Supporting Information

Synthesis of Substituted Isoquinolines Utilizing Palladium-Catalyzed α-Arylation of Ketones

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General methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ and referenced to residual solvent peaks or to $SiMe_4$ as an internal standard. Chemical shifts are quoted in ppm (parts per million) to the nearest 0.01 ppm with signal splittings recorded as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), septet (sept.) and broad singlet (br. s). Coupling constants, *J*, are measured in Hz to the nearest 0.1 Hz. ^{1}H and ^{13}C NMR spectra were recorded at room temperature. Assignments were based upon DEPT, COSY and HMQC experiments and by comparison with data of known compounds.

Infrared spectra were recorded neat on a Bruker Tensor 27 FT-IR spectrometer equipped with Attenuated Total Reflectance sampling accessories. Absorption maxima are quoted in wavenumbers (cm^{-1}) for the range 3500-800 cm^{-1} and labelled as strong (s), medium (m), weak (w) and broad (br.). Mass spectra were recorded on a Fisons Platform II spectrometer under electrospray ionisation (ESI) or electron impact (EI). Relative intensities of assignable peaks are quoted as percentage values. High resolution mass spectra are given to four decimal places and were recorded on a Bruker MicroTof (resolution = 10000 FWHM). Calibration was *via* the lock-mass of tetraoctylammonium bromide for positive and sodium dodecyl sulfate for negative ions. Melting points (m.p.) were obtained from recrystallized samples using a Lecia VMTG heated-stage microscope and are uncorrected. The solvent systems used for recrystallization are quoted in parentheses. Optical rotations were recorded on a Perkin Elmer 241 Polarimeter (using the sodium D line, 589 nm) and $[\alpha]_D^{20}$ are given in units of deg dm^{-1} cm^3 g^{-1}; concentrations given in brackets are in g $(100\ mL)^{-1}$.

Flash column chromatography was performed using silica gel (60 Å, 0.033-0.070 mm, BDH) for all compounds apart from isoquinoline *N*-oxides **5a,f,l** where it was performed using basic alumina (pH 9.5, 58 Å, 150 mesh, Aldrich). TLC analyses were performed on Merck Kiesegel 60 F_{254} 0.25 mm precoated silica plates for all compounds apart from isoquinoline *N*-oxides **5a,f,l** where analyses were performed on Macherey-Nagel Alugram Alox N/UV_{254} 0.20 mm precoated alumina plates. Petrol refers to petroleum ether in the boiling range 40-60 °C. Product spots were visualized under UV light (λ_{max} = 254 nm) and/or by staining with potassium permanganate or vanillin solutions as deemed appropriate. Reagents obtained from Aldrich, Alfa and TCI suppliers were used directly as supplied. 1,1'-Bis(di*tert*-butylphosphino)ferrocene palladium dichloride ((D*t*BPF)$PdCl_2$) and Dichlorobis(*p*-dimethylamino phenyldi*tert*-butylphosphine) palladium (II) ($PdCl_2$(Amphos)$_2$) were obtained from Johnson Matthey. Sodium *tert*-butoxide, (D*t*BPF)$PdCl_2$ and $PdCl_2$(Amphos)$_2$ were stored in a dessicator. Any compounds **2a-t** and **3a-t** that contained acetals of electron rich benzaldehydes were found to undergo slow hydrolysis (over a period of weeks) due to atmospheric moisture. The stability of these compounds could be increased to many months by storage in a dessicator. All anhydrous reactions were carried out in flame-dried glassware and under an inert atmosphere of argon. THF was dried by purification through two activated alumina purification columns.

General Procedure 1: Cyclic acetal protection of aldehydes/ketones

para-Toluenesulfonic acid monohydrate (2.0 mol%) was added to a solution of the aldehyde/ketone (1.0 eq.) and ethanediol (1.3 eq.) in toluene (10 mL $mmol^{-1}$ substrate) in a round-bottomed flask. The flask was attached to a Dean Stark apparatus and the solution was stirred at reflux for 18 h. The reaction mixture was cooled to room temperature and quenched by addition of saturated aqueous $NaHCO_3$ (50 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 2a: Palladium-catalyzed α-arylation

A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (2.0 mol%) and sodium *tert*-butoxide (2.5 eq.) were added to the tube. The aryl halide (1.0 eq.) was dissolved in dry THF (5 mL $mmol^{-1}$ substrate) and the resulting solution was added *via* syringe to the tube. The ketone (1.2 eq.) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 2b: Palladium-catalyzed α-arylation

A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (5.0 mol%) and sodium *tert*-butoxide (2.5 eq.) were added to the tube. The aryl halide (1.0 eq.) was dissolved in dry THF (5 mL $mmol^{-1}$ substrate) and the resulting solution was added *via* syringe to the tube. The ketone (2.0 eq.) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 3: Isoquinoline formation where R^1 = H

A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was added to the cyclization substrate (1.0 eq.) in a resealable reaction tube containing a magnetic follower. The tube was sealed with a screw cap and heated at 90 °C for 24 h. The reaction was then cooled to room temperature and quenched by the addition of saturated aqueous $NaHCO_3$ (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 4: Isoquinoline formation where R^1 = Me

A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was added to the cyclization substrate (1.0 eq.) in a resealable reaction tube containing a magnetic follower. The tube was sealed with a screw cap and heated at 90 °C for 18 h. A solution of NH_4HCO_3 (2.0 M in H_2O) was

then added until the pH of the reaction mixture had been adjusted to approximately pH 9. The tube was resealed and heated for a further 24 h at 90 °C. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 5: Isoquinoline-*N*-oxide formation

A solution of $NH_2OH.HCl$ (10 eq., 1.0 M in 9:1 EtOH/H_2O) was added to the cyclization substrate (1.0 eq.) in a resealable reaction tube containing a magnetic follower. The tube was sealed with a screw cap and heated at 90 °C for 2 h. The reaction was then cooled to room temperature and the solvent removed *in vacuo* using a toluene azeotrope to give the crude product which was purified as specified.

General Procedure 6: One-Pot Isoquinoline Formation: where R^1 = H

A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (2.0 mol%) and sodium *tert*-butoxide (2.5 eq.) were added to the tube. The aryl halide (1.0 eq.) was dissolved in dry THF (5 mL $mmol^{-1}$ substrate) and the resulting solution was added *via* syringe to the tube. The ketone (1.2 eq.) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and acidified to pH 5 by the addition of aqueous HCl (1.0 M). A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was then added and the tube resealed and heated at 90 °C for 24 h. The reaction was then cooled to room temperature and quenched by the addition of saturated aqueous $NaHCO_3$ (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 7a: One-Pot Isoquinoline Formation: where R^1 = Me

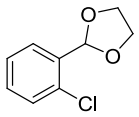
A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (2.0 mol%) and sodium *tert*-butoxide (2.5 eq.) were added to the tube. The aryl halide (1.0 eq.) was dissolved in dry THF (5 mL $mmol^{-1}$ substrate) and the resulting solution was added *via* syringe to the tube. The ketone (1.2 eq.) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and acidified to pH 5 by the addition of aqueous HCl (1.0 M). A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was then added and the tube resealed and heated at 90 °C for 18 h. The reaction was then cooled to room temperature, a solution of NH_4HCO_3 (2.0 M in H_2O) was then added to adjust the pH to approximately 9 and the tube resealed and heated at 90 °C for 24 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

General Procedure 7b: One-Pot Isoquinoline Formation: where R^1 = Me

A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (5.0 mol%) and sodium *tert*-butoxide (2.5 eq.) were added to the tube. The aryl halide (1.0 eq.) was dissolved in dry THF (5 mL $mmol^{-1}$ substrate) and the resulting solution was added *via* syringe to the tube. The ketone (2.0 eq.) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and acidified to pH 5 by the addition of aqueous HCl (1.0 M). A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was then added and the tube resealed and heated at 90 °C for 18 h. The reaction was then cooled to room temperature, a solution of NH_4HCO_3 (2.0 M in H_2O) was then added to adjust the pH to approximately 9 and the tube resealed and heated at 90 °C for 24 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified.

Preparation and spectroscopic data for compounds

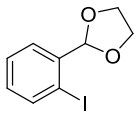
2-(2-Chlorophenyl)-1,3-dioxolane **2b**



2-Chlorobenzaldehyde (2.04 g, 14.5 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *acetal* **2b** (2.50 g, 13.5 mmol, 93 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.63 (1H, dd, *J* 5.7, 3.7, *H*C_{Ar}), 7.41-7.37 (1H, m, *H*C_{Ar}), 7.32-7.27 (2H, m, 2 × *H*C_{Ar}), 6.17 (1H, s, C*H*$(OR)_2$), 4.18-4.12 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.11-4.05 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 135.1, 133.5 (2 × *C*$_{Ar}$), 130.3, 129.7, 127.6, 126.8 (4 × H*C*$_{Ar}$), 100.7 (*C*H$(OR)_2$), 65.5 (*C*H_2OR). Data were consistent with those previously reported.[1]

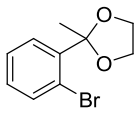
2-(2-Iodophenyl)-1,3-dioxolane **2c**



2-Iodobenzaldehyde (500 mg, 2.16 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *acetal* **2c** (518 mg, 1.87 mmol, 87 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.86 (1H, d, *J* 7.8, *H*C_{Ar}), 7.56 (1H, dd, *J* 7.8, 1.5, *H*C_{Ar}), 7.38 (1H, t, *J* 7.6, *H*C_{Ar}), 7.07 (1H, td, *J* 7.6, 1.5, *H*C_{Ar}), 5.93 (1H, s, C*H*$(OR)_2$), 4.20-4.14 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.13-4.07 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 139.7 (H*C*$_{Ar}$), 139.3 (*C*$_{Ar}$), 130.9, 128.2, 127.6 (3 × H*C*$_{Ar}$), 106.4 (*C*H$(OR)_2$), 97.1 (*C*$_{Ar}$), 65.5 (*C*H_2OR). Data were consistent with those previously reported.[2]

2-(2-Bromophenyl)-2-methyl-1,3-dioxolane **2f**

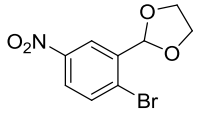


2'-Bromoacetophenone (1.98 g, 9.92 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *ketal* **2f** (2.26 g, 9.31 mmol, 94 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.67 (1H, dd, *J* 7.9, 1.8, *H*C_{Ar}), 7.59 (1H, dd, *J* 8.1, 1.3, *H*C_{Ar}), 7.28 (1H, td, *J* 7.6, 1.1, *H*C_{Ar}), 7.13 (1H, td, *J* 7.6, 1.7, *H*C_{Ar}), 4.10-4.01 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 3.80-3.71 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 1.81 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ_C: 141.1 (C_{Ar}), 134.9, 129.5, 127.9, 127.1 (4 × HC_{Ar}), 120.5 (C_{Ar}), 108.7 ($C(OR)_2$), 64.2 (CH_2OR), 25.3 (CH_3). Data were consistent with those previously reported.[3]

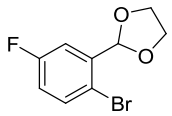
2-(2-Bromo-5-nitrophenyl)-1,3-dioxolane **2k**



2-Bromo-5-nitrobenzaldehyde (978 mg, 4.25 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *acetal* **2k** (1.10 g, 4.00 mmol, 94 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.44 (1H, d, *J* 2.8, HC_{Ar}), 8.08 (1H, dd, *J* 8.6, 2.8, HC_{Ar}), 7.76 (1H, d, *J* 8.9, HC_{Ar}), 6.10 (1H, s, C*H*$(OR)_2$), 4.24-4.16 (2H, m, C$H_a$$H_bCH_a$$H_b$), 4.16-4.08 (2H, m, C$H_a$$H_bCH_a$$H_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 147.3, 139.0, (2 × C_{Ar}), 134.1 (HC_{Ar}), 130.1 (C_{Ar}), 125.0, 123.0 (2 × HC_{Ar}), 101.5 (*C*H$(OR)_2$), 65.7 (CH_2OR); **m.p.** 95-96 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[4]

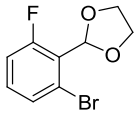
2-(2-Bromo-5-fluorophenyl)-1,3-dioxolane **2l**



2-Bromo-5-fluorobenzaldehyde (1.98 g, 9.74 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *acetal* **2l** (2.35 g, 9.53 mmol, 98 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.52 (1H, dd, *J* 8.4, 5.3, HC_{Ar}), 7.34 (1H, dd, *J* 9.3, 2.4, HC_{Ar}), 6.96 (1H, td, *J* 8.1, 2.3, HC_{Ar}), 6.04 (1H, s, C*H*$(OR)_2$), 4.17-4.06 (4H, m, 2 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 162.0 (d, ^1J 247.7, C_{Ar}), 139.0 (d, ^3J 8.0, C_{Ar}), 134.3 (d, ^3J 8.0, HC_{Ar}), 117.7 (d, ^2J 22.3, HC_{Ar}), 116.8 (d, ^4J 3.2, C_{Ar}), 115.1 (d, ^2J 25.4, HC_{Ar}), 102.0 (*C*H$(OR)_2$), 65.5 (CH_2OR); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −113.9; **IR** ν_{max} (thin film)/cm^{-1} 2958w, 2889w, 1583m, 1468s, 1415m, 1390m, 1263s, 1221w, 1158s, 1118s, 1080s, 1029s, 964m, 941s, 880s, 814s; **m/z** (EI/FI^+) $C_9H_8{}^{79}BrFO_2$ predicted 245.9692, found 245.9691, (Δ + 0.3 ppm).

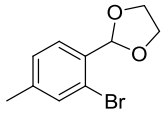
2-(2-Bromo-6-fluorophenyl)-1,3-dioxolane **2m**



2-Bromo-6-fluorobenzaldehyde (991 mg, 4.88 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *acetal* **2m** (1.16 g, 4.69 mmol, 96 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.37 (1H, d, *J* 8.1, *H*C$_{Ar}$), 7.20 (1H, ddd, *J* 8.4, 8.1, 5.6, *H*C$_{Ar}$), 7.04 (1H, dd, *J* 9.6, 8.4, *H*C$_{Ar}$), 6.33 (1H, s, C*H*(OR)$_2$), 4.29-4.22 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.09-4.02 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 162.1 (d, ^{1}J 256.5, *C*$_{Ar}$), 131.4 (d, ^{3}J 10.3, H*C*$_{Ar}$), 129.2 (d, ^{4}J 3.9, H*C*$_{Ar}$), 124.3 (d, ^{2}J 12.8, *C*$_{Ar}$), 123.9 (d, ^{3}J 4.8, *C*$_{Ar}$), 115.9 (d, ^{2}J 23.2, H*C*$_{Ar}$), 102.0 (d, ^{3}J 2.4, *C*H(OR)$_2$), 66.0 (*C*H$_2$OR); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −112.4; **IR** ν_{max} (thin film)/cm^{-1} 2969w, 2896w, 1602m, 1574m, 1457s, 1410m, 1391m, 1246s, 1209s, 1178w, 1167w, 1138w, 1096s, 1059s, 1027m, 959s, 941s, 881s, 804w; **m/z** (EI/FI$^+$) $C_9H_8{}^{79}BrFO_2$ predicted 245.9692, found 245.9689, (Δ + 1.1 ppm).

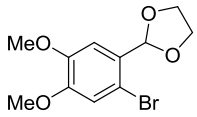
2-(2-Bromo-4-methylphenyl)-1,3-dioxolane **2n**



2-Bromo-4-methylbenzaldehyde (879 mg, 4.42 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *acetal* **2n** (1.07 g, 4.41 mmol, 100 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.48 (1H, d, *J* 7.8, *H*C$_{Ar}$), 7.40 (1H, s, *H*C$_{Ar}$), 7.15 (1H, d, *J* 7.8, *H*C$_{Ar}$), 6.08 (1H, s, C*H*(OR)$_2$), 4.17-4.11 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.10-4.04 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 2.34 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 140.9, 133.6 (2 × *C*$_{Ar}$), 133.4, 128.2, 127.6, (3 × H*C*$_{Ar}$), 122.7 (*C*$_{Ar}$), 102.7 (*C*H(OR)$_2$), 65.4 (*C*H$_2$OR), 20.8 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2885w, 1608m, 1567w, 1450w, 1381m, 1271m, 1218m, 1141m, 1086s, 1038s, 972m, 942s, 869m, 825s; **m/z** (EI/FI$^+$) $C_{10}H_{11}{}^{79}BrO_2$ predicted 241.9942, found 241.9943, (Δ − 0.2 ppm).

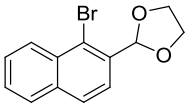
2-(2-Bromo-4,5-dimethoxyphenyl)-1,3-dioxolane **2o**



2-Bromo-4,5-dimethoxybenzaldehyde (2.00 g, 8.15 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 9:1 grading to 4:1] to furnish *acetal* **2o** (2.29 g, 7.91 mmol, 97 %) as needles.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.11 (1H, s, *H*C$_{Ar}$), 7.01 (1H, s, *H*C$_{Ar}$), 5.99 (1H, s, C*H*(OR)$_2$), 4.19-4.16 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.07-4.04 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 3.89 (3H, s, OC*H*$_3$), 3.87 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 150.2, 148.5, 128.2 (3 × *C*$_{Ar}$), 115.4 (H*C*$_{Ar}$), 113.4 (*C*$_{Ar}$), 110.1 (H*C*$_{Ar}$), 102.6 (*C*H(OR)$_2$), 65.4 (*C*H$_2$OR), 56.2, 56.0 (2 × O*C*H$_3$); **m.p.** 108-110 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[5]

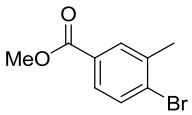
2-(1-Bromonaphthalen-2-yl)-1,3-dioxolane **2p**



1-Bromo-2-naphthaldehyde (1.20 g, 5.08 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *acetal* **2p** (1.41 g, 5.03 mmol, 99 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.40 (1H, d, *J* 8.6, *H*C_{Ar}), 7.85 (1H, d, *J* 8.6, *H*C_{Ar}), 7.84 (1H, d, *J* 8.1, *H*C_{Ar}), 7.71 (1H, d, *J* 8.6, *H*C_{Ar}), 7.63 (1H, td, *J* 7.1, 1.3, *H*C_{Ar}), 7.56 (1H, td, *J* 8.3, 1.0, *H*C_{Ar}), 6.44 (1H, s, C*H*$(OR)_2$), 4.28-4.20 (2H, m, C$H_a$$H_bCH_a$$H_b$), 4.18-4.10 (2H, m, C$H_a$$H_bCH_a$$H_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 135.0, 134.6, 132.2 (3 × C_{Ar}), 128.2, 128.0, 127.6, 127.5, 127.2, 124.2 (6 × HC_{Ar}), 124.0 (C_{Ar}), 103.5 (*C*H$(OR)_2$), 65.7 (*C*H_2OR); **IR** ν_{max} (thin film)/cm^{-1} 2960w, 2885w, 1557w, 1501w, 1464w, 1399w, 1344w, 1324m, 1260m, 1224m, 1134m, 1094s, 1026m, 1000m, 961s, 943s, 864m, 818s; **m/z** (EI/FI^+) $C_{13}H_{11}{}^{79}BrO_2$ predicted 277.9942, found 277.9940, (Δ + 0.9 ppm).

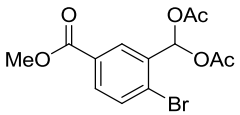
Methyl 4-bromo-3-methylbenzoate **S1**



4-Bromo-3-methyl-benzoic acid (2.50 g, 11.6 mmol) and concentrated aqueous H_2SO_4 (2 mL) were added to MeOH (15 mL) and the reaction heated at reflux for 18 h. The solvent was removed *in vacuo* and then the residue was taken up in EtOAc (100 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL), H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was taken up in CH_2Cl_2 and passed through a plug of silica to furnish *ester* **S1** (2.54 g, 11.1 mmol, 95 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.89 (1H, d, *J* 1.7, *H*C_{Ar}), 7.69 (1H, dd, *J* 8.3, 2.0, *H*C_{Ar}), 7.59 (1H, d, *J* 8.3, *H*C_{Ar}), 3.90 (3H, s, OCH_3), 2.43 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 166.6 (*C*=O), 138.2 (C_{Ar}), 132.5, 131.7 (2 × HC_{Ar}), 130.4, 129.2 (2 × C_{Ar}), 128.3 (HC_{Ar}), 52.2 (O*C*H_3), 22.9 (*C*H_3); **m.p.** 38-39 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[6]

(2-Bromo-5-(methoxycarbonyl)phenyl)methylene diacetate **S2**

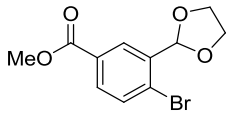


Chromium trioxide (3.35 g, 33.5 mmol) was added portionwise over 30 min to a solution of ester **S1** (2.40 g, 11.2 mmol), concentrated aqueous H_2SO_4 (2 mL) and acetic anhydride (14.7 g, 144 mmol) in AcOH (14 mL) at 0 °C. The reaction was warmed to room temperature and stirred for another 4 h at this temperature. The mixture was poured on to iced H_2O (150 mL),

stirred for 30 min and then filtered. The precipitate was taken up in EtOAc (150 mL), washed with H_2O (5 × 50 mL), dried over Na_2SO_4 and concentrated *in vacuo* to furnish *diacetate* **S2** (1.94 g, 5.61 mmol, 50 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.21 (1H, d, *J* 2.1, *H*C_{Ar}), 7.92 (1H, s, C*H*$(OAc)_2$), 7.91 (1H, dd, *J* 8.5, 2.0, *H*C_{Ar}), 7.68 (1H, d, *J* 8.4, *H*C_{Ar}), 3.94 (3H, s, OCH_3), 2.16 (6H, s, 2 × CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 168.4, 165.8 (2 × *C*=O), 135.5 (*C*$_{Ar}$), 133.5, 131.7 (2 × H*C*$_{Ar}$), 129.8 (*C*$_{Ar}$), 129.1 (H*C*$_{Ar}$), 127.8 (*C*$_{Ar}$), 88.6 (*C*H$(OAc)_2$), 52.5 (OCH_3), 20.7 (CH_3); **m.p.** 45-47 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[6]

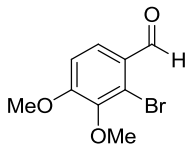
Methyl 4-bromo-3-(1,3-dioxolan-2-yl)benzoate **2q**



Diacetate **S2** (1.78 g, 5.16 mmol) and concentrated aqueous H_2SO_4 (0.2 mL) in a solution of MeOH/H_2O (16 mL, 1:1) were heated at reflux for 1 h. The reaction mixture was diluted with H_2O (50 mL) and then extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was then subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *acetal* **2q** (1.01 g, 3.52 mmol, 68 %) as rods.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.23 (1H, d, *J* 2.3, *H*C_{Ar}), 7.87 (1H, dd, *J* 8.3, 2.3, *H*C_{Ar}), 7.64 (1H, d, *J* 8.3, *H*C_{Ar}), 6.10 (1H, s, C*H*$(OR)_2$), 4.20-4.13 (2H, m, CH_aH$_b$CH_aH$_b$), 4.12-4.05 (2H, m, CH$_a$$H_bCH_a$$H_b$), 3.91 (3H, s, OC$H_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 166.1 (*C*=O), 137.3 (*C*$_{Ar}$), 133.3, 131.3 (2 × H*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 129.0 (H*C*$_{Ar}$), 128.3 (*C*$_{Ar}$), 102.1 (*C*H$(OR)_2$), 65.6 (*C*H$_2$OR), 52.3 (O*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2953w, 2890w, 1720s, 1436m, 1395w, 1292s, 1239s, 1203s, 1107s, 1086s, 1026s, 989m, 943m, 927m, 808w; **m/z** (ESI$^+$) 309.0 [100, (M + Na)$^+$], 595.0 [30, (2M + Na)$^+$], $C_{11}H_{11}{}^{79}BrNaO_4$ predicted 308.9733, found 308.9729, (Δ + 1.2 ppm); **m.p.** 69-71 °C (petrol/CH_2Cl_2).

2-Bromo-3,4-dimethoxybenzaldehyde **S3**

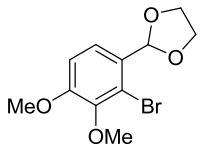


Powdered NaOH (649 mg, 16.2 mmol) was stirred in DMSO (6.9 mL) for 5 min at room temperature. A solution of 2-bromo-3-hydroxy-4-methoxybenzaldehyde (1.50 g, 6.49 mmol) in DMSO (1.0 mL) and iodomethane (1.01 g, 7.14 mmol) were then added. The reaction was stirred for a further 30 min and then the reaction mixture was poured on to 80 mL of 2 M aqueous HCl. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude

product. Purification by flash column chromatography [Petrol/EtOAc 9:1 grading to 4:1] furnished *ether* **S3** (1.32 g, 5.39 mmol, 83 %) as needles.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 10.25 (1H, s, C*H*O), 7.74 (1H, d, *J* 8.8, *H*C$_{Ar}$), 6.96 (1H, d, *J* 8.9, *H*C$_{Ar}$), 3.96 (3H, s, OC*H*$_3$), 3.89 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 190.9 (*C*HO), 158.6, 146.4, 127.3 (3 × *C*$_{Ar}$), 126.5 (H*C*$_{Ar}$), 123.1 (*C*$_{Ar}$), 110.9 (H*C*$_{Ar}$), 60.6, 56.3 (2 × O*C*H$_3$); **m.p.** 82-84 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[7]

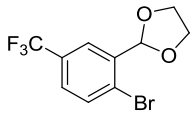
2-(2-Bromo-3,4-dimethoxyphenyl)-1,3-dioxolane **2r**



2-Bromo-3,4-dimethoxybenzaldehyde (1.08 g, 4.42 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 9:1 grading to 4:1] to furnish *acetal* **2r** (1.16 g, 4.02 mmol, 91 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.34 (1H, d, *J* 8.9, *H*C$_{Ar}$), 6.89 (1H, d, *J* 8.6, *H*C$_{Ar}$), 6.07 (1H, s, C*H*(OR)$_2$), 4.17-4.11 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.10-4.04 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 3.89 (3H, s, OC*H*$_3$), 3.86 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 154.3, 146.4, 129.5 (3 × *C*$_{Ar}$), 123.0 (H*C*$_{Ar}$), 118.8 (*C*$_{Ar}$), 111.0 (H*C*$_{Ar}$), 102.7 (*C*H(OR)$_2$), 65.4 (*C*H$_2$OR), 60.5, 56.1 (2 × O*C*H$_3$); **m.p.** 71-73 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[8]

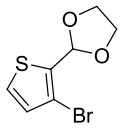
2-(2-Bromo-5-(trifluoromethyl)phenyl)-1,3-dioxolane **2s**



2-Bromo-5-(trifluoromethyl)benzaldehyde (1.00 g, 3.97 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 99:1 grading to 49:1] to furnish *acetal* **2s** (1.10 g, 3.69 mmol, 93 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.88 (1H, d, *J* 2.0, *H*C$_{Ar}$), 7.69 (1H, dd, *J* 8.0, 3.6, *H*C$_{Ar}$), 7.47 (1H, dd, *J* 8.4, 2.6, *H*C$_{Ar}$), 6.10 (1H, d, *J* 2.8, C*H*(OR)$_2$), 4.19-4.14 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.10-4.06 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 138.0 (*C*$_{Ar}$), 133.6 (H*C*$_{Ar}$), 129.9 (q, ^2J 32.7, *C*$_{Ar}$), 127.1 (q, ^3J 2.4, H*C*$_{Ar}$), 126.8 (q, ^4J 1.6, *C*$_{Ar}$), 124.9 (q, ^3J 4.0, H*C*$_{Ar}$), 123.7 (q, ^1J 272.4, *C*F$_3$), 101.8 (*C*H(OR)$_2$), 65.6 (*C*H$_2$OR); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −62.7; **IR** ν_{max} (thin film)/cm^{-1} 2893w, 1608w, 1583w, 1476w, 1395w, 1326s, 1256s, 1199m, 1168s, 1123s, 1078s, 1027s, 975m, 944m, 900m, 828m; **m/z** (EI/FI$^+$) $C_{10}H_8{}^{79}BrF_3O_2$ predicted 295.9660, found 295.9671, (Δ − 3.8 ppm).

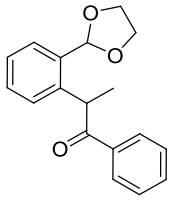
2-(3-Bromothiophen-2-yl)-1,3-dioxolane **2t**



3-Bromothiophene-2-carboxaldehyde (867 mg, 4.53 mmol) was subjected to General Procedure 1. The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 19:1] to furnish *acetal* **2t** (1.02 g, 4.34 mmol, 96 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.31 (1H, d, *J* 4.5, *H*C(5)), 6.98 (1H, d, *J* 5.0, *H*C(4)), 6.14 (1H, s, C*H*$(OR)_2$), 4.20-4.12 (2H, m, C$H_aH_bCH_aH_b$), 4.07-3.99 (2H, m, $CH_aH_bCH_aH_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 136.0 (*C*(2)), 130.4 (H*C*(4)), 126.5 (H*C*(5)), 110.2 (*C*(3)), 99.5 (*C*H$(OR)_2$), 65.4 (*C*H_2OR). Data were consistent with those previously reported.[9]

2-(2-(1,3-Dioxolan-2-yl)phenyl)-1-phenylpropan-1-one **3a**



Entry	X	Cat. Loading [mol%]	Ketone [mol%]	Time [h]	Yield [%]
1	Br	0.5[a]	120	18	71
2	Br	0.5[a]	200	18	74
3	Br	2.0[a]	120	18	82
4	Br	2.0[a]	200	18	83
5	Br	5.0[a]	200	18	89
6	I	2.0[a]	120	18	79
7	Cl	5.0[a]	200	18	30
8	Cl	5.0[b]	200	18	45
9	Cl	5.0[b] × 2	200	96	74
10	Br	2.0[b]	120	18	82

Selected Entries:

Entry 3: Acetal **2a** (56.0 mg, 0.244 mmol) was subjected to General Procedure 2a with propiophenone (39.4 mg, 0.293 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 14:1] to furnish *ketone* **3a** (56.7 mg, 0.201 mmol, 82 %) as prisms.

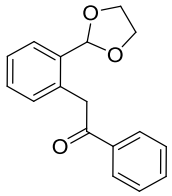
Entry 5: Acetal **2a** (85.5 mg, 0.373 mmol) was subjected to General Procedure 2b with propiophenone (100 mg, 0.746 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 14:1] to furnish *ketone* **3a** (93.4 mg, 0.331 mmol, 89 %) as prisms.

Entry 9: A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. $PdCl_2$(Amphos)$_2$ (13.8 mg, 0.0195 mmol) and sodium *tert*-butoxide (93.5 mg, 0.973 mmol) were added to the tube. Acetal **2c** (71.9 mg, 0.389 mmol) was dissolved in dry THF (1.95 mL) and the resulting solution was

added *via* syringe to the tube. Propiophenone (105 mg, 0.779 mmol) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^{o}C for 48 h. Additional $PdCl_2(Amphos)_2$ (13.8 mg, 0.0195 mmol) was added and the tube was heated at 70 ^{o}C for a further 48 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified as specified. Purification by flash column chromatography [Petrol/EtOAc 19:1 grading to 14:1] furnished *ketone* **3a** (80.8 mg, 0.286 mmol, 74 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.04 (2H, d, *J* 7.6, 2 × *H*C$_{Ar}$), 7.62-7.59 (1H, m, *H*C$_{Ar}$), 7.45 (1H, t, *J* 7.3, *H*C$_{Ar}$), 7.36 (2H, t, *J* 7.6, 2 × *H*C$_{Ar}$), 7.26-7.21 (2H, m, 2 × *H*C$_{Ar}$), 7.11-7.08 (1H, m, *H*C$_{Ar}$), 6.14 (1H, s, C*H*(OR)$_2$), 5.12 (1H, q, *J* 6.8, C*H*CH$_3$), 4.21-4.09 (4H, m, 2 × C*H*$_2$), 1.54 (3H, d, *J* 6.8, CHC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 200.9 (*C*=O), 140.6, 136.5, 133.7 (3 × *C*$_{Ar}$), 132.6, 129.8, 129.0, 128.4, 127.7, 127.4, 126.8 (7 × H*C*$_{Ar}$), 102.6 (*C*H(OR)$_2$), 65.3, 65.1 (2 × *C*H$_2$OR), 43.7 (*C*HCH$_3$), 19.2 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3064w, 2976m, 2888m, 1682s, 1597w, 1581w, 1490w, 1449m, 1373w, 1222s, 1181w, 1111m, 1084s, 1057s, 1026w, 1002w, 968m, 950s; **m/z** (ESI$^+$) 305.1 [100, (M + Na)$^+$], 587.3 [60, (2M + Na)$^+$], $C_{18}H_{18}NaO_3$ predicted 305.1148, found 305.1148, (Δ + 0.2 ppm); **m.p.** 76-78 °C (petrol/CH_2Cl_2).

2-(2-(1,3-Dioxolan-2-yl)phenyl)-1-phenylethanone **3b**



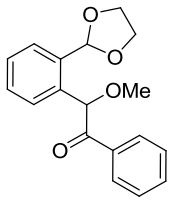
Acetal **2a** (56.0 mg, 0.244 mmol) was subjected to General Procedure 2a with acetophenone (35.2 mg, 0.293 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3b** (53.1 mg, 0.201 mmol, 82 %) as prisms.

Acetal **2a** (68.7 mg, 0.300 mmol) was subjected to General Procedure 2b with acetophenone (72.1 mg, 0.600 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3b** (74.0 mg, 0.276 mmol, 92 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.06 (2H, dd, *J* 7.3, 0.8, 2 × *H*C$_{Ar}$), 7.58 (2H, td, *J* 8.0, 1.0, 2 × *H*C$_{Ar}$), 7.49 (2H, t, *J* 7.7, 2 × *H*C$_{Ar}$), 7.36-7.30 (2H, m, 2 × *H*C$_{Ar}$), 7.19 (1H, d, *J* 6.6, *H*C$_{Ar}$), 5.89 (1H, s, C*H*(OR)$_2$), 4.51 (2H, s, C*H*$_2$), 4.03-3.99 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 3.97-3.93 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 197.6 (*C*=O), 137.0, 135.6, 133.6 (3 × *C*$_{Ar}$), 133.0, 131.5, 129.2, 128.6, 128.4, 127.0, 127.0 (7 × H*C*$_{Ar}$), 102.8 (*C*H(OR)$_2$), 65.0 (*C*H$_2$OR), 42.6 (*C*H$_2$); **IR** ν_{max} (thin film)/cm^{-1} 2890w, 1687s, 1597w, 1580w, 1490w, 1448m, 1403w, 1333m, 1271w, 1214s, 1112m, 1073s, 1044w, 1023w, 993s, 943s; **m/z**

(ESI$^+$) 291.1 [55, (M + Na)$^+$], 559.2 [100, (2M + Na)$^+$], $C_{17}H_{16}NaO_3$ predicted 291.0992, found 291.0994, (Δ − 0.7 ppm); **m.p.** 87-89 °C (petrol/CH_2Cl_2).

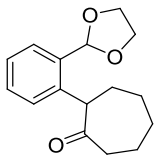
2-(2-(1,3-Dioxolan-2-yl)phenyl)-2-methoxy-1-phenylethanone **3c**



A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (10.1 mg, 0.0156 mmol) and potassium phosphate (165 mg, 0.778 mmol) were added to the tube. Acetal **2a** (71.3 mg, 0.311 mmol) was dissolved in dry THF (1.56 mL) and the resulting solution was added *via* syringe to the tube. The ketone (56.1 mg, 0.374 mmol) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified by flash column chromatography [Petrol/Et_2O 49:1 grading to 9:1] to furnish *ketone* **3c** (80.3 mg, 0.269 mmol, 87 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.01 (2H, d, *J* 7.7, 2 × *H*C_{Ar}), 7.65-7.63 (1H, m, *H*C_{Ar}), 7.51 (1H, t, *J* 7.3, *H*C_{Ar}), 7.41 (2H, t, *J* 7.7, 2 × *H*C_{Ar}), 7.39-7.33 (3H, m, 3 × *H*C_{Ar}), 6.13 (1H, s, C*H*$(OR)_2$), 6.12 (1H, s, C*H*OMe), 4.14-4.02 (4H, m, 2 × CH_2OR), 3.50 (3H, s, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 196.8 (*C*=O), 136.0, 135.7, 134.8 (3 × C_{Ar}), 133.0, 129.5, 128.9, 128.7 (2 signals), 128.5, 127.1 (7 × HC_{Ar}), 102.0 (*C*H$(OR)_2$), 81.6 (*C*HOMe), 65.1, 65.1 (2 × *C*H_2OR), 58.1 (O*C*H_3); **IR** ν_{max} (thin film)/cm^{-1} 2891w, 1693s, 1597w, 1448m, 1212m, 1105s, 1072s, 1044m, 969m, 944s, 859w; **m/z** (ESI$^+$) 321.1 [100, (M + Na)$^+$], 619.2 [90, (2M + Na)$^+$], $C_{18}H_{18}NaO_4$ predicted 321.1097, found 321.1098, (Δ − 0.2 ppm).

2-(2-(1,3-Dioxolan-2-yl)phenyl)cycloheptanone **3d**

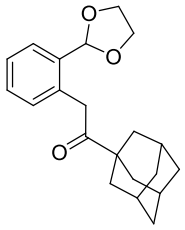


Acetal **2a** (166 mg, 0.726 mmol) was subjected to General Procedure 2b with cycloheptanone (163 mg, 1.45 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3d** (137 mg, 0.527 mmol, 73 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.53 (1H, dd, *J* 10.6, 1.0, *H*C_{Ar}), 7.37 (1H, td, *J* 7.4, 1.3 *H*C_{Ar}), 7.30 (1H, dd, *J* 7.8, 1.3, *H*C_{Ar}), 7.26 (1H, td, *J* 7.3, 1.5, *H*C_{Ar}), 6.01 (1H, s, C*H*$(OR)_2$), 4.36 (1H, dd, *J* 10.9, 2.6, C*H*), 4.12-3.99 (4H, m, 2 × CH_2OR), 2.73 (1H, dt, *J* 16.0, 4.8,

CH_aH$_b$C=O), 2.61 (1H, ddd, *J* 15.7, 11.8, 3.8, CH$_a$$H_b$C=O), 2.12-1.90 (5H, m, 2 × CH_2 + CH_aH$_b$CH$_2$C=O), 1.83-1.71 (1H, m, CH$_a$$H_bCH_2$C=O), 1.63-1.52 (1H, m, CH_aH$_b$), 1.46-1.34 (1H, m, CH$_a$$H_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 213.0 (*C*=O), 140.1, 134.5 (2 × C_{Ar}), 129.0, 128.6, 126.4, 126.2 (4 × HC_{Ar}), 102.5 (*C*H(OR)$_2$), 65.1, 64.8 (2 × *C*H$_2$OR), 52.5 (*C*H), 43.6 (*C*H$_2$C=O), 33.0, 29.9, 29.4 (3 × *C*H$_2$), 24.3 (*C*H$_2$CH$_2$C=O); **IR** ν_{max} (thin film)/cm^{-1} 2926s, 2857m, 1701s, 1645m, 1606w, 1491m, 1454s, 1346m, 1295m, 1218m, 1179w, 1139m, 1117s, 1099s, 1029s, 974s, 950m, 911s; **m/z** (ESI$^+$) 283.1 [100, (M + Na)$^+$], 543.3 [100, (2M + Na)$^+$], $C_{16}H_{20}NaO_3$ predicted 283.1305, found 283.1306, (Δ − 0.4 ppm).

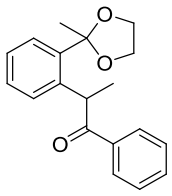
1-Adamantyl-2-(2-(1,3-dioxolan-2-yl)phenyl) ethanone **3e**



Acetal **2a** (175 mg, 0.766 mmol) was subjected to General Procedure 2a with methyl adamantyl ketone (164 mg, 0.919 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 19:1] to furnish *ketone* **3e** (175 mg, 0.536 mmol, 70 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.59 (1H, dd, *J* 7.0, 2.2, *H*C_{Ar}), 7.33-7.26 (2H, m, 2 × *H*C_{Ar}), 7.06 (1H, dd, *J* 6.6, 2.2, *H*C_{Ar}), 5.83 (1H, s, C*H*(OR)$_2$), 4.09-4.03 (2H, m, CH_aH$_b$CH_aH$_b$), 4.03-3.97 (2H, m, CH$_a$$H_bCH_a$$H_b$), 4.00 (2H, s, C$H_2$C=O), 2.09 (3H, br. s, 3 × C*H*), 1.93 (6H, d, *J* 2.8, 3 × CH_2), 1.81-1.72 (6H, m, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 212.2 (*C*=O), 136.0, 133.8, (2 × C_{Ar}), 131.4, 128.8, 126.7, 126.1 (4 × HC_{Ar}), 102.1 (*C*H(OR)$_2$), 64.9 (*C*H$_2$OR), 46.7 (CO*C*R$_3$), 40.3 (CO*C*H$_2$) 38.5, 36.6 (2 × *C*H$_2$), 28.1 (*C*H); **IR** ν_{max} (thin film)/cm^{-1} 2904s, 2850s, 1701s, 1645w, 1491w, 1452m, 1390w, 1344m, 1327m, 1307m, 1223w, 1193w, 1157m, 1112m, 1074s, 1013s, 964m, 944m; **m/z** (ESI$^+$) 349.2 [10, (M + Na)$^+$], 675.4 [100, (2M + Na)$^+$], $C_{21}H_{26}NaO_3$ predicted 349.1774, found 349.1771, (Δ + 0.8 ppm); **m.p.** 69-71 °C (petrol/CH_2Cl_2).

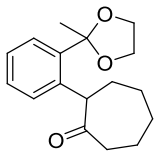
2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-1-phenylpropan-1-one **3f**



Acetal **2f** (66.5 mg, 0.274 mmol) was subjected to General Procedure 2a with propiophenone (44.0 mg, 0.328 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *ketone* **3f** (63.9 mg, 0.216 mmol, 79 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.06-8.03 (2H, m, 2 × *H*C$_{Ar}$), 7.63 (1H, dd, *J* 7.9, 1.6, *H*C$_{Ar}$), 7.51 (1H, tt, *J* 7.4, 1.7, *H*C$_{Ar}$), 7.45-7.40 (3H, m, 3 × *H*C$_{Ar}$), 7.32 (1H, td, *J* 7.8, 1.5, *H*C$_{Ar}$), 7.24 (1H, td, *J* 7.6, 1.3, *H*C$_{Ar}$), 5.11 (1H, q, *J* 7.2, C*H*CH$_3$), 4.04-3.99 (1H, m, C*H*$_a$H$_b$CH$_a$H$_b$), 3.86-3.75 (2H, m, CH$_a$*H*$_b$C*H*$_a$H$_b$), 3.52-3.47 (1H, m, CH$_a$H$_b$CH$_a$*H*$_b$), 1.78 (3H, s, C*H*$_3$), 1.58 (3H, d, *J* 7.1, CHC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 202.1 (*C*=O), 140.0, 138.3, 137.2 (3 × *C*$_{Ar}$), 132.4, 129.4, 128.7, 128.4 (2 signals), 126.7, 126.4 (7 × H*C*$_{Ar}$), 109.3 (*C*(OR)$_2$), 64.4, 64.0 (2 × *C*H$_2$OR), 43.3 (*C*HCH$_3$), 28.1 (*C*H$_3$), 19.7 (CH*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2983w, 2889w, 1681s, 1597w, 1579w, 1481w, 1447m, 1374m, 1289w, 1189s, 1104w, 1035s, 967m, 951m, 867m; **m/z** (ESI$^+$) 319.1 [95, (M + Na)$^+$], 615.3 [100, (2M + Na)$^+$], $C_{19}H_{20}NaO_3$ predicted 319.1305, found 319.1307, (Δ − 0.8 ppm).

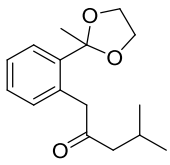
2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)cycloheptanone **3g**



Acetal **2f** (71.1 mg, 0.292 mmol) was subjected to General Procedure 2b with cycloheptanone (65.6 mg, 0.585 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *ketone* **3g** (54.6 mg, 0.199 mmol, 68 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.55 (1H, dd, *J* 7.8, 2.4, *H*C$_{Ar}$), 7.32 (1H, td, *J* 7.5, 1.3 *H*C$_{Ar}$), 7.25 (1H, dd, *J* 7.9, 1.5, *H*C$_{Ar}$), 7.21 (1H, td, *J* 7.5, 1.5, *H*C$_{Ar}$), 4.66 (1H, dd, *J* 11.2, 2.8, C*H*), 3.98 (1H, td, *J* 7.2, 5.9, C*H*$_a$H$_b$CH$_a$H$_b$OR), 3.91 (1H, td, *J* 7.1, 5.6, CH$_a$H$_b$C*H*$_a$H$_b$OR), 3.70 (1H, td, *J* 7.6, 5.7, CH$_a$*H*$_b$CH$_a$H$_b$OR), 3.47 (1H, td, *J* 7.5, 6.0, CH$_a$H$_b$CH$_a$*H*$_b$OR), 2.77 (1H, dt, *J* 16.6, 4.3, C*H*$_a$H$_b$C=O), 2.54 (1H, ddd, *J* 16.5, 11.9, 4.3, CH$_a$*H*$_b$C=O), 2.09-1.96 (4H, m, 2 × C*H*$_2$), 1.94-1.82 (2H, m, C*H*$_2$), 1.73 (3H, s, C*H*$_3$), 1.68-1.57 (1H, m, C*H*$_a$H$_b$), 1.42-1.32 (1H, m, CH$_a$*H*$_b$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 213.3 (*C*=O), 139.5, 139.4 (2 × *C*$_{Ar}$), 129.7, 128.1, 126.3, 125.7 (4 × H*C*$_{Ar}$), 109.0 (*C*(OR)$_2$), 64.1, 63.8 (2 × *C*H$_2$OR), 52.8 (*C*H), 43.8 (*C*H$_2$C=O), 33.4, 30.4, 29.4 (3 × *C*H$_2$), 28.0 (*C*H$_3$), 23.8 (*C*H$_2$); **IR** ν_{max} (thin film)/cm^{-1} 2927m, 2856w, 1703s, 1482w, 1443w, 1375w, 1235m, 1189s, 1140w, 1098w, 1032s, 976w, 951w, 867m; **m/z** (ESI$^+$) 297.2 [90, (M + Na)$^+$], 571.3 [100, (2M + Na)$^+$], $C_{17}H_{22}NaO_3$ predicted 297.1461, found 297.1450, (Δ + 3.6 ppm).

4-Methyl-1-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)pentan-2-one **3h**

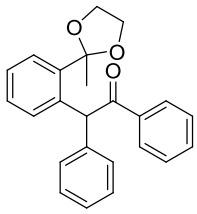


Acetal **2f** (65.3 mg, 0.269 mmol) was subjected to General Procedure 2b with 4-methyl-2-pentanone (53.9 mg, 0.538 mmol). The crude product was purified by flash column

chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *ketone* **3h** (64.7 mg, 0.246 mmol, 92 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.58 (1H, dd, *J* 6.6, 1.6, *H*C_{Ar}), 7.29-7.23 (2H, m, 2 × *H*C_{Ar}), 7.07 (1H, dd, *J* 6.8, 1.5, *H*C_{Ar}), 3.96-3.92 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 3.90 (2H, s, C*H*$_2$C$_{Ar}$), 3.65-3.62 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 2.43 (2H, d, *J* 6.8, C*H*$_2$CH), 2.19 (1H, sept., *J* 6.6, C*H*), 1.65 (3H, s, C*H*$_3$), 0.97 (6H, d, *J* 6.8, CH(C*H*$_3$)$_2$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 207.6 (*C*=O), 140.9 (*C*$_{Ar}$), 132.8 (H*C*$_{Ar}$), 132.0 (*C*$_{Ar}$), 128.0, 126.9, 126.3 (3 × H*C*$_{Ar}$), 109.0 (*C*(OR)$_2$), 64.2 (*C*H$_2$OR), 51.4 (*C*H$_2$CH), 48.3 (*C*H$_2$C$_{Ar}$), 27.5 (*C*H$_3$), 24.3 (*C*H), 22.7 (CH(*C*H$_3$)$_2$); **IR** ν_{max} (thin film)/cm^{-1} 2957s, 2895m, 1720s, 1469w, 1442w, 1419w, 1366m, 1319w, 1260m, 1241m, 1195s, 1143m, 1103m, 1036s, 952w, 870m; **m/z** (ESI$^+$) 285.2 [80, (M + Na)$^+$], 547.3 [100, (2M + Na)$^+$], $C_{16}H_{22}NaO_3$ predicted 285.1461, found 285.1453, (Δ + 3.0 ppm).

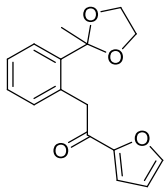
2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-1,2-diphenylethanone **3i**



Acetal **2f** (244 mg, 1.00 mmol) was subjected to General Procedure 2a with deoxybenzoin (236 mg, 1.20 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *ketone* **3i** (233 mg, 0.677 mmol, 68 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.05 (2H, dd, *J* 7.4, 1.2, 2 × *H*C_{Ar}), 7.66-7.64 (1H, m, *H*C_{Ar}), 7.50 (1H, tt, *J* 7.4, 1.9, *H*C_{Ar}), 7.41 (2H, t, *J* 7.7, 2 × *H*C_{Ar}), 7.36-7.32 (2H, m, 2 × *H*C_{Ar}), 7.27-7.23 (5H, m, 5 × *H*C_{Ar}), 7.14-7.11 (1H, m, *H*C_{Ar}), 6.91 (1H, s, C*H*), 4.00-3.95 (1H, m, C*H*$_a$H$_b$CH$_a$H$_b$), 3.78-3.71 (2H, m, CH$_a$*H*$_b$C*H*$_a$H$_b$), 3.51-3.45 (1H, m, CH$_a$H$_b$CH$_a$*H*$_b$), 1.79 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 198.5 (*C*=O), 140.2, 139.6, 137.1, 136.5 (4 × *C*$_{Ar}$), 132.5, 132.2, 129.4, 128.9, 128.9, 128.5, 128.0, 127.0, 126.8, 126.1 (10 × H*C*$_{Ar}$), 109.2 (*C*(OR)$_2$), 64.4, 63.8 (2 × *C*H$_2$OR), 55.5 (*C*H), 28.3 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3062w, 2989w, 2892w, 1686s, 1597w, 1580w, 1495w, 1479w, 1447m, 1374w, 1327w, 1274m, 1262m, 1207s, 1189s, 1100w, 1032s, 951w, 908w, 869s, 803m; **m/z** (ESI$^+$) 381.2 [25, (M + Na)$^+$], 739.3 [100, (2M + Na)$^+$], $C_{24}H_{22}NaO_3$ predicted 381.1461, found 381.1452, (Δ + 2.4 ppm); **m.p.** 134-136 °C (petrol/CH_2Cl_2).

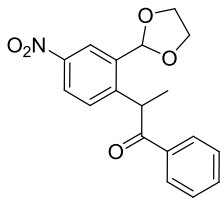
1-(Furan-2-yl)-2-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)ethanone **3j**



Acetal **2f** (83.1 mg, 0.342 mmol) was subjected to General Procedure 2b with 2-furyl methyl ketone (75.3 mg, 0.684 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *ketone* **3j** (75.8 mg, 0.278 mmol, 81 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.62-7.60 (2H, m, *H*C_{Ar} + *H*C(5)), 7.32-7.26 (2H, m, 2 × *H*C_{Ar}), 7.24 (1H, d, *J* 3.5, *H*C(3)), 7.18-7.16 (1H, m, *H*C_{Ar}), 6.56 (1H, dd, *J* 3.6, 1.8 *H*C(4)), 4.40 (2H, s, CH_2), 3.90-3.86 (2H, m, C$H_a$$H_bCH_a$$H_b$), 3.65-3.62 (2H, m, C$H_a$$H_bCH_a$$H_b$), 1.68 (3H, s, C$H_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 186.9 (*C*=O), 152.8 (*C*(2)), 146.0 (H*C*(5)), 141.3 (*C*$_{Ar}$), 133.0 (H*C*$_{Ar}$), 131.4 (*C*$_{Ar}$), 128.1, 127.2, 126.4 (3 × H*C*$_{Ar}$), 116.6 (H*C*(3)), 112.1 (H*C*(4)), 109.0 (*C*(OR)$_2$), 64.2 (*C*H_2OR), 43.5 (*C*H_2), 27.6 (*C*H_3); **IR** ν_{max} (thin film)/cm^{-1} 2959m, 2926m, 1680s, 1569m, 1468s, 1392w, 1375w, 1332w, 1243m, 1195m, 1156m, 1032s, 951w, 882m, 868m; **m/z** (ESI$^+$) 295.1 [80, (M + Na)$^+$], 567.2 [100, (2M + Na)$^+$], $C_{16}H_{16}NaO_4$ predicted 295.0941, found 295.0943, (Δ − 0.6 ppm); **m.p.** 85-88 °C (petrol/CH_2Cl_2).

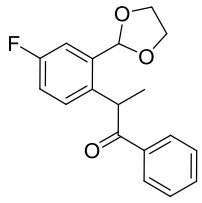
2-(2-(1,3-Dioxolan-2-yl)-4-nitrophenyl)-1-phenylpropan-1-one **3k**



A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. $PdCl_2$(Amphos)$_2$ (8.4 mg, 0.012 mmol) and caesium carbonate (194 mg, 0.595 mmol) were added to the tube. Acetal **2k** (65.3 mg, 0.238 mmol) was dissolved in dry THF (1.19 mL) and the resulting solution was added *via* syringe to the tube. Propiophenone (63.9 mg, 0.477 mmol) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^{o}C for 18 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3k** (68.0 mg, 0.208 mmol, 87 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.49 (1H, d, *J* 2.3, *H*C_{Ar}), 8.10 (1H, dd, *J* 8.6, 2.5, *H*C_{Ar}), 8.00 (2H, d, *J* 7.7, 2 × *H*C_{Ar}), 7.50 (1H, t, *J* 7.3, *H*C_{Ar}), 7.39 (2H, t, *J* 7.6, 2 × *H*C_{Ar}), 7.32 (1H, d, *J* 8.6, *H*C_{Ar}), 6.17 (1H, s, C*H*(OR)$_2$), 5.21 (1H, q, *J* 6.8, C*H*CH$_3$), 4.25-4.11 (4H, m, 2 × CH_2OR), 1.56 (3H, d, *J* 6.9, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 199.6 (*C*=O), 147.6, 146.7, 136.4, 135.9 (4 × *C*$_{Ar}$), 133.2, 129.0, 128.8, 128.7, 124.4, 122.4 (6 × H*C*$_{Ar}$), 100.9 (*C*H(OR)$_2$), 65.5, 65.4 (2 × *C*H_2OR), 43.5 (*C*HCH$_3$), 19.0 (CH*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2894w, 1683s, 1614w, 1592m, 1564w, 1523s, 1485w, 1449m, 1346s, 1221s, 1177w, 1104s, 1072m, 1054m, 1026m, 1000m, 967m, 950m, 907s, 845w; **m/z** (ESI$^+$) 350.1 [85, (M + Na)$^+$], 677.2 [100, (2M + Na)$^+$], $C_{18}H_{17}NNaO_5$ predicted 350.0999, found 350.0986, (Δ + 3.8 ppm).

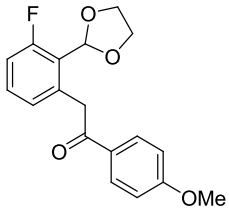
2-(2-(1,3-Dioxolan-2-yl)-4-fluorophenyl)-1-phenylpropan-1-one **3l**



Acetal **2l** (62.4 mg, 0.253 mmol) was subjected to General Procedure 2a with propiophenone (40.6 mg, 0.304 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *ketone* **3l** (58.0 mg, 0.193 mmol, 76 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.01 (2H, dd, *J* 8.6, 1.3, 2 × *H*C_{Ar}), 7.47 (1H, tt, *J* 7.5, 1.3, *H*C_{Ar}), 7.37 (2H, t, *J* 7.6, 2 × *H*C_{Ar}), 7.34 (1H, dd, *J* 9.8, 3.0, *H*C_{Ar}), 7.08 (1H, dd, *J* 8.8, 5.5, *H*C_{Ar}), 6.93 (1H, td, *J* 8.5, 3.0, *H*C_{Ar}), 6.12 (1H, s, C*H*$(OR)_2$), 5.07 (1H, q, *J* 6.8, C*H*CH_3), 4.22-4.16 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.14-4.08 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 1.51 (3H, d, *J* 6.9, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 200.7 (*C*=O), 161.5 (d, ^{1}J 245.3, C_{Ar}), 136.5 (d, ^{3}J 6.4, C_{Ar}), 136.3 (C_{Ar}), 136.0 (d, ^{4}J 4.0, C_{Ar}), 132.8 (HC_{Ar}), 129.4 (d, ^{3}J 8.0, HC_{Ar}), 128.9, 128.5 (2 × HC_{Ar}), 116.4 (d, ^{2}J 21.5, HC_{Ar}), 114.1 (d, ^{2}J 23.2, HC_{Ar}), 101.3 (d, ^{4}J 1.6, (*C*H$(OR)_2$)), 65.4, 65.2 (2 × *C*H_2OR), 43.0 (*C*HCH_3), 19.2 (*C*H_3); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −115.2; **IR** ν_{max} (thin film)/cm^{-1} 2977w, 2932w, 2891w, 1682s, 1595w, 1495m, 1449m, 1375w, 1338w, 1272s, 1222s, 1162s, 1114s, 1071m, 1054s, 1001m, 965s, 949s, 883s, 830m; **m/z** (ESI$^+$) 323.1 [100, (M + Na)$^+$], 623.3 [70, (2M + Na)$^+$], $C_{18}H_{17}FNaO_3$ predicted 323.1054, found 323.1044, (Δ + 3.2 ppm).

2-(2-(1,3-Dioxolan-2-yl)-3-fluorophenyl)-1-(4-methoxyphenyl)ethanone **3m**

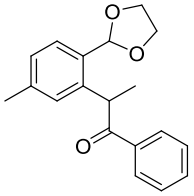


Acetal **2m** (111 mg, 0.447 mmol) was subjected to General Procedure 2a with 4'-methoxyacetophenone (80.6 mg, 0.537 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 9:1] to furnish *ketone* **3m** (122 mg, 0.387 mmol, 86 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.02 (2H, d, *J* 8.8, 2 × *H*C_{Ar}), 7.33-7.29 (1H, m, *H*C_{Ar}), 7.02-6.97 (2H, m, 2 × *H*C_{Ar}), 6.95 (2H, d, *J* 8.8, 2 × *H*C_{Ar}), 6.09 (1H, s, C*H*$(OR)_2$), 4.46 (2H, s, C*H*$_2$), 3.94-3.90 (4H, m, 2 × C*H*$_2$OR), 3.88 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 195.8 (*C*=O), 163.3 (C_{Ar}), 162.3 (d, ^{1}J 249.3, C_{Ar}), 154.1 (d, ^{2}J 21.6, C_{Ar}), 137.5 (d, ^{3}J 2.4, C_{Ar}), 130.8 (d, ^{3}J 9.6, HC_{Ar}), 130.5 (HC_{Ar}), 129.9 (C_{Ar}), 128.0 (d, ^{4}J 3.2, HC_{Ar}), 114.4 (d, ^{2}J 23.2, HC_{Ar}), 113.8 (HC_{Ar}), 98.4 (d, ^{3}J 9.6, (*C*H$(OR)_2$)), 64.9 (*C*H_2OR), 55.5 (O*C*H_3), 42.4 (*C*H_2); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −119.1; **IR** ν_{max} (thin film)/cm^{-1} 2935m, 1682m,

1601s, 1575m, 1510s, 1467s, 1420m, 1249s, 1216w, 1174s, 1085w, 1019s, 944m, 911m, 813m; **m/z** (ESI^+) 339.1 [30, $(M + Na)^+$], 655.2 [100, $(2M + Na)^+$], $C_{18}H_{17}FNaO_4$ predicted 339.1003, found 339.1006, (Δ − 0.9 ppm); **m.p.** 110-112 °C (petrol/CH_2Cl_2).

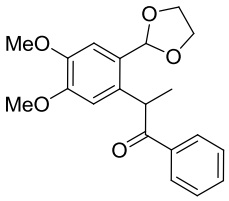
2-(2-(1,3-Dioxolan-2-yl)-5-methylphenyl)-1-phenylpropan-1-one **3n**



Acetal **2n** (177 mg, 0.729 mmol) was subjected to General Procedure 2a with propiophenone (117 mg, 0.875 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *ketone* **3n** (192 mg, 0.648 mmol, 89 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.07-8.04 (2H, m, 2 × *H*C_{Ar}), 7.49-7.43 (2H, m, 2 × *H*C_{Ar}), 7.36 (2H, tt, *J* 7.5, 1.1, 2 × *H*C_{Ar}), 7.04 (1H, d, *J* 7.6, *H*C_{Ar}), 6.89 (1H, s, *H*C_{Ar}), 6.10 (1H, s, C*H*$(OR)_2$), 5.08 (1H, q, *J* 6.8, C*H*CH_3), 4.21-4.15 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.14-4.08 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 2.23 (3H, s, C_{Ar}C*H*$_3$), 1.52 (3H, d, *J* 6.8, CHC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 201.0 (*C*=O), 140.4, 139.7, 136.5 (3 × *C*$_{Ar}$), 132.6 (H*C*$_{Ar}$), 130.6 (*C*$_{Ar}$), 129.0, 128.4, 128.2, 127.6, 127.5 (5 × H*C*$_{Ar}$), 102.8 (*C*H$(OR)_2$), 65.2, 65.1 (2 × *C*H_2OR), 43.6 (*C*HCH$_3$), 21.2 (C_{Ar}*C*H$_3$), 19.2 (CH*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2930w, 1682s, 1608w, 1597w, 1579w, 1449m, 1372w, 1334w, 1297w, 1259m, 1228s, 1211s, 1183w, 1115m, 1075s, 1057s, 1027m, 1001w, 958s, 817s; **m/z** (ESI^+) 319.1 [80, $(M + Na)^+$], 615.3 [100, $(2M + Na)^+$], $C_{19}H_{20}NaO_3$ predicted 319.1305, found 319.1303, (Δ + 0.6 ppm).

2-(2-(1,3-Dioxolan-2-yl)-4,5-dimethoxyphenyl)-1-phenylpropan-1-one **3o**

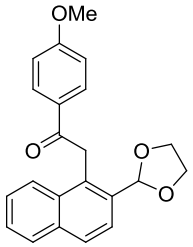


Acetal **2o** (77.4 mg, 0.268 mmol) was subjected to General Procedure 2a with propiophenone (43.1 mg, 0.321 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3o** (81.8 mg, 0.239 mmol, 89 %) as plates.

Acetal **2o** (103 mg, 0.356 mmol) was subjected to General Procedure 2b with propiophenone (95.5 mg, 0.712 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3o** (117 mg, 0.343 mmol, 96 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.02 (2H, dd, *J* 8.6, 1.5, 2 × *H*C_{Ar}), 7.46 (1H, tt, *J* 7.5, 1.6, *H*C_{Ar}), 7.36 (2H, t, *J* 7.6, 2 × *H*C_{Ar}), 7.14 (1H, s, *H*C_{Ar}), 6.56 (1H, s, *H*C_{Ar}), 6.09 (1H, s, C*H*$(OR)_2$), 5.03 (1H, q, *J* 6.8, C*H*CH_3), 4.24-4.18 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.15-4.09 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 3.87 (3H, s, OC*H*$_3$), 3.74 (3H, s, OC*H*$_3$), 1.51 (3H, d, *J* 6.9, CHC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 201.3 (*C*=O), 149.7, 147.5, 136.6, 133.1 (4 × *C*$_{Ar}$), 132.7, 128.9, 128.4 (3 × H*C*$_{Ar}$), 125.8 (*C*$_{Ar}$), 110.3, 110.2 (2 × H*C*$_{Ar}$), 102.1 (*C*H$(OR)_2$), 65.2, 65.1 (2 × *C*H_2OR), 55.8, 55.8 (2 × O*C*H_3), 43.2 (*C*H), 19.3 (CH*C*H_3); **IR** ν_{max} (thin film)/cm^{-1} 2935m, 2892m, 1681s, 1597m, 1517s, 1450m, 1402w, 1343w, 1270s, 1225m, 1202m, 1178m, 1116s, 1081w, 1020m, 993m, 952m, 870w; **m/z** (ESI$^+$) 365.2 [30, (M + Na)$^+$], 707.3 [100, (2M + Na)$^+$], $C_{20}H_{22}NaO_5$ predicted 365.1359, found 365.1362, (Δ − 0.6 ppm); **m.p.** 89-91 °C (petrol/CH_2Cl_2).

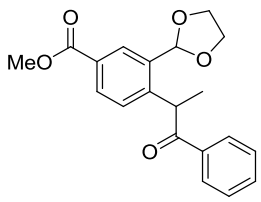
2-(2-(1,3-Dioxolan-2-yl)naphthalen-1-yl)-1-(4-methoxyphenyl)ethanone **3p**



Acetal **2p** (103 mg, 0.372 mmol) was subjected to General Procedure 2a with 4'-methoxyacetophenone (66.9 mg, 0.446 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 9:1] to furnish *ketone* **3p** (108 mg, 0.310 mmol, 83 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.15 (2H, d, *J* 8.6, 2 × *H*C_{Ar}), 7.88-7.85 (2H, m, 2 × *H*C_{Ar}), 7.81-7.75 (2H, m, 2 × *H*C_{Ar}), 7.50-7.43 (2H, m, 2 × *H*C_{Ar}), 7.02 (2H, d, *J* 8.6, 2 × *H*C_{Ar}), 6.09 (1H, s, C*H*$(OR)_2$), 4.96 (2H, s, C*H*$_2$), 4.12-4.06 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.05-3.99 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 3.91 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 195.1 (*C*=O), 163.6, 134.0, 133.8, 133.0, 130.8 (5 × *C*$_{Ar}$), 130.5 (H*C*$_{Ar}$), 130.0 (*C*$_{Ar}$), 128.6, 127.7, 126.4, 126.0, 124.0, 123.7, 113.9 (7 × H*C*$_{Ar}$), 102.7 (*C*H$(OR)_2$), 65.2 (*C*H_2OR), 55.5 (O*C*H_3), 37.7 (*C*H_2); **IR** ν_{max} (thin film)/cm^{-1} 2961w, 2918w, 1681s, 1600s, 1574m, 1510s, 1463w, 1441w, 1419w, 1381w, 1320m, 1258s, 1216m, 1171s, 1096s, 1019s; **m/z** (ESI$^+$) 371.2 [30, (M + Na)$^+$], 719.3 [100, (2M + Na)$^+$], $C_{22}H_{20}NaO_4$ predicted 371.1254, found 371.1243, (Δ + 2.9 ppm); **m.p.** 129-131 °C (petrol/CH_2Cl_2).

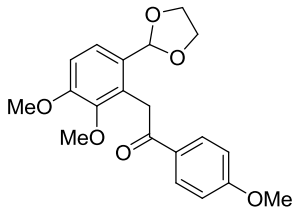
Methyl 3-(1,3-dioxolan-2-yl)-4-(1-oxo-1-phenylpropan-2-yl)benzoate **3q**



A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. $PdCl_2(Amphos)_2$ (12.8 mg, 0.0181 mmol) and potassium phosphate (192 mg, 0.905 mmol) were added to the tube. Acetal **2q** (104 mg, 0.362 mmol) was dissolved in dry THF (1.81 mL) and the resulting solution was added *via* syringe to the tube. Propiophenone (58.2 mg, 0.434 mmol) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^{o}C for 18 h. The reaction was then cooled to room temperature and quenched by the addition of H_2O (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product, which was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 4:1] to furnish *ketone* **3q** (86.4 mg, 2.54 mmol, 70 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (1H, d, *J* 1.8, *H*C$_{Ar}$), 8.02-7.99 (2H, m, 2 × *H*C$_{Ar}$), 7.90 (1H, dd, *J* 8.1, 2.1, *H*C$_{Ar}$), 7.45 (1H, tt, *J* 7.4, 1.3, *H*C$_{Ar}$), 7.35 (2H, tt, *J* 7.8, 1.5, 2 × *H*C$_{Ar}$), 7.17 (1H, d, *J* 8.1, *H*C$_{Ar}$), 6.14 (1H, s, C*H*(OR)$_2$), 5.15 (1H, q, *J* 6.8, C*H*CH$_3$), 4.24-4.17 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.16-4.09 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 3.87 (3H, s, OC*H*$_3$), 1.54 (3H, d, *J* 6.9, CHC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 200.3 (*C*=O), 166.6 (*C*O$_2$CH$_3$), 145.7, 136.2, 134.4 (3 × *C*$_{Ar}$), 132.8, 130.8, 128.9 (3 × H*C*$_{Ar}$), 128.7 (2 signals) (H*C*$_{Ar}$ + *C*$_{Ar}$), 128.5, 128.0 (2 × H*C*$_{Ar}$), 102.0 (*C*H(OR)$_2$), 65.4, 65.2 (2 × *C*H$_2$OR), 52.1 (O*C*H$_3$), 43.8 (*C*HCH$_3$), 19.0 (CH*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2892w, 1720s, 1683s, 1613w, 1437m, 1292s, 1211s, 1112s, 1074m, 1056m, 1000m, 967m, 950m; **m/z** (ESI$^+$) 363.1 [100, (M + Na)$^+$], 703.2 [90, (2M + Na)$^+$], $C_{20}H_{20}NaO_5$ predicted 363.1203, found 363.1210, (Δ − 1.9 ppm).

2-(6-(1,3-Dioxolan-2-yl)-2,3-dimethoxyphenyl)-1-(4-methoxyphenyl)ethanone **3r**

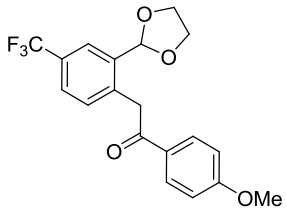


Acetal **2r** (146 mg, 0.509 mmol) was subjected to General Procedure 2a with 4'-methoxyacetophenone (91.8 mg, 0.611 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 9:1 grading to 4:1] to furnish *ketone* **3r** (127 mg, 0.353 mmol, 69 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.06 (2H, d, *J* 8.8, 2 × *H*C$_{Ar}$), 7.28 (1H, d, *J* 9.6, *H*C$_{Ar}$), 6.97 (2H, d, *J* 8.9, 2 × *H*C$_{Ar}$), 6.86 (1H, d, *J* 8.6, *H*C$_{Ar}$), 5.74 (1H, s, C*H*(OR)$_2$), 4.51 (2H, s, C*H*$_2$), 3.98-3.93 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 3.92-3.87 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 3.88 (3H, s, OC*H*$_3$), 3.88 (3H, s, OC*H*$_3$), 3.75 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 196.1 (*C*=O), 163.3, 153.2, 147.8, (3 × *C*$_{Ar}$), 130.4 (H*C*$_{Ar}$), 130.3, 128.7, 128.5 (3 × *C*$_{Ar}$), 122.8, 113.7, 110.4 (3 × H*C*$_{Ar}$), 103.0 (*C*H(OR)$_2$), 64.8 (*C*H$_2$OR), 60.6, 55.6, 55.5 (3 × O*C*H$_3$), 36.0 (*C*H$_2$); **IR** ν_{max} (thin film)/cm^{-1} 2940w, 2839w, 1680s, 1600s, 1576m, 1510m, 1495m, 1457m, 1421m, 1329w, 1308w, 1261s, 1230s, 1169s, 1093m, 1080m, 1035s, 995w, 960w, 938w, 831w, 813w; **m/z** (ESI$^+$) 359.2 [45, (M + H)$^+$], 381.1 [100, (M + Na)$^+$], 739.2 [100, (2M + Na)$^+$],

$C_{20}H_{22}NaO_6$ predicted 381.1309, found 381.1307, (Δ + 0.4 ppm); **m.p.** 114-116 °C (petrol/CH_2Cl_2).

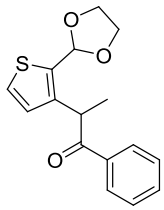
2-(2-(1,3-Dioxolan-2-yl)-4-(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)ethanone **3s**



Acetal **2s** (115 mg, 0.388 mmol) was subjected to General Procedure 2a with 4'-methoxyacetophenone (69.9 mg, 0.465 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *ketone* **3s** (113 mg, 0.308 mmol, 79 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.03 (2H, dt, *J* 8.8, 2.4, 2 × *H*C$_{Ar}$), 7.89 (1H, s, *H*C$_{Ar}$), 7.58 (1H, dd, *J* 8.1, 1.3, *H*C$_{Ar}$), 7.30 (1H, d, *J* 7.9, *H*C$_{Ar}$), 6.97 (2H, dt, *J* 9.0, 2.4, 2 × *H*C$_{Ar}$), 5.91 (1H, s, C*H*(OR)$_2$), 4.51 (2H, s, C*H*$_2$), 4.06-4.01 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.00-3.95 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$) 3.88 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 195.2 (*C*=O), 163.7, 138.1, 137.0 (3 × *C*$_{Ar}$), 131.9, 130.6 (2 × H*C*$_{Ar}$), 129.6 (*C*$_{Ar}$), 129.2 (q, ^2J 32.5, *C*$_{Ar}$), 125.7 (q, ^3J 3.7, H*C*$_{Ar}$), 124.1 (q, ^1J 272.2, *C*F$_3$), 123.6 (q, ^3J 3.4, H*C*$_{Ar}$), 113.9 (H*C*$_{Ar}$), 101.6 (*C*H(OR)$_2$), 65.1 (*C*H$_2$OR), 55.5 (*C*H$_3$), 42.0 (*C*H$_2$); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −62.5; **IR** ν_{max} (thin film)/cm^{-1} 2961w, 1679s, 1599s, 1575m, 1510m, 1421w, 1329s, 1266m, 1226m, 1164s, 1118s, 1085s, 1028m, 990m, 945m, 899m, 832s; **m/z** (ESI$^+$) 367.1 [70, (M + H)$^+$], 389.1 [100, (M + Na)$^+$], 755.1 [95, (2M + Na)$^+$], $C_{19}H_{17}F_3NaO_4$ predicted 389.0971, found 389.0970, (Δ + 0.3 ppm).

2-(2-(1,3-Dioxolan-2-yl)thiophen-3-yl)-1-phenylpropan-1-one **3t**

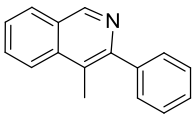


Acetal **2t** (118 mg, 0.500 mmol) was subjected to General Procedure 2a with propiophenone (80.5 mg, 0.600 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *ketone* **3t** (114 mg, 0.396 mmol, 79 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.00 (2H, dd, *J* 7.4, 1.5, 2 × *H*C$_{Ar}$), 7.49 (1H, tt, *J* 7.4, 1.2, *H*C$_{Ar}$), 7.39 (2H, t, *J* 7.6, 2 × *H*C$_{Ar}$), 7.18 (1H, d, *J* 5.3, *H*C(5)), 6.85 (1H, d, *J* 5.0, *H*C(4)), 6.29 (1H, s, C*H*(OR)$_2$), 5.00 (1H, q, *J* 6.8, C*H*CH$_3$), 4.18-4.13 (2H, m, C*H*$_a$H$_b$C*H*$_a$H$_b$), 4.10-4.04 (2H, m, CH$_a$*H*$_b$CH$_a$*H*$_b$), 1.51 (3H, d, *J* 7.0, CHC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 200.2 (*C*=O), 139.8, 136.4, 135.2 (*C*$_{Ar}$ + *C*(2) + *C*(3)), 132.9, 128.7, 128.5 (3 × H*C*$_{Ar}$), 127.7

(H*C*(4)), 125.6 (H*C*(5)), 99.3 (*C*H(OR)$_2$), 65.3, 65.2 (2 × *C*H$_2$OR), 41.3 (*C*HCH$_3$), 18.7 (CH*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2976w, 2933w, 2877w, 1682s, 1448w, 1426w, 1273w, 1218s, 1080m, 967s; **m/z** (ESI$^+$) 311.1 [100, (M + Na)$^+$], $C_{16}H_{16}NaO_3S$ predicted 311.0712, found 311.0724, (Δ − 3.6 ppm); **m.p.** 77-79 °C (petrol/CH_2Cl_2).

