ELECTRONIC SUPPLEMENTARY INFORMATION

Cycloaddition of Tertiary Aziridines and Carbon Dioxide Using a

Recyclable Organocatalyst, 1,3-Di-tert-butylimidazolium-2-carboxylate:

A Straightforward Access to 3-Substituted 2-Oxazolidones

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General information. Solvents were purchased from Kanto Chemical Co., Inc. or Nacalai Tesque, Inc. Et_2O was dried by refluxing over sodium benzophenone ketyl and distilled under argon. 1-(2-Hydroxyethyl)ethyleneimine (**2c**) was purchased from Tokyo Kasei Co. Ltd., and used after purification by distillation under argon. Other reagents were used as delivered. Aziridine substrates of **2a**, **2b** and **2f** were prepared by the literature methods.¹

Synthesis of Aziridines (2d–2e and 2g–2o).

To an Et₂O solution (40.0 mL) of 1-(2-Hydroxyethyl)ethyleneimine (1.50 g, 17.2 mmol) was added NaH (1.2 g, 30 mmmol) under argon atmosphere at 0 °C. The mixture was stirred for 10 minutes, and appropriate organic bromides (17.2 mmol) dissolved in Et₂O (10 mL) was added dropwisely at room temperature over a period of 5 minutes. After stirring for 18 h, H₂O (5.0 mL) was added to the solution. The ethereal solution was washed with brine (50 mL) and dried with Na₂SO₄. The filtrate was concentrated *in vacuo* to give the crude products. The desired aziridines were isolated after purification by column chromatography using alumina and distillation.

N-[2-Benzyloxy]ethyl]aziridine (2d).



The title compound was prepared from benzyl bromide by the procedure described above: yield: 75%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.17 (m, 2H), 1.75 (m, 2H), 2.44 (t, 2H, ³J_{HH} = 5.8 Hz; NCH₂CH₂O), 3.65 (t, 2H, ³J_{HH} = 5.8 Hz; NCH₂CH₂O), 4.57 (s, 2H; CH₂C₆H₅), 7.26-7.37 (m, 4H; CH₂C₆H₅); ¹³C{¹H} NMR

 $(100.5 \text{ MHz}, \text{CDCl}_3) \delta 27.1, 61.1, 69.8, 73.2, 127.4, 127.5, 128.3, 138.4; \text{HRMS (ESI)}$ calcd for C₁₁H₁₆NO 178.1226 (M + H⁺), found 178.1224.

1-[2-(Allyloxy)ethyl]aziridine (2e).

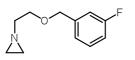
The title compound was prepared from allyl bromide by the procedure described above: yield: 56%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.15 (m, 2H), 1.73 (m, 2H), 2.40 (t, 2H, ³J_{HH} = 5.8 Hz; NCH₂CH₂OCH₂), 3.59 (t, 2H, ³J_{HH} = 5.6 Hz; NCH₂CH₂OCH₂), 4.01 (m, 2H; CH₂CH=CH₂), 5.16 (ddt, 1H, ²J_{HH} = 10.4 Hz, ³J_{HH} = 1.8 Hz, ⁴J_{HH} = 1.2 Hz; CH₂CH=CH₂), 5.30 (ddt, 1H, ²J_{HH} = 17.2 Hz, ³J_{HH} = 1.8 Hz, ⁴J_{HH} = 1.8 Hz; CH₂CH=CH₂), 5.87-5.97 (m, 1H; CH₂CH=CH₂); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 61.1, 69.7, 72.1, 116.7, 134.8; HRMS (ESI) calcd for C₇H₁₄NO 128.1070 (M + H⁺), found 128.1073.

1-[2-(Benzoyloxy)ethyl]aziridine (2g).



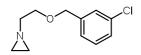
The title compound was prepared from benzoyl bromide by the procedure described above: yield: 55%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.22 (m, 2H), 1.81 (m, 2H), 2.33 (t, 2H, ${}^{3}J_{HH} = 5.5$ Hz; NCH₂CH₂O), 4.49 (t, 2H, ${}^{3}J_{HH} = 5.5$ Hz; NCH₂CH₂O), 7.41-8.07 (m, 5H; COC₆H₅); ${}^{13}C{}^{1}H$ NMR (100.5 MHz, CDCl₃) δ 27.2, 59.8, 128.3, 129.6, 130.1, 132.9, 166.5. Anal. Calcd. for C₁₁H₁₃NO₂: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.47; H, 6.74; N, 7.02.

1-[2-(3-Fluorophenyl)methyloxy]ethyl]aziridine (2h).



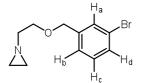
The title compound was prepared from 3-fluorobenzyl bromide by the procedure described above: yield: 72%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.17 (m, 2H), 1.76 (m, 2H), 2.44 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.65 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 4.56 (s, 2H; CH₂C₆H₄F), 7.07-7.31 (m, 4H; CH₂C₆H₄F); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 27.1, 61.0, 70.0, 72.4, 114.1(d), 114.3(d), 122.7, 129.7(d), 141.1, 162.7(d). Anal. Calcd. for C₁₁H₁₄FNO: C, 67.67; H, 7.23; N, 7.17. Found: C, 67.89; H, 6.95; N, 6.80.

1-[2-(3-Chlorophenyl)methyloxy]ethyl]aziridine (2i).



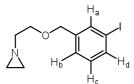
The title compound was prepared from 3-chlorobenzyl bromide by the procedure described above: yield: 62%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.17 (m, 2H), 1.76 (m, 2H), 2.44 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.64 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 4.53 (s, 2H; CH₂C₆H₄Cl), 7.20-7.36 (m, 4H; CH₂C₆H₄Cl); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 27.1, 61.0, 70.0, 72.3, 125.4, 127.4, 127.5, 129.5, 134.2, 140.5. Anal. Calcd. for C₁₁H₁₄ClNO: C, 62.42; H, 6.67; N, 6.62. Found: C, 62.53; H, 6.59; N, 6.23.

1-[2-(3-Bromophenyl)methyloxy]ethyl]aziridine (2j).



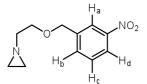
The title compound was prepared from 3-bromobenzyl bromide by the procedure described above: yield: 52%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.17 (m, 2H), 1.76 (m, 2H), 2.44 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.64 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 4.53 (s, 2H; CH₂C₆H₄Br), 7.20 (m, 1H; aromatic), 7.26 (d, 1H, ³J_{HH} = 6.4 Hz; aromatic), 7.41 (d, 1H, ³J_{HH} = 1.2 Hz; aromatic), 7.52 (s, 1H; aromatic); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 27.1, 61.0, 70.0, 72.3, 122.4, 125.9, 129.8, 130.4, 130.5, 140.8; HRMS (ESI) calcd for C₁₁H₁₄BrNONa 278.0157 (M + Na⁺), found 278.0163.

1-[2-(3-Iodophenyl)methyloxy]ethyl]aziridine (2k).



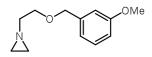
The title compound was prepared from 3-iodobenzyl bromide, but was decomposed at around 200 °C. The product was purified only with column chromatography: yield: 70%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.17 (m, 2H), 1.76 (m, 2H), 2.43 (t, 2H, ${}^{3}J_{HH} = 5.5$ Hz; NCH₂CH₂O), 3.63 (t, 2H, ${}^{3}J_{HH} = 5.5$ Hz; NCH₂CH₂O), 4.50 (s, 2H; CH₂C₆H₄I), 7.07 (dd, 1H; aromatic), 7.29 (d, 1H, ${}^{3}J_{HH} = 6.4$ Hz; aromatic), 7.60 (d, 1H, ${}^{3}J_{HH} = 8.0$ Hz; aromatic), 7.71 (s, 1H; aromatic); ${}^{13}C{}^{1}H$ NMR (100.5 MHz, CDCl₃) δ 27.1, 61.0, 70.0, 72.3, 122.4, 125.9, 129.8, 130.4, 130.5, 140.8. Anal. Calcd. for C₁₁H₁₄INO: C, 43.48; H, 4.66; N, 4.62. Found: C, 43.55; H, 4.64; N, 4.48..

1-[2-(3-Nitrophenyl)methyloxy]ethyl]aziridine (2l).



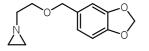
The title compound was prepared from 3-nitrobenzyl bromide by the procedure described above: yield: 40%; orange liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.19 (m, 2H), 1.78 (m, 2H), 2.47 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.69 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 4.66 (s, 2H; CH₂C₆H₄NO₂), 7.50 (m, 1H; aromatic), 7.68 (d, 1H, ³J_{HH} = 7.6 Hz; aromatic), 8.13 (d, 1H, ³J_{HH} = 8.2 Hz; aromatic), 8.23 (s, 1H; aromatic); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 27.2, 61.0, 70.5, 71.8, 122.0, 122.4, 129.2, 133.1, 140.7, 148.1. Anal. Calcd. for C₁₁H₁₄N₂O₃: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.70; H, 6.13; N, 12.26.

1-[2-(3-Methoxyphenyl)methyloxy]ethyl]aziridine (2m).



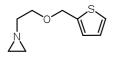
The title compound was prepared from 3-methoxybenzyl bromide by the procedure described above: yield: 60%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.17 (m, 2H), 1.75 (m, 2H), 2.43 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.64 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.80 (s, 2H; OCH₃), 4.54 (s, 2H; CH₂C₆H₄NO₂), 6.80-6.83 (m, 1H), 6.91-6.93 (m, 2H), 7.24 (m, 1H); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 55.1, 61.1, 69.8, 73.0, 112.8, 113.1, 119.7, 129.3, 140.0, 159.6; HRMS (ESI) calcd for C₁₂H₁₈NO 208.1332 (M + H⁺), found 208.1337.

1-[2-(3,4-Methylenedioxyphenylmethyloxy)ethyl]aziridine (2n).



The title compound was prepared from 3,4-methylenedioxybenzyl bromide by the procedure described above: yield: 50%; colorless liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.16 (m, 2H), 1.75 (m, 2H), 2.41 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.61 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.61 (t, 2H, ³J_{HH} = 5.5 Hz; NCH₂CH₂O), 3.39 (s, 2H; CH₂C₅H₃OCH₂O), 5.94 (s, 2H; CH₂C₅H₃OCH₂O), 6.75-6.86 (m, 3H; CH₂C₅H₃OCH₂O); ¹³C{¹H} NMR (100.5 MHz, CDCl₃) δ 27.1, 61.1, 65.5, 73.0, 100.8, 107.9, 108.3, 121.1, 132.3, 146.9, 147.6; HRMS (ESI) calcd for C₁₂H₁₆NO₃ 222.1125 (M + H⁺), found 222.1125.

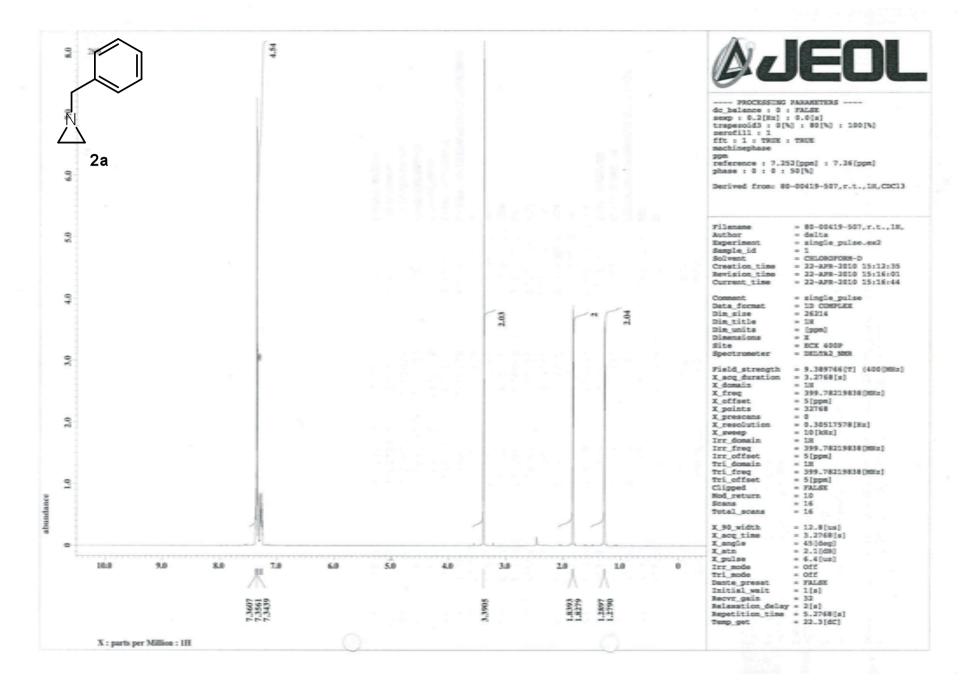
1-[2-(Thiophen-2-ylmethyloxy)ethyl]aziridine (20).

