

Supporting Information

Transformation of *N,N*-Dimethylaniline-*N*-Oxides into Diverse Tetrahydroquinoline Scaffolds via Formal Povarov Reactions

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I. Instrumentation

Proton (^1H), carbon (^{13}C), fluorine (^{19}F), and silicon (^{29}Si) nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV400 CryoPlatform QNP or Bruker AVIII600 SMART NMR spectrometers at 23 °C. Proton chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl_3 : δ 7.26, C_6HD_5 : δ 7.16). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the NMR solvent (CDCl_3 : δ 77.16, C_6D_6 : δ 128.06). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), integration, and coupling constant (J) in Hertz (Hz). High-resolution mass spectra were obtained using an Agilent 1100 quaternary LC system coupled to an Agilent 6210 LC/MSD-TOF fitted with an ESI or an APCI source, or Thermo Q-Exactive Orbitrap using electrospray ionization (ESI) or a Waters GCT Premier spectrometer using chemical ionization (CI). Unless otherwise noted, column chromatography was performed either manually or by use of a Biotage Isolera One unit with 40–63 μm silica gel, and the eluent reported in parentheses. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60-Å pore size, 5–20 μm , Silicycle) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV), then were stained by immersion in iodine-impregnated silica gel, submersion in aqueous ceric ammonium molybdate solution (CAM), ethanolic phosphomolybdic acid solution (PMA), acidic ethanolic *p*-anisaldehyde solution (anisaldehyde), or aqueous potassium permanganate solution (KMnO_4), followed by brief heating on a hot plate (215 °C, 10–15 s).

II. General Experimental Details

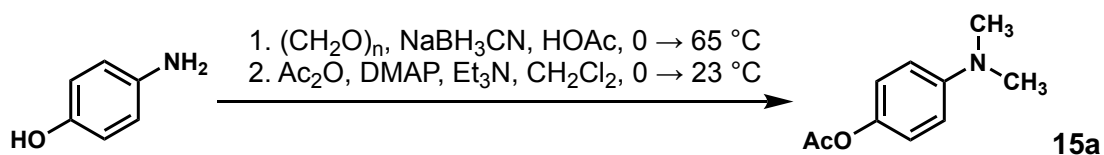
Commercial reagents and solvents were used as received with the following exceptions. Triethylamine, dichloromethane, ethyl ether, dimethylsulfoxide, tetrahydrofuran, hexane, toluene, *N,N*-dimethylformamide, and benzene were purified by the method of Pangborn, et. al.¹ All reactions were performed in single-neck oven- or flame-dried round bottom flasks fitted with

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J.; *Organometallics* **1996**, *15*, 1518-1520.

rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at or below 35 °C at 10 Torr (diaphragm vacuum pump) unless otherwise noted.

*(For clarity, intermediates that have not been assigned numbers in the text are numbered sequentially in the supporting information beginning with **15**).*

III. Synthetic Procedures



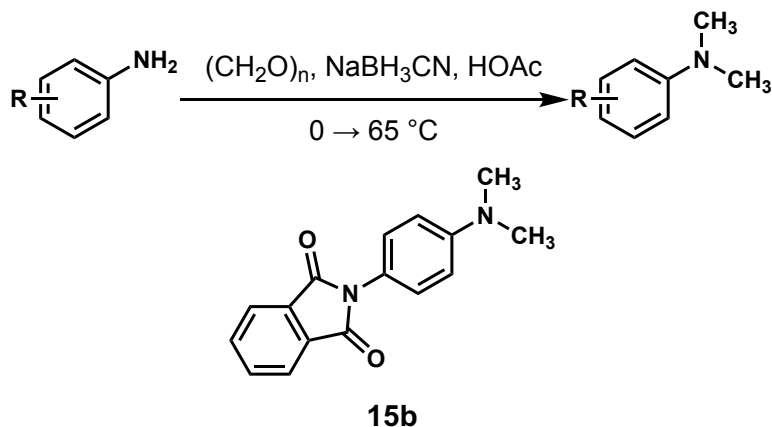
4-(*N,N*-dimethylamino)phenyl acetate (**15a**)²

Sodium cyanoborohydride (1.82 g, 29.0 mmol, 2.1 equiv) was added to a stirred slurry of *p*-aminophenol (1.504 g, 13.78 mmol, 1 equiv) and paraformaldehyde (0.862 g, 28.7 mmol, 2.08 equiv) in glacial acetic acid (15 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 10 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 2 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (53 mL, 265 mmol, 1.01 equiv to acetic acid) and then was diluted with ethyl acetate (20 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed sequentially with water (20 mL) and saturated aqueous sodium chloride solution (20 mL), and then were dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford crude 4-(*N,N*-dimethylamino)phenol. Triethylamine (1.594 g, 2.20 mL, 15.75 mmol, 1.1 equiv) and *N,N*-dimethylaminopyridine (86 mg, 0.70 mmol, 0.05 equiv) were added to a solution of crude 4-(*N,N*-dimethylamino)phenol in dichloromethane (7.5 mL). The resultant solution was cooled to 0 °C whereupon acetic anhydride (1.677 g, 1.55 mL, 16.43 mmol, 1.2 equiv) was added slowly via syringe. The reaction mixture was warmed to 23 °C, and stirred at that temperature for 19 h, and then poured over saturated aqueous sodium bicarbonate solution (15 mL). The biphasic mixture was diluted with dichloromethane (10 mL) and the layers were separated. The aqueous layer was extracted with dichloromethane (1 × 10 mL) and the combined organic layers were washed sequentially with water (15 mL) and saturated aqueous sodium chloride solution (15 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated resulting in an oily residue that was purified by automated flash column chromatography (starting with hexane, grading to 20% ethyl acetate–hexanes) to afford 4-(*N,N*-dimethylamino)phenyl acetate (**15a**) as a white, crystalline solid (1.965 g, 10.96 mmol, 80% yield). TLC: 10% ethyl acetate–hexanes, R_f=0.22, UV. ¹H

² De Carolis, M.; Protti, S.; Fagnoni, M.; Albin, A.; *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 1232-1236.

NMR (400 MHz, CDCl₃), δ : 6.95 (d, J = 9.1 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 2.93 (s, 6H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃), δ : 170.42, 148.81, 141.57, 121.92, 113.20, 41.07, 21.24. HRMS (ESI): Calcd. for C₁₀H₁₄NO₂ [(M+H)⁺]: 180.1019. Found: 180.1020.

Preparation of *N,N*-dimethylanilines³



2-(4-(dimethylamino)phenyl)isoindoline-1,3-dione (15b)⁴

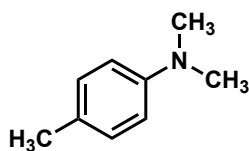
Sodium cyanoborohydride (0.58 g, 9.2 mmol, 2.2 equiv) was added to a stirred slurry of 2-(4-aminophenyl)isoindoline-1,3-dione⁵ (1.009 g, 4.235 mmol, 1 equiv) and paraformaldehyde (0.262 g, 8.72 mmol, 2.06 equiv) in glacial acetic acid (10 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 15 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 3.5 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (38 mL, 190 mmol, 1.1 equiv to acetic acid), diluted with dichloromethane (50 mL), and the resulting emulsion filtered, removing pale aqua solids. The layers were then separated and the aqueous layer was extracted with dichloromethane (1 × 30 mL). The combined organic layers were washed sequentially with water (25 mL) and saturated aqueous sodium chloride solution (25 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a green-yellow residue that was purified by automated flash column chromatography (starting with toluene, grading to 25% ethyl acetate–toluene) to afford 2-(4-

³ adapted from Chandrasekharam, M.; Chiranjeevi, B.; Gupta, K. S.; Sridhar, B.; *J. Org. Chem.* **2011**, 76, 10229-10235.

⁴ Hadad, C.; Ke, X.; Carraro, M.; Sartorel, A.; Bittencourt, C.; Van Tendeloo, G.; Bonchio, M.; Quintana, M.; Prato, M.; *Chem. Commun. (Cambridge, U.K.)* **2014**, 50, 885-887.

⁵ Chang, Y.-T.; Shu, C.-F.; *Macromolecules* **2003**, 36, 661-666.

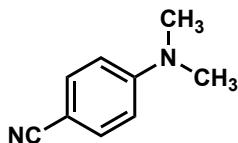
(dimethylamino)phenyl)isoindoline-1,3-dione (**15b**) as fluffy yellow needles (0.505 g, 1.90 mmol, 45% yield). TLC: 10% ethyl acetate–toluene, $R_f=0.39$, UV. $^1\text{H NMR}$ (600 MHz, CDCl_3), δ : 7.93 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.76 (dd, $J = 5.5, 3.0$ Hz, 2H), 7.25 (d, $J = 8.9$ Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 2H), 3.00 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3), δ : 168.05, 150.41, 134.23, 132.16, 127.65, 123.65, 120.24, 112.64, 40.66. HRMS (ESI): Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2$ [(M+H) $^+$]: 267.1128. Found: 267.1128.



15c

4-(dimethylamino)toluene (**15c**)⁶

Sodium cyanoborohydride (2.69 g, 42.8 mmol, 2.1 equiv) was added to a stirred slurry of *p*-toluidine (2.184 g, 20.38 mmol, 1 equiv) and paraformaldehyde (1.262 g, 42.02 mmol, 2.06 equiv) in glacial acetic acid (22 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 15 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 1.5 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (78 mL, 390 mmol, 1.02 equiv to acetic acid) and then diluted with hexanes (30 mL). The layers were separated and the aqueous layer was extracted with hexanes (2 × 20 mL). The combined organic layers were washed sequentially with water (20 mL) and saturated aqueous sodium chloride solution (20 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude oily residue that was purified by automated flash column chromatography (starting with hexane, grading to 20% ethyl acetate–hexanes) to afford 4-(dimethylamino)toluene (**15c**) as a clear, colorless oil (1.245 g, 9.208 mmol, 45% yield). TLC: 5% ethyl acetate–hexanes, $R_f=0.24$, UV. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ : 7.07 (d, $J = 8.1$ Hz, 2H), 6.70 (d, $J = 8.6$ Hz, 2H), 2.91 (s, 6H), 2.27 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3), δ : 148.93, 129.70, 126.23, 113.33, 41.22, 20.39. HRMS (ESI): Calcd. for $\text{C}_9\text{H}_{14}\text{N}$ [(M+H) $^+$]: 136.1121. Found: 136.1121.

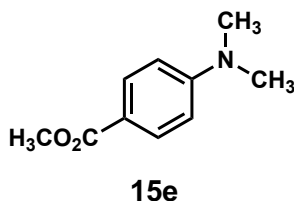


15d

⁶ Selva, M.; Perosa, A.; Tundo, P.; Brunelli, D.; *J. Org. Chem.* **2006**, *71*, 5770-5773.

4-(dimethylamino)benzotrile (**15d**)⁷

Sodium cyanoborohydride (5.70 g, 90.7 mmol, 2.14 equiv) was added to a stirred slurry of *p*-aminobenzotrile (5.01 g, 42.4 mmol, 1 equiv) and paraformaldehyde (2.61 g, 86.9 mmol, 2.06 equiv) in glacial acetic acid (50 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 15 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 8 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (180 mL, 900 mmol, 1.03 equiv to acetic acid) and then diluted with ethyl acetate (50 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 25 mL). The combined organic layers were washed sequentially with water (25 mL) and saturated aqueous sodium chloride solution (25 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford 4-(dimethylamino)benzotrile (**15d**) (6.216 g, 42.52 mmol, quantitative yield) as orange-yellow needles. ¹H NMR (400 MHz, CDCl₃), δ: 7.47 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 3.04 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ: 152.55, 133.54, 120.91, 111.50, 97.43, 40.10. HRMS (ESI): Calcd. for C₉H₁₁N₂ [(M+H)⁺]: 147.0917. Found: 147.0918.

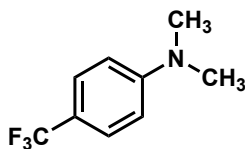


methyl 4-(dimethylamino)benzoate (**15e**)⁶

Sodium cyanoborohydride (1.025 g, 16.31 mmol, 2.17 equiv) was added to a stirred slurry of methyl *p*-aminobenzoate (1.134 g, 7.501 mmol, 1 equiv) and paraformaldehyde (0.458 g, 15.2 mmol, 2.03 equiv) in glacial acetic acid (11 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 15 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 2.5 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (40 mL, 200 mmol, 1.02 equiv to acetic acid) and then diluted with ethyl acetate (20 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (1 × 20 mL). The combined organic layers were washed sequentially with water (20 mL) and saturated aqueous sodium chloride solution (20 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford methyl 4-(dimethylamino)benzoate (**15e**) (1.345 g, 7.505 mmol,

⁷ Kraus, G. A.; Yue, S.; *J. Org. Chem.* **1983**, *48*, 2936-2937.

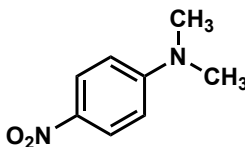
quantitative yield) as white needles. ^1H NMR (400 MHz, CDCl_3), δ : 7.90 (d, J = 9.1 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 3.04 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3), δ : 167.65, 153.39, 131.38, 117.04, 110.80, 51.66, 40.22. HRMS (ESI): Calcd. for $\text{C}_{10}\text{H}_{14}\text{NO}_2$ [(M+H) $^+$]: 180.1019. Found: 180.1020.



15f

***N,N*-dimethyl-4-(trifluoromethyl)aniline (15f)⁷**

Sodium cyanoborohydride (4.55 g, 72.4 mmol, 2.12 equiv) was added to a stirred slurry of *p*-(trifluoromethyl)aniline (5.49 g, 34.1 mmol, 1 equiv) and paraformaldehyde (2.10 g, 69.9 mmol, 2.05 equiv) in glacial acetic acid (50 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 35 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 8.75 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (180 mL, 900 mmol, 1.03 equiv to acetic acid) and then diluted with hexanes (50 mL). The layers were separated and the aqueous layer was extracted with hexanes (2 × 25 mL). The combined organic layers were washed sequentially with water (25 mL) and saturated aqueous sodium chloride solution (25 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford *N,N*-dimethyl-4-(trifluoromethyl)aniline (**15f**) (3.463 g, 18.31 mmol, 54% yield) as pale fluorescent-yellow, crystalline solids. ^1H NMR (400 MHz, CDCl_3), δ : 7.45 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 3.01 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3), δ : 152.38, 126.45 (q, J = 3.8 Hz), 125.31 (q, J = 270.1 Hz), 117.58 (q, J = 32.6 Hz), 111.25, 40.30. ^{19}F NMR (376 MHz, CDCl_3), δ : -60.80 (s, 3F). HRMS (ESI): Calcd. for $\text{C}_9\text{H}_{11}\text{F}_3\text{N}$ [(M+H) $^+$]: 190.0838. Found: 190.0838.

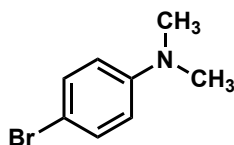


15g

***N,N*-dimethyl-4-nitroaniline (15g)⁷**

Sodium cyanoborohydride (0.987 g, 15.7 mmol, 2.13 equiv) was added to a stirred slurry of *p*-nitroaniline (1.017 g, 7.363 mmol, 1 equiv) and paraformaldehyde (0.451 g, 15.0 mmol, 2.04 equiv) in glacial acetic acid (10 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 15 min

whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 3 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (37.5 mL, 188 mmol, 1.07 equiv to acetic acid) and then diluted with ethyl acetate (20 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed sequentially with water (20 mL) and saturated aqueous sodium chloride solution (20 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford *N,N*-dimethyl-4-nitroaniline (**15g**) (1.203 g, 7.239 mmol, 98% yield) as yellow needles. ¹H NMR (400 MHz, CDCl₃), δ: 8.13 (d, *J* = 9.4 Hz, 2H), 6.61 (d, *J* = 9.4 Hz, 2H), 3.12 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ: 154.30, 136.99, 126.25, 110.32, 40.42. HRMS (ESI): Calcd. for C₈H₁₁N₂O₂ [(M+H)⁺]: 167.0815. Found: 167.0815. Note: if necessary, this material may be recrystallized from toluene.



15h

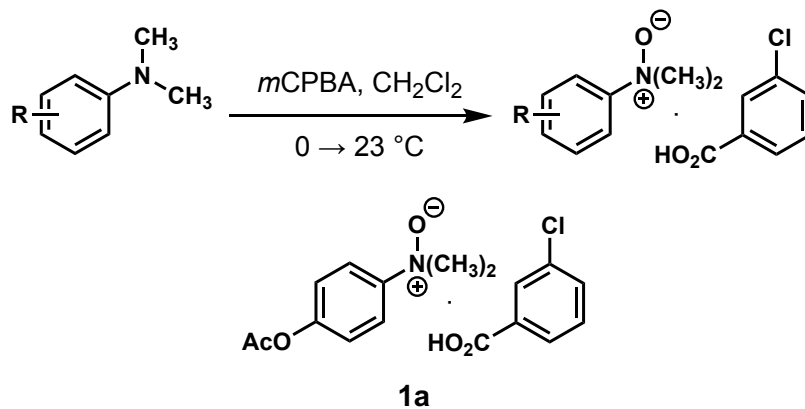
4-bromo-*N,N*-dimethylaniline (**15h**)⁸

Sodium cyanoborohydride (1.13 g, 17.98 mmol, 2.0 equiv) was added to a stirred slurry of *p*-bromoaniline (1.559 g, 9.064 mmol, 1 equiv) and paraformaldehyde (0.560 g, 18.6 mmol, 2.05 equiv) in glacial acetic acid (15 mL) at 0 °C. The resultant mixture was stirred at 0 °C for 25 min whereupon the ice bath was removed and the mixture was heated to 65 °C (external oil bath temperature) and stirred at that temperature for 3 h. The hot reaction mixture was poured over 5M aqueous sodium hydroxide solution (60 mL, 300 mmol, 1.1 equiv to acetic acid) and then diluted with ethyl acetate (30 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed sequentially with water (20 mL) and saturated aqueous sodium chloride solution (20 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford 4-bromo-*N,N*-dimethylaniline (**15h**) (1.803 g, 9.011 mmol, 99% yield) as off-white, crystalline solids. ¹H NMR (600 MHz, CDCl₃), δ: 7.30 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 2.92 (s, 6H). ¹³C NMR (151 MHz, CDCl₃), δ: 149.67, 131.82, 114.25, 108.66, 40.70.

⁸ Goodman, M. A.; Detty, M. R.; *Organometallics* **2004**, 23, 3016-3020.

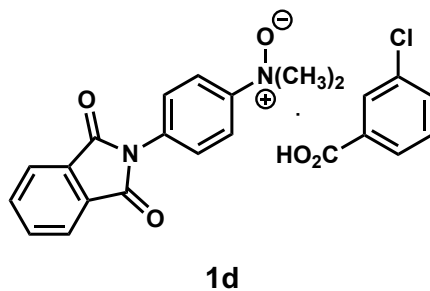
HRMS (ESI): Calcd. for $C_8H_{11}BrN$ $[(M^{79}Br+H)^+]$: 200.0069 and $[(M^{81}Br+H)^+]$: 202.0049. Found: 200.0072 and 202.0045.

Preparation of *N,N*-dimethylaniline-*N*-oxides⁹



4-acetoxy-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid (**1a**)

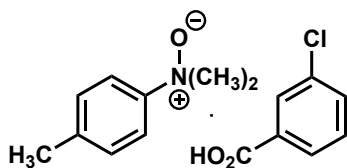
3-chloroperbenzoic acid (*m*CPBA, 1.44 g, 6.42 mmol, 1.10 equiv) was added to a solution of 4-(dimethylamino)phenyl acetate **15a** (1.030 g, 5.747 mmol, 1 equiv) in dichloromethane (7.5 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 30 minutes, after which basic alumina (3.74 g, 1.5 g/ g solids) was charged and stirred an additional 13 minutes. The slurry was filtered and concentrated, then was reslurried in ethyl acetate (20 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1a** (1.952 g, 5.328 mmol, 93% yield, 1:1.093 *N*-oxide to *m*CBA) as a beige, crystalline solid. ¹H NMR (600 MHz, CDCl₃), δ: 8.05 (t, *J* = 1.9 Hz, 1H), 7.99 – 7.92 (m, 3H), 7.44 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 6H), 2.32 (s, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 169.47, 169.04, 151.26, 149.84, 135.68, 134.17, 131.70, 129.96, 129.39, 127.88, 122.79, 121.23, 62.19, 21.19. HRMS (ESI): Calcd. for C₁₀H₁₄NO₃ [(M+H)⁺]: 196.0968. Found: 196.0963. Note: this material has a limited shelf life of ≤1 week.



⁹ Lewis, R. S.; Wisthoff, M. F.; Grissmerson, J.; Chain, W. J.; *Org. Lett.* **2014**, *16*, 3832-3835.

4-(1,3-dioxoisindolin-2-yl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid (**1d**)

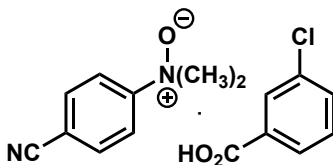
3-chloroperbenzoic acid (*m*CPBA, 0.463 g, 2.06 mmol, 1.10 equiv) was added to a solution of 2-(4-(dimethylamino)phenyl)isoindoline-1,3-dione **15b** (0.505 g, 1.90 mmol, 1 equiv) in dichloromethane (7.5 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 1.25 hours, after which basic alumina (2.14 g, 2.2 g/ g solids) was charged and stirred an additional 10 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (20 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1d** (0.576 g, 1.34 mmol, 70% yield, 1:0.950 *N*-oxide to *m*CBA) as a pale, pastel yellow crystalline solid. ¹H NMR (600 MHz, CDCl₃), δ: 8.11 (d, *J* = 9.1 Hz, 2H), 8.08 (t, *J* = 1.9 Hz, 1H), 7.99 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.96 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.68 (d, *J* = 9.1 Hz, 2H), 7.45 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 3.88 (s, 6H). ¹³C NMR (151 MHz, CDCl₃), δ: 169.47, 166.90, 151.79, 135.57, 134.95, 134.22, 133.13, 131.78, 131.63, 130.02, 129.42, 127.94, 127.27, 124.19, 120.89, 62.34. HRMS (ESI): Calcd. for C₁₆H₁₅N₂O₃ [(M+H)⁺]: 283.1077. Found: 283.1076.



1b

N,N,4-trimethylaniline-*N*-oxide 3-chlorobenzoic acid (**1b**)

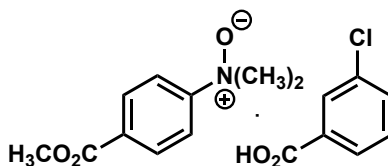
3-chloroperbenzoic acid (*m*CPBA, 2.28 g, 10.2mmol, 1.10 equiv) was added to a solution of 4-(dimethylamino)toluene **15c** (1.245 g, 9.208 mmol, 1 equiv) in dichloromethane (9.3 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 30 minutes, after which basic alumina (5.36 g, 1.5 g/ g solids) was charged and stirred an additional 5 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (20 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1b** (2.609 g, 7.959 mmol, 86% yield, 1:1.128 *N*-oxide to *m*CBA) as beige, crystalline solids. ¹H NMR (600 MHz, CDCl₃), δ: 8.06 (t, *J* = 1.9 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.43 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 6H), 2.39 (s, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 169.64, 150.03, 140.10, 136.03, 134.13, 131.56, 130.26, 129.98, 129.35, 127.89, 119.45, 61.84, 21.02. HRMS (ESI): Calcd. for C₉H₁₄NO [(M+H)⁺]: 152.1070. Found: 152.1070.



1e

4-cyano-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid (1e)

3-chloroperbenzoic acid (*m*CPBA, 4.36 g, 19.4 mmol, 1.10 equiv) was added to a solution of 4-(dimethylamino)benzonitrile **15d** (2.578 g, 17.63 mmol, 1 equiv) in dichloromethane (19.3 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 1 hour, after which basic alumina (14.1 g, 2.5 g/g solids) was charged and stirred an additional 15 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (30 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1e** (4.93 g, 14.4 mmol, 81% yield, 1:1.159 *N*-oxide to *m*CBA) as light beige needles. ¹H NMR (600 MHz, CDCl₃), δ: 8.15 (d, *J* = 8.9 Hz, 2H), 8.04 (t, *J* = 1.9 Hz, 1H), 7.94 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.48 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 3.84 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ: 169.02, 155.97, 134.30, 134.19, 133.70, 132.15, 129.85, 129.46, 127.81, 121.21, 117.21, 114.16, 62.07. HRMS (ESI): Calcd. for C₉H₁₁N₂O [(M+H)⁺]: 163.0866. Found: 163.0865.

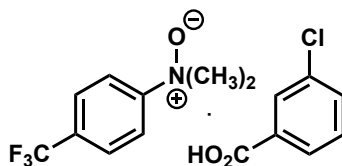


1c

4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid (1c)

3-chloroperbenzoic acid (*m*CPBA, 1.914 g, 8.540 mmol, 1.10 equiv) was added to a solution of methyl 4-(dimethylamino)benzoate **15e** (1.406 g, 7.845 mmol, 1 equiv) in dichloromethane (10.5 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 3 hours, after which basic alumina (2.63 g, 2 g/g solids) was charged and stirred an additional 10 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (20 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1c** (2.127 g, 5.644 mmol, 72% yield, 1:1.16 *N*-oxide to *m*CBA) as pale yellow solids (*N*-oxide to *m*CBA). ¹H NMR (400 MHz, CDCl₃), δ: 8.18 (d, *J* = 8.9 Hz, 2H), 8.08 – 8.01 (m, 3H), 7.93 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.45 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ: 169.37, 165.60, 155.99, 135.22, 134.18, 131.88,

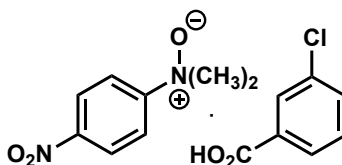
131.65, 131.23, 129.94, 129.45, 127.88, 120.13, 62.03, 52.75. HRMS (ESI): Calcd. for $C_{10}H_{14}NO_3 [(M+H)^+]$: 196.0968. Found: 196.0968.



1f

***N,N*-dimethyl-4-(trifluoromethyl)aniline-*N*-oxide 3-chlorobenzoic acid (1f)**

3-chloroperbenzoic acid (*m*CPBA, 4.55 g, 20.3 mmol, 1.10 equiv) was added to a solution of *N,N*-dimethyl-4-(trifluoromethyl)aniline **15f** (3.464 g, 18.31 mmol, 1 equiv) in dichloromethane (26 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 2 hours, after which basic alumina (12.0 g, 1.5 g/ g solids) was charged and stirred an additional 10 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (40 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1f** (5.909 g, 15.76 mmol, 86% yield, 1:1.084 *N*-oxide to *m*CBA) as pastel yellow, crystalline solids. 1H NMR (400 MHz, $CDCl_3$), δ : 8.12 (d, $J = 8.4$ Hz, 2H), 8.04 (t, $J = 1.9$ Hz, 1H), 7.94 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.46 (ddd, $J = 8.0, 2.2, 1.1$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 3.86 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$), δ : 169.30, 155.46, 134.98, 134.23, 132.24 (q, $J = 33.3$ Hz), 132.01, 129.95, 129.50, 127.89, 127.11 (q, $J = 3.7$ Hz), 123.33 (q, $J = 272.6$ Hz), 120.77, 62.21. ^{19}F NMR (376 MHz, $CDCl_3$), δ : -62.77 (s, 3F). HRMS (ESI): Calcd. for $C_9H_{11}F_3NO [(M+H)^+]$: 206.0787. Found: 206.0787.

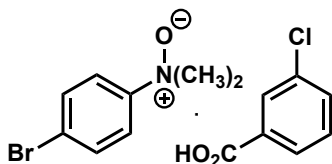


1g

***N,N*-dimethyl-4-nitroaniline-*N*-oxide 3-chlorobenzoic acid (1g)**

3-chloroperbenzoic acid (*m*CPBA, 1.780 g, 7.942 mmol, 1.10 equiv) was added to a solution of *N,N*-dimethyl-4-nitroaniline **15g** (1.203 g, 7.239 mmol, 1 equiv) in dichloromethane (12 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 3 hours, after which basic alumina (6.04 g, 2 g/ g solids) was charged and stirred an additional 10 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (30 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1g** (2.090 g, 5.986 mmol, 83% yield, 1:1.060 *N*-oxide to *m*CBA) as bright yellow solids. 1H NMR

(600 MHz, CDCl₃), δ : 8.39 (d, J = 9.2 Hz, 2H), 8.22 (d, J = 9.2 Hz, 2H), 8.04 (t, J = 1.8 Hz, 1H), 7.93 (dt, J = 7.7, 1.3 Hz, 1H), 7.48 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 3.87 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ : 169.10, 157.32, 148.23, 134.42, 134.27, 132.23, 129.92, 129.57, 127.89, 125.19, 121.69, 62.33. HRMS (ESI): Calcd. for C₈H₁₁N₂O₃ [(M+H)⁺]: 183.0764. Found: 183.0764.

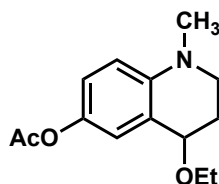
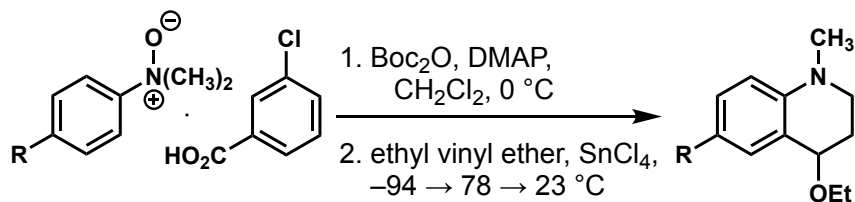


1h

4-bromo-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid (**1h**)

3-chloroperbenzoic acid (*m*CPBA, 1.230 g, 5.488 mmol, 1.10 equiv) was added to a solution of 4-bromo-*N,N*-dimethylaniline **15h** (1.000 g, 4.998 mmol, 1 equiv) in dichloromethane (7.5 mL) at 0 °C. The resulting slurry was stirred at 0 °C for 1 hour, after which basic alumina (4.48 g, 2 g/ g solids) was charged and stirred an additional 10 minutes. The slurry was filtered and concentrated, then reslurried in ethyl acetate (20 mL) and dried azeotropically (3 iterations) then in vacuo affording *N,N*-dimethylaniline-*N*-oxide co-crystallized with 3-chlorobenzoic acid **1h** (1.405 g, 3.681 mmol, 74% yield, 1:1.058 *N*-oxide to *m*CBA) as light beige crystalline solids. ¹H NMR (600 MHz, CDCl₃), δ : 8.05 (t, J = 1.9 Hz, 1H), 7.94 (dt, J = 7.7, 1.3 Hz, 1H), 7.84 (d, J = 9.1 Hz, 2H), 7.64 (d, J = 9.1 Hz, 2H), 7.45 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 3.83 (s, 6H). ¹³C NMR (151 MHz, CDCl₃), δ : 169.32, 151.90, 135.21, 134.26, 132.85, 131.93, 130.00, 129.46, 127.92, 123.94, 121.73, 62.18. HRMS (ESI): Calcd. for C₈H₁₁BrNO [(M⁷⁹Br+H)⁺]: 216.0019. Found: 216.0019.

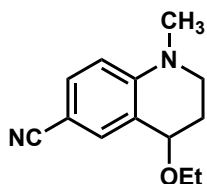
Preparation of 4-ethoxy-1,2,3,4-tetrahydro-1-methylquinolines



7a

4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinolin-6-yl acetate (7a)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-acetoxy-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1a** (380 mg, 1.00 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 559 mg, 2.56 mmol, 2.6 equiv), and ethyl vinyl ether (358 mg, 4.96 mmol, 5.0 equiv) in dichloromethane (7.75 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C with liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at –78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude oil that was purified by automated flash column chromatography (starting with 2% diethyl ether–toluene, grading to 8% diethyl ether–toluene) to afford 4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinolin-6-yl acetate (**7a**) as a clear, amber syrup (196 mg, 0.786 mmol, 78% yield). TLC: 5% diethyl ether–toluene, R_f=0.23, UV. ¹H NMR (600 MHz, CDCl₃), δ: 6.91 – 6.86 (m, 2H), 6.58 (d, *J* = 8.6 Hz, 1H), 4.31 (t, *J* = 4.0 Hz, 1H), 3.61 (dq, *J* = 9.1, 7.0 Hz, 1H), 3.55 (dq, *J* = 9.1, 7.0 Hz, 1H), 3.38 (td, *J* = 11.4, 3.4 Hz, 1H), 3.11 (dtd, *J* = 11.3, 4.5, 0.8 Hz, 1H), 2.90 (s, 3H), 2.25 (s, 3H), 2.09 (dtd, *J* = 13.4, 4.5, 3.3 Hz, 1H), 1.94 (dddd, *J* = 13.4, 11.5, 4.4, 3.6 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 170.39, 144.45, 140.66, 122.79, 122.23, 122.01, 111.77, 72.95, 63.31, 46.64, 39.28, 27.52, 21.25, 15.72. HRMS (ESI): Calcd. for C₁₄H₂₀NO₃ [(M+H)⁺]: 250.1438. Found: 250.1428.

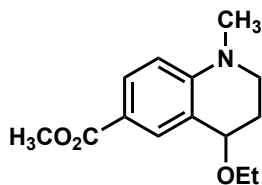


7b

4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline-6-carbonitrile (7b)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-cyano-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1e** (346 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 263 mg, 1.21 mmol, 1.2 equiv), and ethyl vinyl ether (190 mg,

2.63 mmol, 2.6 equiv) in dichloromethane (7.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, amber solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting thin, peach slurry was stirred at -78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (5 mL). The layers were separated and the aqueous layer extracted with dichloromethane (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, brown oil that was purified by flash column chromatography (starting with 5% ethyl acetate-hexanes, grading to 15% ethyl acetate-hexanes) to afford 4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline-6-carbonitrile (**7b**) as a faintly orange-brown syrup (91 mg, 0.421 mmol, 42% yield). TLC: 20% ethyl acetate-hexanes, R_f=0.52, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.39 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 4.28 (t, *J* = 3.7 Hz, 1H), 3.63 – 3.48 (m, 3H), 3.22 (dddd, *J* = 11.9, 4.8, 3.9, 0.8 Hz, 1H), 2.98 (s, 3H), 2.11 (dq, *J* = 13.5, 4.0 Hz, 1H), 1.88 (dddd, *J* = 13.5, 11.9, 4.9, 3.1 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 148.83, 133.85, 133.62, 121.35, 120.94, 110.83, 96.53, 72.31, 63.42, 46.21, 38.68, 26.66, 15.59. HRMS (ESI): Calcd. for C₁₃H₁₇N₂O [(M+H)⁺]: 217.1335. Found: 217.1334.

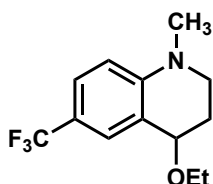


7c

methyl 4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline-6-carboxylate (7c)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (372 mg, 1.00 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 241 mg, 1.10 mmol, 1.1 equiv), and ethyl vinyl ether (362 mg, 5.02 mmol, 5.0 equiv) in dichloromethane (7.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting opaque amber-orange solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N₂, then tin(IV)

chloride (1.0 M in dichloromethane, 250 μ L, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting opaque, yellow-orange solution was stirred at -78 $^{\circ}$ C for a minimum of 1 hour, then allowed to warm slowly to 23 $^{\circ}$ C with stirring over an additional 3 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1×10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, light amber syrup that was purified by automated flash column chromatography (starting with hexanes, grading to 30% ethyl acetate–hexanes) to afford methyl 4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline-6-carboxylate (**7c**) as pale orange-yellow needles (150 mg, 0.602 mmol, 60% yield). TLC: 10% ethyl acetate–hexanes, $R_f=0.13$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.83 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.78 (d, $J = 2.2$ Hz, 1H), 6.56 (d, $J = 8.8$ Hz, 1H), 4.34 (t, $J = 3.4$ Hz, 1H), 3.85 (s, 3H), 3.64 – 3.56 (m, 2H), 3.56 – 3.50 (m, 1H), 3.22 – 3.15 (m, 1H), 3.00 (s, 3H), 2.13 (dq, $J = 13.5, 3.5$ Hz, 1H), 1.91 – 1.82 (m, 1H), 1.21 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3), δ : 167.66, 149.57, 132.30, 131.63, 120.08, 116.10, 110.10, 72.76, 63.20, 51.59, 46.13, 38.79, 27.00, 15.64. HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ $[(\text{M}+\text{H})^+]$: 250.1438. Found: 250.1435.

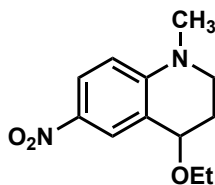


7d

4-ethoxy-1-methyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (7d)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of *N,N*-dimethyl-4-(trifluoromethyl)aniline-*N*-oxide 3-chlorobenzoic acid salt **1f** (381 mg, 1.02 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 555 mg, 2.54 mmol, 2.5 equiv), and ethyl vinyl ether (365 mg, 5.06 mmol, 5.0 equiv) in dichloromethane (7.75 mL) under an atmosphere of Ar and cooled to 0 $^{\circ}$ C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 $^{\circ}$ C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μ L, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at -78 $^{\circ}$ C for a minimum of 1 hour, then allowed to warm slowly to 23 $^{\circ}$ C with stirring over an additional 4.5 hours. The clear, amber reaction mixture was poured

over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude residue that was purified by automated flash column chromatography (isocratic toluene) to afford 4-ethoxy-1-methyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (**7d**) as a clear, pale yellow oil (148 mg, 0.571 mmol, 56% yield). TLC: toluene, $R_f=0.42$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.37 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.34 (d, $J = 2.3$ Hz, 1H), 6.60 (d, $J = 8.7$ Hz, 1H), 4.33 (t, $J = 3.7$ Hz, 1H), 3.66 – 3.48 (m, 3H), 3.19 (dt, $J = 10.7, 3.9$ Hz, 1H), 2.97 (s, 3H), 2.12 (dq, $J = 13.6, 3.9$ Hz, 1H), 1.90 (dddd, $J = 13.5, 12.1, 4.7, 3.2$ Hz, 1H), 1.24 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3), δ : 148.39, 127.24 (q, $J = 3.7$ Hz), 126.55 (q, $J = 3.8$ Hz), 125.32 (q, $J = 270.0$ Hz), 120.83, 116.62 (q, $J = 32.6$ Hz), 110.49, 72.75, 63.34, 46.19, 38.82, 26.94, 15.67. ^{19}F NMR (565 MHz, CDCl_3), δ : -60.75 (s, 3F). HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{NO}$ [(M+H) $^+$]: 260.1257. Found: 260.1254.

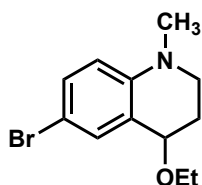


7e

4-ethoxy-1-methyl-6-nitro-1,2,3,4-tetrahydroquinoline (**7e**)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of *N,N*-dimethyl-4-nitroaniline-*N*-oxide 3-chlorobenzoic acid salt **1g** (373 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 552 mg, 2.53 mmol, 2.5 equiv), and ethyl vinyl ether (356 mg, 4.94 mmol, 4.9 equiv) in dichloromethane (7.7 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, bright yellow-orange solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, bright red-orange solution was stirred at -78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 4 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was

filtered and concentrated to afford a crude residue that was purified by automated flash column chromatography (starting with toluene, grading to 5% diethyl ether–toluene) to afford 4-ethoxy-1-methyl-6-nitro-1,2,3,4-tetrahydroquinoline (**7e**) as mustard yellow needles (171 mg, 0.723 mmol, 72% yield). TLC: 5% diethyl ether–toluene, $R_f=0.37$, UV. $^1\text{H NMR}$ (600 MHz, CDCl_3), δ : 8.07 (dd, $J = 9.1, 2.1$ Hz, 1H), 8.02 (d, $J = 2.9$ Hz, 1H), 6.53 (d, $J = 9.2$ Hz, 1H), 4.35 (t, $J = 3.6$ Hz, 1H), 3.68 – 3.52 (m, 3H), 3.27 (dt, $J = 12.2, 4.3$ Hz, 1H), 3.07 (s, 3H), 2.19 – 2.12 (m, 1H), 1.94 – 1.85 (m, 1H), 1.23 (td, $J = 7.0, 1.1$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3), δ : 150.74, 136.17, 126.56, 126.51, 120.16, 109.76, 72.42, 63.51, 46.44, 39.06, 26.68, 15.57. HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_3$ [(M+H) $^+$]: 237.1234. Found: 237.1229.



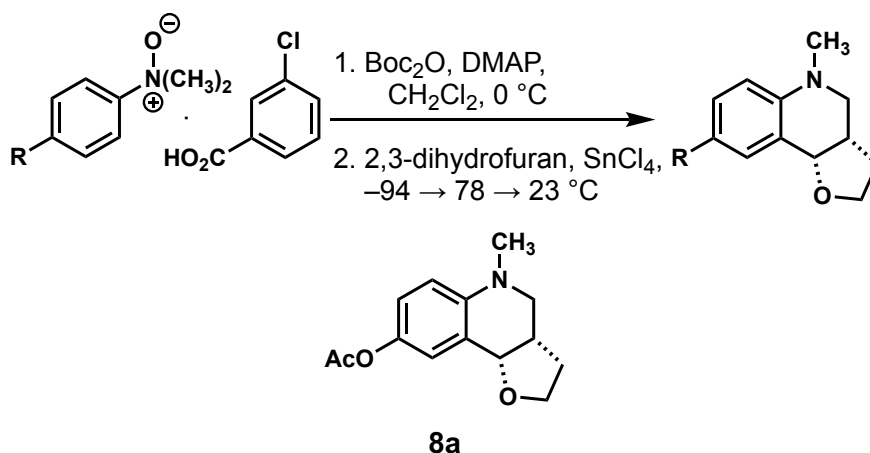
7f

6-bromo-4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline (7f)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.098 mmol, 0.1 equiv) was charged to a clear, orange-yellow solution of 4-bromo-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1h** (383 mg, 1.00 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 558 mg, 2.56 mmol, 2.6 equiv), and ethyl vinyl ether (360 mg, 4.99 mmol, 5.0 equiv) in dichloromethane (8.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, orange-amber solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 16 hours. The thin, light pink-brown slurry was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (2 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, brown-amber syrup that was purified by automated flash column chromatography (starting with toluene, grading to 5% ethyl acetate–toluene) to afford 6-bromo-4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline (**7f**) as a clear, faintly amber syrup (117 mg, 0.433 mmol, 43% yield). TLC: 2.5% ethyl acetate–toluene, $R_f=0.38$, UV. $^1\text{H NMR}$ (600 MHz, C_6D_6), δ : 7.33 (d, $J = 2.4$ Hz, 1H),

7.28 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.16 (d, $J = 8.8$ Hz, 1H), 3.88 (t, $J = 3.7$ Hz, 1H), 3.29 (dq, $J = 8.9, 6.9$ Hz, 1H), 3.24 (ddd, $J = 12.1, 11.1, 3.5$ Hz, 1H), 3.18 (dq, $J = 8.9, 7.0$ Hz, 1H), 2.58 (dtd, $J = 11.2, 4.3, 3.9, 0.8$ Hz, 1H), 2.32 (s, 3H), 1.77 (dq, $J = 13.3, 3.8$ Hz, 1H), 1.51 (dddd, $J = 13.3, 12.1, 4.7, 3.2$ Hz, 1H), 1.02 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3), δ : 145.35, 132.55, 131.89, 123.57, 113.06, 107.33, 72.76, 63.41, 46.35, 39.02, 27.28, 15.72. HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{17}\text{BrNO}$ [$(\text{M}^{79}\text{Br}+\text{H})^+$]: 270.0488 and [$(\text{M}^{81}\text{Br}+\text{H})^+$]: 272.0468. Found: 270.0494 and 272.0467.

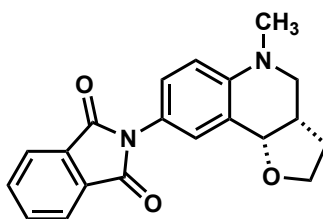
Preparation of *cis*-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolines



cis-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolin-8-yl acetate (**8a**)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-acetoxy-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1a** (385 mg, 1.02 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 552 mg, 2.53 mmol, 2.5 equiv), and 2,3-dihydrofuran (363 mg, 5.18 mmol, 5.1 equiv) in dichloromethane (7.75 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, brown solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at -78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3.5 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1×10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude oil that was purified by automated flash column

chromatography (starting with hexanes, grading to 40% ethyl acetate–hexanes) to afford *cis*-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolin-8-yl acetate (**8a**) as light brown needles (187 mg, 0.756 mmol, 74% yield). TLC: 20% ethyl acetate–hexanes, $R_f=0.13$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.08 (d, $J = 2.8$ Hz, 1H), 6.92 (dd, $J = 8.9, 2.8$ Hz, 1H), 6.66 (d, $J = 8.9$ Hz, 1H), 4.58 (d, $J = 5.7$ Hz, 1H), 3.92 (td, $J = 8.4, 5.8$ Hz, 1H), 3.80 (td, $J = 8.7, 6.3$ Hz, 1H), 3.03 (dd, $J = 11.3, 5.2$ Hz, 1H), 2.88 (s, 3H), 2.77 (dd, $J = 10.9$ Hz, 1H), 2.54 (ddtd, $J = 10.9, 8.5, 5.5, 3.2$ Hz, 1H), 2.25 (s, 3H), 2.27 – 2.20 (m, 1H), 1.77 (dddd, $J = 12.7, 8.3, 6.3, 3.2$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3), δ : 170.23, 145.32, 142.09, 123.74, 122.88, 122.05, 112.47, 75.73, 65.48, 52.86, 39.71, 36.35, 30.12, 21.21. HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ [(M+H) $^+$]: 248.1281. Found: 248.1272.

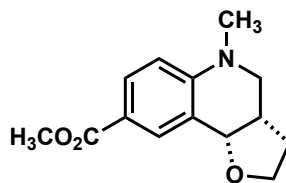


8b

2-(*cis*-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolin-8-yl)isoindoline-1,3-dione (8b**)**

4-(dimethylamino)pyridine (DMAP, 8 mg, 0.06 mmol, 0.1 equiv) was added to a solution of 4-(1,3-dioxisoindolin-2-yl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1d** (285 mg, 0.661 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 360 mg, 1.65 mmol, 2.5 equiv), and 2,3-dihydrofuran (228 mg, 3.25 mmol, 4.9 equiv) in dichloromethane (6.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, bright yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 165 μL , 0.165 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 12.5 hours. The clear, amber-orange reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (1 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford an orange glass that was purified by automated flash column chromatography (starting with toluene, grading to 10% acetone–toluene) to afford 2-(*cis*-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolin-8-

yl)isoindoline-1,3-dione (**8b**) as a yellow-orange solid (130 mg, 0.389 mmol, 59% yield). TLC: 5% acetone–toluene, $R_f=0.17$, UV. $^1\text{H NMR}$ (600 MHz, CDCl_3), δ : 7.92 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.75 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.39 (d, $J = 2.5$ Hz, 1H), 7.22 (dd, $J = 8.8, 2.6$ Hz, 1H), 6.78 (d, $J = 8.8$ Hz, 1H), 4.64 (d, $J = 5.5$ Hz, 1H), 3.94 (td, $J = 8.4, 5.8$ Hz, 1H), 3.80 (td, $J = 8.8, 6.2$ Hz, 1H), 3.08 (dd, $J = 11.3, 5.2$ Hz, 1H), 2.94 (s, 3H), 2.86 (dd, $J = 11.0$ Hz, 1H), 2.55 (ddtd, $J = 10.8, 8.4, 5.4, 3.1$ Hz, 1H), 2.24 (dddd, $J = 12.6, 9.0, 8.1, 5.8$ Hz, 1H), 1.78 (dddd, $J = 12.6, 8.4, 6.2, 3.1$ Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3), δ : 167.85, 147.09, 134.23, 132.14, 129.57, 127.56, 123.66, 122.35, 121.11, 112.20, 75.65, 65.38, 52.51, 39.52, 36.09, 30.05. HRMS (ESI): Calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3$ [(M+H) $^+$]: 335.1390. Found: 335.1389.

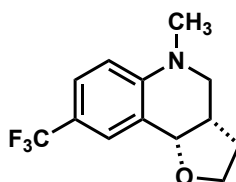


8c

methyl *cis*-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline-8-carboxylate (8c**)**

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (372 mg, 1.00 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 241 mg, 1.10 mmol, 1.1 equiv), and 2,3-dihydrofuran (360 mg, 5.14 mmol, 5.1 equiv) in dichloromethane (7.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting opaque amber-orange solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting pale yellow-orange slurry was stirred at –78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3.5 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a light amber syrup that was purified by automated flash column chromatography (starting with hexane, grading to 40% ethyl acetate–hexanes) to afford methyl *cis*-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline-8-carboxylate (**8c**) as a clear, orange-yellow syrup (132 mg, 0.534 mmol, 53% yield). TLC: 25% ethyl acetate–hexanes, $R_f=0.28$, UV. $^1\text{H NMR}$ (600 MHz, CDCl_3), δ : 8.02 (d, $J = 2.2$

Hz, 1H), 7.87 (dd, $J = 8.7, 2.2$ Hz, 1H), 6.65 (d, $J = 8.7$ Hz, 1H), 4.56 (d, $J = 5.1$ Hz, 1H), 3.95 (td, $J = 8.6, 6.0$ Hz, 1H), 3.84 (s, 3H), 3.87 – 3.80 (m, 1H), 3.09 (dd, $J = 11.6, 5.1$ Hz, 1H), 2.97 (s, 3H), 2.92 (dd, $J = 11.3$ Hz, 1H), 2.48 (ddtd, $J = 10.7, 7.8, 5.3, 2.5$ Hz, 1H), 2.25 (dddd, $J = 12.7, 9.3, 7.9, 6.0$ Hz, 1H), 1.75 (dddd, $J = 12.7, 8.6, 6.0, 2.6$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3), δ : 167.34, 150.40, 133.44, 131.27, 120.25, 118.19, 110.93, 75.67, 65.13, 51.93, 51.61, 39.25, 35.35, 29.93. HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ [(M+H) $^+$]: 248.1281. Found: 248.1280.

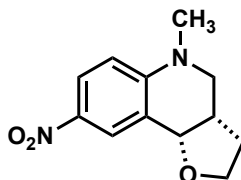


8d

***cis*-5-methyl-8-(trifluoromethyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (8d)**

4-(dimethylamino)pyridine (DMAP, 11 mg, 0.090 mmol, 0.090 equiv) was added to a solution of *N,N*-dimethyl-4-(trifluoromethyl)aniline-*N*-oxide 3-chlorobenzoic acid salt **1f** (374 mg, 0.998 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 546 mg, 2.50 mmol, 2.5 equiv), and 2,3-dihydrofuran (361 mg, 5.15 mmol, 5.2 equiv) in dichloromethane (7.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at –78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 5.25 hours. The clear, light amber-orange reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, faintly yellow oil that was purified by automated flash column chromatography (isocratic toluene) to afford *cis*-5-methyl-8-(trifluoromethyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (**8d**) as white needles (126 mg, 0.490 mmol, 49% yield). TLC: toluene, $R_f=0.22$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.58 (d, $J = 2.3$ Hz, 1H), 7.41 (dd, $J = 8.7, 2.3$ Hz, 1H), 6.70 (d, $J = 8.7$ Hz, 1H), 4.57 (d, $J = 5.3$ Hz, 1H), 3.95 (td, $J = 8.5, 5.9$ Hz, 1H), 3.84 (td, $J = 8.9, 6.1$ Hz, 1H), 3.08 (dd, $J = 11.5, 5.4$ Hz, 1H), 2.95 (s, 3H), 2.88 (dd, $J = 11.2$ Hz, 1H), 2.51 (ddtd, $J = 10.8, 8.0, 5.3, 2.7$ Hz, 1H), 2.27 (dddd, $J = 12.6, 9.2, 8.0, 5.9$ Hz, 1H), 1.77 (dddd, $J = 12.6, 8.7, 6.1, 2.7$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3), δ : 149.36, 128.58

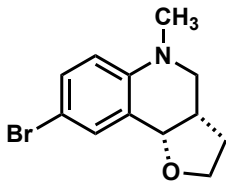
(q, $J = 3.8$ Hz), 126.35 (q, $J = 3.8$ Hz), 125.05 (q, $J = 270.4$ Hz), 121.06, 118.79 (q, $J = 32.8$ Hz), 111.36, 75.52, 65.27, 52.07, 39.31, 35.60, 29.97. ^{19}F NMR (565 MHz, CDCl_3), δ : -61.09 (s, 3F). HRMS Calcd. for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}$ [(M+H) $^+$]: 258.1100. Found: 258.1100.



8e

***cis*-5-methyl-8-nitro-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (8e)**

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of *N,N*-dimethyl-4-nitroaniline-*N*-oxide 3-chlorobenzoic acid salt **1g** (373 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 552 mg, 2.53 mmol, 2.5 equiv), and 2,3-dihydrofuran (370 mg, 5.28 mmol, 5.2 equiv) in dichloromethane (7.7 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, bright yellow-orange solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, bright red-orange solution was stirred at -78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3.25 hours. The clear, dark brown reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (2 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude residue that was purified by automated flash column chromatography (starting with toluene, grading to 5% diethyl ether-toluene) to afford *cis*-5-methyl-8-nitro-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (**8e**) as fine, yellow needles (119 mg, 0.508 mmol, 50% yield). TLC: 5% diethyl ether-toluene, $R_f=0.13$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 8.25 (d, $J = 2.8$ Hz, 1H), 8.09 (dd, $J = 9.2, 2.7$ Hz, 1H), 6.62 (d, $J = 9.2$ Hz, 1H), 4.57 (d, $J = 4.9$ Hz, 1H), 3.97 (td, $J = 8.6, 6.0$ Hz, 1H), 3.88 (td, $J = 9.1, 5.9$ Hz, 1H), 3.18 (dd, $J = 12.0, 5.6$ Hz, 1H), 3.06 (s, 3H), 3.03 (dd, $J = 11.5$ Hz, 1H), 2.50 (ddtd, $J = 10.6, 7.8, 5.3, 2.6$ Hz, 1H), 2.29 (dddd, $J = 12.8, 9.5, 7.7, 6.0$ Hz, 1H), 1.77 (dddd, $J = 12.7, 8.5, 5.9, 2.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3), δ : 151.38, 137.55, 128.09, 126.03, 119.94, 110.56, 75.23, 65.17, 51.62, 39.51, 34.90, 29.67. HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_3$ [(M+H) $^+$]: 235.1077. Found: 235.1073.



8f

***cis*-8-bromo-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (**8f**)¹⁰¹¹¹²**

4-(dimethylamino)pyridine (DMAP, 11 mg, 0.090 mmol, 0.1 equiv) was added to a solution of 4-bromo-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1h** (318 mg, 0.833 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 467 mg, 2.14 mmol, 2.6 equiv), and 2,3-dihydrofuran (295 mg, 4.21 mmol, 5.0 equiv) in dichloromethane (6.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, orange-yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 210 μL, 0.210 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, amber-brown solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 16.25 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, golden-yellow oil that was purified by automated flash column chromatography (starting with toluene, grading to 3% ethyl acetate–toluene) to afford *cis*-8-bromo-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (**8f**) as a brown-yellow syrup (162 mg, 0.604 mmol, 73% yield). TLC: 5% ethyl acetate–toluene, R_f=0.38, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.44 (d, *J* = 2.5 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 4.53 (d, *J* = 5.6 Hz, 1H), 3.93 (td, *J* = 8.5, 5.8 Hz, 1H), 3.81 (td, *J* = 8.8, 6.2 Hz, 1H), 3.02 (dd, *J* = 11.3, 5.2 Hz, 1H), 2.86 (s, 3H), 2.77 (dd, *J* = 11.0 Hz, 1H), 2.52 (ddtd, *J* = 10.9, 8.3, 5.4, 3.0 Hz, 1H), 2.29 – 2.19 (m, 1H), 1.80 – 1.72 (m, 1H). ¹³C NMR (151 MHz, CDCl₃), δ: 146.31,

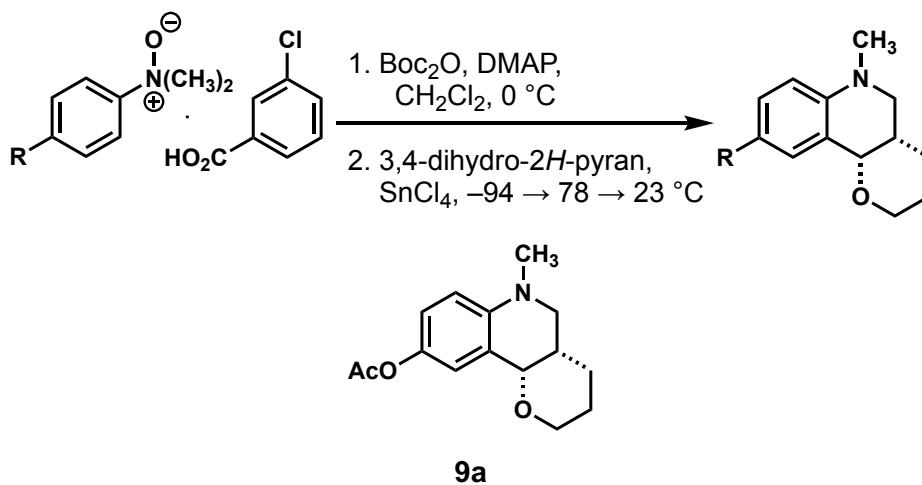
¹⁰ Reddy, B. V. S.; Grewal, H.; *Tetrahedron Lett.* **2011**, 52, 761-763.

¹¹ Kawade, R. K.; Huple, D. B.; Lin, R. J.; Liu, R. S.; *Chem. Commun. (Cambridge, U.K.)* **2015**, 51, 6625-6628.

¹² Huo, C.; Chen, F.; Quan, Z.; Dong, J.; Wang, Y.; *Tetrahedron Lett.* **2016**, 57, 5127-5131.

133.69, 131.82, 123.97, 113.67, 109.45, 75.50, 65.43, 52.54, 39.48, 36.13, 30.08. HRMS (ESI): Calcd. for C₁₂H₁₅BrNO [(M⁷⁹Br+H)⁺]: 268.0332 and [(M⁸¹Br+H)⁺]: 270.0311. Found: 268.0331 and 270.0310.

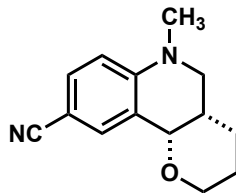
Preparation of *cis*-6-methyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinolines



cis-6-methyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinolin-9-yl acetate (**9a**)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-acetoxy-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1a** (382 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 572 mg, 2.62 mmol, 2.6 equiv), and 3,4-dihydro-2*H*-pyran (429 mg, 5.10 mmol, 5.0 equiv) in dichloromethane (7.75 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, dark brown solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at -78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3.5 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, dark red oil that was purified by automated flash column chromatography (starting with toluene, grading to 10% diethyl ether-toluene) to afford *cis*-6-methyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinolin-9-yl acetate (**9a**) as off-white to beige needles (157 mg, 0.601 mmol, 59% yield). TLC: 5% diethyl ether-toluene, R_f=0.12, UV.

^1H NMR (600 MHz, CDCl_3), δ : 6.97 (d, $J = 2.8$ Hz, 1H), 6.88 (dd, $J = 8.9, 2.8$ Hz, 1H), 6.57 (d, $J = 8.9$ Hz, 1H), 4.45 (d, $J = 3.5$ Hz, 1H), 3.89 (dt, $J = 12.6, 4.4$ Hz, 1H), 3.63 (ddd, $J = 11.3, 9.6, 2.9$ Hz, 1H), 3.45 (dd, $J = 10.6$ Hz, 1H), 2.99 (dd, $J = 11.1, 3.9$ Hz, 1H), 2.88 (s, 3H), 2.24 (s, 3H), 2.14 (dp, $J = 8.6, 4.2$ Hz, 1H), 1.86 (ddt, $J = 13.9, 11.1, 4.8$ Hz, 1H), 1.80 – 1.69 (m, 2H), 1.48 (dddd, $J = 13.0, 7.5, 5.1, 3.5$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3), δ : 170.33, 144.69, 141.41, 123.05, 122.30, 122.21, 111.94, 73.78, 66.86, 51.74, 39.46, 32.49, 25.34, 23.00, 21.23. HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{20}\text{NO}_3$ [(M+H) $^+$]: 262.1438. Found: 262.1429.

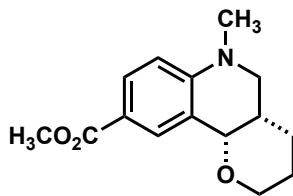


9b

***cis*-6-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline-9-carbonitrile (9b)**

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-cyano-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1e** (346 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 263 mg, 1.21 mmol, 1.2 equiv), and 3,4-dihydro-2H-pyran (252 mg, 3.00 mmol, 3.0 equiv) in dichloromethane (7.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, amber solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at –78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 2.5 hours. The reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (1 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, amber oil that was purified by automated flash column chromatography (starting with 25% dichloromethane–hexanes, grading to dichloromethane) to afford *cis*-6-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline-9-carbonitrile (**9b**) as off-white needles (143 mg, 0.626 mmol, 62% yield). TLC: 50% dichloromethane–hexanes, $R_f=0.07$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.44 (d, $J = 2.2$ Hz, 1H), 7.38 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.54 (d, $J = 8.7$ Hz, 1H), 4.38 (d, $J = 3.0$ Hz, 1H), 3.97 – 3.92 (m, 1H), 3.70 – 3.62 (m, 2H), 3.08 (ddd, $J = 11.7, 4.5, 1.3$ Hz, 1H), 2.96 (s, 3H), 2.12 (ddd, $J = 14.2, 7.7, 4.1$ Hz, 1H), 1.92 –

1.87 (m, 1H), 1.82 – 1.73 (m, 2H), 1.51 – 1.44 (m, 1H). ¹³C NMR (151 MHz, CDCl₃), δ: 149.11, 134.75, 133.73, 121.58, 120.67, 110.98, 97.61, 73.49, 67.65, 50.81, 38.84, 31.63, 25.09, 22.43. HRMS (ESI): Calcd. for C₁₄H₁₇N₂O [(M+H)⁺]: 229.1335. Found: 229.1336.

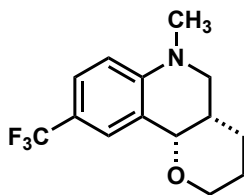


9c

methyl *cis*-6-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline-9-carboxylate (9c)

4-(dimethylamino)pyridine (DMAP, 12 mg, 0.10 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (372 mg, 1.00 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 241 mg, 1.10 mmol, 1.1 equiv), and 3,4-dihydro-2*H*-pyran (422 mg, 5.02 mmol, 5.0 equiv) in dichloromethane (7.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting opaque, amber-orange solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting opaque, pale yellow-orange solution was stirred at –78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 3.75 hours. The pale orange-cream reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (5 mL) and ethyl acetate (5 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, light amber syrup that was purified by automated flash column chromatography (starting with hexanes, grading to 30% ethyl acetate–hexanes) to afford methyl *cis*-6-methyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-c]quinoline-9-carboxylate (**9c**) as waxy, pale yellow needles (110 mg, 0.421 mmol, 42% yield). TLC: 25% ethyl acetate–hexanes, R_f=0.44, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.87 (d, *J* = 2.2 Hz, 1H), 7.82 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 4.40 (d, *J* = 3.0 Hz, 1H), 4.00 – 3.94 (m, 1H), 3.83 (s, 3H), 3.70 – 3.63 (m, 2H), 3.03 (dd, *J* = 11.1, 3.6 Hz, 1H), 2.97 (s, 3H), 2.15 – 2.10 (m, 1H), 1.92 – 1.86 (m, 1H), 1.77 (ddt, *J* = 12.6, 8.6, 3.4 Hz, 2H), 1.49 – 1.42 (m, 1H). ¹³C NMR (151 MHz, CDCl₃), δ: 167.45, 149.76, 132.87, 131.69, 120.61, 117.17, 110.25, 74.14, 67.83, 51.54, 50.78,

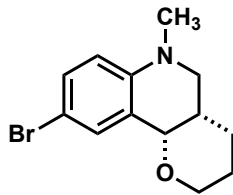
38.90, 31.91, 25.34, 22.41. HRMS (ESI): Calcd. for C₁₅H₂₀NO₃ [(M+H)⁺]: 262.1438. Found: 262.1437.



9d

***cis*-6-methyl-9-(trifluoromethyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline (9d)**

4-(dimethylamino)pyridine (DMAP, 13 mg, 0.11 mmol, 0.1 equiv) was added to a solution of *N,N*-dimethyl-4-(trifluoromethyl)aniline-*N*-oxide 3-chlorobenzoic acid salt **1f** (381 mg, 1.02 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 584 mg, 2.68 mmol, 2.6 equiv), and 3,4-dihydro-2*H*-pyran (434 mg, 5.16 mmol, 5.0 equiv) in dichloromethane (7.75 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at -78 °C for a minimum of 1 hour, then allowed to warm slowly to 23 °C with stirring over an additional 5.5 hours. The clear, yellow reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, orange oil that was purified by automated flash column chromatography (isocratic toluene) to afford *cis*-6-methyl-9-(trifluoromethyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-c]quinoline (**9d**) as white needles (177 mg, 0.652 mmol, 64% yield). TLC: toluene, R_f=0.28, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.44 (d, *J* = 2.3 Hz, 1H), 7.37 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 4.42 (d, *J* = 3.1 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.68 (td, *J* = 11.2, 2.8 Hz, 1H), 3.62 (dd, *J* = 11.2 Hz, 1H), 3.03 (ddd, *J* = 11.3, 4.3, 1.2 Hz, 1H), 2.95 (s, 3H), 2.19 – 2.10 (m, 1H), 1.96 – 1.85 (m, 1H), 1.84 – 1.73 (m, 2H), 1.52 – 1.44 (m, 1H). ¹³C NMR (151 MHz, CDCl₃), δ: 148.66, 127.94 (q, *J* = 3.7 Hz), 126.68 (q, *J* = 3.7 Hz), 125.50 (q, *J* = 270.1 Hz), 121.05, 117.71 (q, *J* = 32.8 Hz), 110.68, 73.90, 67.64, 50.90, 38.97, 32.00, 25.31, 22.55. ¹⁹F NMR (565 MHz, CDCl₃), δ: -60.89 (s, 3F). HRMS (ESI): Calcd. for C₁₄H₁₇F₃NO [(M+H)⁺]: 272.1257. Found: 272.1257.

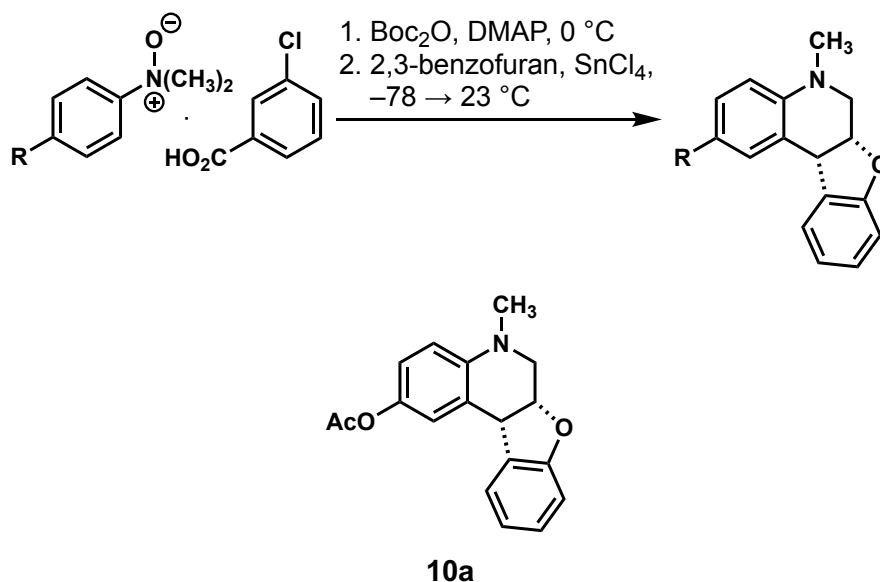


9e

***cis*-9-bromo-6-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline (9e)¹⁰**

4-(dimethylamino)pyridine (DMAP, 11 mg, 0.090 mmol, 0.1 equiv) was added to a solution of 4-bromo-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1h** (304 mg, 0.796 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 428 mg, 1.96 mmol, 2.5 equiv), and 3,4-dihydro-2*H*-pyran (565 mg, 6.72 mmol, 8.4 equiv) in dichloromethane (6.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, orange-yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 200 μL, 0.200 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, amber-brown solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 16.75 hours. The clear, black-green reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (2 × 10 mL). The combined clear, yellow organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, golden-yellow oil that was purified by automated flash column chromatography (starting with toluene, grading to 5% ethyl acetate–toluene) to afford *cis*-9-bromo-6-methyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-c]quinoline (**9e**) as a clear, faintly amber syrup (163 mg, 0.578 mmol, 72% yield). TLC: 2.5% ethyl acetate–toluene, R_f=0.28, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.30 (d, *J* = 2.3 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.47 (d, *J* = 8.8 Hz, 1H), 4.38 (d, *J* = 3.3 Hz, 1H), 3.94 (dt, *J* = 11.6, 3.7 Hz, 1H), 3.65 (ddd, *J* = 11.3, 10.0, 2.8 Hz, 1H), 3.49 (dd, *J* = 11.0 Hz, 1H), 2.97 (ddd, *J* = 11.2, 4.1, 1.2 Hz, 1H), 2.87 (s, 3H), 2.16 – 2.07 (m, 1H), 1.93 – 1.83 (m, 1H), 1.81 – 1.70 (m, 2H), 1.52 – 1.43 (m, 1H). ¹³C NMR (151 MHz, CDCl₃), δ: 145.62, 133.04, 132.08, 123.65, 113.17, 108.17, 73.79, 67.39, 51.23, 39.17, 32.35, 25.40, 22.71. HRMS (ESI): Calcd. for C₁₃H₁₇BrNO [(M⁷⁹Br+H)⁺]: 282.0488 and [(M⁸¹Br+H)⁺]: 284.0468. Found: 282.0488 and 284.0466.