4-Methyl-3-phenylisoquinoline **4a**

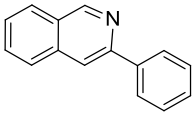


Ketone **3a** (57.8 mg, 0.205 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 14:1 grading to 9:1] to furnish *isoquinoline* **4a** (41.3 mg, 0.188 mmol, 92 %) as prisms.

Acetal **2a** (51.0 mg, 0.223 mmol) was subjected to General Procedure 6 with propiophenone (35.8 mg, 0.267 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *isoquinoline* **4a** (35.8 mg, 0.163 mmol, 73 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.22 (1H, s, *H*C(1)), 8.07 (1H, d, *J* 8.6, *H*C(8)), 8.01 (1H, d, *J* 8.3, *H*C(5)), 7.77 (1H, t, *J* 7.6, *H*C(7)), 7.65-7.60 (3H, m, *H*C(6) + 2 × *H*C$_{Ar}$), 7.50 (2H, d, *J* 8.6, 2 × *H*C$_{Ar}$), 7.42 (1H, t, *J* 7.3, *H*C$_{Ar}$), 2.67 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 151.9 (*C*(3)), 150.2 (H*C*(1)), 141.3, 136.2 (2 × *C*$_{Ar}$), 130.4 (H*C*(7)), 129.9, 128.1 (2 × H*C*$_{Ar}$), 128.1 (H*C*(5)), 127.6 (H*C*$_{Ar}$), 127.3 (*C*$_{Ar}$), 126.6 (H*C*(6)), 124.0 (*C*(4)), 123.6 (H*C*(8)), 15.5 (*C*H$_3$); **m.p.** 96-98 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[10]

3-Phenylisoquinoline **4b**



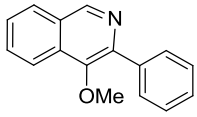
Ketone **3b** (48.9 mg, 0.182 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *isoquinoline* **4b** (35.9 mg, 0.175 mmol, 96 %) as prisms.

Acetal **2a** (66.7 mg, 0.291 mmol) was subjected to General Procedure 6 with acetophenone (42.0 mg, 0.349 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *isoquinoline* **4b** (44.2 mg, 0.215 mmol, 74 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.36 (1H, s, *H*C(1)), 8.15 (2H, d, *J* 7.3, 2 × *H*C$_{Ar}$), 8.08 (1H, s, *H*C(4)), 8.01 (1H, d, *J* 8.1, *H*C(8)), 7.89 (1H, d, *J* 8.3, *H*C(5)), 7.71 (1H, t, *J* 7.6, *H*C(6)), 7.60 (1H, t, *J* 7.6, *H*C(7)), 7.53 (2H, t, *J* 7.7, 2 × *H*C$_{Ar}$), 7.43 (1H, t, *J* 7.4, *H*C$_{Ar}$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 152.4 (H*C*(1)), 151.3 (*C*(3)), 139.6, 136.7 (2 × *C*$_{Ar}$), 130.5

(H*C*(6)), 128.8, 128.5 (2 × HC_{Ar}), 127.8 (C_{Ar}), 127.6 (H*C*(8)), 127.1 (H*C*(7)), 127.0 (HC_{Ar}), 126.9 (H*C*(5)), 116.5 (H*C*(4)); **m.p.** 98-99 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[11]

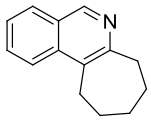
4-Methoxy-3-phenylisoquinoline **4c**



Ketone **3c** (46.4 mg, 0.156 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 4:1] to furnish *isoquinoline* **4c** (36.3 mg, 0.154 mmol, 99 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.16 (1H, s, *H*C(1)), 8.22 (1H, d, *J* 8.6, *H*C(5)), 8.10 (2H, d, *J* 8.3, 2 × *H*C_{Ar}), 8.01 (1H, d, *J* 8.1, *H*C(8)), 7.75 (1H, t, *J* 7.6, *H*C(7)), 7.62 (1H, t, *J* 7.6, *H*C(6)), 7.52 (2H, t, *J* 7.7, 2 × *H*C_{Ar}), 7.42 (1H, t, *J* 7.5, *H*C_{Ar}), 3.70 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 149.0 (*C*(3)), 147.8 (H*C*(1)), 143.1 (*C*(4)), 138.1, 131.9 (2 × C_{Ar}), 130.3 (H*C*(7)), 129.3 (C_{Ar}), 129.2, 128.4, 128.1 (3 × HC_{Ar}), 127.4 (H*C*(8)), 127.3 (H*C*(6)), 121.6 (H*C*(5)), 61.2 (O*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 1622w, 1565w, 1498w, 1454w, 1362s, 1333w, 1309w, 1280w, 1249w, 1155m, 1116m, 1066m, 984m, 918w, 884w, 866w; **m/z** (ESI$^+$) 236.1 [95, (M + H)$^+$], 258.1 [100, (M + Na)$^+$], 493.2 [85, (2M + Na)$^+$], $C_{16}H_{13}NNaO$ predicted 258.0889, found 258.0891, (Δ − 0.8 ppm).

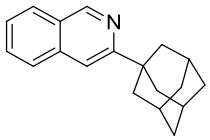
8,9,10,11-Tetrahydro-7H-cyclohepta[c]isoquinoline **4d**



Ketone **3d** (66.4 mg, 0.255 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 14:1 grading to 4:1] to furnish *isoquinoline* **4d** (39.6 mg, 0.201 mmol, 79 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.01 (1H, s, *H*C(1)), 8.06 (1H, d, *J* 8.6, *H*C(8)), 7.93 (1H, d, *J* 8.3, *H*C(5)), 7.68 (1H, ddd, *J* 8.4, 6.8, 1.3, *H*C(7)), 7.51 (1H, td, *J* 7.5, 0.7, *H*C(6)), 3.28-3.25 (2H, m, C*H*$_2$C$_{Ar}$), 3.22-3.19 (2H, m, C*H*$_2$C$_{Ar}$), 1.98-1.92 (2H, m, C*H*$_2$), 1.78-1.70 (4H, m, 2 × C*H*$_2$CH$_2$C$_{Ar}$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 156.5 (*C*(3)), 149.2 (H*C*(1)), 134.7 (C_{Ar}), 131.0 (*C*(4)), 129.9 (H*C*(7)), 128.2 (H*C*(5)), 127.2 (C_{Ar}), 125.5 (H*C*(6)), 122.3 (H*C*(8)), 38.9 (*C*H$_2$C$_{Ar}$), 32.4 (*C*H$_2$), 27.0, 26.7, 26.3 (*C*H$_2$C$_{Ar}$ + 2 × *C*H$_2$CH$_2$C$_{Ar}$); **IR** ν_{max} (thin film)/cm^{-1} 2920s, 2851m, 1775w, 1698w, 1621s, 1575s, 1498m, 1454s, 1374s, 1260s, 1241s, 1221w, 1204w, 1154w, 1139w, 1093m, 1019s, 955s, 923w, 898m; **m/z** (ESI$^+$) 198.1 [100, (M + H)$^+$], $C_{14}H_{16}N$ predicted 198.1277, found 198.1280, (Δ − 1.6 ppm); **m.p.** 77-79 °C (petrol/CH_2Cl_2).

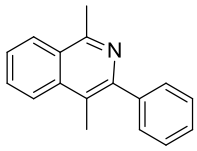
3-Adamantylisoquinoline **4e**



Ketone **3e** (30.4 mg, 0.0931 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *isoquinoline* **4e** (23.3 mg, 0.0885 mmol, 95 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.25 (1H, s, *H*C(1)), 7.92 (1H, d, *J* 8.1, *H*C(8)), 7.78 (1H, d, *J* 8.4, *H*C(5)), 7.64 (1H, ddd, *J* 7.9, 6.9, 1.1, *H*C(6)), 7.54-7.50 (2H, m, *H*C(4) + *H*C(7)), 2.18-2.14 (3H, m, 3 × C*H*), 2.11 (6H, d, *J* 2.7, RC(CH_2)$_3$), 1.84 (6H, t, *J* 3.0, 3 × CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 162.9 (*C*(3)), 151.8 (H*C*(1)), 136.6 (*C*$_{Ar}$), 129.9 (H*C*(6)), 127.3 (H*C*(8)), 127.0 (*C*$_{Ar}$), 126.6 (H*C*(5)), 126.3 (H*C*(7)), 114.3 (H*C*(4)), 42.0 (RC(*C*H_2)$_3$), 38.6 (R*C*(CH$_2$)$_3$), 36.9 (*C*H$_2$), 28.8 (*C*H); **IR** ν_{max} (thin film)/cm^{-1} 2902s, 2882s, 2848s, 1628s, 1585m, 1490m, 1451s, 1382w, 1366w, 1344w, 1316w, 1278w, 1260s, 1180w, 1099s, 1036s, 977m, 943m, 880s, 856w; **m/z** (ESI$^+$) 264.2 [100, (M + H)$^+$], $C_{19}H_{22}N$ predicted 264.1747, found 264.1742, (Δ + 1.7 ppm); **m.p.** 106-108 °C (petrol/CH_2Cl_2).

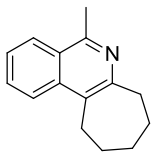
1,4-Dimethyl-3-phenylisoquinoline **4f**



Ketone **3f** (53.2 mg, 0.180 mmol) was subjected to General Procedure 4. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *isoquinoline* **4f** (35.2 mg, 0.151 mmol, 84 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.18 (1H, d, *J* 8.3, *H*C(8)), 8.07 (1H, d, *J* 8.3, *H*C(5)), 7.76 (1H, ddd, *J* 8.2, 6.8, 1.2, *H*C(6)), 7.64-7.58 (3H, m, *H*C(6) + 2 × *H*C$_{Ar}$), 7.50-7.47 (2H, m, 2 × *H*C$_{Ar}$), 7.40 (1H, tt, *J* 7.3, 1.3, 2 × *H*C$_{Ar}$), 3.00 (3H, s, C(1)C*H*$_3$), 2.61 (3H, s, C(4)C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 155.9 (*C*(3)), 150.7 (*C*(1)), 141.6, 136.3 (2 × *C*$_{Ar}$), 129.9 (2 signals) (H*C*$_{Ar}$ + H*C*(6)), 128.1, 127.4 (2 × H*C*$_{Ar}$), 126.3 (H*C*(7)), 126.2 (*C*$_{Ar}$), 126.1 (H*C*(8)), 124.1 (H*C*(5)), 122.2 (*C*(4)), 22.5 (C(1)*C*H$_3$), 15.5 (C(4)*C*H$_3$); **m.p.** 95-97 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[12]

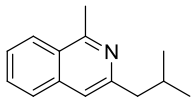
5-Methyl-8,9,10,11-tetrahydro-7H-cyclohepta[c]isoquinoline **4g**



Ketone **3g** (47.3 mg, 0.172 mmol) was subjected to General Procedure 4. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *isoquinoline* **4g** (29.9 mg, 0.142 mmol, 82 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.10 (1H, d, *J* 8.3, *H*C(5)), 8.06 (1H, d, *J* 8.9, *H*C(8)), 7.65 (1H, ddd, *J* 8.0, 6.8, 1.0, *H*C(7)), 7.49 (1H, t, *J* 7.7, *H*C(6)), 3.24-3.21 (2H, m, CH_2C$_{Ar}$), 3.18-3.15 (2H, m, CH_2C$_{Ar}$), 2.93 (3H, s, CH_3), 1.96-1.90 (2H, m, CH_2), 1.77-1.68 (4H, m, 2 × CH_2CH$_2$C$_{Ar}$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 155.0, 154.8 (*C*(3) + *C*(1)), 134.8 (*C*$_{Ar}$), 129.5 (H*C*(7)), 129.2 (*C*$_{Ar}$), 126.2 (H*C*(5)), 125.8 (*C*(4)), 125.1 (H*C*(6)), 122.9 (H*C*(8)), 38.7 (*C*H$_2$C$_{Ar}$), 32.4 (*C*H$_2$), 26.8 (2 signals), 26.4 (*C*H$_2$C$_{Ar}$ + 2 × *C*H$_2$CH$_2$C$_{Ar}$), 22.3 (CH$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3071w, 2921s, 2851s, 1699s, 1617m, 1566s, 1505w, 1450s, 1396s, 1339m, 1263m, 1227w, 1153w, 1026w, 988w, 971w, 956w, 832w; **m/z** (ESI$^+$) 212.1 [100, (M + H)$^+$], $C_{15}H_{18}N$ predicted 212.1434, found 212.1434, (Δ − 0.2 ppm); **m.p.** 65-67 °C (petrol/CH_2Cl_2).

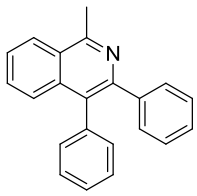
3-Isobutyl-1-methylisoquinoline **4h**



Ketone **3h** (42.0 mg, 0.160 mmol) was subjected to General Procedure 4. The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 14:1] to furnish *isoquinoline* **4h** (29.5 mg, 0.148 mmol, 93 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.08 (1H, d, *J* 8.4, *H*C(8)), 7.73 (1H, d, *J* 8.0, *H*C(5)), 7.63 (1H, ddd, *J* 8.1, 6.9, 1.2, *H*C(6)), 7.52 (1H, ddd, *J* 8.2, 6.9, 1.3, *H*C(7)), 7.29 (1H, s, *H*C(4)), 2.96 (3H, s, CH_3), 2.76 (2H, d, *J* 7.3, CH_2), 2.21 (1H, sept., *J* 6.8, C*H*), 0.97 (6H, d, *J* 6.8, CH(CH_3)$_2$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 158.0 (*C*(1)), 153.5 (*C*(3)), 136.5 (*C*$_{Ar}$), 129.8 (H*C*(6)), 126.8 (H*C*(5)), 126.0 (H*C*(7)), 125.8 (*C*$_{Ar}$), 125.5 (H*C*(8)), 117.6 (H*C*(4)), 47.3 (*C*H$_2$), 28.9 (*C*H), 22.5 (CH(*C*H$_3$)$_2$), 22.3 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2954w, 2927w, 2867w, 1700m, 1625s, 1590s, 1568s, 1497m, 1464s, 1446s, 1390s, 1366s, 1338m, 1262w, 1165m, 1095w, 1026m, 955w, 879s, 849w, 818m; **m/z** (ESI$^+$) 200.1 [100, (M + H)$^+$], $C_{14}H_{18}N$ predicted 200.1434, found 200.1431, (Δ + 1.3 ppm).

1-Methyl-3,4-diphenylisoquinoline **4i**

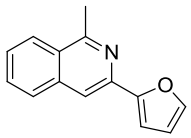


Ketone **3i** (166 mg, 0.463 mmol) was subjected to General Procedure 4. The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *isoquinoline* **4i** (111 mg, 0.375 mmol, 81 %) as plates.

Acetal **2f** (40.7 mg, 0.167 mmol) was subjected to General Procedure 7a with deoxybenzoin (39.4 mg, 0.201 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 49:1 grading to 24:1] to furnish *isoquinoline* **4i** (25.2 mg, 0.0853 mmol, 51 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.24-8.20 (1H, m, *H*C(8)), 7.69-7.66 (1H, m, *H*C(5)), 7.63-7.58 (2H, m, *H*C(6) + *H*C(7)), 7.40-7.33 (5H, m, 5 × *H*C_{Ar}), 7.26-7.18 (5H, m, 5 × *H*C_{Ar}), 3.10 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 157.7 (*C*(1)), 149.4 (*C*(3)), 141.0, 137.6, 136.0 (3 × *C*$_{Ar}$), 131.4, 130.3 (2 × H*C*$_{Ar}$), 129.9 (H*C*(6)), 129.2 (*C*$_{Ar}$), 128.2, 127.6, 127.1, 126.9 (4 × H*C*$_{Ar}$), 126.5 (H*C*(7)), 126.2 (H*C*(5)), 126.2 (*C*(4)), 125.5 (H*C*(8)), 22.7 (*C*H$_3$); **m.p.** 150-152 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[13]

3-(Furan-2-yl)-1-methylisoquinoline **4j**

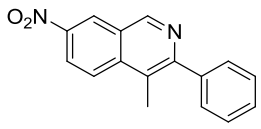


Ketone **3j** (58.3 mg, 0.214 mmol) was subjected to General Procedure 4. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *isoquinoline* **4j** (37.6 mg, 0.180 mmol, 84 %) as an oil.

Acetal **2f** (47.9 mg, 0.197 mmol) was subjected to General Procedure 7b with 2-furyl methyl ketone (43.4 mg, 0.394 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 19:1] to furnish *isoquinoline* **4j** (25.8 mg, 0.123 mmol, 63 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.09 (1H, d, *J* 8.3, *H*C(8)), 7.88 (1H, s, *H*C(4)), 7.82 (1H, d, *J* 8.1, *H*C(5)), 7.65 (1H, ddd, *J* 8.1, 7.0, 1.1, *H*C(6)), 7.56-7.52 (2H, m, *H*C(7) + *H*C(5')), 7.13 (1H, d, *J* 3.3, *H*C(3')), 6.57 (1H, dd, *J* 3.3, 1.8, *H*C(4')), 3.00 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 158.9 (*C*(1)), 154.4 (*C*(2')), 142.9 (H*C*(5')), 142.2 (*C*(3)), 136.5 (*C*$_{Ar}$), 130.2 (H*C*(6)), 127.8 (H*C*(5)), 126.7 (H*C*(7)), 126.6 (*C*$_{Ar}$), 125.8 (H*C*(8)), 113.0 (H*C*(4)), 112.0 (H*C*(4')), 108.0 (H*C*(3'), 23.0 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3068w, 2920w, 1692w, 1621s, 1567s, 1488m, 1436m, 1389s, 1324m, 1287w, 1261w, 1239w, 1216w, 1157s, 1087m, 1006s, 970m, 937w, 882s, 834m, 812s; **m/z** (ESI$^+$) 210.1 [100, (M + H)$^+$], $C_{14}H_{12}NO$ predicted 210.0913, found 210.0921, (Δ − 3.5 ppm).

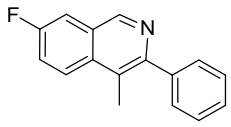
4-Methyl-7-nitro-3-phenylisoquinoline **4k**



Ketone **3k** (49.7 mg, 0.152 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *isoquinoline* **4k** (30.5 mg, 0.116 mmol, 76 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.39 (1H, s, *H*C(1)), 8.95 (1H, d, *J* 2.3, *H*C(8)), 8.52 (1H, dd, *J* 9.5, 2.3, *H*C(6)), 8.22 (1H, d, *J* 9.1, *H*C(5)), 7.63-7.60 (2H, m, 2 × *H*C_{Ar}), 7.52 (2H, t, *J* 6.8, 2 × *H*C_{Ar}), 7.48 (1H, tt, *J* 7.0, 2.6, *H*C_{Ar}), 2.73 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 155.5 (*C*(3)), 151.6 (H*C*(1)), 145.7, 140.2, 138.9 (*C*(7) + 2 × *C*$_{Ar}$), 129.8, 128.3, 128.3 (3 × H*C*$_{Ar}$), 125.9 (*C*(4)), 125.8 (H*C*(5)), 124.7 (H*C*(8)), 124.5 (*C*$_{Ar}$), 123.6 (H*C*(6)), 15.8 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3030w, 1620s, 1588w, 1524s, 1486m, 1448w, 1384w, 1346s, 1248w, 1106w, 1091w, 1007m, 934m, 851w, 820w; **m/z** (ESI$^+$) 265.1 [80, (M + H)$^+$], 287.1 [100, (M + Na)$^+$], 551.2 [30, (2M + Na)$^+$], $C_{16}H_{13}N_2O_2$ predicted 265.0972, found 265.0970, (Δ + 0.7 ppm); **m.p.** 180-182 °C (petrol/CH_2Cl_2).

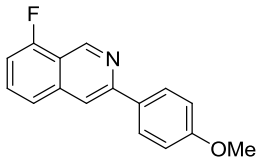
7-Fluoro-4-methyl-3-phenylisoquinoline **4l**



Ketone **3l** (48.2 mg, 0.161 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 14:1] to furnish *isoquinoline* **4l** (34.1 mg, 0.144 mmol, 89 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.16 (1H, s, *H*C(1)), 8.07 (1H, dd, *J* 9.4, 5.1, *H*C(5)), 7.61-7.58 (3H, m, *H*C(8) + 2 × *H*C_{Ar}), 7.55-7.48 (3H, m, *H*C(6) + 2 × *H*C_{Ar}), 7.42 (1H, tt, *J* 7.3, 1.5, *H*C_{Ar}), 2.66 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 160.7 (d, ^1J 248.5, *C*(7)), 151.6 (d, ^6J 2.4, *C*(3)), 149.3 (d, ^4J 5.6, H*C*(1)), 141.0, 133.3 (2 × *C*$_{Ar}$), 129.8, 128.2 (2 × H*C*$_{Ar}$), 128.1 (d, ^3J 8.0, *C*$_{Ar}$), 127.7 (H*C*$_{Ar}$), 126.5 (d, ^3J 8.8, H*C*(5)), 124.2 (d, ^5J 1.6, *C*(4)), 120.7 (d, ^2J 25.5, H*C*(6)), 110.9 (d, ^2J 20.8, H*C*(8)), 15.7 (*C*H$_3$); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −113.0; **IR** ν_{max} (thin film)/cm^{-1} 2925w, 2854w, 1682w, 1624w, 1565m, 1500s, 1445m, 1404w, 1373s, 1333m, 1274m, 1244m, 1224s, 1146s, 1098w, 1072w, 1007m, 953s, 921s, 859s, 835s; **m/z** (ESI$^+$) 238.1 [100, (M + H)$^+$], $C_{16}H_{13}FN$ predicted 238.1027, found 238.1025, (Δ + 0.7 ppm); **m.p.** 112-114 °C (petrol/CH_2Cl_2).

8-Fluoro-3-(4-methoxyphenyl)isoquinoline **4m**

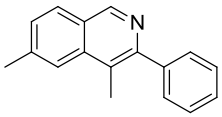


Ketone **3m** (91.7 mg, 0.290 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *isoquinoline* **4m** (70.9 mg, 0.280 mmol, 97 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.58 (1H, s, *H*C(1)), 8.19 (2H, d, *J* 8.9, 2 × *H*C_{Ar}), 7.97 (1H, s, *H*C(4)), 7.62-7.58 (2H, m, *H*C(5) + *H*C(6)), 7.19-7.14 (1H, m, *H*C(7)), 7.05 (2H, d, *J* 8.9, 2 × *H*C_{Ar}), 3.89 (3H, s, OC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 160.4 (*C*$_{Ar}$), 159.4 (d, ^1J 256.8, *C*(8)), 152.0 (*C*(3)), 146.0 (d, ^3J 4.8, H*C*(1)), 138.2 (d, ^3J 4.0, *C*$_{Ar}$), 131.8 (*C*$_{Ar}$), 130.7

(d, ^{3}J 8.8, H*C*(6)), 128.3 (HC_{Ar}), 122.6 (d, ^{4}J 4.0, H*C*(5)), 117.8 (d, ^{2}J 15.9, C_{Ar}), 114.6 (d, ^{4}J 3.2, H*C*(4)), 114.2 (HC_{Ar}), 110.4 (d, ^{2}J 19.2, H*C*(7)), 55.4 (O*C*H$_3$); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −123.3; **IR** ν_{max} (thin film)/cm^{-1} 2961w, 1635m, 1605m, 1574s, 1512s, 1454s, 1438s, 1350m, 1282m, 1244m, 1174m, 1081m, 1032s, 906w, 829s; **m/z** (ESI$^+$) 254.1 [100, $(M + H)^+$], $C_{16}H_{13}FNO$ predicted 254.0976, found 254.0975, (Δ + 0.3 ppm); **m.p.** 132-134 °C (petrol/CH_2Cl_2).

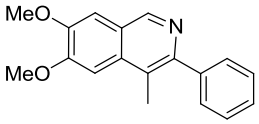
4,6-Dimethyl-3-phenylisoquinoline **4n**



Ketone **3n** (32.0 mg, 0.108 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *isoquinoline* **4n** (24.2 mg, 0.104 mmol, 96 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.15 (1H, s, *H*C(1)), 7.88 (1H, d, *J* 8.3, *H*C(8)), 7.81 (1H, s, *H*C(5)), 7.62-7.59 (2H, m, 2 × *H*C$_{Ar}$), 7.51-7.47 (2H, t, *J* 7.6, 2 × *H*C$_{Ar}$), 7.45-7.39 (2H, m, *H*C(7) + *H*C$_{Ar}$), 2.63 (3H, s, C*H*$_3$), 2.61 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 151.9 (*C*(3)), 149.8 (H*C*(1)), 141.5, 140.7, 136.4 (2 × *C*$_{Ar}$ + *C*(6)), 129.9 (H*C*$_{Ar}$), 128.8 (H*C*(7)), 128.1, 127.9 (2 × H*C*$_{Ar}$), 127.5 (H*C*(8)), 125.7, 123.5 (*C*(4) + *C*$_{Ar}$), 122.7 (H*C*(5)), 22.5 (C(6)*C*H$_3$), 15.5 (C(4)*C*H$_3$); **m.p.** 96-98 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[14]

6,7-Dimethoxy-4-methyl-3-phenylisoquinoline **4o**

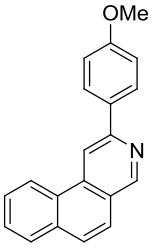


Ketone **3o** (57.8 mg, 0.205 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 14:1 grading to 9:1] to furnish *isoquinoline* **4o** (41.3 mg, 0.188 mmol, 92 %) as needles.

Acetal **2o** (46.8 mg, 0.162 mmol) was subjected to General Procedure 6 with propiophenone (26.1 mg, 0.194 mmol). The crude product was purified by flash column chromatography [Petrol/EtOAc 14:1 grading to 9:1] to furnish *isoquinoline* **4o** (34.6 mg, 0.124 mmol, 77 %) as needles.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.01 (1H, s, *H*C(1)), 7.58 (2H, dd, *J* 8.3, 1.2, 2 × *H*C$_{Ar}$), 7.48 (2H, td, *J* 7.1, 1.7, 2 × *H*C$_{Ar}$), 7.39 (1H, tt, *J* 7.4, 1.2, *H*C$_{Ar}$), 7.25 (1H, s, *H*C(5)), 7.23 (1H, s, *H*C(8)), 4.08 (3H, s, OC*H*$_3$), 4.06 (3H, s, OC*H*$_3$), 2.61 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 152.9 (*C*(3)), 151.0, 149.8 (*C*(6) + *C*(7)), 147.6 (H*C*(1)), 141.6, 132.7 (2 × *C*$_{Ar}$), 129.8, 128.0, 127.3 (3 × H*C*$_{Ar}$), 123.4, 122.8 (*C*$_{Ar}$ + *C*(4)), 105.8 (H*C*(5)), 102.1 (H*C*(8)), 56.0 (O*C*H$_3$), 56.0 (O*C*H$_3$), 15.8 (*C*H$_3$); **m.p.** 155-157 °C (petrol/CH_2Cl_2). Data were consistent with those previously reported.[15]

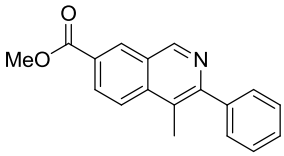
2-(4-Methoxyphenyl)benzo[f]isoquinoline **4p**



Ketone **3p** (66.5 mg, 0.191 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *isoquinoline* **4p** (48.9 mg, 0.171 mmol, 90 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.27 (1H, s, *H*C(1)), 8.74-8.72 (2H, m, *H*C(4) + *H*C_{Ar}), 8.17 (1H, t, *J* 2.6, *H*C_{Ar}), 8.15 (1H, t, *J* 2.5, *H*C_{Ar}), 7.93-7.91 (1H, m, *H*C_{Ar}), 7.81-7.76 (2H, m, *H*C(7) + *H*C(8)), 7.73-7.69 (2H, m, 2 × *H*C_{Ar}), 7.10 (1H, t, *J* 2.4, *H*C_{Ar}), 7.07 (1H, t, *J* 2.6, *H*C_{Ar}), 3.91 (3H, s, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 160.3 (C_{Ar}), 153.1 (*C*(3)), 151.4 (H*C*(1)), 135.6, 133.8, 132.5 (2 × C_{Ar} + *C*(6)), 128.8 (HC_{Ar}), 128.7 (*C*(5)), 128.6, 128.4 (2 × HC_{Ar}), 127.8, 124.7 (H*C*(7) + H*C*(8)), 127.0 (HC_{Ar}), 125.5 (C_{Ar}), 123.1, 114.3 (2 × HC_{Ar}), 111.5 (H*C*(4)), 55.4 (OCH_3); **IR** ν_{max} (thin film)/cm^{-1} 2932w, 1607s, 1591s, 1519s, 1505s, 1480m, 1452s, 1385w, 1299w, 1248s, 1174s, 1030m, 834s, 815w; **m/z** (ESI^+) 286.1 [100, $(M + H)^+$], $C_{20}H_{16}NO$ predicted 286.1226, found 286.1228, (Δ − 0.7 ppm); **m.p.** 91-93 °C (petrol/CH_2Cl_2).

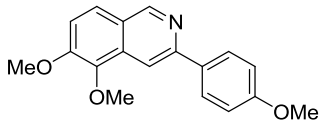
Methyl 4-methyl-3-phenylisoquinoline-7-carboxylate **4q**



Ketone **3q** (45.3 mg, 0.133 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *isoquinoline* **4q** (31.7 mg, 0.114 mmol, 86 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.30 (1H, s, *H*C(1)), 8.76 (1H, s, *H*C(8)), 8.34 (1H, dd, *J* 8.9, 1.5, *H*C(6)), 8.11 (1H, d, *J* 8.9, *H*C(5)), 7.61 (2H, d, *J* 7.1, 2 × *H*C_{Ar}), 7.51 (2H, t, *J* 7.6, 2 × *H*C_{Ar}), 7.44 (1H, t, *J* 7.2, *H*C_{Ar}), 4.03 (3H, s, OCH_3), 2.69 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 166.5 (*C*=O), 154.0 (*C*(3)), 151.3 (H*C*(1)), 140.8, 138.4 (2 × C_{Ar}), 131.1 (H*C*(8)), 129.8, 129.7 (H*C*(6) + HC_{Ar}), 128.2 (HC_{Ar}), 128.2 (C_{Ar}), 127.9 (HC_{Ar}), 126.5, 124.2 (*C*(4) + *C*(7)), 124.1 (H*C*(5)), 52.5 (O*C*H_3), 15.6 (*C*H_3); **IR** ν_{max} (thin film)/cm^{-1} 2999w, 2952w, 1720s, 1624m, 1572w, 1438m, 1379w, 1339w, 1295s, 1262s, 1203s, 1105m, 1007w, 992w, 973w, 940w, 839w, 806w; **m/z** (ESI^+) 278.1 [100, $(M + H)^+$], $C_{18}H_{16}NO_2$ predicted 278.1176, found 278.1179, (Δ − 1.2 ppm); **m.p.** 155-157 °C (petrol/CH_2Cl_2).

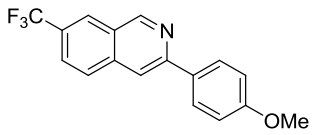
5,6-Dimethoxy-3-(4-methoxyphenyl)isoquinoline **4r**



Ketone **3r** (59.3 mg, 0.165 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 9:1 grading to 4:1] to furnish *isoquinoline* **4r** (38.9 mg, 0.132 mmol, 80 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.19 (1H, s, *H*C(1)), 8.21 (1H, s, *H*C(4)), 8.11 (2H, d, *J* 8.1, 2 × *H*C$_{Ar}$), 7.73 (1H, d, *J* 8.9, *H*C(8)), 7.32 (1H, d, *J* 9.1, *H*C(7)), 7.04 (2H, d, *J* 8.0, 2 × *H*C$_{Ar}$), 4.03 (6H, s, C(5)OCH_3 + C(6)OCH_3), 3.88 (3H, s, C_{Ar}OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 160.1 (C_{Ar}), 151.9 (H*C*(1)), 151.6, 151.0 (*C*(3) + *C*(6)), 141.6 (*C*(5)), 132.6, 132.5 (2 × C_{Ar}), 128.3 (HC_{Ar}), 124.4 (H*C*(8)), 123.6 (C_{Ar}), 115.0 (H*C*(7)), 114.1 (HC_{Ar}), 109.0 (H*C*(4)), 61.2 (C(5)O*C*H$_3$), 56.5 (C(6)O*C*H$_3$), 55.4 (C_{Ar}O*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 2936w, 2837w, 1621m, 1606s, 1514s, 1488s, 1457s, 1425w, 1408w, 1385w, 1339w, 1318w, 1295m, 1278m, 1242s, 1169s, 1110s, 1064s, 1039m, 1024m, 986s, 939w, 870w, 834s, 801m; **m/z** (ESI$^+$) 296.1 [100, (M + H)$^+$], 318.1 [75, (M + Na)$^+$], 613.2 [75, (2M + Na)$^+$], $C_{18}H_{18}NO_3$ predicted 296.1281, found 296.1280, (Δ + 0.5 ppm); **m.p.** 101-102 °C (petrol/CH_2Cl_2).

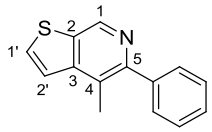
3-(4-Methoxyphenyl)-7-(trifluoromethyl)isoquinoline **4s**



Ketone **3s** (103 mg, 0.280 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 24:1 grading to 14:1] to furnish *isoquinoline* **4s** (72.8 mg, 0.240 mmol, 86 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.38 (1H, s, *H*C(1)), 8.26 (1H, s, *H*C(8)), 8.11 (2H, dt, *J* 8.8, 1.9, 2 × *H*C$_{Ar}$), 8.02 (1H, s, *H*C(4)), 7.93 (1H, d, *J* 8.6, *H*C(5)), 7.82 (1H, dd, *J* 8.6, 1.5, *H*C(6)), 7.05 (2H, dt, *J* 8.9, 1.9, 2 × *H*C$_{Ar}$), 3.89 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 160.6 (C_{Ar}), 153.1 (*C*(3)), 153.0 (H*C*(1)), 138.0, 131.4 (2 × C_{Ar}), 128.4 (HC_{Ar}), 128.4 (q, ^2J 32.7, *C*(7)), 127.9 (H*C*(5)), 126.0 (C_{Ar}), 126.0 (q, ^3J 3.2, H*C*(6)), 125.5 (q, ^3J 4.8, H*C*(8)), 123.9 (q, ^1J 272.4, *C*F$_3$), 114.8 (H*C*(4)), 114.3 (HC_{Ar}), 55.4 (O*C*H$_3$); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −62.5; **IR** ν_{max} (thin film)/cm^{-1} 2918w, 2848w, 1635m, 1602s, 1574m, 1516s, 1452s, 1443s, 1396w, 1333s, 1313s, 1292m, 1273s, 1250s, 1217m, 1186s, 1174s, 1157s, 1121s, 1064s, 1038s, 1022m, 951w, 900m, 881s, 837s; **m/z** (ESI$^+$) 304.1 [100, (M + H)$^+$], $C_{17}H_{13}F_3NO$ predicted 304.0944, found 304.0945, (Δ − 0.5 ppm); **m.p.** 169-171 °C (petrol/CH_2Cl_2).

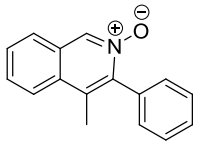
4-Methyl-5-phenylthieno[2,3-c]pyridine **4t**



Ketone **3t** (75.9 mg, 0.263 mmol) was subjected to General Procedure 3. The crude product was purified by flash column chromatography [Petrol/EtOAc 19:1 grading to 9:1] to furnish *thienopyridine* **4t** (43.5 mg, 0.193 mmol, 73 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.10 (1H, s, *H*C(1)), 7.75 (1H, d, *J* 5.5, *H*C(1')), 7.57 (2H, dd, *J* 7.1, 1.3, 2 × *H*C$_{Ar}$), 7.50-7.46 (3H, m, 2 × *H*C$_{Ar}$ + *H*C(2')), 7.41 (1H, tt, *J* 7.4, 2.1, *H*C$_{Ar}$), 2.62 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 152.0 (*C*(5)), 146.0 (*C*$_{Ar}$), 141.6 (H*C*(1)), 140.6, 134.8 (2 × *C*$_{Ar}$), 131.8 (H*C*(1')), 129.6, 128.1, 127.6 (3 × H*C*$_{Ar}$), 124.6 (*C*(4)), 122.1 (H*C*(2')), 16.8 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3058w, 2920w, 1567s, 1495m, 1445s, 1404s, 1380m, 1334m, 1253w, 1224s, 1152m, 1090w, 1073w, 1012s, 910w, 873w, 818m; **m/z** (ESI$^+$) 226.0 [95, (M + H)$^+$], 248.0 [100, (M + Na)$^+$], $C_{14}H_{12}NS$ predicted 226.0685, found 226.0688, (Δ − 1.2 ppm).

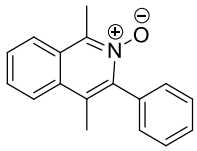
4-Methyl-3-phenylisoquinoline-*N*-oxide **5a**



Ketone **3a** (50.6 mg, 0.179 mmol) was subjected to General Procedure 5. The crude product was purified by flash column chromatography on alumina [EtOAc/MeOH 97:3] to furnish *isoquinoline-N-oxide* **5a** (38.7 mg, 0.166 mmol, 93 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.86 (1H, s, *H*C(1)), 7.93 (1H, dd, *J* 5.0, 4.3, *H*C(8)), 7.74-7.72 (1H, m, *H*C(5)), 7.64-7.59 (2H, m, *H*C(6) + *H*C(7)), 7.54-7.45 (3H, m, 3 × *H*C$_{Ar}$), 7.39 (2H, d, *J* 7.3, 2 × *H*C$_{Ar}$), 2.42 (3H, s, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 146.3 (*C*(3)), 135.0 (H*C*(1)), 133.0, 130.7 (2 × *C*$_{Ar}$), 130.0 (H*C*$_{Ar}$), 129.3 (*C*$_{Ar}$), 128.9, 128.8, 128.7 (H*C*(6) + H*C*(7) + H*C*$_{Ar}$), 128.6 (H*C*$_{Ar}$), 128.6 (*C*(4)), 125.3 (*C*(5)), 124.0 (H*C*(8)), 16.1 (*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 1589w, 1495w, 1468w, 1425m, 1373w, 1314s, 1219m, 1182s, 1127s, 1034w, 1017m, 896w; **m/z** (ESI$^+$) 236.1 [70, (M + H)$^+$], 258.1 [80, (M + Na)$^+$], 493.1 [100, (2M + Na)$^+$], $C_{16}H_{13}NNaO$ predicted 258.0889, found 258.0893, (Δ − 1.6 ppm); **m.p.** 181-184 °C (petrol/EtOAc).

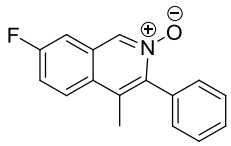
1,4-Dimethyl-3-phenylisoquinoline-*N*-oxide **5f**



Ketone **3f** (53.2 mg, 0.180 mmol) was subjected to General Procedure 5. The crude product was purified by flash column chromatography on alumina [EtOAc/MeOH 97:3] to furnish *isoquinoline-N-oxide* **5f** (44.6 mg, 0.179 mmol, 99 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.00 (1H, dd, *J* 7.8, 1.5, *H*C(8)), 7.96 (1H, dd, *J* 7.2, 1.5, *H*C(5)), 7.67-7.60 (2H, m, *H*C(6) + *H*C(7)), 7.54-7.49 (2H, m, 2 × HC_{Ar}), 7.48-7.43 (1H, m, HC_{Ar}), 7.39-7.37 (2H, m, 2 × HC_{Ar}), 2.91 (3H, s, C(1)CH_3), 2.40 (3H, s, C(4)CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 145.8 (*C*(3)), 143.6 (*C*(1)), 134.0 (C_{Ar}), 129.8 (HC_{Ar}), 128.9 (C_{Ar}), 128.5 (HC_{Ar}), 128.4 (2 signals), 128.0 (HC_{Ar} + H*C*(6) + H*C*(7)), 128.0, 127.7 (C_{Ar} + *C*(4)), 124.4, 124.4 (H*C*(5) + H*C*(8)), 16.0 (C(1)*C*H$_3$) 13.2 (C(4)*C*H$_3$); **IR** ν_{max} (thin film)/cm^{-1} 3058w, 1502w, 1443w, 1386w, 1349m, 1296s, 1214s, 1138m, 1094w, 1019m, 919w; **m/z** (ESI$^+$) 250.1 [55, (M + H)$^+$], 272.1 [55, (M + Na)$^+$], 499.2 [55, (2M + H)$^+$], 521.2 [100, (2M + Na)$^+$], $C_{17}H_{16}NO$ predicted 250.1226, found 250.1229, (Δ − 1.2 ppm); **m.p.** 160-163 °C (petrol/EtOAc).

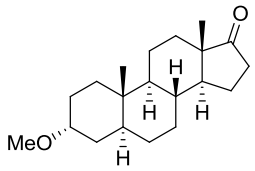
7-Fluoro-4-methyl-3-phenylisoquinoline-*N*-oxide **5l**



Ketone **3l** (52.3 mg, 0.174 mmol) was subjected to General Procedure 5. The crude product was purified by flash column chromatography on alumina [EtOAc/MeOH 97:3] to furnish *isoquinoline-N-oxide* **5l** (37.8 mg, 0.149 mmol, 86 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.80 (1H, s, *H*C(1)), 7.94 (1H, dd, *J* 9.1, 5.1, *H*C(5)), 7.56-7.47 (3H, m, 2 × HC_{Ar} + *H*C(8)), 7.41-7.34 (4H, m, 3 × HC_{Ar} + *H*C(6)), 2.42 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 162.2 (d, ^1J 250.9, *C*(7)), 145.9 (d, ^6J 2.4, *C*(3)), 134.3 (d, ^4J 5.6, H*C*(1)), 132.6, 130.8 (2 × C_{Ar}), 130.0 (HC_{Ar}), 129.8 (d, ^3J 9.6, C_{Ar}), 129.0 (HC_{Ar}), 128.7 (HC_{Ar}), 126.9 (d, ^3J 8.8, H*C*(5)), 126.2 (*C*(4)), 118.7 (d, ^2J 25.6, H*C*(6)), 108.6 (d, ^2J 22.4, H*C*(8)), 16.3 (*C*H$_3$); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ_F: −109.9; **IR** ν_{max} (thin film)/cm^{-1} 3060m, 1629m, 1573w, 1501m, 1443w, 1378s, 1314s, 1230m, 1193s, 1151s, 1033w, 1006w, 965w, 873w, 822m; **m/z** (ESI$^+$) 254.1 [65, (M + H)$^+$], 276.1 [65, (M + Na)$^+$], 507.2 [25, (2M + H)$^+$], 529.1 [100, (2M + Na)$^+$], $C_{16}H_{12}FNNaO$ predicted 276.0795, found 276.0798, (Δ − 1.1 ppm); **m.p.** 216-218 °C (petrol/EtOAc).

Androsterone-3-methyl ether **7**



Trimethyloxonium tetrafluoroborate (112 mg, 0.760 mmol) was added to a solution of androsterone (147 mg, 0.506 mmol) and *N*,*N*,*N*'*N*'-tetramethyl-1,8-naphthalenediamine (217

mg, 1.01 mmol) in CH_2Cl_2 (20 mL) and the reaction was stirred at room temperature for 18 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (50 mL) and the aqueous layer was further extracted with CH_2Cl_2 (2 × 50 mL). The combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product. Purification by flash column chromatography [Petrol/EtOAc 19:1] furnished *ether* **7** (152 mg, 0.500 mmol, 99 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 3.44-3.42 (1H, m, C*H*OCH_3), 3.28 (3H, s, OCH_3), 2.42 (1H, dd, *J* 19.1, 8.8, CH_aH_bC=O), 2.05 (1H, dd, *J* 19.1, 8.8, CH_aH_bC=O), 1.95-1.88 (1H, m, assignment uncertain), 1.82-1.15 (17H, m, assignment uncertain), 1.00 (1H, ddd, *J* 17.2, 12.2, 4.9, assignment uncertain), 0.85 (3H, s, CH_3), 0.81-0.77 (1H, m, assignment uncertain), 0.80 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 221.6 (*C*=O), 75.4 (*C*HOCH$_3$), 55.7 (O*C*H$_3$), 54.3, 51.5 (2 × *C*H), 47.8 (*C*), 39.5 (*C*H), 36.0 (*C*), 35.9 (*C*H$_2$), 35.0 (*C*H), 32.8, 32.5, 31.6, 30.8, 28.3, 25.0, 21.7, 20.0 (8 × *C*H$_2$), 13.8, 11.4 (2 × *C*H$_3$); **m.p.** 120-122 °C (petrol/CH_2Cl_2); **$[\alpha]_D^{20}$** + 88.8 (*c* 1.0, CH_2Cl_2). Data were consistent with those previously reported.[16]

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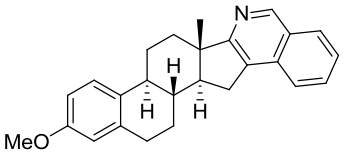
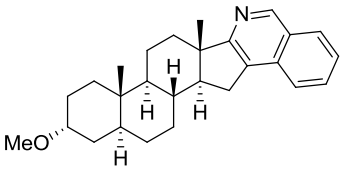


A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (6.5 mg, 0.010 mmol) and sodium *tert*-butoxide (48.1 mg, 0.500 mmol) were added to the tube. Acetal **2a** (68.7 mg, 0.300 mmol) was dissolved in dry THF (1.0 mL) and the resulting solution was added *via* syringe to the tube. Estrone-3-methyl ether (57.0 mg, 0.200 mmol) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and acidified to pH 5 by the addition of aqueous HCl (1.0 M). A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was then added and the tube resealed and heated at 90 °C for 24 h. The reaction was then cooled to room temperature and quenched by the addition of saturated aqueous $NaHCO_3$ (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product. Purification by flash column chromatography [Petrol/EtOAc 24:1 grading to 9:1] furnished *isoquinoline* **8** (46.4 mg, 0.126 mmol, 63 %) as prisms.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.11 (1H, s, *H*C(1)), 7.98 (1H, d, *J* 8.1, *H*C(8)), 7.81 (1H, d, *J* 8.3, *H*C(5)), 7.70 (1H, ddd, *J* 8.1, 6.9, 1.1, *H*C(6)), 7.52 (1H, ddd, *J* 8.0, 6.9, 1.0, *H*C(7)), 7.29 (1H, d, *J* 8.6, *H*C_{Ar}), 6.77 (1H, dd, *J* 8.5, 2.7, *H*C_{Ar}), 6.70 (1H, d, *J* 2.5, *H*C_{Ar}), 3.81 (3H, s, O*CH*$_3$), 3.25 (1H, dd, *J* 14.6, 6.0, CH_aH_bC(4)), 3.08-2.93 (2H, m, CH_2C_{Ar}), 2.79 (1H, dd, *J* 14.1, 12.6, CH_aH_bC(4)), 2.57-2.51 (2H, m, CH_aH_bCH_aH_bCHC_{Ar}), 2.44 (1H, td, *J* 11.0, 4.2, C*H* C_{Ar}), 2.18-2.12 (1H, m, CH_aH_bCH_2C_{Ar}), 2.05 (1H, td, *J* 11.7, 6.4, C*H*CH_2C(4)), 1.95-1.75

(3H, m, $CH_aH_bCH_aH_bCHC_{Ar}$ + $CHCHC_{Ar}$), 1.60 (1H, dtd, *J* 18.6, 12.1, 6.7, $CH_aH_bCH_2C_{Ar}$), 1.07 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 166.0 (*C*(3)), 157.5 (C_{Ar}), 151.2 (H*C*(1)), 137.8, 134.0, 132.7 (3 × C_{Ar}), 130.1 (H*C*(6)), 129.6 (*C*(4)), 128.4 (H*C*(8)), 127.5 (C_{Ar}), 126.2 (HC_{Ar}), 125.7 (H*C*(7)), 123.2 (H*C*(5)), 113.9, 111.5 (2 × HC_{Ar}), 55.5 ($CHCH_2C$(4)), 55.2 (OCH_3), 46.3 (*C*), 44.6 (CHC_{Ar}), 37.6 ($CHCHC_{Ar}$), 34.1, 26.5 ($CH_2CH_2CHC_{Ar}$), 29.7 (CH_2C_{Ar}), 28.0 (CH_2C(4)), 27.6 ($CH_2CH_2C_{Ar}$), 17.8 (CH_3); **IR** ν_{max} (thin film)/cm^{-1} 2927s, 2851m, 1736w, 1625m, 1610m, 1570m, 1500s, 1463m, 1369m, 1280m, 1256s, 1155w, 1103w, 1045m, 857w, 805m; **m/z** (ESI$^+$) 370.2 [100, $(M + H)^+$], $C_{26}H_{28}NO$ predicted 370.2165, found 370.2163, (Δ + 0.5 ppm); **m.p.** 219-221 °C (petrol/CH_2Cl_2); **$[\alpha]_D^{20}$** + 34.8 (*c* 0.25, CH_2Cl_2).

9



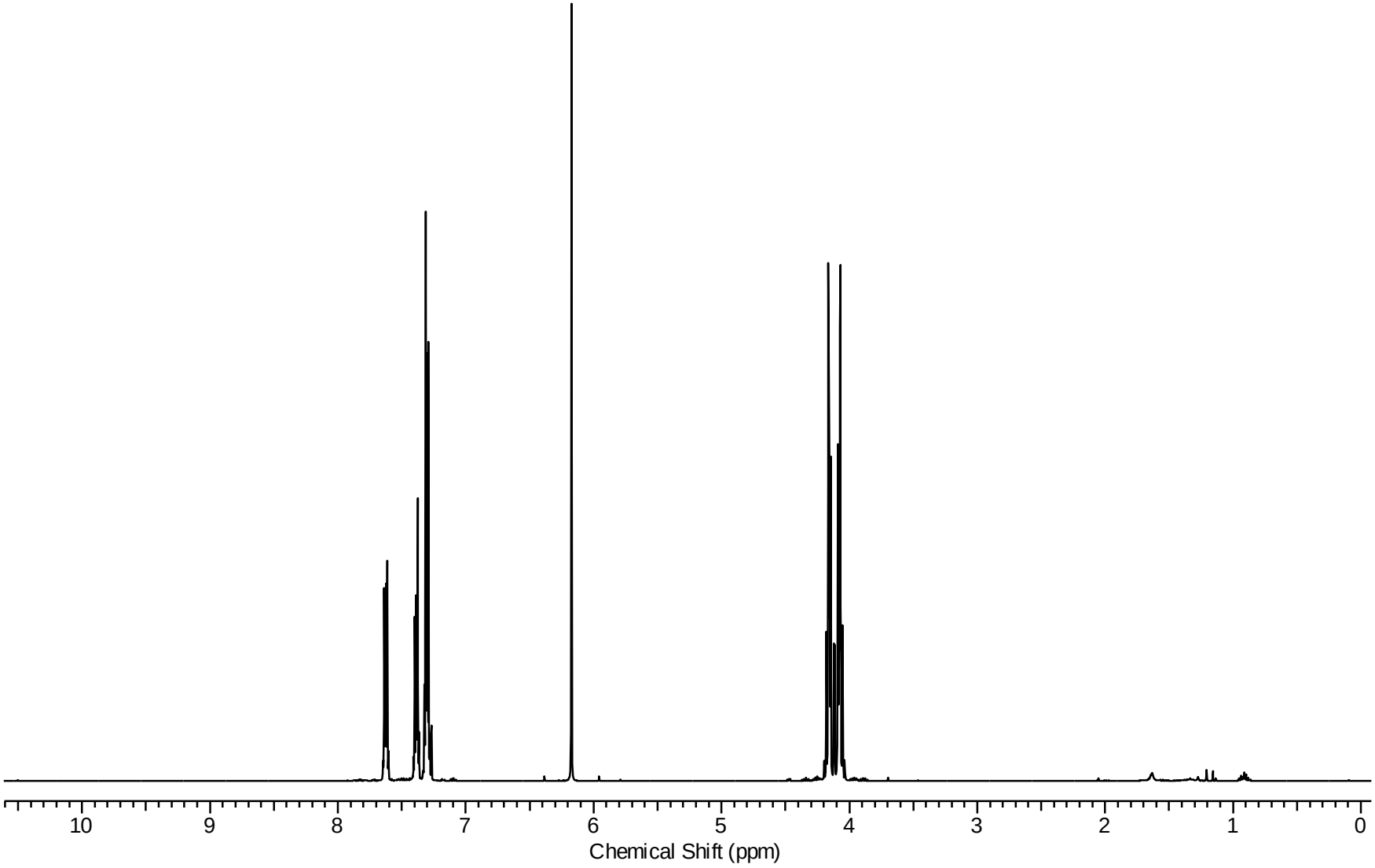
A resealable reaction tube, containing a magnetic follower, was sealed with a rubber septum and flame dried under a flow of argon. (D*t*BPF)$PdCl_2$ (7.4 mg, 0.011 mmol) and sodium *tert*-butoxide (54.5 mg, 0.568 mmol) were added to the tube. Acetal **2a** (77.9 mg, 0.340 mmol) was dissolved in dry THF (1.1 mL) and the resulting solution was added *via* syringe to the tube. Ether **7** (69.0 mg, 0.227 mmol) was then added *via* syringe to the tube. The rubber septum was then replaced with a screw cap and the tube was heated at 70 ^oC for 18 h. The reaction was then cooled to room temperature and acidified to pH 5 by the addition of aqueous HCl (1.0 M). A solution of NH_4Cl (10 eq., 1.0 M in 3:1 EtOH/H_2O) was then added and the tube resealed and heated at 90 °C for 24 h. The reaction was then cooled to room temperature and quenched by the addition of saturated aqueous $NaHCO_3$ (25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product. Purification by flash column chromatography [Petrol/EtOAc 24:1 grading to 9:1] furnished *isoquinoline* **9** (52.0 mg, 0.133 mmol, 59 %) as plates.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.06 (1H, s, H*C*(1)), 7.94 (1H, d, *J* 8.3, H*C*(8)), 7.75 (1H, d, *J* 8.3, H*C*(5)), 7.65 (1H, td, *J* 7.0, 1.1, H*C*(6)), 7.48 (1H, td, *J* 7.6, 0.9, H*C*(7)), 3.46-3.44 (1H, m, $CHOCH_3$), 3.30 (3H, s, OCH_3), 3.11 (1H, dd, *J* 15.1, 5.8, CH_aH_bC(4)), 2.63 (1H, dd, *J* 14.7, 11.4, CH_aH_bC(4)), 2.37-2.33 (1H, m, assignment uncertain), 1.92-1.76 (5H, m, assignment uncertain), 1.68-1.14 (11H, m, assignment uncertain), 1.04-0.96 (1H, m, assignment uncertain), 1.02 (3H, s, CH_3), 0.90 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 166.2 (*C*(3)), 151.0 (H*C*(1)), 133.9 (C_{Ar}), 130.0 (H*C*(6)), 129.7 (*C*(4)), 128.3 (H*C*(8)), 127.5 (C_{Ar}), 125.6 (H*C*(7)), 123.3 (H*C*(5)), 75.5 ($CHOCH_3$), 56.4 (*C*H), 55.7 (OCH_3), 55.1 (*C*H), 46.1 (*C*), 39.8 (*C*H), 36.3 (*C*), 34.4 (*C*H), 34.0, 32.9, 32.4, 31.7, 28.5 (5 × CH_2), 28.2 (CH_2C(4)), 25.1, 20.6 (2 × CH_2), 17.8, 11.5 (2 × CH_3); **IR** ν_{max} (thin film)/cm^{-1} 2924w, 2854w, 1626m, 1570m, 1445m, 1365m, 1259m, 1148w, 1089s, 1030m, 987w, 909s, 878w,

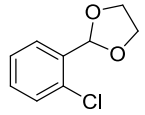
867w, 802s; **m/z** (ESI^+) 390.2 [100, $(M + H)^+$], $C_{27}H_{36}NO$ predicted 390.2791, found 390.2780, (Δ + 2.8 ppm); **m.p.** 178-180 °C (petrol/CH_2Cl_2); $\mathbf{[\alpha]_D^{20}}$ + 7.90 (*c* 1.0, CH_2Cl_2).

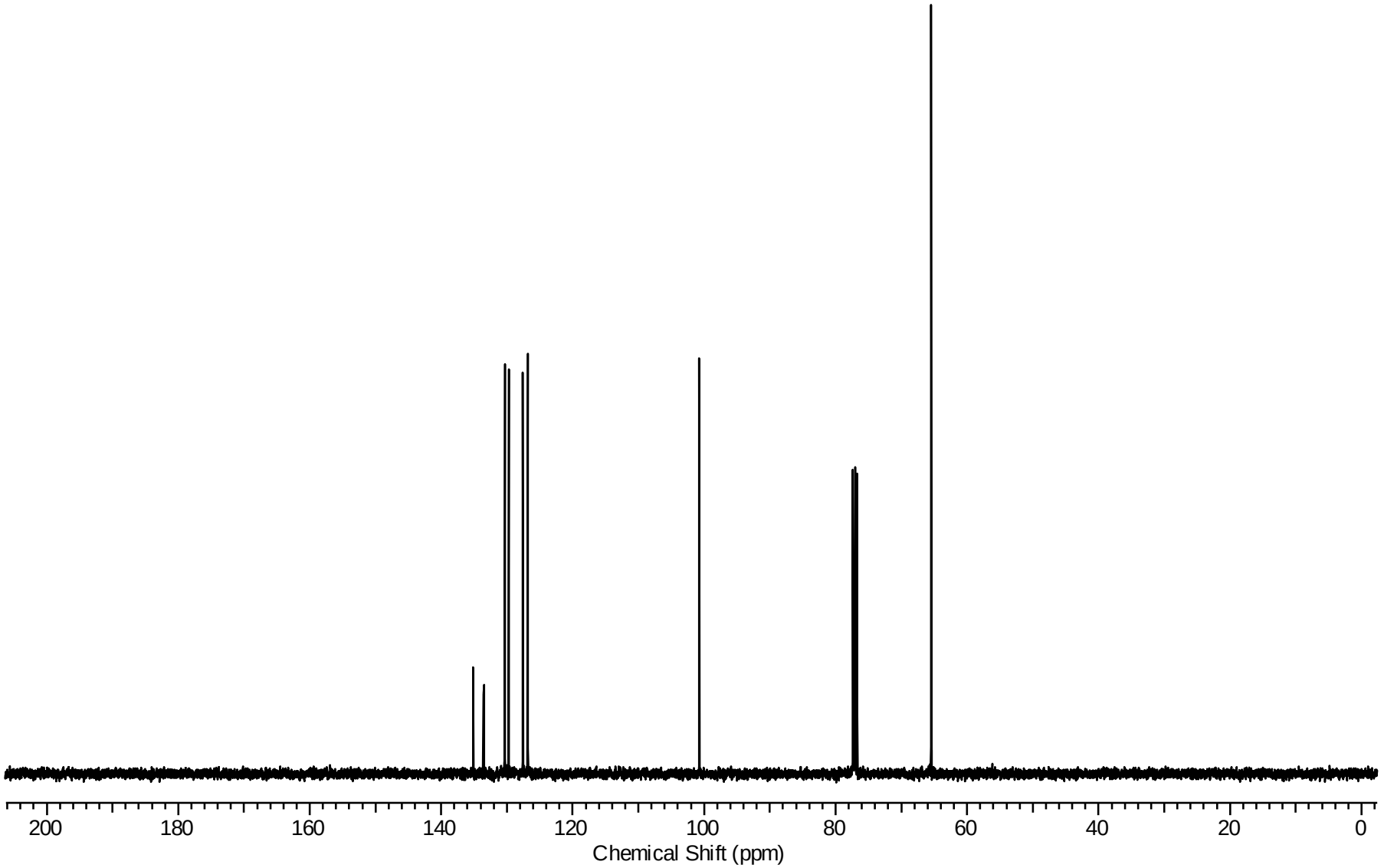
^{1}H NMR and ^{13}C NMR spectra of compounds

2-(2-Chlorophenyl)-1,3-dioxolane **2b**

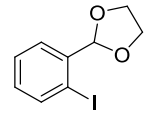


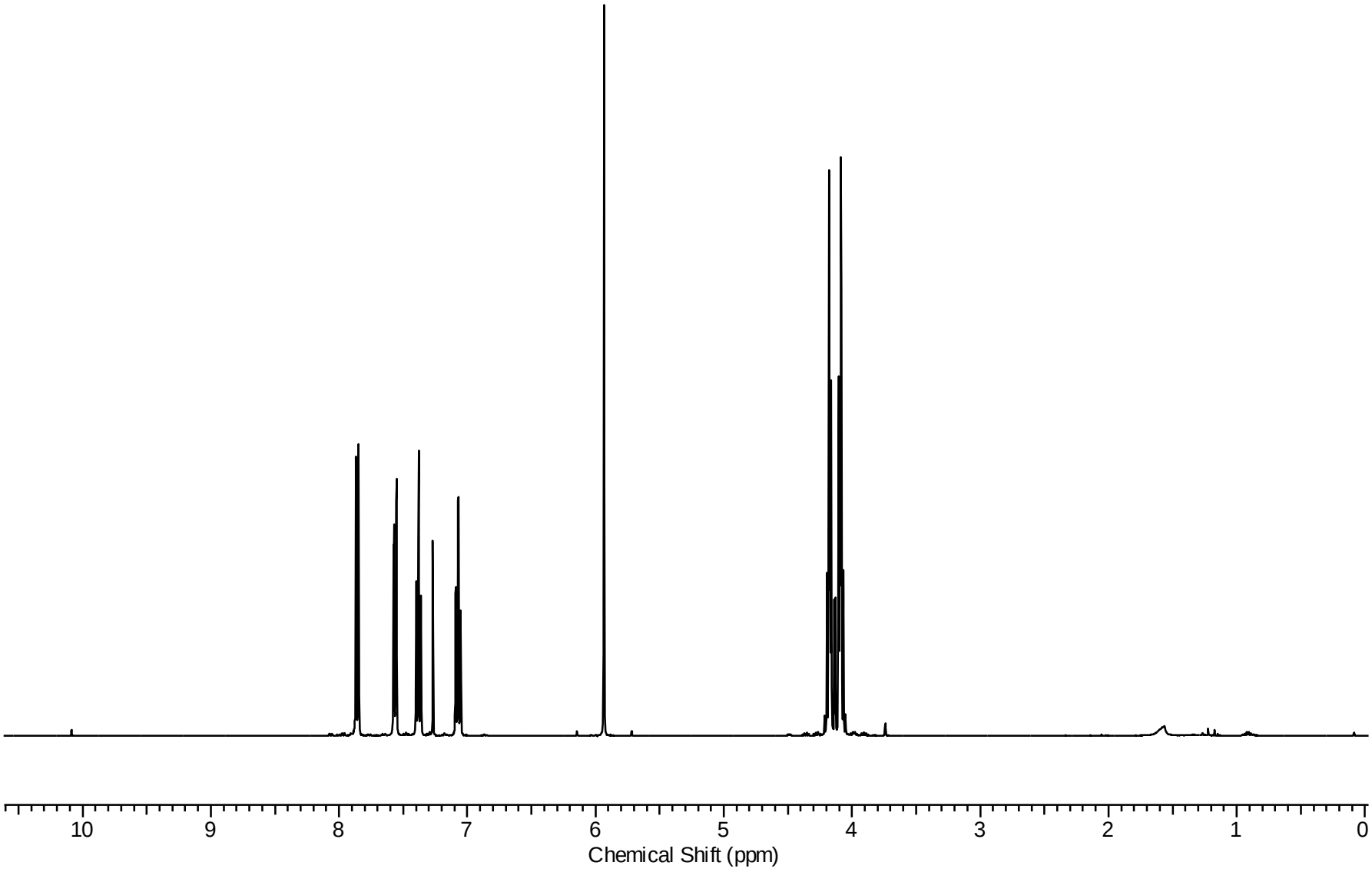
2-(2-Chlorophenyl)-1,3-dioxolane **2b**



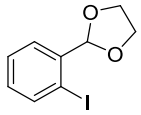


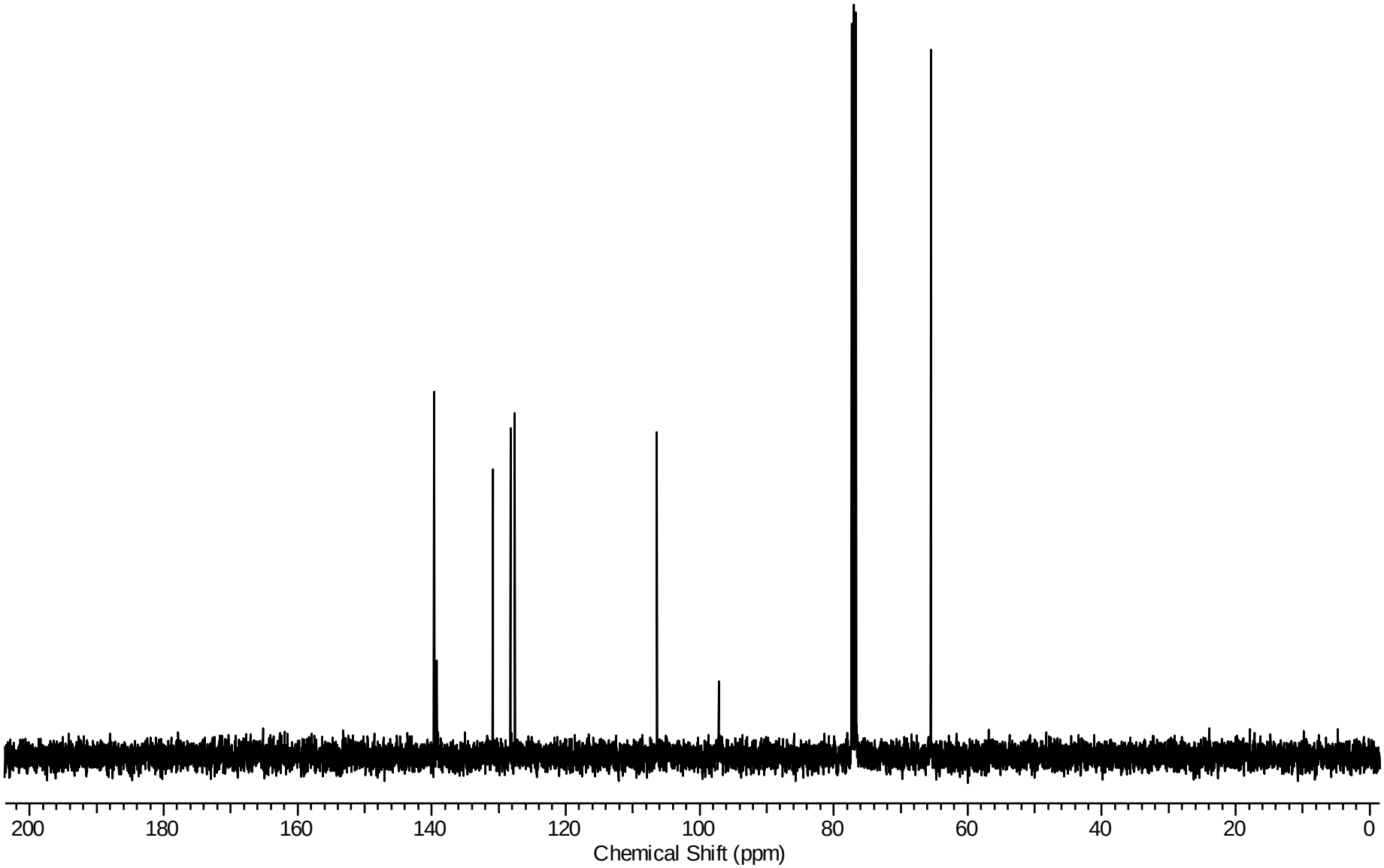
2-(2-Iodophenyl)-1,3-dioxolane **2c**



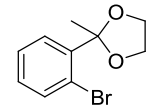


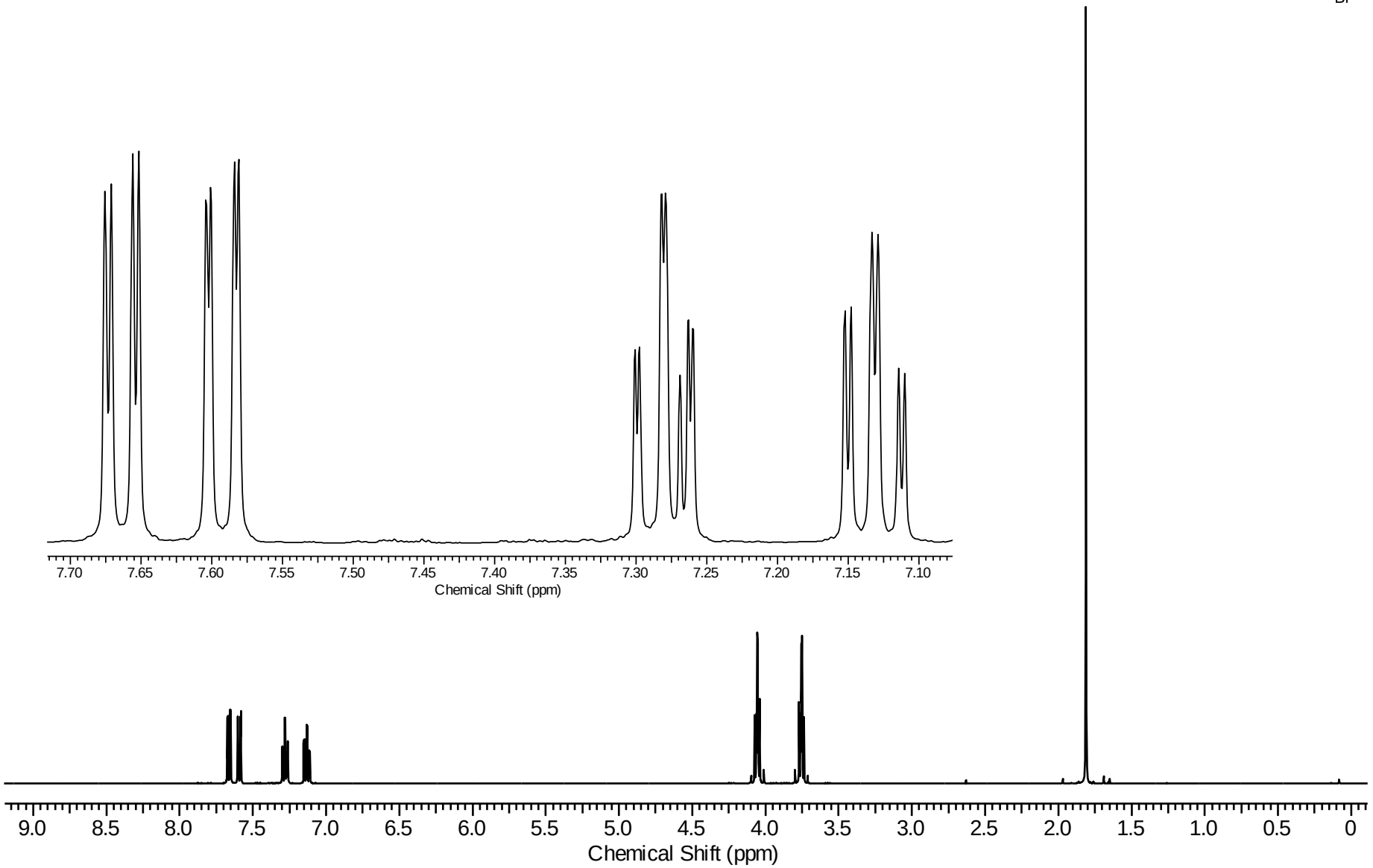
2-(2-Iodophenyl)-1,3-dioxolane **2c**



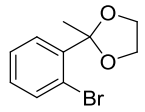


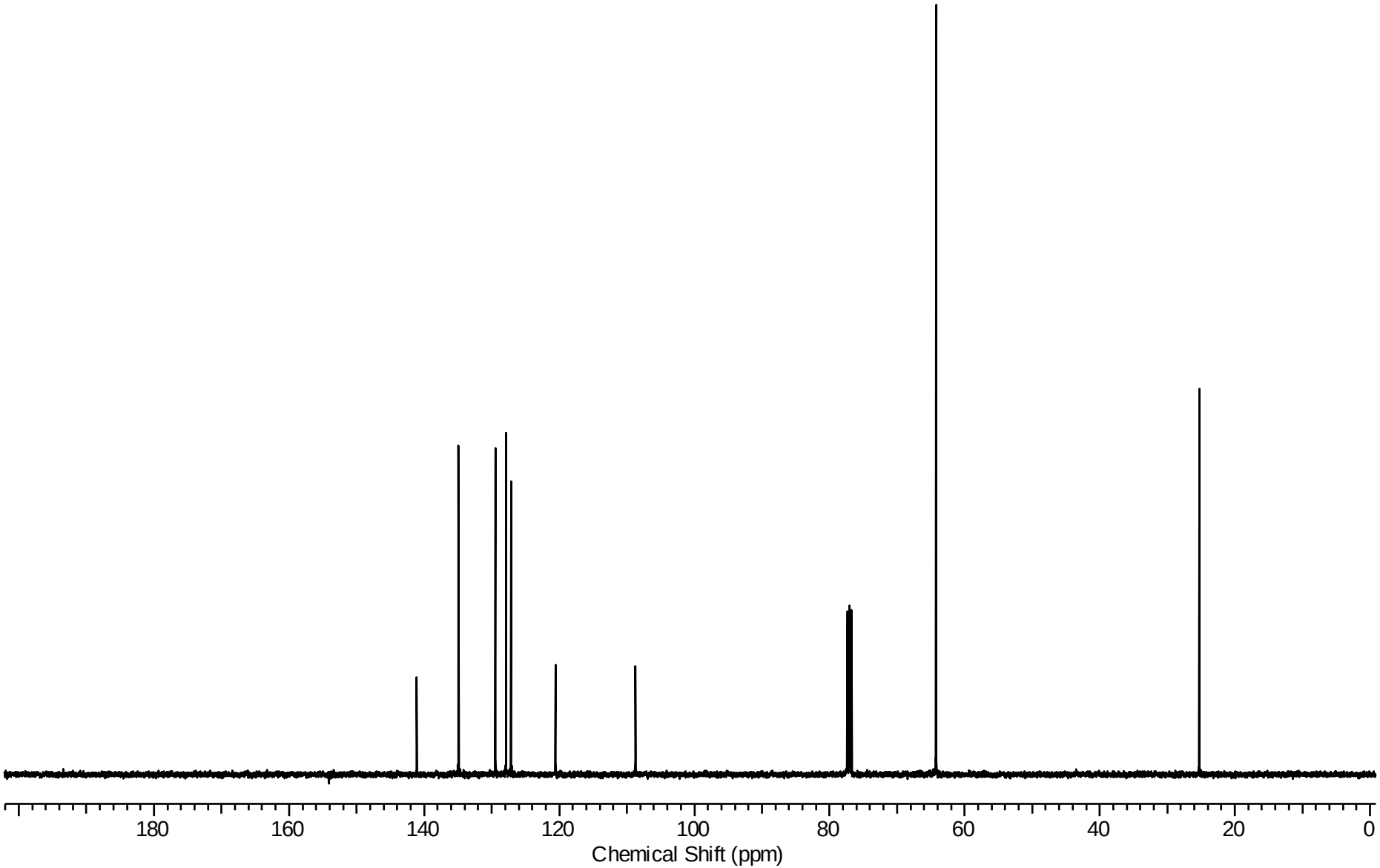
2-(2-Bromophenyl)-2-methyl-1,3-dioxolane **2f**



