

Supplementary Information

Palladium on graphene: the in situ generation of a catalyst for the chemoselective reduction of α,β -unsaturated olefins

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1. General information

^1H (300, 600 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a Varian Mercury300 spectrometers. Proton chemical shifts are relative to solvent peaks [chloroform: 7.27 (^1H), 77.00 (^{13}C); deuterium oxide: 4.79 (^1H)]. IR (ATR) spectra were measured with JASCO ATR PRO450-S with Ge. High-resolution mass spectra were measured by JEOL JMS-700. GC analysis was carried out with Shimadzu GC-2014 equipped with FID detector. The chemical yields were determined using dodecane as an internal standard. TEM image were taken on a JEOL JEM-2100F at an acceleration voltage of 200 kV. XPS spectra were measured by SHIMADZU Kratos AXIS-ULTRA DLD with pass energy of 20 eV. ICP-MS measurement was performed by Agilent 7500c using stock solution of $\text{Pd}(\text{NO}_3)_2$ (0ppb, 1ppb, 10ppb and 100ppb) for calibration. Flash column chromatography was performed with silica gel Merck 60N (spherical, neutral, 20-100 μm) using hexane and ethyl acetate as eluents.

2. Materials

$\text{Pd}(\text{OAc})_2$, PdCl_2 , $\text{Pd}(\text{NO}_3)_2$, Pd/C and Pt/C were purchased from WAKO Pure Chemical Industries, Ltd. and $\text{Pd}(\text{acac})_2$ was purchased from Tokyo Chemical Industry CO., Ltd. Compounds **1a**, **1e**, **1g**, **1i**, **1l**, **1m**, **1n**, **1p** and **3c** were purchased from Tokyo Chemical Industry CO., Ltd. Compounds **1b**,¹ **1c**,² **1d**,³ **1f**,⁴ **1h**,⁵ **1j**,⁶ **1k**,⁶ **1o**,⁷ **3a**,⁸ **3b**⁹ were synthesized by literature procedures.

Products **2a**,¹⁰ **2b**,¹⁰ **2c**,¹¹ **2e**,¹² **2g**,¹⁰ **2h**,¹⁰ **2i**,¹³ **2j**,¹⁴ **2k**,¹⁵ **2l**,¹⁶ **2m**,¹⁷ **2n**,¹⁸ **2o**,¹⁹ **2p**,²⁰ **4a**,²¹ **4b**,²² **4c**²³ were known compounds.

3. Preparation of graphene oxide (GO)

GO was prepared from natural graphite flakes (SP-1, BAY CARBON, Inc.) according to Hummers method.²⁴

4. Preparation of Pd-graphene oxide (Pd/GO)

For the preparation of Pd/GO, 1 g of 3 w% aq. dispersion of GO was suspended in 25 mL of distilled water. To the solution of the aqueous GO was added 25 mL of EtOH at room temperature. After being stirred at the same temperature for 10 min, Pd source (0.005 mmol) was added and then stirred vigorously for 1 h. The suspension of Pd/GO was washed with distilled water by centrifugation for 3 times.

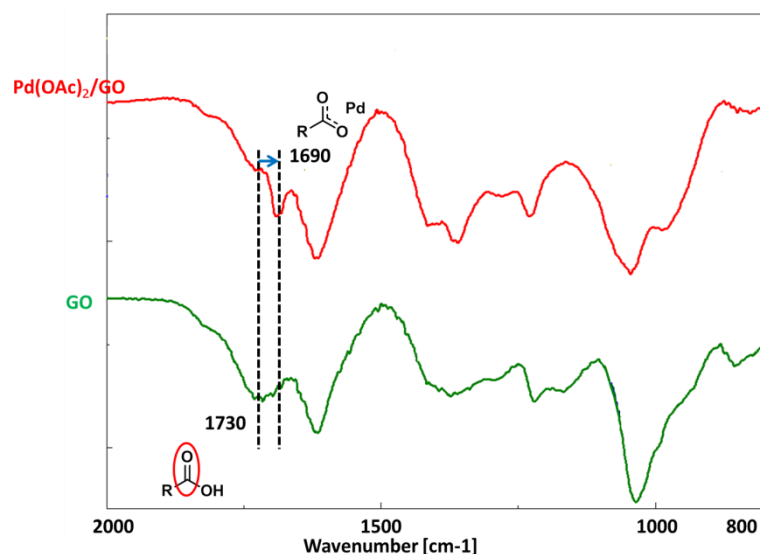
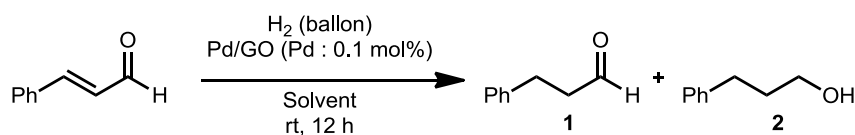


