SUPPORTING INFORMATION

Organic and Biomolecular Chemistry

TBD/Al_2O_3: A Novel Catalytic System for Dynamic Intermolecular Aldol Reactions that Exhibit Complex System Behaviour

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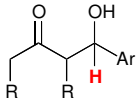
General Information

All commercially available reagents and solvents were used without further purification unless otherwise stated. Liquid aldehydes were in all cases distilled before use. Flash chromatography of reaction products was carried out using Silica 60A, particle size 230-400 micron (Merk). Analytical thin layer chromatography (TLC) was performed on DC-Alufolien Kieselgel $60F_{254}$ 0.2 mm plates (Merck) and compounds were visualised by UV fluorescence or 5% phosphomolybdic acid in methanol. ^{1}H NMR, ^{13}C NMR and ^{19}F NMRspectra were recorded on a Bruker AC-300 or a Bruker DPX-300 spectrometer, using deuterated solvents and were referenced internally to the residual solvent peak (δ_H = 7.26 ppm, δ_C = 77.36 ppm) signal,[1] or to CF_3CO_2H (δ_F = -76.55 ppm) for ^{19}F spectra. Coupling constants (*J*-Values) are given in hertzs (Hz). The DEPT 135 technique was used to assign (*C*H2) signals. Chemical shifts are reported as follows: value (number of protons, description of absorption, coupling constant(s) where applicable, and assignment). NMR spectra assignation was aided by comparison with literature values for similar compounds. In all this experimental section only clear identifiable peaks are assigned.

[1] H.E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512.

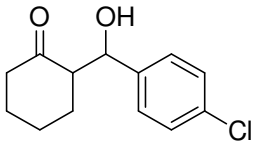
Overview of the characteristic ^{1}H NMR resonances for aldols **3**, **4**:



Aldol	δ_H (ppm) *anti*	δ_H (ppm) *syn*
3a[2]	4.76, dd, J = 8.8, 2.5 Hz	5.35, s
3b[3]	4.78, d, J = 8.8 Hz	5.38, s
3c[4]	4.77, dd, J = 8.8, 2.2 Hz	5.35, s
	δ_F (ppm): -115.4	δ_F (ppm): -116.8
3d[5]	4.84, d, J = 8.6 Hz	5.43, s
3e[1]	4.89, dd, J = 8.6, 3.1 Hz	5.48, s
3f[2]	4.76, d, J = 8.6 Hz	5.36
3g[1]	4.83, d, J = 8.6 Hz	5.43, s
4c[6]	4.68, d, J = 9.1 Hz	5.25, s
	δ_F (ppm): -115.3	δ_F (ppm): -116.4
4e[1]	4.84, d, J = 9.0 Hz	5.38, d, J = 2.7 Hz

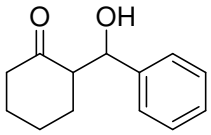
[2] A. Martínez-Castañeda, B. Poladura, H. Rodríguez-Solla, C. Concellón and V. del Amo, *Org. Lett.*, 2011, **13**, 3032-3035.
[3] J. G. Hernández and E. Juaristi, *J. Org. Chem.*, 2011, **76**, 1464-1467.
[4] R. A. Flowers II, X. Xu, C. Timmons, and G. Li, *Eur. J. Org. Chem.*, 2004, 2988.
[5] V. Maya, M. Raj and V. K. Singh, *Org. Lett.*, 2007, **9**, 2593.
[6] G. L. Puleo and A. Iuliano, *Tet. Asymmetry*, 2007, **18**, 2894-2900.

2-(Hydroxy(4-chlorophenyl)methyl)cyclohexan-1-one (3a)



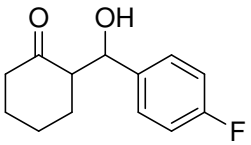
^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 7.33-7.22 (8 H, m, Ar*H*), 5.35 (1 H, s, C*H*OH), 4.76 (1 H, d, *J* = 8.8 Hz, C*H*OH), 3.97 (1 H, s, O*H*), 3.04 (1 H, s, O*H*), 2.58-2.29 (6 H, m, C*H* + CH_2), 2.12-2.06 (2 H, m, CH_2), 1.87-1.46 (8 H, m, 2 x CH_2), 1.35-1.21 (2 H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 215.6 (*C*=O), 215.0 (*C*=O), 140.3 (Ar*C*), 139.8 (Ar*C*), 133.9 (Ar*C*), 133.0 (Ar*C*), 128.9 (2 x Ar*C*H), 128.7 (2 x Ar*C*H), 128.7 (2 x Ar*C*H), 127.5 (2 x Ar*C*H), 74.5 (*C*HOH), 70.5 (*C*HOH), 57.7 (*C*H), 57.4 (*C*H), 43.0 (2 x *C*H_2), 31.1 (*C*H_2), 28.3 (*C*H_2), 28.1 (*C*H_2), 26.3 (*C*H_2), 25.2 (*C*H_2), 25.1 (*C*H_2).

2-(Hydroxy(phenyl)methyl)cyclohexan-1-one (3b)



^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 7.30-7.18 (10 H, m, Ar*H*), 5.32 (1 H, s, C*H*OH), 4.72 (1 H, d, *J* = 8.7 Hz, C*H*OH), 3.91 (1 H, s, O*H*), 3.02 (1 H, s, O*H*), 2.60-2.23 (6 H, m, C*H* + CH_2), 2.04-1.98 (2 H, m, CH_2), 1.80-1.41 (8 H, m, 4 x CH_2), 1.30-1.16 (2 H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 215.8 (*C*=O), 215.0 (*C*=O), 141.8 (Ar*C*), 141.3 (Ar*C*), 128.6 (2 x Ar*C*H), 128.4 (2 x Ar*C*H), 128.2 (Ar*C*H), 127.3 (2 x Ar*C*H), 127.2 (Ar*C*H), 126.0 (2 x Ar*C*H), 75.0 (*C*HOH), 70.9 (*C*HOH), 57.7 (*C*H), 57.5 (*C*H), 42.9 (2 x *C*H_2), 31.1 (*C*H_2), 28.2 (*C*H_2), 28.1 (*C*H_2), 26.3 (*C*H_2), 25.1 (*C*H_2), 25.0 (*C*H_2).

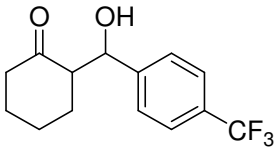
2-(Hydroxy(4-fluorophenyl)methyl)cyclohexan-1-one (3c)



^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 7.31-7.24 (4 H, m, Ar*H*), 7.10-7.00 (4 H, m, Ar*H*), 5.34 (1 H, s, C*H*OH), 4.77 (1 H, d, *J* = 8.7 Hz, C*H*OH), 4.00 (1 H, s, O*H*), 3.08 (1 H, s, O*H*), 2.61-2.29 (6 H, m, 2 x C*H* + 2 x CH_2), 2.12-2.05 (2 H, m, CH_2), 1.81-1.50 (8 H, m, 4 x CH_2), 1.34-1.20 (2 H, m, CH_2); ^{13}C NMR (75

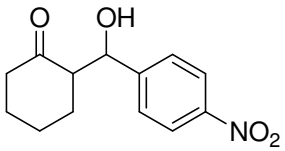
MHz, $CDCl_3$): δ = (both diastereoisomers) 215.7 (*C*=O), 215.0 (*C*=O), 164.3 (d, $^1J_{C\text{-}F}$ = 246 Hz, Ar*C*F), 163.8 (d, $^1J_{C\text{-}F}$ = 245 Hz, Ar*C*F), 137.5 (d, $^4J_{C\text{-}F}$ = 3.2 Hz, Ar*C*), 137.1 (d, $^4J_{C\text{-}F}$ = 3.2 Hz, Ar*C*), 128.9 (d, $^3J_{C\text{-}F}$ = 8.1 Hz, 2 x Ar*C*H), 127.7 (d, $^3J_{C\text{-}F}$ = 7.9 Hz, 2 xAr*C*H), 115.5 (d, $^2J_{C\text{-}F}$ = 21.4 Hz, 2 x Ar*C*H), 115.3 (d, $^2J_{C\text{-}F}$ = 21.2, 2 x Ar*C*H), 74.4 (*C*HOH), 70.5 (*C*HOH), 57.8 (*C*H), 57.5 (*C*H), 43.0 (2 x *C*H_2), 31.1 (*C*H_2), 28.2 (*C*H_2), 28.0 (*C*H_2), 26.3 (*C*H_2), 25.2 (*C*H_2), 25.0 (*C*H_2). ^{19}F NMR (282 MHz, $CDCl_3$): δ = (both diastereoisomers) -115.4 (*anti*), -116.8 (*syn*).

2-(Hydroxy(4-(trifluoromethyl)phenyl)methyl)cyclohexan-1-one (3d)



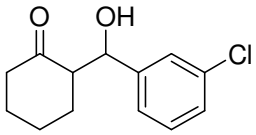
White solid. Purified by flash chromatography (Hex/EtOAc, 3:1).
^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 7.61-7.57 (4 H, m, Ar*H*), 7.45-7.41 (4 H, m, Ar*H*), 5.43 (1 H, s, C*H*OH), 4.84 (1 H, d, *J* = 8.6 Hz, C*H*OH), 4.05 (1 H, s, O*H*), 3.16 (1 H, s, O*H*), 2.63-2.30 (6 H, m, C*H* + CH_2), 2.13-2.05 (2 H, m, CH_2), 1.82-1.52 (8 H, m, 2 x CH_2), 1.40-1.25 (2 H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 215.4 (*C*=O), 214.6 (*C*=O), 146.0 (Ar*C*), 145.3 (Ar*C*), 130.4 (q, $^2J_{C\text{-}F}$ = 30.2 Hz, 2 x Ar*C*), 127.7 (2 x Ar*C*H), 126.4 (2 x Ar*C*H), 125.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, 2 x Ar*C*H), 125.4 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, 2 x Ar*C*H), 74.6 (*C*HOH), 70.5 (*C*HOH), 57.6 (*C*H), 57.3 (*C*H), 43.0 (2 x *C*H_2), 31.1 (*C*H_2), 28.2 (*C*H_2), 28.0 (*C*H_2), 26.2 (*C*H_2), 25.1 (*C*H_2), 25.0 (*C*H_2).

