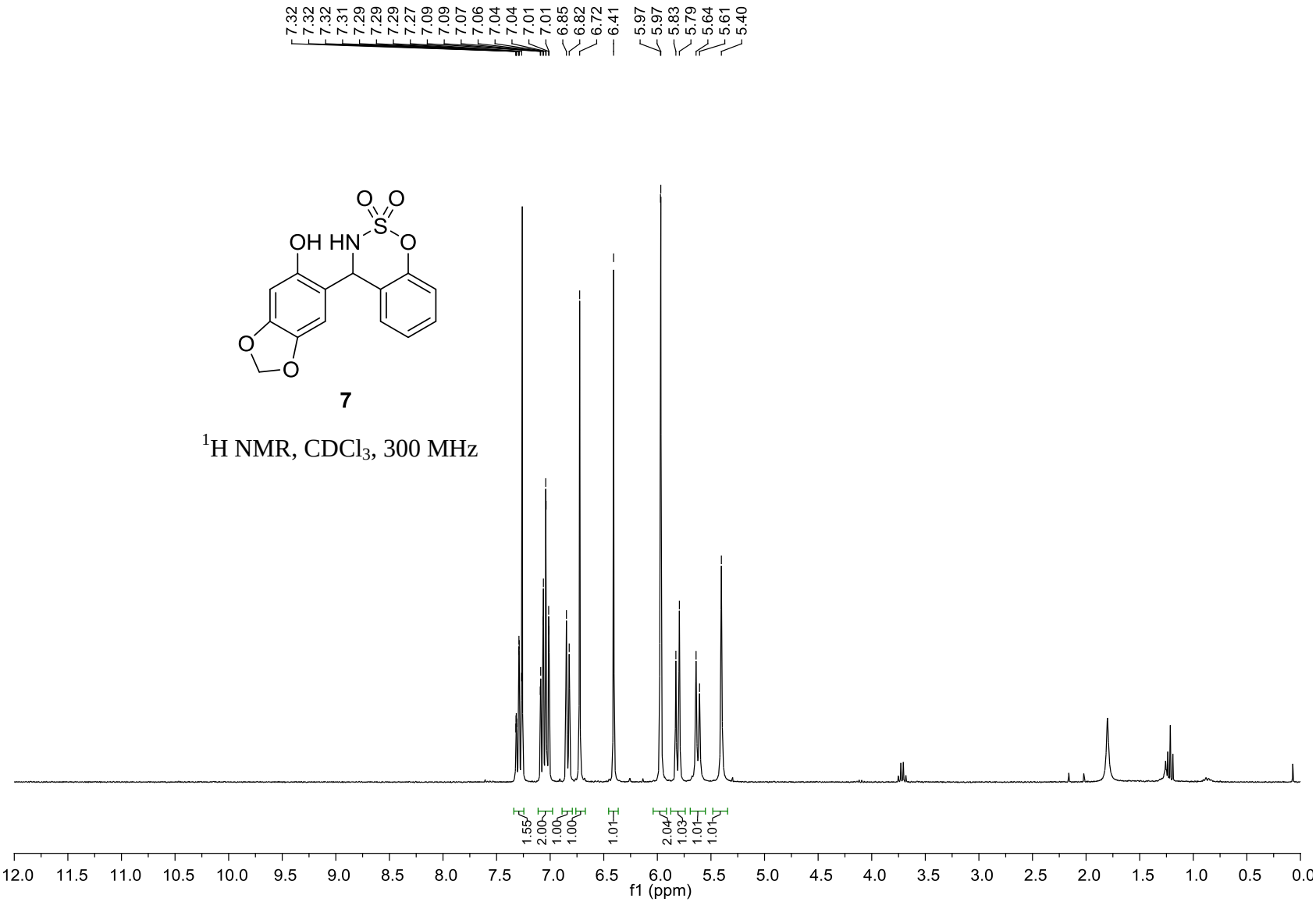


^{1}H NMR, $CDCl_3$, 300 MHz


168.34
153.18
151.31
133.57
129.07
128.79
128.14
127.54
126.55
126.25
124.90
122.88
119.59
119.50
118.11
114.76
54.91
52.36
OH HN
O
O
S
O
COOMe
3fa
^{13}C NMR, $CDCl_3$, 75 MHz
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)

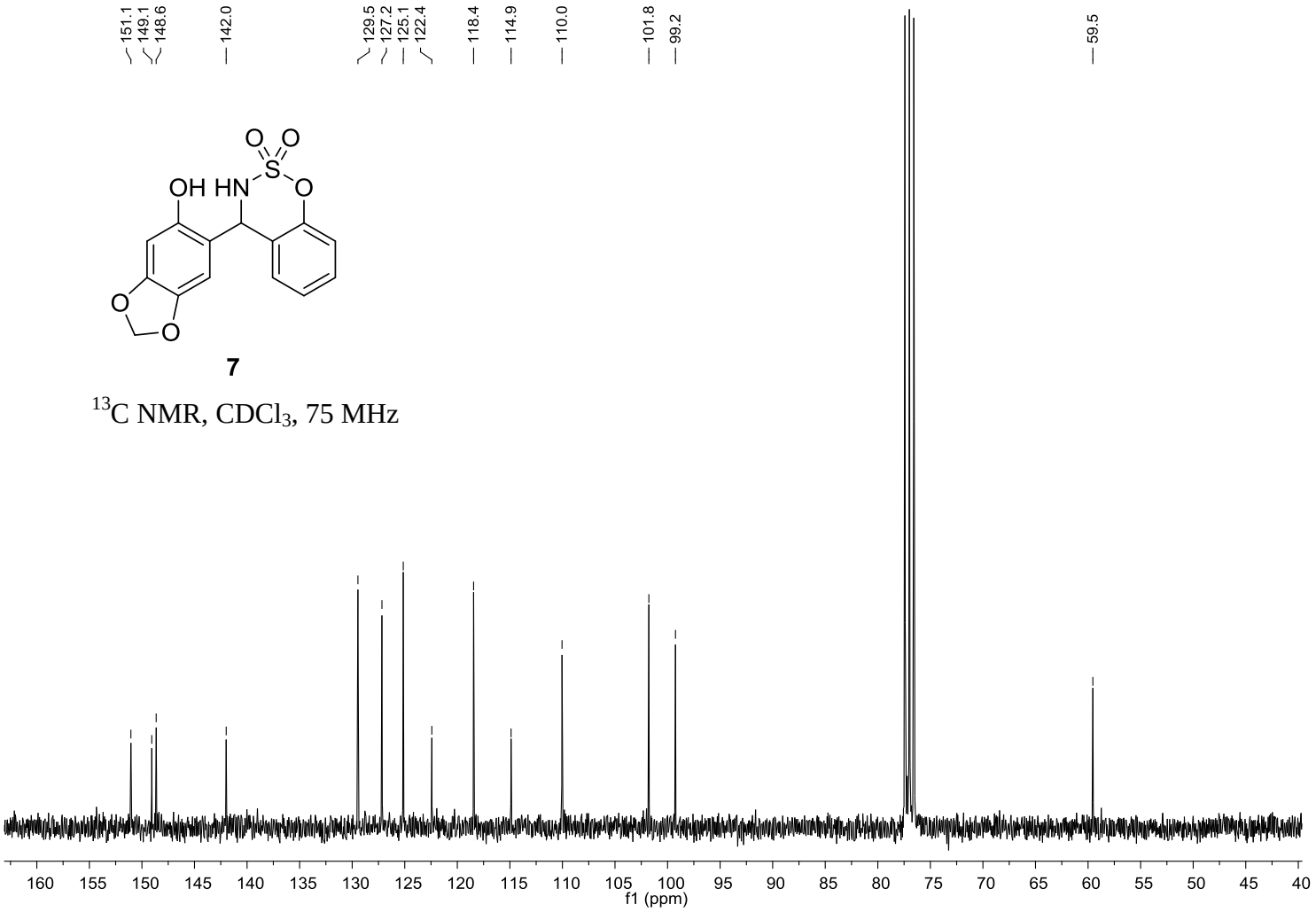

8.41 8.40 8.39 8.38 8.38 8.37 8.37 8.37 8.37 8.36 8.35 8.35 8.14 7.93 7.92 7.91 7.91 7.90 7.89 7.88 7.61 7.60 7.59 7.58 7.58 7.57 7.56 7.55 7.53 7.50 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.14 7.12 7.09 7.09 6.87 6.87 6.85 6.84 6.84 6.60
OH HN
O O
S
O
6
1H NMR, d6-acetone, 300MHz
1.14 0.73 1.11 1.98 1.03 2.01 1.99 1.00 0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.7
151.7
135.7
130.1
129.1
128.8
127.7
127.6
126.6
126.2
125.8
124.2
122.6
121.6
120.0
119.0
57.1
O
O
S
OH HN
O
6
^{13}C NMR, d^6-acetone, 75 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



