

(L)-Prolinamide imidazolium hexafluorophosphate ionic liquid as an efficient reusable organocatalyst for direct asymmetric aldol reaction in solvent-free condition

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(2*S*,4*R*)-1-(*tert*-butoxycarbonyl)-4-hydroxypyrrolidine-2-carboxylic acid (5**)¹**

Trans-4-hydroxy-*L*-proline **4** (2.5 g, 19 mmol) was dissolved in 38 mL of THF/H₂O (2/1) and then treated with 10% aqueous NaOH (8 mL) followed by addition of di-*tert*-butyldicarbonate (6.0 g, 28 mmol). The reaction mixture was stirred at room temperature overnight and then THF was removed by rotary vapor. The residue was adjusted to pH 2 by the addition of 10% aqueous KHSO₄. The acidic solution was extracted several times with ethyl acetate. The combined organic extracts were washed with H₂O and brine, dried over anhydrous Na₂SO₄. The solvent was removed by rotavapor afforded compound **5** as a syrup (4.4 g, 100%), which was used without purification for next step. $[\alpha]_{\text{D}}^{25} = -68.1$ (*c* 1.3, MeOH). IR (KBr) 3462, 2976, 2934, 1740, 1639 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): $\delta = 7.52$ (brs, 1H), 4.44–4.12 (m, 1H), 3.50–3.32 (m, 2H), 2.10–1.80 (m, 4H), 1.47 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 174.90, 153.68, 79.51, 68.81, 57.51, 53.14, 30.52, 27.73$ ppm.

(2*S*, 4*R*)-*tert*-Butyl-4-hydroxy-2-((*S*)-1-phenylethylcarbamoyl)pyrrolidine-1-carboxylate (6**)¹**

Compound **5** (2.14 g, 9.3 mmol) was dissolved in dry dichloromethane (25 mL), triethylamine (1.54 mL, 11.1 mmol) and ethyl chloroformate (1.05 mL, 11.1 mmol, in dichloromethane (5 mL)) were added slowly at 0°C and stirred for 15 min. (*S*)-1-Phenylethylamine (1.19 mL, 9.3 mmol) in 5 mL dichloromethane was added to above solution and reaction mixture was allowed to attain room temperature and stirred for 5 h. Reaction mixture was concentrated by rota vapor. The resulting oil was purified on silica gel using 30% ethyl acetate in hexane giving colourless oil **6** (2.5 g, 81%). $[\alpha]_{\text{D}}^{25} = -97.3$ (*c* 2.0, MeOH). IR (K Br): 3302, 2976, 1666, 1547 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.51$ (brs, 1H), 7.24–7.16 (m, 5H), 5.04–4.95 (m, 1H), 4.53–4.21 (m, 2H), 3.51–3.28 (m, 2H), 2.32–2.19 (m, 1H), 1.93–1.91 (m, 1H), 1.39 (s, 9H), 1.29–1.17 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 171.77, 155.57, 143.00, 128.12$ (2C), 126.61, 125.81 (2C), 80.14, 69.09, 59.39, 54.08, 48.37, 36.36, 27.86, 21.43 ppm.

4.2.2 General procedure for asymmetric aldol reaction.

The organocatalyst (**IL-3**) (10.8 mg, 0.02 mmol), cyclohexanone (0.310 mL, 3 mmol) and acetic acid (1.1 μ L, 0.02 mmol) was stirred for 20 min at –15 °C, then 4-nitrobenzaldehyde **10** (151 mg, 1 mmol) was added. The reaction mixture was stirred for a specified reaction time period at same temperature. The crude aldol product was purified by flash column chromatography on silica gel (hexane/ethyl acetate (3/1)). The diastereomeric ratio was determined by ¹H-NMR of the crude product. The *ee* of the aldol product was determined by HPLC using chiral column (chiralpak AD-H and OD-H) using hexane/2-propanol as mobile phase.

(*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)cyclohexanone (Table 1, entry 2)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 8.14$ (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 4.84 (dd, *J* = 7.60, 3.2 Hz, 1H), 4.12 (s, OH, 1H), 2.64–2.52 (m, 1H), 2.48–2.41 (m, 1H), 2.34–2.26 (m, 1H), 2.08–2.02 (m, 1H), 1.81–1.78 (m, 1H), 1.66–1.45 (m, 3H), 1.36–1.26 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 214.93, 148.49, 147.68, 127.88$ (2C), 123.44 (2C), 73.97, 57.20, 42.66, 30.75,

27.71, 24.69 ppm. HPLC analysis: Chiralpak AD-H (Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C): $t_{\text{minor}} = 22.6$ min, $t_{\text{major}} = 30.9$ min, *ee*: 94%.

(S)-2-((R)-Hydroxy(phenyl)methyl)cyclohexanone (Table 3, entry 1)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.34\text{--}7.24$ (m, 5H), 4.76 (d, *J* = 9.16 Hz, 1H), 3.96 (brs, 1H), 2.63–2.56 (m, 1H), 2.44–2.43 (m, 1H), 2.37–2.29 (m, 1H), 2.09–2.02 (m, 1H), 1.77–1.73 (m, 1H), 1.66–1.46 (m, 3H), 1.32–1.23 (m, 1H) ppm. HPLC analysis: Chiralpak AD-H (Hexane/ *i*-PrOH = 97/3, 1.0 mL/min, 222 nm, 25 °C): $t_{\text{minor}} = 32.3$ min, $t_{\text{major}} = 33.6$ min, *ee*: 98%.

(S)-2-((R)-Hydroxy(naphthyl)methyl)cyclohexanone (Table 3, entry 2)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 8.23$ (d, *J* = 7.63 Hz, 1H), 7.89–7.74 (m, 2H), 7.55–7.43 (m, 4H), 5.57 (d, *J* = 9.16 Hz, 1H), 3.01–3.94 (m, 1H), 2.51–2.32 (m, 2H), 2.04–2.02 (m, 1H), 1.69–1.63 (m, 2H), 1.44–1.24 (m, 3H) ppm. HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 90/10, 0.5 mL/min, 280 nm, 25 °C): $t_{\text{minor}} = 28.4$ min, $t_{\text{major}} = 30.5$ min, *ee*: 93%.

(S)-2-((R)-Hydroxy(2-nitro-phenyl)methyl)cyclohexanone (Table 3, entry 3)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.77$ (d, *J* = 6.87 Hz, 1H), 7.69 (d, *J* = 7.63 Hz, 1H), 7.57 (t, *J* = 7.63 Hz, 1H), 7.37 (t, *J* = 6.87 Hz, 1H), 5.38 (d, *J* = 6.87 Hz, 1H), 4.13 (brs, OH, 1H), 2.72–2.66 (m, 1H), 2.37–2.26 (m, 2H), 2.02–2.01 (m, 1H), 1.67–1.56 (m, 5H) ppm. HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm, 25 °C): $t_{\text{major}} = 16.0$ min, $t_{\text{minor}} = 18.4$ min, *ee*: 97%.

(S)-2-((R)-Hydroxy(2-fluoro-phenyl)methyl)cyclohexanone (Table 3, entry 4)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.49\text{--}7.42$ (m, 1H), 7.24–7.08 (m, 2H), 6.96 (t, *J* = 9.92 Hz, 1H), 5.15 (d, *J* = 8.39 Hz, 1H), 4.03 (brs, OH, 1H), 2.67–2.60 (m, 1H), 2.44–2.26 (m, 2H), 2.04–2.02 (m, 1H), 1.81–1.74 (m, 1H), 1.65–1.38 (m, 4H) ppm. HPLC analysis: Chiralcel OD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 220 nm, 25 °C): $t_{\text{major}} = 6.4$ min, $t_{\text{minor}} = 7.7$ min, *ee*: 91%.

(S)-2-((R)-Hydroxy(4-fluoro-phenyl)methyl)cyclohexanone (Table 3, entry 5)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.30\text{--}7.24$ (m, 2H), 7.05–6.99 (m, 2H), 4.76 (d, *J* = 8.39 Hz, 1H), 4.03 (brs, OH, 1H), 2.59–2.30 (m, 3H), 2.11–2.05 (m, 1H), 2.80–2.77 (m, 1H), 1.67–1.51 (m, 3H), 1.31–1.21 (m, 1H) ppm. HPLC analysis: Chiralcel OD-H (Hexane/ *i*-PrOH = 95/5, 1.0 mL/min, 254 nm, 25 °C): $t_{\text{major}} = 11.3$ min, $t_{\text{minor}} = 17.1$ min, *ee*: 93%.

(S)-2-((R)-Hydroxy(2-chloro-phenyl)methyl)cyclohexanone (Table 3, entry 6)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.50$ (dd, *J* = 7.63, 1.53 Hz, 1H), 7.24–7.19 (m, 2H), 7.13–7.09 (m, 1H), 5.26 (d, *J* = 7.93 Hz, 1H), 2.62–2.56 (m, 1H), 2.39–2.21 (m, 2H), 1.98–1.96 (m, 1H), 1.73–1.70 (m, 1H), 1.65–1.43 (m, 3H), 1.21–1.17 (m, 1H) ppm. HPLC analysis: Chiralcel OD-H (Hexane/ *i*-PrOH = 92/8, 0.5 mL/min, 220 nm, 25 °C): $t_{\text{major}} = 14.2$ min, $t_{\text{minor}} = 16.5$ min, *ee*: 97%.

(S)-2-((R)-Hydroxy(4-chloro-phenyl)methyl)cyclohexanone (Table 3, entry 7)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.58$ (d, *J* = 7.63 Hz, 2H), 7.42 (d, *J* = 8.39 Hz, 2H), 4.82 (d, *J* = 8.39 Hz, 1H), 4.03 (brs, 1H), 2.60–2.54 (m, 1H), 2.49–1.39 (m, 1H), 2.38–2.30 (m, 1H), 2.11–2.06 (m, 1H), 1.81–1.77 (m, 1H), 1.66–1.51 (m, 3H), 1.37–1.23 (m, 1H) ppm. HPLC analysis: Chiralpak

AD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 222 nm, 25 °C): $t_{\text{minor}} = 13.1$ min, $t_{\text{major}} = 15.8$ min, *ee*: 91%.

(S)-2-((R)-Hydroxy(2-bromo-phenyl)methyl)cyclohexanone (Table 3, entry 8)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.49\text{--}7.32$ (m, 2H), 7.32 (t, $J = 7.63$ Hz, 1H), 7.12–7.08 (m, 1H), 5.27 (d, $J = 8.39$ Hz, 1H), 4.08 (brs, OH, 1H), 2.69–2.62 (m, 1H), 2.42–2.29 (m, 2H), 2.07–2.04 (m, 1H), 1.86–1.75 (m, 2H), 1.73–1.46 (m, 3H) ppm. HPLC analysis: Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 220 nm, 25 °C): $t_{\text{major}} = 10.5$ min, $t_{\text{minor}} = 12.2$ min, *ee*: 97%.

(S)-2-((R)-Hydroxy(4-bromo-phenyl)methyl)cyclohexanone (Table 3, entry 9)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.44$ (d, $J = 8.39$ Hz, 2H), 7.17 (d, $J = 6.87$ Hz, 2H), 4.72 (d, $J = 8.39$ Hz, 1H), 3.97 (brs, OH, 1H), 2.56–2.43 (m, 2H), 2.38–2.28 (m, 1H), 2.07–2.04 (m, 1H), 1.83–1.53 (m, 4H), 1.31–1.20 (m, 1H) ppm. HPLC analysis: Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 0.3 mL/min, 222 nm, 25 °C): $t_{\text{minor}} = 45.7$ min, $t_{\text{major}} = 54.6$ min, *ee*: 98%.

(S)-2-((R)-Hydroxy(2-methoxy-phenyl)methyl)cyclohexanone (Table 3, entry 10)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.39$ (dd, $J = 7.63, 1.53$ Hz, 1H), 7.26–7.21 (m, 1H), 6.96 (t, $J = 7.63$ Hz, 1H), 6.84 (d, $J = 8.39$ Hz, 1H), 5.24 (d, $J = 8.39$ Hz, 1H), 3.82 (s, 3H), 2.75–2.68 (m, 1H), 2.47–2.32 (m, 2H), 2.06–1.99 (m, 1H), 1.79–1.44 (m, 5H) ppm. HPLC analysis: Chiralpak OD-H (Hexane/ *i*-PrOH = 97/3, 0.5 mL/min, 210 nm, 25 °C): $t_{\text{major}} = 33.7$ min, $t_{\text{minor}} = 36.5$ min, *ee*: 91%.

(S)-2-((R)-Hydroxy(4-methoxy-phenyl)methyl)cyclohexanone (Table 3, entry 11)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.24\text{--}7.20$ (m, 2H), 6.87–6.85 (m, 2H), 4.73 (d, $J = 8.54$ Hz, 1H), 3.81 (s, 3H), 2.62–2.55 (m, 1H), 2.45–2.33 (m, 2H), 2.07–2.04 (m, 1H), 1.78–1.54 (m, 3H), 1.30–1.23 (m, 2H) ppm. HPLC analysis: Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C): $t_{\text{minor}} = 21.8$ min, $t_{\text{major}} = 22.7$ min, *ee*: 52%.

(S)-2-((R)-Hydroxy(2-trifluoromethyl-phenyl)methyl)cyclohexanone (Table 3, entry 12)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.69$ (d, $J = 7.63$ Hz, 1H), 7.62–7.52 (m, 2H), 7.39 (t, $J = 7.63$ Hz, 1H), 5.28 (d, $J = 8.39$ Hz, 1H), 2.76–2.69 (m, 1H), 2.50–2.31 (m, 2H), 2.09–2.05 (m, 1H), 1.83–1.23 (m, 5H) ppm. HPLC analysis: Chiralcel AD-H (Hexane/ *i*-PrOH = 90/10, 0.5 mL/min, 254 nm, 25 °C): $t_{\text{major}} = 20.1$ min, $t_{\text{minor}} = 21.8$ min, *ee*: 99%.

(S)-2-((R)-Hydroxy(4-trifluoromethyl-phenyl)methyl)cyclohexanone (Table 3, entry 13)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.58$ (d, $J = 7.63$ Hz, 2H), 7.42 (d, $J = 8.39$ Hz, 2H), 4.82 (d, $J = 8.39$ Hz, 1H), 4.04 (brs, OH, 1H), 2.60–2.29 (m, 3H), 2.10–2.04 (m, 1H), 1.80–1.50 (m, 4H), 1.36–1.22 (m, 1H) ppm. HPLC analysis: Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 0.5 mL/min, 230 nm, 25 °C): $t_{\text{minor}} = 20.2$ min, $t_{\text{major}} = 25.5$ min, *ee*: 91%.

2-[Hydroxy(2-nitro-phenyl)methyl]-cyclopentanone (Table 4, Entry 1)¹

¹H NMR (400 MHz, CDCl₃): $\delta = 7.97$ (d, $J = 7.63$ Hz, 1H), 7.87–7.77 (m, 2H), 7.65–7.61 (m, 1.64H), 7.41 (t, $J = 8.39$ Hz, 1H), 5.89 (d, $J = 2.29$ Hz, 1H *syn*), 5.42 (d, $J = 8.39$ Hz, 0.41H *anti*), 2.76–2.69 (m, 1H), 2.51–2.25 (m, 2H), 2.16–2.09 (m, 1H), 2.06–2.00 (m, 2H), 1.73–1.62 (m, 4H) ppm. HPLC analysis: Chiralcel OD-H (Hexane/ *i*-PrOH = 95/5, 1.0 mL/min, 254 nm, 25 °C): *syn*: $t_{\text{minor}} = 13.1$ min, $t_{\text{major}} = 17.1$ min, *ee*: 28%; *anti*: $t_{\text{major}} = 23.7$ min (*S, R*), $t_{\text{minor}} = 24.8$ min (*R, S*), *ee*: 99%.

2-[Hydroxy(4-nitro-phenyl)methyl]-cyclopentanone (Table 4, Entry 2)¹

¹H NMR (400 MHz, CDCl₃): δ = 8.19 (d, J = 6.87 Hz, 3H), 7.50 (t, J = 7.63 Hz, 4H), 5.40 (d, J = 3.05 Hz, 1H *syn*), 4.82 (d, J = 9.16 Hz, 0.74H *anti*), 2.48–2.08 (m, 5H), 2.04–1.87 (m, 2H), 1.79–1.46 (m, 5H) ppm. HPLC analysis Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C): *syn*: t_{major} 14.9 min, t_{minor} 19.5 min, *ee*: 40%; *anti*: t_{minor} 23.5 min (*R, S*), t_{major} 25.0 min (*S, R*), *ee*: 66%.

2-[Hydroxy(2-fluoro-phenyl)methyl]-cyclopentanone (Table 4, entry 3)¹

¹H NMR (400 MHz, CDCl₃): δ = 7.48–7.40 (m, 1H), 7.19–7.10 (m, 1H), 7.04 (t, J = 7.63 Hz, 1.9H), 6.88 (t, J = 8.39 Hz, 1H), 5.48 (d, J = 3.05 Hz, 1H *syn*), 4.99 (d, J = 9.16 Hz, 0.23 *anti*), 2.49–2.40 (m, 1H), 2.38–2.12 (m, 2H), 2.06–1.97 (m, 1H), 1.93–1.82 (m, 2H), 1.67–1.48 (m, 2.6H) ppm. HPLC analysis Chiralpak AD-H (Hexane/ *i*-PrOH = 90/0, 1 mL/min, 220 nm, 25 °C): *syn*: t_{minor} 11.5 min, t_{major} 14.7 min, *ee*: 61%; *anti*: t_{major} 20.8 (*S, R*) min, t_{minor} 22.4 min (*R, S*), *ee*: 76%.

2-[Hydroxy-(4-fluoro-phenyl)methyl]-cyclopentanone (Table 4, entry 4)¹

¹H NMR (400 MHz, CDCl₃): δ = 7.29–7.24 (m, 4H), 6.98 (dd, J = 9.16, 3.05 Hz, 4H), 5.23 (d, J = 3.05 Hz, 1H *syn*), 4.65 (d, J = 9.16 Hz, 1H *anti*), 2.42–2.32 (m, 3H), 2.29–2.04 (m, 1H), 2.00–1.89 (m, 4H), 1.79–1.61 (m, 4H), 1.49–1.41 (m, 2H) ppm. HPLC analysis: Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 222 nm, 25 °C): *syn*: t_{major} 8.2 min, t_{minor} 9.8 min, *ee*: 20%; *anti*: t_{major} 11.0 min (*S, R*), t_{minor} 12.0 min (*R, S*), *ee*: 82%.

2-[Hydroxy-(2-chloro-phenyl)methyl]-cyclohexanone (Table 4, entry 5)¹

¹H NMR (400 MHz, CDCl₃): δ = 7.58–7.54 (m, 1H), 7.31–7.24 (m, 3H), 7.21–7.15 (m, 1H), 5.67 (d, J = 2.29 Hz, 1H *syn*), 5.27 (d, J = 9.16 Hz, 0.27H *anti*), 2.66–2.62 (m, 1H), 2.55–2.27 (m, 1H), 2.17–2.08 (m, 1H), 2.02–1.93 (m, 3H), 1.77–1.60 (m, 3H) ppm. HPLC analysis ChiralcelOD-H (Hexane/ *i*-PrOH = 95/5, 1.0 mL/min, 222 nm, 25 °C): *syn*: t_{minor} 7.5 min, t_{major} 8.6 min *ee*: 45%; *anti*: t_{major} 12.0 min (*S, R*), t_{minor} 12.5 min (*R, S*), *ee*: 99%.

2-[Hydroxy-(4-chloro-phenyl)methyl]-cyclohexanone (Table 4, entry 6)¹

¹H NMR (400 MHz, CDCl₃): δ = 7.44–7.21 (m, 6.37H), 5.23 (d, J = 3.05 Hz, 0.62H *syn*), 4.66 (d, J = 8.39 Hz, 1H *anti*), 2.93–2.28 (m, 1H), 2.43–2.32 (m, 3H), 2.05–1.89 (m, 3H), 1.77–1.61 (m, 3H), 1.47–1.42 (m, 1H), ppm. HPLC analysis Chiralpak AD-H (Hexane/ *i*-PrOH = 90/10, 1.0 mL/min, 222 nm, 25 °C): *syn*: t_{major} 8.1 min, t_{minor} 9.9 min, *ee*: 26%; *anti*: t_{major} 11.5 min (*S, R*), t_{minor} 11.2 min (*S, R*), *ee*: 84%.

2-[Hydroxy-(2-methoxy-phenyl)methyl]-cyclopentanone (Table 4, entry 7)¹

¹H NMR (400 MHz, CDCl₃): δ = 7.42 (d, J = 7.63 Hz, 1H), 7.25–7.22 (m, 2H), 6.96 (t, J = 7.63 Hz, 1H), 6.84–6.82 (m, 1H), 5.56 (d, J = 2.29 Hz, 1H *syn*), 5.18 (d, J = 11.44 Hz, 0.32H *anti*), 3.85 (s, 0.25H), 3.80 (s, 3H), 2.65–2.58 (m, 1H), 2.54–2.24 (m, 2H), 2.20–2.09 (m, 1H), 2.03–1.91 (m, 2H), 1.74–1.58 (m, 3H) ppm. HPLC analysis Chiralpak AD-H (Hexane/ *i*-PrOH = 95/5, 0.5 mL/min, 222 nm, 25 °C): *syn*: t_{major} 38.9 min, t_{minor} 49.2 min, *ee*: 33%; *anti*: t_{major} 44.1 min (*S, R*), and t_{minor} 45.0 min (*R, S*), *ee*: 97%.

2-[Hydroxy-(4-methoxy-phenyl)methyl]-cyclopentanone (Table 4, entry 8)¹

¹H NMR (400 MHz, CDCl₃): δ = 7.57–7.51 (m, 0.7H), 7.24–7.20 (m, 2H), 6.93 (d, J = 8.54 Hz, 1H), 6.83 (d, J = 8.54 Hz, 2H), 5.19 (d, J = 3.66 Hz, 1H *syn*), 4.62 (d, J = 12.82 Hz, 0.4 *anti*), 3.82 (s,

0.62), 3.76 (s, 3H), 3.05 (m, 1H), 2.45–2.30 (m, 2H), 2.14–2.13 (m, 1H), 2.02–1.88 (m, 2H), 1.86–1.78 (m, 1H), 1.74–1.61 (m, 1H), 1.47–1.22 (m, 2H) ppm. HPLC analysis Chiralpak AD-H (Hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C): *syn*: t_{major} 13.8 min, t_{minor} 15.8 min, *ee*: 8%; *anti*: t_{major} 18.3 min (*S*, *R*), and t_{minor} 20.0 min (*R*, *S*), *ee*: 86%.

Typical procedure for continuous use of IL 3 (Table 5)

A mixture of cyclohexanone (310 μ L, 3 mmol), 4-nitrobenzaldehyde (**10**) (151 mg, 1 mmol), **IL-3** (10.8 mg, 2 mol%), and acetic acid (1.1 μ L, 2 mol%) was stirred at -15°C temperature for 24 h. After complete consumption of **10** (TLC and HPLC analysis), cyclohexanone (3 mmol) and **10** (1 mmol) were added to the reaction mixture without any additional catalyst or additives. The crude product was obtained after repeating this procedure for another 6 catalytic cycles.

References

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Table 1: Comparisons of literature reported recoverable proline and prolinamide catalysts with **IL 3** for direct asymmetric aldol reaction between cyclohexanone and 4-nitrobenzaldehyde.

Entry	Recoverable organocatalyst Catalyst	Catalyst Loading, reaction time	Yield (%) (<i>anti/syn</i>)	Ee (<i>anti</i>) (%)	TON	TOF (h ⁻¹) x 10 ⁻²	References
1	L-Prolinamide as a Recoverable	5 mol%, 30 h	95 (93/7)	96	19	63	3r
2	Polymer supported <i>L</i> -prolinamide	10 mol%, 96 h	91 (89/11)	87	9.1	9.4	3n
3	imidazolium-based chiral proline analogous	30 mol%, 2 d	83 (86/14)	86	2.8	5.7	3p
4	polyvinylidene chloride-supported ionic liquid/ <i>L</i> -proline	12 mol%, 2 d	99 (94/6)	98	7.2	17	3k
5	silica magnetic microspheres supported proline	20 mol%, 24 h	63 (76/24)	85	4.3	13	3l
6	pyrrolidine-type FILs	20 mol%, 12 h	93 (50/50)	10	9.3	38.7	3d
7	Guanidinium Salt/Proline	15 mol%, 96 h	92 (92/8)	99	6.1	6	3j
8	fluorous <i>b</i> -aminosulfonamide	10 mol%, 20 h	82 (80/20)	92	8.2	41	3g, 3i
9	IL tagged proline	20 mol%, 24 h	95 (98/2)	98	4.8	19.7	3f
10	Silica supported <i>L</i> -prolinamide	60 mol%, 4 d	87 (85/15)	96	1.5	1.5	3e
11	Dendritic supported <i>N</i> -polylysulfonamide	10 mol%, 24 h	>99 (99/1)	>99	9.9	41	3a
12	Polystyrene-Supported Hydroxyproline	10 mol%, 18 h	85 (98/2)	97	8.5	47	3b
13	Polystyrene-Supported <i>L</i> -Proline	10 mol%, 22 h	82 (95/5)	98	8.2	37	3c
14	Silica-gel supported binam-prolinamides	10 mol%, 6 h	86 (94/6)	95	8.6	143	3m
15	Recoverable (<i>S</i>)-Binam- <i>L</i> -Prolinamides	5 mol%, 2 h	80 (90/10)	86	16	800	3q
16	Polystyrene supported <i>N</i> -Sulfonyl-(<i>Ra</i>)-binam- <i>D</i> -prolinamide	20 mol%, 24h	83 (95:5)	88	4.4	18.3	3s
17	Recyclable silica-supported prolinamide	10 mol%, 24h	88 (86/14)	86	8.6	35.8	3t
18	O-acylation serine derivatives	10 mol%, 20 h	90 (94/6)	98	9.0	45	3h
19	(<i>S</i>)-prolinamide modified by an ionic liquid	2 mol%, 18 h	98 (99/1)	99	49	272	3o
20	(1 <i>R</i> ,2 <i>R</i>)-Bis(<i>S</i>)-prolinamido]cyclohexane Modified with Ionic Groups	10 mol%, 72 h	72 (92/8)	98	7.2	10	2
21	Ionic liquid of <i>trans</i> -4-hydroxy- <i>L</i> -Prolinamide	2 mol%, 24 h	99 (97/3)	94	49.5	206	This paper

$$\text{TOF} = [\text{product}]/[\text{catalyst}][\text{Time}] \quad \text{and} \quad \text{TON} = \text{Product (moles)}/\text{Catalyst (moles)}$$

Mass spectra

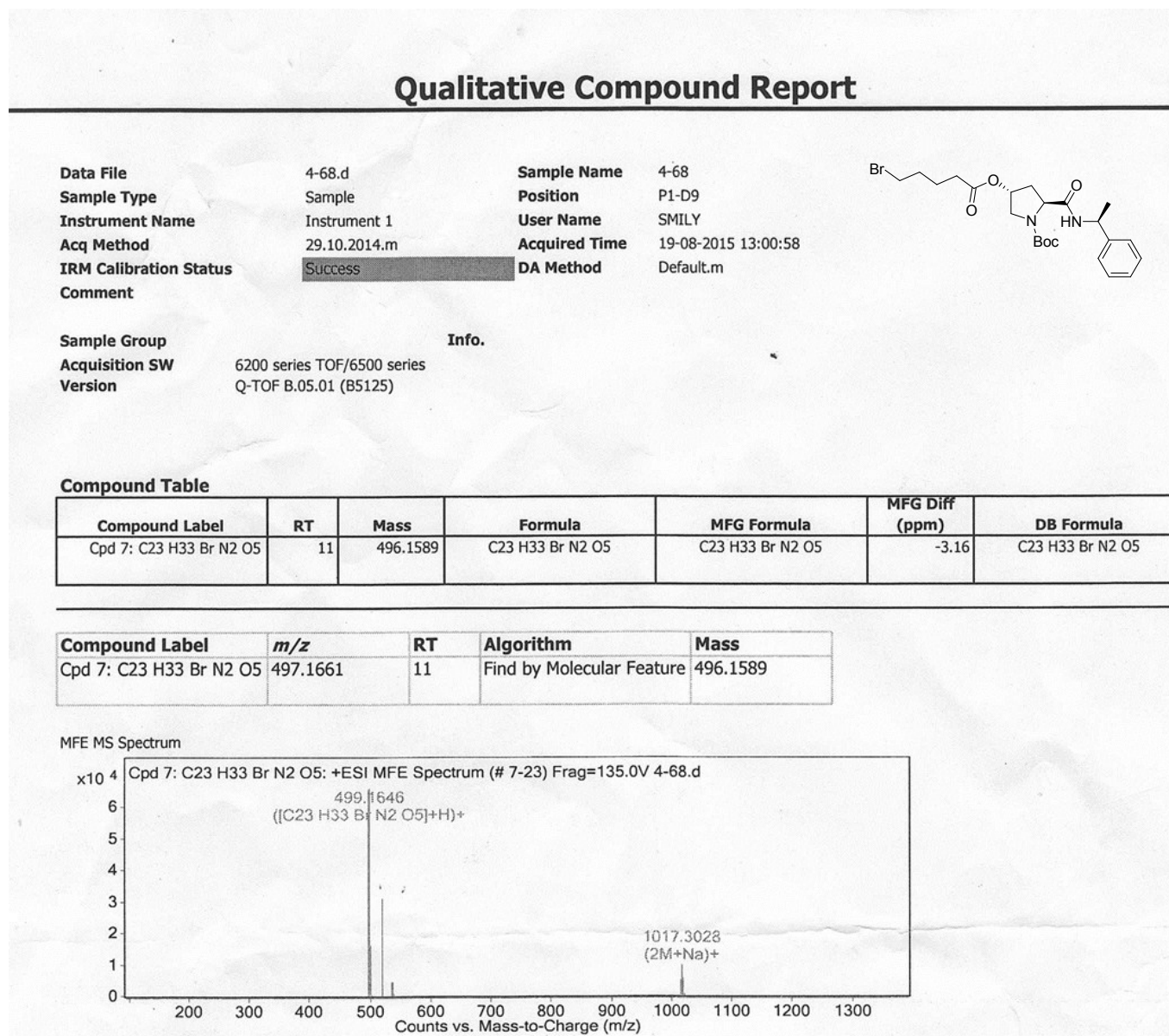
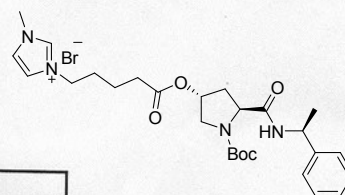


Figure1: HRMS of compound 7

Qualitative Compound Report

Data File	GY433.d	Sample Name	GY433
Sample Type	Sample	Position	P1C9
Instrument Name	6530 QTOF LCMS	User Name	lcmsdu-PC\admin
Acq Method	Union.m	Acquired Time	21-08-2014 14:28:34
IRM Calibration Status	Success	DA Method	Default.m
Comment			

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	



Compound Table

Compound Label	RT	Mass	MFG Formula
Cpd 1: 0.195	0.195	498.2843	<none>

Compound Label	m/z	RT	Algorithm	Mass
Cpd 1: 0.195	499.2916	0.195	Find by Molecular Feature	498.2843