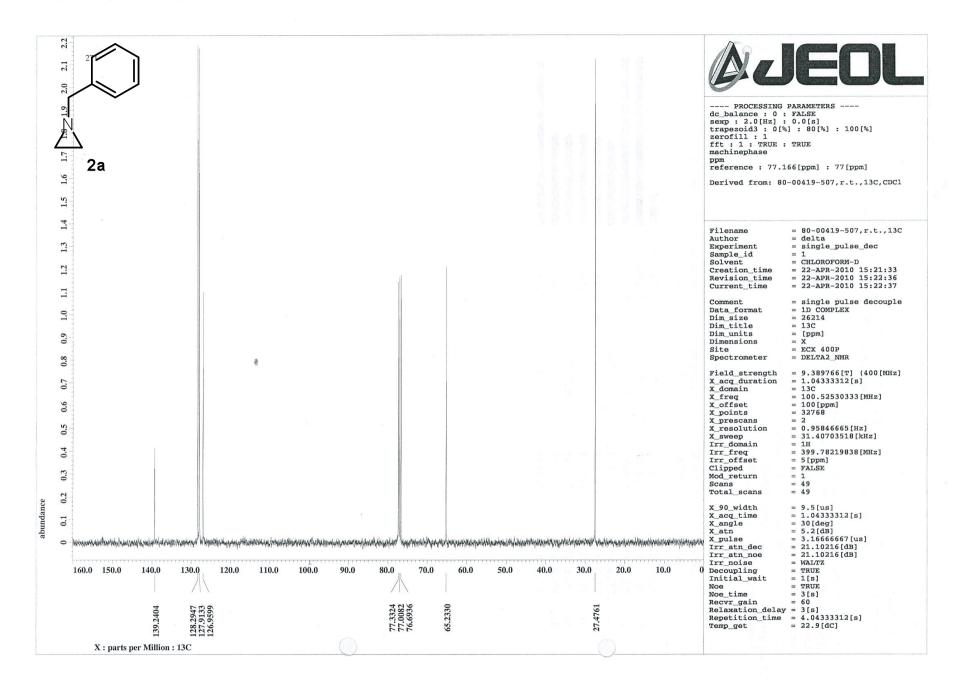


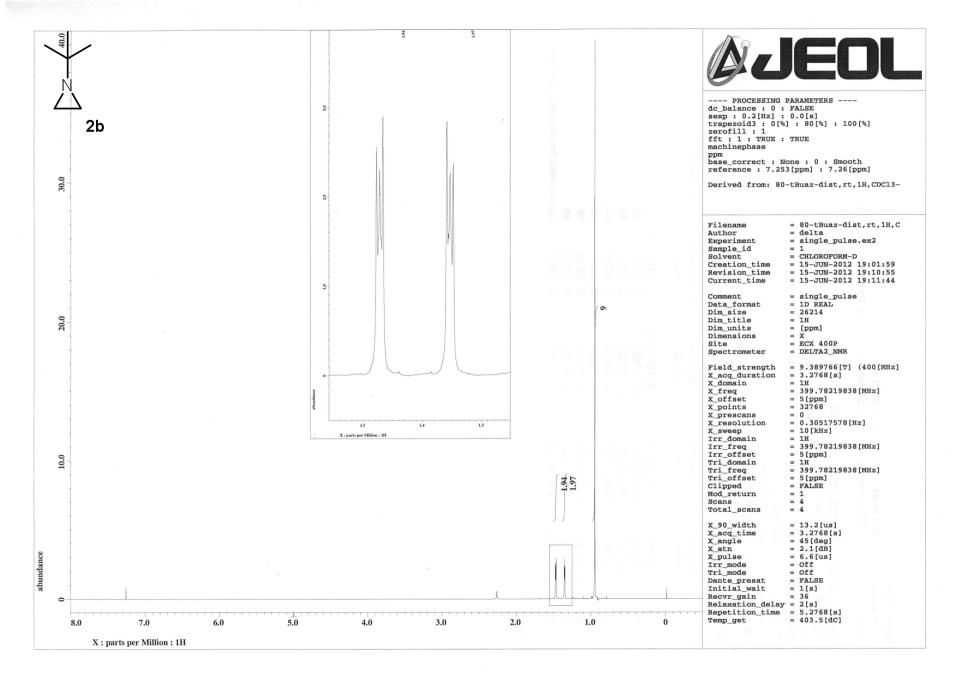
The title compound was prepared from 2-bromothiophene by the procedure described above: yield: 62%; pale yellow liquid. ¹H NMR (399.8 MHz, CDCl₃) δ 1.16 (m, 2H), 1.74 (m, 2H), 2.42 (t, 2H, ${}^{3}J_{HH} = 5.5$ Hz; NCH₂CH₂O), 3.65 (t, 2H, ${}^{3}J_{HH} = 5.5$ Hz; NCH₂CH₂O), 4.72 (s, 2H; CH₂C₄H₃S), 6.96-7.27 (m, 3H; CH₂C₄H₃S); ${}^{13}C{}^{1}H$ NMR (100.5 MHz, CDCl₃) δ 27.1, 61.0, 67.7, 69.4, 125.6, 126.2, 126.5, 141.1. Anal. Calcd. for C₉H₁₃NOS: C, 58.98; H, 7.15; N, 7.64. Found: C, 58.67; H, 7.04; N, 7.39.

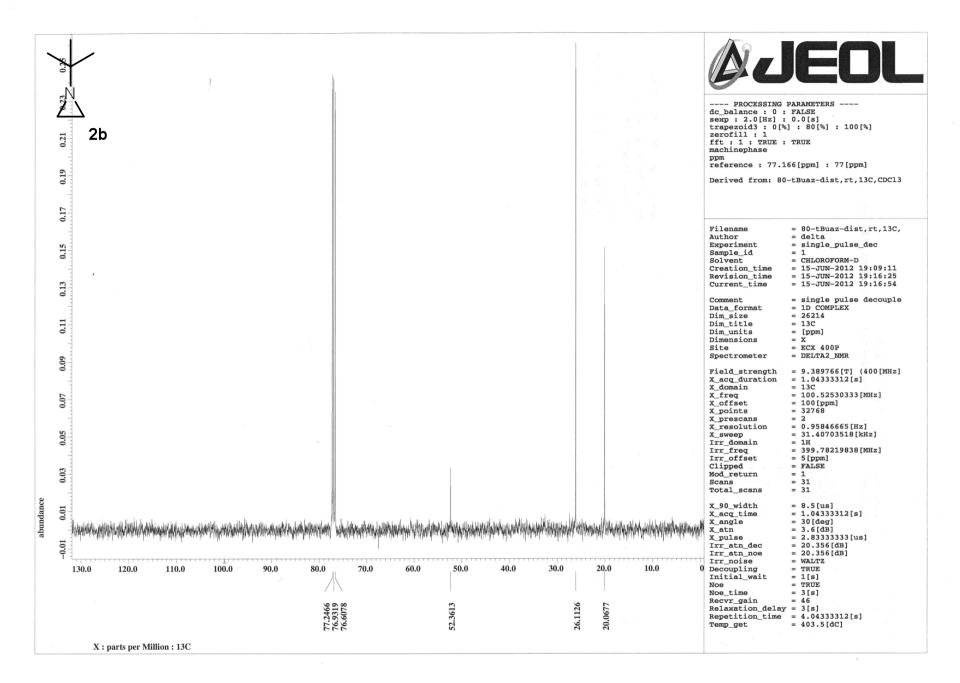
References

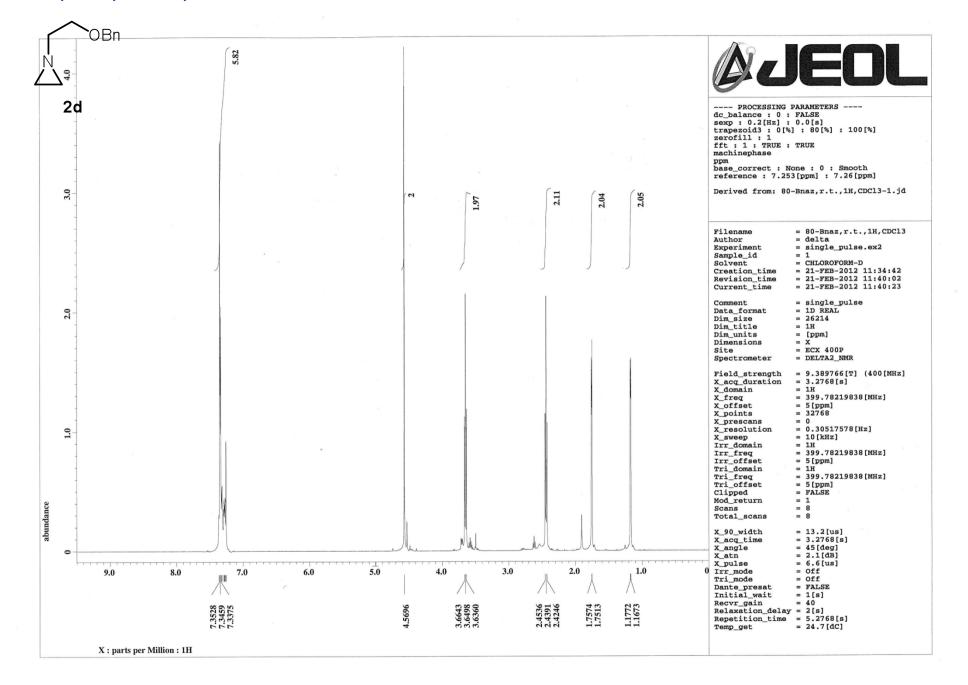
¹(*a*) H. Wenker, *J. Am. Chem. Soc.*, 1935, **57**, 2328. (*b*) T. Munegumi, I. Azumaya, T. Kato, H. Masu and S. Saito, *Org. Lett.*, 2006, **27**, 379–382.