2-(Hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (3e)



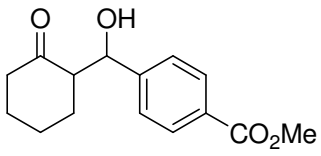
^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 8.20 (4 H, dd , *J* = 8.0, 1.3 Hz, Ar*H*), 7.52-7.46 (4 H, m, Ar*H*), 5.48 (1 H, s, C*H*OH), 4.90 (1 H, d, *J* = 8.4 Hz, C*H*OH), 4.07 (1 H, s, O*H*), 3.18 (1 H, s, O*H*), 2.66-2.30 (6 H, m, 2 x C*H* + 2 x CH_2), 2.16-2.08 (2 H, m, CH_2), 1.88-1.43 (8 H, m, CH_2), 0.90-0.83 (2 H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 215.1 (*C*=O), 214.4 (*C*=O), 149.4 (Ar*C*), 148.7 (Ar*C*), 147.9 (Ar*C*), 147.4 (Ar*C*), 128.2 (2 x Ar*C*H), 126.9 (2 x Ar*C*H), 123.9 (2 x Ar*C*H), 123.8 (2 x Ar*C*H), 74.3 (*C*HOH), 70.4 (*C*HOH), 57.5 (*C*H), 57.1 (*C*H), 43.0 (*C*H_2), 42.9 (*C*H_2), 31.1 (*C*H_2), 28.2 (*C*H_2), 28.0 (*C*H_2), 26.2 (*C*H_2), 25.1 (*C*H_2), 25.0 (*C*H_2).

2-(Hydroxy(3-chlorophenyl)methyl)cyclohexan-1-one (3f)



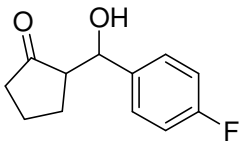
White solid. Purified by flash chromatography (Hex/EtOAc, 3:1).
^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 7.34-7.16 (8 H, m, Ar*H*), 5.36 (1 H, s, C*H*OH), 4.76 (1 H, d, *J* = 8.6 Hz, C*H*OH), 4.03 (1 H, s, O*H*), 3.14 (1 H, d, *J* = 2.2 Hz, O*H*), 2.62-2.30 (m, 6 H, C*H* + CH_2), 2.12-2.04 (2 H, m, CH_2), 1.88-1.49 (8 H, m, CH_2), 1.37-1.23 (2 H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 215.4 (*C*=O), 214.7 (*C*=O), 144.0 (Ar*C*), 143.4 (Ar*C*), 134.6 (Ar*C*), 134.5 (Ar*C*), 129.9 (Ar*C*H), 129.7 (Ar*C*H), 128.3 (Ar*C*H), 127.4 (Ar*C*H), 127.4 (Ar*C*H), 126.3 (Ar*C*H), 125.6 (Ar*C*H), 124.2 (Ar*C*H), 74.5 (*C*HOH), 70.3 (*C*HOH), 57.5 (*C*H), 57.3 (*C*H), 42.9 (CH_2), 42.9 (CH_2), 31.1 (CH_2), 28.2 (CH_2), 28.0 (CH_2), 26.2 (CH_2), 25.1 (CH_2), 25.0 (CH_2).

2-(Hydroxy(4-methoxycarbonyl)phenyl)methyl)cyclohexan-1-one (3g)



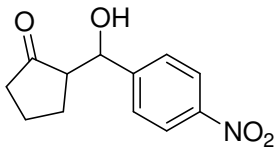
^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 8.04-7.99 (4 H, m, Ar*H*), 7.40-7.36 (4 H, m, Ar*H*), 5.43 (1 H, d, *J* = 2.0 Hz, C*H*OH), 4.84 (1 H, d, *J* = 8.5 Hz, C*H*OH), 3.90 (6 H, s, 2 x CO_2CH_3), 2.64-2.30 (6 H, m, 2 x C*H* + 2 x CH_2), 2.12-2.03 (2 H, m, CH_2), 1.85-1.47 (8 H, m, 4 x CH_2), 1.37-1.22 (2 H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 215.4 (*C*=O), 214.7 (*C*=O), 167.3 (CO_2Me), 167.2 (CO_2Me), 147.1 (Ar*C*), 146.4 (Ar*C*), 130.4 (Ar*C*), 130.0 (2 x Ar*C*H), 129.8 (2 x Ar*C*H), 129.2 (Ar*C*), 127.4 (2 x Ar*C*H), 126.1 (2 x Ar*C*H), 74.7 (*C*HOH), 70.7 (*C*HOH), 57.6 (*C*H), 57.3 (*C*H), 52.4 (CO_2CH_3), 52.4 (CO_2CH_3), 43.0 (2 x CH_2), 31.1 (CH_2), 28.2 (CH_2), 28.0 (CH_2), 26.2 (CH_2), 25.1 (CH_2), 25.0 (CH_2).

2-((4-fluorophenyl)(hydroxy)methyl)cyclopentanone (4c)



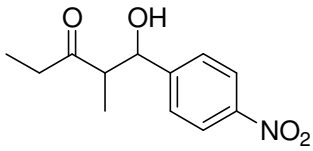
^{1}H NMR (300 MHz, $CDCl_3$): δ = (both diastereoisomers) 7.34-7.25 (4 H, m, Ar*H*), 7.06-6.97 (4 H, m, Ar*H*), 5.26 (1 H, d, *J* = 1.8 Hz C*H*OH), 4.69 (1 H, d, *J* = 9.2 Hz, C*H*OH), 4.59 (1 H, s, O*H*), 2.66 (1 H, s, O*H*), 2.48-2.23(4 H, m, 2 x CH_2), 2.20-1.90 (4 H, m, 2 x CH_2), 1.84-1.41 (6 H, m, 2 x C*H* + 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 223.2 (*C*=O), 220.7 (*C*=O), 162.7 (d, $^{1}J_{C\text{-}F}$ = 244 Hz, Ar*C*F), 162.3 (d, $^{1}J_{C\text{-}F}$ = 244 Hz, Ar*C*F), 138.8 (d, $^{4}J_{C\text{-}F}$ = 2.6 Hz, Ar*C*), 137.6 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz, Ar*C*), 128.5 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz, Ar*C*H), 127.5 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz, 2 x Ar*C*H), 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz, Ar*C*H), 115.5 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz, 2 x Ar*C*H), 74.9 (*C*HOH), 71.2 (*C*HOH), 56.5 (*C*H), 55.7 (*C*H), 39.5 (*C*H_2), 39.0 (*C*H_2), 29.5 (*C*H_2), 27.2 (*C*H_2), 23.0 (*C*H_2), 20.8 (*C*H_2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = (both diastereoisomers) -115.3 (*anti*), -116.4 (*syn*).

2-(hydroxy(4-nitrophenyl)methyl)cyclopentanone (4e)



^{1}H NMR (300MHz, $CDCl_3$): δ = (both diastereoisomers) 8.20 (4 H, dd , *J* = 8.7, 1.7 Hz, Ar*H*), 7.54-7.50 (4 H, m, Ar*H*), 5.41 (1 H, d, *J* = 2.1 Hz, C*H*OH), 4.84 (1 H, d, *J* = 9.1 Hz, C*H*OH), 2.51-2.29 (4 H, m, 2 x CH_2), 2.26-1.85 (6 H, m, 2 x C*H* + 2 x CH_2), 1.74-1.50 (4 H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (both diastereoisomers) 222.5 (*C*=O), 220.0 (*C*=O), 150.5 (2 x Ar*C*), 149.0 (Ar*C*), 147.5 (Ar*C*), 127.7 (2 x Ar*C*H), 126.7 (2 x Ar*C*H), 124.0 (2 x Ar*C*H), 123.9 (2 x Ar*C*H), 74.7 (*C*HOH), 70.8 (*C*HOH), 56.4 (*C*H), 55.4 (*C*H), 39.2 (*C*H_2), 38.9 (*C*H_2), 27.1 (*C*H_2), 22.7 (*C*H_2), 20.7 (*C*H_2), 20.6 (*C*H_2).

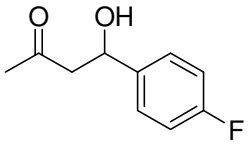
1-hydroxy-2-methyl-1-(4-nitrophenyl)pentan-3-one (5e)



Yellow solid. Purified by flash chromatography (Hex/EtOAc, 3:1).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = (both diastereoisomers) 8.20 (4 H, d, *J* = 8.7 Hz, ArC*H*), 7.51 (4 H, d, *J* = 8.4 Hz, ArC*H*), 5.22 (1 H, s, C*H*OH), 4.87 (1 H, dd, *J* = 7.5, 4.2 Hz, C*H*OH), 3.59 (1 H, s, O*H*), 3.36 (1 H, d, *J* = 5.2 Hz, O*H*), 2.91 (1 H, quintet, *J* = 7.2 Hz, C*H*), 2.83 (1 H, dq, *J* = 7.3, 2.9 Hz, C*H*), 2.67-2.31 (4 H, m, 2 x CH_2), 1.08-0.99 (12 H, m, 4 x CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = (both diastereoisomers) 216.5 (*C*=O), 215.9 (*C*=O), 149.9 (Ar*C*), 149.4 (Ar*C*), 147.8 (Ar*C*), 147.5 (Ar*C*), 127.7 (Ar*C*H), 127.1 (Ar*C*H), 124.0 (Ar*C*H), 123.8 (Ar*C*H), 75.9 (*C*HOH), 72.3 (*C*HOH), 52.6 (*C*H), 51.7 (*C*H), 36.7 (*C*H_2), 35.5 (*C*H_2), 14.8 (*C*H_3), 10.2 (*C*H_3), 7.9 (*C*H_3), 7.7 (*C*H_3).

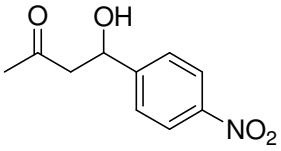
4-(4-Fluorophenyl)-4-hydroxybutan-2-one (6c)[7]



White solid. Purified by flash chromatography (Hex/EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (2H, dd, *J* = 8.5, 5.7 Hz, Ar*H*), 7.06-7.00 (2H, m, Ar*H*), 5.13 (1H, dd, *J* = 8.1, 4.2 Hz, C*H*OH), 2.88-2.77 (2H, m, CH_2), 2.20 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.4 (*C*=O), 162.5 (d, $^1J_{C\text{-}F}$ = 244 Hz, Ar*C*F), 138.8 (d, $^4J_{C\text{-}F}$ = 3.2 Hz, Ar*C*), 127.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, 2 x Ar*C*H), 115.7 (d, $^2J_{C\text{-}F}$ = 21.3 Hz, 2 x Ar*C*H), 69.5 (*C*HOH), 52.2 (*C*H_2), 31.1 (*C*H_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = -114.9.

4-Hydroxy-4-(4-nitrophenyl)butan-2-one (6e)[2]



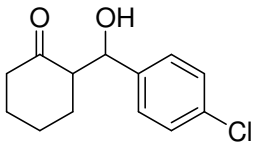
Orange solid. Purified by flash chromatography (Hex/EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21-8.17 (2H, m, Ar*H*), 7.55-7.51 (2H, m, Ar*H*), 5.26 (1H, dd, *J* = 7.3, 5.2 Hz, C*H*OH), 3.54 (1H, s, CHO*H*), 2.86-2.83 (2H, m, CH_2), 2.21 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.8 (*C*=O), 150.3 (Ar*C*), 147.7 (Ar*C*), 126.7 (2 x Ar*C*H), 124.1 (2 x Ar*C*H), 69.2 (*C*HOH), 51.8 (*C*H_2), 31.0 (*C*H_3).

