Supporting Information

Stereodivergent Access to 5–6–5, 5–6–6, and 5–6–7 Fused Tricyclic Indolizidine Cores *via* Ring-Size-Dependent Fragmentation of Overbred Intermediates

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1. **General Information**: All reactions were performed in oven-dried or flame-dried round-bottom flasks fitted with rubber septa and were conducted under positive argon pressure using standard Schlenk techniques, unless noted otherwise. Cannula or gas-tight syringes with stainless steel needles were used to transfer air or moisture-sensitive liquids. Where necessary (so noted), solutions were degassed by sparging with argon for a minimum of 10 min. Commercial reagents and solvents were purified and stored according to procedures prescribed in the literature[1]. All commercial reagents were obtained from Merck, TCI and Spectrochem. Reaction progress was monitored by TLC on aluminium-backed silica gel 60 F_{254} plates (Merck), visualized by UV light (254 nm) and/or staining with iodine or phosphomolybdic acid. Column chromatography was performed on silica gel (100–200 mesh) using n-hexane/ethyl acetate mixtures. NMR (Nuclear Magnetic Resonance) spectra were recorded on Bruker 500 MHz spectrometers (500 MHz for ^{1}H and 126 MHz for ^{13}C respectively), Bruker 600 MHz spectrometers (600 MHz for ^{1}H and 151 MHz for 13C respectively), and JEOL ECS 500 MHz spectrometers (500 MHz for ^{1}H and 126 MHz for ^{13}C respectively) using deuterated solvent. Chemical shifts are reported in ppm, proton coupling constants (J) are reported as absolute values in Hz, and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or combinations thereof). NMR spectra data are described in terms of chemical shift (δ in ppm) relative to TMS (δ = 0.00 ppm) or $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and the central line of $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. HRMS (High-Resolution Mass Spectrometry) was performed on SCIEX X500R QTOF (TOF-MS) mass spectrometer. Single crystal X-ray diffraction measurements were carried out on Rigaku: XTALAB Synergy-I.

2. General Procedure for synthesis of compounds 16 to 28

General Procedure A[2]

To an oven-dried 50 mL two-neck round-bottom flask equipped with a magnetic stir bar, Palladium(II) acetate (10 mol%) and the allylic acetate (1.5 equiv.) were added. The flask was evacuated and backfilled with argon (3 cycles). Anhydrous THF (3.5 ml $mmol^{-1}$) was added *via* syringe, and the mixture was degassed with an argon balloon for 15 minutes. Subsequently, Tributylphosphine (PBu_3, 50% solution in ethyl acetate, 40 mol%) was added dropwise. The resulting mixture was stirred for 5 minutes at room temperature. A solution of the bicyclic ketone (1 equiv.) in anhydrous THF (3.5 mL $mmol^{-1}$) was then added to the reaction mixture dropwise (resulting in a final reaction concentration of approx. 0.14 M). The reaction was stirred at room

temperature under an argon atmosphere for 10 hours. Upon completion (monitored by TLC), the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to afford the desired product.

General Procedure B

To a stirred solution of the appropriate starting material (1.0 equiv) in DCM (10 mL $mmol^{-1}$) was added trifluoroacetic acid (TFA) (5.0 equiv) at 25 ºC. The reaction mixture (approx. 0.1 M) was stirred for 5 h. After the reaction time, the volatiles were removed under reduced pressure. The resulting residue was dissolved in ethyl acetate and washed with saturated aqueous $NaHCO_3$ solution and water (2 ×). The aqueous layer was further extracted with EtOAc (2 ×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to afford the desired product and recovered starting material. The recovered starting material was subjected again to the identical reaction conditions (25 ºC, 5.0 equiv TFA). This cycle was repeated two more times (total three cycles). The yields reported correspond to the combined yield of the isolated product from these cycles.

General Procedure C

To a stirred solution of the appropriate starting material (1.0 equiv) in DCM (10 mL $mmol^{-1}$) was added trifluoroacetic acid (TFA) (5.0 equiv) at 25 ºC. The reaction mixture (approx. 0.1M) was stirred at this temperature for 24 h. After completion of the reaction (monitored by TLC), the volatiles were removed under reduced pressure. The resulting residue was dissolved in ethyl acetate (EtOAc) and washed with saturated aqueous $NaHCO_3$ solution. The aqueous layer was further extracted with EtOAc (2 ×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to afford the desired product.

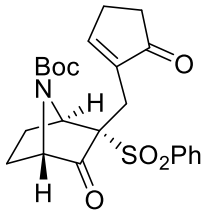
General Procedure D[3]

To a stirred solution of the appropriate starting material (1.0 equiv) in dry methanol (7.2 mL $mmol^{-1}$) was added sodium methoxide (NaOMe) (0.5 equiv) at room temperature under an argon atmosphere (Note: In the case of substrate **17**, gentle warming (approx. 55 to 60 °C) was required to achieve a clear solution prior to the addition of NaOMe). The reaction mixture (approx.

0.14 M) was stirred at room temperature for 30 minutes. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure. The resulting residue was dissolved in ethyl acetate (EtOAc) and washed with water (2 ×). The aqueous layer was further extracted with EtOAc (2 ×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane, to afford the desired product.

3. Characterization of compounds 16 to 29

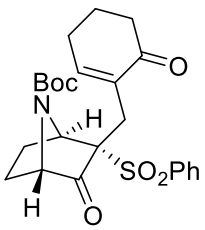
Synthesis of (1*R*,2*S*,4*S*)- *tert*-butyl 3-oxo-2-((5-oxocyclopent-1-en-1-yl)methyl)-2-(phenylsulfonyl)-7 azabicyclo[2.2.1]heptane-7-carboxylate (16)



16

Prepared according to General Procedure A using bicyclic ketone **12** (300 mg, 0.854 mmol) and allyl acetate **13** (197.5 mg, 1.282 mmol). Purification by column chromatography (silica gel 100-200mesh, 20% EtOAc in hexanes) afforded **16** as a white solid (350 mg, 92% yield). R_f = 0.25 (30% ethyl acetate in hexane), mp = 158-160 °C, $[\alpha]_D^{25}$ = +65.6 (*c* 2.8, $CHCl_3$) ; **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.02 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.18 (m, 1H), 4.61 (d, *J* = 4.3 Hz, 1H), 4.33 (br s, 1H), 2.86 – 2.78 (m, 1H), 2.67 (d, *J* = 14.5 Hz, 1H), 2.54 – 2.42 (m, 2H), 2.39 (d, *J* = 14.6 Hz, 1H), 2.25 – 2.21 (m, 2H), 2.17 – 2.04 (m, 2H), 1.89 (br s, 1H), 1.41 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ (ppm) 208.1, 199.9, 160.3, 153.9, 139.4, 137.6, 134.5, 130.5, 129.1, 81.5, 78.4, 64.9, 62.4, 33.8, 29.5, 28.2, 27.0, 26.0, 25.8. HRMS (ESI-TOF) m/z: [M + Na]+ calcd. for $C_{23}H_{27}NO_6SNa$ 468.1451; Found 468.1455.

Synthesis of (1*R*,2*S*,4*S*)-*tert*-butyl 3-oxo-2-((6-oxocyclohex-1-en-1-yl)methyl)-2-(phenylsulfonyl)-7-azabicyclo[2.2.1]heptane-7-carboxylate (17)

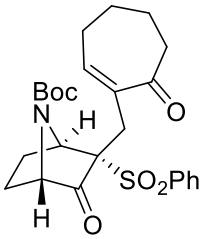


17

Prepared according to General Procedure A using bicyclic ketone **12** (500 mg, 1.424 mmol) and allyl acetate **14** (359 mg, 2.136 mmol). Purification by column chromatography (silica gel 100-200mesh, 20% EtOAc in hexanes) afforded **17** as a white solid (621 mg, 95% yield). R_f = 0.3 (30% ethyl acetate in hexane), mp = 134-136 °C, $[\alpha]_D^{25}$= +54.7 (*c* 2.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 7.9 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 6.77 – 6.34 (m, 1H), 4.54 (d, *J* = 3.1 Hz, 1H), 4.25 (br s, 1H), 2.86 – 2.52 (m, 2H), 2.36 – 2.17 (m, 5H), 2.09 (br s, 2H), 1.93 – 1.79 (m, 3H), 1.43 (s, 9H). **^{13}C{^{1}H}**

NMR (126 MHz, $CDCl_3$): δ (ppm) 200.1, 198.4, 154.6, 148.9, 137.8, 134.3, 133.9, 130.6, 129.1, 81.5, 78.6, 65.4, 62.5, 38.0, 35.3, 28.3, 26.4, 26.3, 26.2, 22.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. For $C_{24}H_{29}NO_6SNa$ 482.1608; Found 482.1599.

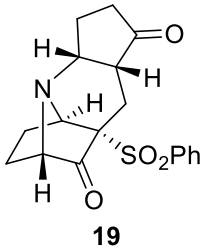
Synthesis of (1*R*,2*S*,4*S*)-*tert*-butyl 3-oxo-2-((7-oxocyclohept-1-en-1-yl)methyl)-2-(phenylsulfonyl)-7-azabicyclo[2.2.1]heptane-7-carboxylate (18)



18

Prepared according to General Procedure A using bicyclic ketone **12** (300 mg, 0.854 mmol) and allyl acetate **15** (233.4 mg, 1.282 mmol). Purification by column chromatography (silica gel 100-200mesh, 20% EtOAc in hexanes) afforded **18** as a white semi solid (352 mg, 87% yield). R_f = 0.33 (30% ethyl acetate in hexane), mp = 96-104 °C, $[\alpha]_D^{25}$= +28.0 (*c* 0.4, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 7.9 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 6.46 – 6.17 (m, 1H), 4.52 (d, *J* = 3.8 Hz, 1H), 4.25 (br s, 1H), 2.88 – 2.64 (m, 2H), 2.50 – 2.40 (m, 3H), 2.34 – 2.21 (m, 2H), 2.08 (br s, 1H), 1.89 (br s, 1H), 1.70 – 1.60 (m, 4H), 1.55 (d, *J* = 5.3 Hz, 1H), 1.43 (s, 9H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ (ppm) 202.8, 200.3, 154.7, 147.0, 145.9, 137.8, 134.3, 130.6, 129.1, 81.6, 78.8, 65.6, 62.6, 42.0, 38.5, 28.3, 28.1, 26.4, 25.6, 25.2, 21.4. HRMS (ESI-TOF) m/z: [M + Na]+ calcd. For $C_{25}H_{31}NO_6SNa$ 496.1764; Found 496.1758.

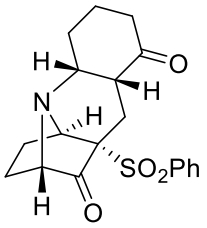
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,8a*R*)-4-(phenylsulfonyl)decahydro-6*H*-1,4-methanocyclopenta[*e*]indolizine-6,10-dione (19)



19

Prepared according to General Procedure C using **16** (200 mg, 0.449 mmol). Purification by column chromatography (silica gel 100-200mesh, 70% EtOAc in hexanes) afforded **19** as a white solid (144.2 mg, 93% yield). R_f = 0.2 (60% ethyl acetate in hexane), mp = 150-152 °C, $[\alpha]_D^{25}$ = +138.1 (*c* 2.2, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 3.85 (d, *J* = 4.1 Hz, 1H), 3.63 – 3.57 (m, 2H), 2.80 – 2.73 (m, 1H), 2.45 – 2.37 (m, 1H), 2.29 – 2.17 (m, 3H), 2.15 – 2.05 (m, 2H), 2.02 – 1.97 (m, 1H), 1.95 – 1.88 (m, 1H), 1.87 – 1.77 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ (ppm) 216.1, 206.7, 136.4, 134.4, 130.2, 129.1, 73.1, 73.0, 63.1, 56.7, 41.7, 36.8, 29.6, 27.4, 24.8, 23.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{19}NO_4SNa$ 368.0927; Found 368.0921.

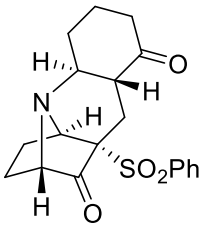
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,9a*R*)-4-(phenylsulfonyl)decahydro-1,4-methanopyrrolo[1,2-*a*]quinoline-6,11(1*H*)-dione (20)



20

Prepared according to General Procedure B using **17** (300 mg, 0.653 mmol). Purification by column chromatography (silica gel 100-200mesh, 50% EtOAc in hexanes). The resulting solid was triturated with ethyl acetate to afford **20** as a white solid (117.3 mg, 50% BRSM yield). R_f = 0.25 (60% ethyl acetate in hexane), mp = 168-170 ºC, $[\alpha]_D^{25}$ = +65.1 (*c* 1.4, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.98 (d, *J* =8.1 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 2H), 4.02 (d, *J* = 4.5 Hz, 1H), 3.50 (d, *J* = 5.2 Hz, 1H), 3.30 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.64 – 2.54 (m, 1H), 2.44 – 2.33 (m, 2H), 2.28 (dt, *J* = 15.2, 4.9 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.98 – 1.87 (m, 3H), 1.84 – 1.76 (m, 1H), 1.69 – 1.57 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ (ppm) 209.8, 207.4, 136.6, 134.4, 130.3, 129.1, 74.1, 71.6, 62.3, 56.7, 46.8, 38.7, 30.6, 28.4, 24.6, 24.1, 21.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{21}NO_4SNa$ 382.1083; Found 382.1081.

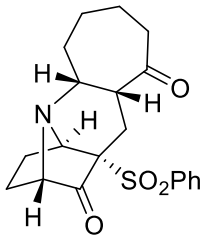
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,9a*S*)-4-(phenylsulfonyl)decahydro-1,4-methanopyrrolo[1,2-*a*]quinoline-6,11(1*H*)-dione (21)



21

Prepared according to General Procedure C using **17** (200 mg, 0.435 mmol). Purification by column chromatography (silica gel 100-200mesh, 50% EtOAc in hexanes) afforded **21** as a white solid (124.1 mg, 95% yield). R_f = 0.25 (60% ethyl acetate in hexane), mp = 156-158 ºC, $[\alpha]_D^{25}$ = +56.1 (*c* 1.1, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.99 (d, *J* = 8.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 3.74 (d, *J* = 4.2 Hz, 1H), 3.70 (d, *J* = 5.8 Hz, 1H), 3.02 (t, *J* = 11.5 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.40 (td, *J* = 12.1, 4.3 Hz, 1H), 2.29 (d, *J* = 13.8 Hz, 1H), 2.19 – 2.13 (m, 2H), 2.12 – 2.02 (m, 3H), 1.91 (td, *J* = 12.2, 5.8 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.78 (dd, *J* = 12.9, 4.3 Hz, 1H), 1.65 – 1.57 (m, 2H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$)**:** δ (ppm) 208.0, 206.9, 136.7, 134.4, 130.1, 129.2, 74.6, 69.2, 66.3, 61.7, 51.0, 40.5, 30.6, 30.2, 24.8, 23.9, 23.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{19}H_{22}NO_4S$ 360.1264; Found 360.1257.

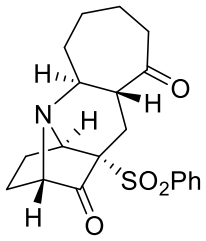
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,10a*R*)-4-(phenylsulfonyl)dodecahydro-6*H*-1,4-methanocyclohepta[*e*]indolizine-6,12-dione (22)



22

Prepared according to General Procedure C using **18** (150 mg, 0.317 mmol). Purification by column chromatography (silica gel 100-200mesh, 35% EtOAc in hexanes) afforded **22** as a brown semi solid (71 mg, 60% yield). R_f = 0.45 (60% ethyl acetate in hexane), mp = 96-102 ºC, $[\alpha]_D^{25}$ = +109.2 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J* = 7.9 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 3.73 (d, *J* = 3.7 Hz, 1H), 3.58 (d, *J* = 6.2 Hz, 1H), 3.56 – 3.51 (m, 1H), 2.79 – 2.70 (m, 2H), 2.48 (dd, *J* = 18.1, 7.1 Hz, 1H), 2.32 – 2.26 (m, 1H), 2.13 – 2.03 (m, 2H), 1.94 – 1.75 (m, 6H), 1.62 – 1.54 (m, 1H), 1.50 (dd, *J* = 12.6, 10.2 Hz, 1H), 1.46 – 1.37 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ (ppm) 210.6, 208.3, 136.5, 134.3, 130.2, 129.1, 74.3, 71.0, 62.4, 55.9, 48.4, 41.8, 33.6, 29.6, 28.9, 28.3, 24.8, 24.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{23}NO_4SNa$ 396.1240; Found 396.1232.

Synthesis of (1*S*,3a*R*,4*S*,5a*R*,10a*S*)-4-(phenylsulfonyl)dodecahydro-6*H*-1,4-methanocyclohepta[*e*]indolizine-6,12-dione (23)

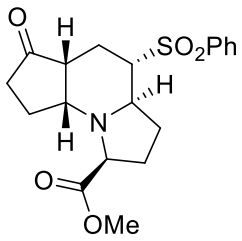


23

Prepared according to General Procedure B using **18** (150 mg, 0.317 mmol). Purification by column chromatography (silica gel 100-200mesh, 30% EtOAc in hexanes) afforded **23** as a white solid (59.1 mg, 50% BRSM yield). R_f = 0.5 (60% ethyl acetate in hexane), mp = 152-154 ºC, $[\alpha]_D^{25}$ = +60.6 (*c* 2.8, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 3.75 (d, *J* = 3.7 Hz, 1H), 3.71 (d, *J* = 5.8 Hz, 1H), 2.86 (td, *J* = 10.9, 2.9 Hz, 1H), 2.81 – 2.75 (m, 1H), 2.72 – 2.65 (m, 1H), 2.59 – 2.53 (m, 1H), 2.42 – 2.36 (m, 1H), 2.31 (ddd, *J* = 17.3, 12.0, 5.4 Hz, 1H), 2.08 (d, *J* = 13.4 Hz, 1H), 2.01 (dt, *J* = 11.9, 7.0 Hz, 1H), 1.94 – 1.77 (m, 4H), 1.60 – 1.51 (m, 2H), 1.44 (td, *J* = 13.7, 2.6 Hz, 1H), 1.17 – 1.08 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ (ppm) 210.7, 207.9, 136.8, 134.2, 130.2, 129.1, 73.8, 68.2, 65.9, 58.3, 49.9, 44.0, 37.3, 31.9, 25.7, 24.3, 24.0, 22.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{23}NO_4SNa$ 396.1240; Found 396.1230.

Synthesis of (1*S*,3a*R*,4*S*,5a*R*,8a*R*)-methyl 6-oxo-4-(phenylsulfonyl)decahydro-1*H*-cyclopenta[*e*]indolizine-1-carboxylate (24)

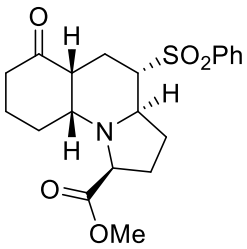
Prepared according to General Procedure D using **19** (50mg, 0.145 mmol). Purification by column chromatography (silica gel 100-200 mesh, 50% EtOAc in hexane) afforded **24** as pale red semi solid (46.4 mg, 85% yield). R_f = 0.3 (60% ethyl acetate in hexane), mp = 104-110 ºC, $[\alpha]_D^{25}$ = +4.0 (*c* 0.4, $CHCl_3$) ; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.79 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 3.78 – 3.73 (m, 1H), 3.68 (s, 3H), 3.48 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.07 – 3.01 (m, 1H), 2.98 (td, *J* = 9.6, 5.5 Hz, 1H), 2.44 (dd, *J* = 19.3, 8.5 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.18 – 2.11 (m, 1H), 2.10 – 2.02 (m, 1H), 1.98 – 1.91 (m, 2H), 1.90 – 1.83 (m, 1H), 1.81 – 1.75 (m, 1H), 1.71 (ddd, *J* = 13.4, 6.5, 3.0 Hz, 1H), 1.43 (q, *J* = 13.1 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ (ppm) 215.8, 173.7, 137.7, 134.1, 129.4, 128.5, 64.6, 60.2, 55.4, 54.5, 52.2, 45.5, 36.7, 29.2, 27.2, 22.9, 16.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{23}NO_5SNa$ 400.1189; Found 400.1185.



24

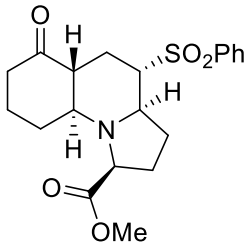
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,9a*R*)-methyl-6-oxo-4-(phenylsulfonyl)dodecahydropyrrolo[1,2-a]quinoline-1-carboxylate (25)

Prepared according to General Procedure D using **20** (50mg, 0.139 mmol). Purification by column chromatography (silica gel 100-200 mesh, 40% EtOAc in hexane) afforded **25** as white solid (52.3 mg, 96% yield). R_f = 0.35 (60% ethyl acetate in hexane), mp = 180-182 ºC, $[\alpha]_D^{25}$ = +61.7 (*c* 1.2, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.81 (d, *J* = 7.9 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 3.67 (s, 3H), 3.56 (dd, *J* = 9.6, 5.1 Hz, 1H), 3.32 – 3.26 (m, 1H), 3.17 (td, *J* = 9.6, 5.7 Hz, 1H), 3.05 – 2.99 (m, 1H), 2.63 (dd, *J* = 8.5, 4.8 Hz, 1H), 2.34 – 2.23 (m, 3H), 2.06 – 1.94 (m, 3H), 1.89 (q, *J* = 13.0 Hz, 1H), 1.82 – 1.67 (m, 3H), 1.63 (dt, *J* = 12.9, 3.9 Hz, 1H), 1.45 – 1.37 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ (ppm) 211.3, 173.7, 137.9, 134.2, 129.5, 128.6, 65.7, 59.8, 55.5, 54.0, 52.2, 51.5, 37.9, 30.1, 27.4, 24.7, 21.6, 16.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{25}NO_5SNa$ 400.1189; Found 400.1185.



25

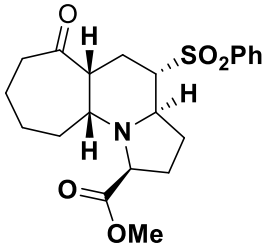
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,9a*S*)-methyl-6-oxo-4-(phenylsulfonyl)dodecahydropyrrolo[1,2-*a*]quinoline-1-carboxylate (26)



26

Prepared according to General Procedure D using **21** (50mg, 0.139 mmol). Purification by column chromatography (silica gel 100-200 mesh, 50% EtOAc in hexane) afforded **26** as white solid (47.9 mg, 88% yield). R_f = 0.25 (60% ethyl acetate in hexane), mp = 166-168 °C, $[\alpha]_D^{25}$ = +18.1 (*c* 1.1, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.88 – 7.85 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 3.72 (s, 3H), 3.31 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.23 (br s, 1H), 2.55 (dd, *J* = 11.8, 7.3 Hz, 1H), 2.46 – 2.38 (m, 2H), 2.33 – 2.29 (m, 1H), 2.26 – 2.13 (m, 3H), 2.01 (ddd, *J* = 9.1, 6.0, 2.6 Hz, 1H), 1.94 (dt, *J* = 13.8, 3.7 Hz, 1H), 1.92 – 1.83 (m, 3H), 1.67 – 1.58 (m, 2H), 1.58 – 1.49 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ (ppm) 207.9, 175.5, 137.8, 134.0, 129.4, 128.8, 67.2, 64.7, 63.6, 62.7, 52.9, 52.4, 40.7, 30.2, 29.7, 29.0, 25.5, 23.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{20}H_{26}NO_5S$ 392.1526; Found 392.1519.

Synthesis of (1*S*,3a*R*,4*S*,5a*R*,10a*R*)-methyl-6-oxo-4-(phenylsulfonyl)dodecahydro-1*H*-cyclohepta[*e*]indolizine-1-carboxylate (27)

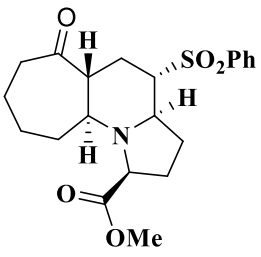


27

Prepared according to General Procedure D using **22** (50mg, 0.133 mmol). Purification by column chromatography (silica gel 100-200 mesh, 30% EtOAc in hexane) afforded **27** as pale red semi solid (48.9 mg, 88% yield). R_f = 0.5 (60% ethyl acetate in hexane), mp = 130-136 °C, $[\alpha]_D^{25}$ = +22.8 (*c* 0.6, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.83 – 7.80 (m, 2H), 7.60 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 3.67 (s, 3H), 3.61 (br s, 1H), 3.43 (t, *J* = 7.2 Hz, 1H), 2.95 (br s, 1H), 2.79 (dd, *J* = 15.0, 9.3 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.30 – 2.22 (m, 2H), 2.12 (dt, *J* = 14.1, 4.1 Hz, 1H), 1.98 (dd, *J* = 14.4, 8.6 Hz, 2H), 1.85 (dd, *J* = 11.9, 8.9 Hz, 2H), 1.74 – 1.66 (m, 1H), 1.63 (d, *J* = 14.2 Hz, 1H), 1.57 – 1.50 (m, 1H), 1.40 – 1.32 (m, 1H), 1.22 – 1.13 (m, 2H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ (ppm) 211.8, 173.9, 137.9, 134.0, 129.4, 128.8, 66.1, 59.8, 55.8, 54.6, 52.2, 51.5, 42.0, 29.8, 28.9, 27.5, 27.2, 22.9, 22.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{21}H_{27}NO_5SNa$ 428.1502; Found 428.1497.

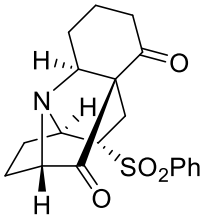
Synthesis of (1*S*,3a*R*,4*S*,5a*R*,10a*S*)-methyl-6-oxo-4-(phenylsulfonyl)dodecahydro-1*H*-cyclohepta[*e*]indolizine-1-carboxylate (28)

Prepared according to General Procedure D using **23** (50mg, 0.133 mmol). Purification by column chromatography (silica gel 100-200 mesh, 30% EtOAc in hexane) afforded **28** as pale red solid (46.2 mg, 88% yield). R_f = 0.5 (60% ethyl acetate in hexane), mp = 146-148 °C, $[\alpha]_D^{25}$ = +9.6 (*c* 0.28, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 3.67 (s, 3H), 3.35 – 3.31 (m, 1H), 3.23 – 3.14 (m, 1H), 2.78 – 2.71 (m, 1H), 2.67 – 2.62 (m, 1H), 2.48 – 2.43 (m, 1H), 2.41 – 2.34 (m, 2H), 2.26 – 2.20 (m, 1H), 2.12 – 2.05 (m, 1H), 1.99 – 1.91 (m, 1H), 1.88 – 1.76 (m, 5H), 1.66 – 1.57 (m, 2H), 1.40 – 1.33 (m, 1H), 1.17 – 1.09 (m, 1H). **^{13}C{^{1}H}** NMR (151 MHz, $CDCl_3$): *δ* (ppm) 211.7, 176.0, 137.8, 134.0, 129.3, 128.8, 64.6, 64.2, 63.4, 62.7, 53.0, 52.3, 43.2, 35.1, 30.0, 29.1, 28.4, 24.6, 22.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{21}H_{27}NO_5SNa$ 428.1502; Found 428.1495.



28

Synthesis of (1S,3aR,4S,5aS,9aS)-4-(phenylsulfonyl)decahydro-6H-1,5a-methanopyrrolo[1,2-a]quinoline-6,11-dione (29)

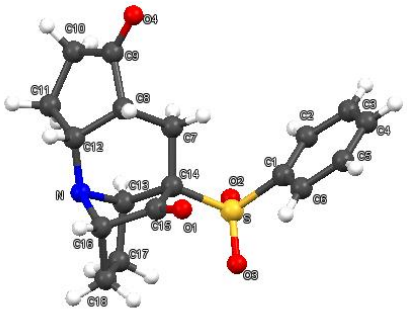


29

A crude diastereomeric mixture containing compounds **20** (*cis*) and **21** (*trans*) (ca. 2.25:1) was dissolved in dry THF (0.1 M) under an argon atmosphere. To this stirred solution was added DBU (2.0 equiv) at room temperature, and the reaction mixture was stirred for 2 h. Upon completion, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to afford the ring-opened product **29**, arising from selective conversion of the *trans* isomer **21**, while the *cis* isomer **20** remained unreacted. When the reaction was performed using the isolated *trans* isomer **21** (50 mg, 0.139 mmol) under identical conditions, product **29** was obtained as a pale yellow solid (47.5 mg, 95% yield). R_f = 0.2 (60% ethyl acetate in hexane), mp = 192-194 °C; $[\alpha]_D^{25}$= +17.1 (*c* 0.38, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): *δ* (ppm) 7.82 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 2H), 4.14 – 4.09 (m, 1H), 3.83 (d, *J* = 9.3 Hz, 1H), 3.67 (dd, *J* = 10.2, 5.8 Hz, 1H), 2.94 (dd, *J* = 18.2, 9.0 Hz, 1H), 2.39 (d, *J* = 14.7 Hz, 1H), 2.34 – 2.27 (m, 2H), 2.25 – 2.14 (m, 3H), 2.08 – 1.91 (m, 3H), 1.85 – 1.80 (m, 1H), 1.62 – 1.50 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): *δ* (ppm) 216.8, 203.6, 137.3, 134.5, 129.7, 128.8, 65.8, 65.7, 60.6, 59.2, 59.1, 40.2, 34.8, 32.3, 28.1, 25.1, 21.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{21}NO_4SNa$ 382.1083; Found 382.1090.

4. X-Ray Crystallography

X-Ray Crystal Analysis of Compound 19 (CCDC No. 2521102)



Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.

Bond precision: C-C = 0.0046 A Wavelength=1.54184

Cell: a=8.0410 (1) b=7.5103 (1) c=13.5277 (2)
alpha=90 beta=102.460 (1) gamma=90

Temperature: 298 K

	Calculated	Reported
Volume Space	797.701 (19)	797.701 (19)
group Hall	P 21	P 1 21 1
group	P 2yb	P 2yb
Moiety formula	C18 H19 N O4 S	C18 H19 N O4 S
Sum formula	C18 H19 N O4 S	C18 H19 N O4 S
Mr	345.40	345.40
Dx,g cm-3	1.438	1.438
Z	2	2
Mu (mm-1)	2.003	2.003
F000	364.0	364.0
F000’	365.73	
h,k,lmax	9,9,16	9,8,16
Nref	2912[1577]	2245
Tmin,Tmax	0.887,0.905	0.827,1.000
Tmin’	0.818	

Correction method= # Reported T Limits: Tmin=0.827 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.42/0.77 Theta(max)= 67.989

R(reflections)= 0.0309(2184) wR2(reflections)= 0.0803(2245)

S = 1.040 Npar= 217

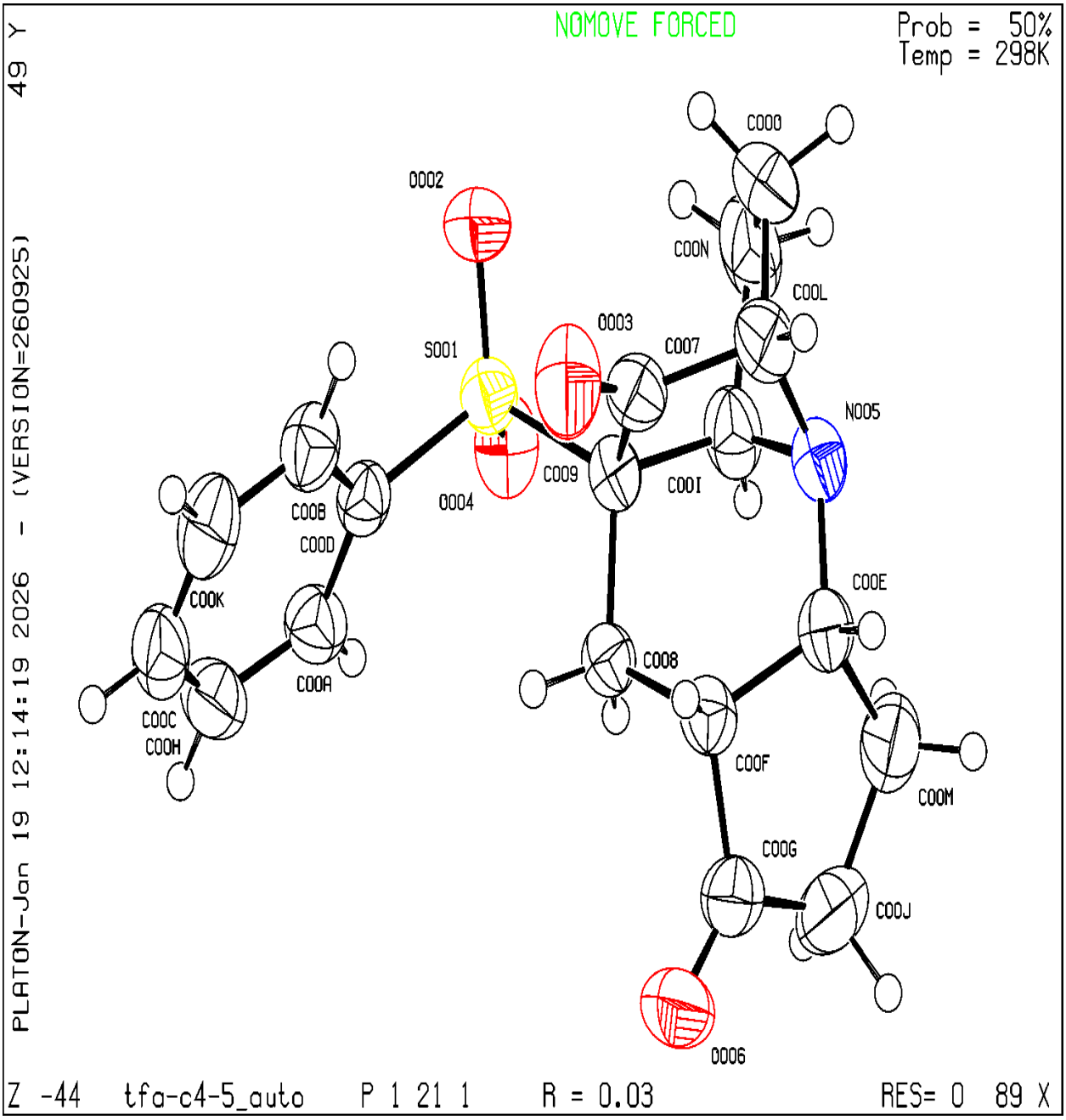
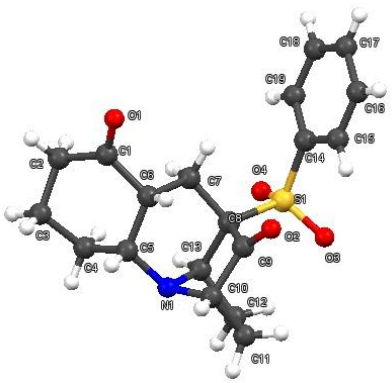


Figure S1. Thermal Ellipsoid are plotted at the 50% probability level

X-Ray Crystal Analysis of Compound 20 (CCDC No. 2433359)

Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.



Bond precision:	C-C = 0.0044 A	Wavelength=1.54184	
Cell:	a=8.0273 (1)	b=7.6845 (1)	c=13.7609 (2)
	alpha=90	beta=100.662 (1)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume Space	834.20 (2)	834.197 (19)
group Hall	P 21	P 1 21 1
group	P 2yb	P 2yb
Moiety formula	C19 H21 N O4 S	C19 H21 N O4 S
Sum formula	C19 H21 N O4 S	C19 H21 N O4 S
Mr	359.43	359.43
Dx,g cm-3	1.431	1.431
Z	2	2
Mu (mm-1)	1.937	1.937
F000	380.0	380.0
F000'	381.77	
h,k,lmax	9,9,16	9,9,16
Nref	3051[1649]	2799
Tmin,Tmax	0.947,0.955	0.697,1.000
Tmin'	0.947	

Correction method= # Reported T Limits: Tmin=0.697 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.70/0.92 Theta(max)= 68.114 wR2(reflections)= 0.0867(2799)

R(reflections)= 0.0335(2676)

S = 1.025 Npar= 226

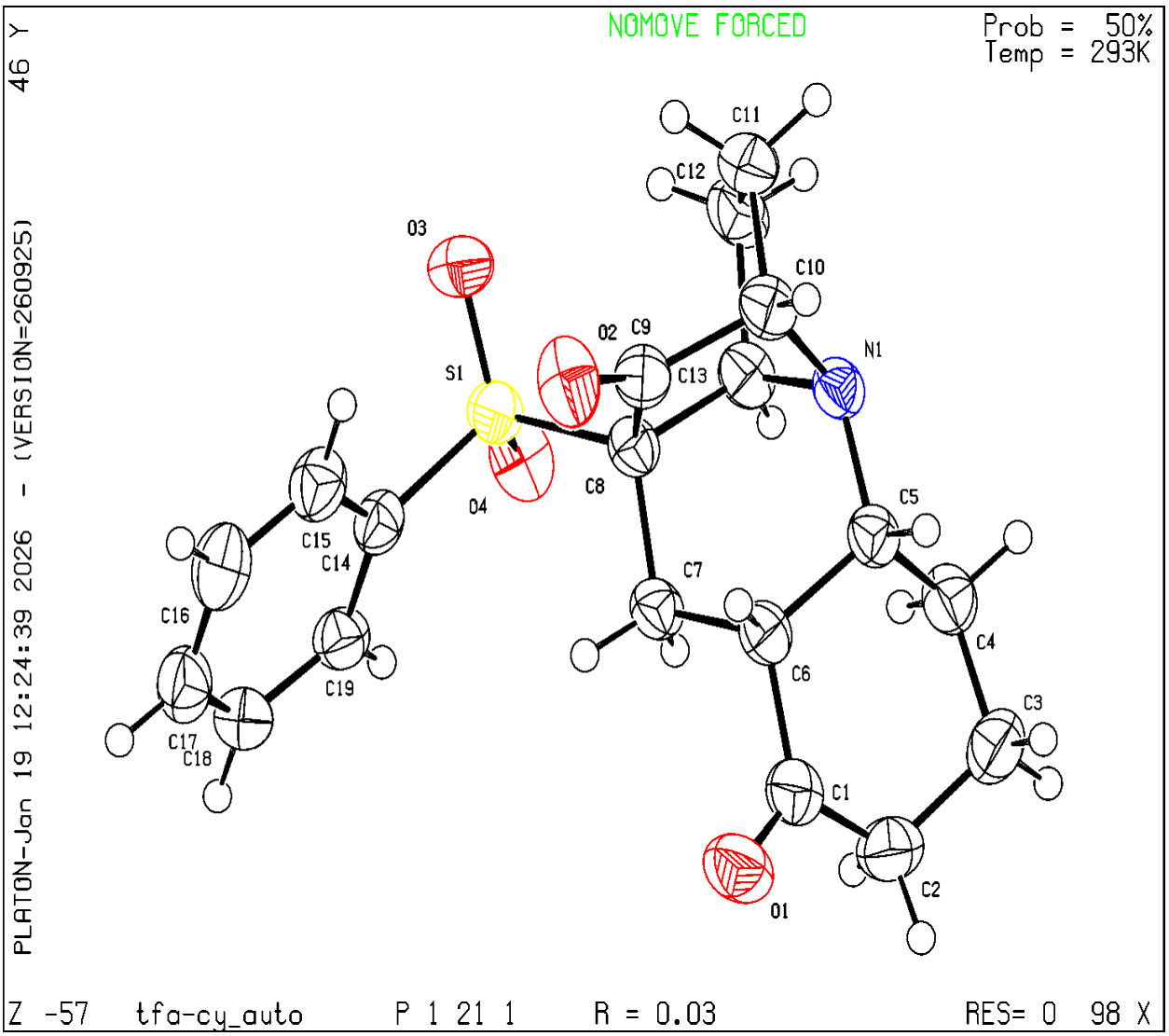
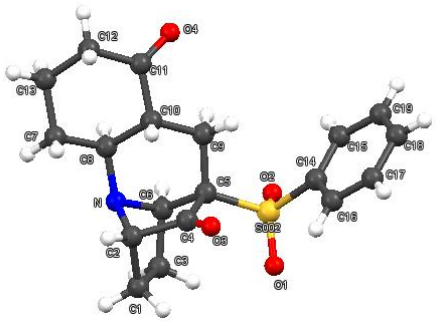


Figure S2. Thermal Ellipsoid are plotted at the 50% probability level

X-Ray Crystal Analysis of Compound 21 (CCDC No. 2521350)



Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.

Bond precision: C-C = 0.0048 A Wavelength=1.54184

Cell: a=9.9321 (1) b=19.3107 (2) c=10.3792 (1)
alpha=90 beta=117.980 (2) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume Space	1758.00 (4)	1758.00 (4)
group Hall	P 21	P 1 21 1
group	P 2yb	P 2yb
Moiety formula	C19 H21 N O4 S	2(C19 H21 N O4 S)
Sum formula	C19 H21 N O4 S	C38 H42 N2 O8 S2
Mr	359.43	718.85
Dx,g cm-3	1.358	1.358
Z	4	2
Mu (mm-1)	1.839	1.839
F000	760.0	760.0
F000’	763.53	
h,k,lmax	11,23,12	11,23,12
Nref	6419[3312]	4747
Tmin,Tmax	0.832,0.912	0.941,1.000
Tmin’	0.832	

Correction method= # Reported T Limits: Tmin=0.941 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.43/0.74 Theta(max)= 68.099

R(reflections)= 0.0312(4600) wR2(reflections)= 0.0790(4747)

S = 1.049 Npar= 451

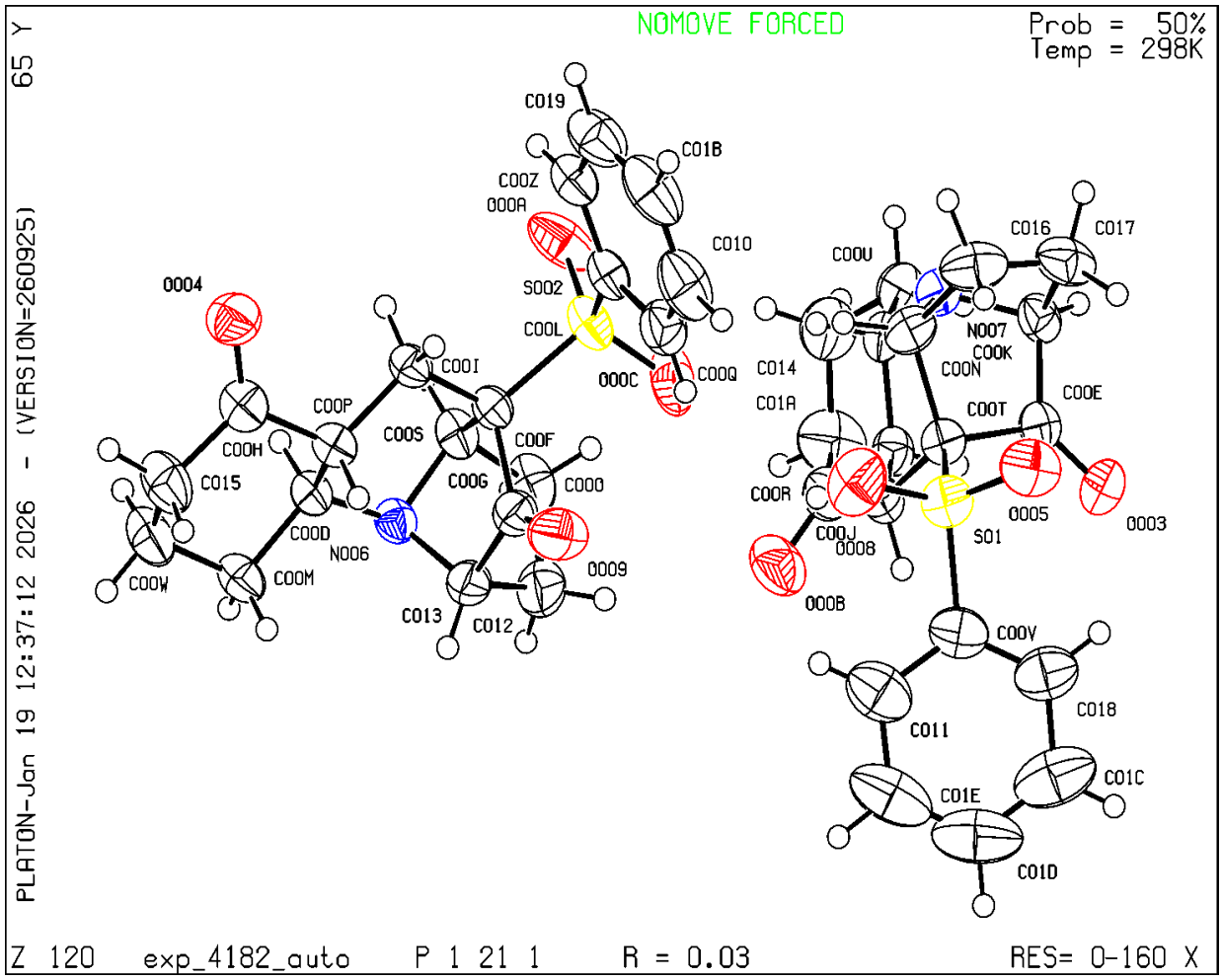
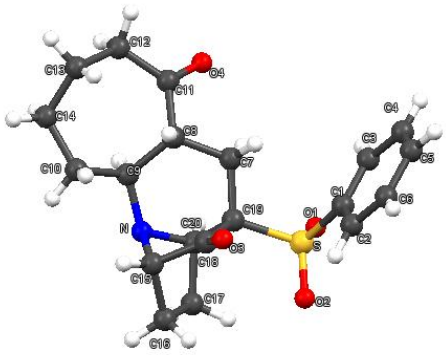


Figure S3. Thermal Ellipsoid are plotted at the 50% probability level

X-Ray Crystal Analysis of Compound 23 (CCDC No. 2521140)



Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.

