Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Chiral Sultams with Two Adjacent Stereocenters via Palladium-catalyzed Dynamic Kinetic Resolution

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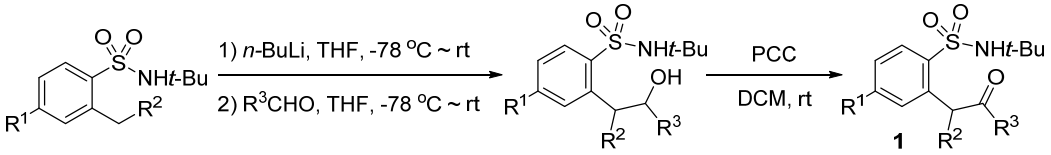
1. General

All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Enantiomeric excess was determined by HPLC analysis using chiral column. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh).

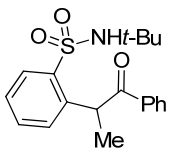
2. Preparation of Keto Sulfonamides

Keto sulfonamides **1** were prepared from the corresponding aldehydes and *N*-*tert*-butyl-2-substituted benzenesulfonamide according to the modified procedures reported in the literature.[1]

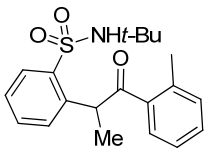


To a cooled (-78 °C) solution of *N*-*tert*-butyl-2-substitued-benzenesulfonamide (4.0 mmol) in THF (15 mL) was added *n*-butyl lithium (3.5 mL, 8.8 mmol, 2.5 M in *n*-hexane). After stirring the resulting mixture for 2 hours, the temperature was elevated to room temperature and stired for one hour. Then the mixture was cooled to -78 °C, and a solution of aldehyde (4.4 mmol) in THF (10 mL) was added dropwise over a period of 20 min and stirring was continued for additional 3 hours and the temperature was allowed to be elevated to room temperature, the mixture was poured into a saturated aqueous ammonium chloride solution (20 mL). The aqueous layer was extracted three times with ethyl acetate (20 mL×3), and the organic extracts were dried over anhydrous sodium sulfate. After concentration in *vacuo*, the residue was finally purified by flash chromatography to afford the corresponding alcohol. To a solution of the entire amount of intermediate alcohol in dichloromethane (25 mL) was added PCC (1.724 g, 8.0 mmol). The resulting dark-brown solution was stirred for overnight at ambient temperature. After addition of diethyl ether (10 mL) and additional stirring (30 min), the mixture was filtered through a pad of silica gel. Concentration in *vacuo* afforded the analytically pure keto sulfonamide compounds **1**. The yields given are overall yields for two steps.

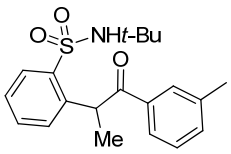
***N*-*tert*-Butyl-2-(1-*oxo*-1-phenylpropan-2-yl)-benzenesulfonamide (1a):** 0.717 g, 52% yield (4 mmol scale), white solid, mp 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.04 (m, 3H), 7.44-7.26 (m, 6H), 5.70 (q, *J* = 6.8 Hz, 1H), 5.01 (s, 1H), 1.58 (d, *J* = 6.9 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 140.4, 140.3, 136.3, 133.1, 133.0, 130.1, 129.6, 129.2, 128.7, 127.1, 55.7, 43.5, 30.1, 19.5. HRMS Calculated for $C_{19}H_{24}NO_3S$ $[M+H]^+$ 346.1471, found: 346.1472.



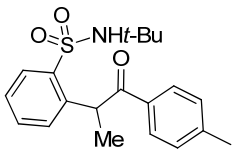
***N*-*tert*-Butyl-2-(1-*oxo*-1-(*o*-tolyl)-propan-2-yl)-benzenesulfonamide (1b):** 1.026 g, 71% yield (4 mmol scale), white solid, mp 81-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.27-7.26 (m, 2H), 7.18-7.15 (m, 2H), 5.65 (q, *J* = 6.9 Hz, 1H), 5.04 (br, 1H), 2.47 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 140.5, 140.0, 138.5, 137.3, 132.6, 131.8, 131.2, 129.9, 129.4, 128.9, 126.9, 125.8, 55.4, 45.5, 30.0, 21.3, 19.2. HRMS Calculated for $C_{20}H_{26}NO_3S$ $[M+H]^+$ 360.1628, found: 360.1630.



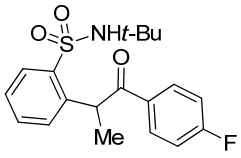
***N-tert*-Butyl-2-(1-*oxo*-1-(*m*-tolyl)propan-2-yl)-benzenesulfonamide (1c):** 0.997 g, 69% yield (4 mmol scale), white solid, mp 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 1H), 7.93-7.89 (m, 2H), 7.44-7.40 (m, 1H), 7.33-7.24 (m, 4H), 5.71 (q, *J* = 6.9 Hz, 1H), 4.83 (br, 1H), 2.34 (s, 3H), 1.58 (d, *J* = 6.9 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 140.2, 140.2, 138.5, 136.1, 133.8, 132.8, 130.0, 129.5, 129.4, 128.5, 126.9, 126.3, 55.6, 43.2, 30.0, 21.3, 19.4. HRMS Calculated for $C_{20}H_{26}NO_3S$ $[M+H]^+$ 360.1628, found: 360.1630.



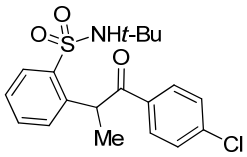
***N-tert*-Butyl-2-(1-*oxo*-1-(*p*-tolyl)propan-2-yl)-benzenesulfonamide (1d):** 0.740 g, 68% yield (3 mmol scale), white solid, mp 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.44-7.42 (m, 1H), 7.34-7.27 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.69 (q, *J* = 6.9 Hz, 1H), 4.65 (d, *J* = 5.3 Hz, 1H), 2.34 (s, 3H), 1.58 (d, *J* = 6.9 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 144.0, 140.5, 140.3, 133.8, 133.0, 130.2, 129.6, 129.5, 129.3, 127.0, 55.7, 43.3, 30.1, 21.8, 19.5. HRMS Calculated for $C_{20}H_{26}NO_3S$ $[M+H]^+$ 360.1628, found: 360.1626.



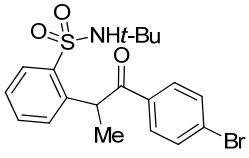
***N-tert*-Butyl-2-(1-(4-fluorophenyl)-1-*oxo*-propan-2-yl)-benzenesulfonamide (1e):** 0.735 g, 67% yield (3 mmol scale), white solid, mp 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.12 (m, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.46-7.42 (m, 1H), 7.33-7.26 (m, 2H), 7.05-7.01 (m, 2H), 5.64 (q, *J* = 6.7 Hz, 1H), 4.64 (br, 1H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 165.6 (d, *J* = 254.8 Hz), 140.0 (d, *J* = 2.5 Hz), 133.0, 132.4 (d, *J* = 2.9 Hz), 131.8, 131.8, 129.6 (d, *J* = 28.2 Hz), 127.1, 115.8, 115.6, 55.7, 43.5, 30.0, 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.2. HRMS Calculated for $C_{19}H_{23}FNO_3S$ $[M+H]^+$ 364.1377, found: 364.1379.



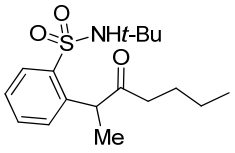
***N-tert*-Butyl-2-(1-(4-chlorophenyl)-1-*oxo*-propan-2-yl)-benzenesulfonamide (1f):** 0.721 g, 63% yield (3 mmol scale), white solid, mp 153-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.03(m, 3H), 7.44-8.41 (m, 1H), 7.33-7.24 (m, 4H), 5.65-5.61 (m, 1H), 4.72 (br, 1H), 1.58 (d, *J* = 6.4 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 140.3, 140.1, 139.6, 134.6, 133.1, 130.7, 129.9, 129.7, 129.1, 127.3, 55.9, 43.8, 30.2, 19.4. HRMS Calculated for $C_{19}H_{23}ClNO_3S$ $[M+H]^+$ 380.1082, found: 380.1083.



***N-tert*-Butyl-2-(1-(4-bromophenyl)-1-*oxo*-propan-2-yl)-benzenesulfonamide (1g):** 0.694 g, 41% yield (4 mmol scale), white solid, mp 149-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43-7.41 (m, 1H), 7.33-7.31 (m, 1H), 7.27-7.23 (m, 1H), 5.61 (q, *J* = 6.7 Hz, 1H), 4.66 (br, 1H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 140.2, 140.0, 135.0, 133.2, 132.1, 130.8, 129.9, 129.7, 128.4, 127.3, 55.9, 43.8, 30.2, 19.3. HRMS Calculated for $C_{19}H_{23}BrNO_3S$ $[M+H]^+$ 424.0577, found: 424.0575.

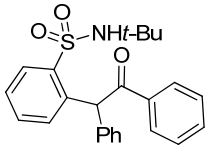


***N-tert*-Butyl-2-(3-*oxo*-heptan-2-yl)-benzenesulfonamide (1h):** 1.209 g, 47% yield (8 mmol scale), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.53-7.49 (m, 1H), 7.38-7.34 (m, 1H), 7.27-7.25 (m, 1H), 5.14 (br, 1H), 4.81 (q, *J* = 6.8 Hz, 1H), 2.50-2.31 (m, 2H), 1.50-1.42 (m, 5H), 1.29 (s, 9H), 1.20-1.16 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz,

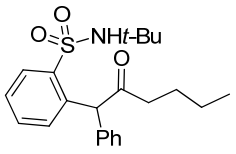


$CDCl_3$) δ 210.5, 141.1, 139.7, 132.8, 129.4, 129.3, 127.0, 55.4, 47.8, 41.0, 30.1, 25.8, 22.1, 17.9, 13.8. HRMS Calculated for $C_{17}H_{28}NO_3S$ $[M+H]^+$ 326.1786, found: 326.1786.

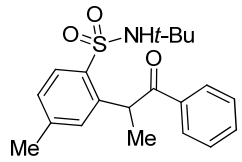
***N-tert*-Butyl-2-(2-*oxo*-1,2-diphenylethyl)-benzenesulfonamide (1i):** 0.380 g, 33% yield (2.8 mmol scale), white solid, mp 136-137 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.4 Hz, 1H), 8.07 (d, J = 7.5 Hz, 2H), 7.50-7.28 (m, 12H), 4.03 (br, 1H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 140.6, 138.3, 136.9, 136.1, 133.3, 132.5, 132.5, 129.9, 129.5, 129.3, 129.2, 128.8, 127.7, 127.4, 55.1, 54.2, 29.6. HRMS Calculated for $C_{24}H_{26}NO_3S$ $[M+H]^+$ 406.1628, found: 406.1629.



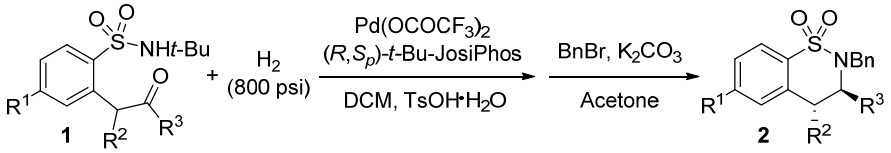
***N-tert*-Butyl-2-(2-*oxo*-1-phenylhexyl)-benzenesulfonamide (1j):** 0.443 g, 41% yield (2.8 mmol scale), white solid, mp 96-97 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 1H), 7.35-7.33 (m, 1H), 7.31-7.21 (m, 7H), 6.36 (s, 1H), 4.88 (s, 1H), 2.66-2.52 (m, 2H), 1.57-1.52 (m, 2H), 1.28-1.21 (m, 2H), 1.07 (s, 9H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 141.2, 137.9, 136.5, 132.2, 132.0, 129.3, 129.3, 129.0, 127.5, 127.2, 58.9, 55.2, 42.4, 29.8, 25.8, 22.1, 13.9. HRMS Calculated for $C_{22}H_{30}NO_3S$ $[M+H]^+$ 388.1941, found: 388.1940.



***N*-(*tert*-Butyl)-4-methyl-2-(1-*oxo*-1-phenylpropan-2-yl)-benzenesulfonamide (1k):** 1.060 g, 74% yield (4 mmol scale), white solid, mp 150-151 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.49-7.46 (m, 1H), 7.40-7.37 (m, 2H), 7.10-7.07 (m, 2H), 5.68 (q, J = 6.8 Hz, 1H), 4.58 (br, 1H), 2.30 (s, 3H), 1.58 (d, J = 6.8 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 143.6, 139.9, 137.2, 136.1, 133.0, 130.4, 129.8, 129.1, 128.6, 127.6, 55.5, 43.2, 30.0, 21.4, 19.3. HRMS Calculated for $C_{20}H_{25}NO_3SNa$ $[M+Na]^+$ 382.1447, found: 382.1452.



3. Procedure for Asymmetric Intramolecular Reductive Amination

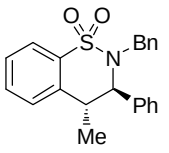


Bisphosphine ligand (R,S_p)-*t*-Bu-JosiPhos (3.6 mg, 0.0066 mmol) and $Pd(OCOCF_3)_2$ (2.0 mg, 0.006 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in dichloromethane (1.0 mL). To the mixture of keto sulfonamides **1** (0.2 mmol) and *para*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) in dochloromethane was added this catalyst solution, and then the mixture was transferred to an autoclave, which was charged hydrogen gas (800 psi). The autoclave was stirred under directed condition (oil bath temperature was showed if it was heated). After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. To a solution of the crude product in acetone (5.0 mL) was added benzyl bromide (30 μL, 0.25 mmol), potassium carbonate (69 mg, 0.50 mmol). Then the mixture was heated to reflux for overnight. The reaction mixture was evaporated. Purification was performed on silica gel using *n*-hexane/ethyl acetate as the eluent to give the chiral products **2**. The enantiomeric excesses were determined by chiral HPLC.

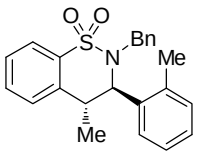
Racemates of **2** was prepared by the reduction amination of the corresponding keto sulfona-

mides catalyzed by racemic catalyst.

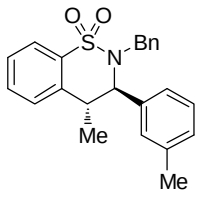
(+)-*N*-Benzyl-3,4-dihydro-3-phenyl-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2a): 64 mg, 89% yield (0.2 mmol scale), 94% ee, white solid, mp 90-92 ^{o}C, $[\alpha]^{20}_{D}$ = +43.59 (*c* 0.64, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 1H), 7.51-7.45 (m, 2H), 7.37-7.27 (m, 5H), 7.24-7.20 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 2H), 5.15-5.11 (m, 1H), 4.30-4.21 (m, 2H), 3.51-3.47 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.5, 136.2, 135.4, 132.3, 129.0, 128.7, 128.4, 128.3, 128.0, 127.8, 127.0, 126.3, 121.4, 64.7, 47.4, 33.4, 14.2. HPLC: Chiracel AD-H column, 254 nm, 30 ^{o}C, *n*-hexane/*i*-propanol = 95/5, flow = 0.7 mL/min, retention time 14.7 min and 24.6 min (maj). HRMS Calculated for $C_{22}H_{22}NO_2S$ $[M+H]^+$ 364.1365, found: 364.1364.



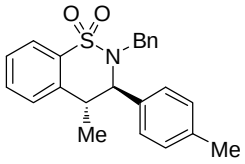
(+)-*N*-Benzyl-3,4-dihydro-3-(*o*-Tolyl)-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2b): 65 mg, 86% yield (0.2 mmol scale), 57% ee, white solid, mp 123-124 ^{o}C, $[\alpha]^{20}_{D}$ = +18.28 (*c* 2.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 1H), 7.55-7.48 (m, 2H), 7.37-7.27 (m, 5H), 7.13-7.05 (m, 3H), 6.88-6.81 (m, 1H), 6.17 (d, *J* = 7.5 Hz, 1H), 5.17-5.13 (m, 1H), 4.76-4.72 (m, 1H), 4.34-4.27 (m, 1H), 3.46-3.42 (m, 1H), 1.89 (s, 3H), 1.05 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 138.5, 137.8, 137.1, 134.3, 133.1, 131.4, 129.5, 129.5. 128.7, 128.5, 127.8, 127.6, 127.2, 127.1, 122.2, 59.3, 48.5, 34.8, 20.1, 13.9. HPLC: Chiracel OD-H column, 230 nm, 30 ^{o}C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 11.7 min (maj) and 14.9 min. HRMS Calculated for $C_{23}H_{24}NO_2S$ $[M+H]^+$ 378.1522, found: 378.1516.



(+)-*N*-Benzyl-3,4-dihydro-3-(*m*-Tolyl)-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2c): 68 mg, 90% yield (0.2 mmol scale), 94% ee, white solid, mp 117-118 ^{o}C, $[\alpha]^{20}_{D}$ = +37.29 (*c* 1.70, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.4 Hz, 1H), 7.51-7.45 (m, 2H), 7.34-7.30 (m, 5H), 7.04-7.00 (m, 3H), 6.34-6.32 (m, 2H), 5.11 (d, *J* = 15.8 Hz, 1H), 4.25-4.22 (m, 2H), 3.53-3.49 (m, 1H), 2.16 (s, 3H), 1.01 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.9, 137.6, 136.3, 135.2, 132.2, 129.1, 128.9, 128.6, 128.6, 128.1, 127.7, 126.9, 126.2, 125.1, 121.4, 64.7, 47.4, 33.4, 21.4, 14.2. HPLC: Chiracel OD-H column, 230 nm, 30 ^{o}C, *n*-hexane/*i*-propanol = 90/10, flow = 0.7 mL/min, retention time 10.2 min and 12.7 min (maj). HRMS Calculated for $C_{23}H_{24}NO_2S$ $[M+H]^+$ 378.1522, found: 378.1516.

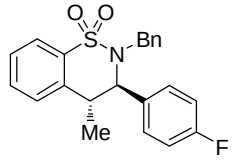


(+)-*N*-Benzyl-3,4-dihydro-3-(*p*-Tolyl)-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2d): 69 mg, 91% yield (0.2 mmol scale), 94% ee, colorless oil, $[\alpha]^{20}_{D}$ = +63.33 (*c* 2.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.7 Hz, 1H), 7.52-7.48 (m, 2H), 7.38-7.33 (m, 5H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.43 (d, *J* = 7.8 Hz, 2H), 5.15-5.10 (m, 1H), 4.27-4.21 (m, 2H), 3.51-3.47 (m, 1H), 2.27 (s, 3H), 1.01 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.1, 137.6, 136.3, 132.2, 132.2, 129.0, 129.0, 128.7, 127.9, 127.7, 127.0, 126.2, 121.3, 64.4, 47.2, 33.4, 21.1, 14.2. HPLC: Chiracel OD- H column, 230 nm, 30 ^{o}C, *n*-hexane/*i*-propanol = 90/10, flow = 0.7 mL/min, retention time 10.7 min and 14.4 min (maj). HRMS Calculated for $C_{23}H_{24}NO_2S$ $[M+H]^+$ 378.1522, found: 378.1516.

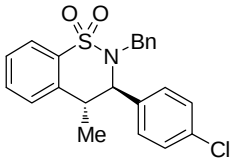


(+)-*N*-Benzyl-3,4-dihydro-3-(4-fluorophenyl)-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2e): 73 mg, 96% yield (0.2 mmol scale), 95% ee, white solid, mp 135-137 ^{o}C, $[\alpha]^{20}_{D}$ =

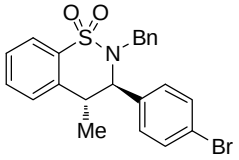
+41.23 (*c* 0.73, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 1H), 7.53-7.47 (m, 2H), 7.37-7.30 (m, 5H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.85-6.81 (m, 2H), 6.53-6.50 (m, 2H), 5.14-5.10 (m, 1H), 4.29-4.22 (m, 2H), 3.53-3.49 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.3 Hz), 139.0, 137.2, 135.9, 132.4, 131.2 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 8.1 Hz), 128.9, 128.7, 127.9, 127.2, 126.2, 121.5, 115.3 (d, *J* = 21.5 Hz), 64.1, 47.4, 33.4, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4. HPLC: Chiracel AD-H column, 230 nm, 30 °C, *n*-hexane/*i*-propanol = 95/5, flow = 0.7 mL/min, retention time 19.1 min (maj) and 21.5 min. HRMS Calculated for $C_{22}H_{21}FNO_2S$ $[M+H]^+$ 382.1272, found: 382.1269.



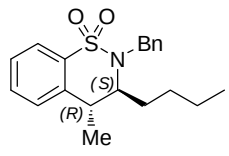
(+)-*N*-Benzyl-3,4-dihydro-3-(4-chlorophenyl)-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2f): 70 mg, 89% yield (0.2 mmol scale), 92% ee, white solid, mp 120-122 °C, $[\alpha]^{20}_D$ = +82.99 (*c* 0.70, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 1H), 7.54-7.47 (m, 2H), 7.34-7.30 (m, 5H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.04-7.03 (m, 1H), 6.48 (d, *J* = 8.4 Hz, 2H), 5.15-5.11 (m, 1H), 4.27-4.23 (m, 2H), 3.51-3.47 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.1, 135.8, 134.2, 134.0, 132.4, 129.3, 128.9, 128.8, 128.6, 127.9, 127.2, 126.2, 121.5, 64.1, 47.4, 33.3, 14.2. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 90/10, flow = 0.7 mL/min, retention time 13.8 min (maj) and 14.7 min. HRMS Calculated for $C_{22}H_{21}ClNO_2S$ $[M+H]^+$ 398.0976, found: 398.0973.



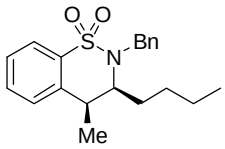
(+)-*N*-Benzyl-3,4-dihydro-3-(4-bromophenyl)-4-methyl-2*H*-1λ^6-benzo[*e*][1,2]thiazine 1,1-dioxide (2g): 75 mg, 85% yield (0.2 mmol scale), 90% ee, white solid, mp 118-119 °C, $[\alpha]^{20}_D$ = +65.91 (*c* 1.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 1H), 7.53-7.47 (m, 2H), 7.37-7.26 (m, 7H), 7.08-7.02 (m, 1H), 6.44-6.41 (m, 2H), 5.15-5.11 (m, 1H), 4.25-4.22 (m, 2H), 3.51-3.47 (m, 1H), 1.01 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.0, 135.8, 134.5, 132.4, 131.5, 129.6, 128.9, 128.7, 127.9, 127.2, 126.2, 122.4, 121.5, 64.2, 47.4, 33.2, 14.2. HPLC: Chiracel AD-H column, 220 nm, 30 °C, *n*-hexane/*i*-propanol = 80/20, flow = 0.7 mL/min, retention time 23.7 min and 29.6 min (maj). HRMS Calculated for $C_{22}H_{21}BrNO_2S$ $[M+H]^+$ 442.0476, found: 442.0450.



(3*S*,4*R*)-(-)-*N*-Benzyl-3-*n*-butyl-4-methyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (2h): 39 mg, 57% yield (0.2 mmol scale), 85% ee, colorless oil, $[\alpha]^{20}_D$ = -34.66 (*c* 0.75, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 1H), 7.30-7.25 (m, 6H), 4.22-4.13 (m, 2H), 3.28-3.23 (m, 1H), 3.00-2.93 (m, 1H), 1.85-1.82 (m, 1H), 1.68-1.64 (m, 1H), 1.30-1.23 (m, 4H), 1.16-1.12 (m, 3H), 0.77 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 136.6, 136.2, 132.2, 129.1, 128.3, 127.9, 127.7, 126.9, 124.5, 64.6, 51.6, 34.8, 32.8, 28.4, 22.4, 19.3, 13.9. HPLC: Chiracel OD-H column, 220 nm, 30 °C, *n*-hexane/*i*-propanol = 95/5, flow = 0.7 mL/min, retention time 12.5 min (maj) and 13.2 min. HRMS Calculated for $C_{20}H_{26}NO_2S$ $[M+H]^+$ 344.1679, found: 344.1674. To futher confirm the relative configuration, 2D-NMR spectra including the NOESY and COSY were run. No NOE cross peak between C-3 H and C-4 H was observed in NOESY spectra, which indicates relative configuration of C-3 H and C-4 H is *trans* configuration. The absolute configuration was assigned by comparison with the analogue.

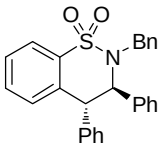


(3*S*,4*S*)-(-)-*N*-Benzyl-3-*n*-butyl-4-methyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (2h´): 24 mg, 35% yield (0.2 mmol scale), 91% ee, colorless oil, $[\alpha]^{20}_{D}$ = -36.89 (*c* 0.45, $CHCl_3$).



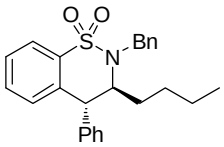
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.50-7.26 (m, 8H), 4.71-4.67 (m, 1H), 4.51-4.47 (m, 1H), 4.02-3.97 (m, 1H), 3.21-3.15 (m, 1H), 1.79-1.71 (m, 1H), 1.60-1.49 (m, 1H), 1.38-1.31 (m, 4H), 1.28-1.12 (m, 3H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.3, 136.9, 132.1, 128.5, 128.3, 127.8, 127.5, 127.5, 124.5, 60.3, 49.8, 34.5, 28.8, 28.2, 22.4, 16.9, 13.9. HPLC: Chiracel OD-H column, 220 nm, 30 °C, *n*-hexane/*i*-propanol = 95/5, flow = 0.7 mL/min, retention time 18.7 min (maj) and 24.6 min. HRMS Calculated for $C_{20}H_{26}NO_2S$ $[M+H]^+$ 344.1679, found: 344.1674. To futher confirm the relative configuration, 2D-NMR spectra including the NOESY and COSY spectrum were run. A NOE cross peak (4.00, 3.18) between C-3 H and C-4 H was observed in NOESY spectra, which indicates relative configuration of C-3 H and C-3 H is *cis* configuration. The absolute configuration was assigned by comparison with the analogue.

(-)-*N*-Benzyl-3-phenyl-4-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (2i): 72 mg, 85% yield (0.2 mmol scale), 97% ee, white solid, mp 137-138 °C, $[\alpha]^{20}_{D}$ = -76.58 (*c* 1.55, $CHCl_3$).



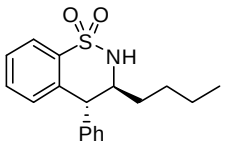
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32-7.20 (m, 7H), 7.14-7.03 (m, 5H), 6.58 (d, *J* = 7.4 Hz, 2H), 6.43 (d, *J* = 7.6 Hz, 2H), 5.41 (d, *J* = 6.2 Hz, 1H), 5.18-5.14 (m, 1H), 4.45 (d, *J* = 6.2 Hz, 1H), 3.62-3.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 136.8, 136.7, 136.6, 135.4, 132.9, 132.4, 129.9, 129.8, 129.5, 129.5, 129.0, 128.9, 128.7, 128.7, 128.6, 128.1, 122.7, 66.3, 48.6, 48.1.HPLC: Chiracel OD-H column, 220 nm, 30 °C, *n*-hexane/*i*-propanol = 80/20, flow = 0.7 mL/min, retention time 13.1 min (maj) and 17.7 min. HRMS Calculated for $C_{27}H_{24}NO_2S$ $[M+H]^+$ 426.1522, found: 426.1514.

(-)-*N*-Benzyl-3-*n*-Butyl-4-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (2j): 72 mg, 89% yield (0.2 mmol scale), 99% ee, white solid, mp 118-119 °C, $[\alpha]^{20}_{D}$ = -112.55 (*c* 0.90, $CHCl_3$).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 1H), 7.39-7.23 (m, 10H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), 4.28 (s, 2H), 4.08-4.07 (m, 2H), 1.72-1.66 (m, 1H), 1.45-1.40 (m, 1H), 1.19-1.17 (m, 1H), 1.04-0.85 (m, 3H), 0.60 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.5, 136.8, 136.6, 132.1, 130.1, 129.6, 129.0, 128.8, 128.3, 127.6, 127.5, 127.1, 124.4, 64.5, 51.0, 47.4, 32.4, 28.1, 22.0, 13.7. HPLC: Chiracel OD-H column, 220 nm, 30 °C, *n*-hexane/*i*-propanol = 80/20, flow = 0.7 mL/min, retention time 6.9 min and 20.3 min (maj). HRMS Calculated for $C_{25}H_{28}NO_2S$ $[M+H]^+$ 406.1835, found: 406.1834.

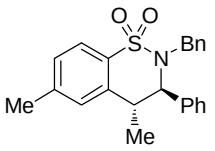
(3*S*,4*R*)-(-)-3-*n*-Butyl-4-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (2j´): 59 mg, 89% yield (0.2 mmol scale), white solid, mp 108-110 °C, $[\alpha]^{20}_{D}$ = -18.33 (*c* 0.60, $CHCl_3$). ^{1}H



NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 1H), 7.37-7.21 (m, 5H), 7.14-7.12 (m, 2H), 6.72-6.71 (m, 1H), 4.87-4.84 (m, 1H), 4.04-3.95 (m, 1H), 3.84-3.82 (m, 1H), 1.59-1.47 (m, 2H), 1.44-1.11 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.8, 137.3, 132.0, 130.9, 129.4, 129.1, 127.6, 127.3, 123.4, 59.2, 50.9, 32.7, 27.1, 22.1, 13.8. HRMS Calculated for $C_{18}H_{22}NO_2S$ $[M+H]^+$ 316.1366, found: 316.1368.

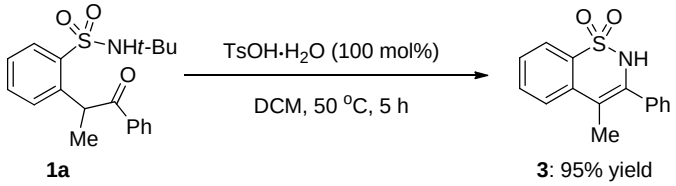
(+)-*N*-Benzyl-4,6-dimethyl-3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (2k): 70 mg, 92% yield (0.2 mmol scale), 94% ee, colorless oil, $[\alpha]^{20}_{D}$ = +43.00 (*c* 1.15, $CHCl_3$). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.41-7.21 (m, 7H), 7.15 (t, *J* = 7.5 Hz, 2H), 6.82 (s, 1H), 6.58 (d, *J* = 7.4 Hz, 2H), 5.12 (d, *J* = 15.9 Hz, 1H), 4.28-4.27 (m, 1H), 4.24-4.17 (m, 1H), 3.49 (d, *J* = 15.9 Hz, 1H), 2.37 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 137.3, 136.3, 136.2, 135.6, 129.0, 128.6, 128.3, 128.2, 128.1, 127.7, 127.4, 126.9, 121.5, 64.8, 47.3, 33.4, 21.9, 14.2. HPLC: Chiracel OD-H column, 220 nm, 30 °C, *n*-hexane/*i*-propanol = 93/7, flow = 0.7 mL/min, retention time 11.3 min and 15.0 min (maj). HRMS Calculated for $C_{23}H_{24}NO_2S$ $[M+H]^+$ 378.1522, found: 378.1529.



4. Control Experiments

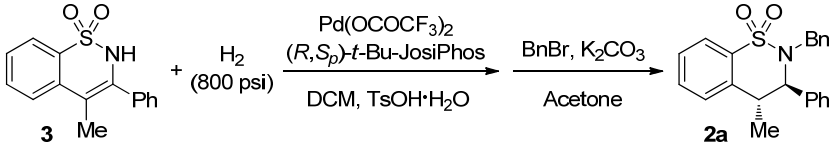
Enesulfonamide intermidate **3** can be synthesized from the keto sulfonamide **1a** according to the following procedures.



1a **3**: 95% yield

To a solution of keto sulfonamides **1a** (69 mg, 0.20 mmol) in dichloromethane (5.0 mL) was added *para*-toluenesulfonic acid monohydrate (38 mg, 0.20 mmol). Then the resulting solution was stirred for 5 hours at 50 °C. The reaction mixture was evaporated. Purification was performed on silica gel using *n*-hexanes/ethyl acetate as the eluent to give the enesulfonamide product **3**.

4-Methyl-3-phenyl-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide (3): 50 mg, 95% yield (0.2 mmol scale), white solid, mp 122-123 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.5 Hz, 2H), 7.93-7.89 (m, 2H), 7.70-7.66 (m, 1H), 7.60-7.57 (m, 1H), 7.54-7.45 (m, 3H), 2.89 (s, 1H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.0, 134.9, 132.4, 132.1, 130.0, 129.6, 128.6, 127.3, 125.3, 121.2, 112.7, 15.7. HRMS Calculated for $C_{15}H_{14}NO_2S$ $[M+H]^+$ 272.0740, found: 272.0740.



The *in situ* prapared bisphosphine ligand (*R*,S_p)-*t*-Bu-JosiPhos (3.6 mg, 0.0066 mmol) and $Pd(OCOCF_3)_2$ (2.0 mg, 0.006 mmol) complex was taken into a glove box and added to the mixture of enesulfonamide **3** (0.2 mmol) and *para*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) in dichloromethane. Then, the mixture was transferred to an autoclave, which was charged hydrogen gas (800 psi). The autoclave was stirred at 100 °C for 48 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. To a solution of the crude product in acetone (5.0 mL) was added benzyl bromide (30 uL, 0.25 mmol), potassium carbonate (69 mg, 0.50 mmol). Then the mixture was heated to reflux for overnight. The reaction mixture was evaporated. Purification was performed on silica gel using *n*-hexane/ethyl acetate as the eluent to give the chiral product **2a** 65 mg, 89% yield, 92% ee.

