Organocatalytic Stereoselective Construction of Polycyclic Benzo[*b*]thiophenes from 2-Aminobenzo[*b*]thiophenes and Alkynyl-substituted Enones

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Supporting Information

Content

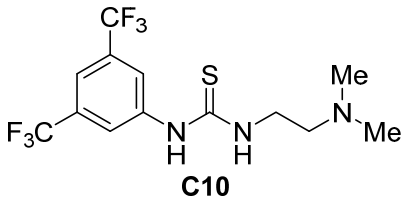
1. General information and starting materials

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 (or 700 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). ^{19}F NMR spectra were measured at 376 MHz with a Bruker Ascend 400 MHz spectrometer. 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 column. Optical rotations were measured with a Krüss P8000 polarimeter at the indicated concentration with the units of grams per 100 mL.

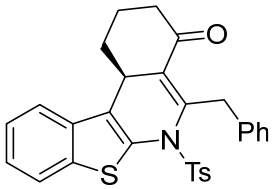
Starting materials. Substrate **1** were prepared according to the literature [1]. Substrate **2** were prepared according to the literature [2]. The organocatalysts were prepared according to the literature [3].

2. Enantioselective synthesis and characterization of compounds 3

sulfonamide **1** (0.1 mmol), 2-alkynyl cycloenone **2** (0.12 mmol), and catalyst **C2** (3.0 mg, 0.005 mmol) were dissolved in toluene (1.0 mL), and the mixture was stirred at room temperature for about 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 = 8/1 to 6:1) to afford the pure products **3**. Racemates were prepared following a similar procedure using following **C10** as catalyst (5 mol%).

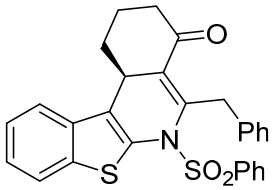


C10



3a

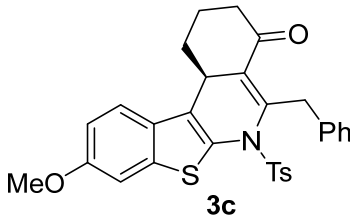
***(S)*-5-Benzyl-6-tosyl-2,3,6,11*c*-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3a).** White solid (44.5 mg, 89% yield), m.p. 179 – 180 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 14.5 (minor), t_R = 23.8 min (major); 96% ee. $[\alpha]_D^{25}$ = –126.5° (*c* = 1.09, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 –7.72 (m, 1H, ArH), 7.52 (d, *J* = 8.0 Hz, 2H, ArH), 7.46 (d, *J* = 7.6 Hz, 2H, ArH), 7.42 – 7.40 (m, 1H, ArH), 7.33 – 7.29 (m, 2H, ArH), 7.23 (d, *J* = 8.0 Hz, 4H, ArH), 7.16 (t, *J* = 7.4 Hz, 1H, ArH), 4.52 (d, *J* = 14.8 Hz, 1H, CH_2), 4.37 (d, *J* = 14.4 Hz, 1H, CH_2), 3.49 (dd, J_1 = 12.0 Hz, J_2 = 4.8 Hz, 1H, CH), 2.58 (dt, J_1 = 15.6 Hz, J_2 = 5.4 Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.30 – 2.22 (m, 1H, CH_2), 2.12 – 2.05 (m, 1H, CH_2), 1.85 – 1.67 (m, 2H, CH_2), 0.28 – 0.18 (m, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 145.0, 140.6, 138.4, 138.1, 137.0, 135.1, 132.1, 129.33, 129.27, 128.5, 128.2, 126.3, 125.4, 124.7, 124.2, 122.2, 120.5, 42.4, 38.1, 36.1, 30.5, 23.1, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{26}NO_3S_2$ $[M + H]^+$ 500.1349, found 500.1353.



3b

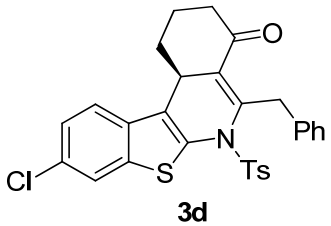
(*S*)-5-benzyl-6-(phenylsulfonyl)-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3b). White solid (39.8 mg, 82% yield), m.p. 187–189 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.3 (minor), t_R = 18.3 min (major); 95% ee. $[\alpha]_D^{25}$ = –105.9° (*c* = 1.52, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 1H, ArH), 7.64 (d, *J* = 7.7 Hz, 2H, ArH), 7.59 (t, *J* = 7.4 Hz, 1H, ArH), 7.47 – 7.43 (m, 4H, ArH), 7.40 (d, *J* = 7.7 Hz, 1H, ArH), 7.31 – 7.28 (m, 2H, ArH), 7.24 (t, *J* = 7.0 Hz, 2H, ArH), 7.16 (t, *J* = 7.4 Hz, 1H, ArH), 4.52 (d, *J* = 14.4 Hz, 1H, CH_2), 4.37 (d, *J* = 14.7 Hz, 1H, CH_2), 3.46 (dd, J_1 = 11.9 Hz, J_2 = 4.9 Hz, 1H, CH), 2.57 (dt, 1H, J_1 = 15.4 Hz, J_2 = 5.6 Hz, 1H, CH_2), 2.26 – 2.21 (m, 1H, CH_2), 2.07 – 2.03 (m, 1H, CH_2), 1.81 – 1.74 (m, 1H, CH_2), 1.72 – 1.67 (m, 1H, CH_2), 0.16 – 0.10 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.4, 140.3, 138.3, 138.0, 136.8, 135.1, 134.8, 133.9, 132.3, 129.3, 128.8, 128.4, 128.2, 126.3, 125.5, 124.8, 124.3, 122.2, 120.5, 42.5, 38.2, 36.1, 30.6, 23.1 ppm. HRMS

(ESI): *m*/*z* calcd. for $C_{28}H_{23}NNaO_3S_2$ $[M + Na]^+$ 508.1012, found 508.1017.



3c

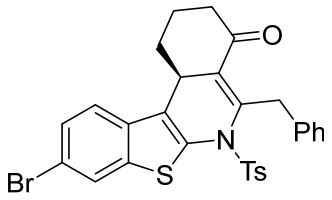
(S)-5-benzyl-9-methoxy-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3c). White solid (36.0 mg, 68% yield), m.p. 165 – 166 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 31.0 (major), t_R = 39.7 min (minor); 93% ee. $[\alpha]_D^{25}$ = –114.5 ° (*c* = 1.34, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.7 Hz, 2H, ArH), 7.46 (d, *J* = 7.7 Hz, 2H, ArH), 7.28 (d, *J* = 9.1 Hz, 1H, ArH), 7.25 – 7.22 (m, 4H, ArH), 7.19 (d, *J* = 2.1 Hz, 1H, ArH), 7.16 (t, *J* = 7.4 Hz, 1H, ArH), 6.90 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H, ArH), 4.52 (d, *J* = 14.7 Hz, 1H, CH_2), 4.35 (d, *J* = 14.0 Hz, 1H, CH_2), 3.84 (s, 3H, CH_3), 3.41 (dd, J_1 = 11.9 Hz, J_2 = 4.9 Hz, 1H, CH), 2.56 (dt, 1H, J_1 = 15.4 Hz, J_2 = 5.3 Hz, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.26 – 2.22 (m, 1H, CH_2), 2.07 – 2.03 (m, 1H, CH_2), 1.79 – 1.73 (m, 1H, CH_2), 1.71 – 1.67 (m, 1H, CH_2), 0.24 – 0.18 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.5, 157.6, 145.0, 140.7, 139.6, 138.5, 134.2, 132.1, 131.9, 129.3, 128.9, 128.5, 128.2, 126.3, 125.3, 121.4, 114.0, 104.8, 55.6, 42.4, 38.2, 36.2, 30.4, 23.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{28}NO_4S_2$ $[M + H]^+$ 530.1454, found 530.1464.



3d

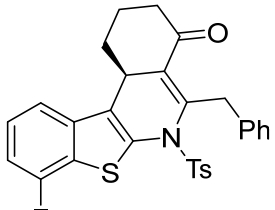
(*S*)-5-benzyl-9-chloro-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3d). White solid (39.4 mg, 74% yield), m.p. 176 – 178 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 17.9 (minor), t_R = 27.8 min (major); 97% ee. $[\alpha]_D^{25}$ = –101.9 ° (*c* = 0.80, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.70 (d, *J* = 1.4 Hz, 1H, ArH), 7.51 (d, *J* = 7.7 Hz, 2H, ArH), 7.46 (d, *J* = 7.7 Hz, 2H, ArH), 7.30 (d, *J* = 8.4 Hz, 1H, ArH), 7.26 – 7.24 (m, 5H, ArH), 7.17 (t, *J* = 7.4 Hz, 1H, ArH), 4.51 (d, *J* = 14.0 Hz, 1H, CH_2), 4.35 (d, *J* = 14.0 Hz, 1H, CH_2), 3.44 (dd, J_1 = 12.3 Hz, J_2 = 4.6 Hz, 1H, CH), 2.57 (dt, 1H, J_1 = 15.8 Hz, J_2 = 5.3 Hz, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.28 – 2.23 (m, 1H, CH_2), 2.05 – 2.02 (m, 1H, CH_2), 1.81 – 1.75 (m, 1H, CH_2), 1.73 – 1.69 (m, 1H, CH_2), 0.25 – 0.16 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.3, 145.2, 140.6,

139.0, 138.3, 137.4, 133.5, 132.0, 131.8, 130.8, 129.4, 129.3, 128.5, 128.3, 126.4, 125.10, 125.06, 121.8, 121.5, 42.4, 38.0, 36.1, 30.5, 23.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{25}{}^{35}ClNO_3S_2$ $[M + H]^+$ 534.0959; found 534.0903; calcd. for $C_{29}H_{25}{}^{37}ClNO_3S_2$ $[M + H]^+$ 536.0929, found 536.0924.



3e

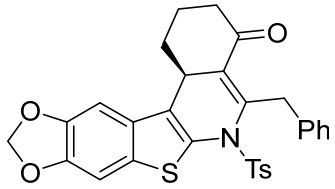
(*S*)-5-benzyl-9-bromo-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3e). White solid (42.2 mg, 73% yield), m.p. 165 – 167 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 65/35, flow rate 1.0 mL/min, detection at 254 nm): t_R = 19.4 (minor), t_R = 27.0 min (major); 93% ee. $[\alpha]_D^{25}$ = –130.7 ° (*c* = 1.07, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.84 (s, 1H, ArH), 7.50 (d, *J* = 7.7 Hz, 2H, ArH), 7.46 (d, *J* = 7.7 Hz, 2H, ArH), 7.37 (d, *J* = 8.4 Hz, 1H, ArH), 7.26 – 7.23 (m, 5H, ArH), 7.17 (t, *J* = 7.4 Hz, 1H, ArH), 4.51 (d, *J* = 14.7 Hz, 1H, CH_2), 4.35 (d, *J* = 14.7 Hz, 1H, CH_2), 3.44 (dd, J_1 = 11.9 Hz, J_2 = 4.9 Hz, 1H, CH), 2.57 (dt, 1H, J_1 = 15.4 Hz, J_2 = 5.6 Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.28 – 2.23 (m, 1H, CH_2), 2.04 – 2.00 (m, 1H, CH_2), 1.81 – 1.75 (m, 1H, CH_2), 1.73 – 1.68 (m, 1H, CH_2), 0.24 – 0.18 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.3, 145.2, 140.6, 139.4, 138.3, 137.4, 133.8, 131.9, 131.8, 129.4, 129.3, 128.4, 128.3, 127.7, 126.4, 125.1, 124.7, 121.7, 118.4, 42.4, 37.9, 36.1, 30.5, 23.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{25}{}^{79}BrNO_3S_2$ $[M + H]^+$ 578.0454, found 578.0457; calcd. for $C_{29}H_{25}{}^{81}BrNO_3S_2$ $[M + H]^+$ 580.0434, found 580.0438.



3f

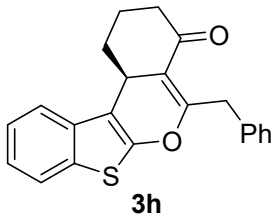
(*S*)-5-benzyl-6-(methylsulfonyl)-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3f). White solid (41.9 mg, 81% yield), m.p. 188 – 189 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 12.0 (minor), t_R = 25.5 min (major); 95% ee. $[\alpha]_D^{25}$ = –106.7° (*c* = 0.55, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.4 Hz, 2H, ArH), 7.46 (d, *J* = 7.7 Hz, 2H, ArH), 7.26 – 7.24 (m, 5H, ArH), 7.20 – 7.17 (m, 2H, ArH), 7.13 (t, *J* = 8.8 Hz, 2H, ArH), 4.51 (d, *J* = 14.7 Hz, 1H, CH_2), 4.37 (d, *J* = 14.7 Hz, 1H, CH_2), 3.47 (dd, J_1 = 11.9 Hz, J_2 = 4.9 Hz, 1H, CH), 2.58 (dt,

1H, J_1 = 15.8 Hz, J_2 = 5.3 Hz, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.29 – 2.24 (m, 1H, CH_2), 2.09 – 2.05 (m, 1H, CH_2), 1.82 – 1.76 (m, 1H, CH_2), 1.74 – 1.69 (m, 1H, CH_2), 0.28 – 0.23 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.3, 157.1 (d, $^1J_{C–F}$ = 247.8 Hz), 145.2, 140.7, 138.3, 138.19, 138.16, 132.0, 131.9, 129.4 (d, $^2J_{C–F}$ = 23.6 Hz), 128.5, 128.3, 126.4, 125.8 (d, $^4J_{C–F}$ = 1.8 Hz), 125.7 (d, $^3J_{C–F}$ = 7.0 Hz), 124.9 (d, $^3J_{C–F}$ = 18.1 Hz), 116.44, 116.42, 110.1 (d, $^2J_{C–F}$ = 18.5 Hz), 42.4, 38.2, 36.1, 30.5, 23.0, 21.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ –114.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{25}FNO_3S_2$ $[M + H]^+$ 518.1254, found 518.1257.



3g

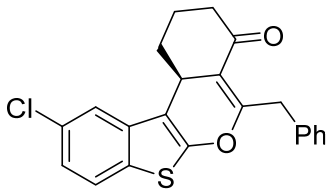
(*S*)-5-benzyl-6-tosyl-2,3,6,12c-tetrahydro-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3g). White solid (47.8 mg, 88% yield), m.p. 173 – 175 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 24.4 (major), t_R = 31.4 min (minor); 93% ee. $[\alpha]_D^{25}$ = –148.8 ° (*c* = 1.39, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 4H, ArH), 7.23 (d, *J* = 7.6 Hz, 4H, ArH), 7.15 (t, *J* = 7.2 Hz, 1H, ArH), 7.10 (s, 1H, ArH), 6.77 (s, 1H, ArH), 5.96 (d, *J* = 0.8 Hz, 2H, CH_2), 4.51 (d, *J* = 14.4 Hz, 1H, CH_2), 4.34 (d, *J* = 14.4 Hz, 1H, CH_2), 3.37 (dd, J_1 = 12.0 Hz, J_2 = 4.8 Hz, 1H, CH), 2.55 (dt, J_1 = 15.6 Hz, J_2 = 5.2 Hz, 1H, CH_2), 2.28 – 2.20 (m, 1H, CH_2), 2.01 – 1.95 (m, 1H, CH_2), 1.81 – 1.64 (m, 2H, CH_2), 0.18 – 0.08 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.5, 146.6, 146.5, 145.0, 140.5, 138.4, 134.9, 132.0, 131.4, 129.27, 129.25, 128.5, 128.2, 126.3, 125.4, 101.7, 101.3, 99.8, 42.4, 38.1, 36.1, 30.3, 23.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{25}KNO_5S_2$ $[M + K]^+$ 582.0806, found 582.0806.



3h

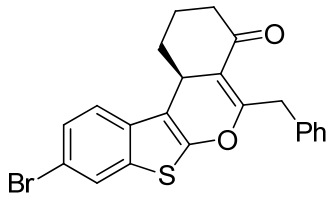
(*S*)-5-benzyl-1,2,3,11c-tetrahydro-4*H*-benzo[4,5]thieno[2,3-*c*]isochromen-4-one (3h). White solid (30.8 mg, 89% yield), m.p. 107 – 108 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 4.9 (major), t_R = 5.5 min (minor); 96% ee. $[\alpha]_D^{25}$ = +19.6 ° (*c* = 0.76, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1H, ArH), 7.55 (d, *J* = 7.6 Hz, 1H, ArH), 7.39 (d, *J* = 7.2 Hz, 2H, ArH),

7.35 – 7.28 (m, 3H, ArH), 7.27 – 7.21 (m, 2H, ArH), 4.02 – 3.87 (m, 3H, CH + CH_2), 2.75 – 2.61 (m, 2H, CH_2), 2.53 – 2.45 (m, 1H, CH_2), 2.09 – 2.02 (m, 2H, CH_2), 1.89 – 1.79 (m, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 155.4, 151.1, 137.1, 136.2, 132.0, 129.0, 128.4, 126.6, 124.6, 123.6, 122.5, 121.0, 113.3, 111.0, 41.3, 36.6, 34.5, 30.8, 22.1 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{19}O_2S$ $[M + H]^+$ 347.1100, found 347.1100.



3i

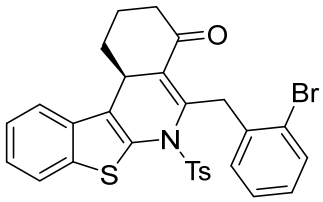
(*S*)-5-benzyl-10-chloro-1,2,3,11c-tetrahydro-4*H*-benzo[4,5]thieno[2,3-*c*]isochromen-4-one (3i). White solid (29.7 mg, 78% yield), m.p. 108 – 110 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 5.2 (major), t_R = 6.3 min (minor); 90% ee. $[\alpha]_D^{25}$ = +17.4 ° (*c* = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.8 Hz, 1H, ArH), 7.51 (d, *J* = 2.0 Hz, 1H, ArH), 7.39 (d, *J* = 7.2 Hz, 2H, ArH), 7.31 (t, *J* = 7.4 Hz, 2H, ArH), 7.23 – 7.20 (m, 2H, ArH), 3.98 – 3.84 (m, 3H, CH + CH_2), 2.70 – 2.62 (m, 2H, CH_2), 2.53 – 2.45 (m, 1H, CH_2), 2.10 – 2.03 (m, 2H, CH_2), 1.89 – 1.79 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 201.6, 155.2, 152.6, 137.4, 137.0, 131.0, 129.9, 129.0, 128.5, 126.7, 123.9, 123.6, 120.7, 113.3, 110.7, 41.3, 36.5, 34.4, 30.8, 22.1 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{18}ClO_2S$ $[M + H]^+$ 381.0711, found 381.0709.



3j

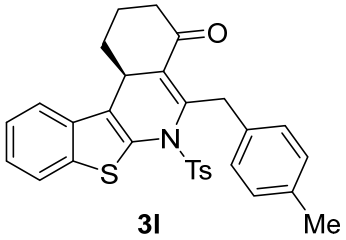
(*S*)-5-benzyl-9-bromo-1,2,3,11c-tetrahydro-4*H*-benzo[4,5]thieno[2,3-*c*]isochromen-4-one (3j). White solid (21.3 mg, 50% yield), m.p. 113 – 114 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.9 (major), t_R = 8.4 min (minor); 92% ee. $[\alpha]_D^{25}$ = +22.0 ° (*c* = 0.87, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 2.0 Hz, 1H, ArH), 7.51 (d, *J* = 8.4 Hz, 1H, ArH), 7.39 (d, *J* = 7.2 Hz, 2H, ArH), 7.35 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.31 (t, *J* = 7.4 Hz, 2H, ArH), 7.24 – 7.21 (m, 1H, ArH), 3.98 – 3.86 (m, 3H, CH + CH_2), 2.71 – 2.62 (m, 2H, CH_2), 2.54 – 2.46 (m, 1H, CH_2), 2.10 – 2.03 (m, 2H, CH_2), 1.89 – 1.79 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 201.6, 155.2, 152.5, 137.9, 136.9, 130.5, 129.0, 128.5, 126.7, 126.6, 123.9, 123.7, 118.7, 113.3, 110.6, 41.3, 36.5, 34.4, 30.8, 22.1 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{18}{}^{79}BrO_2S$ $[M + H]^+$ 425.0205,

found 425.0200; calcd. for $C_{22}H_{18}{}^{81}BrO_2S$ $[M + H]^+$ 427.0185, found 427.0191.



3k

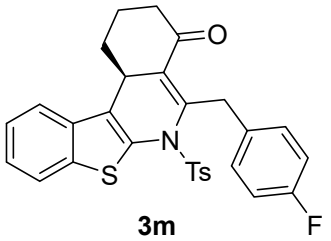
(*S*)-5-(2-bromobenzyl)-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3k). White solid (53.8 mg, 93% yield), m.p. 112 – 113 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 85/15, flow rate 1.0 mL/min, detection at 254 nm): t_R = 17.6 (minor), t_R = 18.7 min (major); 93% ee. $[\alpha]_D^{25}$ = +4.6 ° (*c* = 1.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.77 (m, 1H, ArH), 7.53 – 7.49 (m, 4H, ArH), 7.37 – 7.31 (m, 2H, ArH), 7.20 – 7.15 (m, 4H, ArH), 7.06 – 7.01 (m, 1H, ArH), 4.64 (d, *J* = 16.8 Hz, 1H, CH_2), 4.37 (d, *J* = 16.8 Hz, 1H, CH_2), 3.33 (dd, J_1 = 11.8 Hz, J_2 = 5.0 Hz, 1H, CH), 2.52 (dt, J_1 = 15.6 Hz, J_2 = 5.0 Hz, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.35 – 2.28 (m, 1H, CH_2), 2.23 – 2.15 (m, 1H, CH_2), 1.83 – 1.73 (m, 2H, CH_2), 0.79 – 0.69 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.8, 145.0, 139.9, 138.2, 138.0, 136.9, 135.1, 134.6, 132.6, 131.7, 130.3, 129.3, 128.5, 127.7, 127.2, 126.0, 124.7, 124.2, 122.5, 121.2, 42.1, 38.6, 38.3, 30.4, 23.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{25}{}^{79}BrNO_3S_2$ $[M + H]^+$ 578.0454, found 578.0457; calcd. for $C_{29}H_{25}{}^{81}BrNO_3S_2$ $[M + H]^+$ 580.0434, found 580.0438.



3l

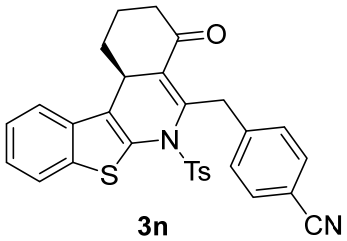
(*S*)-5-(4-methylbenzyl)-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3l). White solid (33.4 mg, 65% yield), m.p. 193 – 194 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 8.1 (major), t_R = 12.4 min (minor); 88% ee. $[\alpha]_D^{25}$ = –117.0 ° (*c* = 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.72 (m, 1H, ArH), 7.52 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 – 7.40 (m, 1H, ArH), 7.35 (d, *J* = 8.0 Hz, 2H, ArH), 7.32 – 7.29 (m, 2H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 7.05 (d, *J* = 8.0 Hz, 2H, ArH), 4.48 (d, *J* = 14.4 Hz, 1H, CH_2), 4.32 (d, *J* = 14.4 Hz, 1H, CH_2), 3.49 (dd, J_1 = 11.8 Hz, J_2 = 5.0 Hz, 1H, CH), 2.57 (dt, J_1 = 15.6 Hz, J_2 = 5.4 Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.30 – 2.22 (m, 4H, CH_2 + CH_3), 2.11 – 2.04 (m, 1H, CH_2), 1.85 – 1.67 (m, 2H, CH_2), 0.27 – 0.15 (m, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 145.0, 140.9, 138.1, 137.1, 135.8, 135.4, 135.2, 132.1, 131.8, 129.3, 129.1, 129.0, 128.5, 125.4, 124.7, 124.2,

122.2, 120.5, 42.4, 38.1, 35.7, 30.5, 23.0, 21.6, 21.0 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{28}NO_3S_2$ $[M + H]^+$ 514.1505, found 514.1506.



3m

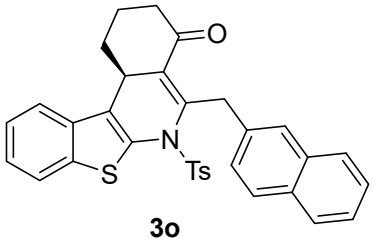
(*S*)-5-(4-fluorobenzyl)-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3m). White solid (38.3 mg, 74% yield), m.p. 173 – 174 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.0 (major), t_R = 12.7 min (minor); 94% ee. $[\alpha]_D^{25}$ = –79.9° (*c* = 2.34, CH_2Cl_2). (*c* = 2.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.72 (m, 1H, ArH), 7.51 (d, *J* = 8.0 Hz, 2H, ArH), 7.46 – 7.39 (m, 3H, ArH), 7.32 – 7.29 (m, 2H, ArH), 7.22 (d, *J* = 8.0 Hz, 2H, ArH), 6.92 (t, *J* = 8.8 Hz, 2H, ArH), 4.48 (d, *J* = 14.4 Hz, 1H, CH_2), 4.31 (d, *J* = 14.4 Hz, 1H, CH_2), 3.50 (dd, J_1 = 12.0 Hz, J_2 = 4.8 Hz, 1H, CH), 2.59 (dt, J_1 = 15.6 Hz, J_2 = 5.6 Hz, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.31 – 2.23 (m, 1H, CH_2), 2.09 – 2.02 (m, 1H, CH_2), 1.85 – 1.67 (m, 2H, CH_2), 0.22 – 0.12 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.6, 161.6 (d, $^1J_{C–F}$ = 244.5 Hz), 145.2, 140.1, 138.0, 136.8, 135.1, 134.0 (d, $^4J_{C–F}$ = 2.5 Hz), 131.9 (d, $^2J_{C–F}$ = 28.2 Hz), 130.8 (d, $^3J_{C–F}$ = 7.9 Hz), 129.3, 128.4, 125.3, 124.8, 124.3, 122.2, 120.5, 115.0, 114.9, 42.5, 38.0, 35.1, 30.5, 23.1, 21.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{25}FNO_3S_2$ $[M + H]^+$ 518.1254, found 518.1258.



3n

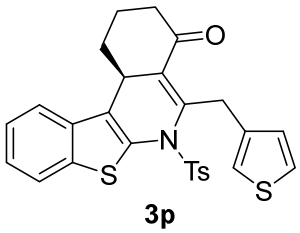
(*S*)-4-((4-oxo-6-tosyl-1,2,3,4,6,11c-hexahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-5-yl)methyl)benzonitrile (3n). White solid (45.6 mg, 87% yield), m.p. 174 – 175 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 10.1 min (major), t_R = 19.7 min (minor); 91% ee. $[\alpha]_D^{25}$ = –113.0 ° (*c* = 2.13, CH_2Cl_2). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.7 Hz, 1H, ArH), 7.59 (d, *J* = 7.7 Hz, 2H, ArH), 7.52 – 7.48 (m, 4H, ArH), 7.42 (d, *J* = 7.7 Hz, 1H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.23 (d, *J* = 7.7 Hz, 2H, ArH), 4.59 (d, *J* = 14.7 Hz, 1H, CH_2), 4.40 (d, *J* = 14.7 Hz, 1H, CH_2), 3.54 (dd, J_1 = 11.9 Hz, J_2 = 4.9 Hz, 1H, CH), 2.61 (dt, J_1 = 15.4 Hz, J_2 = 5.3 Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.31 – 2.26 (m, 1H, CH_2), 2.08 – 2.05 (m, 1H, CH_2), 1.85 – 1.79 (m, 1H, CH_2), 1.73 –

1.69 (m, 1H, CH_2), 0.15 – 0.09 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.5, 145.4, 144.0, 138.7, 137.9, 136.5, 134.9, 132.8, 132.1, 131.6, 130.0, 129.4, 128.4, 125.3, 124.9, 124.4, 122.2, 120.5, 119.1, 110.1, 42.3, 37.9, 36.0, 30.4, 22.9, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{25}N_2O_3S_2$ $[M + H]^+$ 525.1301, found 525.1309.



3o

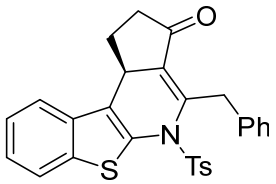
(*S*)-5-(naphthalen-2-ylmethyl)-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3o). White solid (40.7 mg, 74% yield), m.p. 183 – 185 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.7 (major), t_R = 18.5 min (minor); 65% ee. $[\alpha]_D^{25}$ = –85.3° (*c* = 0.81, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H, ArH), 7.78 – 7.69 (m, 4H, ArH), 7.61 (d, *J* = 8.4 Hz, 1H, ArH), 7.53 (d, *J* = 8.0 Hz, 2H, ArH), 7.38 (s, 3H, ArH), 7.28 – 7.20 (m, 4H, ArH), 4.68 (d, *J* = 14.4 Hz, 1H, CH_2), 4.54 (d, *J* = 14.4 Hz, 1H, CH_2), 3.51 (dd, J_1 = 11.8 Hz, J_2 = 4.2 Hz, 1H, CH), 2.60 (dt, J_1 = 15.0 Hz, J_2 = 4.6 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3), 2.32 – 2.24 (m, 1H, CH_2), 2.10 – 2.05 (m, 1H, CH_2), 1.82 – 1.67 (m, 2H, CH_2), 0.23 – 0.17 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 201.6, 145.1, 140.4, 138.0, 136.9, 135.9, 135.1, 133.5, 132.2, 132.0, 129.3, 128.5, 128.0, 127.8, 127.7, 127.6, 127.5, 125.6, 125.4, 125.2, 124.7, 124.2, 122.2, 120.5, 42.5, 38.1, 36.2, 30.5, 23.0, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{28}NO_3S_2$ $[M + H]^+$ 550.1505, found 550.1506.



3p

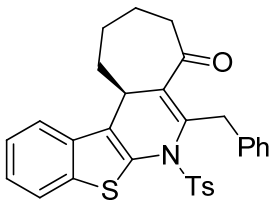
(*S*)-5-(thiophen-3-ylmethyl)-6-tosyl-2,3,6,11c-tetrahydrobenzo[4,5]thieno[2,3-*c*]isoquinolin-4(1*H*)-one (3p). White solid (41.9 mg, 83% yield), m.p. 184 – 185 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 15.9 min (major), t_R = 32.3 min (minor); 97% ee. $[\alpha]_D^{25}$ = –122.5° (*c* = 2.61, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 1H, ArH), 7.50 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 – 7.39 (m, 1H, ArH), 7.33 – 7.28 (m, 2H, ArH), 7.25 – 7.20 (m, 3H, ArH), 7.16 – 7.14 (m, 2H, ArH), 4.55 (d, *J* = 14.8 Hz, 1H, CH_2), 4.34 (d, *J* = 14.8 Hz, 1H, CH_2), 3.47 (dd, J_1 = 15.8 Hz, J_2 = 5.0 Hz, 1H, CH_2), 2.57 (dt, J_1 = 15.6 Hz, J_2 = 5.6 Hz, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.29 –

2.21 (m, 1H, CH_2), 2.12 – 2.05 (m, 1H, CH_2), 1.84 – 1.64 (m, 2H, CH_2), 0.29 – 0.19 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 201.5, 145.1, 140.3, 138.2, 138.0, 136.9, 135.1, 132.0, 131.4, 129.3, 128.8, 128.4, 125.4, 124.8, 124.7, 124.2, 122.6, 122.2, 120.5, 42.3, 37.9, 31.2, 30.4, 22.8, 21.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{23}NaNO_3S_3$ $[M + Na]^+$ 528.0732, found 528.0740.



3q

(*S*)-4-benzyl-5-tosyl-1,2,5,10c-tetrahydro-3*H*-benzo[4,5]thieno[2,3-*b*]cyclopenta[*d*]pyridin-3-one (3q). White solid (38.8 mg, 80% yield), m.p. 180 – 181 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.6 min (minor), t_R = 10.7 min (major); 70% ee. $[\alpha]_D^{25}$ = –137.0° (*c* = 1.69, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.72 (m, 1H, ArH), 7.60 – 7.58 (m, 1H, ArH), 7.45 (d, *J* = 8.4 Hz, 2H, ArH), 7.32 – 7.29 (m, 2H, ArH), 7.24 – 7.19 (m, 4H, ArH), 7.16 – 7.14 (m, 3H, ArH), 5.34 (d, *J* = 14.8 Hz, 1H, CH_2), 4.39 (dd, J_1 = 14.8 Hz, J_2 = 2.8 Hz, 1H, CH_2), 2.83 – 2.74 (m, 2H, CH_2), 2.47 – 2.28 (m + s, 5H, CH_2 + CH_3), 1.94 – 1.82 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 204.8, 148.9, 145.1, 139.4, 138.0, 136.7, 134.7, 133.0, 130.6, 130.3, 129.6, 129.0, 128.3, 127.8, 126.4, 124.6, 124.2, 122.7, 122.5, 39.1, 38.4, 35.3, 26.9, 21.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{23}NNaO_3S_2$ $[M + Na]^+$ 508.1012, found 508.1003.



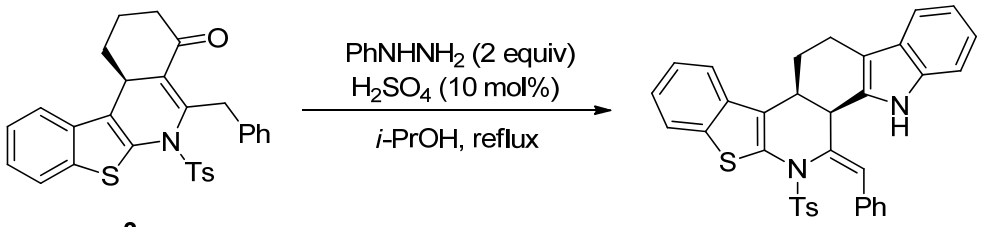
3r

(*S*)-6-benzyl-7-tosyl-1,2,3,4,7,12c-hexahydro-5*H*-benzo[4,5]thieno[2,3-*b*]cyclohepta[*d*]pyridin-5-one (3r). White solid (42.1 mg, 82% yield), m.p. 182 – 183 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 10.4 min (minor), t_R = 13.5 min (major); 92% ee. $[\alpha]_D^{25}$ = –155.8° (*c* = 2.29, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.68 (m, 1H, ArH), 7.61 (d, *J* = 8.4 Hz, 2H, ArH), 7.39 – 7.37 (m, 3H, ArH), 7.32 – 7.27 (m, 2H, ArH), 7.24 – 7.20 (m, 4H, ArH), 7.15 (t, *J* = 7.2 Hz, 1H, ArH), 4.47 (d, *J* = 15.2 Hz, 1H, CH_2), 4.17 (d, *J* = 15.2 Hz, 1H, CH_2), 3.49 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H, CH_2), 2.67 – 2.49 (m, 2H, CH_2), 2.36 (s, 3H, CH_3), 1.87 – 1.83 (m, 1H, CH_2), 1.65 – 1.60 (m, 1H, CH_2), 1.55 – 1.35 (m, 2H, CH_2), –0.15 – –0.25 (m, 1H, CH_2)

ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 205.4, 144.9, 142.3, 138.7, 138.0, 136.5, 135.7, 134.4, 133.8, 129.5, 129.1, 128.8, 128.2, 128.1, 126.2, 124.6, 124.3, 122.3, 119.7, 43.8, 37.3, 36.9, 36.7, 30.0, 23.2, 21.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{27}NNaO_3S_2$ $[M + H]^+$ 536.1325, found 536.1327.

3. Synthetic procedure and the characterization data of compound 4

To solution of **3a** (89.9 mg, 0.2 mmol), phenylhydrazine (43.2 mg, 0.4 mmol), and concentrated sulfuric acid (4.0 mg, 0.04 mmol) in isopropanol (4 mL), and the resulting suspension was stirred at 85 °C (oil bath temperature) for 12 h. Then concentrated the mixture. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 – 10/1) to afford compound **4**.



3a **4**

(5b*S*,12c*S*,*Z*)-6-benzylidene-7-tosyl-5b,6,7,12c,13,14-hexahydro-5*H*-benzo[4',5']thieno-[3',2':5,6]pyrido[3,4-*a*]carbazole (4). White solid (47.0 mg, 41% yield), m.p. 169 – 170 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 5.4 min (minor), t_R = 7.5 min (major); >99% ee. $[\alpha]_D^{25}$ = +85.2° (*c* = 1.85, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.80 (m, 2H, ArH), 7.74 (d, *J* = 8.0 Hz, 2H, ArH), 7.61 (dd, J_1 = 7.4 Hz, J_2 = 1.8 Hz, 1H, ArH), 7.54 – 7.49 (m, 3H, ArH), 7.45 (d, *J* = 8.4 Hz, 1H, ArH), 7.39 – 7.33 (m, 2H, ArH), 7.29 – 7.21 (m, 6H, ArH + NH), 7.15 (t, *J* = 7.4 Hz, 1H, ArH), 6.01 (s, 1H, CH), 3.27 – 3.24 (m, 2H, CH + CH), 2.91 – 2.75 (m, 2H, CH_2), 2.40 – 2.35 (m, 4H, CH_2 + CH_3), 1.84 – 1.72 (m, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 145.0, 136.54, 136.48, 136.41, 136.36, 134.6, 134.5, 134.4, 130.6, 130.2, 129.9, 129.6, 128.3, 128.2, 127.8, 127.0, 124.5, 124.4, 124.3, 122.5, 122.3, 120.8, 119.6, 118.4, 112.9, 111.0, 36.8, 36.6, 24.7, 21.6, 20.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{35}H_{29}N_2O_2S_2$ $[M + H]^+$ 573.1665, found 573.1665.

