

Supporting Information for

Diastereoselective Base-Catalyzed Formal [4+2] Cycloadditions of *N*-Sulfonyl Imines and Cyclic Anhydrides

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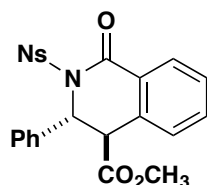
Experimental Details and Compound Characterization

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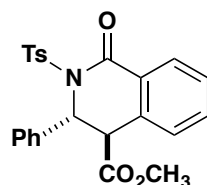
1. Materials and Instrumentation

Unless otherwise specified, all commercially available reagents were used as received. All reactions using dried solvents were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Dry solvent was dispensed from a solvent purification system that passes solvent through two columns of dry neutral alumina. ^1H NMR spectra and proton-decoupled ^{13}C NMR spectra were obtained on a 400 MHz Bruker or 600 MHz Varian NMR spectrometer. ^1H Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS (s, δ 0). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hexet), and m (multiplet). Complex splitting will be described by a combination of these abbreviations, i.e. dd (doublet of doublets). ^{13}C NMR chemical shifts are reported relative to CDCl_3 (t, δ 77.4) unless otherwise noted. High-resolution mass spectra were recorded on positive ESI mode unless otherwise noted. Melting points were taken on an EZ-melting apparatus and were uncorrected. Infrared spectra were taken on a Bruker Tensor 27 spectrometer. Chromatographic purifications were performed by flash chromatography with silica gel (Fisher, 40–63 μm) packed in glass columns. The eluting solvent for the purification of each compound was determined by thin-layer chromatography (TLC) on glass plates coated with silica gel 60 F254 and visualized by ultraviolet light.

2. Experimental procedures for the synthesis of lactams 16a-u.



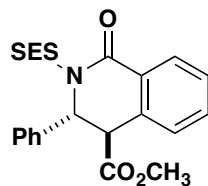
methyl (3R,4R)-2-((4-nitrophenyl)sulfonyl)-1-oxo-3-phenyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16a). Imine **15a** (49.5 mg, 0.17 mmol) and anhydride **8** (27.7 mg, 0.17 mmol) were dissolved in CH_2Cl_2 (1.7 mL) and diisopropylethylamine (30 μL , 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 and three times with EtOAc. The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH_3OH (0.67 mL) and acetyl chloride (6 μL , 0.09 mmol) was added. The reaction mixture was allowed to stir for 15 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-40% EtOAc:hex) to yield **16a** (67.9 mg, 86%), a single diastereomer, as a white amorphous solid: mp 80.6-84.5 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 8.29 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.4 Hz, 2H), 8.05 (dd, J = 1.4, 7.8 Hz, 1H), 7.49 (td, J = 1.5, 7.5 Hz, 1H), 7.41 (td, J = 1.2, 7.7 Hz, 1H), 7.21-7.29 (m, 4H), 7.16-7.07 (m, 2H), 6.49 (d, J = 1.5 Hz, 1H), 4.15 (d, J = 1.6 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 162.5, 150.5, 144.3, 137.9, 134.4, 132.9, 131.0, 129.9, 129.1, 129.0, 128.8, 128.5, 127.3, 126.2, 123.4, 59.9, 53.2, 51.2; IR: 1739, 1668, 1532, 1310, 1159 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_7\text{S}^+$ $[\text{M}+\text{H}]^+$ 467.0907, found 467.0927.



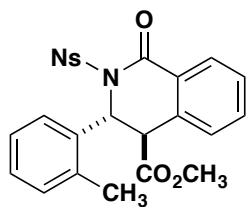
methyl (3R,4R)-1-oxo-3-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16b). Imine **15b** (44.0 mg, 0.17 mmol) and anhydride **8** (27.5 mg, 0.17 mmol) were dissolved in CH_3CN

(1.7 mL) and diisopropylethylamine (30 μ L, 0.17 mmol) was added. The reaction mixture was allowed to stir for 24 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 and three times with EtOAc. The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH_3OH (0.68 mL) and acetyl chloride (6 μ L, 0.09 mmol) was added. The reaction mixture was allowed to stir for 15 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-40% EtOAc:hex) to yield **16b** (70.3 mg, 95%), a single diastereomer, as a white amorphous solid; mp 75.8-77.3 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 8.06 (dd, J = 1.2, 7.7 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.43 (td, J = 1.4, 7.5 Hz, 1H), 7.36 (td, J = 1.2, 7.6 Hz, 1H), 7.29-7.08 (m, 8H), 6.51 (d, J = 1.4 Hz, 1H), 4.13 (d, J = 1.5 Hz, 1H), 3.69 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.5, 140.8, 123.1, 116.7, 114.3, 112.1, 111.3, 107.9, 107.9, 107.3, 107.1, 107.0, 106.4, 106.4, 104.5, 55.6, 38.2, 31.4, 30.0; IR: 1734, 1683, 1352, 1242, 1165 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_5\text{S}^+$ $[\text{M}+\text{H}]^+$ 436.1213, found 436.1230.

16b Scale-up. Imine **15b** (350 mg, 1.35 mmol) and anhydride **8** (219 mg, 1.350 mmol) were dissolved in CH_3CN (13.5 mL) and diisopropylethylamine (47 μ L, 0.27 mmol, 20 mol%) was added. The reaction mixture was allowed to stir for 24 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 and three times with EtOAc. The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH_3OH (13.5 mL) and EtOAc (5 mL), and acetyl chloride (96 μ L, 1.4 mmol) was added. After 15 h, esterification was incomplete so another portion of acetyl chloride (96 μ L, 1.4 mmol) was added. After 24 h, the reaction mixture was concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-50% EtOAc:hexanes) to yield a spectroscopically identical sample of **16b** as a single diastereomer (530 mg, 90%).

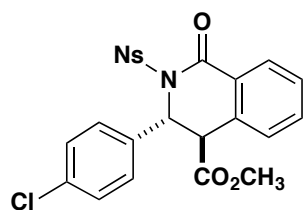


methyl (3R,4R)-1-oxo-3-phenyl-2-((2-(trimethylsilyl)ethyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16c). Imine **15c** (40.4 mg, 0.17 mmol) and anhydride **8** (24.6 mg, 0.17 mmol) were dissolved in CH₂Cl₂ (1.7 mL) and tetramethylguanidine (20 μL, 0.15 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.60 mL) and acetyl chloride (5 μL, 0.08 mmol) was added. The reaction mixture was allowed to stir for 19 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-35% EtOAc:hex) to yield **16c** (55.4 mg, 83%), a single diastereomer, as a white amorphous solid: mp 160.7-161.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.55-7.42 (m, 2H), 7.28-7.12 (m, 6H), 6.19 (d, *J* = 1.6 Hz, 1H), 4.13 (d, *J* = 1.8 Hz, 1H), 3.80-3.45 (m, 2H), 3.75 (s, 3H), 1.06-0.89 (m, 2H), 0.02 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 163.8, 138.6, 134.0, 133.1, 129.4, 129.0, 128.9, 128.8, 128.3, 128.2, 126.2, 59.4, 53.0, 51.7, 51.1, 9.5, -2.0; IR: 1732, 1672, 1349, 1236, 1155 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₂H₂₈NO₅SSi⁺ [M+H]⁺ 446.1452, found 446.1474.



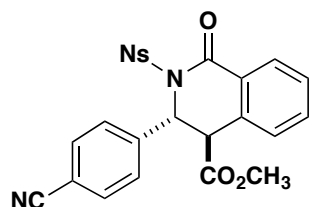
methyl (3R,4R)-2-((4-nitrophenyl)sulfonyl)-1-oxo-3-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16d). Imine **15d** (60.9 mg, 0.20 mmol) and anhydride **8** (32.1 mg, 0.20 mmol) were dissolved in CH₂Cl₂ (2.0 mL) and tetramethylguanidine (25 μL, 0.20 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined

organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.80 mL) and acetyl chloride (8 μ L, 0.10 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (20-25% EtOAc:hex) to yield **16d** (74.0 mg, 77%), a single diastereomer, as a white amorphous solid: mp 78.1-81.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 1.5 Hz, 2H), 8.11 (d, *J* = 1.6 Hz, 2H), 8.08 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.49 (td, *J* = 1.6, 7.5 Hz, 1H), 7.43 (td, *J* = 1.4, 7.5 Hz, 1H), 7.26-7.14 (m, 3H), 6.91-6.84 (m, 1H), 6.68 (d, *J* = 1.4 Hz, 1H), 6.59 (dd, *J* = 1.3, 7.8 Hz, 1H), 3.96 (d, *J* = 1.4 Hz, 1H), 3.76 (s, 3H), 2.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 162.8, 150.5, 144.3, 135.7, 134.5, 134.3, 132.6, 131.4, 131.0, 130.1, 129.1, 128.7, 128.5, 127.4, 126.3, 125.7, 123.4, 56.8, 53.3, 49.5, 19.3; IR: 1738, 1681, 1527, 1244, 1170 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₄H₂₁N₂O₇S⁺ [M+H]⁺ 481.1064, found 481.1086.

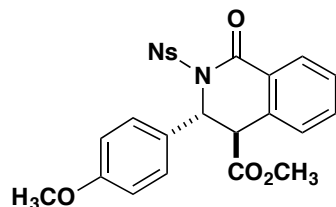


methoxy (3R,4R)-3-(4-chlorophenyl)-2-((4-nitrophenyl)sulfonyl)-1-oxo-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16e). Imine **15e** (55.2 mg, 0.17 mmol) and anhydride **8** (27.4 mg, 0.17 mmol) were dissolved in CH₂Cl₂ (1.7 mL) and diisopropylethylamine (30 μ L, 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.68 mL) and acetyl chloride (6 μ L, 0.09 mmol) was added. The reaction mixture was allowed to stir for 14 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-40% EtOAc:hex) to yield **16e** (61.5 mg, 72%), a single diastereomer, as a white amorphous solid: mp 84.9-88.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.37-8.31 (m, 2H), 8.31-8.26 (m, 2H), 8.03 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.51 (td, *J* = 1.5, 7.5 Hz, 1H), 7.42 (td, *J* = 1.3, 7.6 Hz, 1H), 7.28-7.20 (m, 3H), 7.12-7.06 (m, 2H), 6.49-6.43 (m, 1H), 4.10 (d, *J* = 1.6 Hz, 1H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 162.3, 150.7, 144.2, 136.6, 134.5, 132.6, 131.1, 129.9, 129.3, 129.2, 128.9, 127.5, 127.2, 123.6, 59.3, 53.3, 51.1; IR: 1732,

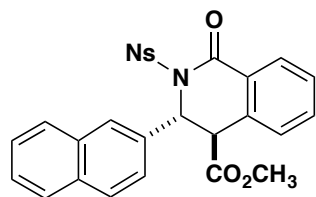
1676, 1347, 1256, 1168 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{18}\text{ClN}_2\text{O}_7\text{S}^+$ $[\text{M}+\text{H}]^+$ 501.0518, found 501.0535.



methyl (3R,4R)-3-(4-cyanophenyl)-2-((4-nitrophenyl)sulfonyl)-1-oxo-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16f). Imine **15f** (53.7 mg, 0.17 mmol) and anhydride **8** (27.6 mg, 0.17 mmol) were dissolved in CH_2Cl_2 (1.7 mL) and diisopropylethylamine (30 μL , 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH_3OH (0.68 mL) and acetyl chloride (6 μL , 0.09 mmol) was added. The reaction mixture was allowed to stir for 14 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (30-35% EtOAc:hex) to yield **16f** (51.0 mg, 61%), a single diastereomer, as a white amorphous solid: mp 65.7-70.0 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 4H), 8.04 (dd, J = 1.5, 7.9 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.52 (td, J = 1.5, 7.5 Hz, 1H), 7.44 (td, J = 1.3, 7.6 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.5 Hz, 1H), 6.55-6.49 (m, 1H), 4.11 (d, J = 1.6 Hz, 1H), 3.71 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 162.0, 150.8, 144.0, 143.3, 134.7, 132.9, 132.1, 131.1, 129.8, 129.4, 128.9, 127.0, 126.9, 123.6, 117.9, 112.7, 59.5, 53.4, 50.7; IR: 1734, 1681, 1535, 1245, 1169 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{18}\text{N}_3\text{O}_7\text{S}^+$ $[\text{M}+\text{H}]^+$ 492.0860, found 492.0880.

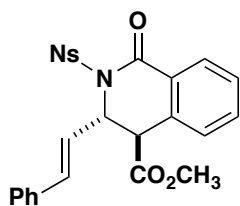


methyl (3R,4R)-3-(4-methoxyphenyl)-2-((4-nitrophenyl)sulfonyl)-1-oxo-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16g). Imine **15g** (54.5 mg, 0.17 mmol) and anhydride **8** (27.7 mg, 0.17 mmol) were dissolved in CH₂Cl₂ (1.7 mL) and diisopropylethylamine (30 μ L, 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.68 mL) and acetyl chloride (6 μ L, 0.09 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-40% EtOAc:hex) to yield **16g** (59.2 mg, 70%), a single diastereomer, as a white amorphous solid: mp 68.5-70.1 $^{\circ}$ C; ¹H NMR (400 MHz, CDCl₃) δ 8.33-8.25 (m, 2H), 8.29 (d, *J* = 1.7 Hz, 2H), 8.19 (d, *J* = 1.9 Hz, 2H), 8.04 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.51 (td, *J* = 1.5, 7.6 Hz, 1H), 7.42 (td, *J* = 1.1, 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 1.9 Hz, 2H), 6.80-6.71 (m, 2H), 6.43 (d, *J* = 1.6 Hz, 1H), 4.10 (d, *J* = 1.7 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 162.5, 159.6, 150.5, 144.5, 134.4, 133.1, 131.0, 129.9, 129.9, 129.0, 128.8, 127.5, 127.4, 123.5, 114.3, 59.5, 55.3, 53.2, 51.3; IR: 1734, 1684, 1530, 1349, 1243 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₄H₂₁N₂O₈S⁺ [M+H]⁺ 497.1013, found 497.1028.



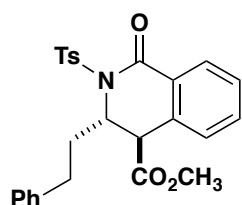
methyl (3R,4R)-3-(naphthalen-2-yl)-2-((4-nitrophenyl)sulfonyl)-1-oxo-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16h). Imine **15h** (68.1 mg, 0.20 mmol) and anhydride **8** (32.4 mg, 0.20 mmol) were dissolved in CH₂Cl₂ (2.0 mL) and tetramethylguanidine (25 μ L, 0.20

mmol) was added. The reaction mixture was allowed to stir for 2 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.80 mL) and acetyl chloride (8 μL, 0.10 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (20-25% EtOAc:hex) to yield **16h** (73.9 mg, 72%), a single diastereomer, as a white amorphous solid: mp 86.3-95.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.32-8.25 (m, 4H), 8.08 (dd, *J* = 1.6, 7.7 Hz, 1H), 7.81-7.71 (m, 2H), 7.69-7.61 (m, 1H), 7.59-7.52 (m, 1H), 7.50-7.43 (m, 3H), 7.39 (td, *J* = 1.4, 7.6 Hz, 1H), 7.25-7.21 (m, 2H), 6.66 (s, 1H), 4.26 (d, *J* = 1.6 Hz, 1H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 162.6, 144.4, 135.2, 134.4, 133.0, 132.9, 132.9, 131.1, 129.9, 129.1, 129.1, 128.9, 128.1, 127.6, 127.4, 126.8, 126.8, 125.7, 123.5, 123.3, 60.1, 53.3, 51.2; IR: 1735, 1676, 1532, 1349, 1165 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₇H₂₁N₂O₇S⁺ [M+H]⁺ 517.1064, found 517.1080.



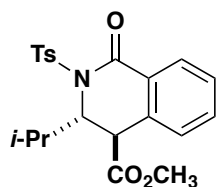
methyl (3S,4R)-2-((4-nitrophenyl)sulfonyl)-1-oxo-3-((E)-styryl)-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16i). Imine **15i** (53.8 mg, 0.17 mmol) and anhydride **8** (27.6 mg, 0.17 mmol) were dissolved in CH₂Cl₂ (1.7 mL) and diisopropylethylamine (30 μL, 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.68 mL) and acetyl chloride (6 μL, 0.09 mmol) was added. The reaction mixture was allowed to stir for 16 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (25-40% EtOAc:hex) to yield **16i** (42.5 mg, 51%), a single diastereomer, as a white amorphous solid: mp 83.6-88.0 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.38 (d,

$J = 9.1$ Hz, 2H), 8.31 (d, $J = 9.1$ Hz, 2H), 8.01 (dd, $J = 1.2, 7.9$ Hz, 1H), 7.58 (td, $J = 1.4, 7.5$ Hz, 1H), 7.43 (td, $J = 1.1, 7.7$ Hz, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.30-7.23 (m, 4H), 6.80 (d, $J = 14.9$ Hz, 1H), 6.10-5.97 (m, 2H), 4.05 (d, $J = 1.4$ Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 161.2, 150.6, 144.6, 135.1, 134.9, 134.4, 133.5, 131.0, 129.9, 129.1, 129.1, 128.7, 127.1, 126.8, 124.6, 123.6, 77.3, 58.9, 53.2, 49.2; IR: 1734, 1686, 1530, 1348, 1170 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_7\text{S}^+ [\text{M}+\text{H}]^+$ 493.1064, found 493.1085.



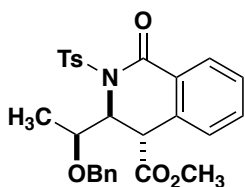
methyl (3*S*,4*R*)-1-oxo-3-phenethyl-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16j).

Imine **15j** (48.9 mg, 0.17 mmol) and anhydride **8** (27.6 mg, 0.17 mmol) were dissolved in CH_2Cl_2 (1.7 mL) and tetramethylguanidine (20 μL , 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH_3OH (0.68 mL) and acetyl chloride (6 μL , 0.09 mmol) was added. The reaction mixture was allowed to stir for 16 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (30-35% EtOAc:hex) to yield **16j** (26.8 mg, 34%), a single diastereomer, as a white amorphous solid: mp 102.5-105.0 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.10-7.93 (m, 3H), 7.51 (td, $J = 1.4, 7.5$ Hz, 1H), 7.39 (td, $J = 1.2, 7.6$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.28-7.08 (m, 5H), 5.38 (ddd, $J = 1.7, 5.9, 8.1$ Hz, 1H), 3.88 (d, $J = 1.9$ Hz, 1H), 3.59 (s, 3H), 2.80 (dddd, $J = 5.9, 10.3, 13.9, 42.5$ Hz, 2H), 2.40 (s, 3H), 2.23-2.08 (m, 1H), 1.96-1.80 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 161.8, 144.8, 140.2, 136.1, 133.7, 133.6, 129.5, 129.4, 129.0, 129.0, 128.7, 128.5, 128.2, 127.9, 126.3, 57.7, 52.8, 47.7, 36.4; 32.6, 21.6; IR: 1729, 1689, 1341, 1244, 1160 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_5\text{S}^+ [\text{M}+\text{H}]^+$ 464.1526, found 464.1542.



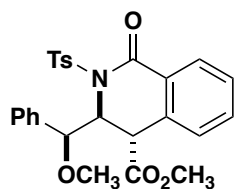
methyl (3*S*,4*R*)-3-isopropyl-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16k).

Imine **15k** (45.1 mg, 0.20 mmol) and anhydride **8** (32.2 mg, 0.20 mmol) were dissolved in CH₂Cl₂ (2.0 mL) and tetramethylguanidine (25 μL, 0.20 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.80 mL) and acetyl chloride (7 μL, 0.10 mmol) was added. The reaction mixture was allowed to stir for 17 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (20-25% EtOAc:hex) to yield **16k** (36.7 mg, 46%), a single diastereomer, as a white amorphous solid: mp 60.3-63.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.99 (dd, *J* = 1.4, 7.8 Hz, 1H), 7.51 (td, *J* = 1.4, 7.5 Hz, 1H), 7.38 (td, *J* = 1.2, 7.7 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.30-7.26 (m, 1H), 5.02 (dd, *J* = 1.7, 8.4 Hz, 1H), 4.03 (d, *J* = 1.5 Hz, 1H), 3.59 (s, 3H), 2.40 (s, 3H), 1.89 (dp, *J* = 6.8, 8.4 Hz, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 162.1, 144.7, 136.0, 134.3, 133.6, 129.9, 129.0, 128.9, 128.9, 128.6, 128.4, 63.5, 52.8, 46.2, 32.4, 21.7, 20.3, 19.6; IR: 1727, 1684, 1349, 1243, 1164 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₁H₂₄NO₅S⁺ [M+H]⁺ 402.1370, found 402.1388.



methyl 3-((*S*)-1-(benzyloxy)ethyl)-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16l)

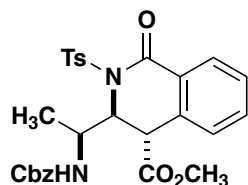
Imine **15l** (93 mg, 0.29 mmol, 1 equiv.) and homophthalic anhydride (48 mg, 0.29 mmol, 1 equiv.) were combined in anhydrous CH₃CN (2.9 mL). Tetramethylguanidine (37 μ L, 0.29 mmol, 1 equiv.) was added, and the reaction mixture immediately turned bright orange. After 23 h, 10% aqueous HCl solution (1.5 mL) and brine (1.5 mL) were added. The layers were separated, and the aqueous portion was extracted with CH₂Cl₂ (3 x 15 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude acid was dissolved in CH₃OH (1.2 mL) and treated with AcCl (11 μ L, 0.15 mmol, 0.5 equiv.). After 19 h, the reaction mixture was concentrated *in vacuo*. The crude product mixture was purified by flash column chromatography (100:0 to 70:30 hexanes:EtOAc) to produce ester **16l** (102 mg, 71%) as an 88:12:0:0 mixture of diastereomers. Major product: ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.91 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 – 7.21 (m, 3H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.98 (m, 2H), 5.24 (dd, *J* = 7.3, 1.6 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.36 (d, *J* = 1.6 Hz, 1H), 4.15 (d, *J* = 11.6 Hz, 1H), 3.61 (s, 3H), 2.39 (s, 3H), 1.45 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (151 MHz, cdcl₃) δ 170.9, 162.0, 144.7, 137.6, 136.0, 134.4, 133.4, 129.8, 129.1, 128.9, 128.6, 128.2, 128.1, 127.6, 127.5, 110.0, 75.7, 71.2, 61.1, 52.7, 44.3, 21.6, 16.5. IR (thin film) 1733, 1686, 1348, 1243, 1166 cm⁻¹; AMM (ESI-TOF) calcd for C₂₇H₂₈NO₆S⁺ [M+H]⁺ 494.1632, found 494.1634.



methyl 3-((S)-methoxy(phenyl)methyl)-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16m)

Aminosulfone **15m** (60 mg, 0.13 mmol, 1 equiv.) and homophthalic anhydride (22 mg, 0.13 mmol, 1 equiv.) were combined in anhydrous CH₃CN (1.35 mL). Tetramethylguanidine (17 μ L, 0.13 mmol, 1 equiv.) was added, and the solution immediately turned bright orange. After 24 h, 10% aqueous HCl solution (1.5 mL) and brine (1.5 mL) were added. The aqueous portion was extracted with CH₂Cl₂ (3 x 15 mL), and the combined organics were dried over Na₂SO₄, filtered, and

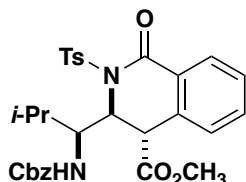
concentrated *in vacuo*. The crude acid was dissolved in CH₃OH (1 mL) and treated with AcCl (10 μ L, 1 equiv.). After 22 h, the reaction mixture was concentrated *in vacuo*. The crude product mixture was purified by flash column chromatography (100:0 to 60:40 hexanes:EtOAc, *R*_f = 0.42 in 60:40 hexanes:EtOAc) to produce ester **16m** (54 mg, 83% over 2 steps) as a 79:21:0:0 mixture of diastereomers. Spectroscopic data for major diastereomer: ¹H NMR (600 MHz, CDCl₃) δ 8.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.33 – 7.29 (m, 3H), 7.27 (dd, *J* = 1.4, 0.7 Hz, 2H), 5.47 (dd, *J* = 5.2, 1.4 Hz, 1H), 4.56 (d, *J* = 5.1 Hz, 1H), 4.05 (d, *J* = 1.3 Hz, 1H), 3.57 (s, 3H), 3.07 (s, 3H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.7, 162.6, 144.5, 136.9, 134.5, 133.2, 129.5, 128.9, 128.8, 128.6, 128.6, 128.4, 128.2, 128.0, 127.4, 127.1, 85.5, 61.0, 58.1, 52.7, 43.5, 21.6. IR (thin film) 1734, 1687, 1241, 1164, 699 cm⁻¹; AMM (ESI-TOF) calcd for C₂₆H₂₆NO₆S⁺ [M+H]⁺ 480.1475, found 480.1491.



methyl 3-(((S)-1-(((benzyloxy)carbonyl)amino)ethyl)-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16n)

Aminosulfone **15n** (150 mg, 0.282 mmol, 1 equiv.) and homophthalic anhydride (46 mg, 0.28 mmol, 1 equiv) were combined in dry CH₃CN (2.8 mL) and treated with TMG (35 μ L, 0.28 mmol, 1 equiv.). After 23 h, 3M aqueous HCl solution (3 mL) and brine (1 mL) were added. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 x 7 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude acid was dissolved in CH₃OH (2.8 mL) and treated with AcCl (20 μ L, 0.28 mmol, 1 equiv). After 15 h, the mixture was concentrated *in vacuo*. The crude product mixture was purified by flash column chromatography (100:0 to 50:50 hexanes:EtOAc) to produce ester **16n** (95 mg, 63%) as a 78:22:0:0 mixture of diastereomers. Major product: ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.97 (m, 4H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.30 – 7.22 (m, 6H), 5.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 5.05 (dd, *J* = 11.0, 4.3 Hz, 2H), 4.87 (d, *J* = 12.1 Hz, 1H), 4.01 (s, 1H), 3.88 (tt, *J* = 11.7, 6.1 Hz,

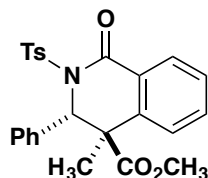
1H), 3.57 (s, 3H), 2.38 (s, 3H), 1.31 (d, $J = 6.8$ Hz, 3H). IR (thin film) 1709, 1682, 1528, 1228, 1165 cm^{-1} ; AMM (ESI-TOF) calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_6\text{S}^+$ $[\text{M}+\text{H}]^+$ 537.1690, found 537.1704.



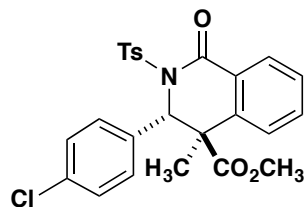
methyl 3-((*S*)-1-(((benzyloxy)carbonyl)amino)-2-methylpropyl)-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16o**)**

Aminosulfone **15o** (73 mg, 0.19 mmol, 1 equiv.) and homophthalic anhydride (31 mg, 0.19 mmol, 1 equiv) were dissolved in anhydrous CH_3CN (1.9 mL). Tetramethylguanidine (24 μL , 0.19 mmol, 1 equiv.) was added, and the solution immediately became an orange-brown color. After 22 h, H_2O (1 mL), 1 M HCl (1 mL), and brine (1 mL) were added, and the aqueous portion was extracted with CH_2Cl_2 (3 x 15 mL). The combined organics were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude acid was dissolved in CH_3OH (0.57 mL) and THF (1.9 mL). TMSCHN_2 in hexane (115 μL , 0.226 mmol, 1.2 equiv.) was added. After 1.5 h, 10% HCl (1 mL) was added, and the resulting mixture was diluted to 10 mL with CH_2Cl_2 . The aqueous portion was extracted with CH_2Cl_2 (3 x 10 mL), and the combined organics were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude product mixture was purified by flash column chromatography (100:0 to 50:50 hexanes:EtOAc, $R_f = 0.37$ in 50:50 hexanes:EtOAc) to produce **16o** (103 mg, 97% over two steps) as an 85:15:0:0 mixture of diastereomers. Spectroscopic data for major diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 7.98 (m, 4H), 7.52 (td, $J = 7.5, 1.5$ Hz, 1H), 7.46 – 7.21 (m, 10H), 5.26 (dd, $J = 9.8, 1.8$ Hz, 1H), 5.12 (d, $J = 12.1$ Hz, 1H), 5.09 (d, $J = 10.7$ Hz, 1H), 4.98 (d, $J = 12.1$ Hz, 1H), 3.94 (d, $J = 1.8$ Hz, 1H), 3.64 (td, $J = 10.1, 3.7$ Hz, 1H), 3.54 (s, 3H), 2.38 (s, 3H), 1.97 – 1.88 (m, 1H), 1.02 (d, $J = 6.9$ Hz, 3H), 0.91 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 161.9, 156.8, 144.8, 136.6, 136.0, 133.5, 132.6, 129.8, 129.2, 129.1, 129.0, 128.9, 128.6, 128.4, 128.2, 127.9, 67.3, 59.7, 56.5, 52.9, 46.9, 28.8, 21.7, 20.5, 15.2. IR (thin film)

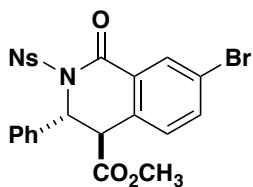
1689, 1721, 1162, 1234, 1347 cm^{-1} ; AMM (ESI-TOF) calcd for $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_7\text{S}^+$ $[\text{M}+\text{H}]^+$ 565.2003, found 565.2038.



methyl (3*S*,4*R*)-4-methyl-1-oxo-3-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16p). Imine **15p** (44.2 mg, 0.17 mmol) and anhydride **17a** (30.3 mg, 0.17 mmol) were dissolved in CH_3CN (1.7 mL) and tetramethylguanidine (21 μL , 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH_3OH (0.52 mL), THF (1.7 mL), and TMSCHN_2 (105 μL , 0.20 mmol) was added. The reaction mixture was allowed to stir for 1 h, and then CH_2Cl_2 and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude mixture was purified by flash column chromatography (25-30% EtOAc:hex) to yield **16p** (55.9 mg, 73%), a single diastereomer, as a white amorphous solid: mp 73.9-76.3 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (dd, J = 1.2, 7.8 Hz, 1H), 7.59-7.52 (m, 3H), 7.44 (t, J = 7.3 Hz, 1H), 7.28-7.22 (m, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.97-6.91 (m, 2H), 6.25 (s, 1H), 3.66 (s, 3H), 2.35 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 162.5, 144.5, 138.0, 136.0, 135.6, 133.9, 129.3, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 126.6, 77.2, 65.3, 53.4, 50.5, 21.6, 21.3; IR: 1729, 1682, 1355, 1248, 1167 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_5\text{S}^+$ $[\text{M}+\text{H}]^+$ 450.1370, found 450.1384.

