

Article

Novel Fluorinated Indanone, Tetralone and Naphthone Derivatives: Synthesis and Unique Structural Features

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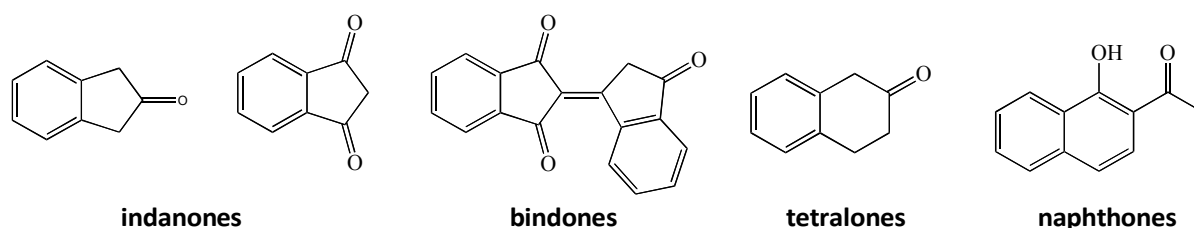
Abstract: Several fluorinated and trifluoromethylated indanone, tetralone and naphthone derivatives have been prepared via Claisen condensations and selective fluorinations in yields ranging from 22–60%. In addition, we report the synthesis of new, selectively fluorinated bindones in yields ranging from 72–92%. Of particular interest is the fluorination and trifluoroacetylation regiochemistry observed in these fluorinated products. We also note unusual transformations including a novel one pot, dual trifluoroacetylation, trifluoroacetylnaphthone synthesis via a deacetylation as well as an acetyl-trifluoroacetyl group exchange. Solid-state structural features exhibited by these compounds were investigated using crystallographic methods. Crystallographic results, supported by spectroscopic data, show that trifluoroacetylated ketones prefer a chelated cis-enol form whereas fluorinated bindone products exist primarily as the cross-conjugated triketo form.

Keywords: 2-trifluoroacetyl-1,3-Diketone; 1,3,5-triketone; tautomerism; X-ray crystallography

1. Introduction

Molecules which have medicinal, industrial and herbicidal properties are of continued interest to the pharmaceutical, chemical and agrochemical communities. For example, indanone derivatives have anticoagulant properties and are used in elaborating latent fingerprints, bindone variants comprise components of near infrared dyes while certain tetralones and naphthones, ketones similar in structure to those shown in Figure 1, have demonstrated bioactive properties [1–6]. Since bioactivity is known to be enhanced in many classes of fluorinated molecules [3,7], it is desirable to prepare fluorine-containing molecules with similar architecture and gain a better understanding of their structure-property relationships.

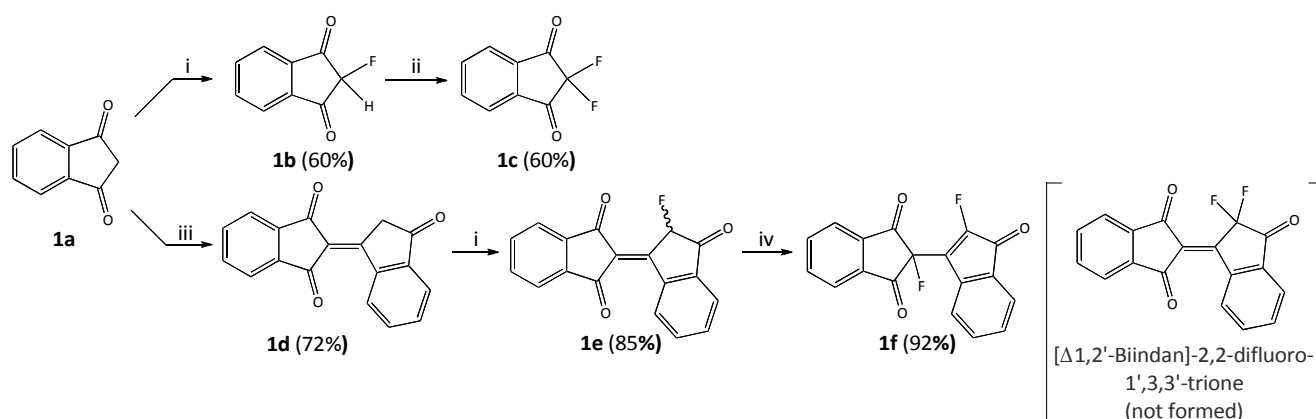
Figure 1. Medicinally and industrially important ketones.



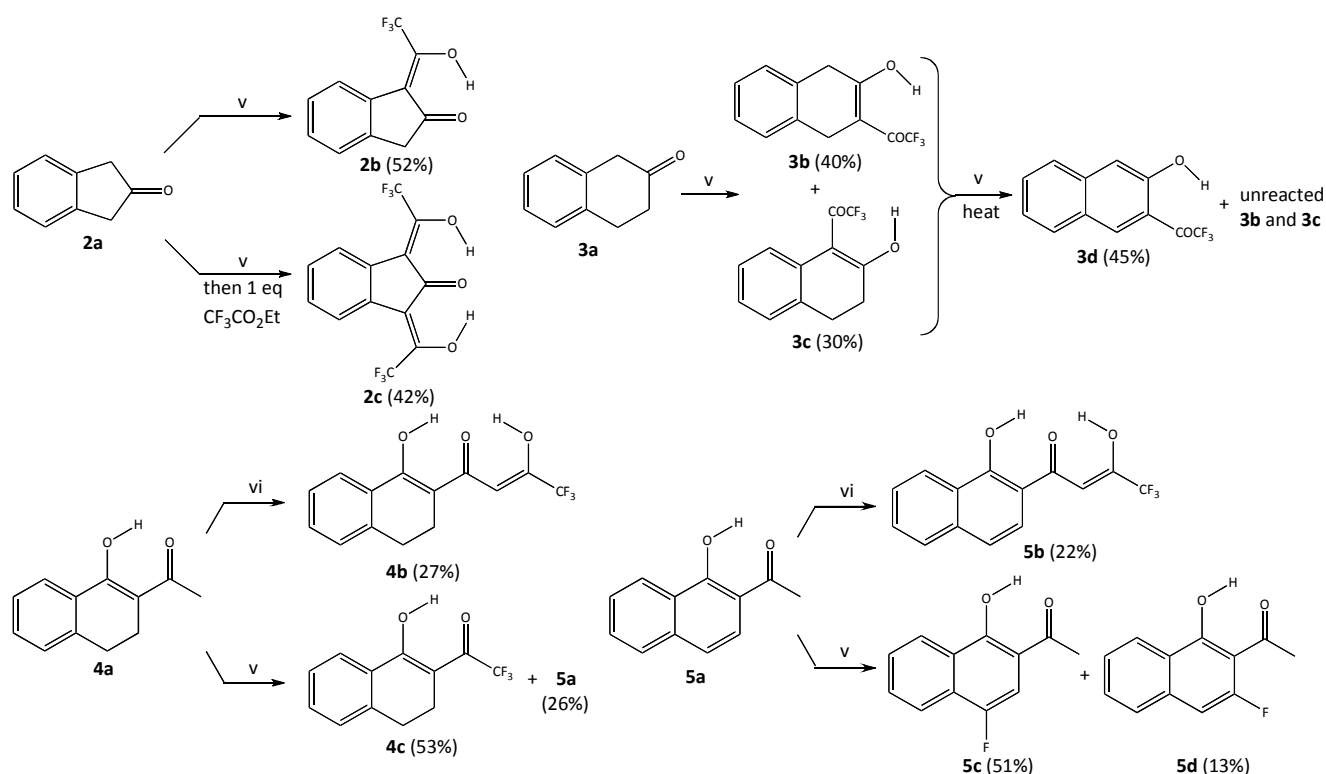
Previously, we reported the preparation and structure-property relationships of acyclic fluorinated and trifluoromethylated β -diketones, precursors to a variety of heterocyclic molecules [8–10]. While the syntheses and properties of these molecules have been investigated thoroughly, the preparation and study of selectively fluorinated, cyclic ketones containing the structural features of the molecules depicted in Figure 1 remains relatively limited [11].

The molecules of interest in this study, shown in Scheme 1, provide this sort of molecular architecture. This paper addresses the design and synthetic approach to prepare these novel molecules, the interesting synthetic results and the unique solid-state structural features that differentiate these molecules.

Scheme 1. Synthesis of fluorinated ketones.



Scheme 1. Cont.



Conditions: i. 1.1 eq Selectfluor[®], MeCN, reflux, 10 h; ii. 1.5 eq Selectfluor[®], MeCN, RT, 18–30 h; iii. H_2SO_4 , MeOH, reflux, 24 h; iv. 1.1 eq Selectfluor[®], MeCN, reflux, 16 h; v. $\text{CF}_3\text{CO}_2\text{Et}$, NaOMe, Et_2O , rt, 18 h; vi. (1) 3.0 eq LDA, Et_2O , 0 °C; (2) 2 eq $\text{CF}_3\text{CO}_2\text{Et}$, 0 °C → rt, 24 h; (3) 2 eq $\text{CF}_3\text{CO}_2\text{Et}$.

2. Experimental Section

2.1. Chemicals

All chemicals were obtained from the Aldrich Chemical Company, Eastman Kodak, or Fisher Chemical Company. All solvents (spectrophotometric grade) and starting materials were checked for purity by mass spectrometry prior to use.

2.2. Instrumentation

Melting points were obtained on a Mel-Temp melting point apparatus and are uncorrected. NMR data were collected using a Varian VXR-200 spectrometer with a broad band probe operating at 200.0 MHz for ^1H , 188.2 MHz for ^{19}F and 50.3 MHz for ^{13}C , and/or a Bruker Avance 300 spectrometer operating at 300.0 MHz for ^1H , 282.0 MHz for ^{19}F and 75.4 MHz for ^{13}C . Unless otherwise noted, CDCl_3 was used as the solvent and internal standard for ^1H and ^{13}C NMR experiments while CFCl_3 served as the internal standard for ^{19}F NMR experiments. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer. See the appendix for complete crystallographic experimental details.

2.3. General Procedure for the Preparation of Trifluoromethyl- β -Diketones and Triketones [12]

A 100 mL round bottom flask equipped with a magnetic stirrer is charged with 50 mL diethyl ether and 60 mmol of sodium methoxide is added slowly. Then, 1eq (60 mmol) of trifluoromethyl ethyl acetate is added dropwise slowly while stirring. After 5 minutes, 1eq (60 mmol) of the ketone is added dropwise and stirred overnight at room temperature under a calcium chloride drying tube. The resulting solution is evaporated to dryness under reduced pressure and the solid residue dissolved in 30 mL 3M sulfuric acid. This solution is extracted with ether, and the organic layer dried over Na₂SO₄. The solvent is evaporated under reduced pressure and the crude diketone purified by radial chromatography.

2.4. General Procedure for the Preparation of Selectively Fluorinated Ketones [10,13]

A 100 mL round bottom flask equipped with a magnetic stirrer is charged with 40 mL CH₃CN and the ketone (1 eq: 1–10 mmol). Then, Selectfluor[®] (1–3 eq (3–30 mmol)) dissolved in 30 mL CH₃CN is added slowly while stirring. The solution is either allowed to stir at room temperature or refluxed as required. Times range from 10–30 h. The resulting solution is evaporated to dryness under reduced pressure and the solid residue taken up in distilled water. This solution is extracted with CH₂Cl₂, and the organic layer dried over Na₂SO₄. The solvent is evaporated under reduced pressure and the crude fluorinated ketone purified by radial chromatography.

2-fluoro-1,3-indanedione (**1b**). This compound was obtained in 60% yield as pale yellow crystals (EtOH), m.p. 97–99 °C lit [14] (m.p. 96–98 °C). NMR: ¹H: δ 5.4 (d, ¹J_{H-F} = 51.0 Hz, 1H), 7.65–8.22 (m, 4H). ¹³C: δ 90.1 (d, ¹J_{C-F} = 211.2 Hz, CF), 125.3, 138.9, 141.9, 193.5 (d, ²J_{C-F} = 24.0 Hz, C-CF). ¹⁹F: δ -207.3 (d, ¹J_{F-H} = 51.1 Hz, 1F). HRMS (ESI+) Calcd. for C₉H₅FO₂: 164.02740. Found: 164.027580.

2,2-difluoro-1,3-indanedione (**1c**). This compound was obtained in 60% yield from fluorination of **1b** as described in the general procedure above as yellowish-brown crystals (EtOH), m.p. 116–117 °C, lit [15] (m.p. 117–118 °C). NMR: ¹H: δ 8.0–8.15 (m, 4H). ¹³C: δ 104.0 (t, ¹J_{C-F} = 264 Hz, CF₂), 128.8, 138.2, 139.3 (t, ³J_{C-F} = 4.3 Hz), 185.8 (t, ²J_{C-F} = 24.0 Hz, C-CF₂). ¹⁹F: δ -125.9 (s, 2F).

[Δ 1,2'-Biindan]-1',3,3'-trione (**1d**). This compound was obtained in 72% yield as orange crystals (EtOH), m.p. 207–209 °C, lit [16] (m.p. 205–208 °C). NMR: ¹H: δ 4.17 (s, 2H), 7.74–8.04 (m, 8H), 9.50 (d, J = 7.8 Hz, 1H). ¹³C: δ 43.4, 123.0, 123.4, 123.5, 125.8, 131.7, 134.2, 135.3, 135.4, 140.4, 141.2, 141.6, 145.9, 155.4, 189.5, 191.0, 201.2.

[Δ 1,2'-Biindan]-2-fluoro-1',3,3'-trione (**1e**). This compound was obtained in 85% yield from fluorination of **1d** as described in the general procedure above as orange crystals (EtOH), m.p. 165–168 °C (dec). NMR: ¹H: δ 6.45 (d, ¹J_{H-F} = 46.1 Hz, 1H), 7.75–8.20 (m, 7H), 9.50 (d, J = 7.7 Hz, 1H). ¹³C: δ 70.8 (d, ¹J_{C-F} = 194 Hz, CF), 125.4, 126.6, 129.3, 130.1, 132.0, 137.7, 138.5, 166.3, 189.3, 191.2, 204.1 (d, ²J_{C-F} = 24 Hz, C-CF). ¹⁹F: δ -182.4 (d, ¹J_{F-H} = 46.0 Hz, 1F). Analysis calcd for C₁₈H₉FO₃: C, 73.97, H, 3.10. Found: C, 74.06, H, 3.21.

2-fluoro-2-(2'-fluoro-3'-oxoindenyl)-1,3-indanedione (**1f**). This compound was obtained in 92% yield from fluorination of **1e** as described in the general procedure above as yellow crystals (EtOH), m.p. 126–129 °C. NMR: ¹H: 7.8–8.25 (7H, m), 9.53 (1H, d, J = 6.9 Hz). ¹³C: δ 89.9, 125.1, 126.3, 129.5, 130.0, 132.2, 137.1, 138.0 (d, ¹J_{C-F} = 254 Hz, CF), 166.1, 185.9, 189.1. ¹⁹F: δ -137.3 (s, 1F),

−176.7 (s, 1F). HRMS (ESI+) calcd for $C_{18}H_8F_2O_3$: 310.04415. Found: 310.04415.

1-trifluoroacetyl-2-indanone (**2b**). This compound was obtained in 52% yield as a brown oil. NMR: 1H : δ 3.73 (2H, s), 7.29 (2H, m), 7.60 (2H, m), 14.19 (1H, bs), ^{13}C : δ 40.9, 111.5, 120.4 (CF_3 , q, $^1J_{C-F}$ = 277 Hz), 122.9, 123.0, 124.9, 127.7, 128.1, 128.8, 129.6, 154.5 (C- CF_3 , q, $^2J_{C-F}$ = 37 Hz), 203.0. ^{19}F : −68.59 (s, 3F). Analysis calcd for $C_{11}H_7F_3O_2$: C, 57.90, H, 3.09. Found: C, 58.04, H, 3.02.