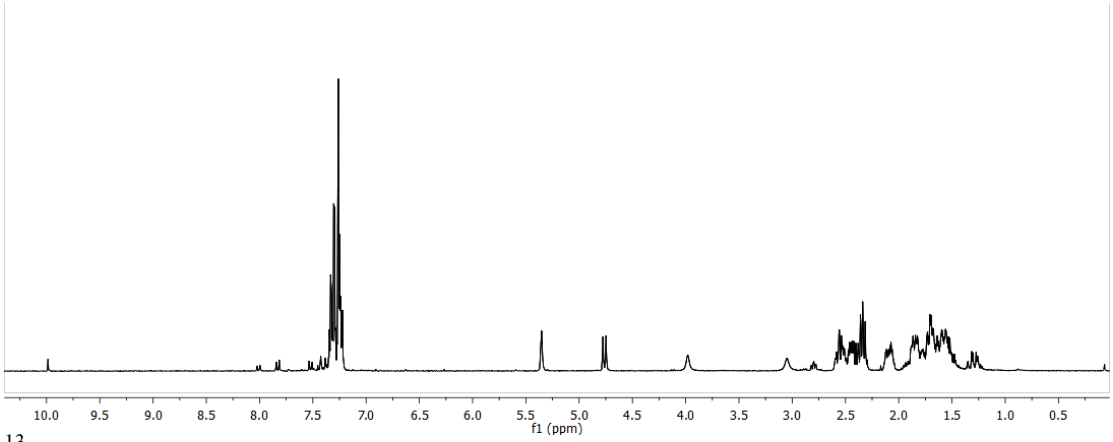
[7] R. Fernández-López, J. Kofoed, M. Manchuqueiro and T. Darbre, *Eur. J. Org. Chem.*, 2005, 5268.

Collection of ^{1}H and ^{13}C NMR spectra for aldols 3a-g, 4c, 4e, 5e, 6c and 6e:

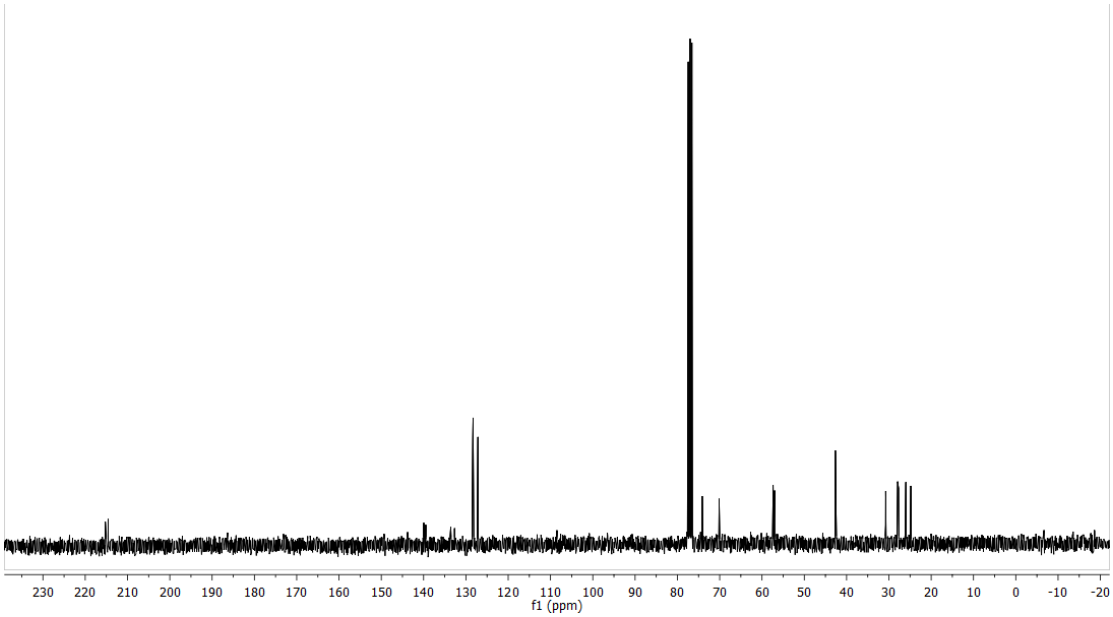
Crude 2-(Hydroxy(4-chlorophenyl)methyl)cyclohexan-1-one (3a) prepared as in Table 3.



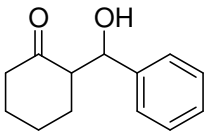
^{1}H



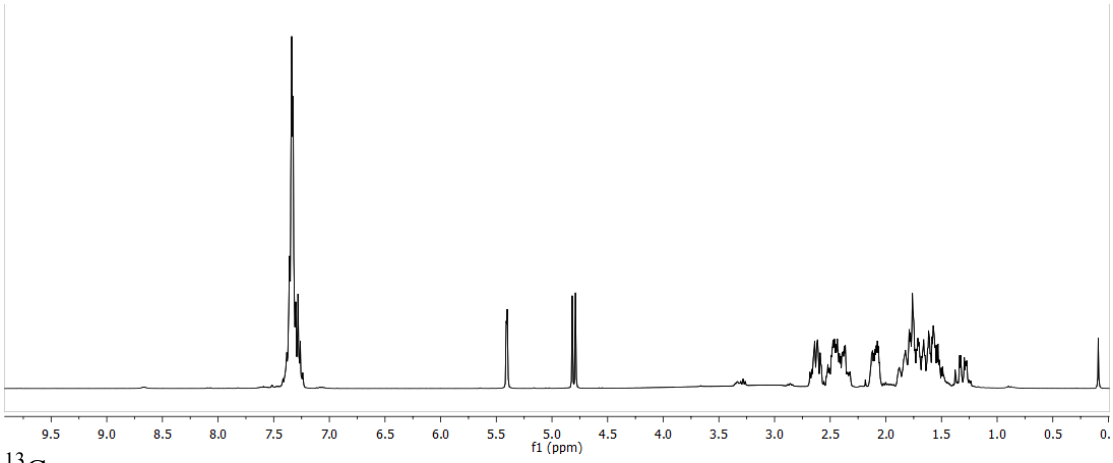
^{13}C



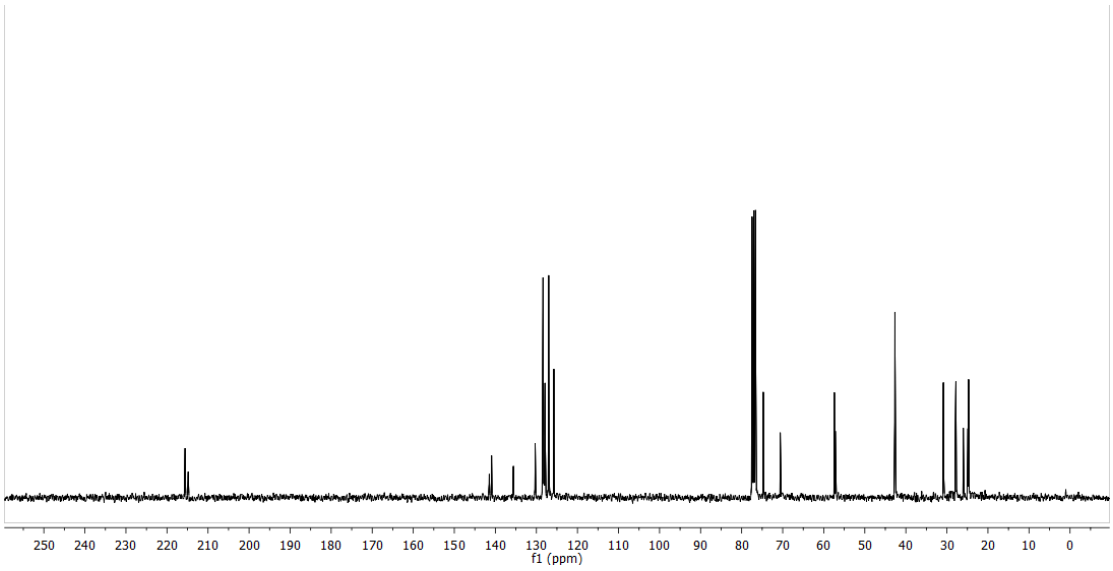
Crude 2-(Hydroxy(phenyl)methyl)cyclohexan-1-one (3b), prepared as in Table 3.



