Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Isothiourea-catalysed Enantioselective Annulation of 2-Aminobenzothiophenes with *α*, *β*-Unsaturated Anhydrides

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Supporting Information

Content

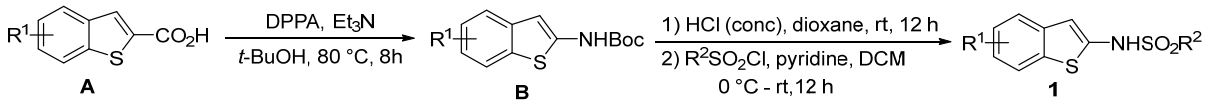
1. General information

Commercially available reagents were used without further purification. Some benzo thiophene-2-carboxylic acid were purchased from Shanghai Haohong Scientific Co., Ltd. A Column chromatography was performed with silica gel (200-300 mesh). Melting points were determined with an XT-4 melting-point apparatus and are uncorrected. ^{1}H NMR spectra were measured with Bruker Ascend 400 MHz spectrometer in $CDCl_3$, chemical shifts were reported in δ (ppm) units relative to tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were measured at 100 MHz (or 176 MHz) with a Bruker Ascend 400 MHz (or 700 MHz) spectrometer, chemical shifts were reported in δ (ppm) relative to tetramethylsilane and referenced to the solvent peak ($CDCl_3$ at 77.0 ppm). High resolution mass spectra were measured with an Agilent 6520 Accurate-Mass-Q-TOF MS system equipped with an electrospray ionization (ESI) source. Enantiomeric excesses were determined by chiral HPLC analysis using an Agilent 1200 LC instrument with a Daicel Chiralpak AD-H, IA and IB column. Optical rotations were measured with a Krüss P8000 polarimeter at the indicated concentration with the units of grams per 100 mL.

2. Starting materials

2a–**2k** were prepared according to the literature.[1] The isothiourea organocatalysts were prepared according to the literature.[2]

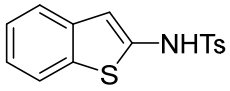
1a–**1j** were prepared according to the following method.[3] **1k** were prepared according to the literature.[4]



A mixture of benzo[*b*]thiophene-2-carboxylic acid **A** (10 mmol, 1.0 equiv), Et_3N (10.5 mmol, 1.05 equiv), diphenyl azidophosphate (DPPA, 12 mmol, 1.2 equiv), and *t*-BuOH (20 mL) was heated at 80 °C for 8 h. Afterwards the solvent was evaporated by reduce pressure and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford product **B**.

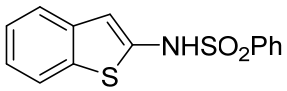
To solution of **B** (5.0 mmol) in dioxane (8.5 mL) followed by HCl (conc., 1.5 mL) was added dropwise, and the resulting suspension was stirred at room temperature for 24 h. Then the mixture was filtered. The precipitate was washed with MTBE (3 × 5 mL) and drying. To a solution of precipitate (1.0 mmol, 1.0 equiv) in dry DCM (5 mL) and cooled to 0 °C, pyridine (2.5 mmol, 2.5 equiv) followed by the corresponding sulfonyl chloride (1.2 mmol, 1.2 equiv) was added dropwise, and the resulting suspension was stirred at room temperature for about 6

h (monitored by TLC). Then 0.5 N HCl (20 mL) was added and extracted with DCM (3 × 10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 3:1) to afford compound **1.**



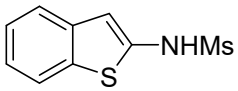
1a

***N*-(Benzo[*b*]thiophen-2-yl)-4-methylbenzenesulfonamide (1a).** Pink solid (0.6978 g, 46% yield for three steps), m.p. 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 1H, ArH), 7.62 – 7.55 (m, 3H, ArH), 7.29 – 7.20 (m, 4H, ArH + NH), 6.91 (s, 1H, ArH), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 137.9, 137.6, 136.6, 135.1, 129.7, 127.5, 124.6, 124.2, 123.2, 121.9, 116.3, 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{14}NO_2S_2$ $[M + H]^+$ 304.0460, found 304.0461.



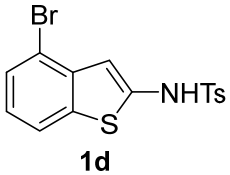
1b

***N*-(Benzo[*b*]thiophen-2-yl)benzenesulfonamide (1b).** Brown solid (0.7959 g, 55% yield for three steps), m.p. 119–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H, ArH), 7.62 – 7.52 (m, 4H, ArH + NH), 7.43 (t, *J* = 7.6 Hz, 2H, ArH), 7.30 – 7.22 (m, 2H, ArH), 6.93 (s, 1H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.9, 137.3, 136.7, 133.4, 129.1, 127.4, 124.7, 124.4, 123.3, 122.0, 116.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{12}NO_2S_2$ $[M + H]^+$ 290.0304, found 290.0281.



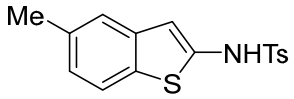
1c

***N*-(Benzo[*b*]thiophen-2-yl)methanesulfonamide (1c).** Pink solid (0.6364 g, 56% yield for three steps), m.p. 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.67 (m, 2H, ArH), 7.37 – 7.29 (m, 2H, ArH), 7.13 (s, 1H, ArH), 7.11 (br s, 1H, NH), 3.11 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 138.1, 137.2, 136.5, 125.0, 124.7, 123.5, 122.1, 116.8, 39.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_9H_{10}NNaO_2S_2$ $[M + Na]^+$ 249.9967, found 224.9952.



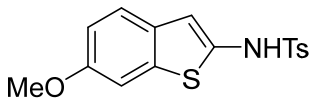
1d

***N*-(4-Bromobenzo[*b*]thiophen-2-yl)-4-methylbenzenesulfonamide (1d).** Pink solid (0.7073 g, 37% yield for three steps), m.p. 125–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H, ArH), 7.55 (d, J = 8.0 Hz, 1H, ArH), 7.43 (dd, J_1 = 7.6, J_2 = 0.8 Hz, 1H, ArH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 7.08 (t, J = 8.0 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 2.37 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 144.6, 138.7, 137.9, 136.8, 135.0, 129.9, 127.9, 127.5, 125.0, 121.0, 116.6, 115.2, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{13}{}^{79}BrNO_2S_2$ $[M + H]^+$ 381.9566, found 381.9567, calcd. for $C_{15}H_{13}{}^{81}BrNO_2S_2$ $[M + H]^+$ 383.9546, found 383.9546.



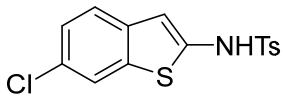
1e

4-Methyl-*N*-(5-methylbenzo[*b*]thiophen-2-yl)benzenesulfonamide (1e). Pink solid (0.4920 g, 31% yield for three steps), m.p. 149–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H, ArH), 7.51 (d, J = 8.0 Hz, 1H, ArH), 7.41 (s, 1H, ArH), 7.24 (d, J = 8.4 Hz, 2H, ArH), 7.10 (dd, J_1 = 8.2, J_2 = 1.0 Hz, 1H, ArH), 6.95 (br s, 1H, NH), 6.87 (s, 1H, ArH), 2.41 (s, 3H, CH_3), 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 138.2, 137.4, 135.3, 134.5, 133.8, 129.7, 127.5, 126.1, 123.4, 121.7, 116.8, 21.6, 21.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{16}NO_2S_2$ $[M + H]^+$ 318.0617, found 318.0613.



1f

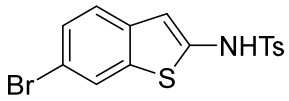
***N*-(6-Methoxybenzo[*b*]thiophen-2-yl)-4-methylbenzenesulfonamide (1f).** Pink solid (0.2506 g, 15% yield for three steps), m.p. 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H, ArH), 7.47 (d, J = 8.8 Hz, 1H, ArH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.17 (s, 1H, NH), 7.10 (d, J = 2.4 Hz, 1H, ArH), 6.91 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 1H, ArH), 6.85 (s, 1H, ArH), 3.81 (s, 3H, CH_3), 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 157.4, 144.2, 138.5, 135.3, 134.6, 131.6, 129.7, 127.5, 124.2, 117.9, 114.4, 104.8, 55.5, 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{16}NO_3S_2$ $[M + H]^+$ 334.0566, found 334.0552.



1g

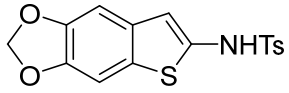
***N*-(6-Chlorobenzo[*b*]thiophen-2-yl)-4-methylbenzenesulfonamide (1g).** White solid (0.2871 g, 17% yield for three steps), m.p. 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H, ArH), 7.58 (d, J = 1.6 Hz, 1H, ArH), 7.49 (br s, 1H, NH), 7.47 (d, J = 8.4 Hz, 1H, ArH), 7.25 – 7.23 (m, 3H, ArH), 6.88 (s, 1H, ArH), 3.81 (s, 3H, CH_3), 2.38 (s, 3H, CH_3)

ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 144.6, 138.0, 137.5, 136.3, 135.0, 130.2, 129.8, 127.5, 125.5, 124.1, 121.6, 115.9, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{13}ClNO_2S_2$ $[M + H]^+$ 338.0071, found 338.0072.



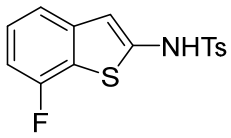
1h

***N*-(6-Bromobenzo[*b*]thiophen-2-yl)-4-methylbenzenesulfonamide (1h).** White solid (0.7646 g, 40% yield for three steps), m.p. 154–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.72 (m, 3H, ArH), 7.45 – 7.38 (m, 2H, ArH), 7.25 (d, J = 6.8 Hz, 3H, NH + ArH), 6.88 (s, 1H, ArH), 2.39 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 144.6, 138.1, 137.9, 136.6, 135.1, 129.8, 128.1, 127.5, 124.5, 124.4, 117.9, 116.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{13}{}^{79}Br\,NNaO_2S_2$ $[M + Na]^+$ 403.9385, found 403.9377, calcd. for $C_{15}H_{13}{}^{81}BrNNaO_2S_2$ $[M + Na]^+$ 405.9365, found 405.9357.



1i

4-Methyl-*N*-(thieno[2',3':4,5]benzo[1,2-*d*][1,3]dioxol-6-yl)benzenesulfonamide (1i). White solid (0.1911 g, 11% yield for three steps), mp 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, J = 8.4 Hz, 2H, ArH), 7.04 (br s, 1H, NH), 7.01 (s, 1H, ArH), 6.98 (s, 1H, ArH), 6.81 (s, 1H, ArH), 5.96 (s, 2H, CH_2), 2.39 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 146.7, 146.6, 144.3, 135.3, 135.2, 131.9, 130.5, 129.7, 127.5, 118.6, 102.4, 101.4, 101.2, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{13}NNaO_4S_2$ $[M + Na]^+$ 370.0178, found 370.0170.

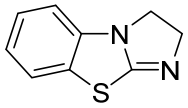


1j

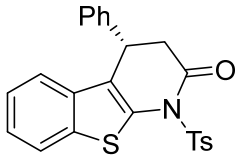
***N*-(7-Fluorobenzo[*b*]thiophen-2-yl)-4-methylbenzenesulfonamide (1j).** White solid (0.8839 g, 55% yield for three steps), m.p. 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2H, ArH), 7.67 (br s, 1H, NH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.25 – 7.20 (m, 3H, ArH), 6.96 – 6.92 (m, 2H, ArH), 2.37 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0 (d, $^1J_{C–F}$ = 245.4 Hz), 144.6, 140.9 (d, $^3J_{C–F}$ = 4.7 Hz), 138.8 (d, $^4J_{C–F}$ = 1.3 Hz), 135.0, 129.8, 127.5, 125.9 (d, $^3J_{C–F}$ = 6.9 Hz), 123.2 (d, $^2J_{C–F}$ = 9.0 Hz), 119.0 (d, $^4J_{C–F}$ = 3.4 Hz), 116.1 (d, $^4J_{C–F}$ = 2.3 Hz), 109.4 (d, $^2J_{C–F}$ = 18.3 Hz), 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{13}FNO_2S_2$ $[M + H]^+$ 322.0366, found 322.0348.

3. Enantioselective synthesis and characterization of compounds 3

Benzenesulfonamide **1** (0.1 mmol), cinnamic acid anhydride **2** (0.12 mmol), $NaHCO_3$ (8.4 mg, 0.1 mmol), and catalyst **C1** (2.5 mg, 0.01 mmol) were dissolved in toluene (1.0 mL), and the mixture was stirred at room temperature for 24 – 72 h (monitored by TLC). After completion of the reaction, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 9:1 to 7:1) to afford the pure products **3**. Racemates were prepared following a similar procedure using 2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole as catalyst (10 mol%).

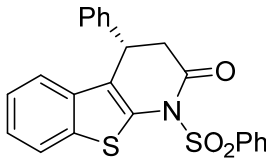


2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole



3aa

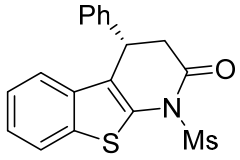
(*S*)-4-Phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3aa). White solid (39.9 mg, 92% yield, 96:4 er), m.p. 149–150 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.0 (minor), t_R = 13.9 min (major); 96:4 er. $[\alpha]_D^{25}$ = +30.1° (*c* = 2.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 2H, ArH), 7.81 – 7.78 (m, 1H, ArH), 7.45 – 7.42 (m, 1H, ArH), 7.31 – 7.29 (m, 2H, ArH), 7.23 (d, *J* = 8.4 Hz, 2H, ArH), 7.09 (t, *J* = 7.2 Hz, 1H, ArH), 6.99 (t, *J* = 7.4 Hz, 2H, ArH), 6.80 (d, *J* = 7.6 Hz, 2H, ArH), 4.43 (dd, J_1 = 7.0 Hz, J_2 = 1.8 Hz, 1H, CH), 3.18 (dd, J_1 = 15.0 Hz, J_2 = 7.0 Hz, 1H, CH_2), 2.92 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2), 2.42 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 168.3, 145.6, 139.6, 136.7, 135.4, 135.0, 134.5, 129.4, 128.71, 128.66, 127.1, 126.5, 124.8, 124.4, 121.9, 120.8, 120.6, 41.5, 36.3, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{20}NO_3S_2$ $[M + H]^+$ 434.0879, found 434.0871.



3ba

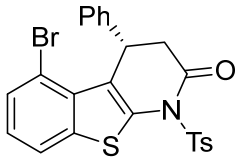
(*S*)-4-Phenyl-1-(phenylsulfonyl)-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ba). White solid (35.7 mg, 85% yield, 95:5 er), m.p. 193–195 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 95:5, flow rate 1.0 mL/min, detection at 254 nm): t_R = 52.7 (major), t_R = 56.6 min (minor); 95:5 er. $[\alpha]_D^{25}$ = +23.1° (*c* = 2.70, CH_2Cl_2). ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.06 – 8.04 (m, 2H, ArH), 7.84 – 7.81 (m, 1H, ArH), 7.64 (t, J = 7.6 Hz, 1H, ArH), 7.50 – 7.44 (m, 3H, ArH), 7.33 – 7.31 (m, 2H, ArH), 7.09 (t, J = 7.2 Hz, 1H, ArH), 7.00 (t, J = 7.4 Hz, 2H, ArH), 6.80 (d, J = 7.6 Hz, 2H, ArH), 4.45 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H, CH), 3.23 (dd, J_1 = 15.4 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.95 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 168.3, 139.5, 137.6, 136.8, 135.4, 135.0, 134.4, 128.9, 128.8, 128.7, 127.3, 126.5, 124.9, 124.5, 121.9, 120.8, 120.7, 41.6, 36.4 ppm. HRMS (ESI): m/z calcd. for $C_{23}H_{18}NO_3S_2$ $[M + H]^+$ 420.0723, found 420.0723.



3ca

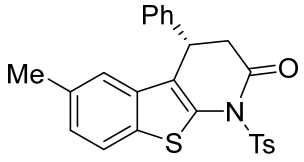
(*S*)-1-(Methylsulfonyl)-4-phenyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ca). White solid (28.6 mg, 80% yield, 96:4 er), m.p. 178–179 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 11.0 (minor), t_R = 22.8 min (major); 96:4 er. $[\alpha]_D^{25}$ = +16.9° (c = 1.54, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.76 (m, 1H, ArH), 7.48 – 7.46 (m, 1H, ArH), 7.32 – 7.28 (m, 4H, ArH), 7.26 – 7.24 (m, 1H, ArH), 7.17 (d, J = 7.2 Hz, 2H, ArH), 4.58 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H, CH), 3.37 (s, 3H, CH_3), 3.28 (dd, J_1 = 15.4 Hz, J_2 = 7.0 Hz, 1H, CH_2), 3.16 (dd, J_1 = 15.4 Hz, J_2 = 2.6 Hz, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 169.9, 139.5, 136.7, 134.7, 129.1, 127.7, 126.7, 124.9, 124.5, 121.9, 120.9, 120.2, 42.4, 41.6, 35.9 ppm. HRMS (ESI): m/z calcd. for $C_{18}H_{16}NO_3S_2$ $[M + H]^+$ 358.0566, found 358.0564.



3da

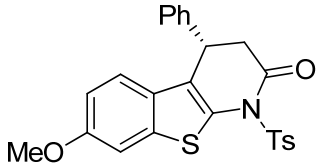
(*S*)-5-Bromo-4-phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3da). White solid (48.7 mg, 95% yield, 96:4 er), m.p. 199–201 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.3 (major), t_R = 10.9 min (minor); 96:4 er. $[\alpha]_D^{25}$ = +95.1° (c = 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.4 Hz, 2H, ArH), 7.77 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H, ArH), 7.50 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.14 (t, J = 7.8 Hz, 1H, ArH), 7.07 (t, J = 7.4 Hz, 1H, ArH), 6.99 (t, J = 7.6 Hz, 2H, ArH), 6.81 (d, J = 7.6 Hz, 2H, ArH), 5.44 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H, CH), 3.13 (dd, J_1 = 15.0 Hz, J_2 = 6.6 Hz, 1H, CH_2), 2.94 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2), 2.41 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 145.6, 139.7, 139.0, 137.7, 134.5, 132.3, 130.4, 129.4, 128.7, 128.5, 127.0, 126.8, 125.1,

121.9, 121.3, 115.7, 41.5, 36.4, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{19}{}^{79}Br\,NO_3S_2$ $[M + H]^+$ 511.9984, found 511.9982, calcd. for $C_{24}H_{19}{}^{81}BrNO_3S_2$ $[M + H]^+$ 513.9964, found 513.9966.



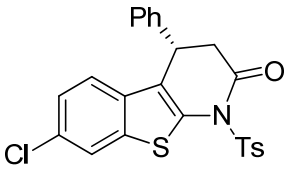
3ea

(*S*)-6-Methyl-4-phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ea). White solid (35.8 mg, 80% yield, 98:2 er), m.p. 83–84 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.1 (minor), t_R = 10.6 min (major); 98:2 er. $[\alpha]_D^{25}$ = +69.7° (*c* = 1.71, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 7.68 (d, *J* = 8.0 Hz, 1H, ArH), 7.24 – 7.22 (m, 3H, ArH), 7.14 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H, ArH), 7.09 (t, *J* = 7.4 Hz, 1H, ArH), 6.99 (t, *J* = 7.6 Hz, 2H, ArH), 6.80 (d, *J* = 7.6 Hz, 2H, ArH), 4.41 (dd, J_1 = 7.0 Hz, J_2 = 1.8 Hz, 1H, CH), 3.17 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.91 (dd, J_1 = 15.2 Hz, J_2 = 2.0 Hz, 1H, CH_2), 2.42 (s, 3H, CH_3), 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 145.5, 139.6, 135.6, 135.2, 134.7, 134.6, 134.0, 129.4, 128.72, 128.67, 127.1, 126.6, 126.1, 121.6, 120.8, 120.4, 41.6, 36.3, 21.7, 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}NO_3S_2$ $[M + H]^+$ 448.1036, found 448.1031.



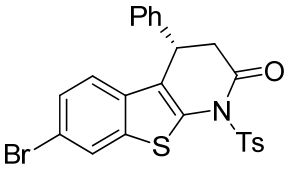
3fa

(*S*)-7-Methoxy-4-phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3fa). White solid (44.5 mg, 96% yield, 97:3 er), m.p. 88–89 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.6 (major), t_R = 16.2 min (minor); 97:3 er. $[\alpha]_D^{25}$ = +91.4° (*c* = 3.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 – 7.28 (m, 2H, ArH), 7.23 (d, *J* = 8.4 Hz, 2H, ArH), 7.08 (t, *J* = 7.2 Hz, 1H, ArH), 6.98 (t, *J* = 7.6 Hz, 2H, ArH), 6.92 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.79 (d, *J* = 7.6 Hz, 2H, ArH), 4.37 (dd, J_1 = 7.0 Hz, J_2 = 2.2 Hz, 1H, CH), 3.85 (s, 3H, CH_3), 3.17 (dd, J_1 = 15.0 Hz, J_2 = 7.0 Hz, 1H, CH_2), 2.90 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2), 2.42 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 157.4, 145.5, 139.6, 138.3, 134.5, 132.7, 129.4, 128.8, 128.7, 128.6, 127.1, 126.5, 121.6, 120.5, 114.5, 104.6, 55.6, 41.5, 36.4, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}NO_4S_2$ $[M + H]^+$ 464.0985, found 464.0979.



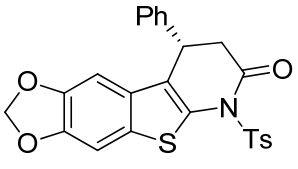
3ga

(S)-7-Chloro-4-phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ga). White solid (43.1 mg, 92% yield, 90:10 er), m.p. 110–112 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 11.6 (minor), t_R = 12.6 min (major); 90:10 er. $[\alpha]_D^{25}$ = +95.1° (*c* = 2.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 7.76 (d, *J* = 1.6 Hz, 1H, ArH), 7.32 (d, *J* = 8.4 Hz, 1H, ArH), 7.27 – 7.23 (m, 3H, ArH), 7.11 (t, *J* = 7.4 Hz, 1H, ArH), 7.00 (t, *J* = 7.6 Hz, 2H, ArH), 6.78 (d, *J* = 7.6 Hz, 2H, ArH), 4.40 (dd, J_1 = 7.0 Hz, J_2 = 2.2 Hz, 1H, CH), 3.19 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.92 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 168.0, 145.7, 139.3, 137.7, 135.8, 134.4, 133.4, 130.3, 129.5, 128.8, 128.7, 127.3, 126.5, 125.6, 121.7, 121.5, 120.1, 41.4, 36.4, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{19}ClNO_3S_2$ $[M + H]^+$ 468.0489, found 468.0490.



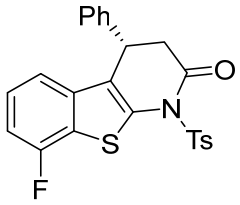
3ha

(*S*)-7-Bromo-4-phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ha). White solid (44.1 mg, 86% yield, 92:8 er), m.p. 161–162 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 12.5 (minor), t_R = 13.7 min (major); 92:8 er. $[\alpha]_D^{25}$ = +99.9° (*c* = 3.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.90 (m, 3H, ArH), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H, ArH), 7.27 – 7.25 (m, 3H, ArH), 7.11 (t, *J* = 7.4 Hz, 1H, ArH), 7.01 (t, *J* = 7.6 Hz, 2H, ArH), 6.78 (d, *J* = 7.6 Hz, 2H, ArH), 4.40 (dd, J_1 = 7.0 Hz, J_2 = 2.2 Hz, 1H, CH), 3.20 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.92 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 145.7, 139.3, 138.1, 135.8, 134.4, 133.8, 129.5, 128.8, 128.7, 128.2, 127.3, 126.4, 124.3, 122.0, 120.1, 117.9, 41.4, 36.4, 21.7 ppm. *m*/*z* calcd. for $C_{24}H_{19}{}^{79}Br\ NO_3S_2$ $[M + H]^+$ 511.9984, found 511.9971, calcd. for $C_{24}H_{19}{}^{81}BrNO_3S_2$ $[M + H]^+$ 513.9964, found 513.9956.



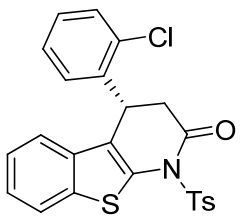
3ia

(*S*)-9-Phenyl-6-tosyl-8,9-dihydro-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5]thieno[2,3-*b*]pyridin-7(6*H*)-one (3ia). White solid (112.1 mg, 80% yield, 97:3 er), m.p. 126–129 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 17.3 (minor), t_R = 19.9 min (major); 97:3 er. $[\alpha]_D^{25}$ = +65.7° (*c* = 2.57, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 7.24 (d, *J* = 8.8 Hz, 2H, ArH), 7.19 (s, 1H, ArH), 7.10 (t, *J* = 7.4 Hz, 1H, ArH), 7.00 (t, *J* = 7.6 Hz, 2H, ArH), 6.81 – 6.77 (m, 3H, ArH), 5.98 (d, *J* = 1.2 Hz, 1H, CH_2), 5.94 (d, *J* = 0.8 Hz, 1H, CH_2), 4.30 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H, CH), 3.19 (dd, J_1 = 15.0 Hz, J_2 = 7.0 Hz, 1H, CH_2), 2.90 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 146.9, 146.4, 145.5, 139.5, 134.5, 133.4, 130.1, 129.4, 128.7, 128.6, 127.1, 126.5, 120.6, 101.35, 101.27, 100.1, 41.5, 36.6, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{20}NO_5S_2$ $[M + H]^+$ 478.0777, found 478.0780.



3ja

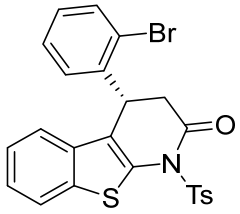
(*S*)-8-Fluoro-4-phenyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ja). White solid (37.0 mg, 82% yield, 76:24 er), m.p. 212–214 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): t_R = 17.8 (minor), t_R = 19.5 min (major); 76:24 er. $[\alpha]_D^{25}$ = +55.5° (*c* = 0.73, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.29 – 7.26 (m, 3H, ArH), 7.22 (t, *J* = 7.6 Hz, 1H, ArH), 7.11 (t, *J* = 7.4 Hz, 3H, ArH), 6.80 (d, *J* = 7.2 Hz, 2H, ArH), 4.43 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H, CH), 3.22 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.95 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 157.2 (d, $^1J_{C–F}$ = 246.2 Hz), 145.8, 139.3, 138.2 (d, $^3J_{C–F}$ = 4.8 Hz), 136.6 (d, $^4J_{C–F}$ = 1.3 Hz), 134.5, 129.5, 128.85, 128.77, 127.3, 126.5, 126.3 (d, $^3J_{C–F}$ = 7.0 Hz), 123.5 (d, $^2J_{C–F}$ = 17.8 Hz), 120.8 (d, $^4J_{C–F}$ = 2.3 Hz), 116.7 (d, $^4J_{C–F}$ = 3.4 Hz), 109.4 (d, $^2J_{C–F}$ = 18.4 Hz), 41.4, 36.6, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{19}FNO_3S_2$ $[M + H]^+$ 452.0785, found 452.0785.



3ab

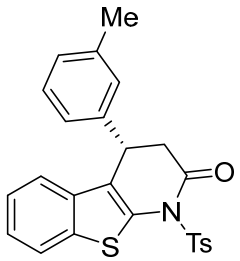
(*R*)-4-(2-Chlorophenyl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one

(3ab). White solid (44.5 mg, 95% yield, 97:3 er), m.p. 153–154 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.8 (minor), t_R = 8.6 min (major); 97:3 er. $[\alpha]_D^{25}$ = +152.5° (*c* = 1.94, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H, ArH), 7.81 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 1H, CH_2), 7.35 – 7.28 (m, 6H, ArH), 7.04 (td, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 1H, ArH), 6.58 (t, *J* = 7.4 Hz, 1H, ArH), 6.28 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H, ArH), 4.93 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H, CH), 3.20 (dd, J_1 = 15.2 Hz, J_2 = 7.6 Hz, 1H, CH_2), 2.93 (dd, J_1 = 15.2 Hz, J_2 = 2.0 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 145.8, 136.6, 136.3, 134.7, 133.0, 130.1, 129.5, 128.8, 128.7, 127.6, 126.9, 124.9, 124.5, 121.8, 120.7, 118.9, 40.0, 33.4, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{19}ClNO_3S_2$ $[M + H]^+$ 468.0489, found 468.0496.



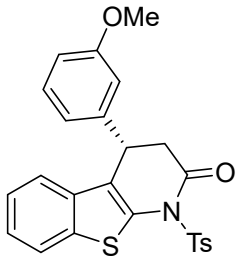
3ac

(*R*)-4-(2-Bromophenyl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ac). White solid (46.1 mg, 90% yield, 96:4 er), m.p. 148–149 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.0 (minor), t_R = 9.1 min (major); 96:4 er. $[\alpha]_D^{25}$ = +115.5° (*c* = 3.06, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 2H, ArH), 7.81 (dd, J_1 = 6.2 Hz, J_2 = 1.8 Hz, 1H, CH_2), 7.53 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, CH_2), 7.34 – 7.28 (m, 5H, ArH), 6.95 (td, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H, ArH), 6.61 (td, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1H, ArH), 6.27 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, ArH), 4.91 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H, CH), 3.19 (dd, J_1 = 15.2 Hz, J_2 = 7.6 Hz, 1H, CH_2), 2.93 (dd, J_1 = 15.0 Hz, J_2 = 1.8 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 145.8, 137.9, 136.5, 134.70, 134.67, 133.4, 129.6, 129.0, 128.8, 127.7, 127.5, 124.9, 124.5, 123.5, 121.8, 120.7, 119.1, 40.1, 36.0, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{19}{}^{79}Br\ NO_3S_2$ $[M + H]^+$ 511.9984, found 511.9985, calcd. for $C_{24}H_{19}{}^{81}BrNO_3S_2$ $[M + H]^+$ 513.9964, found 513.9966.



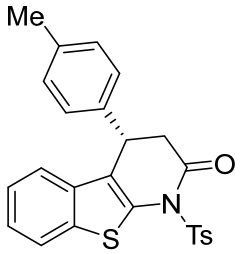
3ad

(*S*)-4-(*m*-Tolyl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ad). White solid (43.0 mg, 96% yield, 96:4 er), m.p. 85–86 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.2 (minor), t_R = 10.6 min (major); 96:4 er. $[\alpha]_D^{25}$ = +74.5° (*c* = 3.01, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H, ArH), 7.82 – 7.78 (m, 1H, ArH), 7.45 – 7.42 (m, 1H, ArH), 7.32 – 7.28 (m, 2H, ArH), 7.25 (d, *J* = 8.0 Hz, 2H, ArH), 6.91 – 6.85 (m, 2H, ArH), 6.66 (s, 1H, ArH), 6.58 (d, *J* = 7.2 Hz, 1H, ArH), 4.40 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H, CH), 3.19 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.91 (dd, J_1 = 15.2 Hz, J_2 = 2.0 Hz, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.08 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 145.5, 139.7, 138.5, 136.7, 135.3, 135.1, 134.7, 129.5, 128.7, 128.6, 128.0, 127.2, 124.8, 124.3, 123.6, 121.8, 120.8, 120.4, 41.5, 36.4, 21.7, 21.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}NO_3S_2$ $[M + H]^+$ 448.1036, found 448.1036.



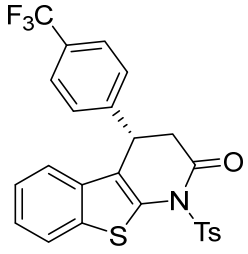
3ae

(*S*)-4-(3-Methoxyphenyl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ae). White solid (95.8 mg, 82% yield, 96:4 er), m.p. 79–80 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 11.9 (minor), t_R = 14.3 min (major); 96:4 er. $[\alpha]_D^{25}$ = +77.0° (*c* = 1.81, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H, ArH), 7.81 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 1H, ArH), 7.45 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 1H, ArH), 7.31 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 1H, ArH), 7.24 (d, *J* = 8.8 Hz, 2H, ArH), 6.91 (t, *J* = 8.0 Hz, 1H, ArH), 6.64 (dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, 1H, ArH), 6.50 (t, *J* = 1.8 Hz, 1H, ArH), 6.37 (d, *J* = 7.6 Hz, 1H, ArH), 4.42 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H, CH), 3.64 (s, 3H, CH_3), 3.19 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.95 (dd, J_1 = 15.2 Hz, J_2 = 2.0 Hz, 1H, CH_2), 2.42 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 159.8, 145.5, 141.3, 136.7, 135.5, 135.0, 134.6, 129.8, 129.4, 128.6, 124.8, 124.4, 121.9, 120.8, 120.4, 118.7, 112.7, 112.3, 55.0, 41.3, 36.3, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}NO_4S_2$ $[M + H]^+$ 464.0985, found 464.0990.



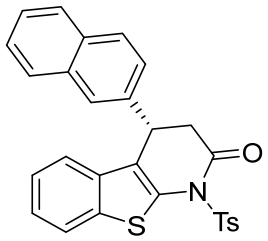
3af

(*S*)-4-(*p*-Tolyl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3af). White solid (39.8 mg, 89% yield, 96:4 er), m.p. 199–200 °C. HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 95:5, flow rate 1.0 mL/min, detection at 254 nm): t_R = 25.3 (major), t_R = 28.0 min (minor); 96:4 er. $[\alpha]_D^{25}$ = +84.5° (*c* = 1.78, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 7.81 – 7.78 (m, 1H, ArH), 7.44 – 7.42 (m, 1H, ArH), 7.31 – 7.28 (m, 2H, ArH), 7.25 – 7.23 (m, 2H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.68 (d, *J* = 8.0 Hz, 2H, ArH), 4.41 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1H, CH), 3.15 (dd, J_1 = 15.2 Hz, J_2 = 7.2 Hz, 1H, CH_2), 2.89 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2), 2.43 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 168.4, 145.5, 136.75, 136.73, 136.5, 135.3, 135.0, 134.6, 129.41, 129.38, 128.7, 126.4, 124.8, 124.3, 121.8, 120.9, 120.8, 41.6, 36.0, 21.6, 20.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{22}NO_3S_2$ $[M + H]^+$ 448.1036, found 448.1034.



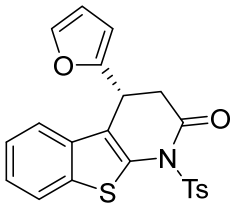
3ag

(*S*)-1-Tosyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ag). Yellow solid (45.6 mg, 91% yield, 96:4 er), m.p. 172–173 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 8.6 (major), t_R = 9.7 min (minor); 96:4 er. $[\alpha]_D^{25}$ = +65.2° (*c* = 1.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H, ArH), 7.84 – 7.81 (m, 1H, ArH), 7.46 – 7.44 (m, 1H, ArH), 7.35 – 7.32 (m, 2H, ArH), 7.22 (d, *J* = 8.4 Hz, 4H, ArH), 6.92 (d, *J* = 8.4 Hz, 2H, ArH), 4.50 (d, *J* = 6.0 Hz, 1H, CH), 3.22 (dd, J_1 = 15.2 Hz, J_2 = 6.8 Hz, 1H, CH_2), 2.95 (dd, J_1 = 15.0 Hz, J_2 = 2.2 Hz, 1H, CH_2), 2.41 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 167.9, 145.9, 143.5, 136.9, 136.0, 134.6, 134.4, 129.5, 129.4 (q, $^2J_{C-F}$ = 32.4 Hz), 128.6, 126.9, 125.6, 125.0, 124.6, 123.8 (q, $^1J_{C-F}$ = 271.9 Hz), 122.0, 120.5, 120.0, 41.1, 35.7, 21.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{18}F_3NO_3S_2$ $[M + H]^+$ 502.0753, found 502.0752.



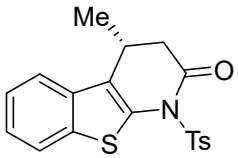
3ah

(*S*)-4-(Naphthalen-2-yl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ah). White solid (35.3 mg, 73% yield, 95:5 er), m.p. 180–182 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 12.8 (major), t_R = 15.1 min (minor); 95:5 er. $[\alpha]_D^{25}$ = +90.0° (*c* = 1.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 –7.80 (m, 3H, ArH), 7.71 –7.69 (m, 1H, ArH), 7.55 (d, *J* = 8.4 Hz, 1H, ArH), 7.52 –7.49 (m, 1H, ArH), 7.42 –7.39 (m, 3H, ArH), 7.34 –7.31 (m, 2H, ArH), 7.16 (s, 1H, ArH), 7.07 –7.01 (m, 3H, ArH), 4.60 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 1H, CH), 3.25 (dd, J_1 = 15.2 Hz, J_2 = 6.8 Hz, 1H, CH_2), 3.09 (dd, J_1 = 15.2 Hz, J_2 = 2.4 Hz, 1H, CH_2), 2.25 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 145.5, 137.1, 136.9, 135.7, 135.1, 134.5, 133.1, 132.4, 129.3, 128.8, 128.5, 127.8, 127.4, 126.0, 125.9, 125.0, 124.9, 124.5, 122.0, 120.9, 120.8, 41.1, 36.1, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{28}HNO_3S_2$ $[M + H]^+$ 484.1036, found 484.1034.



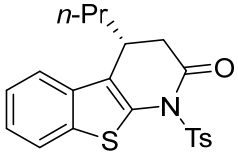
3ai

(*R*)-4-(Furan-2-yl)-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ai). White solid (39.0 mg, 92% yield, 96:4 er), m.p. 149–150 °C HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 8.6 (minor), t_R = 10.6 min (major); 96:4 er. $[\alpha]_D^{25}$ = +50.1° (*c* = 1.64, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.2 Hz, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.59 (d, *J* = 8.0 Hz, 1H, ArH), 7.39 – 7.31 (m, 2H, ArH), 7.25 (d, *J* = 8.0 Hz, 2H, ArH), 6.95 (s, 1H, ArH), 6.00 – 5.99 (m, 1H, ArH), 5.67 (s, 1H, ArH), 4.46 (d, *J* = 6.4 Hz, 1H, CH), 3.11 – 3.05 (m, 1H, CH_2), 2.99 (d, *J* = 15.2 Hz, 1H, CH_2), 2.42 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 152.4, 145.4, 142.1, 136.7, 135.6, 134.7, 134.6, 129.3, 128.7, 124.8, 124.4, 121.9, 120.6, 118.7, 110.0, 105.8, 38.6, 30.2, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{18}NO_4S_2$ $[M + H]^+$ 424.0672, found 424.0669.



3aj

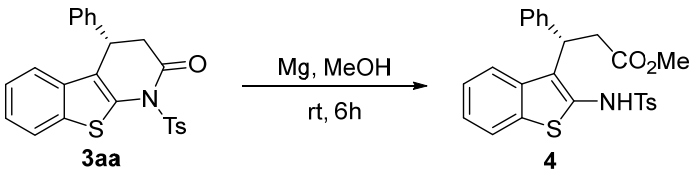
(*R*)-4-Methyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3aj). White solid (35.3 mg, 95% yield, 98:2 er), m.p. 52–53 °C HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.5 (minor), t_R = 8.0 min (major); 98:2 er. $[\alpha]_D^{25}$ = +40.8° (*c* = 2.75, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H, ArH), 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.56 (d, *J* = 8.0 Hz, 1H, ArH), 7.38 (t, *J* = 7.4 Hz, 1H, ArH), 7.34 – 7.29 (m, 3H, ArH), 3.35 – 3.28 (m, 1H,CH), 2.91 (dd, J_1 = 15.2 Hz, J_2 = 6.4 Hz, 1H, CH_2), 2.58 (d, *J* = 15.2 Hz, 1H, CH_2), 2.41 (s, 3H, CH_3), 1.00 (d, *J* = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 145.6, 136.8, 134.9, 134.5, 133.6, 129.4, 128.5, 124.7, 124.2, 123.7, 121.9, 120.2, 40.9, 25.6, 21.7, 19.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{18}NO_3S_2$ $[M + H]^+$ 372.0723, found 372.0725.



3ak

(*R*)-4-Propyl-1-tosyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (3ak). White solid (32.8 mg, 82% yield, 98:2 er), m.p. 158–159 °C. HPLC (Daicel Chiralpak IB, *n*-hexane/EtOAc = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 4.2 (major), t_R = 7.2 min (minor); 98:2 er. $[\alpha]_D^{25}$ = +64.5° (*c* = 1.73, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H, ArH), 7.79 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (d, *J* = 7.6 Hz, 1H, ArH), 7.40 – 7.29 (m, 4H, ArH), 3.20 – 3.15 (m, 1H, CH), 2.85 (dd, J_1 = 15.2 Hz, J_2 = 6.4 Hz, 1H, CH_2), 2.58 (dd, J_1 = 15.4 Hz, J_2 = 1.8 Hz, 1H, CH_2), 2.42 (s, 3H, CH_3) 1.29 – 1.07 (m, 4H, CH_2), 0.70 (t, *J* = 7.0 Hz, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 145.6, 137.0, 135.2, 134.7, 134.0, 129.4, 128.6, 124.6, 124.2, 123.7, 121.9, 120.7, 39.5, 36.5, 30.7, 21.6, 20.1, 13.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{22}NO_3S_2$ $[M + H]^+$ 400.1036, found 400.1032.

4. Synthetic procedure and the characterization data of compounds 4–6

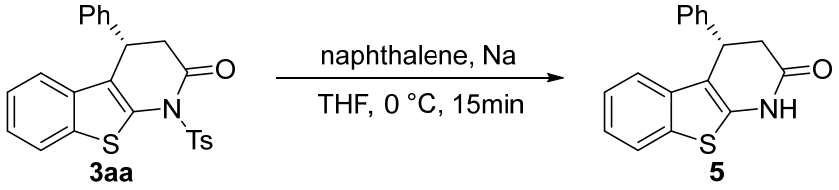


3aa **4**

To solution of **3aa** (43.4 mg, 0.1 mmol) in dry MeOH (5 mL) followed by Mg powder (12.0

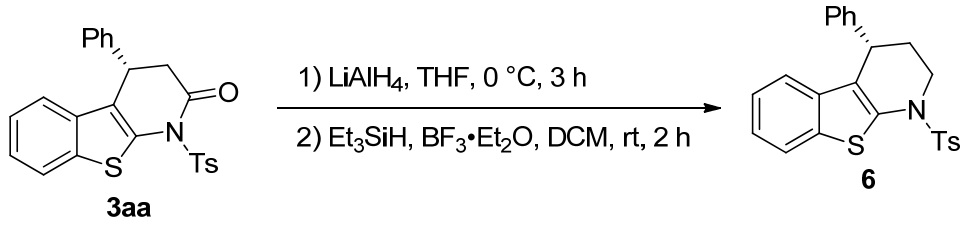
mg, 0.5 mmol) was added, and the resulting suspension was stirred at room temperature for 6 h. Then the mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford compound **4**.

Methyl (*S*)-3-(2-((4-methylphenyl)sulfonamido)benzo[*b*]thiophen-3-yl)-3-phenyl-propanoate (4). White solid (41.9 mg, 90% yield, 96:4 er), m.p. 88–90 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 80:20, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.3 (major), t_R = 22.8 min (minor); 96:4 er. $[\alpha]_D^{25}$ = +125.5° (*c* = 1.58, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H, NH), 7.82 (d, *J* = 8.0 Hz, 2H, ArH), 7.67 (d, *J* = 8.0 Hz, 1H, ArH), 7.20 – 7.16 (m, 3H, ArH), 7.12 – 7.01 (m, 5H, ArH), 6.67 (d, *J* = 7.2 Hz, 2H, ArH), 4.66 (dd, J_1 = 11.2 Hz, J_2 = 3.6 Hz, 1H, CH_2), 3.62 (s, 3H, CH_3), 3.28 (dd, J_1 = 16.8 Hz, J_2 = 3.6 Hz, 1H, CH_2), 3.11 (dd, J_1 = 16.8 Hz, J_2 = 11.2 Hz, 1H, CH_2), 2.35 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 144.0, 139.6, 137.3, 136.4, 135.4, 134.8, 129.8, 128.4, 128.2, 127.5, 126.9, 126.5, 124.1, 123.9, 122.7, 122.4, 52.3, 36.9, 35.9, 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{24}NO_4S_2$ $[M + H]^+$ 466.1141, found 66.1139.



To solution of naphthalene (128.2 mg, 1.0 mmol) in dry THF (5 mL) and cooled to 0 °C under argon atmosphere, Na (23.0 mg, 1.0 mmol) was added, and the resulting suspension was stirred at 0 °C for 1 h, and the solution turned dark green. Then, **3aa** (86.7 mg, 0.2 mmol) was added to the solution and the reaction was stirred at 0 °C for 15 min. Then H_2O (10 mL) was added and extracted with DCM (3 × 10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 to 2:1) to afford compound **5**.

(*S*)-4-Phenyl-3,4-dihydrobenzo[4,5]thieno[2,3-*b*]pyridin-2(1*H*)-one (5). Yellow solid (18.4mg, 33% yield, 95:5 er). m.p. 219–221 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.7 (major), t_R = 9.4 min (minor); 95:5 er. $[\alpha]_D^{25}$ = +142.2° (*c* = 1.93, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H, NH), 7.71 – 7.69 (m, 1H, ArH), 7.30 – 7.28 (m, 2H, ArH), 7.24 – 7.17 (m, 6H, ArH), 4.50 (dd, J_1 = 7.8 Hz, J_2 = 3.8 Hz, 1H, CH), 3.22 (dd, J_1 = 16.4 Hz, J_2 = 8.0 Hz, 1H, CH_2), 2.96 (dd, J_1 = 16.4 Hz, J_2 = 4.0 Hz, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 141.6, 137.3, 137.0, 133.8, 129.0, 127.3, 127.0, 125.0, 123.1, 122.5, 120.6, 114.4, 39.5, 37.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{14}NOS$ $[M + H]^+$ 280.0791, found 280.0789.



To solution of **3aa** (43.4 mg, 0.1 mmol) in dry THF (5 mL) and cooled to 0 °C under argon atmosphere, $LiAlH_4$ (0.2 mmol, 7.6 mg) was added, and the resulting suspension was stirred at 0 °C for 3 h. Then quenched with water (10 mL) and extracted with DCM (3 × 10 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. In the next step, the residue was dissolved in dry DCM, Et_3SiH (23.2 mg, 0.2 mmol) and $BF_3 \cdot OEt_2$ (21.3 mg, 0.15 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. Then quenched with trace water and concentrated. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford compound **6**.

(*S*)-4-Phenyl-1-tosyl-1,2,3,4-tetrahydrobenzo[4,5]thieno[2,3-*b*]pyridine (6). White solid (34.8 mg, 83% yield, 95:5 er). m.p. 80–82 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 60:40, flow rate 1.0 mL/min, detection at 254 nm): t_R = 5.3 (minor), t_R = 5.7 min (major); 95:5 er. $[\alpha]_D^{25}$ = +18.1° (*c* = 1.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.4 Hz, 2H, ArH), 7.65 (d, *J* = 8.0 Hz, 1H, ArH), 7.16 – 7.12 (m, 3H, ArH), 7.10 – 7.05 (m, 3H, ArH), 6.98 – 6.96 (m, 2H, ArH), 6.67 (dd, J_1 = 7.0 Hz, J_1 = 1.4 Hz, 2H, ArH), 4.43 (dd, J_1 = 12.4 Hz, J_2 = 4.4 Hz, 1H, CH), 3.89 – 3.85 (m, 1H, CH_2), 3.21 (td, *J* = 11.4 Hz, J_2 = 2.7 Hz, 1H, CH_2), 2.59 – 2.51 (m, 1H, CH_2), 2.33 (s, 3H, CH_3), 2.17 – 2.10 (m, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.4, 137.4, 136.1, 135.7, 134.7, 129.9, 128.4, 128.0, 127.5, 127.2, 126.0, 124.0, 123.7, 123.1, 122.3, 60.1, 36.7, 32.2, 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{22}NO_2S_2$ $[M + H]^+$ 420.1086, found 420.1028.

5. Crystal data and structure refinement

Crystal data and structure refinement for 3fa

Identification code	1_a (CCDC 2180150)
Empirical formula	$C25H_{21}NO_3S_2$
Formula weight	447.55
Temperature/K	296(2)
Wavelength/Å	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	6.4600(17)
b/Å	13.975(4)
c/Å	24.315(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2195.2(10)
Z	4
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	0.270
F(000)	936
Crystal size/mm^3	0.200 × 0.200 × 0.200
Completeness to theta = 25.117°	99.7 %
Θ range for data collection/°	2.905 to 25.117
Index ranges	$-7 \le h \le 6$, $-16 \le k \le 16$, $-26 \le l \le 28$
Reflections collected	25109
Independent reflections	3905 [$R_{(int)}$ = 0.1295]
Data/restraints/parameters	3905/0/246
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.1646, wR_2 = 0.1811
Largest diff. peak/hole / e Å^{-3}	0.233/-0.318
Absolute structure parameter	-0.10(8)

6. Reference

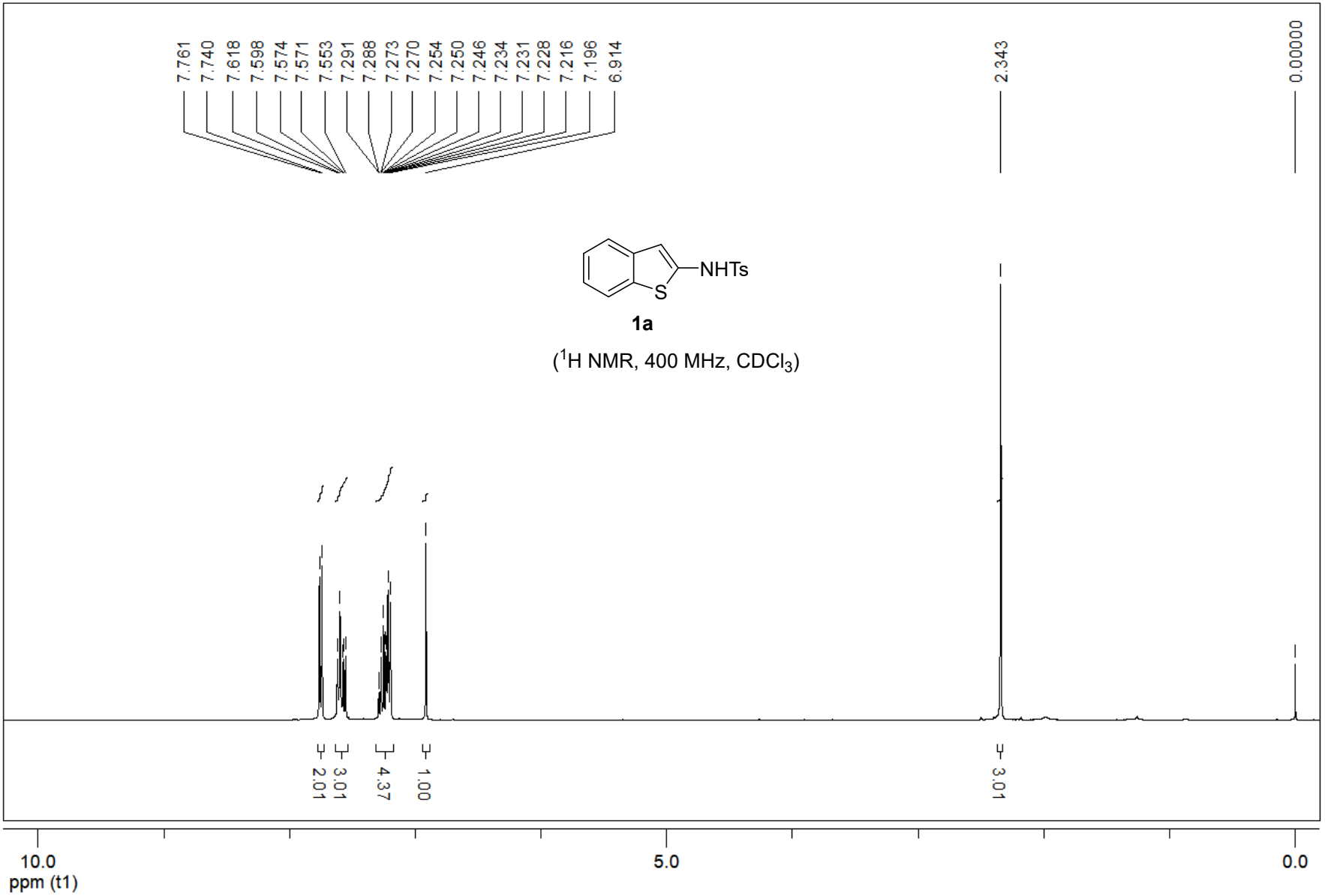
[1] E. R. T. Robinson, C. Fallan, C. Simal, A. M. Z. Slawin and A. D. Smith, Anhydrides as α, β-unsaturated acyl ammonium precursors: isothiourea-promoted catalytic asymmetric annulation processes, *Chem. Sci.*, 2013, **4**, 2193-2200. b) E. R. T. Robinson, D. M. Walden, C. Fallan, M. D. Greenhalgh, P. H.-Y. Cheong and A. D. Smith, Non-bonding 1,5-S…O interactions govern chemo- and enantioselectivity in isothiourea-catalyzed annulations of benzazoles, *Chem. Sci.*, 2016, **7**, 6919-6927.