Fig S1. IR spectra of Pd/GO (red) and GO (green). The peak of GO at 1730 cm^{-1} shifted to 1690 cm^{-1} after the reaction with Pd(OAc)₂. For clearance, ten times larger amount of Pd(OAc)₂ was added to GO.

5. Typical procedure for Hydrogenation

To the solution of 50% aq. EtOH (3.00 mL) was added Pd/GO (Pd: 0.0003 mmol, 0.1 mol%) in the presence of chalcone (0.300 mmol). The mixture was evacuated and flushed 3 times with H₂ to remove air. Then the mixture was stirred at room temperature under ambient pressure of hydrogen (balloon). After the reaction, the reaction mixture was analyzed by gas chromatography using dodecane as an internal standard (Tables 1 and 2) or isolated by flash column chromatography (Tables 3 and 4).

Table S1 Solvent effect for the chemoselective reduction of cinnamaldehyde.

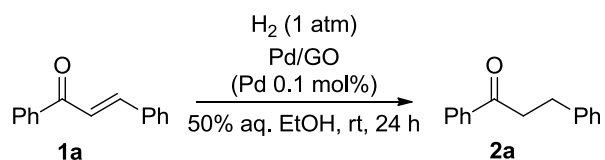


Solvent	1	2
THF	68	19
1,4-dioxane	91	4
EtOH	84	12
DMA	24	1
DMA + 50% aq. EtOH^a	98	2

^aDMA : EtOH : H₂O = 2 : 1 : 1

6. Catalyst recycling

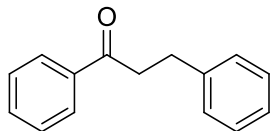
After the reaction, the catalyst was washed with THF and centrifuged for 3 times. Then, 50% aq. EtOH was added and centrifuged for 3 times to replace the solvent, and reused for next reaction.



Cycle	Yield/%
1	99
2	94
3	95
4	98
5	98

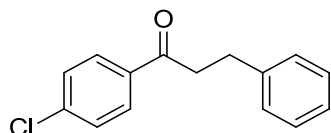
7. Product data

3-Phenylpropiophenone (2a)



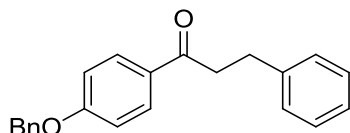
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.95 (d, $J = 7.1$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.19-7.32 (m, 5H), 3.30 (t, $J = 7.8$ Hz, 2H), 3.06 (t, $J = 7.8$ Hz, 2H)

1-(4-Chlorophenyl)-3-phenyl-1-propanone (2b)



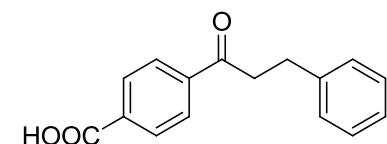
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.75 (d, $J = 9.0$ Hz, 2H), 7.27 (d, $J = 8.8$ Hz, 2H), 7.07-7.19 (m, 5H), 3.13 (t, $J = 8.1$ Hz, 2H), 2.92 (t, $J = 8.1$ Hz, 2H)

3-Phenyl-1-[4-(phenylmethoxy)phenyl]-1-propanone (2c)



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.84 (d, $J = 8.8$ Hz, 2H), 7.11-7.32 (m, 10H), 6.90 (d, $J = 8.9$ Hz, 2H), 5.01 (s, 2H), 3.15 (t, $J = 8.1$ Hz, 2H), 2.96 (t, $J = 8.1$ Hz, 2H)

4-(1-Oxo-3-phenylpropyl)-benzoic acid (2d)



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.19 (d, $J = 8.6$ Hz, 2H), 8.04 (d, $J = 8.6$ Hz, 2H), 7.22-7.34 (m, 5H), 3.35 (t, $J = 7.5$ Hz, 2H), 3.09 (t, $J = 7.5$ Hz, 2H)