5. Determination of Absolute Configurations

The single crystal of (-)-3-*n*-butyl-4-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,2]thiazine 1,1-dioxide **2j´** was grown from the solution of *n*-hexane and diethyl ether, which is suitable for X-ray diffraction analysis. The structure in **Figure S1** showed that the absolute configuration of (-)-**2j´** is (3*S*,4*R*). [CCDC 1469313] contains the structure and supplementary crystallographic data for (-)-**2j´**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

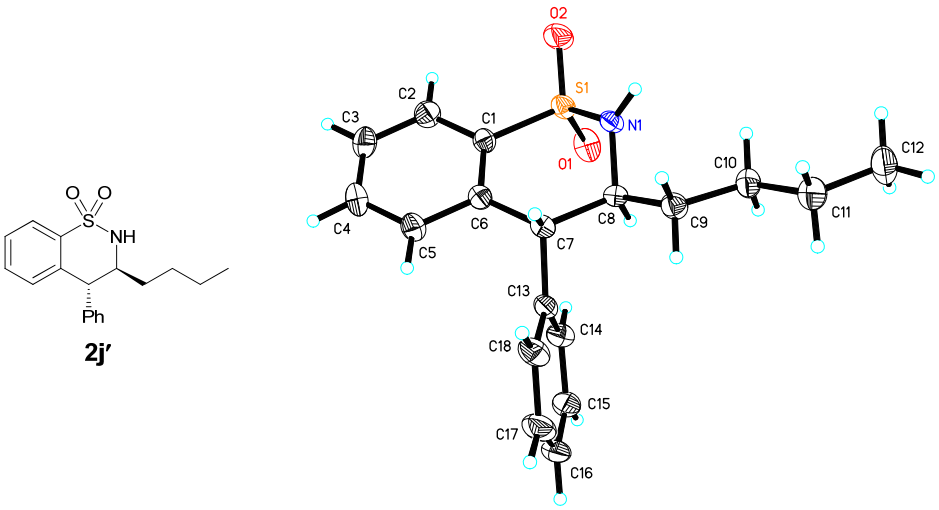
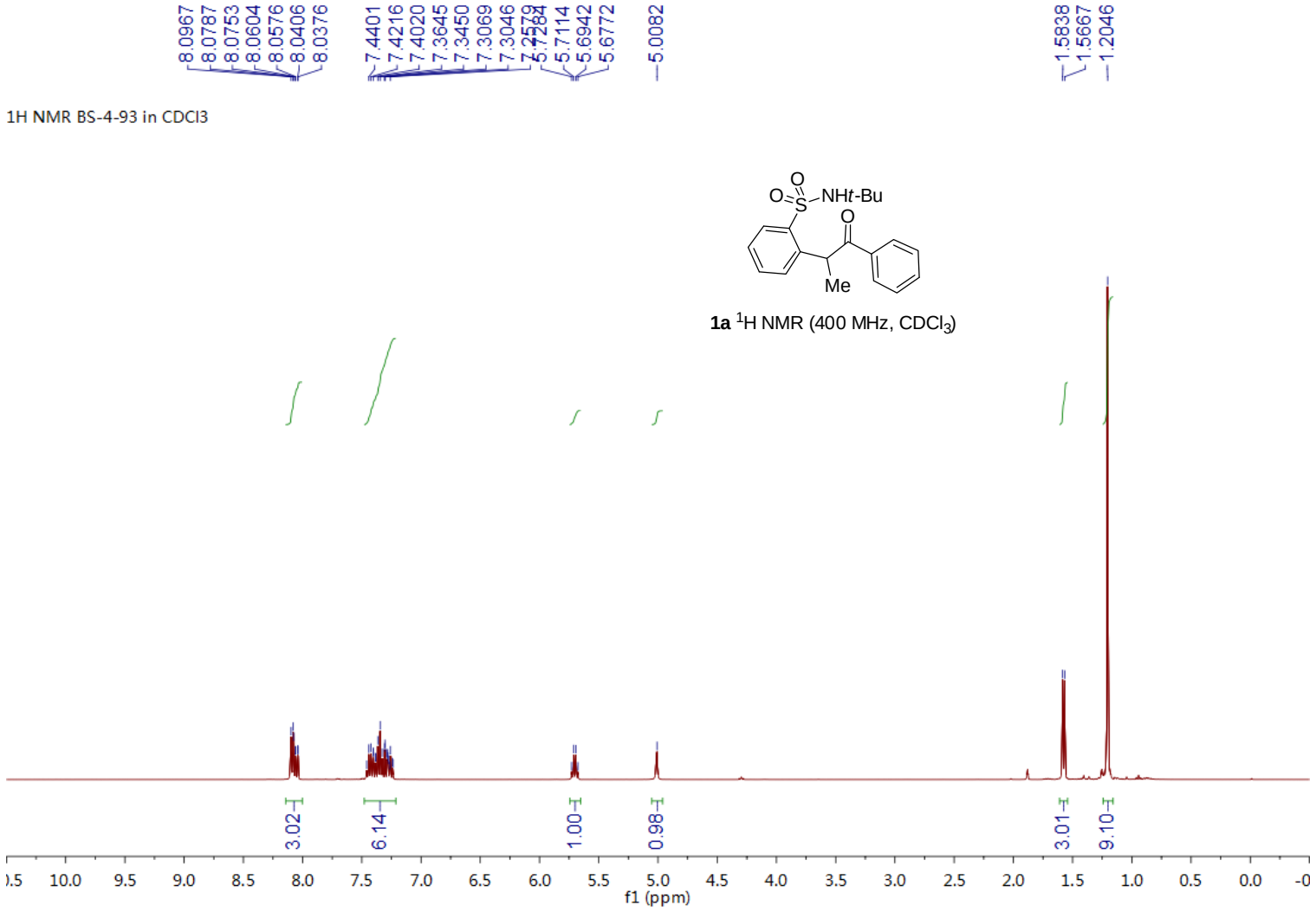


Figure S2. X-ray crystallographic analysis of (3*S*,4*R*)-(-)-**2j´**

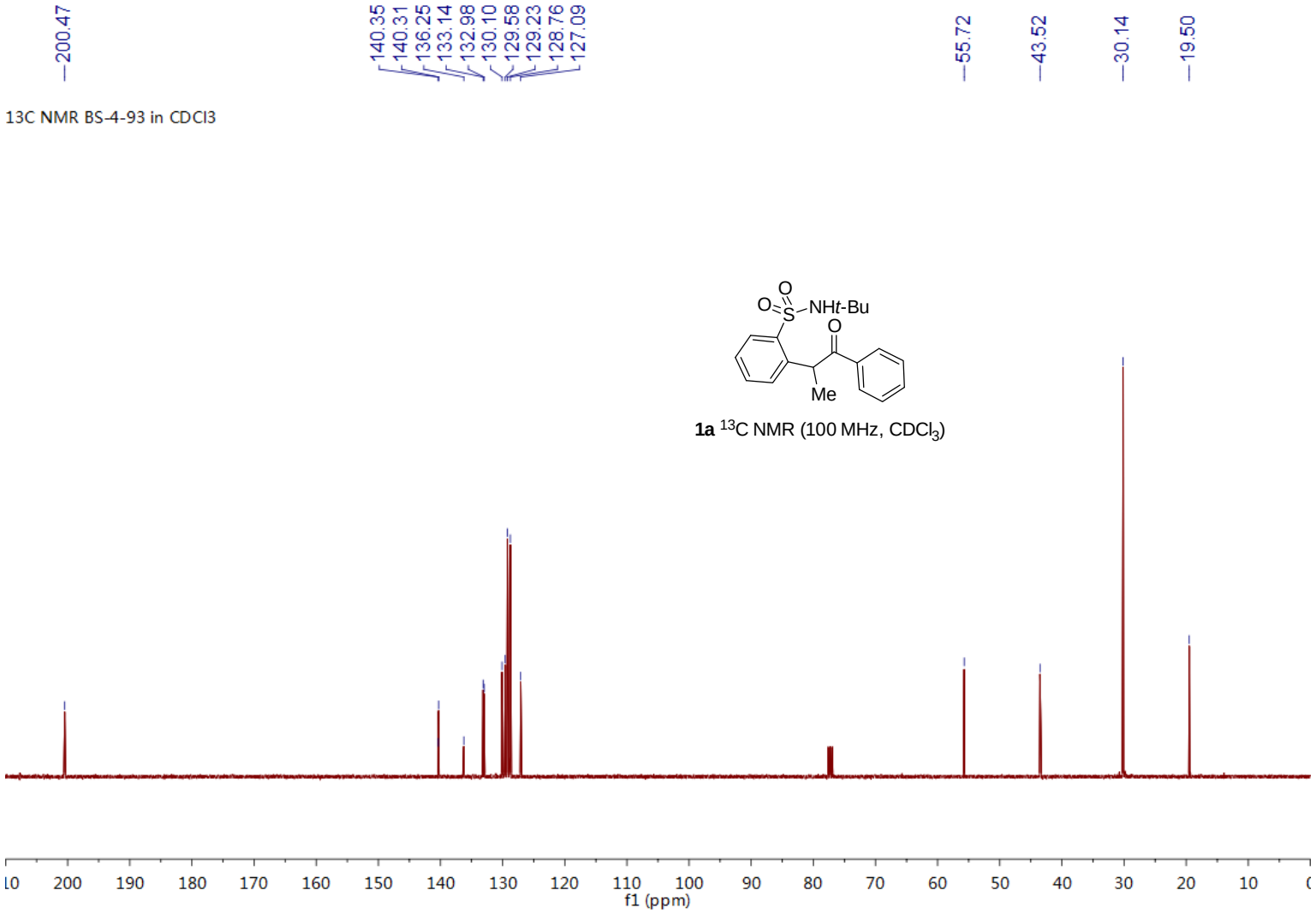
6. References

1) C.-B. Yu, K. Gao, D.-S. Wang, L. Shi and Y.-G. Zhou, *Chem. Commun.*, 2011, **47**, 5052.

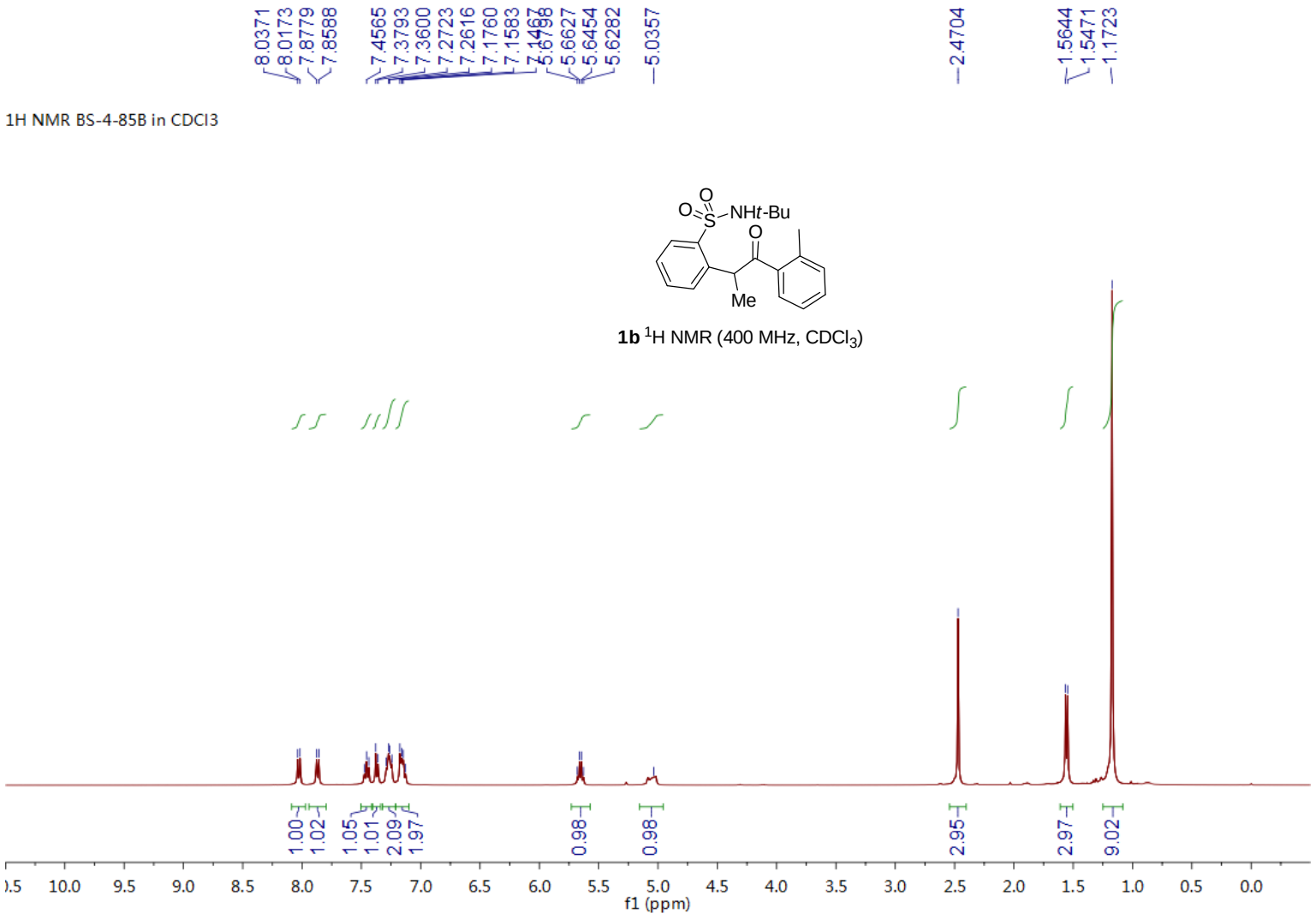
7. Copy of NMR and HPLC for the Compounds



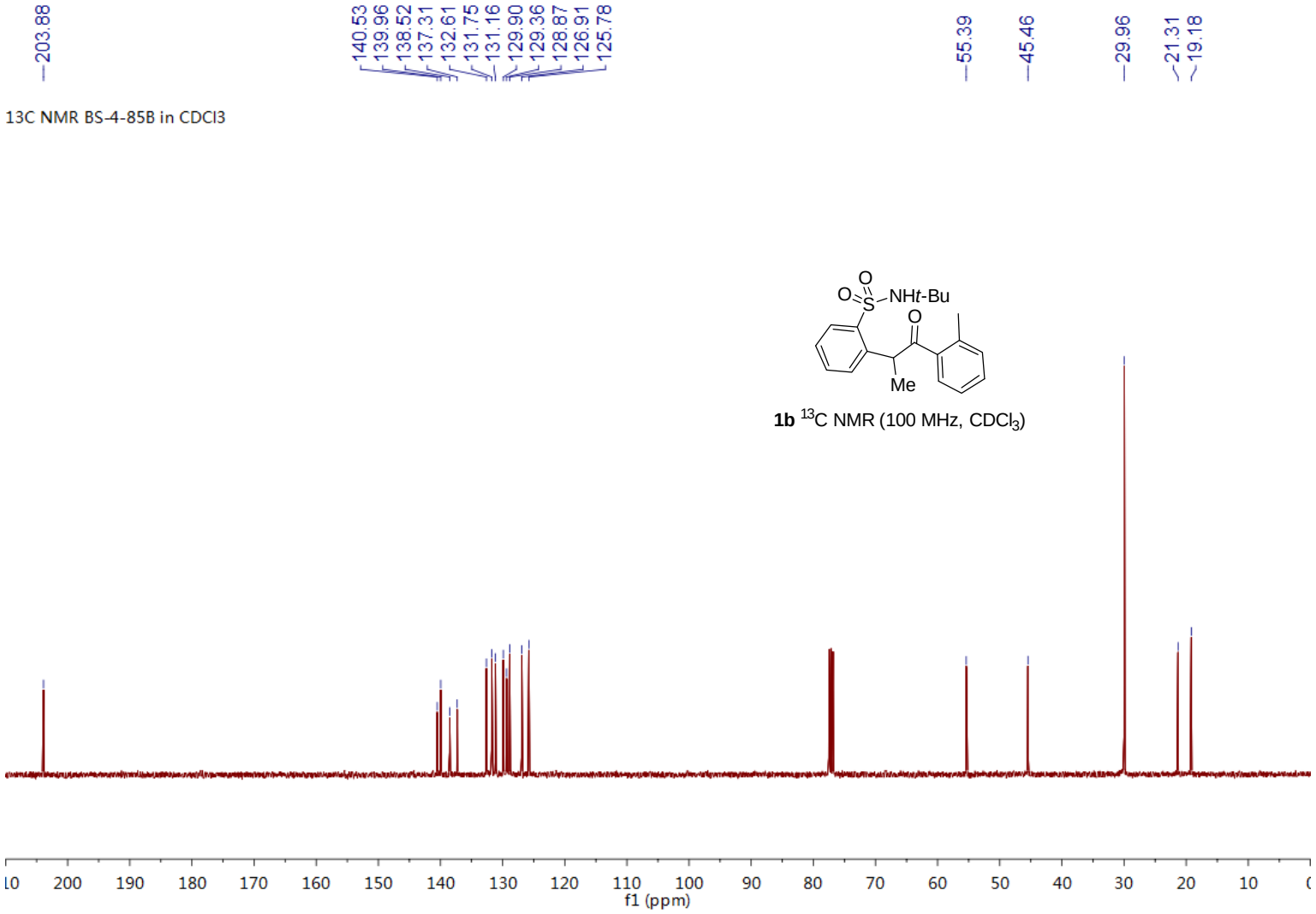
1a ^{1}H NMR (400 MHz, $CDCl_3$)



1a ^{13}C NMR (100 MHz, $CDCl_3$)

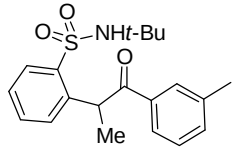


1b ^{1}H NMR (400 MHz, $CDCl_3$)

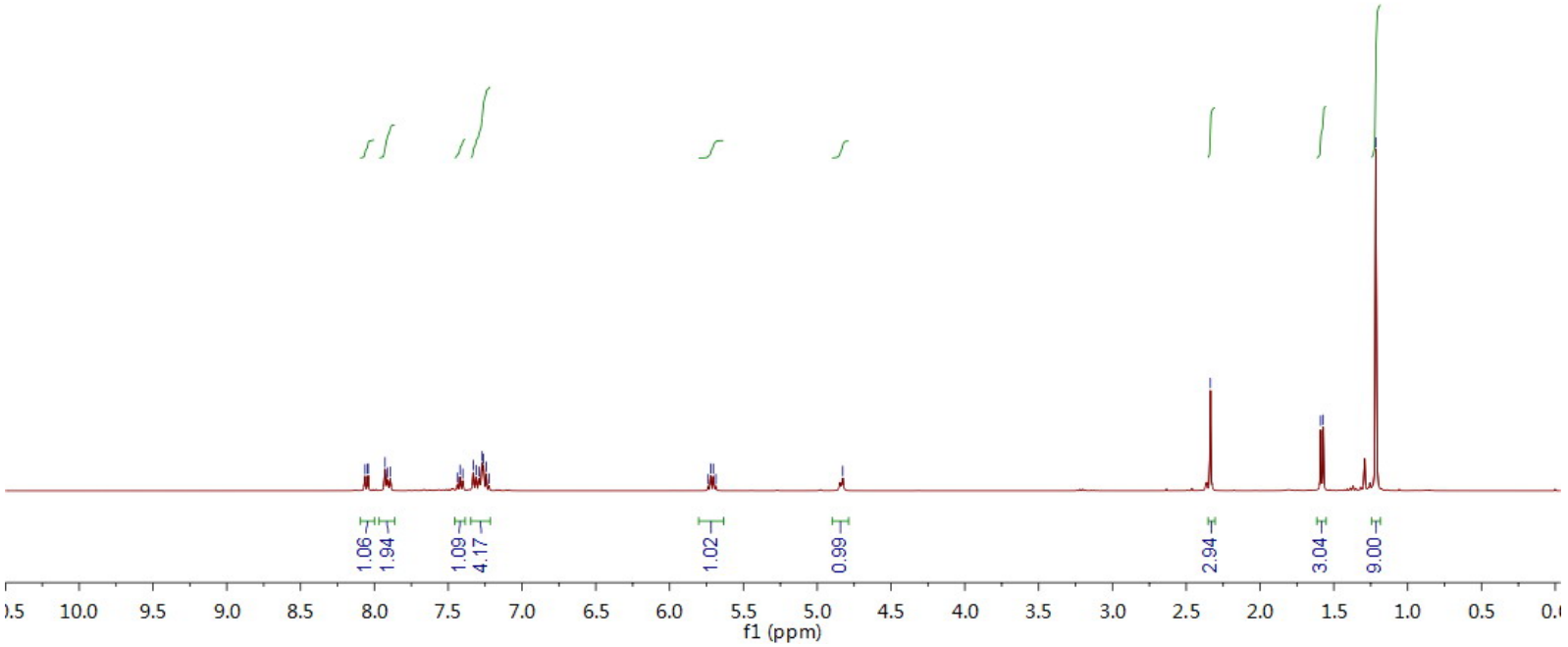


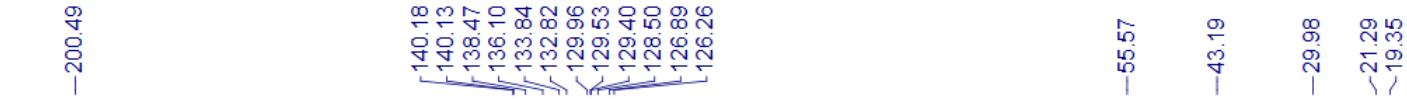
1b ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR BS-4-85C in CDCL3

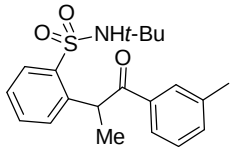


1c ^{1}H NMR (400 MHz, $CDCl_3$)

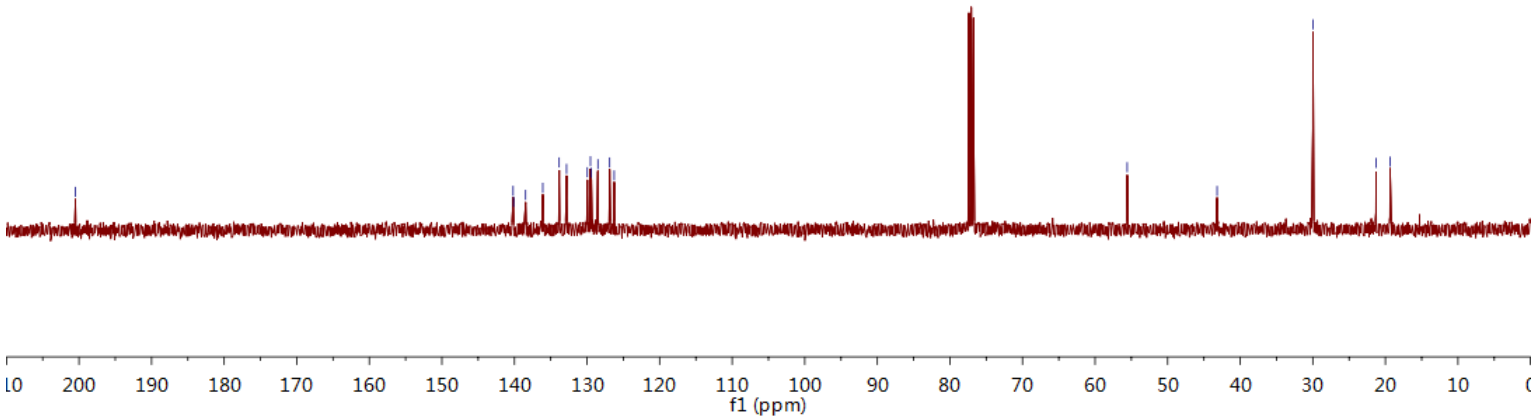


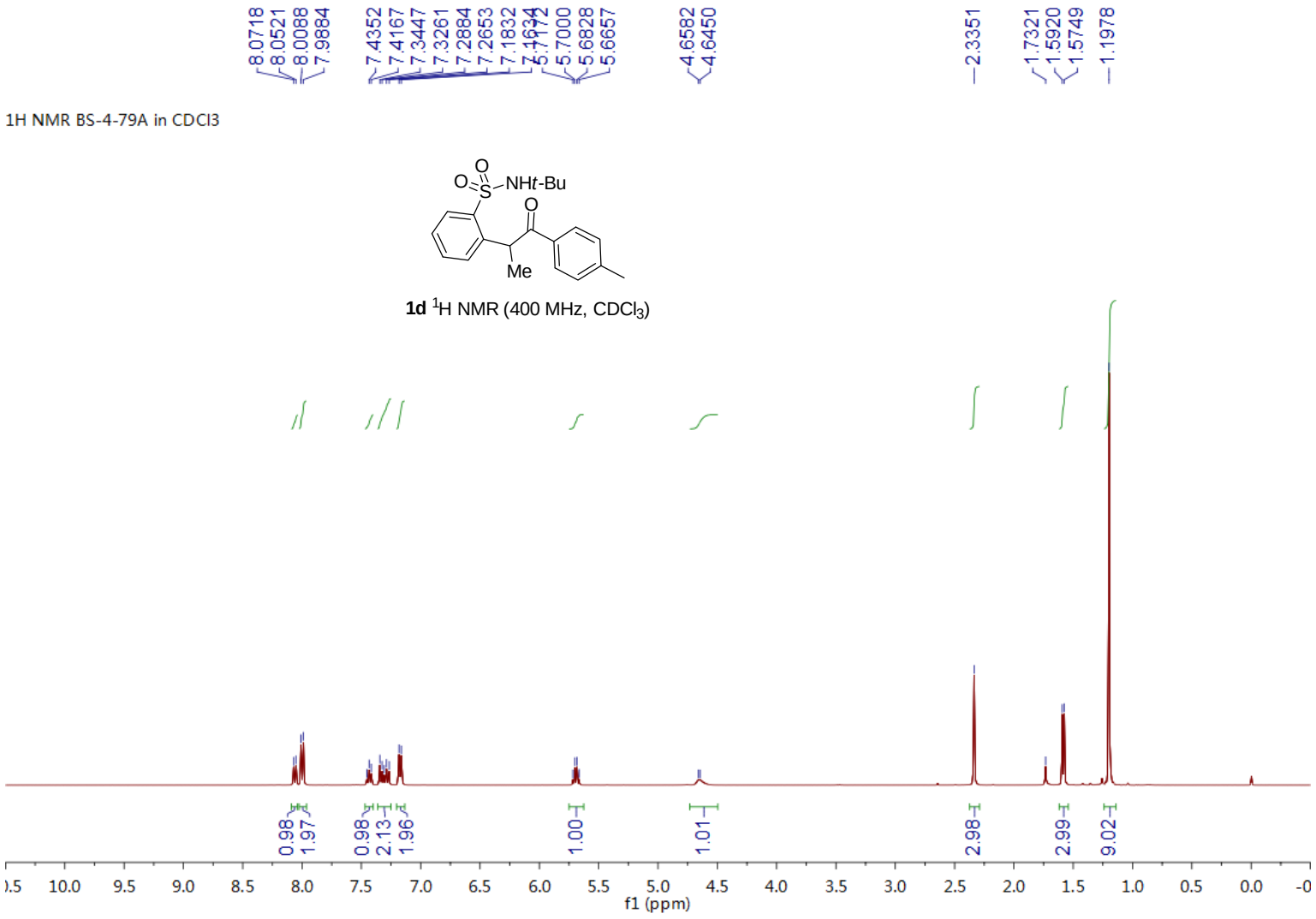


13C NMR BS-4-85C in CDCl3

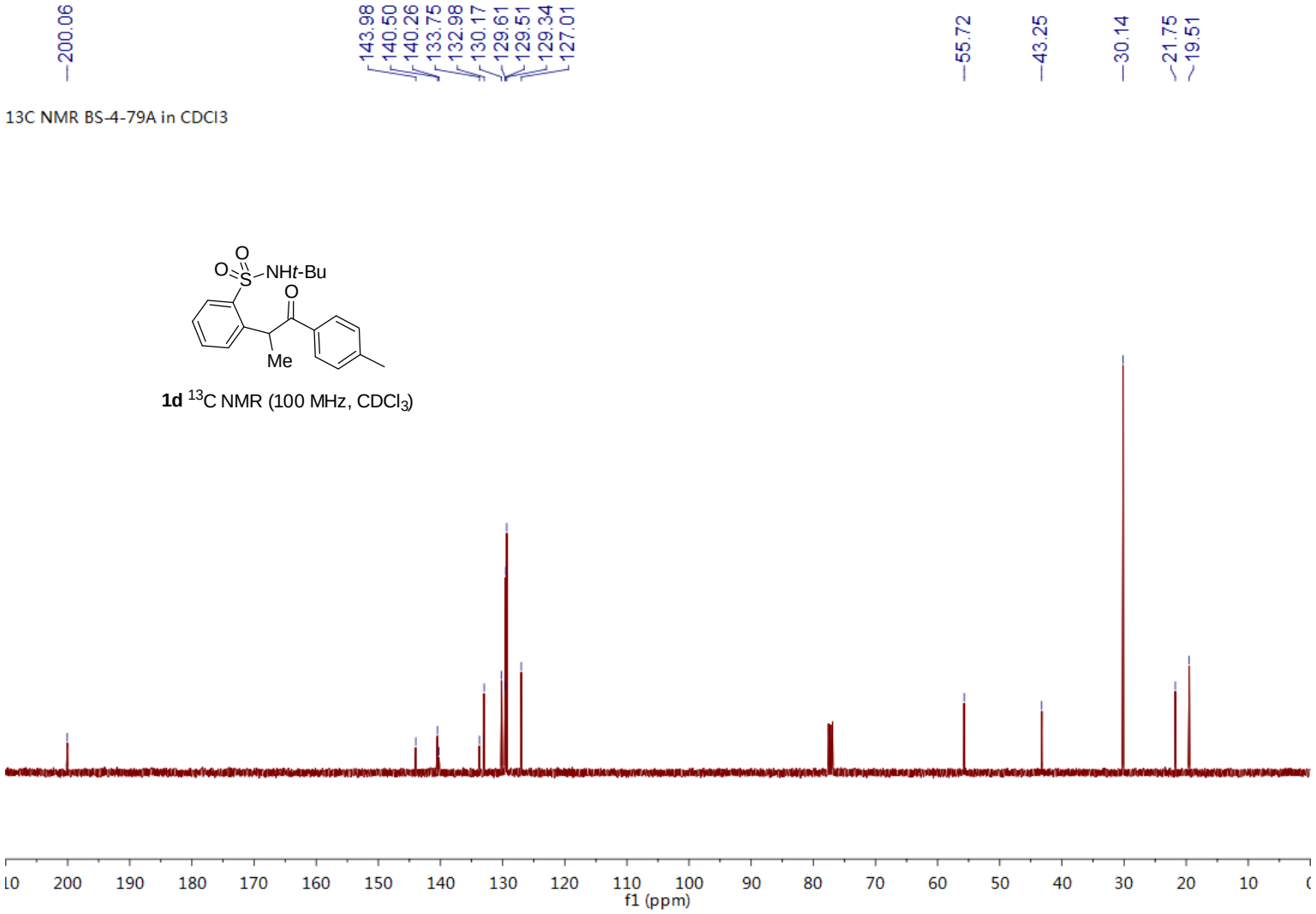


1c ^{13}C NMR (100 MHz, $CDCl_3$)

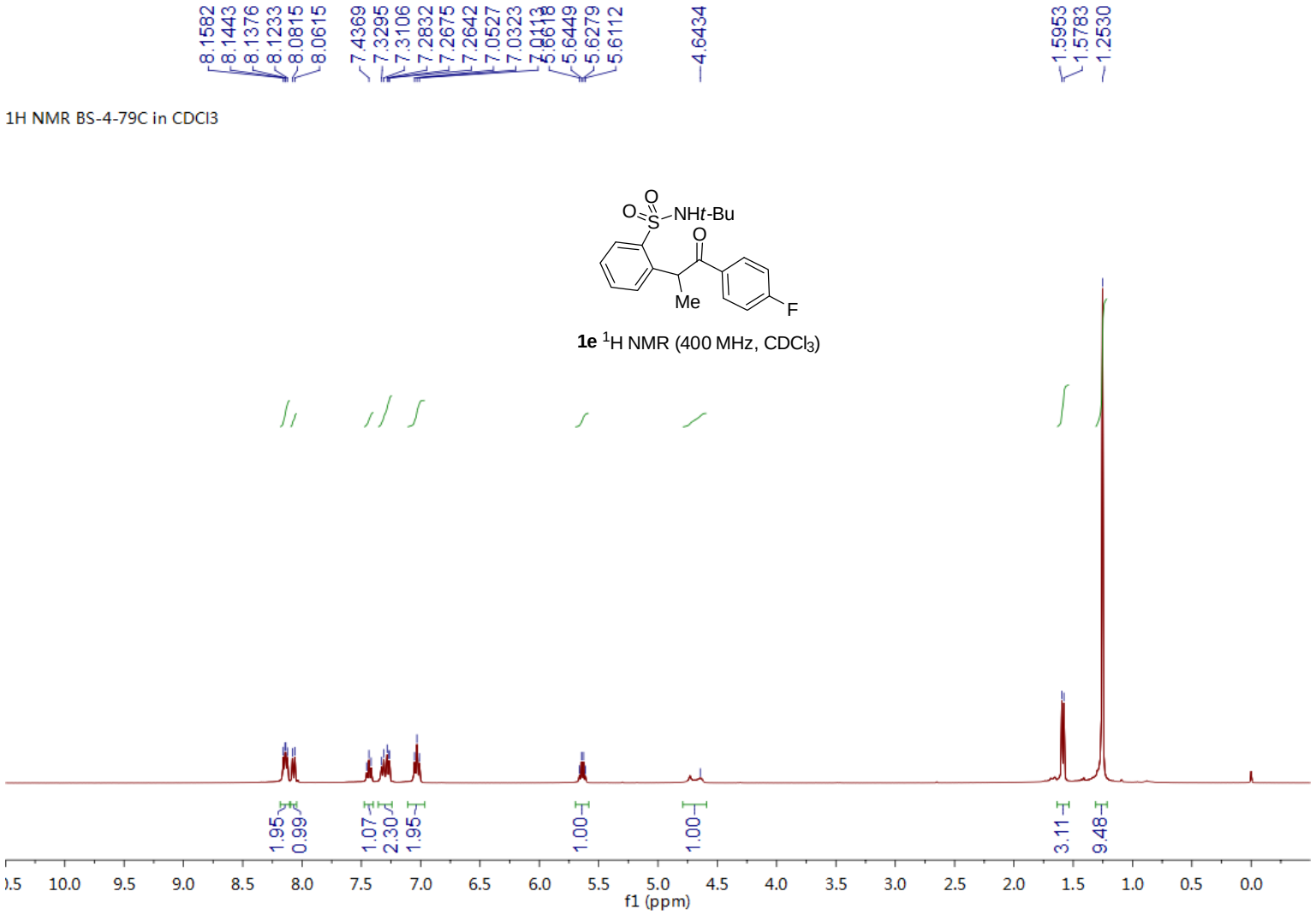




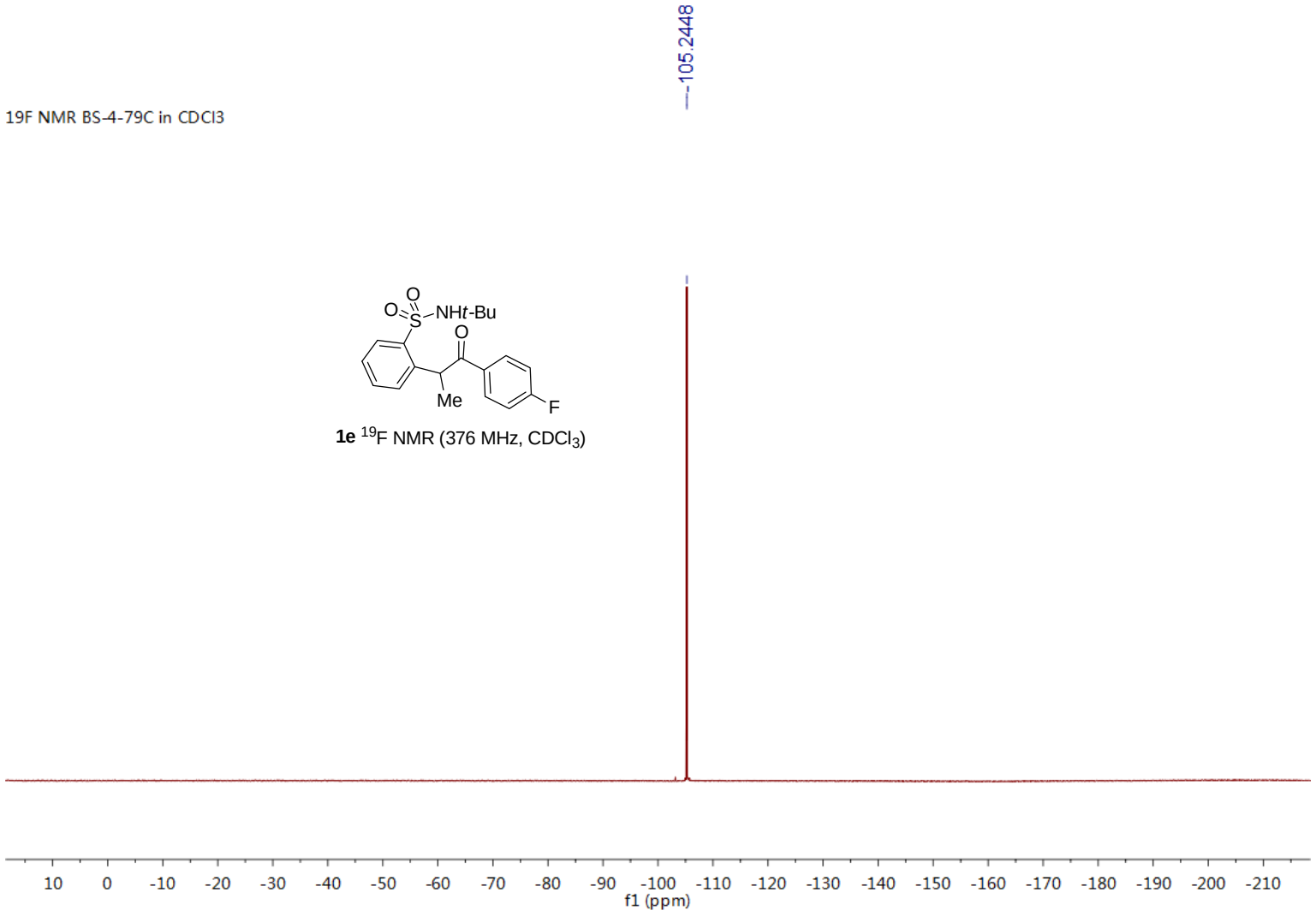
1d ^{1}H NMR (400 MHz, $CDCl_3$)



