Supporting Information

for

Highly efficient gold(I)-catalyzed Overman rearrangement in water

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^{1}H NMR data and NMR spectra of products 2a–2d, 2g–2i.

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^{1}H NMR data of the products

Compound **2a** [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (br, 1H), 5.77 (ddd, *J* = 17.1, 10.4, 5.7 Hz, 1H), 5.22–5.15 (m, 2H), 4.35–4.28 (m, 1H), 1.69–1.59 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

Compound **2b** [1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (br, 1H), 5.85 (ddd, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.26–5.15 (m, 2H), 4.53–4.50 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 3H).

Compound **2c** [1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (br, 1H), 5.78 (ddd, *J* = 17.0, 10.4, 5.6 Hz, 1H), 5.21 (d, *J* = 17.6 Hz, 1H), 5.17 (d, *J* = 10.5 Hz, 1H), 4.45–4.34 (m, 1H), 1.67–1.51 (m, 2H), 1.44–1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

Compound **2d** [1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.17 (m, 5H), 6.56 (br, 1H), 5.84 (ddd, *J* = 16.3, 10.4, 5.6 Hz, 1H), 5.29–5.23 (m, 2H), 4.52–4.45 (m, 1H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.04–1.94 (m, 2H).

Compound **2e**: a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (br, 1H), 5.78 (ddd, *J* = 17.4, 10.3, 5.5 Hz, 1H), 5.23–5.18 (m, 2H), 4.55–4.51 (m, 1H) 1.47–1.38 (m, 3H), 1.36–1.21 (m, 2H), 0.96–0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.2, 135.7, 116.3, 55.1, 45.1, 22.4, 21.8, 11.6; IR (CH_2Cl_2): 3425, 2970, 1713, 1512, 1265 cm^{-1}; LRMS (EI, 20 eV) *m*/*z* 236 (M^+ – Cl, 2), 202 (25), 166 (100), 132 (19); HRMS (EI) calcd for $C_{10}H_{16}Cl_2NO$ (M^+ – Cl) 236.0603, found 236.0604.

Compound **2h** [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (br, 1H), 5.85 (ddd, *J* = 16.9, 10.4, 5.7 Hz, 1H), 5.28 (d, *J* = 18.8 Hz, 1H), 5.24 (d, *J* = 10.8 Hz, 1H), 4.47–4.43 (m, 1H), 3.83–3.70 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H).

Compound **2i**: a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (br, 1H), 5.87