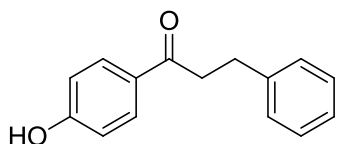
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 30.10, 41.04, 126.43, 128.18, 128.57, 128.75, 130.64,

133.02, 140.87, 141.04, 198.85

IR 2903, 2666, 2538, 1678, 1424, 1281, 1203, 1200, 941, 866, 757, 692 cm^{-1}

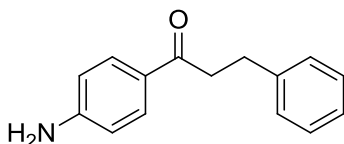
HRMS (ESI+) Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_3$ (ESI+) 255.10212, Found 255.10211.

1-(4-Hydroxyphenyl)-3-phenyl-1-propanone (2e)



^1H NMR (300 MHz, CDCl_3) δ 7.92 (d, $J = 8.9$ Hz, 2H), 7.22-7.33 (m, 5H), 6.94 (d, $J = 8.9$ Hz, 2H), 3.29 (t, $J = 8.0$ Hz, 2H), 3.07 (t, $J = 8.0$ Hz, 2H)

1-(4-Aminophenyl)-3-methylphenyl-1-propanone (2f)



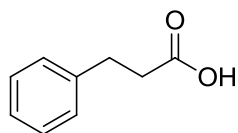
^1H NMR (300 MHz, CDCl_3) δ 7.25-7.31 (m, 4H), 7.14-7.23 (m, 5H), 2.90 (t, $J = 7.8$ Hz, 2H), 2.72 (t, $J = 7.8$ Hz, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 29.85, 44.64, 126.25, 128.44, 128.63, 141.13, 209.26

IR 3085, 3060, 3027, 2938, 1712, 1604, 1493, 1452, 1367, 1262, 1092, 1075, 1031, 982, 913, 747, 696 cm^{-1}

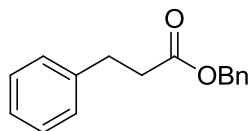
HRMS (ESI+) Calcd for $\text{C}_{15}\text{H}_{16}\text{NO}$ (ESI+) 226.12319, Found 226.12325.

Benzenepropanoic acid (2g)



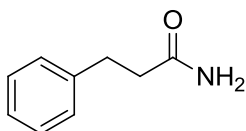
^1H NMR (300 MHz, CDCl_3) δ 7.26-7.31 (m, 2H), 7.18-7.22 (m, 3H), 2.95 (t, $J = 7.7$ Hz, 2H), 2.67 (t, $J = 7.7$ Hz, 2H)

Benzenepropanoic acid phenylmethyl ester (2h)



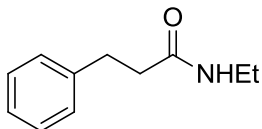
^1H NMR (300 MHz, CDCl_3) δ 7.15-7.25 (m, 7H), 7.07–7.12 (m, 3H), 5.01 (s, 2H), 2.88 (t, $J = 7.8$ Hz, 2H), 2.58 (t, $J = 7.8$ Hz, 2H)

Benzenepropanamide (2i)



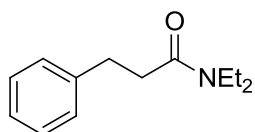
^1H NMR (300 MHz, CDCl_3) δ 7.21-7.26 (m, 2H), 7.12–7.16 (m, 3H), 2.91 (t, $J = 7.8$ Hz, 2H), 2.47 (t, $J = 7.8$ Hz, 2H)

N-Ethyl-benzenepropanamide (2j)



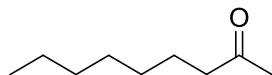
^1H NMR (300 MHz, CDCl_3) δ 7.33-7.36 (m, 2H), 7.23–7.26 (m, 3H), 5.70 (br, 1H), 3.30 (q, $J = 7.2$ Hz, 2H), 3.01 (t, $J = 7.6$ Hz, 2H), 2.51 (t, $J = 7.6$ Hz, 2H), 1.12 (t, $J = 7.2$ Hz, 3H)

N,N-Diethyl-benzenepropanamide (2k)



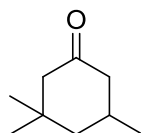
^1H NMR (300 MHz, CDCl_3) δ 7.19-7.33 (m, 5H), 3.40 (q, $J = 7.1$ Hz, 2H), 3.24 (q, $J = 7.1$ Hz, 2H), 3.01 (t, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.09–1.16 (m, 6H)