Bond precision: C-C = 0.0035 A Wavelength=1.54184

Cell: a=7.6680 (1) b=8.1645 (1) c=28.5824 (3)
alpha=90 beta=90 gamma=90

Temperature: 298 K

	Calculated	Reported
Volume Space	1789.41 (4)	1789.41 (4)
group Hall	P 21 21 21	P 21 21 21
group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H23 NO4 S	C20 H23 N O4 S
Sum formula	C20 H23 NO4 S	C20 H23 N O4 S
Mr	373.45	373.45
Dx,g cm-3	1.386	1.386
Z	4	4
Mu (mm-1)	1.827	1.827
F000	792.0	792.0
F000'	795.60	
h,k,lmax	9,9,34	9,9,34
Nref	3269[1914]	3241
Tmin,Tmax	0.833,0.913	0.854,1.000
Tmin'	0.833	

Correction method= # Reported T Limits: Tmin=0.854 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.69/0.99 Theta(max)= 68.128

R(reflections)= 0.0297(3140) wR2(reflections)= 0.0737(3241)

S = 1.076 Npar= 235

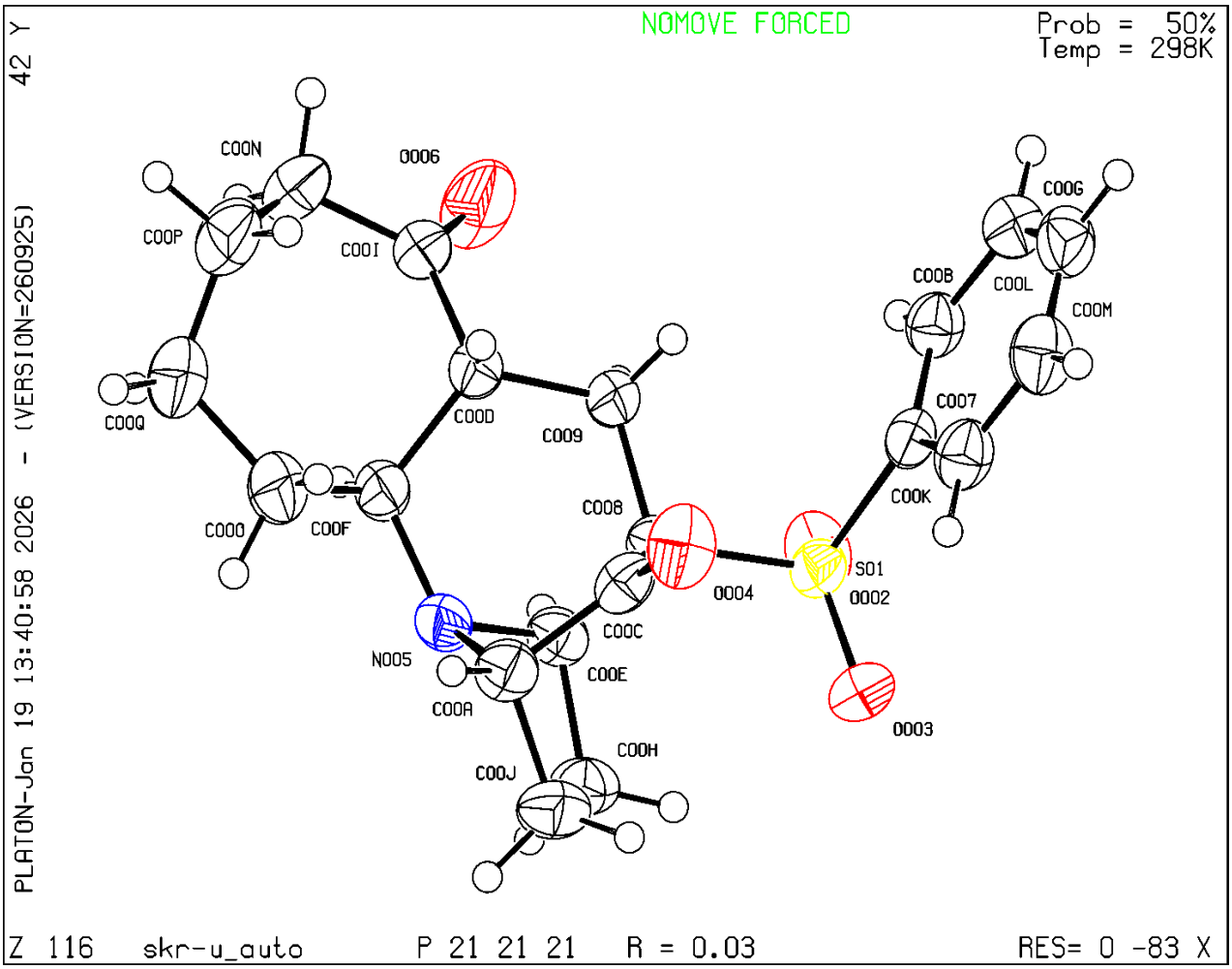
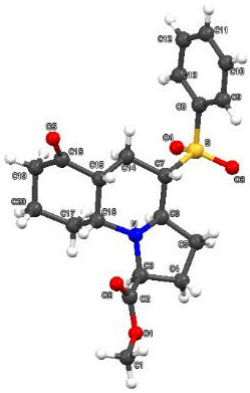


Figure S4. Thermal Ellipsoid are plotted at the 50% probability level

X-Ray Crystal Analysis of Compound 25 (CCDC No. 2521133)

Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.



Bond precision: C-C = 0.0073 A Wavelength=1.54184

Cell: a=5.3763 (1) b=16.9985 (2) c=11.0435 (2)
alpha=90 beta=103.368(2) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume Space	981.91 (3)	981.91 (3)
group Hall	P 21	P 1 21 1
group	P 2yb	P 2yb
Moiety formula	C20 H25 N O5 S	C20 H25 N O5 S
Sum formula	C20 H25 N O5 S	C20 H25 N O5 S
Mr	391.47	391.47
Dx,g cm-3	1.324	1.324
Z	2	2
Mu (mm-1)	1.727	1.727
F000	416.0	416.0
F000'	417.90	
h,k,lmax	6,20,13	6,20,13
Nref	3582[1857]	3535
Tmin,Tmax	0.841,0.841	0.508,1.000
Tmin'	0.841	

Correction method= # Reported T Limits: Tmin=0.508 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.90/0.99 Theta(max)= 68.056

R(reflections)= 0.0428(3355) wR2(reflections)= 0.1191(3535)

S = 1.053 Npar= 245

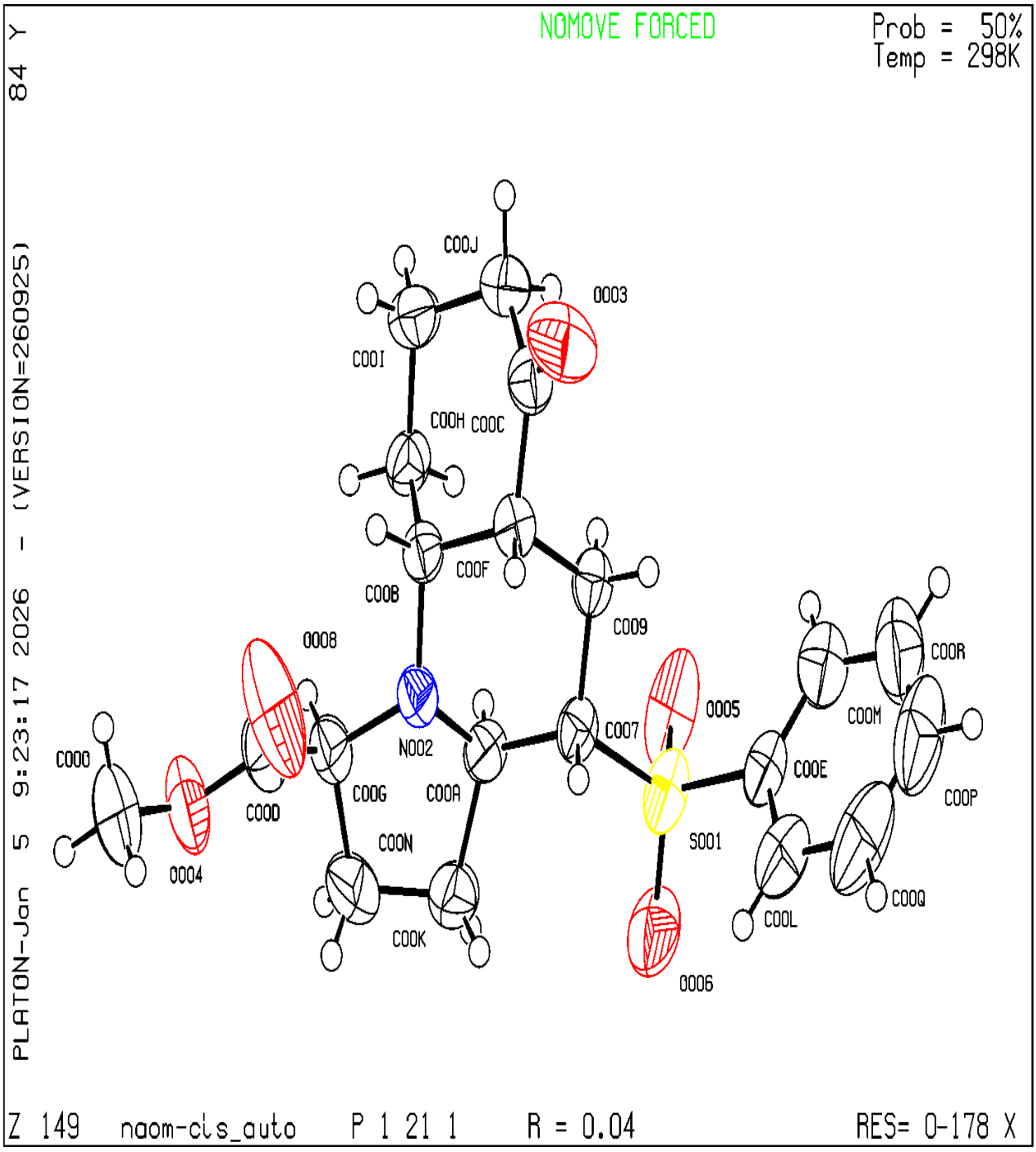
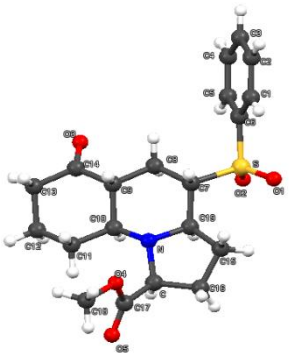


Figure S5. Thermal Ellipsoid are plotted at the 50% probability level

X-Ray Crystal Analysis of Compound 26 (CCDC No. 2521137)

Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.



Bond precision: C-C = 0.0023 A Wavelength=1.54184

Cell: a=9.1584 (1) b=19.4423 (2) c=10.9820 (1)
alpha=90 beta=104.240(1) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume Space	1895.38 (3)	1895.37 (3)
group Hall	P 21/c	P 1 21/c 1
group	-P 2ybc	-P 2ybc
Moiety formula	C20 H25 N O5 S	C20 H25 N O5 S
Sum formula	C20 H25 N O5 S	C20 H25 N O5 S
Mr	391.47	391.47
Dx,g cm-3	1.372	1.372
Z	4	4
Mu (mm-1)	1.789	1.789
F000	832.0	832.0
F000'	835.79	
h,k,lmax	11,23,13	11,23,13
Nref	3445	3438
Tmin,Tmax	0.836,0.914	0.690,1.000
Tmin'	0.836	

Correction method= # Reported T Limits: Tmin=0.690 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 68.080

R(reflections)= 0.0369(3168) wR2(reflections)= 0.1035(3438)

S = 1.034 Npar= 245

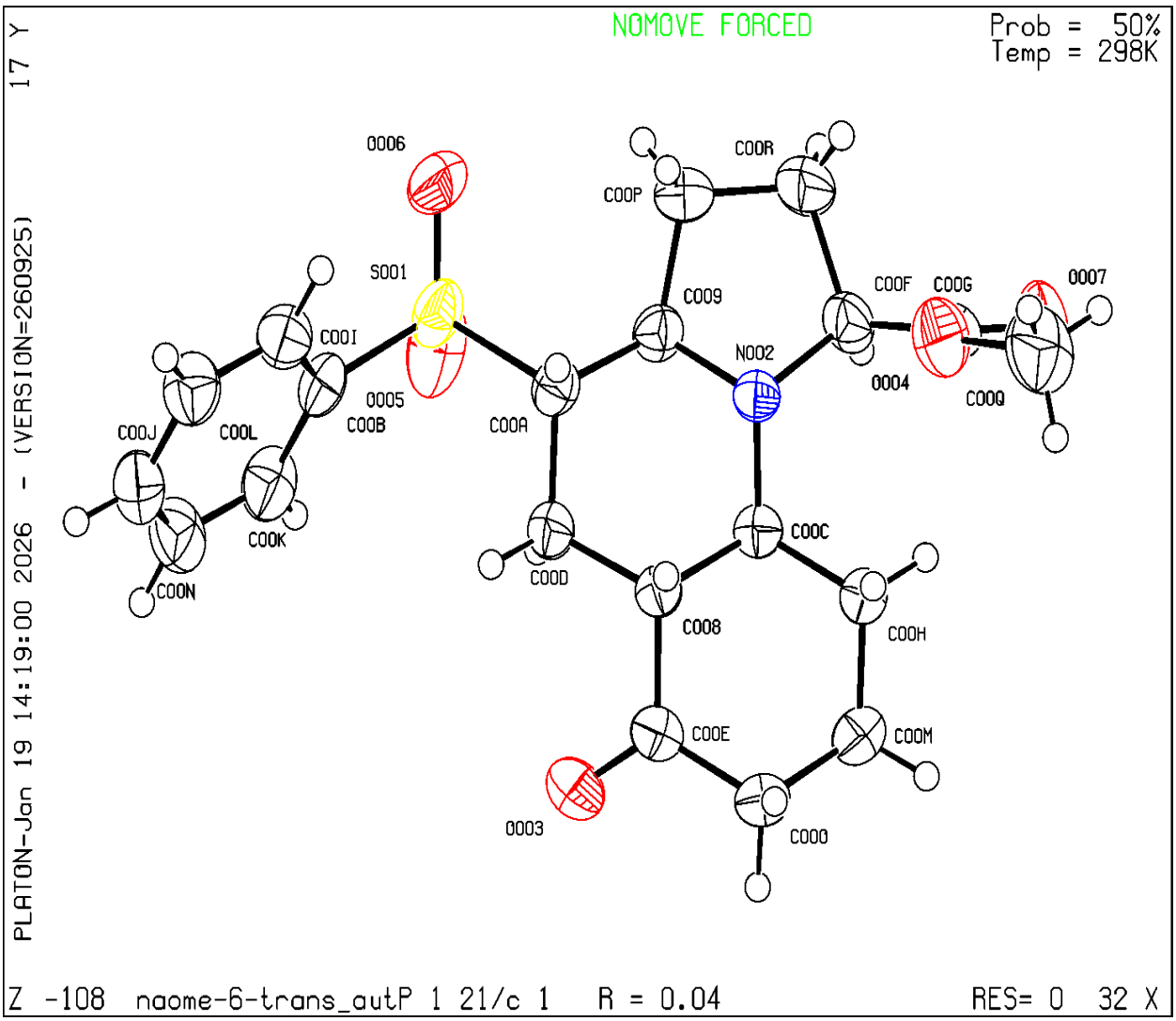
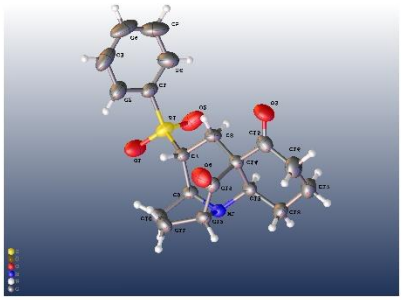


Figure S6. Thermal Ellipsoid are plotted at the 50% probability level

X-Ray Crystal Analysis of Compound 29 (CCDC No. 2546665)

Crystals were grown using ethyl acetate (major)/hexane(minor) as a solvent in a conical. Gradual evaporation of solvent at room temperature was carried out for crystallization.



Bond precision: C-C = 0.0045 A Wavelength=1.54184

Cell: a=6.1617(1) b=11.2010(2) c=25.0765(4)
alpha=90 beta=90 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume Space	1730.71(5)	1730.71(5)
group Hall	P 21 21 21	P 21 21 21
group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C19 H21 N O4 S	C19 H21 N O4 S
Sum formula	C19 H21 N O4 S	C19 H21 N O4 S
Mr	359.43	359.43
Dx,g cm-3	1.379	1.379
Z	4	4
Mu (mm-1)	1.868	1.868
F000	760.0	760.0
F000'	763.53	
h,k,lmax	7,13,30	7,13,30
Nref	3167[1859]	3101
Tmin,Tmax	0.546,0.571	0.765,1.000
Tmin'	0.495	

Correction method= # Reported T Limits: Tmin=0.765 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.67/0.98 Theta(max)= 68.191

R(reflections)= 0.0318(2868) wR2(reflections)= 0.0733(3101)

S = 1.016 Npar= 226

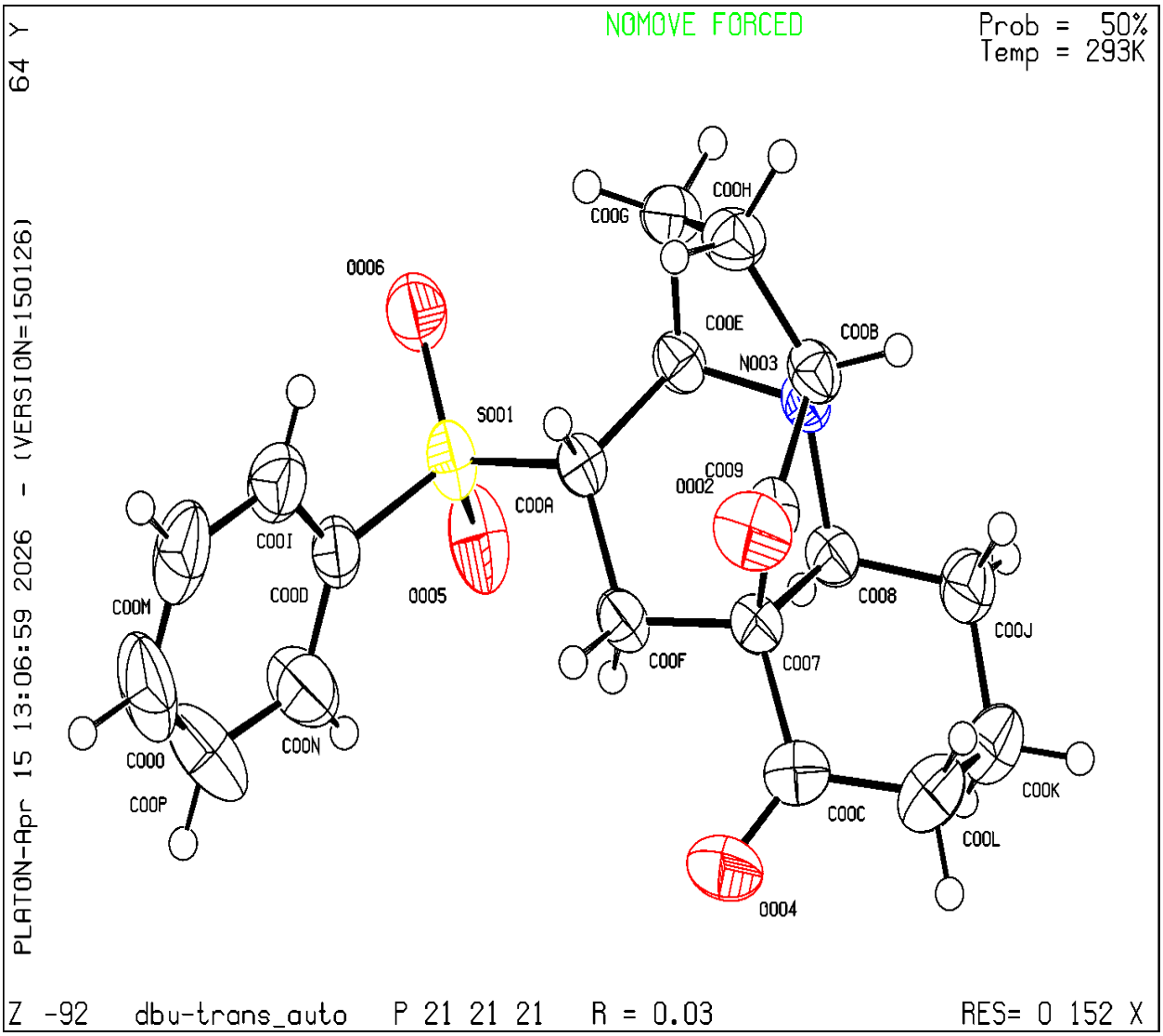
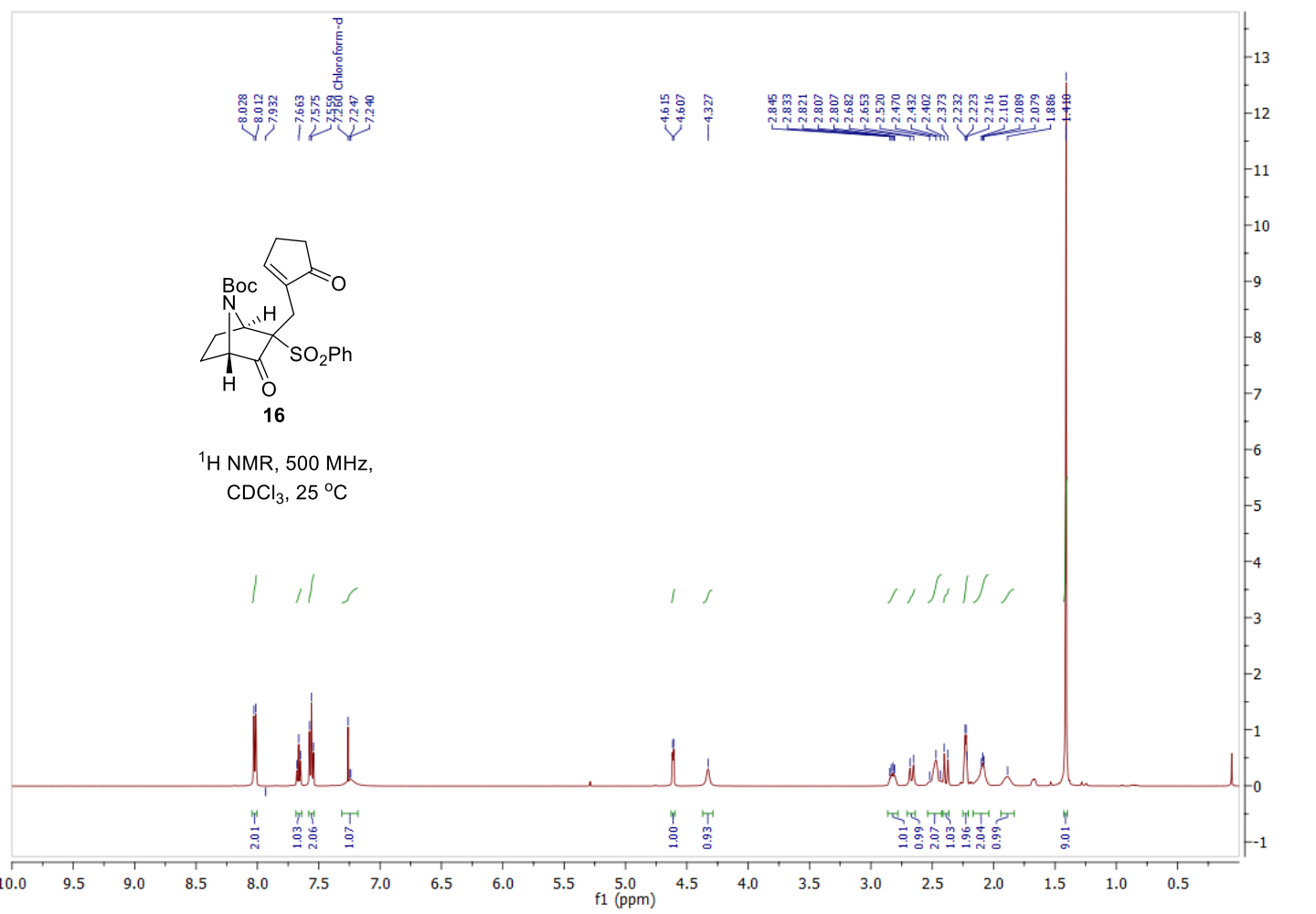
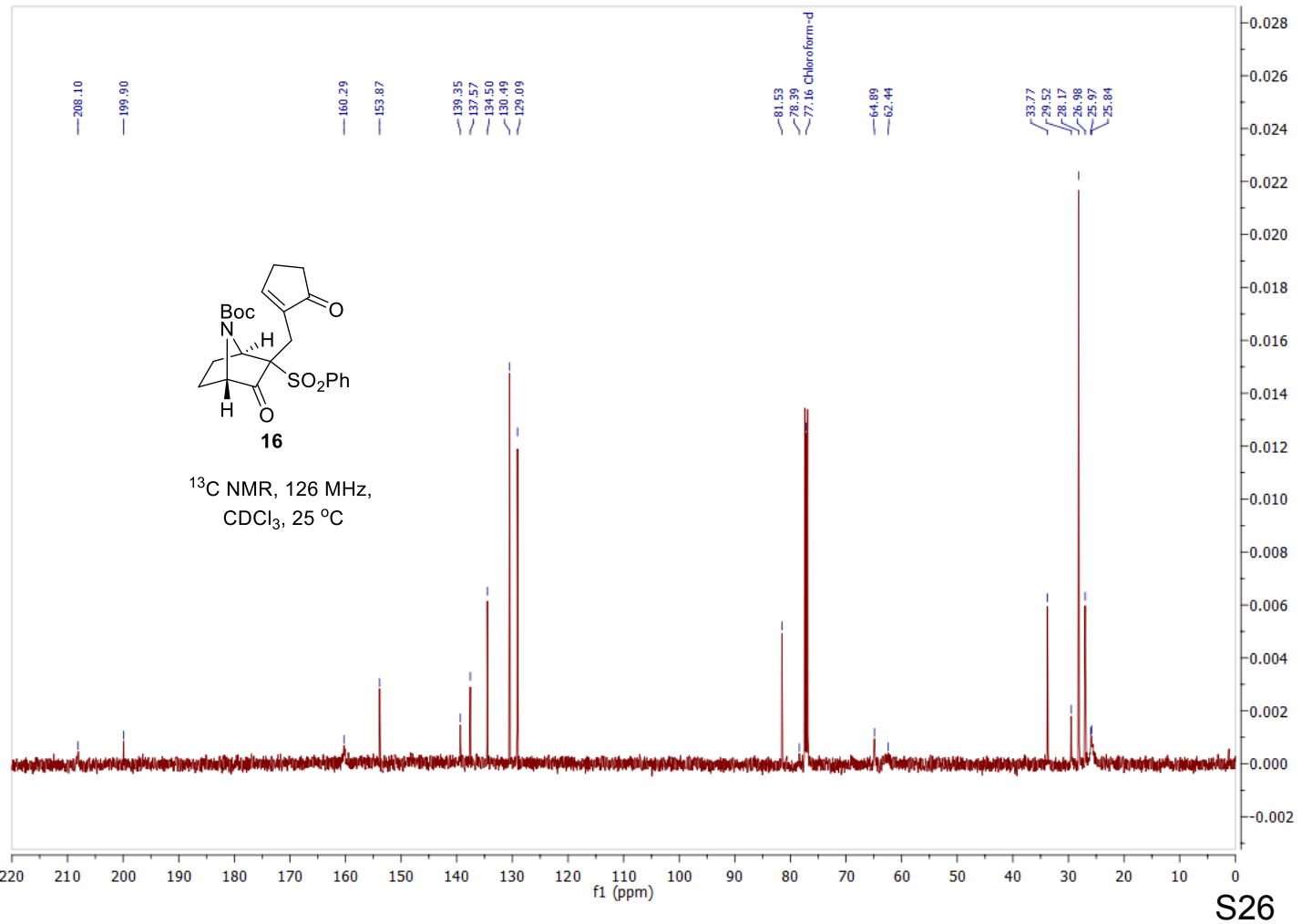


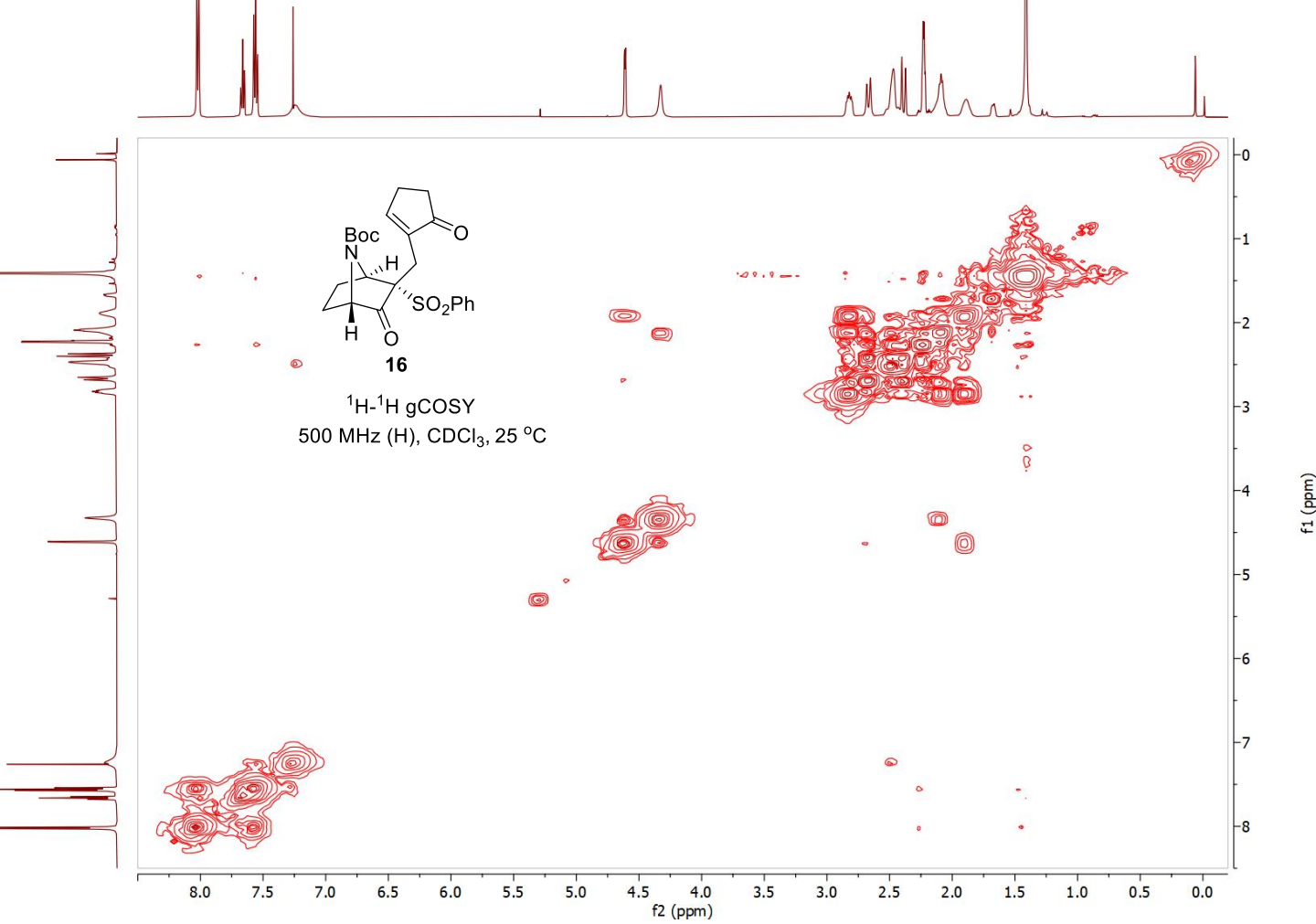
Figure S7. Thermal Ellipsoid are plotted at the 50% probability level

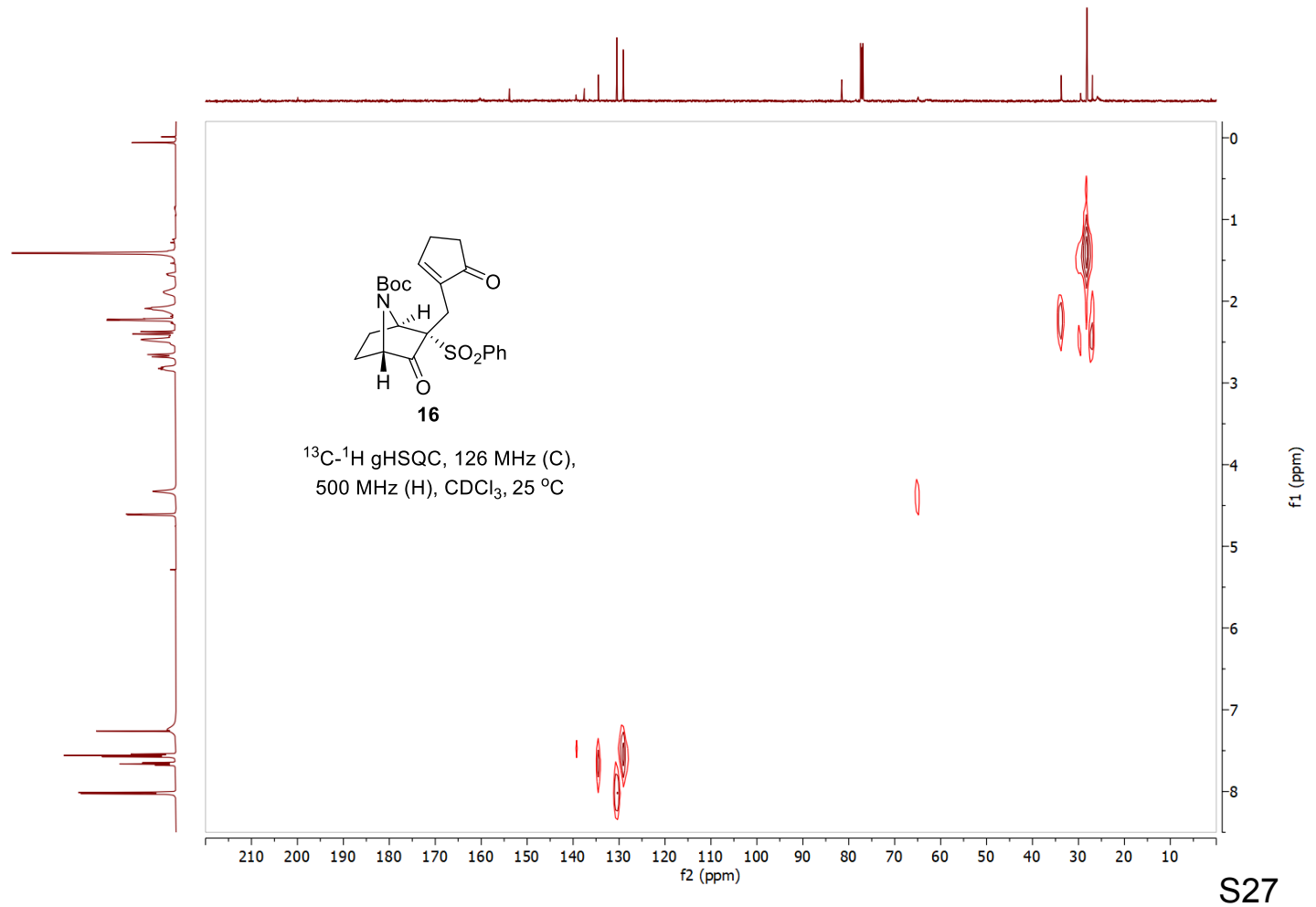
5. References

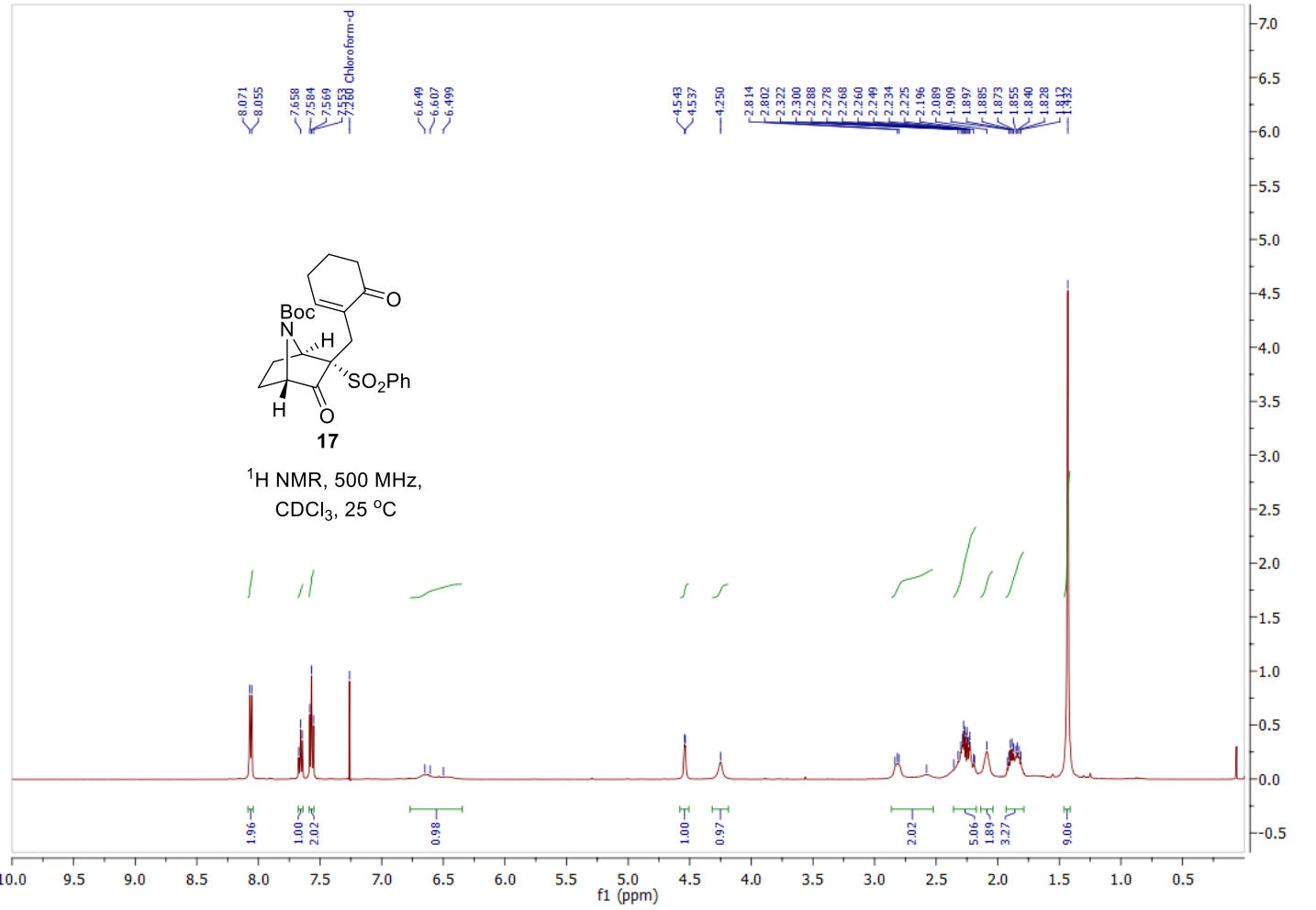
1. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996.
2. R. Varkhedkar, S. Dogra, D. Tiwari, Y. Hussain, P. N. Yadav and G. Pandey, *ChemMedChem* 2018, **13**, 384–395.
3. (a) E. Moreno-Clavijo, A. J. Moreno-Vargas, R. Kieffer, T. Sigstam, A. T. Carmona and I. Robina, *Org. Lett*. 2011, **13**, 6244–6247. (b) G. Pandey, R. Varkhedkar and D. Tiwari, *Org. Biomol. Chem.* 2015, **13**, 4438–4448.