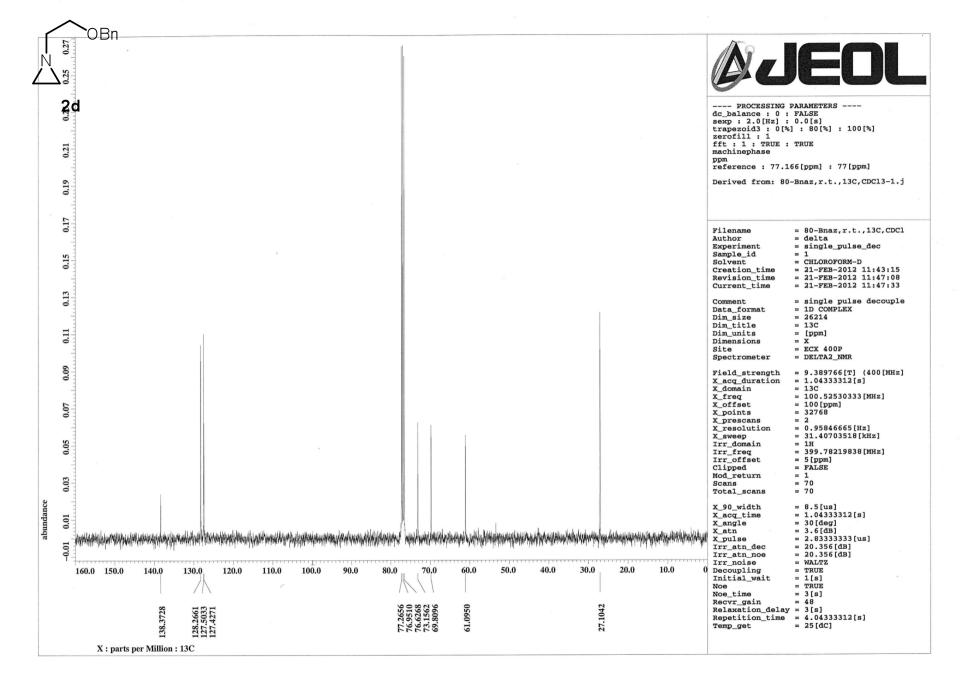


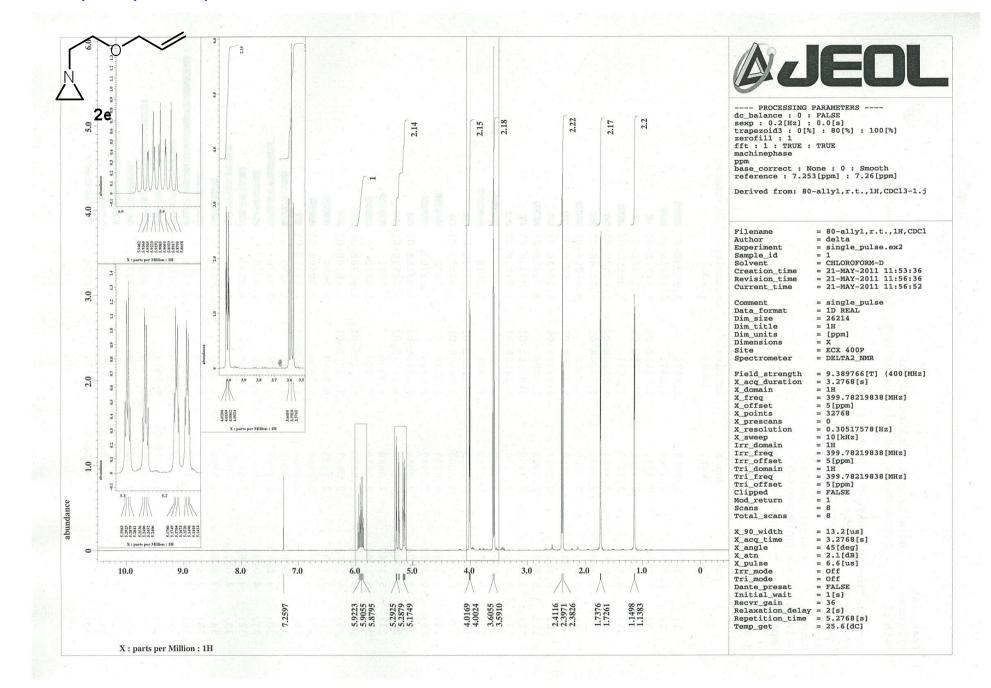


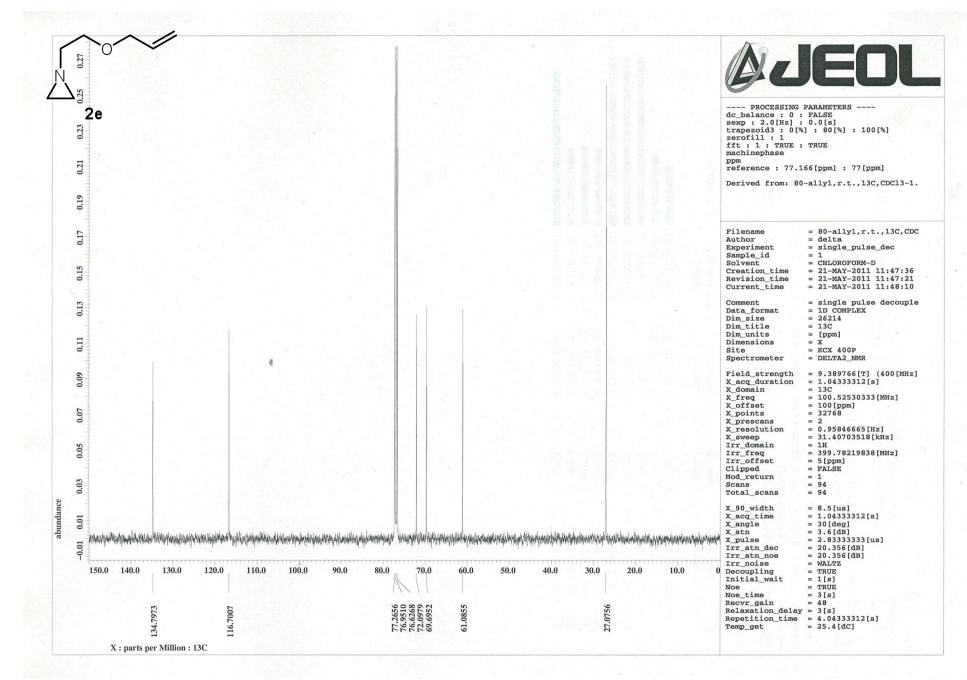


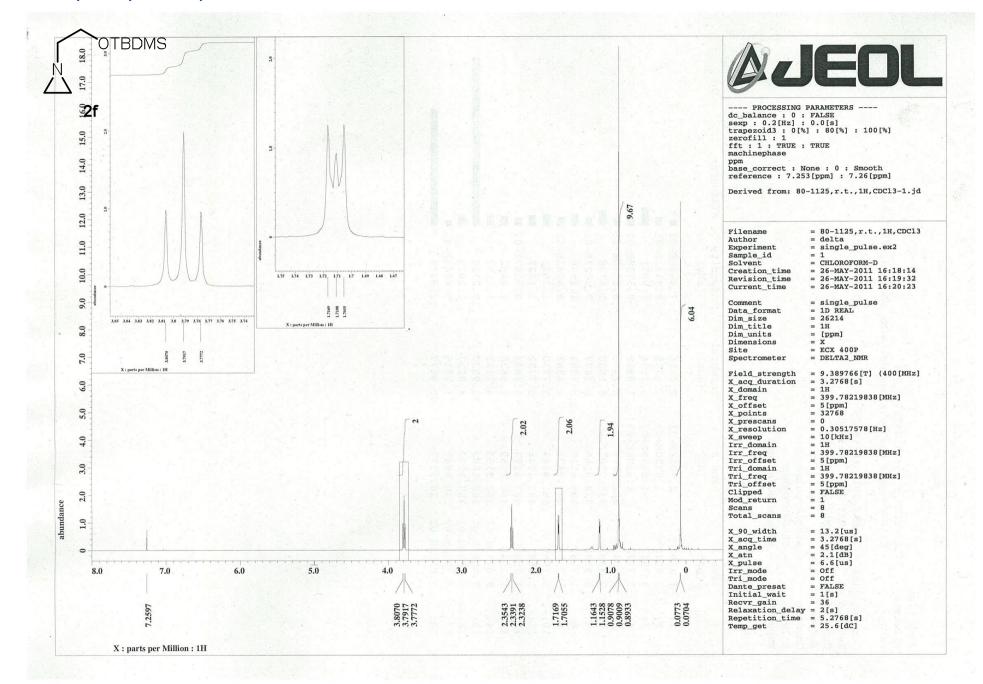


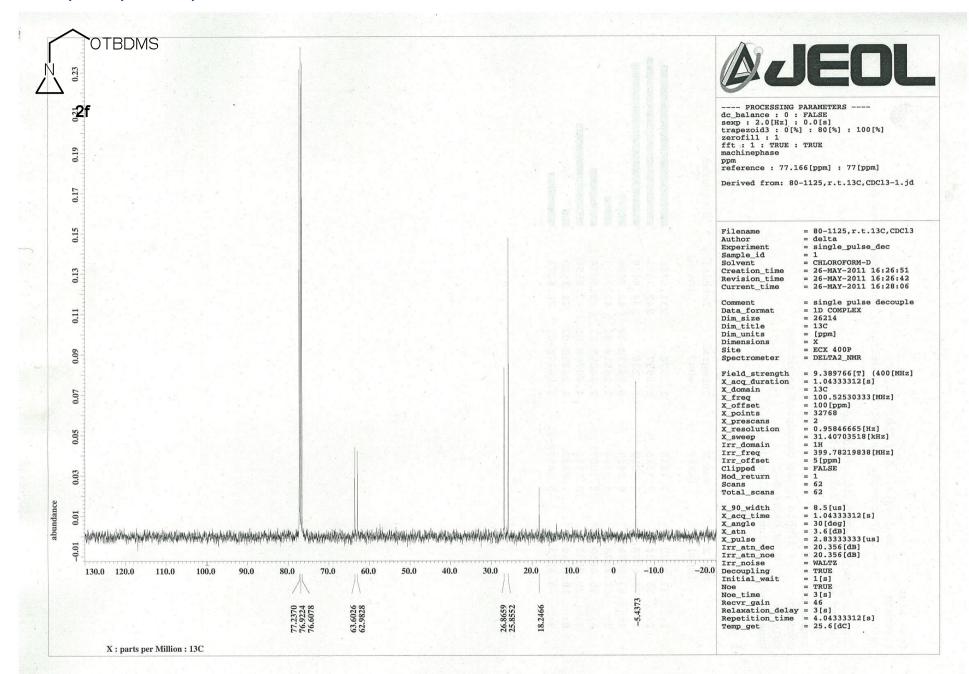


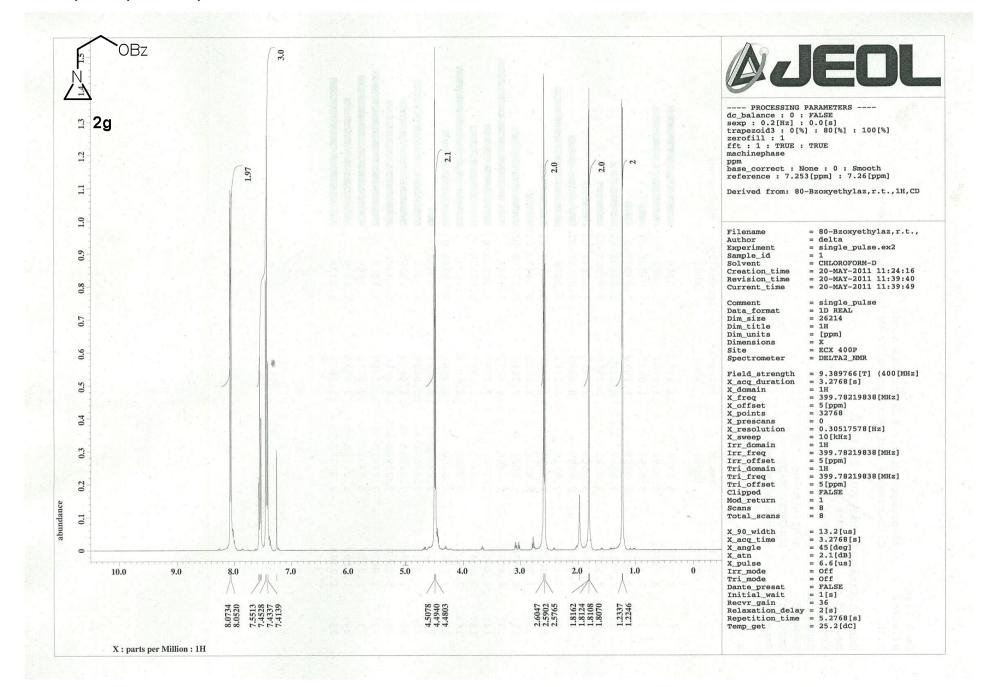


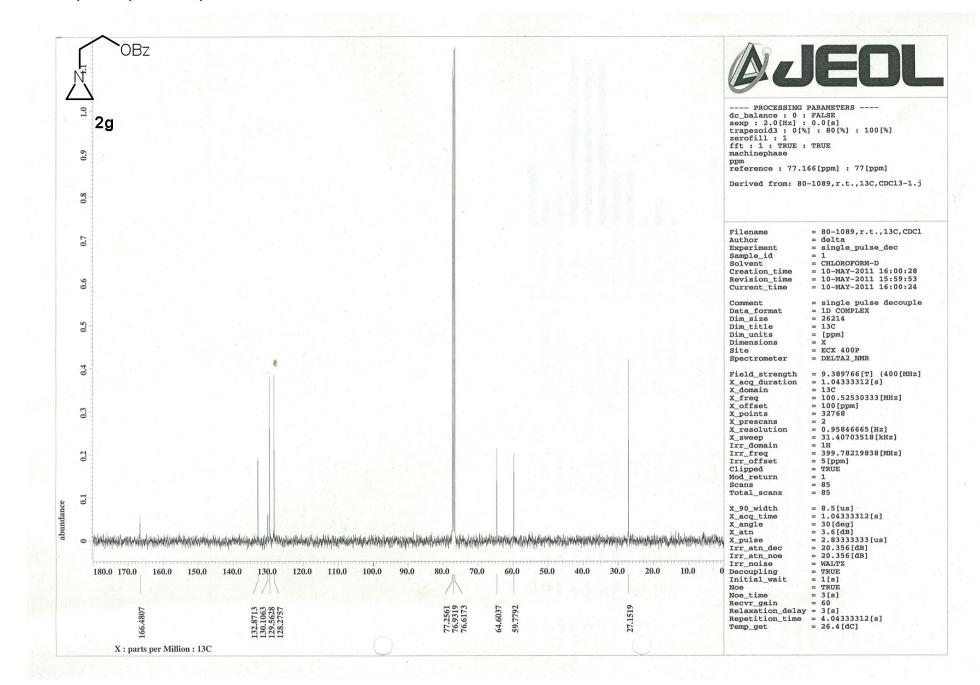


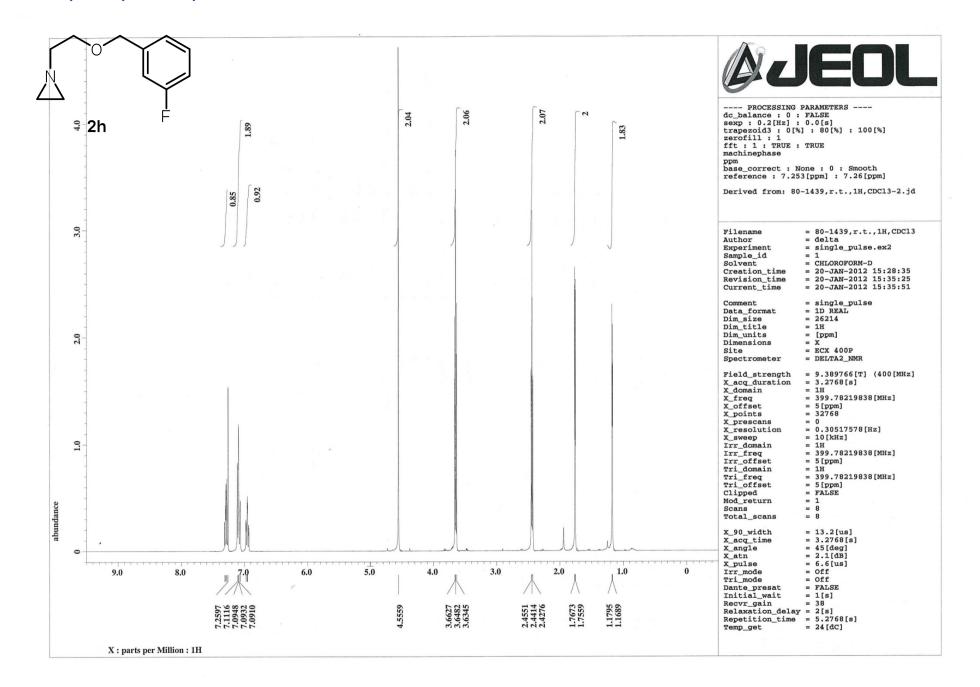


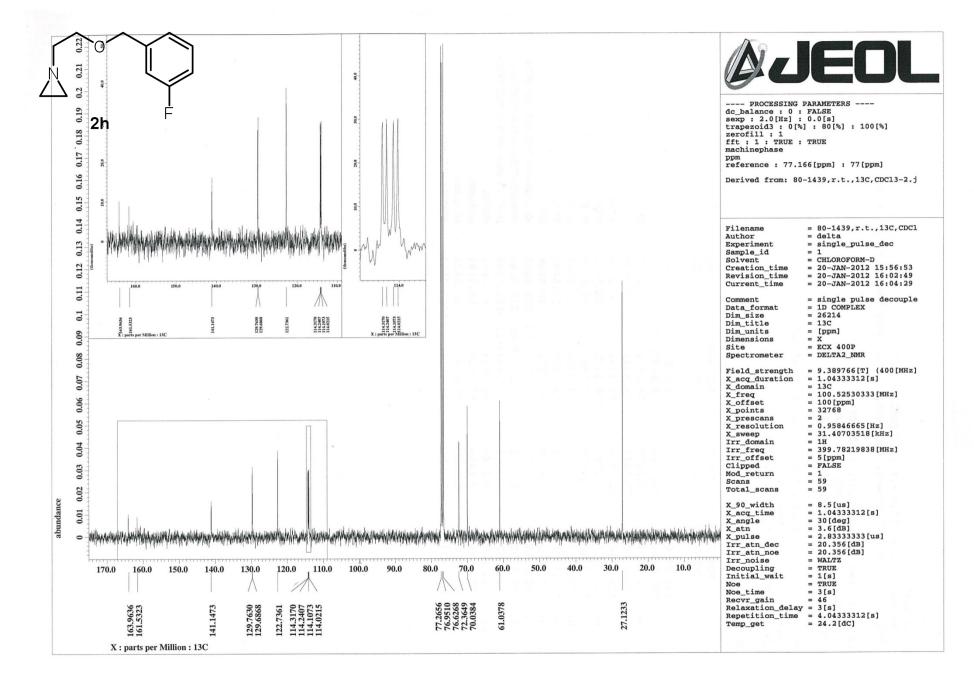


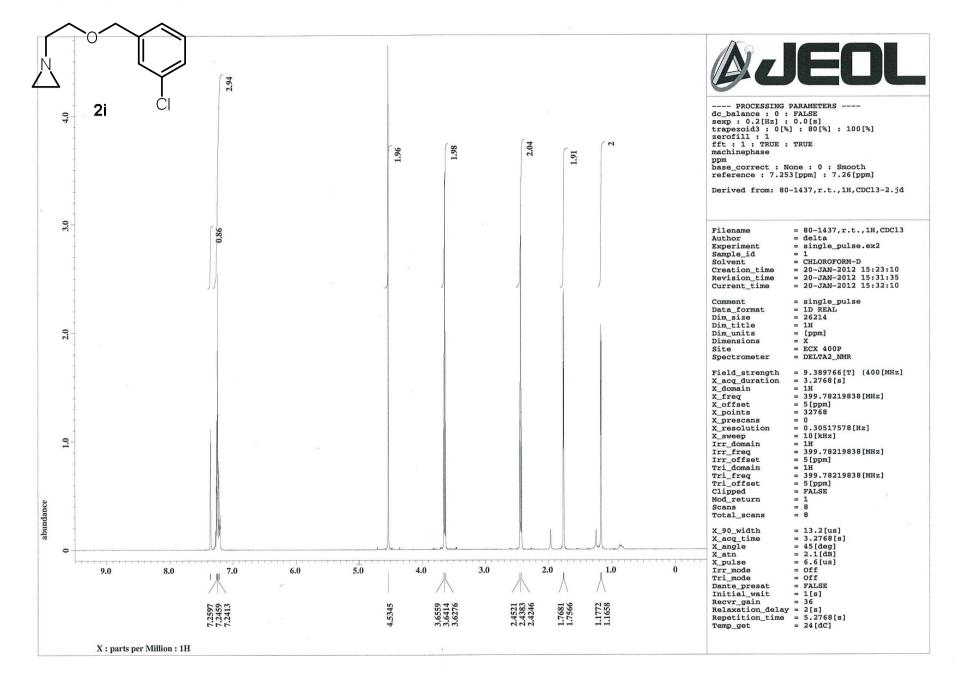


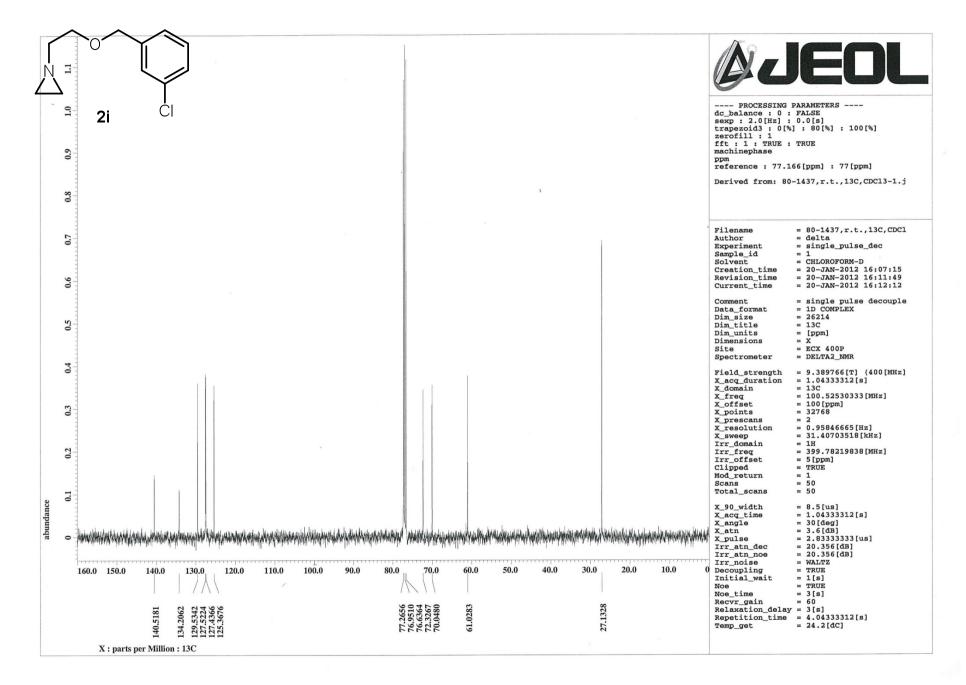


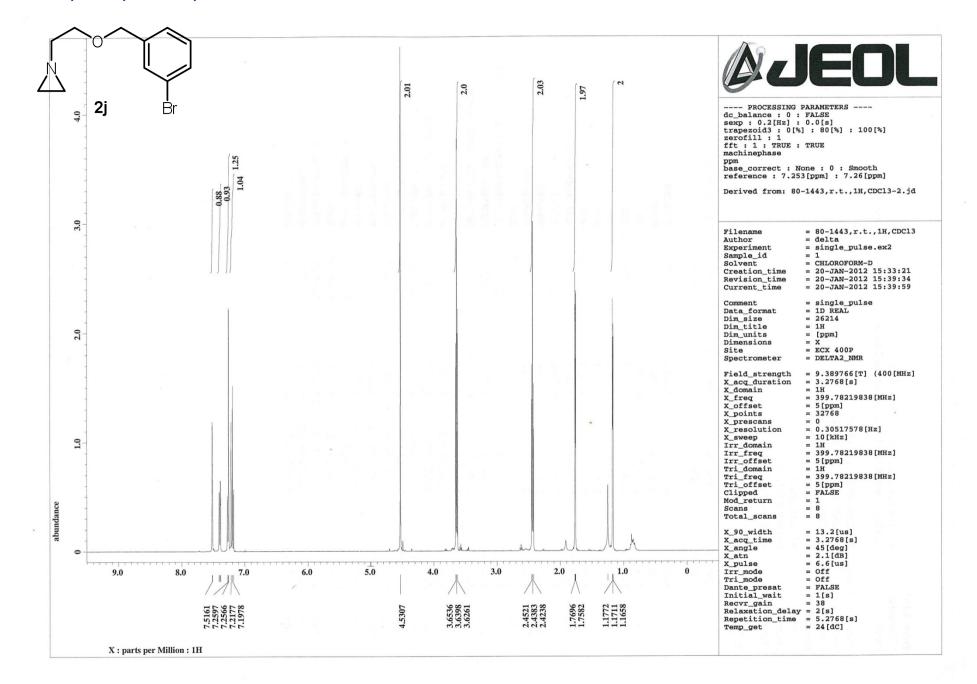


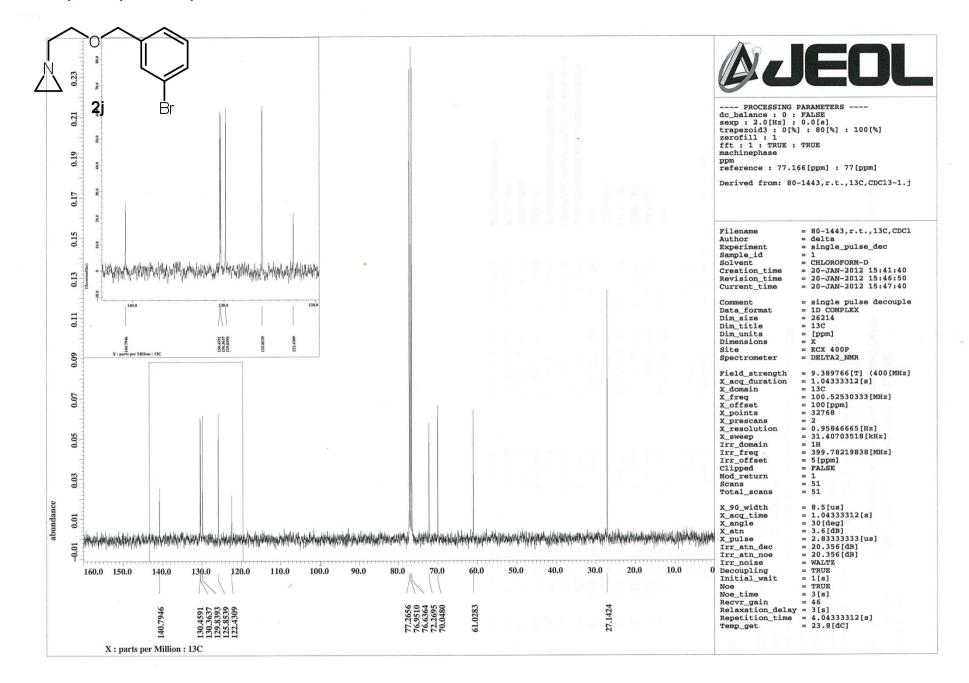


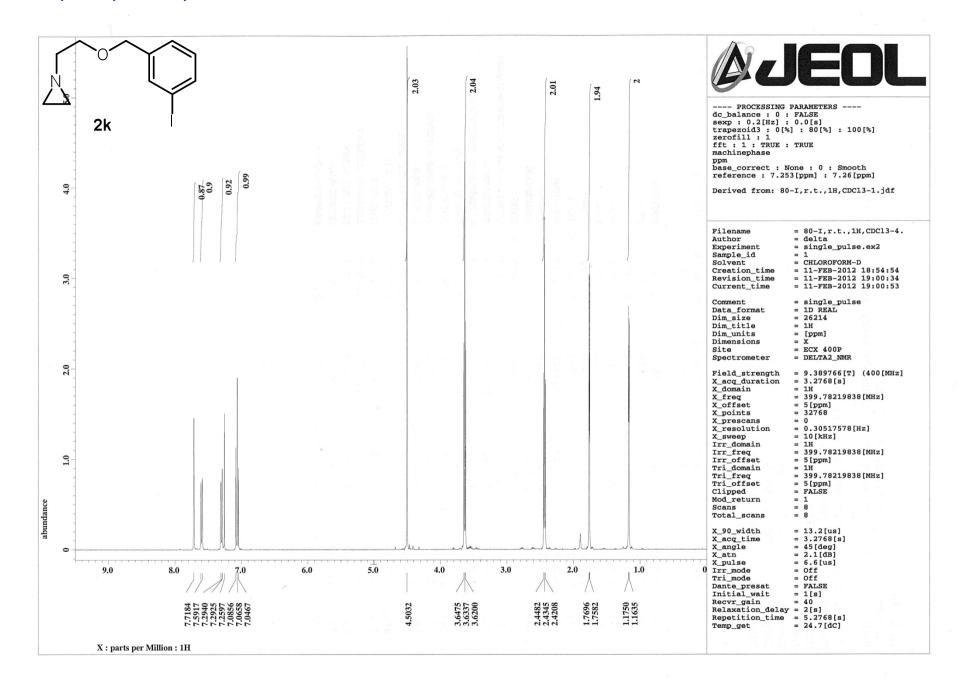




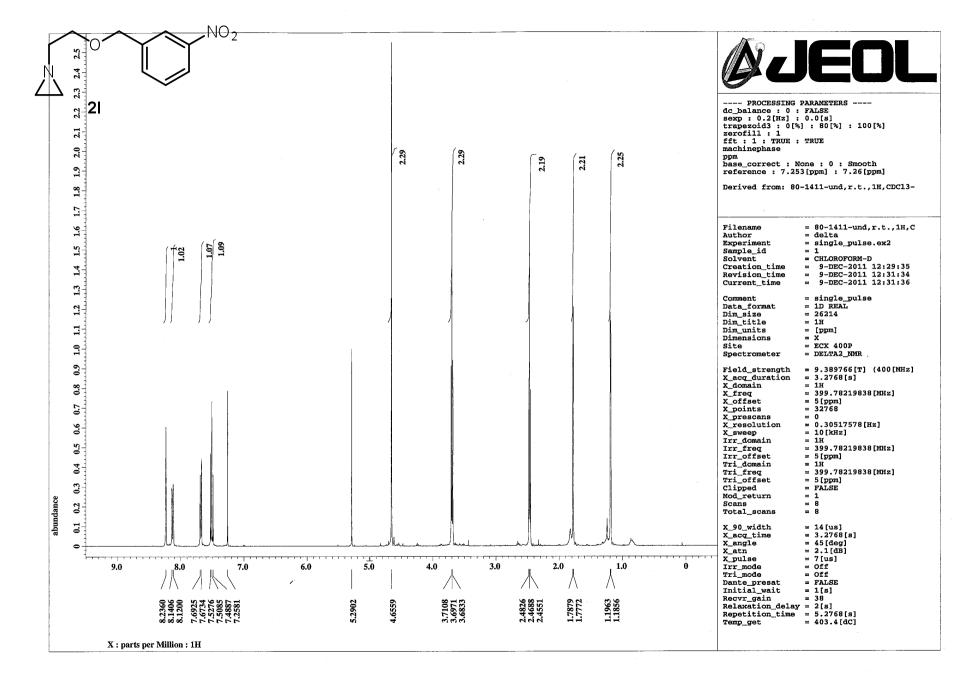


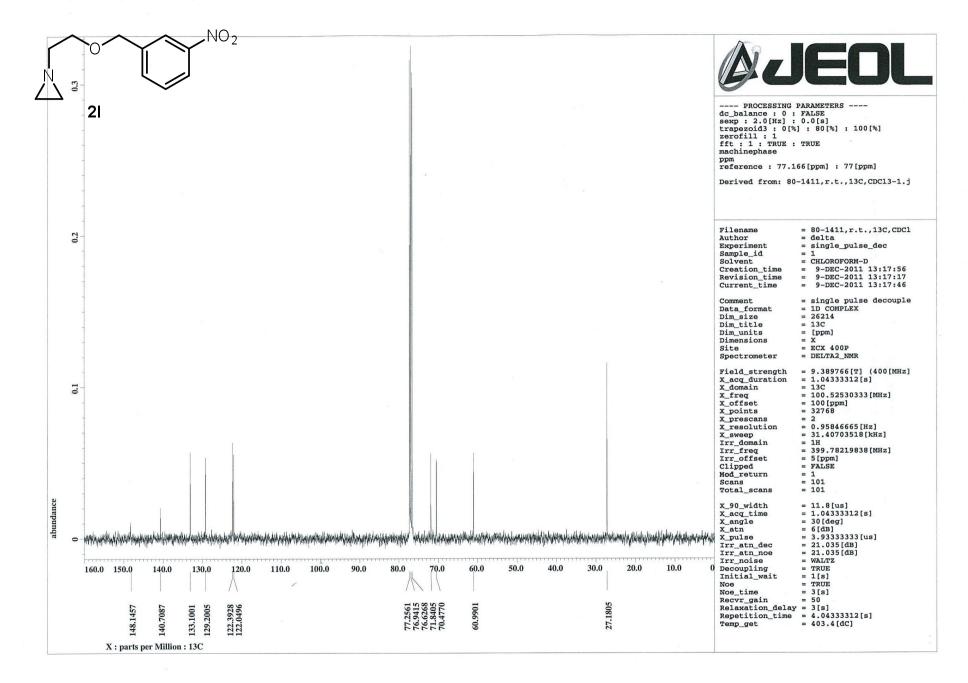


