

Supporting Information

Synthesis of 2,5-disubstituted pyrroles via dehydrogenative condensation of secondary alcohols and 1,2-amino alcohols by supported platinum catalysts

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Ken-ichi Shimizu

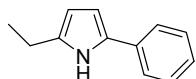
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NMR and GC/MS analysis

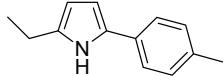
¹H and ¹³C NMR spectra for 2,5-disubstituted pyrroles of Table-3 were assigned and reproduced to the corresponding literature. ¹H and ¹³C NMR spectra were recorded using at ambient temperature on JEOL-ECX 600 operating at 600.17 and 150.92 MHz, respectively with tetramethylsilane as an internal standard. Abbreviations used in the NMR experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC-MS spectra was taken by SHIMADZU QP2010.

2-Ethyl-5-phenyl-1*H*-pyrrole:¹



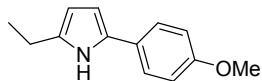
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.17 (br s, 1H), 7.43-7.42 (m, 2H), 7.32 (t, J = 7.56 Hz, 2H), 7.15 (t, J = 7.56 Hz, 1H), 6.41 (t, J = 3.42 Hz, 1H), 5.98 (t, J = 3.44 Hz, 1H), 2.67 (q, J = 7.56 Hz, 2H), 1.28 (t, J = 7.56 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 135.59, 132.96, 130.56, 128.78 (C×2), 125.63, 123.37 (C×2), 106.19, 105.95, 20.97, 113.58; GC-MS m/e 171.105.

2-Ethyl-5-*p*-tolyl-1*H*-pyrrole:



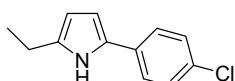
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.15 (br s, 1H), 7.46-7.44 (m, 2H), 7.36-7.33 (m, 2H), 6.43 (t, J = 3.09 Hz, 1H), 5.99 (t, J = 3.1 Hz, 1H), 2.69 (q, J = 7.56 Hz, 2H), 1.58 (s, 3H), 1.31 (t, J = 7.56 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 136.24, 134.33, 130.48 (C×2), 128.89, 124.94 (C×2), 122.89, 106.96, 104.79, 24.91, 20.62, 12.60; GC-MS m/e 185.125.

2-Ethyl-5-(4-methoxyphenyl)-1*H*-pyrrole:



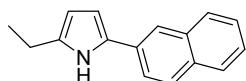
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.45 (br s, 1H), 7.35 (d, *J* = 8.94 Hz, 2H), 6.85 (d, *J* = 8.94 Hz, 2H), 6.27 (t, *J* = 2.76 Hz, 1H), 5.93 (t, *J* = 2.76 Hz, 1H), 3.76 (s, 3H) 2.62 (q, *J* = 7.56 Hz, 2H), 1.25 (t, *J* = 7.56 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 157.51, 134.81, 130.39, 126.11, 124.58 (C×2), 113.96 (C×2), 105.49, 104.41, 55.01, 20.71, 13.45; GC-MS m/e 201.120.

2-Ethyl-5-(4-chloro phenyl)-1*H*-pyrrole:



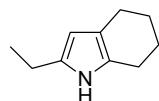
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.17 (br s, 1H), 7.36-7.35 (m, 2H), 7.28-7.26 (m, 2H), 6.38 (t, *J* = 2.76 Hz, 1H), 5.92 (t, *J* = 2.81 Hz, 1H), 2.63 (q, *J* = 7.52 Hz, 2H), 1.27 (t, *J* = 7.56 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 135.83, 135.31, 131.94, 126.96 (C×2), 128.09 (C×2), 122.78, 105.55, 105.06, 20.35, 13.13; GC-MS m/e 205.075.

2-Ethyl-5-naphthalen-2-yl-1*H*-pyrrole:²



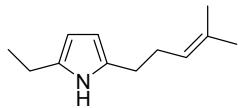
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.43 (br s, 1H), 7.91 (s, 1H), 7.76 (d, *J* = 6.22 Hz, 1H), 7.63 (d, *J* = 8.18 Hz, 2H), 7.45 (d, *J* = 8.22 Hz, 1H), 7.37 (d, *J* = 7.56 Hz, 2H), 6.54-6.53 (m, 1H), 6.02-6.01 (m, 1H), 2.69 (q, *J* = 7.62 Hz, 2H), 1.31 (t, *J* = 7.89 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 136.03, 133.79, 133.15, 131.74, 128.32, 128.13 (C×2), 126.24, 125.89(C×2), 123.09, 120.11, 106.60, 106.24, 25.18, 13.58.; GC-MS m/e 221.125.