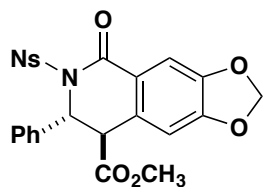


methyl (3*S*,4*R*)-3-(4-chlorophenyl)-4-methyl-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16q). Imine **15q** (294.3 mg, 1.0 mmol) and anhydride **17a** (176.2 mg, 1.0 mmol) were dissolved in CH₂Cl₂ (10.0 mL) and tetramethylguanidine (125 μ L, 1.0 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (3.0 mL), CH₂Cl₂ (3.0 mL), and TMSCHN₂ (0.6 mL, 1.2 mmol) was added. The reaction mixture was allowed to stir for 1 h, and then CH₂Cl₂ and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was purified by flash column chromatography (20-30% EtOAc:hex) to yield **16q** (316.5 mg, 65%), a single diastereomer, as a white amorphous solid: mp 70.4-74.1 $^{\circ}$ C; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.56 (td, *J* = 1.3, 7.7 Hz, 1H), 7.45 (td, *J* = 1.2, 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.23 (s, 1H), 3.62 (s, 3H), 2.37 (s, 3H), 1.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 162.3, 144.8, 137.7, 135.9, 134.7, 134.3, 134.1, 130.0, 129.3, 128.9, 128.7, 128.7, 128.6, 128.5, 126.7, 64.7, 53.4, 50.4, 21.7, 21.2; IR: 1732, 1672, 1349, 1236, 1155 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₅H₂₃ClNO₅S⁺ [M+H]⁺ 484.0980, found 484.0996.



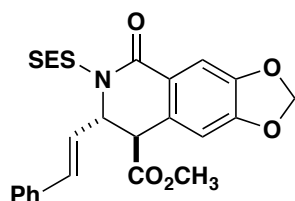
methyl (3*R*,4*R*)-7-bromo-2-((4-nitrophenyl)sulfonyl)-1-oxo-3-phenyl-1,2,3,4-tetrahydroisoquinoline-4-carboxylate (16r). Imine **15a** (58.3 mg, 0.20 mmol) and anhydride **17b**

(47.9 mg, 0.20 mmol) were dissolved in CH₂Cl₂ (2.0 mL) and tetramethylguanidine (25 μ L, 0.20 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.80 mL) and acetyl chloride (8 μ L, 0.10 mmol) was added. The reaction mixture was allowed to stir for 19 h, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (20-30% EtOAc:hex) to yield **16r** (56.0 mg, 53%), a single diastereomer, as a white amorphous solid: mp 87.8-93.5 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.20-8.15 (m, 4H), 7.60 (dd, *J* = 2.1, 8.1 Hz, 1H), 7.33-7.22 (m, 3H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.10-7.07 (m, 2H), 6.49 (d, *J* = 1.3 Hz, 1H), 4.11 (m, 1H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 161.2, 150.6, 143.9, 137.4, 137.3, 131.7, 131.6, 131.5, 131.1, 129.1, 128.9, 128.7, 126.1, 123.5, 123.2, 59.8, 53.4, 50.8; IR: 1743, 1676, 1525, 1352, 1166 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₃H₁₈BrN₂O₇S⁺ [M+H]⁺ 545.0013, found 545.0032.



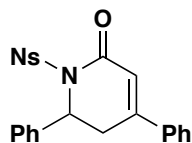
methyl (7R,8R)-6-((4-nitrophenyl)sulfonyl)-5-oxo-7-phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinoline-8-carboxylate (16s). Imine **15a** (49.2 mg, 0.17 mmol) and anhydride **17c** (35.0 mg, 0.17 mmol) were dissolved in CH₂Cl₂ (1.7 mL) and tetramethylguanidine (21 μ L, 0.17 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.68 mL) and acetyl chloride (6 μ L, 0.09 mmol) was added. The reaction mixture was allowed to stir for 1.5 d, and then concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (30-40% EtOAc:hex) to yield **16s** (63.9 mg, 74%), a single diastereomer, as a white amorphous solid: mp 97.3-103.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.9 Hz, 2H), 8.16 (d, *J* = 9.0 Hz, 2H), 7.41 (s, 1H), 7.30-7.26

(m, 2H), 7.23 (m, 1H), 7.18-7.09 (m, 2H), 6.62 (s, 1H), 6.43 (d, $J = 1.4$ Hz, 1H), 6.00 (d, $J = 1.6$ Hz, 2H), 4.01 (d, $J = 1.5$ Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 161.8, 152.7, 150.5, 148.6, 144.4, 137.9, 130.9, 129.0, 128.5, 126.2, 123.4, 121.5, 109.4, 107.9, 102.3, 77.2, 59.7, 53.2, 51.1; IR: 1733, 1677, 1529, 1259, 1169 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_9\text{S}^+$ $[\text{M}+\text{H}]^+$ 511.0806, found 511.0823.



methyl (7*S*,8*R*)-5-oxo-7-((*E*)-styryl)-6-((2-(trimethylsilyl)ethyl)sulfonyl)-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline-8-carboxylate (16t) Imine **15t** (150 mg, 0.51 mmol) and 4,5-methylenedioxyhomophthalic anhydride (**17c**) (105 mg, 0.510 mmol) were dissolved in acetonitrile (5.1 mL) and tetramethylguanidine (64 μL , 0.51 mmol) was added. The reaction was stirred for 19 h, and then water and 10% aq. HCl (30 mL) were added to the mixture. The biphasic mixture was extracted three times with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 and solvent was evaporated *in vacuo*. The crude material was purified by flash column chromatography (0:100 $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$ to 10:90 $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$) to yield acid (197 mg, 77%).

Purified acid (1.38 g, 2.75 mmol) was dissolved in CH_3OH (11 mL) and treated with acetyl chloride (90.0 μL , 1.38 mmol). The mixture was stirred for 19 hours and then concentrated *in vacuo*. The crude material was purified by flash column chromatography (20:80 EtOAc:hexanes) to yield ester **16t** (593 mg, 42%). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.26-7.19 (m, 5H), 6.75-6.70 (m, 2H), 6.06-5.99 (m, 3H), 5.69 (ddd, $J = 7.4, 1.5, 1.5$ Hz, 1H), 3.86 (d, $J = 1.8$ Hz, 1H), 3.72 (s, 3H), 3.66-3.51 (m, 3H), 3.05-3.00 (m, 1H), 1.11-1.05 (m, 1H), 1.04-0.94 (m, 2H), -0.02 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.1, 162.6, 152.6, 148.6, 135.6, 134.6, 129.9, 128.7, 126.9, 125.2, 122.3, 109.3, 108.7, 102.4, 58.2, 53.1, 51.7, 49.3, 11.1, 10.2, -1.9; IR: 1736, 1672, 1342, 1253, 1149 cm^{-1} ; AMM (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{30}\text{NO}_7\text{SSi}^+$ $[\text{M}+\text{H}]^+$ 516.1507, found 516.1519.



1-((4-nitrophenyl)sulfonyl)-4,6-diphenyl-5,6-dihydropyridin-2(1H)-one (16u). Imine **15a** (37.2 mg, 0.13 mmol) and anhydride **17d** (24.4 mg, 0.13 mmol) were dissolved in CH₃CN (1.3 mL) and tetramethylguanidine (16 μ L, 0.13 mmol) was added. The reaction mixture was allowed to stir for 22 h, and then water and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was dissolved in CH₃OH (0.39 mL), CH₂Cl₂ (1.3 mL), and TMSCHN₂ (80 μ L, 1.5 mmol) was added. The reaction mixture was allowed to stir for 1 h, and then CH₂Cl₂ and 10% HCl in water were added to the mixture. The biphasic mixture was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and solvent was evaporated *in vacuo*. The crude mixture was purified by flash column chromatography (20-30% EtOAc:hex) to yield **16u** (11.8 mg, 17%) as a white amorphous solid: mp 196.0-197.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.43-7.21 (m, 7H), 7.16 (d, *J* = 7.2 Hz, 3H), 6.30 (d, *J* = 2.7 Hz, 1H), 6.08 (d, *J* = 6.8 Hz, 1H), 3.63 (ddd, *J* = 17.7, 7.4, 2.7 Hz, 1H), 3.17 (dd, *J* = 17.8, 1.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 152.3, 150.4, 144.1, 139.2, 136.2, 130.8, 130.8, 129.0, 129.0, 128.6, 126.5, 126.1, 123.3, 118.4, 57.8, 35.3; IR: 1669, 1526, 1348, 1237, 1168 cm⁻¹; AMM (ESI-TOF) *m/z* calcd for C₂₃H₁₉N₂O₅S⁺ [M+H]⁺ 435.1009, found 435.1025.

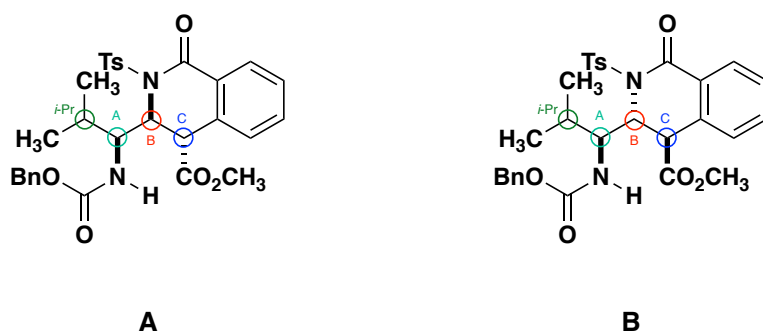
3. Computational NMR Spectroscopy Data

For each diastereomer of the 2 compounds of interest (**16o** and **16m**), we first performed conformational search using *Spartan10*,¹ and kept 100 lowest-energy conformers that were within 200 kcal/mol of electronic energy computed with MMFF force field.² Using *Gaussian09*,³ for each conformer library, we computed electronic energies of all the conformers (without optimization) with DFT method, M06-2X/6-31G(d),^{4,5} to rank them in relative uncorrected electronic energies. The conformers, which were within ~17kcal/mol of the lowest-energy structure, were then fully optimized with frequency calculation (to check for true minima) with B3LYP/6-31G(d).^{6,7} To ensure that we have adequately sample the conformational space, we used the lowest-energy conformer for each diastereomer to perform 2 more rounds of conformational searches in *Spartan10*, until we see redundant outputs of conformations.

Proton-proton Fermi constants were then calculated, using B3LYP/6-31+G(d,p), for conformers that were within 2 kcal/mol of the B3LYP/6-31G(d) Free energy and then scaled to coupling constant using the scaling factor of 0.9117.⁸ Boltzmann weighed average of coupling constants were also determined to account for conformational flexibility.

For the conformers that were within 10kcal/mol of Free energy determined by B3LYP/6-31G(d), full optimization and frequency calculations were performed using B3LYP/6-31+G(d,p) to determine a more accurate Free energy profile. NMR calculations were then calculated for conformers that were within 2 kcal/mol of the new energies, using mPW1PW91/6-311+G(2d,p)⁹ in chloroform (SMD solvation model).¹⁰ Chemical shifts were scaled using scaling factors available at the cheshirenmr.info website (slope=-1.0936 for ¹H, and intercept= 31.8018 for ¹H).¹¹ For methyl group, averages of the computed values of the three hydrogens were used to compare to the experimental numbers. Boltzmann weighed average chemical shifts were also determined to account for conformational flexibility in real time NMR, and DP4 statistical analysis¹² were performed to check for the probability that our assignment were correct.

16o:



Scheme S1: Structures of two possible diastereomers **16o**.

Since there are only one set of experimental NMR data, which was for the observed major product, we calculated the computed NMR for both **A** and **B** to compare. Boltzmann weighed average chemical shifts from all the contributing conformers of **A** and **B** indicated that **A** is the major diastereomer product as its chemical shifts, as well as proton-proton coupling constants, matched better to the experimental values.

Structure A	
opt/freq	B3LYP/6-31+G(d,p)
Name	% of the population
conf 4	48.61
conf 9	15.59
conf 1	12.10
conf 6	8.95
conf 5	7.13
conf 2	4.66
conf 38	1.50
conf 40	1.45

Structure B	
opt/freq	B3LYP/6-31+G(d,p)
Name	% of the population
conf 51	80.79
conf 14	9.39
conf 47	6.22
conf 8	2.35
conf 34	1.25

Table S1: contributing conformers of **A** and **B** (conformers within 2kcal/mol of Free energy)

opt/freq	B3LYP/6-31+G(d,p)		
NMR	mPW1PW91/6-311+G(2d,p)		
	Conformers of A		Conformers of B
	Boltzmann. Ave δ (ppm)	Exp. δ (ppm)	Boltzmann. Ave δ (ppm)
Hb	5.17	5.29	4.77
Hc	4.00	3.97	4.12
Ha	3.54	3.67	3.43
Hi-Pr	1.90	1.94	2.38
DP4 Stat.	97.90%		2.10%

Table S2: Computed Boltzmann weighed average chemical shifts, and experimental NMR of major product.

opt/freq	B3LYP/6-31+G(d,p)		
NMR	mPW1PW91/6-311+G(2d,p)		
	Average Conformers of A		Average Conformers of B
	Δ (comp – exp)	Exp. δ (ppm)	Δ (comp – exp)
Hb	-0.12	5.29	-0.52
Hc	0.03	3.97	0.15
Ha	-0.13	3.67	-0.24
Hi-Pr	-0.04	1.94	0.44
DP4 Stat.	97.90%		2.10%

Table S3: shift by shift deviations and experimental NMR of major product.

opt/freq	B3LYP/6-31G(d)		
NMR	B3LYP/6-31G(d,p)		
	Conformers of A	Exp. Coupling constant (Hz)	Conformers of B
	Boltzmann. Ave coupling (Hz)		Boltzmann. Ave coupling (Hz)
Ha--Hb	9.07	9.8-10.3	6.34
Hb--Hc	1.89	1.7-1.8	1.45
Ha--Hi-Pr	4.73	3.7-3.8	10.30

Table S4: proton-proton coupling constant and experimental coupling constants of major product.

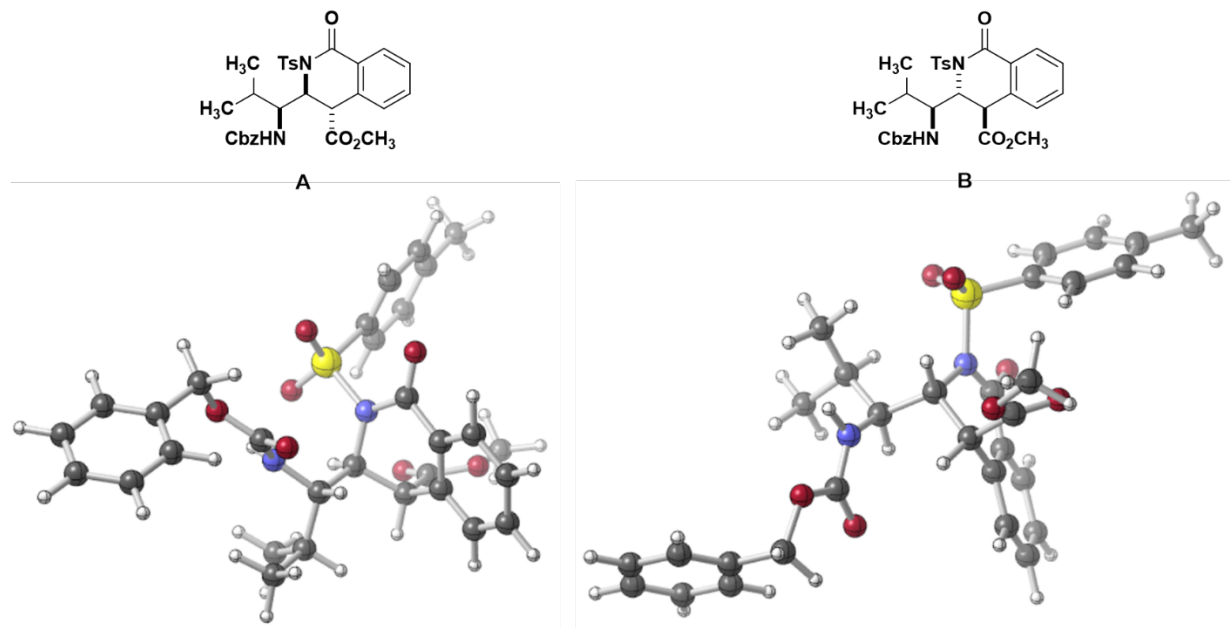
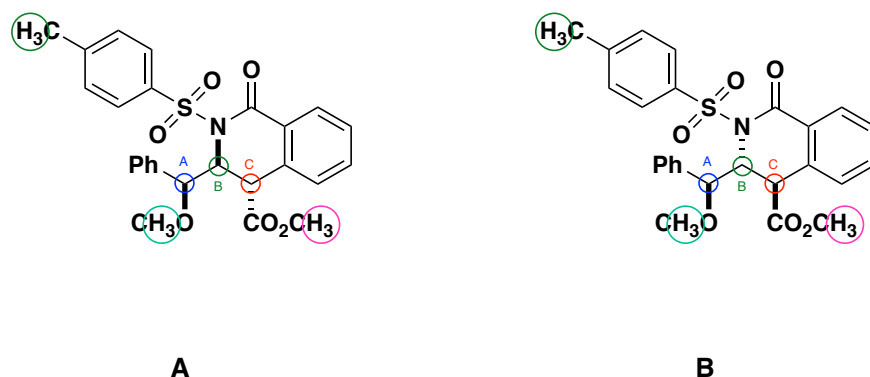


Figure S1: Bond-and-stick pictures of the optimized lowest-energy conformers of **A** and **B** for **16o**.

16m:

Unlike the previous system, we also have experimental NMR for the minor diastereomer product for this system. First when we calculated the coupling constant for A and B after taking into consideration all the contributing conformers based on the calculated B3LYP/6-31G(d) Free energies, the coupling constant of A match well to the experimental data of the major diastereomer; however, the computed values of B did not match to either the major or minor. Upon inspecting the optimized conformers that were within 5kcal/mol of free energies, we notice that some conformers give computed coupling constant that matched well to the experimental value, but their B3LYP Free energies were much higher, making them not weighed much in the Boltzmann average. As the result, we reoptimized with frequency calculation for all the conformers of A and B that were within the 5kcal/mol energy window, using ω B97XD/6-31+G(d,p) and used the new energies to calculate the Boltzmann distribution, while using the same NMR method. Boltzmann weighed average chemical shifts and coupling constant from all the contributing conformers of **A** and **B** indicated that **A** is the major diastereomer product as its chemical shifts matched better to the experimental values.



Scheme S2: Structures of two possible diastereomers of **16m**.

structure A	B3LYP/6-31+G(d,p)	ω B97XD/6-31+G(d,p)
conf name	ΔG (kcal/mol)	ΔG (kcal/mol)
1.first	0.00	0.00
10.first	1.02	0.10
11.first	-1.10	-1.02
23.first	-0.97	1.00
25.first	-0.97	1.00
29.first		-0.03
33.first	2.78	1.54
35.first	2.78	
36.first		1.52
41.first	2.31	3.64
45.first	2.31	3.64
47.first		2.96
71.first	3.38	4.74
9.first	0.00	0.00
13.second	3.96	5.32
15.second	3.37	4.75
18.second	1.61	1.31
2.second	-0.01	0.00
21.second	1.30	0.13
3.second	-1.10	-1.01
36.second	-1.01	1.01
4.second		-0.04
7.second	1.21	0.24
8.second	2.39	4.19
9.second	1.92	4.03

structure B	B3LYP/6-31+G(d,p)	ω B97XD/6-31+G(d,p)
conf name	ΔG (kcal/mol)	ΔG (kcal/mol)
1.first	0.00	0.00
13.first	1.46	
15.first	1.41	
17.first	1.41	1.79
19.first	2.36	
20.first	2.36	
21.first	2.36	
23.first	1.41	
25.first	1.40	
31.first	4.97	
5.first	-1.22	0.13
55.first	1.39	
56.first	2.45	
57.first	2.44	
1.second	0.00	0.00
10.second	4.60	
14.second	1.39	-0.07
15.second	2.55	0.64
16.second	2.42	-0.47
2.second	-1.22	
21.second	1.47	1.55
25.second	1.39	1.45
26.second	1.58	1.16
3.second	1.09	1.24
35.second	1.08	1.46
39.second	1.09	1.24
5.second	2.36	1.54
6.second	1.40	1.55
7.second	4.80	1.33
1.third	1.98	0.82
28.third	2.43	-0.47
2.third	1.44	-0.04
33.third	2.55	0.64

Table S5: Free energies computed at B3LYP/6-31+G(d,p) and ω B97XD/6-31+G(d,p) for conformers of **A** and **B**.

Structure A	
opt/freq	ω B97XD/6-31+G(d,p)
Name	% of the population
conf 11	59.02
conf 29	11.07
conf 2	10.59
conf 10	8.92
conf 21	8.45
conf 36	1.94

Structure B	
opt/freq	ω B97XD/6-31+G(d,p)
Name	% of the population
conf 28	32.35
conf 14	16.62
conf 2	15.85
conf 1a	14.70
conf 5	11.83
conf 33	4.96
conf 1	3.69

Table S6: contributing conformers of **A** and **B** (conformers within 2kcal/mol of Free energy).

COMPARING TO THE EXPERIMENTAL MAJOR PRODUCT:

opt/freq	B3LYP/6-31+G(d,p)		
NMR	mPW1PW91/6-311+G(2d,p)		
	Conformers of A	major prod	Conformers of B
	Boltzmann. Ave δ (ppm)	Exp. δ (ppm)	Boltzmann. Ave δ (ppm)
Ha	4.55	4.56	3.98
Hb	5.44	5.46	5.45
Hc	4.44	4.05	4.51
MeEster	3.44	3.57	3.39
MeEther	3.18	3.06	2.80
MeTosyl	2.43	2.39	2.36
MAD =	0.12		0.25
DP4 Stat.	99.80%		0.20%

Table S7: Computed Boltzmann weighed average chemical shifts, and experimental NMR of major product.

opt/freq	B3LYP/6-31+G(d,p)		
NMR	mPW1PW91/6-311+G(2d,p)		
	Average Conformers of A	major prod	Average Conformers of B
	Δ (comp – exp)	Exp. δ (ppm)	Δ (comp – exp)
Ha	-0.01	4.56	-0.58
Hb	-0.02	5.46	-0.01
Hc	0.39	4.05	0.46
MeEster	-0.13	3.57	-0.18
MeEther	0.12	3.06	-0.26
MeTosyl	0.04	2.39	-0.03
MAD =	0.12		0.25
DP4 Stat.	99.80%		0.20%

Table S8: shift by shift deviations and experimental NMR of major product.

COMPARING TO THE EXPERIMENTAL MINOR PRODUCT:

opt/freq	B3LYP/6-31+G(d,p)		
NMR	mPW1PW91/6-311+G(2d,p)		
	Conformers of A	minor prod	Conformers of B
	Boltzmann. Ave δ (ppm)	Exp. δ (ppm)	Boltzmann. Ave δ (ppm)
Ha	4.55	4.14	3.98
Hb	5.44	5.57	5.45
Hc	4.44	3.81	4.51
MeEster	3.44	3.62	3.39
MeEther	3.18	3.17	2.80
MeTosyl	2.43	2.41	2.36
MAD =	0.23		0.27
DP4 Stat.	46.90%		53.10%

Table S9: Computed Boltzmann weighed average chemical shifts, and experimental NMR of minor product.

opt/freq	B3LYP/6-31+G(d,p)		
NMR	mPW1PW91/6-311+G(2d,p)		
	Average Conformers of A	minor prod	Average Conformers of B
	Δ (comp – exp)	Exp. δ (ppm)	Δ (comp – exp)
Ha	0.41	4.14	-0.16
Hb	-0.13	5.57	-0.12
Hc	0.63	3.81	0.70
MeEster	-0.18	3.62	-0.23
MeEther	0.01	3.17	-0.37
MeTosyl	0.02	2.41	-0.05
MAD =	0.23		0.27
DP4 Stat.	46.90%		53.10%

Table S8: shift by shift deviations and experimental NMR of minor product.

The computed and experimental chemical shifts together suggest that **B** is the minor product; however, the Boltzmann average of Hc chemical shift is off by 0.7ppm from the experimental value. As we look closer at all the structures of the contributing conformers, this proton is pointing directly at the ether oxygen and on average is just 2.3Å apart (figure S2; **conf 28**). This suggests that the deviation could be the result of this proton involving in CH – O interaction. In supporting this hypothesis, **conf 1a** and **conf 5** (figure S2), where Hc isn't in close proximity to the ether oxygen, Hc's chemical shifts are both at around 3.94 ppm, which is only 0.13 ppm away from the experimental value of 3.81 ppm. We are currently investigating the effect of this CH – O interaction in computed chemical shifts for hexa-cyclic peptide, and deviations are typically observed when C-H is about 2-2.5 Å away from the oxygen, and the effect can be alleviated by elongating these distance to about 3.0 Å (more details to follow).

Also, as another experiment, we elongated the distance between the problematic CH and ether-O and then optimized the molecules with the distance constrained. From that geometry, we calculated the chemical shifts, and Hc (in the original **conf 28** deviated by 0.9 ppm from the experimental value) is now only 0.4 ppm off from the experimental chemical shift.

In addition, we are confident that **B** is the minor product as its computed coupling constant matched well with the experimental minor product.

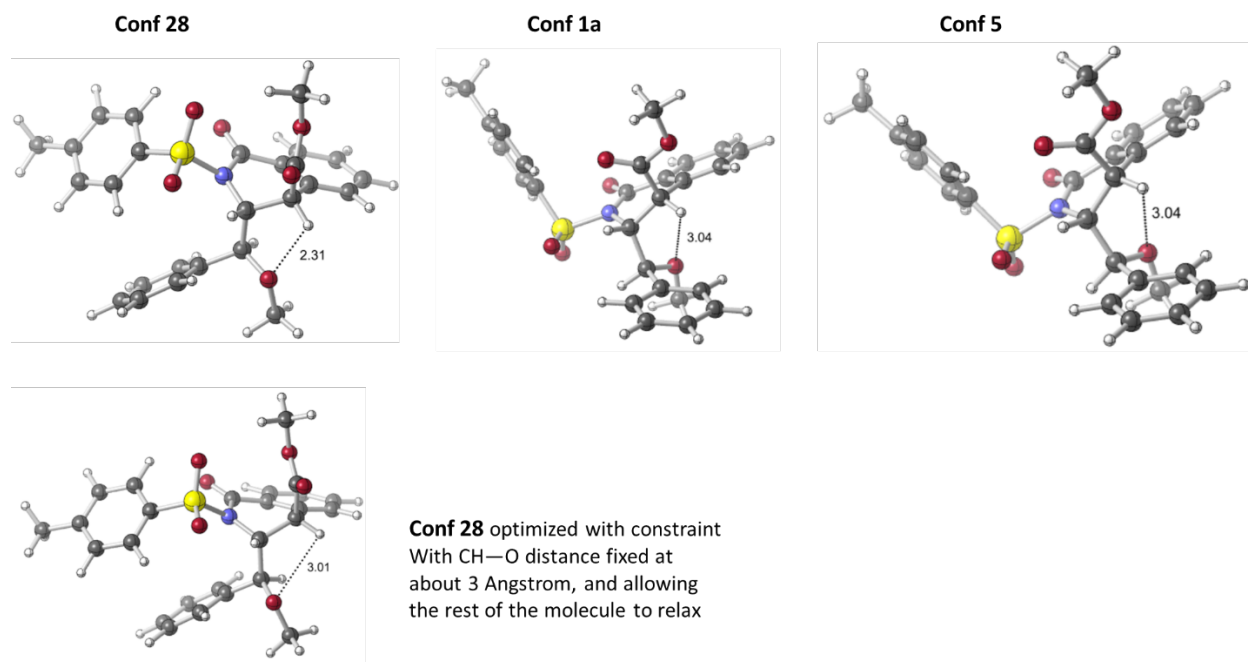


Figure S3: Bond-and-stick pictures of the conformers with the problematic proton, Hc. Distance shown are in Å.

Proton-proton coupling constants:

opt/freq	B3LYP/6-31G(d)	
NMR	B3LYP/6-31G(d,p)	
	Conformers of A	Exp. Coupling constant (Hz)
	Boltzmann. Ave coupling (Hz)	
		Major Prod
Ha--Hb	5.82	5.2
Hb--Hc	1.00	1.4-1.5
	Conformers of B	Exp. Coupling constant (Hz)
	Boltzmann. Ave coupling (Hz)	
		Minor Prod
Ha--Hb	7.94	8.2-8.4
Hb--Hc	1.80	1.4-1.5

Table S11: Computed and experimental proton-proton coupling constants.

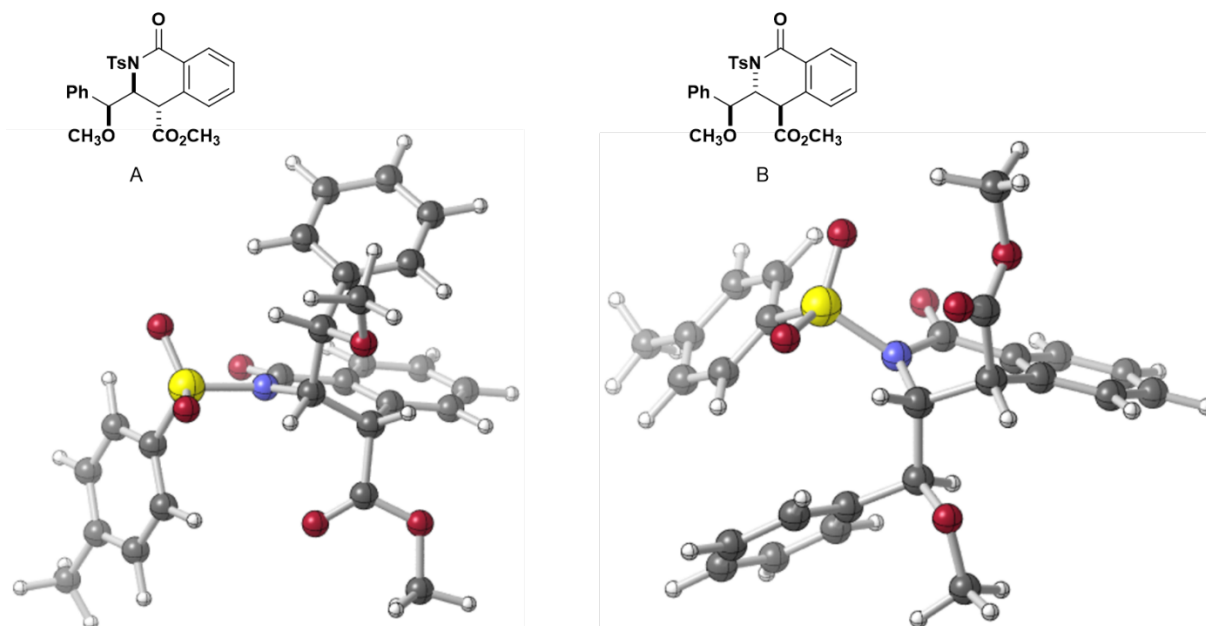


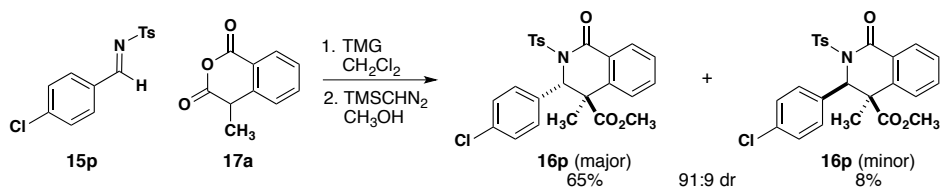
Figure S3: Bond-and-stick pictures of the optimized lowest-energy conformers of **A** and **B** for **16m**.

