Electronic Supporting Information

Activation of the hypervalent fluoroiodane reagent by hydrogen bonding to hexafluoroisopropanol

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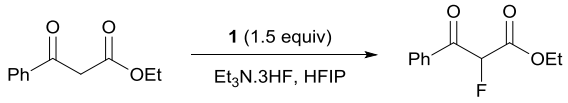
Table S1 Optimisation of the fluorination of ethyl 3-oxo-3-phenylpropanoate in HFIP.[a]



Entry	Temp (°C)	Time (h)	$Et_3N.3HF$ (equiv.)	Yield[b,c] (%)
1	40	6	2.7	98 (98)
2	40	6	0.5	87 (87)
3	40	6	0	70 (58)
4	60	6	0	79 (77)
5	80	6	0	69
6	60	4	0	76 (73)

[a] Reaction conditions: substrate (0.72 mmol), fluoroiodane **1** (1.08 mmol), the required amount of $Et_3N.3HF$ and HFIP (1.2 mL). [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield in parenthesis.

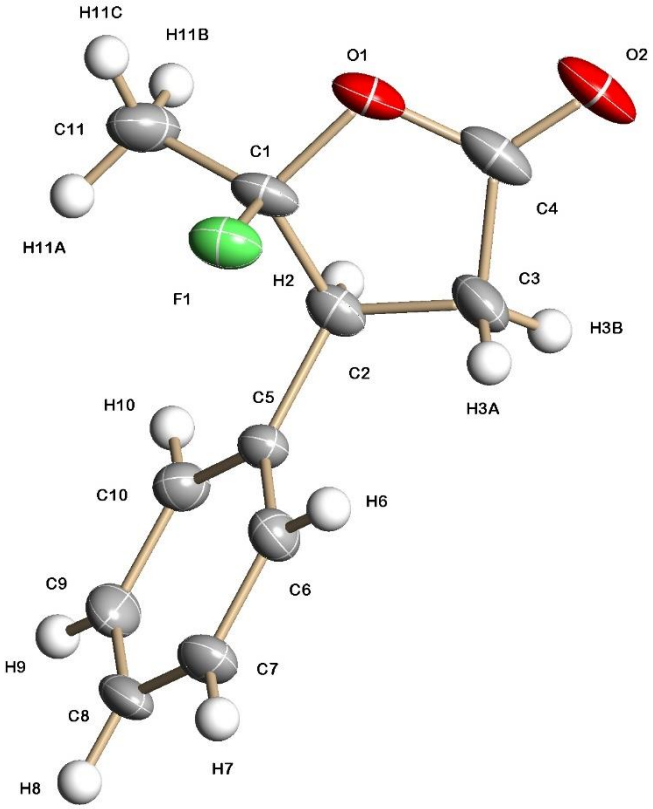


Figure 2. Molecular structure of (4*S*,5*R*)/(4*R*,5*S*)-5-fluoro-5-methyl-4-phenyldihydrofuran-2-one **4h** showing 50% displacement ellipsoids

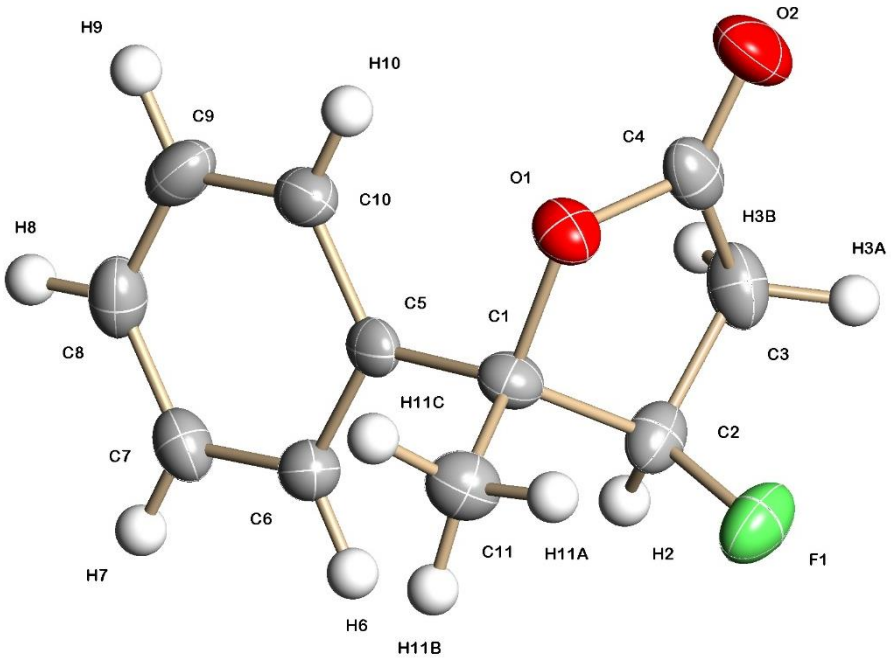


Figure 3. Molecular structure of (4*S*,5*R*)/(4*R*,5*S*)-4-fluoro-5-methyl-5-phenyldihydrofuran-2-one **5** showing 50% displacement ellipsoids

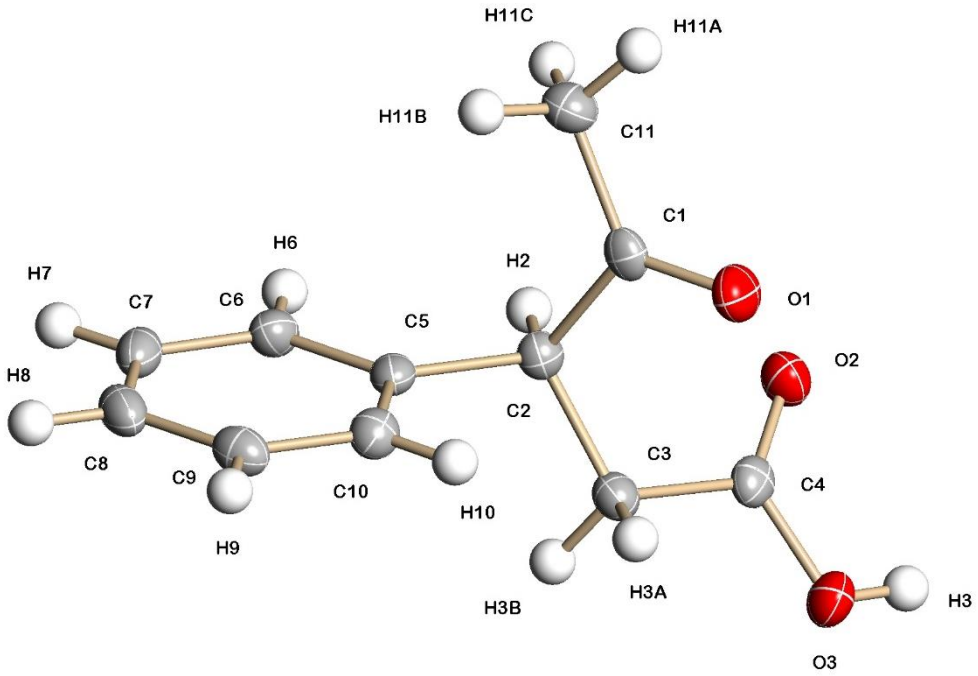


Figure 4. Molecular structure of 4-oxo-3-phenylpentanoic acid **6** showing 50% displacement ellipsoids

Table S2 Selected bond lengths (Å) and bond angles (º) with estimated standard deviations (e.s.d.s.) in parenthesis for compounds **4h**, **5** and **6**

	4h	**5**	**6**
C(1)-O(1)	1.421(3)	1.468(3)	1.218(3)
C(1)-F(1)	1.404(3)	-	-
C(2)-F(1)	-	1.407(2)	-
C(4)-O(1)	1.372(4)	1.360(3)	-
C(4)-O(2)	1.198(4)	1.197(3)	1.203(3)
C(4)-O(3)	-	-	1.335(3)
O(1)-C(1)-C(2)	105.5(2)	102.77(17)	120.3(2)
O(1)-C(1)-C(11)	-	-	122.2(3)
C(1)-C(2)-C(3)	101.5(2)	103.26(18)	111.82(19)
C(2)-C(3)-C(4)	103.2(3)	103.9(2)	112.9(2)
C(3)-C(4)-O(1)	109.3(3)	109.2(2)	-
C(3)-C(4)-O(2)	-	-	124.6(2)
C(4)-O(1)-C(1)	110.4(2)	111.28(18)	-
C(3)-C(4)-O(3)	-	-	111.5(2)

Experimental

Proton, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 400.13, 376.46 and 100.62 MHz respectively and were referenced to external $SiMe_4$ (^{1}H), external $CFCl_3$ (^{19}F) and to external $SiMe_4$ (^{13}C) using the high frequency positive convention. Atmospheric Solids Analysis Probe (ASAP) mass spectra were recorded on a Xevo QTof mass spectrometer (Waters) and Electrospray (ES) mass spectra were obtained by LC-MS using a Xevo QTof mass spectrometer (Waters) coupled to an Acquity LC system (Waters) with an Acquity UPLC BEH C18 column (2.1 x 50 mm). X-ray crystallography data were collected on a Bruker Apex SMART 2000 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å).

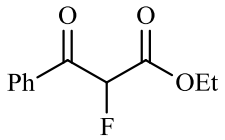
Dichloromethane was obtained dry from a distillation machine model Puresolve^{TM} and was stored in sealed ampoules over 4Å molecular sieves under an atmosphere of dry nitrogen. Hexafluoroisopropan-2-ol was purchased from Fluorochem Ltd and stored in a Schlenk flask over

4Å molecular sieves under an atmosphere of dry nitrogen. The hypervalent fluoroiodane reagent **1**,[3a] the unsaturated carboxylic acids (**3a** to **3e**),[3c] (*E*)-4-phenylbut-3-enoic acid **3g**,[16] and (*E*)-4-phenylpent-3-enoic acid **3h**[17] were prepared following the literature procedures.

Procedure for the fluorination of 1,3-dicarbonyl compounds in HFIP (Table 1, Entries 1-5)

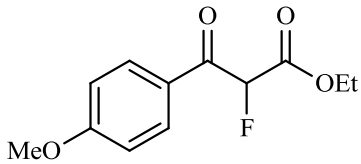
The flask was charged with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.300 g, 1.08 mmol), hexafluoroisopropanol (1.2 mL) and the 1,3-dicarbonyl substrate (0.72 mmol). The flask was then sealed and either heated to 65 ^{o}C (drysyn bath temperature) for 4 hours (entries 1-4) or stirred at room temperature for 1 hour (entry 5). After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^{1}H and ^{19}F NMR spectroscopy. The crude product was purified by column chromatography (1% methanol in dichloromethane) on silica gel.

Ethyl 2-fluoro-3-oxo-3-phenylpropanoate 2a



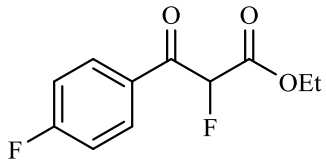
Ethyl 2-fluoro-3-oxo-3-phenylpropanoate **2a** was obtained as a yellow oil (0.111 g, 73%). The characterisation data was in agreement with the literature.[18] δ_H ($CDCl_3$, 400 MHz) 1.22 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.27 (2H, m_{AB}, dq, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 7.2 Hz, OCH_AH_B), 5.87 (1H, d, $^2J_{HF}$ = 50.0 Hz, CHF), 7.48 (2H, t, $^3J_{HH}$ = 8.0 Hz, ArH), 7.61 (1H, t, $^3J_{HH}$ = 8.0 Hz, ArH), 8.02 (2H, d, $^3J_{HH}$ = 8.0 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -190.8 (s); δ_C ($CDCl_3$, 100 MHz) 14.5 (CH_3), 62.9 (CH_2), 90.0 (d, $^1J_{CF}$ = 197.2 Hz, CH), 128.8 (CH), 129.5 (CH), 133.4 (C), 134.5 (CH), 164.9 (d, $^2J_{CF}$ = 24.1 Hz, CO), 189.5 (d, $^2J_{CF}$ = 20.1 Hz, CO); *m/z* (ASAP) 211.0760 (MH^+. $C_{11}H_{12}FO_3$ requires 211.0770, 100 %).