2-Nonanone (2l)



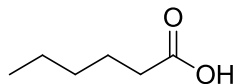
^1H NMR (300 MHz, CDCl_3) δ 2.40 (t, $J = 7.5$ Hz, 2H), 2.12 (s, 3H), 1.52–1.58 (m, 2H), 1.20–1.35 (m, 8H), 0.87 (t, $J = 7.0$ Hz, 3H)

3,3,5-Trimethyl-cyclohexanone (2m)



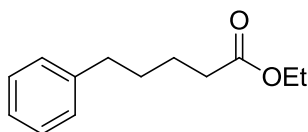
^1H NMR (300 MHz, CDCl_3) δ 2.23-2.29 (m, 1H), 2.09–2.14 (m, 1H), 1.79–2.03 (m, 3H), 1.49-1.57 (m, 1H), 1.25 (t, $J = 12.6$ Hz, 1H), 1.00 (s, 3H), 0.97 (d, $J = 6.3$ Hz, 3H), 0.83 (s, 3H)

Hexanoic acid (2n)



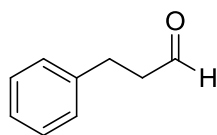
^1H NMR (300 MHz, CDCl_3) δ 10.43 (br, 1H), 2.34 (t, $J = 7.5$ Hz, 2H), 1.58–1.68 (m, 2H), 1.29–1.34 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H)

Benzenepentanoic acid ethyl ester (2o)



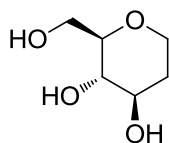
^1H NMR (300 MHz, CDCl_3) δ 7.27-7.31 (m, 2H), 7.17-7.20 (m, 3H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.64 (t, $J = 7.1$ Hz, 2H), 2.32 (t, $J = 7.1$ Hz, 2H), 1.60–1.70 (m, 4H), 1.25 (t, $J = 7.1$ Hz, 3H)

Benzenepropanal (2p)



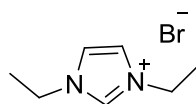
^1H NMR (300 MHz, CDCl_3) δ 9.87 (s, 1H), 7.23-7.38 (m, 5H), 3.01 (t, $J = 7.5$ Hz, 2H), 2.83 (t, $J = 7.5$ Hz, 2H)

1,5-Anhydro-2-deoxy-D-arabino-hexitol (4a)



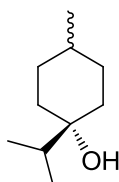
^1H NMR (300 MHz, D_2O) δ 3.97 (dd, $J = 1.6, 14.9$ Hz, 1H), 3.86 (dd, $J = 2.0, 12.3$ Hz, 1H), 3.60-3.71 (m, 2H), 3.46-3.55 (m, 1H), 3.20–3.30 (m, 2H), 1.94–2.02 (m, 1H), 1.53-1.68 (m, 1H)

1,3-Diethyl-1*H*-imidazolium bromide (4b)