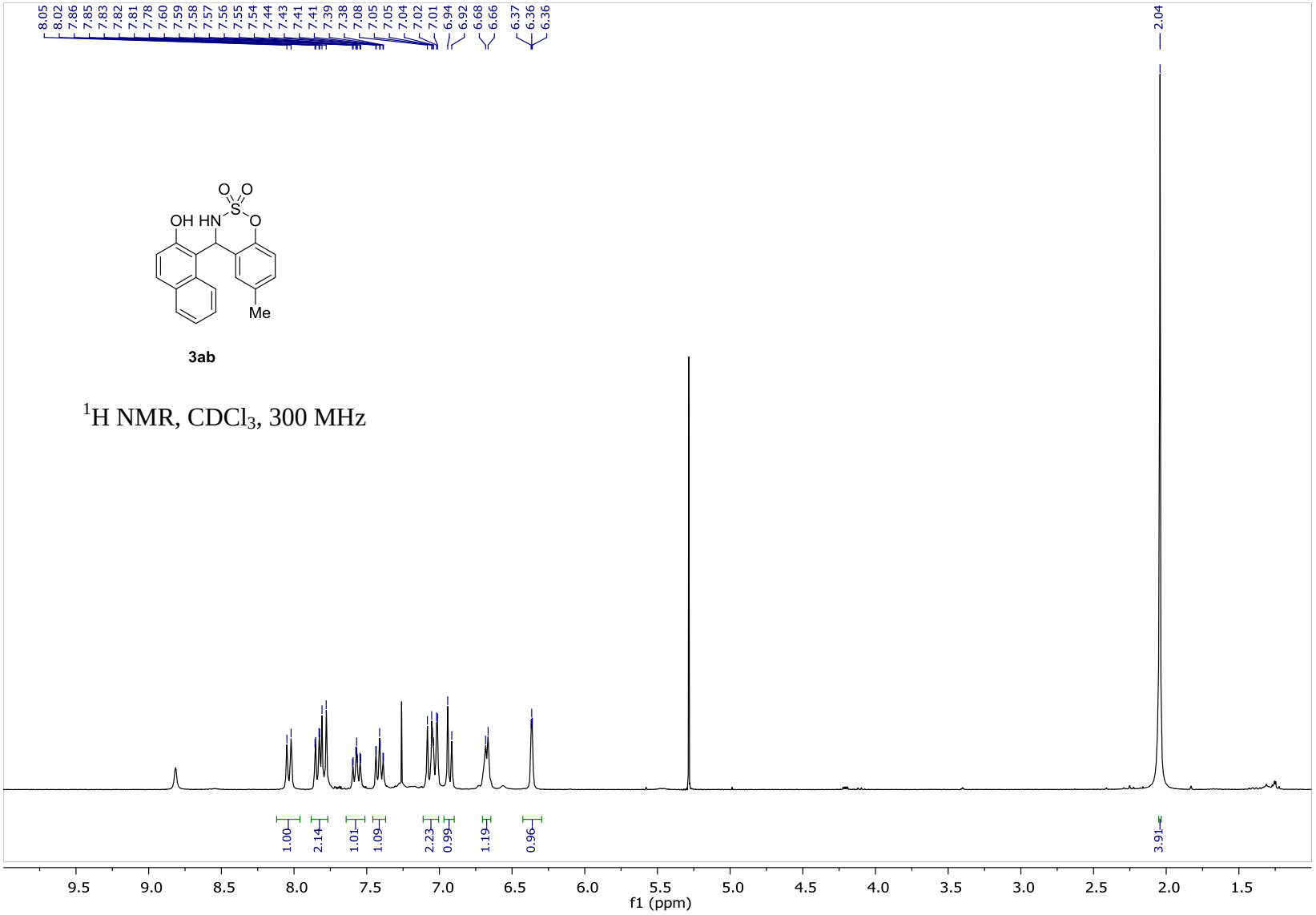
7

^{1}H NMR, $CDCl_3$, 300 MHz



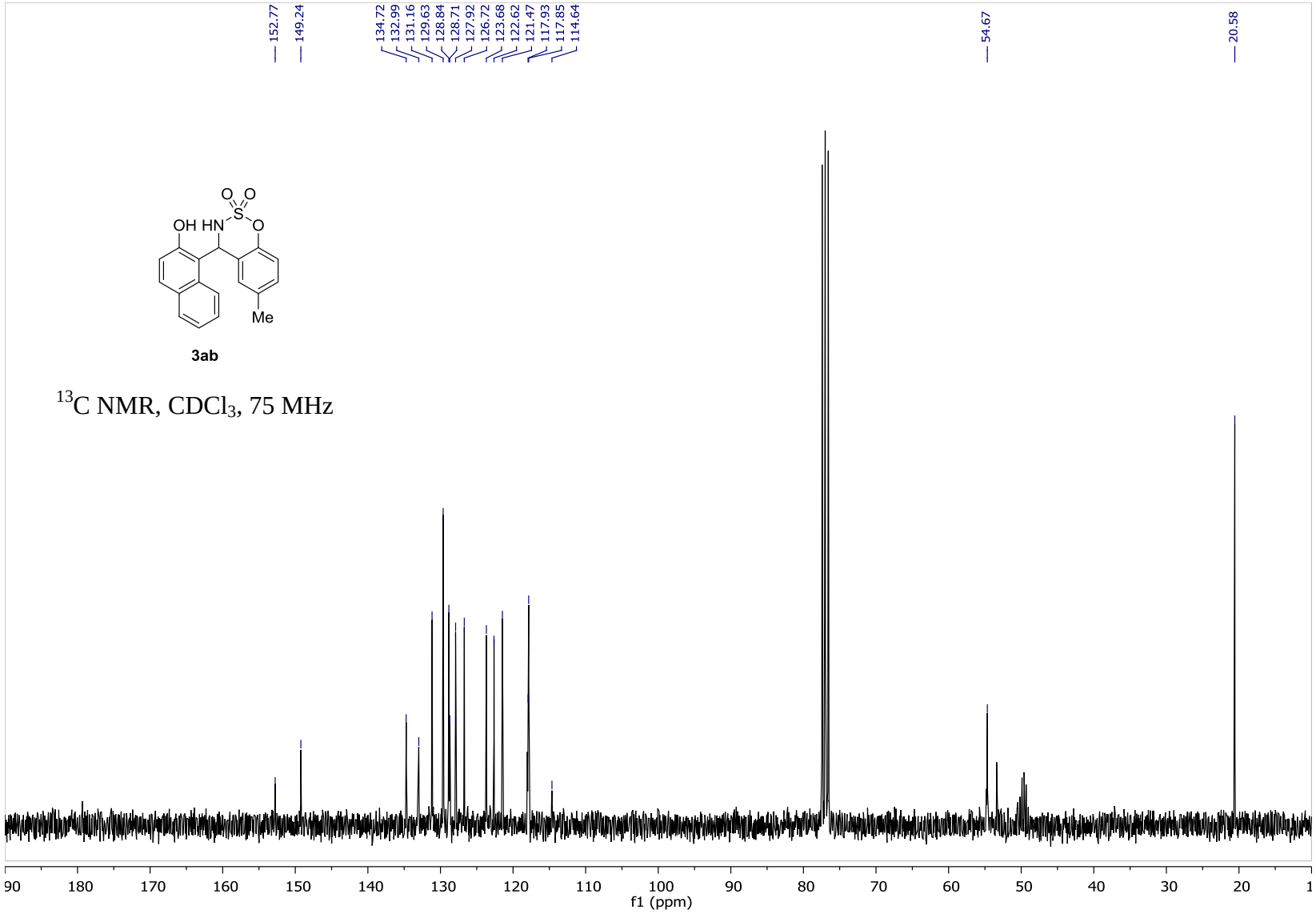
7

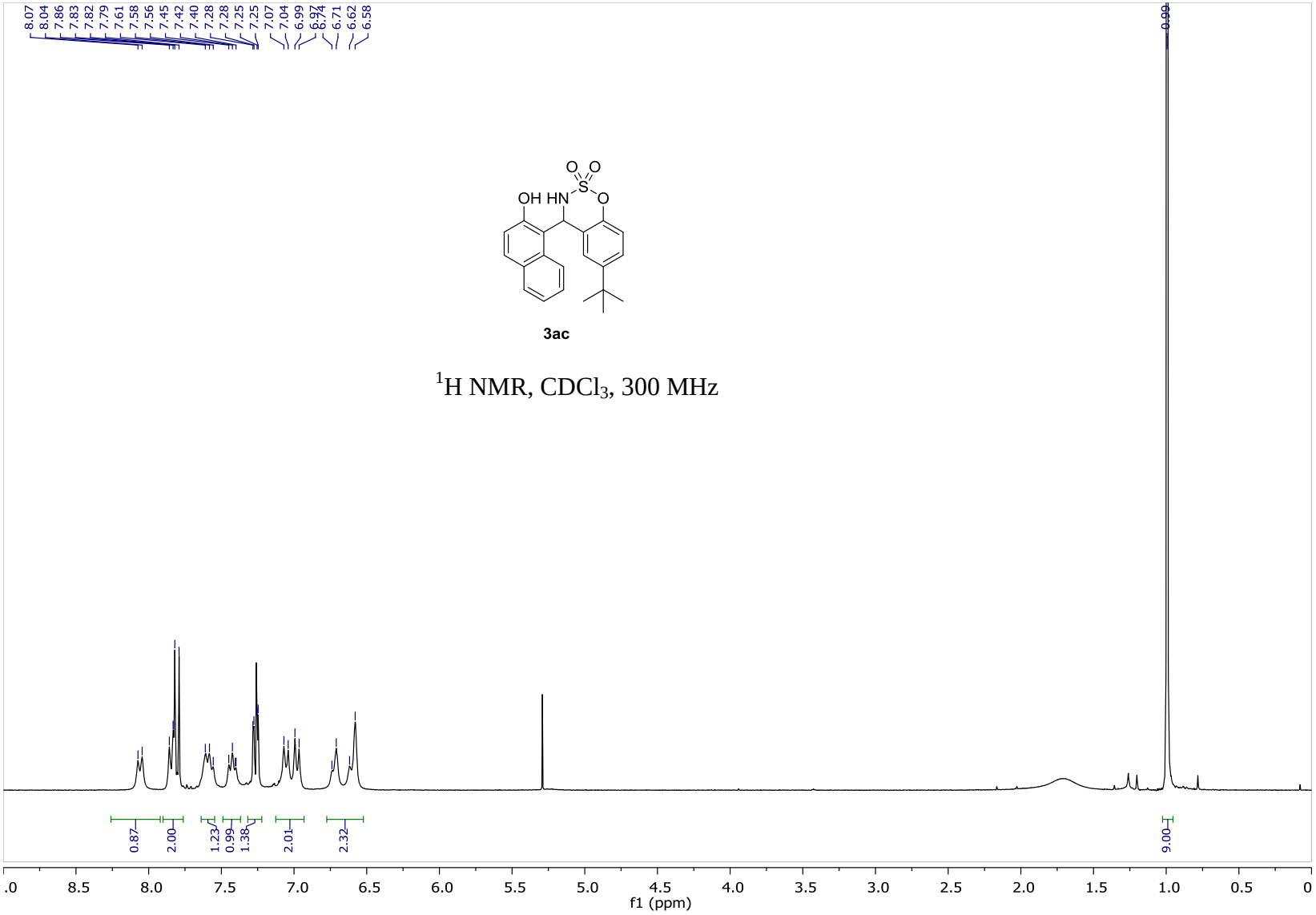
^{13}C NMR, $CDCl_3$, 75 MHz



3ab

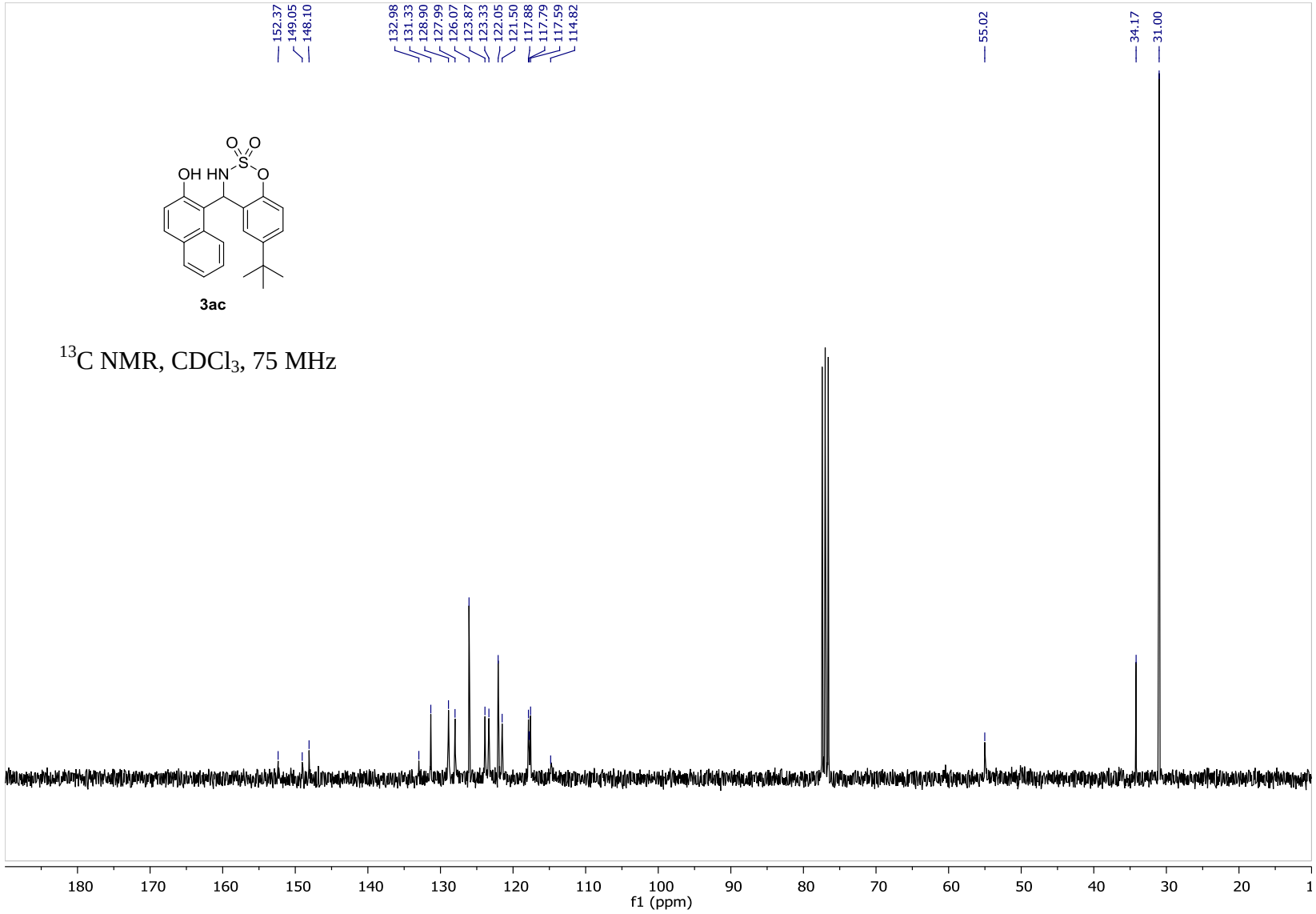
^{1}H NMR, $CDCl_3$, 300 MHz

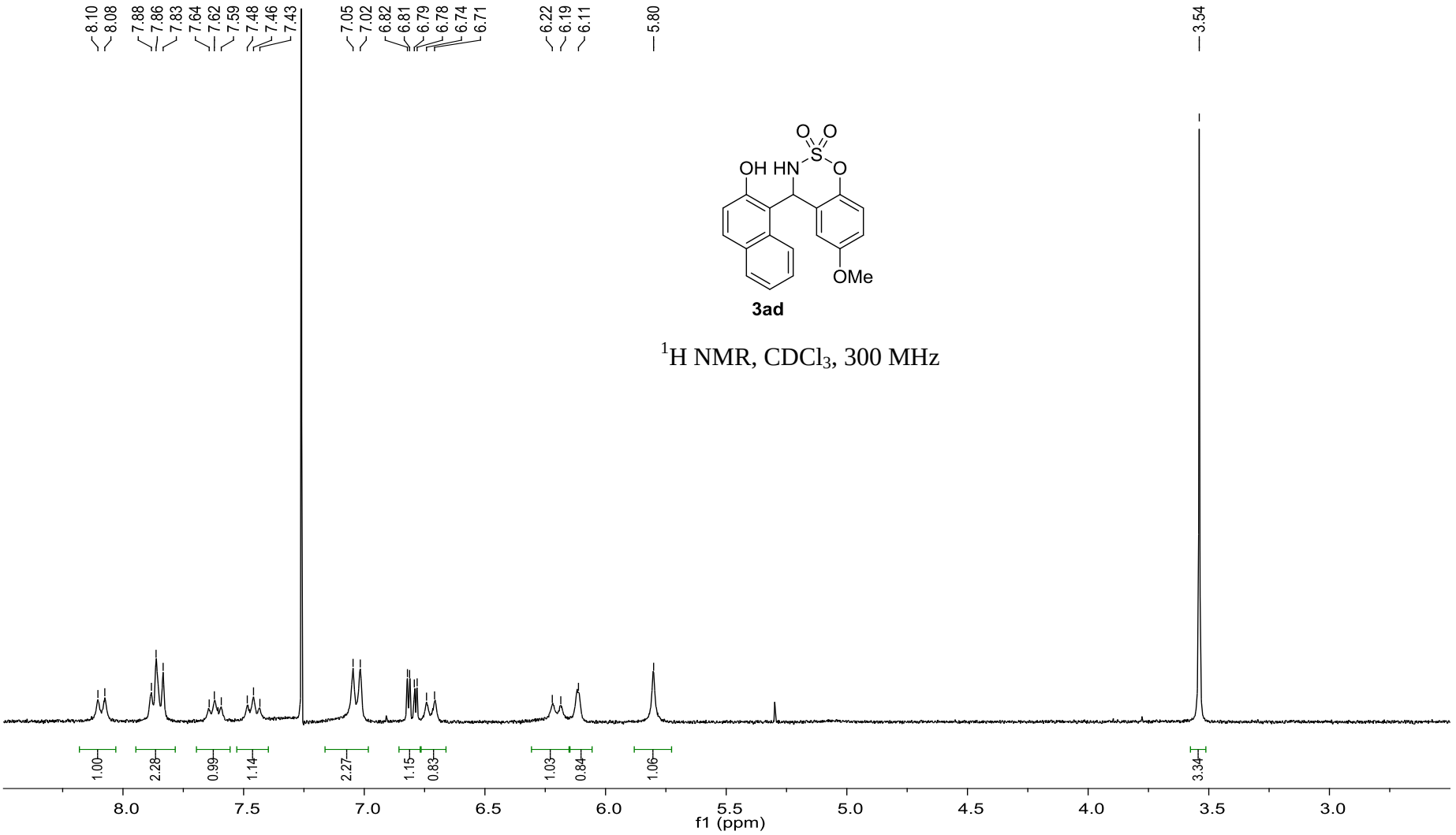

152.77
149.24
134.72
132.99
131.16
129.63
128.84
128.71
127.92
126.72
123.68
122.62
121.47
117.93
117.85
114.64
54.67
20.58
O
O
S
OH HN
O
Me
3ab
^{13}C NMR, $CDCl_3$, 75 MHz
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)