Ethyl 2-fluoro-3-(4-methoxyphenyl)-3-oxo-propanoate 2b



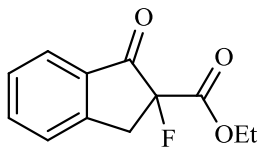
Ethyl 2-fluoro-3-(4-methoxyphenyl)-3-oxo-propanoate **2b** was obtained as a colourless oil (0.155 g, 90%). The characterisation data was in agreement with the literature.[19] δ_H ($CDCl_3$, 400 MHz) 1.23 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 3.86 (3H, s, OMe), 4.30 (2H, m_{AB}, dq, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 7.1 Hz, OCH_AH_B), 5.82 (1H, d, $^2J_{HF}$ = 48.9 Hz, CHF), 6.97 (2H, d, $^3J_{HH}$ = 9.0 Hz, ArH), 8.04 (2H, d, $^3J_{HH}$ = 9.0 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -189.6 (s); δ_C ($CDCl_3$, 100 MHz) 13.0 (CH_3), 54.6 (CH_3), 61.6 (CH_2), 89.2 (d, $^1J_{CF}$ = 197.6 Hz, CH), 113.1 (CH), 125.3 (C), 131.0 (d, $^4J_{CF}$ = 3.1 Hz, CH), 163.6 (C), 164.2 (d, $^2J_{CF}$ = 24.1 Hz, CO), 186.8 (d, $^2J_{CF}$ = 20.8 Hz, CO); *m/z* (ES^+) 241.0880 (MH^+, $C_{12}H_{14}FO_4$ requires 241.0876, 60%), 135.0452 (100).

Ethyl 2-fluoro-3-(4-fluorophenyl)-3-oxo-propanoate 2c



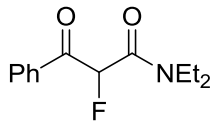
Ethyl 2-fluoro-3-(4-fluorophenyl)-3-oxo-propanoate **2c** was obtained as a colourless oil (0.153 g, 93%). The characterisation data was in agreement with the literature.[20] δ_H ($CDCl_3$, 400 MHz) 1.27 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.31 (2H, m_{AB}, qm, $^3J_{HH}$ = 7.1 Hz, OCH_AH_B), 5.89 (1H, d, $^2J_{HF}$ = 48.9 Hz, CHF), 7.18 (2H, dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{HF}$ = 7.5 Hz, ArH), 8.08-8.12 (2H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -101.8 (1F, s, ArF), -189.6 (1F, s, CHF); δ_C ($CDCl_3$, 100 MHz) 13.9 (CH_3), 62.8 (CH_2), 90.2 (d, $^1J_{CF}$ = 197.2 Hz, CH), 116.1 (d, $^2J_{CF}$ = 22.1 Hz, CH), 129.8 (C), 132.4 (dd, $^3J_{CF}$ = 10.1 Hz, $^4J_{CF}$ = 3.0 Hz, CH), 164.8 (d, $^2J_{CF}$ = 24.1 Hz, CO), 166.5 (d, $^1J_{CF}$ = 257.6 Hz, C), 188.0 (d, $^2J_{CF}$ = 20.1 Hz, CO); *m/z* (ES^+) 229.0679 (MH^+, $C_{11}H_{11}F_2O_3$ requires 229.0676, 100%).

Ethyl 1-indanone-2-fluoro-2-carboxylate 2d



Ethyl 1-indanone-2-fluoro-2-carboxylate **2d** was obtained as a colourless oil (0.129 g, 81%). The characterisation data was in agreement with the literature.[21] δ_H ($CDCl_3$, 400 MHz) 1.26 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 3.44 (1H, dd, $^3J_{HF}$ = 22.6 Hz, $^2J_{HH}$ = 17.6 Hz, ring CH_AH$_B$), 3.80 (1H, dd, $^2J_{HH}$ = 17.6 Hz, $^3J_{HF}$ = 11.7 Hz, ring CH$_A$$H_B$), 4.28 (2H, q, $^3J_{HH}$ = 7.1 Hz, OCH_2), 7.47 (1H, t, $^3J_{HH}$ = 7.9 Hz, ArH), 7.51 (1H, d, $^3J_{HH}$ = 7.9 Hz, ArH), 7.71 (1H, t, $^3J_{HH}$ = 7.9 Hz, ArH), 7.84 (1H, d, $^3J_{HH}$ = 7.9 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -164.4 (s); δ_C ($CDCl_3$, 100 MHz) 14.0 (CH_3), 38.3 (d, $^2J_{CF}$ = 24.0 Hz, CH_2), 62.6 (CH_2), 94.5 (d, $^1J_{CF}$ = 202.7 Hz, C), 125.6 (CH), 126.6 (CH), 128.6 (CH), 133.3 (C), 136.7 (CH), 150.9 (d, $^3J_{CF}$ = 3.1 Hz, C), 167.3 (d, $^2J_{CF}$ = 27.3 Hz, CO), 195.3 (d, $^2J_{CF}$ = 18.4 Hz, CO); *m/z* (ES^+): 245.0583 (MNa^+, $C_{12}H_{11}FO_3Na$ requires 245.0590, 100%), 223.0771 (MH^+, $C_{12}H_{12}FO_3$ requires 223.0770, 47%), 195.0455 (38%).

***N*,*N*-diethyl-2-fluoro-3-oxo-3-phenylpropanamide 2e**



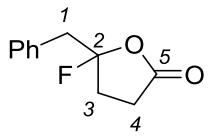
N,*N*-diethyl-2-fluoro-3-oxo-3-phenylpropanamide **2e** was obtained as a yellow oil (0.121 g, 71%). The characterisation data was in agreement with the literature.[22] δ_H ($CDCl_3$, 400 MHz) 1.02 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.11 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 3.30 (2H, q, $^3J_{HH}$ = 7.1 Hz, NCH_2), 3.41 (2H, m, NCH_2), 6.04 (1H, d, $^2J_{HF}$ = 49.1 Hz, CHF), 7.40 (2H, t, $^3J_{HH}$ = 7.7 Hz, ArH), 7.52 (1H, t, $^3J_{HH}$ = 7.7 Hz, ArH), 8.05 (2H, d, $^3J_{HH}$ = 7.7 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -186.6 (s); δ_C ($CDCl_3$, 100 MHz): 12.4 (CH_3), 14.1 (CH_3), 40.9 (CH_2), 41.6 (d, $^4J_{CF}$ = 4.8 Hz, CH_2), 92.5 (d, $^1J_{CF}$ = 197.5 Hz, CHF), 128.6 (CH), 129.6 (d, $^4J_{CF}$ = 2.2 Hz, CH), 133.7 (C), 134.2 (CH), 163.4 (d, $^2J_{CF}$ = 20.6 Hz, CO), 191.9 (d, $^2J_{CF}$ = 20.7 Hz, CO);

m/z (ES^+) 260.1083 (MNa^+, $C_{13}H_{16}FNO_2Na$ requires 260.1063, 55%), 238.1245 (MH^+, $C_{13}H_{17}FNO_2$ requires 238.1243, 100%), 100.0748 ($CONEt_2^+$, 45%).

Procedure for the intramolecular fluorocyclisations in HFIP (Table 2, Entries 1-8)

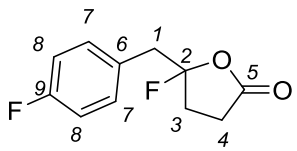
A small Schlenk flask was charged with powdered 4 Å molecular sieves (0.11 g), 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.38 g, 1.36 mmol), substrate (0.9 mmol) and hexafluoroisopropanol (3 mL). The flask was then sealed and the contents were stirred at 40 °C for either one hour (entries 1-5 and 8) or four hours (entries 6-7). After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^1H and ^{19}F NMR spectroscopy. The crude product was purified by column chromatography on silica gel.

5-Benzyl-5-fluorodihydrofuran-2(3*H*)-one 4a



4-Phenylpent-4-enoic acid **3a** (0.15 g, 0.85 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.36 g, 1.29 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-benzyl-5-fluorodihydrofuran-2(3*H*)-one **4a** as a colourless oil (0.139 g, 84%). The characterisation data was in agreement with the literature.[3c] δ_H ($CDCl_3$, 400 MHz) 2.15-2.30 (2H, m, H_3 and $H_{3'}$), 2.42 (1H, dm, on fluorine decoupling simplifies to ddd, $^2J_{HH}$ = 17.8 Hz, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 3.1 Hz, H_4), 2.74 (1H, ddd, $^2J_{HH}$ = 17.8 Hz, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 9.3 Hz, $H_{4'}$), 3.29 (2H, d, $^3J_{HF}$ = 14.7 Hz, H_1 and $H_{1'}$), 7.28 – 7.36 (5H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -97.0 (s); δ_C ($CDCl_3$, 100 MHz) 27.0 (CH_2), 30.9 (d, $^2J_{CF}$ = 27.7 Hz, CH_2), 42.7 (d, $^2J_{CF}$ = 28.0 Hz, CH_2), 119.2 (d, $^1J_{CF}$ = 230.7 Hz, C), 127.6 (CH), 128.6 (CH), 130.4 (CH), 133.0 (d, $^3J_{CF}$ = 5.1 Hz, C), 174.7 (CO); *m/z* (ASAP) 195.0822 (MH^+. $C_{11}H_{12}FO_2$ requires 195.0821, 20 %), 175.0722 ($(M-F)^+$, 100%).

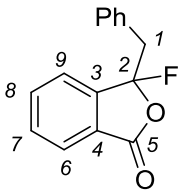
5-Fluoro-5-(4-fluorobenzyl)dihydrofuran-2(3*H*)-one 4b



4-(4-Fluorophenyl)pent-4-enoic acid **3b** (0.15 g, 0.77 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.32 g, 1.14 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-fluoro-5-(4-fluorobenzyl)-dihydrofuran-2(3*H*)-one **4b** as a colourless oil (0.130 g, 80%). The characterisation data was in

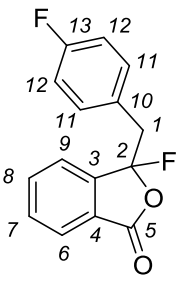
agreement with the literature.[3c] δ_H ($CDCl_3$, 400 MHz) 2.14-2.34 (2H, m, H_3 and $H_{3'}$), 2.42 – 2.49 (1H, m, on fluorine decoupling simplifies to ddd, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 2.3 Hz, H_4), 2.75 (1H, ddd, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 9.4 Hz, $H_{4'}$), 3.26 (2H, d, $^3J_{HF}$ = 14.8 Hz, H_1 and $H_{1'}$), 7.02 (2H, t, $^3J_{HF}$ = $^3J_{HH}$ = 8.7 Hz, ArH), 7.26 (2H, dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HF}$ = 5.5 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -97.8 (1F, s, CF), -114.8 (1F, s, ArF); δ_C ($CDCl_3$, 100 MHz) 26.9 (CH_2), 30.9 (d, $^2J_{CF}$ = 28.8 Hz, CH_2), 41.8 (d, $^2J_{CF}$ = 28.1 Hz, CH_2), 115.5 (d, $^2J_{CF}$ = 22.2 Hz, CH), 118.9 (d, $^1J_{CF}$ = 231.4 Hz, C), 128.7 (C), 131.9 (d, $^3J_{CF}$ = 8.0 Hz, CH), 162.3 (d, $^1J_{CF}$ = 245.9 Hz, C), 174.7 (CO); *m/z* (ASAP) 193.0664 ($(M-F)^+$. $C_{11}H_{10}FO_2$ requires 193.0665, 100 %).