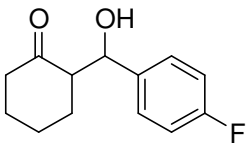
^{1}H



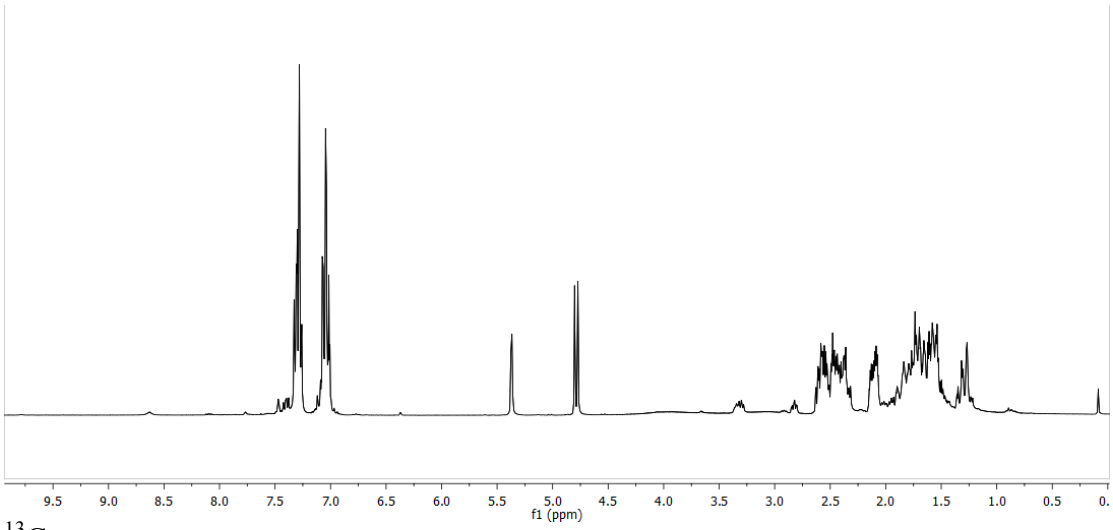
^{13}C



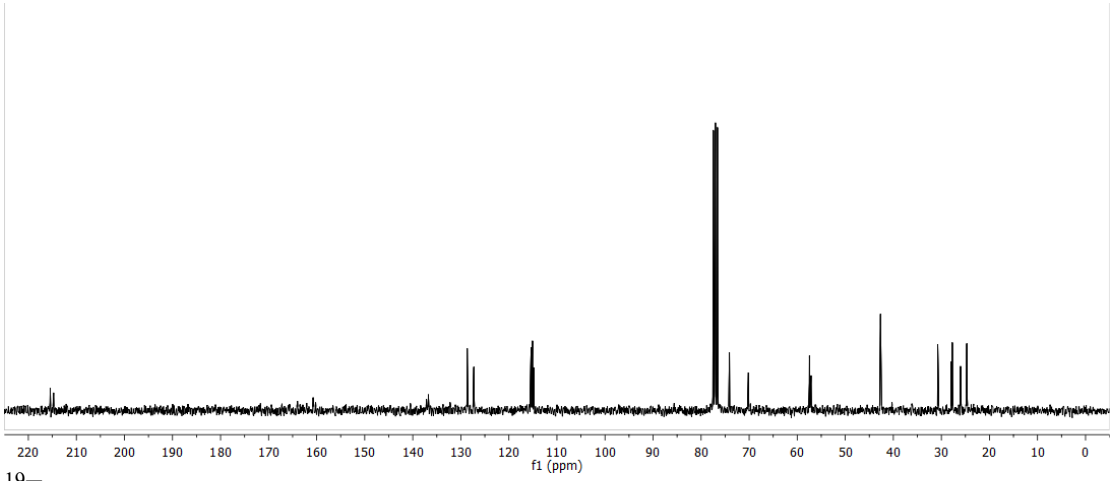
Crude 2-(Hydroxy(4-fluorophenyl)methyl)cyclohexan-1-one (3c), prepared as in Table 3.



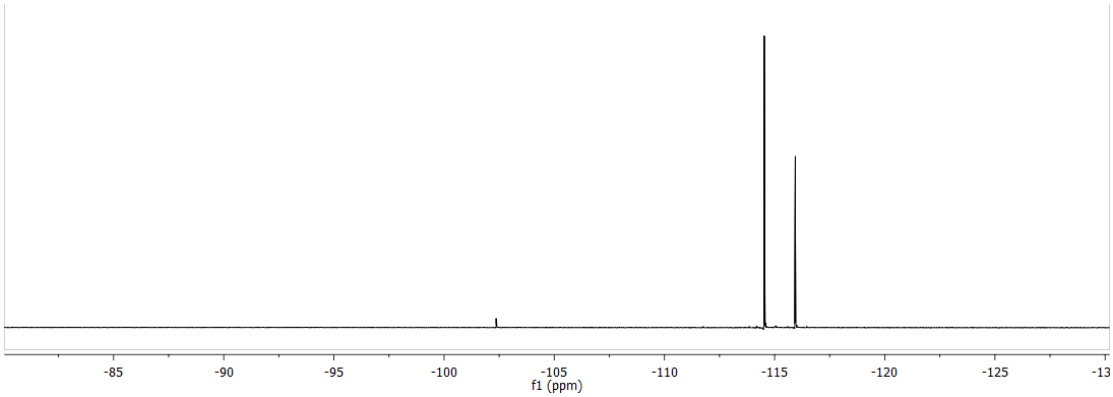
^{1}H



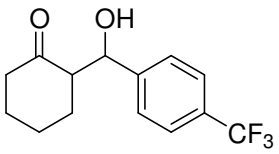
^{13}C



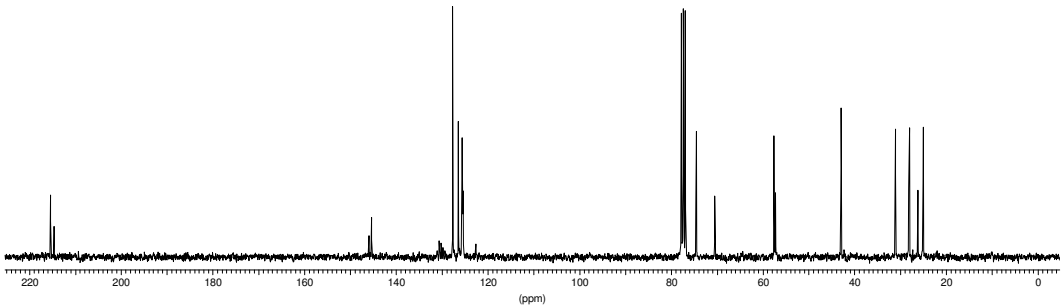
^{19}F



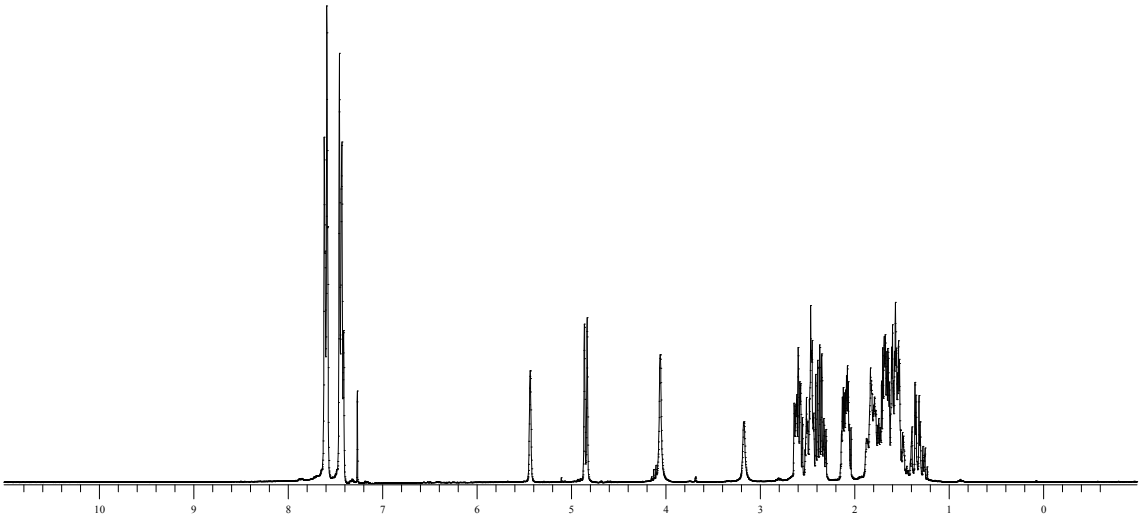
2-(Hydroxy(4-(trifluoromethyl)phenyl)methyl)cyclohexan-1-one (3d), prepared as in Table 2.



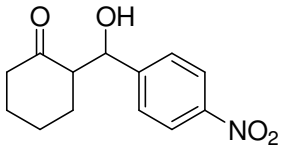
^{1}H



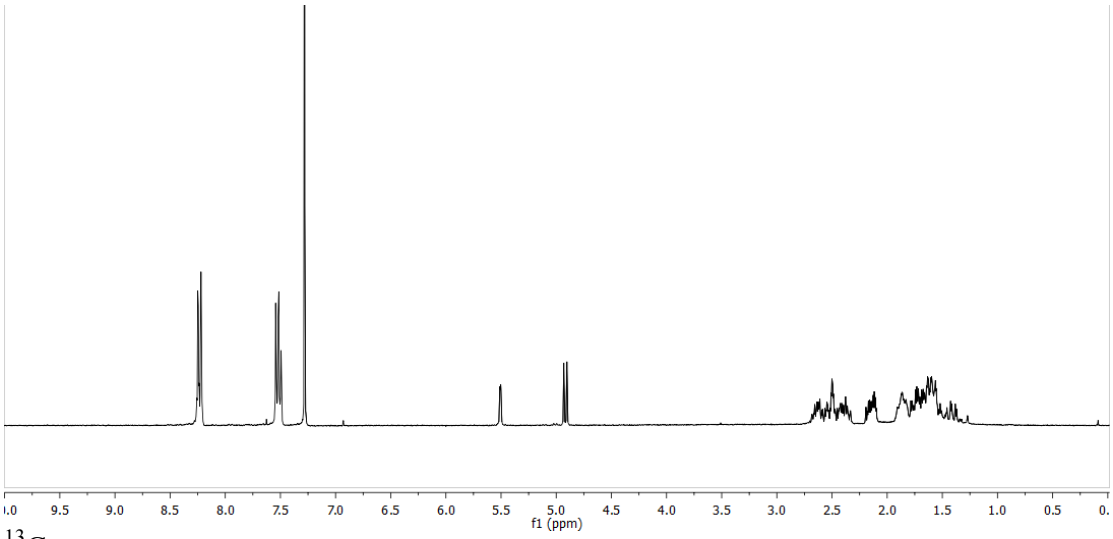
^{13}C



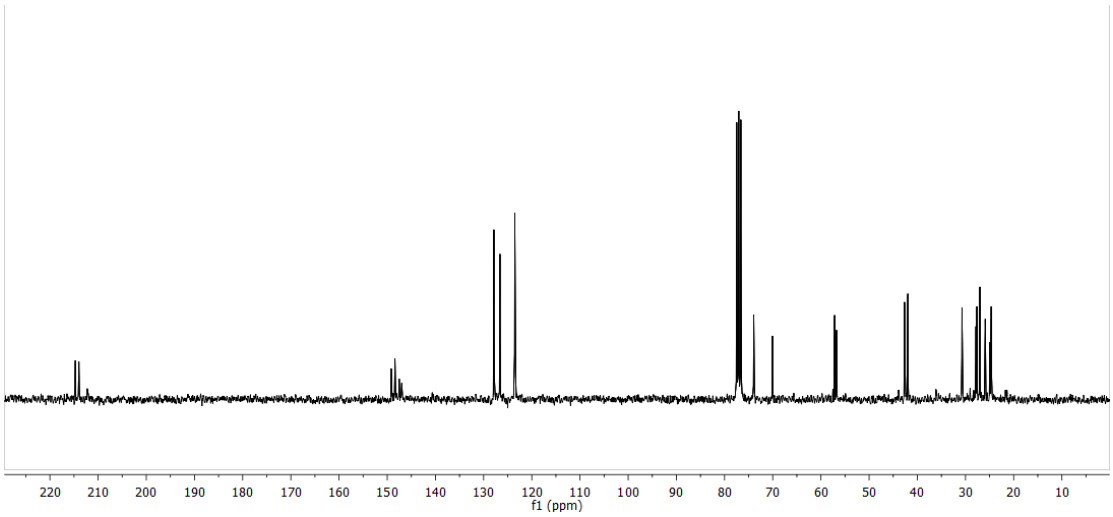
Crude 2-(Hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (3e), prepared as in Table 3.