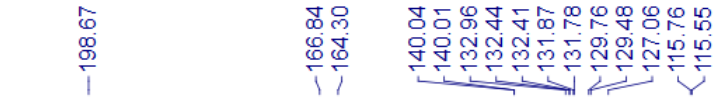
1d ^{13}C NMR (100 MHz, $CDCl_3$)


8.1582
8.1443
8.1376
8.1233
8.0815
8.0615
7.4369
7.3295
7.3106
7.2832
7.2675
7.2642
7.0527
7.0323
5.6449
5.6279
5.6112
4.6434
1.5953
1.5783
1.2530
1H NMR BS-4-79C in CDCl3
NHt-Bu
Me
F
1e 1H NMR (400 MHz, CDCl3)
1.95
0.99
1.07
2.30
1.95
1.00
1.00
3.11
9.48
f1 (ppm)

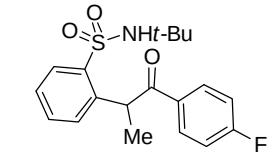
19F NMR BS-4-79C in CDCl3



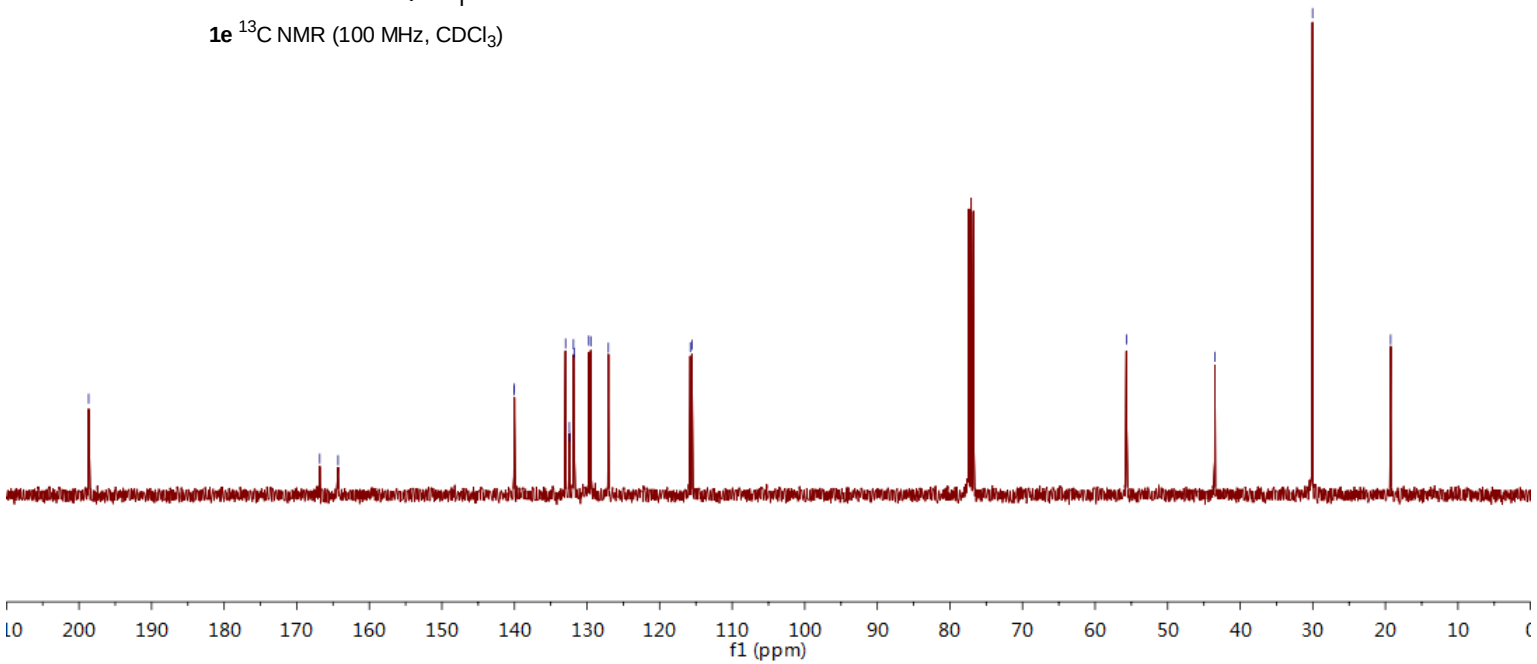
1e ^{19}F NMR (376 MHz, $CDCl_3$)

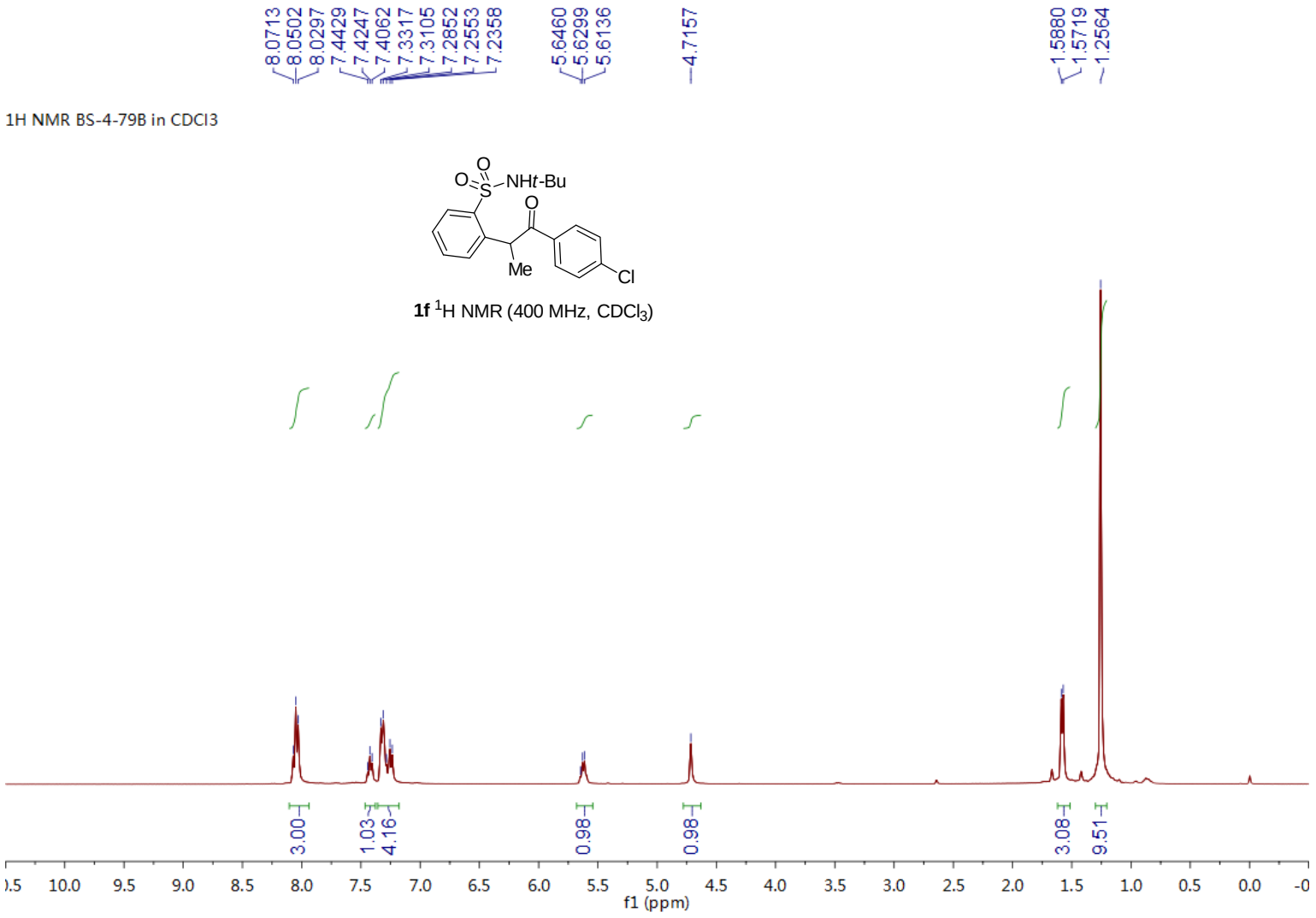


13C NMR BS-4-79C in CDCl3

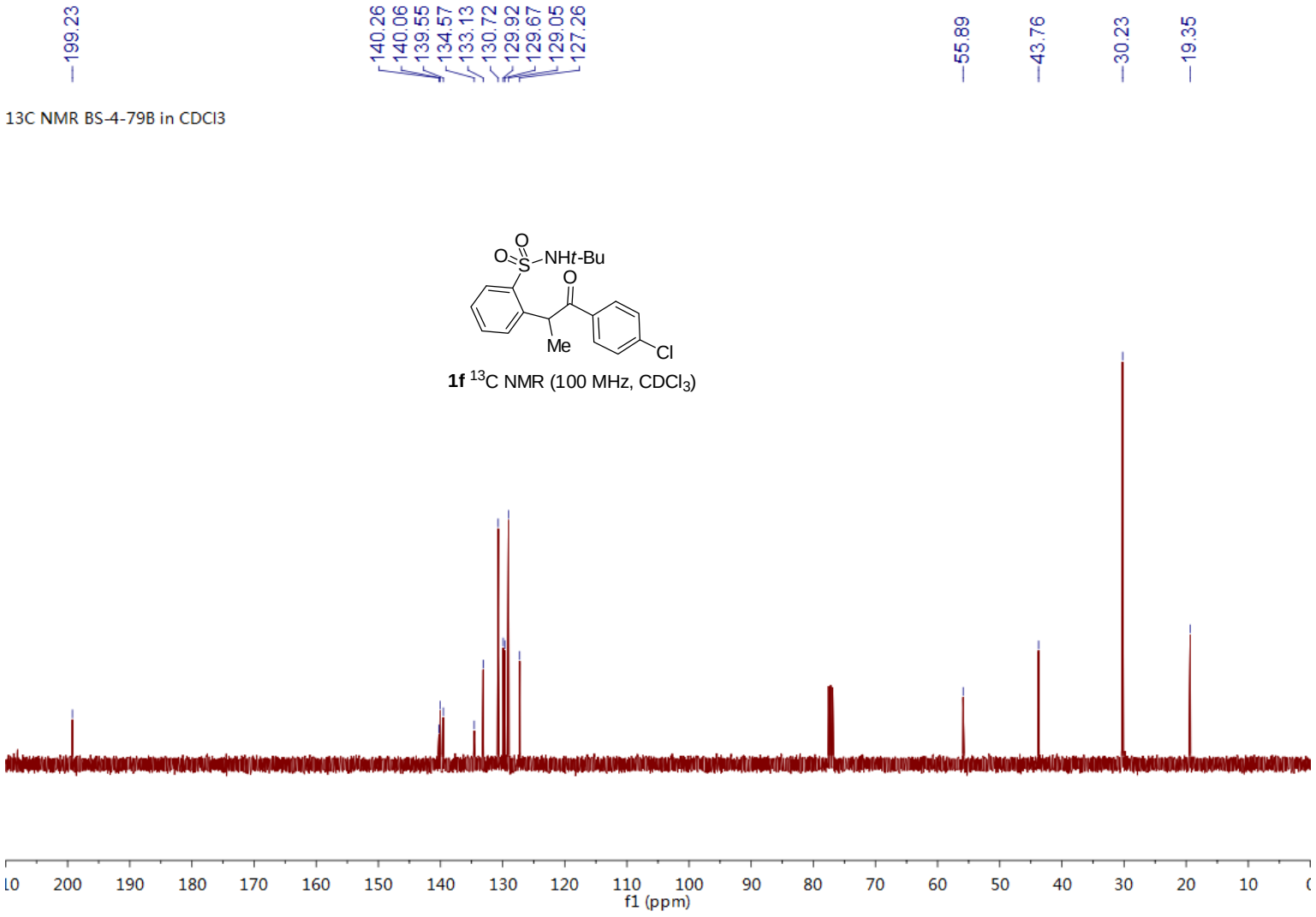


1e ^{13}C NMR (100 MHz, $CDCl_3$)

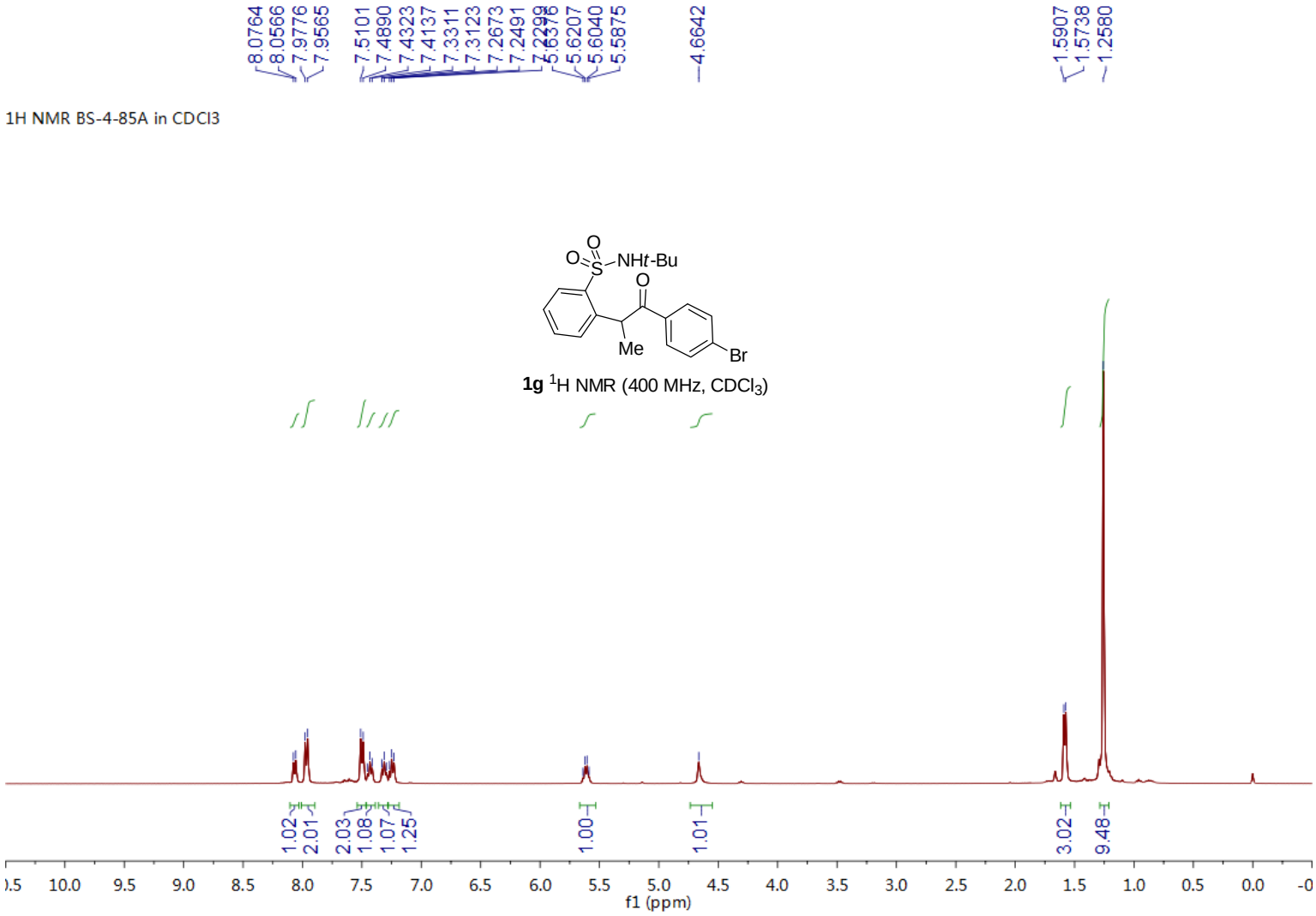


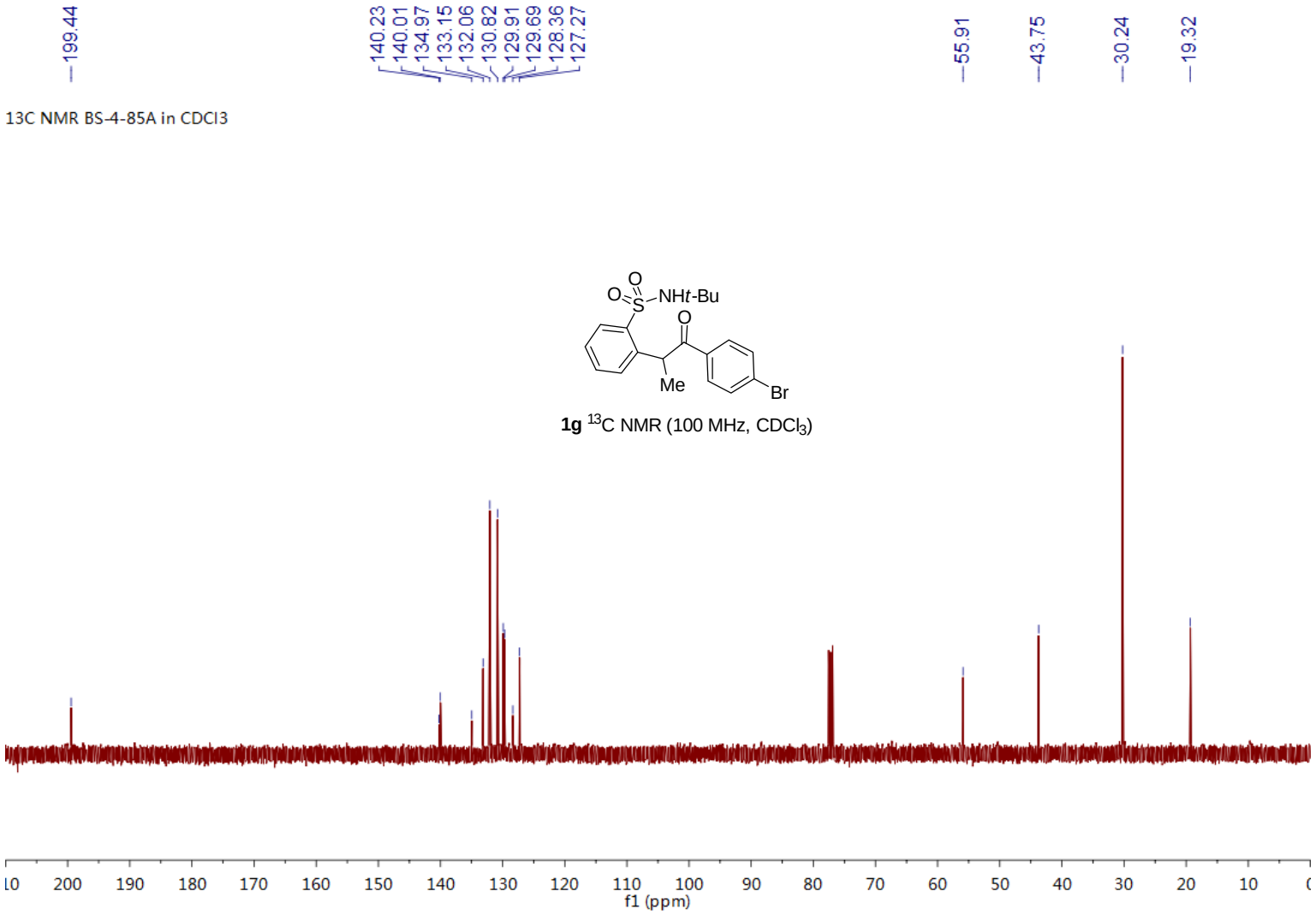


1f ^{1}H NMR (400 MHz, $CDCl_3$)

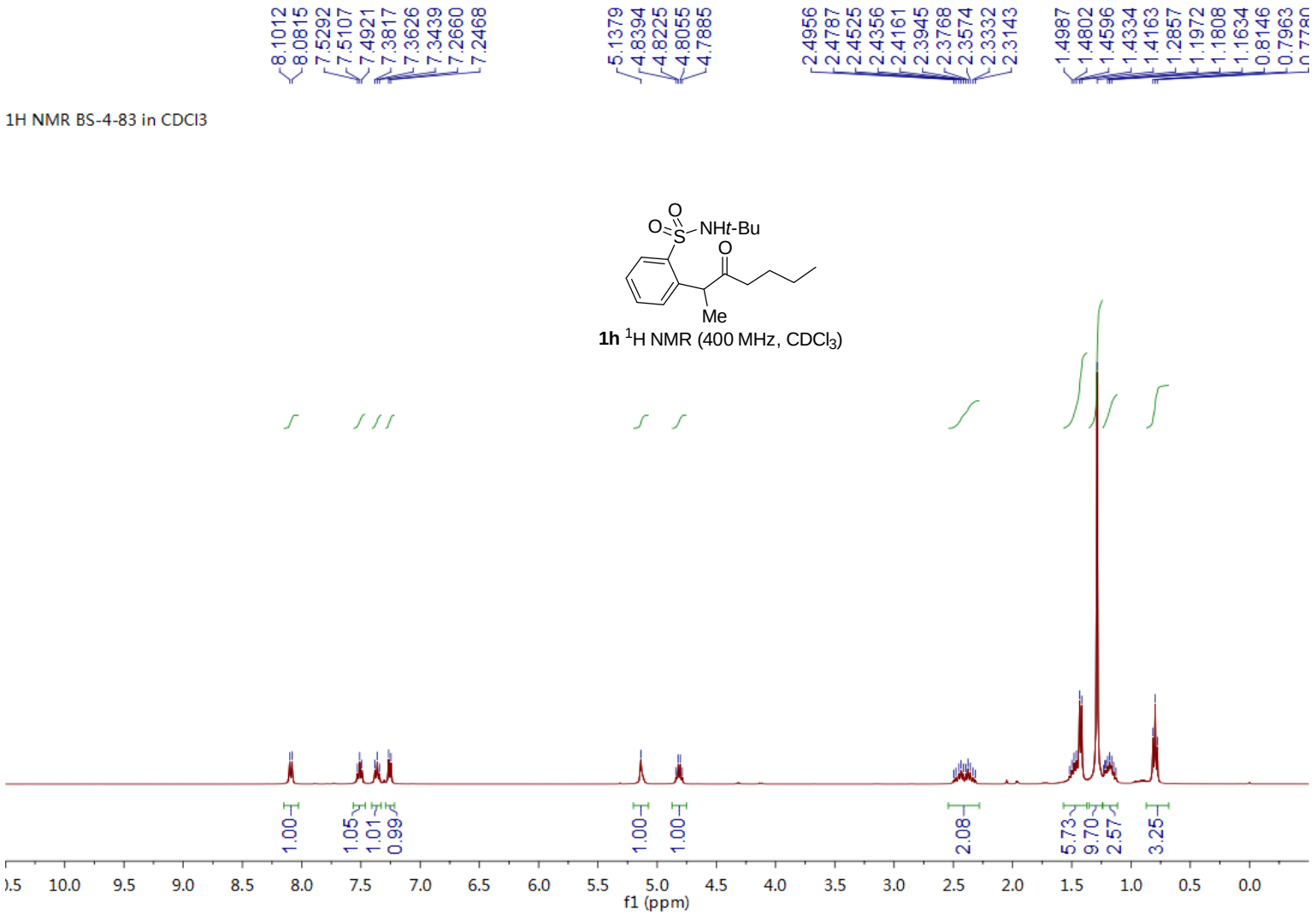


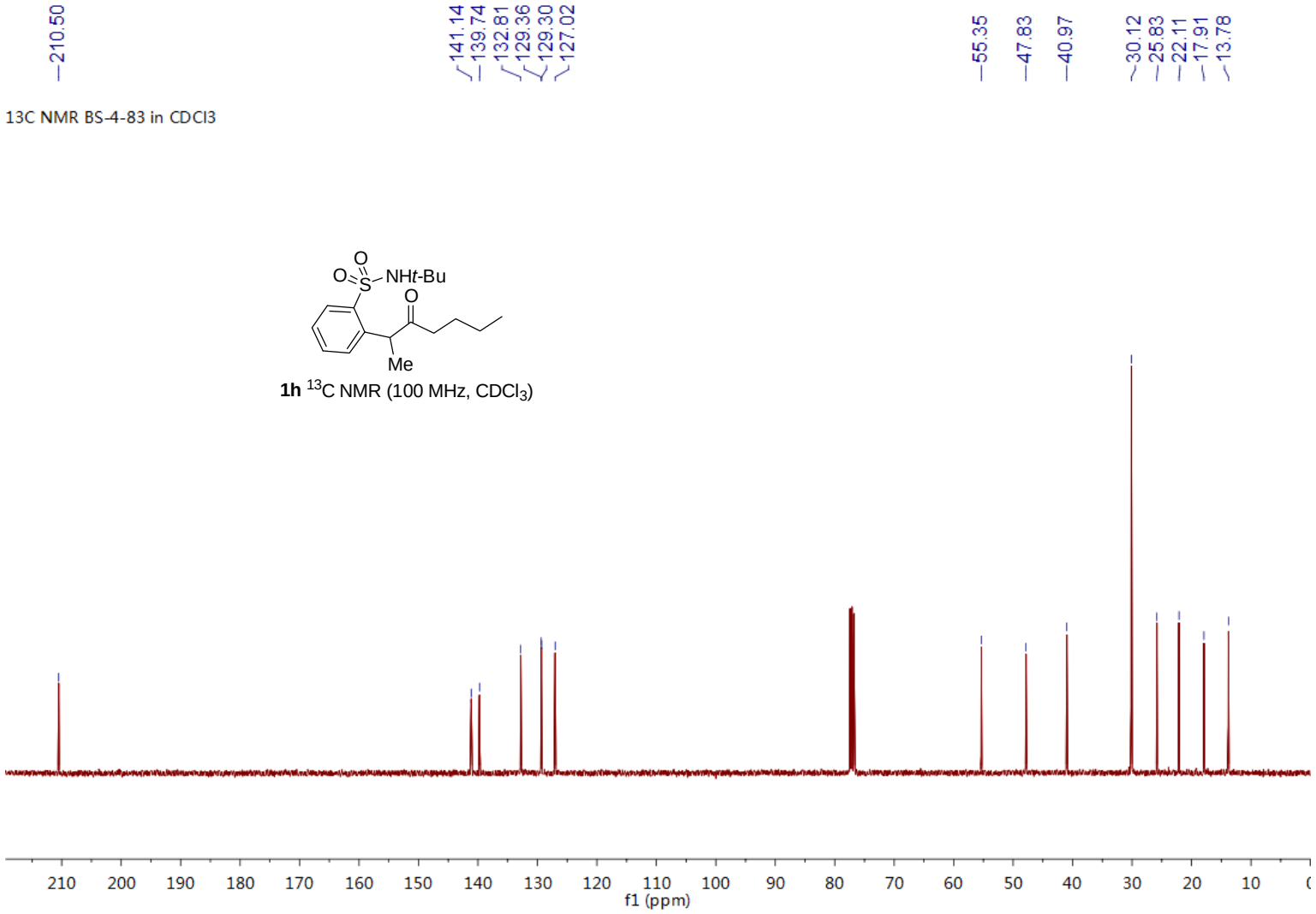
1f ^{13}C NMR (100 MHz, $CDCl_3$)


8.0764
8.0566
7.9776
7.9565
7.5101
7.4890
7.4323
7.4137
7.3311
7.3123
7.2673
7.2491
5.6207
5.6040
5.5875
4.6642
1.5907
1.5738
1.2580
1H NMR BS-4-85A in CDCl3
NHt-Bu
Me
Br
1g 1H NMR (400 MHz, CDCl3)
1.02
2.01
2.03
1.08
1.07
1.25
1.00
1.01
3.02
9.48
f1 (ppm)

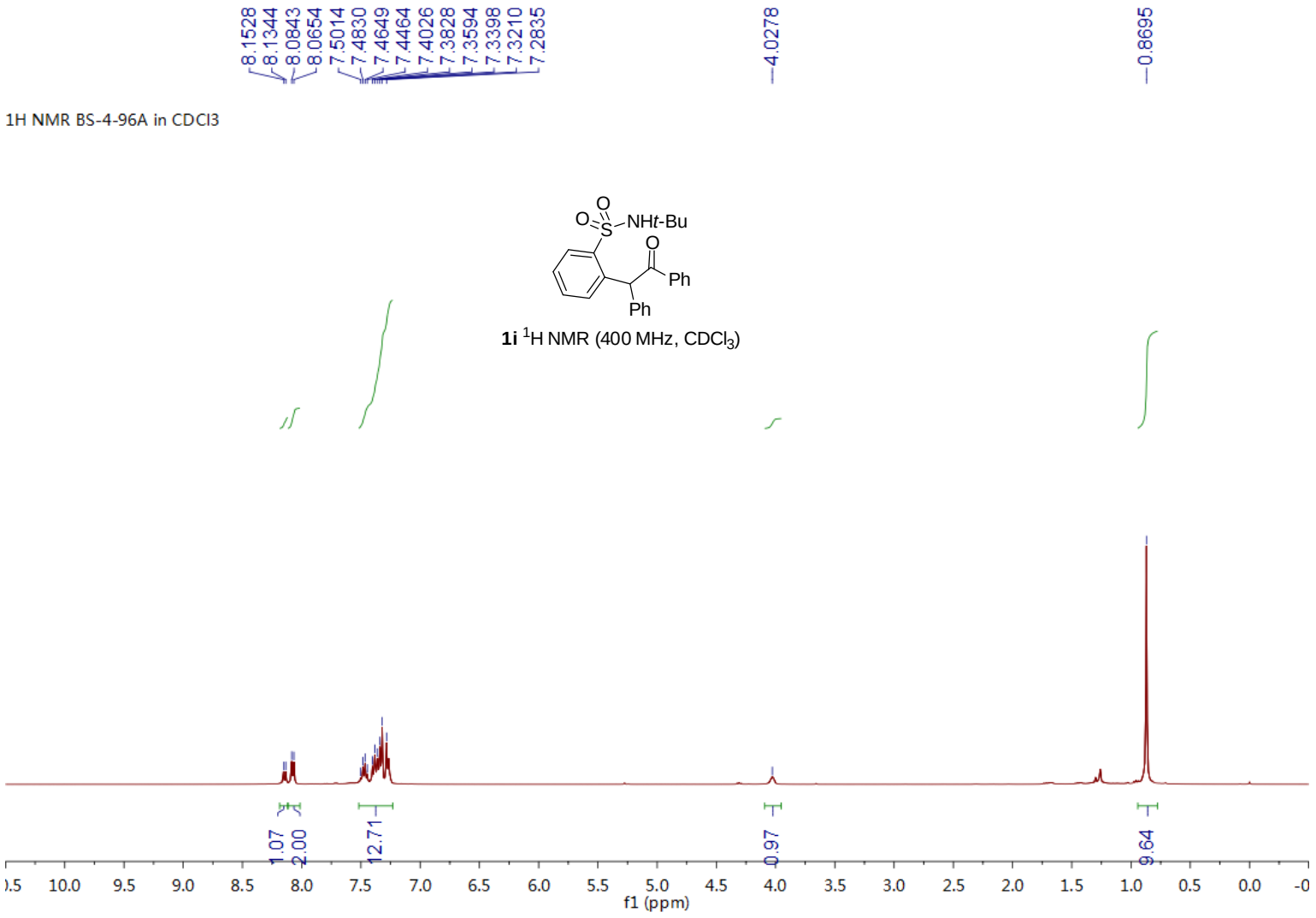


1g ^{13}C NMR (100 MHz, $CDCl_3$)