3-Benzyl-3-fluoroisobenzofuran-1(3*H*)-one 4c



2-(1-Phenylvinyl)benzoic acid **3c** (0.15 g, 0.67 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.28 g, 1.00 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure. The crude product was purified by column chromatography (dichoromethane) to give 3-benzyl-3-fluoroisobenzofuran-1(3*H*)-one **4c** as a colourless oil (0.129 g, 79%). The characterisation data was in agreement with the literature.[3c] δ_H ($CDCl_3$, 400 MHz) 3.52 (1H, dd, $^2J_{HH}$ = 14.4 Hz, $^3J_{HF}$ = 14.3 Hz, H_1), 3.63 (1H, dd, $^2J_{HH}$ = 14.4 Hz, $^3J_{HF}$ = 12.3 Hz, $H_{1'}$), 7.19-7.26 (5H, m, ArH), 7.34 (1H, d, $^3J_{HH}$ = 7.5 Hz, ArH), 7.59 (1H, t, $^3J_{HH}$ = 7.5 Hz, ArH), 7.69 (1H, t, $^3J_{HH}$ = 7.5 Hz, ArH), 7.80 (1H, d, $^3J_{HH}$ = 7.5 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -100.6 (s); δ_C ($CDCl_3$, 100 MHz) 40.6 (d, $^2J_{CF}$ = 28.2 Hz, CH_2), 113.4 (d, $^1J_{CF}$ = 232.2 Hz, C), 121.4 (CH), 124.0 (CH), 124.5 (C), 125.9 (CH), 126.7 (CH), 128.8 (CH), 129.8 (CH), 130.2 (d, $^3J_{CF}$ = 4.5 Hz, C), 132.9 (CH), 142.8 (d, $^2J_{CF}$ = 21.2 Hz, C), 164.8 (CO); *m/z* (ASAP) 223.0758 ($(M-F)^+$. $C_{15}H_{11}O_2$ requires 223.0759, 100%), 195.0813 ($(M-COF)^+$, 70%).

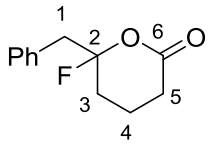
3-Fluoro-3-(4-fluorobenzyl)isobenzofuran-1(3*H*)-one 4d



2-(1-(4-Fluorophenyl)vinyl)benzoic acid **3d** (0.15 g, 0.62 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.26 g, 0.93 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 3-fluoro-3-(4-fluorobenzyl)isobenzofuran-1(3*H*)-one **4d** as a white solid (0.131 g, 81%). The characterisation data was in agreement with the literature.[3c] mp 69 – 71 °C. δ_H ($CDCl_3$, 400 MHz) 3.51 (1H, dd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HF}$ = 14.3 Hz, H_1), 3.57 (1H, dd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HF}$ = 12.7 Hz, $H_{1'}$), 6.93 (2H, t, $^3J_{HH}$ = $^3J_{HF}$ = 8.6 Hz, ArH), 7.17 (2H, dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HF}$ = 5.5 Hz, ArH), 7.37

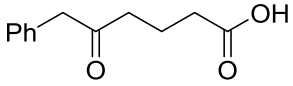
(1H, d, $^3J_{HH}$ = 7.5 Hz, ArH), 7.60 (1H, t, $^3J_{HH}$ = 7.6 Hz, ArH), 7.69 (1H, t, $^3J_{HH}$ = 7.5 Hz, ArH), 7.81 (1H, d, $^3J_{HH}$ = 7.5 Hz, ArH); δ_F ($CDCl_3$, 376 MHz) -101.0 (1F, s, CF), -114.6 (1F, s, ArF); δ_C ($CDCl_3$, 125 MHz) 41.6 (d, $^2J_{CF}$ = 31.3 Hz, CH_2), 115.0 (d, $^1J_{CF}$ = 233.2 Hz, CF), 115.4 (d, $^2J_{CF}$ = 21.7 Hz, CH), 123.0 (CH), 125.8 (CH), 126.3 (d, $^3J_{CF}$ = 1.4 Hz, C), 127.8 (dd, $^3J_{CF}$ = 5.6 Hz, $^4J_{CF}$ = 3.2 Hz, C), 131.7 (d, $^3J_{CF}$ = 2.3 Hz, CH), 132.2 (d, $^3J_{CF}$ = 8.3 Hz, CH), 134.8 (CH), 144.5 (d, $^2J_{CF}$ = 21.2 Hz, C), 162.3 (d, $^1J_{CF}$ = 246.9 Hz, C), 166.4 (d, $^3J_{CF}$ = 2.1 Hz, CO); *m/z* (ASAP) 241.0656 ($(M-F)^+$. $C_{15}H_{10}O_2F$ requires 241.0665, 100%), 213.0694 ($(M-COF)^+$, 95%).

6-Benzyl-6-fluorotetrahydro-2*H*-pyran-2-one 4e



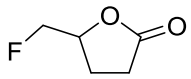
5-Phenylhex-5-enoic acid **3e** (0.15 g, 0.79 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.33 g, 1.18 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 6-benzyl-6-fluorotetrahydro-2*H*-pyran-2-one **4e** as a colourless oil (0.109 g, 66%). The characterisation data was in agreement with the literature.[3c] δ_H ($CDCl_3$, 400 MHz) 1.63 – 1.82 (2H, m, H_3 and H_4), 1.96 – 2.11 (2H, m, $H_{3'}$ and $H_{4'}$), 2.35 – 2.45 (1H, m, H_5), 2.69 (1H, dm, $H_{5'}$), 3.20 (2H, d, $^3J_{HF}$ = 14.8 Hz, H_1 and $H_{1'}$), 7.26 – 7.34 (5H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -96.8 (s); δ_C ($CDCl_3$, 100 MHz) 14.8 (d, $^3J_{CF}$ = 3.2 Hz, CH_2), 28.8 (d, $^2J_{CF}$ = 26.9 Hz, CH_2), 29.1 (CH_2), 45.2 (d, $^2J_{CF}$ = 26.7 Hz, CH_2), 115.5 (d, $^1J_{CF}$ = 228.0 Hz, C), 127.4 (CH), 128.5 (CH), 130.5 (CH), 133.5 (d, $^3J_{CF}$ = 5.5 Hz, C), 168.8 (CO); *m/z* (ASAP) 189.0923 ($(M-F)^+$. $C_{12}H_{13}O_2$ requires 189.0916, 5%), 161.0948 ($(PhCH_2COCH_2CH_2CH_2)^+$, 100%).

5-Oxo-6-phenylhexanoic acid



6-Benzyl-6-fluorotetrahydro-2*H*-pyran-2-one **4e** decomposed in $CDCl_3$ over several hours to give 5-oxo-6-phenylhexanoic acid. The characterisation data was in agreement with the literature.[3c] mp 42 – 44 °C. δ_H ($CDCl_3$, 400 MHz) 1.79 (2H, quintet, $^3J_{HH}$ = 7.4 Hz, CH_2), 2.26 (2H, t, $^3J_{HH}$ = 7.4 Hz, CH_2), 2.47 (2H, t, $^3J_{HH}$ = 7.4 Hz, CH_2), 3.61 (2H, s, CH_2), 7.12 (2H, d, $^3J_{HH}$ = 7.3 Hz, ArH), 7.19 (1H, t, $^3J_{HH}$ = 7.3 Hz, ArH), 7.25 (2H, t, $^3J_{HH}$ = 7.3 Hz, ArH), 10.38 (1H, br s, COOH); δ_C ($CDCl_3$, 100 MHz) 17.4 (CH_2), 31.8 (CH_2), 39.4 (CH_2), 49.1 (CH_2), 126.1 (CH), 127.7 (CH), 128.3 (CH), 133.0 (C), 178.3 (CO), 206.6 (CO); *m/z* (ASAP) 189.0909 ($(M-OH)^+$. $C_{12}H_{13}O_2$ requires 189.0916, 55%), 175.0752 (75%), 161.0941 ($(M-CO_2H)^+$, 60%).

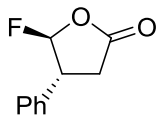
5-(Fluoromethyl)dihydrofuran-2(3*H*)-one 4f



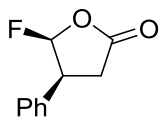
4-Pentenoic acid **3f** (0.15 g, 1.5 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.63 g, 2.25 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 ºC for 4 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-(fluoromethyl)dihydrofuran-2(3*H*)-one **4f** as a yellow oil (0.145 g, 82%). The product was visualised on the TLC plate using $KMnO_4$ stain. The characterisation data was in agreement with the literature.[23] δ_H ($CDCl_3$, 400 MHz) 2.10-2.25 (1H, m, CH_AH_B), 2.35-2.42 (1H, m, CH_AH_B), 2.50-2.69 (2H, m, CH_2), 4.38 (1H, ddd, $^2J_{HF}$ = 47.9 Hz, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 2.4 Hz, CH_CH$_D$F), 4.57 (1H, ddd, $^2J_{HF}$ = 47.9 Hz, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 3.6 Hz, CH$_C$$H_D$F), 4.60-4.68 (1H, m, OCH); δ_F ($CDCl_3$, 376 MHz) -232.5 (s); δ_C ($CDCl_3$, 100 MHz) 22.7 (d, $^3J_{CF}$ = 5.0 Hz, CH_2), 28.1 (CH_2), 82.6 (d, $^2J_{CF}$ = 20.2 Hz, CH), 84.5 (d, $^1J_{CF}$ = 174.3 Hz, CH_2F), 176.5 (CO); m/z (ASAP) 118.0121 (M^+, $C_5H_7FO_2$ requires 118.0120).

5-Fluoro-4-phenyldihydrofuran-2(3*H*)-one 4g

(*E*)-4-Phenylbut-3-enoic acid **3g** (0.15 g, 0.92 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.38 g, 1.36 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 ºC for 4 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-fluoro-4-phenyldihydrofuran-2(3*H*)-one **4g** (0.059 g, 36%) as a 1.6:1 mixture of *anti*-:*syn*-diastereomers.



(4*R*,5*R*)/(4*S*,5*S*)-5-Fluoro-4-phenyldihydrofuran-2(3*H*)-one **4g** was obtained as a yellow oil. δ_H ($CDCl_3$, 400 MHz) 2.59 (1H, dd, $^2J_{HH}$ = 18.3 Hz, $^3J_{HH}$ = 2.2 Hz, COCH_AH_B), 3.15 (1H, dd, $^2J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 9.3 Hz, COCH$_A$$H_B$), 3.76 (1H, m, CHPh), 5.98 (1H, d, $^2J_{HF}$ = 61.0 Hz, CHF), 7.10-7.49 (5H, m, ArH); $^1H\{^{19}F\}$ ($CDCl_3$, 400 MHz) 2.59 (1H, dd, $^2J_{HH}$ = 18.3 Hz, $^3J_{HH}$ = 2.2 Hz, COCH_AH_B), 3.15 (1H, dd, $^2J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 9.3 Hz, COCH$_A$$H_B$), 3.76 (1H, dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 2.0 Hz, CHPh), 6.01 (1H, s, CHF), 7.10-7.49 (5H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -115.0 (s); δ_C ($CDCl_3$, 125 MHz) 32.9 (CH_2), 46.7 (d, $^2J_{CF}$ = 23.8 Hz, CH), 113.2 (d, $^1J_{CF}$ = 233.8 Hz, CH), 126.6 (CH), 128.3 (CH), 129.5 (CH) 137.5 (d, $^3J_{CF}$ = 9.2 Hz, C), 174.6 (CO); m/z (ASAP) 161.0610 ($(M-F)^+$, $C_{10}H_9O_2$ requires 161.0603).