2-Ethyl-1,5,6,7,8-pentahydro-cyclohexa[*b*]pyrrole:³



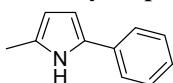
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.29 (br s, 1H), 5.63 (d, *J* = 2.72 Hz, 1H), 2.63-2.60 (m, 4H), 2.53-2.49 (m, 2H), 1.86-1.62 (m, 4H), 1.18 (t, *J* = 7.56 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 132.94, 123.44, 115.93, 104.50, 23.86, 23.39, 22.59, 22.30, 20.77, 14.43; GC-MS m/e 149.130.

2-Ethyl-5-(4-methyl-pent-3-enyl)-1*H*-pyrrole:⁴



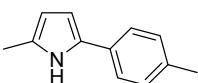
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 7.95 (br s, 1H), 5.73-5.69 (m, 2H), 5.17-5.12 (m, 1H), 2.57-2.42 (m, 4H), 2.16 (q, *J* = 7.56 Hz, 2H), 1.70 (s, 3H), 1.68 (s, 3H), 1.21 (t, *J* = 7.50 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 133.51, 132.39, 131.36, 123.79, 109.27 (C×2), 38.38, 37.21, 25.12, 23.93, 21.64, 17.04; GC-MS m/e 177.155.

2-Methyl-5-phenyl-1*H*-pyrrole:¹



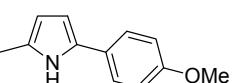
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.82 (br s, 1H), 7.82 (d, *J* = 8.22 Hz, 2H), 7.36 (t, *J* = 7.56 Hz, 2H), 7.22 (t, *J* = 6.26 Hz, 1H), 6.37 (t, *J* = 3.12 Hz, 1H), 5.90 (m, 1H), 2.31 (s, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 134.73, 132.08, 128.80 (C×2), 128.20, 127.92 (C×2), 122.92, 107.22, 105.48, 12.67; GC-MS m/e 157.095.

2-Methyl-5-*p*-tolyl-1*H*-pyrrole:⁵



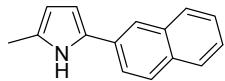
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.31 (br s, 1H), 7.36 (d, *J* = 8.22 Hz, 2H), 7.22 (t, *J* = 7.86 Hz, 2H), 6.31-6.30 (m, 1H), 5.89-5.88 (m, 1H), 2.32 (s, 3H), 2.15 (s, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 136.24, 134.33, 130.48, 128.89 (C×2), 124.94 (C×2), 122.89, 106.96, 104.79, 20.62, 12.60; GC-MS m/e 171.110.

2 (4-Methoxy phenyl)-5-methyl-1*H*-pyrrole:⁶



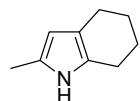
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.32 (br s, 1H), 7.34 (t, *J* = 8.94 Hz, 2H), 6.86 (t, *J* = 8.94 Hz, 2H), 6.26 (t, *J* = 2.70 Hz, 1H), 5.90 (t, *J* = 2.70 Hz, 1H), 3.78 (s, 3H), 2.29 (s, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 157.62, 130.65, 128.21, 126.12, 124.62 (C×2), 114.08 (C×2), 107.37, 104.71, 55.14, 12.95; GC-MS m/e 187.105.

2-Methyl-5-naphthalen-2-yl-1*H*-pyrrole:⁵



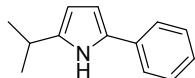
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.56 (br s, 1H), 7.89 (s, 1H), 7.73 (d, *J* = 7.56 Hz, 1H), 7.64 (d, *J* = 8.22 Hz, 2H), 7.43 (d, *J* = 6.86 Hz, 1H), 7.31 (d, *J* = 7.56 Hz, 2H), 6.61-6.59 (m, 1H), 6.16-6.15 (m, 1H), 2.13 (s, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 135.67, 133.86, 133.12, 130.94, 127.98, 128.43 (C×2), 126.46, 125.74 (C×2), 122.89, 119.61, 106.56, 105.98, 14.14.; GC-MS m/e 207.115.

2-Methyl-1,5,6,7,8-pentahydro-cyclohexa[*b*]pyrrole:⁵



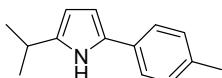
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 7.65 (br s, 1H), 5.68 (s, 1H), 2.62-2.58 (m, 4H), 2.31 (s, 3H), 1.91-1.86 (m, 4H); ¹³C NMR (150.92 MHz, CDCl₃) δ 131.53, 132.92, 119.16, 106.13, 24.24, 23.92, 22.83, 22.16, 14.53; GC-MS m/e 135.115.