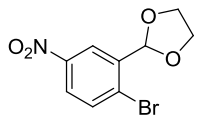


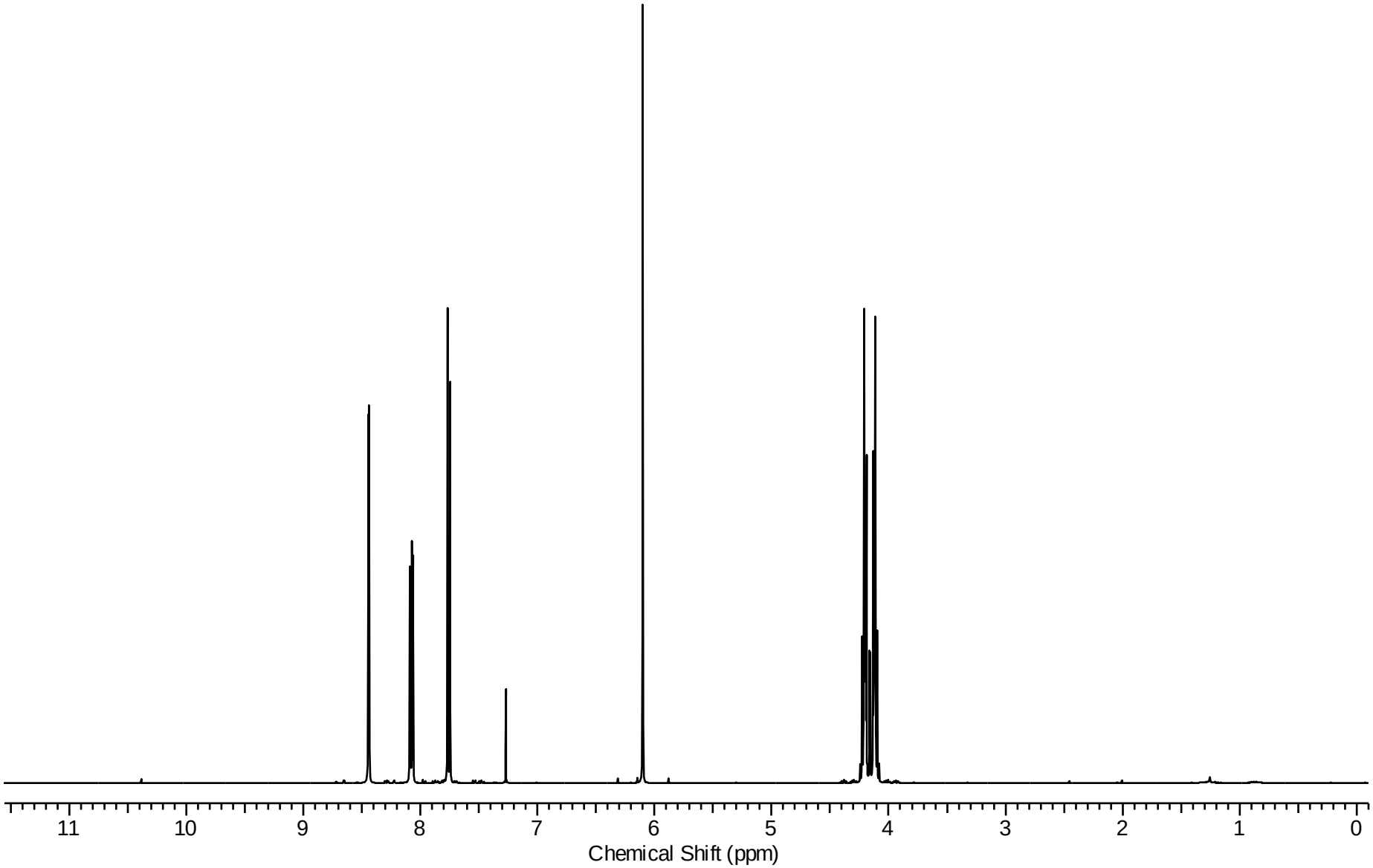
2-(2-Bromophenyl)-2-methyl-1,3-dioxolane **2f**



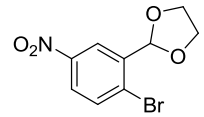


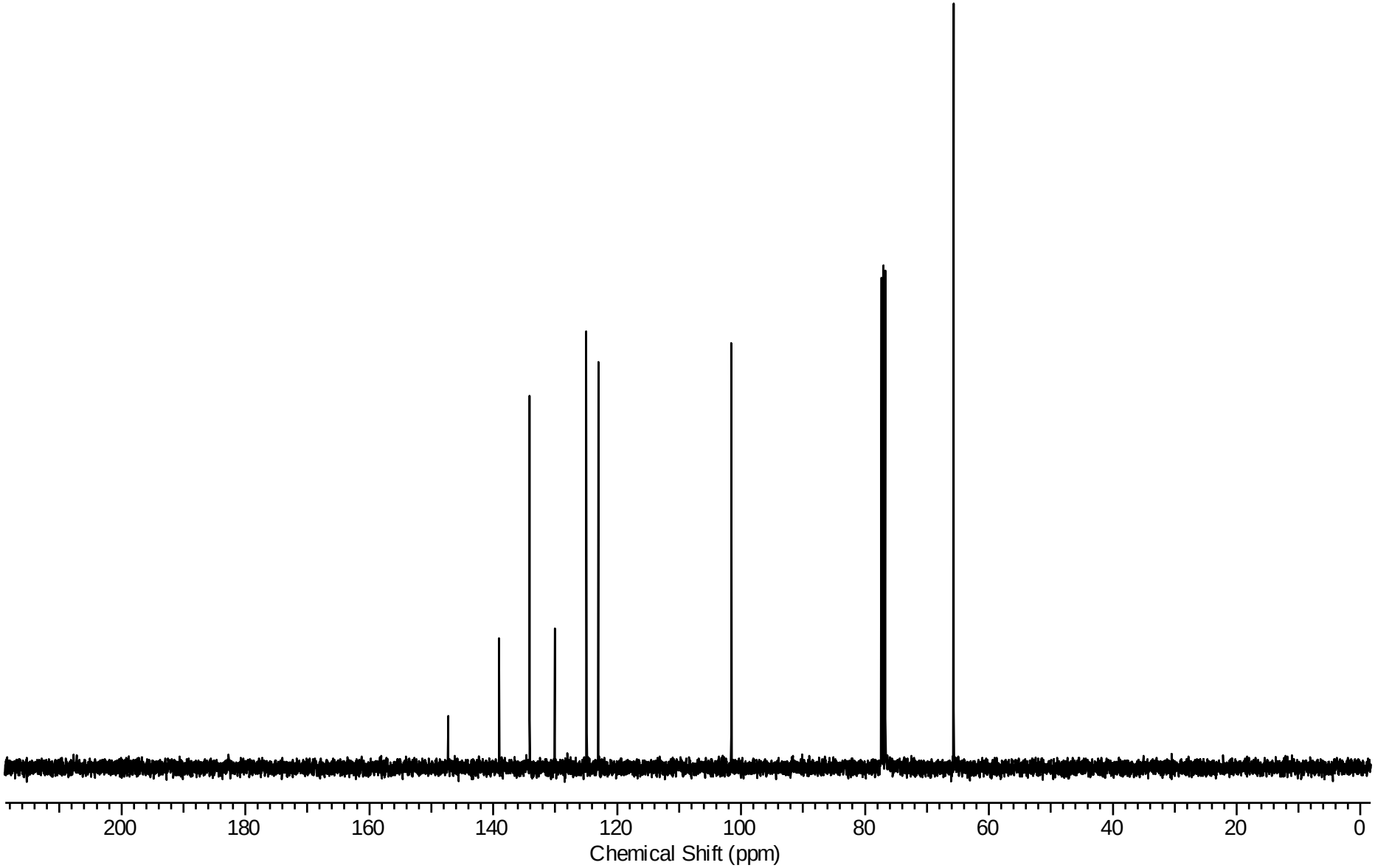
2-(2-Bromo-5-nitrophenyl)-1,3-dioxolane **2k**



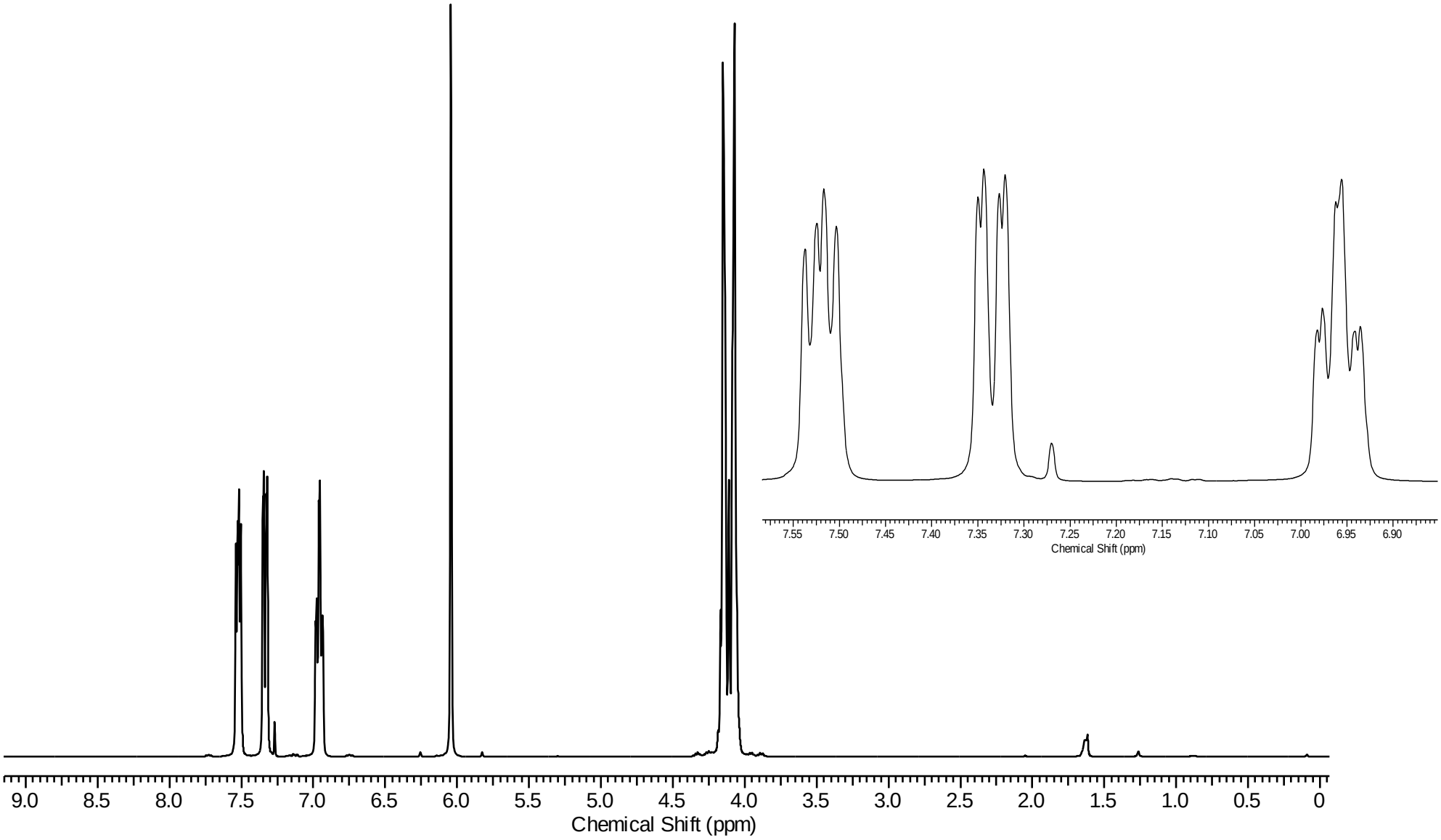


2-(2-Bromo-5-nitrophenyl)-1,3-dioxolane **2k**

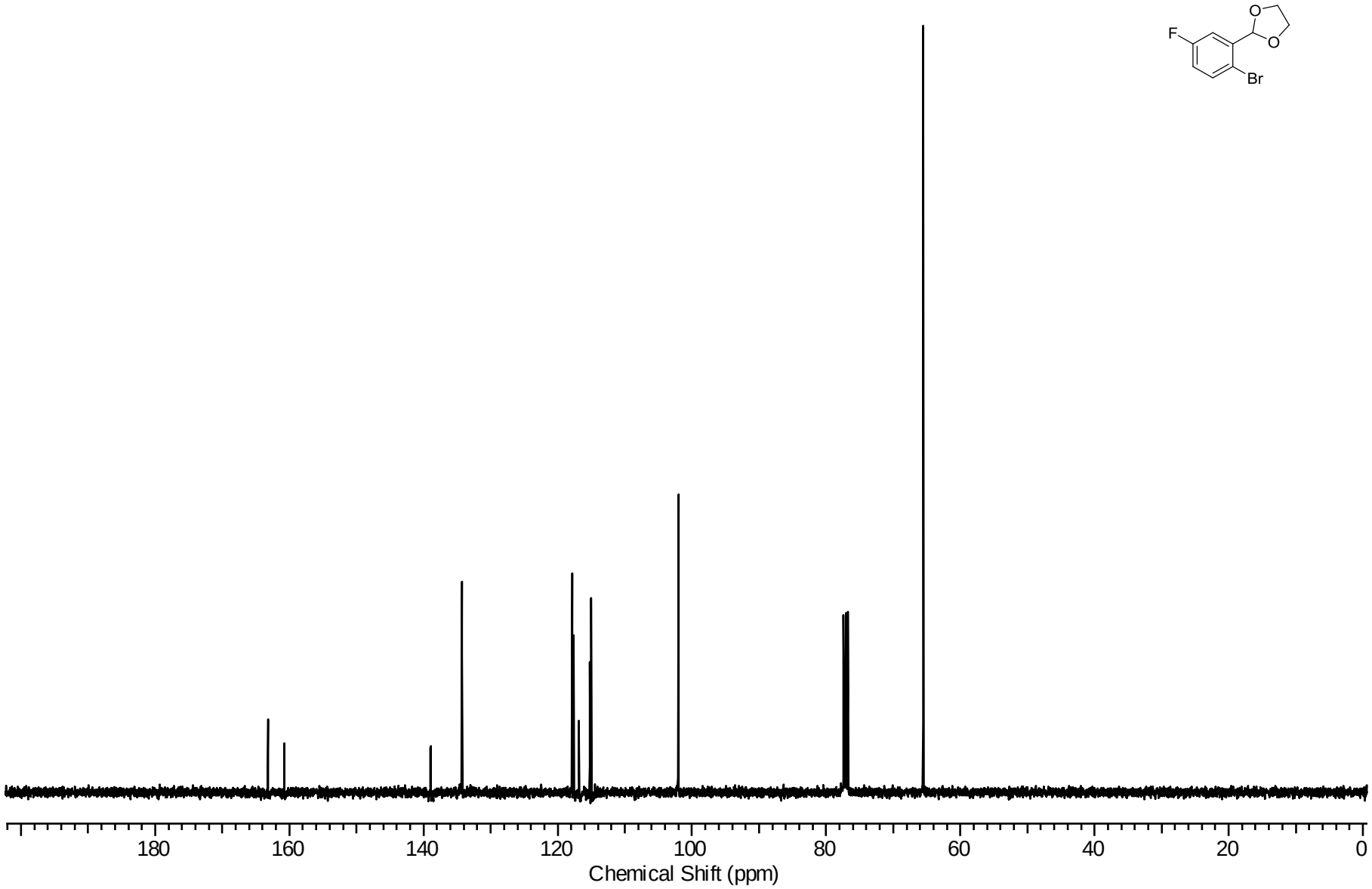




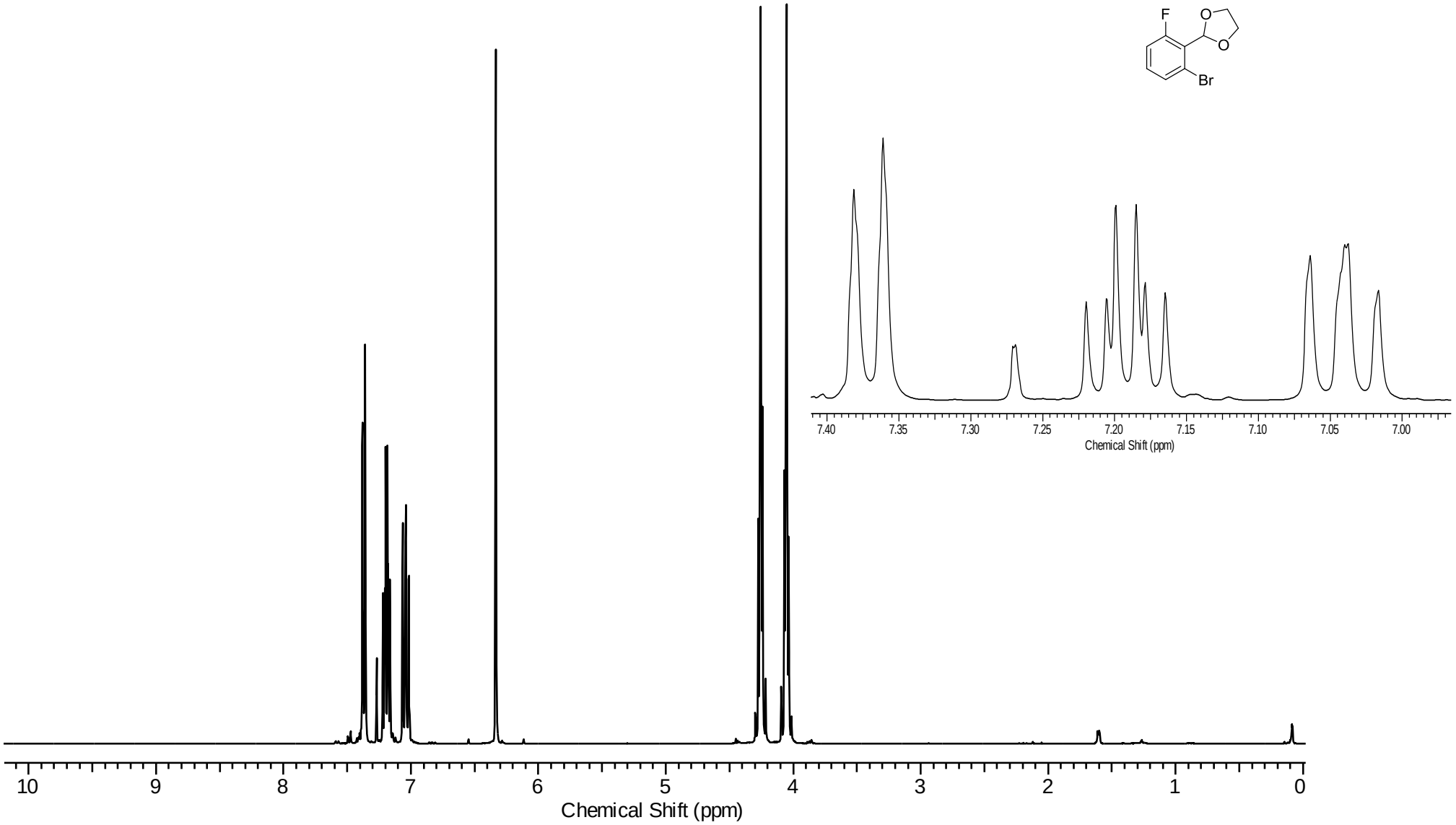
2-(2-Bromo-5-fluorophenyl)-1,3-dioxolane **2l**



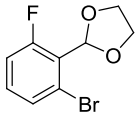
2-(2-Bromo-5-fluorophenyl)-1,3-dioxolane **2l**

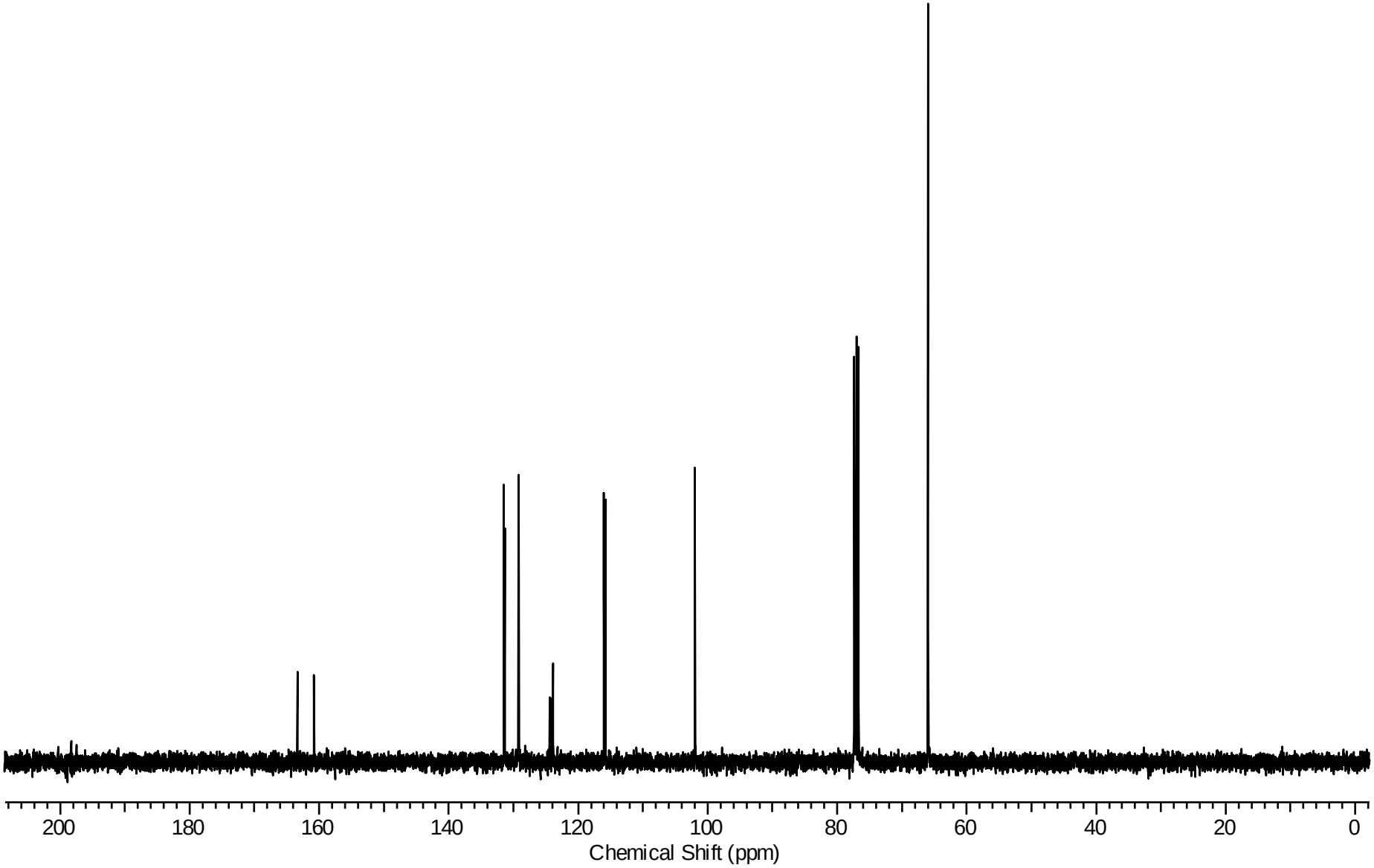


2-(2-Bromo-6-fluorophenyl)-1,3-dioxolane **2m**

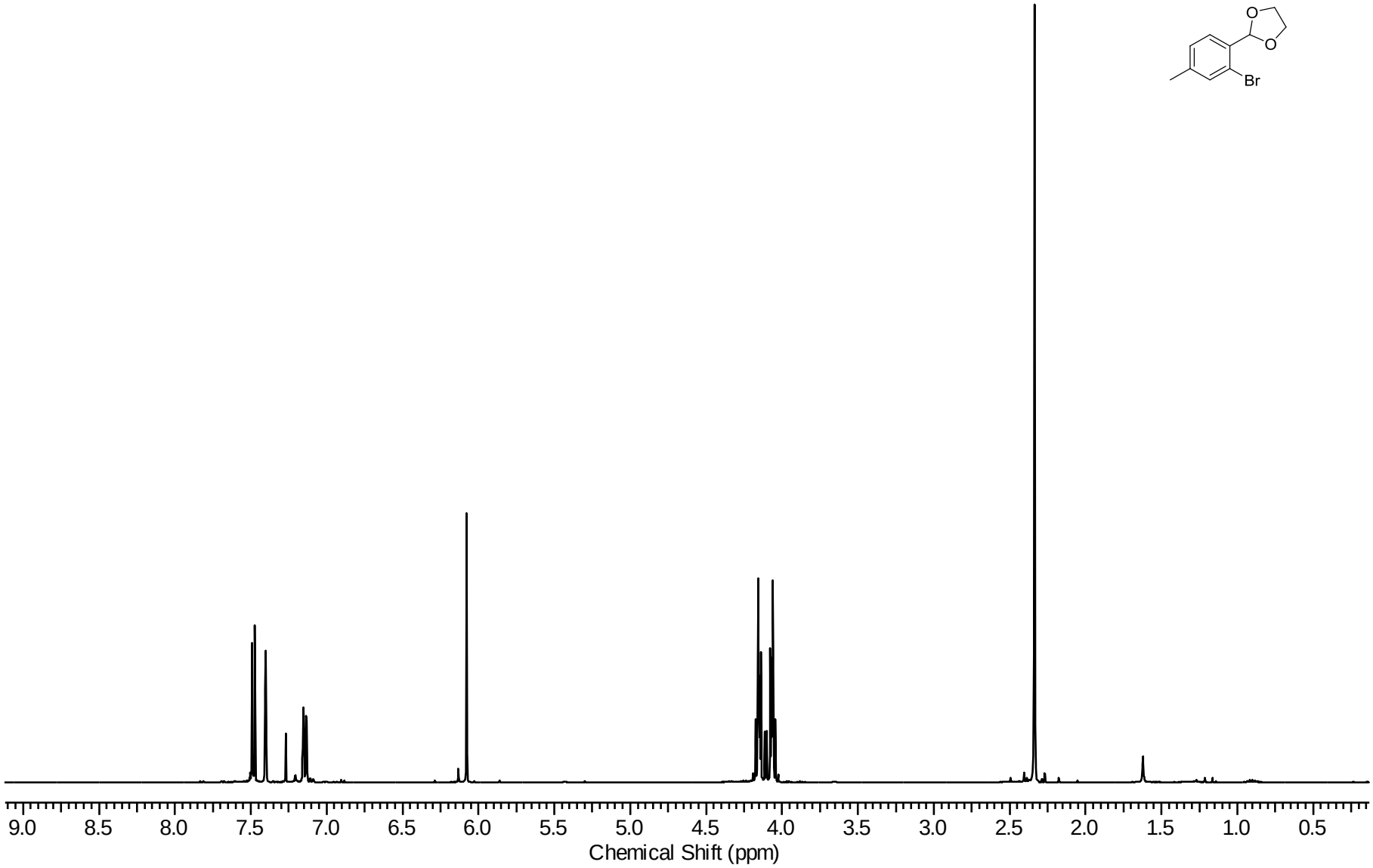


2-(2-Bromo-6-fluorophenyl)-1,3-dioxolane **2m**

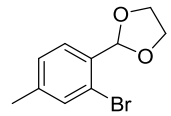


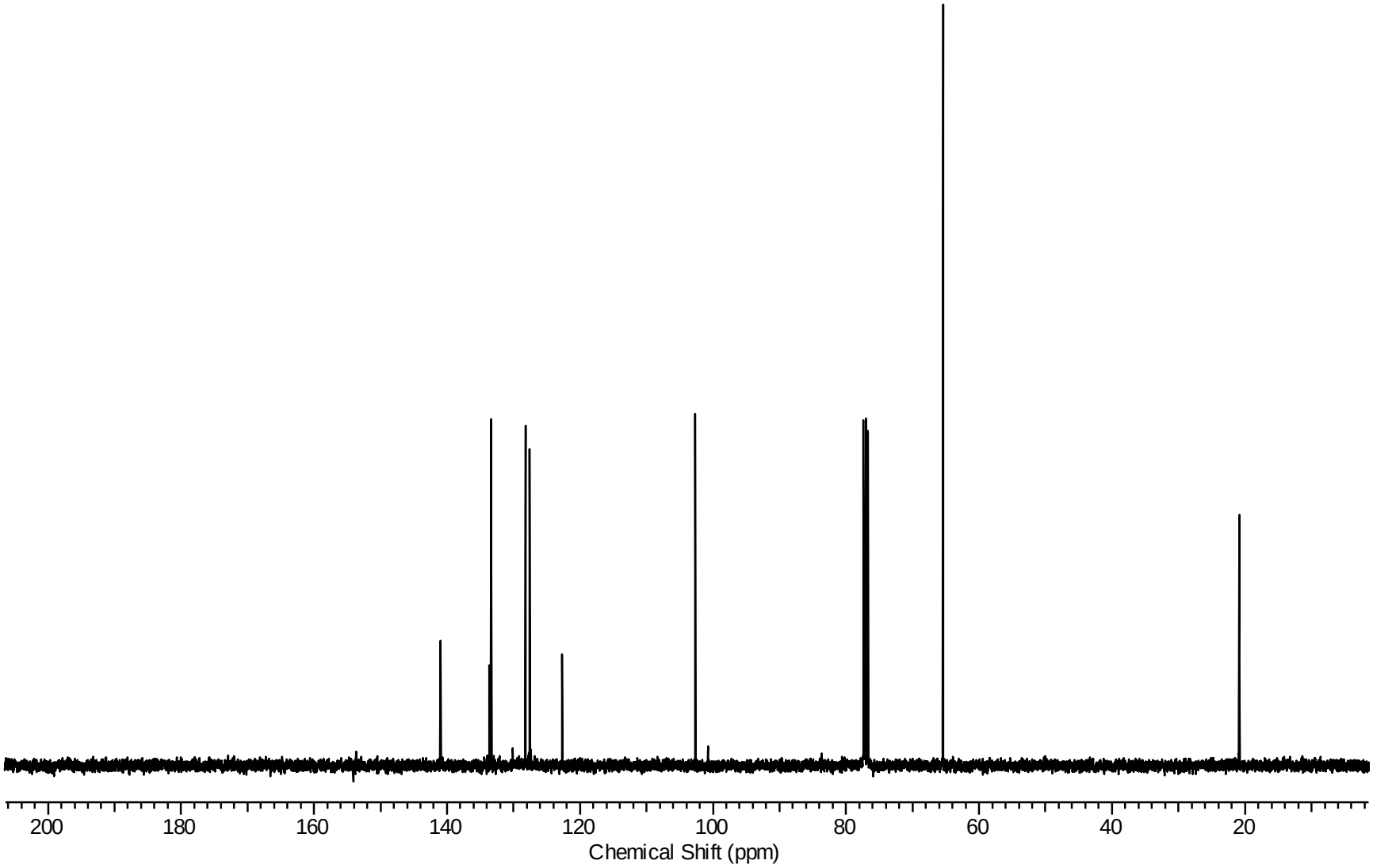


2-(2-Bromo-4-methylphenyl)-1,3-dioxolane **2n**

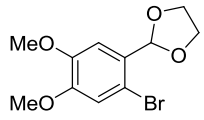


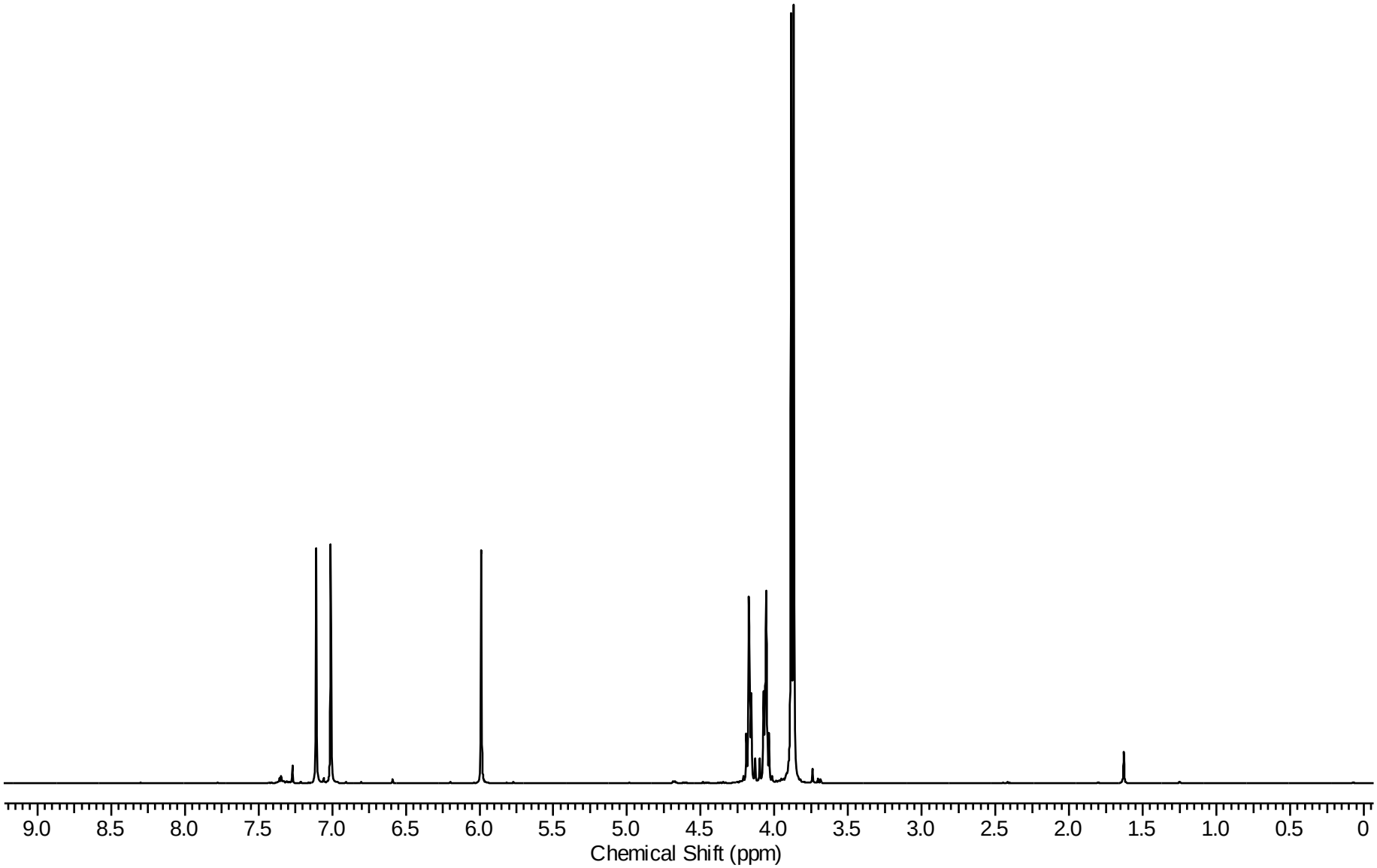
2-(2-Bromo-4-methylphenyl)-1,3-dioxolane **2n**



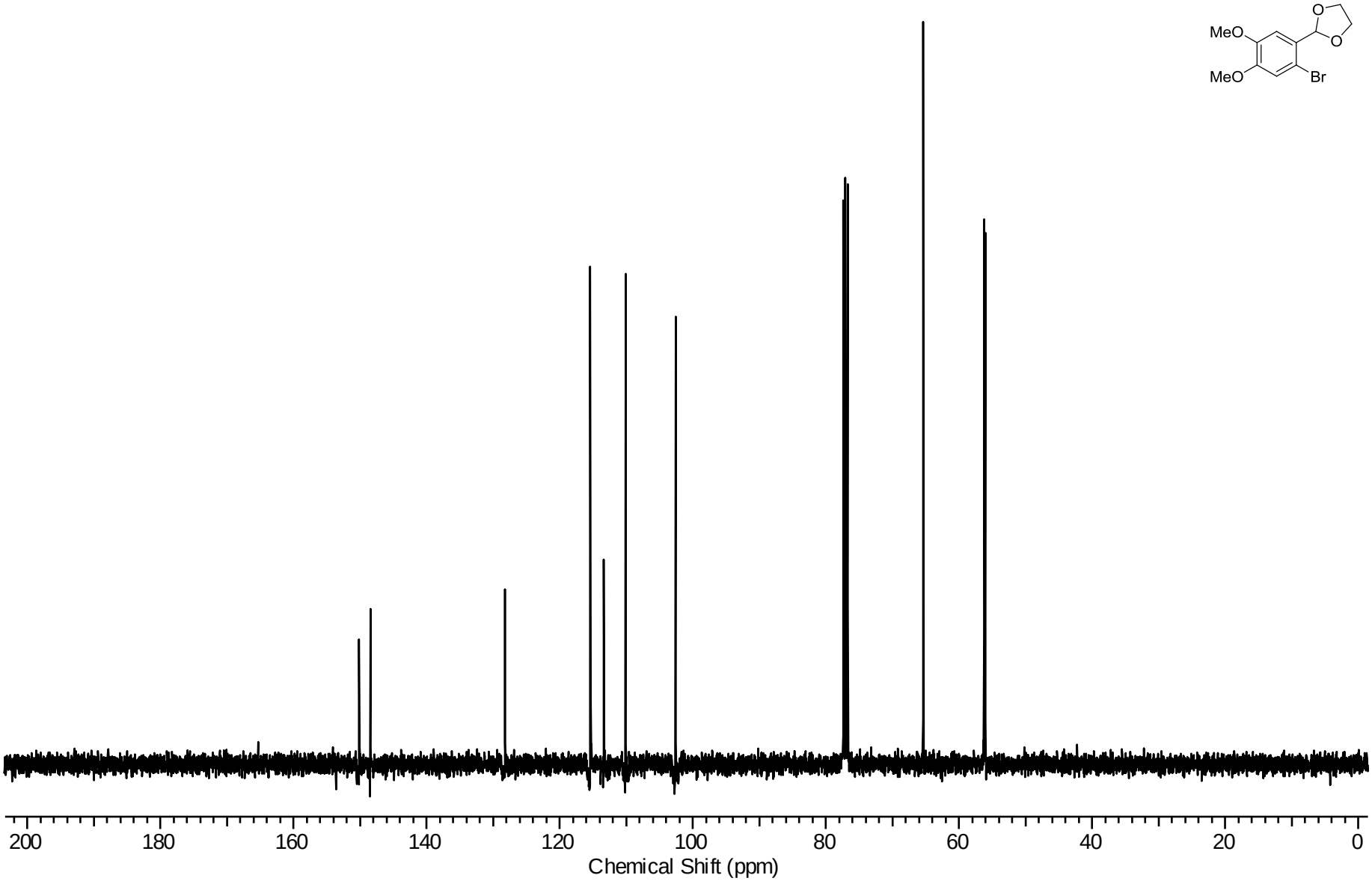


2-(2-Bromo-4,5-dimethoxyphenyl)-1,3-dioxolane **2o**

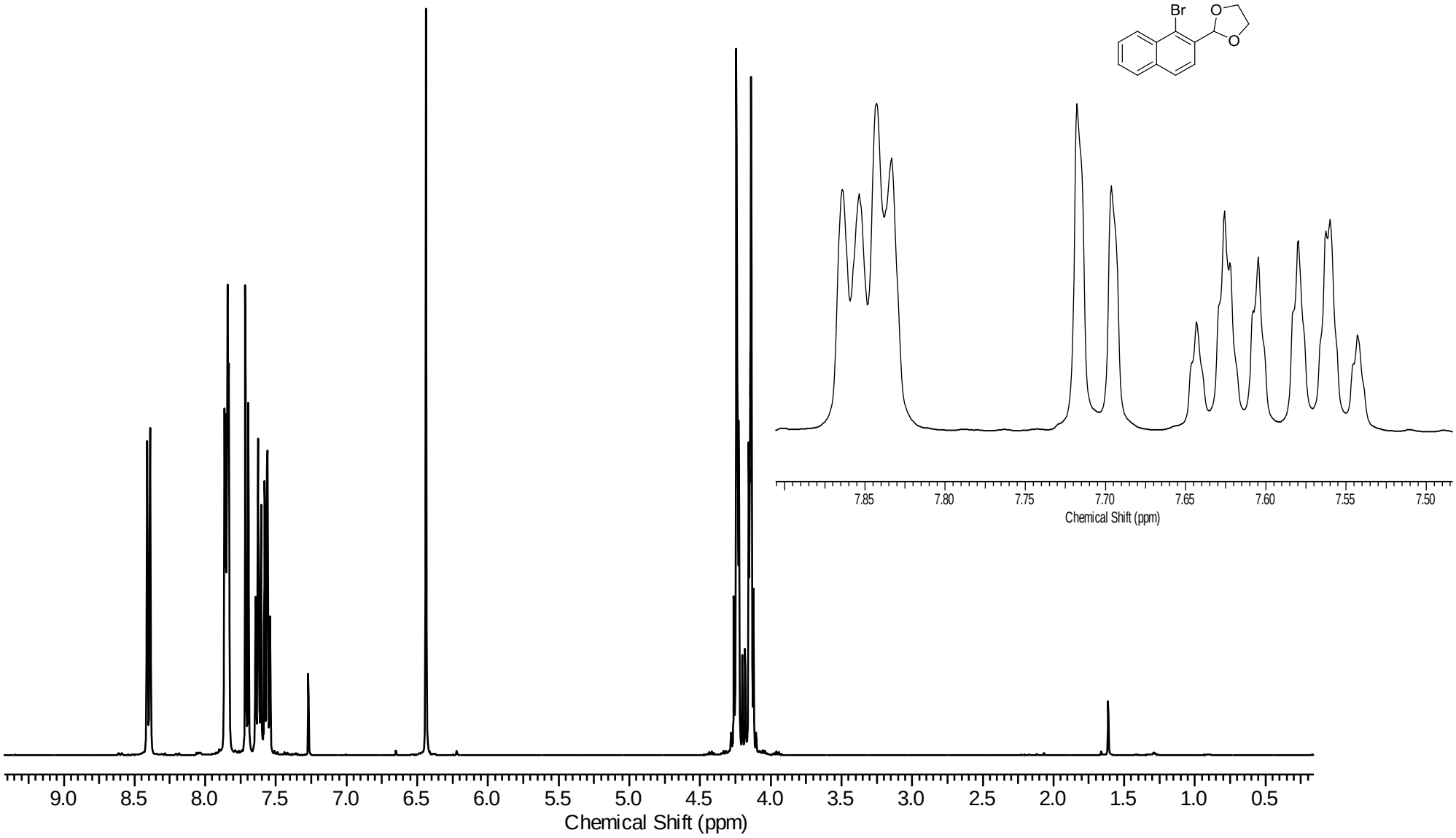




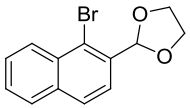
2-(2-Bromo-4,5-dimethoxyphenyl)-1,3-dioxolane **2o**

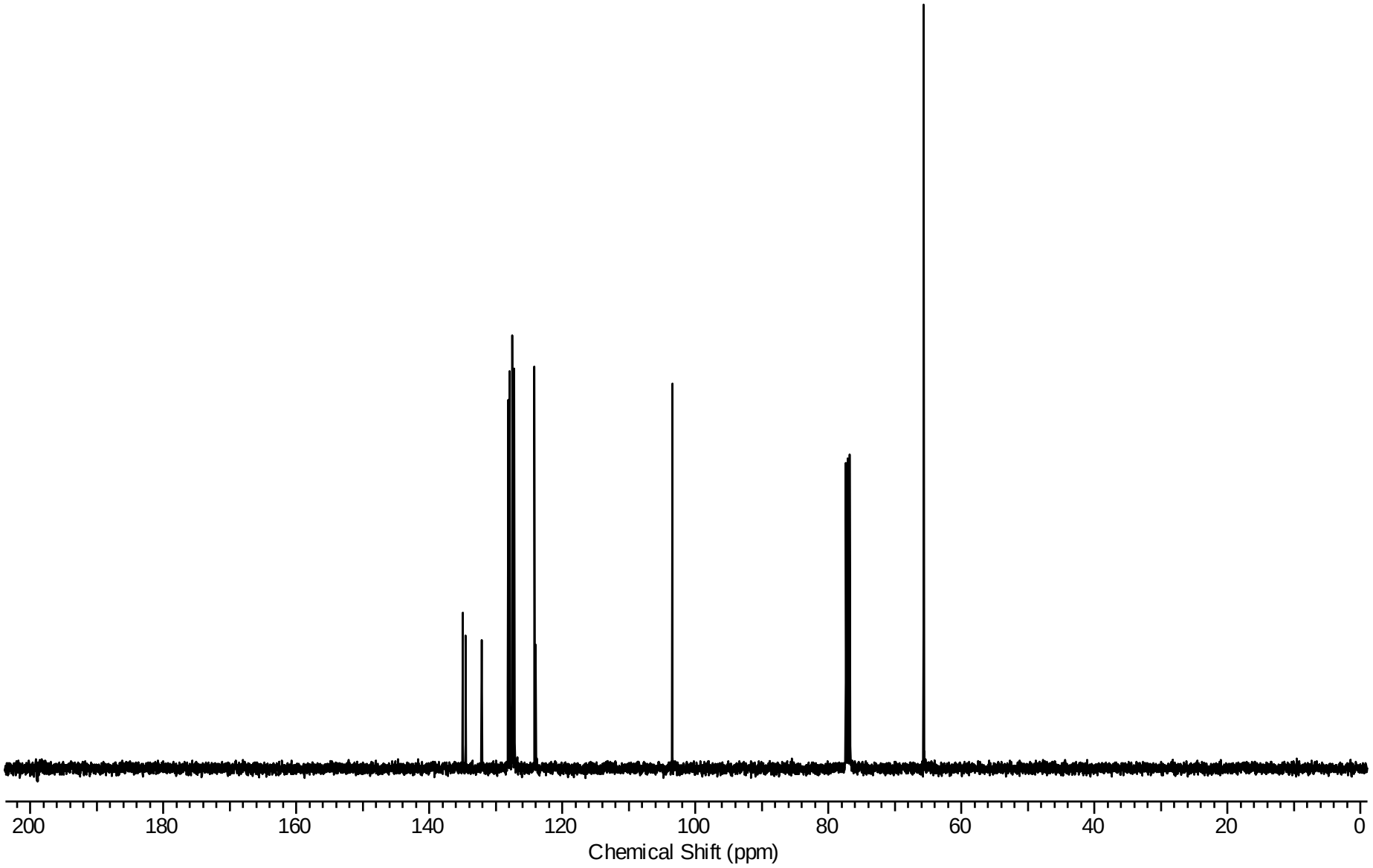


2-(1-Bromonaphthalen-2-yl)-1,3-dioxolane **2p**

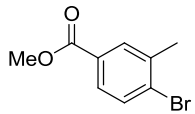


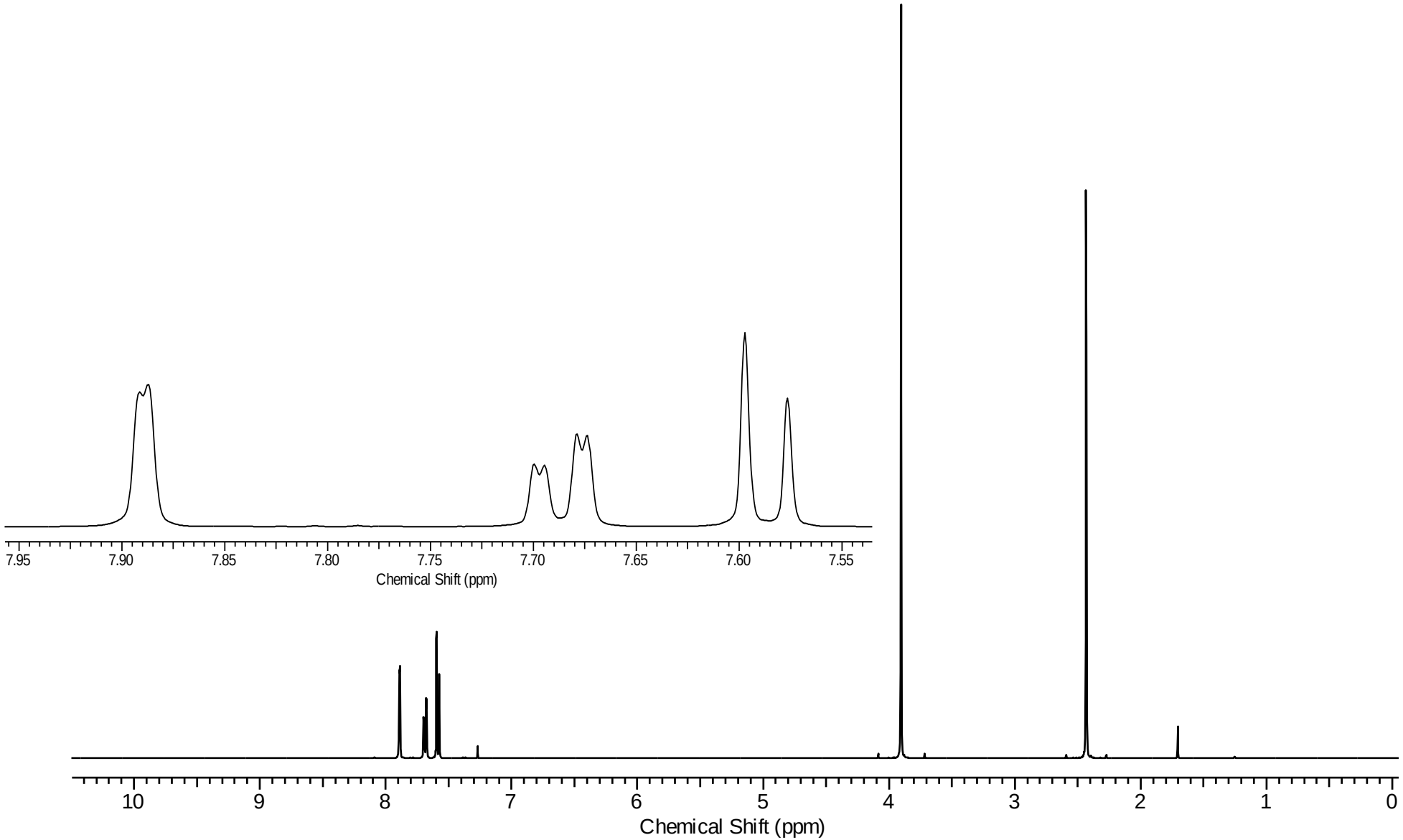
2-(1-Bromonaphthalen-2-yl)-1,3-dioxolane **2p**



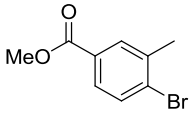


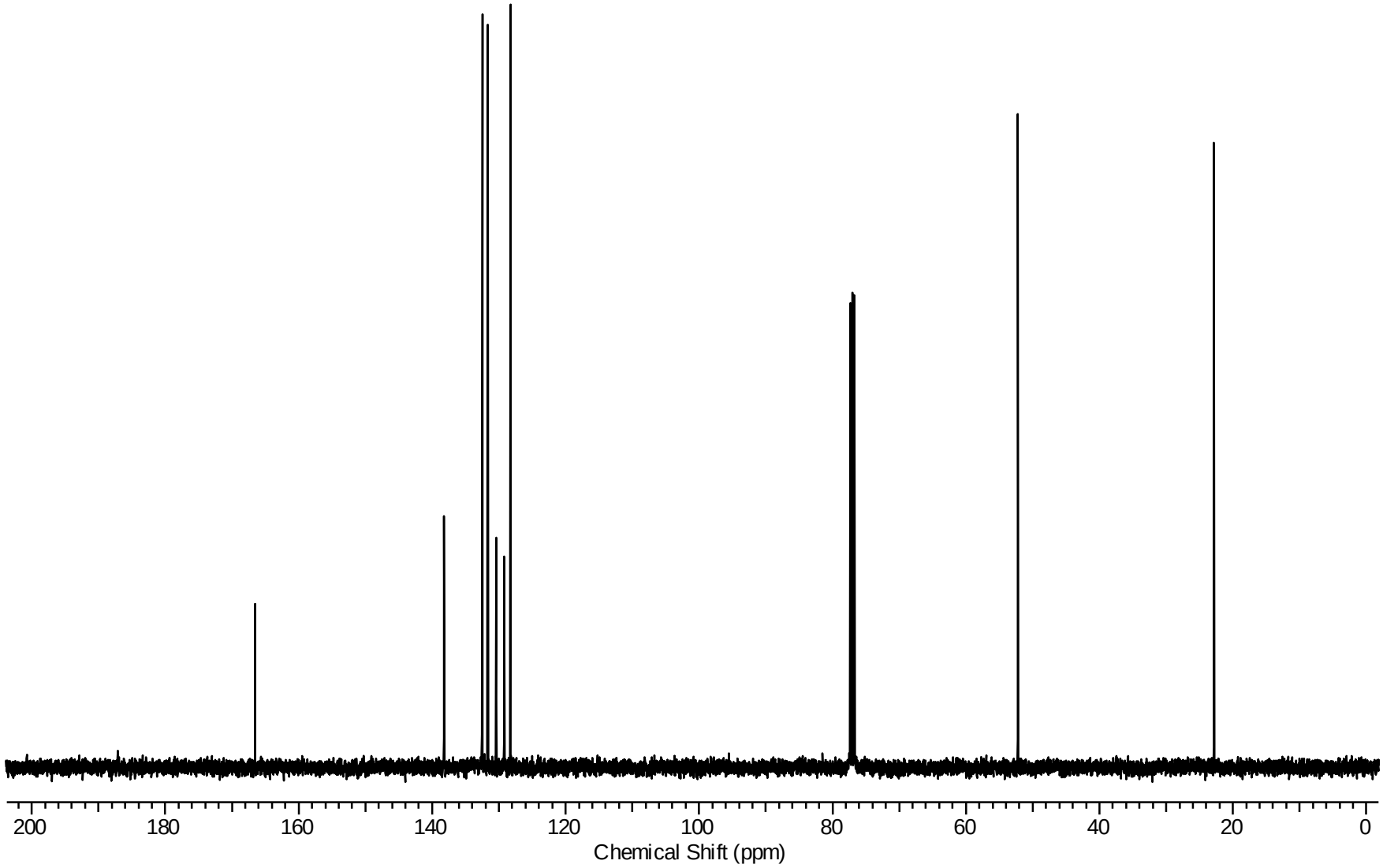
Methyl 4-bromo-3-methylbenzoate **S1**



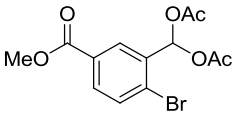


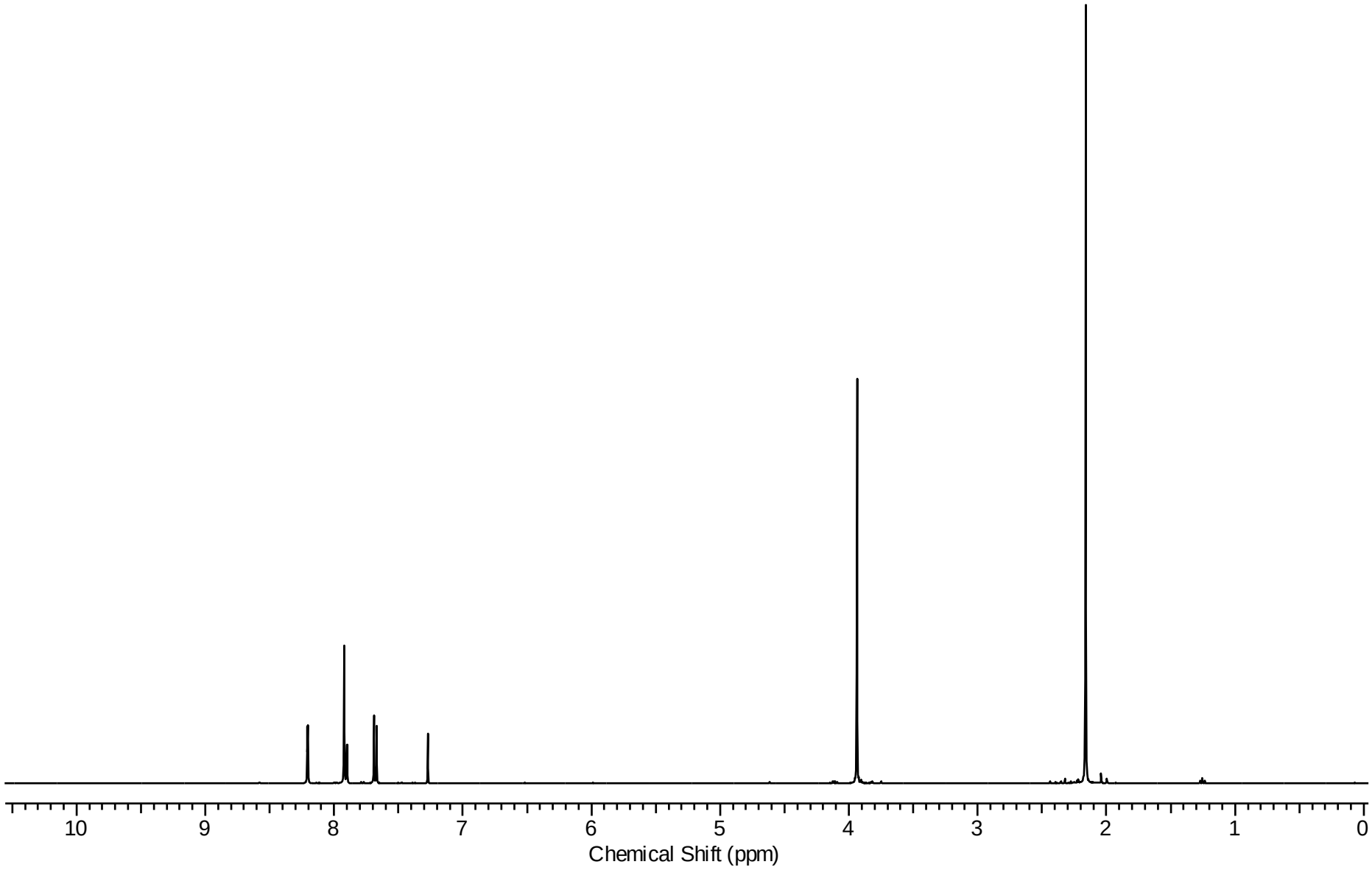
Methyl 4-bromo-3-methylbenzoate **S1**



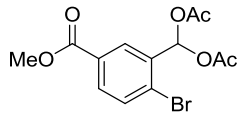


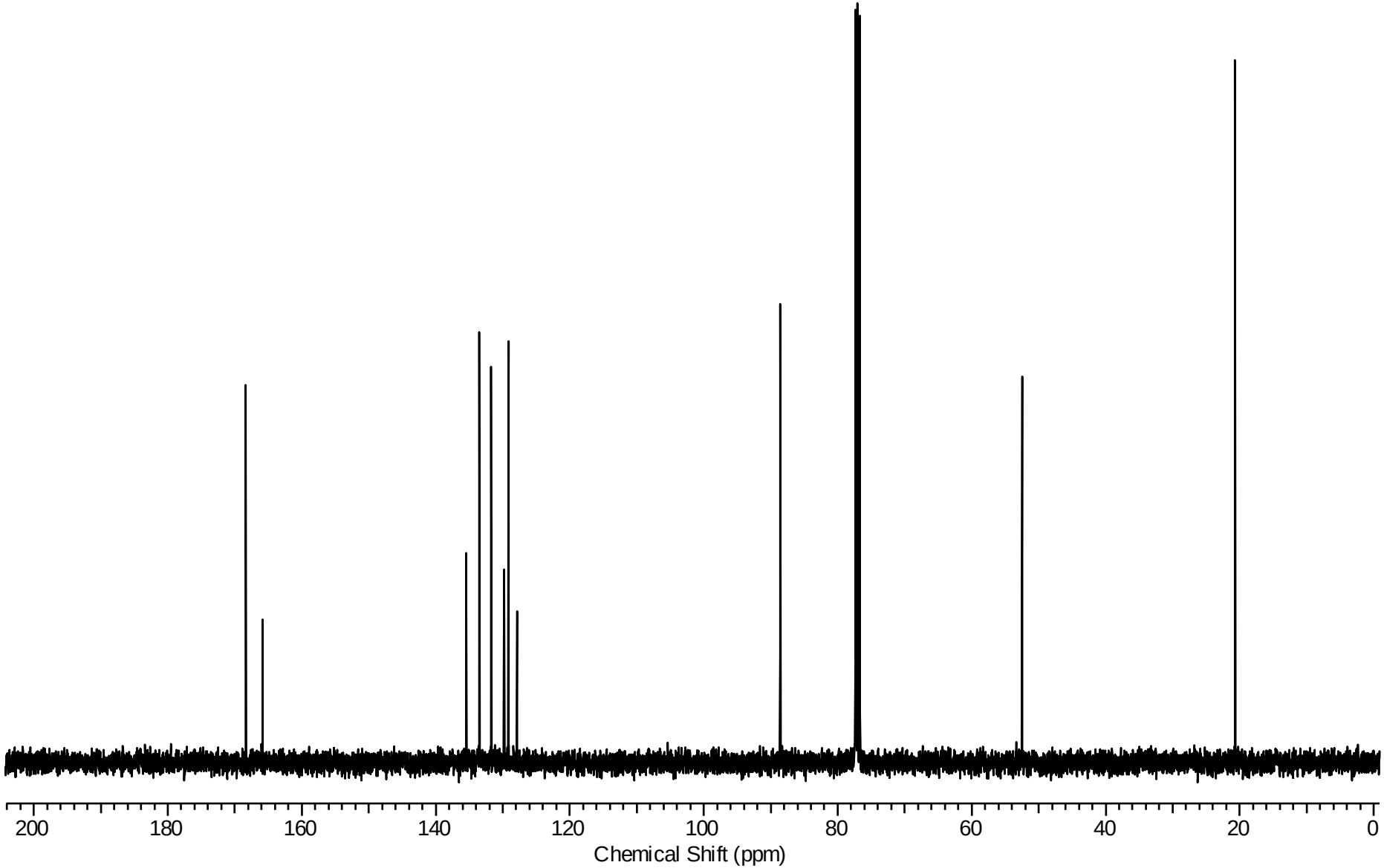
(2-Bromo-5-(methoxycarbonyl)phenyl)methylene diacetate **S2**

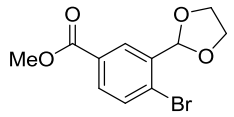




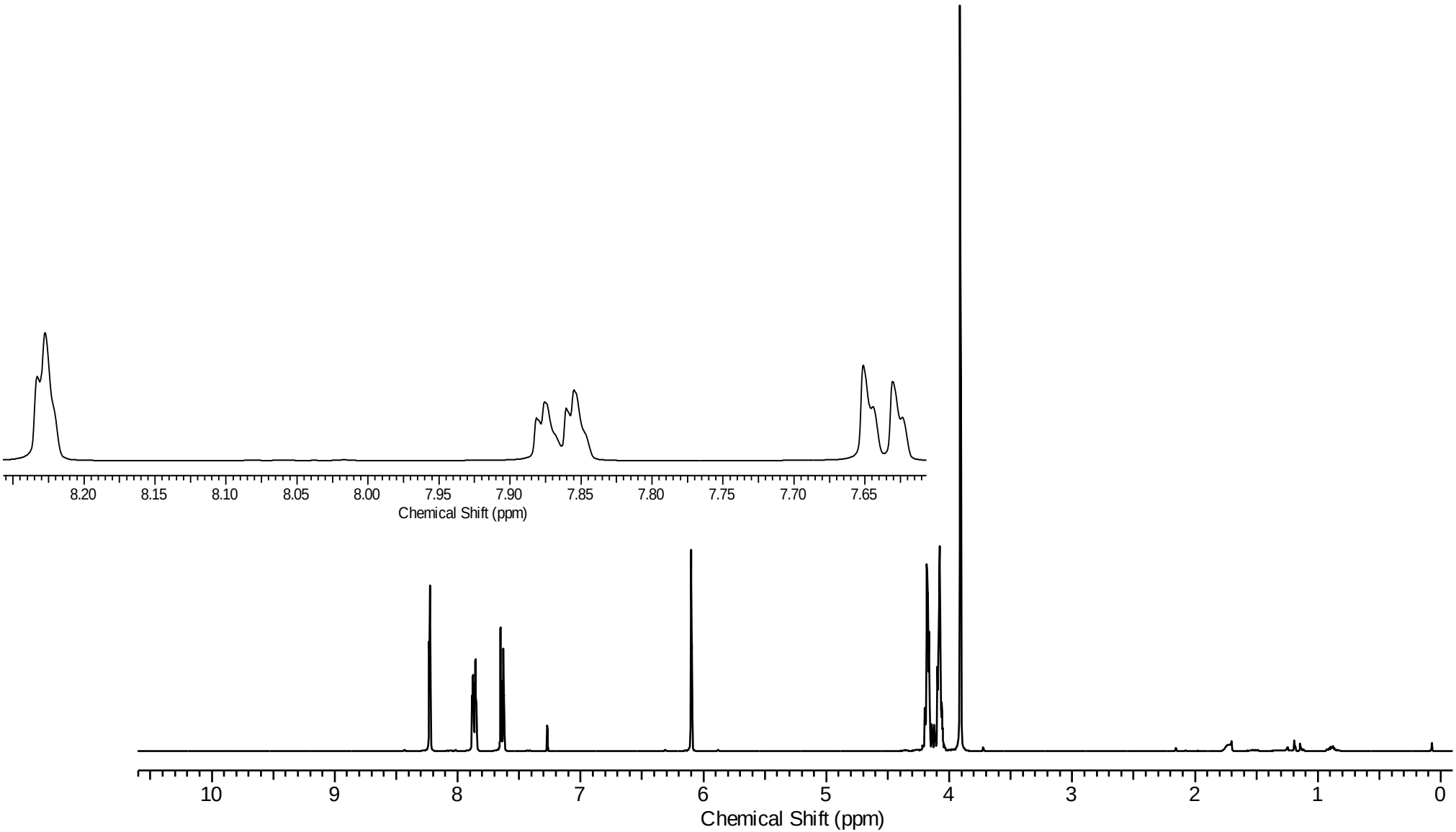
(2-Bromo-5-(methoxycarbonyl)phenyl)methylene diacetate **S2**



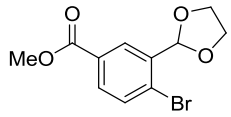


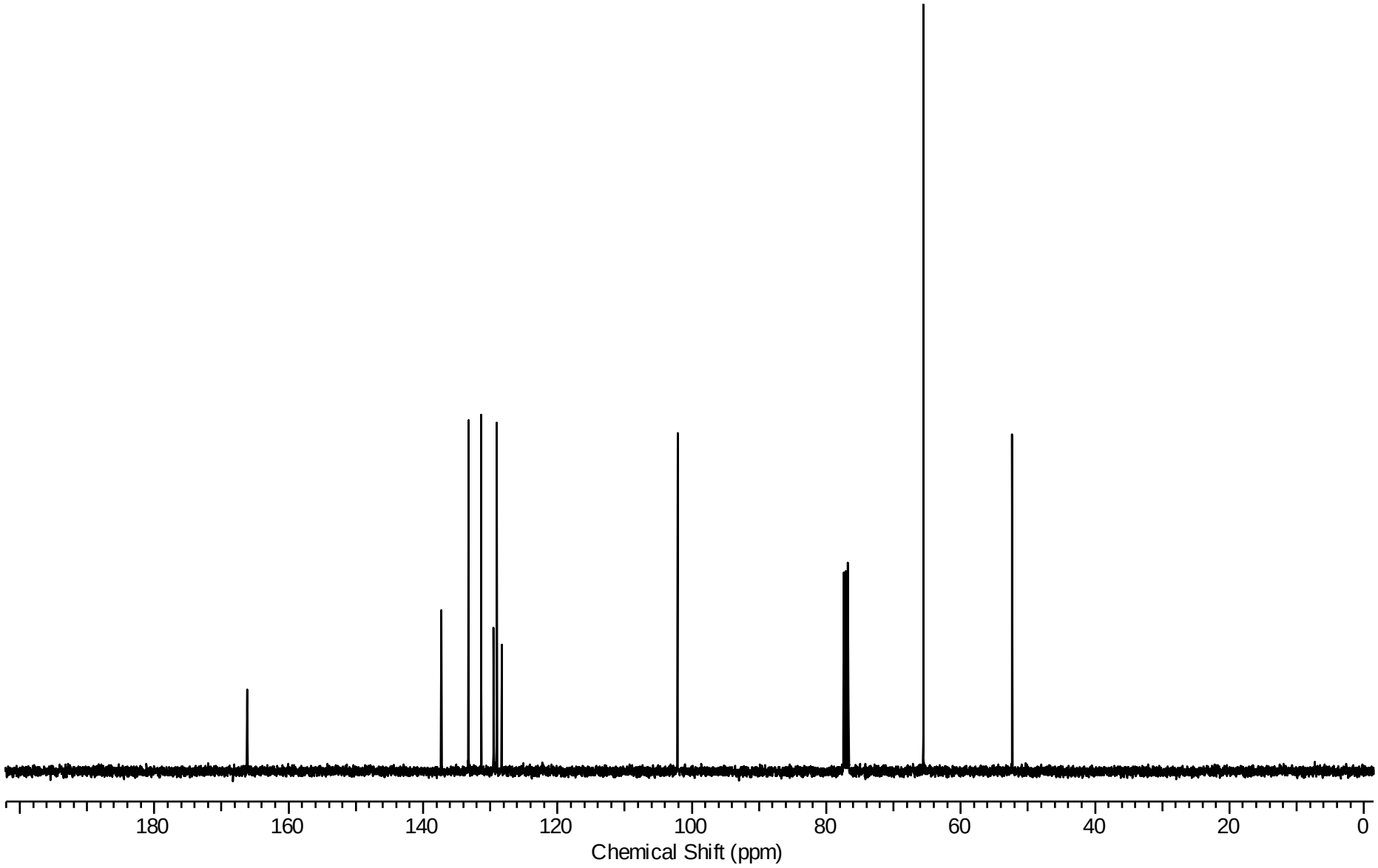


Methyl 4-bromo-3-(1,3-dioxolan-2-yl)benzoate **2q**

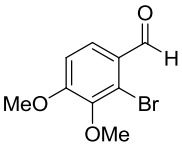


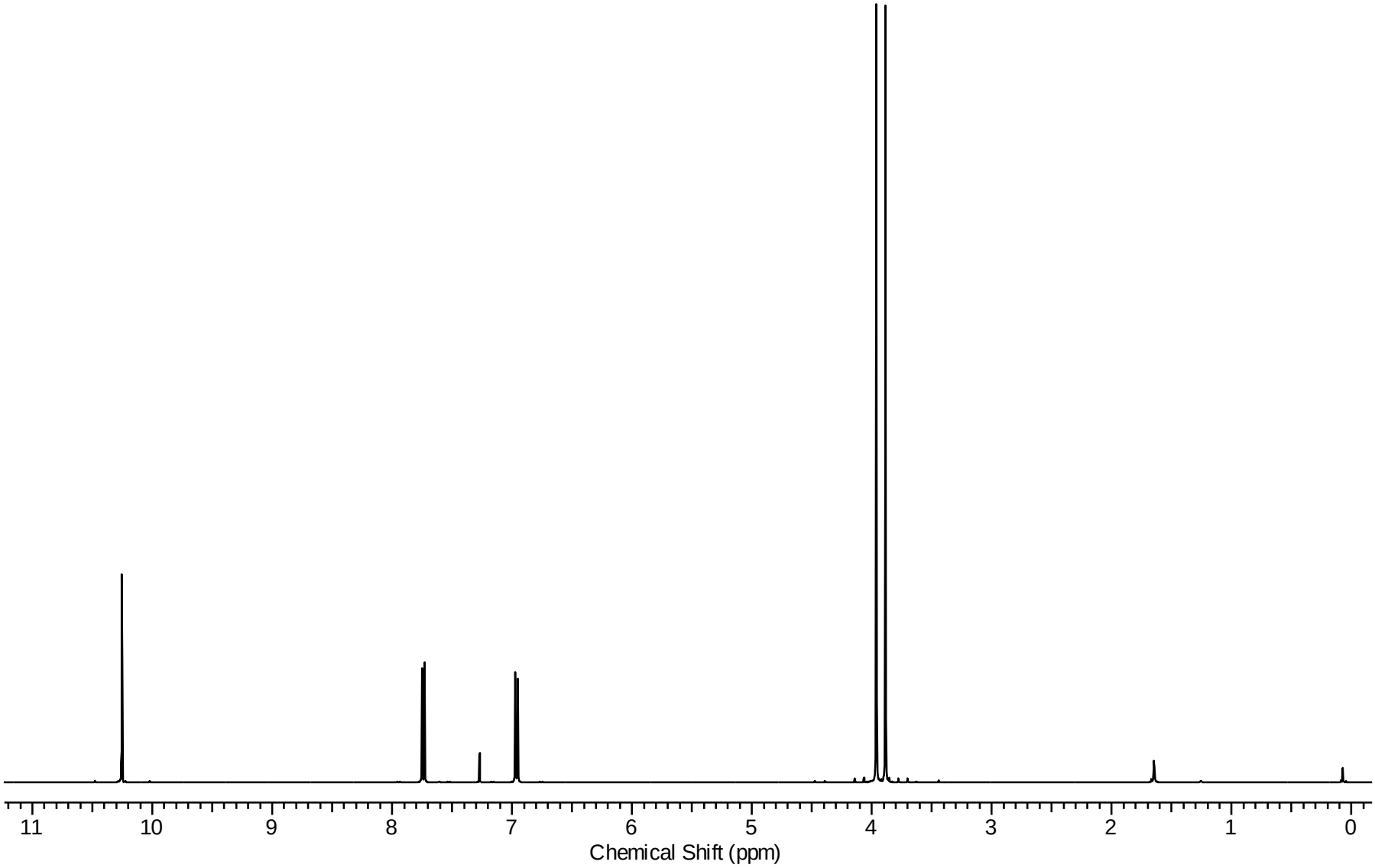
Methyl 4-bromo-3-(1,3-dioxolan-2-yl)benzoate **2q**