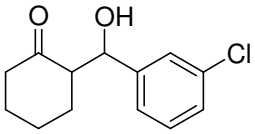
^{1}H



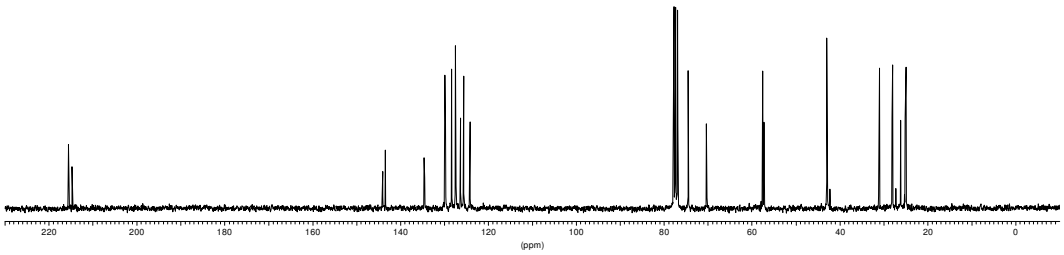
^{13}C



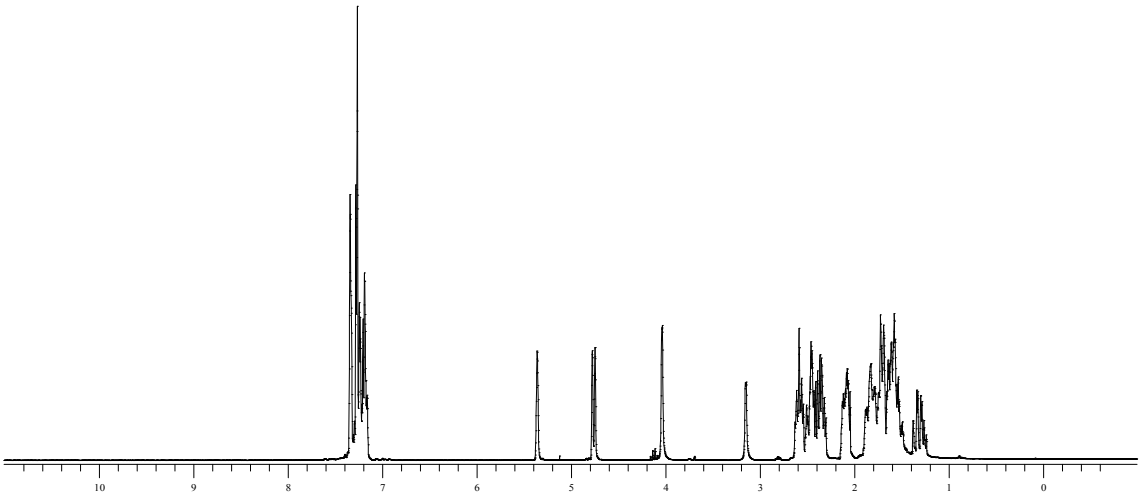
Crude 2-(Hydroxy(3-chlorophenyl)methyl)cyclohexan-1-one (3f), prepared as in Table 3.



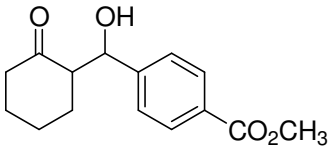
^{1}H



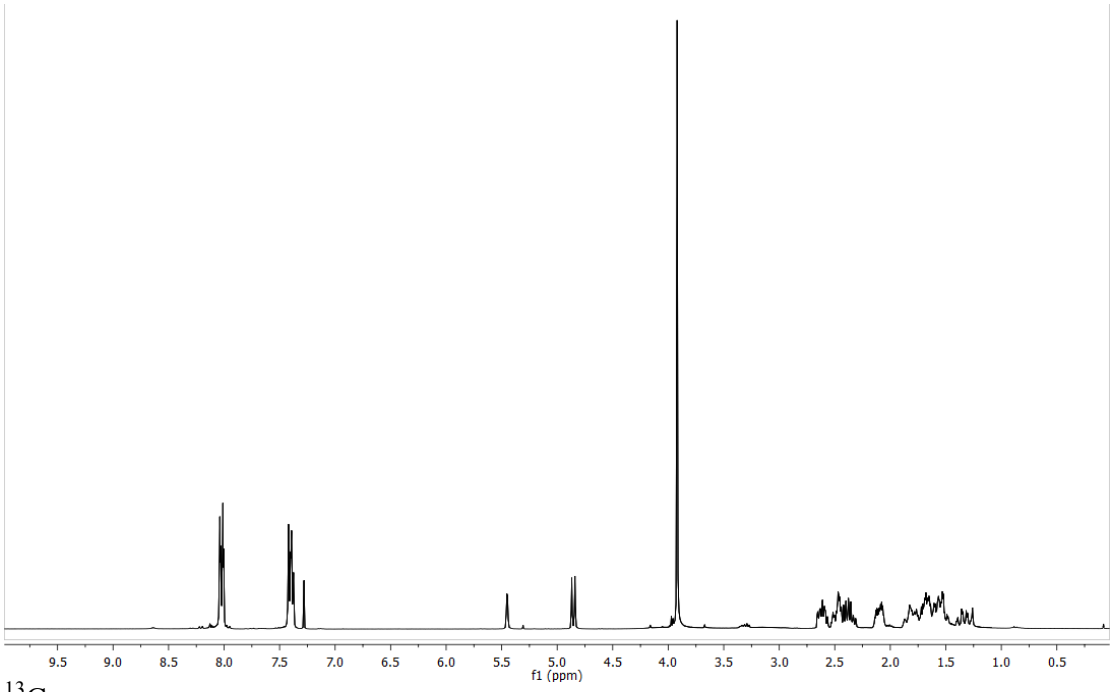
^{13}C



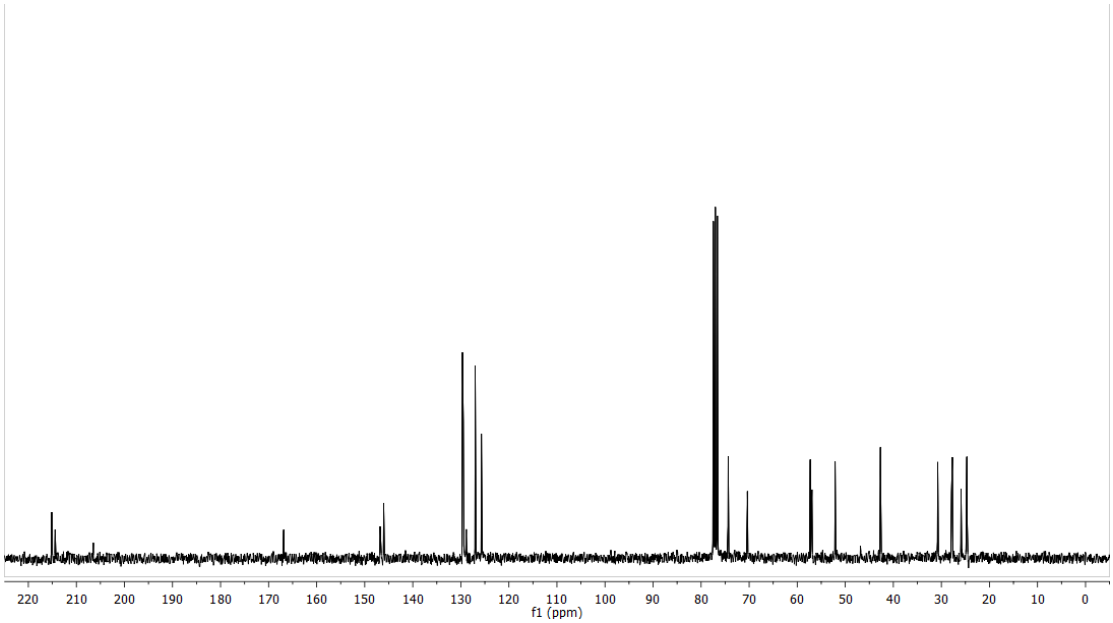
Crude 2-(Hydroxy(4-methoxycarbonyl)phenyl)methyl)cyclohexan-1-one (3g), prepared as in Table 3.



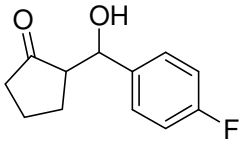
^{1}H



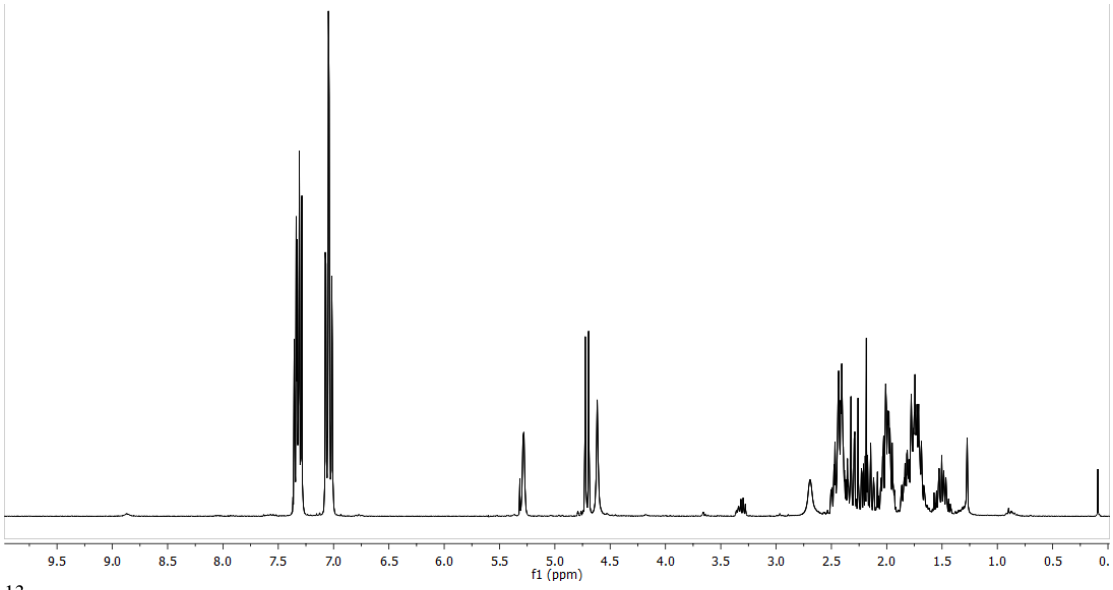
^{13}C



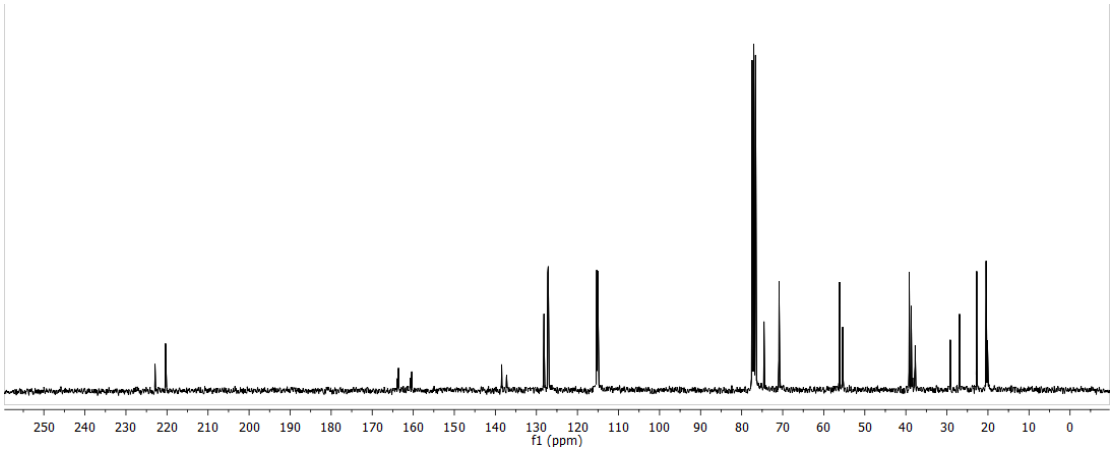
Crude 2-((4-fluorophenyl)(hydroxy)methyl)cyclopentanone (4c), prepared as in Table 3.