3ac

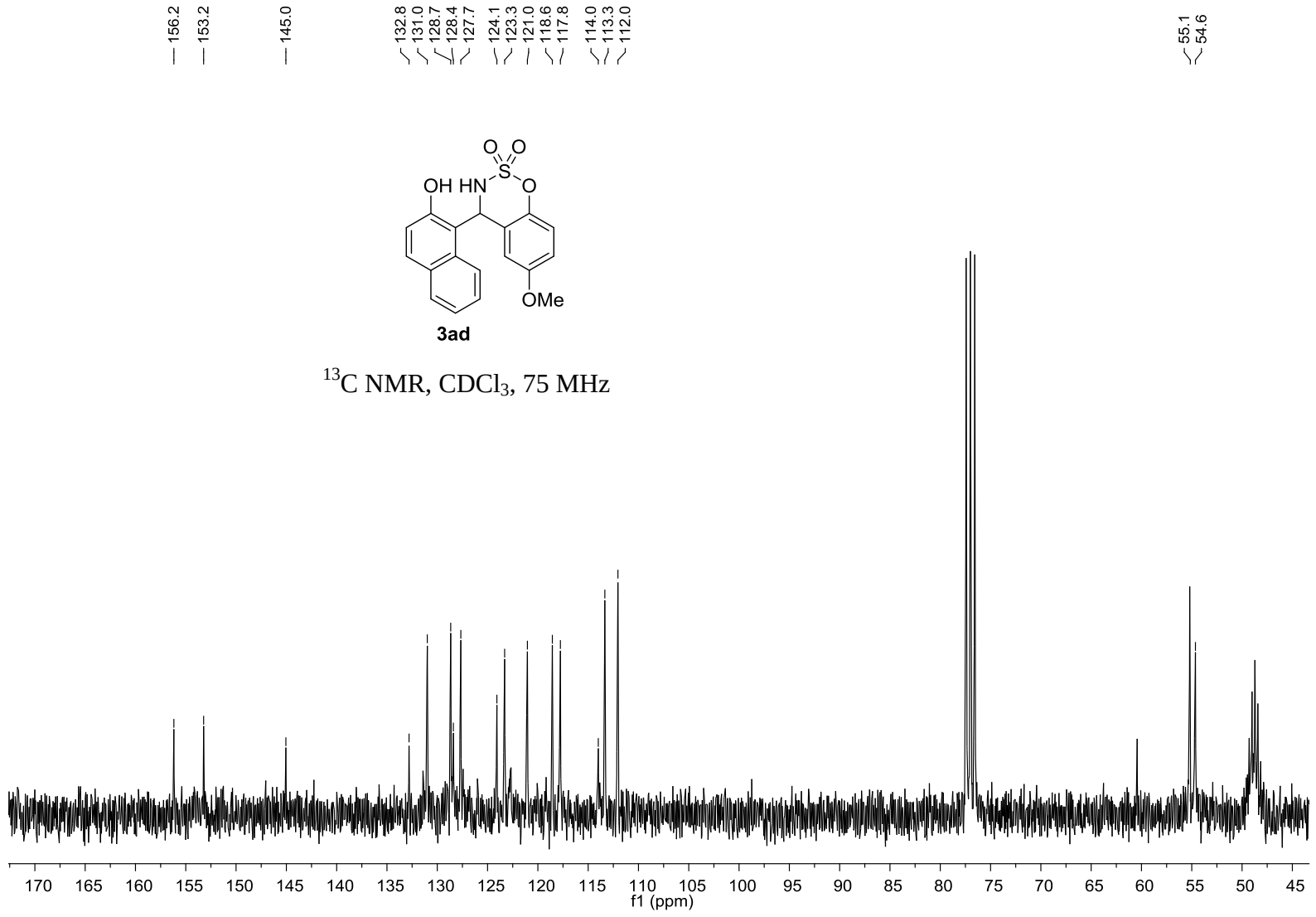
^{1}H NMR, $CDCl_3$, 300 MHz

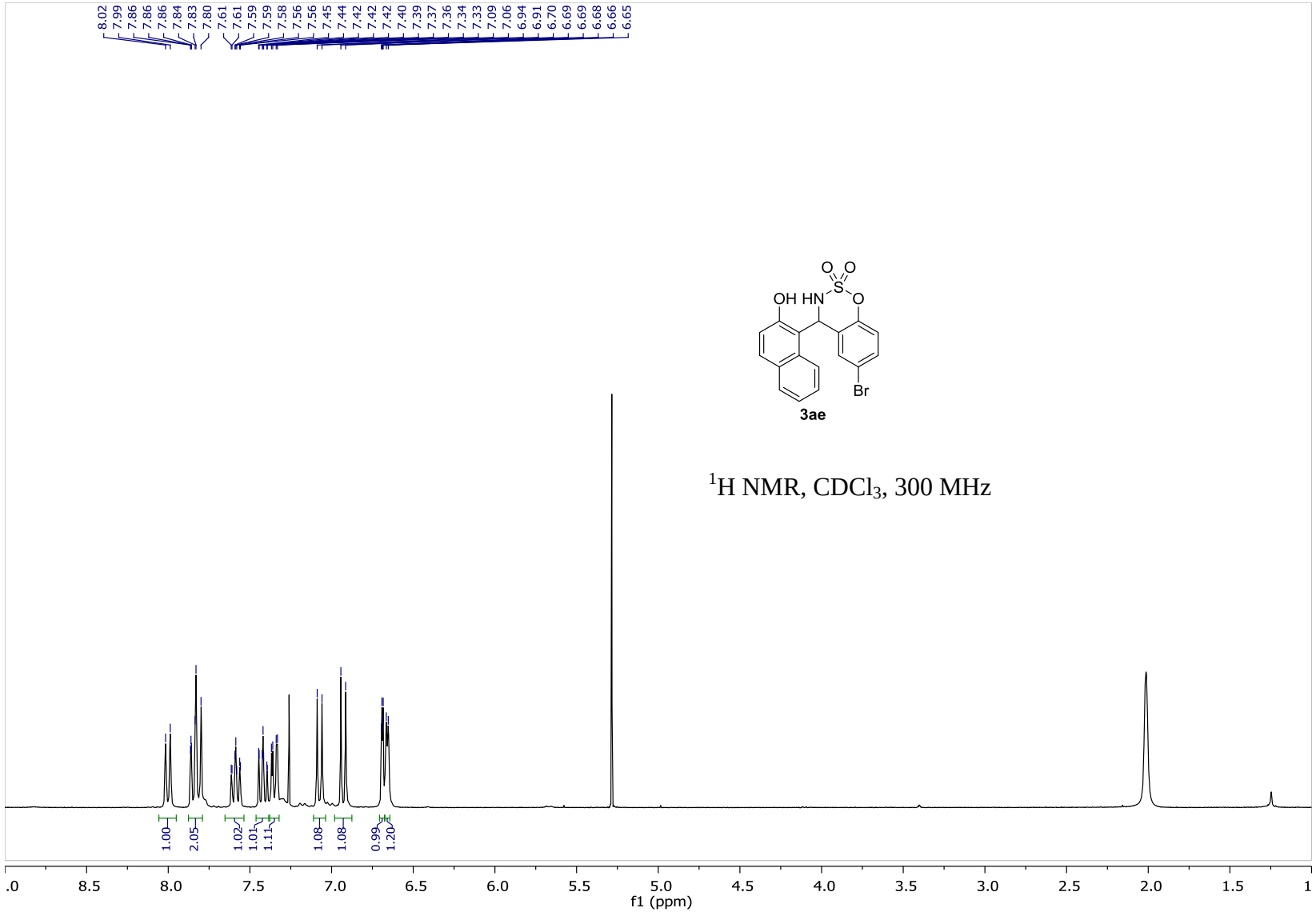

152.37
149.05
148.10
132.98
131.33
128.90
127.99
126.07
123.87
123.33
122.05
121.50
117.88
117.79
117.59
114.82
55.02
34.17
31.00
OH HN
O
O
S
O
3ac
13C NMR, CDCl3, 75 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)



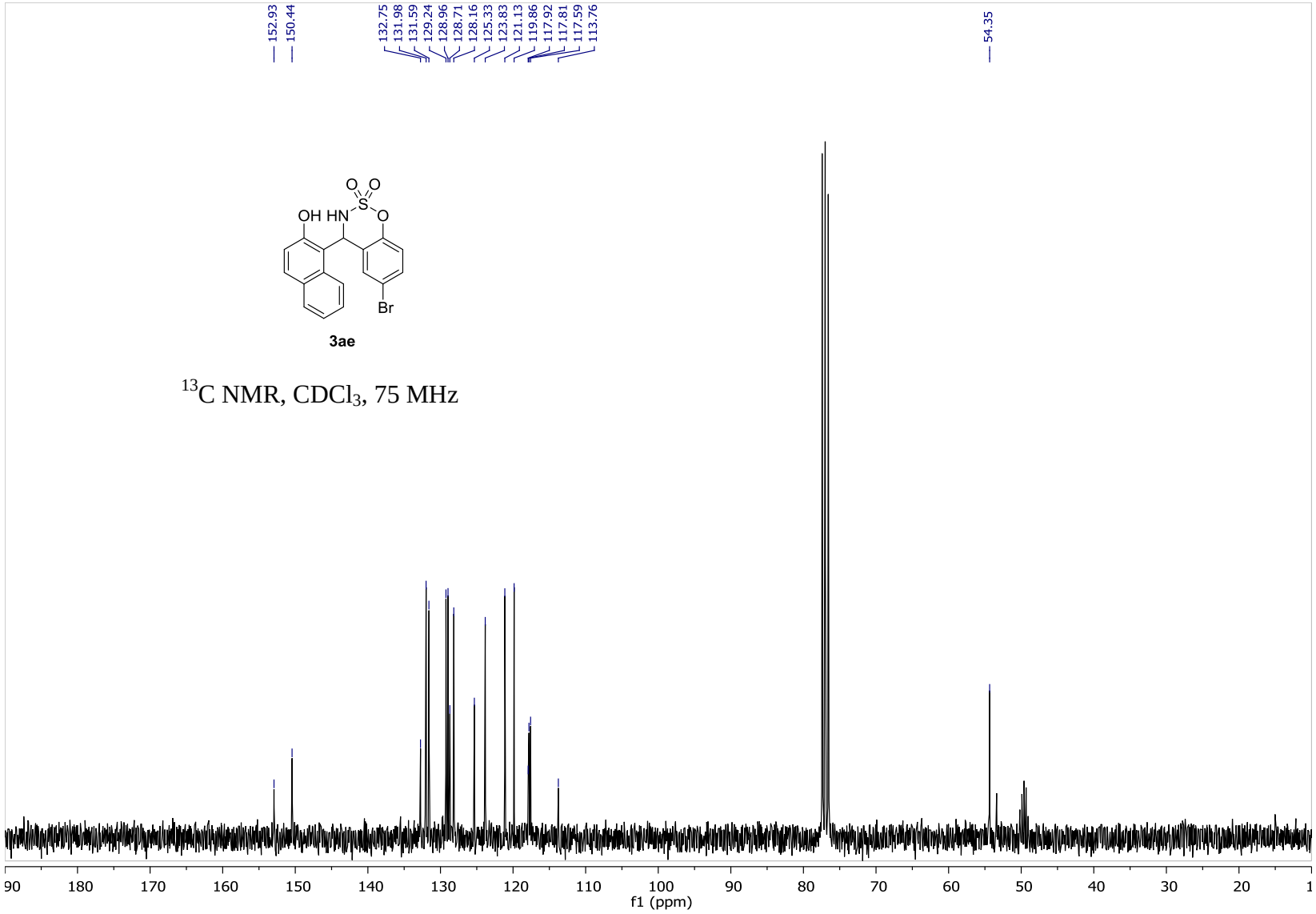
3ad

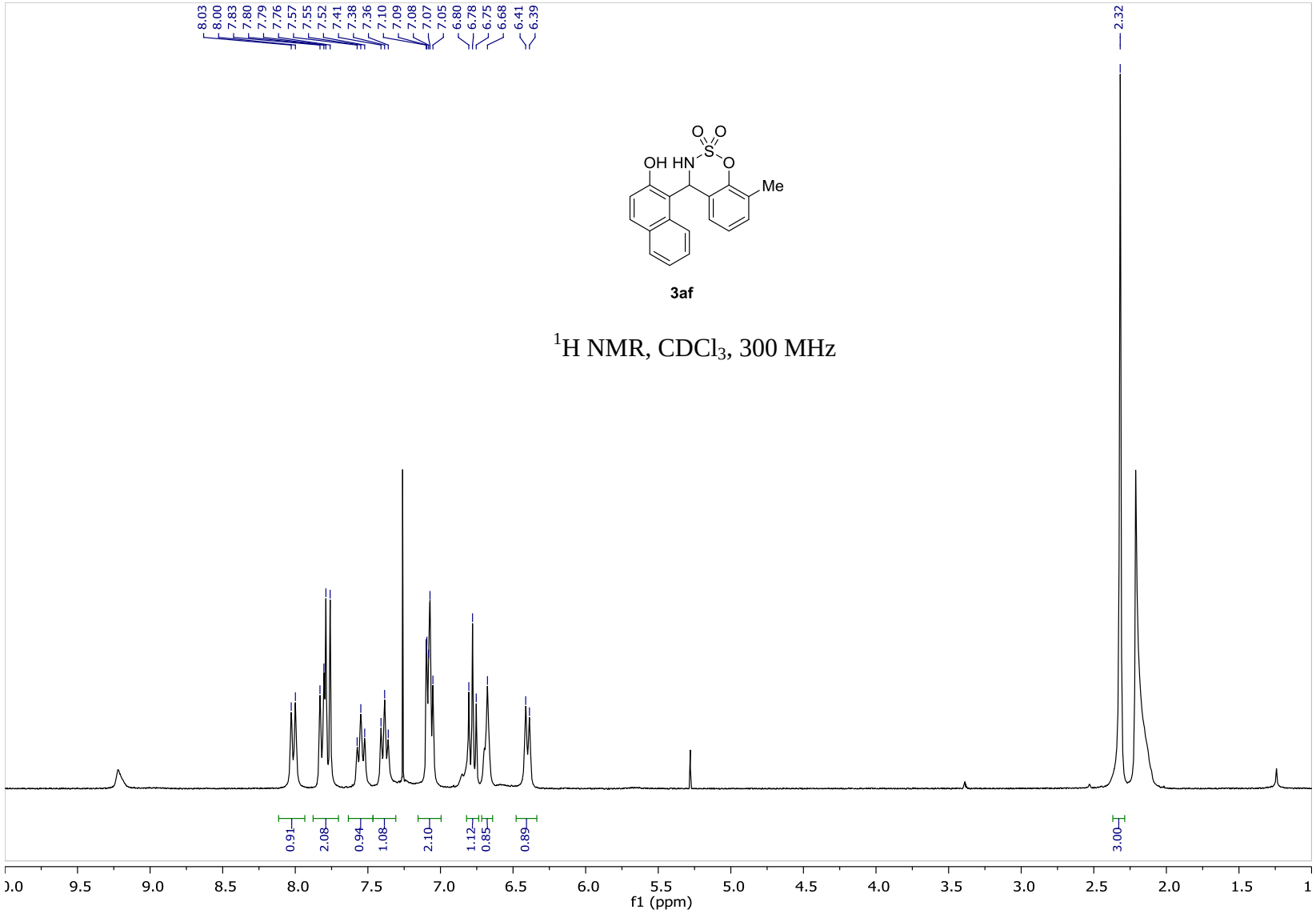
^{1}H NMR, $CDCl_3$, 300 MHz


156.2
153.2
145.0
132.8
131.0
128.7
128.4
127.7
124.1
123.3
121.0
118.6
117.8
114.0
113.3
112.0
55.1
54.6
OH HN
O
O
S
O
OMe
3ad
^{13}C NMR, $CDCl_3$, 75 MHz
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)