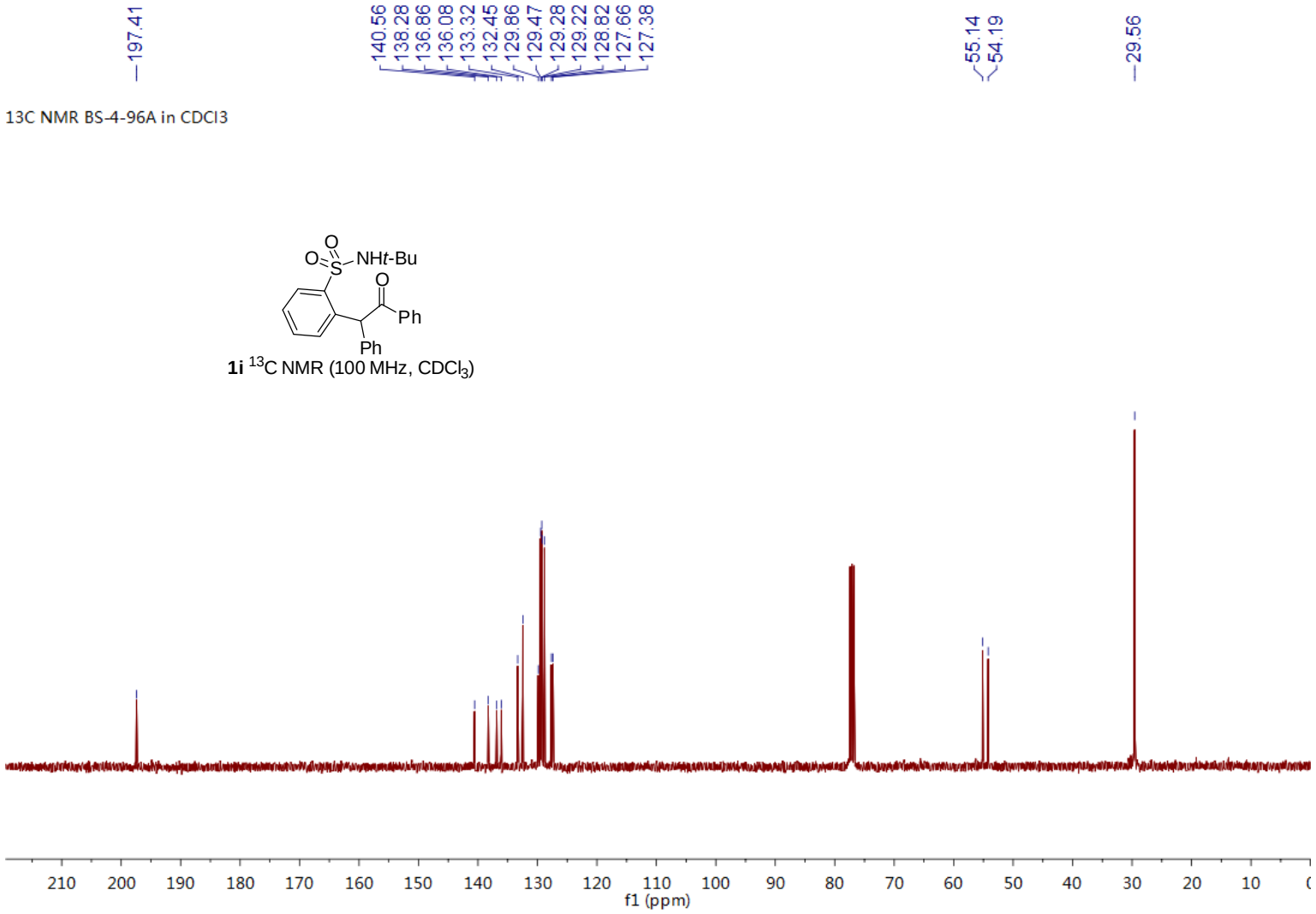

8.1012
8.0815
7.5292
7.5107
7.4921
7.3817
7.3626
7.3439
7.2660
7.2468
5.1379
4.8394
4.8225
4.8055
4.7885
2.4956
2.4787
2.4525
2.4356
2.4161
2.3945
2.3768
2.3574
2.3332
2.3143
1.4987
1.4802
1.4596
1.4334
1.4163
1.2857
1.1972
1.1808
1.1634
0.8146
0.7963
1H NMR BS-4-83 in CDCl3
O
O
S
NHt-Bu
O
Me
1h 1H NMR (400 MHz, CDCl3)
1.00
1.05
1.01
0.99
1.00
1.00
2.08
5.73
9.70
2.57
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



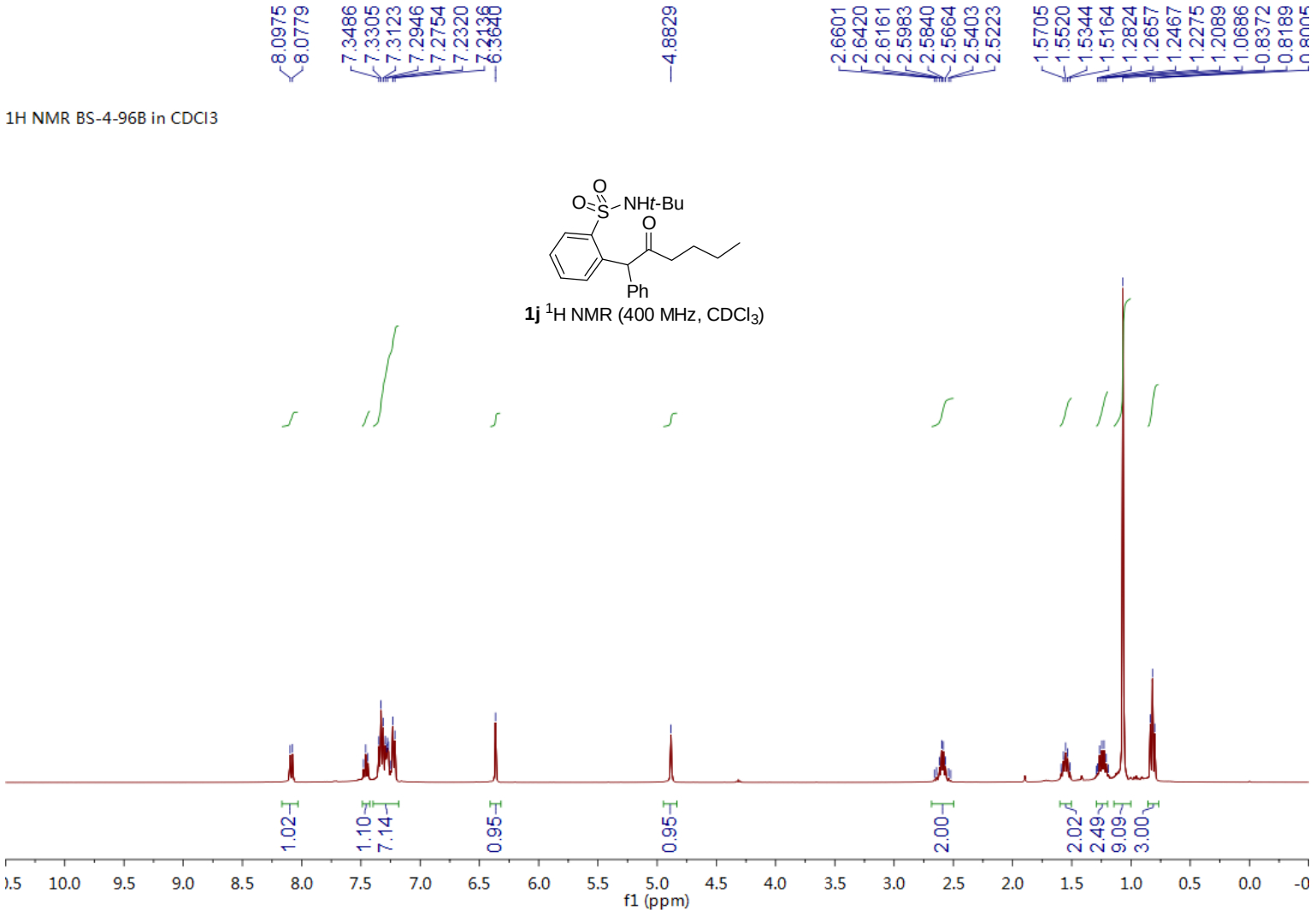
1h ^{13}C NMR (100 MHz, $CDCl_3$)



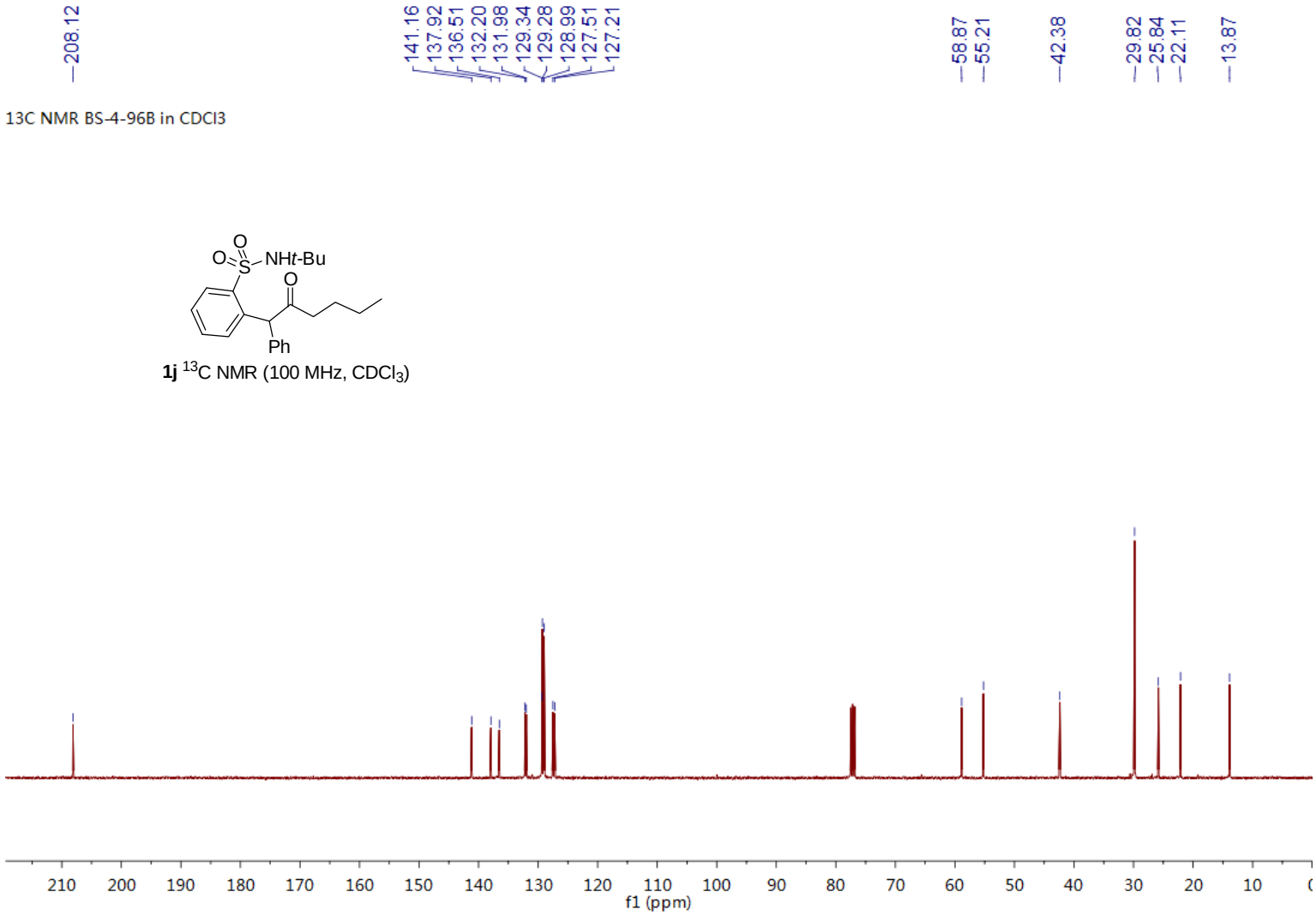
1i ^{1}H NMR (400 MHz, $CDCl_3$)



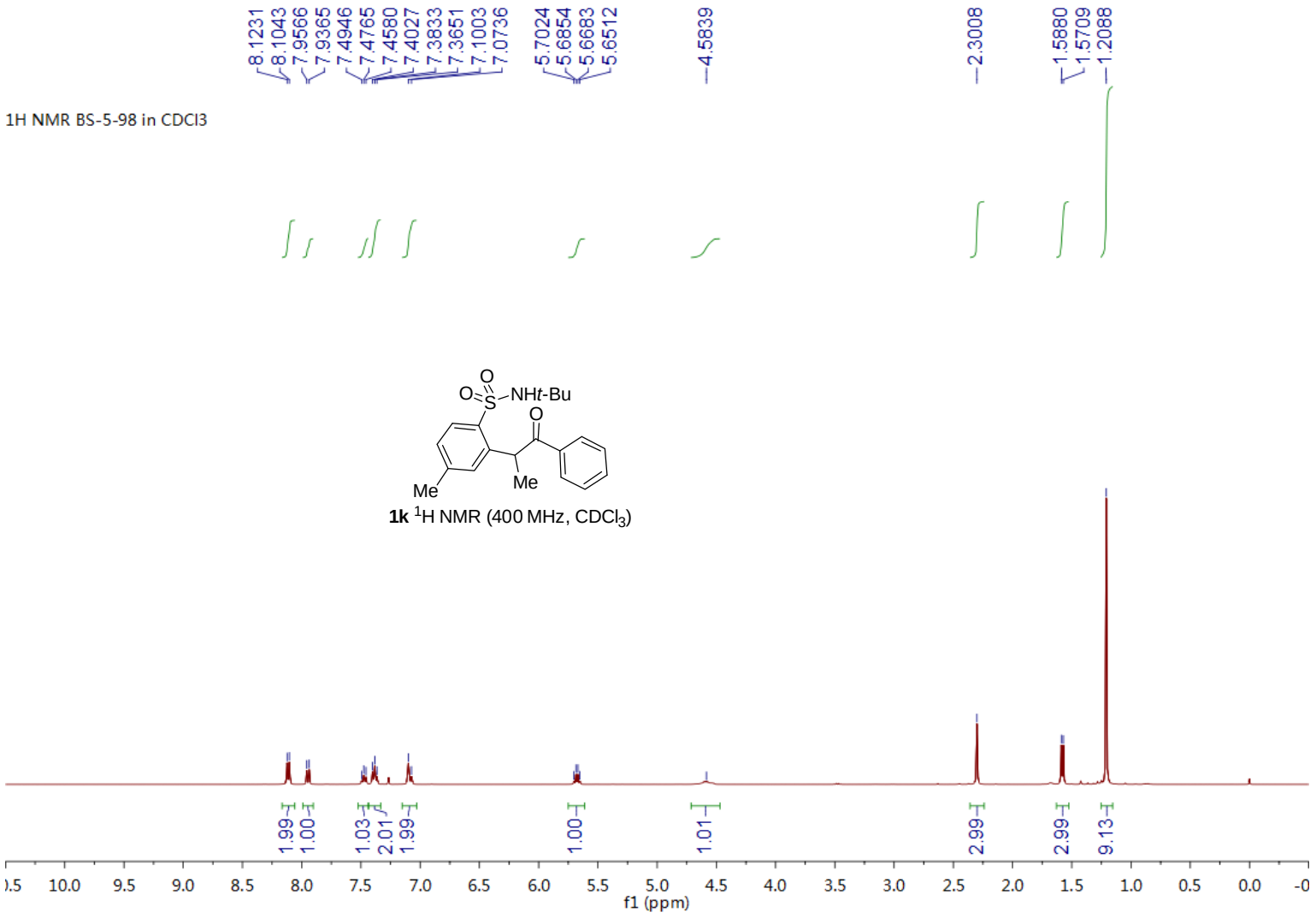
1i ^{13}C NMR (100 MHz, $CDCl_3$)



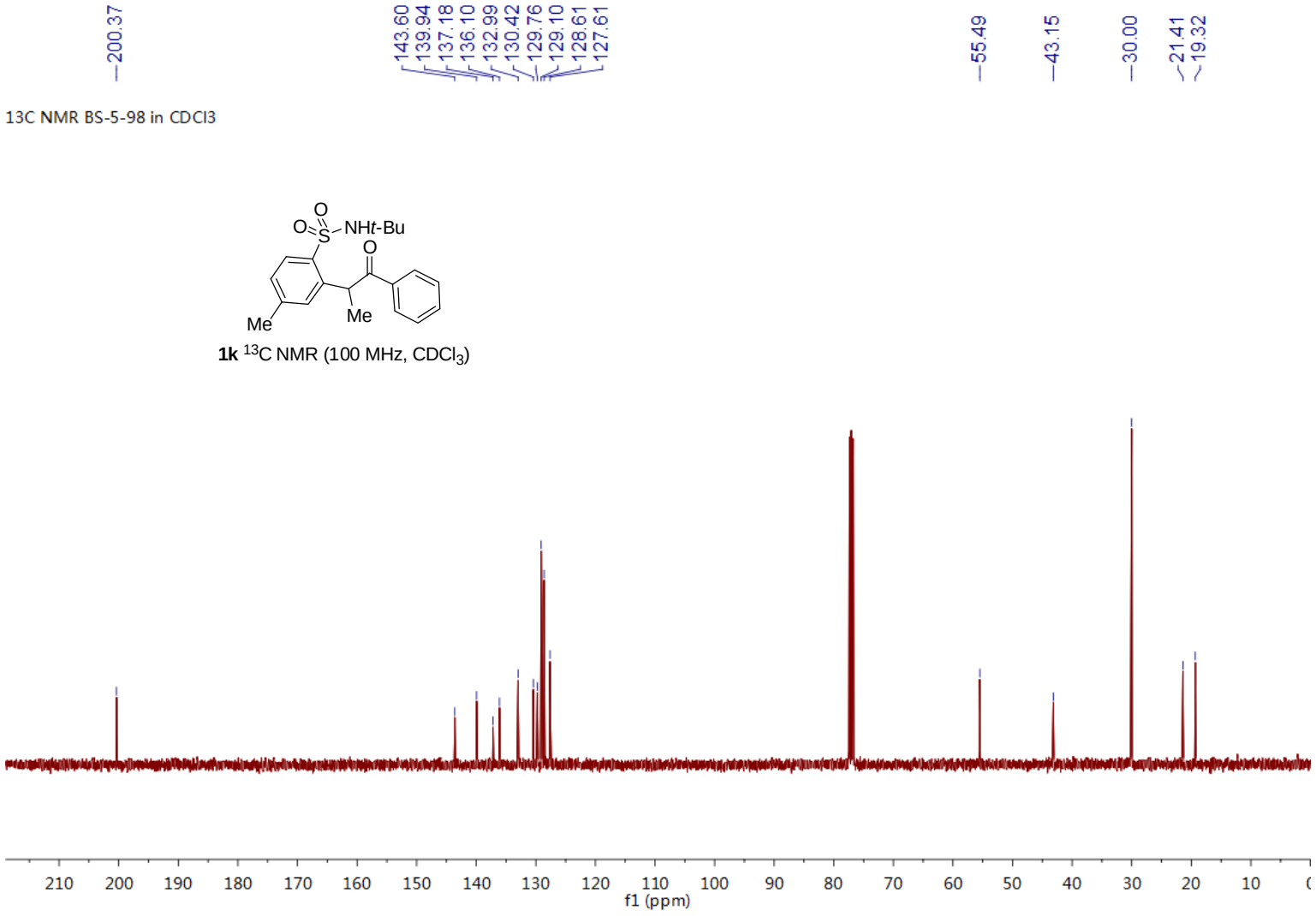
1j ^{1}H NMR (400 MHz, $CDCl_3$)



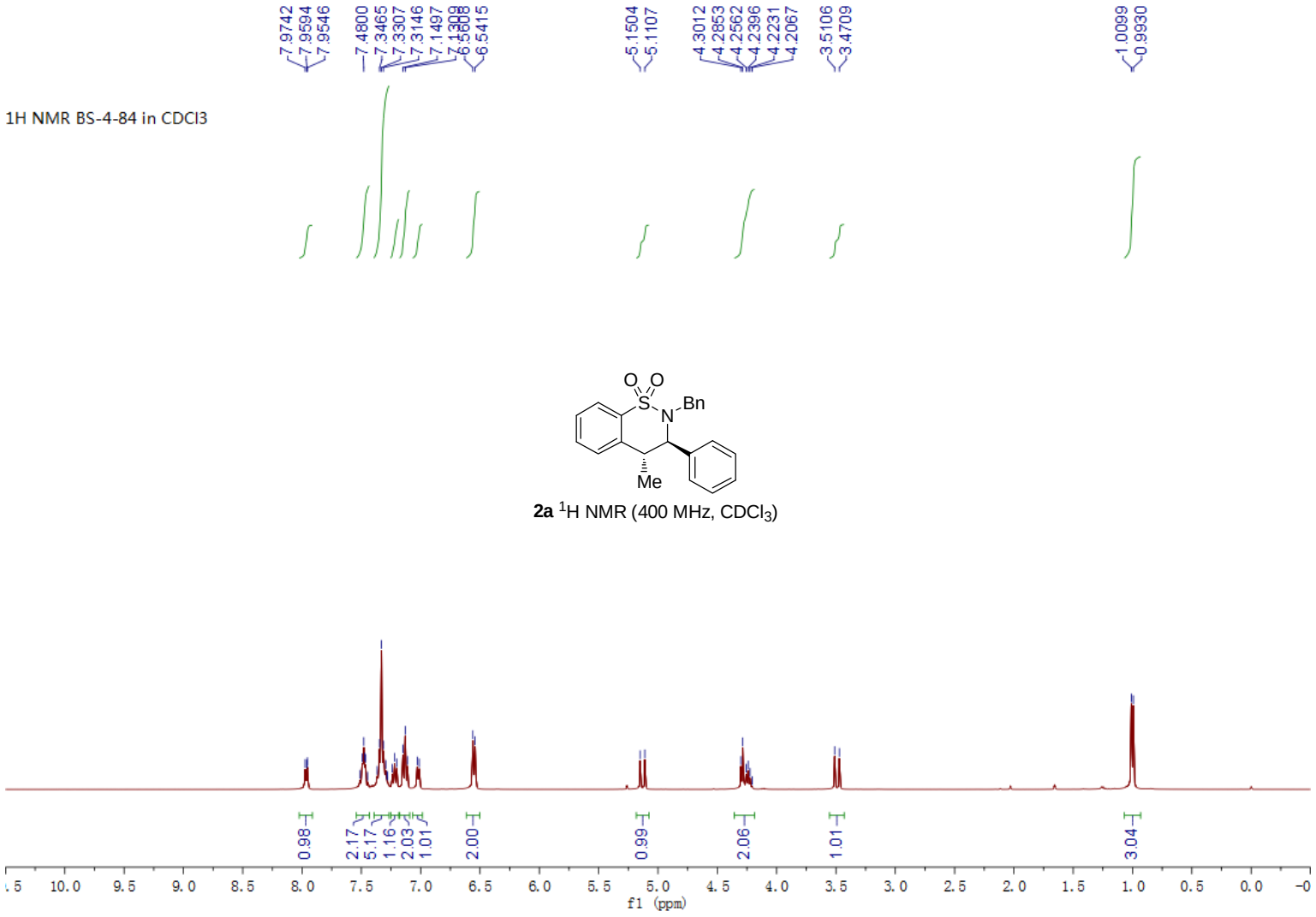
1j ^{13}C NMR (100 MHz, $CDCl_3$)



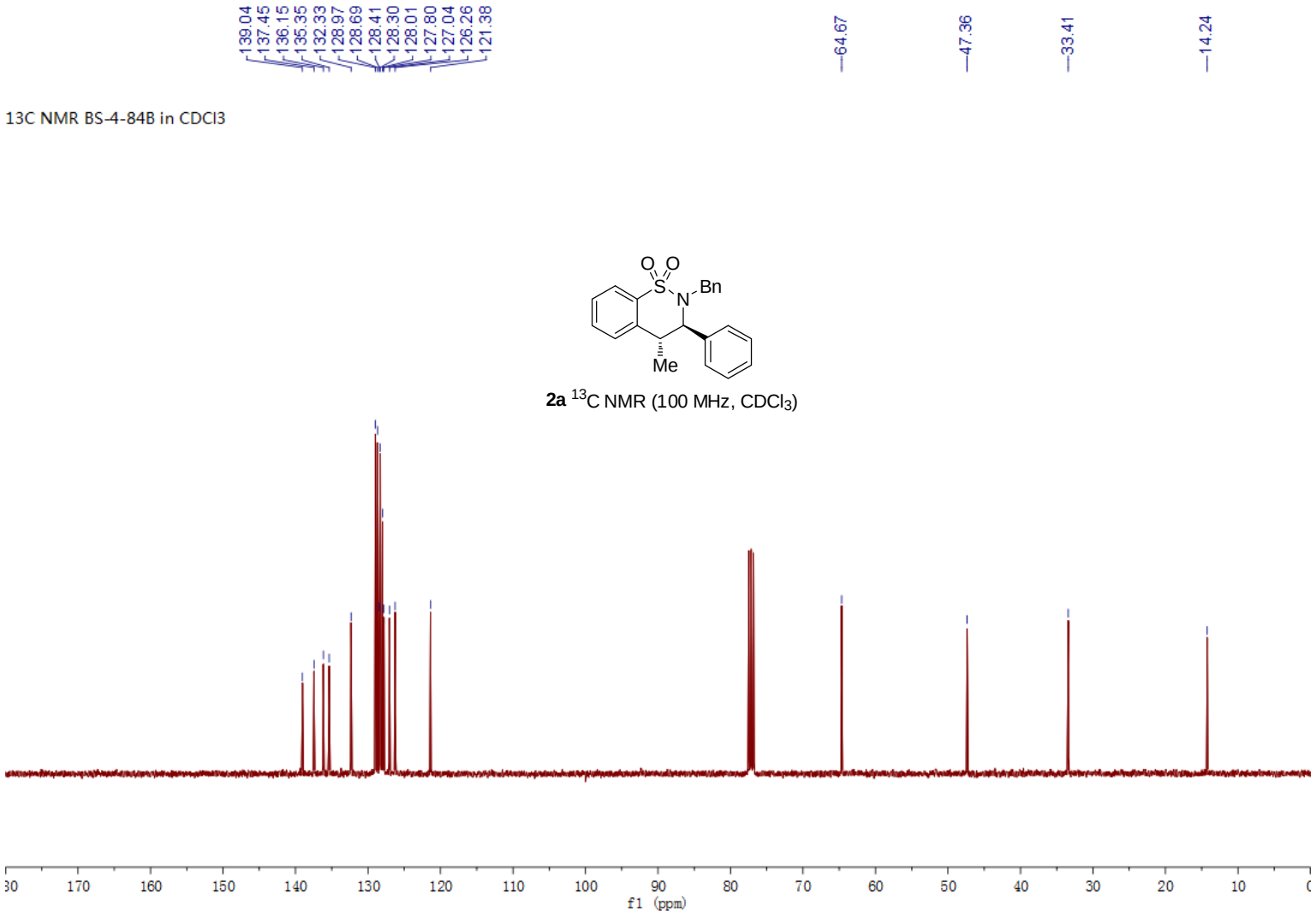
1k ^{1}H NMR (400 MHz, $CDCl_3$)



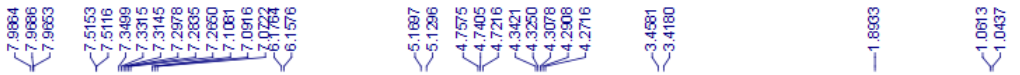
1k ^{13}C NMR (100 MHz, $CDCl_3$)



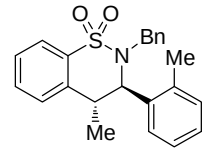
2a ^{1}H NMR (400 MHz, $CDCl_3$)



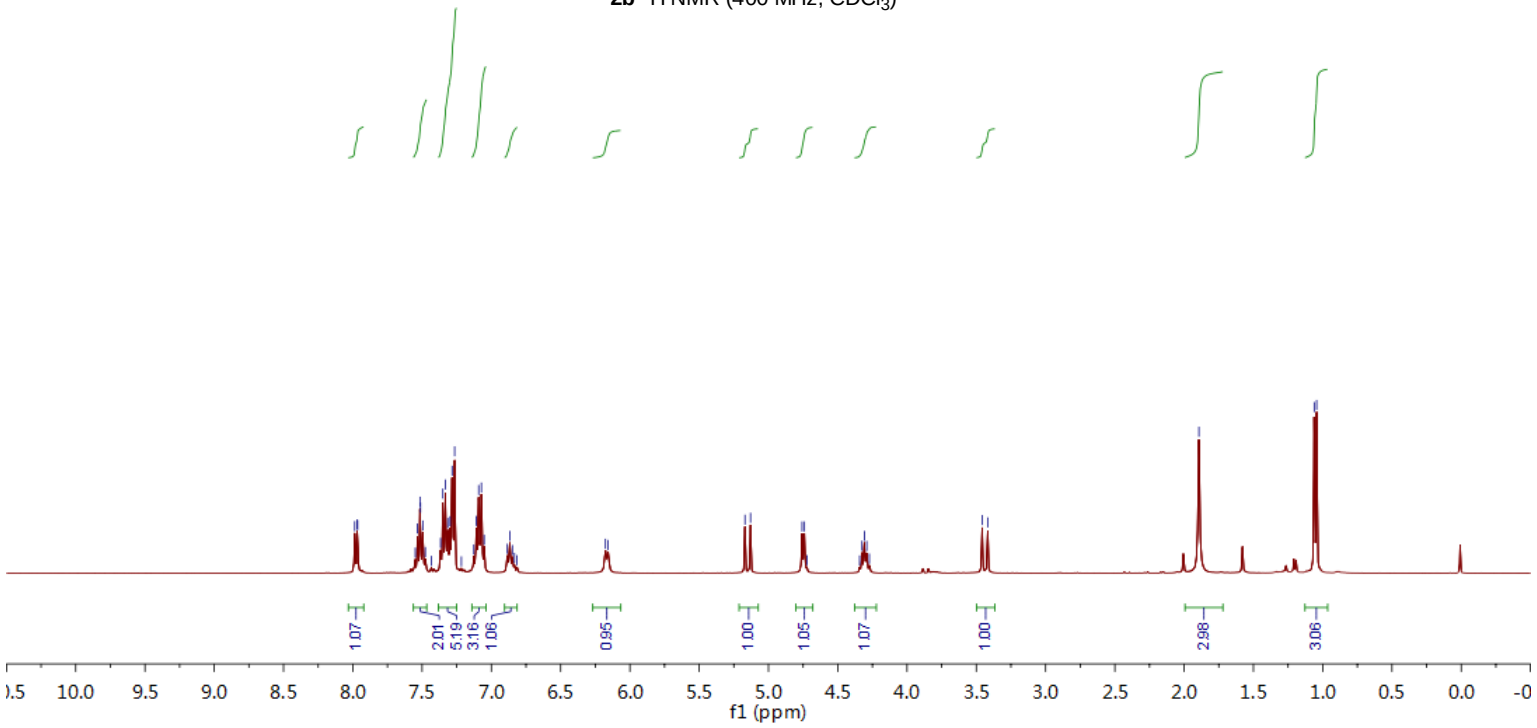
2a ^{13}C NMR (100 MHz, $CDCl_3$)



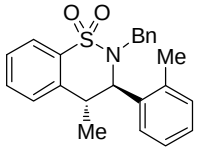
1H NMR BS-5-10 in CDCl3



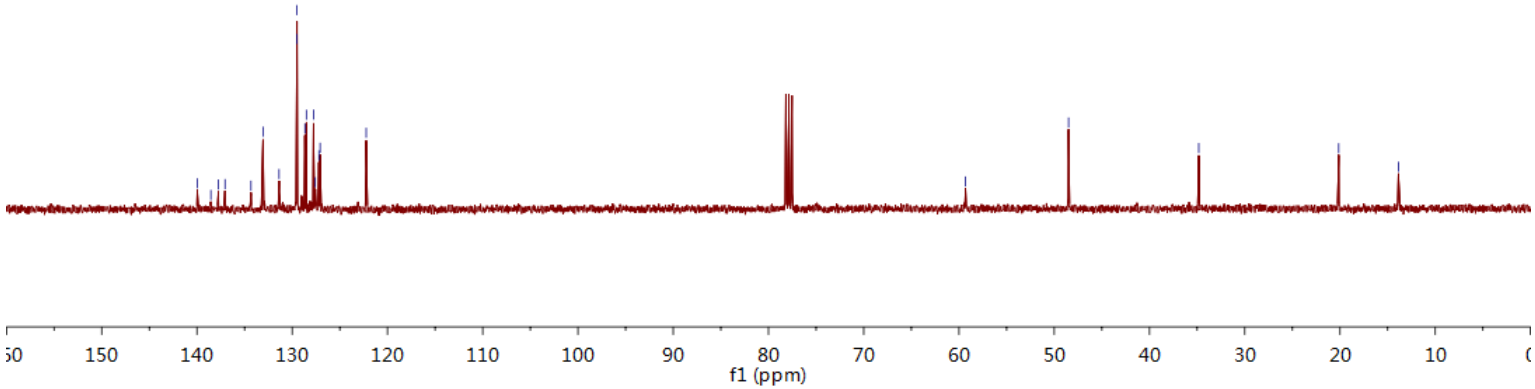
2b ^{1}H NMR (400 MHz, $CDCl_3$)