4. Crystal data and structure refinement

Crystal data and structure refinement for 3n

Identification code	CCDC 2254460
Empirical formula	$C_{30}H_{24}N_2O_3S_2$
Formula weight	524.63
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	$P2_1P2_1P2_1$
a/Å	10.378(2)
b/Å	13.432(3)
c/Å	18.562(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2587(10)
Z	4
ρ_{calc}g/cm^3	1.347
μ/mm^{-1}	0.241
F(000)	1096
Crystal size/mm^3	0.200 × 0.200 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.960 to 50.208
Index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $-22 \le l \le 21$
Reflections collected	58680
Independent reflections	4590 [$R_{(int)}$ = 0.1196]
Data/restraints/parameters	4590/24/345
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0540, wR_2 = 0.0992
Final R indexes [all data]	R_1 = 0.1125, wR_2 = 0.1197
Largest diff. peak/hole / e Å^{-3}	0.210/-0.259
Absolute structure parameter	-0.01(4)

Crystal data and structure refinement for 4

Identification code	CCDC 2270502
Empirical formula	$C_{35}H_{28}N_2O2S_2$
Formula weight	572.71
Temperature/K	300(2)
Crystal system	orthorhombic
Space group	$P2_1P2_1P2_1$
a/Å	9.6474(14)
b/Å	13.1696(19)
c/Å	22.923(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2912.5(7)
Z	4
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	1.931
F(000)	1200
Crystal size/mm^3	0.200 × 0.100 × 0.080
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.714 to 134.732
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 15$, $-27 \le l \le 27$
Reflections collected	30681
Independent reflections	5189 [$R_{(int)}$ = 0.0984]
Data/restraints/parameters	5189/0/323
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1865
Final R indexes [all data]	R_1 = 0.0904, wR_2 = 0.2164
Largest diff. peak/hole / e Å^{-3}	0.205/-0.524
Absolute structure parameter	-0.090(13)

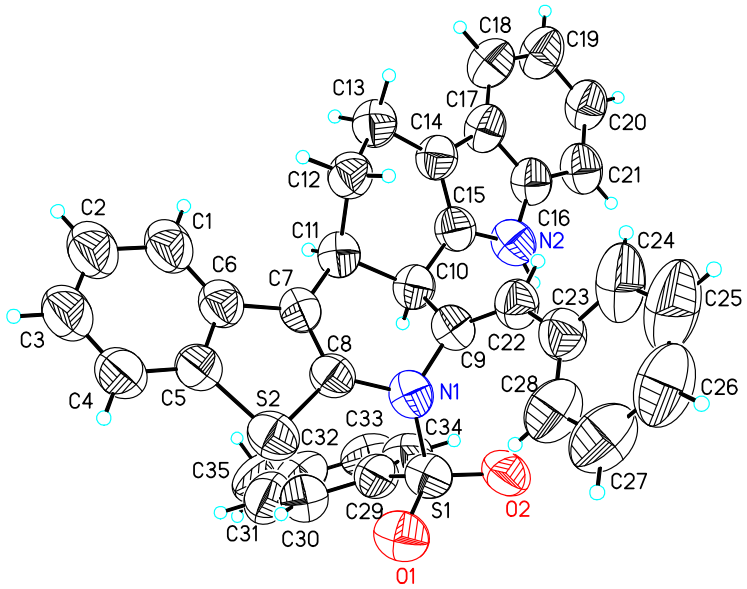


Fig. S1. X-ray structure of **4**

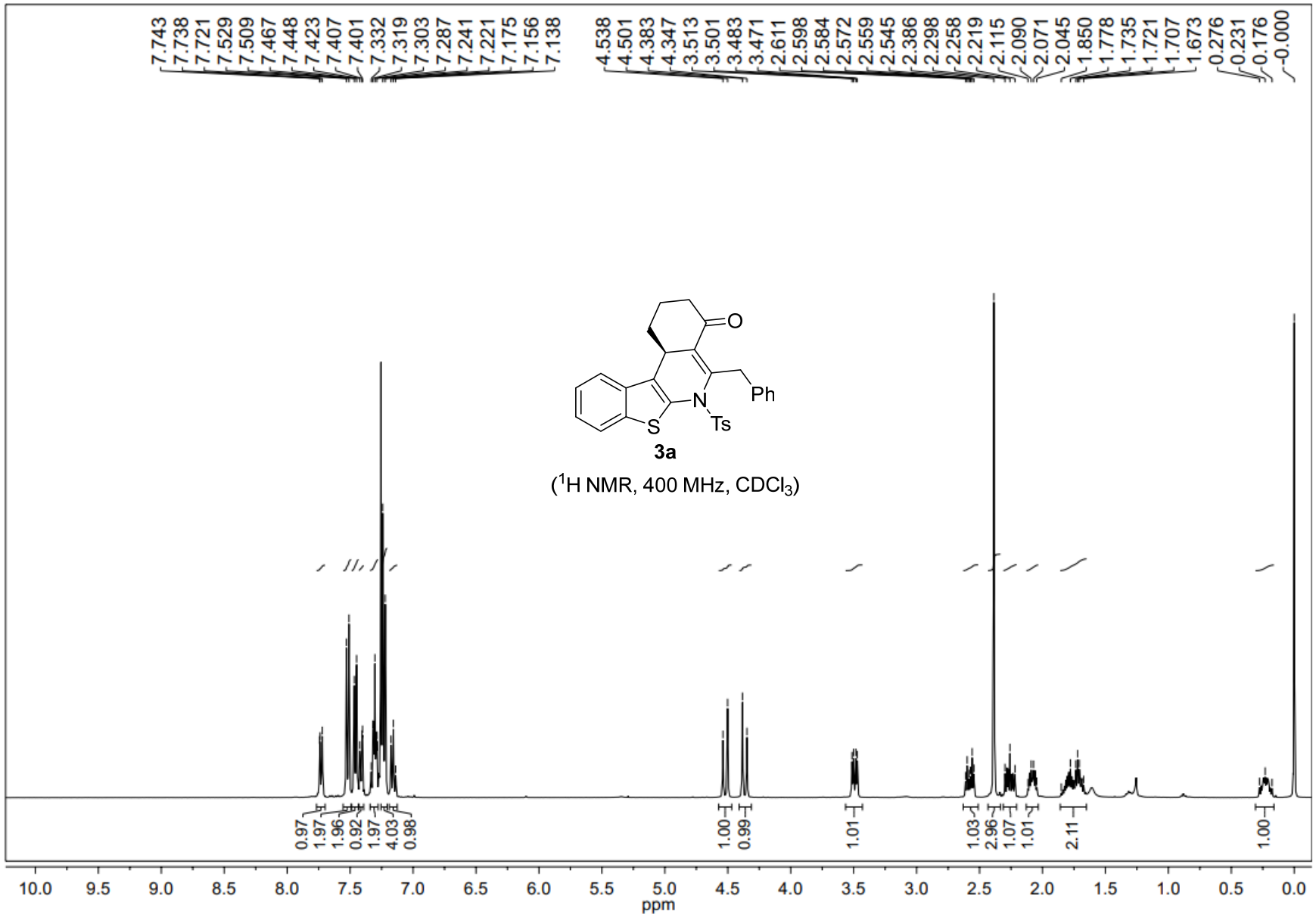
5. Reference

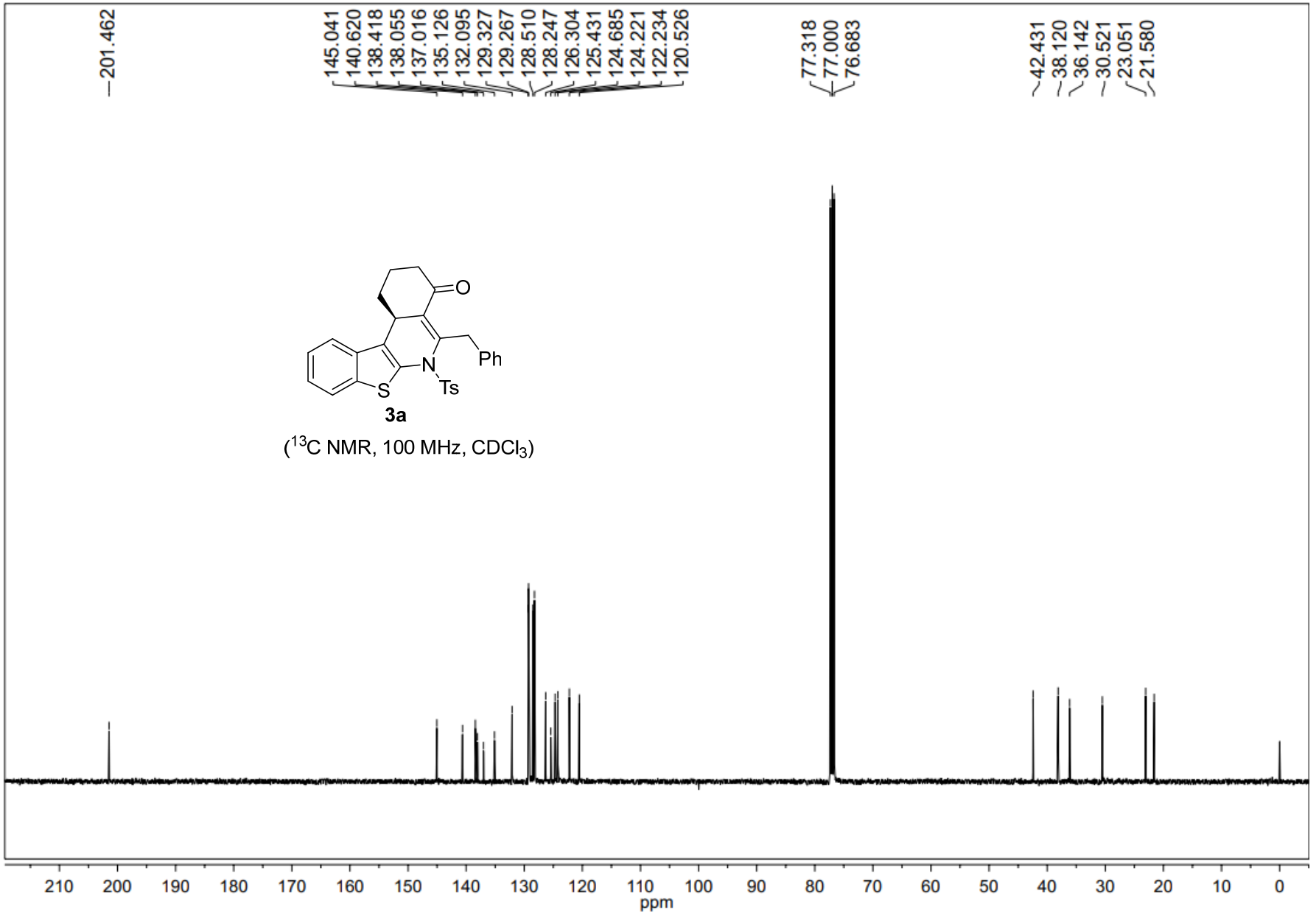
[1] C. Niu, D.-H. Xie and D.-M. Du, Isothiourea-catalysed enantioselective annulation of 2-aminobenzothiophenes with α,β-unsaturated anhydrides, *Org. Chem. Front.*, 2022, **9**, 5551-5556.

[2] a) V. Rauniyar, Z. J. Wang, H. E. Burks and F. D. Toste, Enantioselective synthesis of highly substituted furans by a copper(II)-catalyzed cycloisomerization-indole addition reaction, *J. Am. Chem. Soc.*, 2011, **133**, 8486-8489. b) Q. Li, Z. L. Wang, H. X. Lu and Y. H. Xu, Copper-catalyzed enantioselective 1,4-protosilylation of alkynyl-substituted enones to synthesize the highly diastereomeric chiral homoallenylsilanes, *Org. Lett.*, 2022, **24**, 2832-2836. c) Z. Li, H. Zhou and J. Xu, Access to chiral polycyclic 1,4-dihydropyridines via organocatalytic formal [3 + 3] annulation of 2-(1-alkynyl)-2-alken-1-ones with 3-aminobenzofurans, *Org. Lett.*, 2021, **23**, 6391-6395.

[3] a) W. Yang and D.-M. Du, Highly enantioselective Michael addition of nitroalkanes to chalcones using chiral squaramides as hydrogen bonding organocatalysts, *Org. Lett.*, 2010, **12**, 5450-5453. b) Y. Lin, Y.-X. Song and D.-M. Du, Enantioselective synthesis of CF_3-containing 3,2'-pyrrolidinyl spirooxindoles and dispirooxindoles via thiourea-catalyzed domino Michael/Mannich [3 + 2] cycloaddition reactions, *Adv. Synth. Catal.*, 2019, **361**, 1064-1070. c) N. Hara, S. Nakamura, M. Sano, R. Tamura, Y. Funahashi and N. Shibata, Enantioselective synthesis of AG-041R by using *N*-heteroarenesulfonyl cinchona alkaloid amides as organocatalysts, *Chem. Eur. J.*, 2012, **18**, 9276-9280.

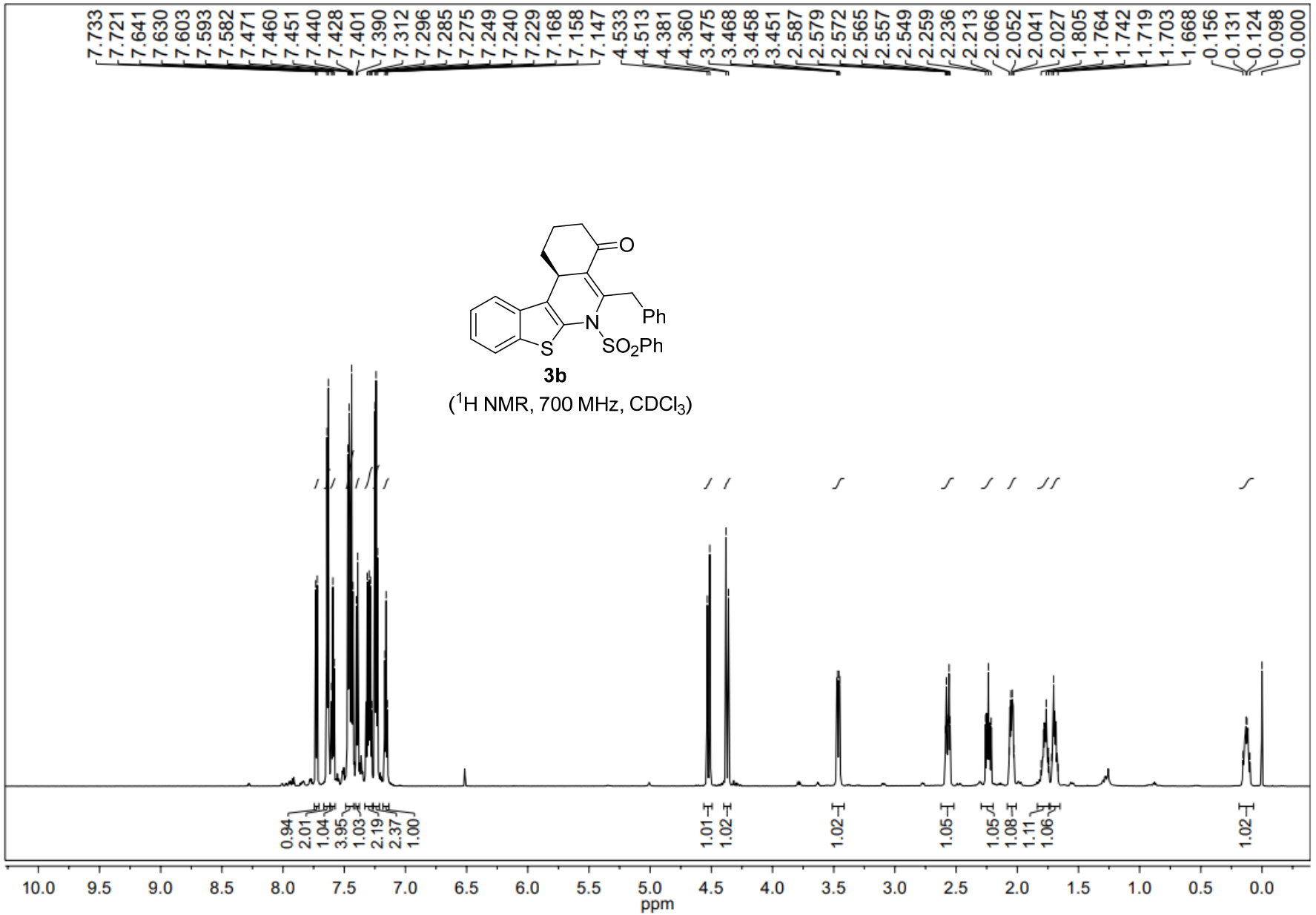
6. Copies of ^{1}H and ^{13}C NMR spectra of new compounds