MFE MS Spectrum

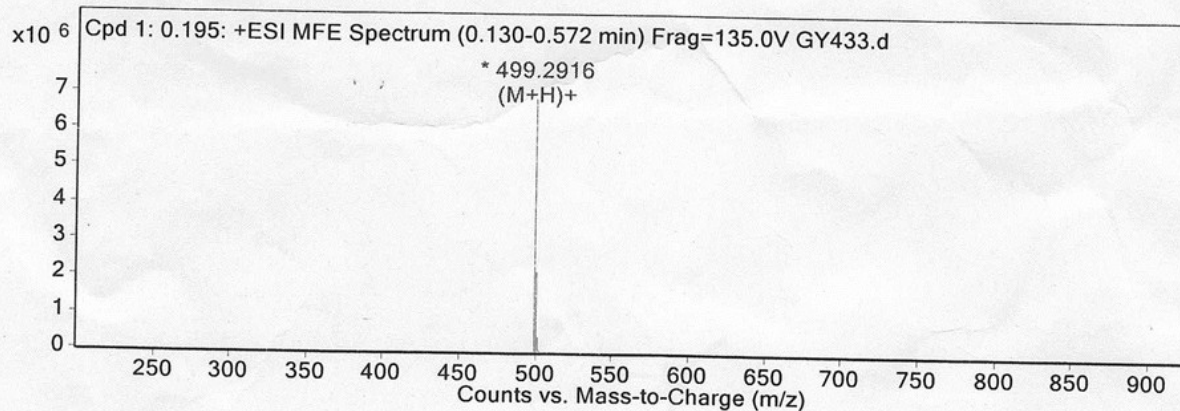


Figure 2: HRMS of compound 8

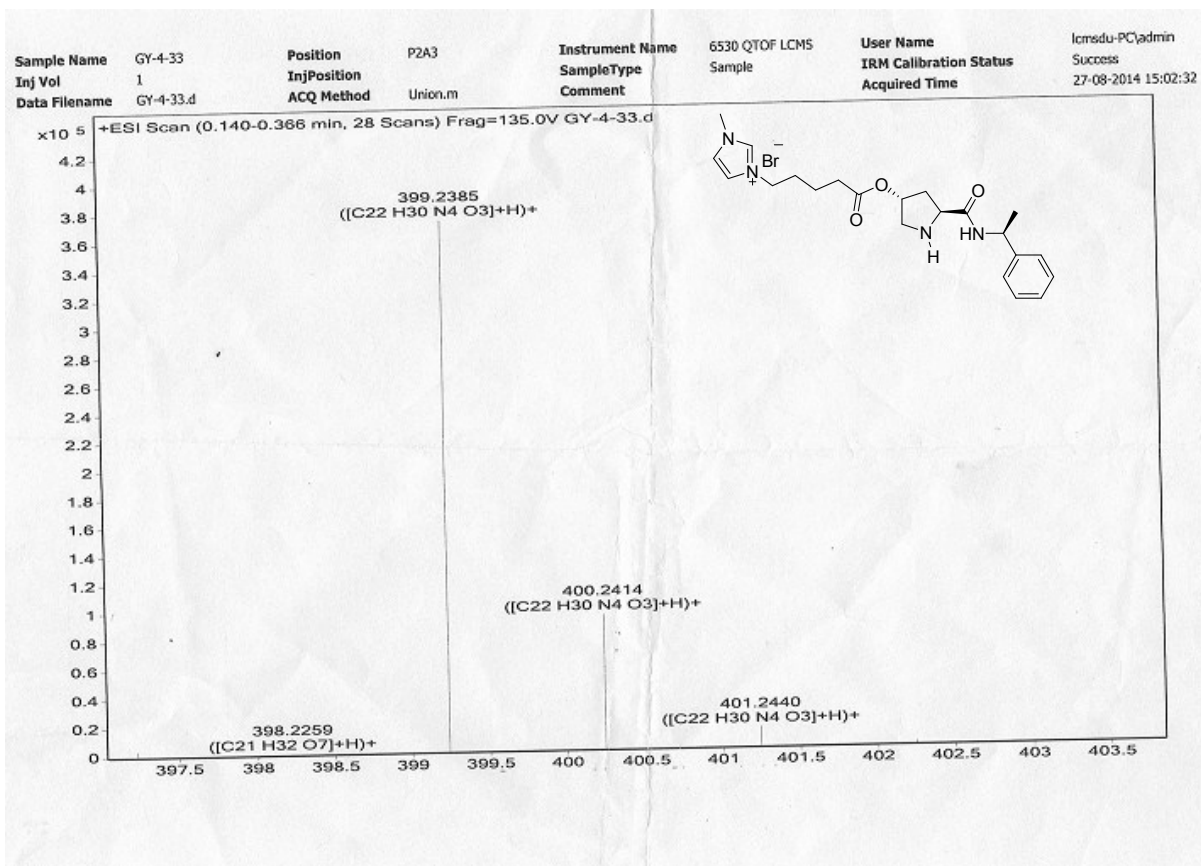


Figure 3: HRMS of IL 2

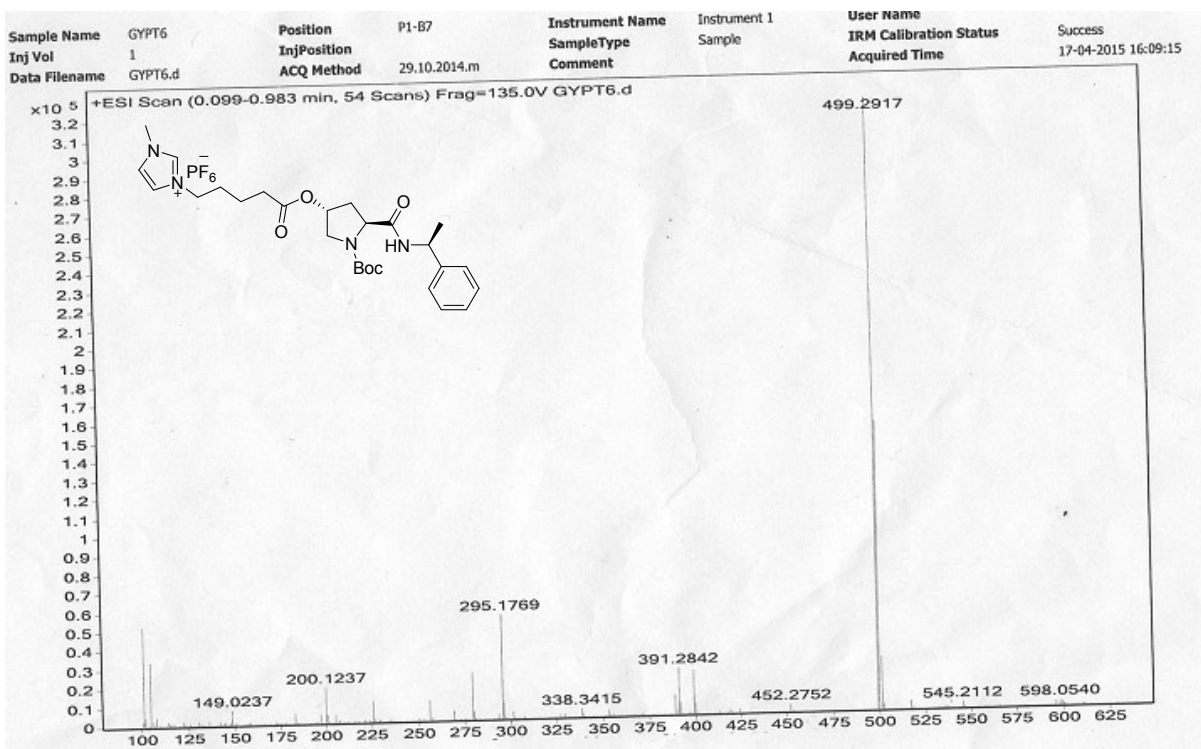


Figure 4: HRMS of compound 9

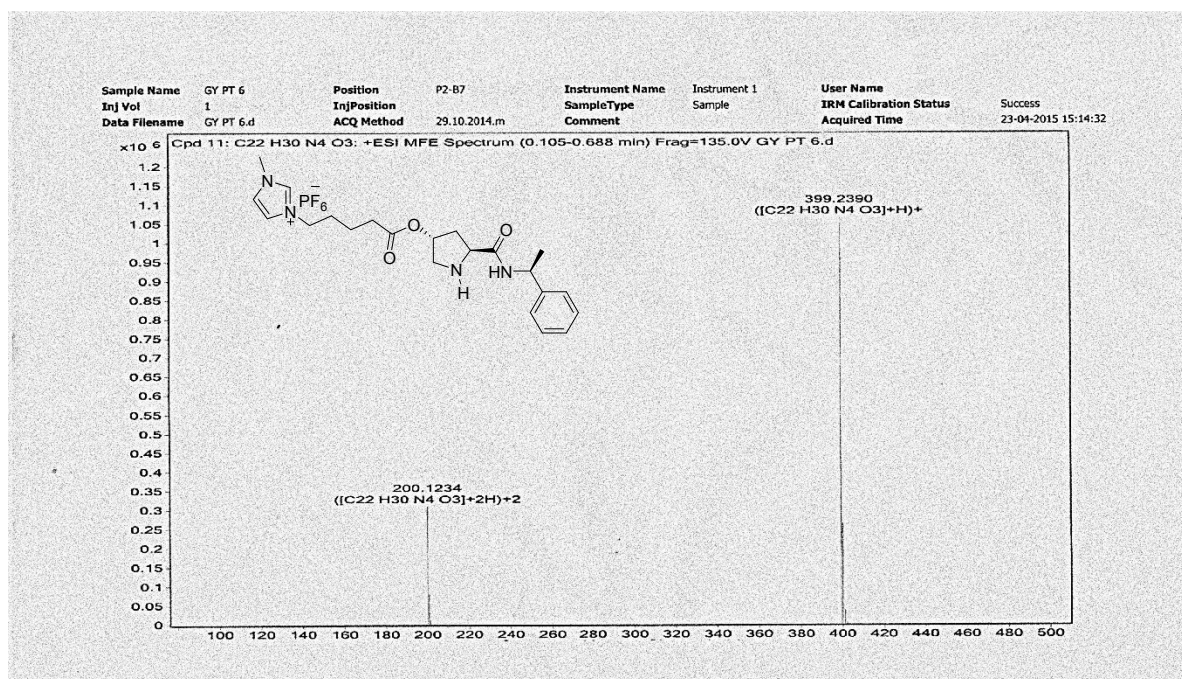
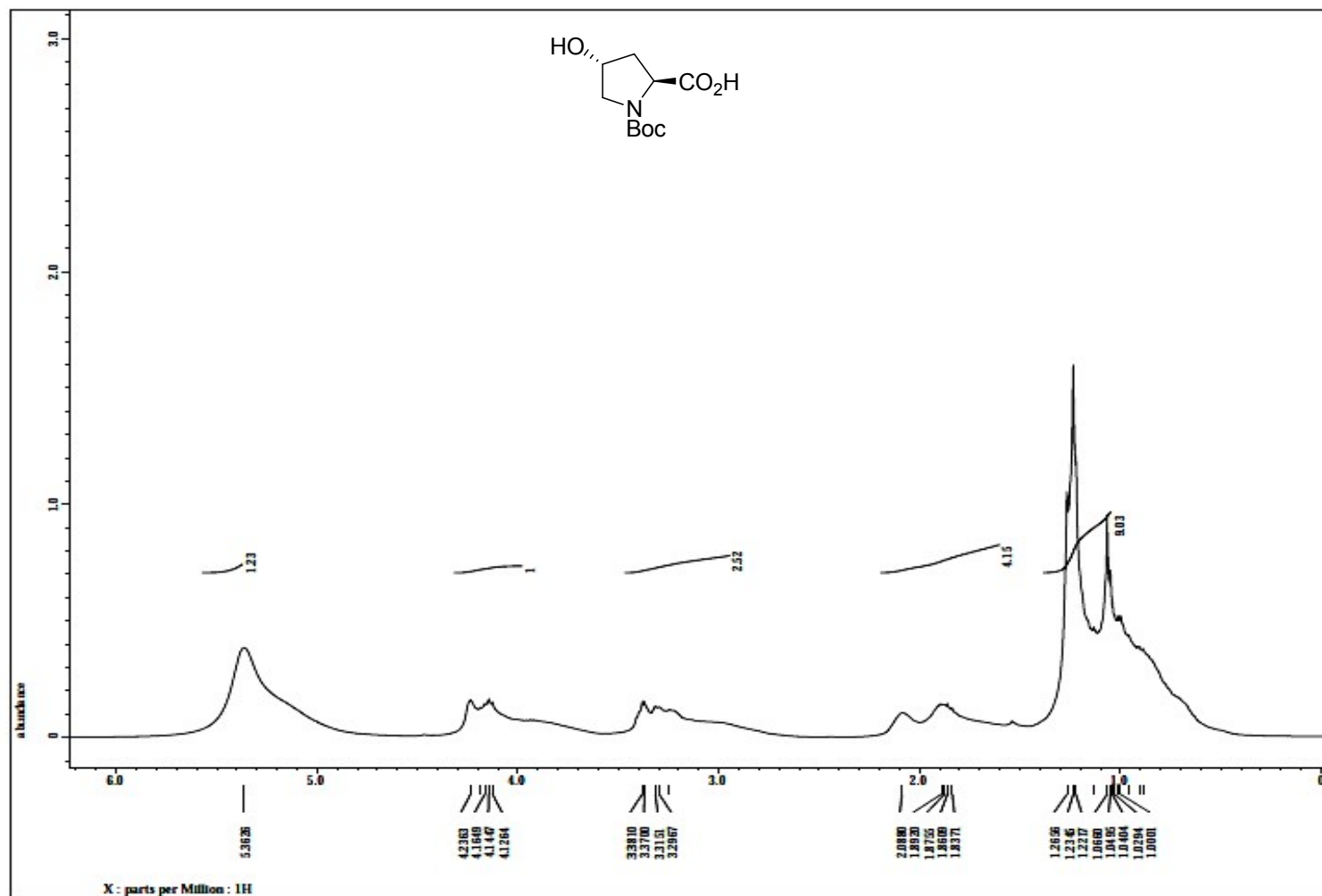
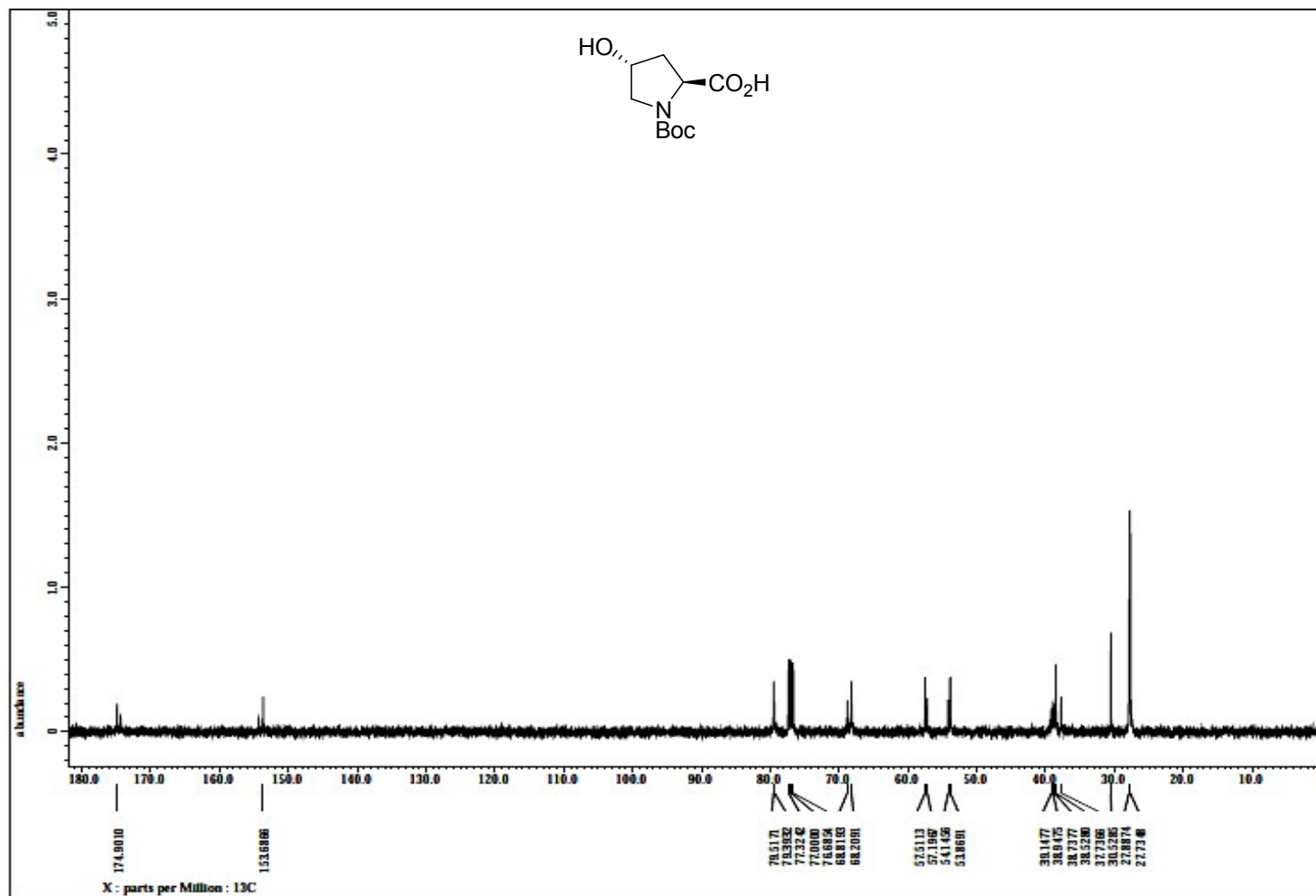
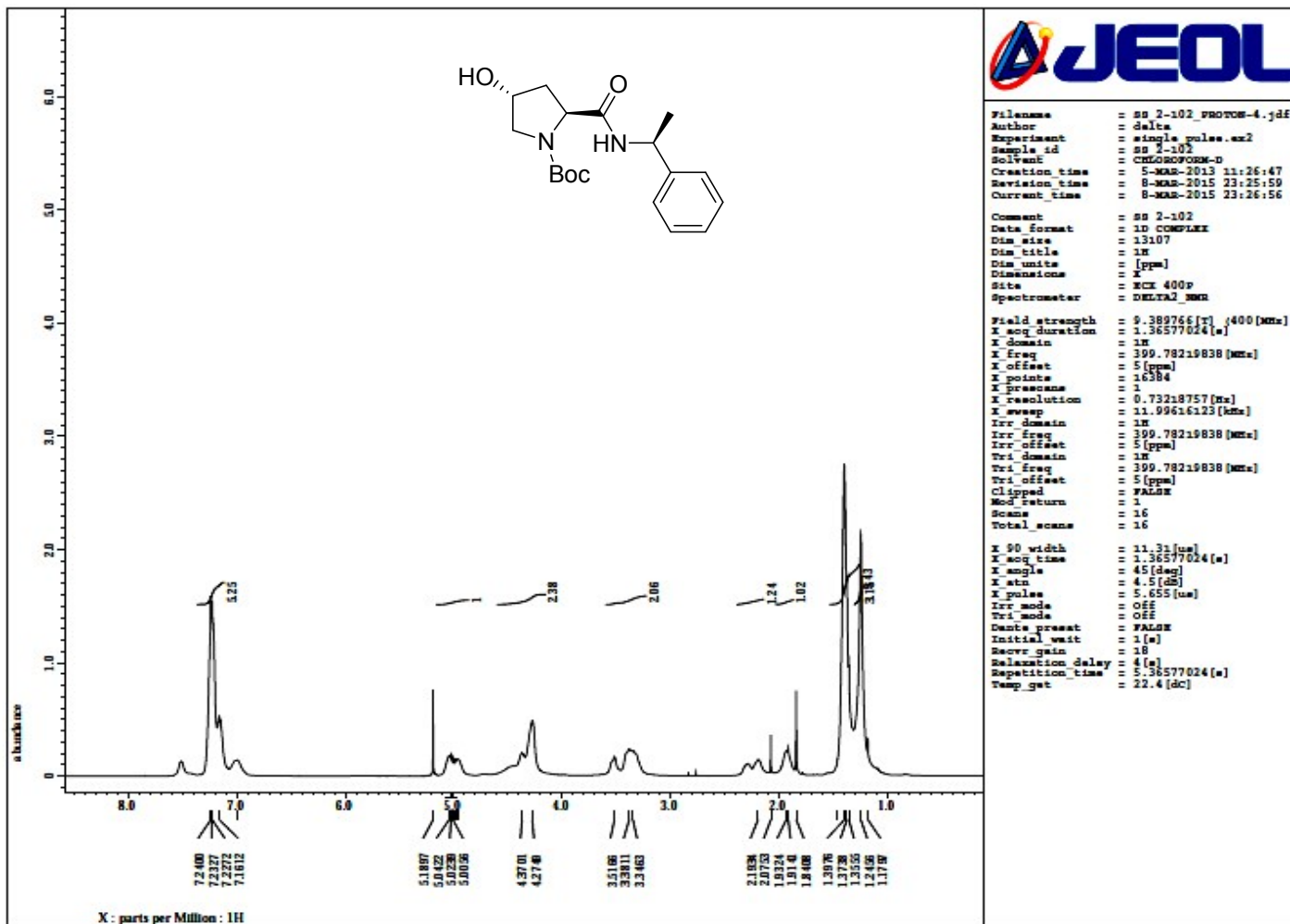