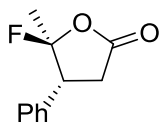


((4*S*,5*R*)/(4*R*,5*S*)-5-Fluoro-4-phenyldihydrofuran-2(3*H*)-one **4g** was obtained as a yellow oil. δ_H ($CDCl_3$, 400 MHz) 2.87 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 8.6 Hz, COCH_AH_B), 3.06 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 12.2 Hz, COCH$_A$$H_B$), 3.79 (1H, m, CHPh), 6.10 (1H, dd, $^2J_{HF}$ = 61.3 Hz, $^3J_{HH}$ = 3.9 Hz, CHF), 7.10-7.49 (5H, m, ArH); $^1H\{^{19}F\}$

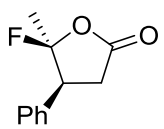
($CDCl_3$, 400 MHz) 2.89 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 8.6 Hz, COCH_AH$_B$), 3.06 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 12.2 Hz, COCH$_A$$H_B$), 3.79 (1H, ddd, $^3J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 3.9 Hz, CHPh), 6.18 (1H, d, $^3J_{HH}$ = 4.0 Hz, CHF), 7.10-7.49 (5H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -134.2 (s); δ_C ($CDCl_3$, 125 MHz) 30.5 (CH_2), 46.3 (d, $^2J_{CF}$ = 23.3 Hz, CH), 109.1 (d, $^1J_{CF}$ = 233.8 Hz, CH), 126.6 (CH), 128.4 (CH), 129.5 (CH), 131.8 (C), 173.9 (CO); m/z (ASAP) 161.0610 ((M-F)$^+$, $C_{10}H_9O_2$ requires 161.0603).

5-Fluoro-5-methyl-4-phenyldihydrofuran-2(3*H*)-one 4h

(*E*)-4-Phenylpent-3-enoic acid **3h** (0.15 g, 0.85 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.36 g, 1.29 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 ^{o}C for 1 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-fluoro-5-methyl-4-phenyldihydrofuran-2(3*H*)-one **4h** (0.142 g, 86%) as a 2.2:1 mixture of *anti*-:*syn*-diastereomers.



(4*R*,5*R*)/(4*S*,5*S*)-5-Fluoro-5-methyl-4-phenyldihydrofuran-2(3*H*)-one **4h** was obtained as a yellow oil. δ_H ($CDCl_3$, 400 MHz) 1.37 (3H, d, $^3J_{HF}$ = 18.9 Hz, CH_3), 2.72 (1H, dd, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 1.6 Hz, COCH_AH$_B$), 3.31 (1H, dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 8.8 Hz, COCH$_A$$H_B$), 3.72 (1H, ddd, $^3J_{HF}$ = 10.3 Hz, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 1.6 Hz, C*H*Ph), 7.14 (2H, dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, ArH), 7.33-7.35 (3H, m, ArH); ^{1}H{^{19}F} NMR ($CDCl_3$, 400 MHz) 1.29 (3H, s, CH_3), 2.64 (1H, dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 1.6 Hz, COCH_AH$_B$), 3.24 (1H, dd, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 8.8 Hz, COCH$_A$$H_B$), 3.66 (1H, dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 1.5 Hz, C*H*Ph), 7.14 (2H, dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, ArH), 7.33-7.35 (3H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -86.3 (s); δ_C ($CDCl_3$, 125 MHz) 20.9 (d, $^2J_{CF}$ = 35.5 Hz, CH_3), 35.0 (CH_2), 50.1 (d, $^2J_{CF}$ = 28.7 Hz, CH), 120.9 (d, $^1J_{CF}$ = 228.6 Hz, C), 127.3 (CH), 128.4 (CH), 129.4 (CH), 137.8 (d, $^3J_{CF}$ = 8.0 Hz, C), 175.1 (CO); m/z (ASAP) 195.0814 (MH$^+$, $C_{11}H_{12}FO_2$ requires 195.0821).



(4*S*,5*R*)/(4*R*,5*S*)-5-Fluoro-5-methyl-4-phenyldihydrofuran-2(3*H*)-one **4h** was obtained as a white solid. mp 53 – 55 °C. δ_H ($CDCl_3$, 400 MHz) 1.69 (3H, d, $^3J_{HF}$ = 17.8 Hz, CH_3), 2.87 (1H, dd, $^2J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 8.5 Hz, COCH_AH$_B$), 3.13 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 12.4 Hz, COCH$_A$$H_B$), 3.55 (1H, ddd, $^3J_{HF}$ = 20.7 Hz, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 8.3 Hz, C*H*Ph), 7.32 – 7.42 (5H, m, ArH); ^{1}H{^{19}F} ($CDCl_3$, 400 MHz) 1.69 (3H, s, CH_3), 2.87 (1H, dd, $^2J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 8.3 Hz, COCH_AH$_B$), 3.14 (1H, dd, $^2J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 12.4 Hz, COCH$_A$$H_B$), 3.56 (1H, dd, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 8.4 Hz, C*H*Ph), 7.32 – 7.42 (5H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -107.8 (s); δ_C ($CDCl_3$, 125 MHz) 21.3 (d, $^2J_{CF}$ = 28.8 Hz, CH_3), 33.5 (CH_2),

50.7 (d, $^{2}J_{CF}$ = 23.8 Hz, CH), 117.9 (d, $^{1}J_{CF}$ = 231.3 Hz, C), 128.5 (CH), 128.8 (CH), 128.9 (CH), 133.0 (C), 173.5 (CO); m/z (ASAP) 195.0814 (MH^+, $C_{11}H_{12}FO_2$ requires 195.0821).

Procedure for the intramolecular fluorocyclisations with $AgBF_4$ (Table 2, Entries 6-8)

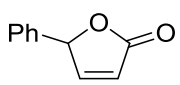
A small Schlenk flask was charged with powdered 4 Å molecular sieves (0.11 g) and $AgBF_4$ (0.17 g, 0.87 mmol) in a glove box. 1-Fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.38 g, 1.36 mmol), substrate (0.9 mmol) and dry dichloromethane (0.7 mL) were added to the flask. The flask was then sealed and the contents were stirred at 40 ^{o}C for either one hour (entries 6 and 8) or four hours (entry 7). After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^{1}H and ^{19}F NMR spectroscopy. The crude product was purified by column chromatography on silica gel.

5-(Fluoromethyl)dihydrofuran-2(3*H*)-one 4f

4-Pentenoic acid (0.15 g, 1.5 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.63 g, 2.25 mmol) and $AgBF_4$ (0.29 g, 1.5 mmol) in the presence of 4 Å molecular sieves (0.11 g) in dry dichloromethane (0.7 mL) at 40 ^{o}C for 1 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-(fluoromethyl)dihydrofuran-2(3*H*)-one **4f** as a yellow oil (0.071 g, 40%).

5-Fluoro-4-phenyldihydrofuran-2(3*H*)-one 4g

(*E*)-4-Phenylbut-3-enoic acid **3g** (0.15 g, 0.92 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.38 g, 1.36 mmol) and $AgBF_4$ (0.17 g, 0.87 mmol) in the presence of 4 Å molecular sieves (0.11 g) in dry dichloromethane (0.7 mL) at 40 ^{o}C for 4 h following the general procedure. The crude product was purified by column chromatography (dichloromethane) to give 5-fluoro-4-phenyldihydrofuran-2(3*H*)-one **4g** (0.072 g, 43%) as a 1.8:1 mixture of *anti*-:*syn*-diastereomers.



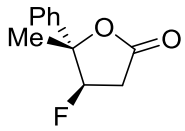
5-Phenylfuran-2(5*H*)-one was obtained (0.011 g, 7%) as a mixture with the iodoalcohol. The characterisation data was in agreement with the literature.[24] δ_H ($CDCl_3$, 400 MHz) 6.01 (1H, dd, $^{3}J_{HH}$ = 1.9 Hz, $^{4}J_{HH}$ = 1.6 Hz, CH), 6.24 (1H, dd, $^{3}J_{HH}$ = 5.6 Hz, $^{4}J_{HH}$ = 2.1 Hz, OCH), 7.27-7.30 (2H, m, ArH), 7.41-7.44 (3H, m, ArH), 7.54 (1H, dd, $^{3}J_{HH}$ = 5.6 Hz, $^{3}J_{HH}$ = 1.6 Hz, CH); δ_C ($CDCl_3$, 100 MHz) 84.4 (CH), 121.0 (CH), 126.5 (CH), 128.9 (CH), 129.5 (CH), 134.2 (C), 155.8 (CH), 173.2 (C=O); m/z (ASAP) 160.0609 (M^+, $C_{10}H_8O_2$ requires 160.0602).

5-Fluoro-5-methyl-4-phenyldihydrofuran-2(3*H*)-one 4h

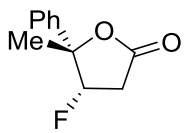
(*E*)-4-Phenylpent-3-enoic acid **3h** (0.15 g, 0.85 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.36 g, 1.29 mmol) and $AgBF_4$ (0.17 g, 0.87 mmol) in the presence of 4 Å molecular sieves (0.11 g) in dry dichloromethane (0.7 mL) at 40 °C for 1 h following the general procedure. The crude mixture was purified by column chromatography (dichloromethane) to give 5-fluoro-5-methyl-4-phenyldihydrofuran-2(3*H*)-one **4h** (0.114 g, 69 %) as a 1:2 mixture of *anti*-:*syn*-diastereomers.

4-Fluoro-5-methyl-5-phenyldihydrofuran-2-one 5

Selectfluor (0.46 g, 1.29 mmol), (*E*)-4-phenylpent-3-enoic acid **3h** (0.15 g, 0.85 mmol) and dry acetonitrile (10 mL) were charged to a small Schlenk flask. The reaction mixture was stirred at room temperature for 20 hours. After removing the solvent under reduced pressure, the residue was dissolved in diethyl ether (15 mL) and a solution of 10% $NaHCO_3$ (15 mL) was added. The aqueous layer was extracted with diethyl ether (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure yielding the crude product. It was purified by column chromatography using dichloromethane as eluent to give (4*R*,5*S*)/(4*S*,5*R*)-4-fluoro-5-methyl-5-phenyldihydrofuran-2-one (0.069 g, 42%) and (4*S*,5*S*)/(4*R*,5*R*)-4-fluoro-5-methyl-5-phenyldihydrofuran-2-one (0.045 g, 27%). The characterisation data was in agreement with the literature.[25]

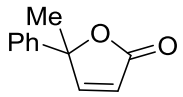


(4*R*,5*S*)/(4*S*,5*R*)-4-Fluoro-5-methyl-5-phenyldihydrofuran-2-one **5** was obtained as a white solid (0.069 g, 42%). mp 49 – 52 ˚C. δ_H ($CDCl_3$, 400 MHz) 1.79 (3H, d, $^4J_{HF}$ = 3.7 Hz, CH_3), 2.66-2.91 (2H, m, CH_2), 5.24 (1H, ddd, $^2J_{HF}$ = 52.5 Hz, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 2.9 Hz, C*H*F), 7.35 (2H, d, $^3J_{HH}$ = 6.2 Hz, ArH), 7.39-7.43 (3H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -182.1 (s); δ_C ($CDCl_3$, 125 MHz) 22.7 (d, $^3J_{CF}$ = 10.0 Hz, CH_3), 35.6 (d, $^2J_{CF}$ = 23.8 Hz, CH_2), 89.6 (d, $^2J_{CF}$ = 21.3 Hz, C), 94.4 (d, $^1J_{CF}$ = 190.0 Hz, CH), 124.3 (CH), 128.5 (CH), 129.1 (CH), 140.7 (d, $^3J_{CF}$ = 5.0 Hz, C), 173.5 (CO); m/z (ASAP) 175.0751 ($(M-F)^+$, $C_{11}H_{11}O_2$ requires 175.0759).