3a

(^{13}C NMR, 100 MHz, $CDCl_3$)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7.721
7.641
7.630
7.603
7.593
7.582
7.471
7.460
7.451
7.440
7.428
7.401
7.390
7.312
7.296
7.285
7.275
7.249
7.240
7.229
7.168
7.158
7.147
4.533
4.513
4.381
4.360
3.475
3.468
3.458
3.451
2.587
2.579
2.572
2.565
2.557
2.549
2.259
2.236
2.213
2.066
2.052
2.041
2.027
1.805
1.764
1.742
1.719
1.703
1.668
0.156
0.131
0.124
0.098
0.000
O
Ph
N
S
SO2Ph
3b
(1H NMR, 700 MHz, CDCl3)
0.94
2.01
1.04
3.95
1.03
2.19
2.37
1.00
1.01
1.02
1.02
1.05
1.05
1.08
1.11
1.06
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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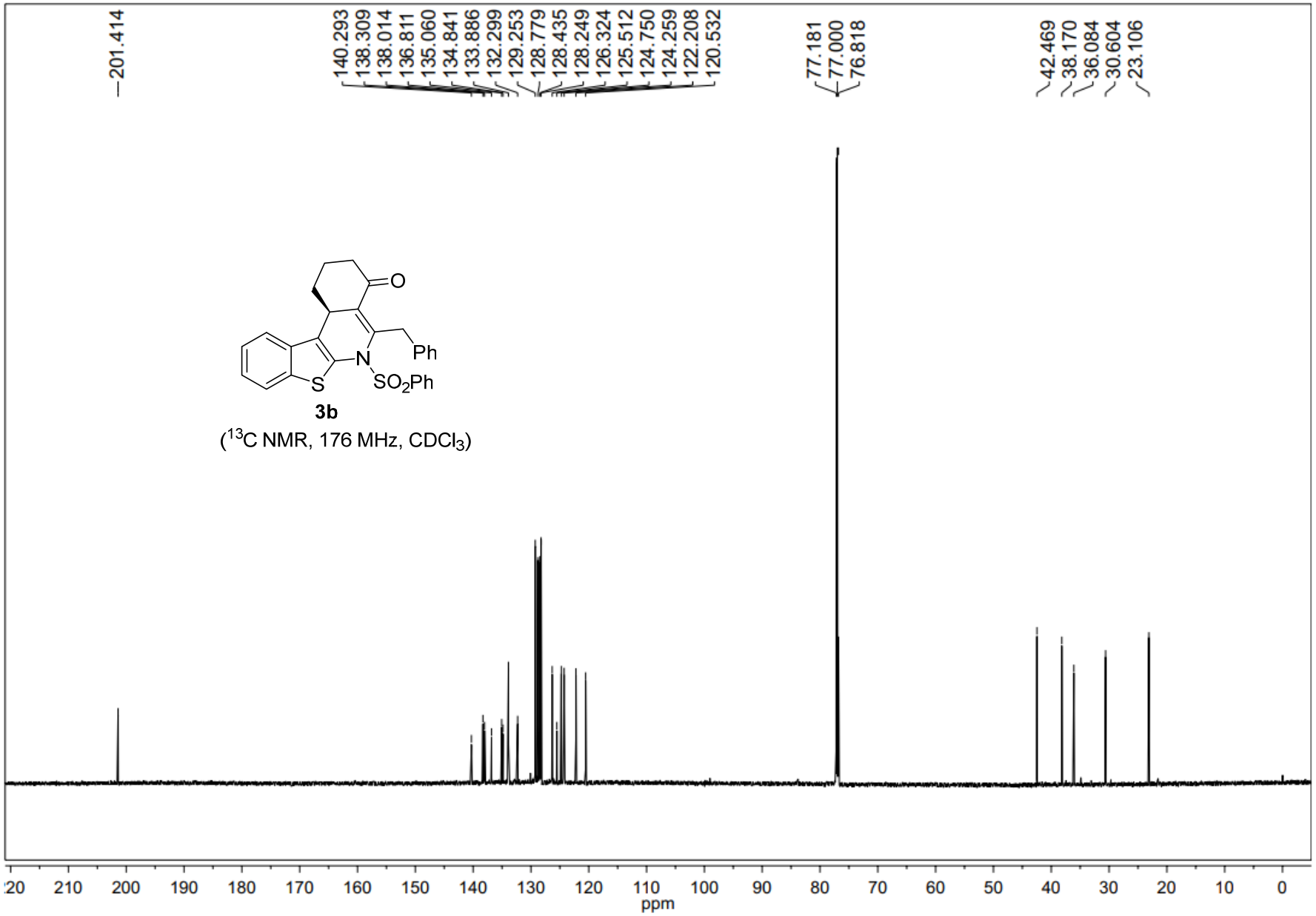
1.0
0.5
0.0
ppm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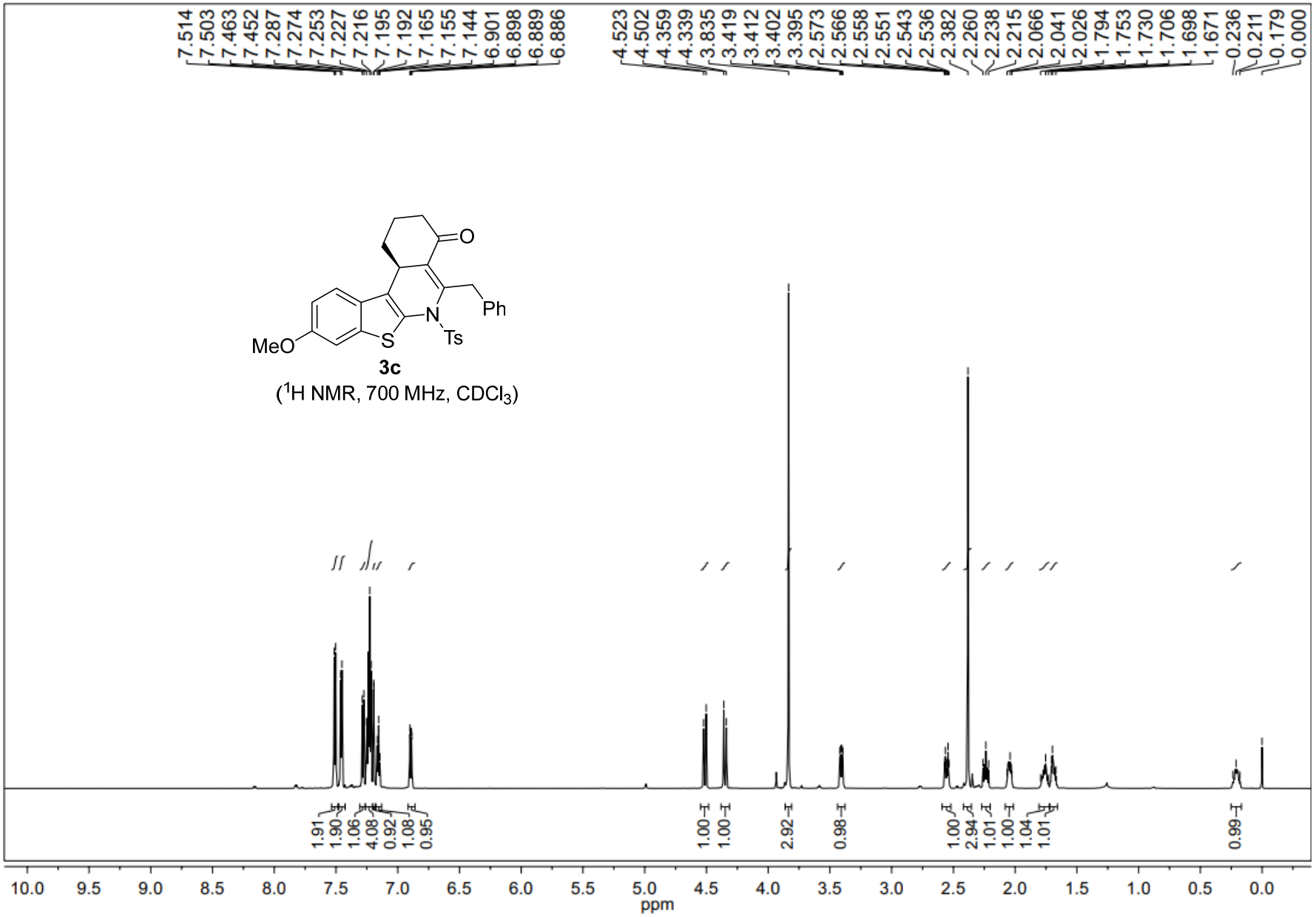
140.293
138.309
138.014
136.811
135.060
134.841
133.886
132.299
129.253
128.779
128.435
128.249
126.324
125.512
124.750
124.259
122.208
120.532
77.181
77.000
76.818
42.469
38.170
36.084
30.604
23.106
O
N
Ph
S
SO2Ph
3b
(13C NMR, 176 MHz, CDCl3)
ppm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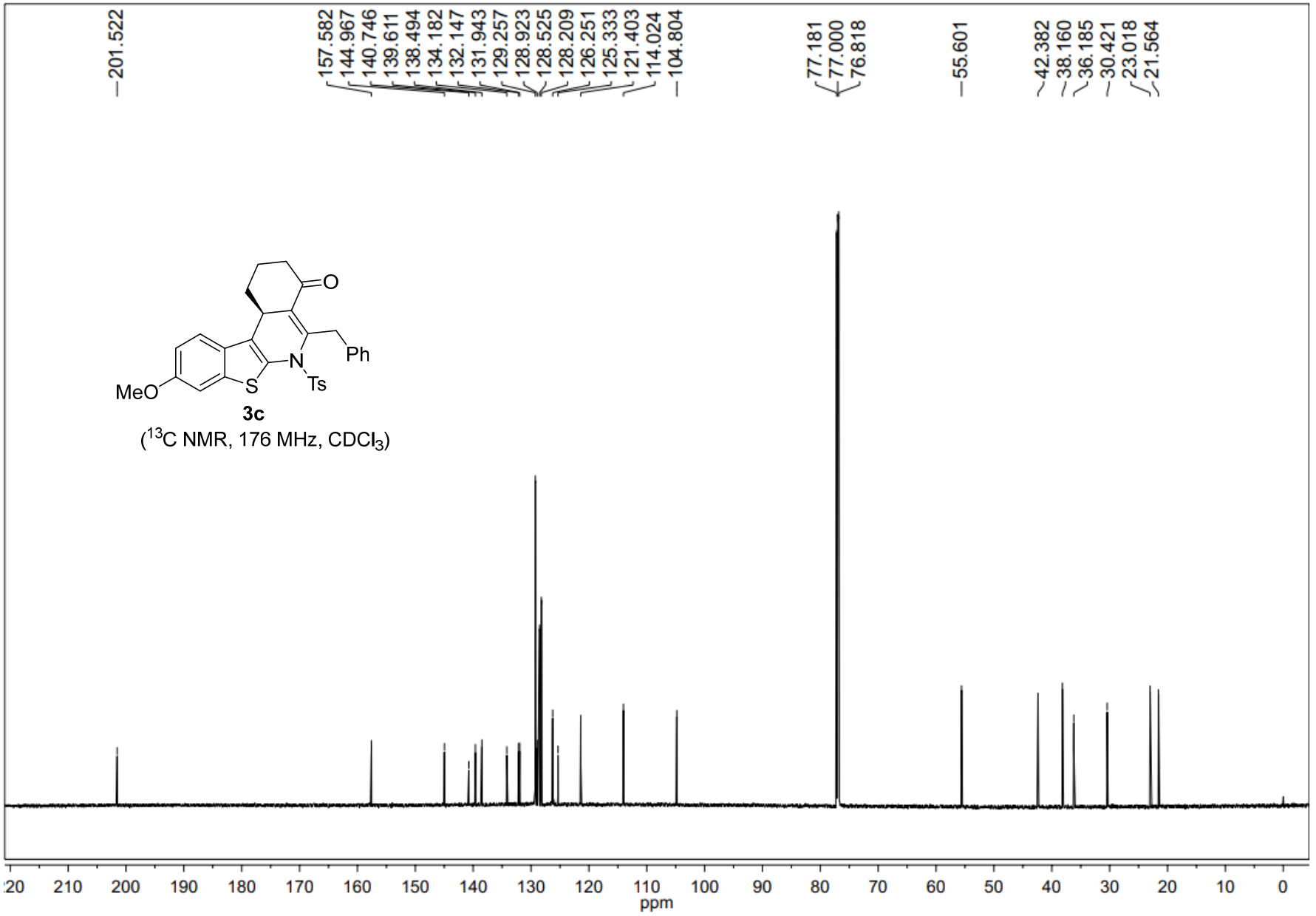
7.503
7.463
7.452
7.287
7.274
7.253
7.227
7.216
7.195
7.192
7.165
7.155
7.144
6.901
6.898
6.889
6.886
4.523
4.502
4.359
4.339
3.835
3.419
3.412
3.402
3.395
2.573
2.566
2.558
2.551
2.543
2.536
2.382
2.260
2.238
2.215
2.066
2.041
2.026
1.794
1.753
1.730
1.706
1.698
1.671
0.236
0.211
0.179
0.000
O
Ph
N
Ts
S
MeO
3c
(1H NMR, 700 MHz, CDCl3)
1.91
1.90
1.06
4.08
0.92
1.08
0.95
1.00
1.00
2.92
0.98
1.00
2.94
1.01
1.00
1.04
1.01
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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144.967
140.746
139.611
138.494
134.182
132.147
131.943
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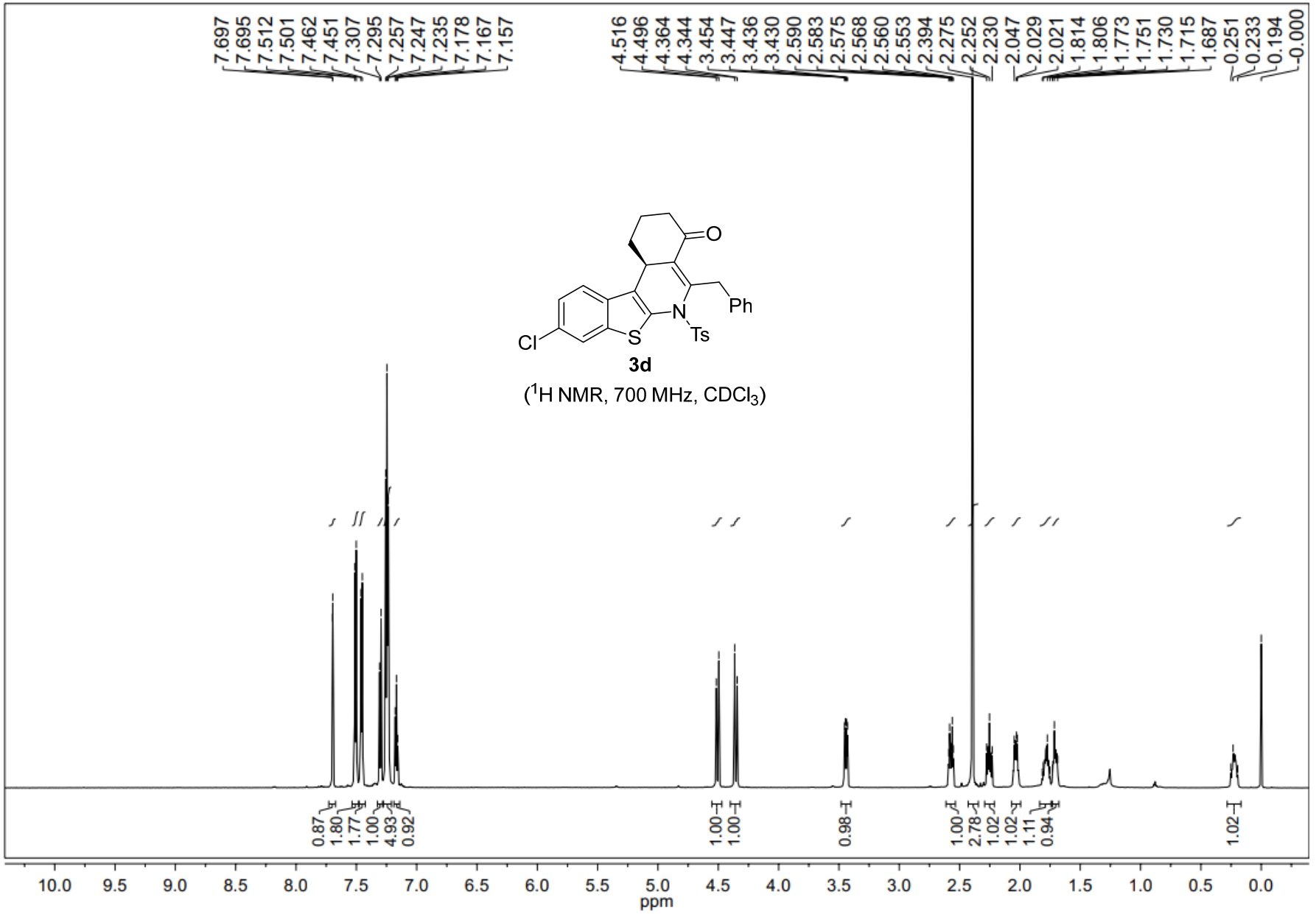
128.923
128.525
128.209
126.251
125.333
121.403
114.024
104.804
77.181
77.000
76.818
55.601
42.382
38.160
36.185
30.421
23.018
21.564
O
Ph
N
Ts
S
MeO
3c
(^{13}C NMR, 176 MHz, $CDCl_3$)
ppm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7.695
7.512
7.501
7.462
7.451
7.307
7.295
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7.247
7.235
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7.167
7.157
4.516
4.496
4.364
4.344
3.454
3.447
3.436
3.430
2.590
2.583
2.575
2.568
2.560
2.553
2.394
2.275
2.252
2.230
2.047
2.029
2.021
1.814
1.806
1.773
1.751
1.730
1.715
1.687
0.251
0.233
0.194
-0.000
O
Ph
N
Ts
S
Cl
3d
(1H NMR, 700 MHz, CDCl3)
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1.80
1.77
1.00
4.93
0.92
1.00
1.00
0.98
1.00
2.78
1.02
1.02
1.11
0.94
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
1.5
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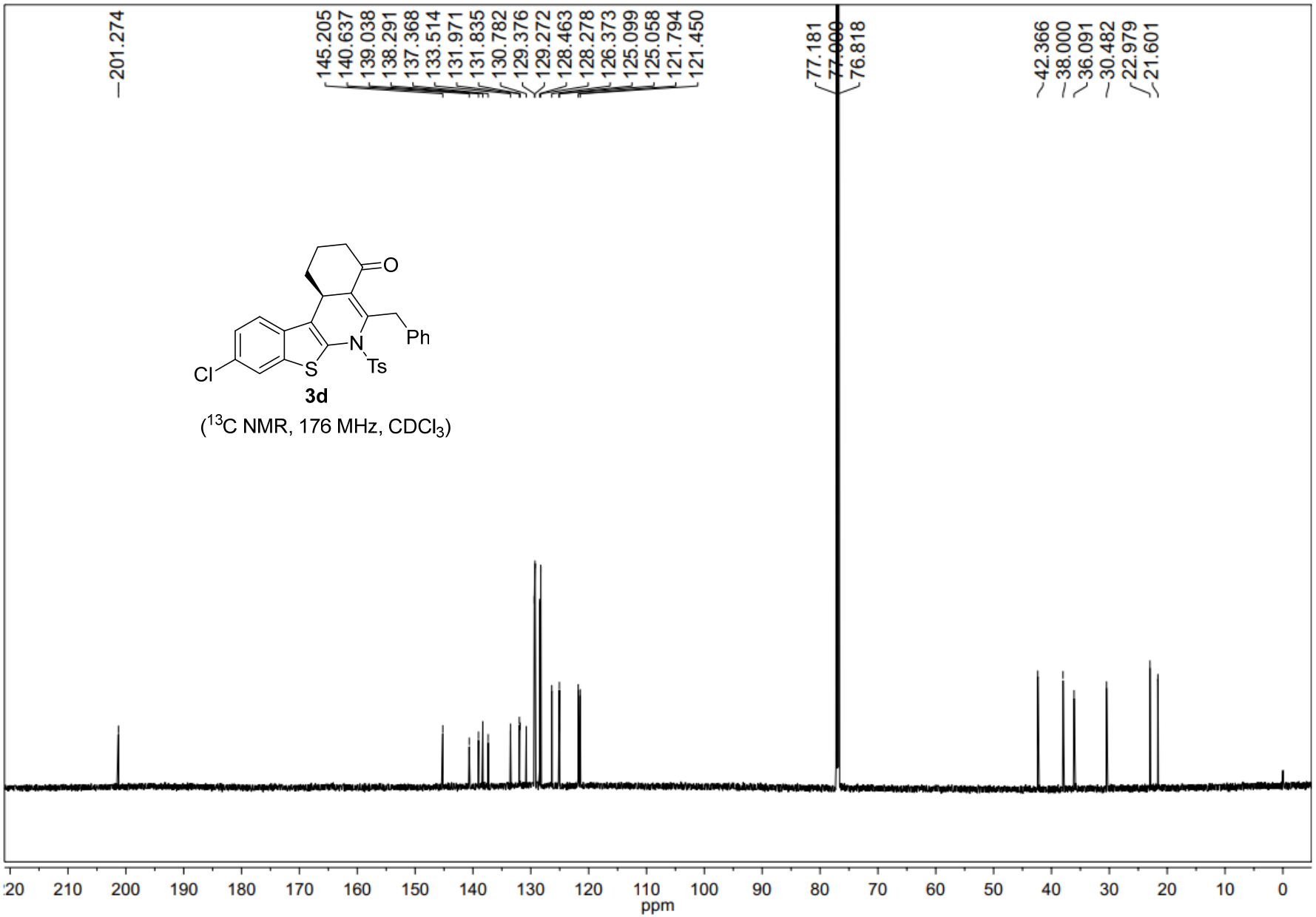
0.5
0.0
ppm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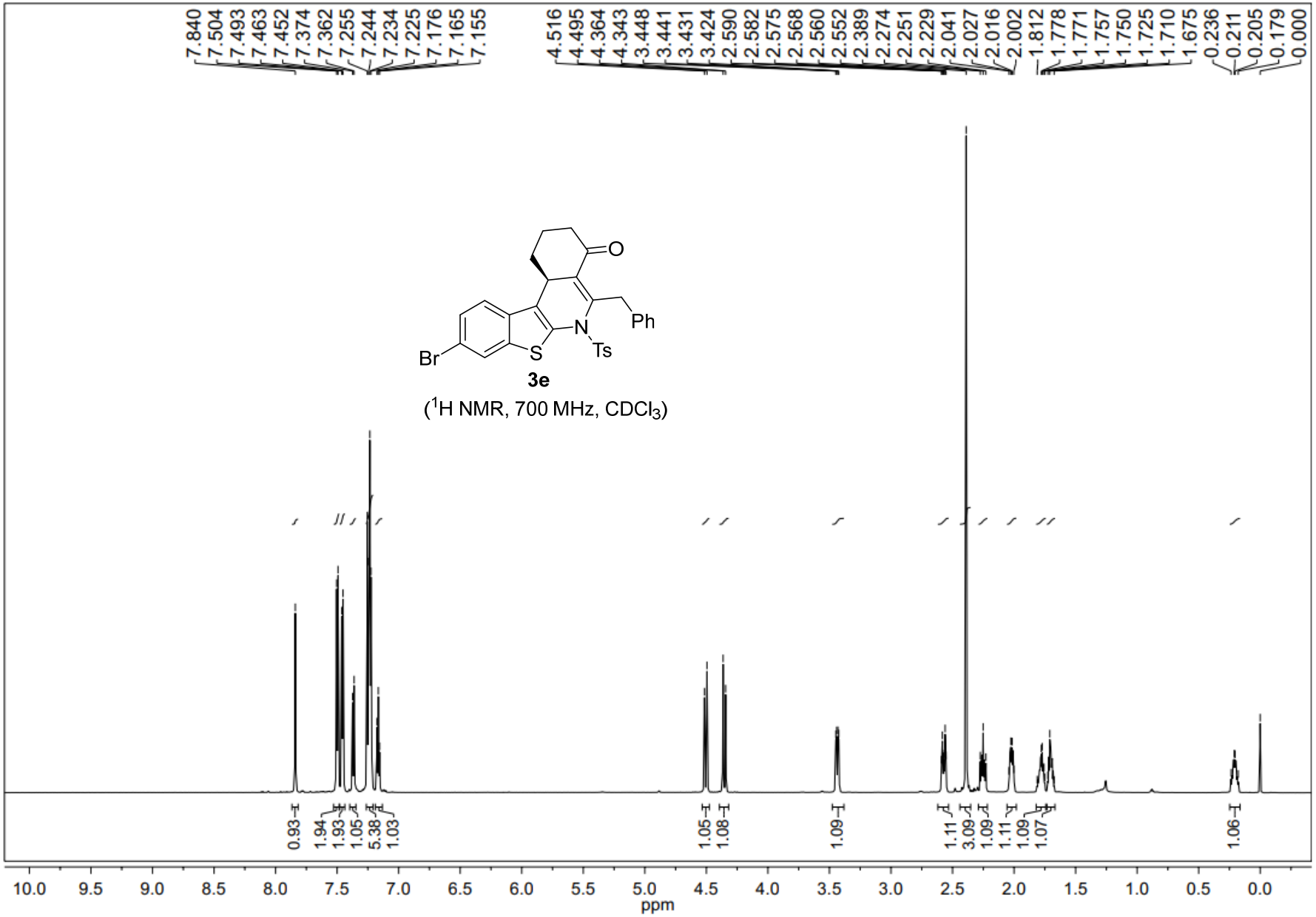
128.463
128.278
126.373
125.099
125.058
121.794
121.450
77.181
77.000
76.818
42.366
38.000
36.091
30.482
22.979
21.601
O
Ph
N
Ts
S
Cl
3d
(^{13}C NMR, 176 MHz, $CDCl_3$)
ppm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7.374
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7.255
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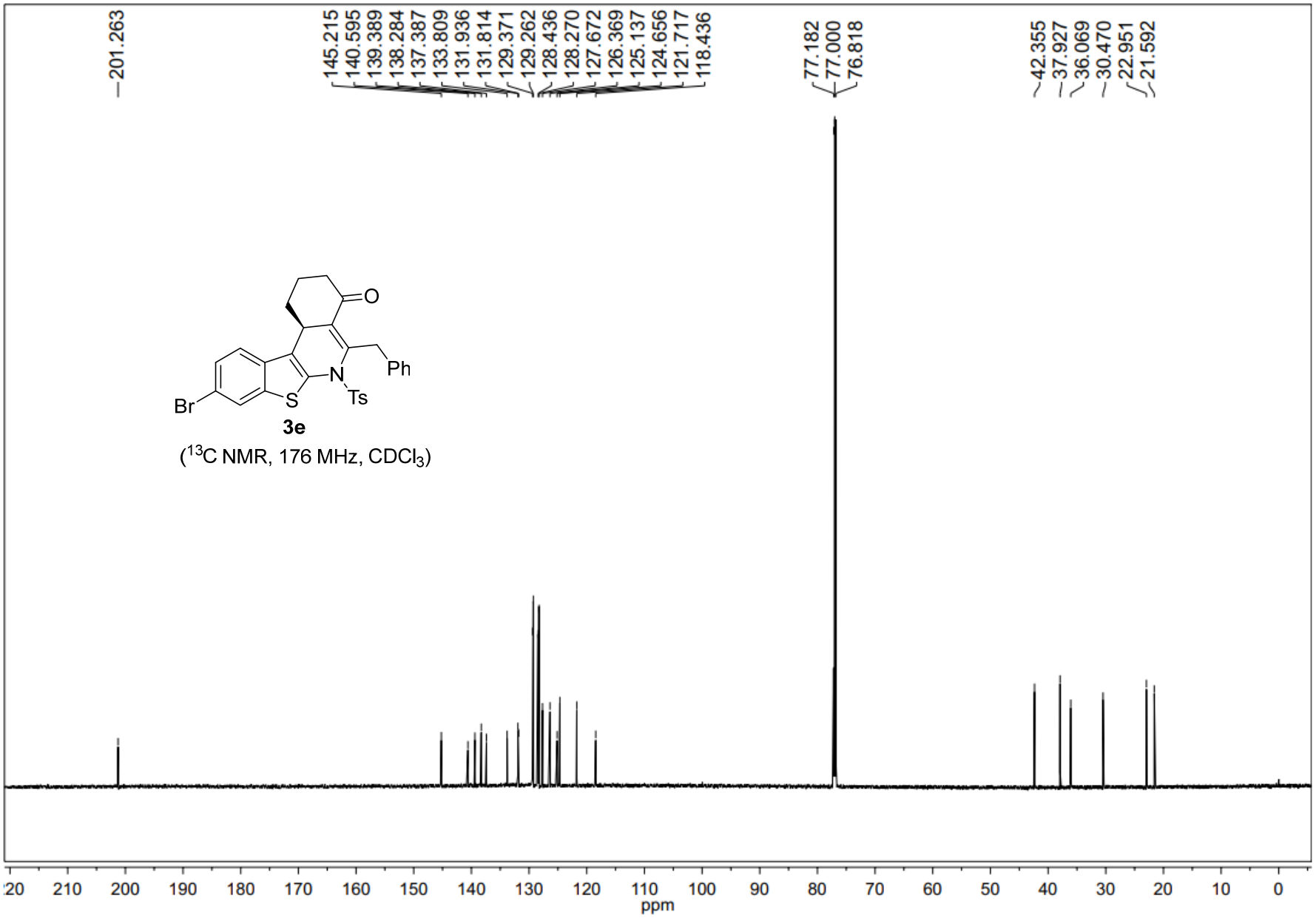
7.234
7.225
7.176
7.165
7.155
4.516
4.495
4.364
4.343
3.448
3.441
3.431
3.424
2.590
2.582
2.575
2.568
2.560
2.552
2.389
2.274
2.251
2.229
2.041
2.027
2.016
2.002
1.812
1.778
1.771
1.757
1.750
1.725
1.710
1.675
0.236
0.211
0.205
0.179
0.000
O
Ph
N
Ts
S
Br
3e
(1H NMR, 700 MHz, CDCl3)
0.93
1.94
1.93
1.05
5.38
1.03
1.05
1.08
1.09
1.11
3.09
1.09
1.11
1.09
1.07
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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139.389
138.284
137.387
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131.936
131.814
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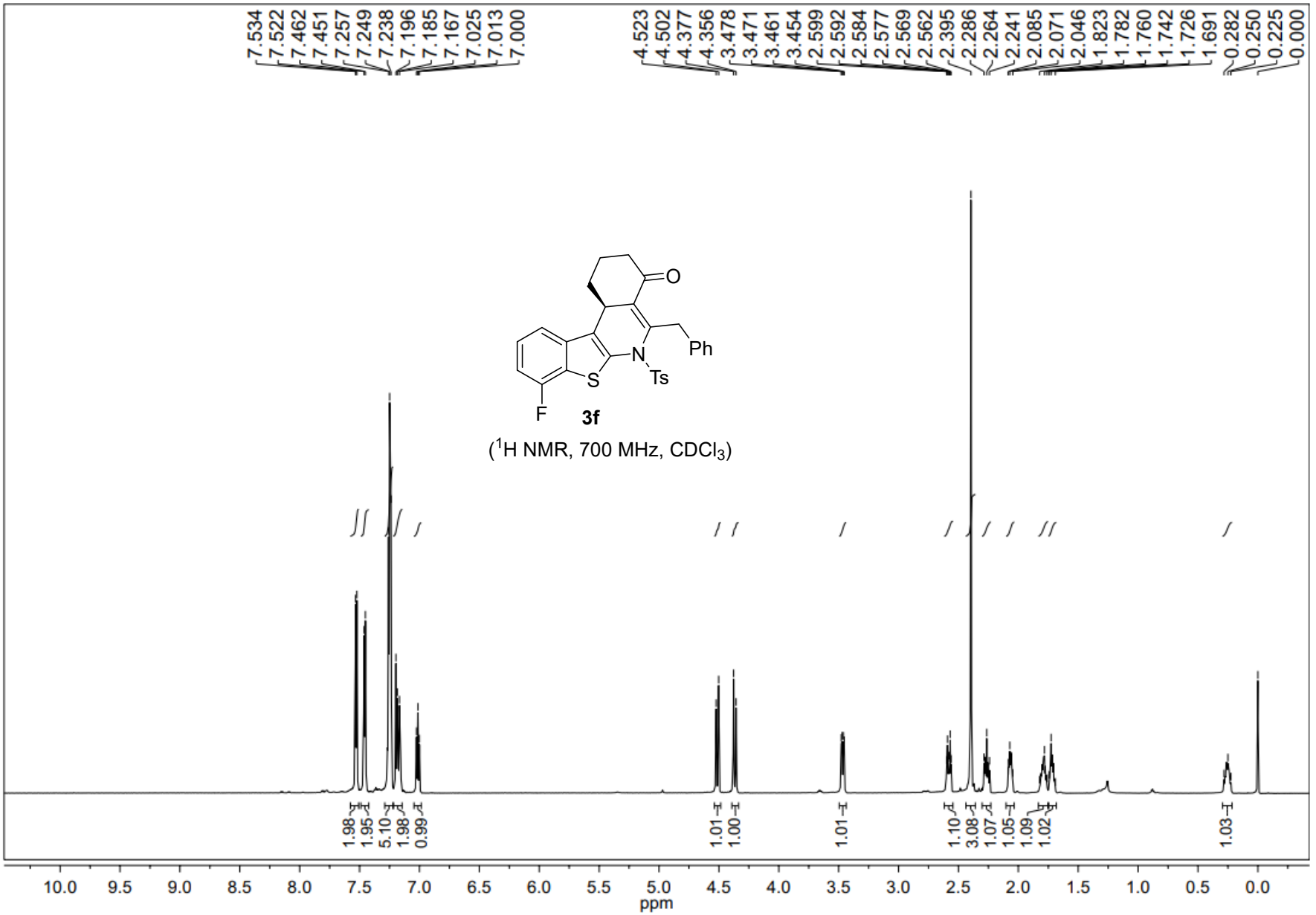
128.270
127.672
126.369
125.137
124.656
121.717
118.436
77.182
77.000
76.818
42.355
37.927
36.069
30.470
22.951
21.592
O
Ph
N
Ts
S
Br
3e
(^{13}C NMR, 176 MHz, $CDCl_3$)
ppm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7.196
7.185
7.167
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7.013
7.000
4.523
4.502
4.377
4.356
3.478
3.471
3.461
3.454
2.599
2.592
2.584
2.577
2.569
2.562
2.395
2.286
2.264
2.241
2.085
2.071
2.046
1.823
1.782
1.760
1.742
1.726
1.691
0.282
0.250
0.225
0.000
O
Ph
N
Ts
S
F
3f
(1H NMR, 700 MHz, CDCl3)
1.98
1.95
5.10
1.98
0.99
1.01
1.00
1.01
1.10
3.08
1.07
1.05
1.09
1.02
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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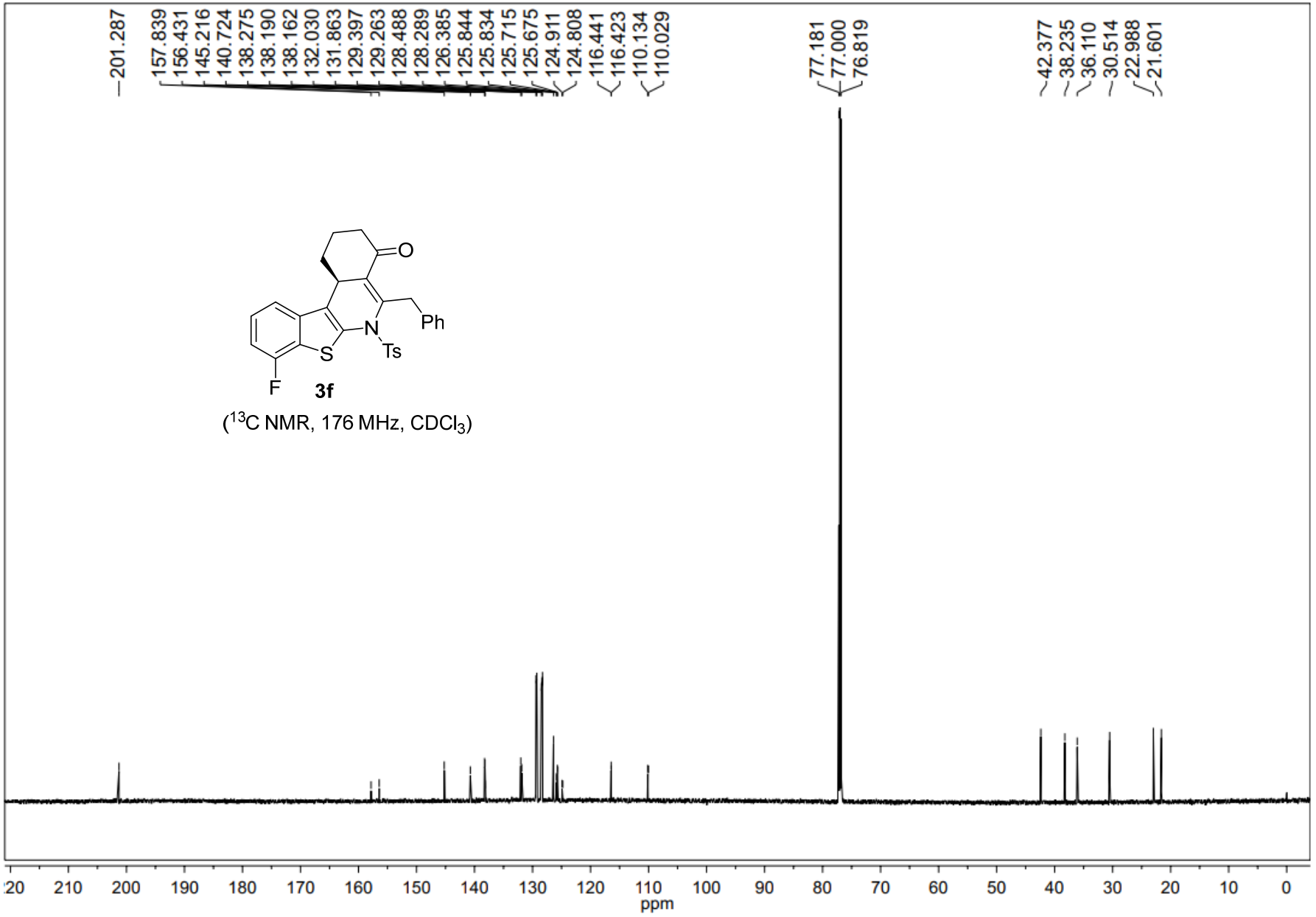
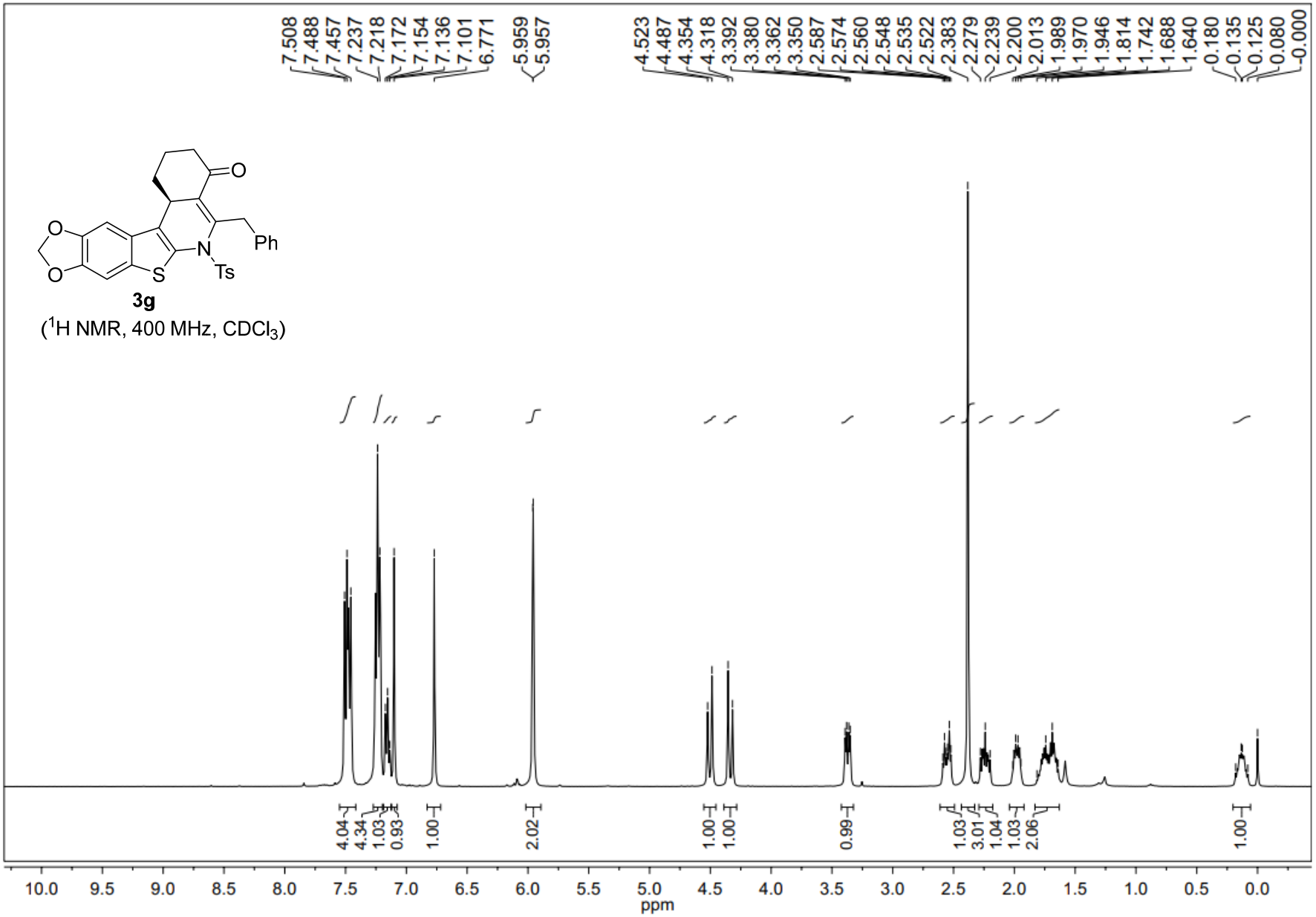
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



(^{13}C NMR, 176 MHz, $CDCl_3$)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7.237
7.218
7.172
7.154
7.136
7.101
6.771
5.959
5.957
4.523
4.487
4.354
4.318
3.392
3.380
3.362
3.350
2.587
2.574
2.560
2.548
2.535
2.522
2.383
2.279
2.239
2.200
2.013
1.989
1.970
1.946
1.814
1.742
1.688
1.640
0.180
0.135
0.125
0.080
-0.000
O
O
O
N
Ts
S
Ph
3g
(1H NMR, 400 MHz, CDCl3)
4.04
4.34
1.03
0.93
1.00
2.02
1.00
1.00
0.99
1.03
3.01
1.04
1.03
2.06
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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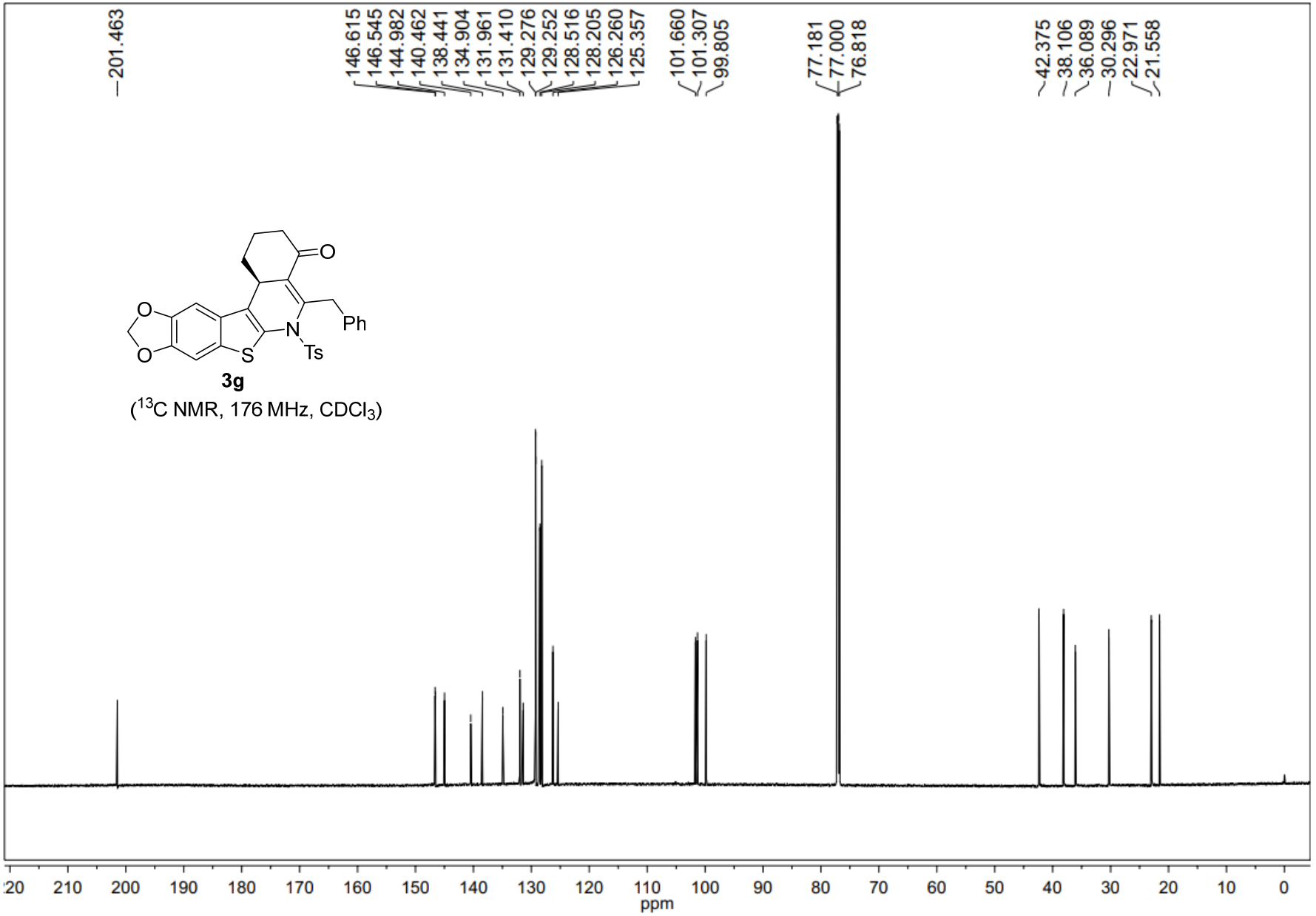
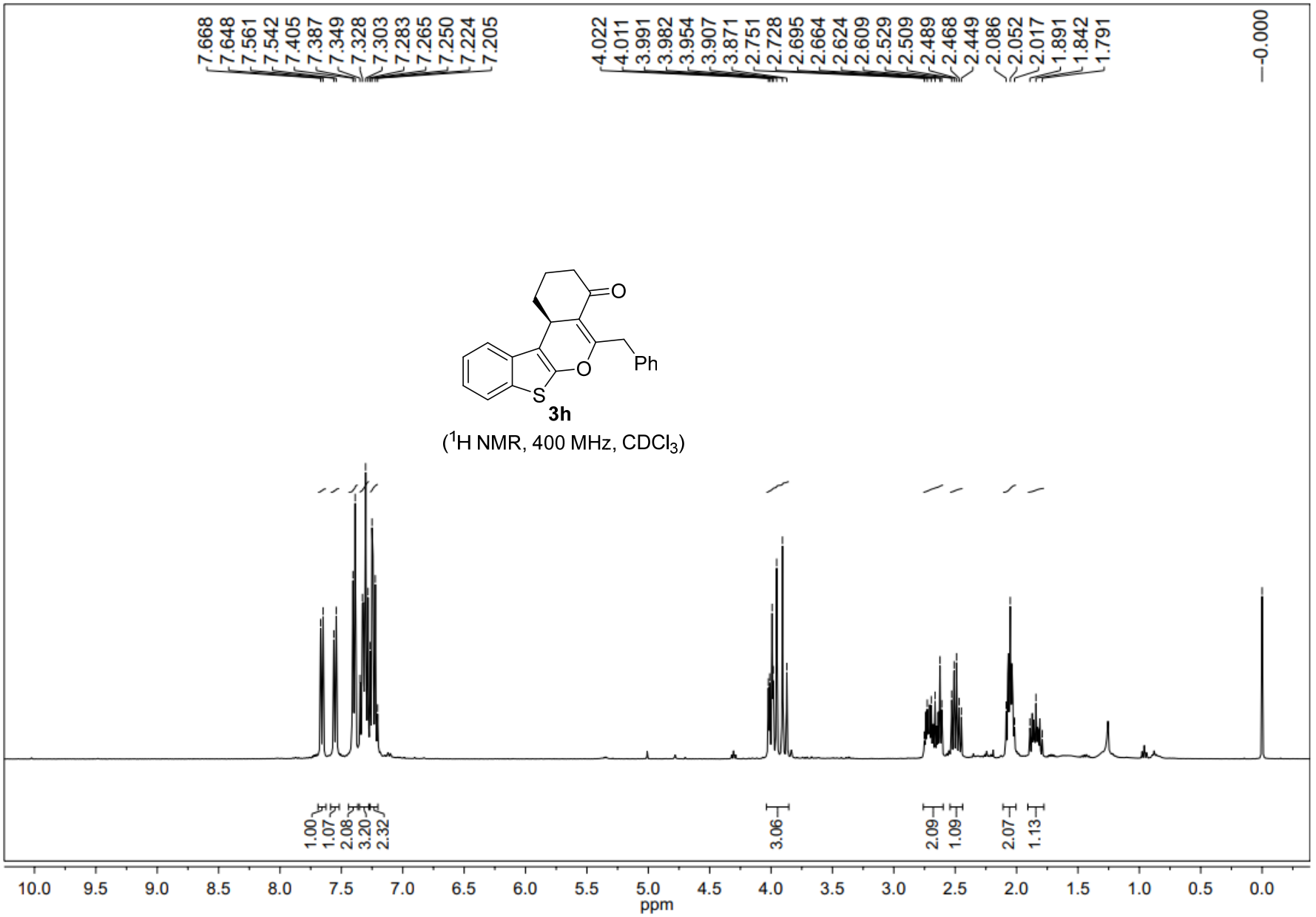
1.5
1.0
0.5
0.0
ppm



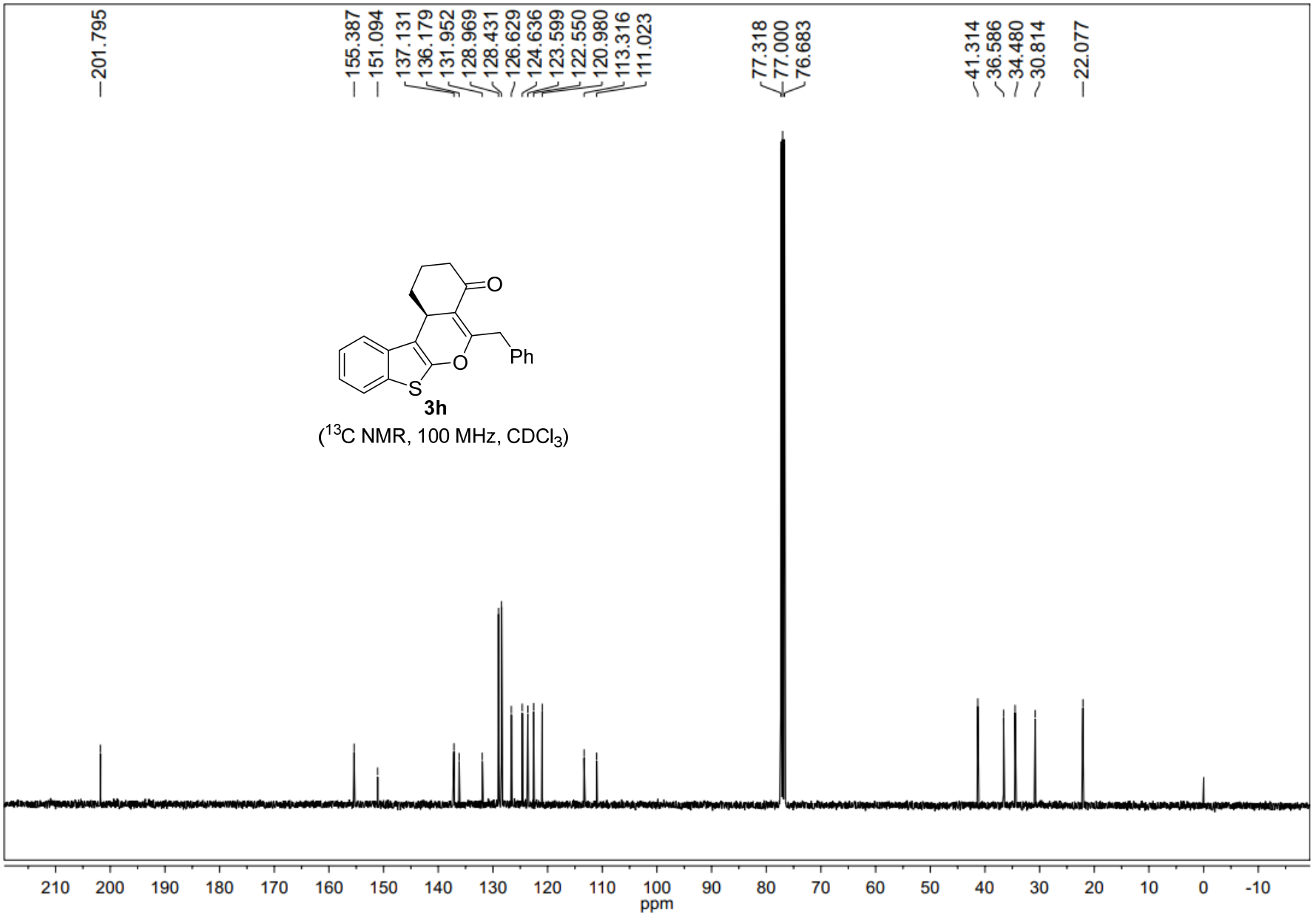
3g

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



3h

(^{1}H NMR, 400 MHz, $CDCl_3$)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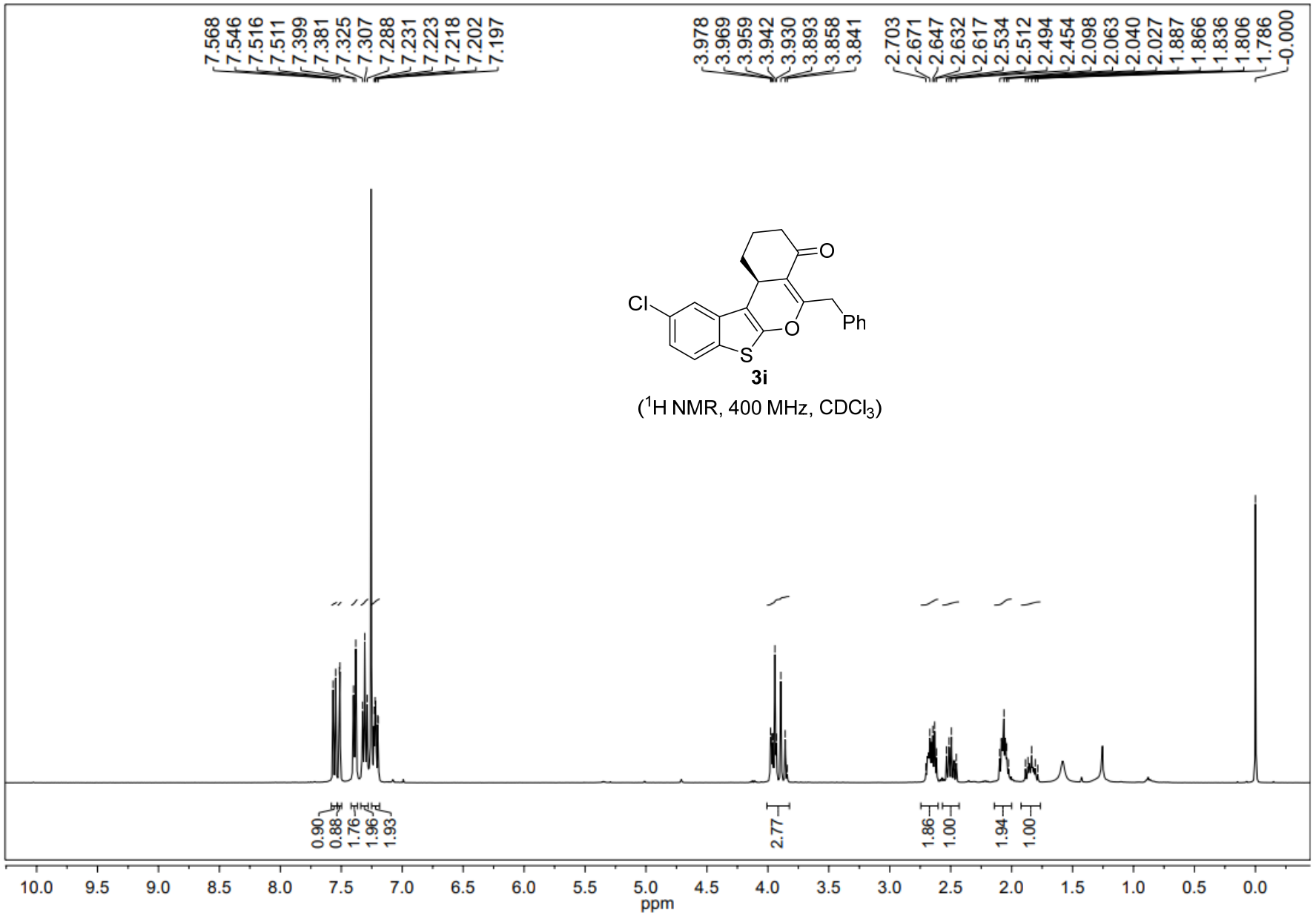
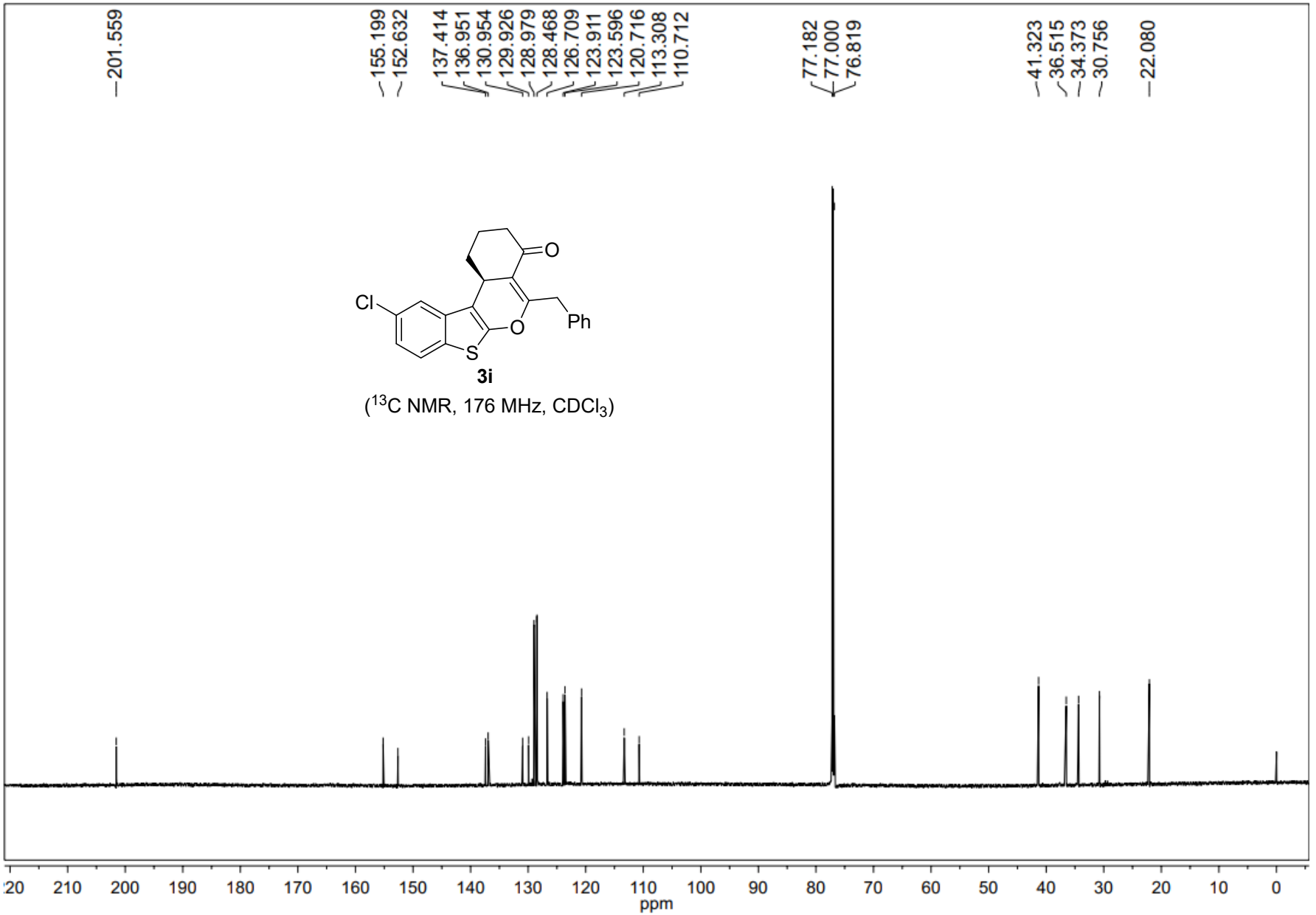
151.094
137.131
136.179
131.952
128.969
128.431
126.629
124.636
123.599
122.550
120.980
113.316
111.023
77.318
77.000
76.683
41.314
36.586
34.480
30.814
22.077
O
O
S
Ph
3h
(13C NMR, 100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