Figure 5: HRMS of fresh IL 3







```

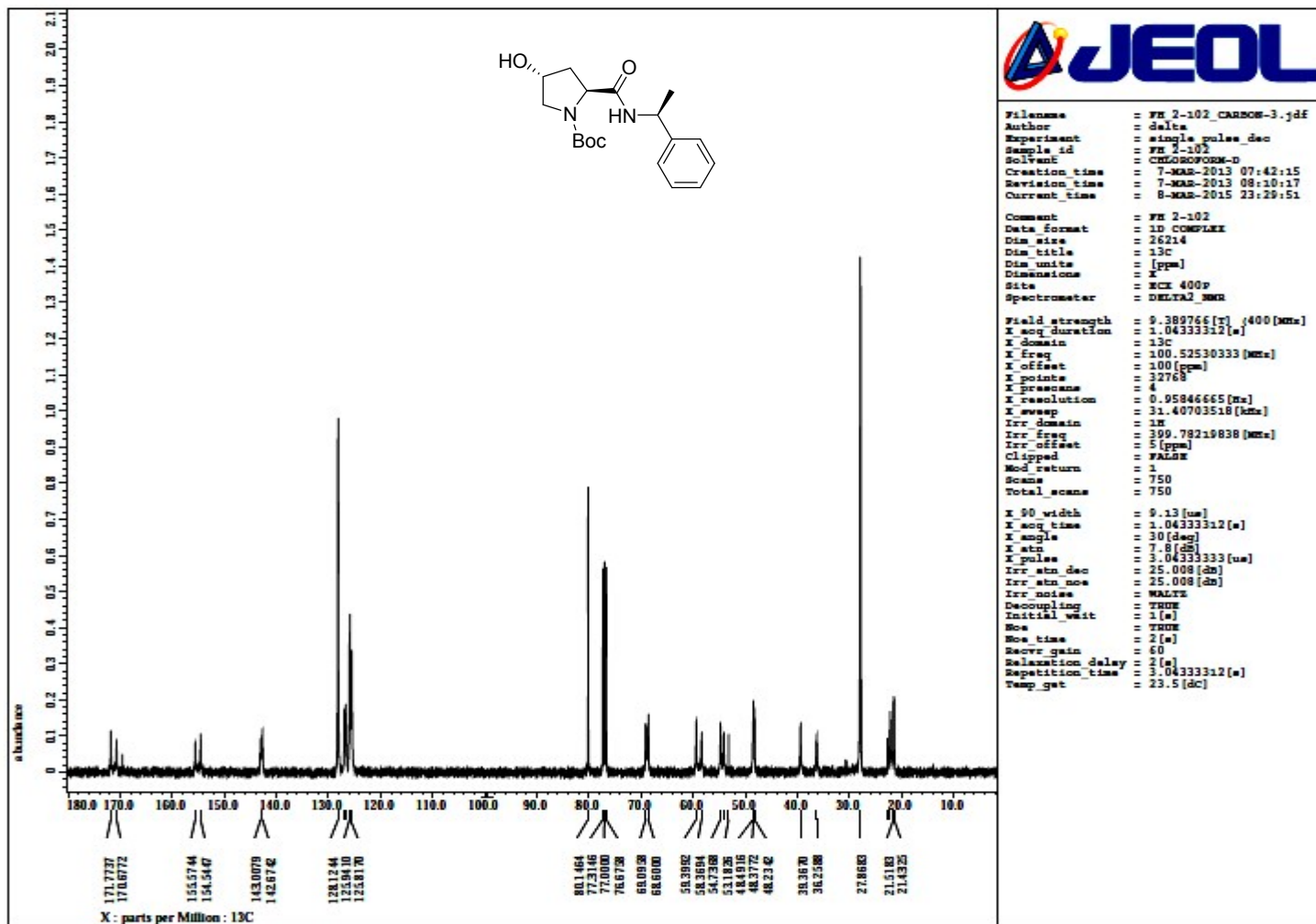
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Revision time = 8-MAR-2015 23:25:59
Current time  = 8-MAR-2015 23:26:56

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Data size    = 13107
Data title   = 1H
Data units   = [ppm]
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X domain       = 1H
X freq         = 399.78219838 [MHz]
X offset       = 5 [ppm]
X points       = 16384
X prescans     = 1
X resolution   = 0.73218757 [Hz]
X sweep        = 11.99616123 [kHz]
Irr domain    = 1H
Irr freq      = 399.78219838 [MHz]
Irr offset    = 5 [ppm]
Tri domain    = 1H
Tri freq      = 399.78219838 [MHz]
Tri offset    = 5 [ppm]
Clipped       = FALSE
Modf return   = 1
Scans         = 16
Total scans   = 16

X 90 width    = 11.31 [us]
X acq time    = 1.36577024 [s]
X angle       = 45 [deg]
X sbn         = 4.5 [dB]
X pulse       = 5.655 [us]
Irr mode      = OFF
Tri mode      = OFF
Dante preset  = FALSE
Initial wait  = 1 [s]
Recv gain     = 18
Relaxation delay = 4 [s]
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```



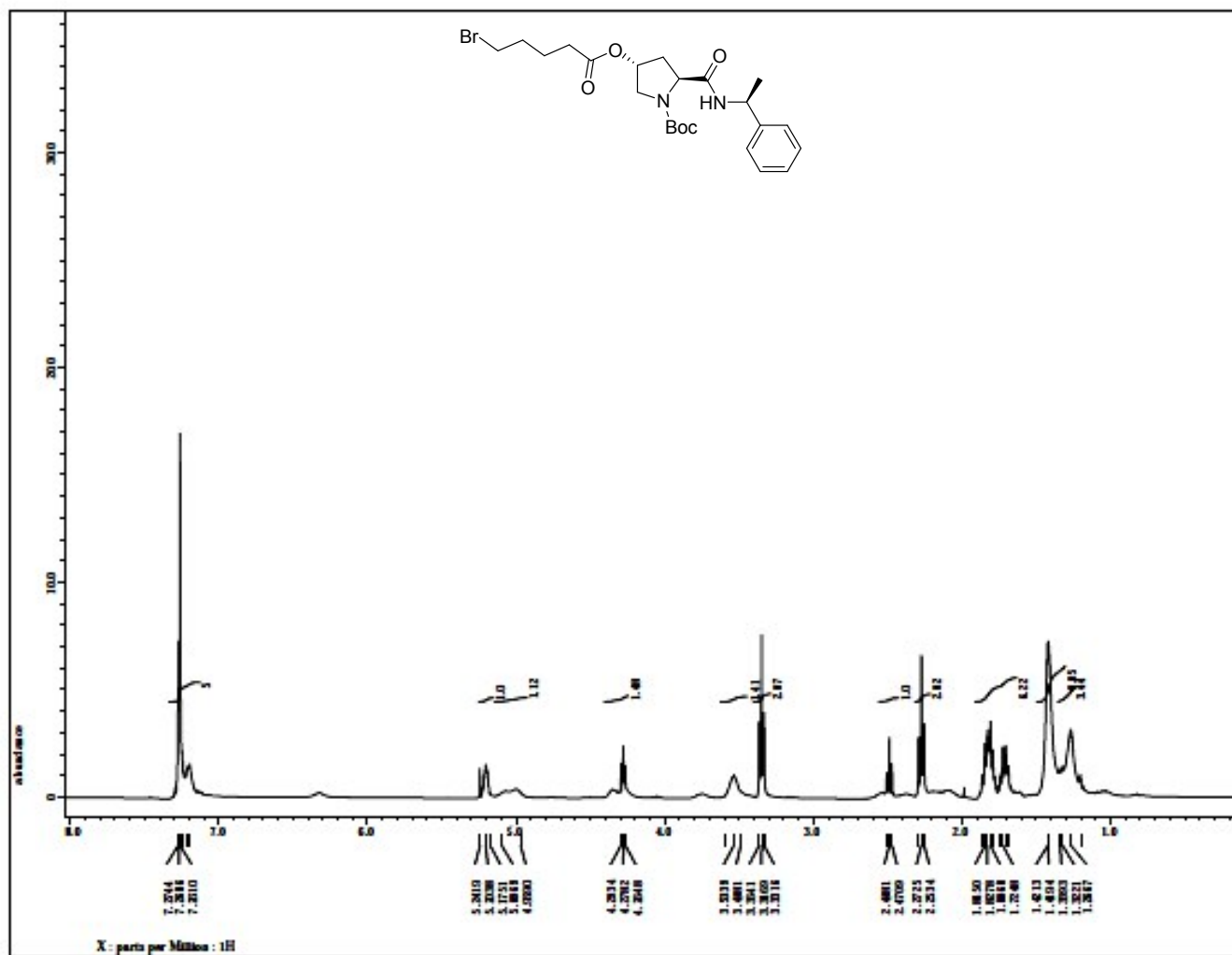
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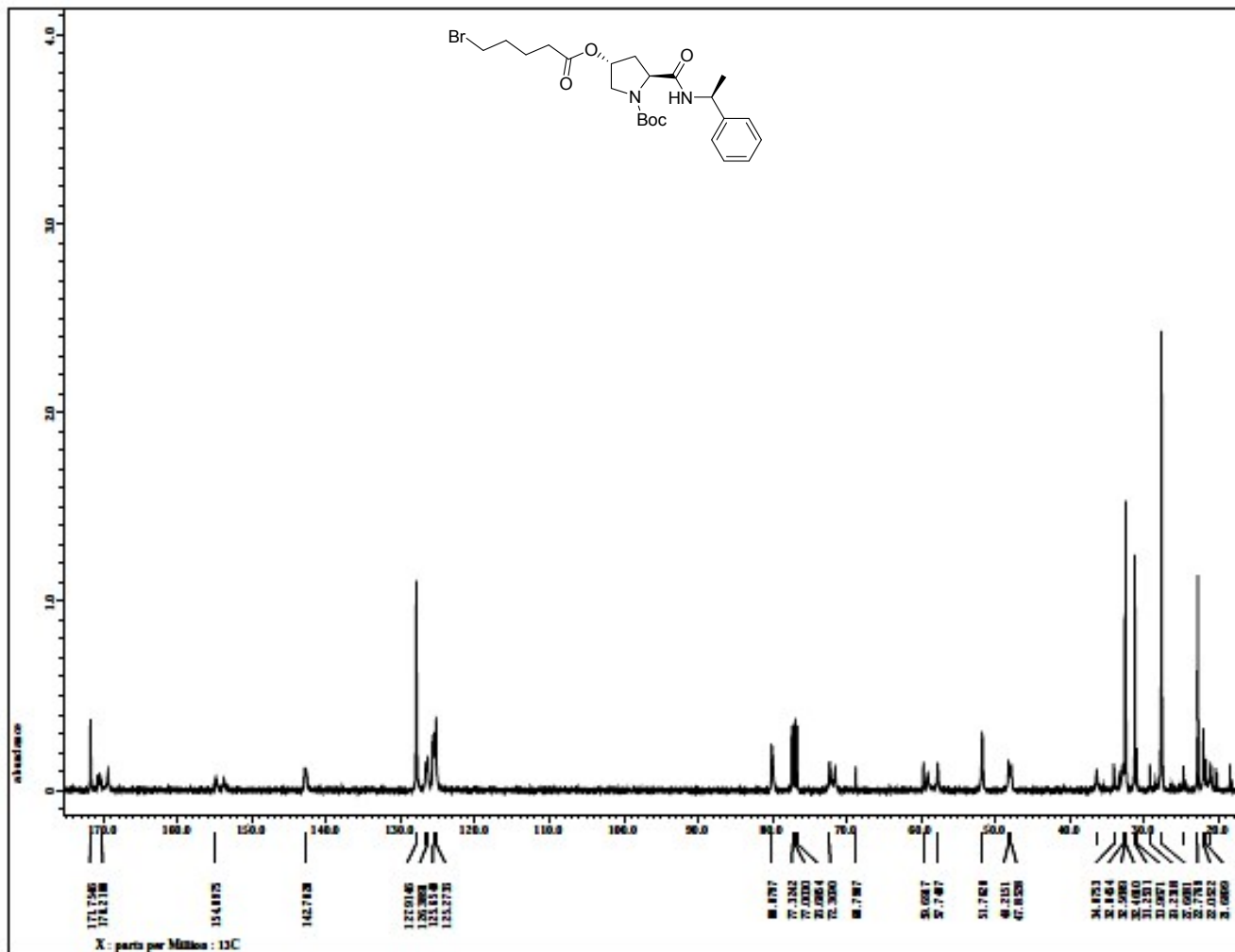
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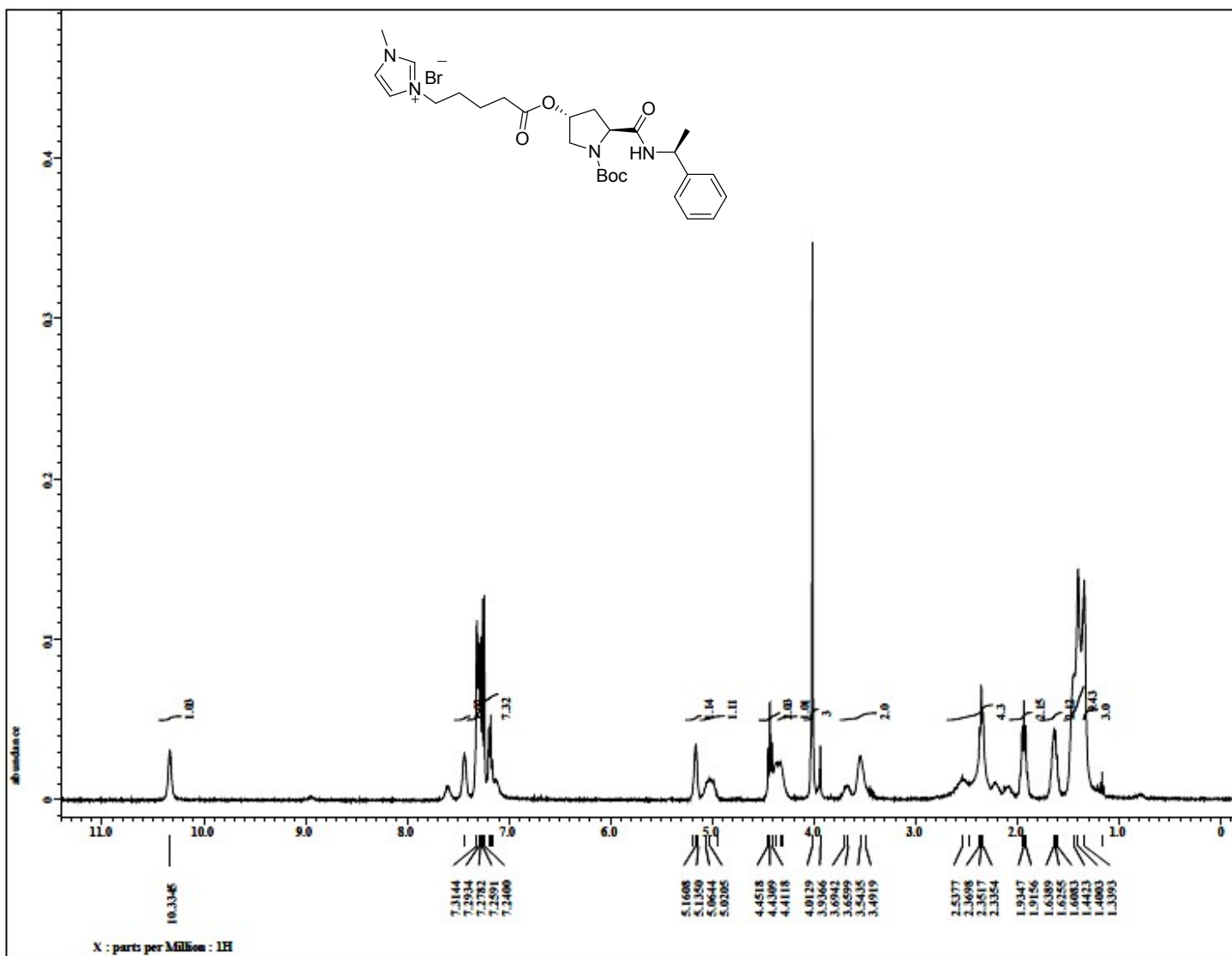
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Spectrometer = DELTA2_MMR

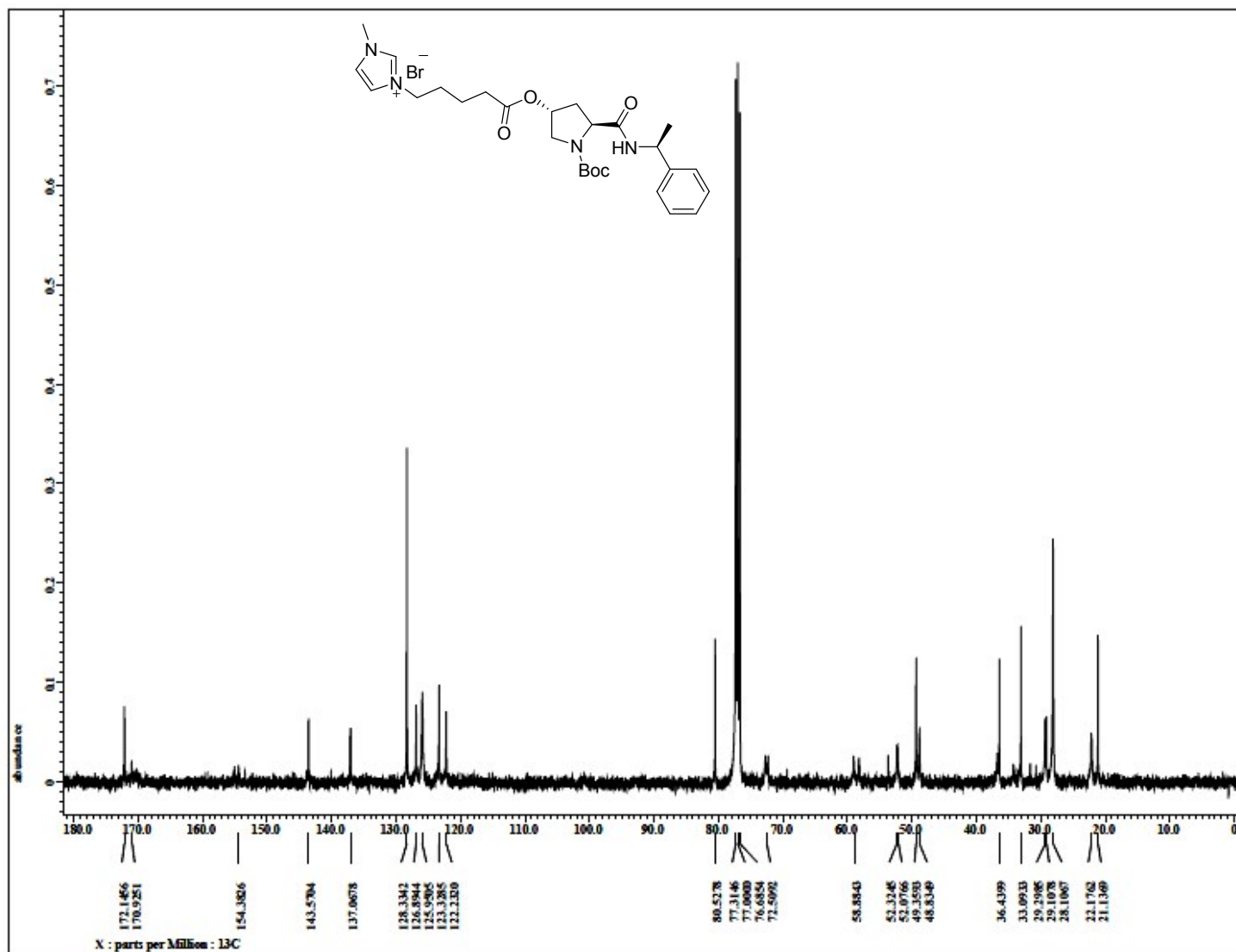
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X points      = 32768
X prescans    = 4
X resolution  = 0.95846665 [Hz]
X sweep       = 31.40703518 [kHz]
Irr domain    = 1H
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Clipped      = FALSE
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Total scans   = 750

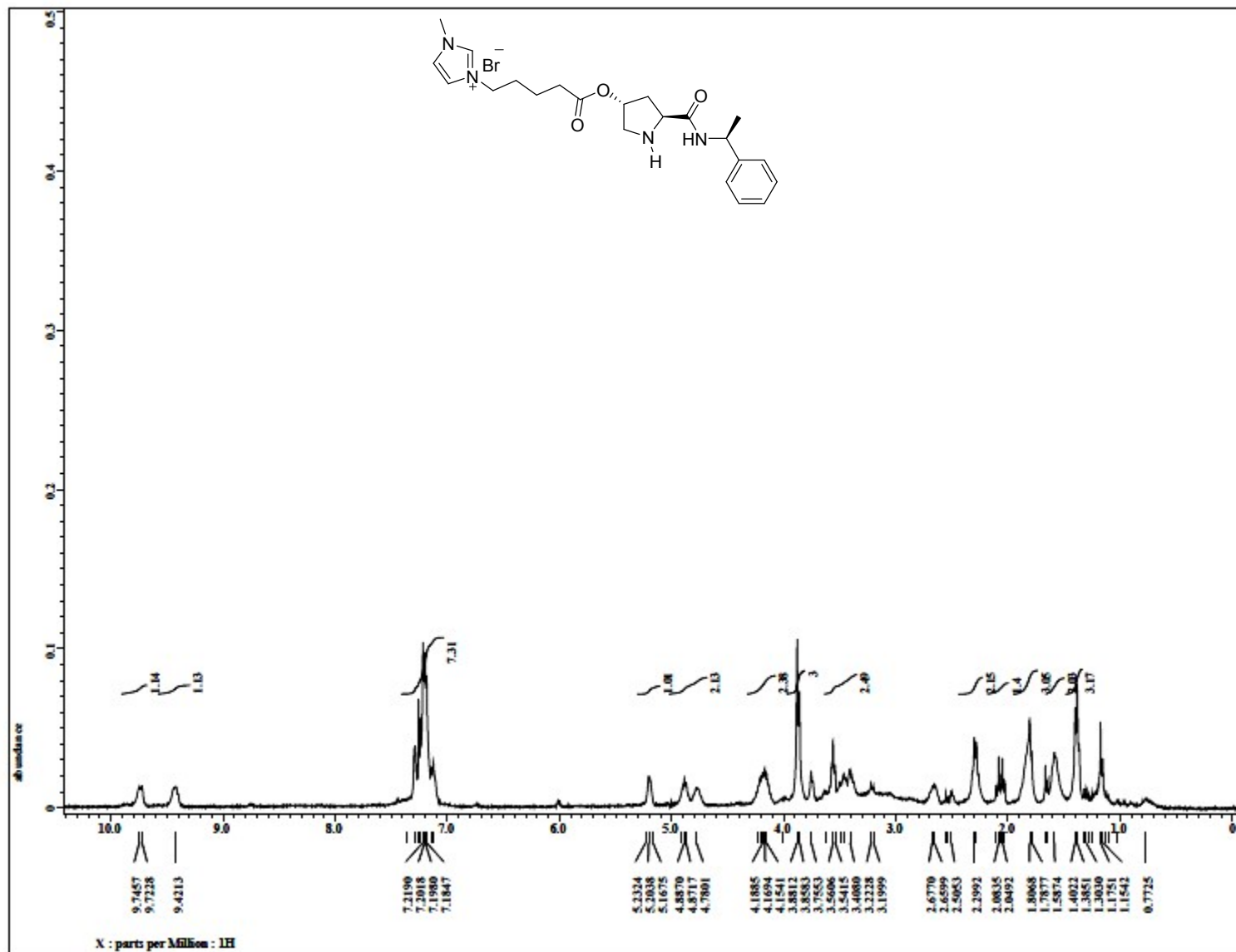
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X acq time    = 1.04333312 [s]
X angle       = 30 [deg]
X stn         = 7.8 [dB]
X pulse       = 3.04333333 [us]
Irr stn_dec   = 25.008 [dB]
Irr stn_noc   = 25.008 [dB]
Irr noise     = WALTZ
Decoupling    = TRUE
Initial wait  = 1 [s]
Noe           = TRUE
Noe time      = 2 [s]
Recvr gain    = 60
Relaxation delay = 2 [s]
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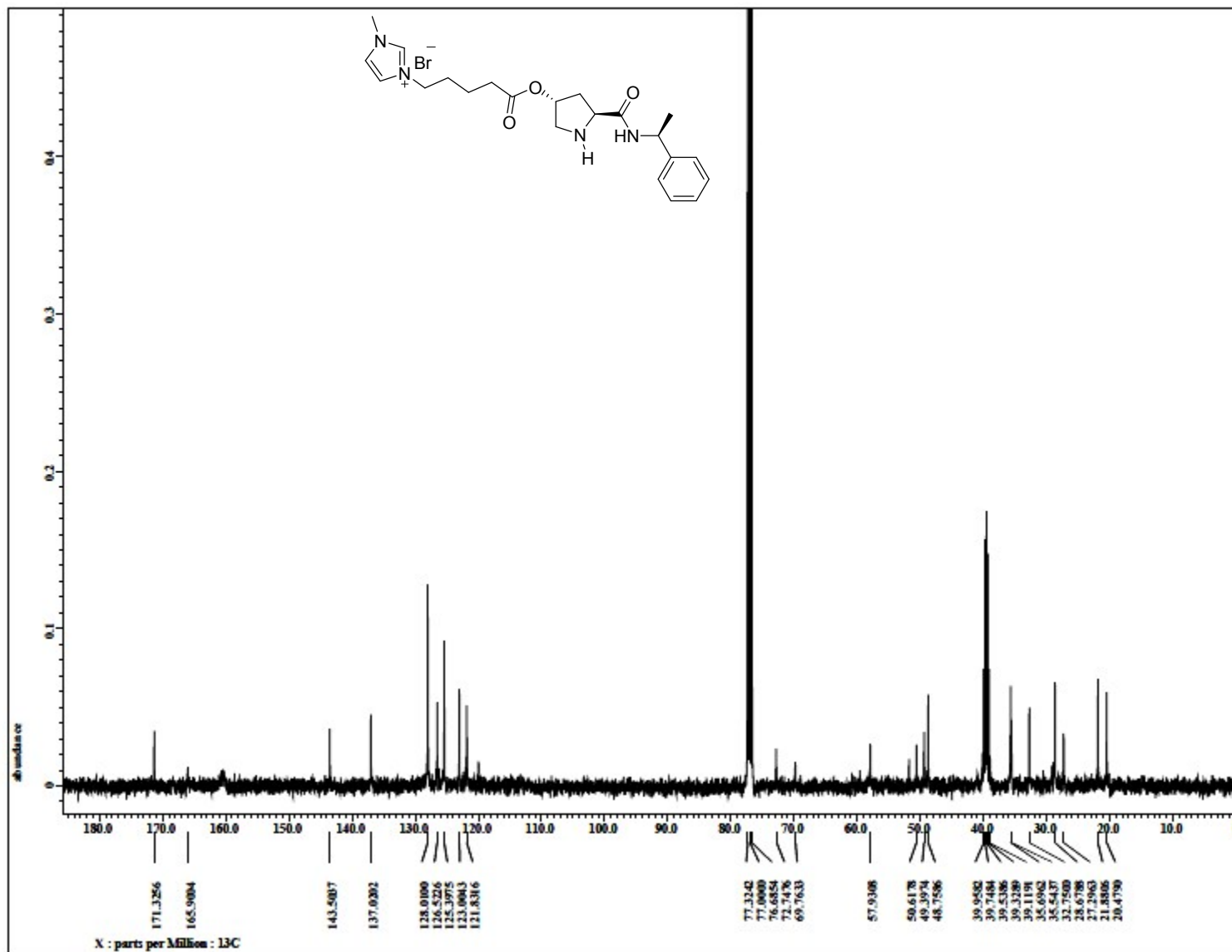


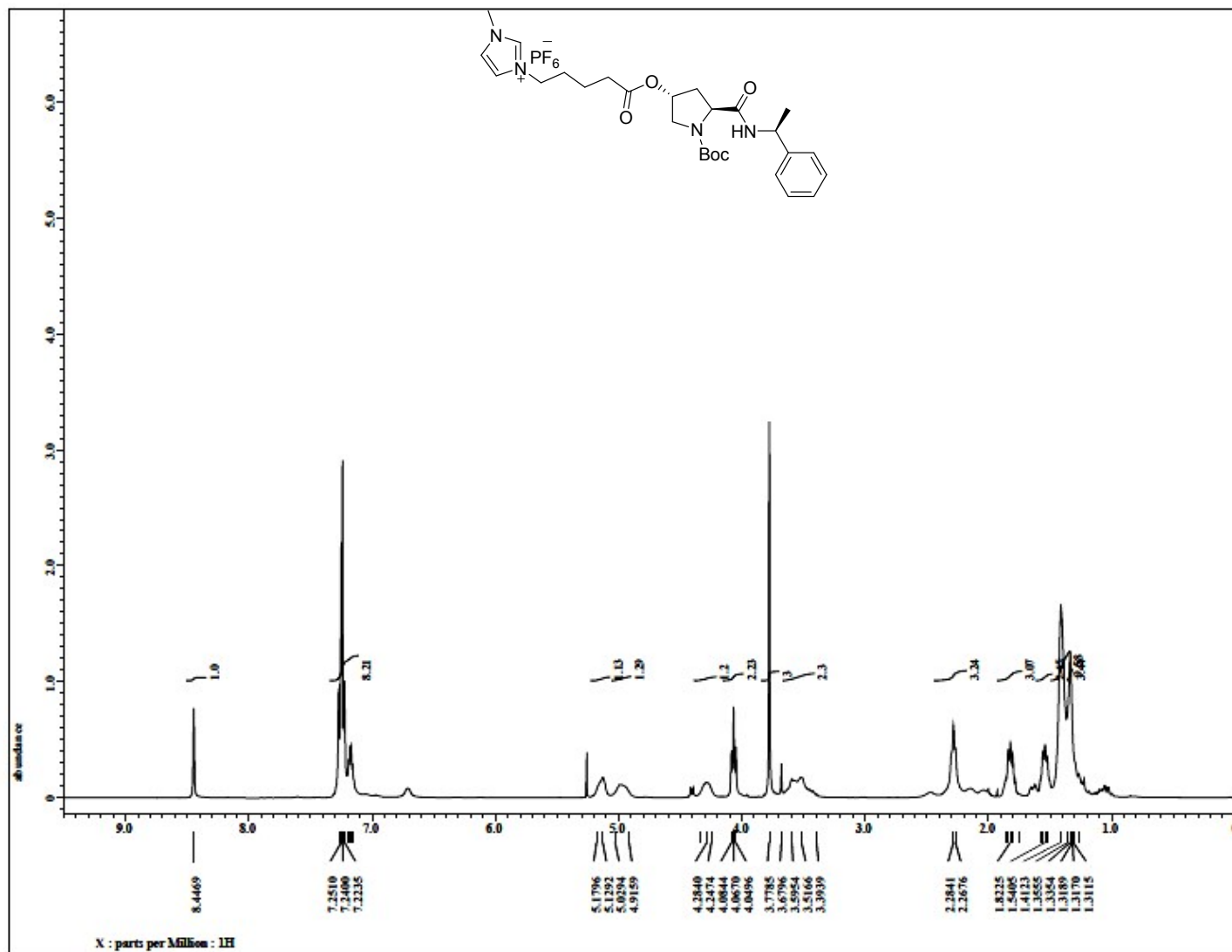


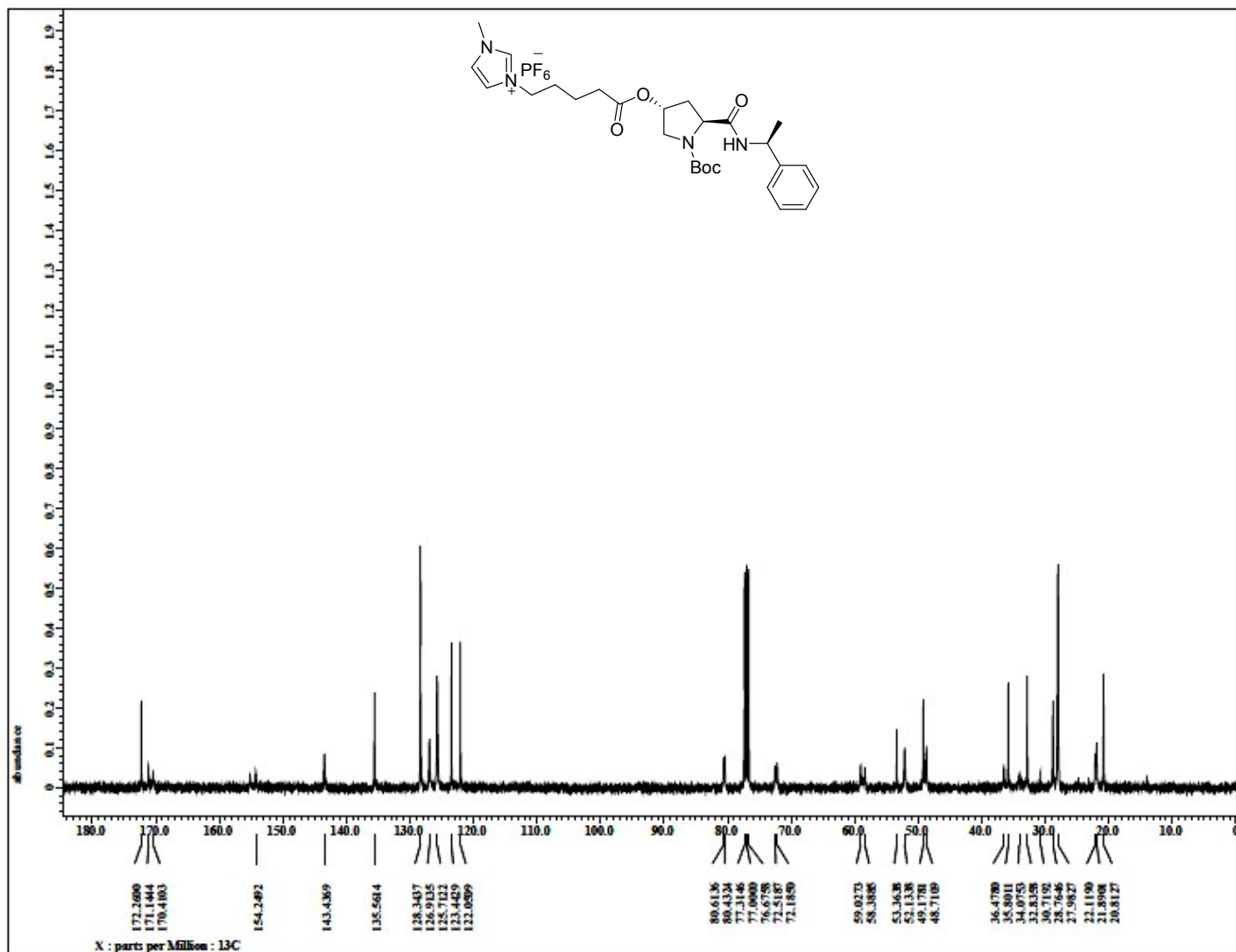


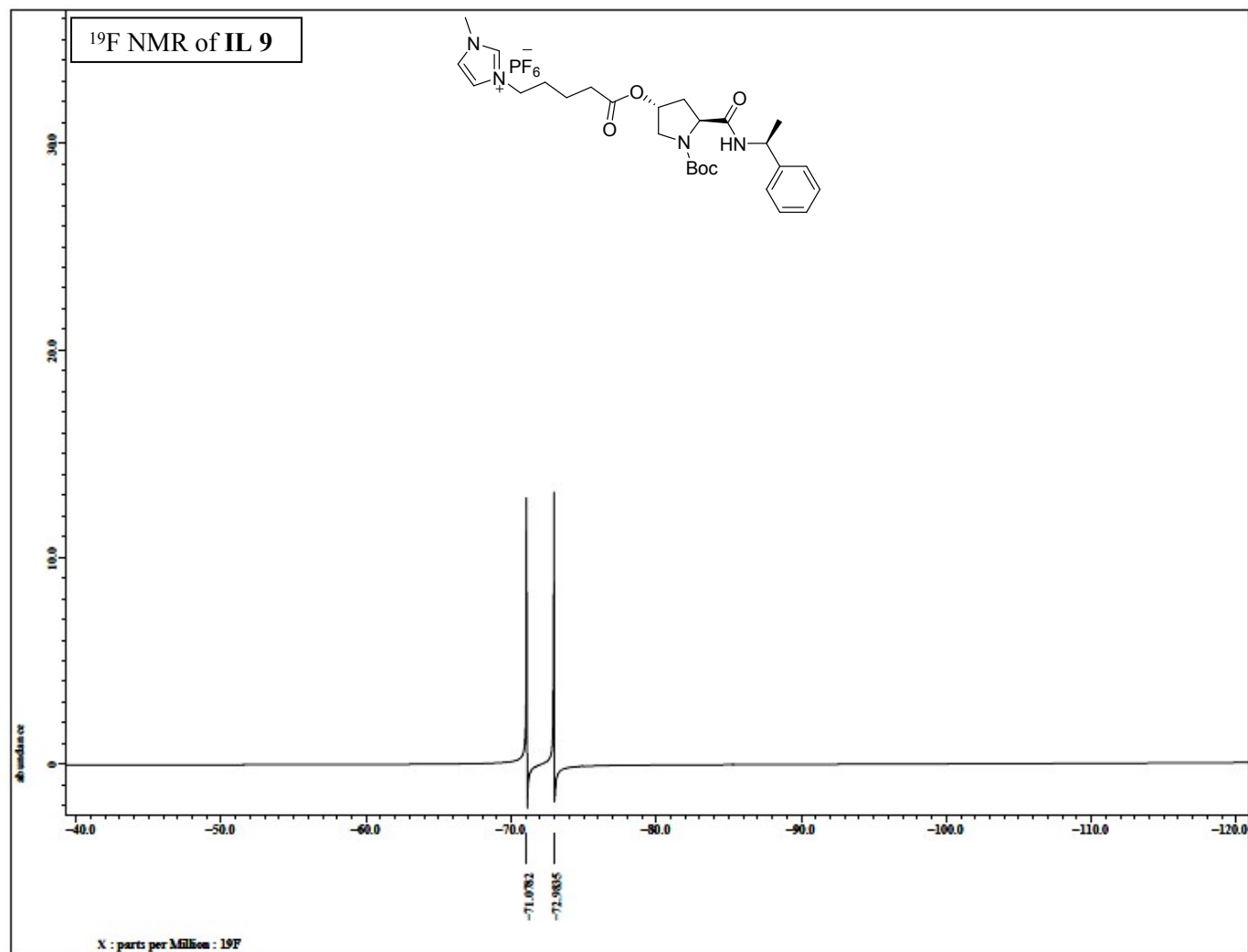


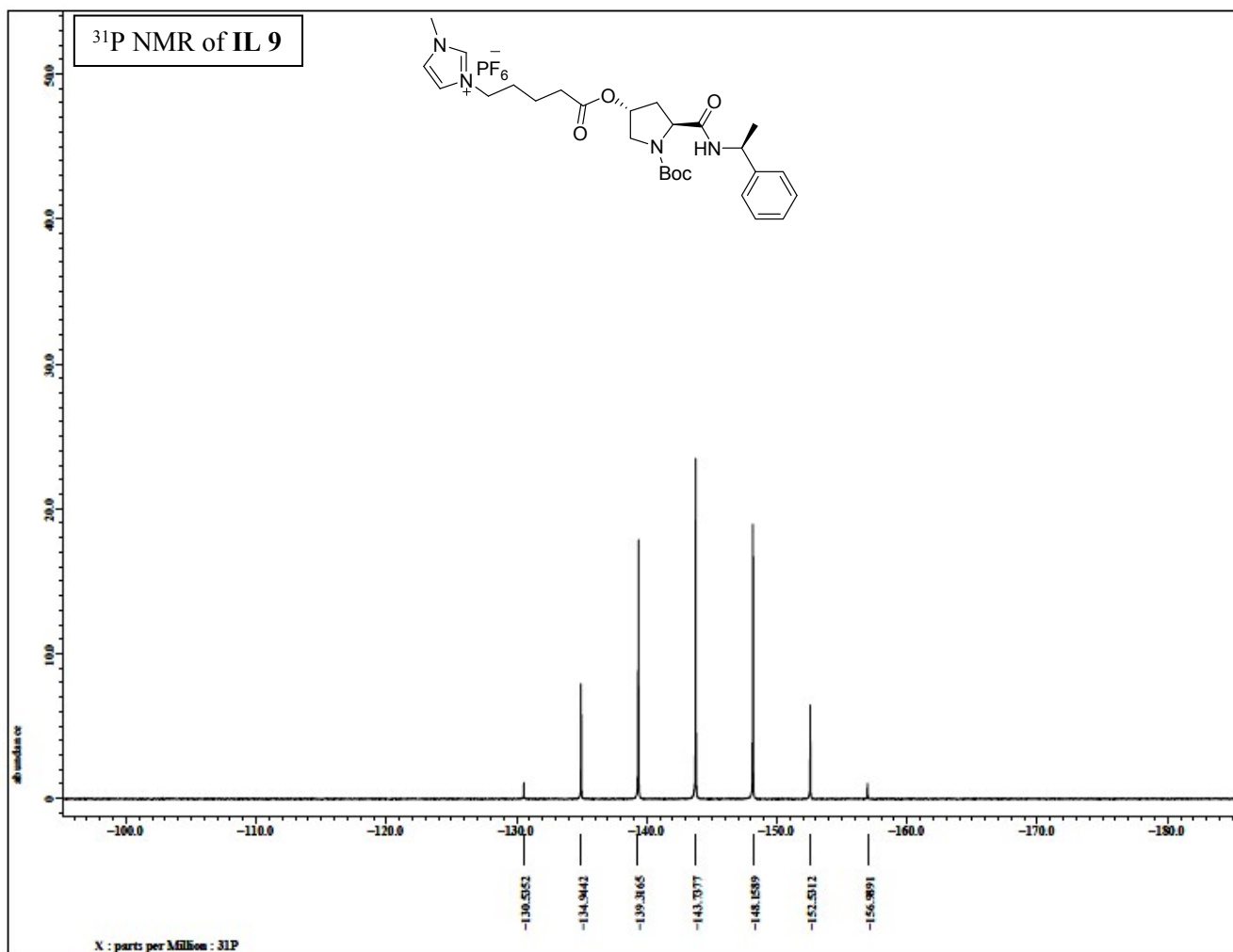


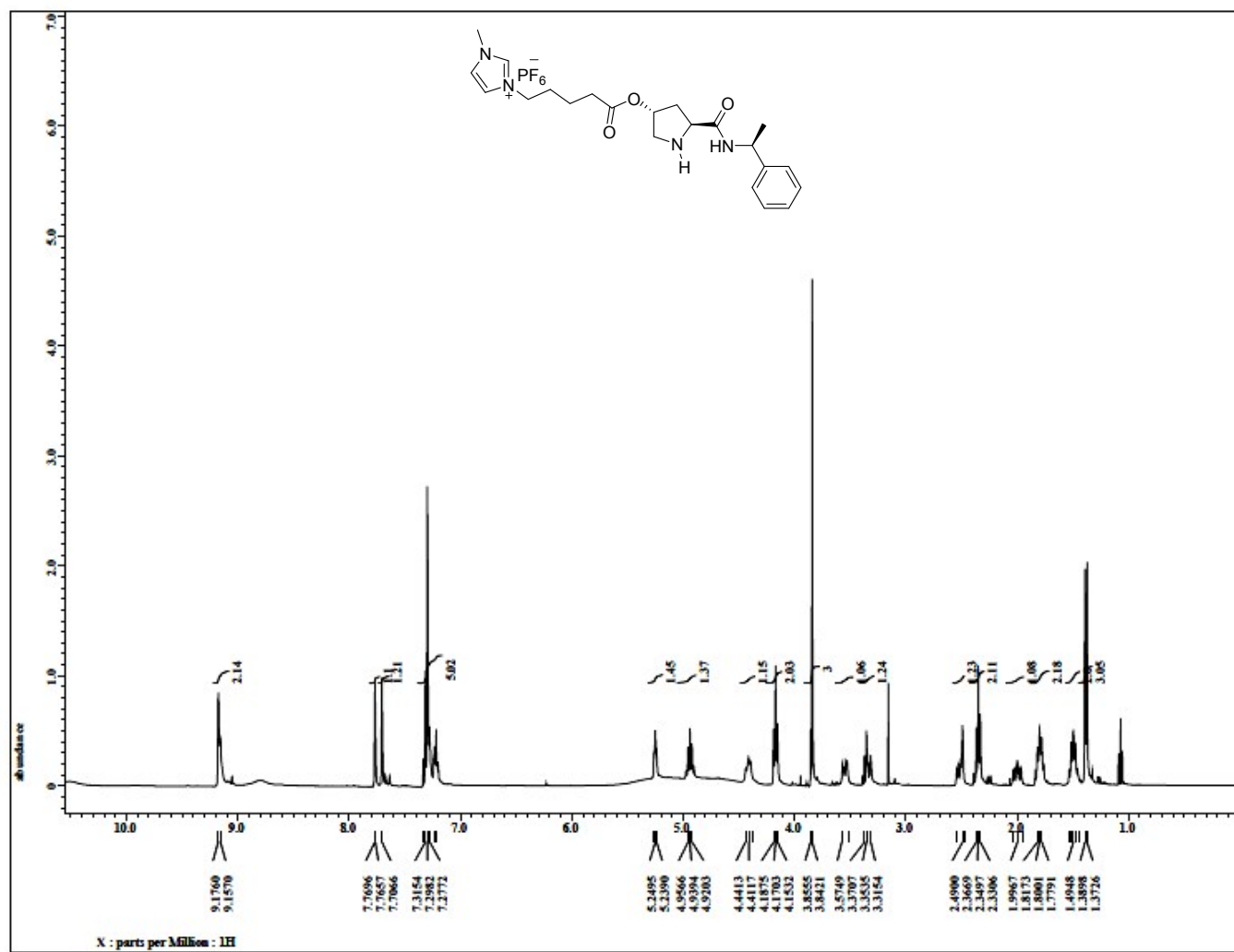


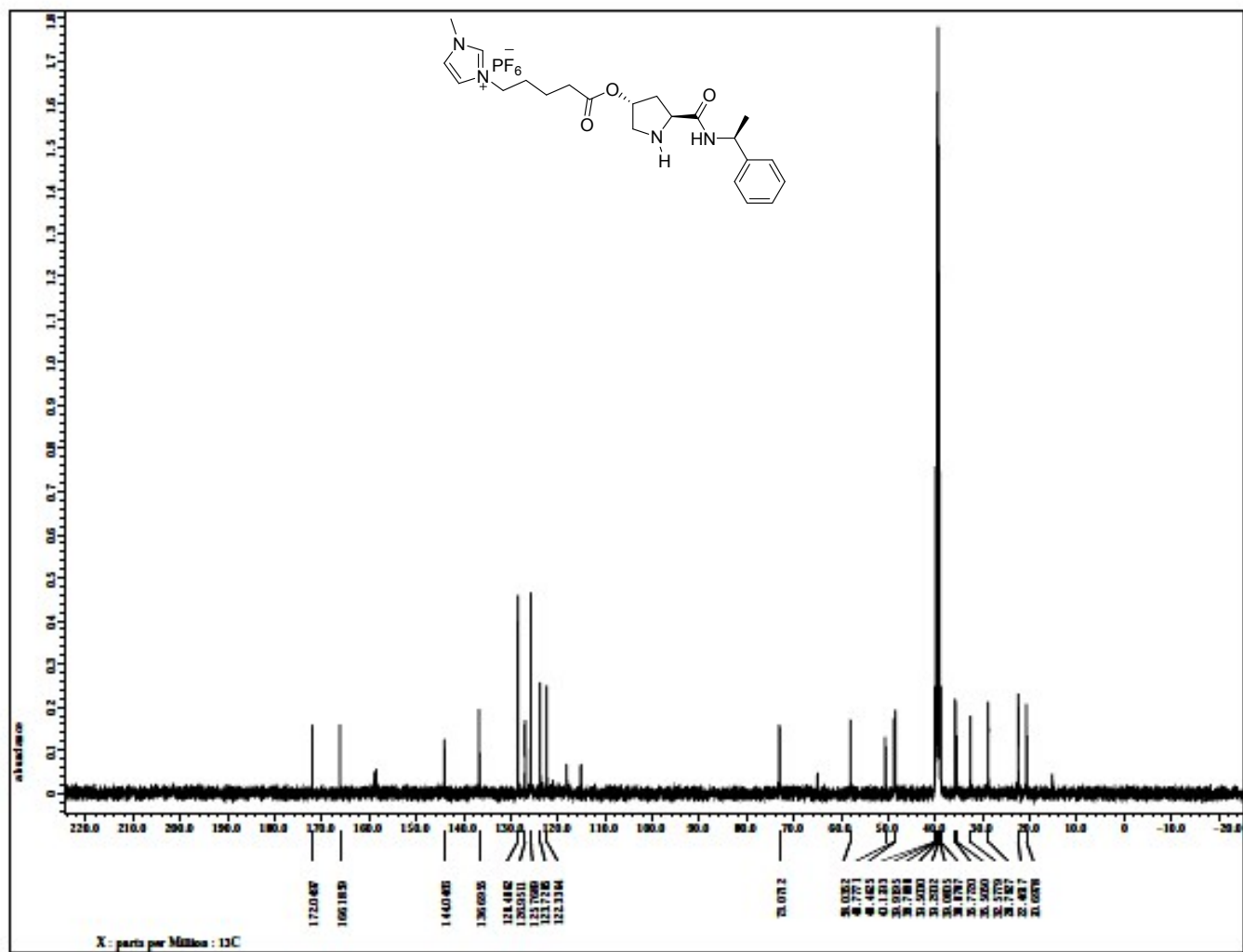




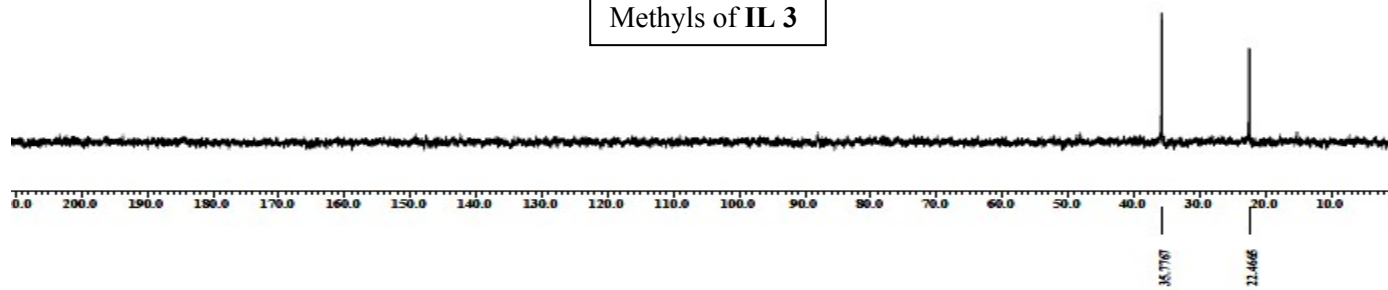




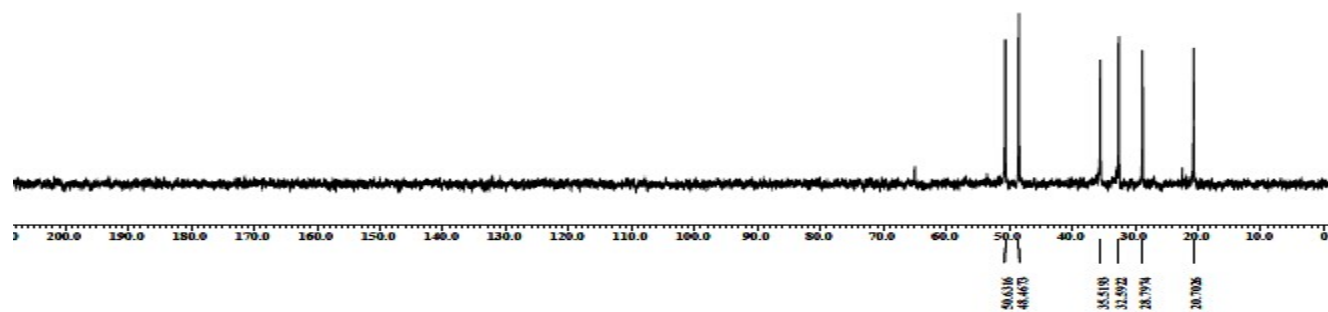




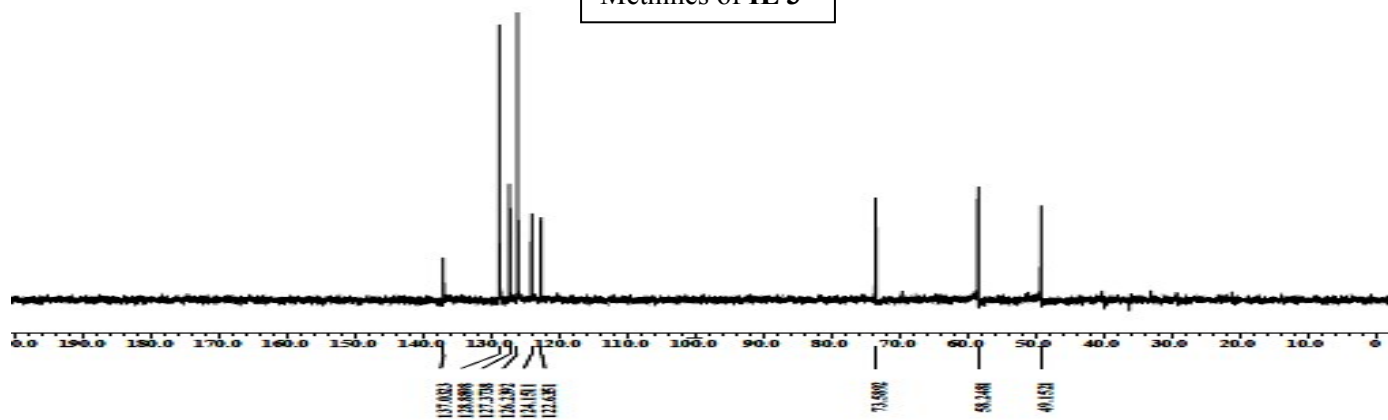
Methyls of IL 3

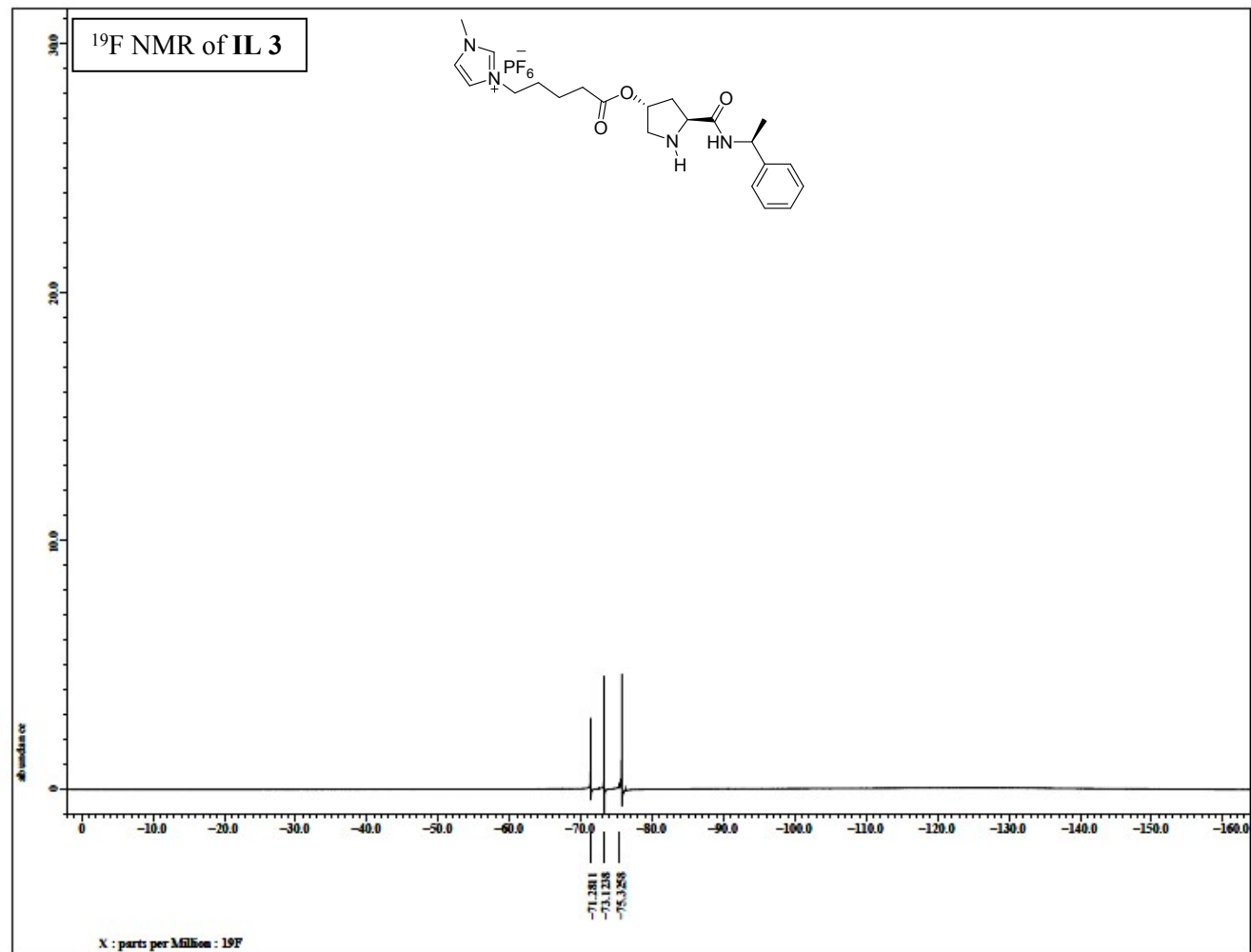


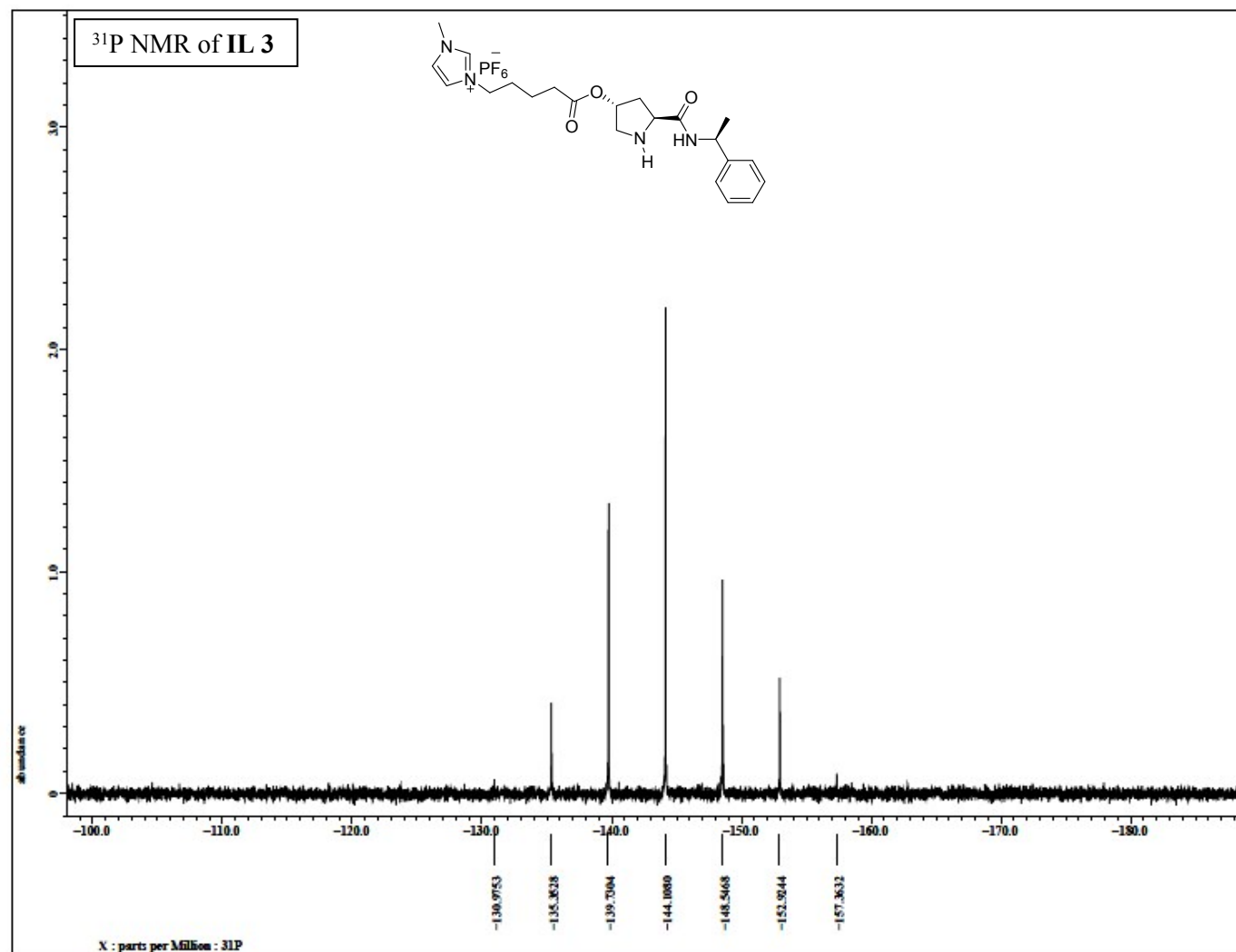
Methylenes of IL 3

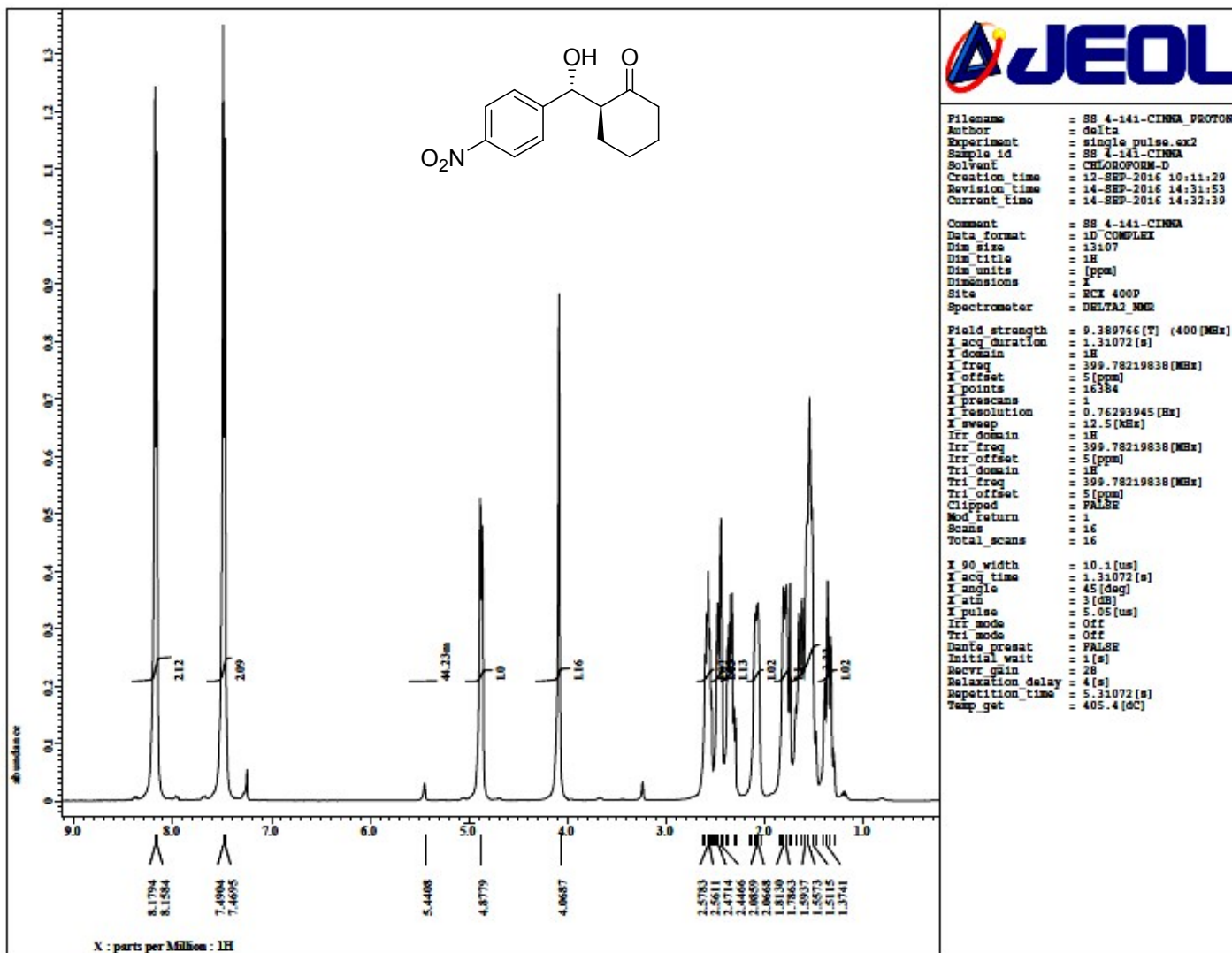


Methines of IL 3









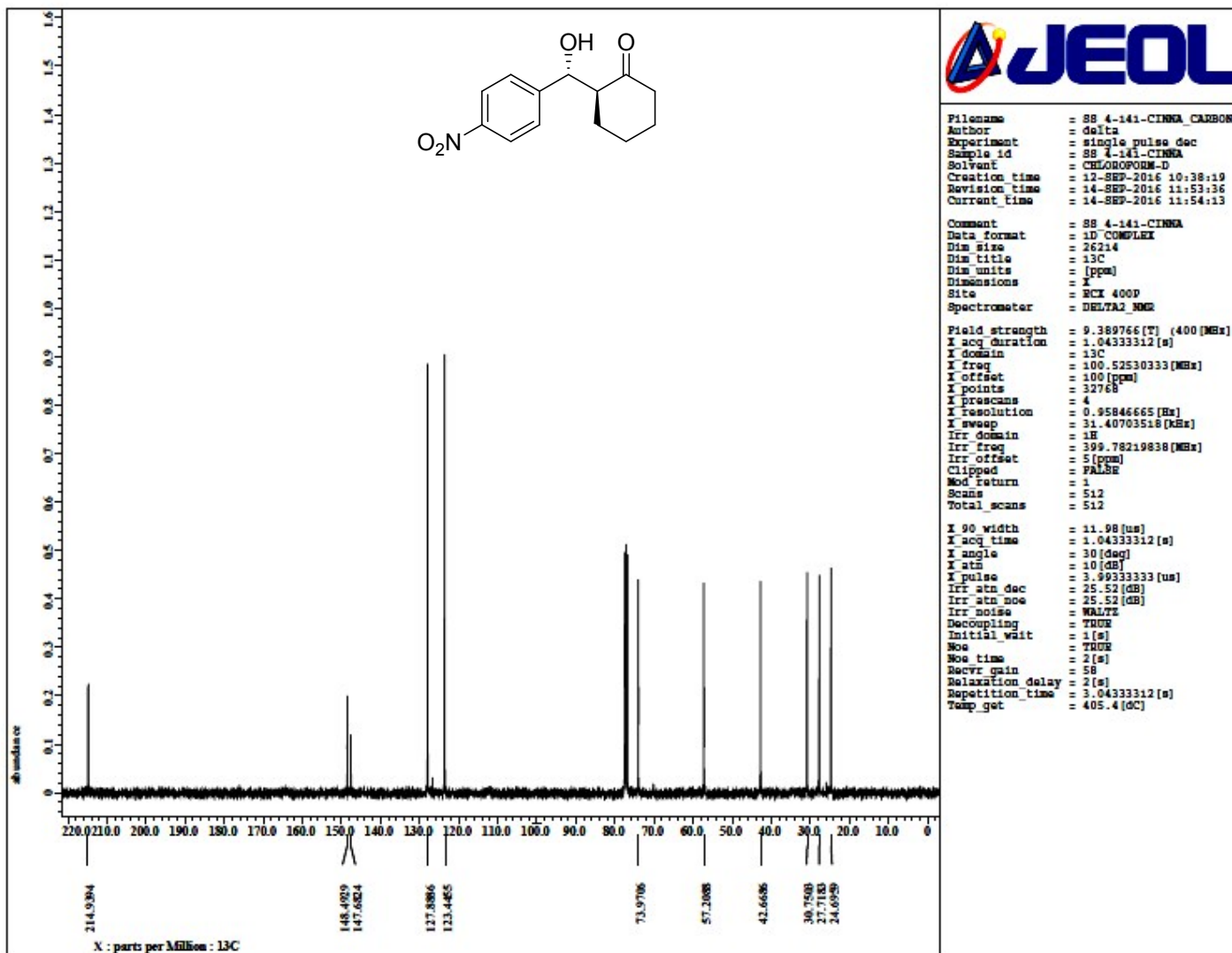
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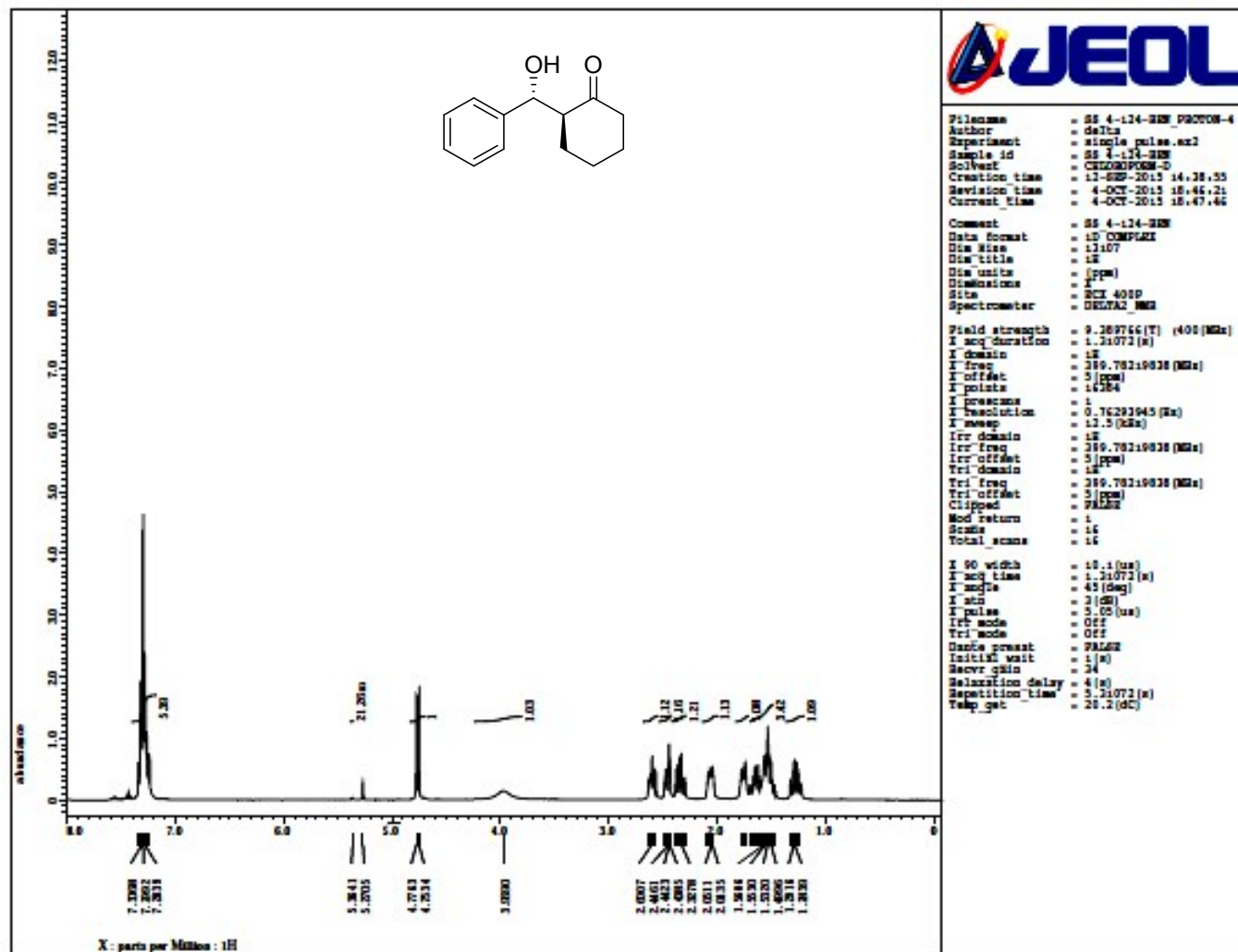
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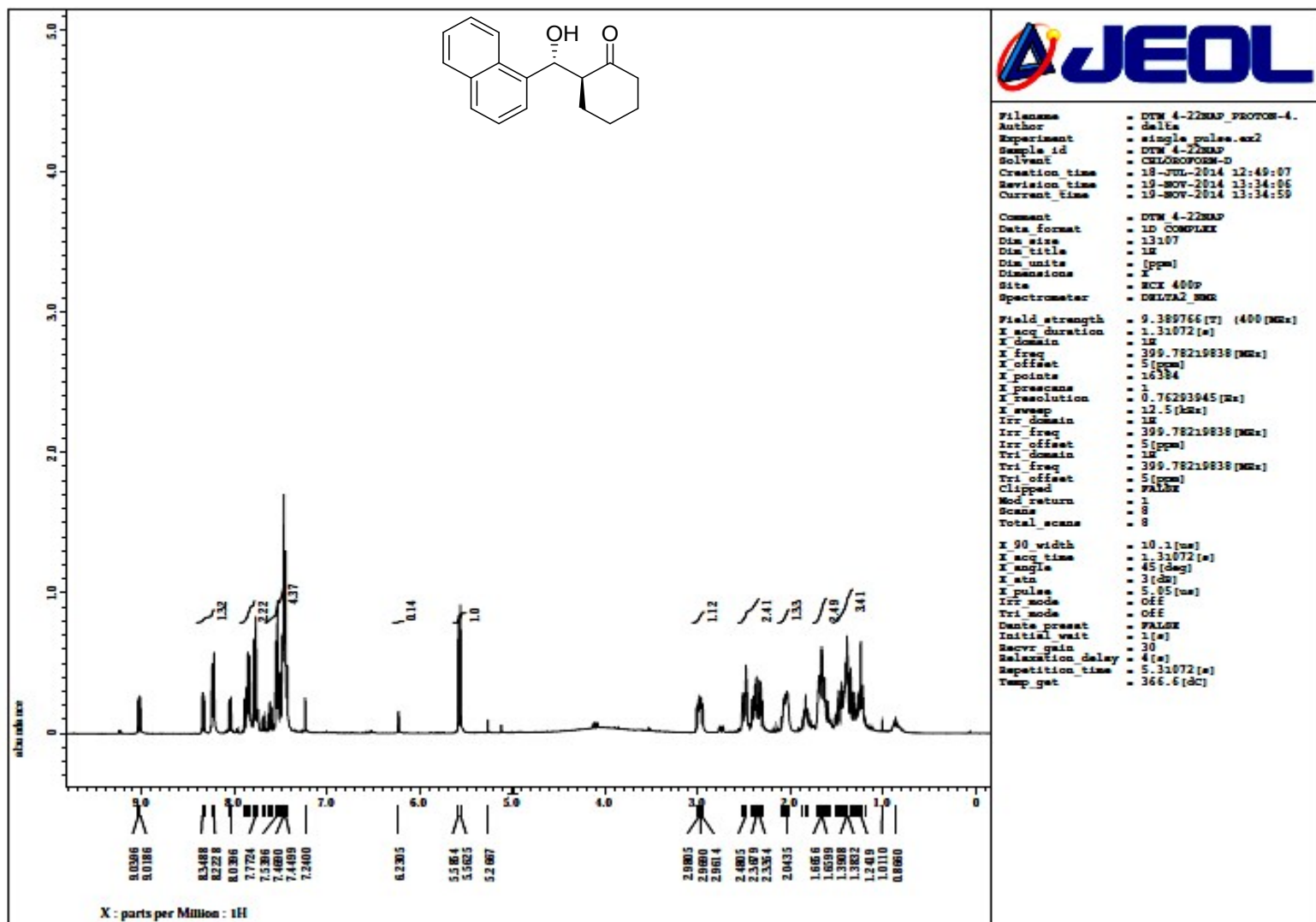
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X_freq         = 399.78219838 [MHz]
X_offset       = 5 [ppm]
X_points       = 16384
X_prescans     = 1
X_resolution   = 0.76293945 [Hz]
X_sweep        = 12.5 [MHz]
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F1_freq        = 399.78219838 [MHz]
F1_offset       = 5 [ppm]
Clipped        = FALSE
Mod return     = 1
Scans          = 16
Total scans    = 16

X_90 width    = 10.1 [us]
X_acq time     = 1.31072 [s]
X_angle        = 45 [deg]
X_atn          = 3 [dB]
X_pulse        = 5.05 [us]
F1_mode        = Off
F1_offset       = Off
Date preset    = FALSE
Initial wait   = 1 [s]
Recvr gain     = 28
Relaxation delay = 4 [s]
Repetition time = 5.31072 [s]
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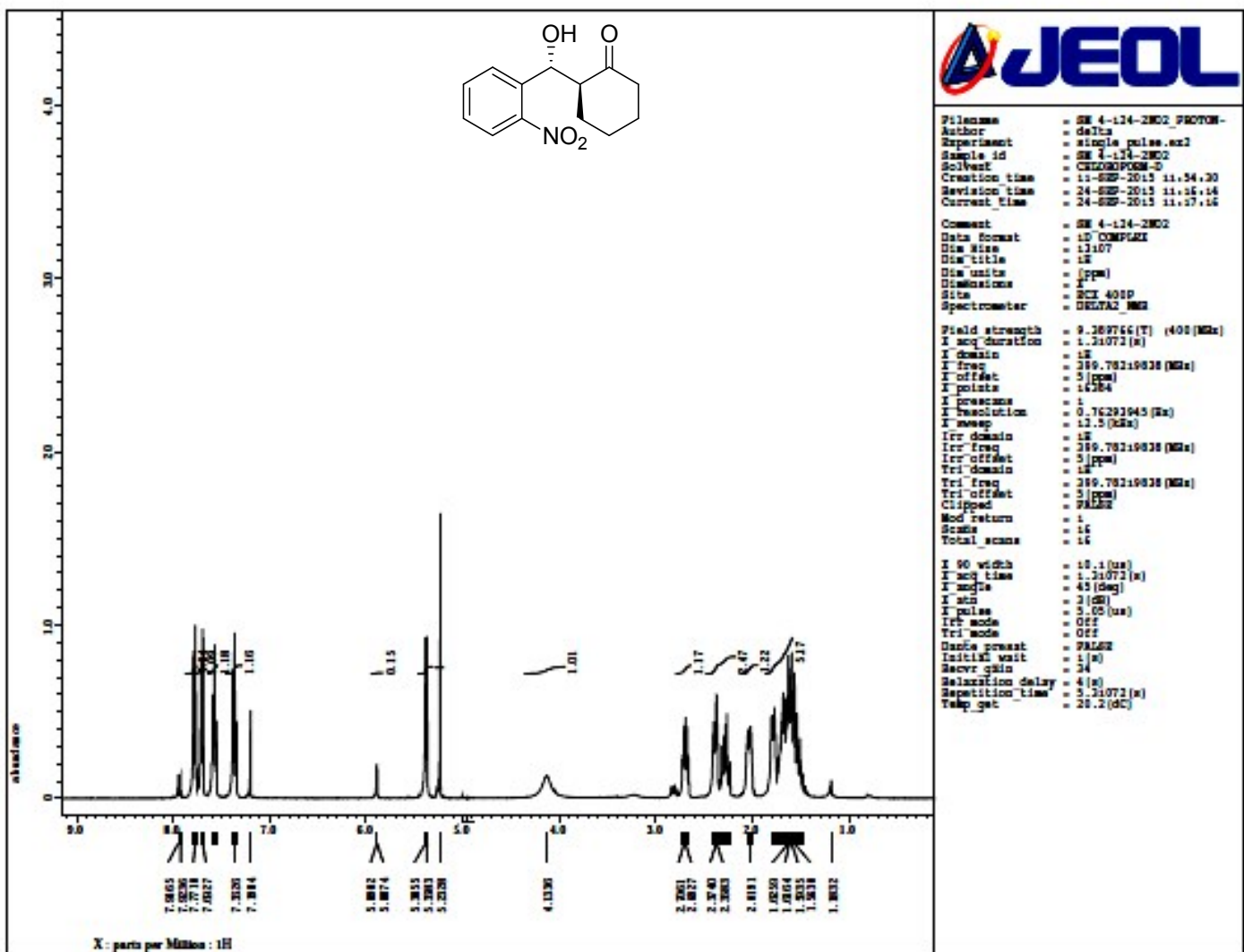
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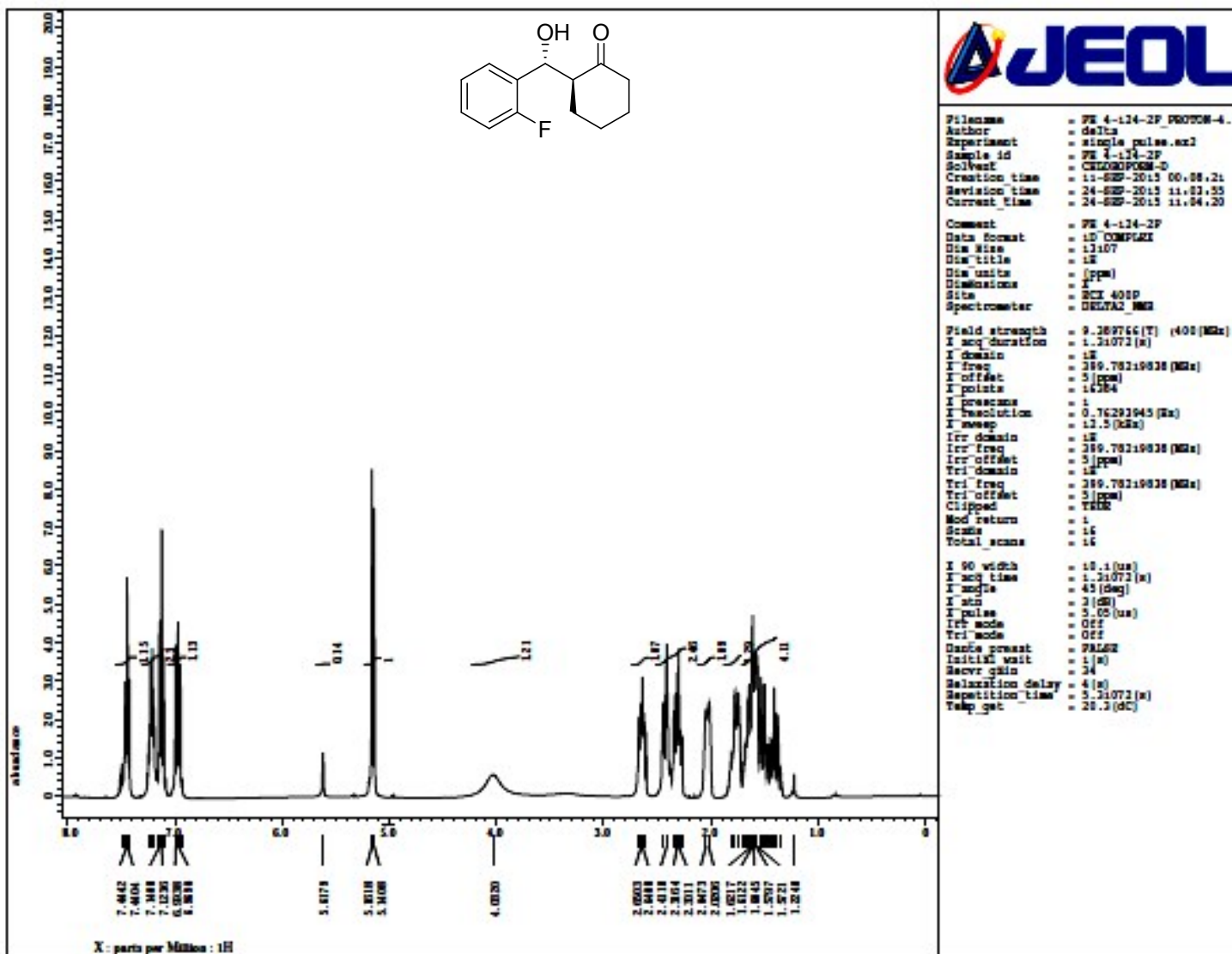
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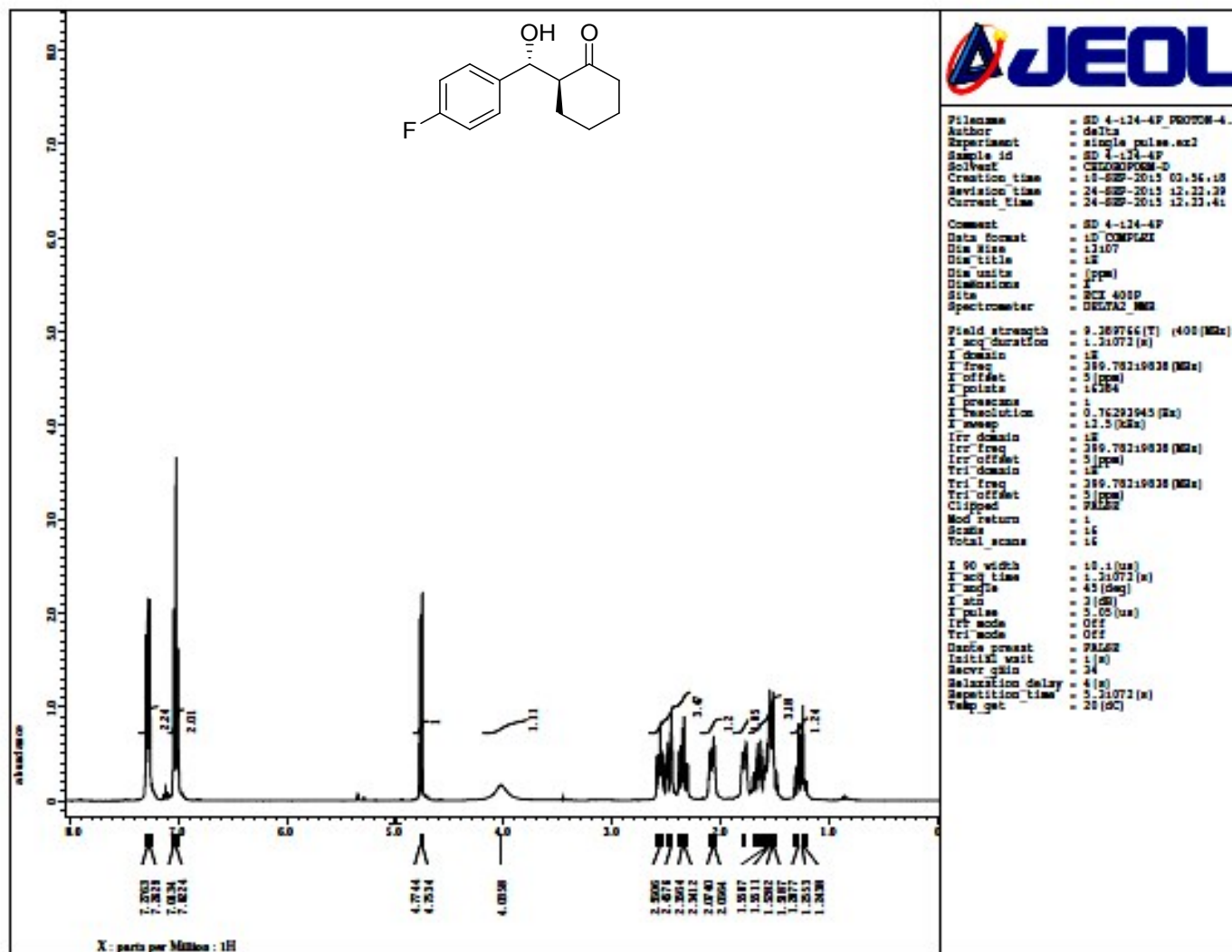
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F1 points      = 16384
F1 prescans    = 1
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F1 sweep       = 12.5 [kHz]
F1r domain     = 1H
F1r freq       = 399.78219838 [MHz]
F1r offset     = 5 [ppm]
F1r points     = 1H
F1r prescans  = 1
F1r resolution = 0.76293945 [Hz]
F1r sweep      = 12.5 [kHz]
F1r domain     = 1H
F1r freq       = 399.78219838 [MHz]
F1r offset     = 5 [ppm]
Clipped       = FALSE
Mod return    = 1
Scans         = 8
Total scans   = 8

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F2r mode      = OEE
Dante preset   = FALSE
Initial wait   = 1 [s]
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Relaxation delay = 4 [s]
Repetition time = 5.31072 [s]
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```

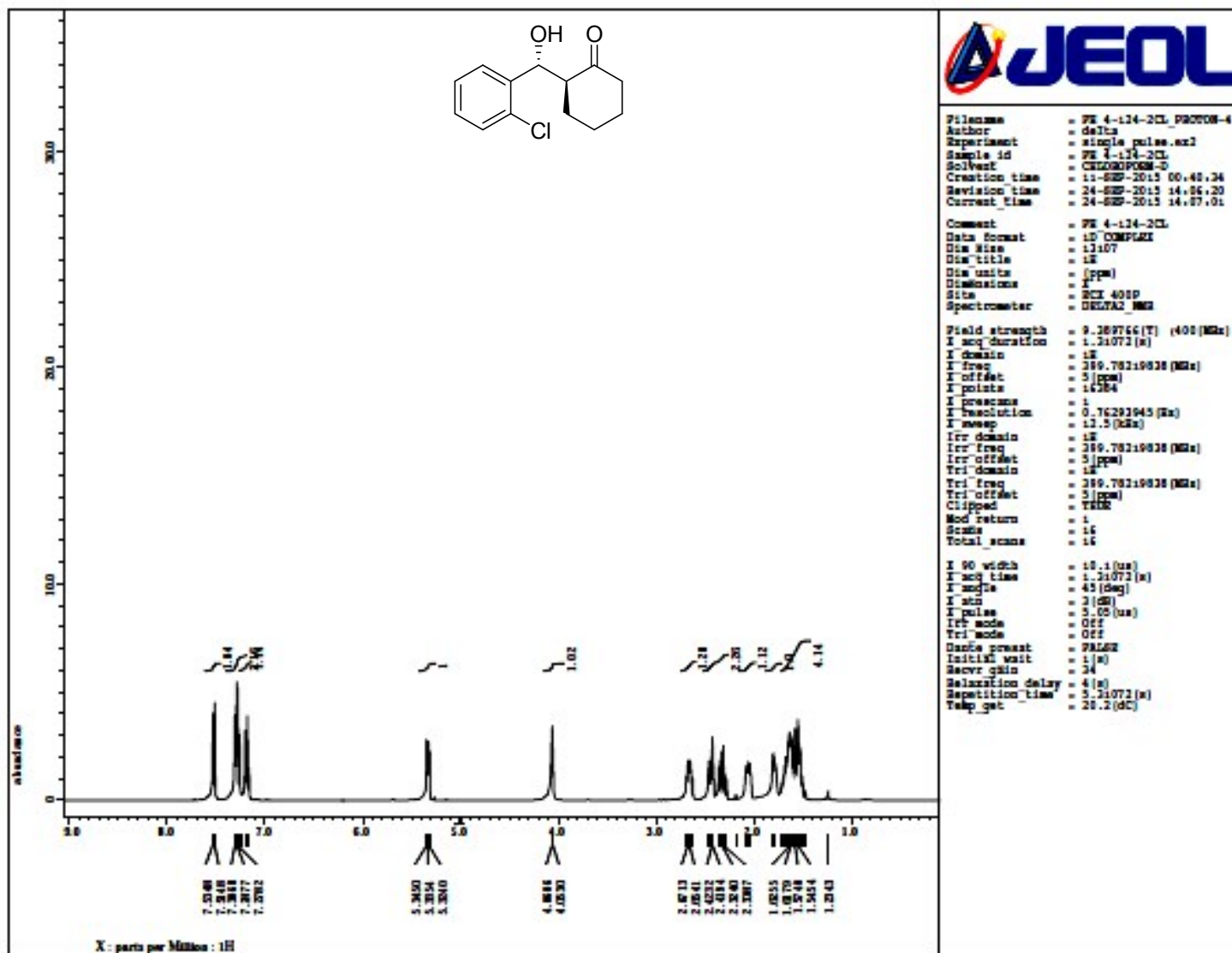
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Revision time = 24-SEP-2015 12:32:39
Current time  = 24-SEP-2015 12:32:41

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Data units    = (ppm)
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F1 freq        = 399.78219838 (MHz)
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F1 points      = 14284
F1 prescans    = 1
F1 resolution  = 0.76293945 (Hz)
F1 sweep       = 12.5 (kHz)
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F1rr freq      = 399.78219838 (MHz)
F1rr offset    = 5 (ppm)
F1rr domain    = 1H
F1rr freq      = 399.78219838 (MHz)
F1rr offset    = 5 (ppm)
Clipped       = FALSE
Mod return    = 1
Scale         = 16
Total scans   = 16

F1 90 width    = 10.1 (us)
F1 acq time    = 1.31072 (s)
F1 angle       = 45 (deg)
F1 str         = 2 (dB)
F1 pulse       = 5.05 (us)
F1r mode       = Off
F1rr mode      = Off
Datae preset   = PALSI
Initia1 wait   = 1 (s)
Recvr gain     = 34
Relaxation delay = 4 (s)
Repetition time = 1.31072 (s)
Temp_get       = 20 (C)