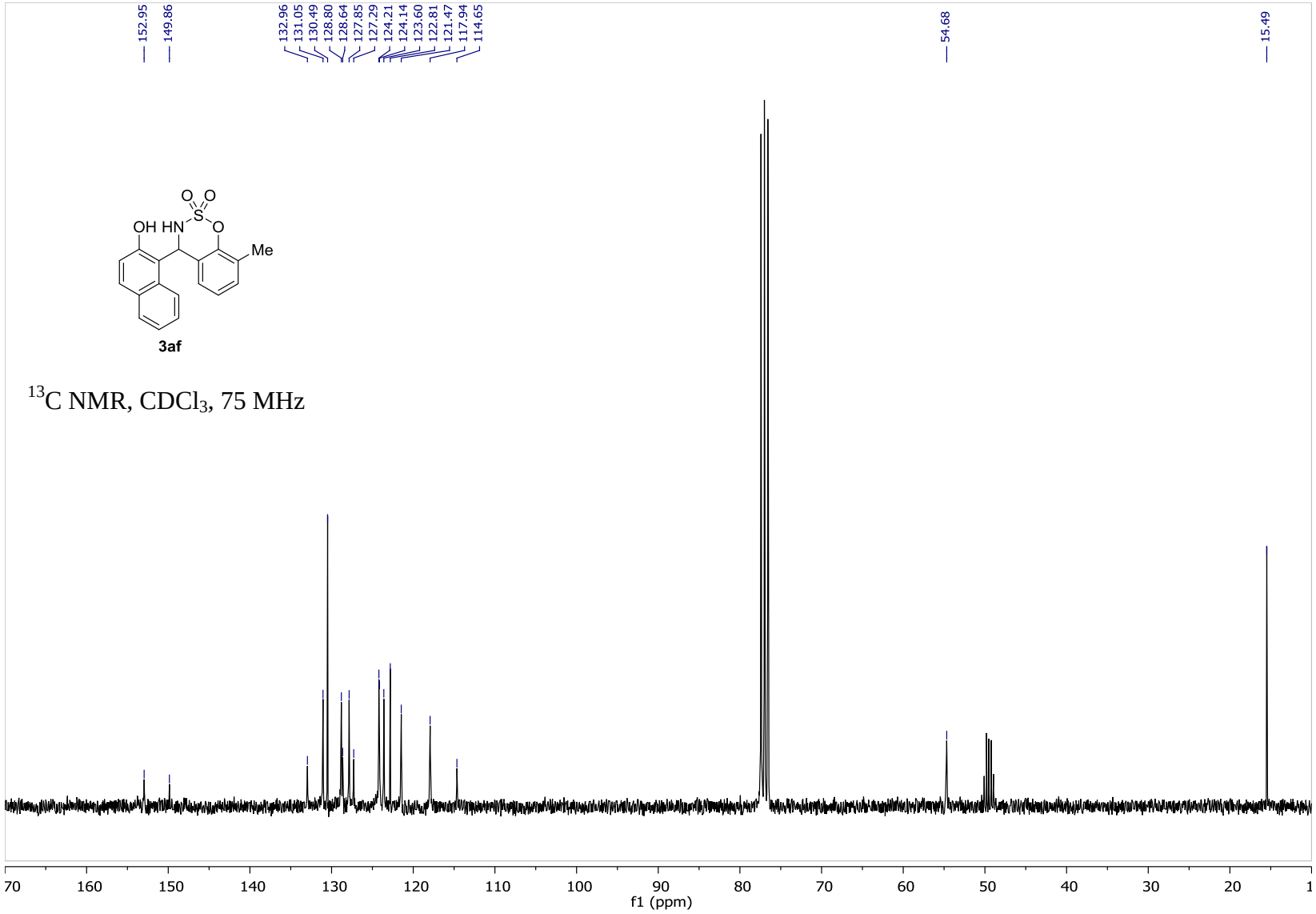
^{1}H NMR, $CDCl_3$, 300 MHz

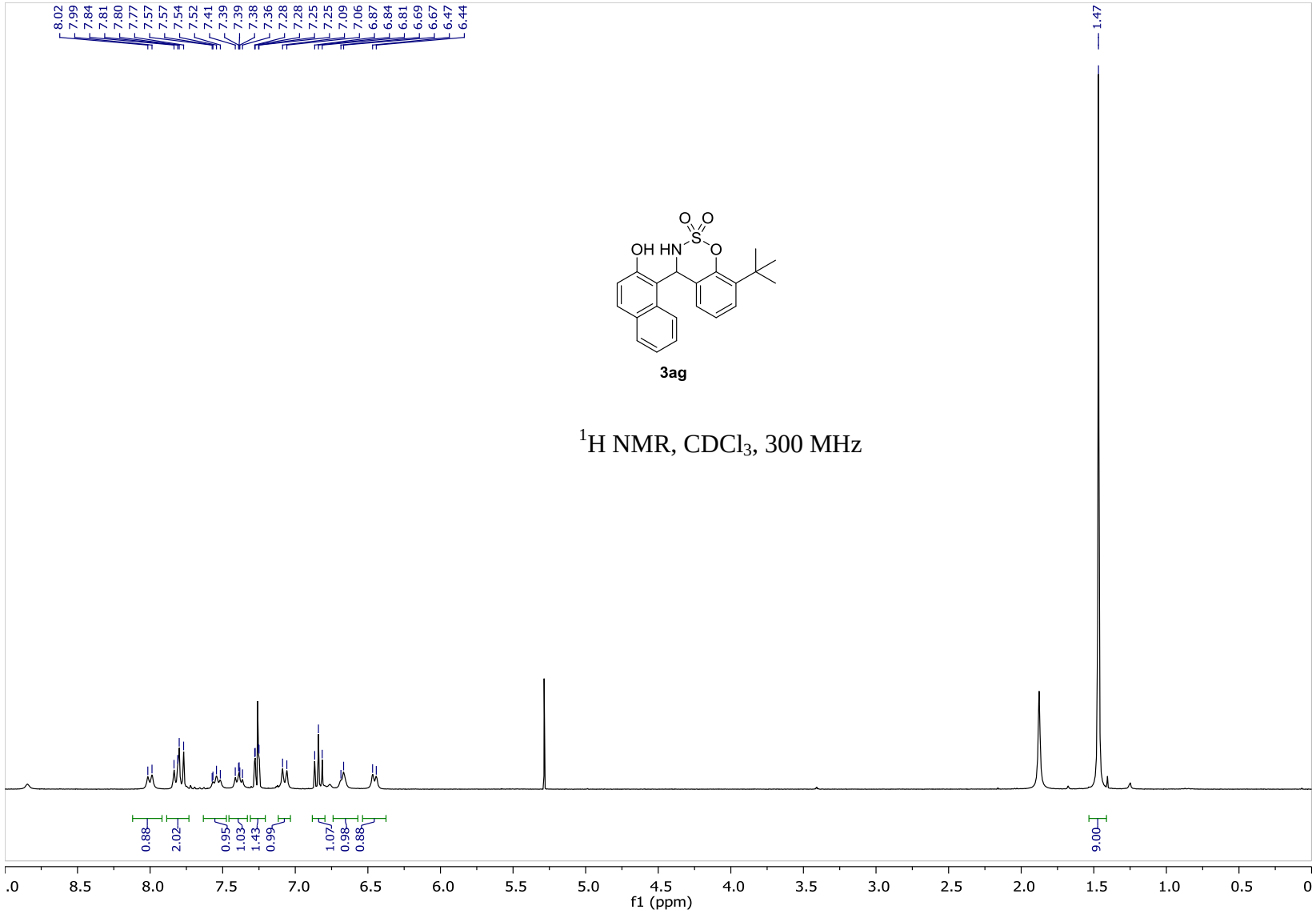

152.93
150.44
132.75
131.98
131.59
129.24
128.96
128.71
128.16
125.33
123.83
121.13
119.86
117.92
117.81
117.59
113.76
54.35
O
O
S
OH HN
O
Br
3ae
^{13}C NMR, $CDCl_3$, 75 MHz
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)



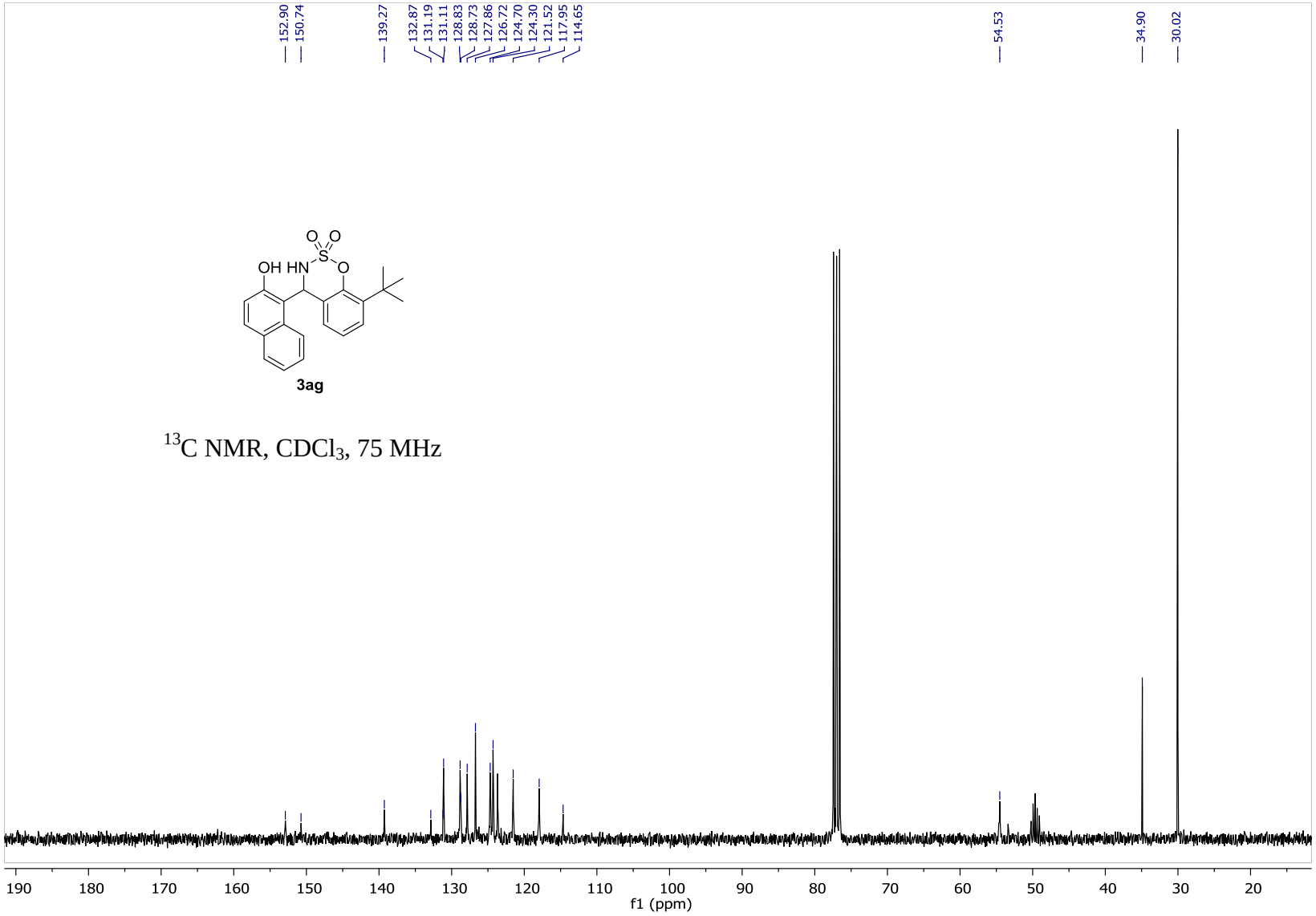
3af

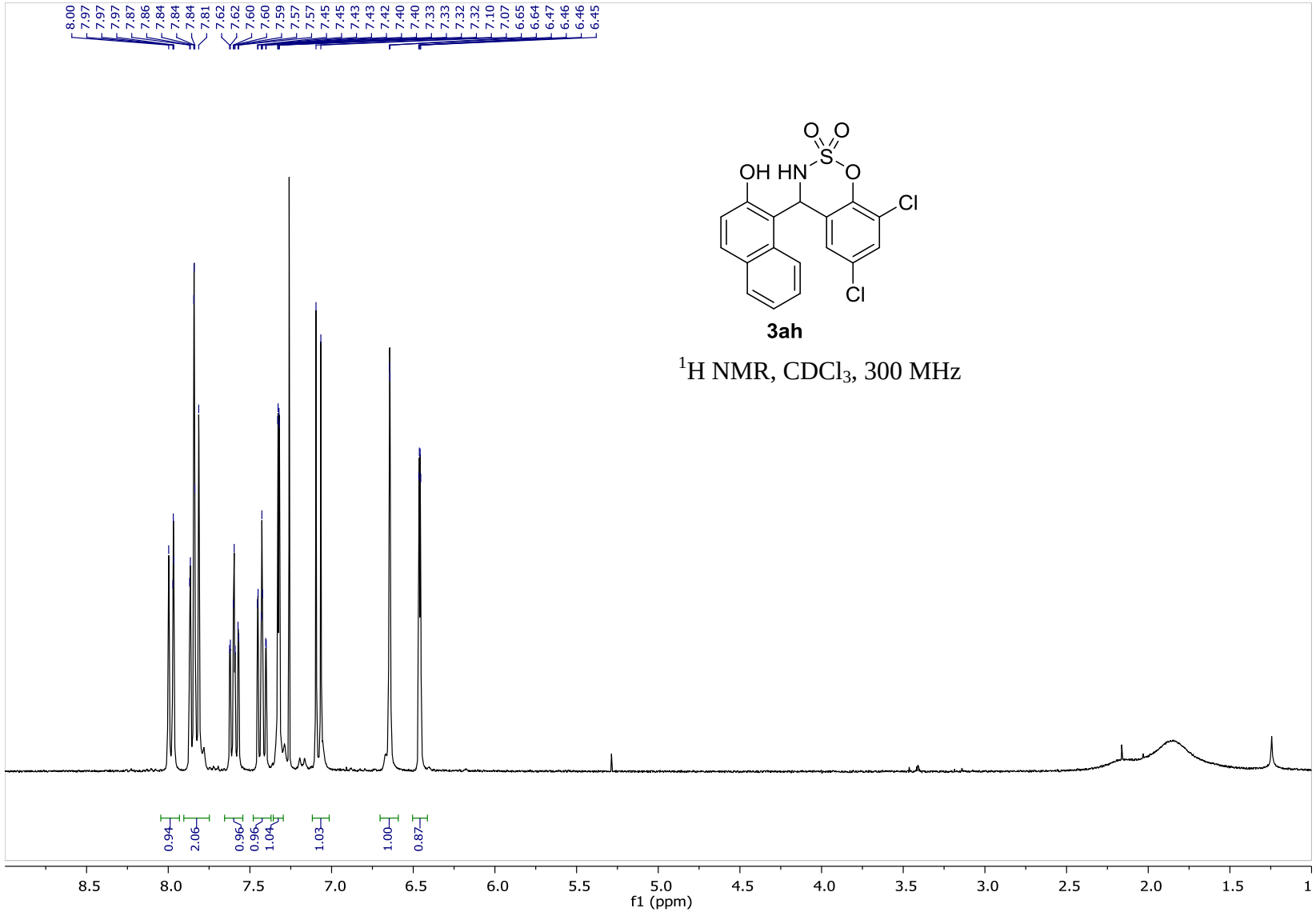
^{1}H NMR, $CDCl_3$, 300 MHz


152.95
149.86
132.96
131.05
130.49
128.80
128.64
127.85
127.29
124.21
124.14
123.60
122.81
121.47
117.94
114.65
54.68
15.49
OH HN
O
O
S
O
Me
3af
^{13}C NMR, $CDCl_3$, 75 MHz
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)



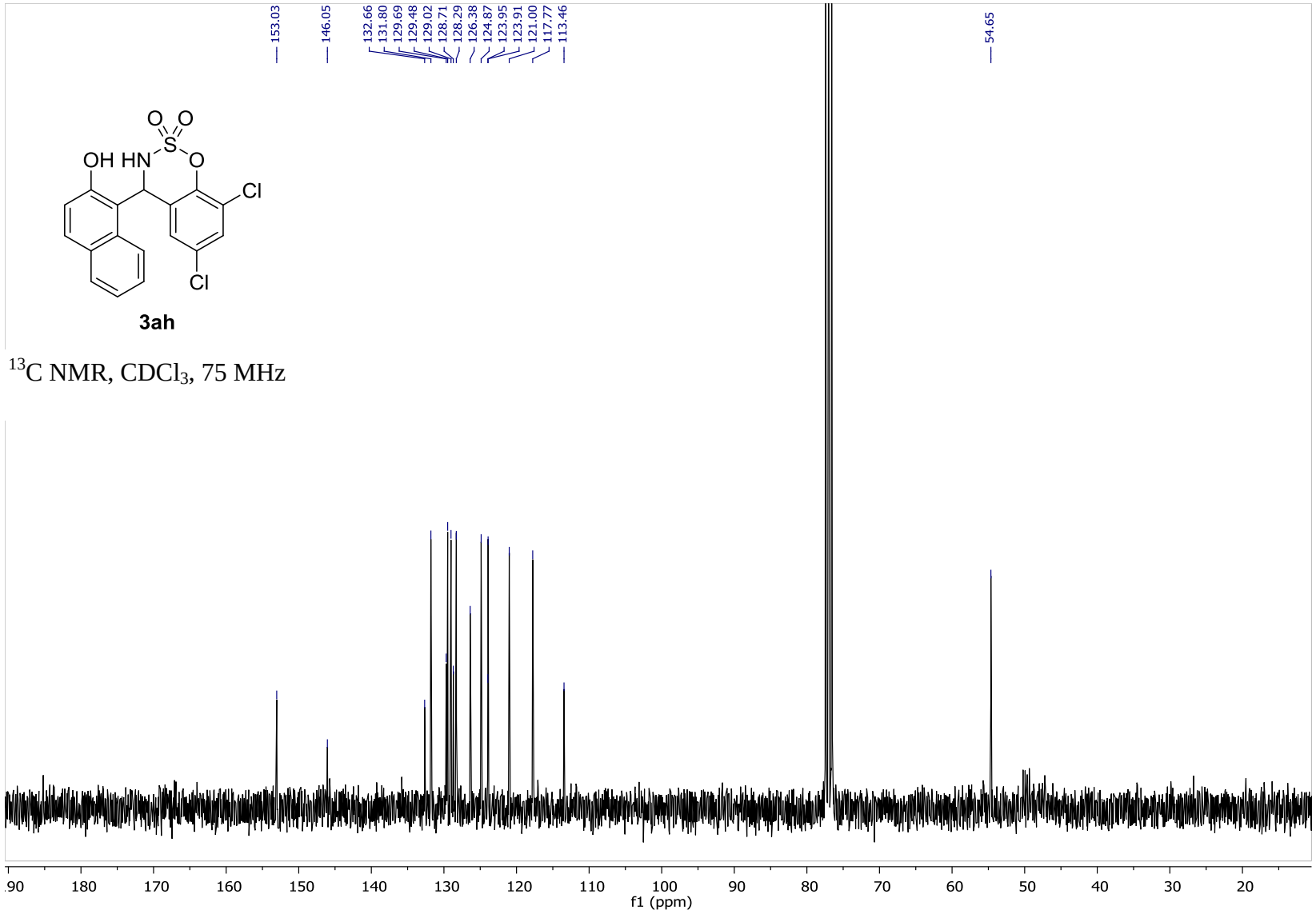
^{1}H NMR, $CDCl_3$, 300 MHz


152.90
150.74
139.27
132.87
131.19
131.11
128.83
128.73
127.86
126.72
124.70
124.30
121.52
117.95
114.65
54.53
34.90
30.02
OH HN
O
S
O
O
3ag
^{13}C NMR, $CDCl_3$, 75 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