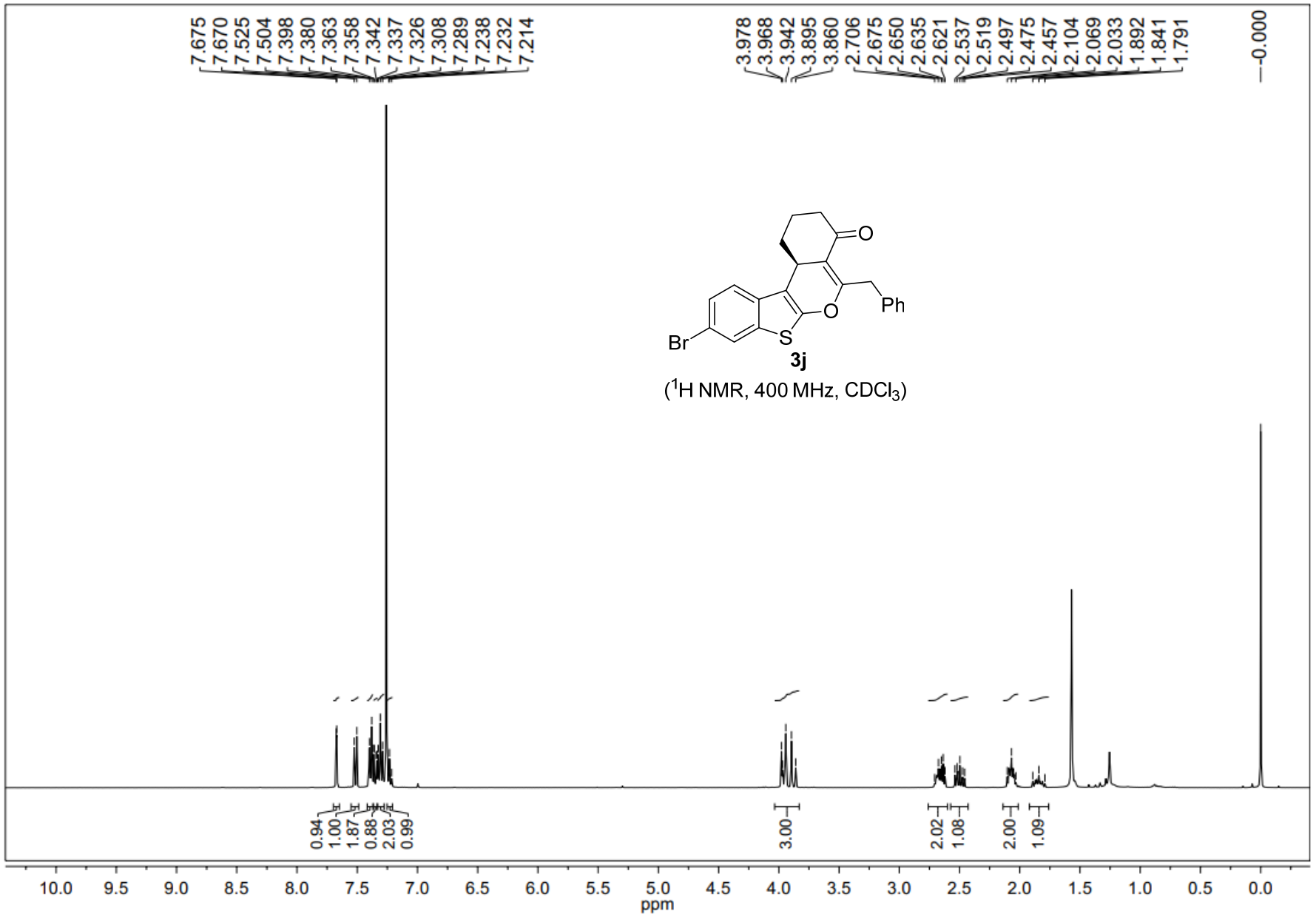
3i

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



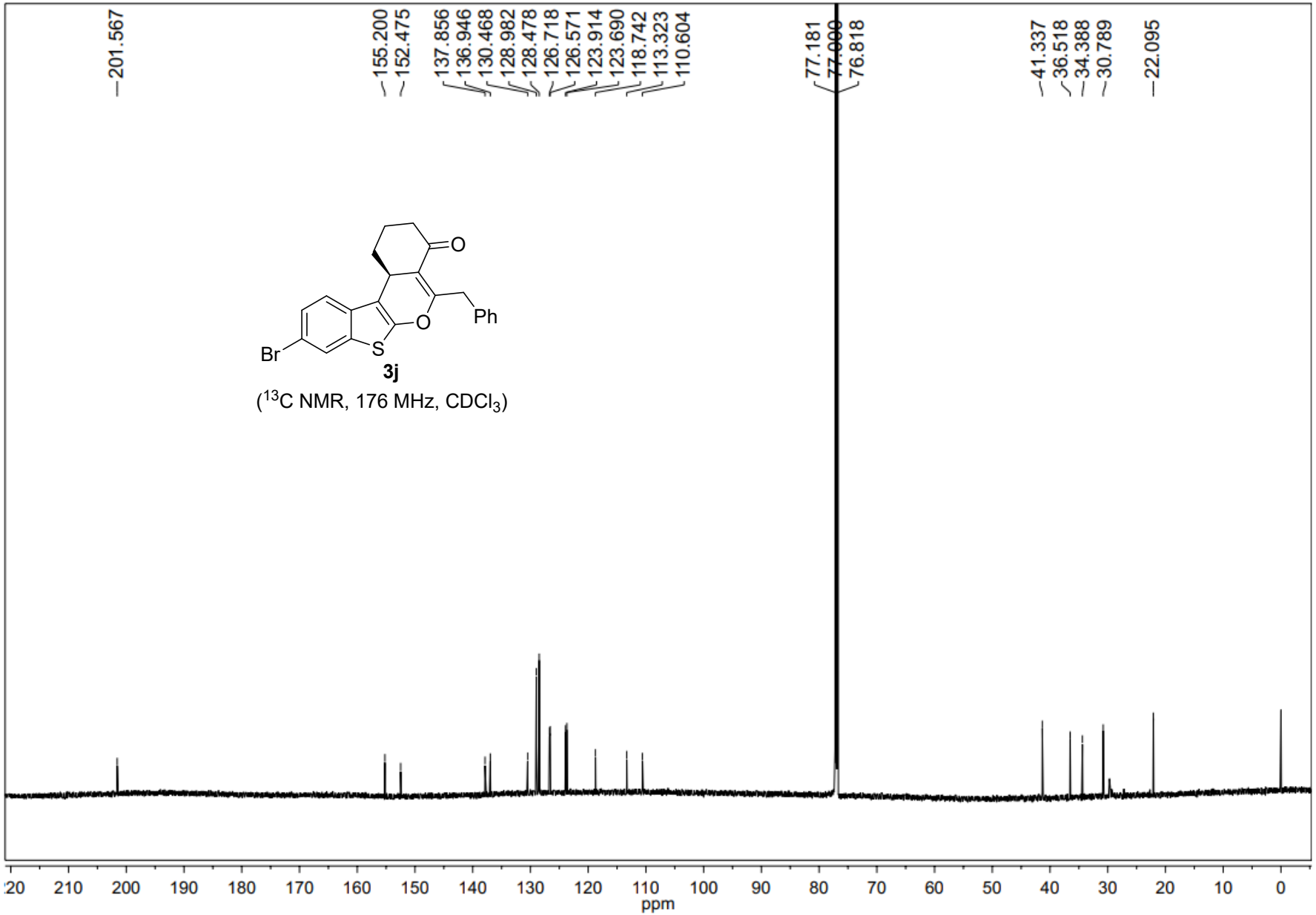
3i

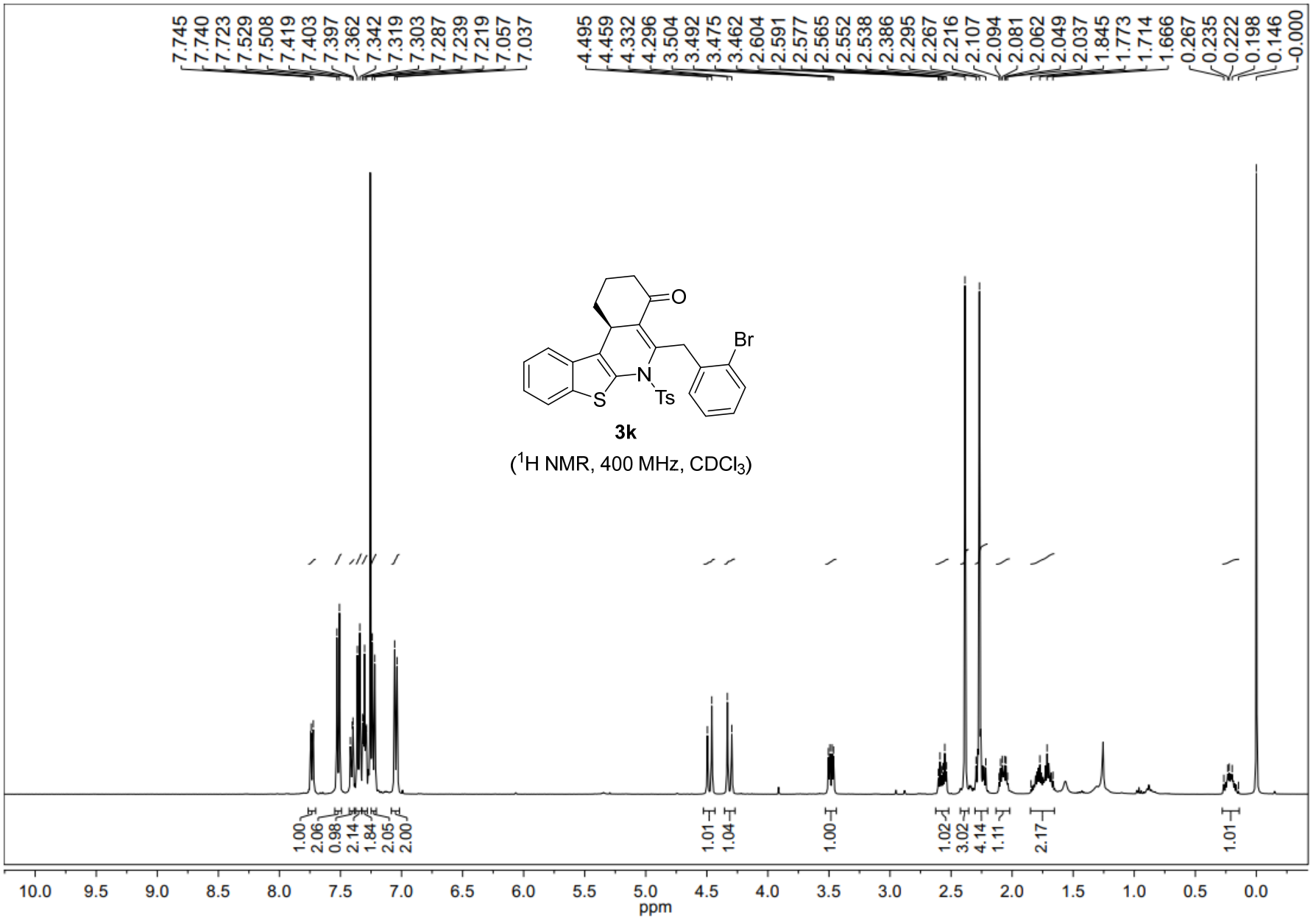
(^{13}C NMR, 176 MHz, $CDCl_3$)



3j

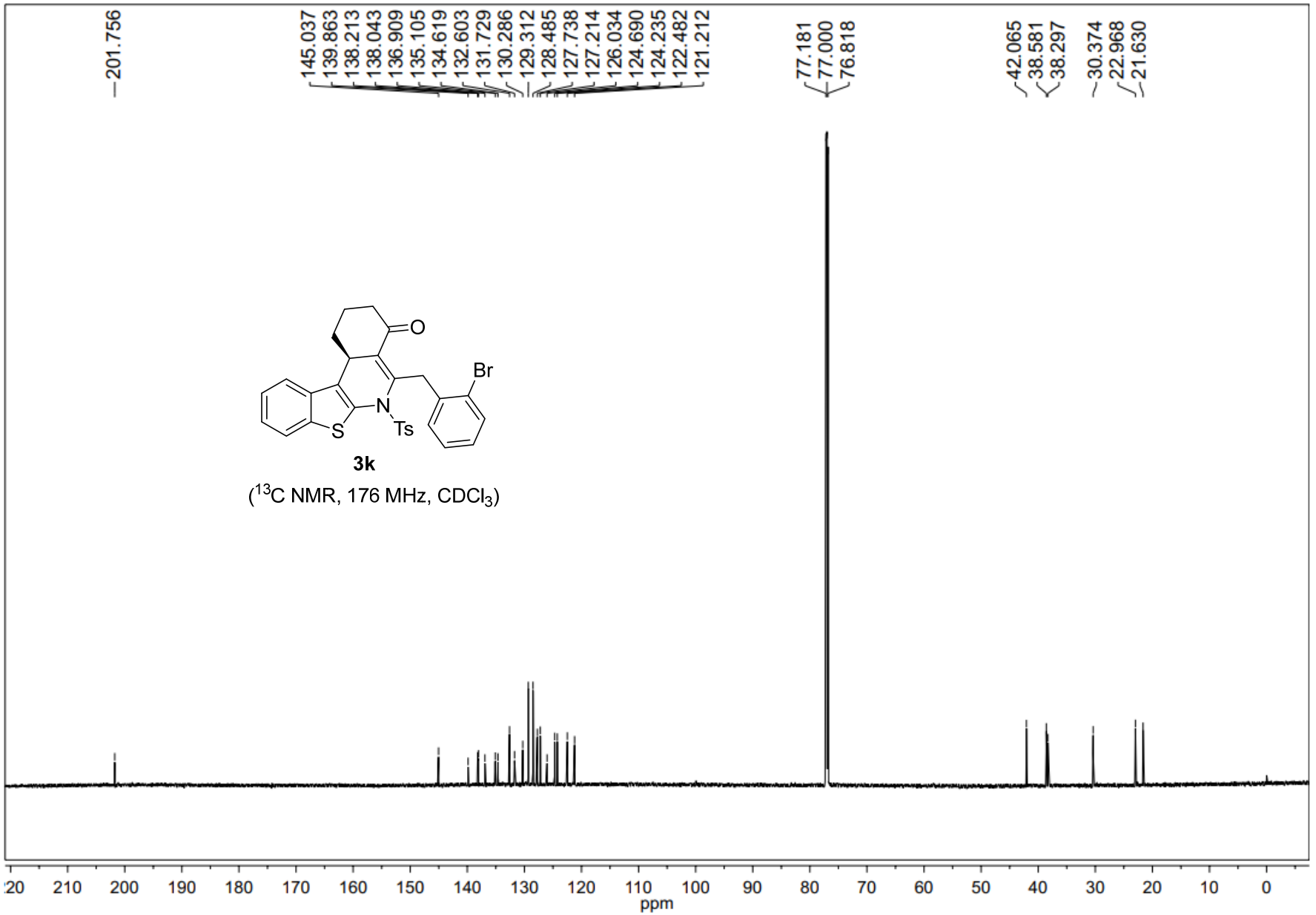
(^{1}H NMR, 400 MHz, $CDCl_3$)

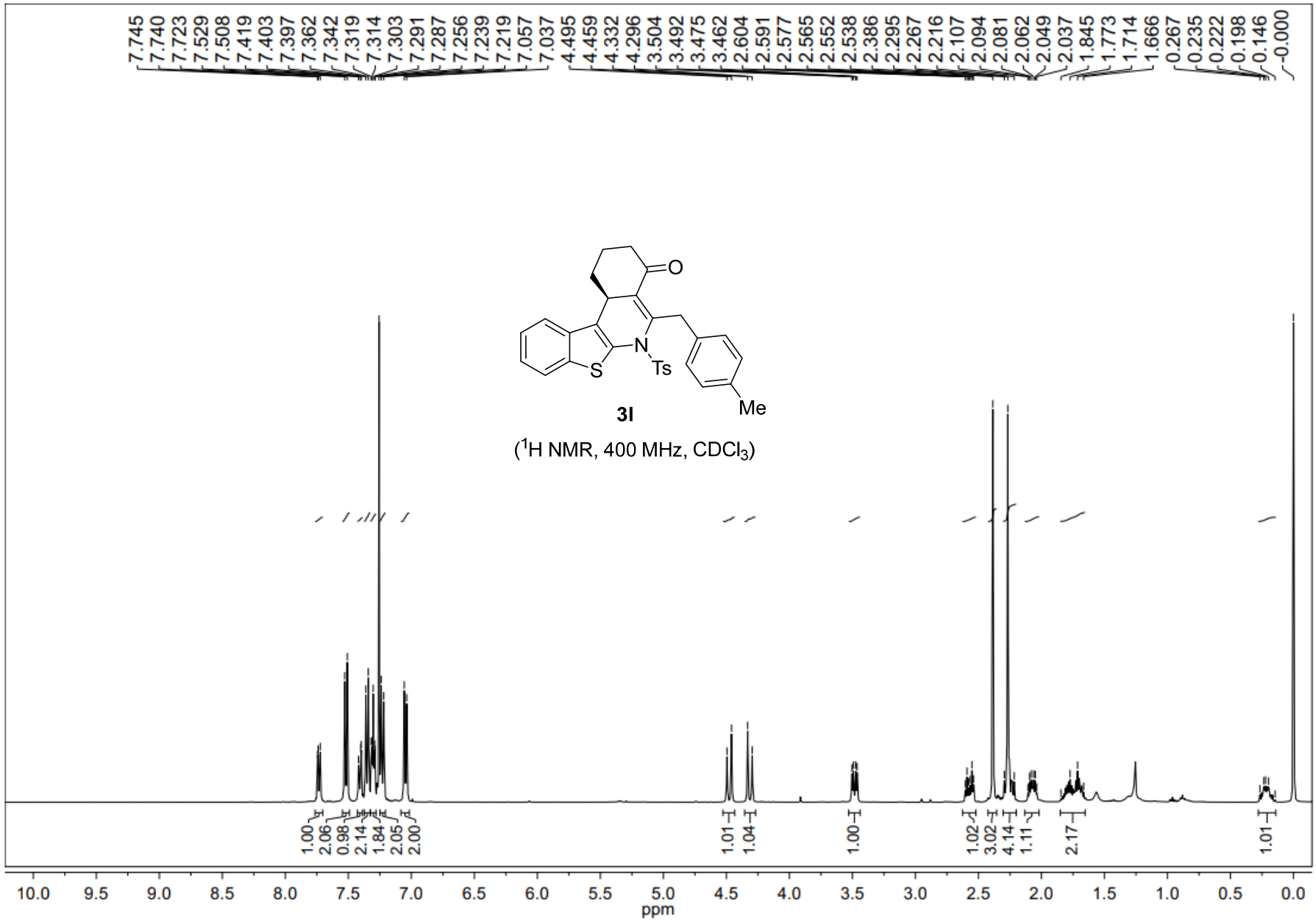

201.567
155.200
152.475
137.856
136.946
130.468
128.982
128.478
126.718
126.571
123.914
123.690
118.742
113.323
110.604
77.181
77.000
76.818
41.337
36.518
34.388
30.789
22.095
O
O
S
Br
Ph
3j
(^{13}C NMR, 176 MHz, $CDCl_3$)
ppm

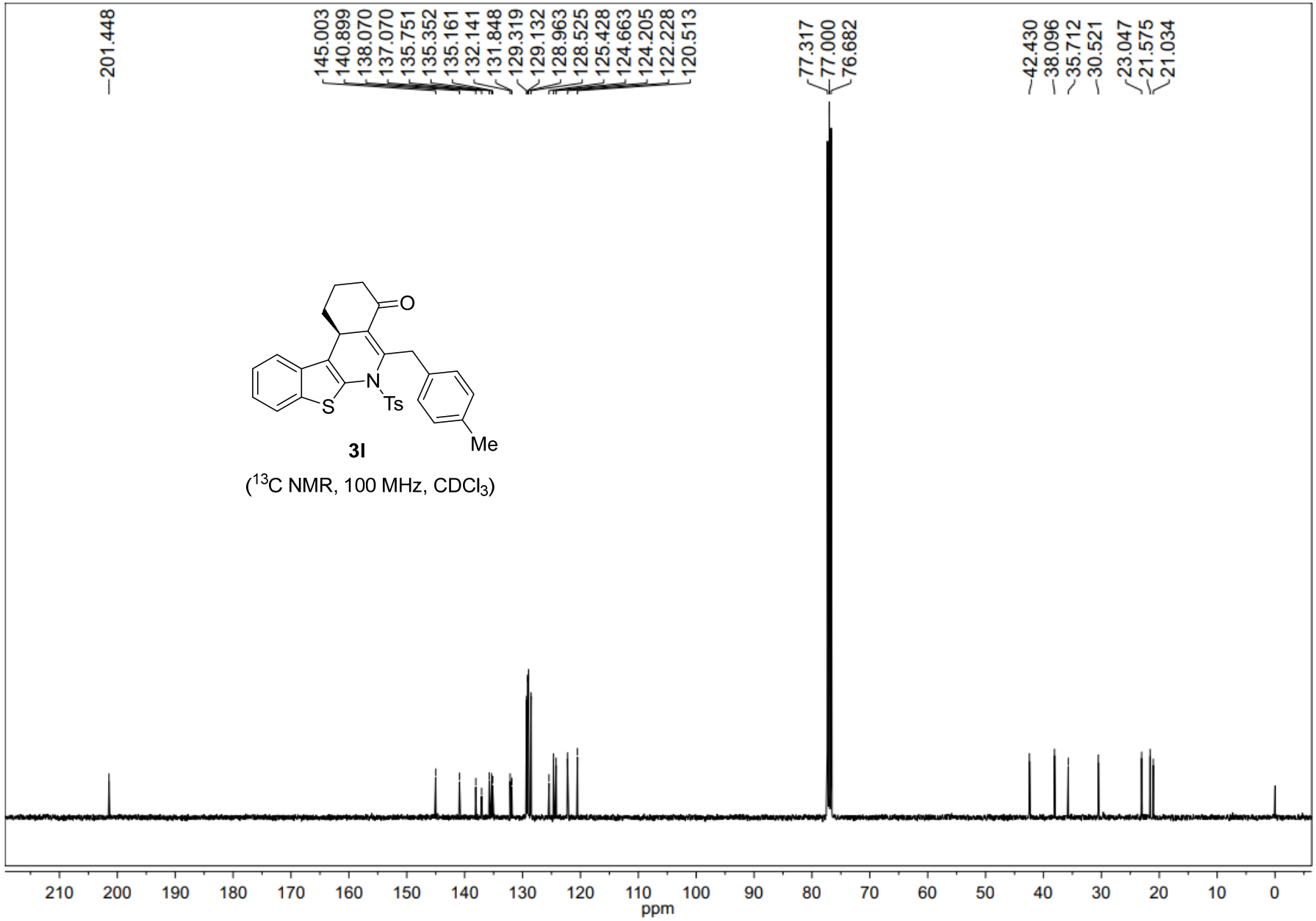


3k

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

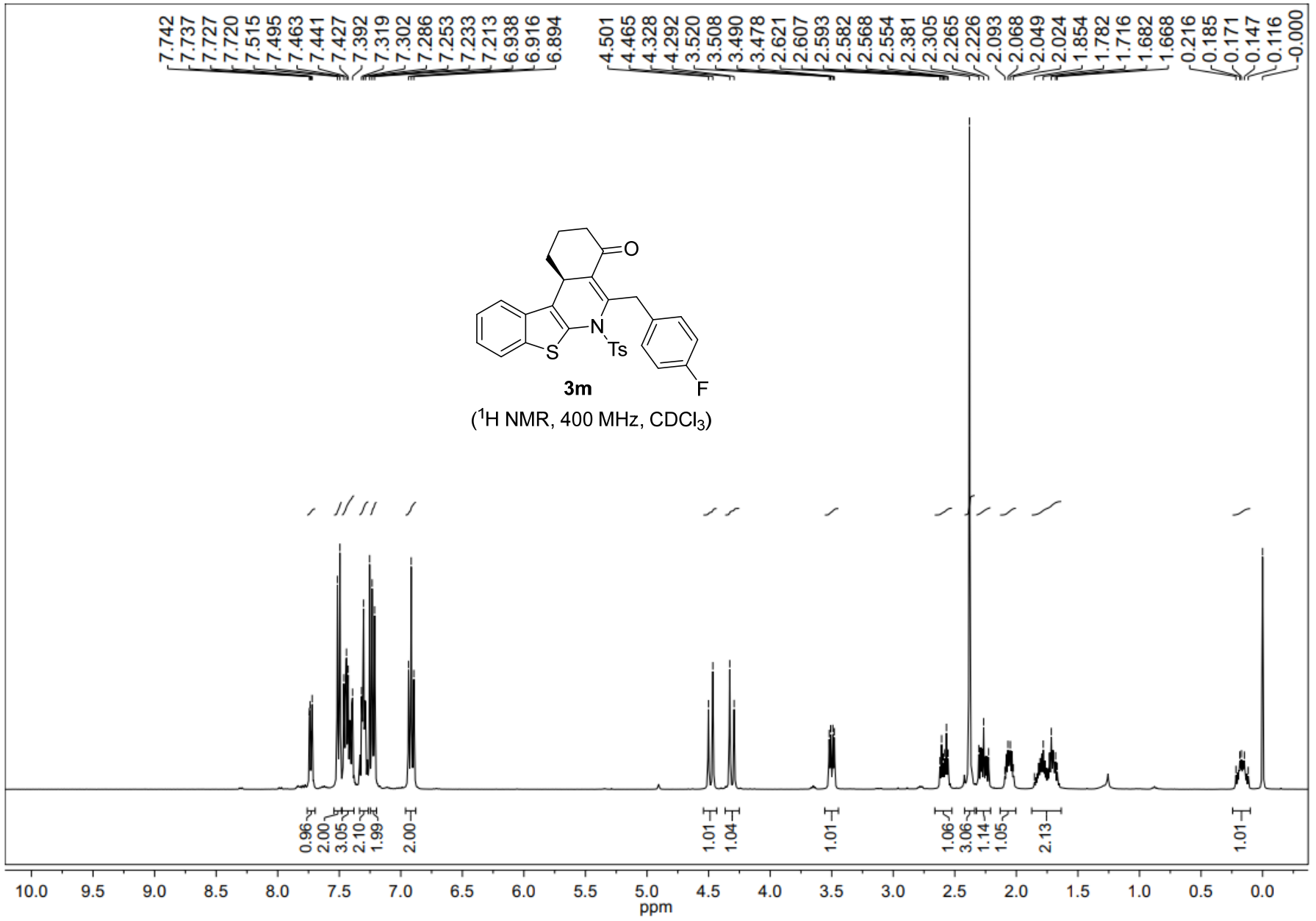

201.756
145.037
139.863
138.213
138.043
136.909
135.105
134.619
132.603
131.729
130.286
129.312
128.485
127.738
127.214
126.034
124.690
124.235
122.482
121.212
77.181
77.000
76.818
42.065
38.581
38.297
30.374
22.968
21.630
O
Br
N
Ts
S
3k
(^{13}C NMR, 176 MHz, $CDCl_3$)
ppm

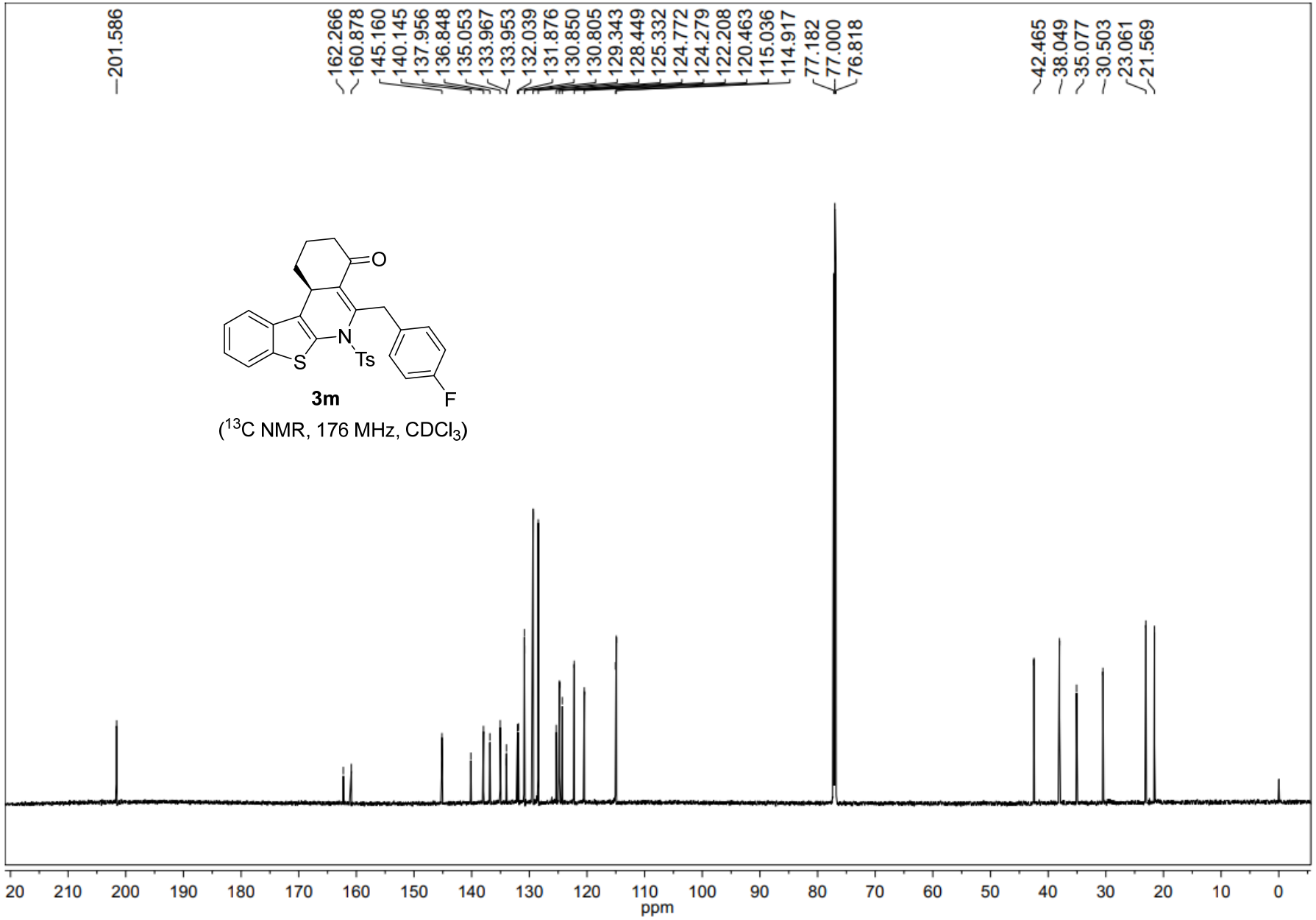

7.745
7.740
7.723
7.529
7.508
7.419
7.403
7.397
7.362
7.342
7.319
7.314
7.303
7.291
7.287
7.256
7.239
7.219
7.057
7.037
4.495
4.459
4.332
4.296
3.504
3.492
3.475
3.462
2.604
2.591
2.577
2.565
2.552
2.538
2.386
2.295
2.267
2.216
2.107
2.094
2.081
2.062
2.049
2.037
1.845
1.773
1.714
1.666
0.267
0.235
0.222
0.198
0.146
-0.000
O
N
Ts
S
Me
3l
(1H NMR, 400 MHz, CDCl3)
1.00
2.06
0.98
2.14
1.84
2.05
2.00
1.01
1.04
1.00
1.02
3.02
4.14
1.11
2.17
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