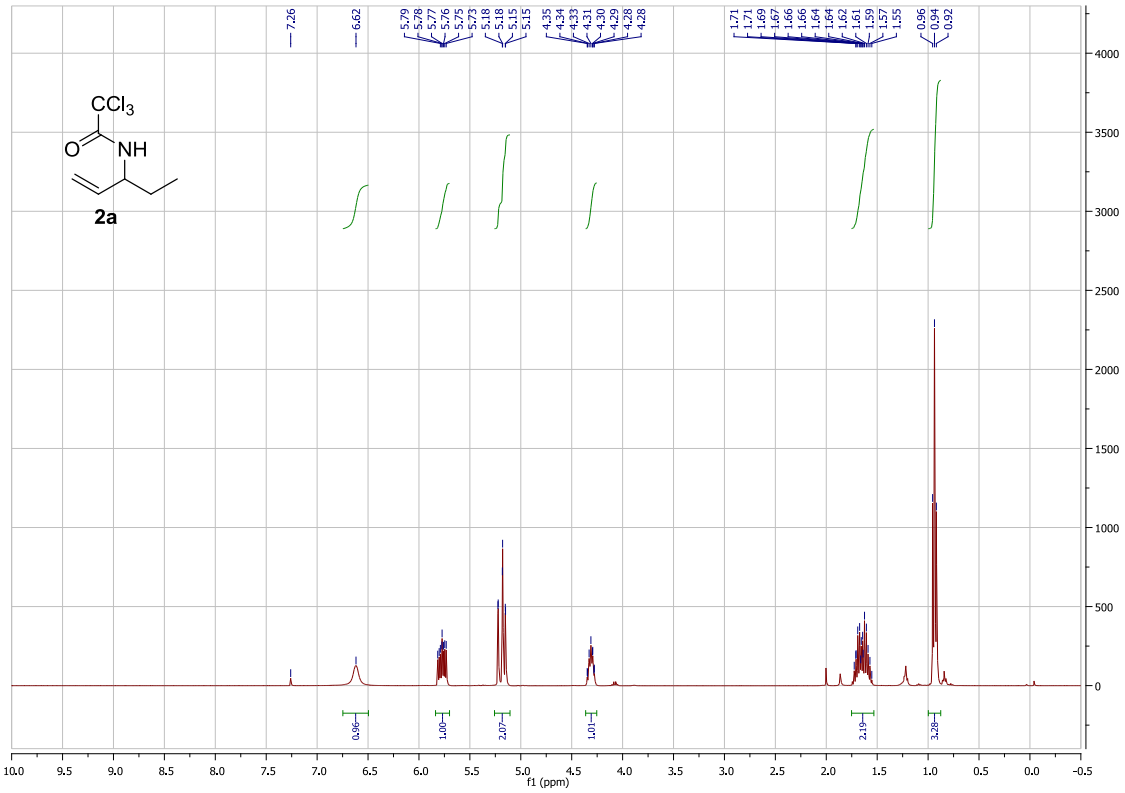
(ddd, *J* = 17.2, 10.5, 5.2 Hz, 1H), 5.35–5.30 (m, 2H), 4.87 (s, 1H), 4.56–4.51 (m, 1H), 4.01–3.98 (m, 1H), 3.92–3.77 (m, 2H), 3.53–3.50 (m, 1H), 3.39–3.37 (m, 1H), 2.34 (s, 1H), 1.87–1.78 (m, 2H), 1.52–1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 133.5, 117.8, 94.5, 63.9, 63.7, 54.8, 31.9, 25.2, 20.3; IR (CH_2Cl_2): 3055, 2986, 1713, 1504, 1427, 1265 cm^{-1}; LRMS (EI, 20 eV) *m*/*z* 199 (M^+ – CH_2OTHP, 69), 166 (100), 132 (81), 71 (35); HRMS (EI) calcd for $C_5H_5Cl_3NO$ (M^+ – CH_2OTHP) 199.9431, found 199.9435.

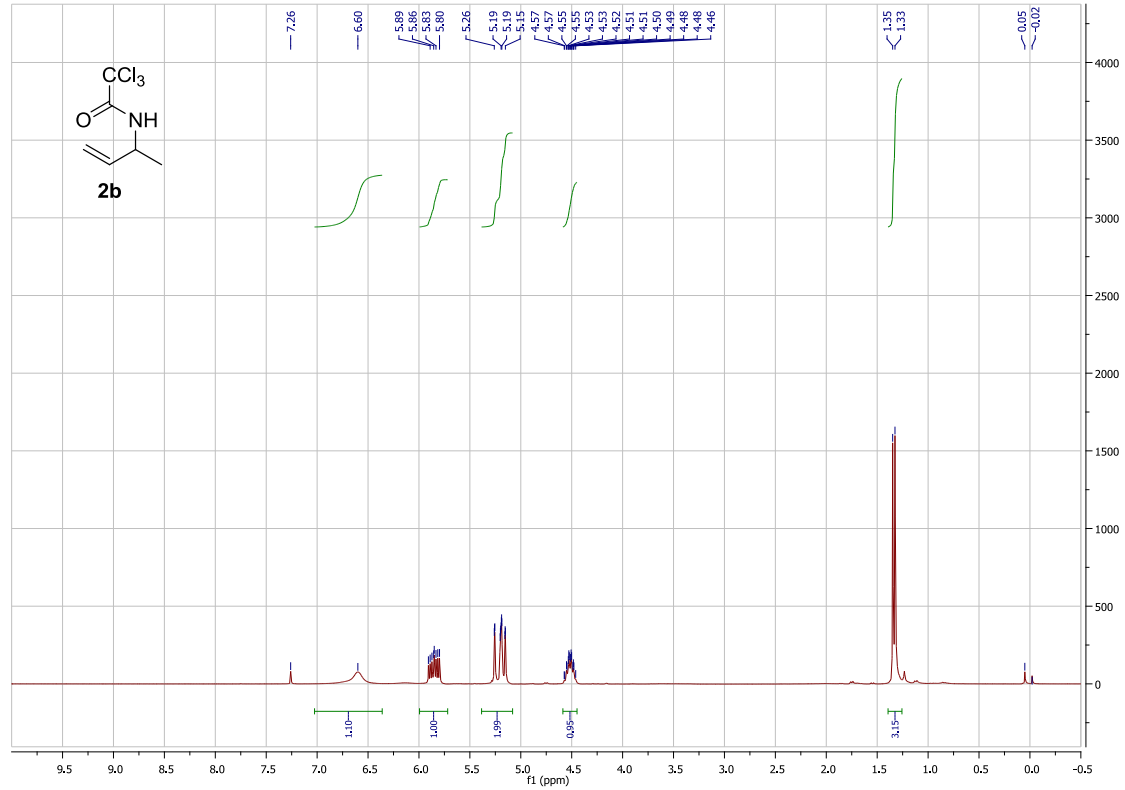
Compound **2j** [1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (br, 1H), 5.78 (ddd, *J* = 17.0, 10.4, 5.6 Hz, 1H), 5.26 (d, *J* = 16.6 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 4.48–4.41 (m, 1H), 3.68 (s, 3H), 2.52–2.36 (m, 2H), 2.07–1.92 (m, 2H).