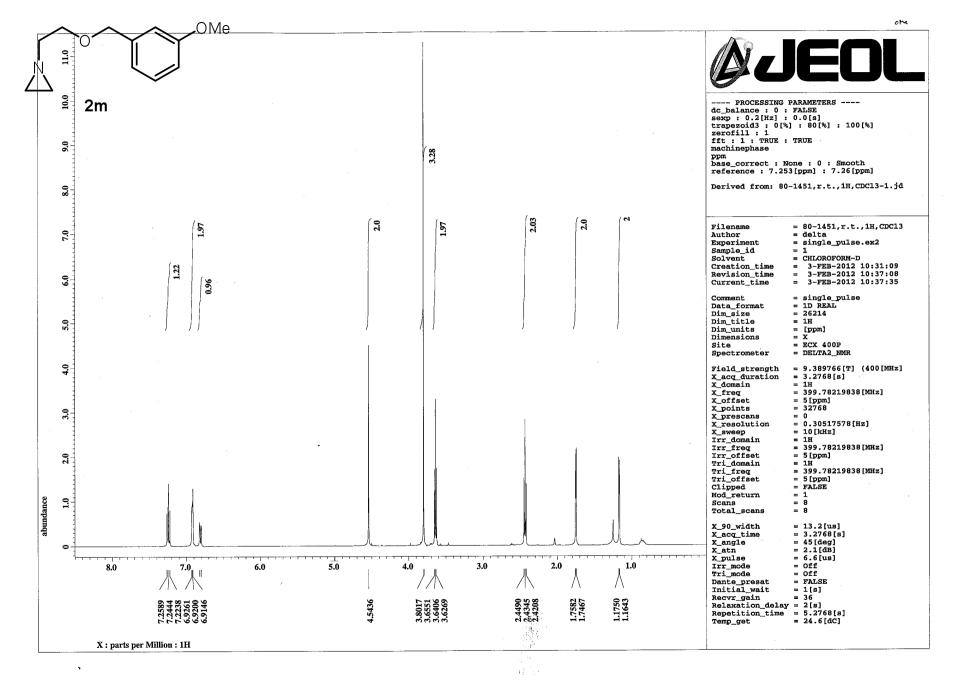


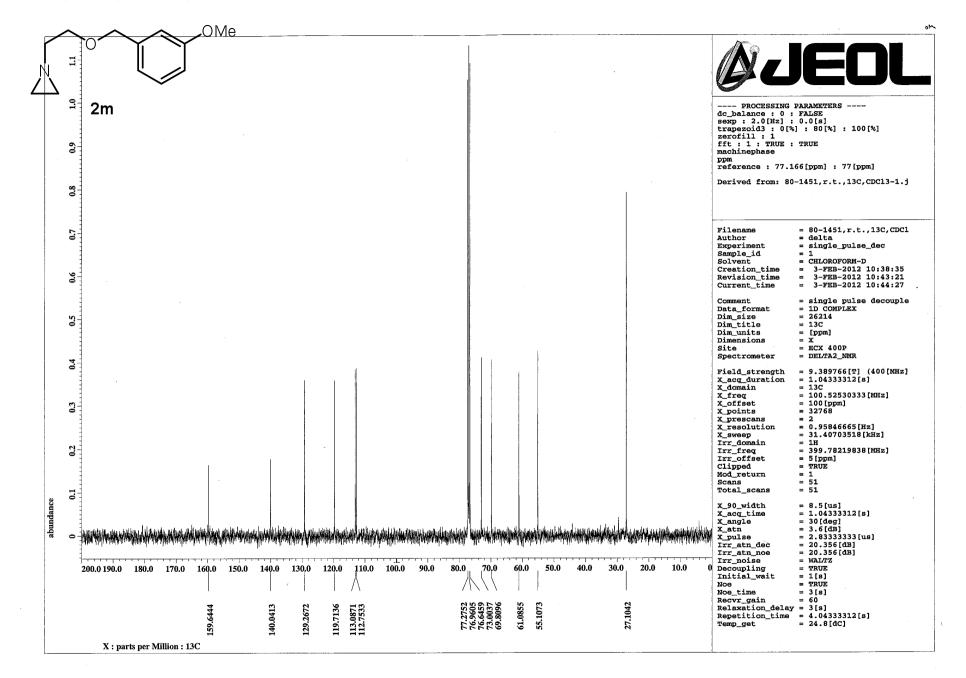


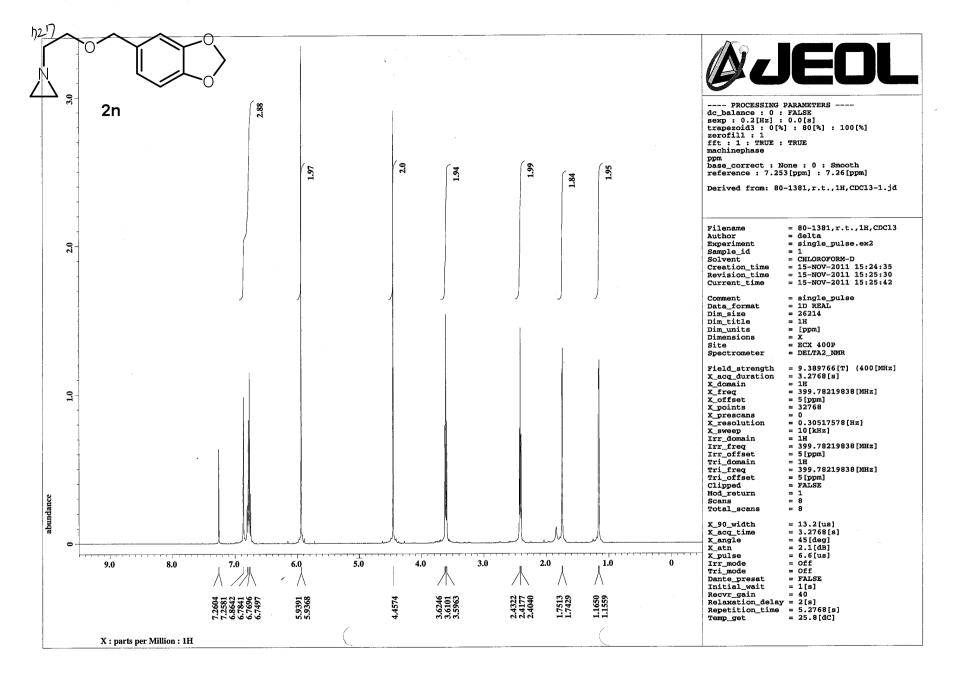
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0.13 0.15			Filename = 80-I-az,r.t.,13C,CDCl Author = delta Experiment = single_pulse_dec Sample_id = 1 Creation_time = 11-FEB-2012 19:24:33 Revision_time = 11-FEB-2012 19:28:46 Current_time = 11-FEB-2012 19:29:20
0.0			Comment = single pulse decouple Data_format = 1D COMPLEX Dim_size = 26214 Dim_title = 13C Dim_units = [ppm] Dimensions = X Site = ECX 400P Spectrometer = DELTA2_NMR