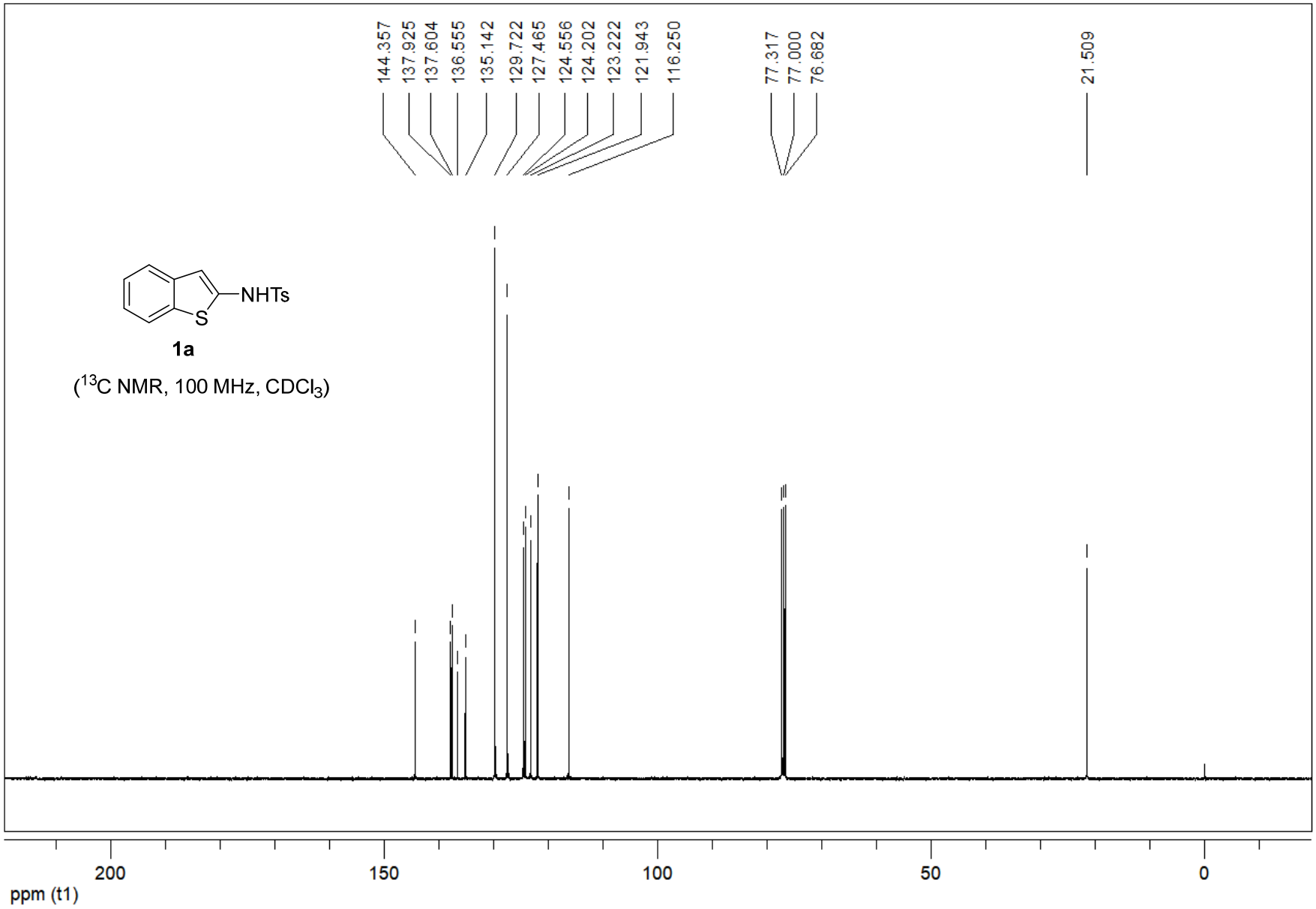
[2] a) L. C. Morrill, J. Douglas, T. Lebl, A. M. Z. Slawin, D. J. Fox and A. D. Smith, Isothiourea-mediated asymmetric Michael-lactonisation of trifluoromethylenones: a synthetic and mechanistic study, *Chem. Sci.*, 2013, **4**, 4146-4155. b) Y. Fukata, K. Asano and S. Matsubara, Facile net cycloaddition approach to optically active 1,5-benzothiazepines, *J. Am. Chem. Soc.*, 2015, **137**, 5320-5323. c) N. R. Guha, R. M. Neyyappadath, M. D. Greenhalgh, R. Chisholm, S. M. Smith, M. L. McEvoy, C. M. Young, C. Rodríguez-Escrich, M. A. Pericàs, G. Hähner and A. D. Smith, Evaluating polymer-supported isothiourea catalysis in industrially-preferable solvents for the acylative kinetic resolution of secondary and tertiary heterocyclic alcohols in batch and flow, *Green Chem.*, 2018, **20**, 4537-4546.

[3] a) C. Galvez, F. Garcia, M. Veiga and P. Viladoms, A convenient preparation of haloaminobenzo[*b*]thiophene derivatives, *Synthesis-Stuttgart*, 1983, 932-933. b) J. K. Augustine, A. Bombrun, A. B. Mandal, P. Alagarsamy, R. N. Atta and P. Selvam, Propylphosphonic anhydride (T3P®)-mediated one-pot rearrangement of carboxylic acids to carbamates, *Synthesis-Stuttgart*, 2011, 1477-1483.

[4] H. Liu, A. M. Z. Slawin and A. D. Smith, Isothiourea-Catalyzed Enantioselective Synthesis of Tetrahydro-alpha-carbolinones, *Org. Lett.*, 2020, **22**, 1301-1305.

7. Copies of ^{1}H and ^{13}C NMR spectra of new compounds

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137.604
136.555
135.142
129.722
127.465
124.556
124.202
123.222
121.943
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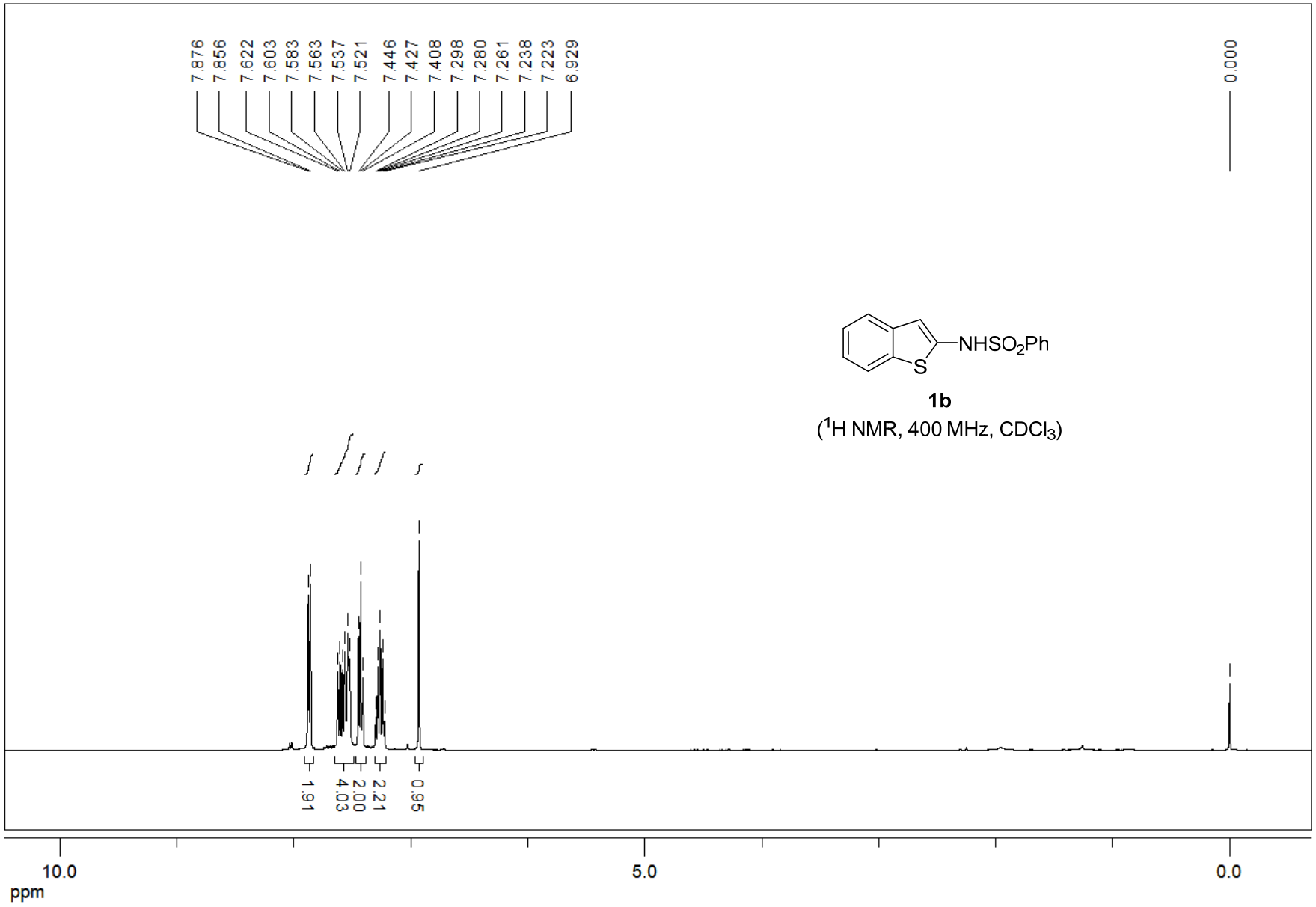
77.317
77.000
76.682
21.509
NHTs
S
1a
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)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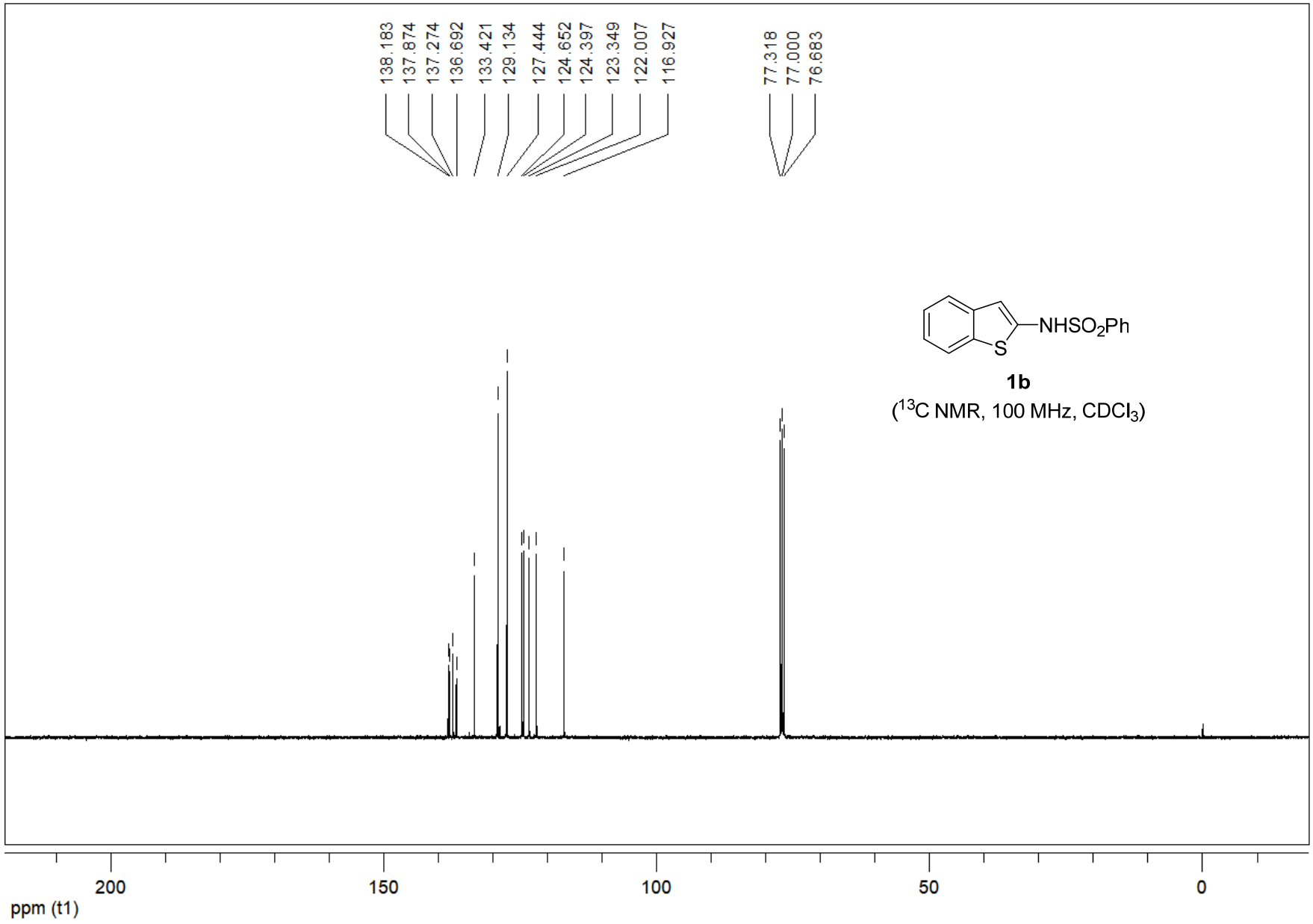
7.856
7.622
7.603
7.583
7.563
7.537
7.521
7.446
7.427
7.408
7.298
7.280
7.261
7.238
7.223
6.929
0.000
NHSO2Ph
S
1b
(1H NMR, 400 MHz, CDCl3)
1.91
4.03
2.00
2.21
0.95
10.0
5.0
0.0
ppm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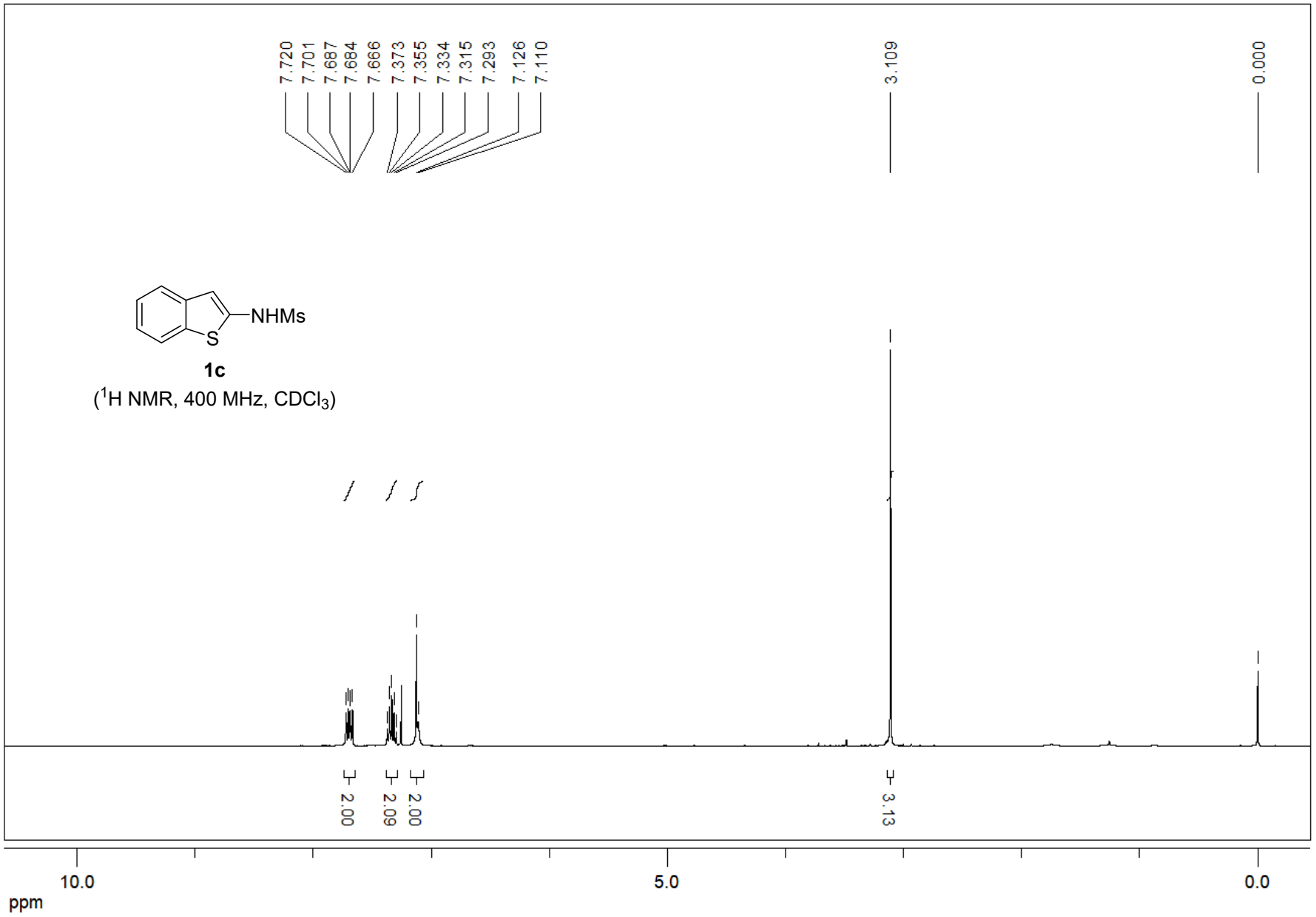
137.874
137.274
136.692
133.421
129.134
127.444
124.652
124.397
123.349
122.007
116.927
77.318
77.000
76.683
NHSO2Ph
S
1b
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm (t1)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7.701
7.687
7.684
7.666
7.373
7.355
7.334
7.315
7.293
7.126
7.110
3.109
0.000
NHMs
S
1c
(1H NMR, 400 MHz, CDCl3)
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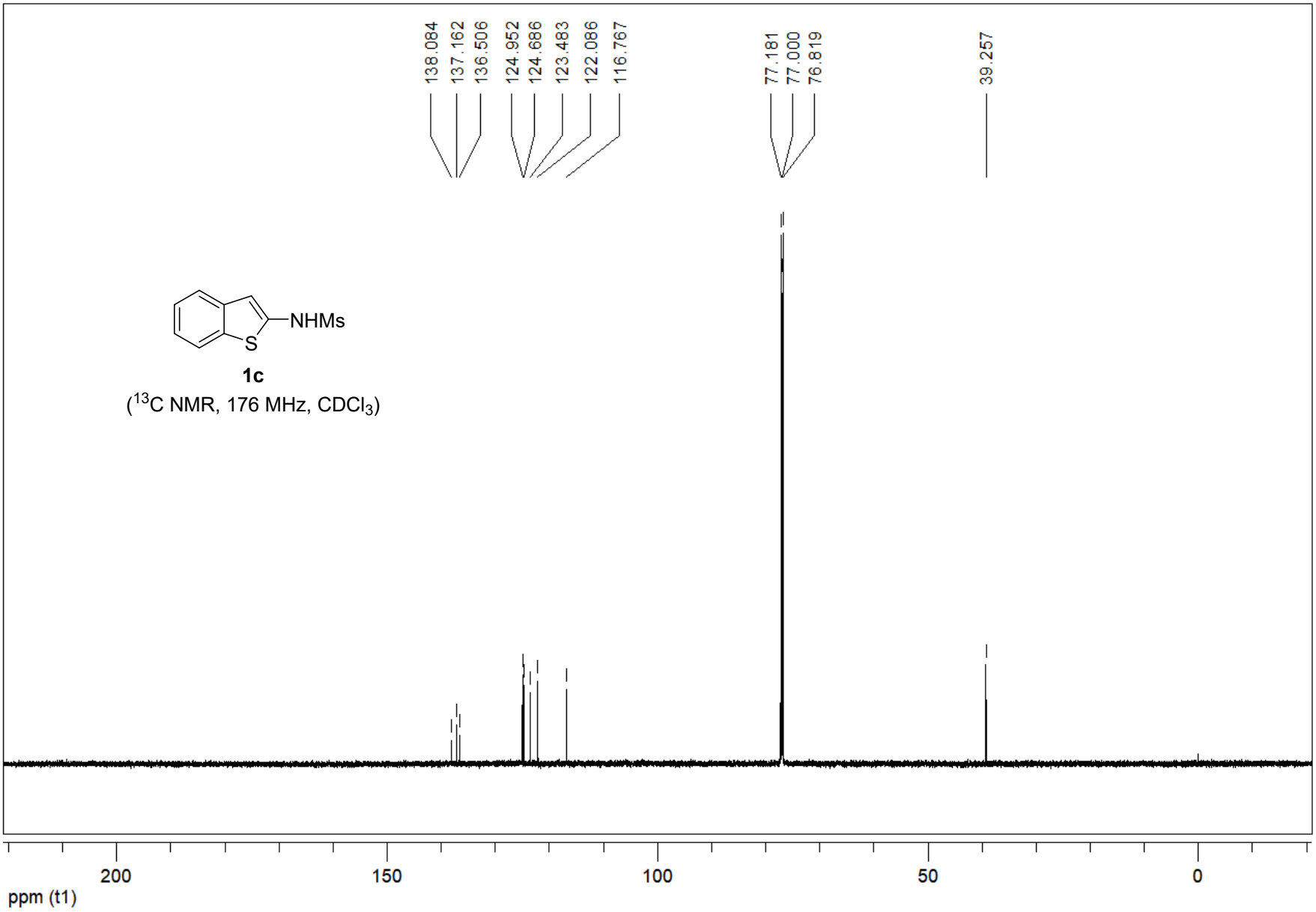
2.00
3.13
10.0
5.0
0.0
ppm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137.162
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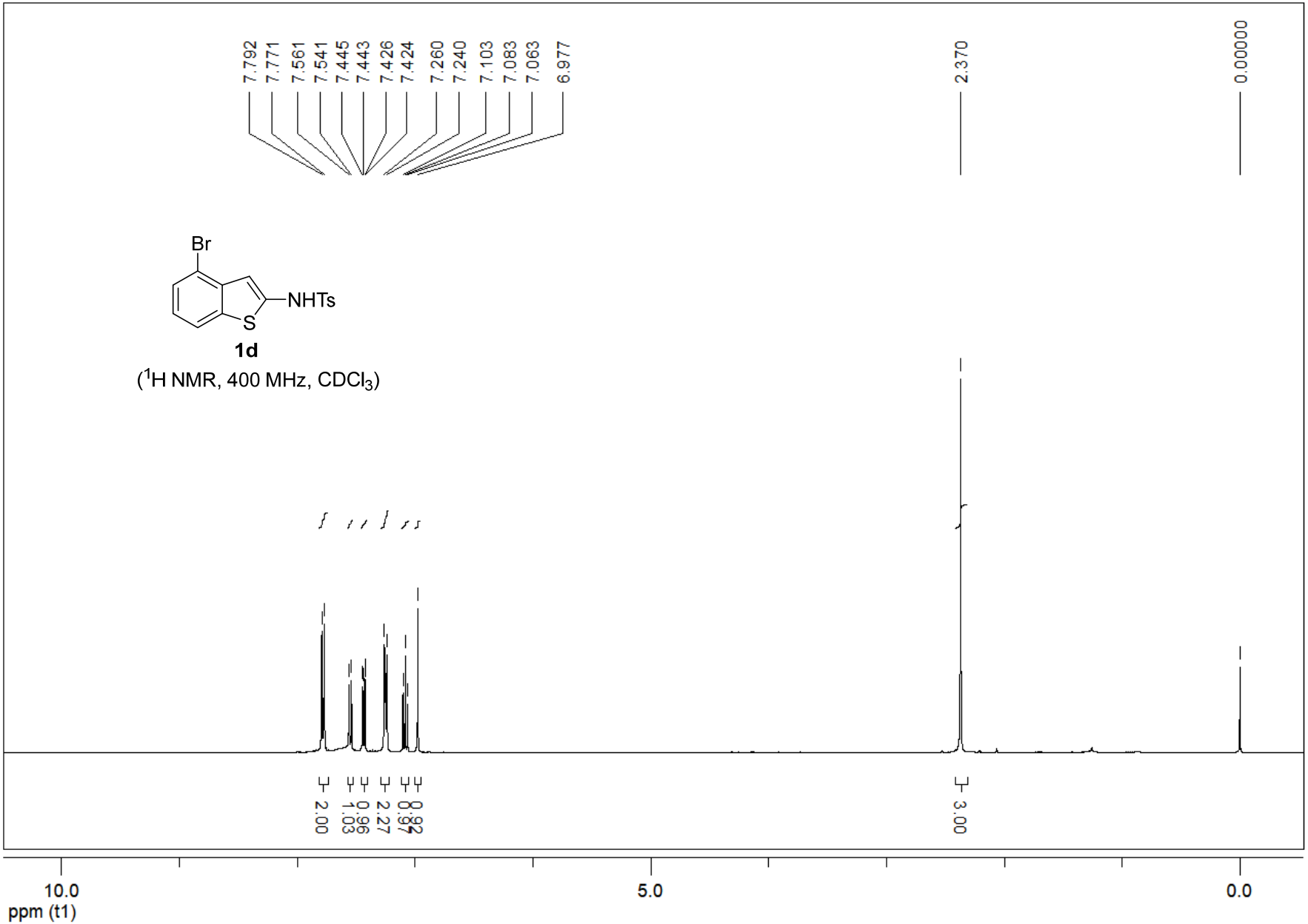
124.952
124.686
123.483
122.086
116.767
77.181
77.000
76.819
39.257
NHMs
S
1c
(^{13}C NMR, 176 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)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7.443
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7.424
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7.240
7.103
7.083
7.063
6.977
2.370
0.00000
Br
NHTs
S
1d
(1H NMR, 400 MHz, CDCl3)
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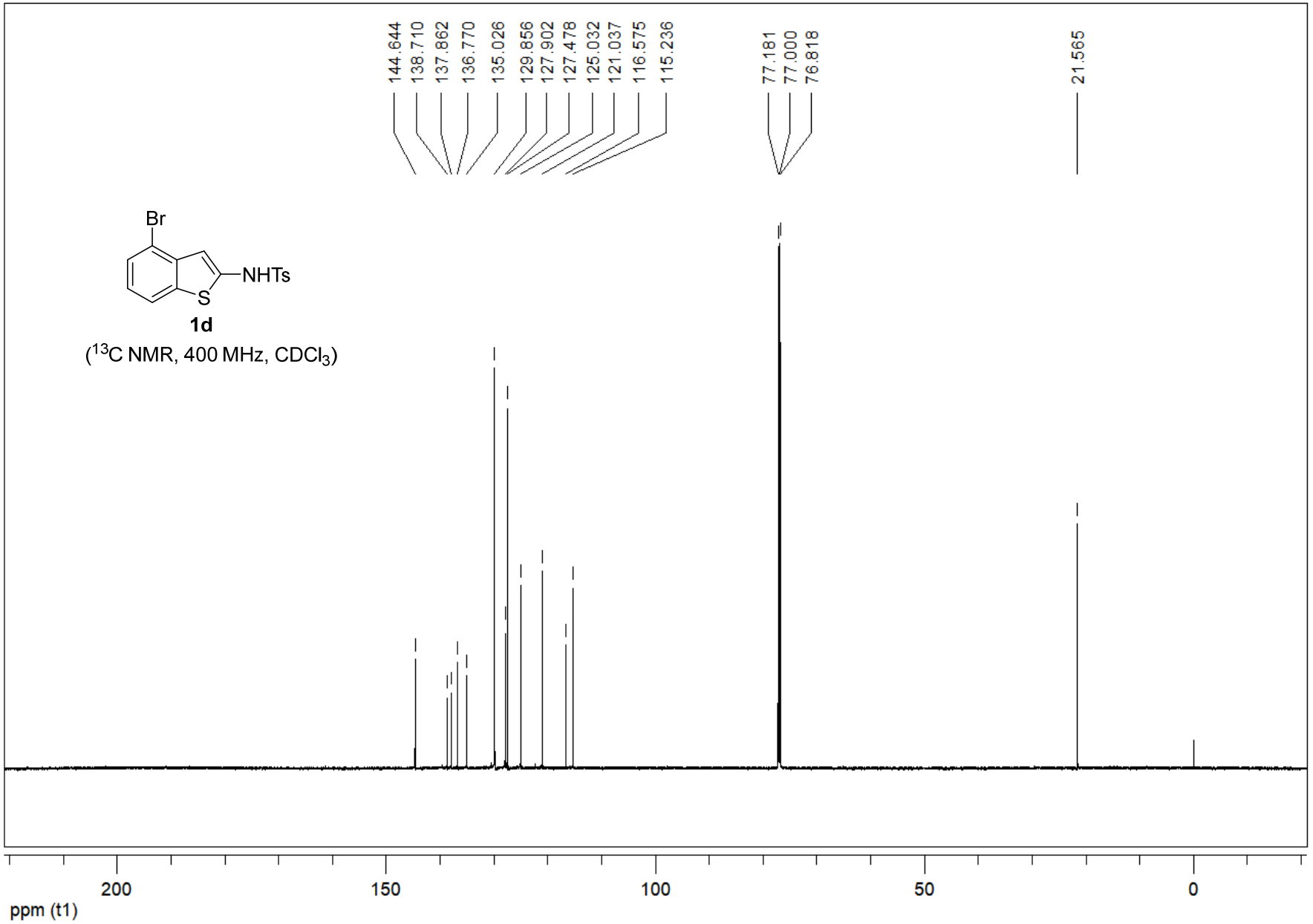
0.96
2.27
0.87
0.82
3.00
10.0
5.0
0.0
ppm (t1)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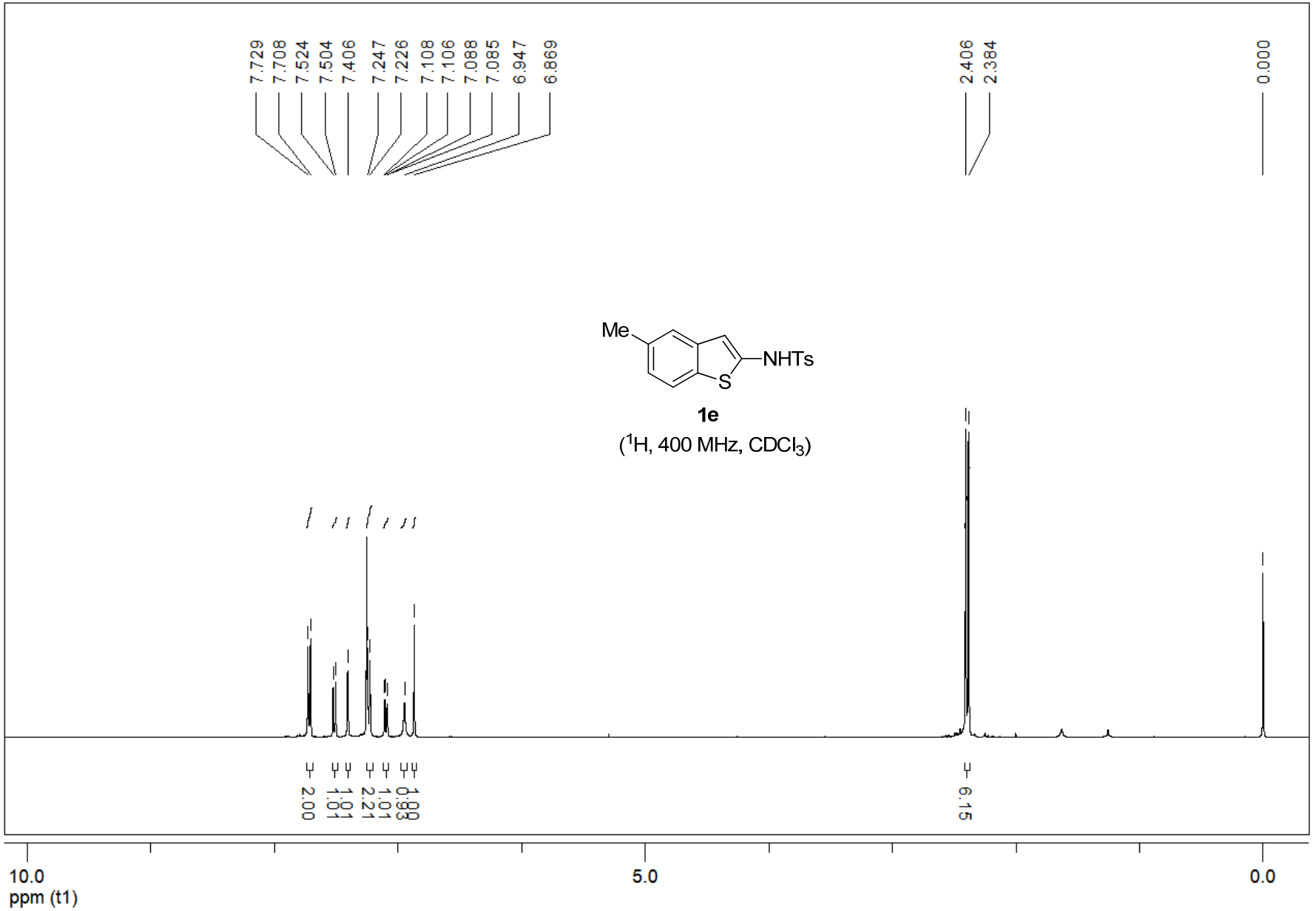
77.181
77.000
76.818
21.565
Br
NHTs
S
1d
(^{13}C NMR, 400 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)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7.524
7.504
7.406
7.247
7.226
7.108
7.106
7.088
7.085
6.947
6.869
2.406
2.384
0.000
Me
NHTs
S
1e
(1H, 400 MHz, CDCl3)
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1.01
2.21
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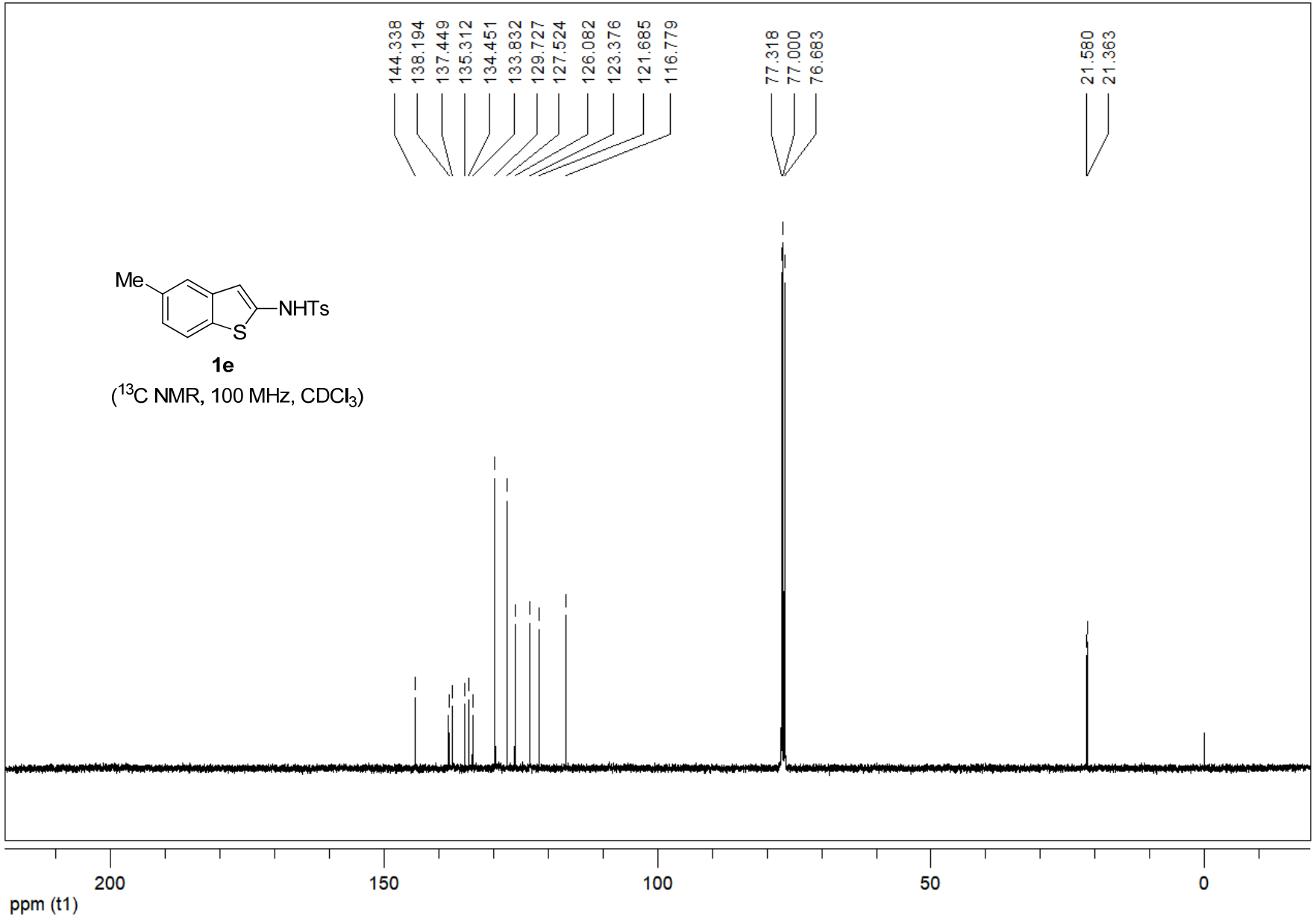
0.83
1.00
6.15
10.0
5.0
0.0
ppm (t1)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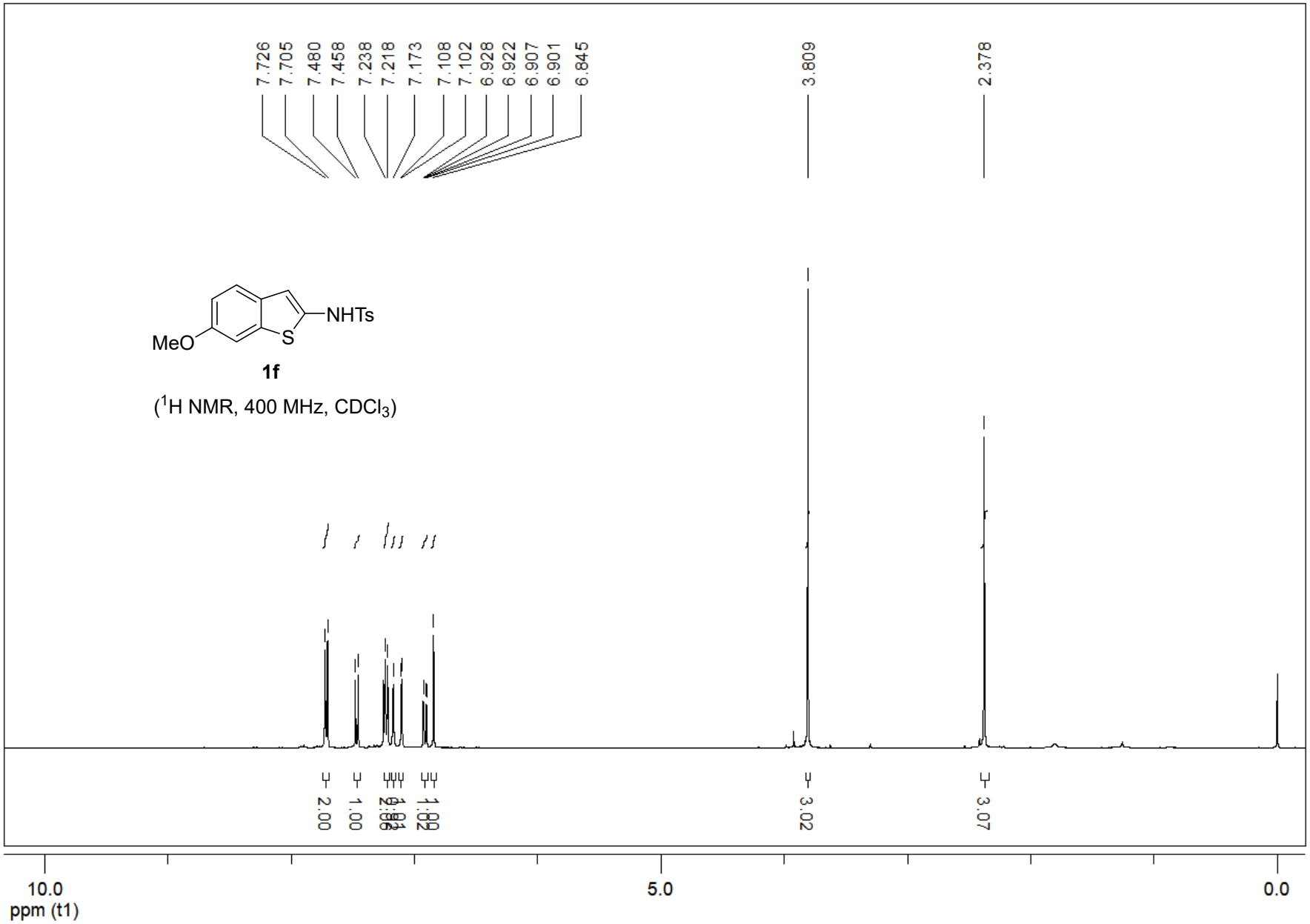
77.000
76.683
21.580
21.363
Me
NHTs
S
1e
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm (t1)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6.928
6.922
6.907
6.901
6.845
3.809
2.378
NHTs
MeO
S
1f
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1.00
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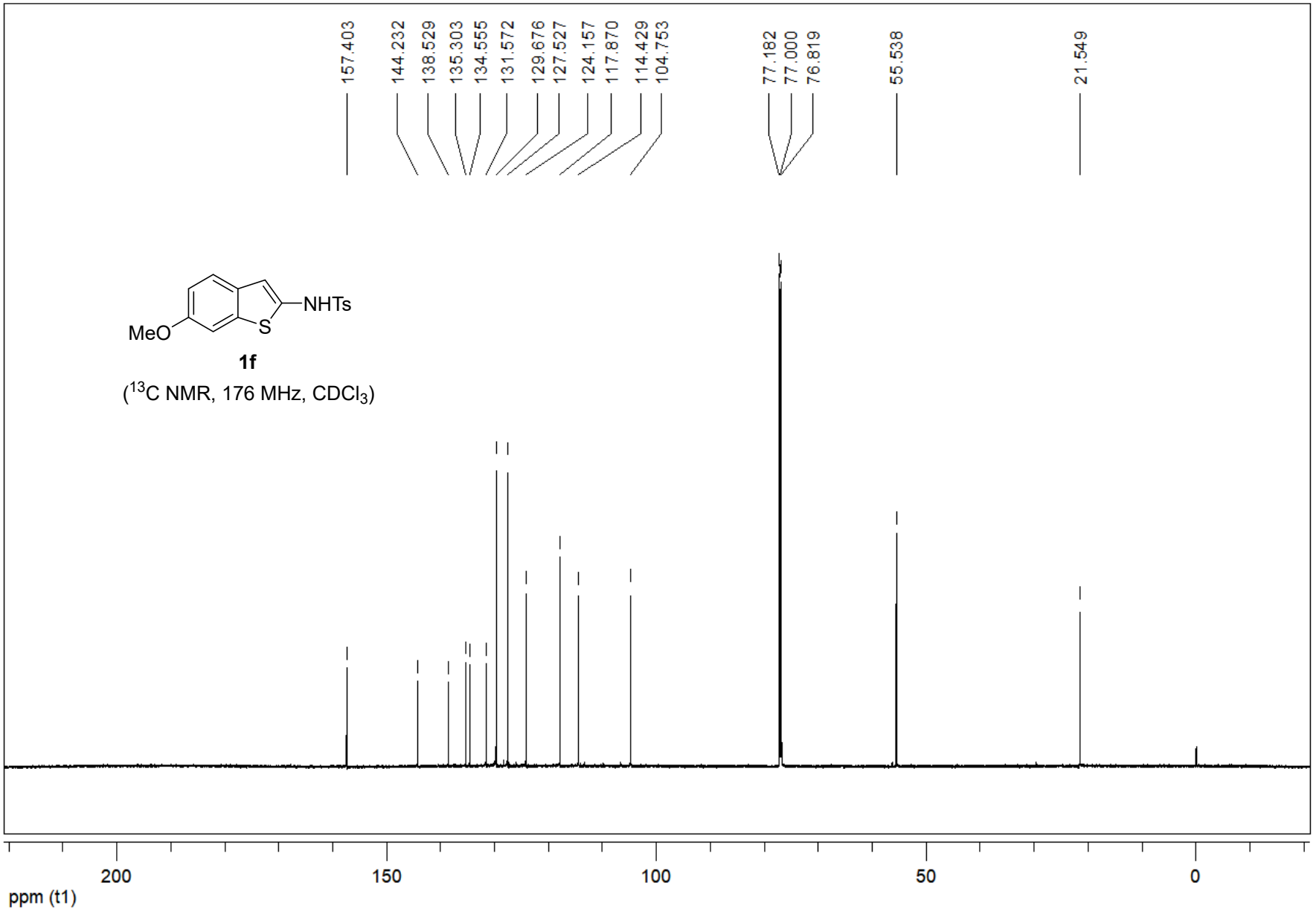
3.02
3.07
10.0
ppm (t1)
5.0
0.0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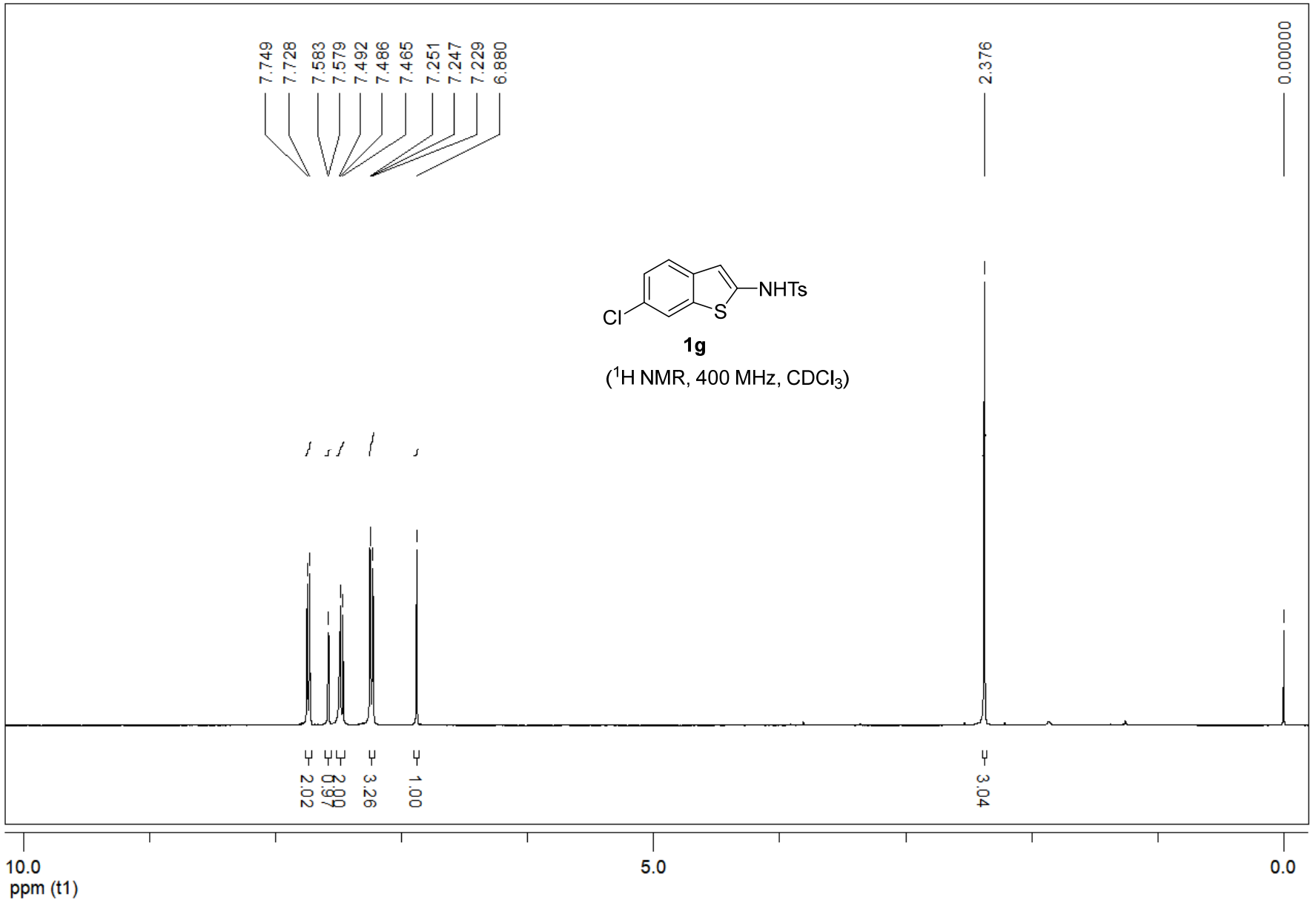
114.429
104.753
77.182
77.000
76.819
55.538
21.549
NHTs
MeO
S
1f
(^{13}C NMR, 176 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)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7.247
7.229
6.880
2.376
0.00000
NHTs
Cl
S
1g
(1H NMR, 400 MHz, CDCl3)
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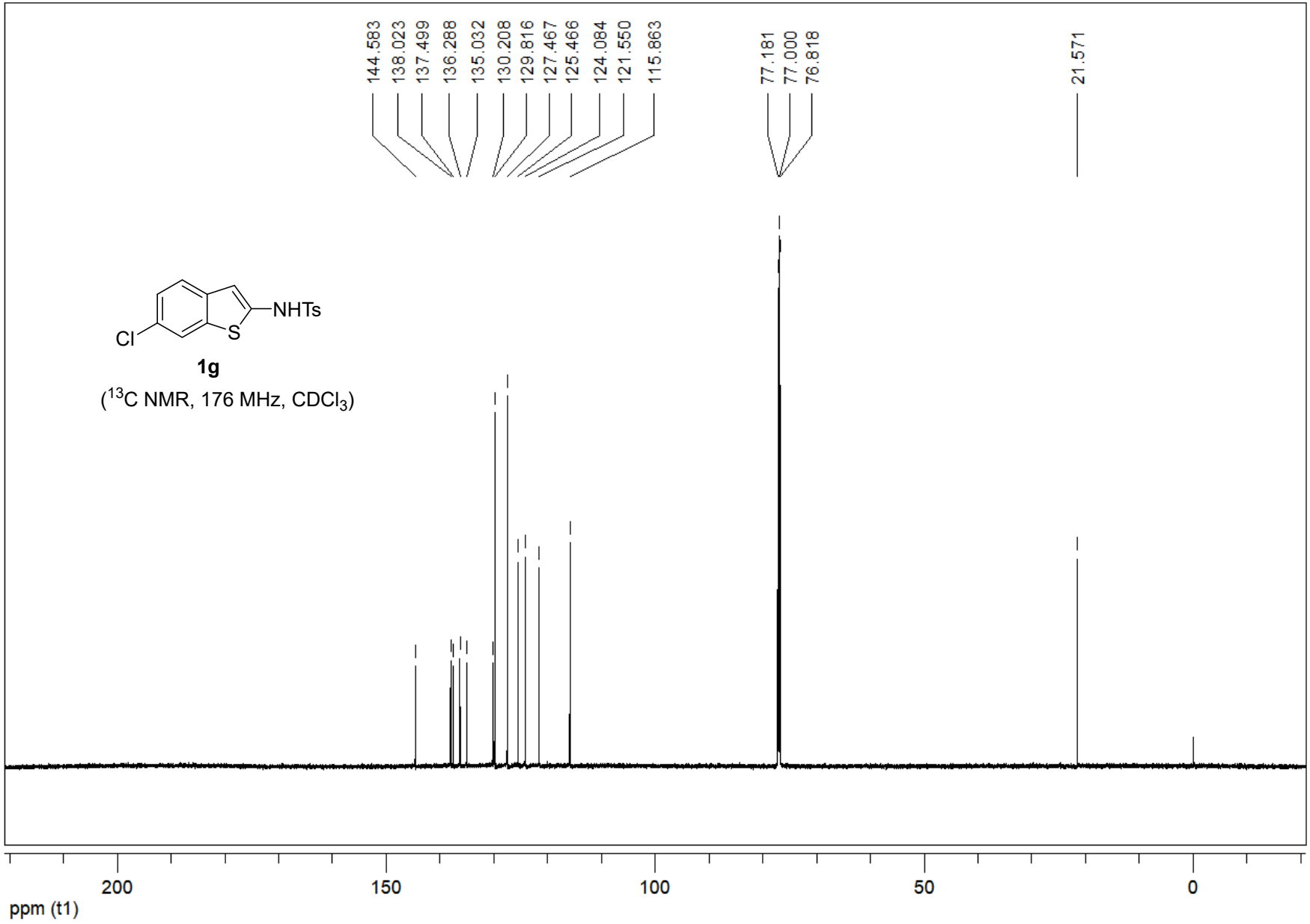
0.97
0.99
3.26
1.00
3.04
10.0
ppm (t1)
5.0
0.0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124.084
121.550
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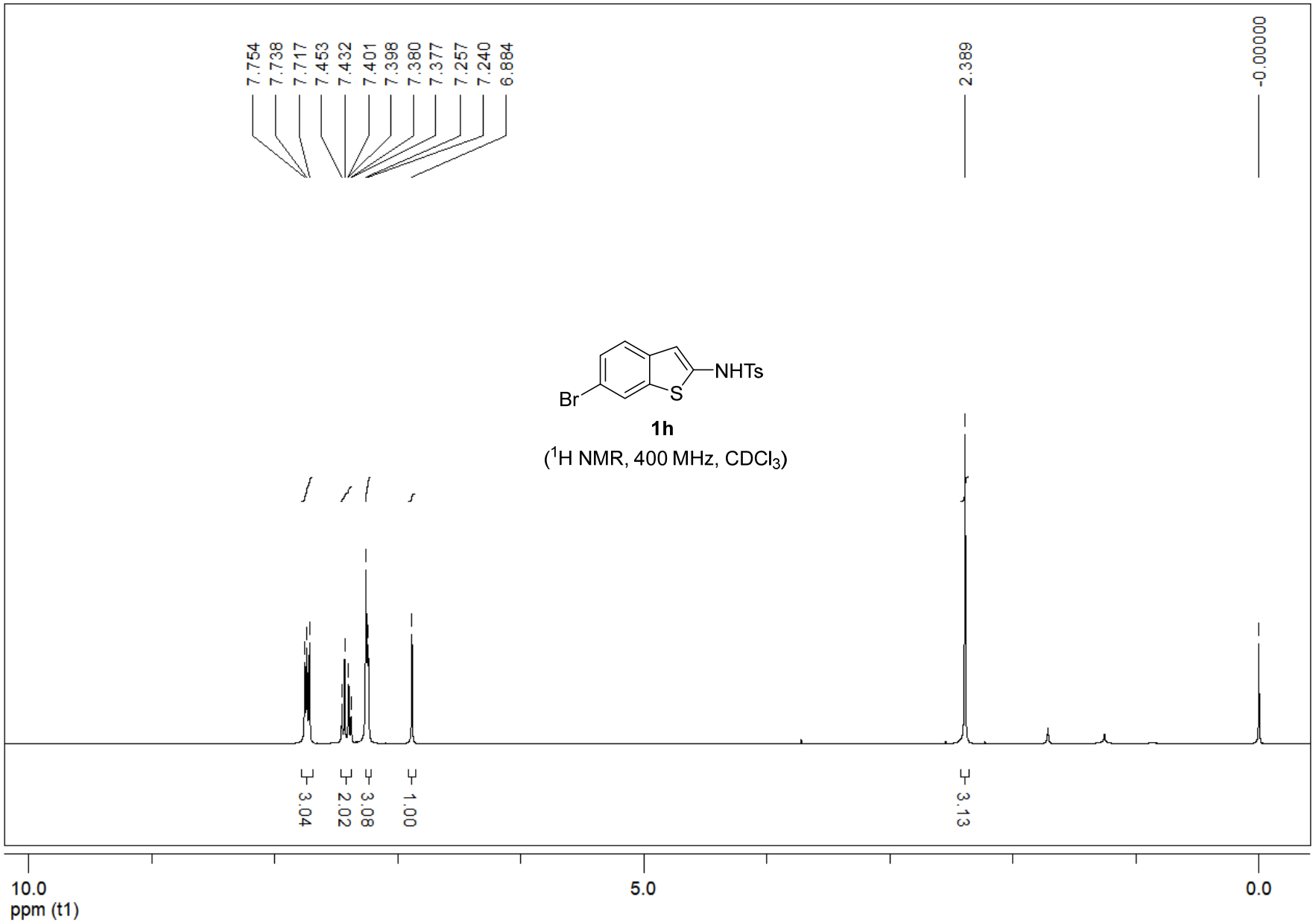
77.181
77.000
76.818
21.571
NHTs
Cl
S
1g
(13C NMR, 176 MHz, CDCl3)
200
150
100
50
0
ppm (t1)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7.257
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-0.00000
NHTs
Br
S
1h
(1H NMR, 400 MHz, CDCl3)
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3.08
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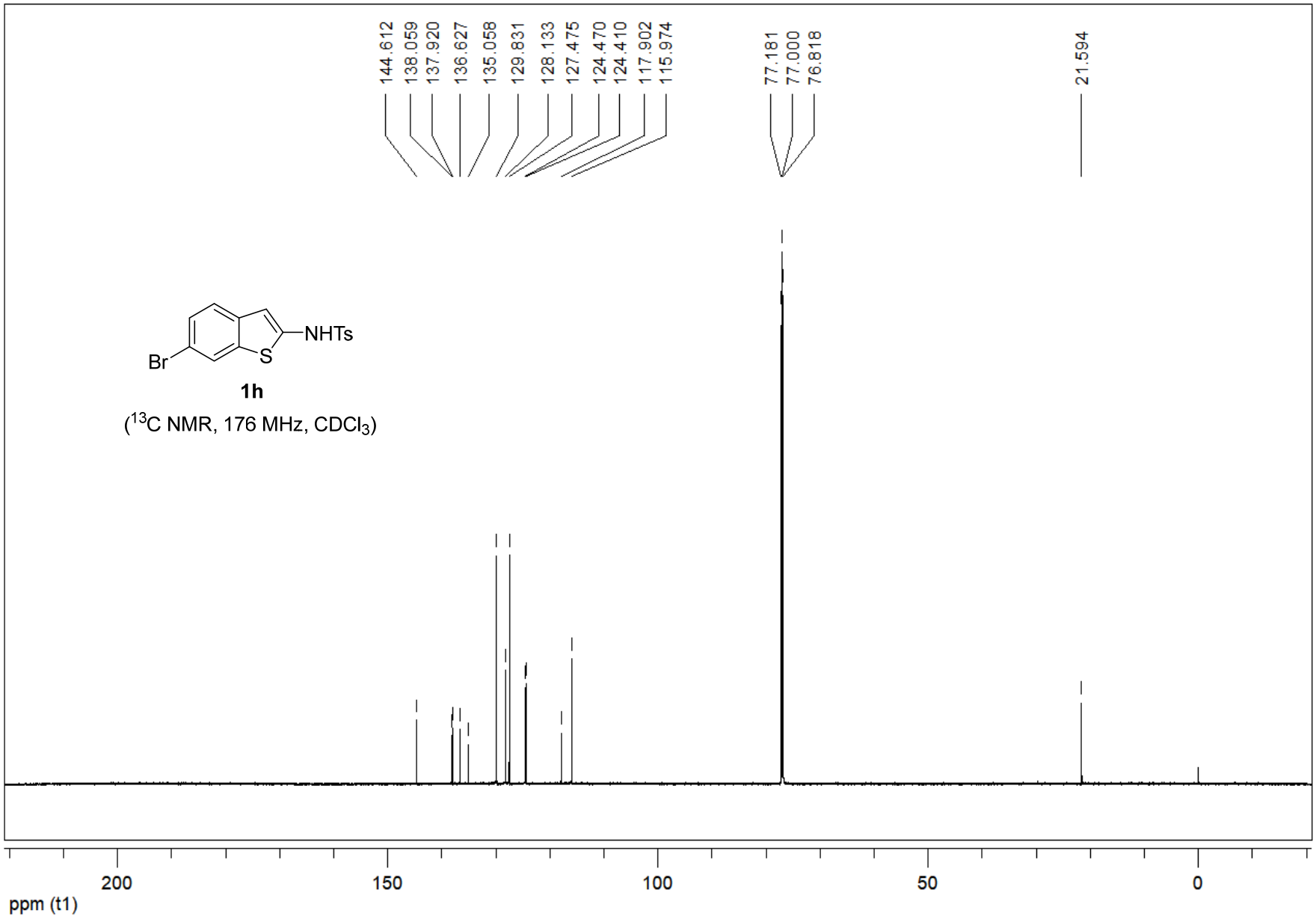
3.13
10.0
ppm (t1)
5.0
0.0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127.475
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124.410
117.902
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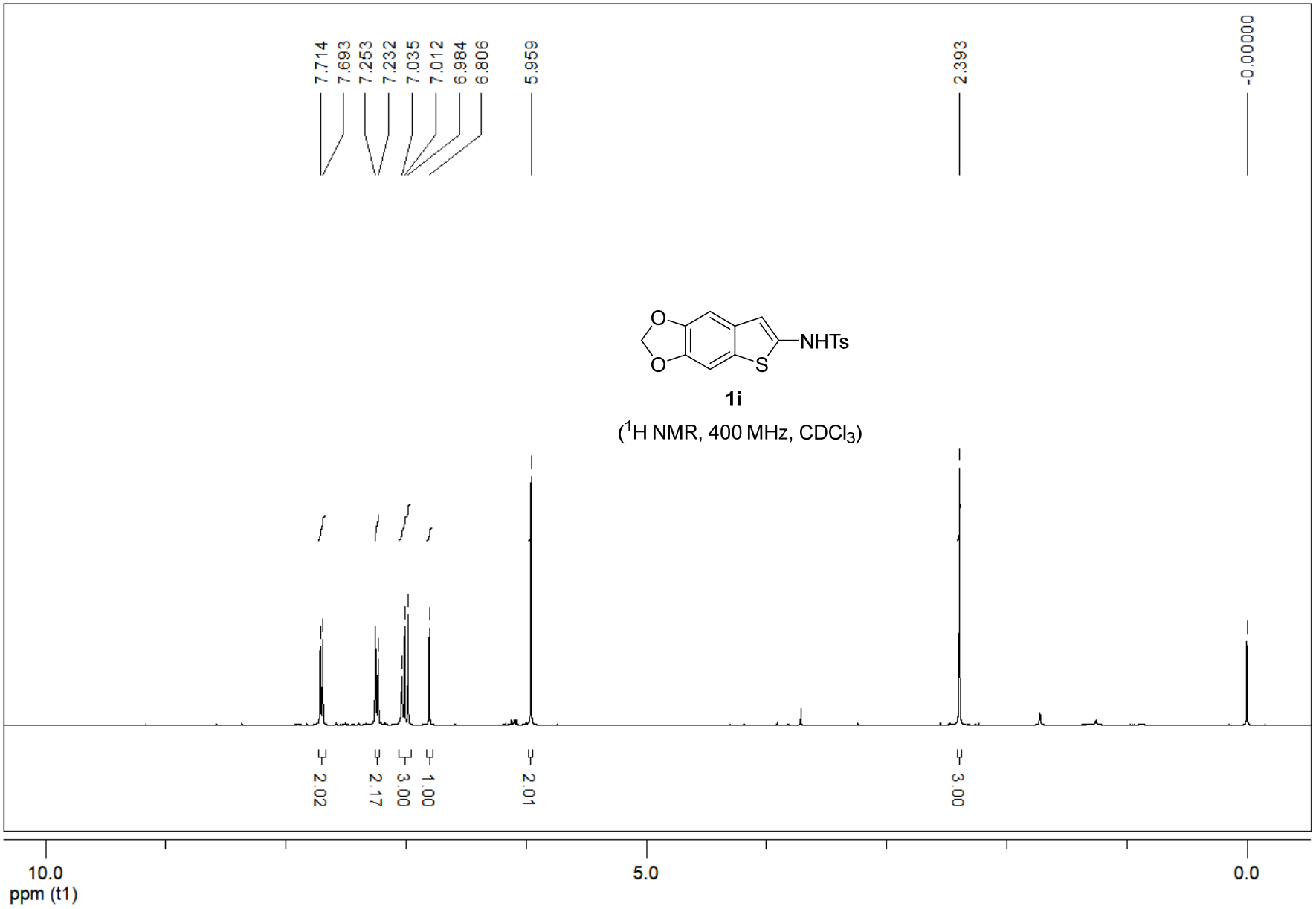
77.181
77.000
76.818
21.594
NHTs
Br
S
1h
(13C NMR, 176 MHz, CDCl3)
200
150
100
50
0
ppm (t1)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7.012
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6.806
5.959
2.393
-0.00000
NHTs
1i
(1H NMR, 400 MHz, CDCl3)
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2.17
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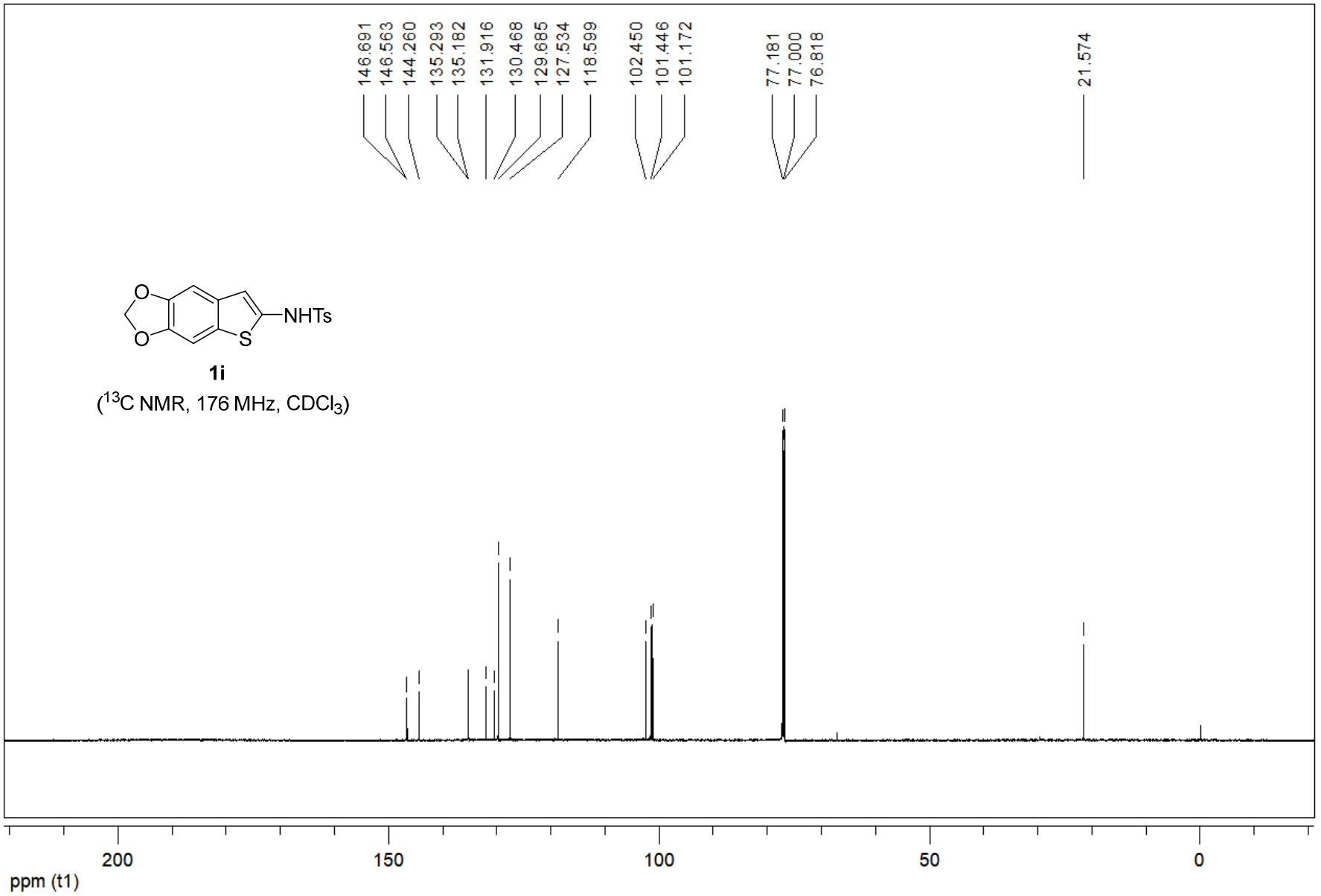
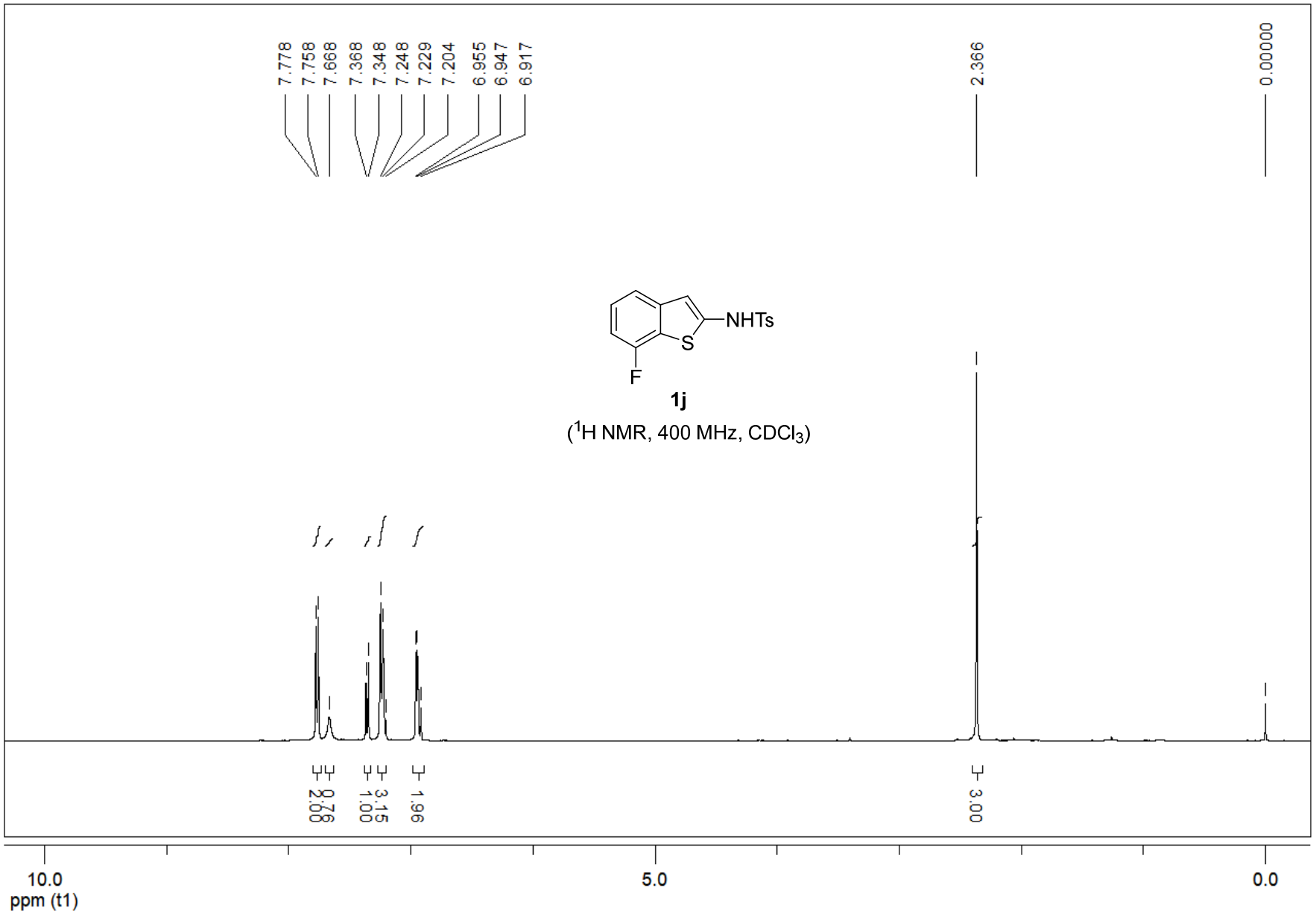
1.00
2.01
3.00
10.0
ppm (t1)
5.0
0.0