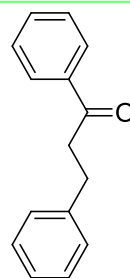
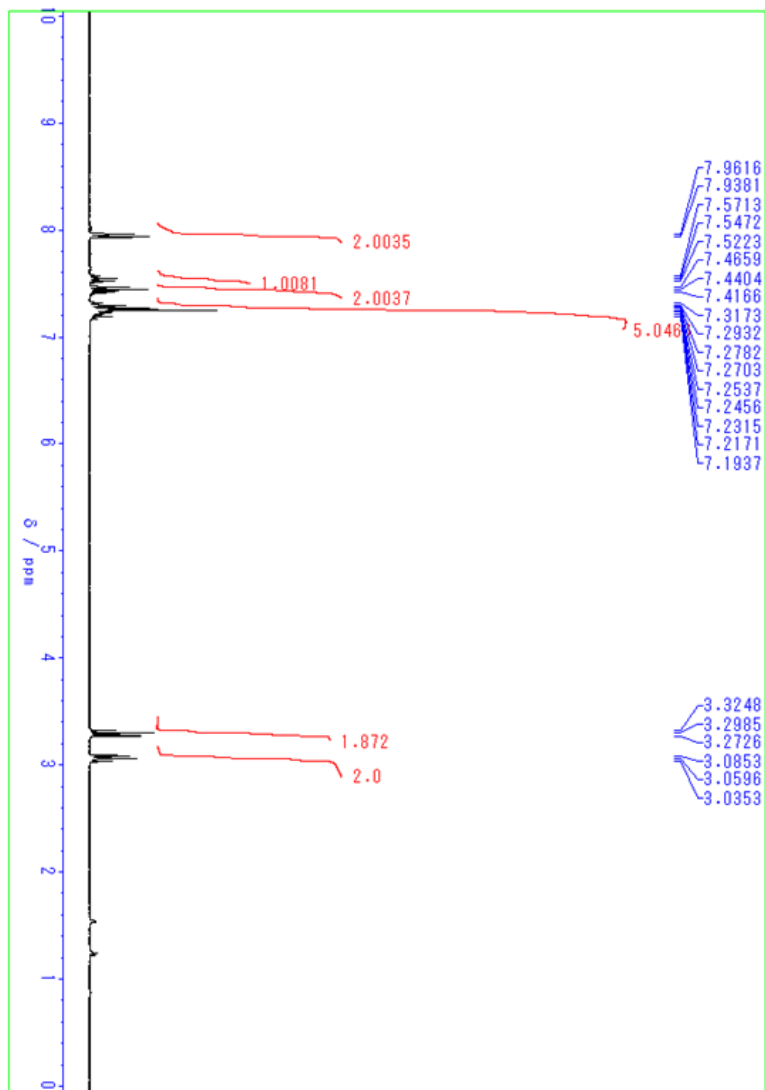
^1H NMR (300 MHz, D_2O) δ 8.77 (s, 1H), 7.49 (d, $J = 1.6$ Hz, 2H), 4.22 (q, $J = 7.4$ Hz, 4H), 1.49 (t, $J = 7.4$ Hz, 6H)

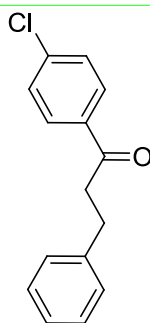
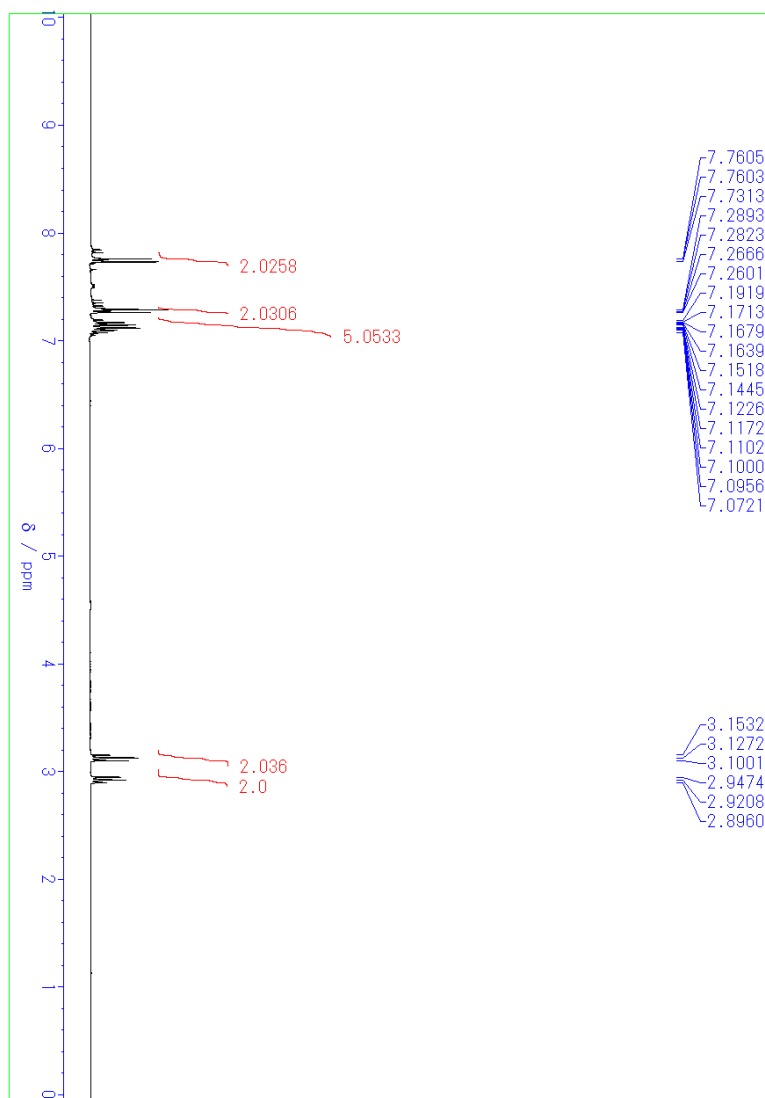
4-Methyl-1-(1-methylethyl)-cyclohexanol (4c)