2-Isopropyl-5-phenyl-1*H*-pyrrole:¹



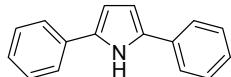
¹H NMR (600.17 MHz, CD₃CN, TMS): δ 8.86 (br s, 1H), 7.47-7.45 (m, 2H), 7.34-7.29 (m, 2H), 7.26-7.22 (m, 1H), 6.39-6.37 (m, 1H), 5.95-5.92 (s, 1H), 2.96-2.93 (m, 1H), 1.29 (d, *J* = 7.23 Hz, 6H); ¹³C NMR (150.92 MHz, CD₃CN) δ 141.72, 132.95, 130.24, 128.37 (C×2), 127.01, 126.53 (C×2), 123.21, 105.32, 104.29, 28.98, 22.49; GC-MS m/e 185.125.

2-Isopropyl-5-*p*-tolyl-1*H*-pyrrole:⁶



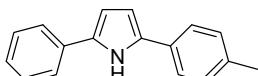
¹H NMR (600.17 MHz, CD₃CN, TMS): δ 8.56 (br s, 1H), 7.35-7.34 (m, 2H), 7.12-7.11 (m, 2H), 6.35-6.33 (m, 1H), 5.95-5.93 (s, 1H), 2.95-2.93 (m, 1H), 2.31 (s, 3H), 1.29 (d, *J* = 7.34 Hz, 6H); ¹³C NMR (150.92 MHz, CD₃CN) δ 139.80, 134.79, 130.43, 129.11 (C×2), 125.11 (C×2), 120.12, 104.77, 104.23, 35.29, 25.25 (C×2), 22.50; GC-MS m/e 199.140.

2,5-Diphenyl-1*H* pyrrole:⁷



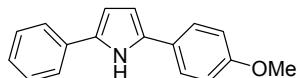
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.39 (br s, 1H), 7.85 (d, J = 8.28 Hz, 4H), 7.60 (d, J = 7.56 Hz, 2H), 7.50 (d, J = 7.56 Hz, 2H), 7.23 (t, J = 6.51 Hz, 2H), 7.16 (t, J = 6.87 Hz, 2H); ¹³C NMR (150.92 MHz, CDCl₃) δ 135.99, 132.43, 129.18, 128.68 (C×2), 128.56, 128.40 (C×2), 128.35, 127.25 (C×2), 126.53, 125.65 (C×2), 106.92, 106.50; GC-MS m/e 219.115.

2-Phenyl-5-*p*-tolyl-1*H* pyrrole:⁸



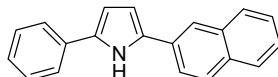
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.49 (br s, 1H), 7.82 (d, J = 8.28 Hz, 2H), 7.56 (d, J = 6.84 Hz, 4H), 7.30 (t, J = 7.20 Hz, 1H), 6.97 (d, J = 7.56 Hz, 2H), 6.54-6.53 (m, 1H), 6.50-6.49 (m, 1H), 1.42 (t, J = 7.20 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 142.96, 136.49, 129.18, 128.95 (C×2), 128.74, 128.47 (C×2), 128.21, 127.09 (C×2), 126.80, 126.29 (C×2), 107.34, 106.90, 20.79 ; GC-MS m/e 233.130.

2-(4-Methoxy phenyl)-5-phenyl-1*H* pyrrole:⁵



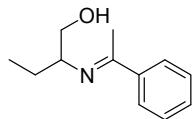
¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.35 (br s, 1H), 7.88 (d, J = 8.94 Hz, 2H), 7.59 (d, J = 6.84 Hz, 2H), 7.53 (d, J = 8.94 Hz, 2H), 7.25-7.21 (m, 1H), 6.88 (d, J = 9.63 Hz, 2H), 6.52-6.51 (m, 1H), 6.42-6.41 (m, 1H), 3.50 (s, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 163.00, 138.09, 130.07 (C×2), 128.14, 127.96, 127.73 (C×2), 126.52 (C×2), 116.92 (C×2), 113.61 (C×2), 106.91, 105.99, 58.33 ; GC-MS m/e 249.120.

2-Naphthalen-2-yl-5-phenyl-1*H*-pyrrole:⁹



¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.38 (br s, 1H), 7.96 (s, 1H), 7.78 (d, J = 6.18 Hz, 1H), 7.59 (d, J = 8.98 Hz, 2H), 7.53 (d, J = 8.42 Hz, 1H), 7.43 (d, J = 6.18 Hz, 2H), 7.40 (d, J = 6.54 Hz, 4H), 7.22 (t, J = 4.83 Hz, 1H), 6.68-6.67 (m, 1H), 6.58-6.57 (m, 1H); ¹³C NMR (150.92 MHz, CDCl₃) δ 143.42, 132.80, 132.24, 128.99, 128.15, 127.84, 127.76, 127.34, 127.18, 126.68, 125.41 (C×2), 125.18, 124.64, 123.53, 123.14, 120.69 (C×2), 107.79, 107.30.; GC-MS m/e 269.130.