1,3-ditrifluoroacetyl-2-indanone (**2c**). To 30 mL dry Et_2O in a round bottom flask equipped with a magnetic stirrer is added sodium methoxide (0.449 g, 8.32 mmol) all at once. Then, trifluoromethyl ethyl acetate (0.903 mL, 7.57 mmol) is added dropwise slowly while stirring. After 5 minutes, 2-indanone (1.00 g, 7.57 mmol) dissolved in 20 mL dry Et_2O is added dropwise and stirred overnight at room temperature under a calcium chloride drying tube. After 24 h, another equivalent of trifluoromethyl ethyl acetate is added dropwise and stirred overnight at room temperature under a calcium chloride drying tube. The reaction mixture is acidified with 30 mL 3M sulfuric acid. The organic layer was separated, washed with deionized water, and the organic layer dried over Na_2SO_4 . The solvent was evaporated under reduced pressure, providing a yellow solid, which when recrystallized, yielded yellow crystals (cyclohexane), in 42% yield, m.p. 111–113 °C. NMR: 1H : δ 7.34 (2H, m), 7.65 (2H, m), 13.50 (2H, bs). ^{13}C : δ 111.5, 118.4 (CF_3 , q, $^1J_{C-F}$ = 273 Hz), 119.6, 122.9, 126.7, 128.4, 128.9, 130.2, 168.5 (C- CF_3 , q, $^2J_{C-F}$ = 35 Hz), 177.0. ^{19}F : −68.53 (s, 3F). HRMS (ESI+) calcd for $C_{13}H_6F_6O_3$: 324.02211, found: 324.02158.

3-trifluoroacetyl-2-tetralone (**3b**) and 1-trifluoroacetyl-2-tetralone (**3c**). These compounds were obtained as a 4:3 mixture of **3b**:**3c**. Radial chromatography (100% CH_2Cl_2 –50/50 CH_2Cl_2 /MeOH) afforded two product fractions. Fraction 1: **3b** as orange crystals (hexane), in 40% yield, m.p. 123–126 °C. NMR: 1H : δ , 3.76 (2H, s), 3.81 (2H, s), 7.25–8.05 (4H, m), 15.01 (1H, bs). ^{13}C : δ 27.8, 38.3, 103.7, 117.5 (CF_3 , q, $^1J_{C-F}$ = 281 Hz), 127.1, 127.3, 127.8, 127.9, 130.5, 133.4, 157.3, 174.8 (C- CF_3 , q, $^2J_{C-F}$ = 35 Hz), 191.0. ^{19}F (C_6F_6 ext. std.): δ −70.62 (s, 3F). HRMS (ESI+) calcd for $C_{12}H_9F_3O_2$: 242.04470, found: 242.04436. Fraction 2: **3c** (30%) as an orange solid, m.p. 88–91 °C. **3c**: NMR: 1H : δ 2.72 (2H, t, 2J = 1.9 Hz), 3.01 (2H, t, 2J = 1.9 Hz), 7.25 (4H, m), 14.98 (1H, bs). ^{13}C : δ 25.0, 30.3, 102.9, 118.6 (CF_3 , q, $^1J_{C-F}$ = 282 Hz), 126.6, 126.9, 127.3, 128.1, 130.2, 133.8, 158.1, 175.4 (C- CF_3 , q, $^2J_{C-F}$ = 35 Hz), 189.1. ^{19}F (C_6F_6 ext. std.): δ −67.70 (s, 3F). HRMS (ESI+) calcd for $C_{12}H_9F_3O_2$: 242.04470, found: 242.04442.

3-trifluoroacetyl-2-naphthol (**3d**). A round bottom flask equipped with a magnetic stirrer containing 30 mL dry Et_2O is charged with 1 equivalent $NaOCH_3$. Then, 1 equivalent ethyl trifluoroacetate is added dropwise slowly and stirred for 15 min. To this solution is added a 4:3 mixture of compounds **3b**:**3c** dissolved in 20 mL Et_2O . The reaction mixture is stirred overnight at room temperature under a calcium chloride drying tube. The solvent is removed under reduced pressure while heating at 60 °C for 20 min. The solid residue is acidified with 30 mL 3M sulfuric acid and extracted with 3–15 mL portions of Et_2O . The organic layers were combined, washed with deionized water, and the organic layer dried over Na_2SO_4 . The solvent was evaporated under reduced pressure, providing a orange solid, which when subjected to radial chromatography, gave a fraction which upon recrystallization, yielded pale, orange crystals (CH_2Cl_2), **3d**, in 45% yield, m.p. 80–83 °C. An additional fraction was collected which contained unreacted **3b** and **3c**. **3d**: NMR: 1H : δ , 7.25–8.05 (6H, m), 14.83 (1H, bs). ^{13}C : δ 119.3 (CF_3 , q, $^1J_{C-F}$ = 284 Hz), 124.9, 125.4, 126.9, 129.9, 130.1, 130.4, 131.4, 135.1, 139.1, 157.3, 184.6 (C- CF_3 , q, $^2J_{C-F}$ = 35 Hz). ^{19}F (C_6F_6 ext. std.): δ −74.25 (s, 3F). Analysis calcd for $C_{12}H_7F_3O_2$:

C, 60.01, H, 2.94. Found: C, 60.13, H, 2.88.

4,4,4-trifluoro-1-(1-oxotetrahydronaphthyl)-1,3-butanedione (**4b**) [17]. A 100 mL round bottom flask is charged with 50 mL dry Et₂O, 5 mL dry diisopropylamine, equipped with a magnetic stir bar and placed under N₂ at 0 °C. To this is added LDA (6.0 mL, 0.0120 mol) and stirred for fifteen minutes. Then, a solution of **4a** (0.752 g, 0.004 mol) in 15 mL dry Et₂O is added dropwise slowly via syringe. After 8 h, ethyl trifluoroacetate (0.96 mL, 0.008 mol) is delivered dropwise slowly via syringe, the reaction mixture is stirred overnight and allowed to warm to rt. A third equivalent of ethyl trifluoroacetate (0.004 mol) is added after 24 hours and the solution is left to stir again overnight. The reaction mixture is acidified with 30 mL 3M sulfuric acid. The organic layer was separated, washed with deionized water, and the organic layer dried over Na₂SO₄. The solvent was evaporated under reduced pressure, and subjected to radial chromatography. After recrystallization from cyclohexane, **4b** was obtained as reddish-brown crystals in 27% yield, mp 133–135 °C. **4b**: NMR: ¹H: δ 2.85 (2H, t, 7.6 Hz), 2.93 (2H, t, 7.6 Hz), 6.76 (s, 1H), 7.37–7.77 (4H, m), 15.68 (2H, bs). ¹³C: δ 20.9, 22.7, 104.6, 118.4 (CF₃, q, ¹J_{C-F} = 270 Hz), 125.9, 126.8, 127.3, 127.4, 128.2, 128.5, 128.6, 129.9, 133.9, 142.8, 177.0 (C-CF₃, q, ²J_{C-F} = 36 Hz), 182.2. ¹⁹F (C₆F₆ ext. std.): δ −72.04 (s, 3F). Analysis calcd for C₁₄H₁₁F₃O₃: C, 59.16, H, 3.90. Found: C, 58.99, H, 4.01.

2-trifluoroacetyl-1-tetralone (**4c**). This compound was obtained as off-white crystals, **4c**, in 53% yield, m.p. 50–52 °C lit [18] (m.p. 51–52 °C). **4c**: NMR: ¹H: δ 2.75 (2H, t, 9.0 Hz), 2.88 (2H, t, 9.0 Hz), 7.16–7.87 (4H, m), 15.62 (1H, bs). ¹³C: δ 21.0, 27.8, 38.3, 103.7, 117.5 (CF₃, q, ¹J_{C-F} = 285 Hz), 127.1, 127.3, 127.8, 127.9, 130.5, 133.4, 157.3, 174.8 (C-CF₃, q, ²J_{C-F} = 35 Hz), 185.0. ¹⁹F (C₆F₆ ext. std.): δ −70.61 (s, 3F). HRMS (ESI+) calcd for C₁₂H₉F₃O₂: 242.04470, found: 242.04436.

4,4,4-trifluoro-1-(1-hydroxynaphthyl)-1,3-butanedione (**5b**) [17]. A 100 mL RBF equipped with a magnetic stir bar is charged with 50 mL dry Et₂O, 5 mL dry diisopropylamine (DIPA) and placed under N₂ at 0 °C. To this is added LDA (6.0 mL, 0.0120 mol) and stirred for fifteen minutes. Then, a solution of **5a** (0.740 g, 0.004 mol) in 15 mL dry Et₂O is added dropwise slowly via syringe. After 8 h, ethyl trifluoroacetate (0.96 mL, 0.008 mol) is delivered dropwise slowly via syringe and the reaction mixture is stirred overnight and allowed to warm to rt. After 24 h, another equivalent of ethyl trifluoroacetate (0.46 mL, 0.004 mol) is added all at once. The reaction is stirred for an additional 24 h. The reaction mixture is acidified with 30 mL 3M sulfuric acid. The organic layer was separated, washed with deionized water, and the organic layer dried over Na₂SO₄. The solvent was evaporated under reduced pressure, and subjected to radial chromatography. After recrystallization (cyclohexane) **5b** was obtained as brown crystals, in 22% yield, m.p. 154–157 °C. **5b**: NMR: ¹H: δ 6.90 (s, 1H), 7.51–8.50 (6H, m), 14.44 (1H, bs), 15.70 (1H, bs). ¹³C: δ 111.9, 115.7 (CF₃, q, ¹J_{C-F} = 271 Hz), 127.1, 127.3, 127.8, 127.9, 130.5, 133.4, 157.3, 174.8 (C-CF₃, q, ²J_{C-F} = 35 Hz), 185.0. ¹⁹F (C₆F₆ ext. std.): δ −71.60 (s, 3F). Analysis calcd for C₁₄H₉F₃O₃: C, 59.59, H, 3.21. Found: C, 59.86, H, 3.16.

2-acetyl-4-fluoro-1-naphthol (**5c**) and 2-acetyl-3-fluoro-1-naphthol (**5d**). These compounds were obtained as a 5:1 mixture of **5c**:**5d**. Radial chromatography (100% CH₂Cl₂–50/50 CH₂Cl₂/MeOH) afforded **5c** as brown crystals (51%, m.p. 93–95 °C) and **5d** as a tan solid (13%, m.p. 88–91 °C). **5c**: NMR: ¹H: δ 2.71 (3H, s), 7.31–8.48 (5H, m), 14.01 (1H, bs). ¹³C: δ 26.9, 113.1, 118.3, 124.9, 126.0, 127.4, 130.1, 137.4, 150.5 (Ar-F, d, ¹J_{C-F} = 243 Hz), 162.4, 204.2. ¹⁹F (C₆F₆ ext. std.): δ −134.0 (s, 1F). Analysis calcd for C₁₂H₉FO₂: C, 70.59, H, 4.44. Found: C, 70.77, H, 4.31. **5d**: NMR: ¹H: δ 2.63 (3H, s), 7.40–8.00 (5H, m), 13.82 (1H, bs). ¹³C: δ 27.6, 111.3, 120.3, 124.6, 125.1, 126.9, 128.6, 130.2,

130.3, 155.5 (Ar-F, d, $^1J_{C-F} = 244$ Hz), 158.7, 203.4. ^{19}F (C_6F_6 ext. std.): $\delta -134.2$ (s, 1F). Analysis calcd for $\text{C}_{12}\text{H}_9\text{FO}_2$: C, 70.59, H, 4.44. Found: C, 70.44, H, 4.49.

3. Results and Discussion

3.1. Synthesis

Compounds **1a–5a** are commercially available and were used without further purification. Compounds **1b** and **1c** have been previously described, but were prepared according to a different method [14,15]. Compound **1d** is known and was synthesized via a previously described method [12,16]. The remaining compounds were prepared using a modified Claisen condensation or direct fluorination with Selectfluor® [10,12,13,18,19]. See Scheme 1.

Recent work by our group showed that regioselective monofluorination and geminal difluorination of acyclic β -diketones could be effected with Selectfluor® under mild conditions without the necessity of specialized glassware or safety precautions [10,14,15]. The current synthetic investigation sought to take advantage of this earlier work by probing Selectfluor®'s efficiency and effectiveness in the mono- and difluorination of 1,3-indanedione and bindone. Our efforts revealed some unexpected findings. The monofluorination of **1a** proceeded with little difficulty to give 2-fluoro-1,3-indanedione (**1b**) in the diketonic form (as evidenced by a doublet signal ($J_{F-H} = 51.1$ Hz) in the ^{19}F NMR at -207.3 ppm), albeit in slightly lower yield compared to fluorination achieved with 5% F_2 in N_2 [10]. Diketone **1b** was also successfully fluorinated (as evidenced by a singlet signal in the ^{19}F NMR at -125.9 ppm), delivering the geminally difluorinated product **1c** in good overall yield.

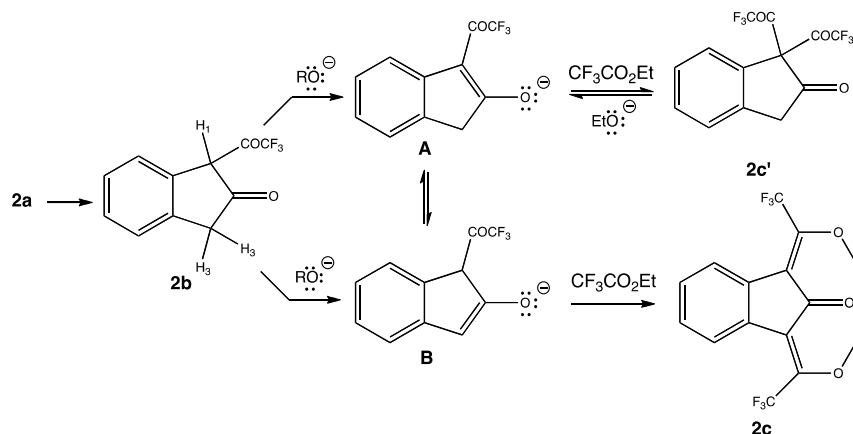
We then examined whether bindone, the aldol self-condensation product of 1,3-indanedione, would react similarly to treatment with Selectfluor®. As expected, monofluorination was achieved in high yield to give **1e** as an enantiomeric triketone pair (^{19}F NMR: -182.4 ppm, $J_{F-H} = 46.0$ Hz), but the site of fluorination was the α -carbon adjacent to the isolated ketone rather than fluorination between the 1,3-diketone residue. Subsequent fluorination of **1e** likewise yielded interesting results. Particularly noteworthy were the fluorination regioselectivity and alkene rearrangement observed during the formation of triketone **1f**. We expected an outcome similar to the fluorination of **1b**, but the occurrence of two distinct signals in the ^{19}F NMR at -137.3 ppm and -176.7 ppm ruled out geminal difluorination. Evidently, the alkene in **1e** retains sufficient nucleophilic nature to permit electrophilic fluorination between the β -dicarbonyl residue. This addition, coupled with a concomitant E1-like elimination leads to **1f**, rather than formation of [Δ 1,2'-Biindan]-2,2-difluoro-1',3,3'-trione, shown in Scheme 1.

While preparing **2b** and **2c**, the previously undescribed one-pot, twin trifluoroacetylation of 2-indanone gave the dual exocyclic enol **2c** in moderate yield (confirmed by the presence of a single ^{19}F NMR resonance at -68.5 ppm) and no **2c'**, Figure 2. In this case, the ethoxide base present following the condensation apparently deprotonates the unsubstituted benzylic α -hydrogen (H_3) rather than the more acidic α -hydrogen H_1 .