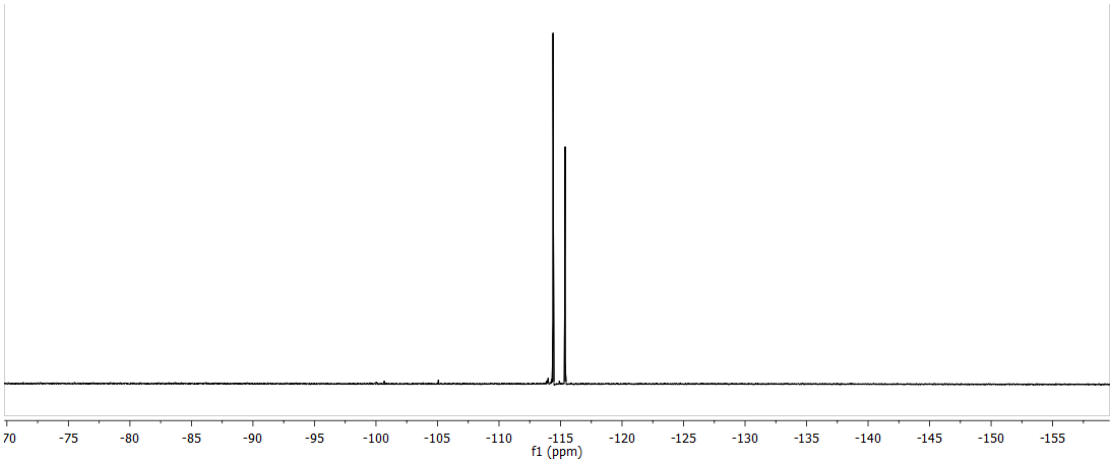
^{1}H



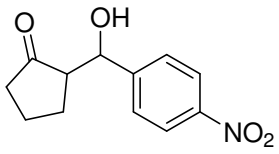
^{13}C



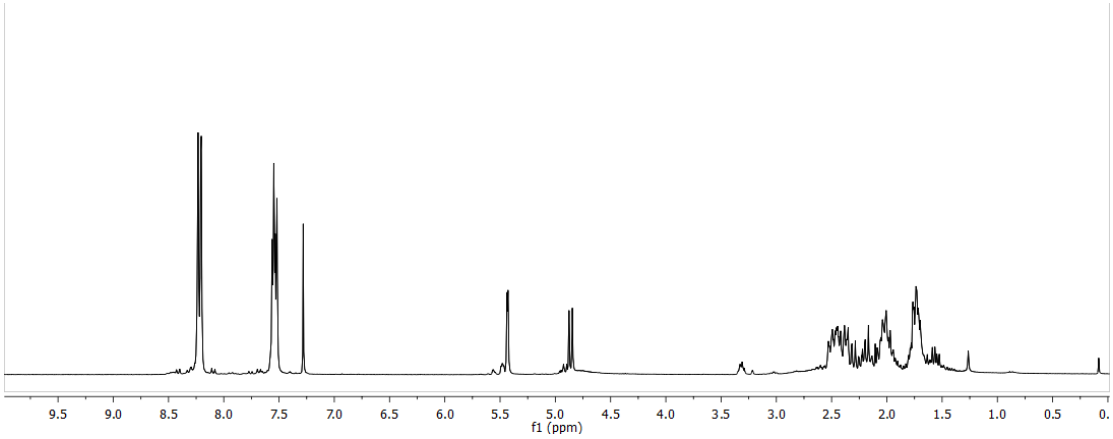
^{19}F



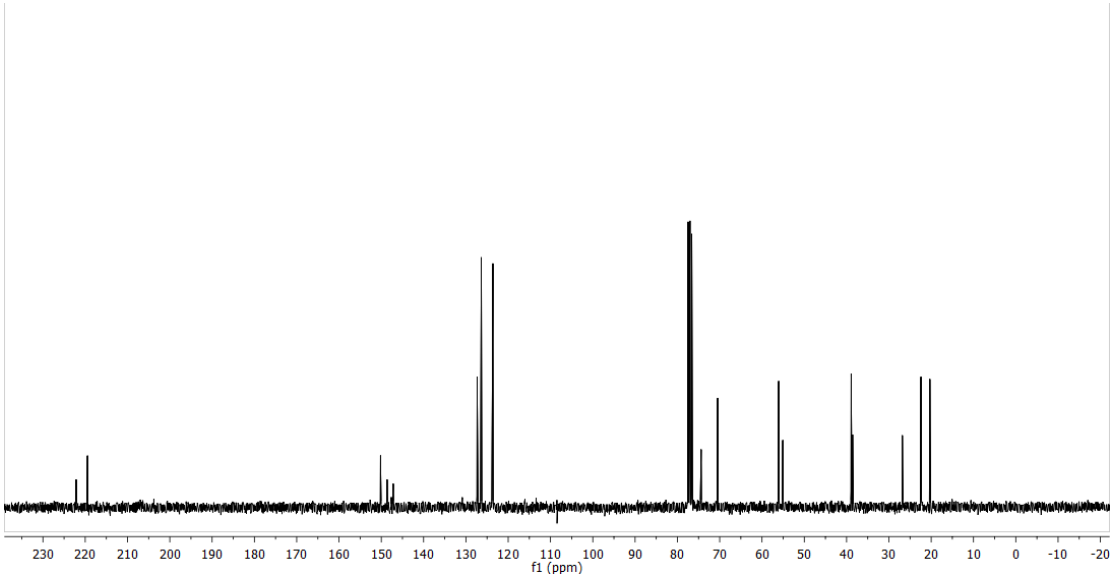
Crude 2-(hydroxy(4-nitrophenyl)methyl)cyclopentanone (4e), prepared as in Table 3.



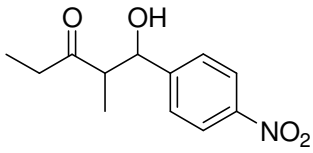
^{1}H



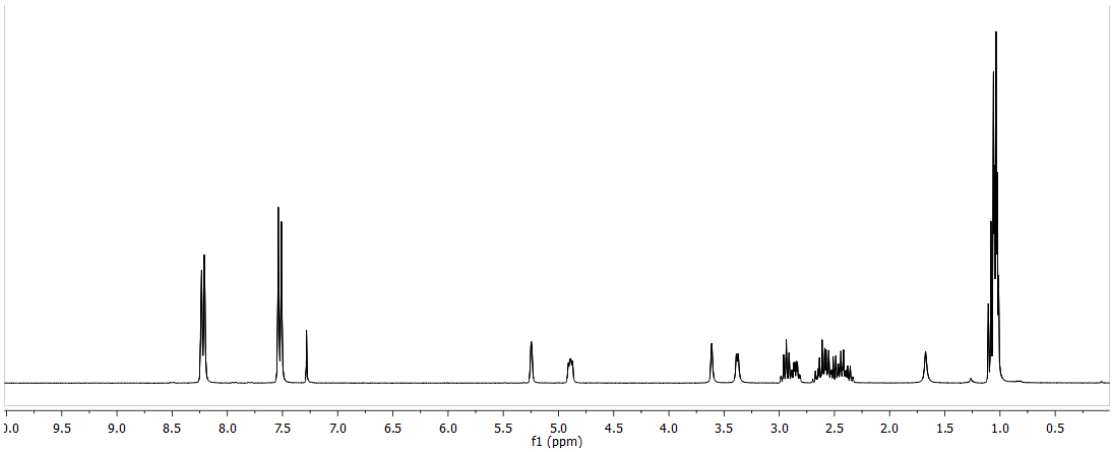
^{13}C



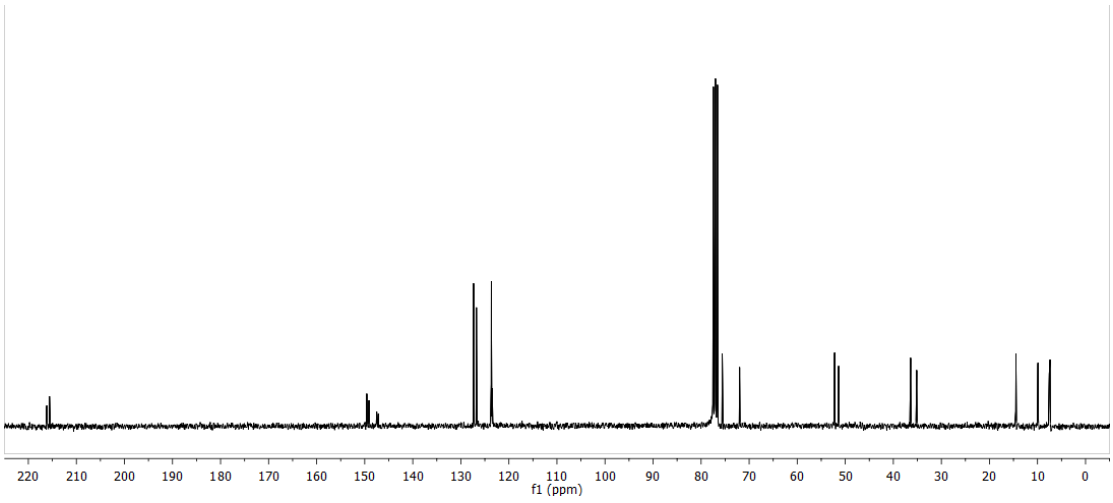
1-hydroxy-2-methyl-1-(4-nitrophenyl)pentan-3-one (5e), prepared as in Table 2.