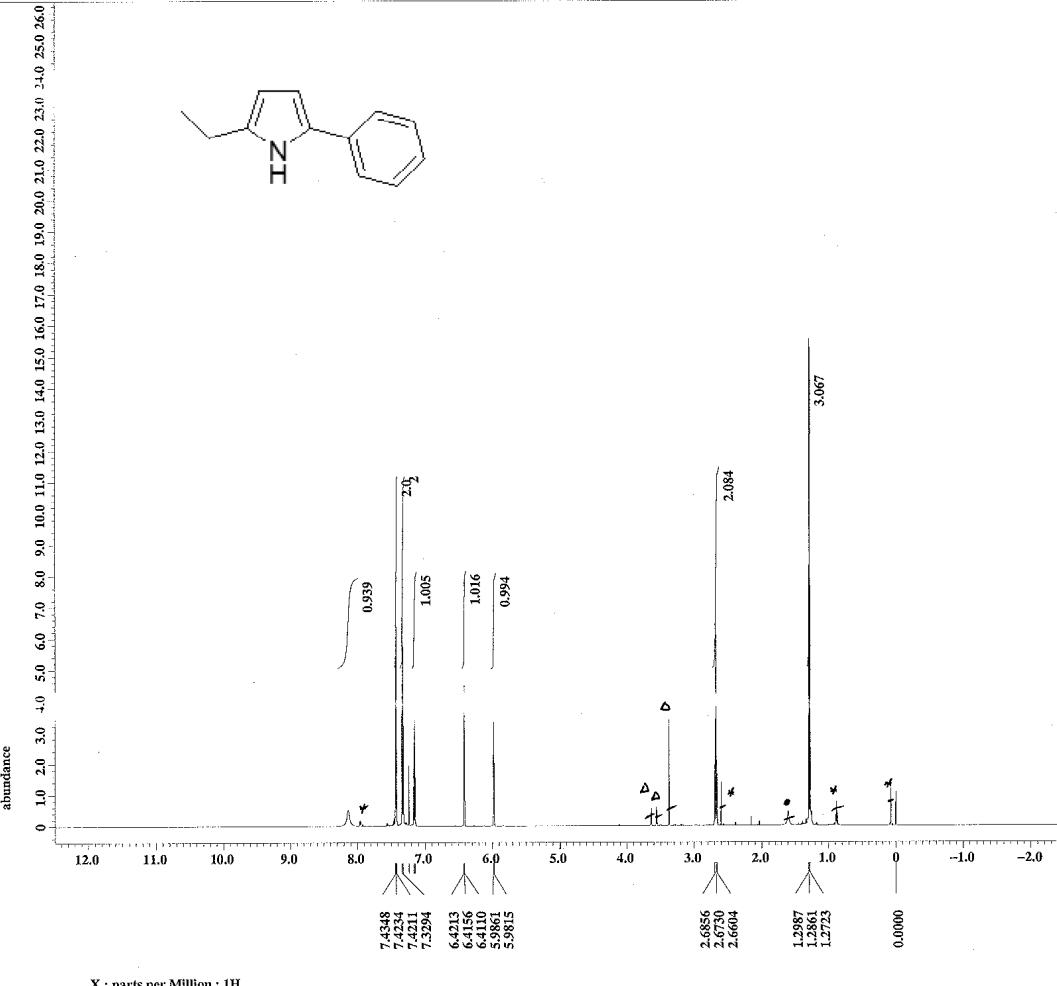
2-(1-Phenyl-ethylideneamino)-1-butanol:⁷ GC-MS m/e 191.135.



Notes and references

- 1 S. Qu, Y. Dang, C. Song, M. Wen, K.-W. Huang and Z.-X. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 4974.
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- 5 J.-L. Zhu and Y.-H. Chan, *Synlett*, 2008, **8**, 1250.
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JEOL