There are several possible explanations for the formation of **2c** and the failure to obtain **2c'**. The most plausible scenario involves initial formation of **2c'**. Given the basic reaction conditions, however, we surmise that upon attachment of the second COCF_3 group, **2c'** may undergo nucleophilic acyl substitution by ethoxide, reverting **2c'** back to enolate **A**. A second possibility for the failure to obtain

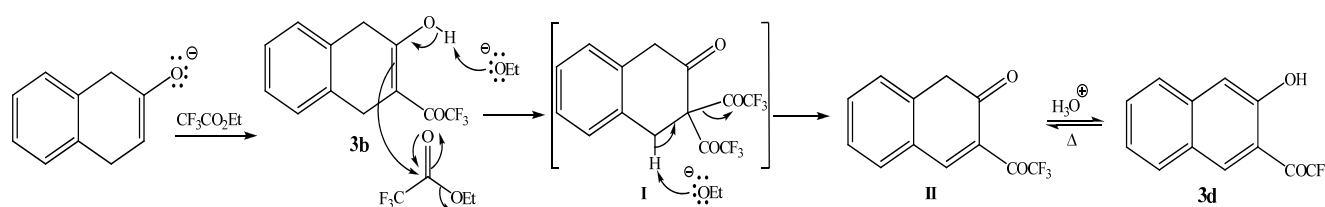
2c' may be larger steric demands in the transition state leading to enolate **A** formation relative to that leading to enolate **B**. Finally, a base-promoted tautomerization from enolate **A** to enolate **B** could occur before formation of **2c'**, ultimately leading to **2c**.

Figure 2. Formation of 1,3-ditrifluoroacetyl-2-indanone (**2c**).



We then attempted a similar strategy with β -tetralone (**3a**) to ascertain whether this ditrifluoroacetylation methodology could be generalized to other ketones with two acidic α -hydrogen sets. Sequential treatment of **3a** with two equivalents of ethyl trifluoroacetate followed by neutralization at room temperature led to a mixture of the 3- and 1-trifluoroacetyl-2-tetralone endocyclic enols **3b** and **3c**, respectively; the formation of 1,3-ditrifluoroacetyl-2-tetralone was not observed. Assignment of the endocyclic enolic structures was based on the observation of a single ¹⁹F NMR resonance at −70.6 ppm for **3b** and −67.7 ppm for **3c**. When the reaction workup conditions were modified by subjecting the enols **3b** and **3c** to an additional equivalent of base and ethyl trifluoroacetate followed by *in vacuo* removal of solvent at elevated temperature, we were surprised to find that aromatization occurred to give the trifluoroacetylated naphthol **3d** in moderate overall yield. Figure 3 depicts a plausible route to naphthol **3d**. We surmise that deprotonation of the less sterically hindered α -hydrogen enroute to **3b** occurs rather than abstraction of the more acidic, benzylic α -hydrogen. Detrifluoroacetylation of triketone **I** followed by tautomerization of diketone **II** under acidic workup provides naphthol **3d**.

Figure 3. Formation of 3-trifluoroacetyl-2-tetralone (**3b**) and 3-trifluoroacetyl-2-naphthol (**3d**).



Application of Light and Hauser's method to **4a** and **5a** produced the cross-conjugated, dienolic 1,3,5-triketones **4b** and **5b** in modest yields [17]. Assignment of the enolic structures was based on a combination of resonances found in their NMR spectra—(**4b**) ¹H: an alkene proton signal @ 6.76 ppm (1H), a broad, unresolvable singlet corresponding to the enol protons @ 15.68 ppm (2H) and ¹⁹F: a

singlet @ -72.0 ppm (3F); for (**5b**) ^1H : an alkene proton signal @ 6.90 ppm (1H), a singlet corresponding to the phenolic enol proton @ 14.44 (1H), a broader singlet @ 15.68 ppm (1H) corresponding to the enol adjacent to the CF_3 group and ^{19}F : a singlet @ -71.6 ppm (3F). Addition of D_2O to the NMR samples of **4b** and **5b** resulted in rapid diminuation of the exchangeable enolic protons in the ^1H NMR. Increasing the molar ratio of ethyl trifluoroacetate:diketone to $>2:1$, although necessary for triketone product formation, also led to *O*-trifluoroacetylated by-products. Fortunately, these were easily separated by chromatography from the desired 1,3,5-triketones. Additionally, we found that when **4a** was subjected to standard Claisen reaction conditions, an unintended acetyl-trifluoroacetyl group exchange occurred to give 2-trifluoroacetyl-1-tetralone (**4c**) in good yield along with, to our surprise, naphthol **5a**. A process similar to the detrifluoroacetylation depicted in Figure 2 may be operating in these cases as well.

Treatment of **5a** with Selectfluor[®] demonstrated the fluorination preference of activated aromatic substrates over acetyl groups [19–21]. The fluorinated naphthols **5c** and **5d** were achieved in good overall yield and a 5:1 ratio of the *para:meta* isomers, respectively. Ring fluorination was confirmed by the observation of resonances in the ^{19}F NMR spectra as singlets: -134.0 ppm (1F) and -134.2 ppm (1F) for **5c** and **5d**, respectively. Preferential *para* fluorination is in accord with the *o-p* directing ability of the hydroxyl group. Use of up to 5 equivalents of Selectfluor[®] to effect fluorination at the acetyl carbon provided only the monofluorinated naphthols **5c** and **5d**.

3.2. Solid State Structural Features: X-ray Crystallography

Several of the target molecules (**1d**, **2c**, **3c** and **4c**) were examined by x-ray crystallography. Crystal data and structure refinement information for **1d** and **2c** are recorded in Figure 4 and Table 1 while Figure 5 and Table 2 contain data for **3d** and **4c**. Critical bond information is listed in Table 3. The crystallographic information files for these molecules have been uploaded to the Cambridge Crystallographic Data Center and have the following control numbers: **1d**: 854704, **2c**: 854697, **3d**: 854705 and **4c**: 854706.

Figure 4. ORTEP drawings of **1d** and **2c**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

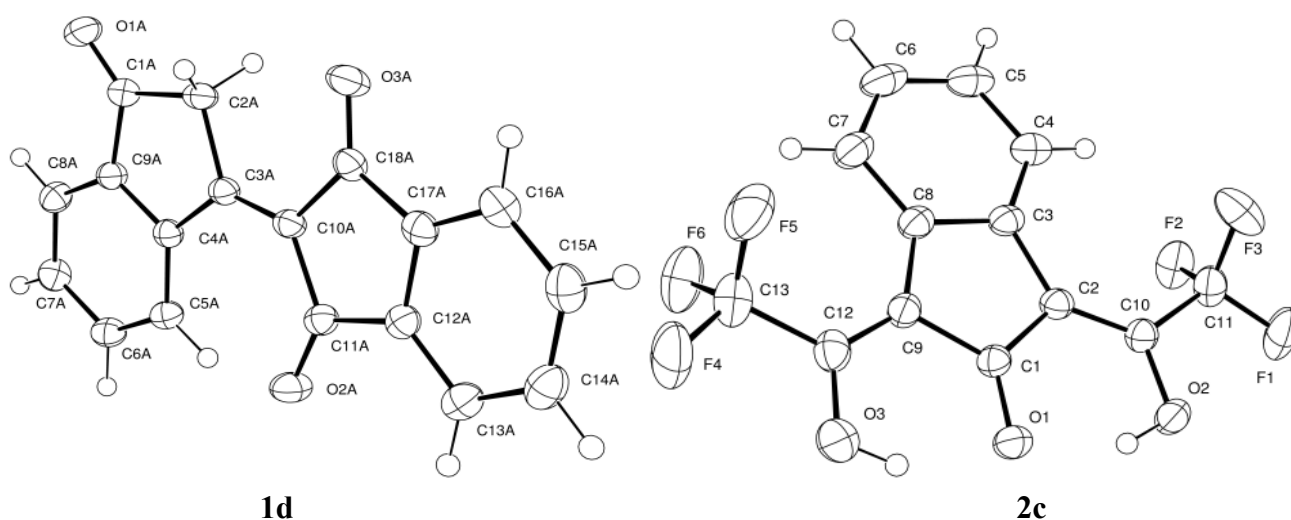


Table 1. Crystal data and structure refinement for **1d** and **2c**.

Compound	1d	2c
Formula	C ₁₈ H ₁₀ O ₃	C ₁₃ H ₆ F ₆ O ₃
Formula Weight (g/mol)	274.26	324.18
Crystal Dimensions (mm)	0.30 × 0.24 × 0.20	1.20 × 0.10 × 0.06
Crystal Color and Habit	clear prism	yellow needle
Crystal System	orthorhombic	monoclinic
Space Group	F d d 2	P 2 ₁ /c
Temperature, K	173	173
a, Å	18.0996(6)	
b, Å	20.9271(7)	18.6978(12)
c, Å	26.0789(8)	13.8431(9)
α, °	90.00	90.0
β, °	90.00	98.964(3)
Compound	1d	2c
γ, °	90.00	90.0
V, Å ³	9878.0(6)	1218.11(14)
Reflections to determine final unit cell	9975	9959
2θ range, °	5.0, 56.84	5.28–57.7
Z	32	4
F(000)	4544	648.71
ρ (g/cm)	1.475	1.768
λ, Å, (MoKα)	0.71070	0.71073
μ, (cm ^{−1})	0.101	0.18
Reflections collected	103146	26516
Unique reflections	6360	3195
R _{merge}	0.0403	0.027
Cut off Threshold Expression	>2sigma(I)	Inet > 1.0sigma(Inet)
Refinement method	full matrix least-sqs using F ²	full matrix least-sqs using F
Weighting Scheme	1/[sigma ² (Fo ²) + (0.0555P) ² + 3.0465P] where P = (Fo ² + 2Fc ²)/3	1/(sigma ² (F) + 0.0005F ²)
R ₁ ^a	0.0342	0.038
wR ₂	0.0846 ^b	0.053 ^c
R ₁ (all data)	0.0400	0.046
wR ₂ (all data)	0.0880	0.054
GOF	1.038 ^d	1.74 ^e

^a R₁ = $\sum(|F_o| - |F_c|)/\sum F_o$; ^b wR₂ = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$; ^c wR₂ = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$;

^d GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(\# \text{ reflns} - \# \text{ params})]^{1/2}$; ^e GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(\text{No. reflns. No. params.})]^{1/2}$.

Figure 5. ORTEP drawings of **3d** and **4c**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

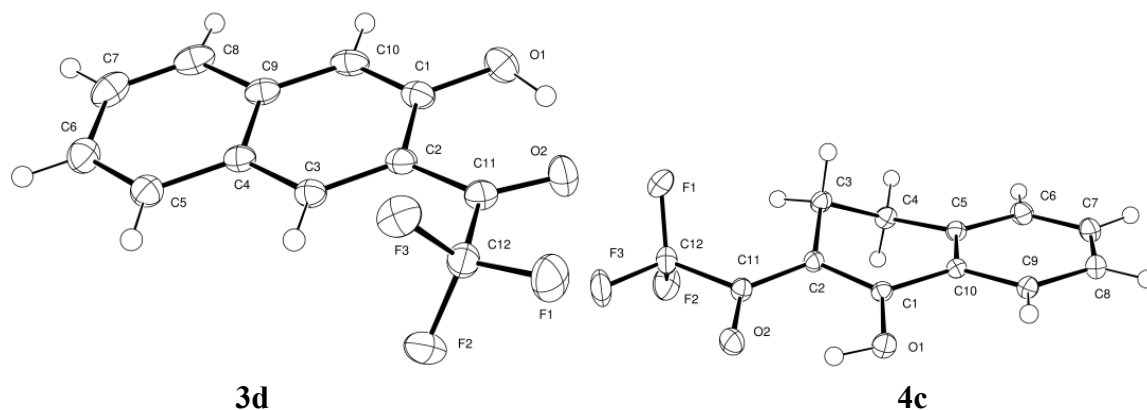


Table 2. Crystal data and structure refinement for **3d** and **4c**.

Compound	3d	4c
Formula	C ₁₂ H ₇ F ₃ O ₂	C ₁₂ H ₉ F ₃ O ₂
Formula Weight (g/mol)	240.18	242.19
crystal size (mm)	0.46 × 0.08 × 0.04	0.38 × 0.28 × 0.04
crystal color/shape	orange yellow needle	colourless plate
cryst syst	orthorhombic	triclinic
space group	P n a 2 ₁	P-1
temp, K	110	110
a, Å	13.5923(5)	7.3528(2)
b, Å	14.9695(5)	7.9165(2)
c, Å	4.8381(2)	9.7991(2)
α, °	90.00	73.0533(11)
β, °	90.00	85.3968(12)
γ, °	90.00	68.3581(11)
V, Å ³	984.41(6)	506.92(2)
Reflections to final unit cell	5859	6416
2θ range, °	5.44–52.66	5.78–71.38
Z	4	2
F(000)	488	248
ρ (g/cm ³)	1.621	1.587
λ, Å, (MoKα)	0.71070	0.71073
μ, (cm ^{−1})	0.147	0.143
Reflections collected	21568	20479
Unique reflections	2632	4691
R _{merge}	0.0444	0.0265
Cut off Threshold Expression	>2sigma(I)	>2sigma(I)
refinement method	full matrix least-sqs using F ²	full matrix least-sqs using F ²
Weighting Scheme	1/[sigma ² (Fo ²) + (0.0406P) ² + 0.0000P] where P = (Fo ² + 2Fc ²)/3	1/[sigma ² (Fo ²) + (0.0707P) ² + 0.0436P] where P = (Fo ² + 2Fc ²)/3
R ₁ ^a	0.0370	0.0382
wR ₂	0.0712	0.1082

Table 2. Cont.

Compound	3d	4c
R ₁ (all data) ^b	0.0538	0.0525
wR ₂ (all data) ^a	0.0762	0.1220
GOF	1.035	1.048

^a $R_1 = \sum(|F_o - F_c|)/\sum F_o$, $wR_2 = [\sum(w(F_o - F_c)^2)/\sum(F_o^2)]^{1/2}$, $GOF = [\sum(w(F_o - F_c)^2)/(\text{No. reflns.} - \text{No. params.})]^{1/2}$;

^b $R_1 = \sum(|F_o| - |F_c|)/\sum F_o$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$, $GOF = [\sum(w(F_o^2 - F_c^2)^2)/(\text{No. reflns.} - \text{No. params.})]^{1/2}$

Table 3. Selected interatomic distances and bond lengths of 1d, 2c, 3d and 4c.

	Interatomic Distances (Å)		Bond Lengths (Å)			Dihedral ∠ (°)
	O···O	O···H	O-H	C-O	C-C	
1d	NA	NA	NA	C _{1A} -O _{1A}	C _{3A} -C _{10A}	O ₃ -C ₁₈ -C ₁₀ -C ₃ -2.4(11)
				1.2143(17)	1.3574(19)	
				C _{11A} -O _{2A}		
				1.2212(17)		
2c	O ₁ ···O ₂	O ₁ ···H ₂	O ₂ -H ₂	C ₁ -O ₁	C ₁ -C ₂	O ₁ -C ₁ -C ₂ -C ₁₀ -1.91(11)
	2.5781(13)	1.75(2)	0.90(2)	1.2576(15)	1.4547(15)	
	O ₁ ···O ₃	O ₁ ···H ₃	O ₃ -H ₃	C ₁₀ -O ₂	C ₂ -C ₁₀	
	2.5926(14)	1.81(2)	0.88(2)	1.3308(15)	1.3593(17)	
3d				C ₁₂ -O ₃	C ₉ -C ₁₂	O ₁ -C ₁ -C ₂ -C ₁₁ 1.9(2)
				1.3242(17)	1.3602(17)	
	O ₁ ···O ₂	O ₂ ···H	O ₁ -H	C ₁ -O ₁	C ₁ -C ₂	
	2.6142(17)	1.75(3)	0.97(3)	1.3588(19)	1.438(2)	
4c				C ₁₁ -O ₂	C ₂ -C ₁₁	O ₁ -C ₁ -C ₂ -C ₁₁ -2.04(11)
				1.2199(18)	1.459(2)	
	O ₁ ···O ₂	O ₂ ···H	O ₁ -H	C ₁ -O ₁	C ₁ -C ₂	
	2.5063(9)	1.72(2)	0.855(19)	1.3215(9)	1.3895(10)	
				C ₁₁ -O ₂	C ₂ -C ₁₁	
				1.2476(10)	1.4193(10)	

In the case of compound **1d**, the small O₃-C₁₀-C₁₈-C₃ dihedral angle of -2.4° shows bond to be nearly planar across the ring bridge in the solid state. The C-O and C₃-C₁₀ bond lengths are consistent with those of typical carbonyls and alkenes, respectively and identify **1d** as a cross-conjugated triketone in the solid state. For **2c**, x-ray crystallography confirms the preference of a previously unreported structure in the solid state: a planar, exocyclic dienol shown in Figure 4. The weak intramolecular H-bonding normally observed in cyclic triketones is clearly supported for **2c** by the interatomic O···H-O distances of 1.75 Å and 1.81 Å and very short O-H bond lengths of 0.88 Å and 0.90 Å [11,22]. The small O₁-C₁-C₂-C₁₀ dihedral angle of -1.91° attests to the planar nature of the cyclopentanone residue.