```



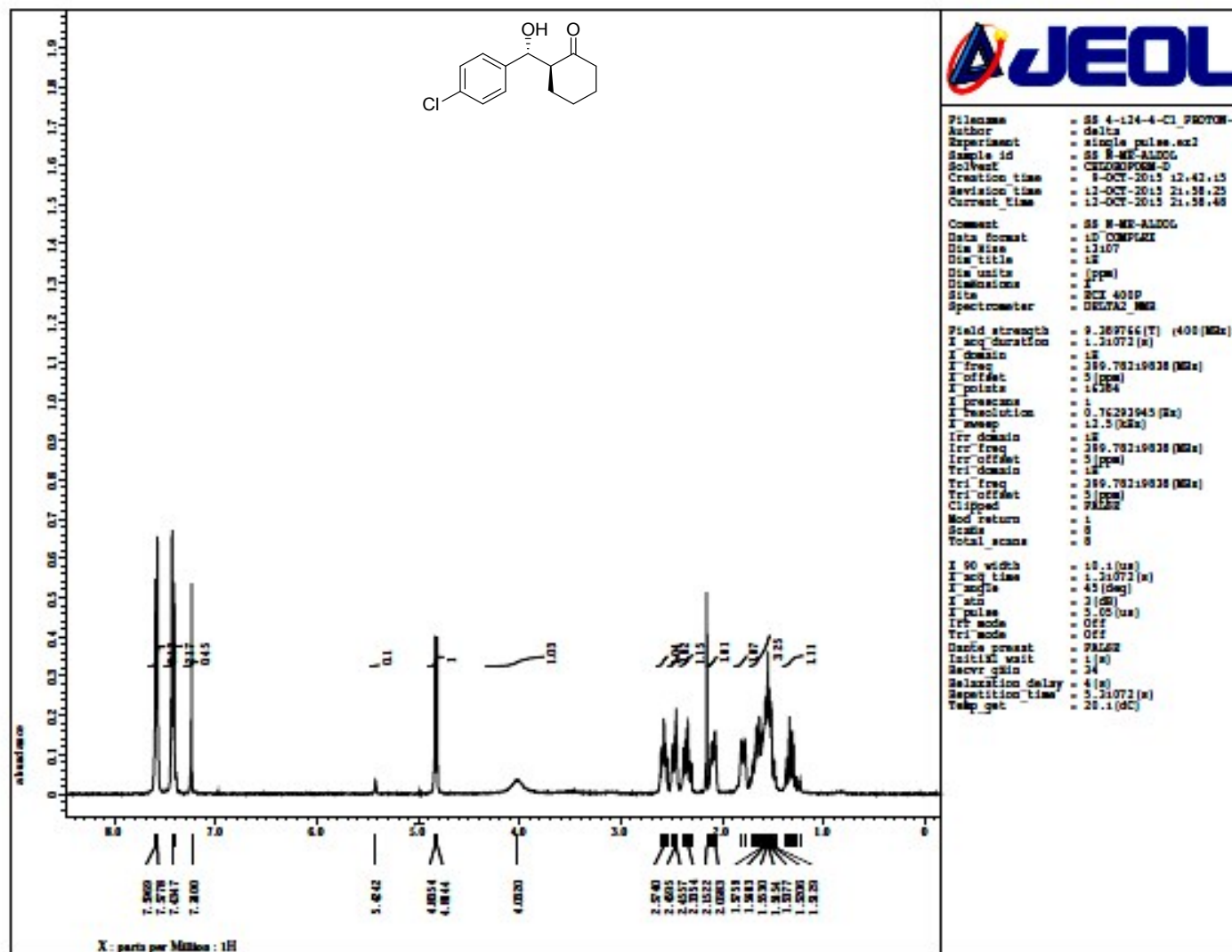
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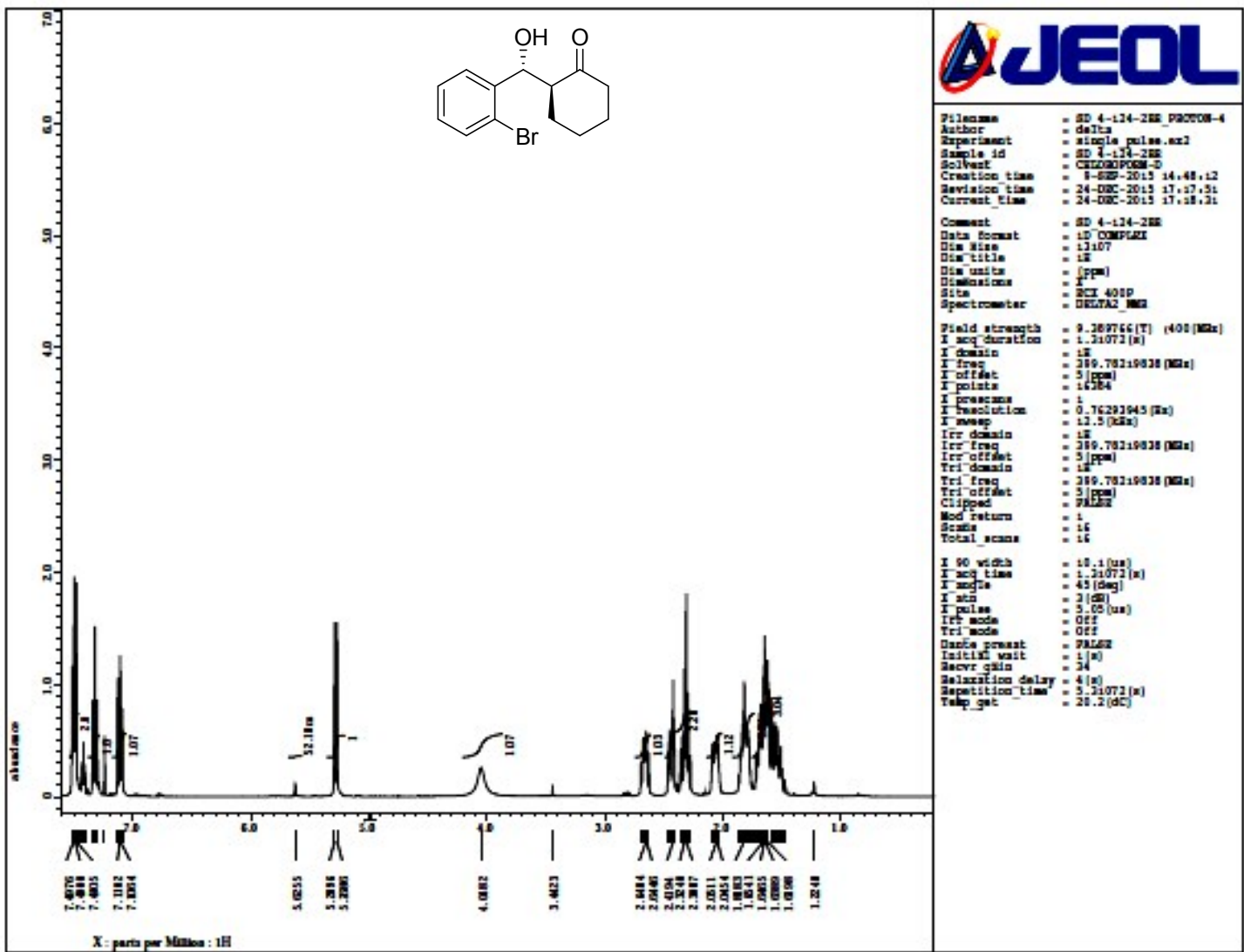
Filename      = PE 4-134-2CL_PROTON-4
Author        = delta
Experiment    = single pulse.sc2
Sample id     = PE 4-134-2CL
Solvent       = CDCl3/PCOM-D
Creation time  = 13-SEP-2013 00:40:34
Revision time = 24-SEP-2013 14:06:20
Current time  = 24-SEP-2013 14:07:01