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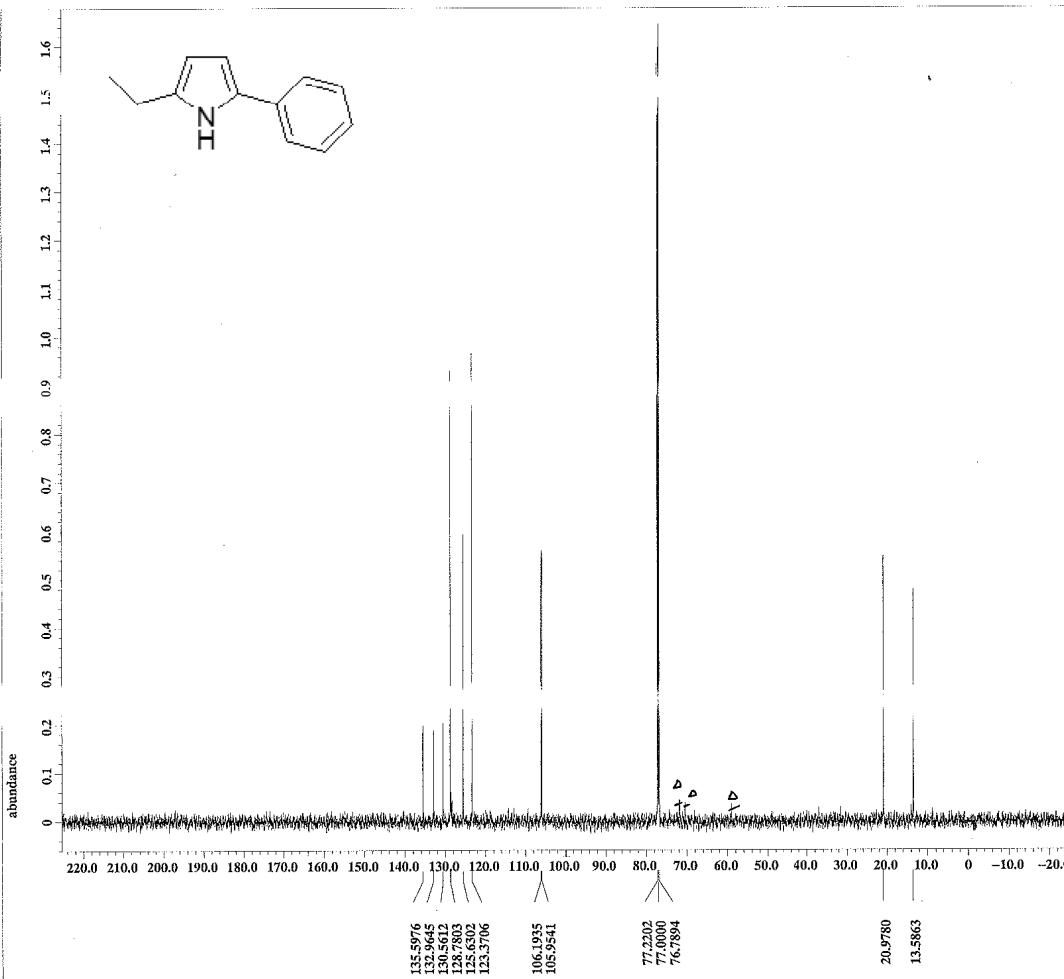
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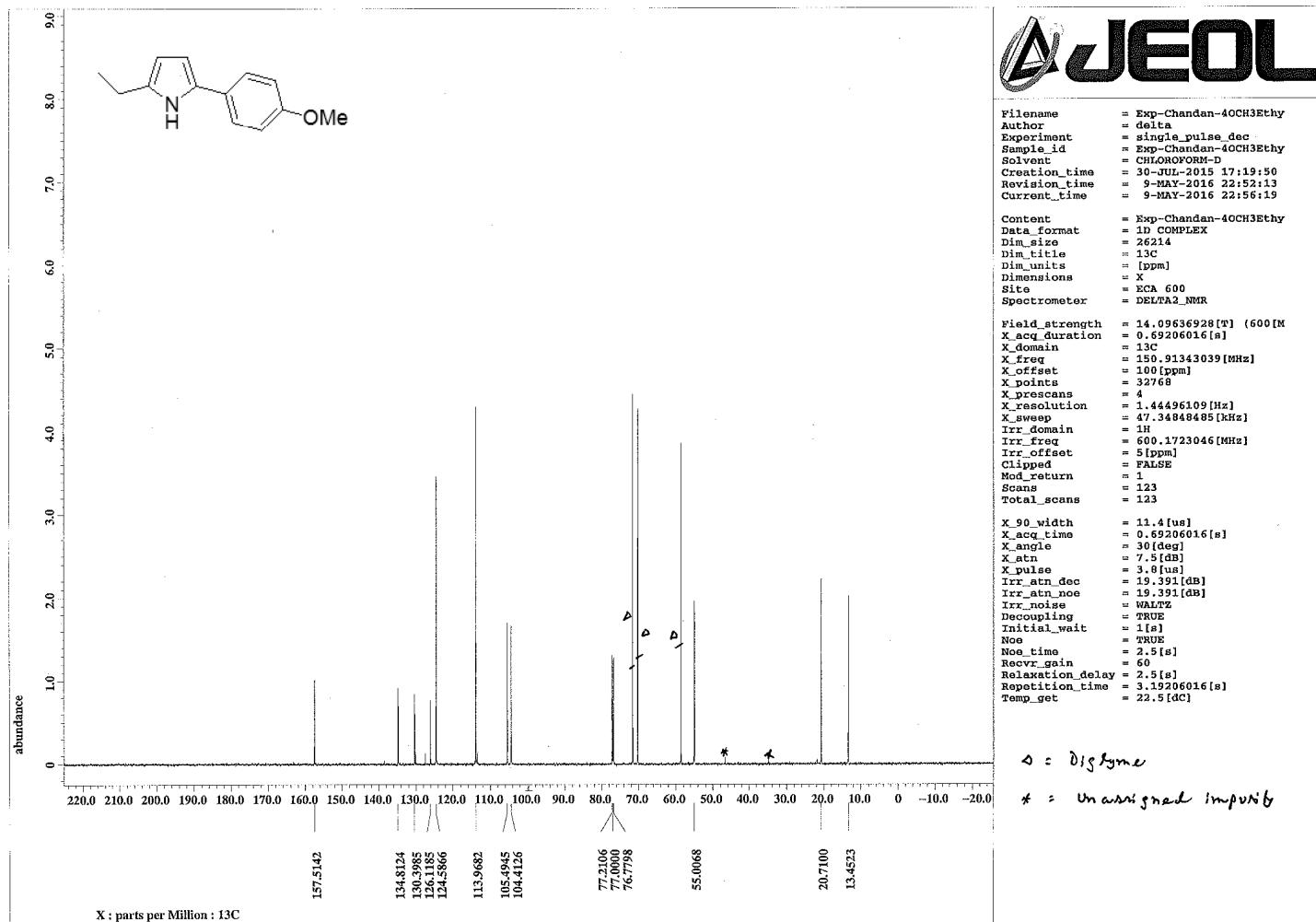
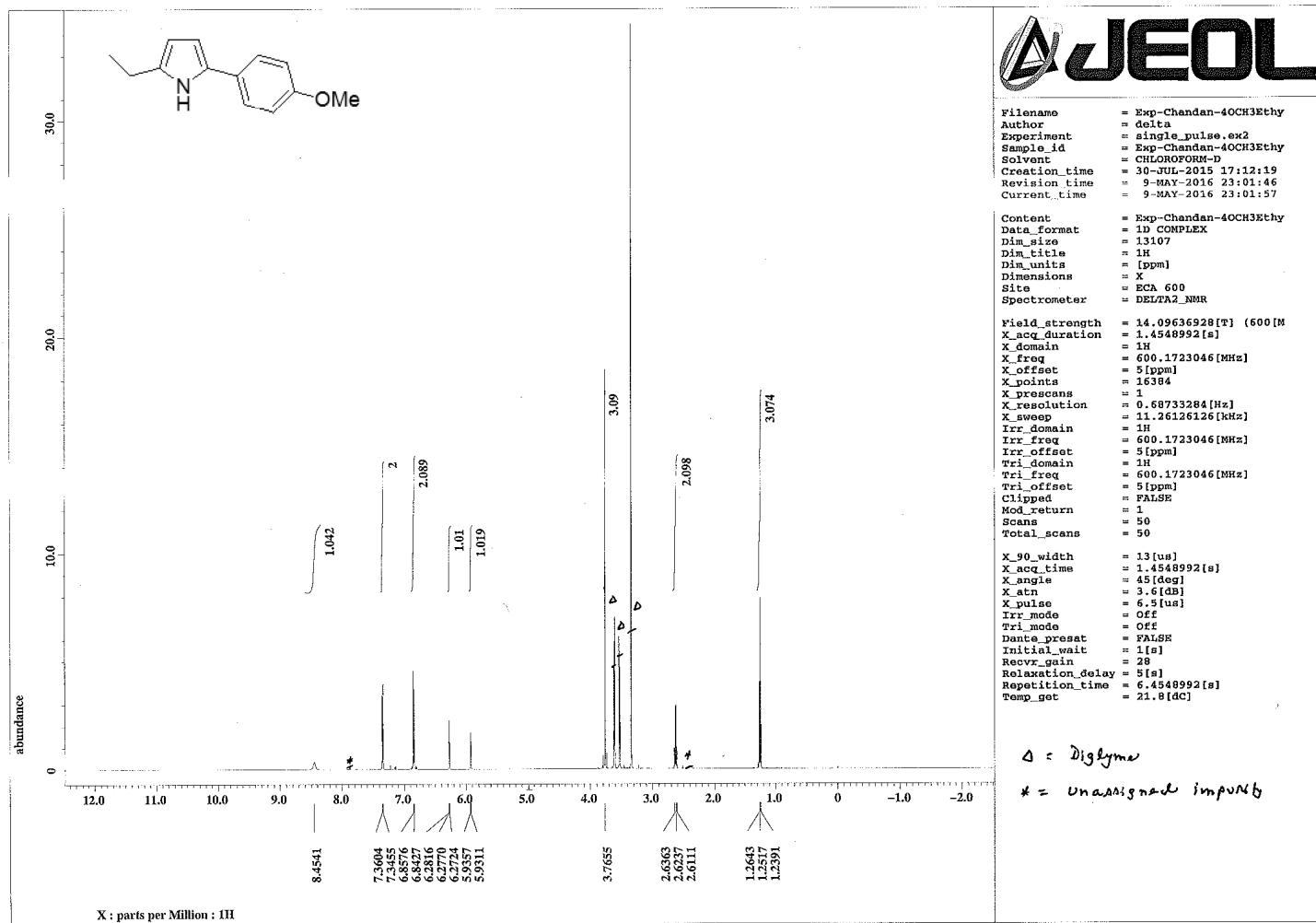
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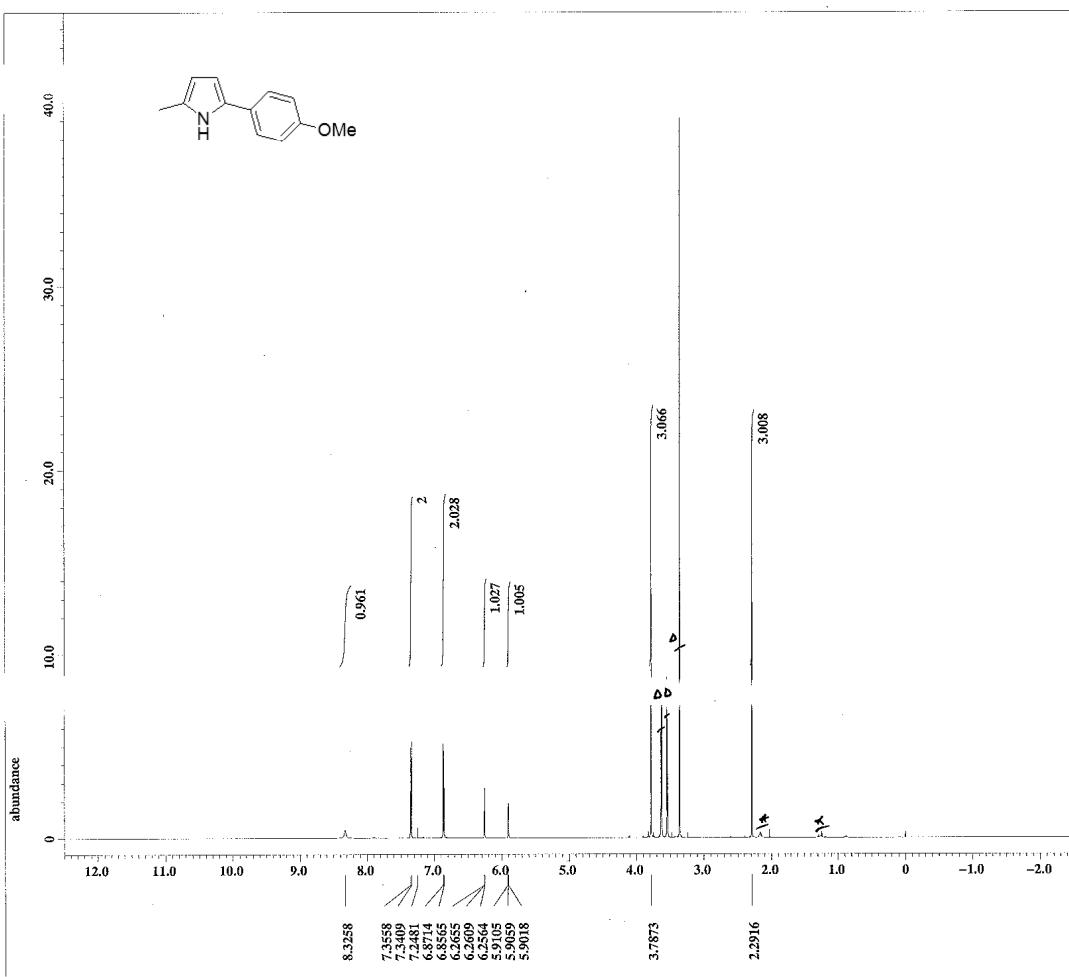
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JEOL



```

Filename = Exp-Chandan-4OCH3Meth
Author = delta
Experiment = single_pulse_ex2
Sample_id = Exp-Chandan-4OCH3Meth
Solvent = CHLOROFORM-D
Creation_time = 30-JUL-2015 17:32:50
Revision_time = 9-MAY-2016 23:08:40