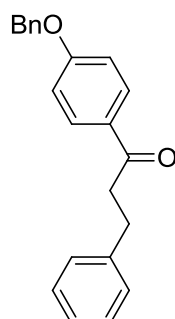
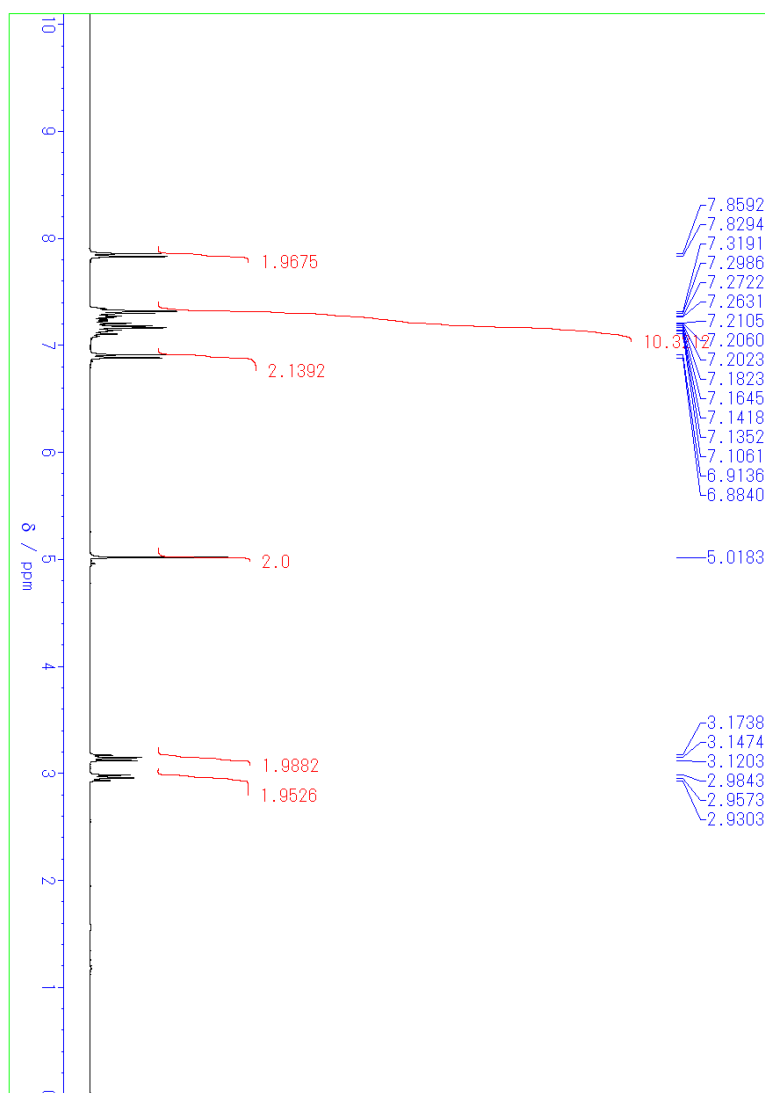