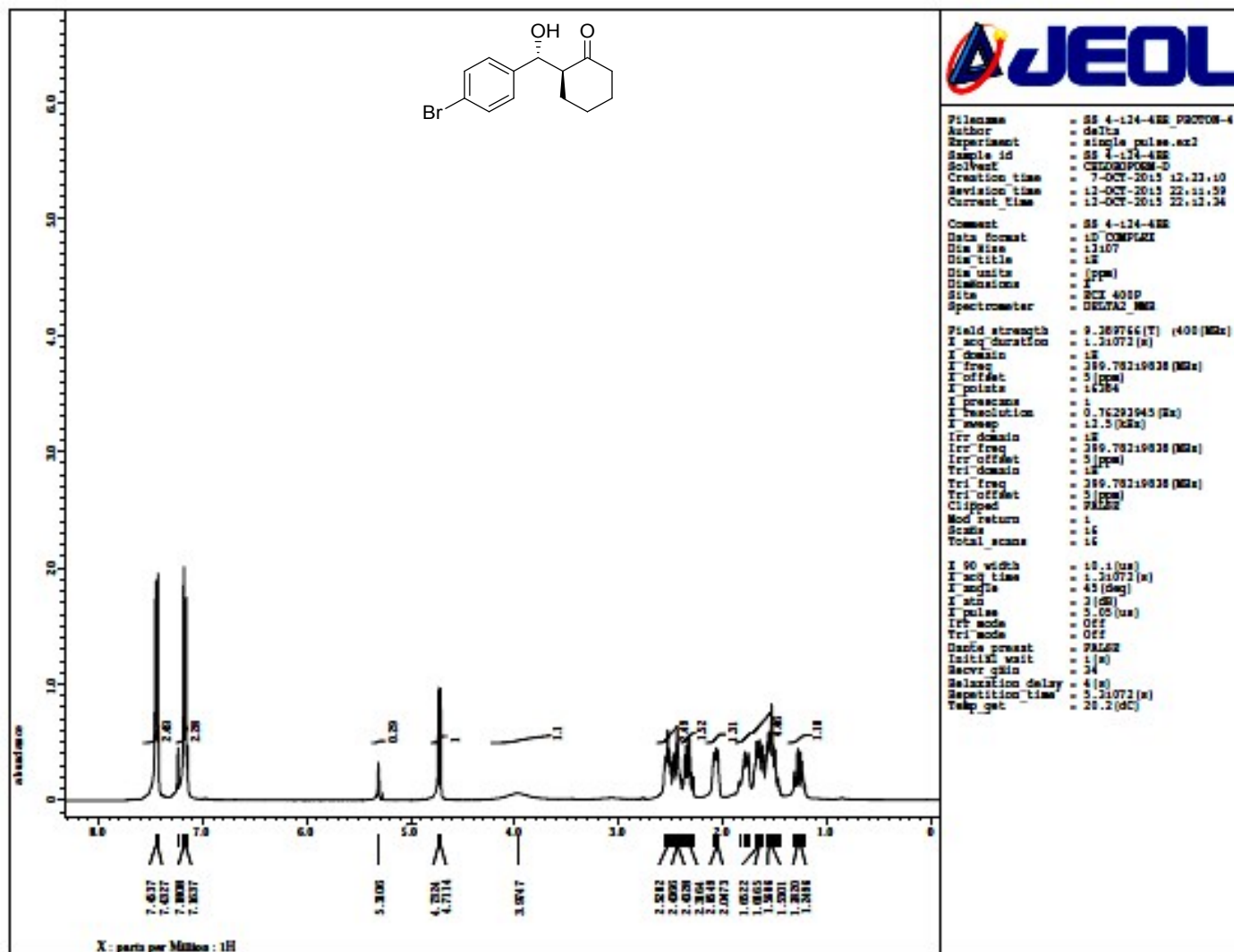
Comment       = PE 4-134-2CL
Data format   = 1D COMPAK
File size     = 13107
Dir title     = 1S
Dir units     = (ppm)
Dimensions    = 1
Site          = RFX 40SP
Spectrometer  = DELTA2 400

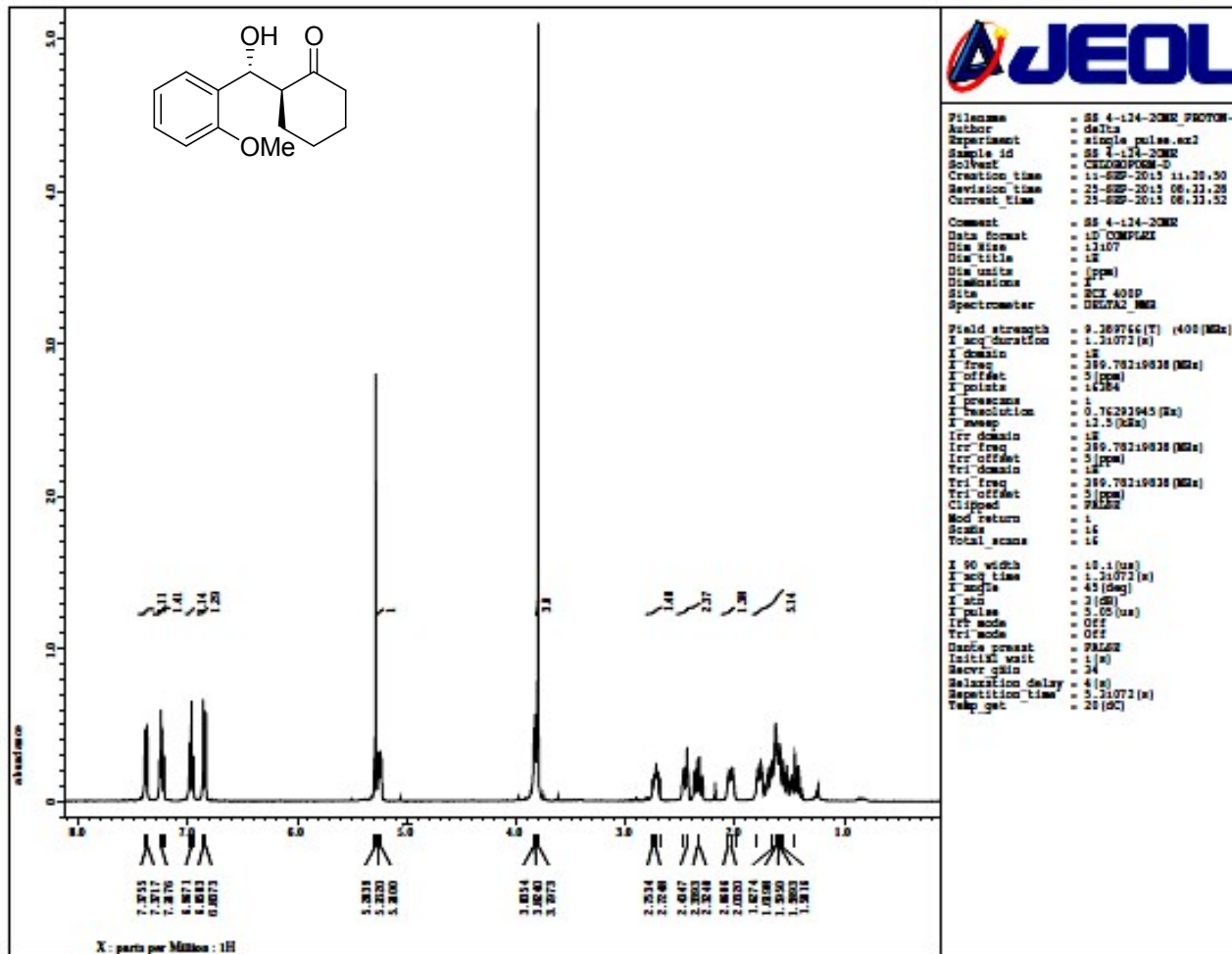
Field strength = 9.39766(T) (400(MHz))
F1 acq duration = 1.21071(s)
F1 domain      = 1S
F1 freq        = 399.7819838 (MHz)
F1 offset      = 5(ppm)
F1 points      = 16384
F1 prescan     = 1
F1 resolution  = 0.76291945 (Hz)
F1 sweep       = 13.5 (kHz)
F1r domain     = 1S
F1r freq       = 399.7819838 (MHz)
F1r offset     = 5(ppm)
F1r points     = 1S
F1r sweep      = 13.5 (kHz)
Tri domain    = 1S
Tri freq      = 399.7819838 (MHz)
Tri offset    = 5(ppm)
Tri points    = 16384
Tri sweep     = 13.5 (kHz)
Mod return    = 1
Scale         = 16
Total scans   = 16

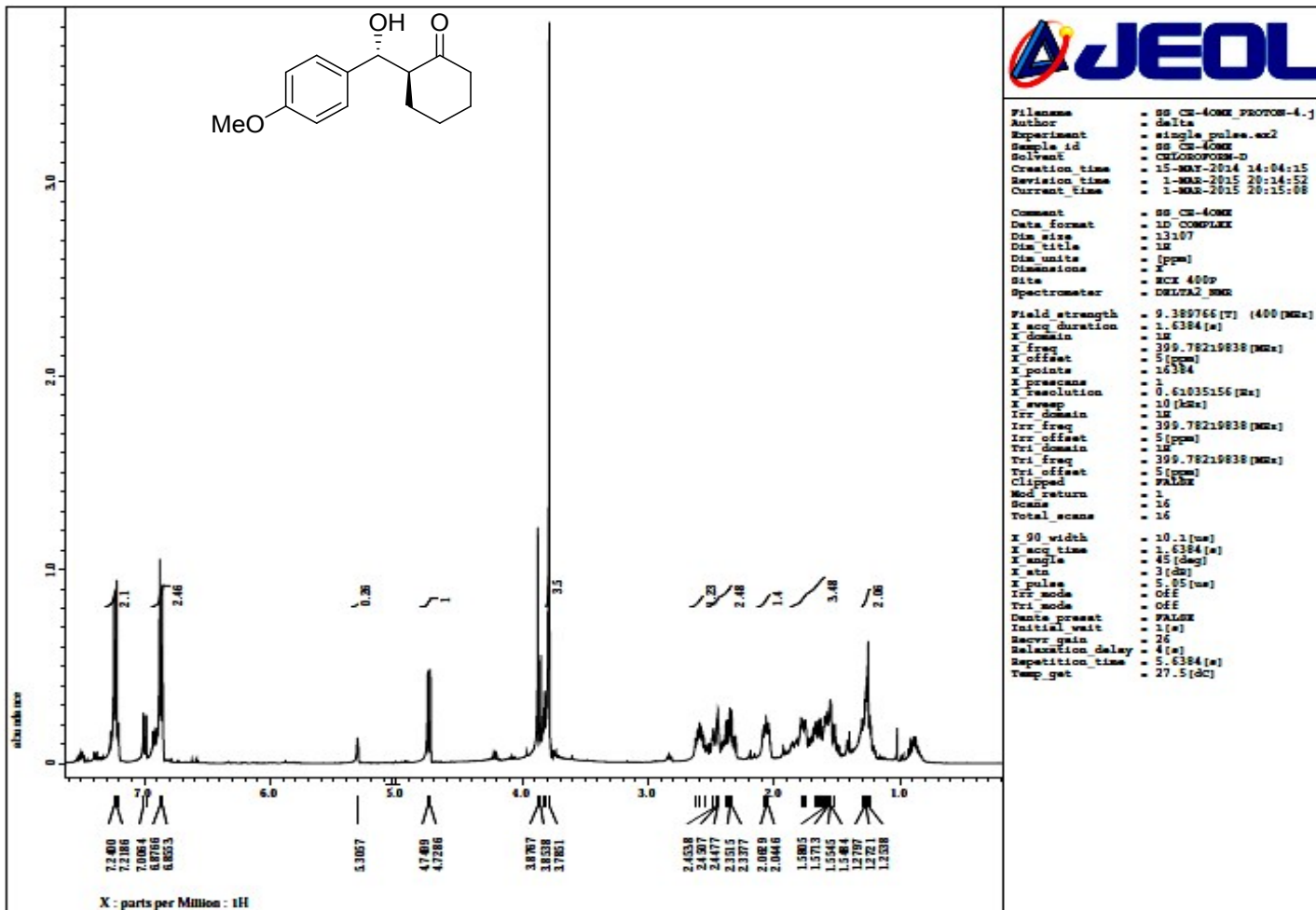
F1 90 width   = 10.1 (us)
F1 acq time   = 1.21071 (s)
F1 mode       = 45 (deg)
F1 pulse      = 3 (dB)
F1r pulse     = 5.05 (us)
F1r mode      = Off
Tri mode      = Off
Dance preset  = PAL62
InitK2 wait   = 1 (s)
Socvr gain    = 34
Relaxation delay = 4 (s)
Repetition time = 5.21071 (s)
Temp_get      = 28.2 (dC)
  
```

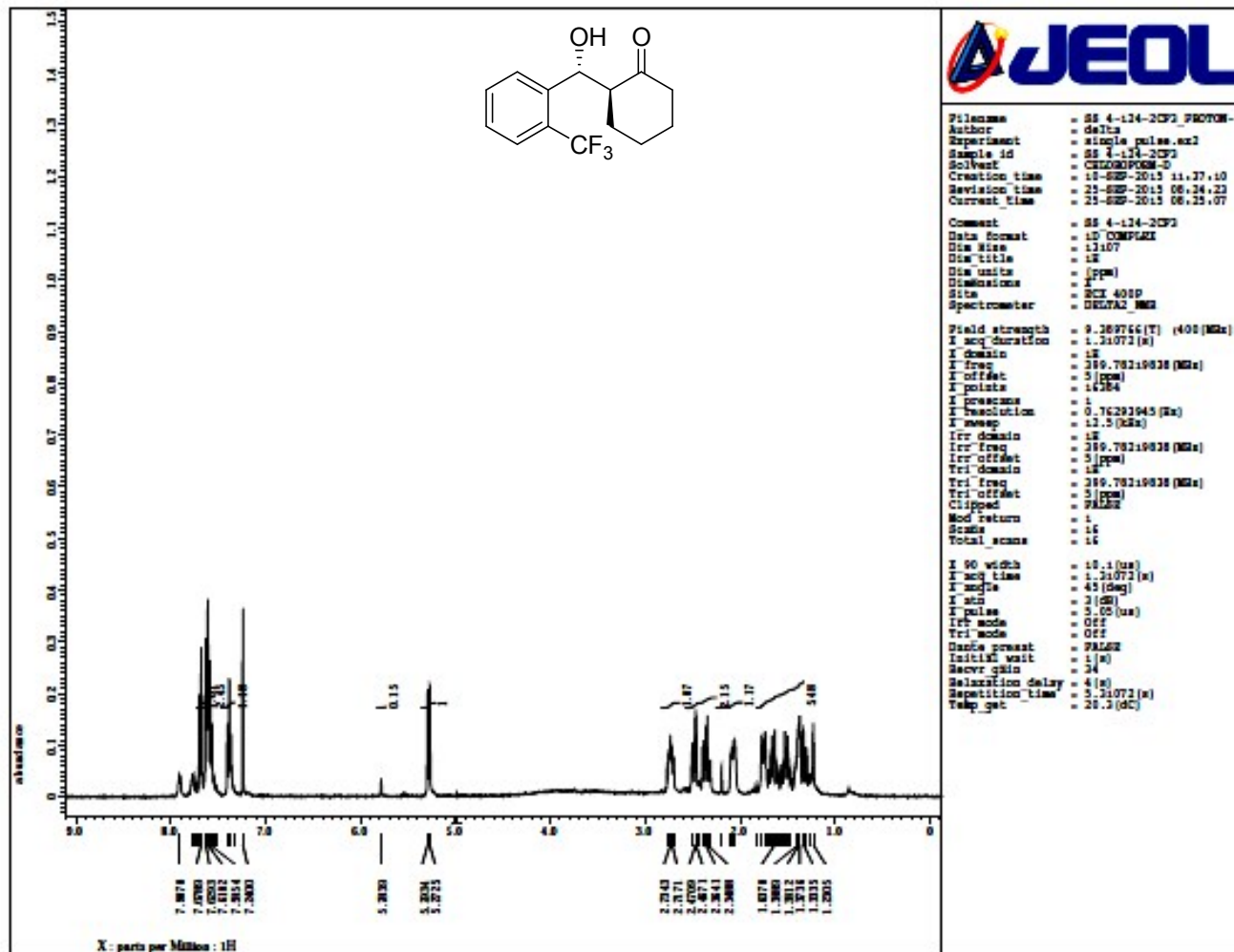












```

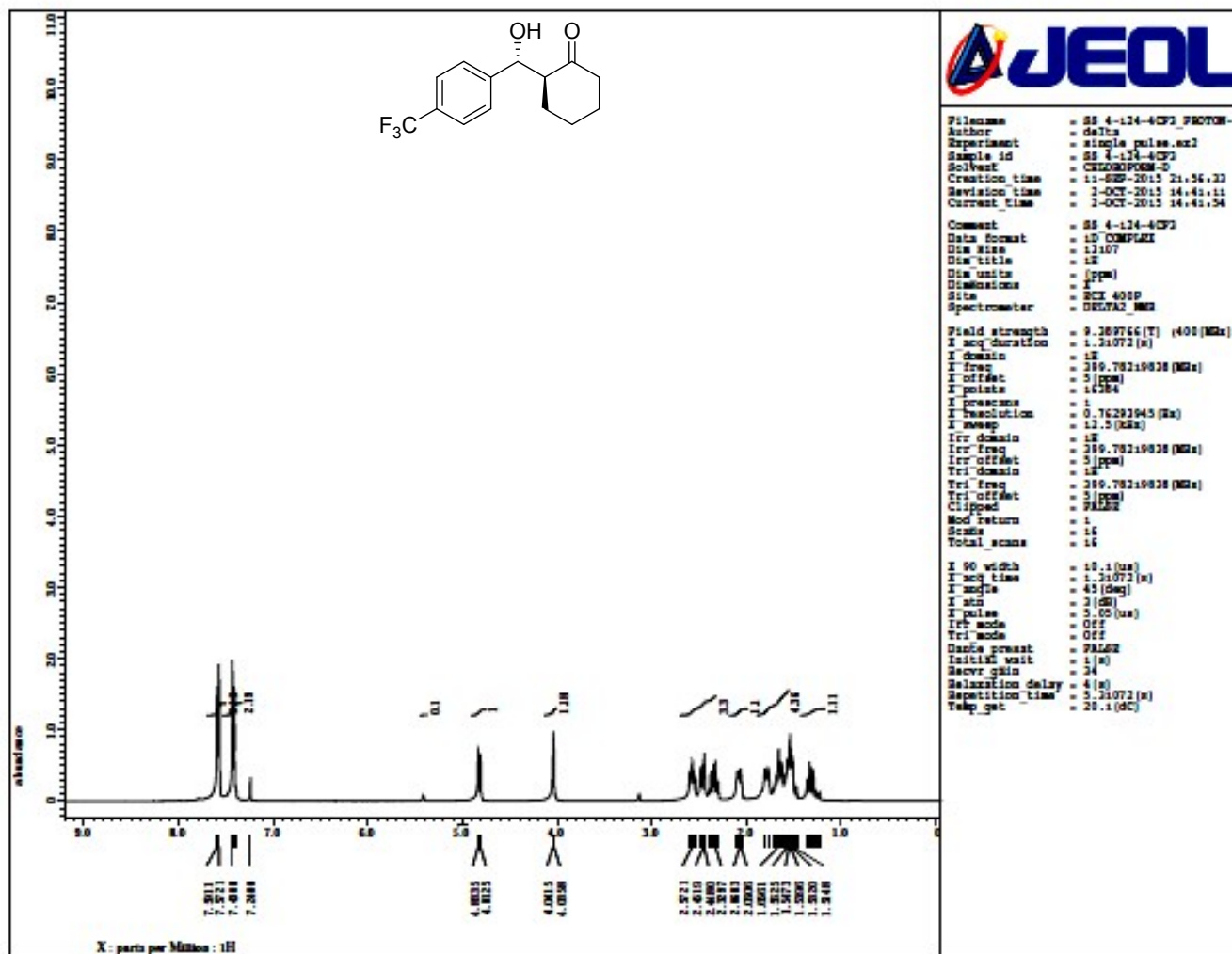
Filename      = SS 4-124-2CF3 PROTON-
Author        = ds1ca
Experiment    = single pulse.ex3
Sample id     = SS 4-124-2CF3
Solvent       = CDCl3/POSS-D
Creation time = 12-SEP-2013 11:37:10
Revision time = 25-SEP-2013 06:34:23
Current time  = 25-SEP-2013 06:35:07

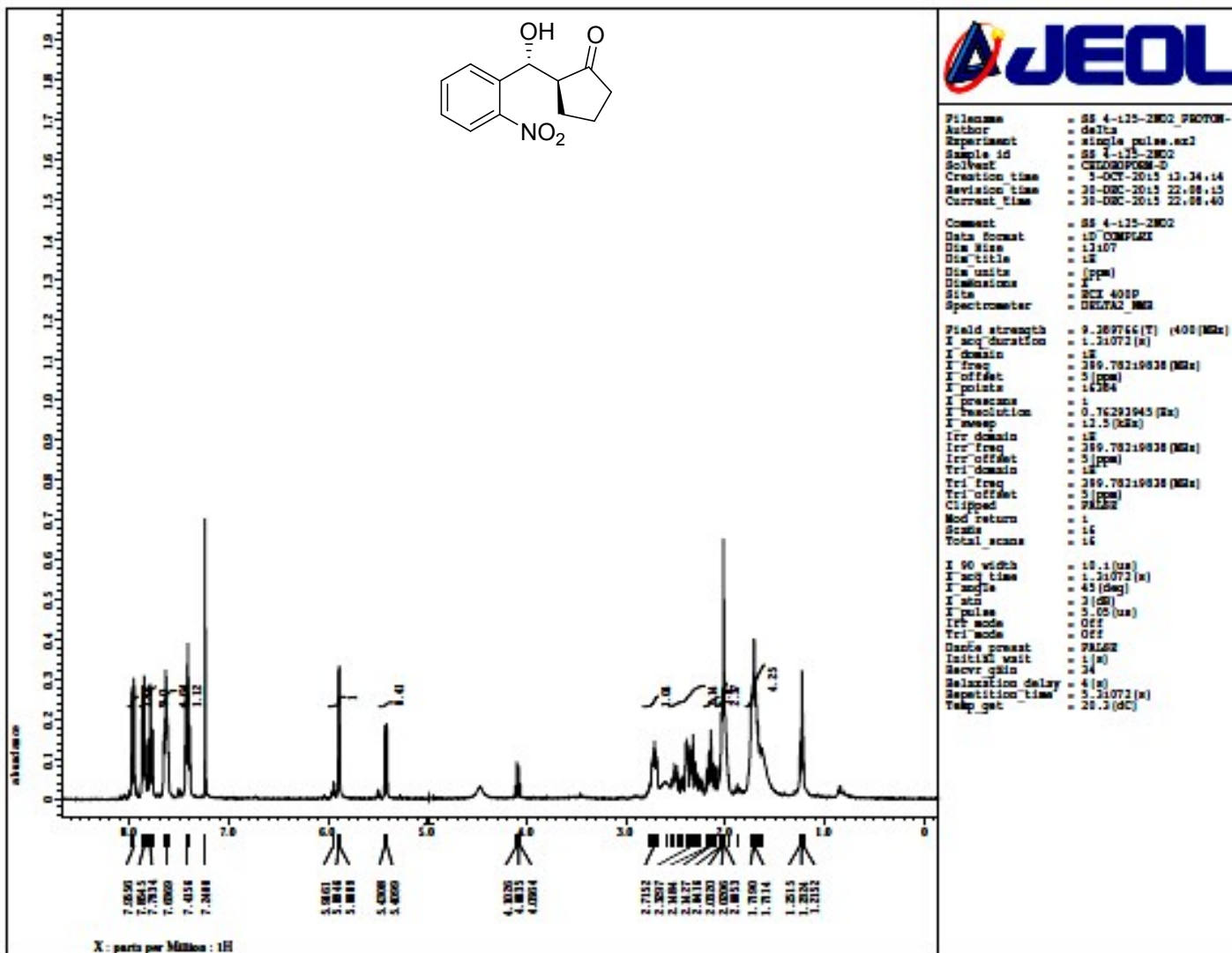
Comment       = SS 4-124-2CF3
Data format   = 1D COMPACT
Daq size      = 13107
Daq title     = 12
Daq units     = (ppm)
Dimensions    = 1
Site          = SCI 400P
Spectrometer  = DELTA2_NMR

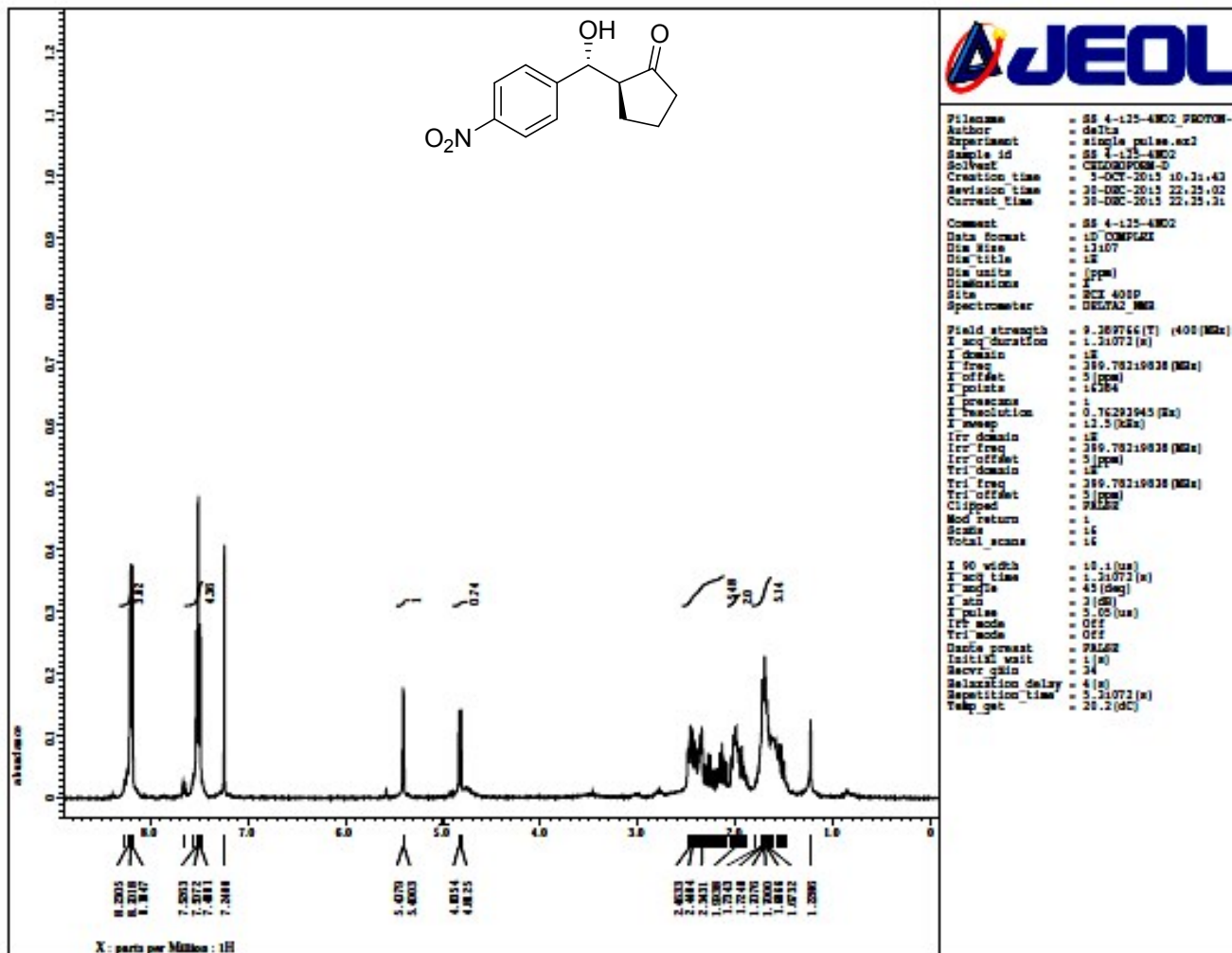
Field strength = 9.269766(T) (400(MHz))
F1 acq duration = 1.31073(s)
F1 domain      = 12
F1 freq        = 399.70219838(MHz)
F1 offset      = 5(ppm)
F1 points      = 14264
F1 prescans    = 1
F1 resolution   = 0.76292945(Hz)
F1 sweep       = 12.5(KHz)
F1r domain     = 12
F1r freq       = 399.70219838(MHz)
F1r offset     = 5(ppm)
F1r domain     = 12
F1r freq       = 399.70219838(MHz)
F1r offset     = 5(ppm)
Clipped       = FALSE
Mod return    = 1
Scale         = 16
Total scans    = 16

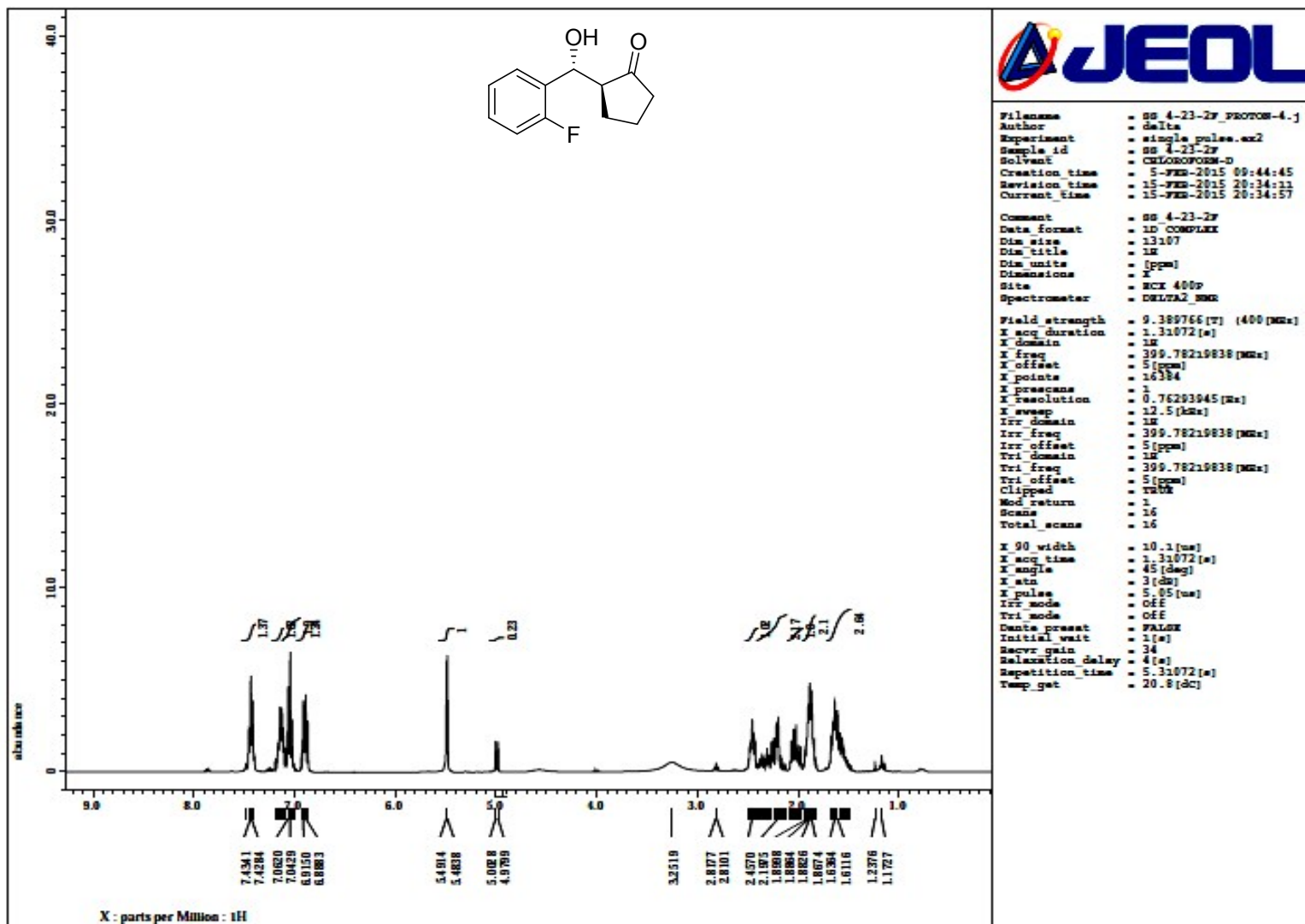
F1 90 width    = 10.1(us)
F1 acq time    = 1.31073(s)
F1 angle       = 45(deg)
F1 sfs         = 3(SM)
F1 pulse       = 9.00(us)
F1r mode       = Off
F1r mode       = Off
Datee preset   = FALSE
Initial wait   = 1(s)
Recvr gain     = 24
Relaxation delay = 4(s)
Repetition time = 5.31073(s)
Temp_set       = 20.2(degC)

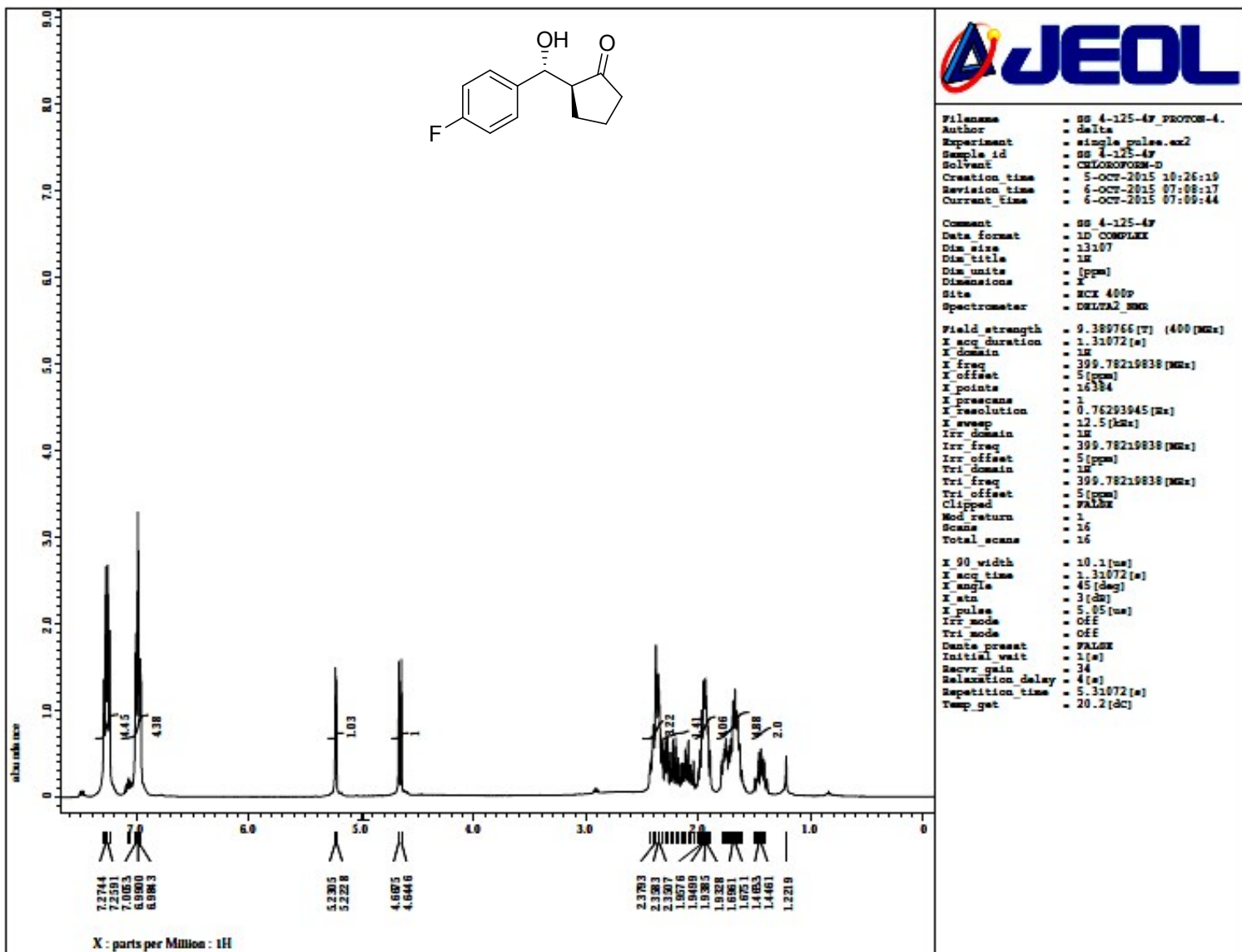
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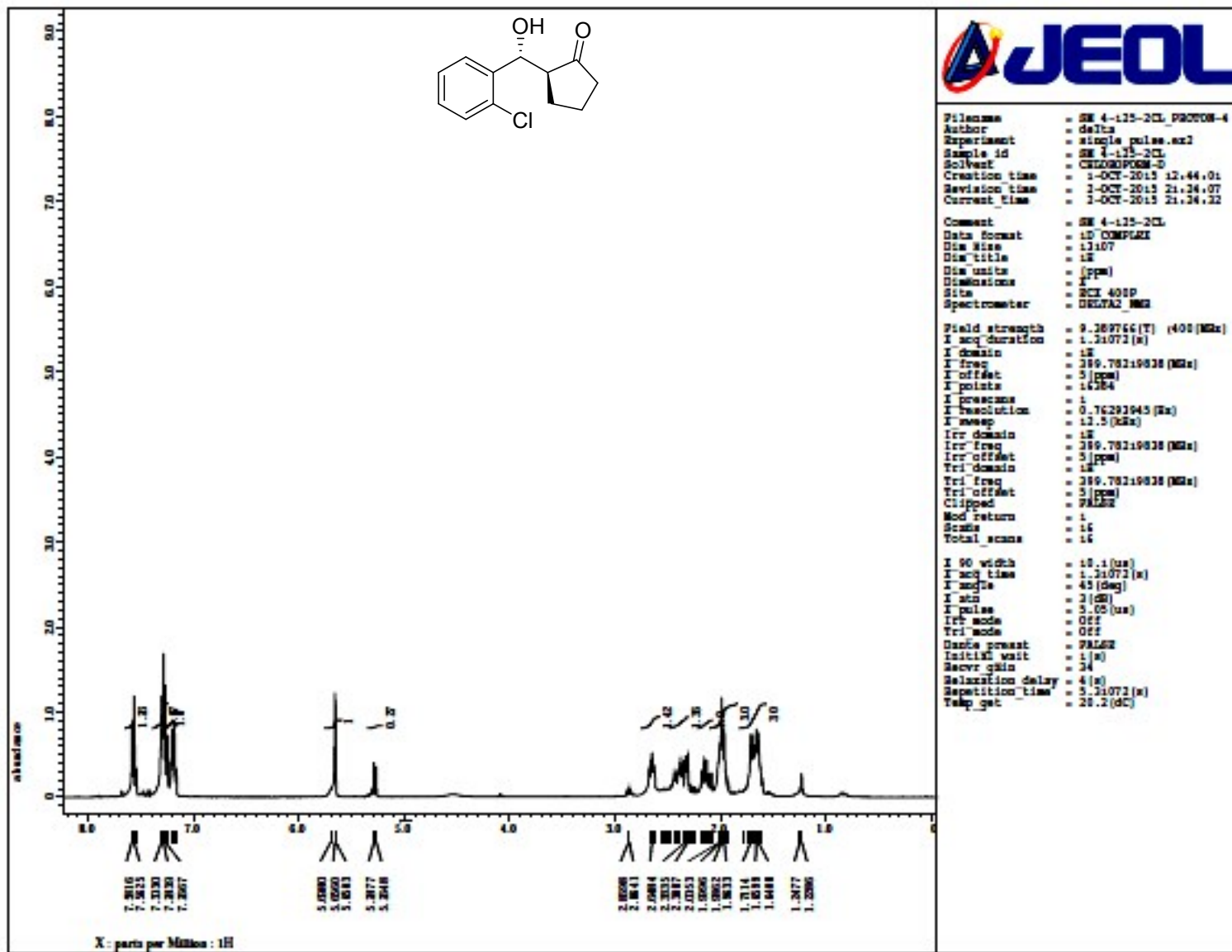