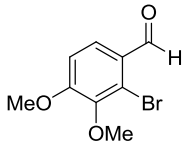


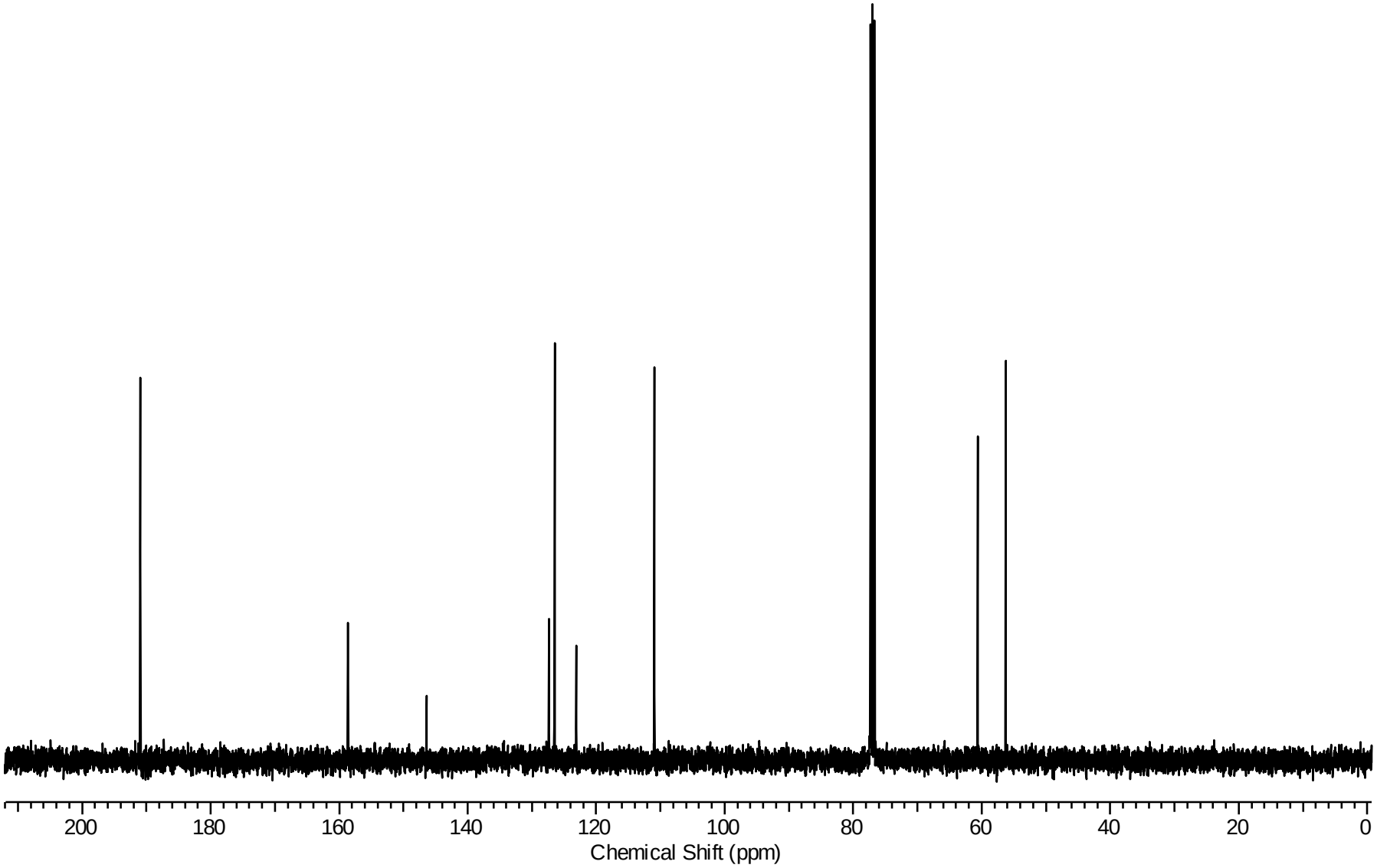
2-Bromo-3,4-dimethoxybenzaldehyde **S3**



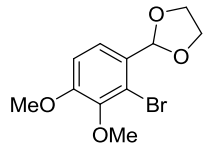


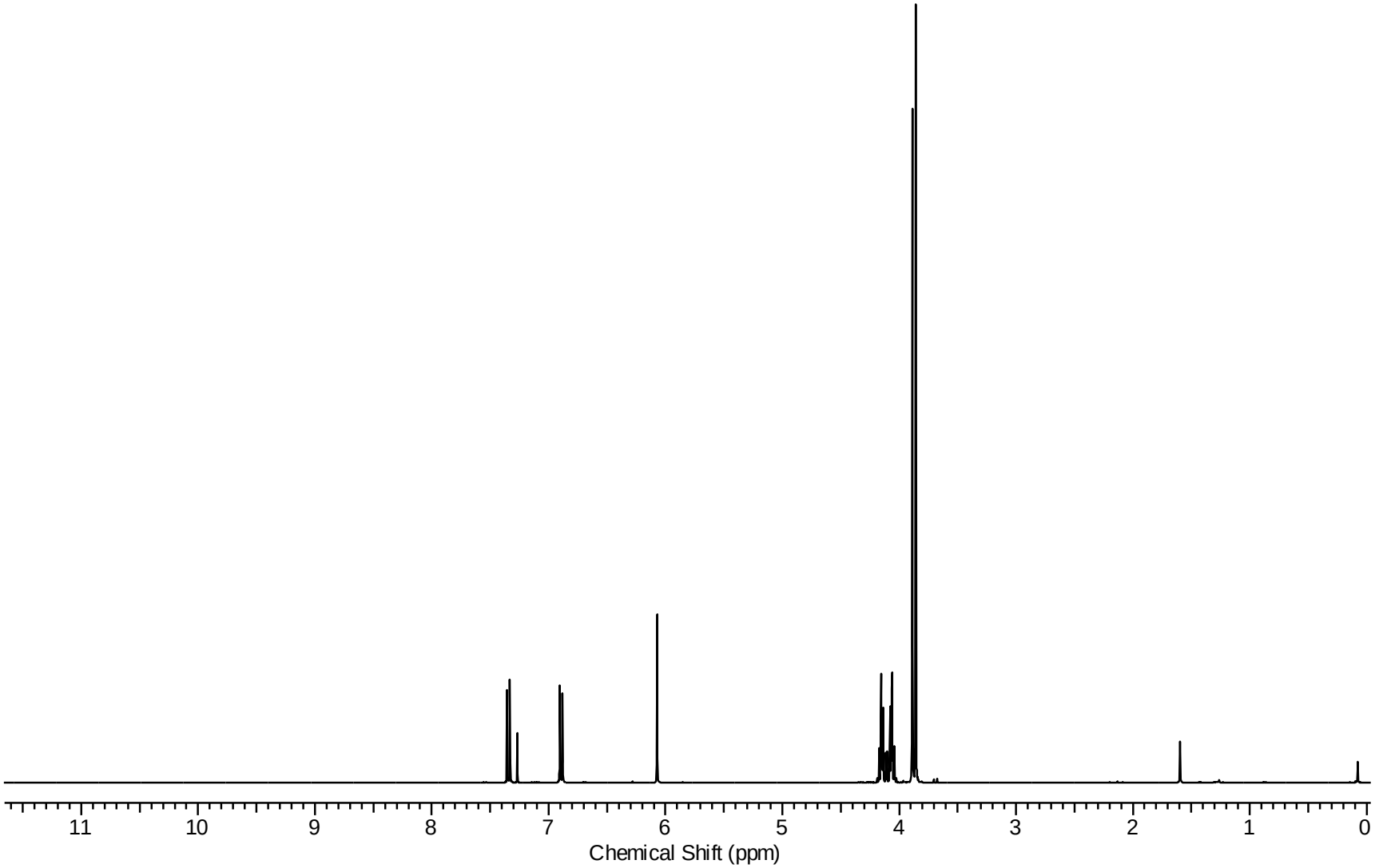
2-Bromo-3,4-dimethoxybenzaldehyde **S3**



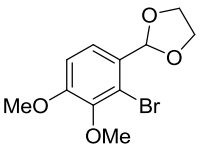


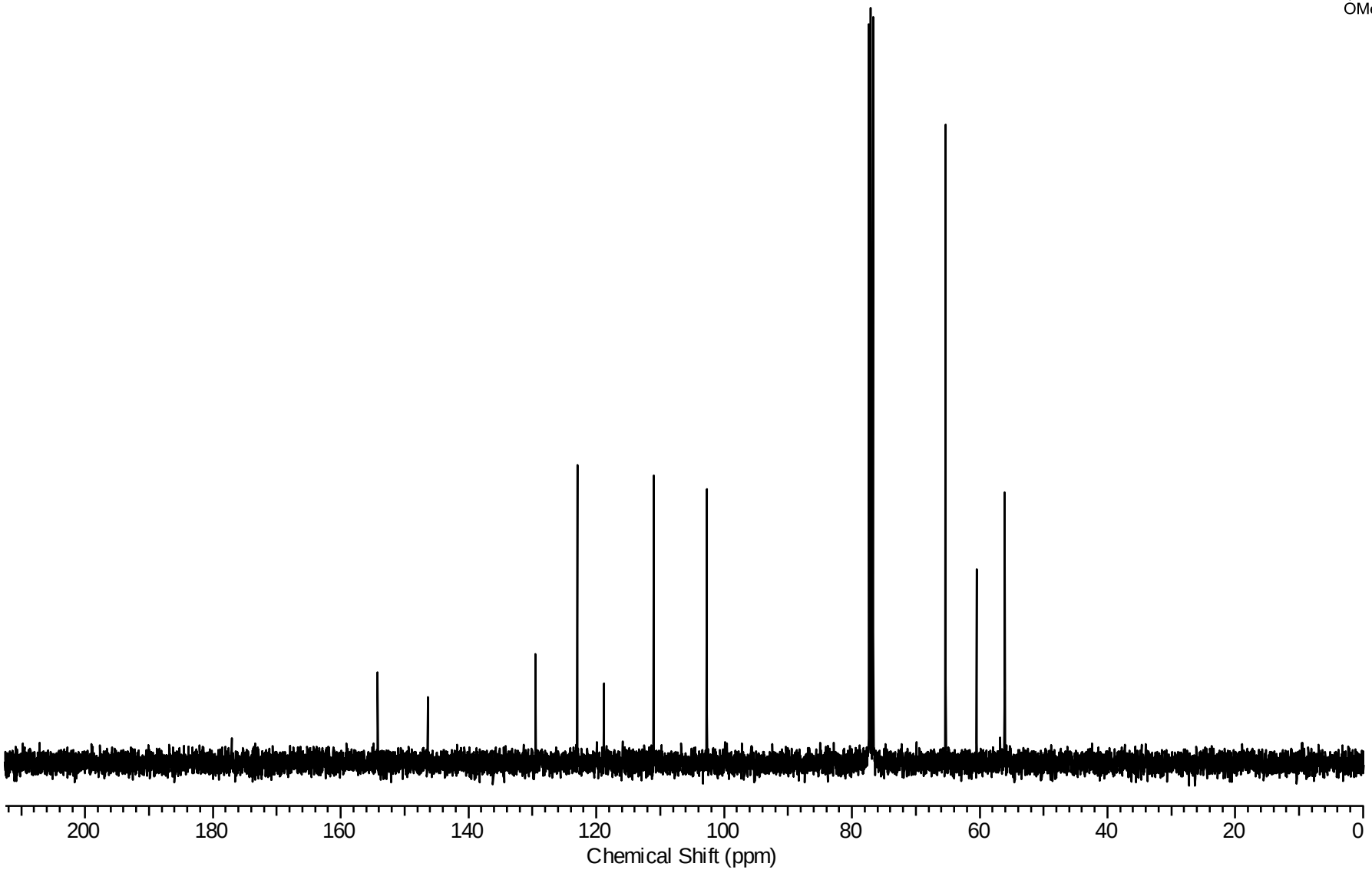
2-(2-Bromo-3,4-dimethoxyphenyl)-1,3-dioxolane **2r**



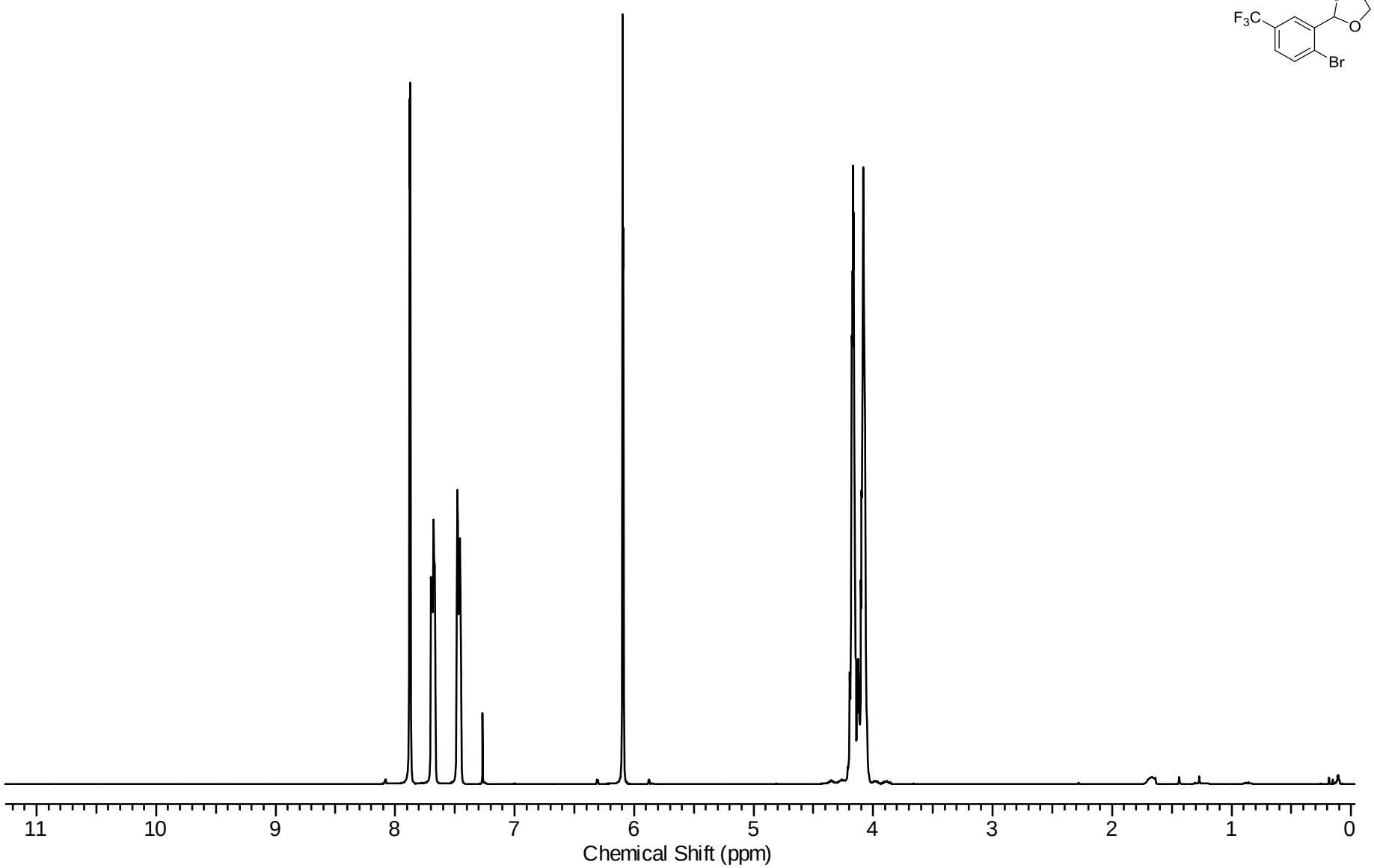


2-(2-Bromo-3,4-dimethoxyphenyl)-1,3-dioxolane **2r**

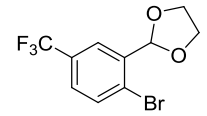


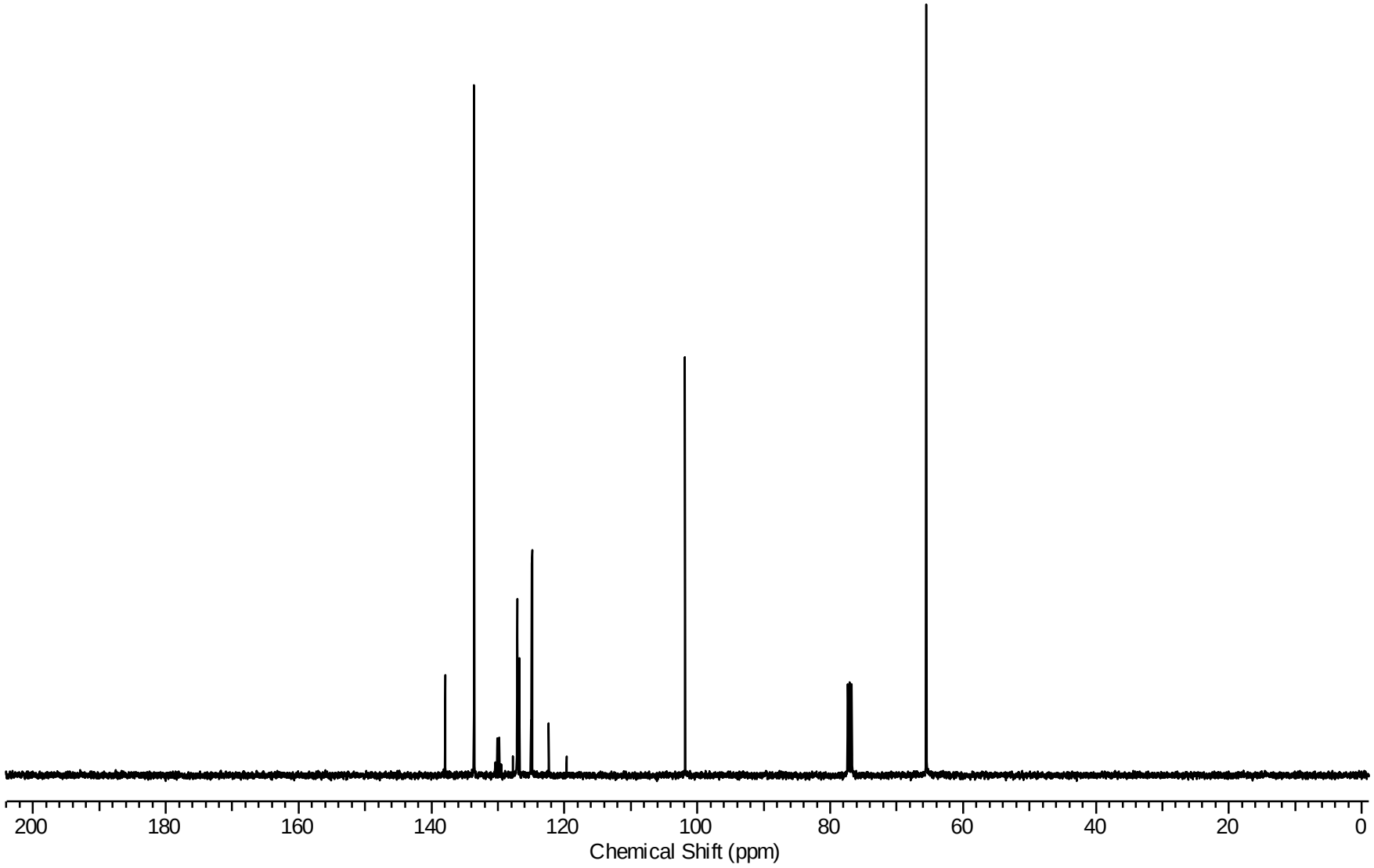


2-(2-Bromo-5-(trifluoromethyl)phenyl)-1,3-dioxolane **2s**

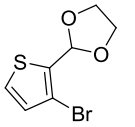


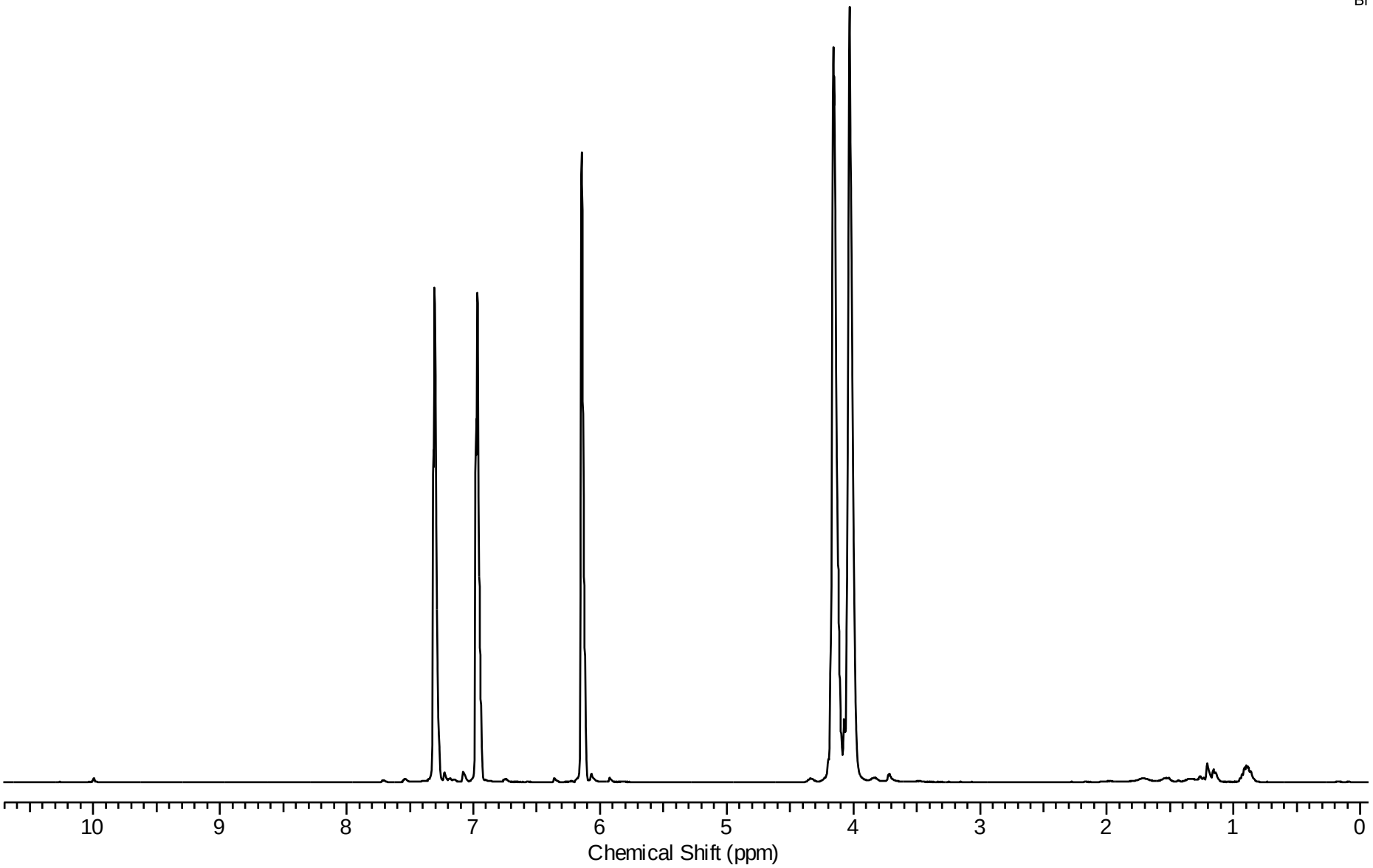
2-(2-Bromo-5-(trifluoromethyl)phenyl)-1,3-dioxolane **2s**



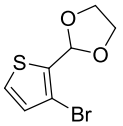


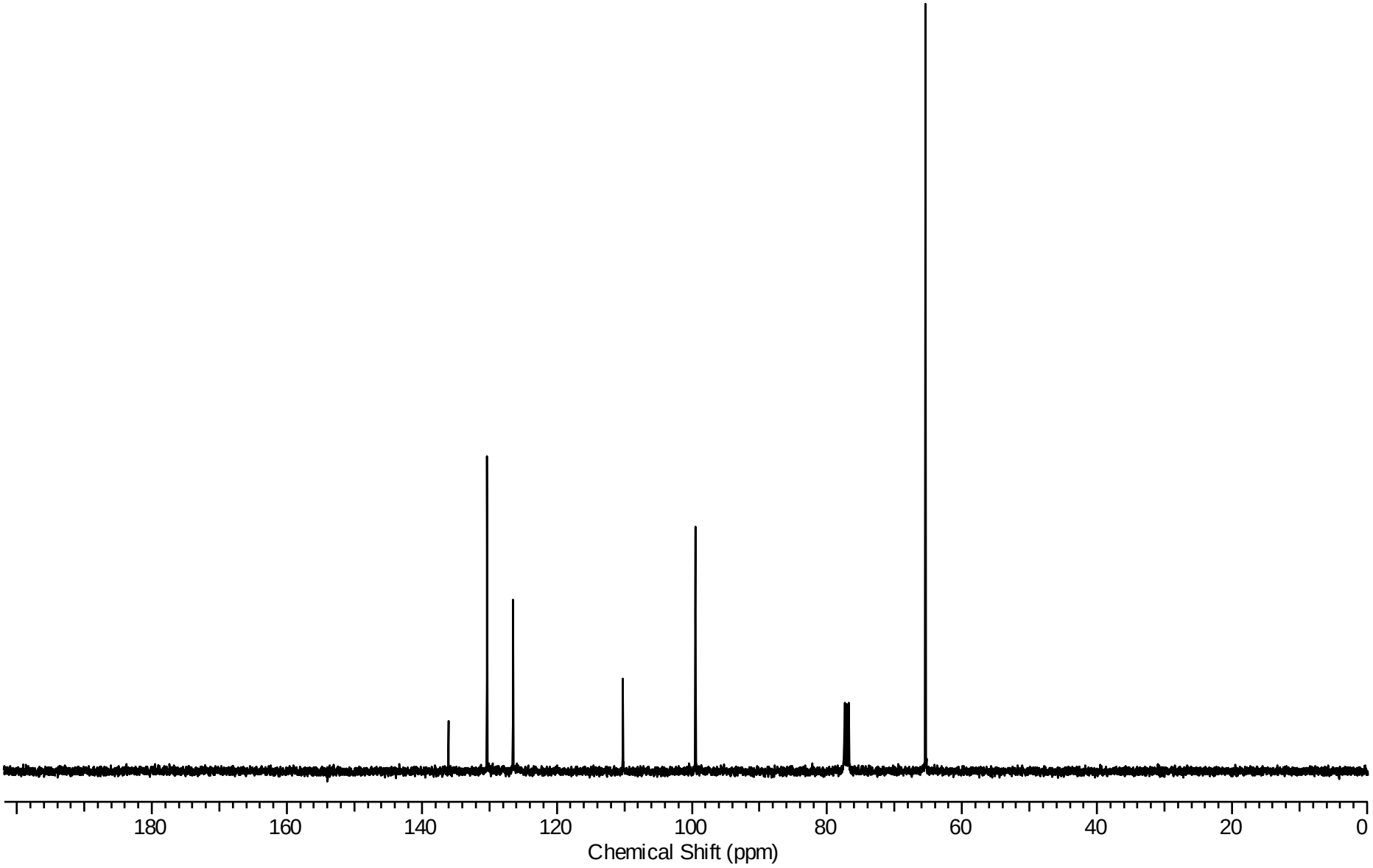
2-(3-Bromothiophen-2-yl)-1,3-dioxolane **2t**



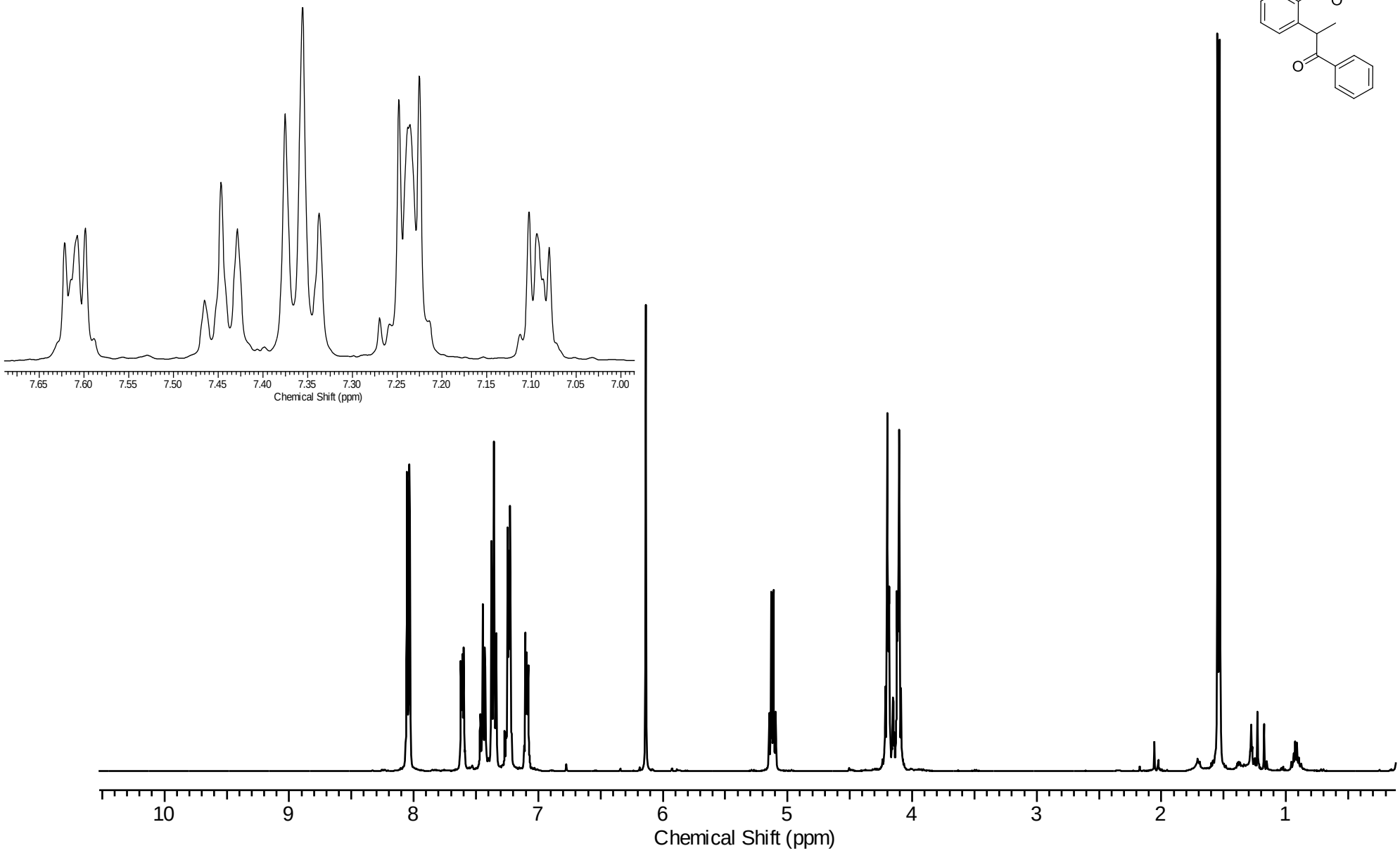


2-(3-Bromothiophen-2-yl)-1,3-dioxolane **2t**

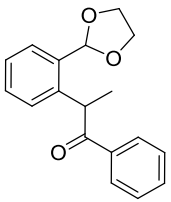


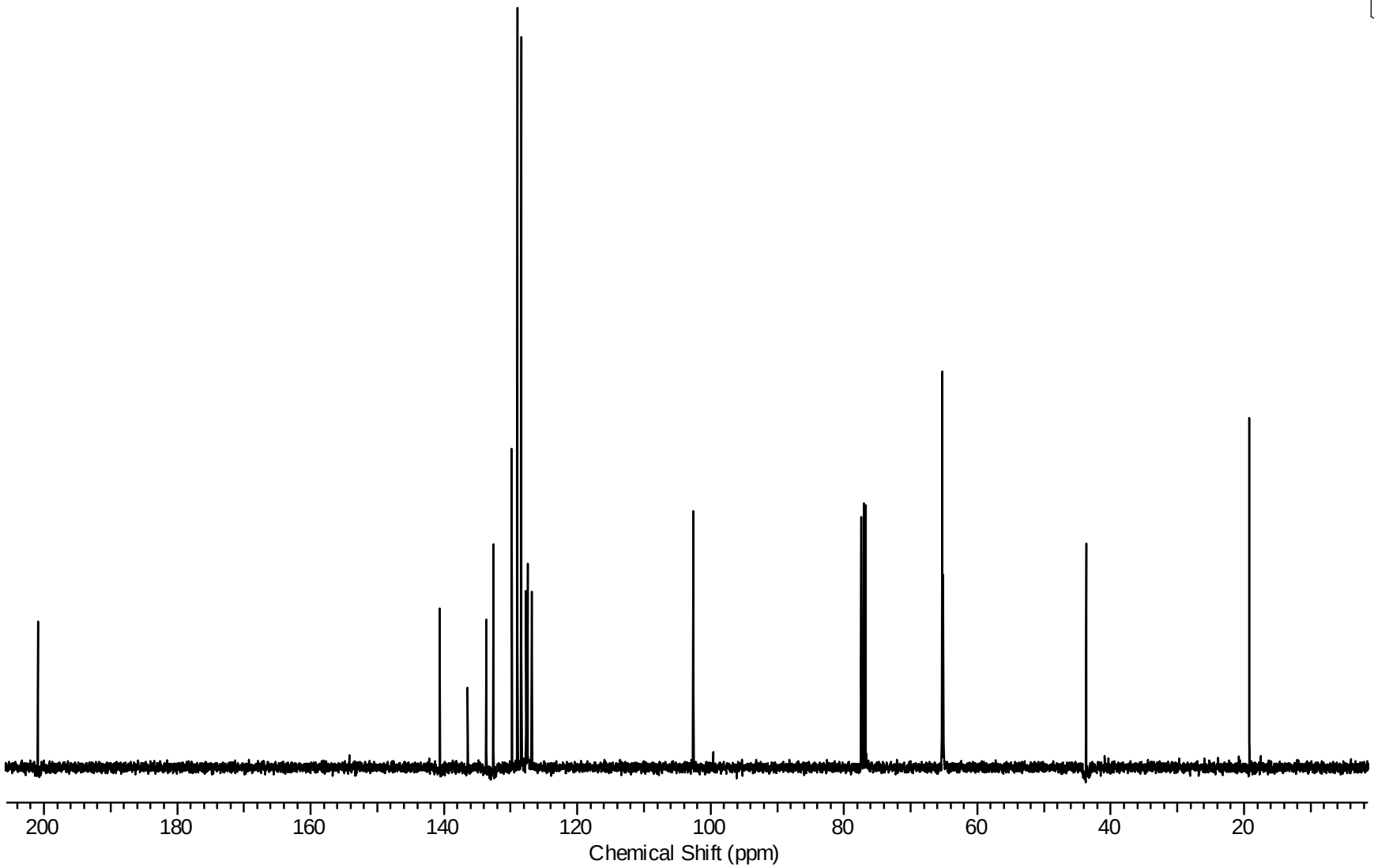


2-(2-(1,3-Dioxolan-2-yl)phenyl)-1-phenylpropan-1-one **3a**

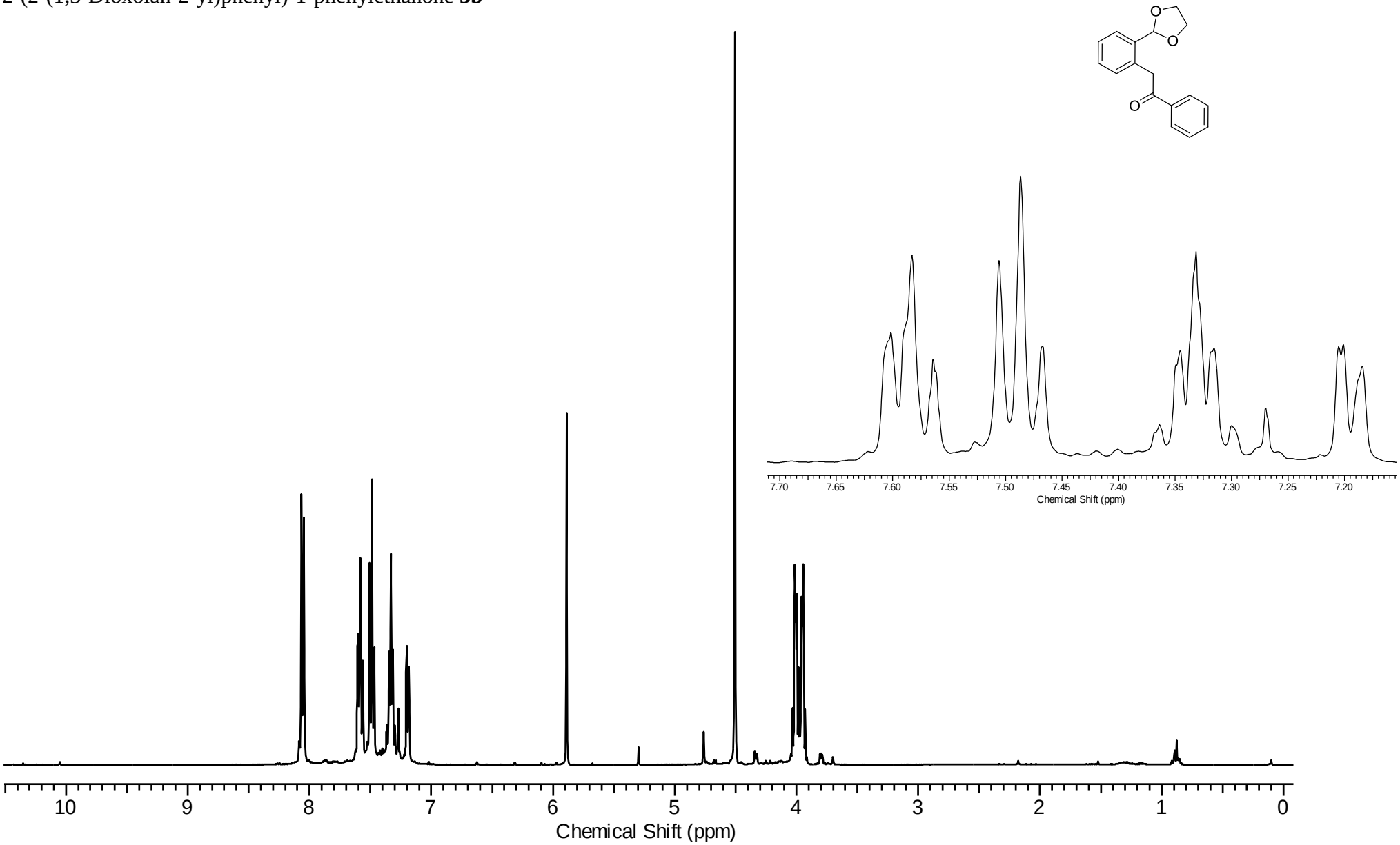


2-(2-(1,3-Dioxolan-2-yl)phenyl)-1-phenylpropan-1-one **3a**

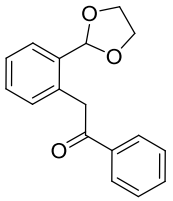


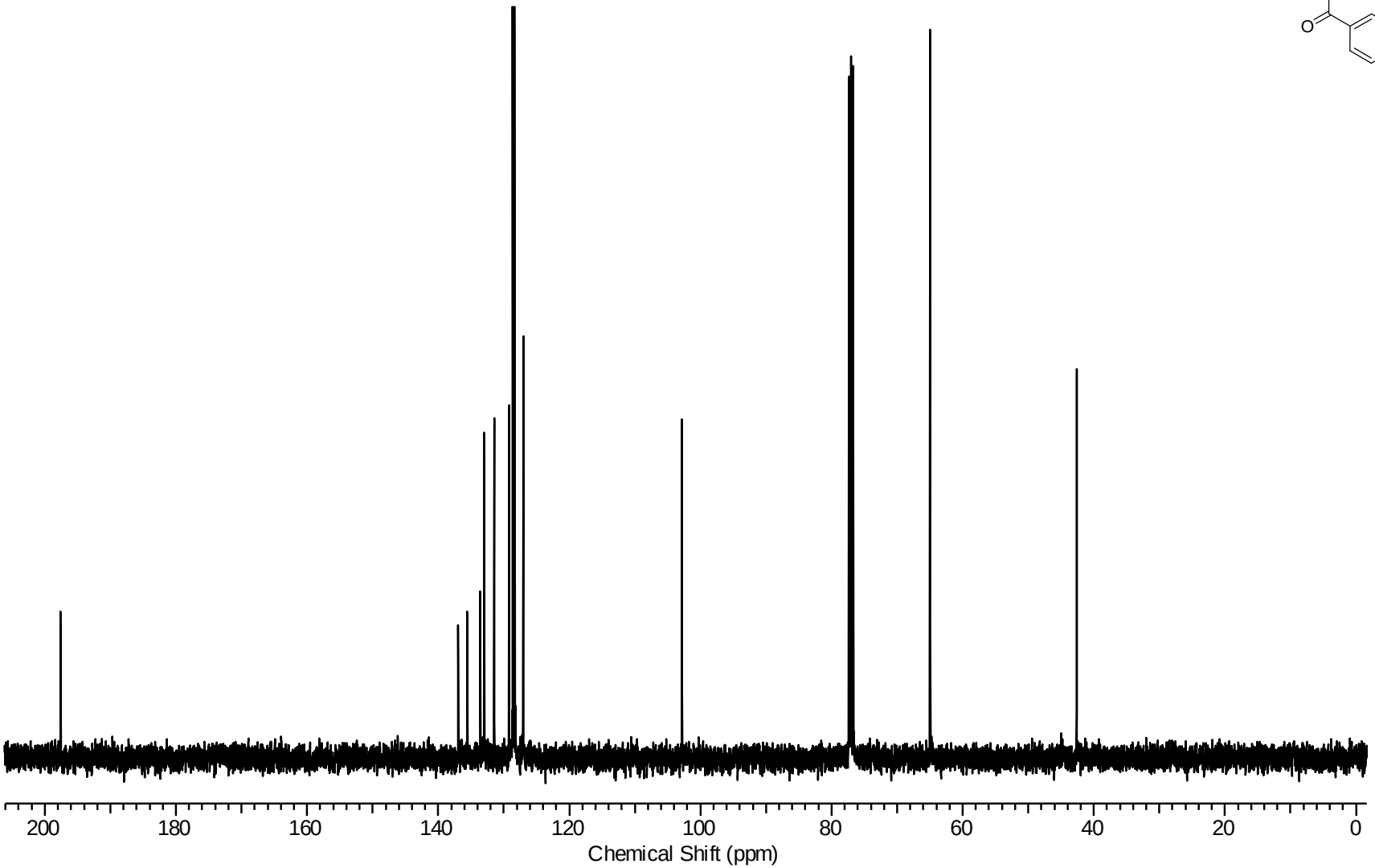


2-(2-(1,3-Dioxolan-2-yl)phenyl)-1-phenylethanone **3b**

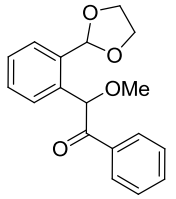


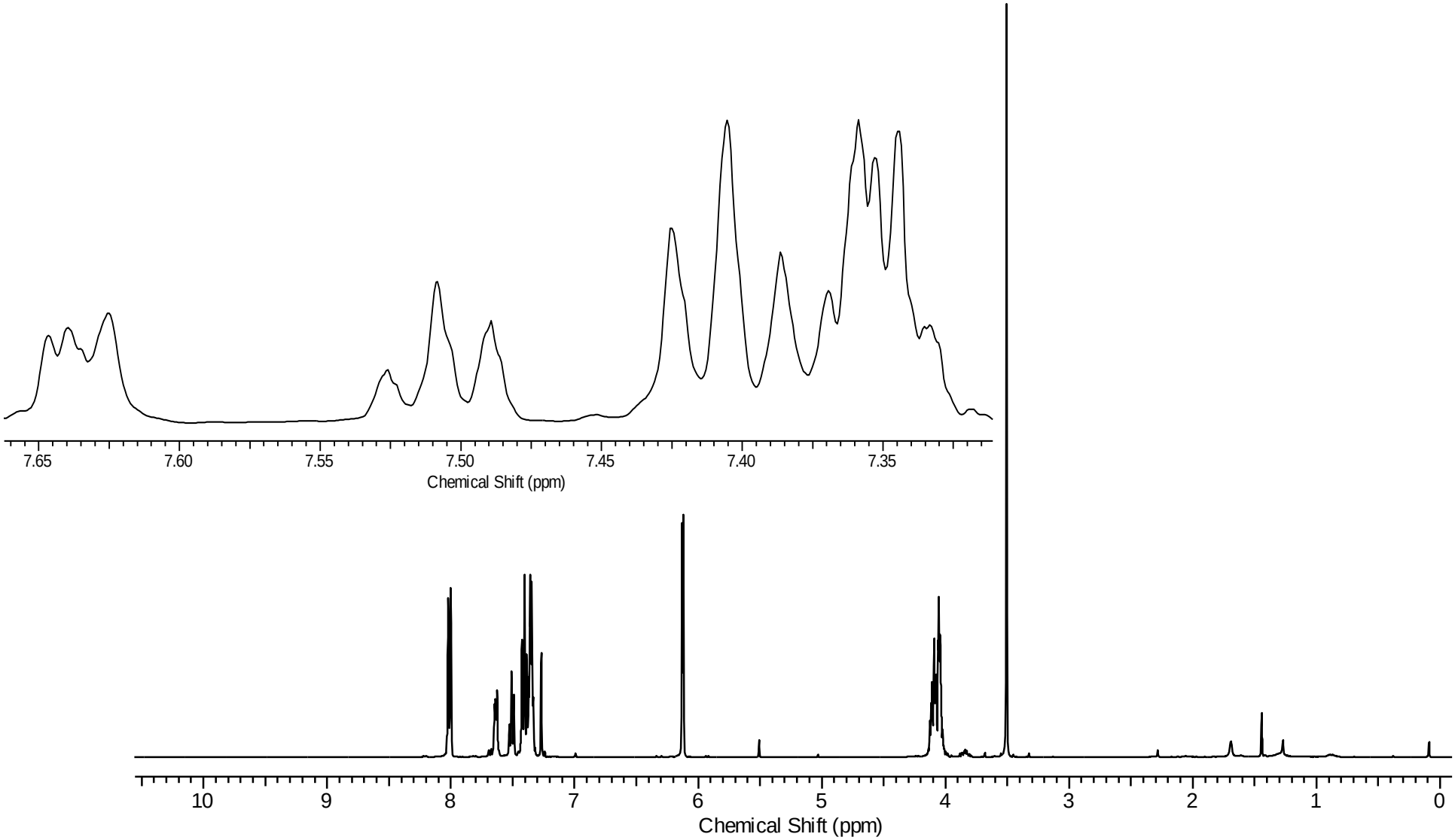
2-(2-(1,3-Dioxolan-2-yl)phenyl)-1-phenylethanone **3b**



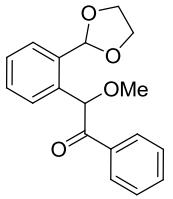


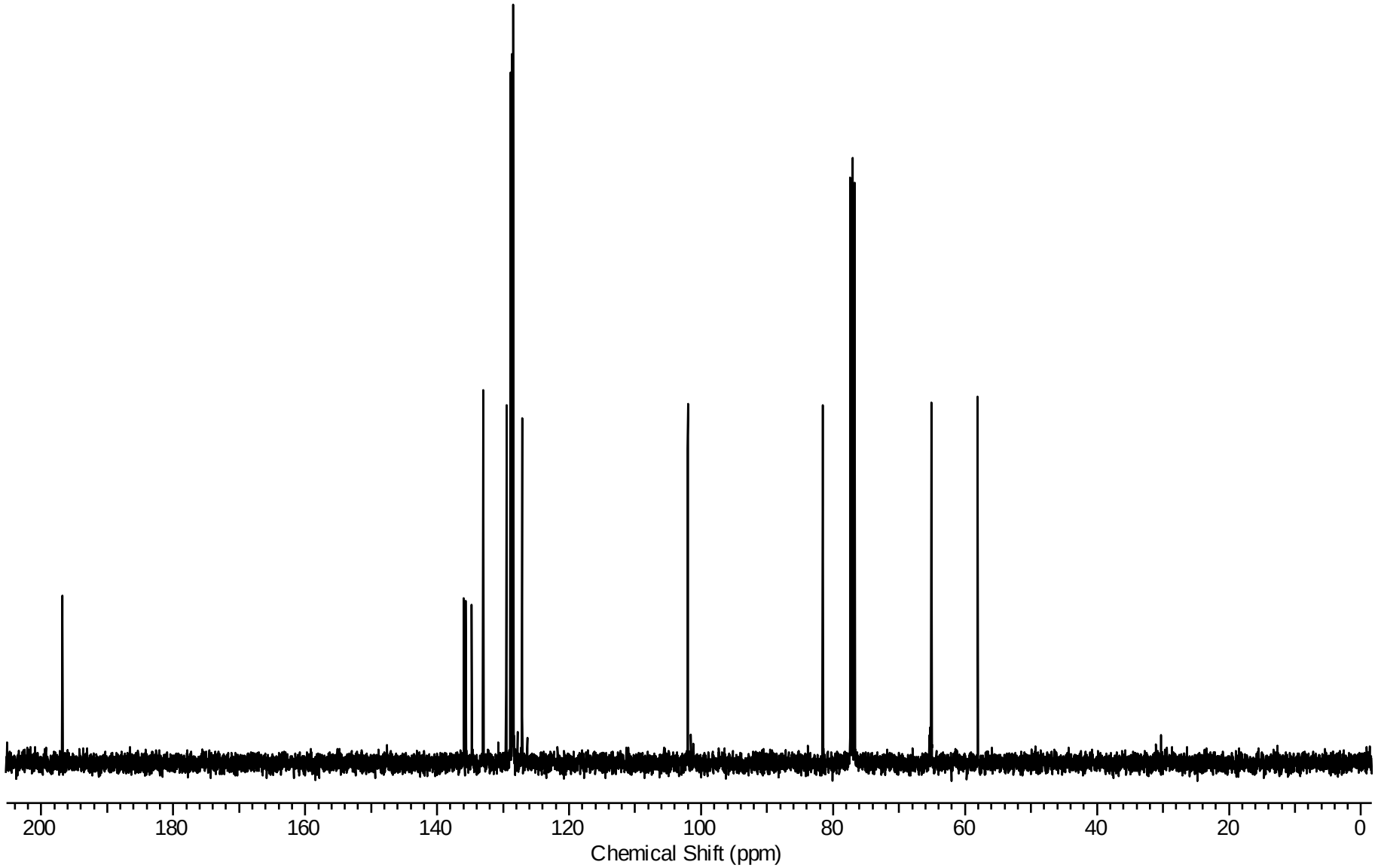
2-(2-(1,3-Dioxolan-2-yl)phenyl)-2-methoxy-1-phenylethanone **3c**



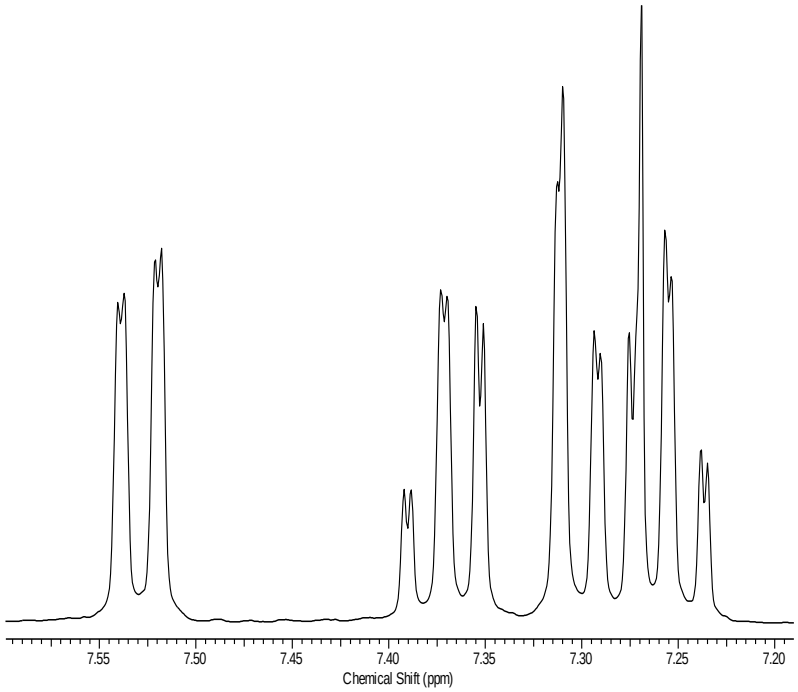


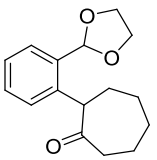
2-(2-(1,3-Dioxolan-2-yl)phenyl)-2-methoxy-1-phenylethanone **3c**



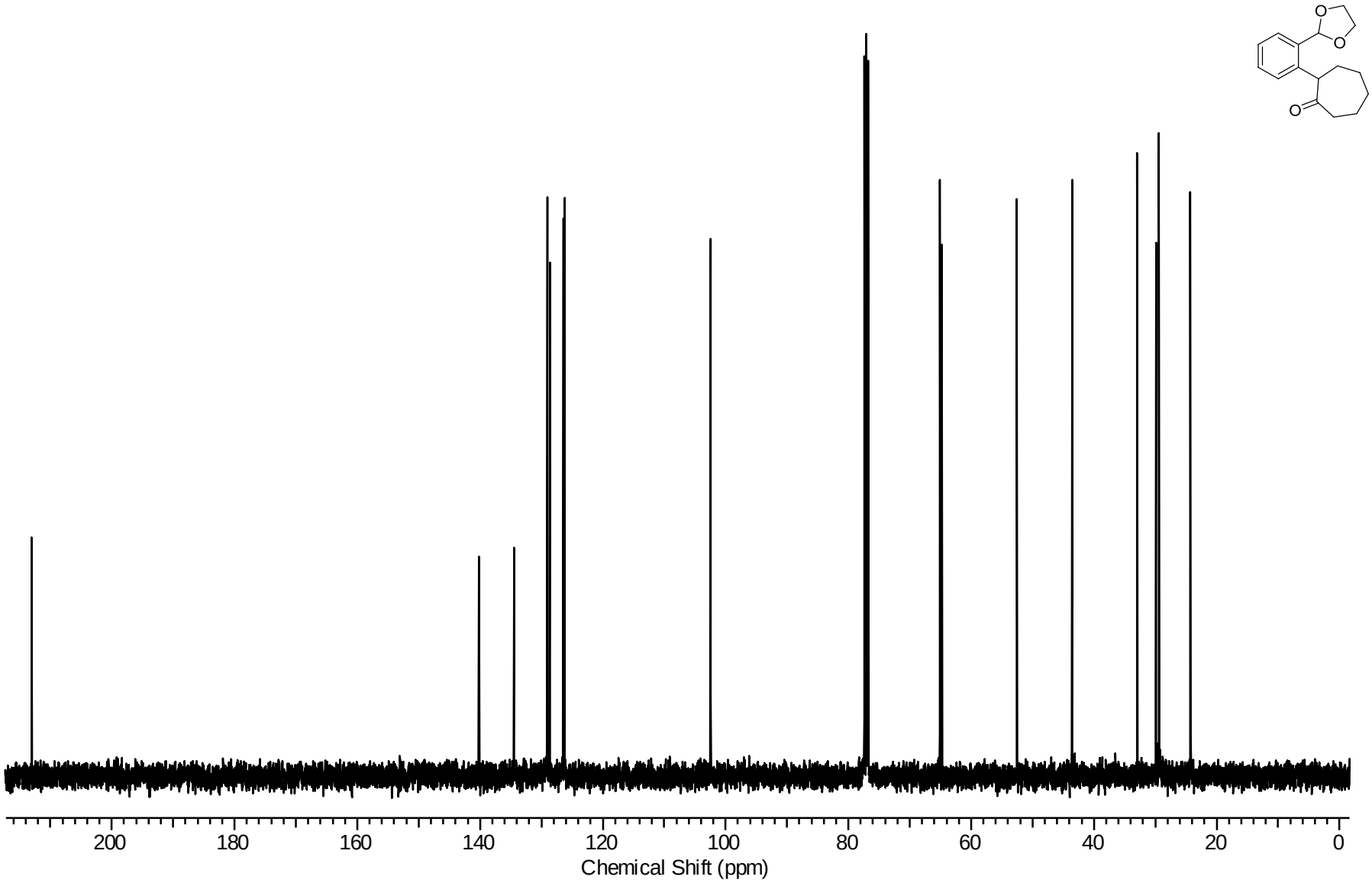


2-(2-(1,3-Dioxolan-2-yl)phenyl)cycloheptanone **3d**

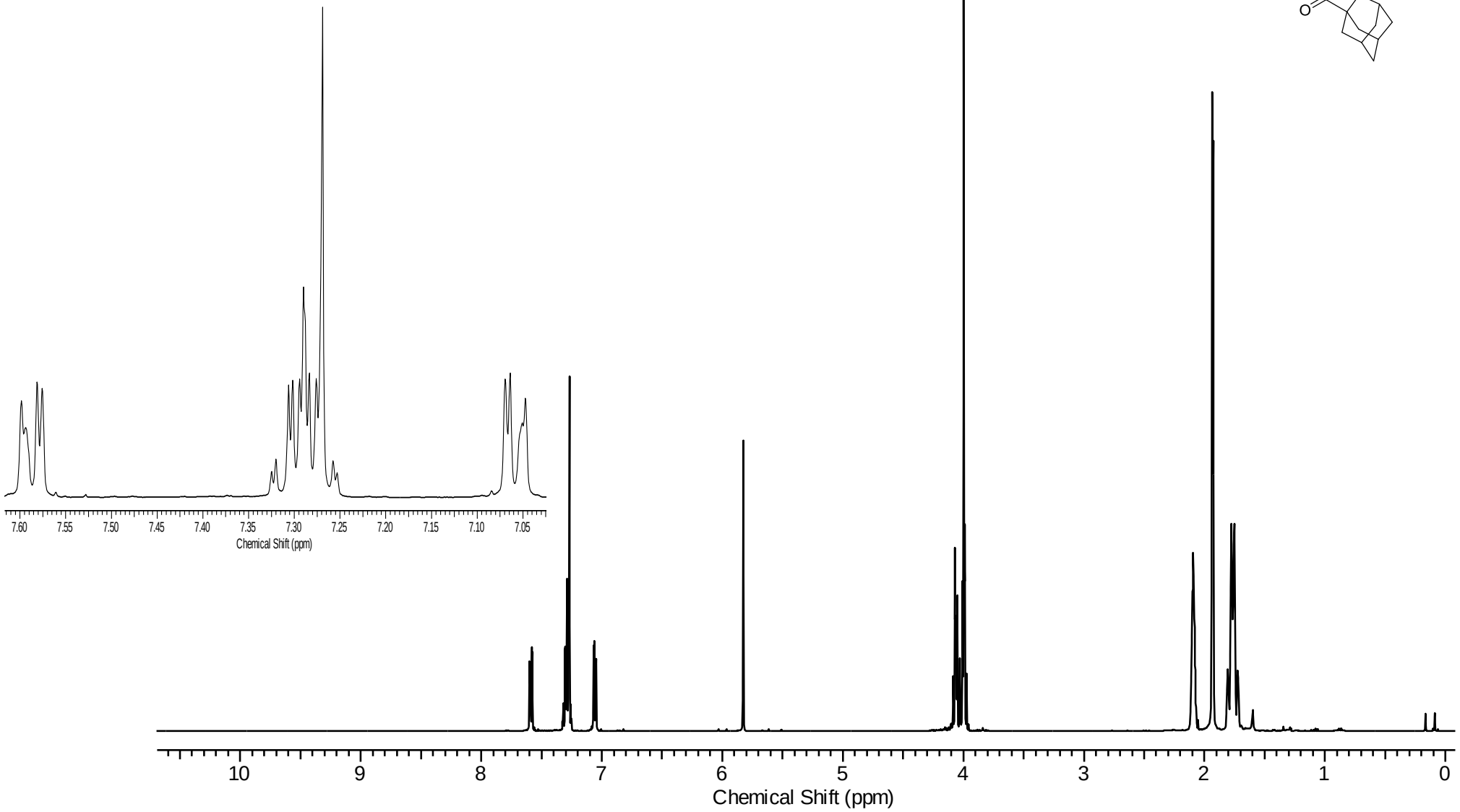




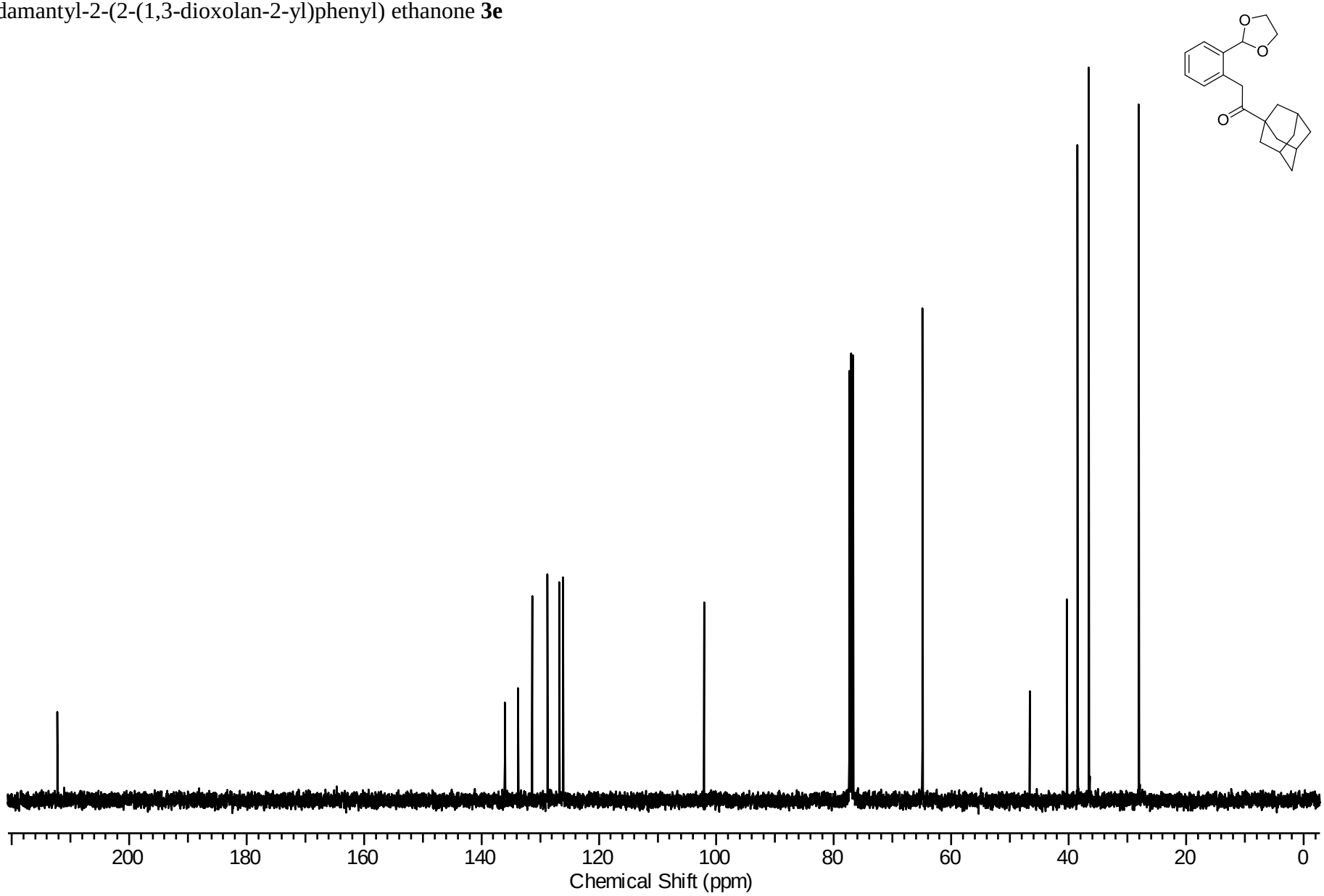
2-(2-(1,3-Dioxolan-2-yl)phenyl)cycloheptanone **3d**



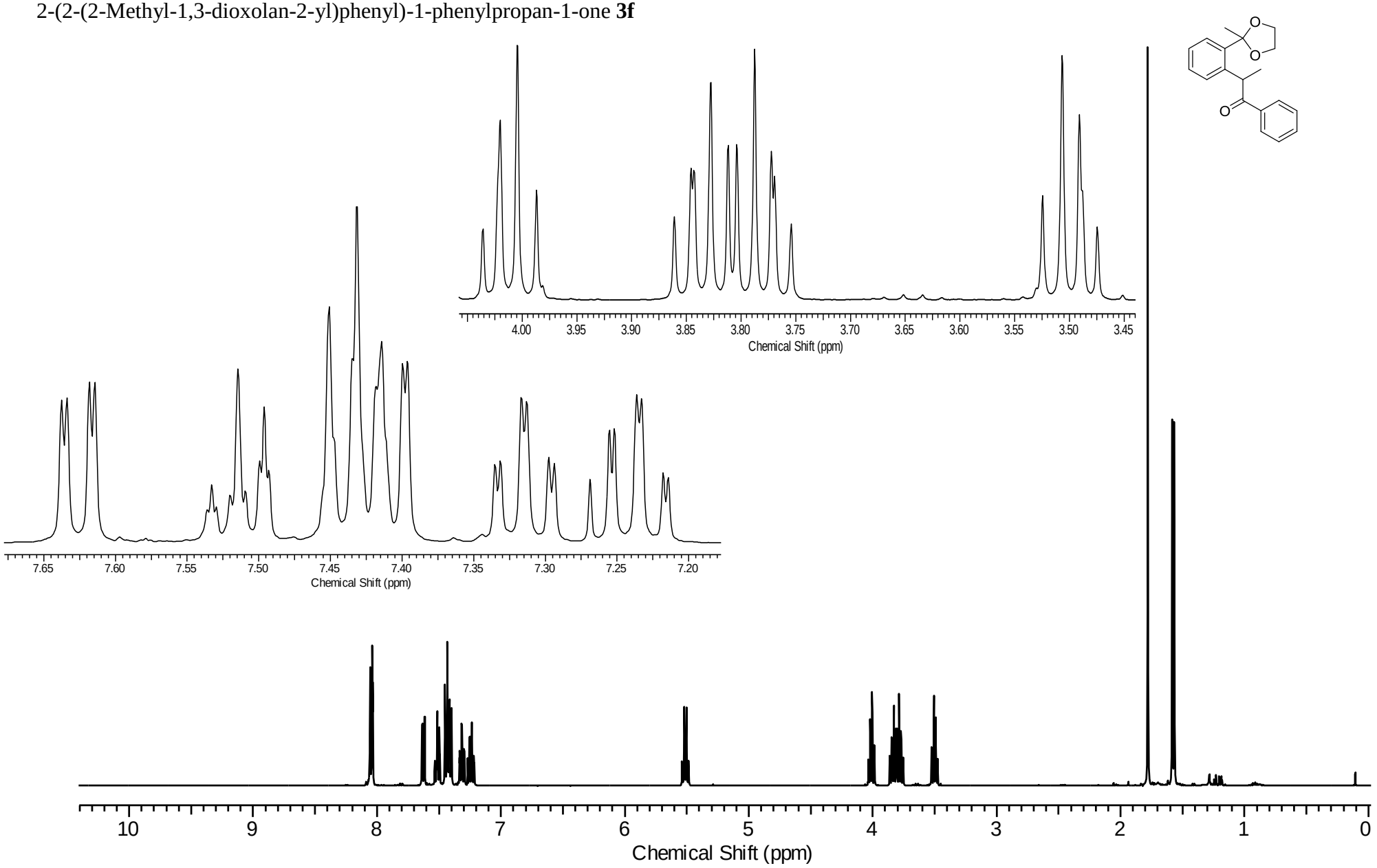
1-Adamantyl-2-(2-(1,3-dioxolan-2-yl)phenyl) ethanone **3e**



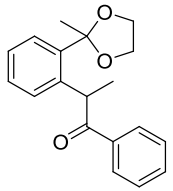
1-Adamantyl-2-(2-(1,3-dioxolan-2-yl)phenyl) ethanone **3e**

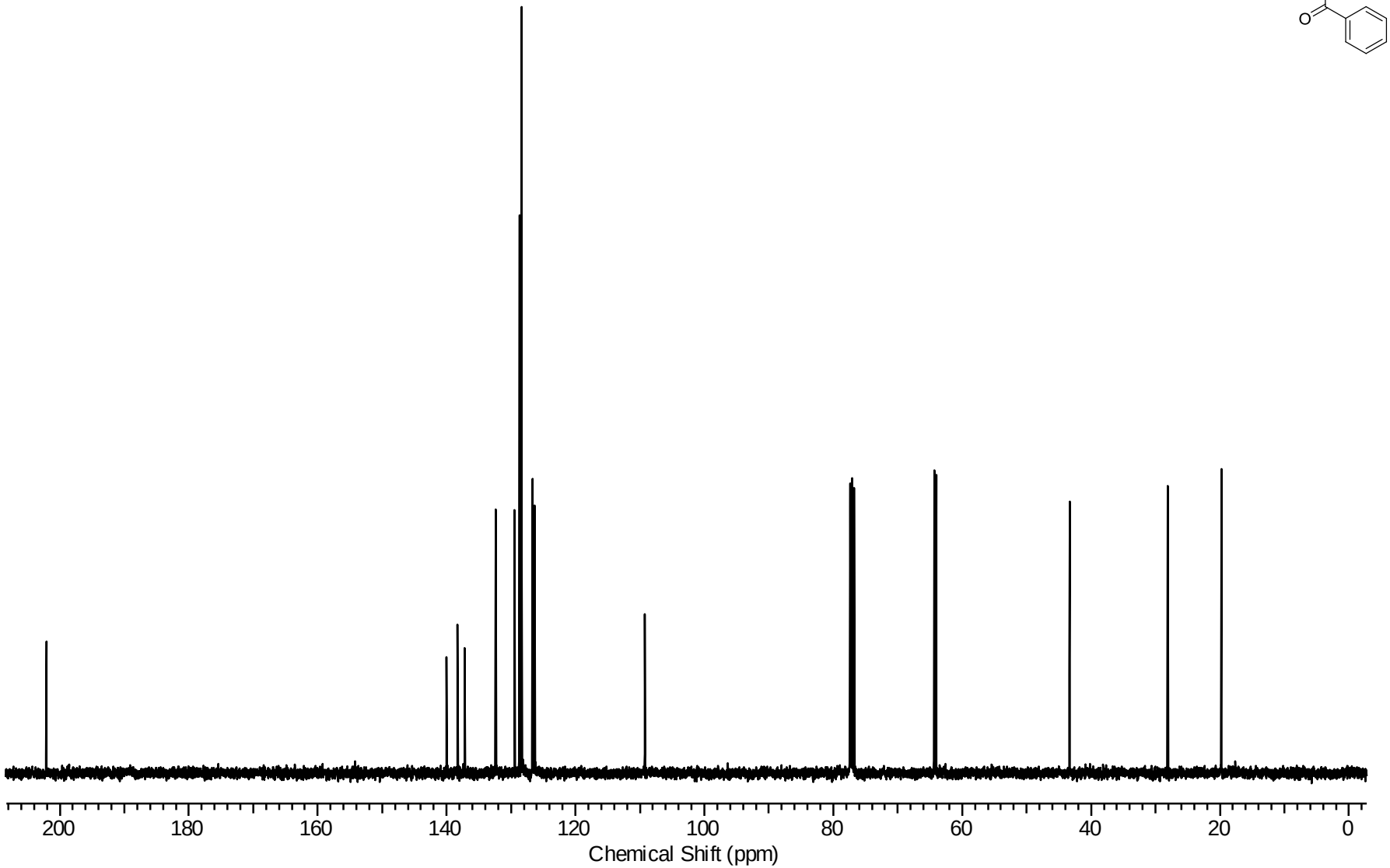


2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-1-phenylpropan-1-one **3f**

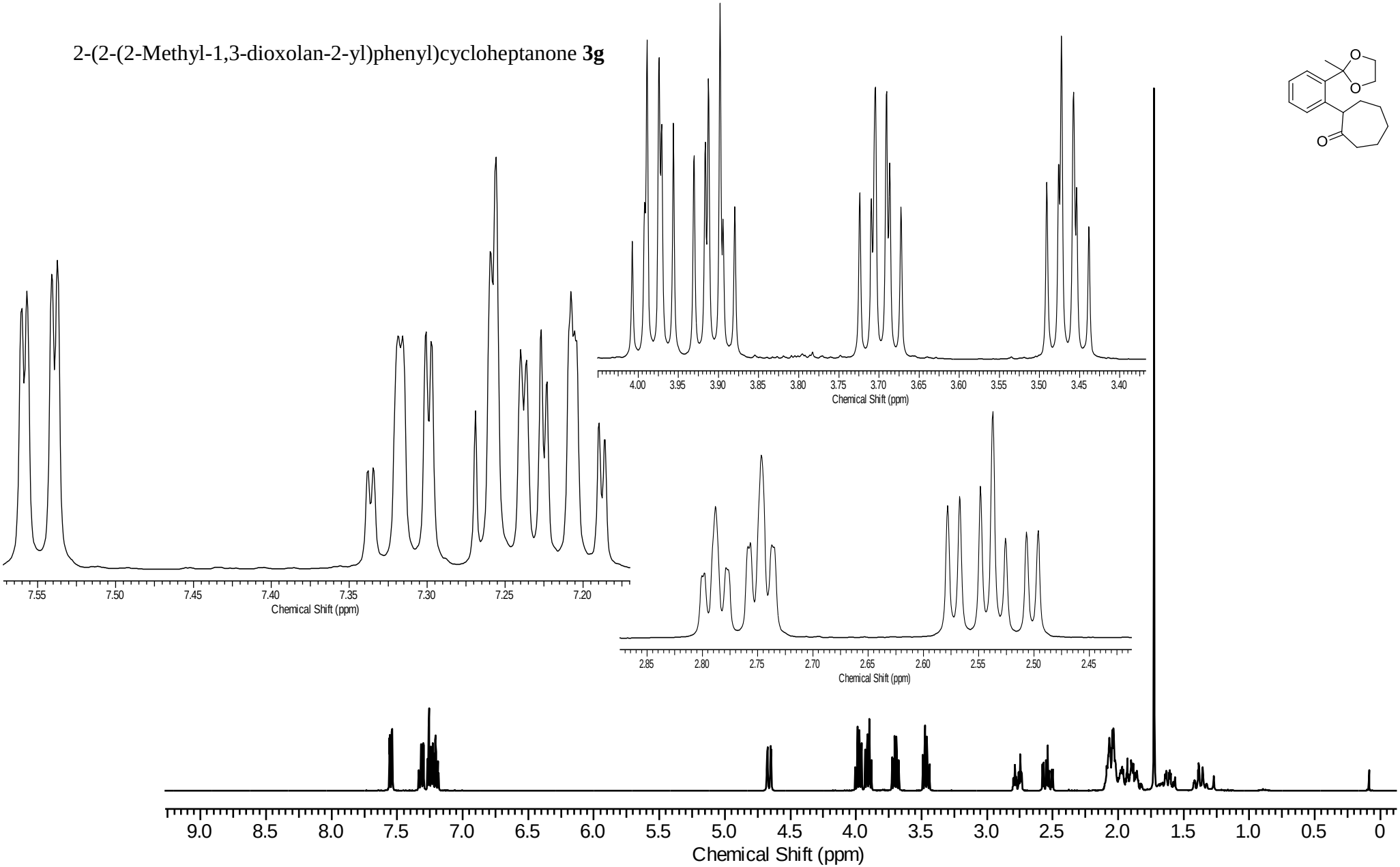


2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-1-phenylpropan-1-one **3f**