0.03 0.05 0.07			<pre>Field_strength = 9.389766[T] (400[MHz] X_acq_duration = 1.0433312[s] X_domain = 13C X_freq = 100.52530333[MHz] X_offset = 100[ppm] X_points = 32768 X_prescans = 2 X_resolution = 0.95846665[Hz] X_resolution = 1.40703518[kHz] Irr_domain = 1.4 Irr_freq = 399.78219838[MHz] Irr_offset = 5[ppm] Clipped = FALSE Mod_return = 1 Comment = 0.0000000000000000000000000000000000</pre>
-0.01 0.01	140.0 130.0 120.0 110.0 100.0 90.0 80.0	70.0 60.0 50.0 40.0 30.0 20.0 10.0 0	Scans = 68 Total_scans = 68 X_90_width = 8.5[us] X_acq_time = 1.04333312[s] X_angle = 30[deg] X_atn = 3.6[dB] Irr_atn_dec = 20.356[dB] Irr_noise = WALTZ Decoupling = TRUE Initial_wait = 1[s]
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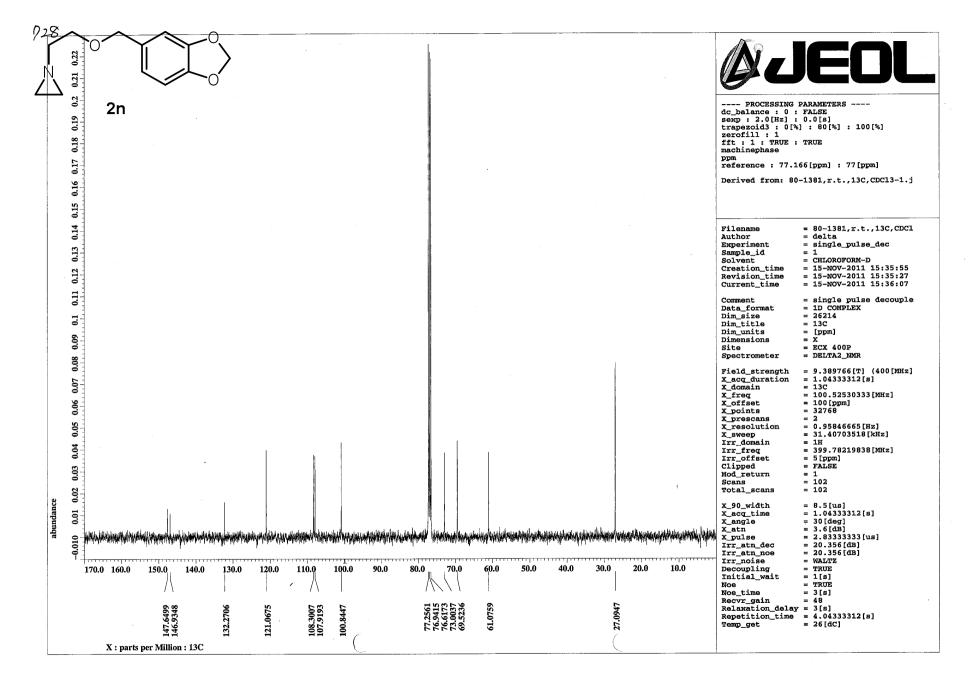