8.028
8.012
7.932
7.663
7.575
7.559
7.260 Chloroform-d
7.247
7.240
4.615
4.607
4.327
2.845
2.833
2.821
2.807
2.807
2.682
2.653
2.520
2.470
2.432
2.402
2.373
2.232
2.223
2.216
2.101
2.089
2.079
1.886
1.410
Boc
N
H
O
SO2Ph
H
O
16
1H NMR, 500 MHz,
CDCl3, 25 °C
2.01
1.03
2.06
1.07
1.00
0.93
1.01
0.99
2.07
1.03
1.96
2.04
0.99
9.01
f1 (ppm)


208.10
199.90
160.29
153.87
139.35
137.57
134.50
130.49
129.09
81.53
78.39
77.16 Chloroform-d
64.89
62.44
33.77
29.52
28.17
26.98
25.97
25.84
Boc
N
H
O
SO2Ph
H
O
16
13C NMR, 126 MHz,
CDCl3, 25 °C
f1 (ppm)

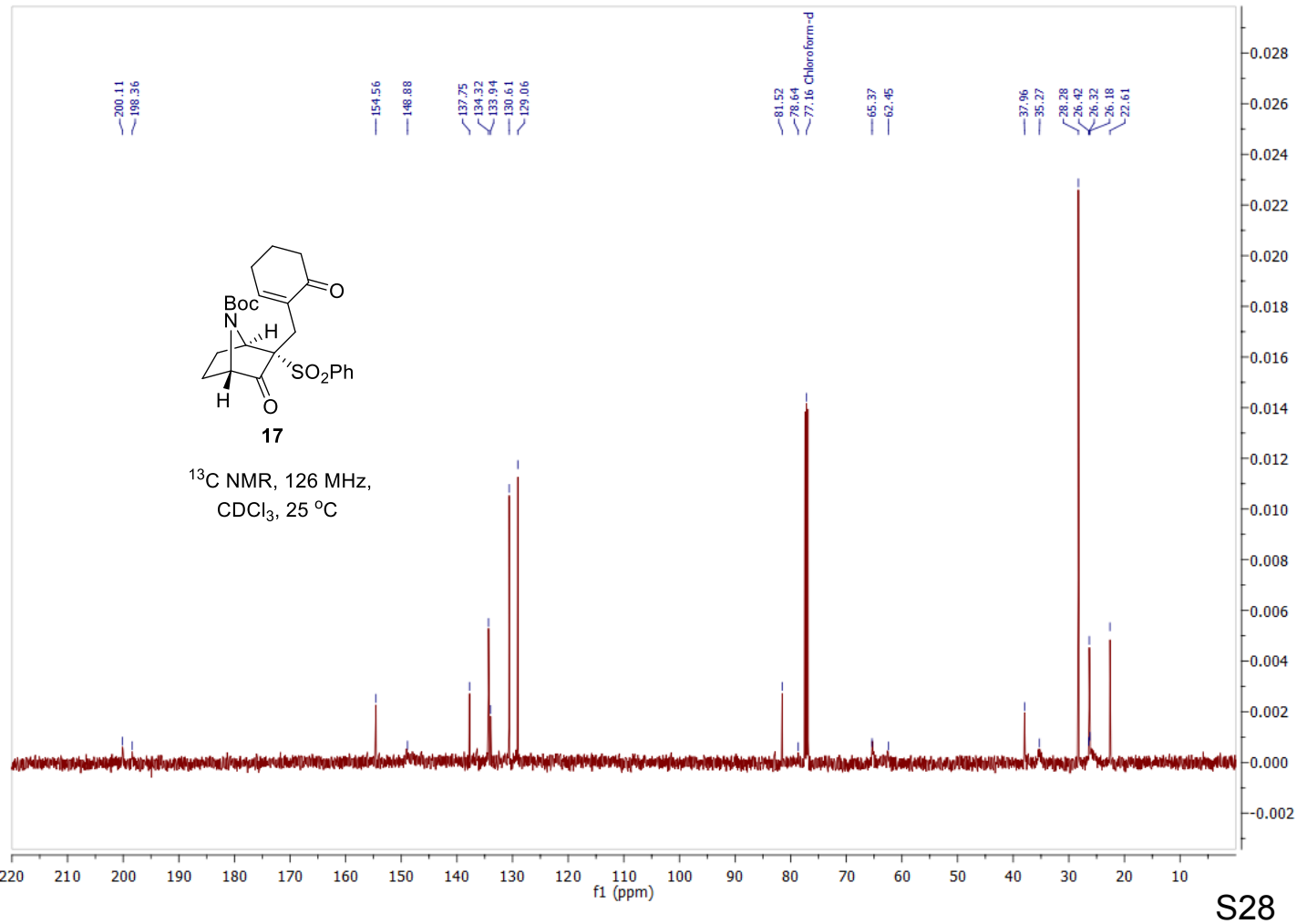

Boc
N
H
O
SO2Ph
H
O
16
1H-1H gCOSY
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


Boc
N
H
O
SO2Ph
H
O
16
13C-1H gHSQC, 126 MHz (C),
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)



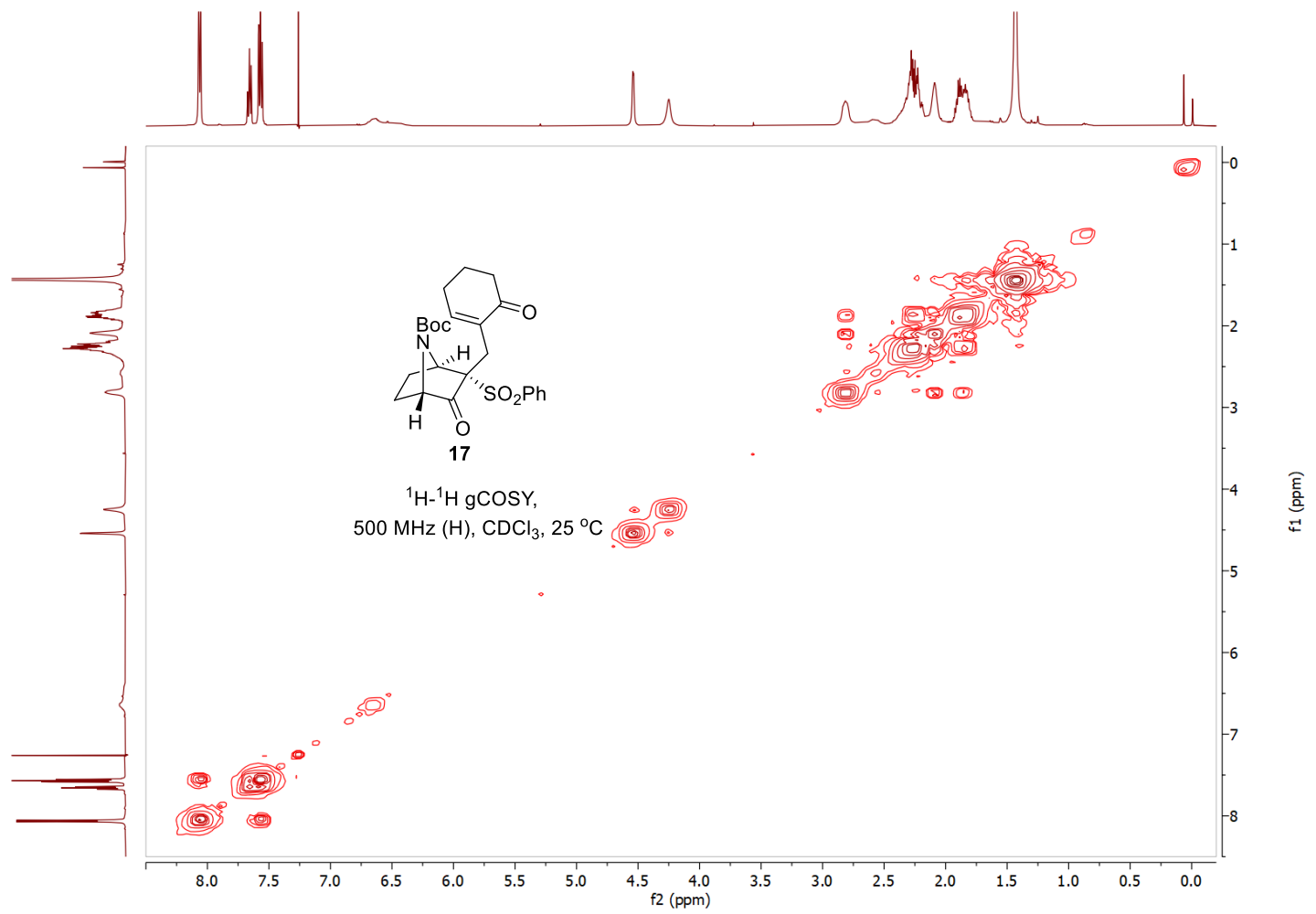
17

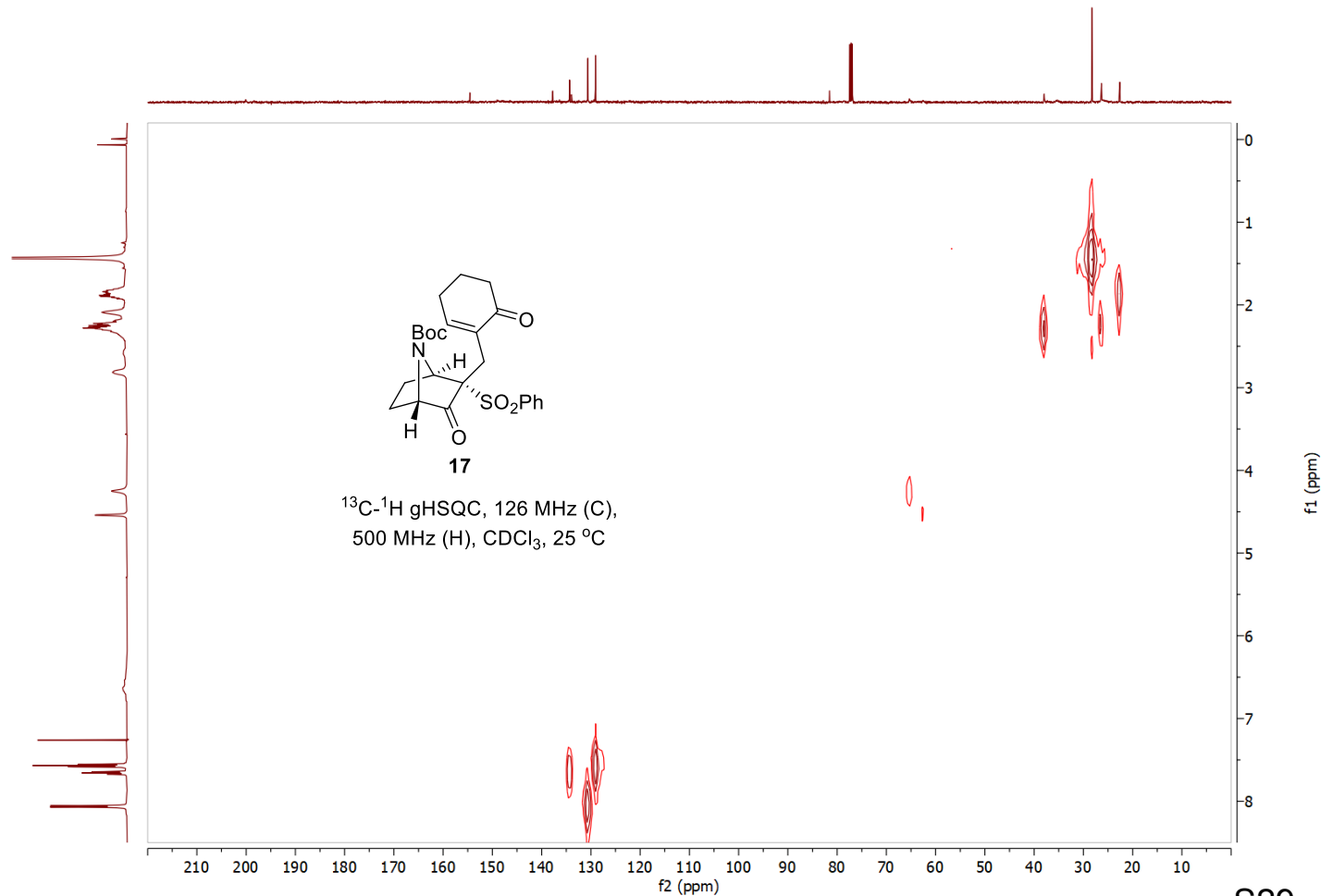
^{1}H NMR, 500 MHz,
$CDCl_3$, 25 °C

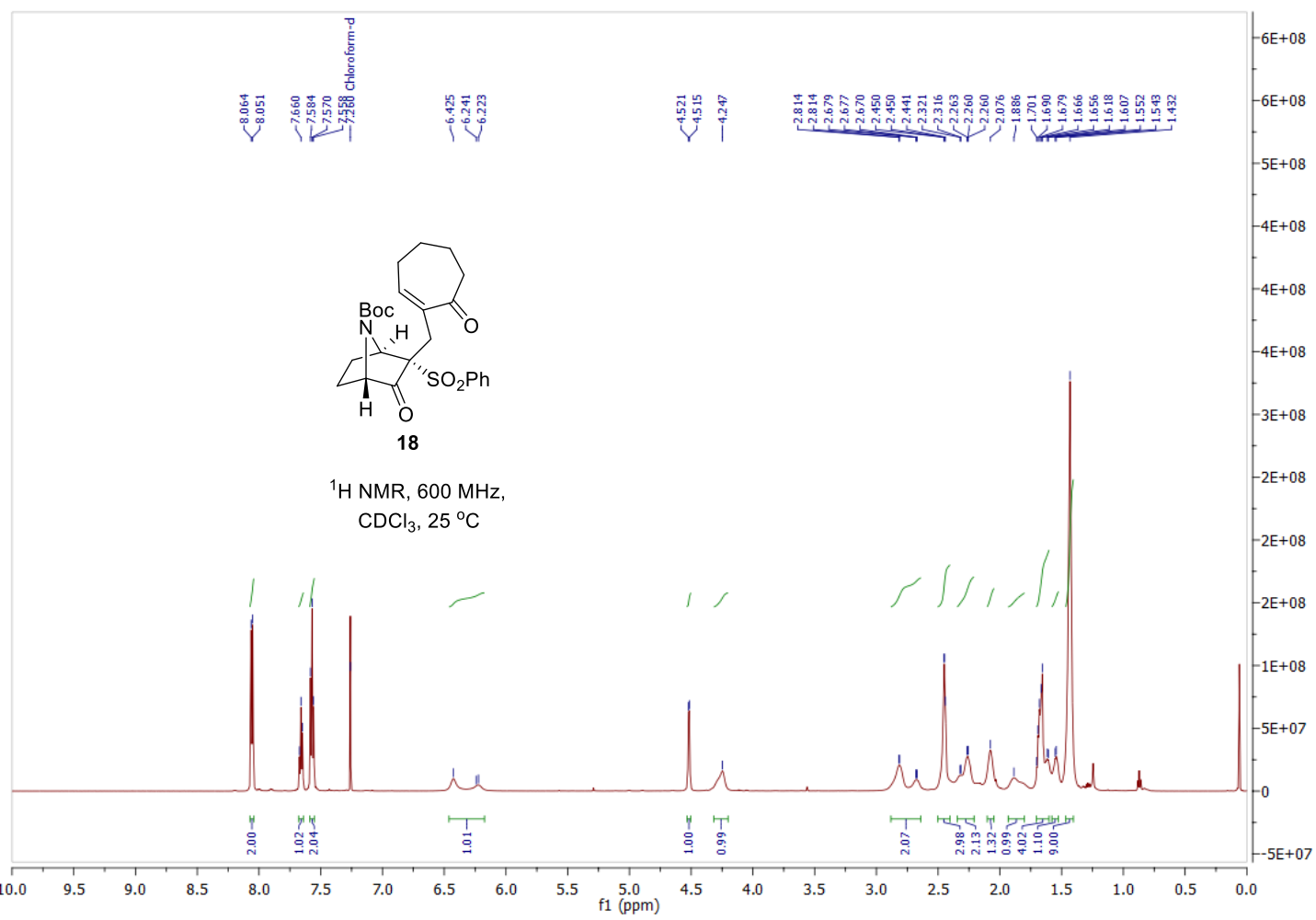


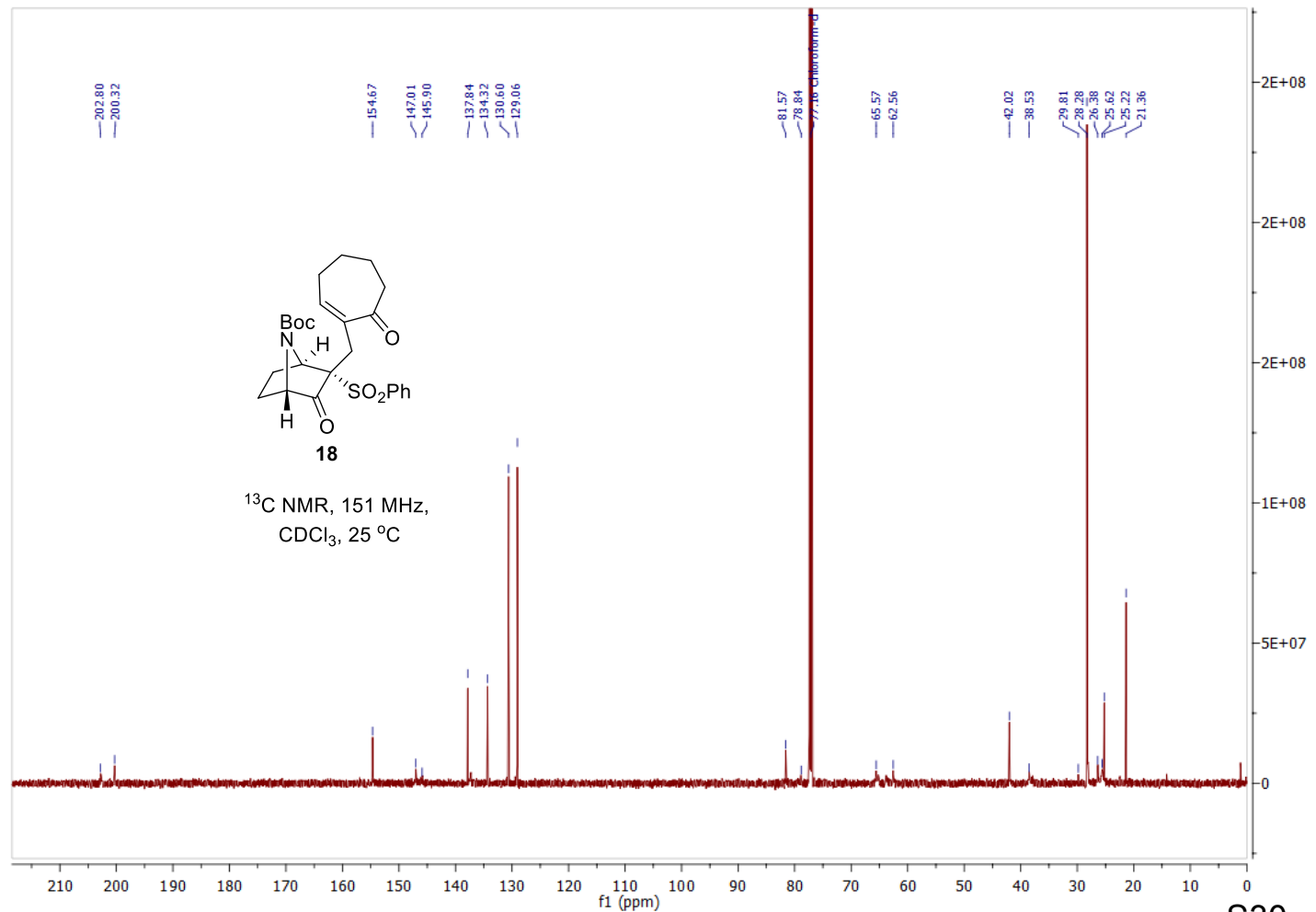
17

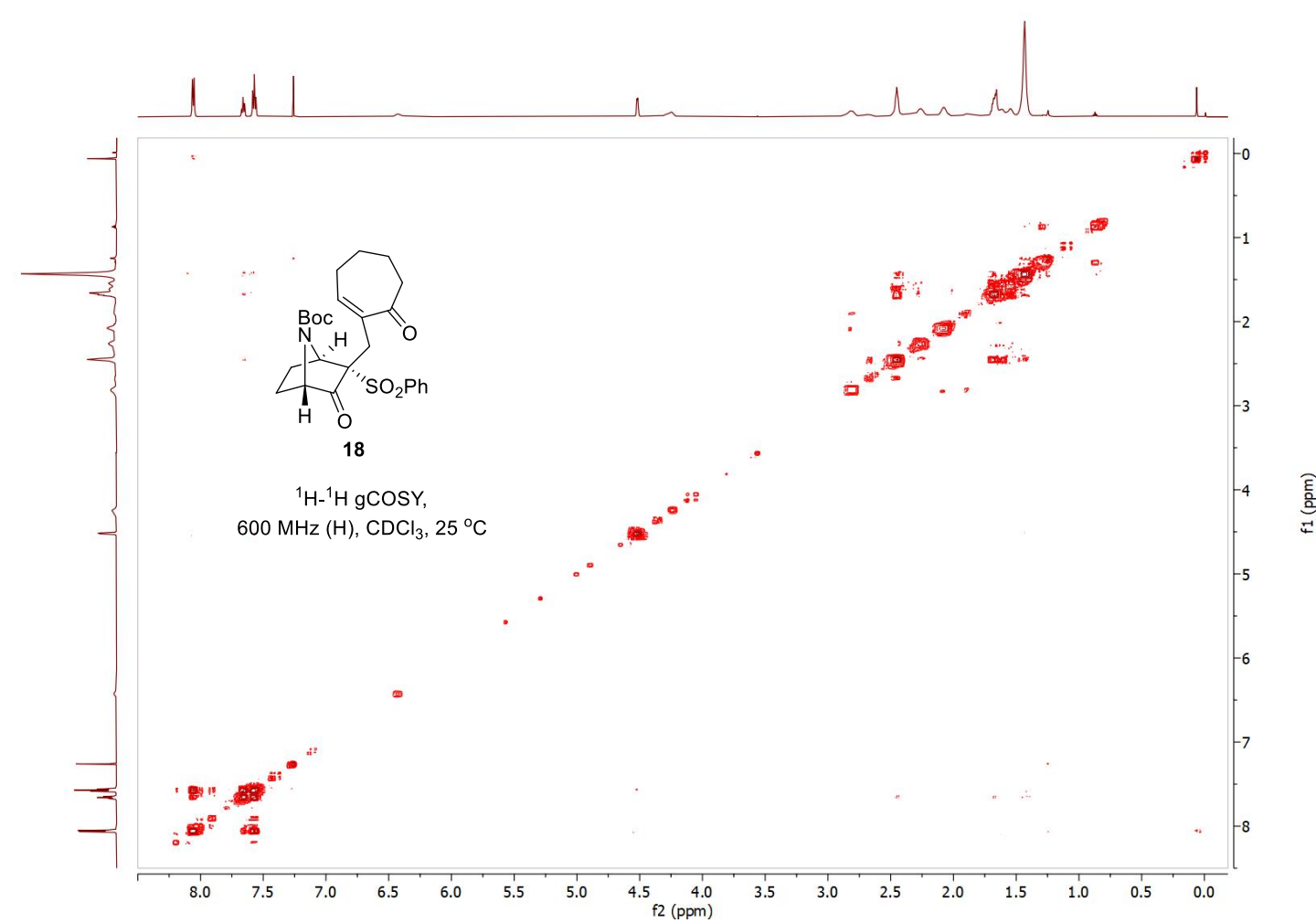
^{13}C NMR, 126 MHz,
$CDCl_3$, 25 °C

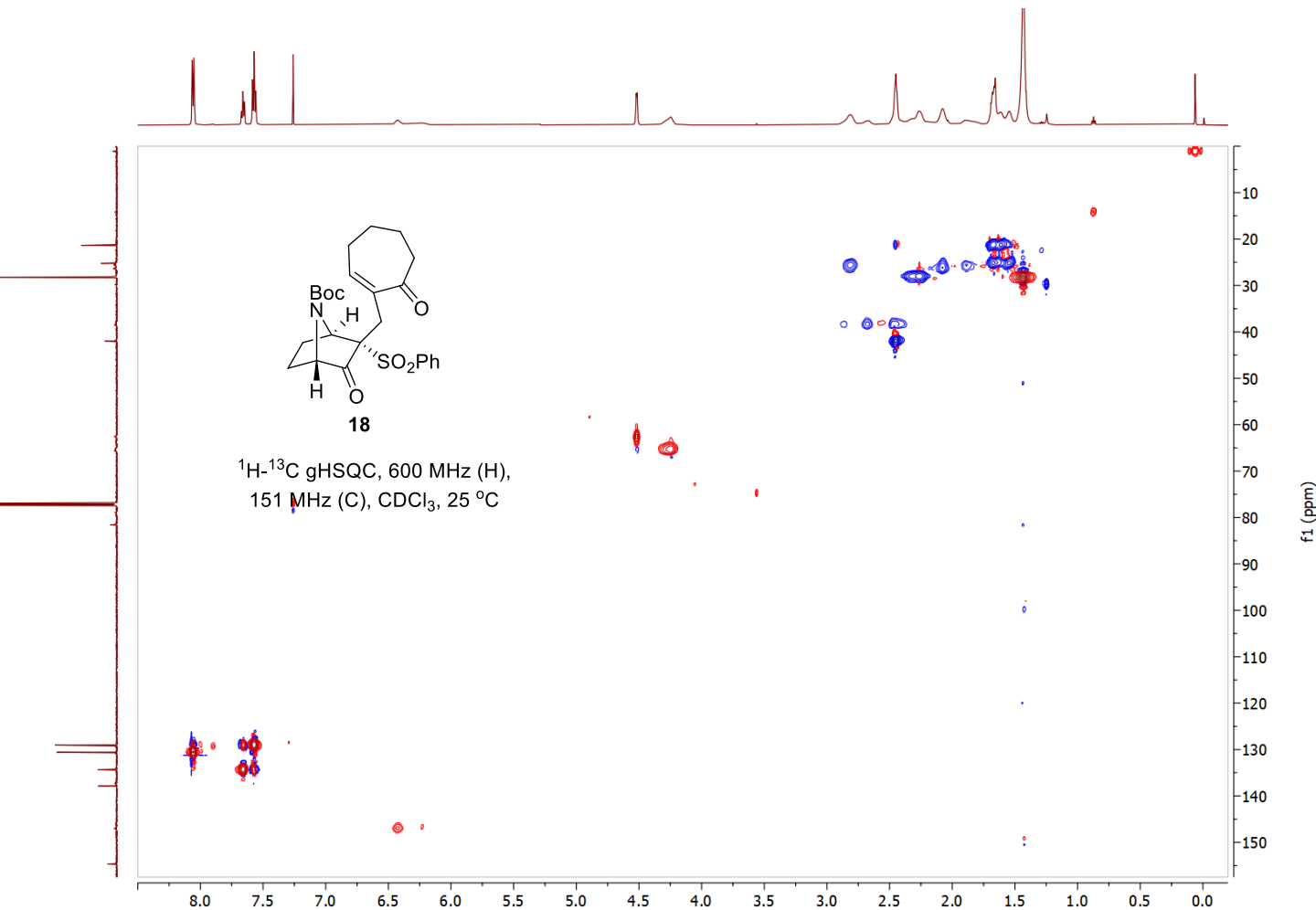

Boc
N
H
O
SO2Ph
H
O
17
1H-1H gCOSY,
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)

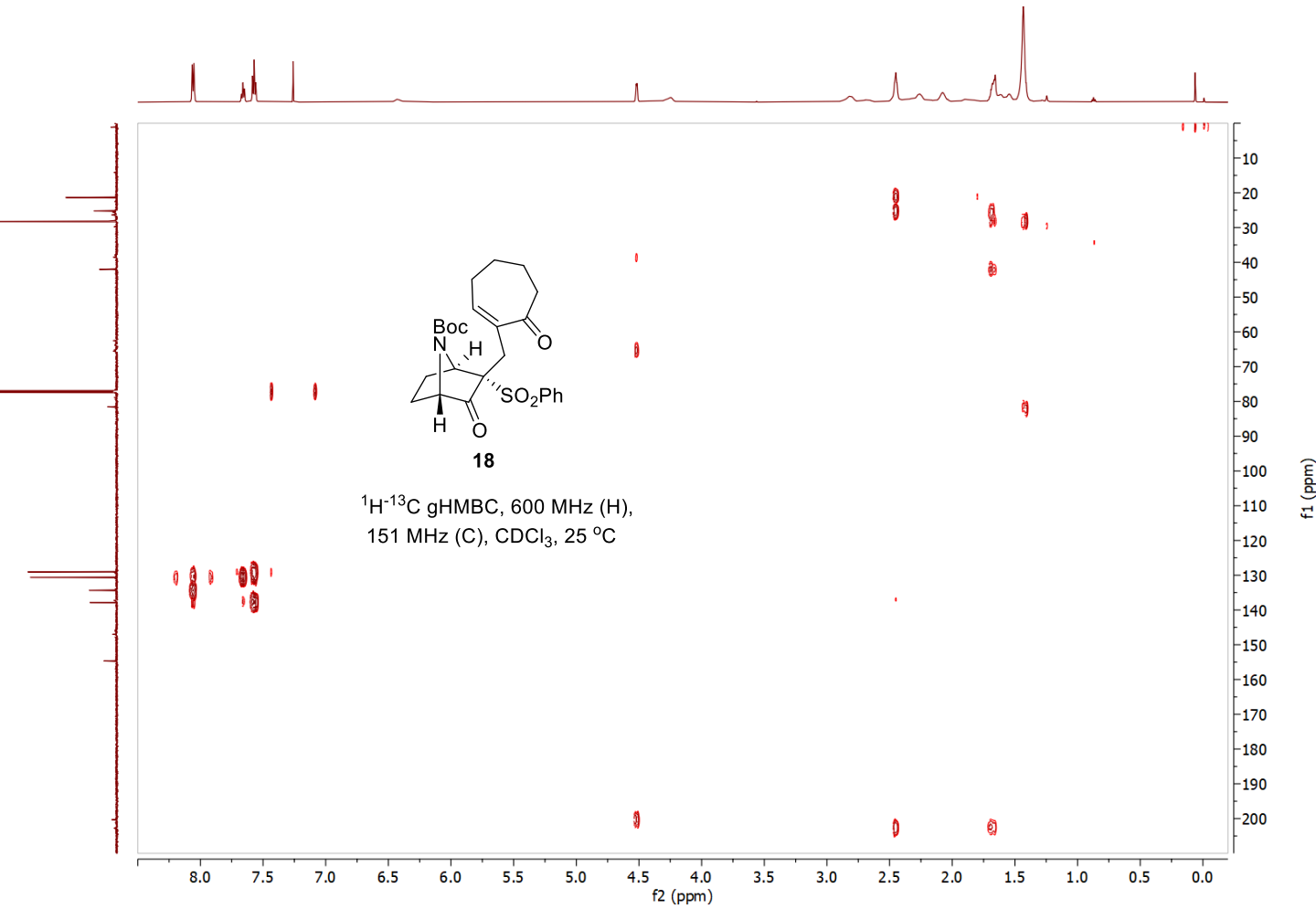

Boc
N
H
O
SO2Ph
H
O
17
13C-1H gHSQC, 126 MHz (C),
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


8.064
8.051
7.660
7.584
7.570
7.558
7.260
Chloroform-d
6.425
6.241
6.223
4.521
4.515
4.247
2.814
2.814
2.679
2.677
2.670
2.450
2.450
2.441
2.321
2.316
2.263
2.260
2.260
2.076
1.886
1.701
1.690
1.679
1.666
1.656
1.618
1.607
1.552
1.543
1.432
Boc
N
H
O
SO2Ph
H
O
18
1H NMR, 600 MHz,
CDCl3, 25 °C
2.00
1.02
2.04
1.01
1.00
0.99
2.07
2.98
2.13
1.32
0.99
4.02
1.10
9.00
f1 (ppm)


202.80
200.32
154.67
147.01
145.90
137.84
134.32
130.60
129.06
81.57
78.84
77.16
Chloroform-d
65.57
62.56
42.02
38.53
29.81
28.28
26.38
25.62
25.22
21.36
Boc
N
H
O
SO2Ph
H
O
18
13C NMR, 151 MHz,
CDCl3, 25 °C
f1 (ppm)

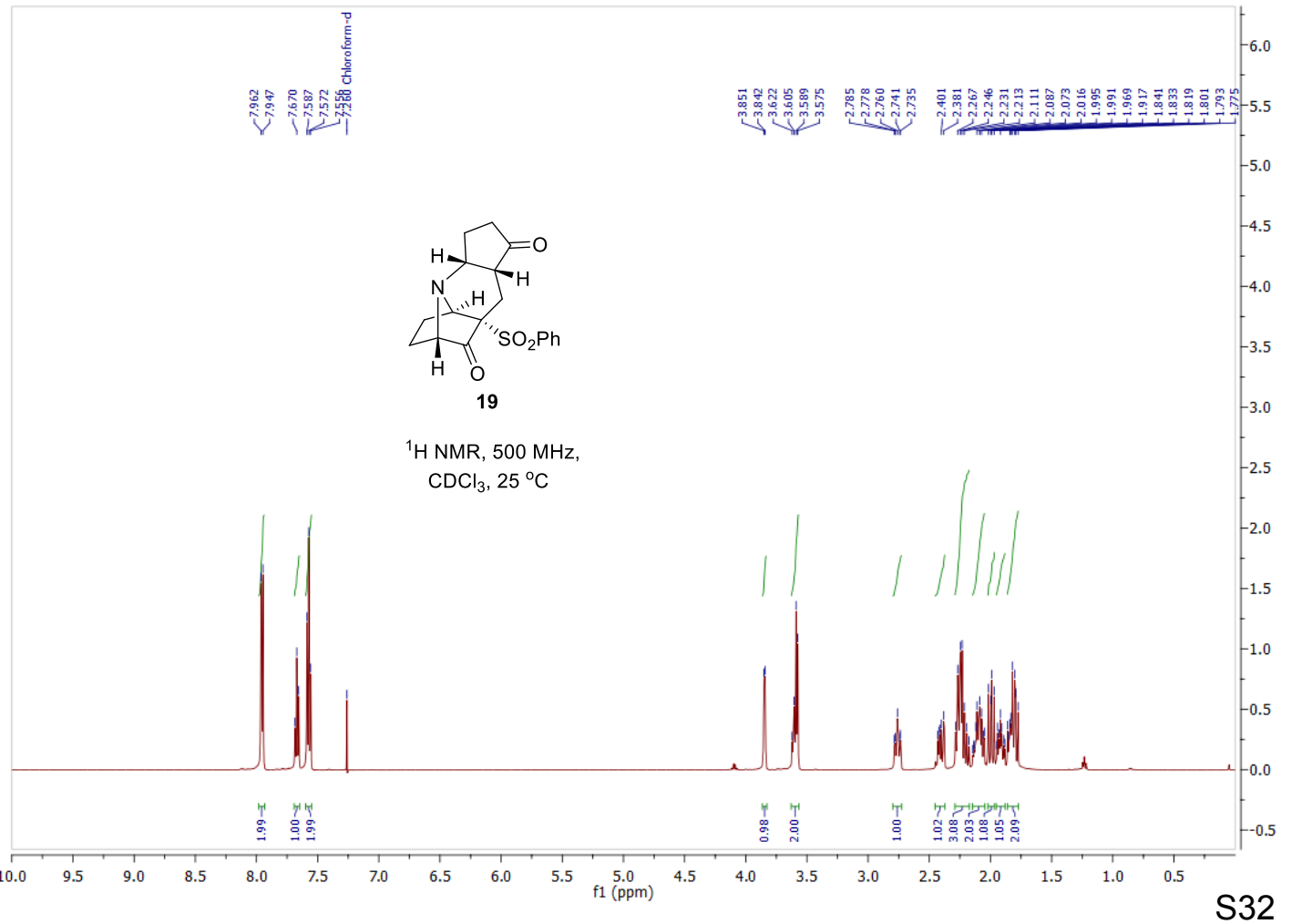

Boc
N
H
O
SO2Ph
H
O
18
1H-1H gCOSY,
600 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


Boc
N
H
O
SO2Ph
H
O
18
1H-13C gHSQC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)



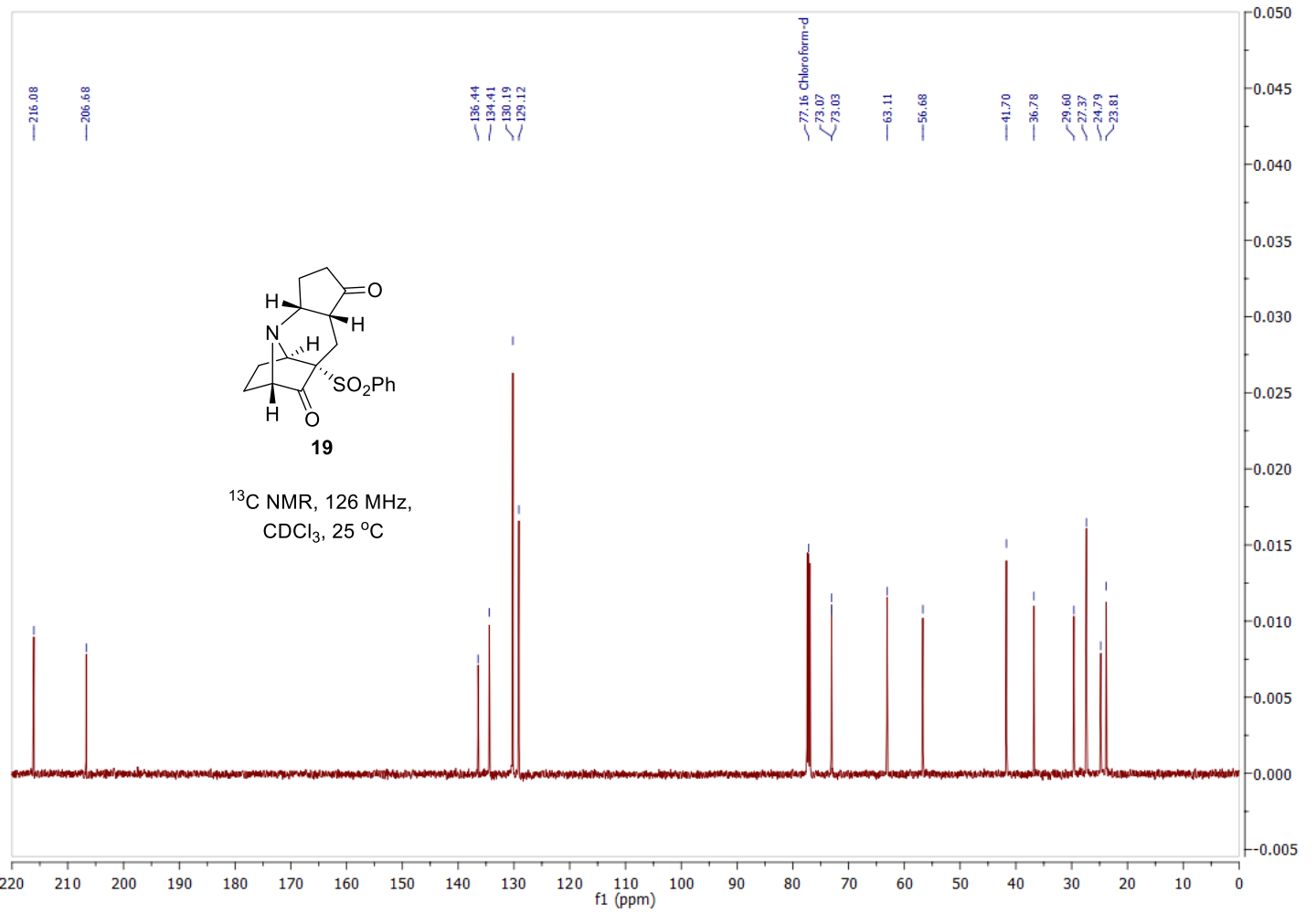
18

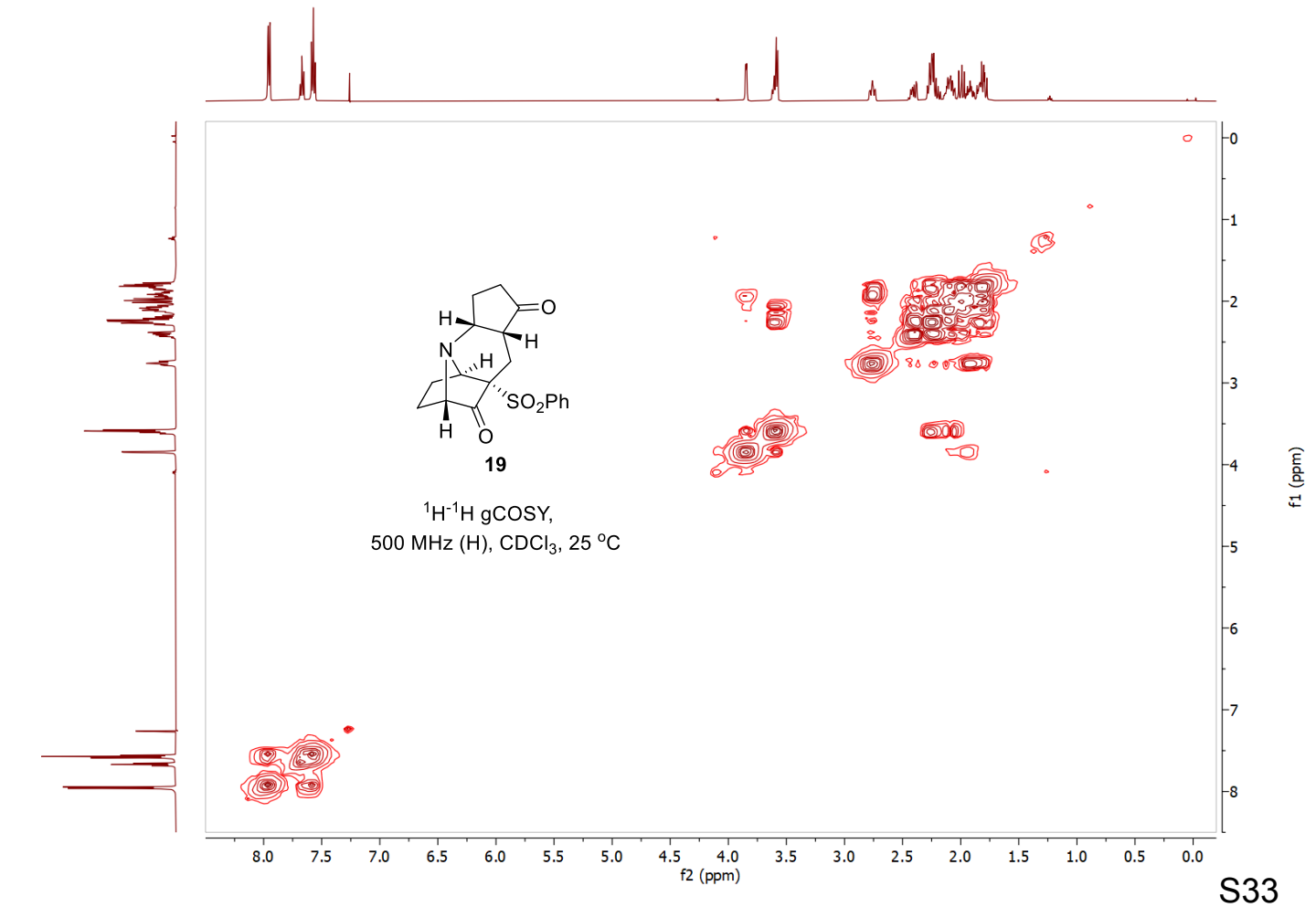
^{1}H-^{13}C gHMBC, 600 MHz (H), 151 MHz (C), $CDCl_3$, 25 °C

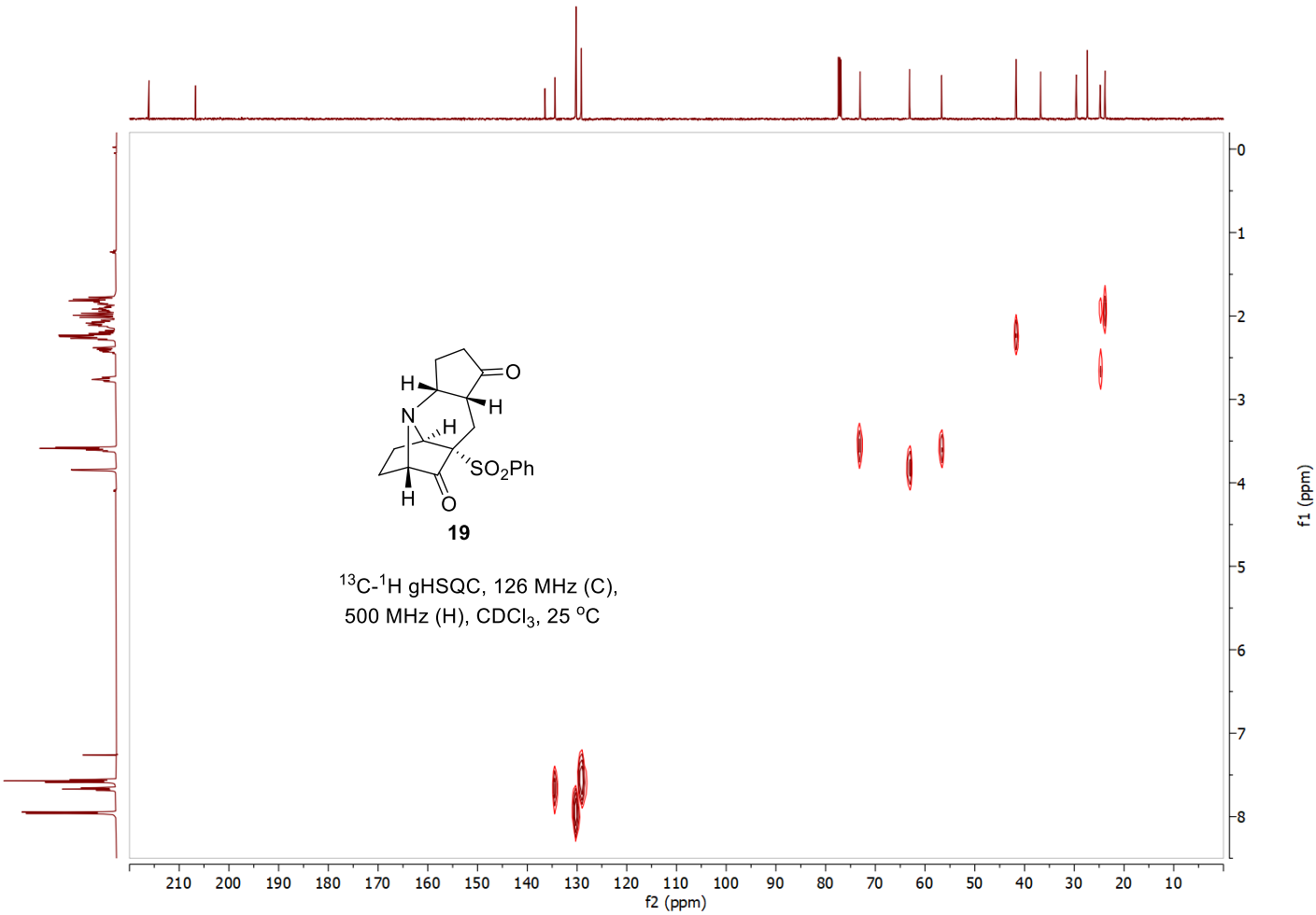


19

^{1}H NMR, 500 MHz, $CDCl_3$, 25 °C


216.08
206.68
136.44
134.41
130.19
129.12
77.16 Chloroform-d
73.07
73.03
63.11
56.68
41.70
36.78
29.60
27.37
24.79
23.81
H
N
H
H
O
O
SO2Ph
H
O
19
13C NMR, 126 MHz,
CDCl3, 25 °C
f1 (ppm)


H
N
H
H
O
O
SO2Ph
H
O
19
1H-1H gCOSY,
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


19
^{13}C-^{1}H gHSQC, 126 MHz (C),
500 MHz (H), $CDCl_3$, 25 °C
f2 (ppm)
f1 (ppm)

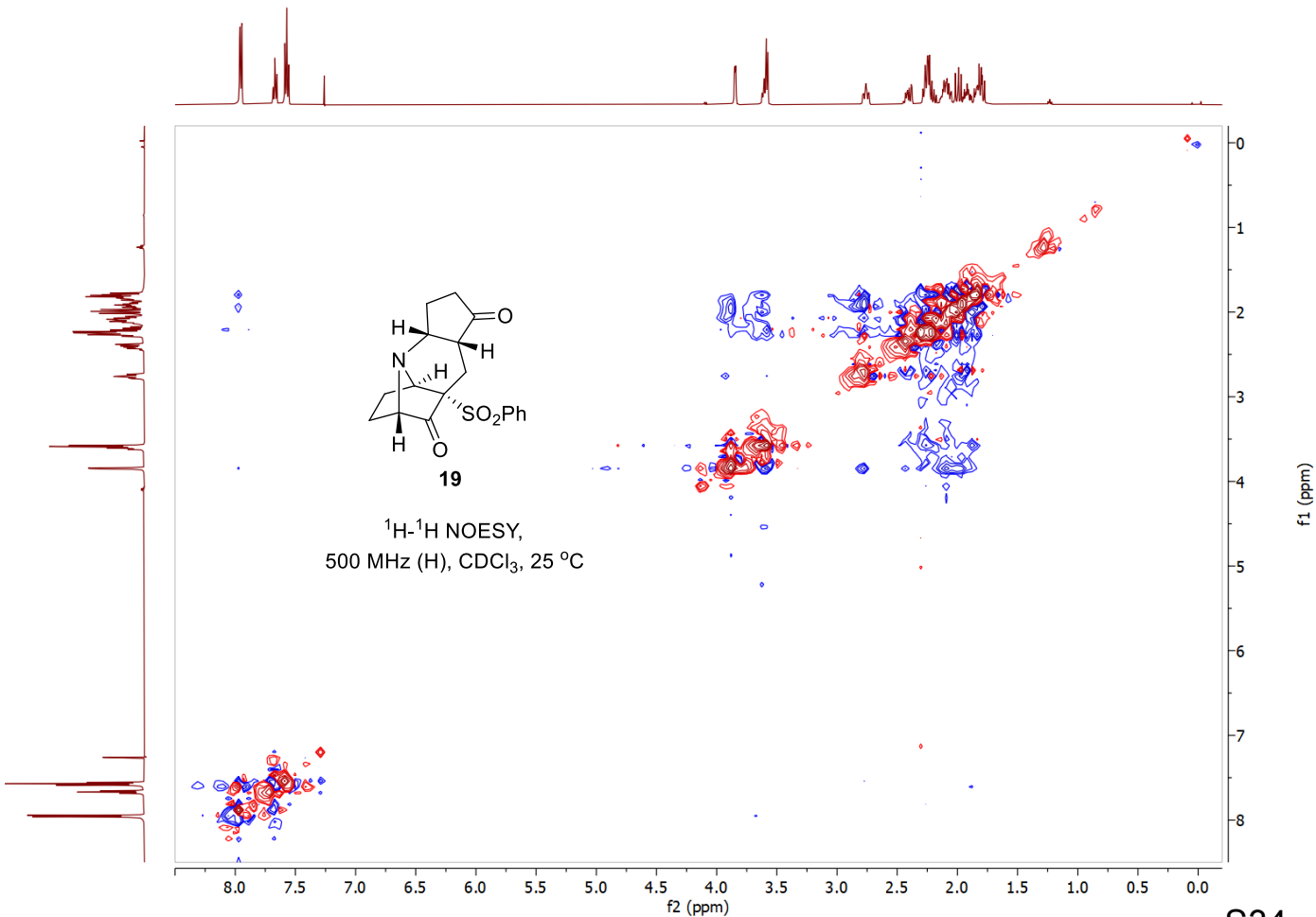

19
^{1}H-^{1}H NOESY,
500 MHz (H), $CDCl_3$, 25 °C
f2 (ppm)
f1 (ppm)