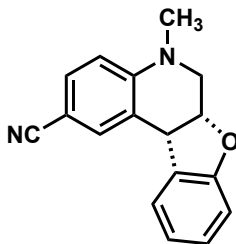
Preparation of *cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-c]quinolines



***cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinolin-2-yl acetate (**10a**)**

4-(dimethylamino)pyridine (DMAP, 16 mg, 0.13 mmol, 0.13 equiv) was added to a solution of 4-acetoxy-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1a** (378 mg, 1.03 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 563 mg, 2.58 mmol, 2.5 equiv), and 2,3-benzofuran (331 mg, 2.80 mmol, 2.7 equiv) in dichloromethane (8.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, light yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.24 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 10 hours. The clear, amber reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, red-brown oil that was purified by automated flash column chromatography (starting with toluene, grading to 5% ethyl acetate–toluene) to afford *cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinolin-2-yl acetate (**10a**) as off-white needles (197 mg, 0.667 mmol, 64% yield). TLC: 5% ethyl acetate–toluene, R_f=0.40, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.18 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 5.27 (dt, *J* = 9.4, 3.7 Hz, 1H), 4.65 (d, *J* = 9.4 Hz, 1H), 3.32 (dd, *J* = 12.4, 3.9 Hz, 1H), 3.14

(dd, $J = 12.4, 3.5$ Hz, 1H), 2.83 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3), δ : 170.19, 159.40, 145.97, 143.14, 129.98, 128.64, 126.03, 124.97, 121.48, 120.86, 120.28, 113.03, 109.61, 81.91, 54.92, 43.22, 39.83, 21.30. HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{18}\text{NO}_3$ $[(\text{M}+\text{H})^+]$: 296.1281. Found: 296.1271.

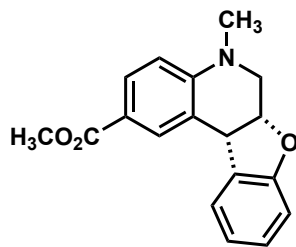


10b

***cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline-2-carbonitrile (10b)**

4-(dimethylamino)pyridine (DMAP, 11 mg, 0.090 mmol, 0.09 equiv) was added to a solution of 4-cyano-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1e** (347 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 557 mg, 2.55 mmol, 2.5 equiv), and 2,3-benzofuran (304 mg, 2.57 mmol, 2.5 equiv) in dichloromethane (7.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to -78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL , 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting thin, orange-beige slurry was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 23.5 hours. The opaque, burnt orange reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude residue that was purified by automated flash column chromatography (starting with hexanes, grading to 20% ethyl acetate-hexanes) to afford *cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline-2-carbonitrile (**10b**) as pale yellow, granular crystals (136 mg, 0.518 mmol, 51% yield). TLC: 20% ethyl acetate-hexanes, $R_f=0.30$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.58 (d, $J = 1.9$ Hz, 1H), 7.40 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.19 (dt, $J = 7.5, 1.2$ Hz, 1H), 7.13 (t, $J = 7.9$ Hz, 1H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.65 (d, $J = 8.6$ Hz, 1H), 5.26 (dt, $J = 9.1, 4.1$ Hz, 1H), 4.63 (d, $J = 9.1$ Hz, 1H), 3.41 (dd, $J = 12.7, 4.3$ Hz, 1H), 3.31 (dd, $J = 12.7, 3.6$ Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3), δ : 159.00, 150.78, 132.29, 132.14, 129.72, 129.07, 124.92, 124.83, 121.25,

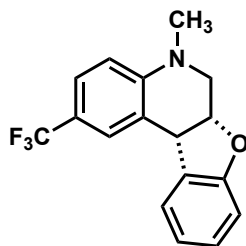
120.23, 112.43, 110.01, 100.53, 80.69, 53.35, 42.52, 39.39. HRMS (ESI): Calcd. for C₁₇H₁₅N₂O [(M+H)⁺]: 263.1179. Found: 263.1173.



10c

methyl *cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline-2-carboxylate (10c)

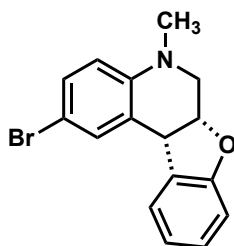
4-(dimethylamino)pyridine (DMAP, 13 mg, 0.11 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (376 mg, 0.998 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 549 mg, 2.52 mmol, 2.5 equiv), and 2,3-benzofuran (300 mg, 2.54 mmol, 2.5 equiv) in dichloromethane (8.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to -78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.24 equiv) slowly charged to the reaction mixture. The resulting clear, golden-yellow solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 20 hours. The opaque pink-peach reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, orange-yellow oil that was purified by automated flash column chromatography (starting with hexanes, grading to 30% ethyl acetate–hexanes) to afford methyl *cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline-2-carboxylate (**10c**) as an off-white powder (256 mg, 0.867 mmol, 87% yield). TLC: 20% ethyl acetate–hexanes, R_f=0.35, UV. ¹H NMR (600 MHz, CDCl₃), δ: 8.04 (d, *J* = 2.1 Hz, 1H), 7.82 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.10 (tt, *J* = 7.6, 1.2 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 1H), 5.27 (dt, *J* = 9.3, 4.1 Hz, 1H), 4.69 (d, *J* = 9.3 Hz, 1H), 3.90 (s, 3H), 3.38 (dd, *J* = 12.5, 4.4 Hz, 1H), 3.27 (dd, *J* = 12.5, 3.7 Hz, 1H), 2.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃), δ: 167.36, 159.01, 151.39, 130.32 (2 C's), 129.79, 128.73, 125.07, 123.93, 121.06, 119.81, 111.71, 109.76, 81.04, 53.70, 51.92, 42.74, 39.55. HRMS (ESI): Calcd. for C₁₈H₁₈NO₃ [(M+H)⁺]: 296.1281. Found: 296.1279.



10d

***cis*-5-methyl-2-(trifluoromethyl)-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline (10d)**

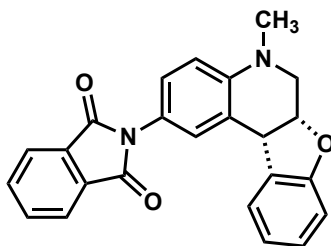
4-(dimethylamino)pyridine (DMAP, 10 mg, 0.082 mmol, 0.08 equiv) was added to a solution of *N,N*-dimethyl-4-(trifluoromethyl)aniline-*N*-oxide 3-chlorobenzoic acid salt **1f** (377 mg, 1.00 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 552 mg, 2.53 mmol, 2.5 equiv), and 2,3-benzofuran (308 mg, 2.60 mmol, 2.6 equiv) in dichloromethane (7.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 250 μL, 0.250 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 11 hours. The clear, yellow reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude residue that was purified by automated flash column chromatography (isocratic toluene) to afford *cis*-5-methyl-2-(trifluoromethyl)-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline (**10d**) as white needles (239 mg, 0.783 mmol, 78% yield). TLC: toluene, R_f=0.55, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.56 (d, *J* = 2.2 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.17 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.12 (td, *J* = 8.0, 7.4, 1.4 Hz, 1H), 6.83 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 5.29 (dt, *J* = 9.3, 3.9 Hz, 1H), 4.69 (d, *J* = 9.3 Hz, 1H), 3.38 (dd, *J* = 12.5, 4.2 Hz, 1H), 3.23 (dd, *J* = 12.5, 3.6 Hz, 1H), 2.90 (s, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 159.20, 150.34, 129.93, 128.86, 125.54 (q, *J* = 3.7 Hz), 124.96 (q, *J* = 3.8 Hz), 124.95 (q, *J* = 270.6 Hz), 124.88, 124.79, 121.08, 120.44 (q, *J* = 32.5 Hz), 112.08, 109.83, 81.29, 54.05, 42.95, 39.54. ¹⁹F NMR (565 MHz, CDCl₃), δ: –61.16 (s, 3F). HRMS (ESI): Calcd. for C₁₇H₁₅F₃NO [(M+H)⁺]: 306.1100. Found: 306.1093.



10e

***cis*-2-bromo-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline (10e)**

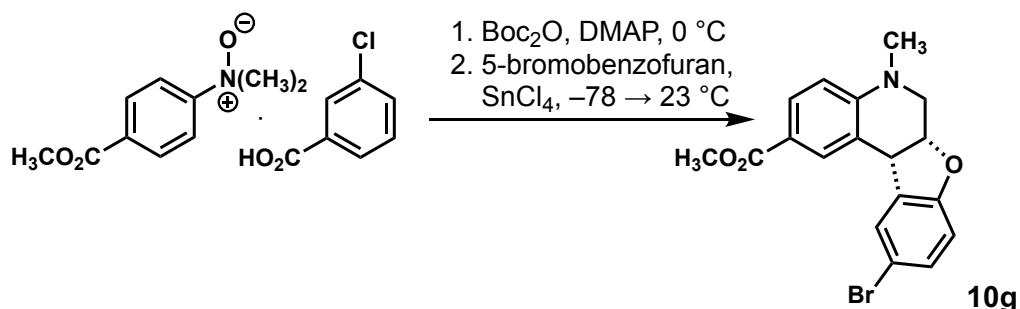
4-(dimethylamino)pyridine (DMAP, 12 mg, 0.098 mmol, 0.1 equiv) was added to a solution of 4-bromo-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1h** (345 mg, 0.904 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 514 mg, 2.36 mmol, 2.6 equiv), and 2,3-benzofuran (281 mg, 2.38 mmol, 2.6 equiv) in dichloromethane (7.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, orange-yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 225 μL, 0.225 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, amber-brown solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 17 hours. The clear, teal reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, golder-yellow oil that was purified by automated flash column chromatography (starting with hexanes, grading to 5% ethyl acetate–hexanes) to afford *cis*-2-bromo-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline (**10e**) as cream-colored needles (240 mg, 0.759 mmol, 84% yield). TLC: 10% ethyl acetate–hexanes, *R*_f=0.39, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.44 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.18 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.11 (tdd, *J* = 7.7, 1.3, 0.6 Hz, 1H), 6.83 (td, *J* = 7.4, 1.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 8.7 Hz, 1H), 5.26 (dt, *J* = 9.4, 3.7 Hz, 1H), 4.62 (d, *J* = 9.4 Hz, 1H), 3.33 (dd, *J* = 12.5, 3.9 Hz, 1H), 3.13 (dd, *J* = 12.5, 3.4 Hz, 1H), 2.82 (s, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 159.37, 147.13, 131.00, 130.37, 129.82, 128.78, 127.29, 124.96, 120.93, 114.28, 110.97, 109.70, 81.74, 54.66, 42.95, 39.65. HRMS (ESI): Calcd. for C₁₆H₁₅BrNO [(M⁷⁹Br+H)⁺]: 316.0332 and [(M⁸¹Br+H)⁺]: 318.0311. Found: 316.0331 and 318.0310.



10f

2-(*cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinolin-2-yl)isoindoline-1,3-dione (10f)

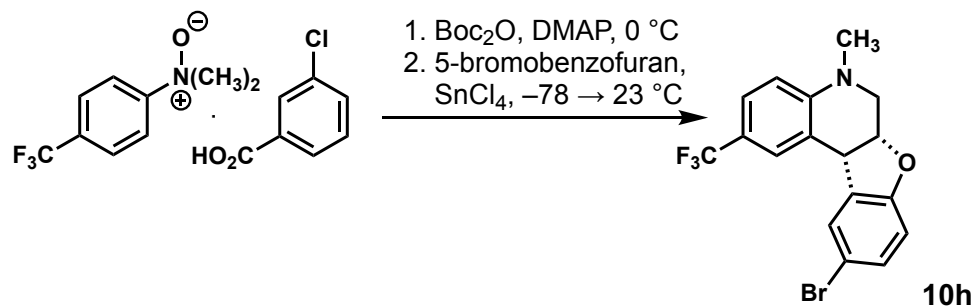
4-(dimethylamino)pyridine (DMAP, 7 mg, 0.06 mmol, 0.09 equiv) was added to a solution of 4-(1,3-dioxoisoindolin-2-yl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1d** (275 mg, 0.638 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 360 mg, 1.65 mmol, 2.6 equiv), and 2,3-benzofuran (194 mg, 1.64 mmol, 2.6 equiv) in dichloromethane (6.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, bright yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to –78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 160 μL, 0.160 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 12.5 hours. The clear, black-brown reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane (1 × 10 mL). The combined golden-yellow organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude residue that was purified by automated flash column chromatography (starting with toluene, grading to 5% ethyl acetate–toluene) to afford 2-(*cis*-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinolin-2-yl)isoindoline-1,3-dione (**10f**) as a light yellow solid (129 mg, 0.337 mmol, 53% yield). TLC: 5% ethyl acetate–toluene, *R*_f=0.28, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.96 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.79 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.42 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.27 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.21 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.84 (td, *J* = 7.4, 1.0 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 5.30 (dt, *J* = 9.4, 3.9 Hz, 1H), 4.72 (d, *J* = 9.4 Hz, 1H), 3.36 (dd, *J* = 12.5, 4.2 Hz, 1H), 3.22 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.89 (s, 3H). ¹³C NMR (151 MHz, CDCl₃), δ: 167.87, 159.24, 147.72, 134.41, 132.09, 130.06, 128.65, 126.75, 125.82, 125.45, 125.18, 123.75, 122.50, 121.06, 112.82, 109.61, 81.56, 54.50, 43.16, 39.68. HRMS (ESI): Calcd. for C₂₄H₁₉N₂O₃ [(M+H)⁺]: 383.1390. Found: 383.1388.



methyl *cis*-10-bromo-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-c]quinoline-2-carboxylate (10g)

4-(dimethylamino)pyridine (DMAP, 7 mg, 57 μmol , 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (214 mg, 0.568 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 317 mg, 1.45 mmol, 2.5 equiv), and 5-bromobenzofuran (198 mg, 1.00 mmol, 1.8 equiv) in dichloromethane (5.0 mL) under an atmosphere of Ar and cooled to $0\text{ }^\circ\text{C}$ in a previously oven-dried flask. The resulting clear, golden-yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to $-78\text{ }^\circ\text{C}$, then tin(IV) chloride (1.0 M in heptane, 145 μL , 145 μmol , 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, amber solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to $23\text{ }^\circ\text{C}$ and stirred for an additional 15 hours. The clear, magenta-red reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane ($1 \times 10\text{ mL}$). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, golden-amber oil that was purified by automated flash column chromatography (isocratic 10% ethyl acetate–hexanes) to afford methyl *cis*-10-bromo-5-methyl-5,6,6a,11b-tetrahydrobenzofuro[2,3-c]quinoline-2-carboxylate (**10g**) as an off-white foam (87 mg, 0.232 mmol, 41% yield). TLC: 10% ethyl acetate–hexanes, $R_f=0.12$, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.97 (d, $J = 2.1\text{ Hz}$, 1H), 7.85 (dd, $J = 8.6, 2.1\text{ Hz}$, 1H), 7.25 (d, $J = 2.1\text{ Hz}$, 1H), 7.19 (dd, $J = 8.5, 2.1\text{ Hz}$, 1H), 6.67 (d, $J = 8.6\text{ Hz}$, 1H), 6.65 (d, $J = 8.5\text{ Hz}$, 1H), 5.29 (dt, $J = 9.3, 3.9\text{ Hz}$, 1H), 4.68 (d, $J = 9.3\text{ Hz}$, 1H), 3.91 (s, 3H), 3.35 (dd, $J = 12.6, 4.2\text{ Hz}$, 1H), 3.22 (dd, $J = 12.6, 3.7\text{ Hz}$, 1H), 2.91 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3), δ : 167.18, 158.37, 151.49, 132.68, 131.58, 130.21, 130.11, 127.98, 123.28, 120.23, 112.69, 111.87, 111.30, 81.89, 53.91, 51.93, 42.94, 39.47. HRMS (ESI): Calcd.

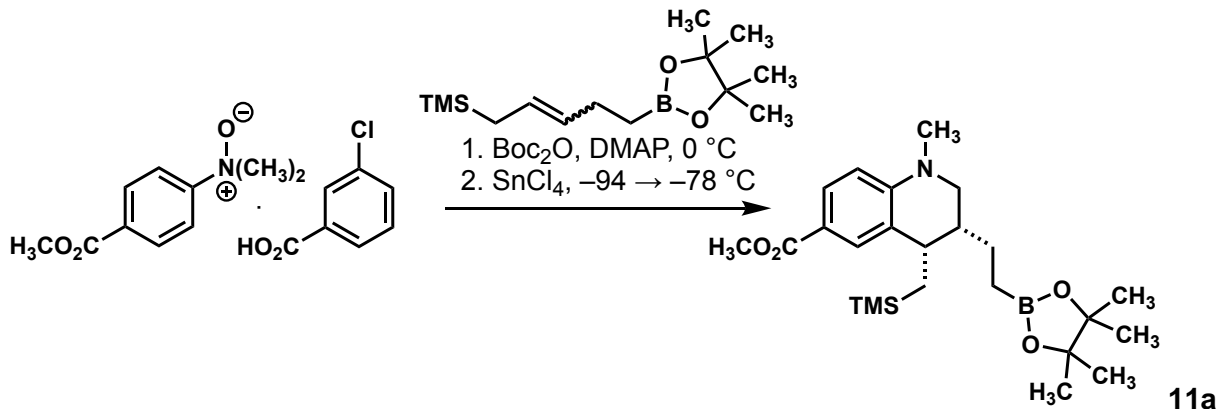
for $C_{18}H_{17}BrNO_3$ $[(M^{79}Br+H)^+]$: 374.0386 and $[(M^{81}Br+H)^+]$: 376.0366. Found: 374.0376 and 376.0353.



***cis*-10-bromo-5-methyl-2-(trifluoromethyl)-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline (10h)**

4-(dimethylamino)pyridine (DMAP, 12 mg, 98 μmol , 0.1 equiv) was added to a solution of *N,N*-dimethyl-4-(trifluoromethyl)aniline-*N*-oxide 3-chlorobenzoic acid salt **1f** (378 mg, 1.01 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 542 mg, 2.48 mmol, 2.5 equiv), and 5-bromobenzofuran (307 mg, 1.56 mmol, 1.5 equiv) in dichloromethane (8.0 mL) under an atmosphere of Ar and cooled to $0\text{ }^\circ\text{C}$ in a previously oven-dried flask. The resulting clear, yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to $-78\text{ }^\circ\text{C}$, then tin(IV) chloride (1.0 M in heptane, 250 μL , 250 μmol , 0.25 equiv) slowly charged to the reaction mixture. The resulting clear, green-yellow solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to $23\text{ }^\circ\text{C}$ and stirred for an additional 15 hours. The clear, blood orange reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer extracted with dichloromethane ($1 \times 10\text{ mL}$). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, golden-amber oil that was purified by automated flash column chromatography (starting with hexanes, grading to 5% ethyl acetate–hexanes) to afford *cis*-10-bromo-5-methyl-2-(trifluoromethyl)-5,6,6a,11b-tetrahydrobenzofuro[2,3-*c*]quinoline (**10h**) as pale mustard-yellow needles (211 mg, 0.549 mmol, 54% yield). TLC: 5% ethyl acetate–hexanes, $R_f=0.17$, UV. ^1H NMR (600 MHz, $CDCl_3$), δ : 7.50 (d, $J = 2.2\text{ Hz}$, 1H), 7.42 (dd, $J = 8.6, 2.2\text{ Hz}$, 1H), 7.20 (dd, $J = 8.4, 2.1\text{ Hz}$, 1H), 7.19 – 7.18 (m, 1H), 6.73 (d, $J = 8.5\text{ Hz}$, 1H), 6.67 (d, $J = 8.4\text{ Hz}$, 1H), 5.31 (dt, $J = 9.4, 3.8\text{ Hz}$, 1H), 4.68 (d, $J = 9.4\text{ Hz}$, 1H), 3.36 (dd, $J = 12.6, 4.0\text{ Hz}$, 1H), 3.19 (dd, $J = 12.6, 3.6\text{ Hz}$, 1H), 2.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ : 158.47, 150.51, 132.21, 131.70, 127.85, 125.37 (q, $J = 3.7$

Hz), 125.31 (q, $J = 3.9$ Hz), 124.80 (q, $J = 271.1$ Hz), 124.14, 120.71 (q, $J = 32.8$ Hz), 112.64, 112.31, 111.33, 82.21, 54.24, 43.00, 39.52. ^{19}F NMR (565 MHz, CDCl_3), δ : -61.15 (s, 3F). HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{14}\text{BrF}_3\text{NO}$ [$(\text{M}^{79}\text{Br}+\text{H})^+$]: 384.0205 and [$(\text{M}^{81}\text{Br}+\text{H})^+$]: 386.0185. Found: 384.0198 and 386.0169.

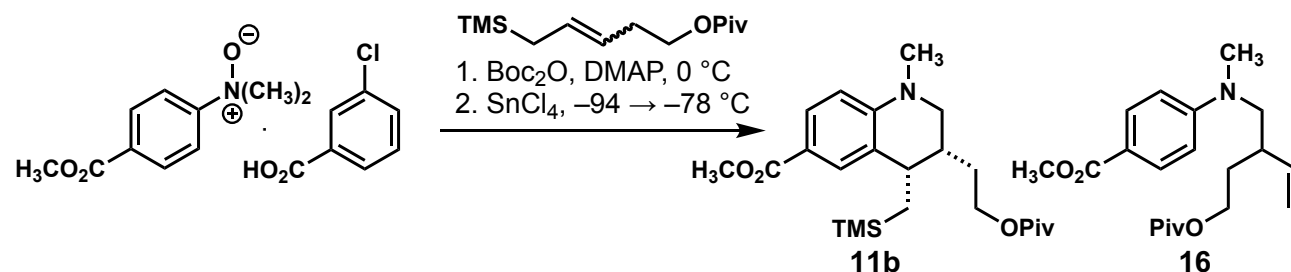


methyl *cis*-1-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-4-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (11a)

4-(dimethylamino)pyridine (DMAP, 9 mg, 0.07 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (243 mg, 0.654 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc_2O , 356 mg, 1.63 mmol, 2.5 equiv), and trimethyl(5-(pinacolboronylethyl)pent-2-enyl)silane¹³ (70:19:11 *E:Z*:vinyl, 375 mg, 1.02 mmol, 1.6 equiv) in dichloromethane (5.0 mL) under an atmosphere of Ar and cooled to $0\text{ }^\circ\text{C}$ in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to $-94\text{ }^\circ\text{C}$ using liquid N_2 , then tin(IV) chloride (1.0 M in dichloromethane, 165 μL , 0.165 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at $-78\text{ }^\circ\text{C}$ for 3.25 hours. The clear, orange-yellow reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 \times 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a clear, faintly beige-peach oil that was purified by automated flash column chromatography (starting with hexanes, grading to 15% ethyl acetate-hexanes) to afford a mixture of the tetrahydroquinoline cyclization adduct and the uncyclized homoallylic amine.

¹³ McAtee, J. R.; Yap, G. P.; Watson, D. A.; *J. Am. Chem. Soc.* **2014**, *136*, 10166-10172.

Removal of the homoallylic amine was achieved by flash column chromatography employing ~10 wt% AgNO₃ impregnated silica gel (starting with toluene, grading to 2% diethyl ether–toluene) to afford methyl *cis*-1-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-4-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (**11a**) as a clear, faintly amber syrup (89 mg, 0.200 mmol, 31% yield). TLC: 5% ethyl acetate–hexanes, R_f=0.20, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.72 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 6.46 (d, *J* = 8.7 Hz, 1H), 3.84 (s, 3H), 3.56 (dd, *J* = 12.1, 3.8 Hz, 1H), 3.01 (dt, *J* = 12.1, 1.8 Hz, 1H), 2.97 (s, 3H), 2.73 (dd, *J* = 9.7, 5.4 Hz, 1H), 1.69 – 1.62 (m, 1H), 1.27 – 1.24 (m, 2H), 1.21 (s, 12H), 0.84 – 0.80 (m, 2H), 0.80 – 0.76 (m, 2H), 0.04 (s, 9H). ¹³C NMR (151 MHz, CDCl₃), δ: 167.82, 148.37, 131.27, 129.36, 126.84, 116.62, 109.08, 83.18, 51.48, 49.97, 39.20, 38.95, 37.75, 28.23, 27.06, 25.04, 25.01, 24.98, –0.40. ²⁹Si NMR (119 MHz, CDCl₃), δ: 0.06. HRMS (ESI): Calcd. for C₂₄H₄₁BNO₄Si [(M+H)⁺]: 446.2892. Found: 446.2893.

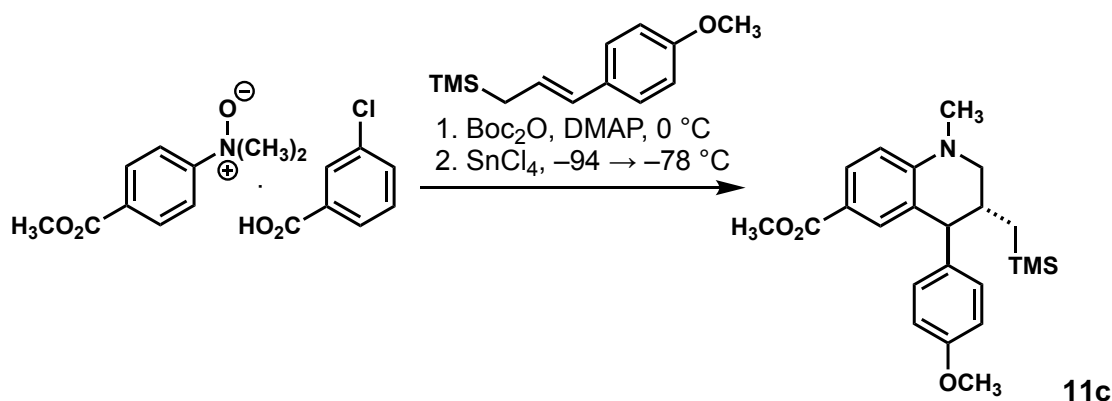


methyl *cis*-1-methyl-3-(2-(pivaloyloxy)ethyl)-4-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (11b) and methyl 4-(methyl(2-(2-(pivaloyloxy)ethyl)but-3-en-1-yl)amino)benzoate (16)

4-(dimethylamino)pyridine (DMAP, 9 mg, 0.07 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (213 mg, 0.569 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 310 mg, 1.42 mmol, 2.5 equiv), and 5-(trimethylsilyl)pent-3-enyl pivalate¹³ (75:12:13 *E:Z*:vinyl, 202 mg, 0.833 mmol, 1.5 equiv) in dichloromethane (4.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 150 μL, 0.150 mmol, 0.26 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at –78 °C for 3.5 hours. The clear, bright yellow reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and

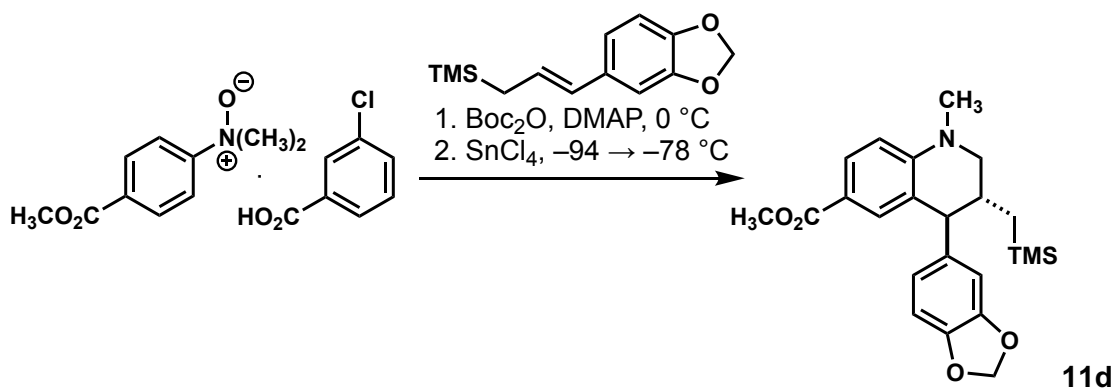
then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude oil that was purified by automated flash column chromatography (starting with hexanes, grading to 15% ethyl acetate–hexanes) to afford methyl *cis*-1-methyl-3-(2-(pivaloyloxy)ethyl)-4-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate and methyl 4-(methyl(2-(2-(pivaloyloxy)ethyl)but-3-en-1-yl)amino)benzoate (**11b**) as a clear, yellow syrup (139 mg, 0.331 mmol, 58% yield). TLC: 10% ethyl acetate–hexanes, R_f = 0.27, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.74 (dd, J = 8.6, 2.1 Hz, 1H), 7.62 (d, J = 2.1 Hz, 1H), 6.51 (d, J = 8.7 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.84 (s, 3H), 3.61 (dd, J = 12.2, 3.6 Hz, 1H), 3.06 – 2.95 (m, 1H), 3.00 (s, 3H), 2.72 – 2.67 (m, 1H), 1.93 – 1.86 (m, 1H), 1.56 – 1.44 (m, 2H), 1.19 (s, 9H), 0.87 (dd, J = 15.1, 5.4 Hz, 1H), 0.82 (dd, J = 15.1, 9.7 Hz, 1H), 0.05 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3), δ : 178.72, 167.68, 148.07, 131.33, 129.58, 126.14, 117.03, 109.37, 62.50, 51.56, 49.62, 39.00, 38.89, 38.32, 33.55, 31.85, 28.12, 27.39, –0.46. ^{29}Si NMR (119 MHz, CDCl_3), δ : 0.04. HRMS (ESI): Calcd. for $\text{C}_{23}\text{H}_{38}\text{NO}_4\text{Si}$ [(M+H) $^+$]: 420.2565. Found: 420.2550.

Additionally, a hazy, yellow syrup (70 mg, 0.201 mmol, 35% yield) corresponding to the uncyclized elimination product (**16**) was also isolated. TLC: 10% ethyl acetate–hexanes, R_f = 0.17, UV. ^1H NMR (600 MHz, CDCl_3), δ : 7.88 (d, J = 9.0 Hz, 2H), 6.60 (d, J = 9.0 Hz, 2H), 5.61 (ddd, J = 17.1, 10.2, 9.0 Hz, 1H), 5.07 (dd, J = 10.2, 1.6 Hz, 1H), 5.02 (ddd, J = 17.1, 1.6, 0.8 Hz, 1H), 4.13 (ddd, J = 11.4, 6.6, 5.0 Hz, 1H), 3.99 (ddd, J = 11.1, 8.5, 6.0 Hz, 1H), 3.85 (s, 3H), 3.45 (dd, J = 14.9, 6.5 Hz, 1H), 3.30 (dd, J = 14.8, 8.3 Hz, 1H), 3.02 (s, 3H), 2.69 – 2.61 (m, 1H), 1.79 (dddd, J = 13.9, 8.5, 6.7, 4.0 Hz, 1H), 1.57 – 1.51 (m, 1H), 1.16 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3), δ : 178.61, 167.58, 152.28, 138.96, 131.46, 117.83, 116.93, 110.68, 62.19, 57.54, 51.66, 40.10, 40.06, 38.84, 31.00, 27.31. HRMS (ESI): Calcd. for $\text{C}_{20}\text{H}_{30}\text{NO}_4$ [(M+H) $^+$]: 348.2169. Found: 348.2159.



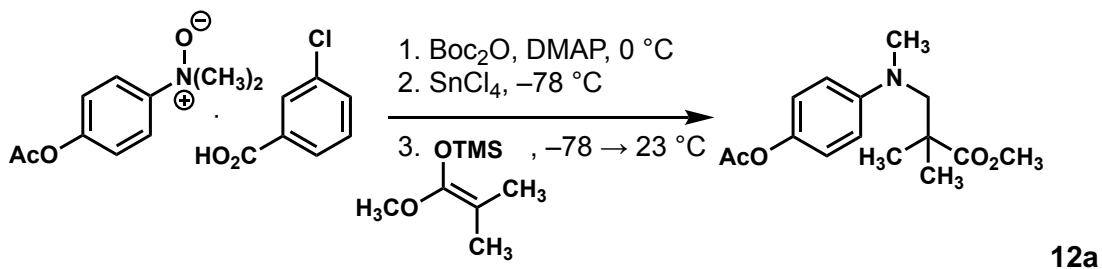
methyl *trans*-4-(4-methoxyphenyl)-1-methyl-3-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (**11c**)

4-(dimethylamino)pyridine (DMAP, 9 mg, 0.07 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (226 mg, 0.600 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 334 mg, 1.53 mmol, 2.5 equiv), and (*E*)-(3-(4-methoxyphenyl)allyl)trimethylsilane¹³ (197 mg, 0.894 mmol, 1.5 equiv) in dichloromethane (5.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to –94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 150 μL, 0.150 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at –78 °C for 3.25 hours. The clear, bright yellow solution was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude oil that was purified by automated flash column chromatography (starting with hexanes, grading to 15% ethyl acetate–hexanes) to afford methyl *trans*-4-(4-methoxyphenyl)-1-methyl-3-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (**11c**) as an orange-yellow syrup (218 mg, 0.548 mmol, 92% yield). TLC: 10% ethyl acetate–hexanes, R_f = 0.26, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.82 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.72 (d, *J* = 4.7 Hz, 1H), 3.30 (dd, *J* = 11.9, 3.5 Hz, 1H), 3.03 (s, 3H), 2.87 (ddd, *J* = 11.9, 4.8, 1.3 Hz, 1H), 2.13 – 2.05 (m, 1H), 0.60 (dd, *J* = 15.0, 5.5 Hz, 1H), 0.52 (dd, *J* = 15.0, 8.3 Hz, 1H), 0.02 (s, 9H). ¹³C NMR (151 MHz, CDCl₃), δ: 167.65, 158.15, 149.60, 138.40, 132.87, 130.02, 129.68, 122.21, 117.13, 113.90, 109.35, 55.40, 54.05, 51.47, 50.95, 39.37, 35.40, 20.64, –0.66. ²⁹Si NMR (119 MHz, CDCl₃), δ: 0.91. HRMS (ESI): Calcd. for C₂₃H₃₂NO₃Si [(M+H)⁺]: 398.2146. Found: 398.2133.



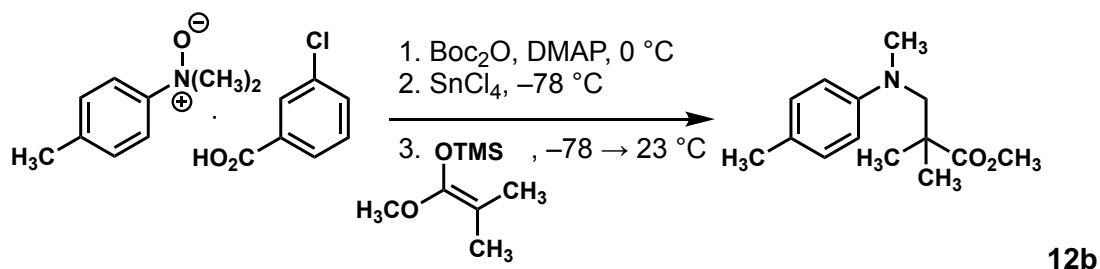
methyl *trans*-4-(benzo[*d*][1,3]dioxol-5-yl)-1-methyl-3-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (11d)

4-(dimethylamino)pyridine (DMAP, 8 mg, 0.06 mmol, 0.1 equiv) was added to a solution of 4-(methoxycarbonyl)-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1c** (228 mg, 0.605 mmol, 1 equiv), di-*tert*-butyl dicarbonate (Boc₂O, 333 mg, 1.52 mmol, 2.5 equiv), and (*E*)-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)trimethylsilane¹³ (223 mg, 0.951 mmol, 1.6 equiv) in dichloromethane (5.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-hexanes bath, cooled further to -94 °C using liquid N₂, then tin(IV) chloride (1.0 M in dichloromethane, 150 μL, 0.150 mmol, 0.25 equiv) slowly charged to the reaction mixture. The resulting solution was stirred at -78 °C for 3 hours. The clear, bright yellow solution was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford a crude oil that was purified by automated flash column chromatography (starting with hexanes, grading to 15% ethyl acetate-hexanes) to afford methyl *trans*-4-(benzo[*d*][1,3]dioxol-5-yl)-1-methyl-3-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (**11d**) as a yellow syrup/ foam (225 mg, 0.547 mmol, 90% yield). TLC: 10% ethyl acetate-hexanes, R_f=0.26, UV. ¹H NMR (600 MHz, CDCl₃), δ: 7.81 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 6.44 (d, *J* = 1.7 Hz, 1H), 6.43 (dd, *J* = 7.8, 1.6 Hz, 1H), 5.92 (d, *J* = 5.3 Hz, 2H), 3.78 (s, 3H), 3.68 (d, *J* = 4.9 Hz, 1H), 3.32 (dd, *J* = 11.9, 3.5 Hz, 1H), 3.02 (s, 3H), 2.88 (dd, *J* = 11.9, 5.0 Hz, 1H), 2.07 (dp, *J* = 9.2, 4.8 Hz, 1H), 0.59 (dd, *J* = 15.0, 5.4 Hz, 1H), 0.51 (dd, *J* = 15.0, 8.3 Hz, 1H), 0.02 (s, 9H). ¹³C NMR (101 MHz, CDCl₃), δ: 167.64, 149.48, 147.70, 145.96, 140.19, 132.83, 130.07, 122.03, 121.91, 117.00, 109.37, 109.02, 108.13, 101.01, 54.00, 51.56, 51.41, 39.39, 35.37, 20.54, -0.66. ²⁹Si NMR (119 MHz, CDCl₃), δ: 0.91. HRMS (ESI): Calcd. for C₂₃H₃₀NO₄Si [(M+H)⁺]: 412.1939. Found: 412.1925.



methyl 3-((4-acetoxyphenyl)(methyl)amino)-2,2-dimethylpropanoate (12a)

4-(dimethylamino)pyridine (DMAP, 5 mg, 0.04 mmol, 0.1 equiv) was added to a solution of 4-acetoxy-*N,N*-dimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1a** (133 mg, 0.363 mmol, 1 equiv) and di-*tert*-butyl dicarbonate (Boc₂O, 210 mg, 0.962 mmol, 2.6 equiv) in dichloromethane (3.0 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting clear, colorless solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to -78 °C, then tin(IV) chloride (1.0 M in dichloromethane, 90 μL, 90 μmol, 0.25 equiv) slowly charged to the reaction mixture, followed by methyl trimethylsilyl dimethylketene acetal (228 mg, 1.31 mmol, 3.6 equiv). The resulting solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to 23 °C and stirred for an additional 9 hours. The clear, faintly lavender reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate (1 × 10 mL). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford an amber-orange oil that was purified by automated flash column chromatography (starting with hexanes, grading to 20% ethyl acetate-hexanes) to afford methyl 3-((4-acetoxyphenyl)(methyl)amino)-2,2-dimethylpropanoate (**12a**) as an opaque, colorless syrup (97 mg, 0.35 mmol, 96% yield). TLC: 20% ethyl acetate-hexanes, *R*_f=0.33, UV. ¹H NMR (400 MHz, CDCl₃), δ: 6.91 (d, *J* = 9.2 Hz, 2H), 6.69 (d, *J* = 9.2 Hz, 2H), 3.62 (s, 3H), 3.51 (s, 2H), 2.90 (s, 3H), 2.26 (s, 3H), 1.23 (s, 6H). ¹³C NMR (101 MHz, CDCl₃), δ: 177.84, 170.40, 148.13, 141.33, 121.80, 112.67, 61.61, 52.11, 45.10, 40.53, 24.06, 21.26. HRMS (ESI): Calcd. for C₁₅H₂₂NO₄ [(M+H)⁺]: 280.1543. Found: 280.1543.

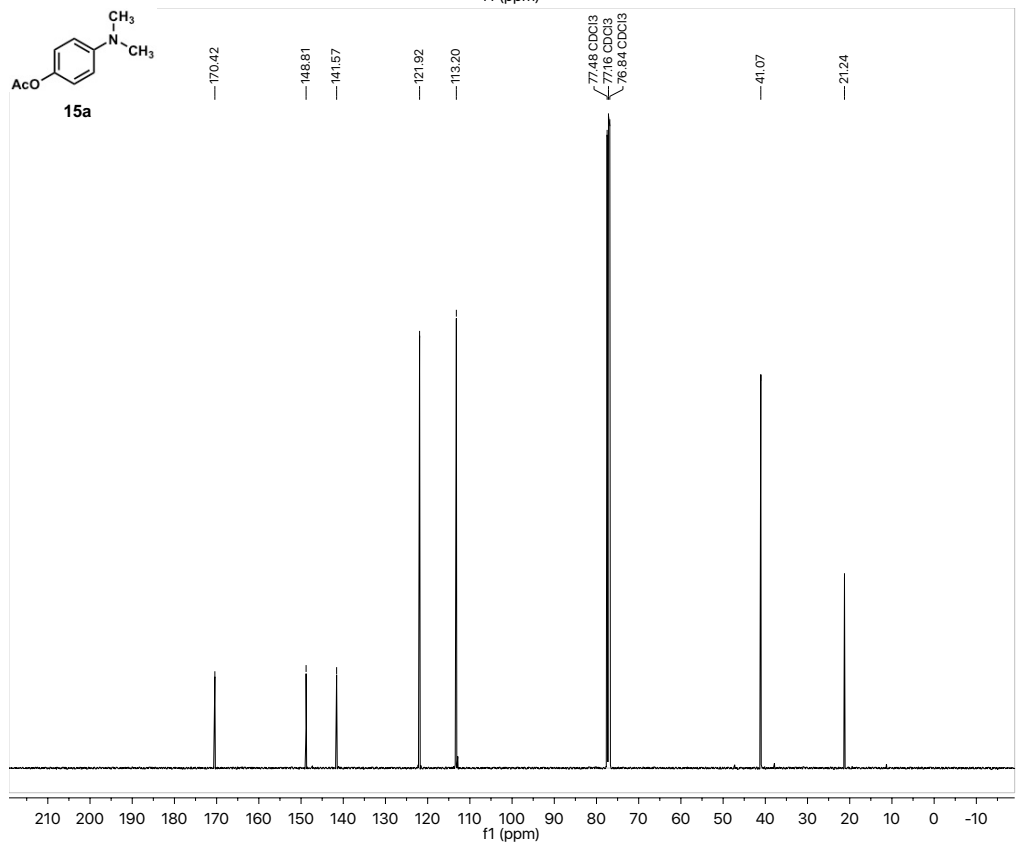
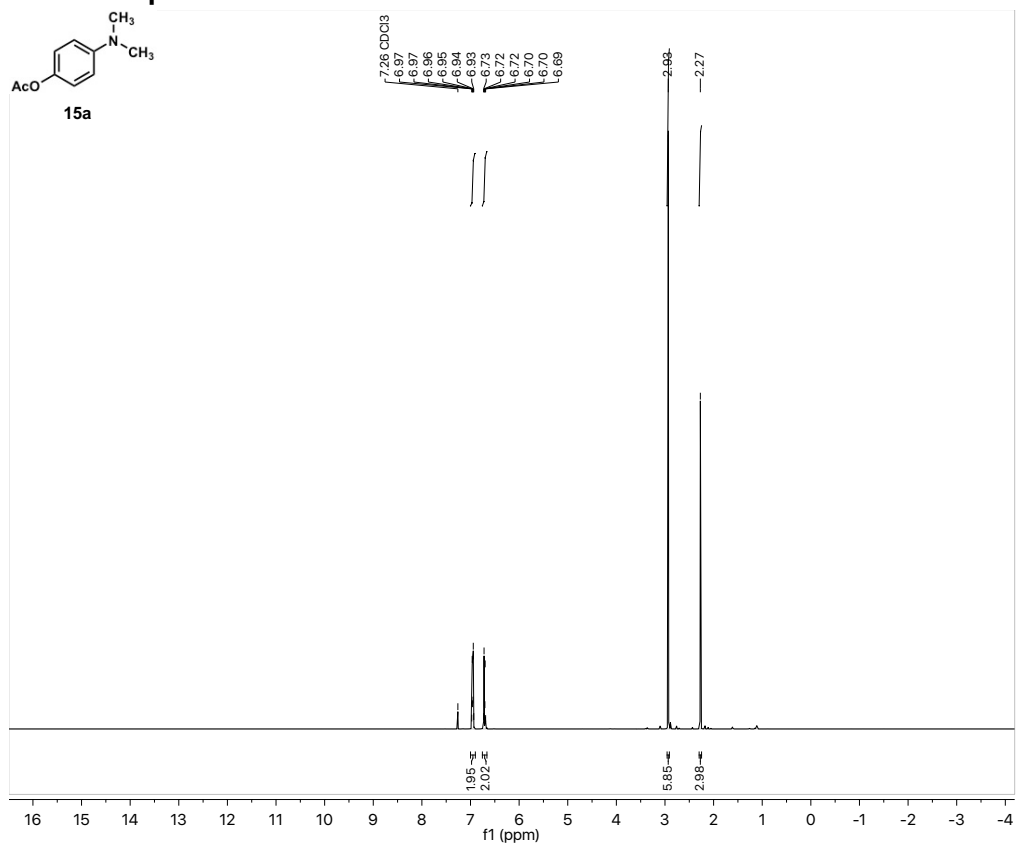


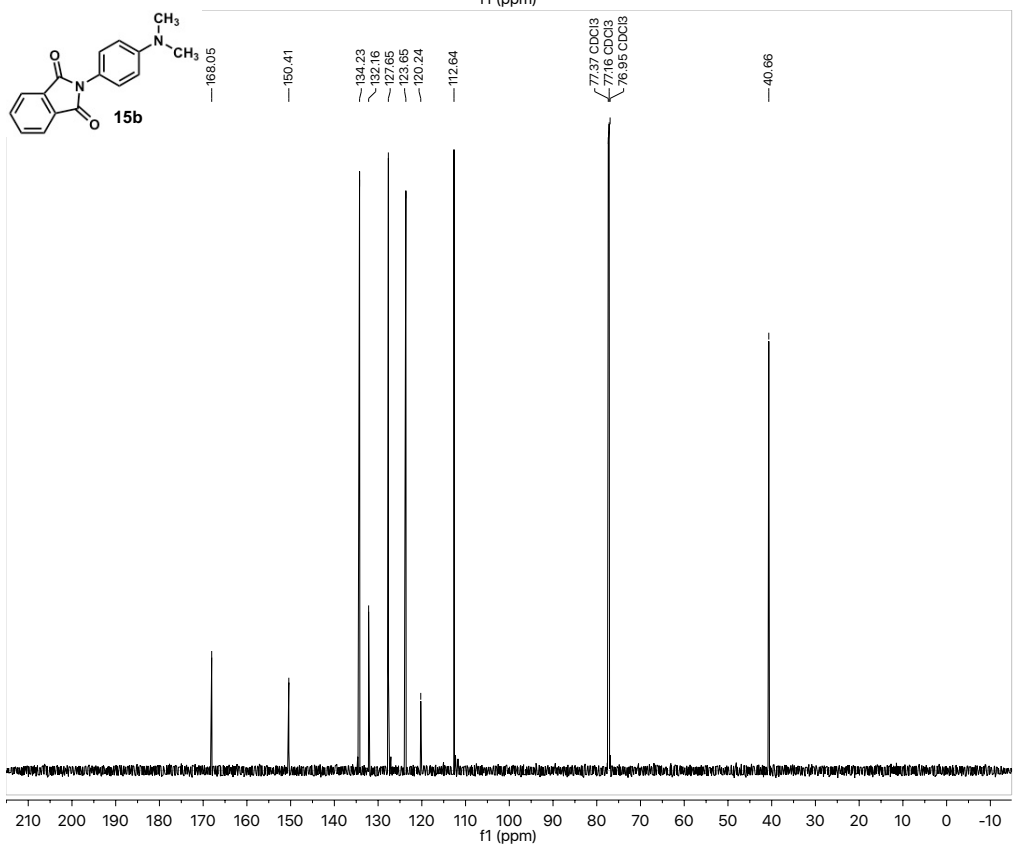
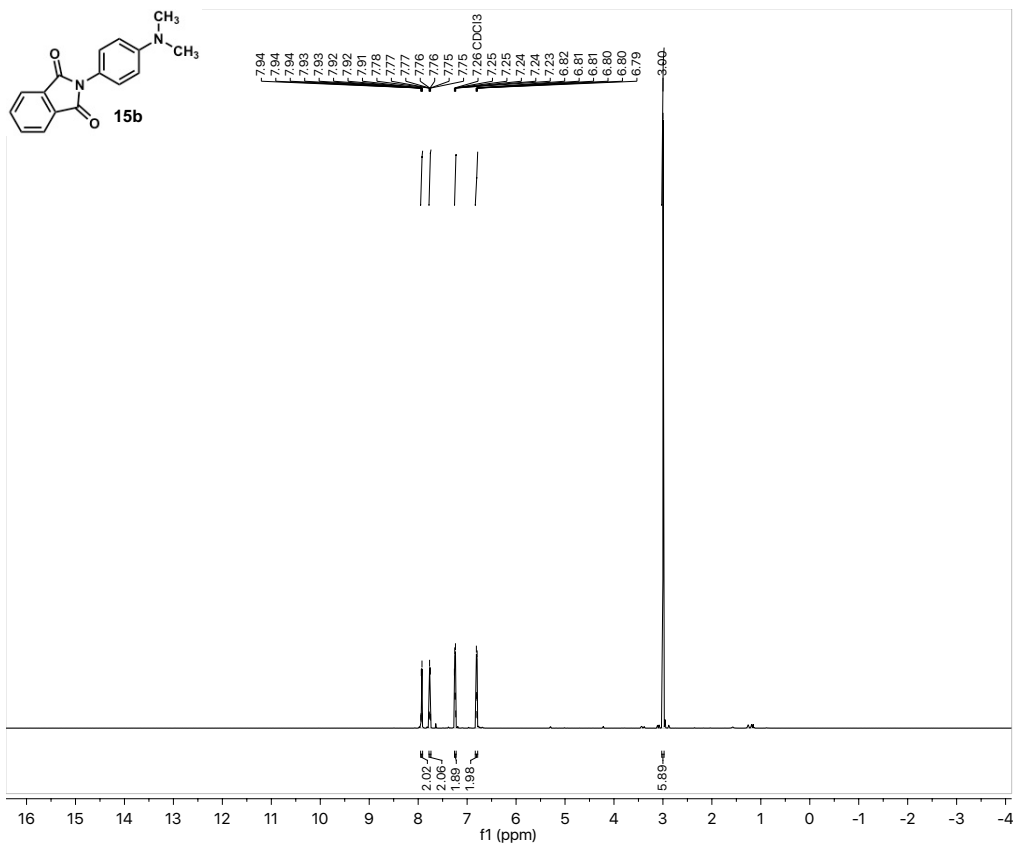
methyl 2,2-dimethyl-3-(methyl(*p*-tolyl)amino)propanoate (12b)

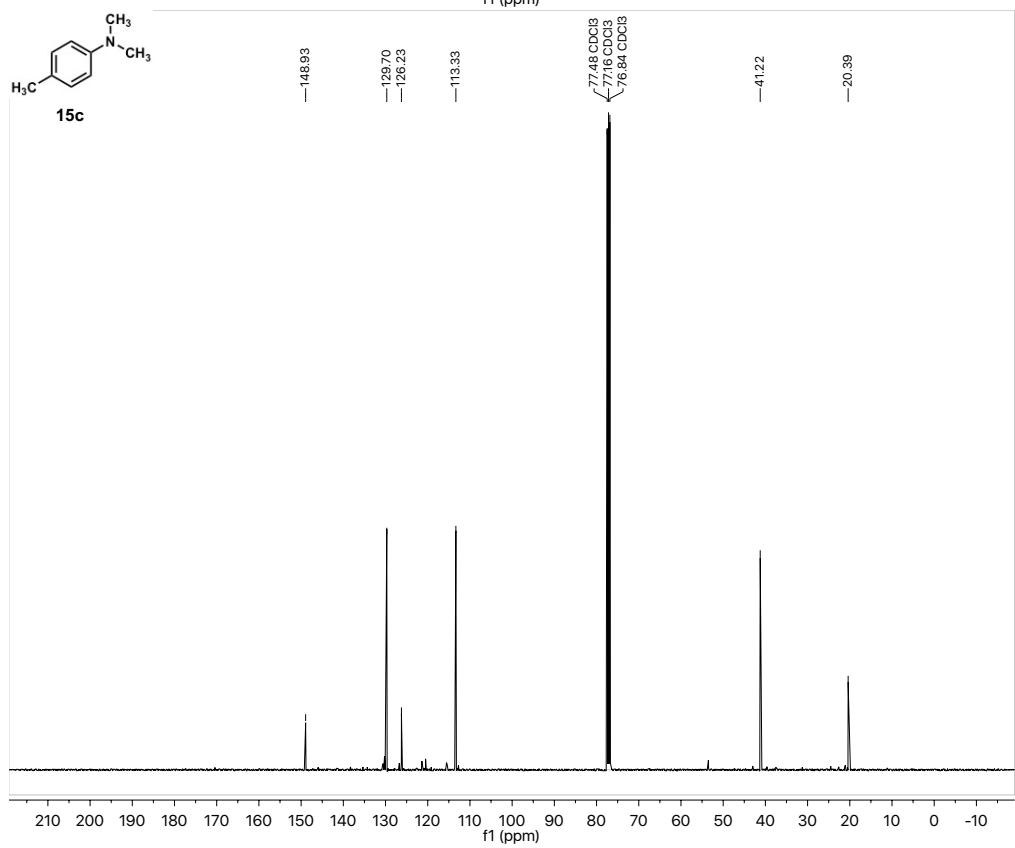
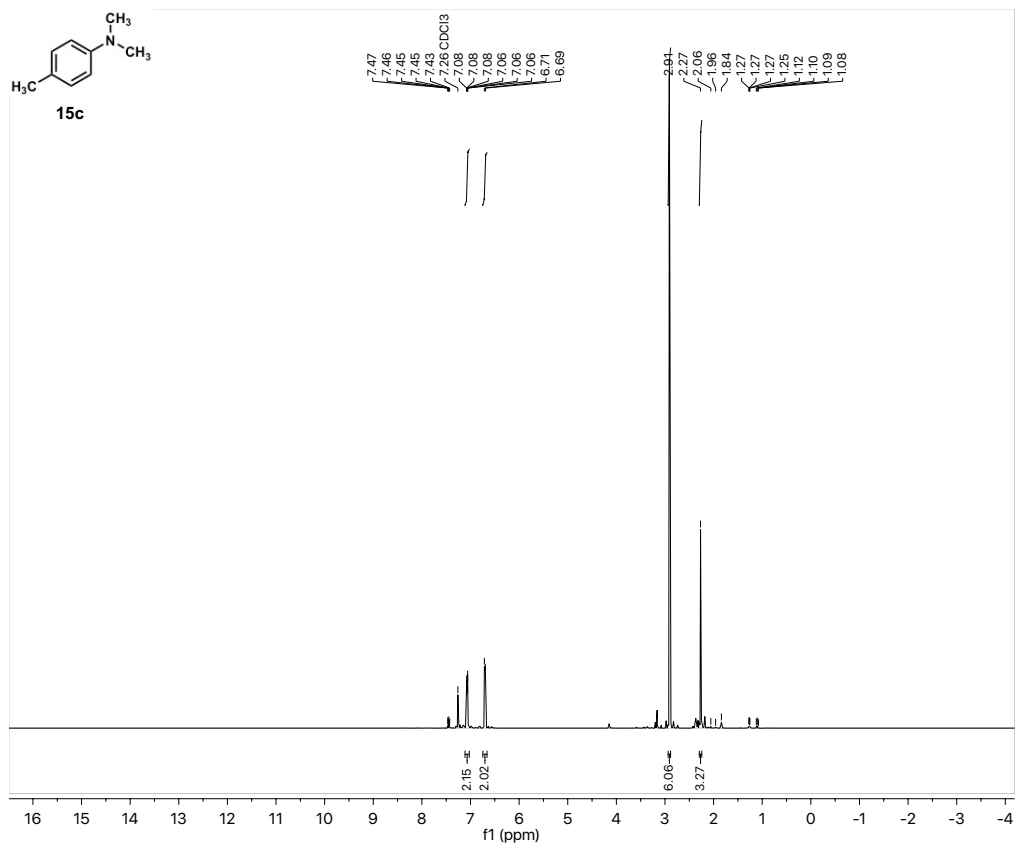
4-(dimethylamino)pyridine (DMAP, 4 mg, 0.03 mmol, 0.09 equiv) was added to a solution of *N,N*,4-trimethylaniline-*N*-oxide 3-chlorobenzoic acid salt **1b** (116 mg, 0.354 mmol, 1 equiv) and di-*tert*-butyl dicarbonate (Boc₂O, 209 mg, 0.958 mmol, 2.7 equiv) in dichloromethane (2.5 mL) under an atmosphere of Ar and cooled to 0 °C in a previously oven-dried flask. The resulting

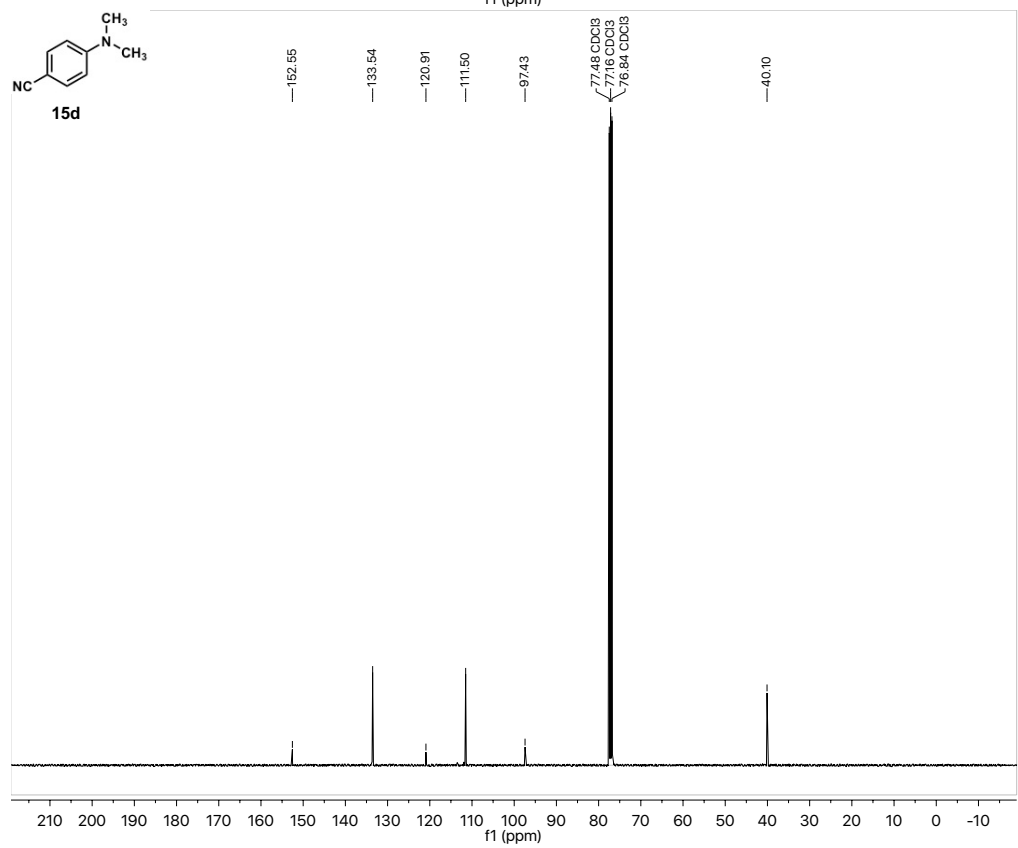
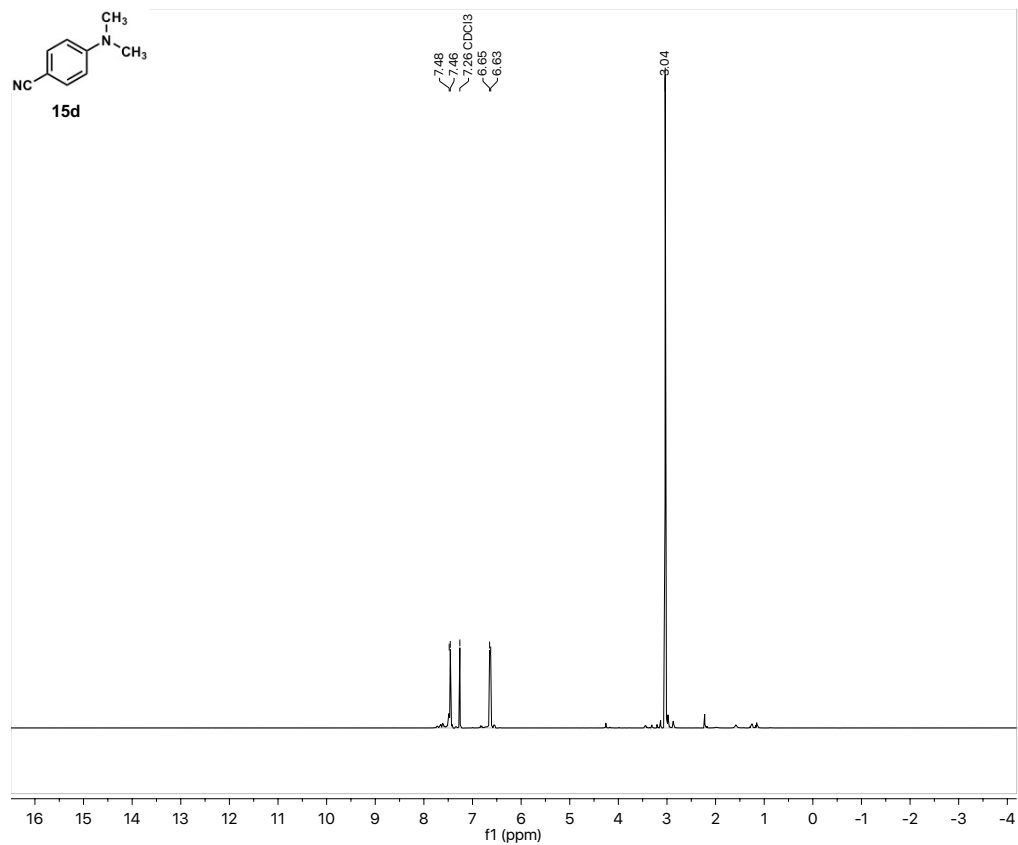
clear, light yellow solution was stirred at that temperature for 1 hour, whereupon the ice bath was removed and replaced with a dry ice-acetone bath, cooled further to $-78\text{ }^{\circ}\text{C}$, then tin(IV) chloride (1.0 M in dichloromethane, 90 μL , 90 μmol , 0.25 equiv) slowly charged to the reaction mixture, followed by methyl trimethylsilyl dimethylketene acetal (226 mg, 1.30 mmol, 3.7 equiv). The resulting solution was stirred at that temperature for a minimum of 1 hour, then allowed to warm slowly to $23\text{ }^{\circ}\text{C}$ and stirred for an additional 9.5 hours. The clear, amber reaction mixture was poured over 1 M aqueous sodium hydroxide (10 mL) and diluted with ethyl acetate (10 mL). The layers were separated and the aqueous layer extracted with ethyl acetate ($1 \times 10\text{ mL}$). The combined organic layers were washed sequentially with water (10 mL) and saturated aqueous sodium chloride (10 mL), and then dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated to afford an amber-brown oil that was purified by automated flash column chromatography (starting with hexanes, grading to 10% ethyl acetate–hexanes) to afford methyl 2,2-dimethyl-3-(methyl(*p*-tolyl)amino)propanoate (**12b**) as a clear, faintly yellow syrup (53 mg, 0.22 mmol, 64% yield). TLC: 5% ethyl acetate–hexanes, $R_f=0.26$, UV. ^1H NMR (400 MHz, CDCl_3), δ : 7.01 (d, $J = 8.9\text{ Hz}$, 2H), 6.66 (d, $J = 8.7\text{ Hz}$, 2H), 3.63 (s, 3H), 3.50 (s, 2H), 2.88 (s, 3H), 2.23 (s, 3H), 1.23 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3), δ : 178.01, 148.15, 129.59, 125.56, 112.46, 61.50, 52.04, 45.14, 40.30, 24.03, 20.28. HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{22}\text{NO}_2$ [(M+H) $^+$]: 236.1645. Found: 236.1642.