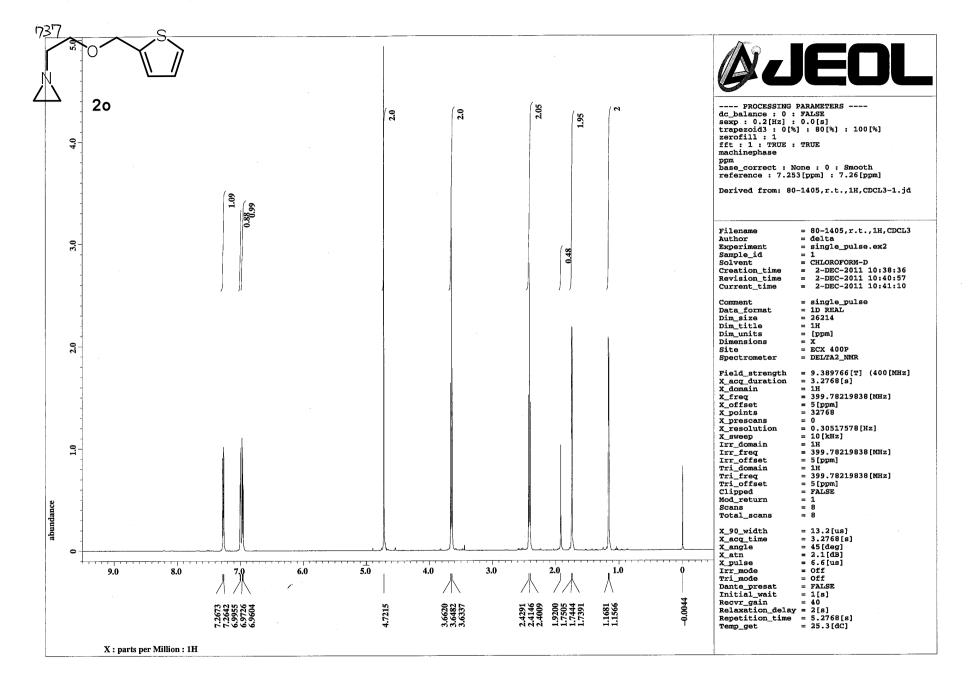


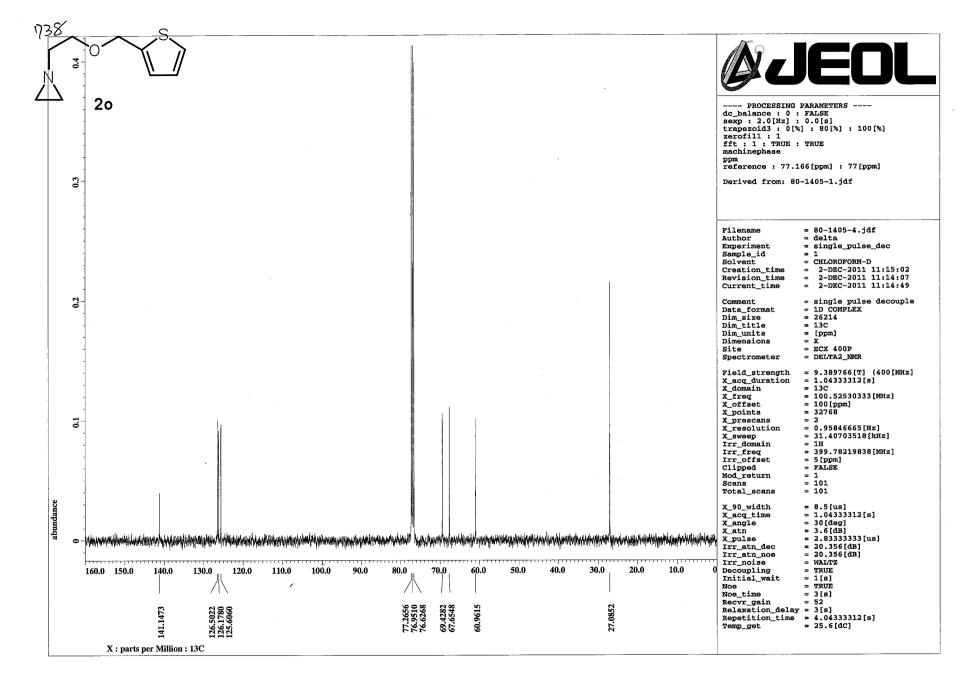


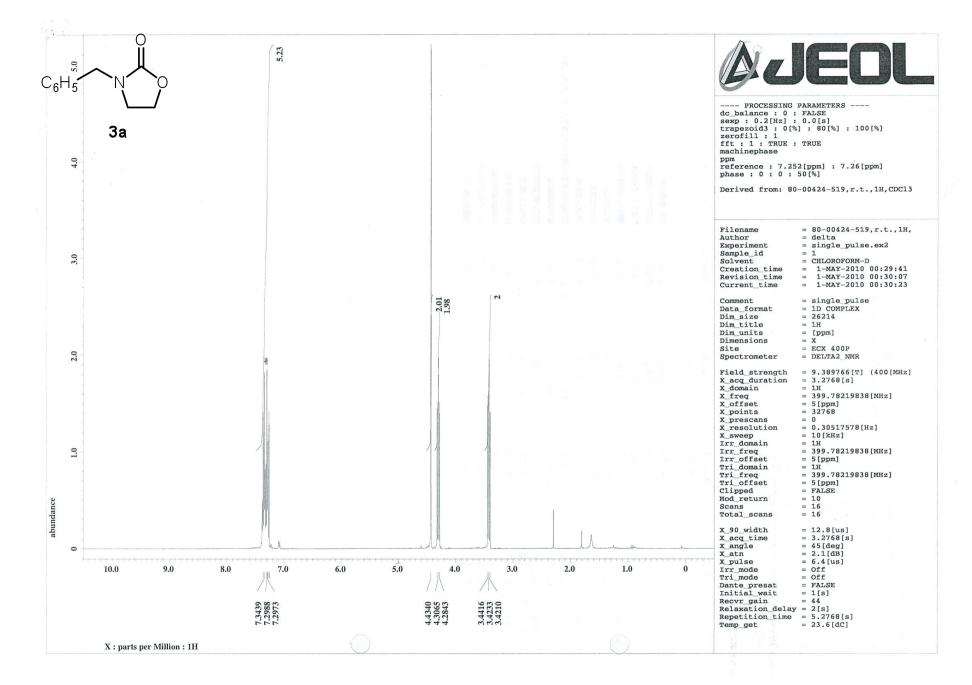


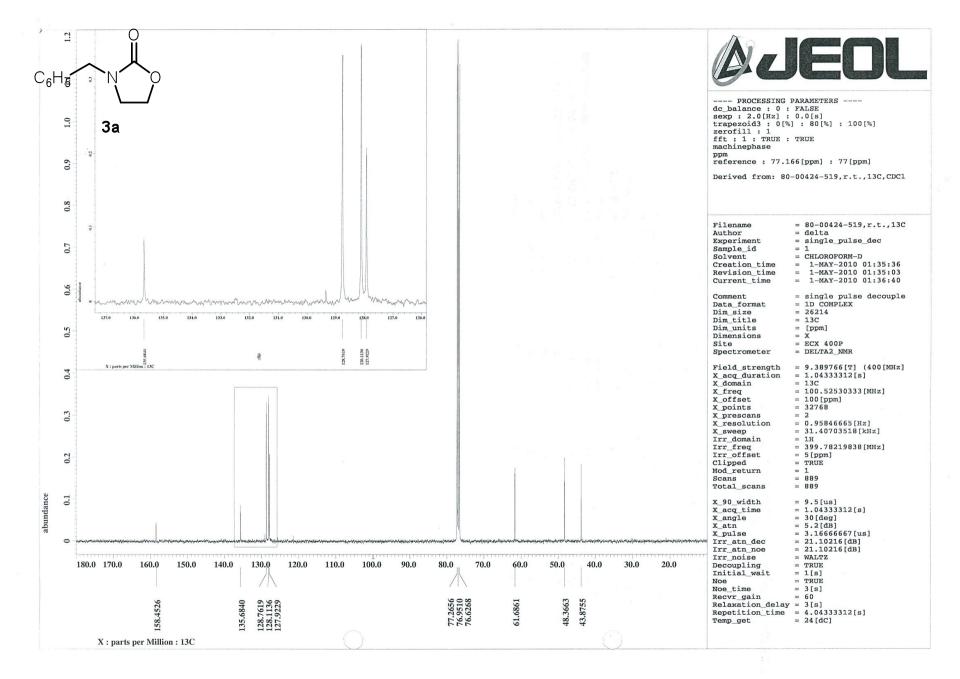


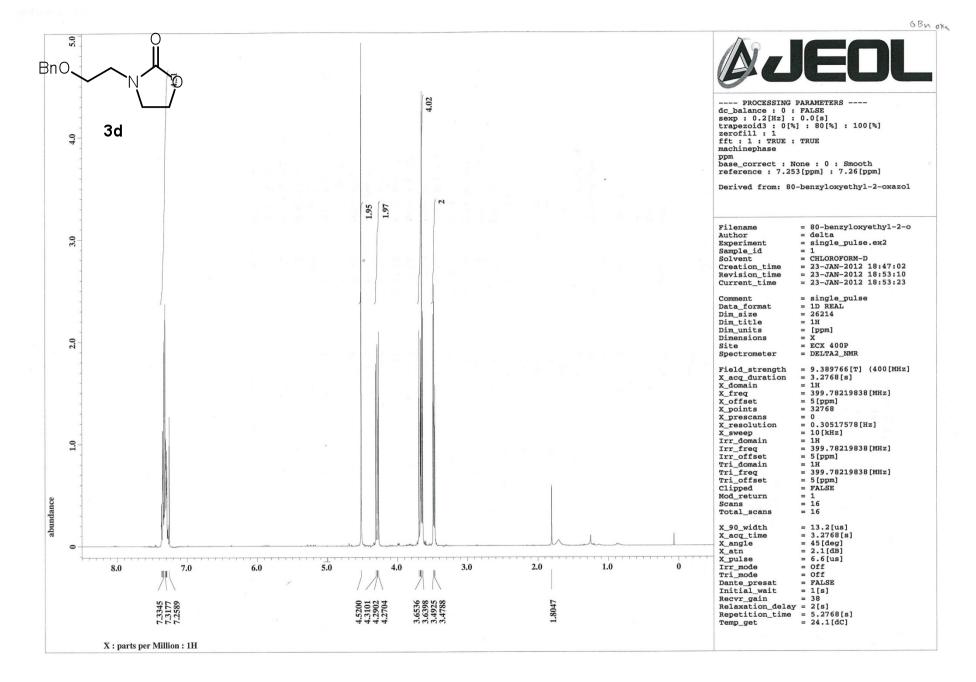


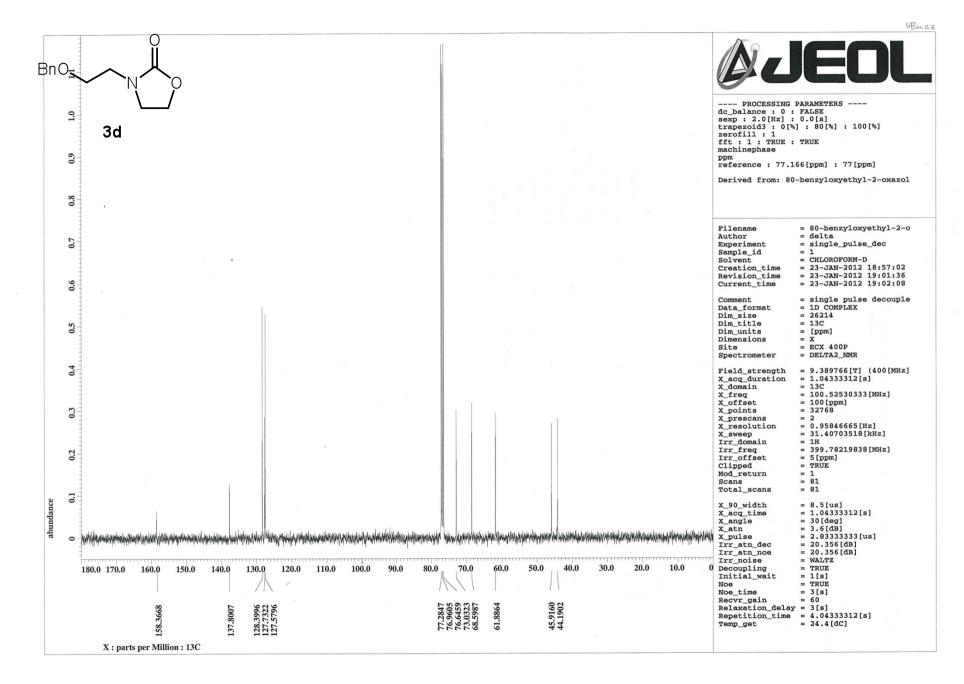


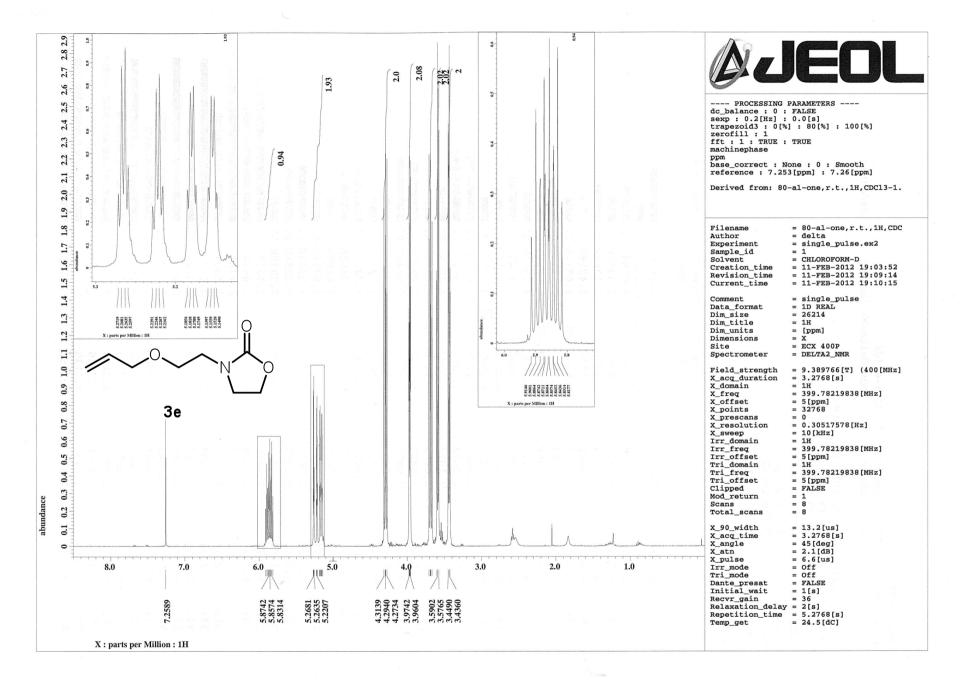