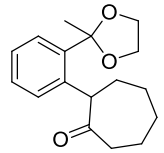


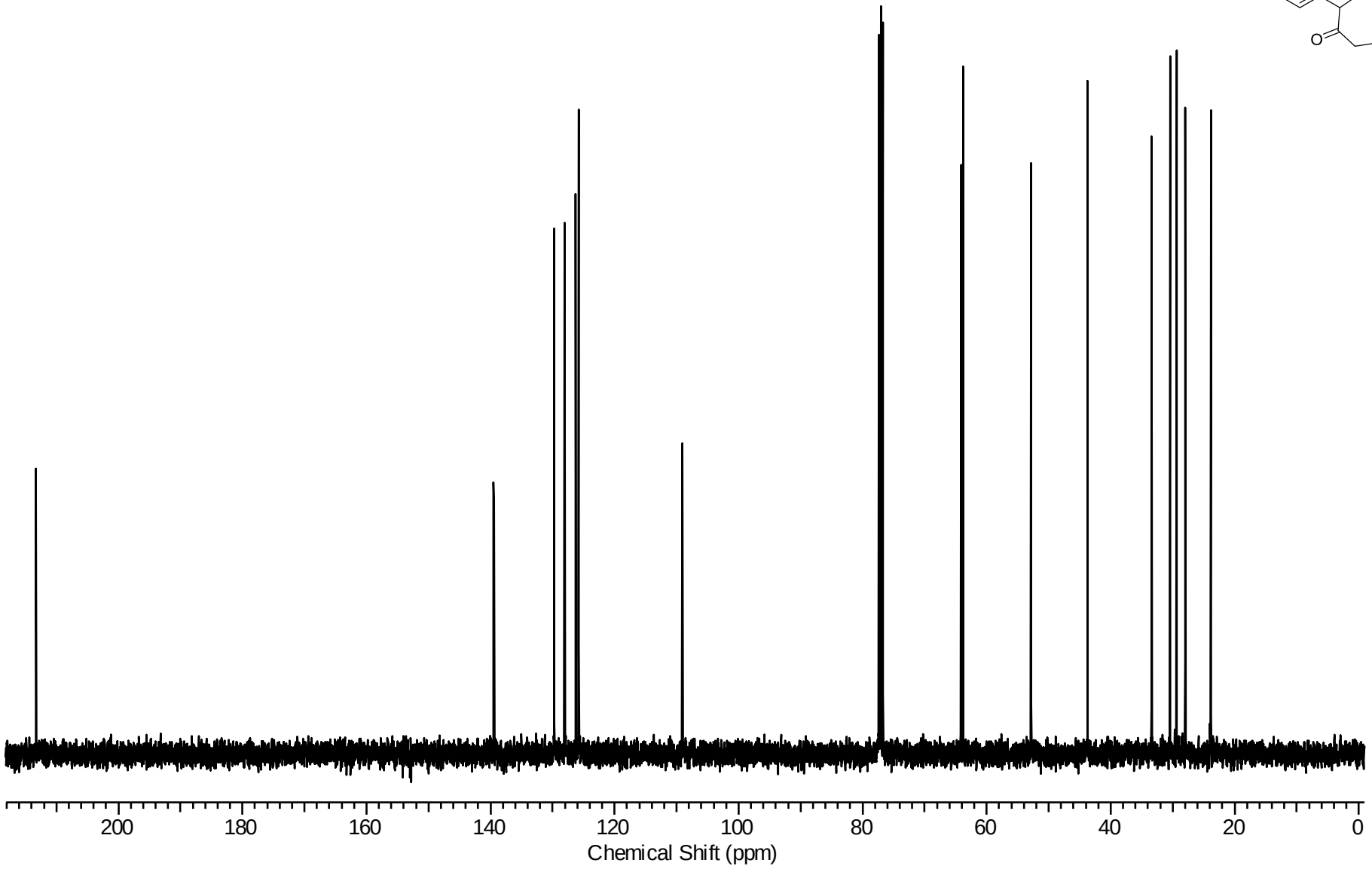


2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)cycloheptanone **3g**

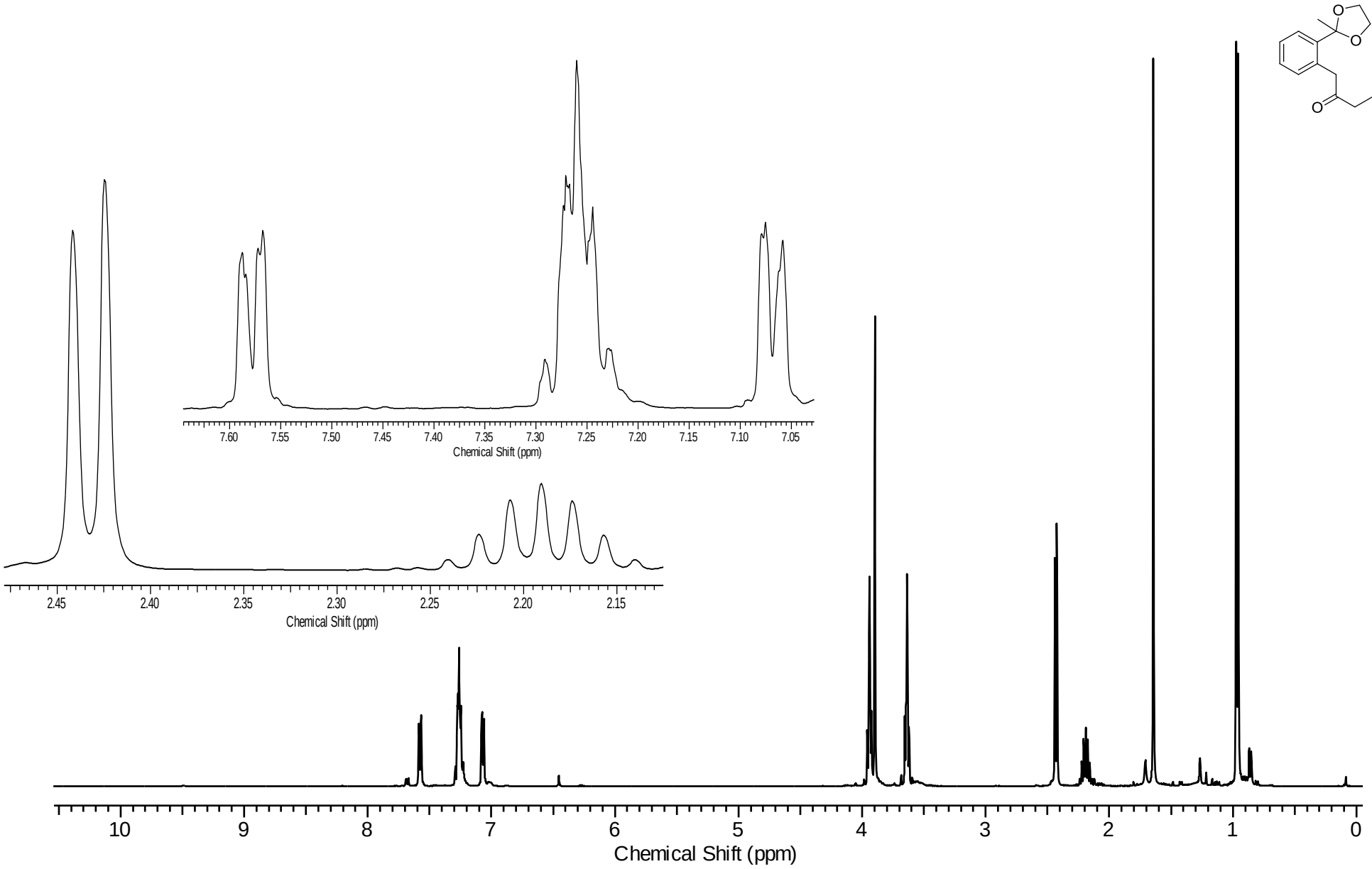


2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)cycloheptanone **3g**

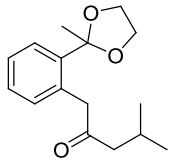




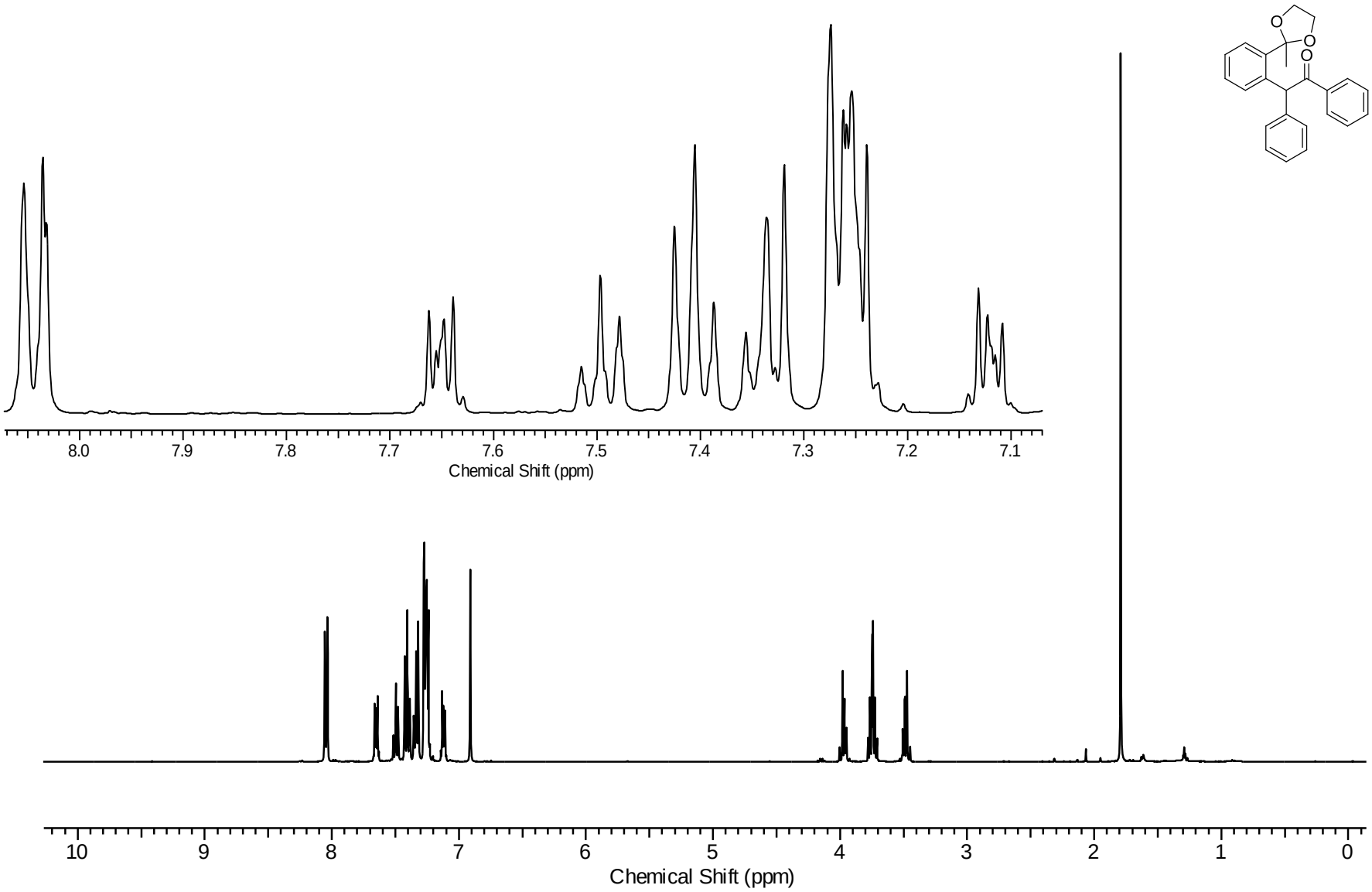
4-Methyl-1-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)pentan-2-one **3h**



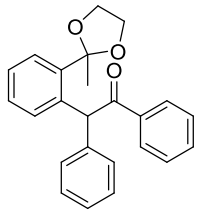
4-Methyl-1-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)pentan-2-one **3h**



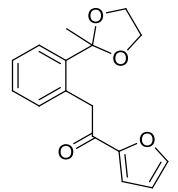
2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-1,2-diphenylethanone **3i**



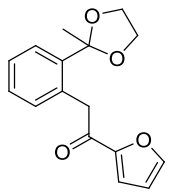
2-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-1,2-diphenylethanone **3i**

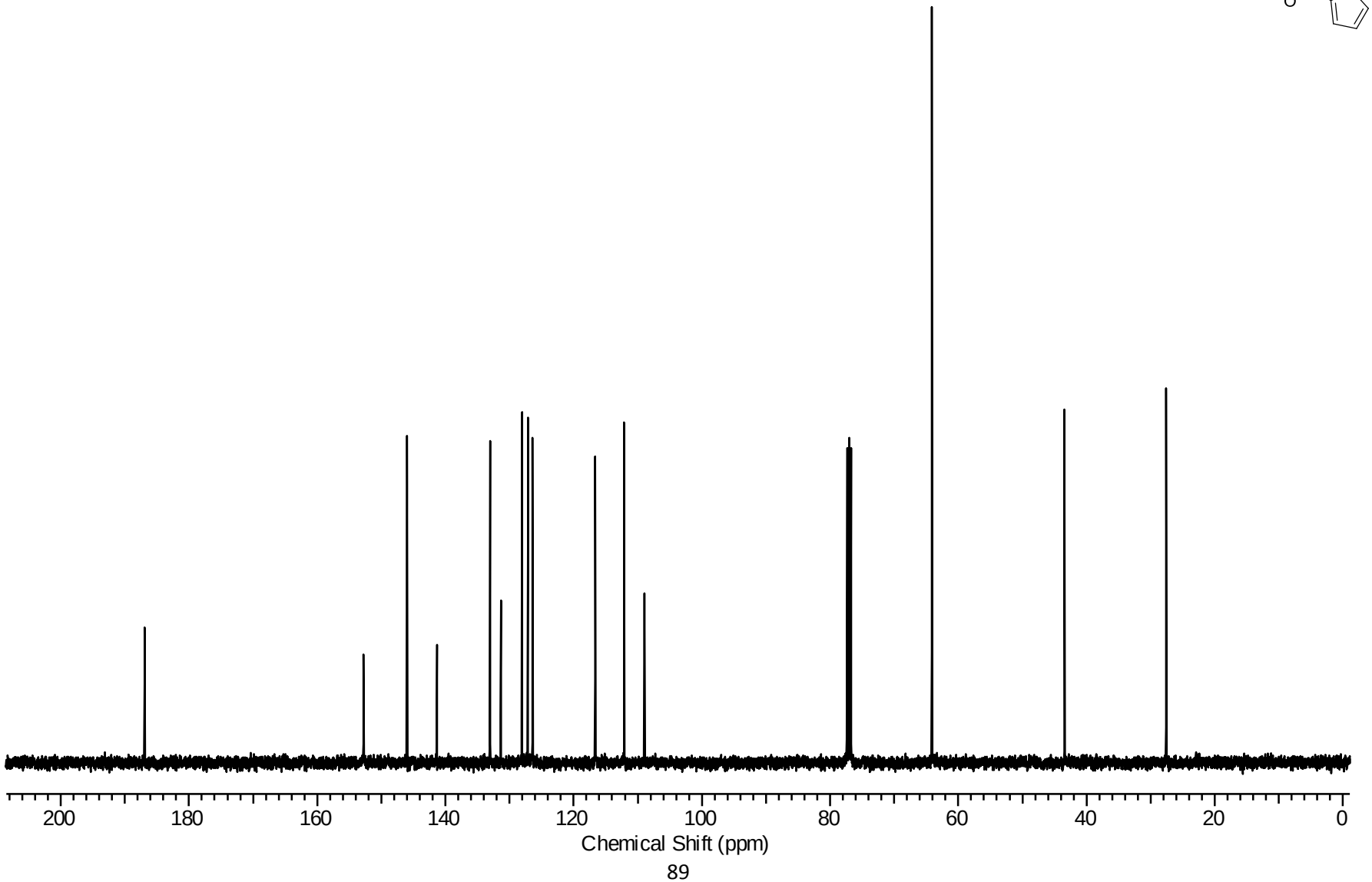


1-(Furan-2-yl)-2-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)ethanone **3j**

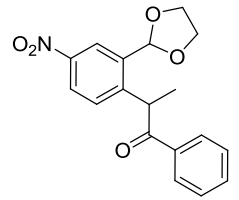


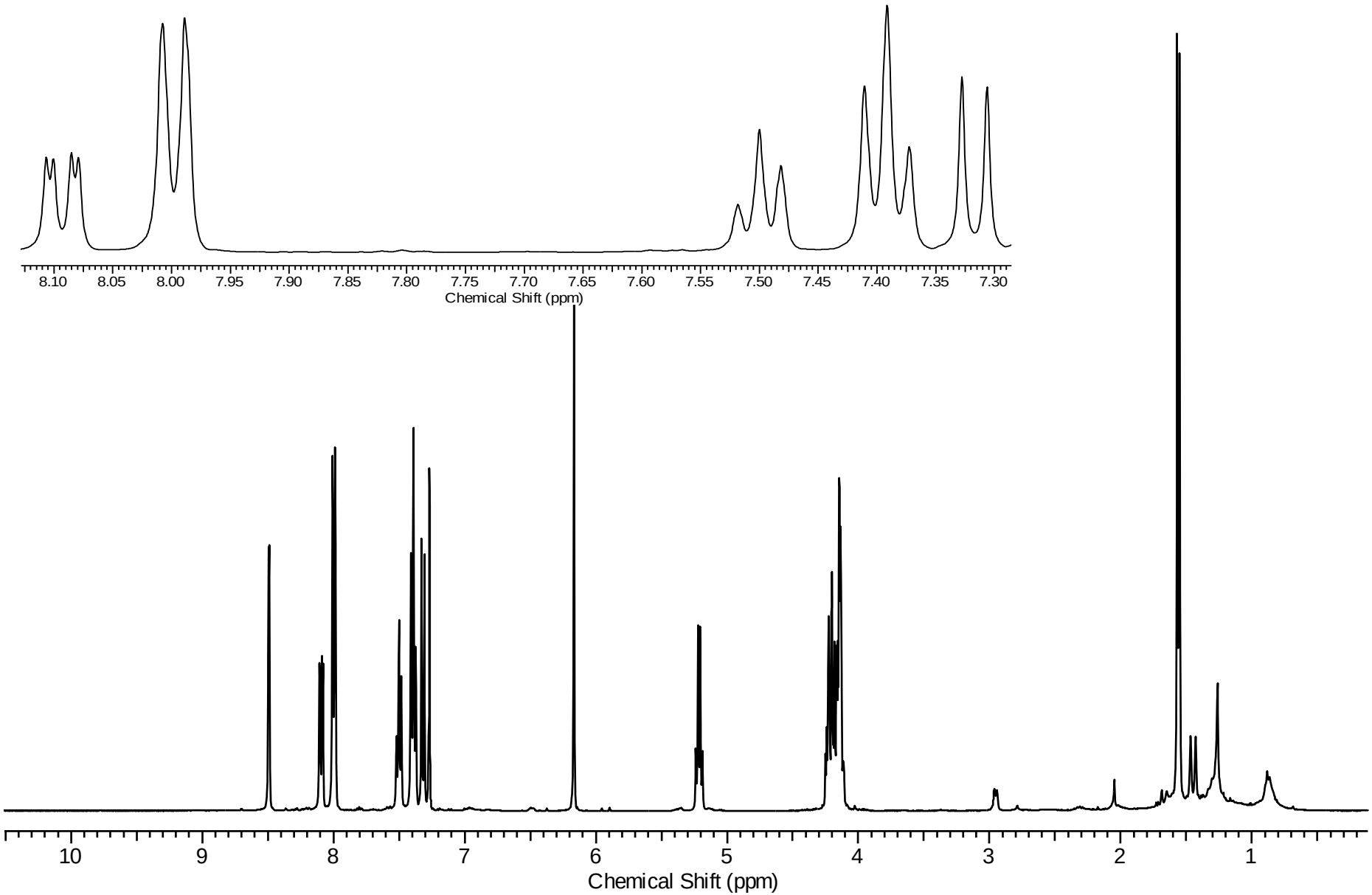
1-(Furan-2-yl)-2-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)ethanone **3j**



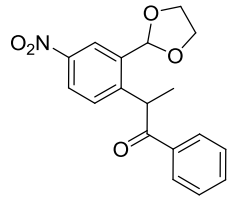


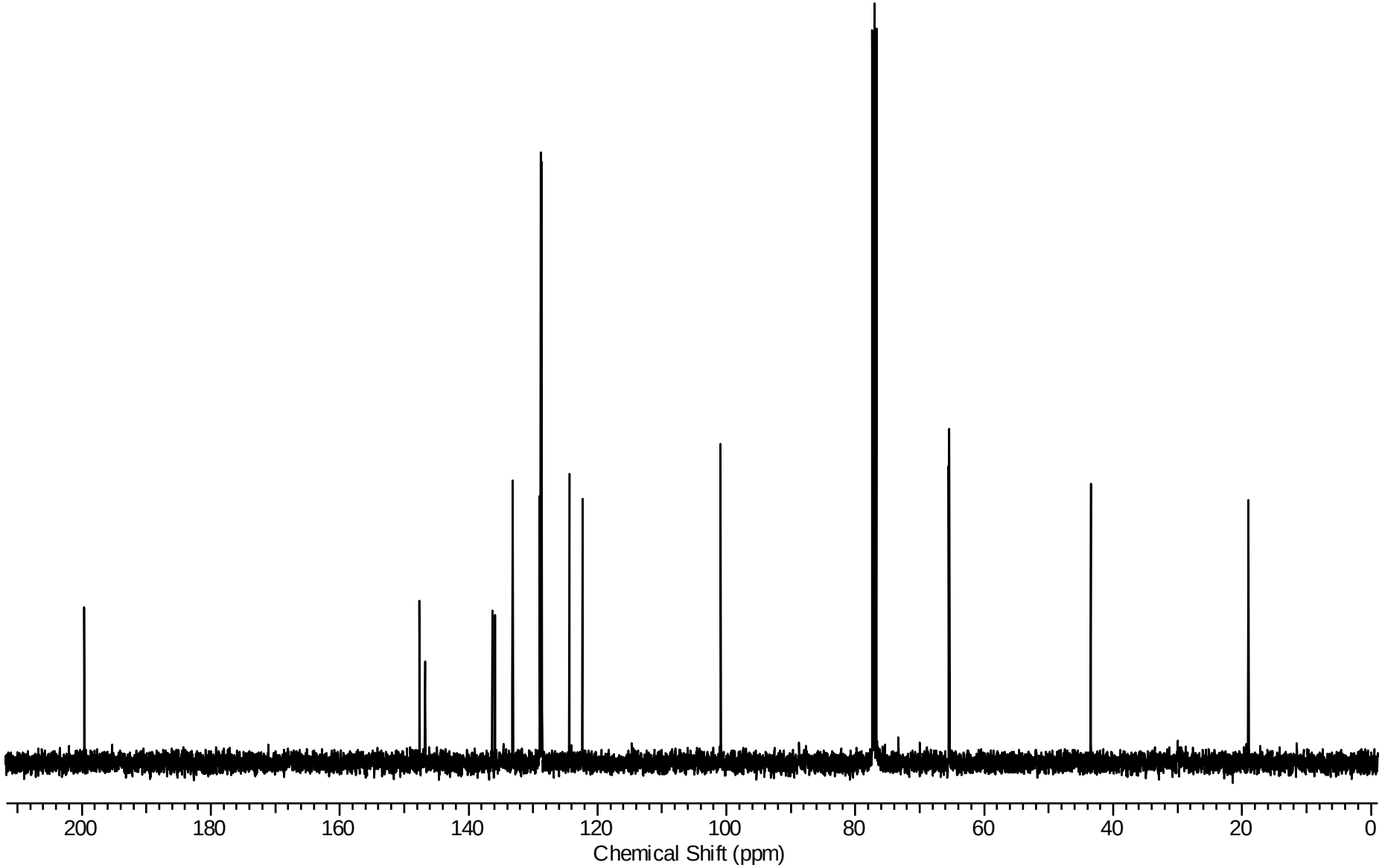
2-(2-(1,3-Dioxolan-2-yl)-4-nitrophenyl)-1-phenylpropan-1-one **3k**



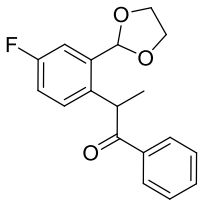


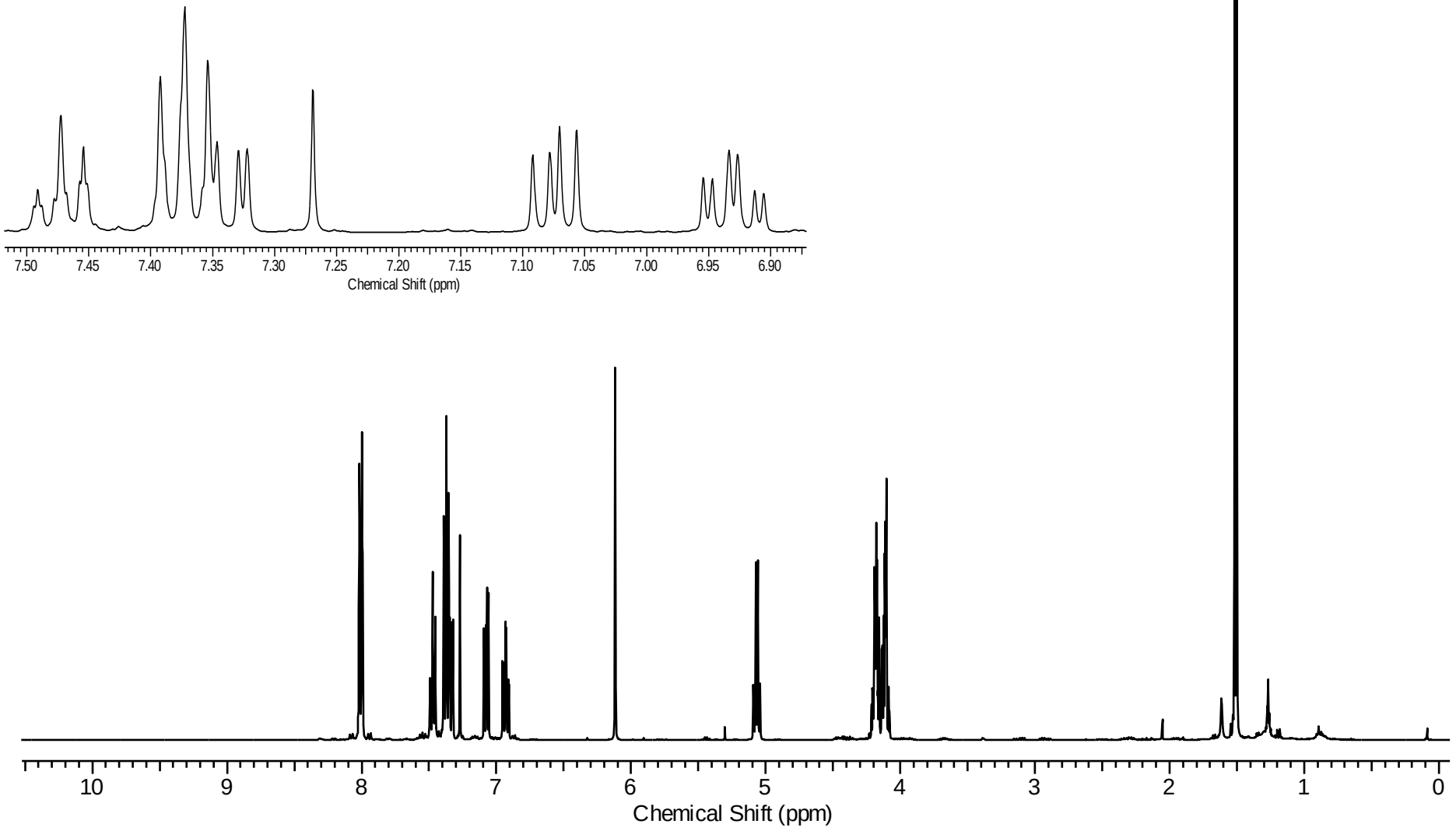
2-(2-(1,3-Dioxolan-2-yl)-4-nitrophenyl)-1-phenylpropan-1-one **3k**



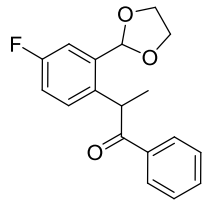


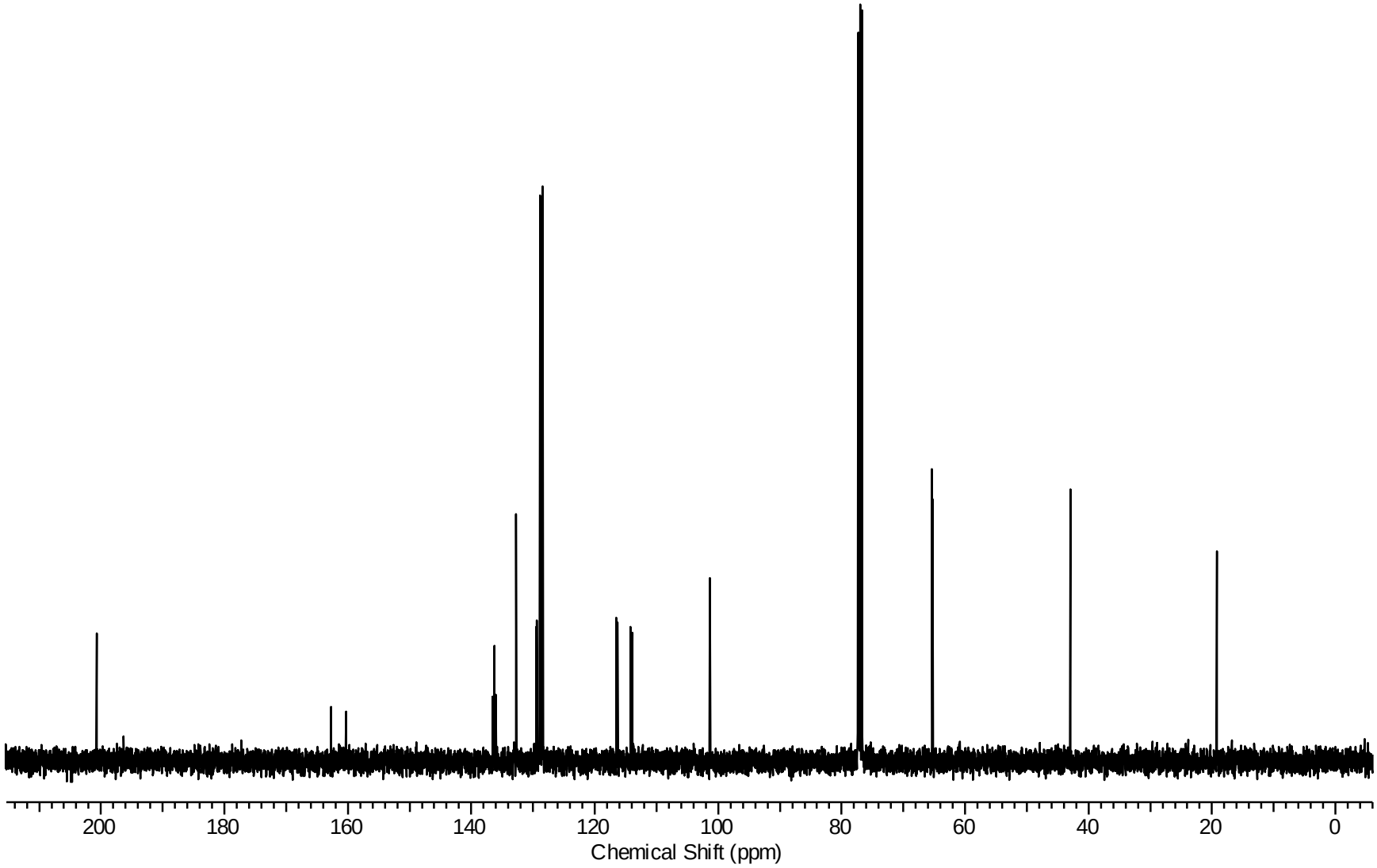
2-(2-(1,3-Dioxolan-2-yl)-4-fluorophenyl)-1-phenylpropan-1-one **3l**



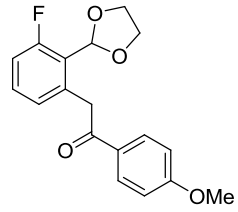


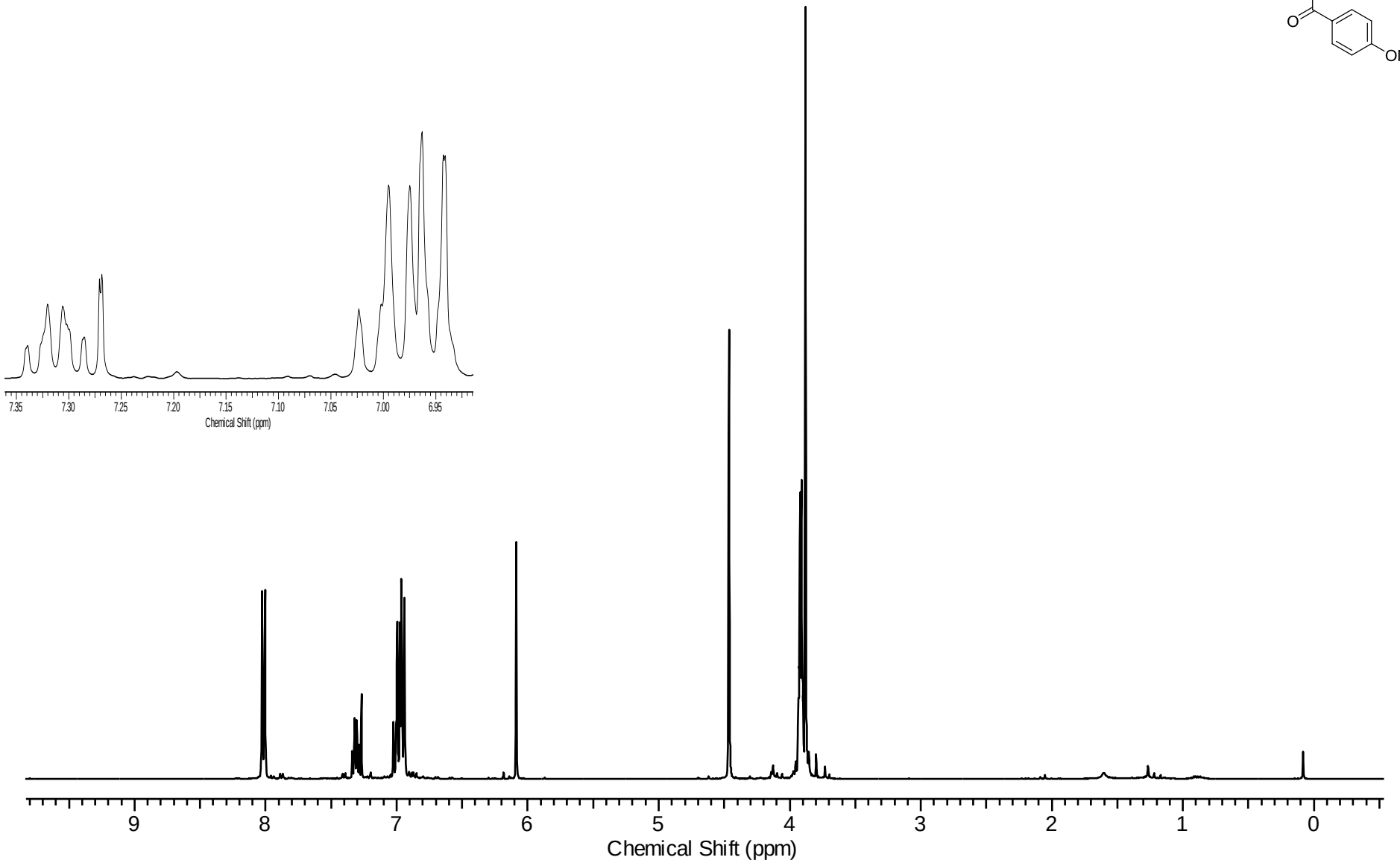
2-(2-(1,3-Dioxolan-2-yl)-4-fluorophenyl)-1-phenylpropan-1-one **3l**



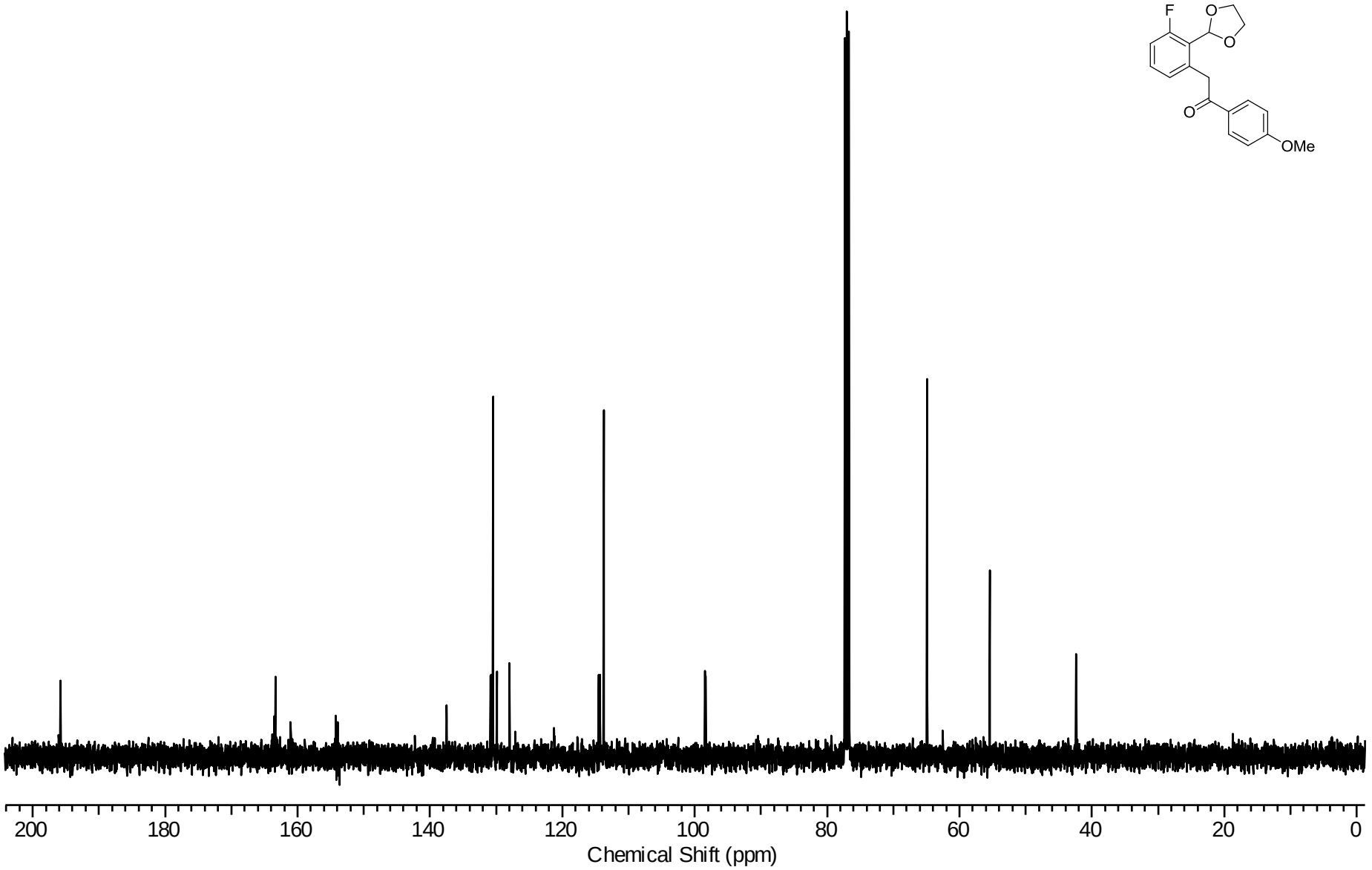


2-(2-(1,3-Dioxolan-2-yl)-3-fluorophenyl)-1-(4-methoxyphenyl)ethanone **3m**

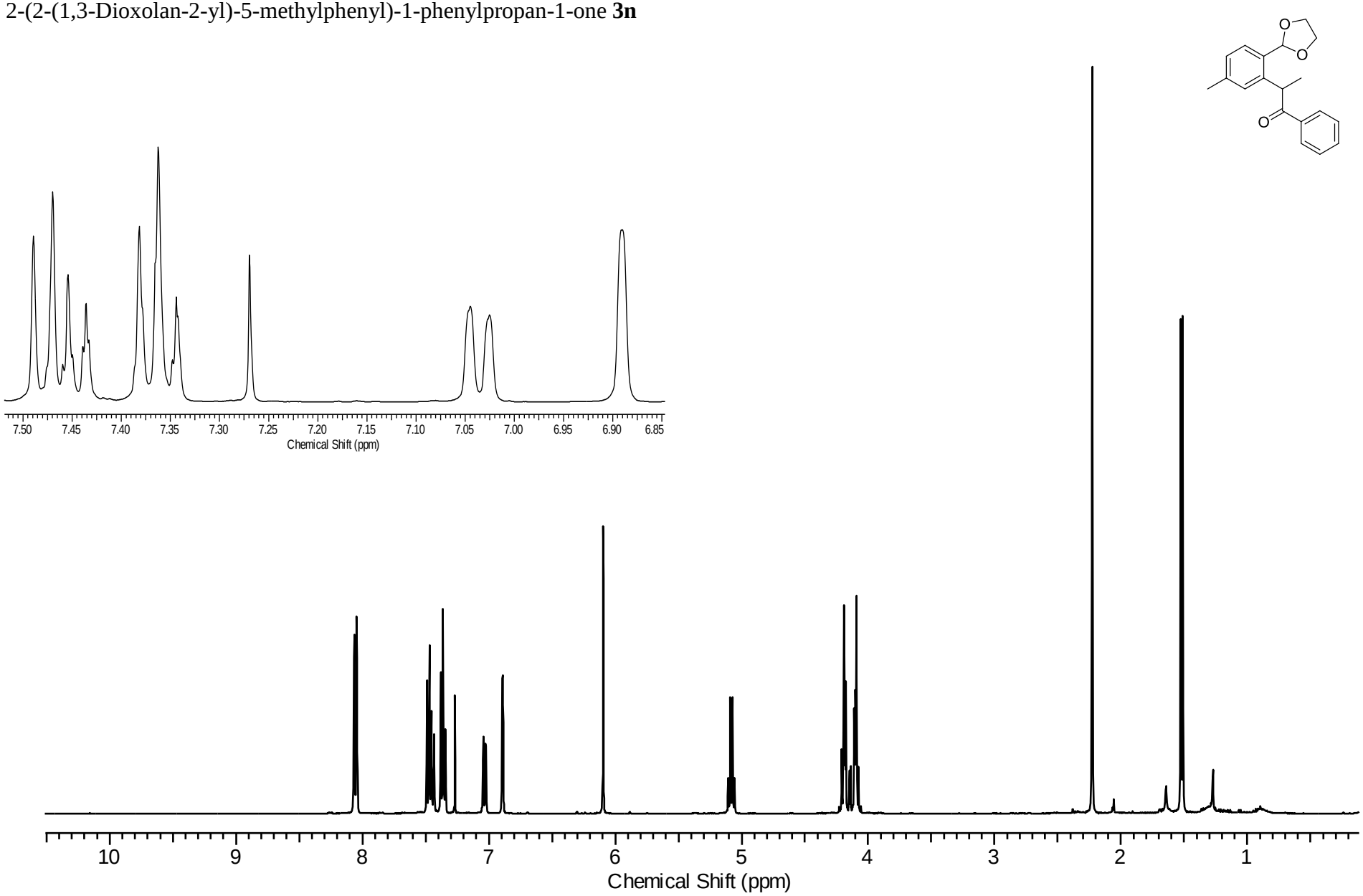




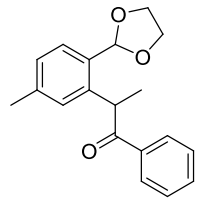
2-(2-(1,3-Dioxolan-2-yl)-3-fluorophenyl)-1-(4-methoxyphenyl)ethanone **3m**

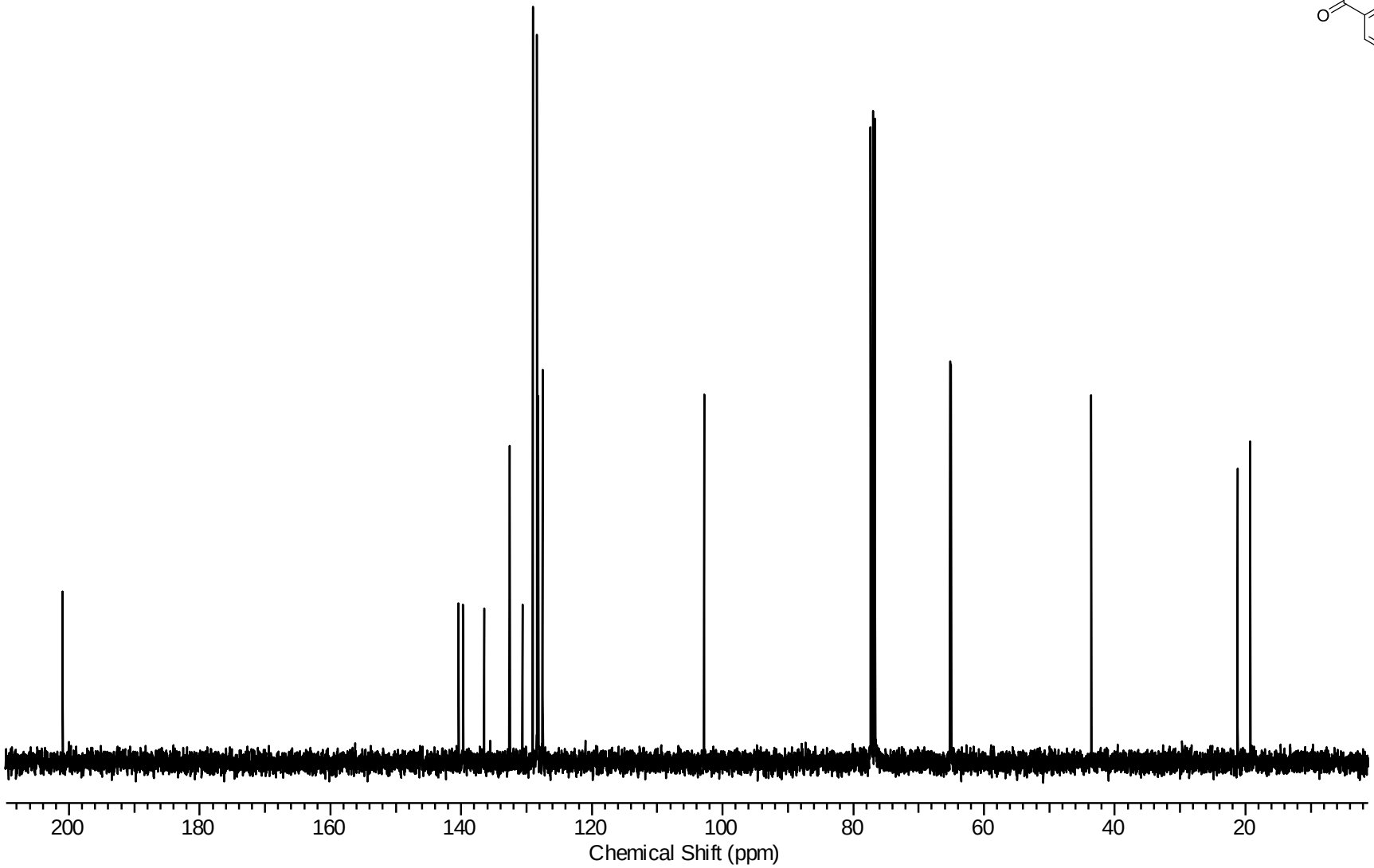


2-(2-(1,3-Dioxolan-2-yl)-5-methylphenyl)-1-phenylpropan-1-one **3n**

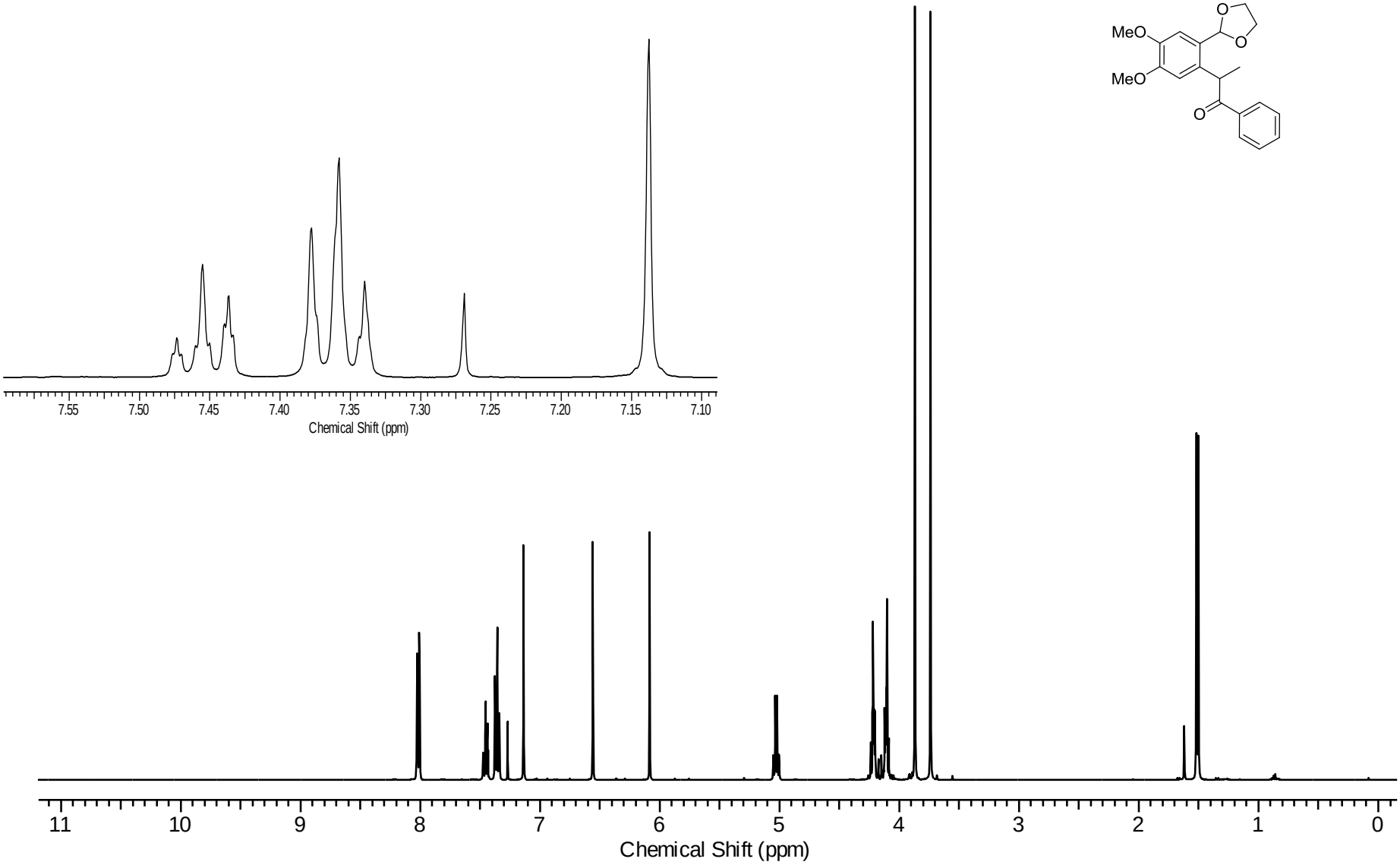


2-(2-(1,3-Dioxolan-2-yl)-5-methylphenyl)-1-phenylpropan-1-one **3n**

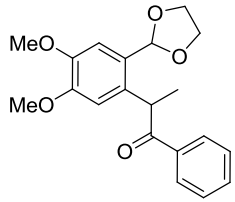


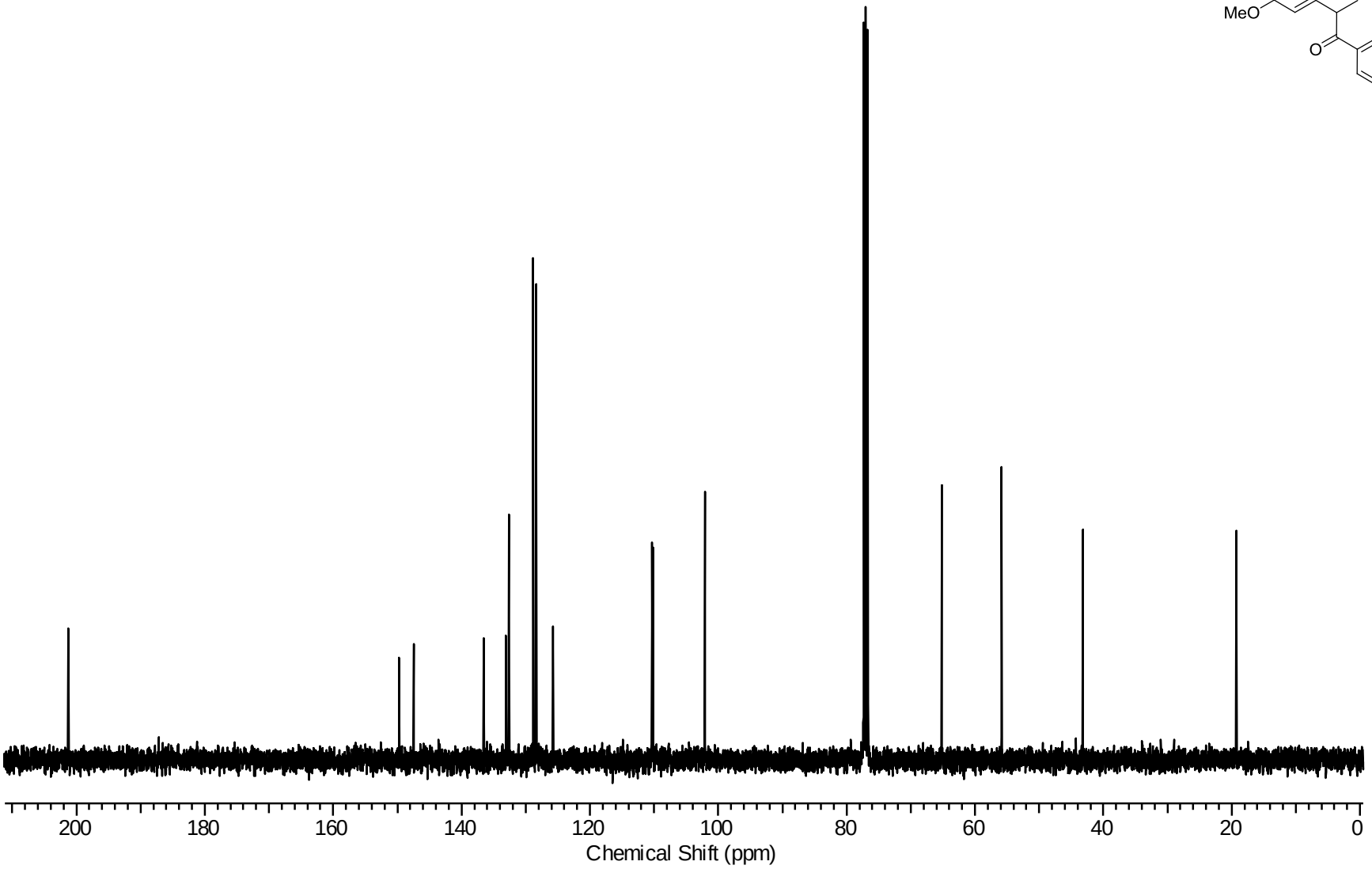


2-(2-(1,3-Dioxolan-2-yl)-4,5-dimethoxyphenyl)-1-phenylpropan-1-one **3o**

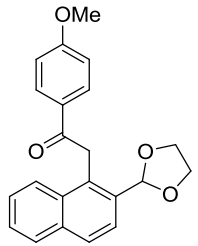


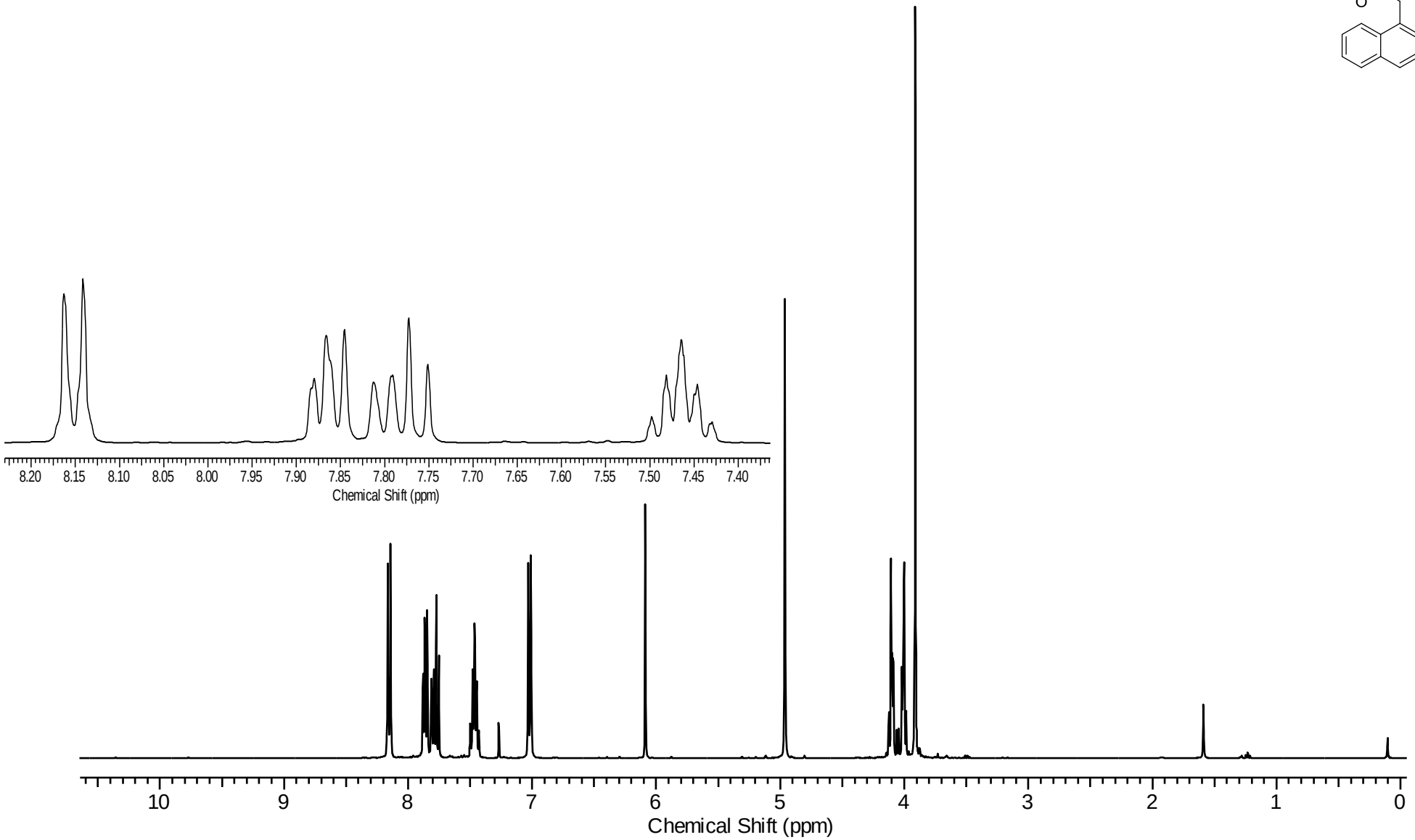
2-(2-(1,3-Dioxolan-2-yl)-4,5-dimethoxyphenyl)-1-phenylpropan-1-one **3o**



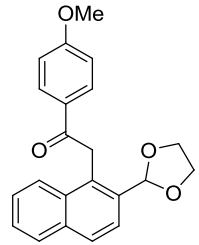


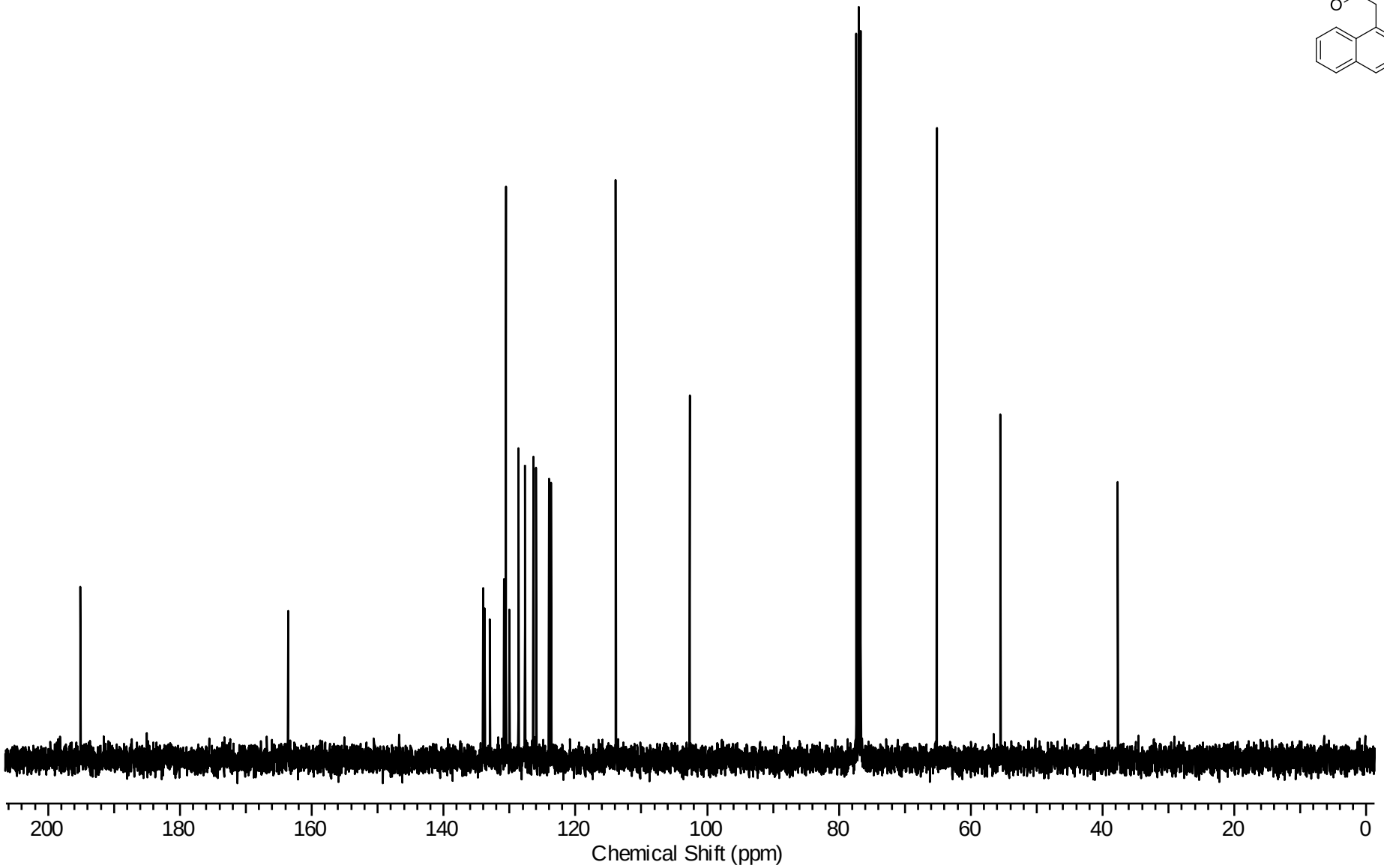
2-(2-(1,3-Dioxolan-2-yl)naphthalen-1-yl)-1-(4-methoxyphenyl)ethanone **3p**



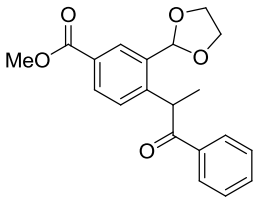


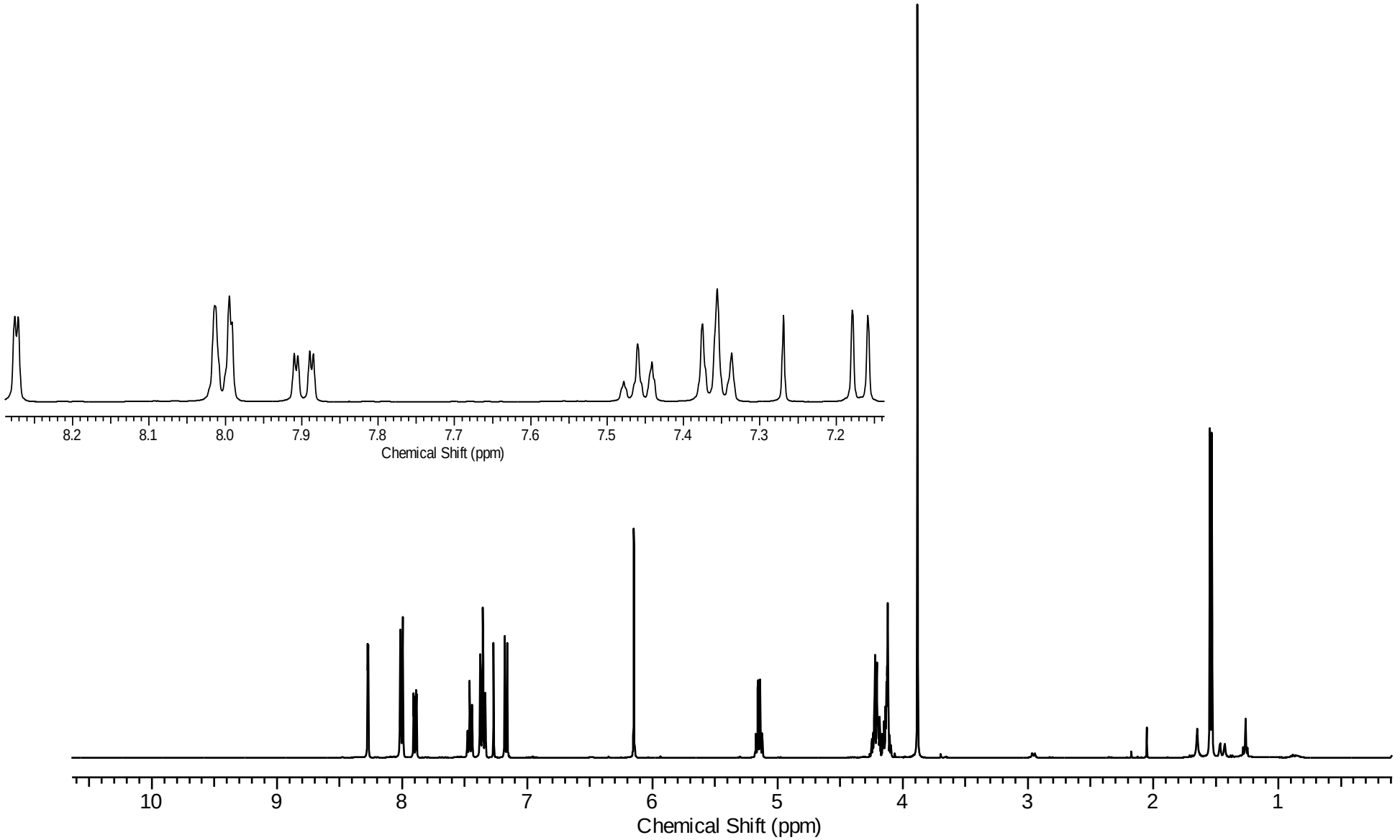
2-(2-(1,3-Dioxolan-2-yl)naphthalen-1-yl)-1-(4-methoxyphenyl)ethanone **3p**



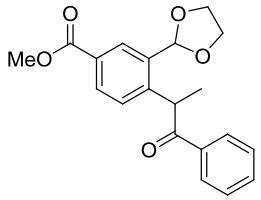


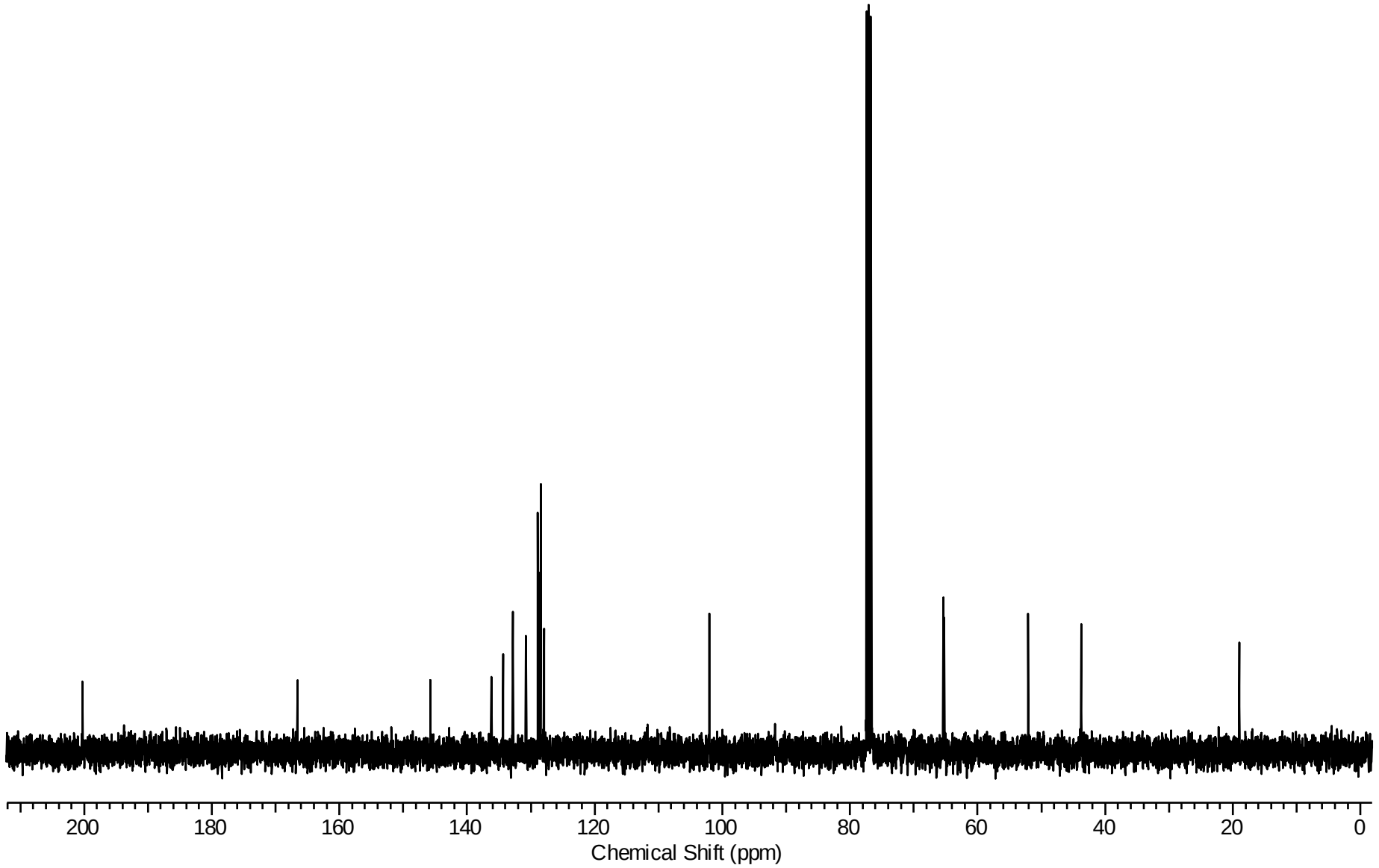
Methyl 3-(1,3-dioxolan-2-yl)-4-(1-oxo-1-phenylpropan-2-yl)benzoate **3q**



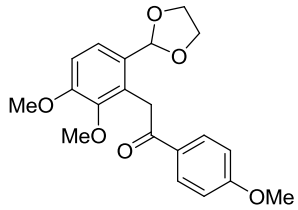


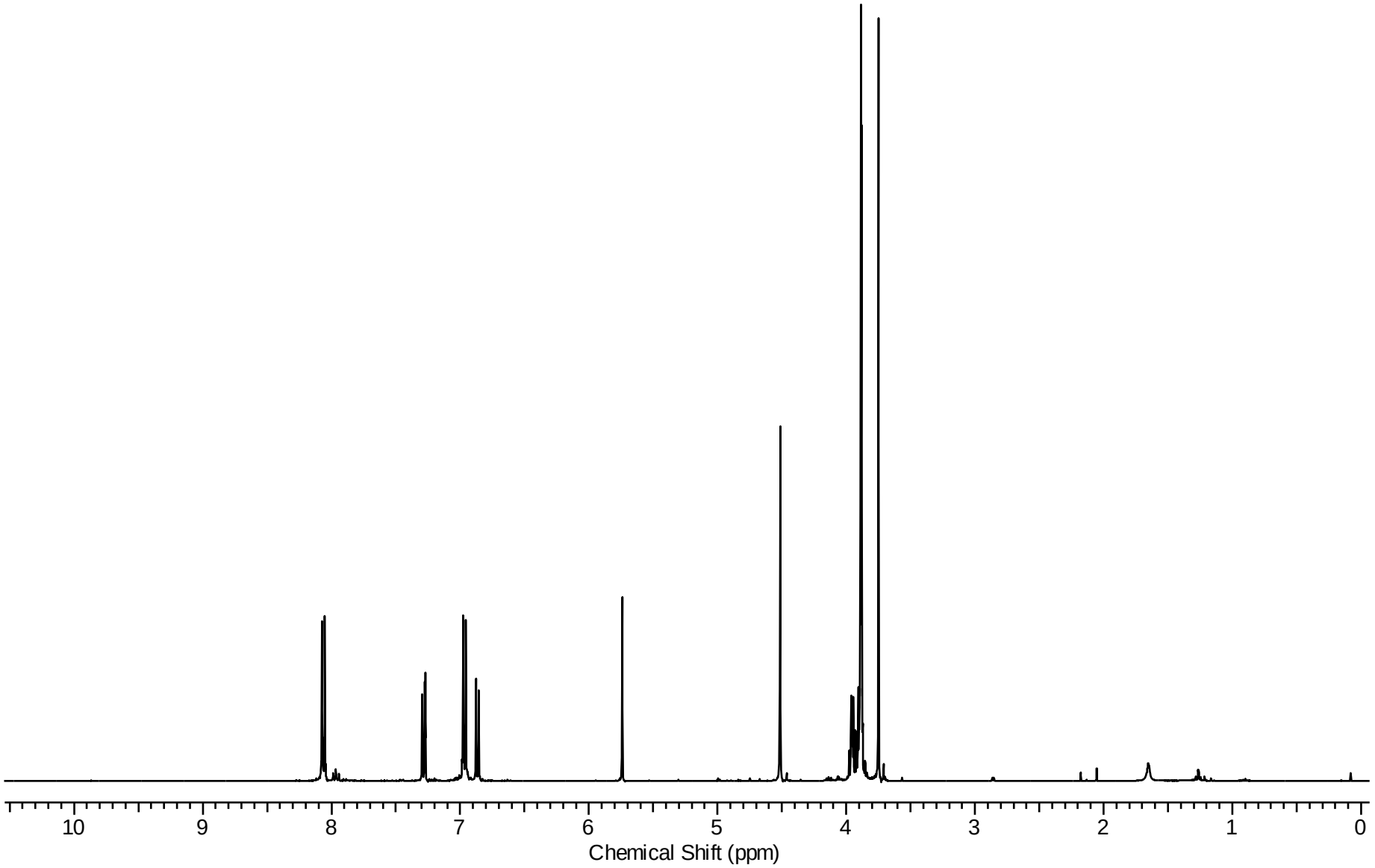
Methyl 3-(1,3-dioxolan-2-yl)-4-(1-oxo-1-phenylpropan-2-yl)benzoate **3q**