Likewise, 3-trifluoroacetyl-2-naphthol (**3d**) and 2-trifluoroacetyl-1-tetralone (**4c**) show trends consistent with a single endocyclic cis-enol tautomer having weak intramolecular H-bonding, e.g.,

interatomic O···H-O distances $>1.7\text{\AA}$, O-H bond lengths $< 1.0\text{\AA}$ and small O₁-C₁-C₂-C₁₁ dihedral angles. For **3d**, the aromatic ring introduces an additional structural constraint prohibiting tautomerism to either the diketo form or any other enolic structure.

Spectral data provided in the experimental section supports the solid-state structural data presented herein [8–10,23–28]. A detailed examination of the absorption, vibrational and magnetic resonance spectroscopy of these molecules is underway to discern the keto-enol and enol-enol behavior of these di- and triketones in various solvent systems and where applicable in the solid-state and/or neat liquid. Those results, along with a comparative ab initio component, will be presented in a future communication.

Acknowledgments

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Appendix. X-Ray Experimental Procedures and Data

1. Compound **1d**

Experimental for C₁₈H₁₀O₃ (**1d**)

Data Collection and Processing. The sample **1d** was submitted by Joseph Sloop of the Sloop research group at Georgia Gwinnett College. The sample was mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at a temperature of 173 K. The unit cell dimensions were determined from a symmetry constrained fit of 9975 reflections with $5.0^\circ < 2\theta < 56.84^\circ$. The data collection strategy was a number of ω and ϕ scans which collected data up to 58.24° (2θ). The frame integration was performed using SAINT [29]. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS [30].

Structure Solution and Refinement. The structure was solved by direct methods using the SIR92 program [31]. All non-hydrogen atoms were obtained from the initial E-map. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on F^2 . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the XL program from SHELXTL [32], graphic plots were produced using the NRCVAX crystallographic program suite. Additional information and other relevant literature references can be found in the reference section of the Facility's Web page (<http://www.xray.ncsu.edu>).

Figure 6. ORTEP drawing of *1d molecule A* showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

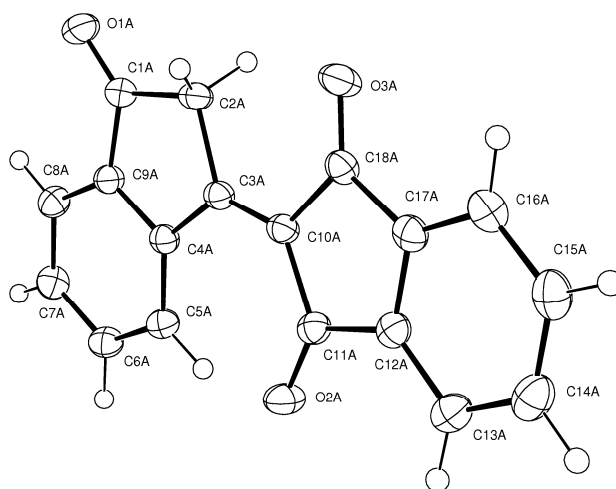


Figure 7. ORTEP drawing of *1d molecule A*. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

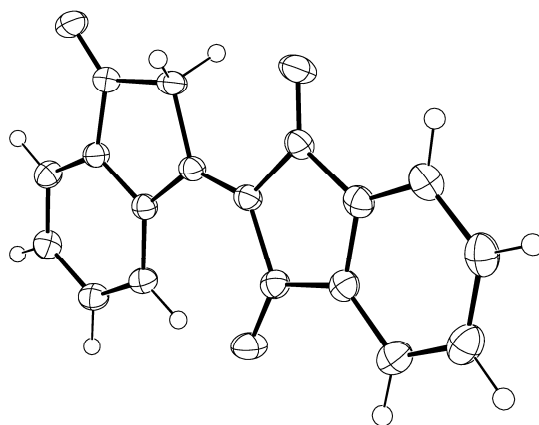


Figure 8. Stereoscopic ORTEP drawing of *1d molecule A*. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

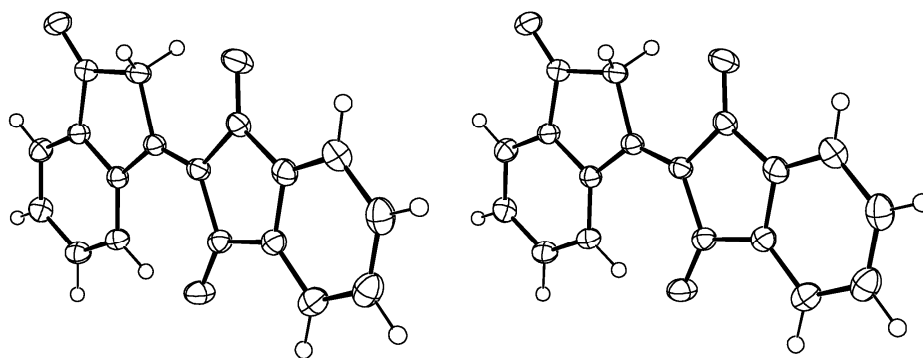


Figure 9. ORTEP drawing of *1d molecule B* showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

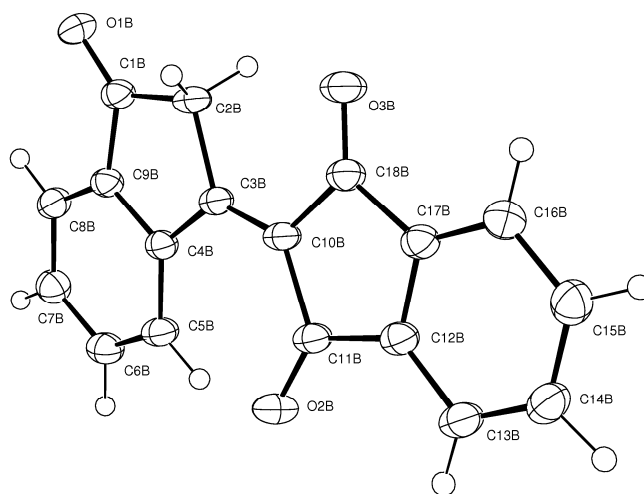


Figure 10. ORTEP drawing of *1d molecule B*. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

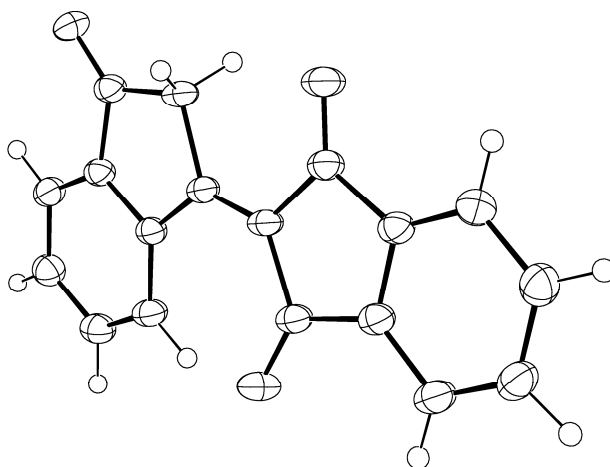


Figure 11. Stereoscopic ORTEP drawing of *1d molecule B*. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

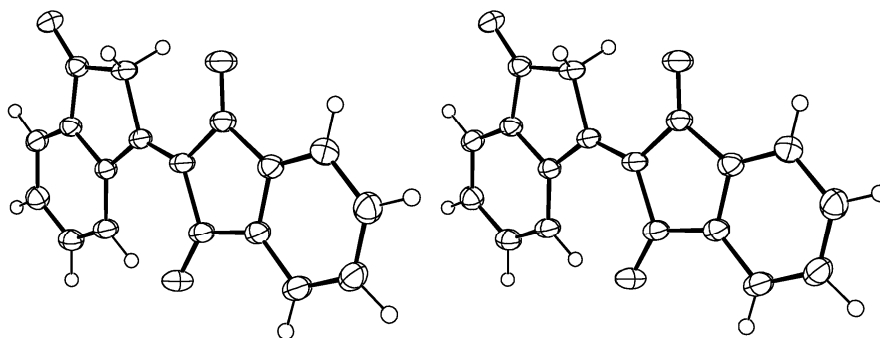


Table 4. Summary of Crystal Data for **Id**.

Formula	C ₁₈ H ₁₀ O ₃
Formula Weight (g/mol)	274.26
Crystal Dimensions (mm)	0.30 × 0.24 × 0.20
Crystal Color and Habit	clear prism
Crystal System	orthorhombic
Space Group	F d d 2
Temperature, K	173
a, Å	18.0996(6)
b, Å	20.9271(7)
c, Å	26.0789(8)
α, °	90.00
β, °	90.00
γ, °	90.00
V, Å ³	9878.0(6)
Number of reflections to determine final unit cell	9975
Min and Max 2θ for cell determination, °	5.0, 56.84
Z	32
F(000)	4544
ρ (g/cm ³)	1.475
λ, Å, (MoKα)	0.71070
μ, (cm ^{−1})	0.101
Diffractionmeter Type	Bruker-Nonius X8 Apex2
Scan Type(s)	omega and phi scans
Max 2θ for data collection, °	58.24
Measured fraction of data	1.000
Number of reflections measured	103146
Unique reflections measured	6360
R _{merge}	0.0403
Number of reflections included in refinement	6360
Cut off Threshold Expression	>2sigma(I)
Structure refined using	full matrix least-squares using F ²
Weighting Scheme	calc w = 1/[sigma ² (F _o ²) + (0.0555P) ² + 3.0465P] where P=(F _o ² + 2F _c ²)/3
Number of parameters in least-squares	458
R ₁	0.0342
wR ₂	0.0846
R ₁ (all data)	0.0400
wR ₂ (all data)	0.0880
GOF	1.038
Maximum shift/error	0.000
Min & Max peak heights on final ΔF Map (e [−] /Å)	−0.219, 0.216

Where:

$$R_1 = \sum (|F_o| - |F_c|) / \sum F_o$$

$$wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$$

$$GOF = [\sum w (F_o^2 - F_c^2)^2 / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$$

Table 5. Atomic Coordinates for *1d*.

Atom	x	y	z	U _{iso} /equiv
O1A	0.20028(6)	0.13639(6)	0.62634(6)	0.0362(3)
O2A	0.36237(6)	0.01557(5)	0.4220	0.0310(2)
O3A	0.40033(6)	−0.02683(5)	0.59892(6)	0.0329(2)
C1A	0.23461(8)	0.12010(7)	0.58853(6)	0.0257(3)
C2A	0.29550(8)	0.07078(7)	0.58765(6)	0.0265(3)
C3A	0.31404(7)	0.06171(6)	0.53149(6)	0.0215(2)
C4A	0.27141(7)	0.10937(6)	0.50228(6)	0.0214(2)
C5A	0.27082(8)	0.12548(7)	0.45022(6)	0.0246(3)
C6A	0.22256(8)	0.17252(7)	0.43340(7)	0.0271(3)
C7A	0.17513(8)	0.20411(7)	0.46700(7)	0.0283(3)
C8A	0.17630(8)	0.19033(7)	0.51873(7)	0.0279(3)
C9A	0.22477(7)	0.14322(7)	0.53572(6)	0.0234(3)
C10A	0.36116(7)	0.01514(6)	0.51589(6)	0.0217(2)
C11A	0.38319(7)	−0.00519(6)	0.46328(6)	0.0228(3)
C12A	0.43567(7)	−0.05931(6)	0.46890(7)	0.0231(3)
C13A	0.47199(8)	−0.09342(7)	0.43109(7)	0.0289(3)
C14A	0.51888(9)	−0.14212(8)	0.44613(8)	0.0328(3)
C15A	0.52844(9)	−0.15676(8)	0.49786(8)	0.0331(3)
C16A	0.49169(8)	−0.12272(7)	0.53601(7)	0.0293(3)
C17A	0.44557(7)	−0.07332(6)	0.52064(7)	0.0242(3)
C18A	0.40165(7)	−0.02813(7)	0.55238(7)	0.0237(3)
O1B	0.14120(7)	0.04113(5)	0.35875(6)	0.0349(2)
O2B	0.25973(7)	−0.11687(6)	0.56110(5)	0.0351(2)
O3B	0.29954(7)	−0.15569(6)	0.38414(6)	0.0367(3)
C1B	0.15538(8)	0.00789(7)	0.39573(6)	0.0270(3)
C2B	0.20581(8)	−0.04922(7)	0.39627(6)	0.0267(3)
C3B	0.21160(8)	−0.06899(7)	0.45205(6)	0.0233(3)
C4B	0.16128(8)	−0.02763(7)	0.48137(7)	0.0241(3)
C5B	0.14109(8)	−0.02690(8)	0.53345(7)	0.0286(3)
C6B	0.09013(9)	0.01792(8)	0.54976(7)	0.0314(3)
C7B	0.05876(9)	0.06238(8)	0.51670(7)	0.0318(3)
C8B	0.07692(9)	0.06178(7)	0.46499(7)	0.0298(3)
C9B	0.12772(8)	0.01681(7)	0.44855(6)	0.0255(3)
C10B	0.25683(8)	−0.11716(7)	0.46724(6)	0.0245(3)
C11B	0.27541(8)	−0.14057(7)	0.52003(7)	0.0259(3)
C12B	0.32241(8)	−0.19790(7)	0.51345(7)	0.0262(3)
C13B	0.35157(9)	−0.23821(8)	0.55099(7)	0.0322(3)
C14B	0.39368(10)	−0.28954(8)	0.53526(8)	0.0352(3)
C15B	0.40794(9)	−0.30056(8)	0.48342(8)	0.0352(3)
C16B	0.37983(9)	−0.25975(7)	0.44609(7)	0.0322(3)
C17B	0.33643(8)	−0.20886(7)	0.46172(7)	0.0264(3)
C18B	0.29790(8)	−0.15934(7)	0.43065(7)	0.0269(3)
H2A1	0.2800(10)	0.0306(10)	0.6041(7)	0.038(5)
H2A2	0.3395(11)	0.0877(9)	0.6072(7)	0.037(5)

Table 5. *Cont.*

H5A	0.3041(10)	0.1074(9)	0.4261(8)	0.033(4)
H6A	0.2211(10)	0.1858(9)	0.3965(7)	0.034(5)
H7A	0.1431(11)	0.2367(9)	0.4567(7)	0.036(5)
H8A	0.1442(12)	0.2130(10)	0.5435(9)	0.045(6)
H13A	0.4637(10)	−0.0835(9)	0.3957(8)	0.036(5)
H14A	0.5436(10)	−0.1635(9)	0.4193(8)	0.035(5)
H15A	0.5585(12)	−0.1908(10)	0.5071(8)	0.044(6)
H16A	0.4962(11)	−0.1324(10)	0.5727(8)	0.041(5)
H2B1	0.2541(12)	−0.0384(10)	0.3821(9)	0.052(6)
H2B2	0.1831(10)	−0.0855(9)	0.3765(8)	0.035(5)
H5B	0.1623(10)	−0.0581(9)	0.5574(7)	0.033(5)
H6B	0.0744(12)	0.0181(10)	0.5865(9)	0.049(6)
H7B	0.0234(10)	0.0921(9)	0.5291(8)	0.035(5)
H8B	0.0572(10)	0.0917(9)	0.4398(8)	0.038(5)
H13B	0.3432(11)	−0.2287(9)	0.5847(8)	0.036(5)
H14B	0.4143(11)	−0.3227(10)	0.5586(8)	0.039(5)
H15B	0.4354(11)	−0.3383(9)	0.4722(8)	0.043(5)
H16B	0.3894(10)	−0.2680(9)	0.4103(7)	0.029(4)

Table 6. Anisotropic Displacement Parameters for *1d*.