Current_time = 9-MAY-2016 23:08:47

Content = Exp-Chandan-4OCH3Meth
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1K
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = DELTA2_NMR

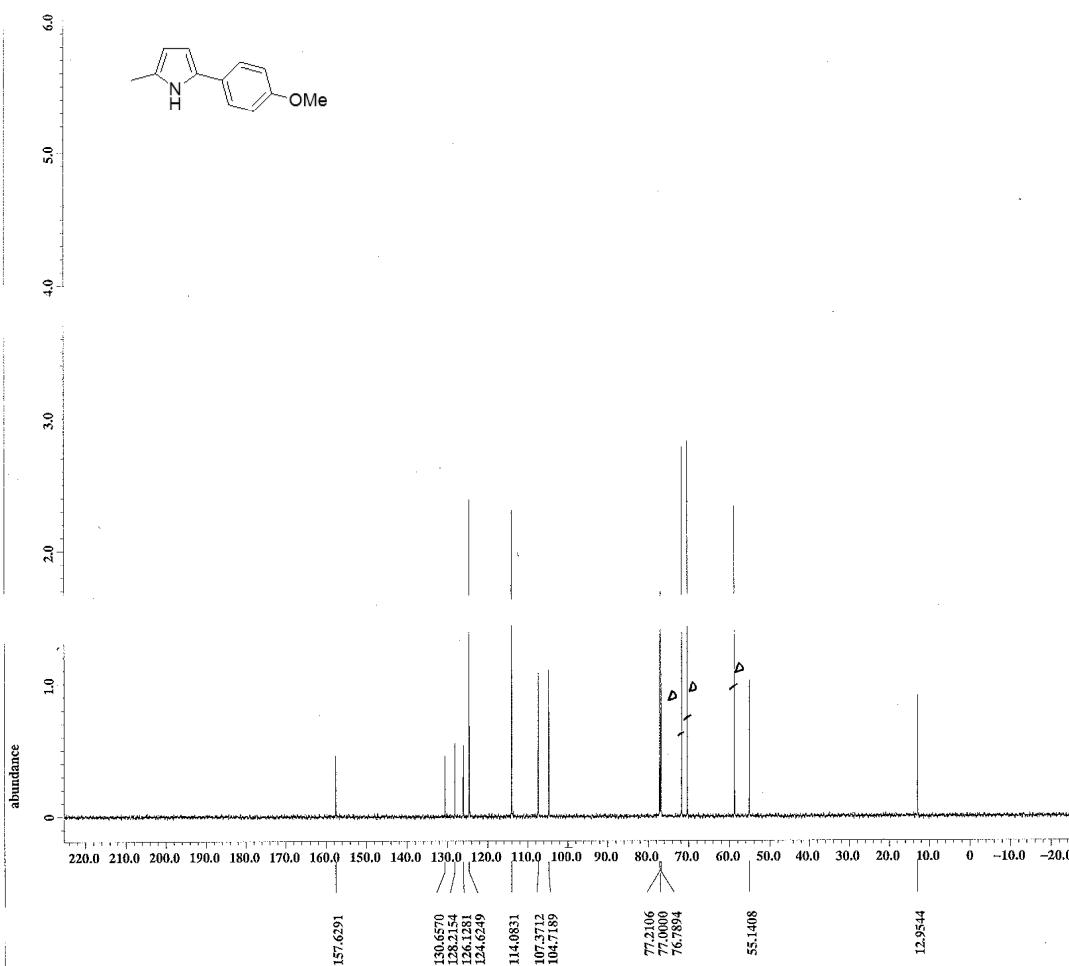
Field_strength = 14.09636928[T] (600[M]
X_acq_duration = 1.4548992[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 51ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.68733284[Hz]
X_sweep = 11.26126126[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 51ppm]
Irr_points = 16384
Irr_resolution = 0.68733284[Hz]
Irr_sweep = 11.26126126[kHz]
Tri_freq = 600.1723046[MHz]
Tri_offset = 51ppm]