Table 1, Entry 1
Crude reaction mixture (20+21)
^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^oC

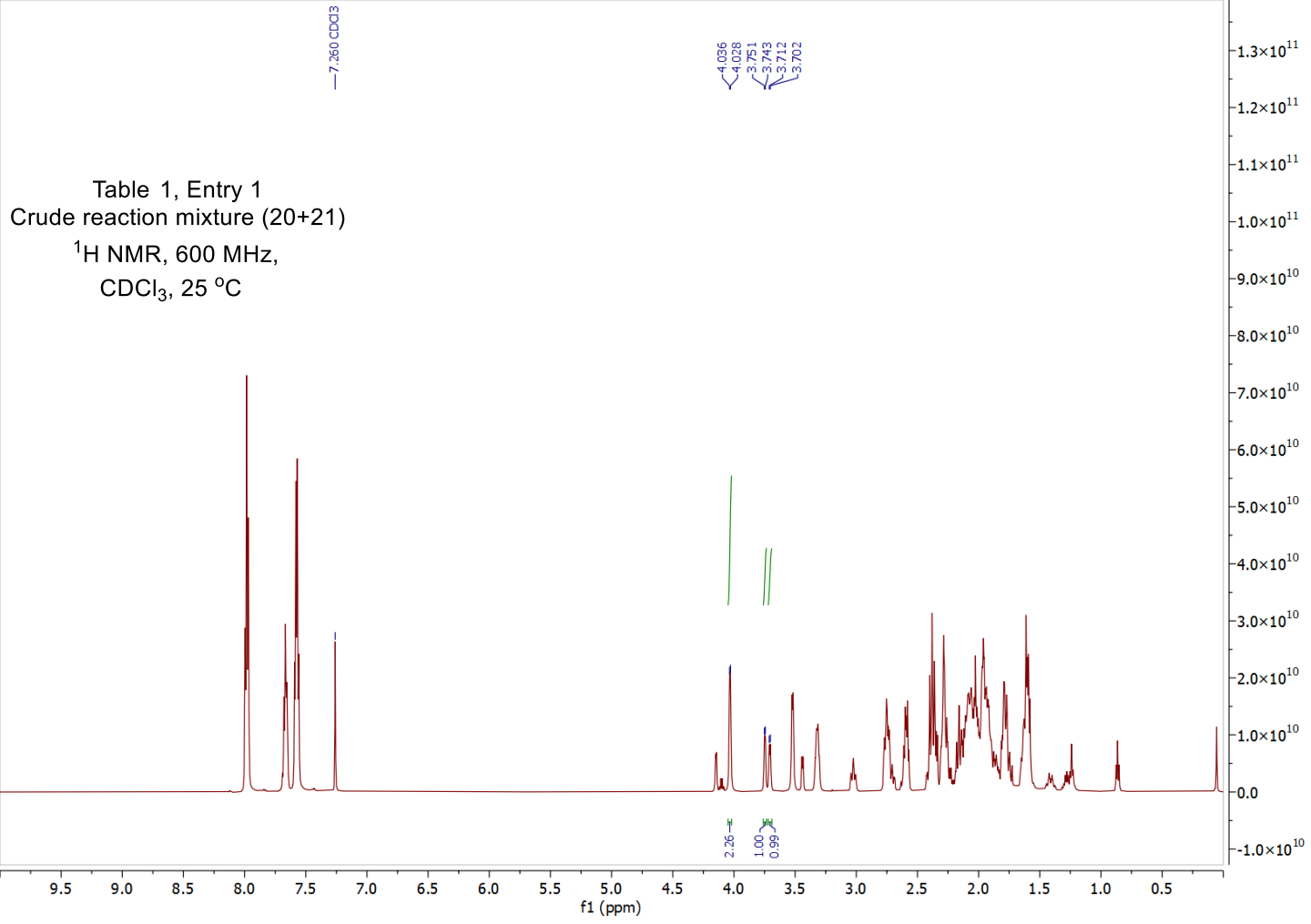


Table 1, Entry 2
Crude reaction mixture (20+21)
^{1}H NMR, 500 MHz,
$CDCl_3$, 25 ^oC

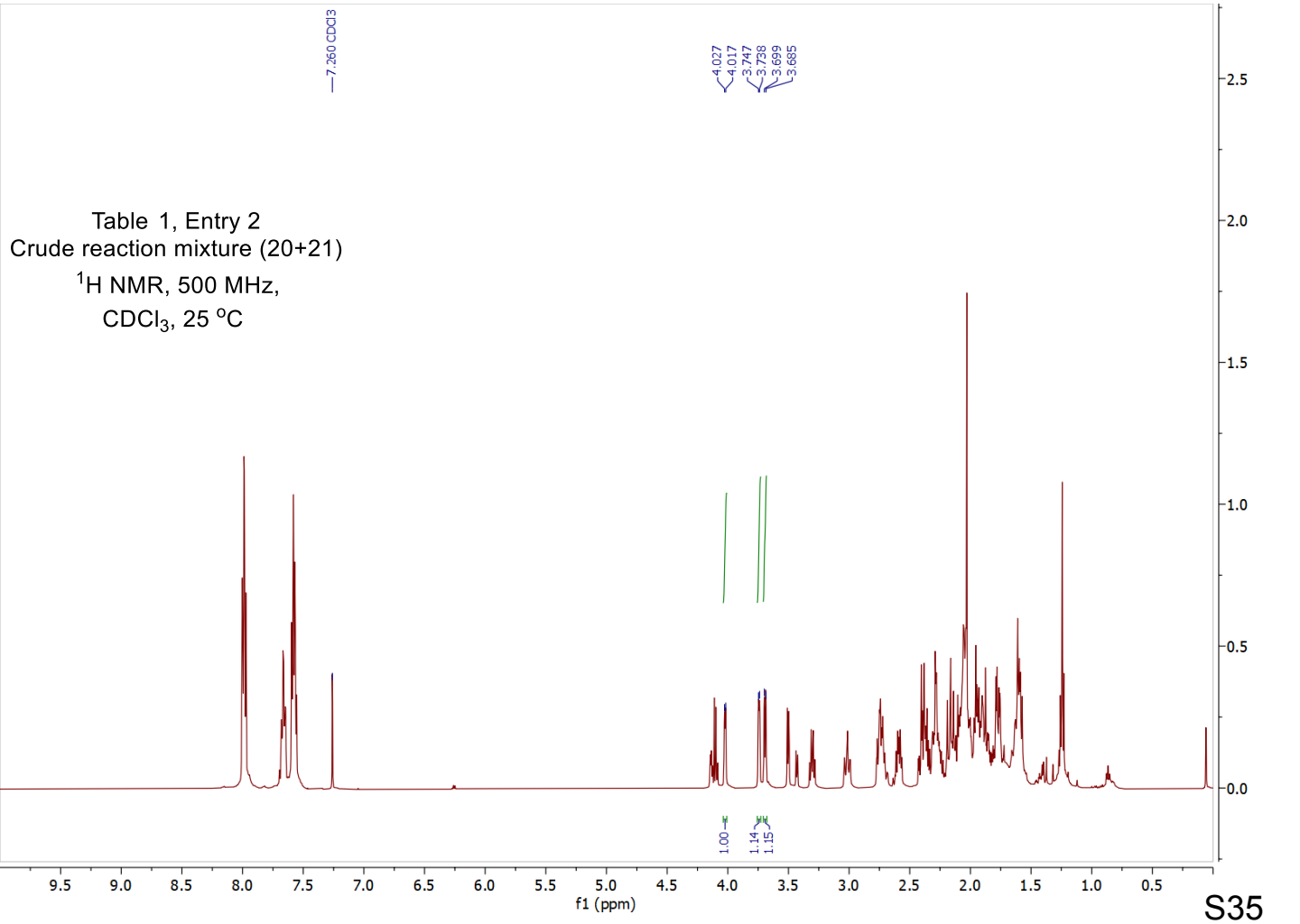


Table 1, Entry 3
Crude reaction mixture (20+21)

^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^oC

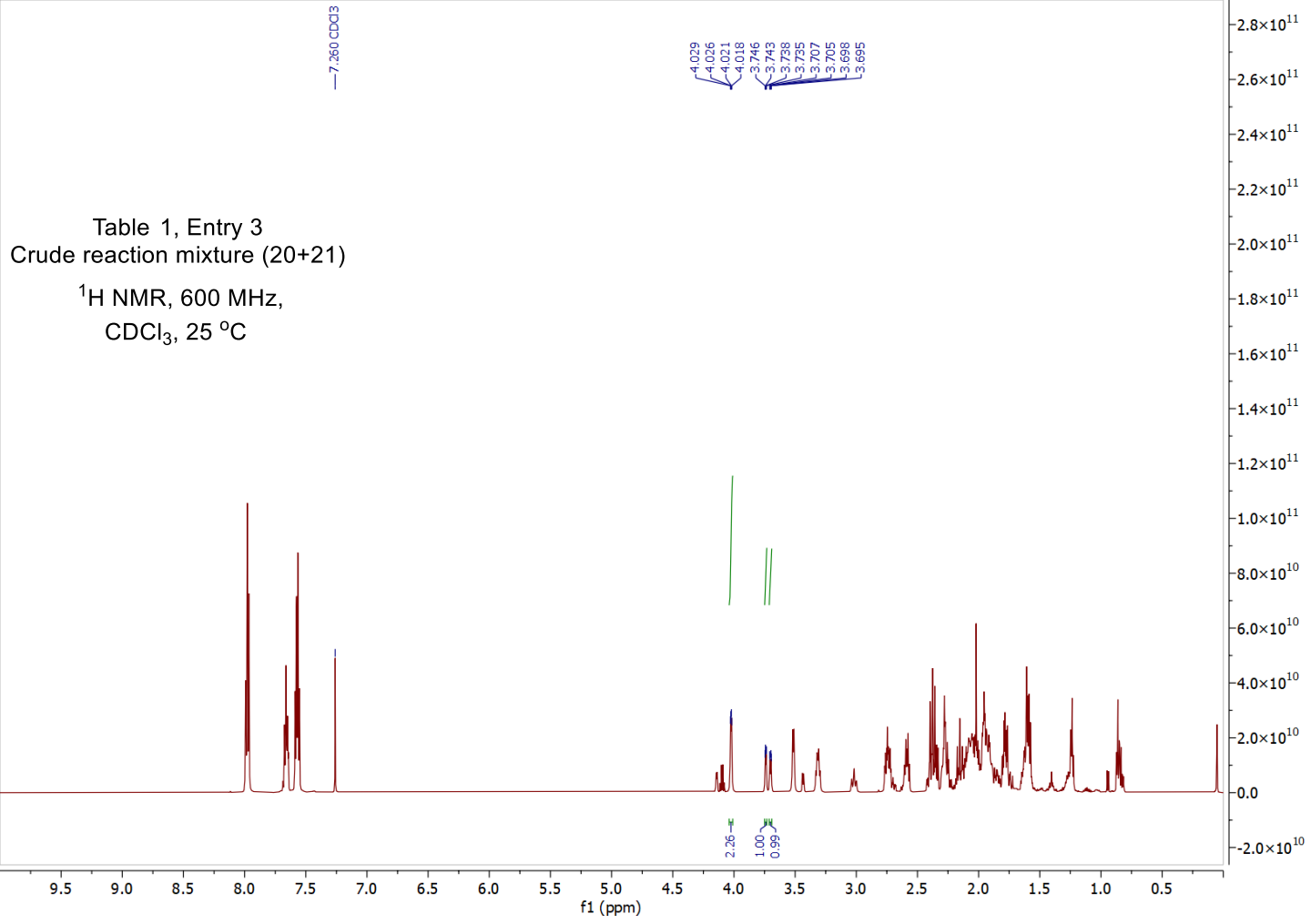
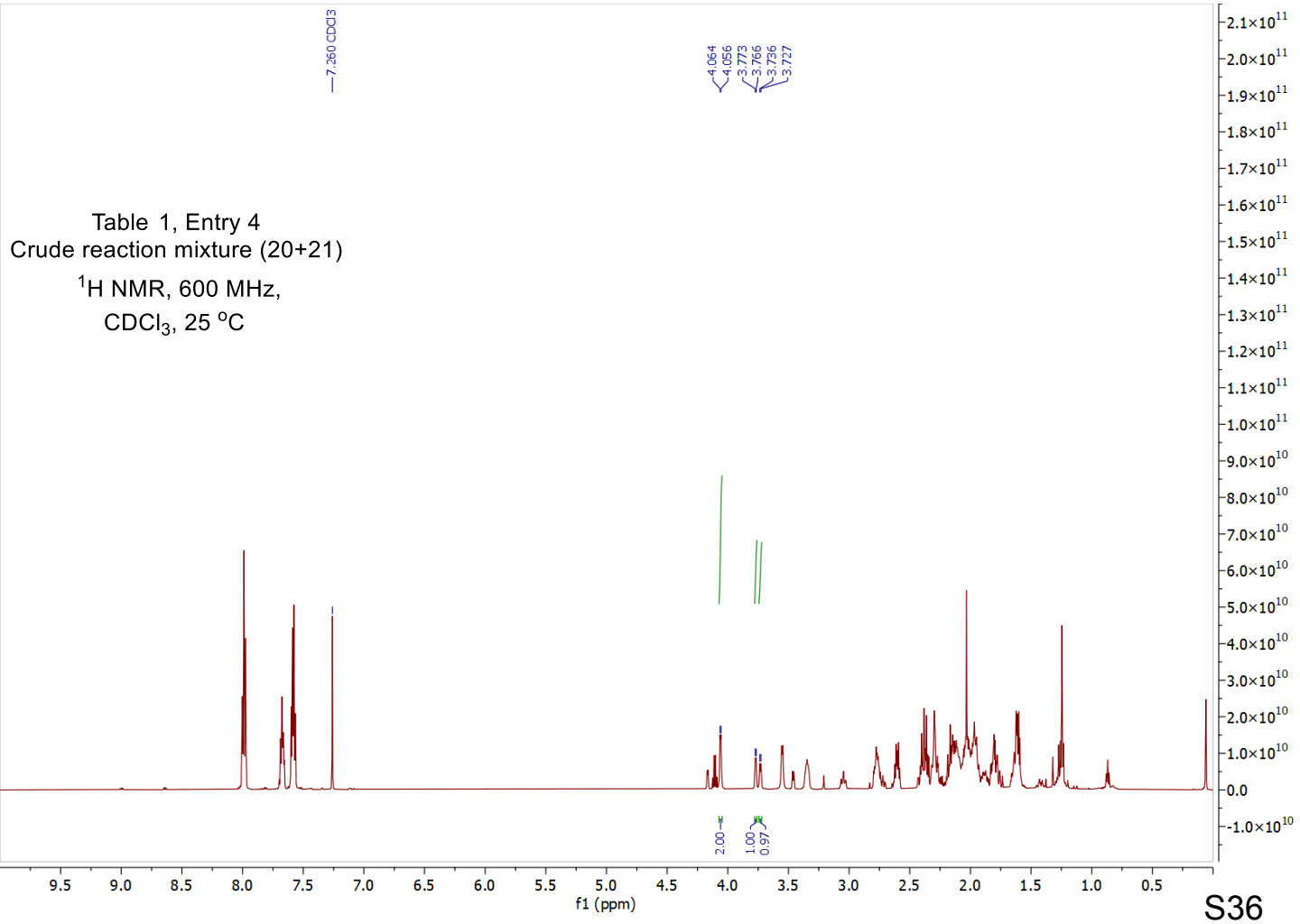
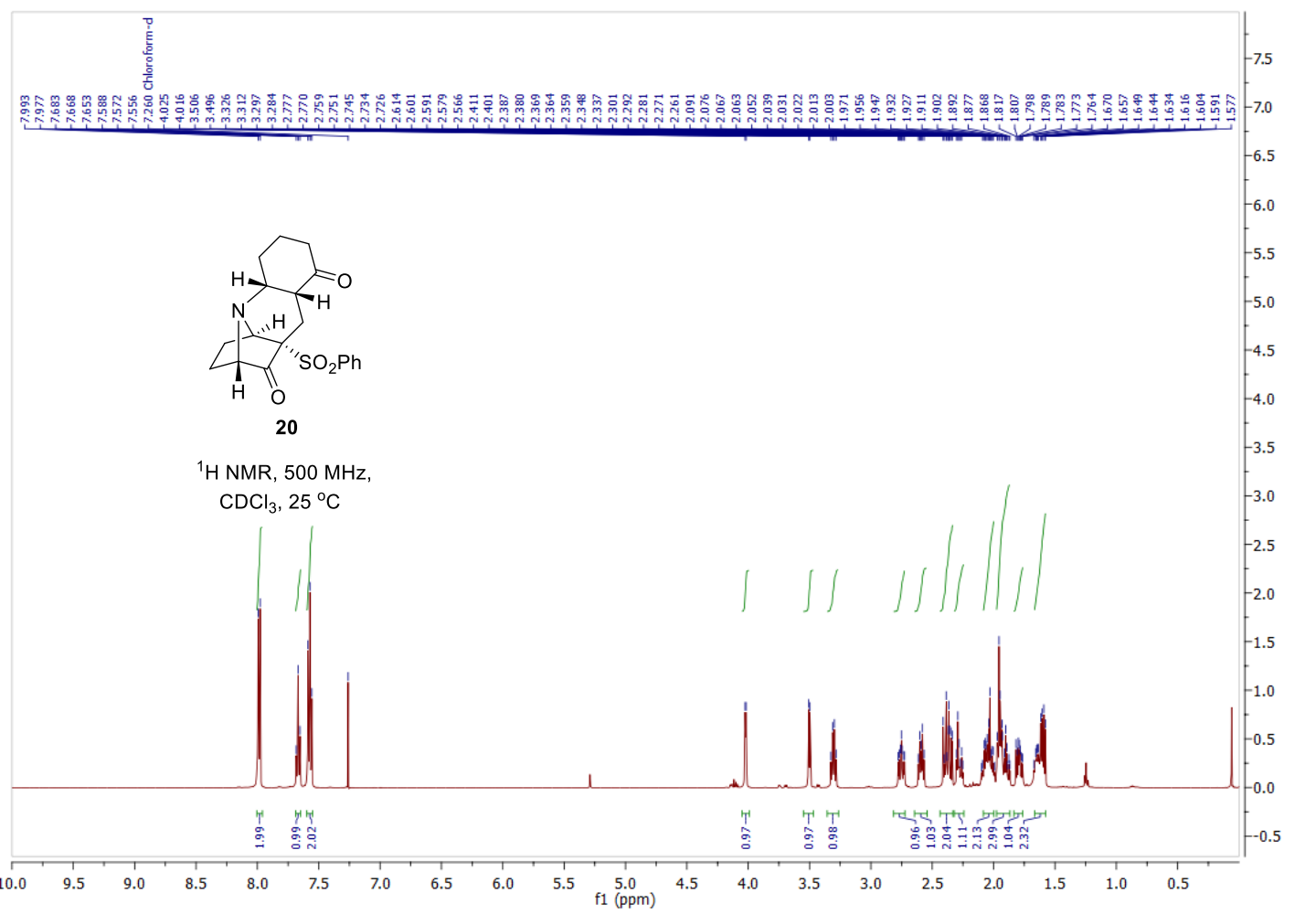
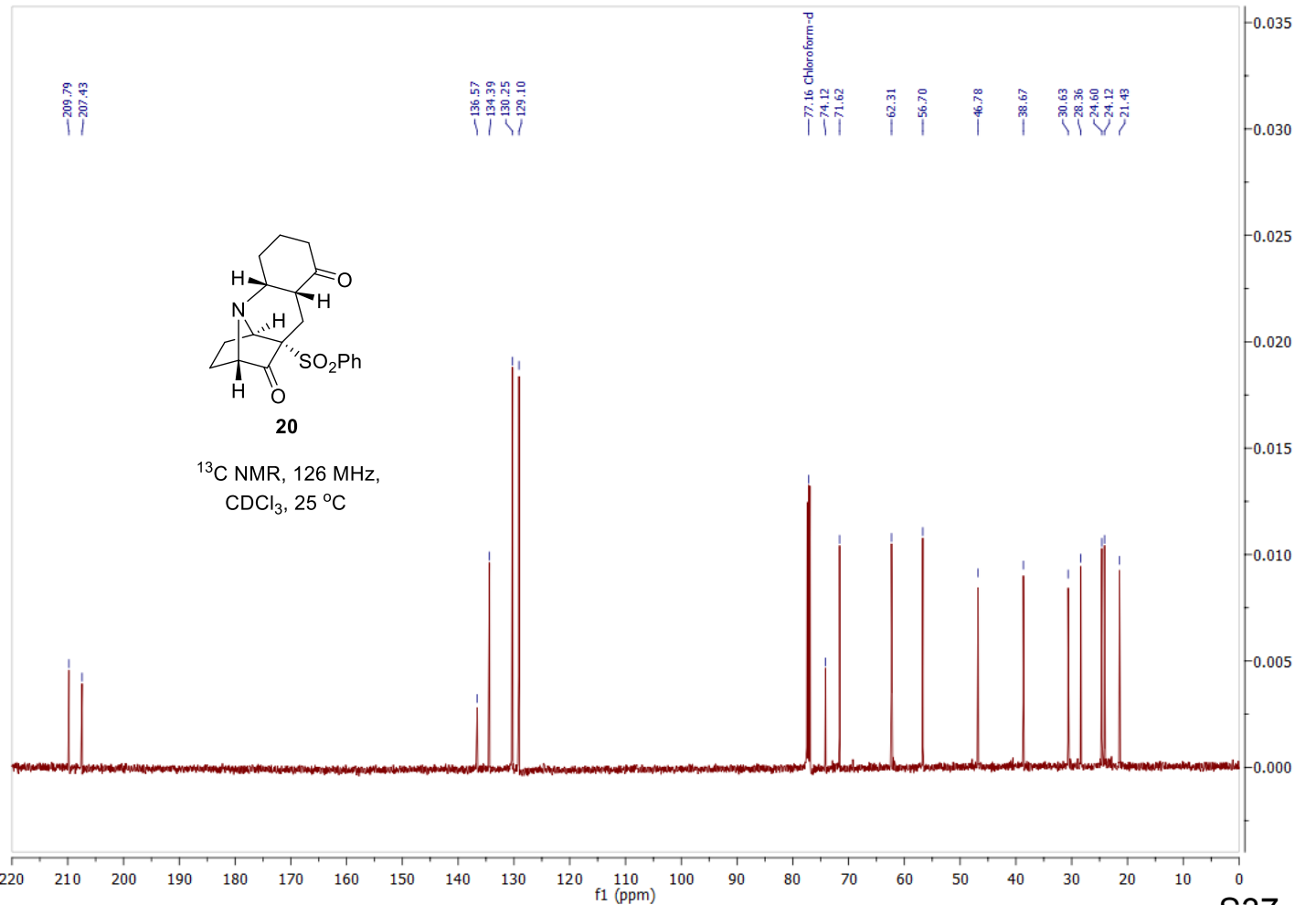


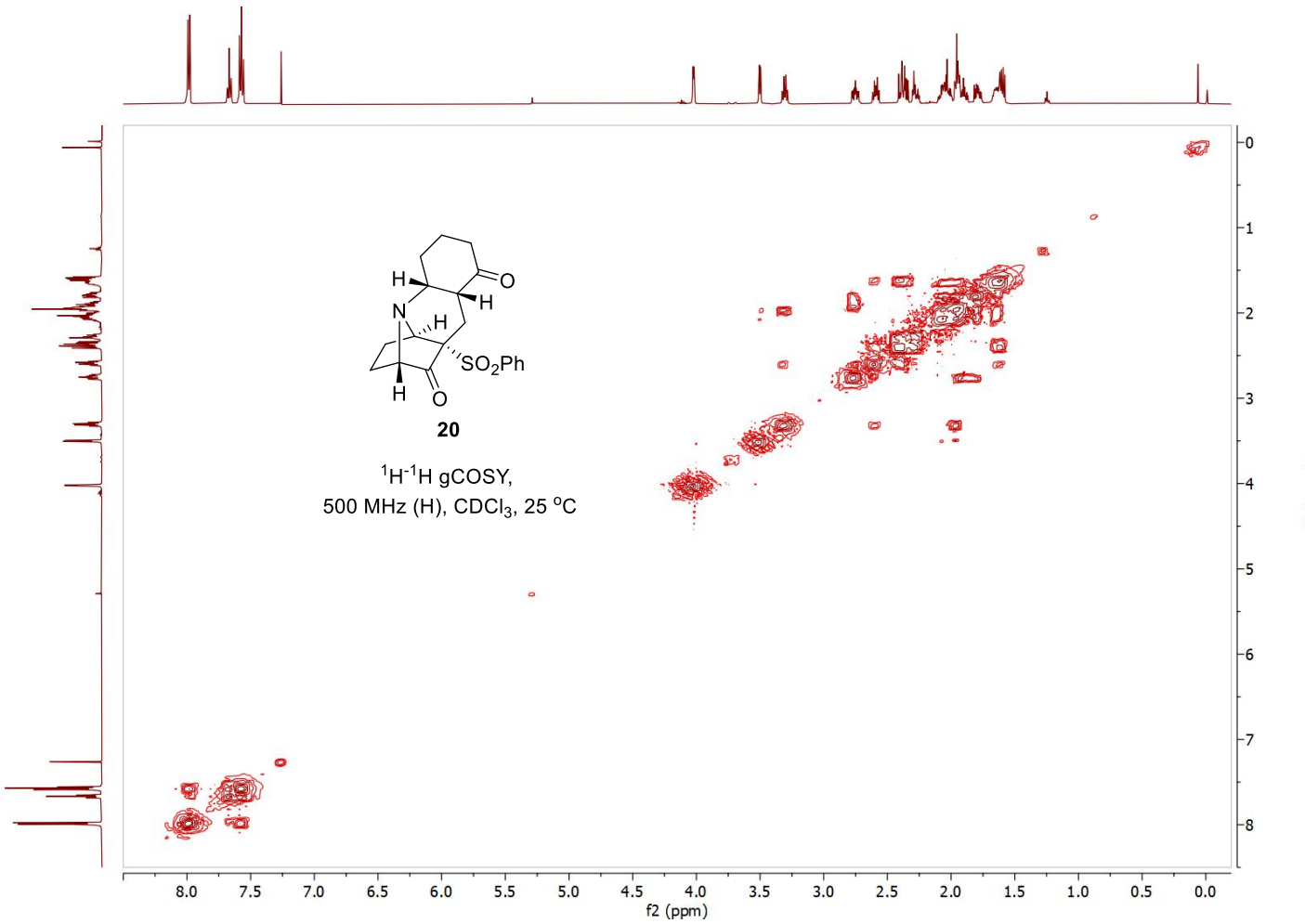
Table 1, Entry 4
Crude reaction mixture (20+21)

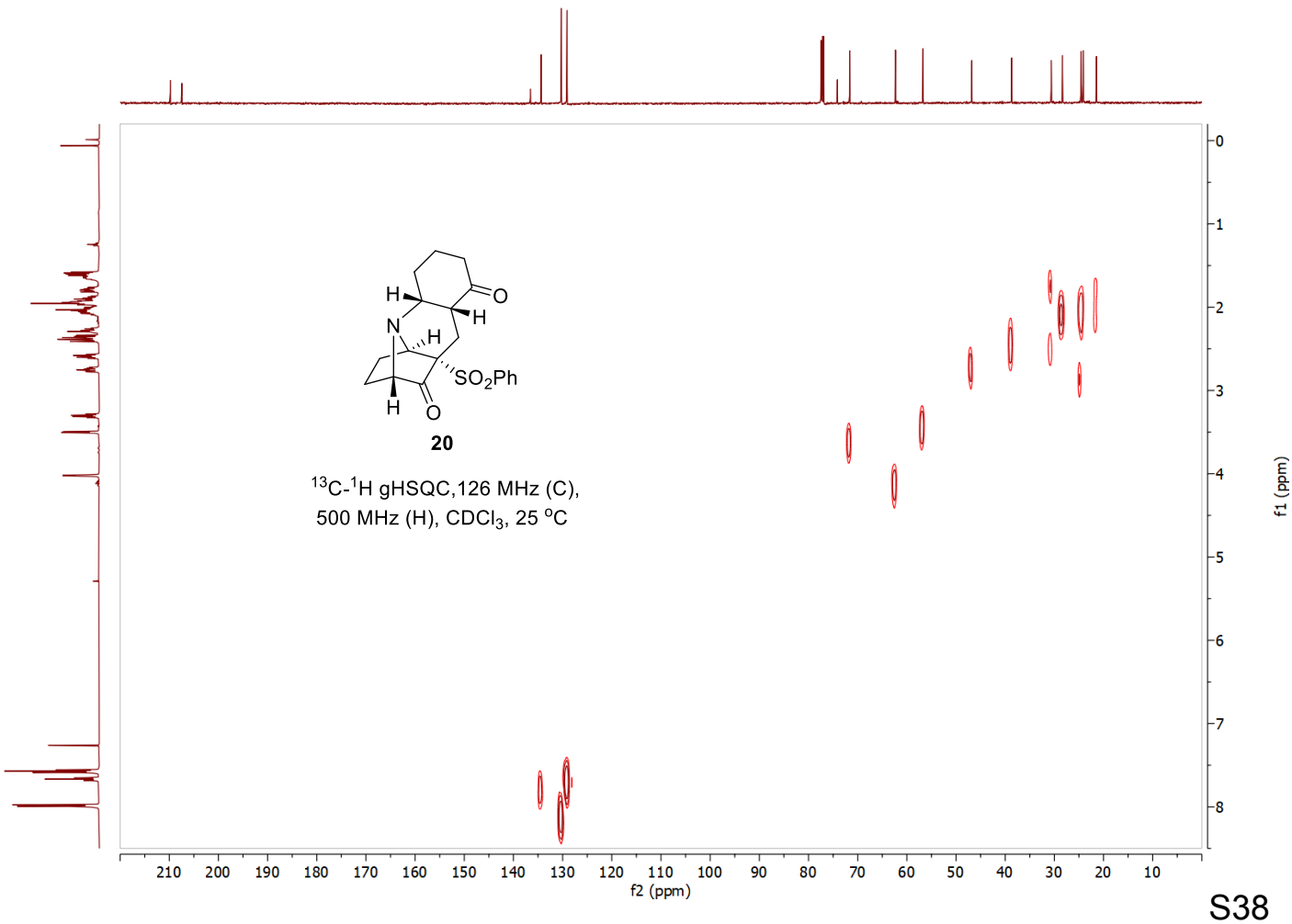
^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^oC

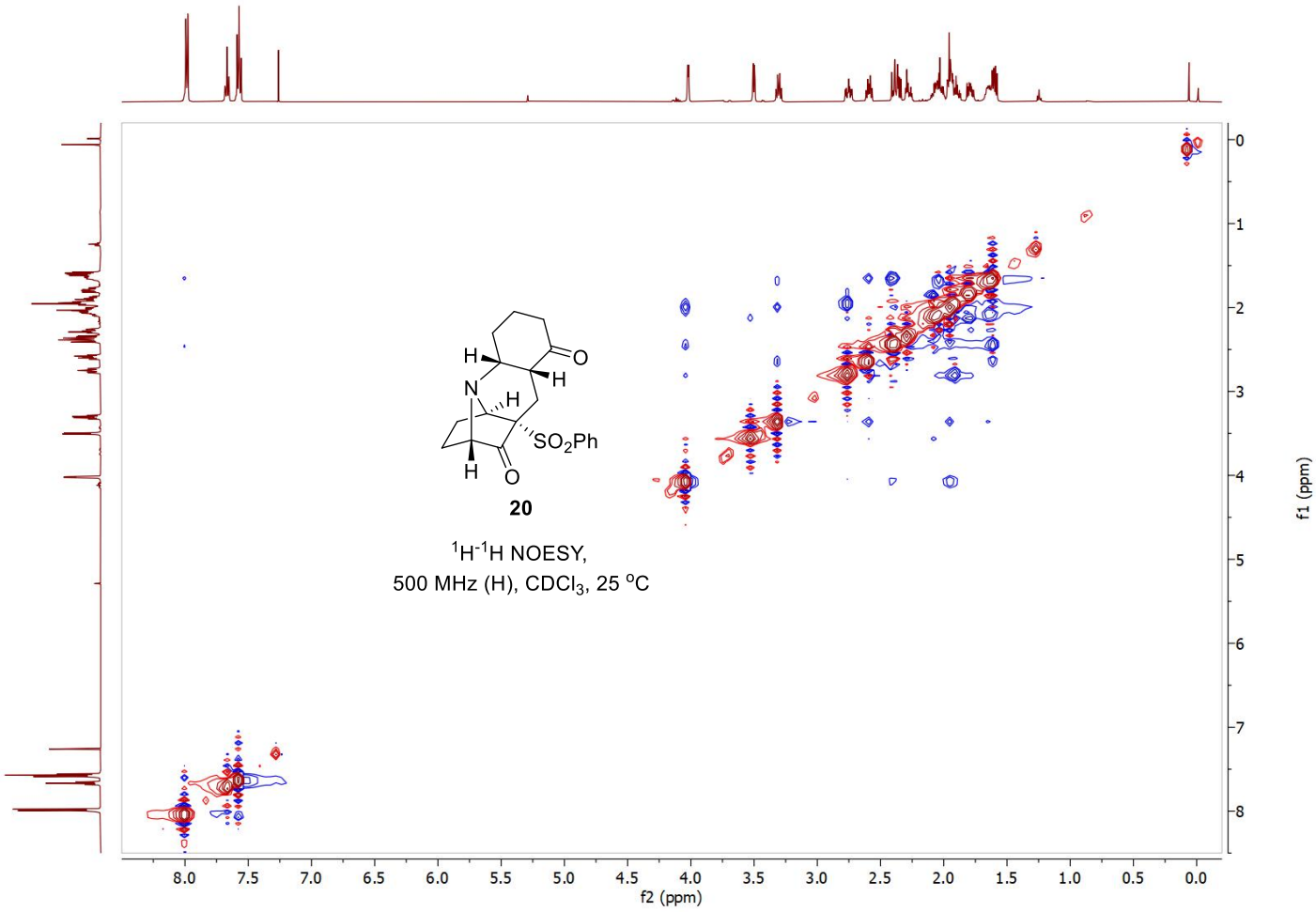



7.993
7.977
7.683
7.668
7.653
7.588
7.572
7.556
7.260 Chloroform-d
4.025
4.016
3.506
3.496
3.326
3.312
3.297
3.284
2.777
2.770
2.759
2.751
2.745
2.734
2.726
2.614
2.601
2.591
2.579
2.566
2.411
2.401
2.387
2.380
2.369
2.364
2.359
2.348
2.337
2.301
2.292
2.281
2.271
2.261
2.091
2.076
2.067
2.063
2.052
2.039
2.031
2.022
2.013
2.003
1.971
1.956
1.947
1.932
1.927
1.911
1.902
1.892
1.877
1.868
1.817
1.807
1.798
1.789
1.783
1.773
1.764
1.670
1.657
1.649
1.644
1.634
1.616
1.604
1.591
1.577
H
N
H
O
H
SO2Ph
H
O
20
1H NMR, 500 MHz,
CDCl3, 25 °C
1.99
0.99
2.02
0.97
0.97
0.98
0.96
1.03
2.04
1.11
2.13
2.99
1.04
2.32
f1 (ppm)


209.79
207.43
136.57
134.39
130.25
129.10
77.16 Chloroform-d
74.12
71.62
62.31
56.70
46.78
38.67
30.63
28.36
24.60
24.12
21.43
H
N
H
O
H
SO2Ph
H
O
20
13C NMR, 126 MHz,
CDCl3, 25 °C
f1 (ppm)

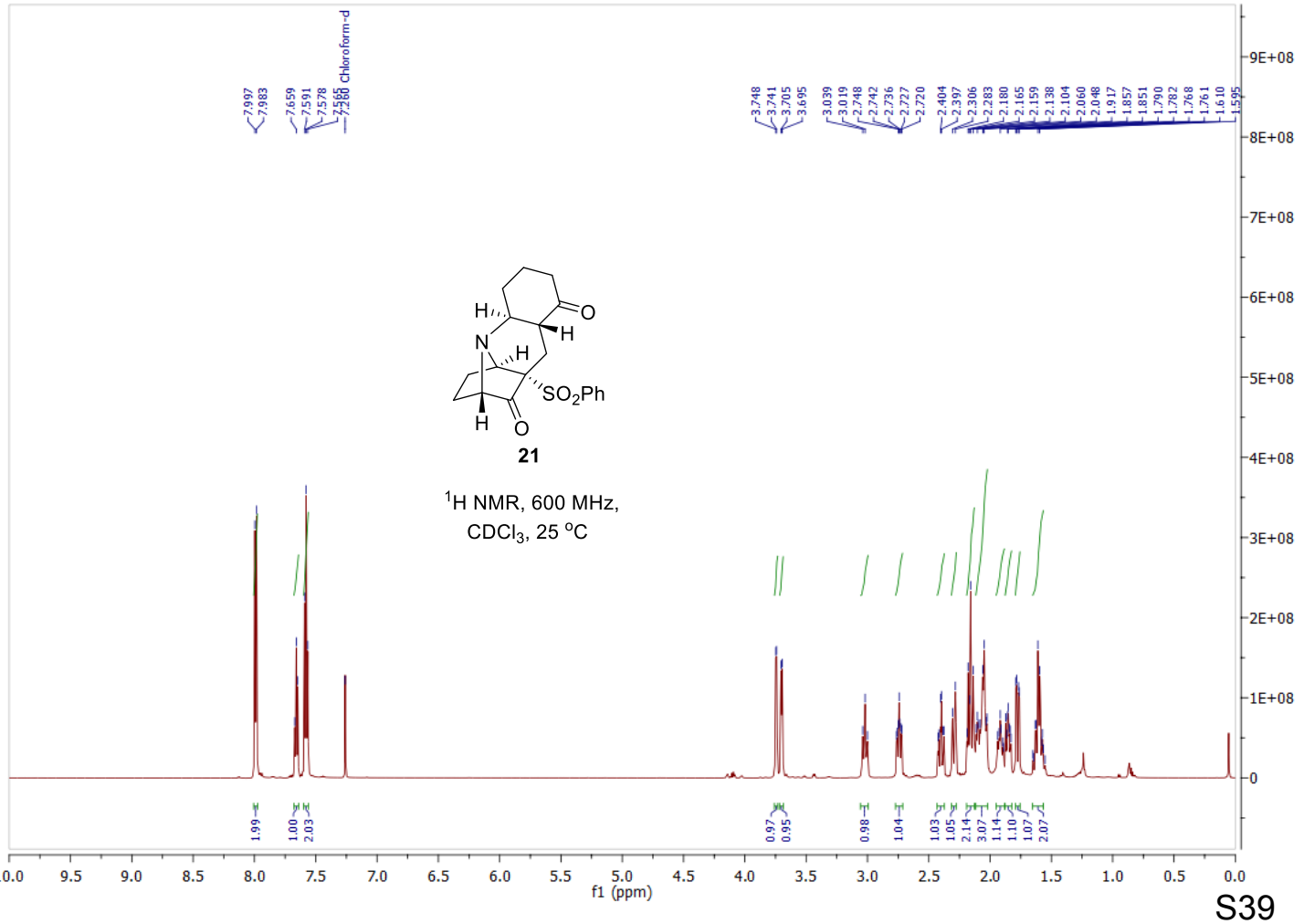

H
O
H
N
H
SO2Ph
H
O
20
1H-1H gCOSY,
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


H
O
H
N
H
SO2Ph
H
O
20
13C-1H gHSQC,126 MHz (C),
500 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)