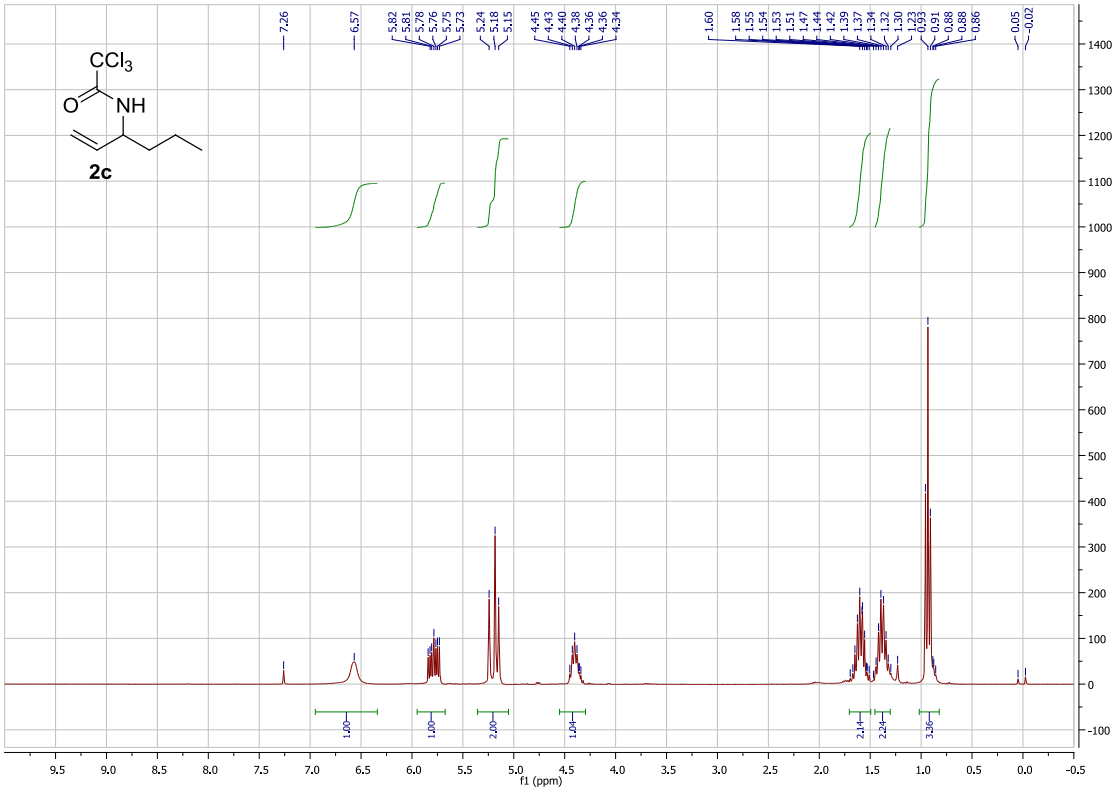
References

1. Anderson, C. E., Overman, L. E. *J. Am. Chem. Soc.* **2003**, *125*, 12412–12413. doi:10.1021/ja037086r