Full Gaussian09 Citation:

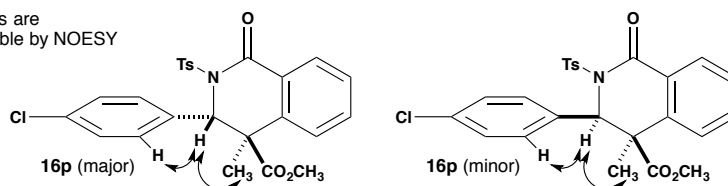
Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

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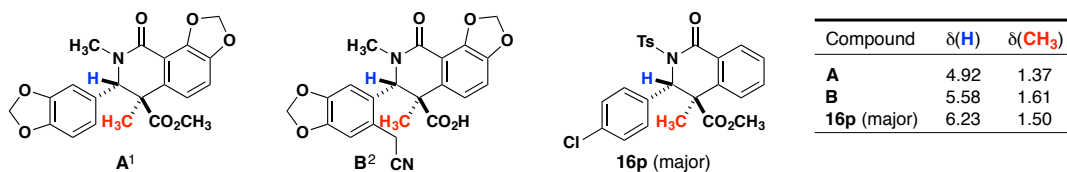
4. Stereochemical Supplement for Lactam 16p Assignment



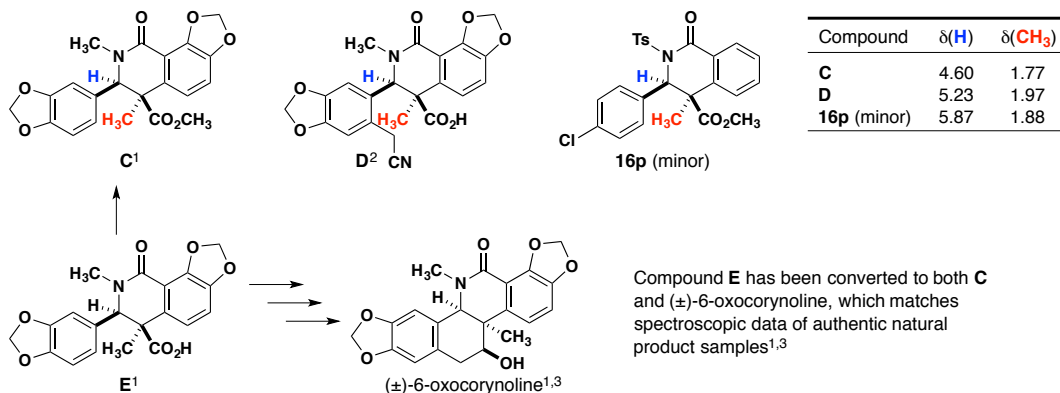
Diastereomers are indistinguishable by NOESY



Relative stereochemistry of **16p** (major) by analogy to literature spectra for compounds **A** and **B**



Relative stereochemistry of **16p** (minor) by analogy to literature spectra for compounds **C** and **D**



References:

A¹; **B²**; **C¹**; **D²**; **E¹**; 6-oxocorynoline^{1,3}

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5. X-ray Crystallography Data

16e

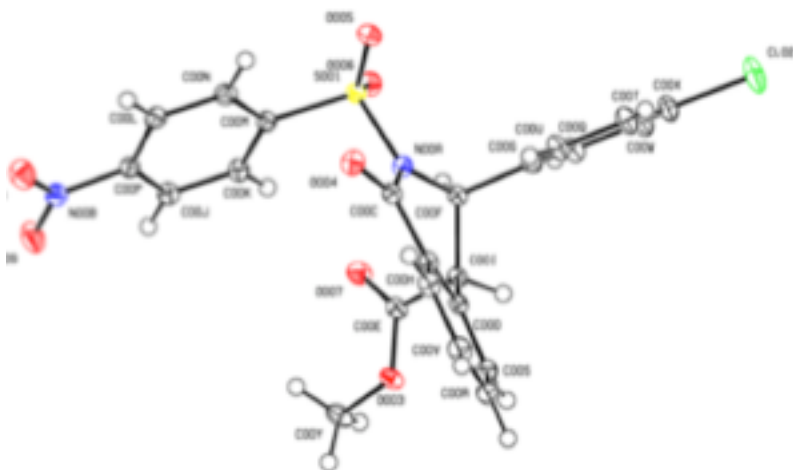


Table 1 Crystal data and structure refinement for 16e.

Identification code	mo_MJD011_0m
Empirical formula	C ₂₃ H ₁₇ N ₂ O ₇ SCl
Formula weight	500.89
Temperature/K	90.15
Crystal system	triclinic
Space group	P-1
a/Å	9.1593(7)
b/Å	11.0566(8)
c/Å	12.4050(9)
α/°	64.9500(10)
β/°	76.9800(10)
γ/°	89.3270(10)
Volume/Å ³	1103.85(14)
Z	2
ρ _{calc} /g/cm ³	1.507
μ/mm ⁻¹	0.317
F(000)	516.0
Crystal size/mm ³	0.385 × 0.28 × 0.224

Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^{\circ}$	3.736 to 66.388
Index ranges	$-14 \leq h \leq 13$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	19981
Independent reflections	7848 [$R_{\text{int}} = 0.0233$, $R_{\text{sigma}} = 0.0275$]
Data/restraints/parameters	7848/0/308
Goodness-of-fit on F^2	1.021
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0373$, $wR_2 = 0.0984$
Final R indexes [all data]	$R_1 = 0.0451$, $wR_2 = 0.1034$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.73/-0.42

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for mo_MJD011_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Ato m	x	y	z	$U(\text{eq})$
S1	5259.9(3)	6953.5(3)	1658.7(2)	14.57(6)
Cl1	8079.4(4)	162.4(3)	4017.4(3)	32.56(8)
O3	-143.4(8)	4297.6(8)	2346.1(7)	16.78(15)
O1	3611.0(9)	6459.0(8)	4051.9(7)	17.98(15)
O4	6423.5(9)	7118.2(9)	2196.2(8)	21.20(16)
O5	5663.8(9)	6800.7(8)	536.3(7)	19.26(16)
O2	1851.2(9)	5629.7(9)	901.0(7)	20.02(16)
O6	1403.5(11)	12136.3(10)	1506.9(9)	25.90(18)
O7	371.3(11)	11535.4(10)	380.9(10)	28.1(2)
N1	4040.9(10)	5607.8(8)	2638.8(8)	12.87(15)
N2	1292.0(11)	11421.5(9)	993.7(9)	17.90(17)
C1	3310.2(11)	5572.8(10)	3774.7(9)	13.34(17)
C7	1571.7(11)	3639.6(10)	4099.8(9)	13.49(17)
C16	1313.1(11)	4721.9(10)	1897.1(9)	14.03(17)
C9	3889.5(11)	4465.4(10)	2325.6(9)	12.79(16)
C10	4965.2(11)	3412.5(10)	2781.0(9)	13.65(17)
C2	2134.2(11)	4443(1)	4564.6(9)	13.57(17)

C8	2236.4(11)	3870.8(10)	2789.7(9)	13.00(17)
C23	2133.7(12)	9495.2(11)	596.2(10)	16.57(18)
C24	3053.4(12)	8449.2(11)	761.7(10)	16.23(18)
C21	3391.9(12)	10231.8(11)	1785.5(10)	16.75(18)
C19	4119.8(11)	8306.1(10)	1441.5(9)	14.62(17)
C20	4310.1(12)	9186.4(11)	1948.5(10)	16.87(18)
C3	1558.3(12)	4239.5(11)	5781.3(9)	17.43(19)
C22	2319.1(12)	10351.4(10)	1121.8(9)	14.95(18)
C15	5606.8(12)	2800.7(11)	2028.4(10)	17.81(19)
C5	-185.2(13)	2456.7(11)	6066.8(10)	19.8(2)
C6	389.2(12)	2652.1(11)	4859.3(10)	16.64(18)
C12	6292.9(13)	2035.3(12)	4291.1(10)	20.7(2)
C11	5328.3(12)	3031.1(11)	3908.3(10)	17.69(19)
C4	405.6(13)	3232.8(12)	6533.6(10)	20.2(2)
C14	6571.2(14)	1802.8(12)	2403.2(11)	21.9(2)
C13	6892.1(13)	1423.2(12)	3538.6(11)	20.3(2)
C18	-1123.6(12)	4945.4(13)	1536(1)	20.9(2)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 16e. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Ato m	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
S1	12.53(11)	14.92(11)	14.53(11)	-5.06(9)	-2.68(8)	1.69(8)
Cl1	36.59(17)	29.86(16)	41.61(18)	-19.60(14)	-21.72(14)	22.43(13)
O3	12.8(3)	22.8(4)	15.2(3)	-7.8(3)	-5.4(3)	3.8(3)
O1	23.3(4)	18.3(4)	16.2(3)	-10.0(3)	-7.0(3)	2.3(3)
O4	14.5(3)	21.7(4)	28.0(4)	-9.7(3)	-8.4(3)	2.1(3)
O5	19.7(4)	19.5(4)	14.5(3)	-6.2(3)	1.2(3)	2.2(3)
O2	17.9(4)	23.7(4)	15.8(3)	-4.5(3)	-7.1(3)	0.9(3)
O6	28.1(4)	27.6(4)	32.5(5)	-21.7(4)	-9.9(4)	8.7(4)
O7	30.0(5)	26.4(4)	39.8(5)	-19.1(4)	-21.7(4)	12.9(4)
N1	14.1(4)	13.5(4)	11.0(3)	-5.8(3)	-2.2(3)	1.1(3)
N2	17.8(4)	16.8(4)	20.0(4)	-8.9(3)	-4.4(3)	2.6(3)

C1	14.9(4)	15.3(4)	10.9(4)	-5.9(3)	-4.8(3)	3.6(3)
C7	13.3(4)	14.8(4)	11.9(4)	-5.0(3)	-3.9(3)	3.6(3)
C16	14.3(4)	17.7(4)	14.3(4)	-9.8(3)	-5.8(3)	3.7(3)
C9	13.5(4)	15.1(4)	11.4(4)	-6.9(3)	-4.1(3)	3.0(3)
C10	12.3(4)	16.5(4)	14.1(4)	-7.8(3)	-4.3(3)	2.5(3)
C2	14.2(4)	14.9(4)	11.3(4)	-5.2(3)	-3.3(3)	3.6(3)
C8	12.8(4)	15.1(4)	12.7(4)	-6.9(3)	-4.4(3)	2.7(3)
C23	18.2(4)	17.7(5)	15.7(4)	-7.9(4)	-6.4(4)	3.0(4)
C24	18.1(4)	16.3(4)	15.6(4)	-7.7(4)	-5.0(4)	2.7(3)
C21	18.3(4)	15.7(4)	17.4(4)	-7.9(4)	-4.9(4)	0.4(3)
C19	14.6(4)	13.9(4)	13.6(4)	-4.5(3)	-3.1(3)	1.5(3)
C20	16.4(4)	17.5(4)	16.8(4)	-6.8(4)	-5.5(4)	0.4(3)
C3	19.6(5)	20.0(5)	12.3(4)	-6.9(4)	-3.5(3)	5.0(4)
C22	15.4(4)	13.4(4)	15.0(4)	-5.5(3)	-3.2(3)	1.7(3)
C15	18.7(5)	22.9(5)	17.3(4)	-12.5(4)	-7.2(4)	6.4(4)
C5	16.8(5)	18.9(5)	16.7(5)	-2.9(4)	-0.8(4)	2.2(4)
C6	15.5(4)	15.7(4)	16.6(4)	-4.7(4)	-4.6(3)	2.3(3)
C12	22.5(5)	23.8(5)	19.1(5)	-10.0(4)	-10.4(4)	9.6(4)
C11	19.0(5)	22.5(5)	15.6(4)	-10.5(4)	-7.2(4)	8.1(4)
C4	20.7(5)	22.6(5)	12.5(4)	-5.1(4)	-0.2(4)	4.5(4)
C14	23.2(5)	26.0(5)	26.3(5)	-18.4(5)	-10.3(4)	10.7(4)
C13	20.0(5)	19.3(5)	25.8(5)	-11.3(4)	-10.6(4)	9.2(4)
C18	15.3(4)	29.8(6)	19.0(5)	-9.6(4)	-9.1(4)	5.2(4)

Table 4 Bond Lengths for 16e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O4	1.4288(8)	C9	C10	1.5205(14)
S1	O5	1.4386(8)	C9	C8	1.5383(14)
S1	N1	1.6834(9)	C10	C15	1.3974(14)
S1	C19	1.7743(11)	C10	C11	1.3968(14)
Cl1	C13	1.7415(11)	C2	C3	1.4012(14)
O3	C16	1.3299(13)	C23	C24	1.3940(15)
O3	C18	1.4529(13)	C23	C22	1.3879(15)
O1	C1	1.2200(12)	C24	C19	1.3946(14)

O2	C16	1.2101(13)	C21	C20	1.3928(15)
O6	N2	1.2237(12)	C21	C22	1.3893(15)
O7	N2	1.2289(13)	C19	C20	1.3947(15)
N1	C1	1.4016(12)	C3	C4	1.3887(16)
N1	C9	1.4865(13)	C15	C14	1.3934(15)
N2	C22	1.4806(14)	C5	C6	1.3932(15)
C1	C2	1.4834(14)	C5	C4	1.3919(17)
C7	C2	1.4018(14)	C12	C11	1.3935(15)
C7	C8	1.5110(14)	C12	C13	1.3879(16)
C7	C6	1.3963(14)	C14	C13	1.3890(16)
C16	C8	1.5323(14)			

Table 5 Bond Angles for 16e.

Ato m	Ato m	Ato m	Angle/°	Ato m	Ato m	Ato m	Angle/°
O4	S1	O5	119.11(5)	C7	C2	C1	121.32(9)
O4	S1	N1	111.29(5)	C3	C2	C1	117.64(9)
O4	S1	C19	108.96(5)	C3	C2	C7	120.98(10)
O5	S1	N1	104.76(5)	C7	C8	C16	113.41(8)
O5	S1	C19	108.56(5)	C7	C8	C9	112.43(8)
N1	S1	C19	102.90(5)	C16	C8	C9	110.36(8)
C16	O3	C18	116.21(8)	C22	C23	C24	118.27(10)
C1	N1	S1	117.38(7)	C23	C24	C19	119.00(10)
C1	N1	C9	122.79(8)	C22	C21	C20	118.31(10)
C9	N1	S1	119.57(6)	C24	C19	S1	118.23(8)
O6	N2	O7	123.83(10)	C24	C19	C20	122.13(10)
O6	N2	C22	118.25(9)	C20	C19	S1	119.65(8)
O7	N2	C22	117.92(9)	C21	C20	C19	118.99(10)
O1	C1	N1	120.54(9)	C4	C3	C2	119.41(10)
O1	C1	C2	123.47(9)	C23	C22	N2	118.08(9)
N1	C1	C2	115.94(9)	C23	C22	C21	123.29(10)
C2	C7	C8	119.61(9)	C21	C22	N2	118.61(9)
C6	C7	C2	118.90(9)	C14	C15	C10	120.75(10)
C6	C7	C8	121.48(9)	C4	C5	C6	120.90(10)

O3	C16	C8	110.94(8)	C5	C6	C7	119.93(10)
O2	C16	O3	124.86(9)	C13	C12	C11	119.24(10)
O2	C16	C8	124.16(9)	C12	C11	C10	120.60(10)
N1	C9	C10	113.11(8)	C3	C4	C5	119.83(10)
N1	C9	C8	109.28(8)	C13	C14	C15	119.06(10)
C10	C9	C8	112.47(8)	C12	C13	C11	119.60(9)
C15	C10	C9	117.75(9)	C12	C13	C14	121.24(10)
C11	C10	C9	123.16(9)	C14	C13	C11	119.16(9)
C11	C10	C15	119.10(10)				

Table 6 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for 16e.

Atom	x	y	z	U(eq)
H9	4147	4837	1410	15
H8	2226	2970	2782	16
H23	1399	9619	136	20
H24	2955	7843	416	19
H21	3497	10847	2120	20
H20	5055	9075	2398	20
H3	1953	4785	6089	21
H15	5383	3068	1252	21
H5	-991	1785	6579	24
H6	-23	2114	4553	20
H12	6538	1778	5058	25
H11	4914	3454	4419	21
H4	21	3074	7365	24
H14	7003	1388	1890	26
H18A	-1023	4591	923	31
H18B	-839	5915	1121	31
H18C	-2170	4768	2017	31

Experimental

Single crystals of $C_{23}H_{17}N_2O_7SCl$ **16e** were grown from a supersaturated solution in methylene chloride. A suitable crystal was selected and mounted on a '**Bruker APEX-II CCD**' diffractometer. The crystal was kept at 90.15 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of **16e**

Crystal Data for $C_{23}H_{17}N_2O_7SCl$ ($M = 500.89$ g/mol): triclinic, space group P-1 (no. 2), $a = 9.1593(7)$ Å, $b = 11.0566(8)$ Å, $c = 12.4050(9)$ Å, $\alpha = 64.9500(10)^\circ$, $\beta = 76.9800(10)^\circ$, $\gamma = 89.3270(10)^\circ$, $V = 1103.85(14)$ Å³, $Z = 2$, $T = 90.15$ K, $\mu(\text{MoK}\alpha) = 0.317$ mm⁻¹, $D_{\text{calc}} = 1.507$ g/cm³, 19981 reflections measured ($3.736^\circ \leq 2\Theta \leq 66.388^\circ$), 7848 unique ($R_{\text{int}} = 0.0233$, $R_{\text{sigma}} = 0.0275$) which were used in all calculations. The final R_1 was 0.0373 ($I > 2\sigma(I)$) and wR_2 was 0.1034 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso
At 1.2 times of:
All C(H) groups
At 1.5 times of:
All C(H,H,H) groups
- 2.a Ternary CH refined with riding coordinates:
C9(H9), C8(H8)
- 2.b Aromatic/amide H refined with riding coordinates:
C23(H23), C24(H24), C21(H21), C20(H20), C3(H3), C15(H15),
C5(H5), C6(H6),
C12(H12), C11(H11), C4(H4), C14(H14)
- 2.c Idealised Me refined as rotating group:
C18(H18A,H18B,H18C)

16f

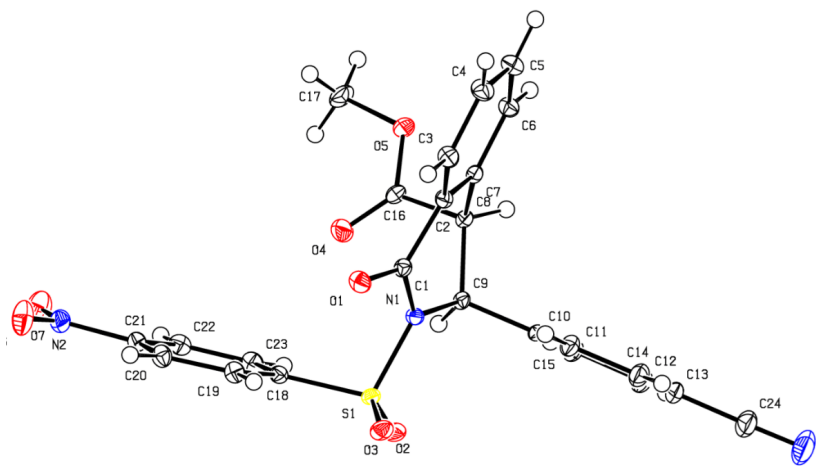


Table 1 Crystal data and structure refinement for 16f.

Identification code	mo_MJD012a
Empirical formula	C ₂₄ H ₁₇ N ₃ O ₇ S
Formula weight	491.46
Temperature/K	99.99
Crystal system	monoclinic
Space group	I2/a
a/Å	13.7214(14)
b/Å	9.2266(9)
c/Å	34.566(4)
α/°	90
β/°	91.593(2)
γ/°	90
Volume/Å ³	4374.4(8)
Z	8
ρ _{calc} /g/cm ³	1.492
μ/mm ⁻¹	0.202
F(000)	2032.0
Crystal size/mm ³	0.403 × 0.398 × 0.36

Radiation MoK α ($\lambda = 0.71073$)
 2 Θ range for data collection/ $^{\circ}$ 4.57 to 61.11
 Index ranges $-19 \leq h \leq 19, -13 \leq k \leq 13, -49 \leq l \leq 49$
 Reflections collected 56151
 Independent reflections 6642 [$R_{\text{int}} = 0.0186, R_{\text{sigma}} = 0.0118$]
 Data/restraints/parameters 6642/0/317
 Goodness-of-fit on F^2 1.049
 Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0326, wR_2 = 0.0880$
 Final R indexes [all data] $R_1 = 0.0357, wR_2 = 0.0900$
 Largest diff. peak/hole / e $\text{\AA}^{-3}$ 0.45/-0.42

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for mo_MJD012a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Ato m	x	y	z	U(eq)
S1	5785.4(2)	2354.9(2)	6690.8(2)	11.63(6)
O1	7013.7(5)	3735.4(9)	6147.3(2)	16.26(15)
O2	6387.2(5)	1223.9(8)	6547.3(2)	16.74(15)
O3	4892.2(5)	2005.5(8)	6875.0(2)	16.23(15)
O5	4160.9(6)	7795.9(8)	6267.2(2)	18.00(15)
O4	4831.0(7)	6303.2(9)	6714.9(2)	22.43(17)
O6	9009.4(6)	6073.6(11)	7747.9(3)	28.6(2)
O7	7677.0(7)	6925.5(10)	7980.5(3)	28.14(19)
N1	5436.8(6)	3454.0(9)	6321.2(2)	11.01(15)
N2	8121.3(7)	6117.3(10)	7765.8(3)	18.38(18)
C9	4388.3(6)	3827.6(10)	6279.3(3)	10.64(16)
C7	4891.7(7)	5586.1(10)	5757.1(3)	11.36(16)
C1	6153.9(7)	4003.3(10)	6082.8(3)	11.68(16)
C10	3797.8(7)	2682.8(10)	6061.2(3)	11.48(16)
C16	4459.8(7)	6512(1)	6399.4(3)	12.40(17)
C8	4252.7(7)	5336.9(10)	6099.1(3)	10.80(16)
C2	5810.6(7)	4934.3(10)	5755.7(3)	11.94(17)

C22	6536.4(7)	5208.9(11)	7521.8(3)	15.66(18)
C21	7543.5(7)	5153.8(11)	7506.5(3)	14.43(18)
C19	7497.1(7)	3399.5(11)	7000.7(3)	14.31(18)
C18	6483.5(7)	3458.2(10)	7009.1(3)	12.12(17)
C15	4193.6(7)	1774.8(11)	5784.9(3)	14.82(18)
C3	6447.8(7)	5211.9(11)	5456.0(3)	15.26(18)
C11	2812.7(7)	2553.7(11)	6148.4(3)	15.88(19)
C6	4615.3(7)	6528.4(11)	5458.4(3)	14.88(18)
C20	8040.2(7)	4257.5(11)	7256.9(3)	15.55(18)
C23	5996.4(7)	4330.7(11)	7269.1(3)	14.84(18)
C14	3611.3(8)	748.0(12)	5593.4(3)	18.2(2)
N0A A	1502.9(10)	-1249.1(15)	5338.5(4)	37.1(3)
C12	2228.3(8)	1527.5(12)	5962.7(3)	19.4(2)
C13	2630.0(8)	629.3(12)	5684.2(3)	18.3(2)
C5	5253.2(8)	6814.6(12)	5162.5(3)	17.55(19)
C4	6165.8(8)	6154.7(12)	5160.1(3)	17.51(19)
C17	4342.7(9)	9024.3(11)	6520.1(3)	21.2(2)
C24	2012.8(9)	-433.1(14)	5491.6(3)	25.0(2)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 16f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Ato m	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
S1	10.63(10)	9.81(10)	14.45(11)	2.04(7)	0.06(8)	-0.92(7)
O1	9.4(3)	20.7(4)	18.6(3)	4.0(3)	0.0(3)	0.1(3)
O2	16.8(3)	10.7(3)	22.7(4)	-0.1(3)	0.0(3)	2.0(3)
O3	12.8(3)	16.6(3)	19.4(3)	5.3(3)	2.1(3)	-3.3(3)
O5	25.4(4)	9.9(3)	18.5(4)	-1.7(3)	-3.2(3)	0.3(3)
O4	33.8(4)	16.2(4)	16.9(4)	-1.8(3)	-6.2(3)	1.4(3)
O6	19.3(4)	39.5(5)	27.0(4)	-8.9(4)	-1.7(3)	-7.5(4)
O7	31.5(5)	29.0(5)	24.1(4)	-12.1(3)	3.1(3)	-1.9(4)
N1	8.4(3)	11.6(3)	13.0(3)	2.1(3)	-0.1(3)	-0.3(3)
N2	21.5(4)	19.7(4)	13.9(4)	-0.6(3)	-1.1(3)	-3.8(3)

C9	7.6(3)	10.7(4)	13.6(4)	0.0(3)	-0.1(3)	-0.5(3)
C7	11.1(4)	10.6(4)	12.3(4)	-1.0(3)	-0.4(3)	-1.4(3)
C1	10.3(4)	12.2(4)	12.6(4)	0.1(3)	0.7(3)	-1.3(3)
C10	10.8(4)	10.4(4)	13.2(4)	1.8(3)	-0.8(3)	-2.0(3)
C16	11.4(4)	11.0(4)	14.9(4)	-0.9(3)	2.8(3)	-1.3(3)
C8	9.7(4)	9.6(4)	13.1(4)	-0.6(3)	0.3(3)	-0.3(3)
C2	10.8(4)	12.7(4)	12.3(4)	0.6(3)	-0.4(3)	-0.9(3)
C22	17.0(4)	16.2(4)	13.8(4)	0.3(3)	1.9(3)	2.3(3)
C21	16.5(4)	14.8(4)	11.9(4)	0.5(3)	-1.3(3)	-1.6(3)
C19	11.9(4)	16.4(4)	14.6(4)	-0.3(3)	1.0(3)	1.0(3)
C18	11.3(4)	12.2(4)	12.8(4)	1.7(3)	-0.8(3)	-0.1(3)
C15	14.2(4)	15.1(4)	15.3(4)	-1.3(3)	1.2(3)	-3.2(3)
C3	12.4(4)	18.6(5)	14.8(4)	1.4(3)	1.4(3)	-0.8(3)
C11	11.3(4)	16.0(4)	20.3(5)	-0.5(4)	0.8(3)	-1.9(3)
C6	15.1(4)	14.6(4)	14.8(4)	1.2(3)	-1.1(3)	1.3(3)
C20	12.1(4)	19.1(5)	15.4(4)	0.1(4)	0.1(3)	-0.4(3)
C23	12.4(4)	17.1(4)	15.1(4)	1.6(3)	1.1(3)	1.7(3)
C14	21.7(5)	17.1(5)	15.7(4)	-2.8(4)	0.3(4)	-5.2(4)
N0						
AA	38.3(6)	41.3(7)	31.4(6)	-6.7(5)	-2.6(5)	-22.3(5)
C12	12.8(4)	21.1(5)	24.2(5)	0.9(4)	-0.7(4)	-5.4(4)
C13	20.3(5)	17.4(5)	17.0(5)	1.4(4)	-4.2(4)	-8.1(4)
C5	20.0(5)	18.1(5)	14.5(4)	3.5(4)	-0.7(4)	0.6(4)
C4	17.2(4)	21.7(5)	13.7(4)	3.1(4)	2.3(3)	-1.3(4)
C17	30.1(6)	10.9(4)	22.5(5)	-4.7(4)	1.6(4)	-3.1(4)
C24	26.0(5)	27.0(6)	22.0(5)	-0.4(4)	-1.8(4)	-12.3(5)

Table 4 Bond Lengths for 16f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.4282(8)	C10	C15	1.3922(14)
S1	O3	1.4335(7)	C10	C11	1.3981(13)
S1	N1	1.6896(8)	C16	C8	1.5223(13)
S1	C18	1.7625(10)	C2	C3	1.3978(13)
O1	C1	1.2198(12)	C22	C21	1.3853(14)

O5	C16	1.3303(12)	C22	C23	1.3901(14)
O5	C17	1.4487(13)	C21	C20	1.3875(14)
O4	C16	1.2062(13)	C19	C18	1.3930(13)
O6	N2	1.2226(13)	C19	C20	1.3890(14)
O7	N2	1.2262(13)	C18	C23	1.3913(14)
N1	C9	1.4827(12)	C15	C14	1.3943(14)
N1	C1	1.3962(12)	C3	C4	1.3894(14)
N2	C21	1.4775(13)	C11	C12	1.3866(14)
C9	C10	1.5187(13)	C6	C5	1.3900(14)
C9	C8	1.5348(13)	C14	C13	1.3954(15)
C7	C8	1.5088(13)	N0AA	C24	1.1471(16)
C7	C2	1.3971(13)	C12	C13	1.3953(16)
C7	C6	1.3942(13)	C13	C24	1.4456(15)
C1	C2	1.4859(13)	C5	C4	1.3927(15)

Table 5 Bond Angles for 16f.

Ato m	Ato m	Ato m	Angle/°	Ato m	Ato m	Ato m	Angle/°
O2	S1	O3	119.98(5)	C7	C8	C9	112.94(8)
O2	S1	N1	109.28(4)	C7	C8	C16	108.92(7)
O2	S1	C18	109.24(5)	C16	C8	C9	110.57(8)
O3	S1	N1	104.08(4)	C7	C2	C1	120.89(8)
O3	S1	C18	108.00(5)	C7	C2	C3	120.45(9)
N1	S1	C18	105.24(4)	C3	C2	C1	118.57(8)
C16	O5	C17	116.31(8)	C21	C22	C23	118.00(9)
C9	N1	S1	117.84(6)	C22	C21	N2	118.28(9)
C1	N1	S1	118.35(6)	C22	C21	C20	123.60(9)
C1	N1	C9	123.76(8)	C20	C21	N2	118.12(9)
O6	N2	O7	124.32(10)	C20	C19	C18	118.87(9)
O6	N2	C21	117.92(9)	C19	C18	S1	119.35(8)
O7	N2	C21	117.76(9)	C23	C18	S1	118.36(7)
N1	C9	C10	112.94(8)	C23	C18	C19	122.27(9)
N1	C9	C8	110.91(7)	C10	C15	C14	120.35(9)
C10	C9	C8	111.87(7)	C4	C3	C2	119.56(9)

C2	C7	C8	118.76(8)	C12	C11	C10	120.56(10)
C6	C7	C8	121.54(8)	C5	C6	C7	119.97(9)
C6	C7	C2	119.53(9)	C21	C20	C19	118.16(9)
O1	C1	N1	120.82(9)	C22	C23	C18	119.06(9)
O1	C1	C2	122.73(9)	C15	C14	C13	119.36(10)
N1	C1	C2	116.44(8)	C11	C12	C13	119.38(10)
C15	C10	C9	123.11(8)	C14	C13	C24	120.42(11)
C15	C10	C11	119.64(9)	C12	C13	C14	120.71(9)
C11	C10	C9	117.25(9)	C12	C13	C24	118.87(10)
O5	C16	C8	110.50(8)	C6	C5	C4	120.40(9)
O4	C16	O5	124.83(9)	C3	C4	C5	120.09(10)
O4	C16	C8	124.67(9)	N0A A	C24	C13	178.15(15)

Table 6 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 16f.