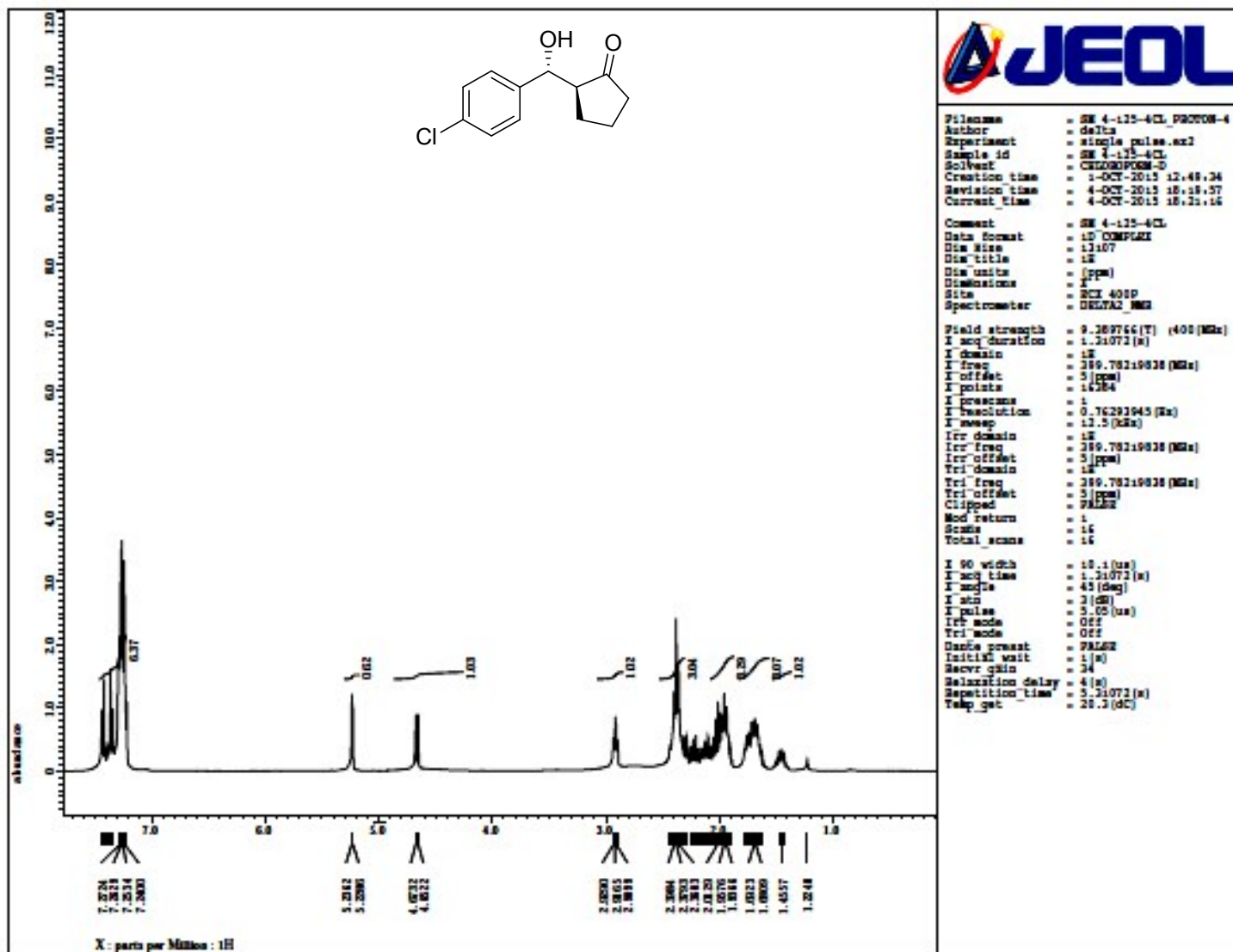
```

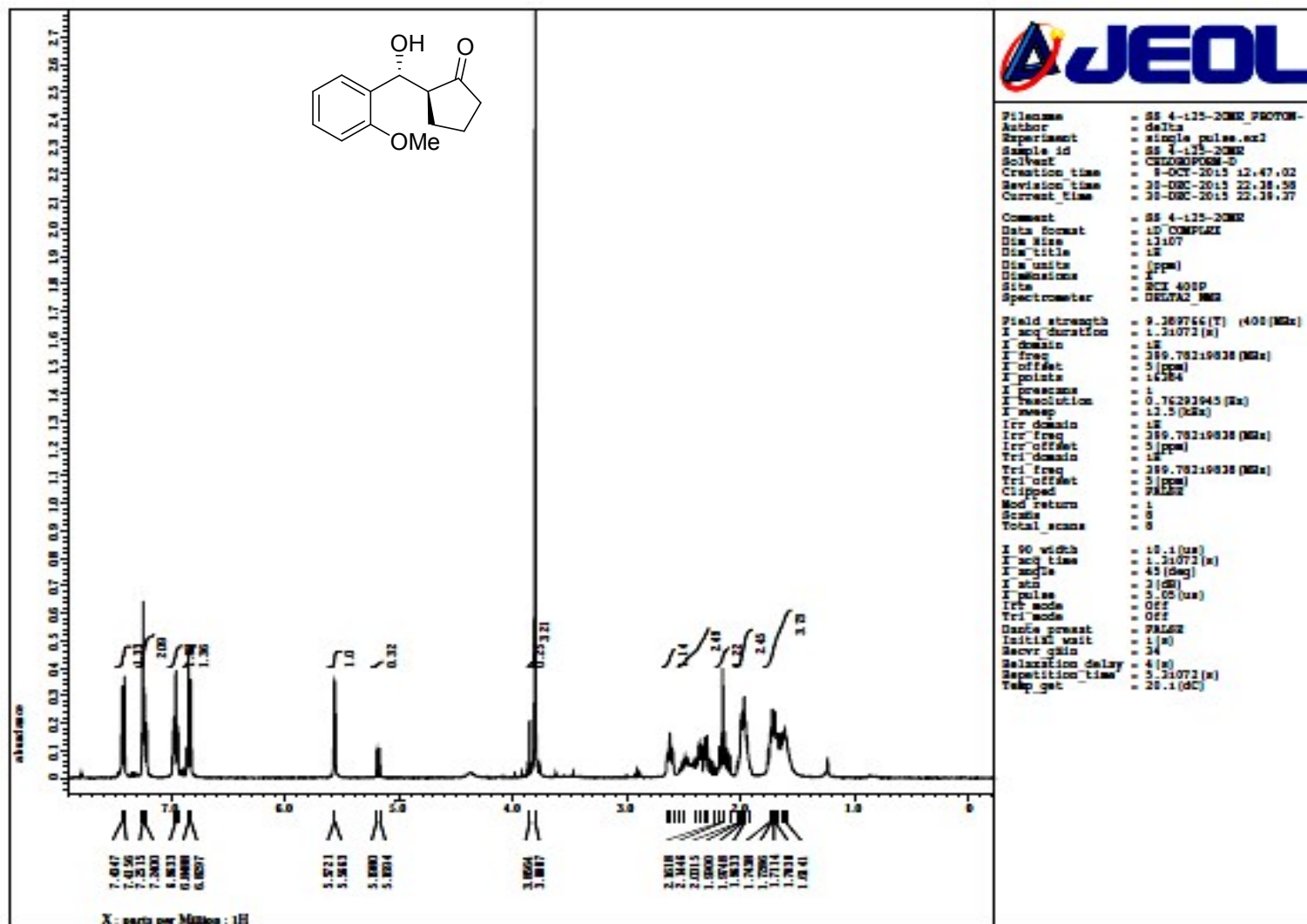
Filename      = SH 4-125-2CL PROTON-4
Author        = delta
Experiment    = single pulse.ex1
Sample id     = SH 4-125-2CL
Solvent       = CDCl3
Creation time = 1-OCT-2015 12:44:01
Revision time = 1-OCT-2015 21:24:07
Current time  = 1-OCT-2015 21:24:22

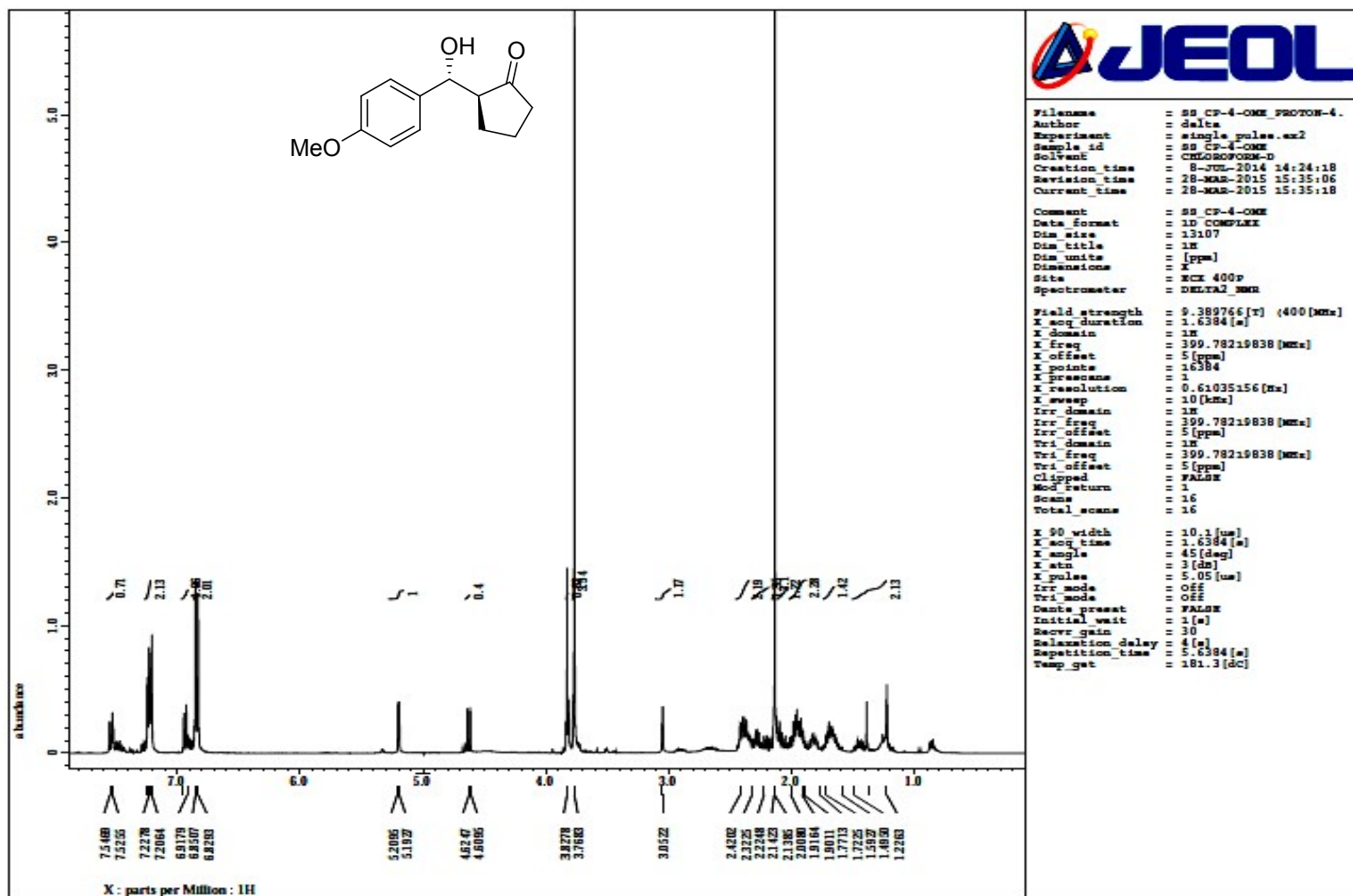
Comment       = SH 4-125-2CL
Data format   = 1D COMPARE
Daq size      = 13107
Daq title     = 1E
Daq units     = (ppm)
Dimensions    = 1
Site          = NCI 400P
Spectrometer  = DELTA 400

Field strength = 9.269766(T) (400(MHz))
F1 acq duration = 1.31073(s)
F1 domain      = 1E
F1 freq        = 399.76219038 (MHz)
F1 offset      = 5(ppm)
F1 points      = 16384
F1 prescans    = 1
F1 resolution  = 0.76292945 (Hz)
F1 sweep       = 13.5 (kHz)
F1r domain     = 1E
F1r freq       = 399.76219038 (MHz)
F1r offset     = 5(ppm)
F1r points     = 16384
F1r prescans   = 1
F1r resolution = 0.76292945 (Hz)
F1r sweep      = 13.5 (kHz)
F1r domain     = 1E
F1r freq       = 399.76219038 (MHz)
F1r offset     = 5(ppm)
Clipped       = FALSE
Mod return    = 1
Scans         = 16
Total scans   = 16

F2 width      = 10.1(us)
F2 acq time   = 1.31073(s)
F2 angle      = 45(deg)
F2 steps     = 2(s)
F2 pulse     = 5.05(us)
F2r mode     = Off
F2r mode     = Off
Data presat  = FALSE
T1 delay     = 1(s)
Recvr gain   = 34
Relaxation delay = 4(s)
Repetition time = 3.31073(s)
Temp set     = 20.2(°C)
  
```

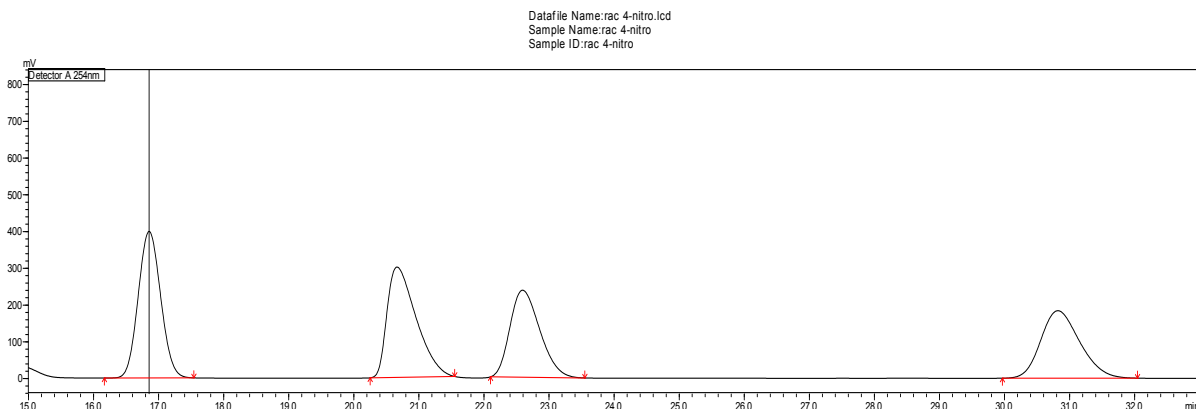




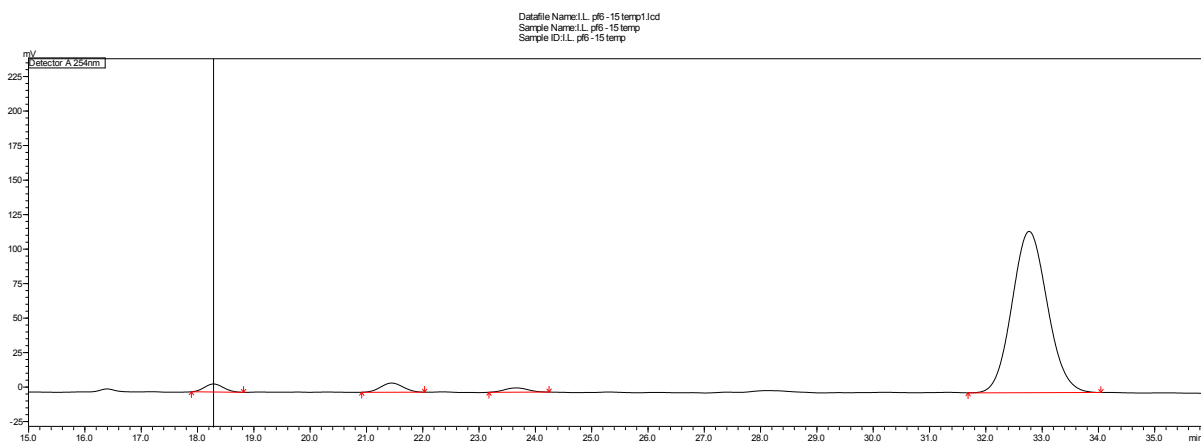


HPLC Chromatogram of the aldol products

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 1, entry 2)

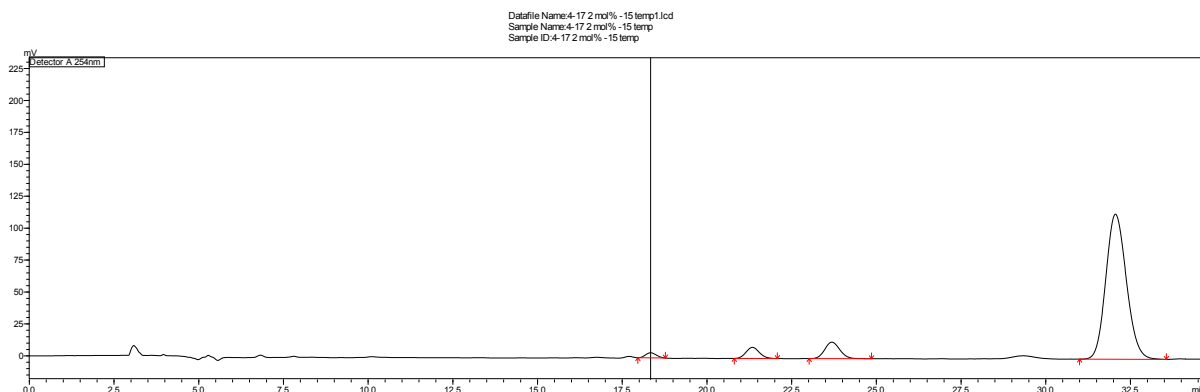


Peak	Ret. Time	Area	Height	Area%	
1	16.855	9562702	398742	28.059	<i>syn</i>
2	20.664	9318086	300259	27.341	<i>syn</i>
3	22.594	7551949	236868	22.159	<i>anti</i>
4	30.820	7648276	183621	22.441	<i>anti</i>
Total		34081013	1119490	100.000	



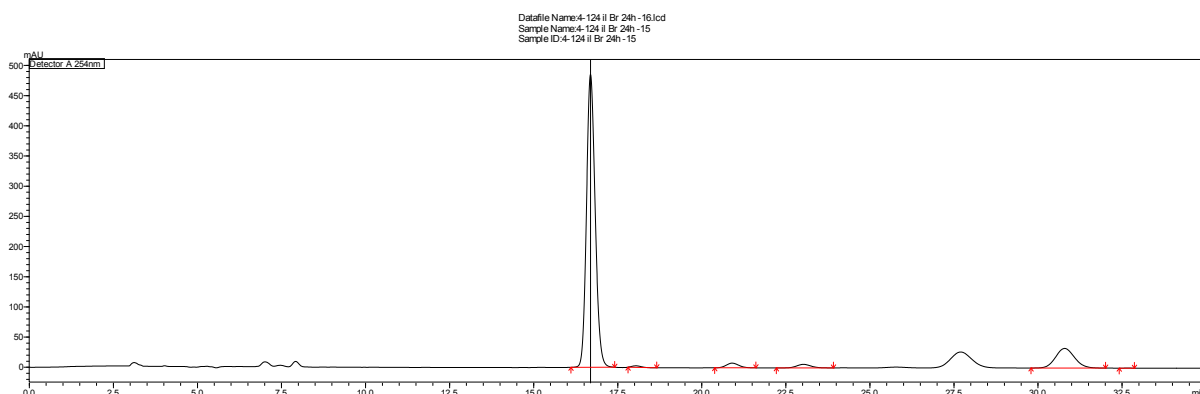
Peak	Ret. Time	Area	Height	Area%	
1	18.284	137353	5839	2.493	<i>syn</i>
2	21.449	184731	6659	3.354	<i>syn</i>
3	23.661	88253	3072	1.602	<i>anti</i>
4	32.768	5098160	116893	92.551	<i>anti</i>
Total		5508498	132463	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 1, entry 5)



Peak	Ret. Time	Area	Height	Area%	
1	18.336	89142	4033	1.612	<i>syn</i>
2	21.341	240374	8705	4.346	<i>syn</i>
3	23.687	399144	12886	7.217	<i>anti</i>
4	32.056	4802012	113602	86.825	<i>anti</i>
Total		5530672	139227	100.000	

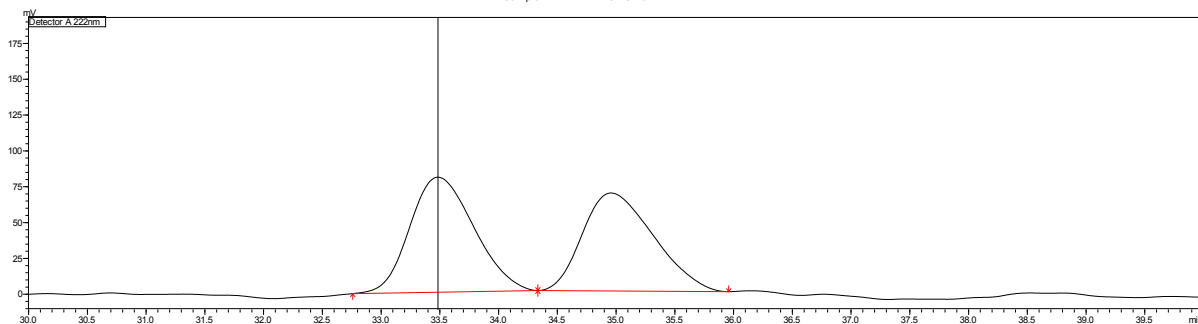
2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 1, entry 6)



Peak	Ret. Time	Area	Height	Area%	
1	16.691	8700518	485385	83.714	4-Nitro-benzaldehyde
2	18.038	44337	2501	0.427	<i>syn</i>
3	20.902	202882	7777	1.952	<i>syn</i>
4	23.024	171125	5872	1.647	<i>anti</i>
5	30.793	1273303	32490	12.251	<i>anti</i>
Total		5508498	132463	100.000	

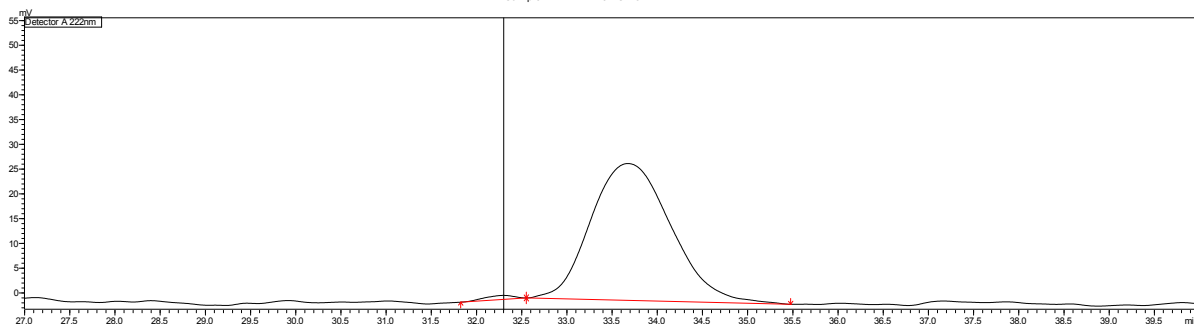
2-[Hydroxy(phenyl)methyl]-cyclohexanone (Table 2, entry 2)

Datafile Name: R 4-124 Ben CHONE1.lcd
 Sample Name: R 4-124 Ben CHONE
 Sample ID: R 4-124 Ben CHONE



Peak	Ret. Time	Area	Height	Area%	
1	33.484	3038337	80257	51.433	<i>anti</i>
2	34.957	2869000	68351	48.567	<i>anti</i>
Total		5907337	148607	100.000	

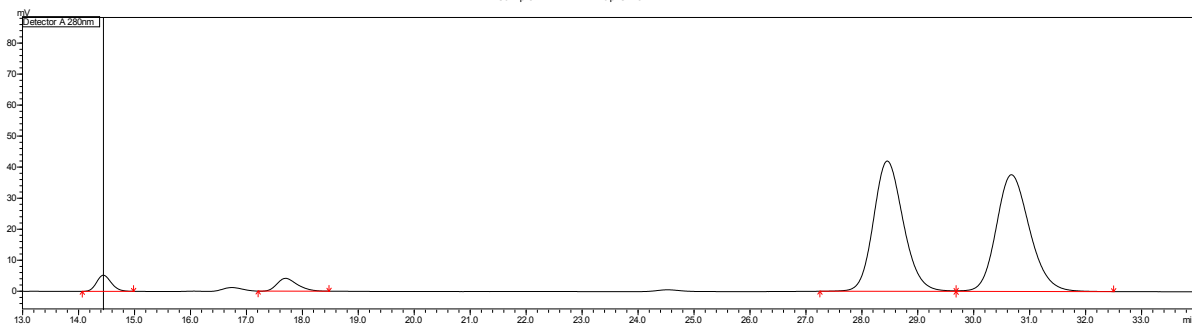
Datafile Name: 4-124 Ben CHONE1.lcd
 Sample Name: 4-124 Ben CHONE
 Sample ID: 4-124 Ben CHONE



Peak	Ret. Time	Area	Height	Area%	
1	32.300	19016	811	1.104	<i>anti</i>
2	33.676	1703268	27641	98.896	<i>anti</i>
Total		1722283	28452	100.000	

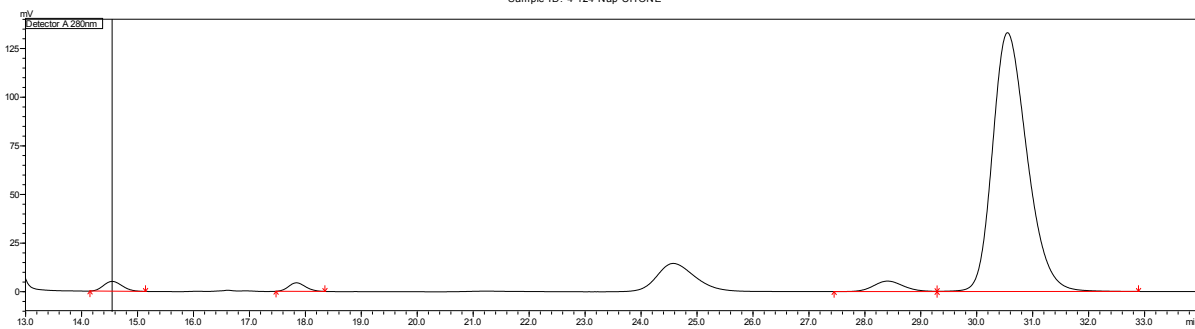
2-[Hydroxy(naphthyl)methyl]-cyclohexanone (Table 2, entry 2)

Datafile Name: R 4-124 Nap CHONE1.lcd
 Sample Name: R 4-124 Nap CHONE
 Sample ID: R 4-124 Nap CHONE



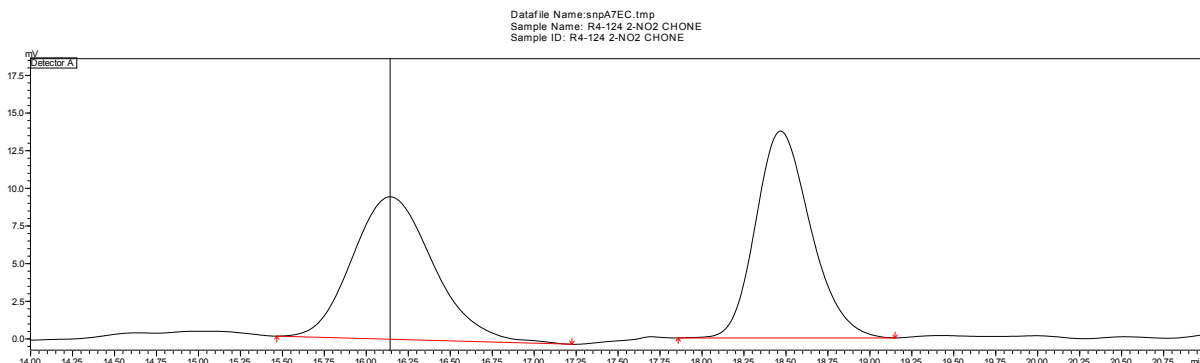
Peak	Ret. Time	Area	Height	Area%	
1	14.443	95221	5205	2.871	<i>syn</i>
2	17.700	104058	4130	3.138	<i>syn</i>
3	28.454	1555667	42020	46.908	<i>anti</i>
4	30.674	1561440	37647	47.083	<i>anti</i>
	Total	3316387	89002	100.000	

Datafile Name: 4-124 Nap CHONE1.lcd
 Sample Name: 4-124 Nap CHONE
 Sample ID: 4-124 Nap CHONE

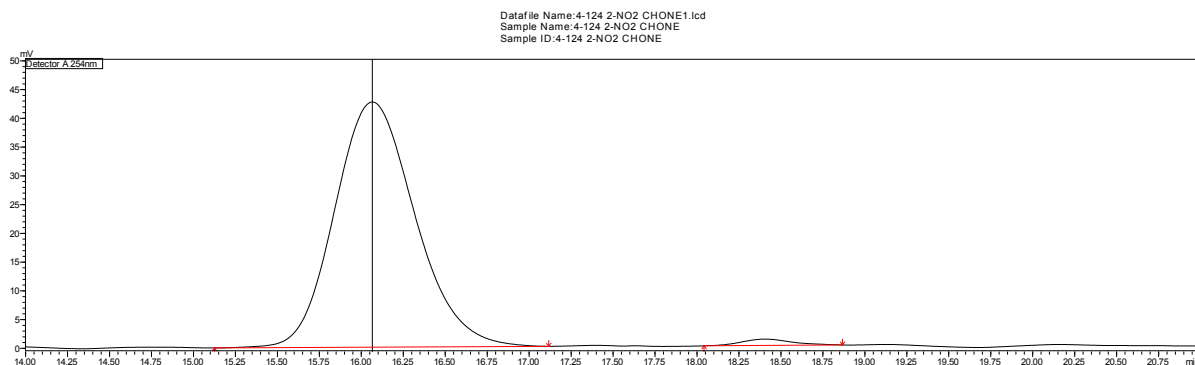


Peak	Ret. Time	Area	Height	Area%	
1	14.546	117229	5031	1.921	<i>syn</i>
2	17.840	92749	4393	1.520	<i>syn</i>
3	28.407	201002	5384	3.293	<i>anti</i>
4	30.550	5692358	133053	93.266	<i>anti</i>
	Total	6103339	147862	100.000	

2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclohexanone (Table 2, entry 3)



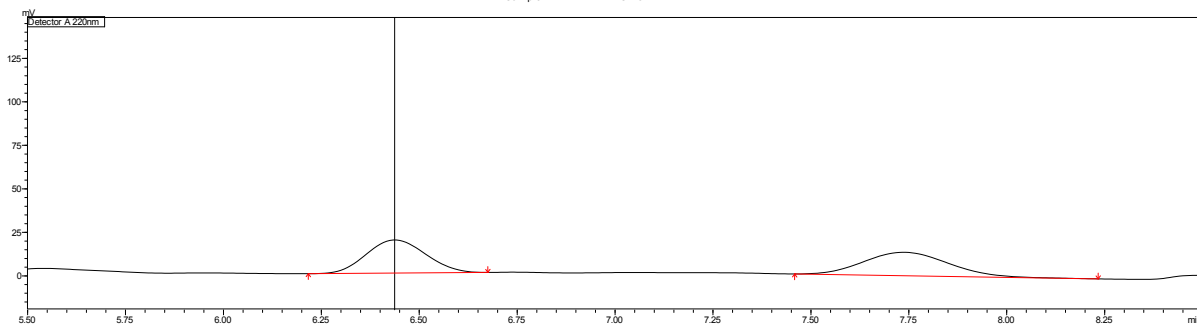
Peak	Ret. Time	Area	Height	Area%	
1	16.142	318790	9465	50.409	<i>anti</i>
2	18.468	313621	13739	49.591	<i>anti</i>
Total		632411	23204	100.000	



Peak	Ret. Time	Area	Height	Area%	
1	16.066	1420282	42657	98.394	<i>anti</i>
2	18.403	23178	1107	1.606	<i>anti</i>
Total		1443459	43764	100.000	

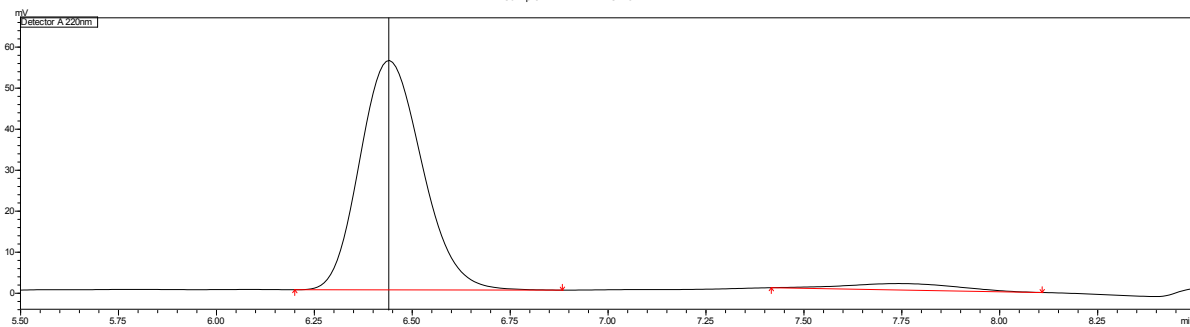
2-[Hydroxy-(2-fluoro-phenyl)methyl]-cyclohexanone (Table 2, entry 4)

Datafile Name: R 4-124 2F CHONE2.lcd
 Sample Name: R 4-124 2F CHONE
 Sample ID: R 4-124 2F CHONE



Peak	Ret. Time	Area	Height	Area%	
1	6.437	200624	19059	49.721	<i>anti</i>
2	7.736	202875	13468	50.279	<i>anti</i>
Total		403499	32528	100.000	

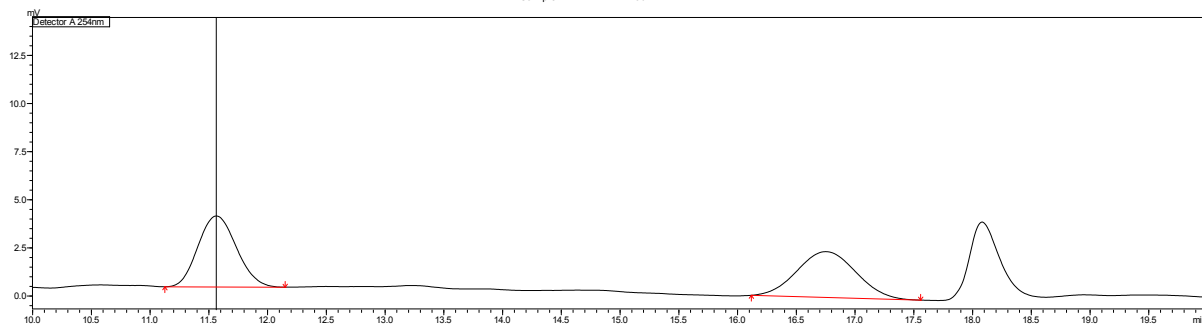
Datafile Name: 4-124 2F CHONE1.lcd
 Sample Name: 4-124 2F CHONE
 Sample ID: 4-124 2F CHONE