1i

(^{13}C NMR, 176 MHz, $CDCl_3$)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7.368
7.348
7.248
7.229
7.204
6.955
6.947
6.917
2.366
0.00000
NHTs
S
F
1j
(1H NMR, 400 MHz, CDCl3)
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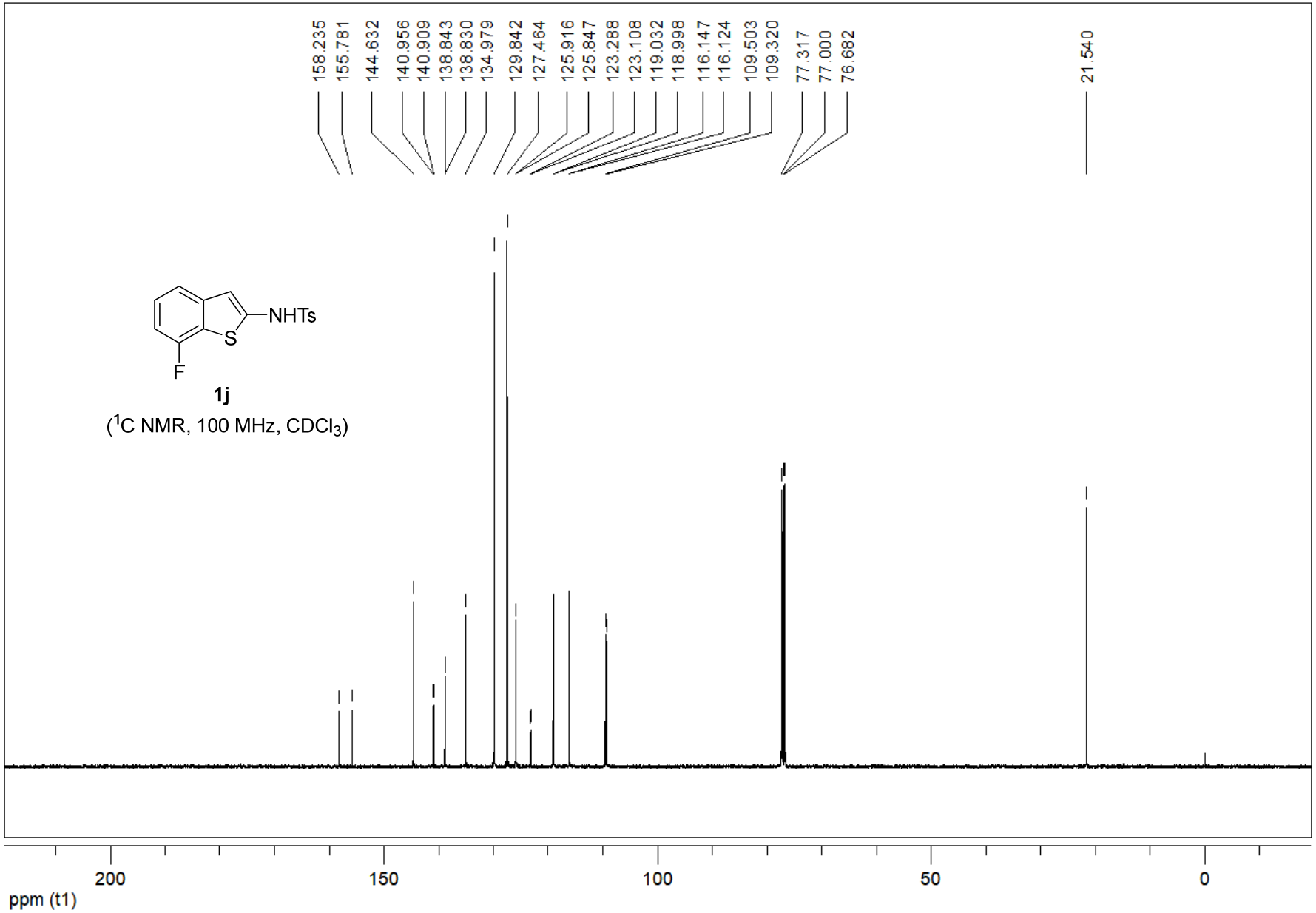
0.76
3.15
1.00
1.96
3.00
10.0
ppm (t1)
5.0
0.0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123.288
123.108
119.032
118.998
116.147
116.124
109.503
109.320
77.317
77.000
76.682
21.540
NHTs
S
F
1j
(1C NMR, 100 MHz, CDCl3)
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150
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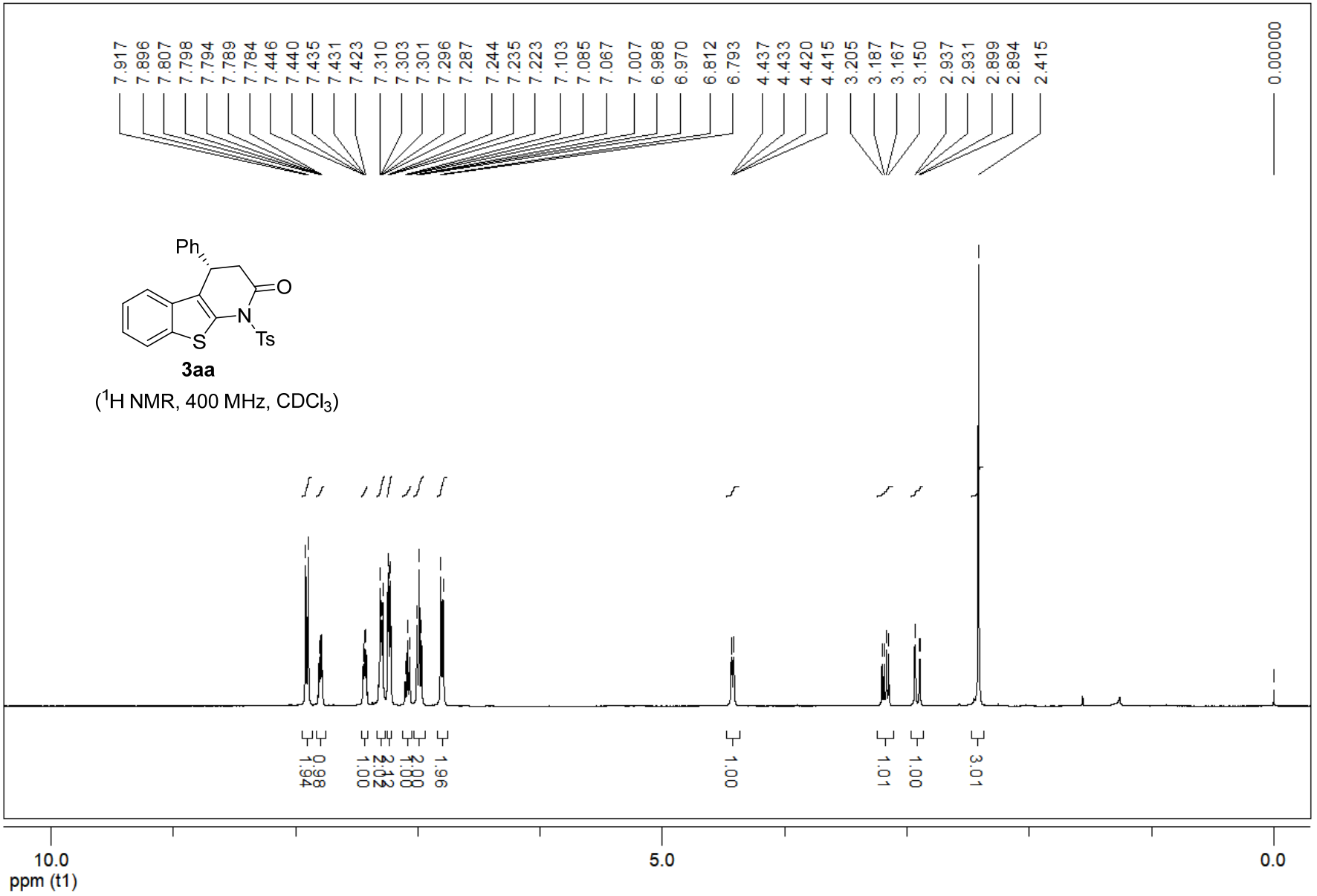
50
0
ppm (t1)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7.303
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4.420
4.415
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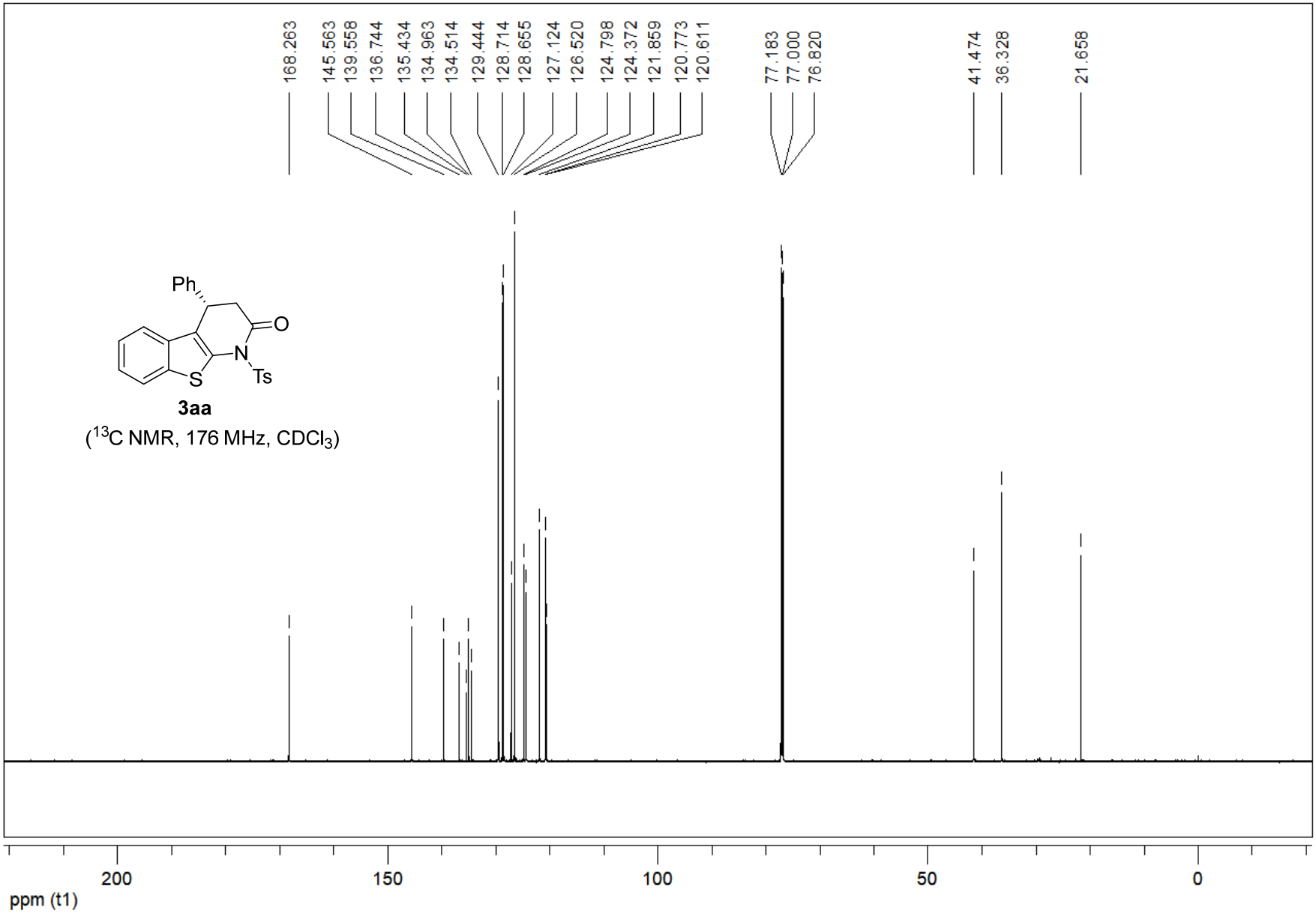
3.167
3.150
2.937
2.931
2.899
2.894
2.415
0.00000
Ph
O
N
Ts
S
3aa
(1H NMR, 400 MHz, CDCl3)
0.98
1.84
1.00
2.12
2.08
1.96
1.00
1.01
1.00
3.01
10.0
ppm (t1)
5.0
0.0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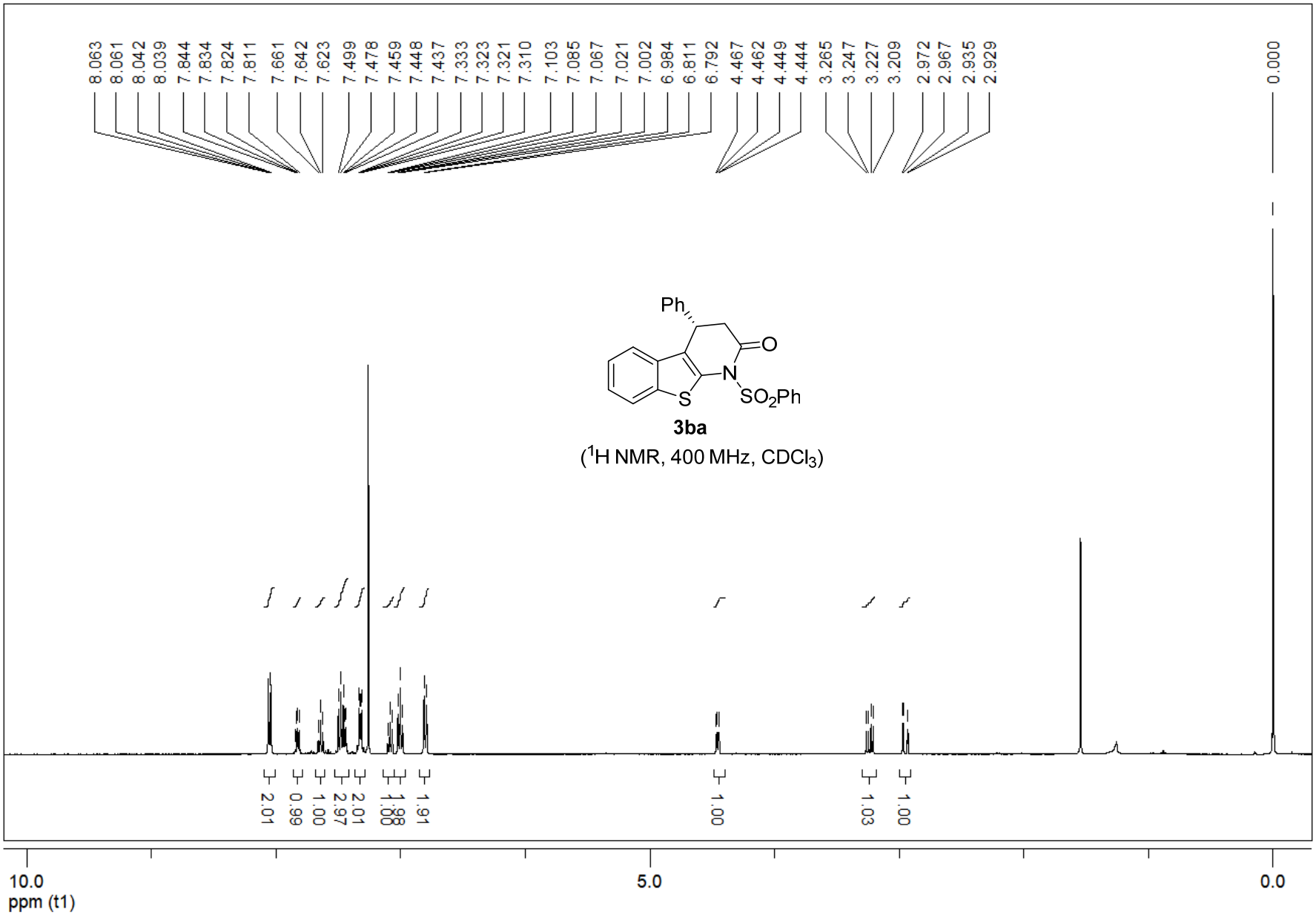
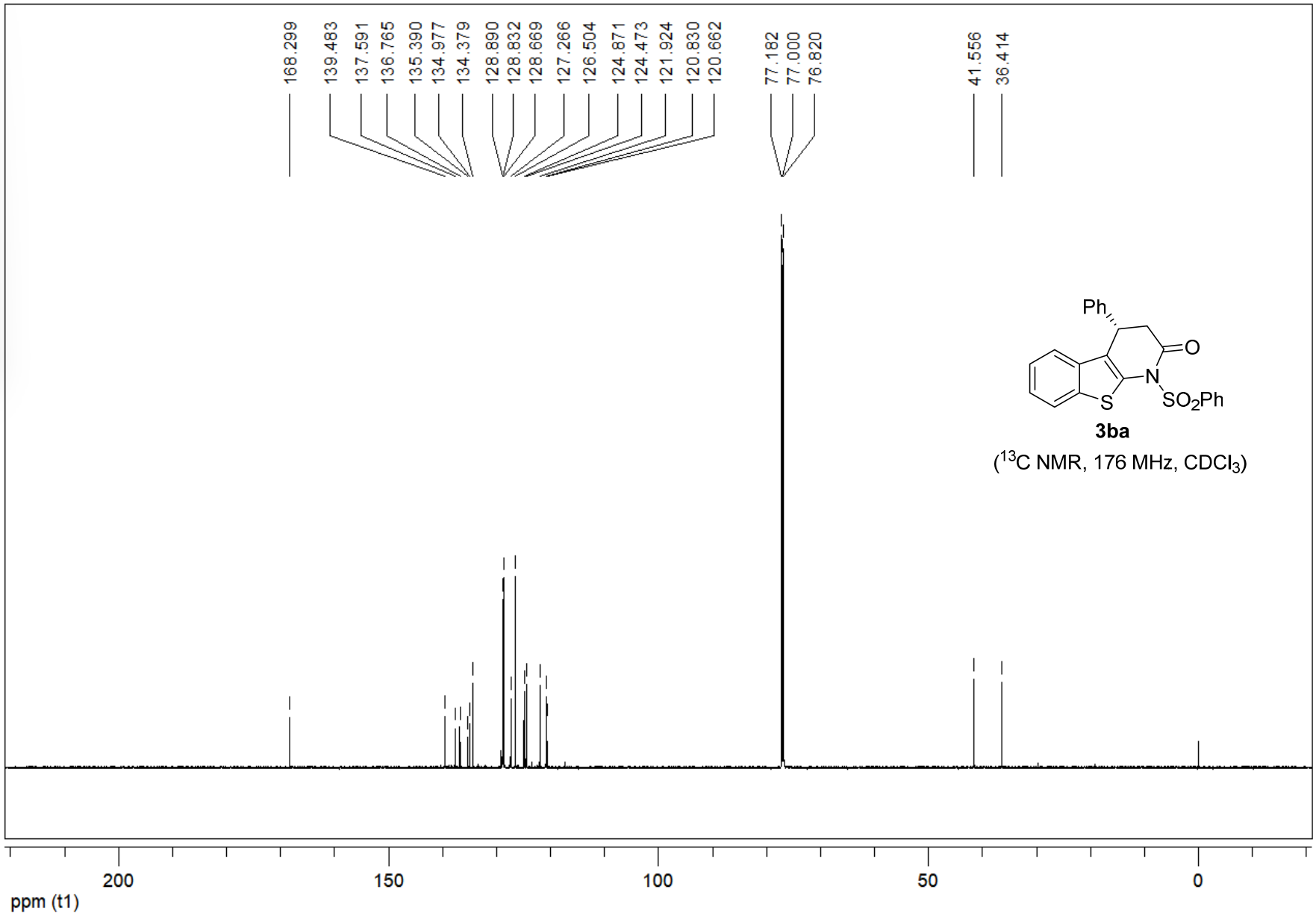
124.372
121.859
120.773
120.611
77.183
77.000
76.820
41.474
36.328
21.658
Ph
O
N
Ts
S
3aa
(^{13}C NMR, 176 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)



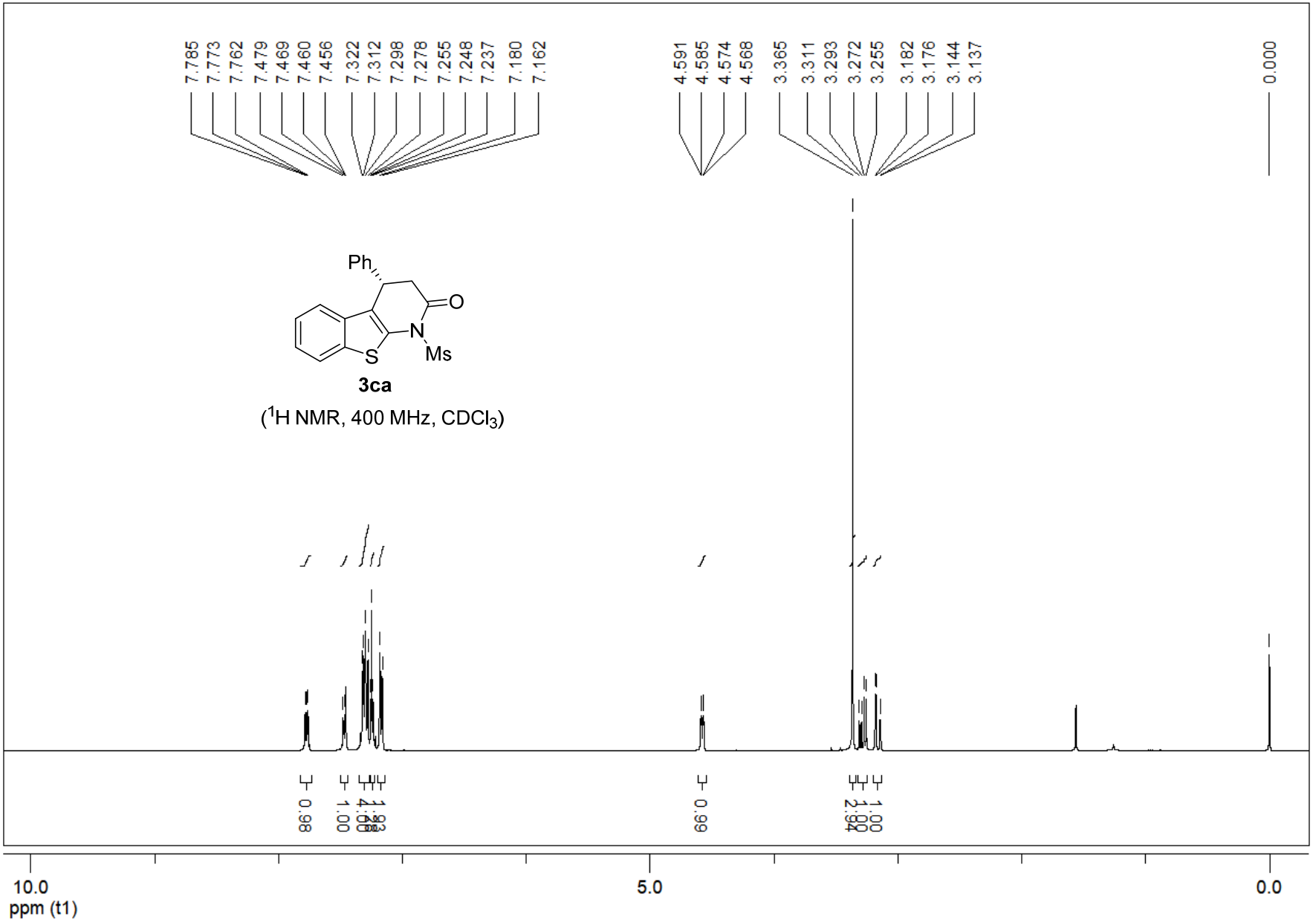
3ba

(^{1}H NMR, 400 MHz, $CDCl_3$)



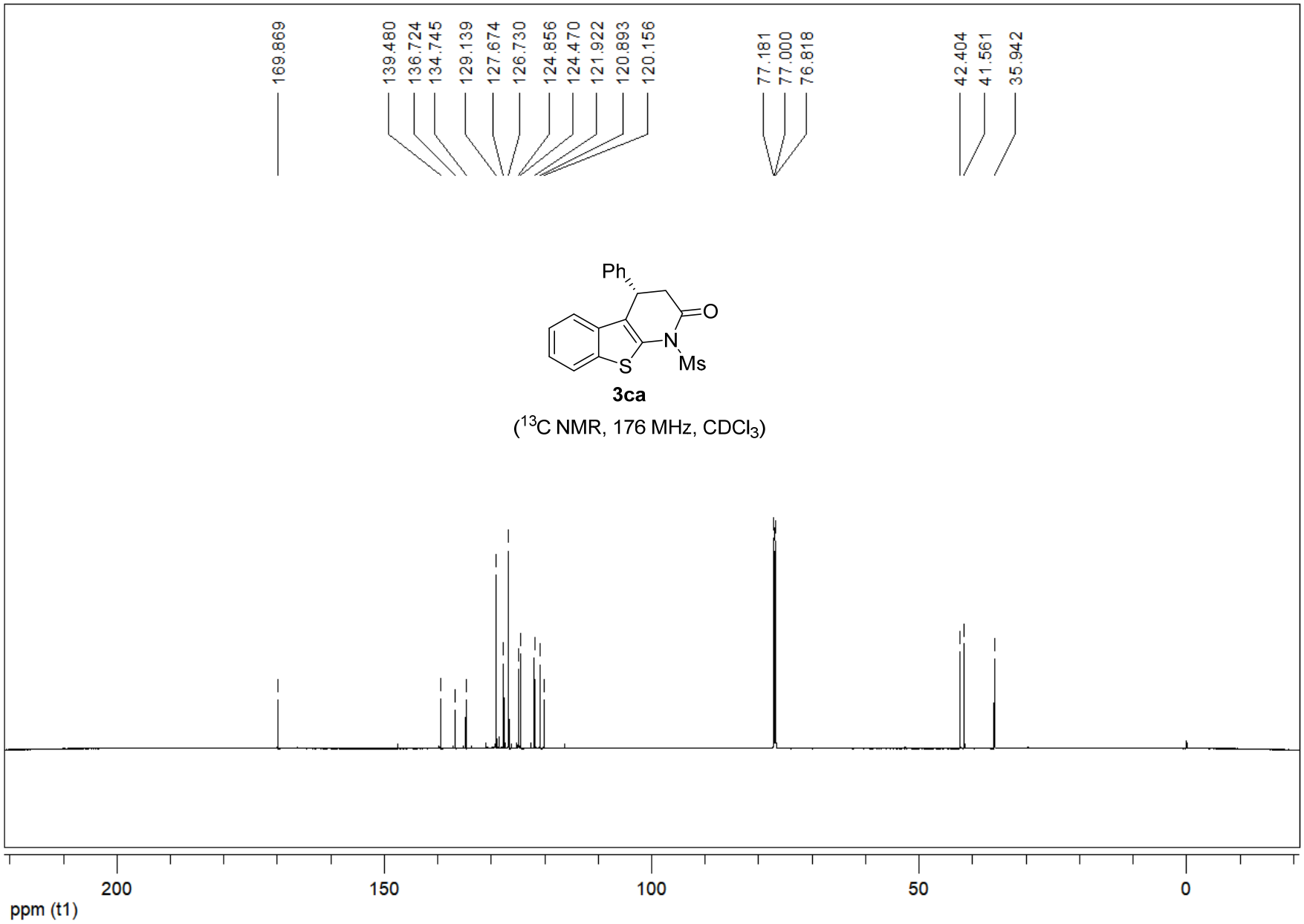
3ba

(^{13}C NMR, 176 MHz, $CDCl_3$)



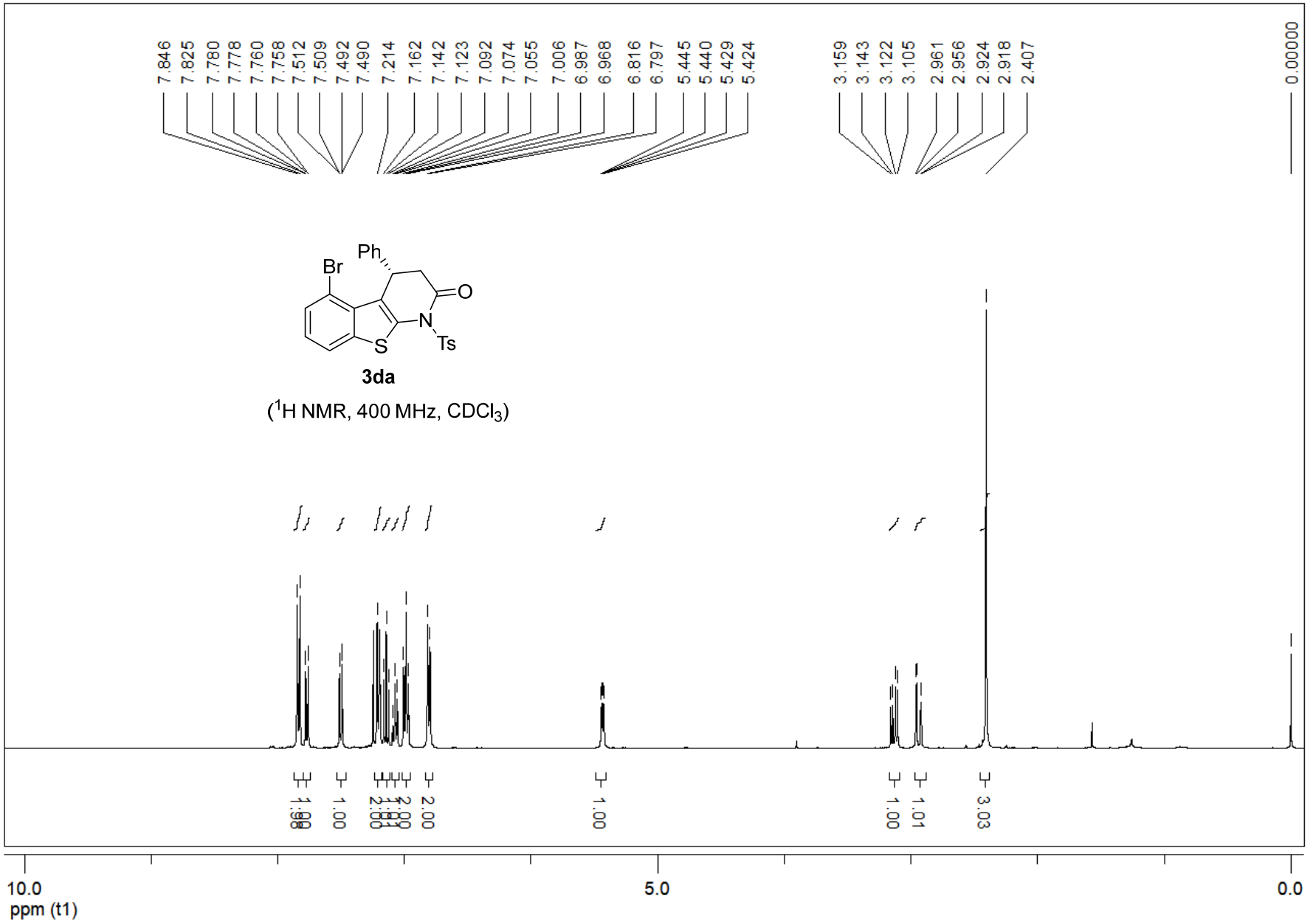
3ca

(^{1}H NMR, 400 MHz, $CDCl_3$)



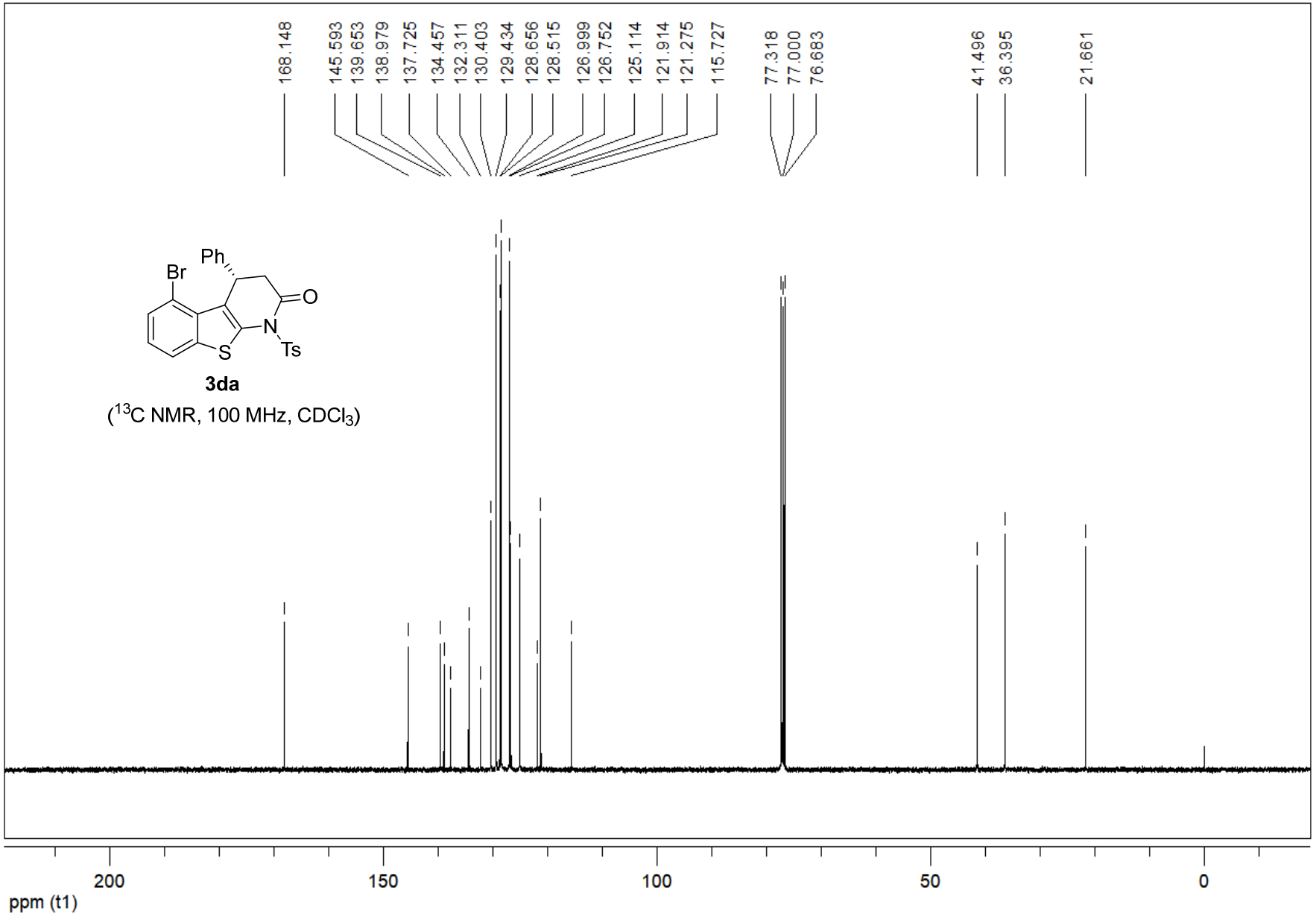
3ca

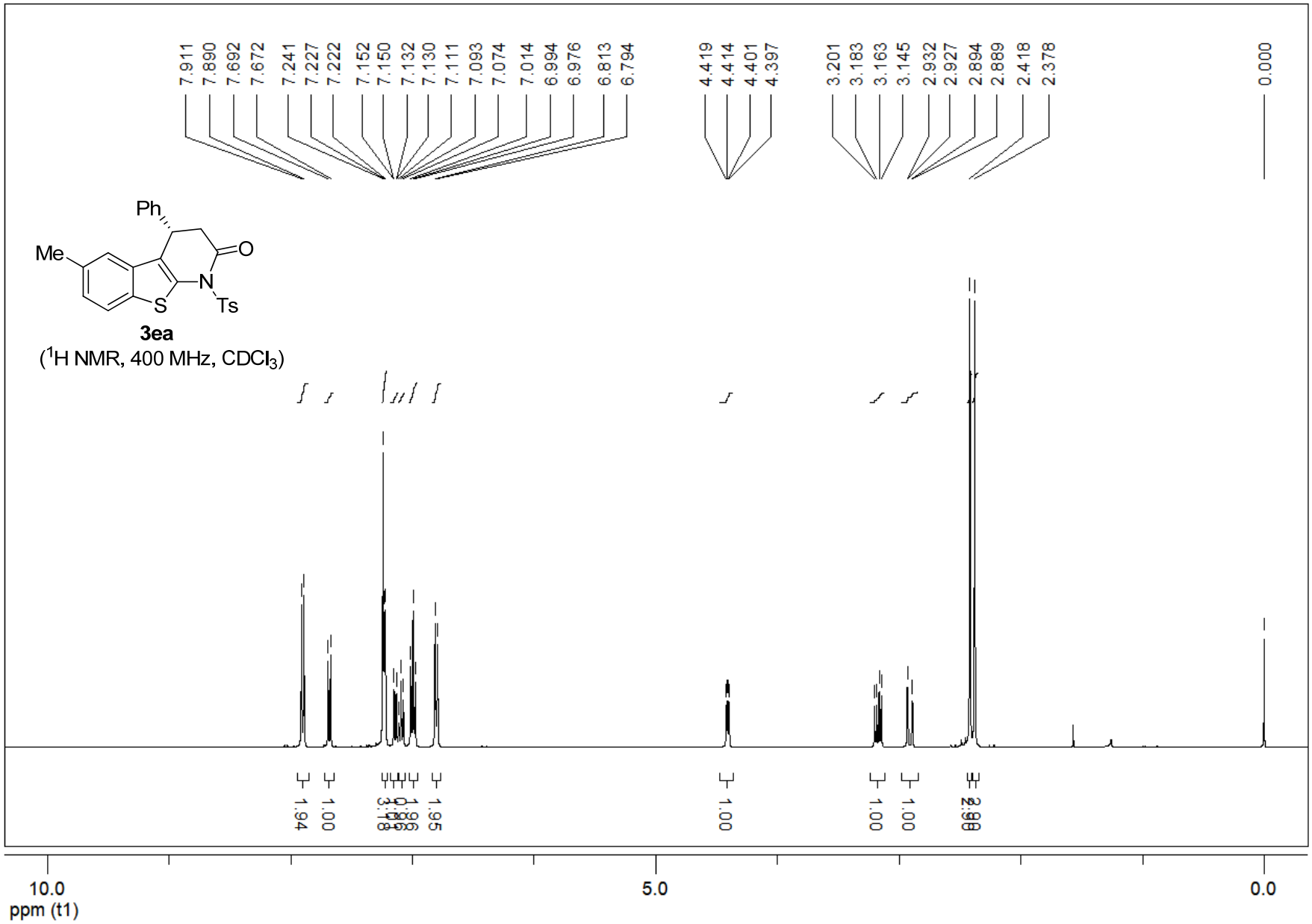
(^{13}C NMR, 176 MHz, $CDCl_3$)