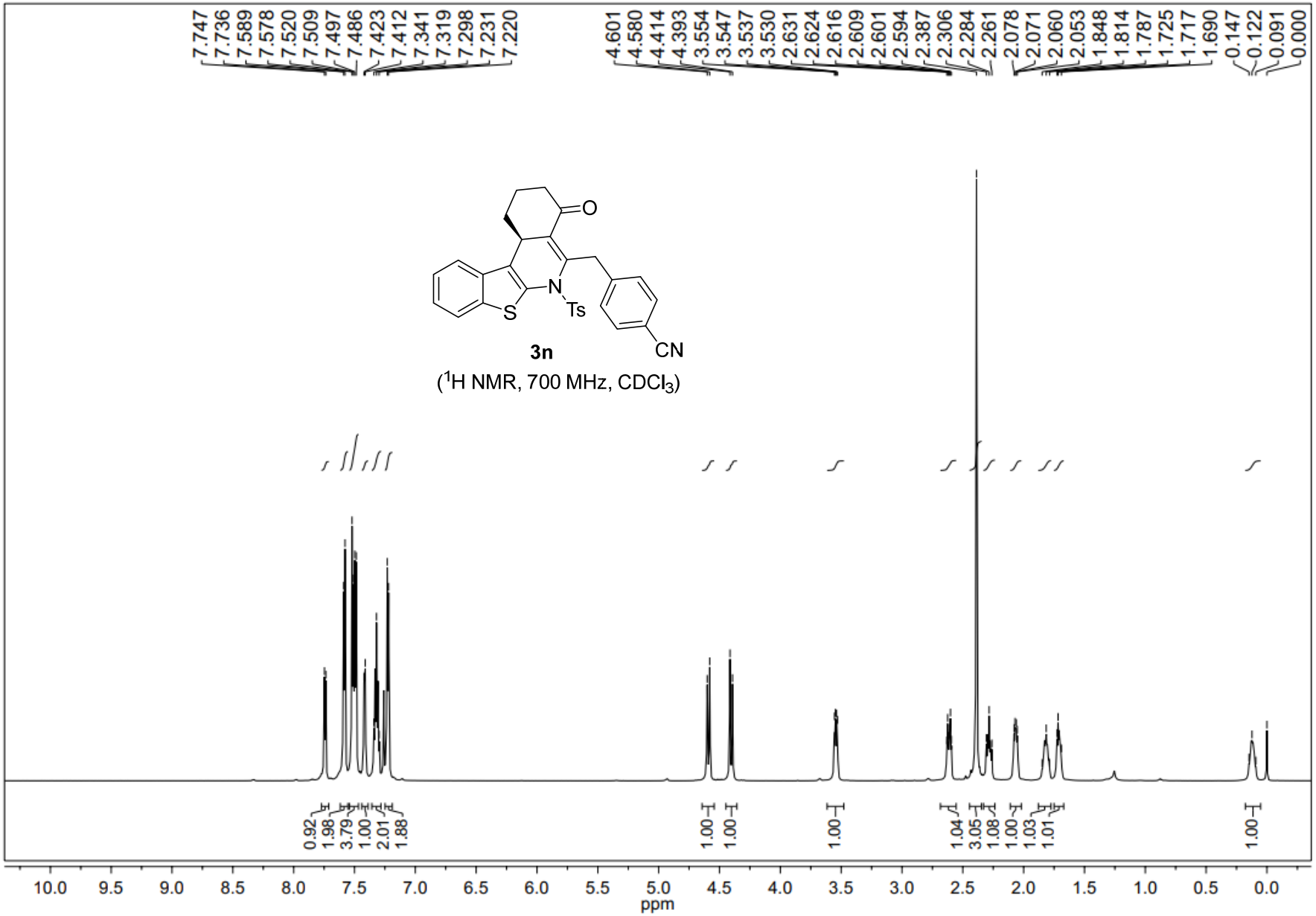


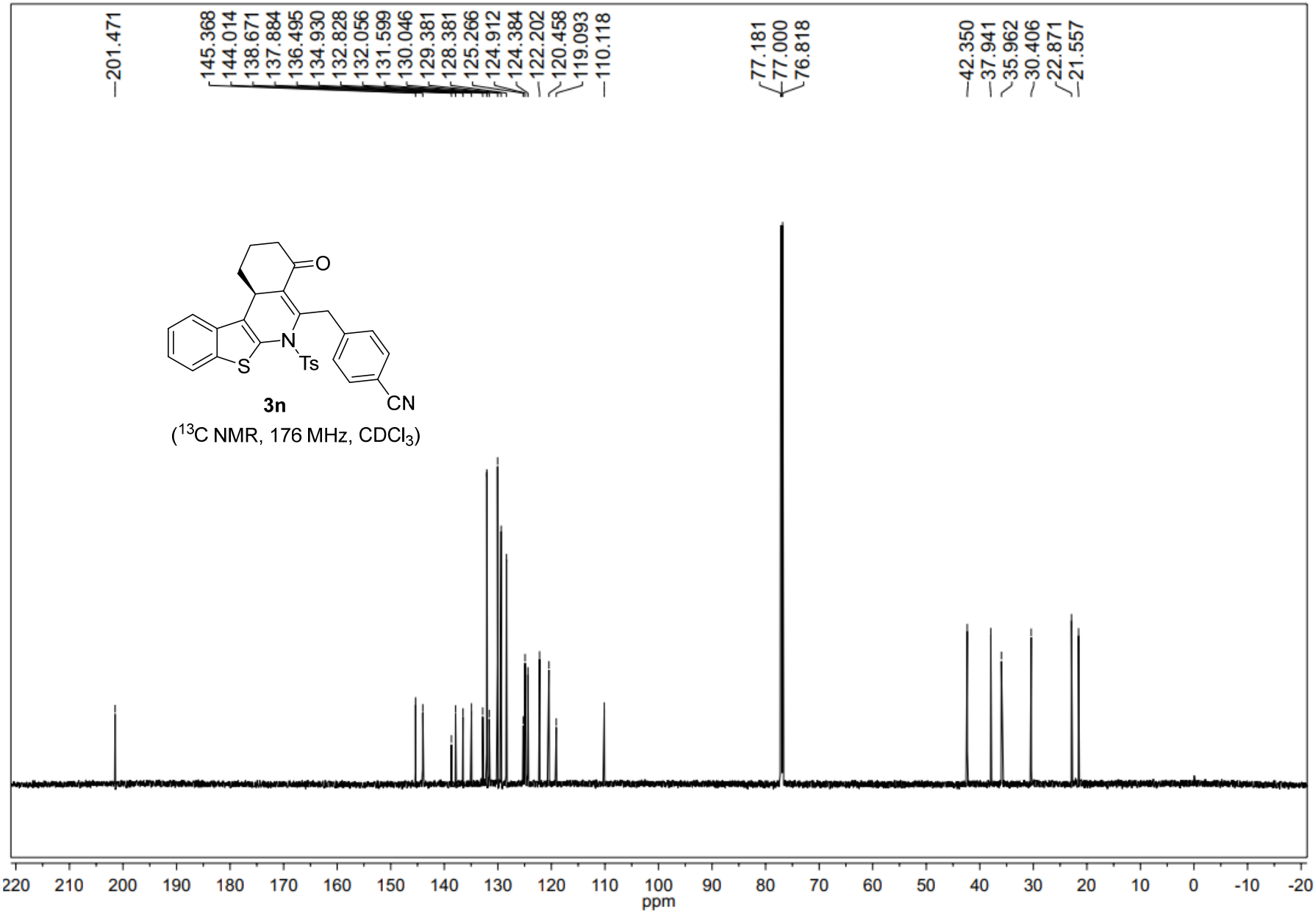
3l

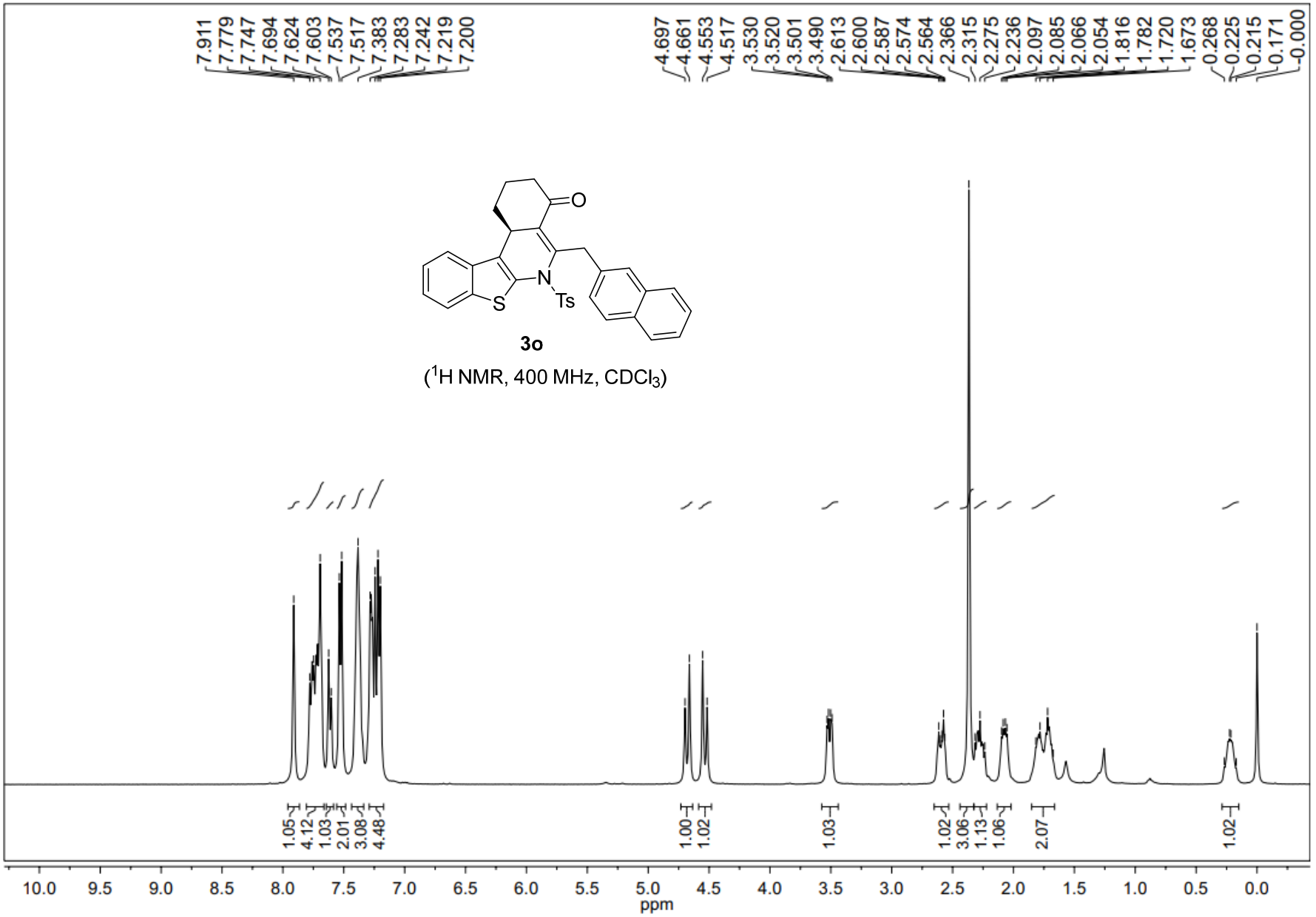
(^{13}C NMR, 100 MHz, $CDCl_3$)


7.742
7.737
7.727
7.720
7.515
7.495
7.463
7.441
7.427
7.392
7.319
7.302
7.286
7.253
7.233
7.213
6.938
6.916
6.894
4.501
4.465
4.328
4.292
3.520
3.508
3.490
3.478
2.621
2.607
2.593
2.582
2.568
2.554
2.381
2.305
2.265
2.226
2.093
2.068
2.049
2.024
1.854
1.782
1.716
1.682
1.668
0.216
0.185
0.171
0.147
0.116
-0.000
O
N
Ts
S
F
3m
(1H NMR, 400 MHz, CDCl3)
0.96
2.00
3.05
2.10
1.99
2.00
1.01
1.04
1.01
1.06
3.06
1.14
1.05
2.13
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


201.586
162.266
160.878
145.160
140.145
137.956
136.848
135.053
133.967
133.953
132.039
131.876
130.850
130.805
129.343
128.449
125.332
124.772
124.279
122.208
120.463
115.036
114.917
77.182
77.000
76.818
42.465
38.049
35.077
30.503
23.061
21.569
O
N
Ts
S
F
3m
(13C NMR, 176 MHz, CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

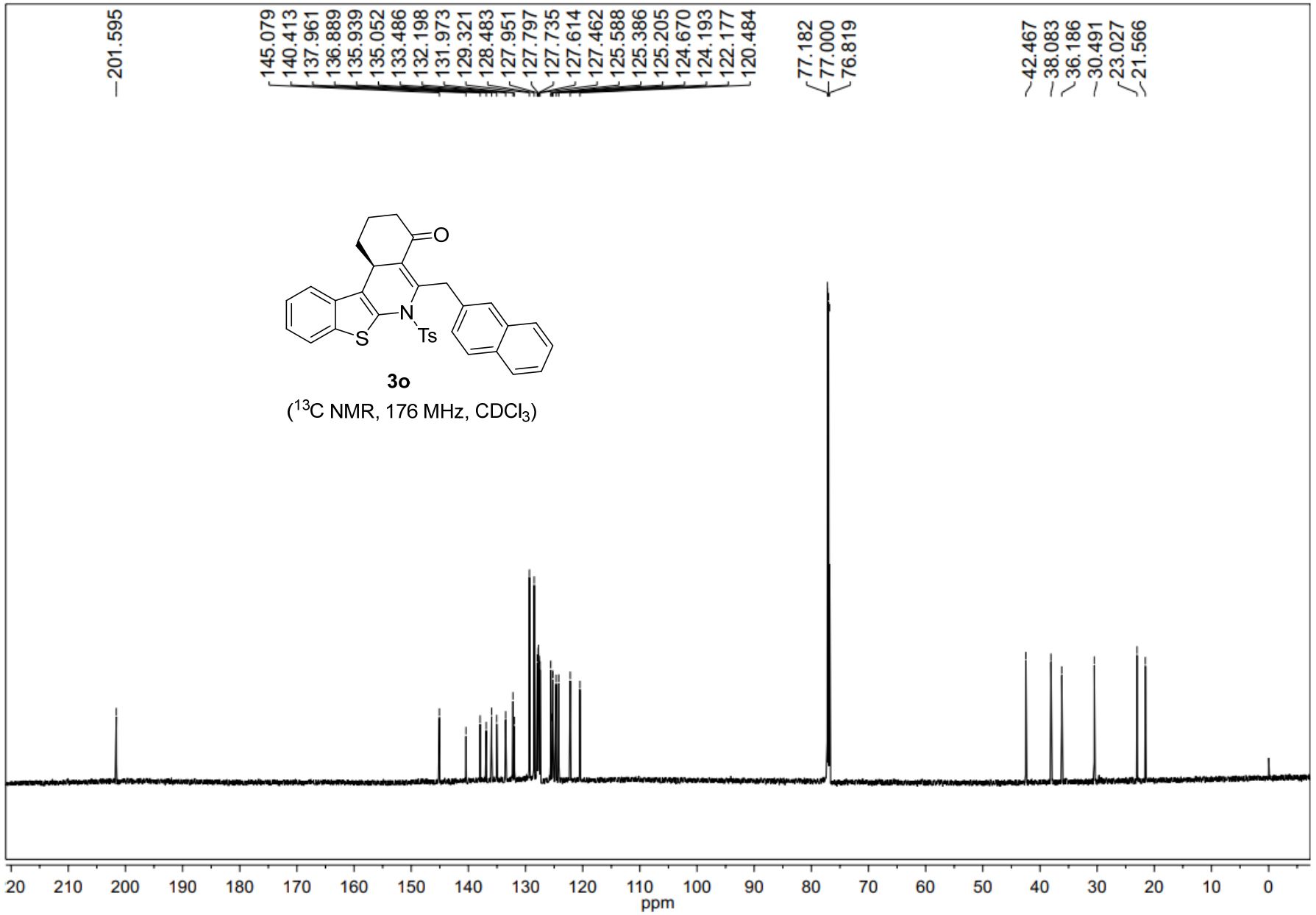

7.747
7.736
7.589
7.578
7.520
7.509
7.497
7.486
7.423
7.412
7.341
7.319
7.298
7.231
7.220
4.601
4.580
4.414
4.393
3.554
3.547
3.537
3.530
2.631
2.624
2.616
2.609
2.601
2.594
2.387
2.306
2.284
2.261
2.078
2.071
2.060
2.053
1.848
1.814
1.787
1.725
1.717
1.690
0.147
0.122
0.091
0.000
O
N
Ts
S
CN
3n
(1H NMR, 700 MHz, CDCl3)
0.92
1.98
3.79
1.00
2.01
1.88
1.00
1.00
1.00
1.04
3.05
1.08
1.00
1.03
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

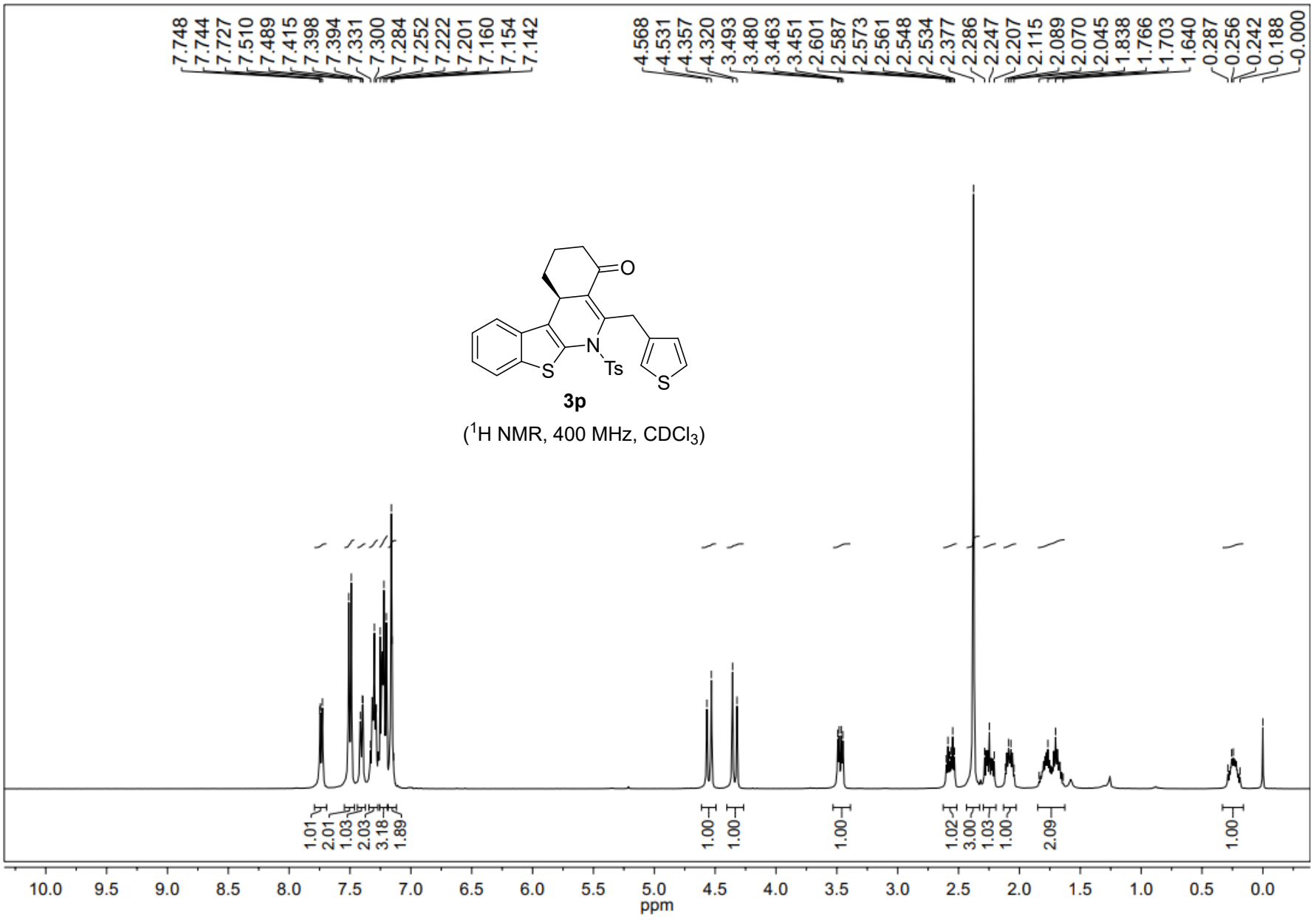

201.471
145.368
144.014
138.671
137.884
136.495
134.930
132.828
132.056
131.599
130.046
129.381
128.381
125.266
124.912
124.384
122.202
120.458
119.093
110.118
77.181
77.000
76.818
42.350
37.941
35.962
30.406
22.871
21.557
O
N
Ts
S
CN
3n
(^{13}C NMR, 176 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm



3o

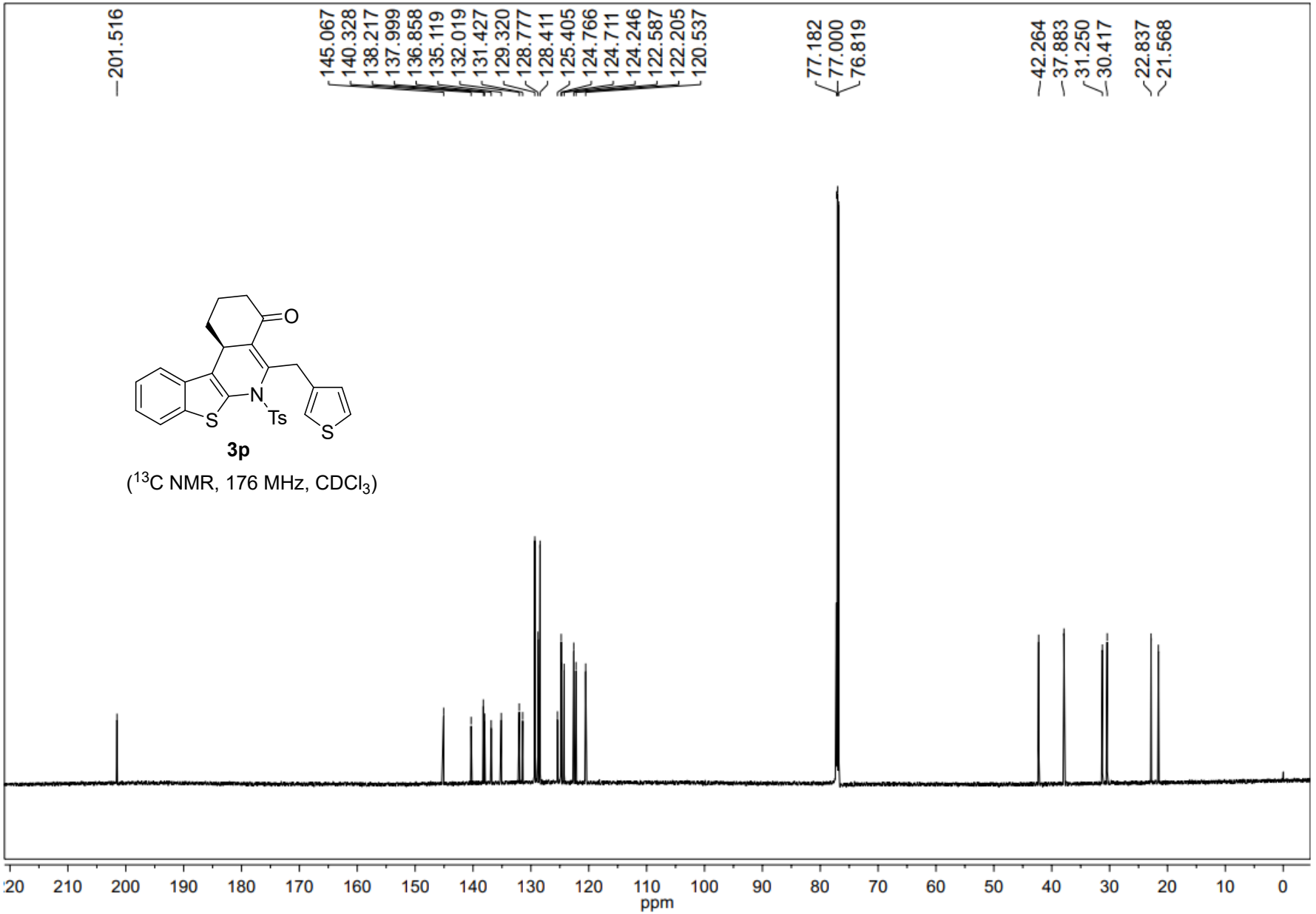
(^{1}H NMR, 400 MHz, $CDCl_3$)


201.595
145.079
140.413
137.961
136.889
135.939
135.052
133.486
132.198
131.973
129.321
128.483
127.951
127.797
127.735
127.614
127.462
125.588
125.386
125.205
124.670
124.193
122.177
120.484
77.182
77.000
76.819
42.467
38.083
36.186
30.491
23.027
21.566
O
N
Ts
S
3o
(^{13}C NMR, 176 MHz, $CDCl_3$)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



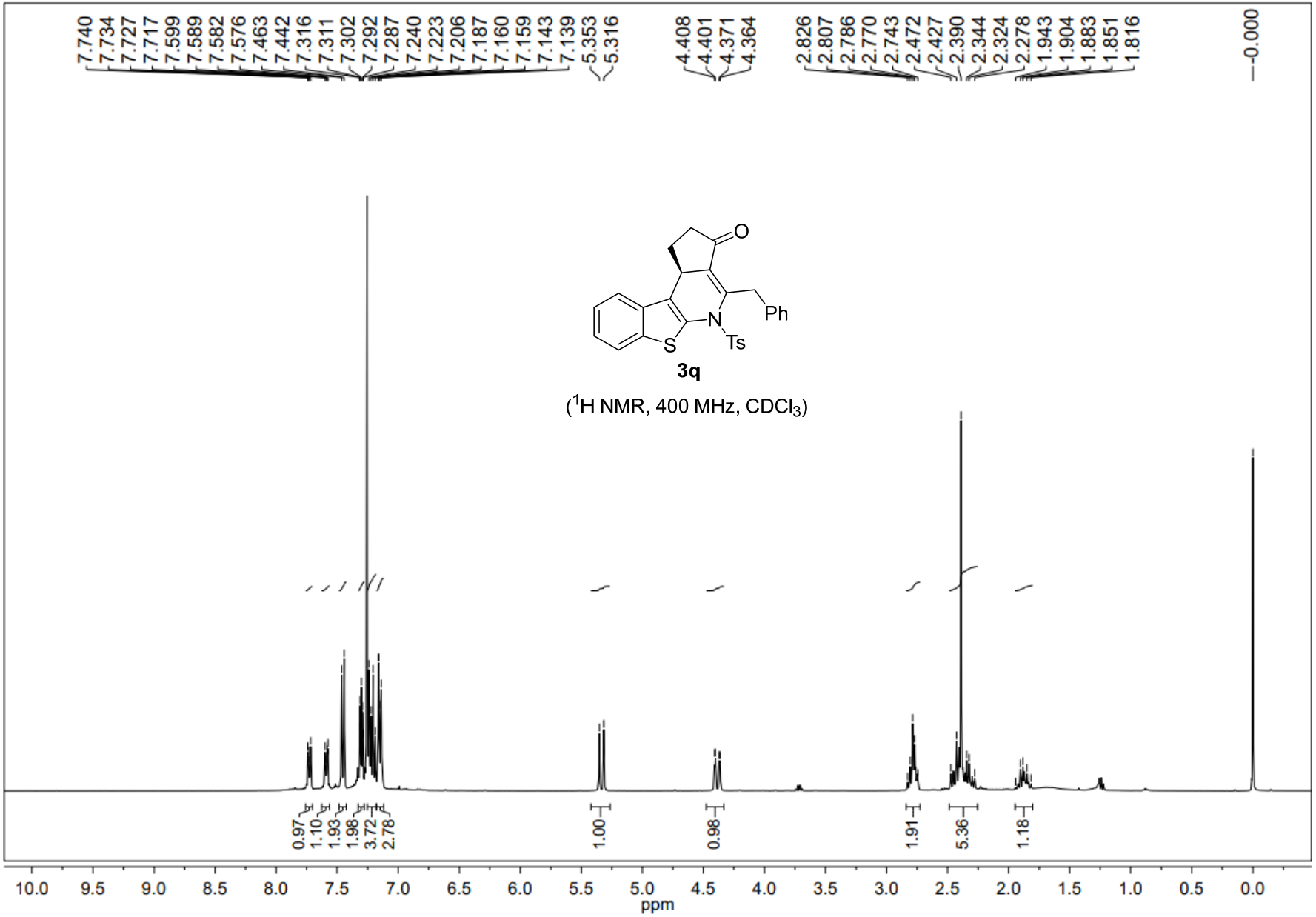
3p

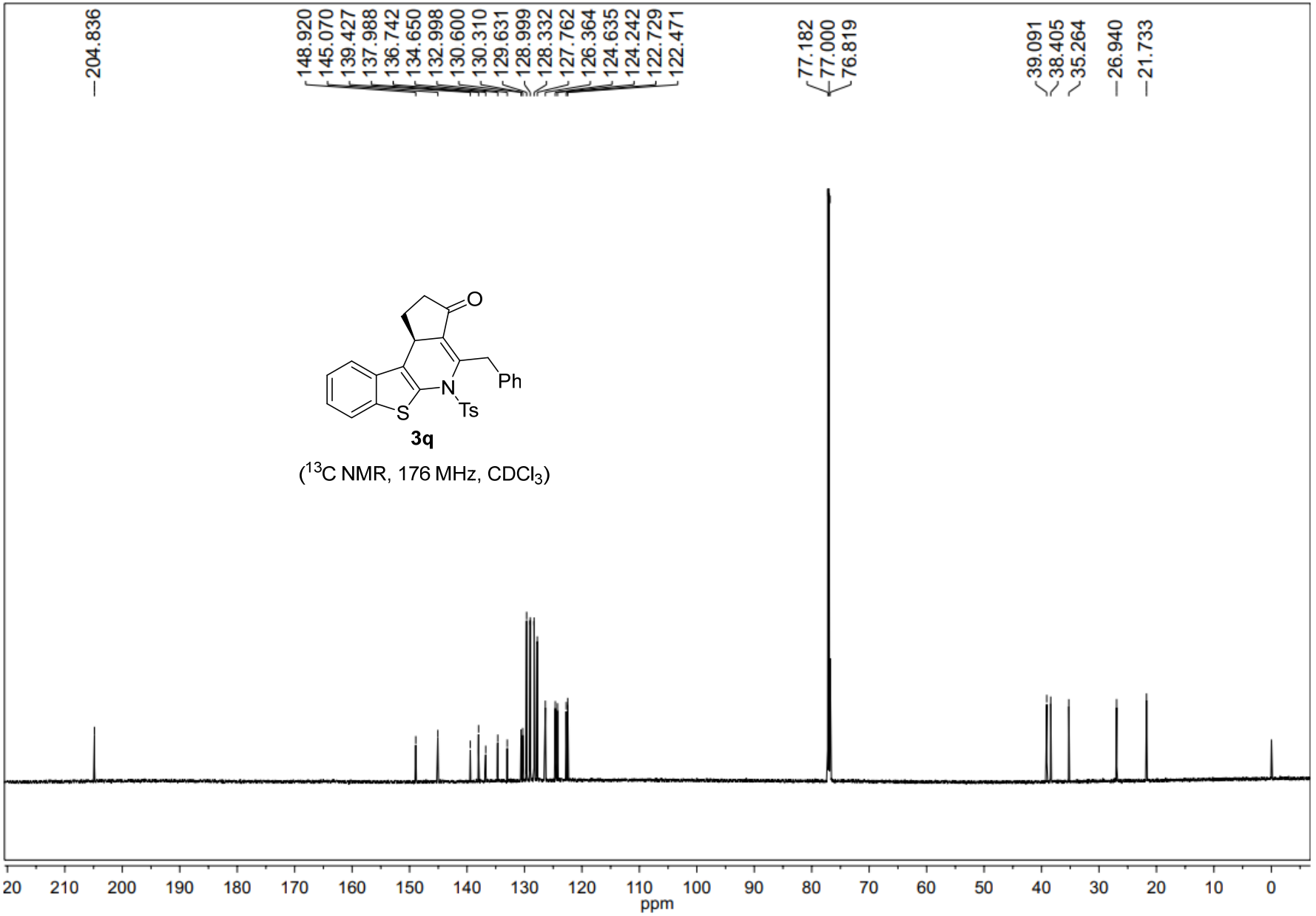
(^{1}H NMR, 400 MHz, $CDCl_3$)



3p

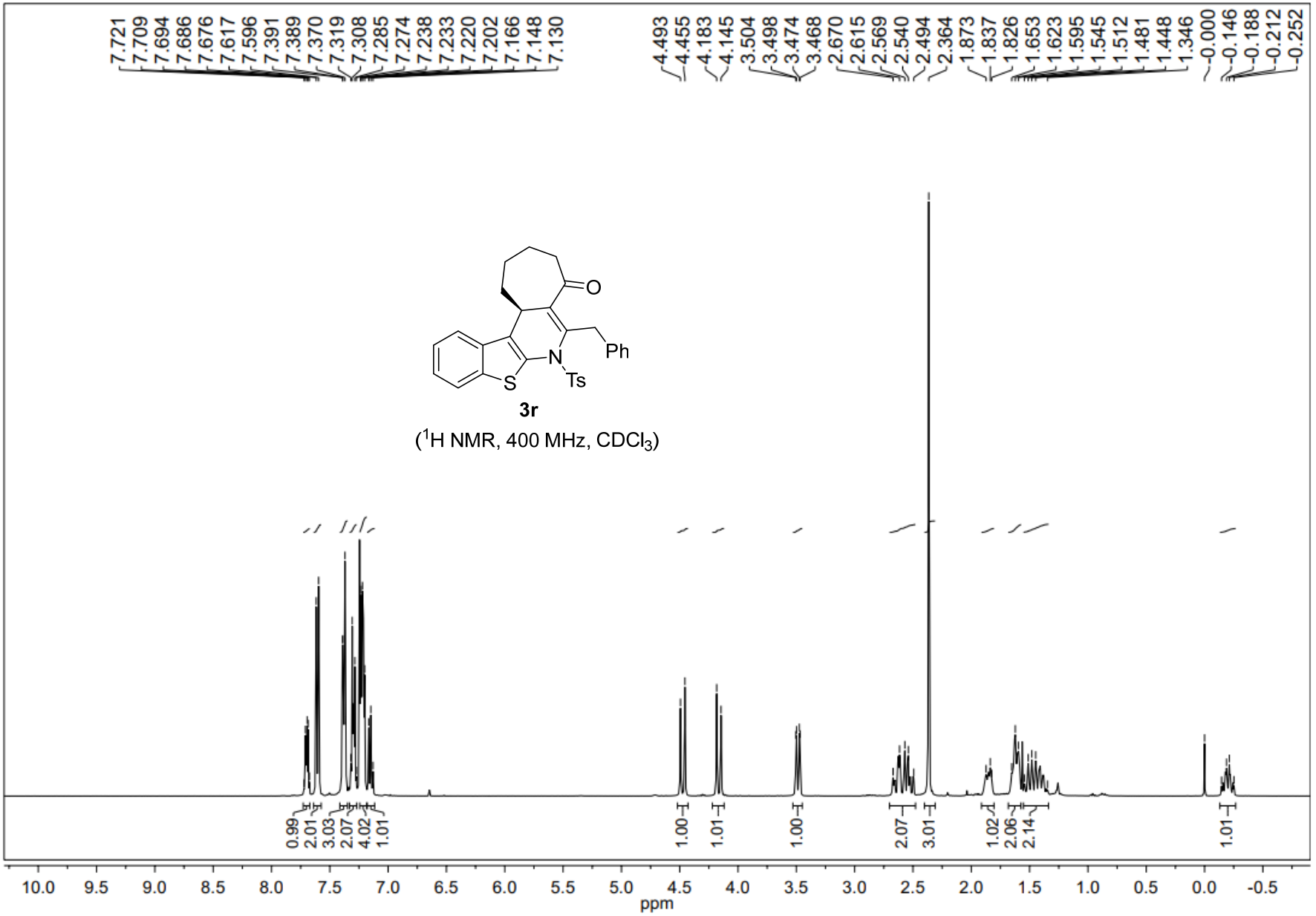
(^{13}C NMR, 176 MHz, $CDCl_3$)


7.740
7.734
7.727
7.717
7.599
7.589
7.582
7.576
7.463
7.442
7.316
7.311
7.302
7.292
7.287
7.240
7.223
7.206
7.187
7.160
7.159
7.143
7.139
5.353
5.316
4.408
4.401
4.371
4.364
2.826
2.807
2.786
2.770
2.743
2.472
2.427
2.390
2.344
2.324
2.278
1.943
1.904
1.883
1.851
1.816
0.000
O
Ph
N
Ts
S
3q
(1H NMR, 400 MHz, CDCl3)
0.97
1.10
1.93
1.98
3.72
2.78
1.00
0.98
1.91
5.36
1.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