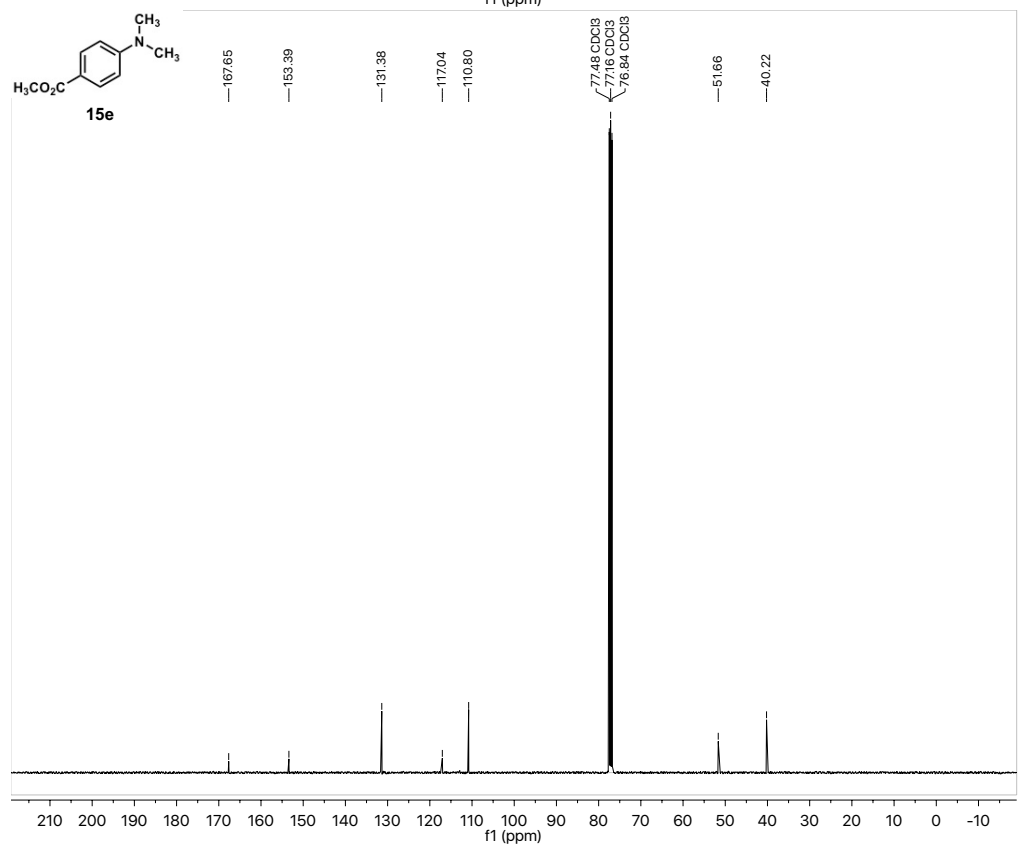
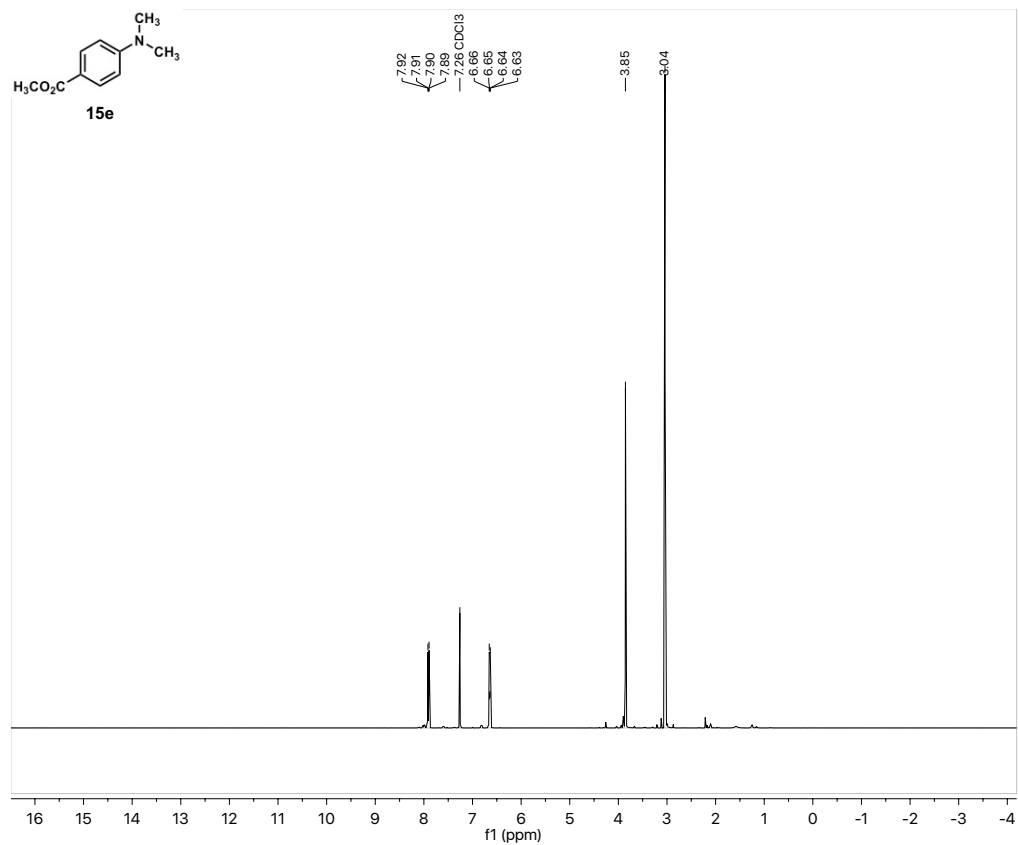
IV. NMR Spectra

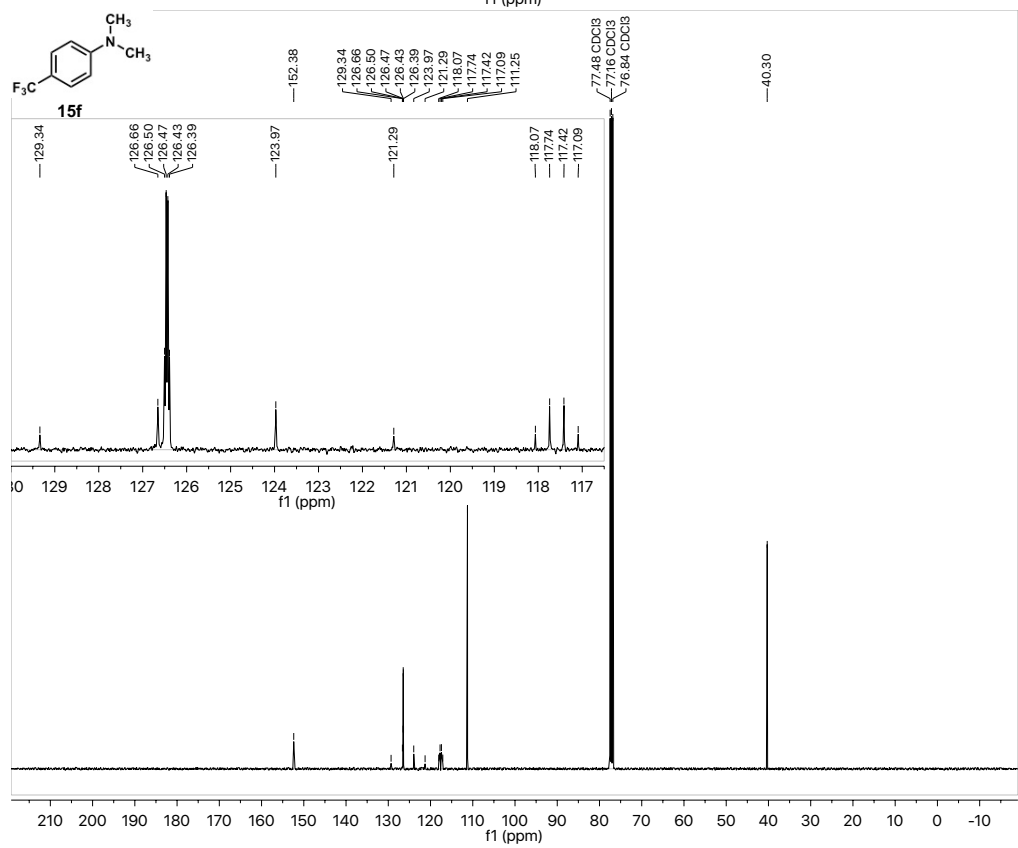
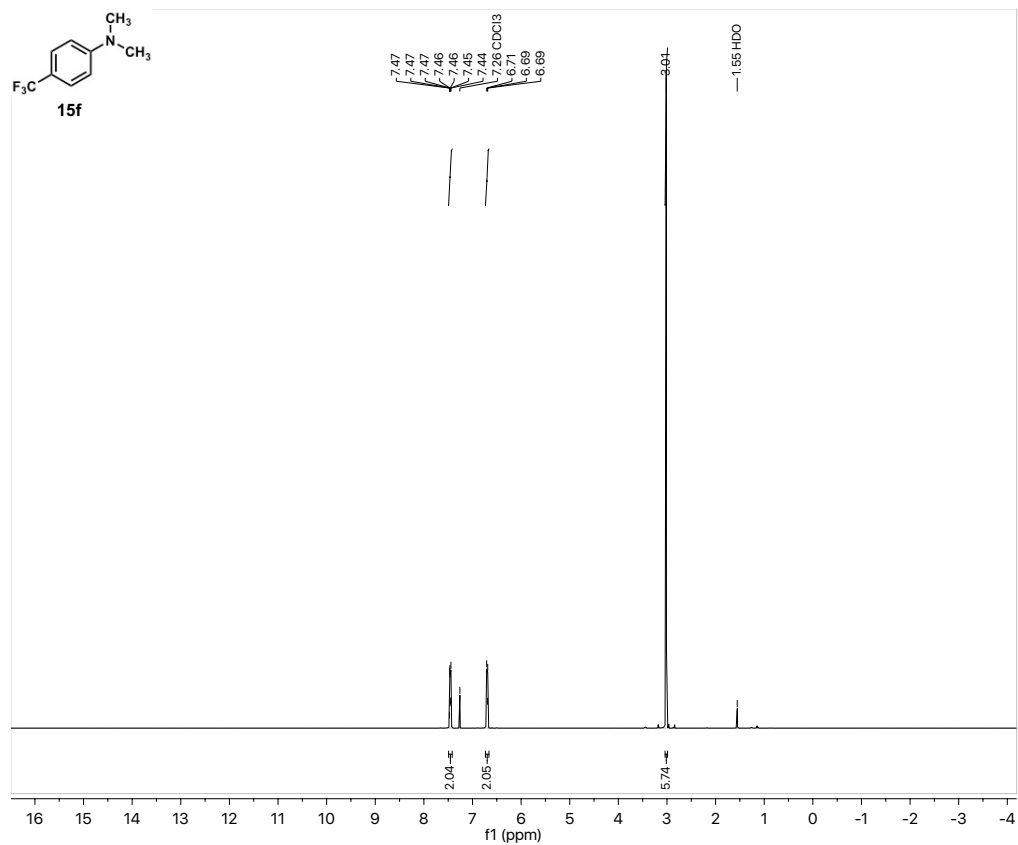


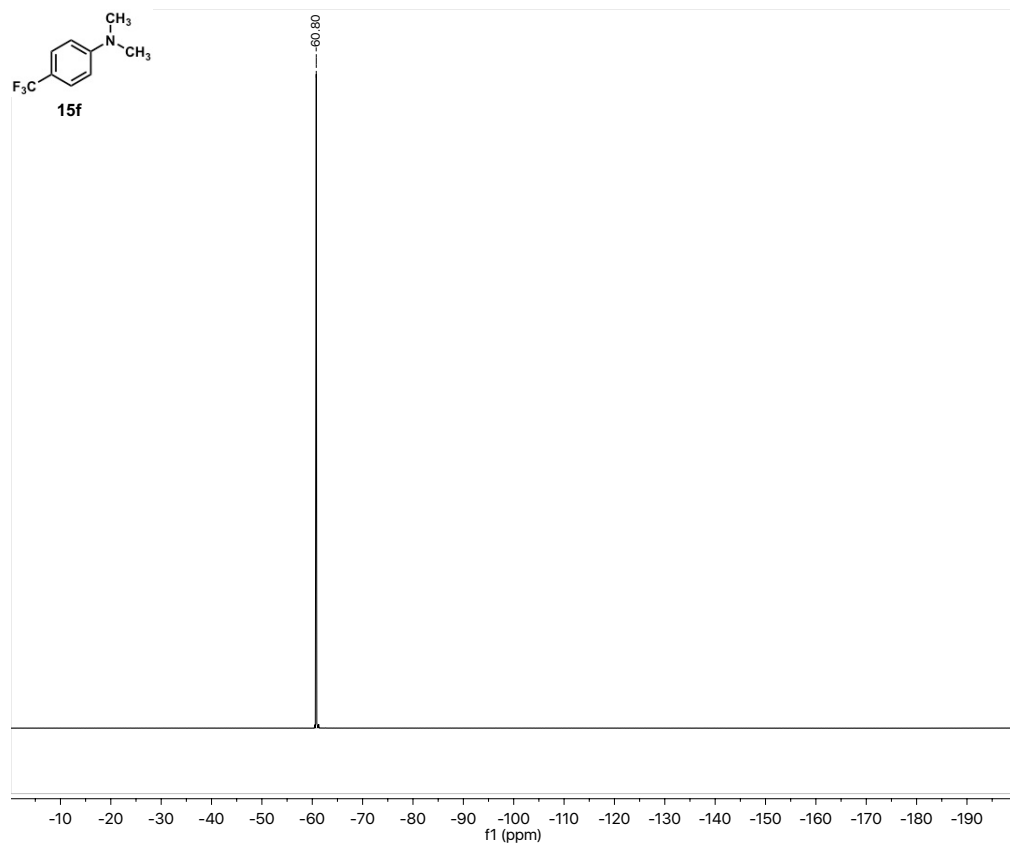


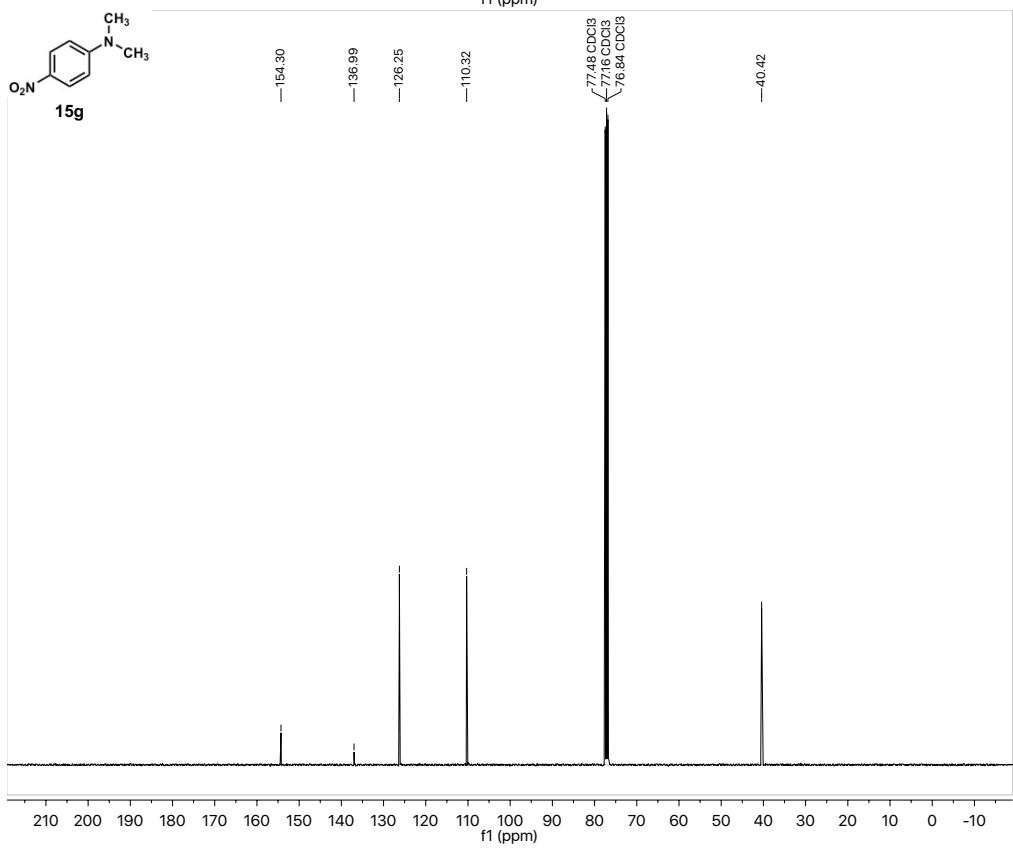
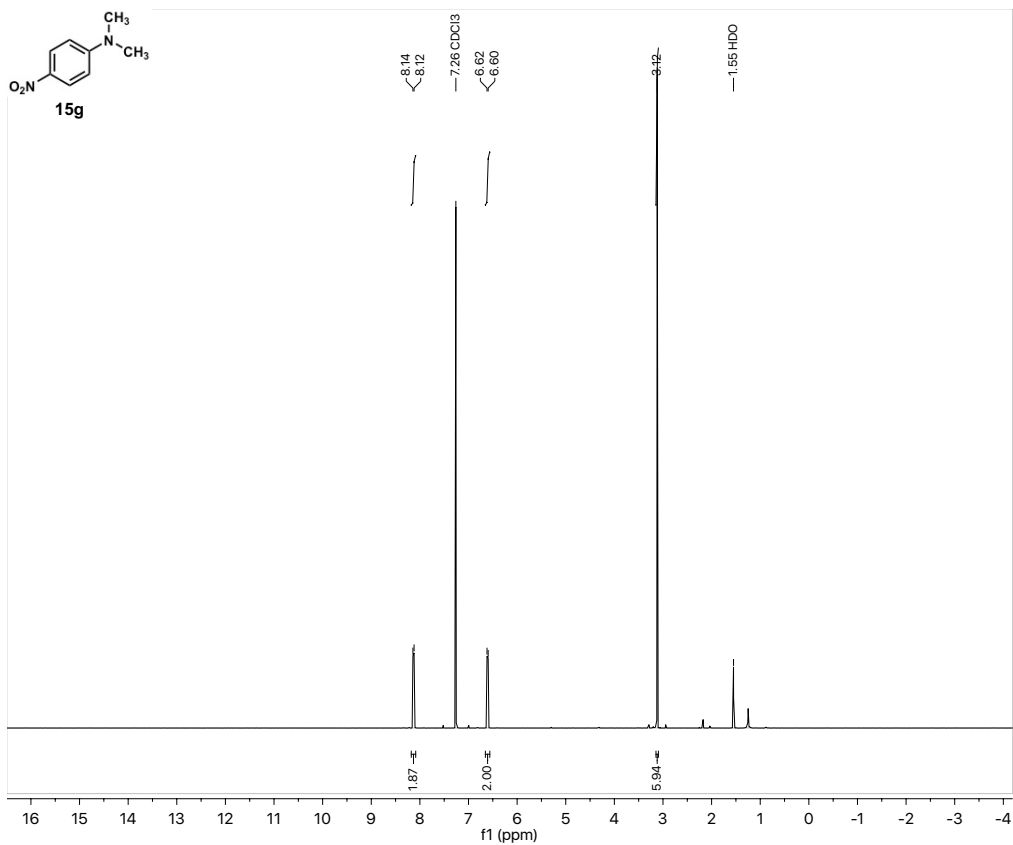


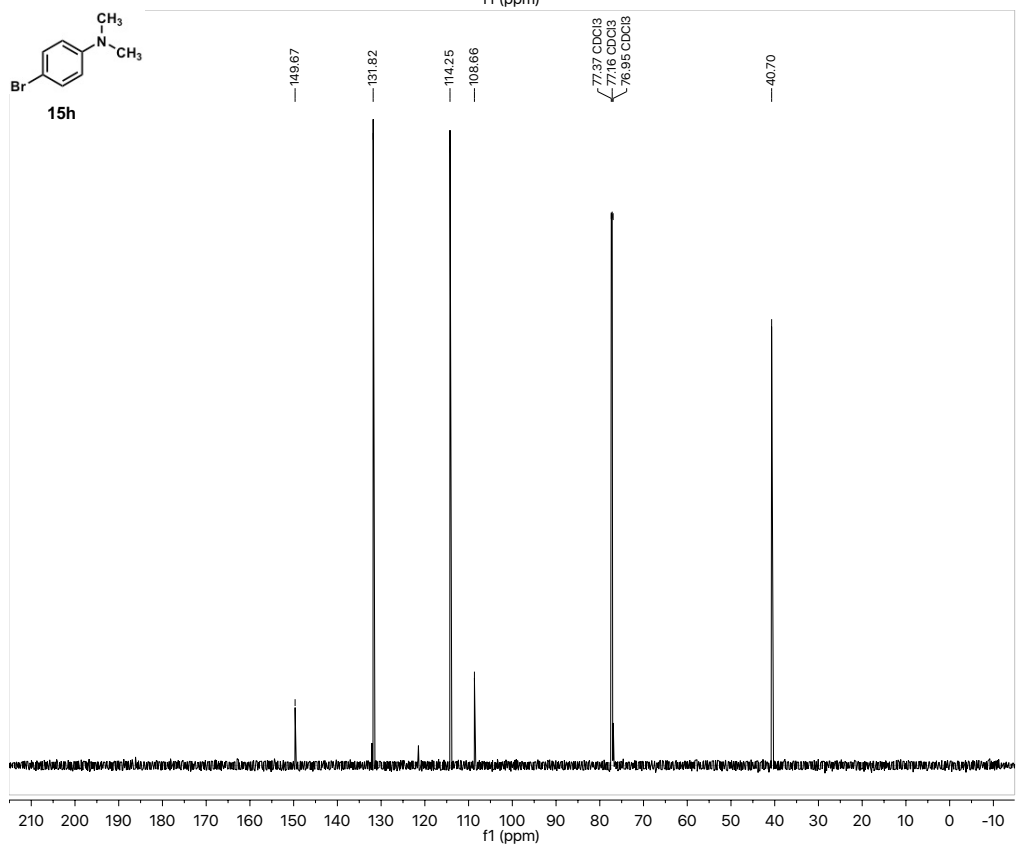
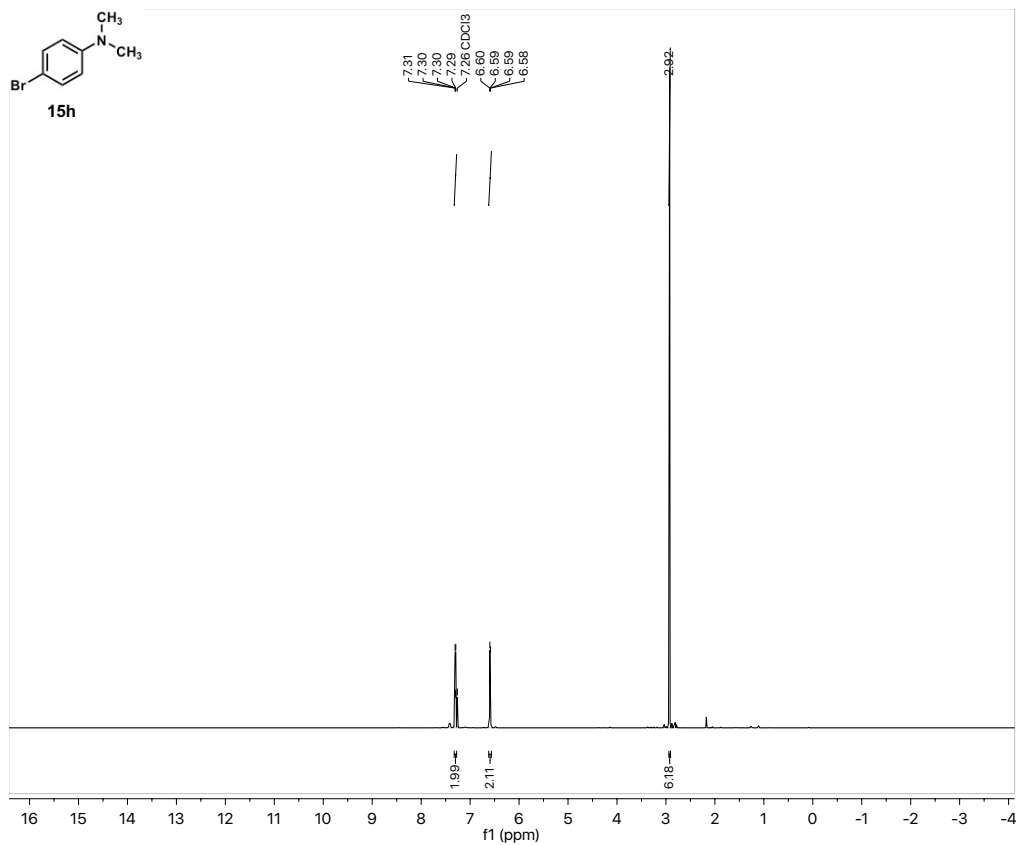


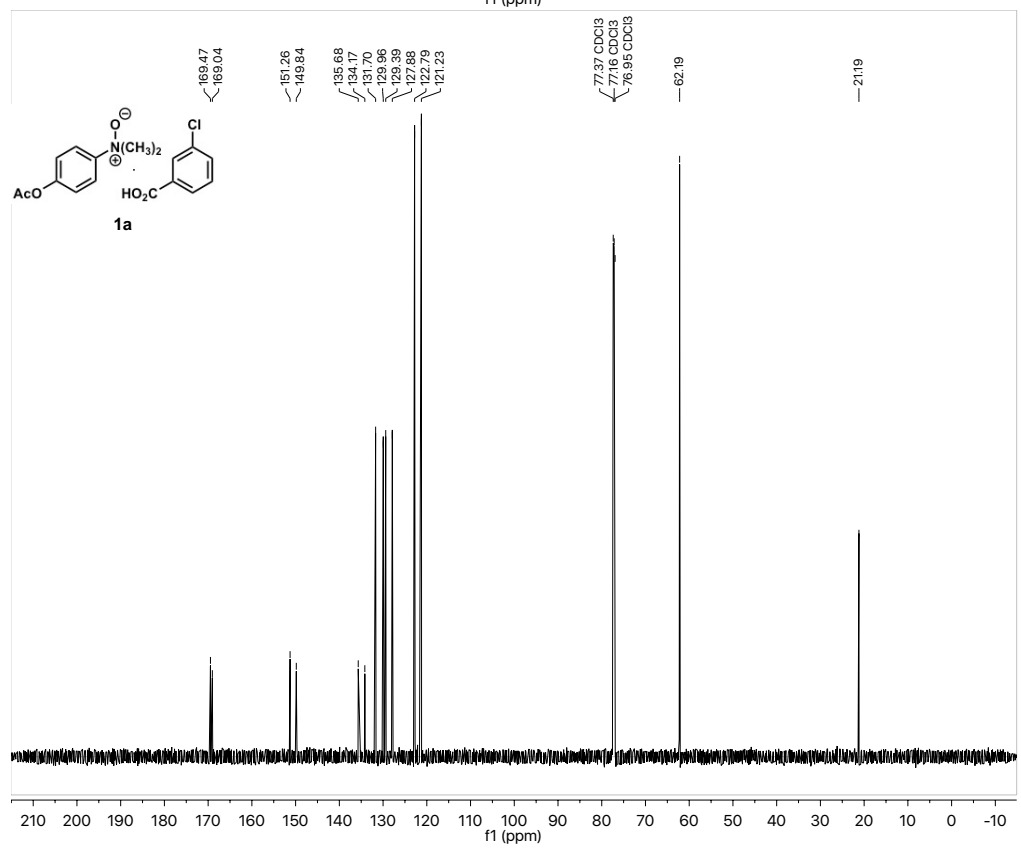
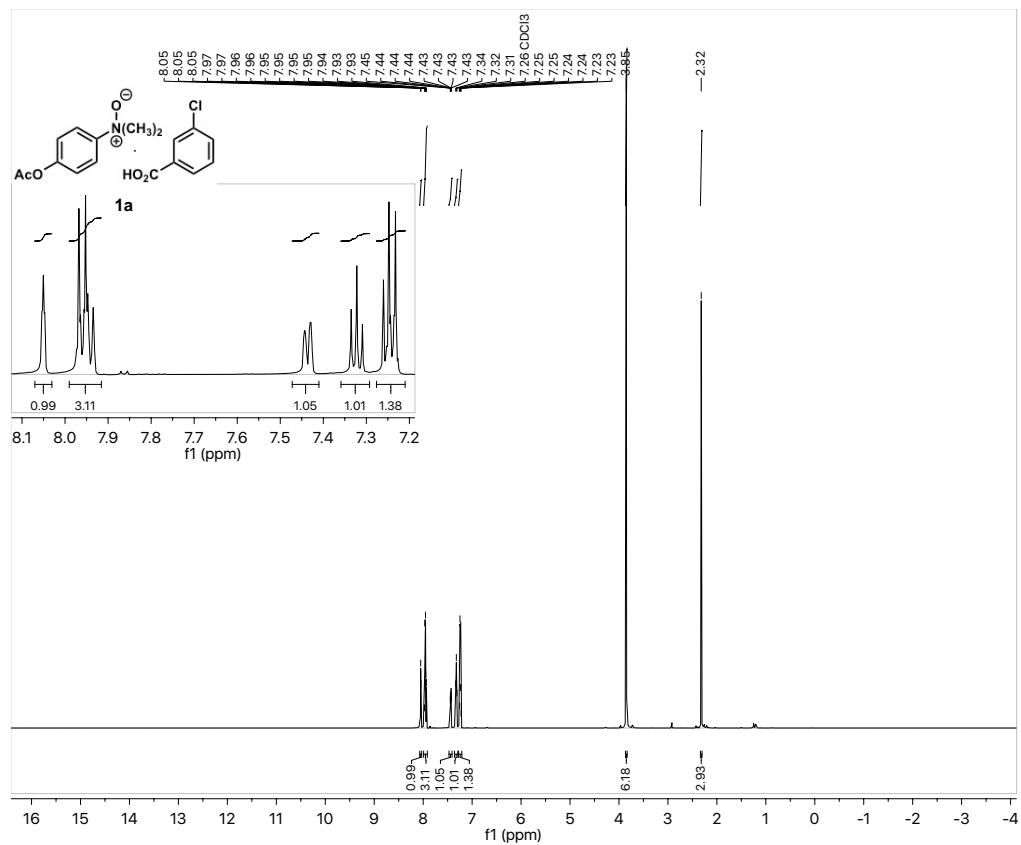


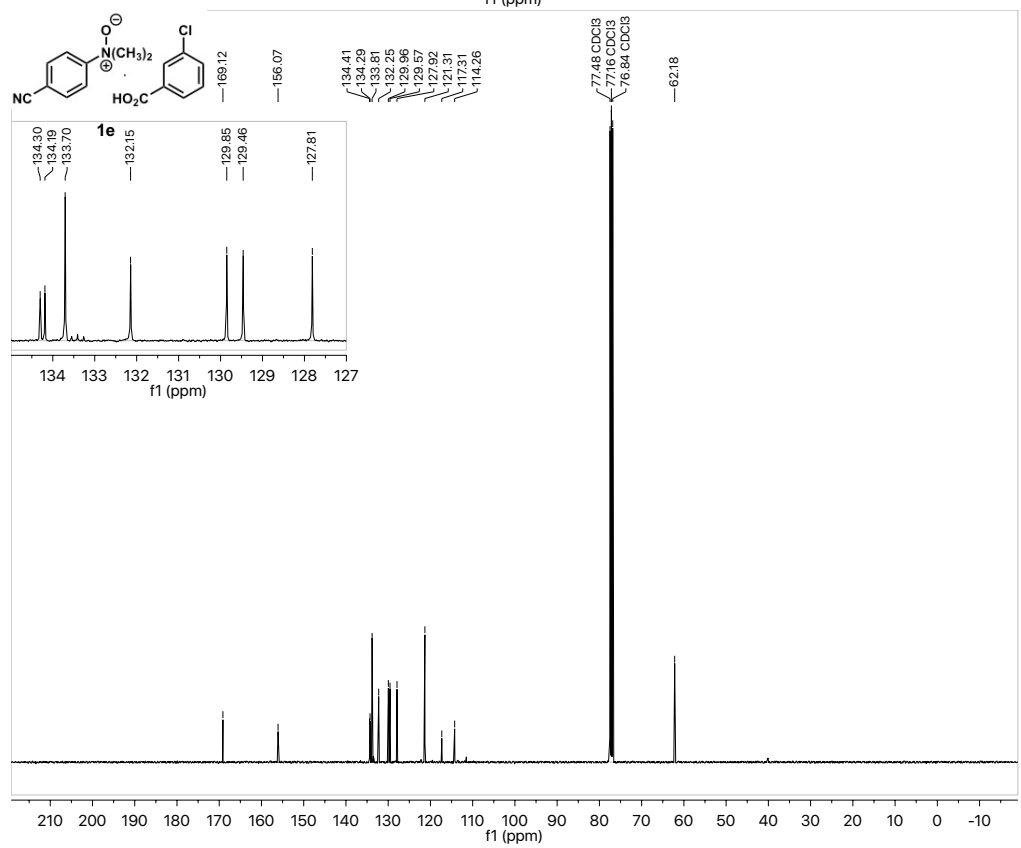
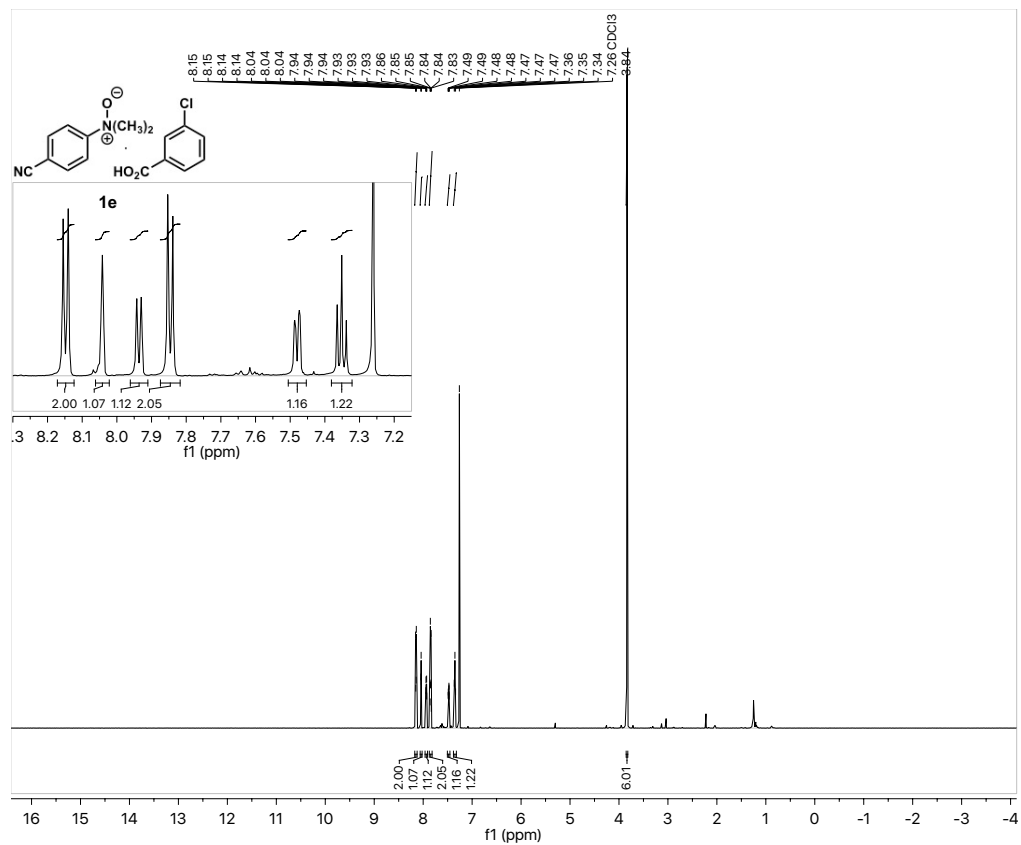


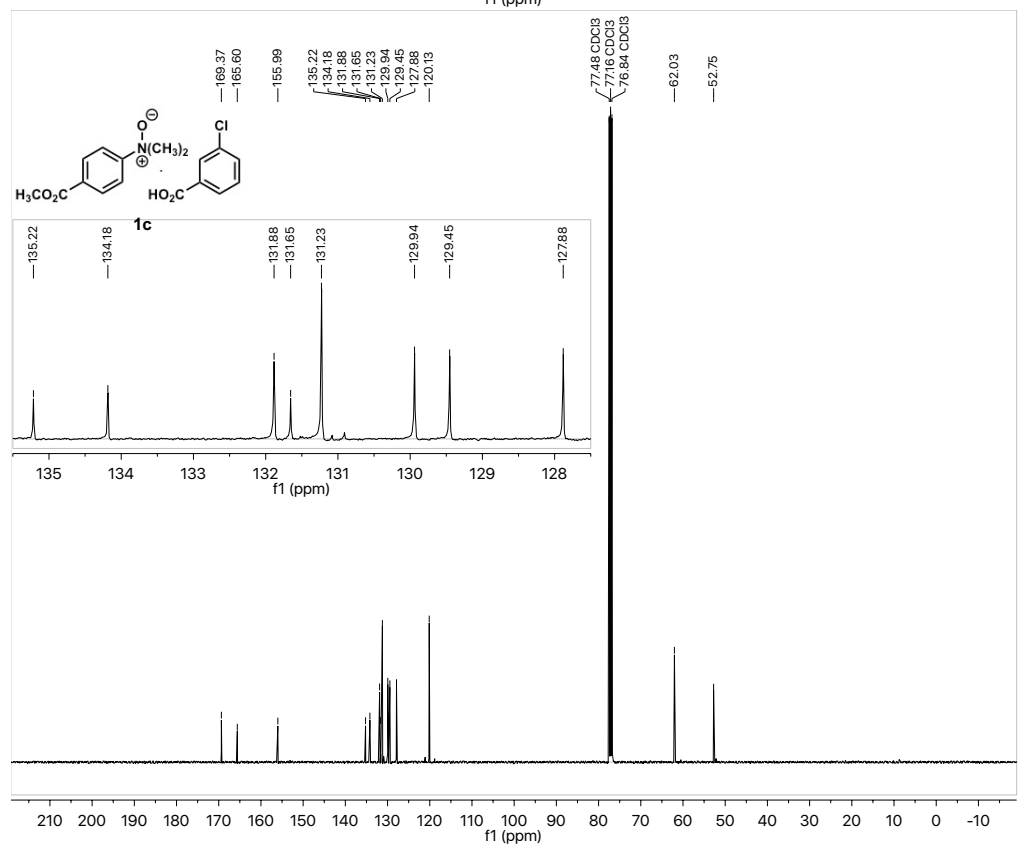
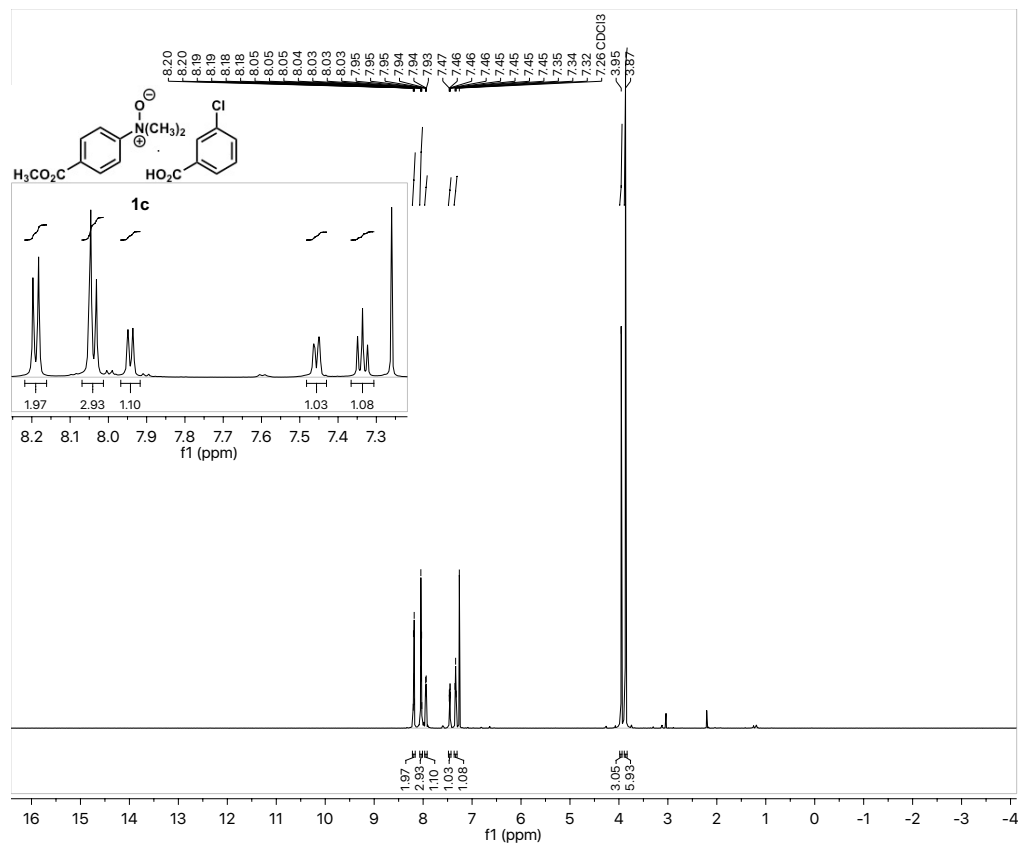


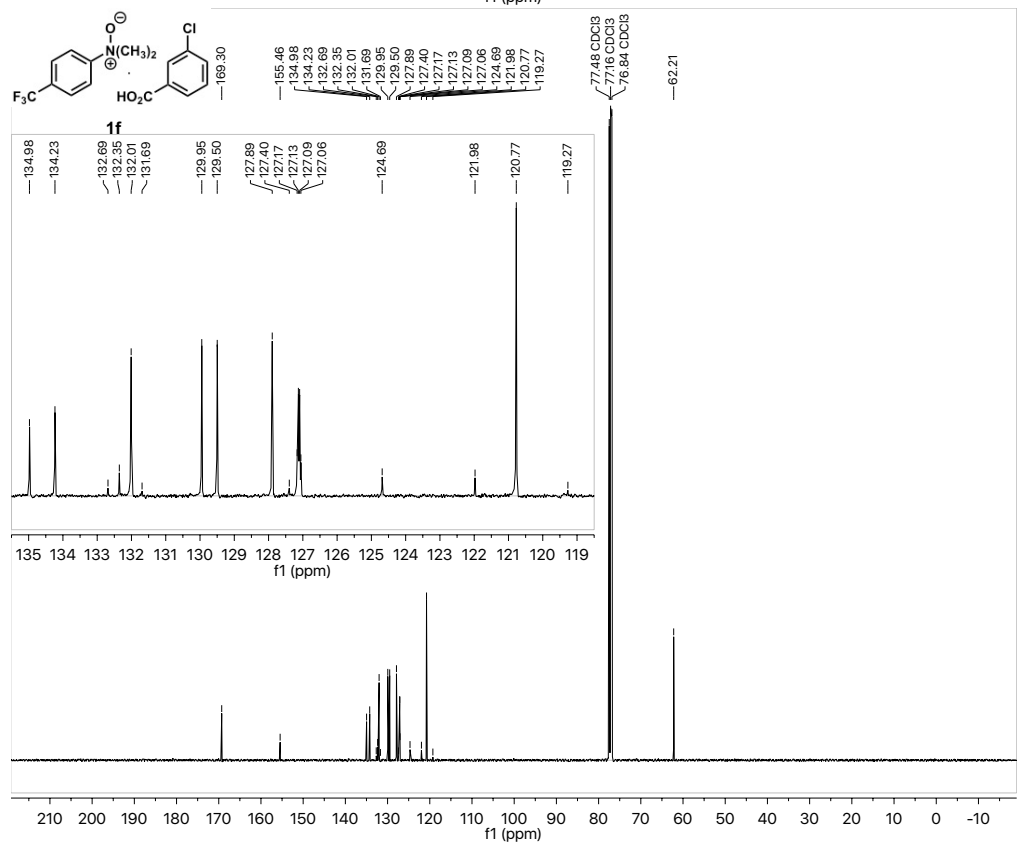
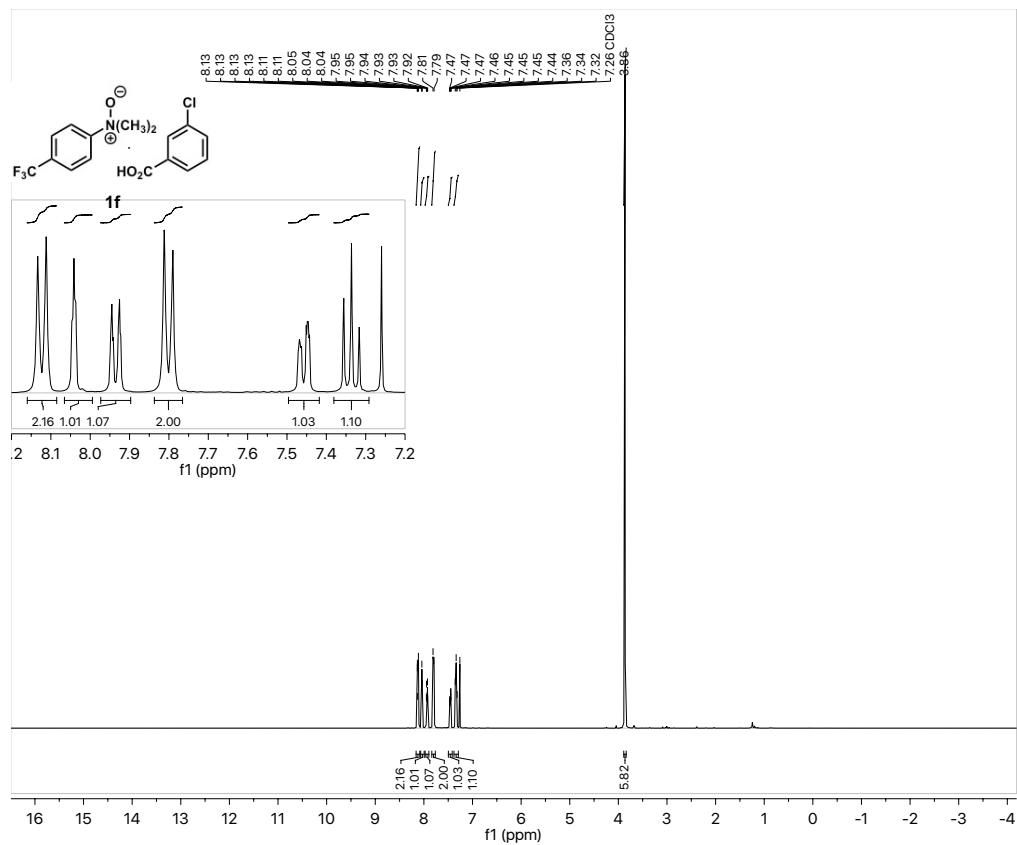


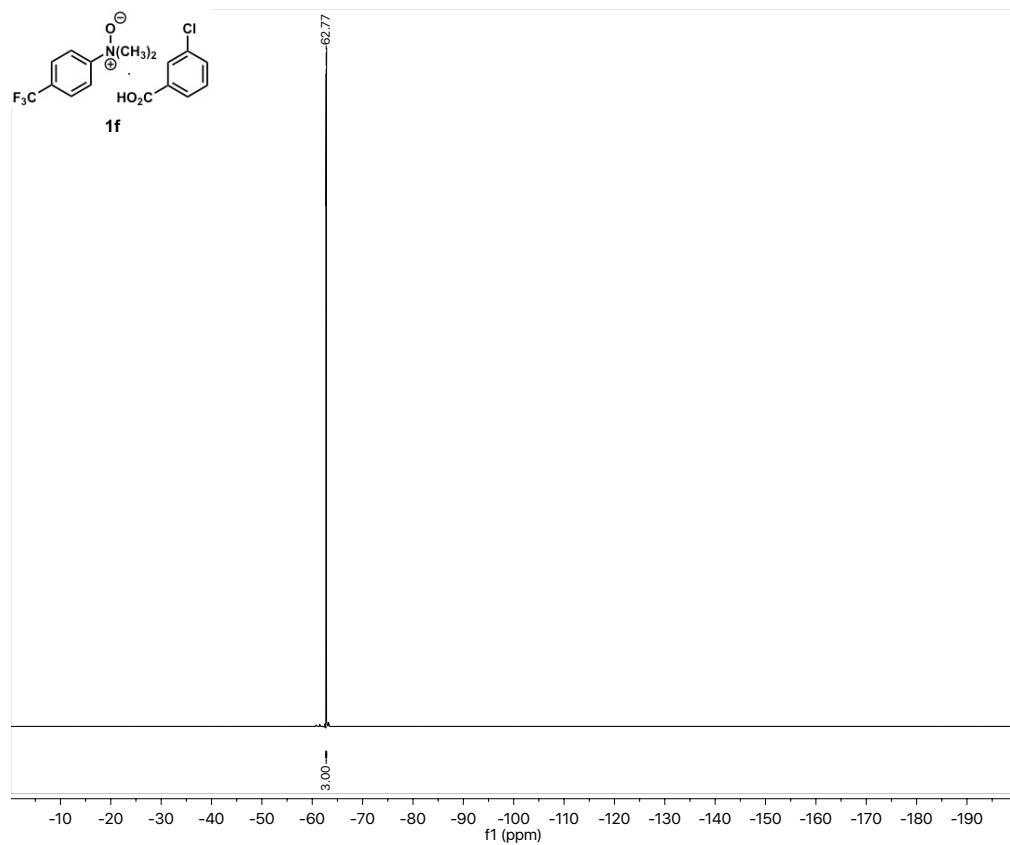


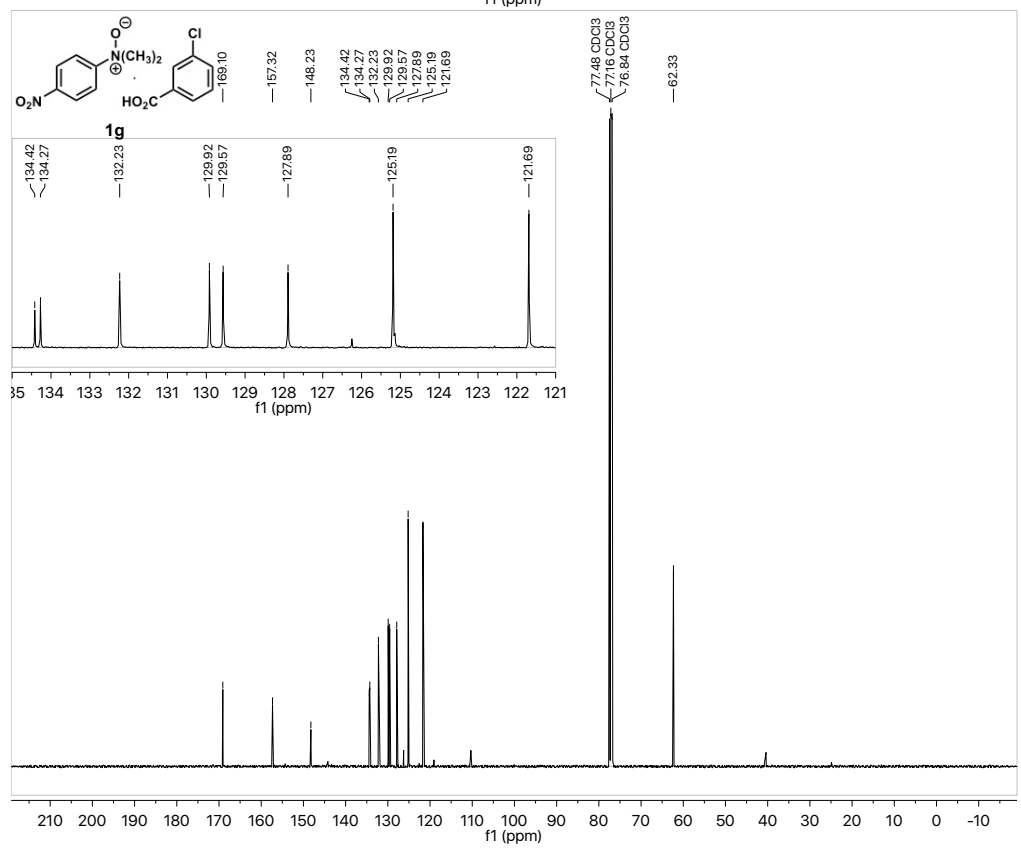
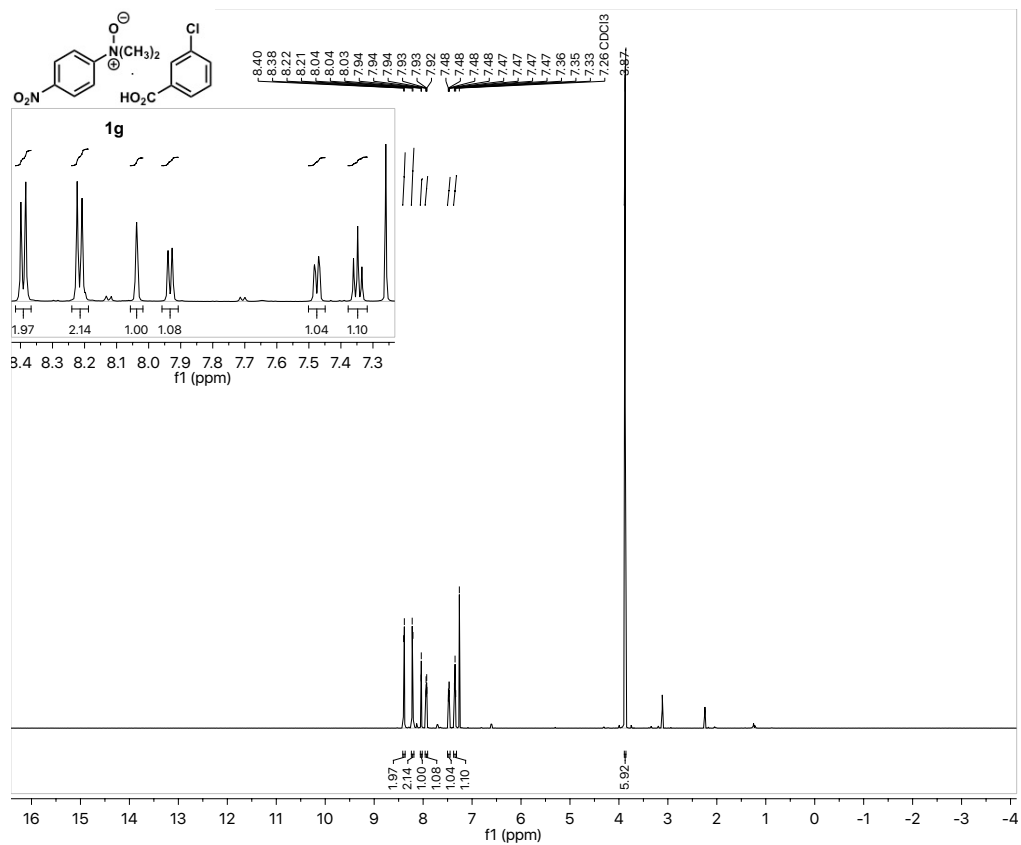


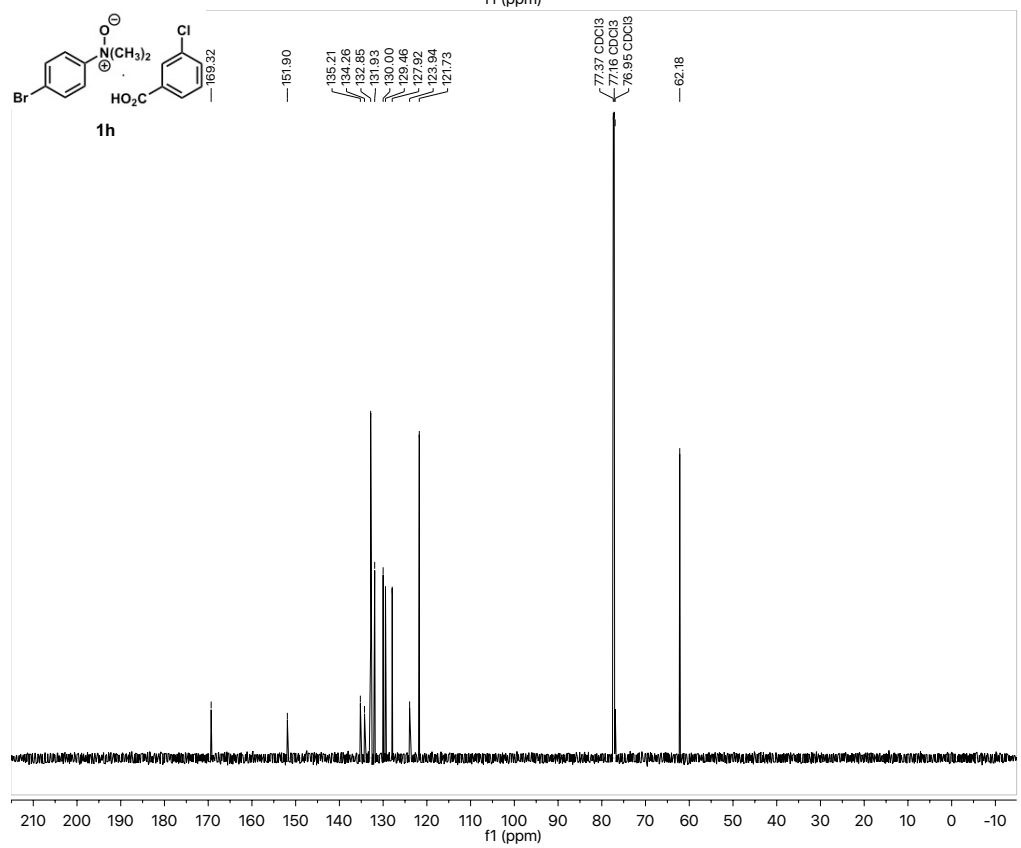
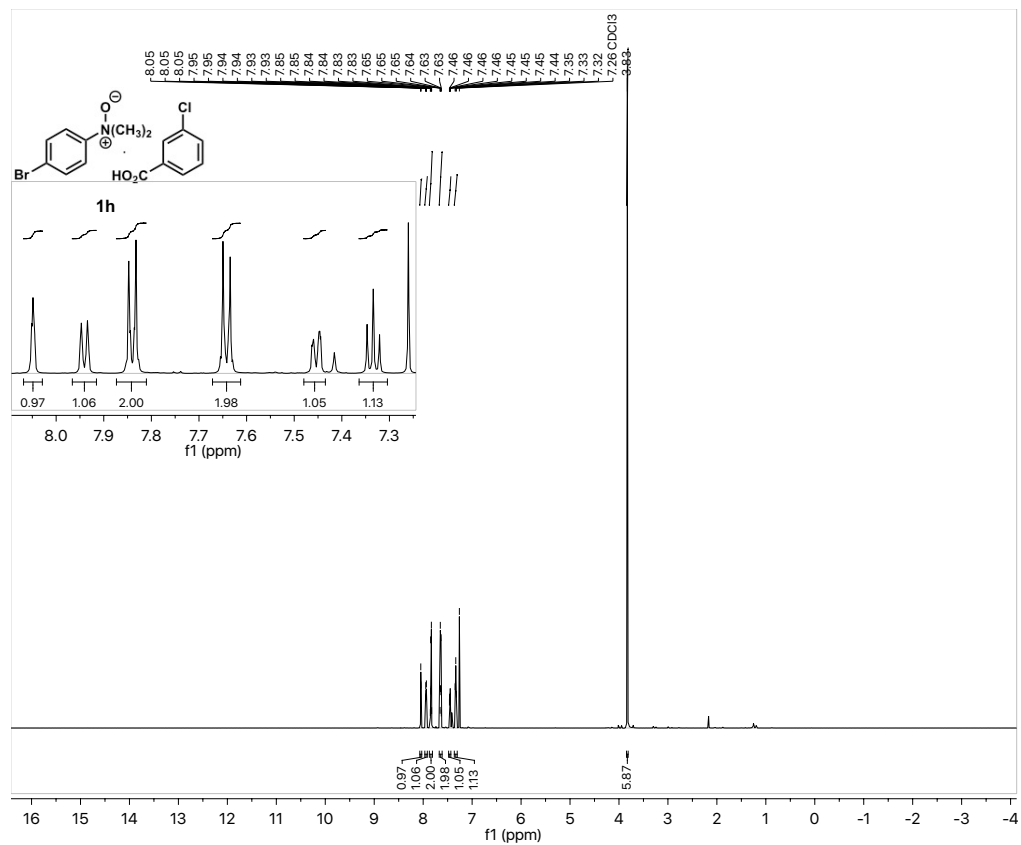


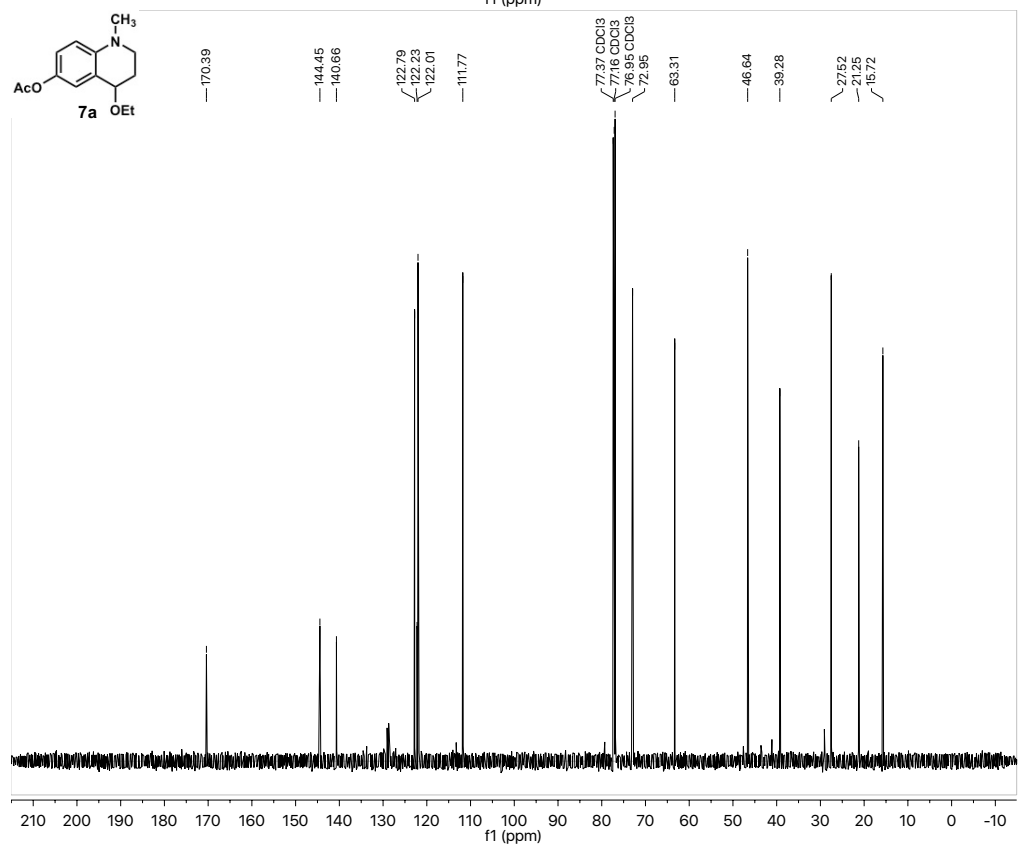
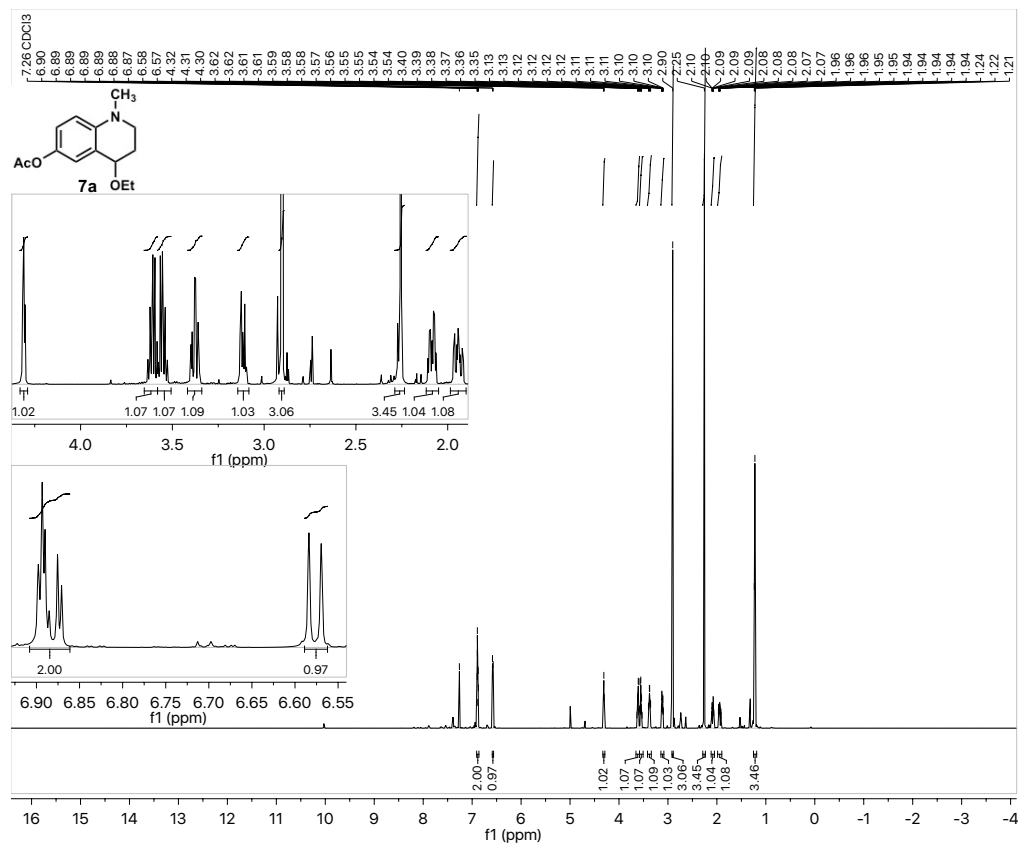


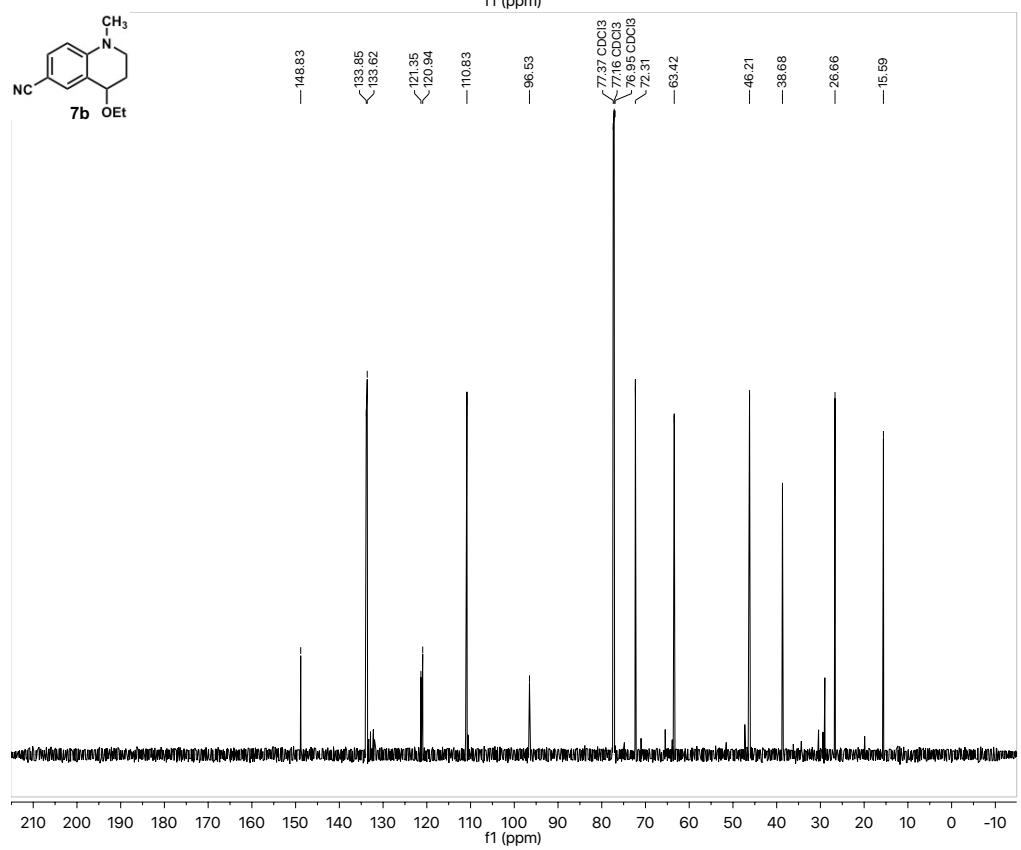
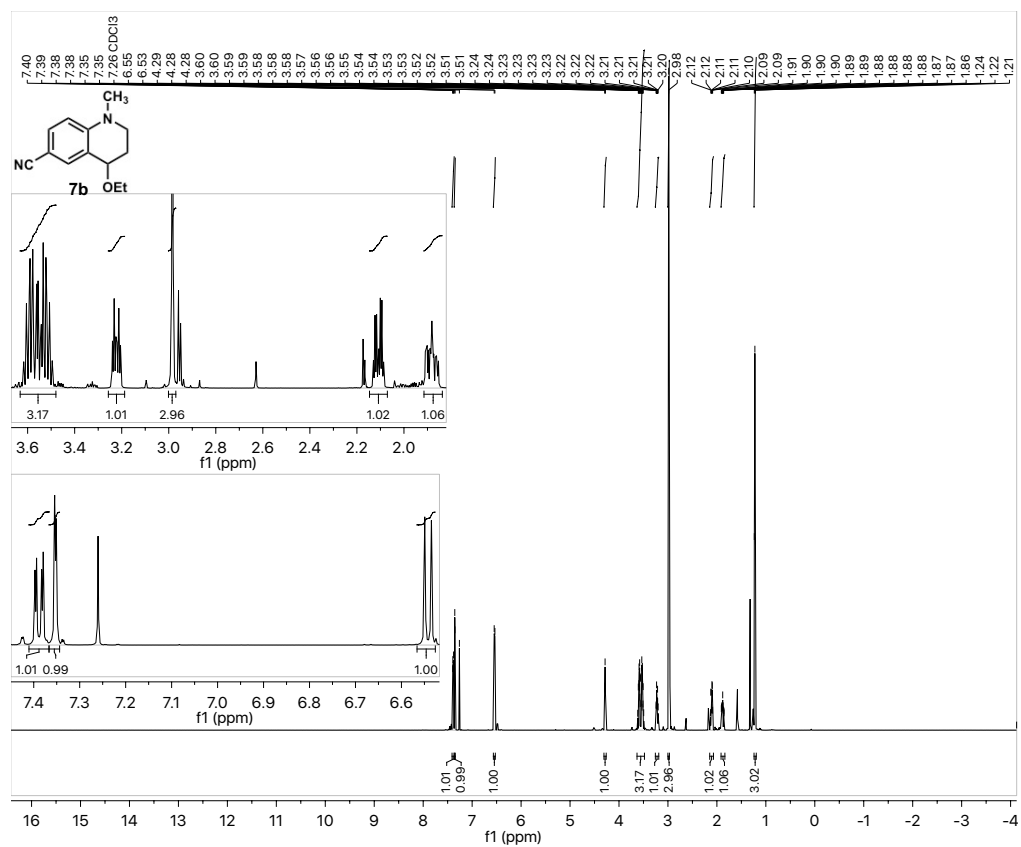


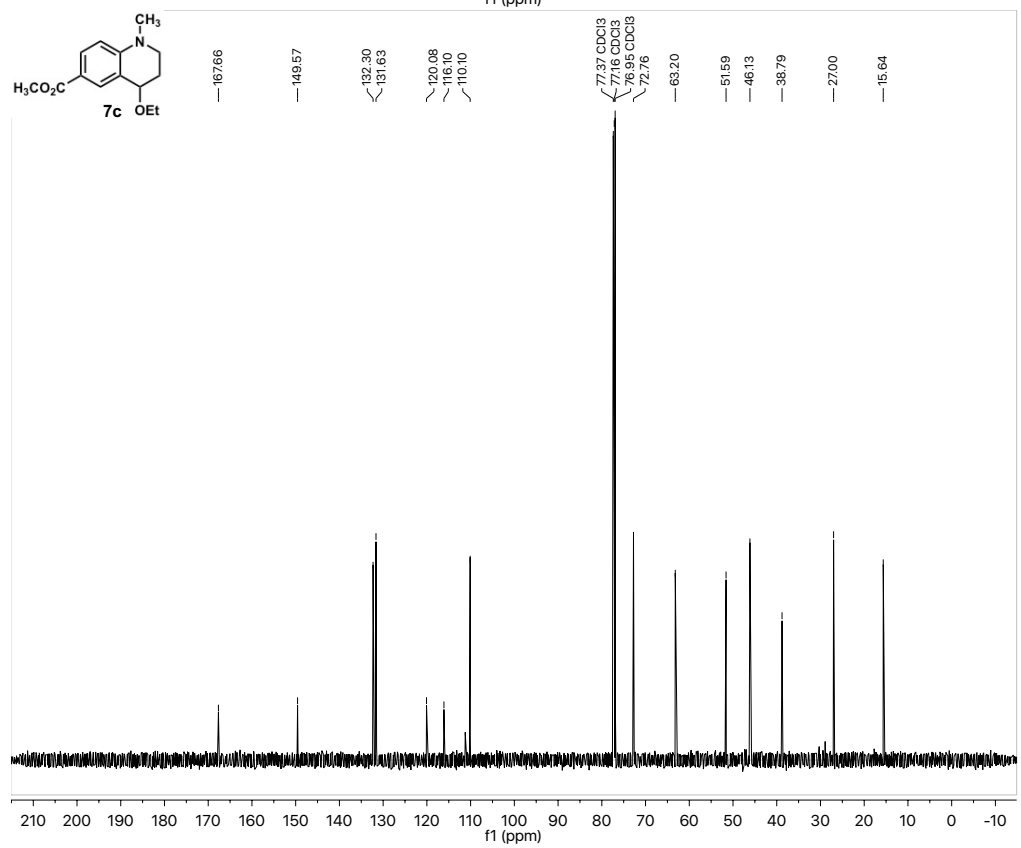
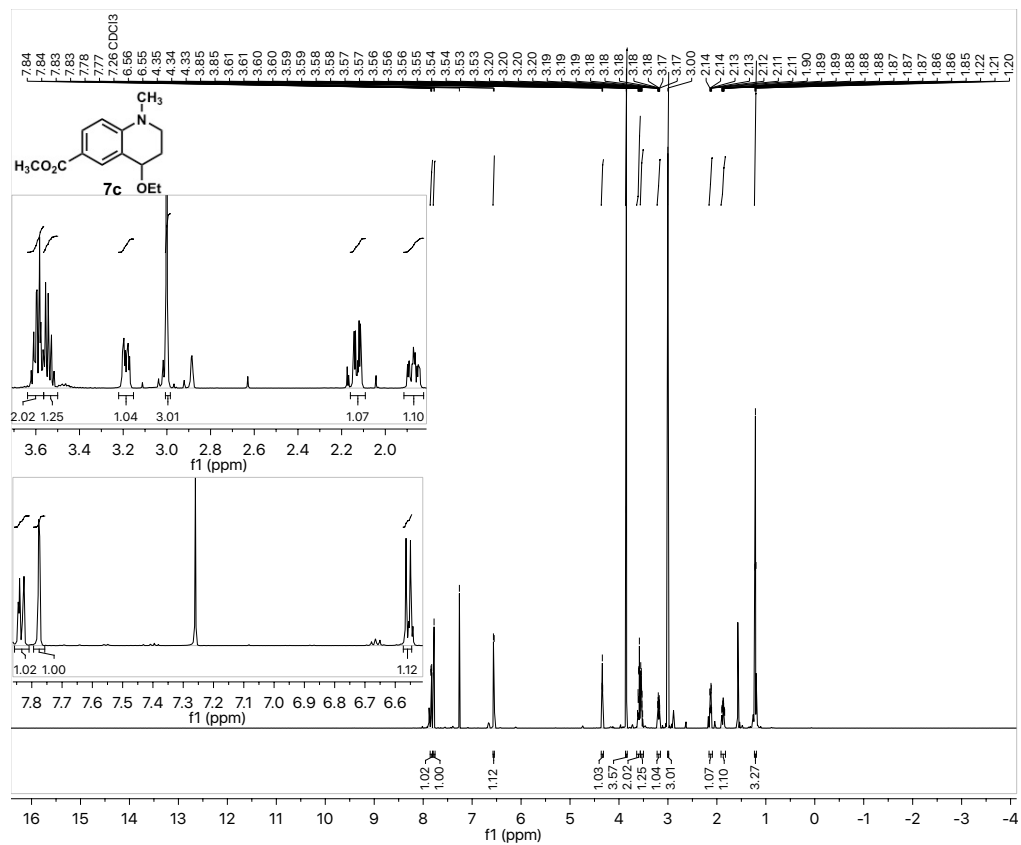