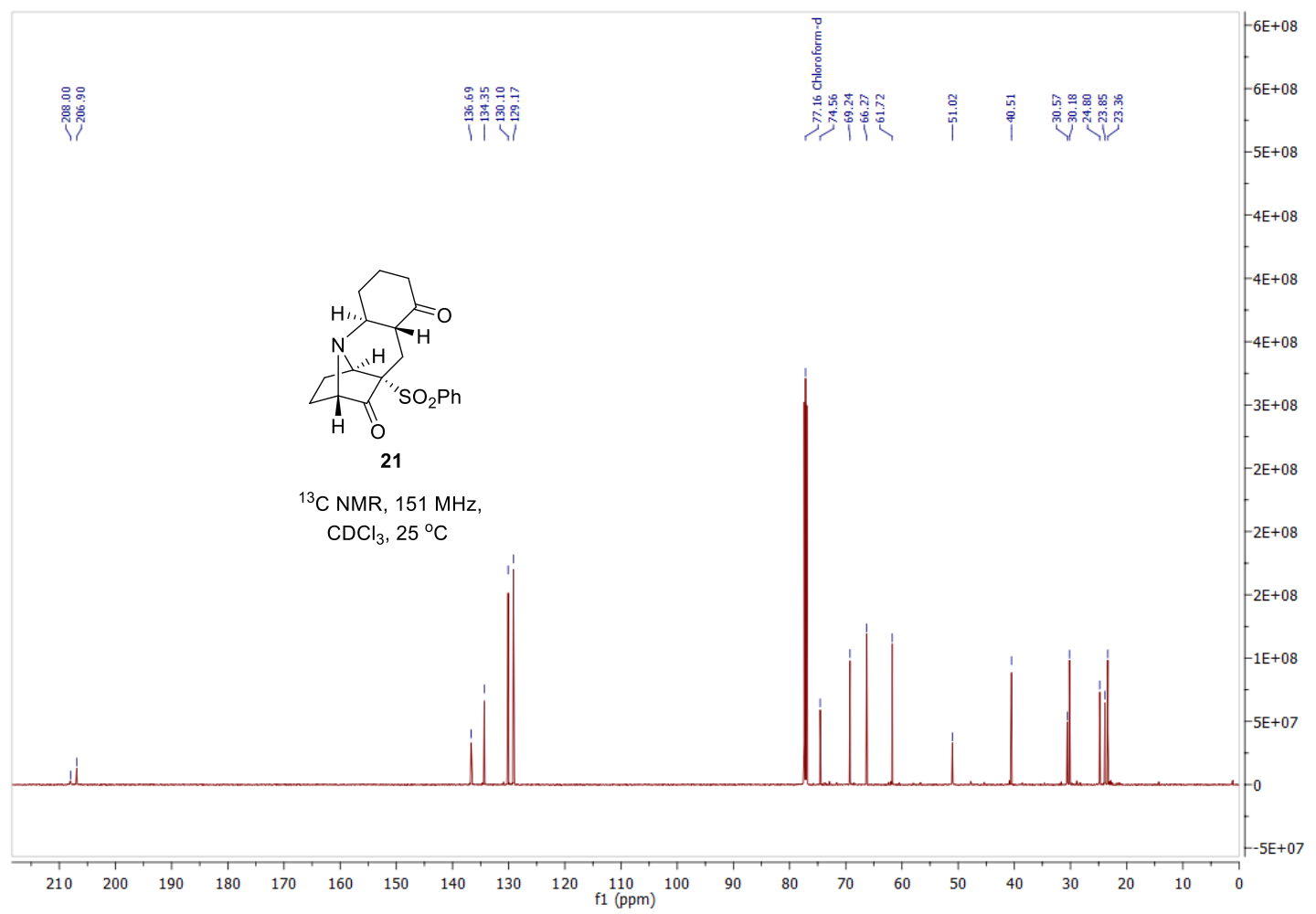
20

^{1}H-^{1}H NOESY,
500 MHz (H), $CDCl_3$, 25 °C



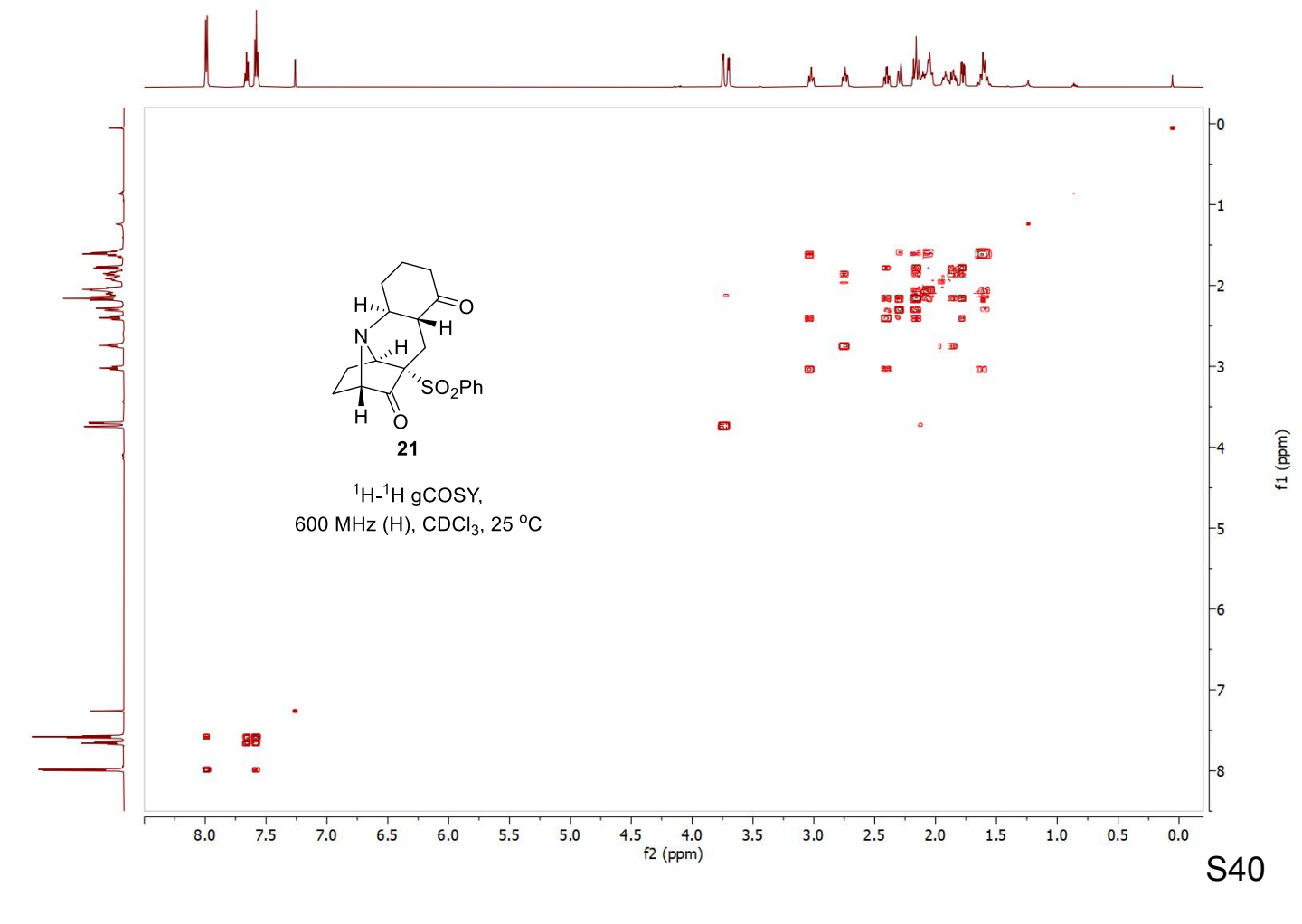
21

^{1}H NMR, 600 MHz,
$CDCl_3$, 25 °C



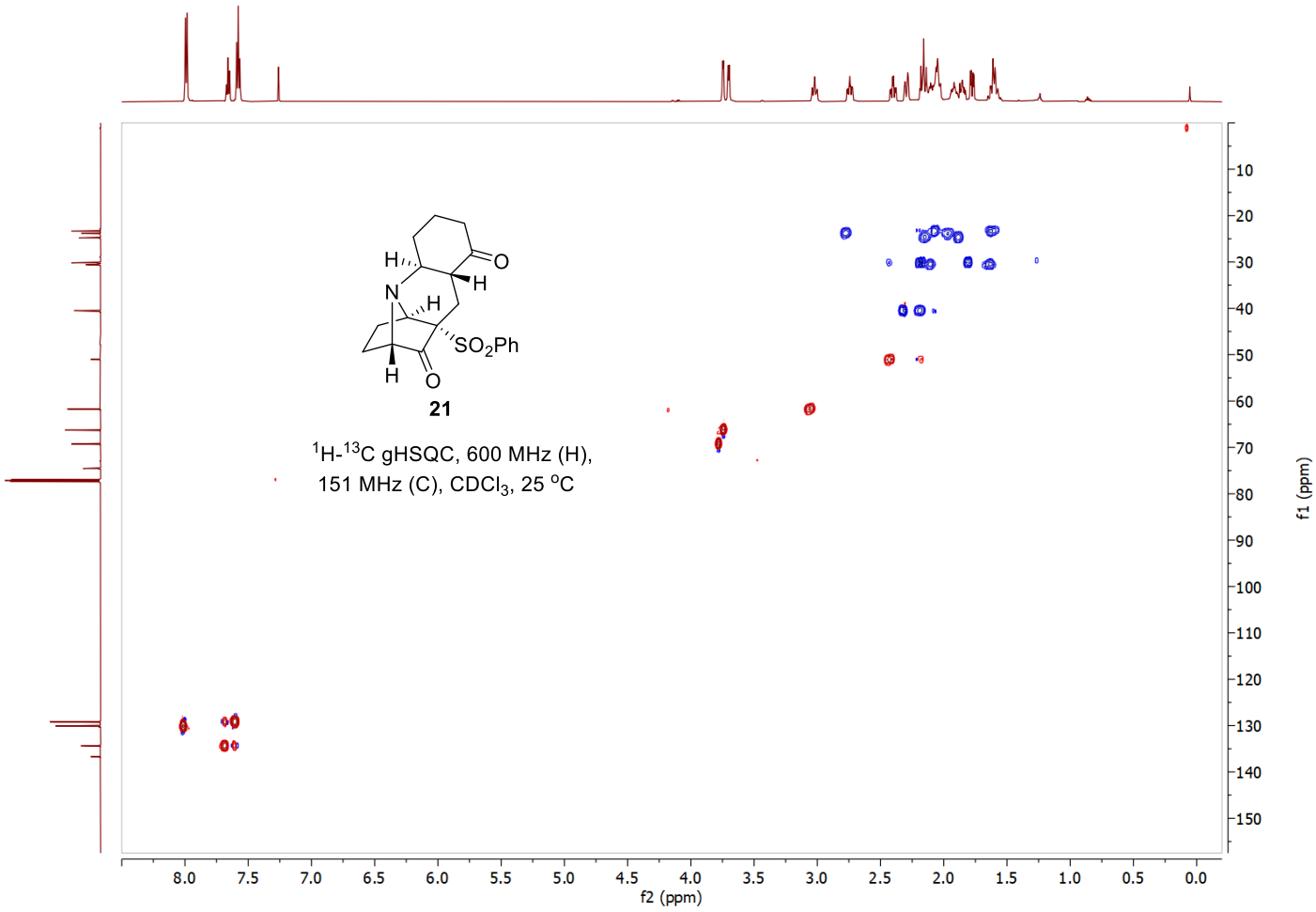
21

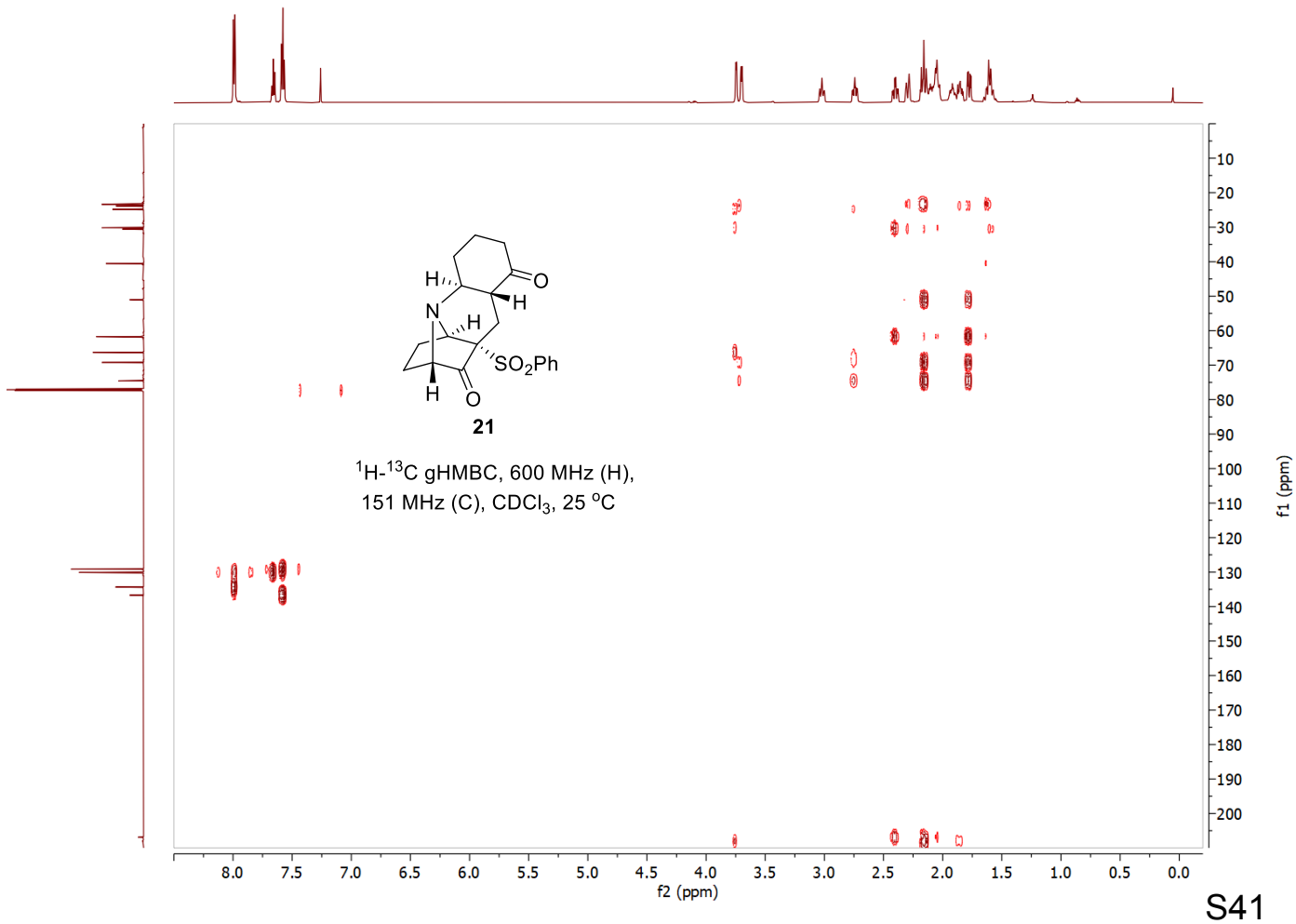
^{13}C NMR, 151 MHz,
$CDCl_3$, 25 ^{o}C

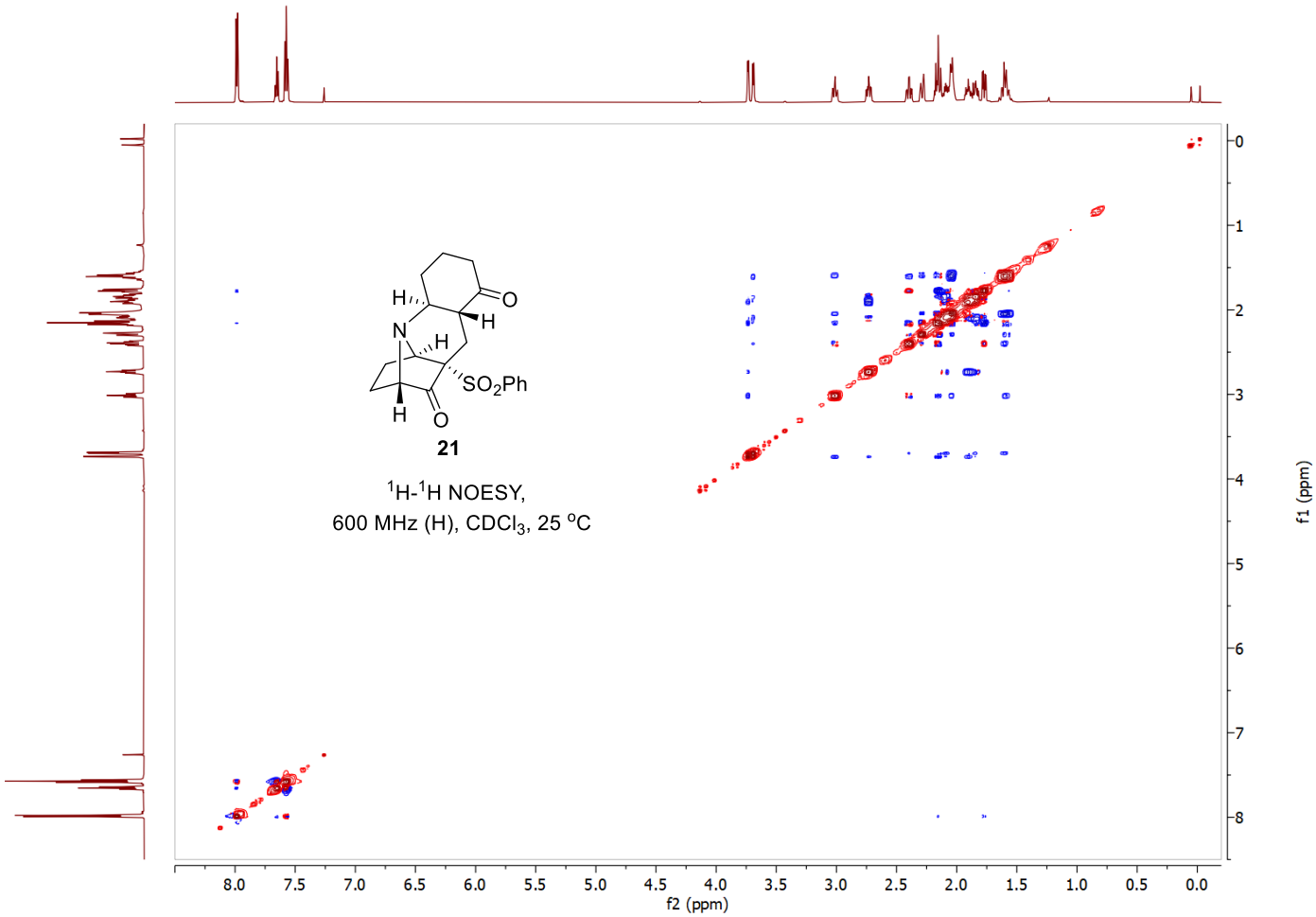


21

^{1}H-^{1}H gCOSY,
600 MHz (H), $CDCl_3$, 25 ^{o}C

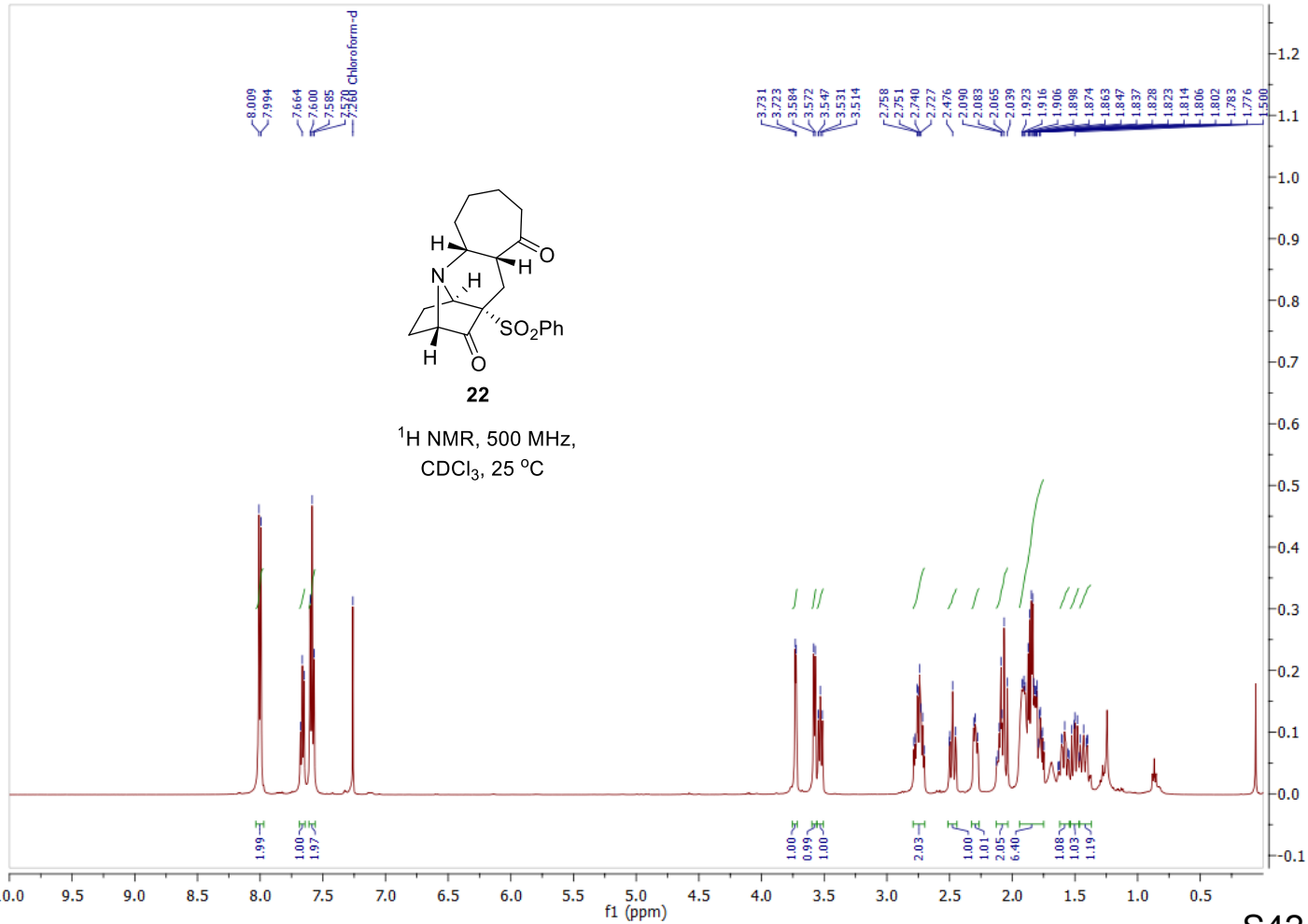

21
^{1}H-^{13}C gHSQC, 600 MHz (H),
151 MHz (C), $CDCl_3$, 25 ^{o}C
f2 (ppm)
f1 (ppm)


21
^{1}H-^{13}C gHMBC, 600 MHz (H),
151 MHz (C), $CDCl_3$, 25 ^{o}C
f2 (ppm)
f1 (ppm)



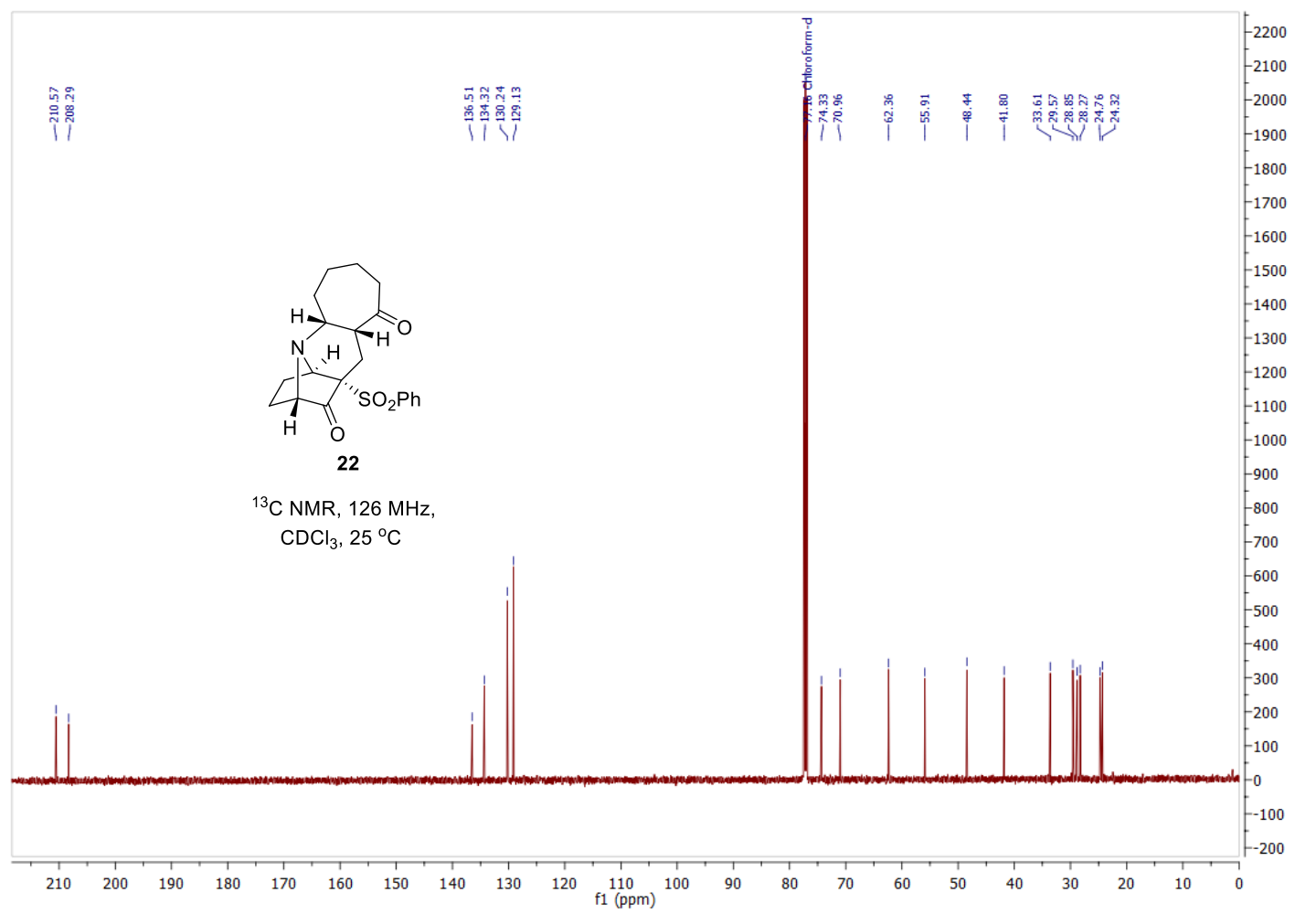
21

^{1}H-^{1}H NOESY,
600 MHz (H), $CDCl_3$, 25 ^oC



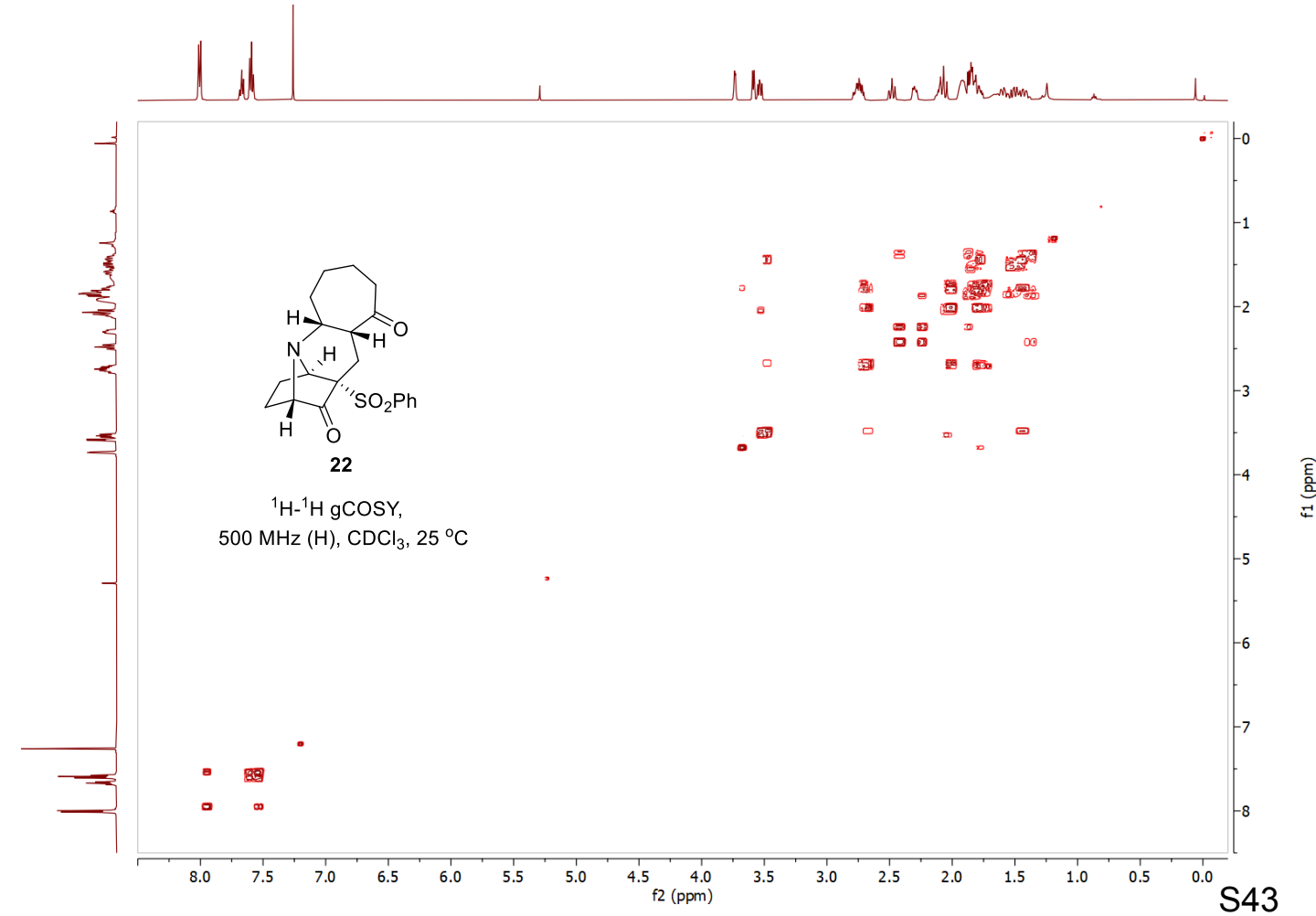
22

^{1}H NMR, 500 MHz,
$CDCl_3$, 25 ^oC



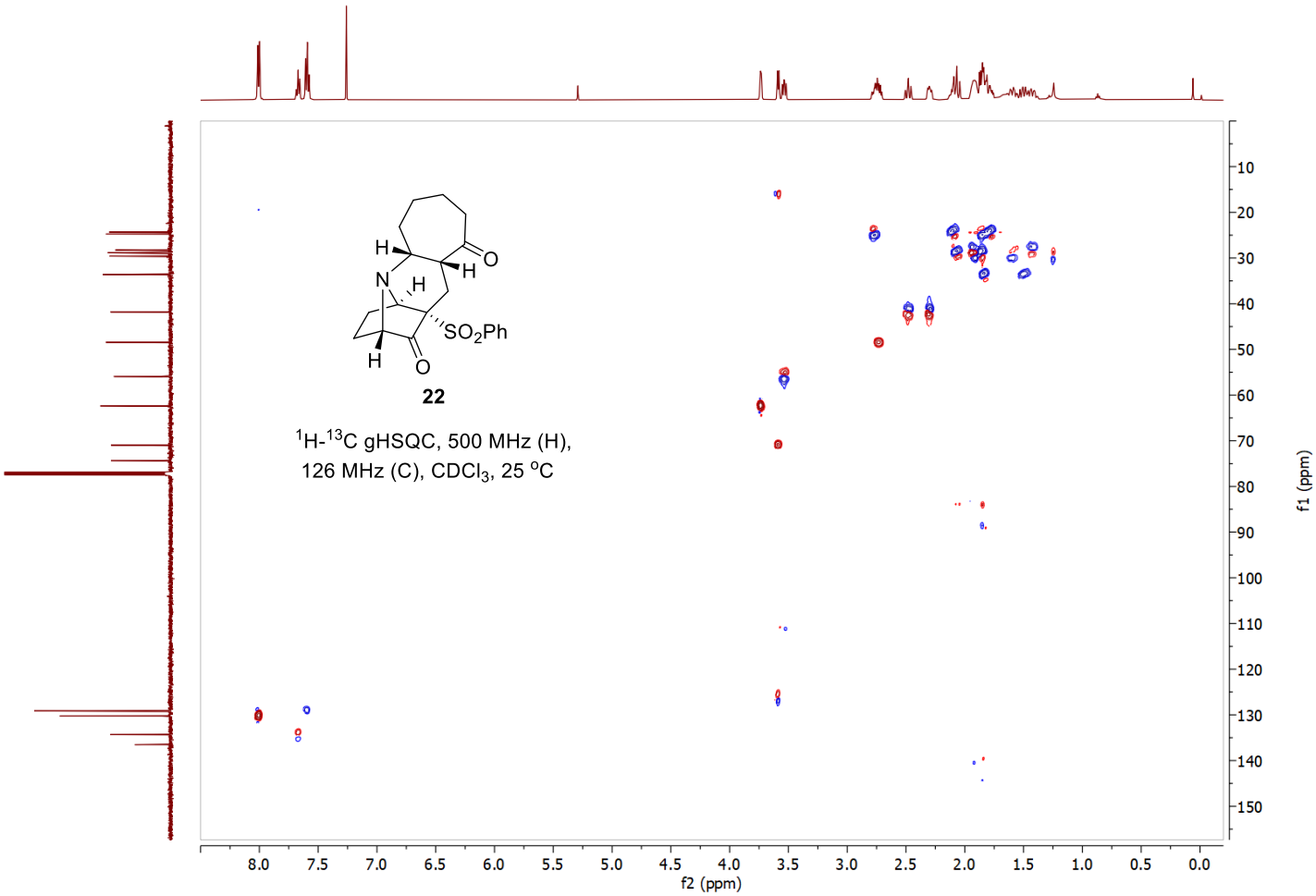
22

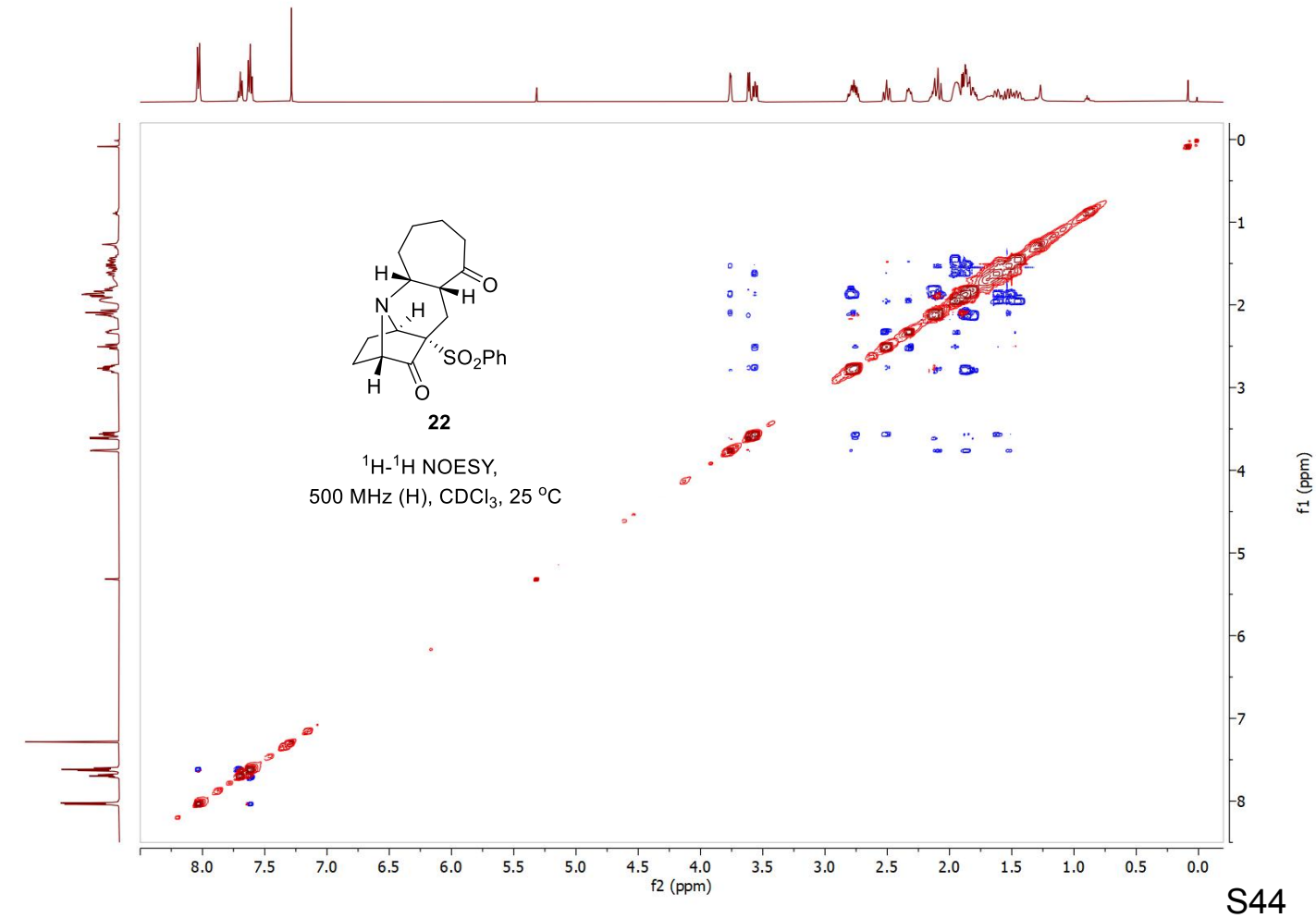
^{13}C NMR, 126 MHz,
$CDCl_3$, 25 °C

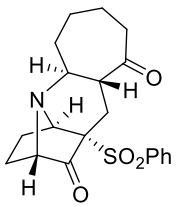


22

^{1}H-^{1}H gCOSY,
500 MHz (H), $CDCl_3$, 25 °C

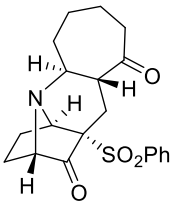

22
^{1}H-^{13}C gHSQC, 500 MHz (H),
126 MHz (C), $CDCl_3$, 25 °C
f2 (ppm)
f1 (ppm)


22
^{1}H-^{1}H NOESY,
500 MHz (H), $CDCl_3$, 25 °C
f2 (ppm)
f1 (ppm)