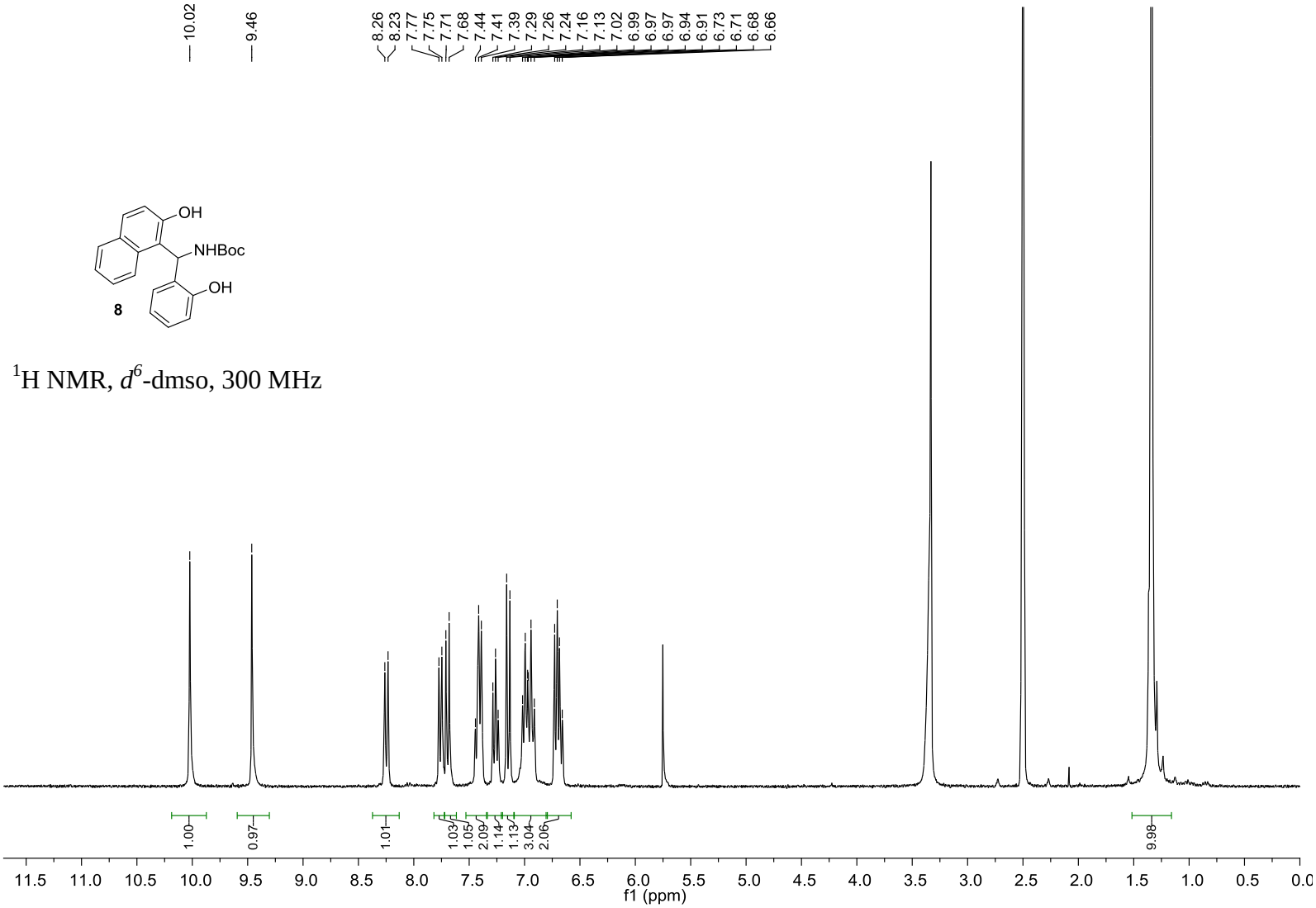


3ah

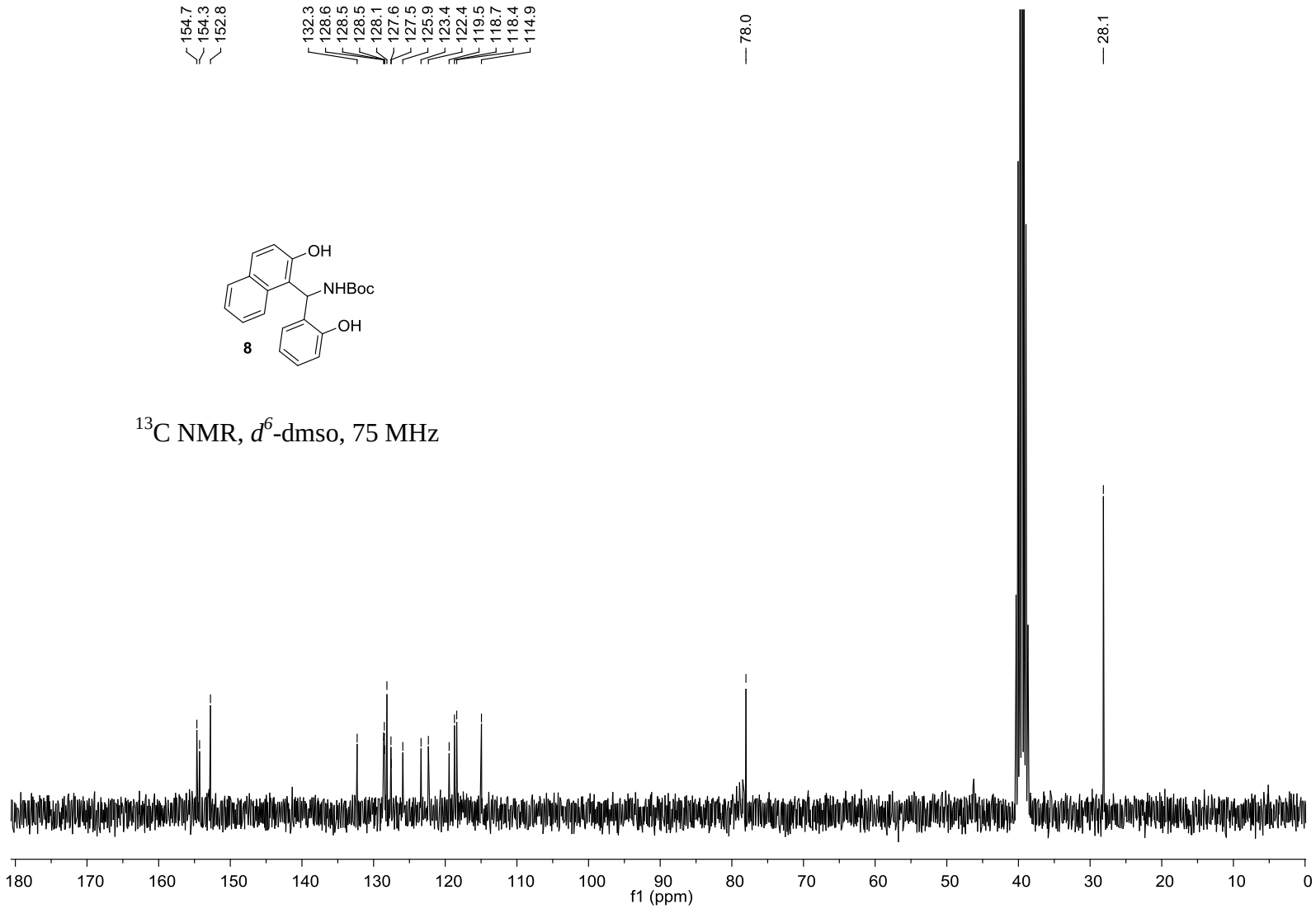
^{1}H NMR, $CDCl_3$, 300 MHz



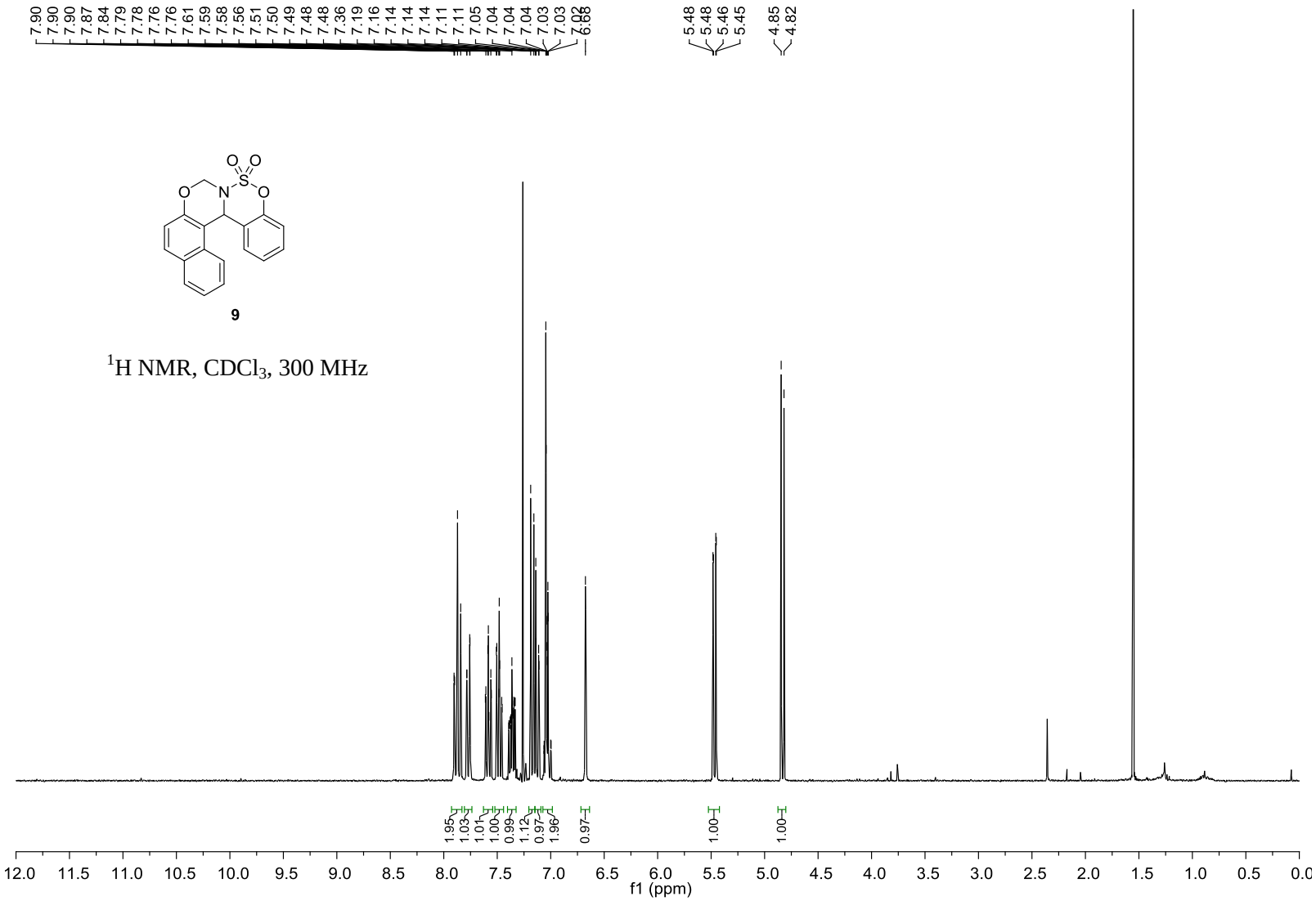
^{13}C NMR, $CDCl_3$, 75 MHz

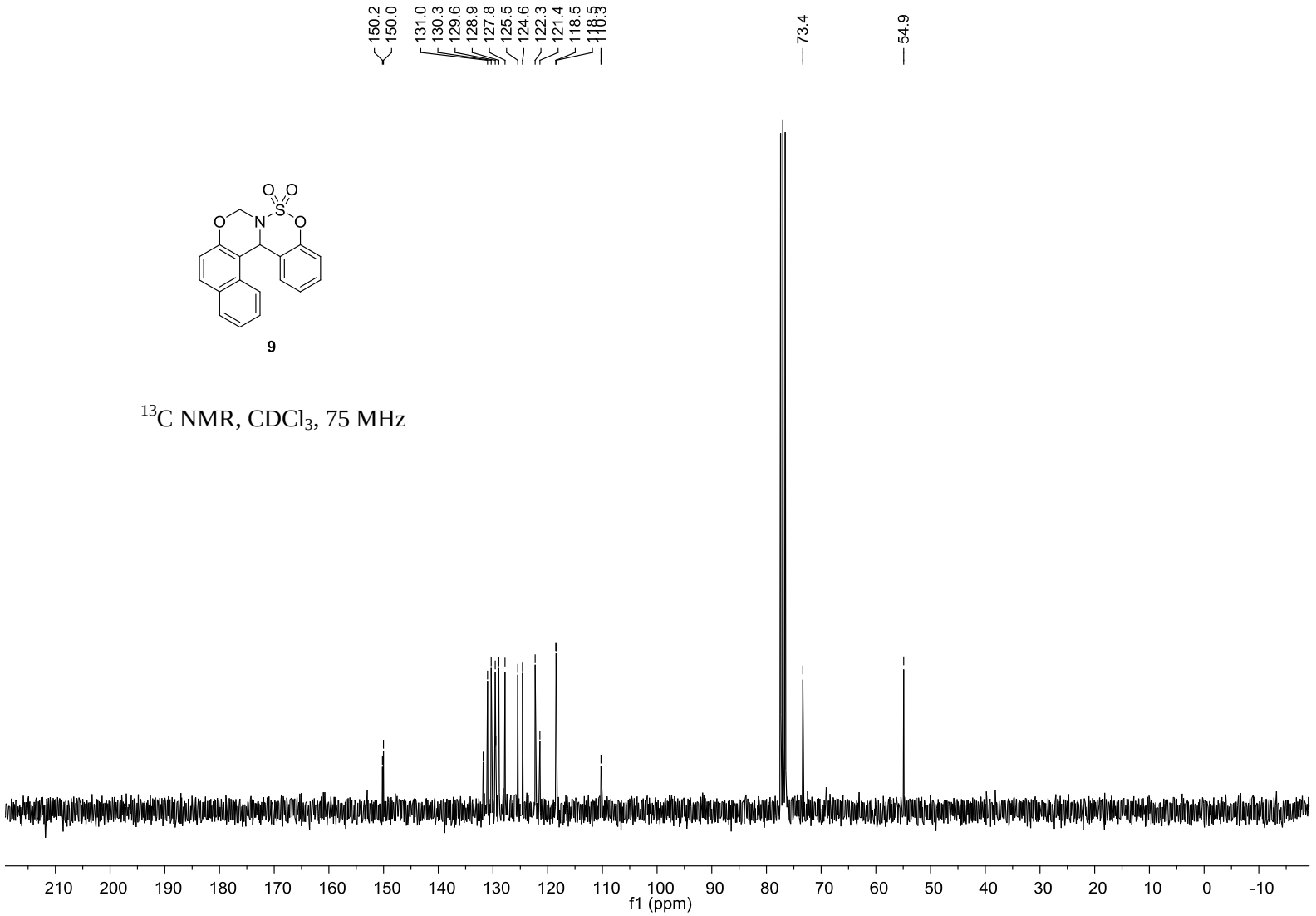


^{1}H NMR, d^{6}-dmso, 300 MHz

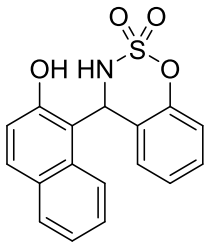


^{13}C NMR, d^6-dmso, 75 MHz

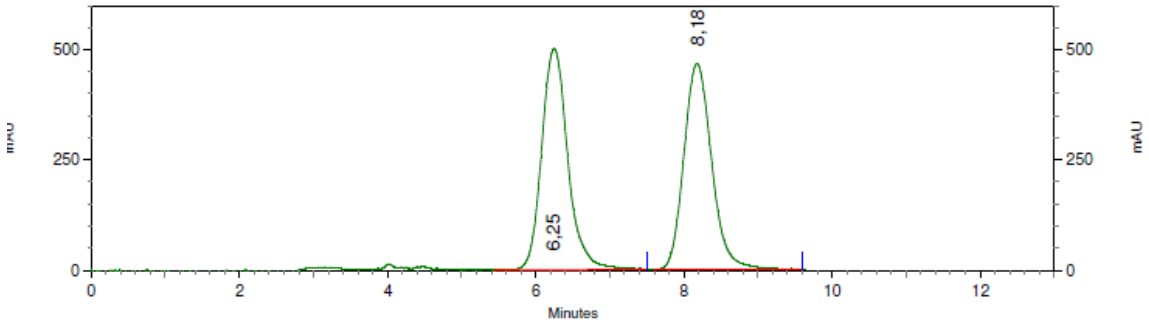

7.90
7.90
7.90
7.87
7.84
7.79
7.78
7.76
7.76
7.61
7.59
7.58
7.56
7.51
7.50
7.49
7.48
7.48
7.36
7.19
7.16
7.14
7.14
7.14
7.11
7.11
7.05
7.04
7.04
7.04
7.03
7.03
7.02
6.68
5.48
5.48
5.46
5.45
4.85
4.82
O
O
O
N
S
O
9
1H NMR, CDCl3, 300 MHz
1.95
1.03
1.01
1.00
0.99
1.12
0.97
1.96
0.97
1.00
1.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