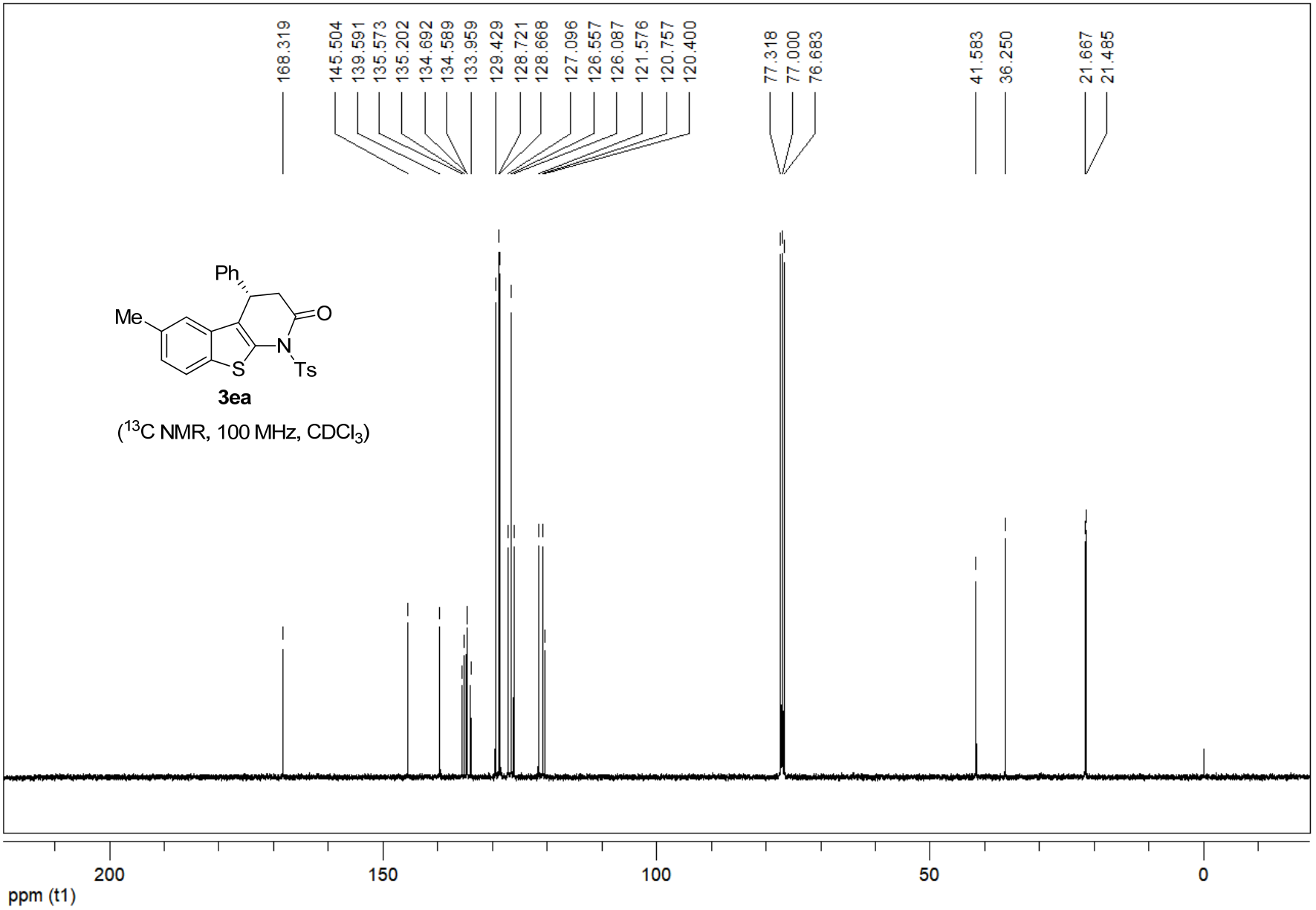


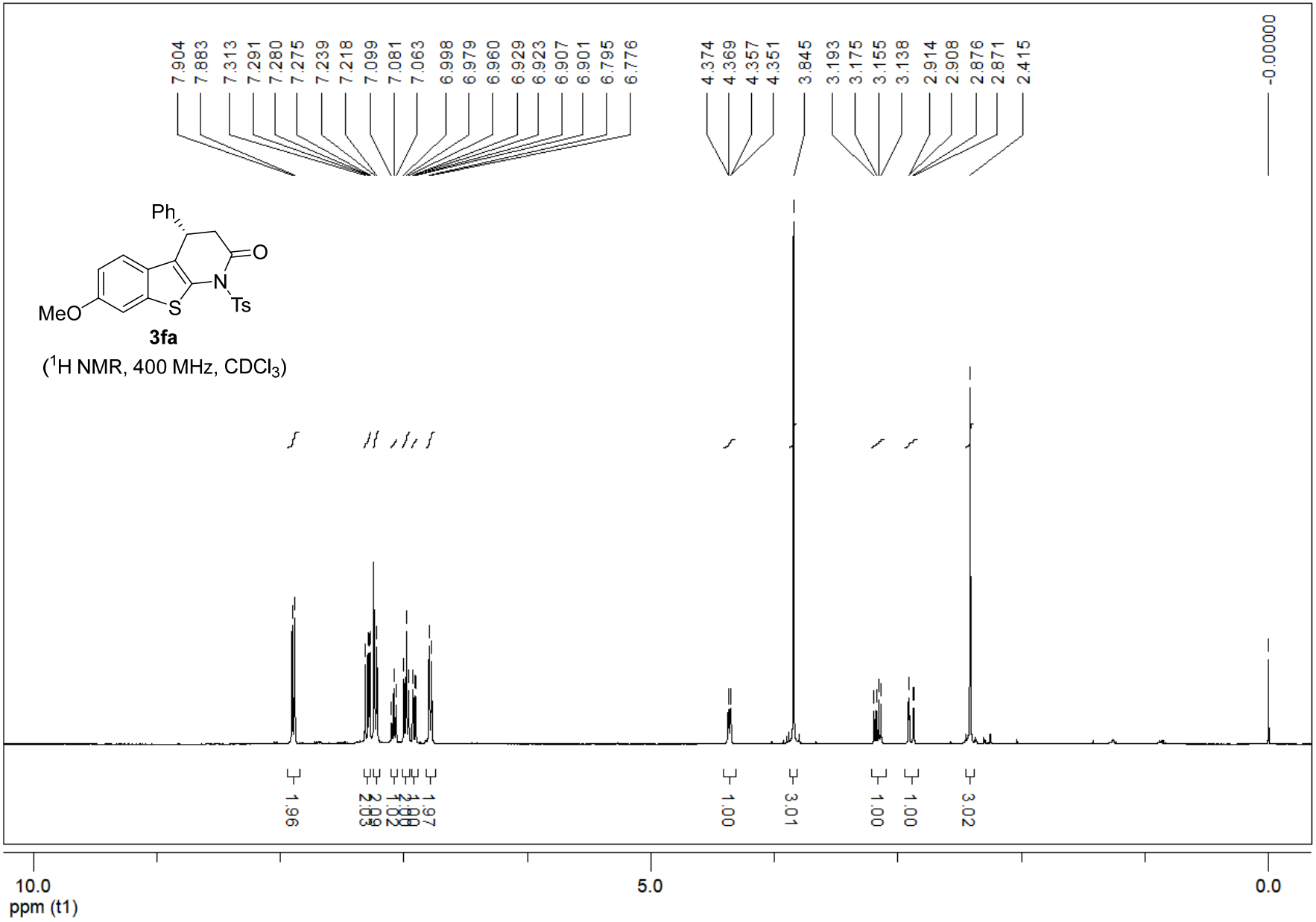
3da

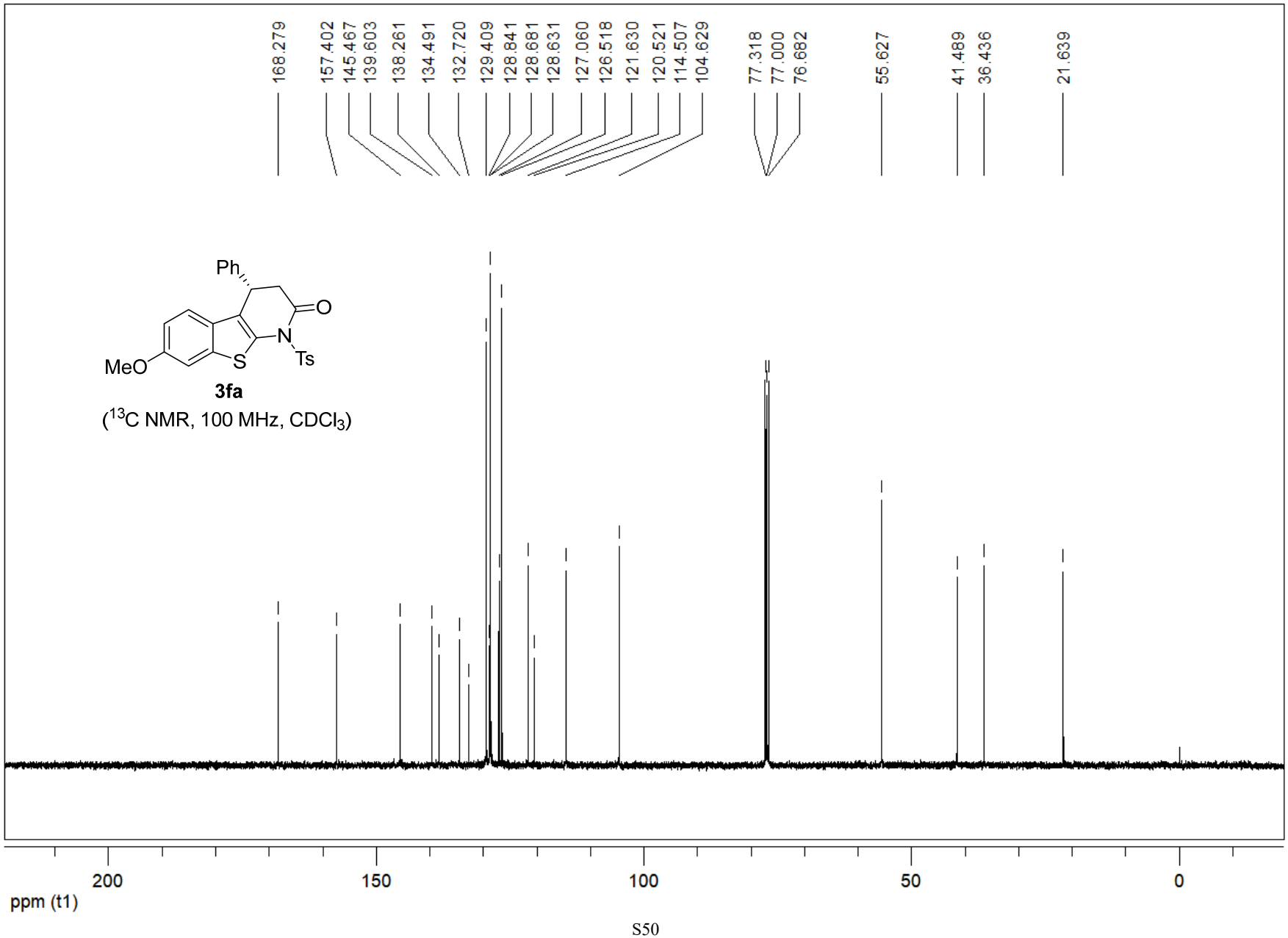
(^{1}H NMR, 400 MHz, $CDCl_3$)

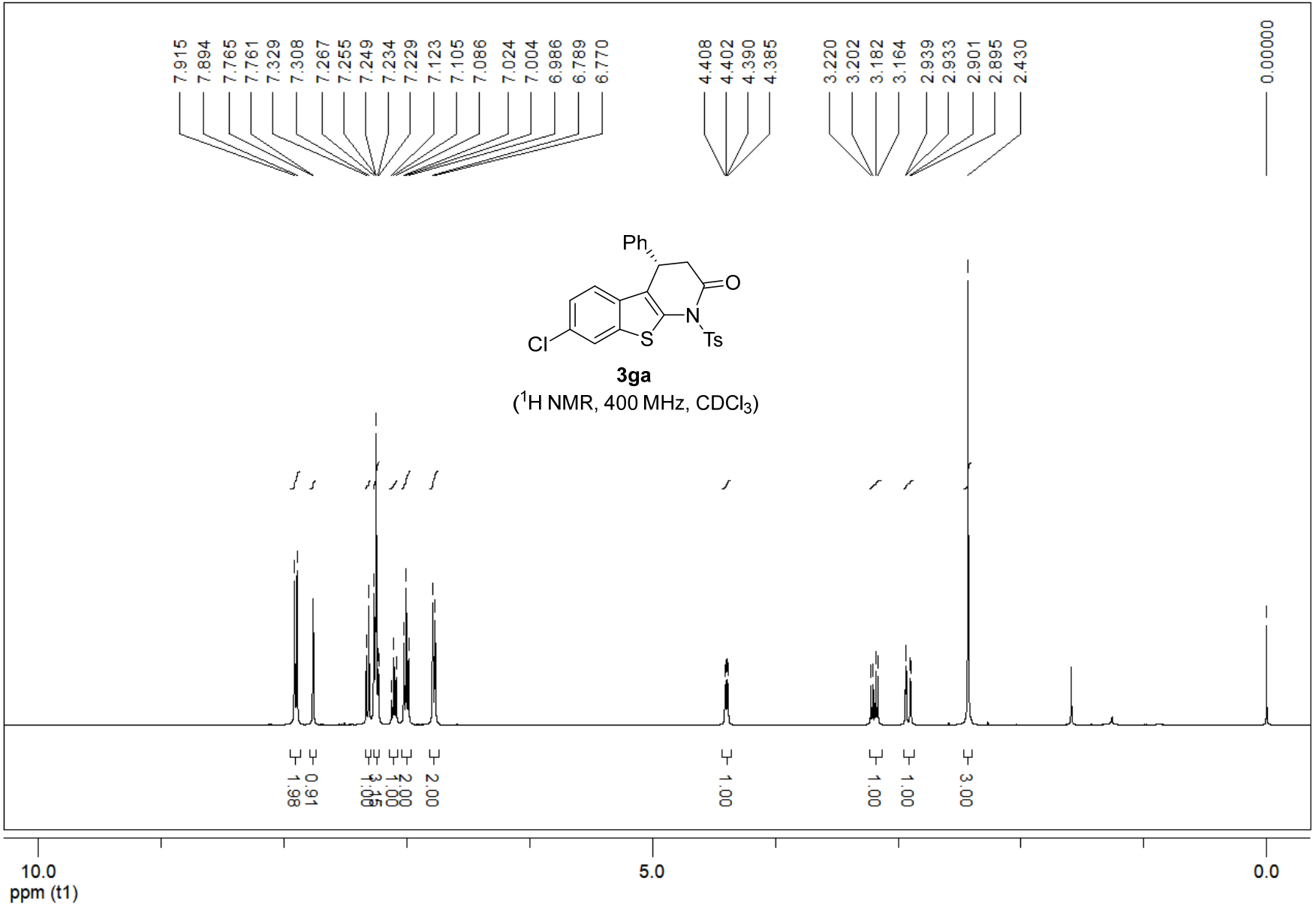

168.148
145.593
139.653
138.979
137.725
134.457
132.311
130.403
129.434
128.656
128.515
126.999
126.752
125.114
121.914
121.275
115.727
77.318
77.000
76.683
41.496
36.395
21.661
Br
Ph
O
N
Ts
S
3da
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)

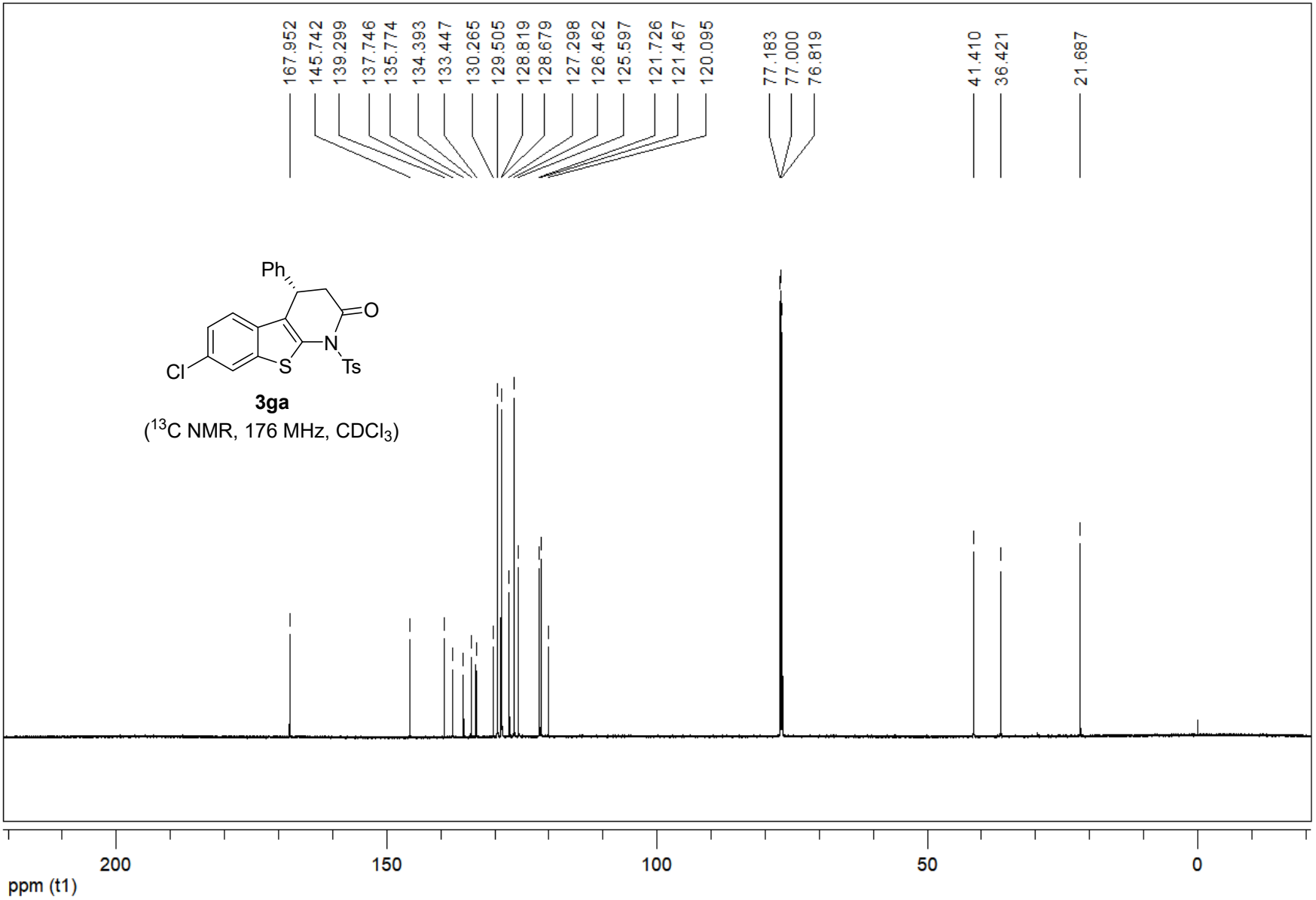

7.911
7.890
7.692
7.672
7.241
7.227
7.222
7.152
7.150
7.132
7.130
7.111
7.093
7.074
7.014
6.994
6.976
6.813
6.794
4.419
4.414
4.401
4.397
3.201
3.183
3.163
3.145
2.932
2.927
2.894
2.889
2.418
2.378
0.000
Ph
Me
O
N
S
Ts
3ea
(1H NMR, 400 MHz, CDCl3)
1.94
1.00
1.00
1.00
1.00
2.90
10.0
ppm (t1)
5.0
0.0


168.319
145.504
139.591
135.573
135.202
134.692
134.589
133.959
129.429
128.721
128.668
127.096
126.557
126.087
121.576
120.757
120.400
77.318
77.000
76.683
41.583
36.250
21.667
21.485
Ph
Me
O
N
S
Ts
3ea
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)


7.904
7.883
7.313
7.291
7.280
7.275
7.239
7.218
7.099
7.081
7.063
6.998
6.979
6.960
6.929
6.923
6.907
6.901
6.795
6.776
4.374
4.369
4.357
4.351
3.845
3.193
3.175
3.155
3.138
2.914
2.908
2.876
2.871
2.415
-0.00000
Ph
O
N
Ts
S
MeO
3fa
(1H NMR, 400 MHz, CDCl3)
1.96
2.03
1.97
1.00
3.01
1.00
1.00
3.02
10.0
ppm (t1)
5.0
0.0

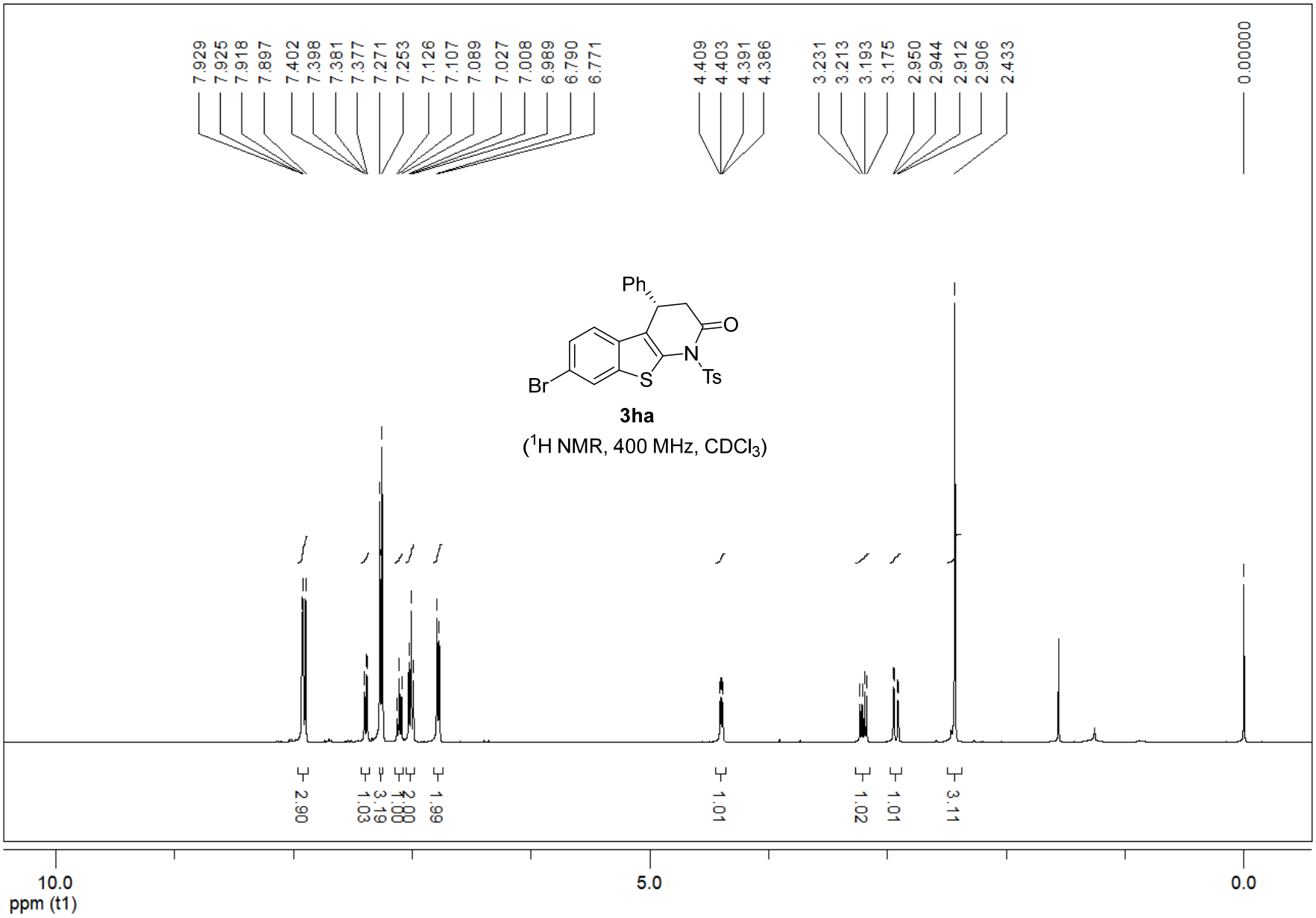

168.279
157.402
145.467
139.603
138.261
134.491
132.720
129.409
128.841
128.681
128.631
127.060
126.518
121.630
120.521
114.507
104.629
77.318
77.000
76.682
55.627
41.489
36.436
21.639
Ph
O
N
Ts
MeO
S
3fa
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm (t1)

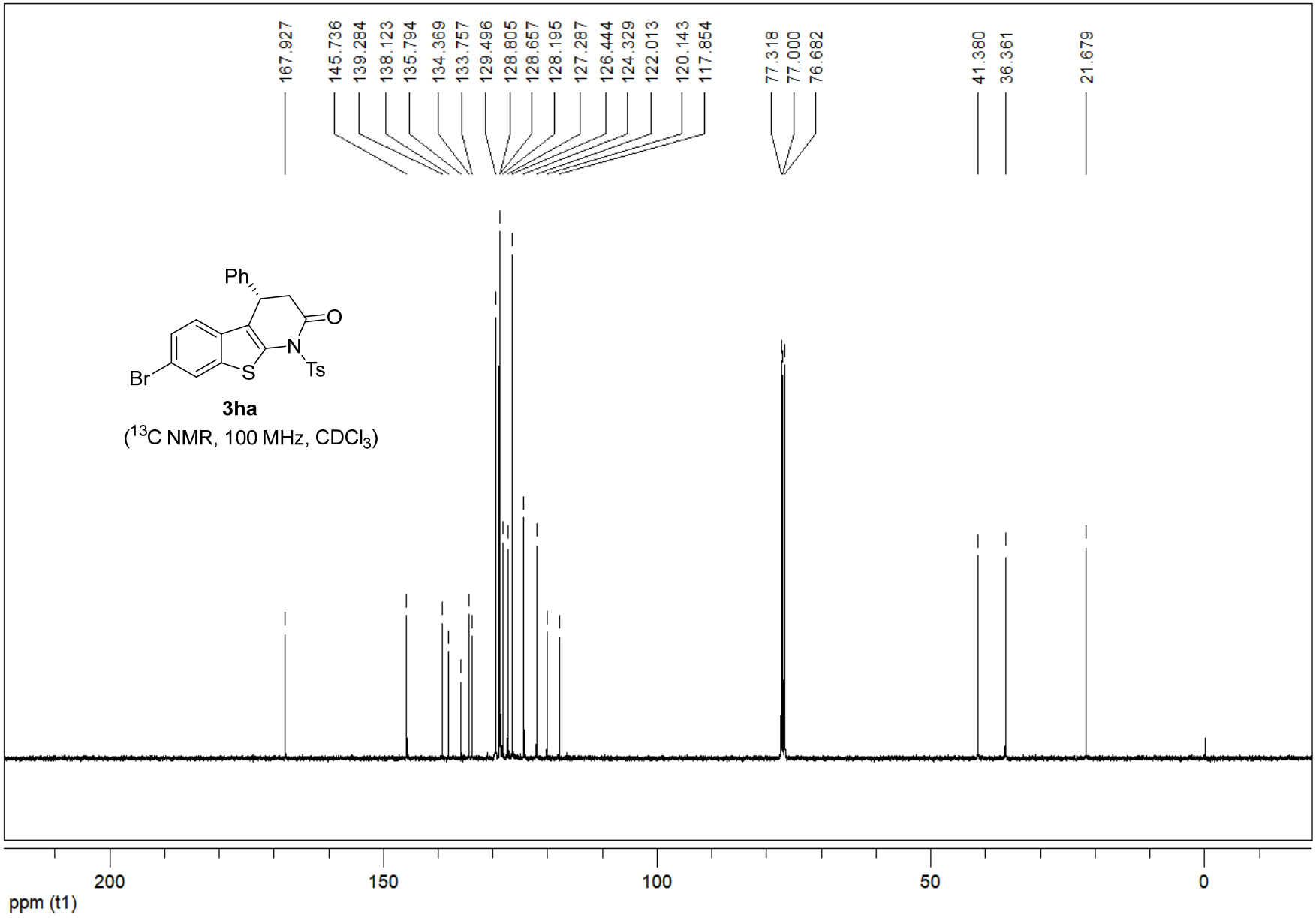

7.915
7.894
7.765
7.761
7.329
7.308
7.267
7.255
7.249
7.234
7.229
7.123
7.105
7.086
7.024
7.004
6.986
6.789
6.770
4.408
4.402
4.390
4.385
3.220
3.202
3.182
3.164
2.939
2.933
2.901
2.895
2.430
0.00000
Ph
O
N
Ts
S
Cl
3ga
(1H NMR, 400 MHz, CDCl3)
1.98
0.91
3.15
1.00
2.00
2.00
1.00
1.00
1.00
3.00
10.0
ppm (t1)
5.0
0.0

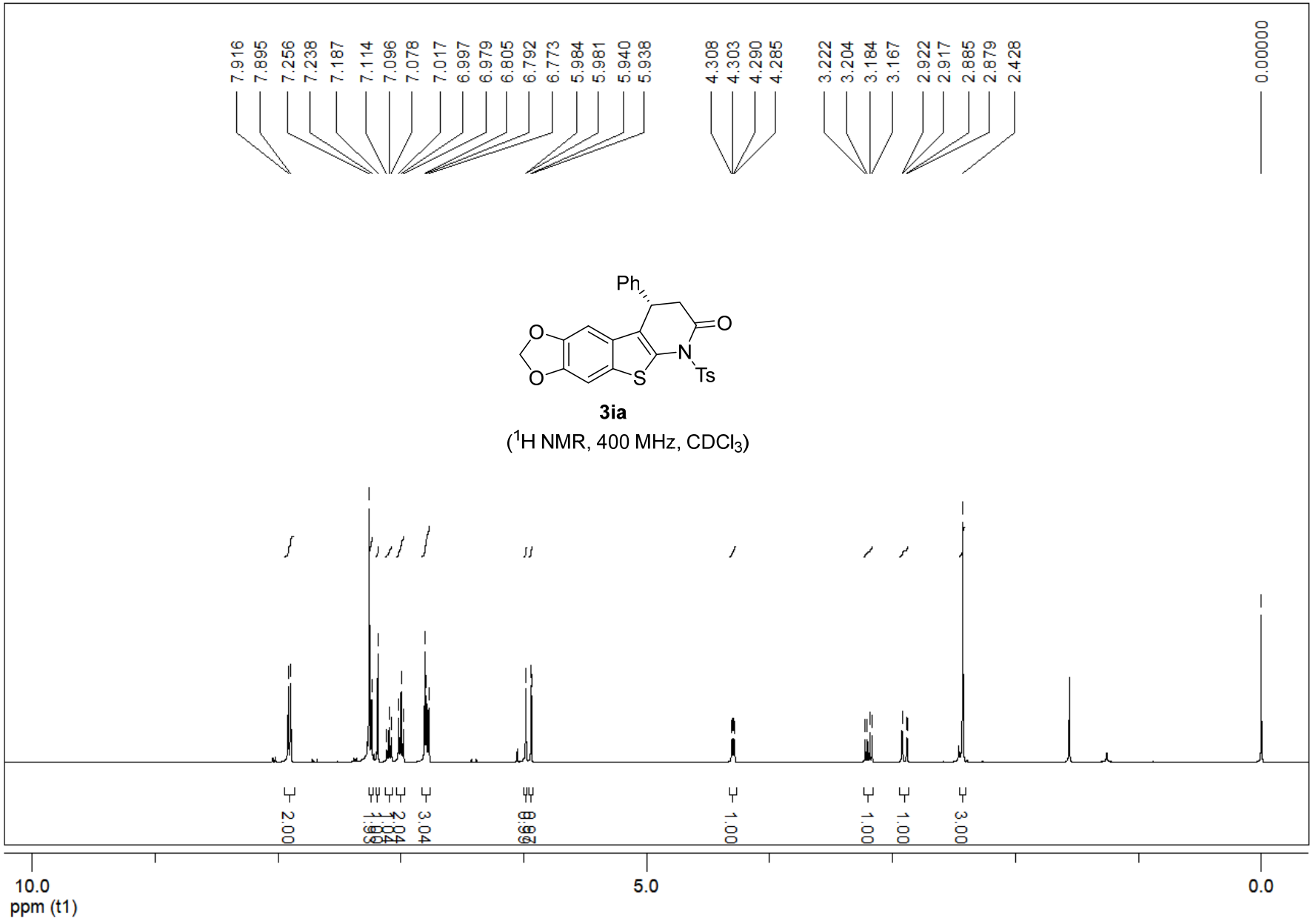


3ga

(^{13}C NMR, 176 MHz, $CDCl_3$)

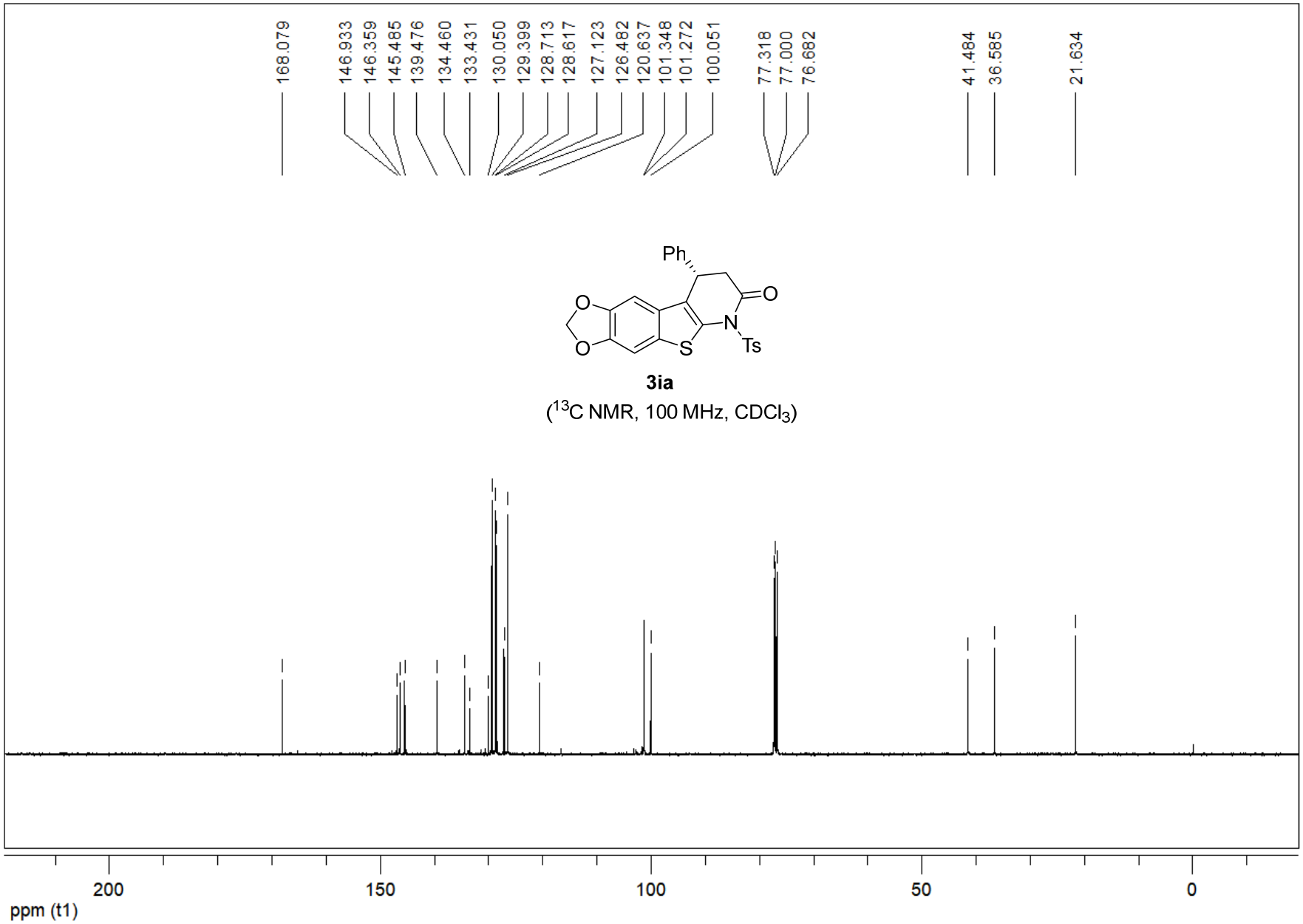

7.929
7.925
7.918
7.897
7.402
7.398
7.381
7.377
7.271
7.253
7.126
7.107
7.089
7.027
7.008
6.989
6.790
6.771
4.409
4.403
4.391
4.386
3.231
3.213
3.193
3.175
2.950
2.944
2.912
2.906
2.433
0.00000
Ph
O
N
Ts
S
Br
3ha
(1H NMR, 400 MHz, CDCl3)
2.90
1.03
3.19
2.00
1.88
1.99
1.01
1.02
1.01
3.11
10.0
ppm (t1)
5.0
0.0


167.927
145.736
139.284
138.123
135.794
134.369
133.757
129.496
128.805
128.657
128.195
127.287
126.444
124.329
122.013
120.143
117.854
77.318
77.000
76.682
41.380
36.361
21.679
Ph
O
N
Ts
S
Br
3ha
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)



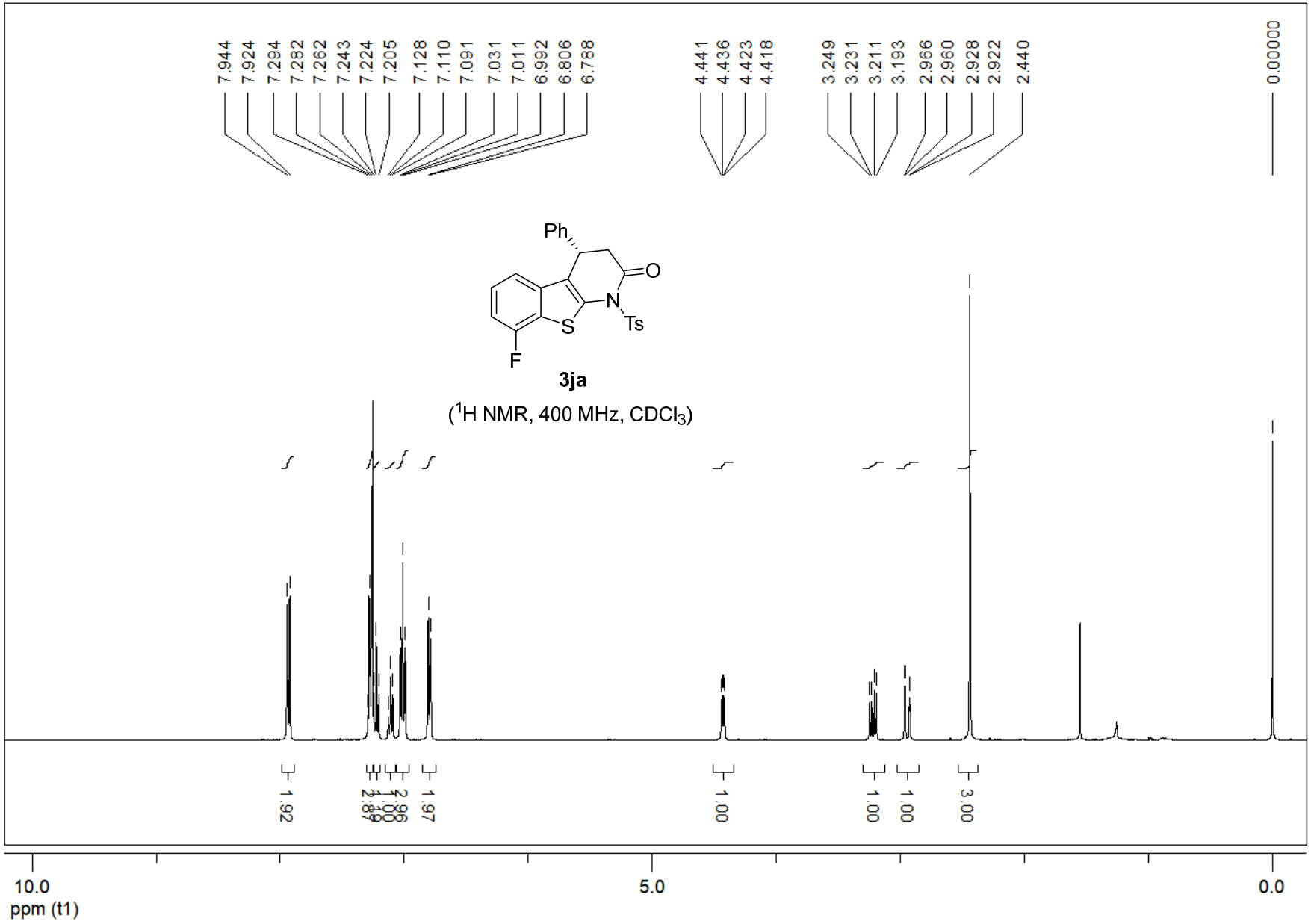
3ia

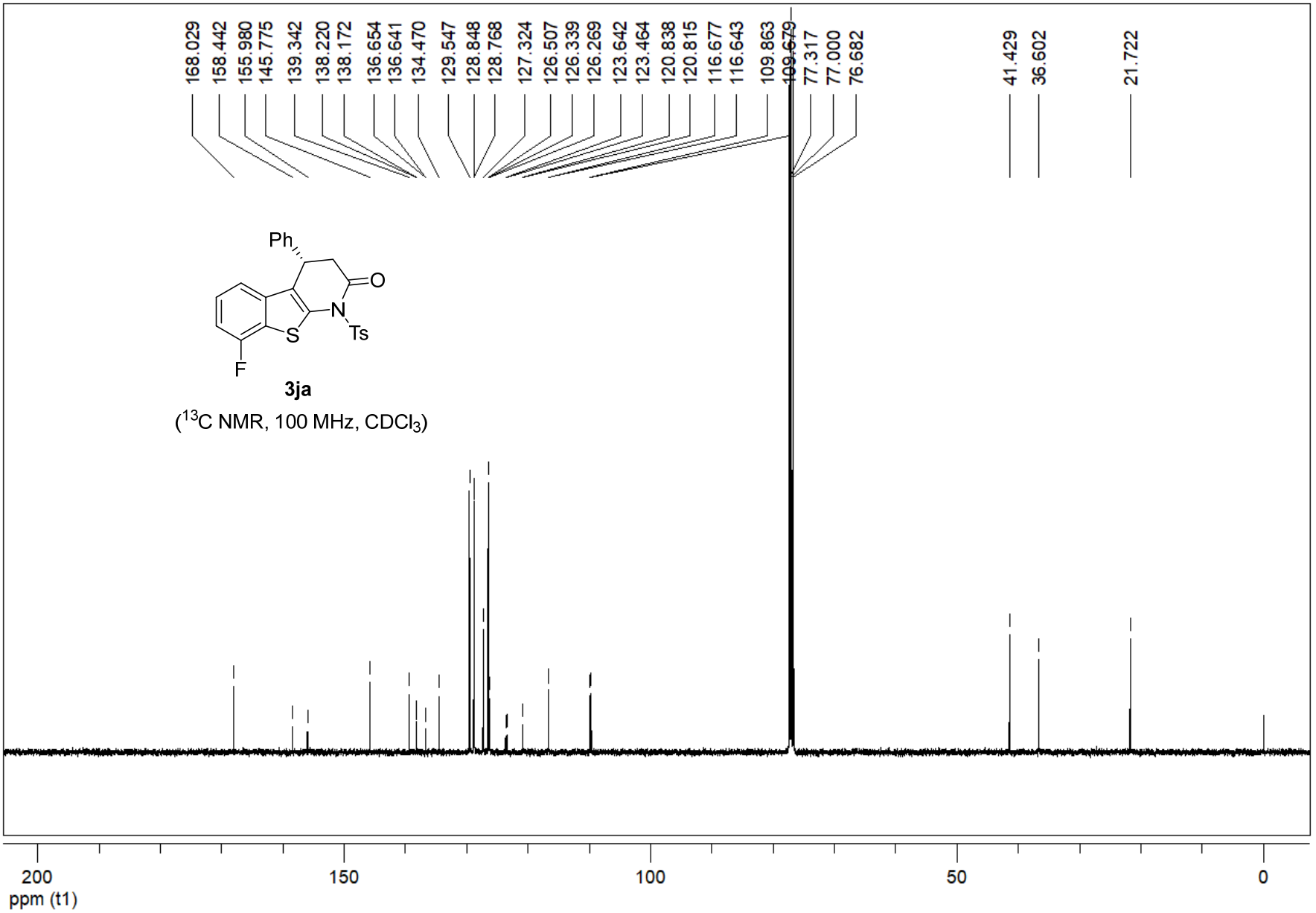
(^{1}H NMR, 400 MHz, $CDCl_3$)

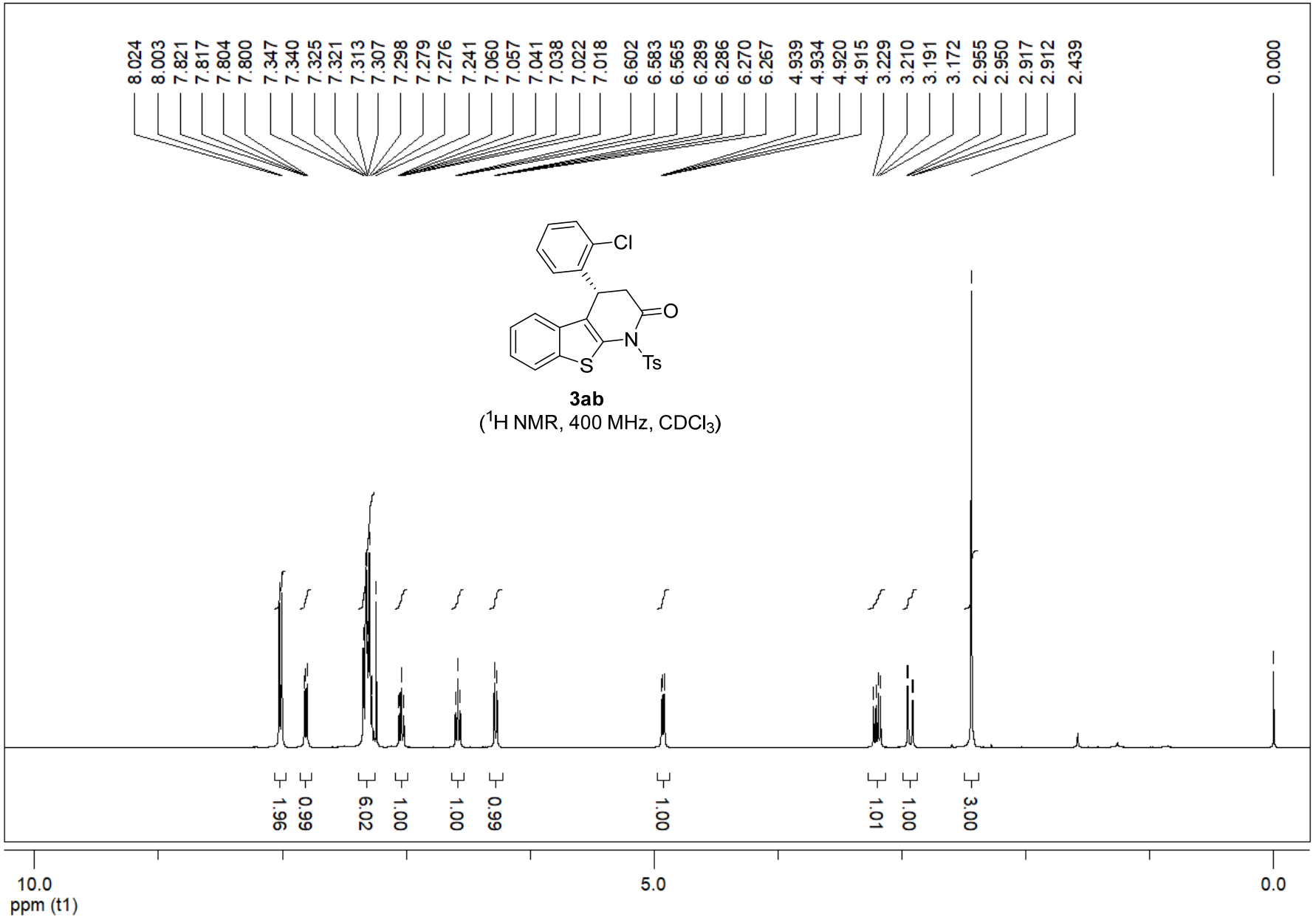


3ia

(^{13}C NMR, 100 MHz, $CDCl_3$)

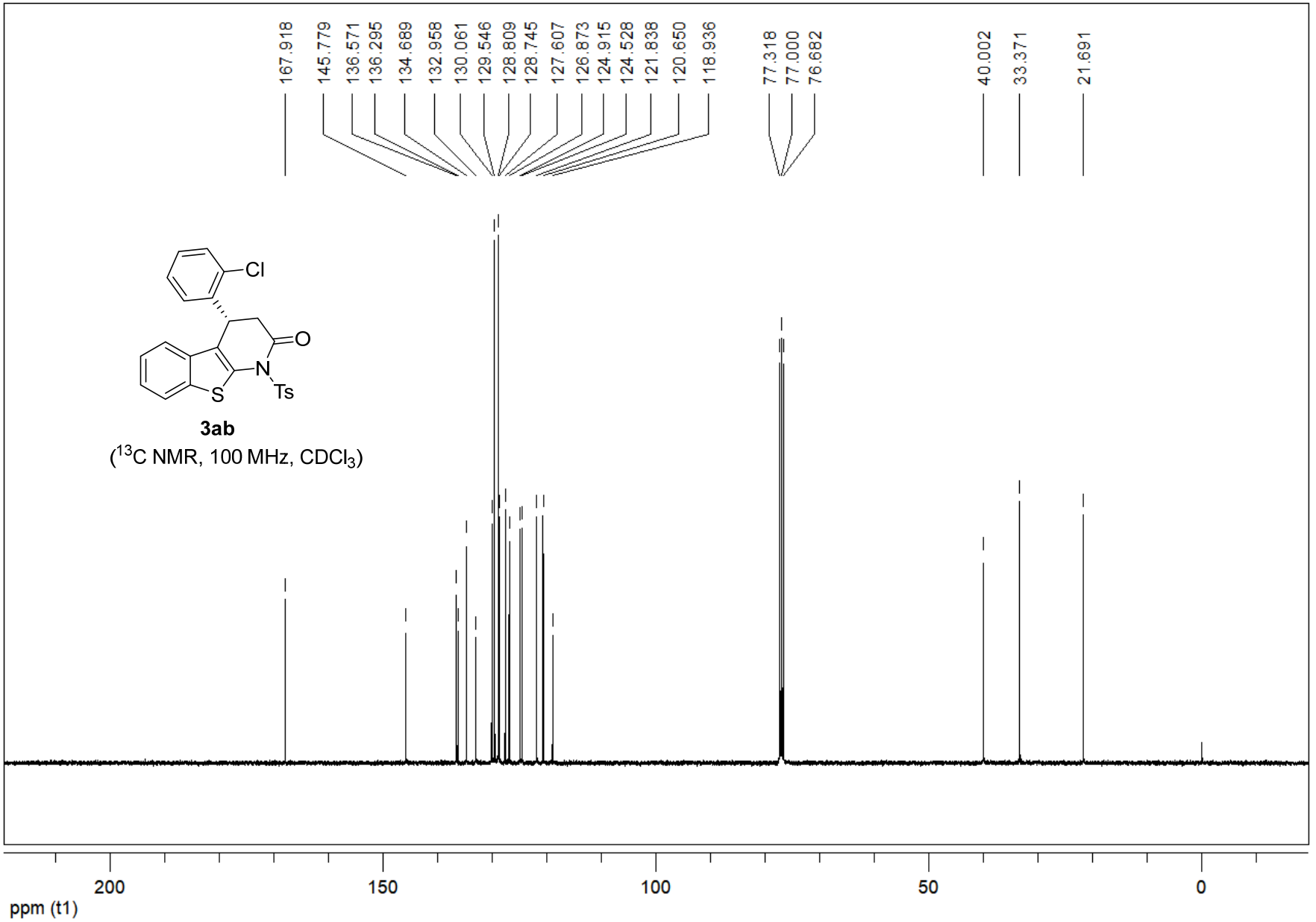

7.944
7.924
7.294
7.282
7.262
7.243
7.224
7.205
7.128
7.110
7.091
7.031
7.011
6.992
6.806
6.788
4.441
4.436
4.423
4.418
3.249
3.231
3.211
3.193
2.966
2.960
2.928
2.922
2.440
0.00000
Ph
O
N
Ts
S
F
3ja
(1H NMR, 400 MHz, CDCl3)
1.92
2.87
2.19
1.00
2.09
1.97
1.00
1.00
1.00
3.00
10.0
ppm (t1)
5.0
0.0