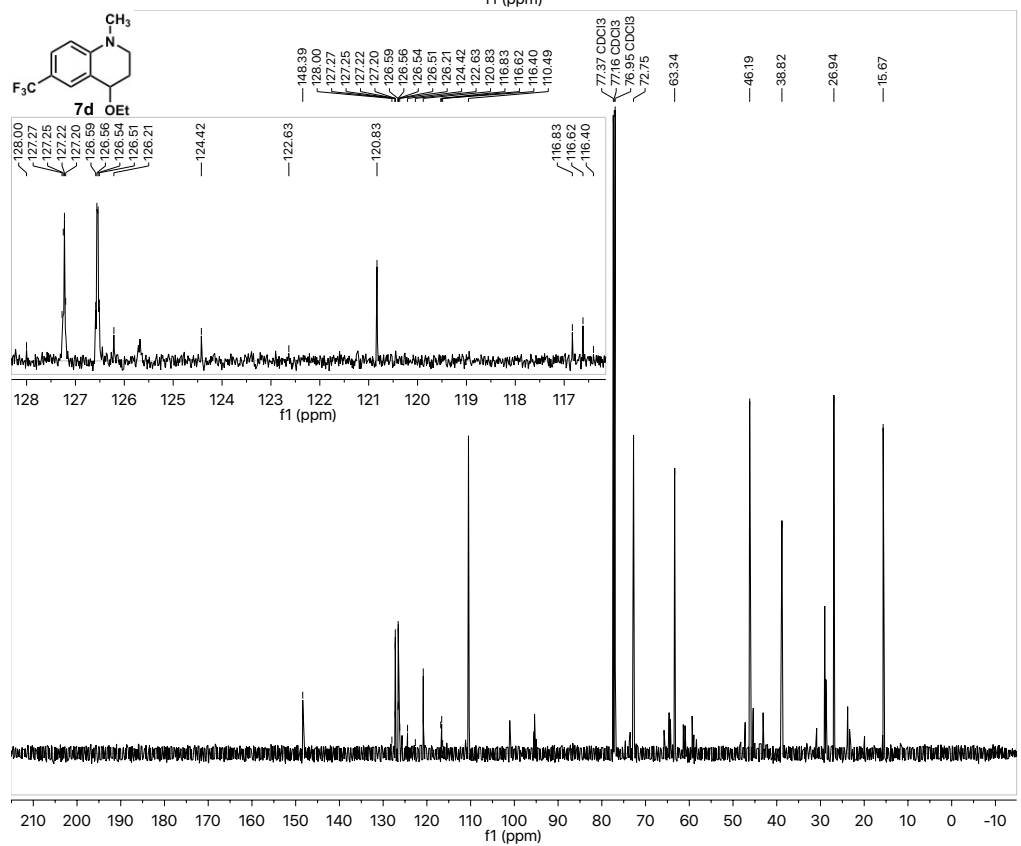
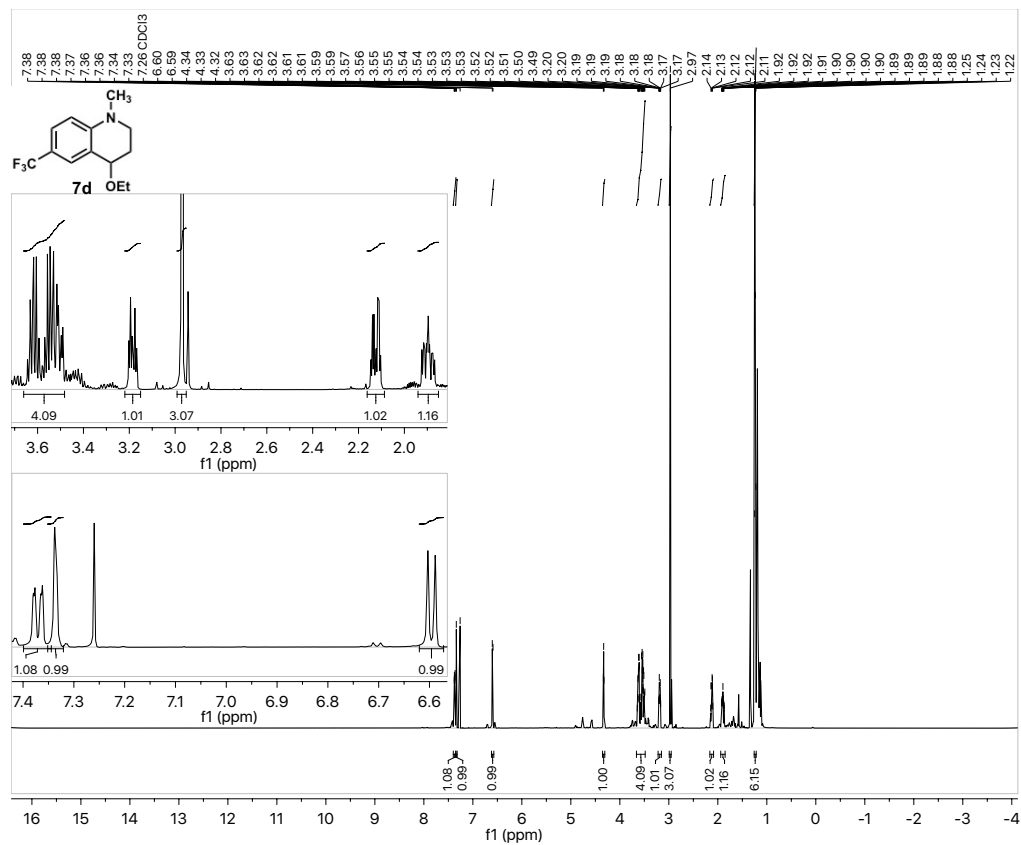


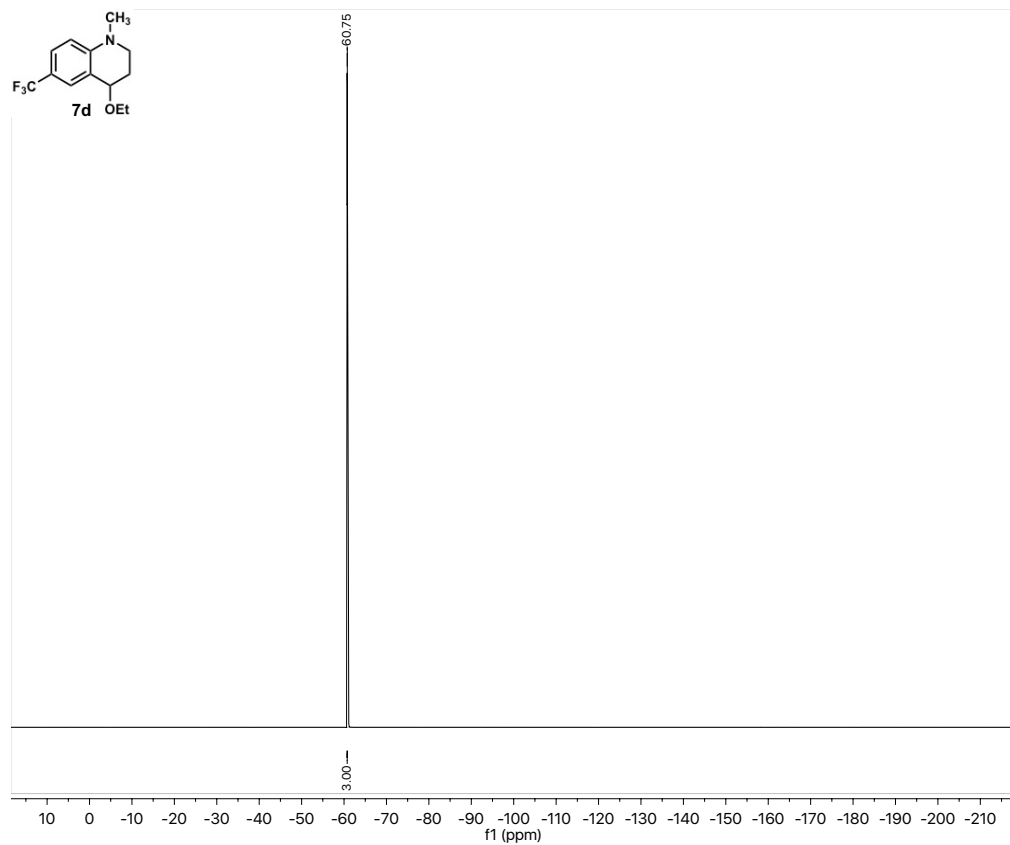


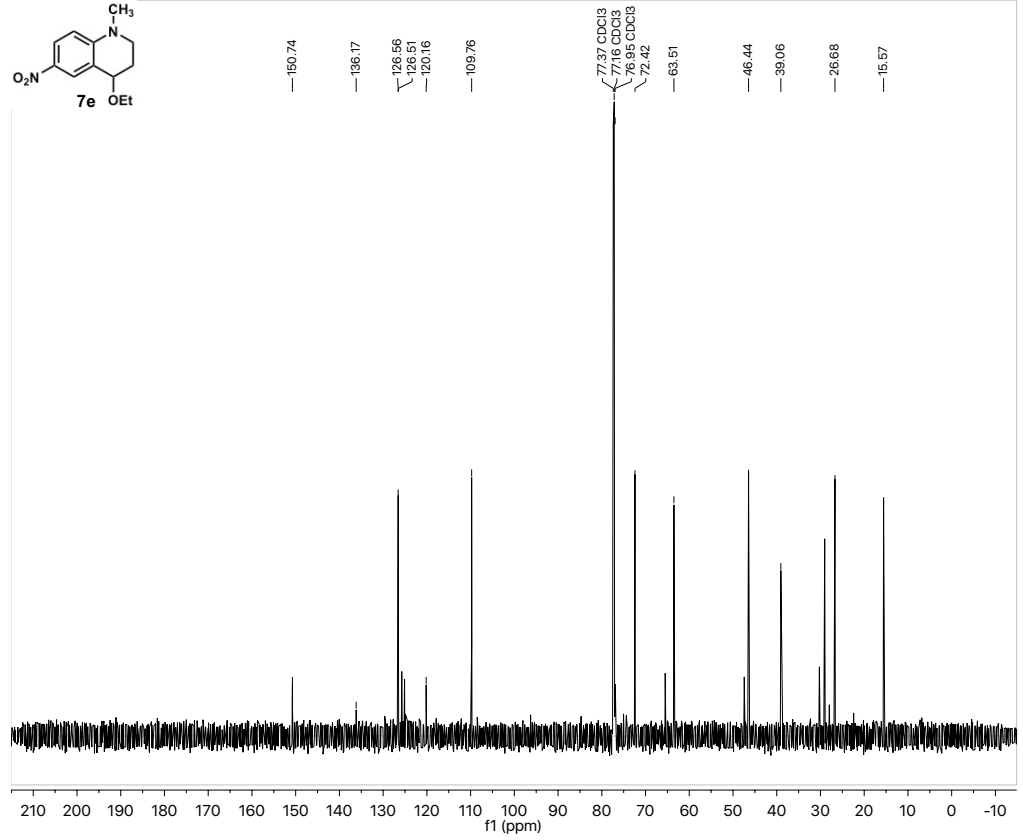
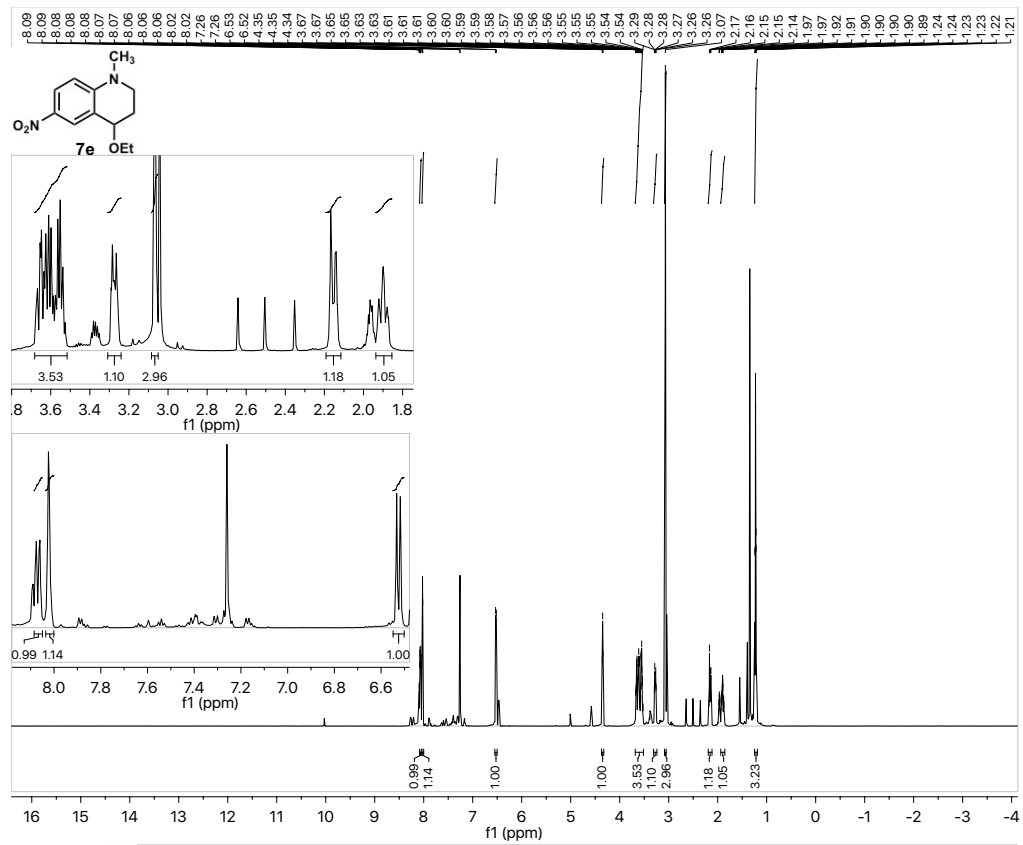


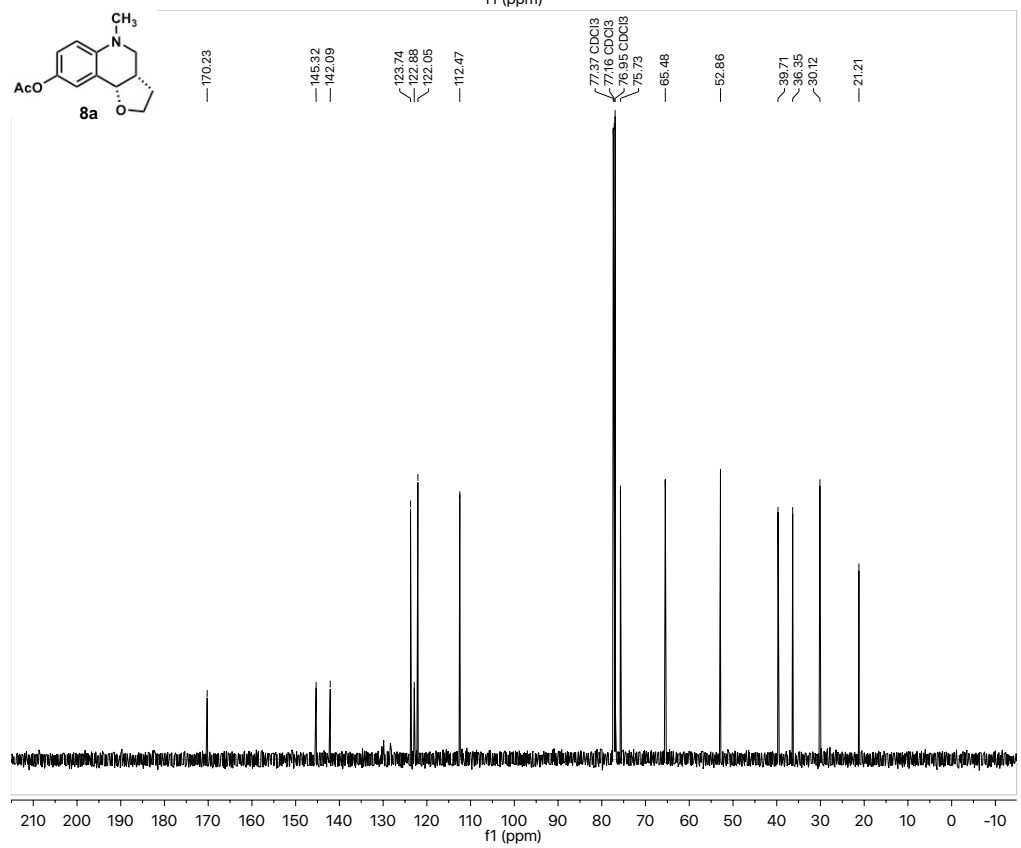
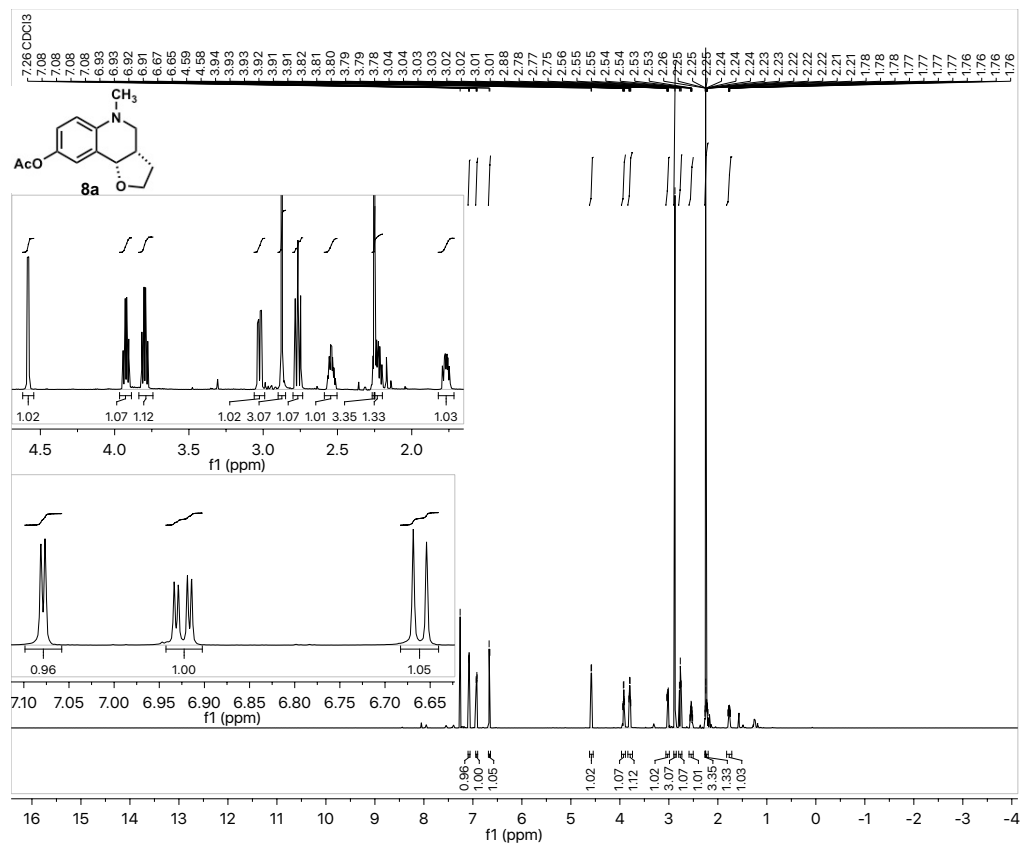


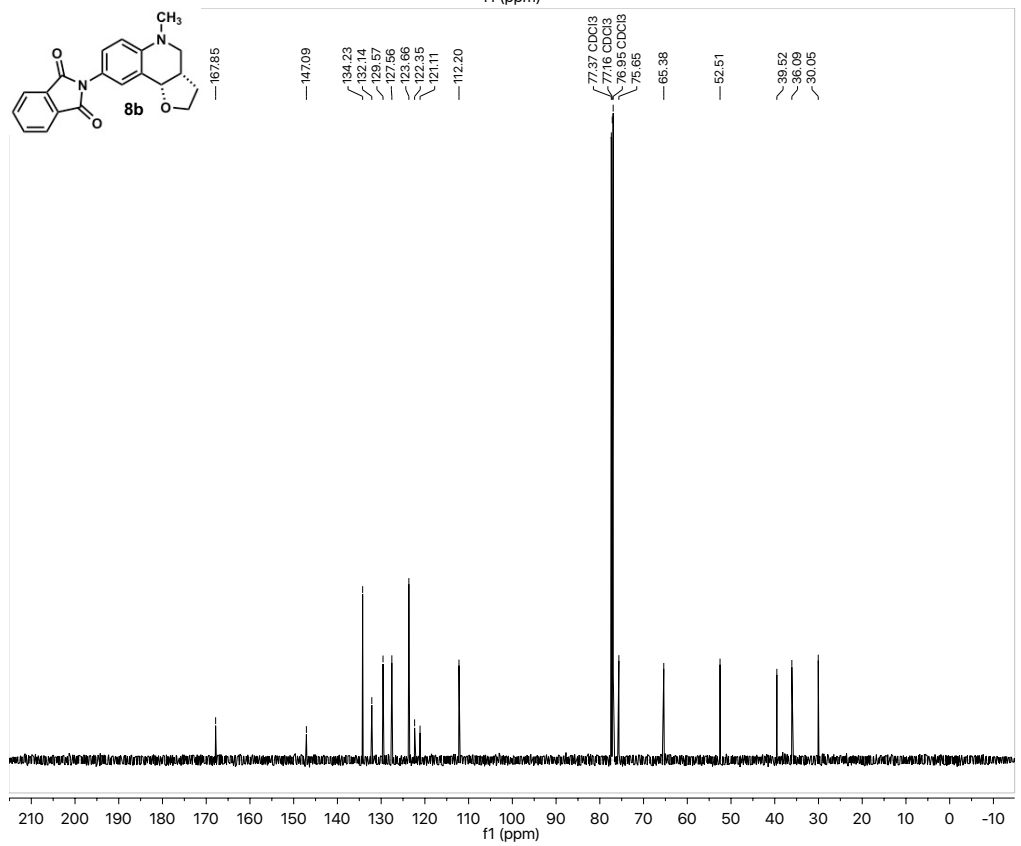
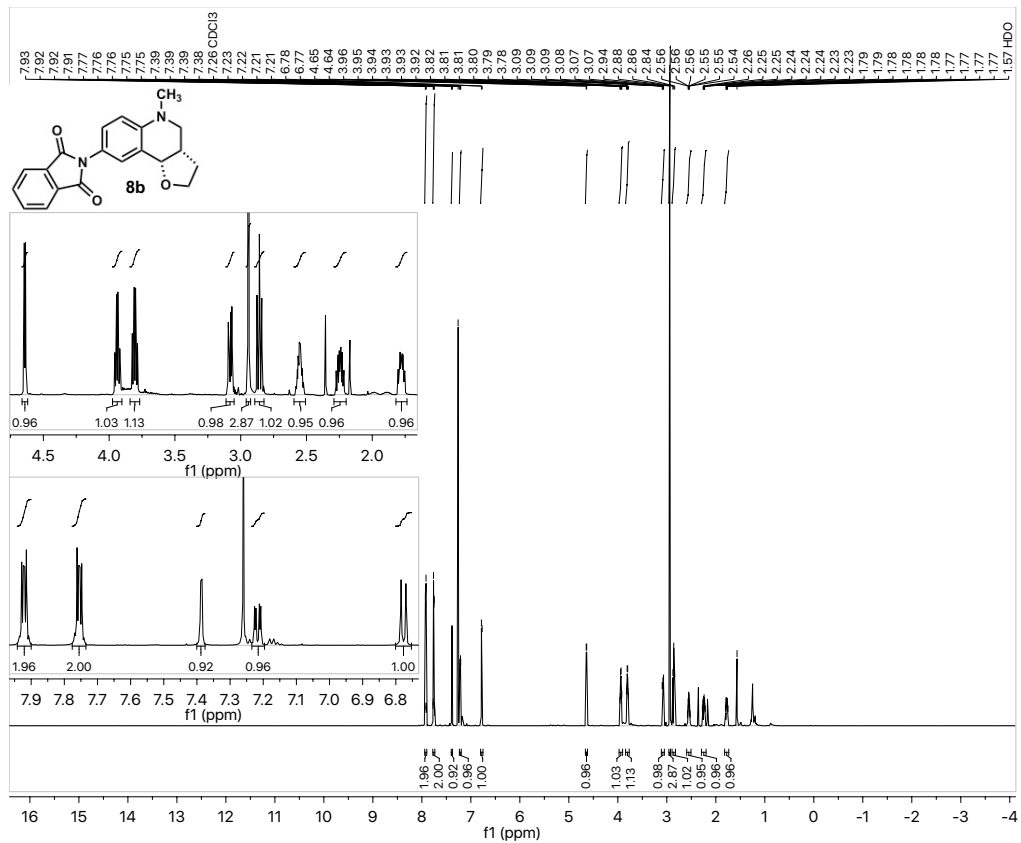


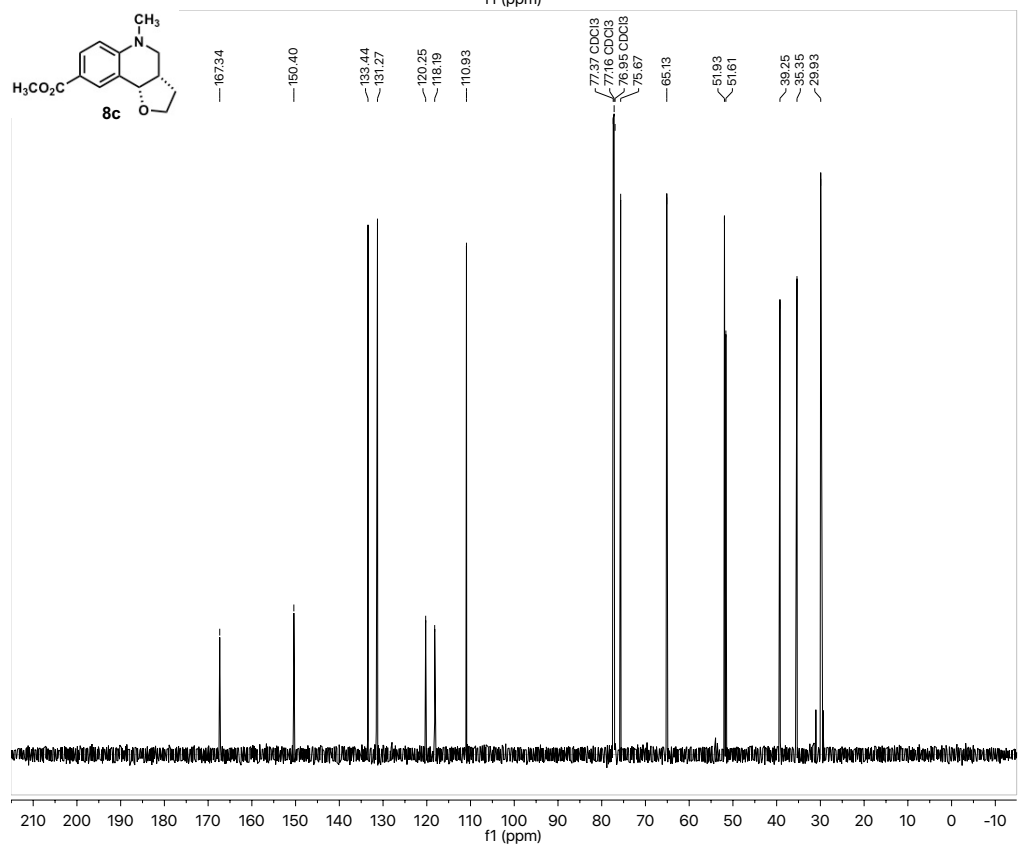
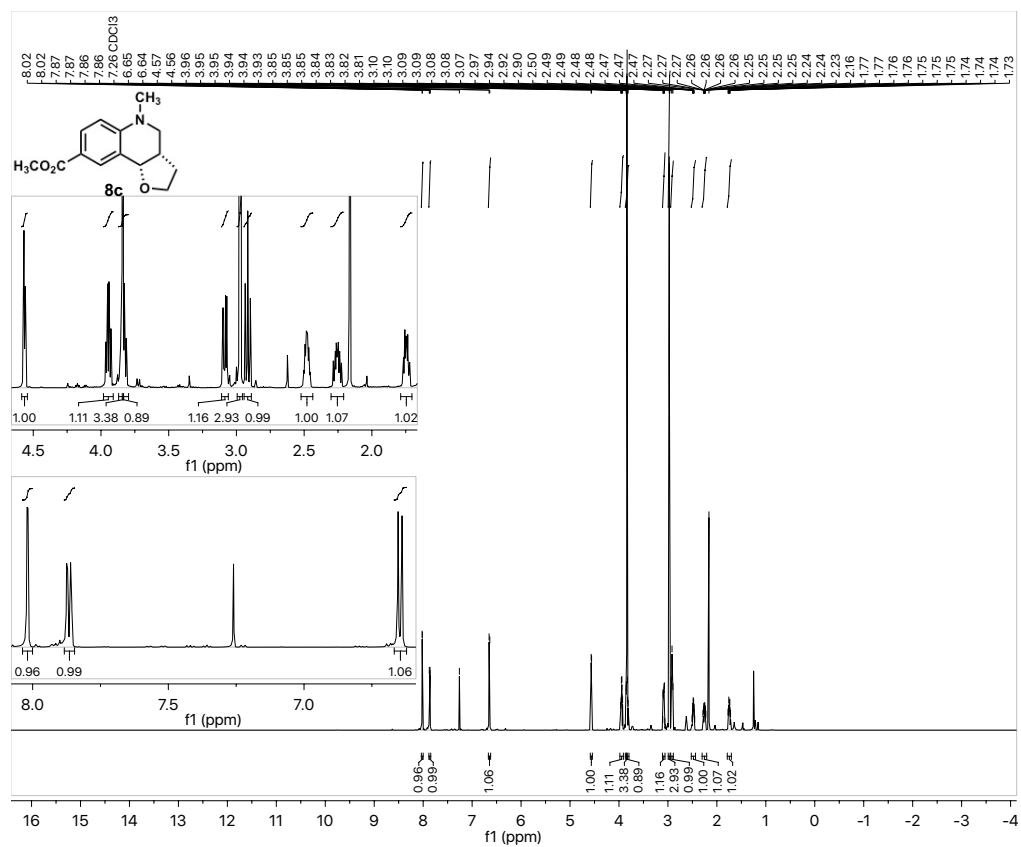


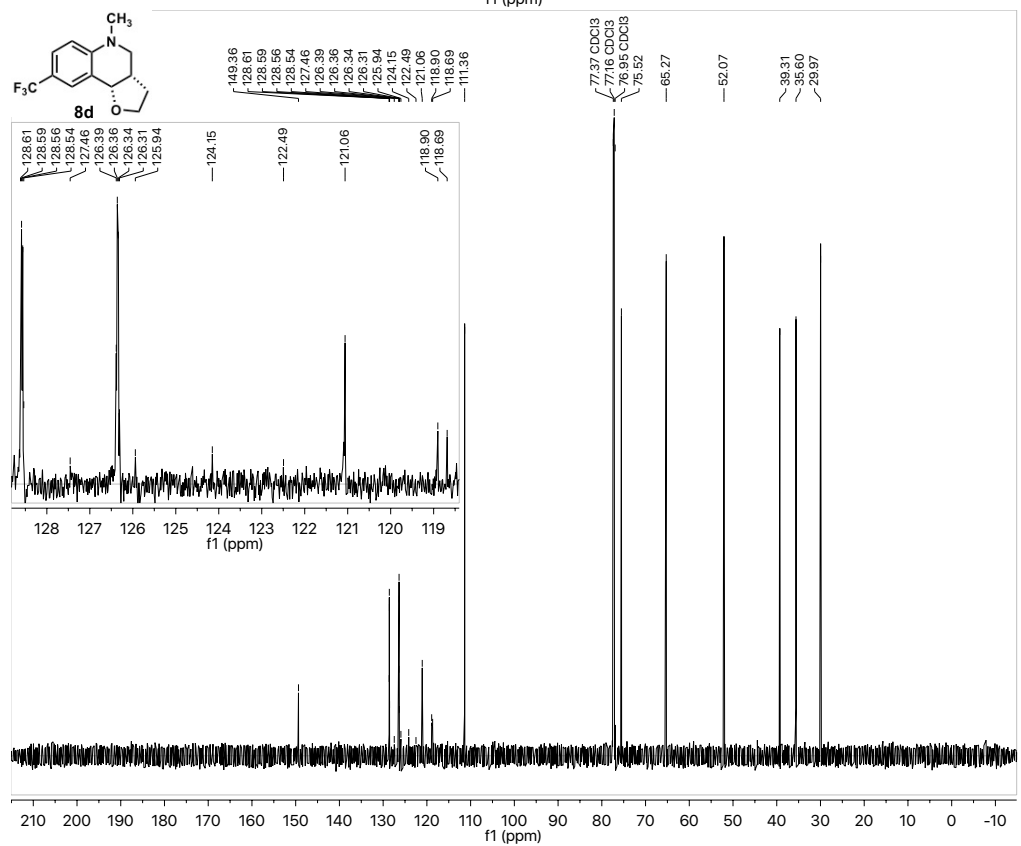
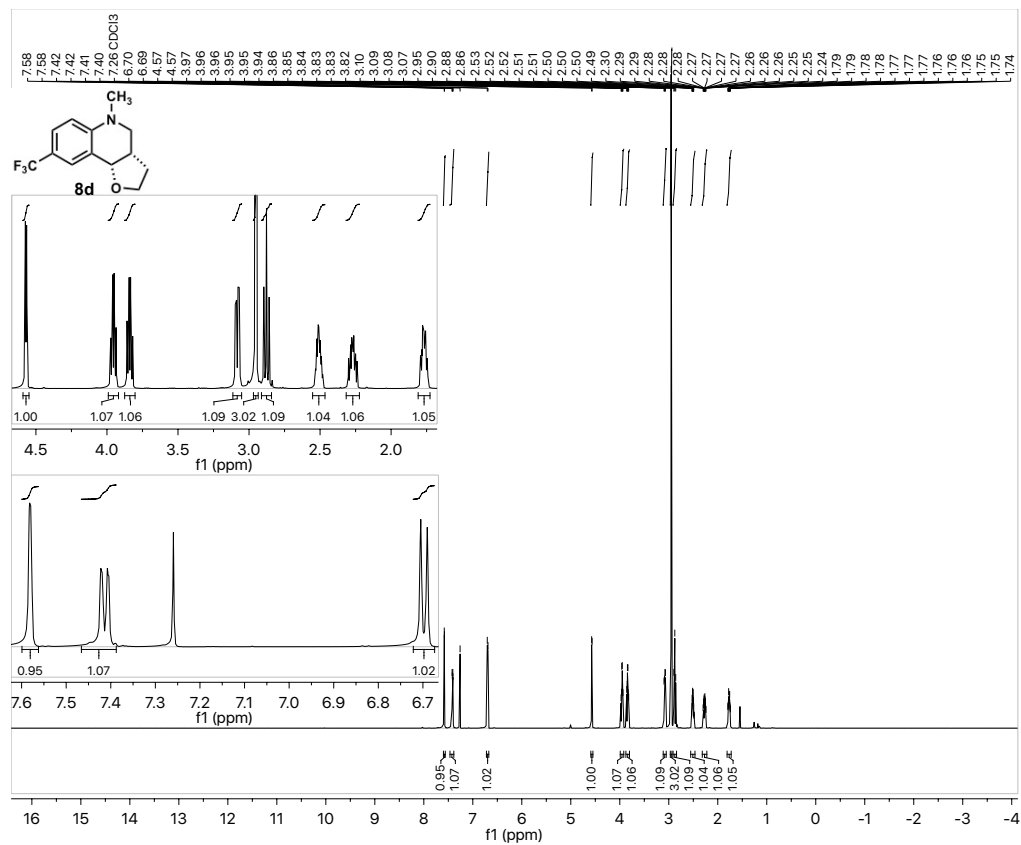


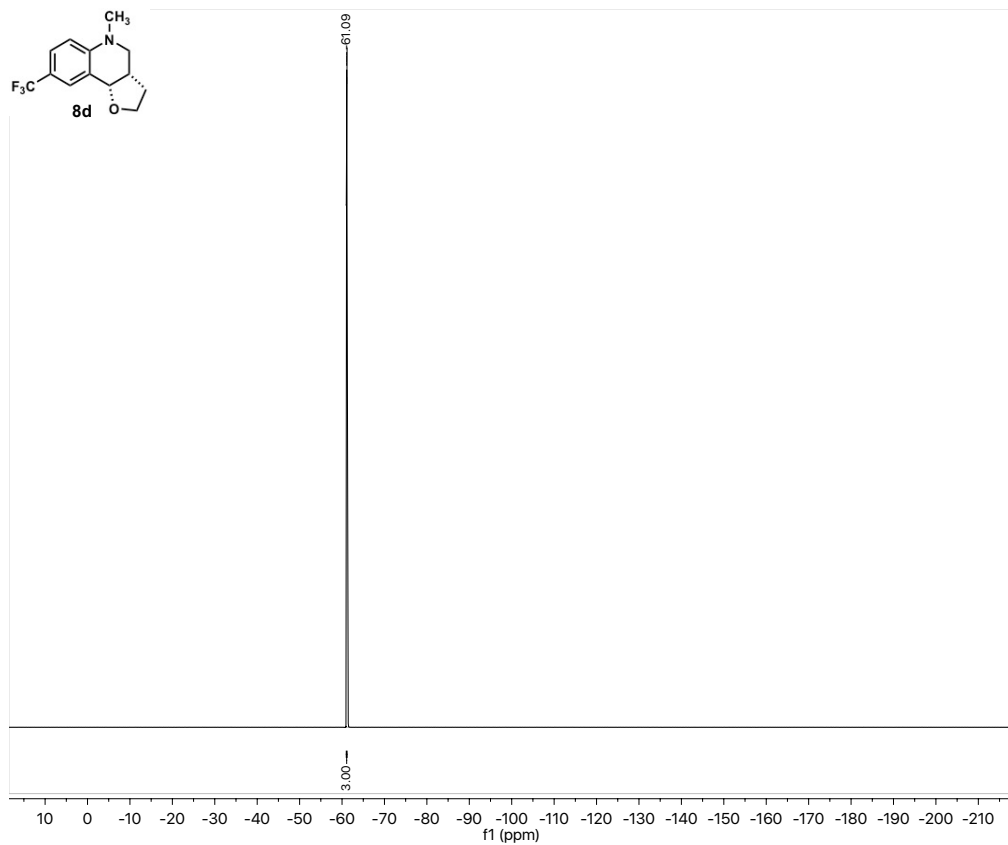


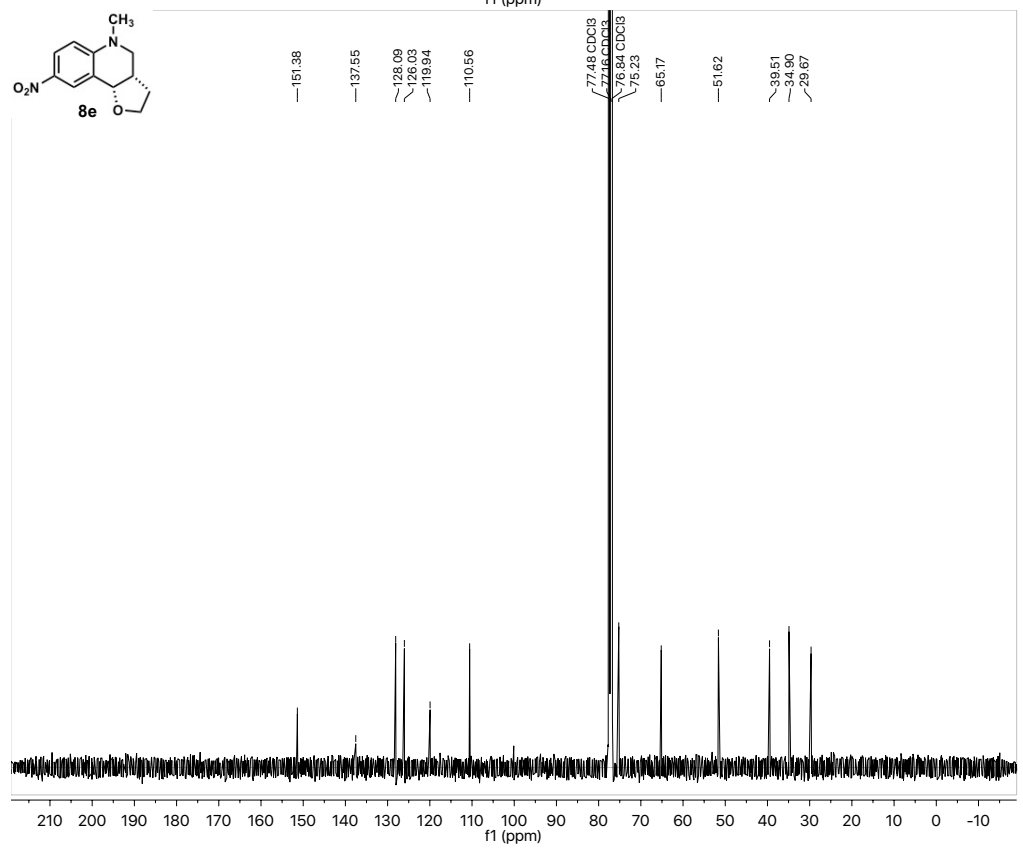
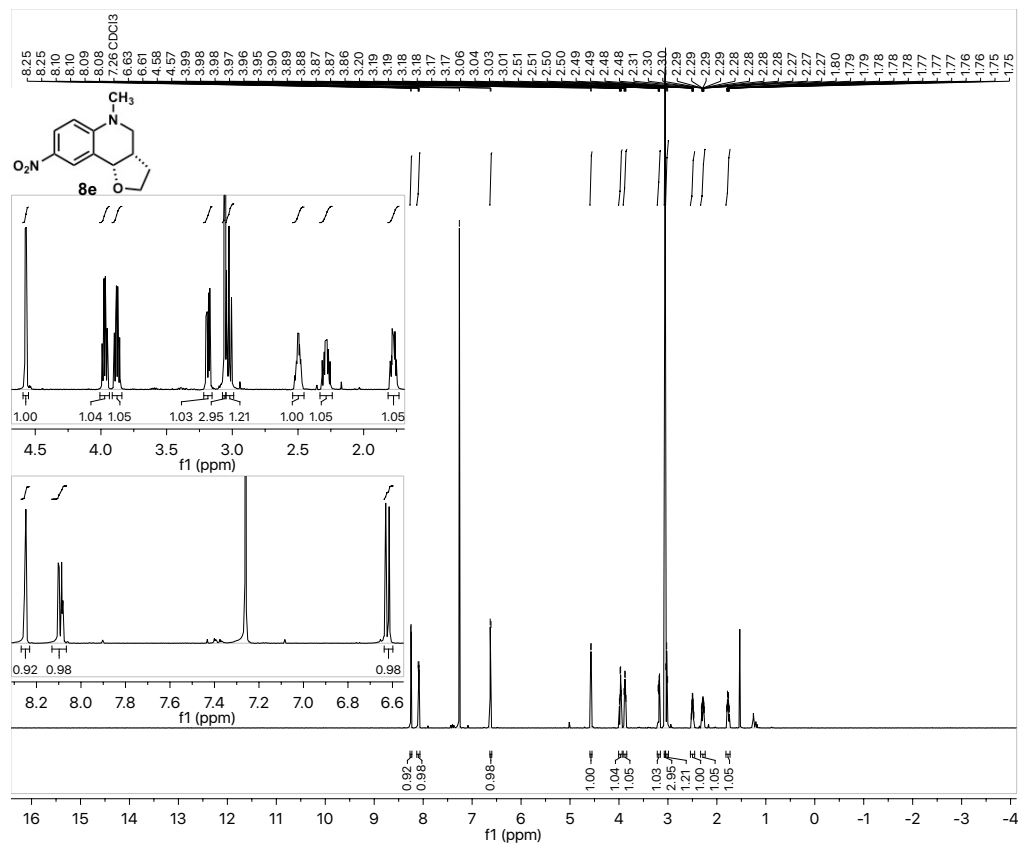


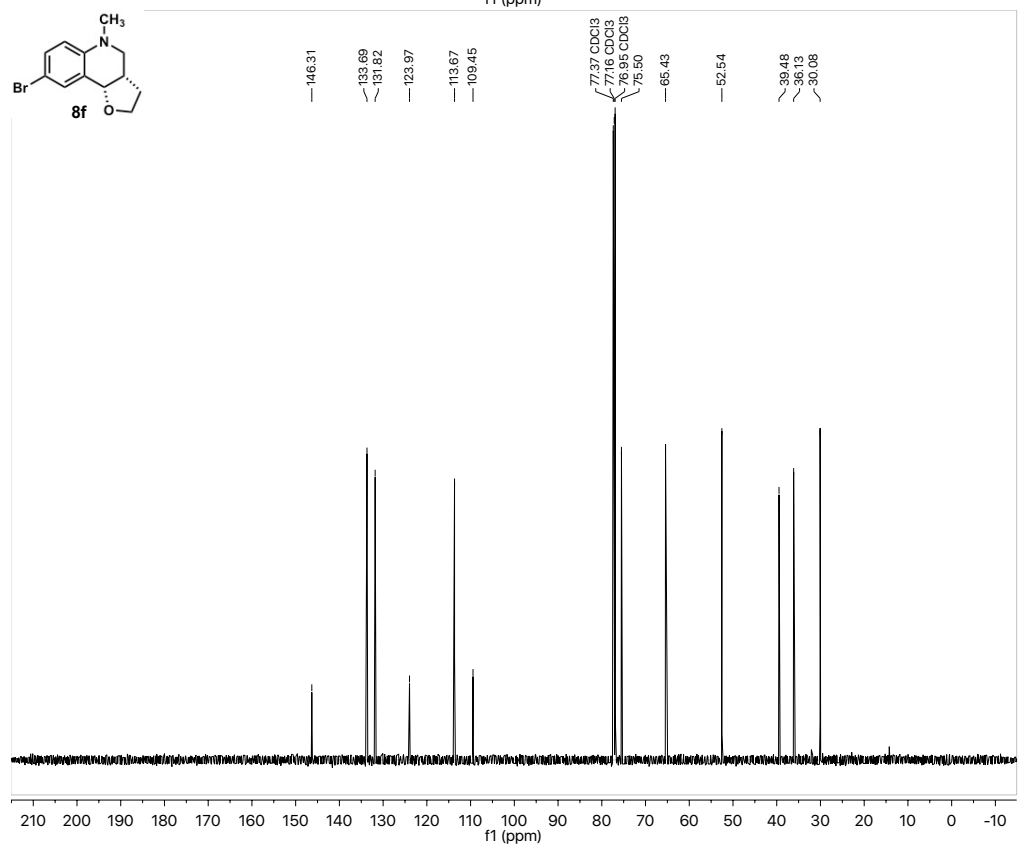
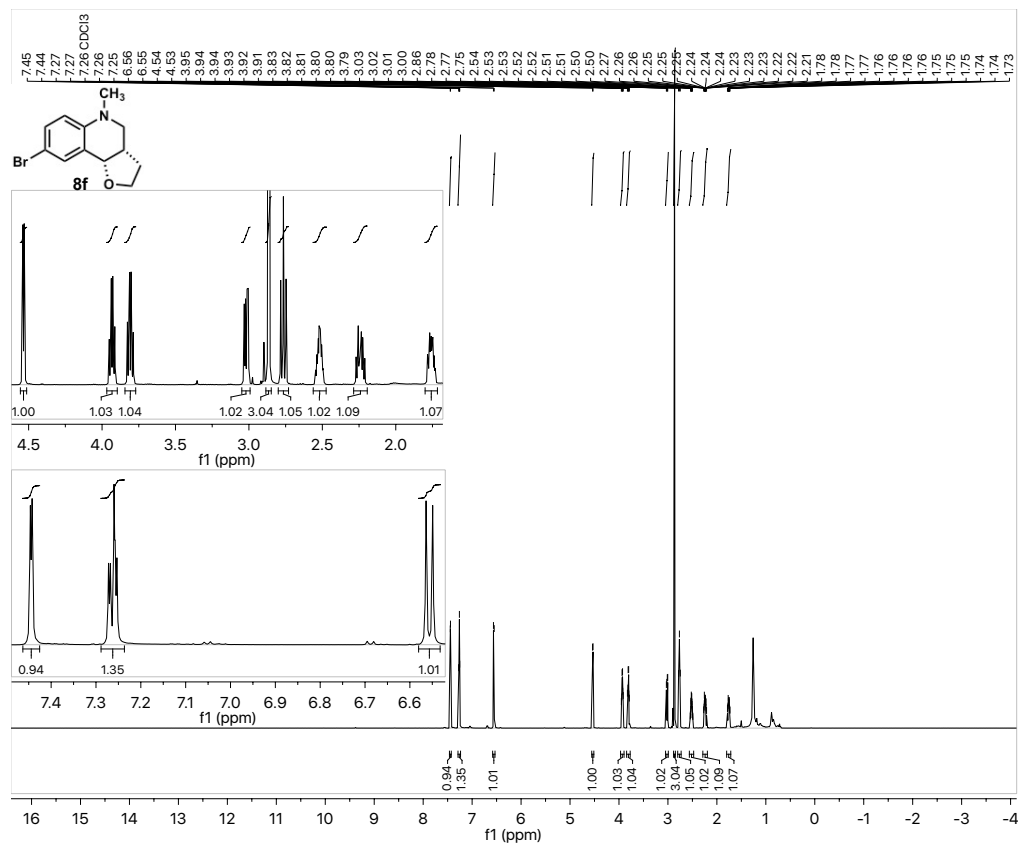


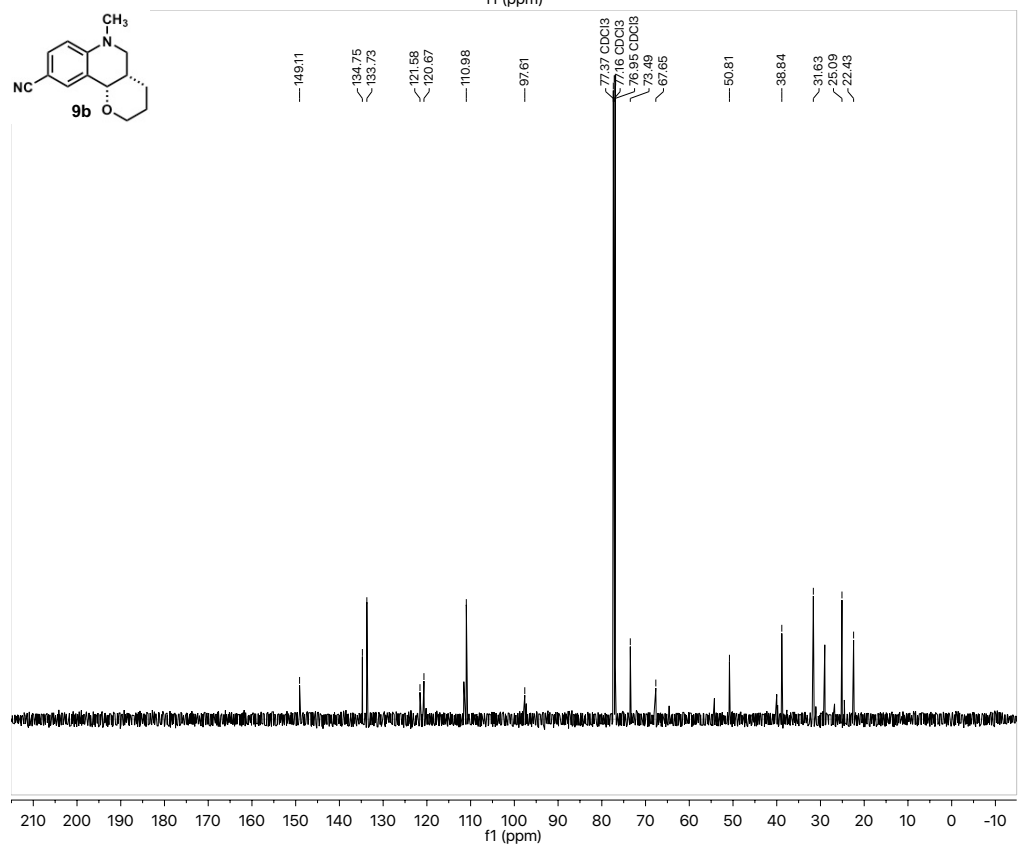
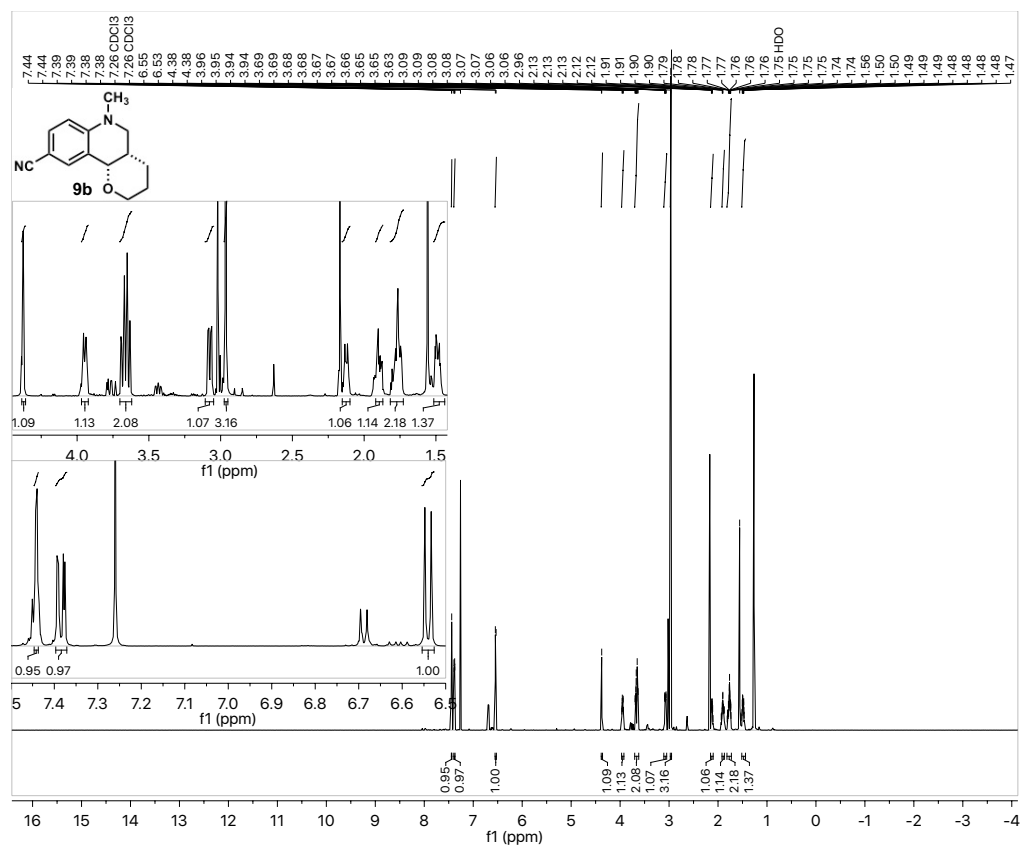


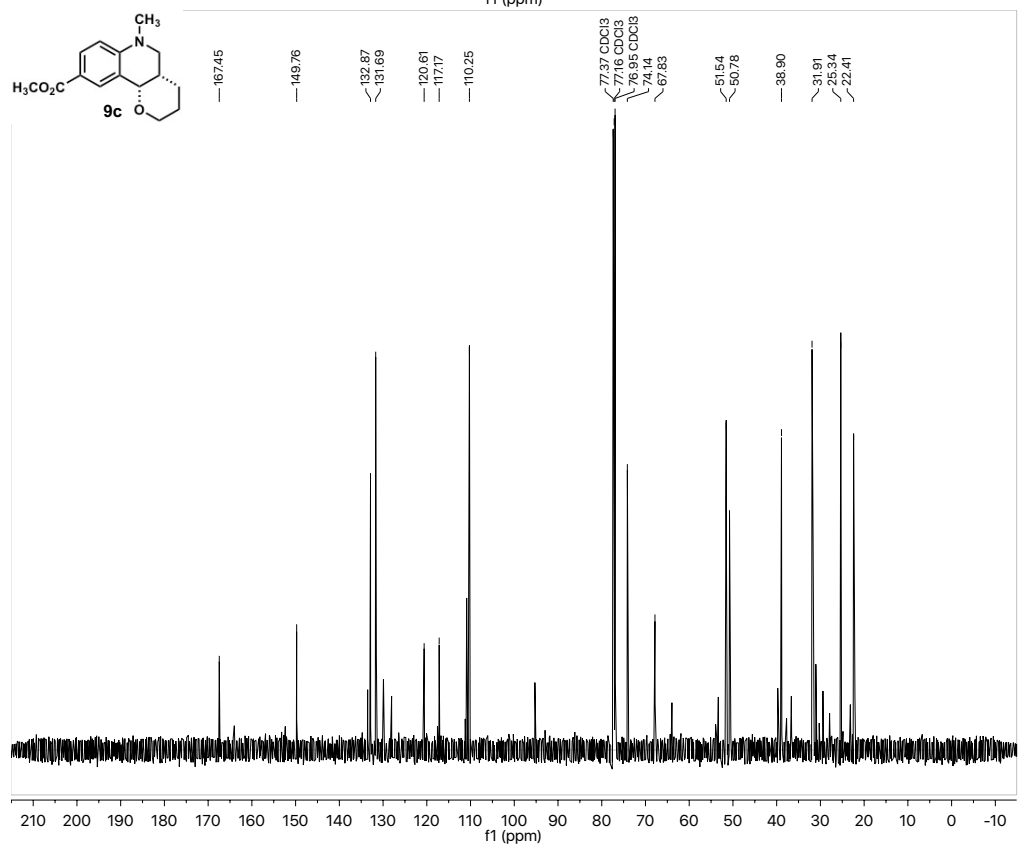
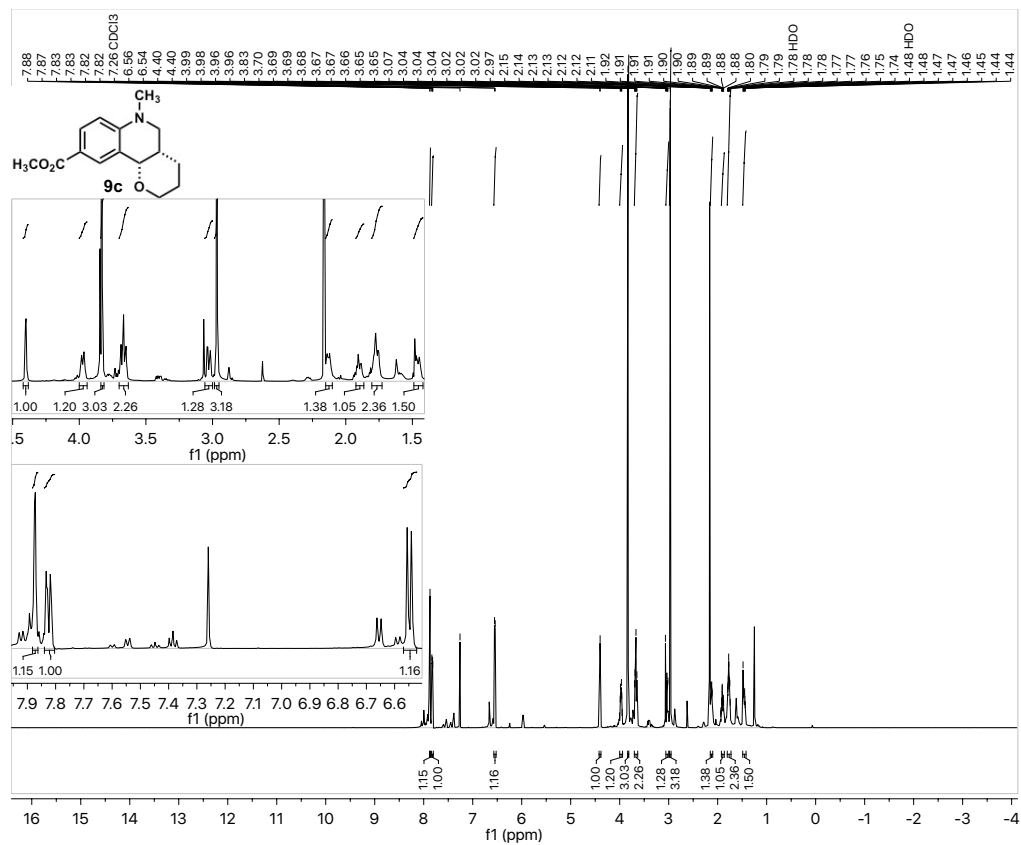


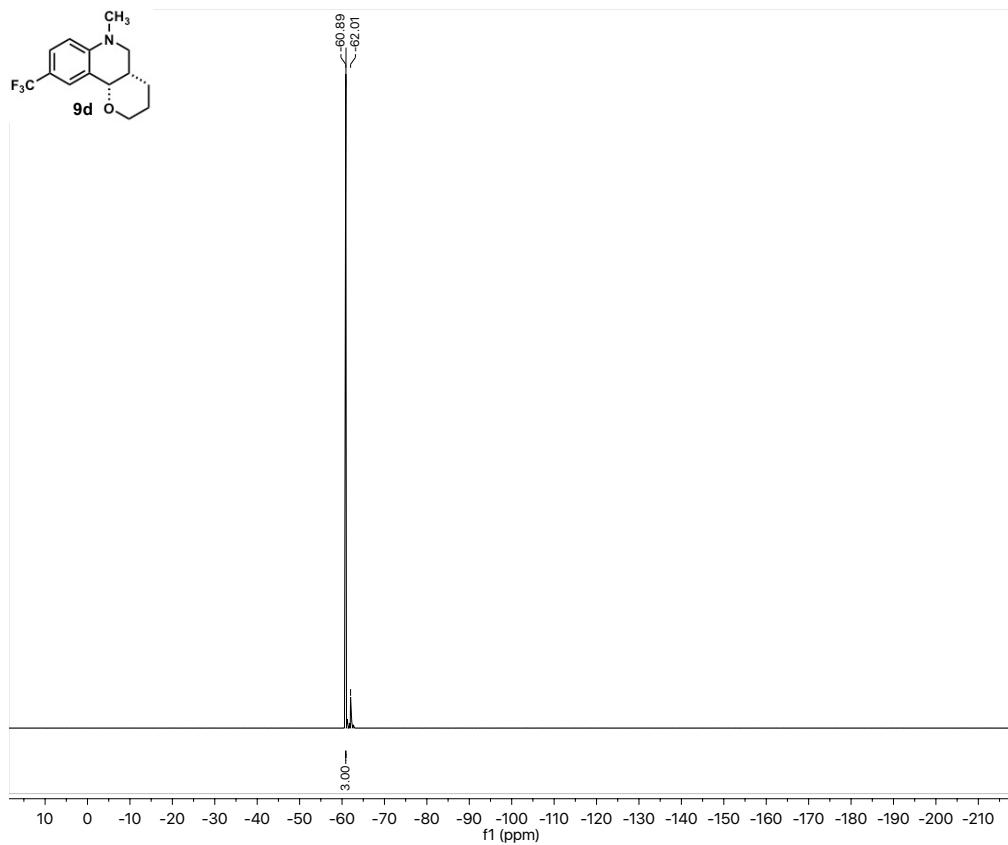


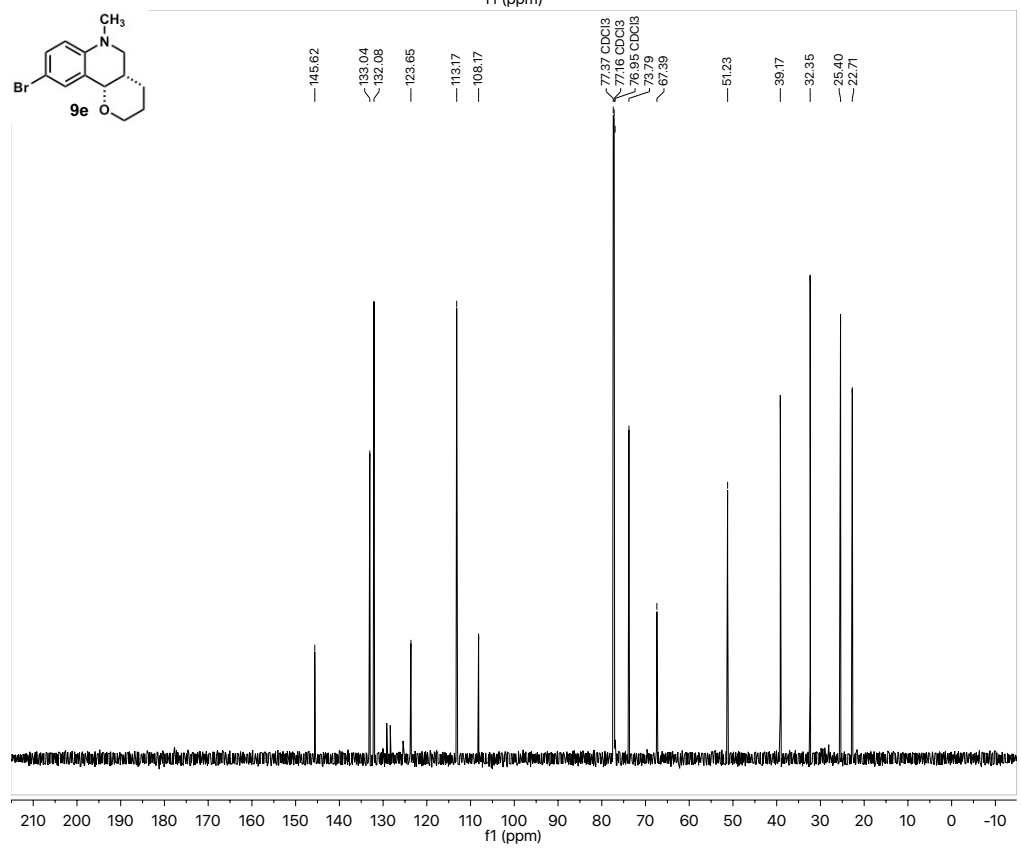
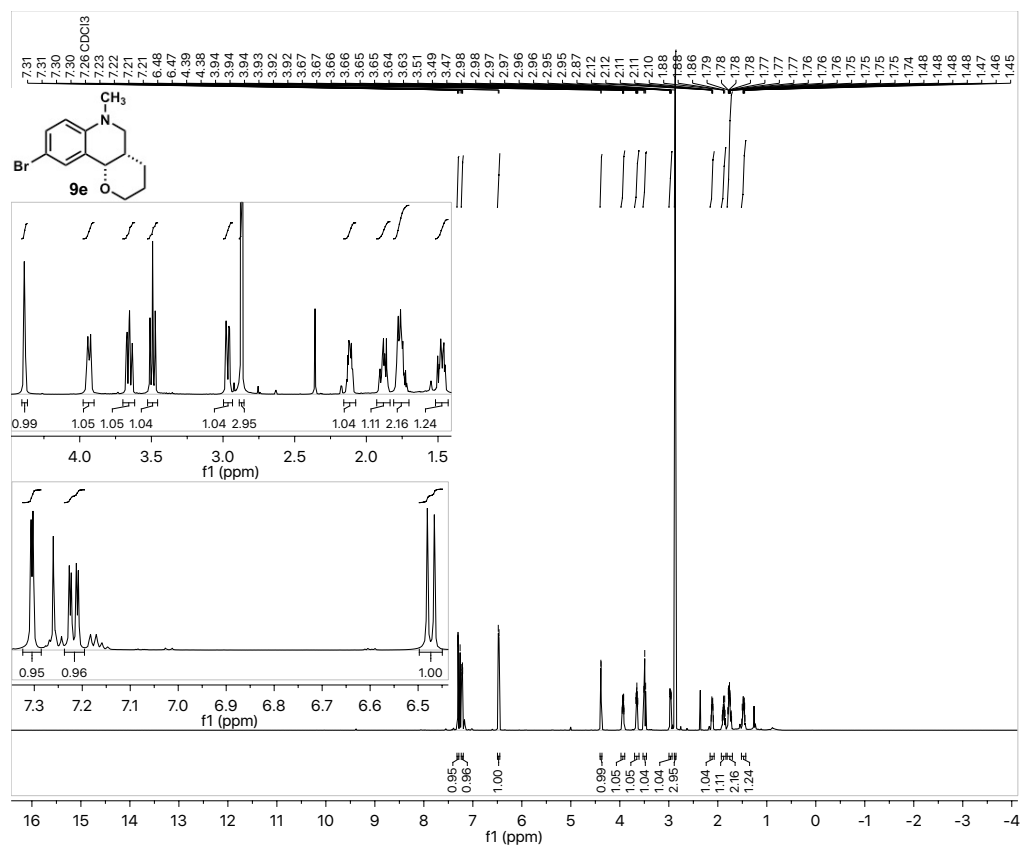