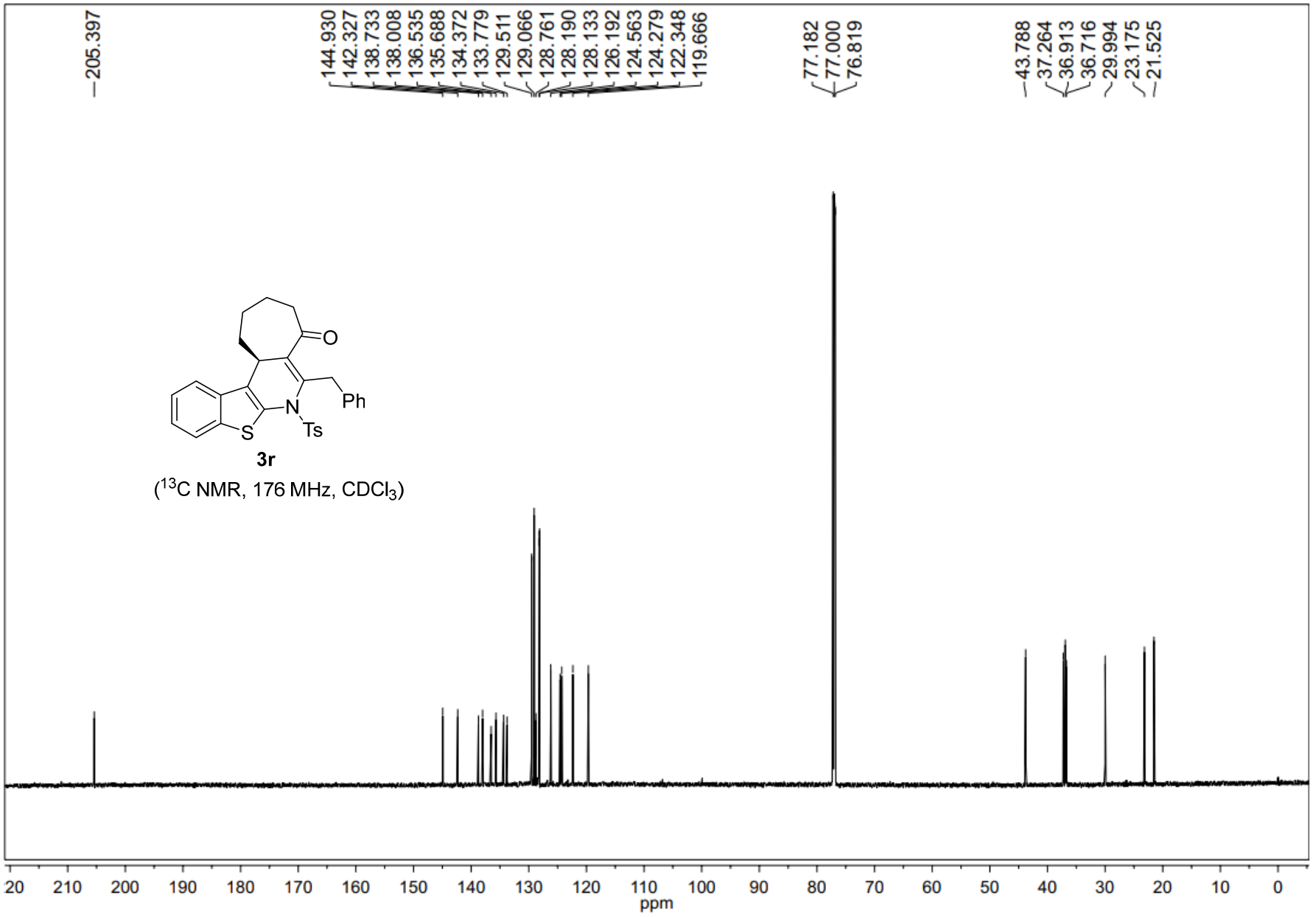
3q

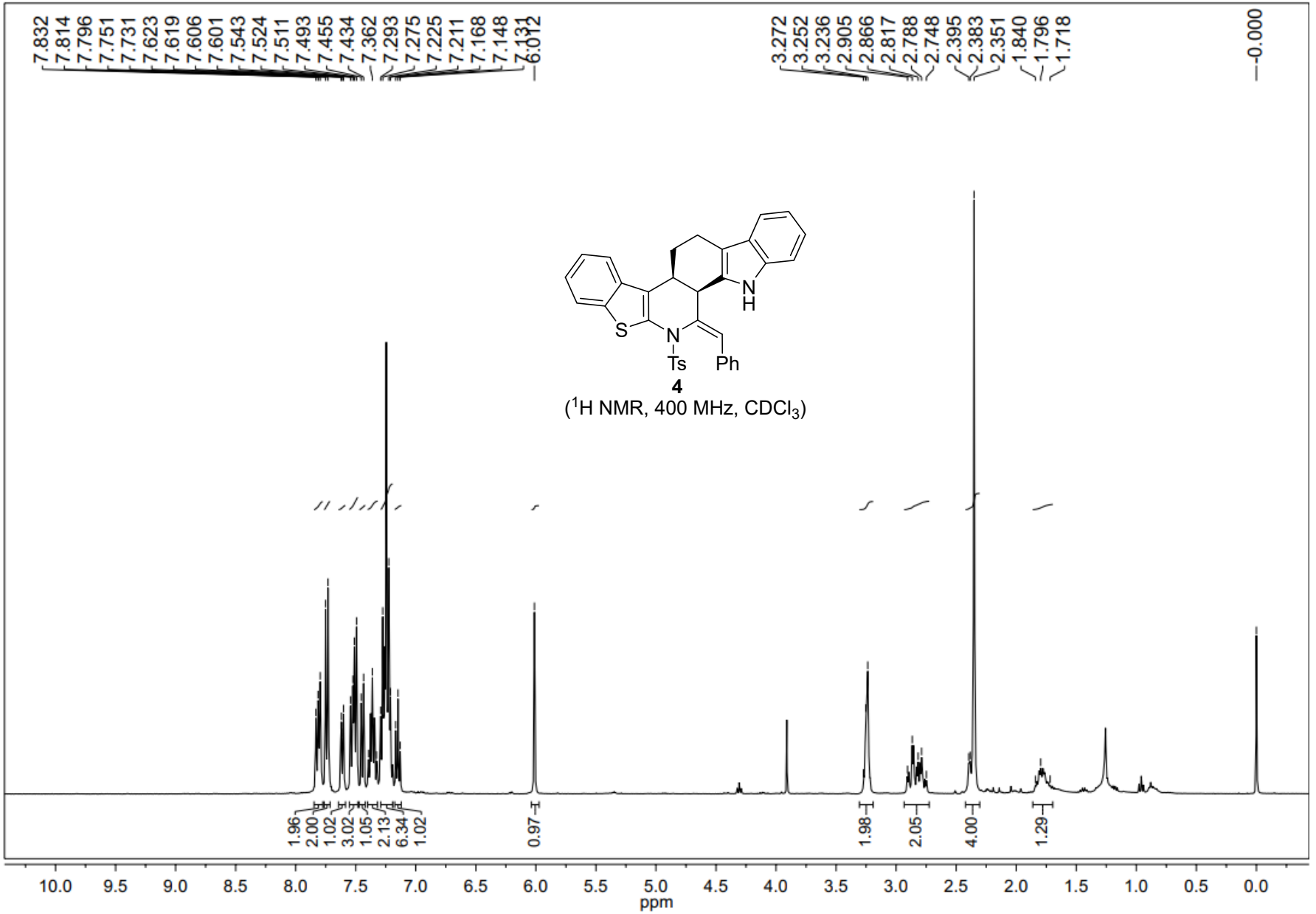
(^{13}C NMR, 176 MHz, $CDCl_3$)



3r

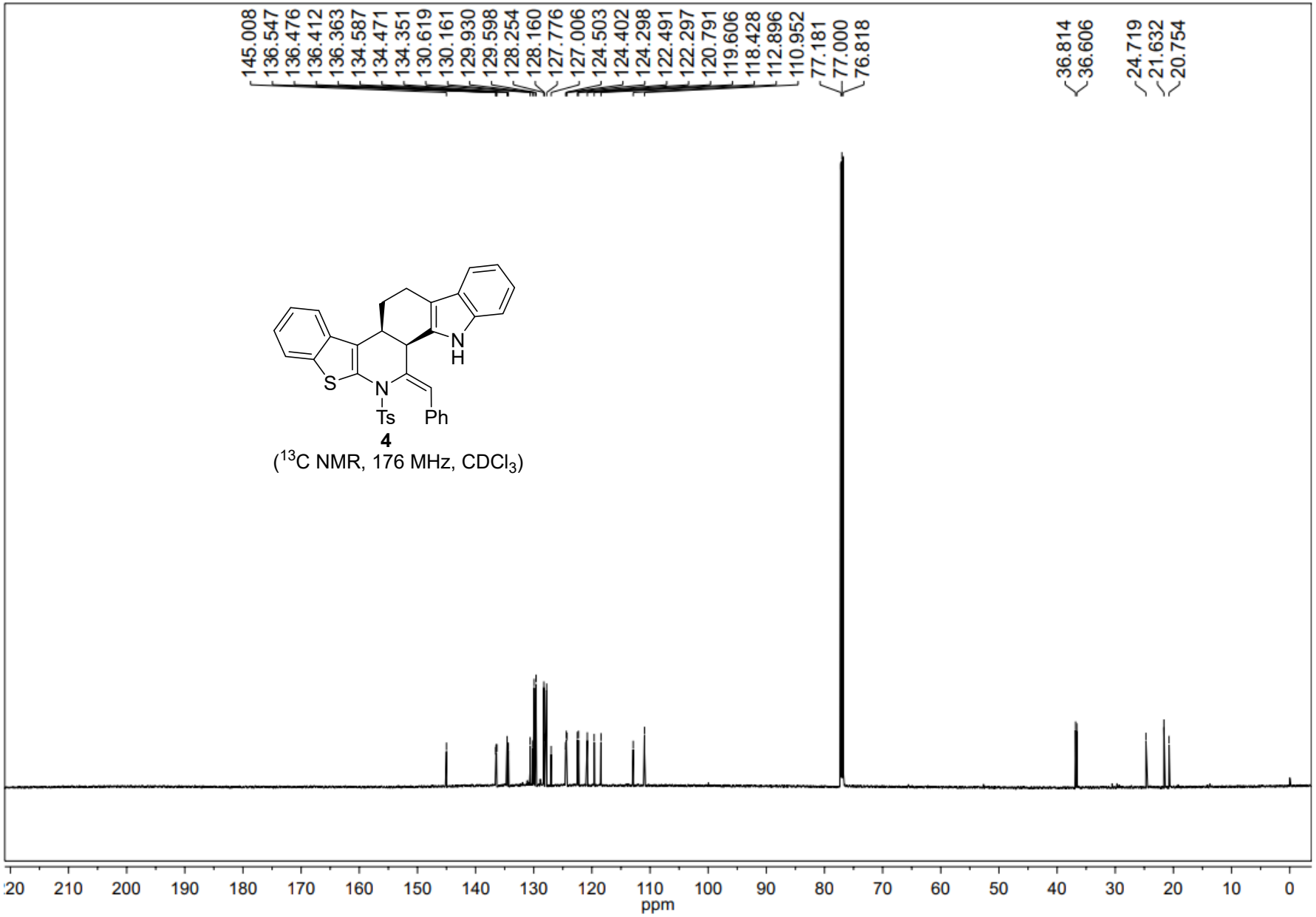
(^{1}H NMR, 400 MHz, $CDCl_3$)


205.397
144.930
142.327
138.733
138.008
136.535
135.688
134.372
133.779
129.511
129.066
128.761
128.190
128.133
126.192
124.563
124.279
122.348
119.666
77.182
77.000
76.819
43.788
37.264
36.913
36.716
29.994
23.175
21.525
O
Ph
N
Ts
S
3r
(^{13}C NMR, 176 MHz, $CDCl_3$)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



4

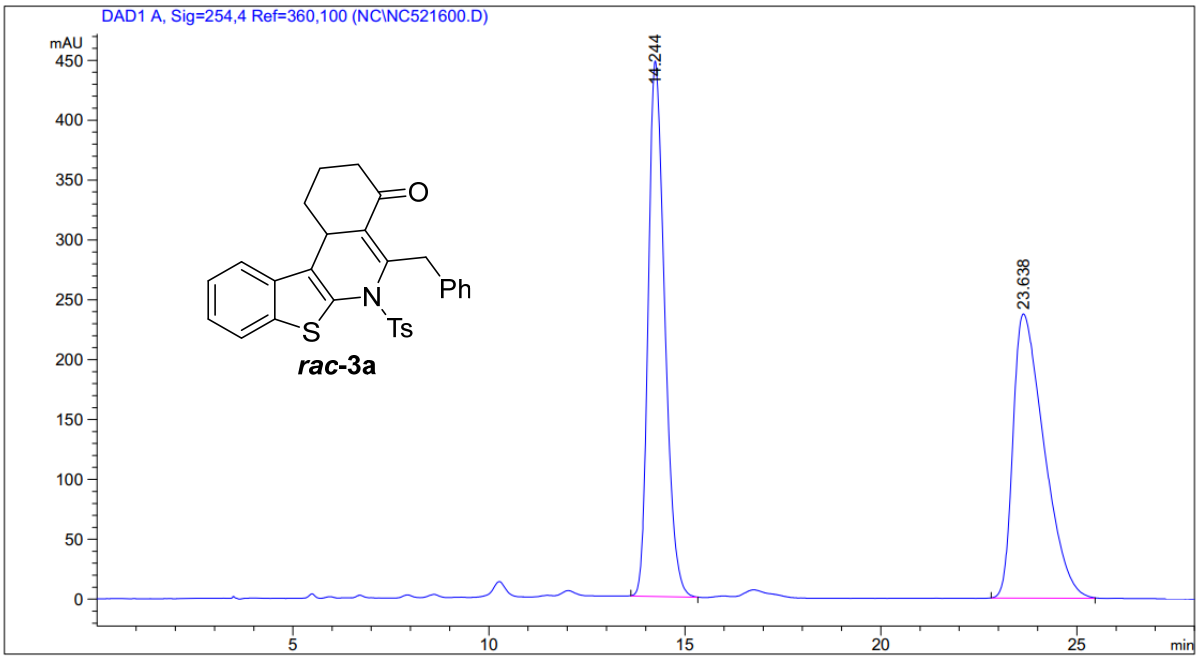
(^{1}H NMR, 400 MHz, $CDCl_3$)



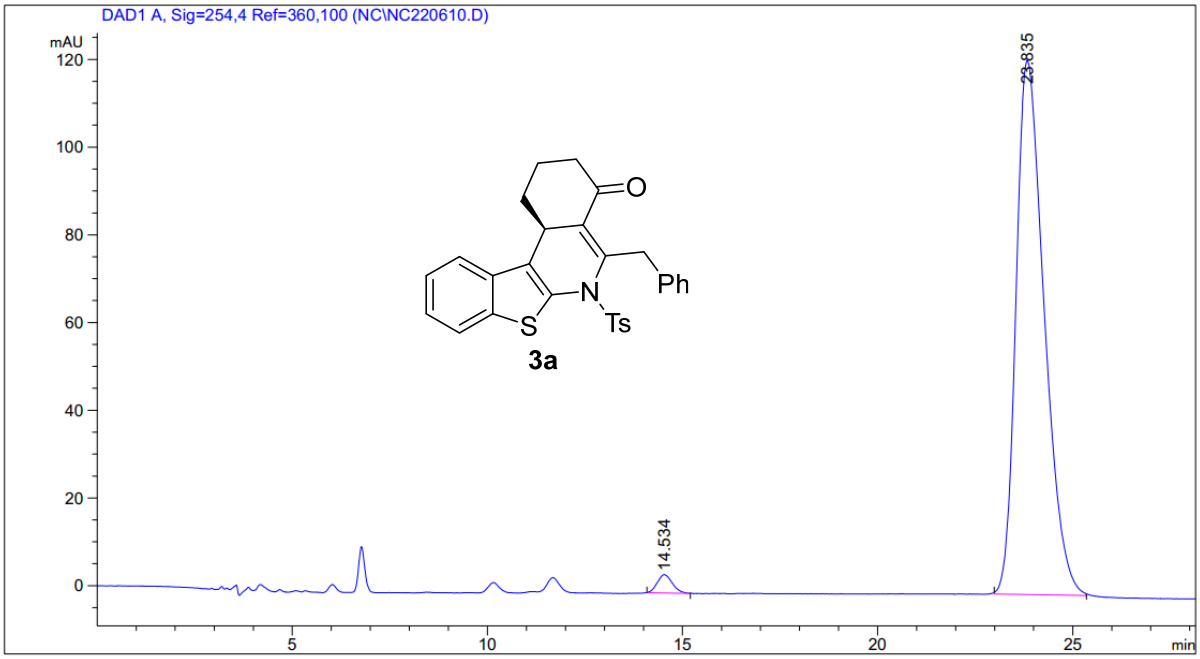
4

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

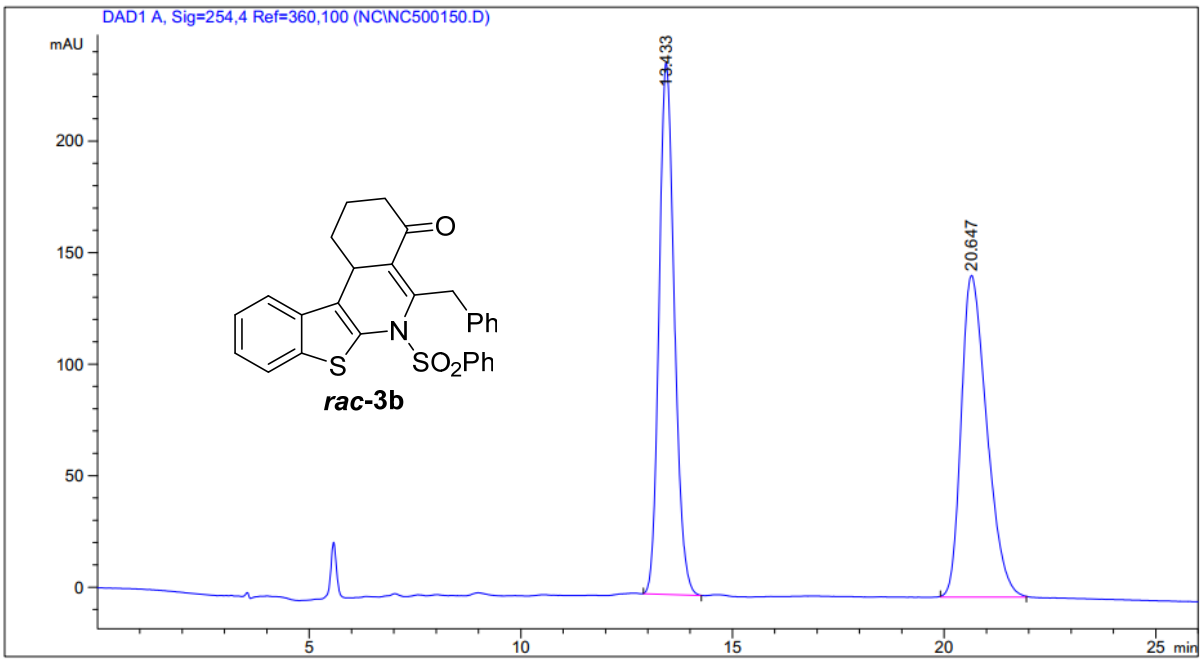
7. Copies of HPLC chromatograms of new products



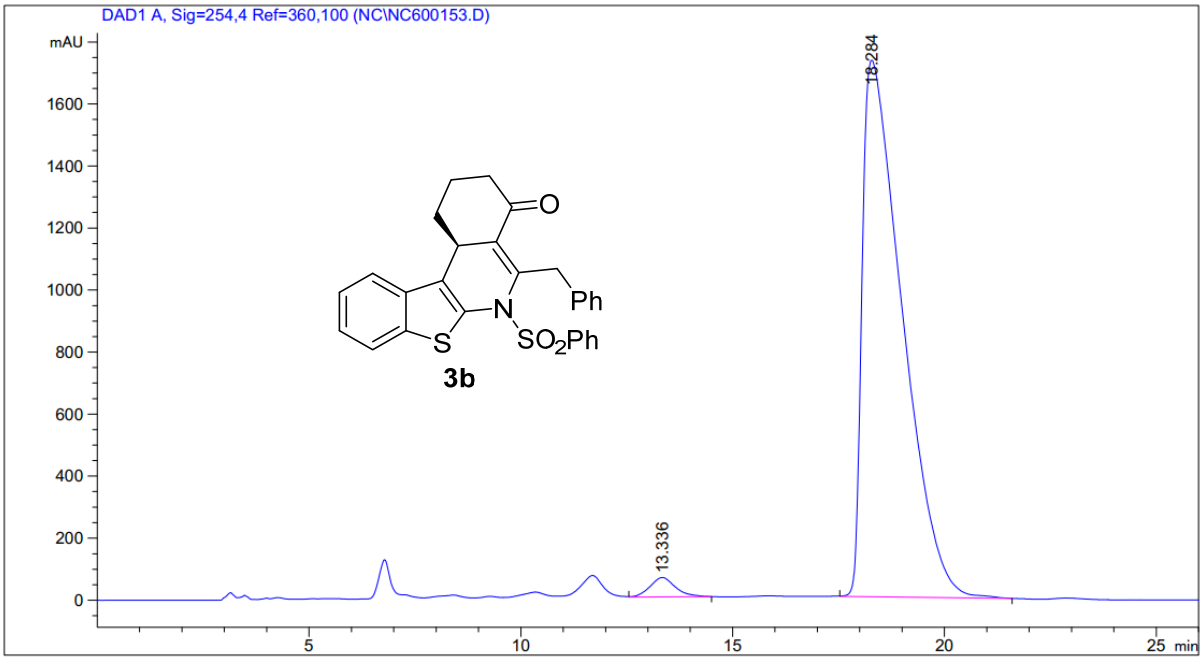
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.244	BB	0.4510	1.30728e4	447.27170	50.0553
2	23.638	BB	0.8248	1.30439e4	237.46489	49.9447



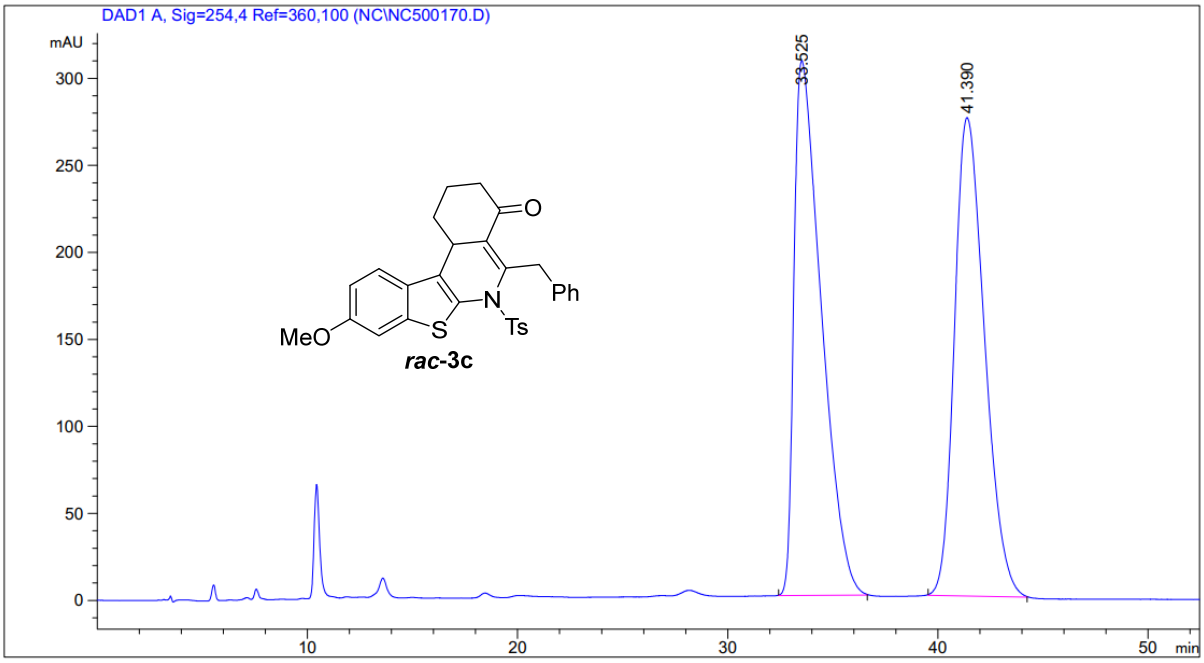
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.534	BB	0.4009	112.92110	4.18356	1.8202
2	23.835	BB	0.7571	6090.70557	121.85439	98.1798



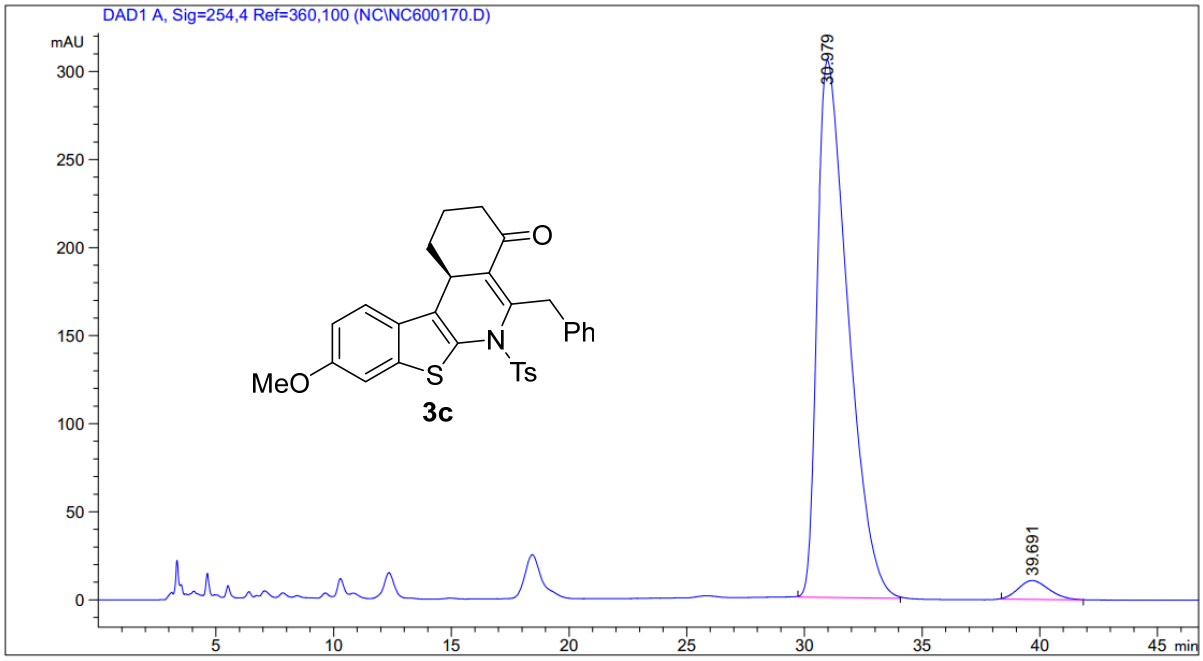
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.434	VV	0.3912	6057.61230	239.40637	49.8980
2	20.648	BB	0.6472	6082.38232	144.45197	50.1020



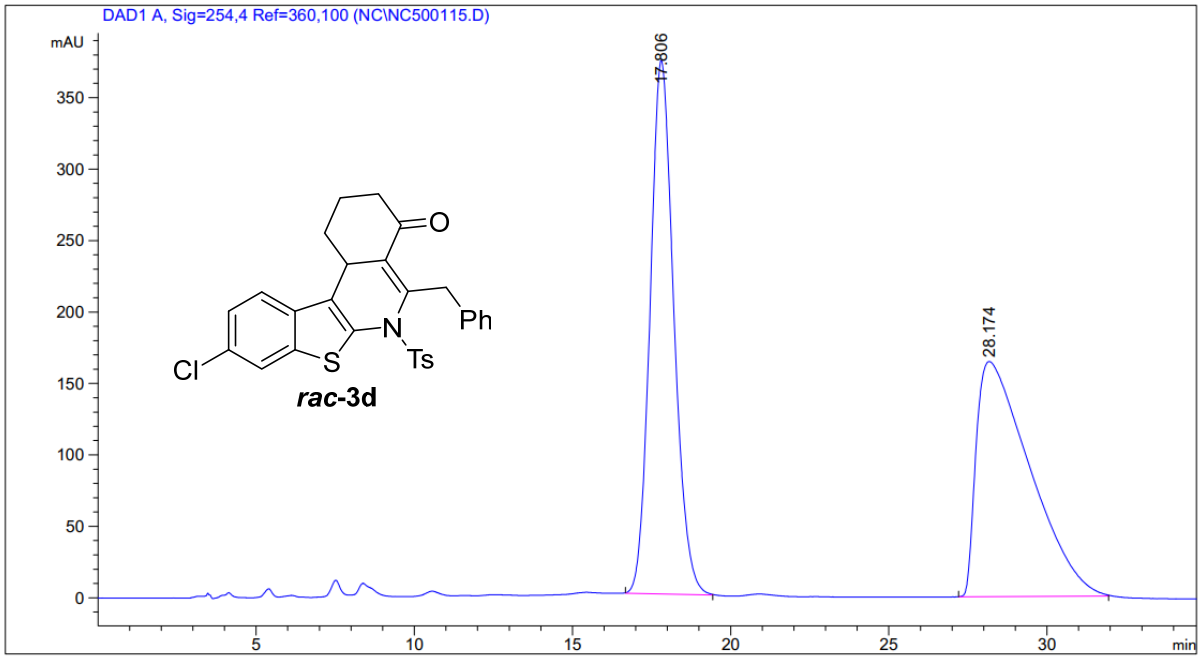
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.336	VB	0.6290	2681.40552	63.19329	2.3163
2	18.284	BB	0.9090	1.13082e5	1729.18054	97.6837



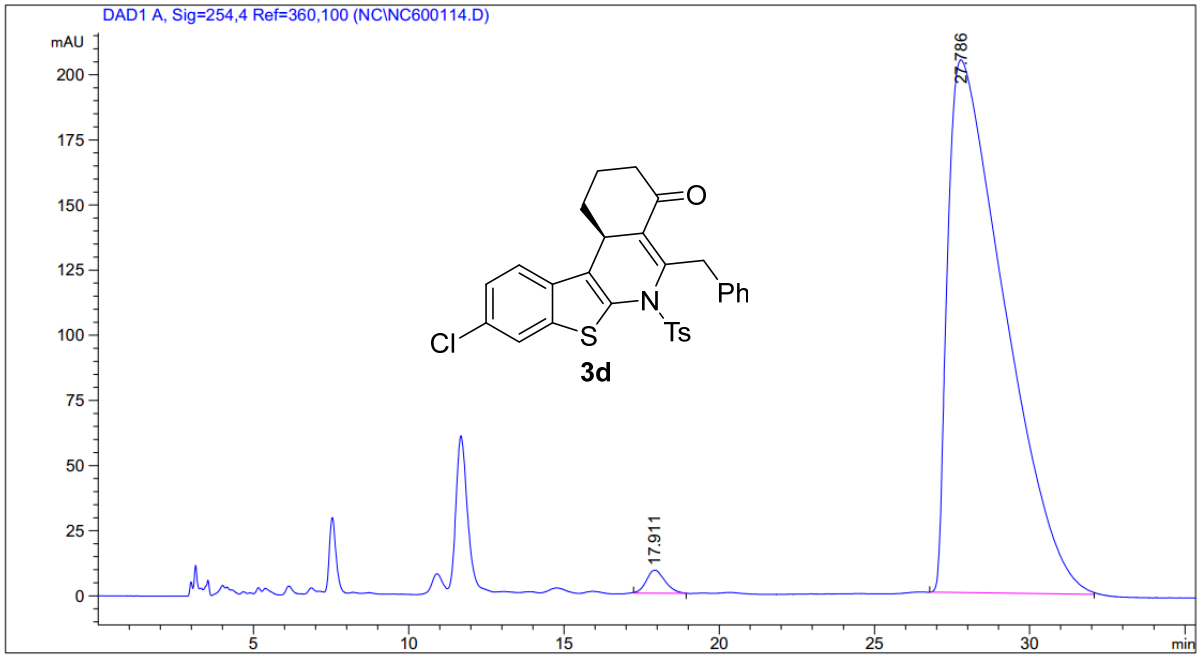
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.527	BB	1.3520	2.78493e4	307.68649	50.2254
2	41.391	BB	1.5600	2.75994e4	275.67569	49.7746



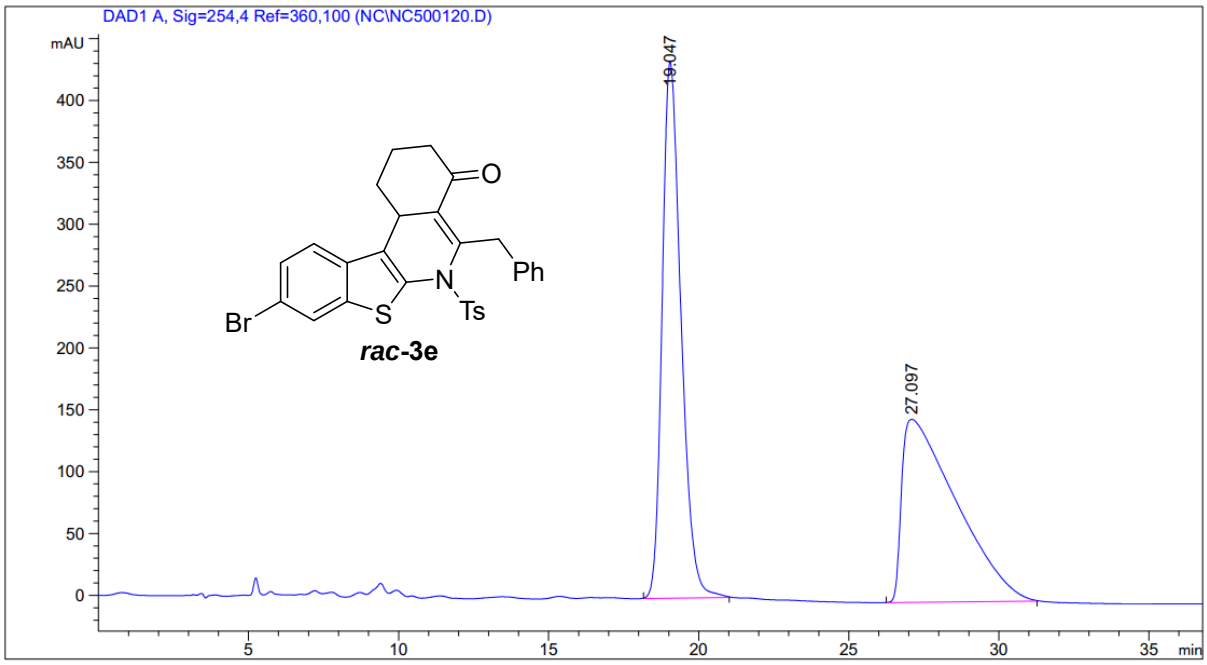
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.979	BB	1.3877	2.78152e4	305.08267	96.4944
2	39.681	BB	1.2905	1010.51318	10.89061	3.5056



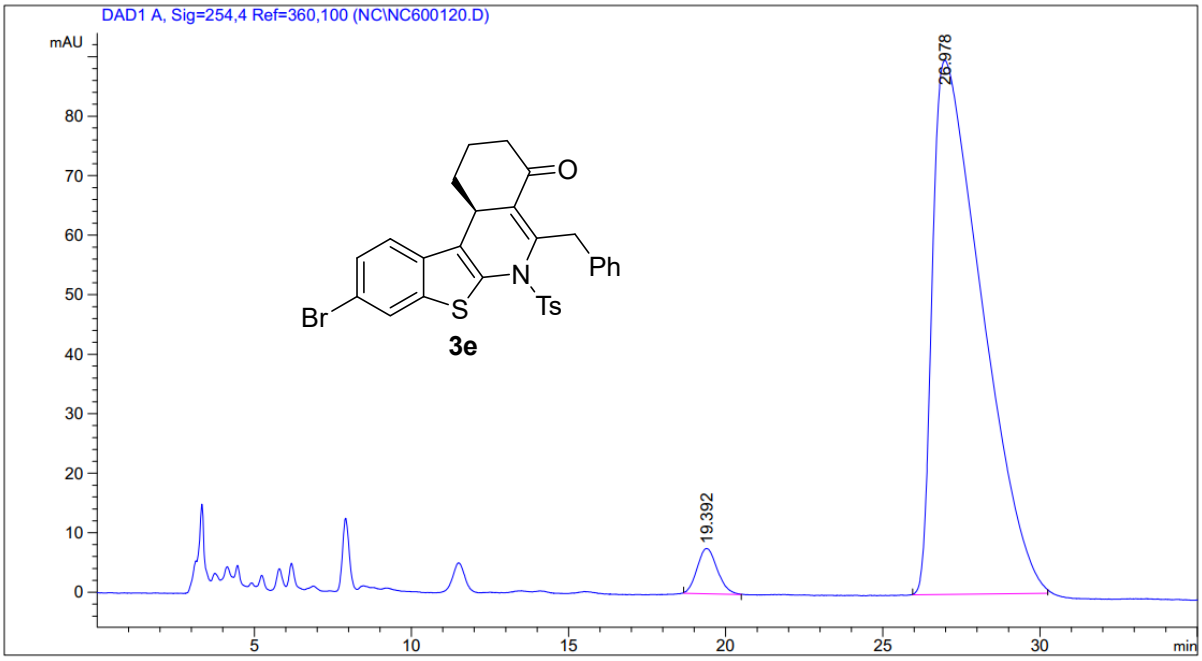
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.806	BB	0.7917	1.94642e4	373.65070	50.0668
2	28.174	BB	1.6010	1.94123e4	164.47571	49.9332