Atom	u ¹¹	u ²²	u ³³	u ¹²	u ¹³	u ²³
O1A	0.0362(6)	0.0485(7)	0.0238(5)	0.0094(5)	0.0051(4)	−0.0015(5)
O2A	0.0394(6)	0.0338(6)	0.0198(5)	0.0040(4)	0.0011(4)	0.0012(4)
O3A	0.0398(6)	0.0369(6)	0.0221(5)	0.0069(5)	−0.0075(4)	−0.0029(4)
C1A	0.0256(6)	0.0301(7)	0.0215(6)	0.0000(5)	−0.0008(5)	−0.0014(5)
C2A	0.0291(7)	0.0326(7)	0.0179(6)	0.0040(6)	−0.0015(5)	−0.0015(5)
C3A	0.0217(6)	0.0238(6)	0.0191(6)	−0.0048(5)	−0.0004(4)	−0.0006(5)
C4A	0.0218(6)	0.0212(6)	0.0213(6)	−0.0030(5)	−0.0006(4)	−0.0007(5)
C5A	0.0276(7)	0.0253(7)	0.0210(6)	−0.0012(5)	0.0020(5)	0.0006(5)
C6A	0.0332(7)	0.0251(7)	0.0230(6)	−0.0029(5)	0.0008(5)	0.0032(5)
C7A	0.0299(7)	0.0245(7)	0.0306(7)	0.0028(5)	−0.0008(6)	0.0047(6)
C8A	0.0283(7)	0.0272(7)	0.0282(7)	0.0019(5)	0.0025(5)	−0.0001(6)
C9A	0.0244(6)	0.0250(6)	0.0209(6)	−0.0010(5)	0.0003(5)	−0.0001(5)
C10A	0.0227(6)	0.0235(6)	0.0190(6)	−0.0021(5)	−0.0016(5)	−0.0008(5)
C11A	0.0232(6)	0.0235(6)	0.0217(6)	−0.0034(5)	0.0019(5)	−0.0011(5)
C12A	0.0223(6)	0.0225(6)	0.0247(6)	−0.0031(5)	0.0014(5)	−0.0011(5)
C13A	0.0300(7)	0.0286(7)	0.0282(7)	−0.0032(6)	0.0055(5)	−0.0030(5)
C14A	0.0305(7)	0.0284(7)	0.0396(8)	−0.0010(6)	0.0067(6)	−0.0076(6)
C15A	0.0266(7)	0.0284(7)	0.0443(9)	0.0033(6)	−0.0025(6)	−0.0028(6)
C16A	0.0279(7)	0.0279(7)	0.0321(8)	0.0000(5)	−0.0052(6)	−0.0001(6)
C17A	0.0225(6)	0.0235(6)	0.0264(6)	−0.0046(5)	−0.0021(5)	−0.0016(5)
C18A	0.0225(6)	0.0249(7)	0.0237(6)	−0.0015(5)	−0.0034(5)	−0.0017(5)
O1B	0.0463(6)	0.0351(6)	0.0235(5)	−0.0023(5)	−0.0037(4)	0.0079(4)
O2B	0.0415(6)	0.0444(6)	0.0192(5)	0.0011(5)	−0.0023(4)	0.0013(4)
O3B	0.0480(6)	0.0425(6)	0.0196(5)	0.0073(5)	−0.0015(4)	0.0010(4)

Table 6. Cont.

C1B	0.0292(7)	0.0303(7)	0.0214(6)	−0.0089(5)	−0.0038(5)	0.0019(5)
C2B	0.0287(7)	0.0344(7)	0.0168(6)	−0.0024(6)	−0.0015(5)	0.0028(5)
C3B	0.0240(6)	0.0277(7)	0.0181(6)	−0.0080(5)	−0.0024(5)	0.0031(5)
C4B	0.0252(6)	0.0271(6)	0.0200(6)	−0.0078(5)	−0.0020(5)	0.0014(5)
C5B	0.0309(7)	0.0349(8)	0.0200(6)	−0.0068(6)	−0.0009(5)	0.0039(5)
C6B	0.0326(8)	0.0379(8)	0.0238(7)	−0.0048(6)	0.0018(5)	−0.0002(6)
C7B	0.0329(7)	0.0330(7)	0.0296(7)	−0.0032(6)	0.0011(6)	−0.0008(6)
C8B	0.0328(7)	0.0306(7)	0.0261(7)	−0.0037(6)	−0.0026(6)	0.0045(6)
C9B	0.0270(7)	0.0288(7)	0.0207(6)	−0.0068(5)	−0.0034(5)	0.0014(5)
C10B	0.0261(7)	0.0310(7)	0.0163(6)	−0.0071(5)	−0.0015(5)	0.0022(5)
C11B	0.0273(7)	0.0313(7)	0.0190(6)	−0.0078(5)	−0.0020(5)	0.0040(5)
C12B	0.0268(6)	0.0289(7)	0.0227(7)	−0.0089(5)	−0.0046(5)	0.0034(5)
C13B	0.0367(8)	0.0351(8)	0.0247(7)	−0.0091(6)	−0.0067(6)	0.0076(6)
C14B	0.0410(9)	0.0304(8)	0.0344(8)	−0.0063(6)	−0.0125(7)	0.0085(6)
C15B	0.0378(8)	0.0293(7)	0.0386(9)	−0.0001(6)	−0.0093(6)	0.0010(6)
C16B	0.0373(8)	0.0315(8)	0.0279(8)	−0.0012(6)	−0.0054(6)	−0.0008(6)
C17B	0.0284(7)	0.0281(7)	0.0228(6)	−0.0064(5)	−0.0043(5)	0.0020(5)
C18B	0.0301(7)	0.0304(7)	0.0203(6)	−0.0048(6)	−0.0030(5)	0.0016(5)

Table 7. Bond Lengths for *1d*.

O1A-C1A	1.2143(17)	O1B-C1B	1.2166(17)
O2A-C11A	1.2212(17)	O2B-C11B	1.2140(18)
O3A-C18A	1.2143(17)	O3B-C18B	1.2159(17)
C1A-C9A	1.4705(19)	C1B-C9B	1.4775(19)
C1A-C2A	1.510(2)	C1B-C2B	1.504(2)
C2A-C3A	1.5145(18)	C2B-C3B	1.5159(17)
C2A-H2A1	0.99(2)	C2B-H2B1	0.98(2)
C2A-H2A2	1.01(2)	C2B-H2B2	1.006(19)
C3A-C10A	1.3574(19)	C3B-C10B	1.358(2)
C3A-C4A	1.4733(19)	C3B-C4B	1.471(2)
C4A-C5A	1.3989(18)	C4B-C9B	1.4025(19)
C4A-C9A	1.4052(19)	C4B-C5B	1.4065(19)
C5A-C6A	1.387(2)	C5B-C6B	1.383(2)
C5A-H5A	0.95(2)	C5B-H5B	0.982(19)
C6A-C7A	1.394(2)	C6B-C7B	1.390(2)
C6A-H6A	1.001(19)	C6B-H6B	1.00(2)
C7A-C8A	1.380(2)	C7B-C8B	1.388(2)
C7A-H7A	0.94(2)	C7B-H7B	0.95(2)
C8A-C9A	1.392(2)	C8B-C9B	1.384(2)
C8A-H8A	0.99(2)	C8B-H8B	0.98(2)
C10A-C11A	1.4908(18)	C10B-C18B	1.497(2)
C10A-C18A	1.5043(19)	C10B-C11B	1.4995(18)
C11A-C12A	1.4855(19)	C11B-C12B	1.481(2)
C12A-C13A	1.383(2)	C12B-C17B	1.3916(19)
C12A-C17A	1.3924(19)	C12B-C13B	1.396(2)

Table 7. Cont

C13A-C14A	1.383(2)	C13B-C14B	1.379(3)
C13A-H13A	0.96(2)	C13B-H13B	0.91(2)
C14A-C15A	1.394(2)	C14B-C15B	1.395(2)
C14A-H14A	0.94(2)	C14B-H14B	1.00(2)
C15A-C16A	1.393(2)	C15B-C16B	1.392(2)
C15A-H15A	0.93(2)	C15B-H15B	0.98(2)
C16A-C17A	1.388(2)	C16B-C17B	1.385(2)
C16A-H16A	0.98(2)	C16B-H16B	0.965(19)
C17A-C18A	1.4870(19)	C17B-C18B	1.489(2)

Table 8. Bond Angles for *Id*.

O1A-C1A-C9A	127.32(14)	O1B-C1B-C9B	126.54(14)
O1A-C1A-C2A	125.28(13)	O1B-C1B-C2B	126.15(13)
C9A-C1A-C2A	107.40(11)	C9B-C1B-C2B	107.30(11)
C1A-C2A-C3A	105.20(11)	C1B-C2B-C3B	105.54(11)
C1A-C2A-H2A1	111.6(11)	C1B-C2B-H2B1	110.9(13)
C3A-C2A-H2A1	112.2(11)	C3B-C2B-H2B1	111.4(13)
C1A-C2A-H2A2	109.2(11)	C1B-C2B-H2B2	110.3(11)
C3A-C2A-H2A2	110.9(11)	C3B-C2B-H2B2	108.3(11)
H2A1-C2A-H2A2	107.7(16)	H2B1-C2B-H2B2	110.2(18)
C10A-C3A-C4A	131.31(12)	C10B-C3B-C4B	131.19(12)
C10A-C3A-C2A	121.27(12)	C10B-C3B-C2B	121.63(13)
C4A-C3A-C2A	107.40(11)	C4B-C3B-C2B	107.18(12)
C5A-C4A-C9A	118.44(12)	C9B-C4B-C5B	118.01(13)
C5A-C4A-C3A	131.98(13)	C9B-C4B-C3B	109.95(12)
C9A-C4A-C3A	109.58(12)	C5B-C4B-C3B	132.01(13)
C6A-C5A-C4A	118.86(13)	C6B-C5B-C4B	118.54(14)
C6A-C5A-H5A	118.3(12)	C6B-C5B-H5B	121.1(11)
C4A-C5A-H5A	122.8(12)	C4B-C5B-H5B	120.3(11)
C5A-C6A-C7A	121.72(13)	C5B-C6B-C7B	122.40(14)
C5A-C6A-H6A	121.2(11)	C5B-C6B-H6B	119.2(12)
C7A-C6A-H6A	117.1(11)	C7B-C6B-H6B	118.4(12)
C8A-C7A-C6A	120.41(14)	C8B-C7B-C6B	120.00(15)
C8A-C7A-H7A	116.4(12)	C8B-C7B-H7B	119.7(12)
C6A-C7A-H7A	123.2(12)	C6B-C7B-H7B	120.2(12)
C7A-C8A-C9A	117.96(14)	C9B-C8B-C7B	117.68(14)
C7A-C8A-H8A	121.9(13)	C9B-C8B-H8B	118.1(12)
C9A-C8A-H8A	120.2(13)	C7B-C8B-H8B	124.2(12)
C8A-C9A-C4A	122.55(13)	C8B-C9B-C4B	123.35(13)
C8A-C9A-C1A	127.40(13)	C8B-C9B-C1B	126.87(13)
C4A-C9A-C1A	110.03(12)	C4B-C9B-C1B	109.78(13)
C3A-C10A-C11A	130.45(12)	C3B-C10B-C18B	123.44(12)
C3A-C10A-C18A	123.28(12)	C3B-C10B-C11B	130.22(13)
C11A-C10A-C18A	106.27(11)	C18B-C10B-C11B	106.33(12)
O2A-C11A-C12A	123.76(13)	O2B-C11B-C12B	124.59(13)

Table 8. Cont.

O2A-C11A-C10A	128.89(12)	O2B-C11B-C10B	128.62(14)
C12A-C11A-C10A	107.32(11)	C12B-C11B-C10B	106.68(12)
C13A-C12A-C17A	121.39(13)	C17B-C12B-C13B	120.75(14)
C13A-C12A-C11A	128.82(13)	C17B-C12B-C11B	110.53(12)
C17A-C12A-C11A	109.79(11)	C13B-C12B-C11B	128.72(14)
C14A-C13A-C12A	118.02(15)	C14B-C13B-C12B	118.09(15)
C14A-C13A-H13A	121.9(11)	C14B-C13B-H13B	123.2(12)
C12A-C13A-H13A	120.1(11)	C12B-C13B-H13B	118.7(12)
C13A-C14A-C15A	120.83(14)	C13B-C14B-C15B	121.28(15)
C13A-C14A-H14A	115.4(12)	C13B-C14B-H14B	124.6(12)
C15A-C14A-H14A	123.7(12)	C15B-C14B-H14B	114.1(12)
C16A-C15A-C14A	121.30(15)	C16B-C15B-C14B	120.57(16)
C16A-C15A-H15A	119.2(13)	C16B-C15B-H15B	118.2(12)
C14A-C15A-H15A	119.5(13)	C14B-C15B-H15B	121.2(12)
C17A-C16A-C15A	117.51(15)	C17B-C16B-C15B	118.27(15)
C17A-C16A-H16A	119.1(12)	C17B-C16B-H16B	121.7(11)
C15A-C16A-H16A	123.4(12)	C15B-C16B-H16B	120.0(11)
C16A-C17A-C12A	120.94(13)	C16B-C17B-C12B	121.03(14)
C16A-C17A-C18A	129.38(13)	C16B-C17B-C18B	129.85(14)
C12A-C17A-C18A	109.68(11)	C12B-C17B-C18B	109.11(13)
O3A-C18A-C17A	125.54(13)	O3B-C18B-C17B	125.12(14)
O3A-C18A-C10A	127.53(13)	O3B-C18B-C10B	127.65(14)
C17A-C18A-C10A	106.93(11)	C17B-C18B-C10B	107.22(11)

Table 9. Torsion Angles for *Id*.

O1A-C1A-C2A-C3A	173.35(14)	O1B-C1B-C2B-C3B	173.77(14)
C9A-C1A-C2A-C3A	−5.93(15)	C9B-C1B-C2B-C3B	−5.04(14)
C1A-C2A-C3A-C10A	−172.45(12)	C1B-C2B-C3B-C10B	−175.90(12)
C1A-C2A-C3A-C4A	6.20(14)	C1B-C2B-C3B-C4B	4.41(14)
C10A-C3A-C4A-C5A	−6.6(2)	C10B-C3B-C4B-C9B	178.21(14)
C2A-C3A-C4A-C5A	174.97(14)	C2B-C3B-C4B-C9B	−2.13(15)
C10A-C3A-C4A-C9A	174.20(13)	C10B-C3B-C4B-C5B	−3.9(2)
C2A-C3A-C4A-C9A	−4.26(15)	C2B-C3B-C4B-C5B	175.74(14)
C9A-C4A-C5A-C6A	−2.2(2)	C9B-C4B-C5B-C6B	−0.83(19)
C3A-C4A-C5A-C6A	178.62(13)	C3B-C4B-C5B-C6B	−178.57(14)
C4A-C5A-C6A-C7A	0.3(2)	C4B-C5B-C6B-C7B	−0.5(2)
C5A-C6A-C7A-C8A	1.6(2)	C5B-C6B-C7B-C8B	1.6(2)
C6A-C7A-C8A-C9A	−1.5(2)	C6B-C7B-C8B-C9B	−1.3(2)
C7A-C8A-C9A-C4A	−0.5(2)	C7B-C8B-C9B-C4B	0.0(2)
C7A-C8A-C9A-C1A	−179.00(14)	C7B-C8B-C9B-C1B	−179.50(14)
C5A-C4A-C9A-C8A	2.4(2)	C5B-C4B-C9B-C8B	1.1(2)
C3A-C4A-C9A-C8A	−178.25(13)	C3B-C4B-C9B-C8B	179.32(13)
C5A-C4A-C9A-C1A	−178.91(12)	C5B-C4B-C9B-C1B	−179.32(12)
C3A-C4A-C9A-C1A	0.45(15)	C3B-C4B-C9B-C1B	−1.12(15)
O1A-C1A-C9A-C8A	2.9(3)	O1B-C1B-C9B-C8B	4.7(2)

Table 9. Cont.