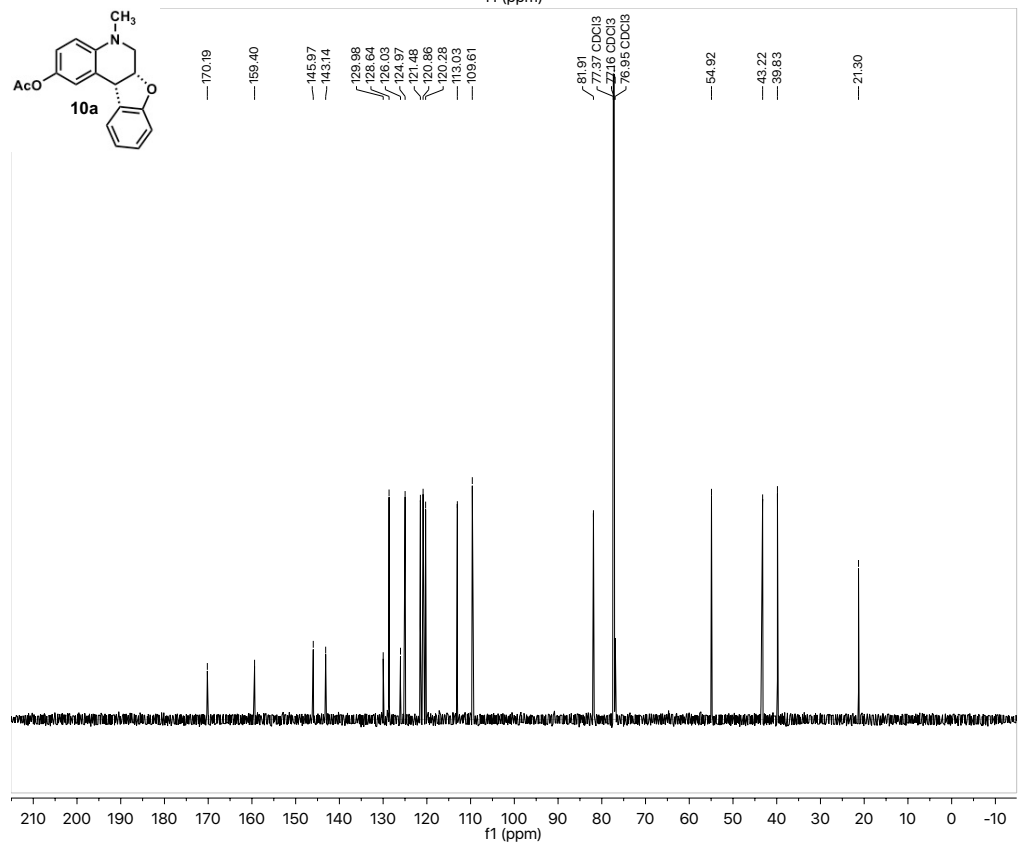
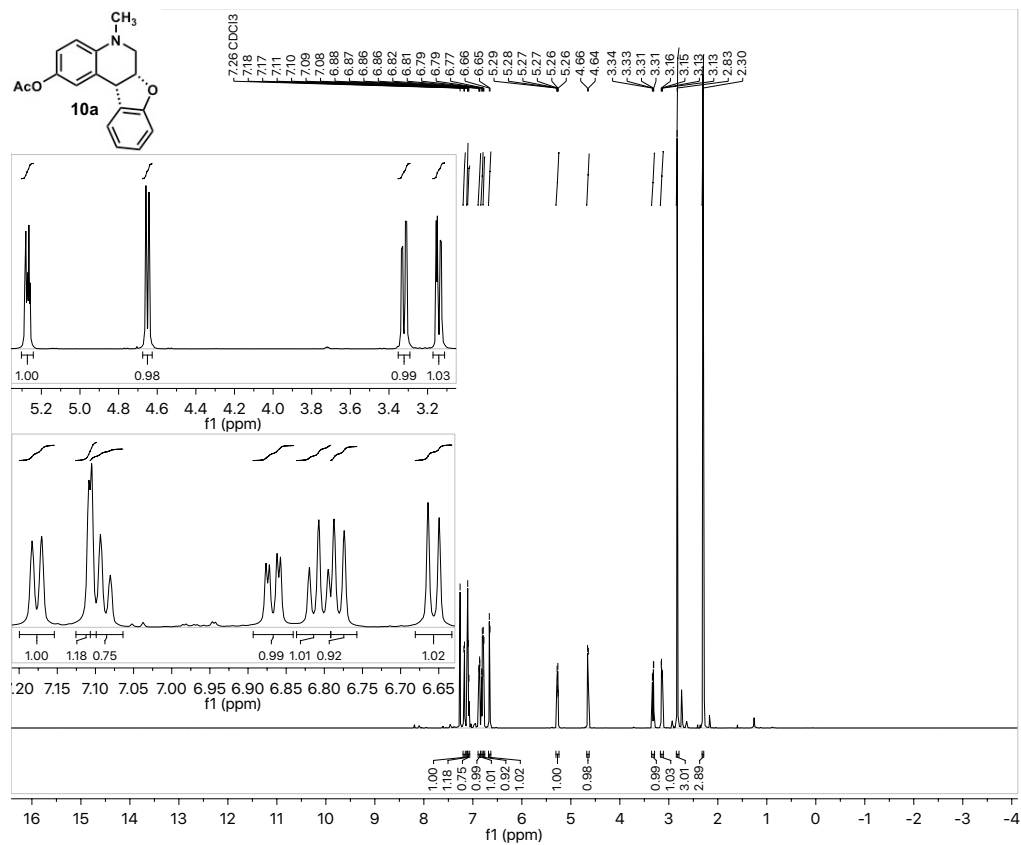


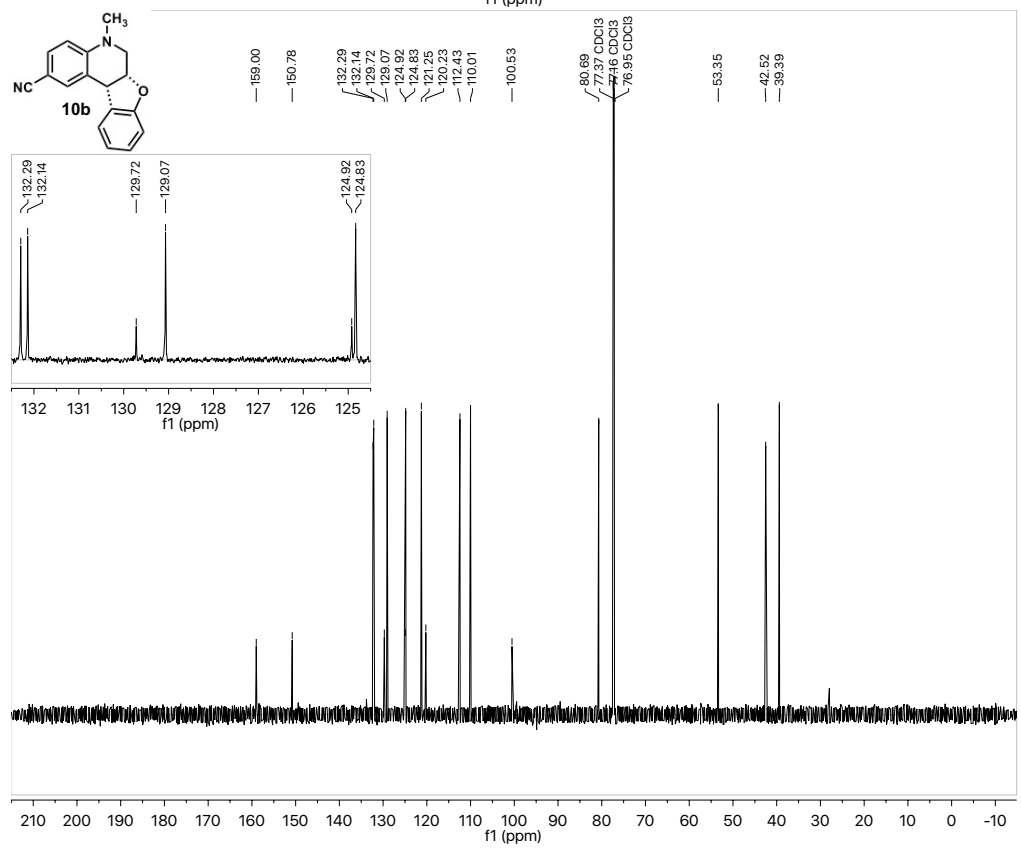
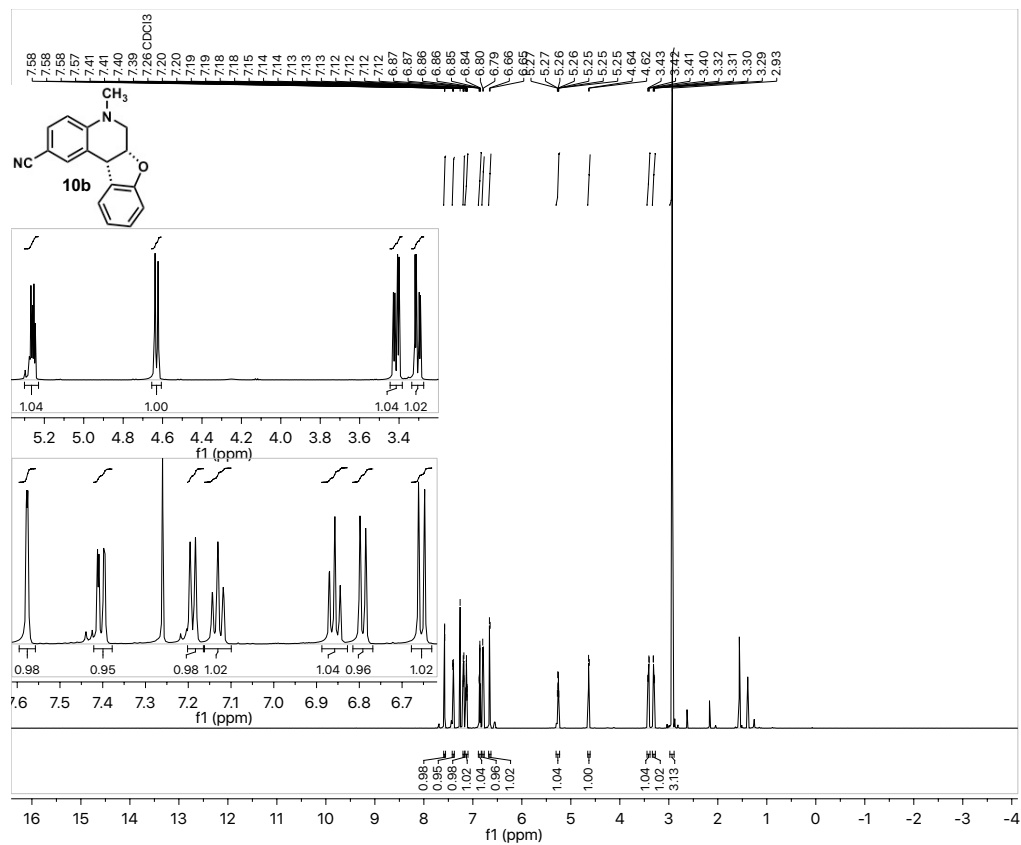


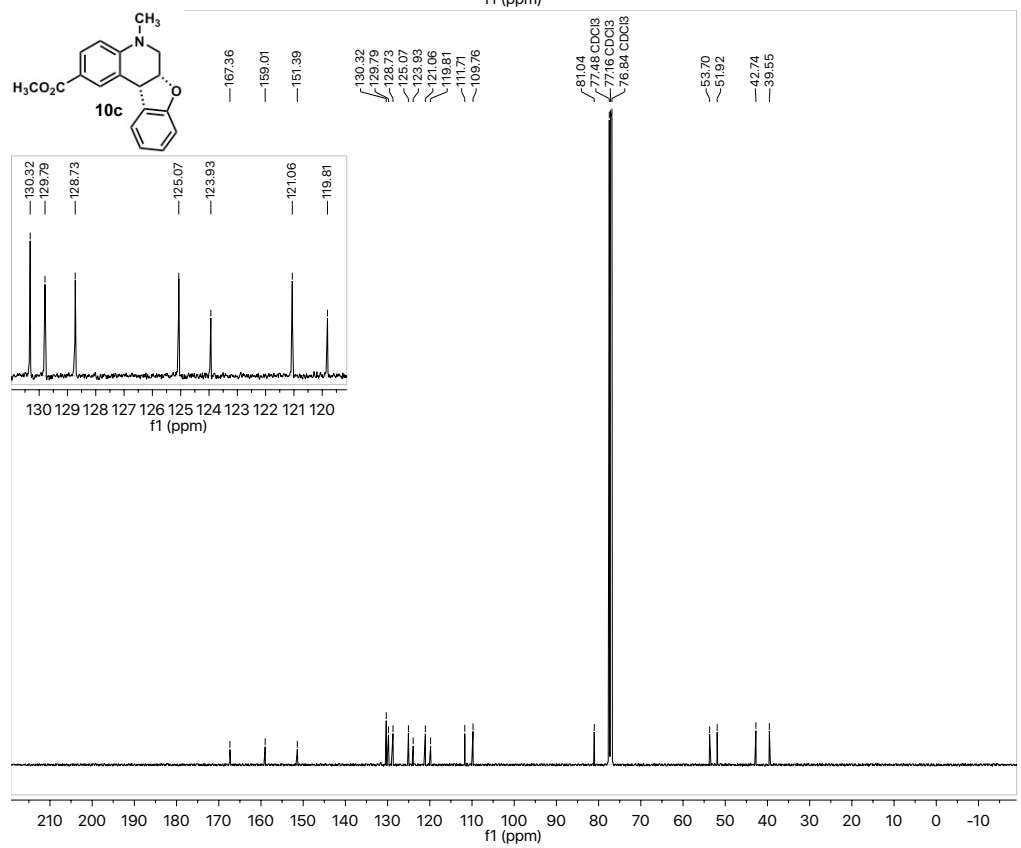
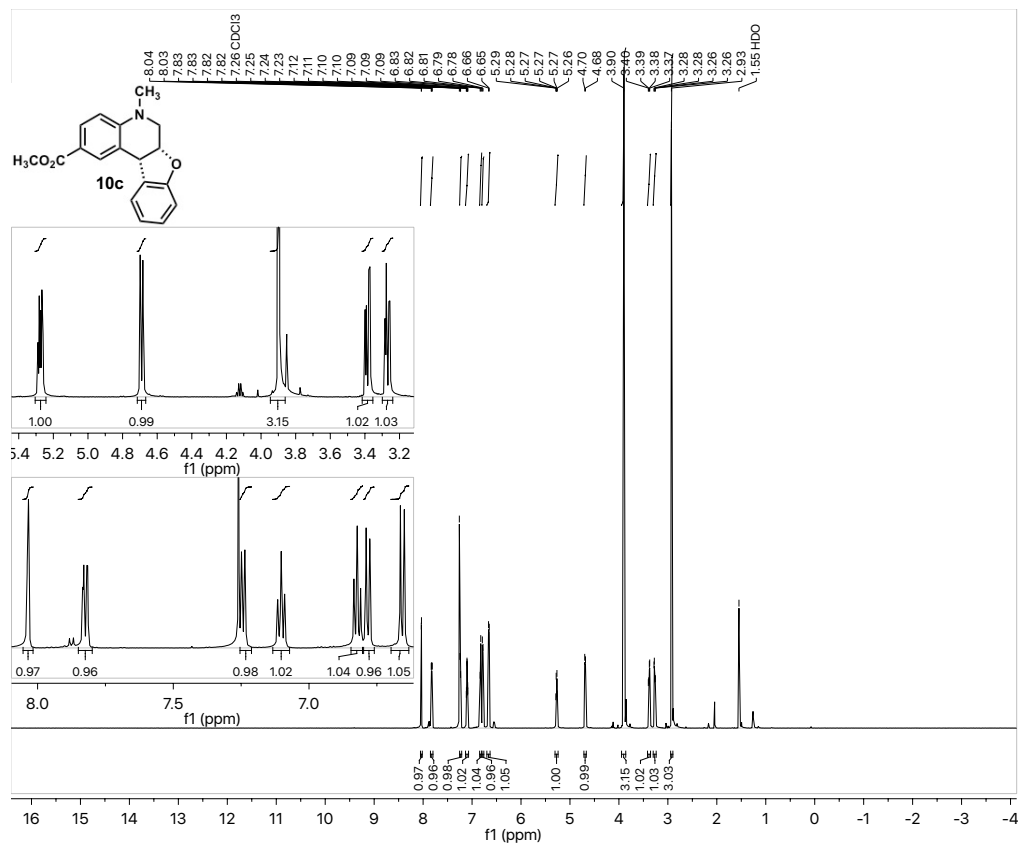


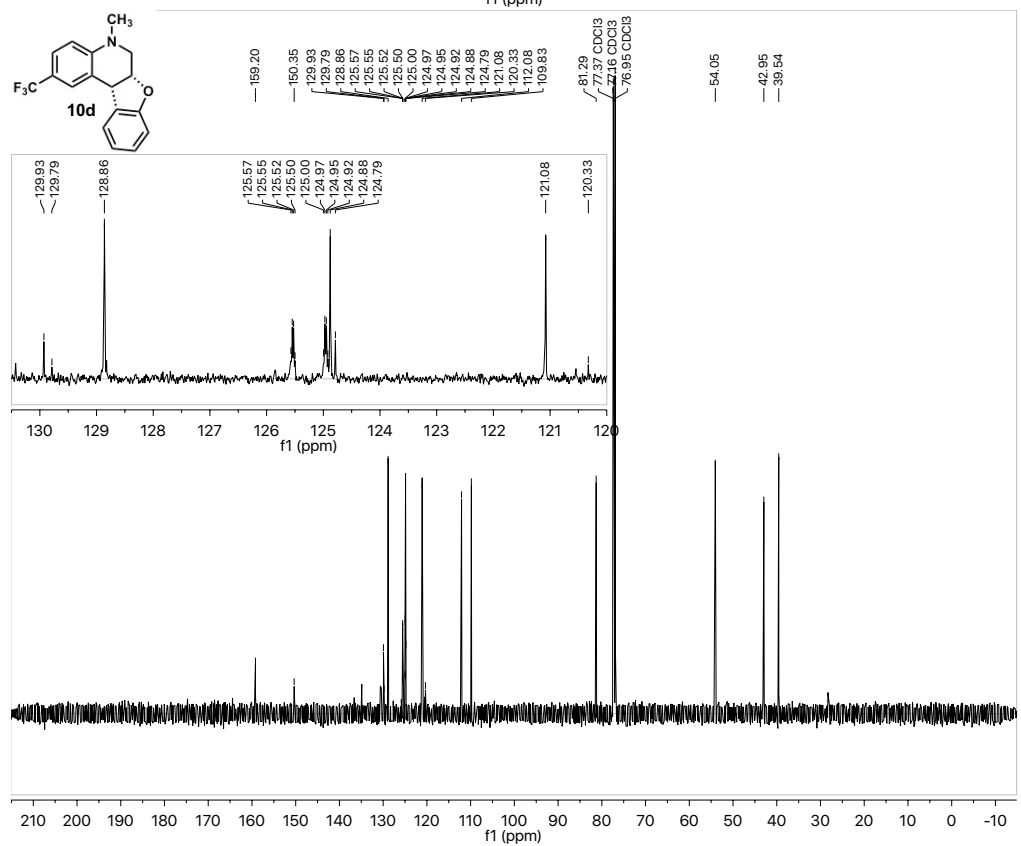
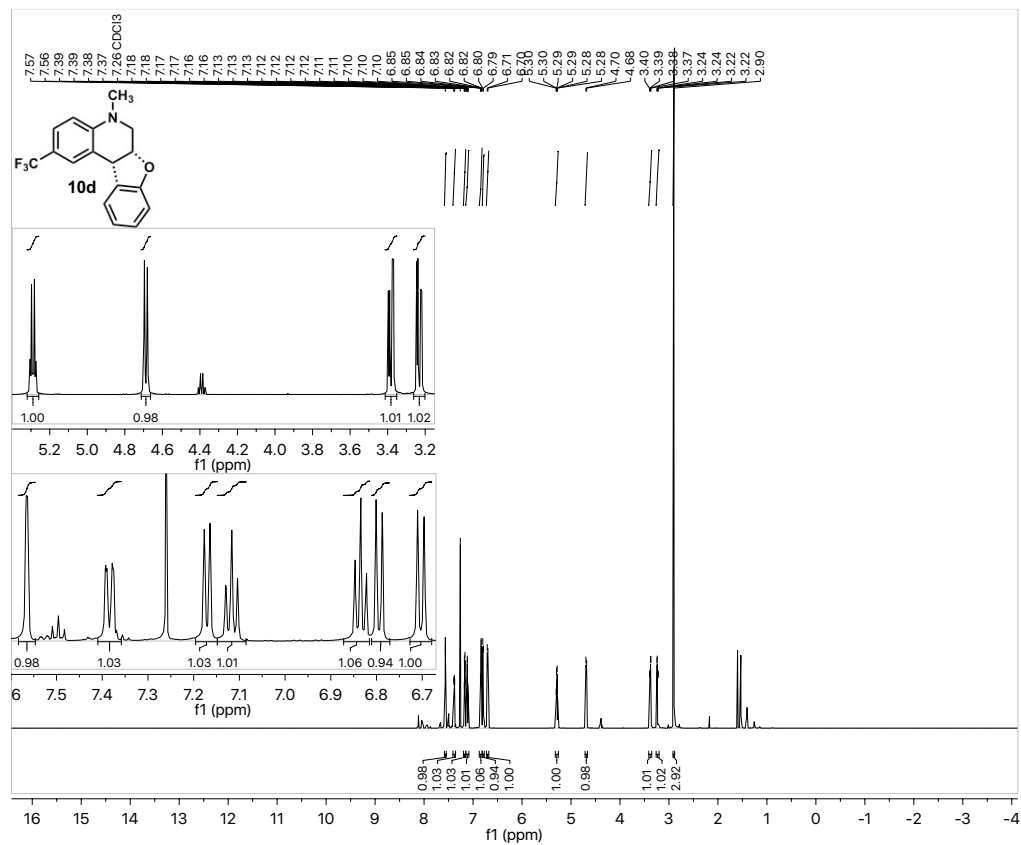


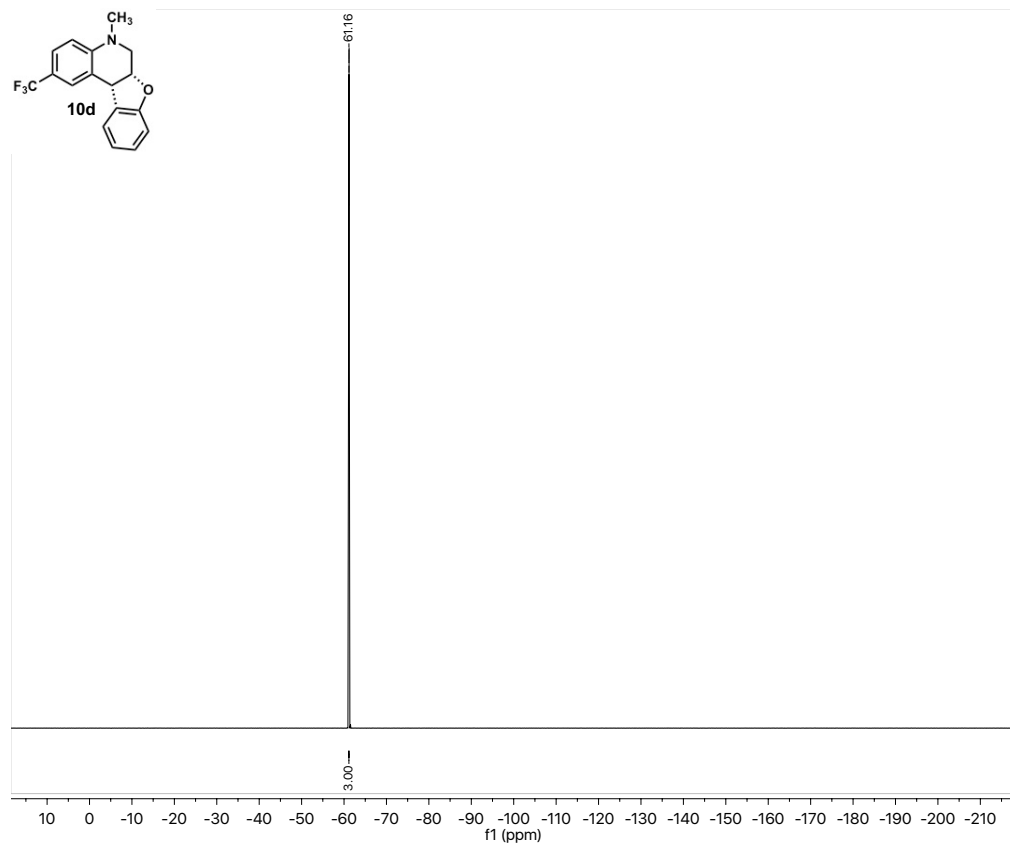


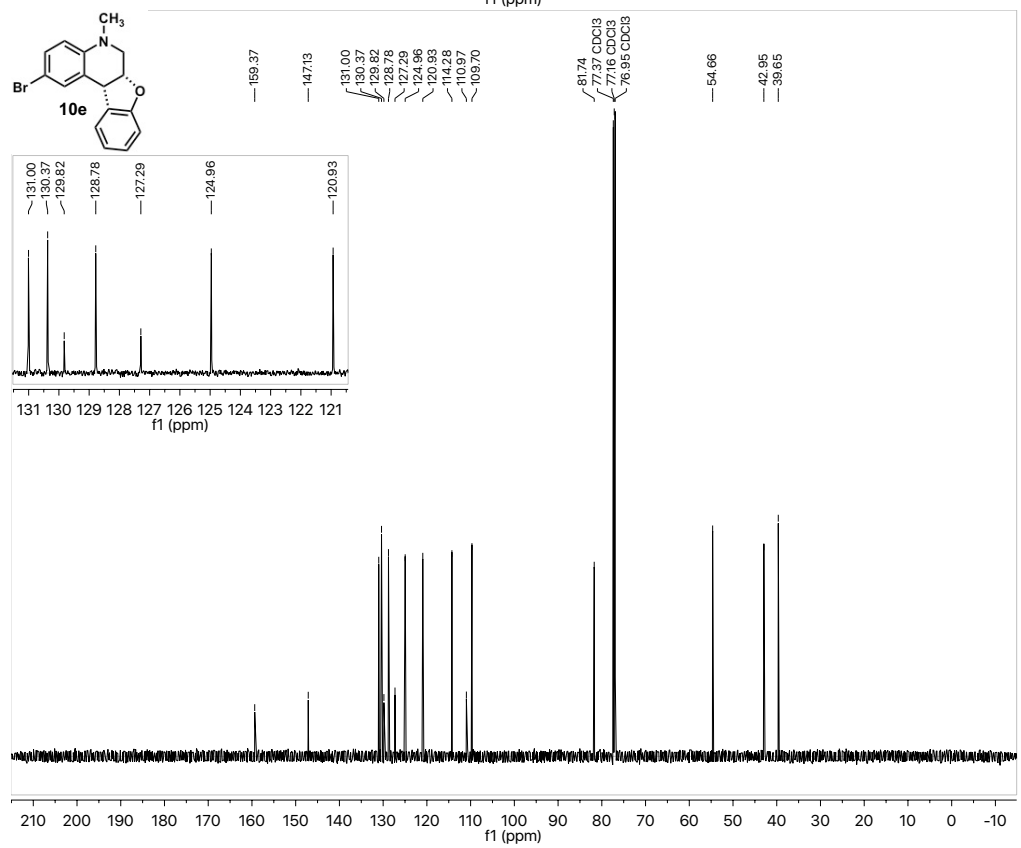
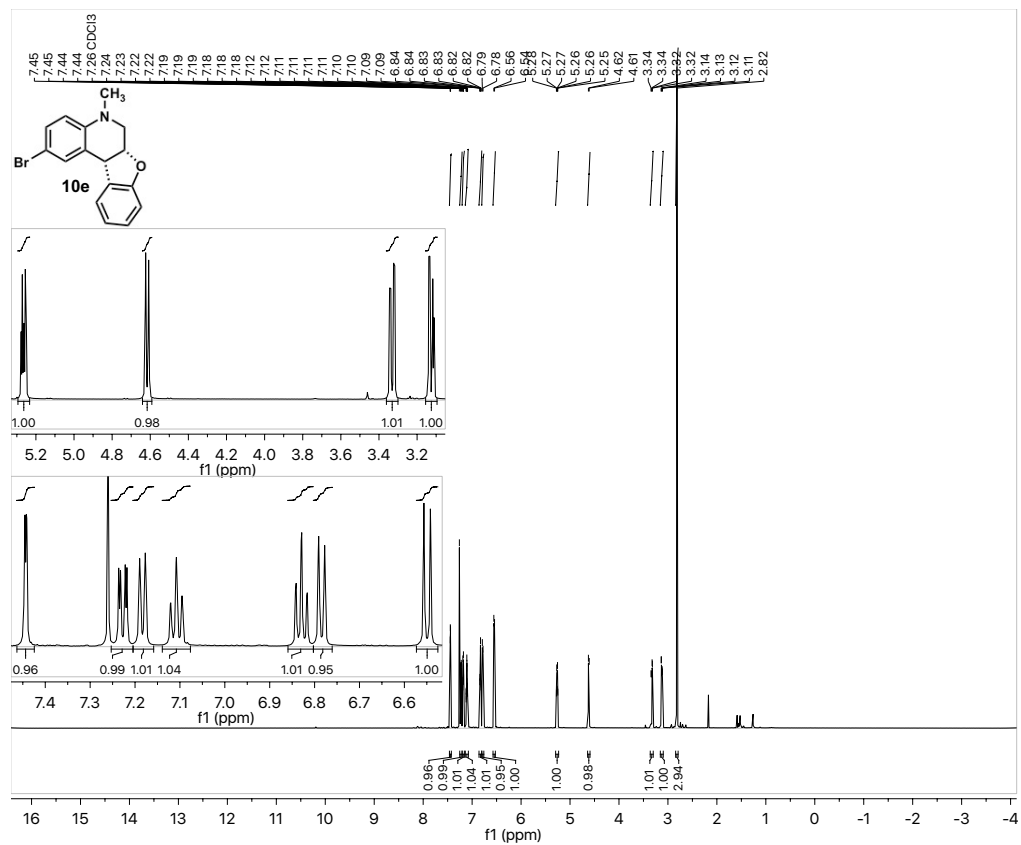


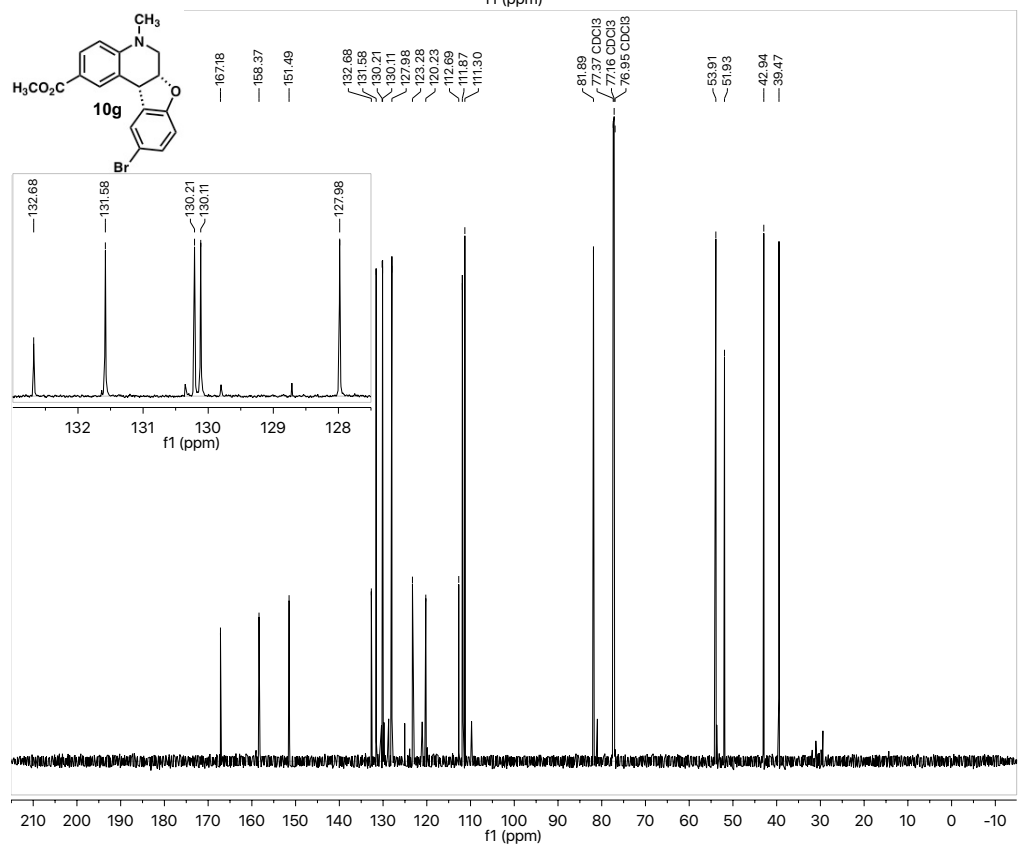
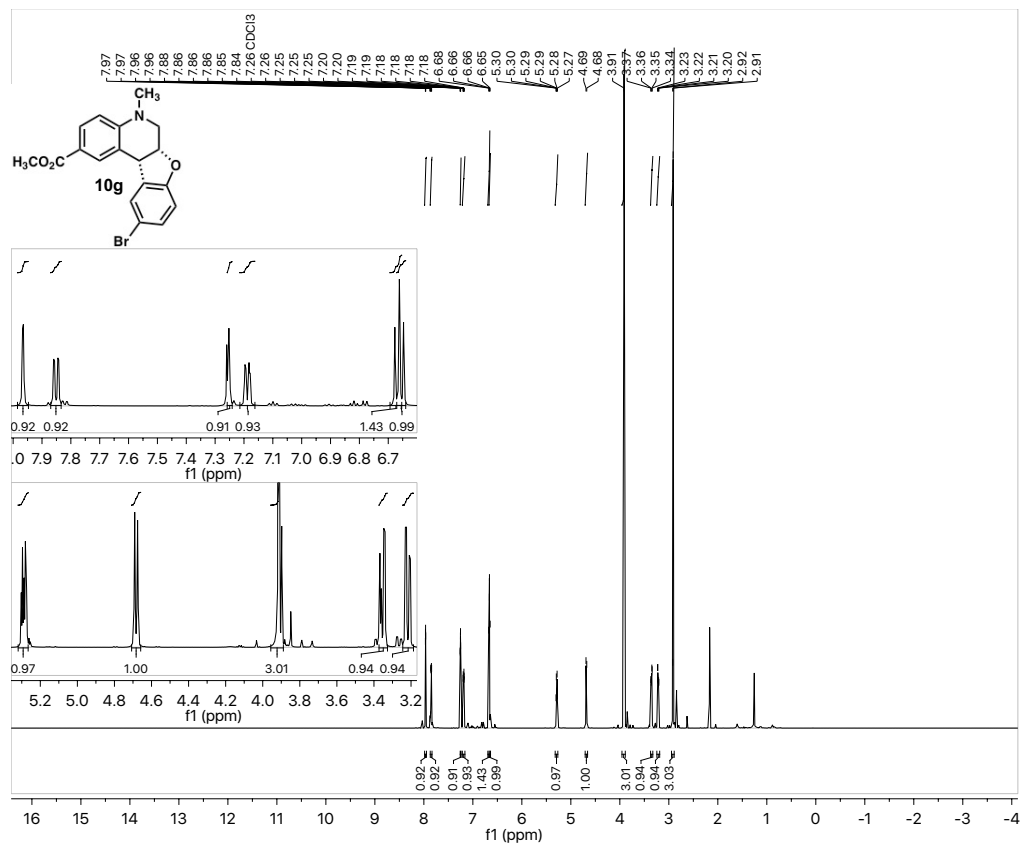


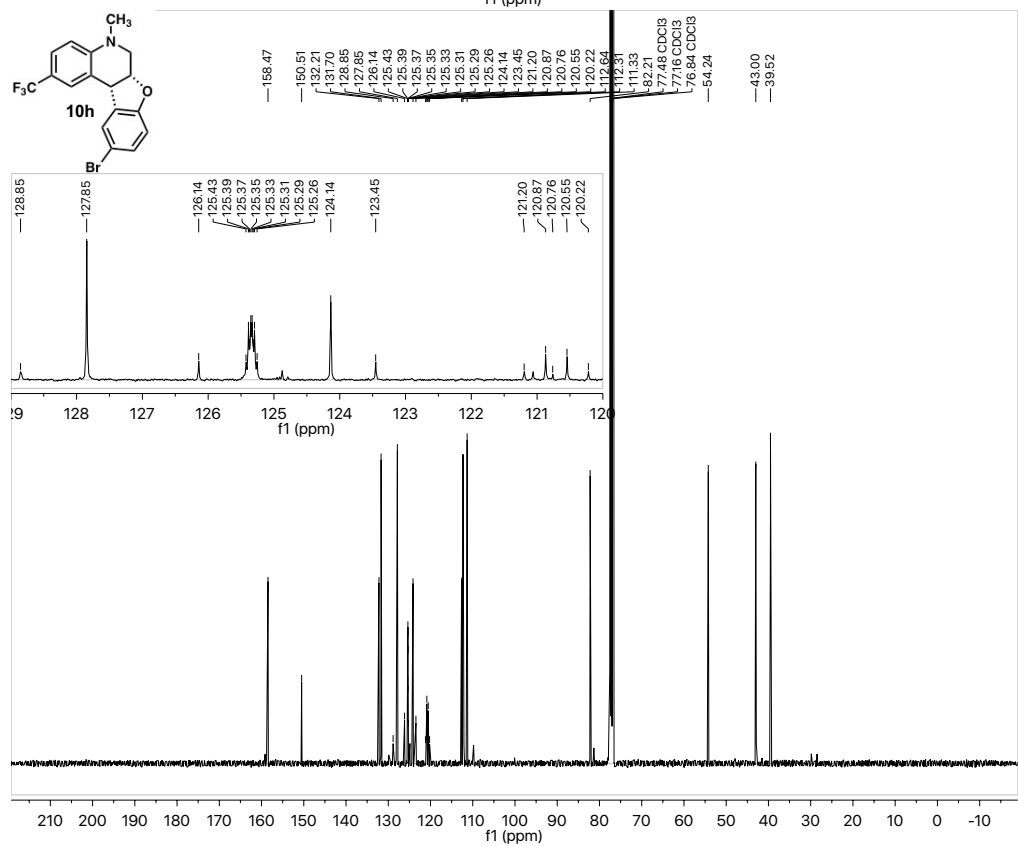
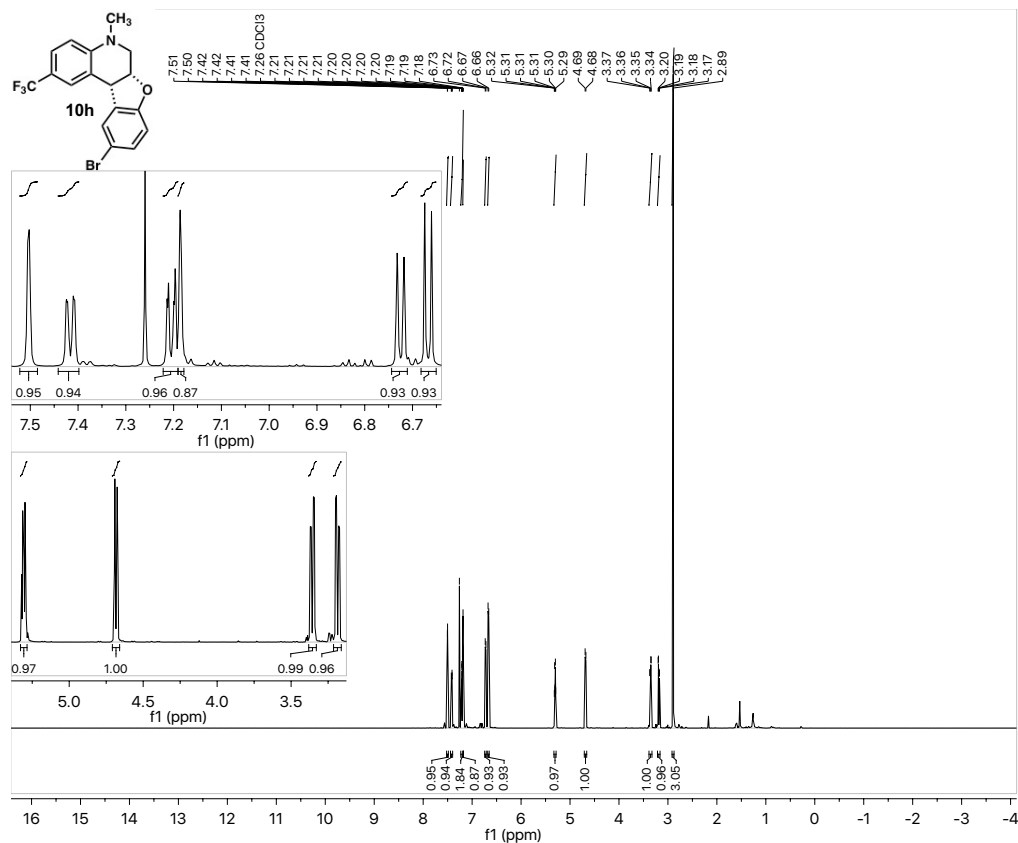


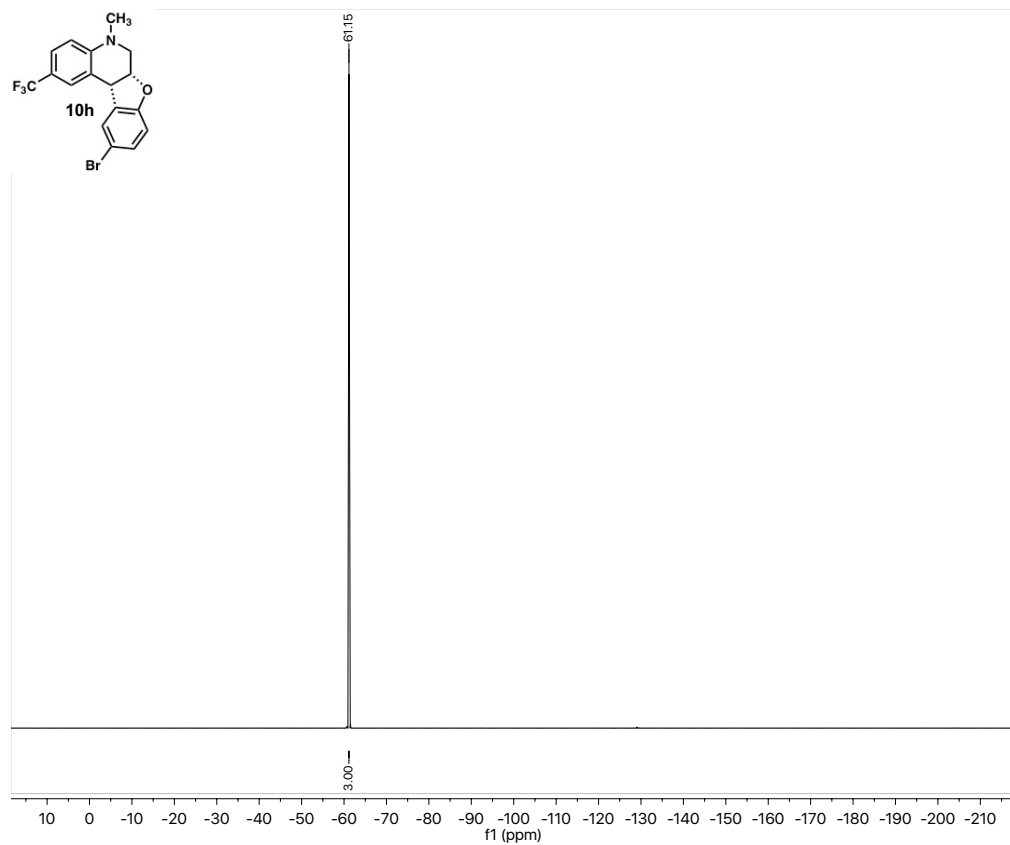


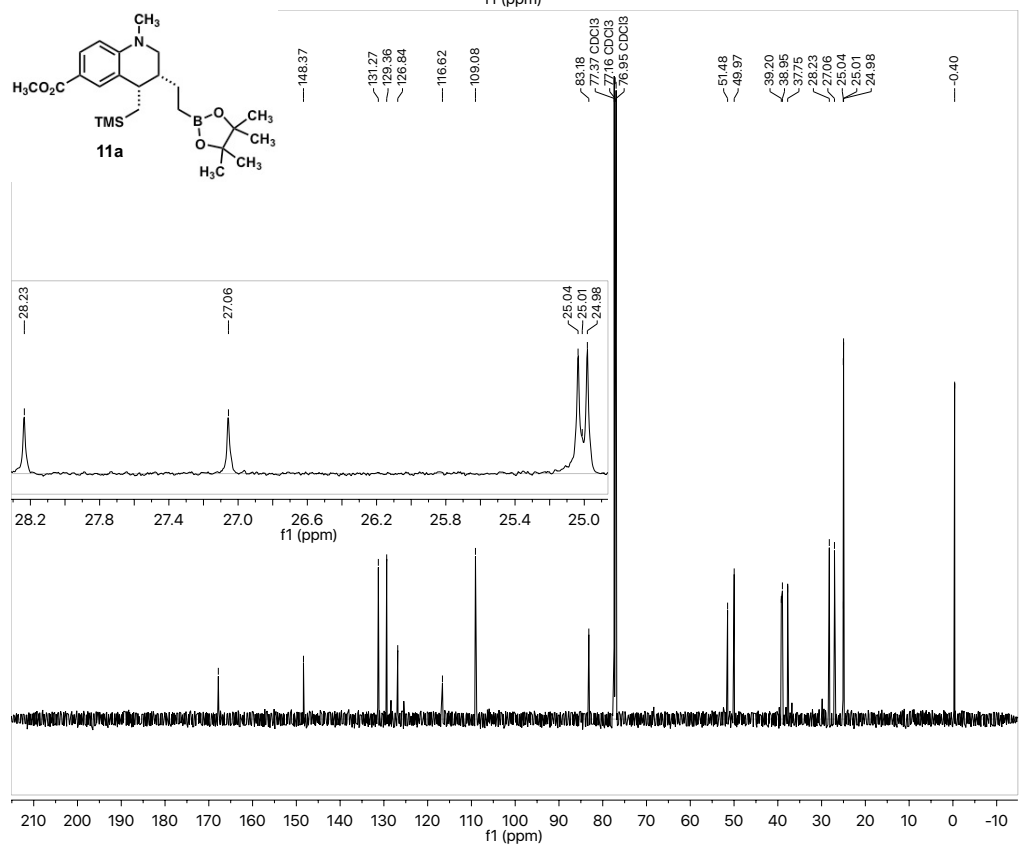
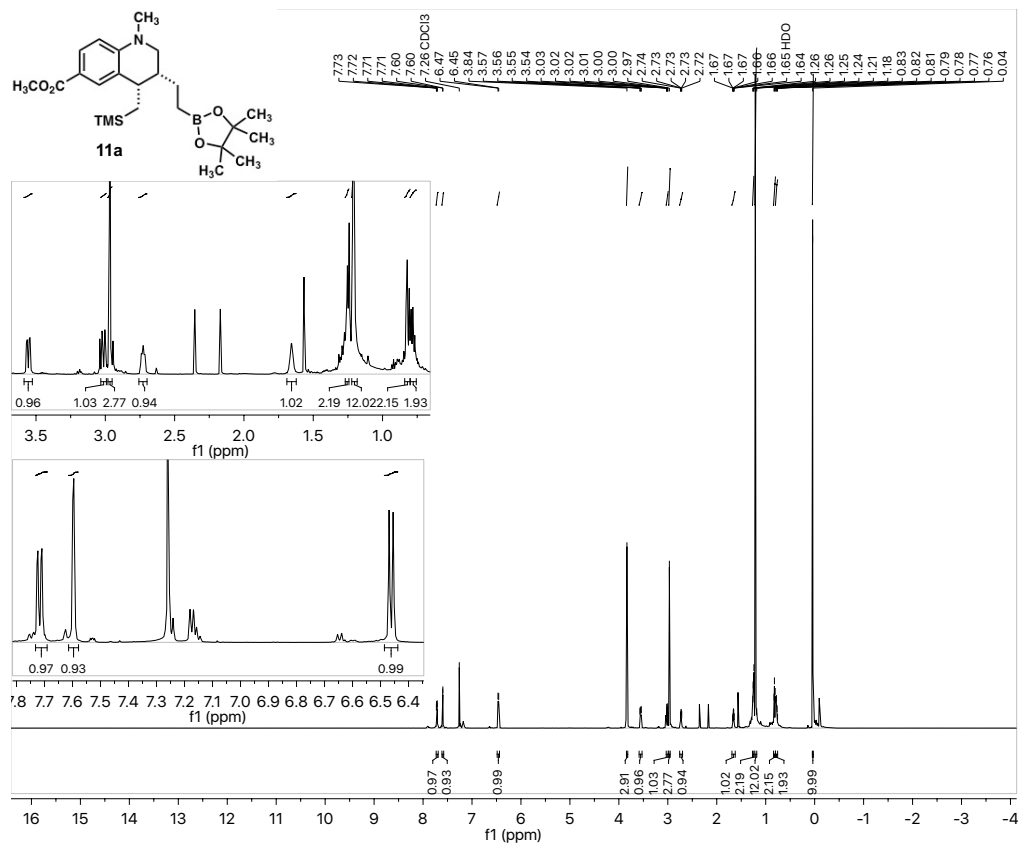


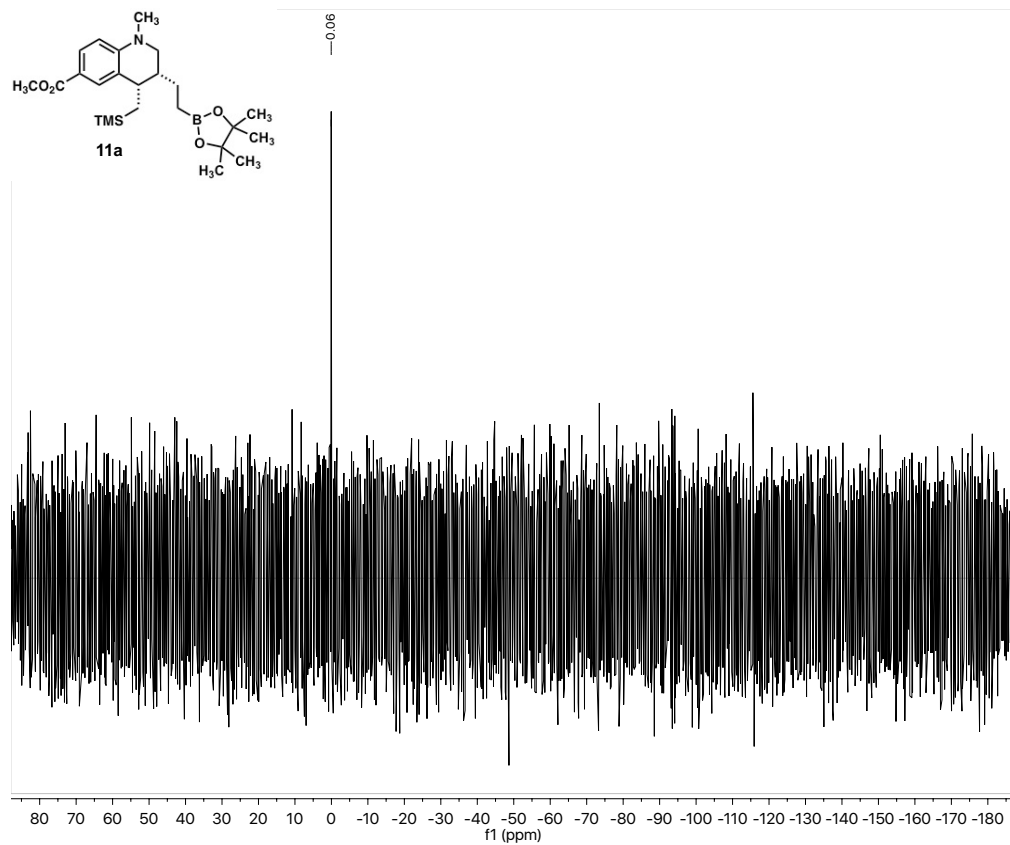


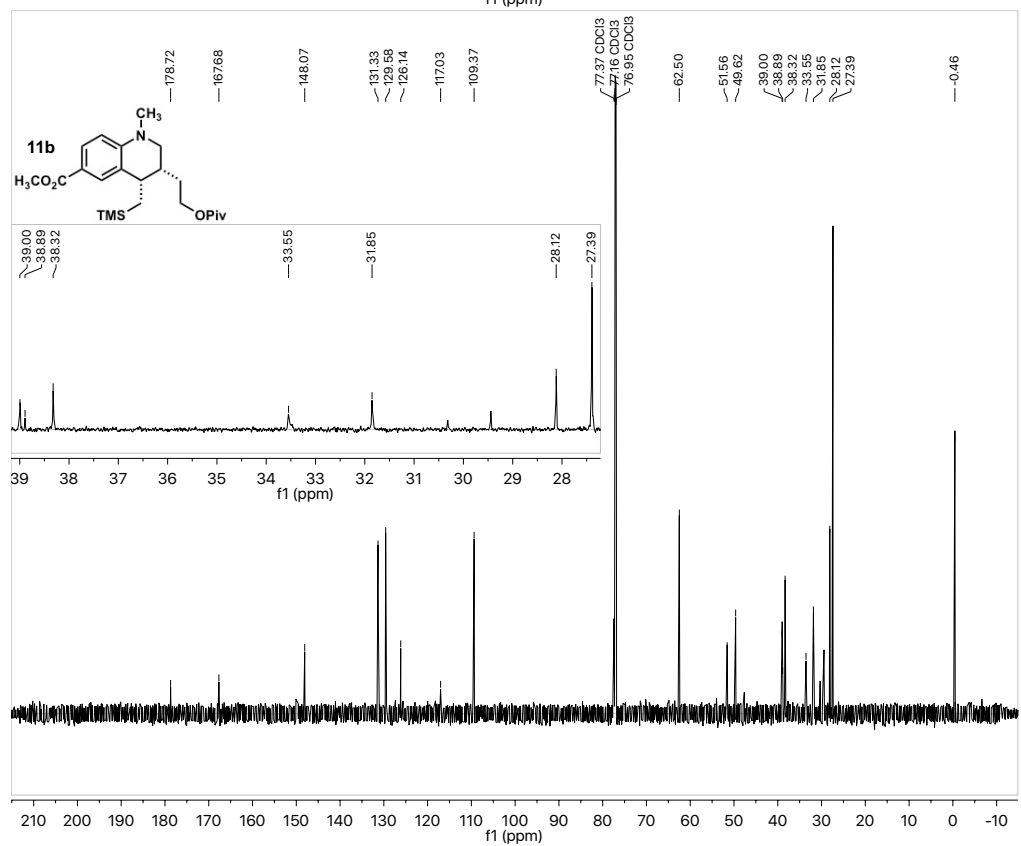
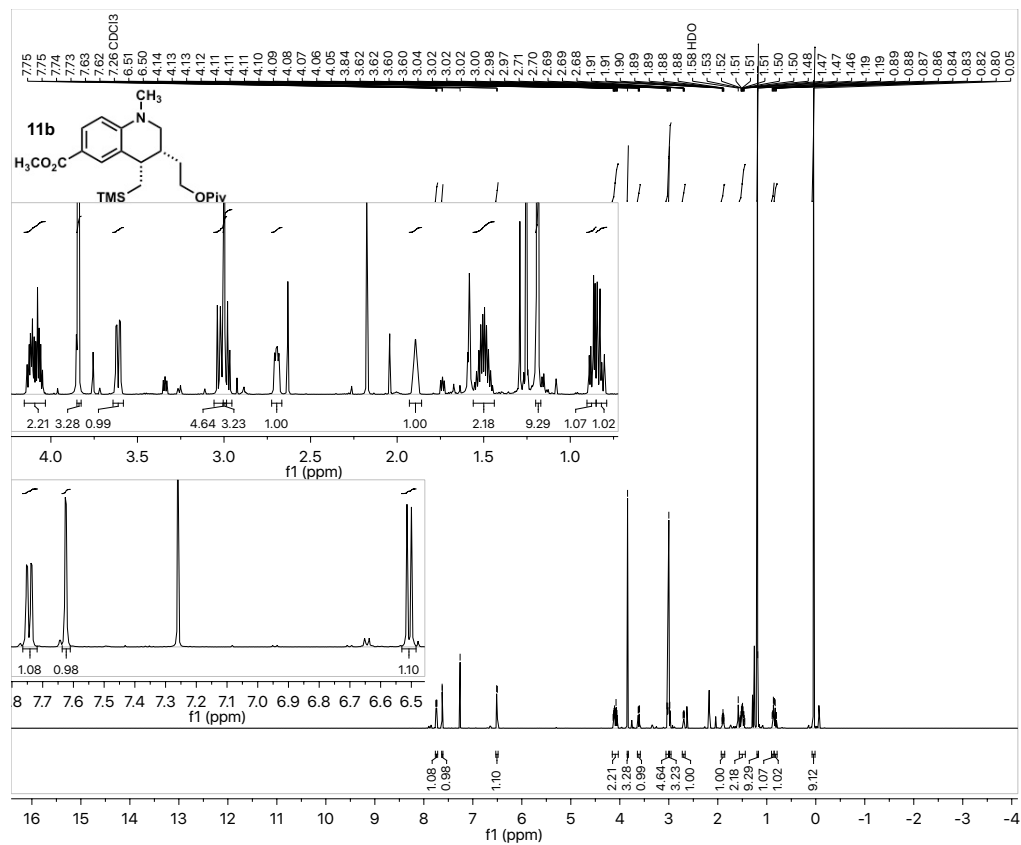


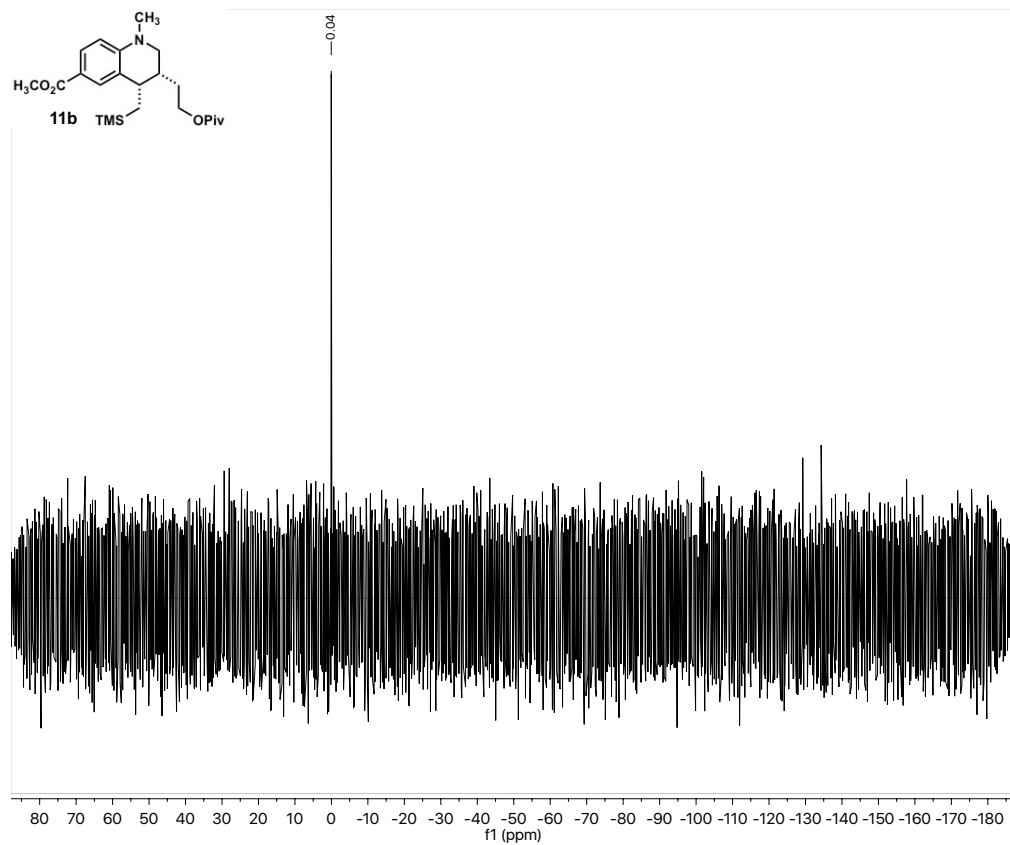


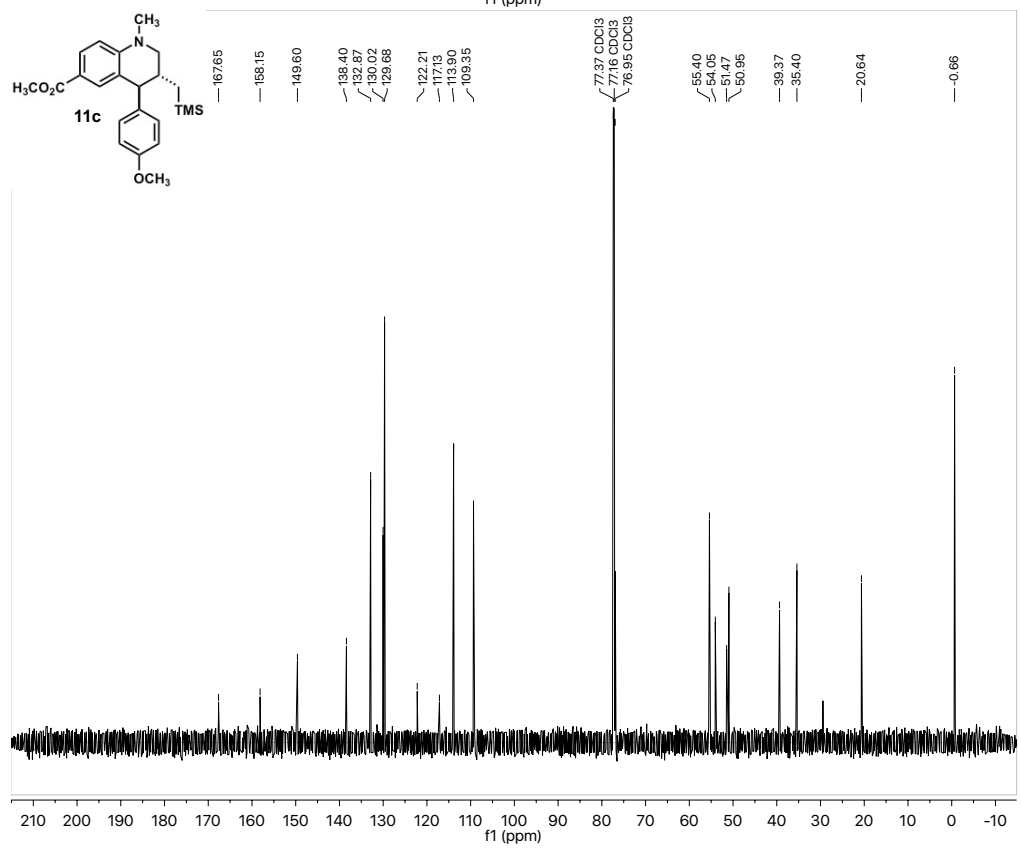
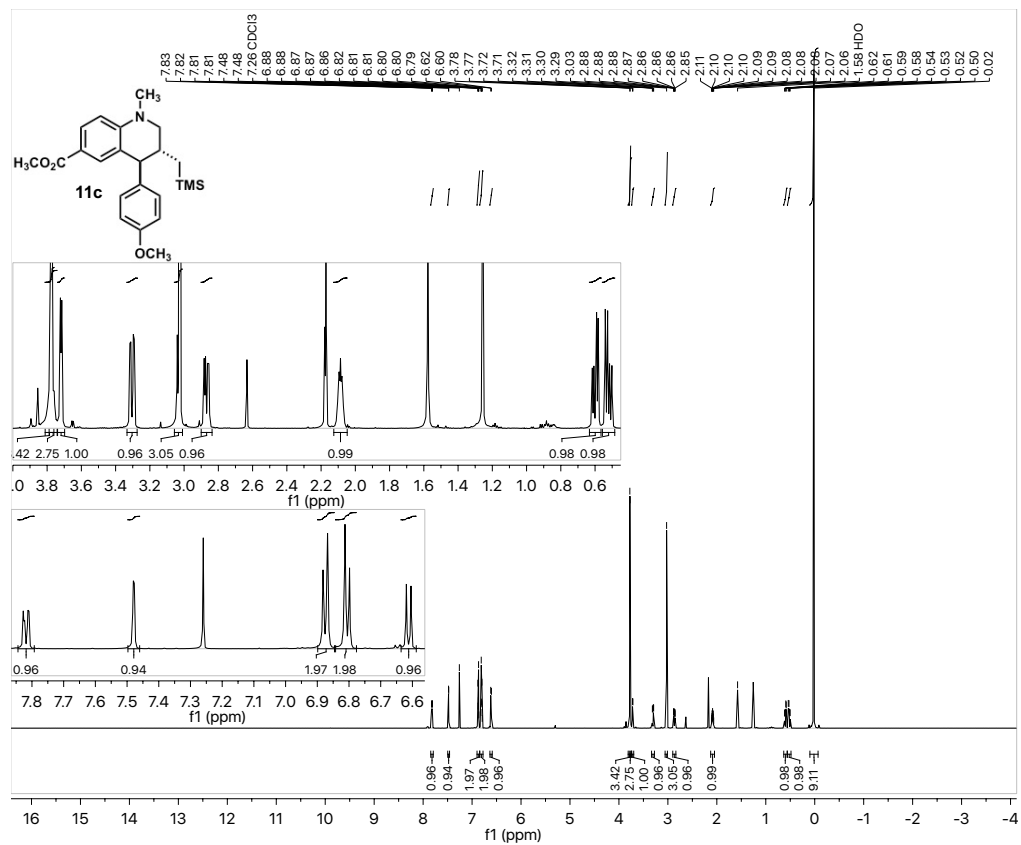