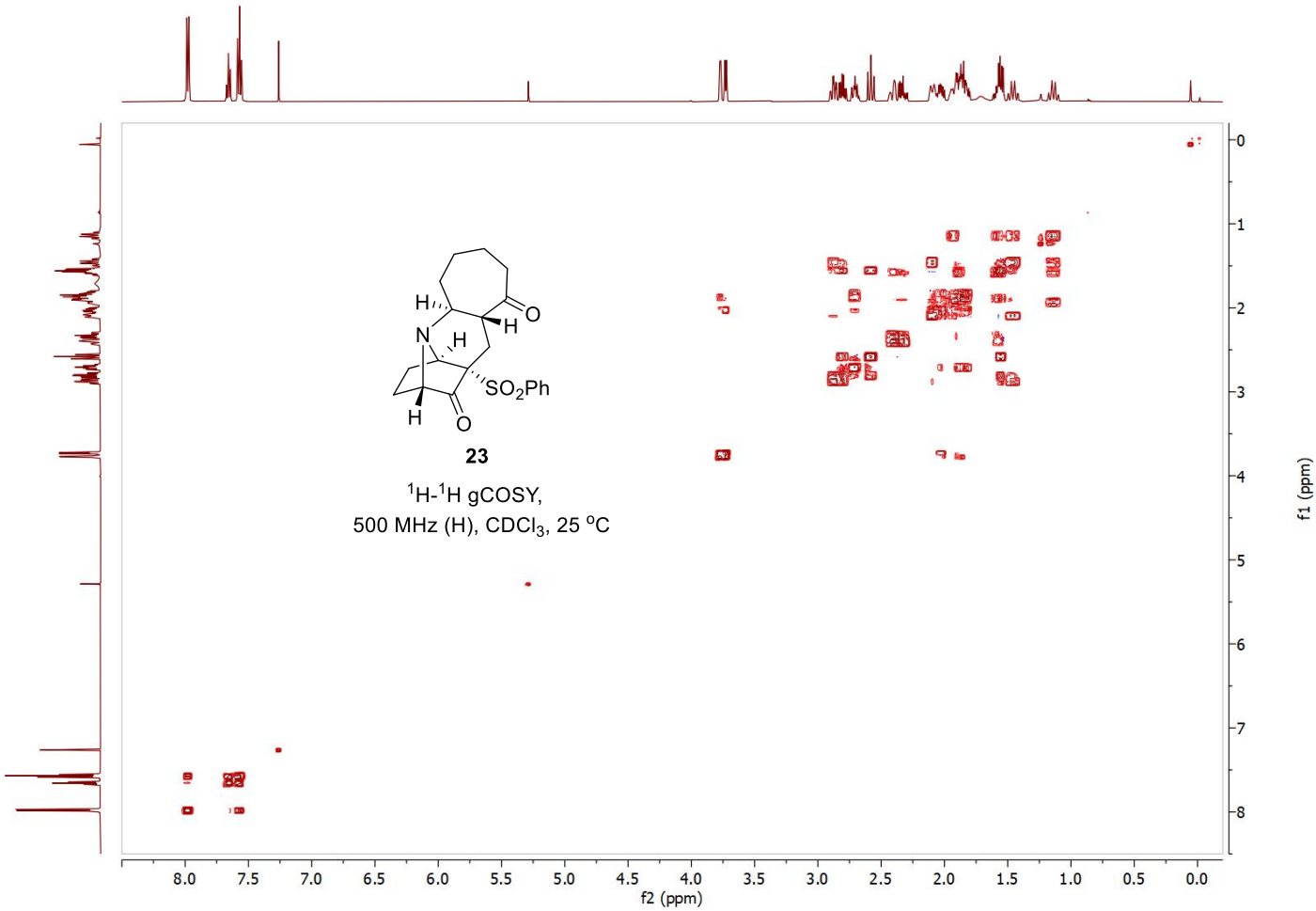
23

^{1}H NMR, 500 MHz,
$CDCl_3$, 25 °C



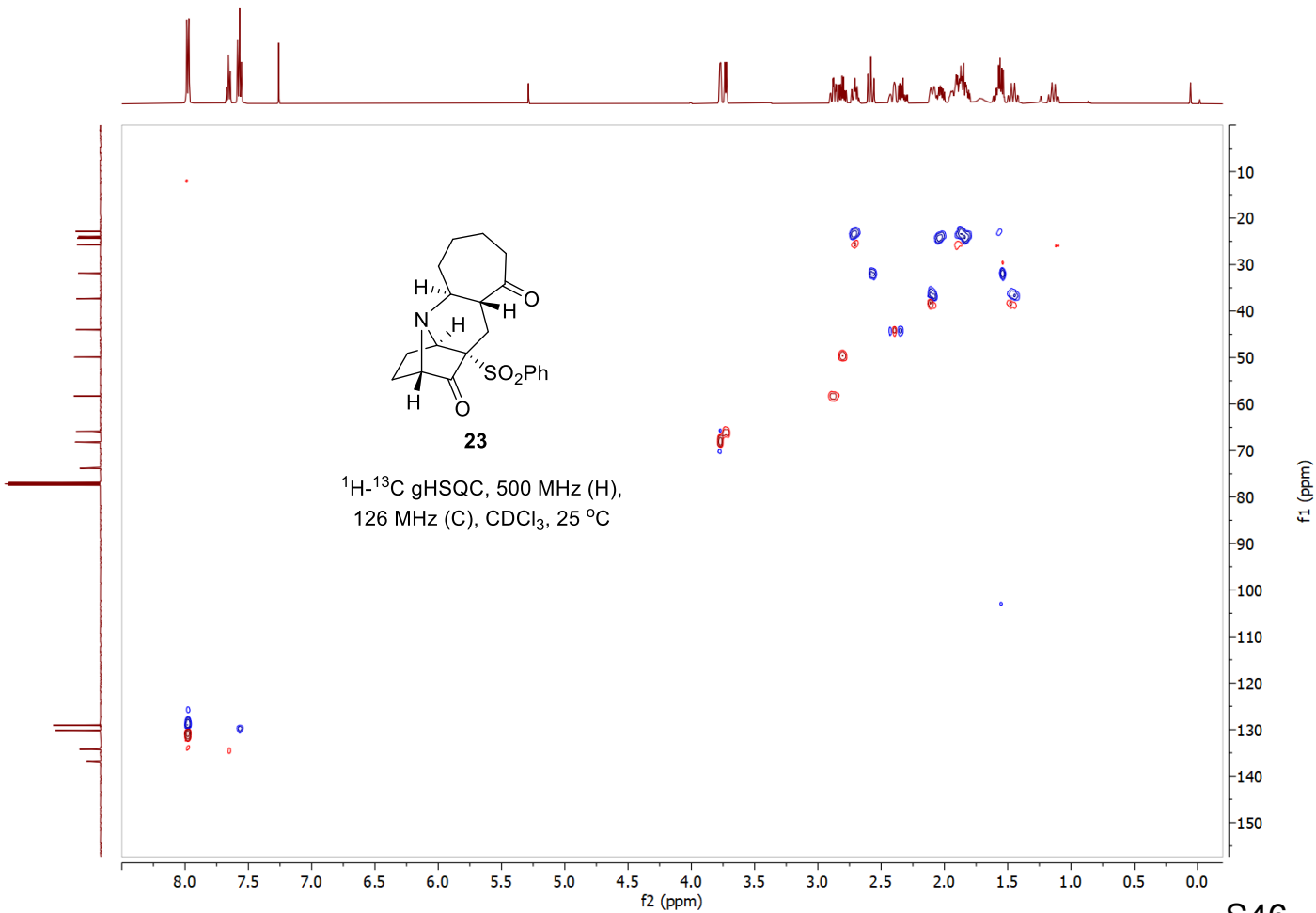
23

^{13}C NMR, 126 MHz,
$CDCl_3$, 25 °C



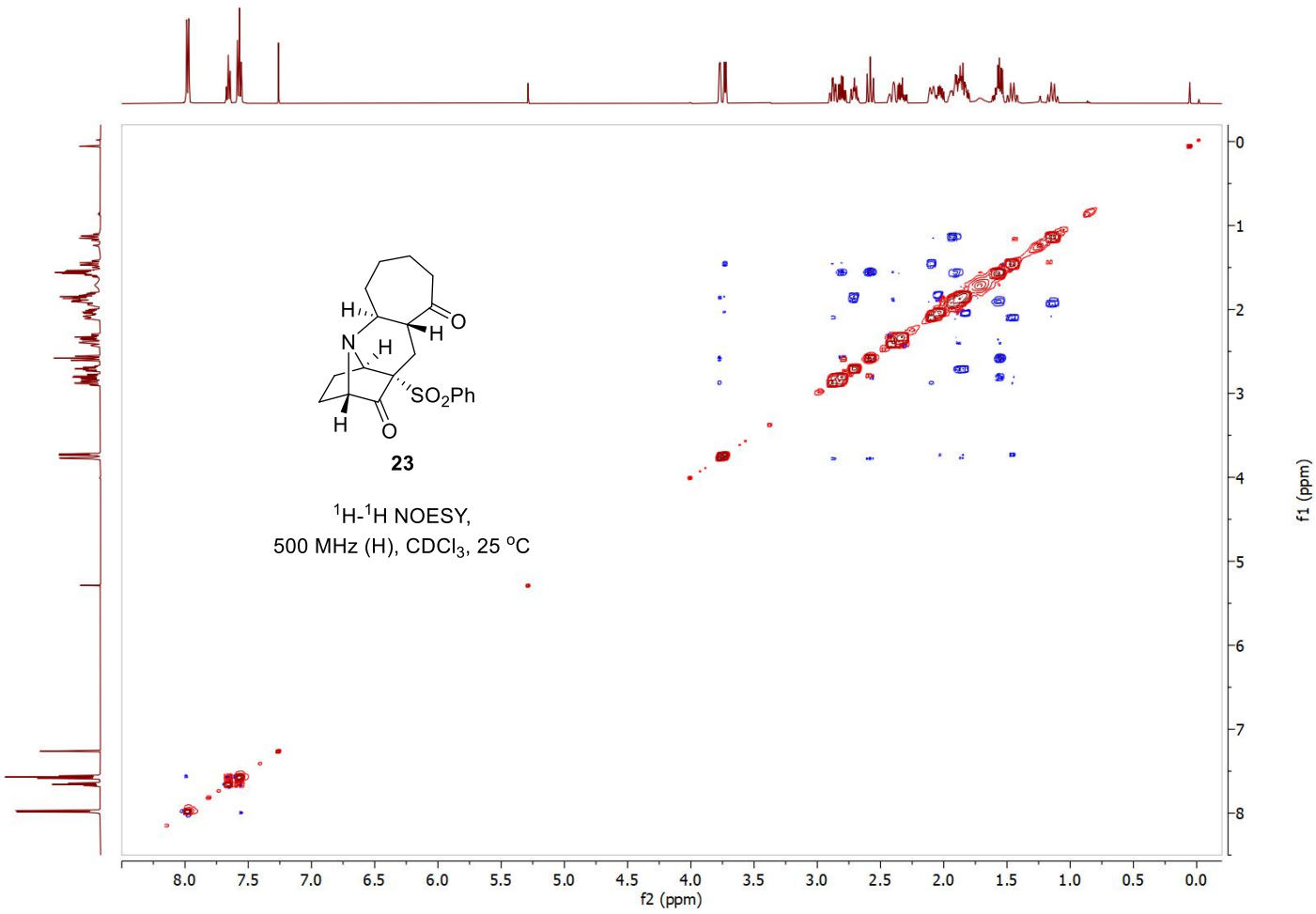
23

^{1}H-^{1}H gCOSY,
500 MHz (H), $CDCl_3$, 25 °C



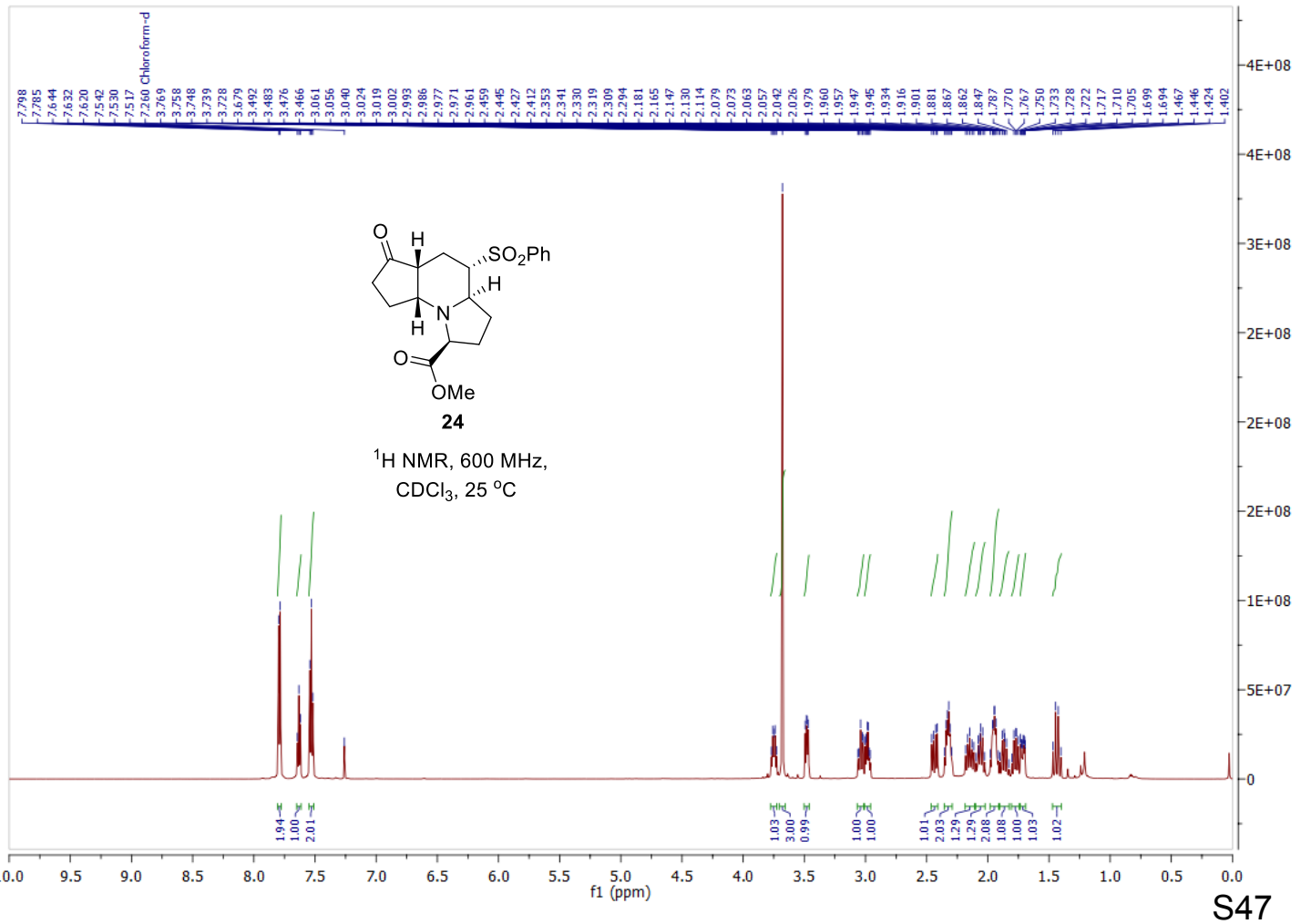
23

^{1}H-^{13}C gHSQC, 500 MHz (H),
126 MHz (C), $CDCl_3$, 25 °C



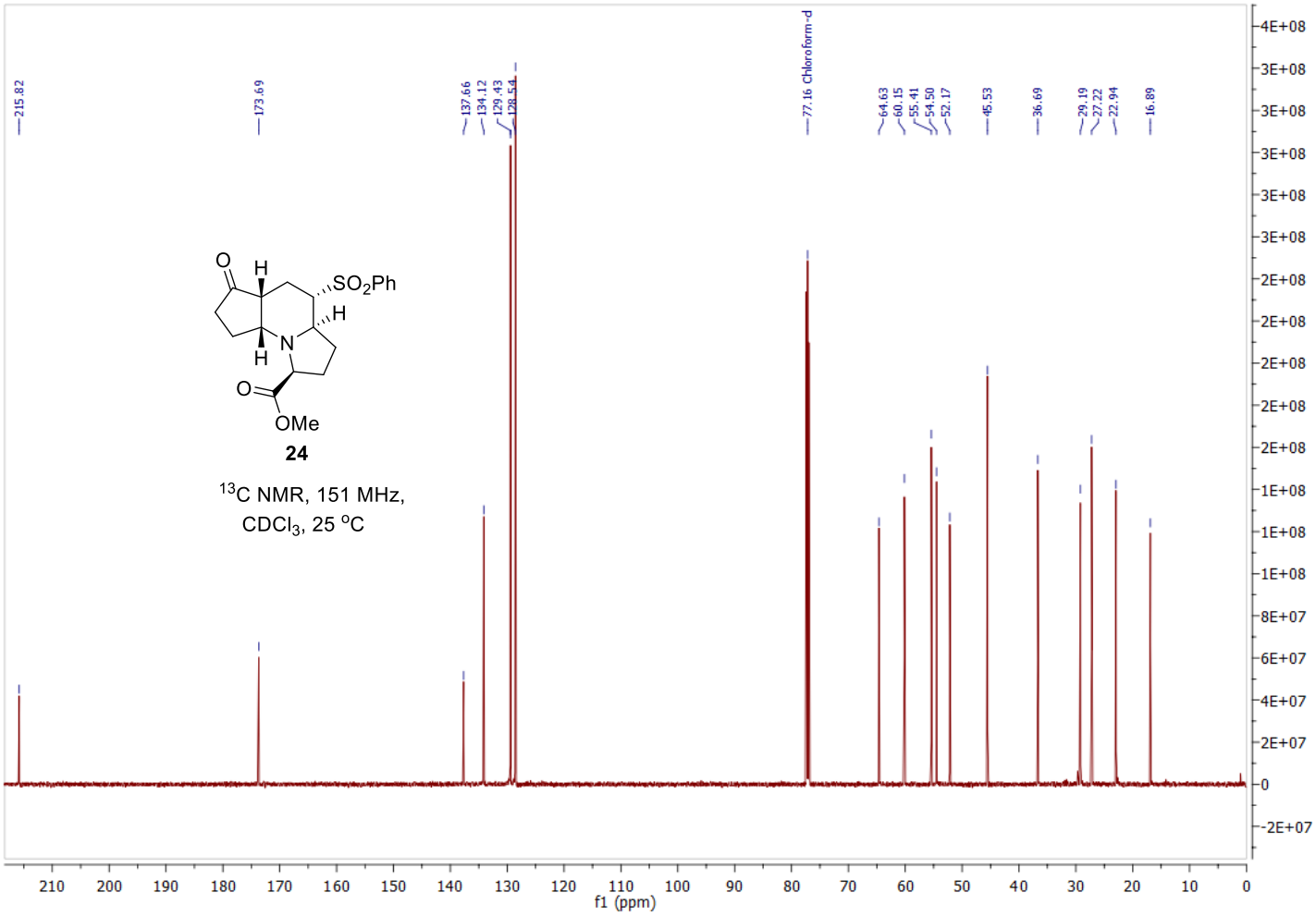
23

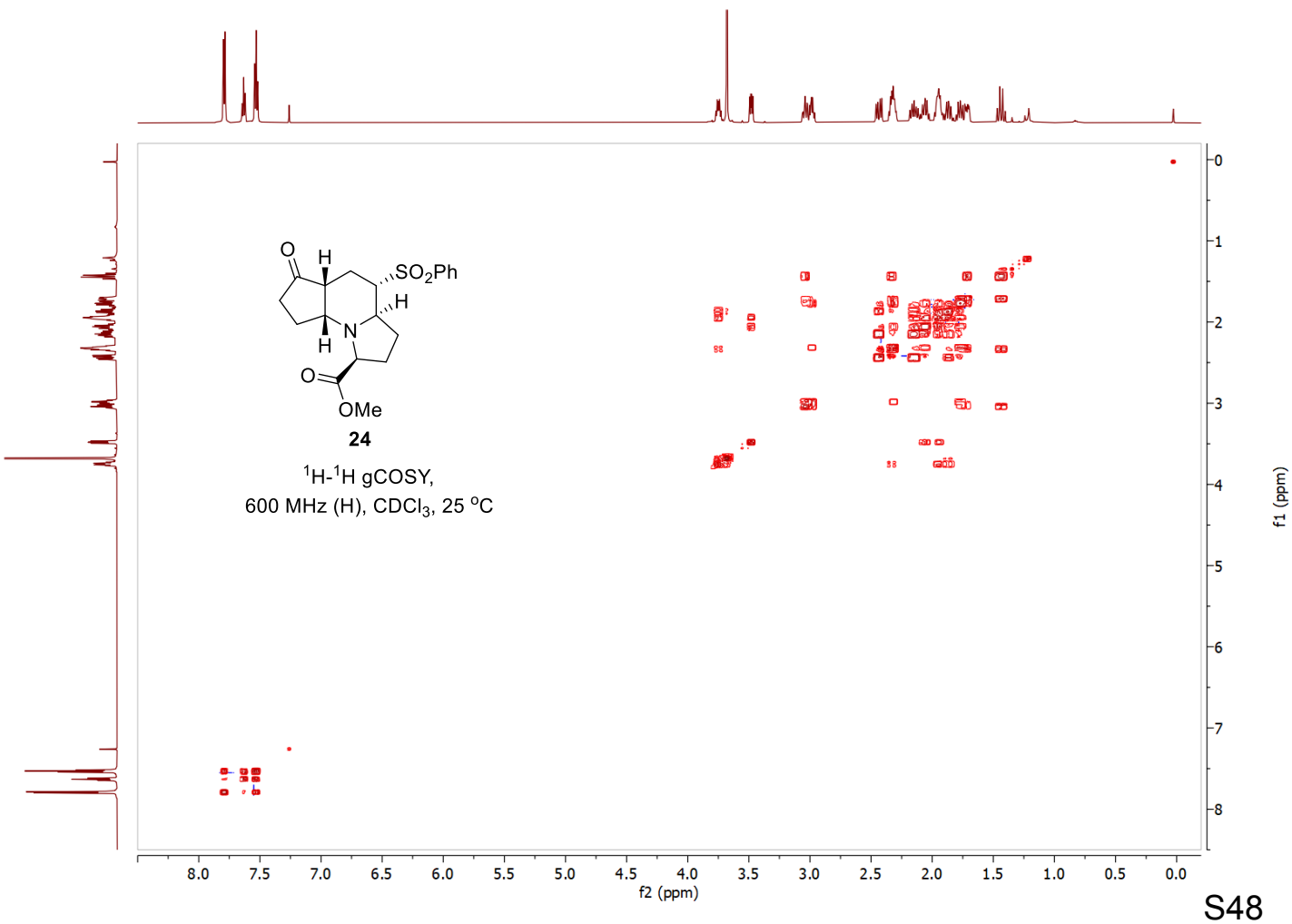
^{1}H-^{1}H NOESY,
500 MHz (H), $CDCl_3$, 25 ^{o}C

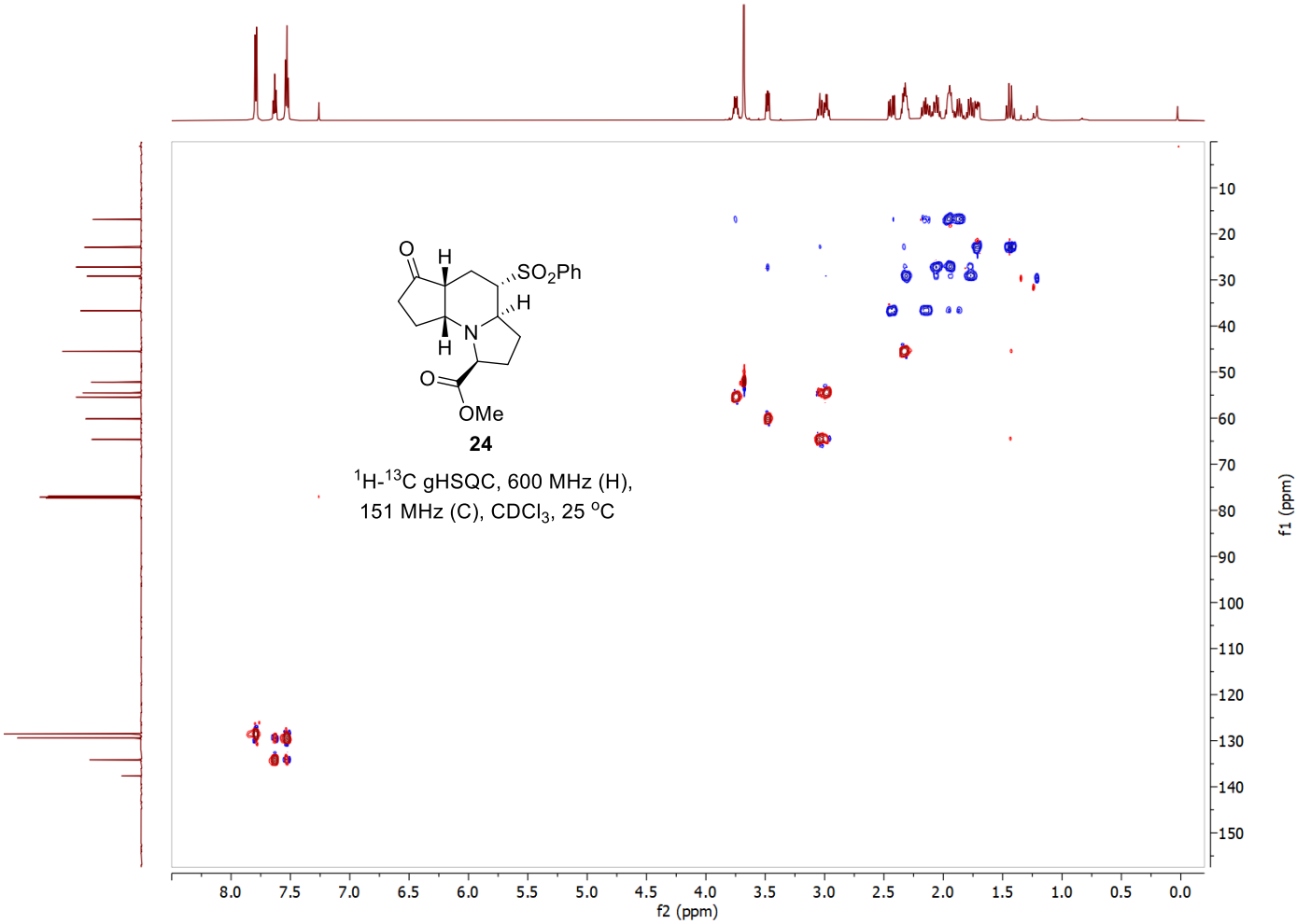


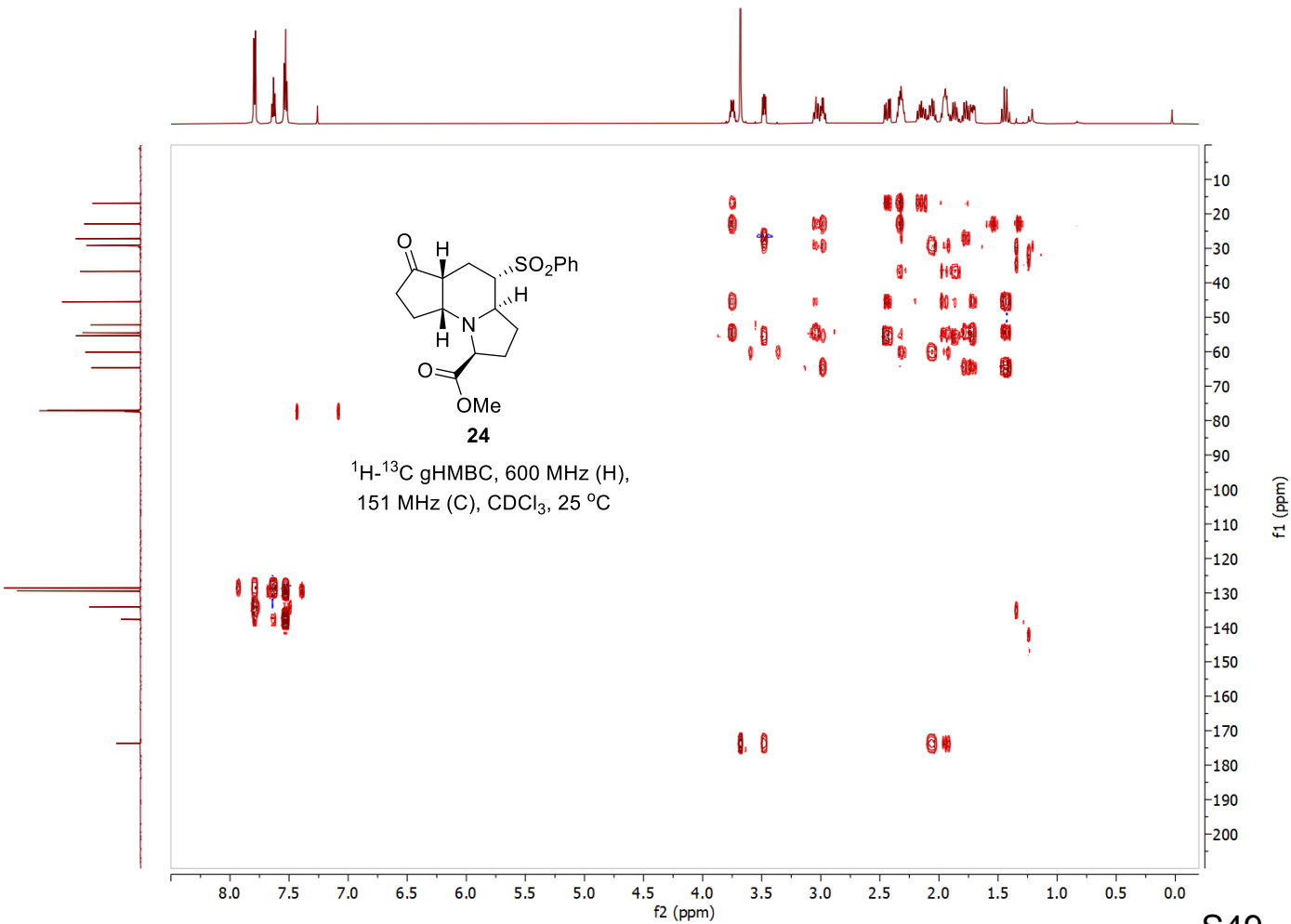
24

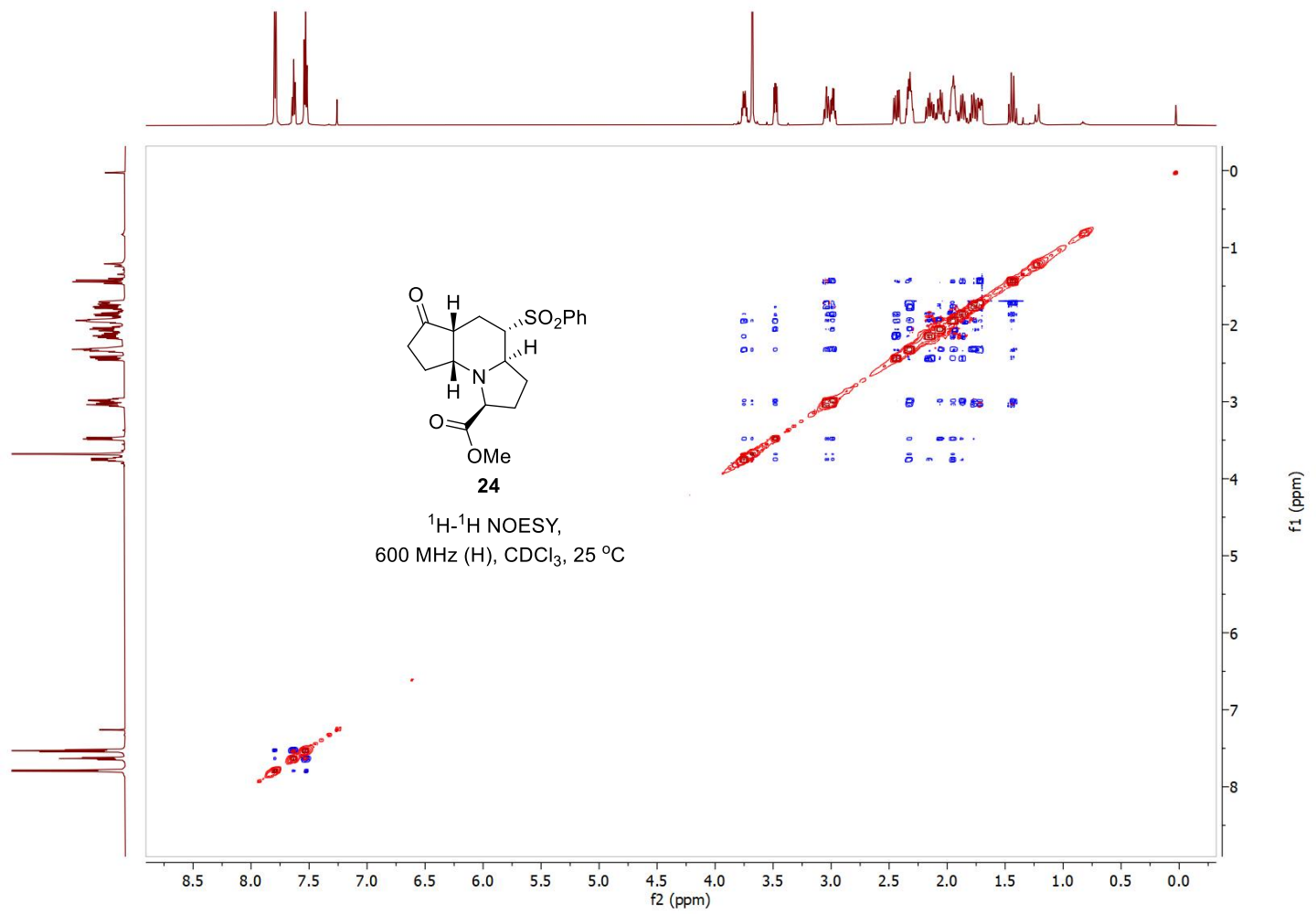
^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^{o}C


215.82
173.69
137.66
134.12
129.43
128.54
77.16 Chloroform-d
64.63
60.15
55.41
54.50
52.17
45.53
36.69
29.19
27.22
22.94
16.89
O
H
SO2Ph
H
N
H
O
OMe
24
13C NMR, 151 MHz,
CDCl3, 25 °C
f1 (ppm)


O
H
SO2Ph
H
N
H
O
OMe
24
1H-1H gCOSY,
600 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)

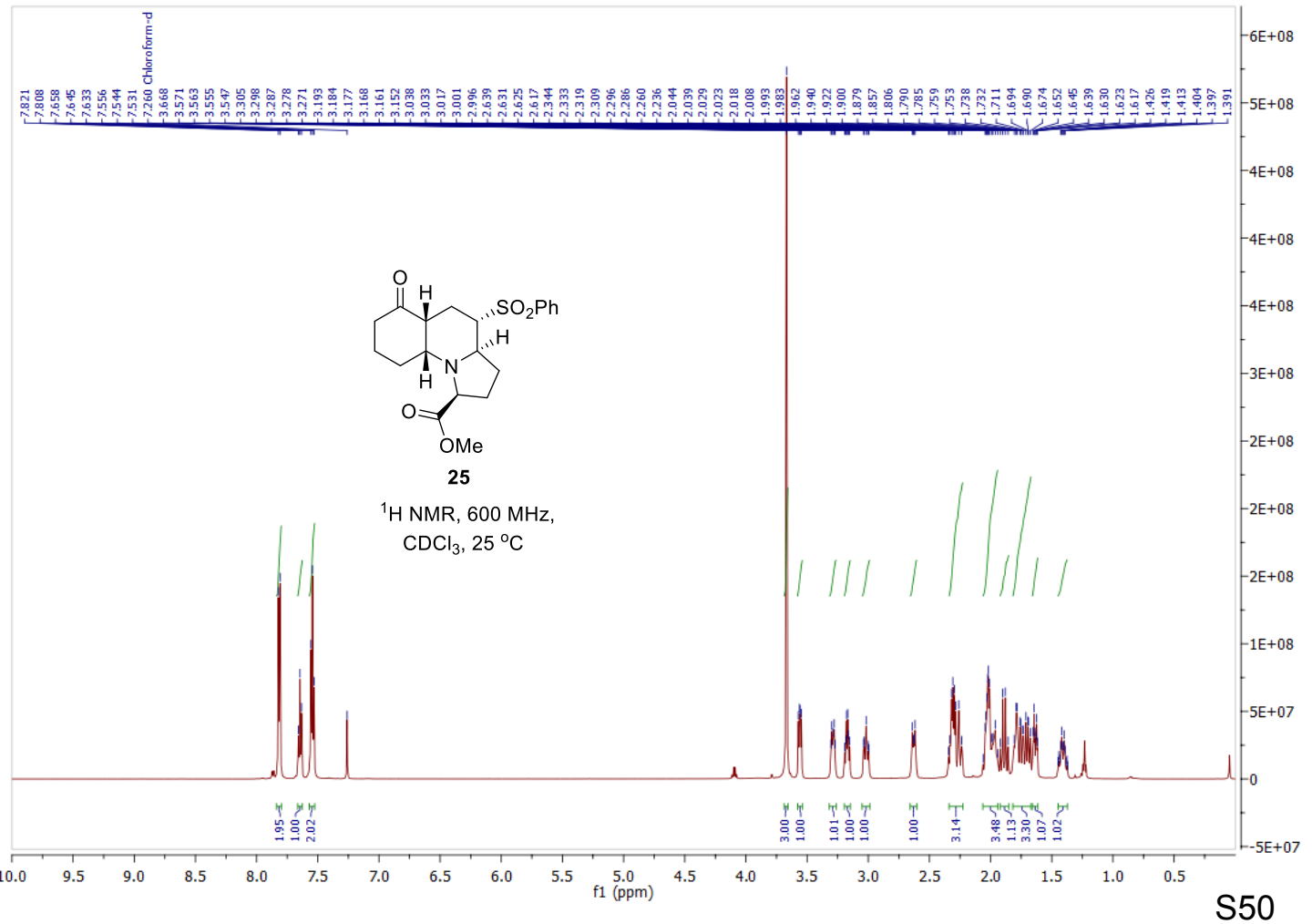

SO2Ph
OMe
24
1H-13C gHSQC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


SO2Ph
OMe
24
1H-13C gHMBC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)



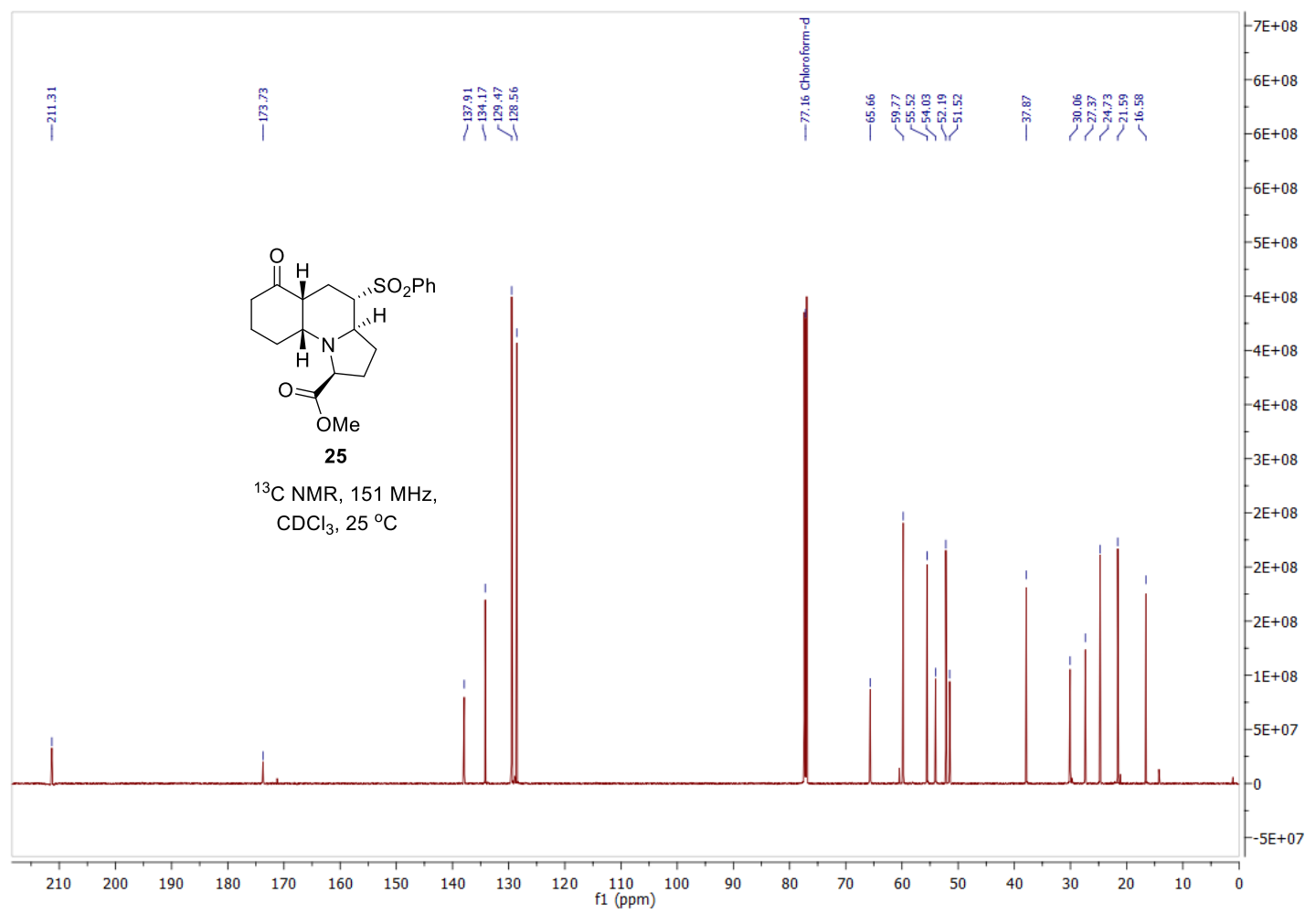
24

^{1}H-^{1}H NOESY,
600 MHz (H), $CDCl_3$, 25 ^{o}C



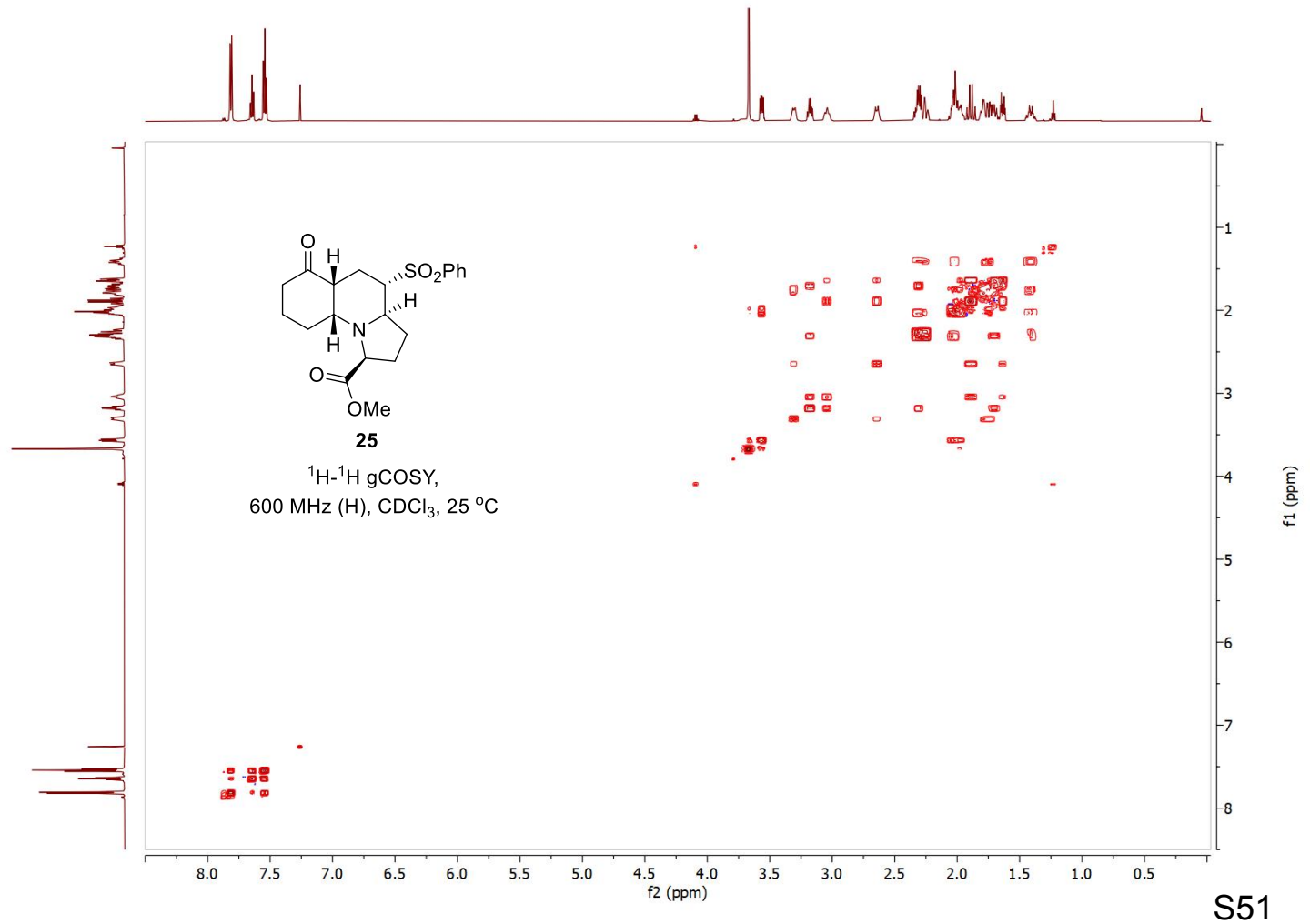
25

^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^{o}C



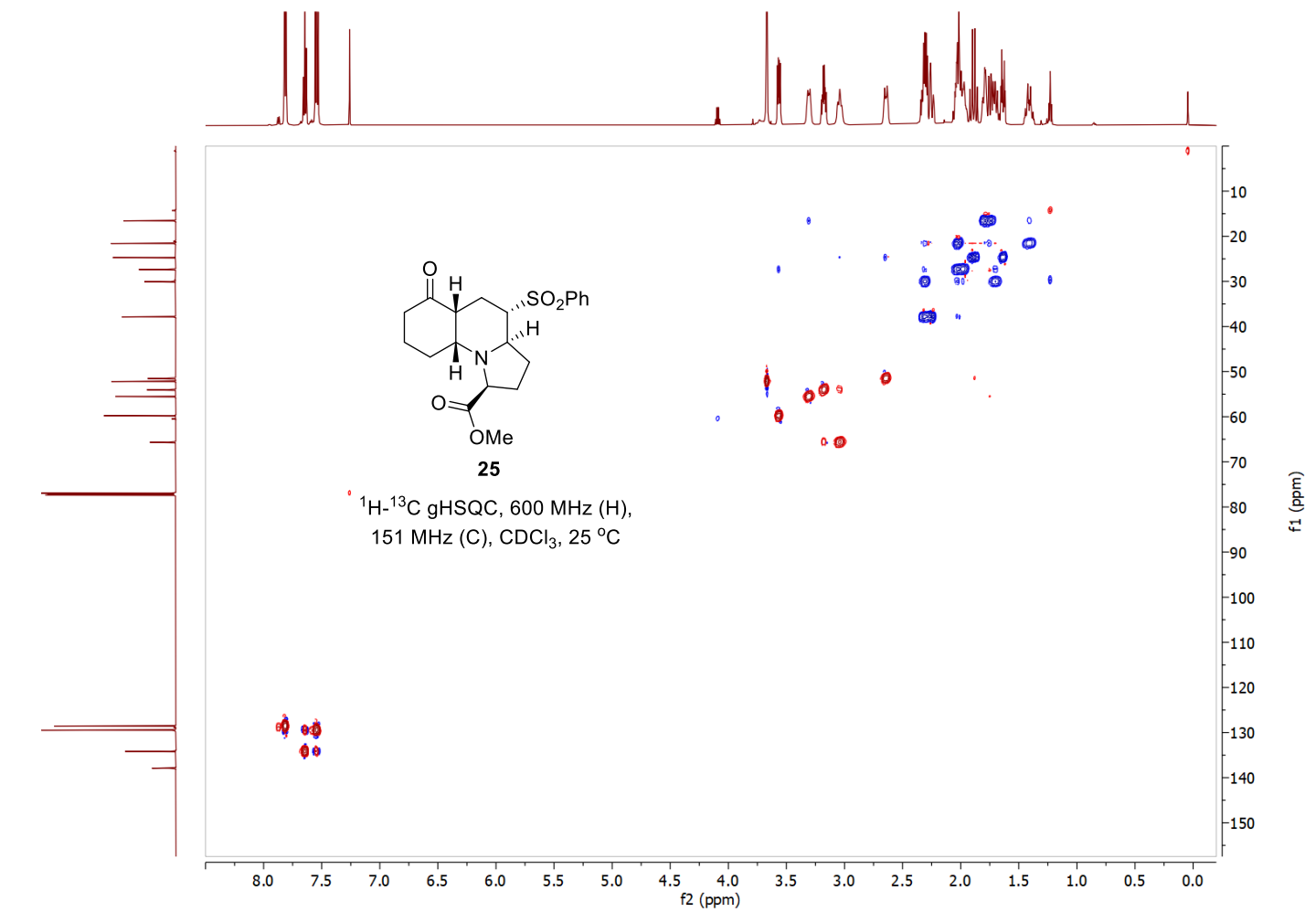
25

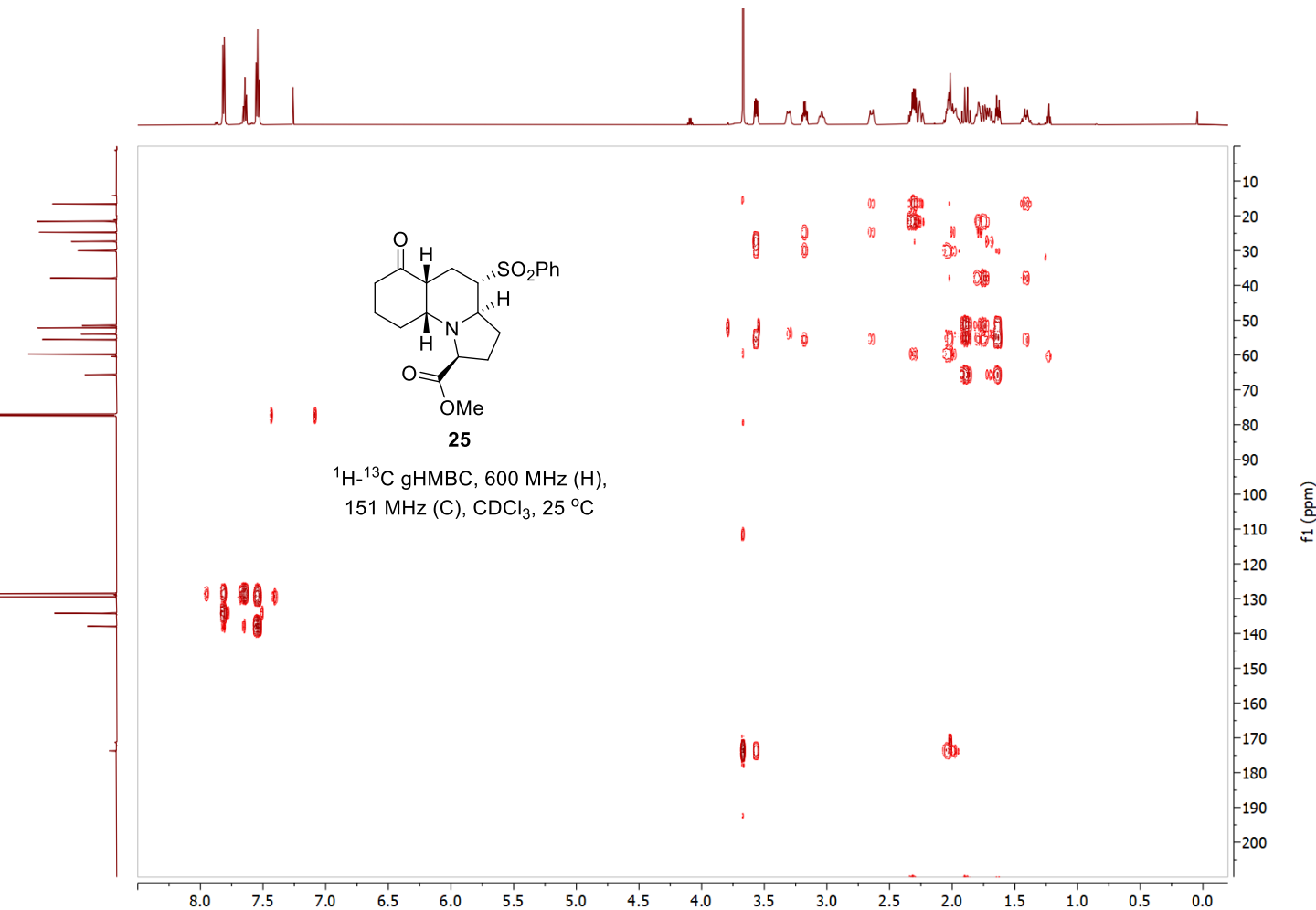
^{13}C NMR, 151 MHz,
$CDCl_3$, 25 °C

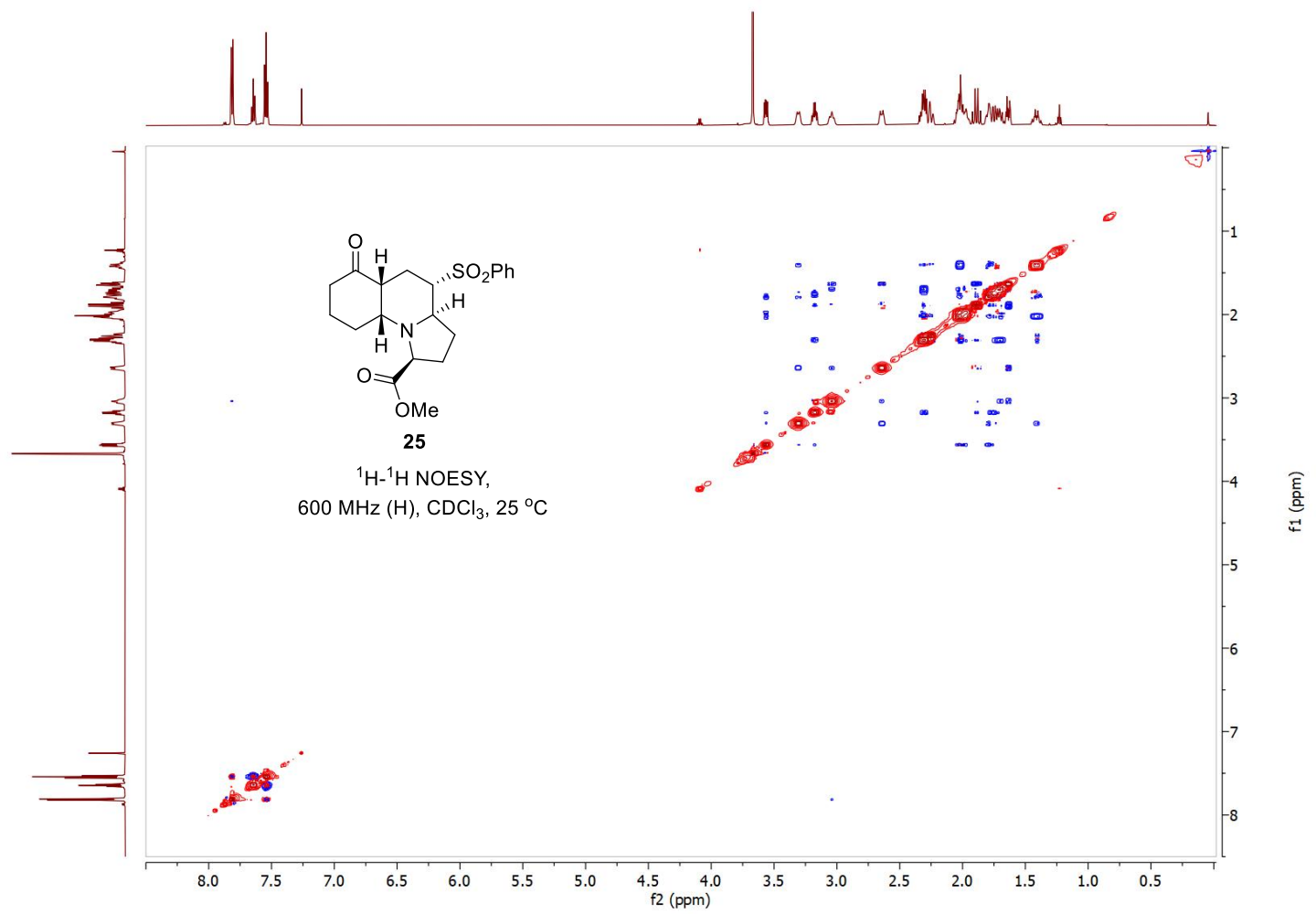


25

^{1}H-^{1}H gCOSY,
600 MHz (H), $CDCl_3$, 25 °C

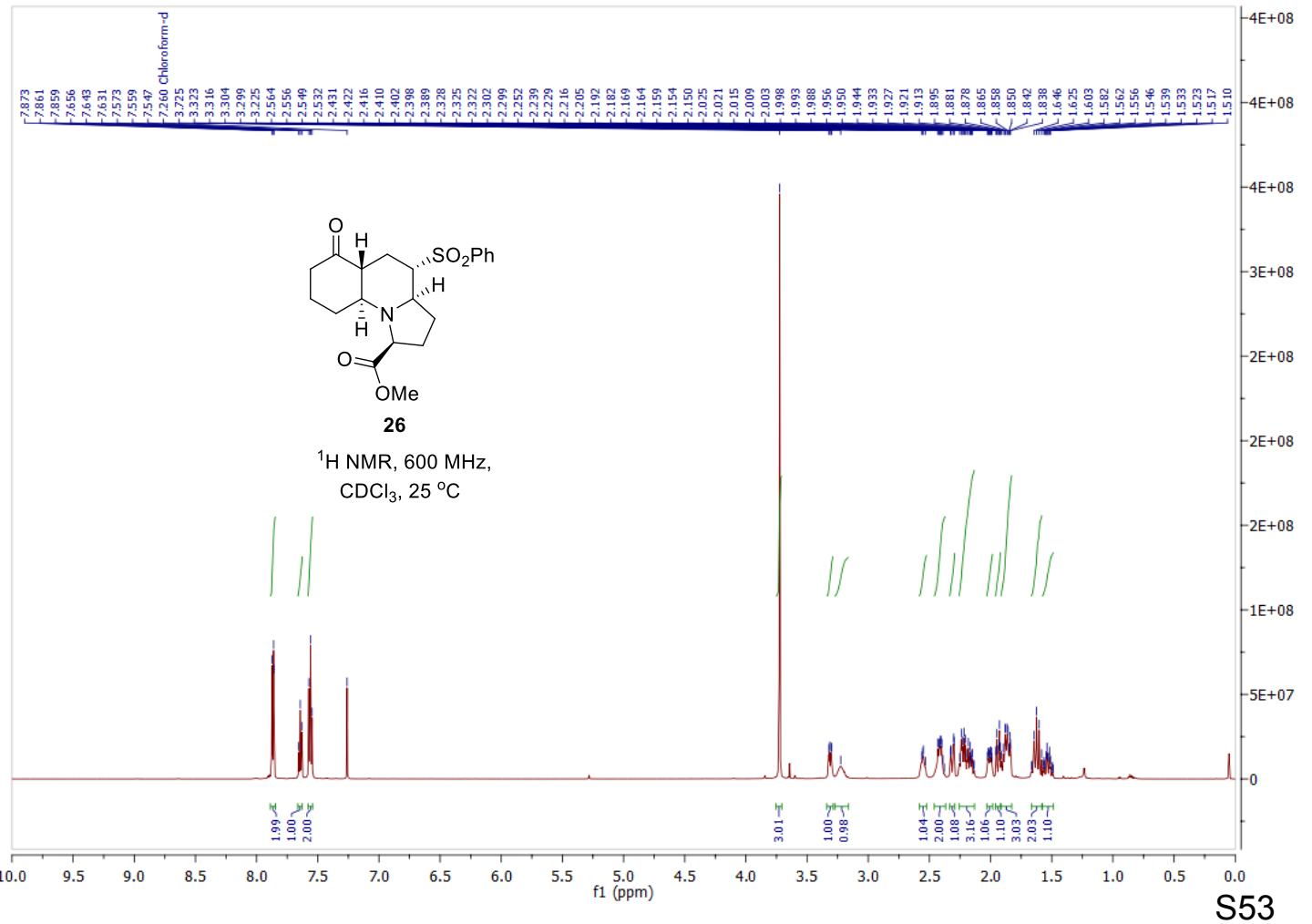

O
H
SO2Ph
H
N
H
O
OMe
25
1H-13C gHSQC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