Atom	x	y	z	U(eq)
H9	4128	3877	6546	13
H8	3557	5431	6008	13
H22	6224	5828	7700	19
H19	7812	2783	6823	17
H15	4864	1855	5726	18
H3	7069	4759	5455	18
H11	2541	3174	6336	19
H6	3991	6975	5457	18
H20	8733	4231	7261	19
H23	5304	4326	7274	18
H14	3880	135	5403	22
H12	1561	1437	6024	23
H5	5066	7464	4961	21
H4	6596	6349	4956	21
H17A	5003	9393	6481	32
H17B	4281	8721	6790	32
H17C	3867	9790	6460	32

Experimental

Single crystals of $C_{24}H_{17}N_3O_7S$ **16f** were grown from a supersaturated solution in methylene chloride. A suitable crystal was selected and mounted on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 99.99 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of **16f**

Crystal Data for $C_{24}H_{17}N_3O_7S$ ($M = 491.46$ g/mol): monoclinic, space group I2/a (no. 15), $a = 13.7214(14)$ Å, $b = 9.2266(9)$ Å, $c = 34.566(4)$ Å, $\beta = 91.593(2)^\circ$, $V = 4374.4(8)$ Å³, $Z = 8$, $T = 99.99$ K, $\mu(\text{MoK}\alpha) = 0.202$ mm⁻¹, $D_{\text{calc}} = 1.492$ g/cm³, 56151 reflections measured ($4.57^\circ \leq 2\Theta \leq 61.11^\circ$), 6642 unique ($R_{\text{int}} = 0.0186$, $R_{\text{sigma}} = 0.0118$) which were used in all calculations. The final R_1 was 0.0326 ($I > 2\sigma(I)$) and wR_2 was 0.0900 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

C9(H9), C8(H8)

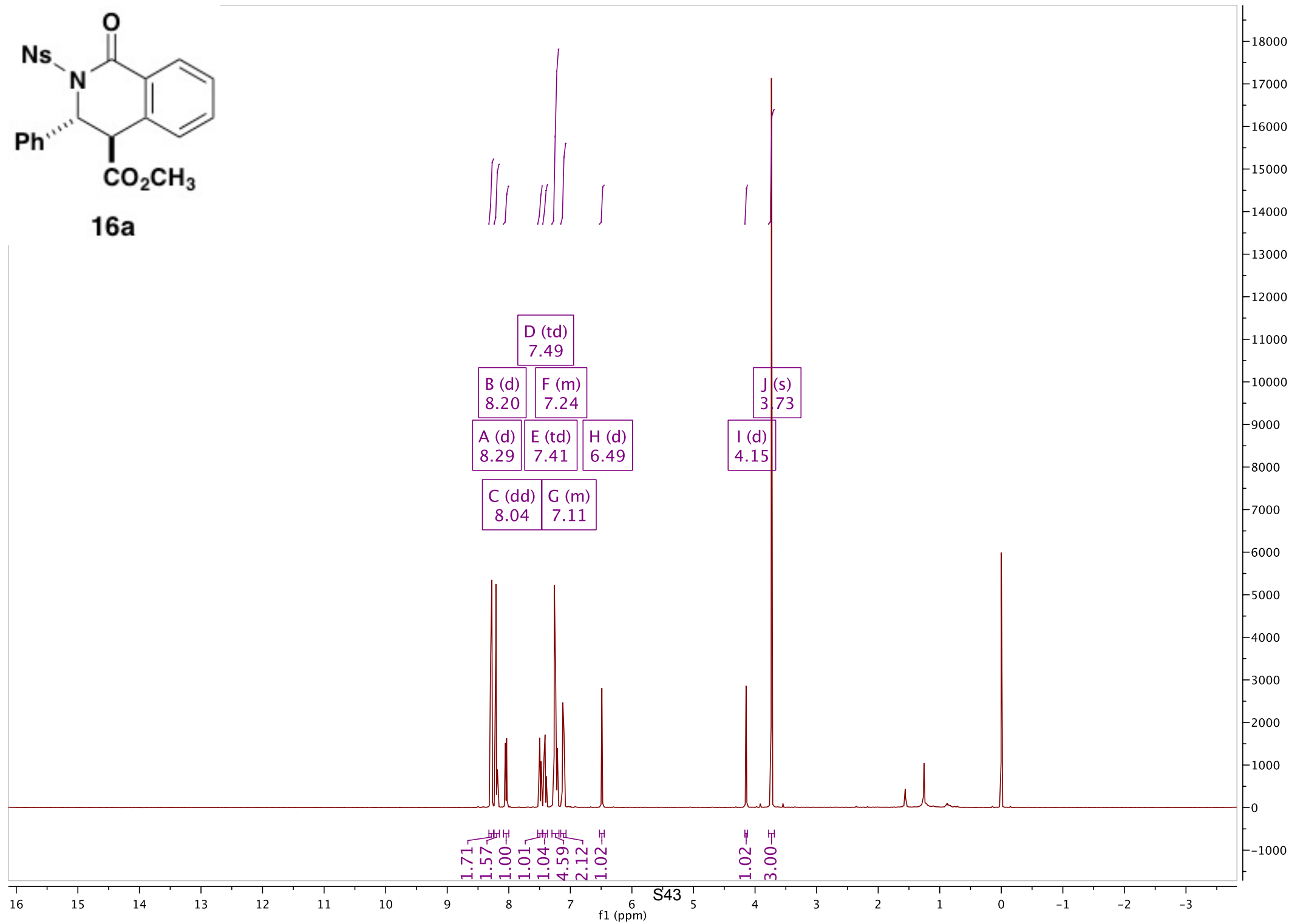
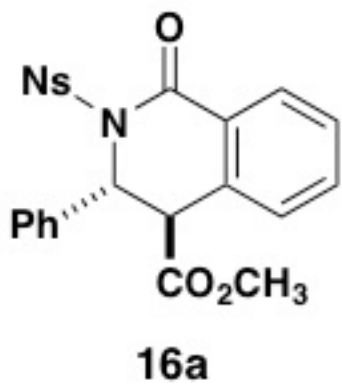
2.b Aromatic/amide H refined with riding coordinates:

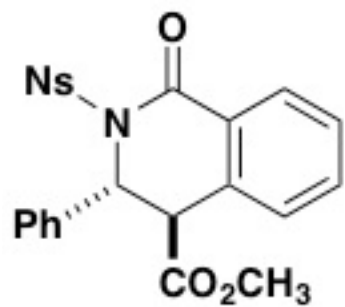
C22(H22), C19(H19), C15(H15), C3(H3), C11(H11), C6(H6),
C20(H20), C23(H23),
C14(H14), C12(H12), C5(H5), C4(H4)

2.c Idealised Me refined as rotating group:

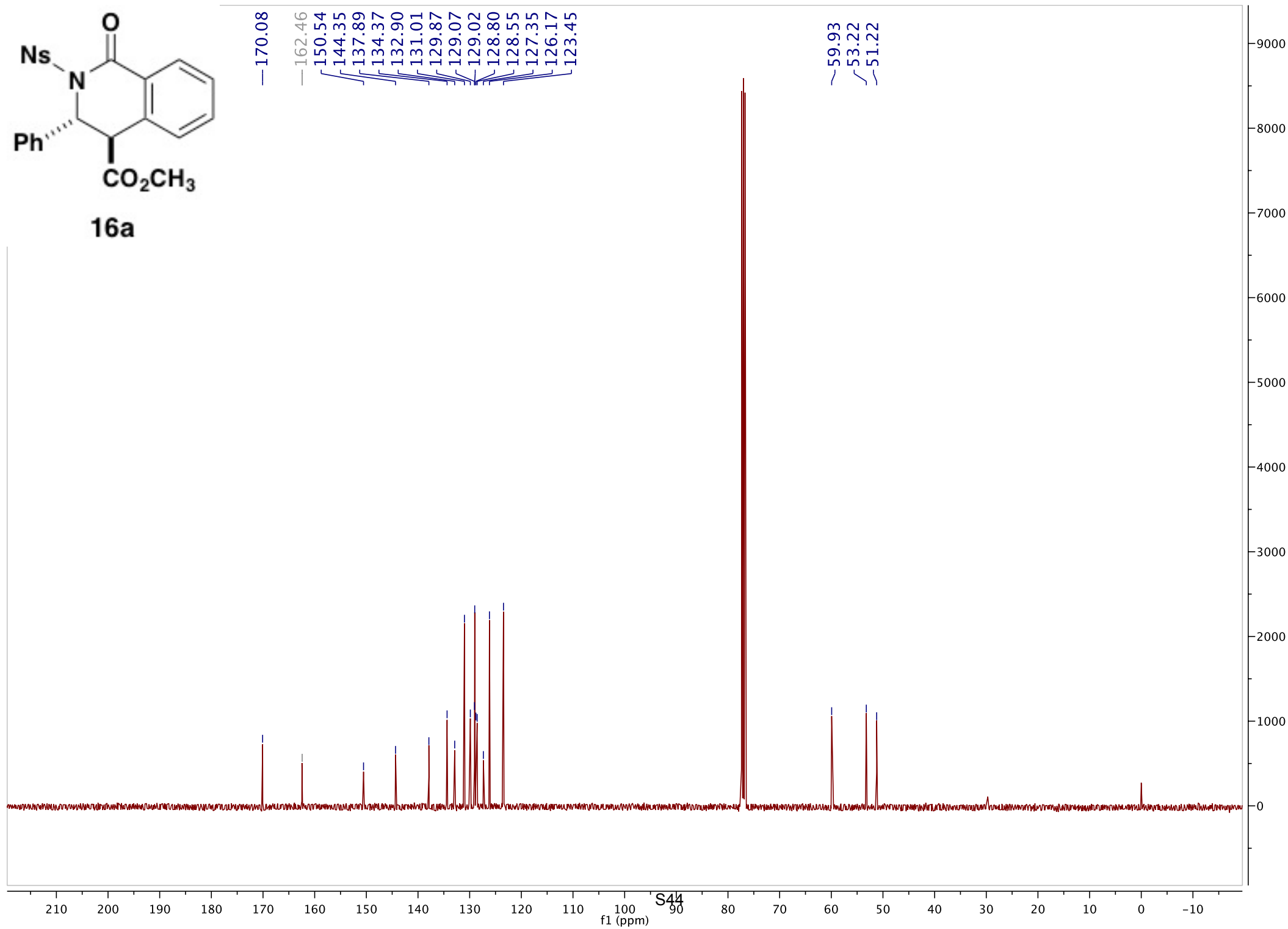
C17(H17A,H17B,H17C)

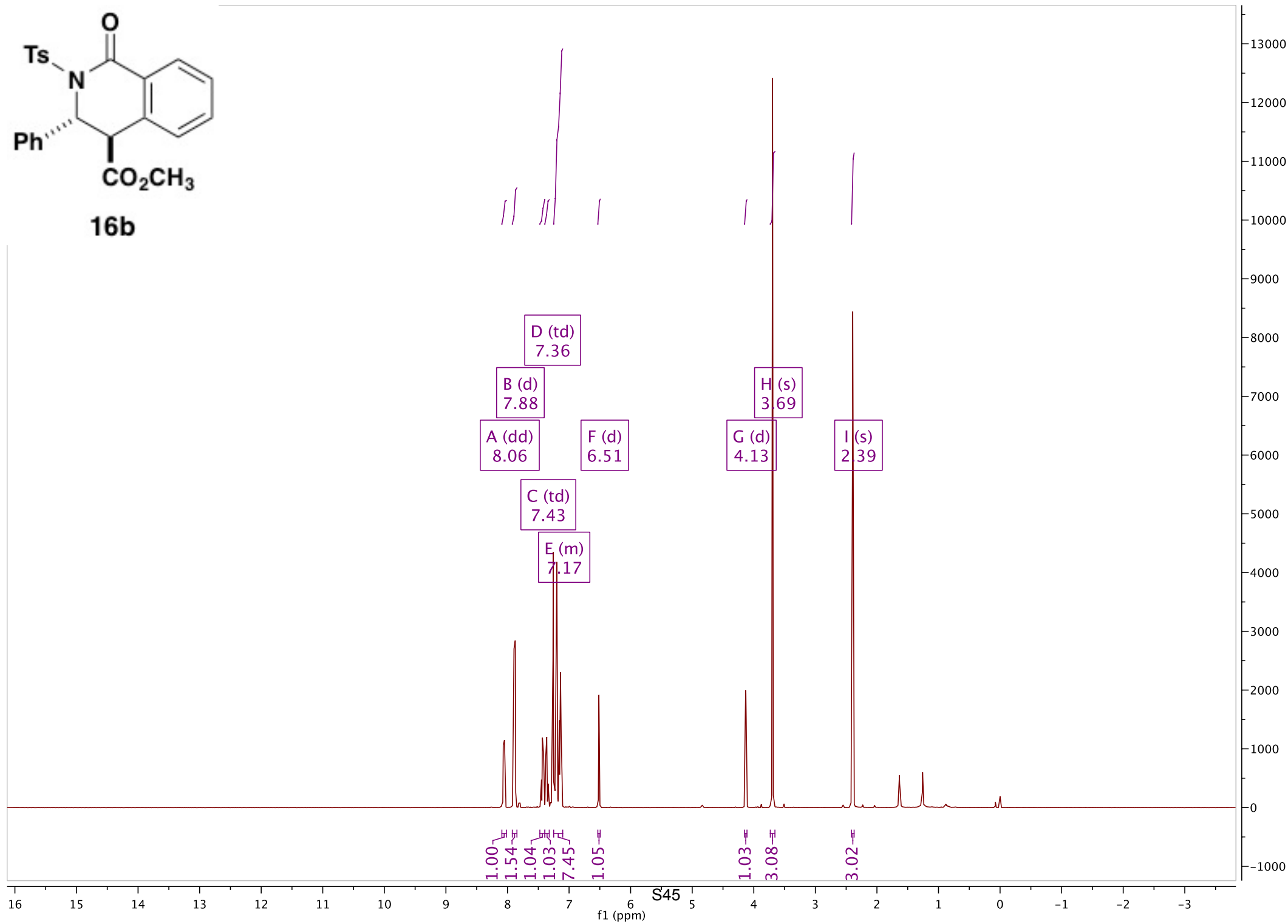
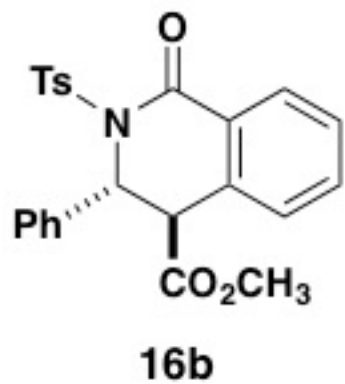
This report has been created with Olex2, compiled on 2016.02.16 svn.r3265 for OlexSys. Please [let us know](#) if there are any errors or if you would like to have additional features.

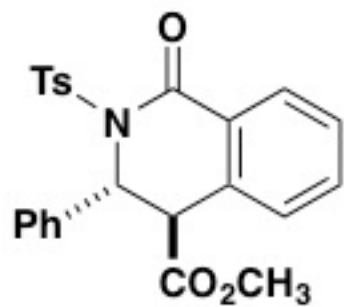




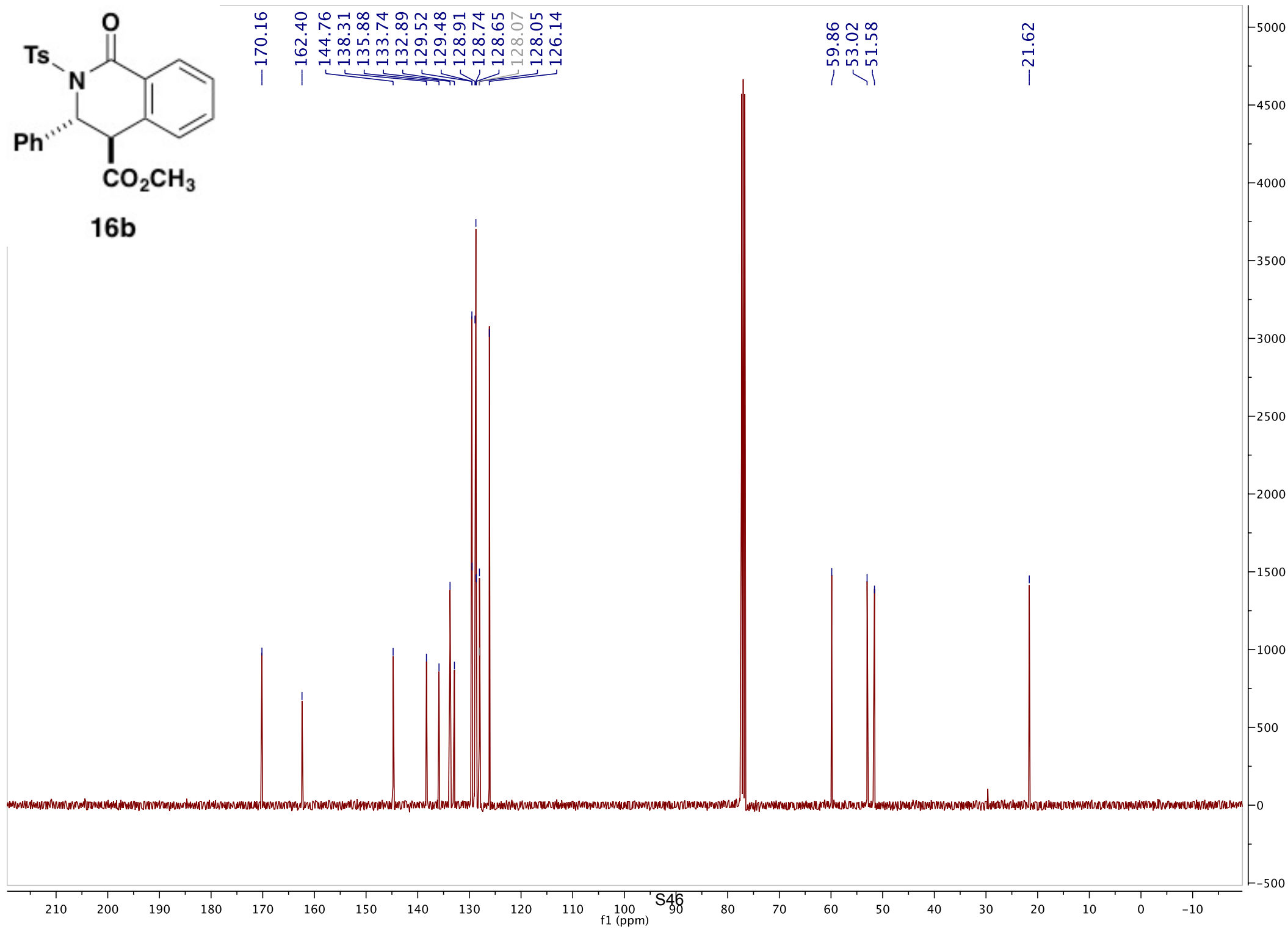
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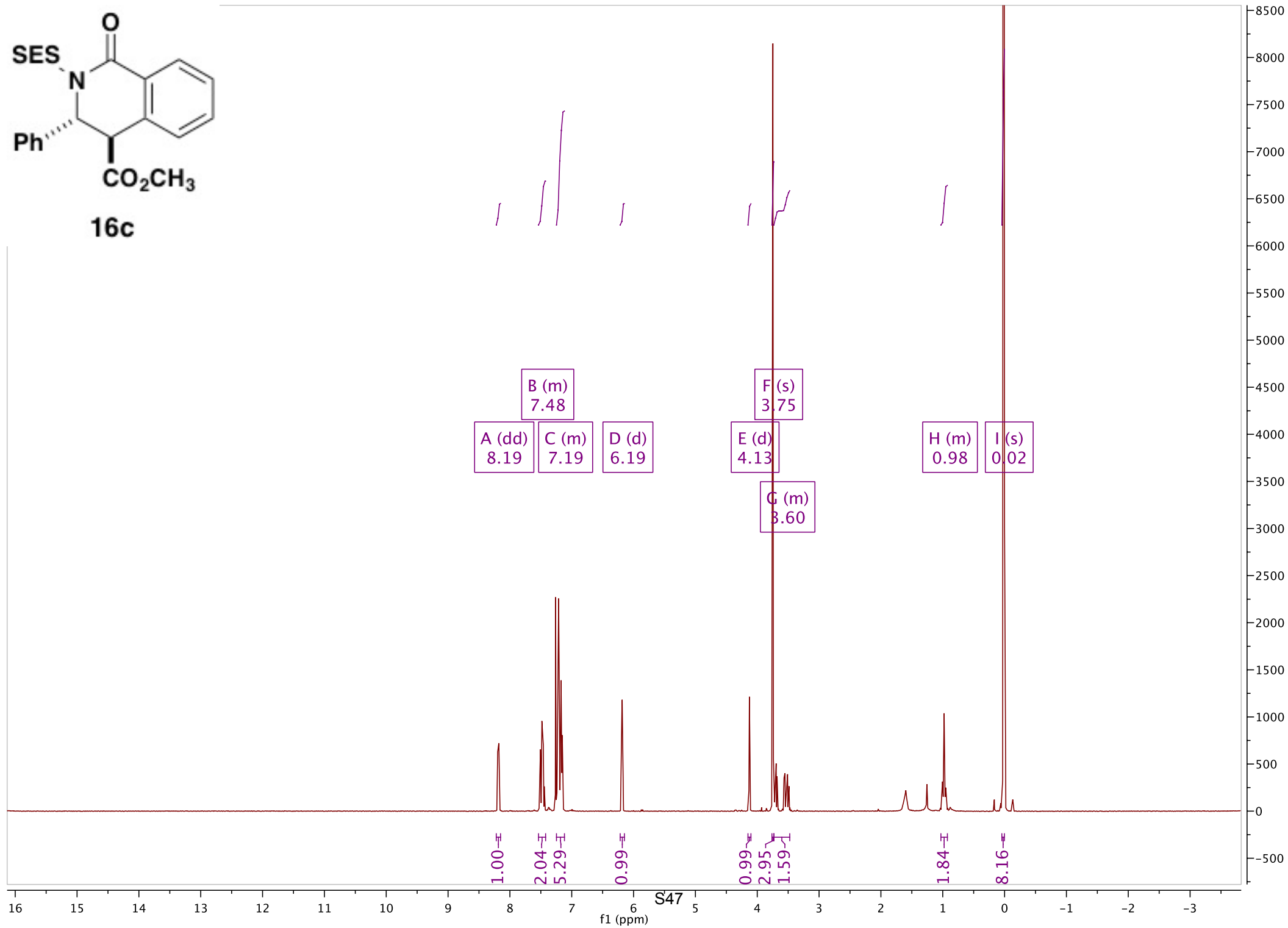
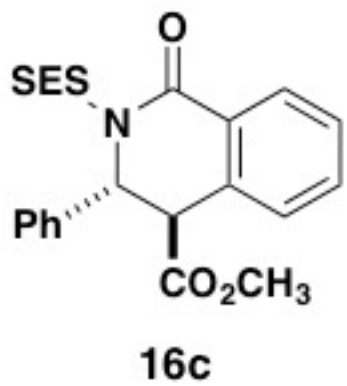


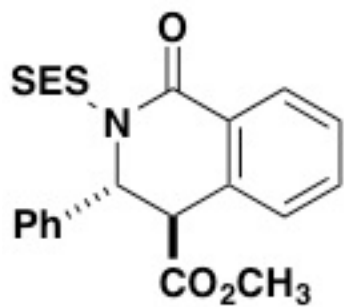




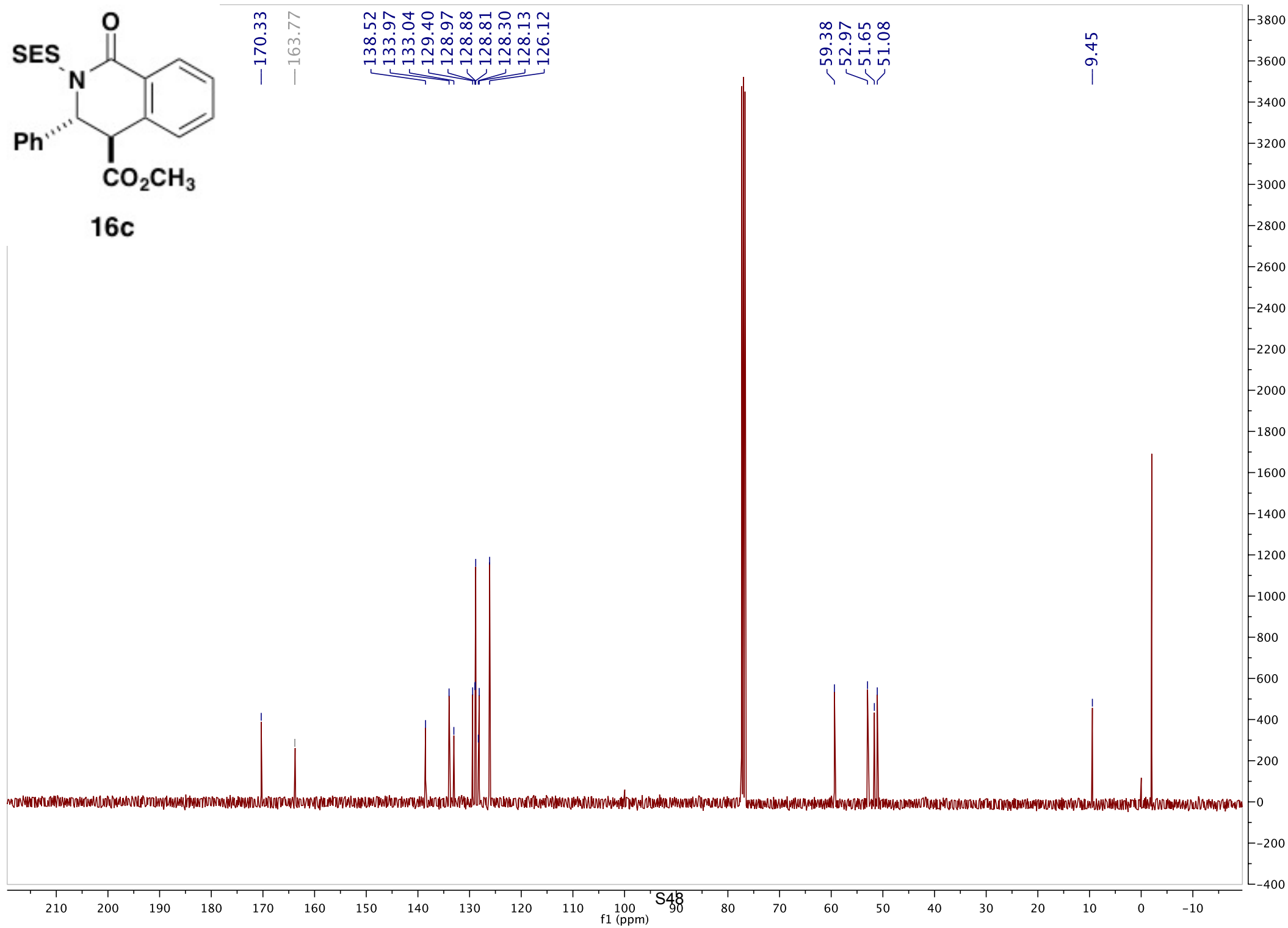
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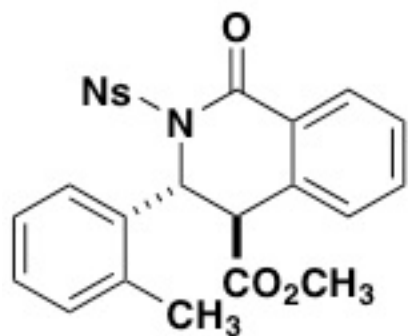