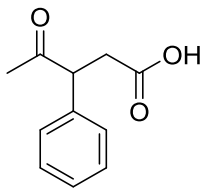
(4*S*,5*S*)/(4*R*,5*R*)-4-Fluoro-5-methyl-5-phenyldihydrofuran-2-one **5** was obtained as a colourless oil (0.045 g, 27%). δ_H ($CDCl_3$, 400 MHz) 1.62 (3H, s, CH_3), 2.82 (1H, dd, $^3J_{HF}$ = 22.5 Hz, $^2J_{HH}$ = 18.6 Hz, CH_AH_B), 3.11 (1H, ddd, $^3J_{HF}$ = 22.3 Hz, $^2J_{HH}$ = 18.6 Hz, $^3J_{HH}$ = 5.0 Hz, CH_AH_B), 5.22 (1H, dd, $^2J_{HF}$ = 52.8 Hz, $^3J_{HH}$ = 5.0 Hz, C*H*F), 7.30-7.34 (5H, m, ArH); δ_F ($CDCl_3$, 376 MHz) -176.0 (s); δ_C ($CDCl_3$, 125 MHz) 26.4 (d, $^3J_{CF}$ = 3.8 Hz, CH_3), 36.3 (d, $^2J_{CF}$ = 26.3 Hz, CH_2), 89.6 (d, $^2J_{CF}$ = 21.1 Hz, C), 92.9 (d, $^1J_{CF}$ = 187.5 Hz, CH), 124.3 (CH),

125.1 (CH), 128.4 (CH), 137.4 (d, $^3J_{CF}$ = 4.4 Hz, C), 172.7 (CO); m/z (ASAP) 175.0751 ((M-F)$^+$, $C_{11}H_{11}O_2$ requires 175.0759).



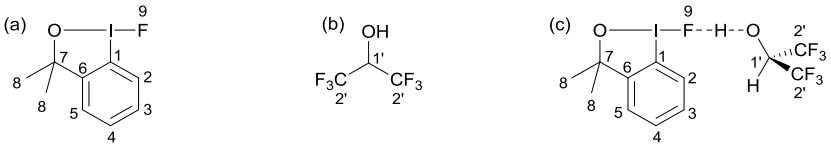
5-Methyl-5-phenylfuran-2-(5*H*)-one (0.008 g, 5%) was isolated together with *anti*-**5** as a white solid. The characterisation data was in agreement with the literature.[26] mp 31 – 35 ˚C (lit.,[27] 34 – 36 ˚C). δ_H ($CDCl_3$, 400 MHz) 1.86 (3H, s, CH_3), 5.98 (1H, d, $^3J_{HH}$ = 5.6 Hz, CH), 7.30-7.43 (5H, m, ArH), 7.59 (1H, d, $^3J_{HH}$ = 5.6 Hz, CH); δ_C ($CDCl_3$, 125 MHz) 29.7 (CH_3), 88.7 (C), 119.4 (CH), 124.8 (CH), 128.4 (CH), 128.8 (CH), 139.1 (C), 160.4 (CH), 172.7 (CO). m/z (ASAP) 175.0715 (MH^+, $C_{11}H_{11}O_2$ requires 175.0722).

4-Oxo-3-phenylpentanoic acid 6



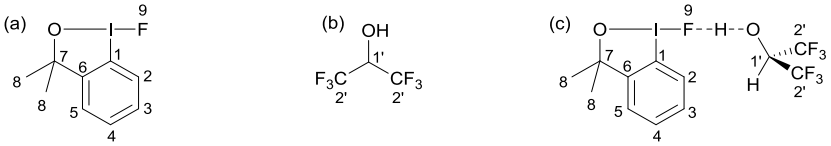
A small Schlenk flask was charged with $AgBF_4$ (0.17 g, 0.87 mmol) in a glove box. 1-Fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.36 g, 1.29 mmol), (*E*)-4-phenylpent-3-enoic acid **3h** (0.15 g, 0.85 mmol) and dry dichloromethane (0.7 mL) were added to the flask. The flask was then sealed and the contents were stirred at 40 ^{o}C for one hour. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^{1}H and ^{19}F NMR spectroscopy. The crude product was purified by column chromatography (dichloromethane) to give 4-oxo-3-phenylpentanoic acid **6** as a yellow solid (0.10 g, 61%). The characterisation data was in agreement with the literature.[27] mp 98 – 100 ˚C (lit.,[27] 98 – 99 ˚C). δ_H ($CDCl_3$, 400 MHz) 2.10 (3H, s, CH_3), 2.59 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 4.9 Hz, CH_AH$_B$), 3.28 (1H, dd, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 9.8 Hz, CH$_A$$H_B$), 4.16 (1H, dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.8 Hz, C*H*Ph), 7.22 (2H, dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.6 Hz, ArH), 7.26-7.36 (3H, m, ArH); δ_C ($CDCl_3$, 125 MHz): 28.8 (CH_3), 36.6 (CH_2), 54.6 (CH), 127.9 (CH), 128.2 (CH), 129.3 (CH), 127.1 (C), 177.4 (CO), 206.6 (CO); m/z (ASAP) 175.0759 ((M-OH)$^+$, $C_{11}H_{11}O_2$ requires 175.0759).

Table S3 Comparison of ^{1}H NMR data for (a) fluoroiodane **1**, (b) HFIP and (c) a 1:1 mixture of **1**:HFIP



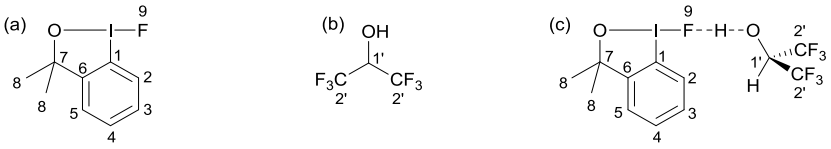
Assignment	(a) Fluoroiodane	(b) HFIP	(c) Adduct	Δδ
2	7.78 dd (8.2, 0.9 Hz)	-	7.72 d (8.1 Hz)	-0.06
3	7.55 td (7.7, 1.5 Hz)	-	7.57 td (7.7, 1.2 Hz)	0.02
4	7.46 td (7.4, 1.1 Hz)	-	7.49 td (7.5, 1.0 Hz)	0.03
5	7.17 dd (7.6, 1.2 Hz)	-	7.18 dd (7.6, 1.2 Hz)	0.01
8	1.52 s	-	1.55 s	0.03
1’	-	4.41 hept (6.0 Hz)	4.37 oct (6.0 Hz)	-0.04
OH	-	2.80 br s	4.92 d (7.5 Hz)	2.12

Table S4 Comparison of ^{19}F NMR data for (a) fluoroiodane **1**, (b) HFIP and (c) a 1:1 mixture of **1**:HFIP



Assignment	(a) Fluoroiodane	(b) HFIP	(c) Adduct	Δδ
9	-142.9 s	-	-142.7 br s	0.2
2’	-	-75.7 d (6.5 Hz)	-75.6 d (6.5 Hz)	0.1

Table S5 Comparison of ^{13}C NMR data for (a) fluoroiodane **1**, (b) HFIP and (c) a 1:1 mixture of **1**:HFIP



Assignment	(a) Fluoroiodane	(b) HFIP	(c) Adduct	Δδ
1	115.9	-	115.7	-0.2
2	128.6	-	128.4	-0.2
3	130.2	-	130.5	0.3
4	130.5	-	130.8	0.3
5	125.9	-	126.1	0.2
6	148.5	-	148.3	-0.2
7	85.2	-	86.1	0.9
8	29.0	-	28.8	-0.2
1’	-	69.6 hept (33.7 Hz)	69.4 hept (33.5 Hz)	-0.2
2’	-	121.3 q (283.5 Hz)	121.7 q (283.7)	0.2

The most significant change found in the ^{1}H NMR spectra is the downfield shift of the OH signal in HFIP from 2.80 to 4.92 ppm in the 1:1 adduct and the OH changed from a broad singlet in HFIP to a doublet in the 1:1 adduct ($^{3}J_{HH}$ = 7.8 Hz). Furthermore, in the ^{13}C NMR spectra there was a downfield shift for the carbon bonded to the oxygen in (a) fluoroiodane from 85.2 to 86.1 ppm in (c) the 1:1 adduct presumably resulting from a change in the O-I-F hypervalent bonding orbital.

Structure solution and refinement

Table S6 summarises the crystallographic data for (4*S*,5*R*)/(4*R*,5*S*)-5-fluoro-5-methyl-4-phenyldihydrofuran-2-one **4h**, (4*S*,5*R*)/(4*R*,5*S*)-4-fluoro-5-methyl-5-phenyldihydrofuran-2-one **5** and 4-oxo-3-phenylpentanoic acid **6**. The data were collected on a Bruker APEX 2000 CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares cycles on F^2 for all data, using SHELXTL version 6.10.[28] All hydrogen atoms were included in calculated positions (C-H = 0.95-1.00 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 Ueq(C) for methyl H atoms and 1.2 Ueq(C) for all other H atoms. All non hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC: 1859674-1859676. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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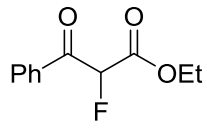
Table S6 Crystallographic data for 5-fluoro-5-methyl-4-phenyldihydrofuran-2-one **4h**, 4-fluoro-5-methyl-5-phenyldihydrofuran-2-one **5** and 4-oxo-3-phenylpentanoic acid **6**

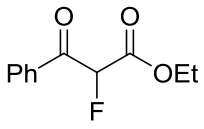
	4h	**5**	**6**
Formula	$C_{11}H_{11}FO_2$	$C_{11}H_{11}FO_2$	$C_{11}H_{12}O_3$
Formula weight	194.20	194.20	192.21
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	P2(1)/c	P2(1)2(1)2(1)	Pna2(1)
Unit cell dimensions			
a (Å)	5.560(5)	5.605(2)	10.1019(17)
b (Å)	7.747(7)	7.129(3)	9.4796(16)
c (Å)	22.119(19)	24.013(9)	9.9375(17)
α (°)	90	90	90
β (°)	91.199(16)	90	90
γ (°)	90	90	90
U (Å^3)	952.4(14)	959.4(6)	951.6(3)
Temperature (K)	150(2)	150(2)	150(2)
Z	4	4	4
D_c (Mg m^{-3})	1.354	1.344	1.342
μ(Mo-Kα) (mm^{-1})	0.105	0.104	0.097
F (000)	408	408	408
Dimensions (mm^3)	0.31 x 0.15 x 0.13	0.46 x 0.27 x 0.08	0.46 x 0.22 x 0.19
Data collection range (°)	1.84 – 26.00	1.70 – 25.98	2.95 – 26.00
Index ranges	$-6 \le h \le 6$	$-6 \le h \le 6$	$-12 \le h \le 12$
	$-9 \le k \le 9$	$-8 \le k \le 8$	$-11 \le k \le 11$
	$-27 \le l \le 26$	$-29 \le l \le 29$	$-12 \le l \le 12$
Reflections	6281	7366	6947
Unique reflections (R_{int})	1872 (0.1163)	1877 (0.0587)	994 (0.0715)
θ_{max} (% complete)	26.00 (99.9)	25.98 (100.0)	26.00 (99.9)
Absorption correction	Empirical	Empirical	Empirical
Max/min transmission	0.970 / 0.060	0.983 / 0.564	0.981 / 0.440
Data/restraints/parameters	1872 / 0 / 128	1877 / 0 / 128	994 / 1 / 128
Goodness of fit on F^2	0.934	1.086	1.035
Final *R* indices [$I > 2\sigma(I)$]			
R_1	0.0756	0.0478	0.0378
wR_2	0.1612	0.1044	0.0851
R indices (all data)			
R_1	0.1177	0.0563	0.0415
wR_2	0.1789	0.1075	0.0865
Largest diff. peak, hole (eÅ^{-3})	0.334, -0.324	0.179, -0.142	0.204, -0.175