O
H
SO2Ph
H
N
H
O
OMe
25
1H-13C gHMBC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)



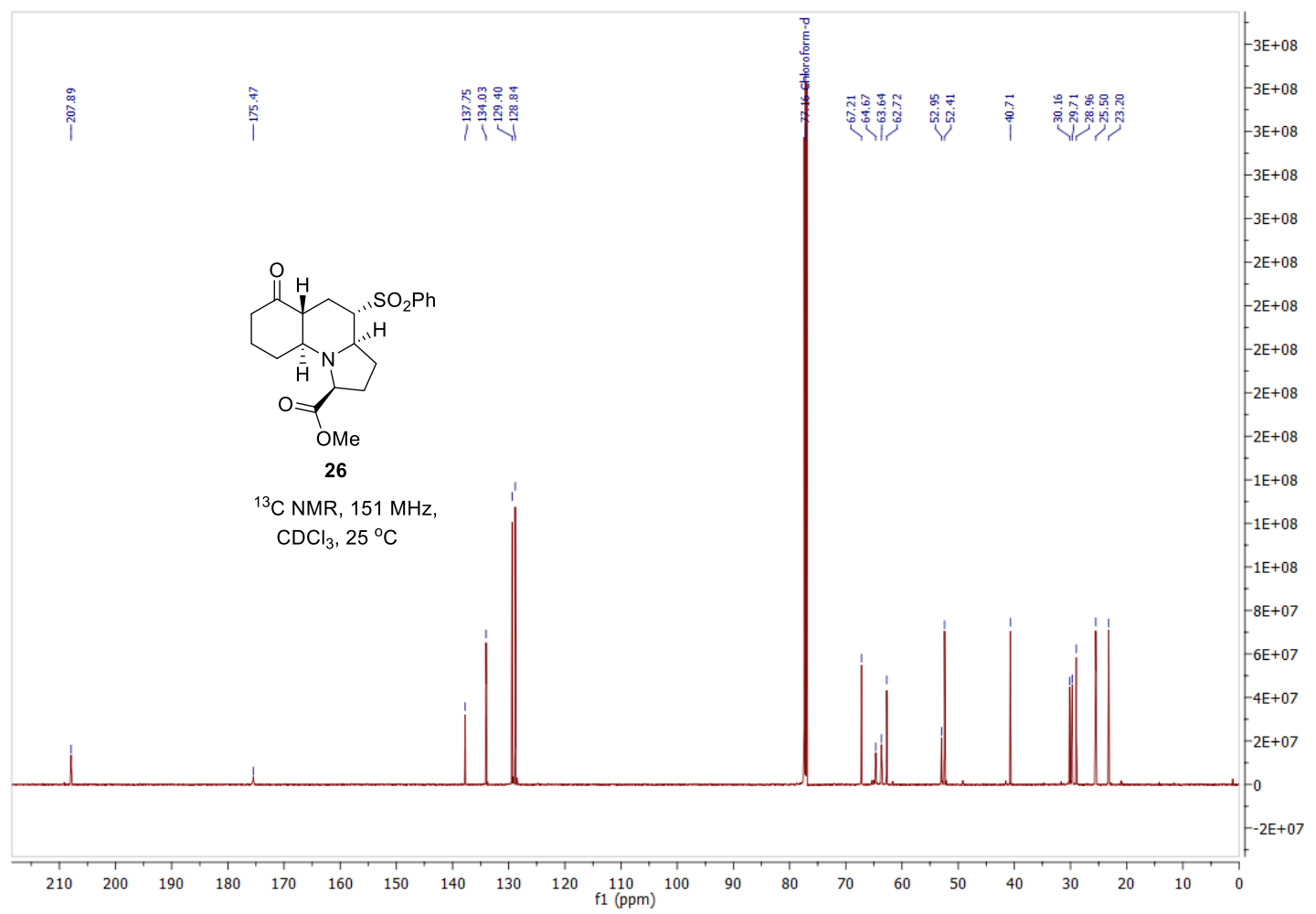
25

^{1}H-^{1}H NOESY,
600 MHz (H), $CDCl_3$, 25 ^{o}C



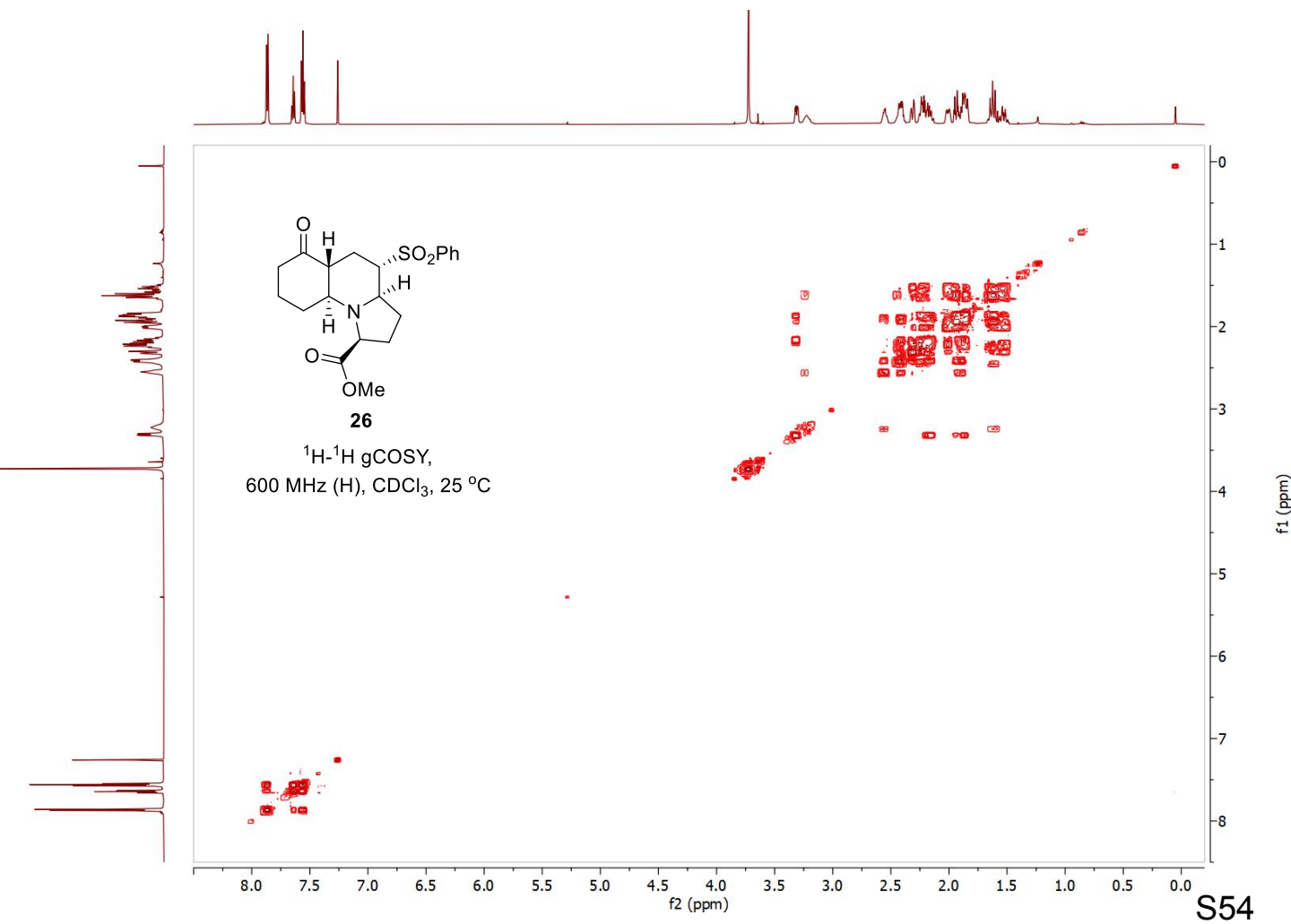
26

^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^{o}C



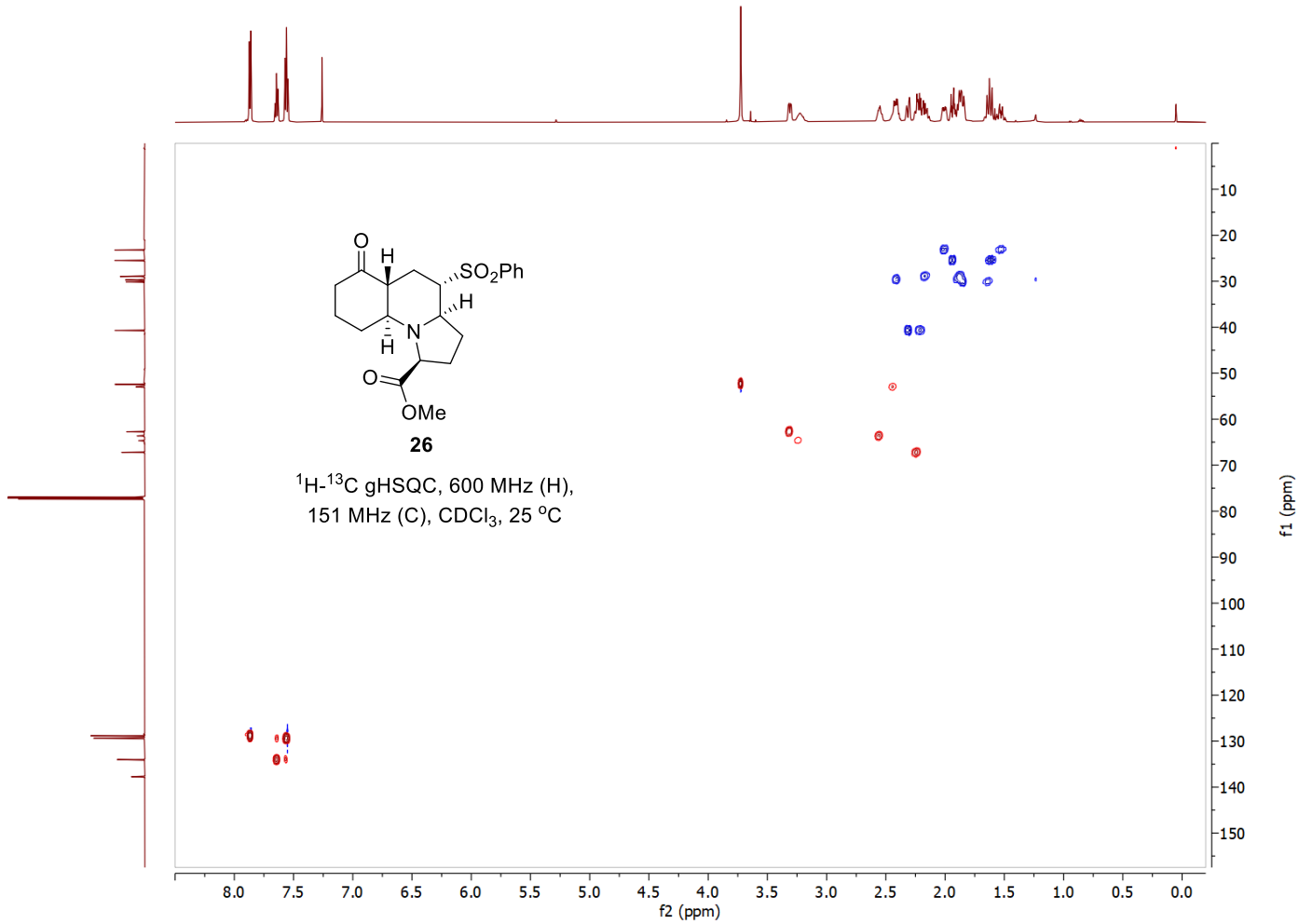
26

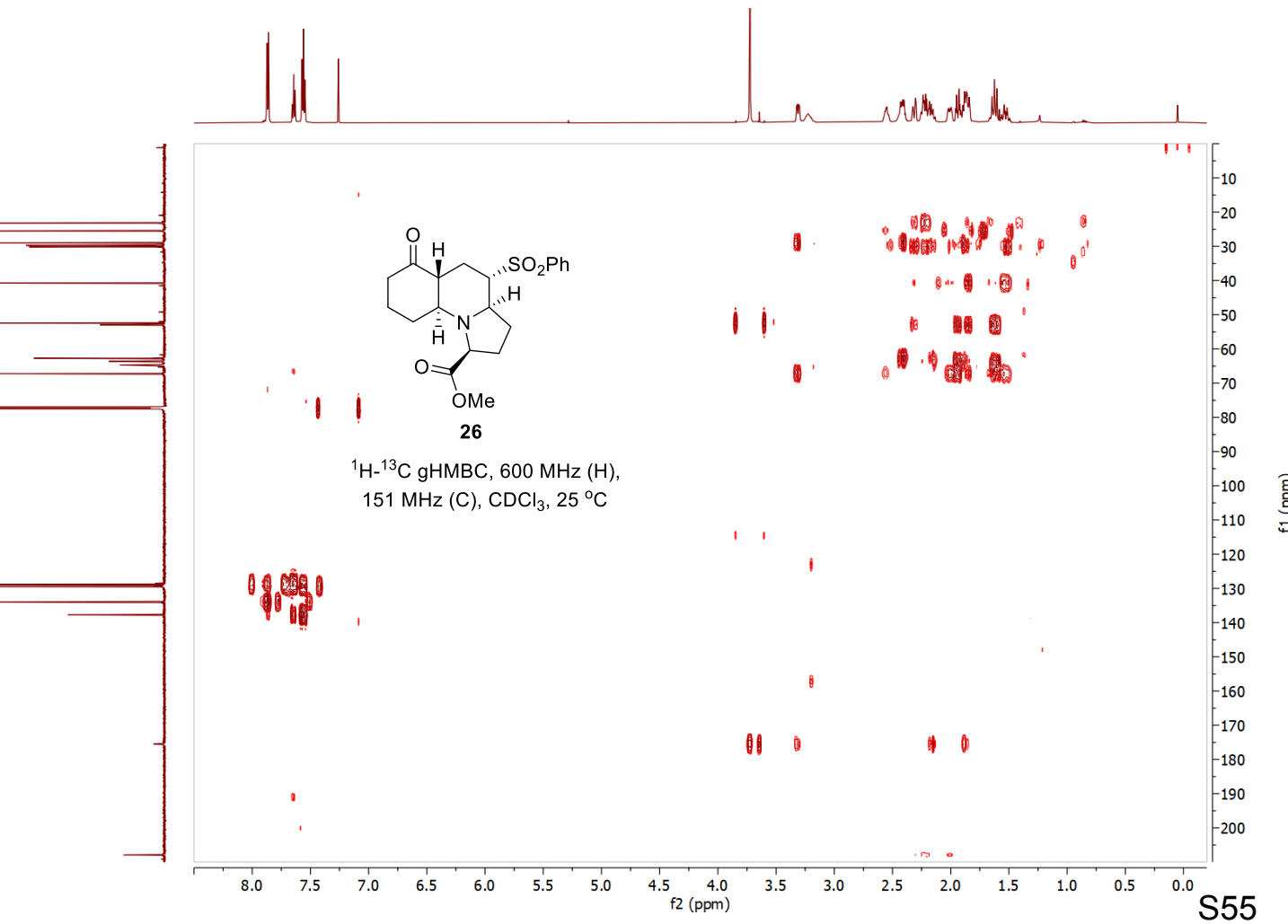
^{13}C NMR, 151 MHz,
$CDCl_3$, 25 °C

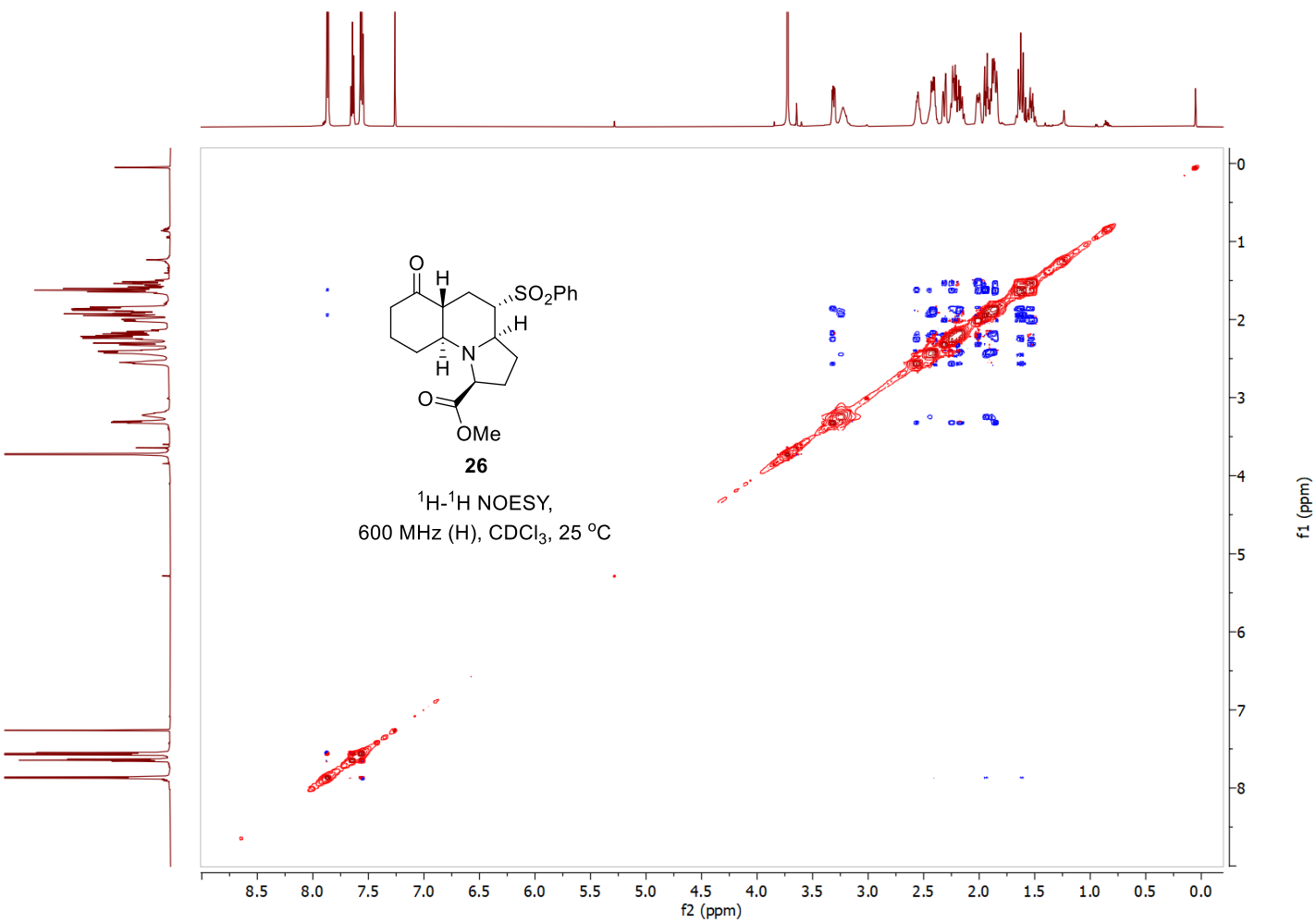


26

^{1}H-^{1}H gCOSY,
600 MHz (H), $CDCl_3$, 25 °C

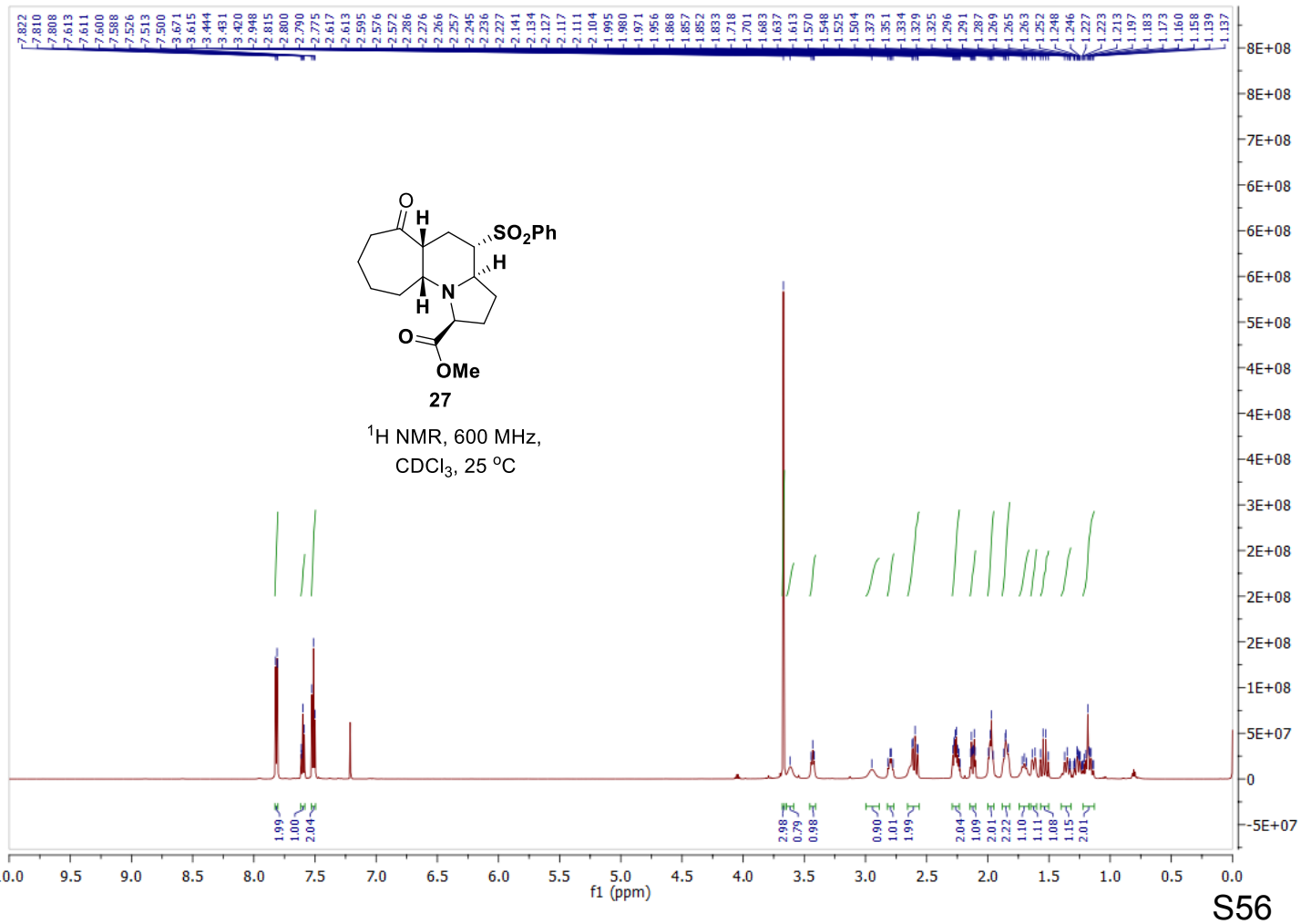

O
H
SO2Ph
H
N
H
O
OMe
26
1H-13C gHSQC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


O
H
SO2Ph
H
N
H
O
OMe
26
1H-13C gHMBC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)