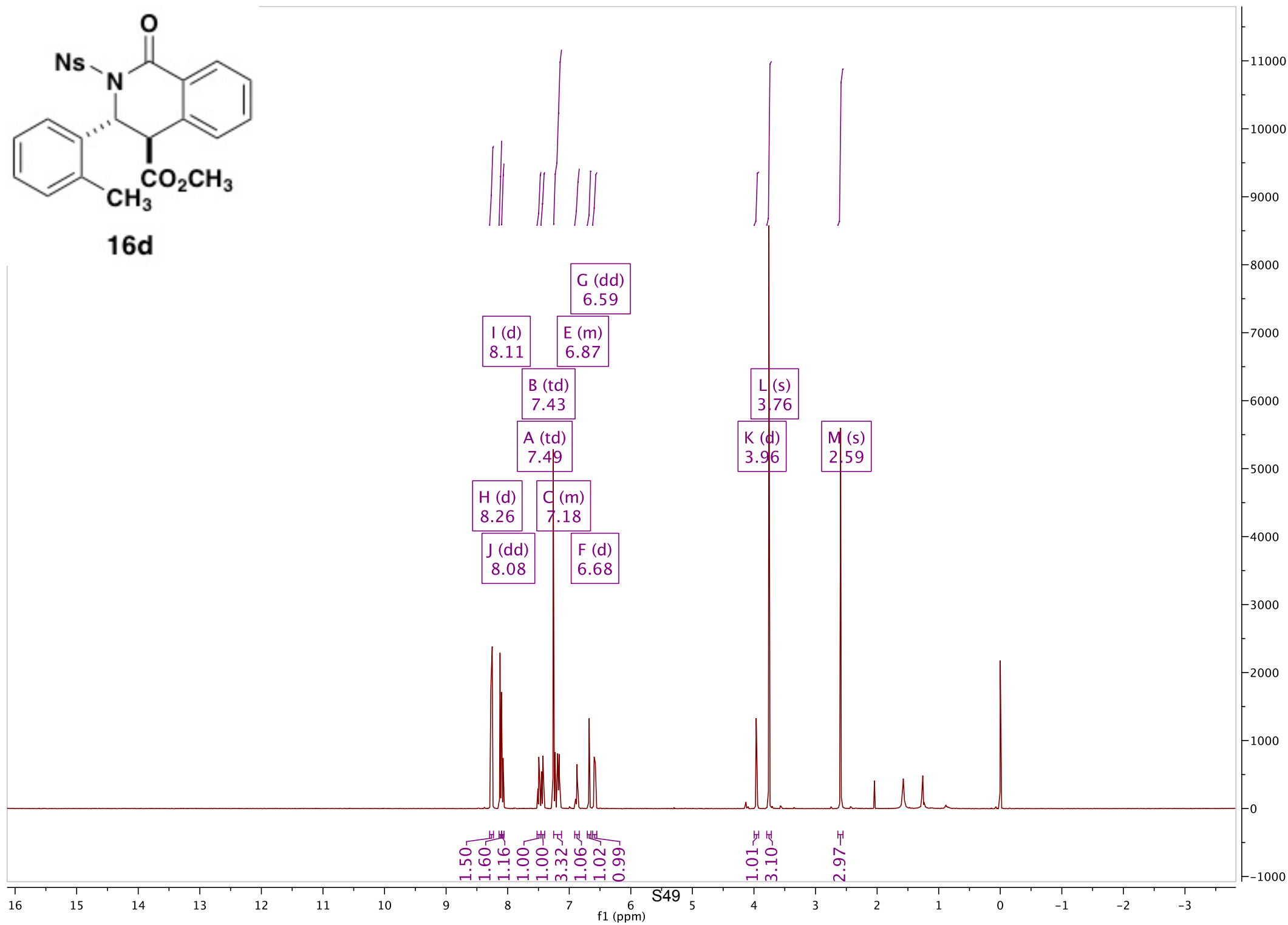


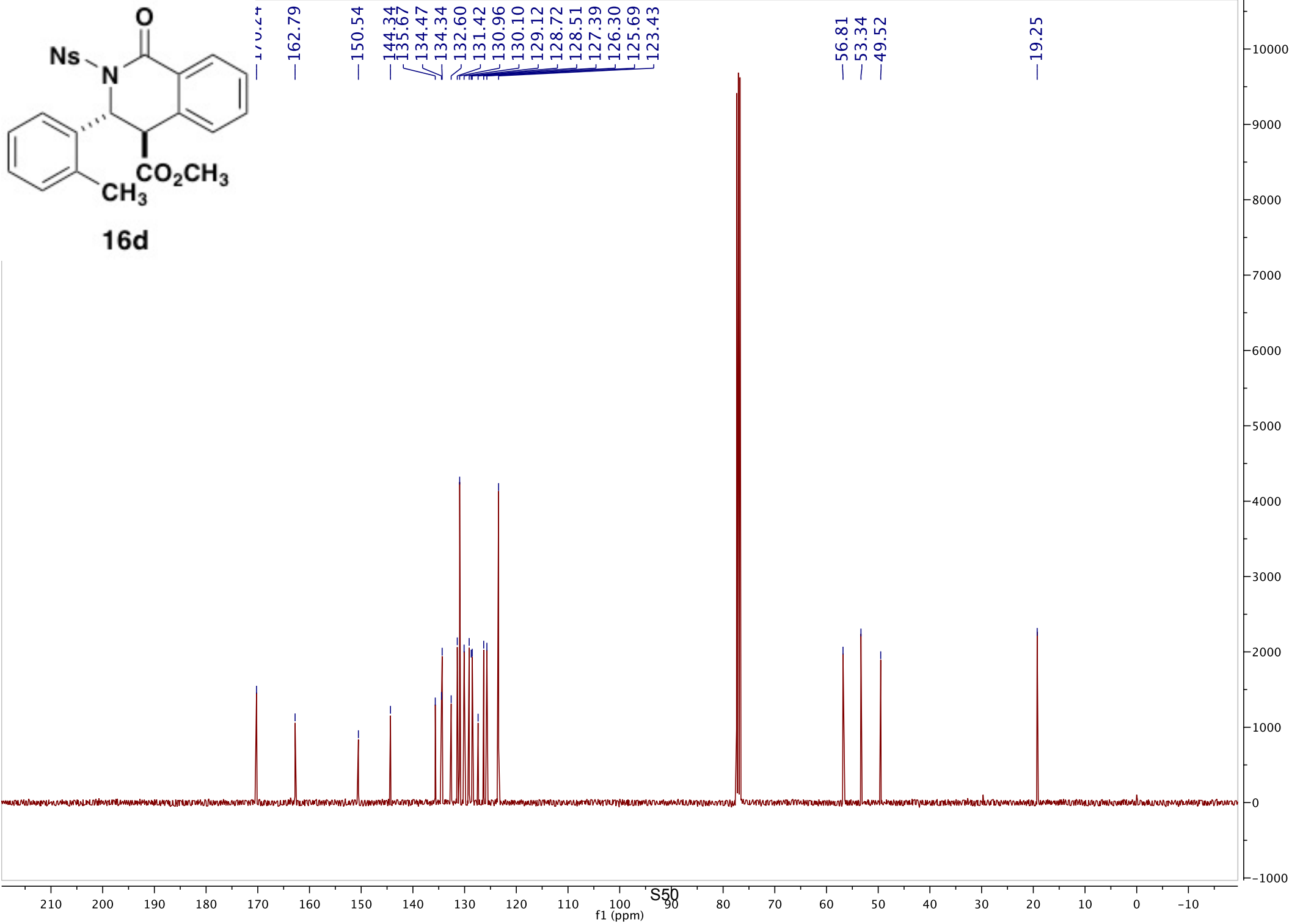
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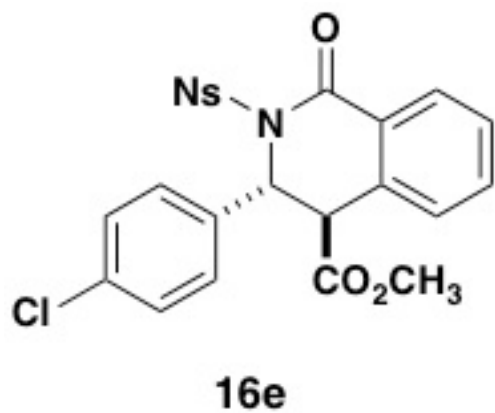


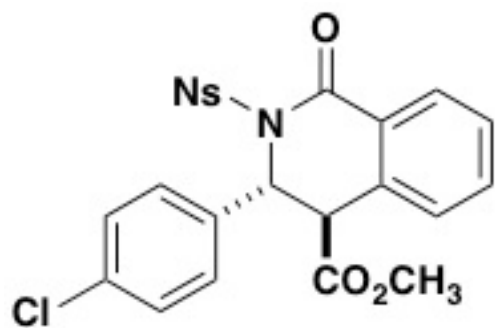


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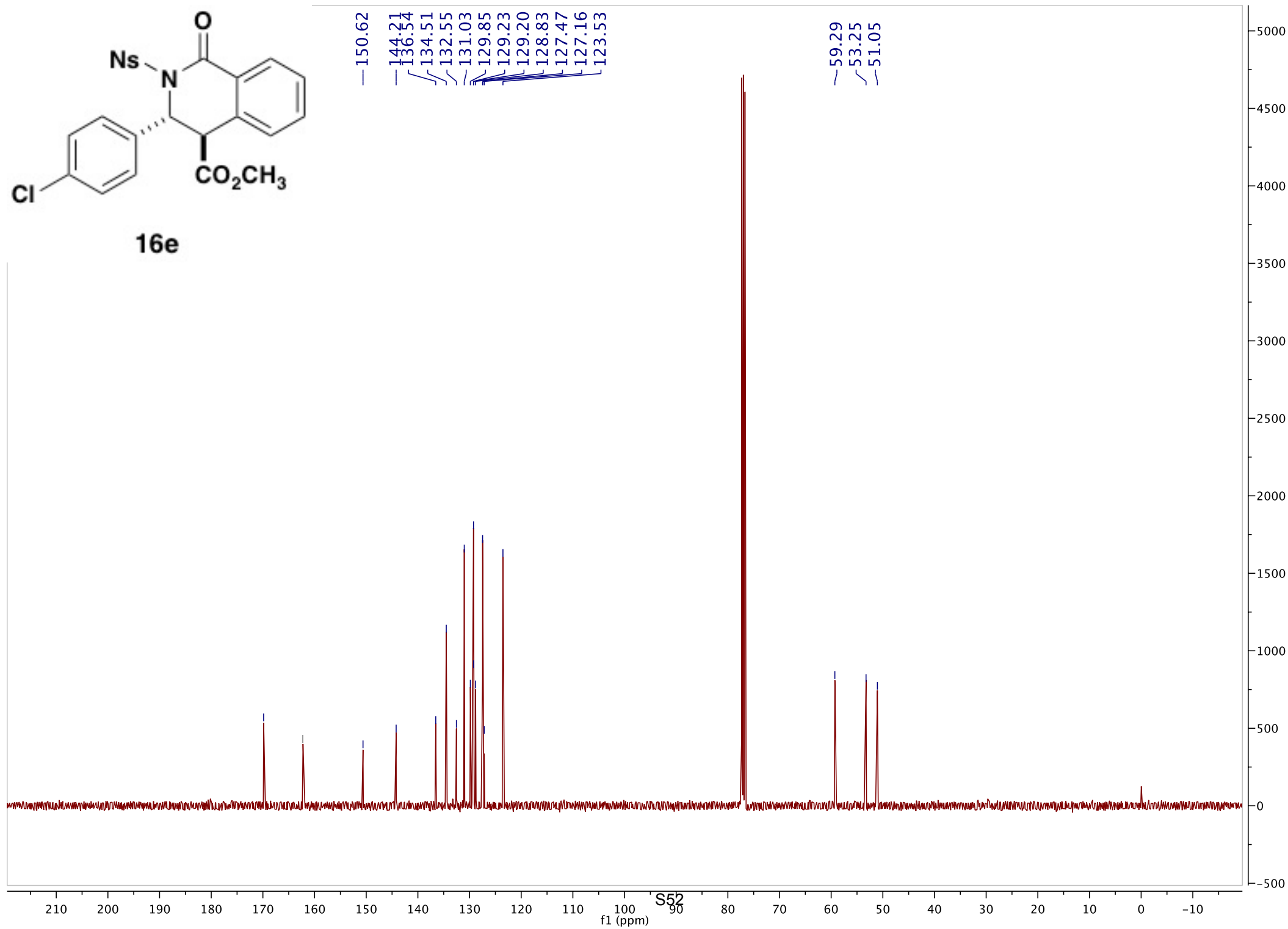


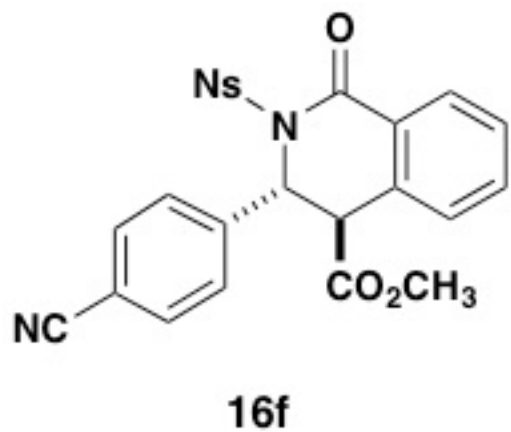


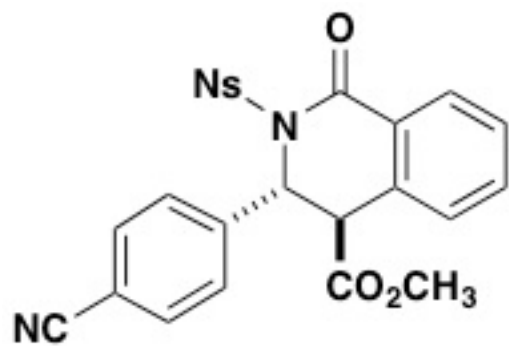




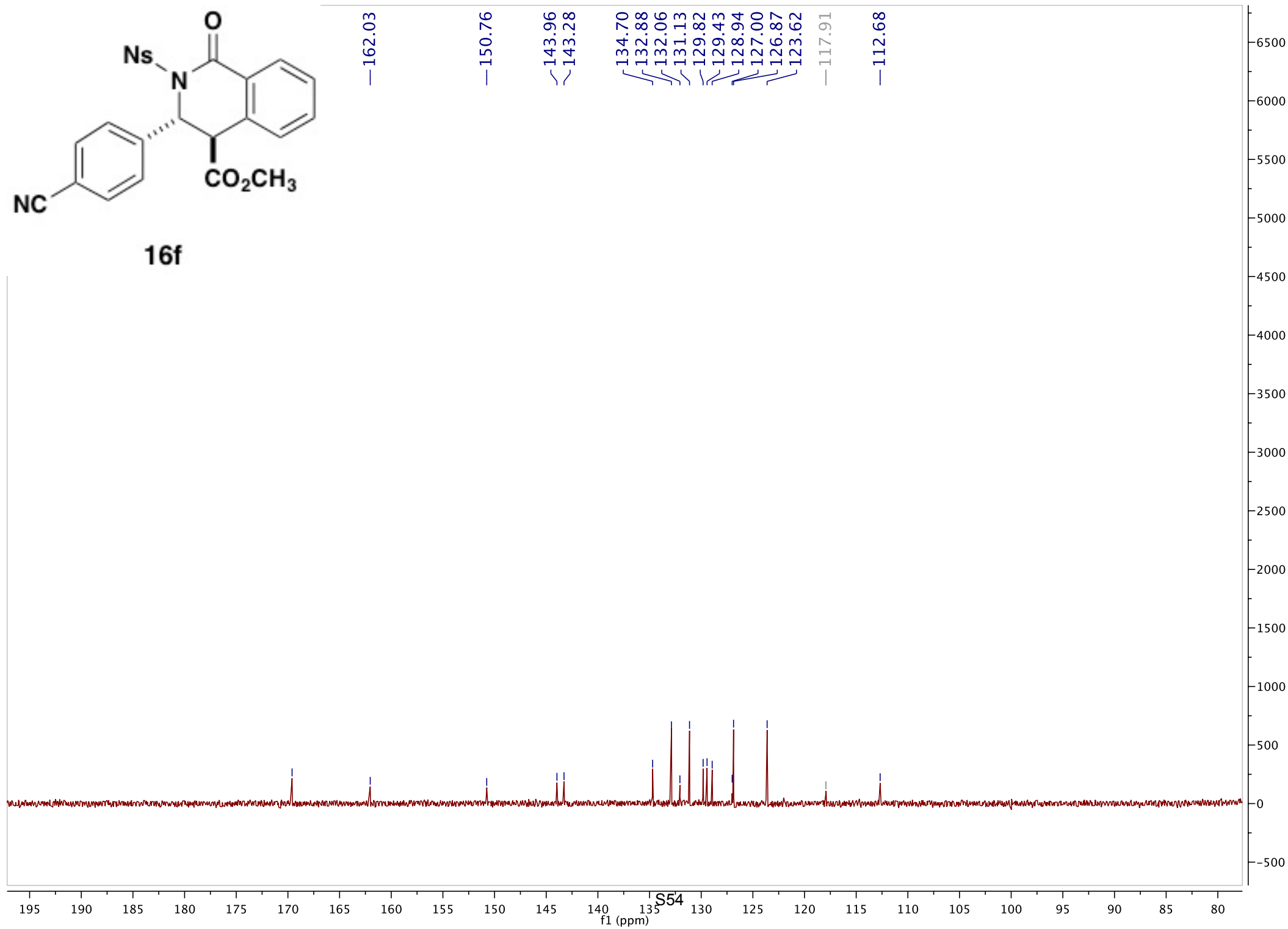
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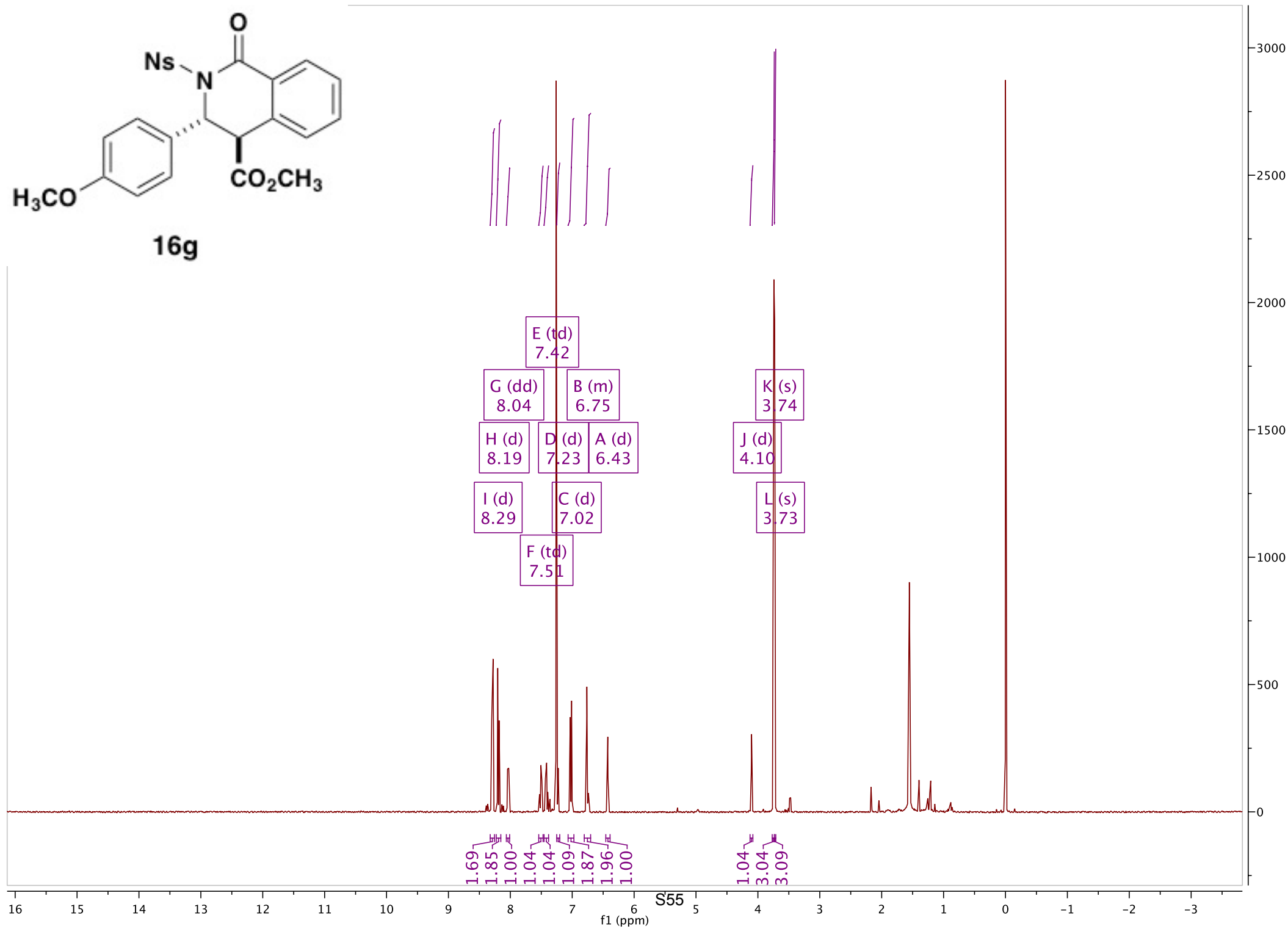
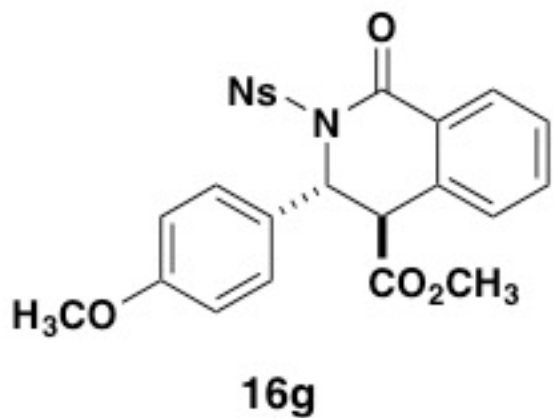


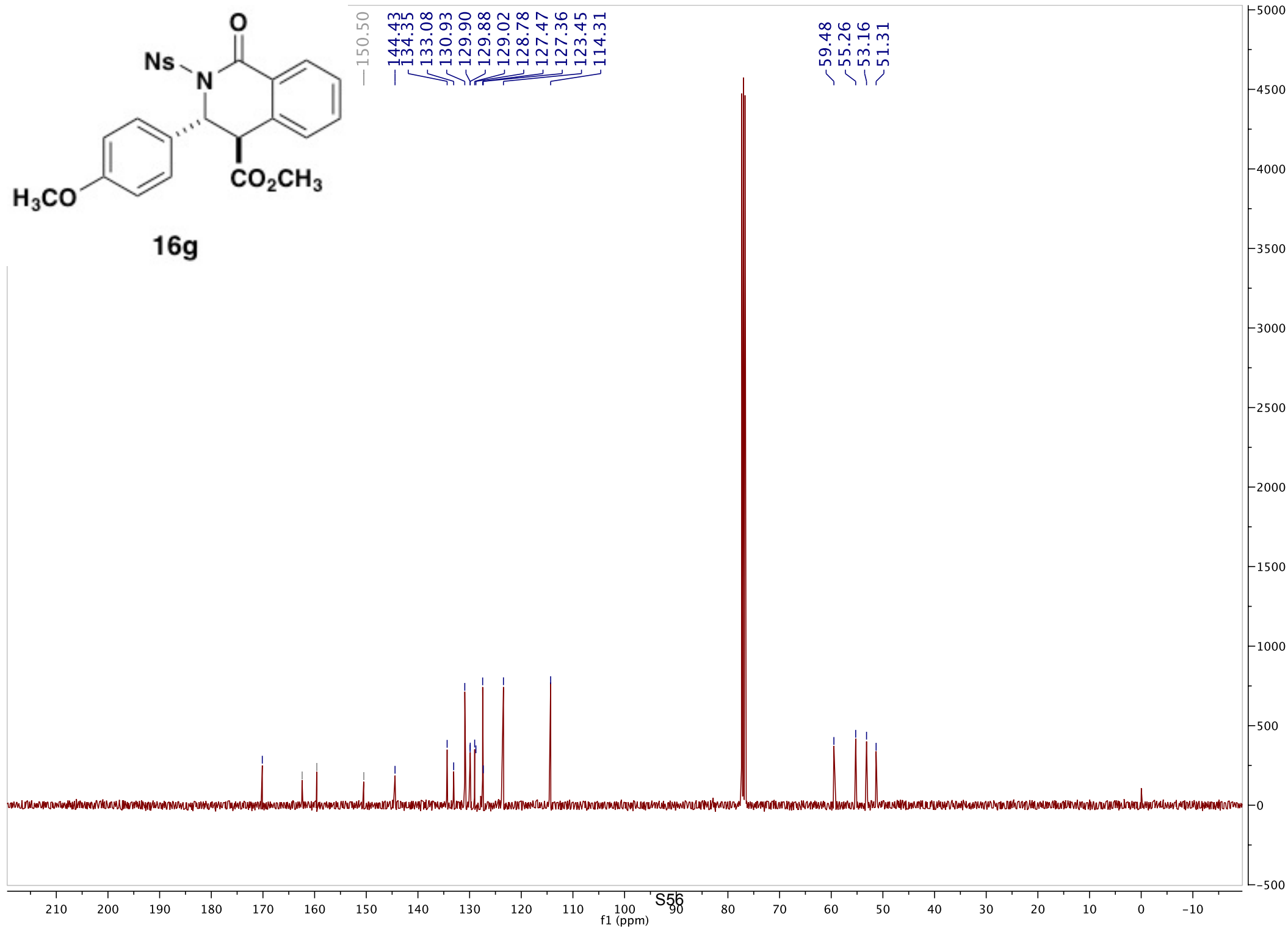
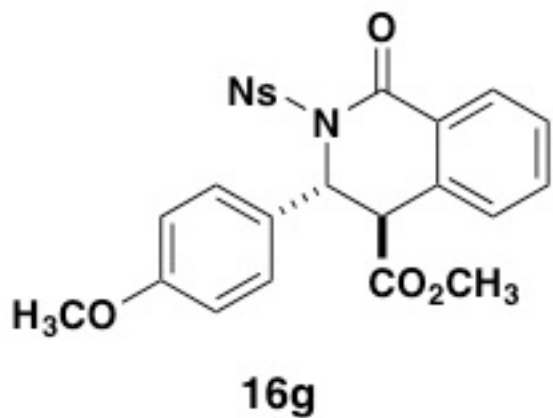


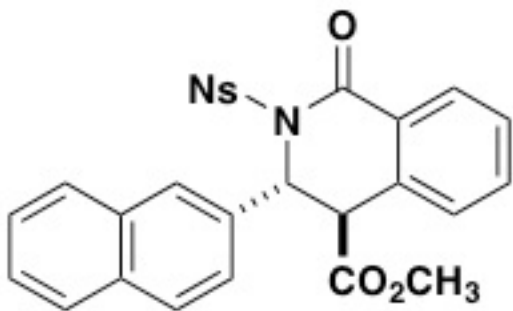


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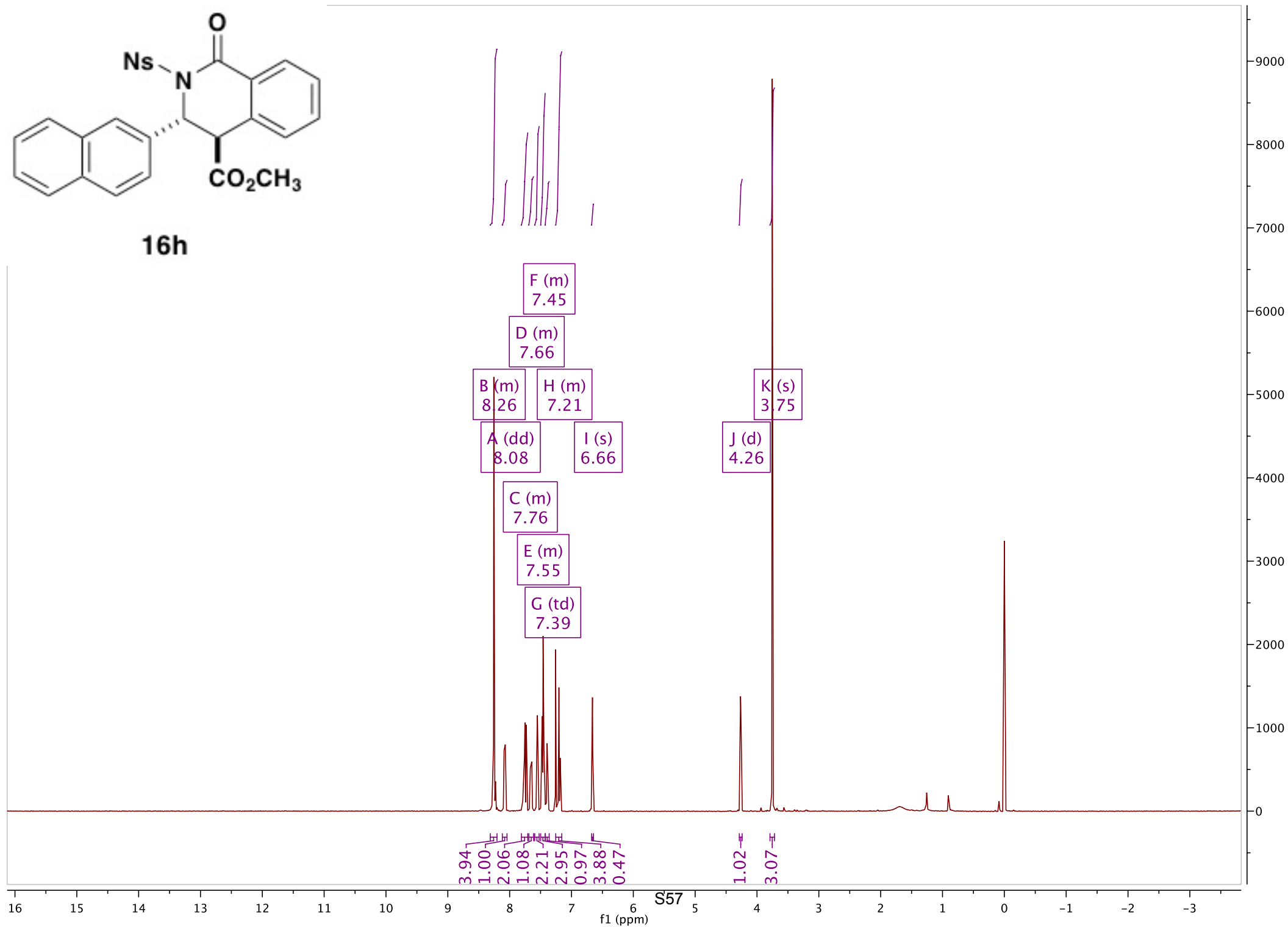