C2A-C1A-C9A-C8A	−177.83(14)	C2B-C1B-C9B-C8B	−176.51(14)
O1A-C1A-C9A-C4A	−175.70(15)	O1B-C1B-C9B-C4B	−174.87(14)
C2A-C1A-C9A-C4A	3.56(15)	C2B-C1B-C9B-C4B	3.94(15)
C4A-C3A-C10A-C11A	−2.9(2)	C4B-C3B-C10B-C18B	172.57(13)
C2A-C3A-C10A-C11A	175.35(13)	C2B-C3B-C10B-C18B	−7.0(2)
C4A-C3A-C10A-C18A	178.09(13)	C4B-C3B-C10B-C11B	−6.0(2)
C2A-C3A-C10A-C18A	−3.6(2)	C2B-C3B-C10B-C11B	174.40(13)
C3A-C10A-C11A-O2A	−1.1(2)	C3B-C10B-C11B-O2B	−8.6(2)
C18A-C10A-C11A-O2A	177.98(14)	C18B-C10B-C11B-O2B	172.65(15)
C3A-C10A-C11A-C12A	−179.17(13)	C3B-C10B-C11B-C12B	175.12(14)
C18A-C10A-C11A-C12A	−0.06(14)	C18B-C10B-C11B-C12B	−3.62(14)
O2A-C11A-C12A-C13A	2.9(2)	O2B-C11B-C12B-C17B	−173.55(14)
C10A-C11A-C12A-C13A	−178.90(13)	C10B-C11B-C12B-C17B	2.91(15)
O2A-C11A-C12A-C17A	−177.23(13)	O2B-C11B-C12B-C13B	6.2(2)
C10A-C11A-C12A-C17A	0.94(15)	C10B-C11B-C12B-C13B	−177.33(14)
C17A-C12A-C13A-C14A	−0.1(2)	C17B-C12B-C13B-C14B	−0.9(2)
C11A-C12A-C13A-C14A	179.72(14)	C11B-C12B-C13B-C14B	179.39(14)
C12A-C13A-C14A-C15A	0.7(2)	C12B-C13B-C14B-C15B	1.0(2)
C13A-C14A-C15A-C16A	−0.5(2)	C13B-C14B-C15B-C16B	0.0(3)
C14A-C15A-C16A-C17A	−0.5(2)	C14B-C15B-C16B-C17B	−1.2(2)
C15A-C16A-C17A-C12A	1.1(2)	C15B-C16B-C17B-C12B	1.3(2)
C15A-C16A-C17A-C18A	−177.97(13)	C15B-C16B-C17B-C18B	−178.14(15)
C13A-C12A-C17A-C16A	−0.8(2)	C13B-C12B-C17B-C16B	−0.3(2)
C11A-C12A-C17A-C16A	179.30(13)	C11B-C12B-C17B-C16B	179.50(13)
C13A-C12A-C17A-C18A	178.41(12)	C13B-C12B-C17B-C18B	179.26(13)
C11A-C12A-C17A-C18A	−1.45(15)	C11B-C12B-C17B-C18B	−0.96(16)
C16A-C17A-C18A-O3A	1.4(2)	C16B-C17B-C18B-O3B	−0.8(2)
C12A-C17A-C18A-O3A	−177.79(14)	C12B-C17B-C18B-O3B	179.73(14)
C16A-C17A-C18A-C10A	−179.45(13)	C16B-C17B-C18B-C10B	178.11(15)
C12A-C17A-C18A-C10A	1.39(15)	C12B-C17B-C18B-C10B	−1.38(15)
C3A-C10A-C18A-O3A	−2.4(2)	C3B-C10B-C18B-O3B	3.1(2)
C11A-C10A-C18A-O3A	178.39(14)	C11B-C10B-C18B-O3B	−178.05(15)
C3A-C10A-C18A-C17A	178.42(12)	C3B-C10B-C18B-C17B	−175.76(12)
C11A-C10A-C18A-C17A	−0.77(14)	C11B-C10B-C18B-C17B	3.10(14)

2. Compound 2c

Experimental for C₁₃H₆F₆O₃ (2c)

Data Collection and Processing. The sample **2c** was submitted by Joseph Sloop of the Sloop research group at Georgia Gwinnett College. The sample was mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at a temperature of 173 K. The unit cell dimensions were determined from a symmetry constrained fit of 9959 reflections with $5.28^\circ < 2\theta < 57.7^\circ$. The data collection strategy was a number of ω and ϕ scans which collected data up to 57.74° (2θ). The frame integration was performed using

SAINT+ [29]. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS [30].

Structure Solution and Refinement. The structure was solved by direct methods using the SIR92 program [31]. All non-hydrogen atoms were obtained from the initial E-map. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on F. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the LSTSQ program from NRCVAX [33], graphic plots were produced using the NRCVAX crystallographic program suite. Additional information and other relevant literature references can be found in the reference section of the Facility's Web page (<http://www.xray.ncsu.edu>).

Figure 12. ORTEP drawing of **2c** showing naming and numbering scheme. Ellipsoids are at the 50%.

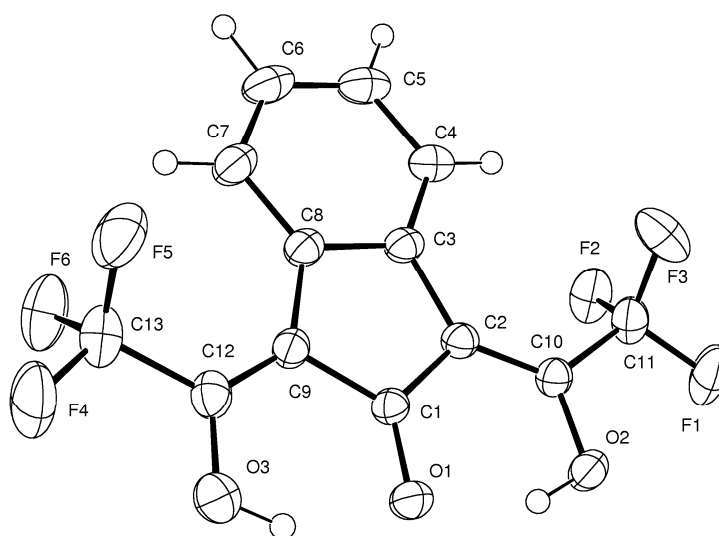


Figure 13. ORTEP drawing of **2c**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

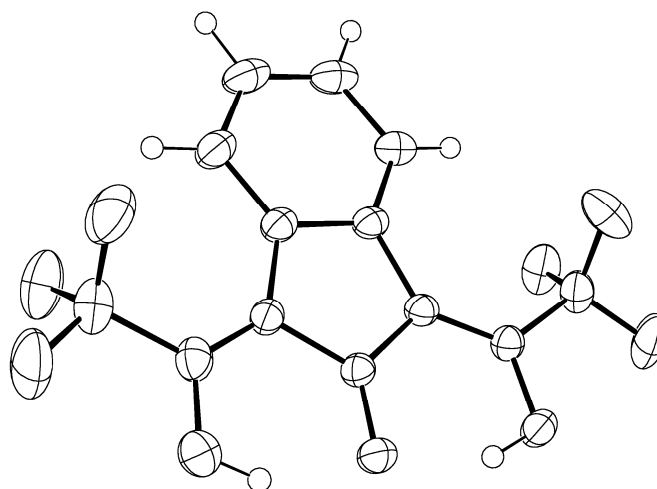


Figure 14. Stereoscopic ORTEP drawing of **2c**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

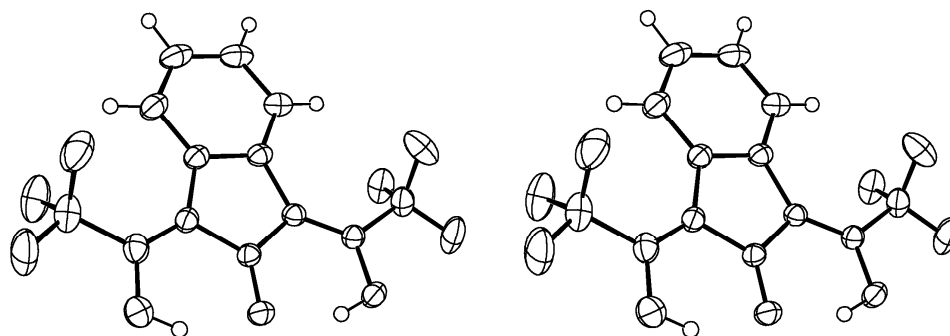


Table 10. Summary of Crystal Data for **2c**.

Formula	C ₁₃ H ₆ F ₆ O ₃
Formula Weight (g/mol)	324.18
Crystal Dimensions (mm)	1.20 × 0.10 × 0.06
Crystal Color and Habit	yellow needle
Crystal System	monoclinic
Space Group	P 2 ₁ /c
Temperature, K	173
a, Å	4.7643(3)
b, Å	18.6978(12)
c, Å	13.8431(9)
α, °	90.0
β, °	98.964(3)
γ, °	90.0
V, Å ³	1218.11(14)
Number of reflections to determine final unit cell	9959
Min and Max 2θ for cell determination, °	5.28, 57.7
Z	4
F(000)	648.71
ρ (g/cm ³)	1.768
λ, Å, (MoKα)	0.71073
μ, (cm ⁻¹)	0.18
Diffractometer Type	Bruker-Nonius X8 Apex2
Scan Type(s)	omega and phi scans
Max 2θ for data collection, °	57.74
Measured fraction of data	0.98
Number of reflections measured	26516
Unique reflections measured	3195
Rmerge	0.027
Number of reflections included in refinement	2755
Cut off Threshold Expression	Inet > 1.0 sigma(Inet)
Structure refined using	full matrix least-squares using F
Weighting Scheme	1/(sigma ² (F) + 0.0005F ²)

Table 10. Cont.

Number of parameters in least-squares	223
R _f	0.038
R _w	0.053
R _f (all data)	0.046
R _w (all data)	0.054
GOF	1.74
Maximum shift/error	0.003
Min & Max peak heights on final ΔF Map (e [−] /Å)	−0.30, 0.35

Where:

$$R_f = \sum (|F_o - F_c|) / \sum F_o$$

$$R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$$

$$GOF = [\sum w(F_o - F_c)^2 / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$$

Table 11. Atomic Coordinates for 2c.

Atom	x	y	z	U _{iso} /equiv
O1	0.81730(18)	0.99675(5)	0.07954(6)	0.0316(4)
O2	0.77456(19)	1.10306(5)	−0.04046(7)	0.0328(5)
O3	0.8507(2)	0.90513(5)	0.22145(8)	0.0392(5)
C1	0.6645(2)	1.03312(6)	0.12739(8)	0.0244(5)
C2	0.5495(2)	1.10365(6)	0.10029(9)	0.0243(5)
C3	0.3836(2)	1.12503(7)	0.17672(8)	0.0257(5)
C4	0.2245(3)	1.18602(8)	0.18650(10)	0.0319(6)
C5	0.0812(3)	1.19205(8)	0.26621(11)	0.0377(7)
C6	0.0964(3)	1.13855(8)	0.33508(11)	0.0396(7)
C7	0.2560(3)	1.07730(8)	0.32738(10)	0.0352(6)
C8	0.4020(2)	1.07009(7)	0.24809(9)	0.0270(5)
C9	0.5808(2)	1.01187(6)	0.22025(8)	0.0263(5)
C10	0.6161(2)	1.13484(7)	0.01809(9)	0.0259(5)
C11	0.5253(3)	1.20877(7)	−0.01820(11)	0.0337(6)
C12	0.6894(3)	0.95005(7)	0.26242(9)	0.0311(6)
C13	0.6515(3)	0.92528(8)	0.36396(11)	0.0401(7)
F1	0.61454(20)	1.22376(5)	−0.10179(7)	0.0526(5)
F2	0.24328(16)	1.21541(5)	−0.03293(6)	0.0430(4)
F3	0.62851(20)	1.25846(5)	0.04657(7)	0.0526(5)
F4	0.8000(2)	0.86675(5)	0.39034(7)	0.0592(6)
F5	0.7410(2)	0.97545(6)	0.43055(6)	0.0548(5)
F6	0.38149(19)	0.91237(6)	0.37079(7)	0.0579(5)
H2	0.822(4)	1.0603(13)	−0.0133(14)	0.064(6)
H3	0.877(5)	0.9223(11)	0.1643(16)	0.072(6)
H4	0.213(3)	1.2212(8)	0.1414(11)	0.030(4)
H5	−0.019(3)	1.2318(8)	0.2728(11)	0.035(4)
H6	−0.004(4)	1.1455(9)	0.3899(12)	0.045(4)
H7	0.272(3)	1.0418(9)	0.3767(12)	0.039(4)

Table 12. Anisotropic Displacement Parameters for **2c**.

Atom	u ¹¹	u ²²	u ³³	u ¹²	u ¹³	u ²³
O1	0.0384(5)	0.0291(5)	0.0291(5)	0.0065(4)	0.0112(4)	0.0003(4)
O2	0.0380(5)	0.0333(5)	0.0302(5)	0.0053(4)	0.0146(4)	0.0045(4)
O3	0.0482(6)	0.0321(5)	0.0380(6)	0.0067(4)	0.0085(5)	0.0061(4)
C1	0.0264(5)	0.0255(6)	0.0214(5)	−0.0027(5)	0.0040(4)	−0.0019(4)
C2	0.0245(5)	0.0243(6)	0.0243(5)	−0.0014(5)	0.0042(4)	−0.0029(4)
C3	0.0230(5)	0.0294(6)	0.0248(6)	−0.0045(5)	0.0042(4)	−0.0063(5)
C4	0.0303(6)	0.0330(7)	0.0321(6)	0.0012(5)	0.0041(5)	−0.0072(5)
C5	0.0313(6)	0.0419(8)	0.0407(7)	0.0023(6)	0.0084(6)	−0.0160(6)
C6	0.0341(6)	0.0531(9)	0.0343(7)	−0.0067(6)	0.0139(6)	−0.0166(7)
C7	0.0358(7)	0.0441(8)	0.0275(6)	−0.0092(6)	0.0112(5)	−0.0064(6)
C8	0.0255(5)	0.0316(6)	0.0242(6)	−0.0068(5)	0.0051(4)	−0.0053(5)
C9	0.0290(5)	0.0282(6)	0.0222(6)	−0.0067(5)	0.0054(5)	−0.0015(4)
C10	0.0241(5)	0.0270(6)	0.0271(6)	−0.0010(5)	0.0051(4)	0.0005(5)
C11	0.0293(6)	0.0323(7)	0.0409(7)	0.0007(5)	0.0096(5)	0.0079(5)
C12	0.0324(6)	0.0314(7)	0.0291(6)	−0.0071(5)	0.0031(5)	0.0023(5)
C13	0.0380(7)	0.0444(8)	0.0374(7)	−0.0058(6)	0.0045(6)	0.0128(6)
F1	0.0516(5)	0.0533(6)	0.0594(6)	0.0131(4)	0.0287(5)	0.0306(5)
F2	0.0296(4)	0.0493(5)	0.0507(5)	0.0088(4)	0.0084(4)	0.0178(4)
F3	0.0538(5)	0.0258(4)	0.0750(7)	0.0008(4)	0.0006(5)	−0.0021(4)
F4	0.0650(6)	0.0577(6)	0.0569(6)	0.0082(5)	0.0154(5)	0.0322(5)
F5	0.0661(6)	0.0702(7)	0.0276(4)	−0.0148(5)	0.0057(4)	0.0044(4)
F6	0.0427(5)	0.0755(7)	0.0574(6)	−0.0133(5)	0.0133(4)	0.0236(5)

Table 13. Bond Lengths for **2c**.

O1-C1	1.2576(15)	C6-C7	1.388(2)
O2-C10	1.3308(15)	C6-H6	0.967(18)
O2-H2	0.90(2)	C7-C8	1.3944(18)
O3-C12	1.3242(17)	C7-H7	0.947(17)
O3-H3	0.88(2)	C8-C9	1.4703(18)
C1-C2	1.4547(17)	C9-C12	1.3602(18)
C1-C9	1.4590(17)	C10-C11	1.5108(18)
C2-C3	1.4714(17)	C11-F1	1.3235(16)
C2-C10	1.3593(17)	C11-F2	1.3329(15)
C3-C4	1.3876(18)	C11-F3	1.3311(17)
C3-C8	1.4186(18)	C12-C13	1.5173(19)
C4-C5	1.3893(20)	C13-F4	1.3233(18)
C4-H4	0.903(15)	C13-F5	1.3375(18)
C5-C6	1.376(2)	C13-F6	1.3267(17)
C5-H5	0.896(17)		

Table 14. Bond Angles for **2c**.