NMR spectra of the products



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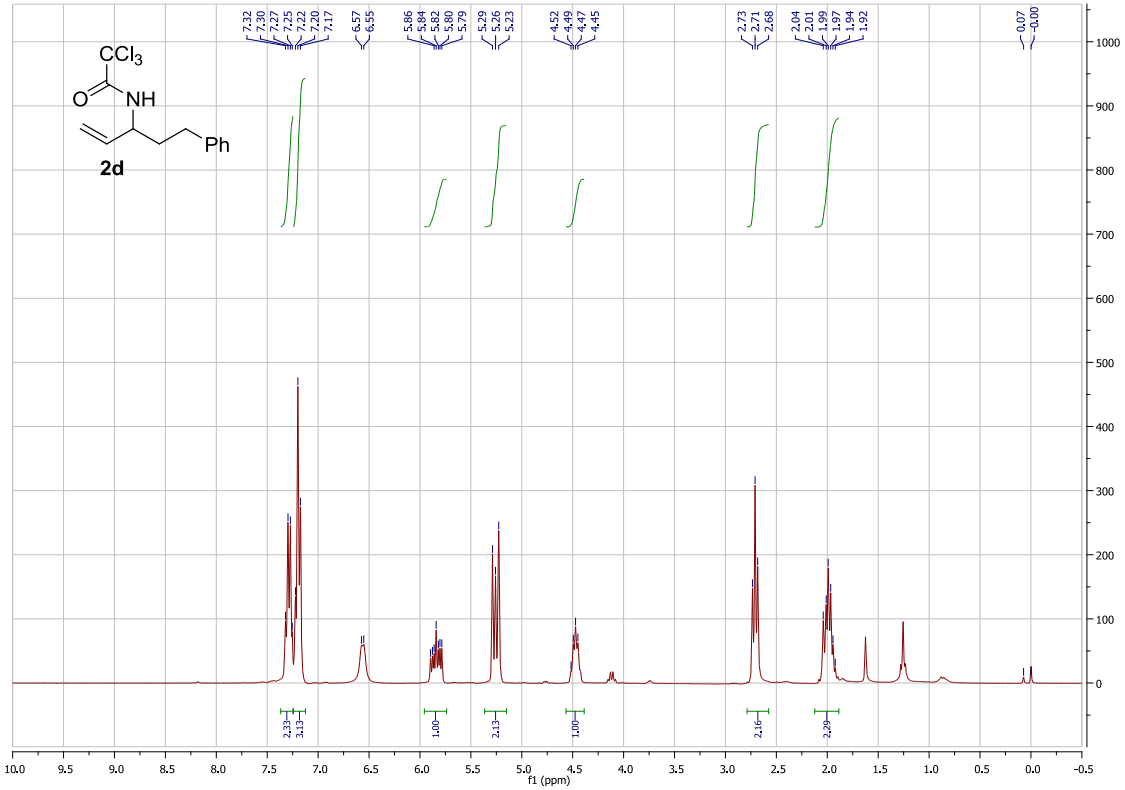
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