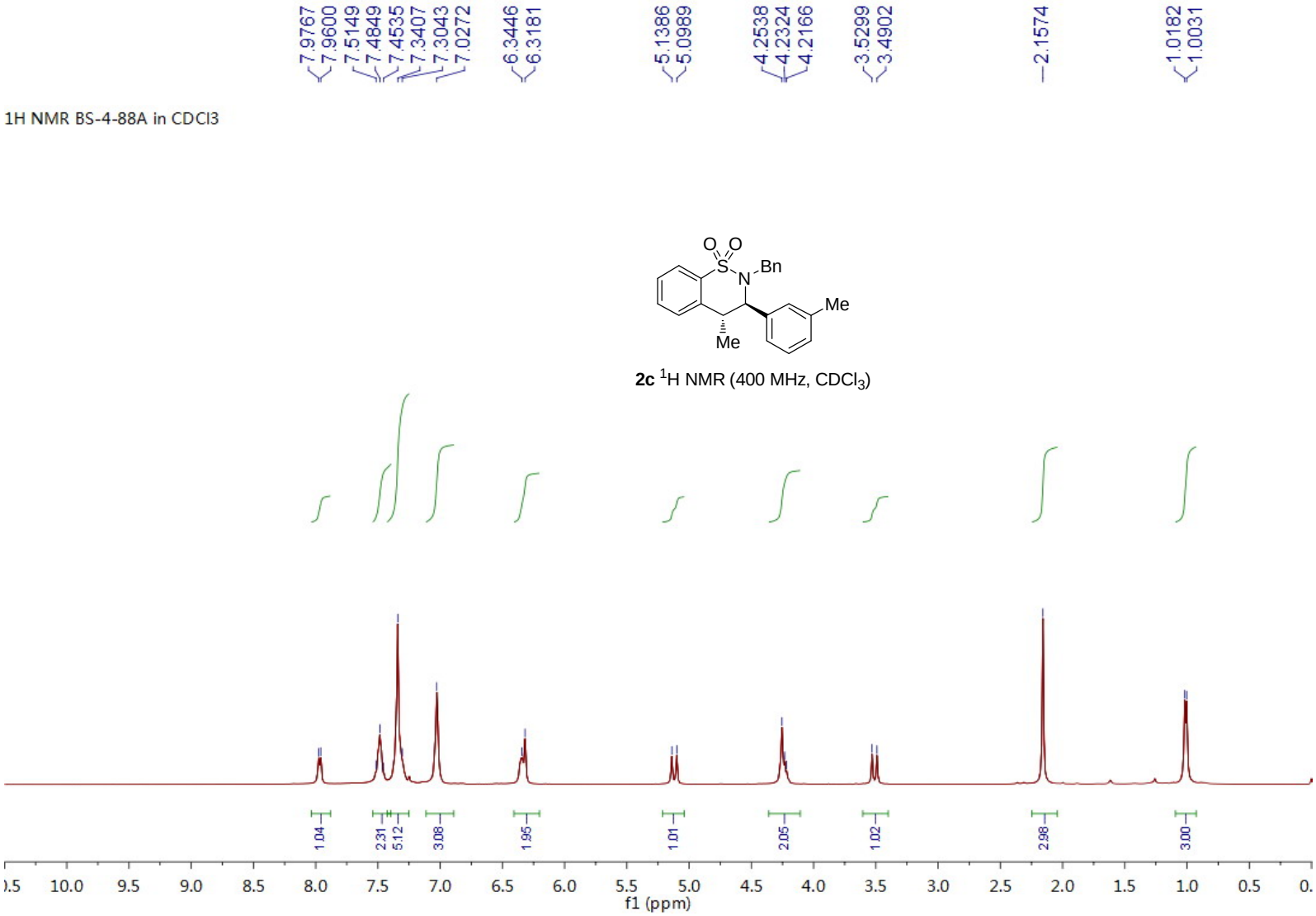


13C NMR BS-5-10 in CDCl3

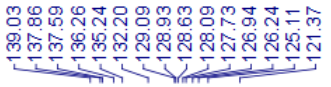


2b ^{13}C NMR (100 MHz, $CDCl_3$)

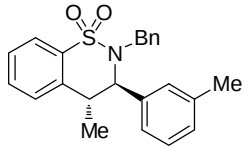




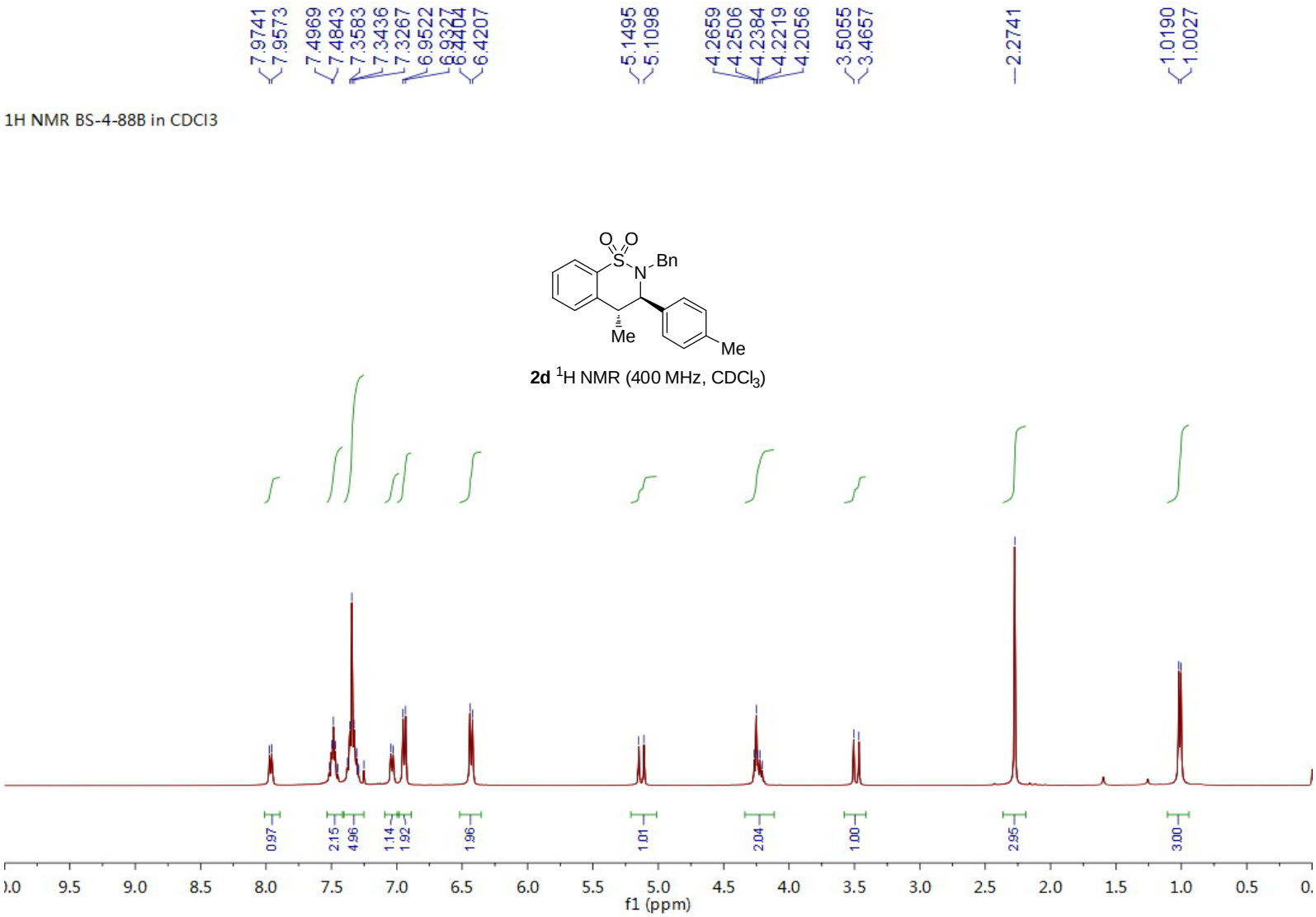
2c ^{1}H NMR (400 MHz, $CDCl_3$)



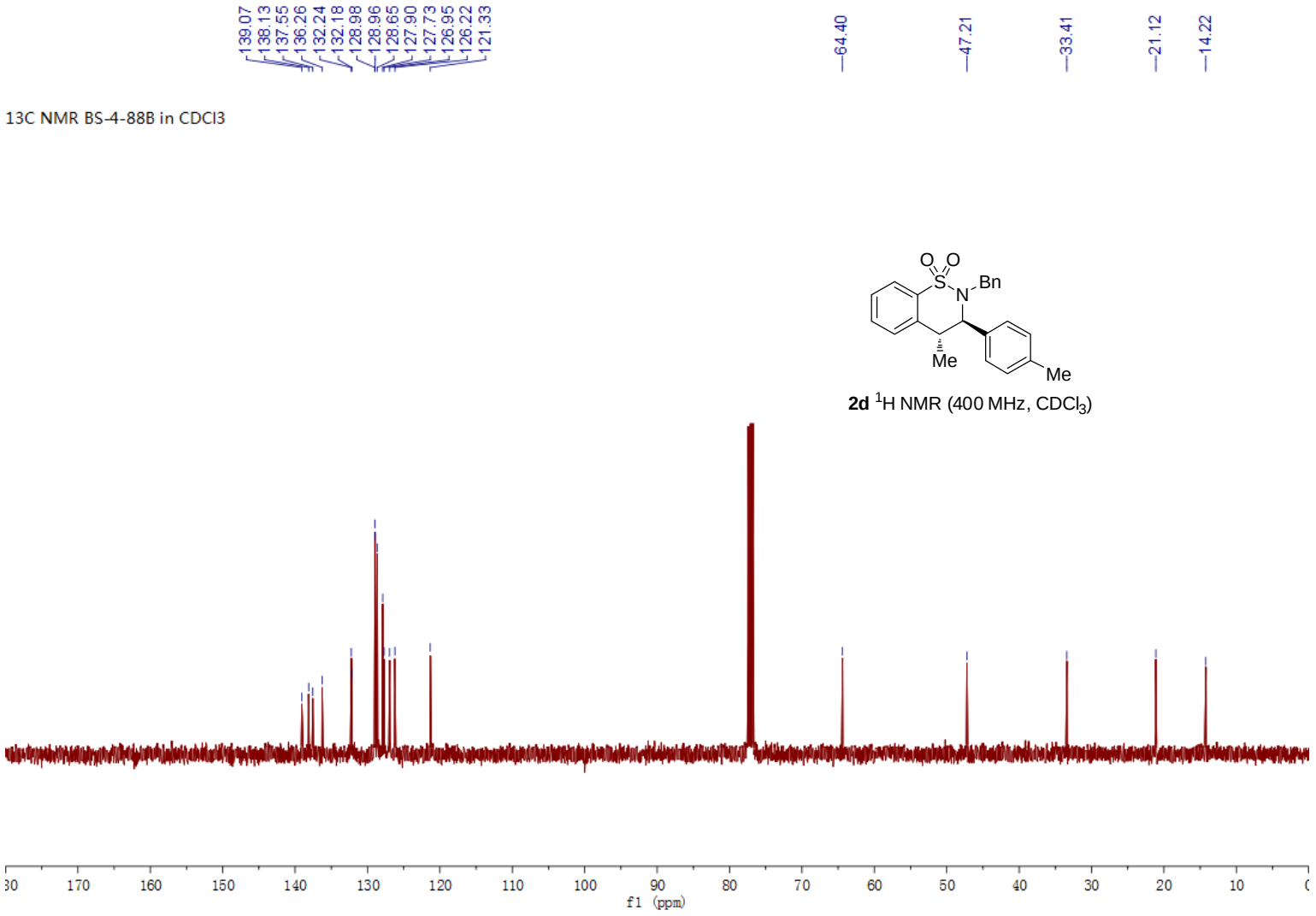
13C NMR BS-4-88A in CDCL3



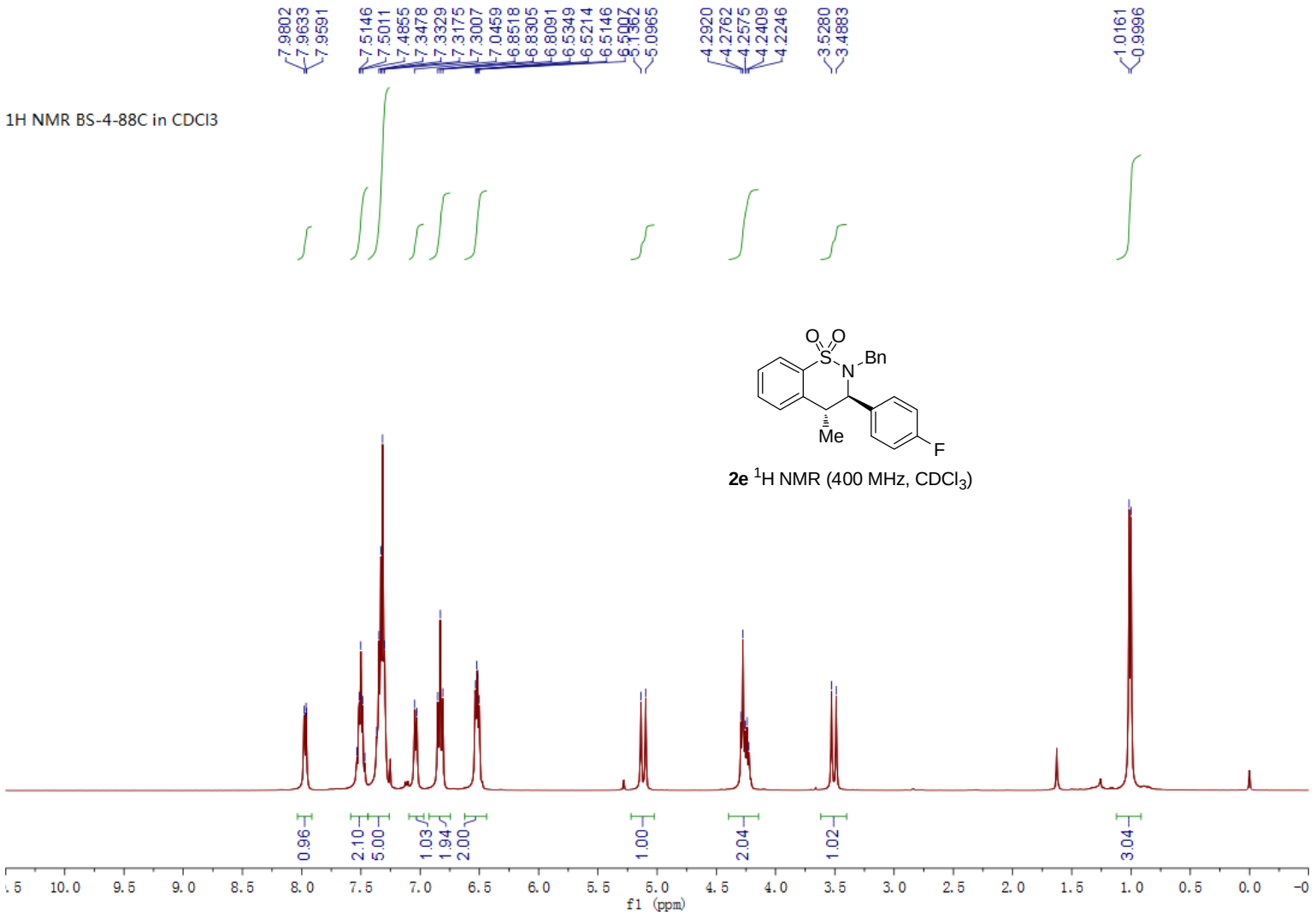
2c ^{13}C NMR (100 MHz, $CDCl_3$)



2d ^{1}H NMR (400 MHz, $CDCl_3$)



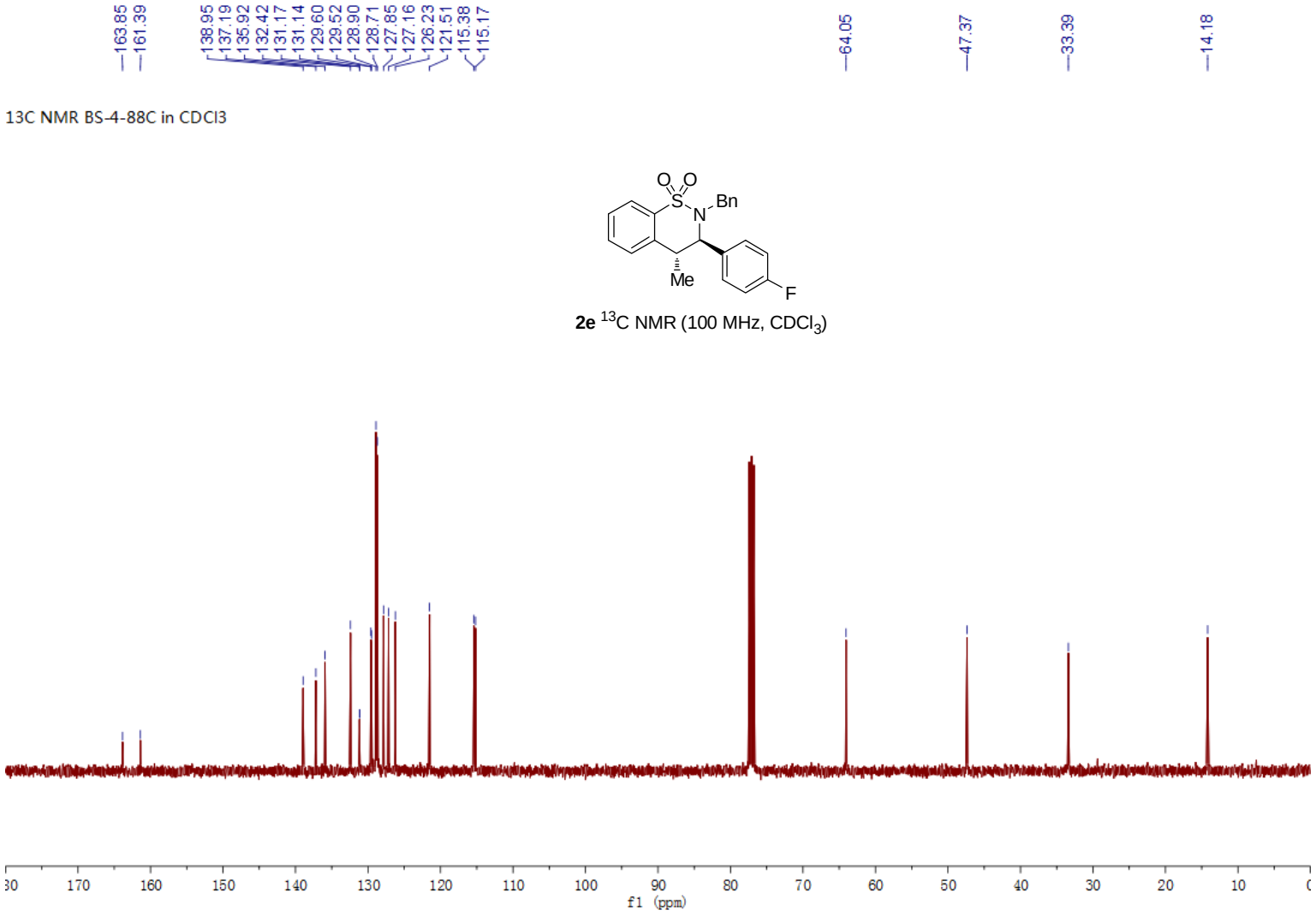
2d ^{1}H NMR (400 MHz, $CDCl_3$)



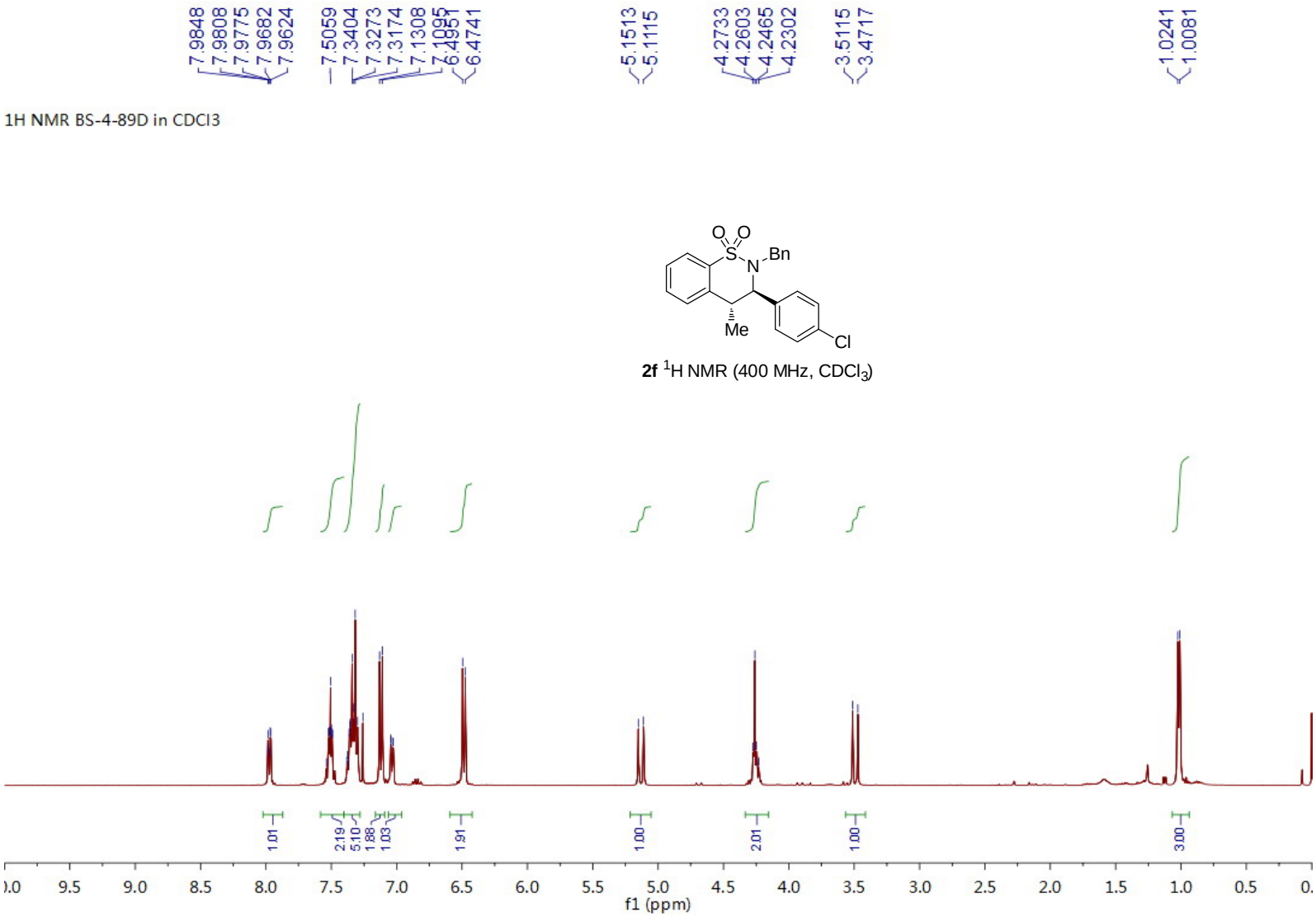
2e ^{1}H NMR (400 MHz, $CDCl_3$)

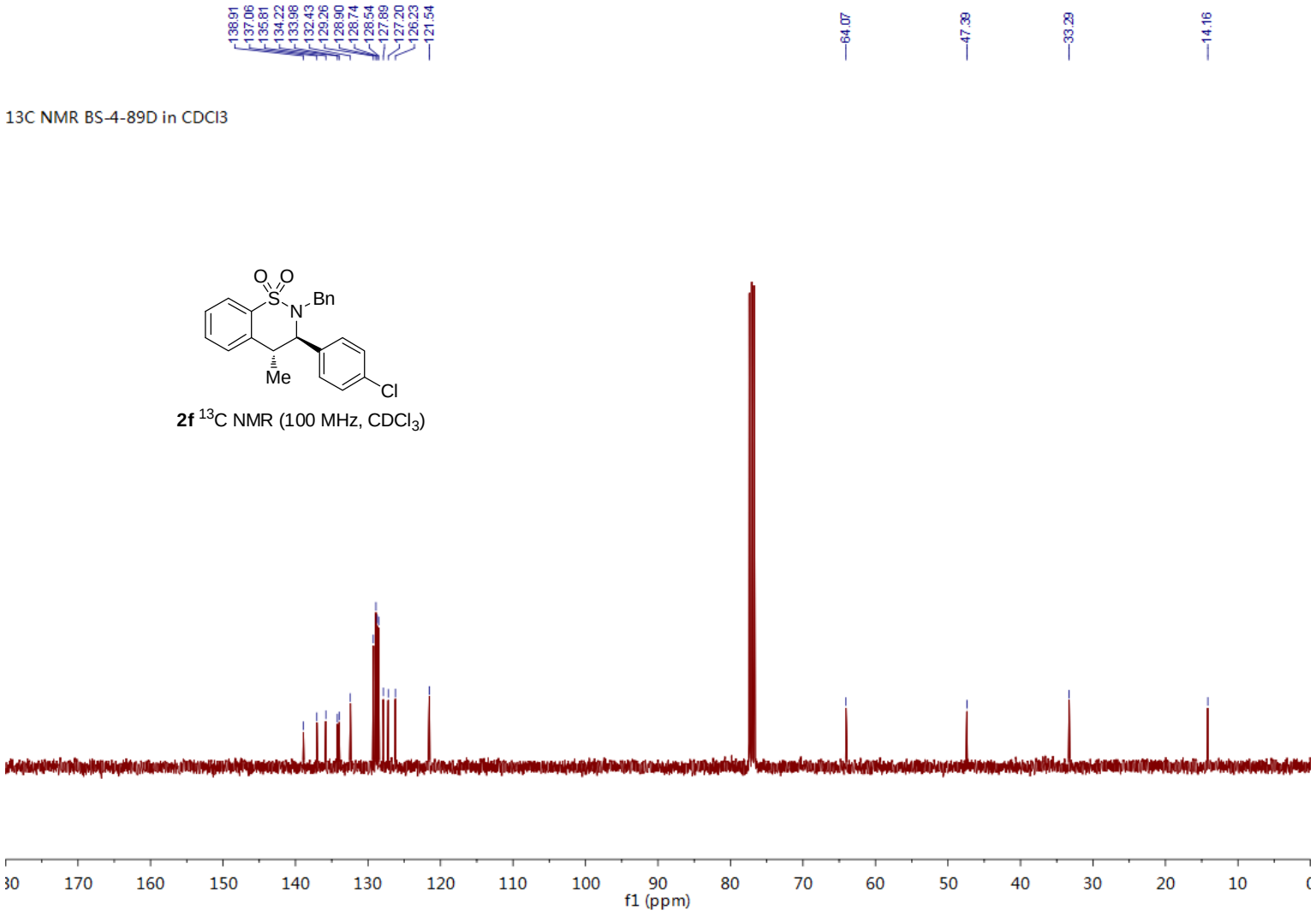
19F NMR BS-4-88C in CDCl3

2e ^{19}F NMR (376 MHz, $CDCl_3$)

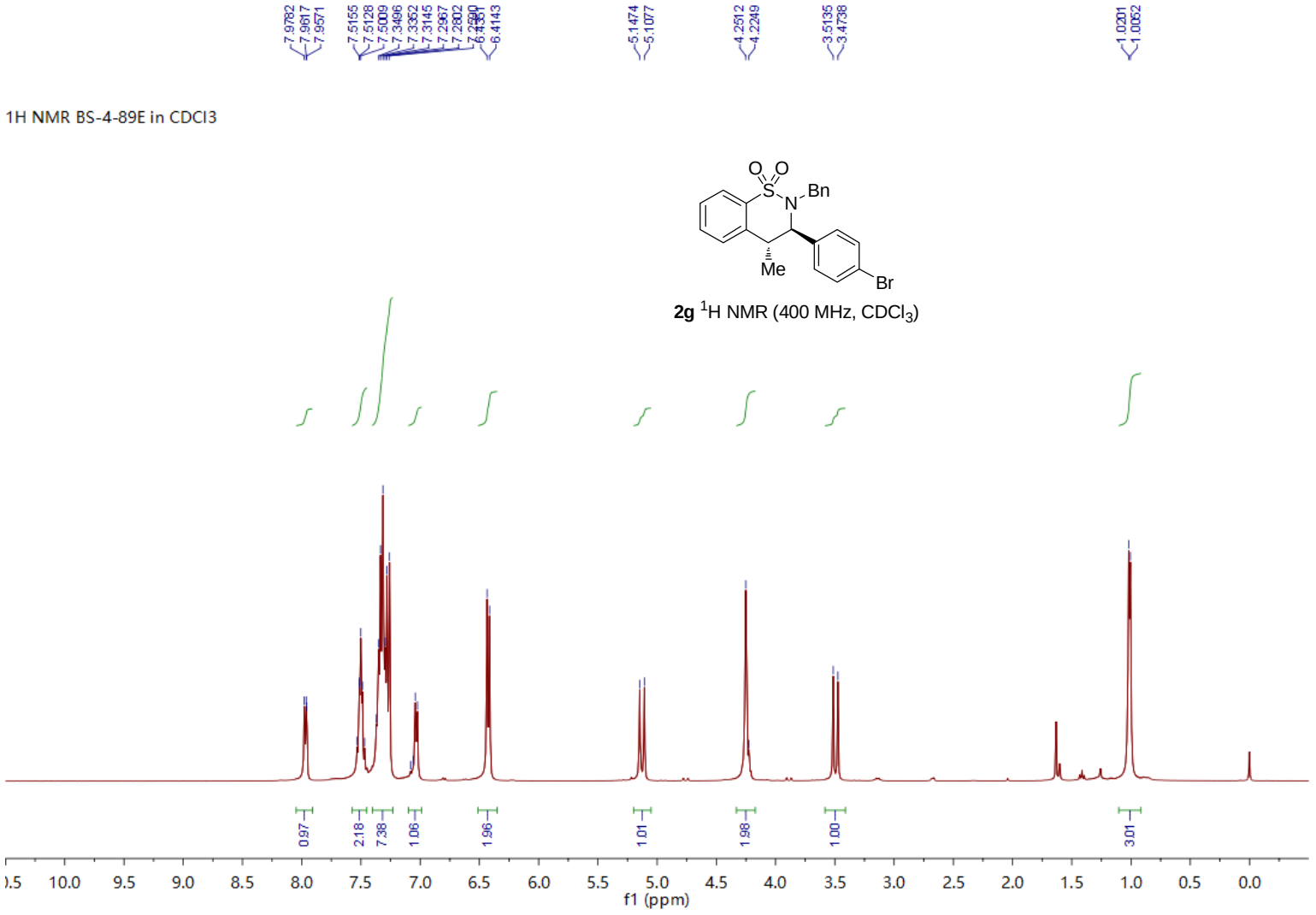


2e ^{13}C NMR (100 MHz, $CDCl_3$)

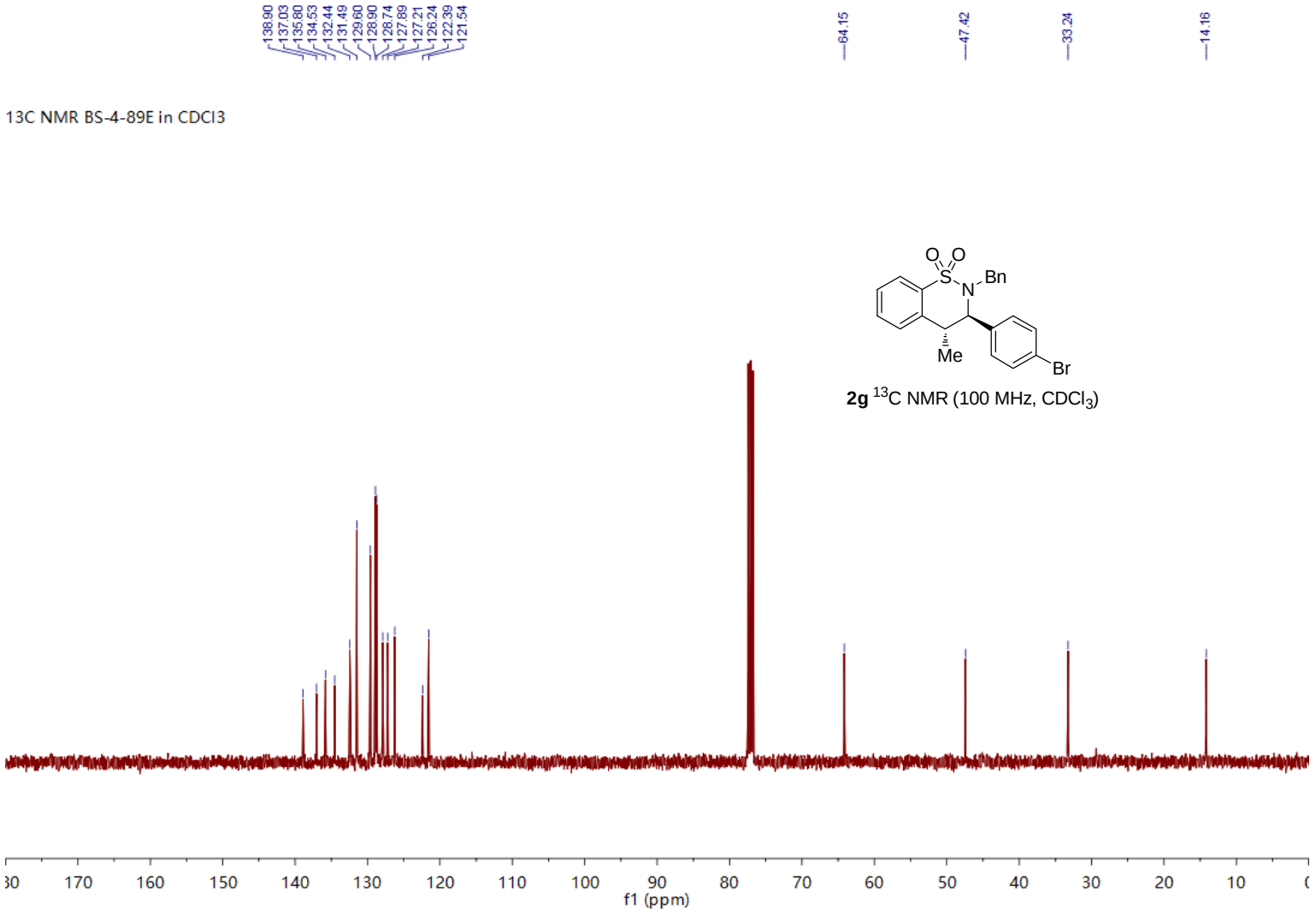

7.9848
7.9808
7.9775
7.9682
7.9624
7.5059
7.3404
7.3273
7.3174
7.1308
7.1095
6.4951
6.4741
5.1513
5.1115
4.2733
4.2603
4.2465
4.2302
3.5115
3.4717
1.0241
1.0081
1H NMR BS-4-89D in CDCl3
O
O
S
N
Bn
Me
Cl
2f 1H NMR (400 MHz, CDCl3)
1.01
2.19
5.10
1.88
1.03
1.91
1.00
2.01
1.00
3.00
f1 (ppm)



2f ^{13}C NMR (100 MHz, $CDCl_3$)