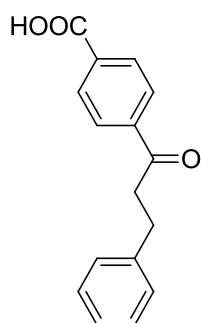
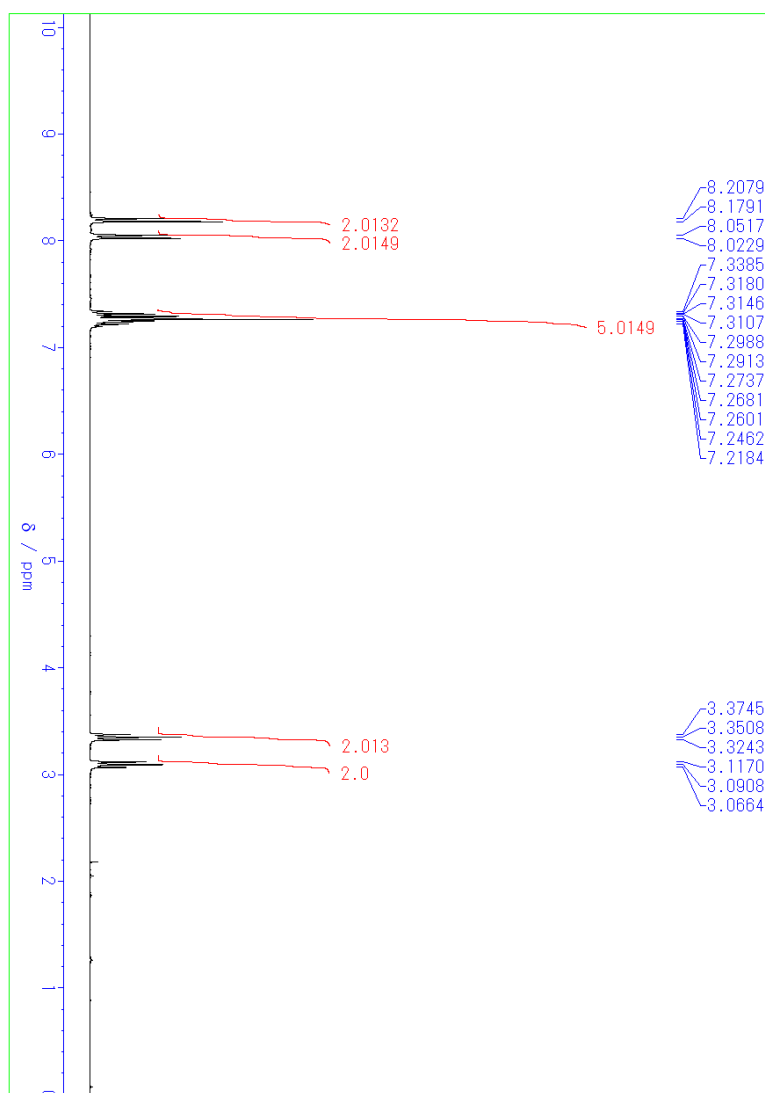
^1H NMR (600 MHz, CDCl_3) δ 1.49-1.58 (m, 4H), 1.25-1.29 (m, 6H), 0.88–0.91 (m, 9H)

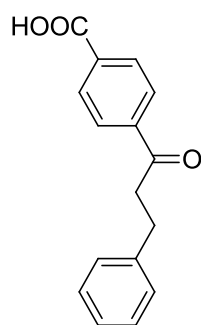
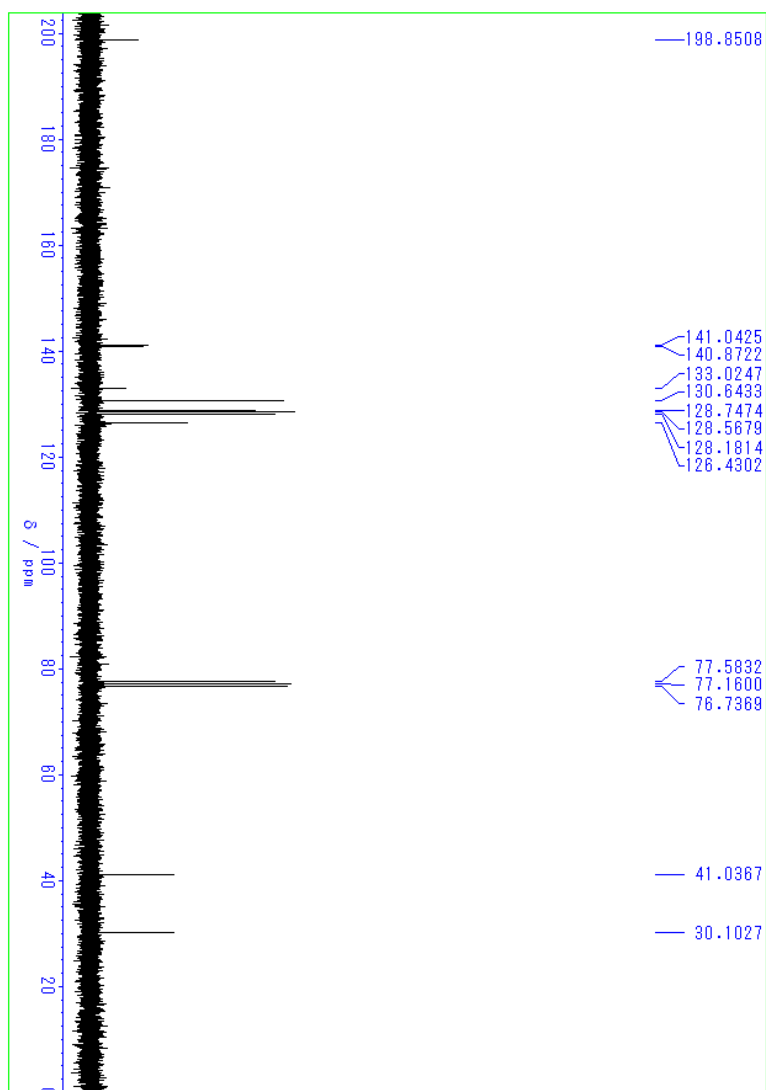
^{13}C NMR (100 MHz, CDCl_3) δ 16.24, 17.04, 22.55, 30.50, 32.50, 33.83, 38.83