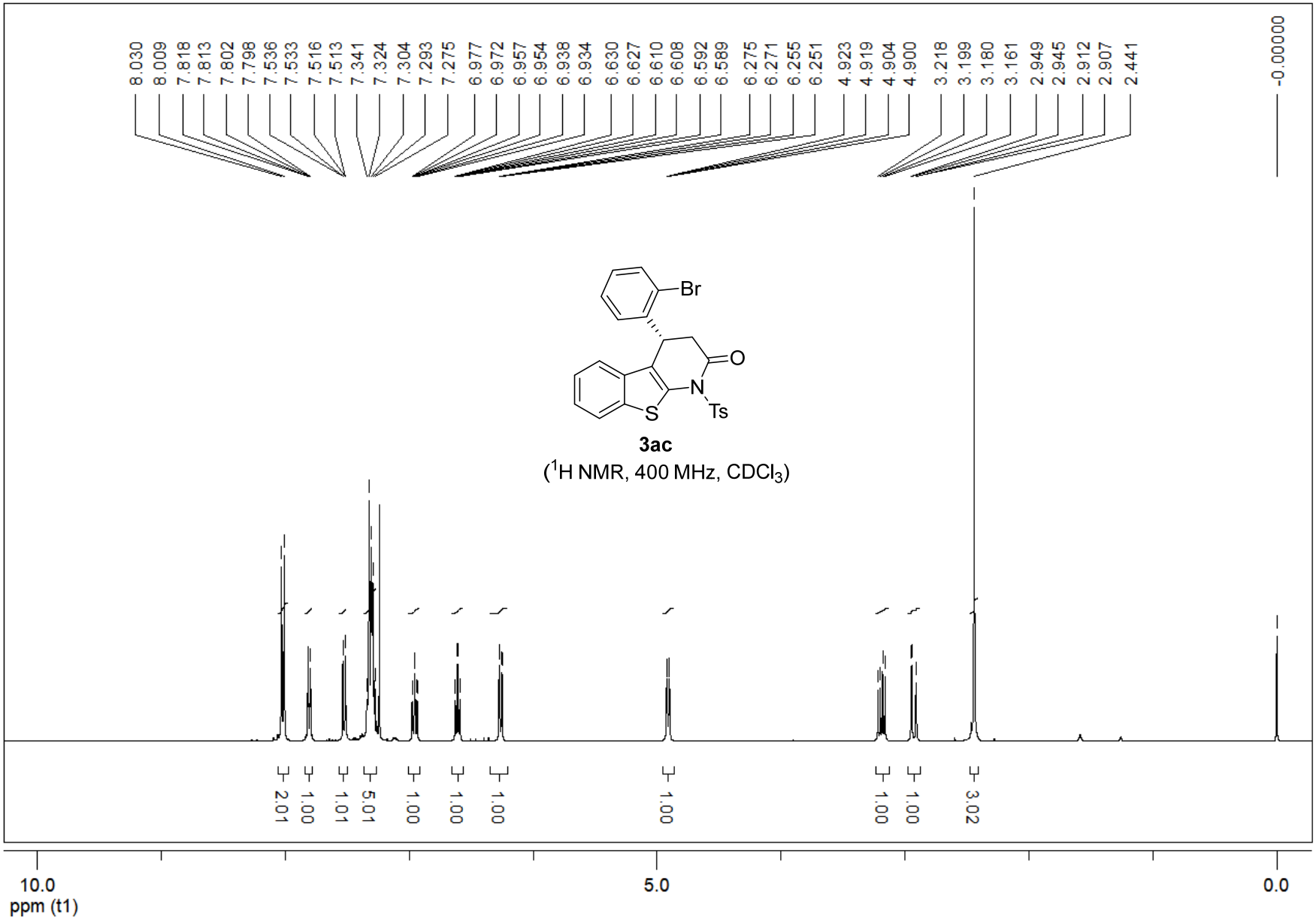

168.029
158.442
155.980
145.775
139.342
138.220
138.172
136.654
136.641
134.470
129.547
128.848
128.768
127.324
126.507
126.339
126.269
123.642
123.464
120.838
120.815
116.677
116.643
109.863
109.679
77.317
77.000
76.682
41.429
36.602
21.722
Ph
O
N
Ts
S
F
3ja
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)



3ab

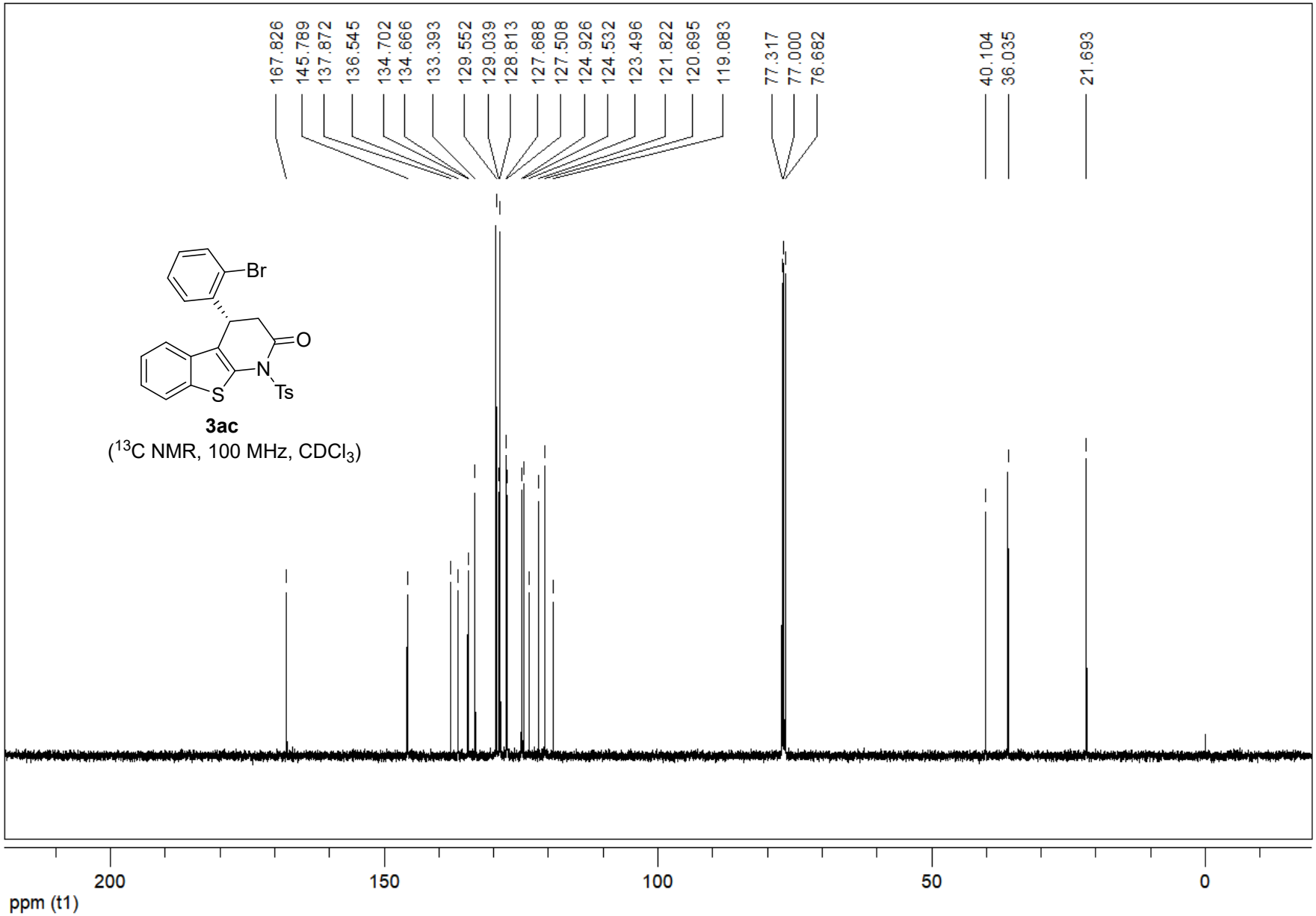
(^{1}H NMR, 400 MHz, $CDCl_3$)

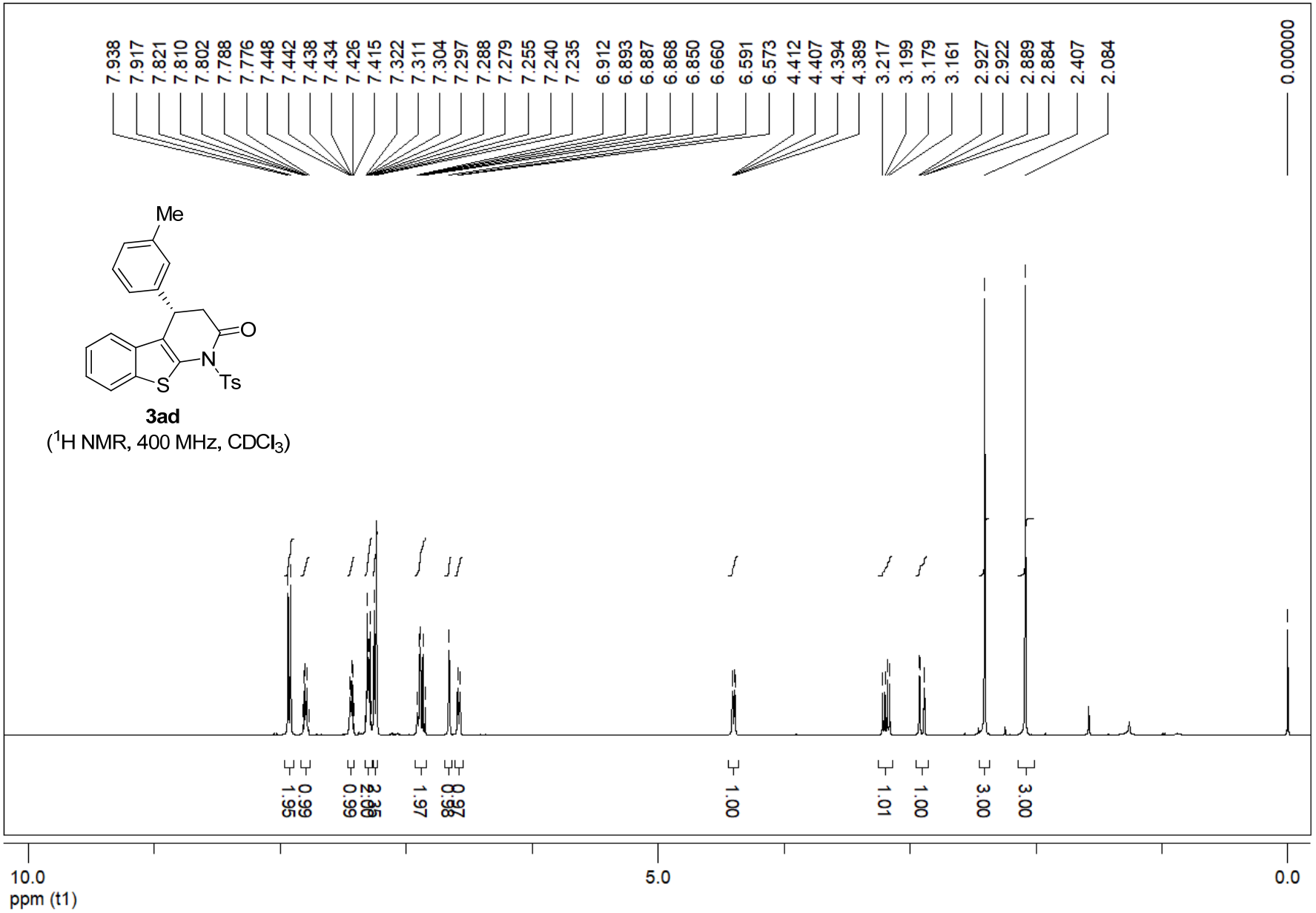

167.918
145.779
136.571
136.295
134.689
132.958
130.061
129.546
128.809
128.745
127.607
126.873
124.915
124.528
121.838
120.650
118.936
77.318
77.000
76.682
40.002
33.371
21.691
Cl
O
N
Ts
S
3ab
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)



3ac

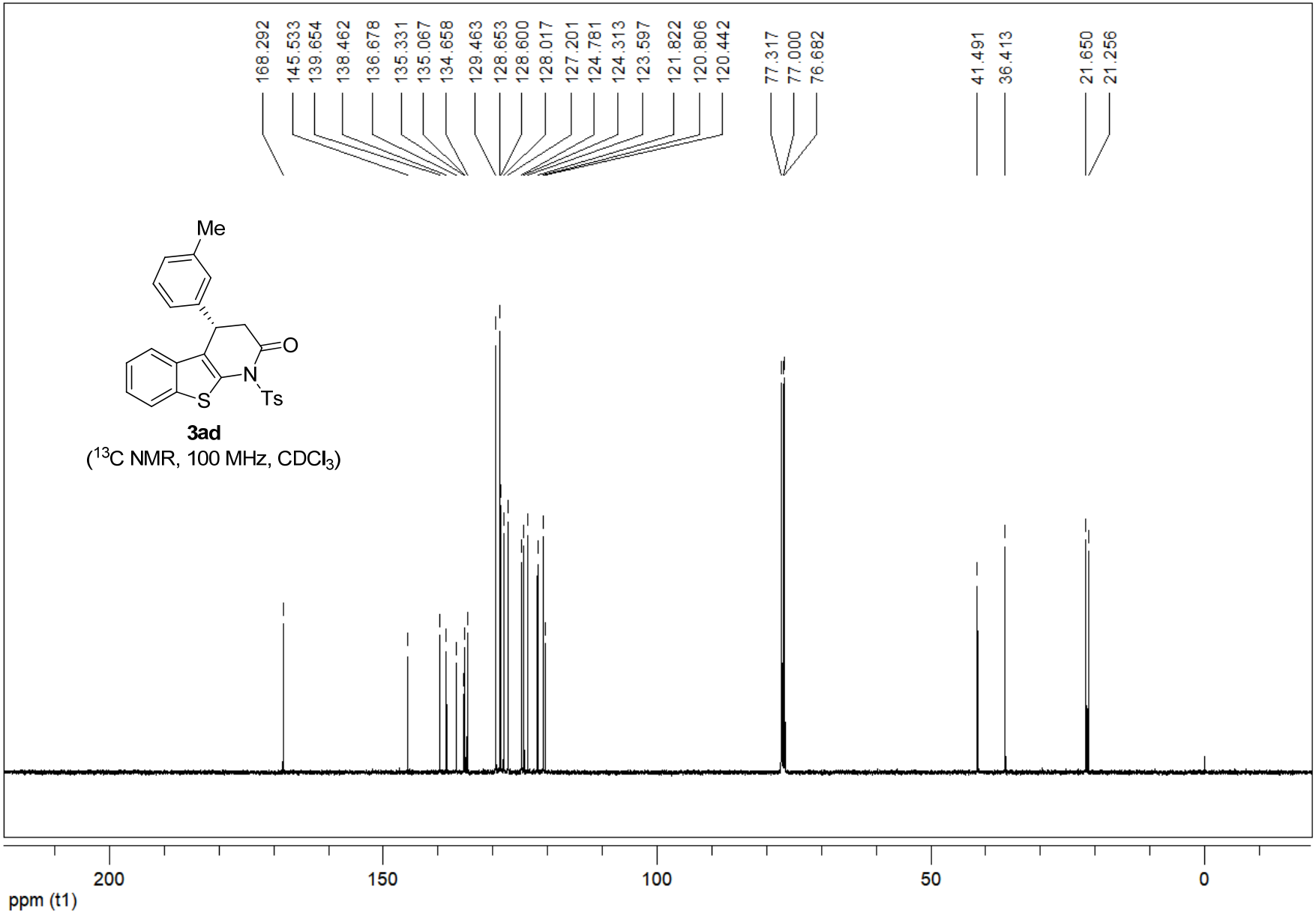
(^{1}H NMR, 400 MHz, $CDCl_3$)

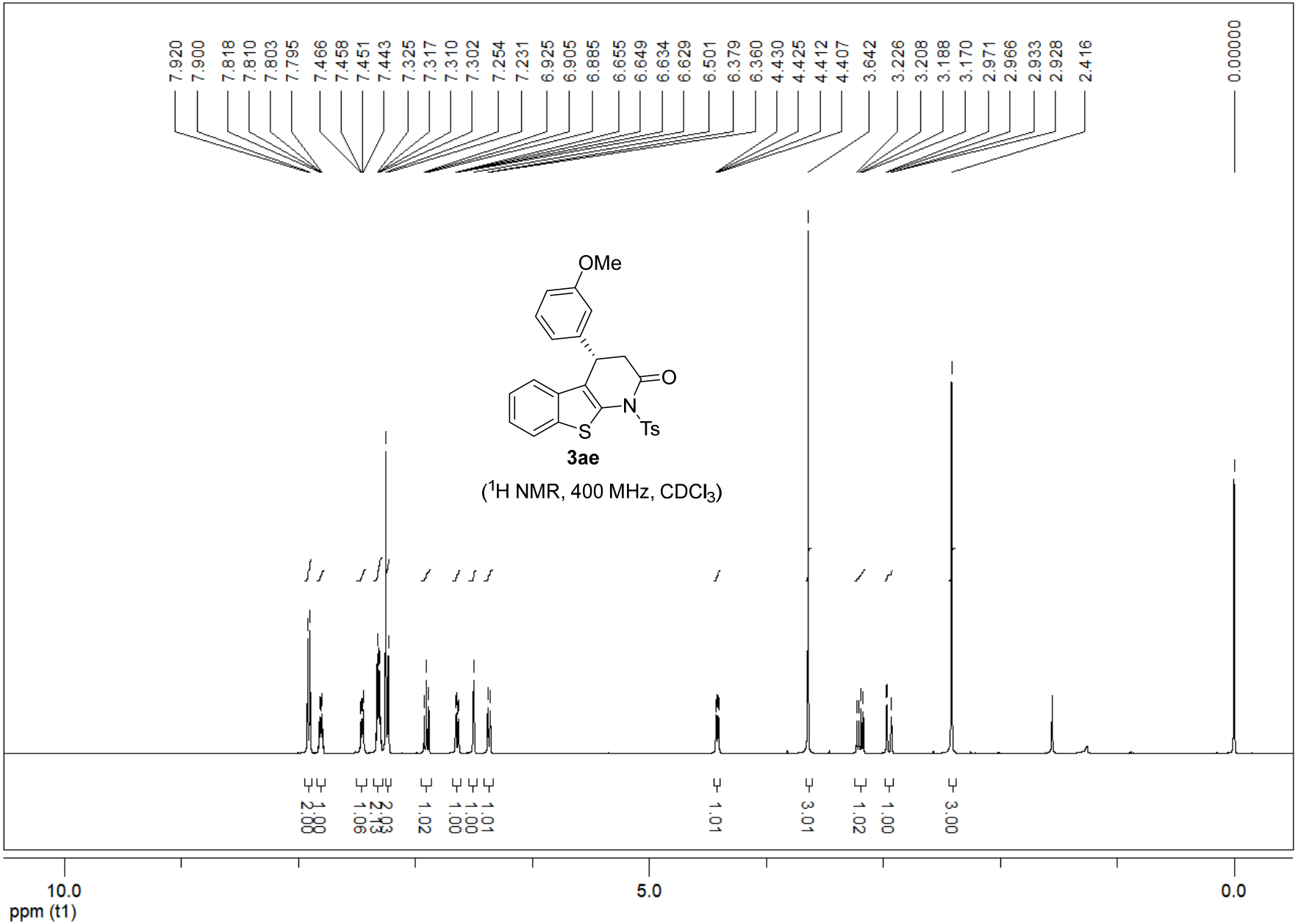

167.826
145.789
137.872
136.545
134.702
134.666
133.393
129.552
129.039
128.813
127.688
127.508
124.926
124.532
123.496
121.822
120.695
119.083
77.317
77.000
76.682
40.104
36.035
21.693
Br
O
N
Ts
S
3ac
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)

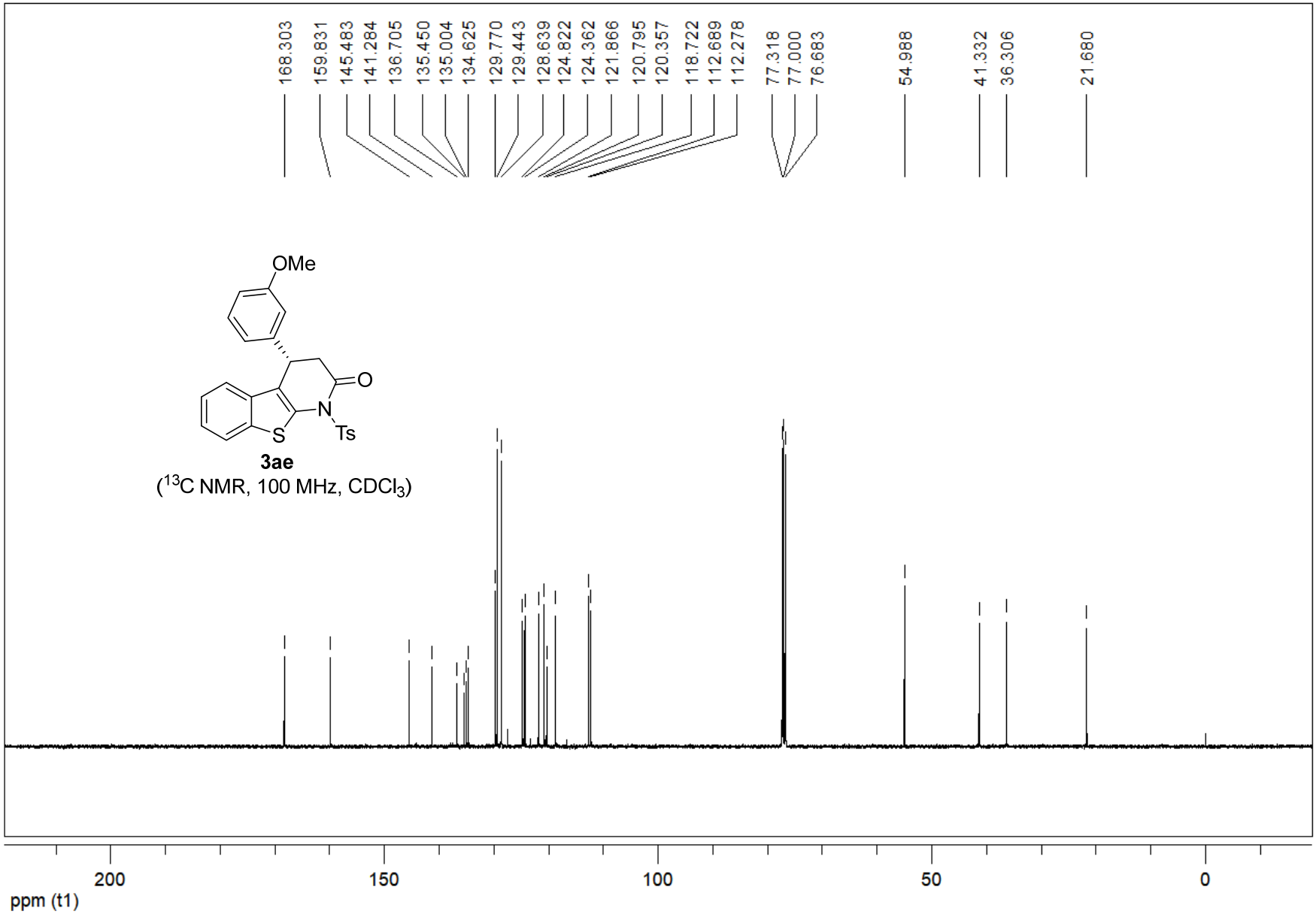


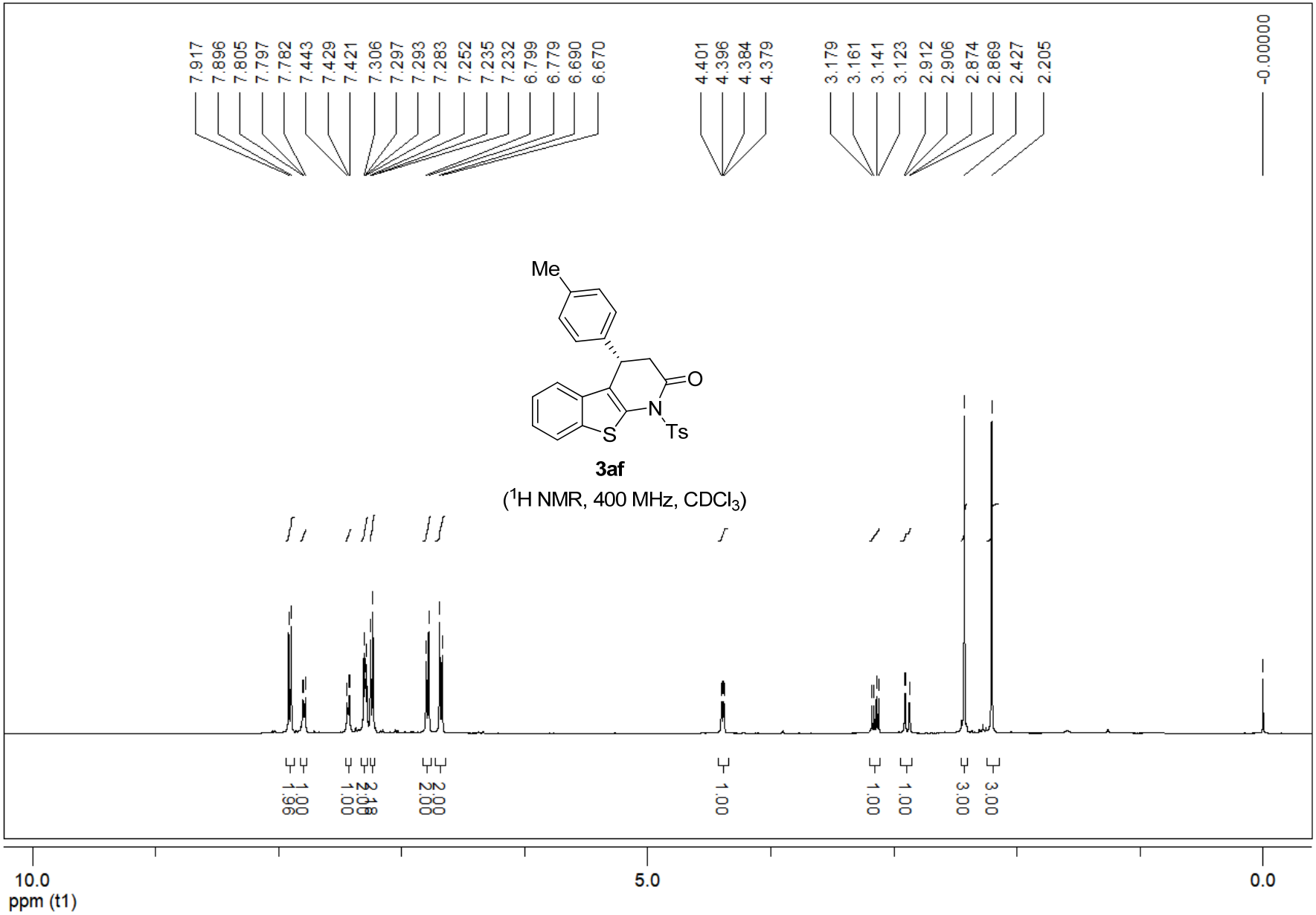
3ad

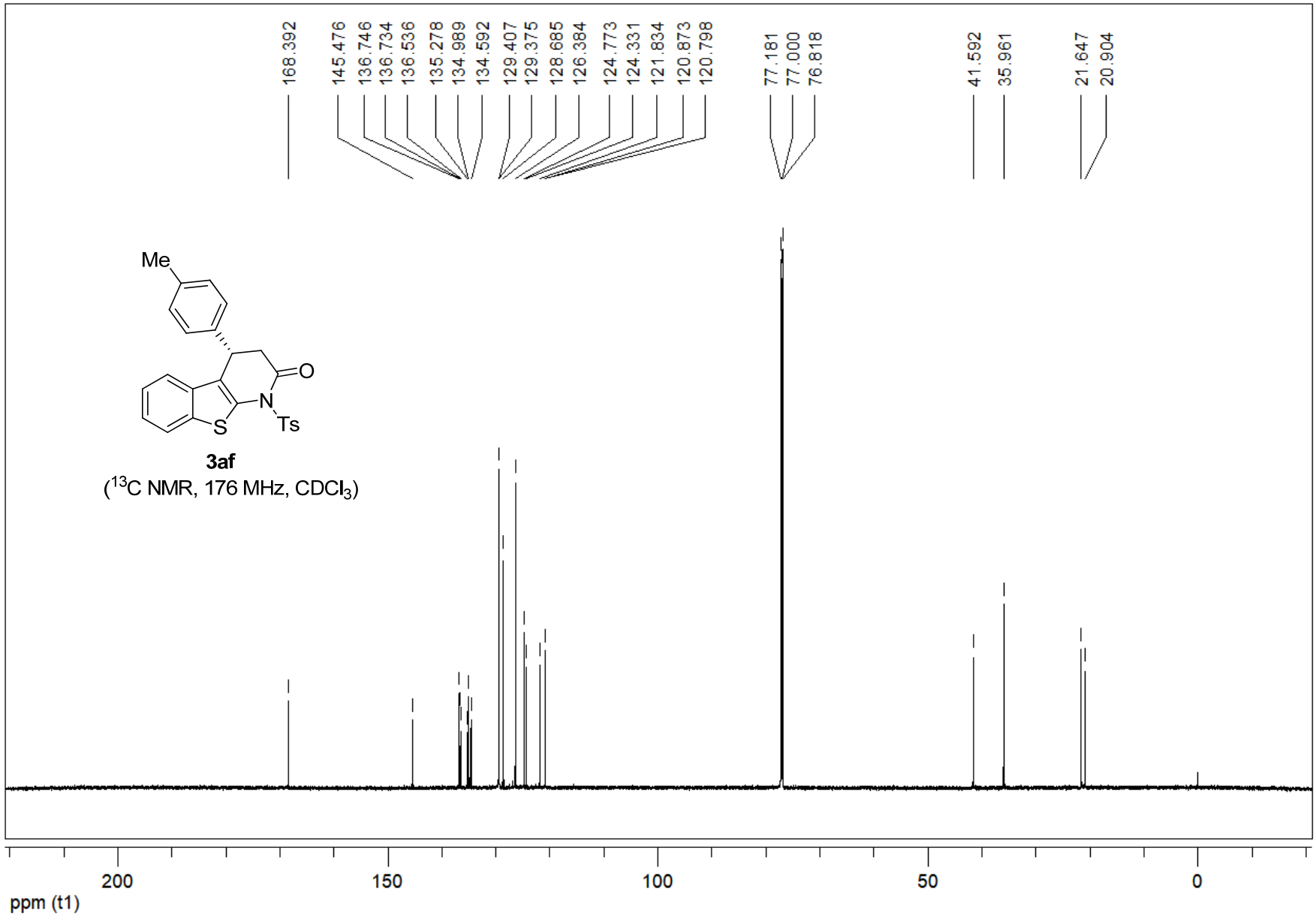
(^{1}H NMR, 400 MHz, $CDCl_3$)

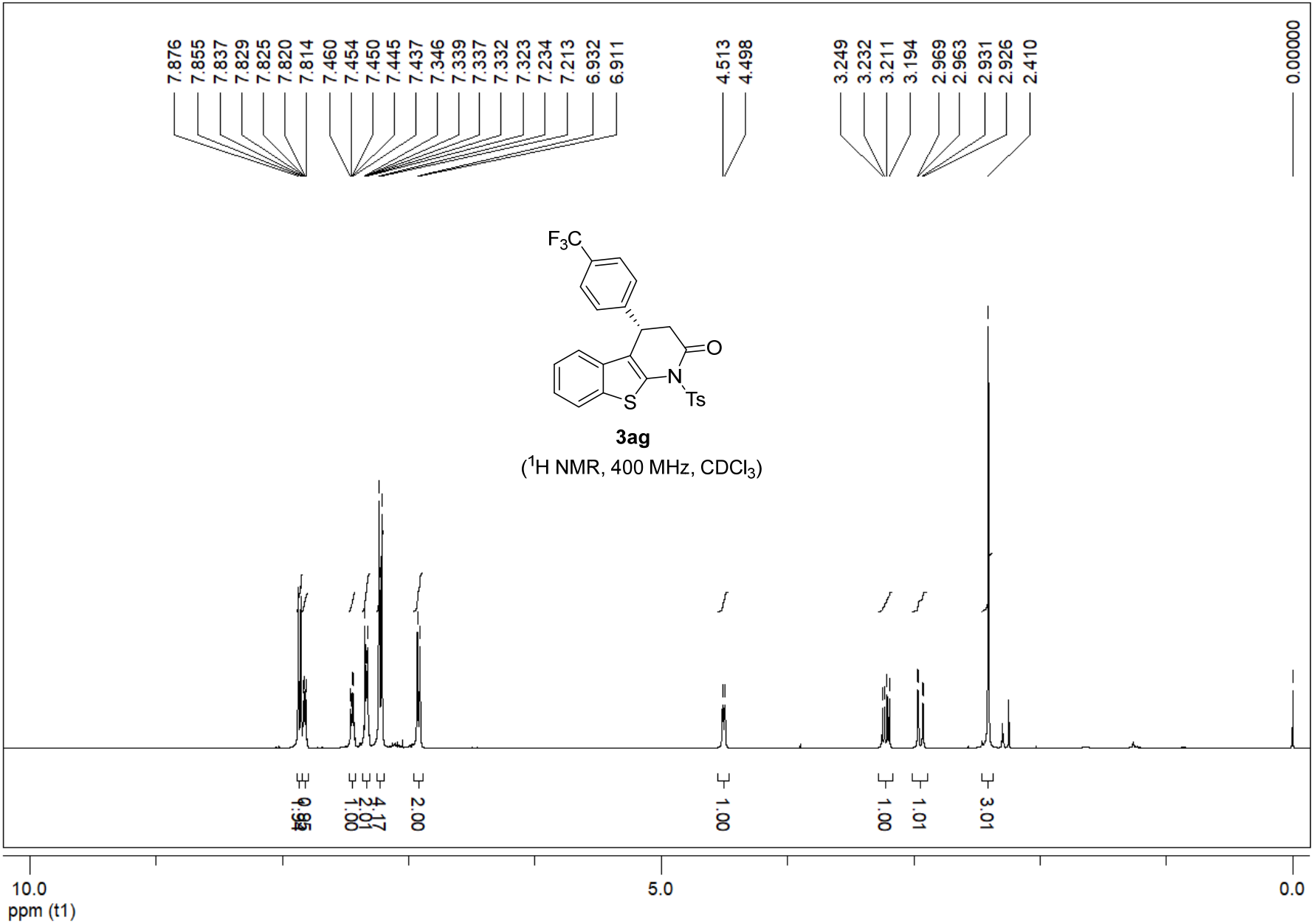

168.292
145.533
139.654
138.462
136.678
135.331
135.067
134.658
129.463
128.653
128.600
128.017
127.201
124.781
124.313
123.597
121.822
120.806
120.442
77.317
77.000
76.682
41.491
36.413
21.650
21.256
Me
O
N
Ts
S
3ad
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)


7.920
7.900
7.818
7.810
7.803
7.795
7.466
7.458
7.451
7.443
7.325
7.317
7.310
7.302
7.254
7.231
6.925
6.905
6.885
6.655
6.649
6.634
6.629
6.501
6.379
6.360
4.430
4.425
4.412
4.407
3.642
3.226
3.208
3.188
3.170
2.971
2.966
2.933
2.928
2.416
0.00000
OMe
O
N
Ts
S
3ae
(1H NMR, 400 MHz, CDCl3)
2.00
1.00
1.06
2.03
2.13
1.02
1.00
1.00
1.01
1.01
3.01
1.02
1.00
3.00
10.0
5.0
0.0
ppm (t1)


168.303
159.831
145.483
141.284
136.705
135.450
135.004
134.625
129.770
129.443
128.639
124.822
124.362
121.866
120.795
120.357
118.722
112.689
112.278
77.318
77.000
76.683
54.988
41.332
36.306
21.680
OMe
O
N
Ts
S
3ae
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)

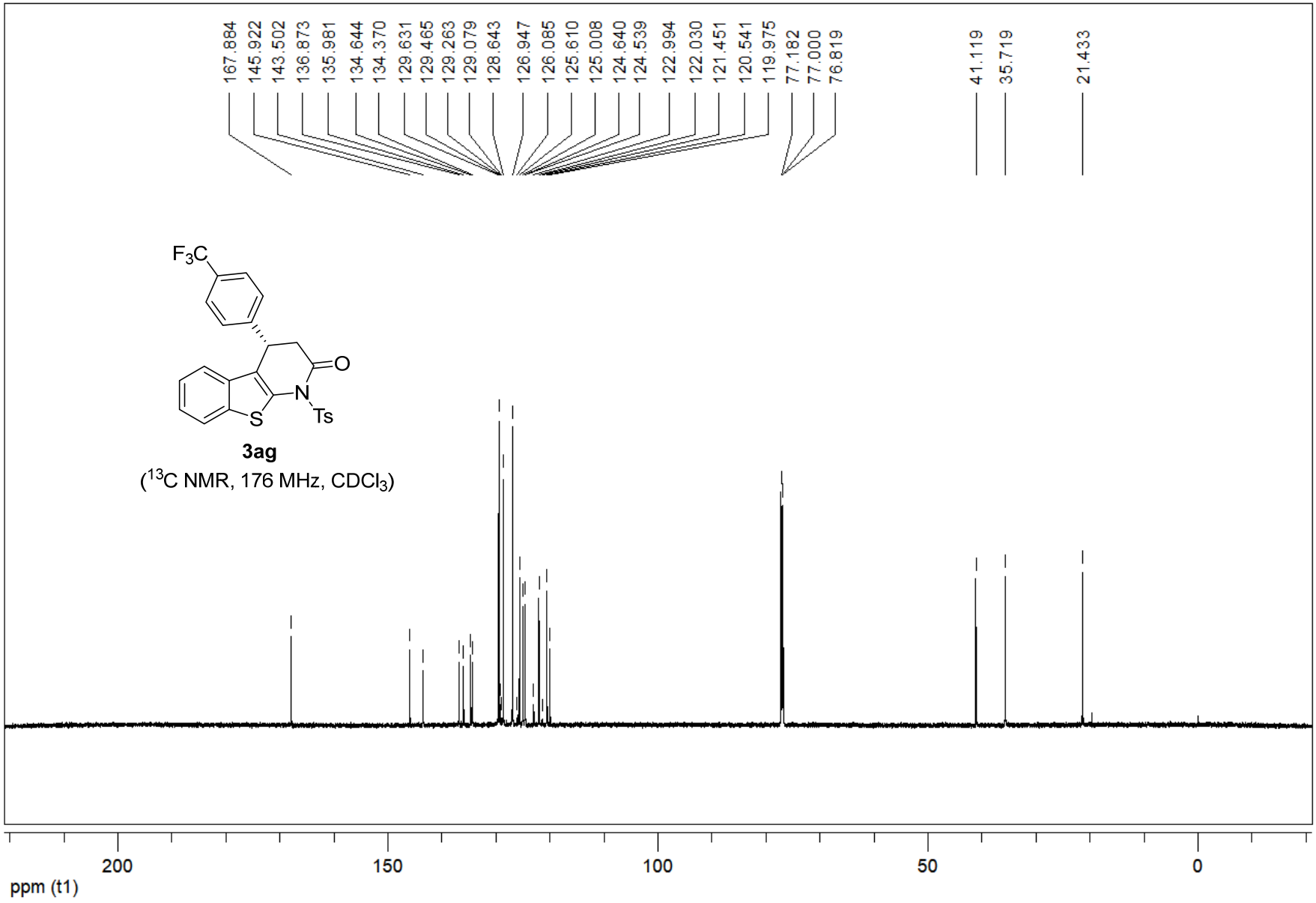

7.917
7.896
7.805
7.797
7.782
7.443
7.429
7.421
7.306
7.297
7.293
7.283
7.252
7.235
7.232
6.799
6.779
6.690
6.670
4.401
4.396
4.384
4.379
3.179
3.161
3.141
3.123
2.912
2.906
2.874
2.869
2.427
2.205
-0.00000
Me
O
N
Ts
S
3af
(1H NMR, 400 MHz, CDCl3)
1.96
1.00
1.00
2.18
2.00
1.00
1.00
1.00
3.00
3.00
10.0
ppm (t1)
5.0
0.0

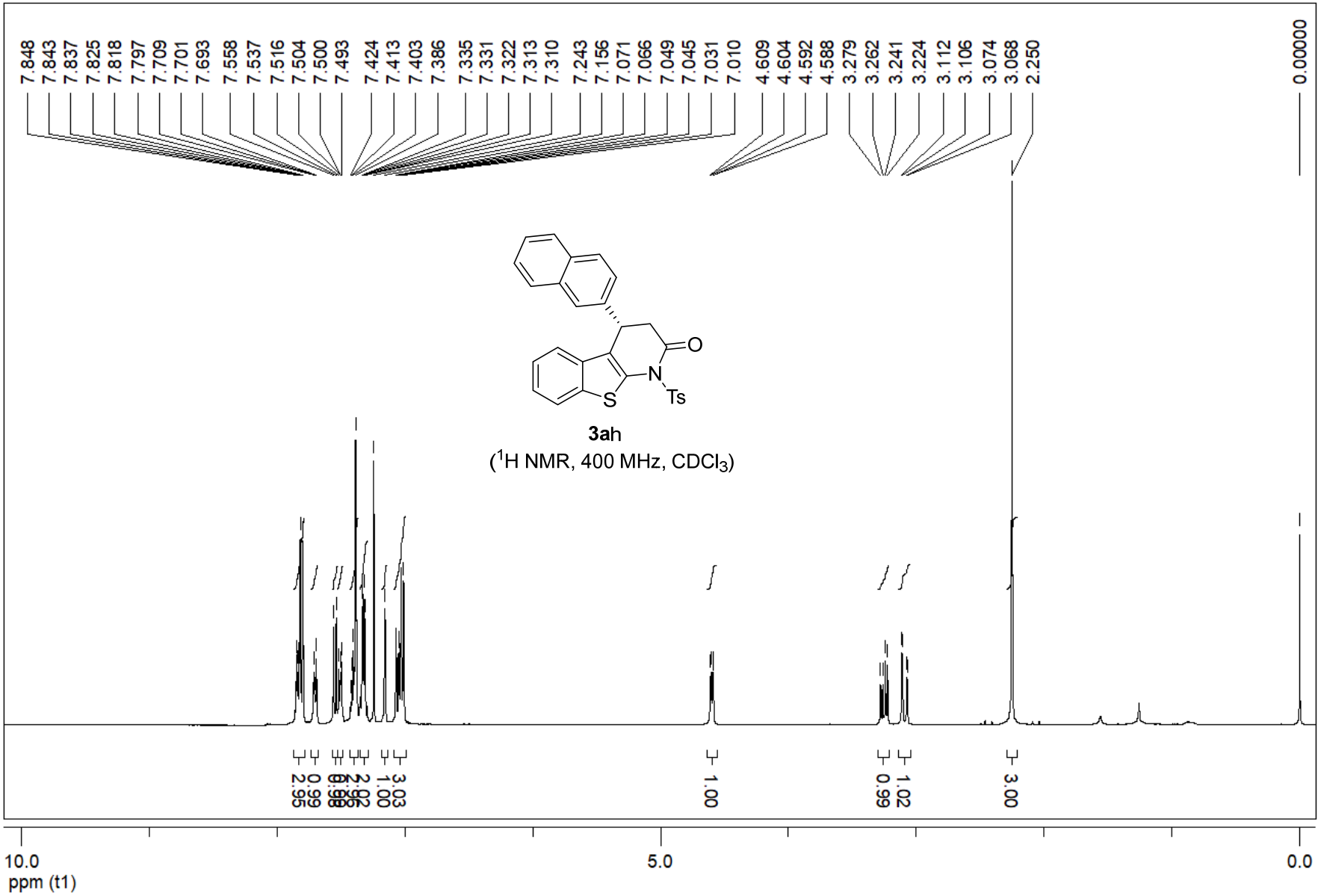

168.392
145.476
136.746
136.734
136.536
135.278
134.989
134.592
129.407
129.375
128.685
126.384
124.773
124.331
121.834
120.873
120.798
77.181
77.000
76.818
41.592
35.961
21.647
20.904
Me
O
N
Ts
S
3af
(^{13}C NMR, 176 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)



3ag

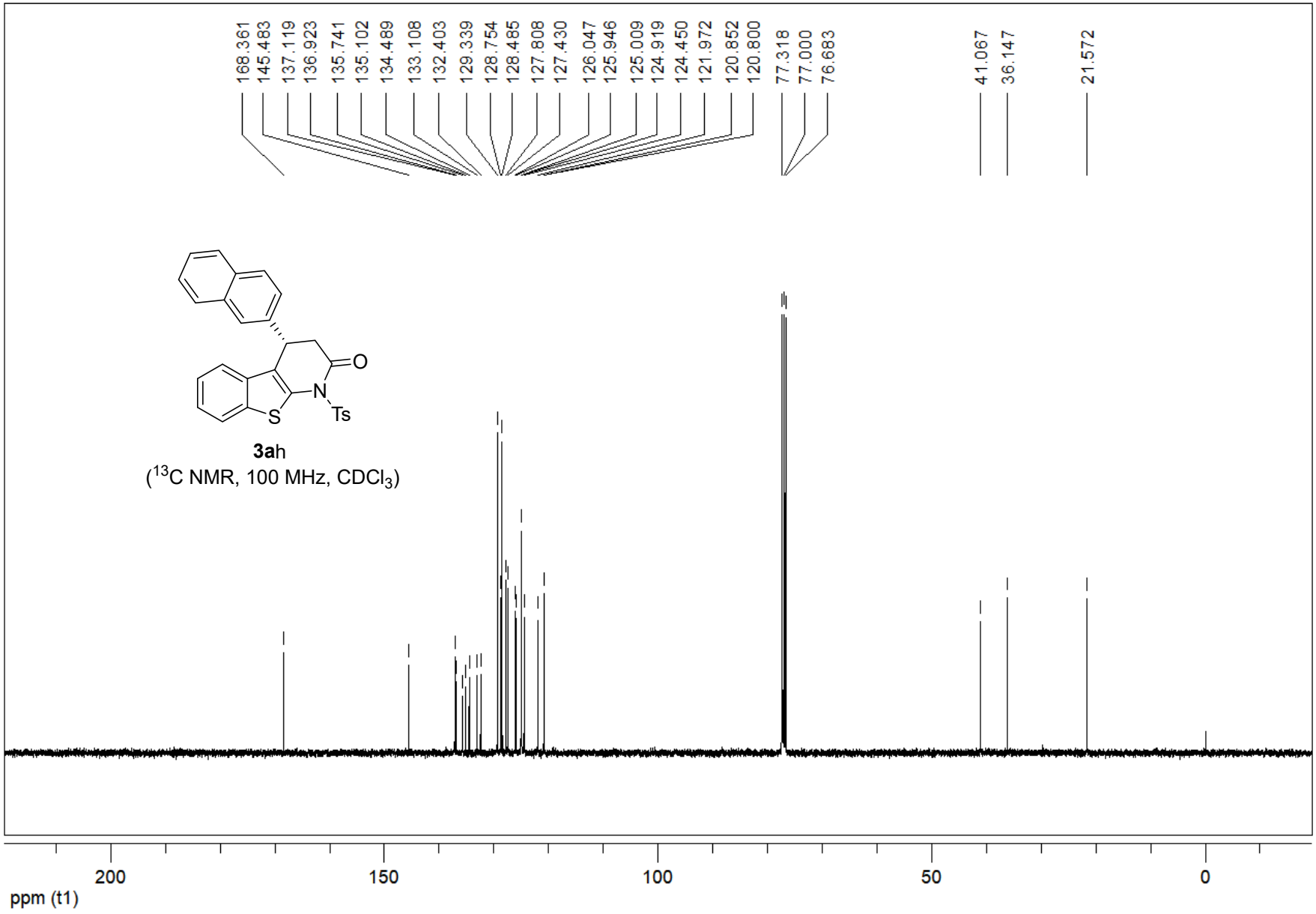
(^{1}H NMR, 400 MHz, $CDCl_3$)


167.884
145.922
143.502
136.873
135.981
134.644
134.370
129.631
129.465
129.263
129.079
128.643
126.947
126.085
125.610
125.008
124.640
124.539
122.994
122.030
121.451
120.541
119.975
77.182
77.000
76.819
41.119
35.719
21.433
F3C
O
N
Ts
S
3ag
(13C NMR, 176 MHz, CDCl3)
200
150
100
50
0
ppm (t1)



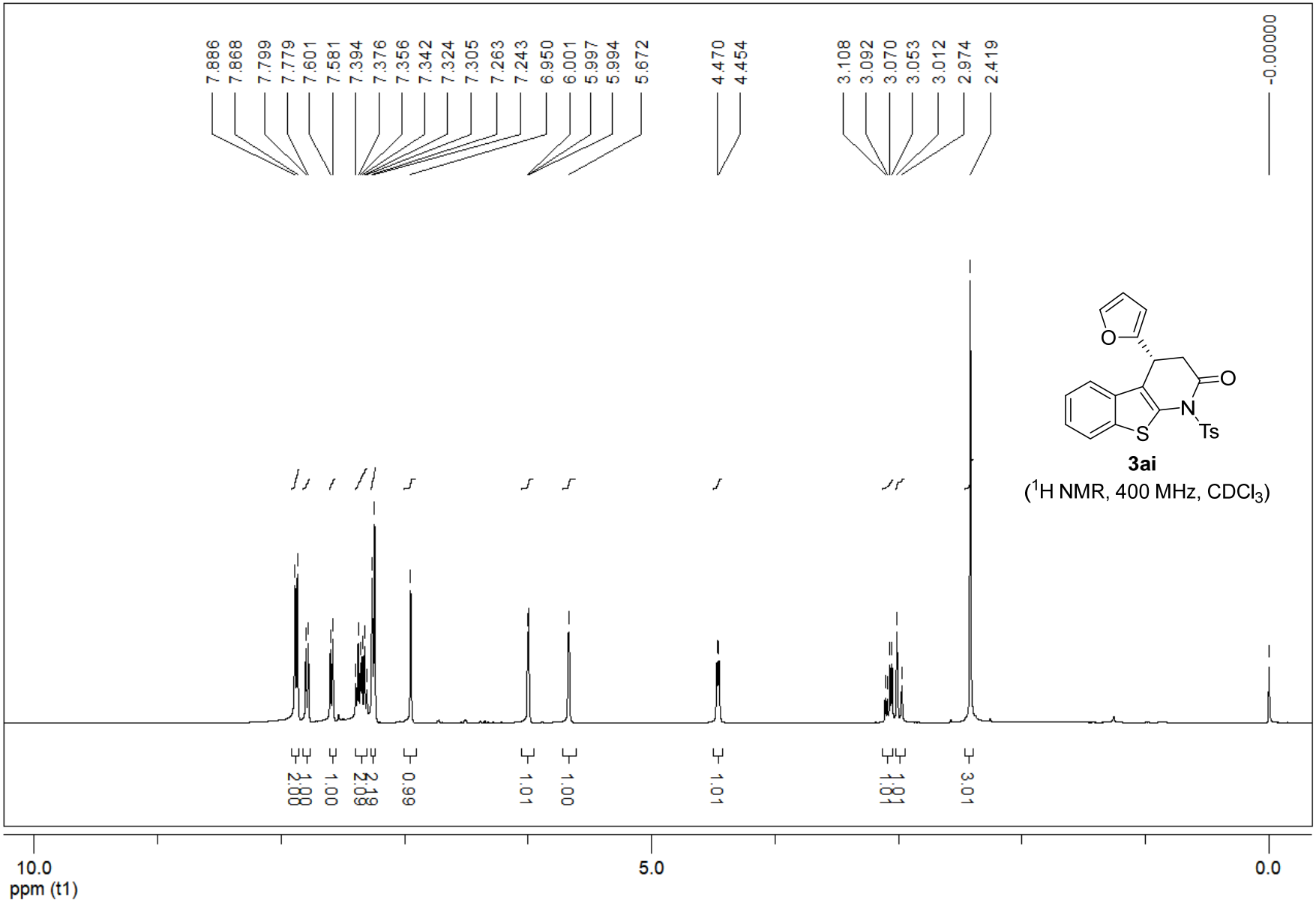
3ah

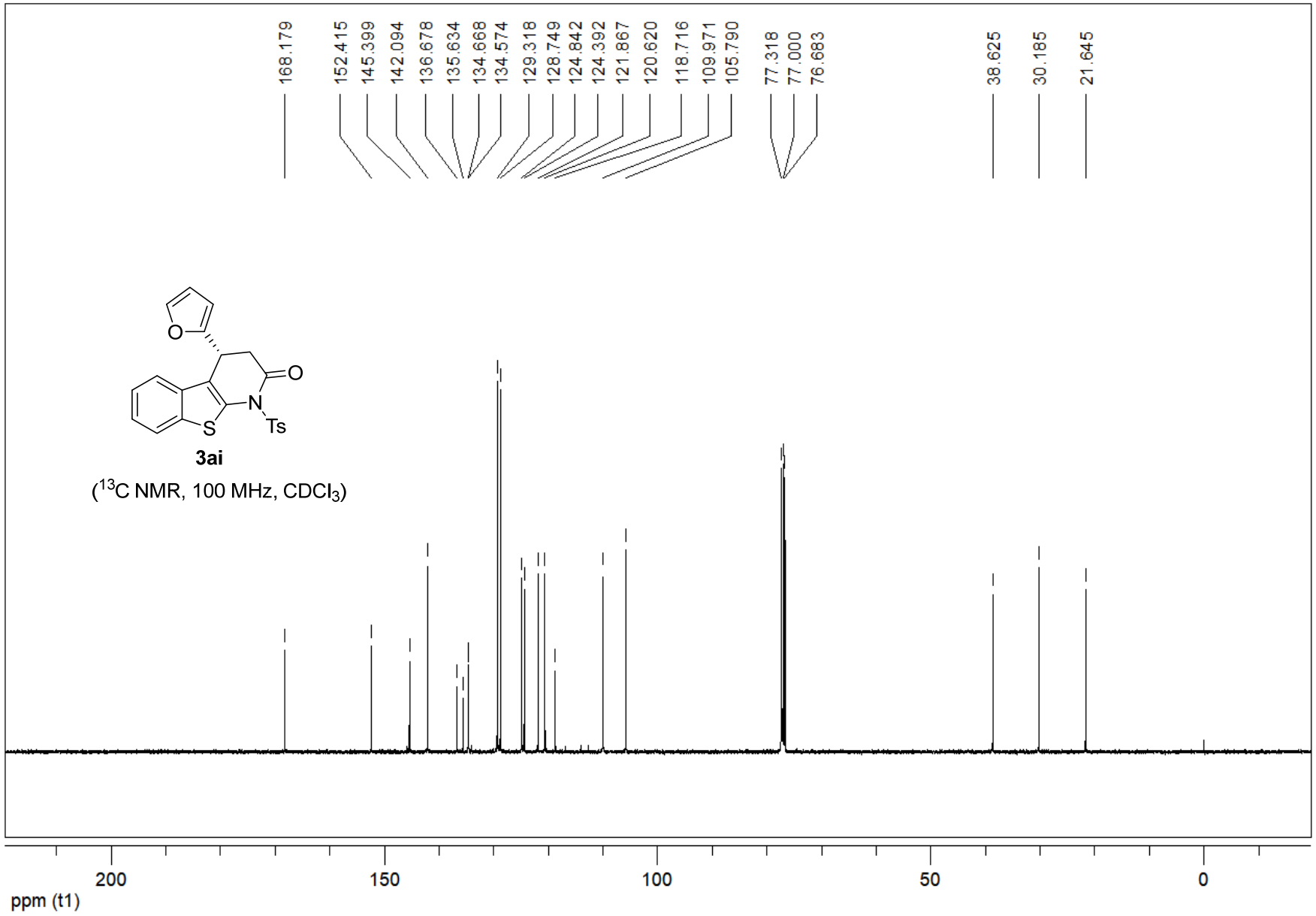
(^{1}H NMR, 400 MHz, $CDCl_3$)