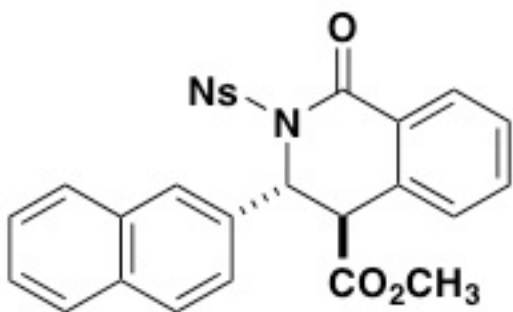




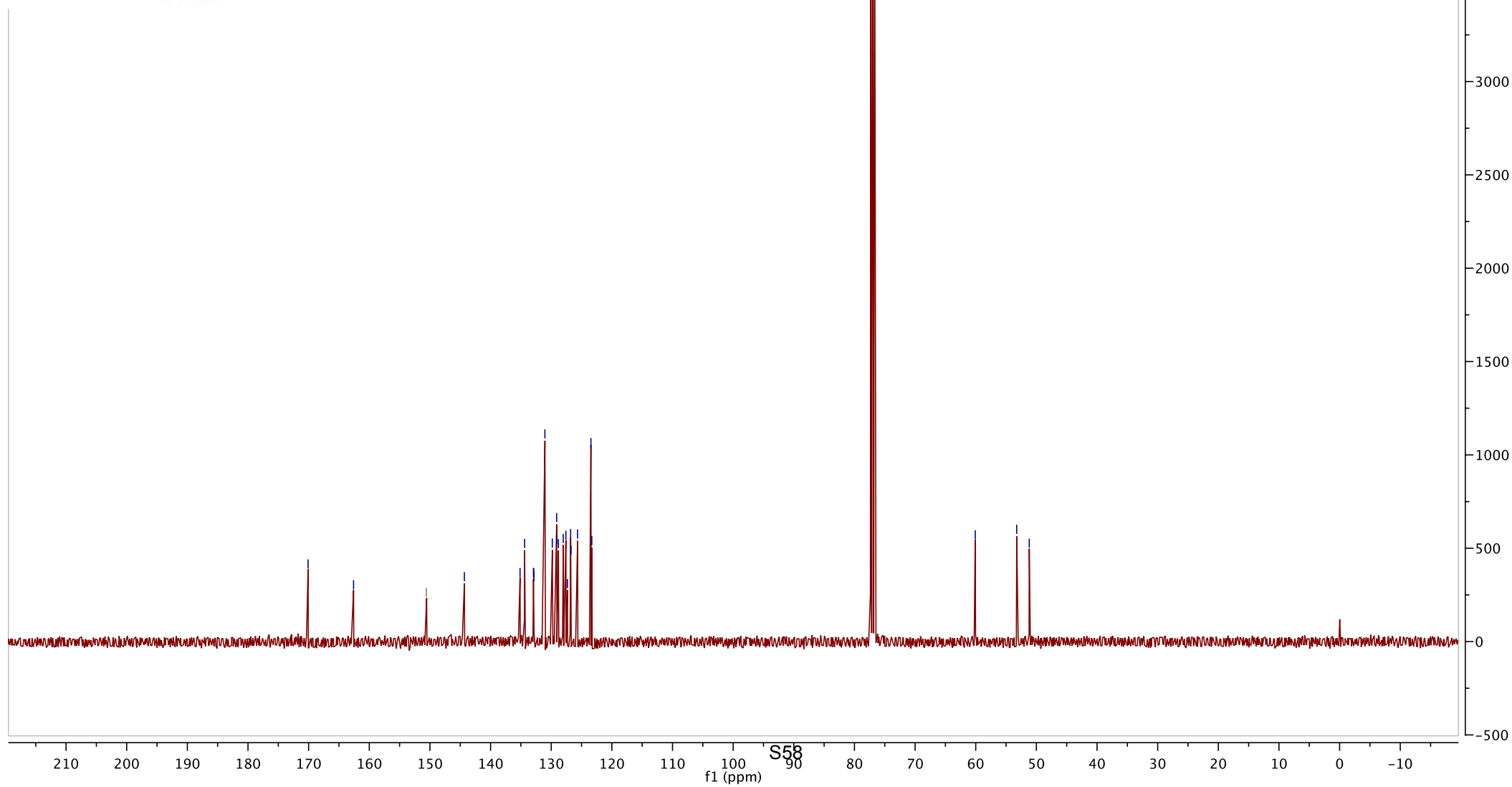


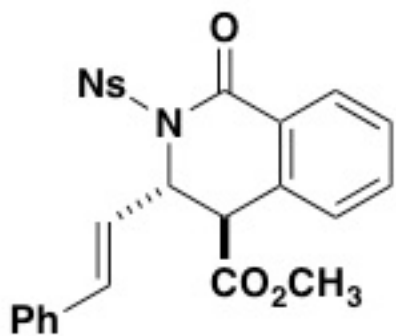
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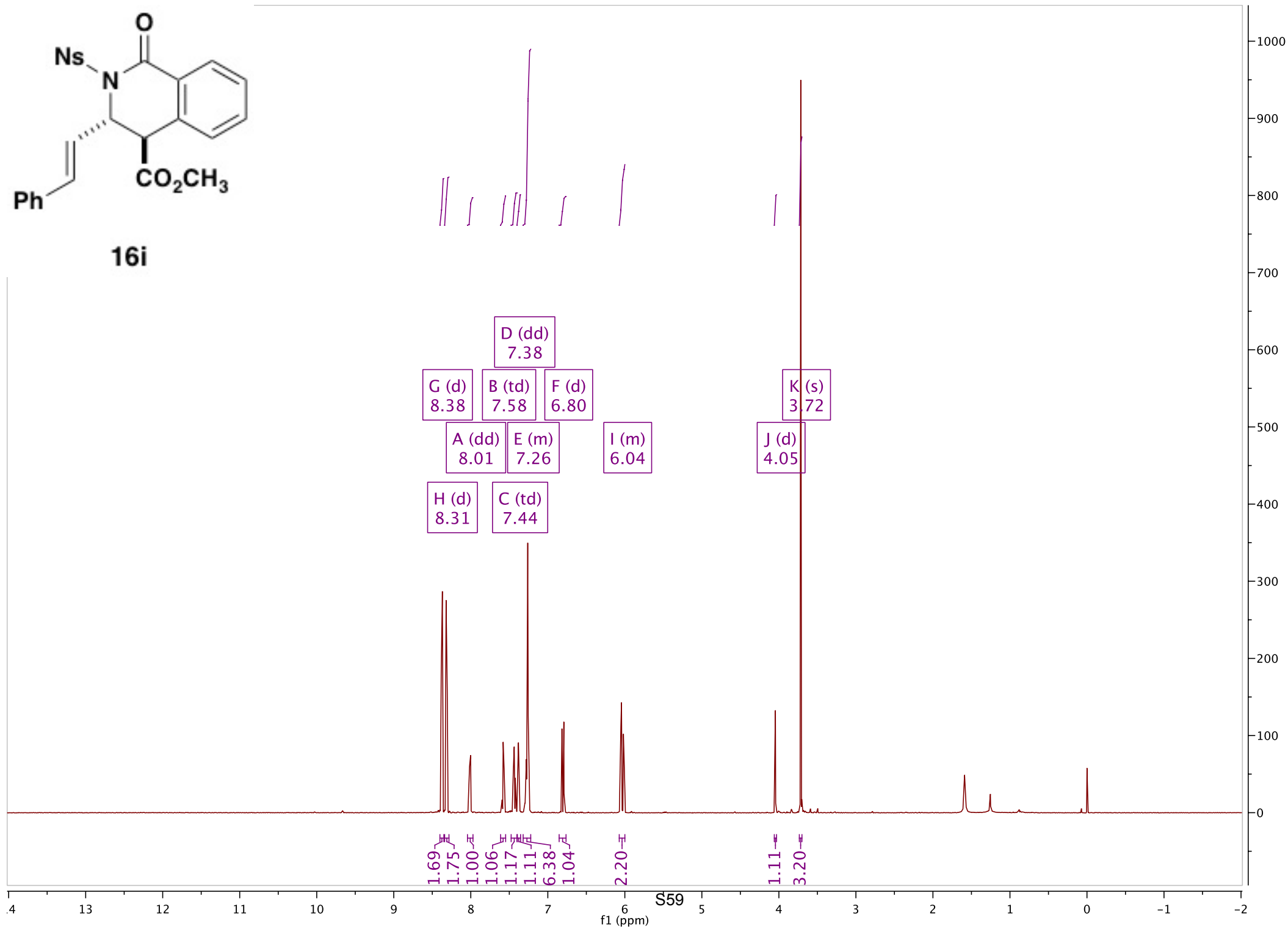


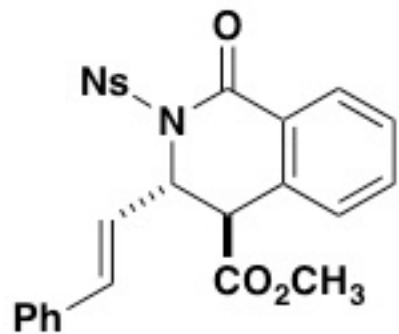
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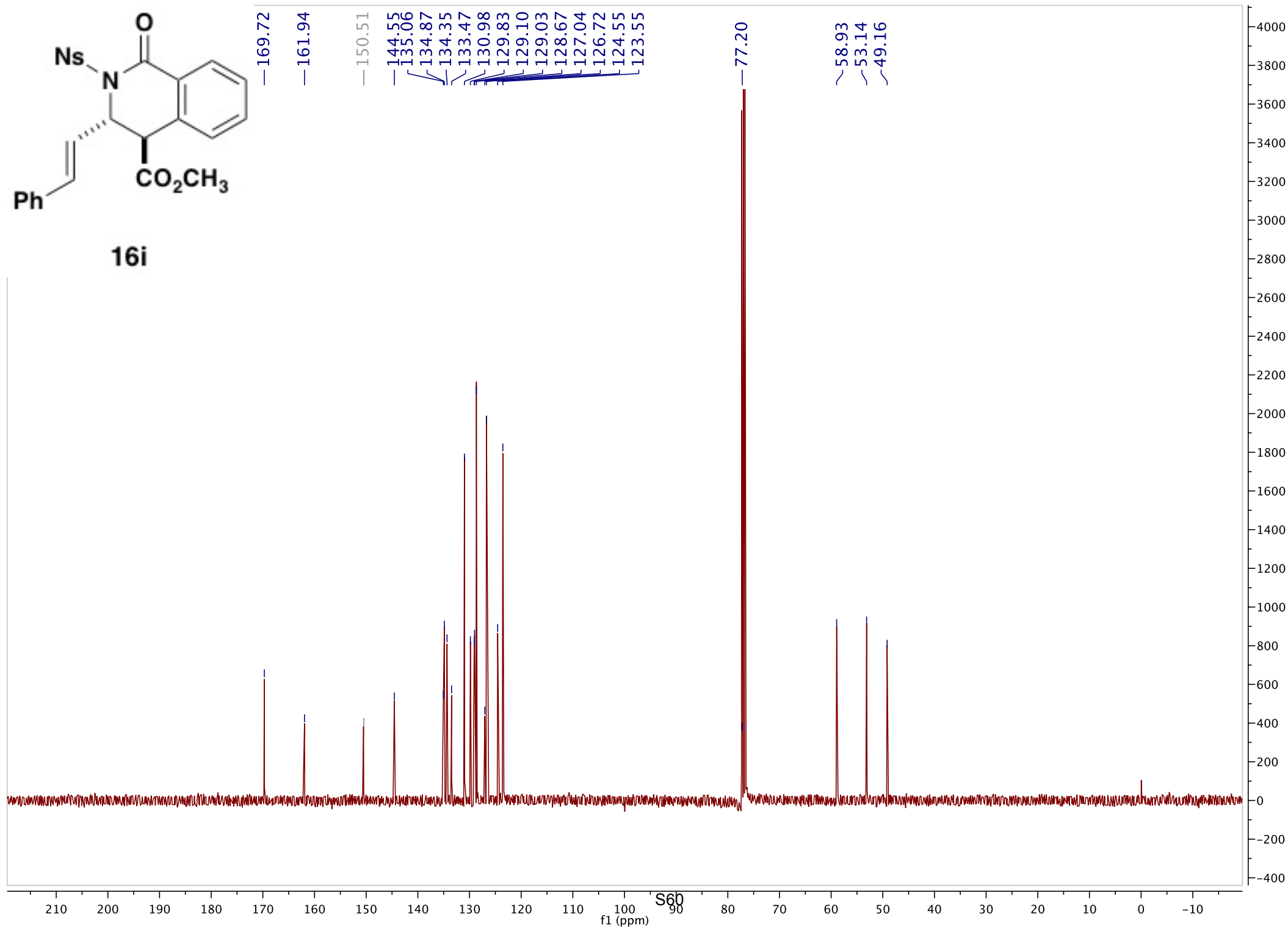


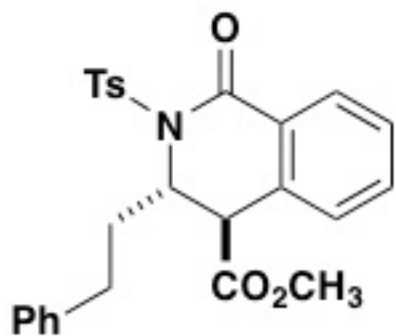
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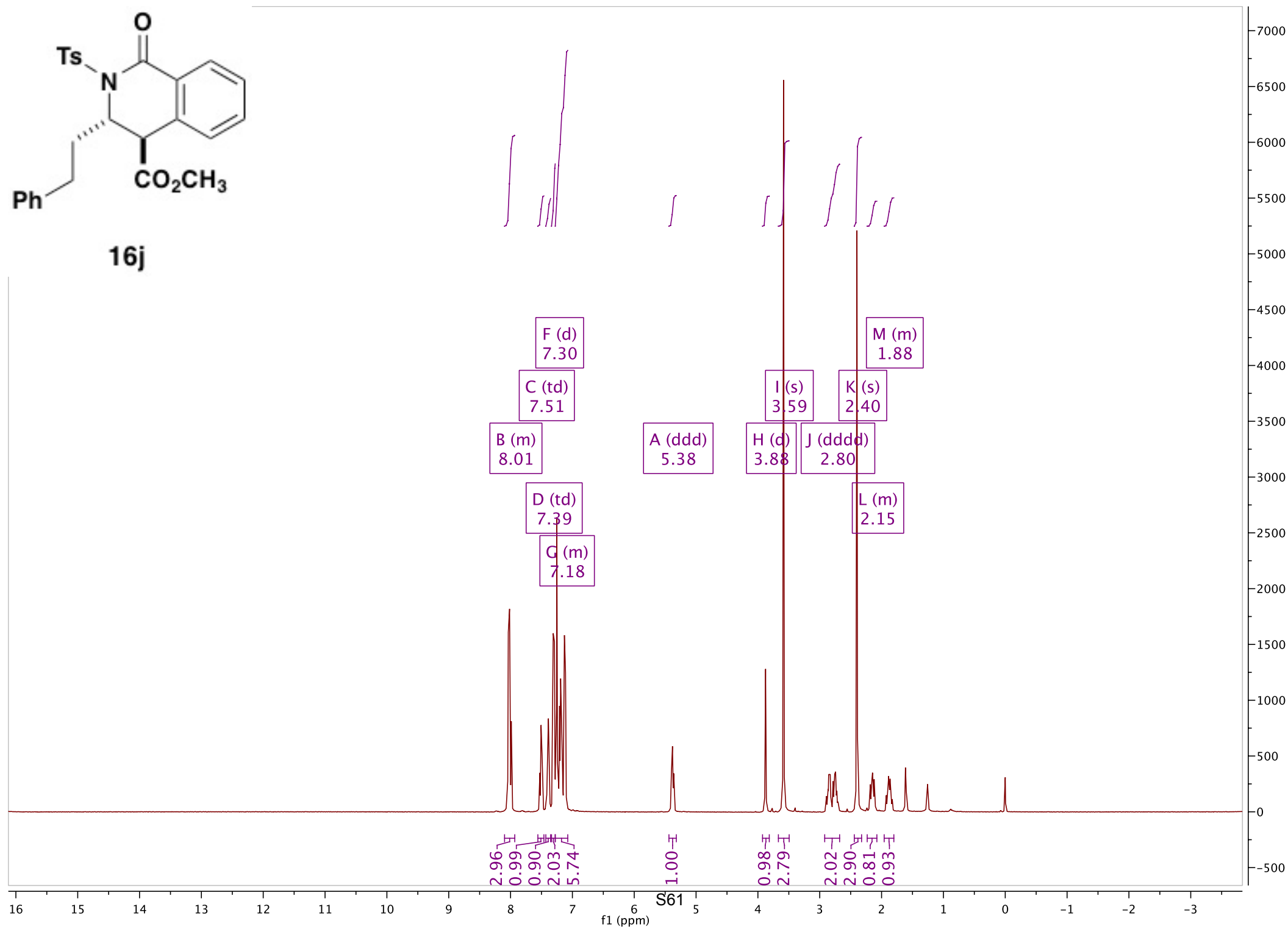


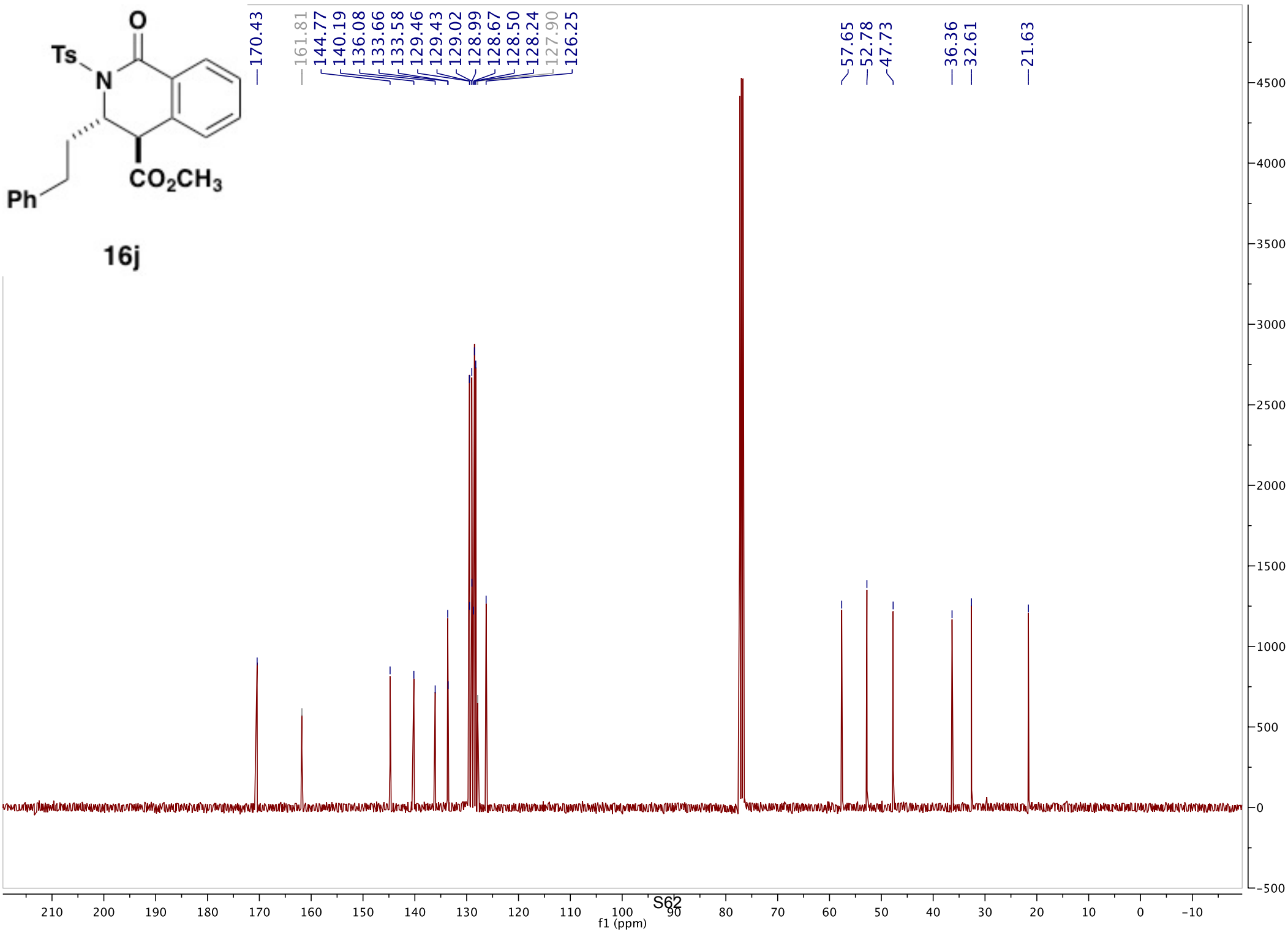
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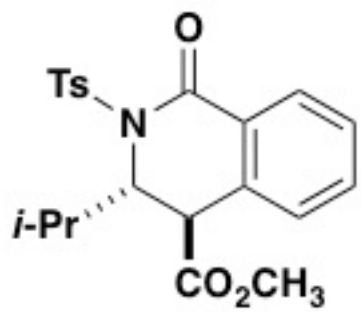




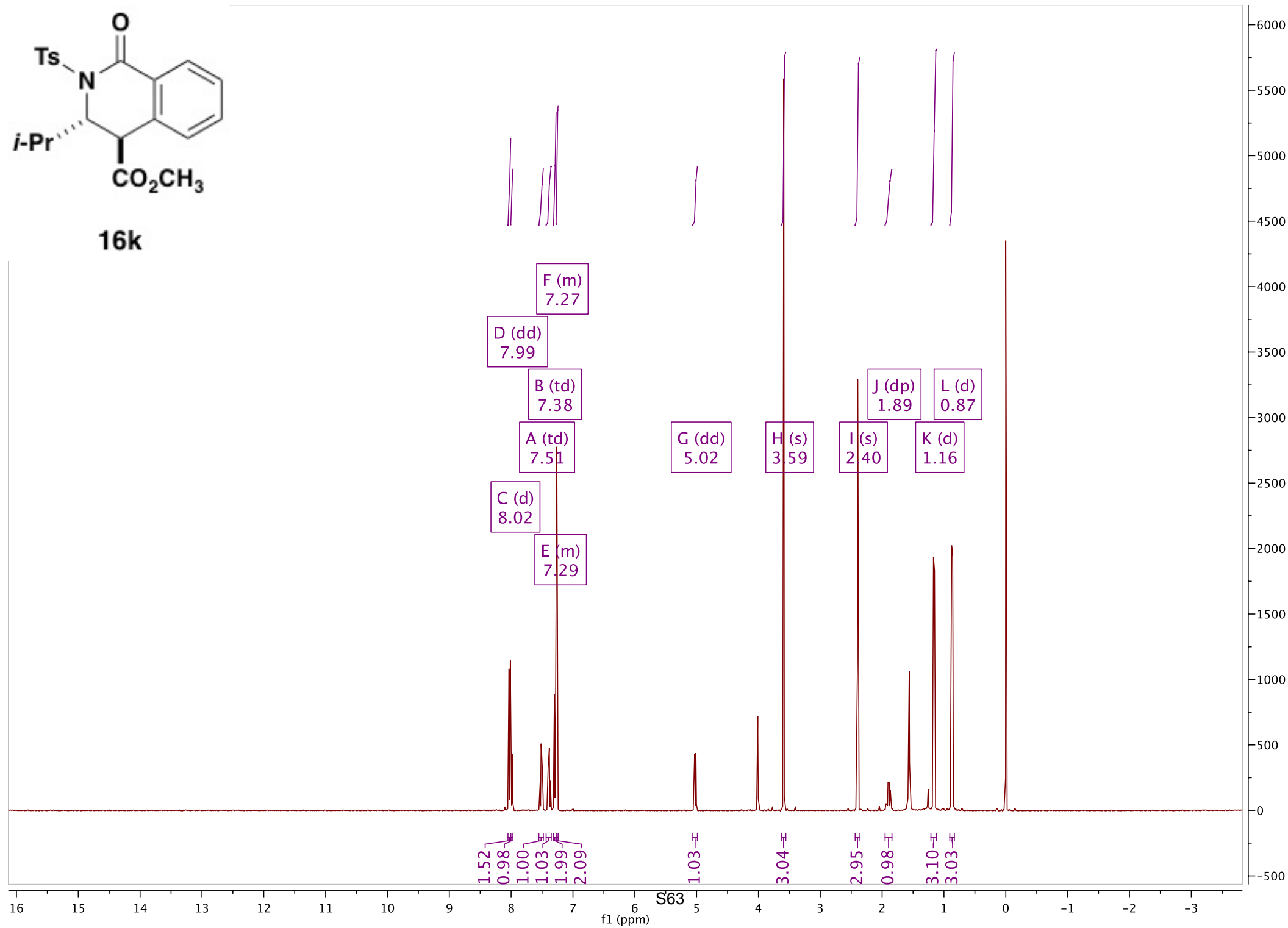
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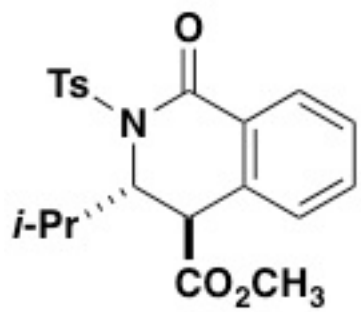




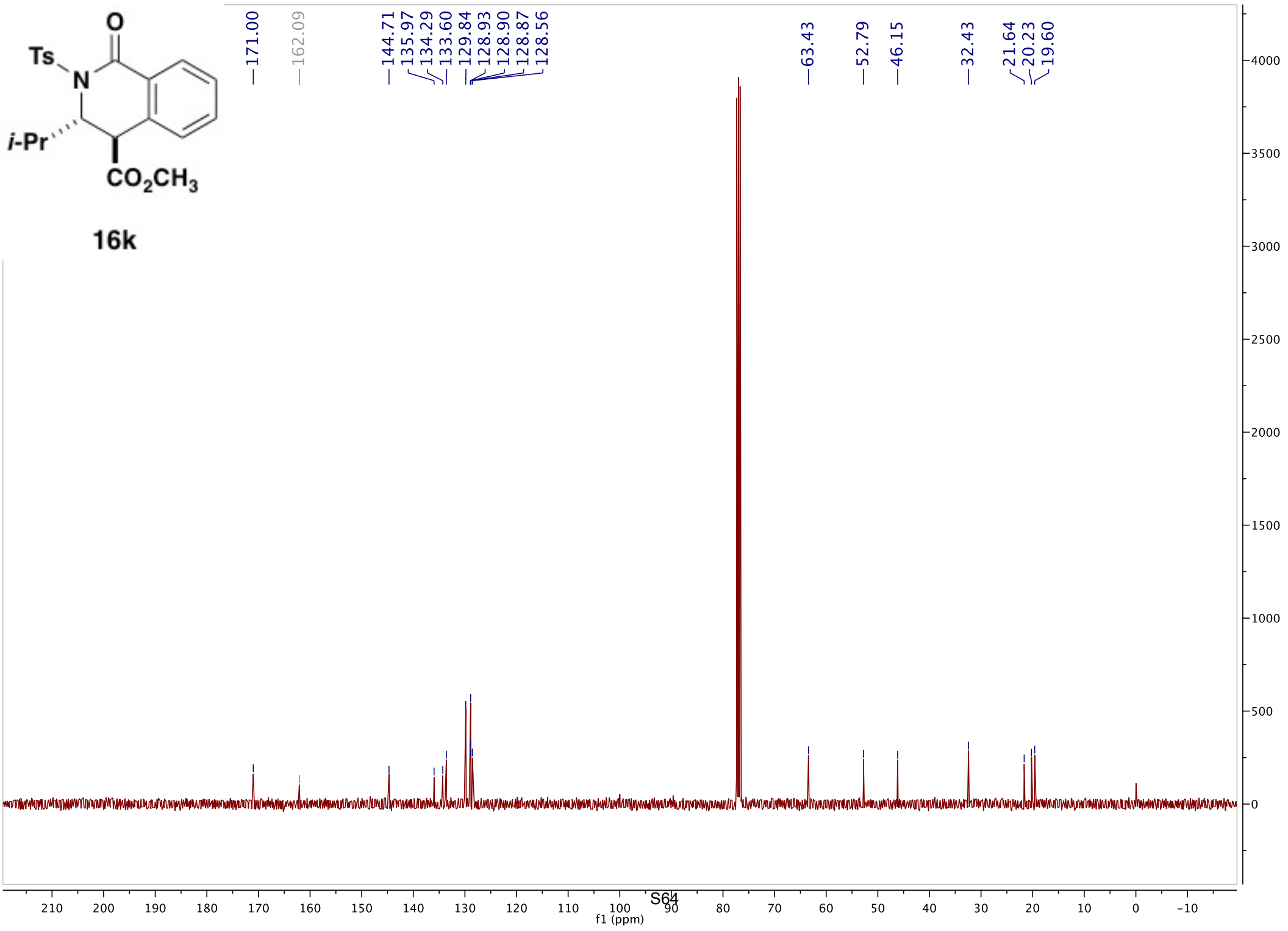


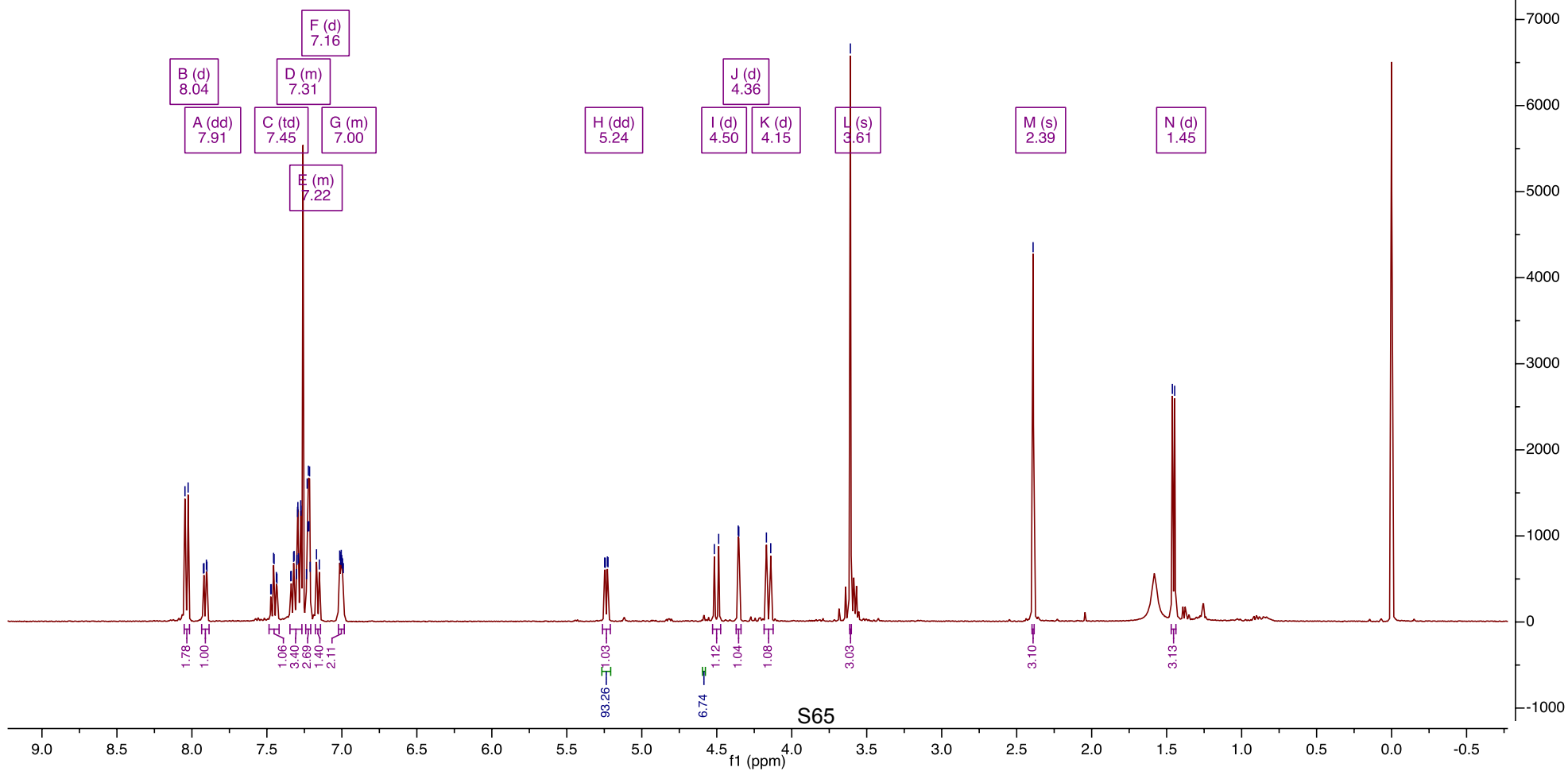
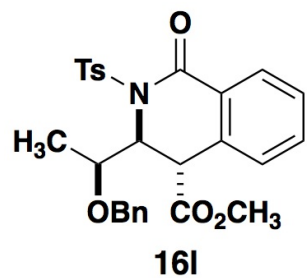
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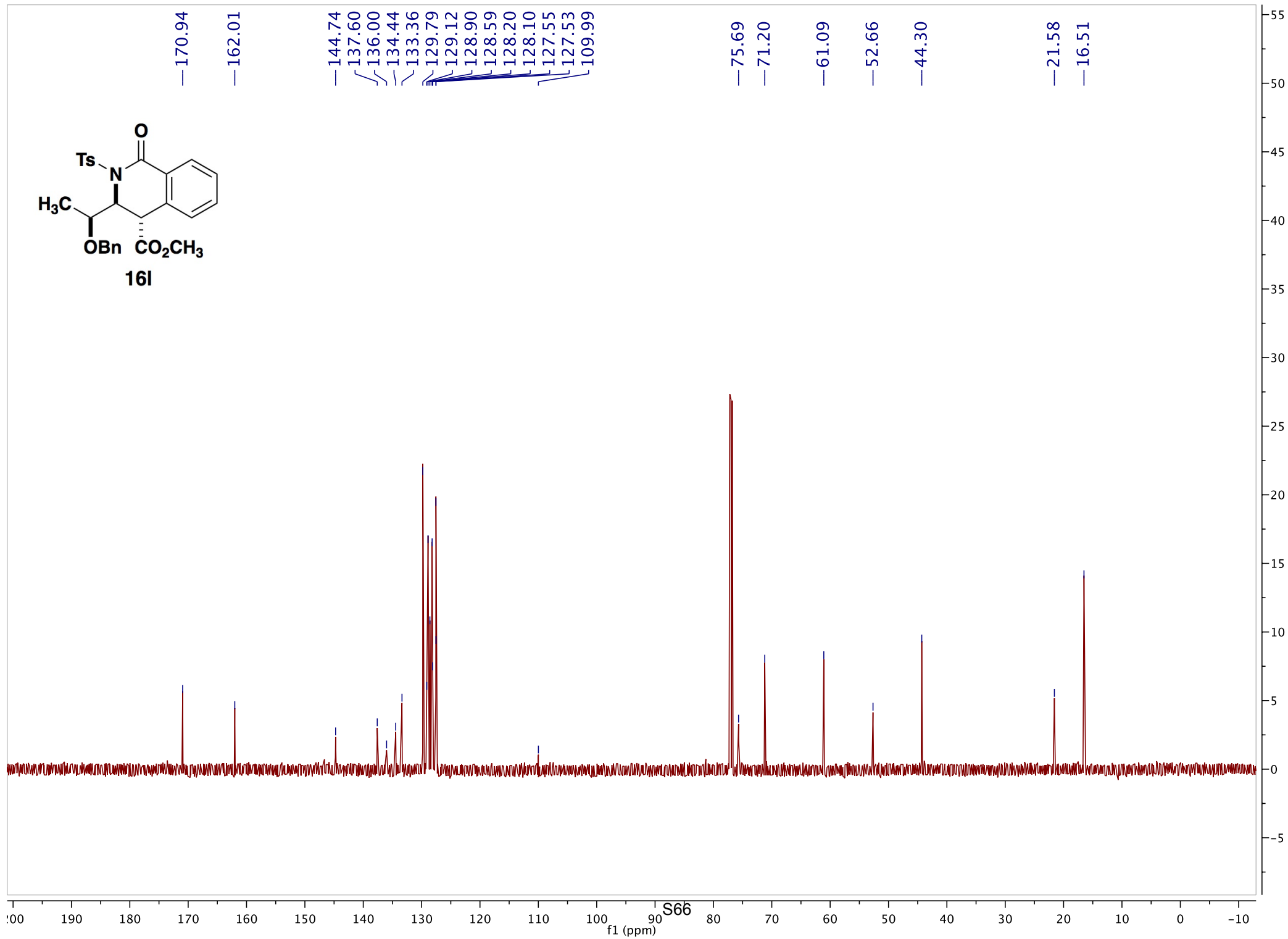
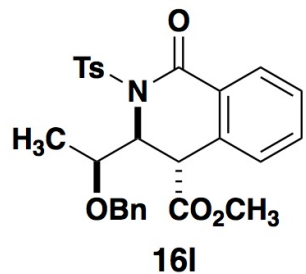