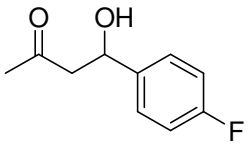
^{1}H



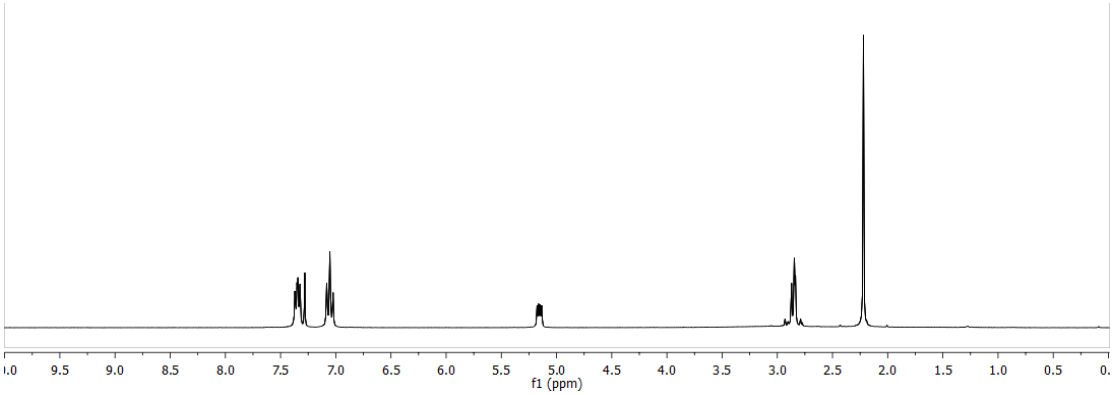
^{13}C



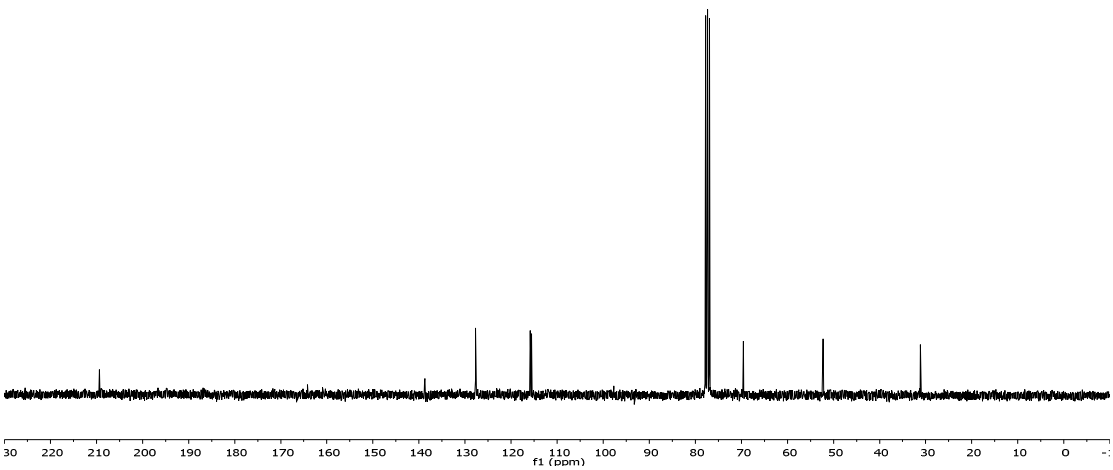
4-(4-Fluorophenyl)-4-hydroxybutan-2-one (6c)



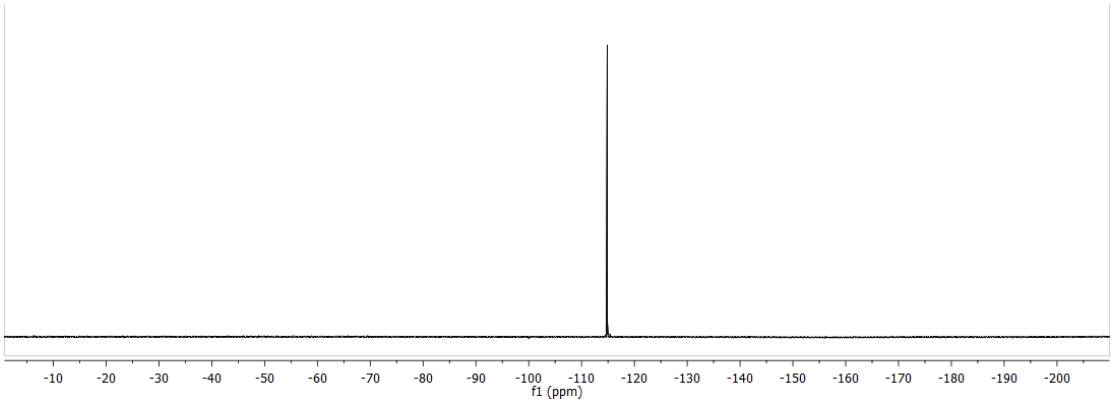
^{1}H



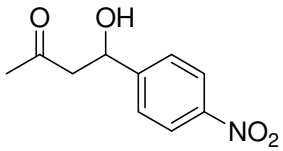
^{13}C



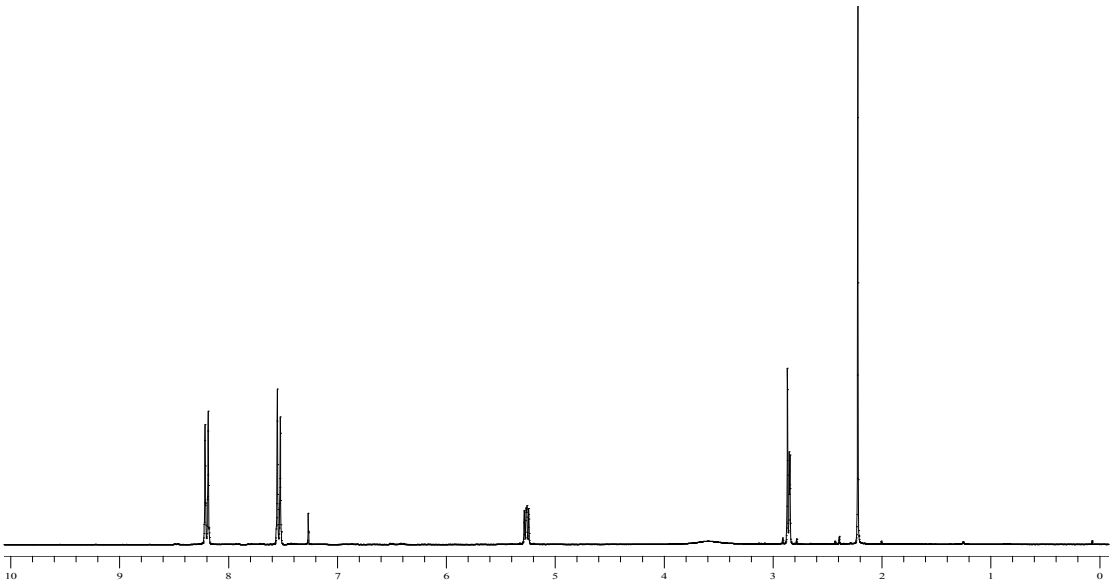
^{19}F



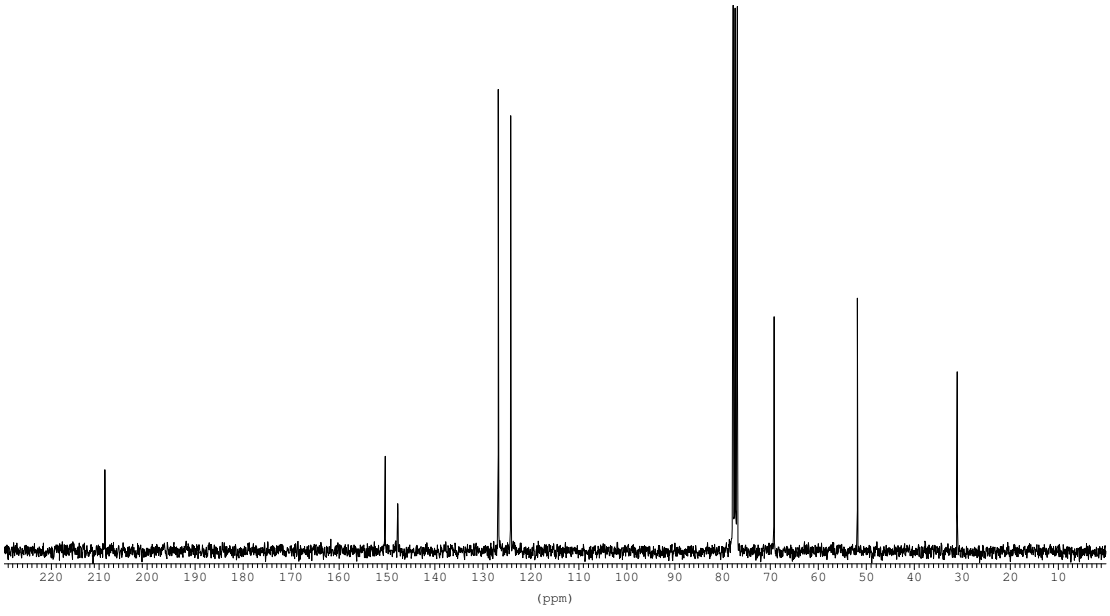
4-Hydroxy-4-(4-nitrophenyl)butan-2-one (6e)