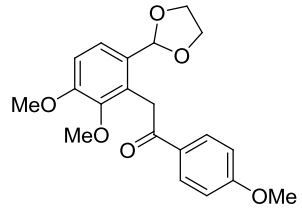


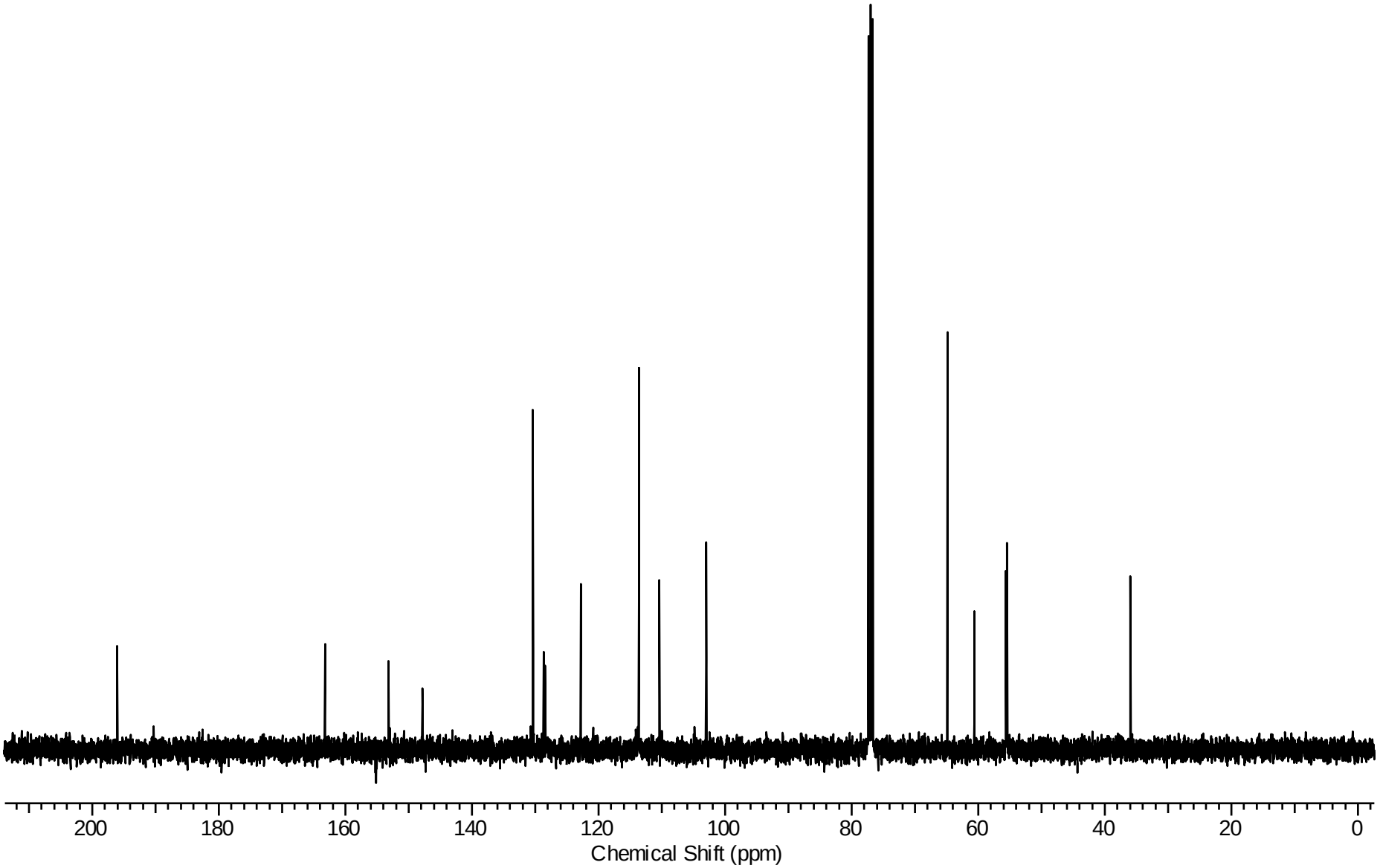
2-(6-(1,3-Dioxolan-2-yl)-2,3-dimethoxyphenyl)-1-(4-methoxyphenyl)ethanone **3r**



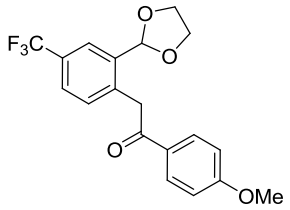


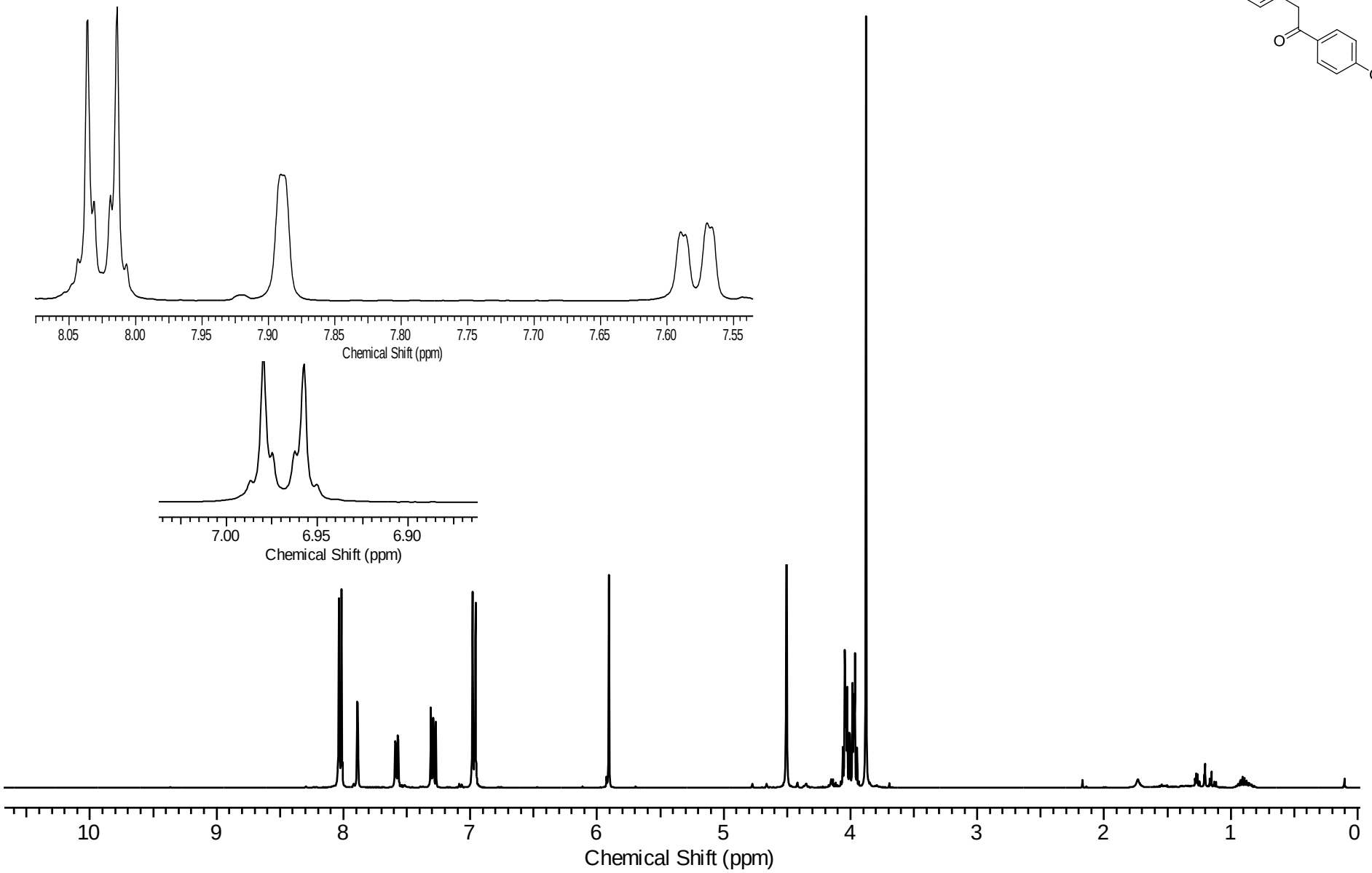
2-(6-(1,3-Dioxolan-2-yl)-2,3-dimethoxyphenyl)-1-(4-methoxyphenyl)ethanone **3r**



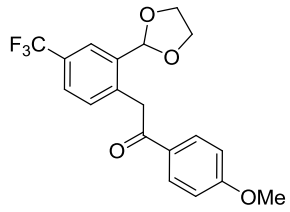


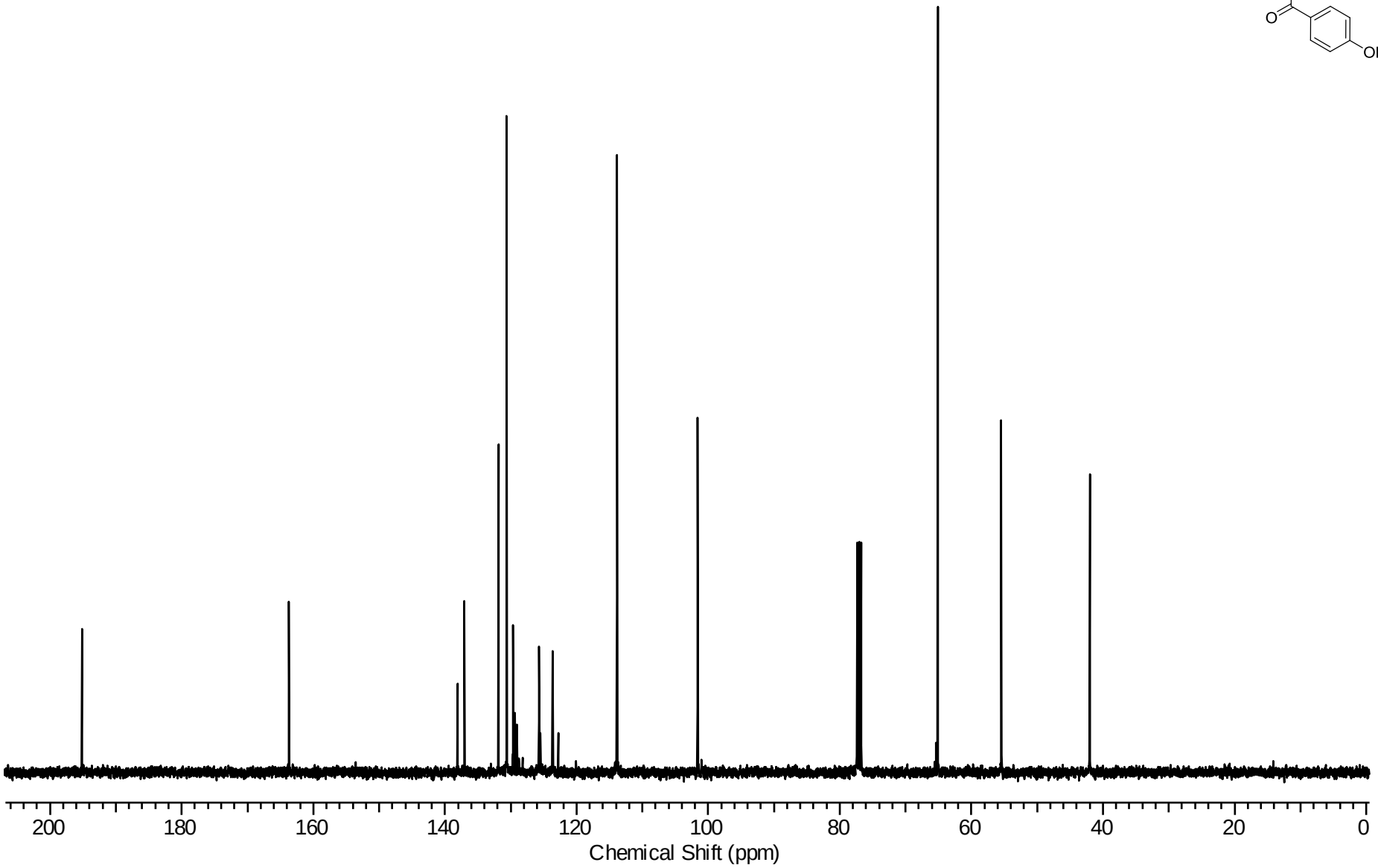
2-(2-(1,3-Dioxolan-2-yl)-4-(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)ethanone **3s**



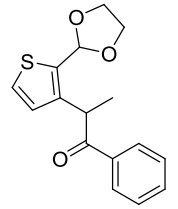


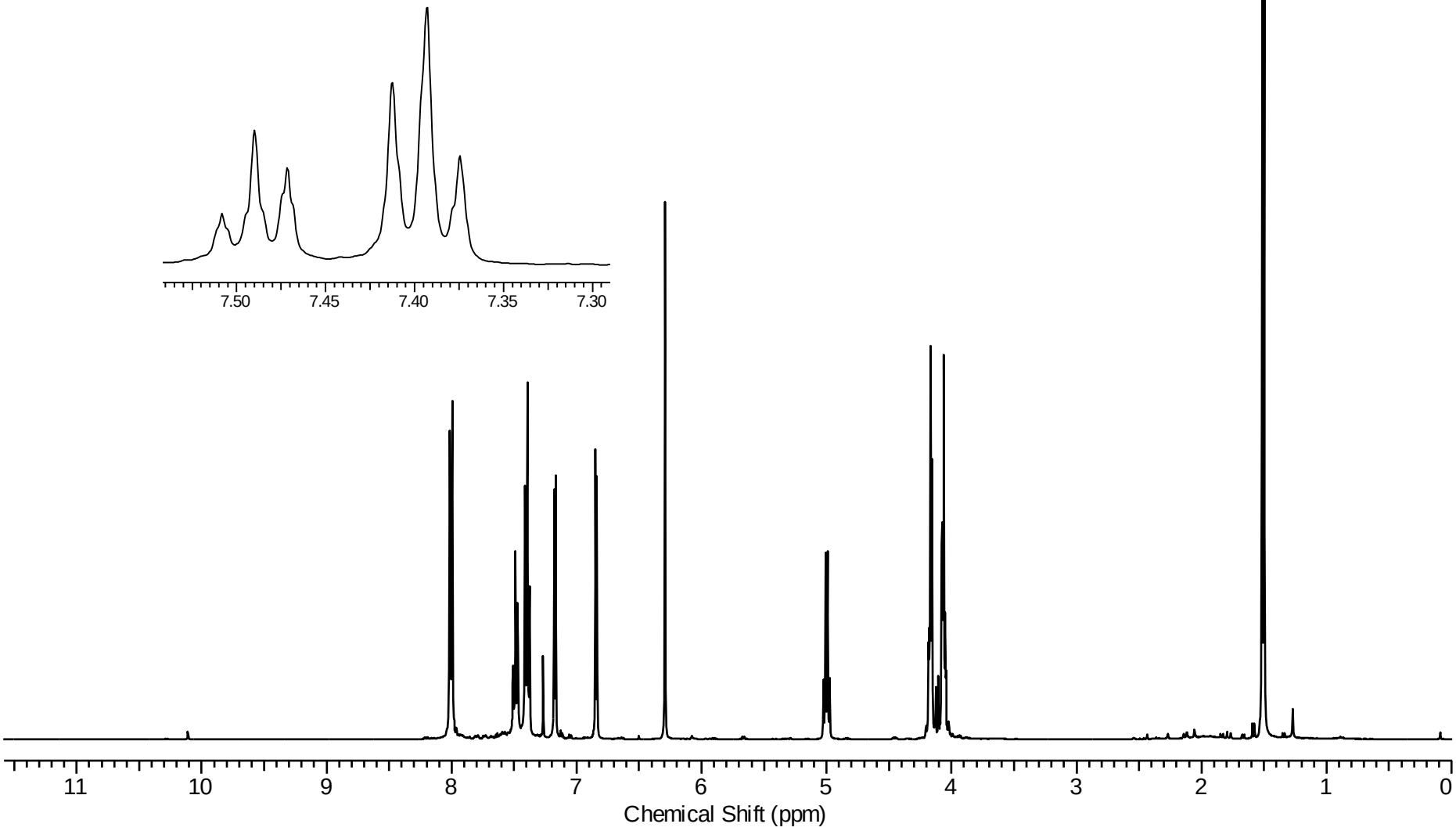
2-(2-(1,3-Dioxolan-2-yl)-4-(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)ethanone **3s**



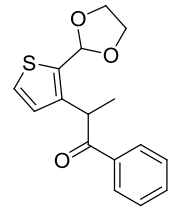


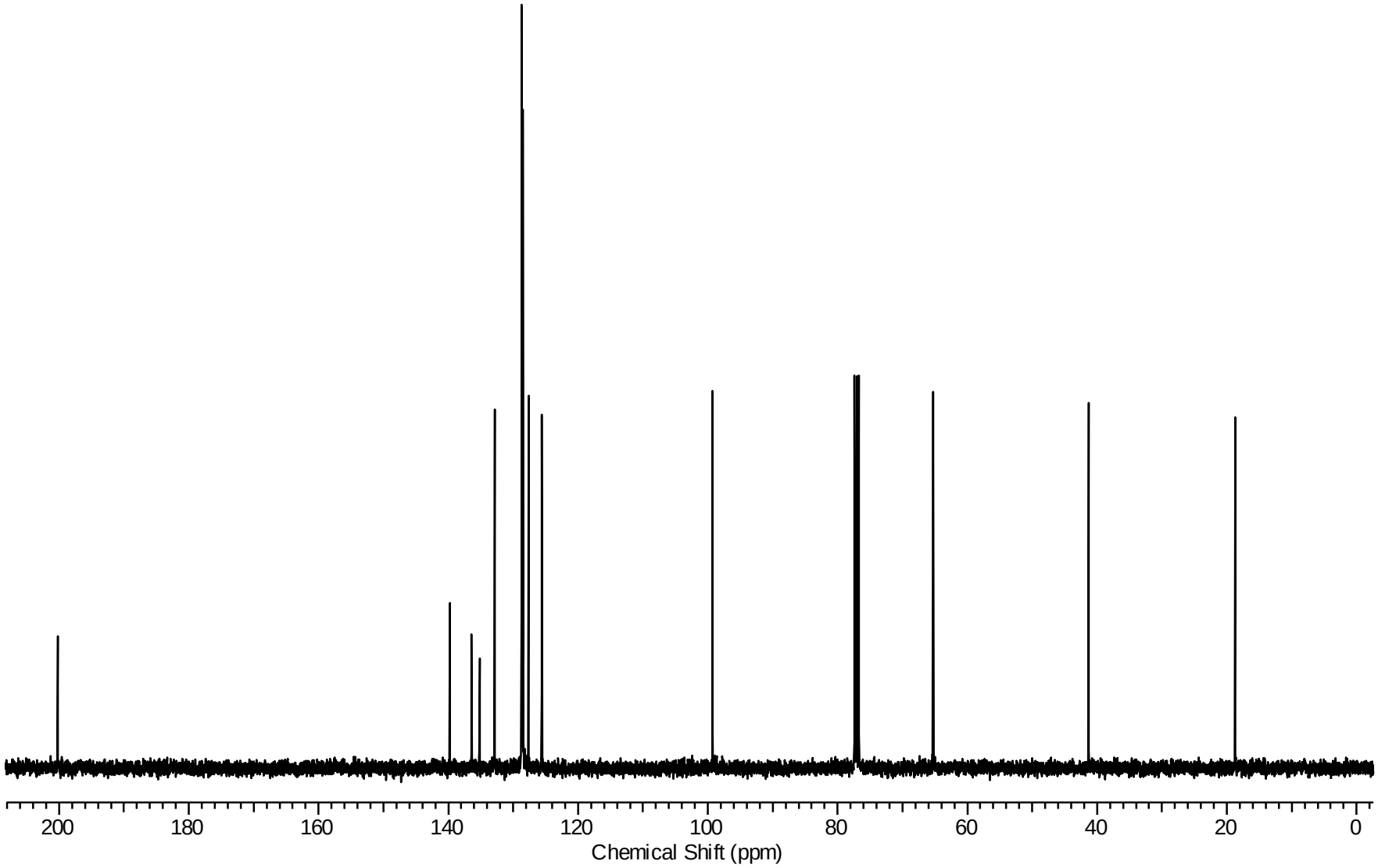
2-(2-(1,3-Dioxolan-2-yl)thiophen-3-yl)-1-phenylpropan-1-one **3t**



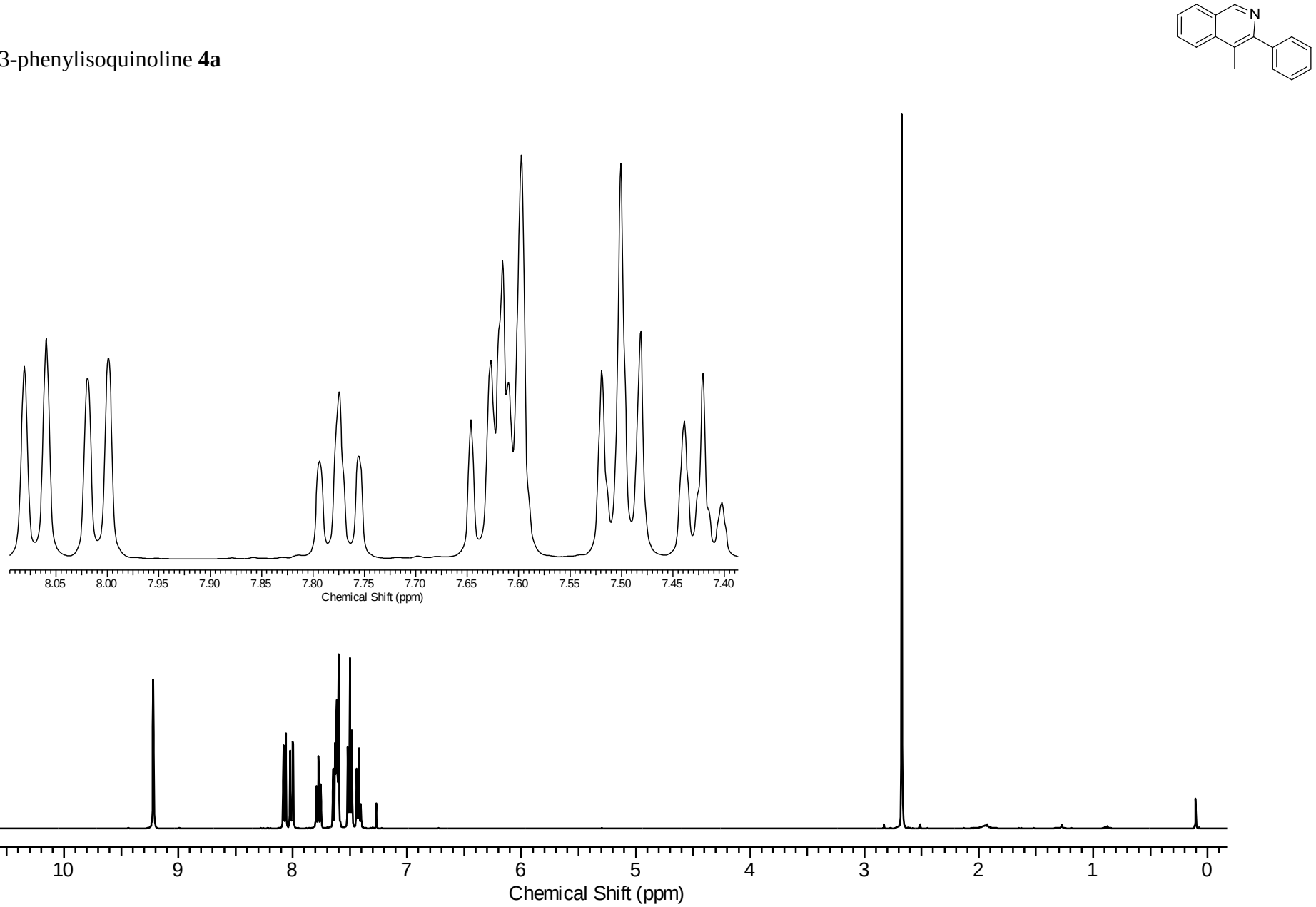


2-(2-(1,3-Dioxolan-2-yl)thiophen-3-yl)-1-phenylpropan-1-one **3t**

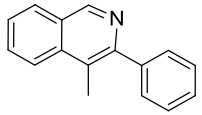


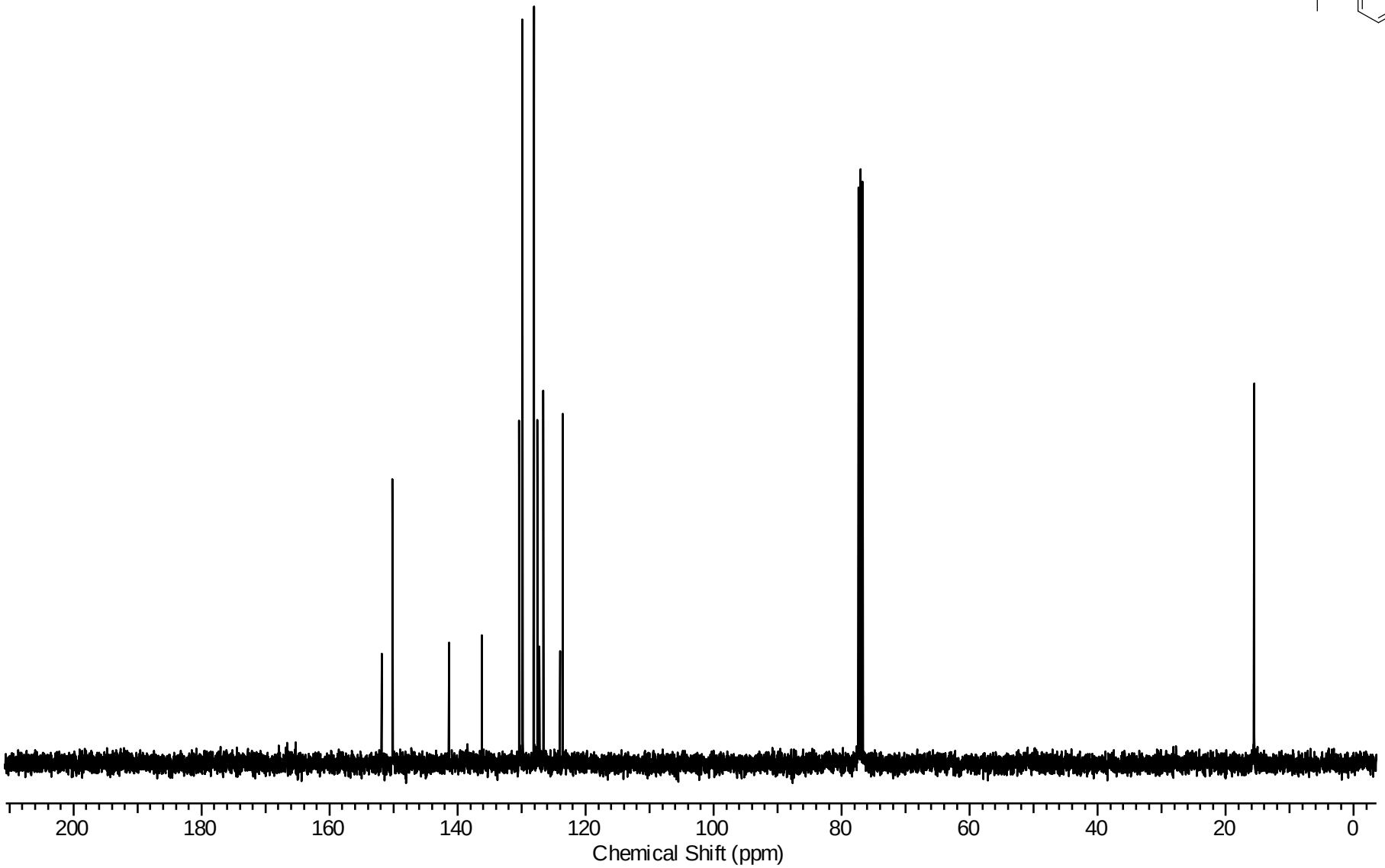


4-Methyl-3-phenylisoquinoline **4a**

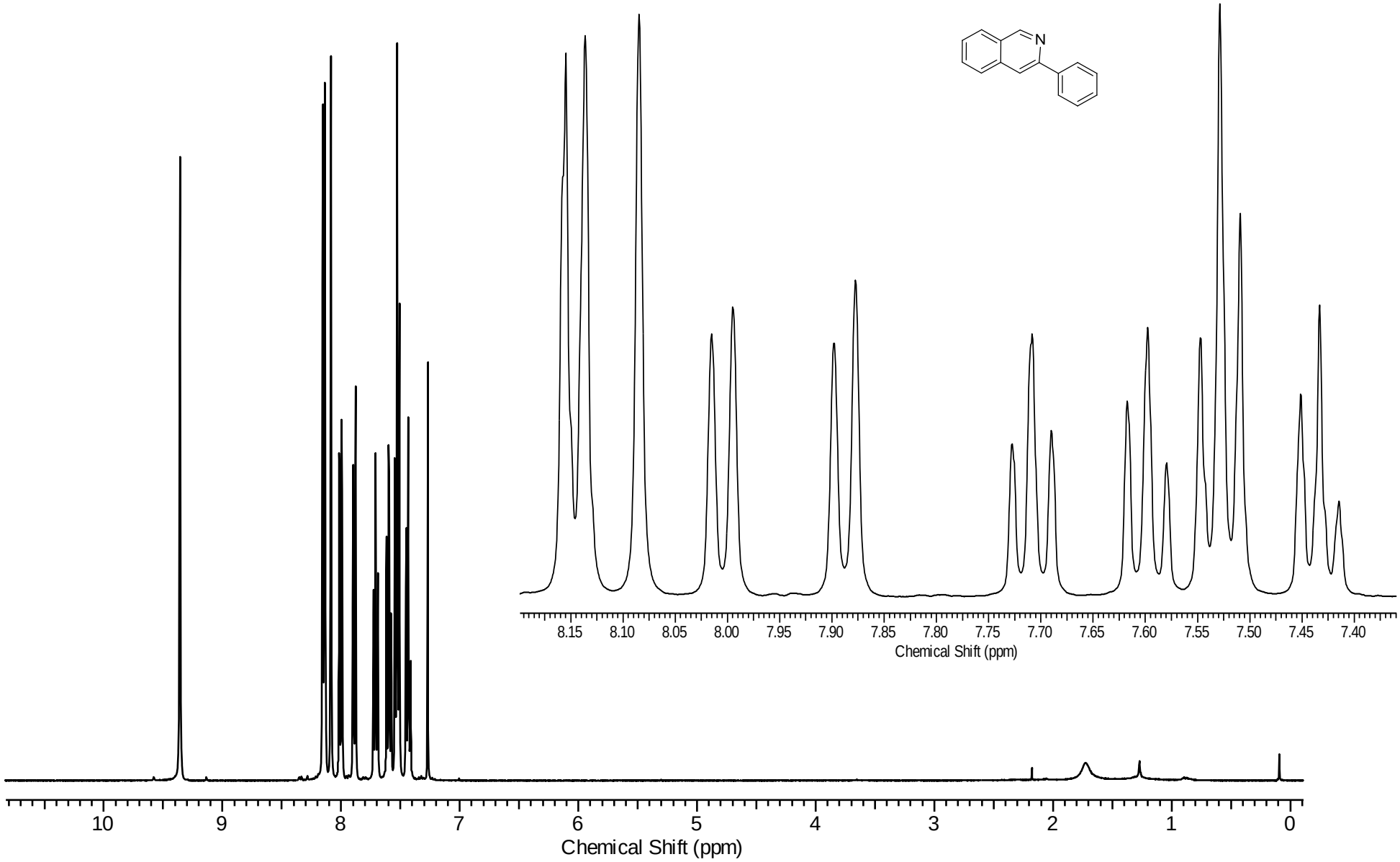


4-Methyl-3-phenylisoquinoline **4a**

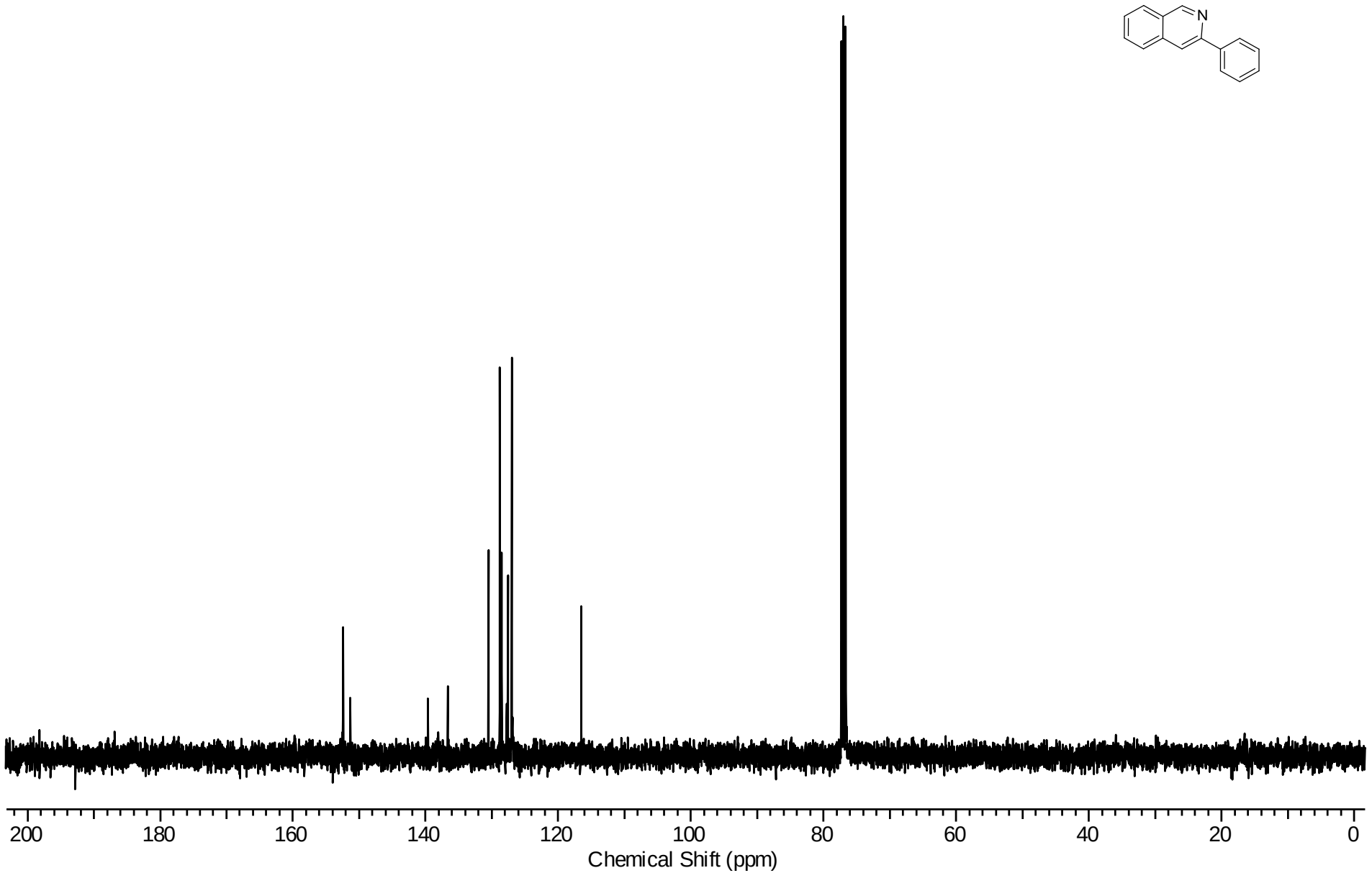


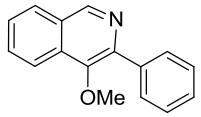


3-Phenylisoquinoline **4b**

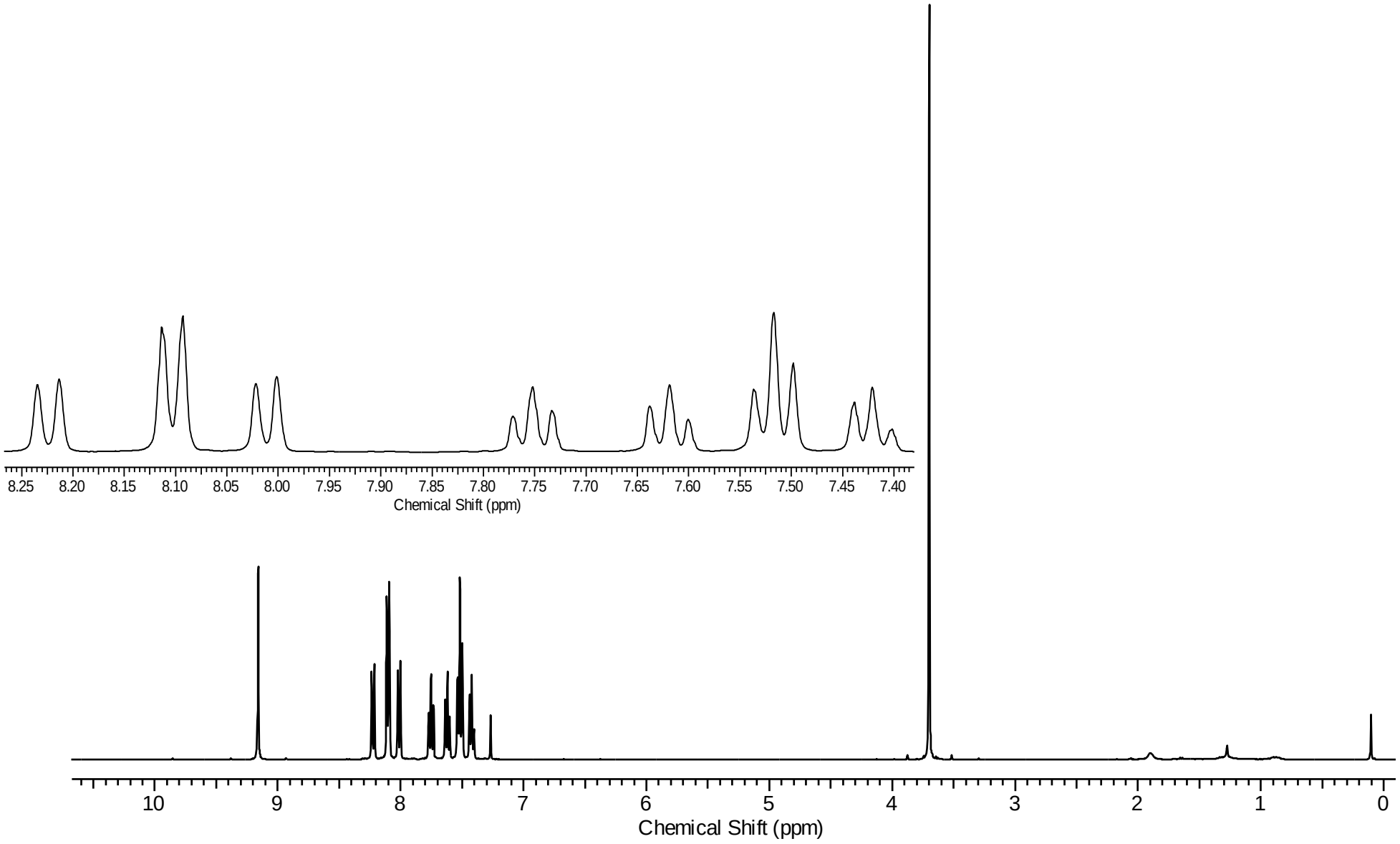


3-Phenylisoquinoline **4b**

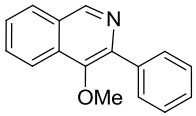


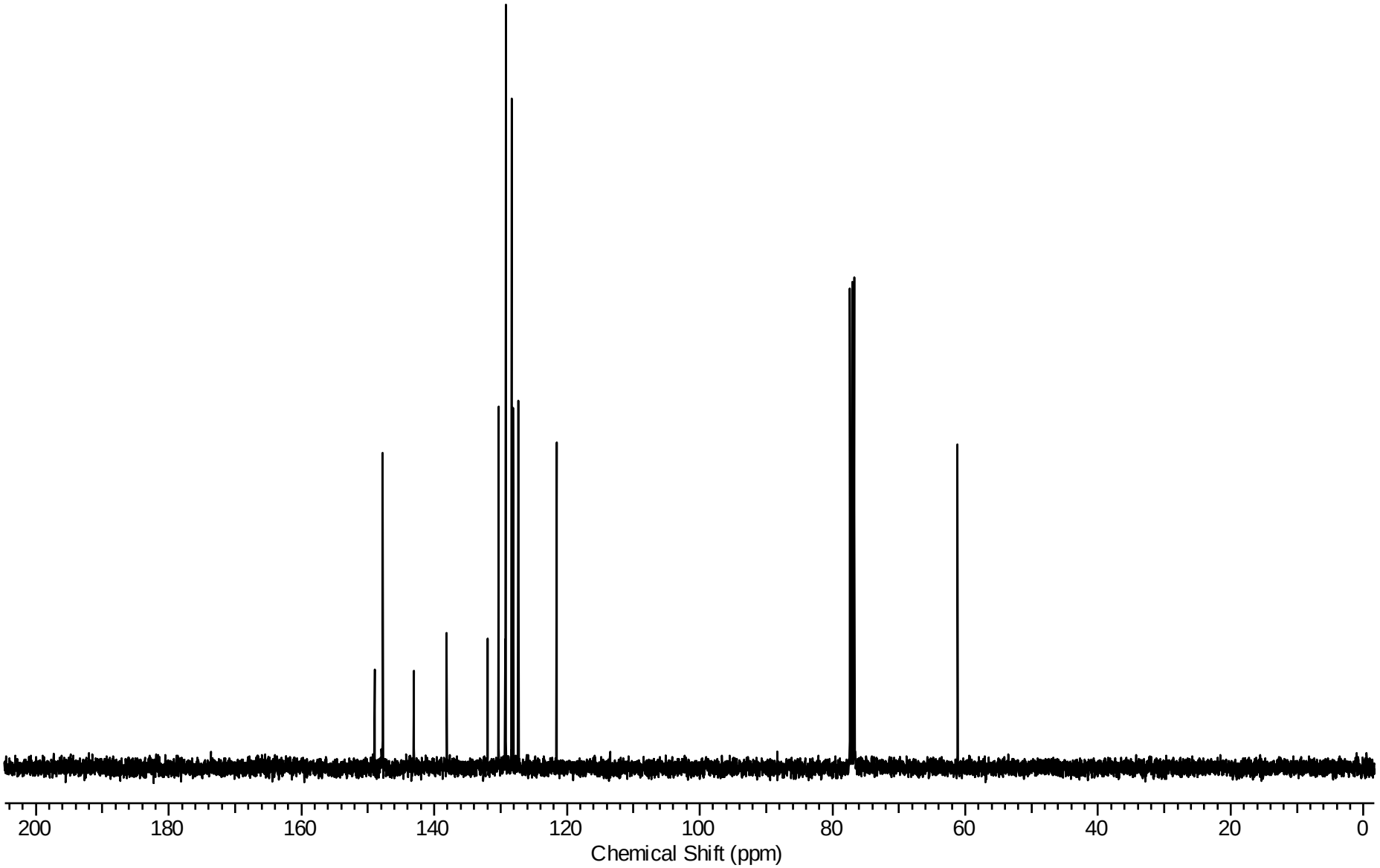


4-Methoxy-3-phenylisoquinoline **4c**

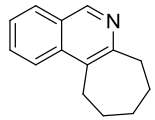


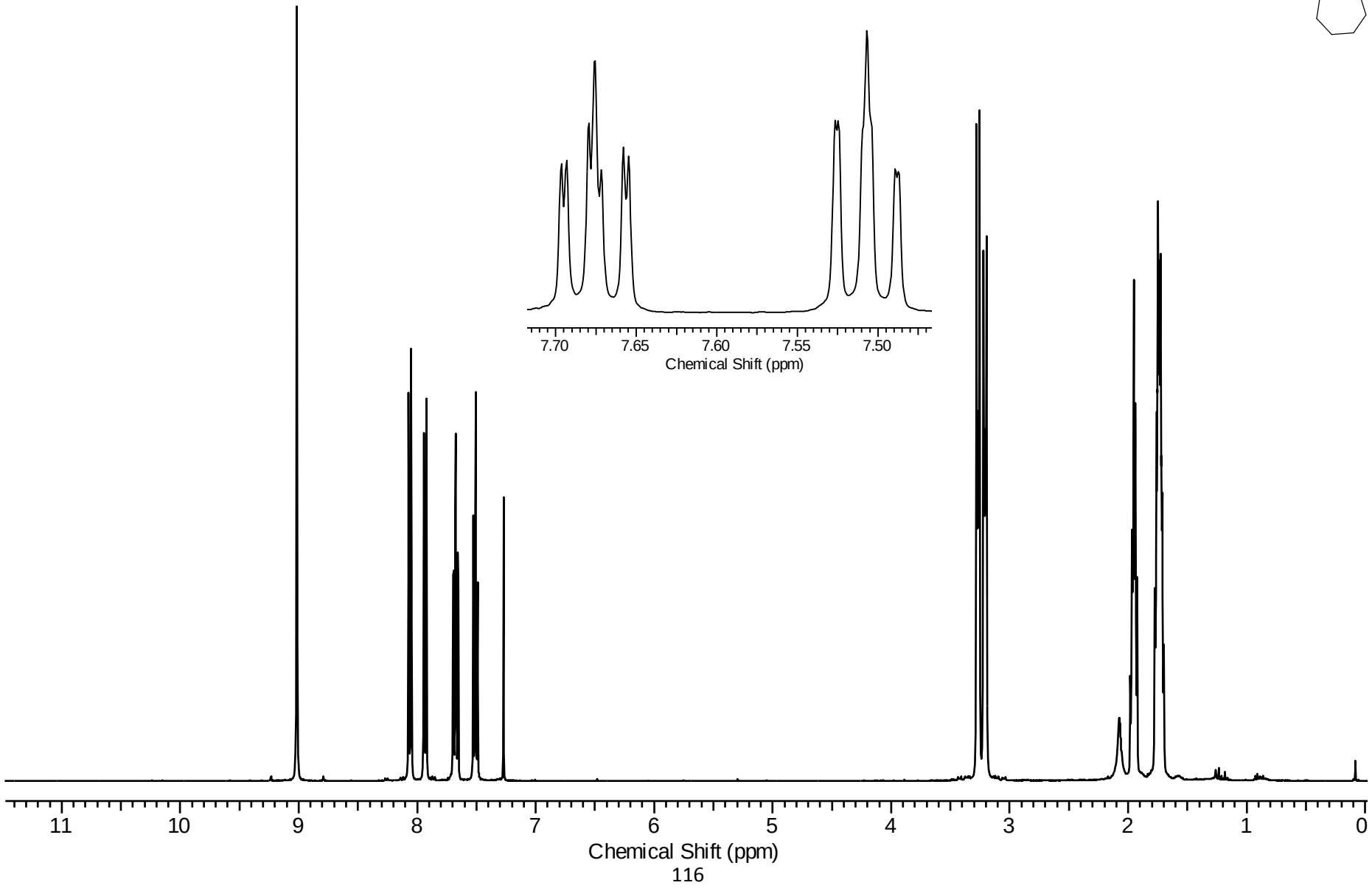
4-Methoxy-3-phenylisoquinoline **4c**



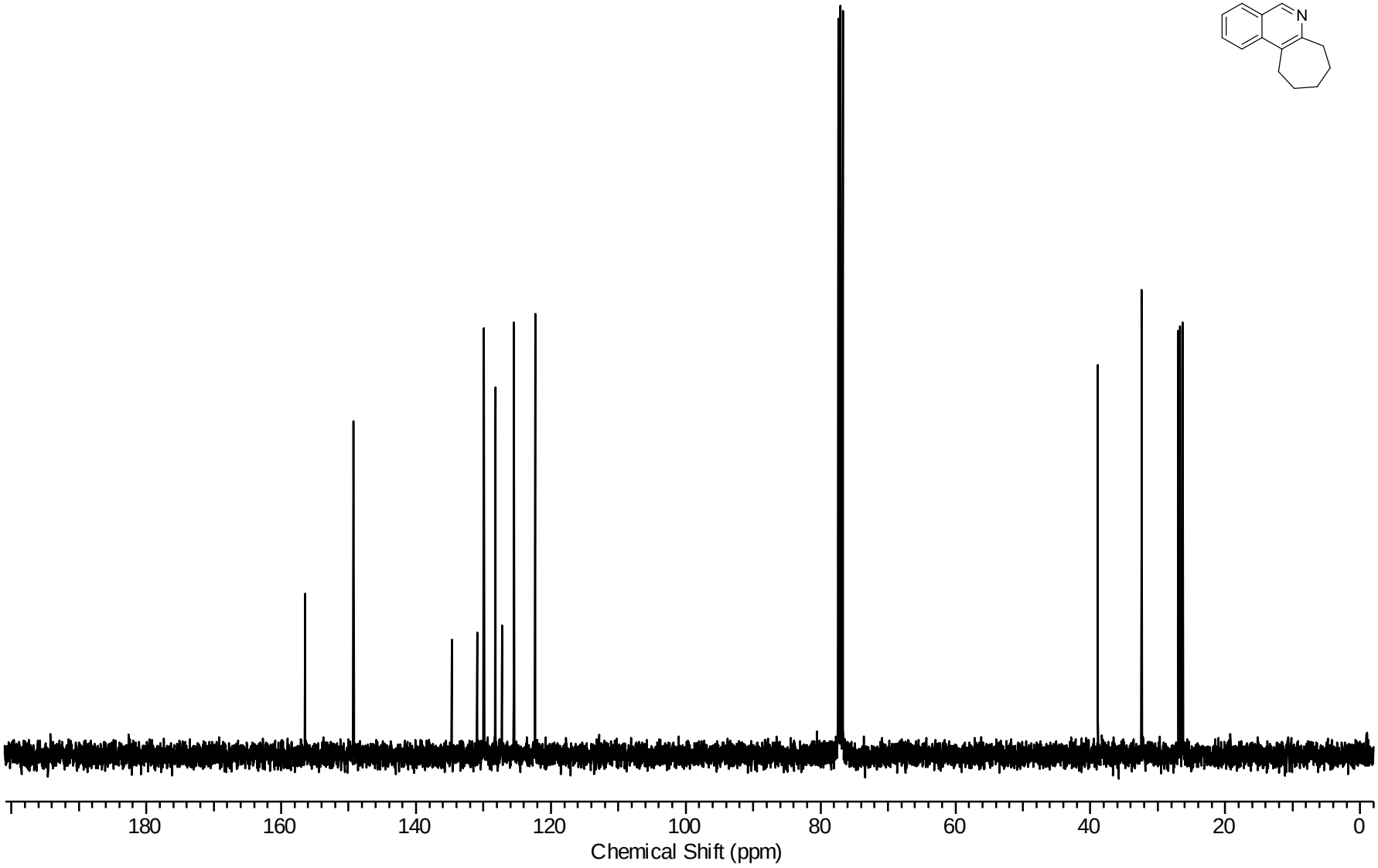


8,9,10,11-Tetrahydro-7H-cyclohepta[c]isoquinoline **4d**

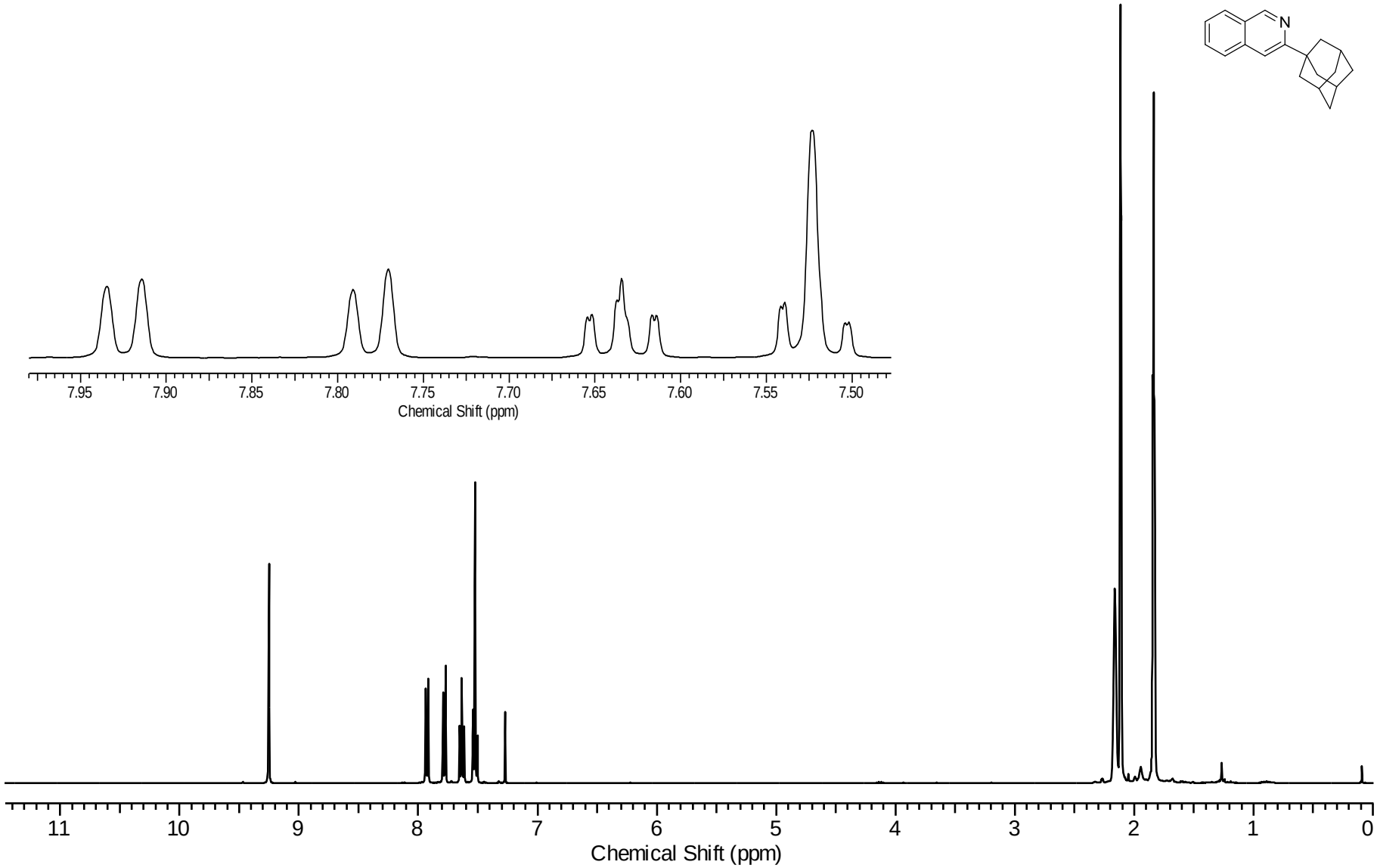




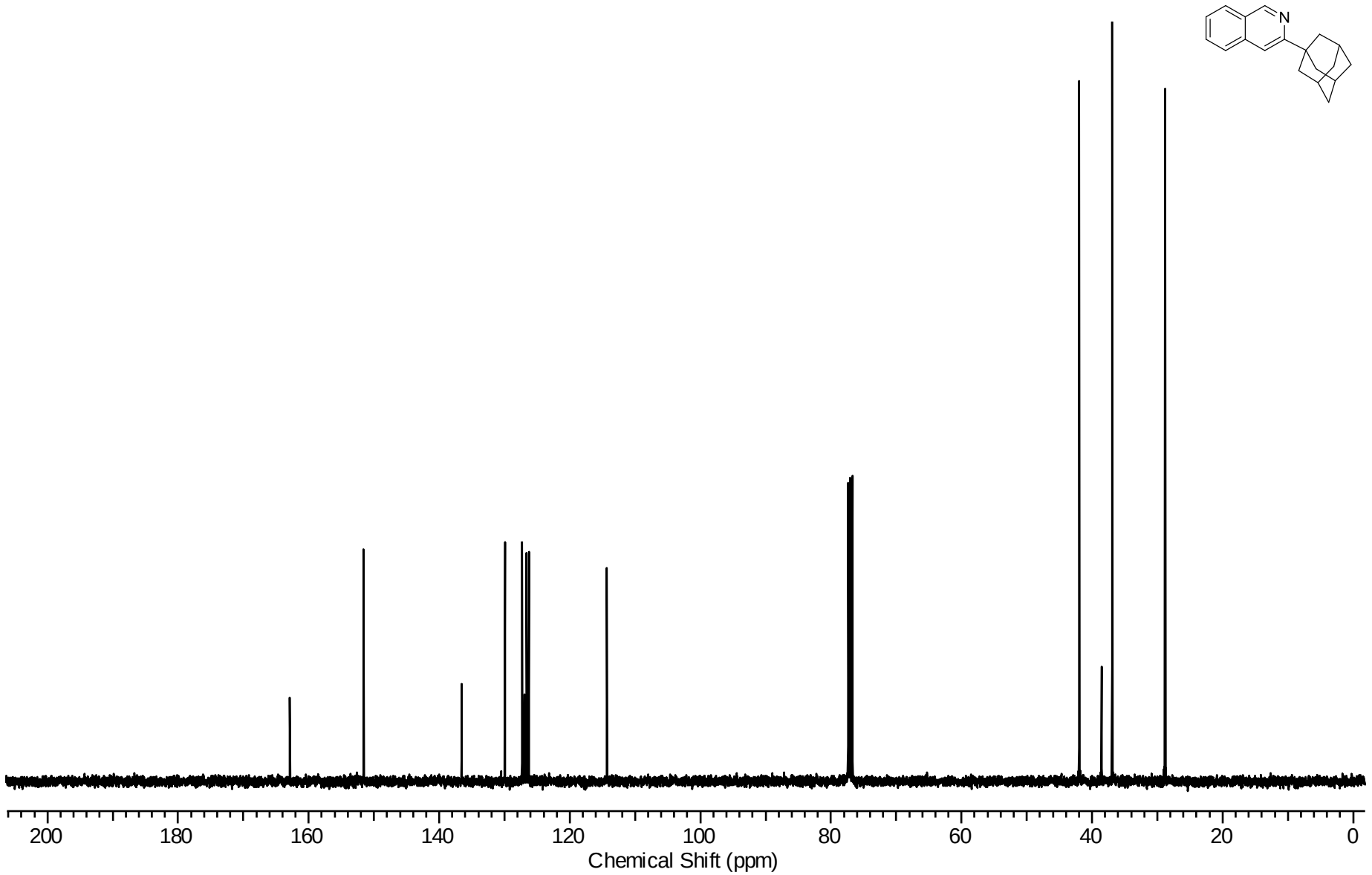
8,9,10,11-Tetrahydro-7H-cyclohepta[c]isoquinoline **4d**



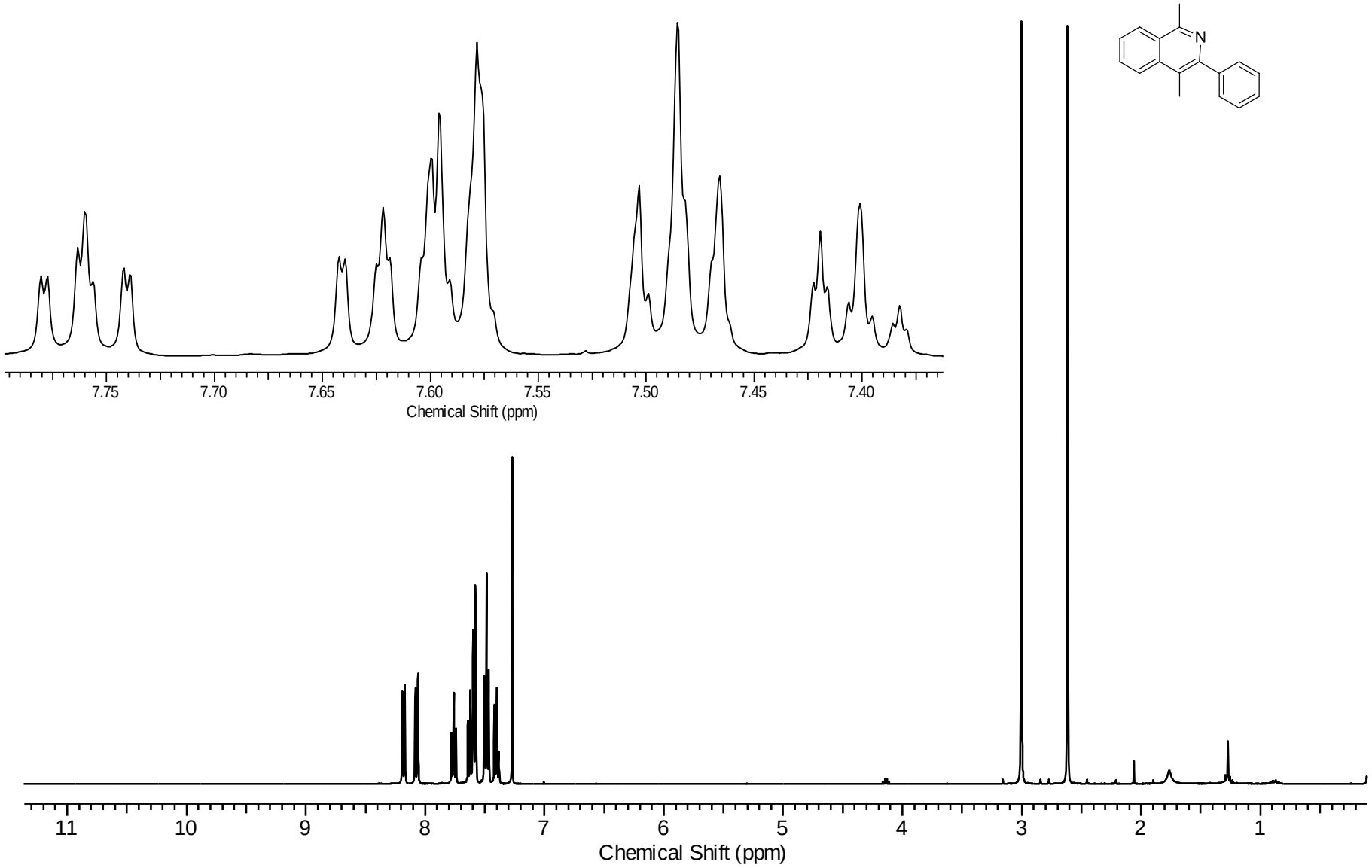
3-Adamantylisoquinoline **4e**



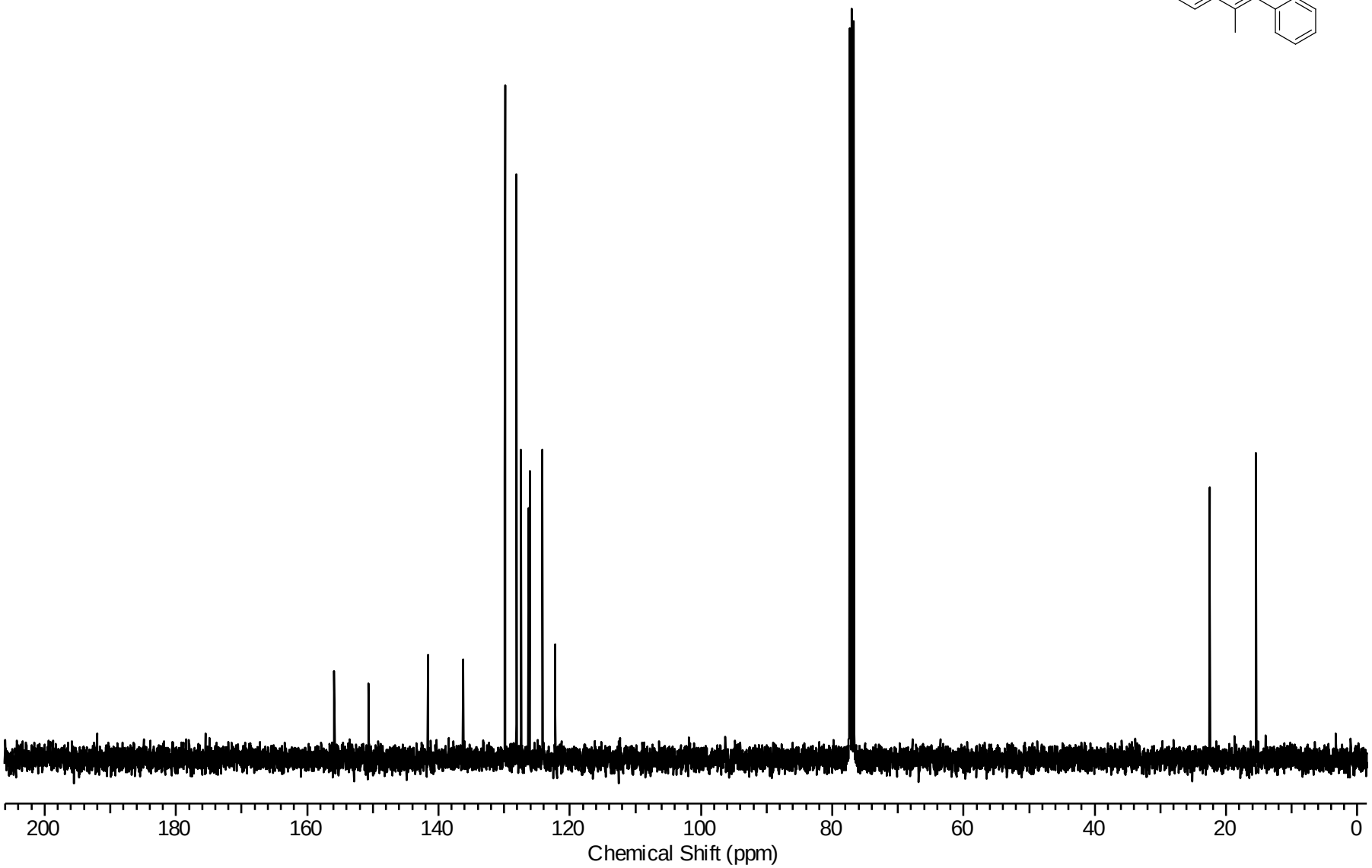
3-Adamantylisoquinoline **4e**



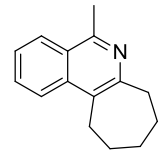
1,4-Dimethyl-3-phenylisoquinoline **4f**

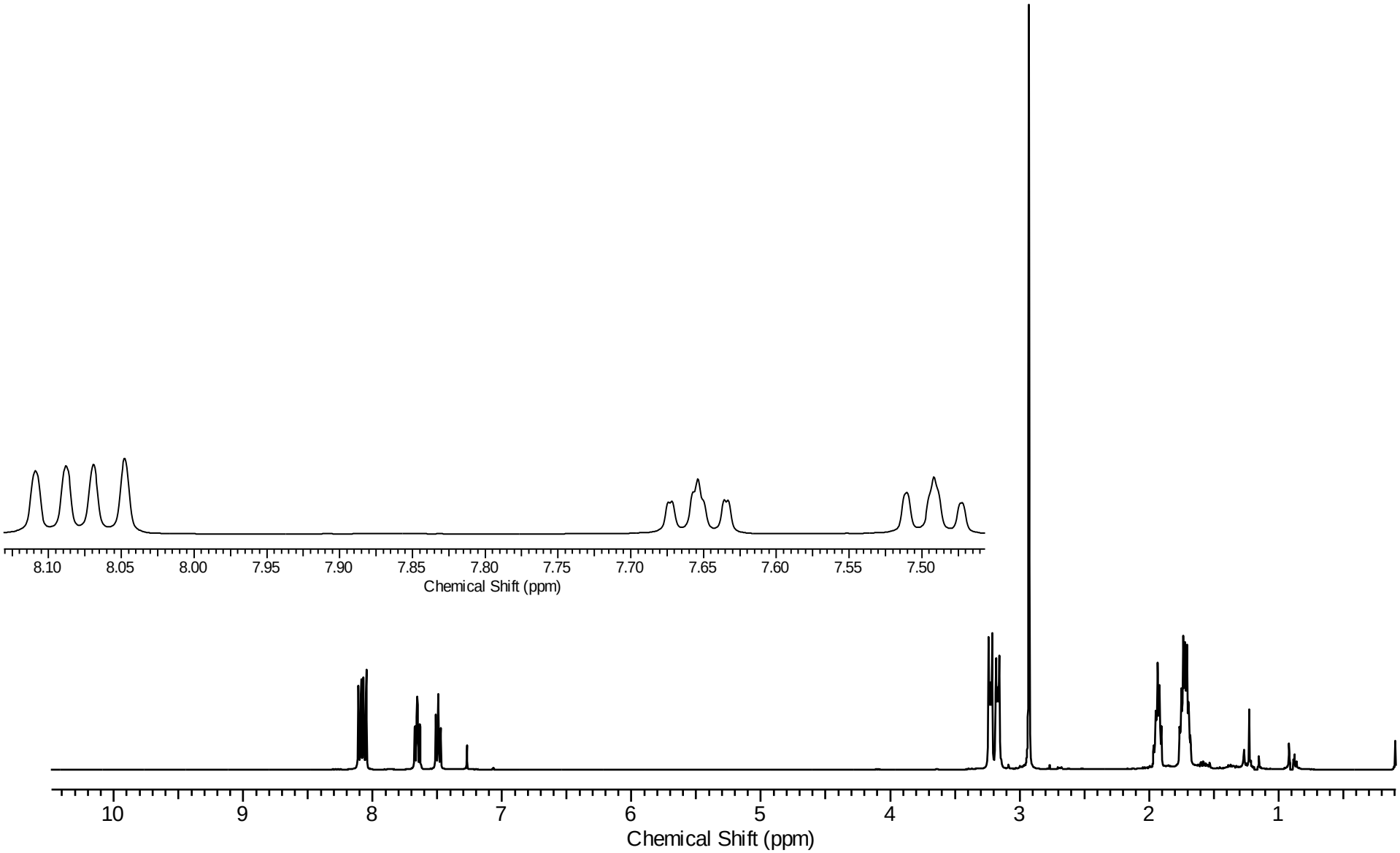


1,4-Dimethyl-3-phenylisoquinoline **4f**

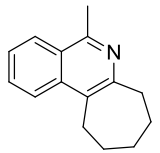


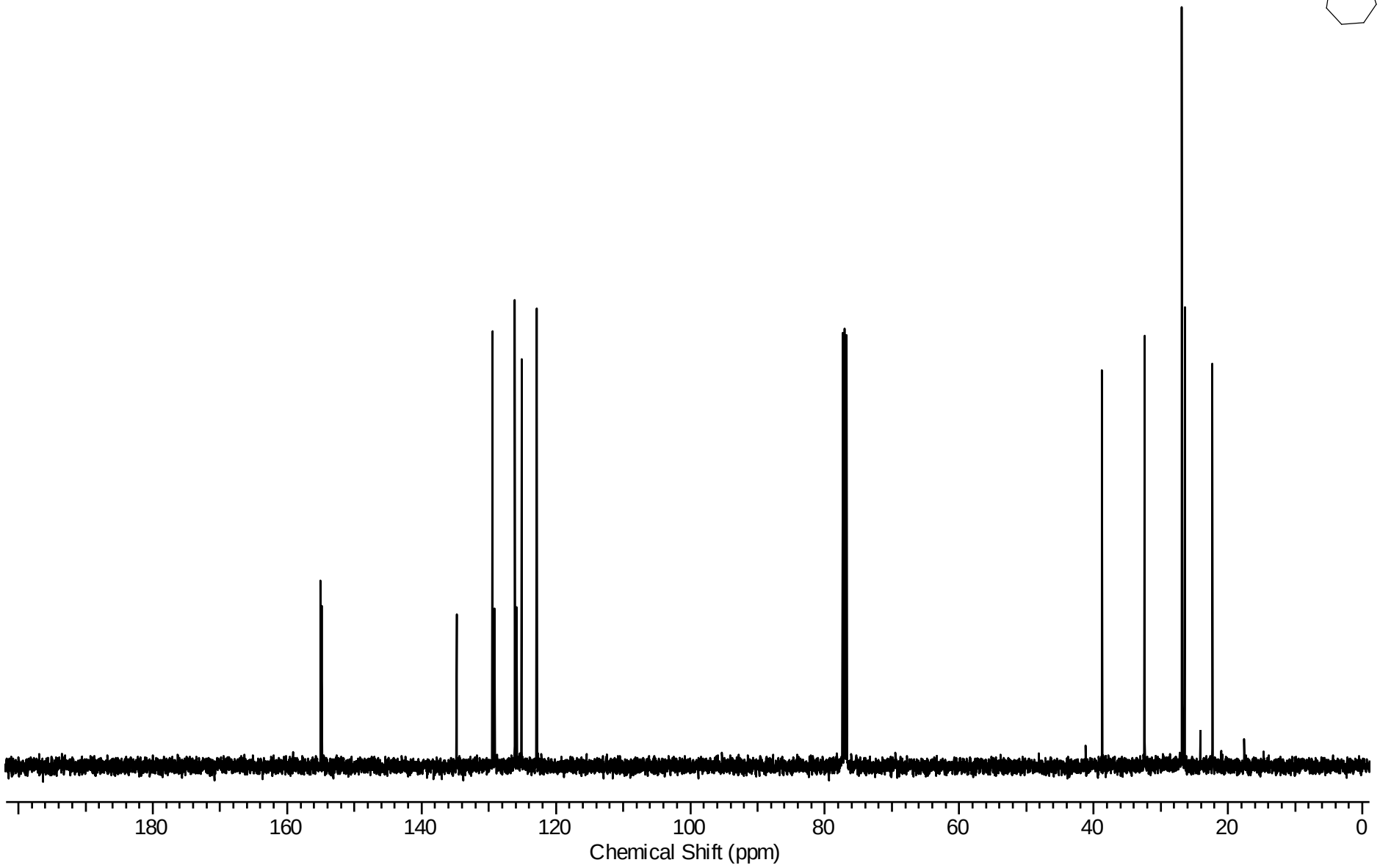
5-Methyl-8,9,10,11-tetrahydro-7H-cyclohepta[c]isoquinoline **4g**