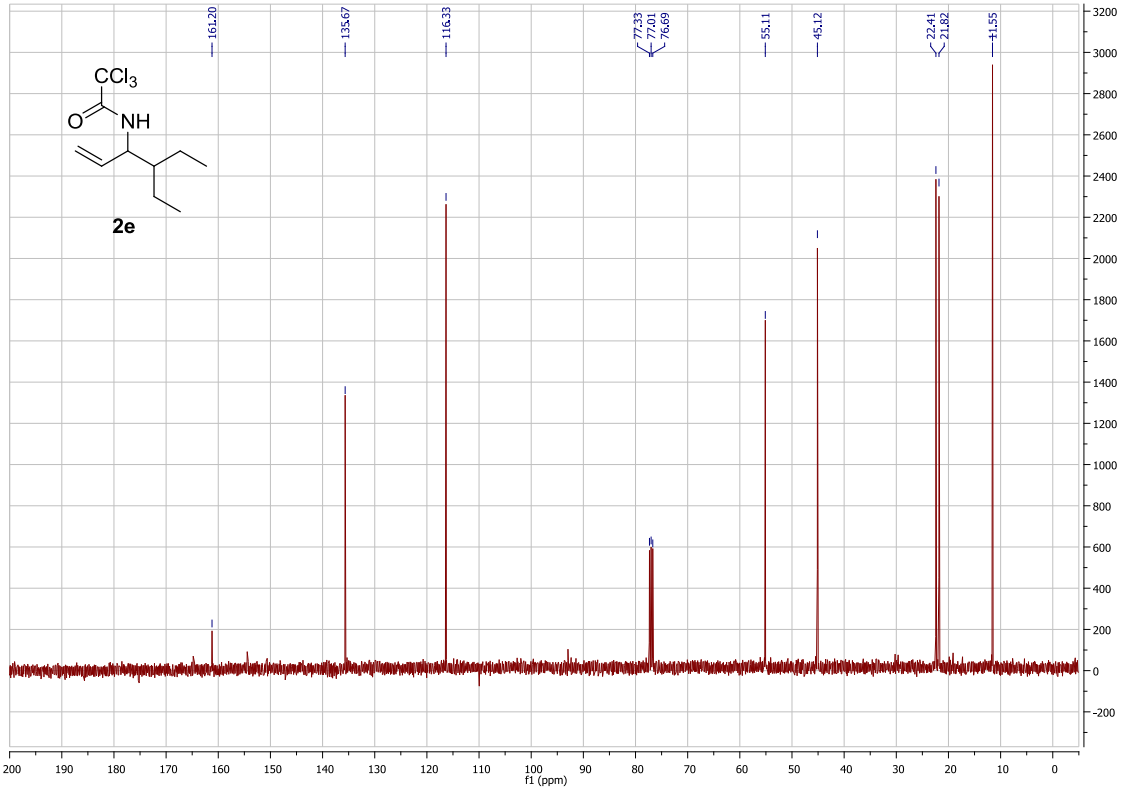
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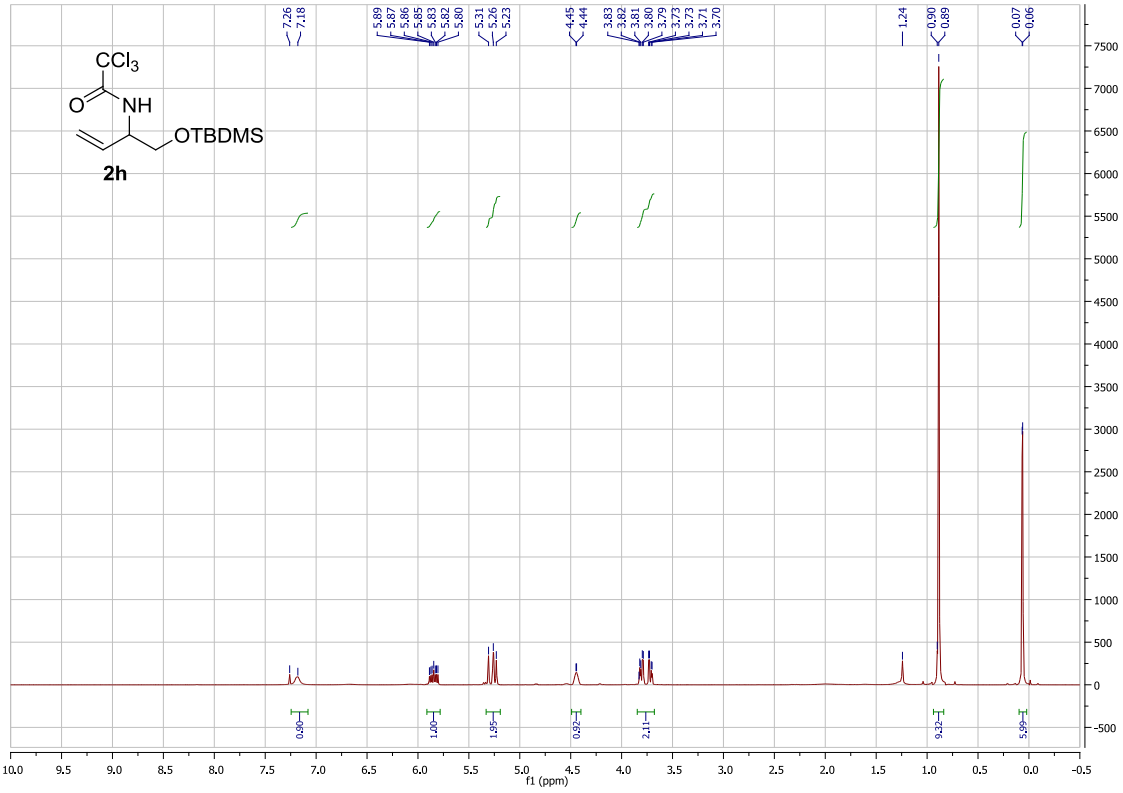