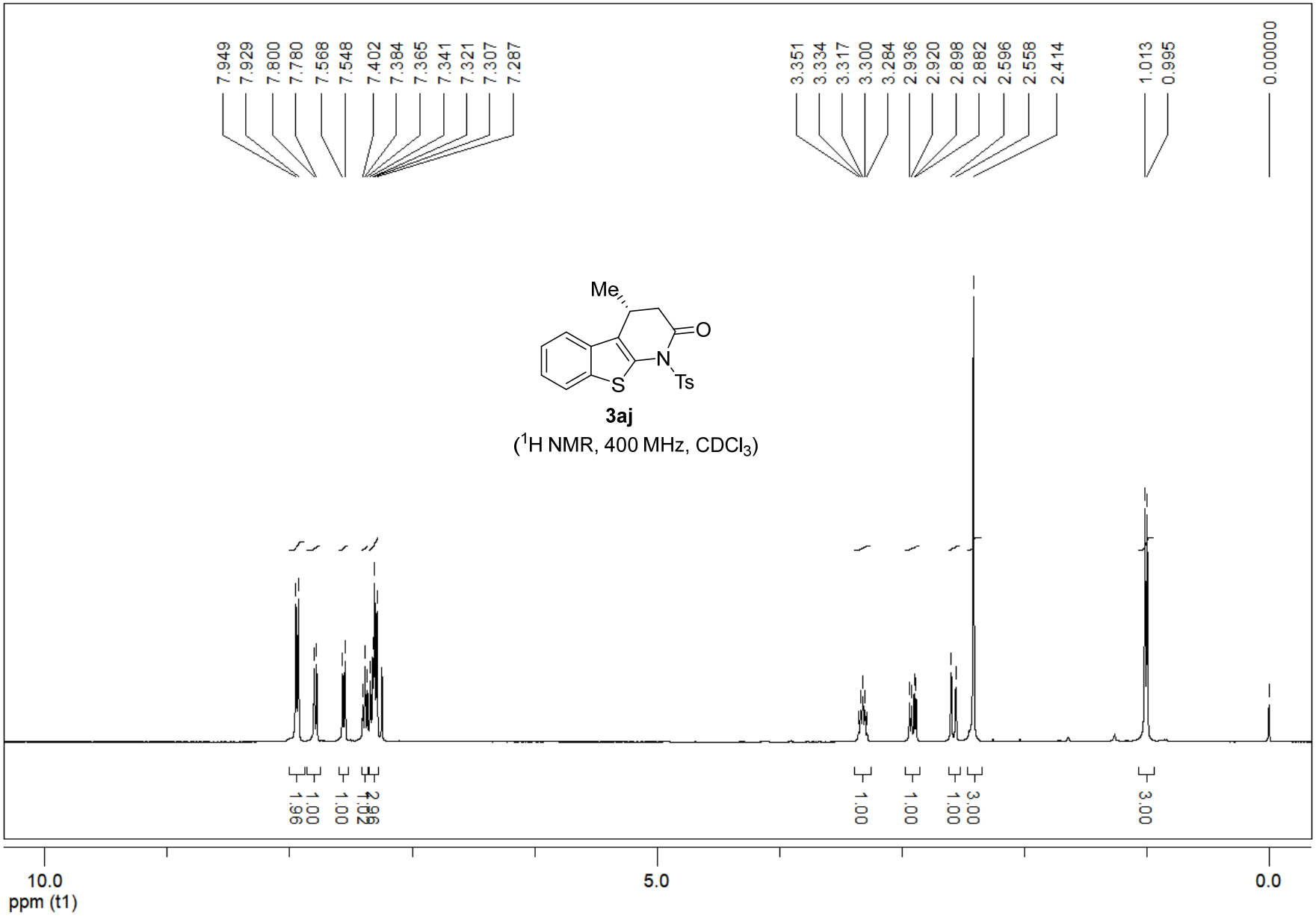


3ah

(^{13}C NMR, 100 MHz, $CDCl_3$)

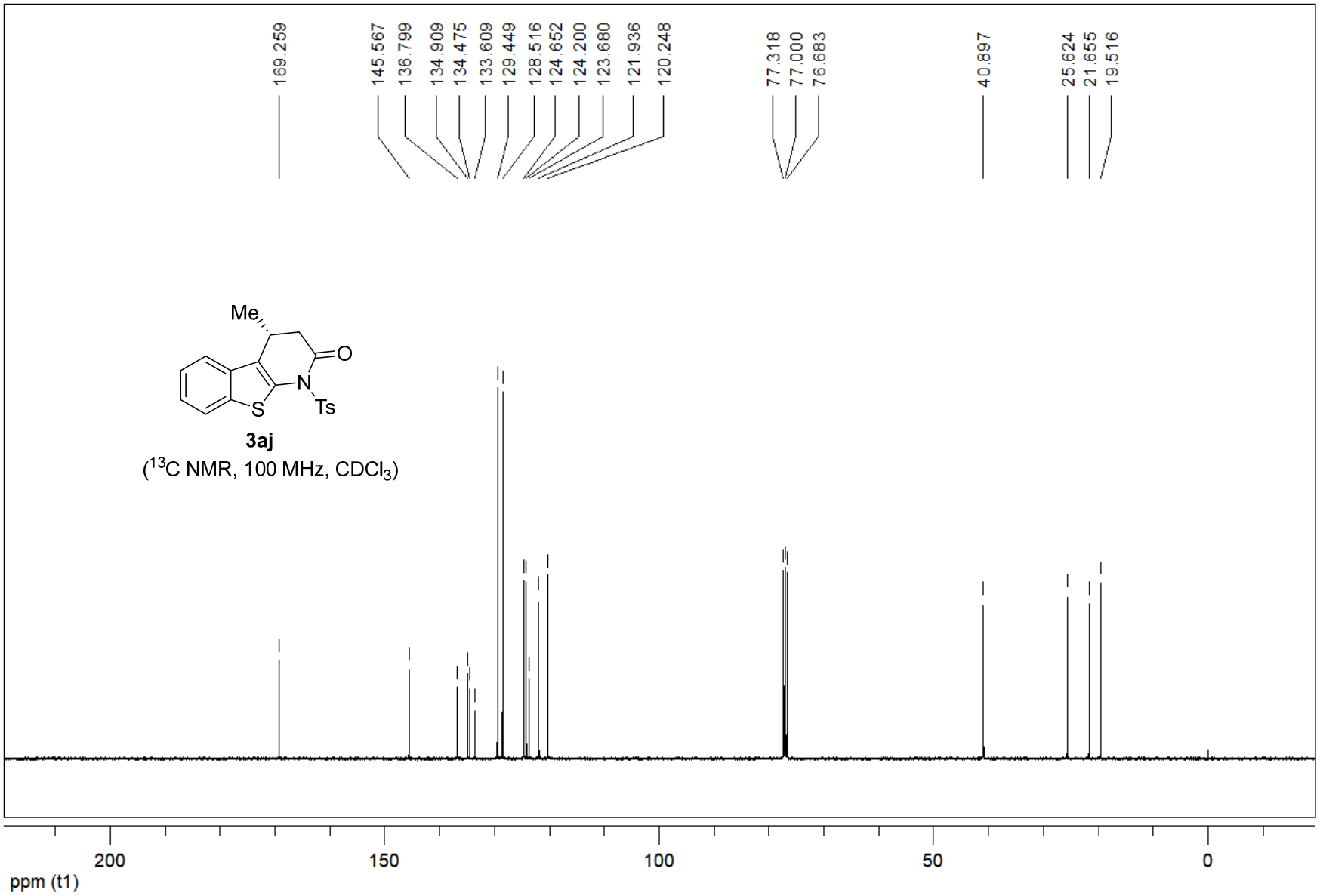

7.886
7.868
7.799
7.779
7.601
7.581
7.394
7.376
7.356
7.342
7.324
7.305
7.263
7.243
6.950
6.001
5.997
5.994
5.672
4.470
4.454
3.108
3.092
3.070
3.053
3.012
2.974
2.419
-0.00000
2.88
1.00
2.09
0.99
1.01
1.00
1.01
1.81
3.01
O
O
N
Ts
S
3ai
(^{1}H NMR, 400 MHz, $CDCl_3$)
10.0
ppm (t1)
5.0
0.0

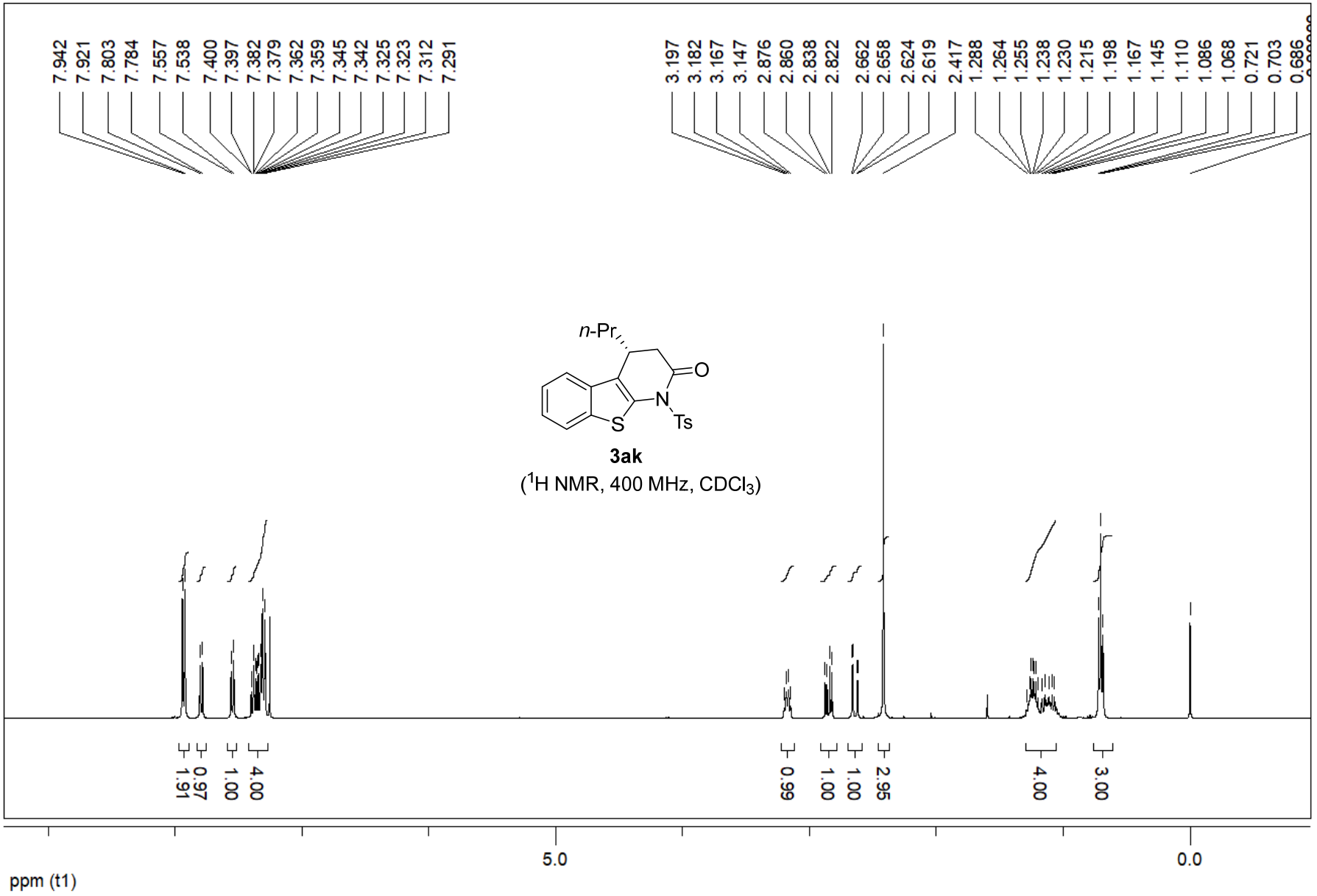

168.179
152.415
145.399
142.094
136.678
135.634
134.668
134.574
129.318
128.749
124.842
124.392
121.867
120.620
118.716
109.971
105.790
77.318
77.000
76.683
38.625
30.185
21.645
O
O
N
S
Ts
3ai
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm (t1)



3aj

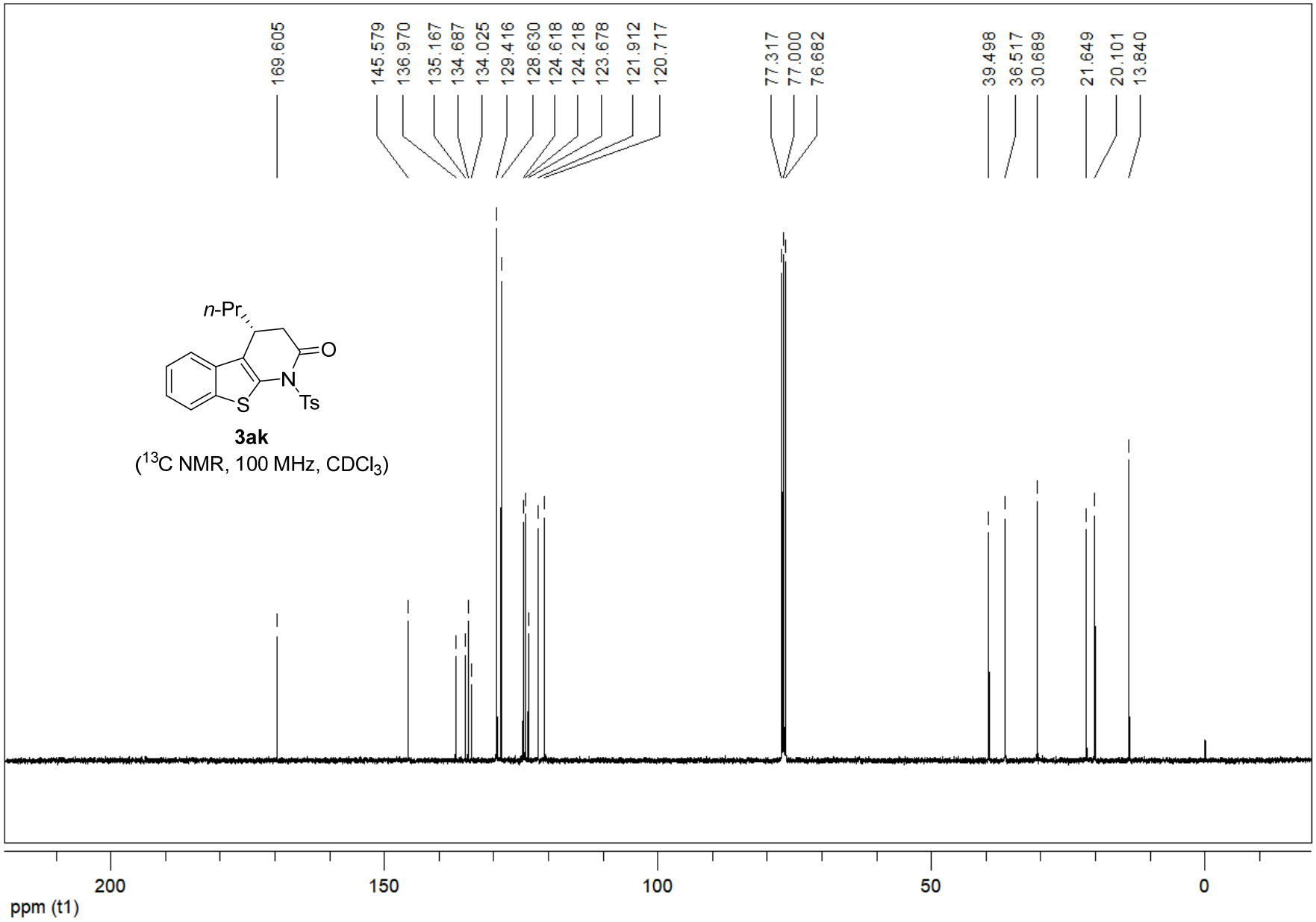
(^{1}H NMR, 400 MHz, $CDCl_3$)

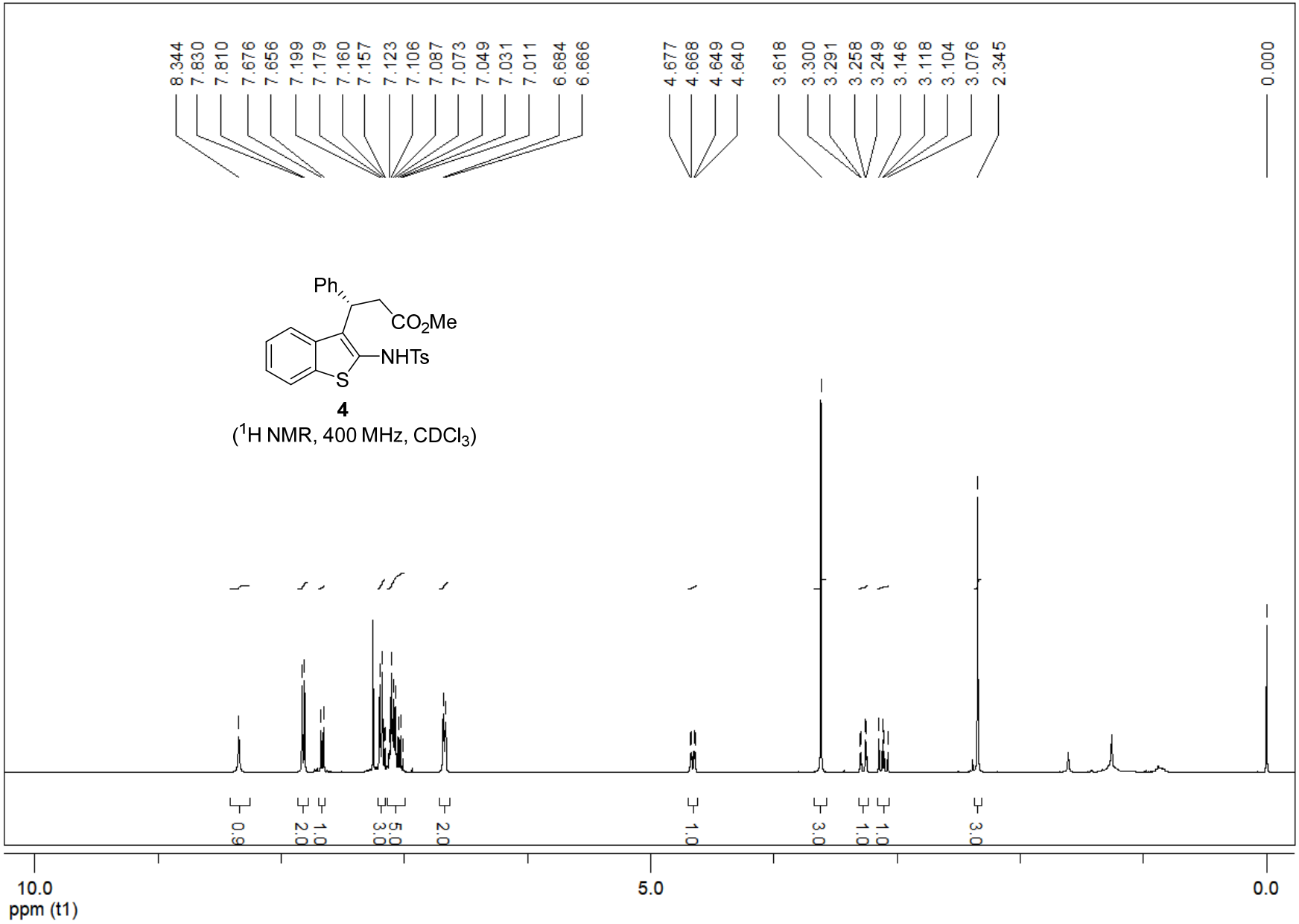

169.259
145.567
136.799
134.909
134.475
133.609
129.449
128.516
124.652
124.200
123.680
121.936
120.248
77.318
77.000
76.683
40.897
25.624
21.655
19.516
Me
O
N
S
Ts
3aj
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm (t1)



3ak

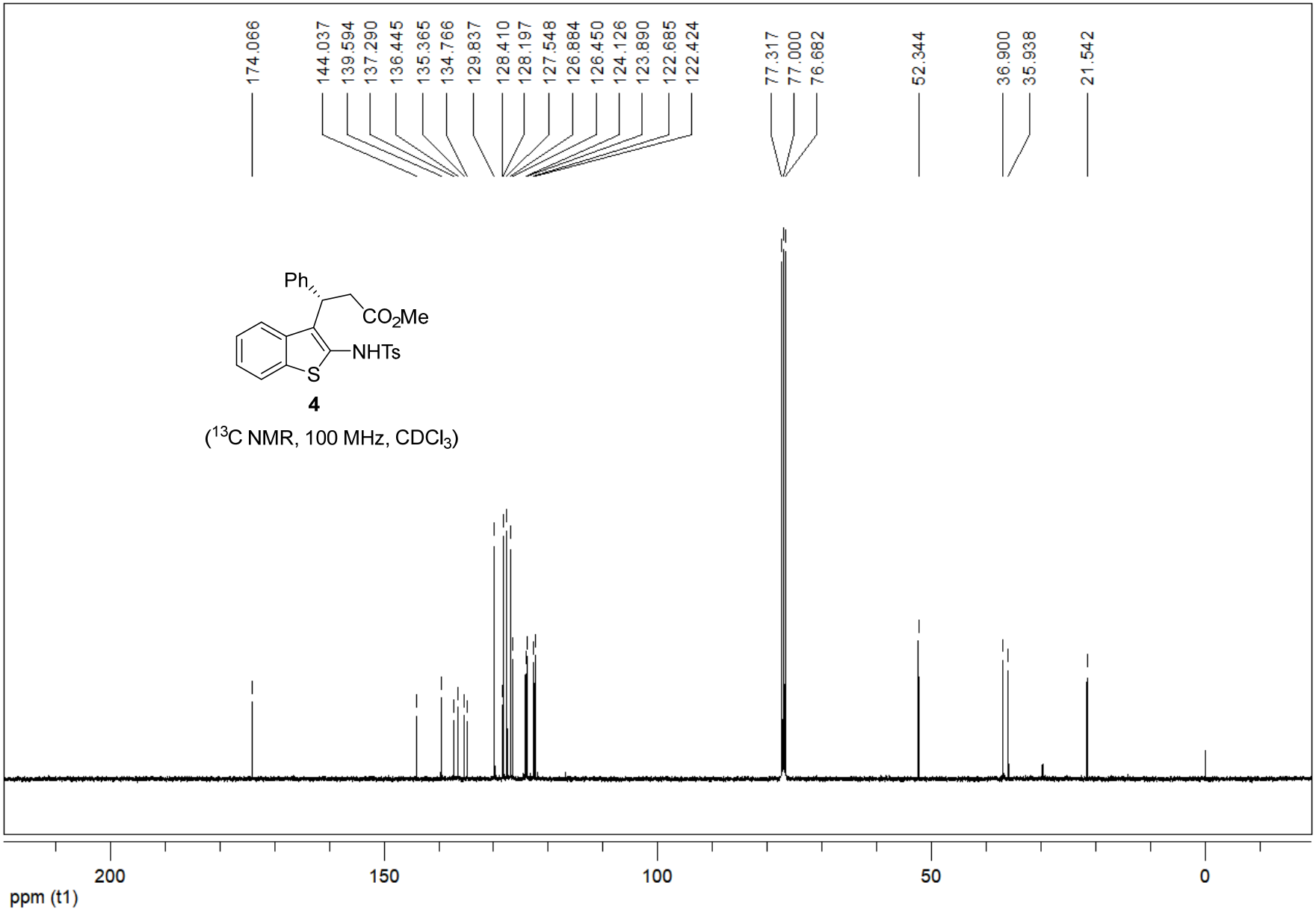
(^{1}H NMR, 400 MHz, $CDCl_3$)


169.605
145.579
136.970
135.167
134.687
134.025
129.416
128.630
124.618
124.218
123.678
121.912
120.717
77.317
77.000
76.682
39.498
36.517
30.689
21.649
20.101
13.840
n-Pr
O
N
Ts
S
3ak
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm (t1)



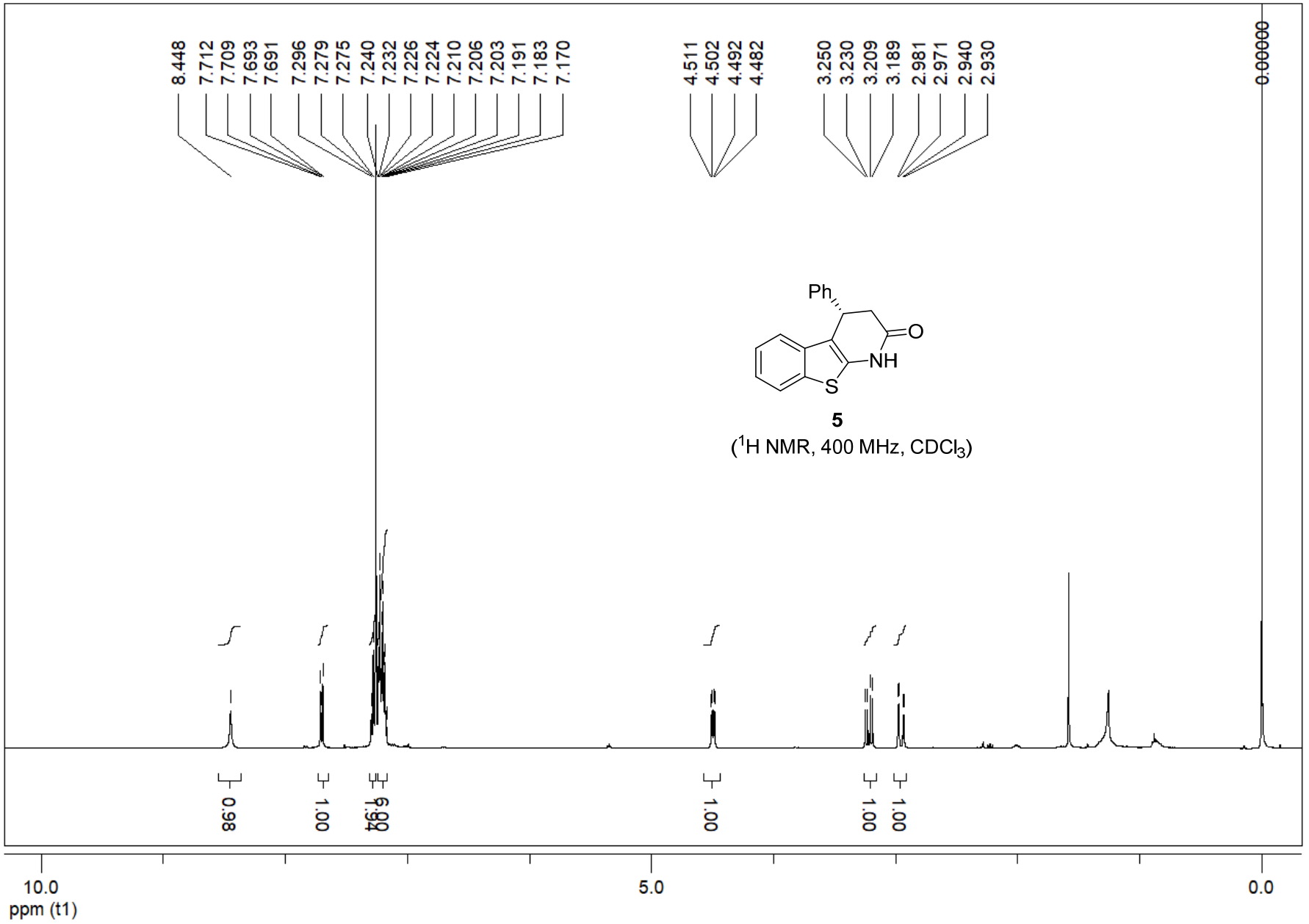
4

(^{1}H NMR, 400 MHz, $CDCl_3$)



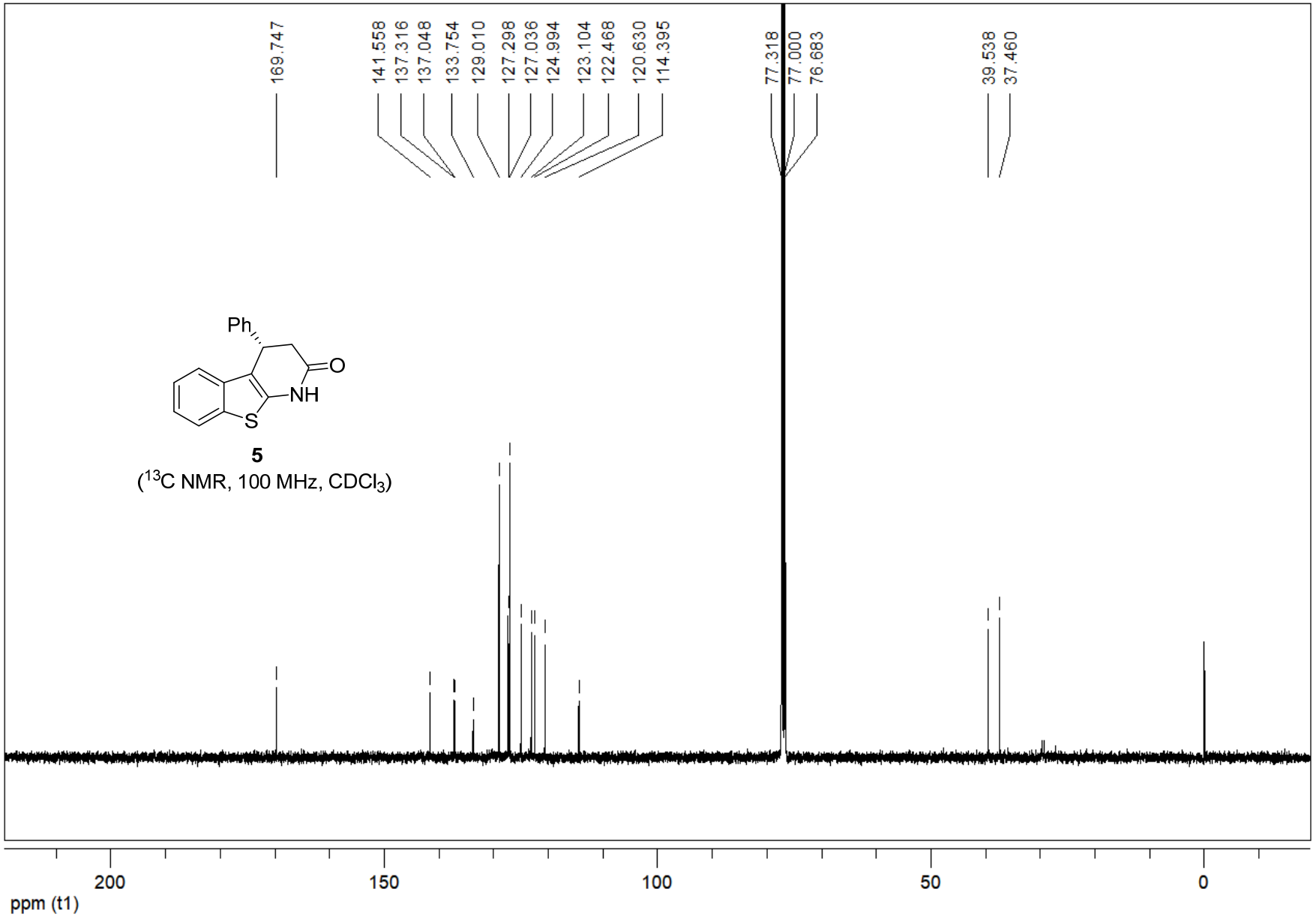
4

(^{13}C NMR, 100 MHz, $CDCl_3$)



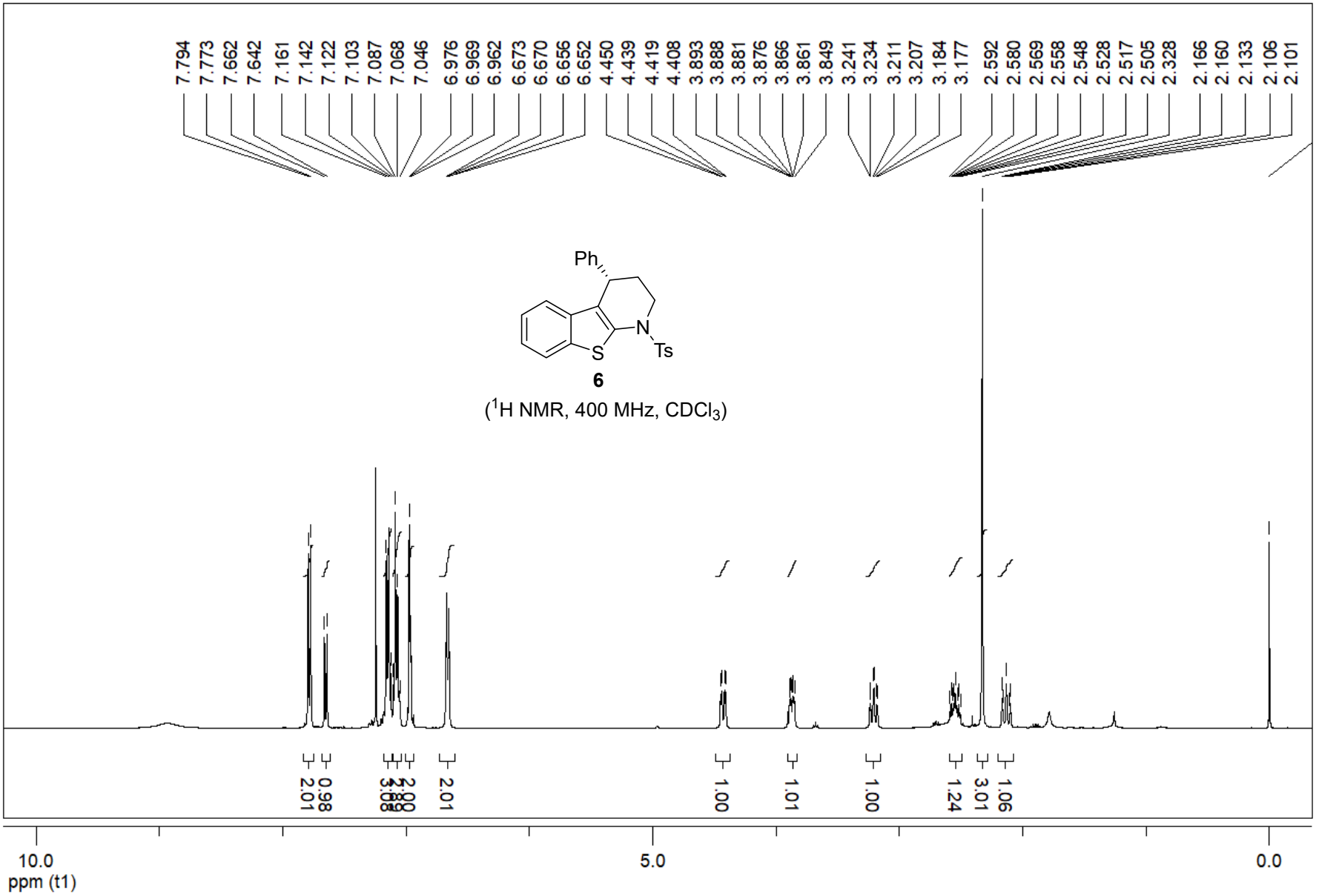
5

(^{1}H NMR, 400 MHz, $CDCl_3$)



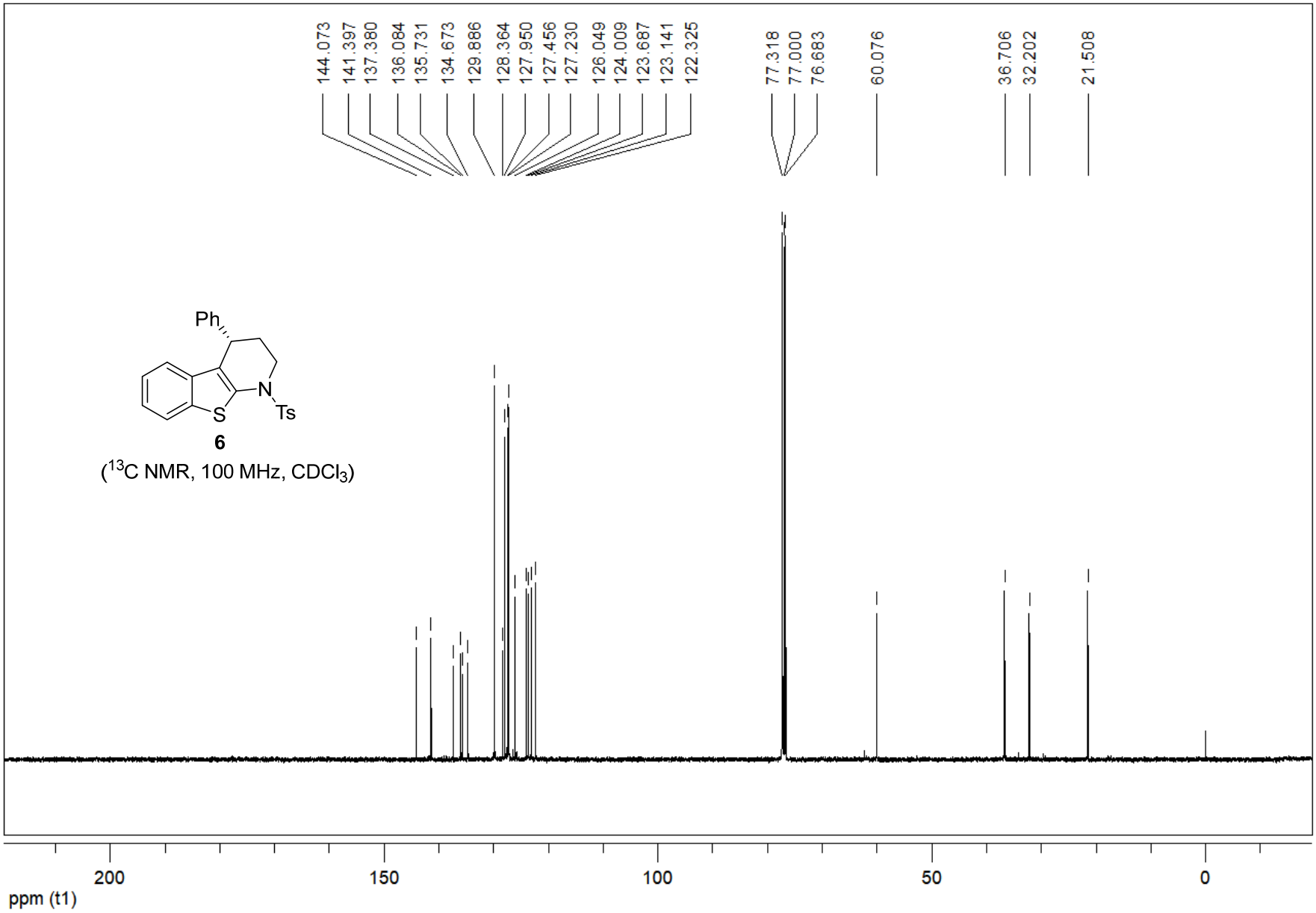
5

(^{13}C NMR, 100 MHz, $CDCl_3$)

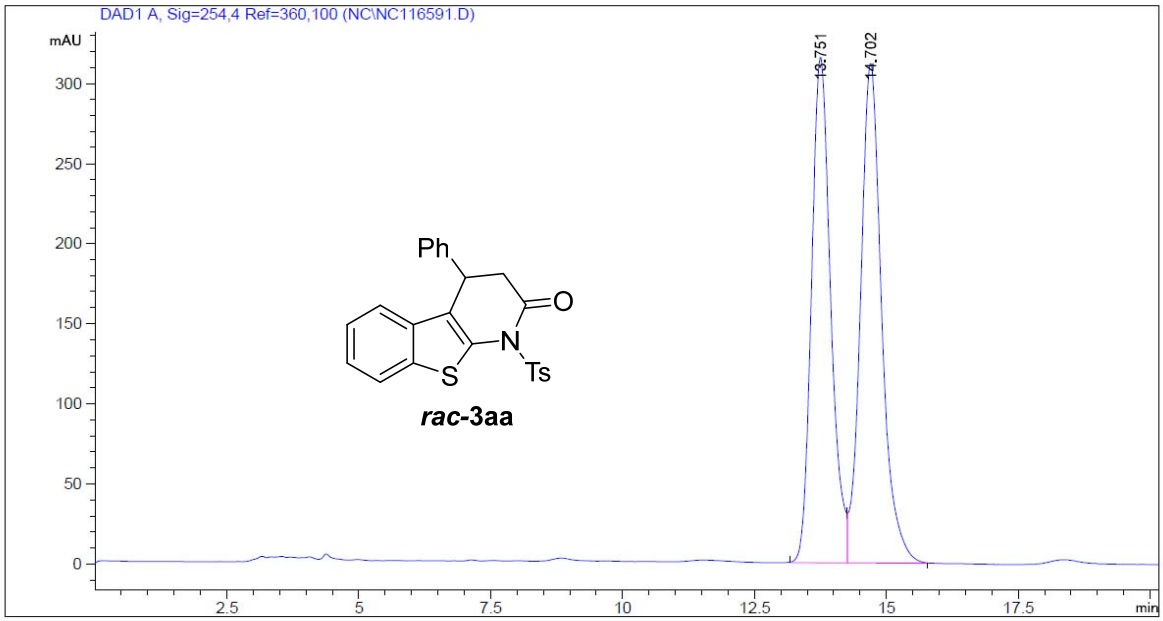


6

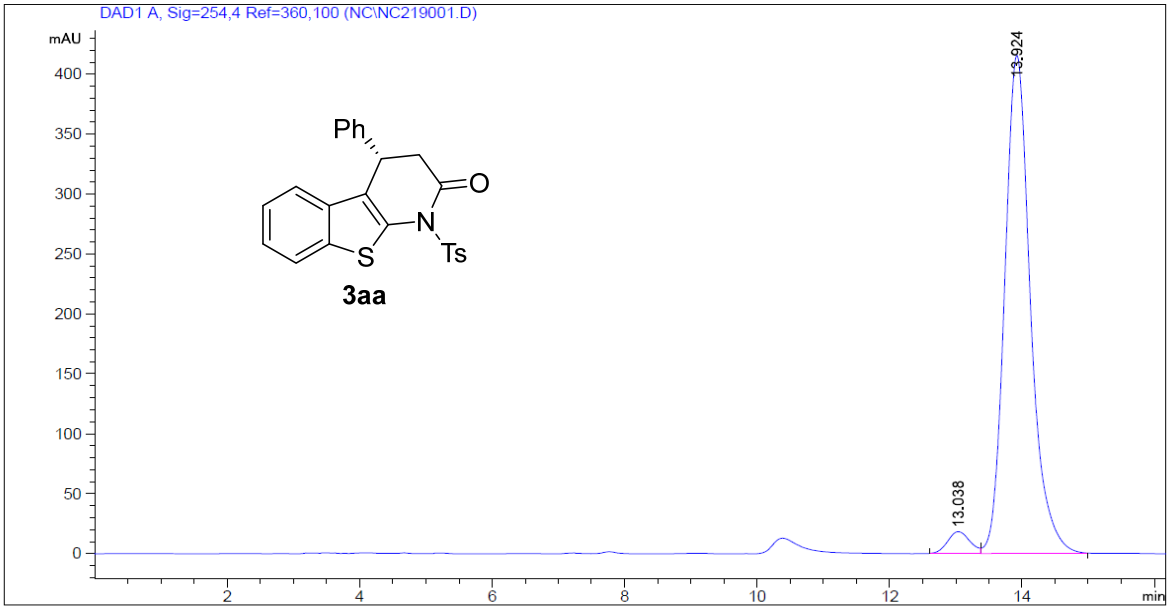
(^{1}H NMR, 400 MHz, $CDCl_3$)


144.073
141.397
137.380
136.084
135.731
134.673
129.886
128.364
127.950
127.456
127.230
126.049
124.009
123.687
123.141
122.325
77.318
77.000
76.683
60.076
36.706
32.202
21.508
Ph
N
S
Ts
6
(^{13}C NMR, 100 MHz, $CDCl_3$)
200
150
100
50
0
ppm (t1)

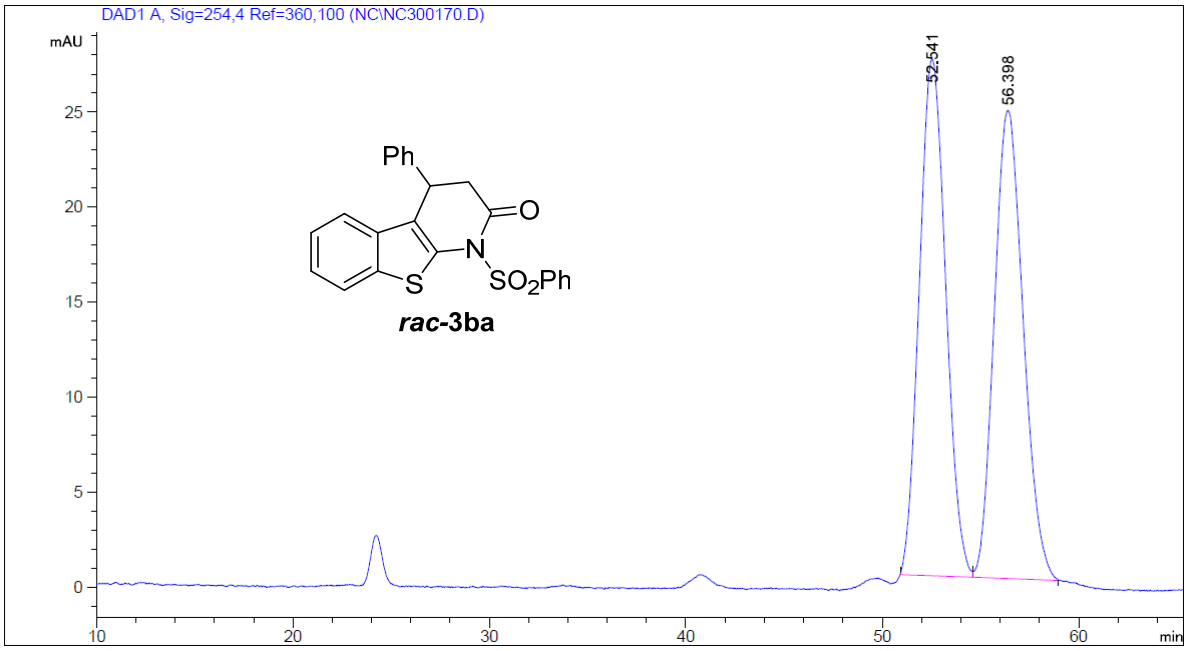
8. Copies of HPLC chromatograms of new products



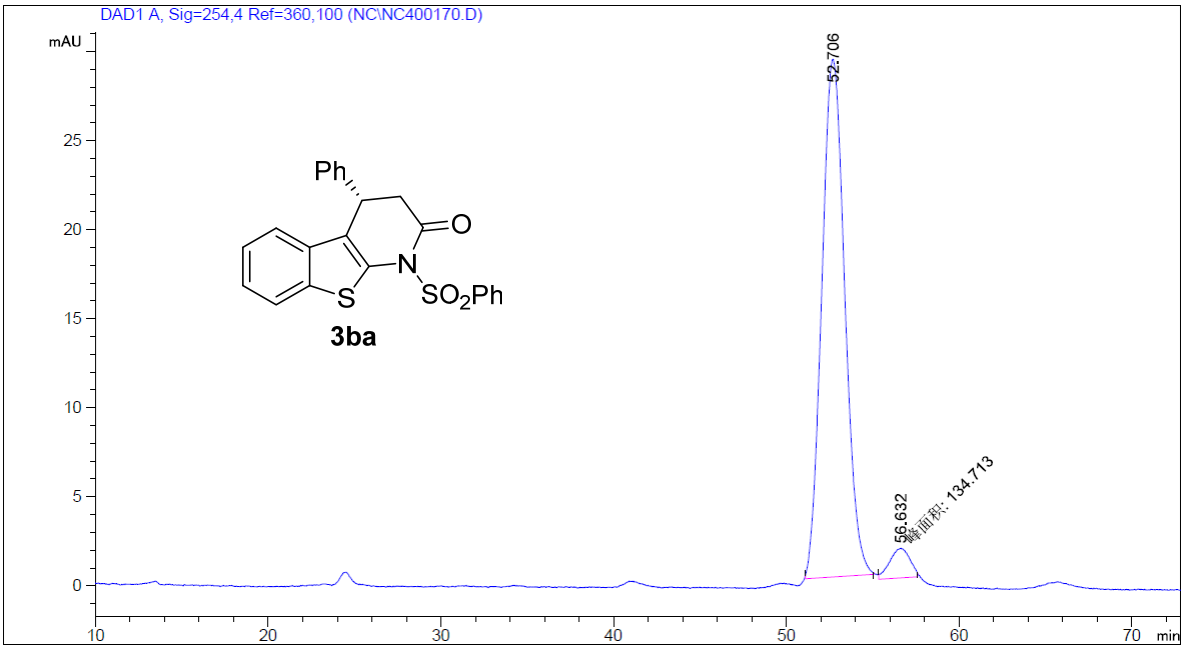
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.751	BV	0.3873	7986.53271	315.55652	47.8116
2	14.702	VB	0.4241	8717.63672	311.93054	52.1884



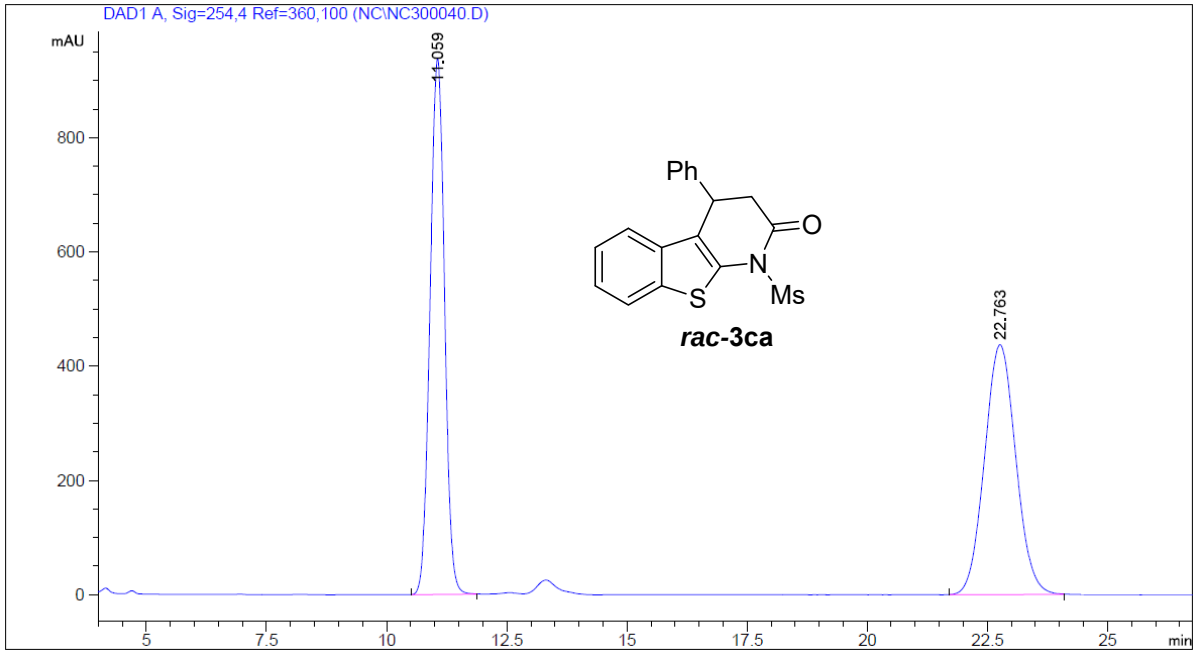
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.038	BV	0.3543	421.42908	18.18786	3.6156
2	13.924	VB	0.4134	1.12345e4	415.61453	96.3844