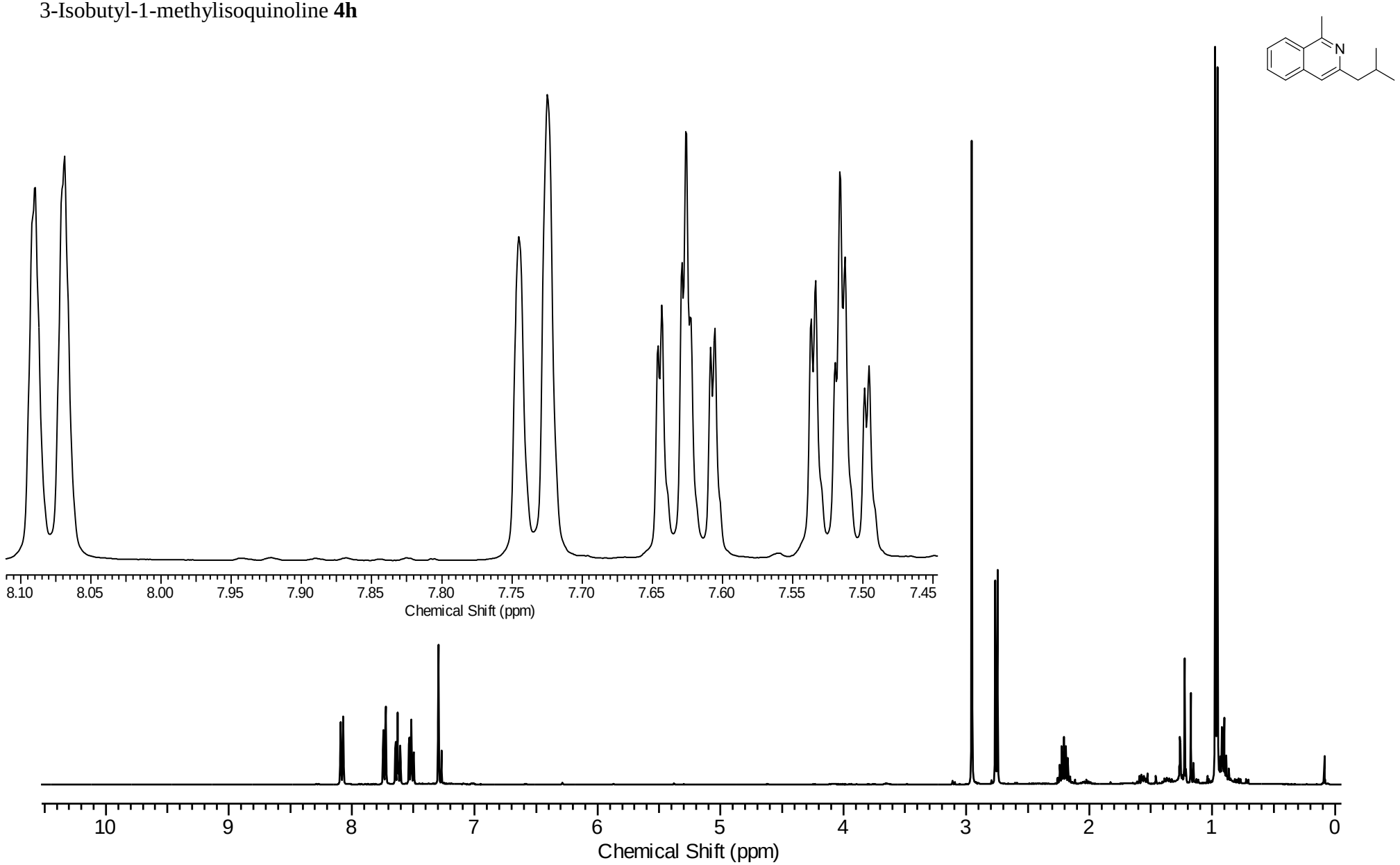


5-Methyl-8,9,10,11-tetrahydro-7H-cyclohepta[c]isoquinoline **4g**

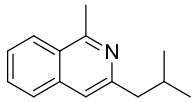


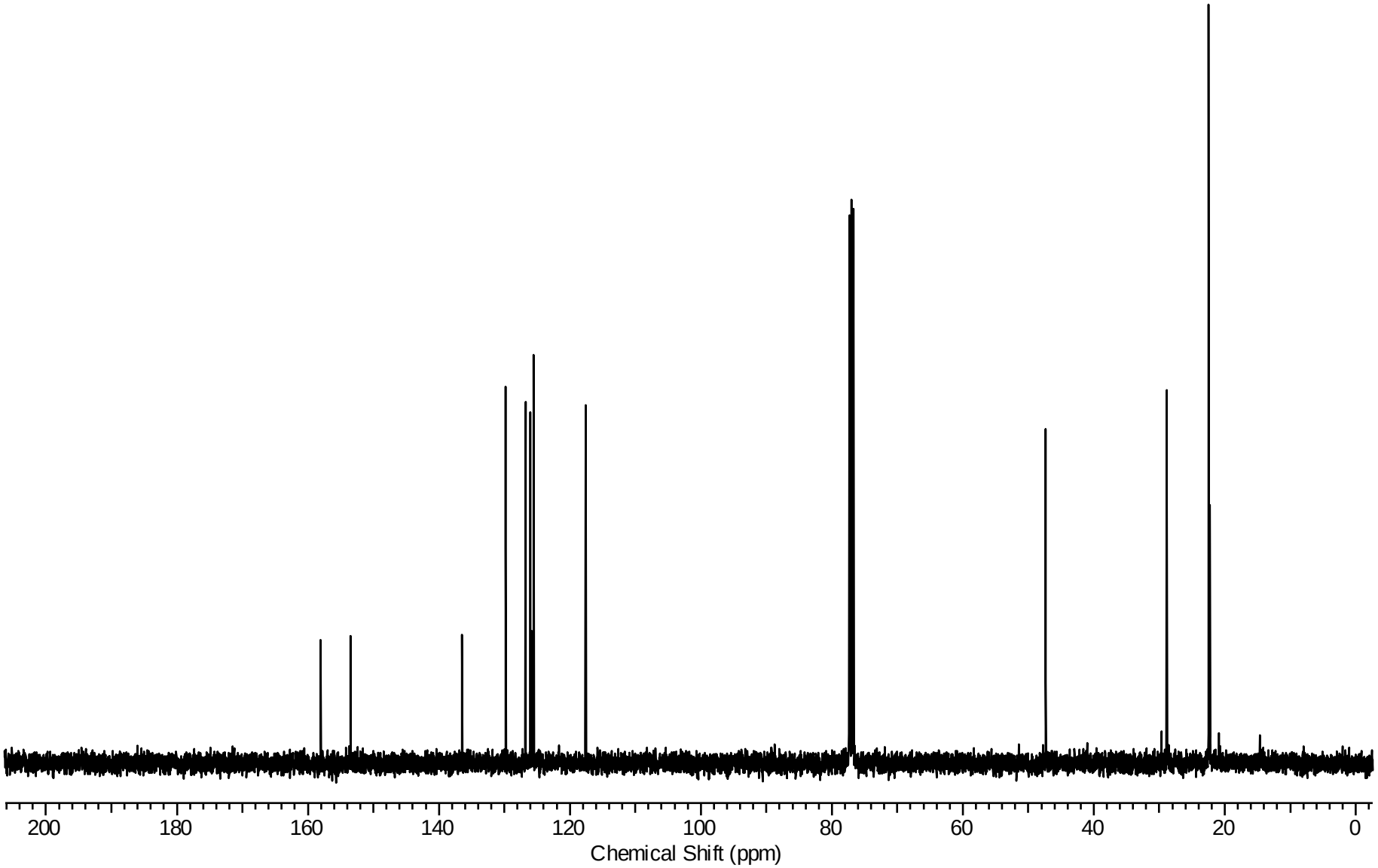


3-Isobutyl-1-methylisoquinoline **4h**

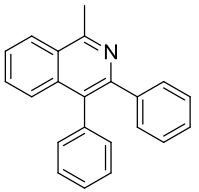


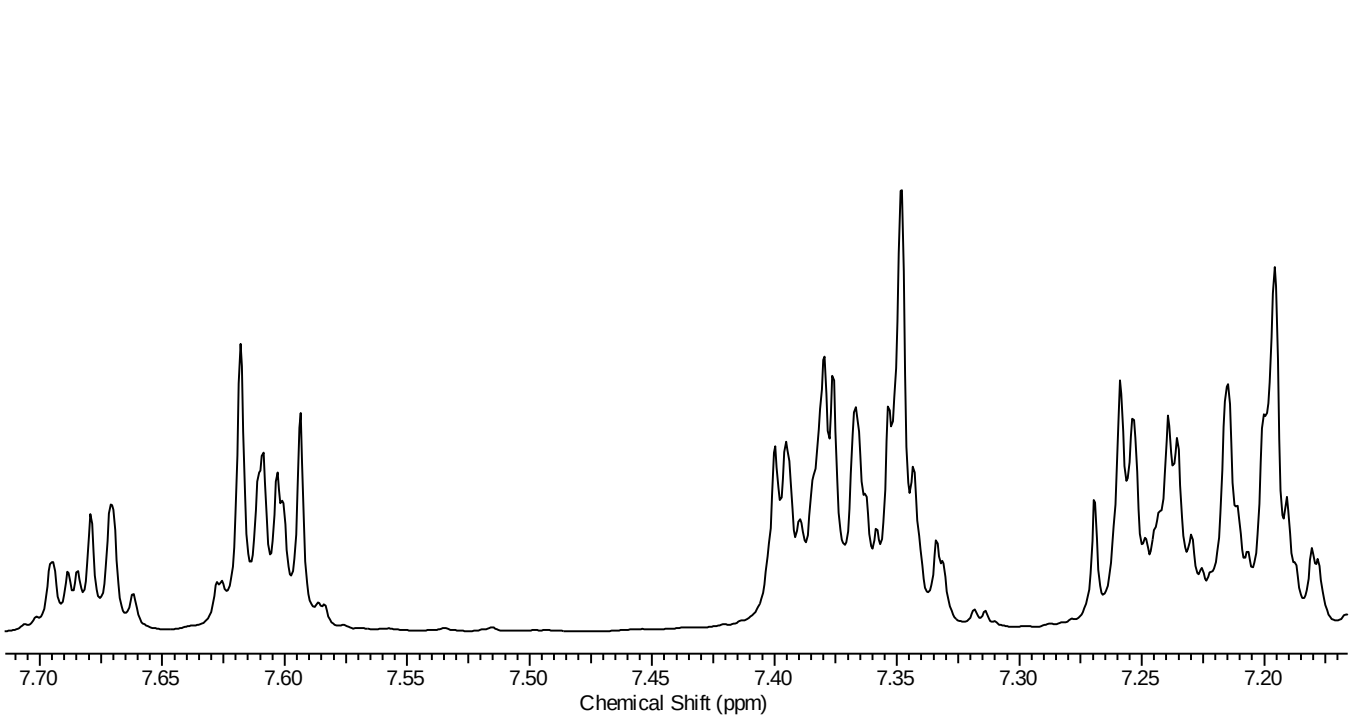
3-Isobutyl-1-methylisoquinoline **4h**

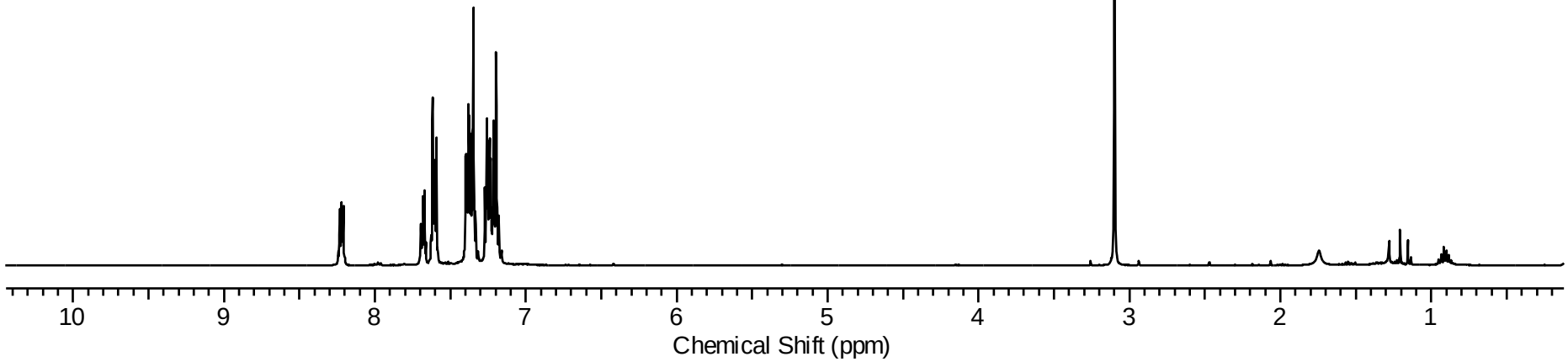




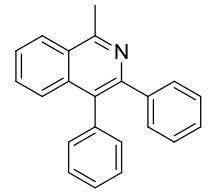
1-Methyl-3,4-diphenylisoquinoline **4i**

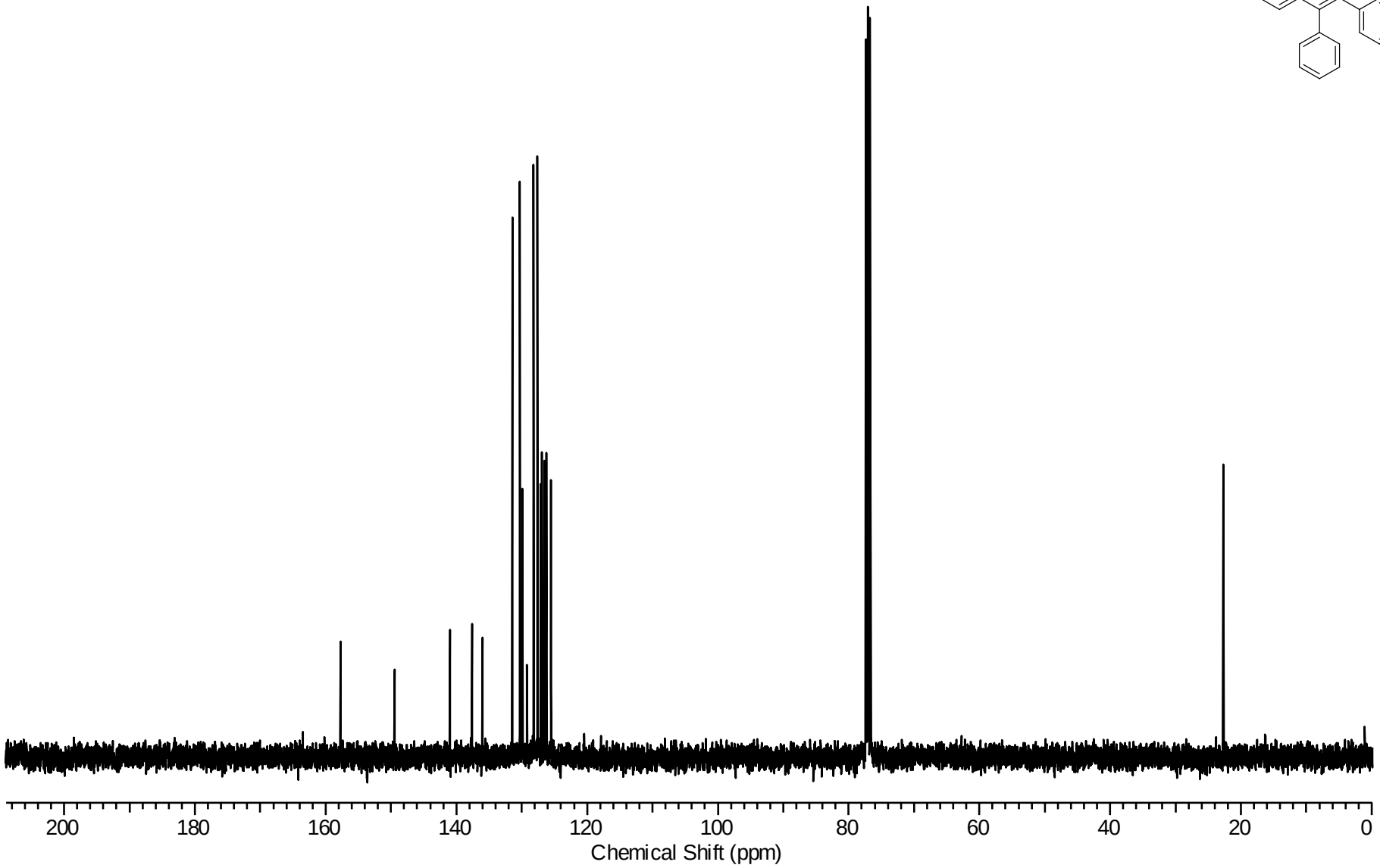




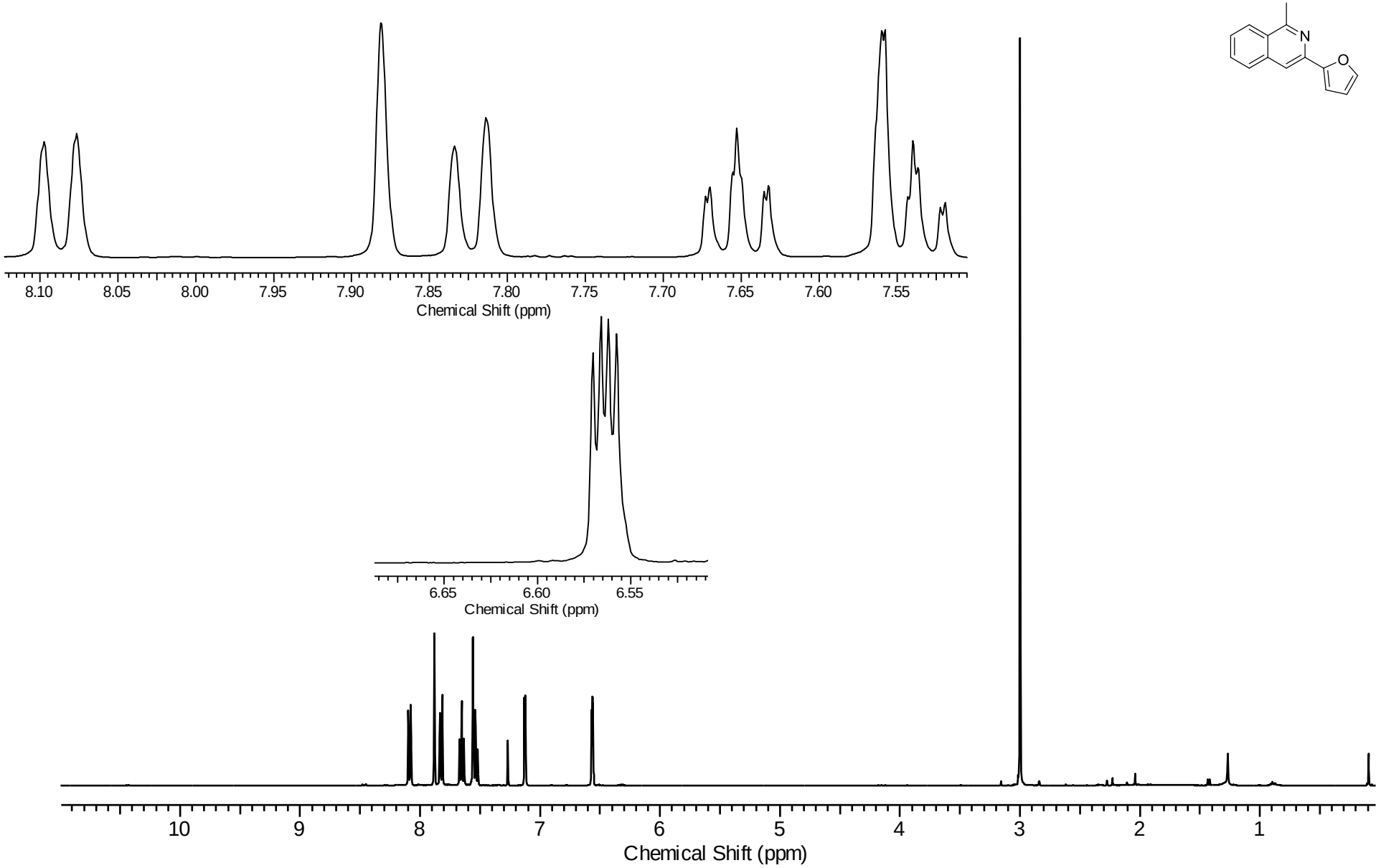


1-Methyl-3,4-diphenylisoquinoline **4i**

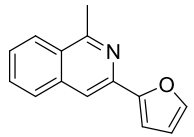


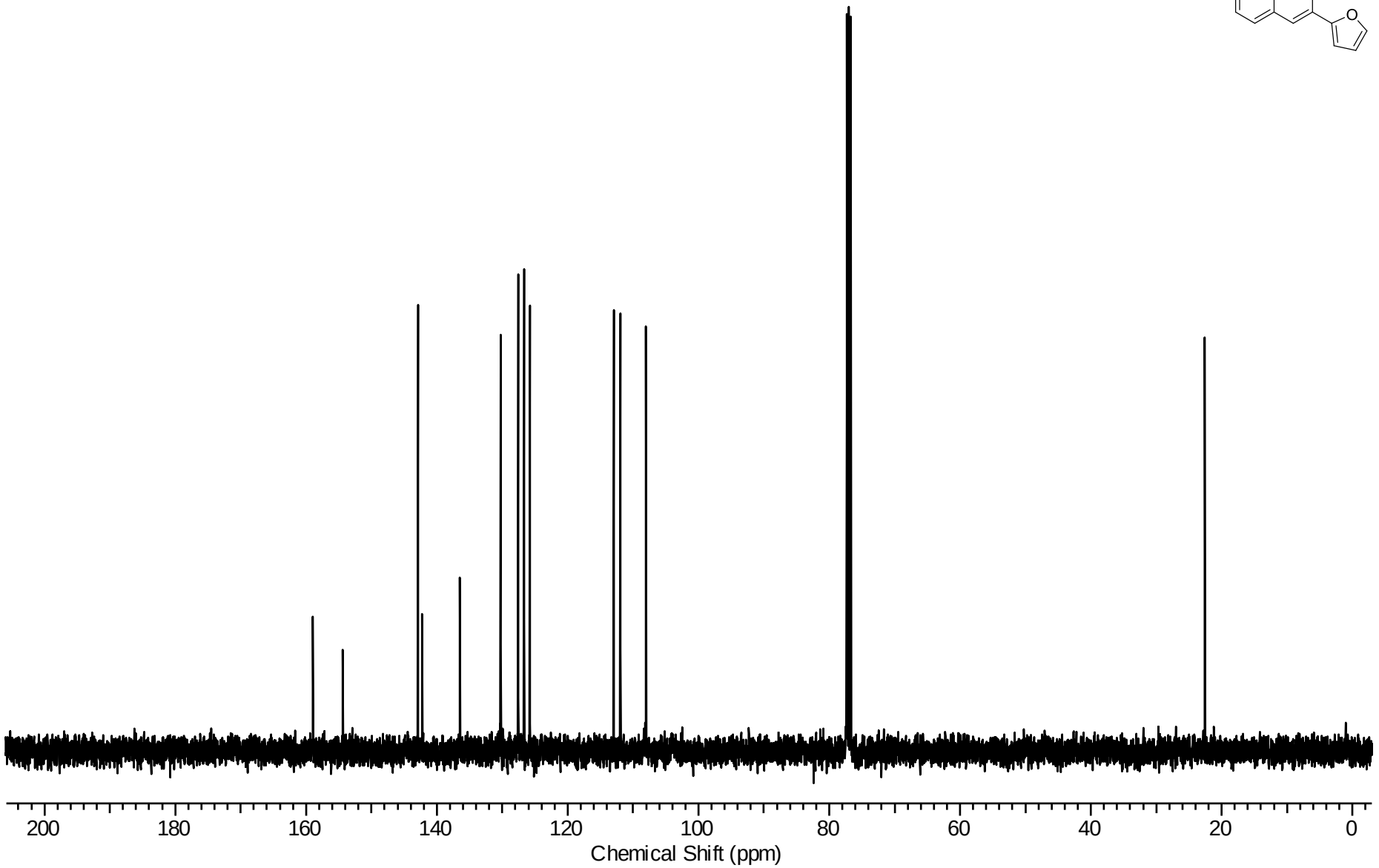


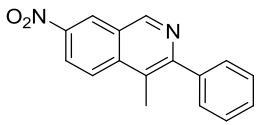
3-(Furan-2-yl)-1-methylisoquinoline **4j**



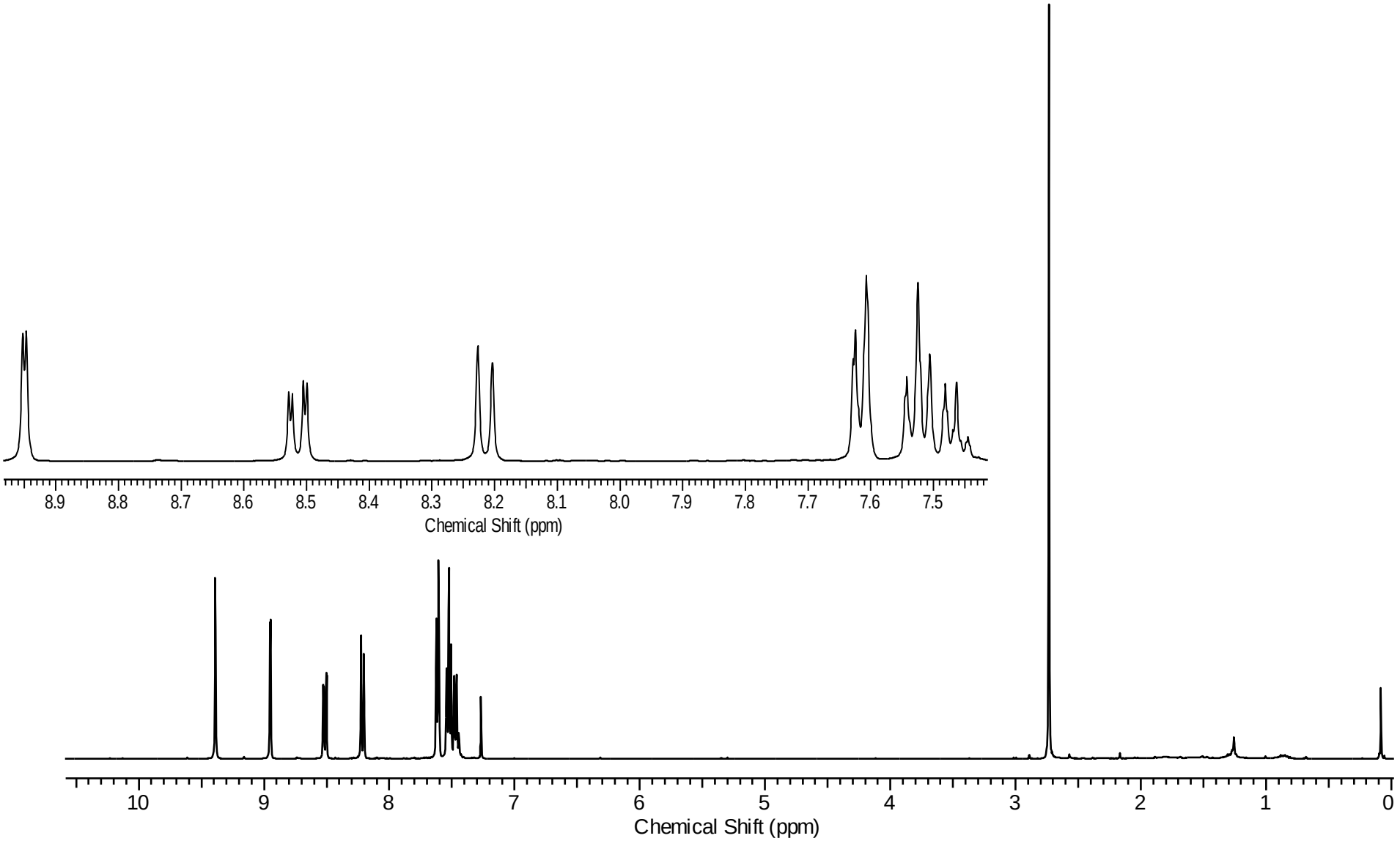
3-(Furan-2-yl)-1-methylisoquinoline **4j**

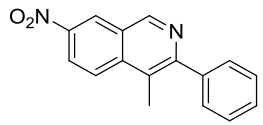




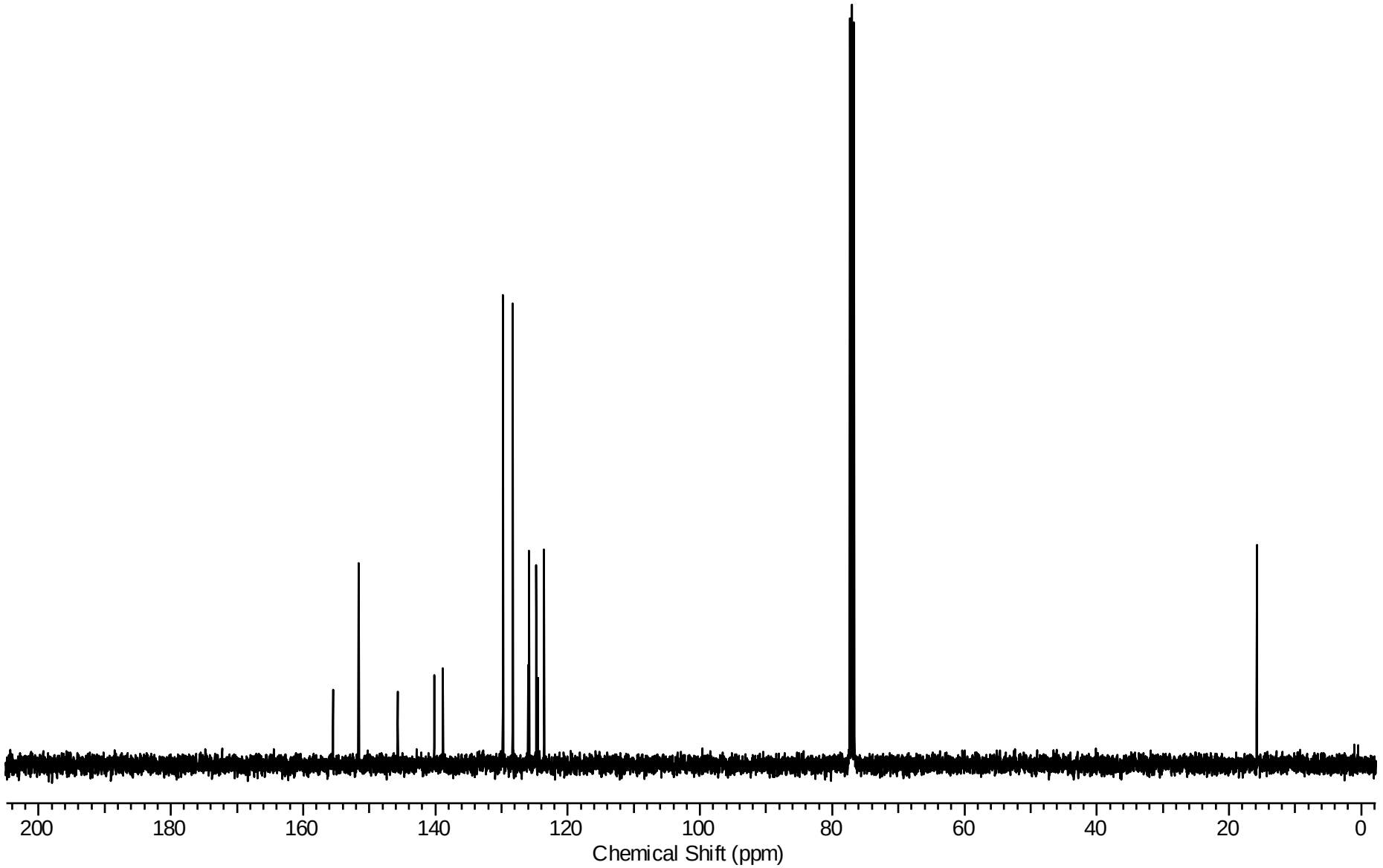


4-Methyl-7-nitro-3-phenylisoquinoline **4k**

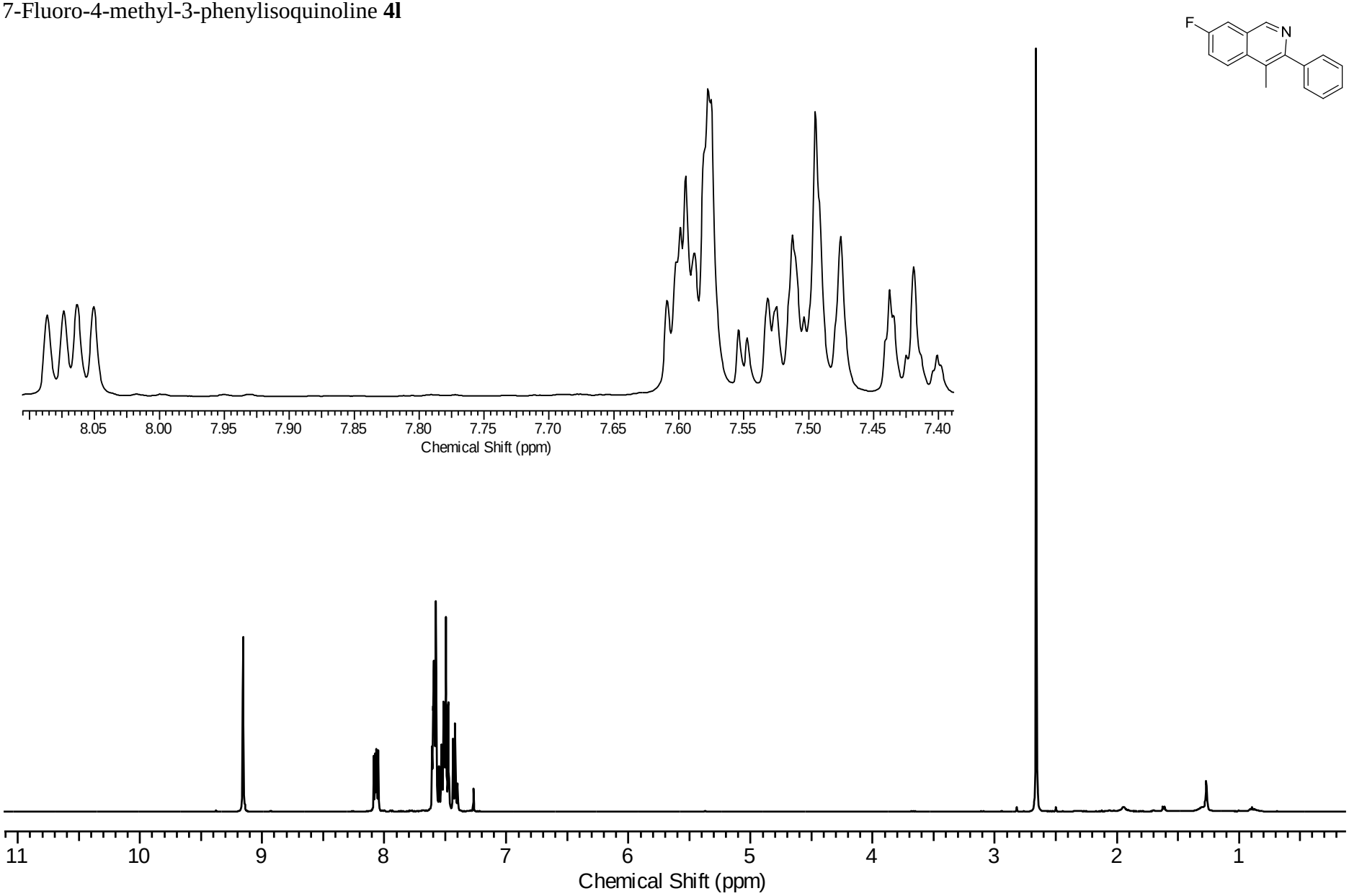




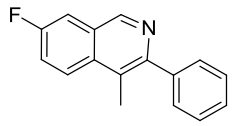
4-Methyl-7-nitro-3-phenylisoquinoline **4k**

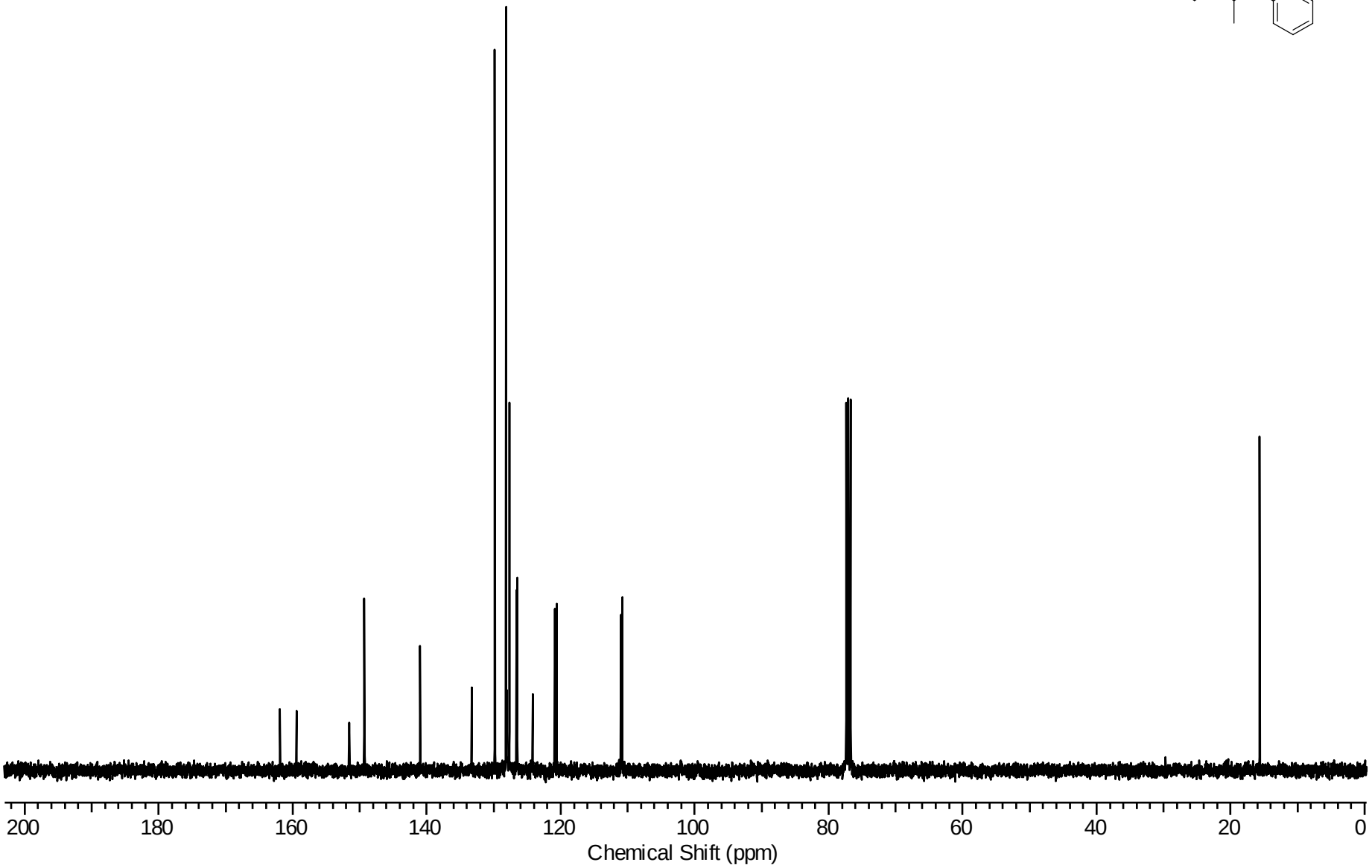


7-Fluoro-4-methyl-3-phenylisoquinoline **4l**

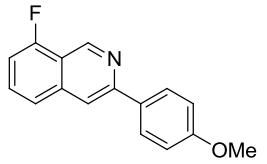


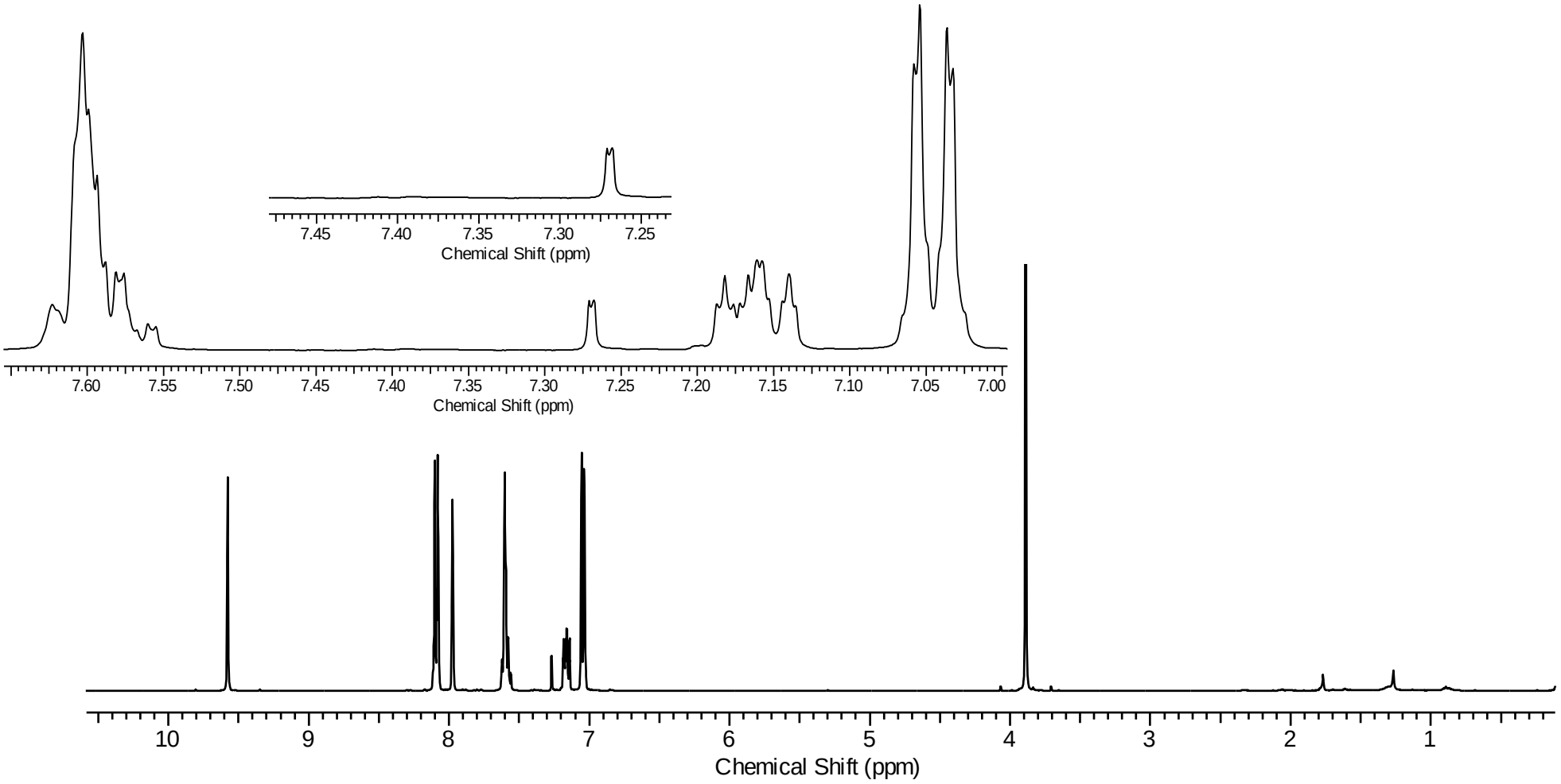
7-Fluoro-4-methyl-3-phenylisoquinoline **4l**



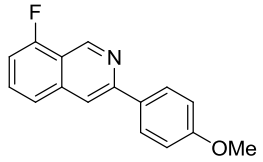


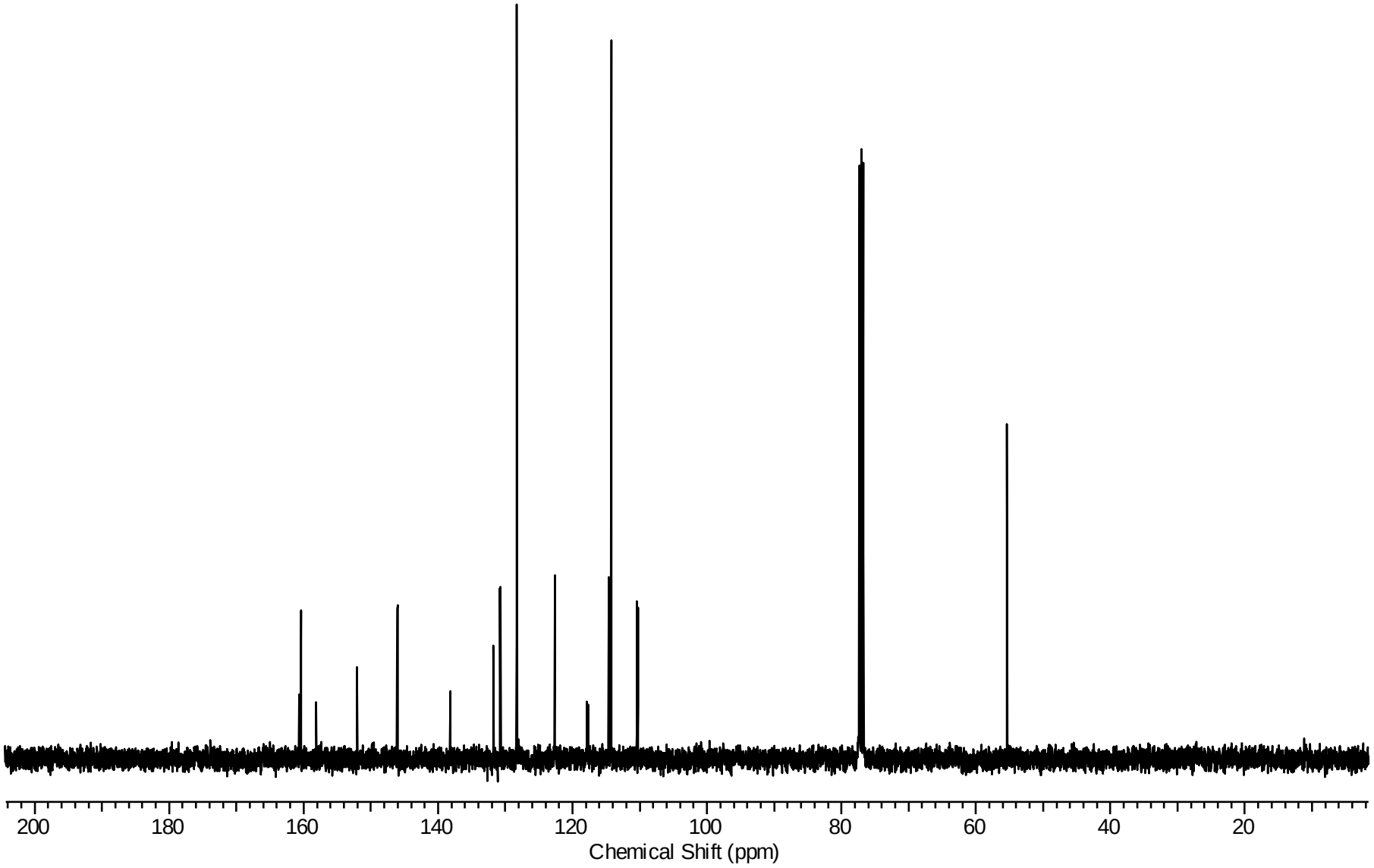
8-Fluoro-3-(4-methoxyphenyl)isoquinoline **4m**



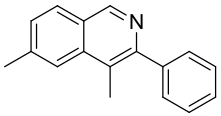


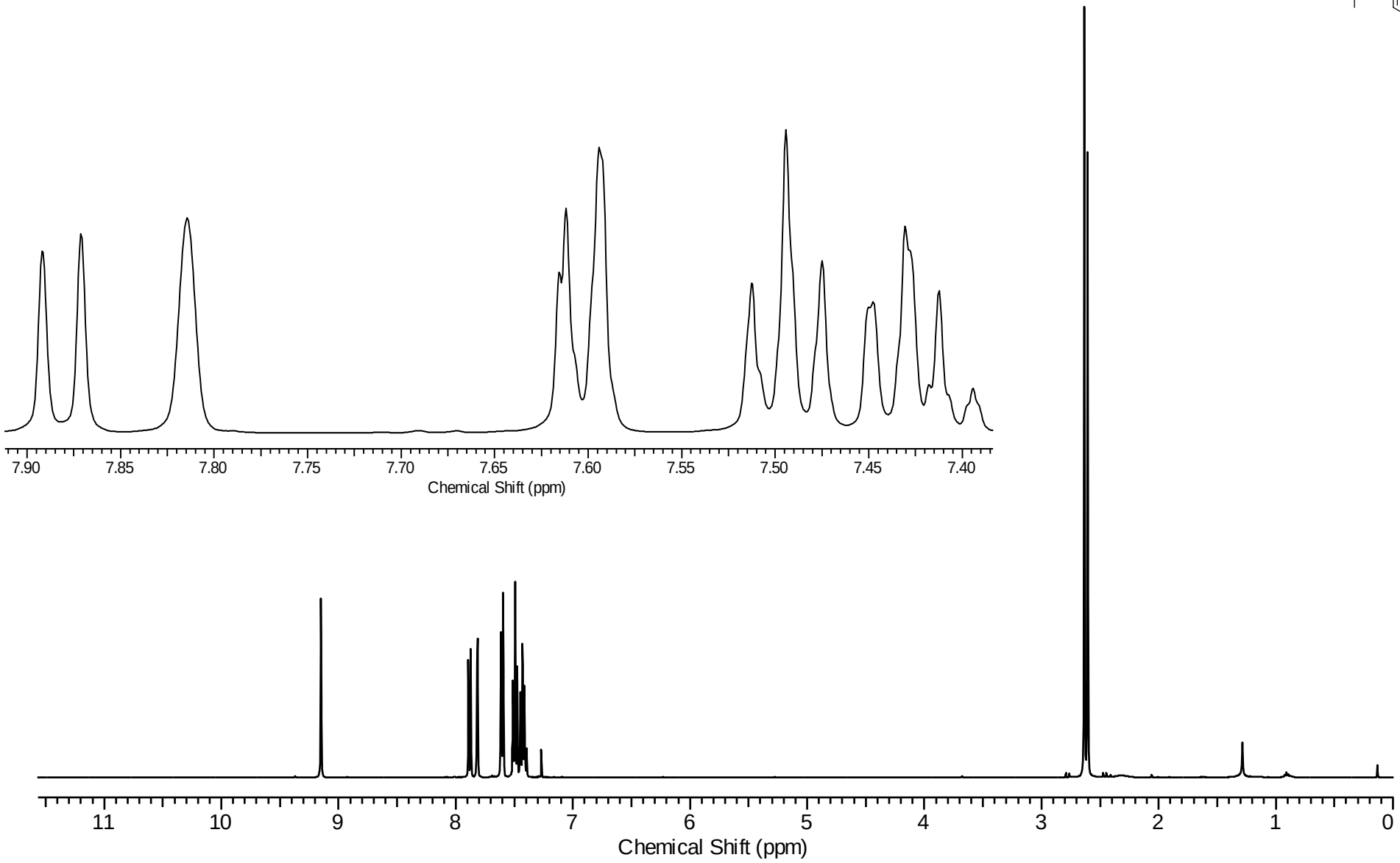
8-Fluoro-3-(4-methoxyphenyl)isoquinoline **4m**



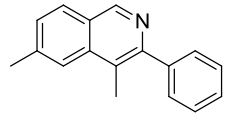


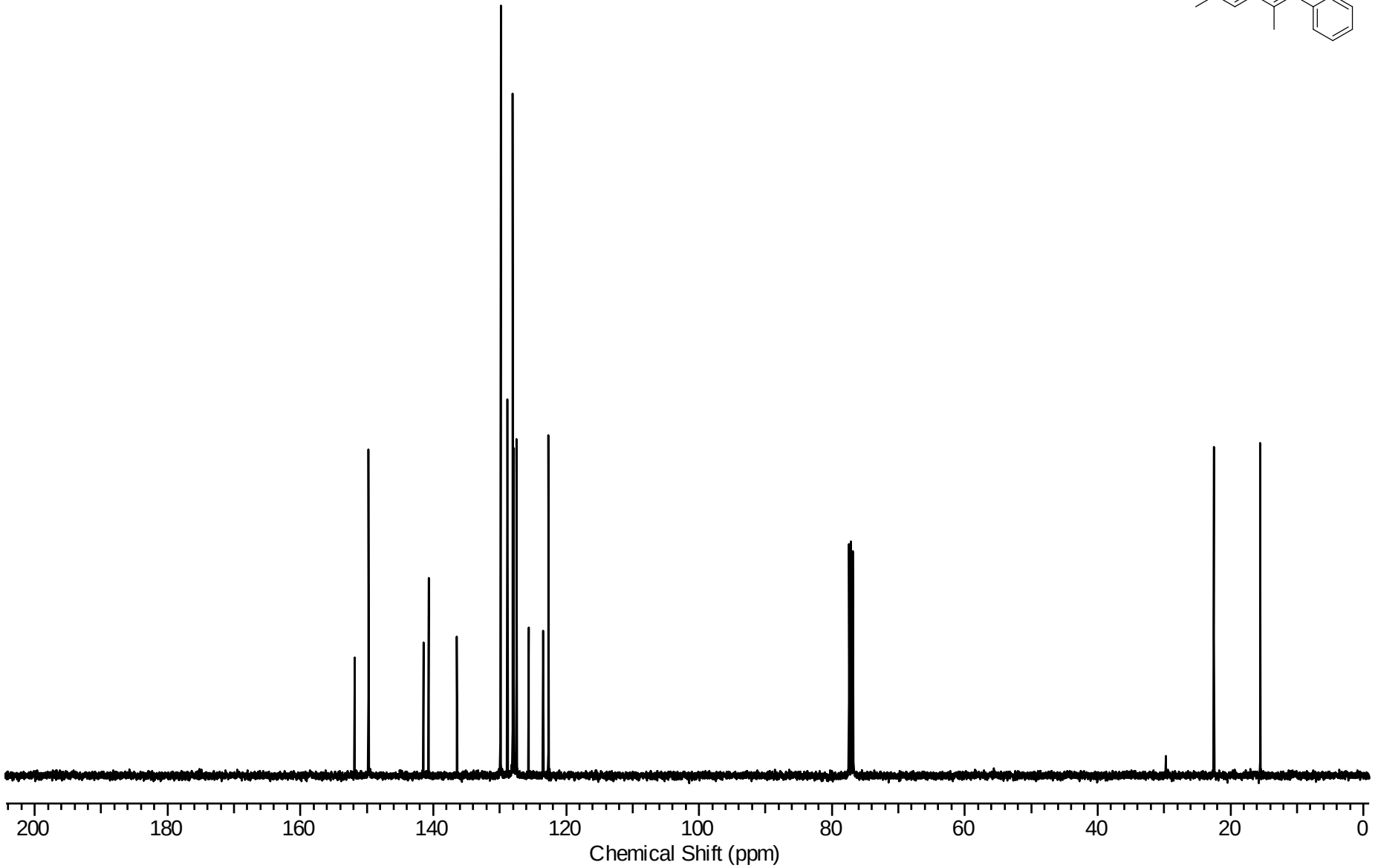
4,6-Dimethyl-3-phenylisoquinoline **4n**



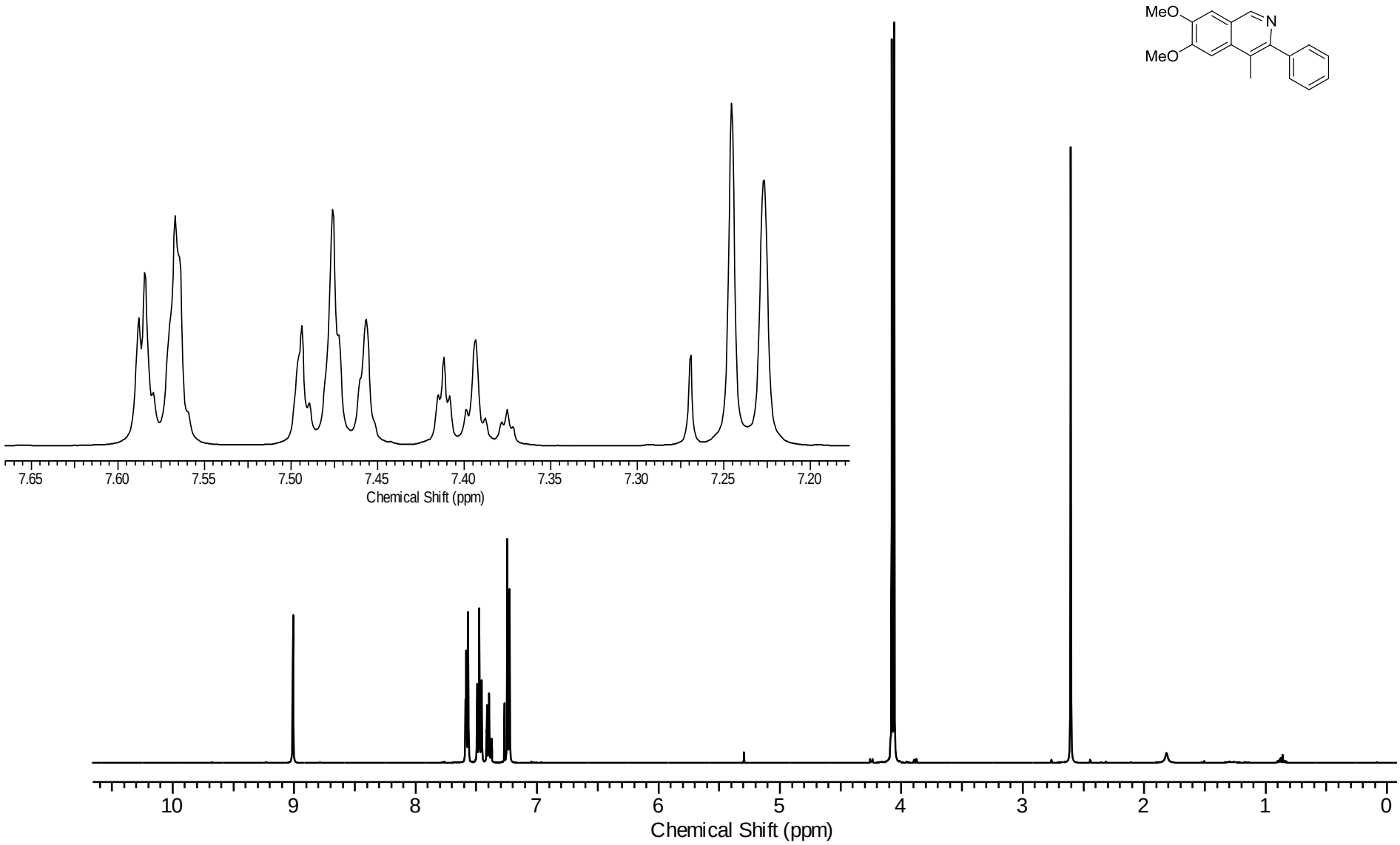


4,6-Dimethyl-3-phenylisoquinoline **4n**

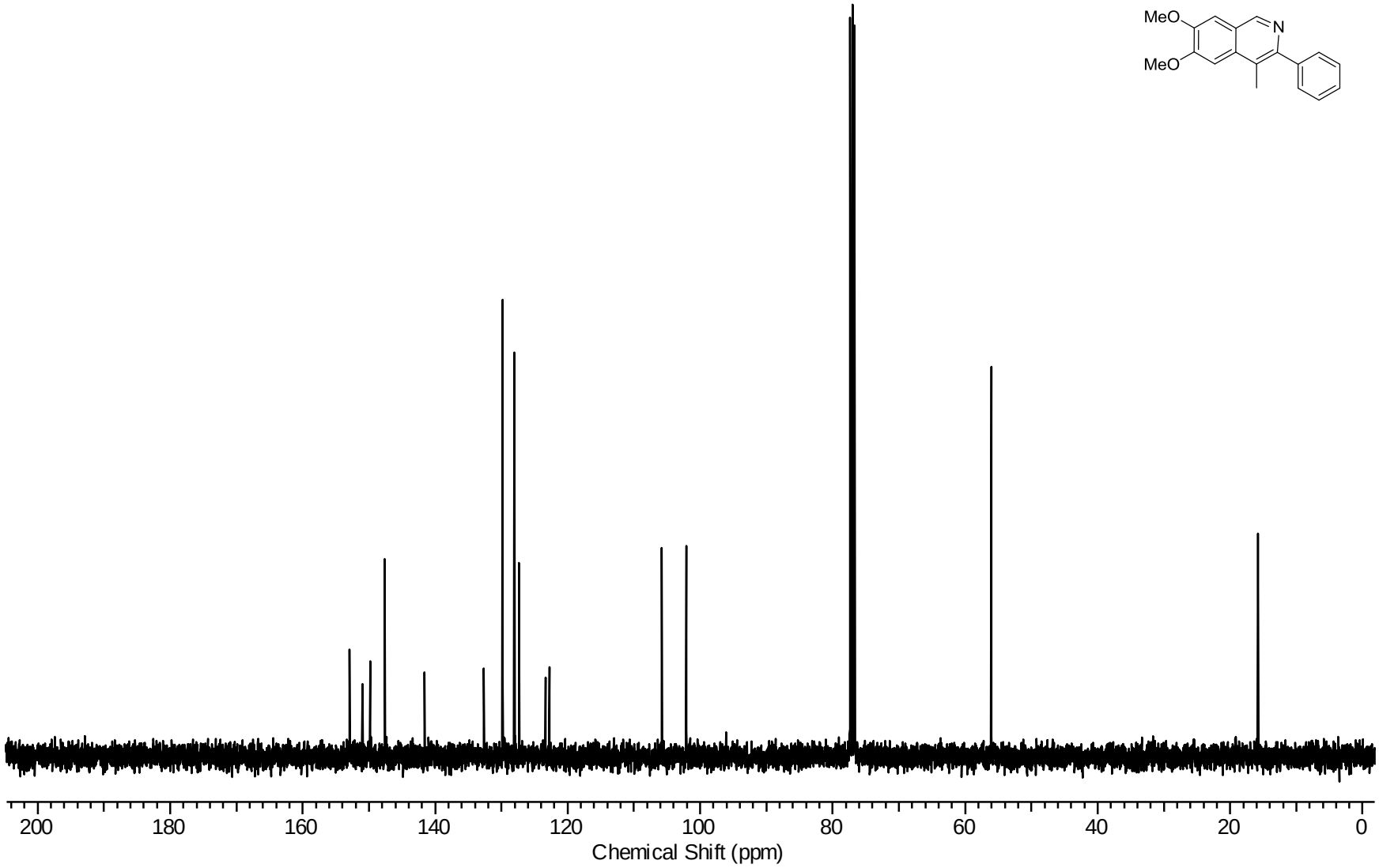




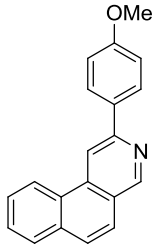
6,7-Dimethoxy-4-methyl-3-phenylisoquinoline **4o**

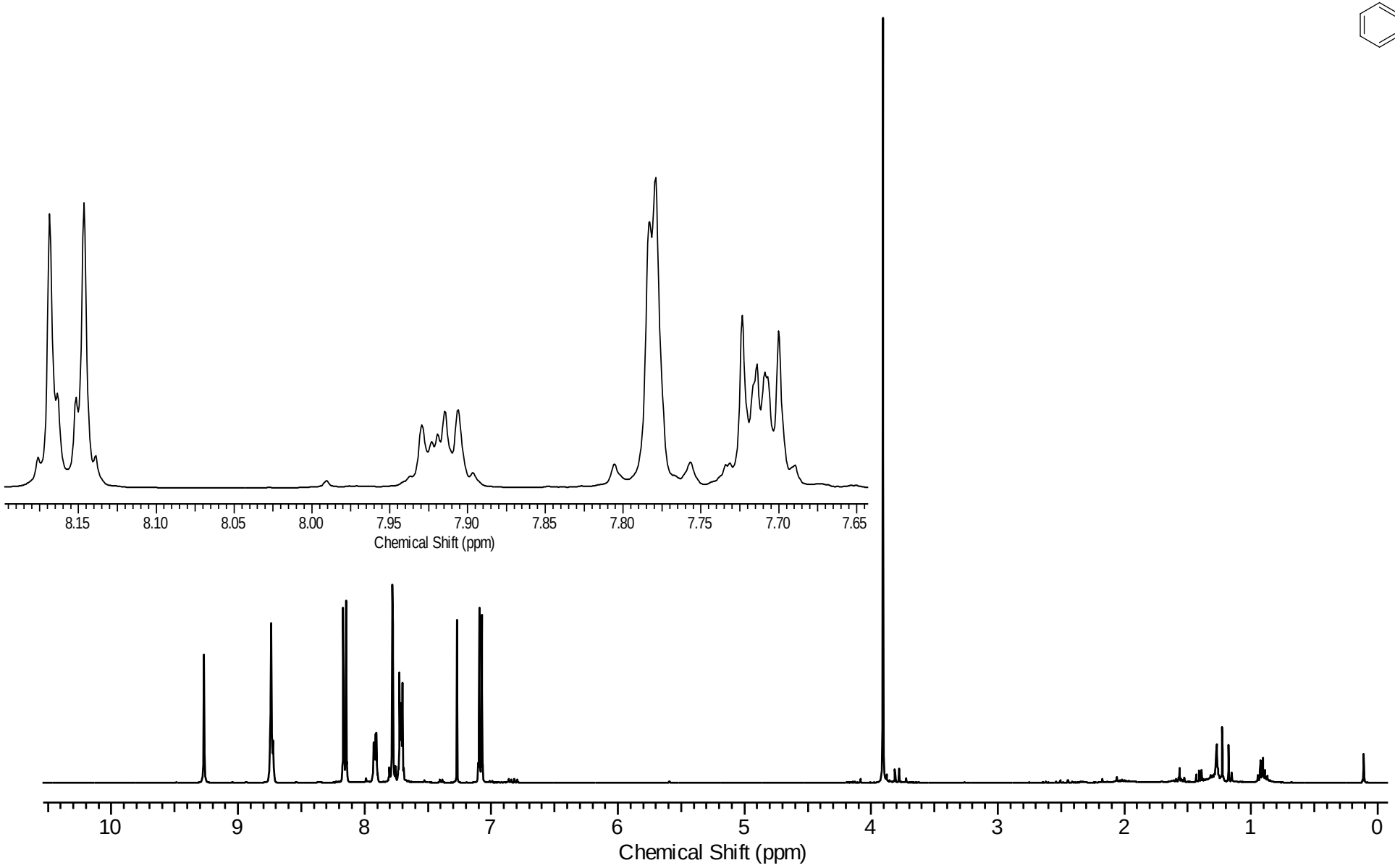


6,7-Dimethoxy-4-methyl-3-phenylisoquinoline **4o**

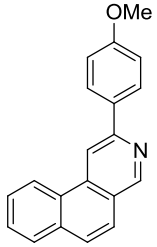


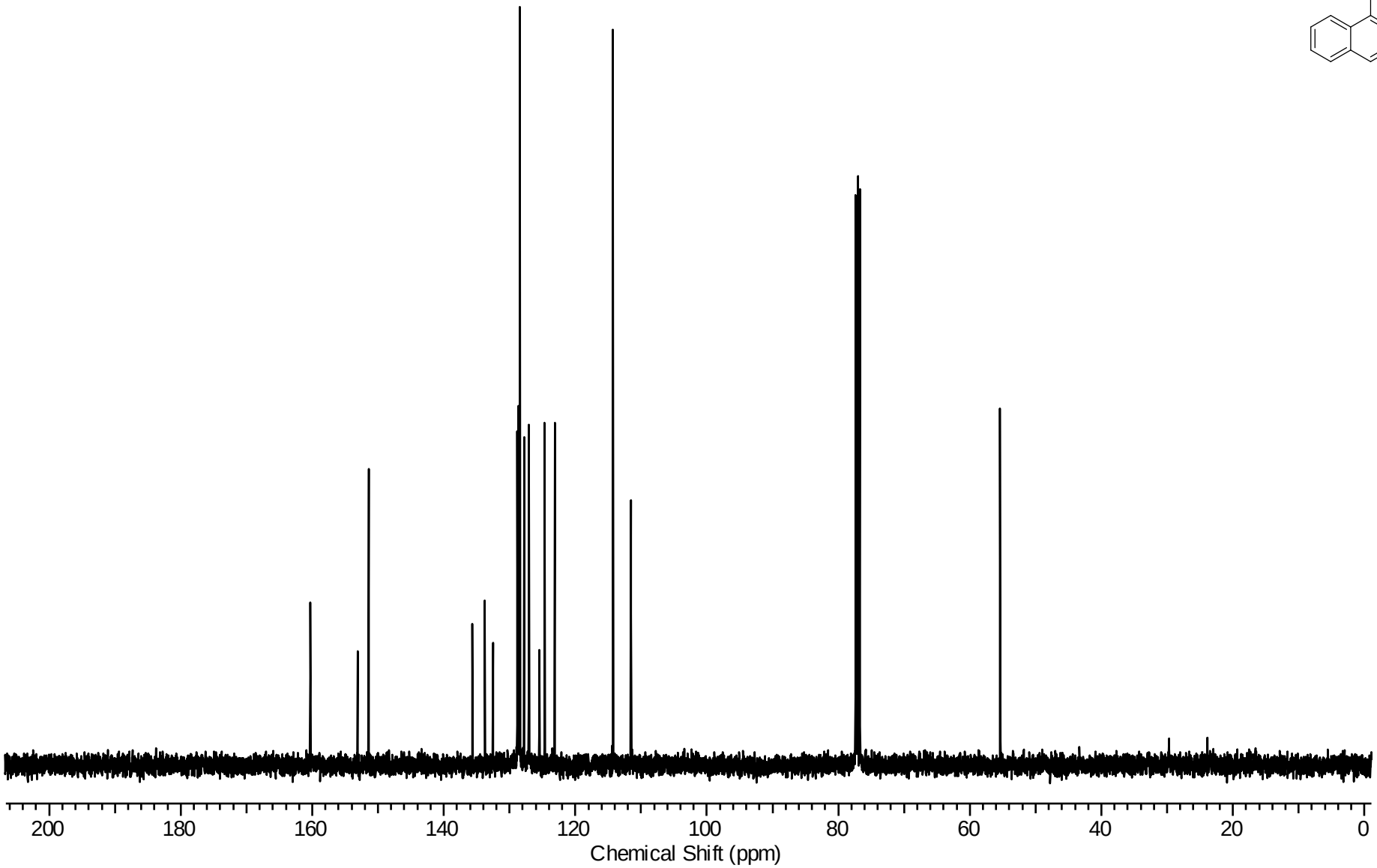
2-(4-Methoxyphenyl)benzo[f]isoquinoline **4p**



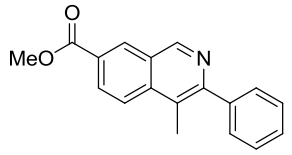


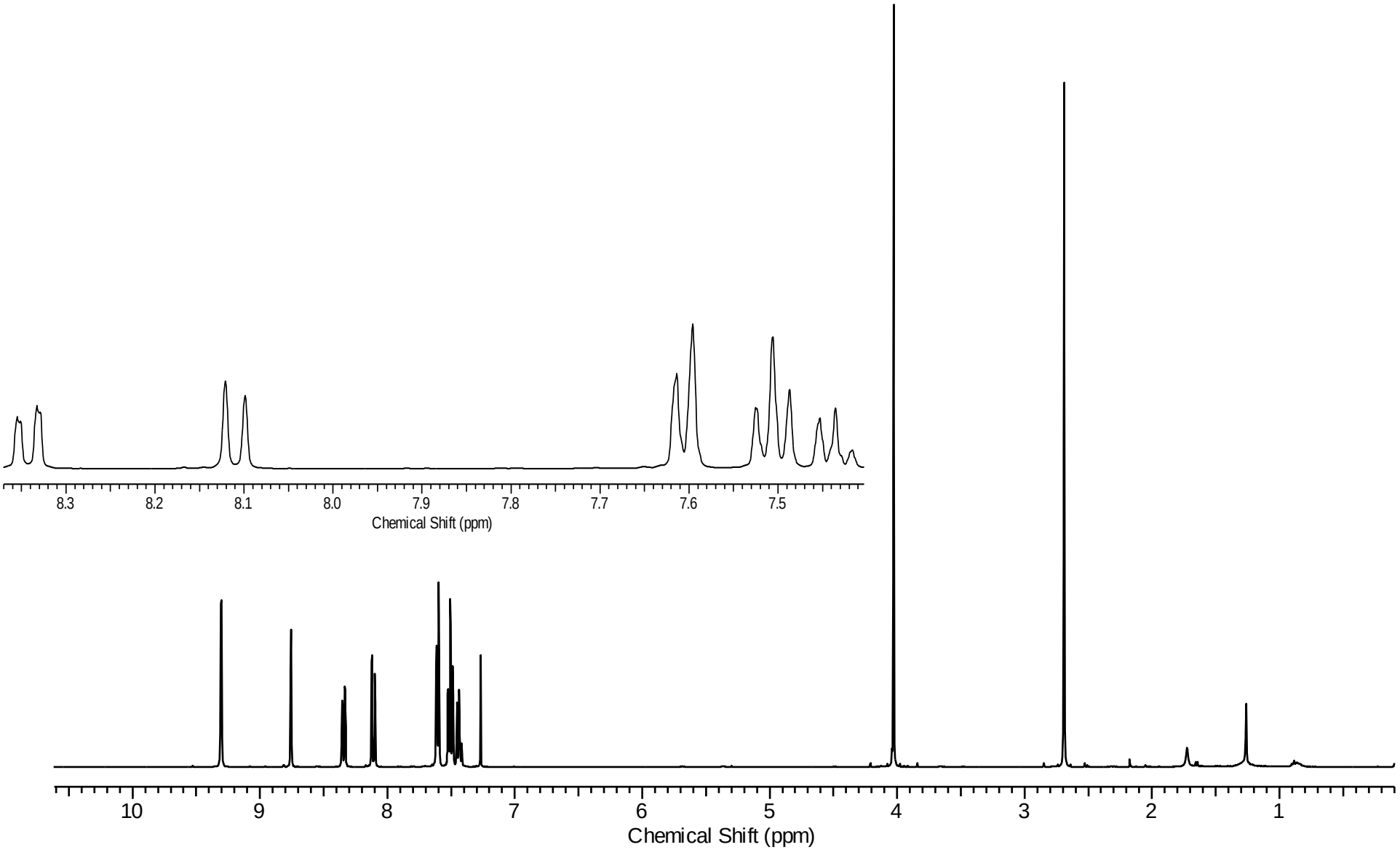
2-(4-Methoxyphenyl)benzo[f]isoquinoline **4p**