Peak	Ret. Time	Area	Height	Area%	
1	6.440	619122	55938	95.242	<i>anti</i>
2	7.741	30928	1559	4.758	<i>anti</i>
Total		650050	57496	100.000	

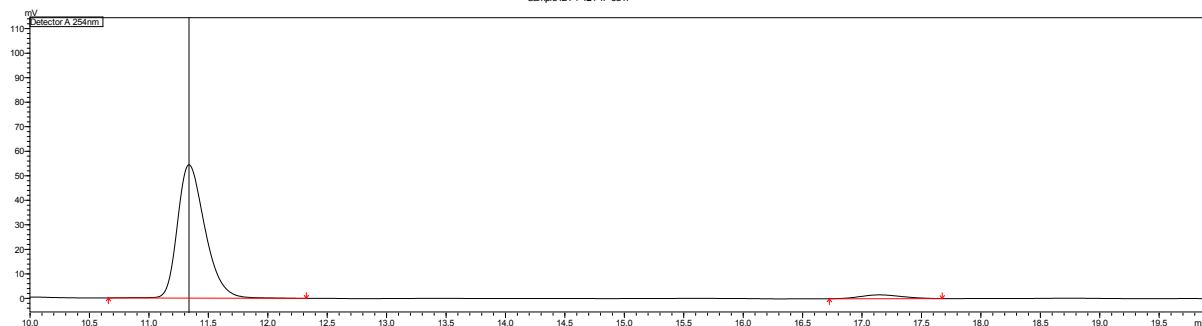
2-[Hydroxy-(4-fluoro-phenyl)methyl]-cyclohexanone (Table 2, entry 5)

Datafile Name: R 4-124 4F od h1.lcd
 Sample Name: R 4-124 4F od h
 Sample ID: R 4-124 4F od h



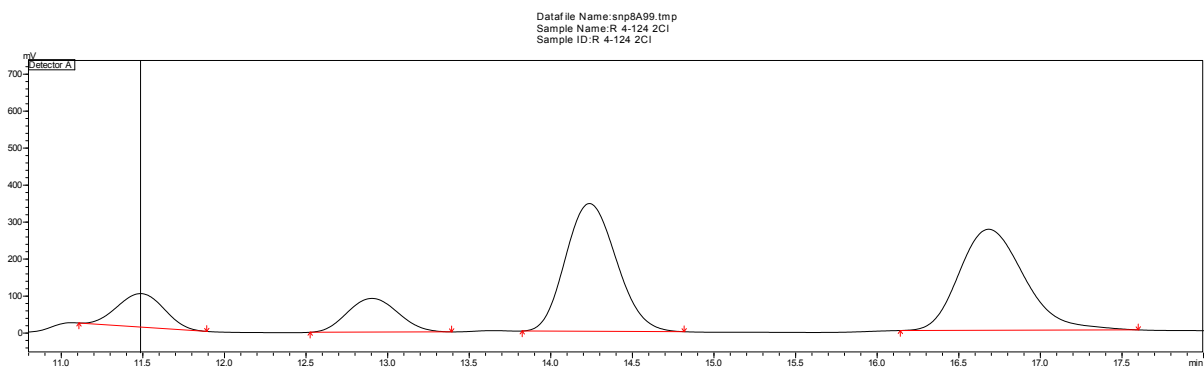
Peak	Ret. Time	Area	Height	Area%	
1	11.564	83742	3688	50.245	<i>anti</i>
2	16.749	82926	2379	49.755	<i>anti</i>
	Total	166668	6067	100.000	

Datafile Name: 4-124 4F od h2.lcd
 Sample Name: 4-124 4F od h
 Sample ID: 4-124 4F od h

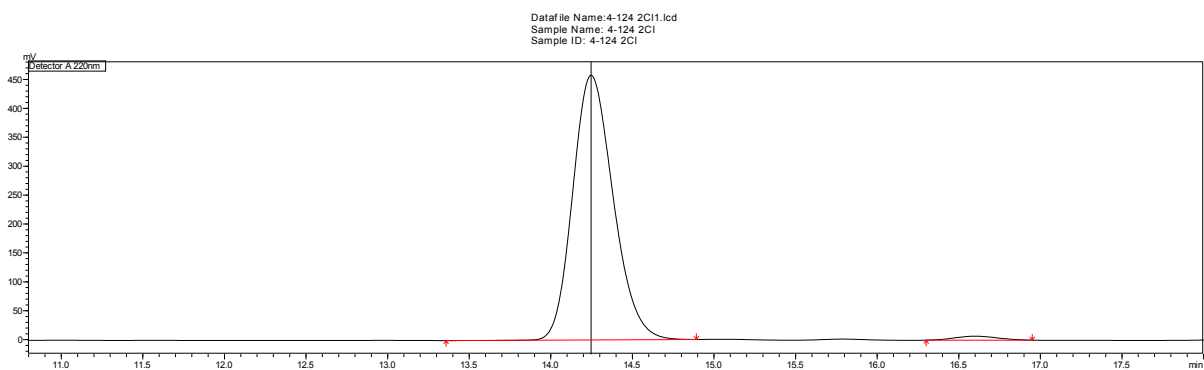


Peak	Ret. Time	Area	Height	Area%	
1	11.337	874282	54356	96.552	<i>anti</i>
2	17.147	31220	1404	3.448	<i>anti</i>
	Total	905502	55759	100.000	

2-[Hydroxy-(2-chloro-phenyl)methyl]-cyclohexanone (Table 2, entry 6)

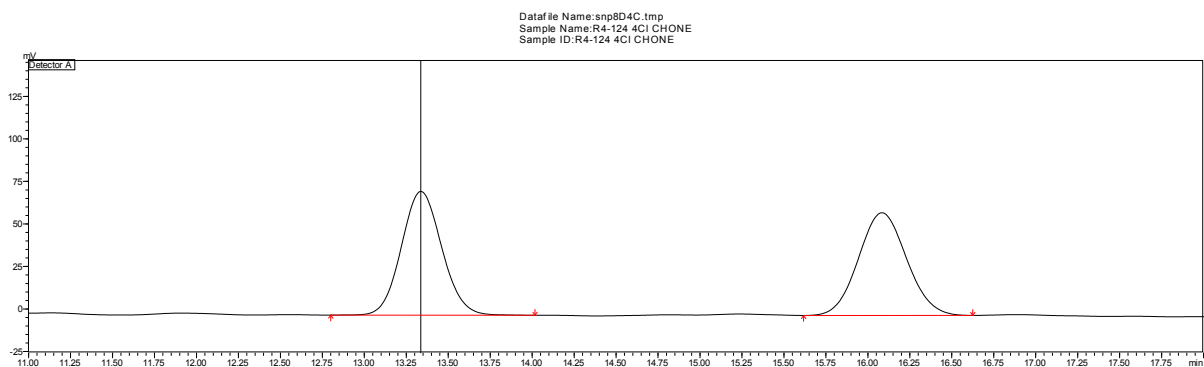


Peak	Ret. Time	Area	Height	Area%	
1	11.486	1790429	90477	9.513	<i>syn</i>
2	12.904	1972025	91012	10.477	<i>syn</i>
3	14.237	7494487	345484	39.818	<i>anti</i>
4	16.683	7564779	273103	40.192	<i>anti</i>
Total		18821719	800077	100.000	

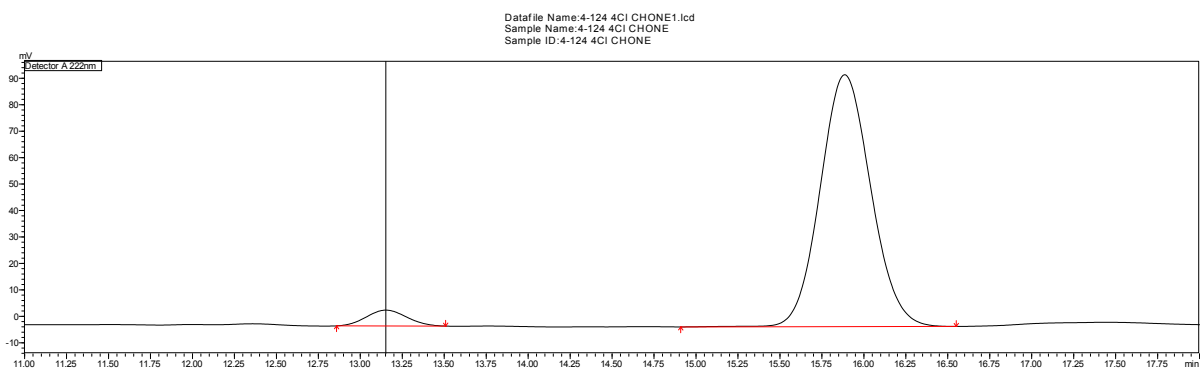


Peak	Ret. Time	Area	Height	Area%	
1	14.247	7886290	457822	98.443	<i>anti</i>
2	16.599	124720	6868	1.557	<i>anti</i>
Total		8011010	464690	100.000	

2-[Hydroxy-(4-chloro-phenyl)methyl]-cyclohexanone (Table 2, entry 7)



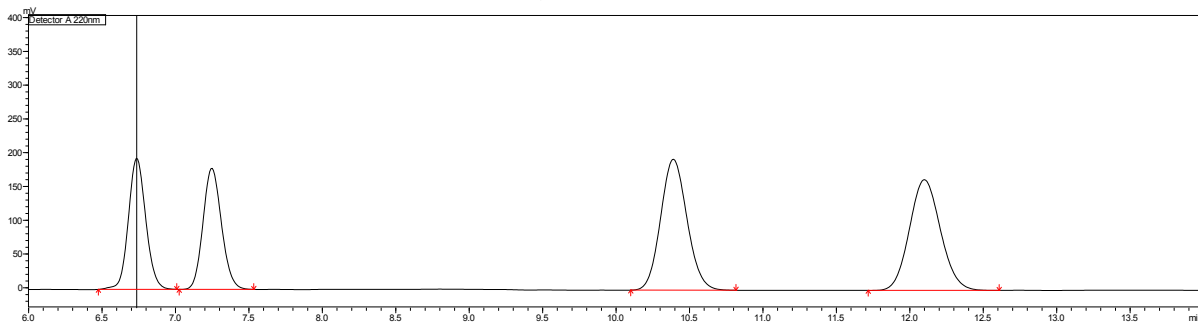
Peak	Ret. Time	Area	Height	Area%	
1	13.337	1220111	72730	50.276	<i>anti</i>
2	16.084	1206725	60377	49.724	<i>anti</i>
Total		2426836	133107	100.000	



Peak	Ret. Time	Area	Height	Area%	
1	13.152	99858	5984	4.762	<i>anti</i>
2	15.886	1997216	95253	95.238	<i>anti</i>
Total		2097074	101237	100.000	

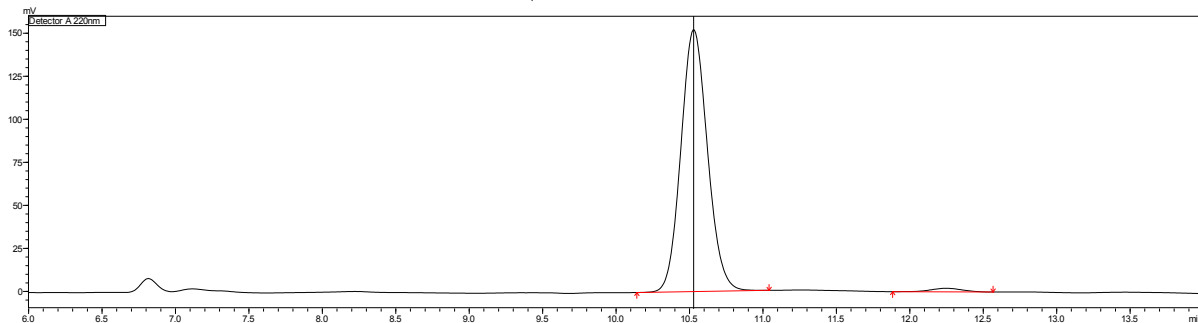
2-[Hydroxy-(2-bromo-phenyl)methyl]-cyclohexanone (Table 2, entry 8)

Datafile Name: R 2Br CHONE2.lcd
 Sample Name: R 2Br CHONE
 Sample ID: R 2Br CHONE



Peak	Ret. Time	Area	Height	Area%	
1	6.736	1601045	193939	19.995	<i>syn</i>
2	7.247	1570953	179235	19.619	<i>syn</i>
3	10.389	2425950	193818	30.297	<i>anti</i>
4	12.099	2409359	163901	30.090	<i>anti</i>
	Total	8007307	730893	100.000	

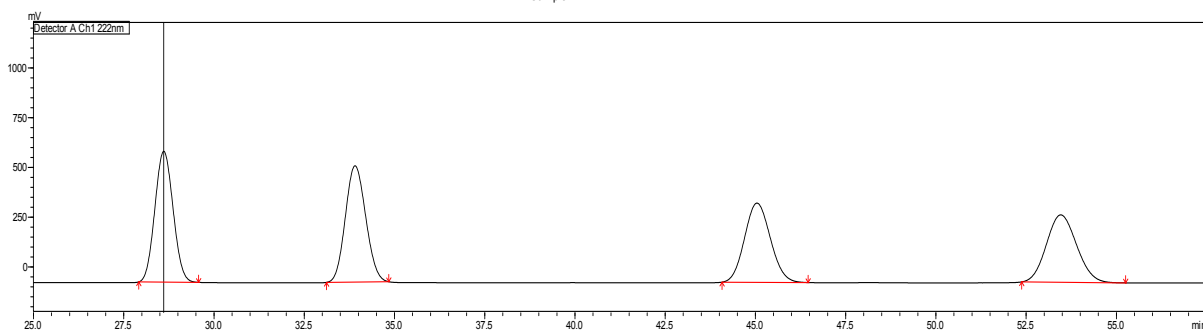
Datafile Name: 4-124 2Br CHONE1.lcd
 Sample Name: 4-124 2Br CHONE
 Sample ID: 4-124 2Br CHONE



Peak	Ret. Time	Area	Height	Area%	
1	10.528	1915424	152111	98.415	<i>anti</i>
2	12.246	30841	2084	1.585	<i>anti</i>
	Total	1946265	154195	100.000	

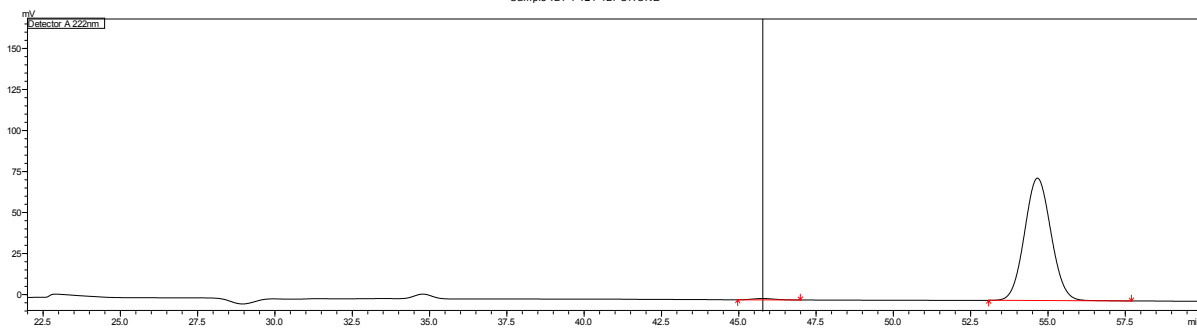
2-[Hydroxy-(4-bromo-phenyl)methyl]-cyclohexanone (Table 2, entry 9)

Datafile Name: R 4-22 4-Br.lcd
 Sample Name: R 4-22 4-Br
 Sample ID: R 4-22 4-Br



Peak	Ret. Time	Area	Height	Area%	
1	28.608	23076716	657179	26.970	<i>syn</i>
2	33.907	22969006	584587	26.844	<i>syn</i>
3	45.043	19835022	398245	23.181	<i>anti</i>
4	53.459	19684507	338683	23.005	<i>anti</i>
Total		85565250	1978694	100.000	

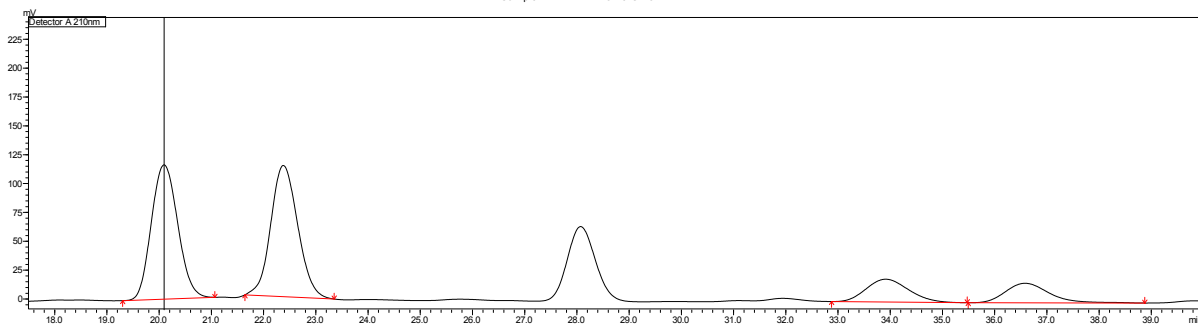
Datafile Name: 4-124 4Br CHONE2.lcd
 Sample Name: 4-124 4Br CHONE
 Sample ID: 4-124 4Br CHONE



Peak	Ret. Time	Area	Height	Area%	
1	45.776	39428	817	0.878	<i>anti</i>
2	54.660	4453109	74635	99.122	<i>anti</i>
Total		4492538	75452	100.000	

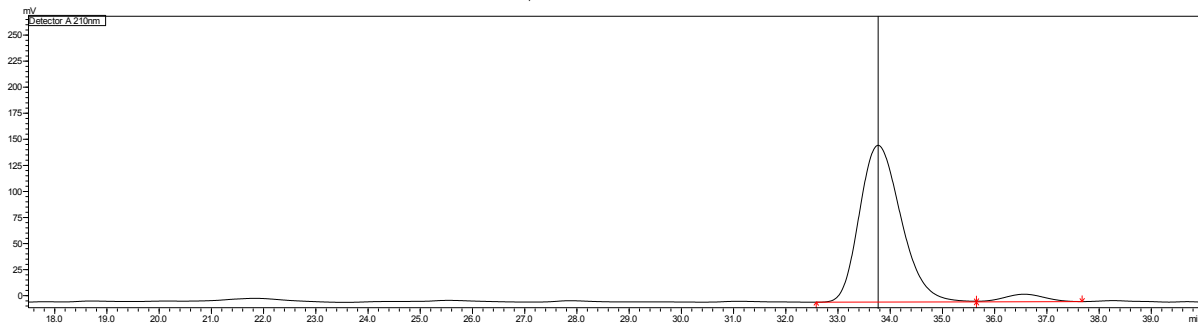
2-[Hydroxy-(2-methoxy-phenyl)methyl]-cyclohexanone (Table 2, entry 10)

Datafile Name: R4-124 2OMe CHONE1.lcd
 Sample Name: R4-124 2OMe CHONE
 Sample ID: R4-124 2OMe CHONE



Peak	Ret. Time	Area	Height	Area%	
1	20.094	4092131	116323	39.806	<i>syn</i>
2	22.377	4084212	113590	39.729	<i>syn</i>
3	33.912	1113897	19756	10.835	<i>anti</i>
4	36.582	989875	16941	9.629	<i>anti</i>
	Total	10280116	266611	100.000	

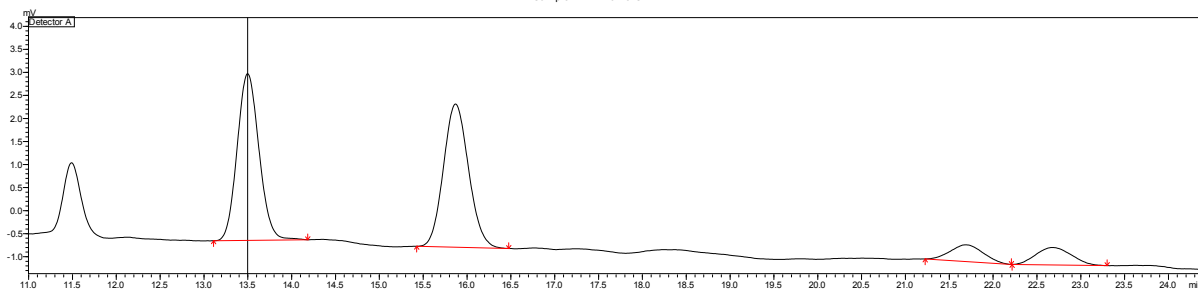
Datafile Name: 4-124 2OMe CHONE2.lcd
 Sample Name: 4-124 2OMe CHONE
 Sample ID: 4-124 2OMe CHONE



Peak	Ret. Time	Area	Height	Area%	
1	33.768	8324265	150418	95.563	<i>anti</i>
2	36.566	386453	7206	4.437	<i>anti</i>
	Total	8710718	157624	100.000	

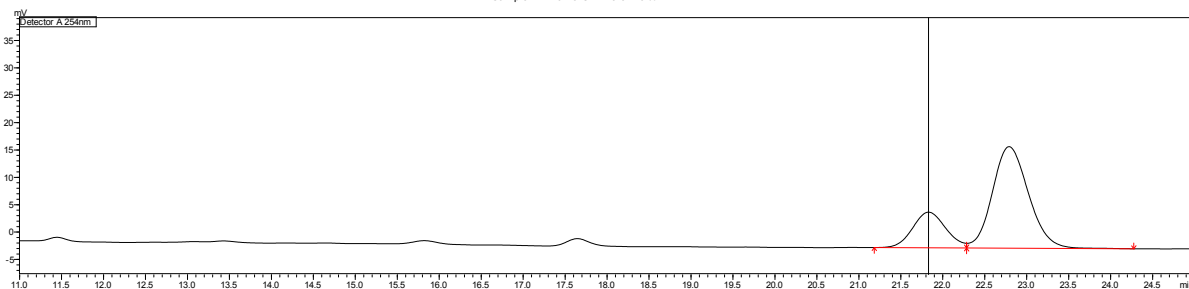
2-[Hydroxy-(4-methoxy-phenyl)methyl]-cyclohexanone (Table 2, entry 11)

Datafile Name: snpD10D.tmp
 Sample Name: R 4-ome CH
 Sample ID: R 4-ome CH



Peak	Ret. Time	Area	Height	Area%	
1	13.498	62822	3619	43.320	<i>syn</i>
2	15.868	62050	3109	42.787	<i>syn</i>
3	21.685	9515	364	6.561	<i>anti</i>
4	22.669	10633	378	7.332	<i>anti</i>
	Total	145020	7470	100.000	

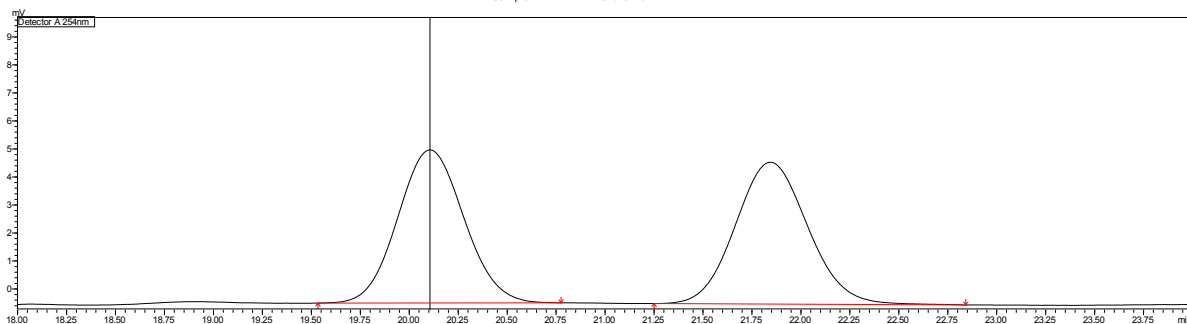
Datafile Name: 4-ome CH -15.5 mol%1.lcd
 Sample Name: 4-ome CH -15.5 mol%
 Sample ID: 4-ome CH -15.5 mol%



Peak	Ret. Time	Area	Height	Area%	
1	21.830	178575	6508	24.334	<i>anti</i>
2	22.790	555262	18543	75.666	<i>anti</i>
	Total	733837	25051	100.000	

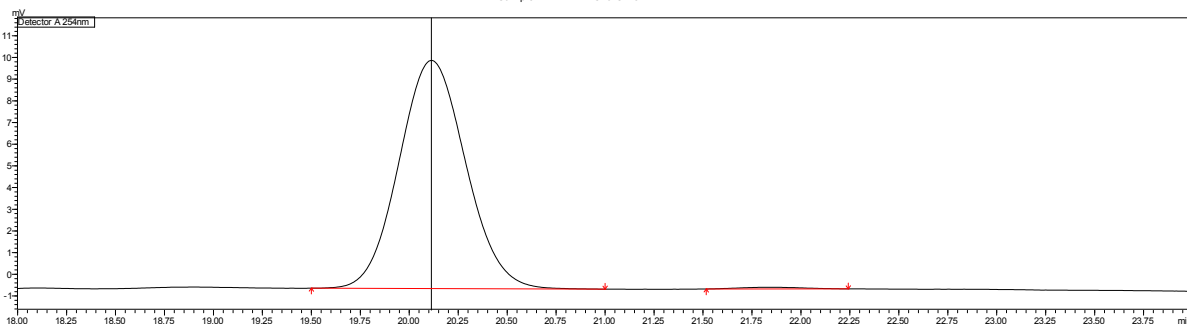
2-[Hydroxy-(2-trifluoromethyl-phenyl)methyl]-cyclohexanone (Table 2, entry 12)

Datafile Name: R 4-124 4C13 CHONE2.lcd
 Sample Name: R 4-124 4C13 CHONE
 Sample ID: R 4-124 4C13 CHONE



Peak	Ret. Time	Area	Height	Area%	
1	20.106	128741	5467	49.676	<i>anti</i>
2	21.845	130422	5064	50.324	<i>anti</i>
Total		259163	10531	100.000	

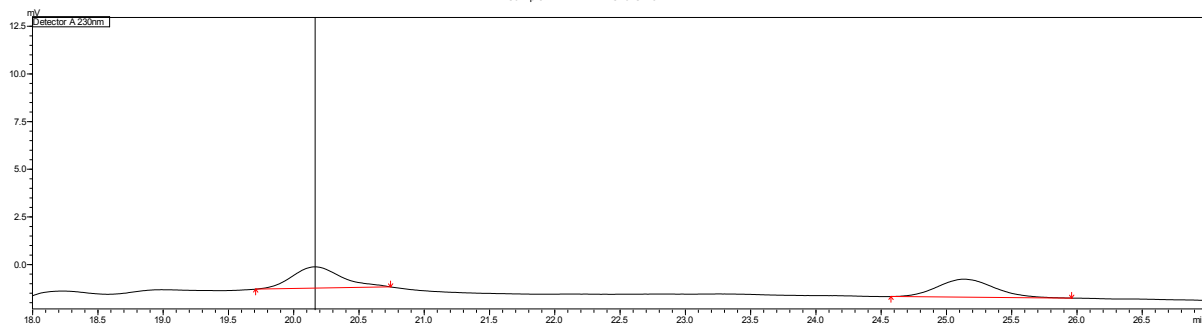
Datafile Name: 4-124 4C13 CHONE2.lcd
 Sample Name: 4-124 4C13 CHONE
 Sample ID: 4-124 4C13 CHONE



Peak	Ret. Time	Area	Height	Area%	
1	20.113	249515	10523	99.321	<i>anti</i>
2	21.835	1705	76	0.679	<i>anti</i>
Total		251220	10598	100.000	

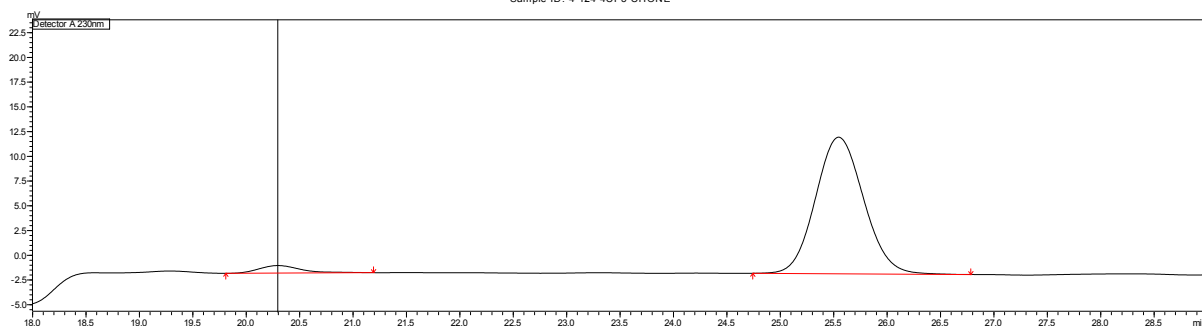
2-[Hydroxy-(4-trifluoromethyl-phenyl)methyl]-cyclohexanone (Table 2, entry 13)

Datafile Name: R4-124 4C13 CHONE1.lcd
Sample Name: R4-124 4C13 CHONE
Sample ID: R4-124 4C13 CHONE



Peak	Ret. Time	Area	Height	Area%	
1	20.164	29462	1119	50.733	<i>anti</i>
2	25.131	28611	942	49.267	<i>anti</i>
	Total	58073	2061	100.000	

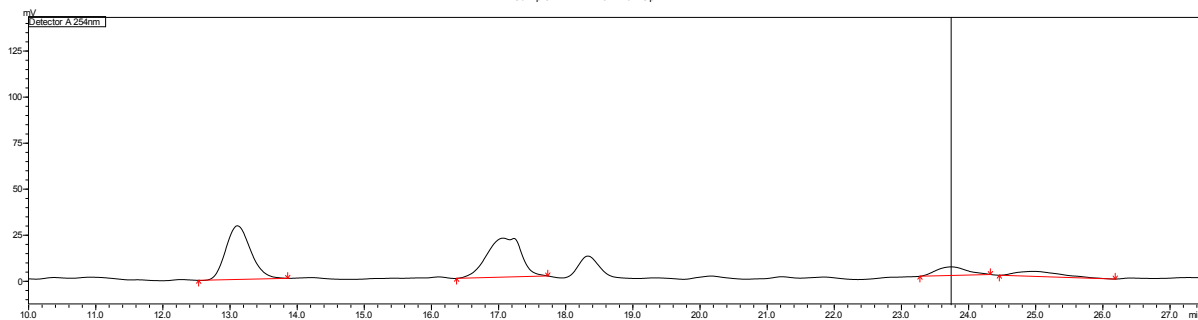
Datafile Name: 4-124 4CF3 CHONE1.lcd
Sample Name: 4-124 4CF3 CHONE
Sample ID: 4-124 4CF3 CHONE



Peak	Ret. Time	Area	Height	Area%	
1	20.295	20775	762	4.588	<i>anti</i>
2	25.546	431988	13800	95.412	<i>anti</i>
	Total	452763	14563	100.000	

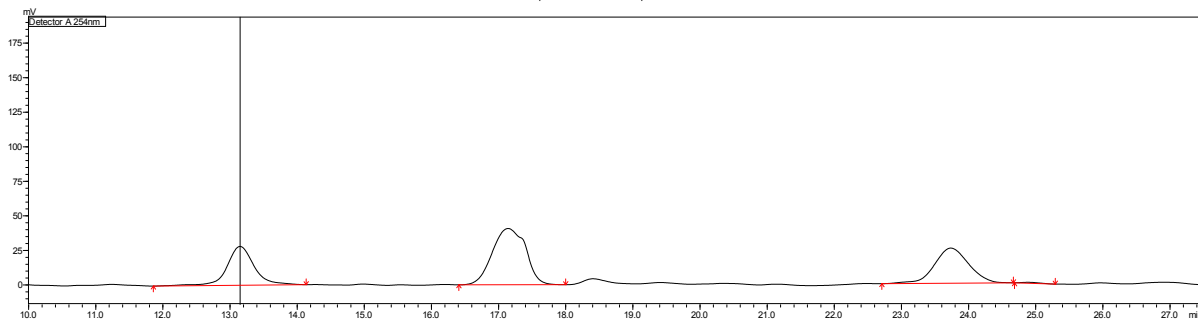
2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclopentanone (Table 3, entry 1)

Datafile Name: R 4-125 2No2 Cp1.lcd
 Sample Name: R 4-125 2No2 Cp
 Sample ID: R 4-125 2No2 Cp



Peak	Ret. Time	Area	Height	Area%	
1	13.110	749394	29152	41.882	<i>syn</i>
2	17.065	762898	21179	42.636	<i>syn</i>
3	23.742	149201	4662	8.338	<i>anti</i>
4	24.964	127825	2700	7.144	<i>anti</i>
	Total	1789319	57693	100.000	

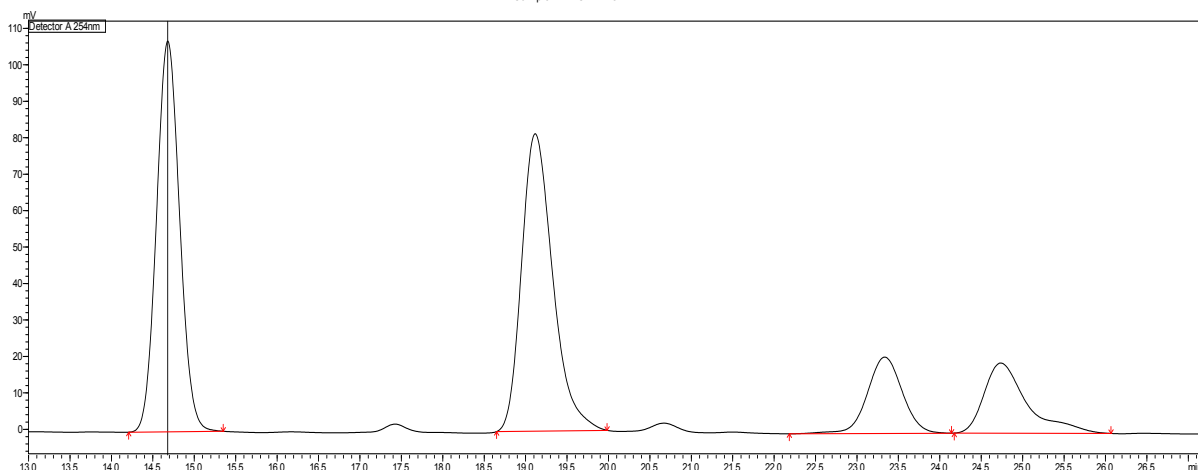
Datafile Name: 4-125 2No2 Cp1.lcd
 Sample Name: 4-125 2No2 Cp
 Sample ID: 4-125 2No2 Cp



Peak	Ret. Time	Area	Height	Area%	
1	13.149	792807	28119	25.438	<i>syn</i>
2	17.141	1411300	40754	45.282	<i>syn</i>
3	23.736	900685	25411	28.899	<i>anti</i>
4	24.884	11889	648	0.381	<i>anti</i>
	Total	3116680	94933	100.000	

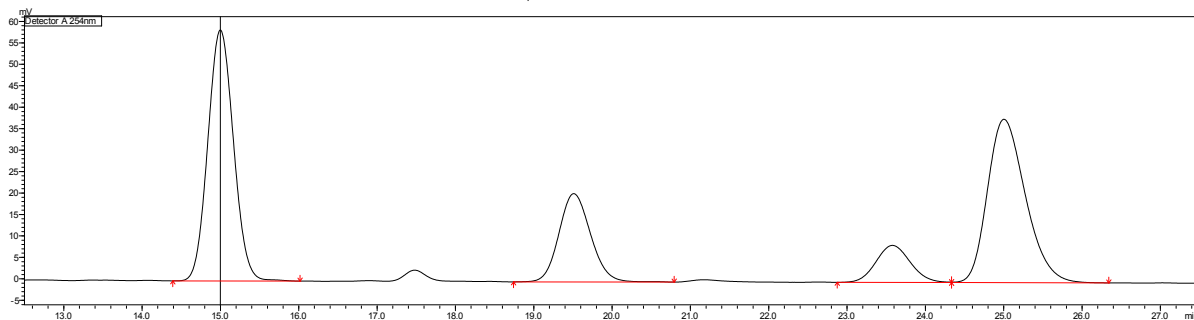
2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclopentanone (Table 3, entry 2)

Datafile Name:RCP 4NO2 AD h1.lcd
 Sample Name:RCP 4NO2 AD h
 Sample ID:RCP 4NO2 AD h



Peak	Ret. Time	Area	Height	Area%	
1	14.680	2081980	107220	37.683	<i>syn</i>
2	19.116	2136189	81607	38.664	<i>syn</i>
3	23.335	614255	20954	11.118	<i>anti</i>
4	24.736	692619	19259	12.536	<i>anti</i>
Total		5525042	229040	100.000	

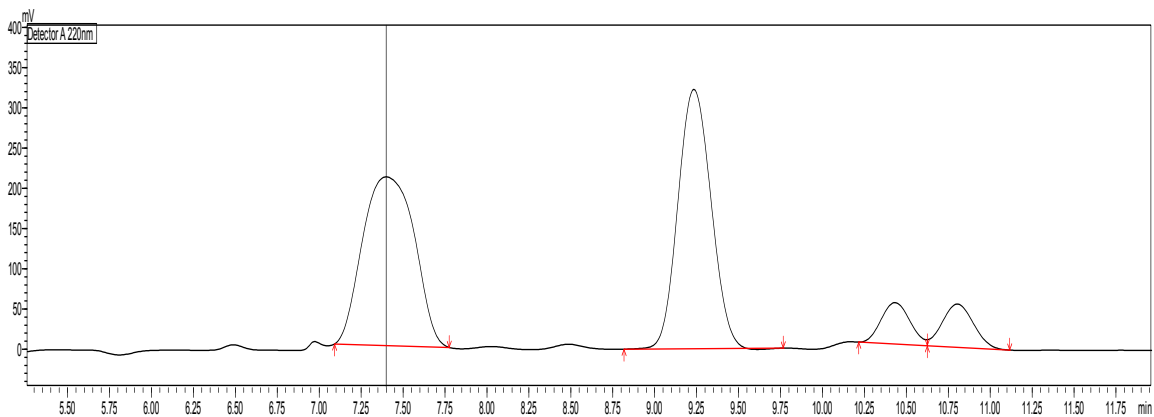
Datafile Name:4-125 4NO2 CPone2.lcd
 Sample Name: 4-125 4NO2 CPone
 Sample ID: 4-125 4NO2 CPone