C10-O2-H2	105.8(12)	C3-C8-C9	109.21(10)
C12-O3-H3	109.1(14)	C7-C8-C9	131.18(12)
O1-C1-C2	125.45(11)	C1-C9-C8	106.17(10)
O1-C1-C9	125.23(11)	C1-C9-C12	118.14(11)
C2-C1-C9	109.30(10)	C8-C9-C12	135.54(12)

Table 14. Cont.

C1-C2-C3	106.48(10)	O2-C10-C2	123.15(11)
C1-C2-C10	118.51(11)	O2-C10-C11	111.48(11)
C3-C2-C10	134.99(11)	C2-C10-C11	125.36(11)
C2-C3-C4	131.02(12)	C10-C11-F1	111.72(11)
C2-C3-C8	108.80(10)	C10-C11-F2	111.45(10)
C4-C3-C8	120.17(11)	C10-C11-F3	110.99(11)
C3-C4-C5	119.18(14)	F1-C11-F2	107.46(11)
C3-C4-H4	120.4(9)	F1-C11-F3	107.80(11)
C5-C4-H4	120.4(9)	F2-C11-F3	107.21(11)
C4-C5-C6	120.80(14)	O3-C12-C9	124.23(12)
C4-C5-H5	119.0(10)	O3-C12-C13	111.34(12)
C6-C5-H5	120.2(10)	C9-C12-C13	124.39(13)
C5-C6-C7	121.13(13)	C12-C13-F4	111.87(13)
C5-C6-H6	117.8(10)	C12-C13-F5	110.68(11)
C7-C6-H6	121.0(10)	C12-C13-F6	112.22(11)
C6-C7-C8	119.11(14)	F4-C13-F5	106.89(12)
C6-C7-H7	120.5(9)	F4-C13-F6	108.20(12)
C8-C7-H7	120.3(9)	F5-C13-F6	106.69(13)
C3-C8-C7	119.60(12)		

Table 15. Torsion Angles for 2c.

O1-C1-C2-C3	179.6(2)	C8-C3-C4-C5	−0.78(13)
O1-C1-C2-C10	−1.91(11)	C2-C3-C8-C7	−178.6(3)
C9-C1-C2-C3	−1.90(11)	C2-C3-C8-C9	0.26(11)
C9-C1-C2-C10	176.6(2)	C4-C3-C8-C7	0.88(13)
O1-C1-C9-C8	−179.4(3)	C4-C3-C8-C9	179.7(3)
O1-C1-C9-C12	4.37(11)	C3-C4-C5-C6	0.17(13)
C2-C1-C9-C8	2.04(11)	C4-C5-C6-C7	0.35(13)
C2-C1-C9-C12	−174.2(3)	C5-C6-C7-C8	−0.25(13)
C1-C2-C3-C4	−178.4(2)	C6-C7-C8-C3	−0.36(13)
C1-C2-C3-C8	1.00(11)	C6-C7-C8-C9	−178.9(3)
C10-C2-C3-C4	3.44(12)	C3-C8-C9-C1	−1.41(11)
C10-C2-C3-C8	−177.2(3)	C3-C8-C9-C12	173.8(3)
C1-C2-C10-O2	2.08(10)	C7-C8-C9-C1	177.3(3)
C1-C2-C10-C11	−177.3(2)	C7-C8-C9-C12	−7.50(13)
C3-C2-C10-O2	−179.9(2)	C1-C9-C12-O3	−4.98(11)
C3-C2-C10-C11	0.67(11)	C1-C9-C12-C13	172.4(3)
C2-C3-C4-C5	178.6(3)		

3. Compound 3d

Experimental for C₁₂H₇F₃O₂ (3d)

Data Collection and Processing. The sample **3d** was submitted by Joseph Sloop of the Sloop research group at Georgia Gwinnett College. The sample was mounted on a nylon loop with a small

amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 5859 reflections with $5.44^\circ < 2\theta < 52.66^\circ$. The data collection strategy was a number of ω and ϕ scans which collected data up to 62.92° (2θ). The frame integration was performed using SAINT [29]. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS [30].

Structure Solution and Refinement. The structure was solved by direct methods using the SIR92 program [31]. All non-hydrogen atoms were obtained from the initial solution. The carbon bound hydrogen atoms were introduced at idealized positions while the hydroxy hydrogen atom position was obtained from a difference Fourier map. All hydrogen atoms were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on F^2 . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The space group is achiral, therefore the structure has an absolute sense to it. However, the anomalous scattering signal is weak due to the absence of any atoms heavier than F, and the absolute structure could not be definitively determined. The structure was refined using the XL program from SHELXTL [32], graphic plots were produced using the NRCVAX crystallographic program suite. Additional information and other relevant literature references can be found in the reference section of the Facility's Web page (<http://www.xray.ncsu.edu>).

Figure 15. ORTEP drawing of **3d** showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

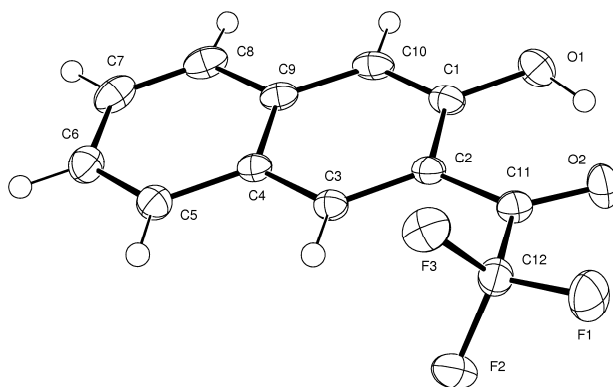


Figure 16. ORTEP drawing of **3d**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

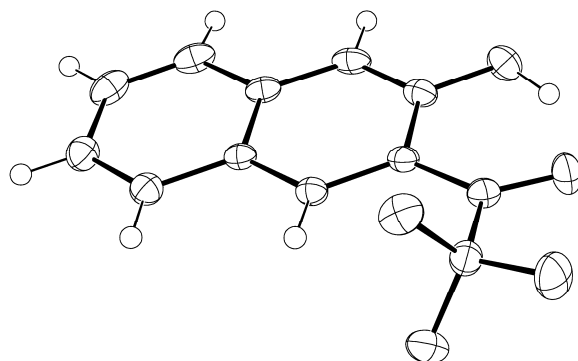


Figure 17. Stereoscopic ORTEP drawing of **3d**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

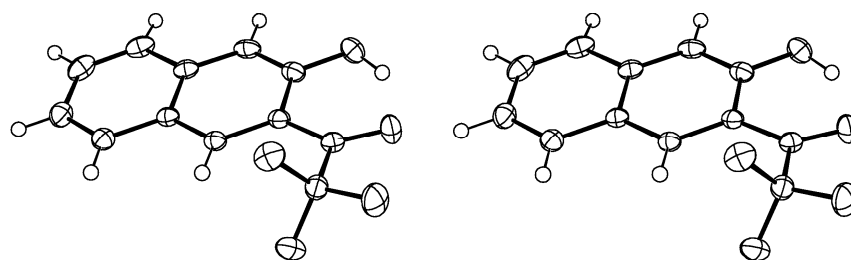


Table 16. Summary of Crystal Data for **3d**.

Formula	C ₁₂ H ₇ F ₃ O ₂
Formula Weight (g/mol)	240.18
Crystal Dimensions (mm)	0.46 × 0.08 × 0.04
Crystal Color and Habit	orange yellow needle
Crystal System	orthorhombic
Space Group	P n a 2 ₁
Temperature, K	110
a, Å	13.5923(5)
b, Å	14.9695(5)
c, Å	4.8381(2)
α, °	90.00
β, °	90.00
γ, °	90.00
V, Å ³	984.41(6)
Number of reflections to determine final unit cell	5859
Min and Max 2θ for cell determination, °	5.44, 52.66
Z	4
F(000)	488
ρ (g/cm ³)	1.621
λ, Å, (MoKα)	0.71070
μ, (cm ⁻¹)	0.147
Diffractometer Type	Bruker-Nonius X8 Apex2
Scan Type(s)	omega and phi scans
Max 2θ for data collection, °	62.92
Measured fraction of data	0.874
Number of reflections measured	21568
Unique reflections measured	2632
R _{merge}	0.0444
Number of reflections included in refinement	2632
Cut off Threshold Expression	>2sigma(I)
Structure refined using	full matrix least-squares using F ²
Weighting Scheme	calc w = 1/[sigma ² (Fo ²) + (0.0406P) ² + 0.0000P] where P=(Fo ² + 2Fc ²)/3
Number of parameters in least-squares	182

Table 16. *Cont.*

R ₁	0.0370
wR ₂	0.0712
R ₁ (all data)	0.0538
wR ₂ (all data)	0.0762
GOF	1.035
Maximum shift/error	0.000
Min & Max peak heights on final ΔF Map (e ⁻ /Å)	−0.229, 0.183

Where:

$$R_1 = \sum (|F_o| - |F_c|) / \sum F_o$$

$$wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$$

$$GOF = [\sum w (F_o^2 - F_c^2)^2 / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$$

Table 17. Atomic Coordinates for **3d**.

Atom	x	y	z	U _{iso/equiv}
O1	0.11391(8)	0.26937(8)	0.6424(3)	0.0315(3)
O2	0.22469(8)	0.37533(7)	0.3464(3)	0.0294(3)
C1	0.19885(11)	0.24126(10)	0.7623(4)	0.0227(3)
C2	0.29250(11)	0.27865(9)	0.6863(4)	0.0190(3)
C3	0.37673(11)	0.24539(9)	0.8101(4)	0.0193(3)
C4	0.37205(11)	0.17792(10)	1.0120(4)	0.0192(3)
C5	0.45775(12)	0.14260(10)	1.1386(4)	0.0230(3)
C6	0.45137(13)	0.07873(10)	1.3373(4)	0.0269(3)
C7	0.35837(14)	0.04578(11)	1.4184(4)	0.0300(4)
C8	0.27466(13)	0.07695(10)	1.3003(4)	0.0275(4)
C9	0.27804(11)	0.14416(10)	1.0917(4)	0.0213(3)
C10	0.19325(12)	0.17720(11)	0.9629(4)	0.0247(3)
C11	0.29517(12)	0.35023(10)	0.4818(4)	0.0217(3)
C12	0.39217(11)	0.40275(10)	0.4367(4)	0.0224(3)
F1	0.37724(7)	0.47125(6)	0.2675	0.0341(3)
F2	0.46266(6)	0.35198(6)	0.3256(3)	0.0286(2)
F3	0.42682(6)	0.43562(6)	0.6742(3)	0.0297(2)
H1	0.1301(19)	0.3131(16)	0.500(7)	0.079(9)
H3	0.4391(12)	0.2686(10)	0.766(4)	0.022(4)
H5	0.5197(14)	0.1674(10)	1.079(4)	0.033(5)
H6	0.5078(13)	0.0544(10)	1.422(4)	0.026(4)
H7	0.3543(13)	0.0040(11)	1.553(4)	0.030(5)
H8	0.2120(15)	0.0566(12)	1.334(5)	0.053(6)

Table 18. Anisotropic Displacement Parameters for **3d**.

Atom	u ¹¹	u ²²	u ³³	u ¹²	u ¹³	u ²³
O1	0.0164(6)	0.0433(7)	0.0347(7)	0.0007(5)	−0.0018(5)	0.0012(6)
O2	0.0251(6)	0.0319(6)	0.0312(6)	0.0036(5)	−0.0074(6)	0.0048(6)
C1	0.0174(8)	0.0271(8)	0.0236(8)	−0.0003(6)	0.0012(6)	−0.0060(7)

Table 18. *Cont.*

C2	0.0180(8)	0.0211(7)	0.0178(7)	0.0006(6)	0.0021(6)	−0.0031(6)
C3	0.0174(8)	0.0209(7)	0.0196(7)	−0.0016(6)	0.0019(6)	−0.0013(7)
C4	0.0199(8)	0.0195(7)	0.0182(7)	−0.0011(6)	0.0023(6)	−0.0032(6)
C5	0.0249(9)	0.0212(8)	0.0229(8)	0.0011(6)	0.0005(7)	−0.0006(6)
C6	0.0338(9)	0.0226(8)	0.0245(8)	0.0051(7)	−0.0020(7)	0.0001(7)
C7	0.0471(11)	0.0208(8)	0.0223(9)	−0.0038(7)	0.0034(7)	0.0020(7)
C8	0.0324(9)	0.0256(8)	0.0247(9)	−0.0107(7)	0.0084(8)	−0.0037(7)
C9	0.0249(8)	0.0193(7)	0.0198(7)	−0.0031(6)	0.0041(6)	−0.0060(6)
C10	0.0178(8)	0.0300(8)	0.0264(8)	−0.0068(7)	0.0072(7)	−0.0062(7)
C11	0.0226(9)	0.0230(8)	0.0195(8)	0.0020(6)	0.0017(6)	−0.0026(6)
C12	0.0238(8)	0.0226(8)	0.0208(7)	0.0010(6)	−0.0013(7)	0.0006(6)
F1	0.0369(6)	0.0279(5)	0.0375(6)	−0.0005(4)	−0.0013(5)	0.0126(5)
F2	0.0238(5)	0.0291(5)	0.0329(5)	0.0011(4)	0.0082(4)	−0.0003(4)
F3	0.0309(5)	0.0300(5)	0.0282(5)	−0.0080(4)	−0.0005(4)	−0.0051(4)

Table 19. Bond Lengths for *3d*.

O1-C1	1.3588(19)	C6-C7	1.412(2)
O1-H1	0.97(3)	C6-H6	0.941(18)
O2-C11	1.2199(18)	C7-C8	1.356(2)
C1-C10	1.367(2)	C7-H7	0.905(18)
C1-C2	1.438(2)	C8-C9	1.426(2)
C2-C3	1.385(2)	C8-H8	0.92(2)
C2-C11	1.459(2)	C9-C10	1.400(2)
C3-C4	1.406(2)	C10-H10	0.939(18)
C3-H3	0.941(16)	C11-C12	1.551(2)
C4-C5	1.418(2)	C12-F1	1.3278(18)
C4-C9	1.427(2)	C12-F3	1.3356(19)
C5-C6	1.359(2)	C12-F2	1.3359(18)
C5-H5	0.963(19)		

Table 20. Bond Angles for *3d*.

C1-O1-H1	108.5(16)	C8-C7-H7	119.3(12)
O1-C1-C10	118.24(14)	C6-C7-H7	119.8(12)
O1-C1-C2	121.49(14)	C7-C8-C9	120.94(15)
C10-C1-C2	120.25(14)	C7-C8-H8	126.2(13)
C3-C2-C1	118.78(13)	C9-C8-H8	112.8(13)
C3-C2-C11	122.46(13)	C10-C9-C8	122.53(15)
C1-C2-C11	118.76(13)	C10-C9-C4	119.43(15)
C2-C3-C4	121.41(13)	C8-C9-C4	118.04(15)
C2-C3-H3	121.0(10)	C1-C10-C9	121.21(15)
C4-C3-H3	117.5(10)	C1-C10-H10	116.9(11)
C3-C4-C5	122.04(13)	C9-C10-H10	121.8(11)
C3-C4-C9	118.85(13)	O2-C11-C2	124.81(14)
C5-C4-C9	119.11(14)	O2-C11-C12	115.85(13)

Table 20. Cont.

C6-C5-C4	121.03(15)	C2-C11-C12	119.28(13)
C6-C5-H5	122.5(11)	F1-C12-F3	107.45(12)
C4-C5-H5	116.5(11)	F1-C12-F2	107.51(13)
C5-C6-C7	119.96(16)	F3-C12-F2	107.63(12)
C5-C6-H6	121.7(10)	F1-C12-C11	110.39(12)
C7-C6-H6	118.3(10)	F3-C12-C11	111.44(13)
C8-C7-C6	120.91(16)	F2-C12-C11	112.21(12)

Table 21. Torsion Angles for **3d**.