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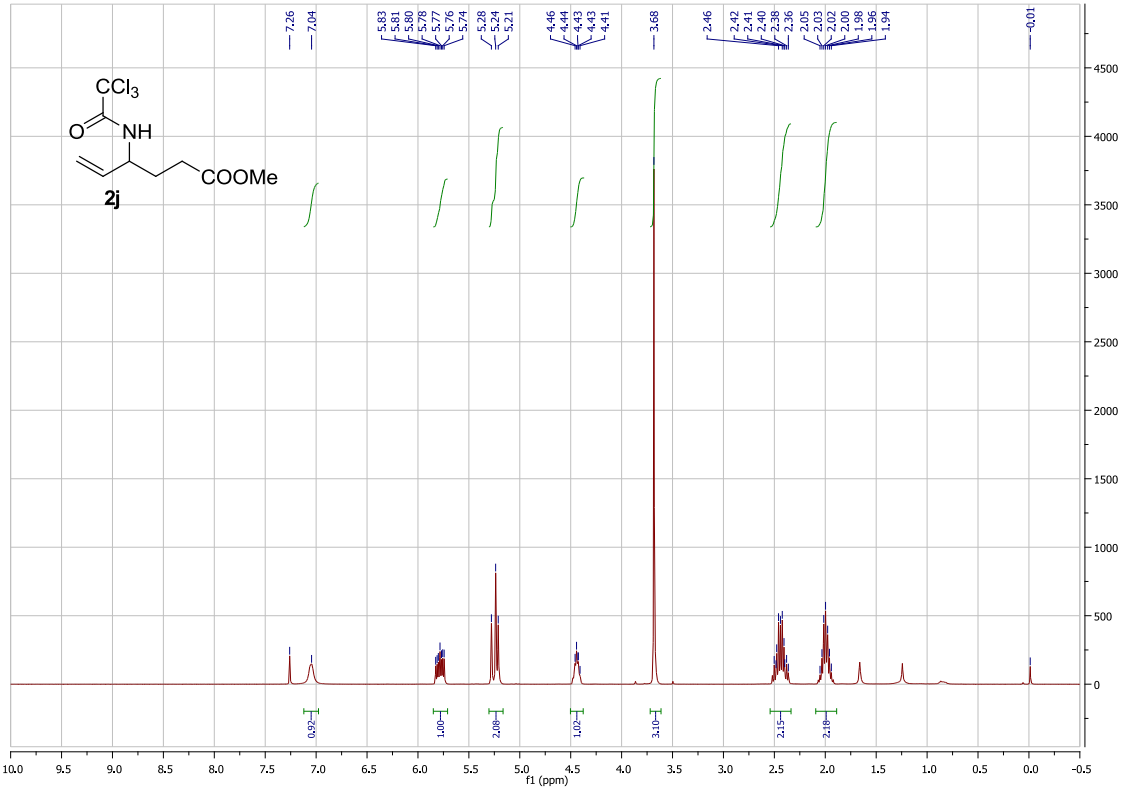
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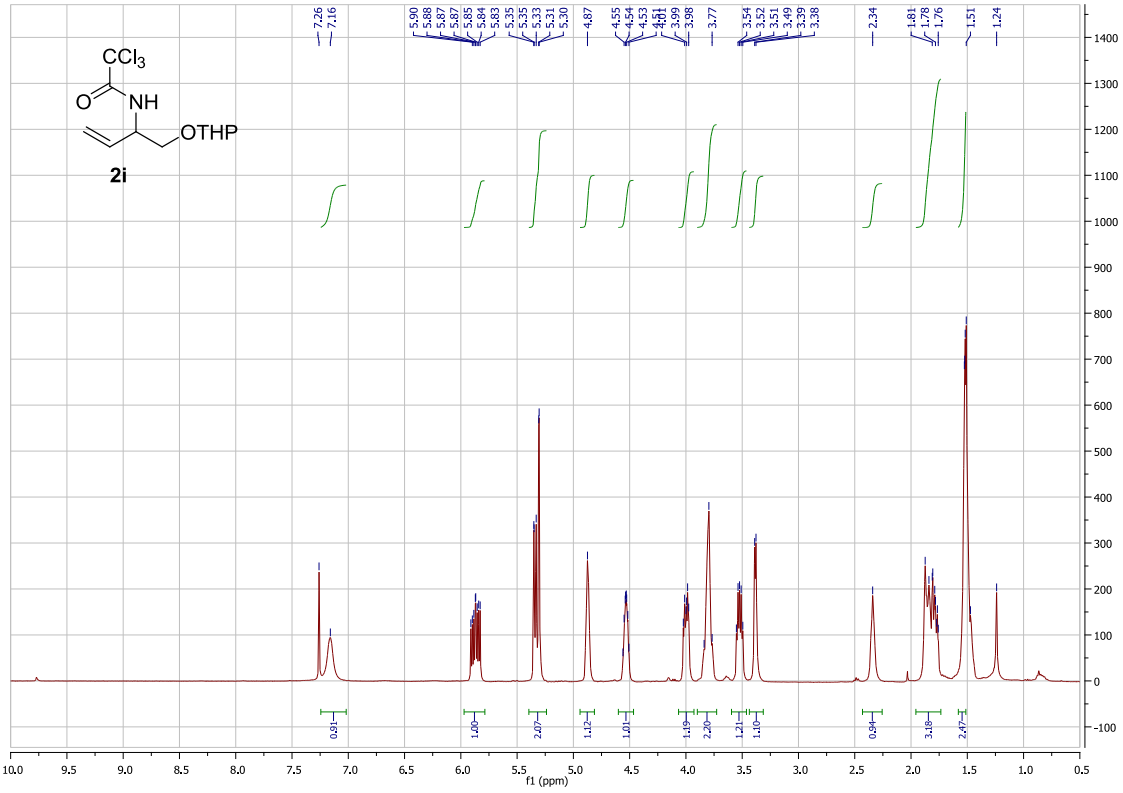