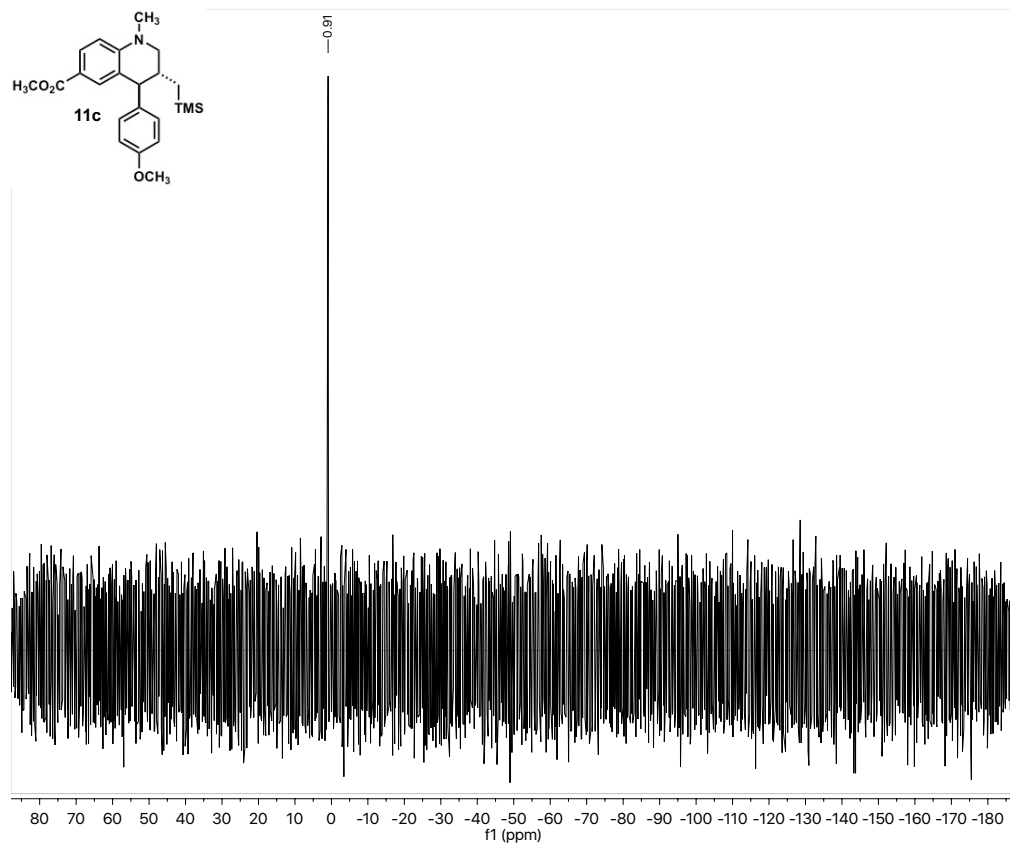


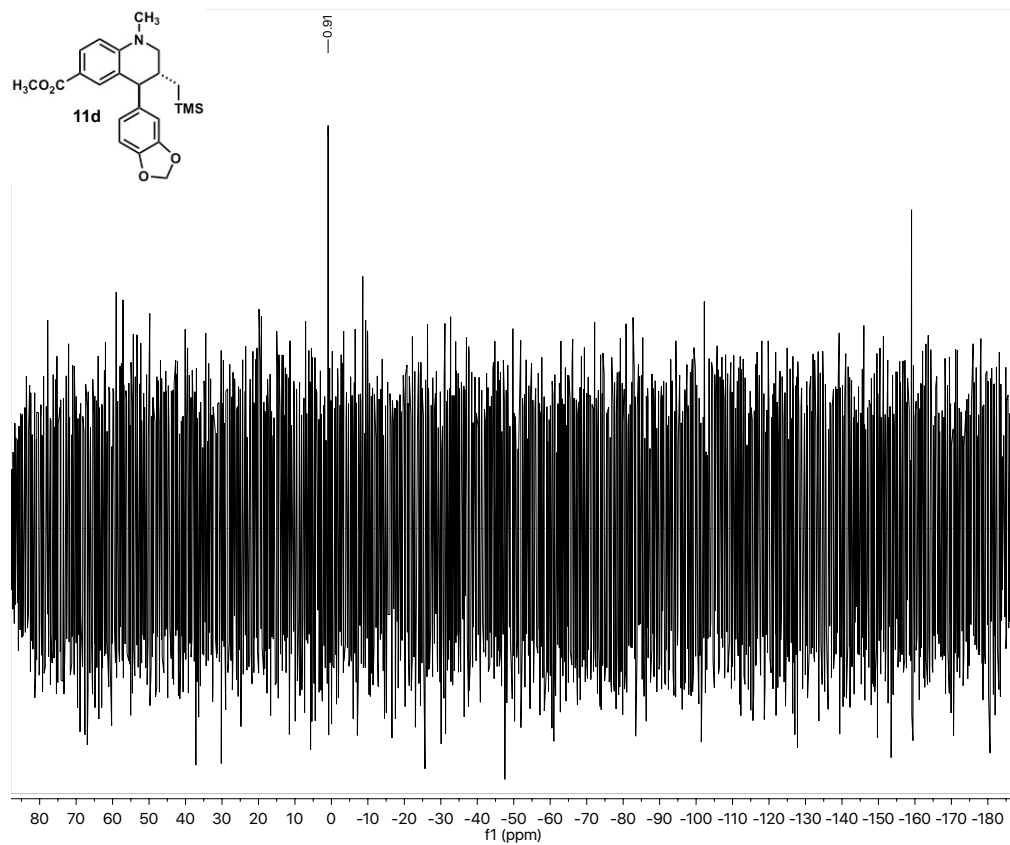


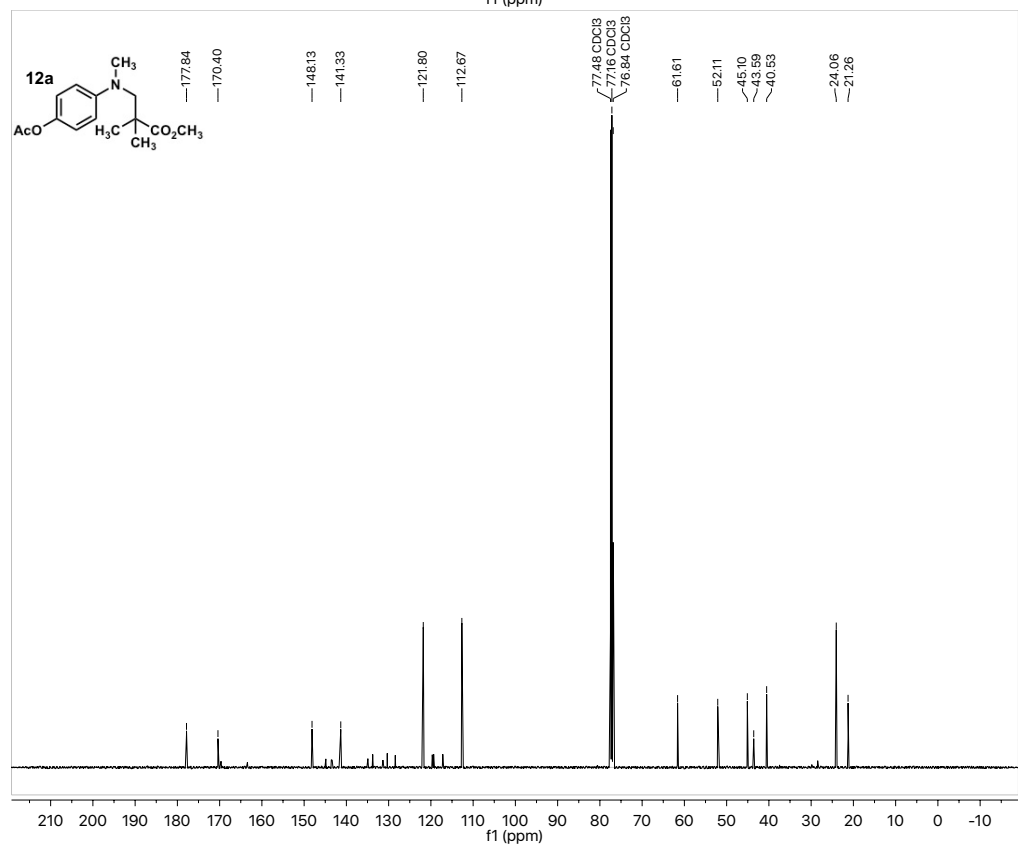
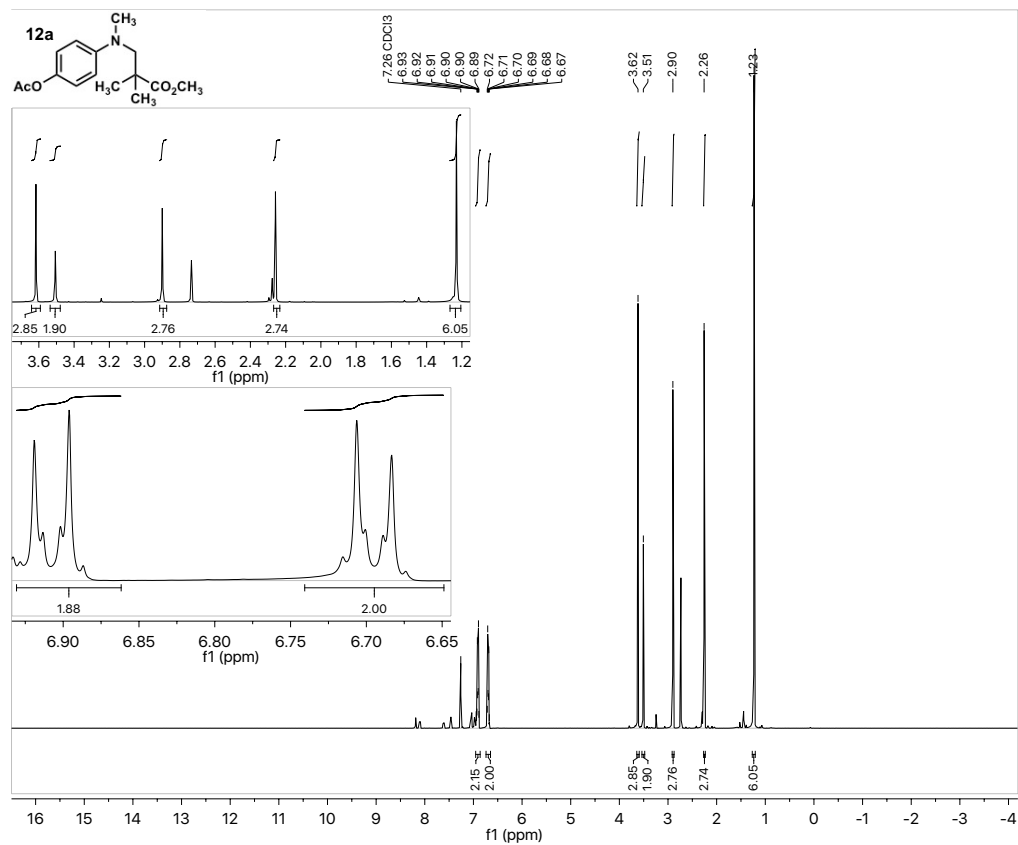


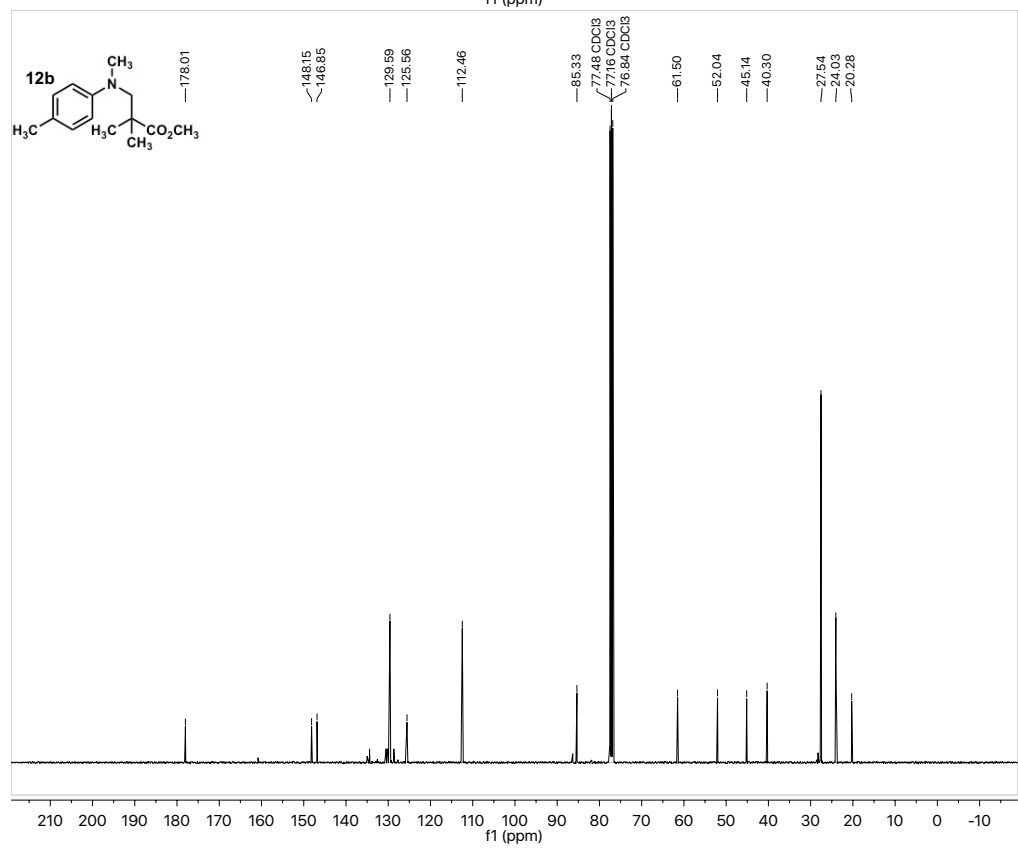
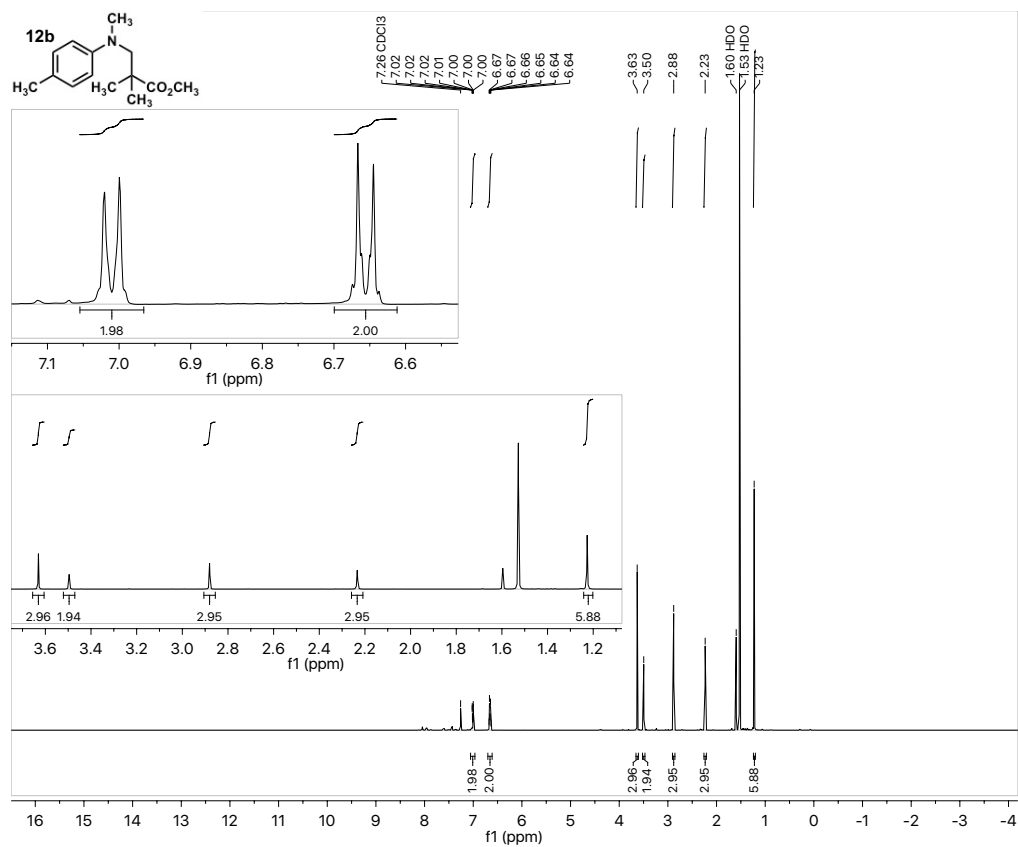




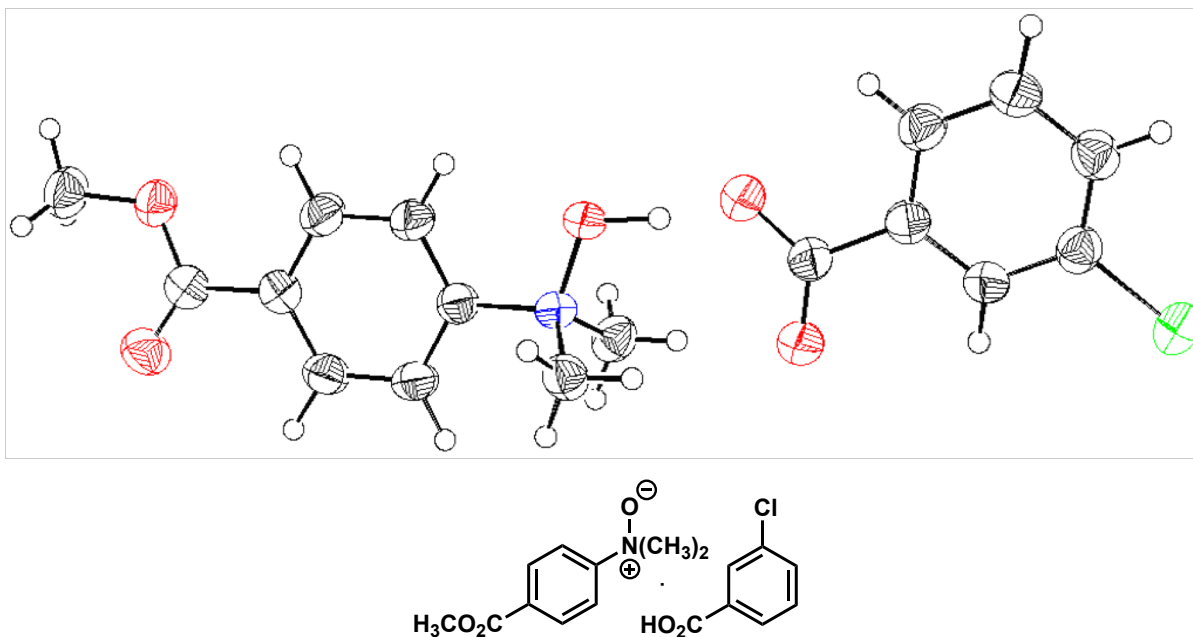








V. Crystallography Data



A specimen of $C_{17}H_{18}ClNO_5$, approximate dimensions 0.046 mm \times 0.199 mm \times 0.217 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 16.17 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 30419 reflections to a maximum θ angle of 75.42° (0.80 Å resolution), of which 3317 were independent (average redundancy 9.171, completeness = 95.6%, $R_{int} = 4.26\%$, $R_{sig} = 2.63\%$) and 2839 (85.59%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 18.4316(6)$ Å, $b = 10.4126(4)$ Å, $c = 8.8302(3)$ Å, $\beta = 98.1000(10)^\circ$, volume = 1677.79(10) Å³, are based upon the refinement of the XYZ-centroids of 9761 reflections above $20 \sigma(I)$ with $4.842^\circ < 2\theta < 150.4^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.784. The Calcd. minimum and maximum transmission coefficients (based on crystal size) are 0.6400 and 0.9030.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with $Z = 4$ for the formula unit, $C_{17}H_{18}ClNO_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 282 variables converged at $R1 = 4.49\%$, for the observed data and $wR2 = 13.78\%$ for all data. The goodness-of-fit was 1.144. The largest peak in the final difference electron density synthesis was 0.236 e⁻/Å³ and the largest hole was -0.309 e⁻/Å³ with an RMS deviation of 0.049 e⁻/Å³. On the basis of the final model, the Calcd. density was 1.393 g/cm³ and $F(000)$, 736 e⁻.

Table 1. Sample and crystal data for 1c.

| | |
|-------------------------------|--|
| Identification code | 1c |
| Chemical formula | C ₁₇ H ₁₈ CINO ₅ |
| Formula weight | 351.77 g/mol |
| Temperature | 200(2) K |
| Wavelength | 1.54178 Å |
| Crystal size | 0.046 × 0.199 × 0.217 mm |
| Crystal system | monoclinic |
| Space group | P 1 21/c 1 |
| Unit cell dimensions | a = 18.4316(6) Å α = 90° b = 10.4126(4) Å β = 98.1000(10)° c = 8.8302(3) Å γ = 90° |
| Volume | 1677.79(10) Å ³ |
| Z | 4 |
| Density (Calcd.) | 1.393 g/cm ³ |
| Absorption coefficient | 2.258 mm ⁻¹ |
| F(000) | 736 |

Table 2. Data collection and structure refinement for 1c.

| | |
|--|---|
| Theta range for data collection | 2.42 to 75.42° |
| Index ranges | -22 ≤ h ≤ 23, -12 ≤ k ≤ 13, -10 ≤ l ≤ 9 |
| Reflections collected | 30419 |
| Independent reflections | 3317 [R(int) = 0.0426] |
| Coverage of independent reflections | 95.6% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9030 and 0.6400 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F ² |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | Σ w(F _o ² - F _c ²) ² |
| Data / restraints / parameters | 3317 / 0 / 282 |
| Goodness-of-fit on F² | 1.144 |
| Final R indices | 2839 data; l > 2σ(l) R1 = 0.0449, wR2 = 0.1330 all data R1 = 0.0496, wR2 = 0.1378 |
| Weighting scheme | w = 1/[σ ² (F _o ²) + (0.0797P) ² + 0.2836P] where P = (F _o ² + 2F _c ²)/3 |
| Extinction coefficient | 0.0051(8) |
| Largest diff. peak and hole | 0.236 and -0.309 eÅ ⁻³ |
| R.M.S. deviation from mean | 0.049 eÅ ⁻³ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters

(Å²) for 1c.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|-------------|-------------|-------------|-----------------|
| Cl1 | 0.09531(3) | 0.47512(6) | 0.07794(6) | 0.0619(2) |
| O1 | 0.93276(8) | 0.59165(16) | 0.33959(16) | 0.0566(4) |
| O2 | 0.90998(7) | 0.67784(13) | 0.56046(16) | 0.0498(3) |
| O3 | 0.54469(7) | 0.63550(14) | 0.38800(14) | 0.0489(4) |
| O4 | 0.41252(7) | 0.64919(13) | 0.36324(15) | 0.0475(3) |
| O5 | 0.38227(8) | 0.53553(19) | 0.15004(18) | 0.0663(5) |
| N1 | 0.57796(8) | 0.57699(14) | 0.27138(15) | 0.0374(3) |
| C1 | 0.76268(11) | 0.66644(19) | 0.4807(2) | 0.0481(4) |
| C2 | 0.80898(10) | 0.61554(16) | 0.3852(2) | 0.0401(4) |
| C3 | 0.77955(11) | 0.5520(2) | 0.2523(2) | 0.0473(4) |
| C4 | 0.70423(11) | 0.5399(2) | 0.2140(2) | 0.0465(4) |
| C5 | 0.65898(9) | 0.59117(16) | 0.31121(19) | 0.0382(4) |
| C6 | 0.68736(11) | 0.6540(2) | 0.4441(2) | 0.0491(5) |
| C7 | 0.55702(12) | 0.43817(19) | 0.2626(2) | 0.0478(4) |
| C8 | 0.55169(11) | 0.6447(2) | 0.1241(2) | 0.0457(4) |
| C9 | 0.36626(10) | 0.59410(17) | 0.2622(2) | 0.0417(4) |
| C10 | 0.28717(10) | 0.60549(16) | 0.28585(19) | 0.0395(4) |
| C11 | 0.23420(10) | 0.54155(18) | 0.1873(2) | 0.0415(4) |
| C12 | 0.16133(10) | 0.55135(18) | 0.2069(2) | 0.0436(4) |
| C13 | 0.13998(11) | 0.62206(19) | 0.3253(2) | 0.0479(4) |
| C14 | 0.19305(11) | 0.6855(2) | 0.4240(2) | 0.0517(5) |
| C15 | 0.26622(11) | 0.67826(18) | 0.4045(2) | 0.0468(4) |
| C16 | 0.89018(10) | 0.62624(17) | 0.4232(2) | 0.0425(4) |
| C17 | 0.98781(11) | 0.6954(2) | 0.6067(3) | 0.0570(5) |

Table 4. Bond lengths (Å) for 1c.

| | | | |
|---------|------------|--------|----------|
| Cl1-C12 | 1.7369(19) | O1-C16 | 1.206(2) |
| O2-C16 | 1.329(2) | O2-C17 | 1.447(2) |
| O3-N1 | 1.4091(18) | O3-H3O | 1.12(3) |
| O4-C9 | 1.280(2) | O4-H3O | 1.31(3) |
| O5-C9 | 1.234(2) | N1-C5 | 1.492(2) |
| N1-C7 | 1.495(2) | N1-C8 | 1.498(2) |
| C1-C2 | 1.387(3) | C1-C6 | 1.386(3) |
| C1-H1 | 0.98(2) | C2-C3 | 1.389(3) |
| C2-C16 | 1.491(2) | C3-C4 | 1.388(3) |
| C3-H3 | 1.04(3) | C4-C5 | 1.386(2) |
| C4-H4 | 0.97(3) | C5-C6 | 1.381(2) |
| C6-H6 | 0.97(3) | C7-H7A | 0.96(2) |

| | | | |
|----------|----------|----------|----------|
| C7-H7B | 0.97(2) | C7-H7C | 0.97(3) |
| C8-H8A | 0.94(2) | C8-H8B | 0.97(3) |
| C8-H8C | 0.98(2) | C9-C10 | 1.506(2) |
| C10-C11 | 1.384(3) | C10-C15 | 1.391(3) |
| C11-C12 | 1.382(3) | C11-H11 | 0.92(2) |
| C12-C13 | 1.381(3) | C13-C14 | 1.383(3) |
| C13-H13 | 0.94(3) | C14-C15 | 1.385(3) |
| C14-H14 | 0.98(2) | C15-H15 | 0.95(2) |
| C17-H17A | 0.98 | C17-H17B | 0.98 |
| C17-H17C | 0.98 | | |

Table 5. Bond angles (°) for 1c.

| | | | |
|-------------|------------|-------------|------------|
| C16-O2-C17 | 116.25(15) | N1-O3-H3O | 113.5(15) |
| C9-O4-H3O | 121.4(13) | O3-N1-C5 | 108.00(12) |
| O3-N1-C7 | 108.66(14) | C5-N1-C7 | 110.50(14) |
| O3-N1-C8 | 108.08(14) | C5-N1-C8 | 110.38(13) |
| C7-N1-C8 | 111.12(14) | C2-C1-C6 | 120.30(17) |
| C2-C1-H1 | 120.3(14) | C6-C1-H1 | 119.4(14) |
| C1-C2-C3 | 119.68(17) | C1-C2-C16 | 121.23(16) |
| C3-C2-C16 | 119.09(16) | C2-C3-C4 | 120.53(17) |
| C2-C3-H3 | 118.5(14) | C4-C3-H3 | 121.0(14) |
| C5-C4-C3 | 118.84(17) | C5-C4-H4 | 123.4(15) |
| C3-C4-H4 | 117.8(15) | C6-C5-C4 | 121.36(17) |
| C6-C5-N1 | 119.60(15) | C4-C5-N1 | 119.05(15) |
| C5-C6-C1 | 119.29(17) | C5-C6-H6 | 120.6(14) |
| C1-C6-H6 | 120.1(14) | N1-C7-H7A | 107.3(15) |
| N1-C7-H7B | 108.3(14) | H7A-C7-H7B | 114.(2) |
| N1-C7-H7C | 106.1(15) | H7A-C7-H7C | 111.(2) |
| H7B-C7-H7C | 110.(2) | N1-C8-H8A | 107.9(13) |
| N1-C8-H8B | 108.0(14) | H8A-C8-H8B | 110.6(19) |
| N1-C8-H8C | 106.6(12) | H8A-C8-H8C | 114.7(19) |
| H8B-C8-H8C | 109.(2) | O5-C9-O4 | 124.75(17) |
| O5-C9-C10 | 119.74(16) | O4-C9-C10 | 115.50(15) |
| C11-C10-C15 | 119.34(17) | C11-C10-C9 | 119.05(16) |
| C15-C10-C9 | 121.61(16) | C12-C11-C10 | 119.84(17) |
| C12-C11-H11 | 119.6(13) | C10-C11-H11 | 120.3(13) |
| C13-C12-C11 | 121.33(18) | C13-C12-Cl1 | 119.47(15) |
| C11-C12-Cl1 | 119.19(15) | C12-C13-C14 | 118.71(19) |
| C12-C13-H13 | 120.5(16) | C14-C13-H13 | 120.8(16) |
| C13-C14-C15 | 120.67(18) | C13-C14-H14 | 115.9(14) |
| C15-C14-H14 | 123.5(14) | C14-C15-C10 | 120.10(18) |

| | | | |
|---------------|------------|---------------|------------|
| C14-C15-H15 | 119.9(14) | C10-C15-H15 | 119.9(14) |
| O1-C16-O2 | 124.08(18) | O1-C16-C2 | 123.98(17) |
| O2-C16-C2 | 111.94(15) | O2-C17-H17A | 109.5 |
| O2-C17-H17B | 109.5 | H17A-C17-H17B | 109.5 |
| O2-C17-H17C | 109.5 | H17A-C17-H17C | 109.5 |
| H17B-C17-H17C | 109.5 | | |

Table 6. Torsion angles (°) for 1c.

| | | | |
|-----------------|-------------|-----------------|-------------|
| C6-C1-C2-C3 | 0.1(3) | C6-C1-C2-C16 | -179.19(18) |
| C1-C2-C3-C4 | 0.4(3) | C16-C2-C3-C4 | 179.70(17) |
| C2-C3-C4-C5 | -0.6(3) | C3-C4-C5-C6 | 0.2(3) |
| C3-C4-C5-N1 | -179.29(16) | O3-N1-C5-C6 | -0.1(2) |
| C7-N1-C5-C6 | -118.87(19) | C8-N1-C5-C6 | 117.82(19) |
| O3-N1-C5-C4 | 179.40(16) | C7-N1-C5-C4 | 60.7(2) |
| C8-N1-C5-C4 | -62.6(2) | C4-C5-C6-C1 | 0.2(3) |
| N1-C5-C6-C1 | 179.77(17) | C2-C1-C6-C5 | -0.4(3) |
| O5-C9-C10-C11 | 4.8(3) | O4-C9-C10-C11 | -175.81(16) |
| O5-C9-C10-C15 | -175.37(19) | O4-C9-C10-C15 | 4.0(2) |
| C15-C10-C11-C12 | 0.5(3) | C9-C10-C11-C12 | -179.73(16) |
| C10-C11-C12-C13 | -1.2(3) | C10-C11-C12-C11 | 177.72(13) |
| C11-C12-C13-C14 | 1.0(3) | C11-C12-C13-C14 | -177.96(15) |
| C12-C13-C14-C15 | 0.0(3) | C13-C14-C15-C10 | -0.8(3) |
| C11-C10-C15-C14 | 0.5(3) | C9-C10-C15-C14 | -179.28(18) |
| C17-O2-C16-O1 | 1.8(3) | C17-O2-C16-C2 | -178.52(16) |
| C1-C2-C16-O1 | -174.74(19) | C3-C2-C16-O1 | 6.0(3) |
| C1-C2-C16-O2 | 5.6(2) | C3-C2-C16-O2 | -173.69(16) |

Table 7. Anisotropic atomic displacement parameters (Å²) for 1c.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Cl1 | 0.0456(3) | 0.0801(4) | 0.0579(4) | -0.0157(2) | -0.0003(2) | -0.0097(2) |
| O1 | 0.0444(7) | 0.0735(10) | 0.0529(8) | -0.0023(7) | 0.0109(6) | 0.0086(7) |
| O2 | 0.0376(7) | 0.0573(8) | 0.0540(8) | -0.0088(6) | 0.0046(5) | -0.0036(6) |
| O3 | 0.0406(7) | 0.0680(9) | 0.0397(7) | -0.0181(6) | 0.0114(5) | -0.0050(6) |
| O4 | 0.0409(7) | 0.0551(8) | 0.0456(7) | -0.0065(5) | 0.0031(5) | -0.0023(5) |
| O5 | 0.0441(8) | 0.1024(13) | 0.0535(9) | -0.0292(8) | 0.0110(6) | -0.0064(8) |
| N1 | 0.0400(7) | 0.0417(7) | 0.0306(7) | -0.0033(5) | 0.0056(5) | -0.0023(6) |
| C1 | 0.0430(10) | 0.0507(10) | 0.0498(11) | -0.0145(8) | 0.0038(7) | -0.0008(8) |
| C2 | 0.0401(9) | 0.0392(8) | 0.0412(9) | 0.0033(6) | 0.0066(7) | 0.0020(7) |
| C3 | 0.0446(10) | 0.0586(11) | 0.0396(10) | -0.0036(8) | 0.0094(7) | 0.0049(8) |

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|------------|------------|------------|-------------|-----------|------------|
| C4 | 0.0476(10) | 0.0569(11) | 0.0344(9) | -0.0068(7) | 0.0040(7) | 0.0012(8) |
| C5 | 0.0396(9) | 0.0385(8) | 0.0365(9) | -0.0004(6) | 0.0050(6) | -0.0008(7) |
| C6 | 0.0435(10) | 0.0554(11) | 0.0488(11) | -0.0180(8) | 0.0077(8) | -0.0019(8) |
| C7 | 0.0529(11) | 0.0430(10) | 0.0461(11) | 0.0022(8) | 0.0018(8) | -0.0079(8) |
| C8 | 0.0431(10) | 0.0545(11) | 0.0395(10) | 0.0086(8) | 0.0061(7) | 0.0012(8) |
| C9 | 0.0405(9) | 0.0468(9) | 0.0378(9) | 0.0005(7) | 0.0047(6) | -0.0024(7) |
| C10 | 0.0409(9) | 0.0409(9) | 0.0363(9) | 0.0039(6) | 0.0042(6) | 0.0007(7) |
| C11 | 0.0433(9) | 0.0466(9) | 0.0350(9) | -0.0010(7) | 0.0071(7) | 0.0001(7) |
| C12 | 0.0421(9) | 0.0464(9) | 0.0413(9) | 0.0035(7) | 0.0022(7) | -0.0021(7) |
| C13 | 0.0437(10) | 0.0491(10) | 0.0511(11) | 0.0005(8) | 0.0076(8) | 0.0054(8) |
| C14 | 0.0512(11) | 0.0524(11) | 0.0525(12) | -0.0109(8) | 0.0115(8) | 0.0052(8) |
| C15 | 0.0469(10) | 0.0445(9) | 0.0485(11) | -0.0068(7) | 0.0045(8) | -0.0013(8) |
| C16 | 0.0446(9) | 0.0398(9) | 0.0431(9) | 0.0035(7) | 0.0056(7) | 0.0021(7) |
| C17 | 0.0396(10) | 0.0643(13) | 0.0652(13) | -0.0089(10) | 0.0013(8) | -0.0018(9) |

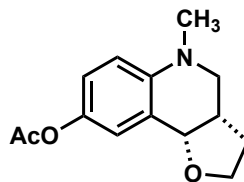
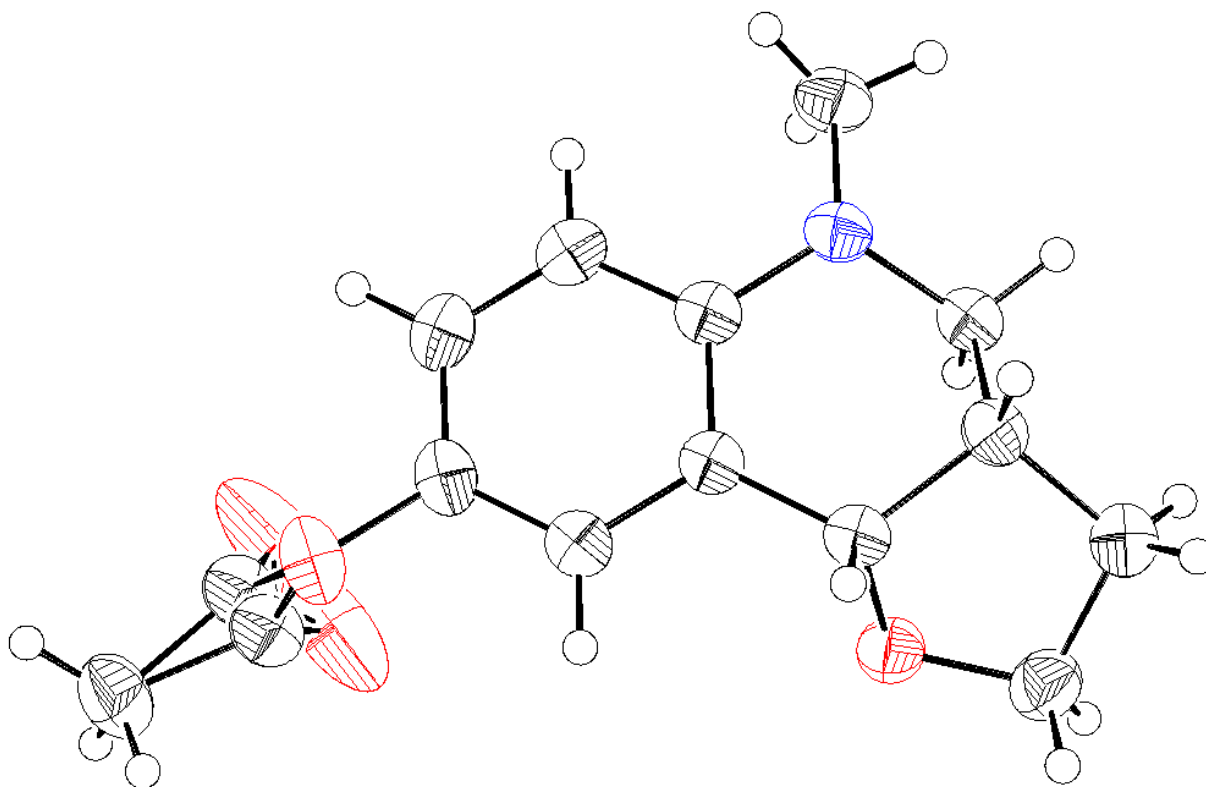
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 1c.

| | x/a | y/b | z/c | U(equiv) |
|------|------------|----------|----------|----------|
| H17A | 1.0125 | 0.6118 | 0.6095 | 0.078(8) |
| H17B | 0.9962 | 0.7345 | 0.7085 | 0.080(8) |
| H17C | 1.0075 | 0.7516 | 0.5333 | 0.073(8) |
| H1 | 0.7829(13) | 0.711(2) | 0.575(3) | 0.057(6) |
| H3 | 0.8151(14) | 0.515(2) | 0.182(3) | 0.059(7) |
| H4 | 0.6860(14) | 0.493(2) | 0.121(3) | 0.057(6) |
| H3O | 0.4833(18) | 0.634(3) | 0.366(3) | 0.087(9) |
| H6 | 0.6551(13) | 0.687(2) | 0.513(3) | 0.057(6) |
| H7A | 0.5725(13) | 0.402(2) | 0.361(3) | 0.056(6) |
| H7B | 0.5790(13) | 0.399(2) | 0.180(3) | 0.052(6) |
| H7C | 0.5040(16) | 0.436(2) | 0.239(3) | 0.065(7) |
| H8A | 0.5740(12) | 0.606(2) | 0.047(2) | 0.044(5) |
| H8B | 0.4990(15) | 0.635(2) | 0.104(3) | 0.058(6) |
| H8C | 0.5636(12) | 0.736(2) | 0.141(2) | 0.051(6) |
| H11 | 0.2475(12) | 0.487(2) | 0.114(2) | 0.043(5) |
| H13 | 0.0905(15) | 0.626(3) | 0.339(3) | 0.066(7) |
| H14 | 0.1752(13) | 0.737(3) | 0.504(3) | 0.061(6) |
| H15 | 0.3023(13) | 0.721(2) | 0.474(3) | 0.054(6) |

Table 9. Hydrogen bond distances (\AA) and angles ($^\circ$) for 1c.

| | Donor-H | Acceptor-H | Donor-Acceptor | Angle |
|-------------|---------|------------|----------------|---------|
| O3-H3O...O4 | 1.12(3) | 1.31(3) | 2.4194(17) | 168.(3) |

| | Donor-H | Acceptor-H | Donor-Acceptor | Angle |
|-------------|----------------|-------------------|-----------------------|--------------|
| O4-H3O...N1 | 1.31(3) | 2.12(3) | 3.349(2) | 154.(2) |



8a

A specimen of $C_{14}H_{17}NO_3$, approximate dimensions 0.373 mm x 0.380 mm x 0.587 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 2.31 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 18942 reflections to a maximum θ angle of 27.69° (0.76 Å resolution), of which 2957 were independent (average redundancy 6.406, completeness = 100.0%, $R_{int} = 2.21\%$, $R_{sig} = 1.36\%$) and 2307 (78.02%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 12.1537(14)$ Å, $b = 12.1840(14)$ Å, $c = 8.5926(10)$ Å, $\beta = 97.5260(10)^\circ$, volume = $1261.4(3)$ Å³, are based upon the refinement of the XYZ-centroids of 6942 reflections above $20\sigma(I)$ with $4.754^\circ < 2\theta < 55.23^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.940. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9480 and 0.9670.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with $Z = 4$ for the formula unit, $C_{14}H_{17}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 178 variables converged at $R1 = 4.24\%$, for the observed data and $wR2 = 14.07\%$ for all data. The goodness-of-fit was 1.020. The largest peak

in the final difference electron density synthesis was $0.200 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.209 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.040 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.302 g/cm^3 and $F(000)$, 528 e^- .

Table 1. Sample and crystal data for 8a.

| | |
|-------------------------------|---|
| Identification code | 8a |
| Chemical formula | $\text{C}_{14}\text{H}_{17}\text{NO}_3$ |
| Formula weight | 247.28 g/mol |
| Temperature | 200(2) K |
| Wavelength | 0.71073 \AA |
| Crystal size | 0.373 x 0.380 x 0.587 mm |
| Crystal system | monoclinic |
| Space group | P 1 21/c 1 |
| Unit cell dimensions | $a = 12.1537(14) \text{\AA}$ $\alpha = 90^\circ$ $b = 12.1840(14) \text{\AA}$ $\beta = 97.5260(10)^\circ$ $c = 8.5926(10) \text{\AA}$ $\gamma = 90^\circ$ |
| Volume | 1261.4(3) \AA^3 |
| Z | 4 |
| Density (calculated) | 1.302 g/cm^3 |
| Absorption coefficient | 0.092 mm^{-1} |
| F(000) | 528 |

Table 2. Data collection and structure refinement for 8a.

| | |
|--|---|
| Theta range for data collection | 1.69 to 27.69° |
| Index ranges | $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-11 \leq l \leq 11$ |
| Reflections collected | 18942 |
| Independent reflections | 2957 [R(int) = 0.0221] |
| Coverage of independent reflections | 100.0% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9670 and 0.9480 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | $\sum w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 2957 / 96 / 178 |
| Goodness-of-fit on F^2 | 1.020 |
| Final R indices | 2307 data; $l > 2\sigma(l)$ $R1 = 0.0424$, $wR2 = 0.1221$ all data $R1 = 0.0567$, $wR2 = 0.1407$ |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.3172P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole | 0.200 and $-0.209 \text{ e}\text{\AA}^{-3}$ |

R.M.S. deviation from mean

0.040 eÅ⁻³**Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 8a.**U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(eq) |
|------|-------------|-------------|-------------|--------------|
| O1 | 0.14913(8) | 0.14119(8) | 0.59594(12) | 0.0405(3) |
| O2 | 0.17391(9) | 0.56669(8) | 0.71666(12) | 0.0463(3) |
| N1 | 0.45756(9) | 0.21379(9) | 0.64292(13) | 0.0356(3) |
| C1 | 0.13765(13) | 0.02436(13) | 0.60678(19) | 0.0457(4) |
| C2 | 0.25282(13) | 0.97919(12) | 0.6616(2) | 0.0485(4) |
| C3 | 0.32282(11) | 0.08041(11) | 0.71409(15) | 0.0347(3) |
| C4 | 0.40202(11) | 0.11036(11) | 0.59809(15) | 0.0349(3) |
| C5 | 0.23667(10) | 0.17076(11) | 0.71830(14) | 0.0326(3) |
| C6 | 0.27736(10) | 0.28418(11) | 0.69001(14) | 0.0312(3) |
| C7 | 0.20754(11) | 0.37320(11) | 0.70526(15) | 0.0352(3) |
| C8 | 0.24442(12) | 0.47907(11) | 0.68790(15) | 0.0373(3) |
| C9 | 0.35123(13) | 0.49876(12) | 0.65821(16) | 0.0405(3) |
| C10 | 0.42155(12) | 0.41139(11) | 0.64184(16) | 0.0381(3) |
| C11 | 0.38660(11) | 0.30235(11) | 0.65629(14) | 0.0323(3) |
| C12 | 0.55828(12) | 0.23294(14) | 0.57202(19) | 0.0460(4) |
| C14 | 0.05154(16) | 0.71224(14) | 0.6476(2) | 0.0561(4) |
| O3A | 0.1701(10) | 0.6310(9) | 0.4781(9) | 0.109(3) |
| C13A | 0.1372(7) | 0.6362(7) | 0.5989(10) | 0.0445(11) |
| O3B | 0.1061(7) | 0.5780(6) | 0.4661(5) | 0.101(2) |
| C13B | 0.1093(6) | 0.6121(6) | 0.5952(7) | 0.0445(11) |

Table 4. Bond lengths (Å) for 8a.

| | | | |
|---------|------------|---------|------------|
| O1-C1 | 1.4345(18) | O1-C5 | 1.4401(15) |
| O2-C13B | 1.340(6) | O2-C13A | 1.350(8) |
| O2-C8 | 1.4108(16) | N1-C11 | 1.3955(17) |
| N1-C12 | 1.4558(18) | N1-C4 | 1.4574(17) |
| C1-C2 | 1.520(2) | C1-H1A | 0.99 |
| C1-H1B | 0.99 | C2-C3 | 1.532(2) |
| C2-H2A | 0.99 | C2-H2B | 0.99 |
| C3-C4 | 1.5180(19) | C3-C5 | 1.5229(18) |
| C3-H3 | 1.0 | C4-H4A | 0.99 |
| C4-H4B | 0.99 | C5-C6 | 1.4984(18) |
| C5-H5 | 1.0 | C6-C7 | 1.3938(18) |
| C6-C11 | 1.4130(18) | C7-C8 | 1.3802(19) |
| C7-H7 | 0.95 | C8-C9 | 1.376(2) |

| | | | |
|----------|------------|----------|----------|
| C9-C10 | 1.384(2) | C9-H9 | 0.95 |
| C10-C11 | 1.4051(19) | C10-H10 | 0.95 |
| C12-H12A | 0.98 | C12-H12B | 0.98 |
| C12-H12C | 0.98 | C14-C13A | 1.493(8) |
| C14-C13B | 1.506(6) | C14-H14A | 0.98 |
| C14-H14B | 0.98 | C14-H14C | 0.98 |
| O3A-C13A | 1.162(8) | O3B-C13B | 1.181(6) |

Table 5. Bond angles (°) for 8a.

| | | | |
|---------------|------------|---------------|------------|
| C1-O1-C5 | 105.65(10) | C13B-O2-C8 | 118.9(3) |
| C13A-O2-C8 | 119.5(4) | C11-N1-C12 | 118.23(12) |
| C11-N1-C4 | 114.87(10) | C12-N1-C4 | 114.44(11) |
| O1-C1-C2 | 106.61(12) | O1-C1-H1A | 110.4 |
| C2-C1-H1A | 110.4 | O1-C1-H1B | 110.4 |
| C2-C1-H1B | 110.4 | H1A-C1-H1B | 108.6 |
| C1-C2-C3 | 104.66(12) | C1-C2-H2A | 110.8 |
| C3-C2-H2A | 110.8 | C1-C2-H2B | 110.8 |
| C3-C2-H2B | 110.8 | H2A-C2-H2B | 108.9 |
| C4-C3-C5 | 109.81(11) | C4-C3-C2 | 112.06(12) |
| C5-C3-C2 | 103.40(11) | C4-C3-H3 | 110.5 |
| C5-C3-H3 | 110.5 | C2-C3-H3 | 110.5 |
| N1-C4-C3 | 110.24(11) | N1-C4-H4A | 109.6 |
| C3-C4-H4A | 109.6 | N1-C4-H4B | 109.6 |
| C3-C4-H4B | 109.6 | H4A-C4-H4B | 108.1 |
| O1-C5-C6 | 109.89(10) | O1-C5-C3 | 104.26(10) |
| C6-C5-C3 | 114.84(11) | O1-C5-H5 | 109.2 |
| C6-C5-H5 | 109.2 | C3-C5-H5 | 109.2 |
| C7-C6-C11 | 119.82(12) | C7-C6-C5 | 118.98(11) |
| C11-C6-C5 | 121.12(11) | C8-C7-C6 | 120.45(13) |
| C8-C7-H7 | 119.8 | C6-C7-H7 | 119.8 |
| C9-C8-C7 | 120.69(13) | C9-C8-O2 | 120.66(13) |
| C7-C8-O2 | 118.36(13) | C8-C9-C10 | 119.66(13) |
| C8-C9-H9 | 120.2 | C10-C9-H9 | 120.2 |
| C9-C10-C11 | 121.36(13) | C9-C10-H10 | 119.3 |
| C11-C10-H10 | 119.3 | N1-C11-C10 | 121.77(12) |
| N1-C11-C6 | 120.21(12) | C10-C11-C6 | 117.99(12) |
| N1-C12-H12A | 109.5 | N1-C12-H12B | 109.5 |
| H12A-C12-H12B | 109.5 | N1-C12-H12C | 109.5 |
| H12A-C12-H12C | 109.5 | H12B-C12-H12C | 109.5 |
| C13A-C14-H14A | 109.5 | C13A-C14-H14B | 109.5 |
| H14A-C14-H14B | 109.5 | C13A-C14-H14C | 109.5 |

| | | | |
|---------------|----------|---------------|----------|
| H14A-C14-H14C | 109.5 | H14B-C14-H14C | 109.5 |
| O3A-C13A-O2 | 121.1(7) | O3A-C13A-C14 | 128.2(7) |
| O2-C13A-C14 | 110.7(5) | O3B-C13B-O2 | 122.0(5) |
| O3B-C13B-C14 | 127.4(5) | O2-C13B-C14 | 110.5(4) |

Table 6. Torsion angles (°) for 8a.

| | | | |
|----------------|-------------|----------------|-------------|
| C5-O1-C1-C2 | -32.89(15) | O1-C1-C2-C3 | 11.97(16) |
| C1-C2-C3-C4 | -106.31(14) | C1-C2-C3-C5 | 11.89(15) |
| C11-N1-C4-C3 | -56.85(14) | C12-N1-C4-C3 | 161.58(11) |
| C5-C3-C4-N1 | 59.17(14) | C2-C3-C4-N1 | 173.49(11) |
| C1-O1-C5-C6 | 164.13(11) | C1-O1-C5-C3 | 40.56(13) |
| C4-C3-C5-O1 | 88.02(12) | C2-C3-C5-O1 | -31.73(13) |
| C4-C3-C5-C6 | -32.28(14) | C2-C3-C5-C6 | -152.03(11) |
| O1-C5-C6-C7 | 68.45(14) | C3-C5-C6-C7 | -174.41(11) |
| O1-C5-C6-C11 | -114.81(13) | C3-C5-C6-C11 | 2.34(16) |
| C11-C6-C7-C8 | -0.11(18) | C5-C6-C7-C8 | 176.68(11) |
| C6-C7-C8-C9 | -1.23(19) | C6-C7-C8-O2 | -175.04(11) |
| C13B-O2-C8-C9 | 90.6(4) | C13A-O2-C8-C9 | 68.7(5) |
| C13B-O2-C8-C7 | -95.6(4) | C13A-O2-C8-C7 | -117.5(5) |
| C7-C8-C9-C10 | 1.6(2) | O2-C8-C9-C10 | 175.23(11) |
| C8-C9-C10-C11 | -0.6(2) | C12-N1-C11-C10 | -16.51(18) |
| C4-N1-C11-C10 | -156.55(12) | C12-N1-C11-C6 | 165.49(12) |
| C4-N1-C11-C6 | 25.44(16) | C9-C10-C11-N1 | -178.77(12) |
| C9-C10-C11-C6 | -0.72(19) | C7-C6-C11-N1 | 179.13(11) |
| C5-C6-C11-N1 | 2.41(17) | C7-C6-C11-C10 | 1.05(18) |
| C5-C6-C11-C10 | -175.67(11) | C8-O2-C13A-O3A | -6.7(9) |
| C8-O2-C13A-C14 | 171.8(3) | C8-O2-C13B-O3B | 3.4(6) |
| C8-O2-C13B-C14 | -173.0(3) | | |

Table 7. Anisotropic atomic displacement parameters (Å²) for 8a.

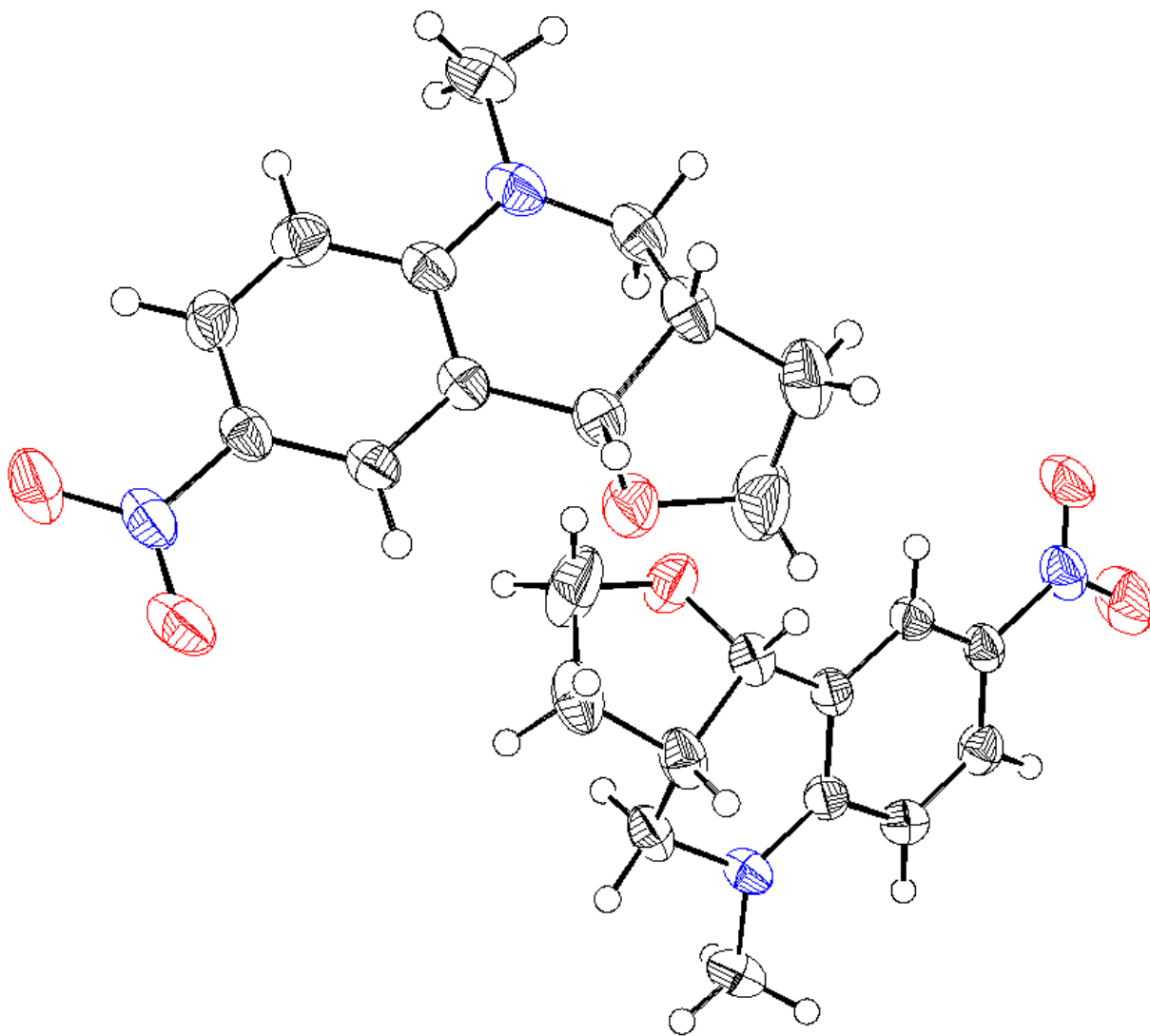
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

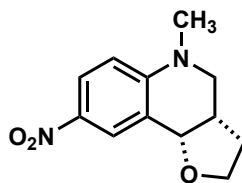
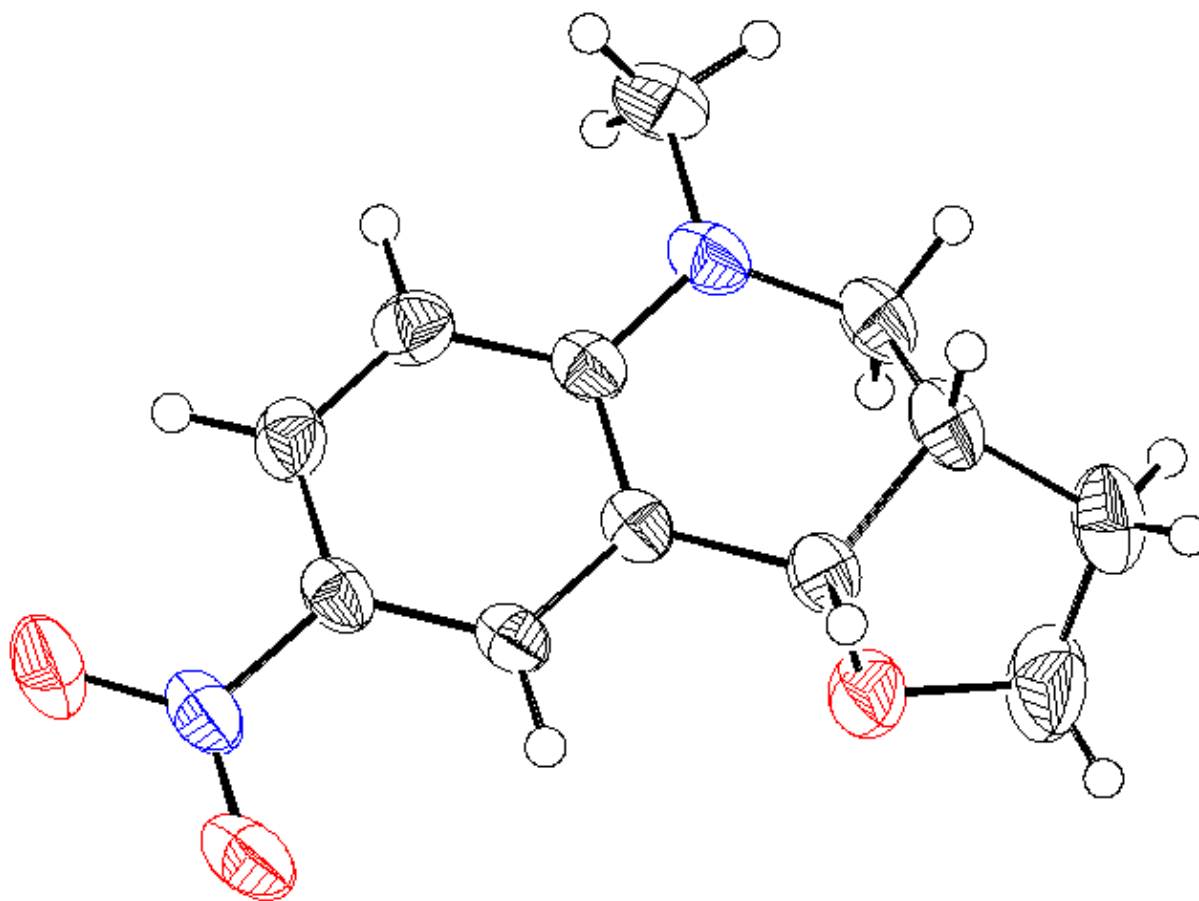
| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| O1 | 0.0362(5) | 0.0398(5) | 0.0428(5) | 0.0007(4) | -0.0042(4) | -0.0009(4) |
| O2 | 0.0630(7) | 0.0394(6) | 0.0363(5) | -0.0004(4) | 0.0054(5) | 0.0142(5) |
| N1 | 0.0313(6) | 0.0411(6) | 0.0347(6) | -0.0009(5) | 0.0059(4) | 0.0012(4) |
| C1 | 0.0443(8) | 0.0431(8) | 0.0486(8) | -0.0029(6) | 0.0019(6) | -0.0059(6) |
| C2 | 0.0456(8) | 0.0380(8) | 0.0626(10) | 0.0000(7) | 0.0099(7) | 0.0011(6) |
| C3 | 0.0366(7) | 0.0368(7) | 0.0299(6) | 0.0034(5) | 0.0015(5) | 0.0040(5) |
| C4 | 0.0352(7) | 0.0399(7) | 0.0289(6) | -0.0021(5) | 0.0023(5) | 0.0043(5) |
| C5 | 0.0325(6) | 0.0373(7) | 0.0278(6) | 0.0000(5) | 0.0032(5) | 0.0009(5) |

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|------------|-----------|------------|-------------|------------|------------|
| C6 | 0.0336(6) | 0.0362(7) | 0.0234(5) | -0.0006(5) | 0.0022(5) | 0.0007(5) |
| C7 | 0.0367(7) | 0.0391(7) | 0.0295(6) | -0.0004(5) | 0.0036(5) | 0.0023(5) |
| C8 | 0.0483(8) | 0.0354(7) | 0.0275(6) | -0.0007(5) | 0.0027(5) | 0.0065(6) |
| C9 | 0.0531(8) | 0.0359(7) | 0.0321(7) | -0.0003(5) | 0.0038(6) | -0.0046(6) |
| C10 | 0.0404(7) | 0.0429(7) | 0.0310(6) | -0.0005(5) | 0.0047(5) | -0.0057(6) |
| C11 | 0.0347(6) | 0.0394(7) | 0.0223(5) | -0.0007(5) | 0.0016(5) | 0.0012(5) |
| C12 | 0.0370(7) | 0.0554(9) | 0.0477(8) | 0.0015(7) | 0.0135(6) | 0.0010(6) |
| C14 | 0.0599(10) | 0.0476(9) | 0.0618(10) | 0.0077(7) | 0.0115(8) | 0.0157(8) |
| O3A | 0.136(6) | 0.148(6) | 0.052(3) | 0.047(3) | 0.040(4) | 0.093(5) |
| C13A | 0.046(3) | 0.047(3) | 0.0413(9) | 0.0080(14) | 0.0062(16) | 0.0048(19) |
| O3B | 0.120(4) | 0.136(4) | 0.0409(15) | -0.0185(19) | -0.015(2) | 0.080(3) |
| C13B | 0.046(3) | 0.047(3) | 0.0413(9) | 0.0080(14) | 0.0062(16) | 0.0048(19) |

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 8a.

| | x/a | y/b | z/c | $U(\text{eq})$ |
|------|--------|---------|--------|----------------|
| H1A | 0.1083 | -0.0068 | 0.5032 | 0.055 |
| H1B | 0.0860 | 0.0055 | 0.6828 | 0.055 |
| H2A | 0.2831 | -0.0592 | 0.5750 | 0.058 |
| H2B | 0.2509 | -0.0726 | 0.7500 | 0.058 |
| H3 | 0.3645 | 0.0686 | 0.8210 | 0.042 |
| H4A | 0.4580 | 0.0515 | 0.5958 | 0.042 |
| H4B | 0.3603 | 0.1171 | 0.4915 | 0.042 |
| H5 | 0.2075 | 0.1688 | 0.8218 | 0.039 |
| H7 | 0.1341 | 0.3609 | 0.7278 | 0.042 |
| H9 | 0.3765 | 0.5720 | 0.6490 | 0.049 |
| H10 | 0.4950 | 0.4254 | 0.6204 | 0.046 |
| H12A | 0.5991 | 0.1638 | 0.5682 | 0.069 |
| H12B | 0.6049 | 0.2866 | 0.6349 | 0.069 |
| H12C | 0.5387 | 0.2613 | 0.4652 | 0.069 |
| H14A | 0.0047 | 0.7397 | 0.5542 | 0.084 |
| H14B | 0.0882 | 0.7741 | 0.7060 | 0.084 |
| H14C | 0.0054 | 0.6728 | 0.7146 | 0.084 |





8e

A specimen of $C_{12}H_{14}N_2O_3$, approximate dimensions 0.054 mm \times 0.125 mm \times 0.339 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 13.91 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13329 reflections to a maximum θ angle of 75.34° (0.80 Å resolution), of which 4208 were independent (average redundancy 3.168, completeness = 99.3%, R_{int} = 2.83%, R_{sig} = 2.82%) and 4006 (95.20%) were greater than $2\sigma(F^2)$. The final cell constants of a = 28.3147(9) Å, b = 10.3899(3) Å, c = 7.7003(2) Å, β = 99.216(2)°, volume = 2236.09(11) Å³, are based upon the refinement of the XYZ-centroids of 8912 reflections above $20\sigma(I)$ with $9.080^\circ < 2\theta < 150.2^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.885. The Calcd. minimum and maximum transmission coefficients (based on crystal size) are 0.7640 and 0.9560.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $C 1 c 1$, with $Z = 8$ for the formula unit, $C_{12}H_{14}N_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 310 variables converged at $R1 = 4.02\%$, for the observed data and $wR2 = 11.21\%$ for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was $0.235 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.165 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.042 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the Calcd. density was 1.392 g/cm^3 and $F(000)$, 992 e^- .