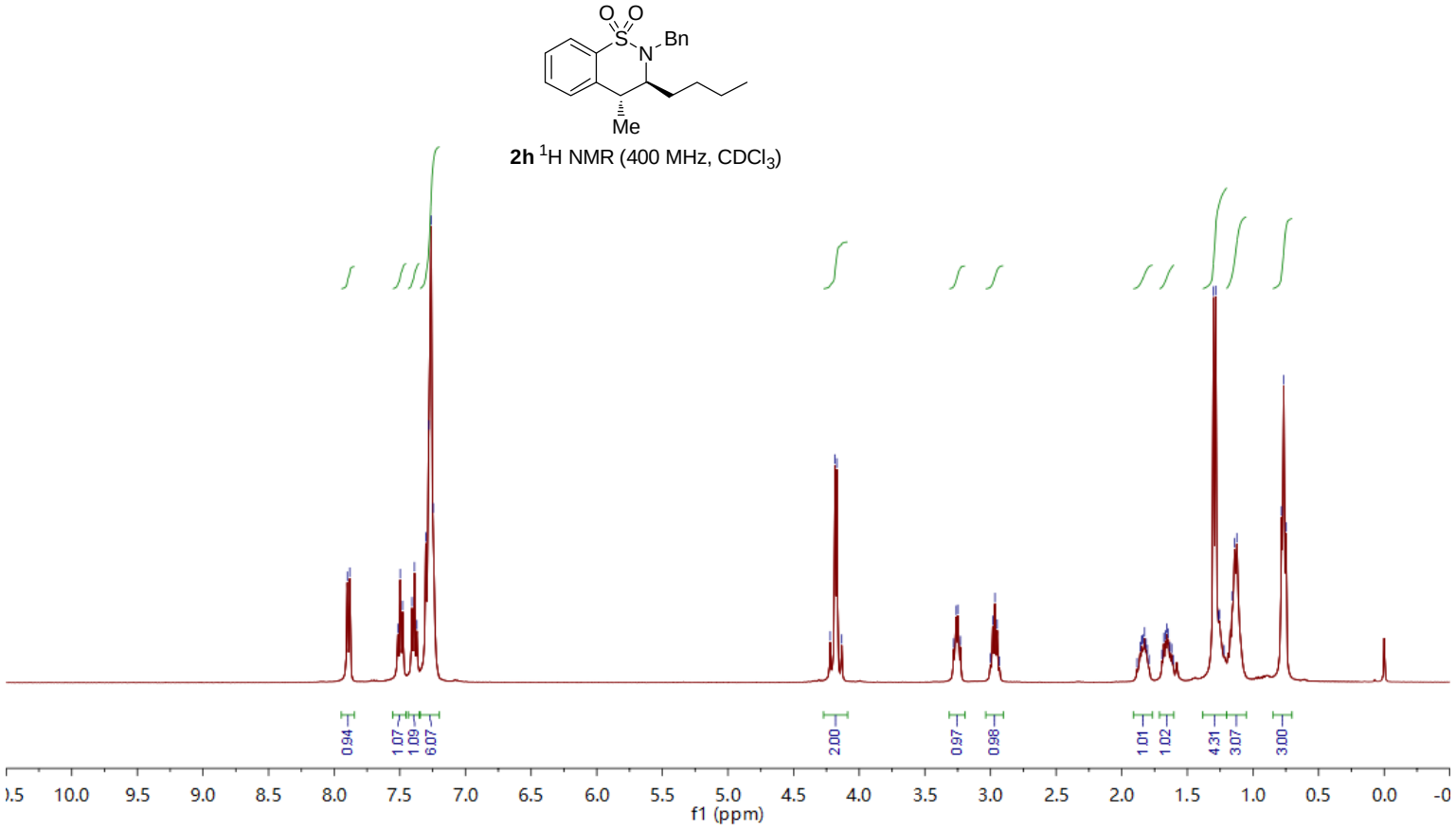


2g ^{1}H NMR (400 MHz, $CDCl_3$)

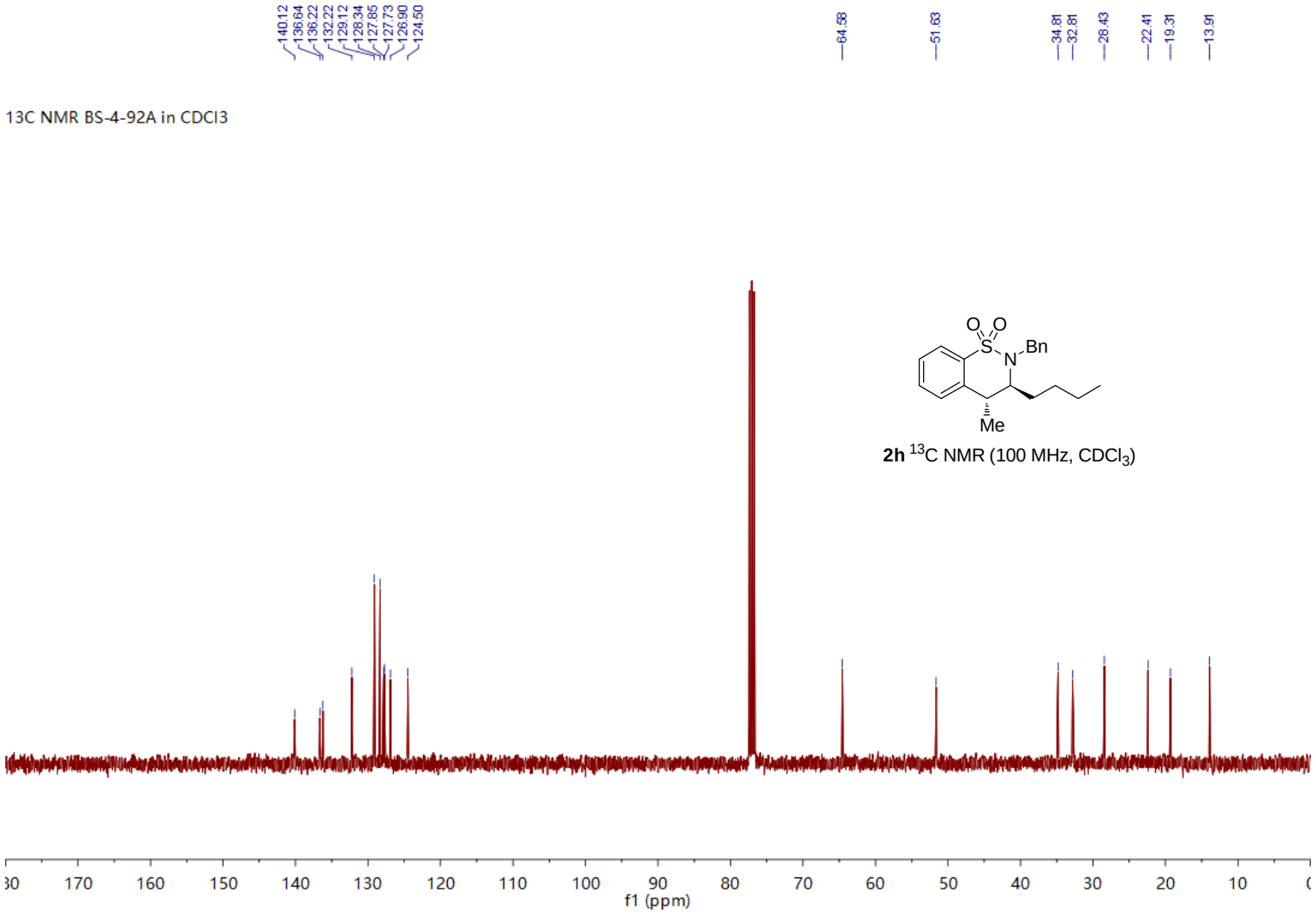


2g ^{13}C NMR (100 MHz, $CDCl_3$)

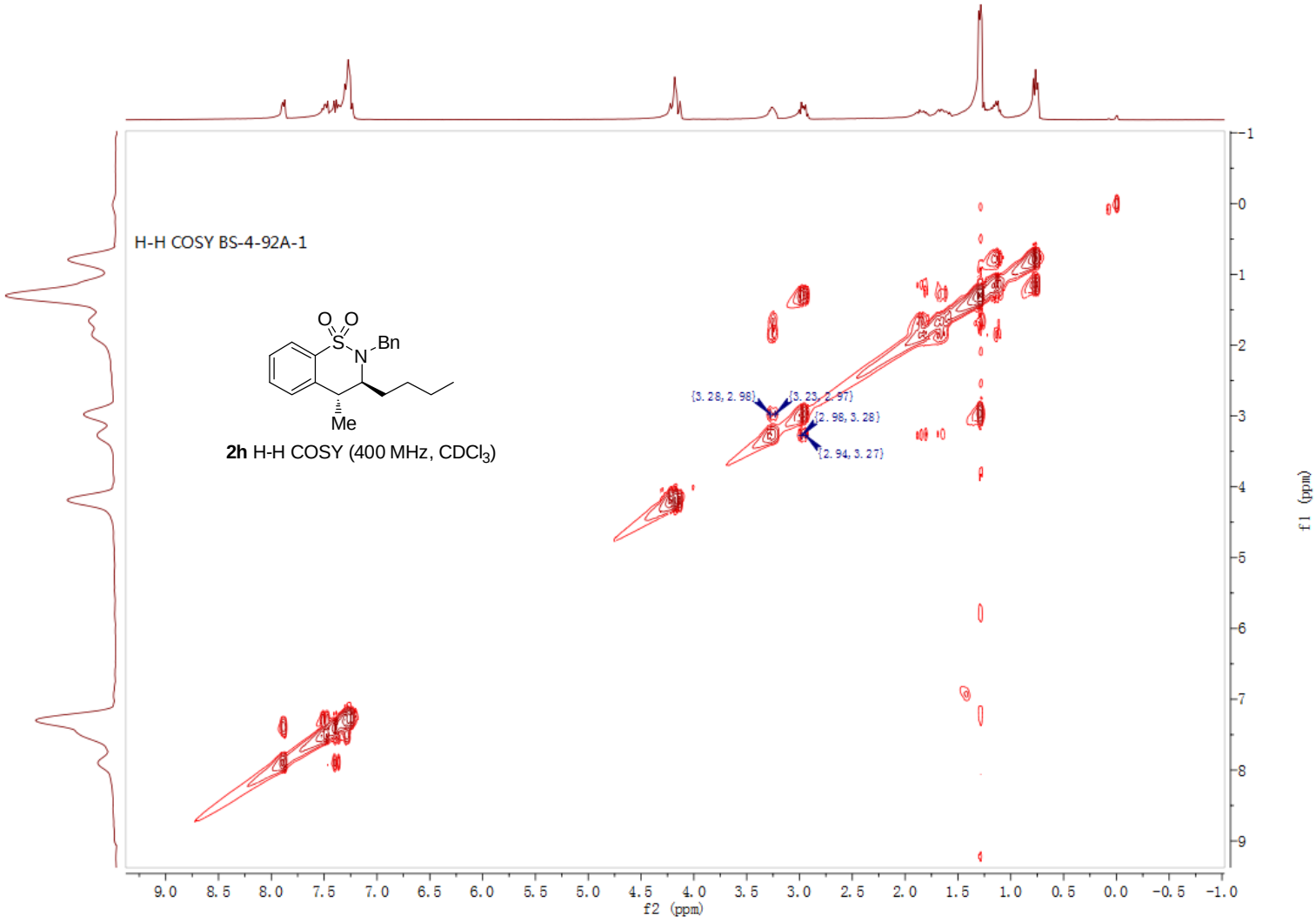
1H NMR BS-4-92A in CDCl3



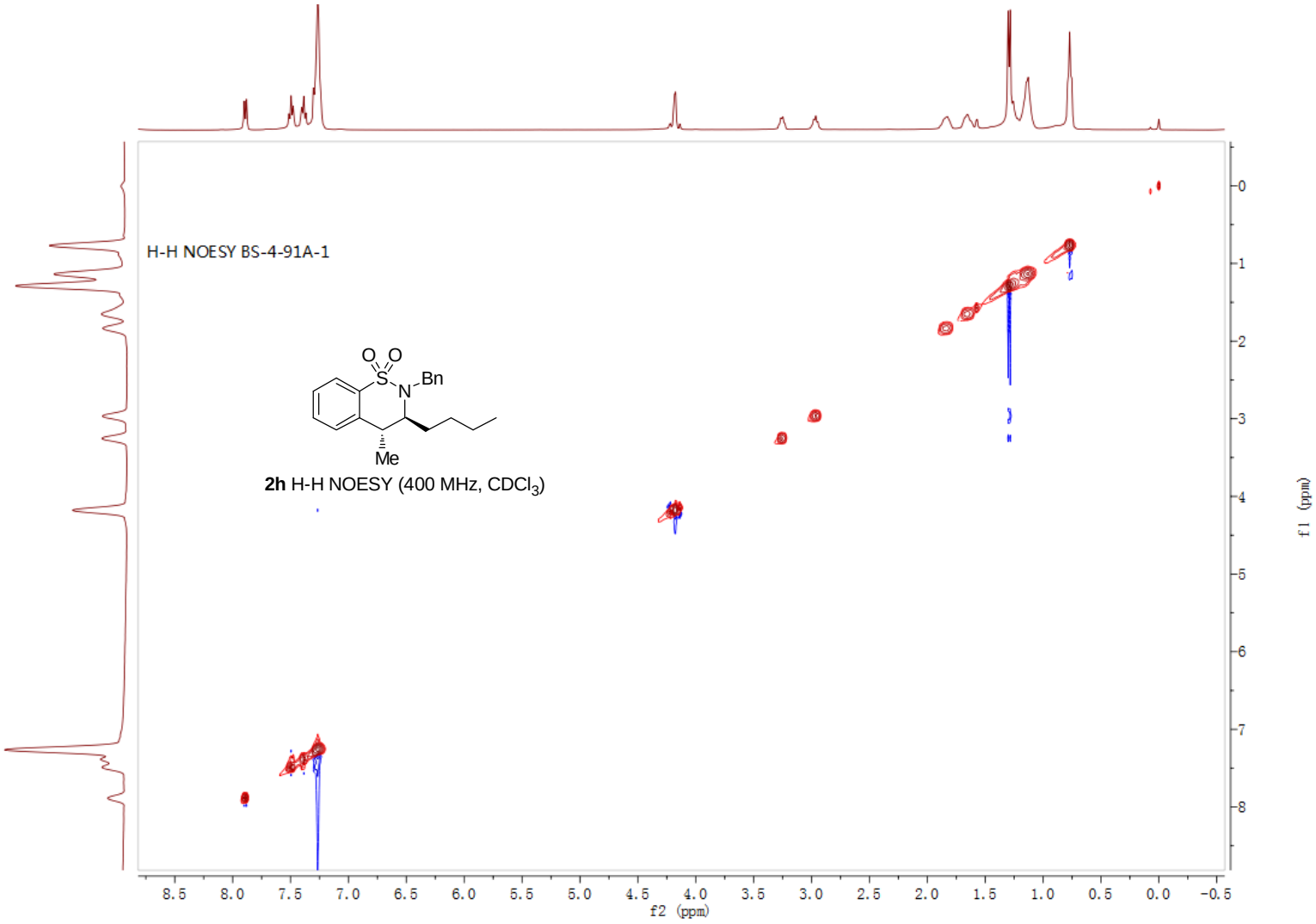
2h ^{1}H NMR (400 MHz, $CDCl_3$)



2h ^{13}C NMR (100 MHz, $CDCl_3$)

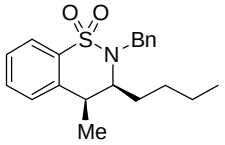


2h H-H COSY (400 MHz, $CDCl_3$)

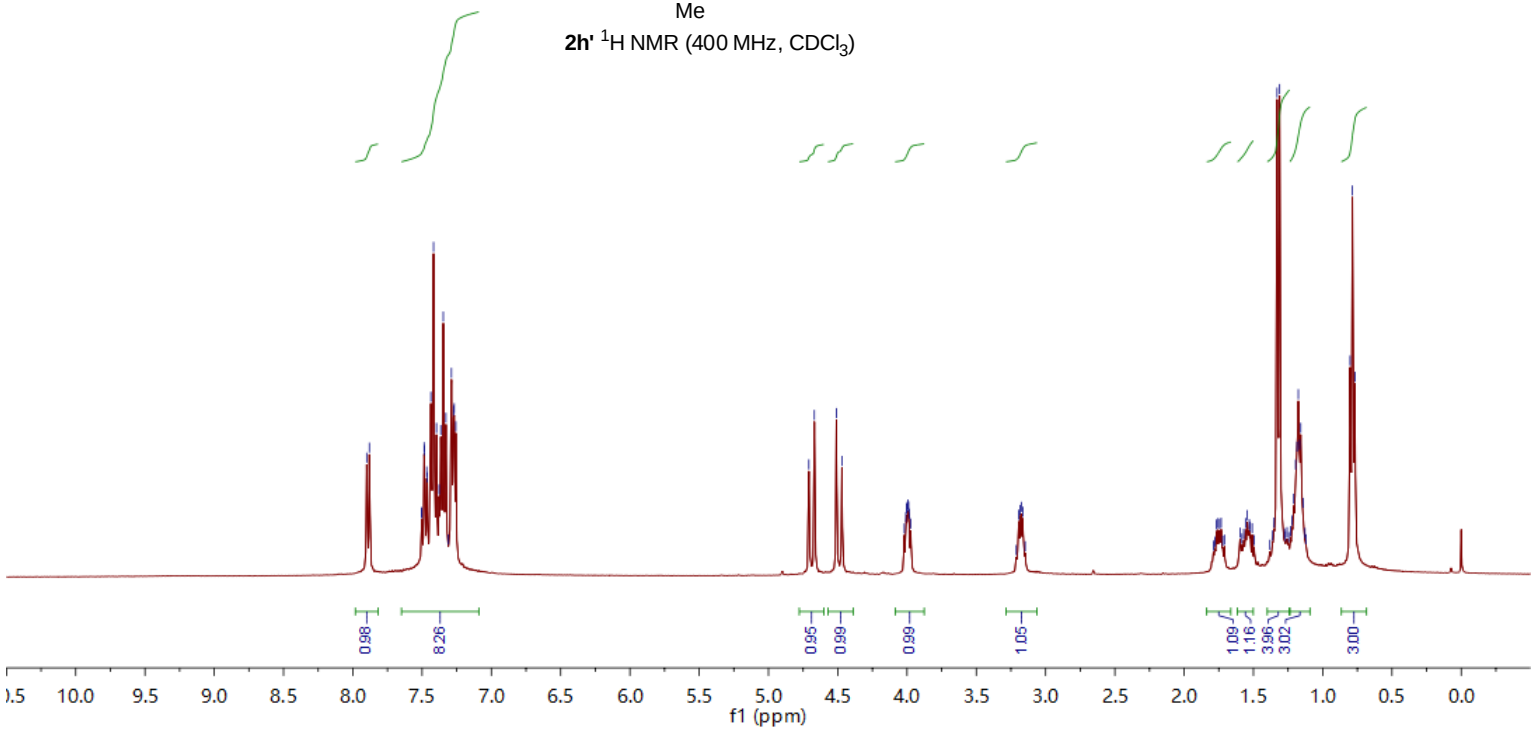


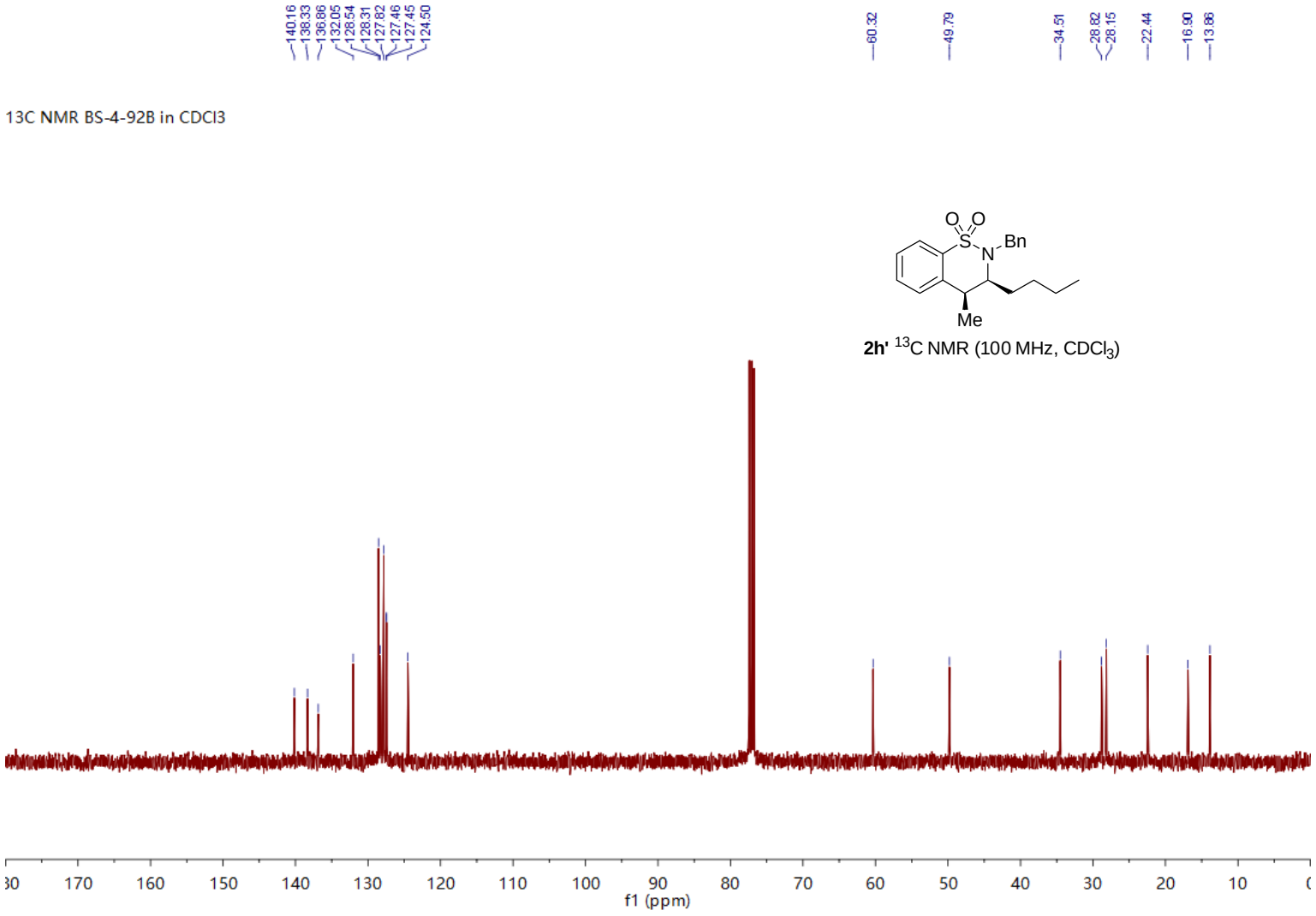
2h H-H NOESY (400 MHz, $CDCl_3$)

1H NMR BS-4-92B in CDCl3

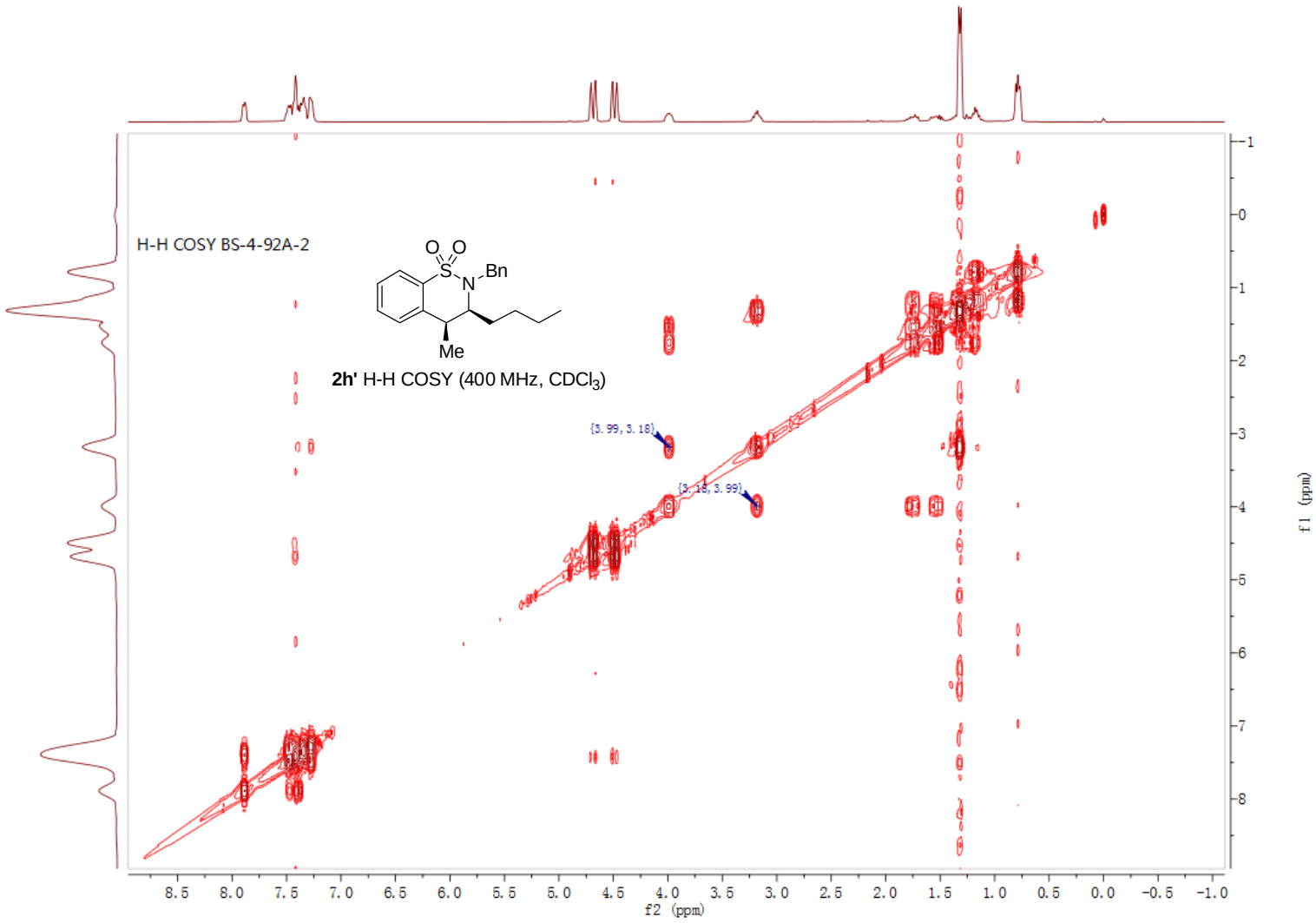


2h' ^{1}H NMR (400 MHz, $CDCl_3$)

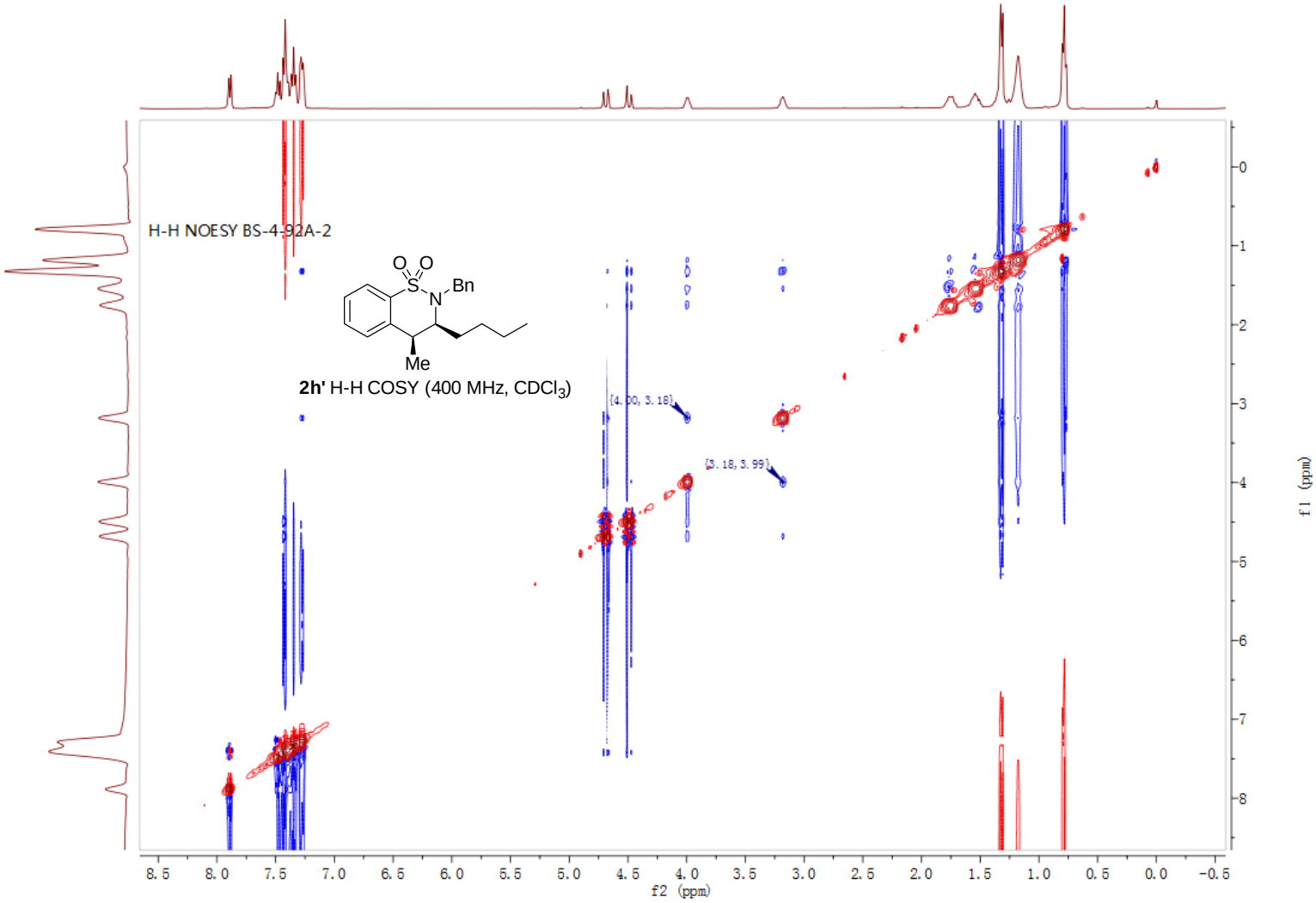




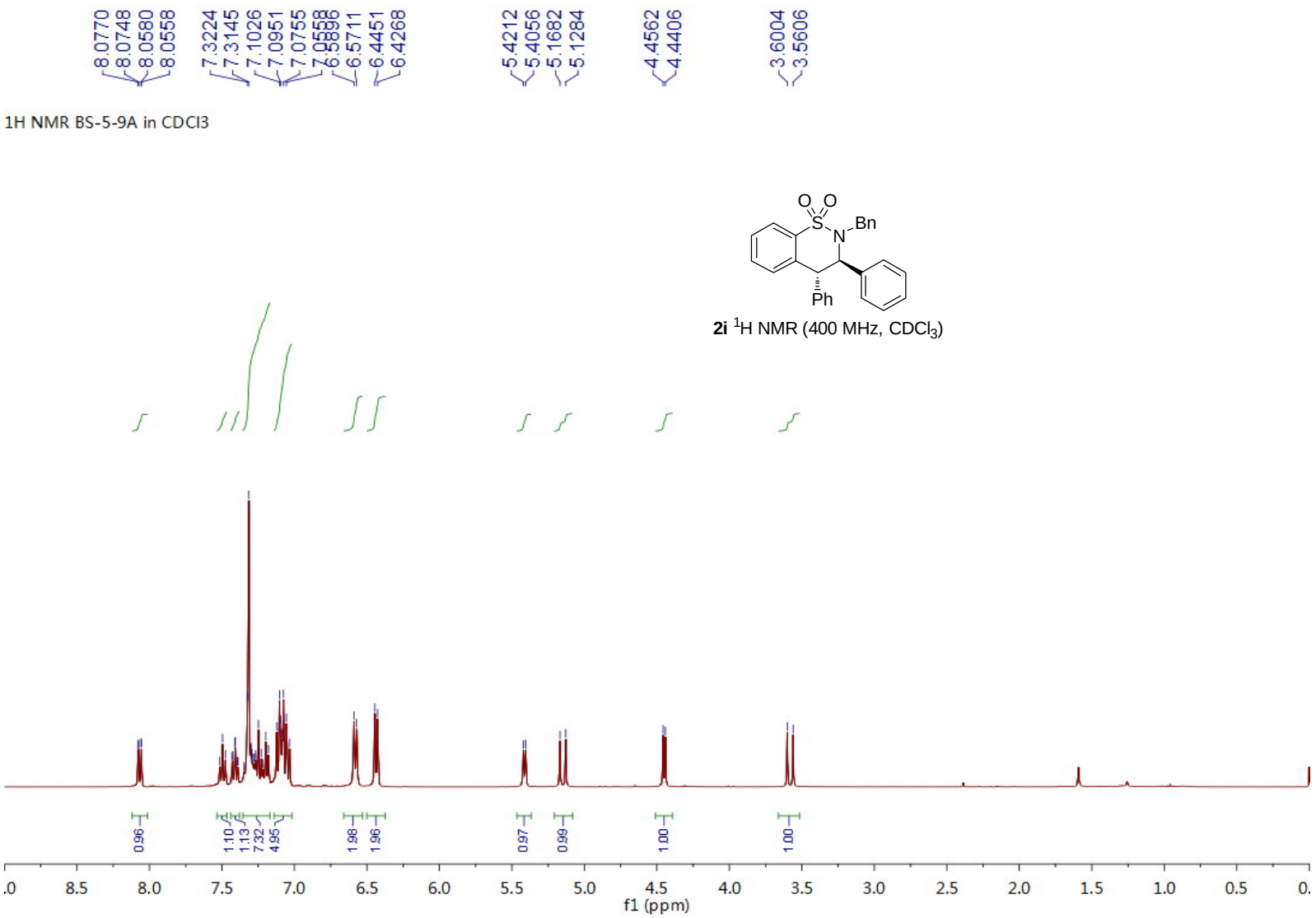
2h' ^{13}C NMR (100 MHz, $CDCl_3$)



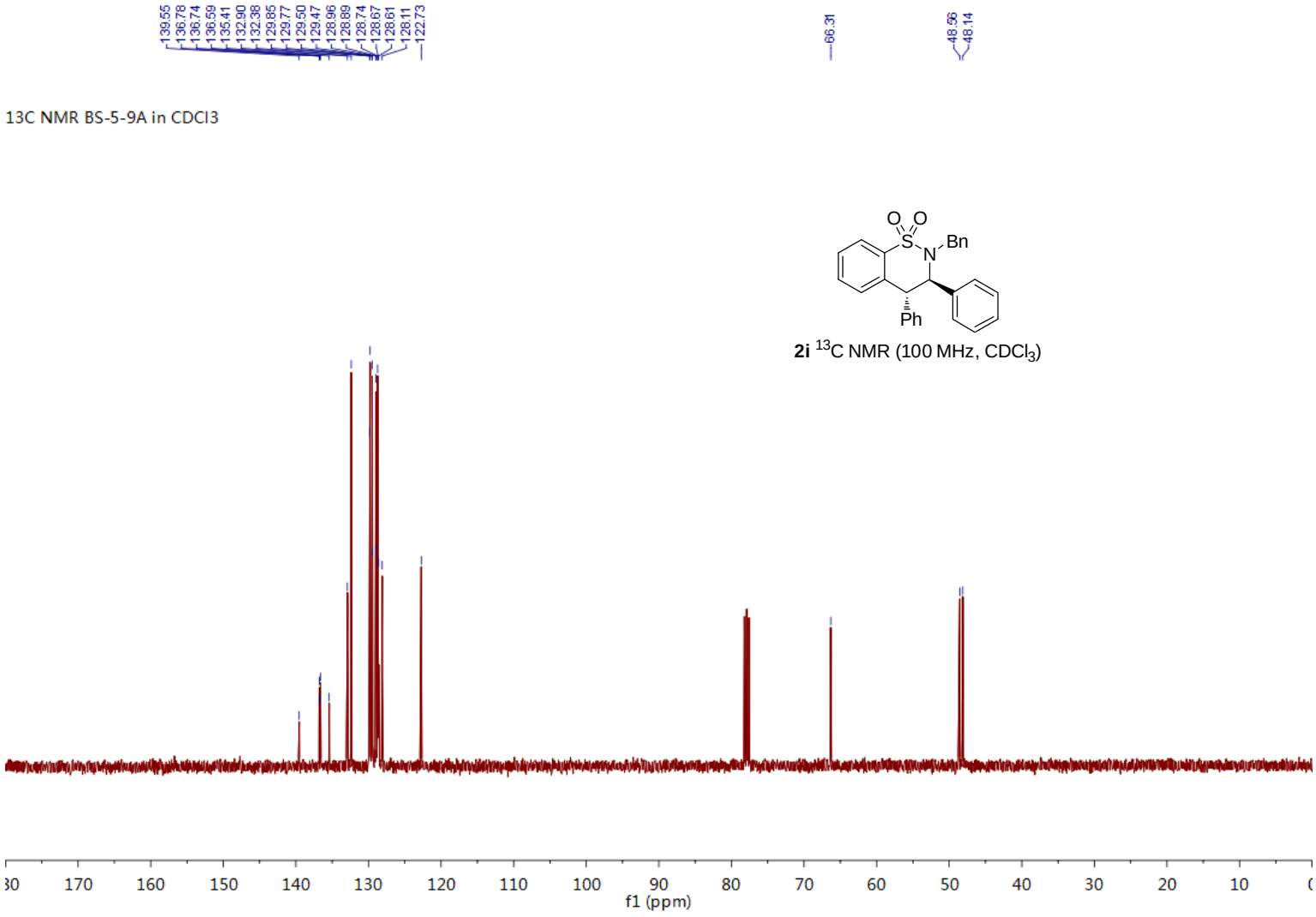
2h' H-H COSY (400 MHz, $CDCl_3$)