Peak	Ret. Time	Area	Height	Area%	
1	14.999	1333087	58505	38.564	<i>syn</i>
2	19.511	577764	20587	16.714	<i>syn</i>
3	23.580	263504	8632	7.623	<i>anti</i>
4	25.003	1282495	38081	37.100	<i>anti</i>
Total		3456849	125805	100.000	

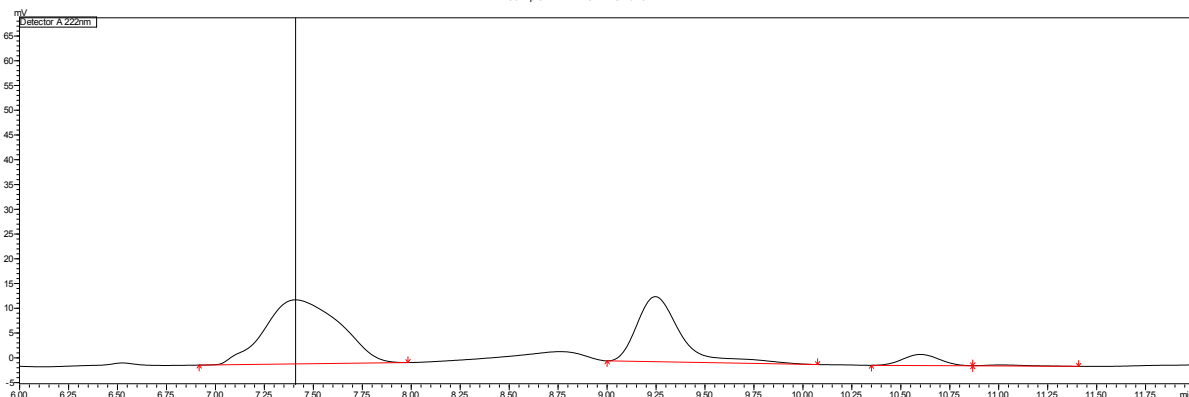
2-[Hydroxy-(2-fluoro-phenyl)-methyl]-cyclopentanone (Table 3, entry 3)

Datafile Name: R_CP 2F1.lcd
 Sample Name: R_CP 2F
 Sample ID: R_CP 2F



Peak	Ret. Time	Area	Height	Area%	
1	7.399	4508736	209627	44.045	<i>syn</i>
2	9.234	4422511	322360	43.202	<i>syn</i>
3	10.432	615946	51474	6.017	<i>anti</i>
4	10.804	689574	53720	6.736	<i>anti</i>
Total		10236766	637181	100.000	

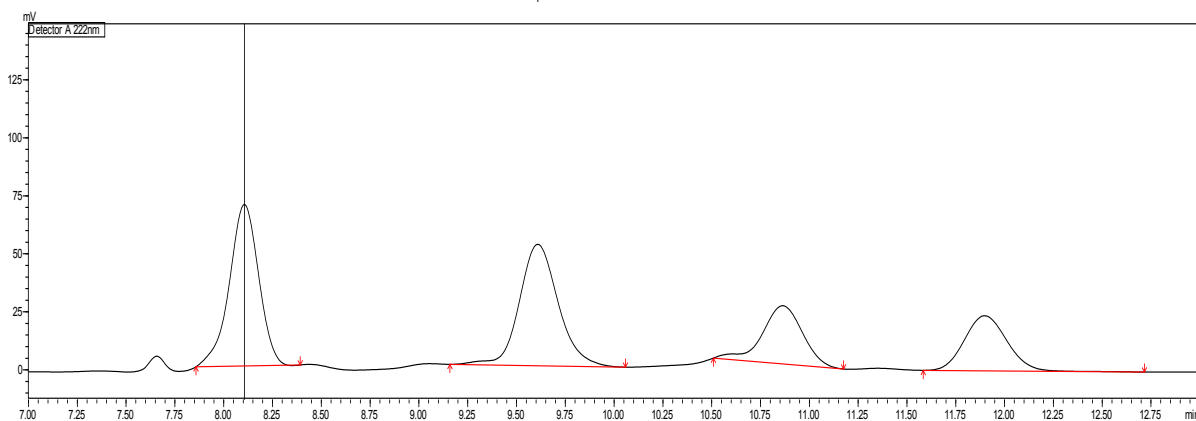
Datafile Name: 4-125 2F CPone2.lcd
 Sample Name: 4-125 2F CPone
 Sample ID: 4-125 2F CPone



Peak	Ret. Time	Area	Height	Area%	
1	7.409	346353	12952	59.430	<i>syn</i>
2	9.246	204349	13145	35.064	<i>syn</i>
3	10.601	29066	2244	4.987	<i>anti</i>
4	11.015	3019	209	0.518	<i>anti</i>
Total		582788	28550	100.000	

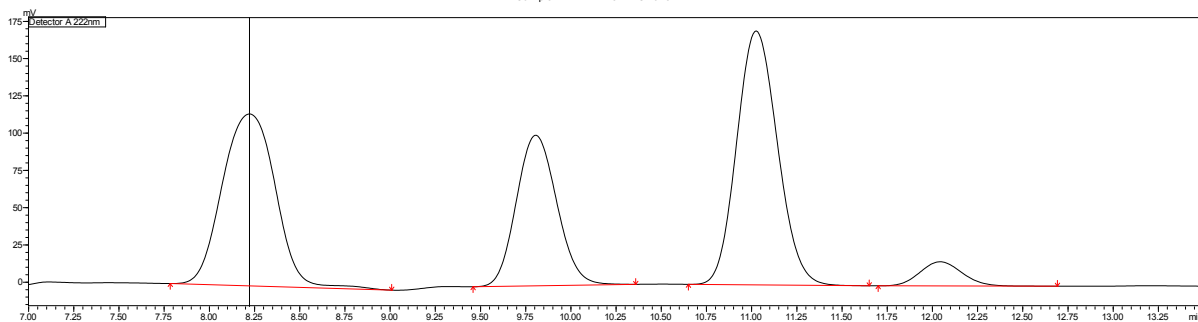
2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclopentanone (Table 3, entry 4)

Datafile Name: R 4-23 4 F ad-h1.lcd
 Sample Name: R 4-23 4 Cl ad-h
 Sample ID: R 4-23 4 Cl ad-h



Peak	Ret. Time	Area	Height	Area%	
1	8.106	727759	69602	33.541	<i>syn</i>
2	9.609	724471	52389	33.390	<i>syn</i>
3	10.863	358024	25047	16.501	<i>anti</i>
4	11.898	359486	23752	16.568	<i>anti</i>
Total		2169740	170789	100.000	

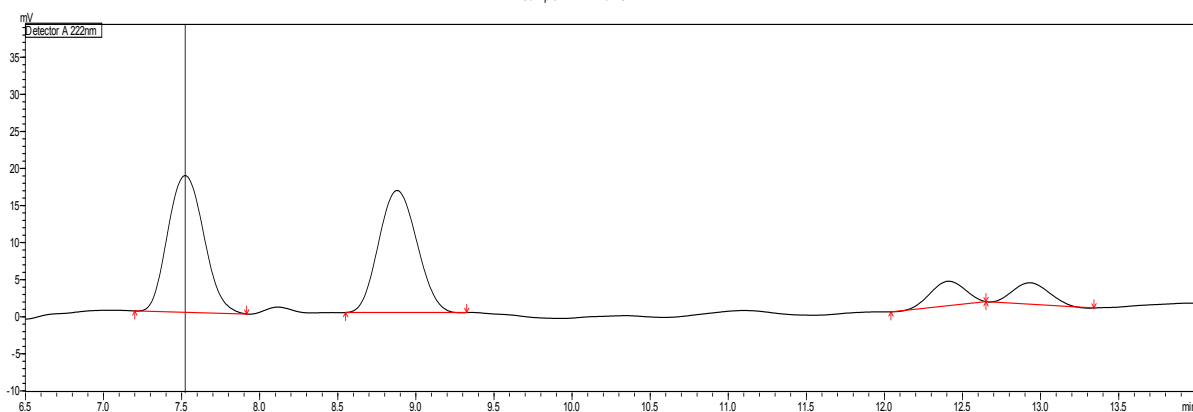
Datafile Name: 4-125 4F CPone1.lcd
 Sample Name: R 4-125 4F CPone
 Sample ID: R 4-125 4F CPone



Peak	Ret. Time	Area	Height	Area%	
1	8.222	2352997	115365	34.313	<i>syn</i>
2	9.805	1568845	101036	22.878	<i>syn</i>
3	11.025	2673358	170413	38.985	<i>anti</i>
4	12.042	262198	16220	3.824	<i>anti</i>
Total		6857399	403034	100.000	

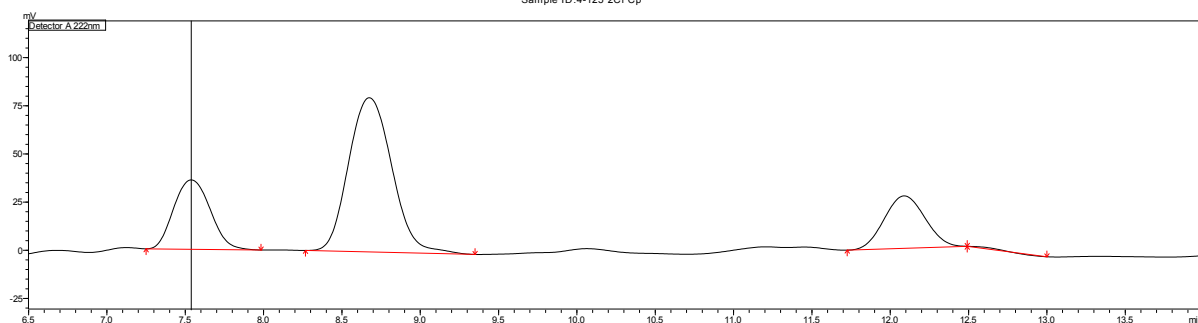
2-[Hydroxy-(2-chloro-phenyl)methyl]-cyclohexanone (Table 3, entry 5)

Datafile Name: R 4-23 2CI1.lcd
 Sample Name: R 4-23 2CI
 Sample ID: R 4-23 2CI



Peak	Ret. Time	Area	Height	Area%	
1	7.522	296558	18441	43.962	<i>syn</i>
2	8.880	280799	16465	41.625	<i>syn</i>
3	12.411	51059	3298	7.569	<i>anti</i>
4	12.930	46168	2890	6.844	<i>anti</i>
Total		674585	41095	100.000	

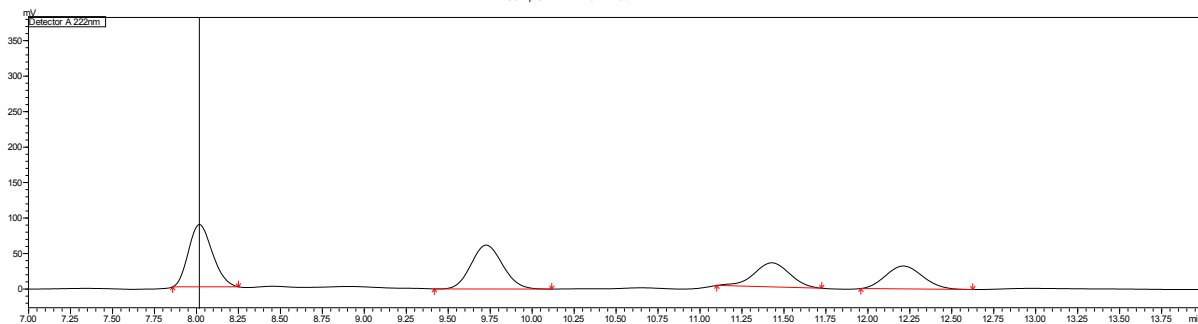
Datafile Name: 4-125 2CI Cp1.lcd
 Sample Name: 4-125 2CI Cp
 Sample ID: 4-125 2CI Cp



Peak	Ret. Time	Area	Height	Area%	
1	7.538	583756	36023	22.284	<i>syn</i>
2	8.674	1540277	80080	58.798	<i>syn</i>
3	12.089	492868	27214	18.815	<i>anti</i>
4	12.504	2695	114	0.103	<i>anti</i>
Total		2619595	143430	100.000	

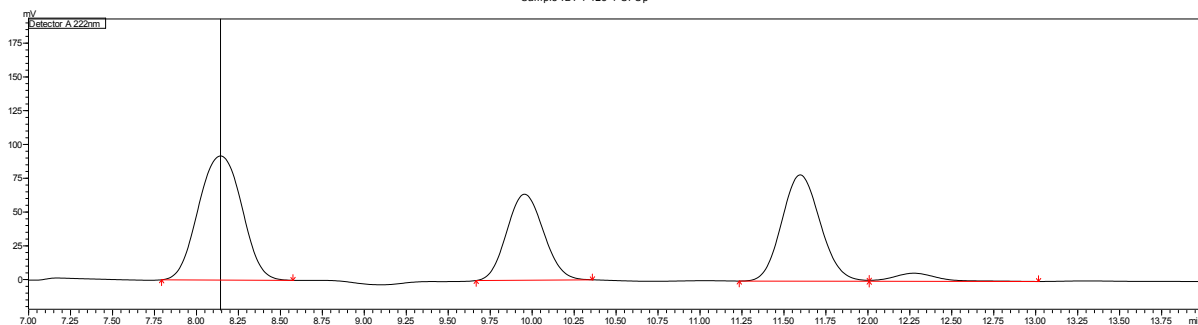
2-[Hydroxy-(4-chloro-phenyl)methyl]-cyclohexanone (Table 3, entry 6)

Datafile Name: R 4-23 4 CI ad-h1 (2).lcl
 Sample Name: R 4-23 4 F ad-h
 Sample ID: R 4-23 4 F ad-h



Peak	Ret. Time	Area	Height	Area%	
1	8.017	869216	87910	32.476	<i>anti</i>
2	9.726	809696	61856	30.252	<i>syn</i>
3	11.427	503213	33958	18.801	<i>syn</i>
4	12.211	494381	32202	18.471	<i>anti</i>
	Total	2676505	215926	100.000	

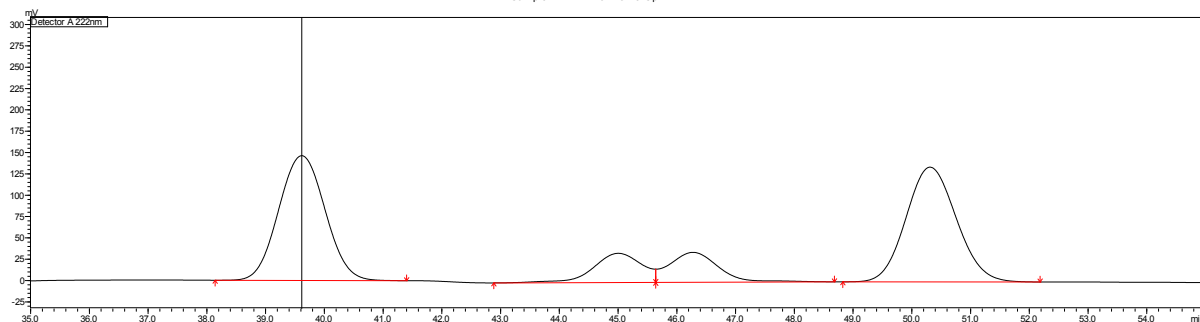
Datafile Name: 4-125 4 CI Cp1.lcl
 Sample Name: 4-125 4 CI Cp
 Sample ID: 4-125 4 CI Cp



Peak	Ret. Time	Area	Height	Area%	
1	8.143	1653487	91829	41.467	<i>anti</i>
2	9.954	971428	63644	24.362	<i>syn</i>
3	11.597	1255214	78623	31.479	<i>syn</i>
4	12.275	107350	5999	2.692	<i>anti</i>
	Total	3987479	240095	100.000	

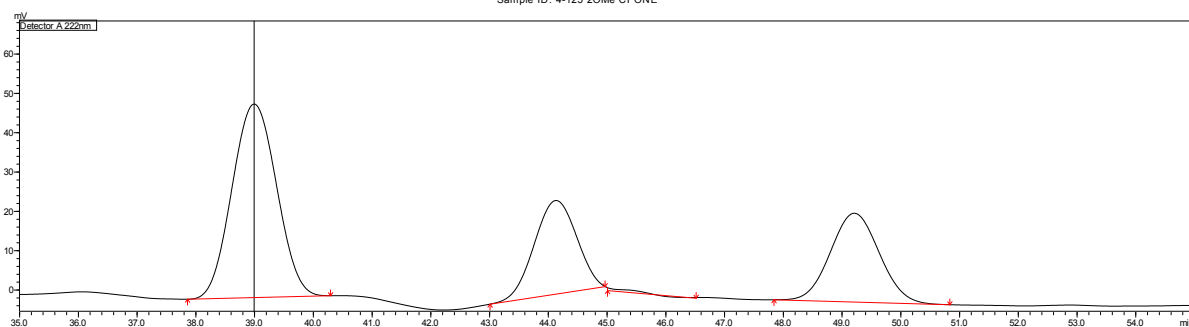
2-[Hydroxy-(2-methoxy-phenyl)methyl]-cyclopentanone (Table 3, entry 7)

Datafile Name: R 4-125 2 OMe Cp2.lcd
 Sample Name: R 4-125 2 OMe Cp
 Sample ID: R 4-125 2 OMe Cp



Peak	Ret. Time	Area	Height	Area%	
1	39.615	8041408	146221	40.125	<i>anti</i>
2	45.003	1971409	34206	9.837	<i>syn</i>
3	46.275	2021712	35043	10.088	<i>syn</i>
4	50.310	8006593	134436	39.951	<i>anti</i>
	Total	20041121	349907	100.000	

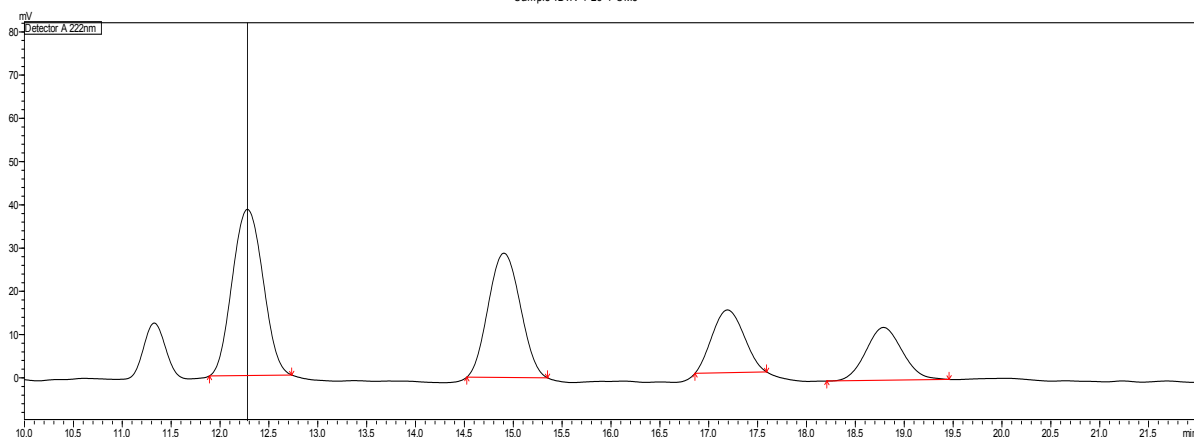
Datafile Name: 4-125 2OMe CPONE1.lcd
 Sample Name: 4-125 2OMe CPONE
 Sample ID: 4-125 2OMe CPONE



Peak	Ret. Time	Area	Height	Area%	
1	38.993	2596848	49221	50.784	<i>anti</i>
2	44.132	1191098	23798	23.293	<i>syn</i>
3	45.021	18701	721	0.366	<i>syn</i>
4	49.207	1306900	22578	25.558	<i>anti</i>
	Total	5113546	96319	100.000	

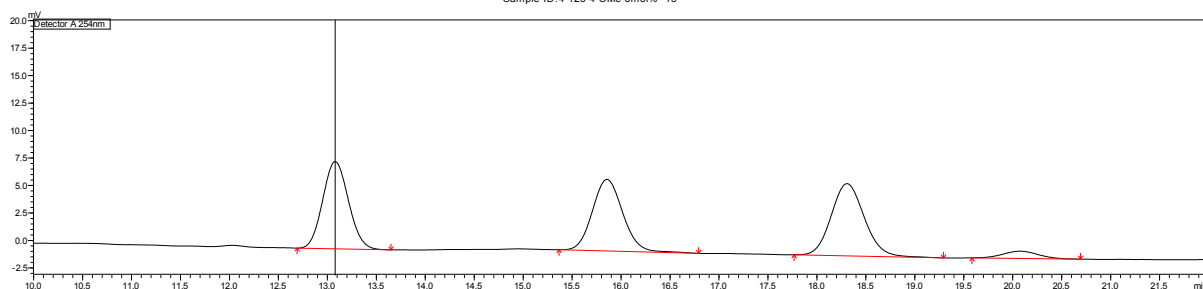
2-[Hydroxy-(4-methoxy-phenyl)methyl]-cyclopentanone (Table 3, entry 8)

Datafile Name: R 4-23 4-OMe1.lcd
 Sample Name: R 4-23 4-OMe
 Sample ID: R 4-23 4-OMe



Peak	Ret. Time	Area	Height	Area%	
1	12.281	640290	33206	33.014	<i>syn</i>
2	14.904	654747	28749	33.012	<i>syn</i>
3	17.192	327404	14515	16.881	<i>anti</i>
4	18.787	317011	12227	16.345	<i>anti</i>
Total		1939451	88696	100.000	

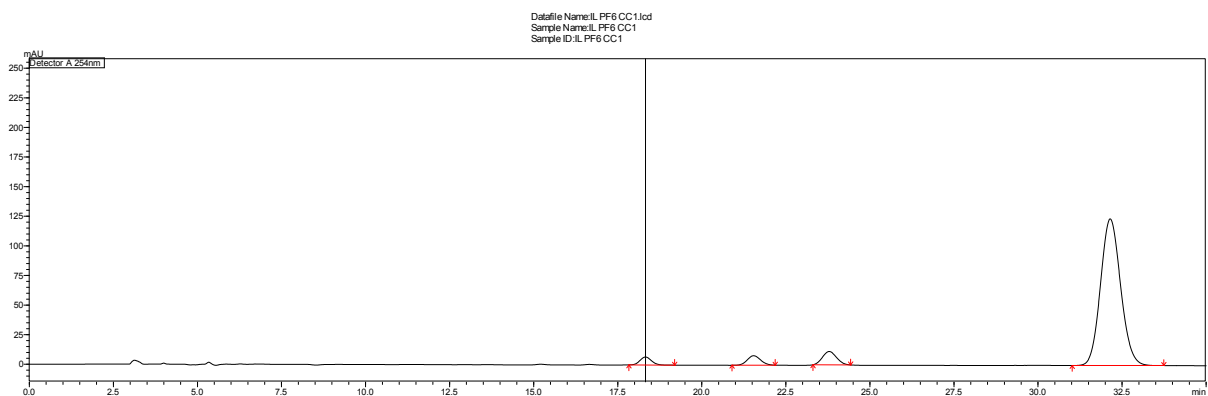
Datafile Name: 4-125 4-OMe 5mol% -16.lcd
 Sample Name: 4-125 4-OMe 5mol% -15
 Sample ID: 4-125 4-OMe 5mol% -15



Peak	Ret. Time	Area	Height	Area%	
1	13.080	145269	7939	31.750	<i>syn</i>
2	15.854	140958	6511	30.808	<i>syn</i>
3	18.306	154808	6575	33.835	<i>anti</i>
4	20.076	16505	660	3.607	<i>anti</i>
Total		457541	21685	100.000	

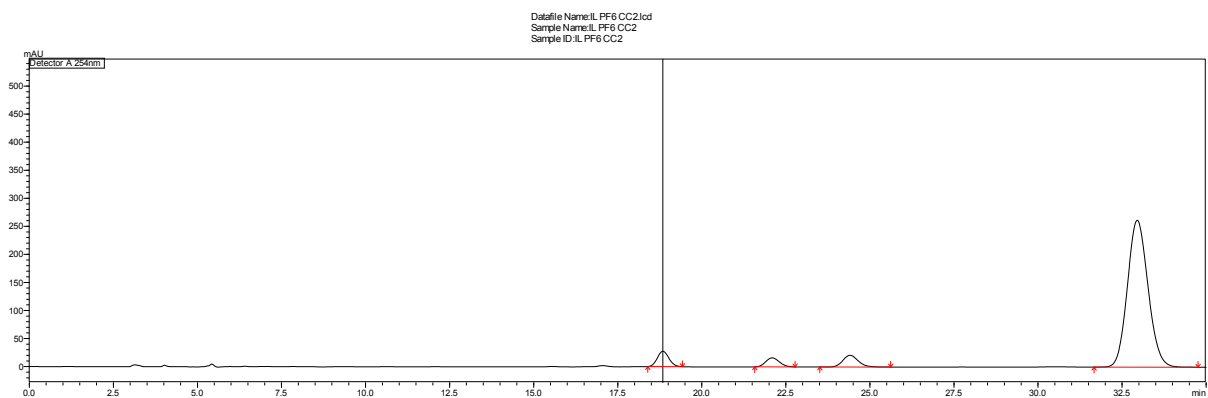
HPLC Data of continuous cycle of IL 3 (Table 4, entry 1-7)

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 1)



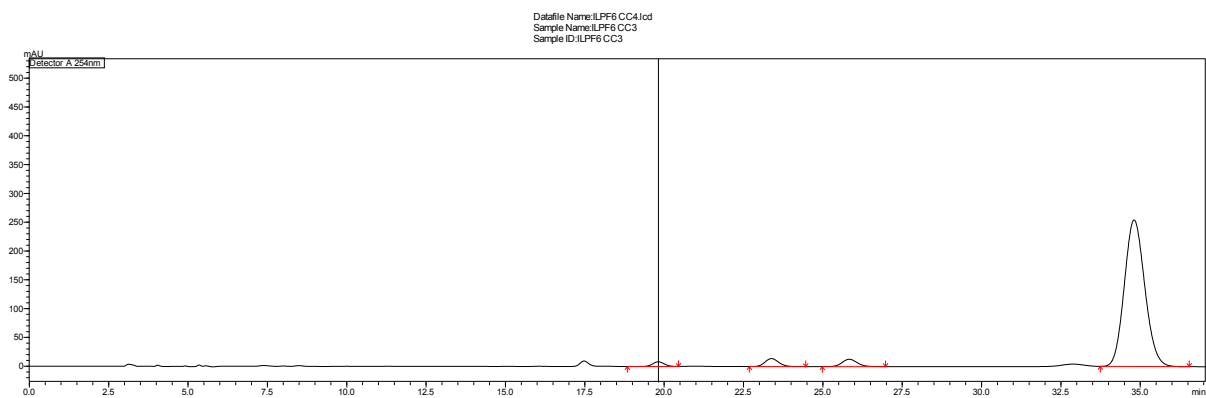
Peak	Ret. Time	Area	Height	Area%	
1	18.325	159105	6704	2.721	<i>syn</i>
2	21.541	221144	8009	3.781	<i>syn</i>
3	23.790	325986	11243	5.574	<i>anti</i>
4	32.147	5142022	123805	87.924	<i>anti</i>
Total		5848257	149760	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 2)



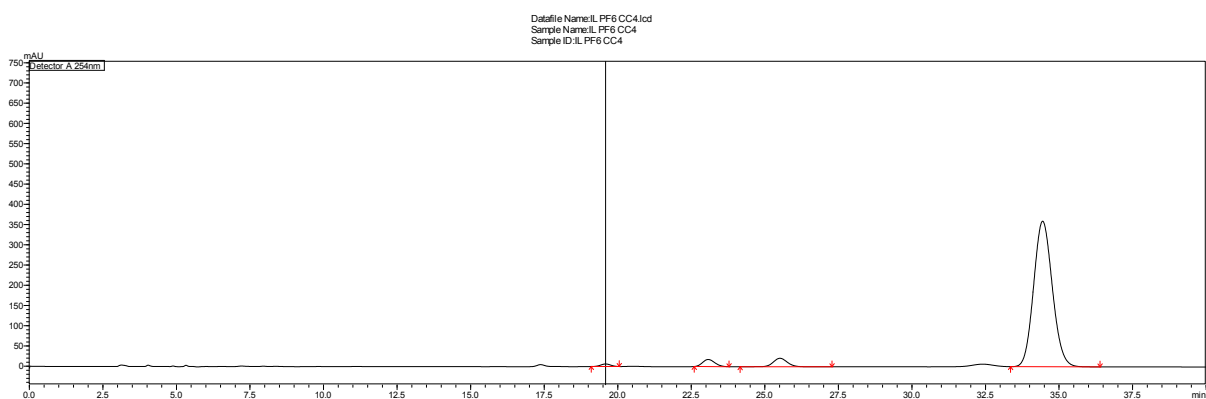
Peak	Ret. Time	Area	Height	Area%	
1	18.842	654529	27351	5.058	<i>syn</i>
2	22.092	453656	16140	3.506	<i>syn</i>
3	24.409	663348	20890	5.126	<i>anti</i>
4	32.951	11168203	261813	86.309	<i>anti</i>
Total		12939734	326194	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 3)



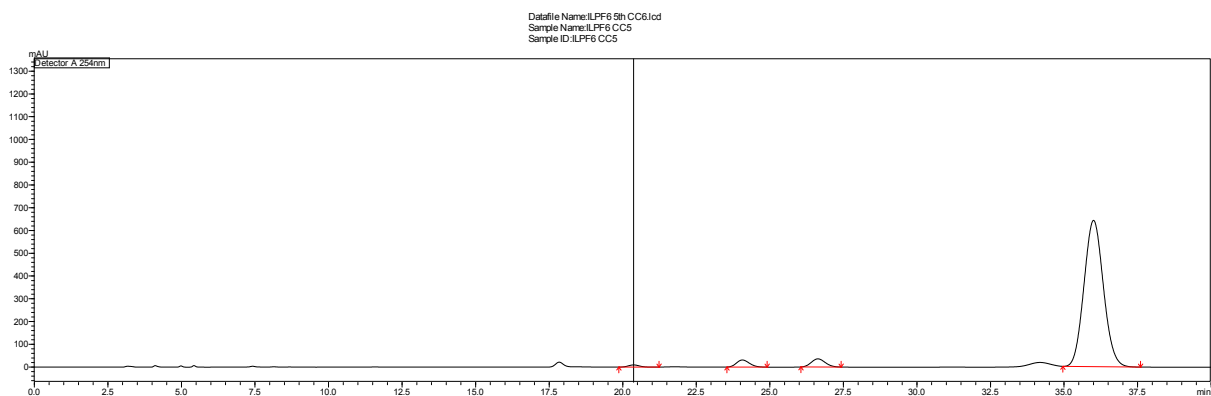
Peak	Ret. Time	Area	Height	Area%	
1	19.818	206054	8071	1.654	<i>syn</i>
2	23.379	411967	13834	3.306	<i>syn</i>
3	25.833	418687	12743	3.360	<i>anti</i>
4	34.806	11423133	254528	91.680	<i>anti</i>
Total		12459840	289177	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 4)



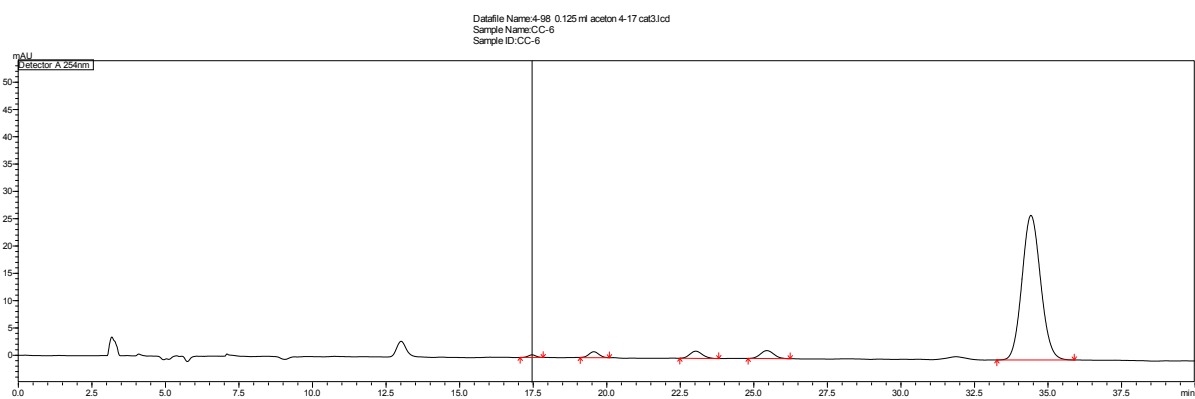
Peak	Ret. Time	Area	Height	Area%	
1	19.587	149874	6289	0.868	<i>syn</i>
2	23.076	506750	17611	2.934	<i>syn</i>
3	25.514	700717	20979	4.056	<i>anti</i>
4	34.443	15916759	359811	92.142	<i>anti</i>
Total		17274100	404690	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 5)



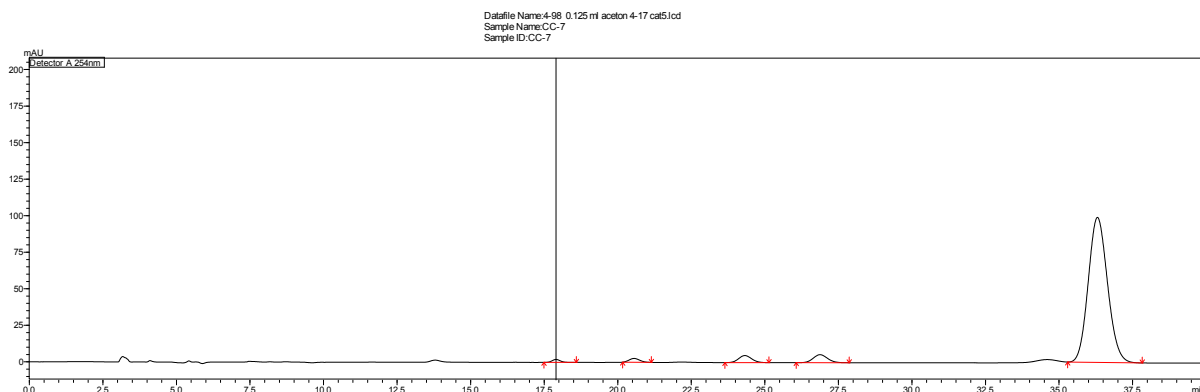
Peak	Ret. Time	Area	Height	Area%	
1	20.369	242451	9466	0.760	<i>syn</i>
2	24.066	951177	31157	2.980	<i>syn</i>
3	26.633	1178656	35736	3.693	<i>anti</i>
4	36.003	29546440	642866	92.568	<i>anti</i>
Total		31918724	719225	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 6)



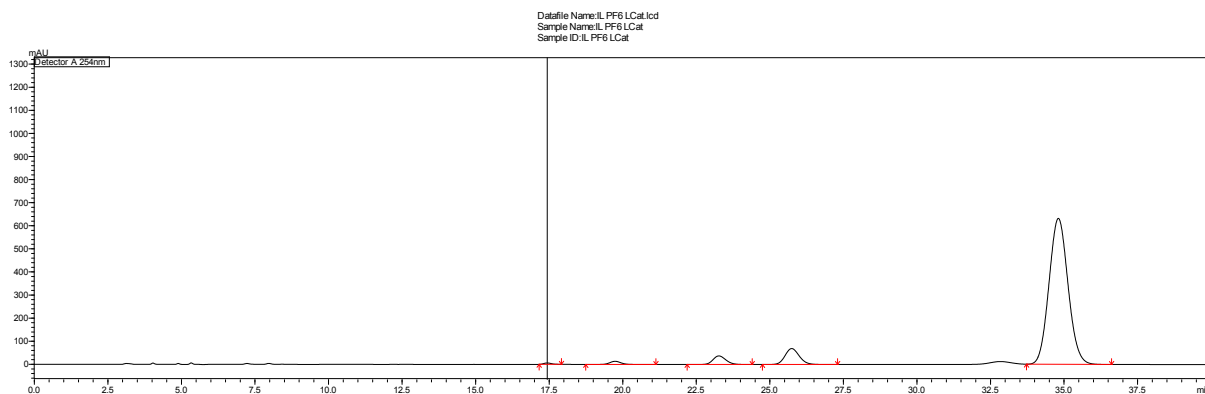
Peak	Ret. Time	Area	Height	Area%	
1	17.463	8645	480	0.669	4-Nitro-benzaldehyde
2	19.558	26156	1091	2.024	<i>syn</i>
3	23.023	38819	1316	3.004	<i>syn</i>
4	25.439	46515	1460	3.600	<i>anti</i>
5	34.419	1171972	26483	90.702	<i>anti</i>
Total		1292108	30829	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (Table 4, entry 7)



Peak	Ret. Time	Area	Height	Area%	
1	17.901	38827	2020	0.782	4-Nitro-benzaldehyde
2	20.556	65048	2612	1.310	<i>syn</i>
3	24.322	149336	4832	3.008	<i>syn</i>
4	26.879	186138	5493	3.750	<i>anti</i>
5	36.305	4524463	99232	91.149	<i>anti</i>
Total		4963813	114190	100.000	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (use of IL3 (0.4 mol%))



Peak	Ret. Time	Area	Height	Area%	
1	17.434	101816	5835	0.316	4-Nitro-benzaldehyde
2	19.740	361530	13691	1.121	<i>syn</i>
3	23.267	1121887	37033	3.477	<i>syn</i>
4	25.743	2301854	68957	7.135	<i>anti</i>
5	34.807	28375453	631909	87.952	<i>anti</i>
Total		32262540	757425	100.000	