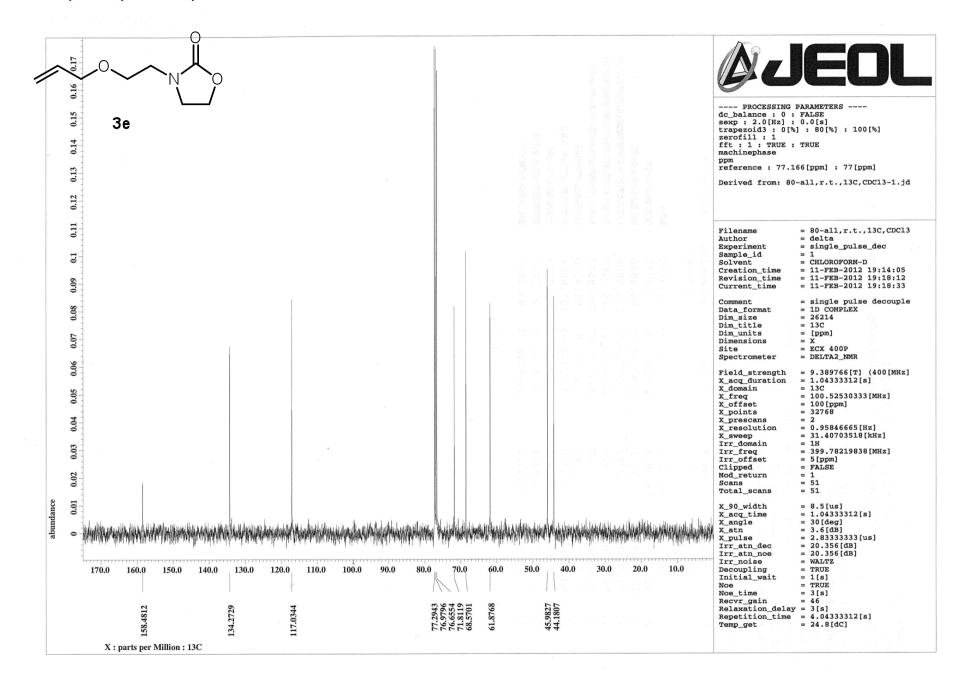


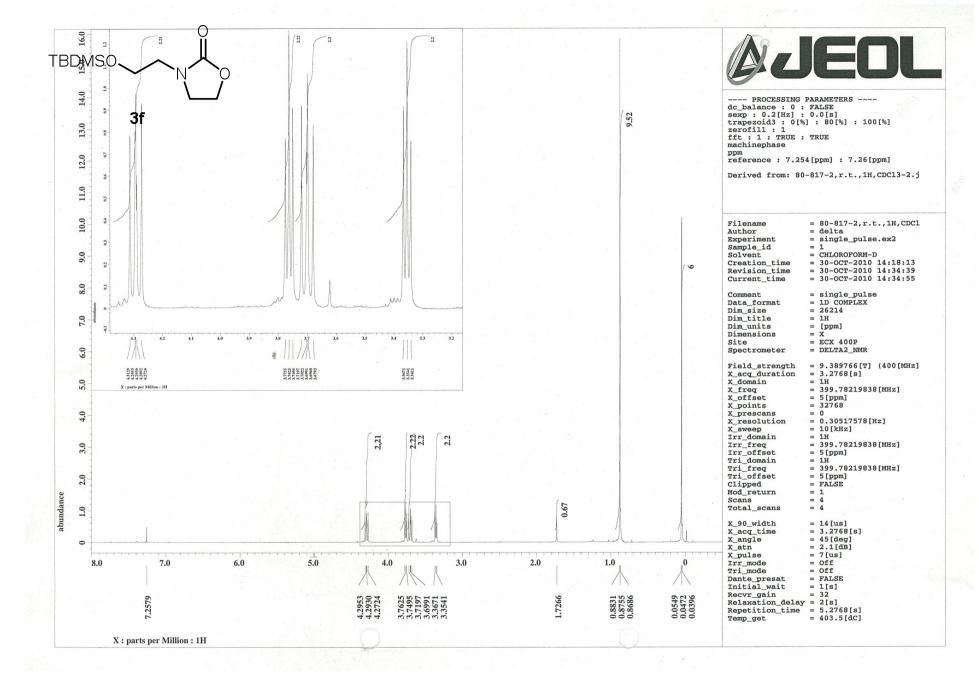


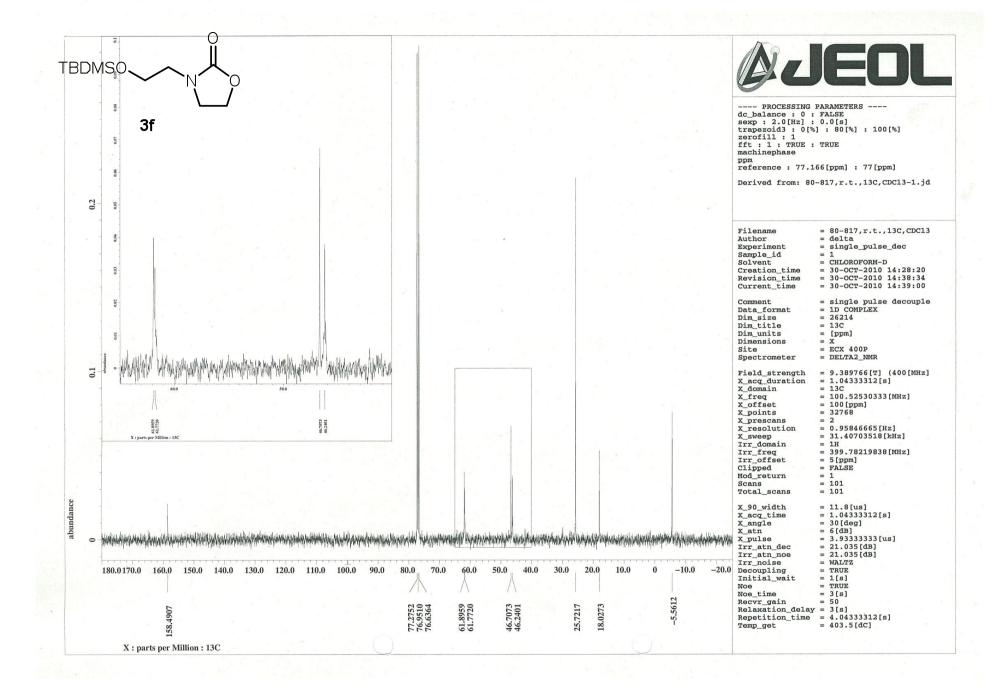


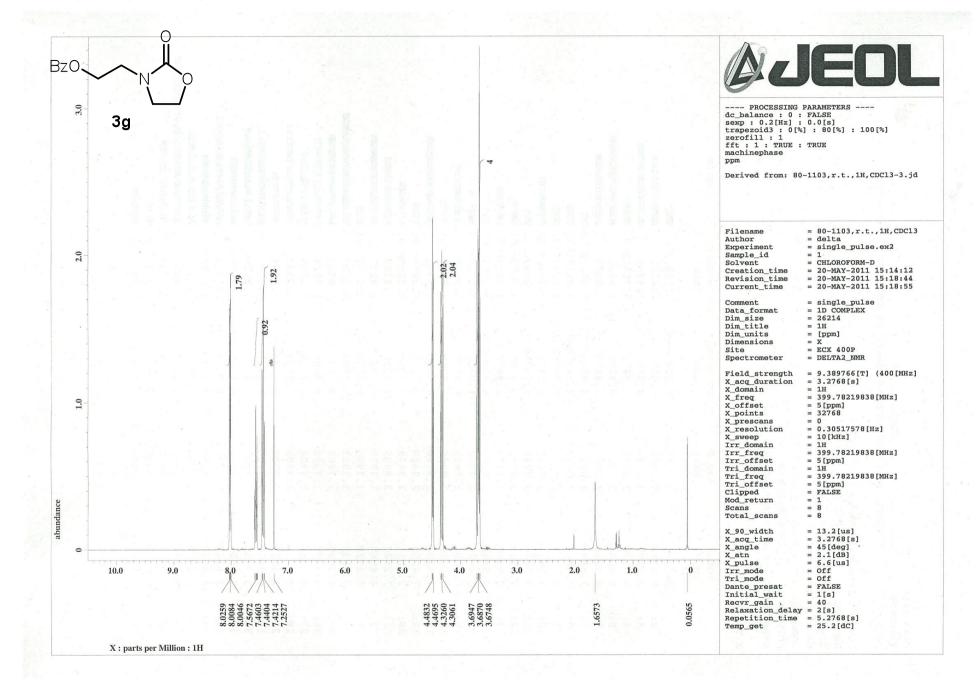


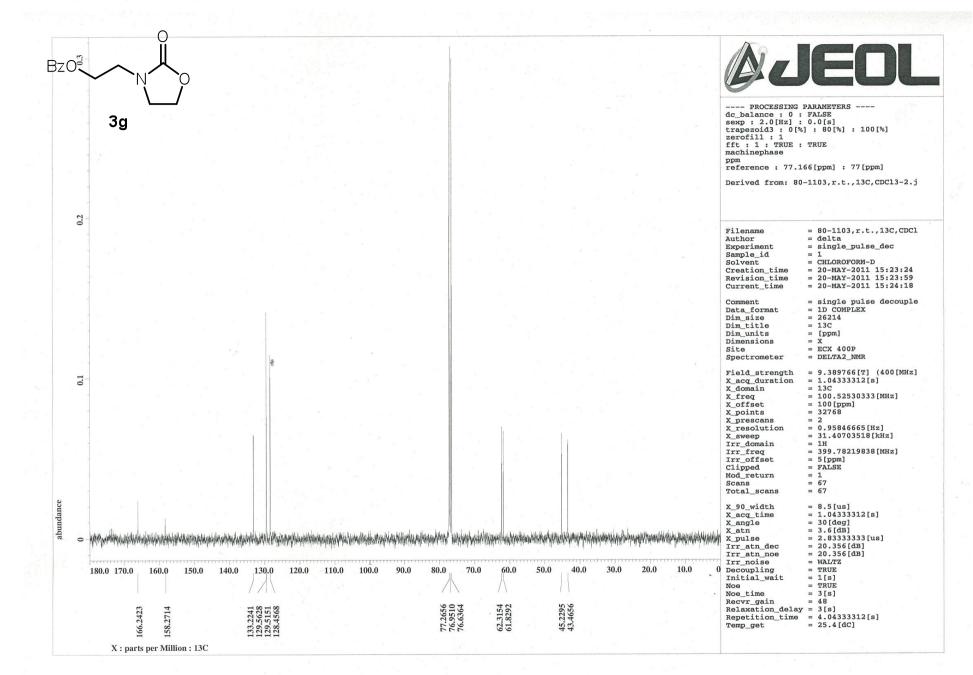


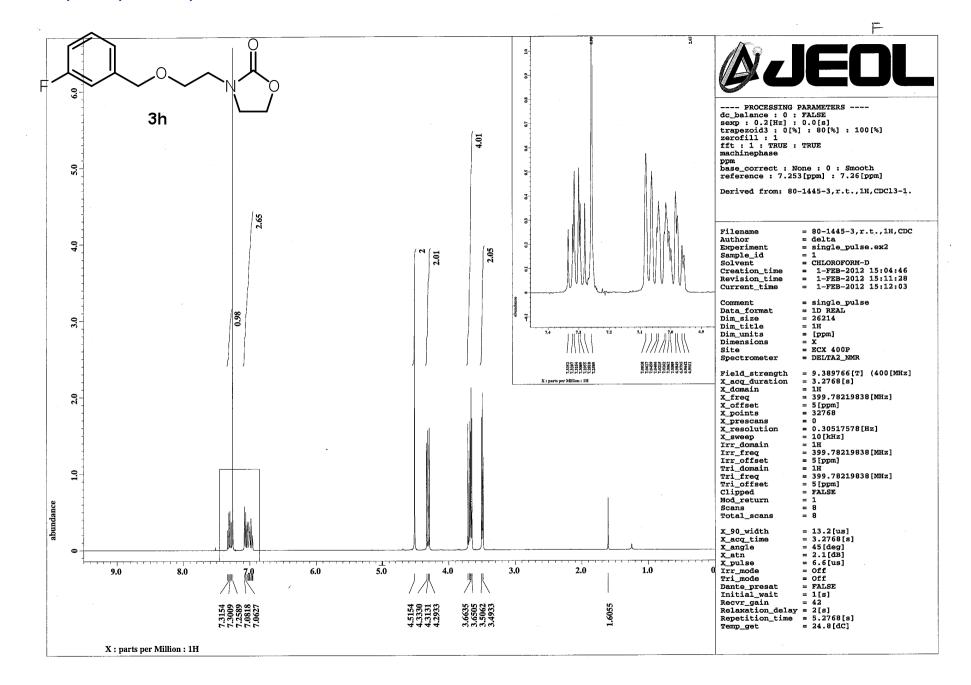


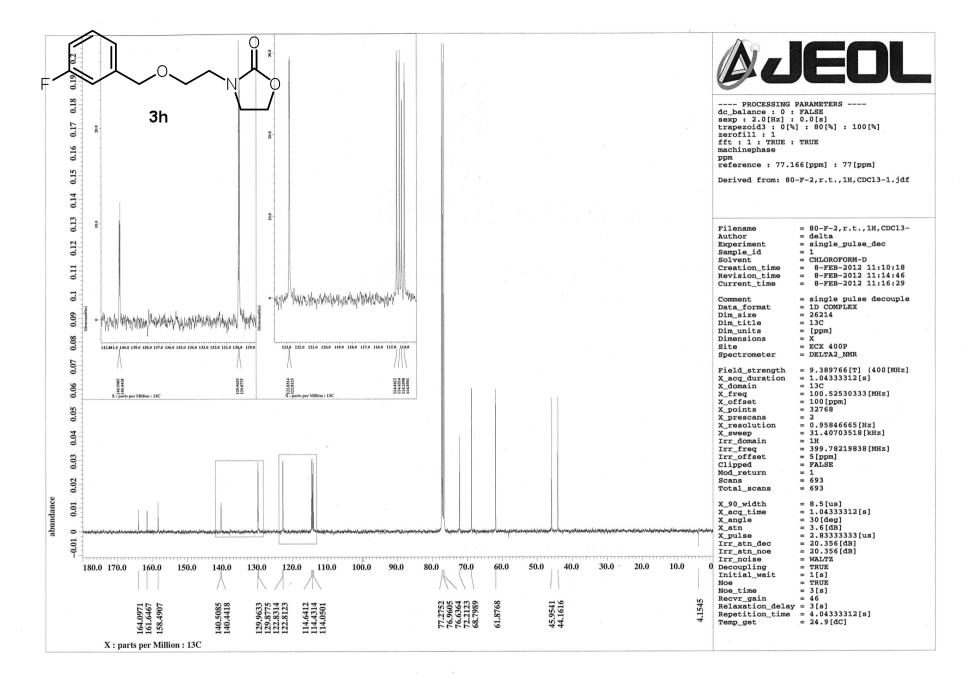