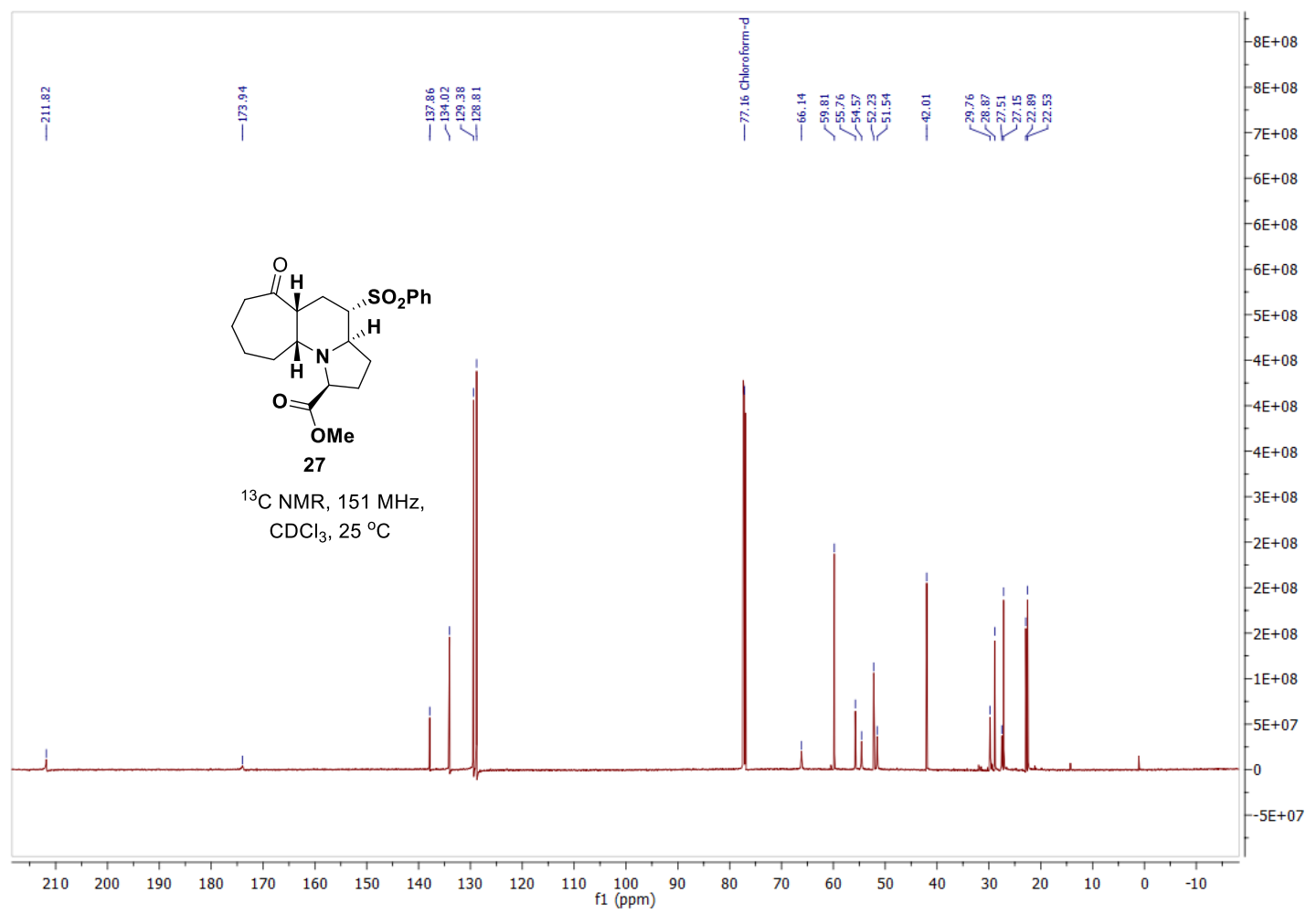
26

^{1}H-^{1}H NOESY,
600 MHz (H), $CDCl_3$, 25 ^{o}C



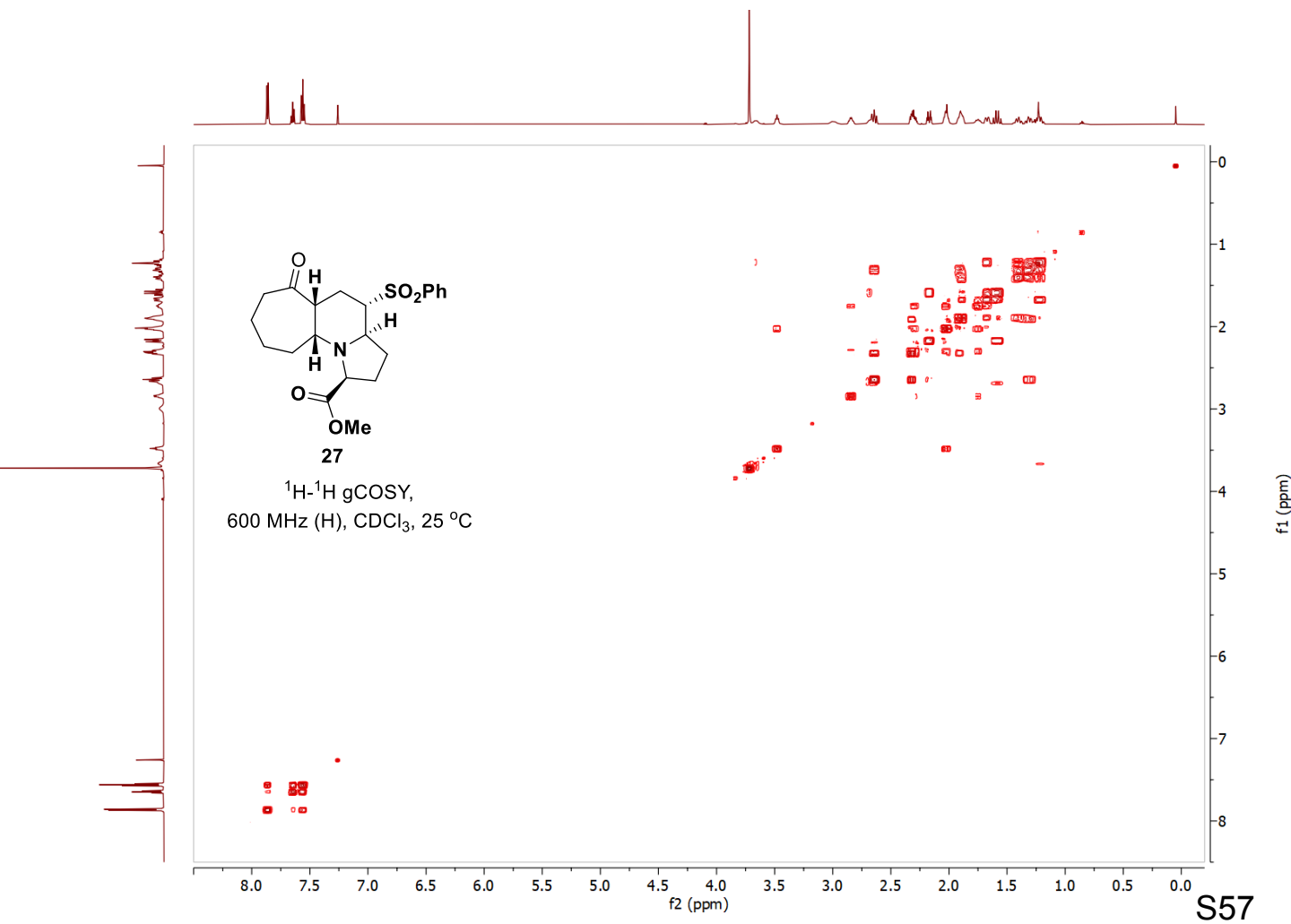
27

^{1}H NMR, 600 MHz,
$CDCl_3$, 25 ^{o}C



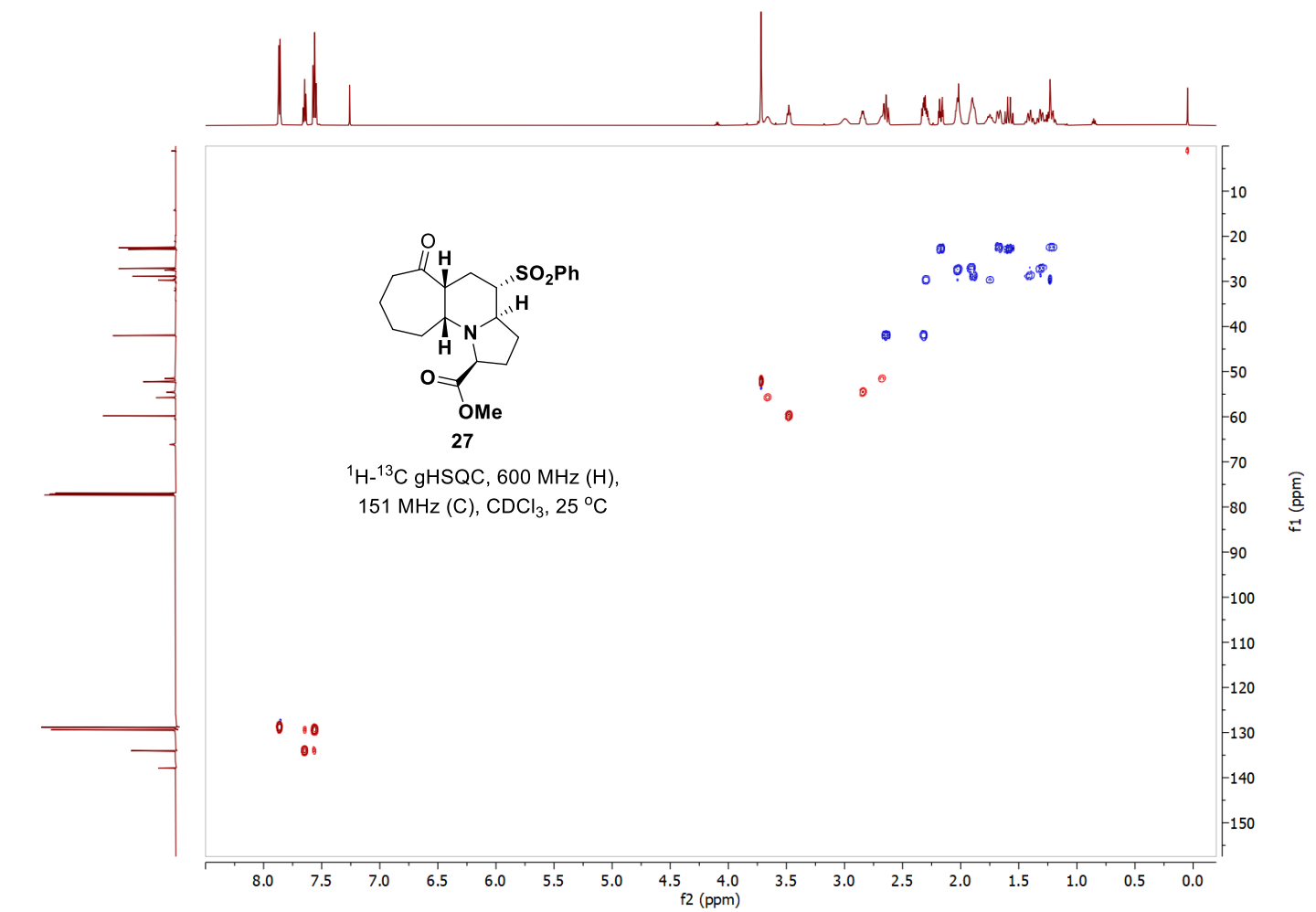
27

^{13}C NMR, 151 MHz,
$CDCl_3$, 25 °C



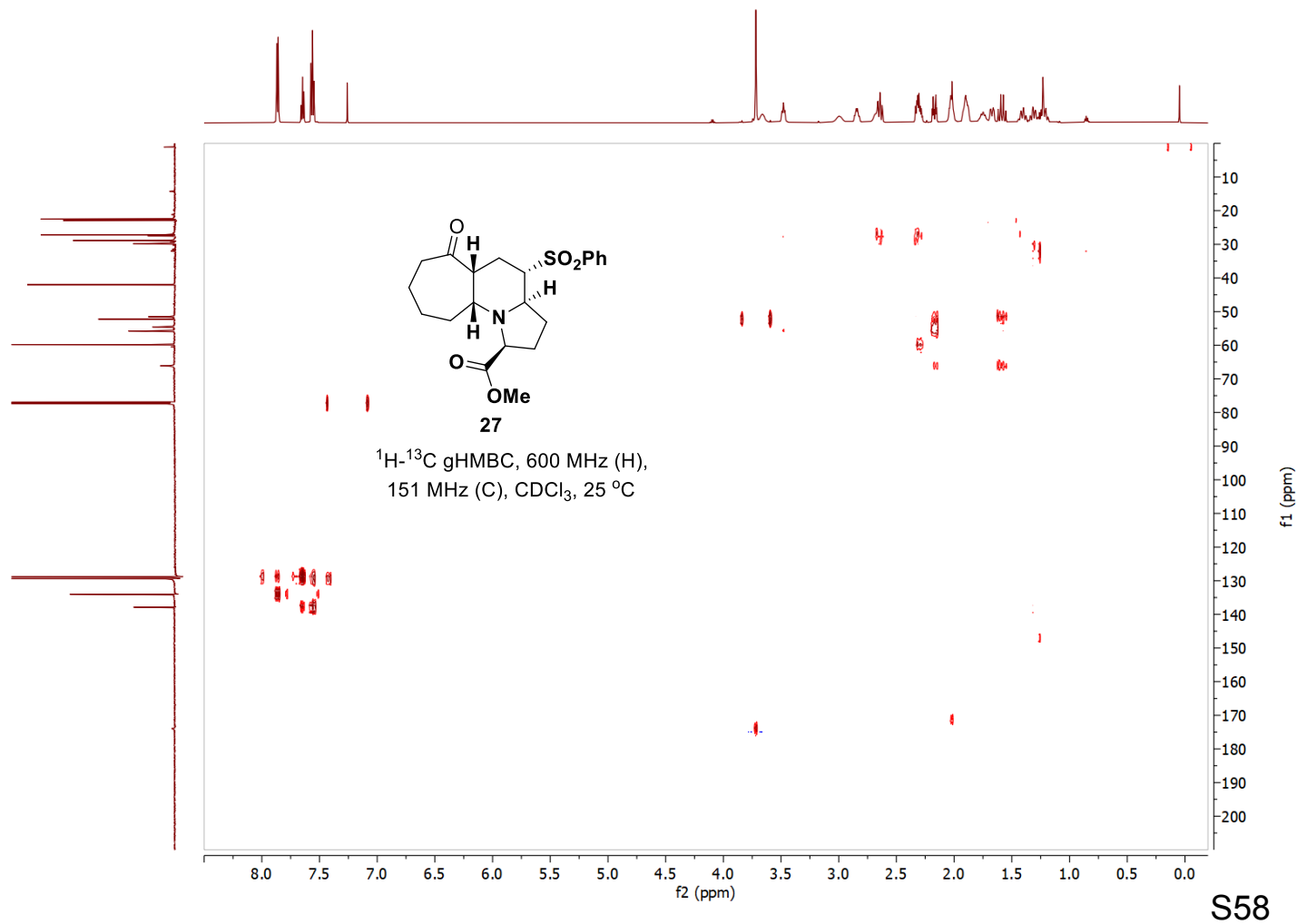
27

^{1}H-^{1}H gCOSY,
600 MHz (H), $CDCl_3$, 25 °C



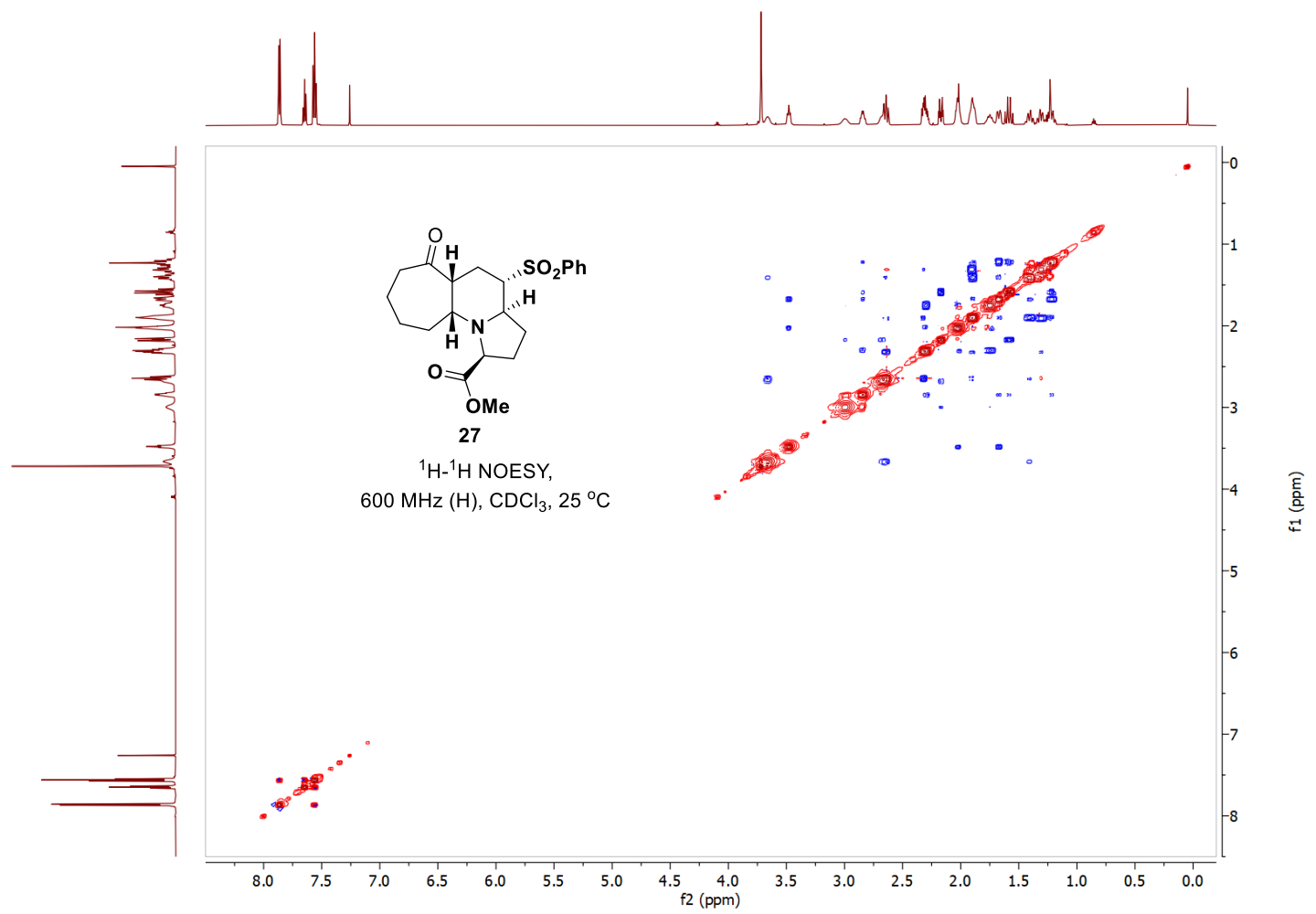
27

^{1}H-^{13}C gHSQC, 600 MHz (H),
151 MHz (C), $CDCl_3$, 25 ^{o}C



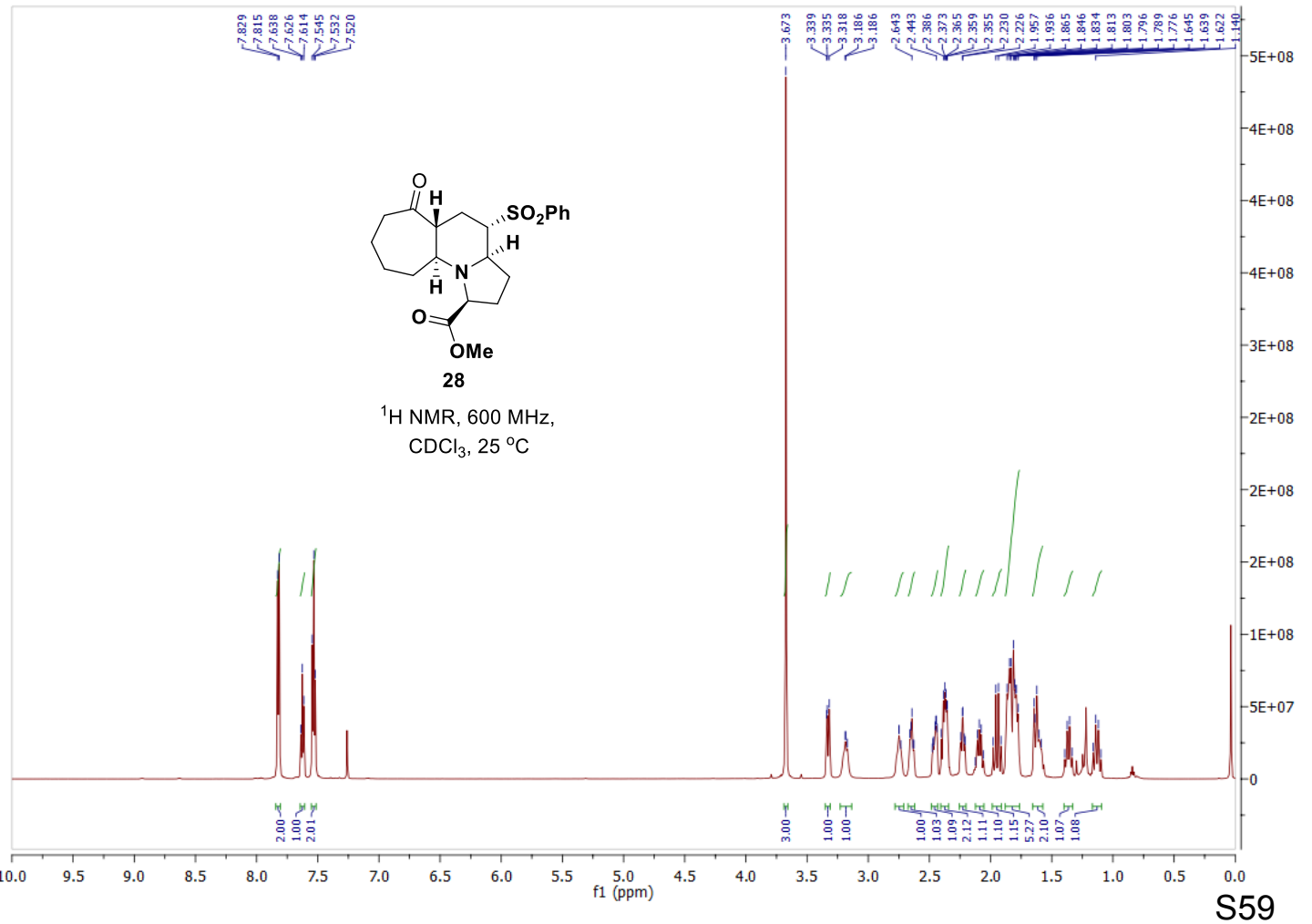
27

^{1}H-^{13}C gHMBC, 600 MHz (H),
151 MHz (C), $CDCl_3$, 25 ^{o}C



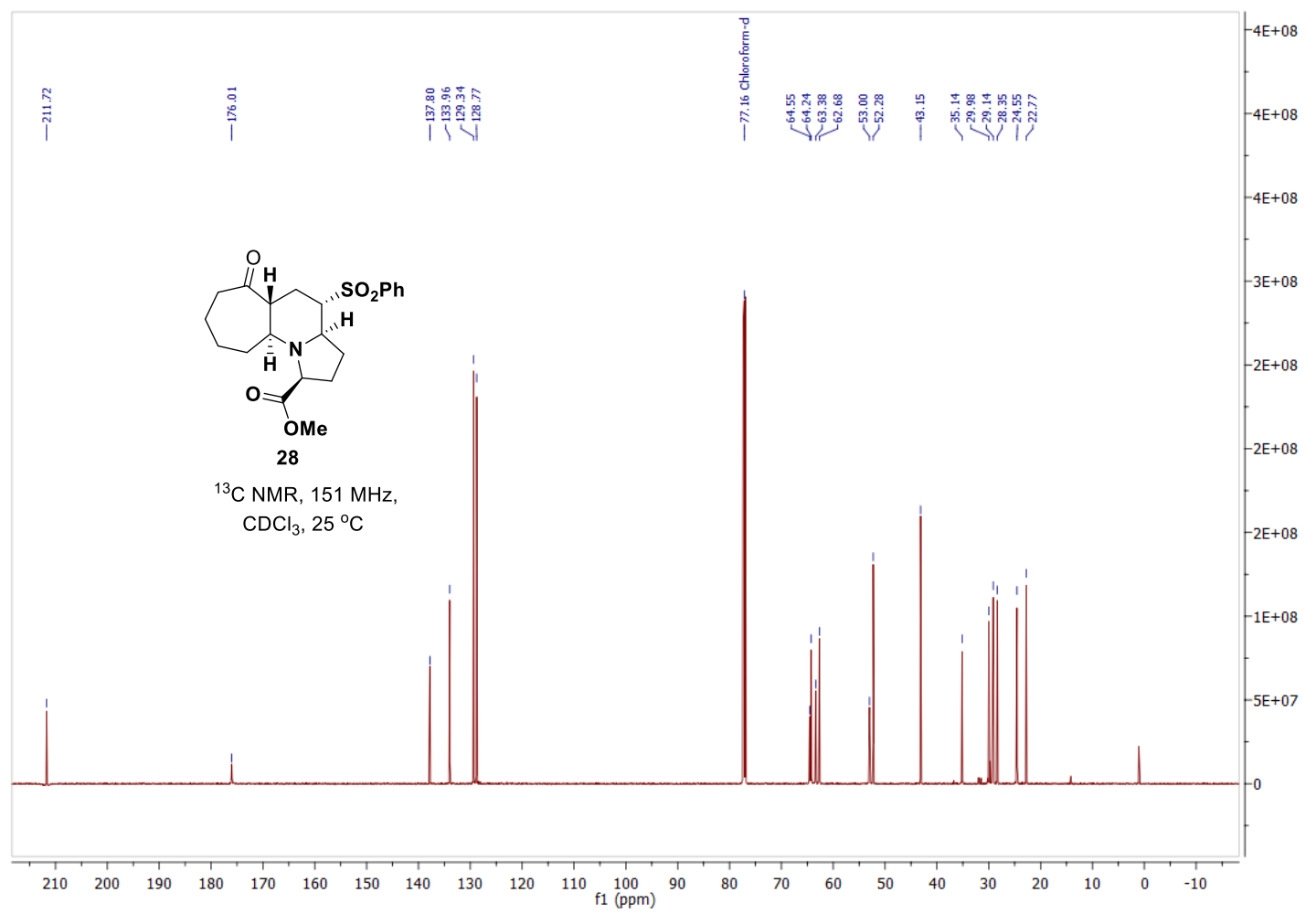
27

^{1}H-^{1}H NOESY,
600 MHz (H), $CDCl_3$, 25 °C



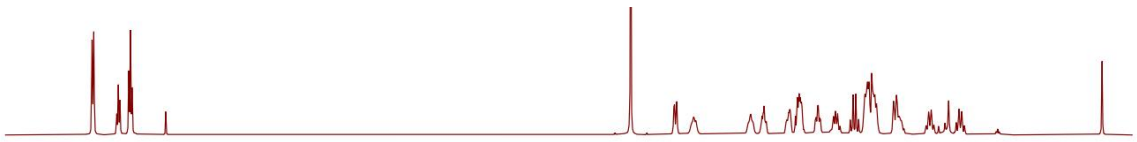
28

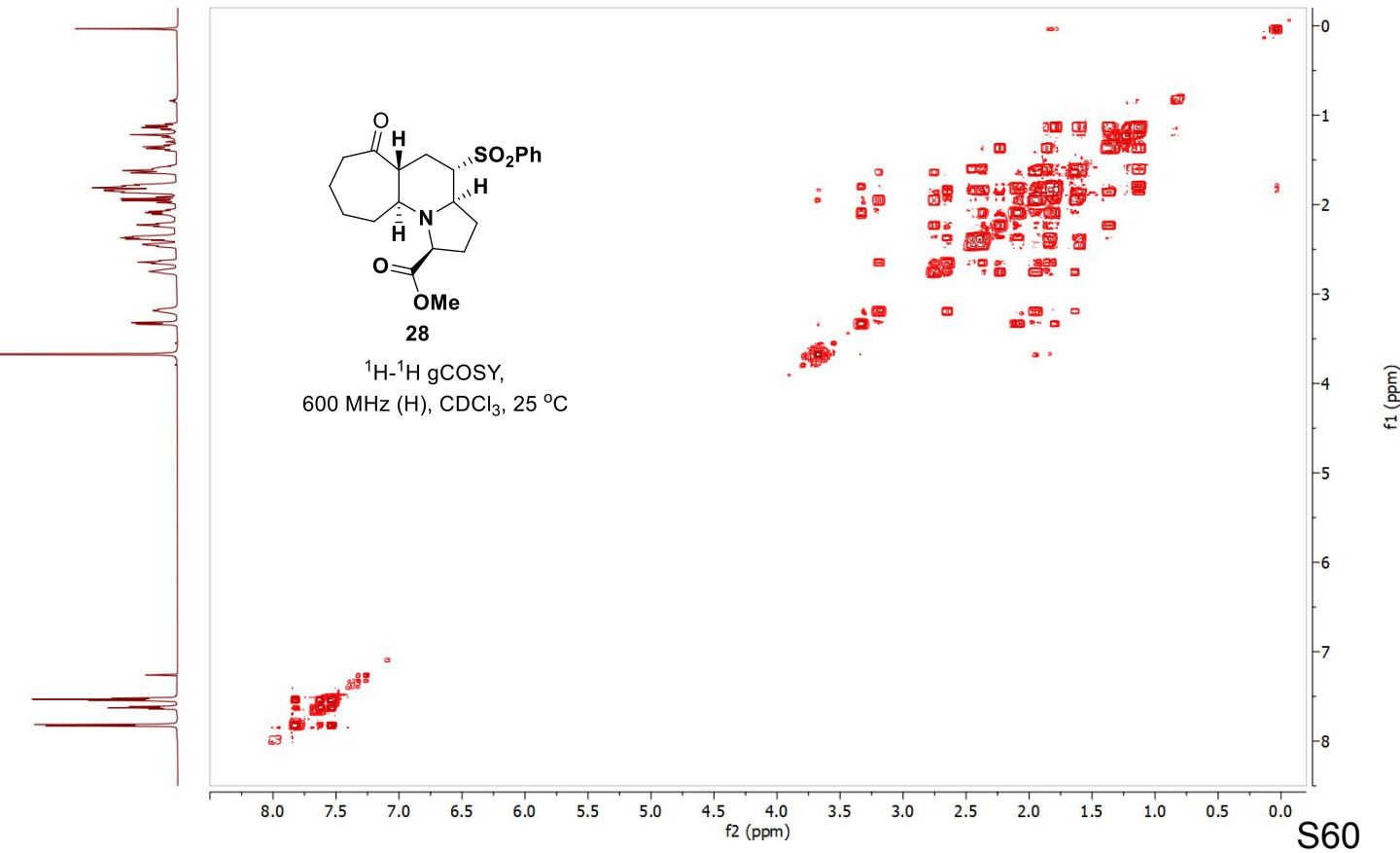
^{1}H NMR, 600 MHz,
$CDCl_3$, 25 °C



28

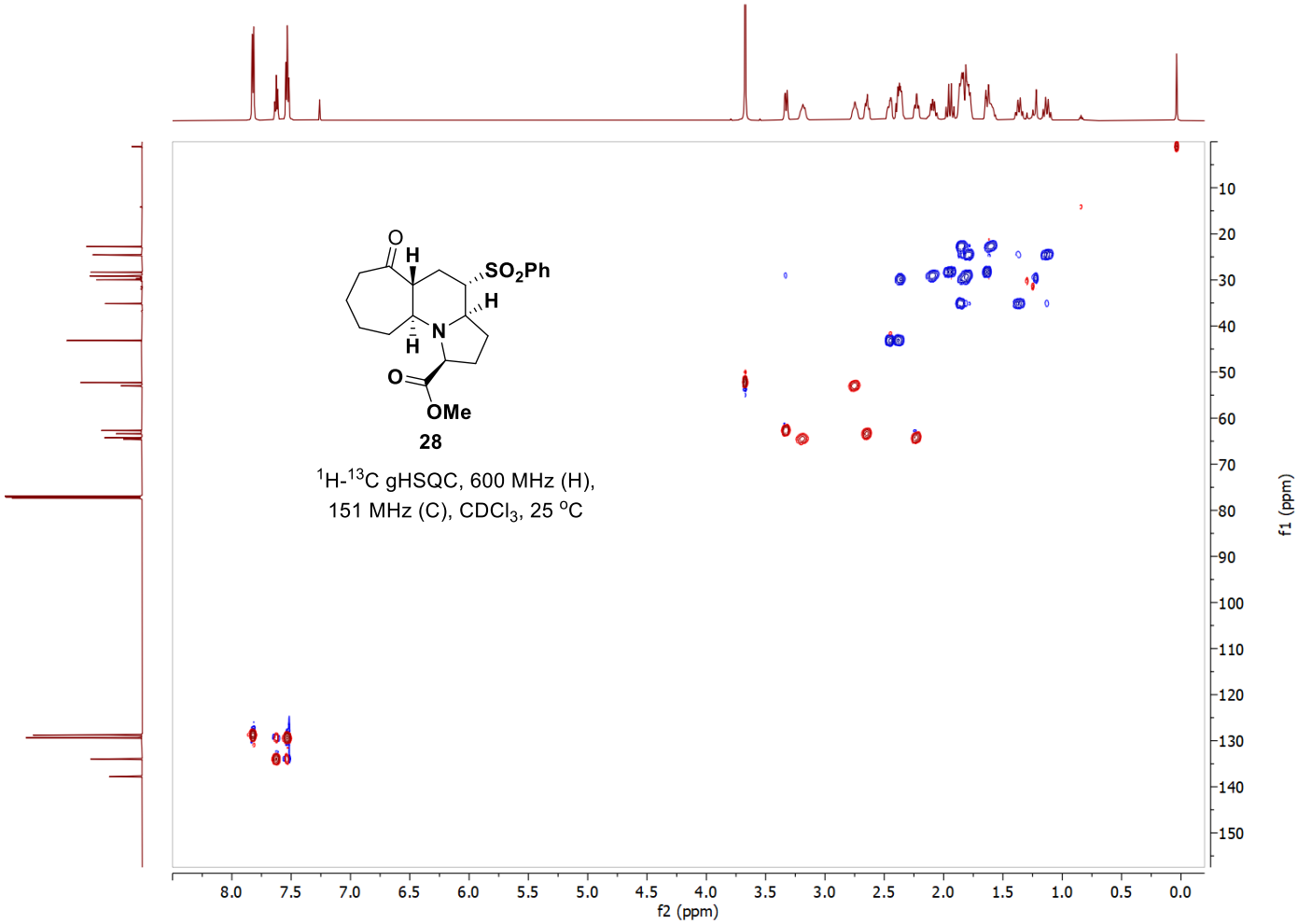
^{13}C NMR, 151 MHz,
$CDCl_3$, 25 °C

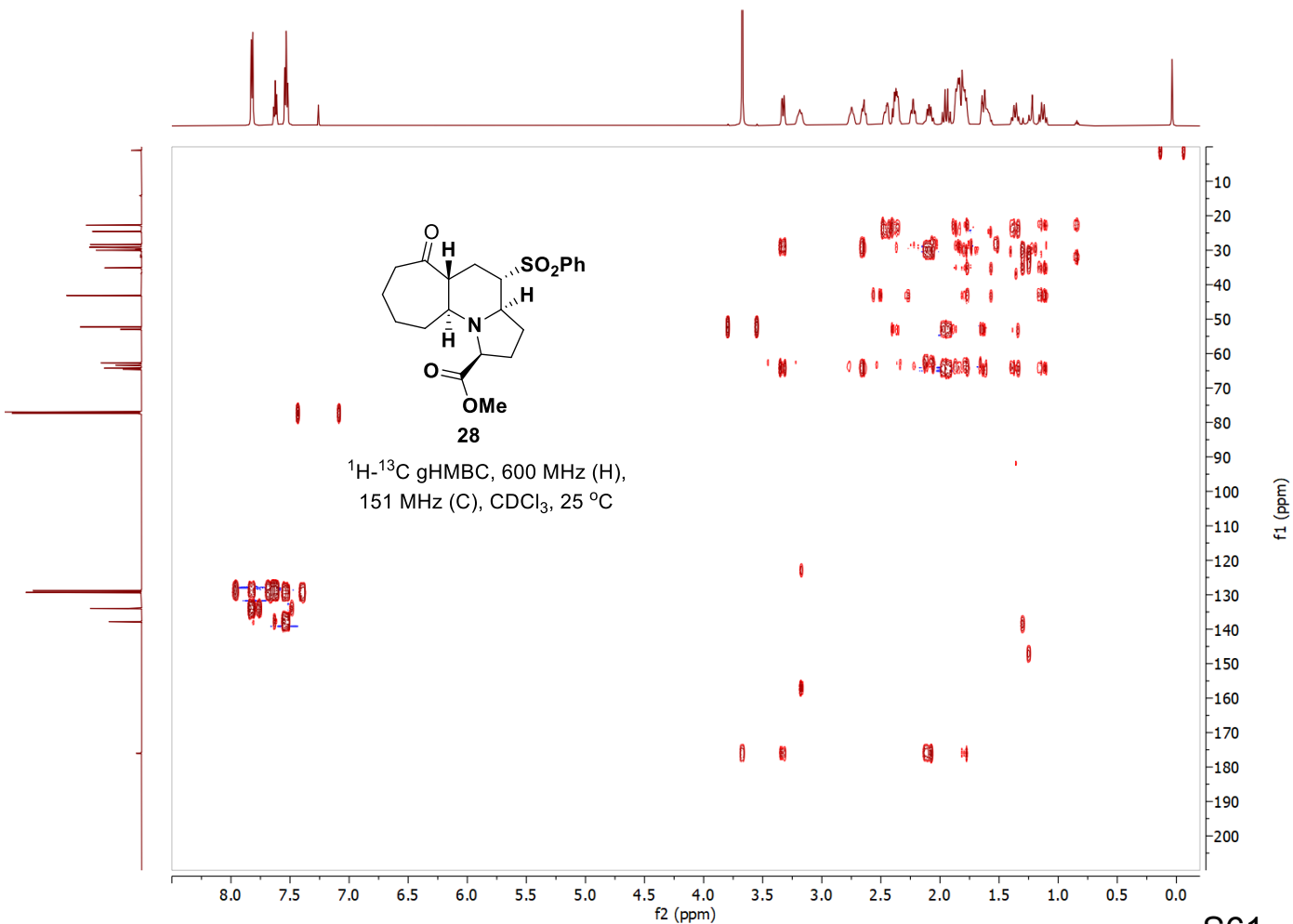


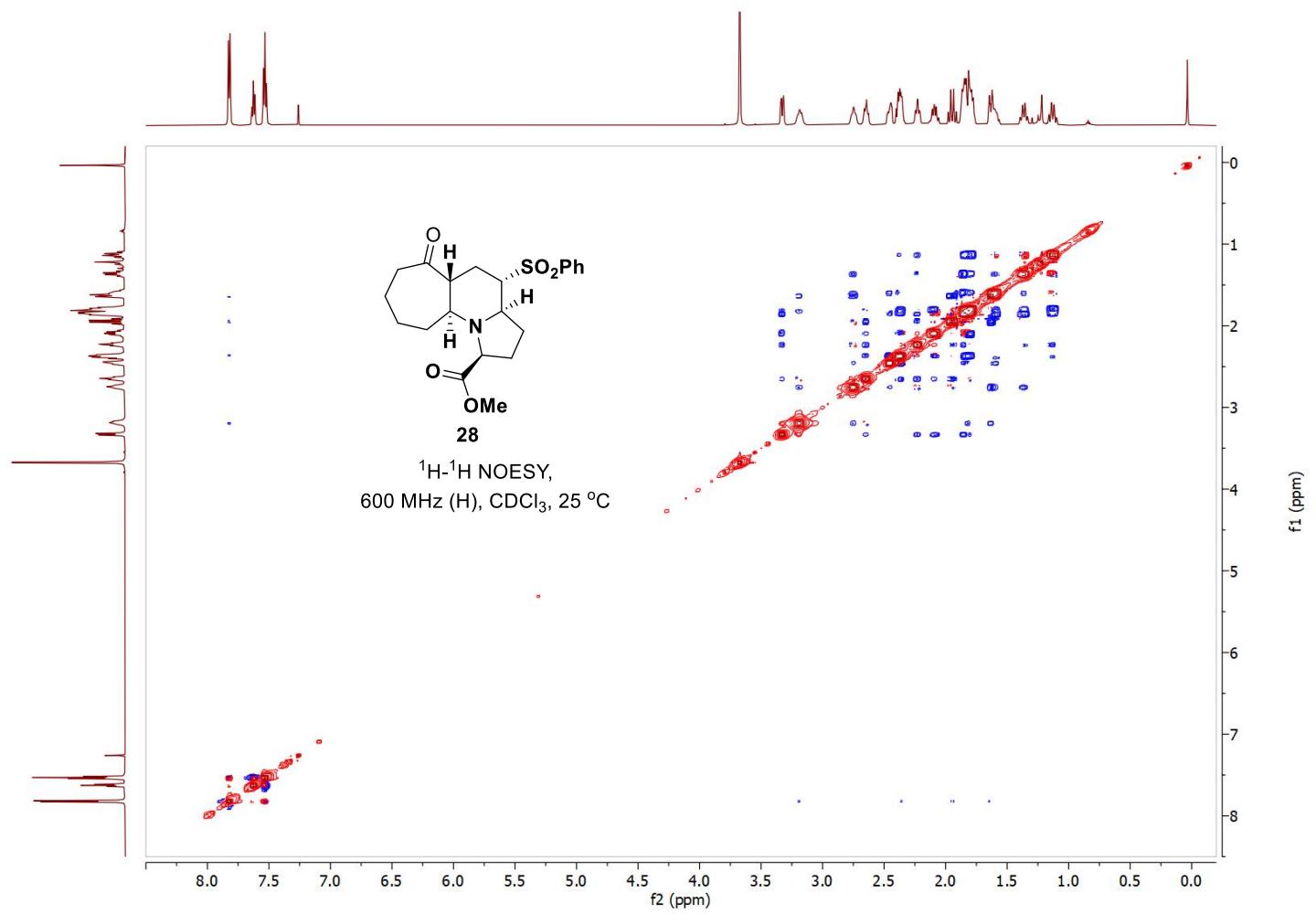


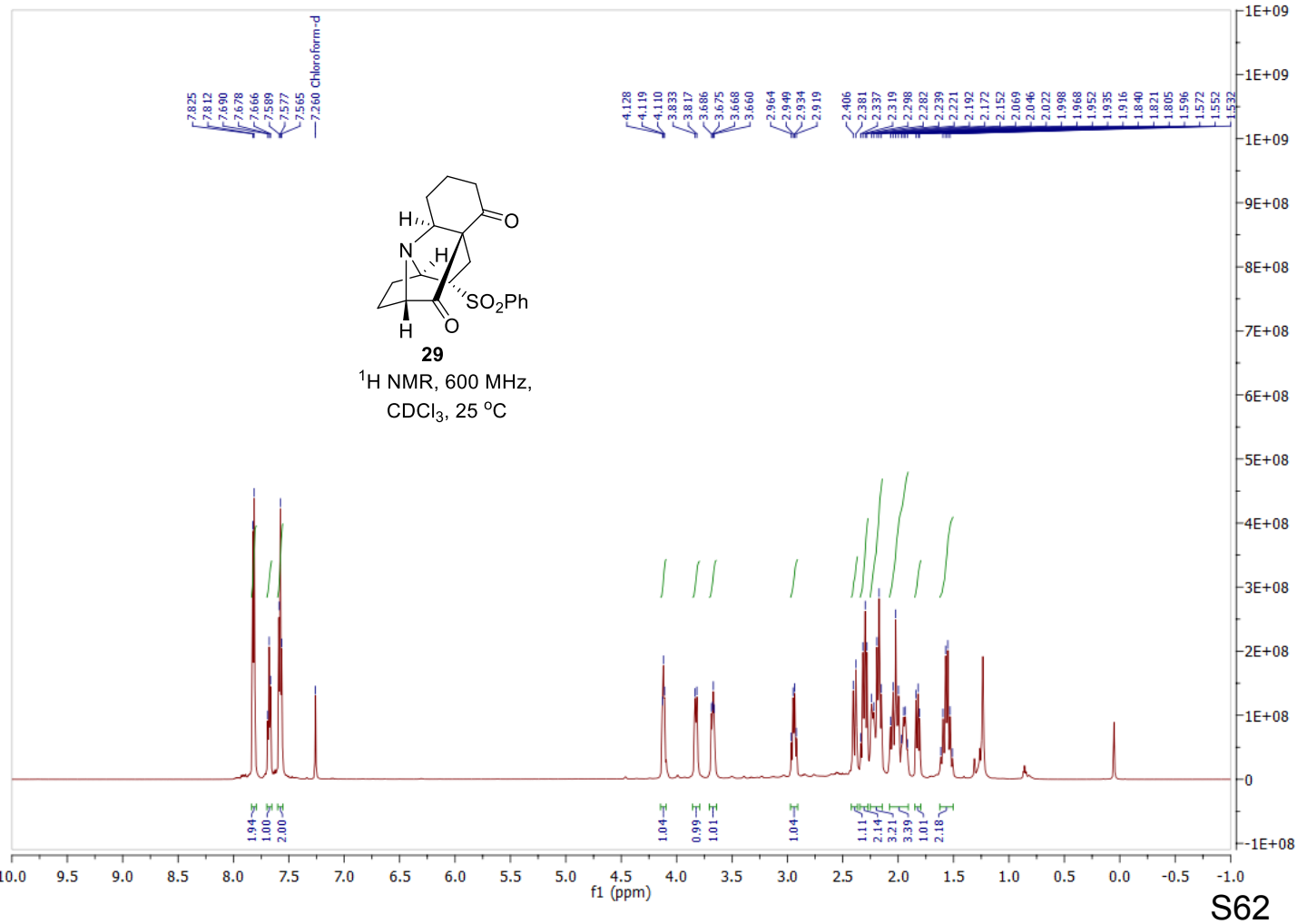
28

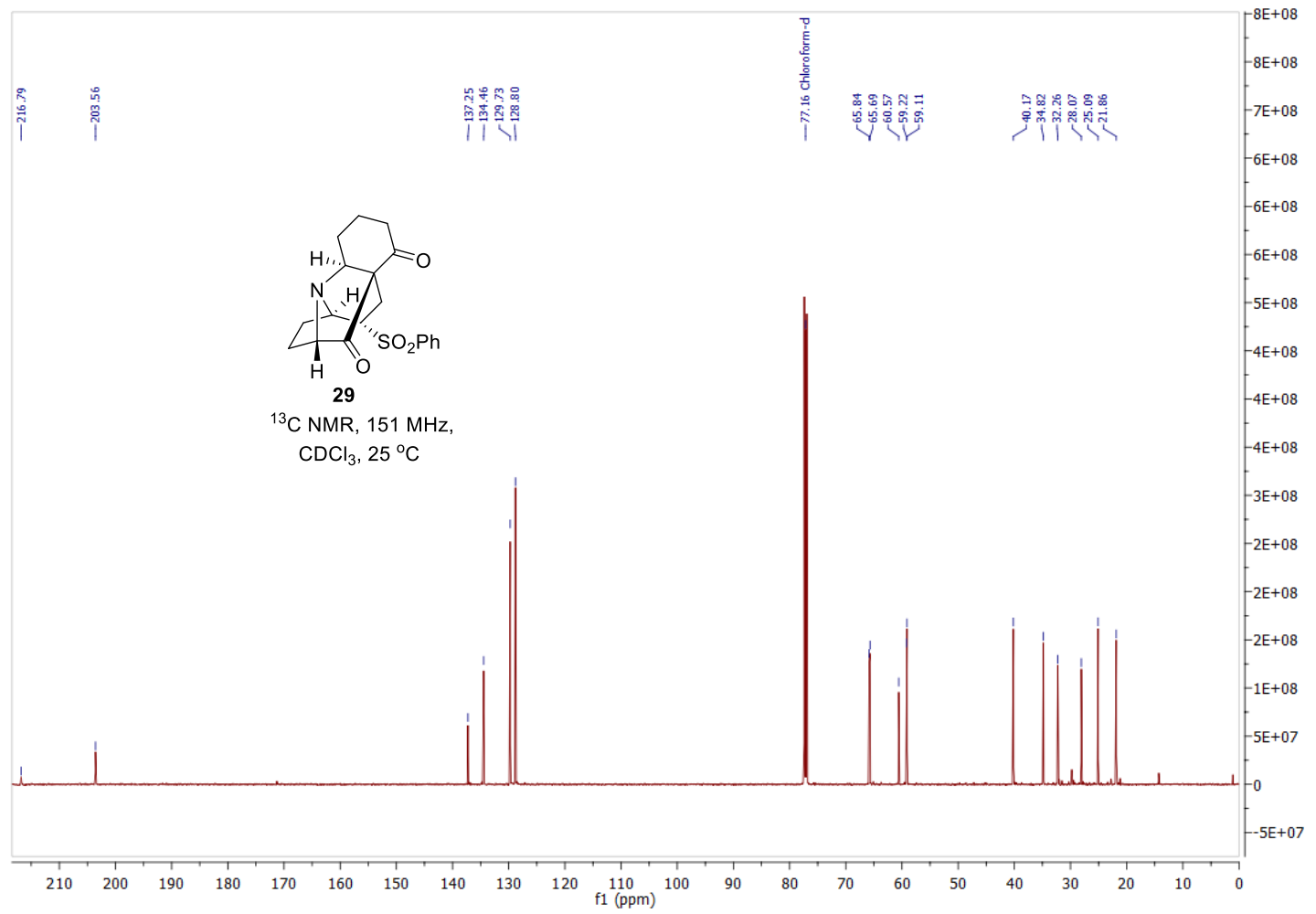
^{1}H-^{1}H gCOSY,
600 MHz (H), $CDCl_3$, 25 °C


O
H
SO2Ph
H
N
H
O
OMe
28
1H-13C gHSQC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


O
H
SO2Ph
H
N
H
O
OMe
28
1H-13C gHMBC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)

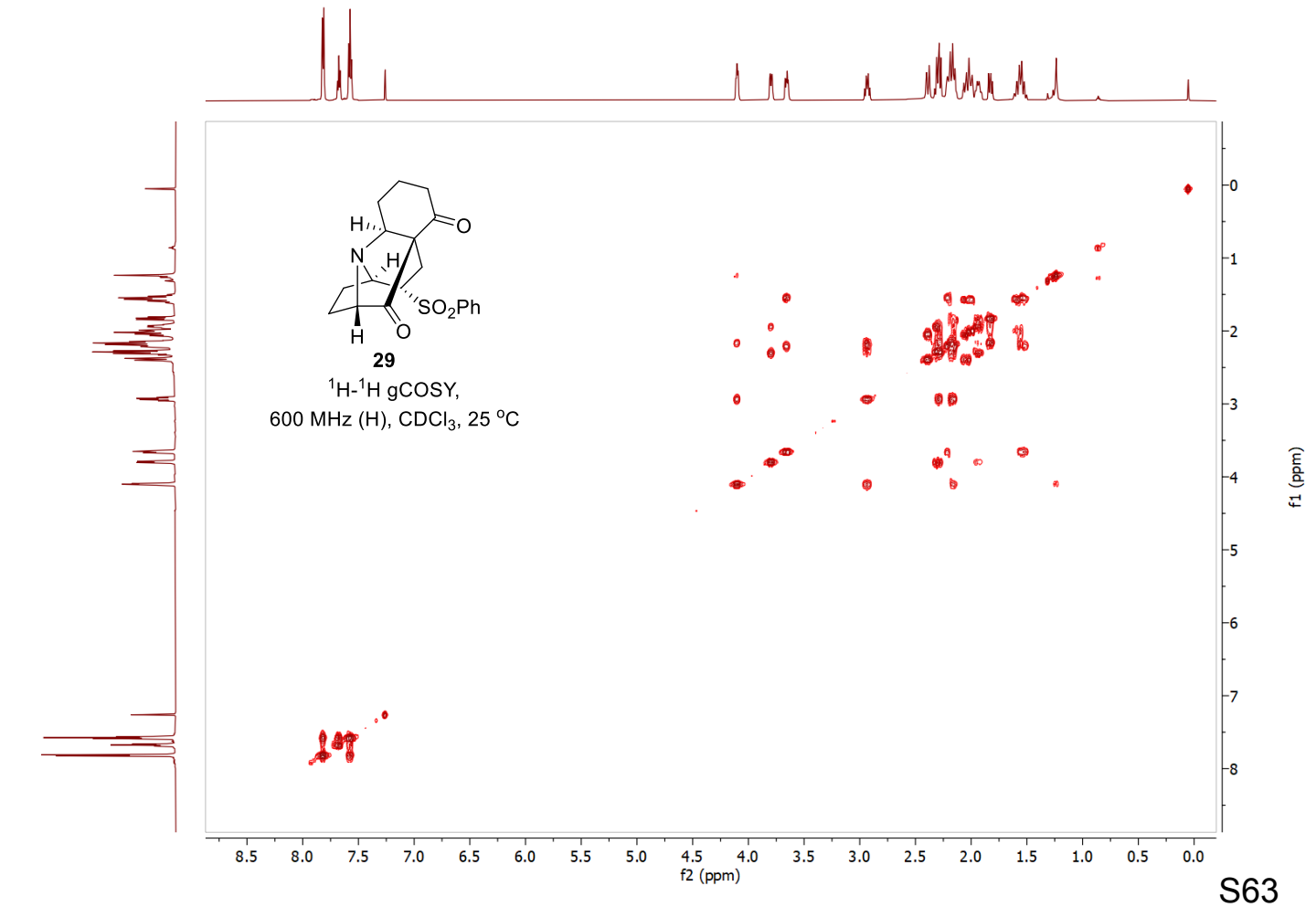

O
H
SO2Ph
H
N
H
O
OMe
28
1H-1H NOESY,
600 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


7.825
7.812
7.690
7.678
7.666
7.589
7.577
7.565
7.260 Chloroform-d
4.128
4.119
4.110
3.833
3.817
3.686
3.675
3.668
3.660
2.964
2.949
2.934
2.919
2.406
2.381
2.337
2.319
2.298
2.282
2.239
2.221
2.192
2.172
2.152
2.069
2.046
2.022
1.998
1.968
1.952
1.935
1.916
1.840
1.821
1.805
1.596
1.572
1.552
1.532
H
N
H
O
SO2Ph
O
H
29
1H NMR, 600 MHz,
CDCl3, 25 °C
1.94
1.00
2.00
1.04
0.99
1.01
1.04
1.11
2.14
3.21
3.39
1.01
2.18
f1 (ppm)



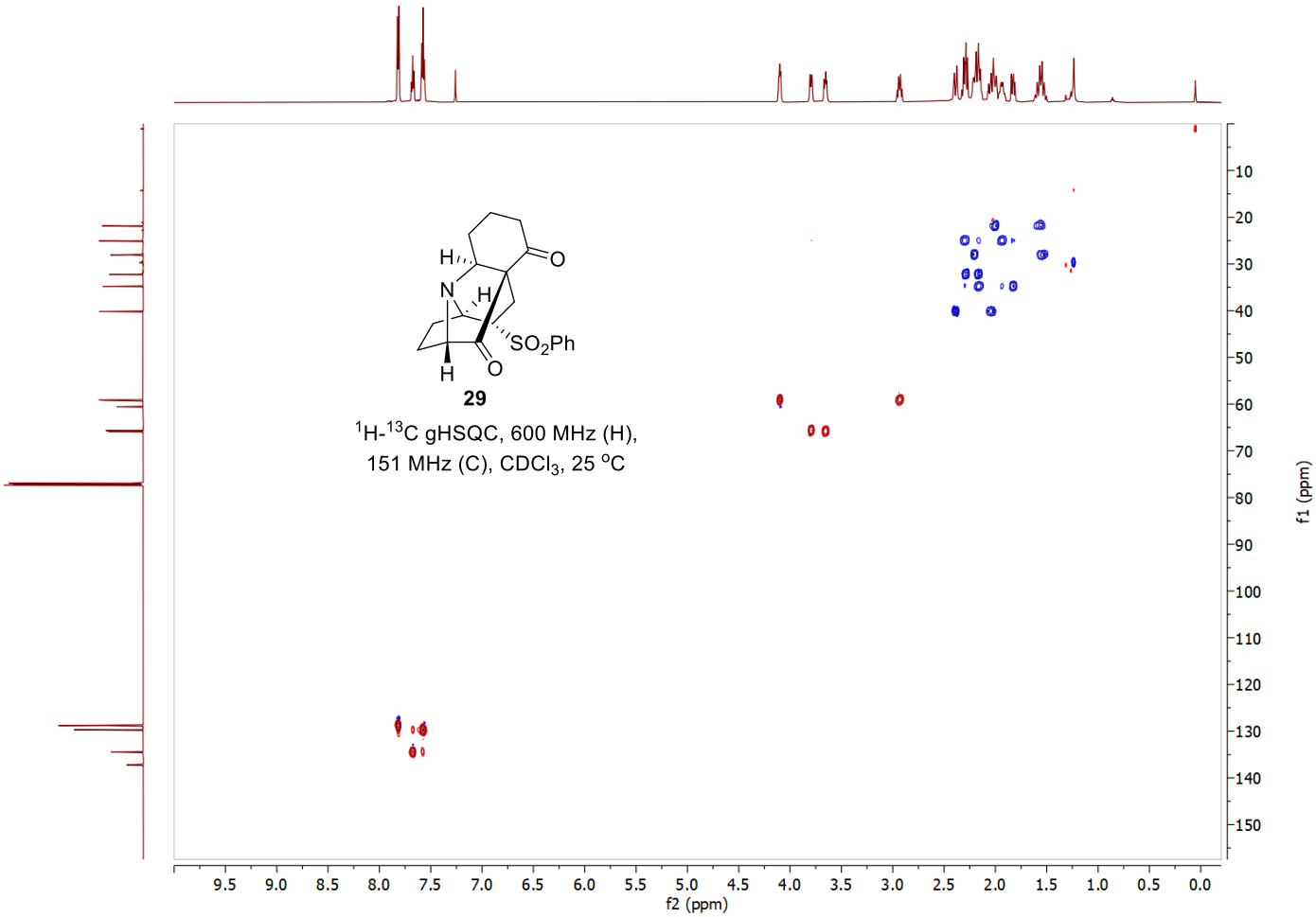
29

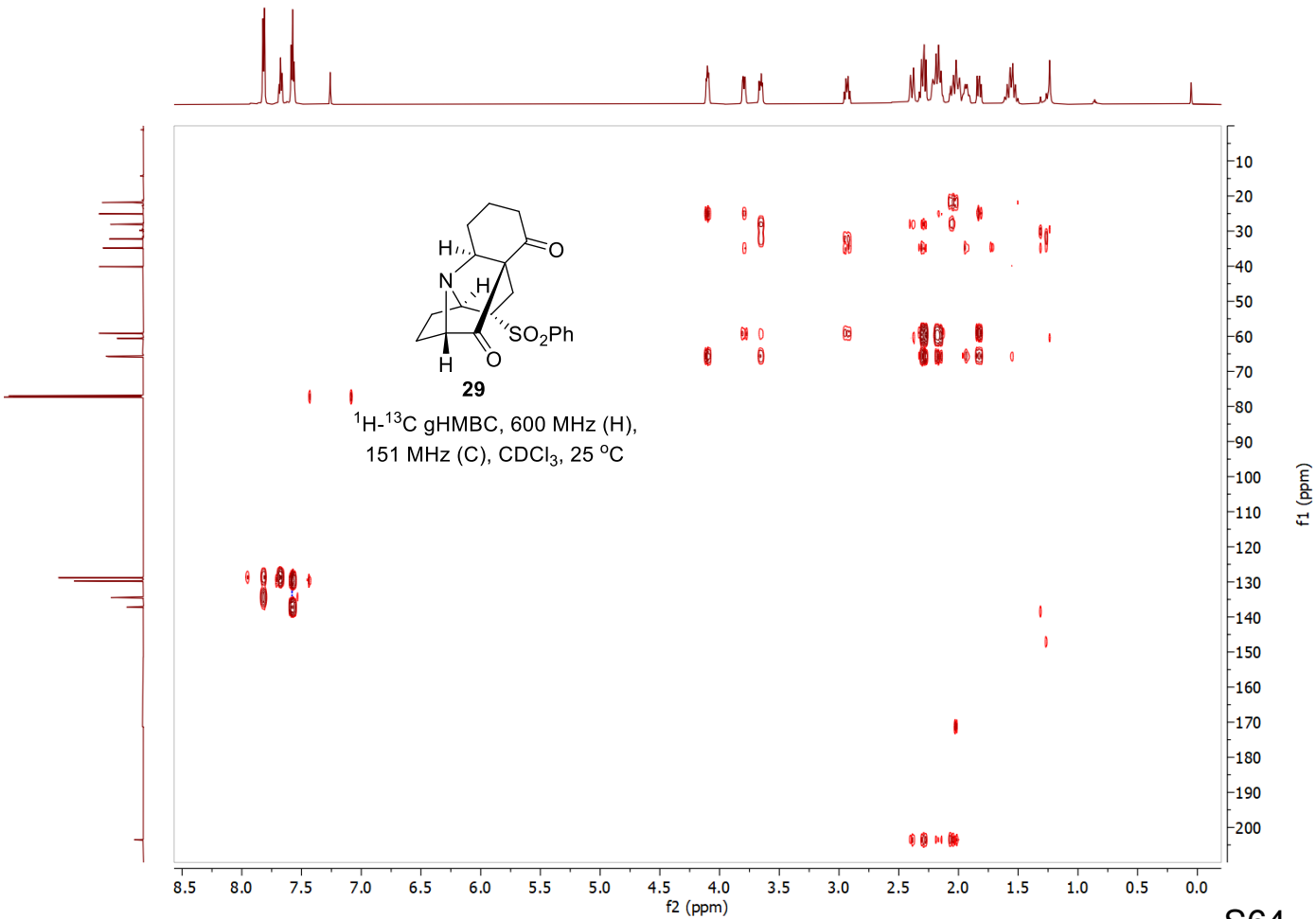
^{13}C NMR, 151 MHz,
$CDCl_3$, 25 °C

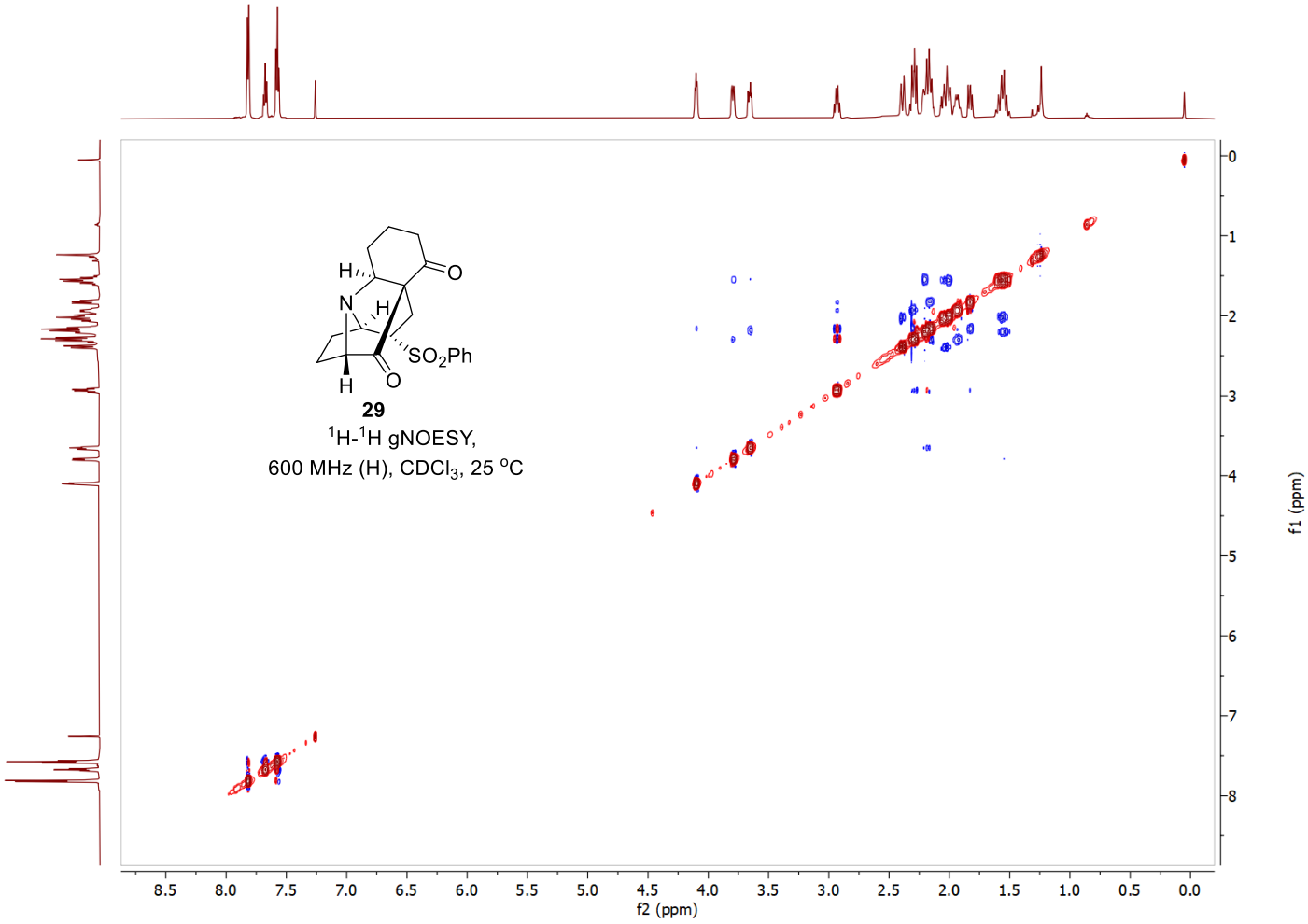


29

^{1}H-^{1}H gCOSY,
600 MHz (H), $CDCl_3$, 25 °C


H
N
H
O
SO2Ph
H
O
29
1H-13C gHSQC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


H
N
H
O
SO2Ph
H
O
29
1H-13C gHMBC, 600 MHz (H),
151 MHz (C), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)


H
N
H
O
SO2Ph
H
O
29
1H-1H gNOESY,
600 MHz (H), CDCl3, 25 °C
f2 (ppm)
f1 (ppm)