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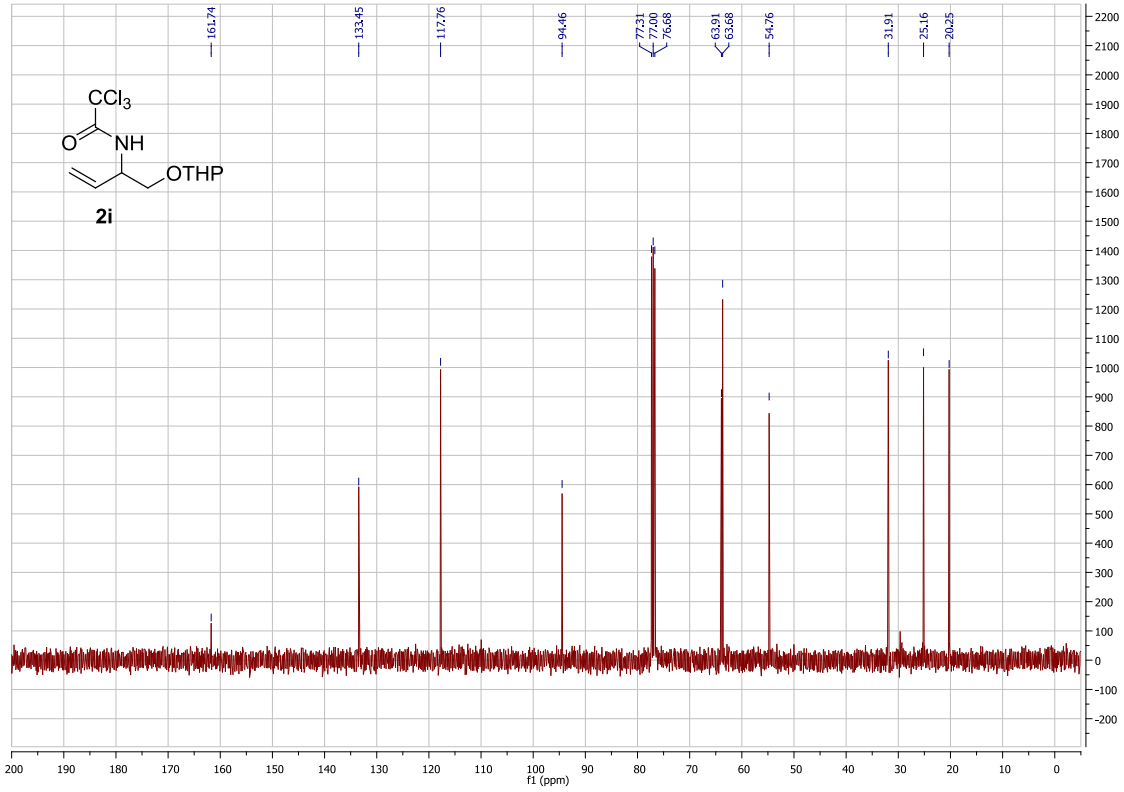
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