^{1}H NMR Spectrum



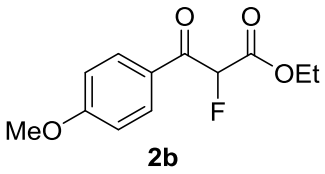
2a

^{19}F NMR Spectrum



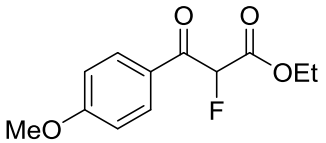
2a

^{1}H NMR Spectrum



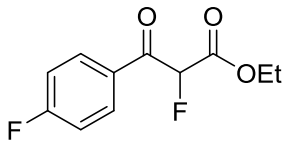
2b

^{19}F NMR Spectrum



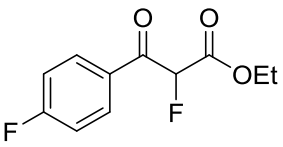
2b

^{1}H NMR Spectrum



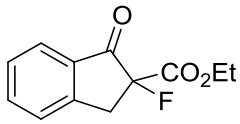
2c

^{19}F NMR Spectrum



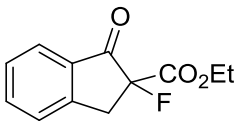
2c

^{1}H NMR Spectrum



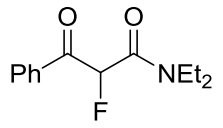
2d

^{19}F NMR Spectrum



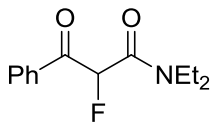
2d

^{1}H NMR Spectrum



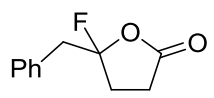
2e

^{19}F NMR Spectrum



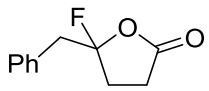
2e

^{1}H NMR Spectrum



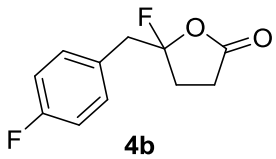
4a

^{19}F NMR Spectrum



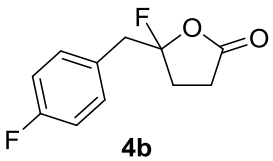
4a

^{1}H NMR Spectrum



4b

^{19}F NMR Spectrum



4b

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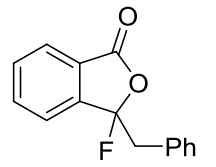
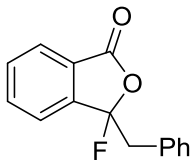


4c

^{19}F NMR Spectrum



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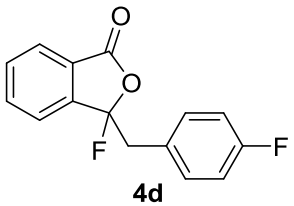
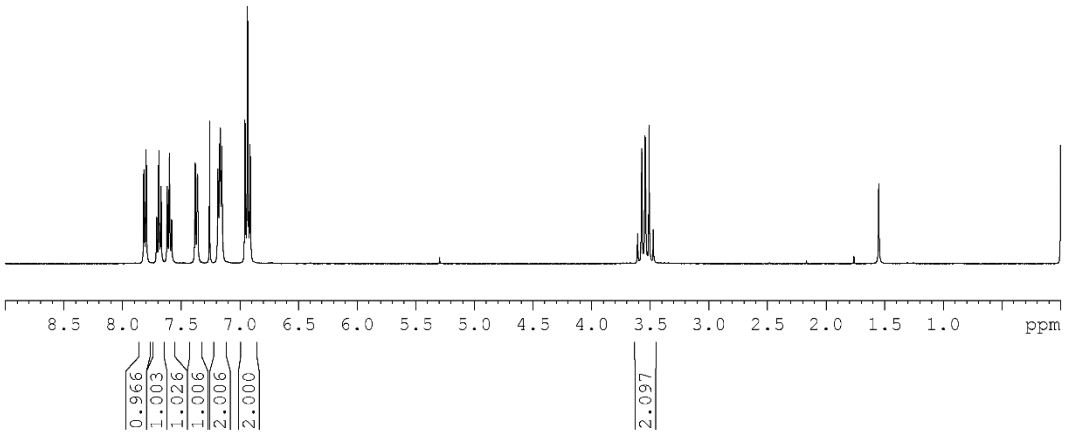
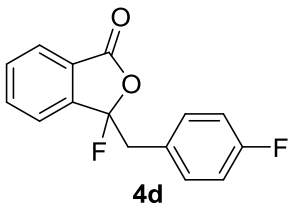