Clipped = FALSE
Mod_return = 1
Scans = 50
Total_scans = 50

X_90_width = 13[us]
X_acq_time = 1.4548992[s]
X_angle = 45[deg]
X_attn = 3.6[dB]
X_pulse = 6.5[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvrv_gain = 34
Relaxation_delay = 5[s]
Repetition_time = 6.4548992[s]
Temp_set = 21.9[dc]

```

△ : Diglyme

* : unassigned impurity



```

Filename = Exp-Chandan-4OCH3Meth
Author = delta
Experiment = single_pulse_dec
Sample_id = Exp-Chandan-4OCH3Meth
Solvent = CHLOROFORM-D
Creation_time = 30-JUL-2015 17:44:16
Revision_time = 9-MAY-2016 23:03:32
Current_time = 9-MAY-2016 23:05:08

Content = Exp-Chandan-4OCH3Meth
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = DELTA2_NMR

Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_resolution = 4
X_sweep = 1.44496109[Hz]
X_sweep = 47.34848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 105
Total_scans = 105

X_90_width = 11.4[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_attn = 7.5[dB]
X_pulse = 3.8[us]
Irr_attn_dec = 19.391[db]
Irr_attn_noe = 19.391[db]
Irr_noise = WALZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2.5[s]
Recvrv_gain = 60
Relaxation_delay = 2.5[s]
Repetition_time = 3.19206016[s]
Temp_set = 22.5[dc]

```

△ : Diglyme