^{13}C NMR, $CDCl_3$, 75 MHz

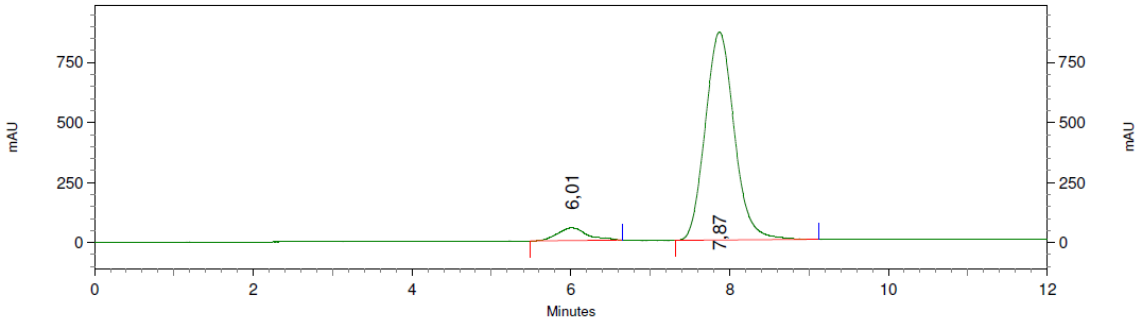


3aa



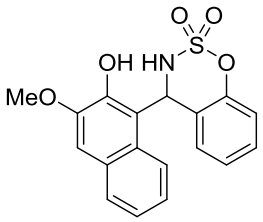
1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
6,25	49227971	50,348
8,18	48548360	49,652

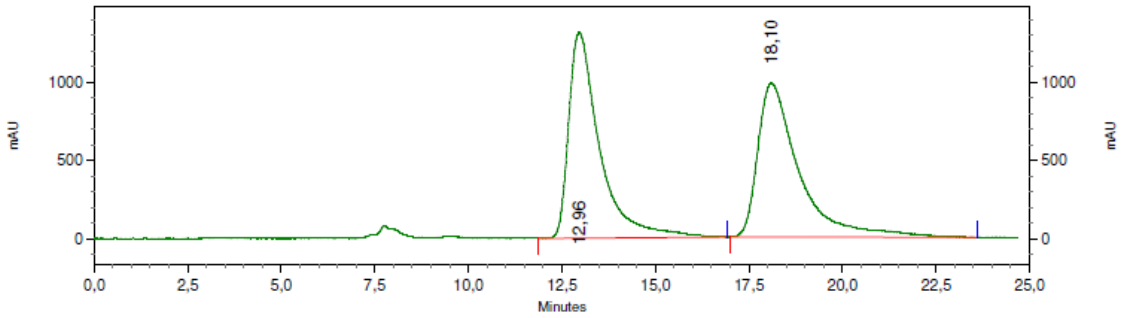


1: 333 nm, 4 nm Results

Retention Time	Area	Area Percent
6,01	5575550	5,952
7,87	88092532	94,048

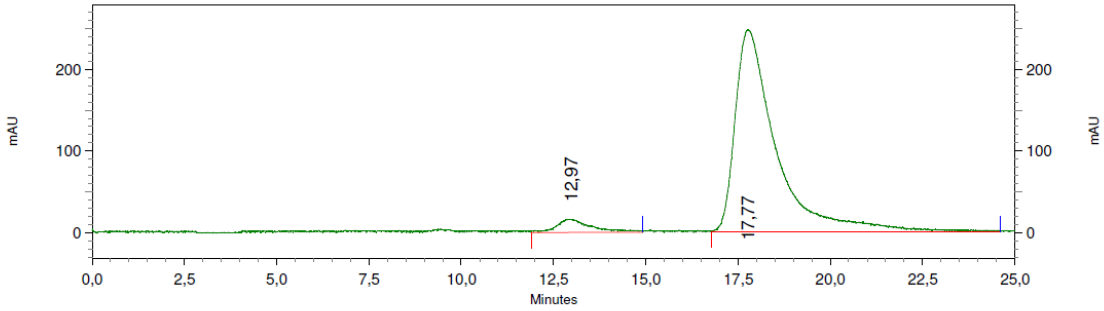


3ba



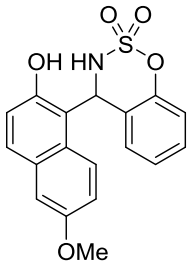
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
12,96	301653835	49,960
18,10	302141065	50,040

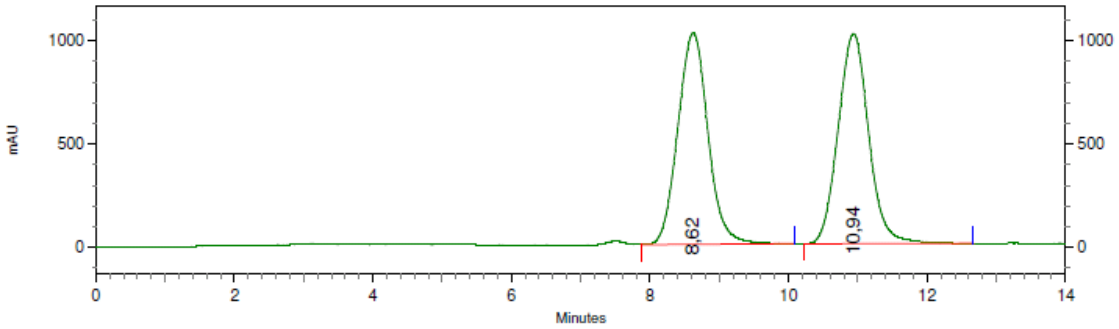


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
12,97	4292430	5,296
17,77	76764459	94,704

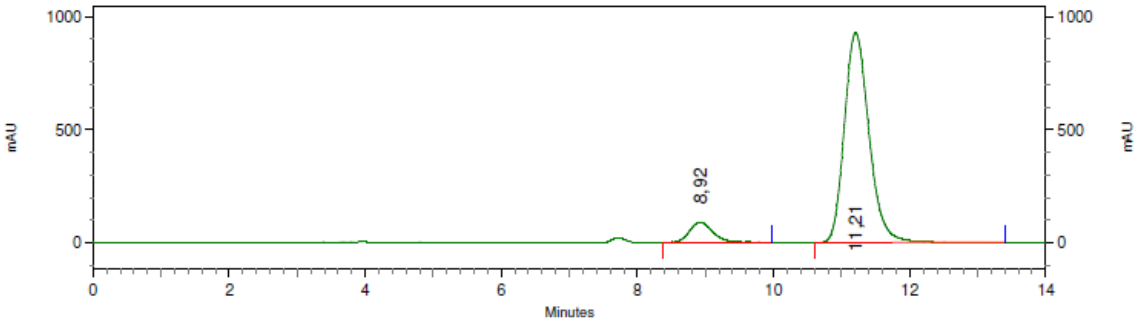


3ca



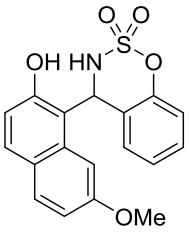
1: 232 nm, 4 nm Results

Retention Time	Area	Area Percent
8,62	123798489	49,809
10,94	124747036	50,191



1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
8,92	8833030	8,622
11,21	93611908	91,378



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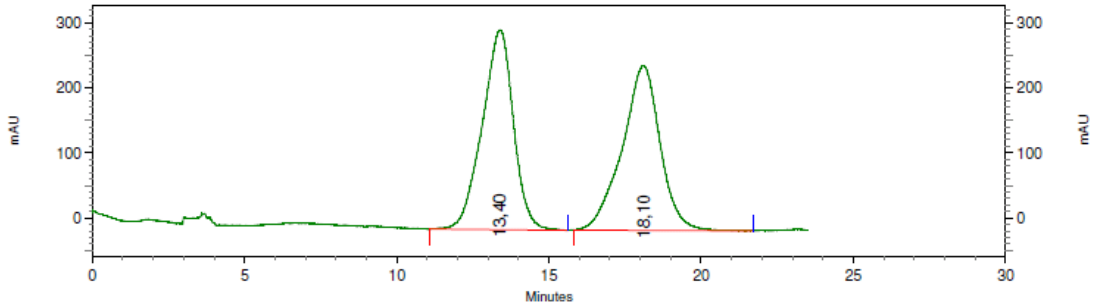
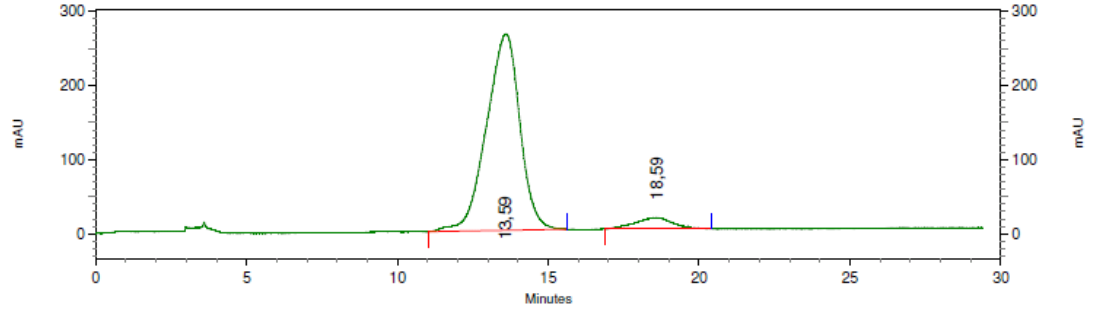


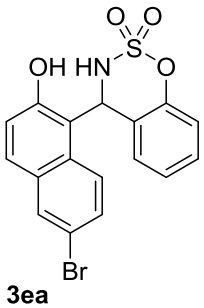
1: 244 nm, 4 nm Results

Retention Time	Area	Area Percent
13,40	87529088	49,885
18,10	87933578	50,115

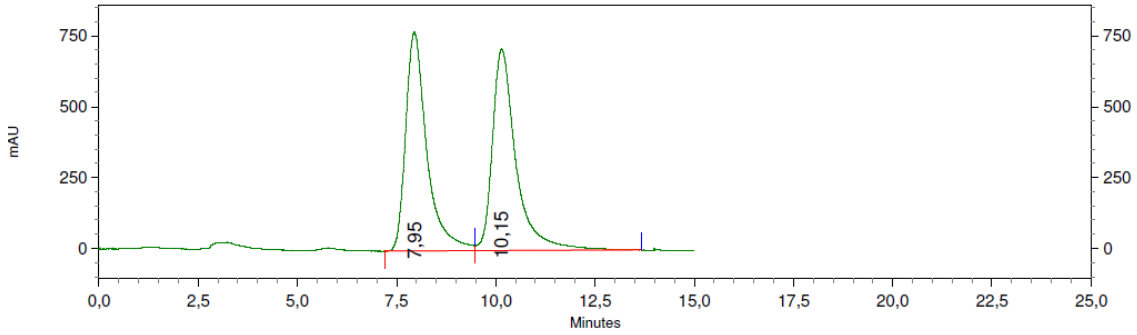


1: 244 nm, 4 nm Results

Retention Time	Area	Area Percent
13,59	81678201	93,924
18,59	5283715	6,076

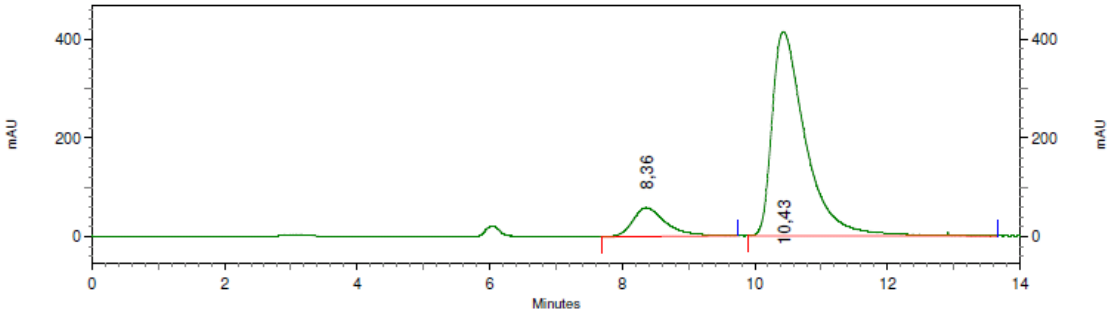


3ea



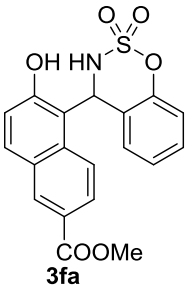
1: 235 nm, 4 nm Results

Retention Time	Area	Area Percent
7,95	114856114	49,336
10,15	117945960	50,664

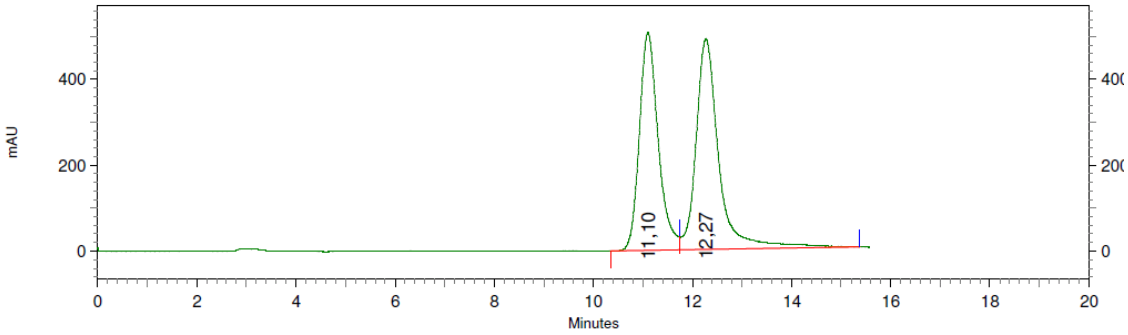


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
8,36	8222884	12,391
10,43	58139334	87,609

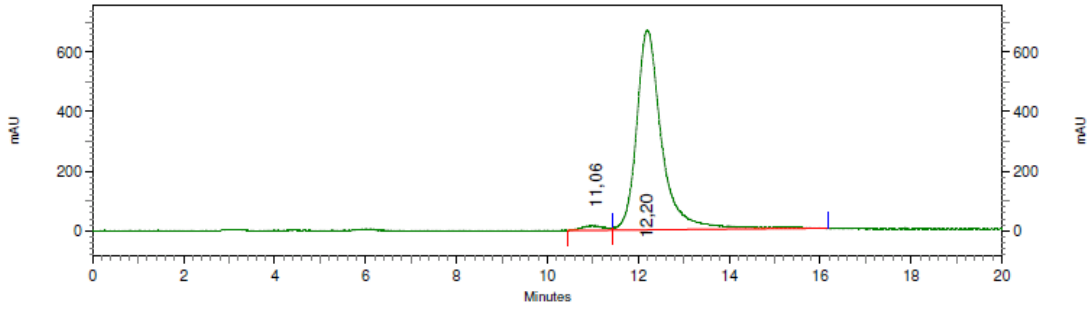


3fa



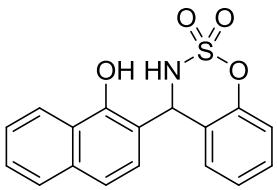
1: 247 nm, 4 nm Results

Retention Time	Area	Area Percent
11,10	53517341	46,114
12,27	62537414	53,886

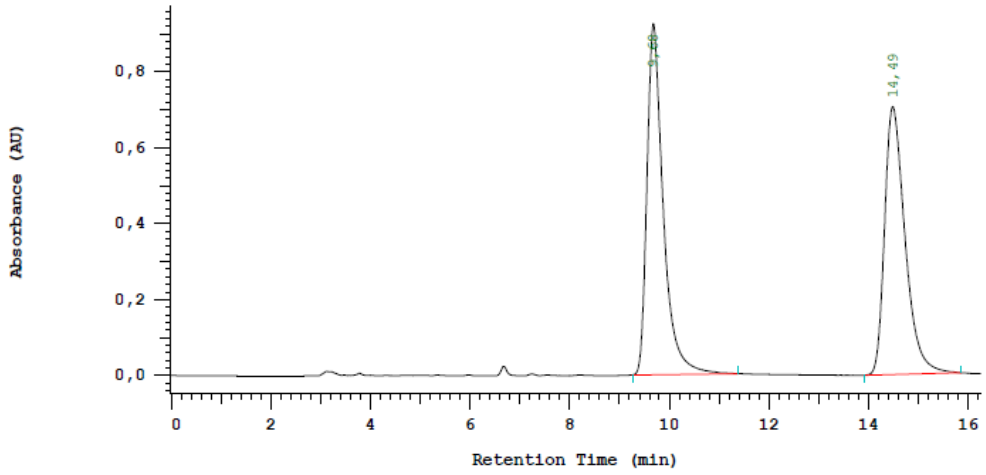


1: 247 nm, 4 nm Results

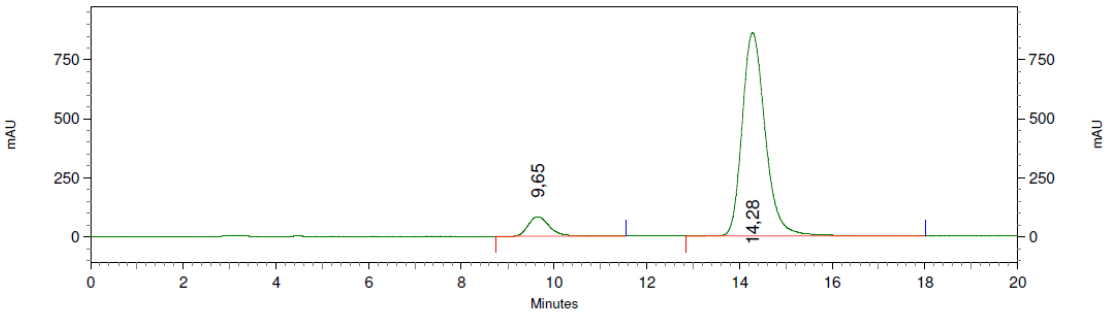
Retention Time	Area	Area Percent
11,06	2126185	2,014
12,20	103455102	97,986