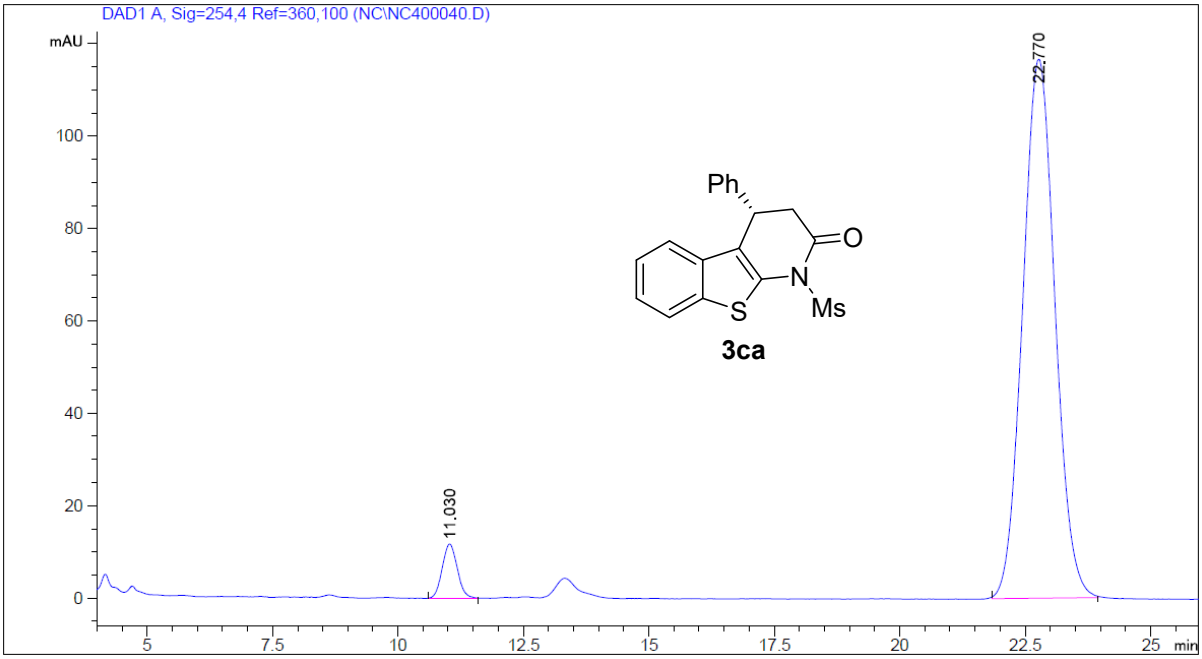
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.541	BV	1.1079	2548.18530	27.17798	50.1770
2	56.398	VB	1.2117	2530.21118	24.64649	49.8230



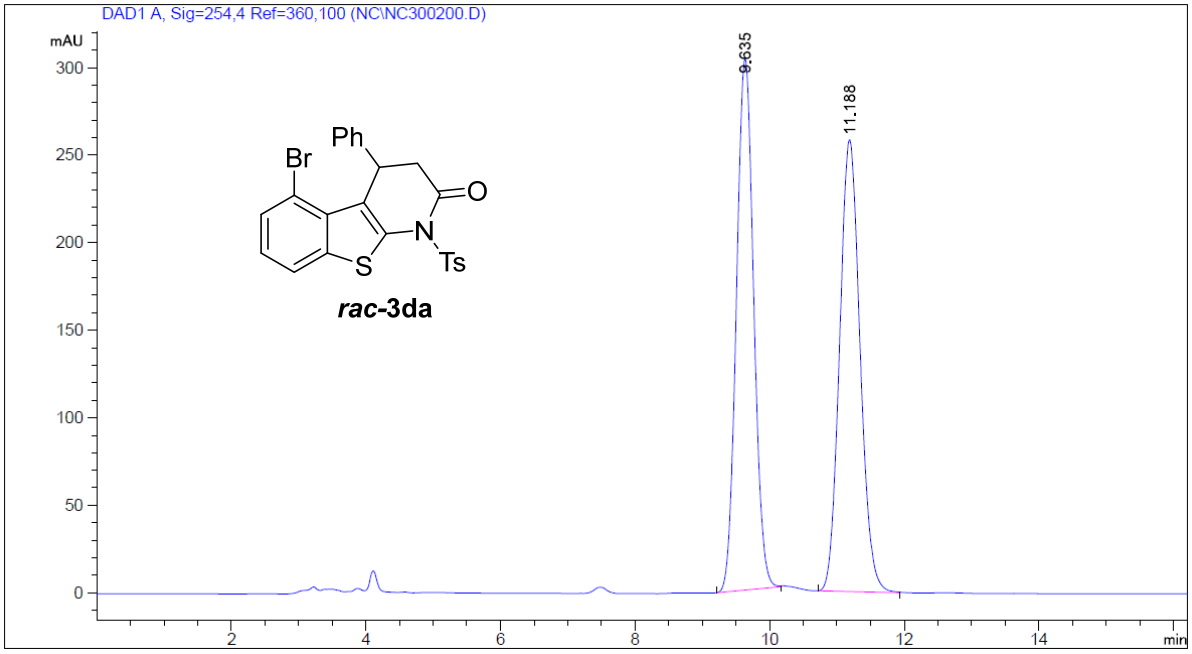
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.706	BB	1.1806	2684.38599	29.08891	95.2214
2	56.632	MM	1.3451	134.71315	1.66917	4.7786



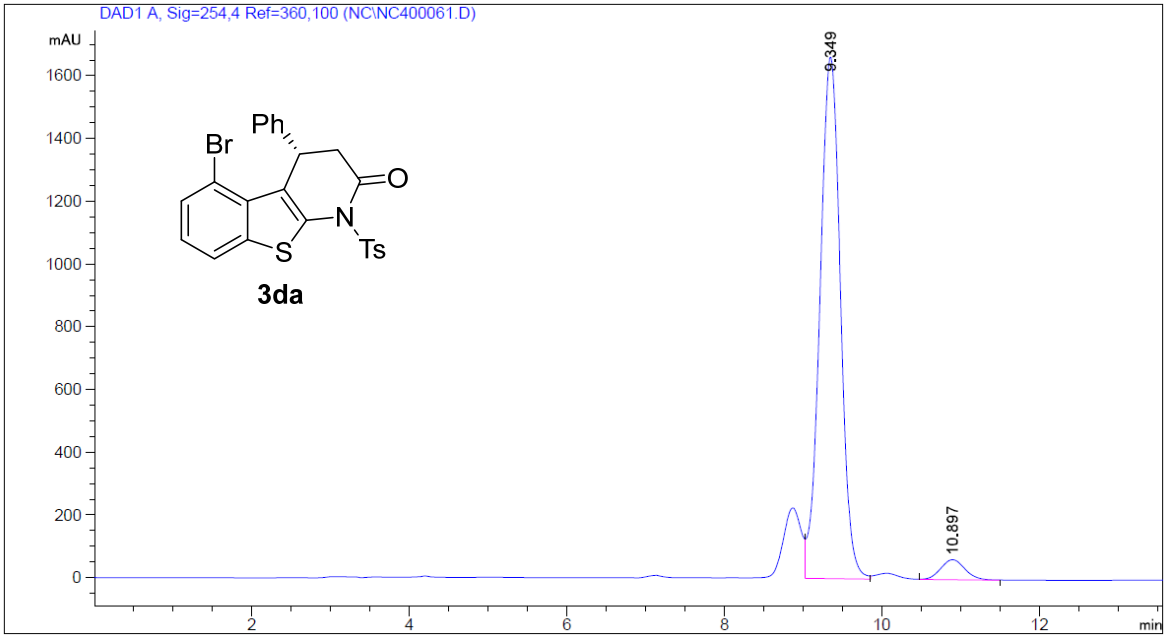
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.059	BB	0.3302	1.96189e4	937.21484	49.8276
2	22.763	BB	0.7052	1.97547e4	437.14502	50.1724



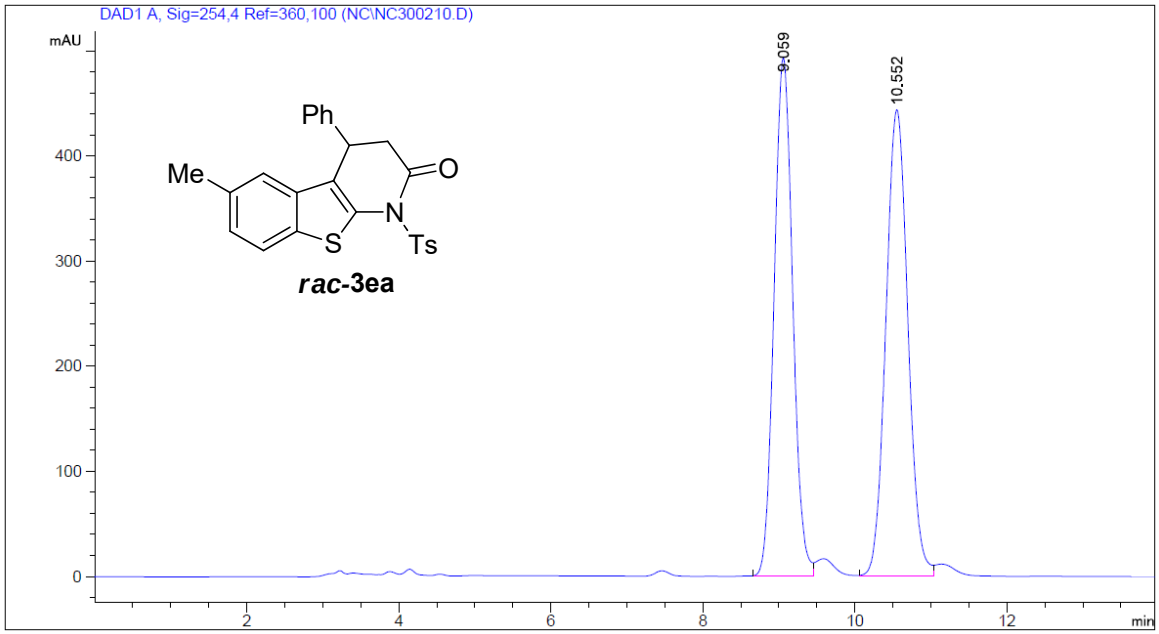
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.030	BB	0.3261	243.51080	11.73695	4.4611
2	22.770	BB	0.6933	5215.04834	116.71575	95.5389



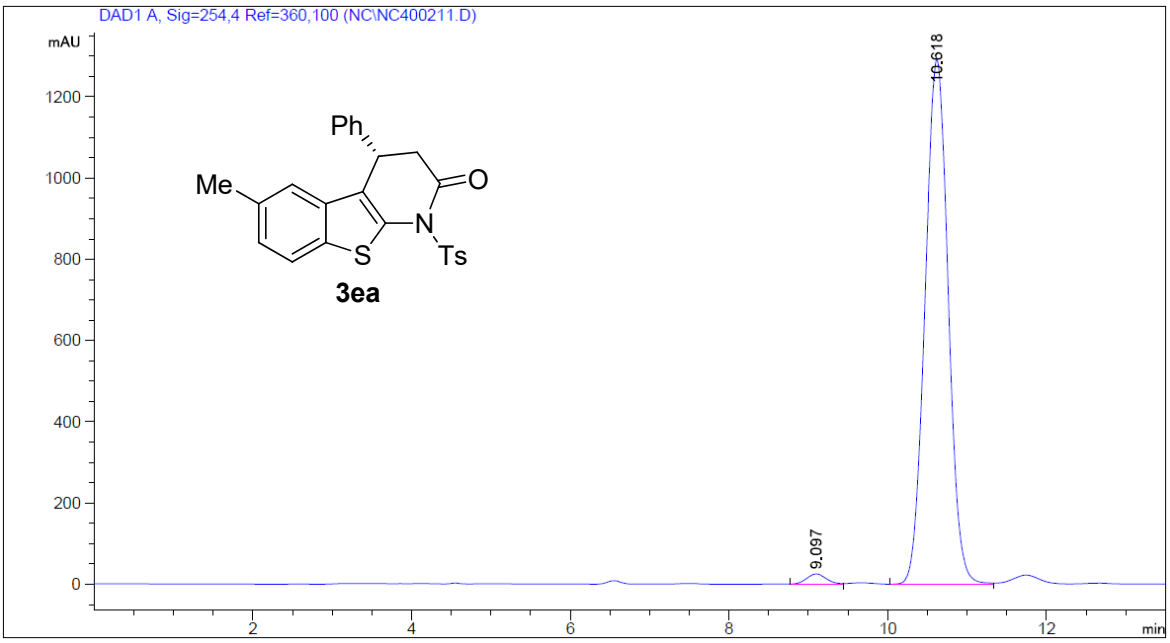
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.635	BB	0.2795	5398.69873	303.52084	49.7906
2	11.188	BB	0.3281	5444.11475	258.07324	50.2094



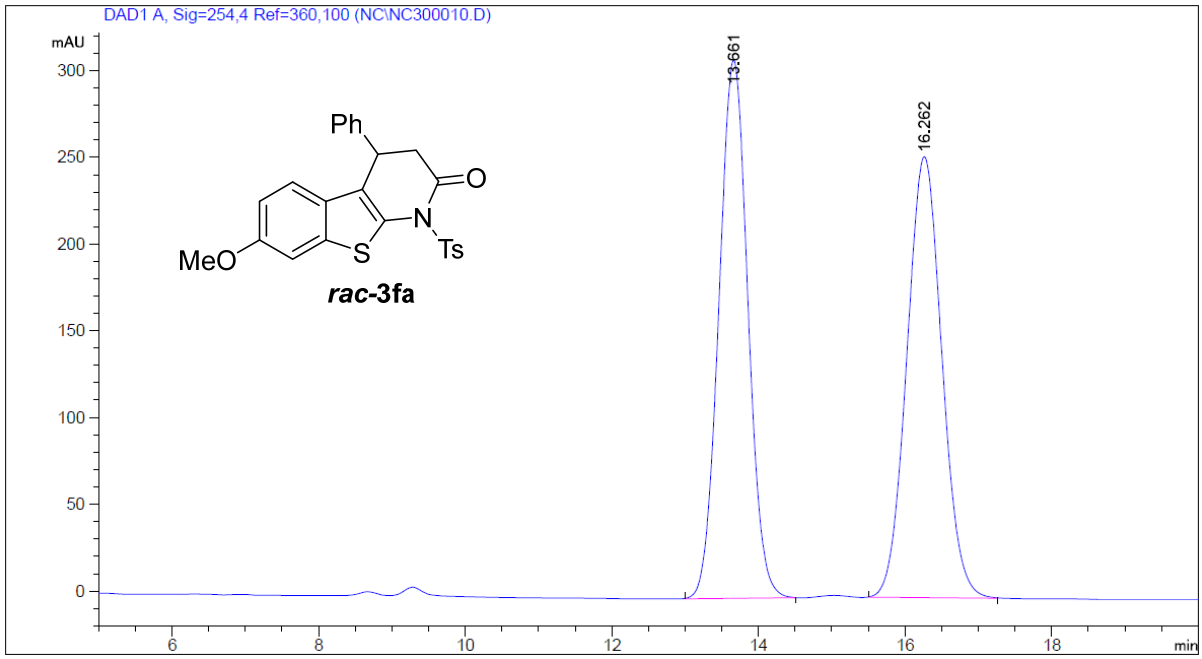
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.349	VV	0.2829	3.00678e4	1663.15540	95.6679
2	10.897	VB	0.3282	1361.55457	64.00226	4.3321



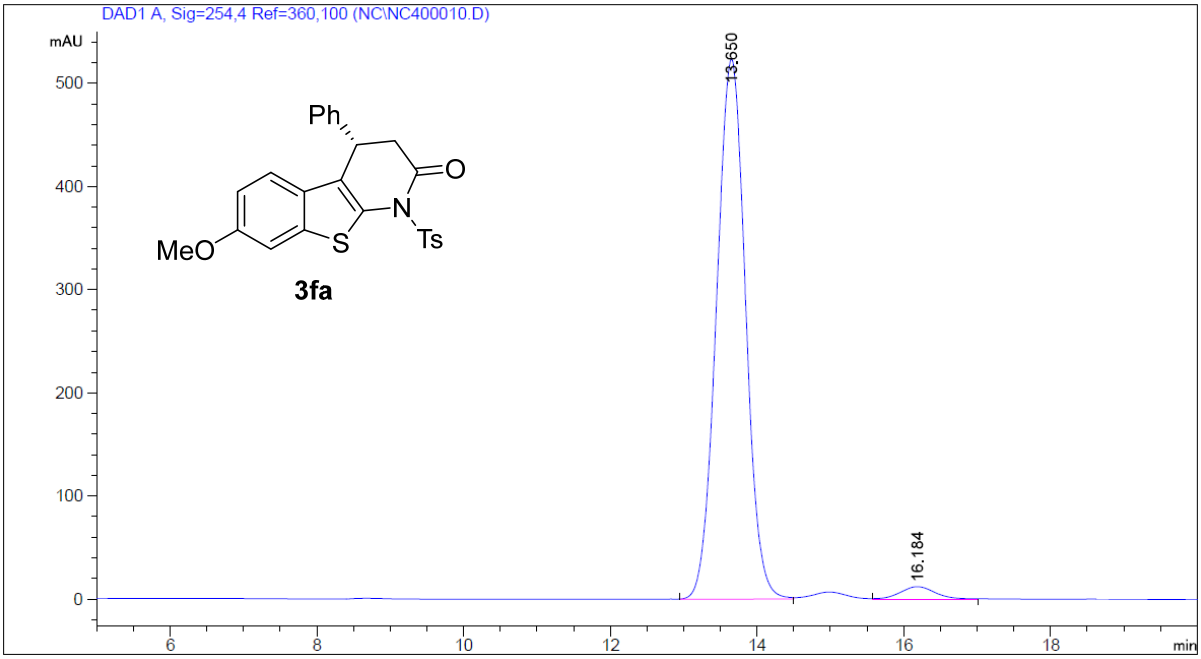
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.059	BV	0.2636	8353.78809	493.13474	48.3554
2	10.552	BV	0.3126	8922.04004	443.64987	51.6446



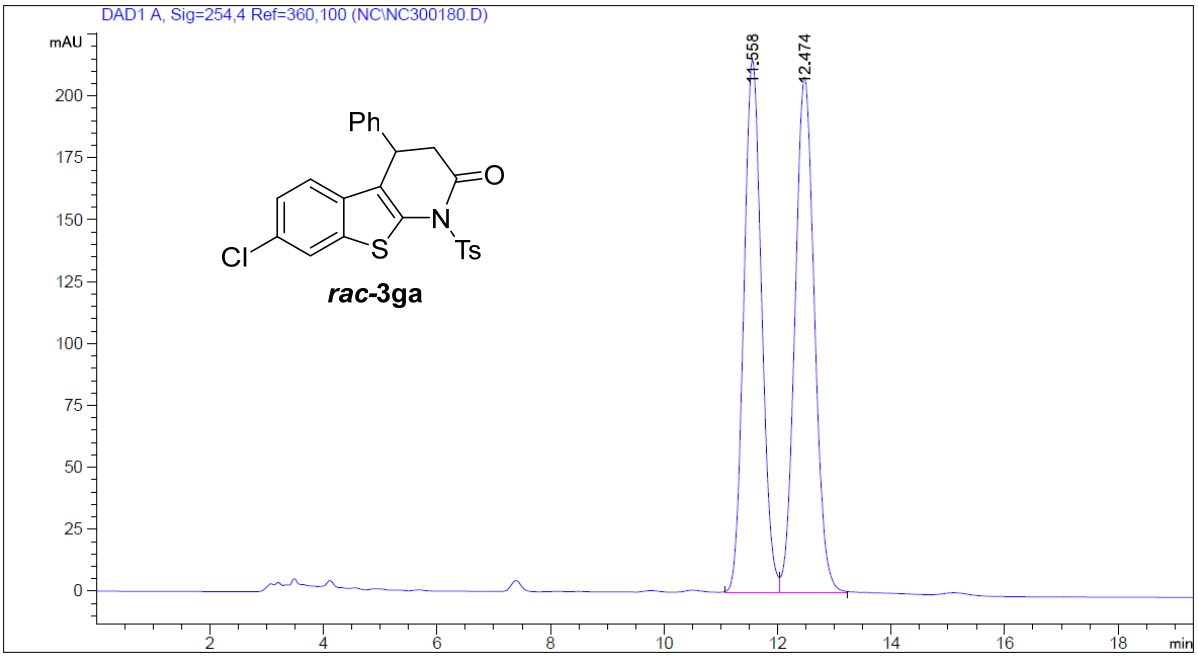
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.097	BV	0.2665	427.37720	24.86376	1.6111
2	10.618	VV	0.3157	2.60999e4	1291.80615	98.3889



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.661	BB	0.4261	8511.75098	310.25751	50.2462
2	16.262	BB	0.5149	8428.33887	254.17671	49.7538

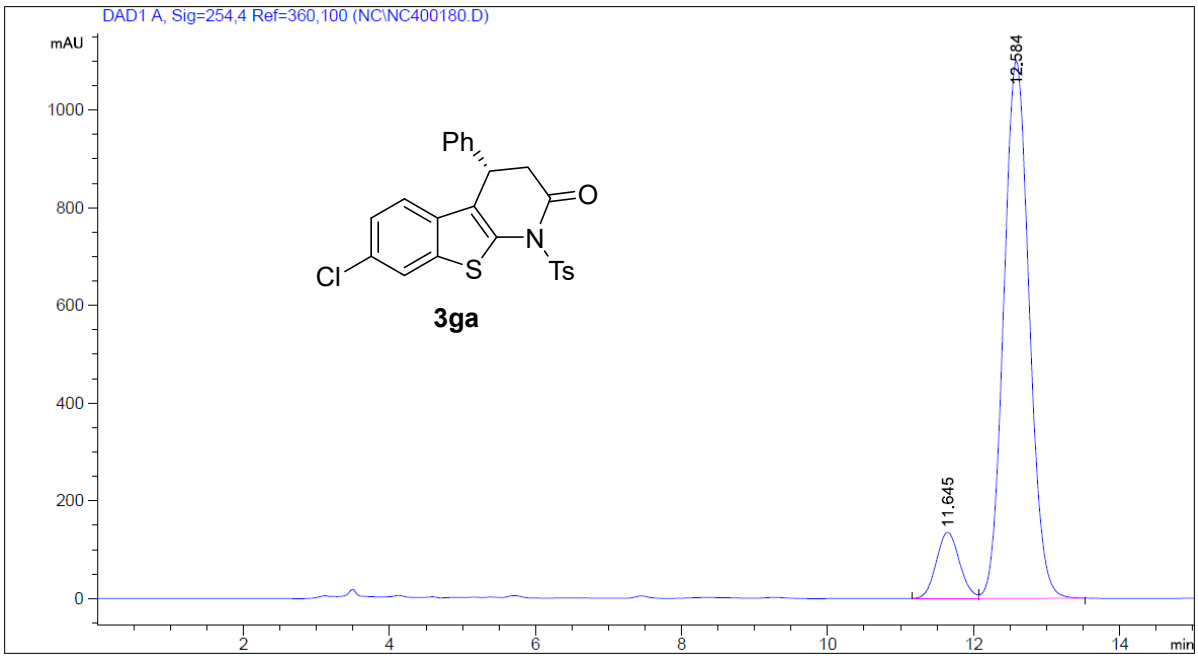


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.650	BB	0.4303	1.43693e4	523.40735	97.3705
2	16.184	VB	0.4804	388.04501	11.90083	2.6295



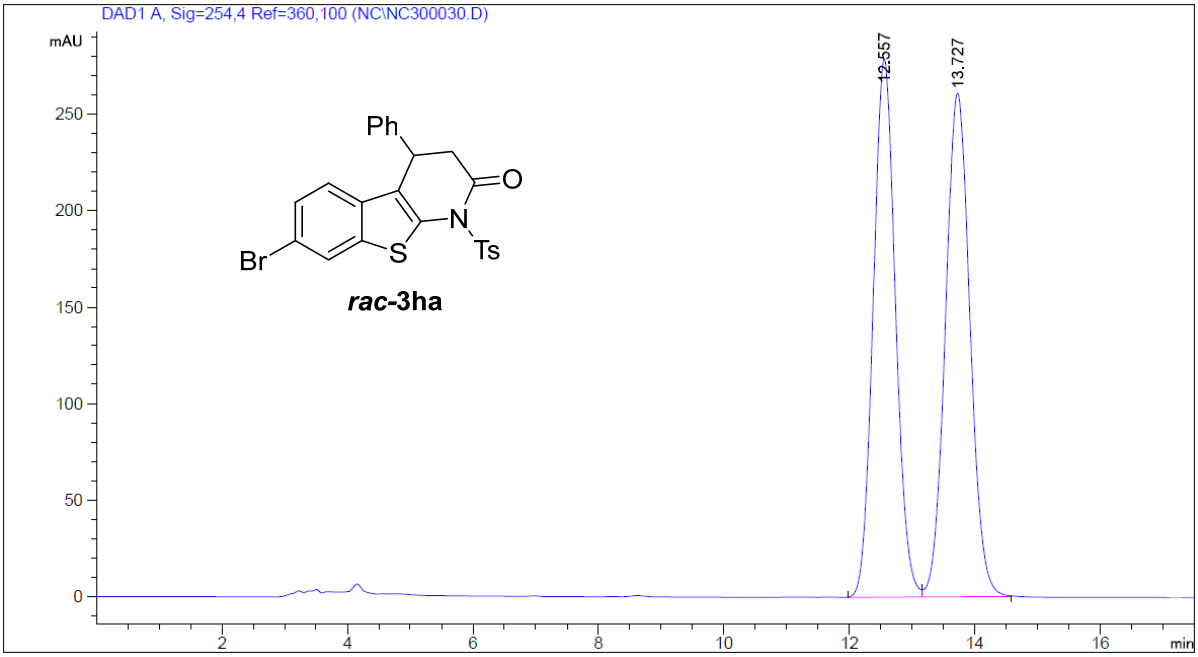
***rac*-3ga**

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.558	BV	0.3397	4676.08008	215.00439	48.6148
2	12.474	VB	0.3691	4942.56348	208.10487	51.3852

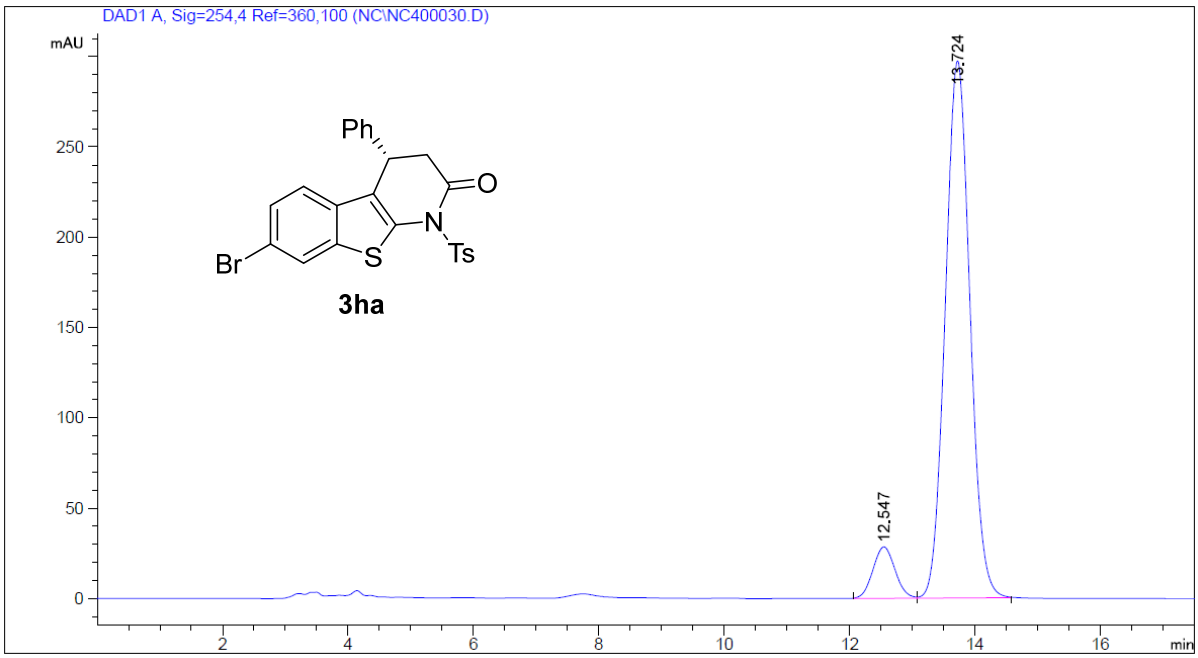


3ga

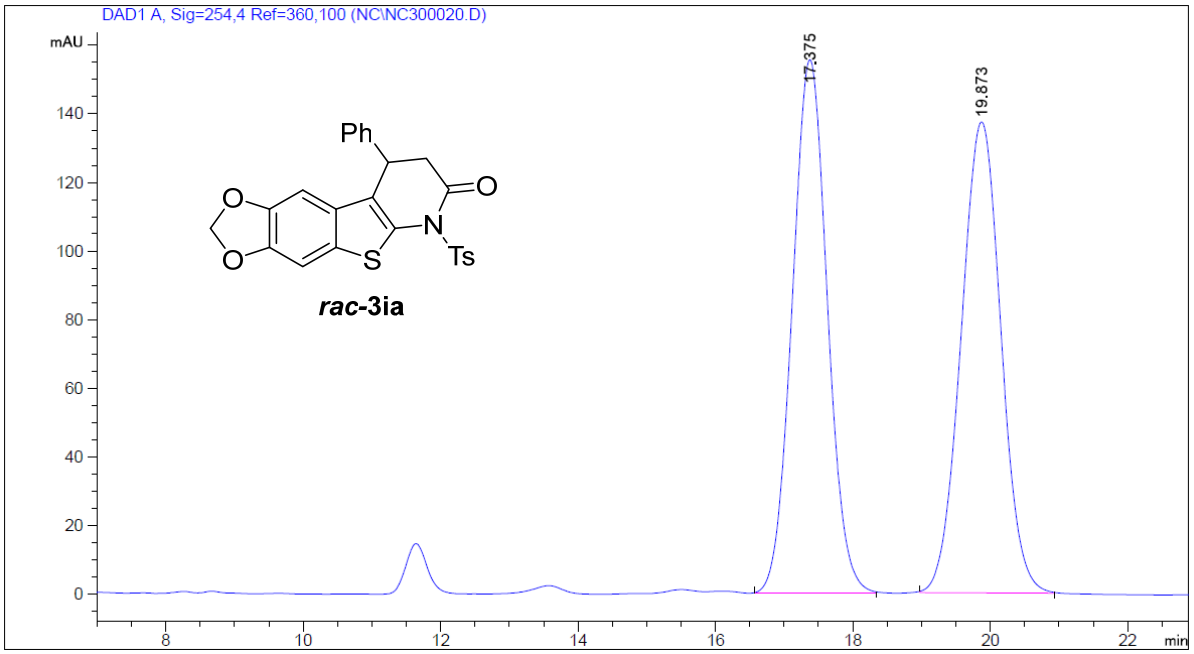
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.645	BV	0.3441	2994.90894	135.36989	10.0956
2	12.584	VB	0.3789	2.66707e4	1099.87000	89.9044



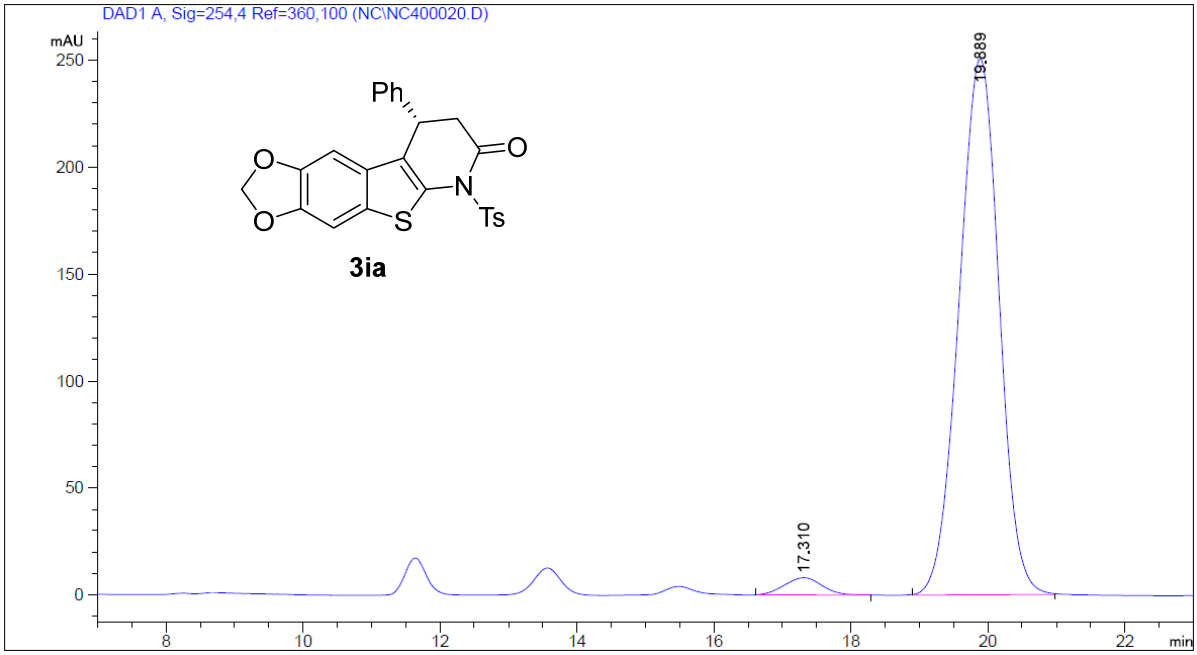
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.557	BV	0.3825	6902.67383	279.15970	49.2203
2	13.727	VB	0.4241	7121.35400	261.20193	50.7797



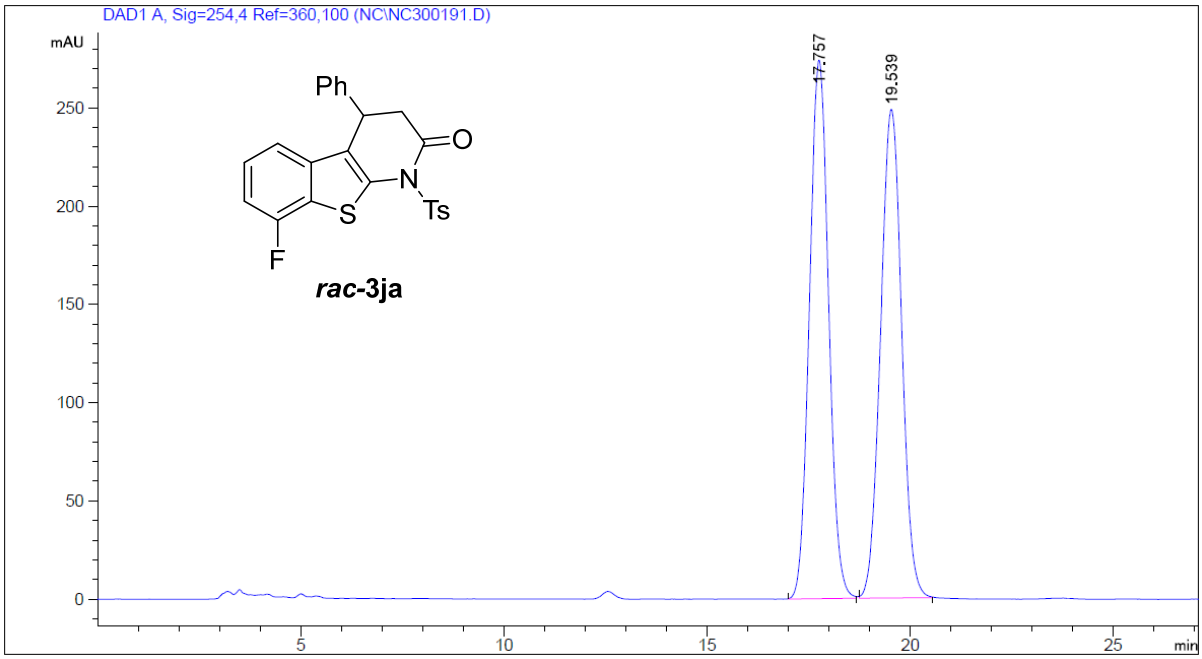
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.547	BV	0.3800	696.96423	28.42969	7.9082
2	13.724	VB	0.4225	8116.26660	297.27014	92.0918



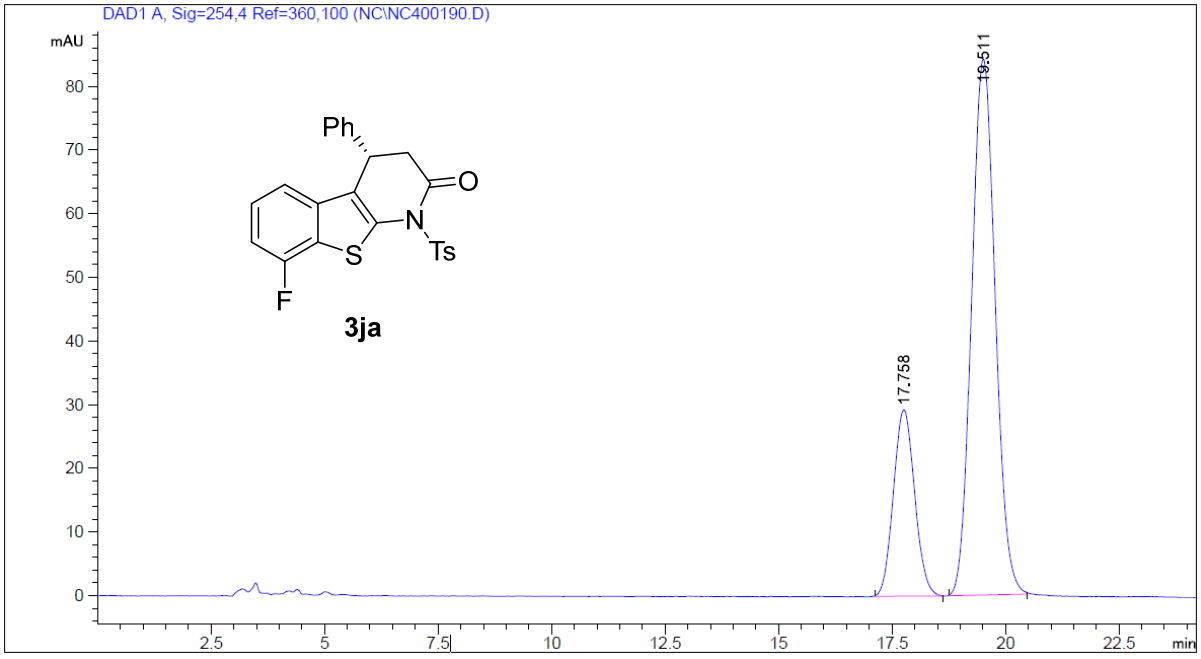
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.375	BB	0.5537	5509.42139	155.36263	49.9181
2	19.873	BB	0.6279	5527.48926	137.24570	50.0819



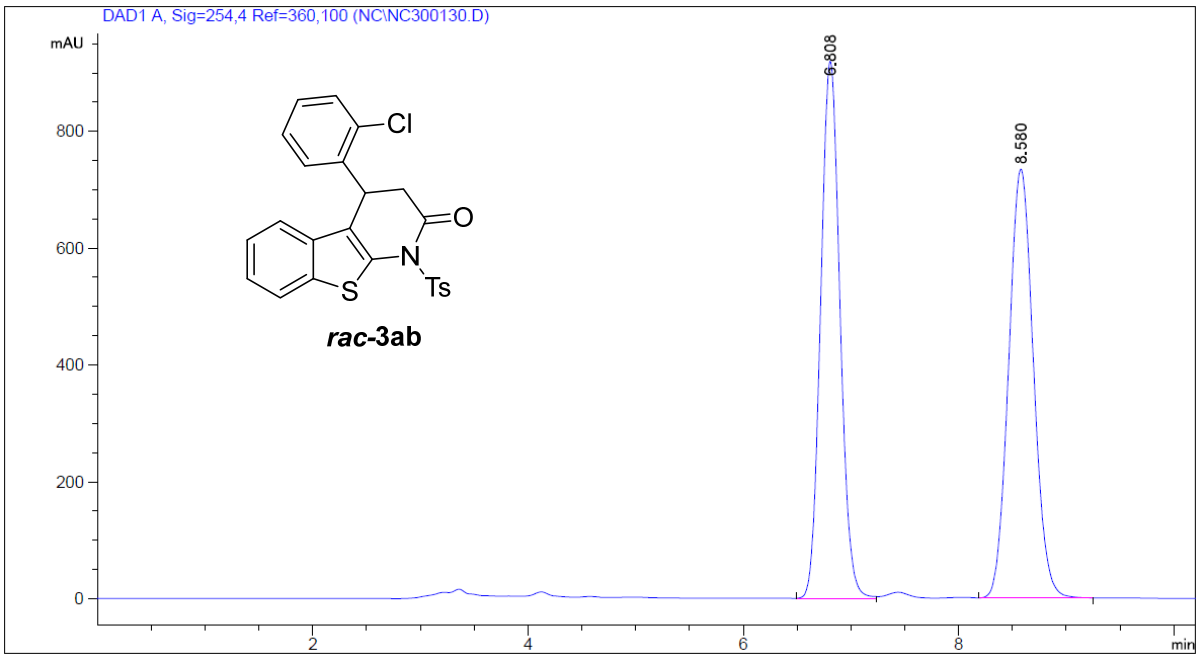
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.310	BB	0.5097	309.14429	8.05665	2.9478
2	19.889	BB	0.6380	1.01782e4	250.52324	97.0522



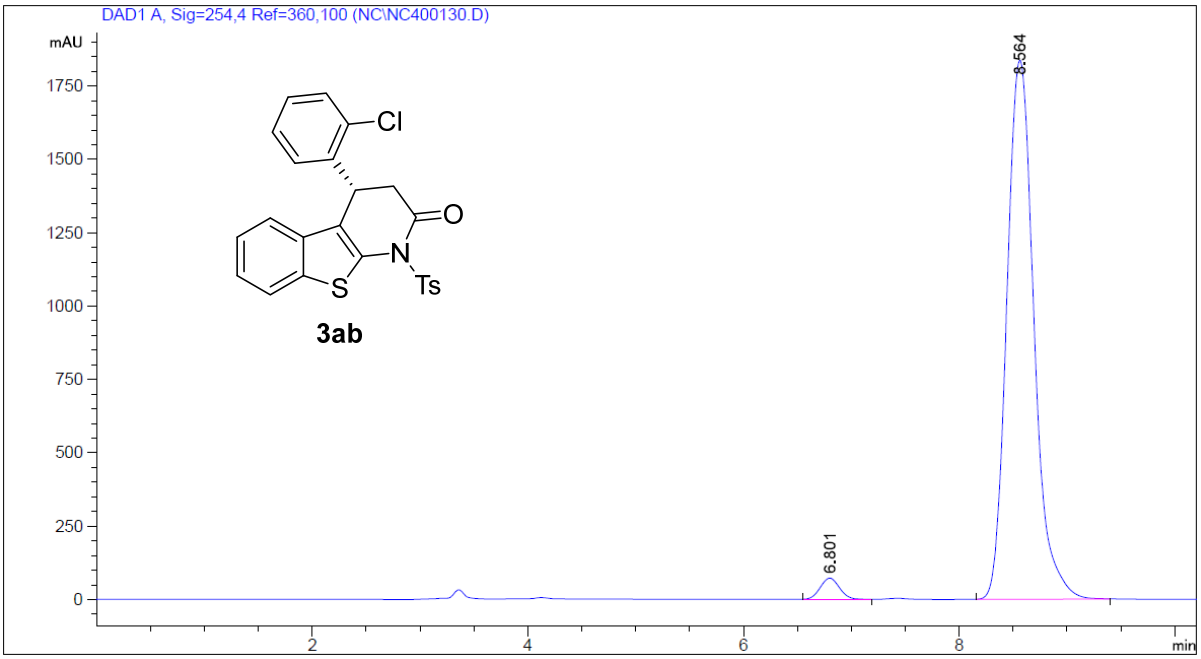
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.757	BB	0.5135	9007.42285	274.02225	50.0805
2	19.539	BB	0.5674	8978.46387	248.60107	49.9195



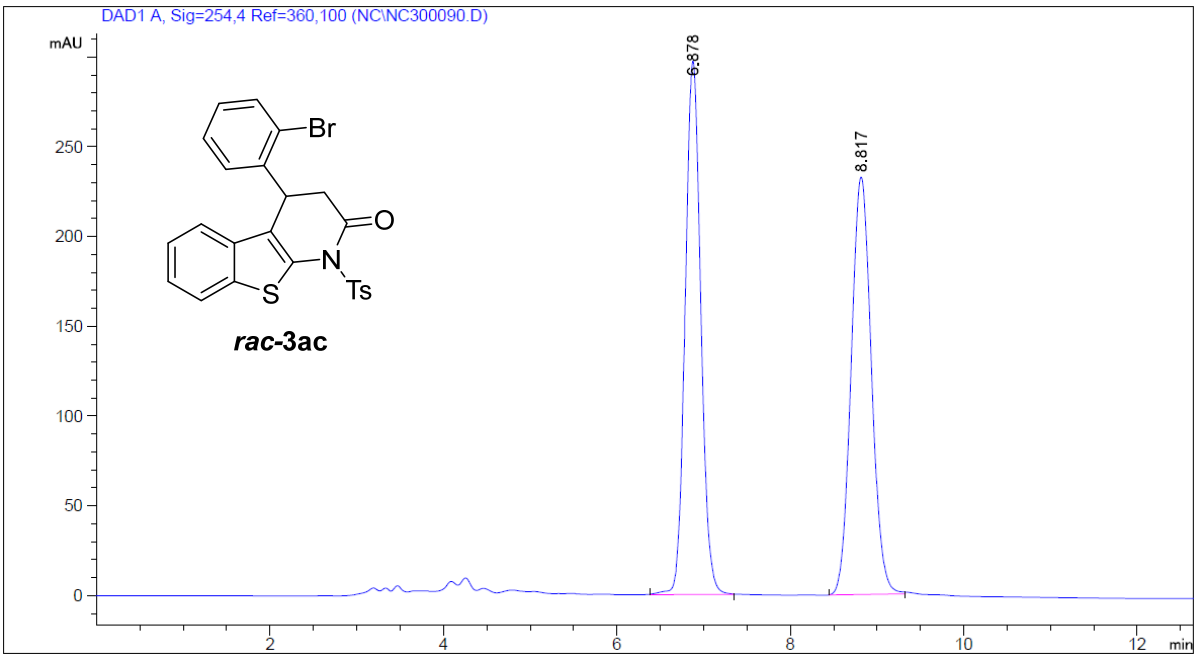
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.758	BB	0.5076	952.75226	29.28067	23.8225
2	19.511	BB	0.5680	3046.62866	84.22534	76.1775



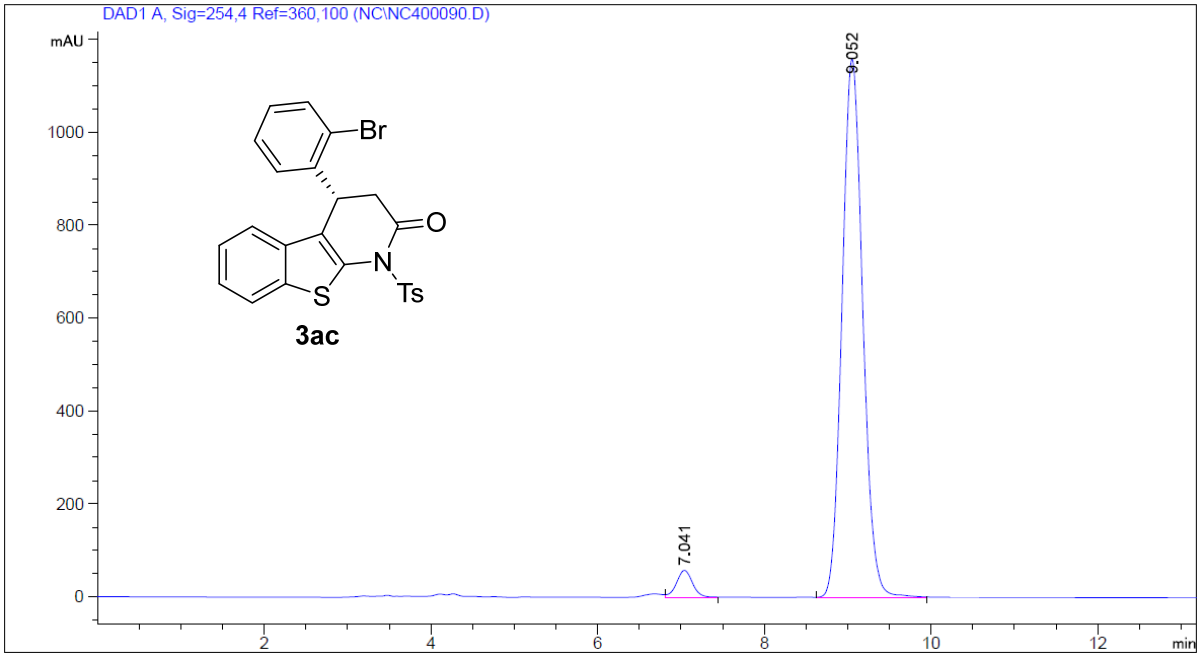
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.808	BV	0.1952	1.14534e4	920.02765	49.4340
2	8.580	VB	0.2501	1.17157e4	734.54230	50.5660



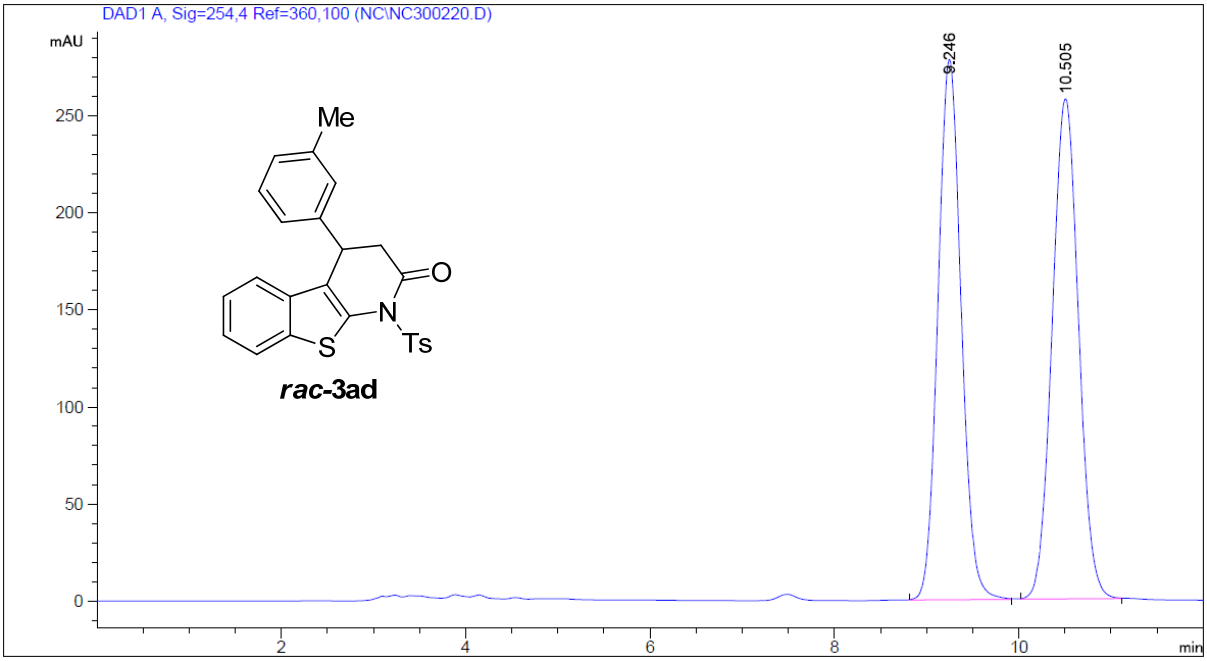
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.801	BB	0.1933	899.92670	72.27006	2.7366
2	8.564	BB	0.2710	3.19851e4	1838.12048	97.2634



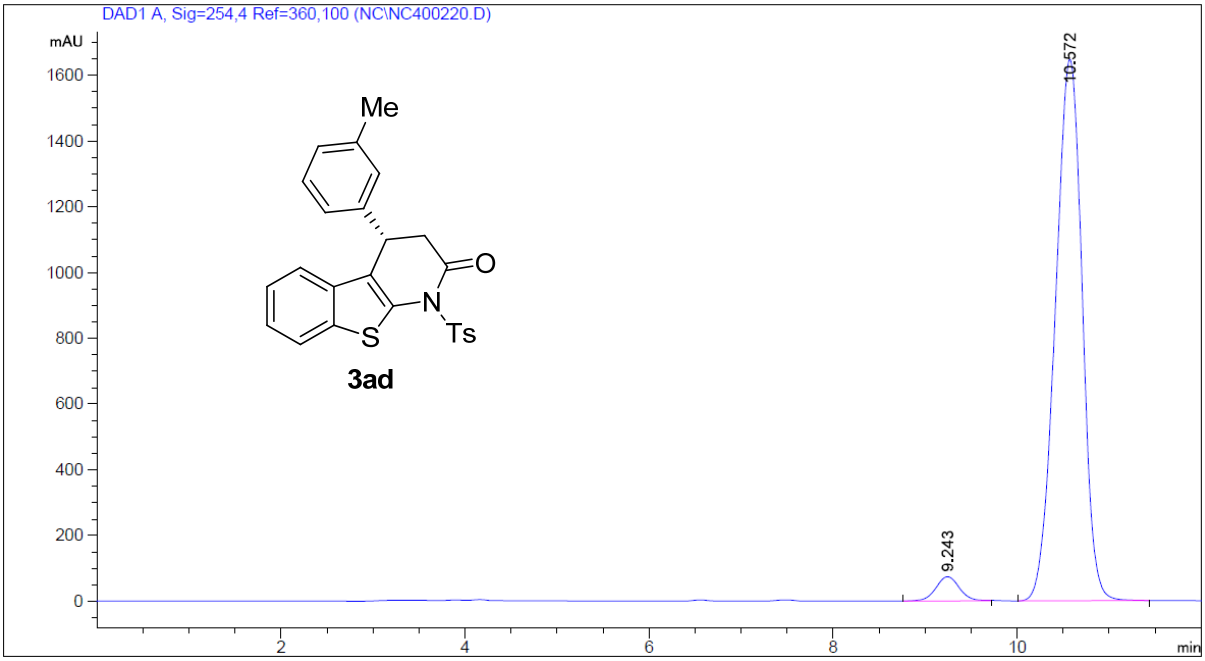
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.878	BB	0.1940	3723.20972	297.44339	49.6803
2	8.817	BB	0.2532	3771.12158	232.58052	50.3197