4d

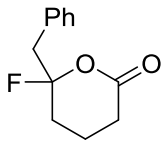


^{19}F NMR Spectrum

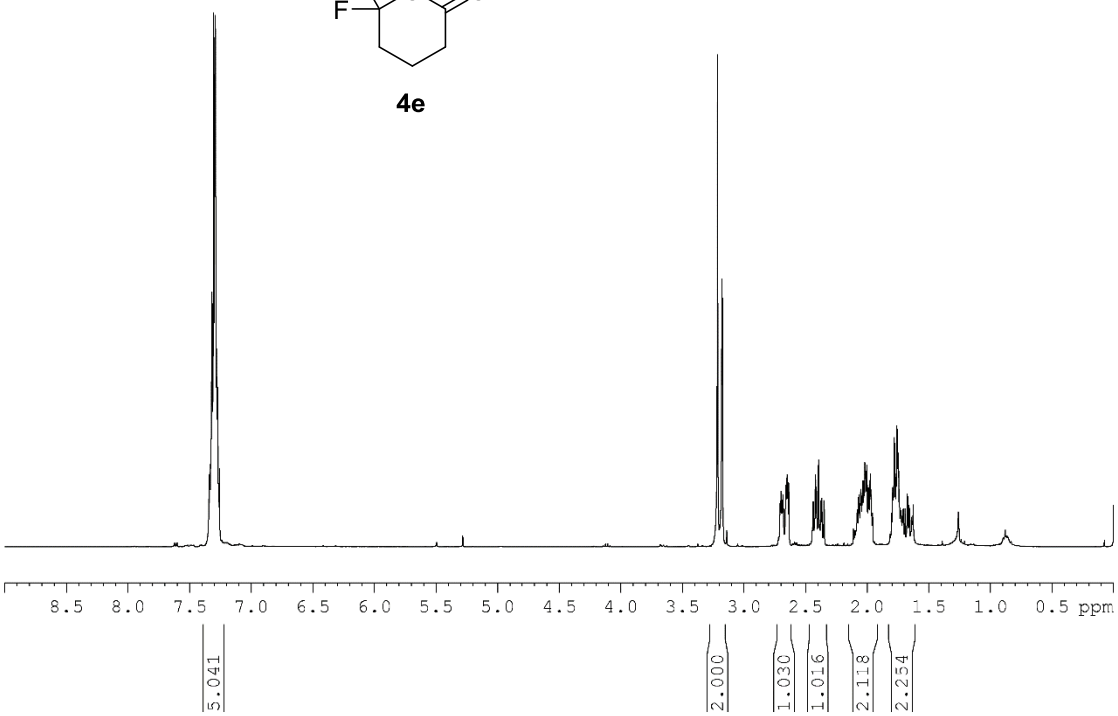


4d

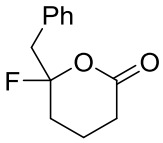
^{1}H NMR Spectrum



4e

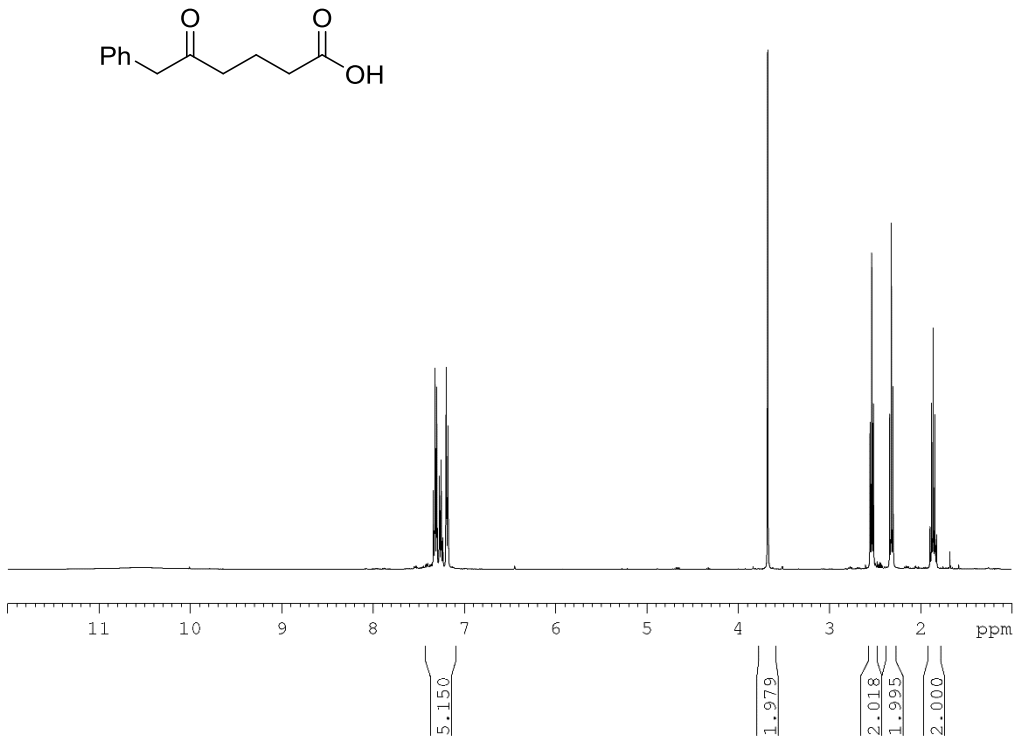


^{19}F NMR Spectrum

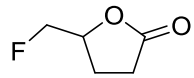


4e

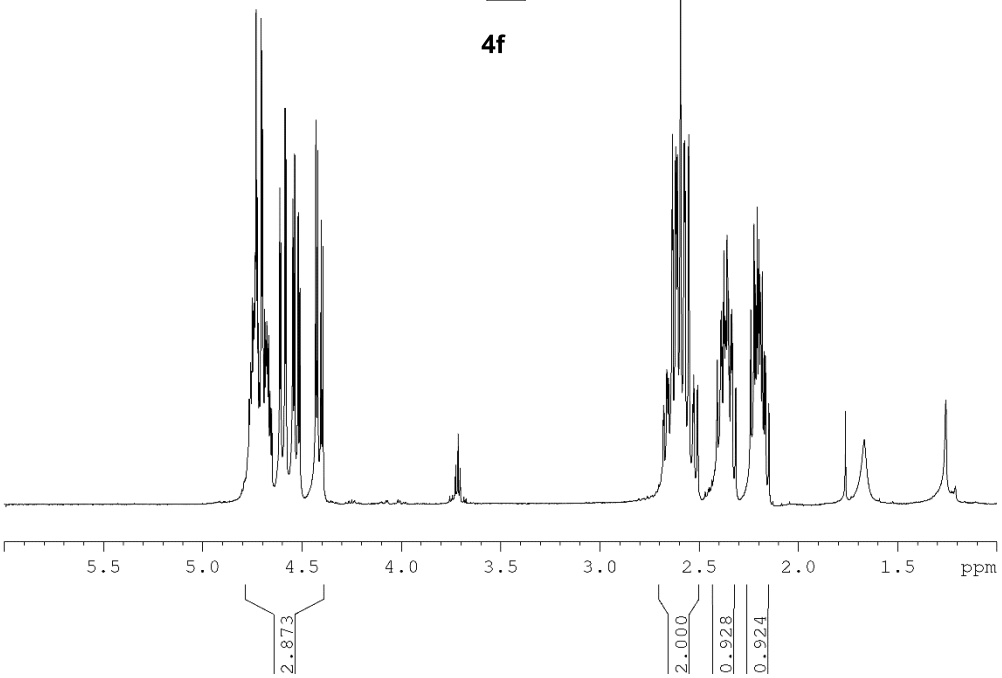
^{1}H NMR Spectrum



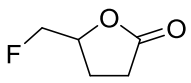
^{1}H NMR Spectrum



4f

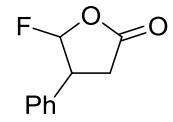


^{19}F NMR Spectrum

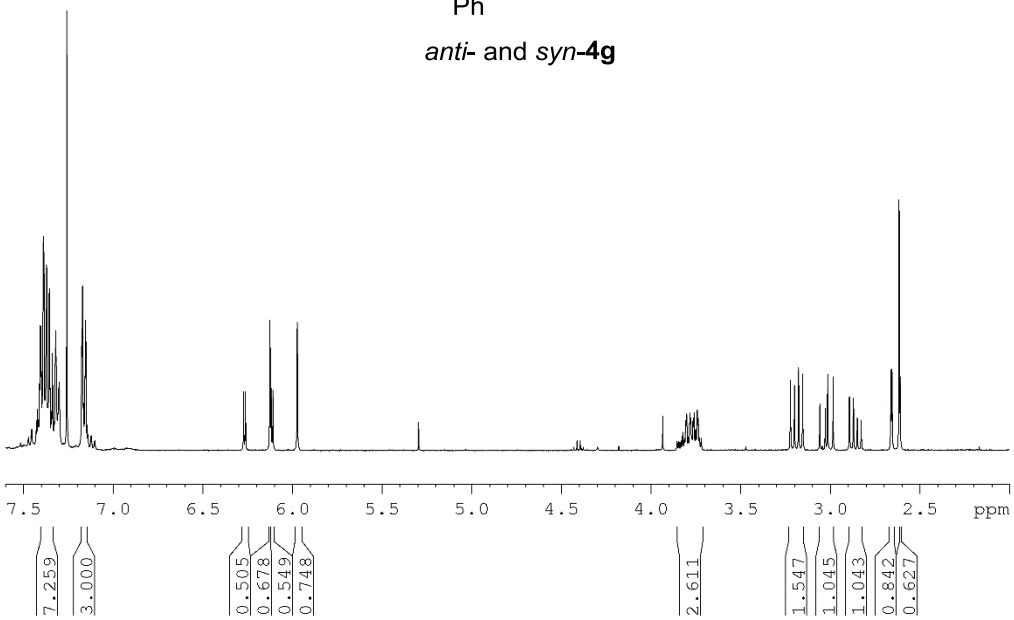


4f

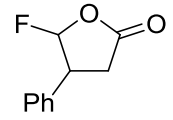
^{1}H NMR Spectrum



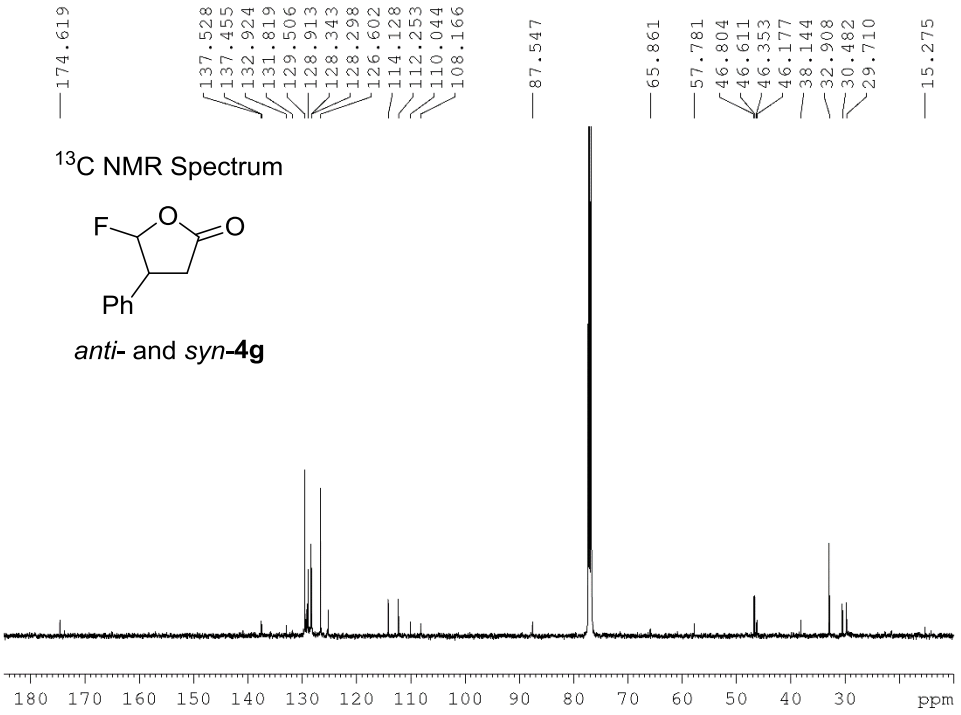
anti- and *syn*-**4g**

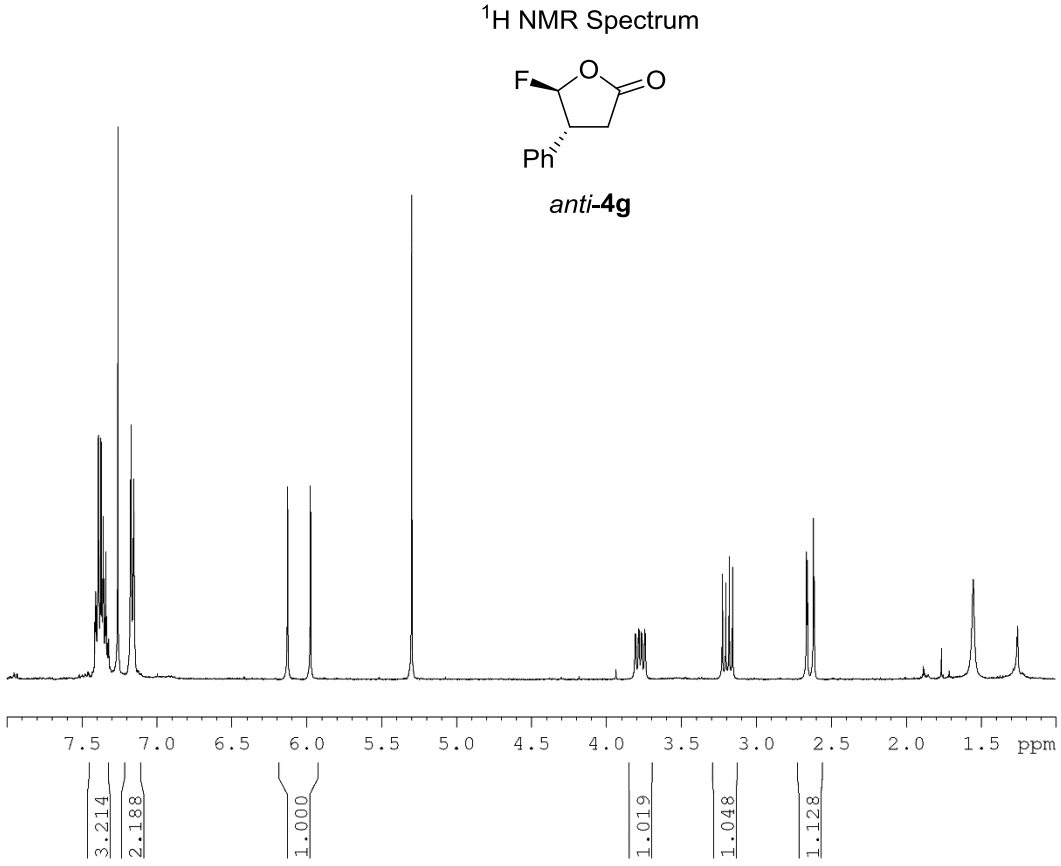


^{19}F NMR Spectrum

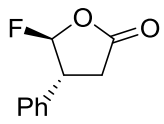


anti- and *syn*-**4g**


174.619
137.528
137.455
132.924
131.819
129.506
128.913
128.343
128.298
126.602
114.128
112.253
110.044
108.166
87.547
65.861
57.781
46.804
46.611
46.353
46.177
38.144
32.908
30.482
29.710
15.275
13C NMR Spectrum
F
O
O
Ph
anti- and syn-4g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

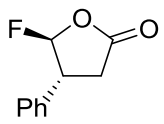

1H NMR Spectrum
F
O
O
Ph
anti-4g
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
3.214
2.188
1.000
1.019
1.048
1.128