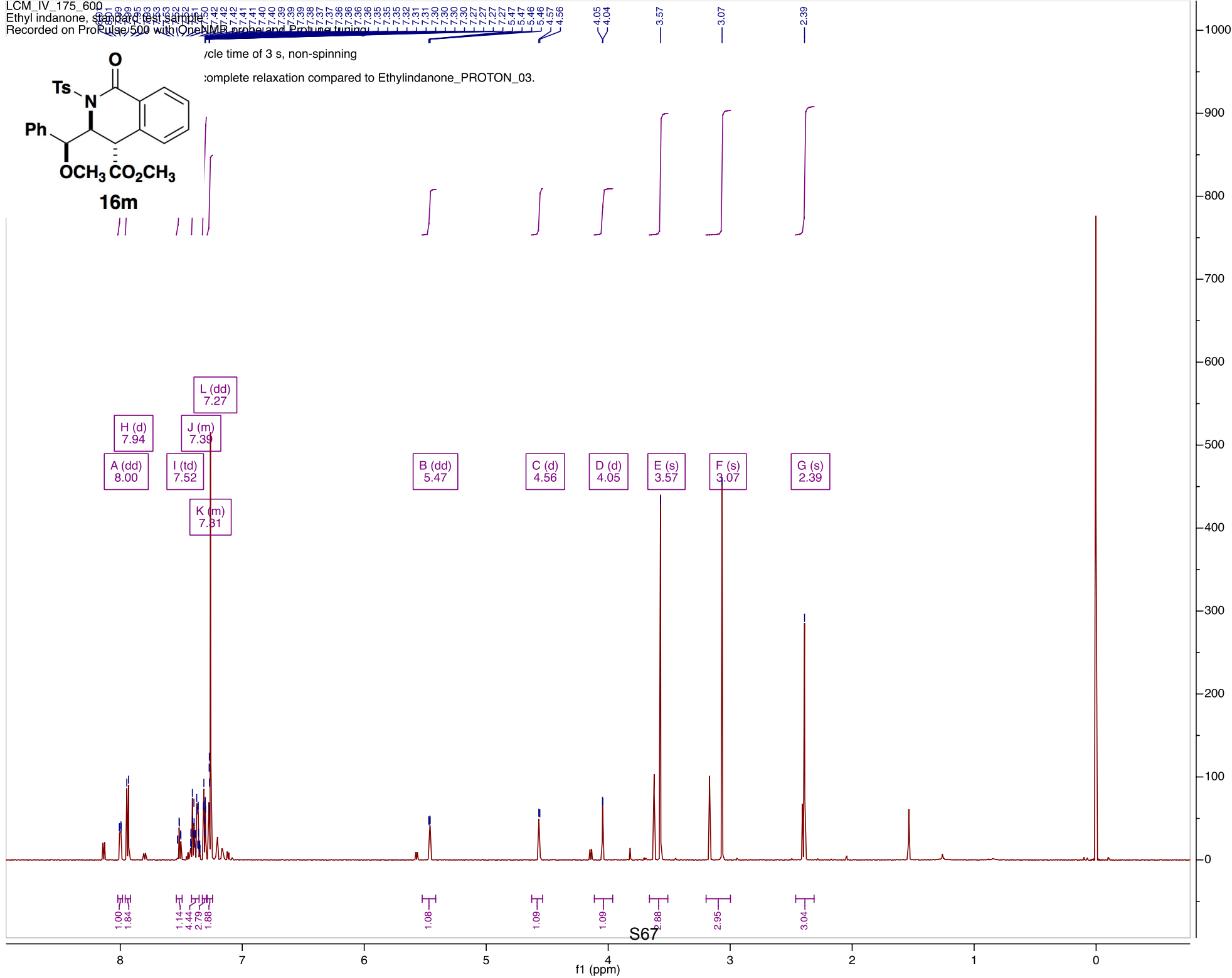
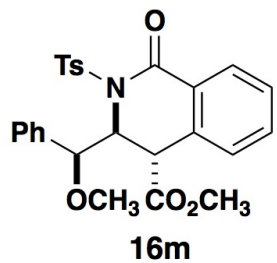
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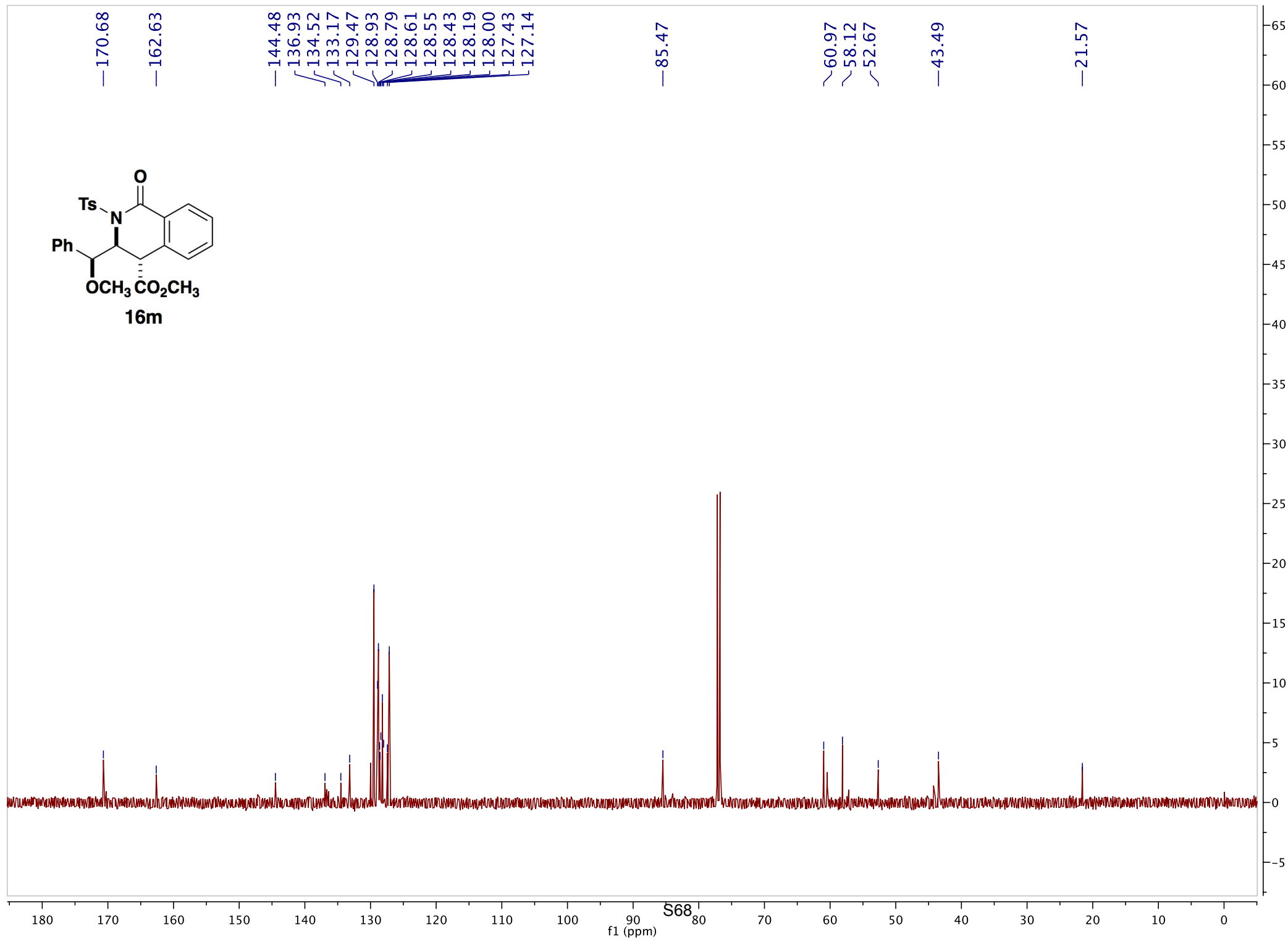
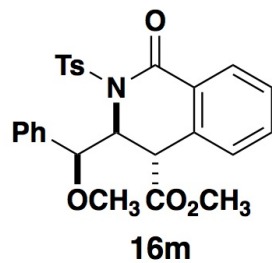


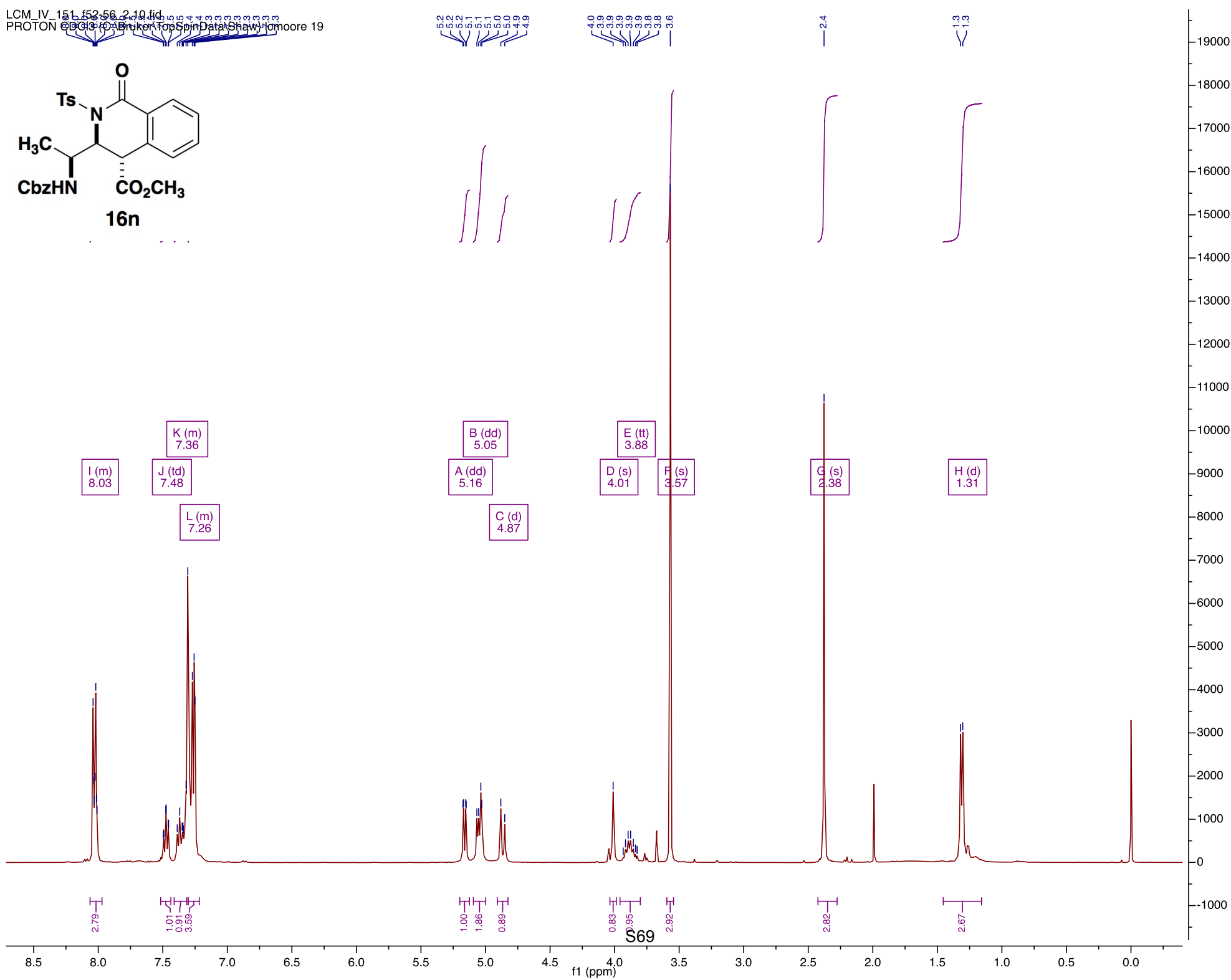
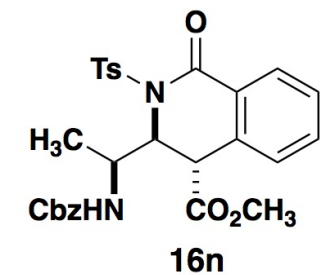


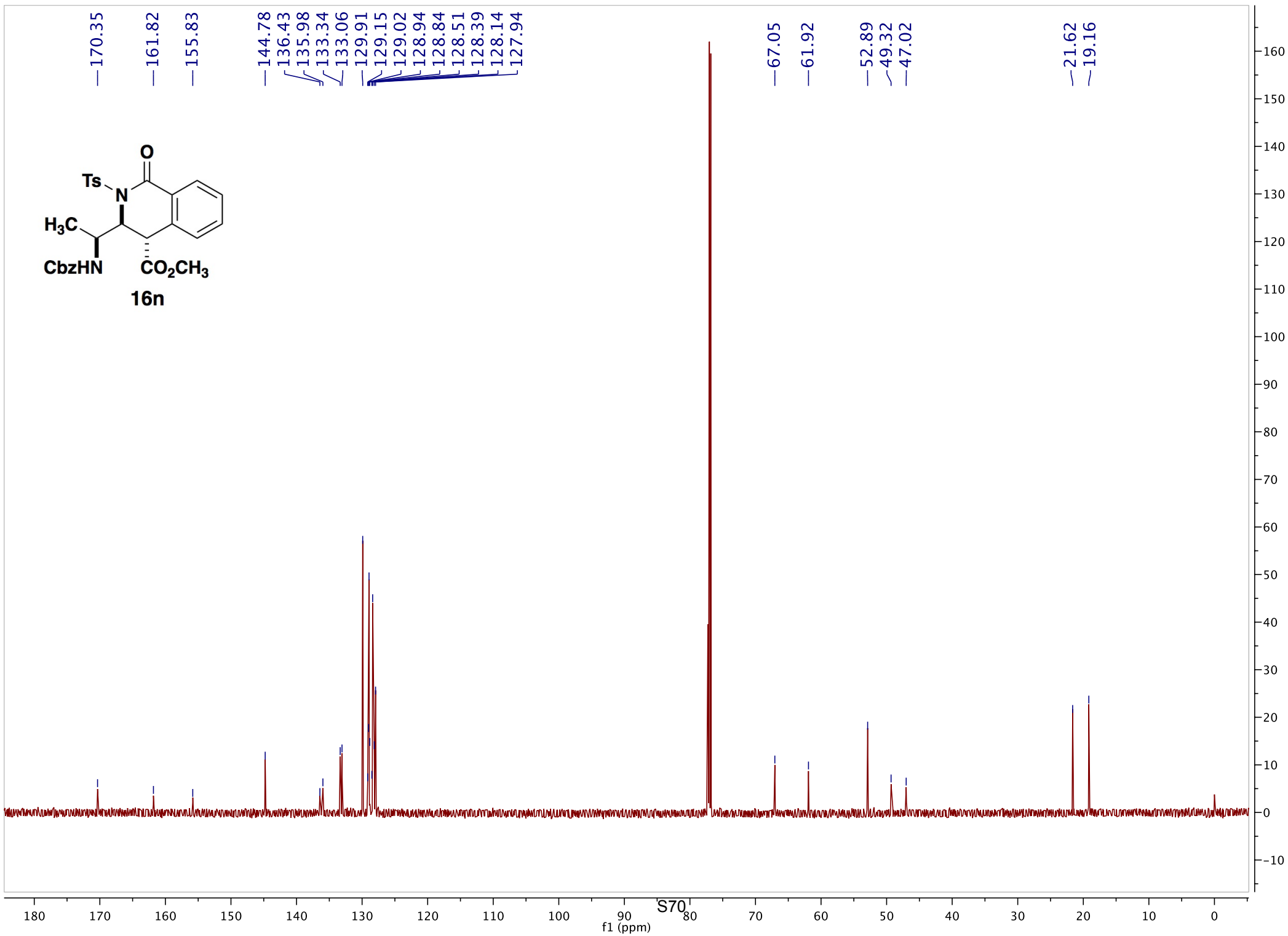
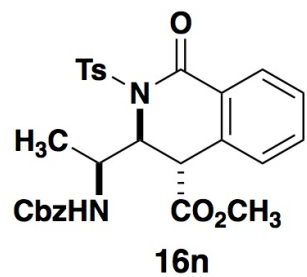


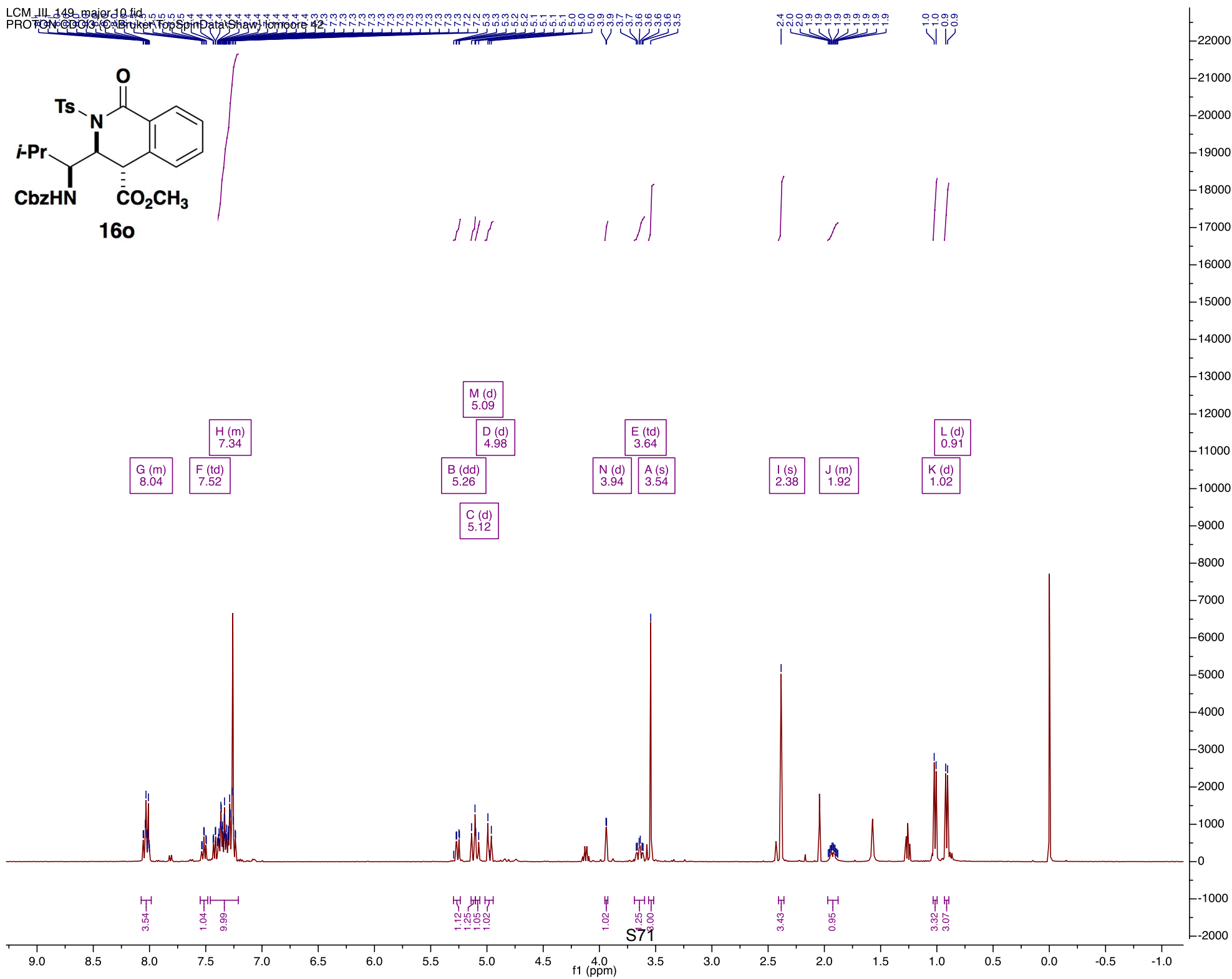
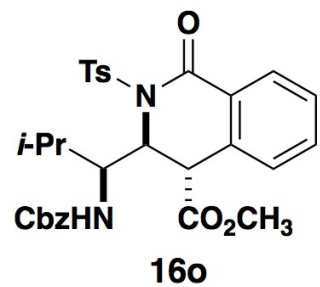
LCM_IV_175_600
Ethyl indanone, standard test sample
Recorded on ProPulse 500 with OneNMR probe and Proton tuning
100% complete relaxation compared to Ethylindanone_PROTON_03.

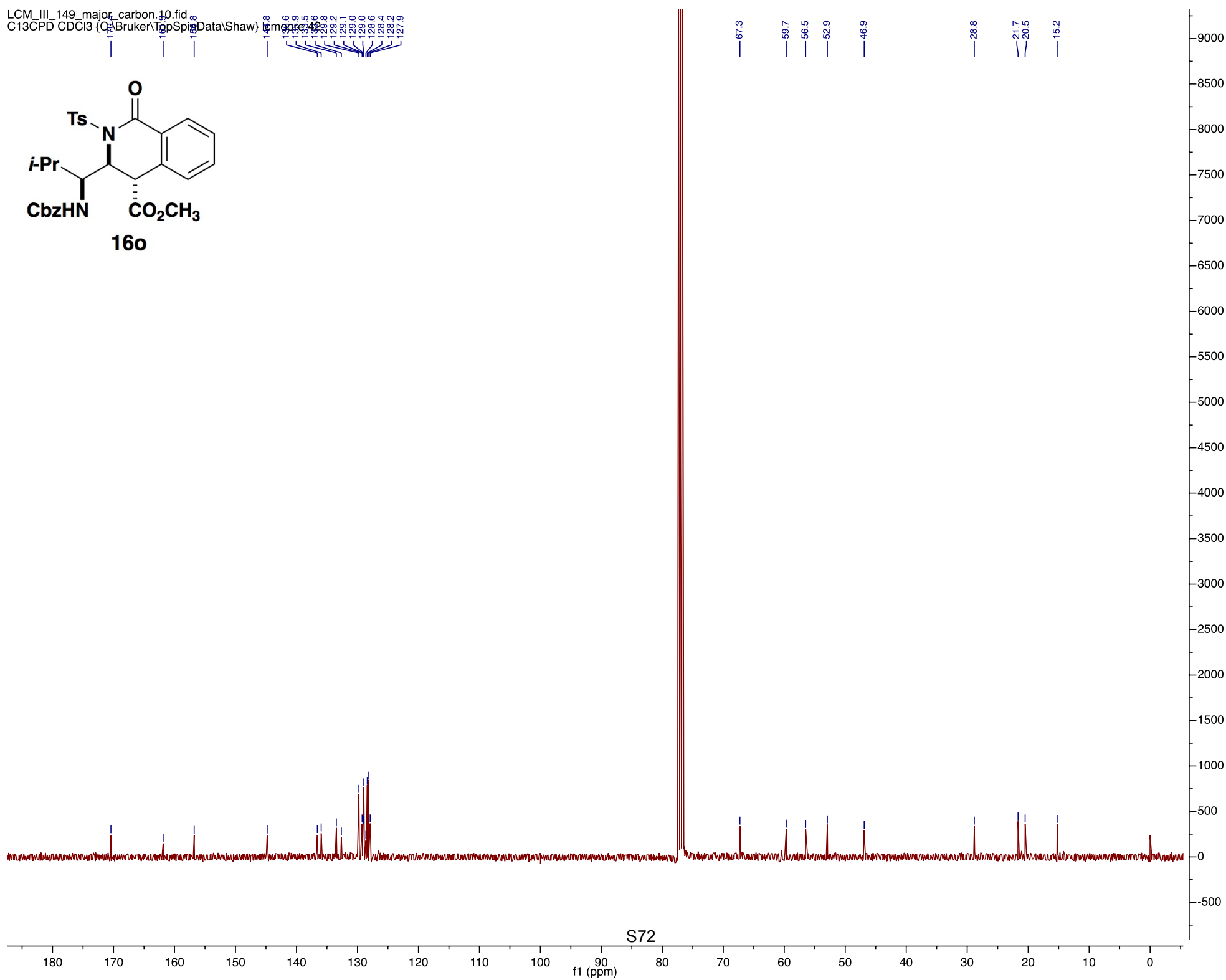
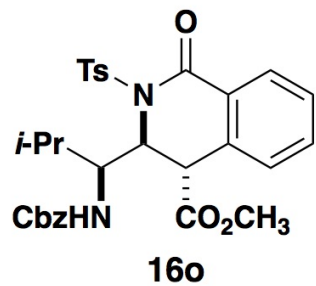


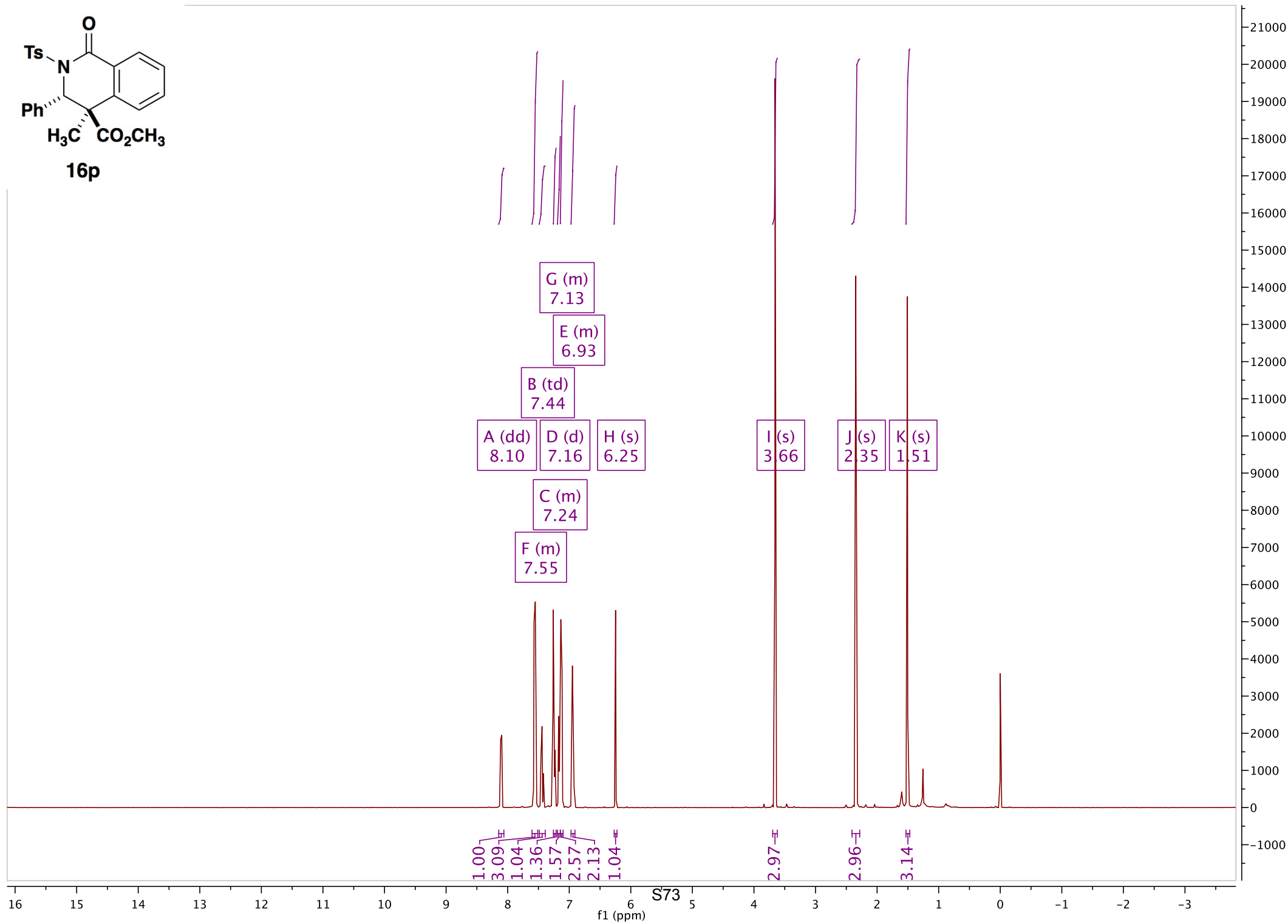
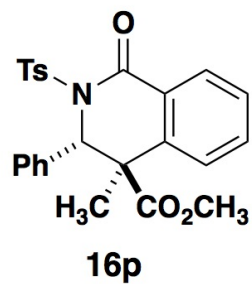