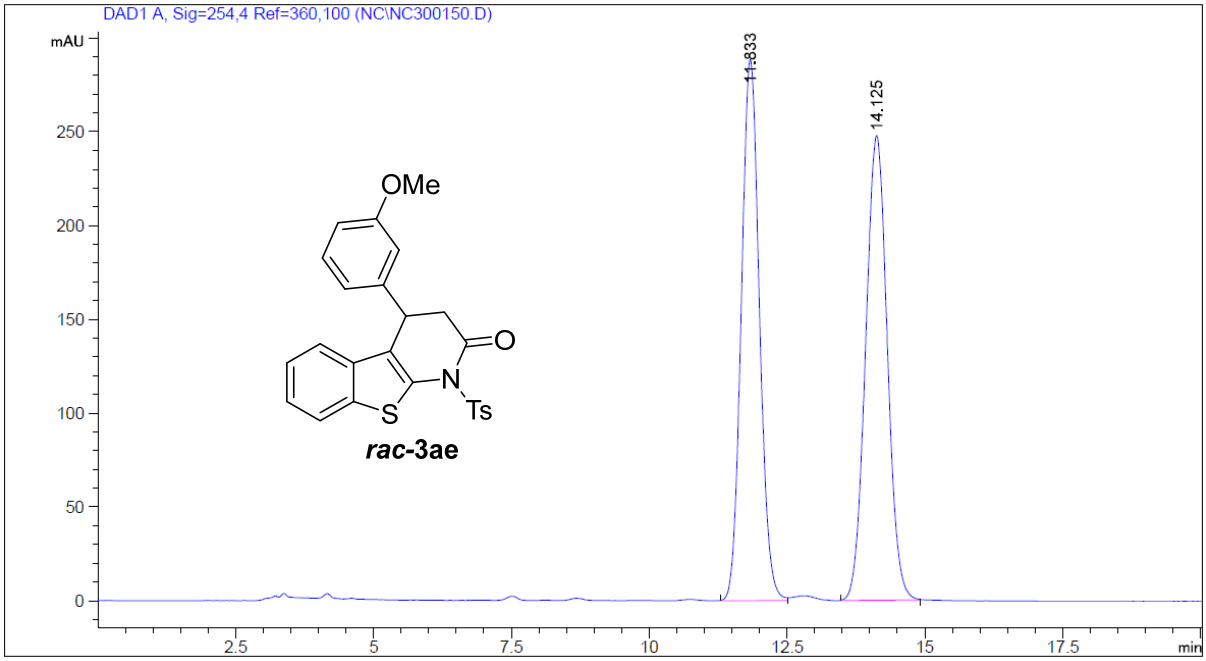
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.041	VB	0.2054	768.51428	57.68219	3.7211
2	9.052	BB	0.2682	1.98844e4	1158.95764	96.2789



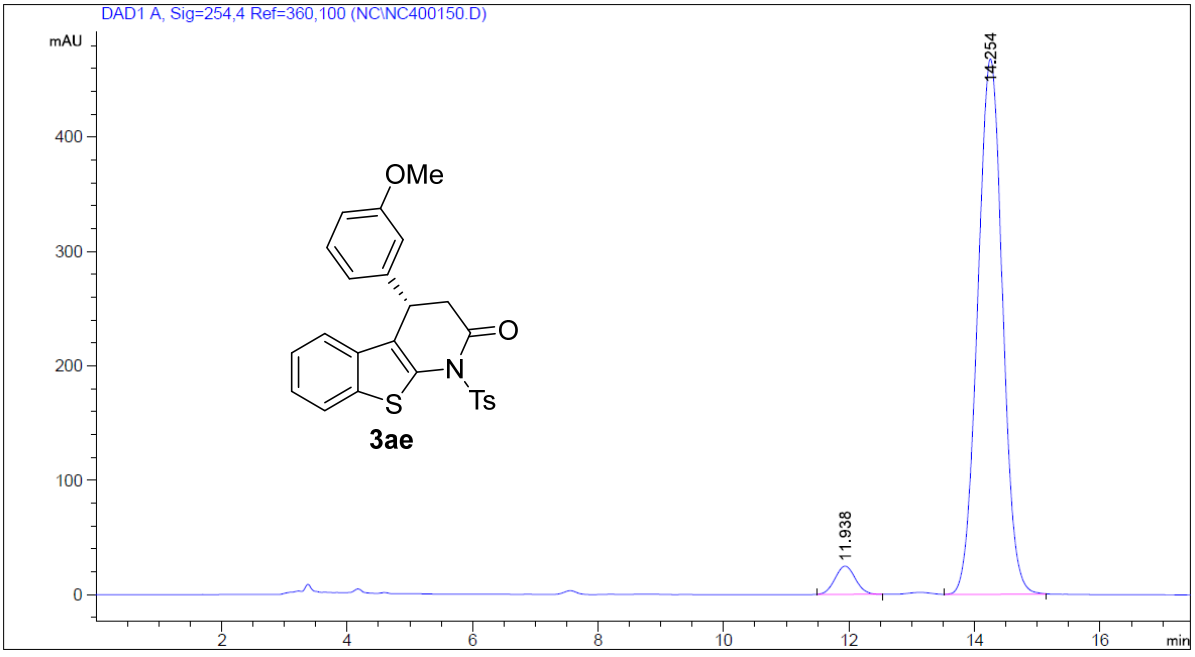
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.246	BB	0.2720	4864.70068	278.26459	48.7113
2	10.505	BB	0.3099	5122.10645	257.64487	51.2887



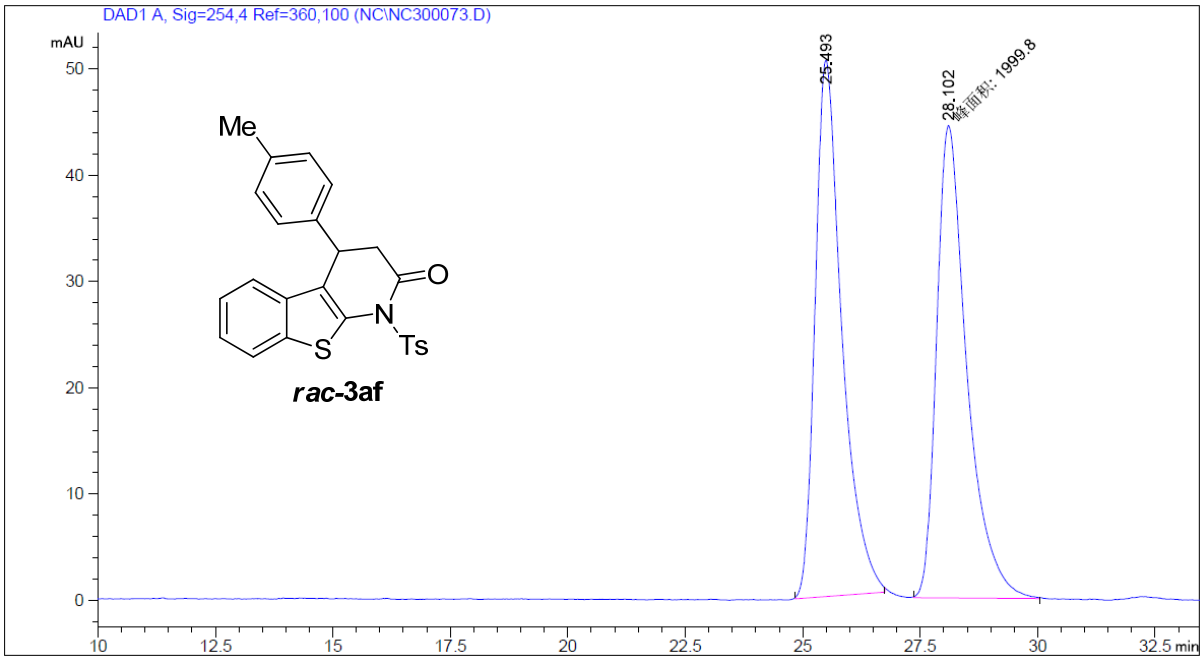
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.243	BB	0.2745	1315.22803	73.58922	3.7989
2	10.572	BB	0.3180	3.33058e4	1646.79858	96.2011



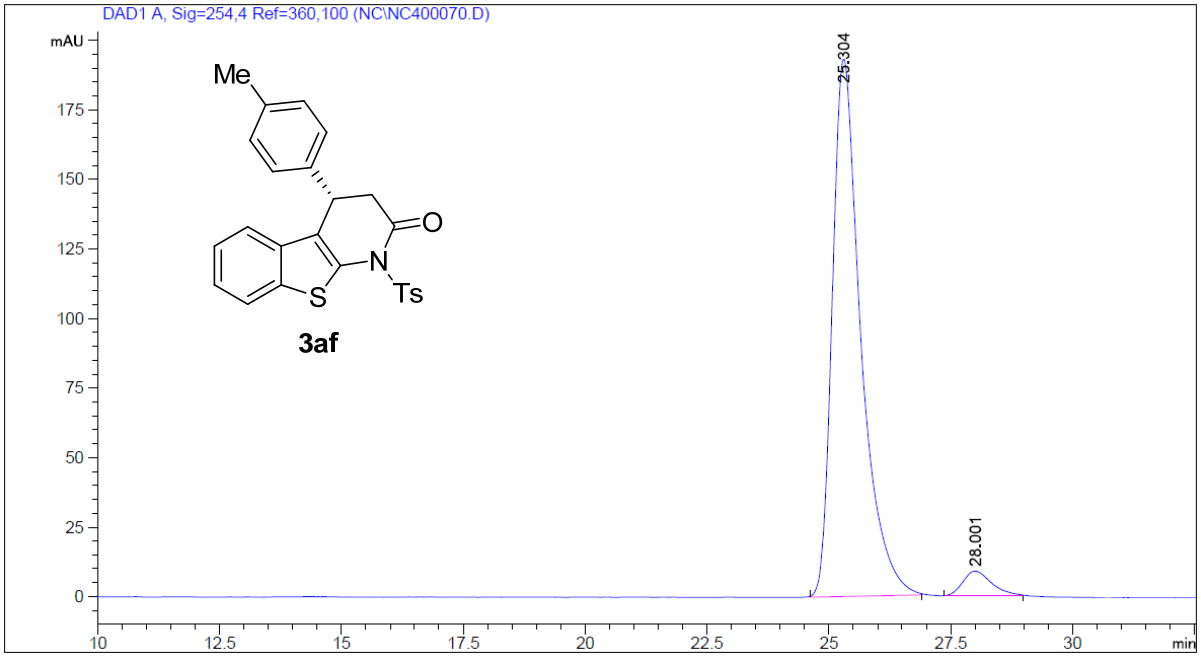
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.833	BB	0.3547	6596.01563	288.57196	49.3728
2	14.125	BB	0.4265	6763.60400	247.71529	50.6272



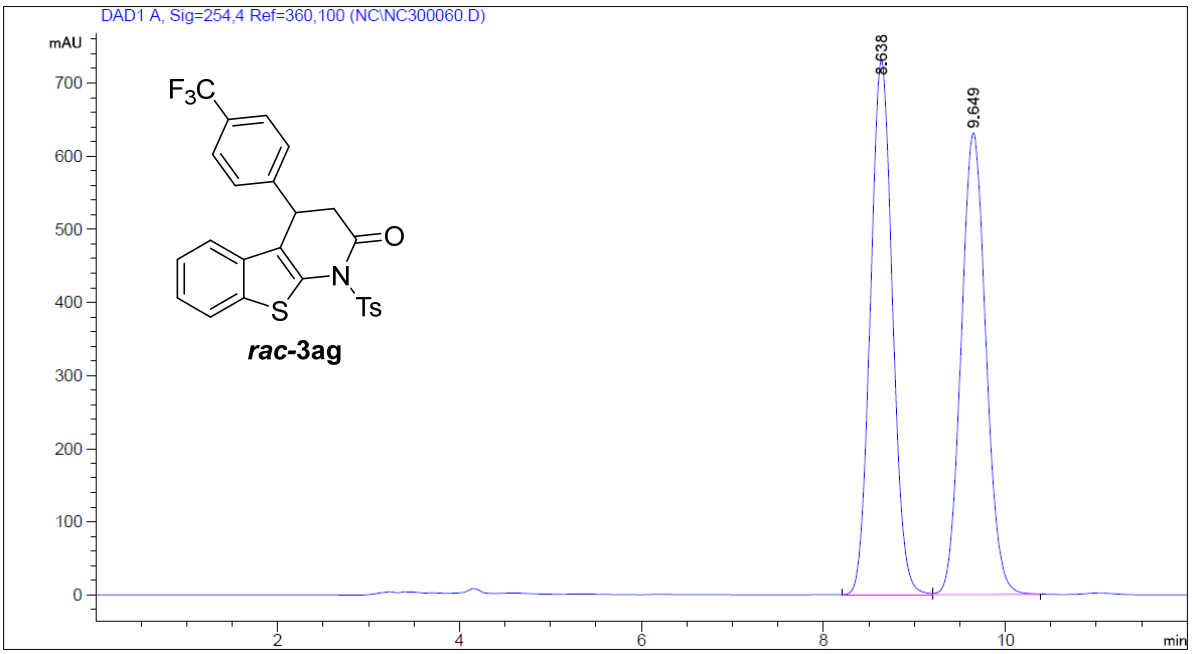
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.938	BB	0.3536	560.50403	24.80362	4.1706
2	14.254	VB	0.4309	1.28788e4	468.21167	95.8294



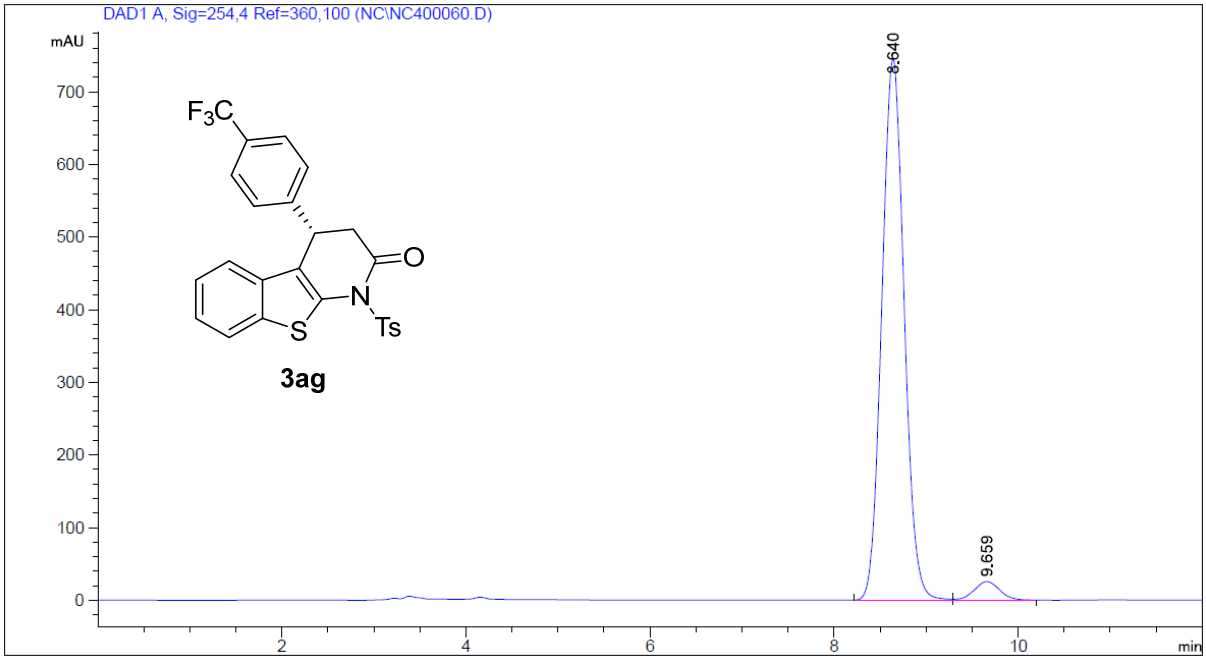
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.493	BB	0.5884	2000.34912	50.46531	50.0069
2	28.102	MM	0.7495	1999.79639	44.46879	49.9931



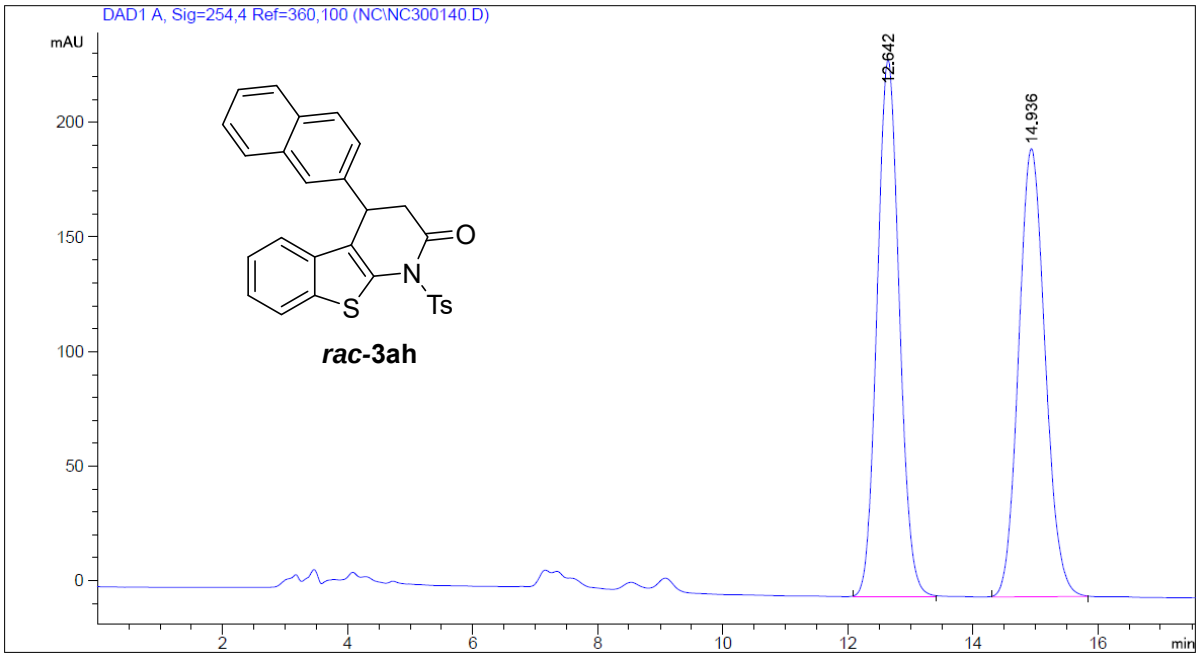
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.304	BB	0.6014	7836.63428	193.12575	95.5616
2	28.001	BB	0.5954	363.97528	8.82138	4.4384



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.638	BV	0.2624	1.22939e4	730.13788	50.7255
2	9.649	VB	0.2949	1.19422e4	630.75793	49.2745



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.640	BB	0.2618	1.25007e4	744.85321	96.2384
2	9.659	BB	0.2962	488.60422	25.42612	3.7616



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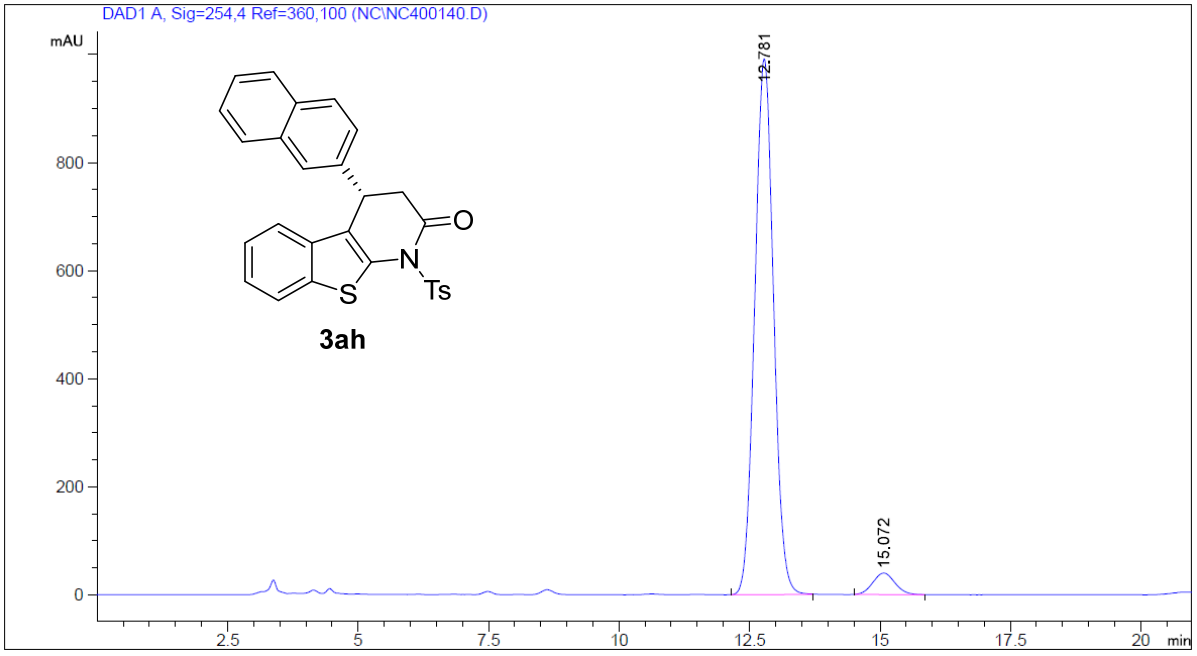
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.642	BB	0.3840	5777.23340	234.03624	50.0611
2	14.936	BB	0.4579	5763.14209	195.50330	49.9389



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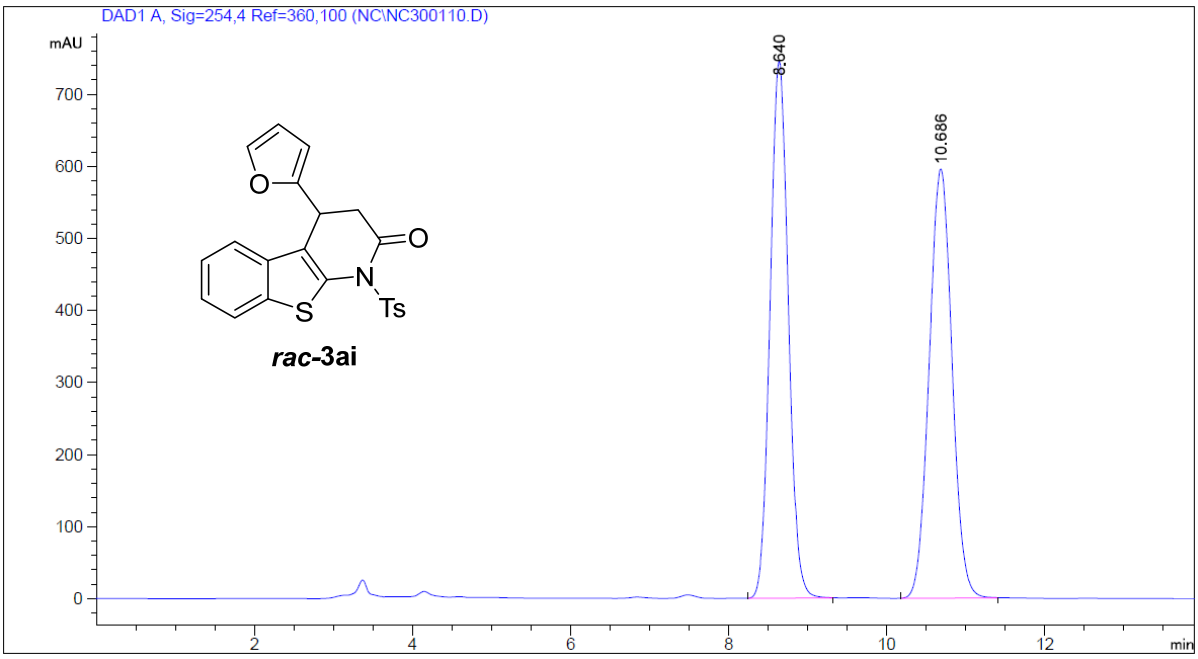
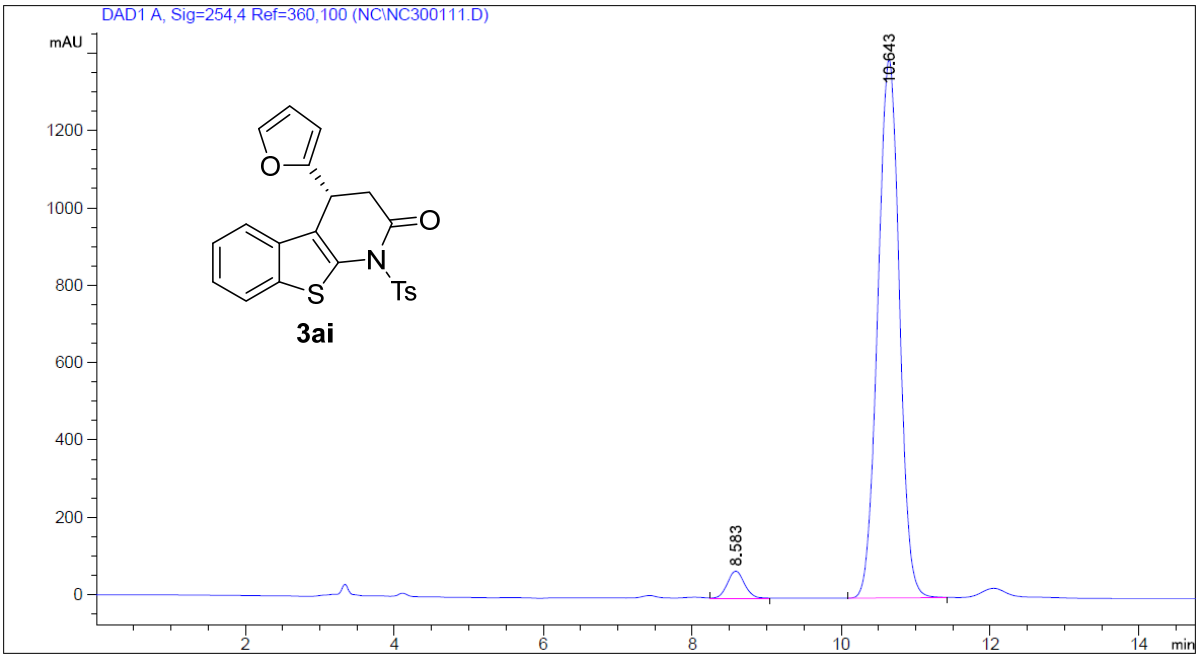
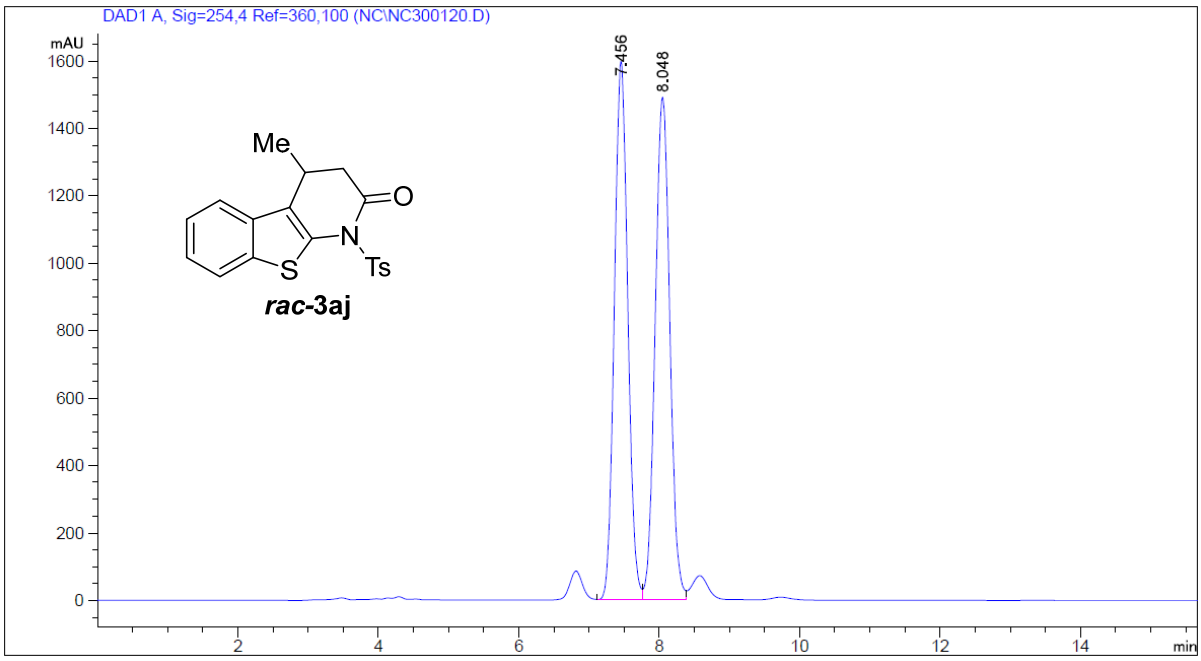
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.781	BB	0.3934	2.49413e4	991.75348	95.4801
2	15.072	BB	0.4623	1180.68152	40.00830	4.5199



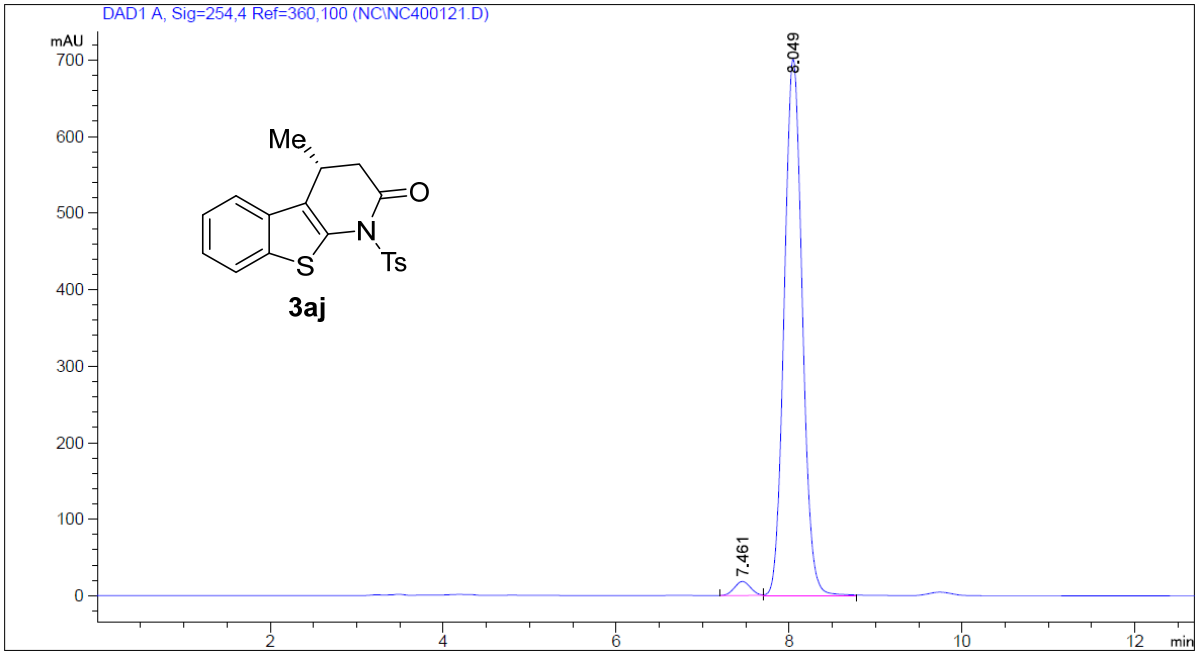
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.640	BB	0.2513	1.19724e4	745.79413	49.9747
2	10.686	BB	0.3146	1.19845e4	595.92627	50.0253



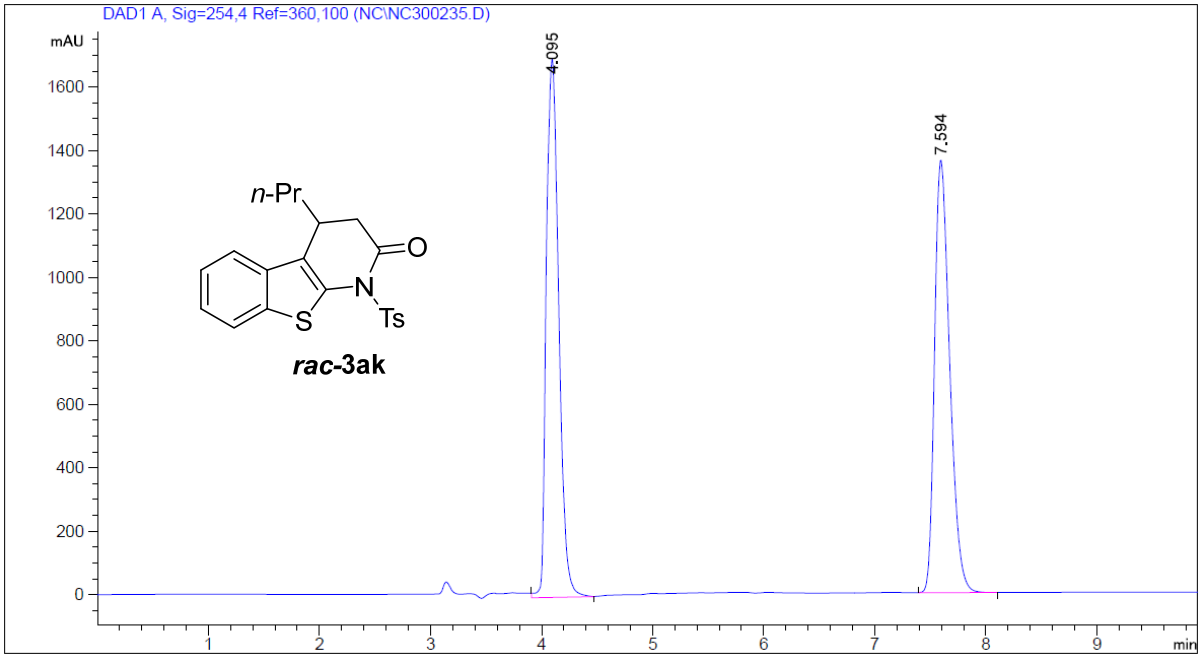
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.583	VB	0.2460	1099.68030	69.72155	3.7774
2	10.643	BB	0.3170	2.80126e4	1390.42419	96.2226



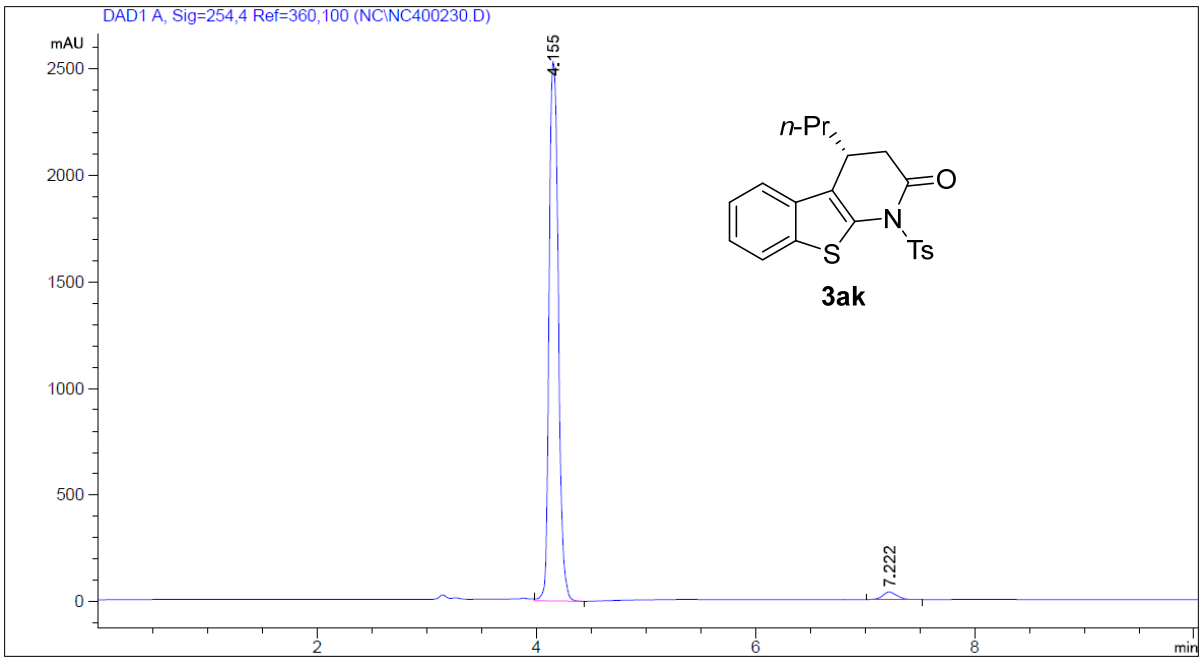
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.456	VV	0.2079	2.13475e4	1597.62170	49.6905
2	8.048	VV	0.2272	2.16134e4	1490.48059	50.3095



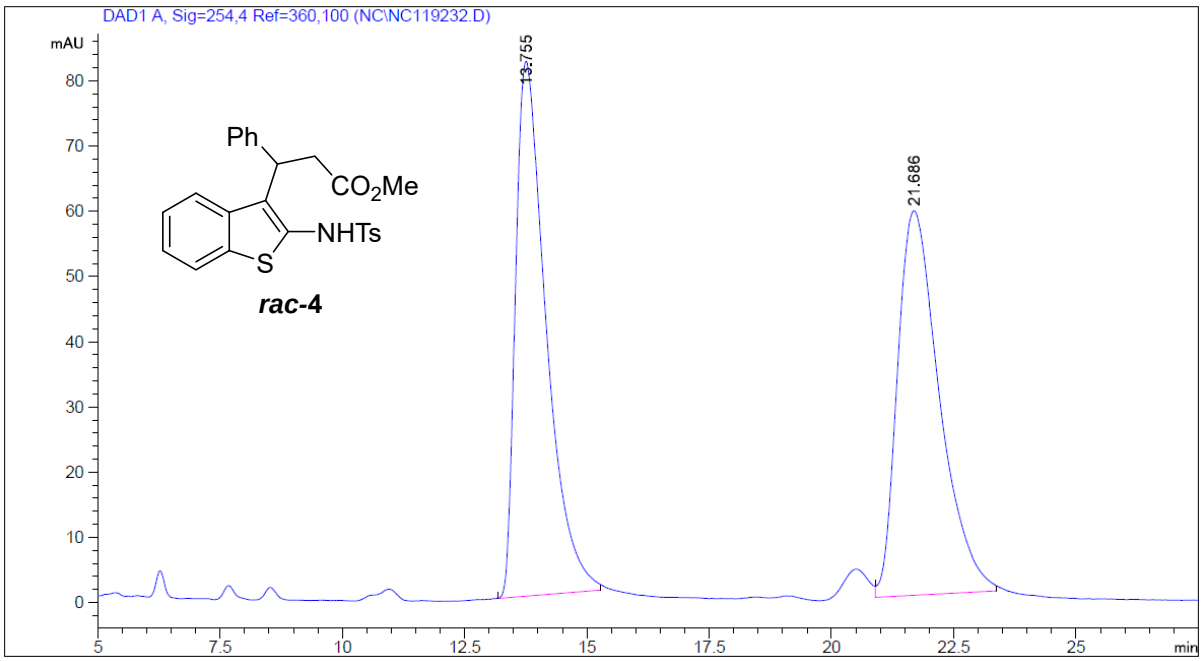
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.461	BV	0.2038	240.95822	18.51769	2.3197
2	8.049	VB	0.2248	1.01467e4	701.26031	97.6803



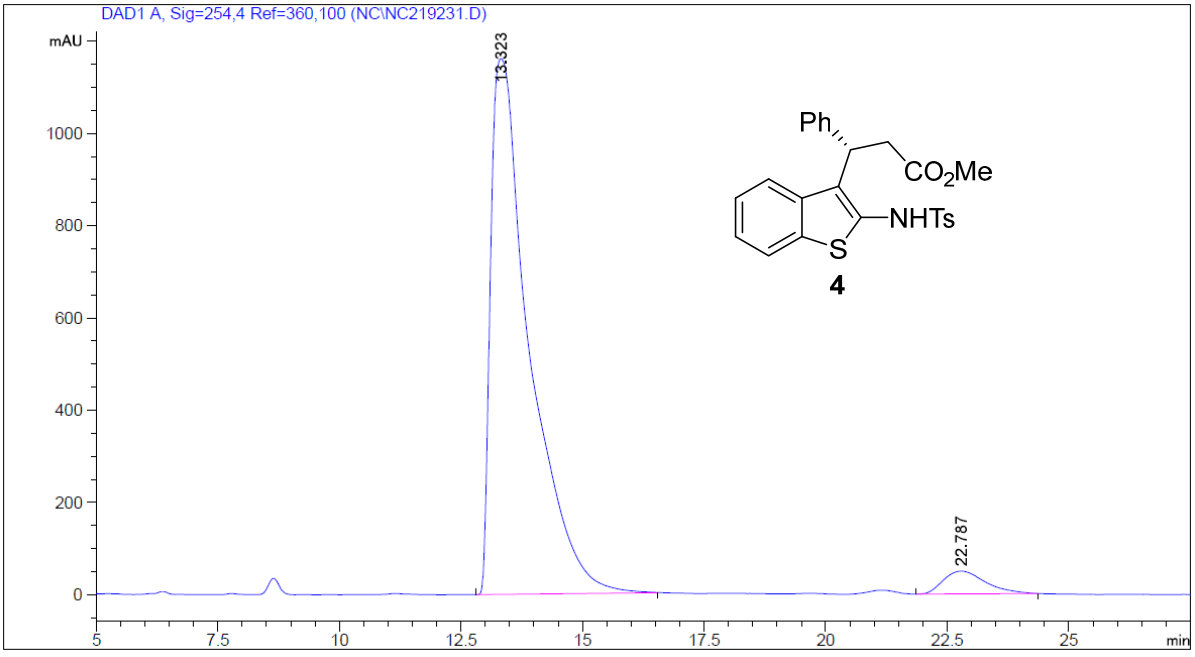
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.095	VV	0.1272	1.32700e4	1697.81409	50.7230
2	7.594	BB	0.1443	1.28917e4	1364.03101	49.2770



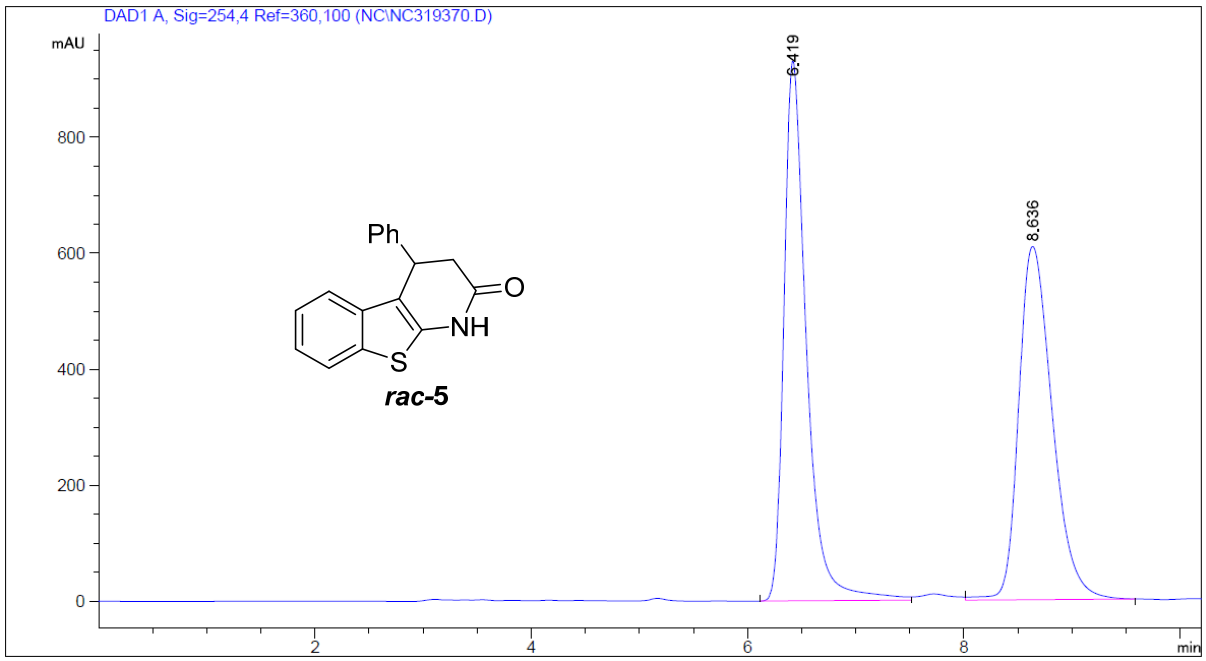
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.155	VV	0.0937	1.47183e4	2535.33423	97.8804
2	7.222	BB	0.1352	318.71704	36.02105	2.1196



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.755	BB	0.6502	3557.63403	82.00054	50.2733
2	21.686	VB	0.8982	3518.95898	58.97158	49.7267



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.323	BB	0.7983	6.43383e4	1161.40356	95.5282
2	22.787	VB	0.9295	3011.77368	49.80738	4.4718



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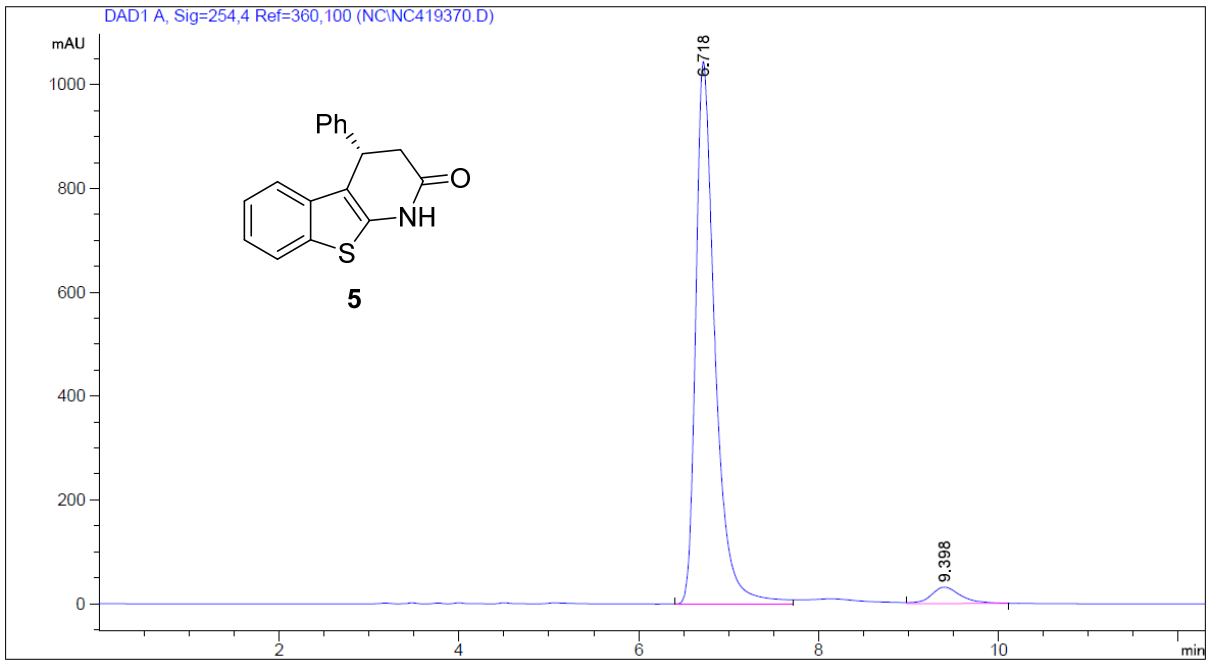
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.419	BB	0.2150	1.34847e4	930.85687	50.6516
2	8.636	VB	0.3337	1.31378e4	609.07458	49.3484



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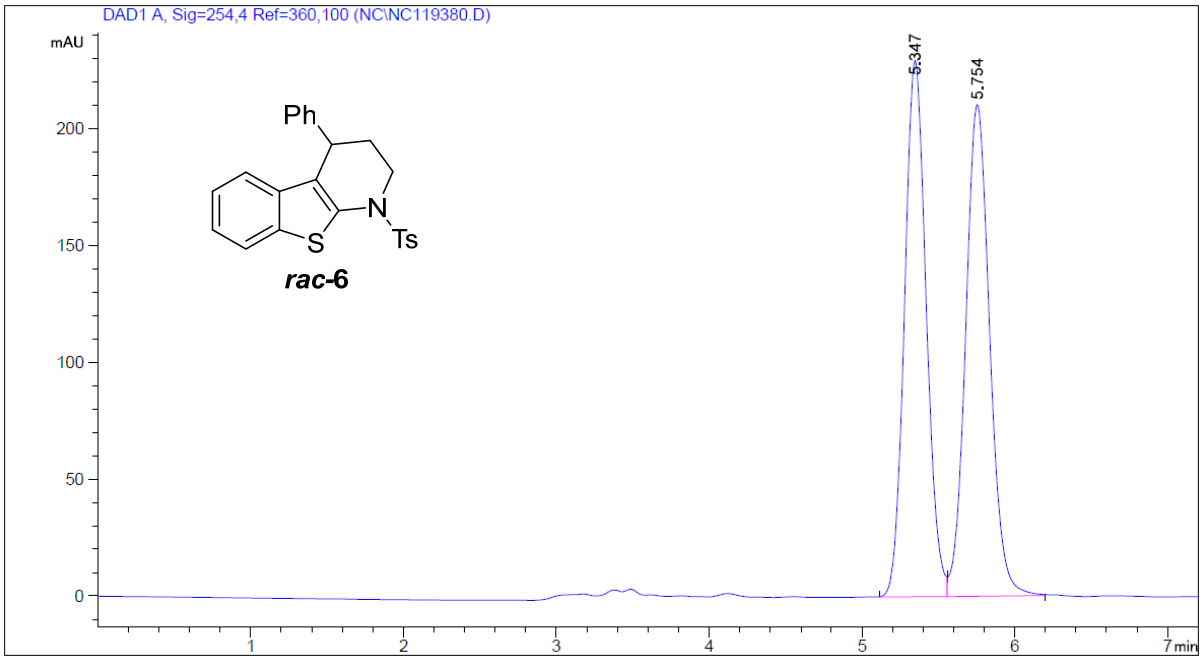
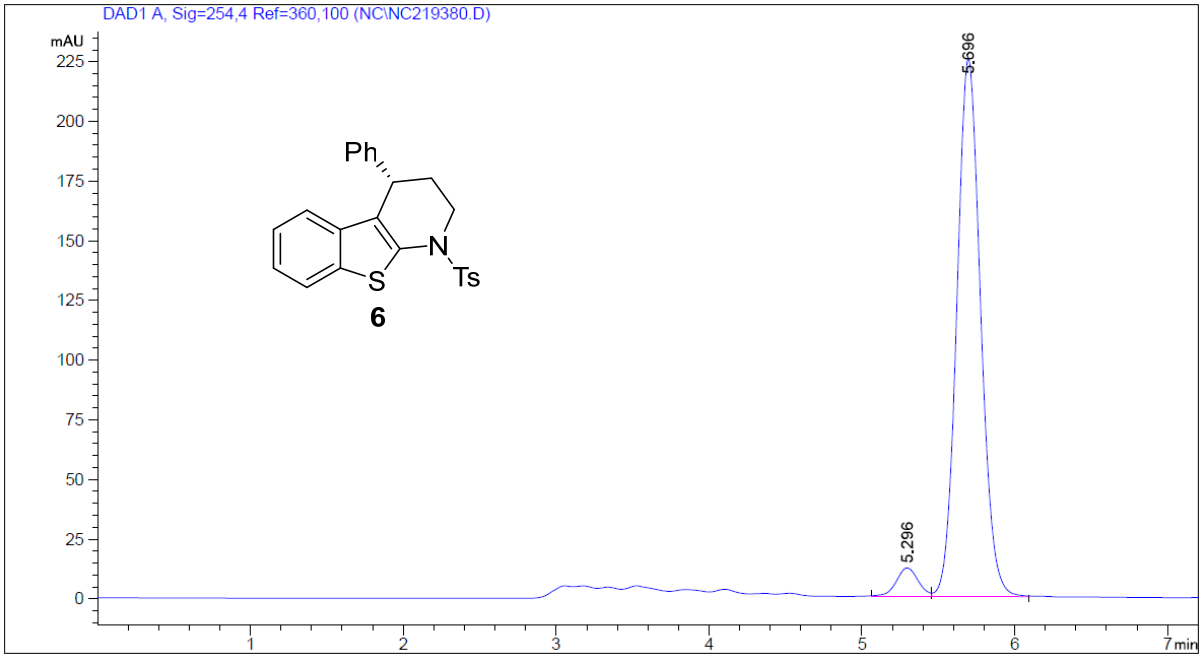
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.718	BB	0.2195	1.55486e4	1045.36438	95.4942
2	9.398	VB	0.3434	733.63898	31.76928	4.5058



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.347	BV	0.1529	2262.88306	229.67741	49.5766
2	5.754	VB	0.1695	2301.53662	210.52612	50.4234



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.296	BV	0.1541	119.09898	11.96582	4.6832
2	5.696	VB	0.1676	2424.03784	225.17192	95.3168