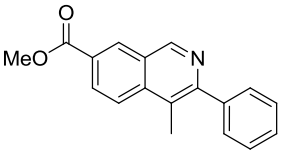


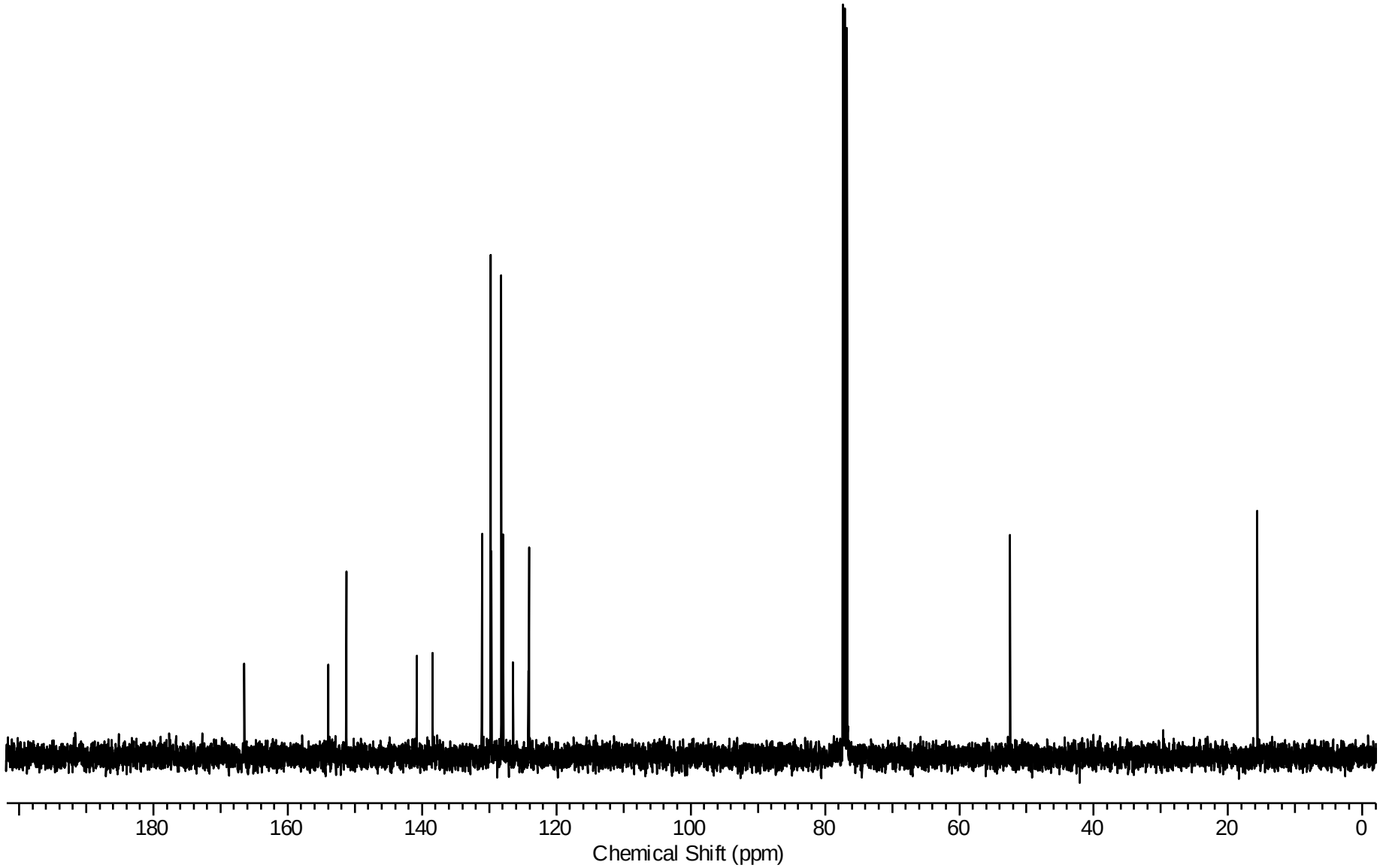
Methyl 4-methyl-3-phenylisoquinoline-7-carboxylate **4q**



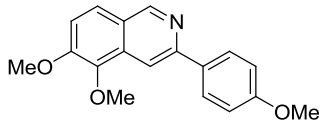


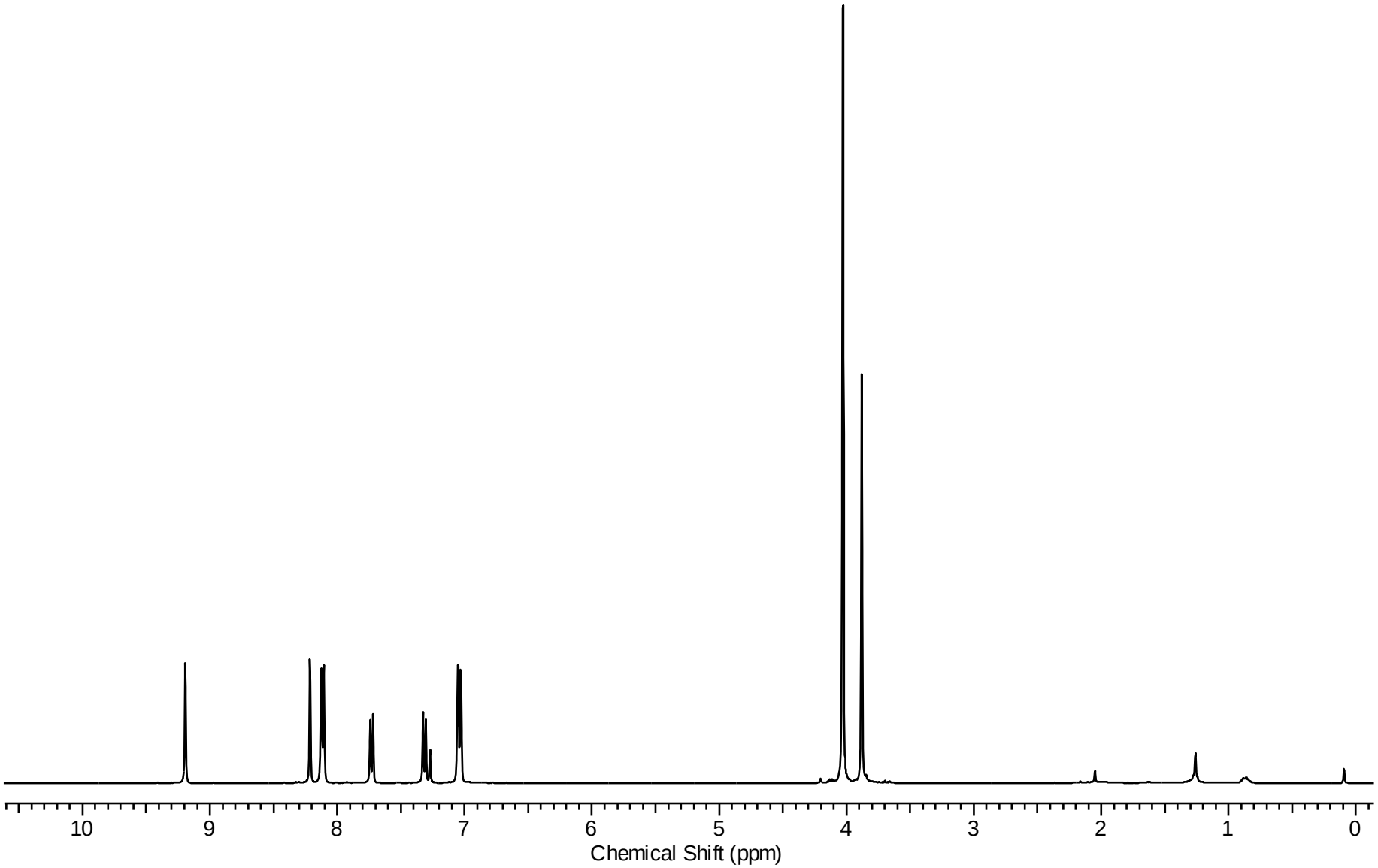
Methyl 4-methyl-3-phenylisoquinoline-7-carboxylate **4q**



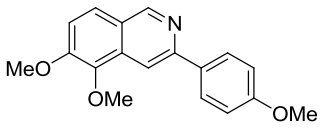


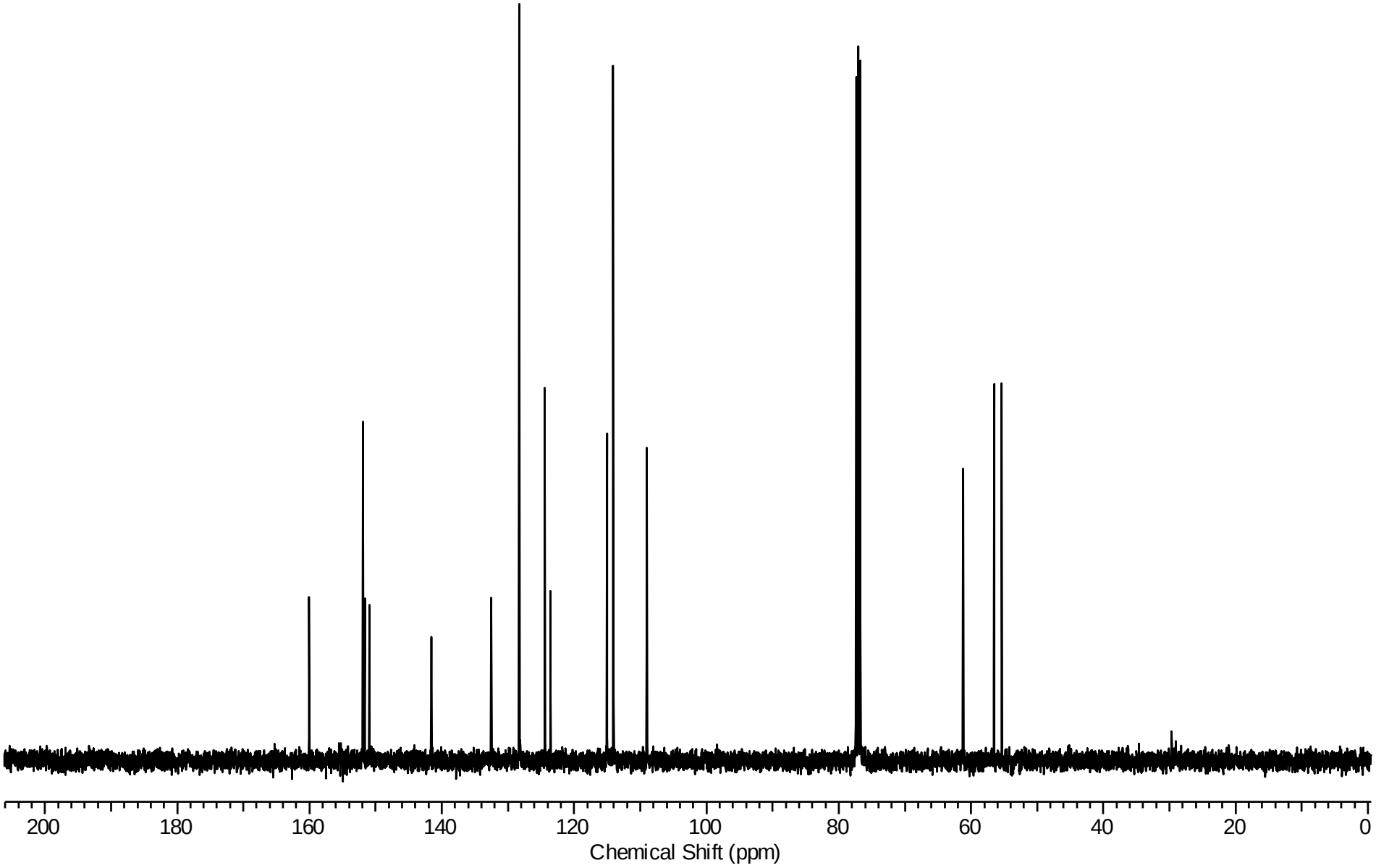
5,6-Dimethoxy-3-(4-methoxyphenyl)isoquinoline **4r**



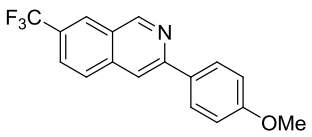


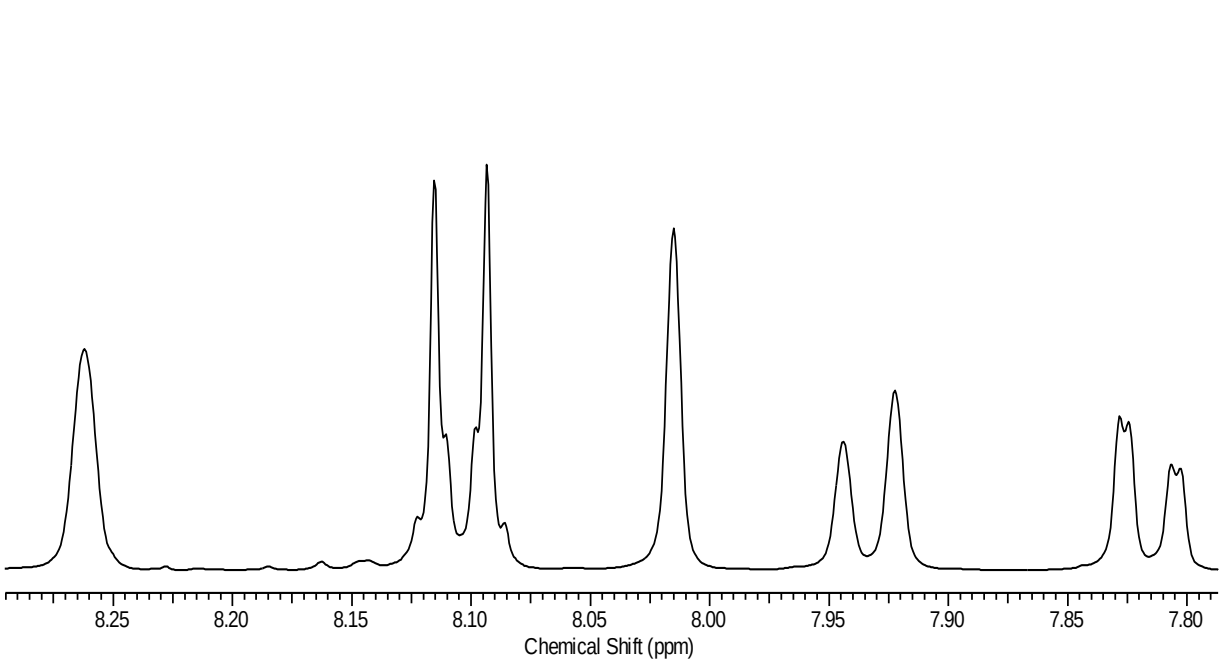
5,6-Dimethoxy-3-(4-methoxyphenyl)isoquinoline **4r**

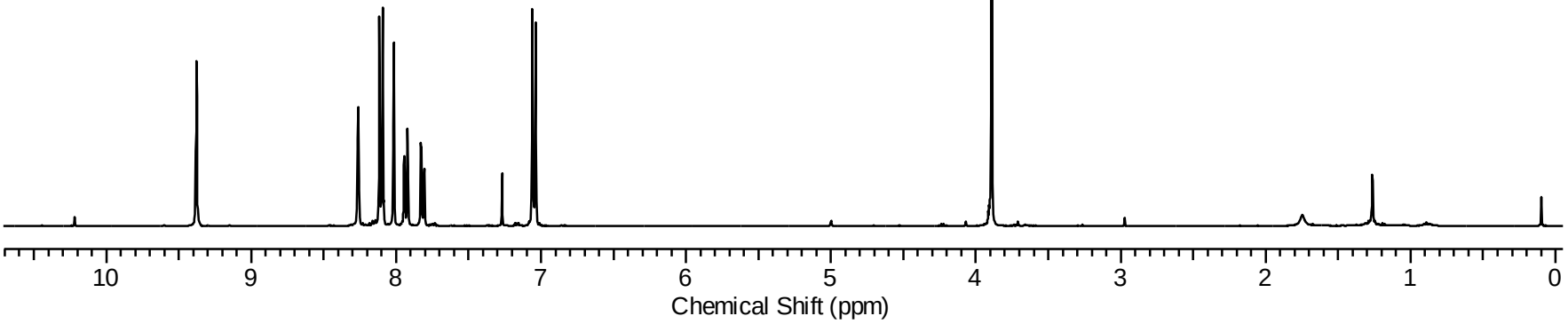




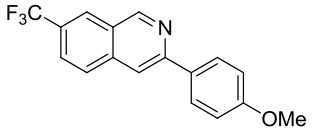
3-(4-Methoxyphenyl)-7-(trifluoromethyl)isoquinoline **4s**

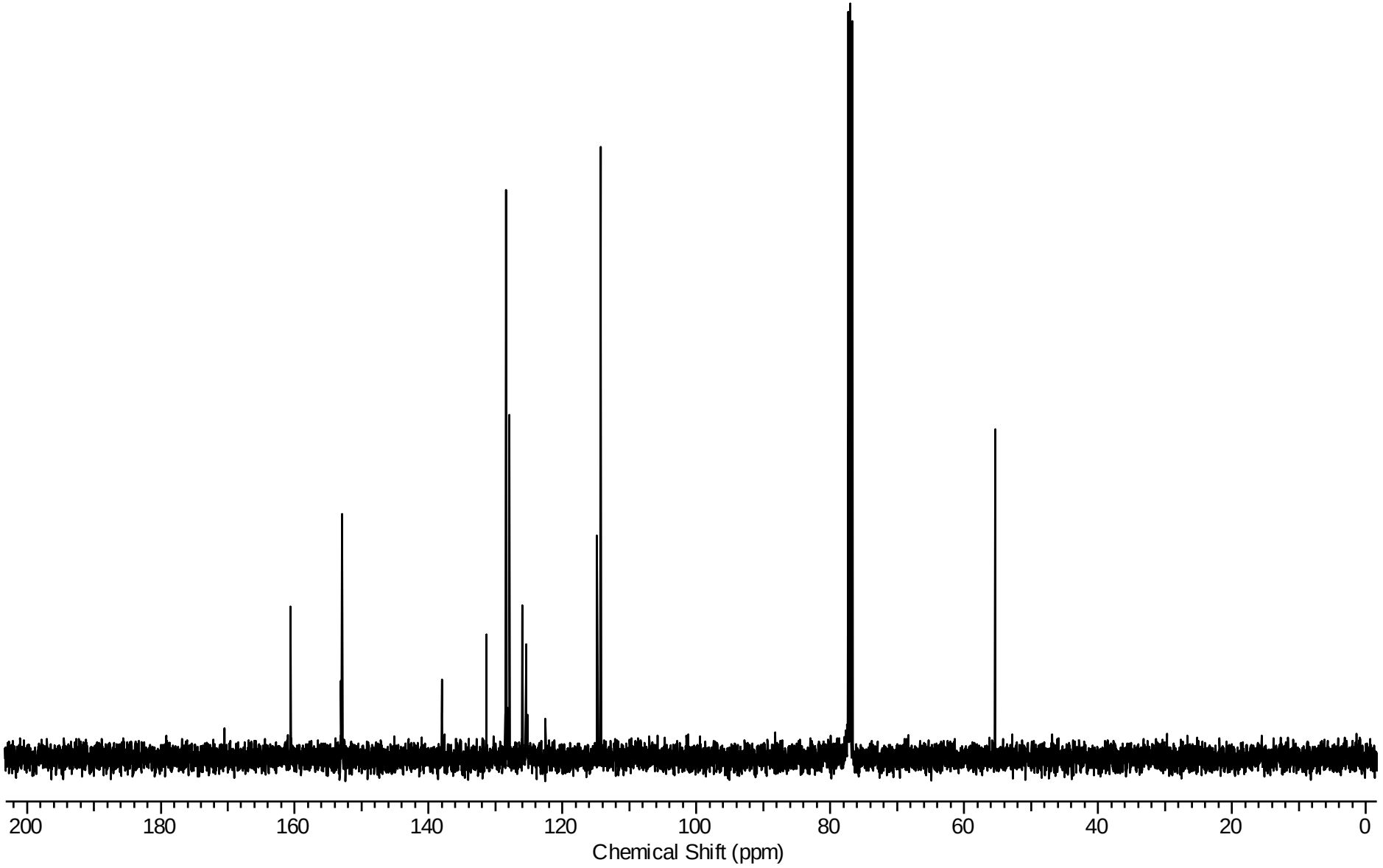




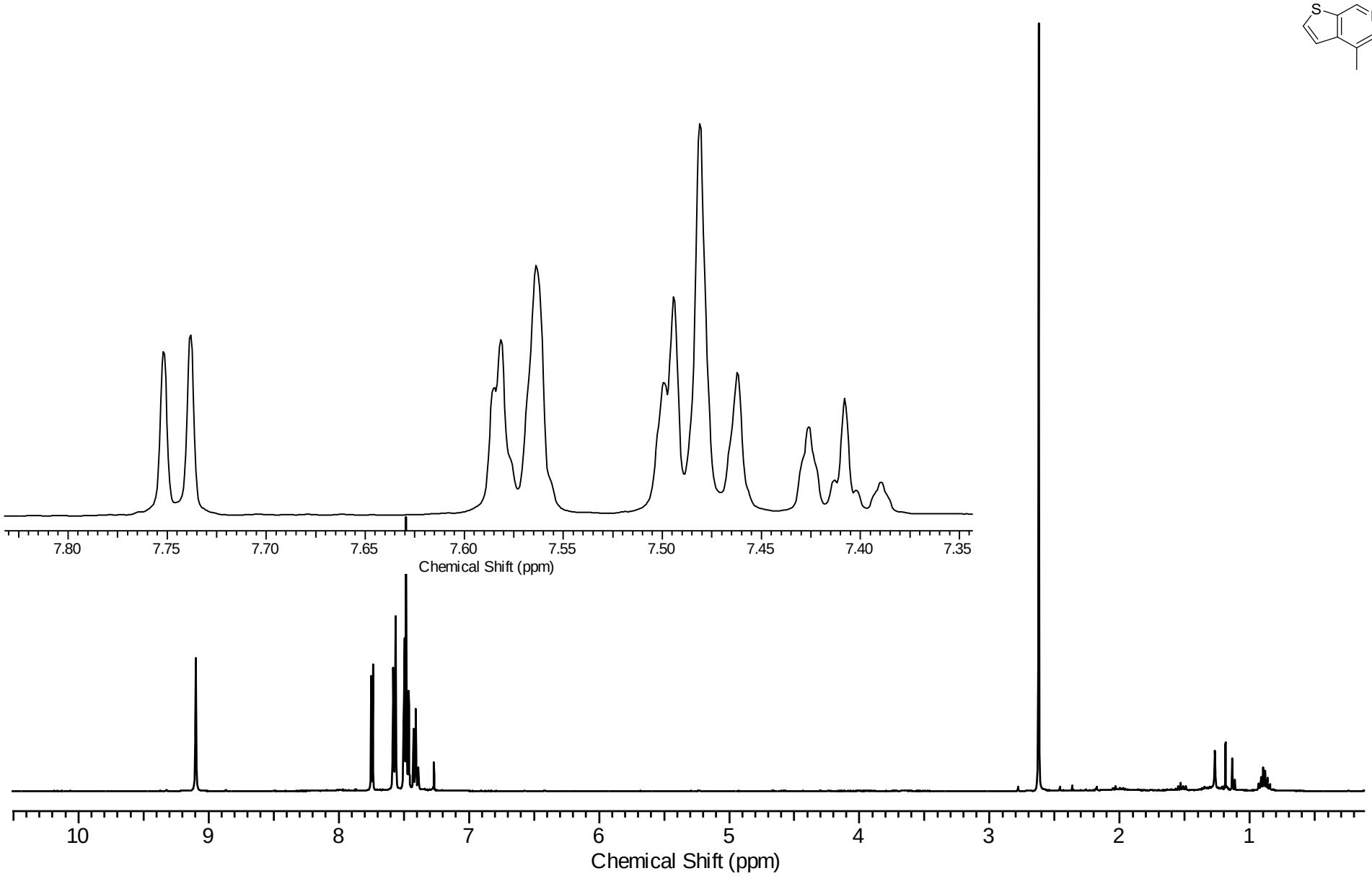


3-(4-Methoxyphenyl)-7-(trifluoromethyl)isoquinoline **4s**

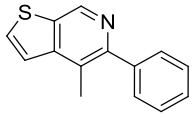


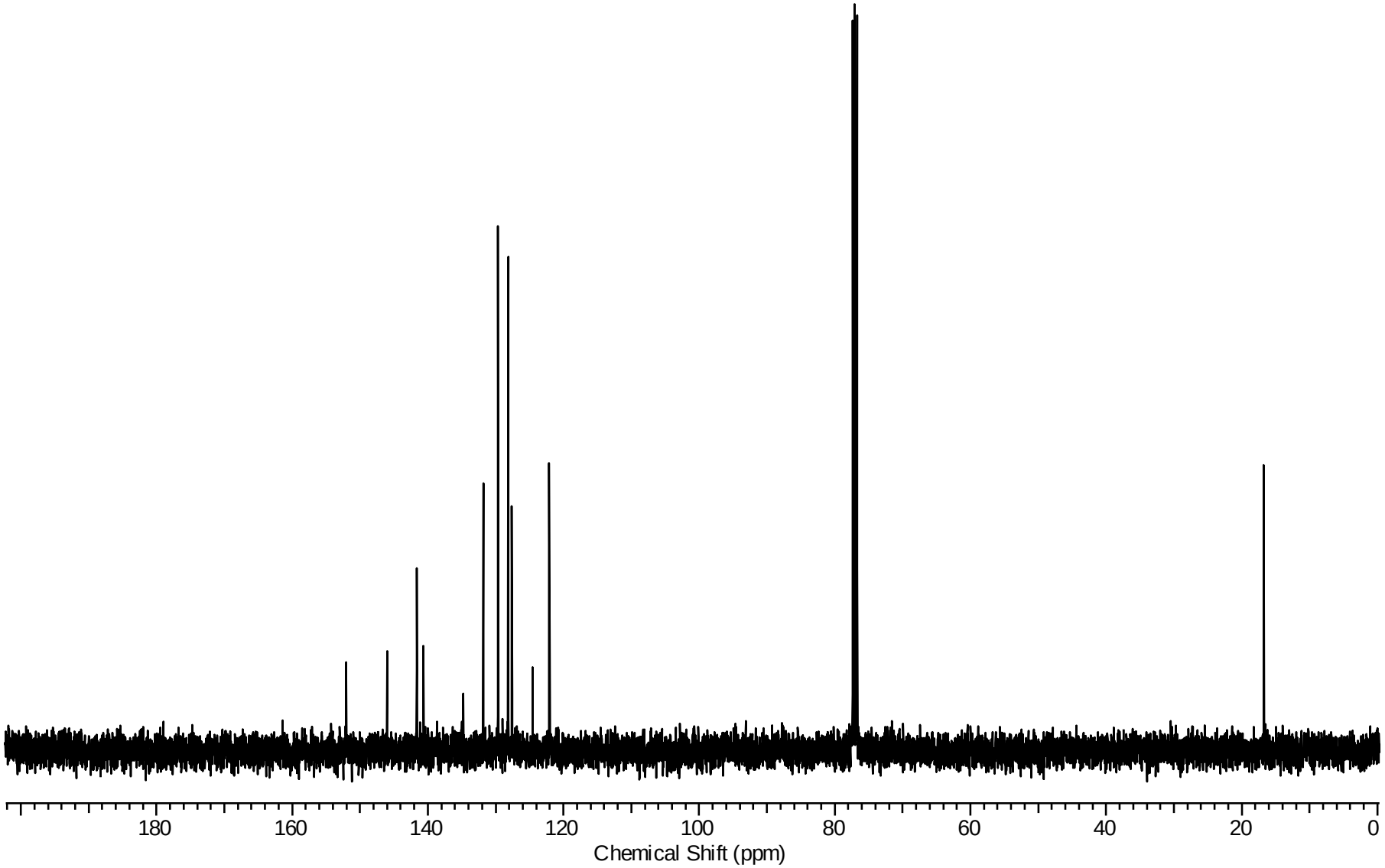


4-Methyl-5-phenylthieno[2,3-c]pyridine **4t**

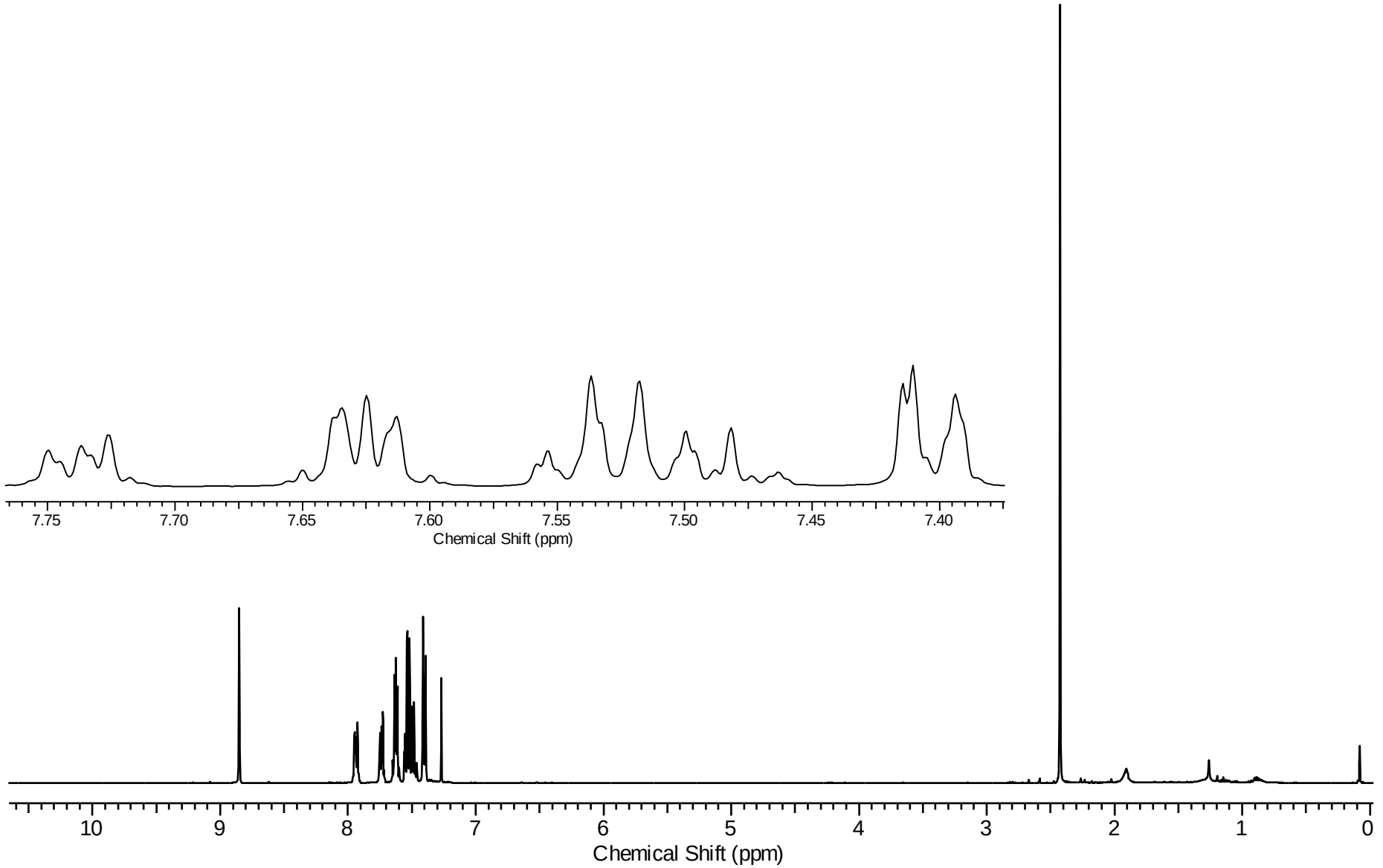


4-Methyl-5-phenylthieno[2,3-c]pyridine **4t**

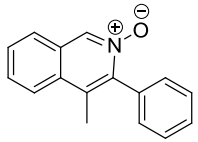


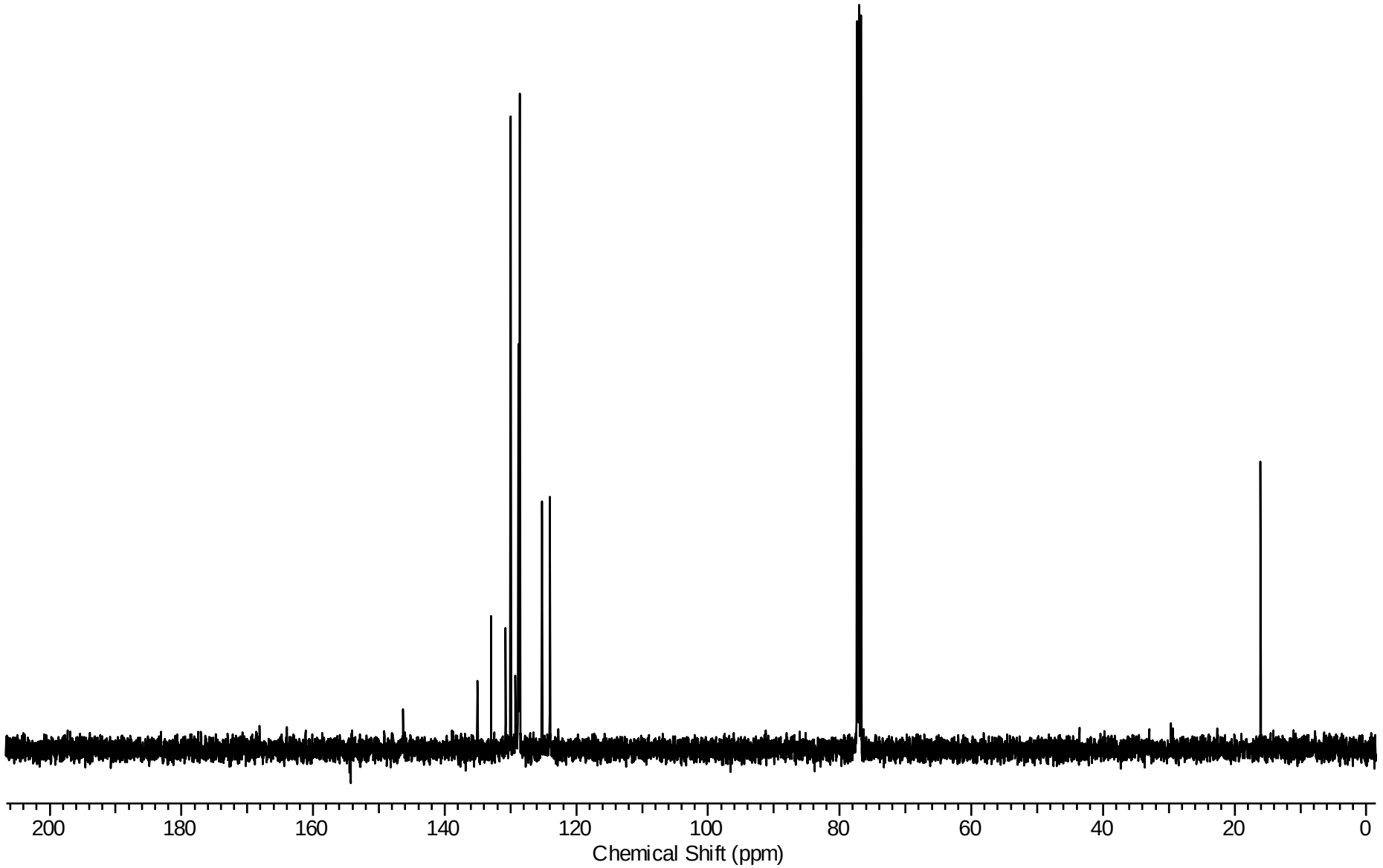


4-Methyl-3-phenylisoquinoline-*N*-oxide **5a**

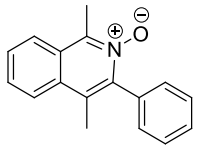


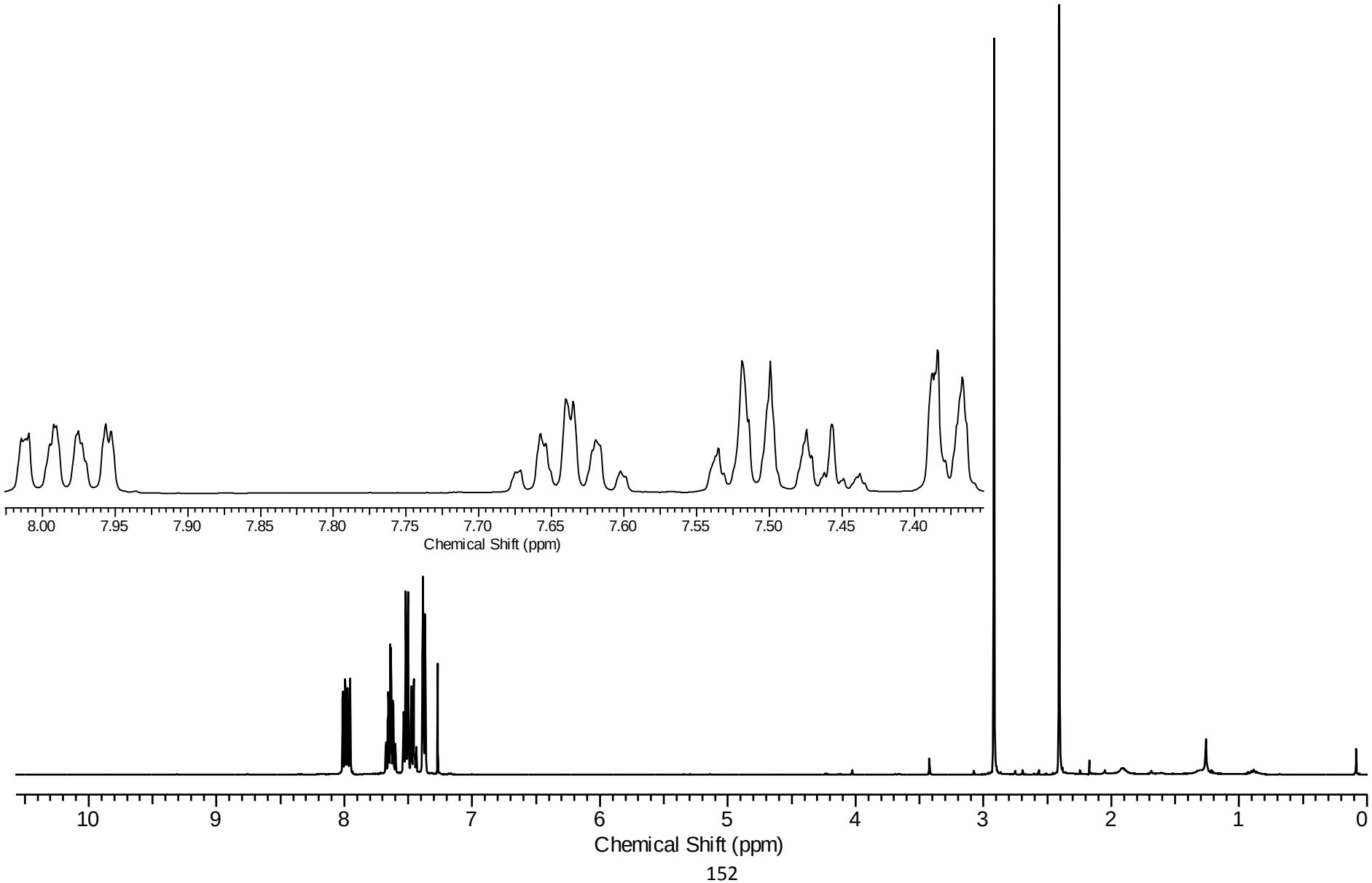
4-Methyl-3-phenylisoquinoline-*N*-oxide **5a**



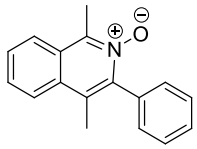


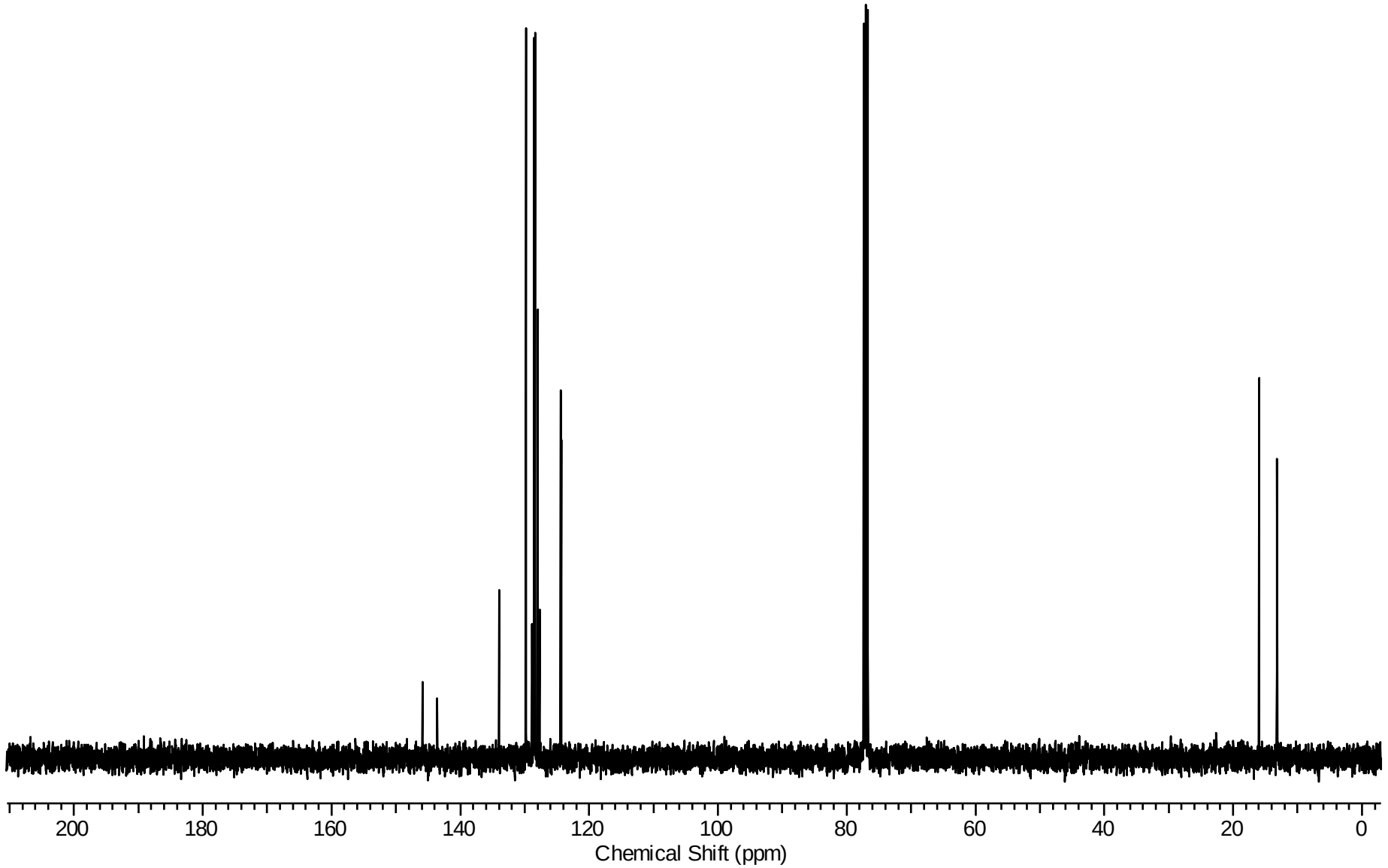
1,4-Dimethyl-3-phenylisoquinoline-*N*-oxide **5f**



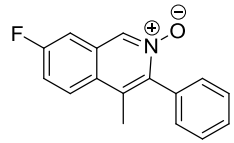


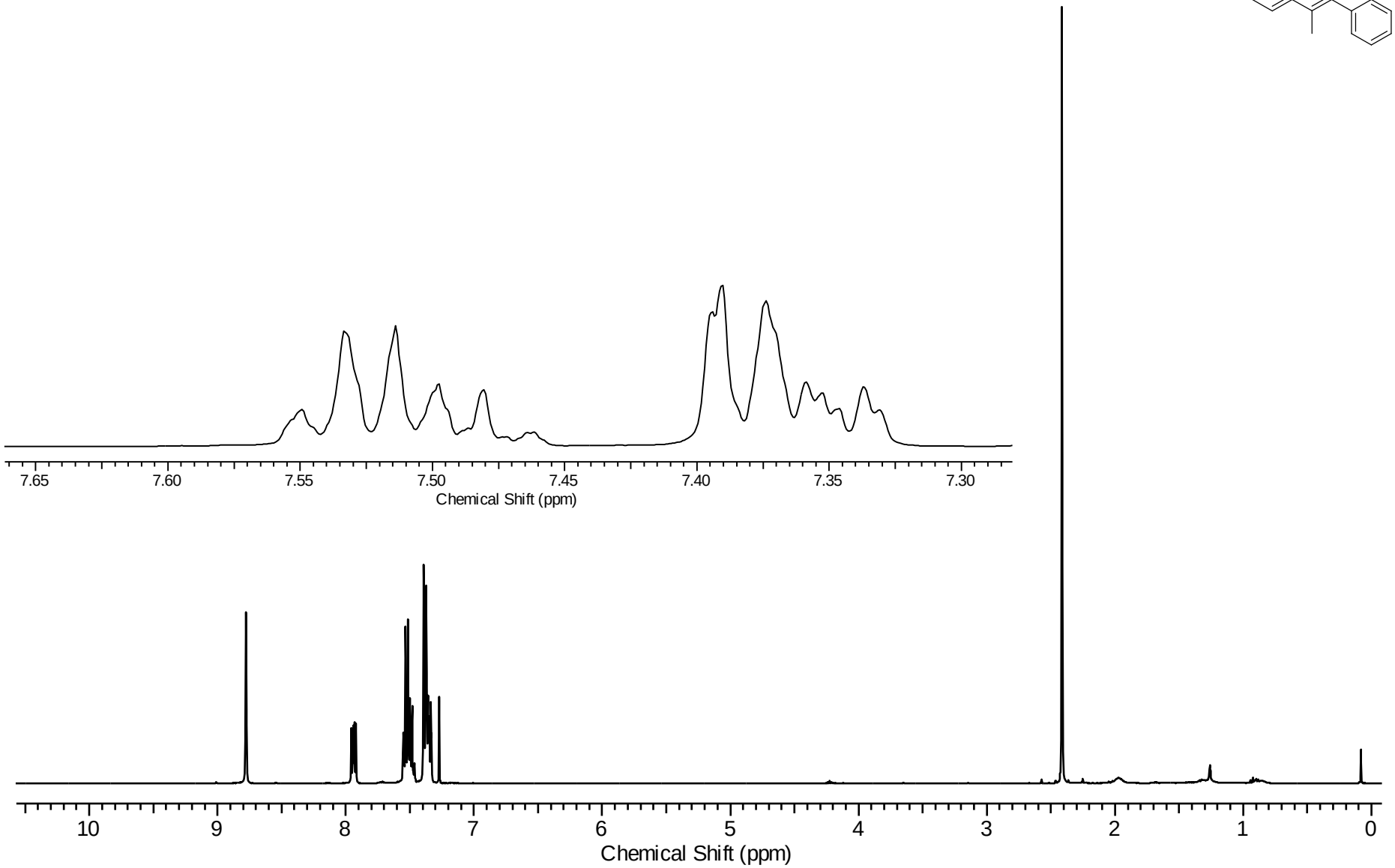
1,4-Dimethyl-3-phenylisoquinoline-*N*-oxide **5f**



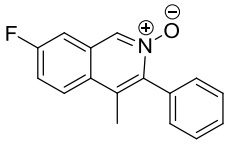


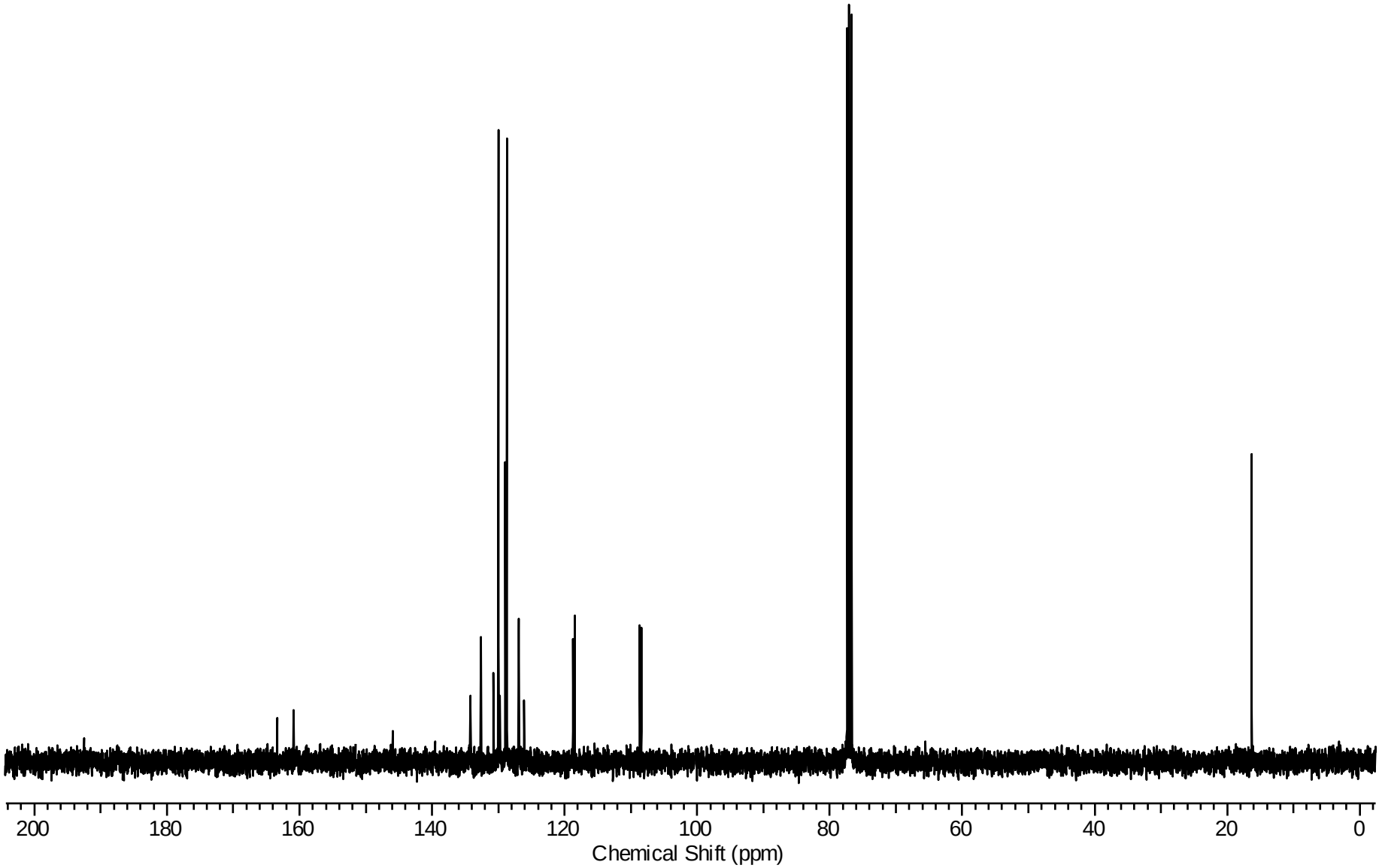
7-Fluoro-4-methyl-3-phenylisoquinoline-*N*-oxide **5m**



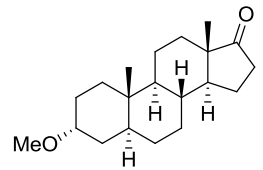


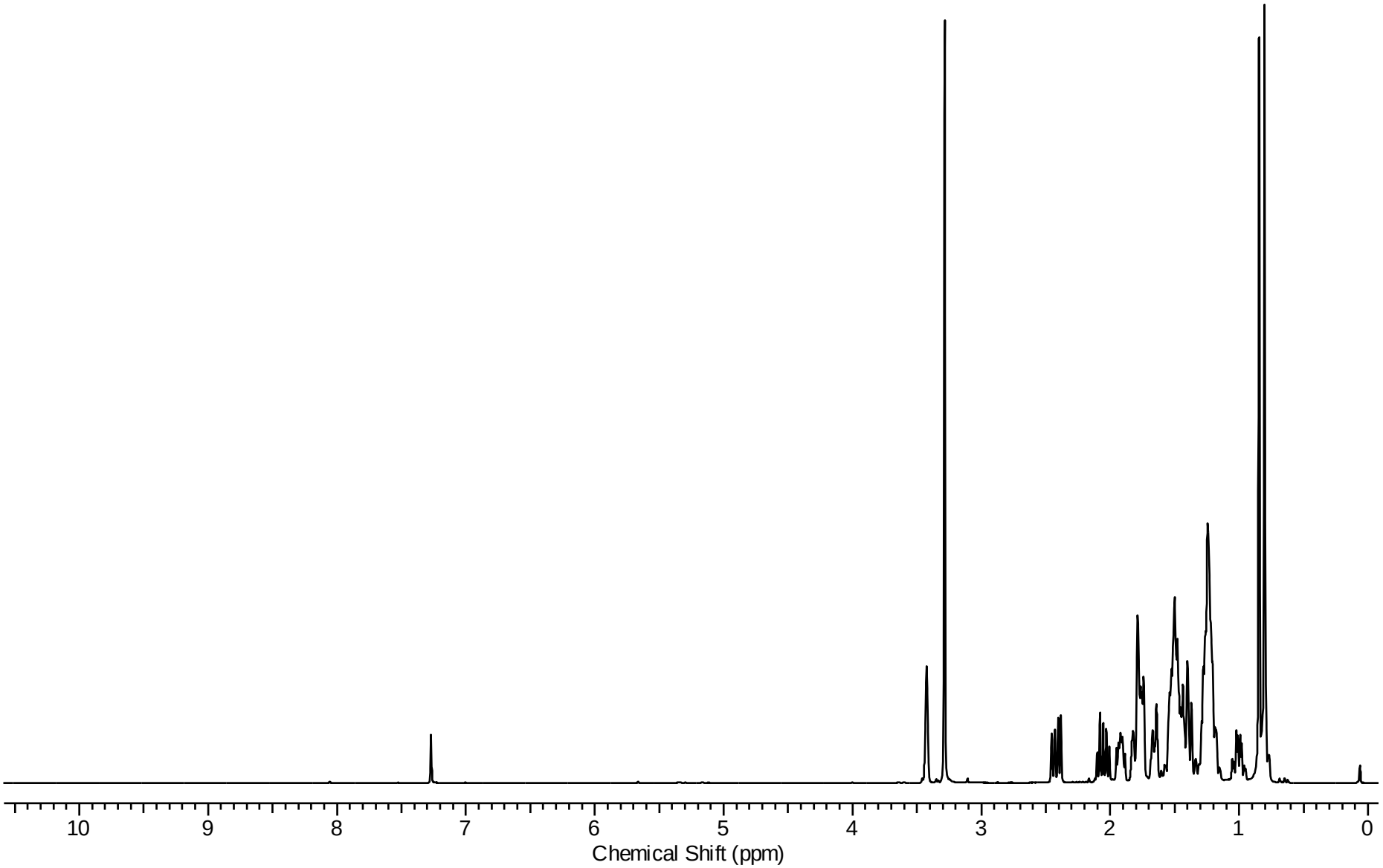
7-Fluoro-4-methyl-3-phenylisoquinoline-*N*-oxide **5m**



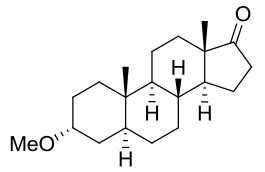


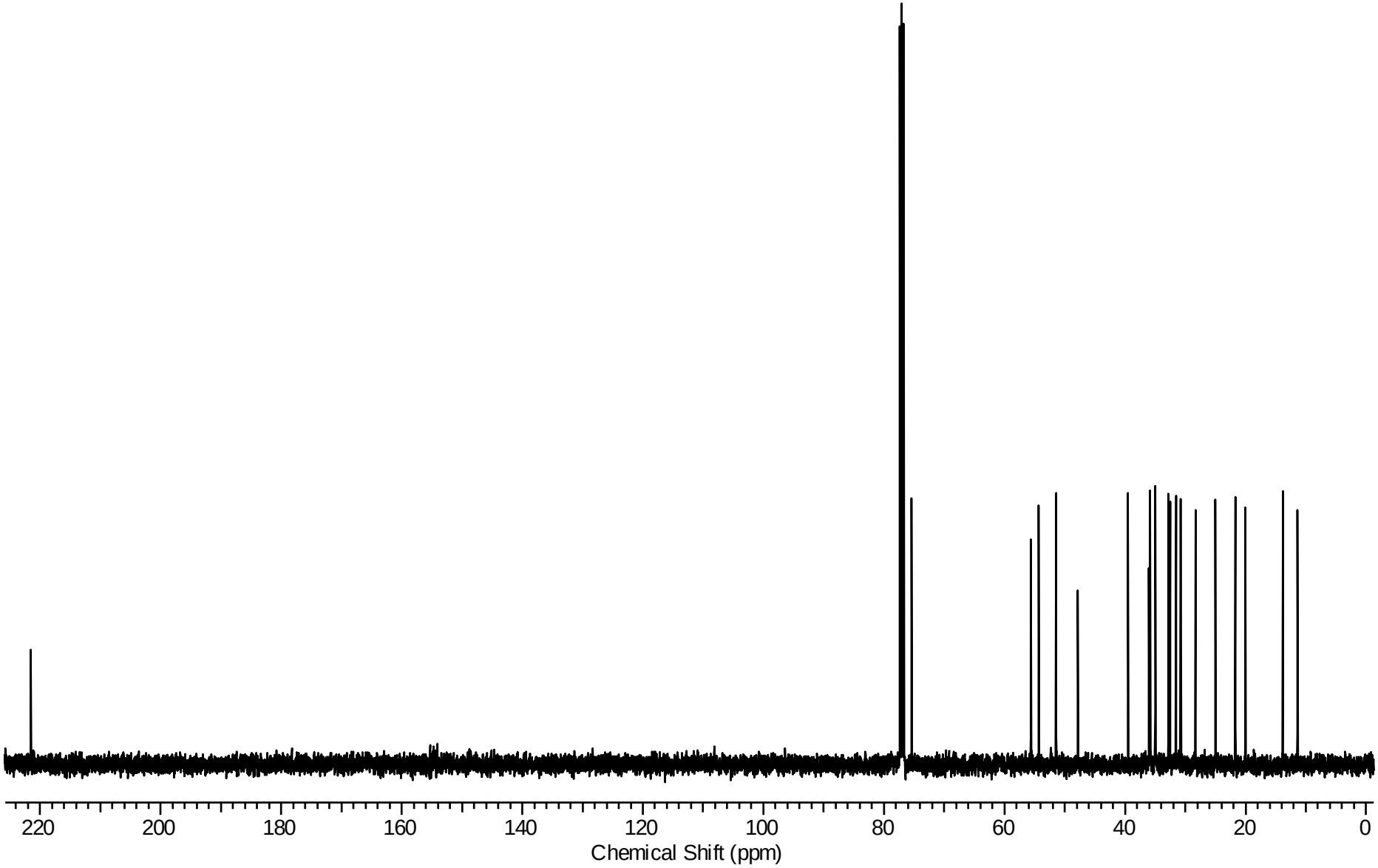
Androsterone-3-methyl ether **7**





Androsterone-3-methyl ether **7**





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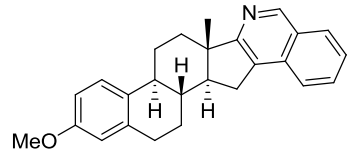
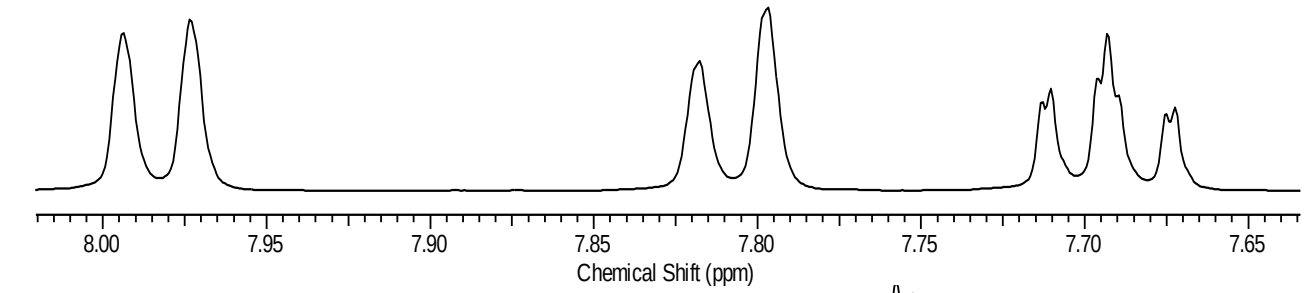
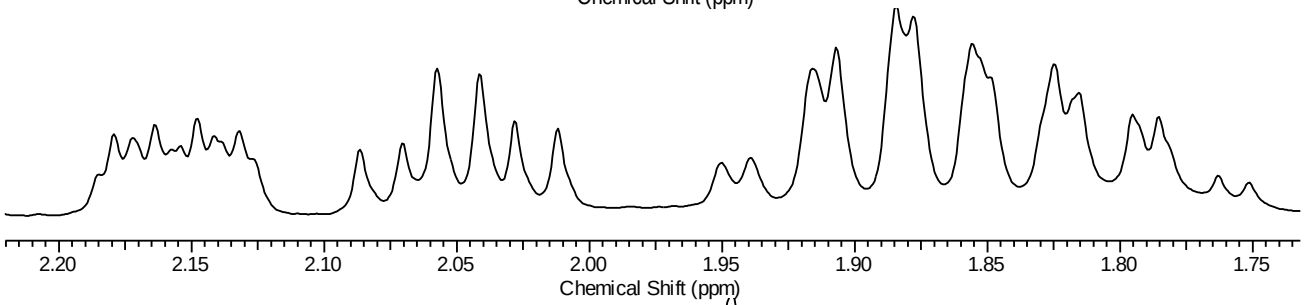
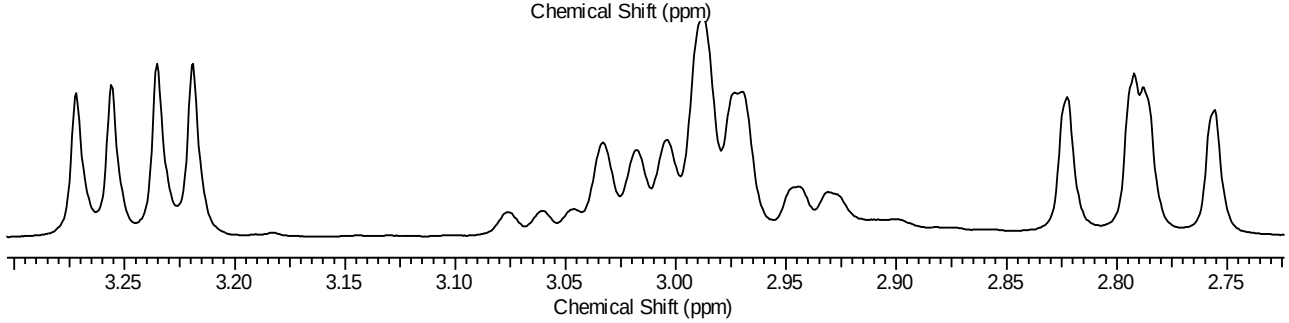
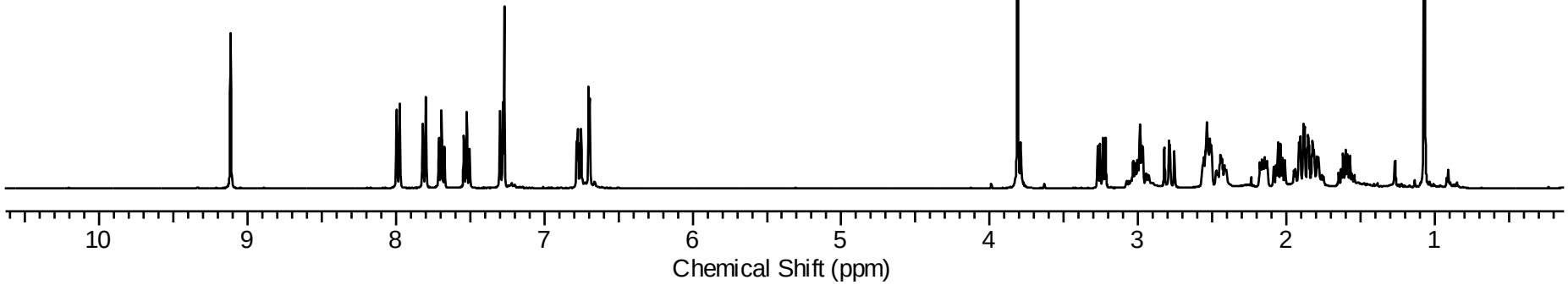

N
H
H
H
MeO

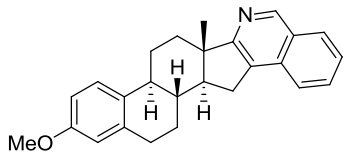

8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
Chemical Shift (ppm)

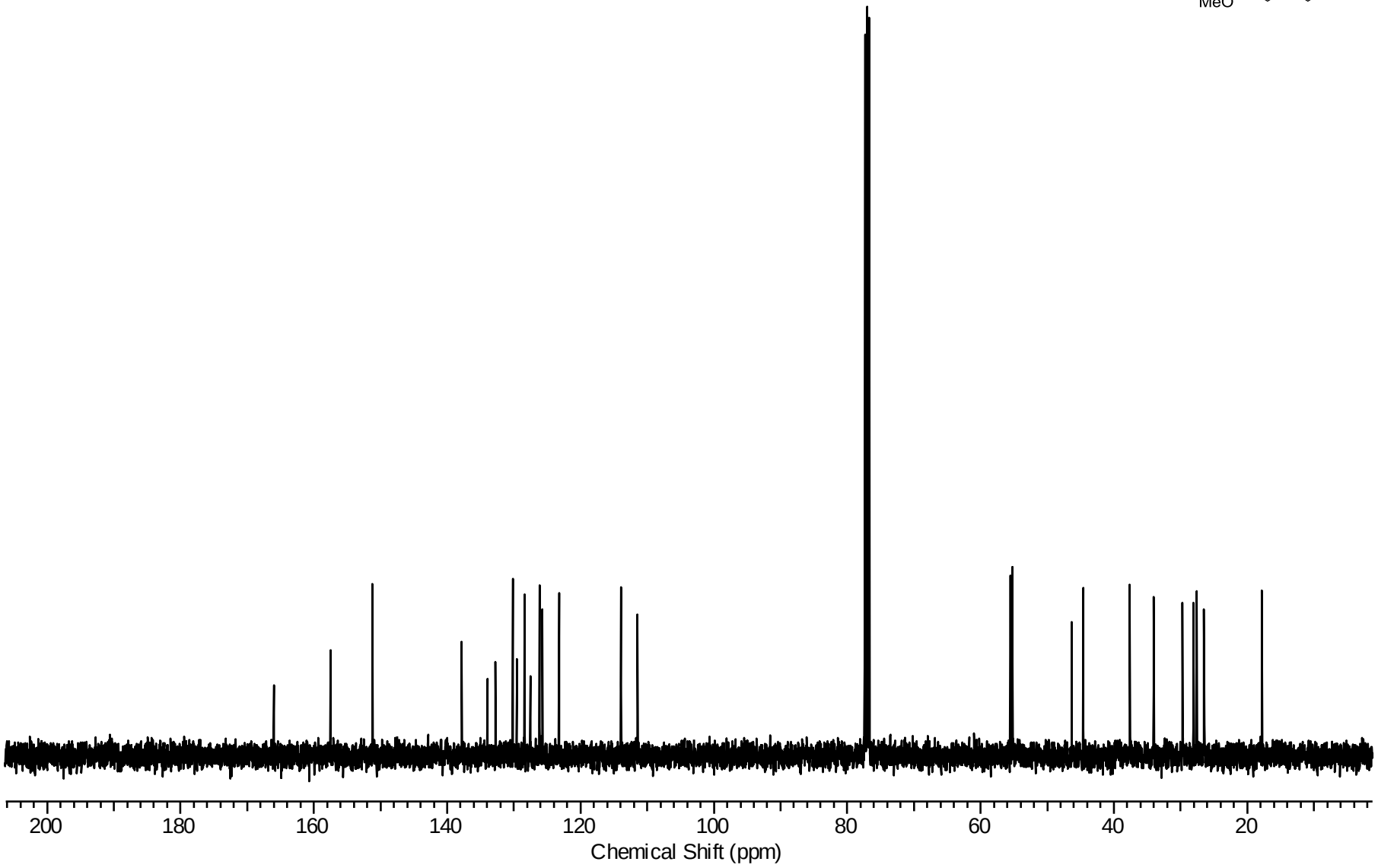

2.20
2.15
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
Chemical Shift (ppm)


3.25
3.20
3.15
3.10
3.05
3.00
2.95
2.90
2.85
2.80
2.75
Chemical Shift (ppm)

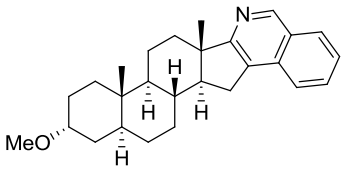

10
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

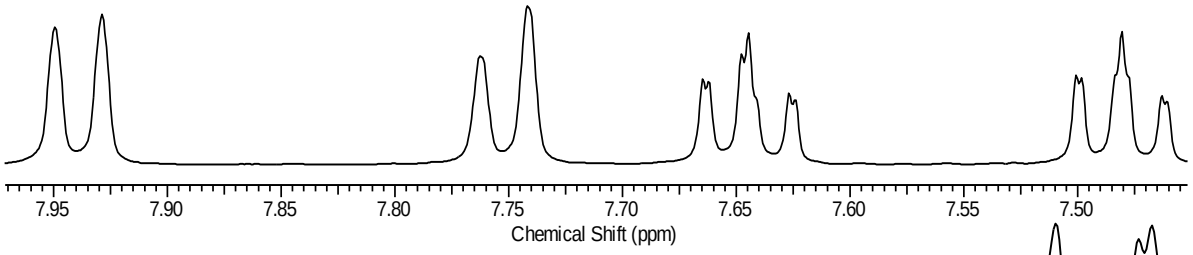
8

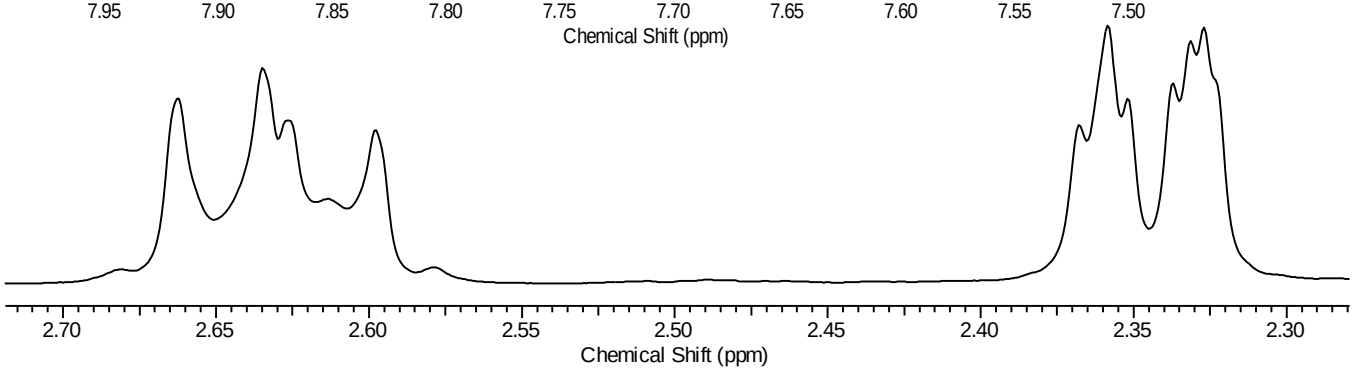




9

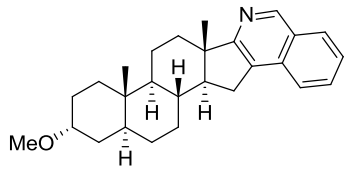

N
H
H
H
MeO
H

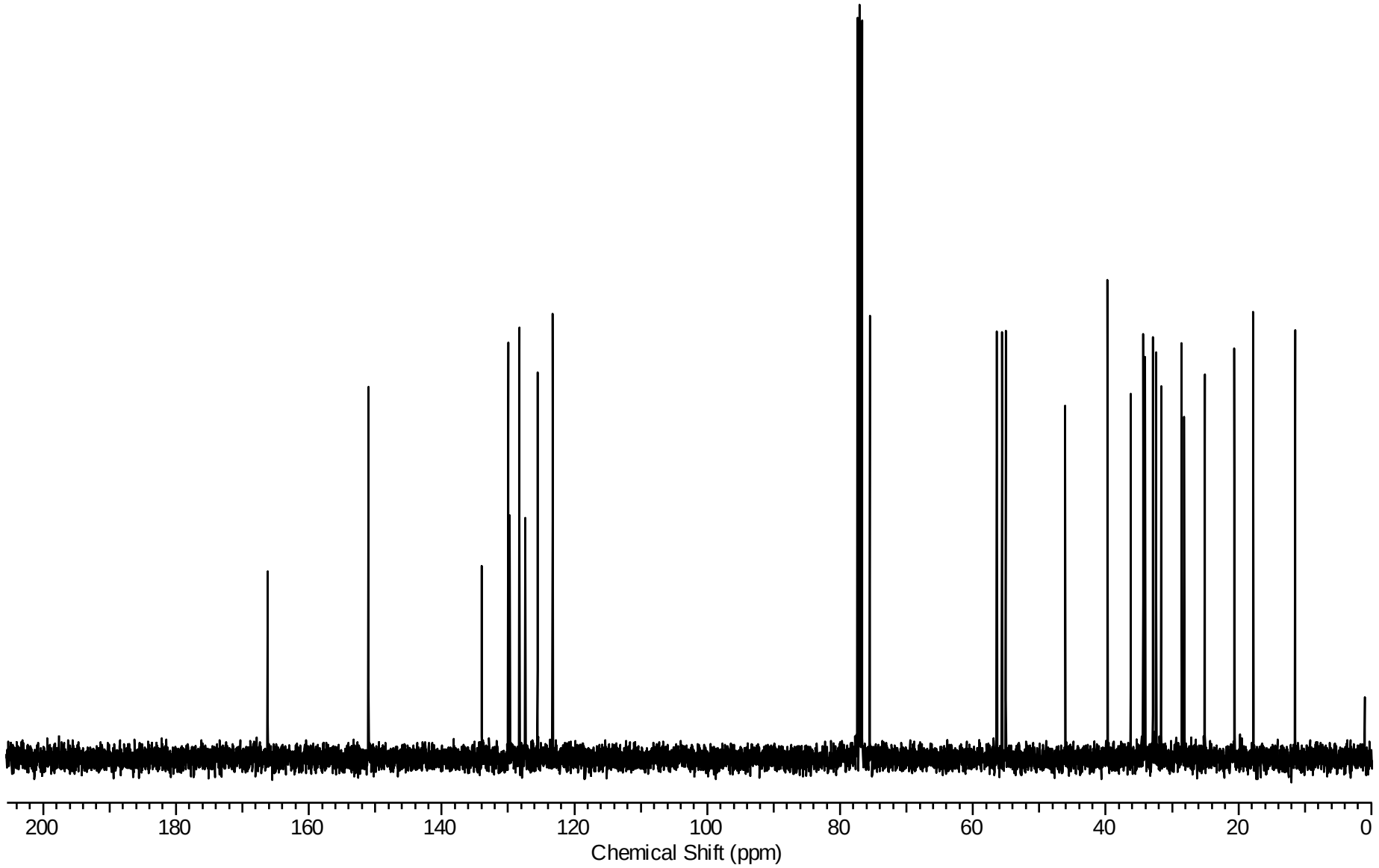

7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
Chemical Shift (ppm)


2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
Chemical Shift (ppm)

10
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

9


N
H
H
H
MeO
H


200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

References

1. Barbasiewicz M, Mąkosza M (2006) Intermolecular Reactions of Chlorohydrine Anions: Acetalization of Carbonyl Compounds under Basic Conditions. *Org Lett* 8:3745-3748.
2. Hanson P, Lövenich PW, Rowell SC, Walton PH, Timms AW (1999) Sandmeyer reactions. Part 4. An investigation into the cyclisation modes of Pschorr phenanthrene synthesis. *J Chem Soc, Perkin Trans 2* 49-64.
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