6

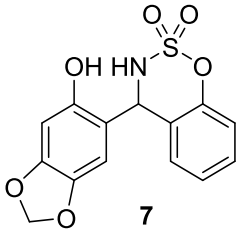


No.	RT	Area	Area %	Name
1	9,68	10488089	50,972	
2	14,49	10088260	49,028	
		20576349	100,000	

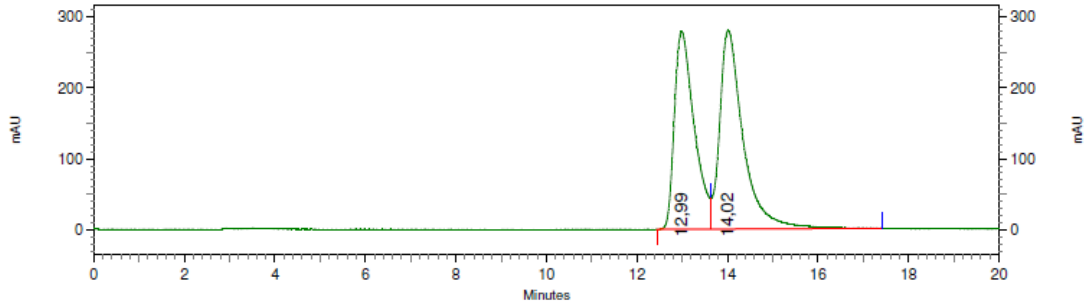


1: 240 nm, 4 nm Results

Retention Time	Area	Area Percent
9,65	10884734	8,326
14,28	119854796	91,674

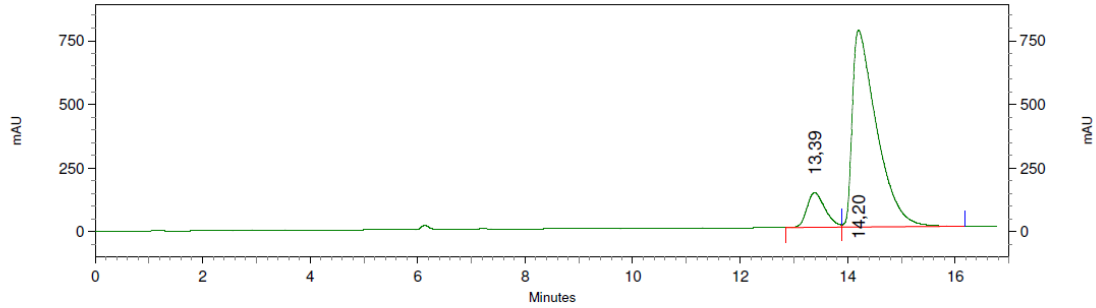


7



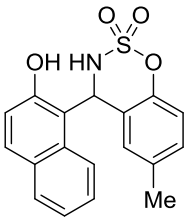
1: 300 nm, 4 nm Results

Retention Time	Area	Area Percent
12,99	33995820	45,608
14,02	40543796	54,392

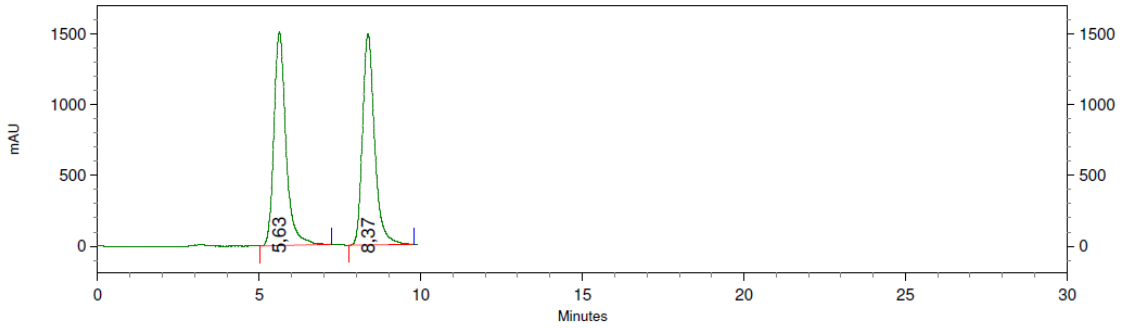


1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent
13,39	12789054	11,609
14,20	97375691	88,391

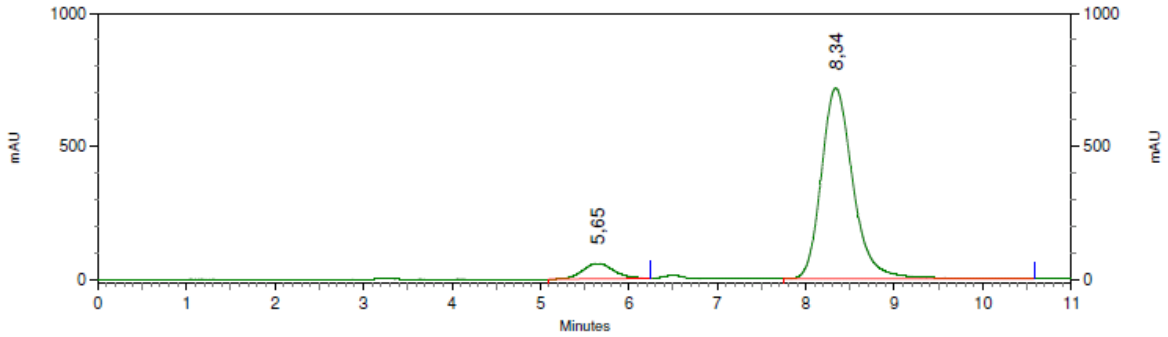


3ab



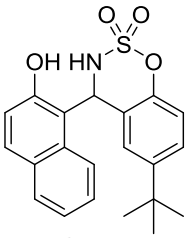
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
5,63	155579602	50,118
8,37	154846311	49,882

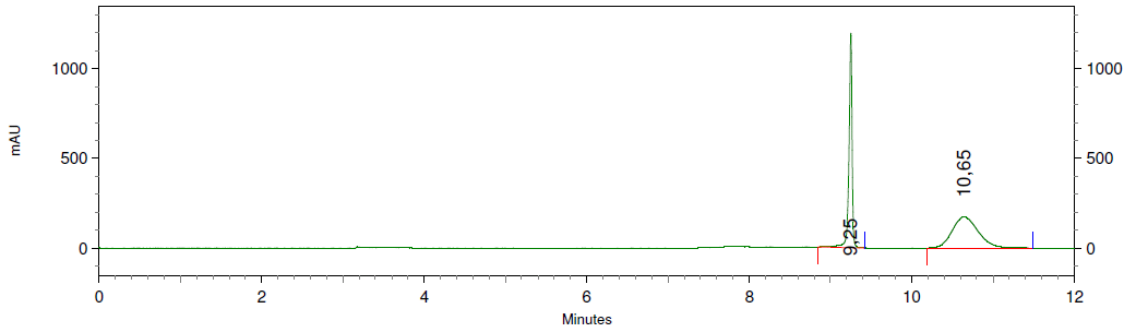


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
5,65	5537525	7,204
8,34	71334316	92,796

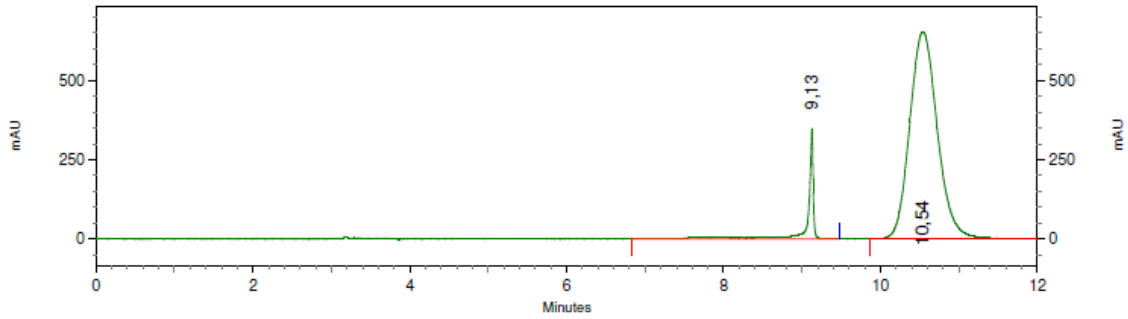


3ac



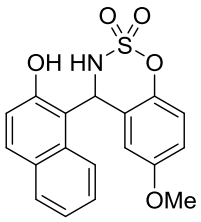
1: 278 nm, 4 nm Results

Retention Time	Area	Area Percent
9,25	12336139	44,212
10,65	15566404	55,788

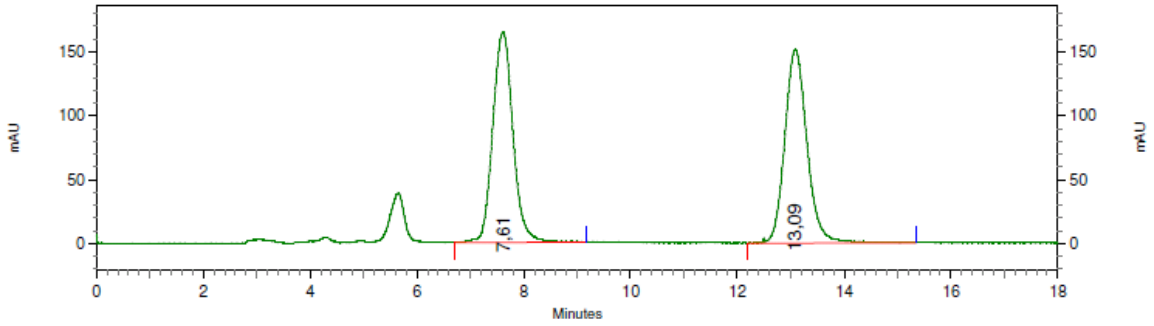


1: 278 nm, 4 nm Results

Retention Time	Area	Area Percent
9,13	6484025	9,131
10,54	64530964	90,869

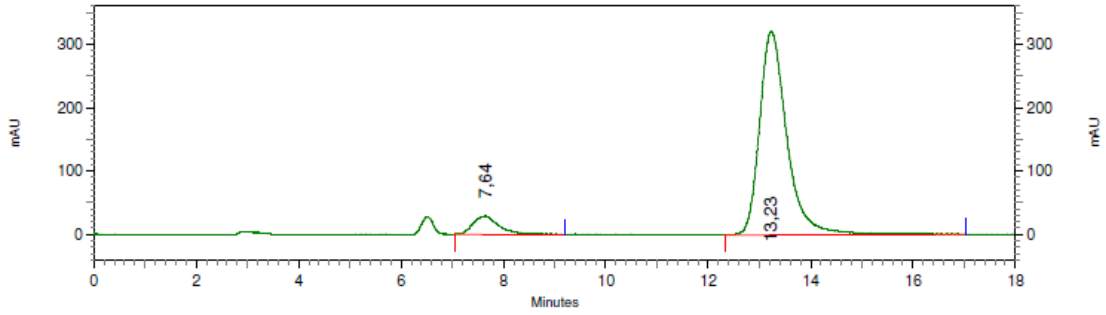


3ad



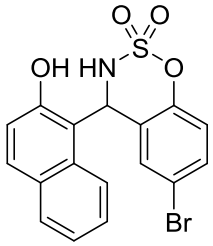
1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
7,61	17334923	49,695
13,09	17547657	50,305

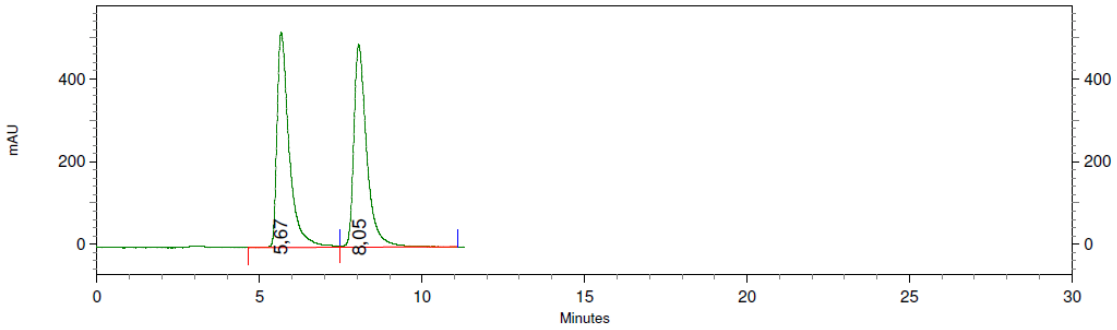


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
7,64	4309996	8,243
13,23	47979000	91,757