^{19}F NMR Spectrum



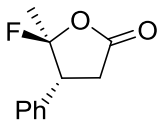
anti-**4g**

^{13}C NMR Spectrum



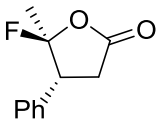
anti-**4g**

^{1}H NMR Spectrum

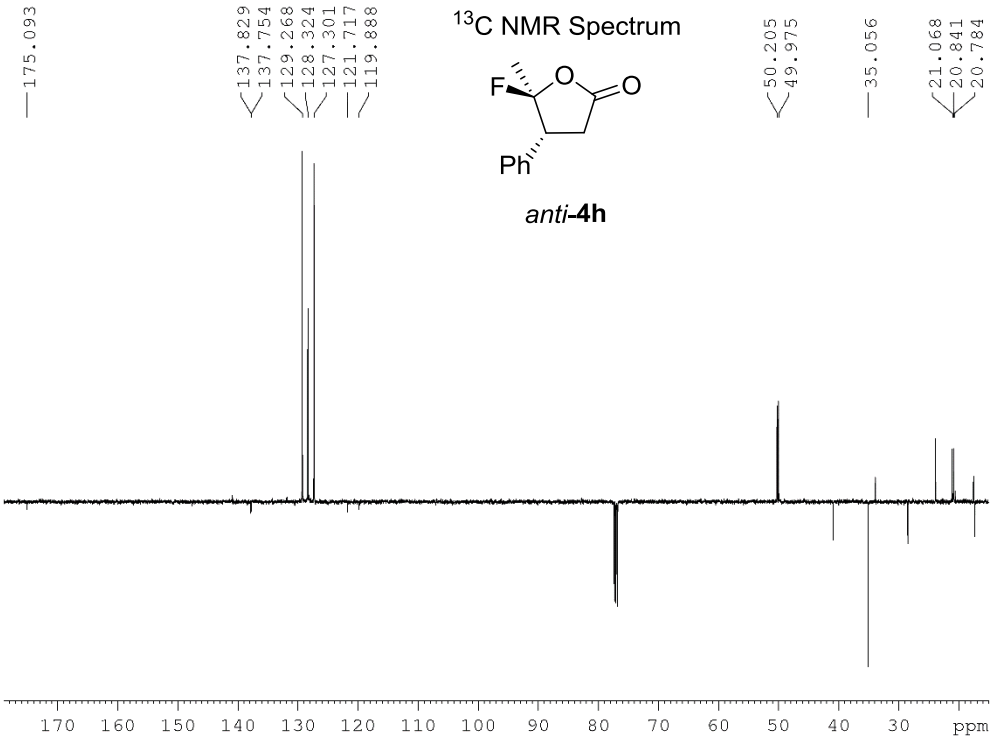


anti-**4h**

^{19}F NMR Spectrum



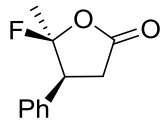
anti-**4h**



^{13}C NMR Spectrum

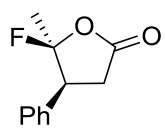
anti-**4h**

^{1}H NMR Spectrum



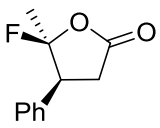
syn-**4h**

^{19}F NMR Spectrum



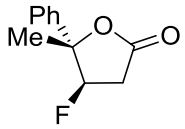
syn-**4h**

^{13}C NMR Spectrum



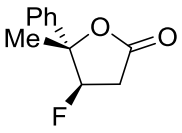
syn-**4h**

^{1}H NMR Spectrum



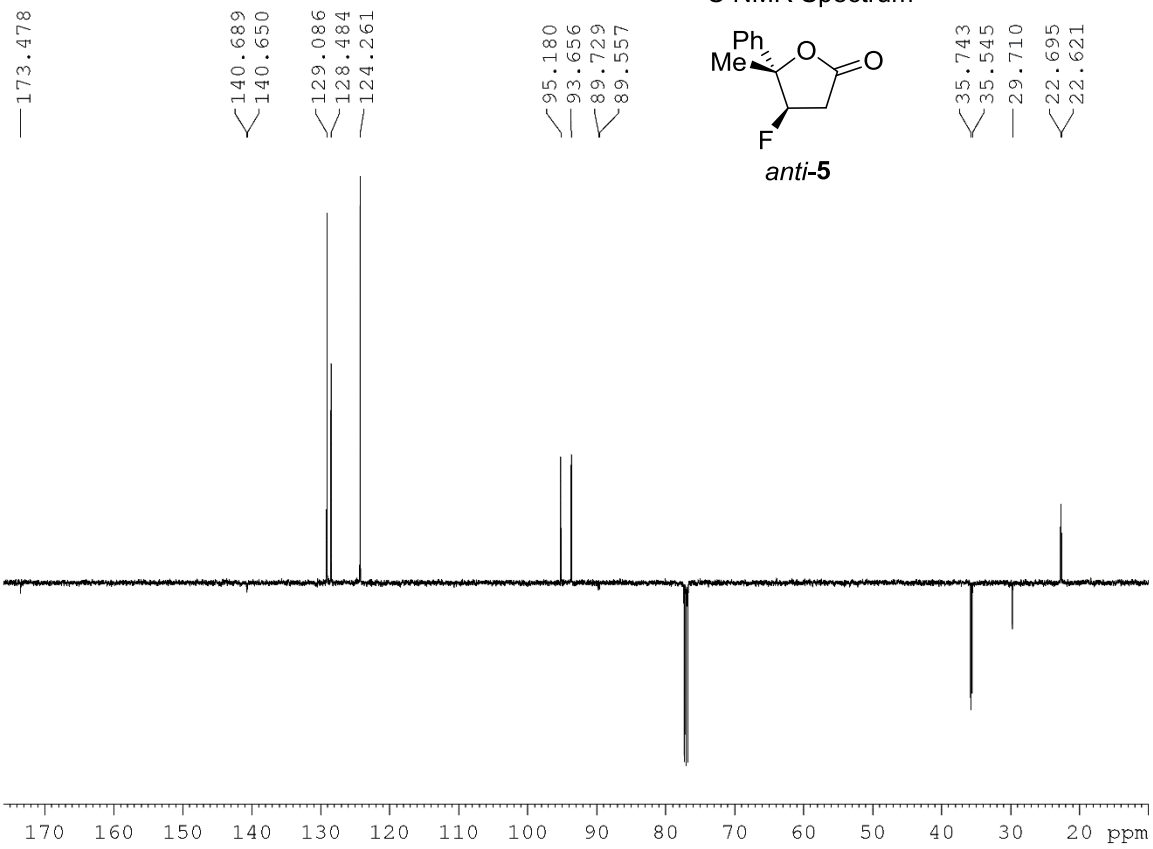
anti-**5**

^{19}F NMR Spectrum



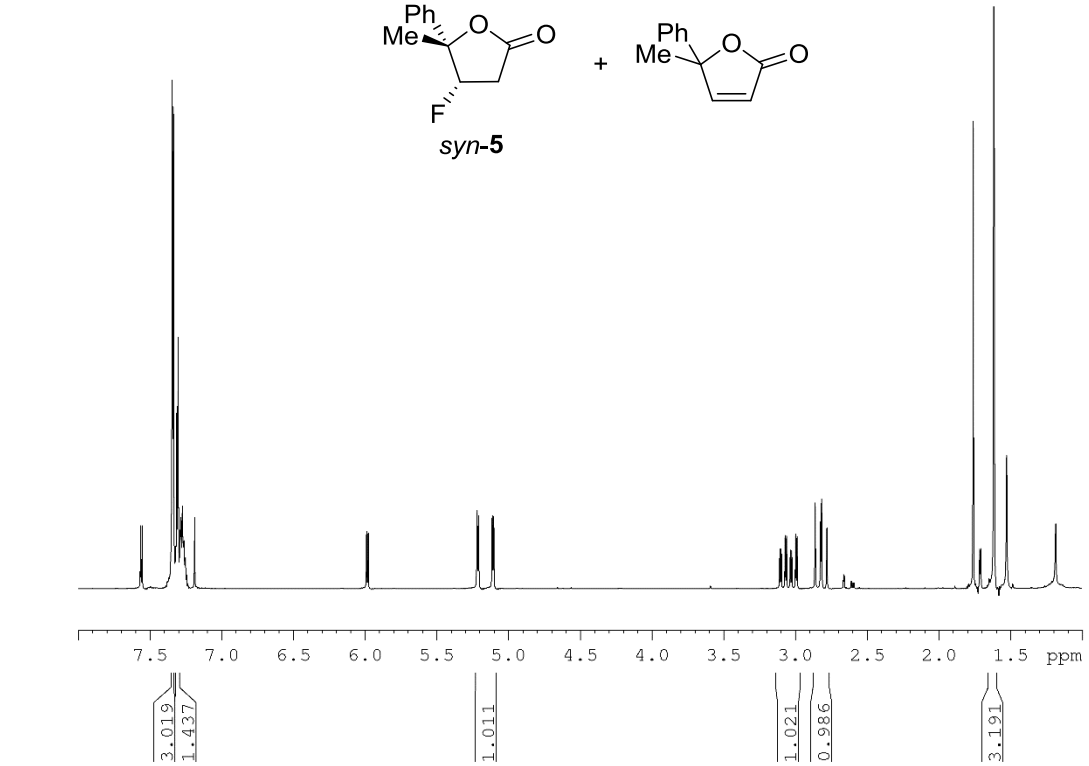
anti-**5**

^{13}C NMR Spectrum



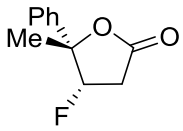
anti-**5**

^{1}H NMR Spectrum



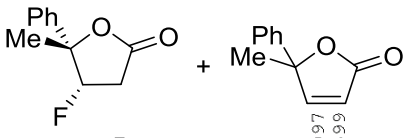
syn-**5**

^{19}F NMR Spectrum

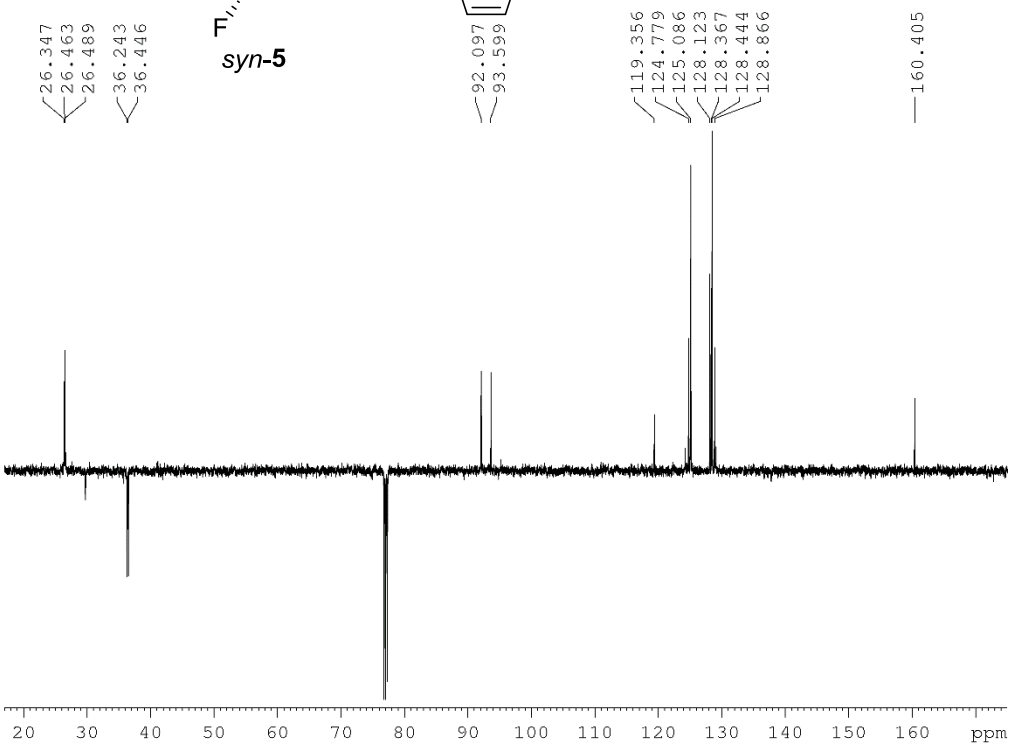


syn-**5**

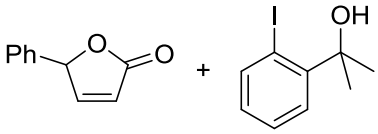
^{13}C NMR Spectrum

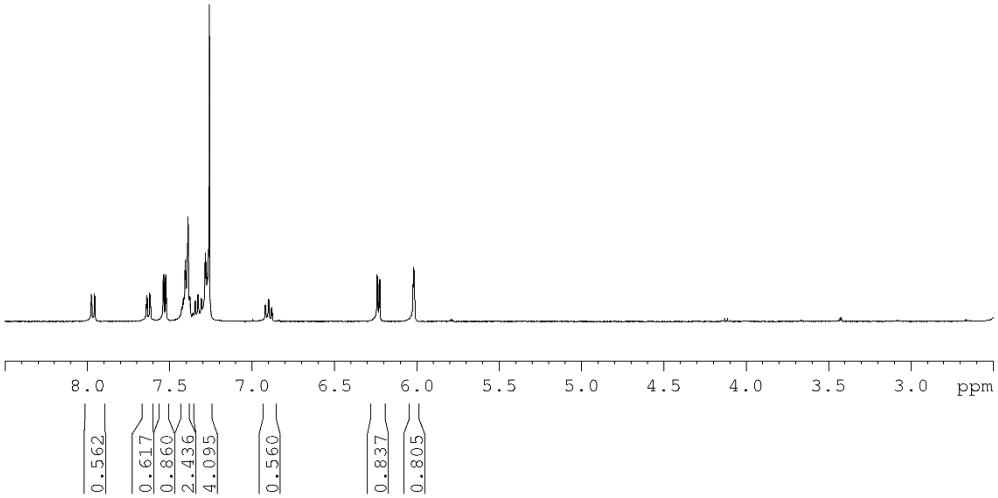


syn-**5**

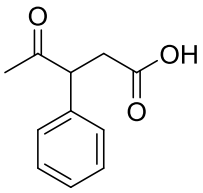


^{1}H NMR Spectrum



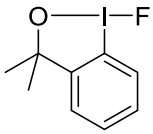


^{1}H NMR Spectrum



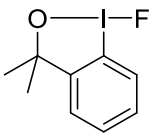
6

^{1}H NMR Spectrum



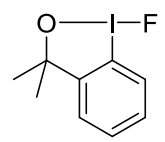
1

^{19}F NMR Spectrum



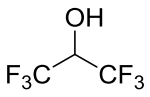
1

^{13}C NMR Spectrum

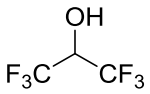


1

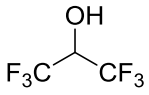
^{1}H NMR Spectrum



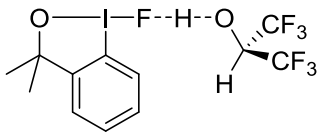
^{19}F NMR Spectrum



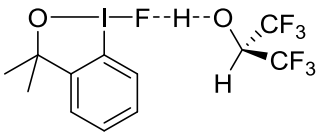
^{13}C NMR Spectrum



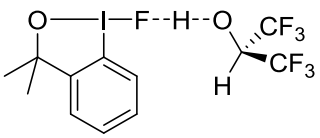
^{1}H NMR Spectrum



^{1}H{^{19}F} NMR Spectrum at 243K



^{19}F NMR Spectrum



^{13}C NMR Spectrum