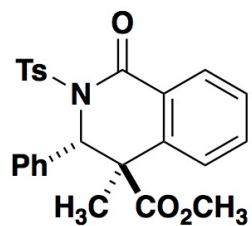




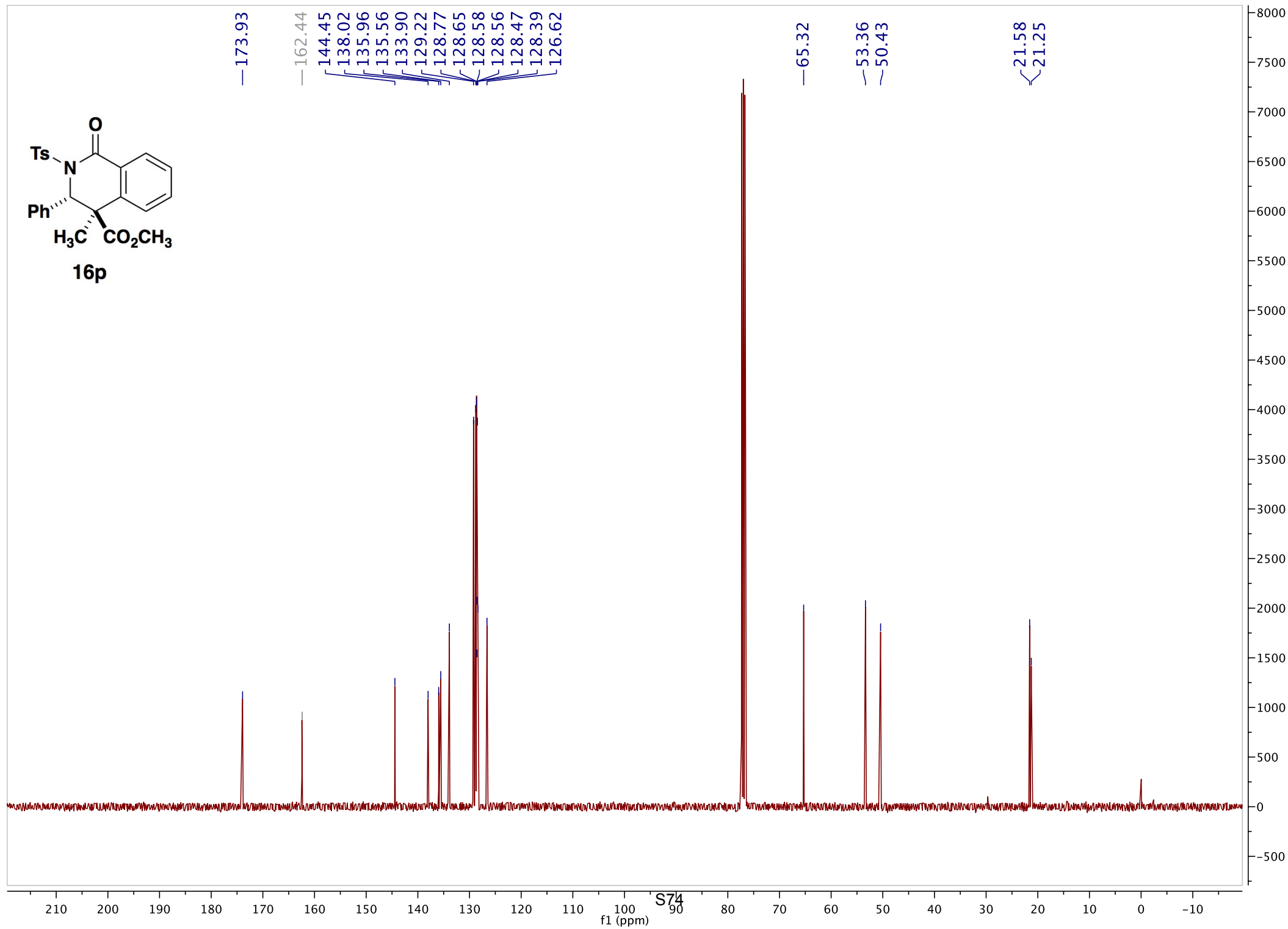


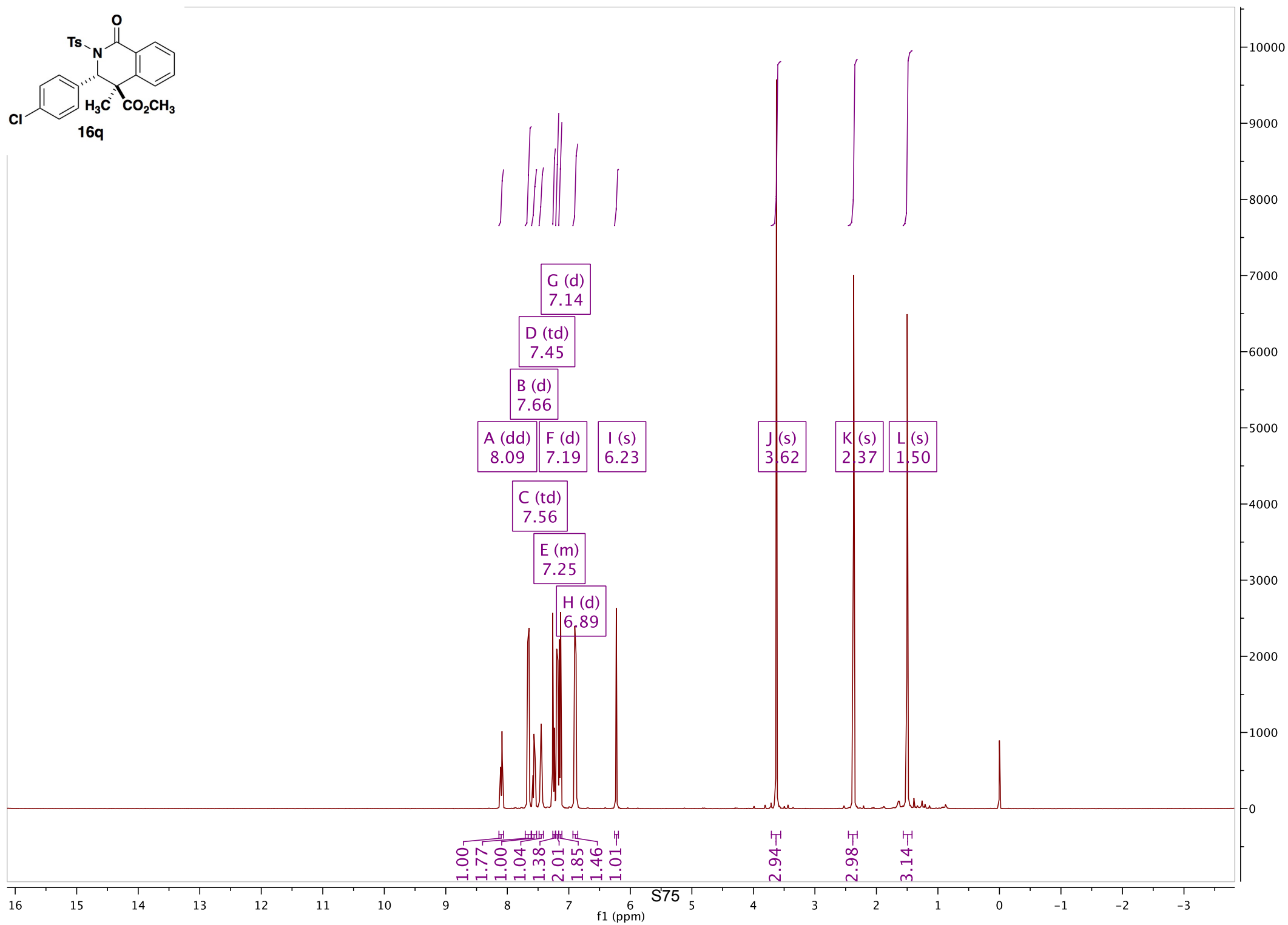
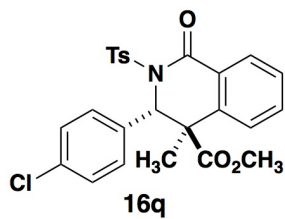


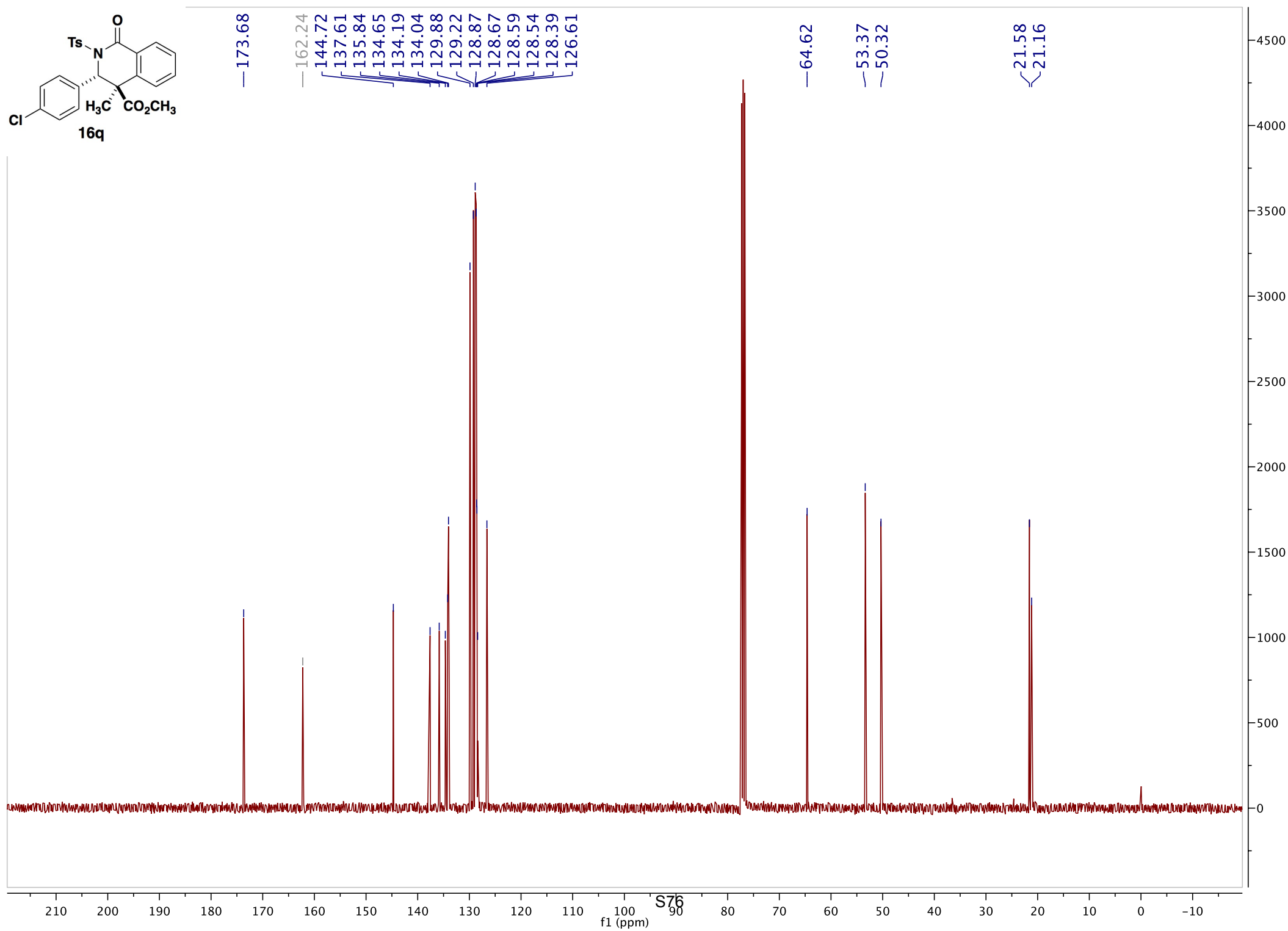
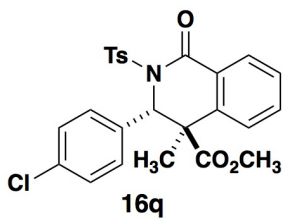


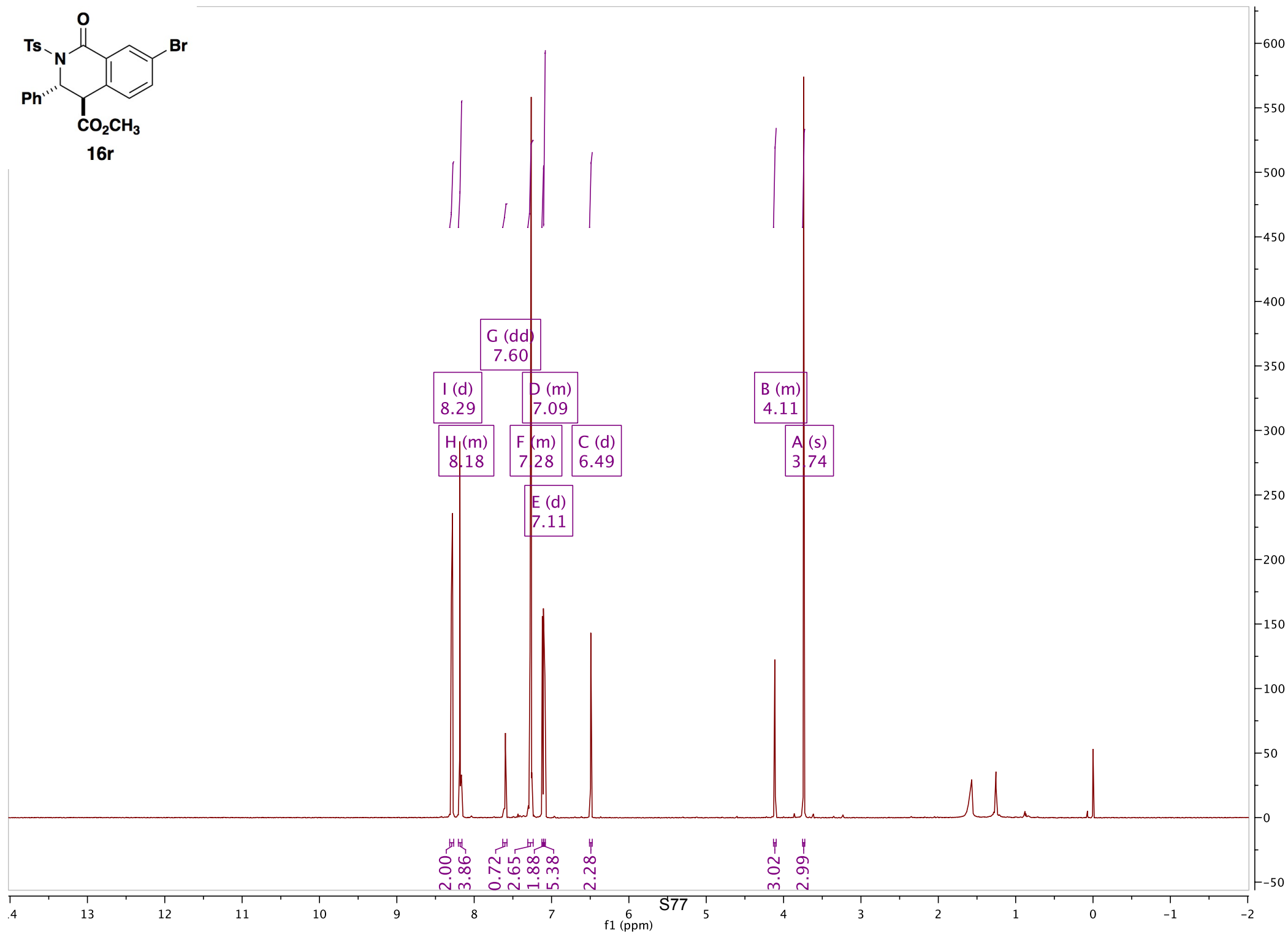
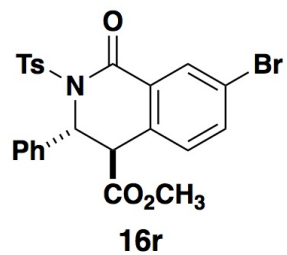


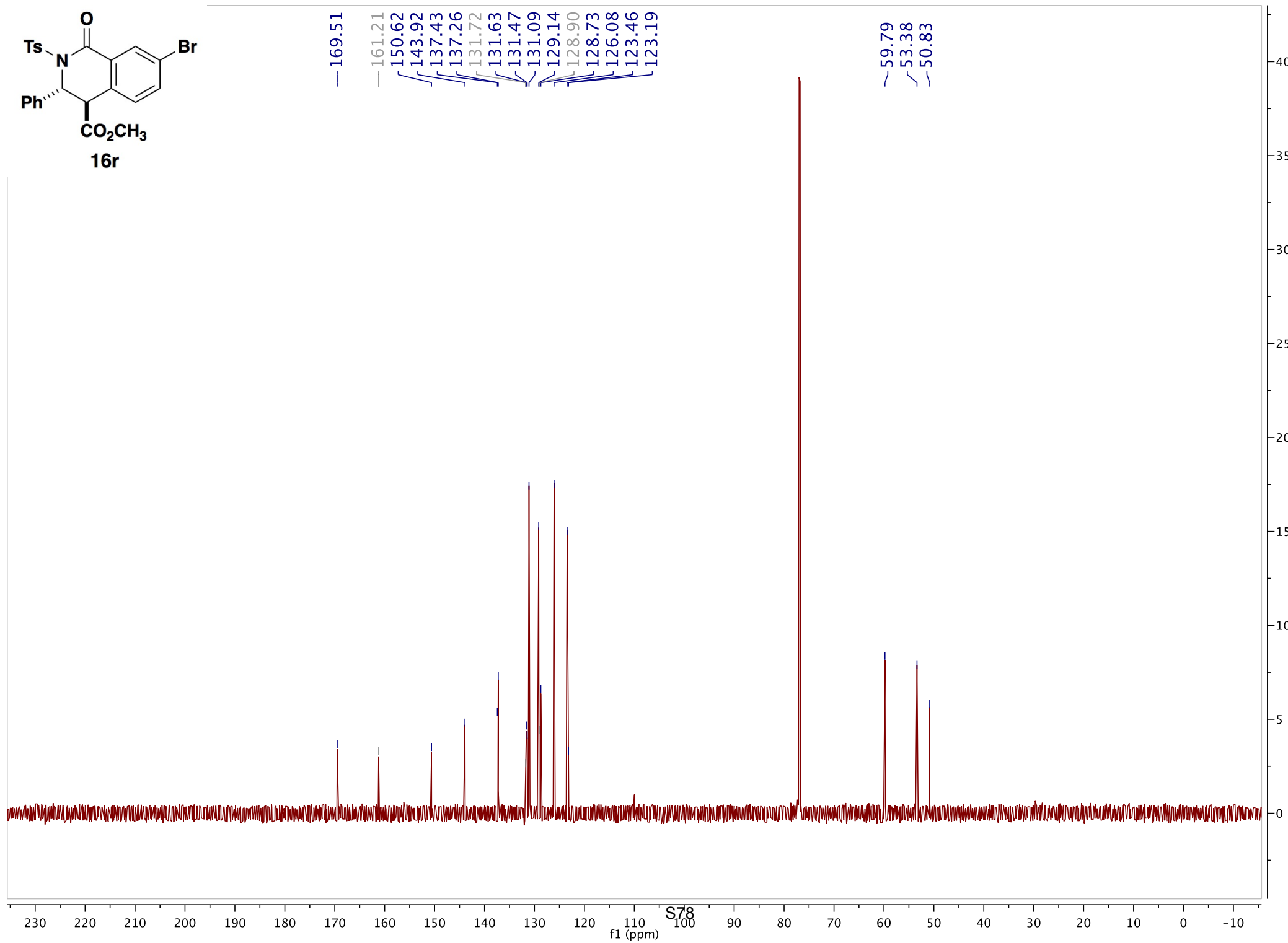
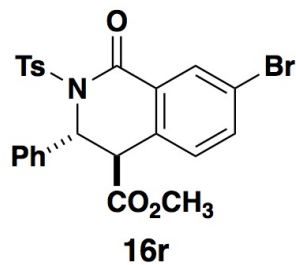
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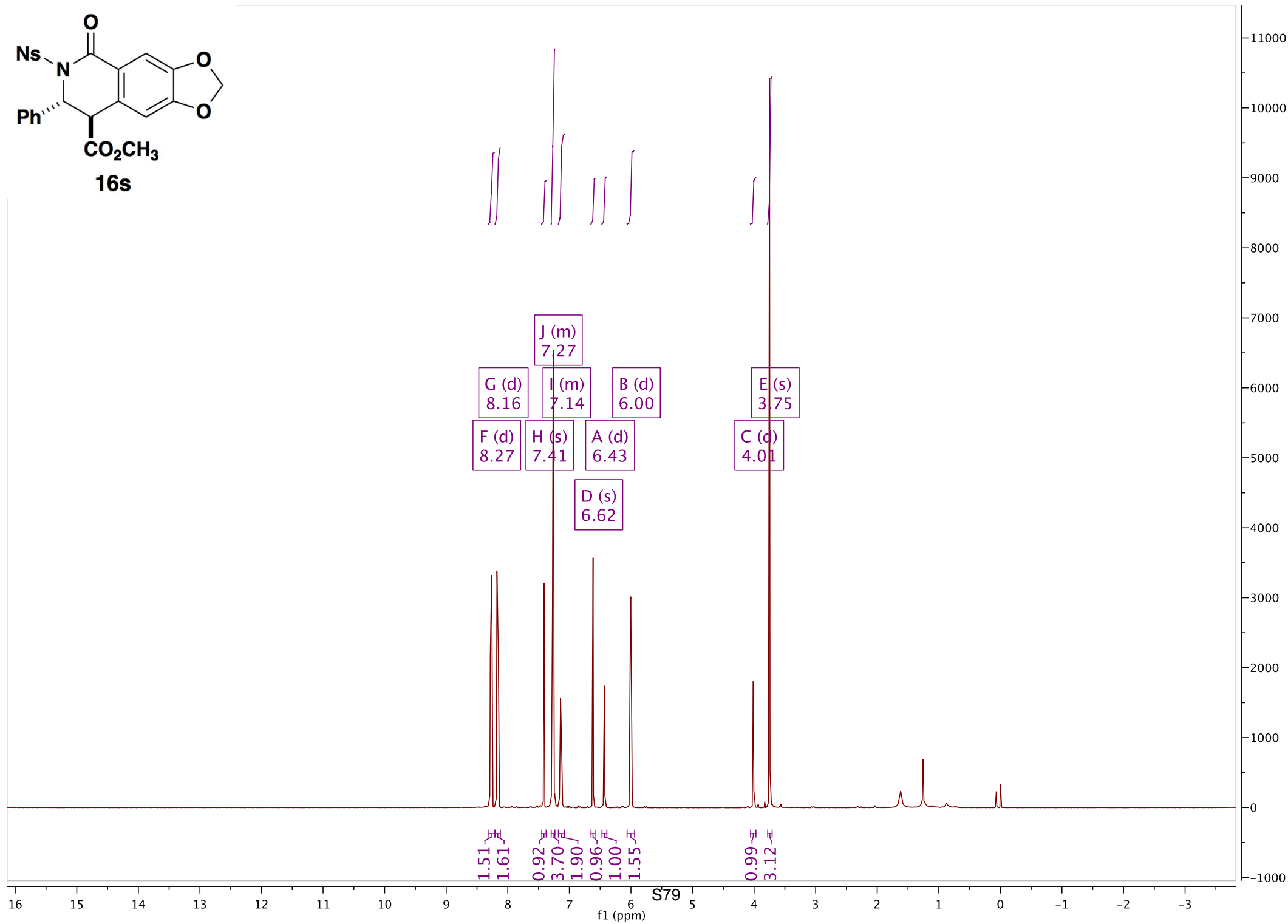
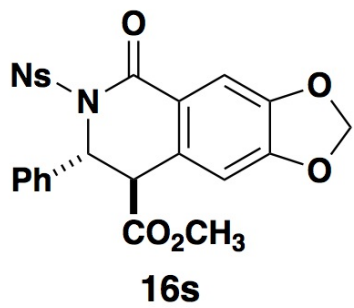


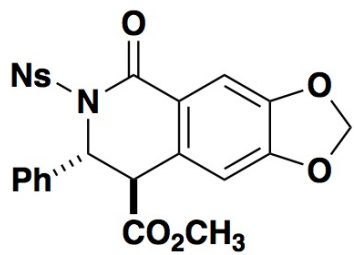




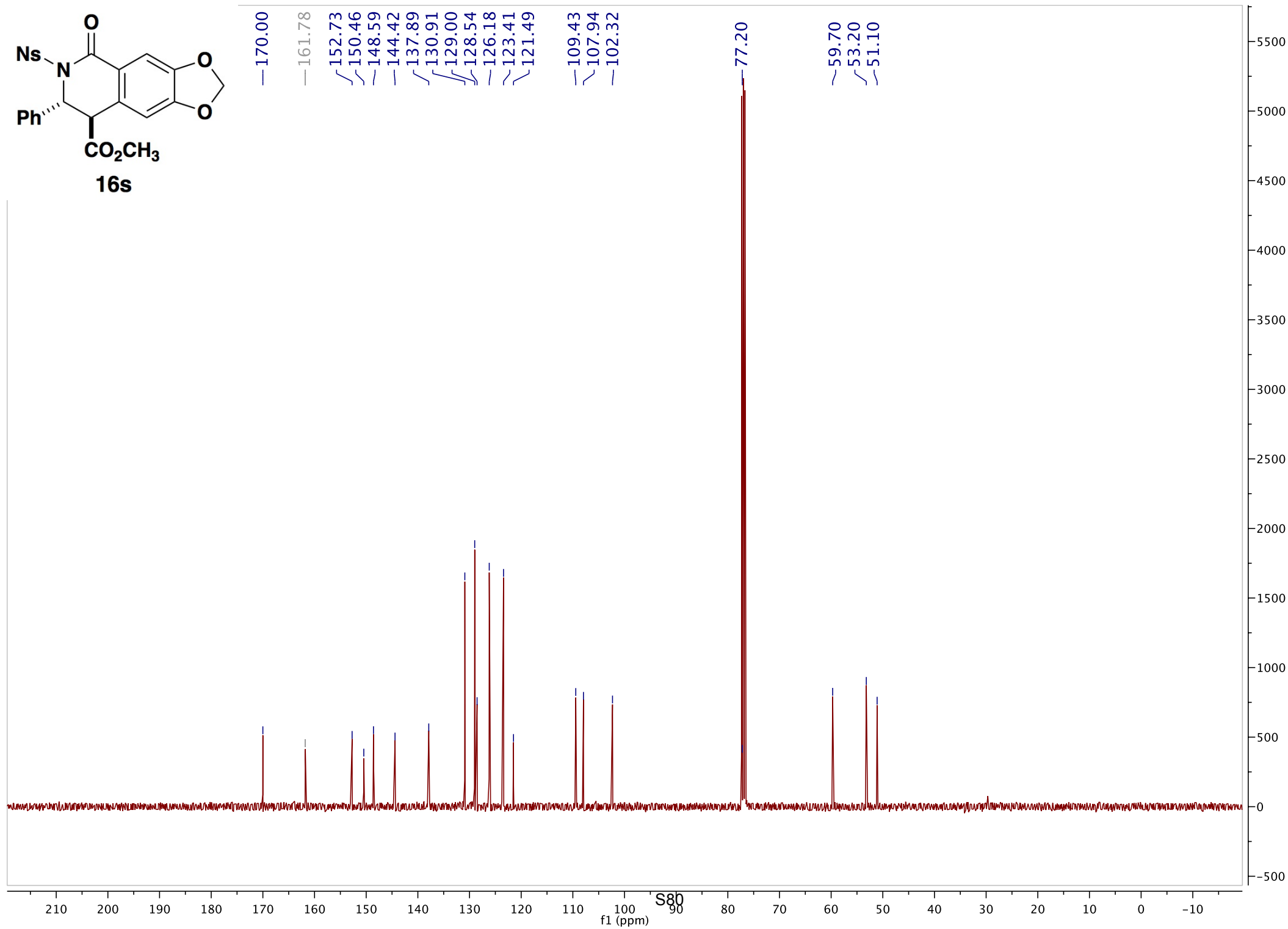


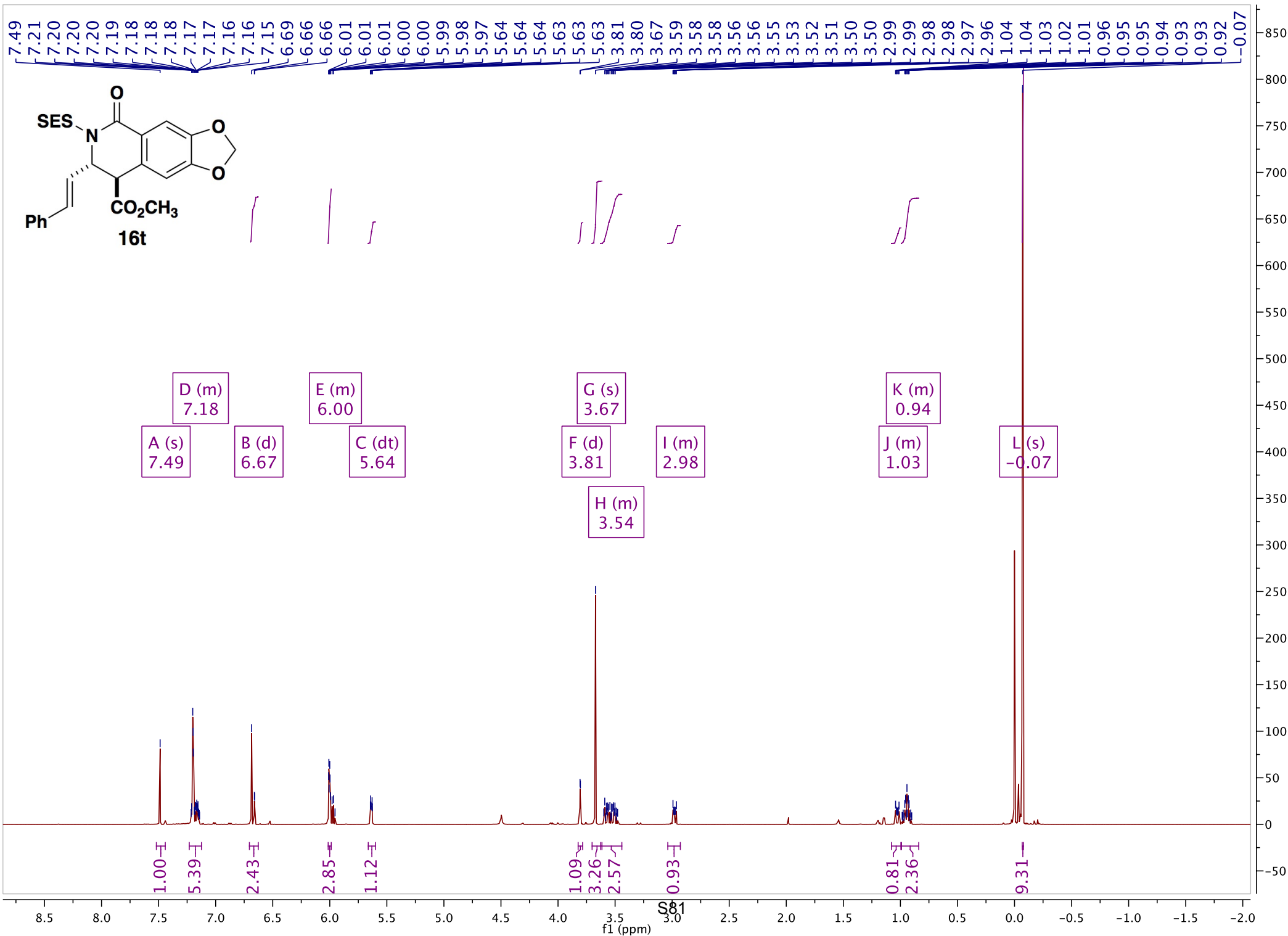


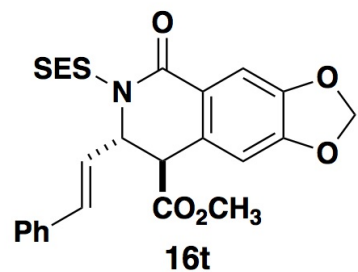




16s







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 -162.64
 -152.62
 -148.66
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 129.88
 128.71
 126.87
 125.20
 122.32
 109.28
 108.74
 102.44

58.26
 53.10
 51.76
 49.31

11.08
 10.17

-1.92