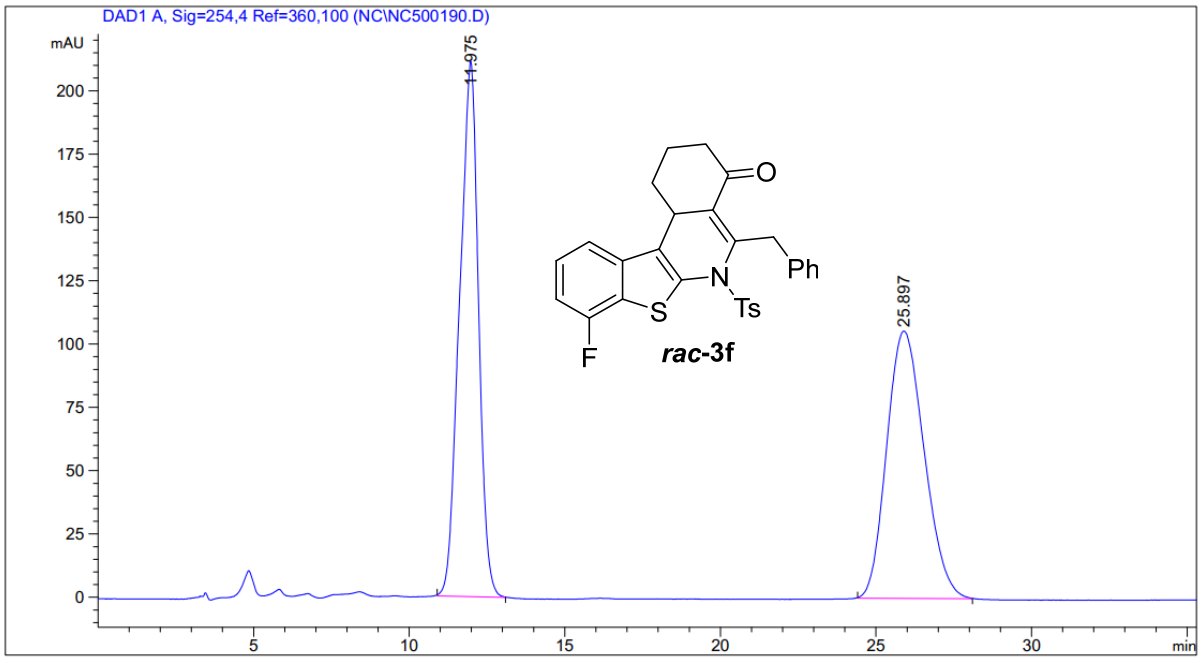
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.911	BB	0.6099	369.92270	8.84541	1.4025
2	27.786	BB	1.7238	2.60052e4	204.46992	98.5975



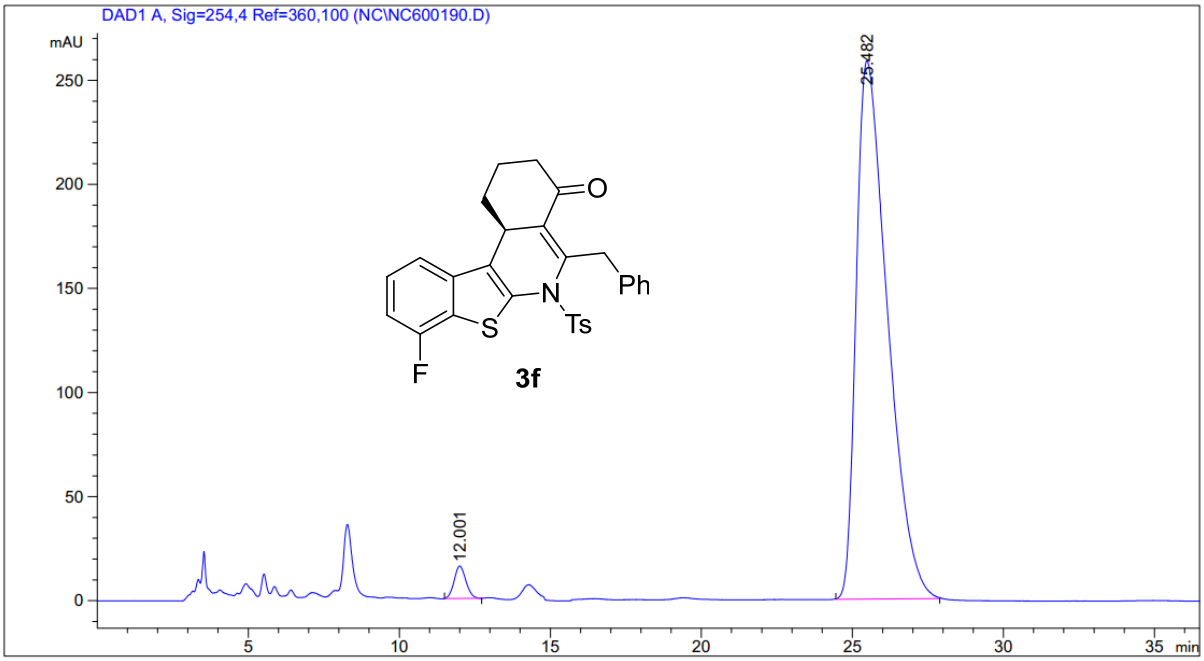
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.048	VB	0.6778	1.91224e4	434.23917	50.2235
2	27.098	BB	1.8037	1.89522e4	148.22449	49.7765



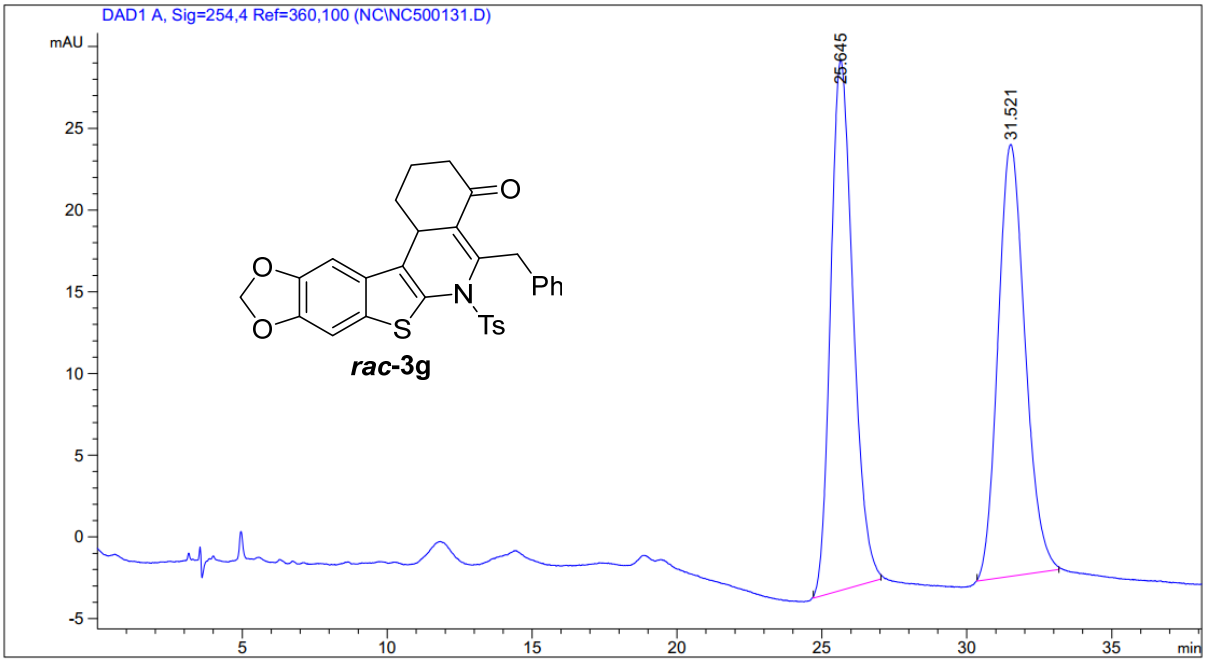
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.390	BB	0.6953	351.74835	7.72446	3.4238
2	26.978	BB	1.5419	9921.93262	90.02073	96.5762



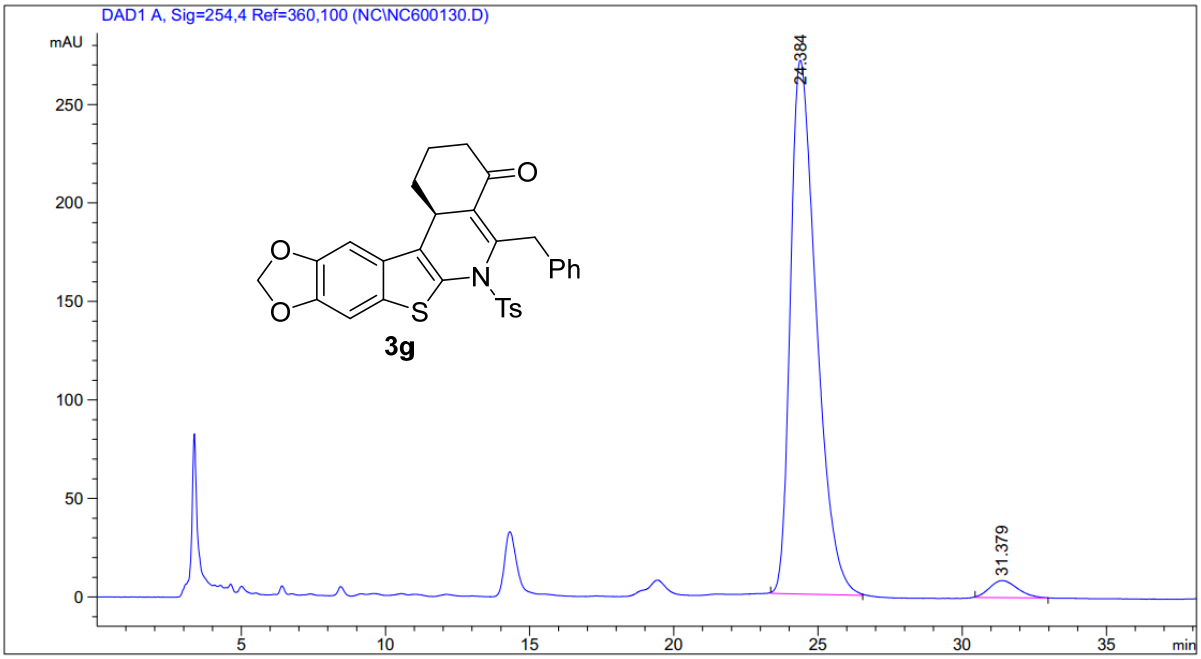
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.974	BB	0.6107	9078.32129	212.38124	50.4604
2	25.897	BB	1.3219	8912.66602	105.89657	49.5396



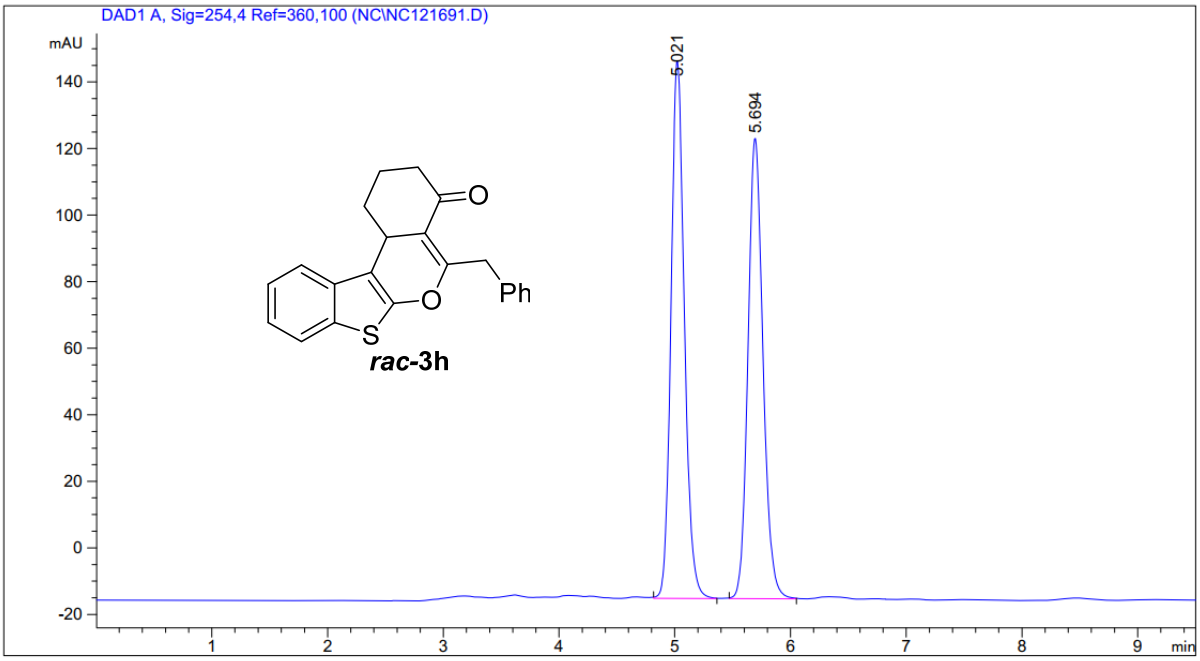
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.001	VB	0.4389	461.79385	16.08665	2.4092
2	25.483	BB	1.0901	1.87061e4	259.15417	97.5908



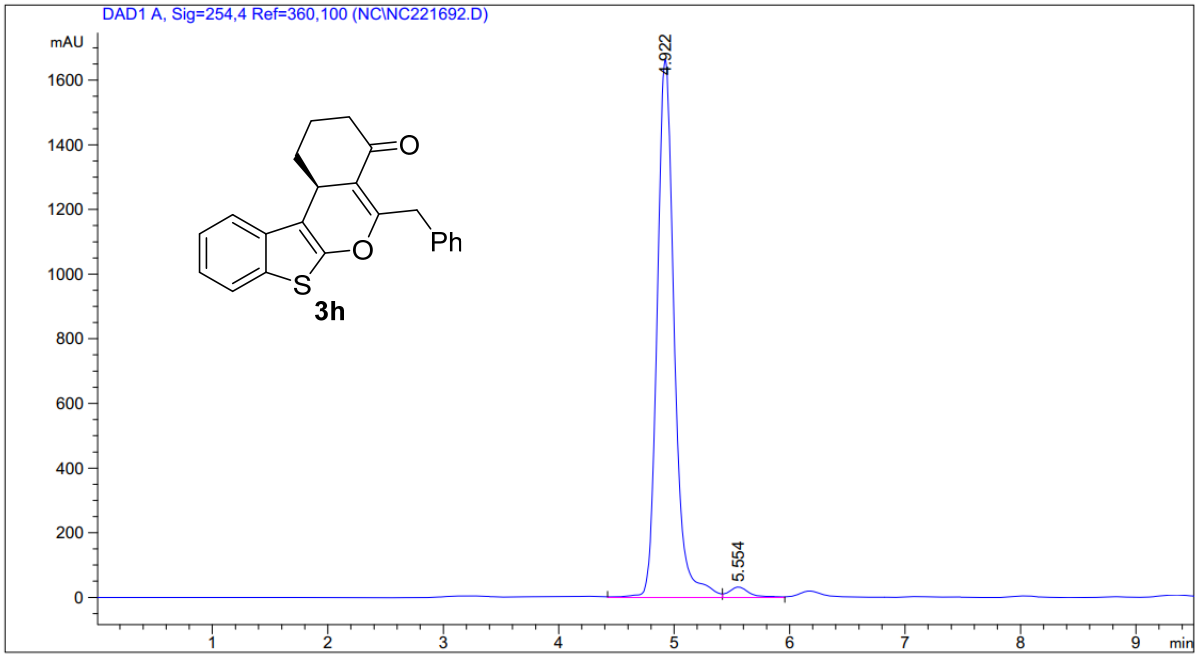
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.645	BB	0.8399	1791.58984	32.66412	50.2714
2	31.516	BB	1.0060	1772.24634	26.71290	49.7286



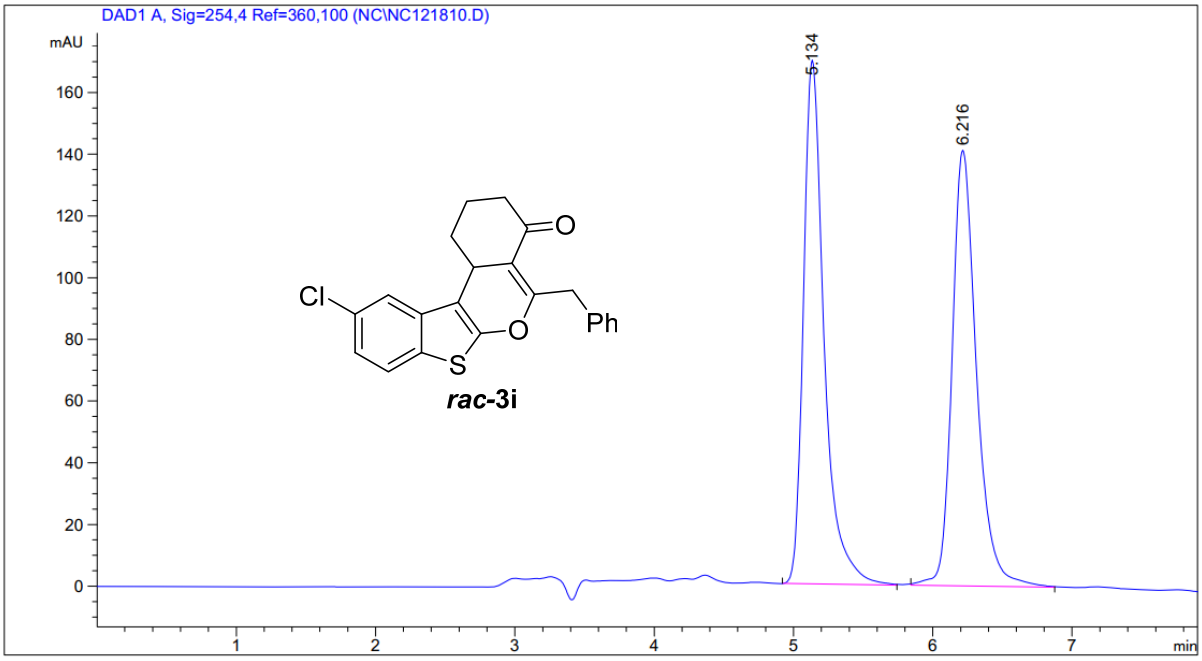
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.384	BB	0.9651	1.70544e4	271.39017	96.4119
2	31.387	BB	1.0575	634.69312	8.97005	3.5881



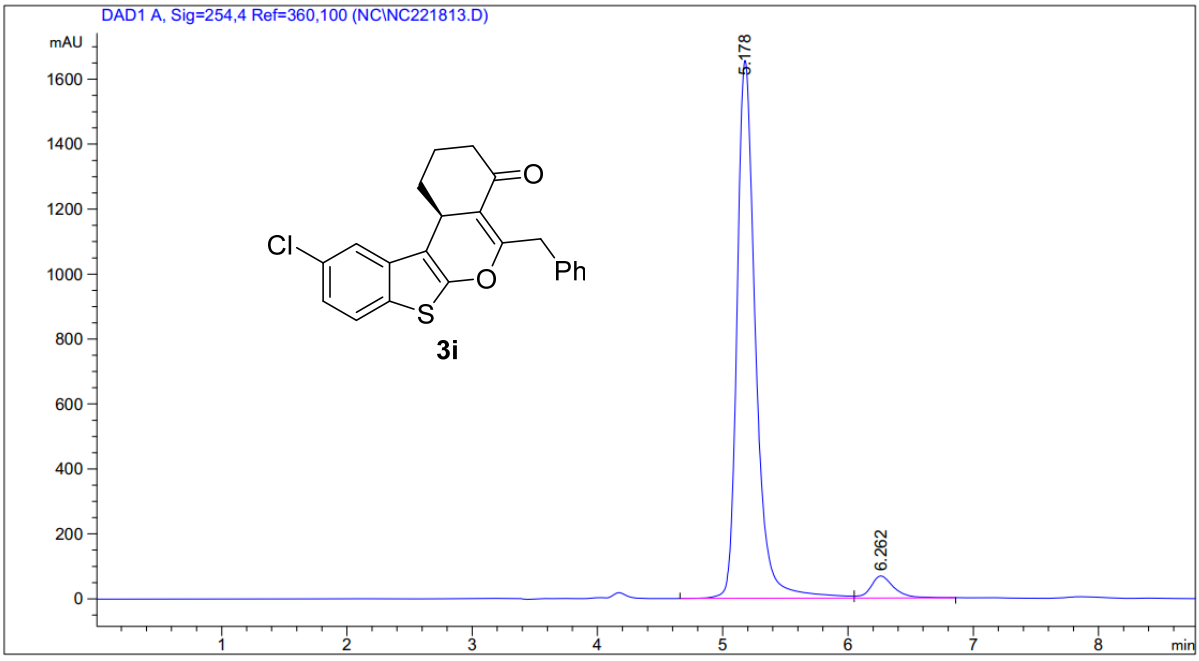
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.021	BB	0.1218	1299.69116	161.65872	51.0383
2	5.694	BB	0.1370	1246.80908	138.52023	48.9617



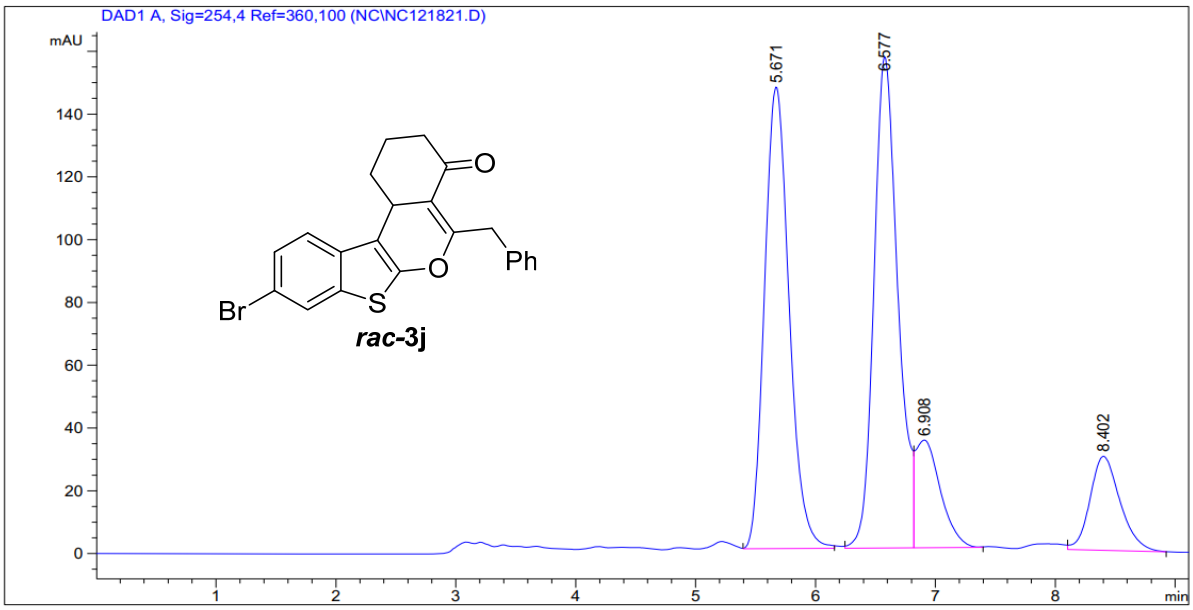
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.922	VV	0.1562	1.71428e4	1664.23840	97.7626
2	5.554	VV	0.1803	392.33682	32.17044	2.2374



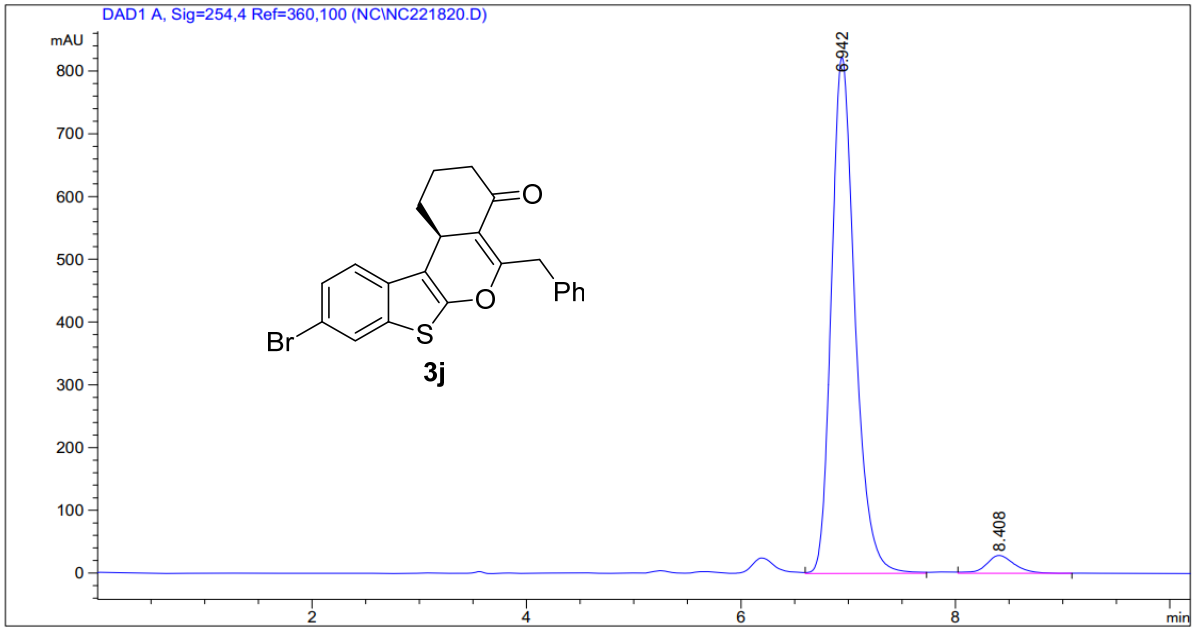
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.134	BB	0.1537	1741.61780	169.78145	50.2464
2	6.216	BB	0.1844	1724.53809	141.25587	49.7536



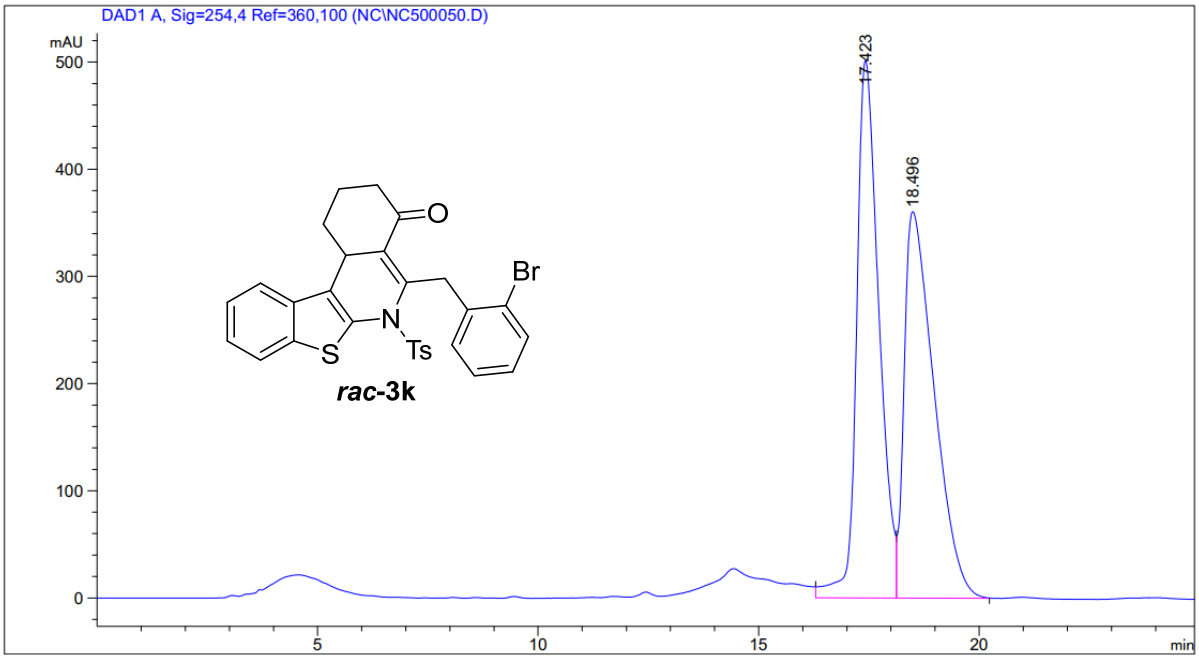
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.178	BV	0.1555	1.69698e4	1656.41589	95.0918
2	6.262	VB	0.1899	875.89337	68.17248	4.9082



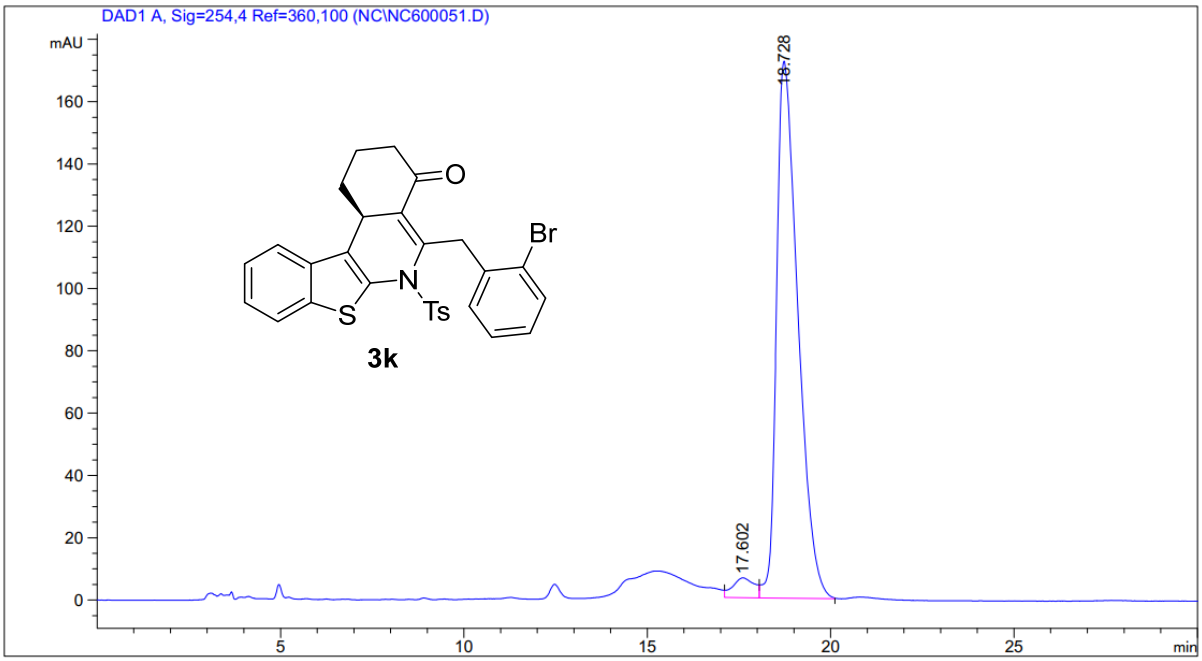
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.671	VB	0.2229	2104.55420	147.09618	39.7631
2	6.577	BV	0.2099	2170.59033	156.37476	41.0108
3	6.908	VB	0.2139	493.37512	34.28854	9.3218
4	8.402	VB	0.2639	524.20593	29.98767	9.9043



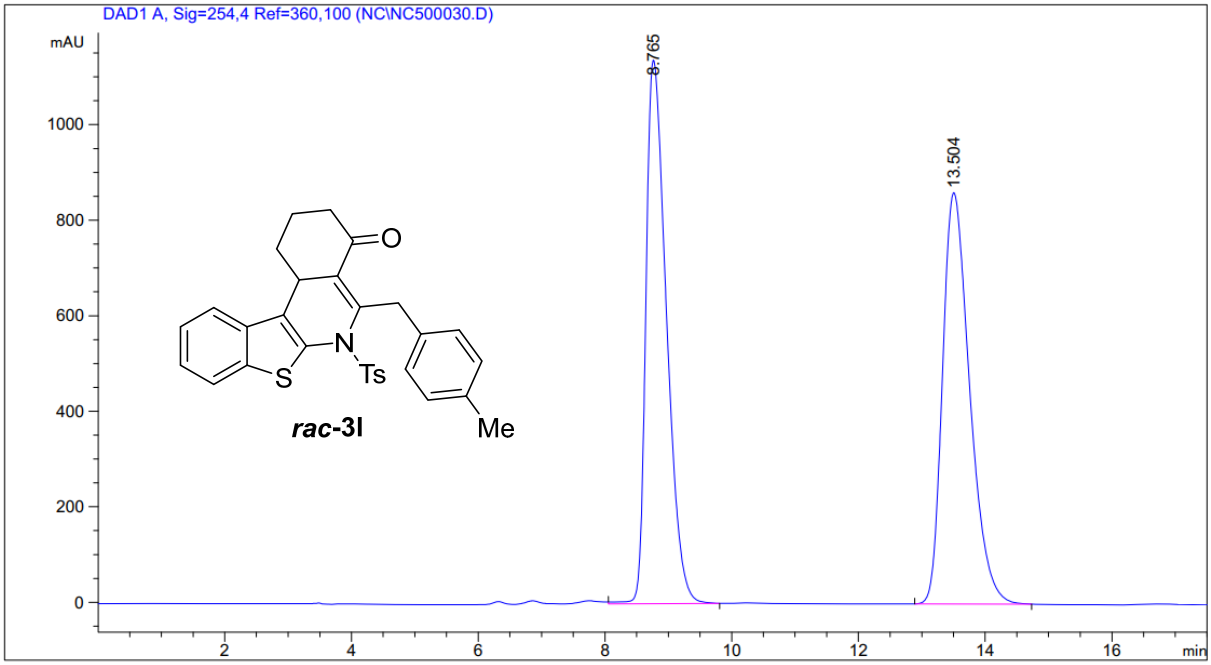
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.942	VV	0.2306	1.25774e4	821.54590	95.9941
2	8.408	VB	0.2749	524.85846	28.49740	4.0059



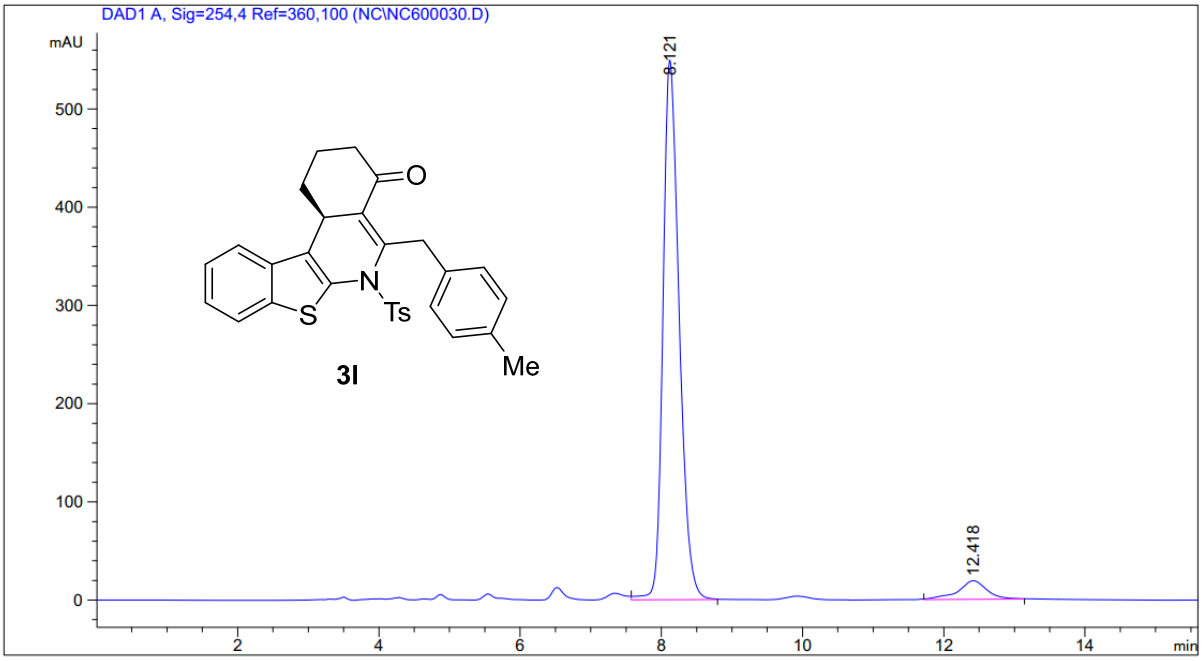
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.423	VV	0.5344	1.76385e4	501.44711	50.9845
2	18.496	VB	0.6967	1.69573e4	360.54755	49.0155