Table 1. Sample and crystal data for 8e.

| | |
|-------------------------------|---|
| Identification code | 8e |
| Chemical formula | $C_{12}H_{14}N_2O_3$ |
| Formula weight | 234.25 g/mol |
| Temperature | 200(2) K |
| Wavelength | 1.54178 \AA |
| Crystal size | 0.054 × 0.125 × 0.339 mm |
| Crystal system | monoclinic |
| Space group | $C 1 c 1$ |
| Unit cell dimensions | $a = 28.3147(9) \text{ \AA}$ $\alpha = 90^\circ$ $b = 10.3899(3) \text{ \AA}$ $\beta = 99.216(2)^\circ$ $c = 7.7003(2) \text{ \AA}$ $\gamma = 90^\circ$ |
| Volume | 2236.09(11) \AA^3 |
| Z | 8 |
| Density (Calcd.) | 1.392 g/cm^3 |
| Absorption coefficient | 0.839 mm^{-1} |
| F(000) | 992 |

Table 2. Data collection and structure refinement for 8e.

| | |
|--|--|
| Theta range for data collection | 3.16 to 75.34° |
| Index ranges | -33 ≤ h ≤ 35, -12 ≤ k ≤ 12, -9 ≤ l ≤ 9 |
| Reflections collected | 13329 |
| Independent reflections | 4208 [R(int) = 0.0283] |
| Coverage of independent reflections | 99.3% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9560 and 0.7640 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | $\sum w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 4208 / 2 / 310 |

| | |
|--|---|
| Goodness-of-fit on F^2 | 1.044 |
| Final R indices | 4006 data; $I > 2\sigma(I)$ $R1 = 0.0402$, $wR2 = 0.1099$ all data $R1 = 0.0421$, $wR2 = 0.1121$ |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 0.2443P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Absolute structure parameter | 0.2(2) |
| Largest diff. peak and hole | 0.235 and -0.165 $e\text{\AA}^{-3}$ |
| R.M.S. deviation from mean | 0.042 $e\text{\AA}^{-3}$ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for 8e.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|-------------|-------------|------------|-----------------|
| O1 | 0.46512(7) | 0.3011(2) | 0.1938(3) | 0.0509(5) |
| O2 | 0.37857(9) | 0.76199(17) | 0.0942(3) | 0.0518(5) |
| O3 | 0.30820(10) | 0.7652(2) | 0.1686(4) | 0.0638(7) |
| O4 | 0.53361(8) | 0.1980(2) | 0.7325(3) | 0.0515(5) |
| O5 | 0.62078(9) | 0.74049(17) | 0.7407(3) | 0.0502(5) |
| O6 | 0.69021(11) | 0.7379(2) | 0.9027(4) | 0.0682(7) |
| N1 | 0.34307(9) | 0.1696(2) | 0.1642(3) | 0.0414(5) |
| N2 | 0.34365(9) | 0.70658(19) | 0.1373(3) | 0.0414(5) |
| N3 | 0.65497(8) | 0.33364(19) | 0.8556(3) | 0.0396(4) |
| N4 | 0.65552(9) | 0.7966(2) | 0.8242(3) | 0.0429(5) |
| C1 | 0.49555(15) | 0.1951(4) | 0.1619(6) | 0.0728(11) |
| C2 | 0.46645(13) | 0.0995(3) | 0.0481(4) | 0.0552(7) |
| C3 | 0.41522(11) | 0.1525(2) | 0.0262(3) | 0.0410(5) |
| C4 | 0.42442(9) | 0.2960(2) | 0.0579(3) | 0.0361(5) |
| C5 | 0.38775(11) | 0.1005(2) | 0.1645(4) | 0.0427(5) |
| C6 | 0.30318(13) | 0.1000(3) | 0.2185(5) | 0.0576(7) |
| C7 | 0.34361(9) | 0.3002(2) | 0.1639(3) | 0.0335(4) |
| C8 | 0.38322(9) | 0.3676(2) | 0.1143(3) | 0.0315(4) |
| C9 | 0.30520(9) | 0.3736(2) | 0.2095(3) | 0.0391(5) |
| C10 | 0.30594(9) | 0.5053(2) | 0.2055(3) | 0.0386(5) |
| C11 | 0.34443(10) | 0.5688(2) | 0.1530(3) | 0.0335(5) |
| C12 | 0.38292(9) | 0.5001(2) | 0.1065(3) | 0.0323(4) |
| C13 | 0.50256(14) | 0.3025(4) | 0.6652(6) | 0.0728(11) |
| C14 | 0.53198(13) | 0.4020(3) | 0.5881(4) | 0.0569(8) |
| C15 | 0.58331(10) | 0.3499(2) | 0.6286(3) | 0.0415(5) |
| C16 | 0.57466(9) | 0.2059(2) | 0.6457(3) | 0.0368(5) |
| C17 | 0.60982(11) | 0.4010(2) | 0.8016(4) | 0.0423(5) |
| C18 | 0.69283(12) | 0.4044(3) | 0.9672(4) | 0.0521(7) |

| | x/a | y/b | z/c | U(equiv) |
|-----|------------|------------|------------|-----------------|
| C19 | 0.65523(9) | 0.2030(2) | 0.8489(3) | 0.0330(4) |
| C20 | 0.61608(8) | 0.1354(2) | 0.7507(3) | 0.0316(4) |
| C21 | 0.69460(9) | 0.1308(2) | 0.9341(3) | 0.0380(5) |
| C22 | 0.69439(9) | 0.9988(2) | 0.9261(3) | 0.0382(5) |
| C23 | 0.65537(9) | 0.9349(2) | 0.8329(3) | 0.0331(4) |
| C24 | 0.61669(8) | 0.0024(2) | 0.7429(3) | 0.0322(4) |

Table 4. Bond lengths (Å) for 8e.

| | | | |
|----------|----------|----------|----------|
| O1-C4 | 1.428(3) | O1-C1 | 1.443(4) |
| O2-N2 | 1.235(4) | O3-N2 | 1.231(3) |
| O4-C16 | 1.433(3) | O4-C13 | 1.441(4) |
| O5-N4 | 1.232(4) | O6-N4 | 1.229(4) |
| N1-C7 | 1.357(3) | N1-C5 | 1.455(4) |
| N1-C6 | 1.458(4) | N2-C11 | 1.437(3) |
| N3-C19 | 1.359(3) | N3-C17 | 1.458(4) |
| N3-C18 | 1.461(4) | N4-C23 | 1.438(3) |
| C1-C2 | 1.484(6) | C1-H1A | 0.99 |
| C1-H1B | 0.99 | C2-C3 | 1.535(4) |
| C2-H2A | 0.99 | C2-H2B | 0.99 |
| C3-C5 | 1.516(4) | C3-C4 | 1.527(3) |
| C3-H3 | 1.0 | C4-C8 | 1.505(3) |
| C4-H4 | 1.0 | C5-H5A | 0.99 |
| C5-H5B | 0.99 | C6-H6A | 0.98 |
| C6-H6B | 0.98 | C6-H6C | 0.98 |
| C7-C9 | 1.418(4) | C7-C8 | 1.425(3) |
| C8-C12 | 1.378(3) | C9-C10 | 1.369(4) |
| C9-H9 | 0.95 | C10-C11 | 1.388(4) |
| C10-H10 | 0.95 | C11-C12 | 1.396(3) |
| C12-H12 | 0.95 | C13-C14 | 1.508(6) |
| C13-H13A | 0.99 | C13-H13B | 0.99 |
| C14-C15 | 1.535(4) | C14-H14A | 0.99 |
| C14-H14B | 0.99 | C15-C17 | 1.516(4) |
| C15-C16 | 1.525(3) | C15-H15 | 1.0 |
| C16-C20 | 1.504(3) | C16-H16 | 1.0 |
| C17-H17A | 0.99 | C17-H17B | 0.99 |
| C18-H18A | 0.98 | C18-H18B | 0.98 |
| C18-H18C | 0.98 | C19-C21 | 1.415(4) |
| C19-C20 | 1.423(4) | C20-C24 | 1.383(3) |
| C21-C22 | 1.373(3) | C21-H21 | 0.95 |
| C22-C23 | 1.387(4) | C22-H22 | 0.95 |

C23-C24

1.389(3)

C24-H24

0.95

Table 5. Bond angles (°) for 8e.

| | | | |
|--------------|------------|---------------|------------|
| C4-O1-C1 | 106.3(2) | C16-O4-C13 | 106.4(2) |
| C7-N1-C5 | 118.9(2) | C7-N1-C6 | 120.4(2) |
| C5-N1-C6 | 117.9(2) | O3-N2-O2 | 122.4(2) |
| O3-N2-C11 | 118.6(3) | O2-N2-C11 | 119.0(2) |
| C19-N3-C17 | 118.6(2) | C19-N3-C18 | 121.2(2) |
| C17-N3-C18 | 116.9(2) | O6-N4-O5 | 122.0(2) |
| O6-N4-C23 | 118.7(2) | O5-N4-C23 | 119.2(2) |
| O1-C1-C2 | 108.7(3) | O1-C1-H1A | 109.9 |
| C2-C1-H1A | 109.9 | O1-C1-H1B | 109.9 |
| C2-C1-H1B | 109.9 | H1A-C1-H1B | 108.3 |
| C1-C2-C3 | 104.5(2) | C1-C2-H2A | 110.9 |
| C3-C2-H2A | 110.9 | C1-C2-H2B | 110.9 |
| C3-C2-H2B | 110.9 | H2A-C2-H2B | 108.9 |
| C5-C3-C4 | 109.22(19) | C5-C3-C2 | 112.2(2) |
| C4-C3-C2 | 101.5(2) | C5-C3-H3 | 111.2 |
| C4-C3-H3 | 111.2 | C2-C3-H3 | 111.2 |
| O1-C4-C8 | 110.01(19) | O1-C4-C3 | 104.47(19) |
| C8-C4-C3 | 114.1(2) | O1-C4-H4 | 109.4 |
| C8-C4-H4 | 109.4 | C3-C4-H4 | 109.4 |
| N1-C5-C3 | 111.5(2) | N1-C5-H5A | 109.3 |
| C3-C5-H5A | 109.3 | N1-C5-H5B | 109.3 |
| C3-C5-H5B | 109.3 | H5A-C5-H5B | 108.0 |
| N1-C6-H6A | 109.5 | N1-C6-H6B | 109.5 |
| H6A-C6-H6B | 109.5 | N1-C6-H6C | 109.5 |
| H6A-C6-H6C | 109.5 | H6B-C6-H6C | 109.5 |
| N1-C7-C9 | 121.9(2) | N1-C7-C8 | 120.1(2) |
| C9-C7-C8 | 118.0(2) | C12-C8-C7 | 120.2(2) |
| C12-C8-C4 | 118.7(2) | C7-C8-C4 | 120.9(2) |
| C10-C9-C7 | 121.1(2) | C10-C9-H9 | 119.4 |
| C7-C9-H9 | 119.4 | C9-C10-C11 | 119.8(2) |
| C9-C10-H10 | 120.1 | C11-C10-H10 | 120.1 |
| C10-C11-C12 | 120.9(2) | C10-C11-N2 | 119.7(2) |
| C12-C11-N2 | 119.3(2) | C8-C12-C11 | 119.9(2) |
| C8-C12-H12 | 120.0 | C11-C12-H12 | 120.0 |
| O4-C13-C14 | 108.3(3) | O4-C13-H13A | 110.0 |
| C14-C13-H13A | 110.0 | O4-C13-H13B | 110.0 |
| C14-C13-H13B | 110.0 | H13A-C13-H13B | 108.4 |
| C13-C14-C15 | 104.1(2) | C13-C14-H14A | 110.9 |

| | | | |
|---------------|------------|---------------|------------|
| C15-C14-H14A | 110.9 | C13-C14-H14B | 110.9 |
| C15-C14-H14B | 110.9 | H14A-C14-H14B | 109.0 |
| C17-C15-C16 | 109.4(2) | C17-C15-C14 | 112.0(2) |
| C16-C15-C14 | 101.7(2) | C17-C15-H15 | 111.1 |
| C16-C15-H15 | 111.1 | C14-C15-H15 | 111.1 |
| O4-C16-C20 | 110.00(19) | O4-C16-C15 | 104.48(19) |
| C20-C16-C15 | 113.7(2) | O4-C16-H16 | 109.5 |
| C20-C16-H16 | 109.5 | C15-C16-H16 | 109.5 |
| N3-C17-C15 | 111.7(2) | N3-C17-H17A | 109.3 |
| C15-C17-H17A | 109.3 | N3-C17-H17B | 109.3 |
| C15-C17-H17B | 109.3 | H17A-C17-H17B | 107.9 |
| N3-C18-H18A | 109.5 | N3-C18-H18B | 109.5 |
| H18A-C18-H18B | 109.5 | N3-C18-H18C | 109.5 |
| H18A-C18-H18C | 109.5 | H18B-C18-H18C | 109.5 |
| N3-C19-C21 | 121.4(2) | N3-C19-C20 | 120.3(2) |
| C21-C19-C20 | 118.3(2) | C24-C20-C19 | 120.1(2) |
| C24-C20-C16 | 118.5(2) | C19-C20-C16 | 121.29(19) |
| C22-C21-C19 | 120.7(2) | C22-C21-H21 | 119.6 |
| C19-C21-H21 | 119.6 | C21-C22-C23 | 119.9(2) |
| C21-C22-H22 | 120.0 | C23-C22-H22 | 120.0 |
| C22-C23-C24 | 121.0(2) | C22-C23-N4 | 119.6(2) |
| C24-C23-N4 | 119.3(2) | C20-C24-C23 | 119.8(2) |
| C20-C24-H24 | 120.1 | C23-C24-H24 | 120.1 |

Table 6. Torsion angles (°) for 8e.

| | | | |
|---------------|------------|----------------|-------------|
| C4-O1-C1-C2 | -20.0(4) | O1-C1-C2-C3 | -4.2(4) |
| C1-C2-C3-C5 | -91.8(3) | C1-C2-C3-C4 | 24.7(3) |
| C1-O1-C4-C8 | 158.9(3) | C1-O1-C4-C3 | 36.0(3) |
| C5-C3-C4-O1 | 81.2(3) | C2-C3-C4-O1 | -37.4(2) |
| C5-C3-C4-C8 | -39.0(3) | C2-C3-C4-C8 | -157.5(2) |
| C7-N1-C5-C3 | -48.3(3) | C6-N1-C5-C3 | 150.5(3) |
| C4-C3-C5-N1 | 57.1(3) | C2-C3-C5-N1 | 168.8(2) |
| C5-N1-C7-C9 | -163.1(2) | C6-N1-C7-C9 | -2.3(4) |
| C5-N1-C7-C8 | 17.8(3) | C6-N1-C7-C8 | 178.6(2) |
| N1-C7-C8-C12 | 177.17(19) | C9-C7-C8-C12 | -1.9(3) |
| N1-C7-C8-C4 | 1.3(3) | C9-C7-C8-C4 | -177.77(19) |
| O1-C4-C8-C12 | 78.0(2) | C3-C4-C8-C12 | -164.93(19) |
| O1-C4-C8-C7 | -106.0(2) | C3-C4-C8-C7 | 11.0(3) |
| N1-C7-C9-C10 | -178.8(2) | C8-C7-C9-C10 | 0.3(3) |
| C7-C9-C10-C11 | 1.1(4) | C9-C10-C11-C12 | -0.9(4) |
| C9-C10-C11-N2 | 175.76(19) | O3-N2-C11-C10 | -1.1(3) |

| | | | |
|-----------------|-------------|-----------------|------------|
| O2-N2-C11-C10 | 178.5(2) | O3-N2-C11-C12 | 175.7(2) |
| O2-N2-C11-C12 | -4.8(3) | C7-C8-C12-C11 | 2.1(3) |
| C4-C8-C12-C11 | 178.1(2) | C10-C11-C12-C8 | -0.7(3) |
| N2-C11-C12-C8 | -177.43(19) | C16-O4-C13-C14 | -20.5(4) |
| O4-C13-C14-C15 | -3.9(4) | C13-C14-C15-C17 | -91.9(3) |
| C13-C14-C15-C16 | 24.8(3) | C13-O4-C16-C20 | 159.1(3) |
| C13-O4-C16-C15 | 36.7(3) | C17-C15-C16-O4 | 80.7(2) |
| C14-C15-C16-O4 | -37.9(2) | C17-C15-C16-C20 | -39.3(3) |
| C14-C15-C16-C20 | -157.9(2) | C19-N3-C17-C15 | -47.0(3) |
| C18-N3-C17-C15 | 153.2(2) | C16-C15-C17-N3 | 57.3(3) |
| C14-C15-C17-N3 | 169.3(2) | C17-N3-C19-C21 | -165.9(2) |
| C18-N3-C19-C21 | -7.0(4) | C17-N3-C19-C20 | 15.9(3) |
| C18-N3-C19-C20 | 174.8(2) | N3-C19-C20-C24 | 179.40(19) |
| C21-C19-C20-C24 | 1.1(3) | N3-C19-C20-C16 | 2.8(3) |
| C21-C19-C20-C16 | -175.4(2) | O4-C16-C20-C24 | 77.1(3) |
| C15-C16-C20-C24 | -166.08(19) | O4-C16-C20-C19 | -106.2(2) |
| C15-C16-C20-C19 | 10.6(3) | N3-C19-C21-C22 | -179.9(2) |
| C20-C19-C21-C22 | -1.7(3) | C19-C21-C22-C23 | 0.3(4) |
| C21-C22-C23-C24 | 1.7(4) | C21-C22-C23-N4 | 179.6(2) |
| O6-N4-C23-C22 | 1.2(4) | O5-N4-C23-C22 | -179.8(2) |
| O6-N4-C23-C24 | 179.2(3) | O5-N4-C23-C24 | -1.8(3) |
| C19-C20-C24-C23 | 0.8(3) | C16-C20-C24-C23 | 177.5(2) |
| C22-C23-C24-C20 | -2.3(3) | N4-C23-C24-C20 | 179.8(2) |

Table 7. Anisotropic atomic displacement parameters (\AA^2) for 8e.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

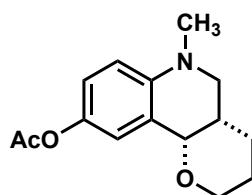
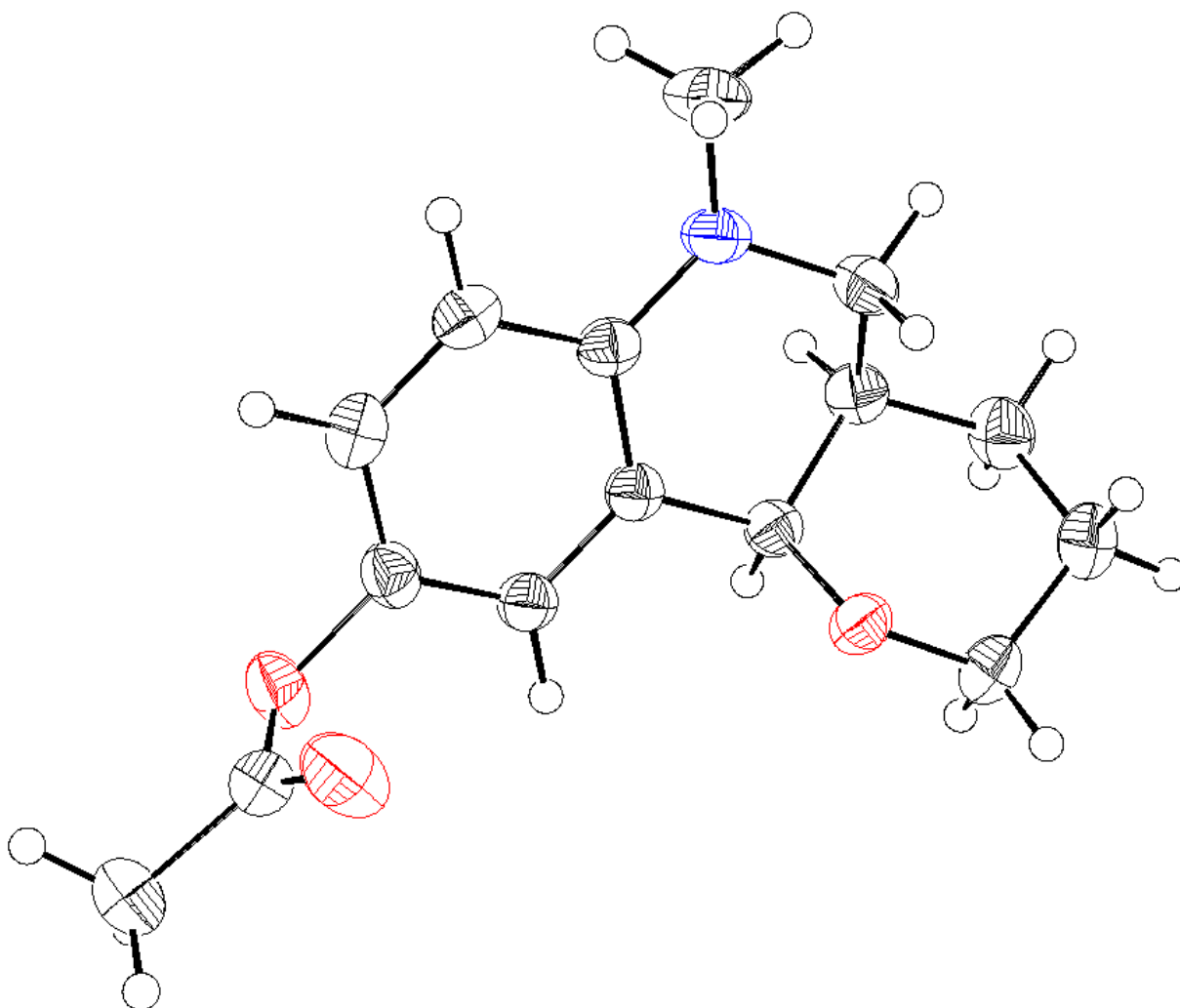
| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|----|------------|------------|------------|-------------|-------------|------------|
| O1 | 0.0400(10) | 0.0488(11) | 0.0594(12) | -0.0085(8) | -0.0058(8) | 0.0099(8) |
| O2 | 0.0648(13) | 0.0276(8) | 0.0601(12) | -0.0007(8) | 0.0015(10) | -0.0046(8) |
| O3 | 0.0653(15) | 0.0341(10) | 0.0899(18) | -0.0084(10) | 0.0056(12) | 0.0154(9) |
| O4 | 0.0394(10) | 0.0512(11) | 0.0662(13) | 0.0137(9) | 0.0156(9) | 0.0087(8) |
| O5 | 0.0622(13) | 0.0270(8) | 0.0623(12) | -0.0015(8) | 0.0124(10) | -0.0033(8) |
| O6 | 0.0754(16) | 0.0366(10) | 0.0869(18) | 0.0065(10) | -0.0044(14) | 0.0197(10) |
| N1 | 0.0484(12) | 0.0289(9) | 0.0456(11) | 0.0019(8) | 0.0041(9) | -0.0047(9) |
| N2 | 0.0501(12) | 0.0265(9) | 0.0430(11) | -0.0047(8) | -0.0060(9) | 0.0046(9) |
| N3 | 0.0449(11) | 0.0268(9) | 0.0478(11) | -0.0024(8) | 0.0095(9) | -0.0040(8) |
| N4 | 0.0559(13) | 0.0277(10) | 0.0469(11) | 0.0035(8) | 0.0138(9) | 0.0058(9) |
| C1 | 0.0561(19) | 0.077(2) | 0.080(2) | -0.0135(19) | -0.0061(16) | 0.0304(18) |
| C2 | 0.069(2) | 0.0409(13) | 0.0578(17) | 0.0060(12) | 0.0175(15) | 0.0204(13) |
| C3 | 0.0597(16) | 0.0291(10) | 0.0331(10) | 0.0002(8) | 0.0043(10) | 0.0075(10) |

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|------------|------------|------------|-------------|------------|-------------|
| C4 | 0.0419(12) | 0.0308(10) | 0.0352(11) | 0.0021(8) | 0.0049(9) | 0.0036(9) |
| C5 | 0.0575(15) | 0.0259(9) | 0.0432(12) | 0.0027(9) | 0.0031(11) | 0.0043(11) |
| C6 | 0.0620(18) | 0.0367(13) | 0.075(2) | 0.0005(13) | 0.0120(15) | -0.0138(12) |
| C7 | 0.0379(11) | 0.0284(10) | 0.0314(10) | 0.0002(8) | -0.0031(8) | -0.0002(9) |
| C8 | 0.0370(12) | 0.0278(10) | 0.0277(9) | 0.0007(7) | -0.0012(8) | 0.0025(9) |
| C9 | 0.0353(11) | 0.0414(13) | 0.0395(12) | 0.0033(9) | 0.0030(9) | -0.0015(9) |
| C10 | 0.0364(12) | 0.0396(12) | 0.0373(11) | -0.0028(9) | -0.0014(9) | 0.0080(9) |
| C11 | 0.0398(11) | 0.0263(10) | 0.0307(10) | -0.0028(7) | -0.0060(8) | 0.0032(8) |
| C12 | 0.0364(11) | 0.0257(10) | 0.0320(9) | -0.0007(8) | -0.0025(8) | -0.0009(8) |
| C13 | 0.0515(19) | 0.081(2) | 0.090(3) | 0.025(2) | 0.0228(18) | 0.0304(18) |
| C14 | 0.066(2) | 0.0430(14) | 0.0590(17) | 0.0011(12) | 0.0024(14) | 0.0217(13) |
| C15 | 0.0562(15) | 0.0308(11) | 0.0390(11) | 0.0050(9) | 0.0123(10) | 0.0094(10) |
| C16 | 0.0415(12) | 0.0318(10) | 0.0374(11) | -0.0009(8) | 0.0068(9) | 0.0041(9) |
| C17 | 0.0567(15) | 0.0264(10) | 0.0456(12) | -0.0013(9) | 0.0132(11) | 0.0045(10) |
| C18 | 0.0566(16) | 0.0340(12) | 0.0655(17) | -0.0049(11) | 0.0088(14) | -0.0118(12) |
| C19 | 0.0369(11) | 0.0289(10) | 0.0357(10) | 0.0016(8) | 0.0130(8) | -0.0011(9) |
| C20 | 0.0371(11) | 0.0273(10) | 0.0320(10) | 0.0008(8) | 0.0109(8) | 0.0024(9) |
| C21 | 0.0350(11) | 0.0372(12) | 0.0417(12) | -0.0014(9) | 0.0055(9) | -0.0033(9) |
| C22 | 0.0361(12) | 0.0375(12) | 0.0410(12) | 0.0050(10) | 0.0058(9) | 0.0079(9) |
| C23 | 0.0412(11) | 0.0250(10) | 0.0353(10) | 0.0028(7) | 0.0132(9) | 0.0041(8) |
| C24 | 0.0348(11) | 0.0275(10) | 0.0354(10) | 0.0008(8) | 0.0089(8) | -0.0009(8) |

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 8e.

| | x/a | y/b | z/c | $U(\text{equiv})$ |
|------|--------|--------|---------|-------------------|
| H1A | 0.5096 | 0.1546 | 0.2749 | 0.087 |
| H1B | 0.5220 | 0.2266 | 0.1034 | 0.087 |
| H2A | 0.4684 | 0.0137 | 0.1047 | 0.066 |
| H2B | 0.4775 | 0.0923 | -0.0673 | 0.066 |
| H3 | 0.3977 | 0.1361 | -0.0952 | 0.049 |
| H4 | 0.4327 | 0.3364 | -0.0513 | 0.043 |
| H5A | 0.3808 | 0.0081 | 0.1418 | 0.051 |
| H5B | 0.4077 | 0.1082 | 0.2820 | 0.051 |
| H6A | 0.2732 | 0.1265 | 0.1451 | 0.086 |
| H6B | 0.3017 | 0.1194 | 0.3421 | 0.086 |
| H6C | 0.3078 | 0.0073 | 0.2050 | 0.086 |
| H9 | 0.2785 | 0.3306 | 0.2435 | 0.047 |
| H10 | 0.2802 | 0.5531 | 0.2385 | 0.046 |
| H12 | 0.4089 | 0.5447 | 0.0695 | 0.039 |
| H13A | 0.4878 | 0.3411 | 0.7613 | 0.087 |

| | x/a | y/b | z/c | U(equiv) |
|------|------------|------------|------------|-----------------|
| H13B | 0.4767 | 0.2705 | 0.5736 | 0.087 |
| H14A | 0.5295 | 0.4870 | 0.6441 | 0.068 |
| H14B | 0.5215 | 0.4105 | 0.4597 | 0.068 |
| H15 | 0.6013 | 0.3682 | 0.5299 | 0.05 |
| H16 | 0.5670 | 0.1668 | 0.5259 | 0.044 |
| H17A | 0.6162 | 0.4940 | 0.7893 | 0.051 |
| H17B | 0.5894 | 0.3910 | 0.8939 | 0.051 |
| H18A | 0.7241 | 0.3764 | 0.9418 | 0.078 |
| H18B | 0.6909 | 0.3875 | 1.0911 | 0.078 |
| H18C | 0.6889 | 0.4968 | 0.9437 | 0.078 |
| H21 | 0.7215 | 0.1742 | 0.9977 | 0.046 |
| H22 | 0.7210 | -0.0487 | 0.9844 | 0.046 |
| H24 | 0.5907 | -0.0426 | 0.6761 | 0.039 |



9a

A clear colourless block-like specimen of $C_{15}H_{19}NO_3$, approximate dimensions 0.132 mm x 0.209 mm x 0.270 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1518 frames were collected. The total exposure time was 18.98 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 21721 reflections to a maximum θ angle of 75.42° (0.80 Å resolution), of which 2756 were independent (average redundancy 7.881, completeness = 99.8%, $R_{int} = 2.59\%$, $R_{sig} = 1.85\%$) and 2526 (91.65%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.8210(3)$ Å, $b = 14.6331(6)$ Å, $c = 20.6577(8)$ Å, volume = $2666.47(18)$ Å³, are based upon the refinement of the XYZ-centroids of 9826 reflections above $20 \sigma(I)$ with $8.560^\circ < 2\theta$

< 150.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.916. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8260 and 0.9090.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pbc_a , with $Z = 8$ for the formula unit, $C_{15}H_{19}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 174 variables converged at $R1 = 4.18\%$, for the observed data and $wR2 = 11.68\%$ for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was $0.180 e^{-}/\text{\AA}^3$ and the largest hole was $-0.265 e^{-}/\text{\AA}^3$ with an RMS deviation of $0.056 e^{-}/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.302 g/cm^3 and $F(000)$, 1120 e^{-} .

Table 1. Sample and crystal data for 9a.

| | |
|-------------------------------|--|
| Identification code | 9a |
| Chemical formula | $C_{15}H_{19}NO_3$ |
| Formula weight | 261.31 g/mol |
| Temperature | 200(2) K |
| Wavelength | 1.54178 Å |
| Crystal size | 0.132 x 0.209 x 0.270 mm |
| Crystal habit | clear colourless block |
| Crystal system | orthorhombic |
| Space group | Pbc_a |
| Unit cell dimensions | $a = 8.8210(3) \text{ \AA}$ $\alpha = 90^\circ$ $b = 14.6331(6) \text{ \AA}$ $\beta = 90^\circ$ $c = 20.6577(8) \text{ \AA}$ $\gamma = 90^\circ$ |
| Volume | $2666.47(18) \text{ \AA}^3$ |
| Z | 8 |
| Density (calculated) | 1.302 g/cm^3 |
| Absorption coefficient | 0.734 mm^{-1} |
| F(000) | 1120 |

Table 2. Data collection and structure refinement for 9a.

| | |
|--|---|
| Theta range for data collection | 4.28 to 75.42° |
| Index ranges | $-11 \leq h \leq 9$, $-18 \leq k \leq 18$, $-24 \leq l \leq 25$ |
| Reflections collected | 21721 |
| Independent reflections | 2756 [R(int) = 0.0259] |
| Coverage of independent reflections | 99.8% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9090 and 0.8260 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |

| | |
|--------------------------------|---|
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 2756 / 0 / 174 |
| Goodness-of-fit on F^2 | 1.040 |
| Final R indices | 2526 data; $l > 2\sigma(l)$ R1 = 0.0418, wR2 = 0.1138 all data R1 = 0.0445, wR2 = 0.1168 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 0.7513P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole | 0.180 and -0.265 eÅ ⁻³ |
| R.M.S. deviation from mean | 0.056 eÅ ⁻³ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 9a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(eq) |
|-----|-------------|-------------|------------|-----------|
| O1 | 0.31546(9) | 0.56231(6) | 0.19503(4) | 0.0340(2) |
| C1 | 0.32661(15) | 0.59018(9) | 0.12886(6) | 0.0390(3) |
| O2 | 0.43895(10) | 0.61876(7) | 0.44066(4) | 0.0414(2) |
| C2 | 0.33333(16) | 0.50810(10) | 0.08426(6) | 0.0427(3) |
| O3 | 0.18871(11) | 0.64515(8) | 0.44125(5) | 0.0547(3) |
| C3 | 0.46751(16) | 0.44814(10) | 0.10268(6) | 0.0423(3) |
| N1 | 0.37978(12) | 0.33034(6) | 0.26379(5) | 0.0365(3) |
| C4 | 0.47091(13) | 0.42654(8) | 0.17542(6) | 0.0337(3) |
| C5 | 0.35572(15) | 0.35523(8) | 0.19619(6) | 0.0365(3) |
| C6 | 0.39361(12) | 0.40195(8) | 0.30769(5) | 0.0303(3) |
| C7 | 0.37951(14) | 0.38717(8) | 0.37474(6) | 0.0357(3) |
| C8 | 0.39233(14) | 0.45862(9) | 0.41855(6) | 0.0370(3) |
| C13 | 0.30587(17) | 0.24682(9) | 0.28471(7) | 0.0476(3) |
| C14 | 0.31227(15) | 0.66265(8) | 0.46085(6) | 0.0364(3) |
| C15 | 0.34864(19) | 0.73384(10) | 0.51033(7) | 0.0502(4) |
| C12 | 0.44800(13) | 0.51293(8) | 0.21537(5) | 0.0300(3) |
| C11 | 0.42596(12) | 0.49157(7) | 0.28622(5) | 0.0288(2) |
| C10 | 0.43767(13) | 0.56220(8) | 0.33084(5) | 0.0315(3) |
| C9 | 0.41912(13) | 0.54600(8) | 0.39602(6) | 0.0337(3) |

Table 4. Bond lengths (Å) for 9a.

| | | | |
|--------|------------|--------|------------|
| O1-C1 | 1.4297(14) | O1-C12 | 1.4372(13) |
| C1-C2 | 1.5150(19) | C1-H1A | 0.99 |
| C1-H1B | 0.99 | O2-C14 | 1.3547(16) |
| O2-C9 | 1.4193(14) | C2-C3 | 1.5217(19) |
| C2-H2A | 0.99 | C2-H2B | 0.99 |
| O3-C14 | 1.1906(16) | C3-C4 | 1.5358(16) |

| | | | |
|----------|------------|----------|------------|
| C3-H3A | 0.99 | C3-H3B | 0.99 |
| N1-C6 | 1.3912(15) | N1-C13 | 1.4511(16) |
| N1-C5 | 1.4588(15) | C4-C5 | 1.5183(17) |
| C4-C12 | 1.5231(15) | C4-H4 | 1.0 |
| C5-H5A | 0.99 | C5-H5B | 0.99 |
| C6-C7 | 1.4073(16) | C6-C11 | 1.4135(16) |
| C7-C8 | 1.3874(18) | C7-H7 | 0.95 |
| C8-C9 | 1.3811(18) | C8-H8 | 0.95 |
| C13-H13A | 0.98 | C13-H13B | 0.98 |
| C13-H13C | 0.98 | C14-C15 | 1.4944(17) |
| C15-H15A | 0.98 | C15-H15B | 0.98 |
| C15-H15C | 0.98 | C12-C11 | 1.5091(15) |
| C12-H12 | 1.0 | C11-C10 | 1.3887(16) |
| C10-C9 | 1.3770(16) | C10-H10 | 0.95 |

Table 5. Bond angles (°) for 9a.

| | | | |
|---------------|------------|---------------|------------|
| C1-O1-C12 | 111.53(9) | O1-C1-C2 | 110.97(10) |
| O1-C1-H1A | 109.4 | C2-C1-H1A | 109.4 |
| O1-C1-H1B | 109.4 | C2-C1-H1B | 109.4 |
| H1A-C1-H1B | 108.0 | C14-O2-C9 | 117.01(9) |
| C1-C2-C3 | 109.60(10) | C1-C2-H2A | 109.8 |
| C3-C2-H2A | 109.8 | C1-C2-H2B | 109.8 |
| C3-C2-H2B | 109.8 | H2A-C2-H2B | 108.2 |
| C2-C3-C4 | 112.24(10) | C2-C3-H3A | 109.2 |
| C4-C3-H3A | 109.2 | C2-C3-H3B | 109.2 |
| C4-C3-H3B | 109.2 | H3A-C3-H3B | 107.9 |
| C6-N1-C13 | 118.66(10) | C6-N1-C5 | 116.67(9) |
| C13-N1-C5 | 115.48(10) | C5-C4-C12 | 109.18(9) |
| C5-C4-C3 | 113.87(10) | C12-C4-C3 | 110.90(10) |
| C5-C4-H4 | 107.5 | C12-C4-H4 | 107.5 |
| C3-C4-H4 | 107.5 | N1-C5-C4 | 110.16(10) |
| N1-C5-H5A | 109.6 | C4-C5-H5A | 109.6 |
| N1-C5-H5B | 109.6 | C4-C5-H5B | 109.6 |
| H5A-C5-H5B | 108.1 | N1-C6-C7 | 121.21(10) |
| N1-C6-C11 | 120.79(10) | C7-C6-C11 | 117.99(10) |
| C8-C7-C6 | 121.27(11) | C8-C7-H7 | 119.4 |
| C6-C7-H7 | 119.4 | C9-C8-C7 | 119.45(11) |
| C9-C8-H8 | 120.3 | C7-C8-H8 | 120.3 |
| N1-C13-H13A | 109.5 | N1-C13-H13B | 109.5 |
| H13A-C13-H13B | 109.5 | N1-C13-H13C | 109.5 |
| H13A-C13-H13C | 109.5 | H13B-C13-H13C | 109.5 |

| | | | |
|---------------|------------|---------------|------------|
| O3-C14-O2 | 123.26(11) | O3-C14-C15 | 125.39(12) |
| O2-C14-C15 | 111.35(11) | C14-C15-H15A | 109.5 |
| C14-C15-H15B | 109.5 | H15A-C15-H15B | 109.5 |
| C14-C15-H15C | 109.5 | H15A-C15-H15C | 109.5 |
| H15B-C15-H15C | 109.5 | O1-C12-C11 | 106.43(9) |
| O1-C12-C4 | 111.51(9) | C11-C12-C4 | 111.75(9) |
| O1-C12-H12 | 109.0 | C11-C12-H12 | 109.0 |
| C4-C12-H12 | 109.0 | C10-C11-C6 | 119.81(10) |
| C10-C11-C12 | 118.68(10) | C6-C11-C12 | 121.51(10) |
| C9-C10-C11 | 120.80(11) | C9-C10-H10 | 119.6 |
| C11-C10-H10 | 119.6 | C10-C9-C8 | 120.62(11) |
| C10-C9-O2 | 119.44(11) | C8-C9-O2 | 119.78(10) |

Table 6. Torsion angles (°) for 9a.

| | | | |
|----------------|-------------|----------------|-------------|
| C12-O1-C1-C2 | 63.77(12) | O1-C1-C2-C3 | -57.69(14) |
| C1-C2-C3-C4 | 50.20(15) | C2-C3-C4-C5 | 75.86(14) |
| C2-C3-C4-C12 | -47.76(14) | C6-N1-C5-C4 | 49.31(14) |
| C13-N1-C5-C4 | -164.20(10) | C12-C4-C5-N1 | -62.79(12) |
| C3-C4-C5-N1 | 172.67(10) | C13-N1-C6-C7 | 18.73(17) |
| C5-N1-C6-C7 | 164.12(11) | C13-N1-C6-C11 | -162.81(11) |
| C5-N1-C6-C11 | -17.42(16) | N1-C6-C7-C8 | -179.59(11) |
| C11-C6-C7-C8 | 1.90(17) | C6-C7-C8-C9 | 0.14(18) |
| C9-O2-C14-O3 | -2.79(18) | C9-O2-C14-C15 | 176.77(11) |
| C1-O1-C12-C11 | 177.29(9) | C1-O1-C12-C4 | -60.60(12) |
| C5-C4-C12-O1 | -74.37(12) | C3-C4-C12-O1 | 51.90(12) |
| C5-C4-C12-C11 | 44.62(13) | C3-C4-C12-C11 | 170.89(9) |
| N1-C6-C11-C10 | 179.31(10) | C7-C6-C11-C10 | -2.17(16) |
| N1-C6-C11-C12 | -0.54(17) | C7-C6-C11-C12 | 177.98(10) |
| O1-C12-C11-C10 | -72.34(12) | C4-C12-C11-C10 | 165.70(10) |
| O1-C12-C11-C6 | 107.51(11) | C4-C12-C11-C6 | -14.44(15) |
| C6-C11-C10-C9 | 0.43(17) | C12-C11-C10-C9 | -179.71(10) |
| C11-C10-C9-C8 | 1.69(17) | C11-C10-C9-O2 | 177.00(10) |
| C7-C8-C9-C10 | -1.97(18) | C7-C8-C9-O2 | -177.26(10) |
| C14-O2-C9-C10 | 96.98(13) | C14-O2-C9-C8 | -87.67(14) |

Table 7. Anisotropic atomic displacement parameters (Å²) for 9a.

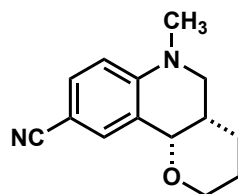
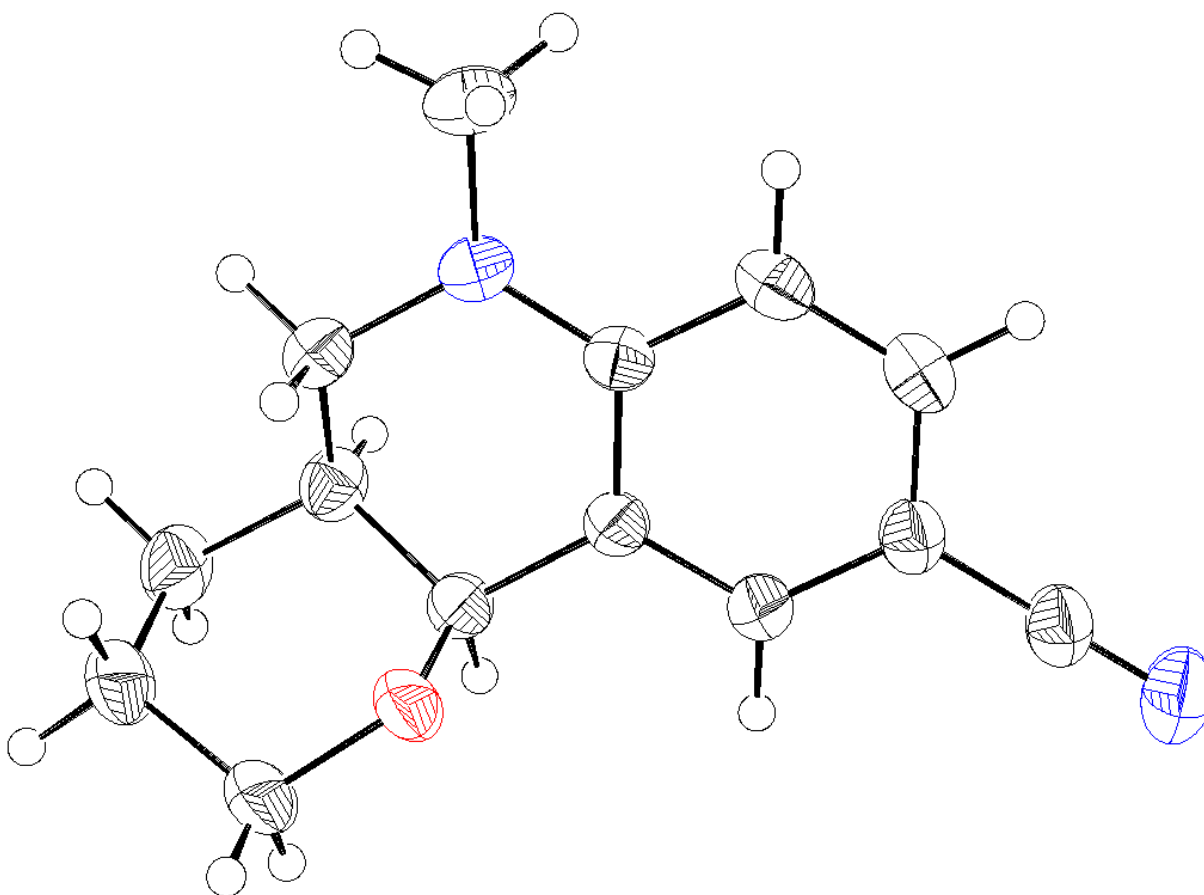
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| O1 | 0.0375(5) | 0.0338(4) | 0.0307(4) | 0.0031(3) | 0.0012(3) | 0.0070(3) |
| C1 | 0.0414(7) | 0.0428(7) | 0.0328(6) | 0.0080(5) | -0.0009(5) | 0.0024(5) |

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| O2 | 0.0391(5) | 0.0478(5) | 0.0373(5) | -0.0126(4) | -0.0063(4) | -0.0003(4) |
| C2 | 0.0448(7) | 0.0526(8) | 0.0306(6) | 0.0007(5) | -0.0026(5) | 0.0008(6) |
| O3 | 0.0429(6) | 0.0545(6) | 0.0665(7) | -0.0221(5) | -0.0091(5) | 0.0069(5) |
| C3 | 0.0434(7) | 0.0492(7) | 0.0344(6) | -0.0052(5) | 0.0071(5) | 0.0033(6) |
| N1 | 0.0433(6) | 0.0256(5) | 0.0405(5) | 0.0001(4) | 0.0009(4) | -0.0011(4) |
| C4 | 0.0302(6) | 0.0350(6) | 0.0359(6) | -0.0020(5) | 0.0027(4) | 0.0043(5) |
| C5 | 0.0409(7) | 0.0306(6) | 0.0380(6) | -0.0059(5) | -0.0010(5) | -0.0002(5) |
| C6 | 0.0262(5) | 0.0291(5) | 0.0357(6) | 0.0012(4) | -0.0002(4) | 0.0022(4) |
| C7 | 0.0351(6) | 0.0338(6) | 0.0382(6) | 0.0073(5) | -0.0003(5) | 0.0005(5) |
| C8 | 0.0348(6) | 0.0459(7) | 0.0304(5) | 0.0034(5) | -0.0014(5) | 0.0015(5) |
| C13 | 0.0594(9) | 0.0256(6) | 0.0578(8) | 0.0001(5) | 0.0062(6) | -0.0031(6) |
| C14 | 0.0439(7) | 0.0331(6) | 0.0322(6) | 0.0008(5) | -0.0032(5) | 0.0019(5) |
| C15 | 0.0636(9) | 0.0440(7) | 0.0430(7) | -0.0112(6) | -0.0065(6) | -0.0001(7) |
| C12 | 0.0284(6) | 0.0294(5) | 0.0323(6) | 0.0007(4) | -0.0009(4) | -0.0019(4) |
| C11 | 0.0251(5) | 0.0293(5) | 0.0321(5) | 0.0003(4) | -0.0018(4) | 0.0006(4) |
| C10 | 0.0296(6) | 0.0293(5) | 0.0355(6) | -0.0001(4) | -0.0047(4) | 0.0003(4) |
| C9 | 0.0304(6) | 0.0374(6) | 0.0332(6) | -0.0060(5) | -0.0047(4) | 0.0020(5) |

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 9a.

| | x/a | y/b | z/c | U(eq) |
|------|------------|------------|------------|--------------|
| H1A | 0.4189 | 0.6277 | 0.1230 | 0.047 |
| H1B | 0.2377 | 0.6283 | 0.1175 | 0.047 |
| H2A | 0.3441 | 0.5287 | 0.0389 | 0.051 |
| H2B | 0.2382 | 0.4726 | 0.0878 | 0.051 |
| H3A | 0.5627 | 0.4796 | 0.0905 | 0.051 |
| H3B | 0.4622 | 0.3902 | 0.0780 | 0.051 |
| H4 | 0.5739 | 0.4021 | 0.1858 | 0.04 |
| H5A | 0.2520 | 0.3798 | 0.1906 | 0.044 |
| H5B | 0.3657 | 0.3003 | 0.1686 | 0.044 |
| H7 | 0.3608 | 0.3271 | 0.3903 | 0.043 |
| H8 | 0.3828 | 0.4475 | 0.4637 | 0.044 |
| H13A | 0.3646 | 0.2190 | 0.3198 | 0.071 |
| H13B | 0.2997 | 0.2041 | 0.2483 | 0.071 |
| H13C | 0.2035 | 0.2609 | 0.3002 | 0.071 |
| H15A | 0.2668 | 0.7791 | 0.5117 | 0.075 |
| H15B | 0.4440 | 0.7641 | 0.4988 | 0.075 |
| H15C | 0.3590 | 0.7050 | 0.5529 | 0.075 |
| H12 | 0.5389 | 0.5532 | 0.2103 | 0.036 |
| H10 | 0.4587 | 0.6224 | 0.3162 | 0.038 |



9b

A clear colourless block-like specimen of $C_{14}H_{16}N_2O$, approximate dimensions $0.238\text{ mm} \times 0.475\text{ mm} \times 0.622\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 414 frames were collected. The total exposure time was 1.73 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 7824 reflections to a maximum θ angle of 29.78° (0.72 \AA resolution), of which 3364 were independent (average redundancy 2.326, completeness = 99.9%, $R_{\text{int}} = 2.55\%$, $R_{\text{sig}} = 3.06\%$) and 2884 (85.73%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 7.4129(13)\text{ \AA}$, $b = 19.814(4)\text{ \AA}$, $c = 8.3185(15)\text{ \AA}$, $\beta = 101.406(3)^\circ$, volume = $1197.7(4)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 3011 reflections above $20\sigma(I)$ with $5.971^\circ < 2\theta < 59.50^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.915. The Calcd. minimum and maximum transmission coefficients (based on crystal size)

are 0.9510 and 0.9810.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 c 1, with Z = 4 for the formula unit, C₁₄H₁₆N₂O. The final anisotropic full-matrix least-squares refinement on F² with 155 variables converged at R1 = 4.20%, for the observed data and wR2 = 11.09% for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 0.159 e⁻/Å³ and the largest hole was -0.208 e⁻/Å³ with an RMS deviation of 0.043 e⁻/Å³. On the basis of the final model, the Calcd. density was 1.266 g/cm³ and F(000), 488 e⁻.

Table 2. Sample and crystal data for 9b.

| | |
|-------------------------------|---|
| Identification code | 9b |
| Chemical formula | C ₁₄ H ₁₆ N ₂ O |
| Formula weight | 228.29 g/mol |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal size | 0.238 × 0.475 × 0.622 mm |
| Crystal habit | clear colourless block |
| Crystal system | monoclinic |
| Space group | C 1 c 1 |
| Unit cell dimensions | a = 7.4129(13) Å α = 90° b = 19.814(4) Å β = 101.406(3)° c = 8.3185(15) Å γ = 90° |
| Volume | 1197.7(4) Å ³ |
| Z | 4 |
| Density (Calcd.) | 1.266 g/cm ³ |
| Absorption coefficient | 0.081 mm ⁻¹ |
| F(000) | 488 |

Table 3. Data collection and structure refinement for 9b.

| | |
|--|--|
| Theta range for data collection | 2.06 to 29.78° |
| Index ranges | -10<=h<=10, -27<=k<=27, -11<=l<=11 |
| Reflections collected | 7824 |
| Independent reflections | 3364 [R(int) = 0.0255] |
| Coverage of independent reflections | 99.9% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9810 and 0.9510 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F ² |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | Σ w(F _o ² - F _c ²) ² |
| Data / restraints / parameters | 3364 / 2 / 155 |

| | |
|--|---|
| Goodness-of-fit on F^2 | 1.049 |
| Final R indices | 2884 data; $I > 2\sigma(I)$ $R1 = 0.0420$, $wR2 = 0.1040$ all data $R1 = 0.0510$, $wR2 = 0.1109$ |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.1977P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Absolute structure parameter | -0.4(6) |
| Largest diff. peak and hole | 0.159 and -0.208 $e\text{\AA}^{-3}$ |
| R.M.S. deviation from mean | 0.043 $e\text{\AA}^{-3}$ |

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for 9b.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|------------|-------------|------------|-----------------|
| O1 | 0.3648(2) | 0.64556(8) | 0.6393(2) | 0.0451(4) |
| N1 | 0.5824(3) | 0.70374(9) | 0.3182(2) | 0.0377(4) |
| N2 | 0.4983(3) | 0.95300(11) | 0.8558(3) | 0.0551(6) |
| C1 | 0.3545(4) | 0.57785(12) | 0.7008(4) | 0.0553(7) |
| C2 | 0.4341(4) | 0.52709(11) | 0.5972(3) | 0.0493(6) |
| C3 | 0.6323(4) | 0.54623(11) | 0.5899(3) | 0.0466(5) |
| C4 | 0.6464(3) | 0.62033(11) | 0.5412(3) | 0.0370(4) |
| C5 | 0.5621(3) | 0.63308(11) | 0.3625(3) | 0.0359(4) |
| C6 | 0.5591(3) | 0.75374(11) | 0.4259(2) | 0.0308(4) |
| C7 | 0.5508(3) | 0.82245(12) | 0.3787(3) | 0.0388(5) |
| C8 | 0.5360(3) | 0.87302(11) | 0.4886(3) | 0.0398(5) |
| C9 | 0.5292(3) | 0.85750(11) | 0.6519(3) | 0.0352(4) |
| C10 | 0.5368(3) | 0.78980(11) | 0.7006(2) | 0.0339(4) |
| C11 | 0.5497(3) | 0.73801(10) | 0.5910(2) | 0.0317(4) |
| C12 | 0.5532(3) | 0.66585(10) | 0.6478(3) | 0.0356(4) |
| C13 | 0.5575(3) | 0.71773(13) | 0.1424(3) | 0.0438(5) |
| C14 | 0.5133(3) | 0.91028(11) | 0.7664(3) | 0.0407(5) |

Table 5. Bond lengths (\AA) for 9b.

| | | | |
|--------|----------|--------|----------|
| O1-C12 | 1.441(3) | O1-C1 | 1.443(3) |
| N1-C6 | 1.370(3) | N1-C5 | 1.463(3) |
| N1-C13 | 1.464(3) | N2-C14 | 1.147(3) |
| C1-C2 | 1.518(3) | C1-H1A | 0.99 |
| C1-H1B | 0.99 | C2-C3 | 1.530(4) |
| C2-H2A | 0.99 | C2-H2B | 0.99 |
| C3-C4 | 1.532(3) | C3-H3A | 0.99 |
| C3-H3B | 0.99 | C4-C5 | 1.515(3) |
| C4-C12 | 1.523(3) | C4-H4 | 1.0 |

| | | | |
|----------|----------|----------|----------|
| C5-H5A | 0.99 | C5-H5B | 0.99 |
| C6-C7 | 1.415(3) | C6-C11 | 1.423(2) |
| C7-C8 | 1.376(3) | C7-H7 | 0.95 |
| C8-C9 | 1.403(3) | C8-H8 | 0.95 |
| C9-C10 | 1.399(3) | C9-C14 | 1.435(3) |
| C10-C11 | 1.389(3) | C10-H10 | 0.95 |
| C11-C12 | 1.505(3) | C12-H12 | 1.0 |
| C13-H13A | 0.98 | C13-H13B | 0.98 |
| C13-H13C | 0.98 | | |

Table 6. Bond angles (°) for 9b.

| | | | |
|-------------|------------|-------------|------------|
| C12-O1-C1 | 111.11(18) | C6-N1-C5 | 119.65(17) |
| C6-N1-C13 | 120.60(19) | C5-N1-C13 | 115.74(18) |
| O1-C1-C2 | 111.16(18) | O1-C1-H1A | 109.4 |
| C2-C1-H1A | 109.4 | O1-C1-H1B | 109.4 |
| C2-C1-H1B | 109.4 | H1A-C1-H1B | 108.0 |
| C1-C2-C3 | 110.0(2) | C1-C2-H2A | 109.7 |
| C3-C2-H2A | 109.7 | C1-C2-H2B | 109.7 |
| C3-C2-H2B | 109.7 | H2A-C2-H2B | 108.2 |
| C2-C3-C4 | 111.36(17) | C2-C3-H3A | 109.4 |
| C4-C3-H3A | 109.4 | C2-C3-H3B | 109.4 |
| C4-C3-H3B | 109.4 | H3A-C3-H3B | 108.0 |
| C5-C4-C12 | 109.02(16) | C5-C4-C3 | 112.51(19) |
| C12-C4-C3 | 110.52(17) | C5-C4-H4 | 108.2 |
| C12-C4-H4 | 108.2 | C3-C4-H4 | 108.2 |
| N1-C5-C4 | 111.34(17) | N1-C5-H5A | 109.4 |
| C4-C5-H5A | 109.4 | N1-C5-H5B | 109.4 |
| C4-C5-H5B | 109.4 | H5A-C5-H5B | 108.0 |
| N1-C6-C7 | 121.25(18) | N1-C6-C11 | 120.62(18) |
| C7-C6-C11 | 118.09(18) | C8-C7-C6 | 121.40(19) |
| C8-C7-H7 | 119.3 | C6-C7-H7 | 119.3 |
| C7-C8-C9 | 120.5(2) | C7-C8-H8 | 119.8 |
| C9-C8-H8 | 119.8 | C10-C9-C8 | 118.91(19) |
| C10-C9-C14 | 120.7(2) | C8-C9-C14 | 120.4(2) |
| C11-C10-C9 | 121.47(19) | C11-C10-H10 | 119.3 |
| C9-C10-H10 | 119.3 | C10-C11-C6 | 119.65(18) |
| C10-C11-C12 | 119.67(18) | C6-C11-C12 | 120.67(17) |
| O1-C12-C11 | 107.06(16) | O1-C12-C4 | 110.68(18) |
| C11-C12-C4 | 111.17(16) | O1-C12-H12 | 109.3 |
| C11-C12-H12 | 109.3 | C4-C12-H12 | 109.3 |
| N1-C13-H13A | 109.5 | N1-C13-H13B | 109.5 |

| | | | |
|---------------|----------|---------------|-------|
| H13A-C13-H13B | 109.5 | N1-C13-H13C | 109.5 |
| H13A-C13-H13C | 109.5 | H13B-C13-H13C | 109.5 |
| N2-C14-C9 | 178.8(3) | | |

Table 7. Torsion angles (°) for 9b.

| | | | |
|----------------|-------------|----------------|-------------|
| C12-O1-C1-C2 | -62.7(3) | O1-C1-C2-C3 | 56.3(3) |
| C1-C2-C3-C4 | -50.7(3) | C2-C3-C4-C5 | -71.5(2) |
| C2-C3-C4-C12 | 50.6(3) | C6-N1-C5-C4 | -40.0(3) |
| C13-N1-C5-C4 | 162.36(18) | C12-C4-C5-N1 | 58.7(2) |
| C3-C4-C5-N1 | -178.29(17) | C5-N1-C6-C7 | -170.62(18) |
| C13-N1-C6-C7 | -14.1(3) | C5-N1-C6-C11 | 11.9(3) |
| C13-N1-C6-C11 | 168.38(18) | N1-C6-C7-C8 | -176.9(2) |
| C11-C6-C7-C8 | 0.7(3) | C6-C7-C8-C9 | 0.2(3) |
| C7-C8-C9-C10 | -0.3(3) | C7-C8-C9-C14 | -179.85(19) |
| C8-C9-C10-C11 | -0.4(3) | C14-C9-C10-C11 | 179.11(19) |
| C9-C10-C11-C6 | 1.3(3) | C9-C10-C11-C12 | -178.60(18) |
| N1-C6-C11-C10 | 176.2(2) | C7-C6-C11-C10 | -1.4(3) |
| N1-C6-C11-C12 | -3.9(3) | C7-C6-C11-C12 | 178.51(19) |
| C1-O1-C12-C11 | -176.66(18) | C1-O1-C12-C4 | 62.0(2) |
| C10-C11-C12-O1 | 83.2(2) | C6-C11-C12-O1 | -96.7(2) |
| C10-C11-C12-C4 | -155.83(19) | C6-C11-C12-C4 | 24.3(3) |
| C5-C4-C12-O1 | 68.5(2) | C3-C4-C12-O1 | -55.7(2) |
| C5-C4-C12-C11 | -50.4(2) | C3-C4-C12-C11 | -174.51(18) |

Table 8. Anisotropic atomic displacement parameters (Å²) for 9b.

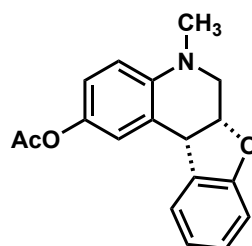
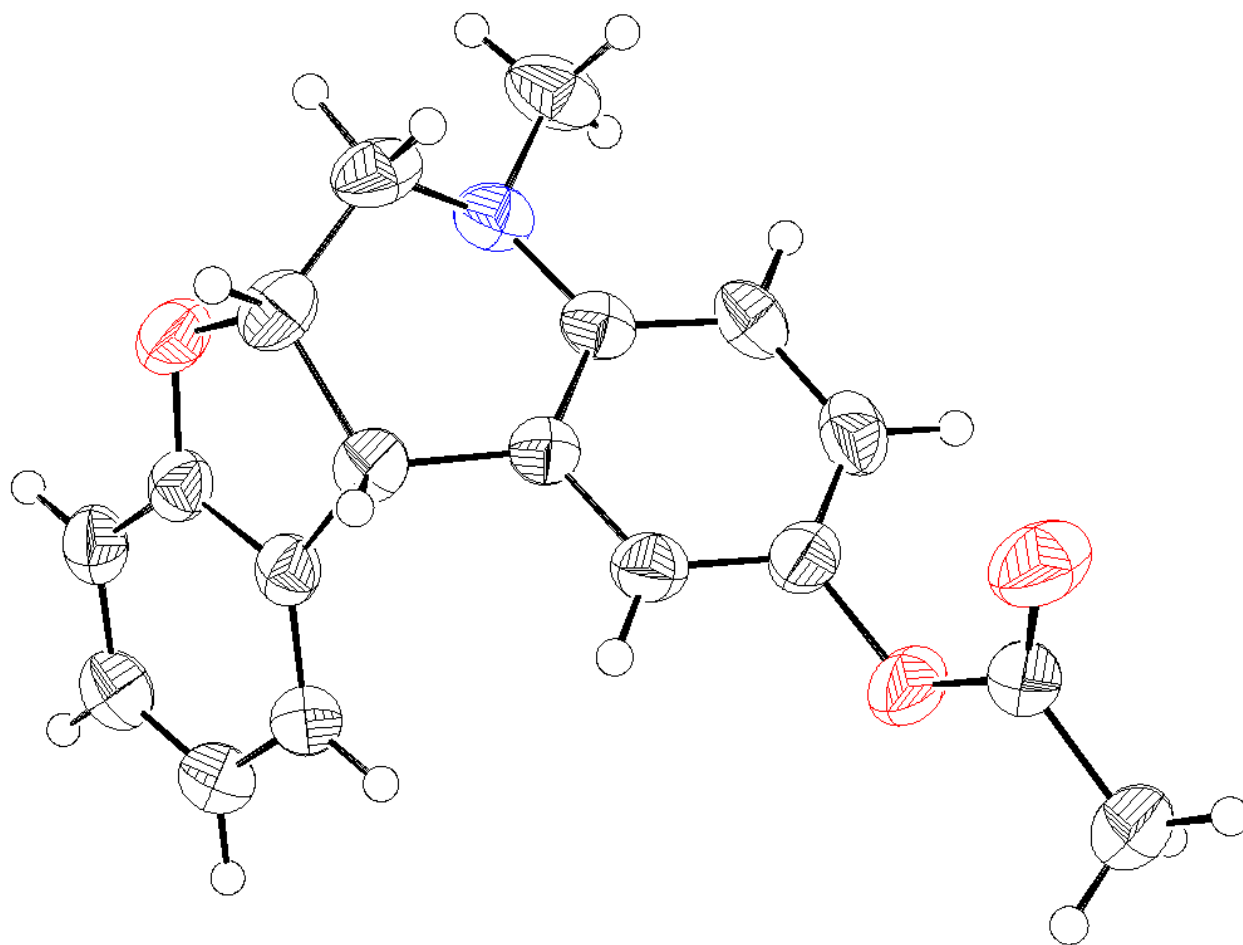
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| O1 | 0.0558(9) | 0.0270(7) | 0.0604(10) | 0.0078(7) | 0.0309(8) | 0.0045(6) |
| N1 | 0.0454(9) | 0.0403(10) | 0.0279(8) | -0.0008(7) | 0.0085(7) | -0.0007(8) |
| N2 | 0.0574(12) | 0.0398(11) | 0.0684(14) | -0.0127(10) | 0.0130(11) | 0.0007(9) |
| C1 | 0.0809(18) | 0.0286(11) | 0.0673(17) | 0.0102(10) | 0.0410(15) | 0.0040(10) |
| C2 | 0.0641(15) | 0.0263(10) | 0.0608(15) | 0.0070(10) | 0.0202(12) | 0.0071(10) |
| C3 | 0.0537(13) | 0.0342(11) | 0.0516(13) | 0.0032(10) | 0.0094(11) | 0.0146(10) |
| C4 | 0.0384(10) | 0.0346(10) | 0.0372(10) | -0.0009(8) | 0.0051(8) | 0.0062(8) |
| C5 | 0.0369(10) | 0.0370(11) | 0.0350(10) | -0.0039(8) | 0.0097(8) | 0.0020(8) |
| C6 | 0.0288(8) | 0.0342(9) | 0.0287(8) | 0.0019(7) | 0.0042(7) | -0.0008(7) |
| C7 | 0.0412(10) | 0.0389(12) | 0.0357(10) | 0.0087(9) | 0.0065(8) | -0.0041(9) |
| C8 | 0.0413(11) | 0.0316(10) | 0.0455(12) | 0.0065(9) | 0.0059(10) | -0.0038(8) |
| C9 | 0.0322(9) | 0.0304(9) | 0.0426(11) | -0.0013(8) | 0.0068(8) | -0.0010(7) |
| C10 | 0.0382(10) | 0.0312(10) | 0.0327(9) | 0.0004(7) | 0.0081(8) | 0.0004(7) |

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| C11 | 0.0345(9) | 0.0307(10) | 0.0303(9) | 0.0018(7) | 0.0072(8) | 0.0018(7) |
| C12 | 0.0468(11) | 0.0303(9) | 0.0305(9) | 0.0045(8) | 0.0093(8) | 0.0059(8) |
| C13 | 0.0447(12) | 0.0588(14) | 0.0277(9) | -0.0003(9) | 0.0066(8) | 0.0002(10) |
| C14 | 0.0375(10) | 0.0319(10) | 0.0527(12) | -0.0027(9) | 0.0089(9) | -0.0021(8) |

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for 9b.

| | x/a | y/b | z/c | U(equiv) |
|------|------------|------------|------------|-----------------|
| H1A | 0.2245 | 0.5663 | 0.7003 | 0.066 |
| H1B | 0.4233 | 0.5755 | 0.8155 | 0.066 |
| H2A | 0.3585 | 0.5262 | 0.4849 | 0.059 |
| H2B | 0.4317 | 0.4814 | 0.6451 | 0.059 |
| H3A | 0.6765 | 0.5170 | 0.5092 | 0.056 |
| H3B | 0.7122 | 0.5384 | 0.6985 | 0.056 |
| H4 | 0.7796 | 0.6328 | 0.5596 | 0.044 |
| H5A | 0.6227 | 0.6038 | 0.2926 | 0.043 |
| H5B | 0.4298 | 0.6212 | 0.3421 | 0.043 |
| H7 | 0.5555 | 0.8339 | 0.2687 | 0.047 |
| H8 | 0.5303 | 0.9188 | 0.4538 | 0.048 |
| H10 | 0.5331 | 0.7790 | 0.8112 | 0.041 |
| H12 | 0.6212 | 0.6631 | 0.7641 | 0.043 |
| H13A | 0.5932 | 0.6780 | 0.0860 | 0.066 |
| H13B | 0.6345 | 0.7562 | 0.1249 | 0.066 |
| H13C | 0.4280 | 0.7284 | 0.0986 | 0.066 |



10a

A clear colourless rod-like specimen of $C_{18}H_{17}NO_3$, approximate dimensions 0.051 mm x 0.091 mm x 0.153 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 3030 frames were collected. The total exposure time was 15.15 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 22058 reflections to a maximum θ angle of 75.30° (0.80 Å resolution), of which 2987 were independent (average redundancy 7.385, completeness = 97.9%, $R_{int} = 4.49\%$, $R_{sig} = 2.58\%$) and 2439 (81.65%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 26.7013(15)$ Å, $b = 12.0354(7)$ Å, $c = 9.2059(6)$ Å, $\beta = 93.351(4)^\circ$, volume = $2953.4(3)$ Å³, are based upon the refinement of the XYZ-centroids of 4604 reflections above $20 \sigma(I)$ with $6.632^\circ < 2\theta < 148.1^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.948. The

Calcd. minimum and maximum transmission coefficients (based on crystal size) are 0.8960 and 0.9630.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $C 1 2/c 1$, with $Z = 8$ for the formula unit, $C_{18}H_{17}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 201 variables converged at $R1 = 3.83\%$, for the observed data and $wR2 = 11.00\%$ for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was $0.187 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.137 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.031 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the Calcd. density was 1.328 g/cm^3 and $F(000)$, 1248 e^- .

Table 1. Sample and crystal data for 10a.

| | |
|-------------------------------|--|
| Identification code | 10a |
| Chemical formula | $C_{18}H_{17}NO_3$ |
| Formula weight | 295.32 g/mol |
| Temperature | 200(2) K |
| Wavelength | 1.54178 Å |
| Crystal size | 0.051 x 0.091 x 0.153 mm |
| Crystal habit | clear colourless rod |
| Crystal system | monoclinic |
| Space group | $C 1 2/c 1$ |
| Unit cell dimensions | $a = 26.7013(15) \text{ \AA}$ $\alpha = 90^\circ$ $b = 12.0354(7) \text{ \AA}$ $\beta = 93.351(4)^\circ$ $c = 9.2059(6) \text{ \AA}$ $\gamma = 90^\circ$ |
| Volume | $2953.4(3) \text{ \AA}^3$ |
| Z | 8 |
| Density (Calcd.) | 1.328 g/cm^3 |
| Absorption coefficient | 0.735 mm^{-1} |
| F(000) | 1248 |

Table 3. Data collection and structure refinement for 10a.

| | |
|--|--|
| Theta range for data collection | 3.32 to 75.30° |
| Index ranges | $-33 \leq h \leq 33$, $-15 \leq k \leq 15$, $-11 \leq l \leq 11$ |
| Reflections collected | 22058 |
| Independent reflections | 2987 [$R(\text{int}) = 0.0449$] |
| Coverage of independent reflections | 97.9% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9630 and 0.8960 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | $\sum w(F_o^2 - F_c^2)^2$ |

| | |
|--|---|
| Data / restraints / parameters | 2987 / 0 / 201 |
| Goodness-of-fit on F² | 1.044 |
| Δ/σ_{\max} | 0.001 |
| Final R indices | 2439 data; $l > 2\sigma(l)$ R1 = 0.0383, wR2 = 0.1041 all data R1 = 0.0482, wR2 = 0.1100 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.7544P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole | 0.187 and -0.137 eÅ ⁻³ |
| R.M.S. deviation from mean | 0.031 eÅ ⁻³ |

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 10a.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|------------|-------------|-------------|-----------------|
| O1 | 0.71226(4) | 0.65221(8) | 0.31717(11) | 0.0500(3) |
| O2 | 0.59533(4) | 0.12154(9) | 0.27486(13) | 0.0595(3) |
| O3 | 0.54164(5) | 0.12584(9) | 0.07974(13) | 0.0652(3) |
| N1 | 0.60542(4) | 0.58101(10) | 0.35674(12) | 0.0432(3) |
| C1 | 0.63938(5) | 0.41128(11) | 0.26280(13) | 0.0358(3) |
| C2 | 0.63587(5) | 0.29766(11) | 0.24024(15) | 0.0422(3) |
| C3 | 0.59544(5) | 0.23854(11) | 0.28726(16) | 0.0448(3) |
| C4 | 0.55740(5) | 0.29093(13) | 0.35407(16) | 0.0483(4) |
| C5 | 0.55989(5) | 0.40470(13) | 0.37467(15) | 0.0454(3) |
| C6 | 0.60070(5) | 0.46641(11) | 0.33231(13) | 0.0378(3) |
| C7 | 0.62575(6) | 0.64071(12) | 0.23508(16) | 0.0508(4) |
| C8 | 0.67775(6) | 0.60199(12) | 0.20770(14) | 0.0460(3) |
| C9 | 0.68506(5) | 0.47436(11) | 0.21733(13) | 0.0388(3) |
| C10 | 0.72997(5) | 0.46555(11) | 0.32495(14) | 0.0376(3) |
| C11 | 0.75748(5) | 0.37522(12) | 0.37529(16) | 0.0462(3) |
| C12 | 0.79756(6) | 0.39241(14) | 0.47663(18) | 0.0546(4) |
| C13 | 0.80914(6) | 0.49827(14) | 0.52671(18) | 0.0537(4) |
| C14 | 0.78205(5) | 0.58995(13) | 0.47666(16) | 0.0471(3) |
| C15 | 0.74282(5) | 0.57061(11) | 0.37524(14) | 0.0394(3) |
| C16 | 0.56613(5) | 0.07363(12) | 0.16785(16) | 0.0454(3) |
| C17 | 0.56883(6) | 0.94996(13) | 0.1772(2) | 0.0610(4) |
| C18 | 0.56345(6) | 0.63717(15) | 0.41897(19) | 0.0606(4) |

Table 5. Bond lengths (Å) for 10a.

| | | | |
|--------|------------|-------|------------|
| O1-C15 | 1.3657(16) | O1-C8 | 1.4567(17) |
| O2-C16 | 1.3494(17) | O2-C3 | 1.4128(17) |
| O3-C16 | 1.1909(17) | N1-C6 | 1.4019(17) |

| | | | |
|----------|------------|----------|------------|
| N1-C18 | 1.4546(18) | N1-C7 | 1.462(2) |
| C1-C2 | 1.3854(18) | C1-C6 | 1.4120(18) |
| C1-C9 | 1.5163(18) | C2-C3 | 1.383(2) |
| C2-H2 | 0.95 | C3-C4 | 1.371(2) |
| C4-C5 | 1.383(2) | C4-H4 | 0.95 |
| C5-C6 | 1.3930(19) | C5-H5 | 0.95 |
| C7-C8 | 1.500(2) | C7-H7A | 0.99 |
| C7-H7B | 0.99 | C8-C9 | 1.5503(19) |
| C8-H8 | 1.0 | C9-C10 | 1.5138(19) |
| C9-H9 | 1.0 | C10-C11 | 1.3771(19) |
| C10-C15 | 1.3829(18) | C11-C12 | 1.393(2) |
| C11-H11 | 0.95 | C12-C13 | 1.384(2) |
| C12-H12 | 0.95 | C13-C14 | 1.384(2) |
| C13-H13 | 0.95 | C14-C15 | 1.3815(19) |
| C14-H14 | 0.95 | C16-C17 | 1.492(2) |
| C17-H17A | 0.98 | C17-H17B | 0.98 |
| C17-H17C | 0.98 | C18-H18A | 0.98 |
| C18-H18B | 0.98 | C18-H18C | 0.98 |

Table 6. Bond angles (°) for 10a.

| | | | |
|------------|------------|-------------|------------|
| C15-O1-C8 | 108.17(10) | C16-O2-C3 | 118.90(11) |
| C6-N1-C18 | 117.15(12) | C6-N1-C7 | 113.24(11) |
| C18-N1-C7 | 113.74(13) | C2-C1-C6 | 119.14(12) |
| C2-C1-C9 | 120.08(12) | C6-C1-C9 | 120.75(12) |
| C3-C2-C1 | 120.53(13) | C3-C2-H2 | 119.7 |
| C1-C2-H2 | 119.7 | C4-C3-C2 | 121.05(13) |
| C4-C3-O2 | 119.76(13) | C2-C3-O2 | 119.05(13) |
| C3-C4-C5 | 119.05(13) | C3-C4-H4 | 120.5 |
| C5-C4-H4 | 120.5 | C4-C5-C6 | 121.43(13) |
| C4-C5-H5 | 119.3 | C6-C5-H5 | 119.3 |
| C5-C6-N1 | 122.96(12) | C5-C6-C1 | 118.76(13) |
| N1-C6-C1 | 118.28(12) | N1-C7-C8 | 111.41(11) |
| N1-C7-H7A | 109.3 | C8-C7-H7A | 109.3 |
| N1-C7-H7B | 109.3 | C8-C7-H7B | 109.3 |
| H7A-C7-H7B | 108.0 | O1-C8-C7 | 108.01(11) |
| O1-C8-C9 | 107.40(11) | C7-C8-C9 | 114.40(12) |
| O1-C8-H8 | 109.0 | C7-C8-H8 | 109.0 |
| C9-C8-H8 | 109.0 | C10-C9-C1 | 113.80(10) |
| C10-C9-C8 | 101.49(10) | C1-C9-C8 | 114.28(11) |
| C10-C9-H9 | 109.0 | C1-C9-H9 | 109.0 |
| C8-C9-H9 | 109.0 | C11-C10-C15 | 119.48(13) |

| | | | |
|---------------|------------|---------------|------------|
| C11-C10-C9 | 131.46(12) | C15-C10-C9 | 109.07(12) |
| C10-C11-C12 | 118.80(14) | C10-C11-H11 | 120.6 |
| C12-C11-H11 | 120.6 | C13-C12-C11 | 120.51(14) |
| C13-C12-H12 | 119.7 | C11-C12-H12 | 119.7 |
| C14-C13-C12 | 121.39(14) | C14-C13-H13 | 119.3 |
| C12-C13-H13 | 119.3 | C15-C14-C13 | 116.86(13) |
| C15-C14-H14 | 121.6 | C13-C14-H14 | 121.6 |
| O1-C15-C14 | 123.74(12) | O1-C15-C10 | 113.30(12) |
| C14-C15-C10 | 122.95(13) | O3-C16-O2 | 122.86(14) |
| O3-C16-C17 | 126.02(14) | O2-C16-C17 | 111.12(12) |
| C16-C17-H17A | 109.5 | C16-C17-H17B | 109.5 |
| H17A-C17-H17B | 109.5 | C16-C17-H17C | 109.5 |
| H17A-C17-H17C | 109.5 | H17B-C17-H17C | 109.5 |
| N1-C18-H18A | 109.5 | N1-C18-H18B | 109.5 |
| H18A-C18-H18B | 109.5 | N1-C18-H18C | 109.5 |
| H18A-C18-H18C | 109.5 | H18B-C18-H18C | 109.5 |

Table 7. Torsion angles (°) for 10a.

| | | | |
|-----------------|-------------|-----------------|-------------|
| C6-C1-C2-C3 | -1.06(18) | C9-C1-C2-C3 | 177.05(11) |
| C1-C2-C3-C4 | 1.52(19) | C1-C2-C3-O2 | -174.11(12) |
| C16-O2-C3-C4 | 80.35(17) | C16-O2-C3-C2 | -103.97(15) |
| C2-C3-C4-C5 | -0.2(2) | O2-C3-C4-C5 | 175.41(12) |
| C3-C4-C5-C6 | -1.6(2) | C4-C5-C6-N1 | -177.38(12) |
| C4-C5-C6-C1 | 2.02(18) | C18-N1-C6-C5 | -4.90(18) |
| C7-N1-C6-C5 | -140.35(13) | C18-N1-C6-C1 | 175.71(12) |
| C7-N1-C6-C1 | 40.26(15) | C2-C1-C6-C5 | -0.67(17) |
| C9-C1-C6-C5 | -178.77(11) | C2-C1-C6-N1 | 178.75(11) |
| C9-C1-C6-N1 | 0.65(17) | C6-N1-C7-C8 | -62.02(15) |
| C18-N1-C7-C8 | 160.98(12) | C15-O1-C8-C7 | 131.53(12) |
| C15-O1-C8-C9 | 7.67(14) | N1-C7-C8-O1 | -77.57(14) |
| N1-C7-C8-C9 | 41.96(16) | C2-C1-C9-C10 | -80.60(14) |
| C6-C1-C9-C10 | 97.48(14) | C2-C1-C9-C8 | 163.44(11) |
| C6-C1-C9-C8 | -18.48(16) | O1-C8-C9-C10 | -6.97(13) |
| C7-C8-C9-C10 | -126.84(12) | O1-C8-C9-C1 | 115.94(12) |
| C7-C8-C9-C1 | -3.93(16) | C1-C9-C10-C11 | 60.91(18) |
| C8-C9-C10-C11 | -175.85(14) | C1-C9-C10-C15 | -119.18(12) |
| C8-C9-C10-C15 | 4.07(13) | C15-C10-C11-C12 | 0.3(2) |
| C9-C10-C11-C12 | -179.77(13) | C10-C11-C12-C13 | 0.6(2) |
| C11-C12-C13-C14 | -1.0(2) | C12-C13-C14-C15 | 0.4(2) |
| C8-O1-C15-C14 | 176.15(12) | C8-O1-C15-C10 | -5.25(14) |
| C13-C14-C15-O1 | 179.09(13) | C13-C14-C15-C10 | 0.6(2) |

| | | | |
|-----------------|-------------|----------------|-------------|
| C11-C10-C15-O1 | -179.59(12) | C9-C10-C15-O1 | 0.49(15) |
| C11-C10-C15-C14 | -1.0(2) | C9-C10-C15-C14 | 179.10(12) |
| C3-O2-C16-O3 | 2.7(2) | C3-O2-C16-C17 | -176.89(13) |

Table 8. Anisotropic atomic displacement parameters (\AA^2) for 10a.