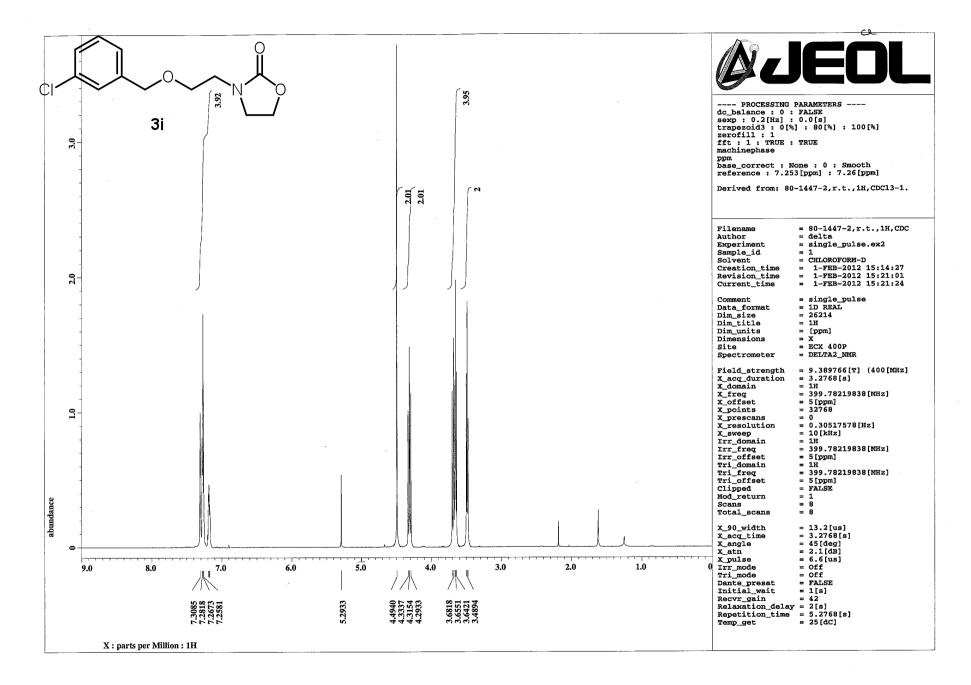


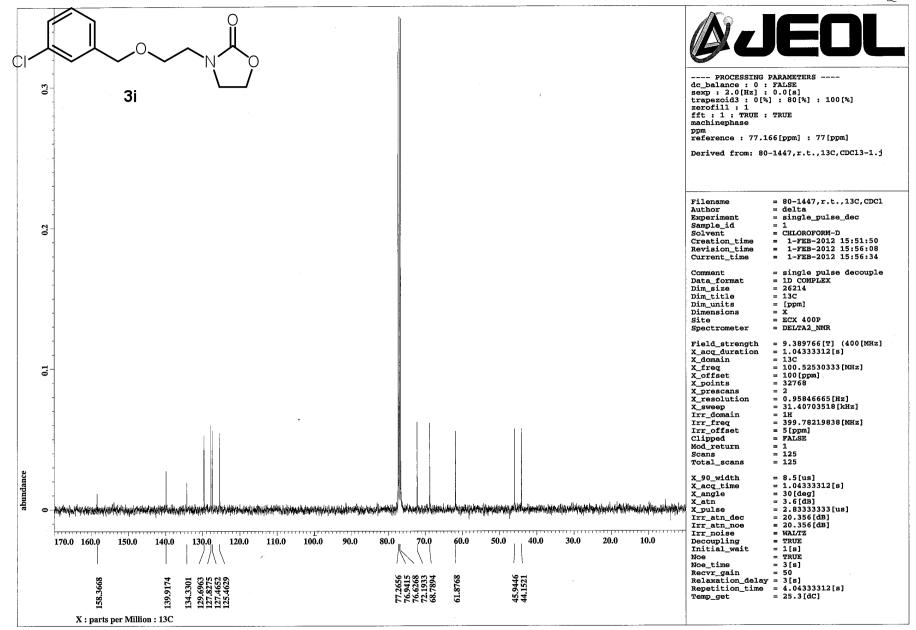






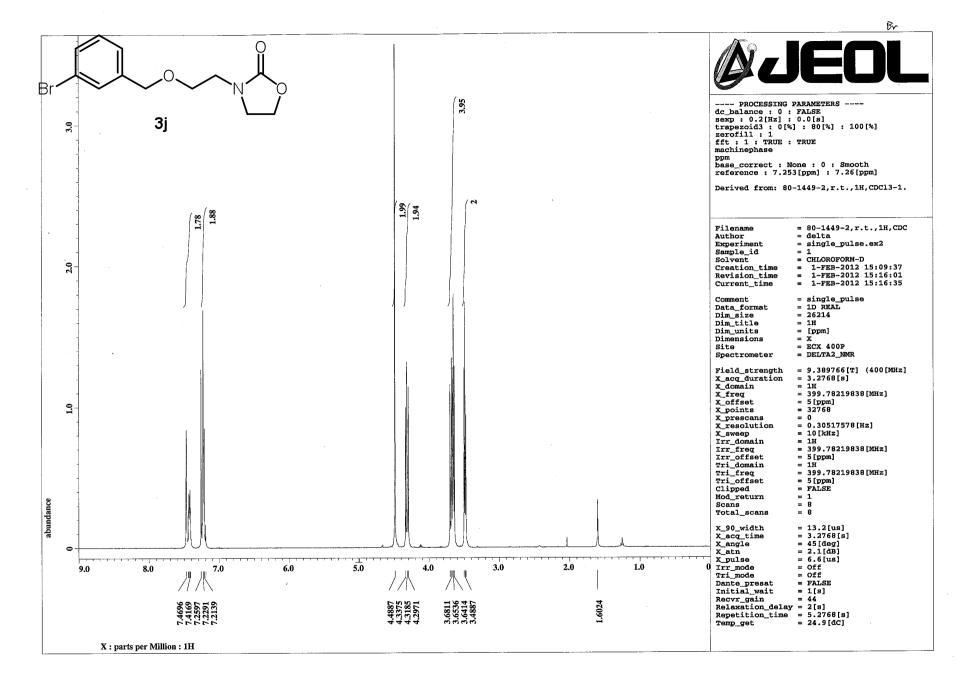


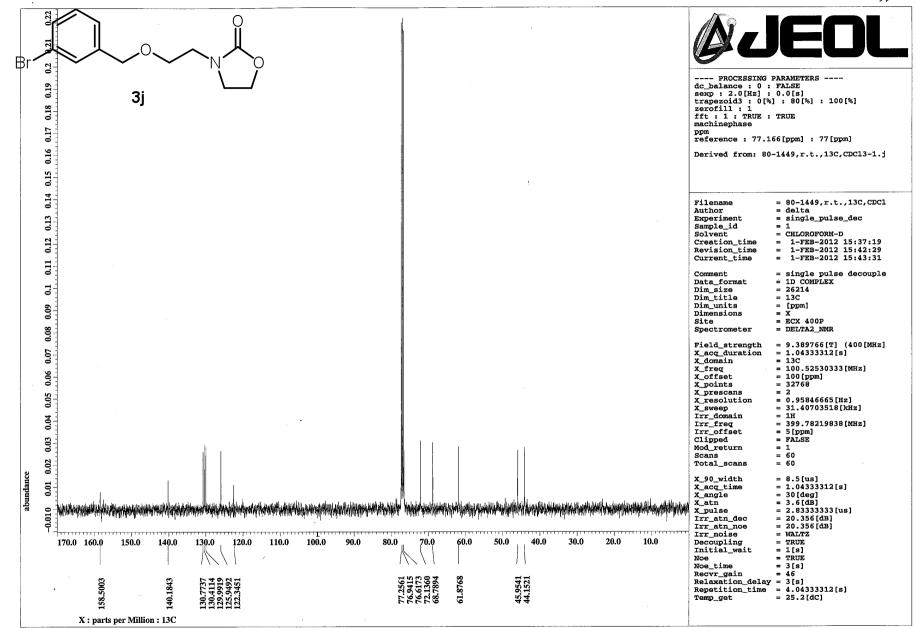




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ce.





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