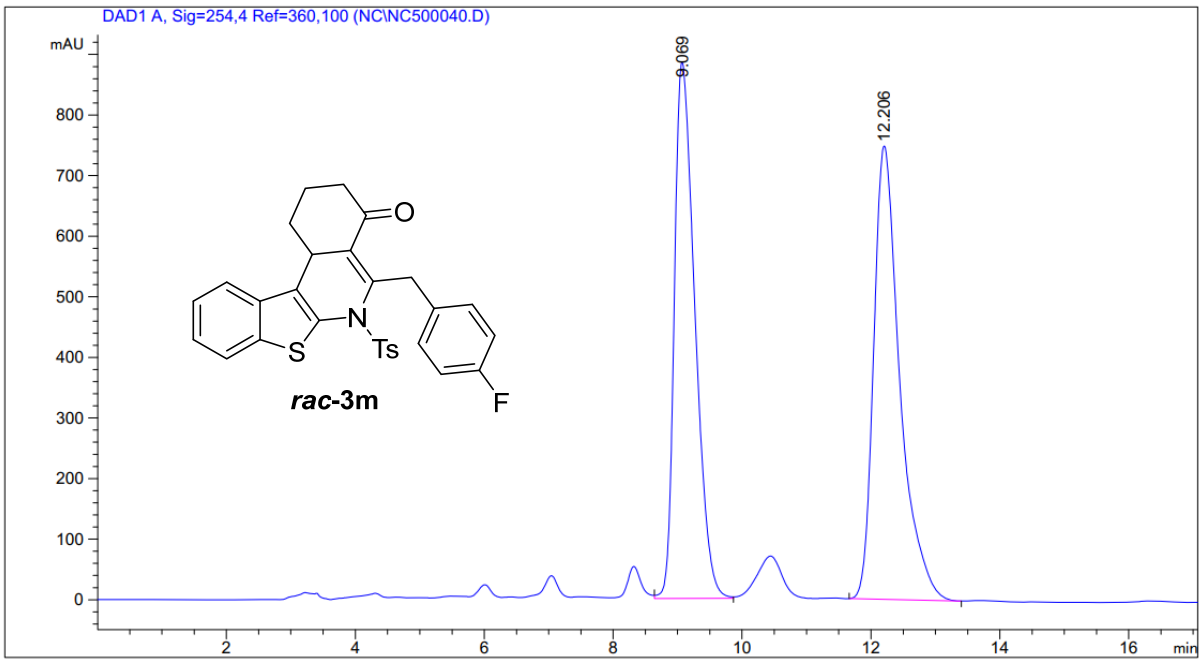
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.602	VV	0.5203	260.61136	6.35661	3.5886
2	18.728	VB	0.6159	7001.69092	172.38318	96.4114



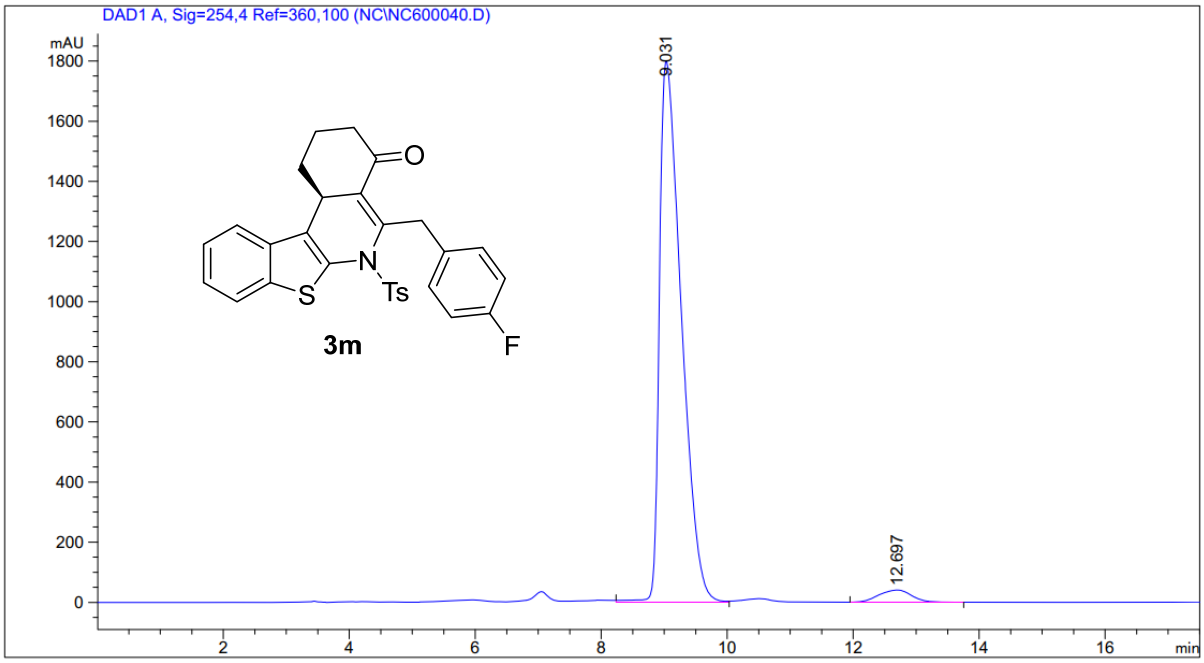
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.765	VB	0.3460	2.55532e4	1138.01672	49.9604
2	13.504	BB	0.4568	2.55937e4	861.04077	50.0396



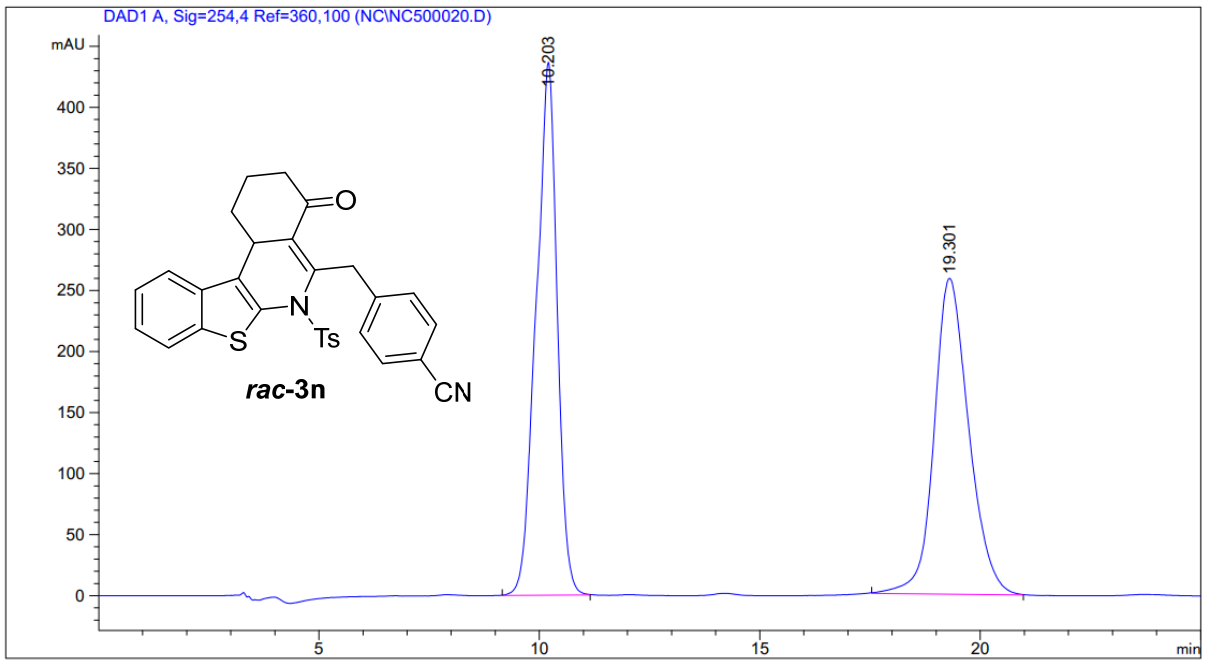
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.121	VB	0.2441	8763.08691	549.45947	94.1448
2	12.418	BB	0.4216	545.01123	19.05851	5.8552



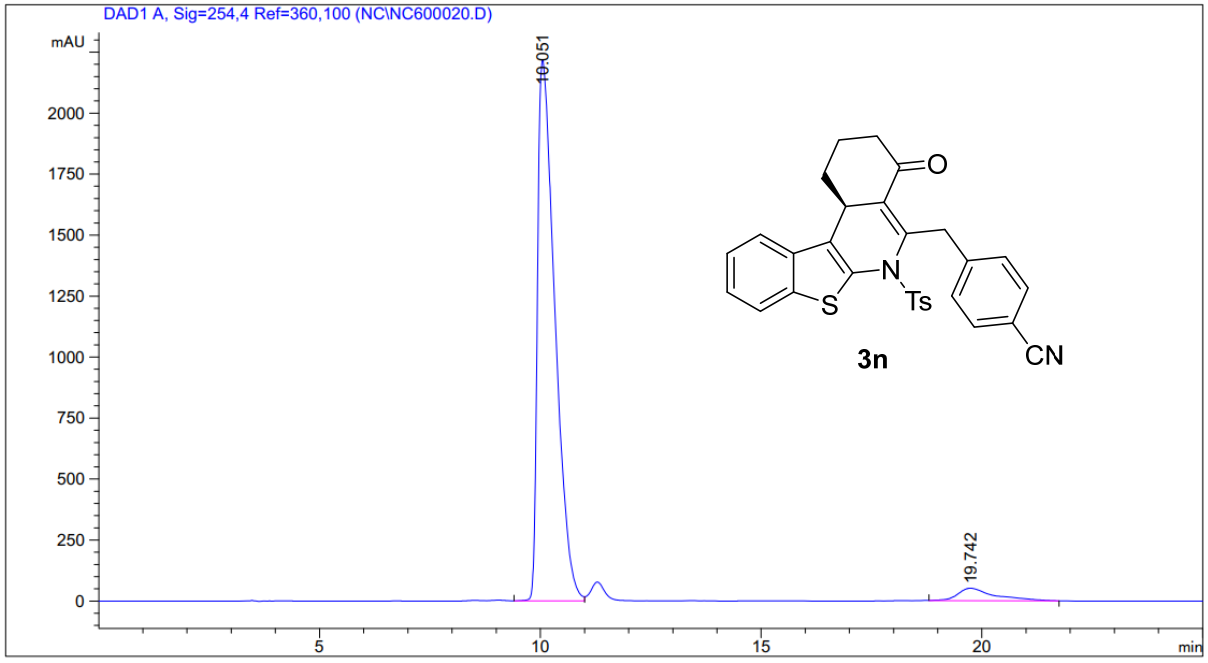
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.069	VV	0.3399	1.95717e4	885.35956	48.1288
2	12.206	BB	0.4228	2.10936e4	748.46857	51.8712



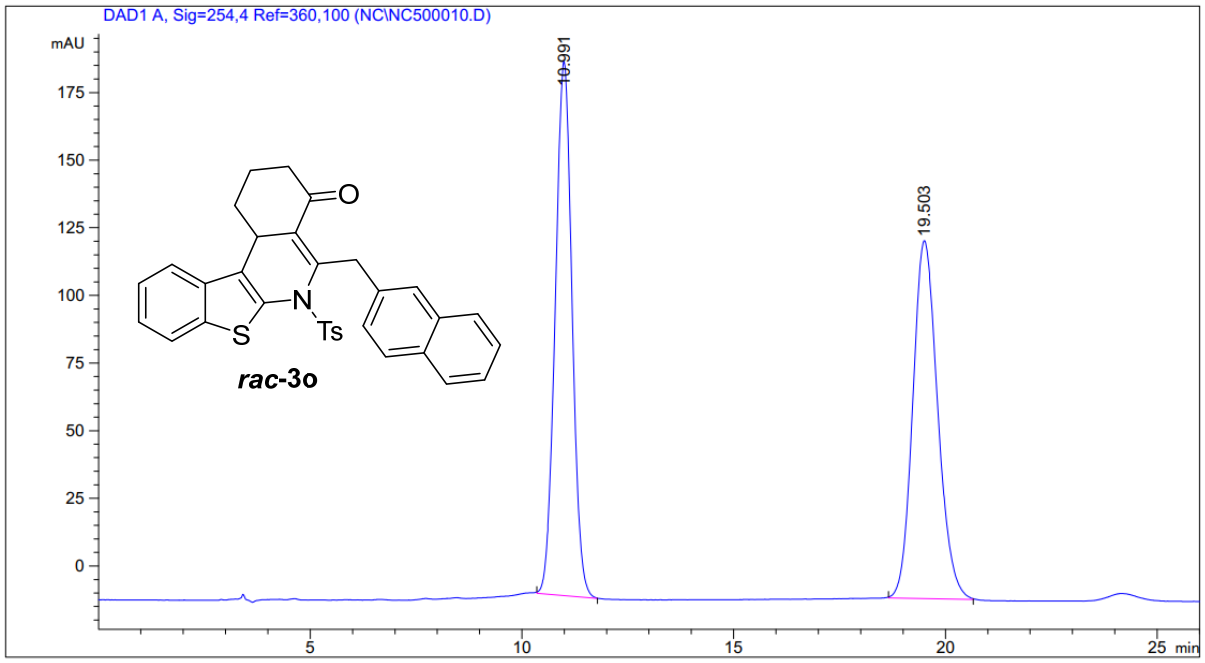
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.031	VB	0.3685	4.32612e4	1799.34534	96.7553
2	12.697	BB	0.5760	1450.75024	40.49120	3.2447



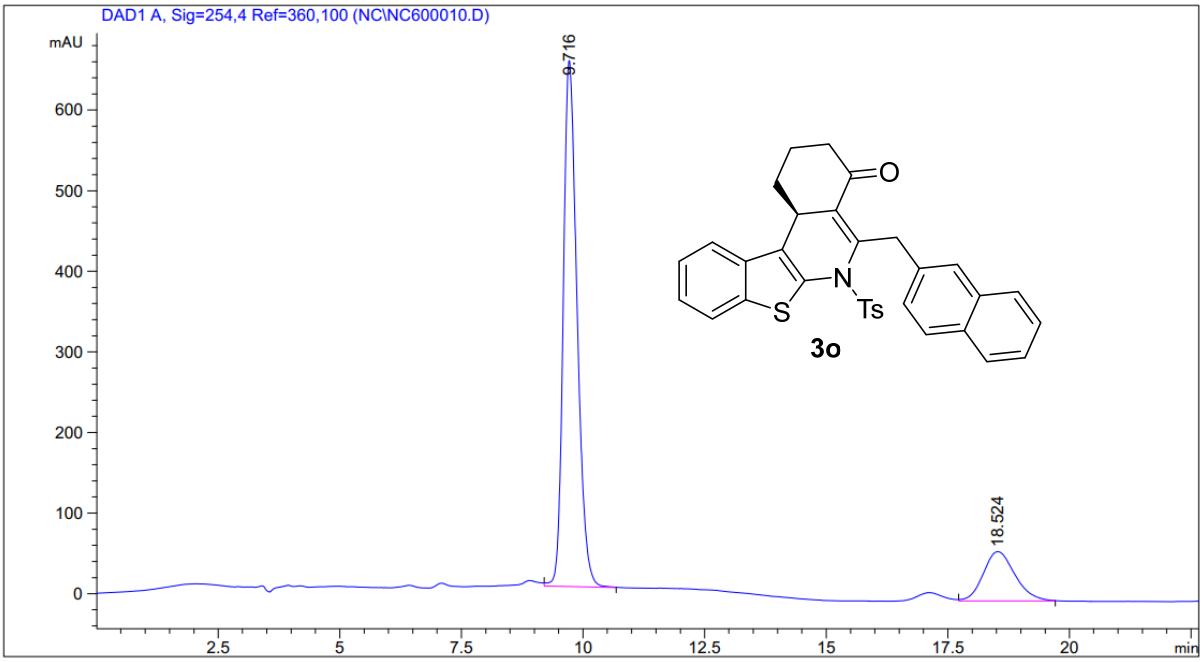
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.203	BB	0.4712	1.44861e4	436.45602	50.5973
2	19.301	BB	0.8259	1.41441e4	258.67941	49.4027



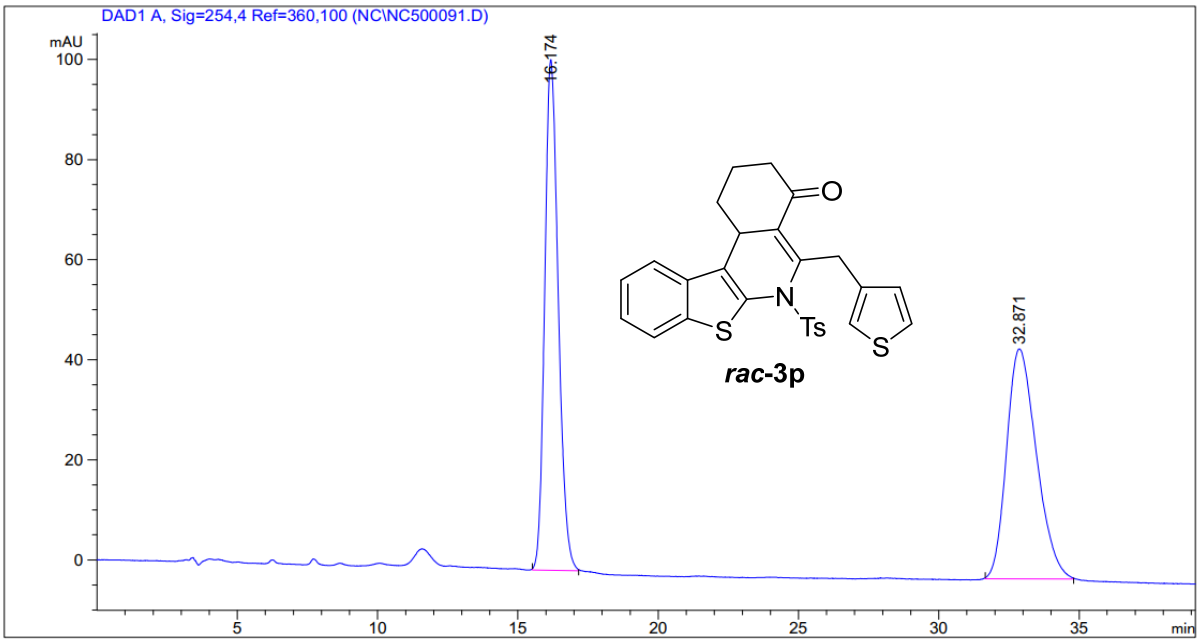
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.051	VV	0.4152	6.06772e4	2217.78467	95.3733
2	19.742	BB	0.8276	2943.52222	50.83016	4.6267



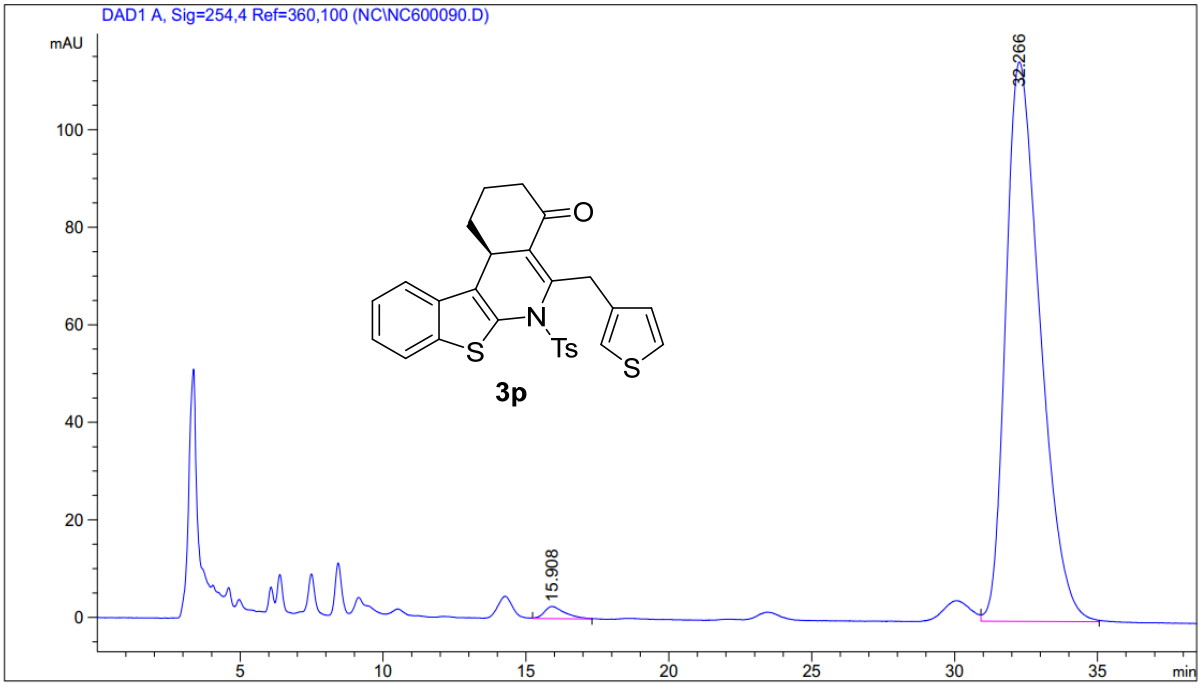
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.991	BB	0.4238	5413.68359	197.48494	50.0157
2	19.503	BB	0.6310	5410.29150	132.32932	49.9843



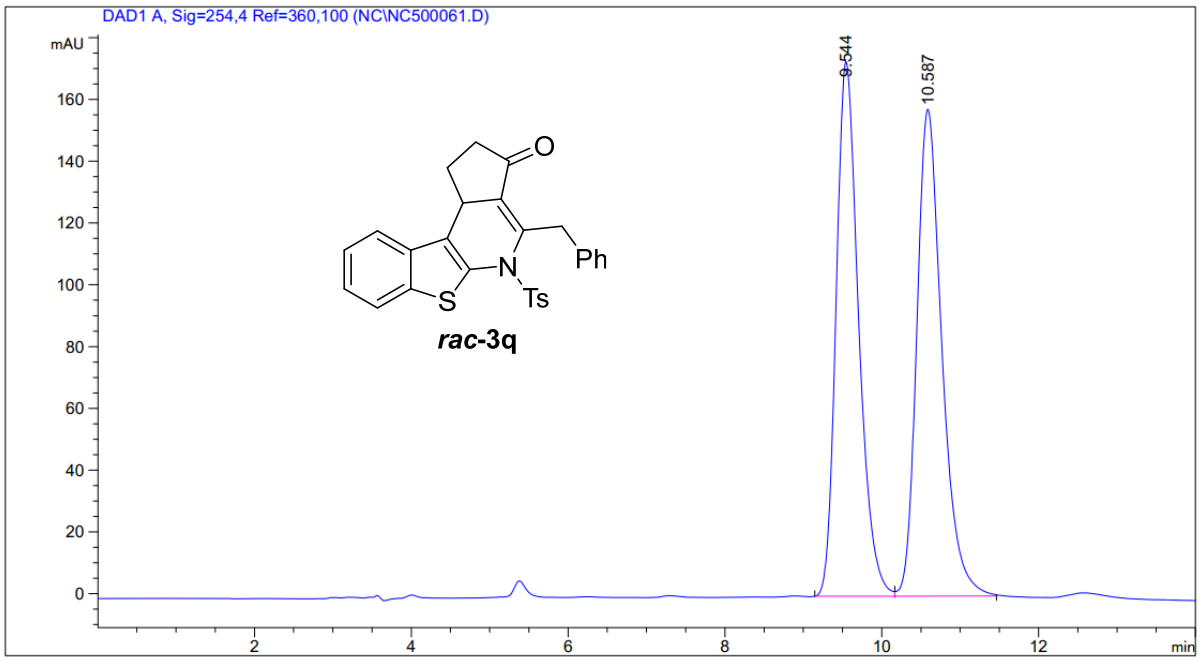
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.716	VB	0.3037	1.28499e4	652.52502	82.2728
2	18.524	VB	0.6763	2768.74194	61.36998	17.7272



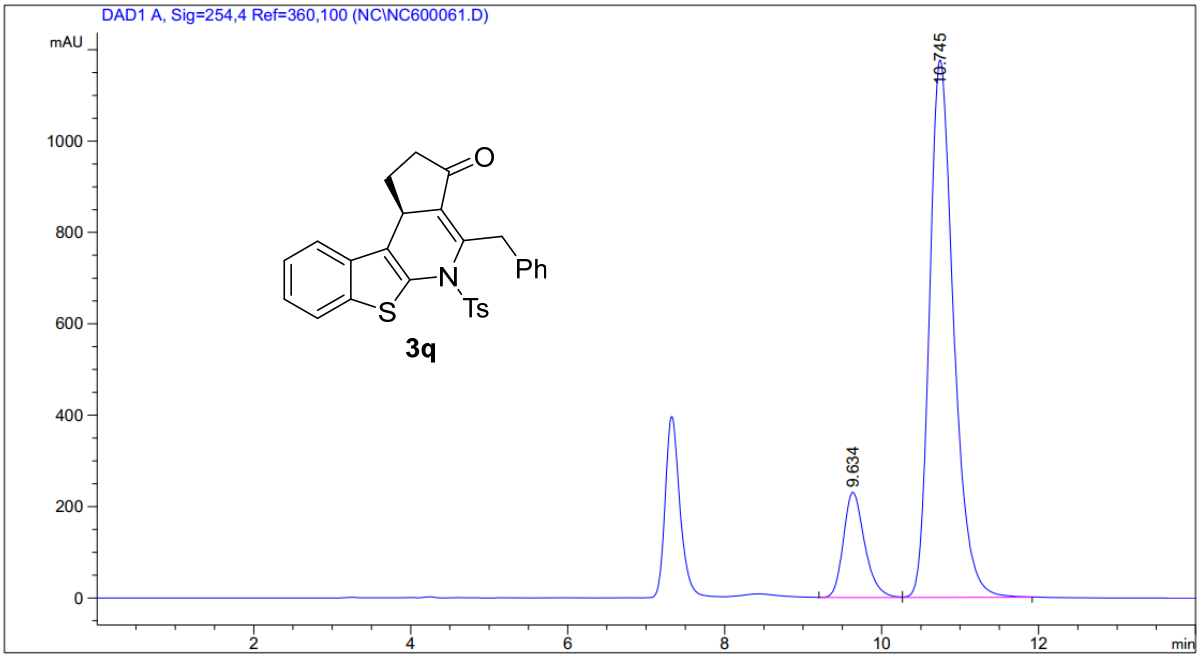
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.174	BB	0.5174	3445.19873	102.17159	49.8729
2	32.871	BB	1.1493	3462.75854	46.25859	50.1271



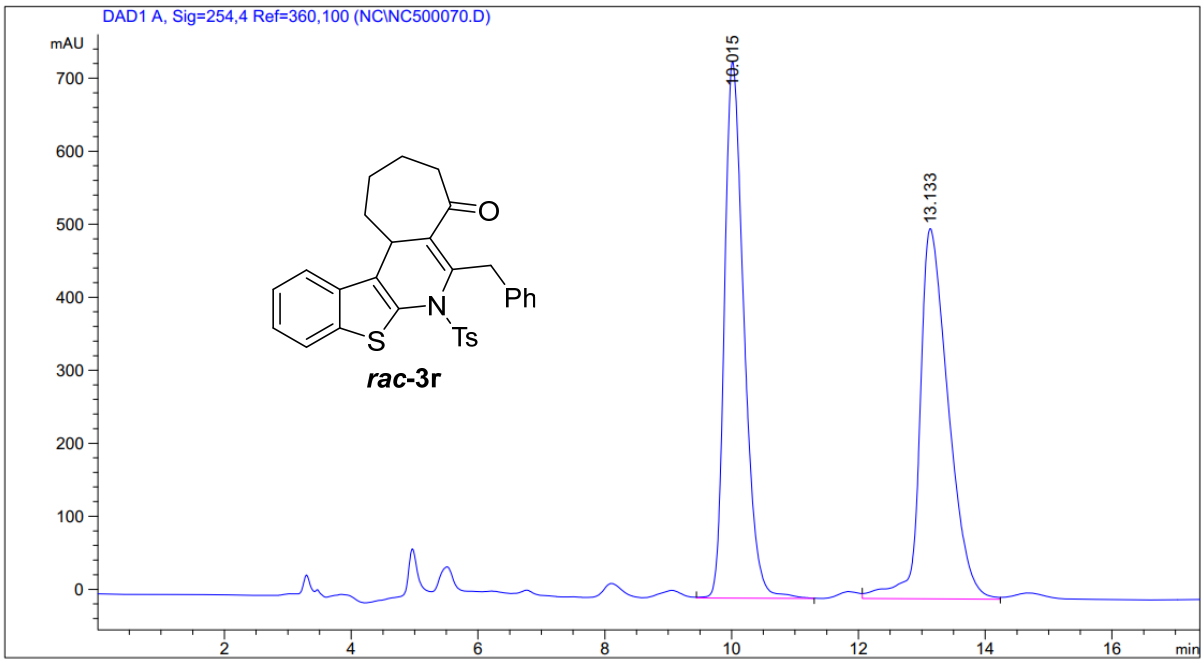
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.908	BB	0.7194	128.85866	2.50812	1.3268
2	32.266	VB	1.2867	9583.40527	114.71129	98.6732



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.544	BV	0.3039	3441.21875	173.10561	49.5217
2	10.587	VB	0.3375	3507.69312	157.67346	50.4783



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.634	VV	0.2880	4350.32080	230.64670	14.7720
2	10.745	VB	0.3269	2.50995e4	1176.33289	85.2280



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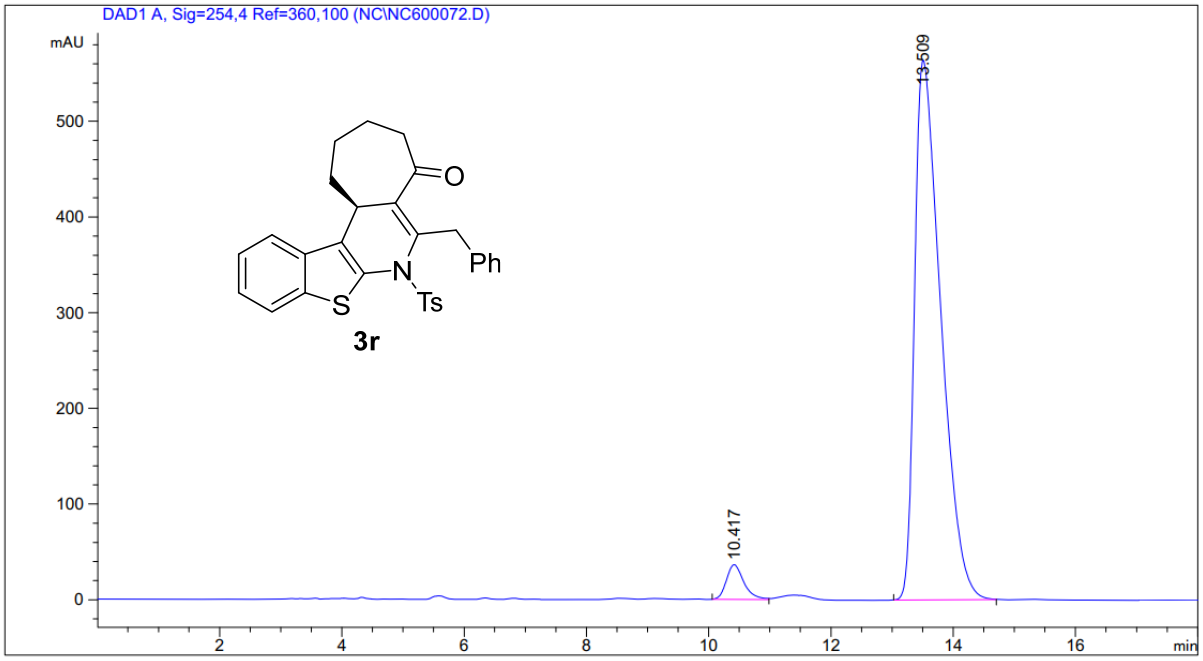
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.015	VB	0.3264	1.56451e4	734.69482	49.6913
2	13.133	VB	0.4743	1.58395e4	507.19946	50.3087



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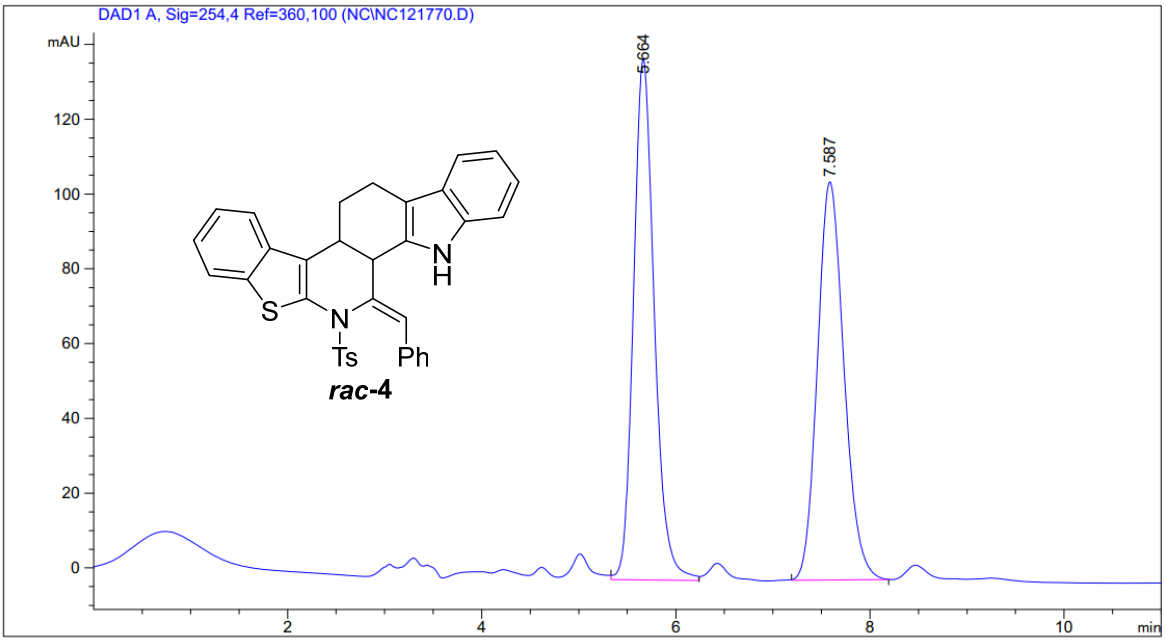
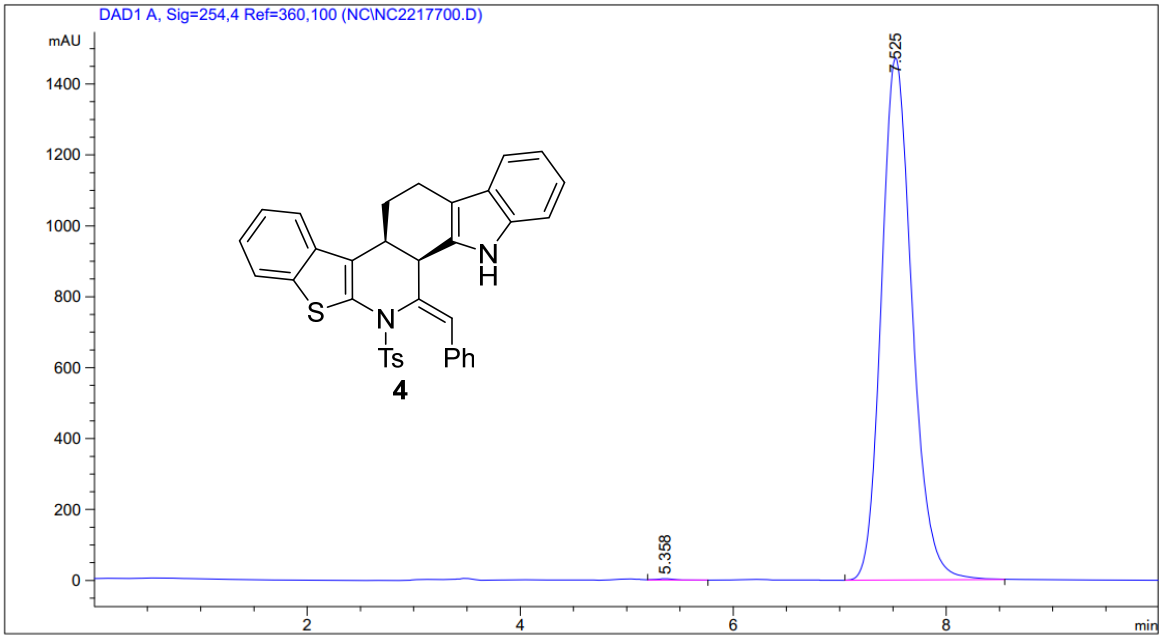
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.417	BB	0.3022	724.33057	36.40049	4.1407
2	13.509	BB	0.4488	1.67687e4	564.10706	95.8593



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.664	VB	0.2281	2078.83862	139.34492	50.6403
2	7.587	BB	0.2940	2026.27222	106.50633	49.3597



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.358	VB	0.1864	43.41637	3.66003	0.1465
2	7.525	BB	0.3085	2.95893e4	1472.02563	99.8535