O1-C1-C2-C3	−178.15(14)	C3-C4-C9-C8	−178.87(13)
C10-C1-C2-C3	3.2(2)	C5-C4-C9-C8	1.1(2)
O1-C1-C2-C11	1.9(2)	O1-C1-C10-C9	178.95(14)
C10-C1-C2-C11	−176.80(13)	C2-C1-C10-C9	−2.3(2)
C1-C2-C3-C4	−1.6(2)	C8-C9-C10-C1	−179.58(14)
C11-C2-C3-C4	178.34(13)	C4-C9-C10-C1	−0.1(2)
C2-C3-C4-C5	179.37(14)	C3-C2-C11-O2	171.95(15)
C2-C3-C4-C9	−0.7(2)	C1-C2-C11-O2	−8.1(2)
C3-C4-C5-C6	178.62(14)	C3-C2-C11-C12	−11.0(2)
C9-C4-C5-C6	−1.3(2)	C1-C2-C11-C12	168.99(13)
C4-C5-C6-C7	0.7(2)	O2-C11-C12-F1	4.49(18)
C5-C6-C7-C8	0.1(2)	C2-C11-C12-F1	−172.83(12)
C6-C7-C8-C9	−0.3(2)	O2-C11-C12-F3	123.80(14)
C7-C8-C9-C10	179.23(15)	C2-C11-C12-F3	−53.51(17)
C7-C8-C9-C4	−0.3(2)	O2-C11-C12-F2	−115.41(15)
C3-C4-C9-C10	1.6(2)	C2-C11-C12-F2	67.28(18)
C5-C4-C9-C10	−178.48(14)		

4. Compound **4c**

Experimental for C₁₂H₉F₃O₂ (**4c**)

Data Collection and Processing. The sample **4c** was submitted by Joseph Sloop of the Sloop research group at Georgia Gwinnett College. The sample was mounted on a nylon loop with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 6416 reflections with $5.78^\circ < 2\theta < 71.38^\circ$. The data collection strategy was a number of ω and ϕ scans which collected data up to 71.58° (2θ). The frame integration was performed using SAINT [29]. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS [30].

Structure Solution and Refinement. The structure was solved by direct methods using the XS program [31]. All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were located from a difference Fourier map and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on F². The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined

using the XL program from SHELXTL [32], graphic plots were produced using the NRCVAX crystallographic program suite. Additional information and other relevant literature references can be found in the reference section of the Facility's Web page (<http://www.xray.ncsu.edu>).

Figure 18. ORTEP drawing of **4c** showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

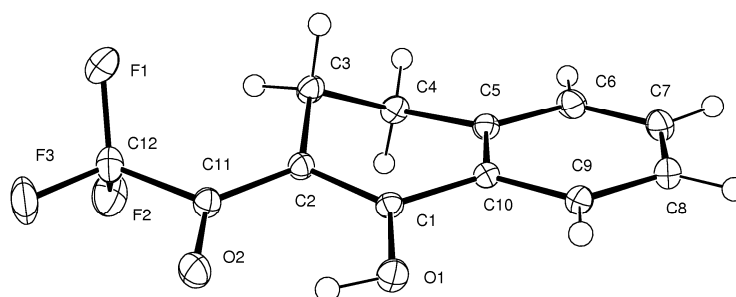


Figure 19. ORTEP drawing of **4c**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

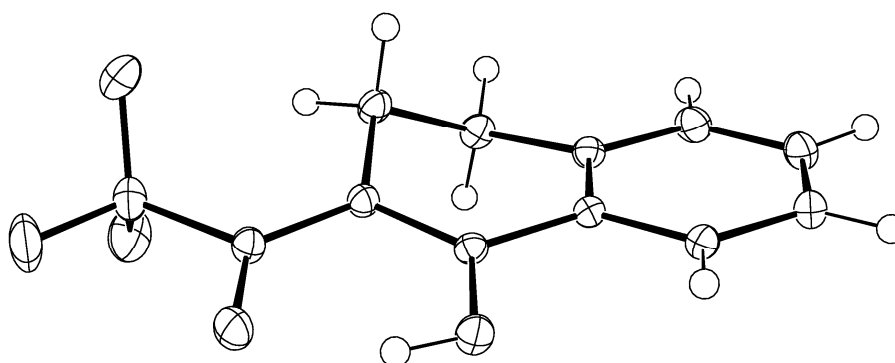


Figure 20. Stereoscopic ORTEP drawing of **4c**. Ellipsoids are at the 50% probability level and hydrogen atoms were drawn with arbitrary radii for clarity.

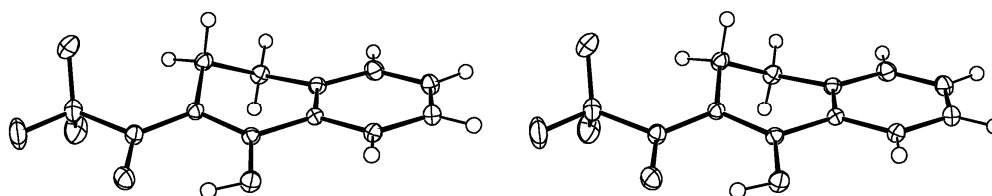


Table 22. Summary of Crystal Data for **4c**.

Formula	C ₁₂ H ₉ F ₃ O ₂
Formula Weight (g/mol)	242.19
Crystal Dimensions (mm)	0.38 × 0.28 × 0.04
Crystal Color and Habit	colourless plate
Crystal System	triclinic
Space Group	P -1

Table 22. Cont.

Temperature, K	110
<i>a</i> , Å	7.3528(2)
<i>b</i> , Å	7.9165(2)
<i>c</i> , Å	9.7991(2)
α , °	73.0533(11)
β , °	85.3968(12)
γ , °	68.3581(11)
<i>V</i> , Å ³	506.92(2)
Reflections to determine final unit cell	6416
Min and Max 2 θ for cell determination, °	5.78, 71.38
<i>Z</i>	2
F(000)	248
ρ (g/cm ³)	1.587
λ , Å, (MoK α)	0.71073
μ , (cm ⁻¹)	0.143
Number of reflections measured	20479
Unique reflections measured	4691
<i>R</i> _{merge}	0.0265
Number of reflections included in refinement	4691
Cut off Threshold Expression	>2sigma(I)
Structure refined using	full matrix least-squares using F ²
Weighting Scheme	$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 0.0436P]$ where $P = (F_o^2 + 2F_c^2)/3$
<i>R</i> ₁	0.0382
<i>wR</i> ₂	0.1082
<i>R</i> ₁ (all data)	0.0525
<i>wR</i> ₂ (all data)	0.1220
GOF	1.048

Where:

$$R_1 = \sum (|F_o| - |F_c|) / \sum F_o$$

$$wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$$

$$GOF = [\sum w (F_o^2 - F_c^2)^2 / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$$

Table 23. Atomic Coordinates for 4c.

Atom	x	y	z	<i>U</i> _{iso/equiv}
O1	0.77448(8)	0.28007(9)	0.27345(6)	0.01748(12)
O2	0.99446(9)	0.28522(9)	0.06442(6)	0.02064(13)
C1	0.92164(10)	0.26838(10)	0.34926(7)	0.01305(12)
C2	1.10003(10)	0.26974(10)	0.29126(8)	0.01358(12)
C3	1.25154(11)	0.27188(11)	0.38557(8)	0.01584(13)
C4	1.24786(11)	0.15172(11)	0.53827(8)	0.01618(13)

Table 23. *Cont.*

C5	1.04451(11)	0.19875(10)	0.59451(8)	0.01444(13)
C6	1.00916(12)	0.18008(12)	0.73914(8)	0.01899(15)
C7	0.82002(13)	0.21517(12)	0.78875(9)	0.02070(15)
C8	0.66361(12)	0.26962(12)	0.69526(9)	0.01971(15)
C9	0.69574(11)	0.28853(11)	0.55100(8)	0.01598(13)
C10	0.88579(10)	0.25358(10)	0.50052(7)	0.01326(12)
C11	1.12232(11)	0.27815(10)	0.14448(8)	0.01590(13)
C12	1.31898(12)	0.27354(12)	0.07494(9)	0.02008(15)
F1	1.37562(8)	0.40737(8)	0.09309(6)	0.02557(13)
F2	1.46211(8)	0.10631(8)	0.12997(6)	0.03004(14)
F3	1.30731(9)	0.29835(10)	−0.06471(6)	0.03180(15)
H1	0.818(3)	0.282(3)	0.190(2)	0.066(5)
H3A	1.2210(17)	0.4028(17)	0.3866(12)	0.018(3)
H3B	1.386(2)	0.2261(18)	0.3516(13)	0.026(3)
H4A	1.3333(19)	0.1700(17)	0.5989(13)	0.021(3)
H4B	1.2933(18)	0.0209(17)	0.5436(13)	0.020(3)
H6	1.120(2)	0.1395(19)	0.8020(14)	0.030(3)
H7	0.806(2)	0.204(2)	0.8859(17)	0.041(4)
H8	0.526(2)	0.304(2)	0.7231(14)	0.033(3)
H9	0.5882(18)	0.3326(17)	0.4836(13)	0.019(3)

Table 24. Anisotropic Displacement Parameters for **4c**.

Atom	u ¹¹	u ²²	u ³³	u ¹²	u ¹³	u ²³
O1	0.0149(2)	0.0246(3)	0.0147(2)	−0.0091(2)	−0.00183(19)	−0.0048(2)
O2	0.0229(3)	0.0269(3)	0.0145(2)	−0.0113(2)	−0.0001(2)	−0.0061(2)
C1	0.0127(3)	0.0135(3)	0.0133(3)	−0.0052(2)	−0.0005(2)	−0.0035(2)
C2	0.0129(3)	0.0155(3)	0.0131(3)	−0.0059(2)	0.0007(2)	−0.0042(2)
C3	0.0137(3)	0.0189(3)	0.0166(3)	−0.0081(2)	0.0007(2)	−0.0046(2)
C4	0.0134(3)	0.0184(3)	0.0162(3)	−0.0059(2)	−0.0019(2)	−0.0035(2)
C5	0.0151(3)	0.0148(3)	0.0143(3)	−0.0062(2)	0.0003(2)	−0.0044(2)
C6	0.0226(4)	0.0212(3)	0.0144(3)	−0.0091(3)	−0.0007(3)	−0.0051(3)
C7	0.0270(4)	0.0225(3)	0.0156(3)	−0.0115(3)	0.0055(3)	−0.0078(3)
C8	0.0210(4)	0.0215(3)	0.0203(3)	−0.0104(3)	0.0077(3)	−0.0097(3)
C9	0.0142(3)	0.0171(3)	0.0185(3)	−0.0069(2)	0.0030(2)	−0.0068(2)
C10	0.0133(3)	0.0143(3)	0.0136(3)	−0.0061(2)	0.0012(2)	−0.0047(2)
C11	0.0174(3)	0.0162(3)	0.0140(3)	−0.0067(2)	0.0021(2)	−0.0038(2)
C12	0.0204(3)	0.0226(4)	0.0166(3)	−0.0077(3)	0.0049(3)	−0.0058(3)
F1	0.0244(3)	0.0283(3)	0.0279(3)	−0.0162(2)	0.0068(2)	−0.0065(2)
F2	0.0215(3)	0.0254(3)	0.0345(3)	−0.0013(2)	0.0080(2)	−0.0070(2)
F3	0.0341(3)	0.0473(4)	0.0169(2)	−0.0181(3)	0.0108(2)	−0.0115(2)

Table 25. Bond Lengths for **4c**.

O1-C1	1.3215(9)	C5-C10	1.4016(10)
O1-H1	0.855(19)	C6-C7	1.3903(12)
O2-C11	1.2476(10)	C6-H6	0.960(14)
C1-C2	1.3895(10)	C7-C8	1.3860(12)
C1-C10	1.4626(10)	C7-H7	0.931(15)
C2-C11	1.4193(10)	C8-C9	1.3877(11)
C2-C3	1.5112(10)	C8-H8	0.984(14)
C3-C4	1.5255(11)	C9-C10	1.3992(10)
C3-H3A	0.979(12)	C9-H9	0.964(12)
C3-H3B	0.984(13)	C11-C12	1.5408(11)
C4-C5	1.5016(10)	C12-F3	1.3298(10)
C4-H4A	0.972(12)	C12-F1	1.3322(10)
C4-H4B	0.950(12)	C12-F2	1.3410(10)
C5-C6	1.3946(10)		

Table 26. Bond Angles for **4c**.

C1-O1-H1	105.2(13)	C7-C6-H6	122.1(8)
O1-C1-C2	123.08(7)	C5-C6-H6	117.4(8)
O1-C1-C10	115.65(6)	C8-C7-C6	120.54(7)
C2-C1-C10	121.28(6)	C8-C7-H7	123.4(9)
C1-C2-C11	116.88(7)	C6-C7-H7	116.1(9)
C1-C2-C3	118.29(6)	C7-C8-C9	119.86(7)
C11-C2-C3	124.76(6)	C7-C8-H8	124.2(8)
C2-C3-C4	111.06(6)	C9-C8-H8	115.9(8)
C2-C3-H3A	108.3(7)	C8-C9-C10	119.82(7)
C4-C3-H3A	108.5(7)	C8-C9-H9	121.1(7)
C2-C3-H3B	113.2(7)	C10-C9-H9	119.0(7)
C4-C3-H3B	108.2(8)	C9-C10-C5	120.59(7)
H3A-C3-H3B	107.4(10)	C9-C10-C1	120.17(7)
C5-C4-C3	112.07(6)	C5-C10-C1	119.22(6)
C5-C4-H4A	110.3(7)	O2-C11-C2	125.09(7)
C3-C4-H4A	109.1(7)	O2-C11-C12	115.47(7)
C5-C4-H4B	105.9(7)	C2-C11-C12	119.42(7)
C3-C4-H4B	111.1(7)	F3-C12-F1	107.53(7)
H4A-C4-H4B	108.2(10)	F3-C12-F2	107.30(7)
C6-C5-C10	118.70(7)	F1-C12-F2	107.24(7)
C6-C5-C4	121.98(7)	F3-C12-C11	110.83(7)
C10-C5-C4	119.24(6)	F1-C12-C11	112.56(6)
C7-C6-C5	120.50(8)	F2-C12-C11	111.13(6)

Table 27. Torsion Angles for **4c**.

O1-C1-C2-C11	−2.04(11)	C4-C5-C10-C9	176.58(7)
C10-C1-C2-C11	177.93(6)	C6-C5-C10-C1	−178.26(7)
O1-C1-C2-C3	175.03(7)	C4-C5-C10-C1	−1.57(10)

Table 27. *Cont.*

C10-C1-C2-C3	−4.99(10)	O1-C1-C10-C9	−12.24(10)
C1-C2-C3-C4	36.71(9)	C2-C1-C10-C9	167.79(7)
C11-C2-C3-C4	−146.47(7)	O1-C1-C10-C5	165.92(6)
C2-C3-C4-C5	−49.62(8)	C2-C1-C10-C5	−14.06(10)
C3-C4-C5-C6	−149.82(7)	C1-C2-C11-O2	0.34(11)
C3-C4-C5-C10	33.60(9)	C3-C2-C11-O2	−176.52(7)
C10-C5-C6-C7	0.04(11)	C1-C2-C11-C12	−178.03(6)
C4-C5-C6-C7	−176.56(7)	C3-C2-C11-C12	5.11(11)
C5-C6-C7-C8	−0.13(12)	O2-C11-C12-F3	6.60(10)
C6-C7-C8-C9	0.30(12)	C2-C11-C12-F3	−174.87(7)
C7-C8-C9-C10	−0.37(11)	O2-C11-C12-F1	127.07(8)
C8-C9-C10-C5	0.28(11)	C2-C11-C12-F1	−54.40(10)
C8-C9-C10-C1	178.41(7)	O2-C11-C12-F2	−112.62(8)
C6-C5-C10-C9	−0.11(11)	C2-C11-C12-F2	65.91(9)

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