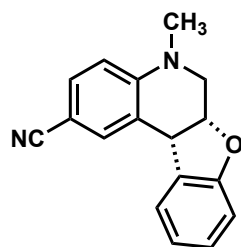
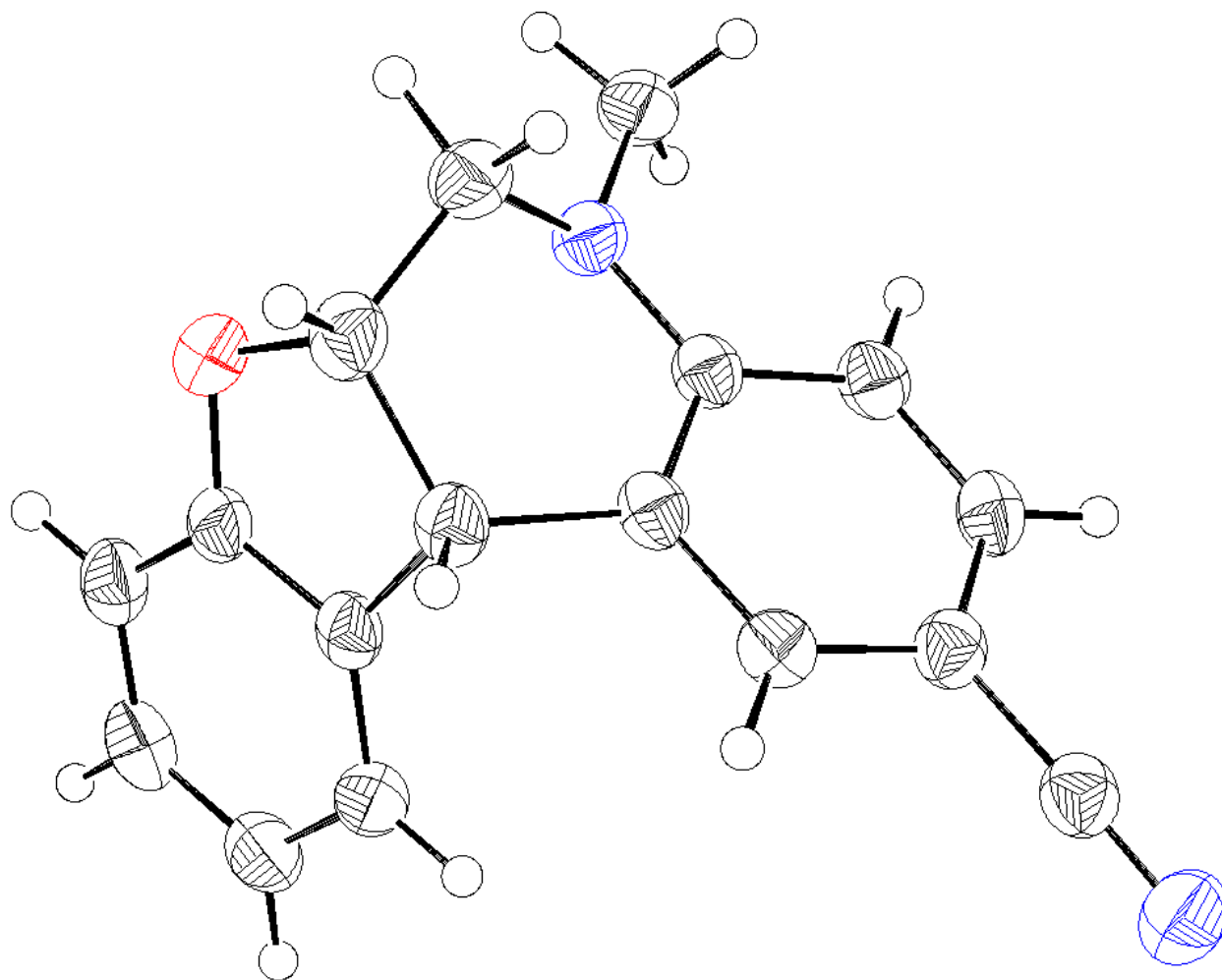
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|-----------|------------|------------|------------|------------|------------|
| O1 | 0.0557(6) | 0.0345(5) | 0.0590(6) | 0.0017(4) | -0.0026(5) | -0.0048(4) |
| O2 | 0.0576(6) | 0.0381(6) | 0.0791(8) | 0.0097(5) | -0.0259(6) | -0.0038(5) |
| O3 | 0.0813(8) | 0.0441(6) | 0.0666(7) | -0.0014(5) | -0.0256(6) | 0.0055(6) |
| N1 | 0.0434(6) | 0.0443(7) | 0.0413(6) | -0.0102(5) | -0.0031(5) | 0.0072(5) |
| C1 | 0.0374(6) | 0.0381(7) | 0.0316(6) | -0.0005(5) | -0.0008(5) | 0.0014(5) |
| C2 | 0.0408(7) | 0.0400(7) | 0.0451(7) | -0.0025(6) | -0.0034(6) | 0.0043(6) |
| C3 | 0.0450(7) | 0.0367(7) | 0.0507(8) | 0.0057(6) | -0.0147(6) | -0.0028(6) |
| C4 | 0.0376(7) | 0.0593(9) | 0.0467(8) | 0.0064(6) | -0.0080(6) | -0.0093(6) |
| C5 | 0.0332(6) | 0.0617(9) | 0.0407(7) | -0.0060(6) | -0.0021(5) | 0.0003(6) |
| C6 | 0.0383(7) | 0.0446(7) | 0.0295(6) | -0.0041(5) | -0.0063(5) | 0.0038(5) |
| C7 | 0.0642(9) | 0.0397(8) | 0.0465(8) | 0.0026(6) | -0.0135(7) | 0.0077(7) |
| C8 | 0.0599(9) | 0.0418(8) | 0.0362(7) | 0.0070(5) | 0.0015(6) | -0.0029(7) |
| C9 | 0.0465(7) | 0.0386(7) | 0.0319(6) | -0.0024(5) | 0.0077(6) | 0.0002(6) |
| C10 | 0.0389(7) | 0.0388(7) | 0.0361(6) | -0.0013(5) | 0.0108(5) | -0.0026(5) |
| C11 | 0.0420(7) | 0.0395(8) | 0.0576(8) | -0.0024(6) | 0.0069(6) | 0.0010(6) |
| C12 | 0.0425(8) | 0.0514(9) | 0.0694(10) | 0.0056(7) | -0.0007(7) | 0.0048(7) |
| C13 | 0.0413(8) | 0.0622(10) | 0.0570(9) | -0.0016(7) | -0.0012(7) | -0.0028(7) |
| C14 | 0.0433(7) | 0.0472(8) | 0.0514(8) | -0.0070(6) | 0.0077(6) | -0.0091(6) |
| C15 | 0.0425(7) | 0.0379(7) | 0.0388(7) | 0.0015(5) | 0.0106(5) | -0.0028(6) |
| C16 | 0.0403(7) | 0.0394(8) | 0.0560(8) | 0.0025(6) | -0.0020(6) | -0.0015(6) |
| C17 | 0.0590(9) | 0.0393(8) | 0.0836(12) | 0.0053(8) | -0.0047(9) | -0.0043(7) |
| C18 | 0.0505(9) | 0.0668(11) | 0.0632(10) | -0.0248(8) | -0.0069(8) | 0.0178(8) |

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 10a.

| | x/a | y/b | z/c | $U(\text{equiv})$ |
|-----|--------|--------|--------|-------------------|
| H2 | 0.6614 | 0.2601 | 0.1921 | 0.051 |
| H4 | 0.5297 | 0.2497 | 0.3858 | 0.058 |
| H5 | 0.5332 | 0.4415 | 0.4187 | 0.054 |
| H7A | 0.6265 | 0.7213 | 0.2567 | 0.061 |
| H7B | 0.6036 | 0.6290 | 0.1464 | 0.061 |
| H8 | 0.6866 | 0.6279 | 0.1092 | 0.055 |
| H9 | 0.6946 | 0.4460 | 0.1207 | 0.047 |

| | x/a | y/b | z/c | U(equiv) |
|------|------------|------------|------------|-----------------|
| H11 | 0.7493 | 0.3025 | 0.3415 | 0.055 |
| H12 | 0.8171 | 0.3310 | 0.5116 | 0.066 |
| H13 | 0.8363 | 0.5082 | 0.5969 | 0.064 |
| H14 | 0.7900 | 0.6628 | 0.5105 | 0.057 |
| H17A | 0.5445 | -0.0827 | 0.1057 | 0.091 |
| H17B | 0.5611 | -0.0739 | 0.2751 | 0.091 |
| H17C | 0.6027 | -0.0747 | 0.1567 | 0.091 |
| H18A | 0.5715 | 0.7160 | 0.4330 | 0.091 |
| H18B | 0.5571 | 0.6034 | 0.5130 | 0.091 |
| H18C | 0.5335 | 0.6299 | 0.3529 | 0.091 |



10b

A specimen of $C_{17}H_{14}N_2O$, approximate dimensions 0.107 mm x 0.136 mm x 0.307 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 2.89 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 12545 reflections to a maximum θ angle of 27.56° (0.77 Å resolution), of which 3021 were independent (average redundancy 4.153, completeness = 99.9%, $R_{\text{int}} = 5.81\%$, $R_{\text{sig}} = 5.95\%$) and 1965 (65.04%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.0288(15)$ Å, $b = 9.0998(17)$ Å, $c = 9.3548(17)$ Å, $\alpha = 105.078(2)^\circ$, $\beta = 96.405(2)^\circ$, $\gamma = 91.196(2)^\circ$, volume = $654.9(2)$ Å³, are based upon the refinement of the XYZ-centroids of 2883 reflections above $20 \sigma(I)$ with $4.544^\circ < 2\theta < 53.95^\circ$. Data were corrected for

absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.965. The Calcd. minimum and maximum transmission coefficients (based on crystal size) are 0.9750 and 0.9910.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, C₁₇H₁₄N₂O. The final anisotropic full-matrix least-squares refinement on F² with 182 variables converged at R1 = 5.49%, for the observed data and wR2 = 13.49% for all data. The goodness-of-fit was 1.012. The largest peak in the final difference electron density synthesis was 0.186 e⁻/Å³ and the largest hole was -0.200 e⁻/Å³ with an RMS deviation of 0.045 e⁻/Å³. On the basis of the final model, the Calcd. density was 1.330 g/cm³ and F(000), 276 e⁻.

Table 1. Sample and crystal data for 10b.

| | |
|-------------------------------|--|
| Identification code | 10b |
| Chemical formula | C ₁₇ H ₁₄ N ₂ O |
| Formula weight | 262.30 g/mol |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal size | 0.107 x 0.136 x 0.307 mm |
| Crystal system | triclinic |
| Space group | P -1 |
| Unit cell dimensions | a = 8.0288(15) Å α = 105.078(2)° b = 9.0998(17) Å β = 96.405(2)° c = 9.3548(17) Å γ = 91.196(2)° |
| Volume | 654.9(2) Å ³ |
| Z | 2 |
| Density (Calcd.) | 1.330 g/cm ³ |
| Absorption coefficient | 0.084 mm ⁻¹ |
| F(000) | 276 |

Table 2. Data collection and structure refinement for 10b.

| | |
|--|------------------------------------|
| Theta range for data collection | 2.27 to 27.56° |
| Index ranges | -10<=h<=10, -11<=k<=11, -12<=l<=12 |
| Reflections collected | 12545 |
| Independent reflections | 3021 [R(int) = 0.0581] |
| Coverage of independent reflections | 99.9% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9910 and 0.9750 |

| | |
|--|---|
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3021 / 0 / 182 |
| Goodness-of-fit on F^2 | 1.012 |
| Final R indices | 1965 data; $I > 2\sigma(I)$ R1 = 0.0549, wR2 = 0.1171 all data R1 = 0.0916, wR2 = 0.1349 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.1080P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole | 0.186 and -0.200 $e\text{\AA}^{-3}$ |
| R.M.S. deviation from mean | 0.045 $e\text{\AA}^{-3}$ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for 10b.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|-------------|-------------|-------------|-----------------|
| O1 | 0.52500(18) | 0.96970(15) | 0.71074(15) | 0.0447(4) |
| N1 | 0.0404(2) | 0.2259(2) | 0.8263(2) | 0.0508(5) |
| N2 | 0.65103(19) | 0.71283(16) | 0.48062(16) | 0.0346(4) |
| C1 | 0.7807(2) | 0.65641(19) | 0.70204(19) | 0.0302(4) |
| C2 | 0.8628(2) | 0.5570(2) | 0.7707(2) | 0.0326(4) |
| C3 | 0.8865(2) | 0.4071(2) | 0.6911(2) | 0.0334(4) |
| C4 | 0.8230(2) | 0.3577(2) | 0.5404(2) | 0.0360(4) |
| C5 | 0.7438(2) | 0.4561(2) | 0.4694(2) | 0.0344(4) |
| C6 | 0.7240(2) | 0.6077(2) | 0.54725(19) | 0.0306(4) |
| C7 | 0.7231(3) | 0.8691(2) | 0.5410(2) | 0.0398(5) |
| C8 | 0.6992(2) | 0.9282(2) | 0.7028(2) | 0.0385(5) |
| C9 | 0.7322(2) | 0.8092(2) | 0.7937(2) | 0.0333(4) |
| C10 | 0.5645(2) | 0.79735(19) | 0.85086(19) | 0.0310(4) |
| C11 | 0.5107(2) | 0.7109(2) | 0.9397(2) | 0.0381(5) |
| C12 | 0.3465(3) | 0.7223(2) | 0.9759(2) | 0.0425(5) |
| C13 | 0.2404(3) | 0.8195(2) | 0.9236(2) | 0.0428(5) |
| C14 | 0.2925(3) | 0.9071(2) | 0.8339(2) | 0.0408(5) |
| C15 | 0.4559(2) | 0.8922(2) | 0.79906(19) | 0.0333(4) |
| C16 | 0.9726(2) | 0.3063(2) | 0.7654(2) | 0.0371(5) |

| | x/a | y/b | z/c | U(equiv) |
|-----|------------|------------|------------|-----------------|
| C17 | 0.5881(3) | 0.6671(2) | 0.3227(2) | 0.0404(5) |

Table 4. Bond lengths (Å) for 10b.

| | | | |
|----------|----------|----------|----------|
| O1-C15 | 1.370(2) | O1-C8 | 1.462(2) |
| N1-C16 | 1.149(2) | N2-C6 | 1.378(2) |
| N2-C17 | 1.454(2) | N2-C7 | 1.467(2) |
| C1-C2 | 1.378(2) | C1-C6 | 1.418(2) |
| C1-C9 | 1.516(2) | C2-C3 | 1.402(3) |
| C2-H2 | 0.95 | C3-C4 | 1.396(3) |
| C3-C16 | 1.433(3) | C4-C5 | 1.374(3) |
| C4-H4 | 0.95 | C5-C6 | 1.403(2) |
| C5-H5 | 0.95 | C7-C8 | 1.504(3) |
| C7-H7A | 0.99 | C7-H7B | 0.99 |
| C8-C9 | 1.551(3) | C8-H8 | 1.0 |
| C9-C10 | 1.515(3) | C9-H9 | 1.0 |
| C10-C15 | 1.377(3) | C10-C11 | 1.379(3) |
| C11-C12 | 1.396(3) | C11-H11 | 0.95 |
| C12-C13 | 1.383(3) | C12-H12 | 0.95 |
| C13-C14 | 1.388(3) | C13-H13 | 0.95 |
| C14-C15 | 1.387(3) | C14-H14 | 0.95 |
| C17-H17A | 0.98 | C17-H17B | 0.98 |
| C17-H17C | 0.98 | | |

Table 5. Bond angles (°) for 10b.

| | | | |
|-----------|------------|-----------|------------|
| C15-O1-C8 | 108.09(14) | C6-N2-C17 | 119.67(15) |
| C6-N2-C7 | 114.63(15) | C17-N2-C7 | 116.86(15) |
| C2-C1-C6 | 119.37(16) | C2-C1-C9 | 120.40(16) |
| C6-C1-C9 | 119.81(16) | C1-C2-C3 | 121.10(17) |
| C1-C2-H2 | 119.5 | C3-C2-H2 | 119.5 |
| C4-C3-C2 | 119.16(17) | C4-C3-C16 | 120.99(17) |
| C2-C3-C16 | 119.84(17) | C5-C4-C3 | 120.53(17) |
| C5-C4-H4 | 119.7 | C3-C4-H4 | 119.7 |
| C4-C5-C6 | 120.62(17) | C4-C5-H5 | 119.7 |
| C6-C5-H5 | 119.7 | N2-C6-C5 | 123.13(16) |
| N2-C6-C1 | 117.76(16) | C5-C6-C1 | 119.11(16) |

| | | | |
|---------------|------------|---------------|------------|
| N2-C7-C8 | 110.82(15) | N2-C7-H7A | 109.5 |
| C8-C7-H7A | 109.5 | N2-C7-H7B | 109.5 |
| C8-C7-H7B | 109.5 | H7A-C7-H7B | 108.1 |
| O1-C8-C7 | 108.02(15) | O1-C8-C9 | 107.49(15) |
| C7-C8-C9 | 113.42(15) | O1-C8-H8 | 109.3 |
| C7-C8-H8 | 109.3 | C9-C8-H8 | 109.3 |
| C10-C9-C1 | 111.81(14) | C10-C9-C8 | 101.60(14) |
| C1-C9-C8 | 113.84(15) | C10-C9-H9 | 109.8 |
| C1-C9-H9 | 109.8 | C8-C9-H9 | 109.8 |
| C15-C10-C11 | 119.64(18) | C15-C10-C9 | 109.32(16) |
| C11-C10-C9 | 131.04(17) | C10-C11-C12 | 119.04(18) |
| C10-C11-H11 | 120.5 | C12-C11-H11 | 120.5 |
| C13-C12-C11 | 120.15(19) | C13-C12-H12 | 119.9 |
| C11-C12-H12 | 119.9 | C12-C13-C14 | 121.53(19) |
| C12-C13-H13 | 119.2 | C14-C13-H13 | 119.2 |
| C15-C14-C13 | 116.87(18) | C15-C14-H14 | 121.6 |
| C13-C14-H14 | 121.6 | O1-C15-C10 | 113.48(17) |
| O1-C15-C14 | 123.76(17) | C10-C15-C14 | 122.76(18) |
| N1-C16-C3 | 179.2(2) | N2-C17-H17A | 109.5 |
| N2-C17-H17B | 109.5 | H17A-C17-H17B | 109.5 |
| N2-C17-H17C | 109.5 | H17A-C17-H17C | 109.5 |
| H17B-C17-H17C | 109.5 | | |

Table 6. Torsion angles (°) for 10b.

| | | | |
|--------------|-------------|--------------|-------------|
| C6-C1-C2-C3 | -2.1(3) | C9-C1-C2-C3 | 170.44(16) |
| C1-C2-C3-C4 | -1.1(3) | C1-C2-C3-C16 | 179.95(16) |
| C2-C3-C4-C5 | 2.4(3) | C16-C3-C4-C5 | -178.60(17) |
| C3-C4-C5-C6 | -0.6(3) | C17-N2-C6-C5 | 1.0(3) |
| C7-N2-C6-C5 | -145.43(17) | C17-N2-C6-C1 | -178.80(16) |
| C7-N2-C6-C1 | 34.8(2) | C4-C5-C6-N2 | 177.63(17) |
| C4-C5-C6-C1 | -2.6(3) | C2-C1-C6-N2 | -176.31(16) |
| C9-C1-C6-N2 | 11.1(2) | C2-C1-C6-C5 | 3.9(2) |
| C9-C1-C6-C5 | -168.69(16) | C6-N2-C7-C8 | -62.4(2) |
| C17-N2-C7-C8 | 150.20(17) | C15-O1-C8-C7 | 124.55(15) |
| C15-O1-C8-C9 | 1.81(18) | N2-C7-C8-O1 | -76.99(19) |
| N2-C7-C8-C9 | 42.1(2) | C2-C1-C9-C10 | -85.8(2) |

| | | | |
|-----------------|-------------|-----------------|-------------|
| C6-C1-C9-C10 | 86.7(2) | C2-C1-C9-C8 | 159.76(16) |
| C6-C1-C9-C8 | -27.7(2) | O1-C8-C9-C10 | -1.46(17) |
| C7-C8-C9-C10 | -120.80(16) | O1-C8-C9-C1 | 118.90(16) |
| C7-C8-C9-C1 | -0.4(2) | C1-C9-C10-C15 | -121.14(16) |
| C8-C9-C10-C15 | 0.64(17) | C1-C9-C10-C11 | 58.5(2) |
| C8-C9-C10-C11 | -179.73(18) | C15-C10-C11-C12 | -0.3(3) |
| C9-C10-C11-C12 | -179.95(17) | C10-C11-C12-C13 | -0.3(3) |
| C11-C12-C13-C14 | 0.4(3) | C12-C13-C14-C15 | 0.1(3) |
| C8-O1-C15-C10 | -1.47(19) | C8-O1-C15-C14 | 178.43(16) |
| C11-C10-C15-O1 | -179.20(15) | C9-C10-C15-O1 | 0.5(2) |
| C11-C10-C15-C14 | 0.9(3) | C9-C10-C15-C14 | -179.42(16) |
| C13-C14-C15-O1 | 179.33(16) | C13-C14-C15-C10 | -0.8(3) |

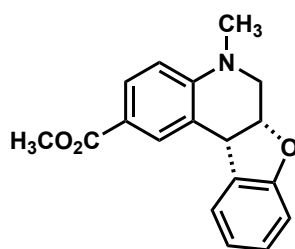
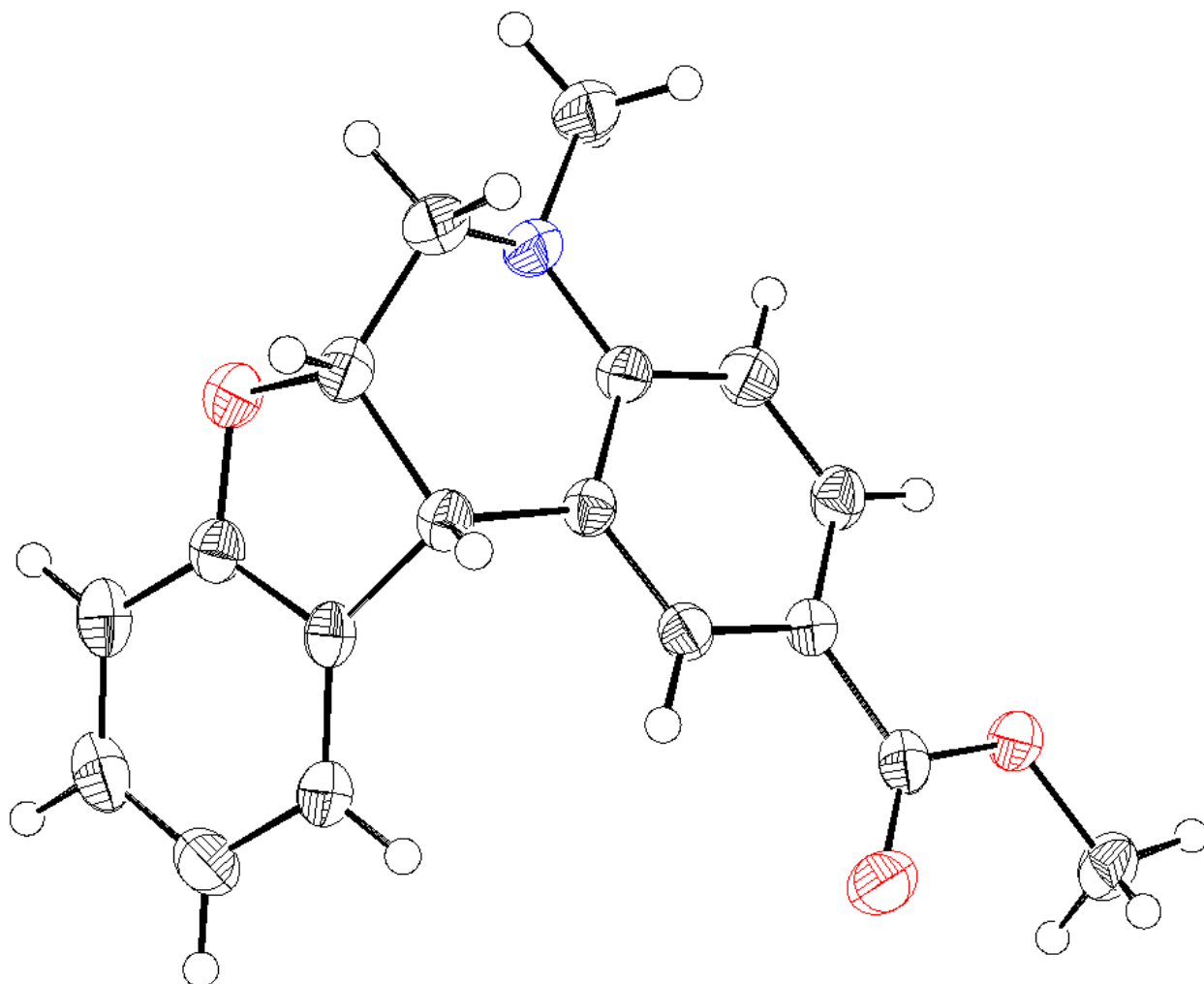
Table 7. Anisotropic atomic displacement parameters (\AA^2) for 10b.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|------------|------------|------------|------------|------------|------------|
| O1 | 0.0555(9) | 0.0369(8) | 0.0476(9) | 0.0173(7) | 0.0141(7) | 0.0152(6) |
| N1 | 0.0482(11) | 0.0523(11) | 0.0582(12) | 0.0236(10) | 0.0088(9) | 0.0133(9) |
| N2 | 0.0420(9) | 0.0295(8) | 0.0307(8) | 0.0063(7) | 0.0019(7) | 0.0011(7) |
| C1 | 0.0281(10) | 0.0295(10) | 0.0309(10) | 0.0035(8) | 0.0055(7) | -0.0006(7) |
| C2 | 0.0296(10) | 0.0362(10) | 0.0305(10) | 0.0069(8) | 0.0019(8) | 0.0003(8) |
| C3 | 0.0285(10) | 0.0347(10) | 0.0378(11) | 0.0101(8) | 0.0061(8) | 0.0038(8) |
| C4 | 0.0371(11) | 0.0293(10) | 0.0384(11) | 0.0016(8) | 0.0082(8) | 0.0033(8) |
| C5 | 0.0368(10) | 0.0334(10) | 0.0291(10) | 0.0016(8) | 0.0032(8) | 0.0012(8) |
| C6 | 0.0279(9) | 0.0315(10) | 0.0319(10) | 0.0067(8) | 0.0060(7) | 0.0006(7) |
| C7 | 0.0468(12) | 0.0326(10) | 0.0413(11) | 0.0116(9) | 0.0078(9) | -0.0015(9) |
| C8 | 0.0425(12) | 0.0287(10) | 0.0416(12) | 0.0047(8) | 0.0051(9) | -0.0013(8) |
| C9 | 0.0354(11) | 0.0296(9) | 0.0301(10) | 0.0013(8) | -0.0010(8) | 0.0009(8) |
| C10 | 0.0355(10) | 0.0266(9) | 0.0253(9) | -0.0014(7) | -0.0005(7) | 0.0016(7) |
| C11 | 0.0476(12) | 0.0362(10) | 0.0294(10) | 0.0072(8) | 0.0018(9) | 0.0073(9) |
| C12 | 0.0486(12) | 0.0398(11) | 0.0381(11) | 0.0056(9) | 0.0124(9) | 0.0007(9) |
| C13 | 0.0388(11) | 0.0428(12) | 0.0391(11) | -0.0037(9) | 0.0068(9) | 0.0029(9) |
| C14 | 0.0434(12) | 0.0378(11) | 0.0346(11) | -0.0001(9) | -0.0015(9) | 0.0106(9) |
| C15 | 0.0426(11) | 0.0265(9) | 0.0272(10) | 0.0010(8) | 0.0021(8) | 0.0048(8) |
| C16 | 0.0336(11) | 0.0375(11) | 0.0411(11) | 0.0102(9) | 0.0088(9) | 0.0025(8) |
| C17 | 0.0466(12) | 0.0420(11) | 0.0320(10) | 0.0097(9) | 0.0021(9) | 0.0034(9) |

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 10b.

| | x/a | y/b | z/c | U(equiv) |
|------|------------|------------|------------|-----------------|
| H2 | 0.9042 | 0.5906 | 0.8736 | 0.039 |
| H4 | 0.8346 | 0.2552 | 0.4865 | 0.043 |
| H5 | 0.7021 | 0.4214 | 0.3665 | 0.041 |
| H7A | 0.6684 | 0.9359 | 0.4836 | 0.048 |
| H7B | 0.8444 | 0.8711 | 0.5305 | 0.048 |
| H8 | 0.7754 | 1.0208 | 0.7487 | 0.046 |
| H9 | 0.8211 | 0.8510 | 0.8795 | 0.04 |
| H11 | 0.5842 | 0.6446 | 0.9757 | 0.046 |
| H12 | 0.3076 | 0.6630 | 1.0366 | 0.051 |
| H13 | 0.1293 | 0.8266 | 0.9496 | 0.051 |
| H14 | 0.2198 | 0.9741 | 0.7981 | 0.049 |
| H17A | 0.5340 | 0.7527 | 0.2944 | 0.061 |
| H17B | 0.5062 | 0.5807 | 0.3032 | 0.061 |
| H17C | 0.6816 | 0.6372 | 0.2642 | 0.061 |



10c

A colorless plate-like specimen of $C_{18}H_{17}NO_3$, approximate dimensions 0.100 mm x 0.267 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 1.15 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 16122 reflections to a maximum θ angle of 27.75° (0.76 Å resolution), of which 3361 were independent (average redundancy 4.797, completeness = 99.9%, $R_{int} = 6.89\%$, $R_{sig} = 5.87\%$) and 2211 (65.78%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 7.311(2)$ Å, $b = 8.940(2)$ Å, $c = 21.909(6)$ Å, $\beta = 93.044(4)^\circ$, volume = $1430.0(7)$ Å³, are based upon the refinement of the XYZ-centroids of 1427 reflections above $20\sigma(I)$ with $4.922^\circ < 2\theta < 44.08^\circ$. Data were corrected for absorption effects using the Multi-

Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.910. The Calcd. minimum and maximum transmission coefficients (based on crystal size) are 0.9720 and 0.9910.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, C₁₈H₁₇NO₃. The final anisotropic full-matrix least-squares refinement on F² with 201 variables converged at R1 = 5.21%, for the observed data and wR2 = 14.06% for all data. The goodness-of-fit was 1.004. The largest peak in the final difference electron density synthesis was 0.208 e⁻/Å³ and the largest hole was -0.247 e⁻/Å³ with an RMS deviation of 0.051 e⁻/Å³. On the basis of the final model, the Calcd. density was 1.372 g/cm³ and F(000), 624 e⁻.

Table 1. Sample and crystal data for 10c.

| | |
|-------------------------------|--|
| Identification code | 10c |
| Chemical formula | C ₁₈ H ₁₇ NO ₃ |
| Formula weight | 295.32 g/mol |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal size | 0.100 x 0.267 x 0.300 mm |
| Crystal habit | colorless plate |
| Crystal system | monoclinic |
| Space group | P 1 21/c 1 |
| Unit cell dimensions | a = 7.311(2) Å α = 90° b = 8.940(2) Å β = 93.044(4)° c = 21.909(6) Å γ = 90° |
| Volume | 1430.0(7) Å ³ |
| Z | 4 |
| Density (Calcd.) | 1.372 g/cm ³ |
| Absorption coefficient | 0.094 mm ⁻¹ |
| F(000) | 624 |

Table 2. Data collection and structure refinement for 10c.

| | |
|--|---|
| Theta range for data collection | 1.86 to 27.75° |
| Index ranges | -9<=h<=9, -11<=k<=11, -28<=l<=27 |
| Reflections collected | 16122 |
| Independent reflections | 3361 [R(int) = 0.0689] |
| Coverage of independent reflections | 99.9% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9910 and 0.9720 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on F ² |
| Refinement program | SHELXL-2018/3 (Sheldrick, 2018) |

| | |
|---|---|
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3361 / 0 / 201 |
| Goodness-of-fit on F² | 1.004 |
| Final R indices | 2211 data; $l > 2\sigma(l)$ R1 = 0.0521, wR2 = 0.1203 all data R1 = 0.0877, wR2 = 0.1406 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.0724P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole | 0.208 and -0.247 eÅ ⁻³ |
| R.M.S. deviation from mean | 0.051 eÅ ⁻³ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 10c.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|-------------|-------------|------------|-----------------|
| O1 | 0.95058(17) | 0.77503(13) | 0.77041(6) | 0.0344(3) |
| O2 | 0.28396(17) | 0.71183(14) | 0.47809(6) | 0.0346(3) |
| O3 | 0.25094(19) | 0.54131(16) | 0.55127(6) | 0.0460(4) |
| N1 | 0.0132(2) | 0.84332(17) | 0.64023(7) | 0.0319(4) |
| C1 | 0.7489(2) | 0.67807(18) | 0.63936(8) | 0.0248(4) |
| C2 | 0.5863(2) | 0.63282(19) | 0.61074(8) | 0.0263(4) |
| C3 | 0.5132(2) | 0.69861(19) | 0.55706(8) | 0.0271(4) |
| C4 | 0.6093(3) | 0.81613(19) | 0.53227(8) | 0.0312(4) |
| C5 | 0.7724(2) | 0.8640(2) | 0.55970(8) | 0.0328(4) |
| C6 | 0.8483(2) | 0.79550(19) | 0.61319(8) | 0.0272(4) |
| C7 | 0.1158(2) | 0.7369(2) | 0.67918(9) | 0.0339(4) |
| C8 | 0.9992(2) | 0.6644(2) | 0.72488(8) | 0.0292(4) |
| C9 | 0.8173(2) | 0.60088(19) | 0.69788(8) | 0.0260(4) |
| C10 | 0.6956(2) | 0.62909(19) | 0.75045(8) | 0.0272(4) |
| C11 | 0.5278(3) | 0.5725(2) | 0.76442(9) | 0.0366(5) |
| C12 | 0.4460(3) | 0.6240(3) | 0.81677(9) | 0.0430(5) |
| C13 | 0.5332(3) | 0.7315(2) | 0.85338(9) | 0.0397(5) |
| C14 | 0.7024(3) | 0.7882(2) | 0.84001(8) | 0.0349(5) |
| C15 | 0.7811(2) | 0.73377(18) | 0.78868(8) | 0.0281(4) |
| C16 | 0.3390(3) | 0.6406(2) | 0.52987(8) | 0.0301(4) |
| C17 | 0.1140(3) | 0.6588(2) | 0.44920(9) | 0.0397(5) |
| C18 | 0.1253(3) | 0.9451(2) | 0.60658(9) | 0.0384(5) |

Table 4. Bond lengths (Å) for 10c.

| | | | |
|--------|----------|--------|----------|
| O1-C15 | 1.373(2) | O1-C8 | 1.462(2) |
| O2-C16 | 1.344(2) | O2-C17 | 1.444(2) |
| O3-C16 | 1.206(2) | N1-C6 | 1.383(2) |

| | | | |
|----------|----------|----------|----------|
| N1-C18 | 1.452(2) | N1-C7 | 1.459(2) |
| C1-C2 | 1.375(2) | C1-C6 | 1.415(2) |
| C1-C9 | 1.517(2) | C2-C3 | 1.396(2) |
| C2-H2 | 0.95 | C3-C4 | 1.390(2) |
| C3-C16 | 1.472(2) | C4-C5 | 1.374(2) |
| C4-H4 | 0.95 | C5-C6 | 1.410(2) |
| C5-H5 | 0.95 | C7-C8 | 1.497(3) |
| C7-H7A | 0.99 | C7-H7B | 0.99 |
| C8-C9 | 1.536(2) | C8-H8 | 1.0 |
| C9-C10 | 1.513(2) | C9-H9 | 1.0 |
| C10-C11 | 1.376(3) | C10-C15 | 1.383(2) |
| C11-C12 | 1.399(3) | C11-H11 | 0.95 |
| C12-C13 | 1.385(3) | C12-H12 | 0.95 |
| C13-C14 | 1.383(3) | C13-H13 | 0.95 |
| C14-C15 | 1.379(3) | C14-H14 | 0.95 |
| C17-H17A | 0.98 | C17-H17B | 0.98 |
| C17-H17C | 0.98 | C18-H18A | 0.98 |
| C18-H18B | 0.98 | C18-H18C | 0.98 |

Table 5. Bond angles (°) for 10c.

| | | | |
|------------|------------|-------------|------------|
| C15-O1-C8 | 105.86(13) | C16-O2-C17 | 115.25(15) |
| C6-N1-C18 | 118.62(15) | C6-N1-C7 | 117.30(15) |
| C18-N1-C7 | 114.79(15) | C2-C1-C6 | 118.91(16) |
| C2-C1-C9 | 119.30(15) | C6-C1-C9 | 121.79(15) |
| C1-C2-C3 | 122.90(16) | C1-C2-H2 | 118.5 |
| C3-C2-H2 | 118.5 | C4-C3-C2 | 117.96(16) |
| C4-C3-C16 | 123.54(16) | C2-C3-C16 | 118.50(16) |
| C5-C4-C3 | 120.59(17) | C5-C4-H4 | 119.7 |
| C3-C4-H4 | 119.7 | C4-C5-C6 | 121.49(17) |
| C4-C5-H5 | 119.3 | C6-C5-H5 | 119.3 |
| N1-C6-C5 | 121.19(16) | N1-C6-C1 | 120.69(15) |
| C5-C6-C1 | 118.11(16) | N1-C7-C8 | 112.34(15) |
| N1-C7-H7A | 109.1 | C8-C7-H7A | 109.1 |
| N1-C7-H7B | 109.1 | C8-C7-H7B | 109.1 |
| H7A-C7-H7B | 107.9 | O1-C8-C7 | 109.37(15) |
| O1-C8-C9 | 106.02(14) | C7-C8-C9 | 114.53(15) |
| O1-C8-H8 | 108.9 | C7-C8-H8 | 108.9 |
| C9-C8-H8 | 108.9 | C10-C9-C1 | 112.76(14) |
| C10-C9-C8 | 100.22(14) | C1-C9-C8 | 113.38(14) |
| C10-C9-H9 | 110.0 | C1-C9-H9 | 110.0 |
| C8-C9-H9 | 110.0 | C11-C10-C15 | 119.57(17) |

| | | | |
|---------------|------------|---------------|------------|
| C11-C10-C9 | 132.45(17) | C15-C10-C9 | 107.98(15) |
| C10-C11-C12 | 119.09(19) | C10-C11-H11 | 120.5 |
| C12-C11-H11 | 120.5 | C13-C12-C11 | 119.96(19) |
| C13-C12-H12 | 120.0 | C11-C12-H12 | 120.0 |
| C14-C13-C12 | 121.38(18) | C14-C13-H13 | 119.3 |
| C12-C13-H13 | 119.3 | C15-C14-C13 | 117.42(19) |
| C15-C14-H14 | 121.3 | C13-C14-H14 | 121.3 |
| O1-C15-C14 | 124.42(17) | O1-C15-C10 | 113.03(15) |
| C14-C15-C10 | 122.54(18) | O3-C16-O2 | 122.35(17) |
| O3-C16-C3 | 124.77(16) | O2-C16-C3 | 112.88(16) |
| O2-C17-H17A | 109.5 | O2-C17-H17B | 109.5 |
| H17A-C17-H17B | 109.5 | O2-C17-H17C | 109.5 |
| H17A-C17-H17C | 109.5 | H17B-C17-H17C | 109.5 |
| N1-C18-H18A | 109.5 | N1-C18-H18B | 109.5 |
| H18A-C18-H18B | 109.5 | N1-C18-H18C | 109.5 |
| H18A-C18-H18C | 109.5 | H18B-C18-H18C | 109.5 |

Table 6. Torsion angles (°) for 10c.

| | | | |
|-----------------|-------------|-----------------|-------------|
| C6-C1-C2-C3 | -0.6(3) | C9-C1-C2-C3 | 179.52(15) |
| C1-C2-C3-C4 | -0.8(3) | C1-C2-C3-C16 | 179.44(16) |
| C2-C3-C4-C5 | 0.8(3) | C16-C3-C4-C5 | -179.40(18) |
| C3-C4-C5-C6 | 0.5(3) | C18-N1-C6-C5 | -12.0(3) |
| C7-N1-C6-C5 | -156.96(16) | C18-N1-C6-C1 | 169.40(16) |
| C7-N1-C6-C1 | 24.4(2) | C4-C5-C6-N1 | 179.40(17) |
| C4-C5-C6-C1 | -1.9(3) | C2-C1-C6-N1 | -179.38(16) |
| C9-C1-C6-N1 | 0.5(3) | C2-C1-C6-C5 | 1.9(3) |
| C9-C1-C6-C5 | -178.21(15) | C6-N1-C7-C8 | -49.3(2) |
| C18-N1-C7-C8 | 164.41(15) | C15-O1-C8-C7 | 148.76(14) |
| C15-O1-C8-C9 | 24.79(17) | N1-C7-C8-O1 | -69.60(18) |
| N1-C7-C8-C9 | 49.2(2) | C2-C1-C9-C10 | -66.4(2) |
| C6-C1-C9-C10 | 113.78(18) | C2-C1-C9-C8 | -179.39(15) |
| C6-C1-C9-C8 | 0.8(2) | O1-C8-C9-C10 | -25.30(16) |
| C7-C8-C9-C10 | -145.99(15) | O1-C8-C9-C1 | 95.10(16) |
| C7-C8-C9-C1 | -25.6(2) | C1-C9-C10-C11 | 76.1(2) |
| C8-C9-C10-C11 | -163.04(19) | C1-C9-C10-C15 | -103.36(16) |
| C8-C9-C10-C15 | 17.50(17) | C15-C10-C11-C12 | 0.9(3) |
| C9-C10-C11-C12 | -178.53(17) | C10-C11-C12-C13 | 0.6(3) |
| C11-C12-C13-C14 | -1.2(3) | C12-C13-C14-C15 | 0.2(3) |
| C8-O1-C15-C14 | 165.40(16) | C8-O1-C15-C10 | -13.87(19) |
| C13-C14-C15-O1 | -177.80(16) | C13-C14-C15-C10 | 1.4(3) |
| C11-C10-C15-O1 | 177.34(15) | C9-C10-C15-O1 | -3.1(2) |

| | | | |
|-----------------|-------------|----------------|-------------|
| C11-C10-C15-C14 | -1.9(3) | C9-C10-C15-C14 | 177.59(15) |
| C17-O2-C16-O3 | -1.3(3) | C17-O2-C16-C3 | 179.63(15) |
| C4-C3-C16-O3 | -178.13(18) | C2-C3-C16-O3 | 1.6(3) |
| C4-C3-C16-O2 | 0.9(3) | C2-C3-C16-O2 | -179.31(15) |

Table 7. Anisotropic atomic displacement parameters (\AA^2) for 10c.

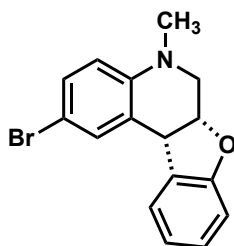
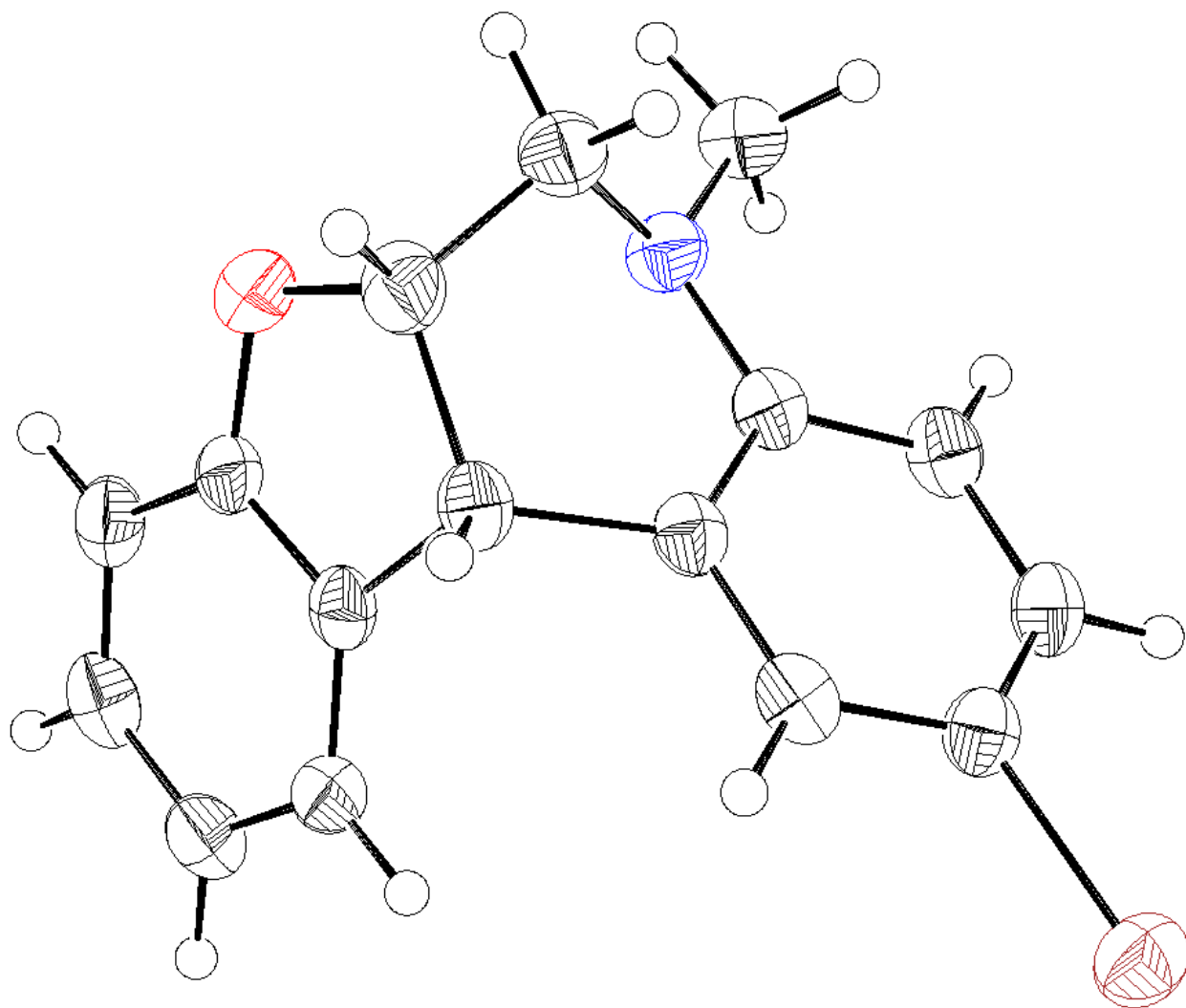
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|------------|------------|------------|------------|------------|------------|
| O1 | 0.0372(8) | 0.0362(7) | 0.0295(7) | -0.0077(5) | -0.0001(6) | -0.0069(6) |
| O2 | 0.0301(7) | 0.0479(8) | 0.0250(7) | 0.0049(6) | -0.0052(6) | -0.0041(6) |
| O3 | 0.0448(9) | 0.0534(9) | 0.0385(8) | 0.0117(7) | -0.0094(7) | -0.0194(7) |
| N1 | 0.0302(8) | 0.0351(8) | 0.0301(8) | 0.0008(7) | -0.0015(7) | -0.0085(7) |
| C1 | 0.0258(9) | 0.0253(9) | 0.0230(9) | -0.0021(7) | 0.0005(7) | 0.0010(7) |
| C2 | 0.0292(9) | 0.0265(9) | 0.0234(9) | 0.0002(7) | 0.0028(8) | -0.0017(7) |
| C3 | 0.0284(9) | 0.0301(9) | 0.0228(9) | -0.0007(7) | 0.0011(7) | -0.0014(7) |
| C4 | 0.0348(10) | 0.0334(10) | 0.0252(10) | 0.0033(7) | -0.0026(8) | 0.0010(8) |
| C5 | 0.0359(10) | 0.0318(10) | 0.0306(10) | 0.0036(8) | 0.0019(8) | -0.0049(8) |
| C6 | 0.0274(9) | 0.0275(9) | 0.0267(9) | -0.0021(7) | 0.0017(8) | -0.0012(7) |
| C7 | 0.0258(9) | 0.0395(10) | 0.0361(11) | -0.0001(8) | -0.0005(8) | 0.0005(8) |
| C8 | 0.0291(9) | 0.0318(10) | 0.0263(10) | -0.0022(7) | -0.0022(8) | 0.0015(8) |
| C9 | 0.0286(9) | 0.0241(9) | 0.0251(9) | -0.0001(7) | -0.0008(7) | 0.0007(7) |
| C10 | 0.0312(9) | 0.0283(9) | 0.0217(9) | 0.0019(7) | -0.0033(7) | 0.0029(8) |
| C11 | 0.0352(11) | 0.0484(12) | 0.0255(10) | 0.0034(8) | -0.0042(8) | -0.0064(9) |
| C12 | 0.0321(11) | 0.0640(14) | 0.0332(12) | 0.0123(10) | 0.0047(9) | 0.0029(10) |
| C13 | 0.0424(12) | 0.0508(12) | 0.0262(10) | 0.0048(9) | 0.0046(9) | 0.0164(10) |
| C14 | 0.0463(12) | 0.0323(10) | 0.0257(10) | -0.0007(8) | -0.0023(9) | 0.0100(8) |
| C15 | 0.0315(10) | 0.0262(9) | 0.0262(9) | 0.0036(7) | -0.0028(8) | 0.0032(8) |
| C16 | 0.0340(10) | 0.0346(10) | 0.0217(9) | -0.0012(8) | 0.0007(8) | 0.0023(8) |
| C17 | 0.0313(10) | 0.0542(13) | 0.0323(11) | -0.0020(9) | -0.0089(9) | 0.0004(9) |
| C18 | 0.0369(11) | 0.0376(11) | 0.0404(12) | -0.0012(9) | 0.0005(9) | -0.0103(9) |

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 10c.

| | x/a | y/b | z/c | $U(\text{equiv})$ |
|-----|--------|--------|--------|-------------------|
| H2 | 0.5208 | 0.5533 | 0.6283 | 0.032 |
| H4 | 0.5619 | 0.8638 | 0.4961 | 0.037 |
| H5 | 0.8353 | 0.9450 | 0.5422 | 0.039 |
| H7A | 1.2189 | 0.7895 | 0.7011 | 0.041 |
| H7B | 1.1680 | 0.6586 | 0.6533 | 0.041 |
| H8 | 1.0705 | 0.5821 | 0.7459 | 0.035 |

| | x/a | y/b | z/c | U(equiv) |
|------|------------|------------|------------|-----------------|
| H9 | 0.8293 | 0.4909 | 0.6907 | 0.031 |
| H11 | 0.4684 | 0.4995 | 0.7389 | 0.044 |
| H12 | 0.3308 | 0.5852 | 0.8272 | 0.052 |
| H13 | 0.4754 | 0.7671 | 0.8884 | 0.048 |
| H14 | 0.7621 | 0.8617 | 0.8652 | 0.042 |
| H17A | 0.0968 | 0.7031 | 0.4084 | 0.059 |
| H17B | 0.0120 | 0.6877 | 0.4739 | 0.059 |
| H17C | 0.1180 | 0.5496 | 0.4457 | 0.059 |
| H18A | 1.1481 | 0.9017 | 0.5666 | 0.058 |
| H18B | 1.2423 | 0.9614 | 0.6296 | 0.058 |
| H18C | 1.0613 | 1.0407 | 0.6008 | 0.058 |



10e

A clear colourless block-like specimen of $C_{16}H_{14}BrNO$, approximate dimensions 0.153 mm x 0.200 mm x 0.356 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 416 frames were collected. The total exposure time was 1.16 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 20215 reflections to a maximum θ angle of 27.71° (0.76 Å resolution), of which 3122 were independent (average redundancy 6.475, completeness = 100.0%, $R_{int} = 5.93\%$, $R_{sig} = 4.29\%$) and 2024 (64.83%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 9.145(3)$ Å, $b = 16.074(4)$ Å, $c = 9.416(3)$ Å, $\beta = 105.913(3)^\circ$, volume = $1331.1(6)$ Å³, are

based upon the refinement of the XYZ-centroids of 2737 reflections above $20 \sigma(I)$ with $5.163^\circ < 2\theta < 42.98^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.869. The Calcd. minimum and maximum transmission coefficients (based on crystal size) are 0.4070 and 0.6500.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P 1 21/n 1$, with $Z = 4$ for the formula unit, $C_{16}H_{14}BrNO$. The final anisotropic full-matrix least-squares refinement on F^2 with 173 variables converged at $R1 = 3.59\%$, for the observed data and $wR2 = 9.68\%$ for all data. The goodness-of-fit was 1.008. The largest peak in the final difference electron density synthesis was $0.711 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.488 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.075 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the Calcd. density was 1.578 g/cm^3 and $F(000)$, 640 e^- .

Table 1. Sample and crystal data for 10e.

| | |
|-------------------------------|--|
| Identification code | 10e |
| Chemical formula | $C_{16}H_{14}BrNO$ |
| Formula weight | 316.19 g/mol |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal size | 0.153 x 0.200 x 0.356 mm |
| Crystal habit | clear colourless block |
| Crystal system | monoclinic |
| Space group | $P 1 21/n 1$ |
| Unit cell dimensions | $a = 9.145(3) \text{ \AA}$ $\alpha = 90^\circ$ $b = 16.074(4) \text{ \AA}$ $\beta = 105.913(3)^\circ$ $c = 9.416(3) \text{ \AA}$ $\gamma = 90^\circ$ |
| Volume | $1331.1(6) \text{ \AA}^3$ |
| Z | 4 |
| Density (Calcd.) | 1.578 g/cm^3 |
| Absorption coefficient | 3.079 mm^{-1} |
| F(000) | 640 |

Table 2. Data collection and structure refinement for 10e.

| | |
|--|--|
| Theta range for data collection | 2.53 to 27.71° |
| Index ranges | $-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-12 \leq l \leq 12$ |
| Reflections collected | 20215 |
| Independent reflections | 3122 [$R(\text{int}) = 0.0593$] |
| Coverage of independent reflections | 100.0% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.6500 and 0.4070 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |

| | |
|--|---|
| Refinement method | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3122 / 0 / 173 |
| Goodness-of-fit on F^2 | 1.008 |
| Δ/σ_{\max} | 0.001 |
| Final R indices | 2024 data; $l > 2\sigma(l)$ R1 = 0.0359, wR2 = 0.0832 all data R1 = 0.0696, wR2 = 0.0968 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.1193P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole | 0.711 and -0.488 $e\text{\AA}^{-3}$ |
| R.M.S. deviation from mean | 0.075 $e\text{\AA}^{-3}$ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for 10e.

U(equiv) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x/a | y/b | z/c | U(equiv) |
|-----|------------|-------------|------------|-----------------|
| Br1 | 0.75618(3) | 0.24723(2) | 0.30885(3) | 0.04244(12) |
| O1 | 0.0323(2) | 0.49284(13) | 0.2653(2) | 0.0436(5) |
| N1 | 0.2803(2) | 0.43471(14) | 0.5205(2) | 0.0342(5) |
| C1 | 0.3589(3) | 0.36619(15) | 0.3277(3) | 0.0291(6) |
| C2 | 0.4663(3) | 0.32275(15) | 0.2791(3) | 0.0317(6) |
| C3 | 0.6100(3) | 0.30974(15) | 0.3739(3) | 0.0320(6) |
| C4 | 0.6486(3) | 0.34087(17) | 0.5148(3) | 0.0349(6) |
| C5 | 0.5412(3) | 0.38286(16) | 0.5657(3) | 0.0344(6) |
| C6 | 0.3945(3) | 0.39525(15) | 0.4743(3) | 0.0297(6) |
| C7 | 0.1312(3) | 0.39649(18) | 0.4611(3) | 0.0391(7) |
| C8 | 0.0800(3) | 0.40702(18) | 0.2961(3) | 0.0385(7) |
| C9 | 0.2080(3) | 0.38975(17) | 0.2207(3) | 0.0318(6) |
| C10 | 0.2166(3) | 0.47251(16) | 0.1458(3) | 0.0288(6) |
| C11 | 0.3062(3) | 0.49875(18) | 0.0589(3) | 0.0357(6) |
| C12 | 0.2928(3) | 0.58033(19) | 0.0071(3) | 0.0427(7) |
| C13 | 0.1907(3) | 0.63402(18) | 0.0444(3) | 0.0403(7) |
| C14 | 0.0982(3) | 0.60812(17) | 0.1291(3) | 0.0383(7) |
| C15 | 0.1141(3) | 0.52706(17) | 0.1787(3) | 0.0312(6) |
| C16 | 0.3157(3) | 0.46602(17) | 0.6708(3) | 0.0395(7) |

Table 4. Bond lengths (\AA) for 10e.

| | | | |
|--------|----------|--------|----------|
| Br1-C3 | 1.903(3) | O1-C15 | 1.364(3) |
| O1-C8 | 1.452(3) | N1-C6 | 1.389(3) |
| N1-C16 | 1.453(3) | N1-C7 | 1.460(3) |

| | | | |
|----------|----------|----------|----------|
| C1-C2 | 1.381(4) | C1-C6 | 1.408(4) |
| C1-C9 | 1.517(3) | C2-C3 | 1.387(3) |
| C2-H2 | 0.95 | C3-C4 | 1.371(4) |
| C4-C5 | 1.382(4) | C4-H4 | 0.95 |
| C5-C6 | 1.395(3) | C5-H5 | 0.95 |
| C7-C8 | 1.504(4) | C7-H7A | 0.99 |
| C7-H7B | 0.99 | C8-C9 | 1.551(4) |
| C8-H8 | 1.0 | C9-C10 | 1.518(4) |
| C9-H9 | 1.0 | C10-C11 | 1.374(4) |
| C10-C15 | 1.379(3) | C11-C12 | 1.393(4) |
| C11-H11 | 0.95 | C12-C13 | 1.386(4) |
| C12-H12 | 0.95 | C13-C14 | 1.377(4) |
| C13-H13 | 0.95 | C14-C15 | 1.378(4) |
| C14-H14 | 0.95 | C16-H16A | 0.98 |
| C16-H16B | 0.98 | C16-H16C | 0.98 |

Table 5. Bond angles (°) for 10e.

| | | | |
|-------------|----------|-------------|----------|
| C15-O1-C8 | 108.6(2) | C6-N1-C16 | 118.5(2) |
| C6-N1-C7 | 113.0(2) | C16-N1-C7 | 117.0(2) |
| C2-C1-C6 | 119.9(2) | C2-C1-C9 | 120.4(2) |
| C6-C1-C9 | 119.5(2) | C1-C2-C3 | 119.8(2) |
| C1-C2-H2 | 120.1 | C3-C2-H2 | 120.1 |
| C4-C3-C2 | 121.0(3) | C4-C3-Br1 | 119.1(2) |
| C2-C3-Br1 | 119.9(2) | C3-C4-C5 | 119.7(2) |
| C3-C4-H4 | 120.2 | C5-C4-H4 | 120.2 |
| C4-C5-C6 | 120.7(2) | C4-C5-H5 | 119.6 |
| C6-C5-H5 | 119.6 | N1-C6-C5 | 123.4(2) |
| N1-C6-C1 | 117.8(2) | C5-C6-C1 | 118.8(2) |
| N1-C7-C8 | 110.0(2) | N1-C7-H7A | 109.7 |
| C8-C7-H7A | 109.7 | N1-C7-H7B | 109.7 |
| C8-C7-H7B | 109.7 | H7A-C7-H7B | 108.2 |
| O1-C8-C7 | 107.7(2) | O1-C8-C9 | 107.6(2) |
| C7-C8-C9 | 113.1(2) | O1-C8-H8 | 109.5 |
| C7-C8-H8 | 109.5 | C9-C8-H8 | 109.5 |
| C1-C9-C10 | 112.0(2) | C1-C9-C8 | 113.8(2) |
| C10-C9-C8 | 101.4(2) | C1-C9-H9 | 109.8 |
| C10-C9-H9 | 109.8 | C8-C9-H9 | 109.8 |
| C11-C10-C15 | 119.5(2) | C11-C10-C9 | 131.4(2) |
| C15-C10-C9 | 109.1(2) | C10-C11-C12 | 119.2(3) |
| C10-C11-H11 | 120.4 | C12-C11-H11 | 120.4 |
| C11-C12-C13 | 119.9(3) | C11-C12-H12 | 120.1 |

| | | | |
|---------------|----------|---------------|----------|
| C13-C12-H12 | 120.1 | C14-C13-C12 | 121.5(3) |
| C14-C13-H13 | 119.3 | C12-C13-H13 | 119.3 |
| C15-C14-C13 | 117.2(3) | C15-C14-H14 | 121.4 |
| C13-C14-H14 | 121.4 | O1-C15-C14 | 124.0(2) |
| O1-C15-C10 | 113.3(2) | C14-C15-C10 | 122.7(3) |
| N1-C16-H16A | 109.5 | N1-C16-H16B | 109.5 |
| H16A-C16-H16B | 109.5 | N1-C16-H16C | 109.5 |
| H16A-C16-H16C | 109.5 | H16B-C16-H16C | 109.5 |

Table 6. Torsion angles (°) for 10e.

| | | | |
|-----------------|-----------|-----------------|------------|
| C6-C1-C2-C3 | -1.6(4) | C9-C1-C2-C3 | 172.8(2) |
| C1-C2-C3-C4 | -1.3(4) | C1-C2-C3-Br1 | 178.24(19) |
| C2-C3-C4-C5 | 2.7(4) | Br1-C3-C4-C5 | -176.9(2) |
| C3-C4-C5-C6 | -1.2(4) | C16-N1-C6-C5 | 1.1(4) |
| C7-N1-C6-C5 | -141.3(3) | C16-N1-C6-C1 | -179.2(2) |
| C7-N1-C6-C1 | 38.4(3) | C4-C5-C6-N1 | 178.0(2) |
| C4-C5-C6-C1 | -1.7(4) | C2-C1-C6-N1 | -176.6(2) |
| C9-C1-C6-N1 | 9.0(4) | C2-C1-C6-C5 | 3.1(4) |
| C9-C1-C6-C5 | -171.3(2) | C6-N1-C7-C8 | -65.5(3) |
| C16-N1-C7-C8 | 151.4(2) | C15-O1-C8-C7 | 123.6(2) |
| C15-O1-C8-C9 | 1.3(3) | N1-C7-C8-O1 | -75.2(3) |
| N1-C7-C8-C9 | 43.6(3) | C2-C1-C9-C10 | -87.7(3) |
| C6-C1-C9-C10 | 86.7(3) | C2-C1-C9-C8 | 158.0(2) |
| C6-C1-C9-C8 | -27.6(3) | O1-C8-C9-C1 | 118.6(2) |
| C7-C8-C9-C1 | -0.3(3) | O1-C8-C9-C10 | -1.8(3) |
| C7-C8-C9-C10 | -120.7(2) | C1-C9-C10-C11 | 59.0(4) |
| C8-C9-C10-C11 | -179.3(3) | C1-C9-C10-C15 | -120.0(2) |
| C8-C9-C10-C15 | 1.8(3) | C15-C10-C11-C12 | 0.7(4) |
| C9-C10-C11-C12 | -178.2(3) | C10-C11-C12-C13 | 0.5(4) |
| C11-C12-C13-C14 | -1.7(4) | C12-C13-C14-C15 | 1.7(4) |
| C8-O1-C15-C14 | -179.7(2) | C8-O1-C15-C10 | -0.2(3) |
| C13-C14-C15-O1 | 179.0(2) | C13-C14-C15-C10 | -0.5(4) |
| C11-C10-C15-O1 | 179.8(2) | C9-C10-C15-O1 | -1.1(3) |
| C11-C10-C15-C14 | -0.7(4) | C9-C10-C15-C14 | 178.4(2) |

Table 7. Anisotropic atomic displacement parameters (Å²) for 10e.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Br1 | 0.04197(19) | 0.03887(19) | 0.0484(2) | -0.00205(14) | 0.01558(14) | 0.00529(13) |
| O1 | 0.0336(10) | 0.0518(13) | 0.0475(12) | 0.0109(10) | 0.0147(9) | 0.0102(9) |

| | U₁₁ | U₂₂ | U₃₃ | U₂₃ | U₁₃ | U₁₂ |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| N1 | 0.0296(12) | 0.0402(13) | 0.0316(12) | -0.0042(10) | 0.0061(10) | -0.0028(10) |
| C1 | 0.0292(13) | 0.0251(13) | 0.0311(15) | 0.0027(11) | 0.0052(11) | -0.0029(11) |
| C2 | 0.0394(15) | 0.0250(14) | 0.0282(14) | -0.0015(11) | 0.0048(12) | -0.0055(11) |
| C3 | 0.0337(14) | 0.0239(13) | 0.0373(16) | 0.0003(11) | 0.0075(12) | 0.0011(11) |
| C4 | 0.0327(14) | 0.0310(14) | 0.0353(16) | 0.0006(12) | 0.0000(12) | 0.0003(12) |
| C5 | 0.0390(15) | 0.0307(14) | 0.0285(15) | -0.0034(11) | 0.0010(12) | -0.0013(12) |
| C6 | 0.0331(14) | 0.0241(13) | 0.0303(15) | -0.0001(11) | 0.0059(11) | -0.0027(11) |
| C7 | 0.0336(15) | 0.0420(17) | 0.0415(17) | 0.0044(13) | 0.0102(13) | -0.0059(13) |
| C8 | 0.0311(14) | 0.0423(17) | 0.0384(17) | 0.0038(13) | 0.0034(12) | -0.0066(13) |
| C9 | 0.0314(14) | 0.0323(15) | 0.0279(14) | -0.0010(11) | 0.0018(11) | -0.0007(11) |
| C10 | 0.0278(13) | 0.0306(14) | 0.0233(13) | -0.0031(10) | -0.0010(10) | 0.0004(11) |
| C11 | 0.0344(15) | 0.0429(16) | 0.0295(14) | 0.0007(13) | 0.0085(12) | 0.0069(13) |
| C12 | 0.0448(17) | 0.0491(18) | 0.0334(16) | 0.0086(14) | 0.0092(13) | 0.0019(15) |
| C13 | 0.0488(18) | 0.0335(16) | 0.0328(16) | 0.0037(12) | 0.0011(14) | 0.0027(13) |
| C14 | 0.0384(15) | 0.0375(16) | 0.0342(16) | 0.0005(13) | 0.0021(13) | 0.0091(13) |
| C15 | 0.0255(13) | 0.0394(15) | 0.0252(13) | -0.0005(11) | 0.0012(11) | 0.0016(11) |
| C16 | 0.0394(16) | 0.0404(16) | 0.0394(16) | -0.0040(13) | 0.0123(13) | -0.0038(13) |

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 10e.

| | x/a | y/b | z/c | U(equiv) |
|------|------------|------------|------------|-----------------|
| H2 | 0.4417 | 0.3018 | 0.1810 | 0.038 |
| H4 | 0.7488 | 0.3336 | 0.5772 | 0.042 |
| H5 | 0.5674 | 0.4035 | 0.6640 | 0.041 |
| H7A | 0.0567 | 0.4229 | 0.5059 | 0.047 |
| H7B | 0.1368 | 0.3365 | 0.4861 | 0.047 |
| H8 | -0.0079 | 0.3692 | 0.2536 | 0.046 |
| H9 | 0.1749 | 0.3452 | 0.1446 | 0.038 |
| H11 | 0.3765 | 0.4617 | 0.0344 | 0.043 |
| H12 | 0.3536 | 0.5991 | -0.0537 | 0.051 |
| H13 | 0.1844 | 0.6900 | 0.0107 | 0.048 |
| H14 | 0.0263 | 0.6446 | 0.1524 | 0.046 |
| H16A | 0.4006 | 0.5054 | 0.6873 | 0.059 |
| H16B | 0.3441 | 0.4195 | 0.7403 | 0.059 |
| H16C | 0.2264 | 0.4943 | 0.6863 | 0.059 |