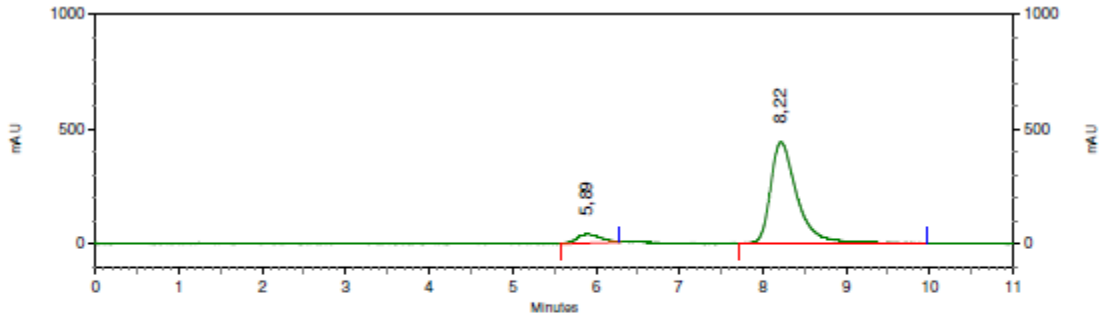


3ae



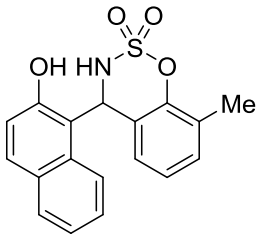
1: 333 nm, 4 nm Results

Retention Time	Area	Area Percent
5,67	54198578	49,995
8,05	54209581	50,005

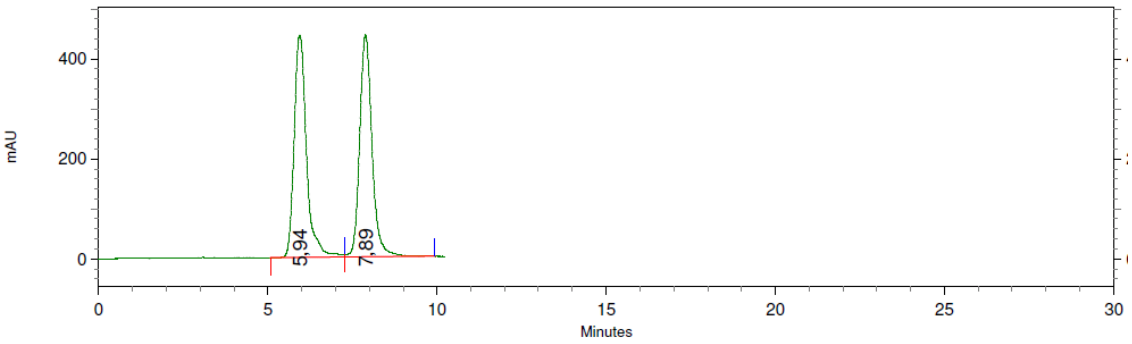


1: 255 nm, 4 nm Results

Retention Time	Area	Area Percent
5,89	3111447	7,229
8,22	39930106	92,771

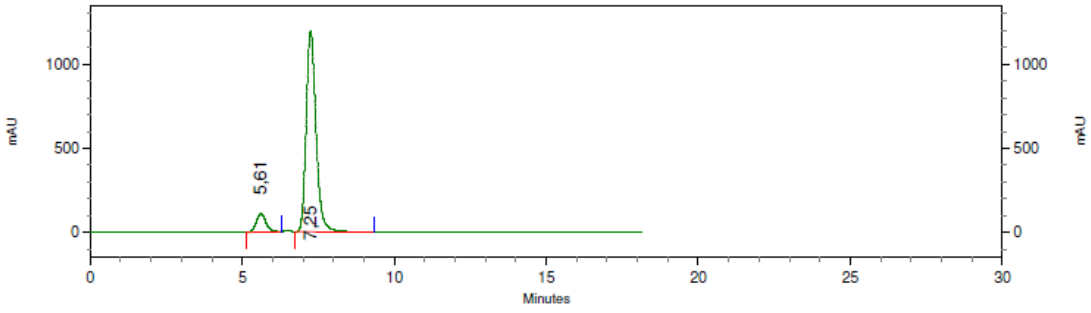


3af



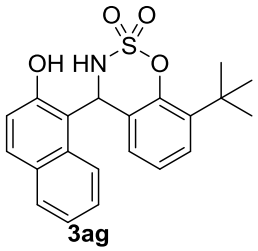
1: 276 nm, 4 nm Results

Retention Time	Area	Area Percent
5,94	45046486	49,998
7,89	45049566	50,002

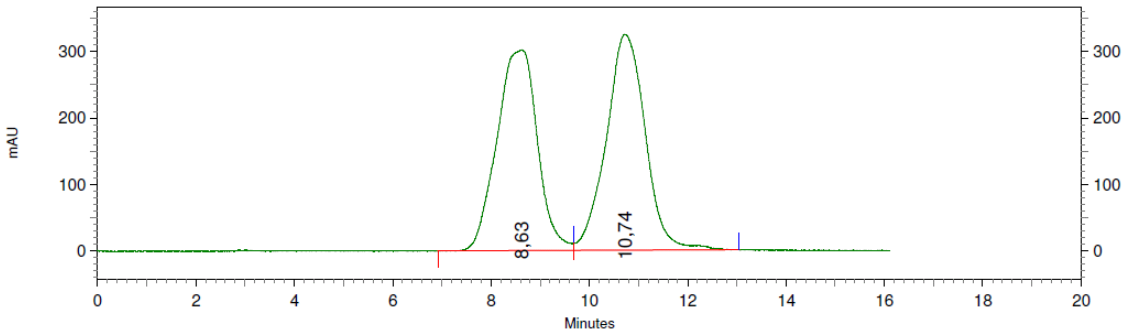


1: 333 nm, 4 nm Results

Retention Time	Area	Area Percent
5,61	9704073	8,276
7,25	107554991	91,724

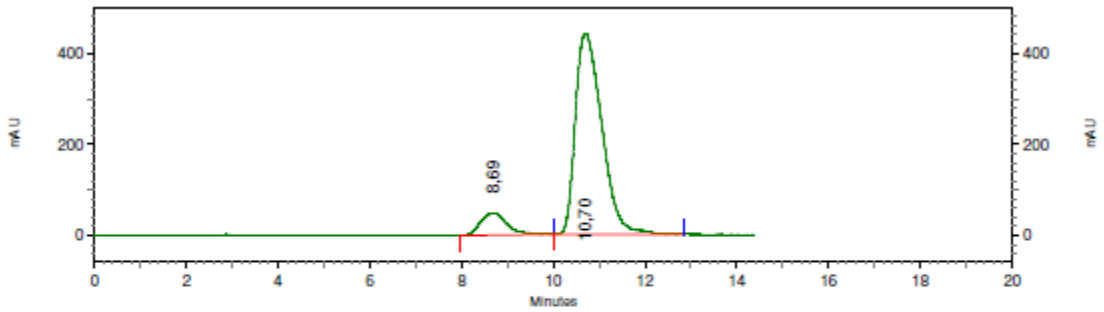


3ag



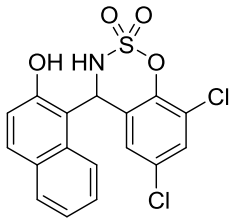
1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
8,63	68998444	49,077
10,74	71592407	50,923

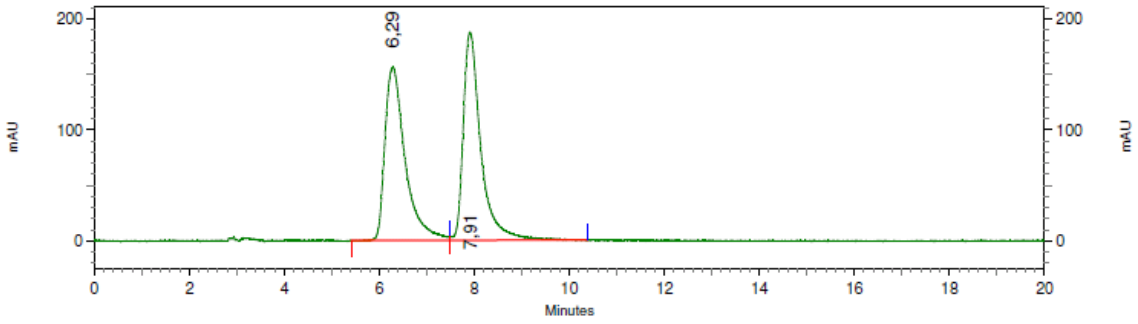


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
8,69	7699711	9,812
10,70	70774310	90,188

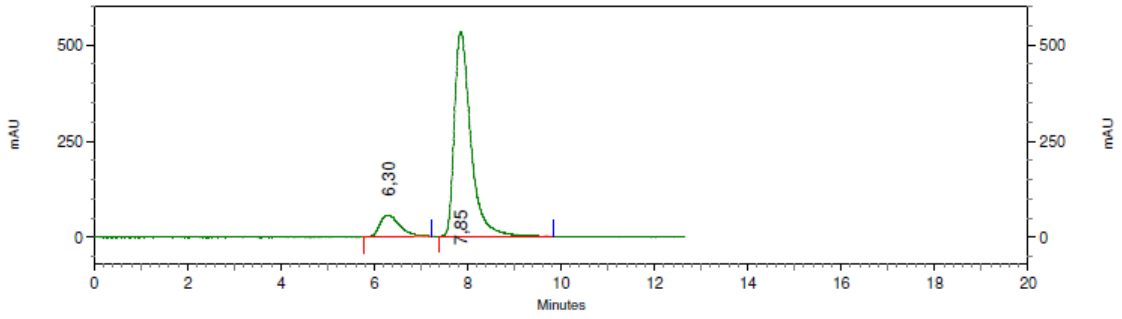


3ah



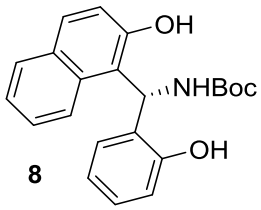
1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
6,29	18477279	49,037
7,91	19203301	50,963

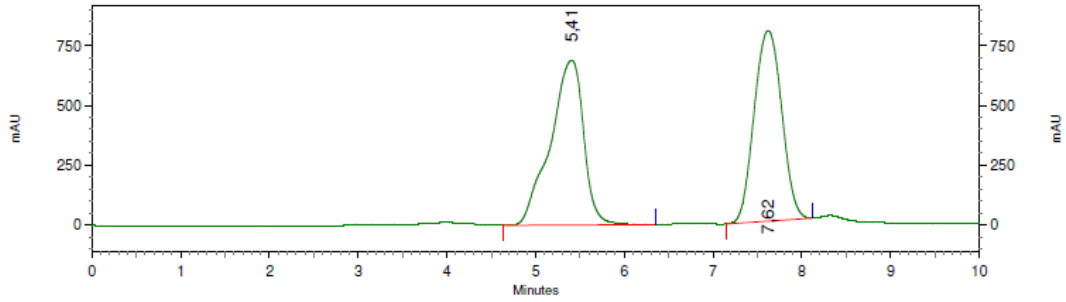


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
6,30	6767314	11,512
7,85	52016162	88,488

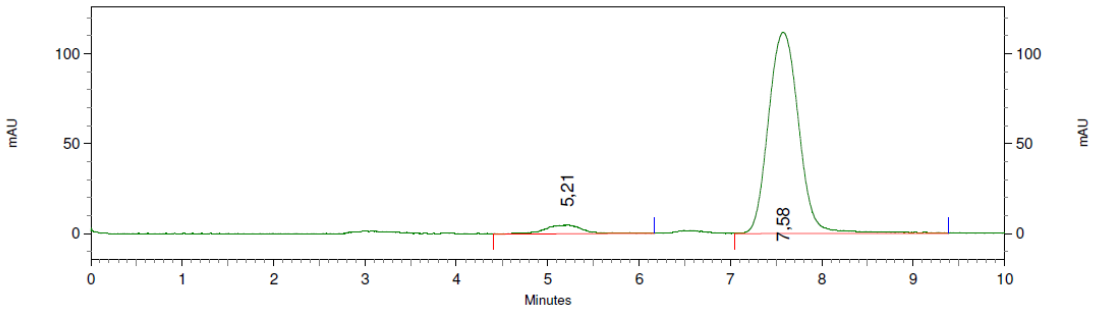


8



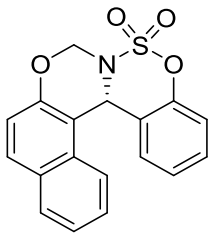
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
5,41	72034383	51,107
7,62	68915154	48,893

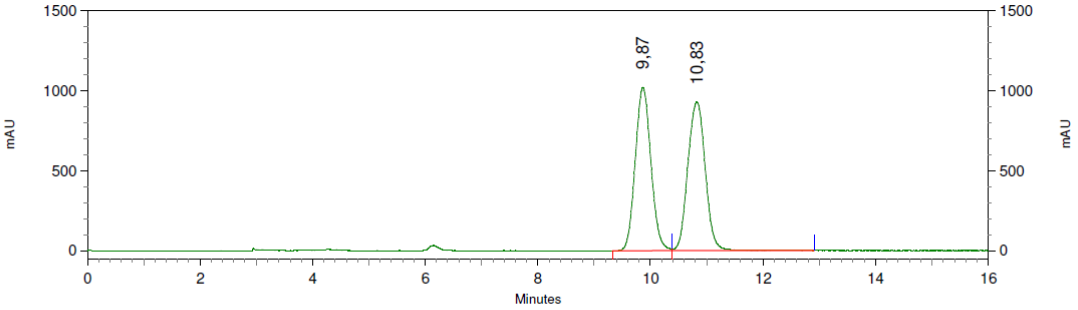


1: 280 nm, 4 nm Results

Retention Time	Area	Area Percent
5,21	596561	5,450
7,58	10350433	94,550

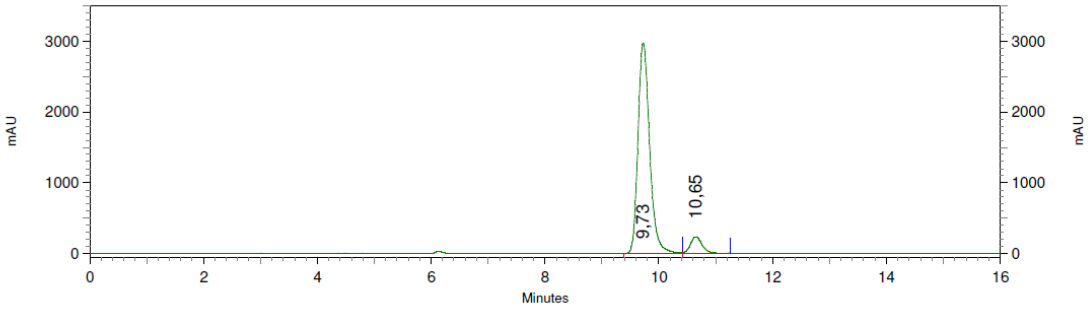


9



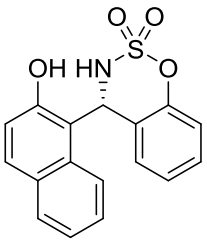
1: 235 nm, 4 nm Results

Retention Time	Area	Area Percent
9,87	78794189	49,612
10,83	80027532	50,388



1: 235 nm, 4 nm Results

Retention Time	Area	Area Percent
9,73	168917945	92,617
10,65	13466273	7,383



3aa

X-ray data for compound **3aa**: crystallized from ethyl acetate/*n*-hexane; $C_{17}H_{13}NSO_4$; Mr=327,35; Diffraction data on prismatic crystals were collected at 293 K with a Nonius Kappa-CCD single crystal diffractometer using Mo K_α (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS97 and refined by full-matrix least squares on F^2 using SHELXL97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions, refined using a riding model and assigned fixed isotropically displacement parameters. The H1 atom was located in a difference map and refined isotropically.

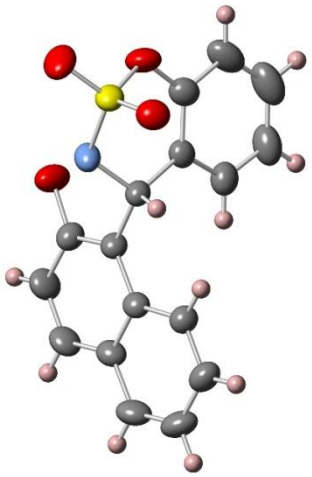
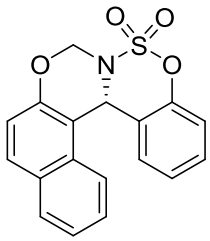


Figure 1. ORTEP plot for the X-ray structure of compound **3aa**.



9

X-ray data for compound **9**: crystallized from ethyl acetate/*n*-hexane; $C_{18}H_{13}NSO_4$; Mr=339,37; Diffraction data on prismatic crystals were collected at 293 K with a Nonius Kappa-CCD single crystal diffractometer using Mo K_α (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS97 and refined by full-matrix least squares on F^2 using SHELXL97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions, refined using a riding model and assigned fixed isotropically displacement parameters. The H1 atom was located in a difference map and refined isotropically.

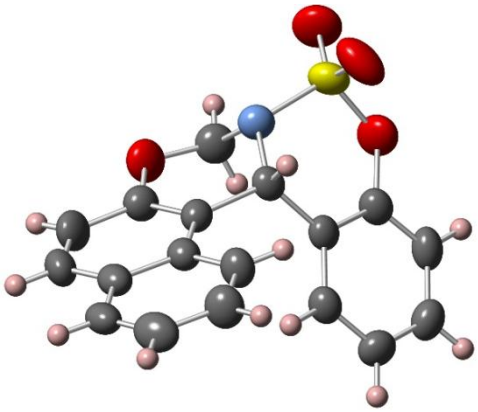


Figure 2. ORTEP plot for the X-ray structure of compound **9**.

References

1 a) Li, H.; Wang, B; Deng, L *J. Am. Chem. Soc.* **2006**, *128*, 732-733. b) Cheng, L.; Liu, L; Jia, H.; Wang, D.; Chen, Y.-J. *J Org Chem*. **2009**, *74*, 4650-4653.

2 a) Luo, Y.; Carnell, A. J.; Lam, H. W. *Angew. Chem Int. Ed*. **2012**, 51, 6762.