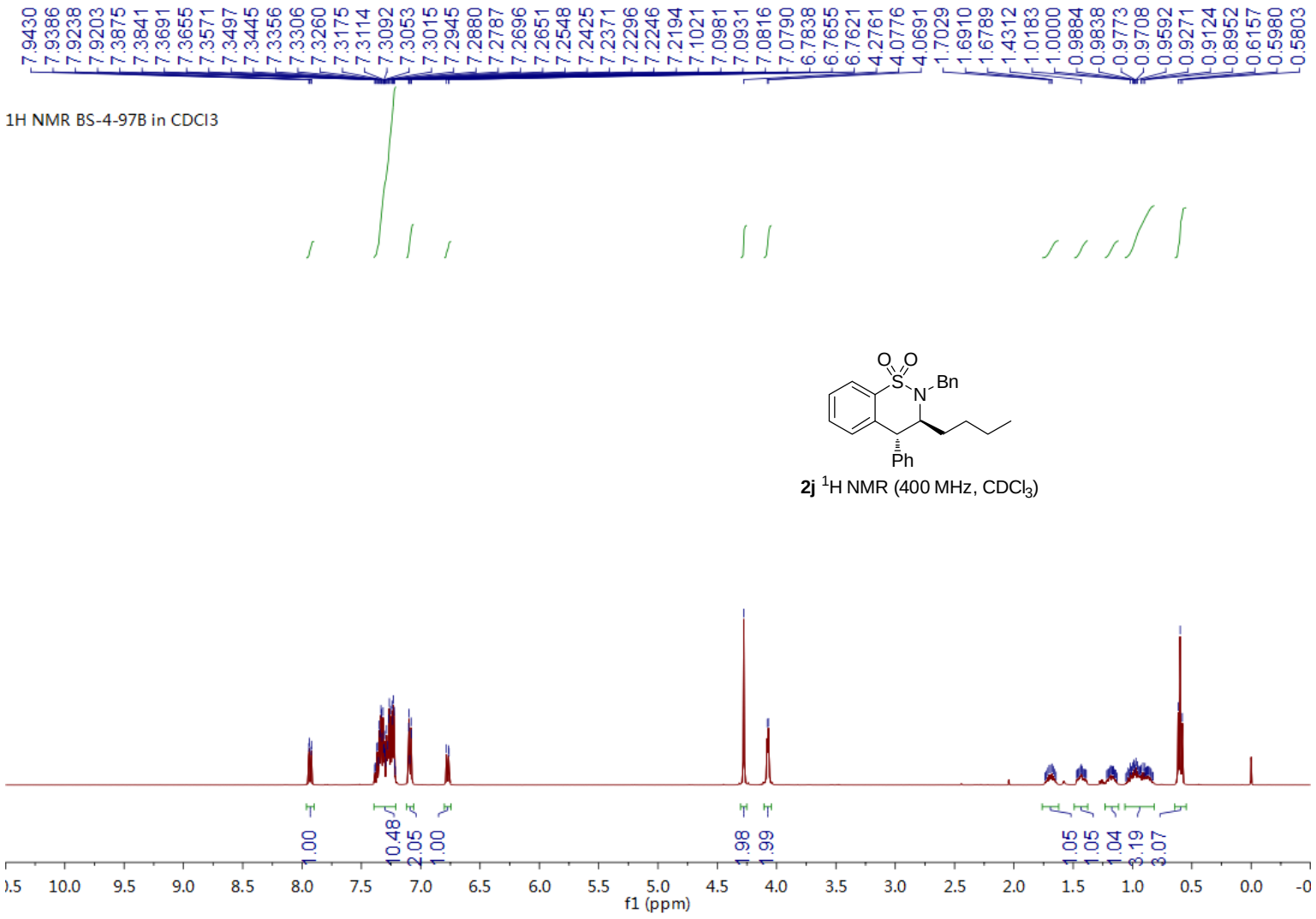
2h' H-H COSY (400 MHz, $CDCl_3$)



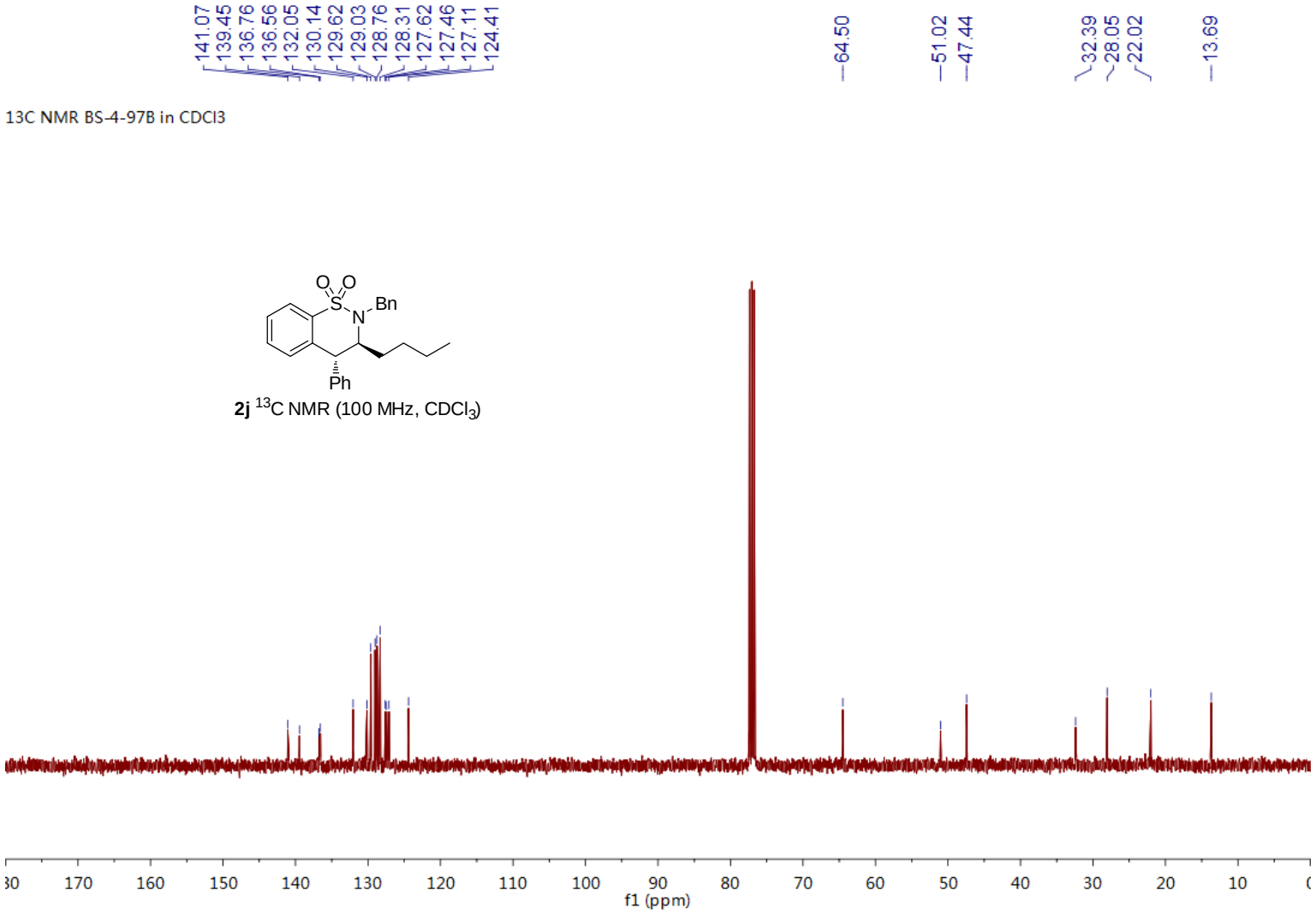
2i ^{1}H NMR (400 MHz, $CDCl_3$)



2i ^{13}C NMR (100 MHz, $CDCl_3$)

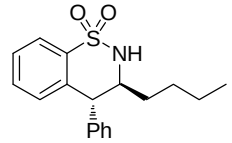


2j ^{1}H NMR (400 MHz, $CDCl_3$)

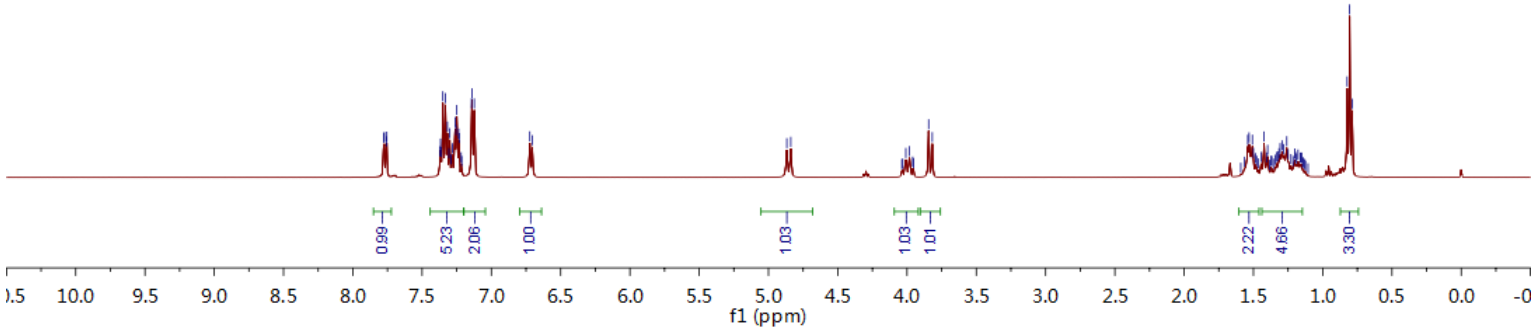


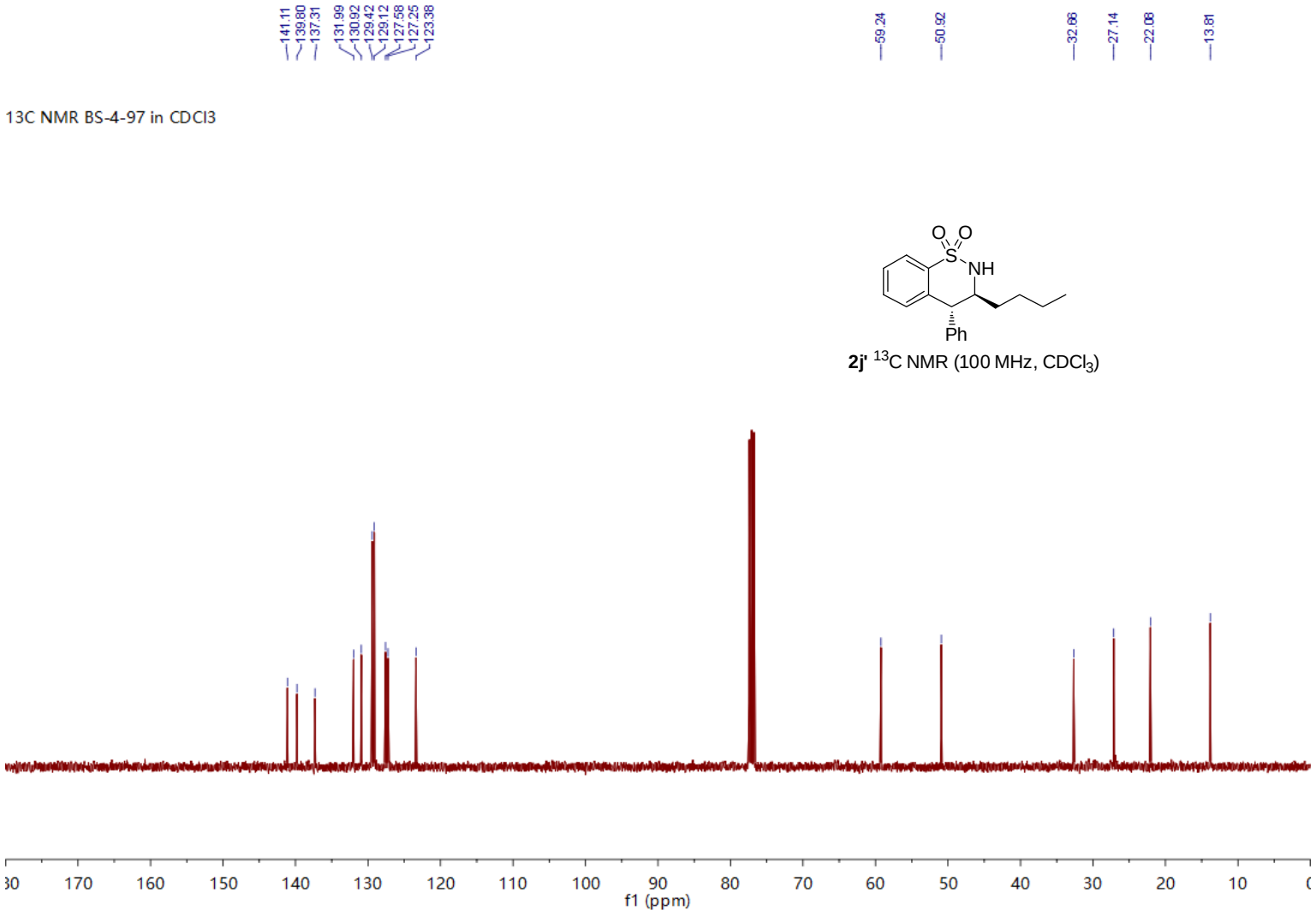
2j ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR BS-4-97 in CDCl3

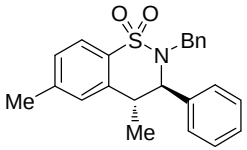


2j' ^{1}H NMR (400 MHz, $CDCl_3$)

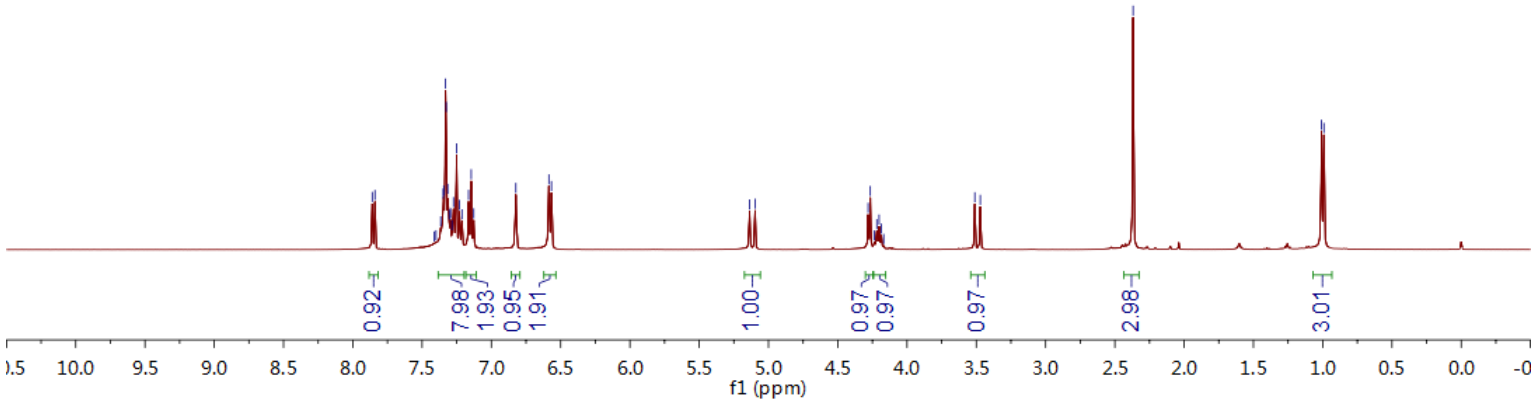


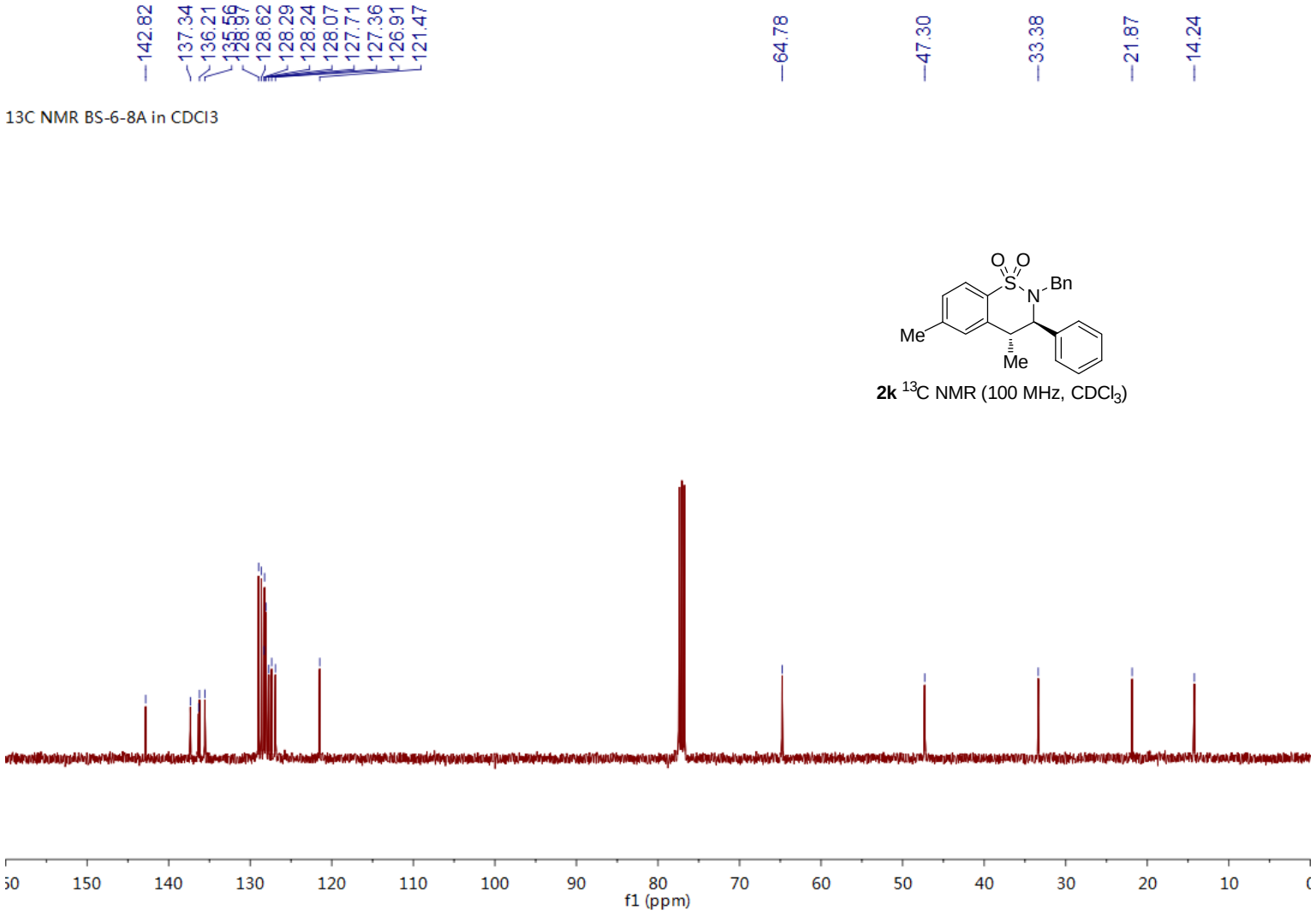


2j' ^{13}C NMR (100 MHz, $CDCl_3$)

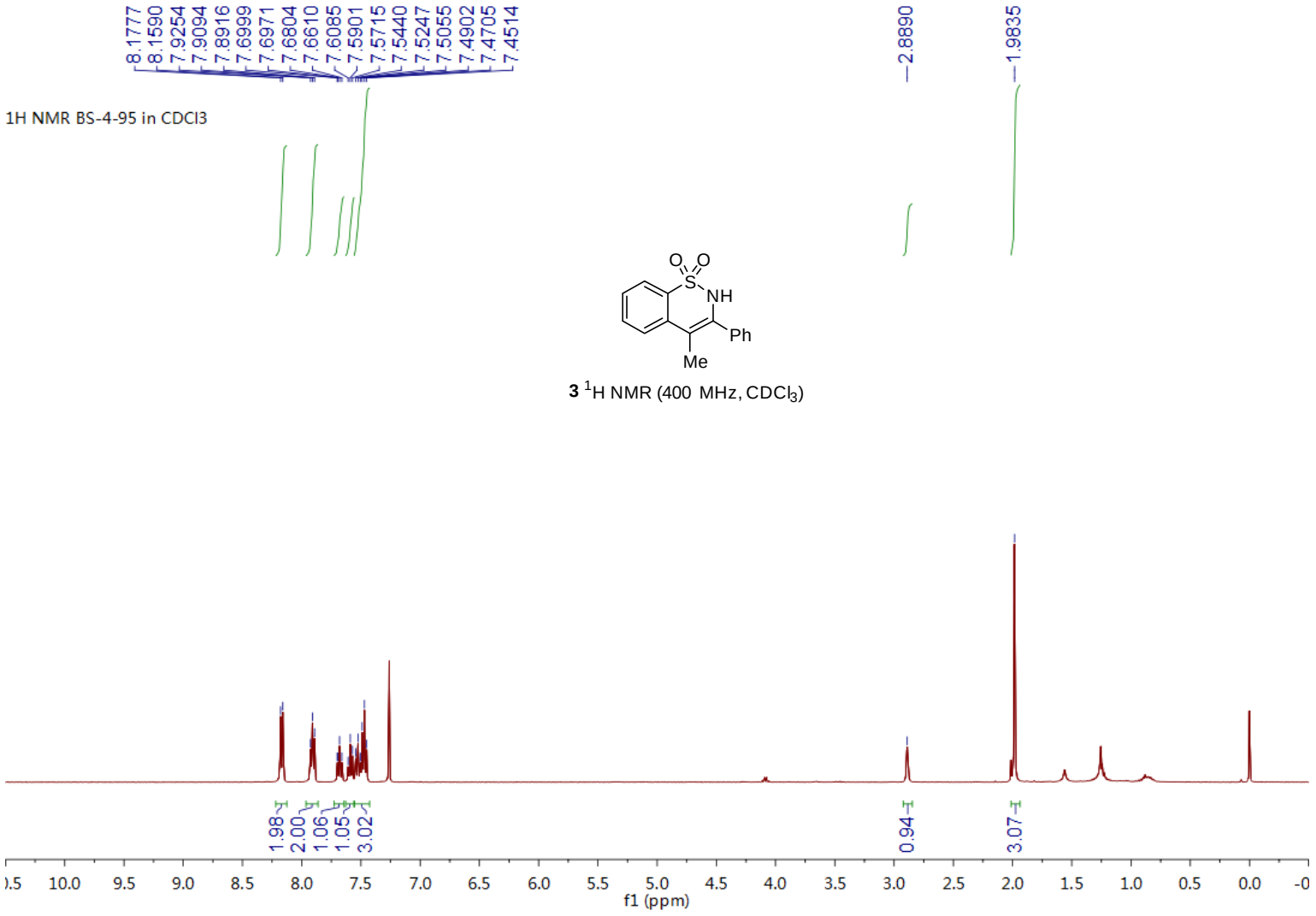


2k ^{1}H NMR (400 MHz, $CDCl_3$)

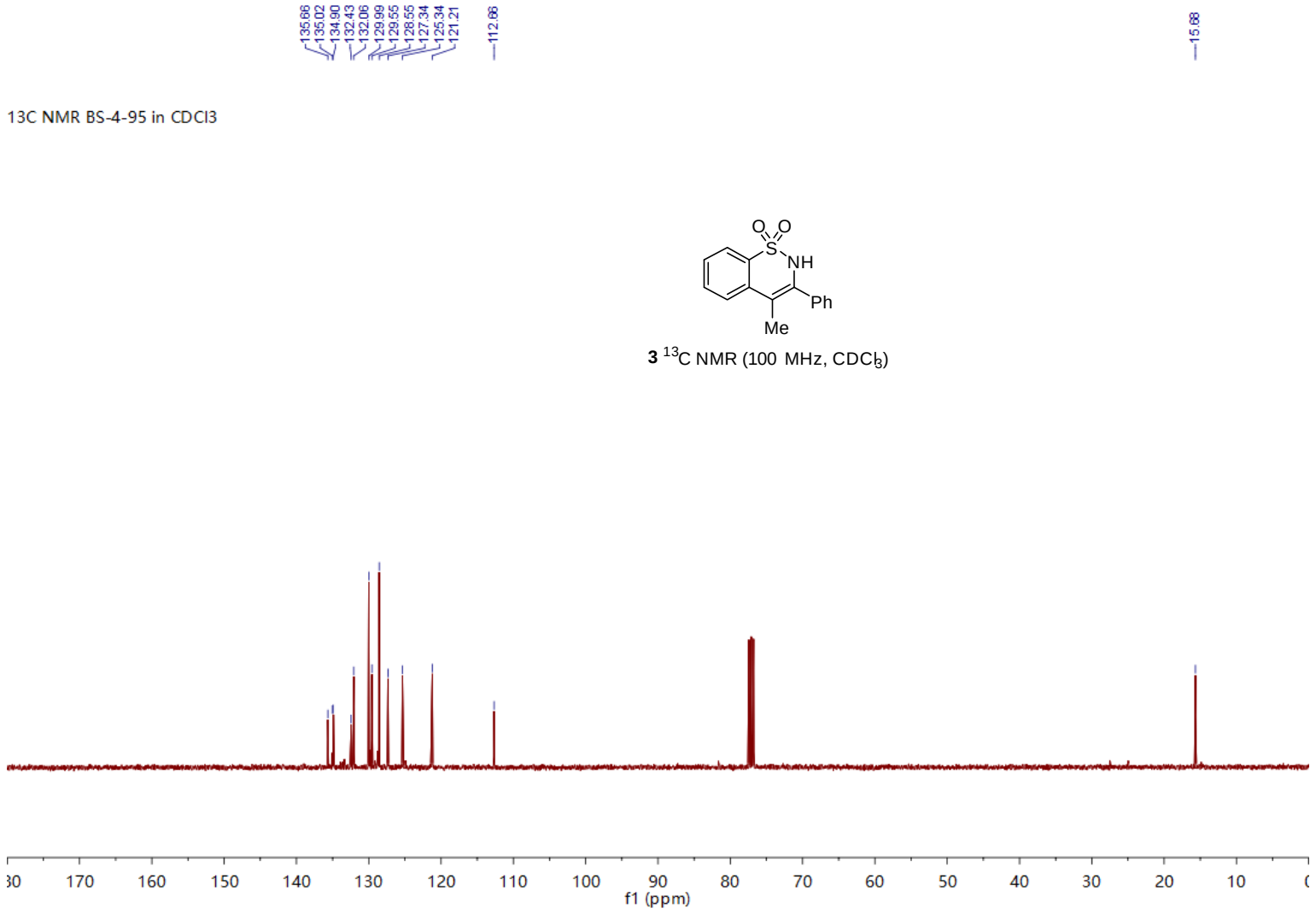




2k ^{13}C NMR (100 MHz, $CDCl_3$)



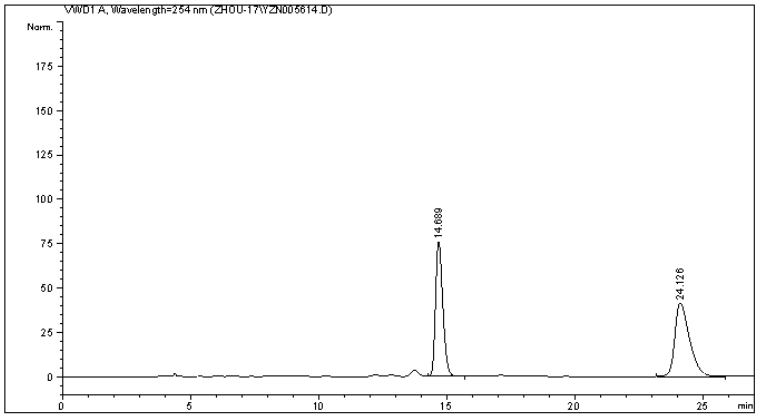
3 ^{1}H NMR (400 MHz, $CDCl_3$)



3 ^{13}C NMR (100 MHz, $CDCl_3$)

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN005614.D
Sample Name: MC-18-23B+-

```
==================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 9/29/2017 9:56:53 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/29/2017 9:55:57 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/6/2017 4:35:26 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 95/5, 0.7 mL/min,  30 oC, 254 nm
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  14.689 VB    0.3078 1508.24463   75.81213  47.9490
   2  24.126 BB    0.5983 1637.27307   41.39853  52.0510

Totals :                  3145.51770  117.21066

==================================================================
                      *** End of Report ***
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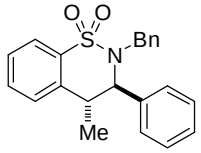
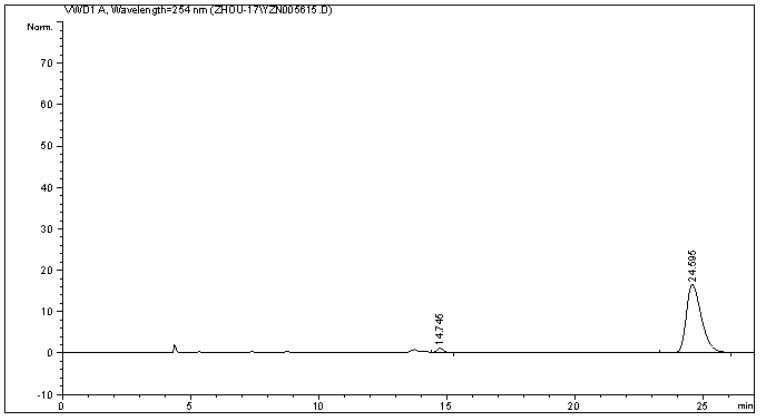


(+/-)-**2a**

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN005615.D
Sample Name: MC-18-23A

```
==================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 9/29/2017 10:25:44 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/29/2017 10:24:02 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/6/2017 4:37:14 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 95/5, 0.7 mL/min,  30 oC, 254 nm
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  14.745 VB    0.3056   21.23040    1.06406   3.0747
   2  24.595 BB    0.6276  669.25604   16.39869  96.9253

Totals :                  690.48644   17.46275

==================================================================
                      *** End of Report ***
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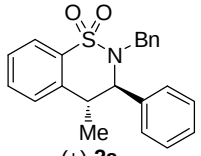
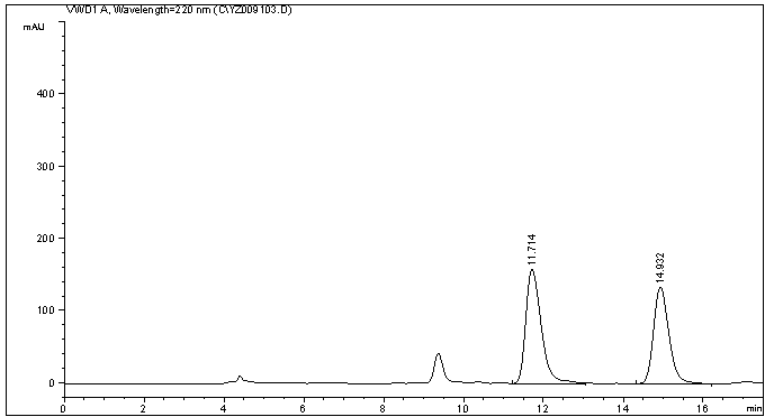


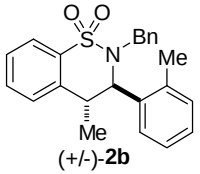
(+)-**2a**

Data File C:\CHEM32\1\DATA\C\YZ009103.D
Sample Name: BS-5-10 (+/-)

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/12/2015 2:37:08 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 11/12/2015 12:42:12 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:24:26 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 220 nm
```



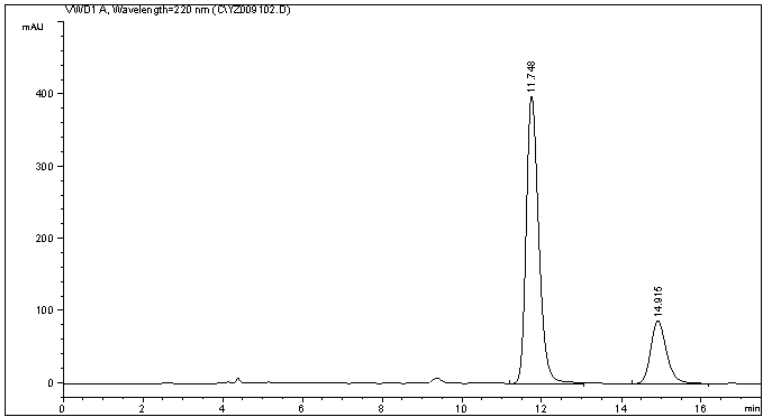

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  11.714 VB    0.4179 4243.04004  158.12268  54.2883
   2  14.932 VB    0.4123 3572.71875  133.64436  45.7117

Totals :                  7815.75879  291.76704


                          *** End of Report ***
```