^{1}H



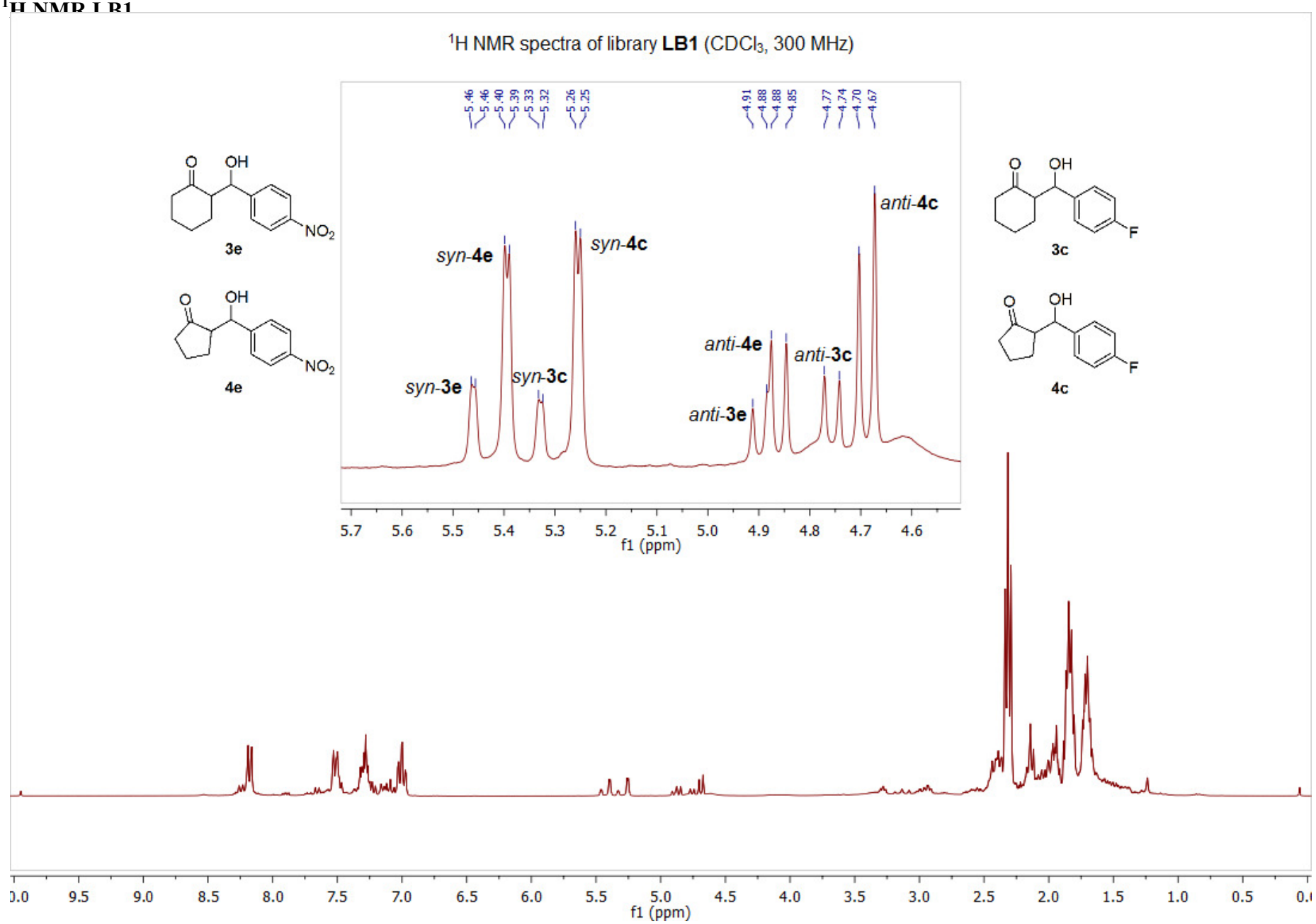
^{13}C



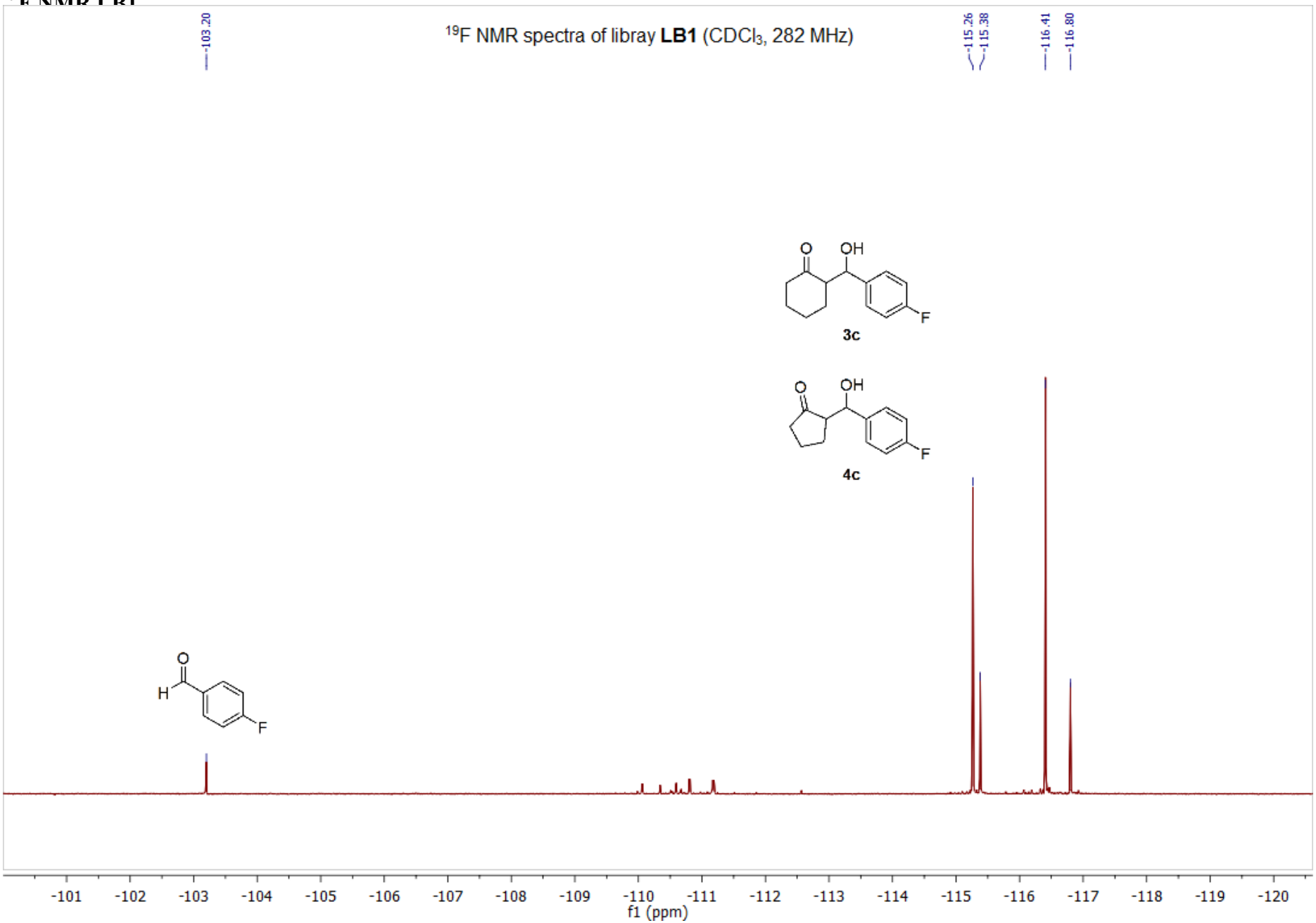
Analysis of libraries LB1 and LB2:

Anti- and *syn*- diasteroisomers of aldols **3c**, **3e**, **4c**, **4e**, were unambiguously distinguished by their ^{1}H and ^{19}F, when corresponds, NMR chemical shifts. Deconvolution of the appropriate resonances allowed inferring the concentration of each aldol in the mixture. Deconvolution was performed using the deconvolution package implemented in MestReNova 7 (v. 7.0.3-8830, 2011) for Macintosh.

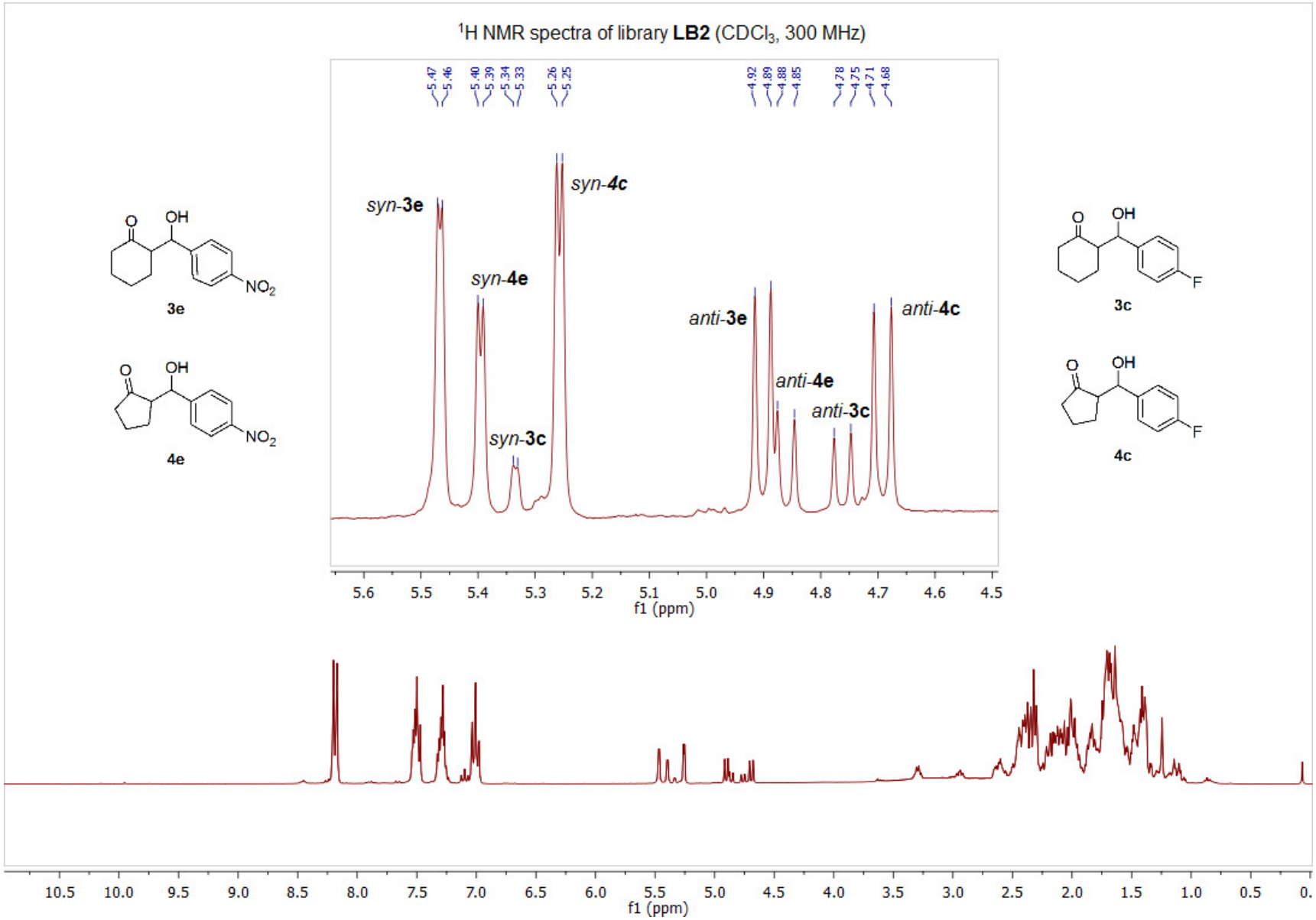
^{1}H NMR LB1



^{19}F NMR LB1



^{1}H NMR LB2



^{19}F NMR LB2