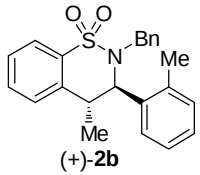
(+/-)-**2b**

Data File C:\CHEM32\1\DATA\C\YZ009102.D
Sample Name: BS-5-10

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/12/2015 2:17:06 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 11/12/2015 12:42:12 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:24:26 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 220 nm
```



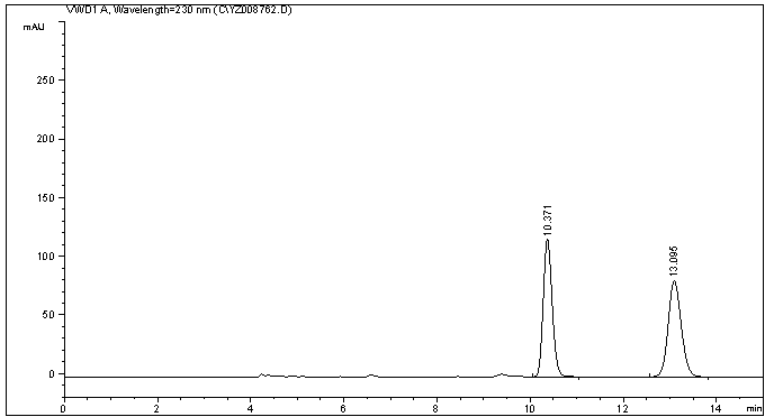

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  11.748 VB    0.3349 8707.44434  398.58865  78.4269
   2  14.915 VB    0.4227 2395.18628   87.10891  21.5731

Totals :                  1.11026e4   485.69756


                          *** End of Report ***
```



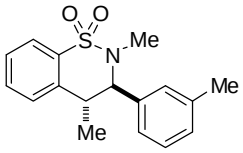
(+)-**2b**

Data File C:\CHEM32\1\DATA\C\YZ008762.D
Sample Name: BS-4-88A(+-)

```
==================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 9/22/2015 4:51:54 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 9/22/2015 4:27:40 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:04:03 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 230 nm
```



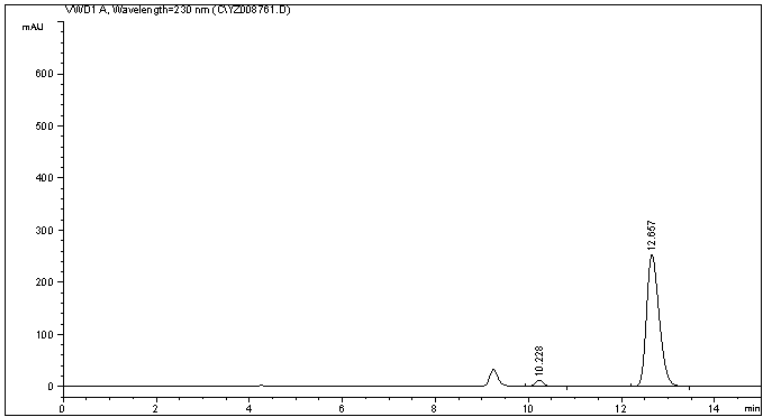

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  10.371 BB    0.2070 1568.68835  117.31021  49.5033
   2  13.095 BB    0.3016 1600.16858   82.12580  50.4967

Totals :                  3168.85693  199.43601

==================================================================
                      *** End of Report ***
```



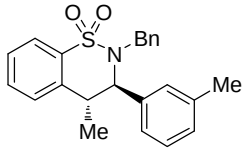
(+/-)-**2c**

Data File C:\CHEM32\1\DATA\C\YZ008761.D
Sample Name: BS-4-88A

```
==================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 9/22/2015 2:14:09 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 9/22/2015 12:06:10 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:03:03 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 230 nm
```



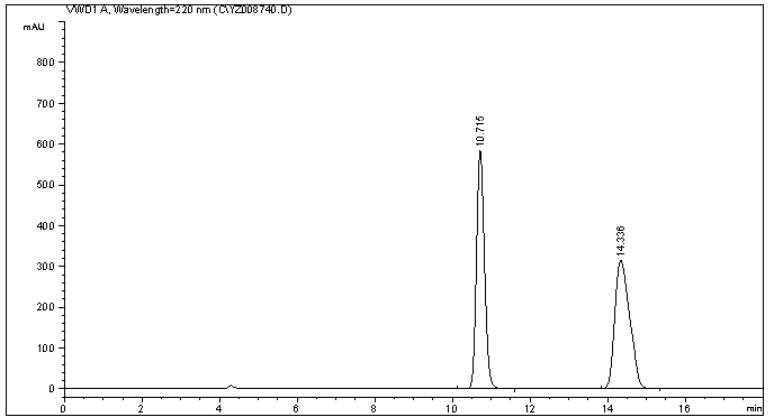

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  10.228 BB    0.2045  157.40727   11.95697   3.1907
   2  12.657 VB    0.2914 4775.92773  253.17534  96.8093

Totals :                  4933.33501  265.13231

==================================================================
                      *** End of Report ***
```



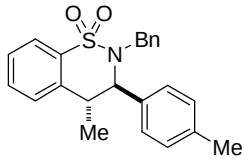
(+)-**2c**

Data File C:\CHEM32\1\DATA\C\YZ008740.D
Sample Name: BS-4-88B(+-)

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 9/19/2015 4:54:48 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 9/19/2015 4:33:12 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 8:56:06 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 220 nm
```



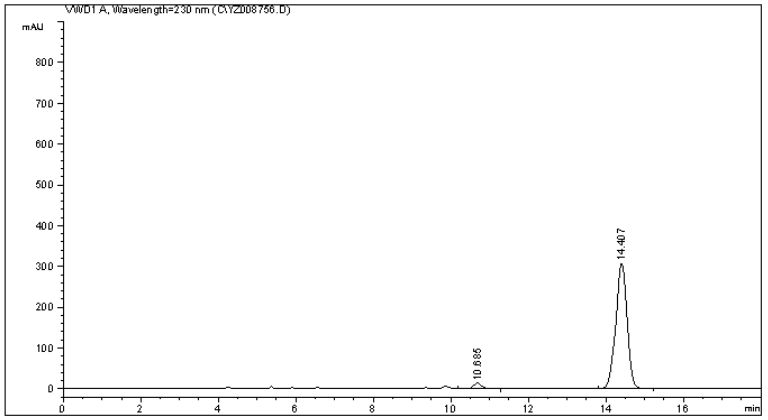

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  10.715 VB    0.2216 8324.21875  584.14319  49.8619
   2  14.336 BB    0.4095 8370.32422  314.48746  50.1381

Totals :                  1.66945e4   898.63065

                          *** End of Report ***
```



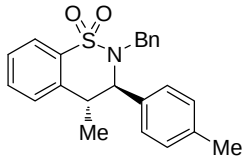
(+/-)-**2d**

Data File C:\CHEM32\1\DATA\C\YZ008756.D
Sample Name: BS-4-88B

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 9/22/2015 12:23:37 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 9/22/2015 12:06:10 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 8:56:06 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 230 nm
```



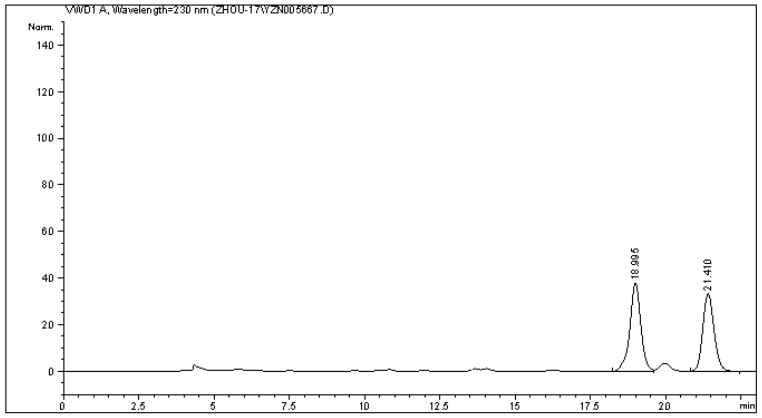

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  10.685 VB    0.2282  198.48097   13.39612   3.0716
   2  14.407 BB    0.3109 6263.27197  306.87427  96.9284

Totals :                  6461.75294  320.27039

                          *** End of Report ***
```



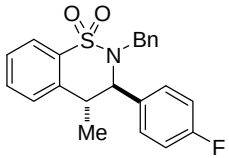
(+)-**2d**

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN005667.D
Sample Name: MC-18-25D

```
==================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 10/11/2017 8:13:47 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 10/11/2017 7:45:08 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/6/2017 4:44:40 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =95/5, 0.7 mL/min,  30 oC, 230 nm
```



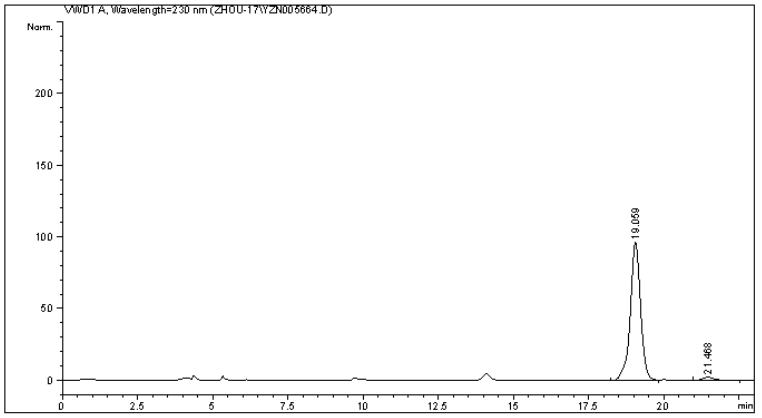

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.995 BV    0.3815  966.39764   37.96130  52.6952
   2  21.410 BB    0.4025  867.53992   33.35485  47.3048

Totals :                  1833.93756   71.31615

==================================================================
                      *** End of Report ***
```



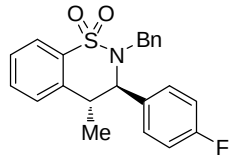
(+/-)-**2e**

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN005664.D
Sample Name: MC-18-25Cl

```
==================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 10/11/2017 4:25:23 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 10/11/2017 4:23:46 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/6/2017 4:39:22 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =95/5, 0.7 mL/min,  30 oC, 230 nm
```



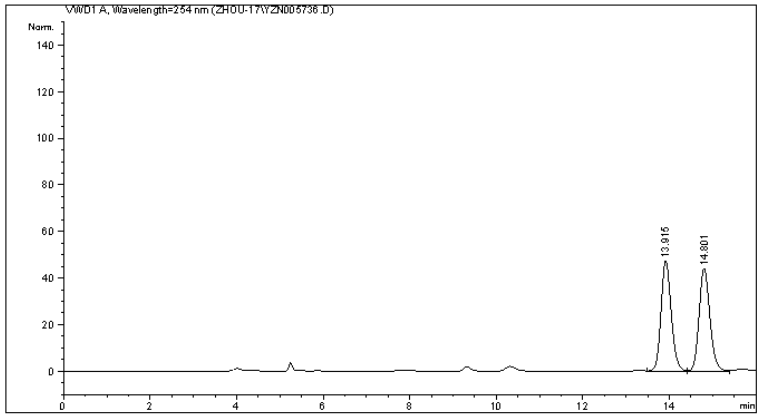

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  19.059 BV    0.3606 2302.26807   96.24651  97.3617
   2  21.468 BB    0.4188   62.38676    2.27596   2.6383

Totals :                  2364.65482   98.52246

==================================================================
                      *** End of Report ***
```



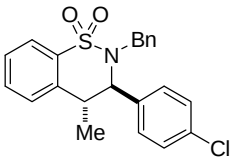
(+)-**2e**

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN005736.D
Sample Name: MC-18-30

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 10/17/2017 1:48:55 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 10/17/2017 1:41:59 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/6/2017 4:47:22 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH=90/10, 0.7 mL/min,  30 oC, 254 nm
```



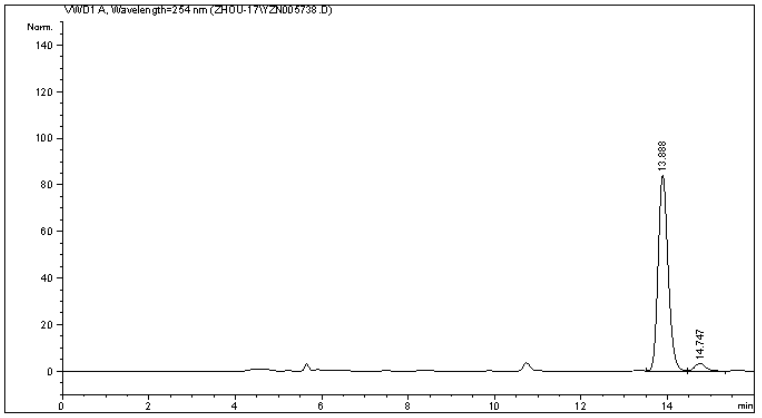

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  13.915 VV    0.2497  777.01904   47.34699  50.3572
   2  14.801 VV    0.2672  765.99658   43.99665  49.6428

Totals :                  1543.01563   91.34364

==========================================================================
                        *** End of Report ***
```



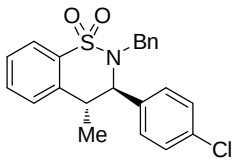
(+/-)-**2f**

Data File C:\CHEM32\1\DATA\ZHOU-17\YZN005738.D
Sample Name: MC-18-25E

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 10/17/2017 2:31:26 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 10/17/2017 2:28:25 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/6/2017 4:48:03 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH=90/10, 0.7 mL/min,  30 oC, 254 nm
```



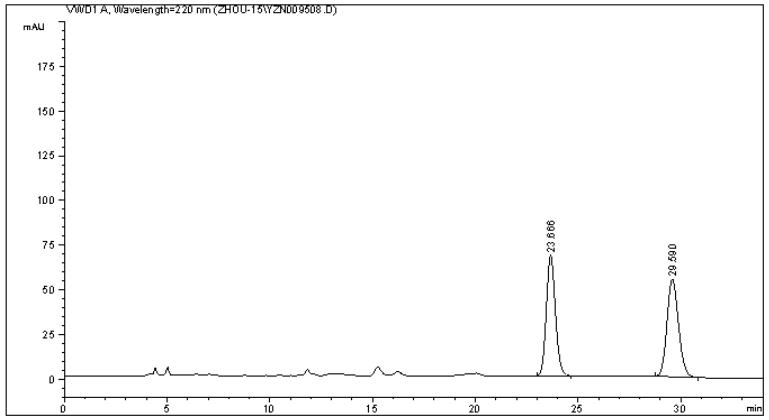

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|--------|
   1  13.888 VV    0.2455 1349.85291   84.09759  95.7132
   2  14.747 VB    0.2751   60.45788    3.34304   4.2868

Totals :                  1410.31078   87.44063

==========================================================================
                        *** End of Report ***
```



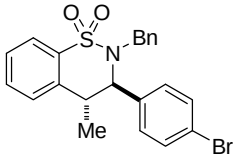
(+)-**2f**

Data File C:\CHEM32\1\DATA\ZHOU-15\YZN009508.D
Sample Name: BS-4-88E(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 9/22/2015 5:04:05 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/22/2015 5:02:45 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:54:02 PM
                  (modified after loading)
Sample Info     : AD, H/i-PrOH = 80/20, 0.7 mL/min, 30 oC, 220nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  23.666 BB    0.4746 2067.68091   67.35074  49.2496
   2  29.590 BB    0.6006 2130.68750   54.62753  50.7504

Totals :                  4198.36841  121.97826
```

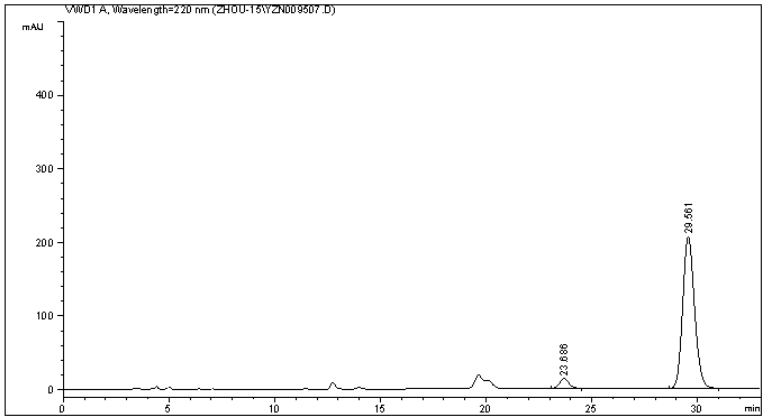


(+/-)-**2g**

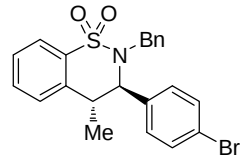
```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-15\YZN009507.D
Sample Name: BS-4-88E

```
Acq. Operator   :
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 9/22/2015 4:29:37 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/22/2015 4:28:55 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:54:45 PM
                  (modified after loading)
Sample Info     : AD, H/i-PrOH = 80/20, 0.7 mL/min, 30 oC, 220nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  23.686 BB    0.4776  399.34097   13.00737   4.7595
   2  29.561 BB    0.6031 7991.00098  205.73053  95.2405

Totals :                  8390.34195  218.73790
```

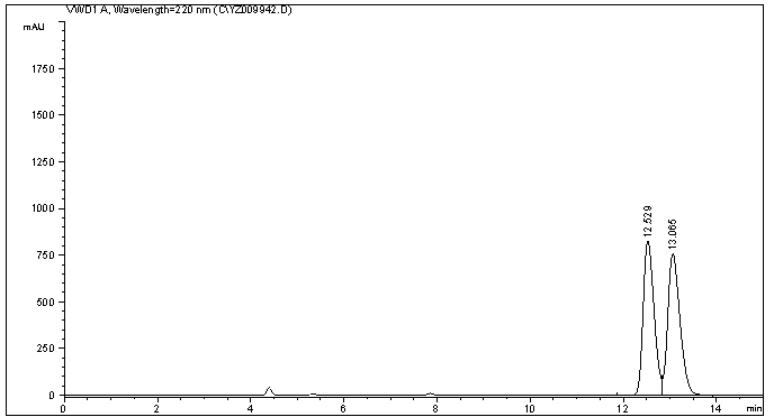


(+)-**2g**

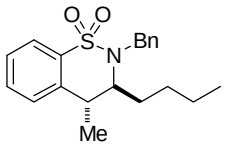
```
                          *** End of Report ***
```

Data File C:\CHEM32\1\DATA\C\YZ009942.D
Sample Name: BS-4-92A(+/-)

```
==========================================================================
Acq. Operator   : j
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/4/2016 12:22:13 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 3/4/2016 12:15:00 PM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 10:23:40 PM
                  (modified after loading)
Sample Info     : OD-H, Hexane/i-PrOH = 95/5, 0.7 mL/min, 30 oC, 220 nm
```



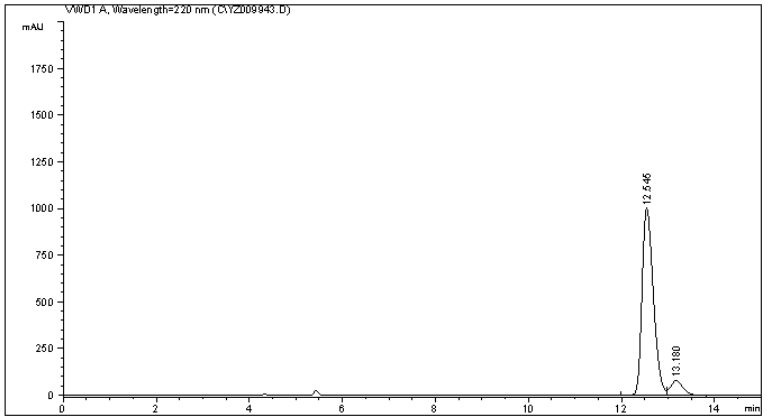

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  12.529 VV    0.2527 1.33561e4   825.89966  49.2877
   2  13.065 VB    0.2787 1.37422e4   757.22931  50.7123

Totals :                  2.70983e4  1583.12897

==========================================================================
                        *** End of Report ***
```



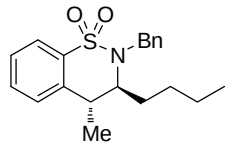
trans-(+/-)-**2h**

Data File C:\CHEM32\1\DATA\C\YZ009943.D
Sample Name: BS-4-92A

```
==========================================================================
Acq. Operator   : j
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/4/2016 12:39:34 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 3/4/2016 12:15:00 PM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 10:24:31 PM
                  (modified after loading)
Sample Info     : OD-H, Hexane/i-PrOH = 95/5, 0.7 mL/min, 30 oC, 220 nm
```



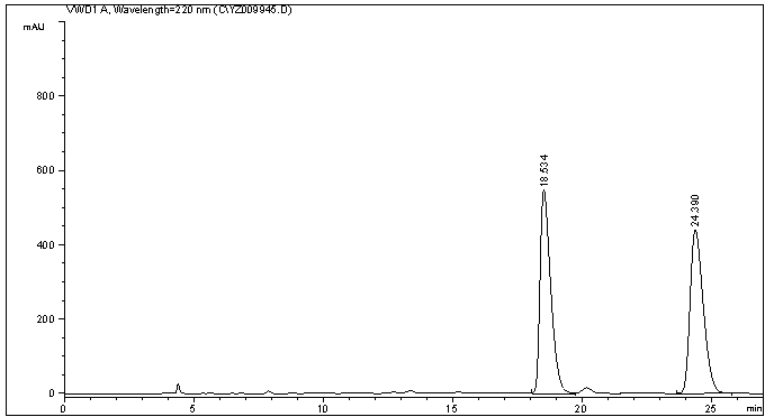

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  12.545 VV    0.2622 1.68785e4  1001.10419  92.1827
   2  13.180 VV    0.2789 1431.34436   78.78201   7.8173

Totals :                  1.83099e4  1079.88619

==========================================================================
                        *** End of Report ***
```



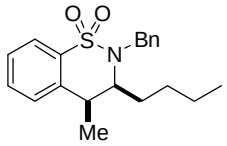
trans-(-)-**2h**

Data File C:\CHEM32\1\DATA\C\YZ009945.D
Sample Name: BS-4-92B(+/-)

```
==================================================================
Acq. Operator   : j
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 3/4/2016 1:28:24 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 3/4/2016 12:15:00 PM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 10:16:50 PM
                  (modified after loading)
Sample Info     : OD-H, Hexane/i-PrOH = 95/5, 0.7 mL/min, 30 oC, 220 nm
```



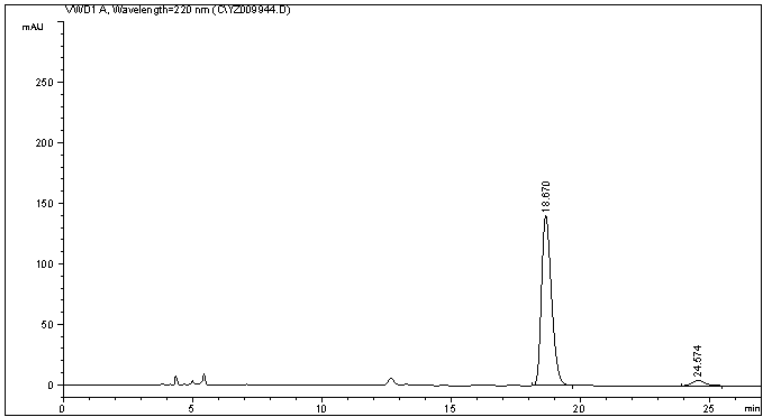

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  18.534 VV    0.4392 1.57366e4   546.72369  50.2497
   2  24.390 BB    0.5460 1.55802e4   441.13898  49.7503

Totals :                  3.13169e4   987.86267


==================================================================
                      *** End of Report ***
```



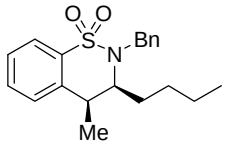
cis-(+/-)-**2h'**

Data File C:\CHEM32\1\DATA\C\YZ009944.D
Sample Name: BS-4-92B

```
==================================================================
Acq. Operator   : j
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 3/4/2016 12:58:18 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 3/4/2016 12:15:00 PM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 10:15:16 PM
                  (modified after loading)
Sample Info     : OD-H, Hexane/i-PrOH = 95/5, 0.7 mL/min, 30 oC, 220 nm
```



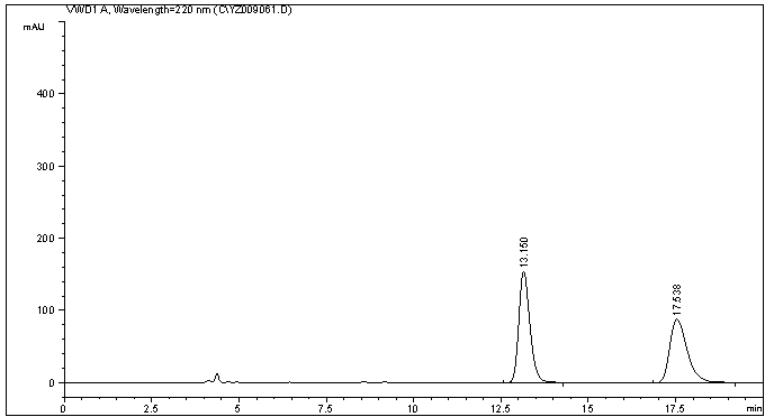

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  18.670 BB    0.4164 3781.77002   140.28308  96.1154
   2  24.574 BB    0.5274  152.84372     4.41802   3.8846

Totals :                  3934.61374   144.70110


==================================================================
                      *** End of Report ***
```



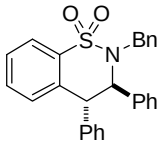
cis-(-)-**2h'**

Data File C:\CHEM32\1\DATA\C\YZ009061.D
Sample Name: BS-5-9A(+/-)

```
==================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/10/2015 1:56:25 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 11/10/2015 12:58:25 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:19:13 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 80/20, 0.7 mL/min, 30 oC, 220 nm
```



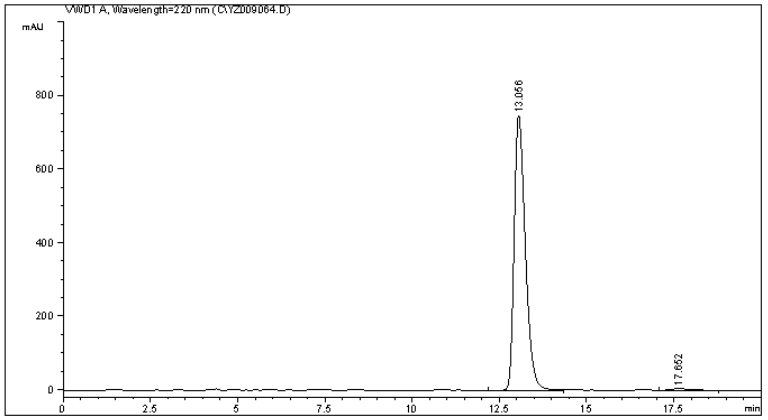

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  13.150 VV    0.3436 3478.50122  154.86357  52.3876
   2  17.538 VB    0.5448 3161.42896   88.82808  47.6124

Totals :                  6639.93018  243.69165

==================================================================
                      *** End of Report ***
```



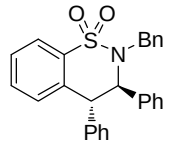
(+/-)-**2i**

Data File C:\CHEM32\1\DATA\C\YZ009064.D
Sample Name: BS-5-9A

```
==================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/10/2015 3:15:02 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 11/10/2015 12:58:25 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:20:11 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 80/20, 0.7 mL/min, 30 oC, 220 nm
```



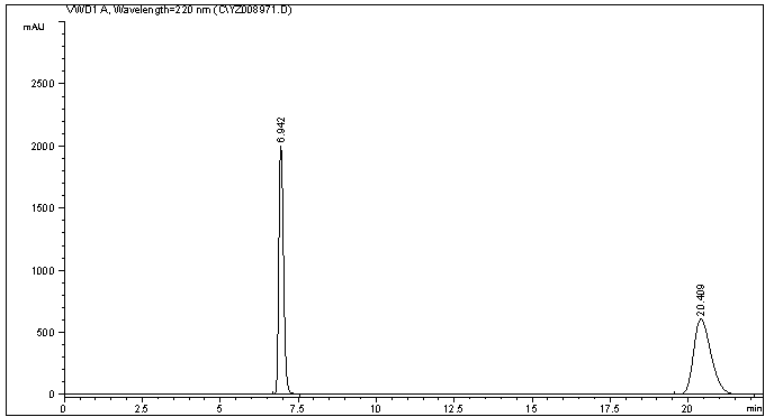

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1  13.056 VV    0.3425 1.67302e4   748.02820  98.5973
   2  17.652 VV    0.6443  238.00883    5.30495   1.4027

Totals :                  1.69682e4   753.33315

==================================================================
                      *** End of Report ***
```



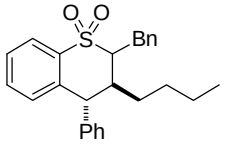
(-)-**2i**

Data File C:\CHEM32\1\DATA\C\YZ008971.D
Sample Name: BS-4-94(+-)

```
==================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 10/27/2015 6:07:28 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 10/27/2015 5:44:25 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:14:04 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 80/20, 0.7 mL/min, 30 oC, 220 nm
```



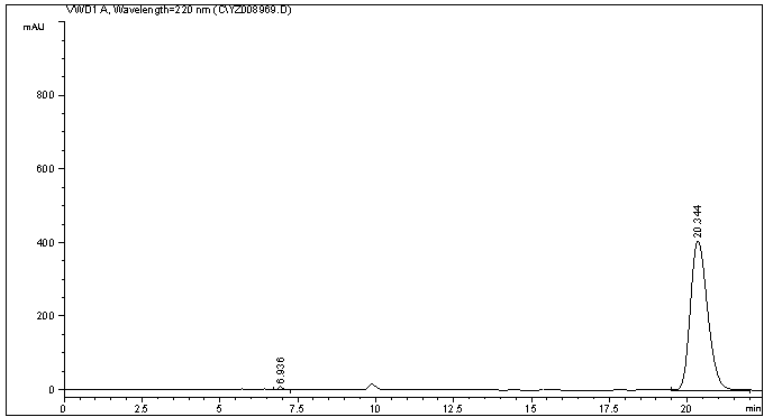

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1   6.942 VV    0.1658 2.11712e4 1998.59863  47.4316
   2  20.409 BB    0.6028 2.34640e4   606.52753  52.5684

Totals :                  4.46351e4  2605.12616

==================================================================
                      *** End of Report ***
```



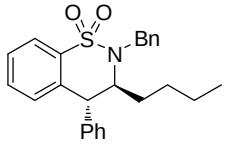
(+/-)-**2j**

Data File C:\CHEM32\1\DATA\C\YZ008969.D
Sample Name: BS-4-94

```
==================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 10/27/2015 2:34:06 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 10/27/2015 1:26:42 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/3/2016 9:15:54 PM
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 80/22, 0.7 mL/min, 30 oC, 220 nm
```



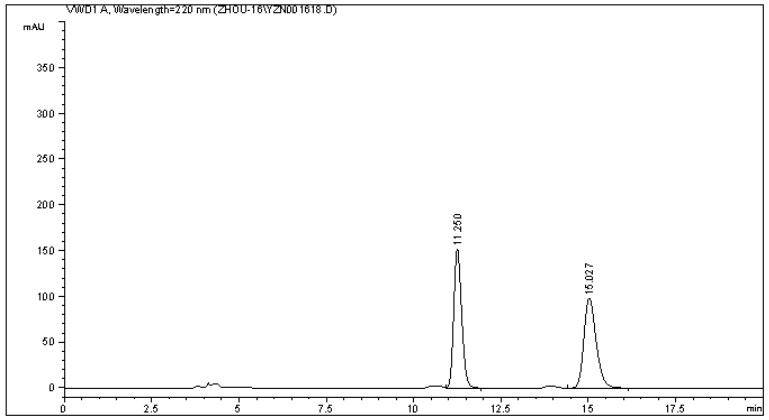

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|--------|
   1   6.936 BB    0.1573   98.31807    9.48963   0.6302
   2  20.344 VB    0.5970 1.55016e4   405.89703  99.3698

Totals :                  1.55999e4   415.38667

==================================================================
                      *** End of Report ***
```



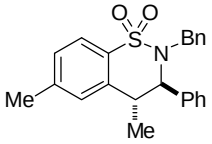
(-)-**2j**

Data File C:\CHEM32\1\DATA\ZHOU-16\YZN001618.D
Sample Name: BS-6-8A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/17/2016 6:04:38 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/17/2016 6:01:09 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/29/2016 3:27:40 PM
                  (modified after loading)
Sample Info     : OD-H, Hex/i-PrOH = 93/07, 0.7 mL/min, 30oC, 20 nm
```



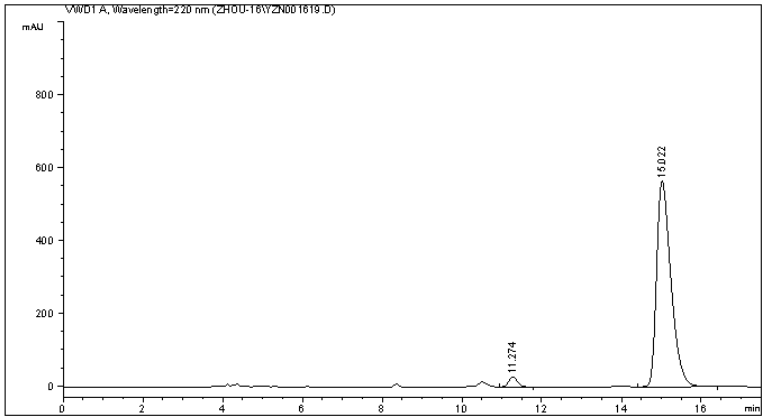

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  11.250 VB    0.2437 2400.69336  152.18907  49.8922
   2  15.027 VB    0.3763 2411.06372   98.33951  50.1078

Totals :                  4811.75708  250.52858

                          *** End of Report ***
```



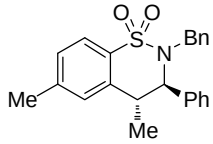
(+/-)-**2k**

Data File C:\CHEM32\1\DATA\ZHOU-16\YZN001619.D
Sample Name: BS-6-8A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/17/2016 8:40:13 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/17/2016 8:25:35 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/29/2016 3:28:20 PM
                  (modified after loading)
Sample Info     : OD-H, Hex/i-PrOH = 93/07, 0.7 mL/min, 30oC, 20 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  11.274 VB    0.2457  436.91373   27.40578   3.0049
   2  15.022 VB    0.3833 1.41029e4   564.39178  96.9951

Totals :                  1.45398e4   591.79756

                          *** End of Report ***
```



(+)-**2k**