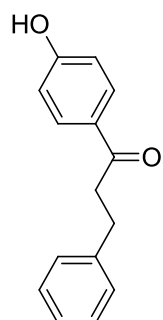
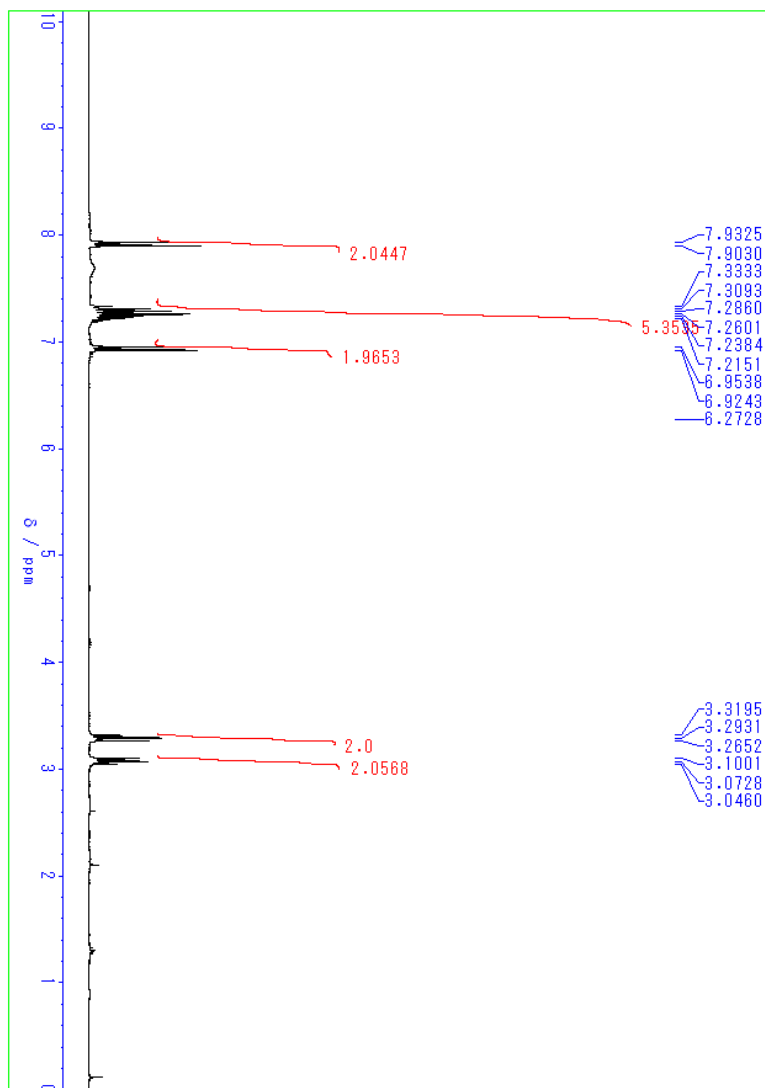


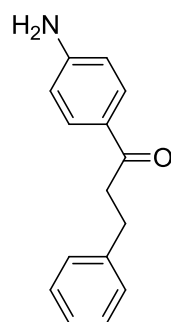
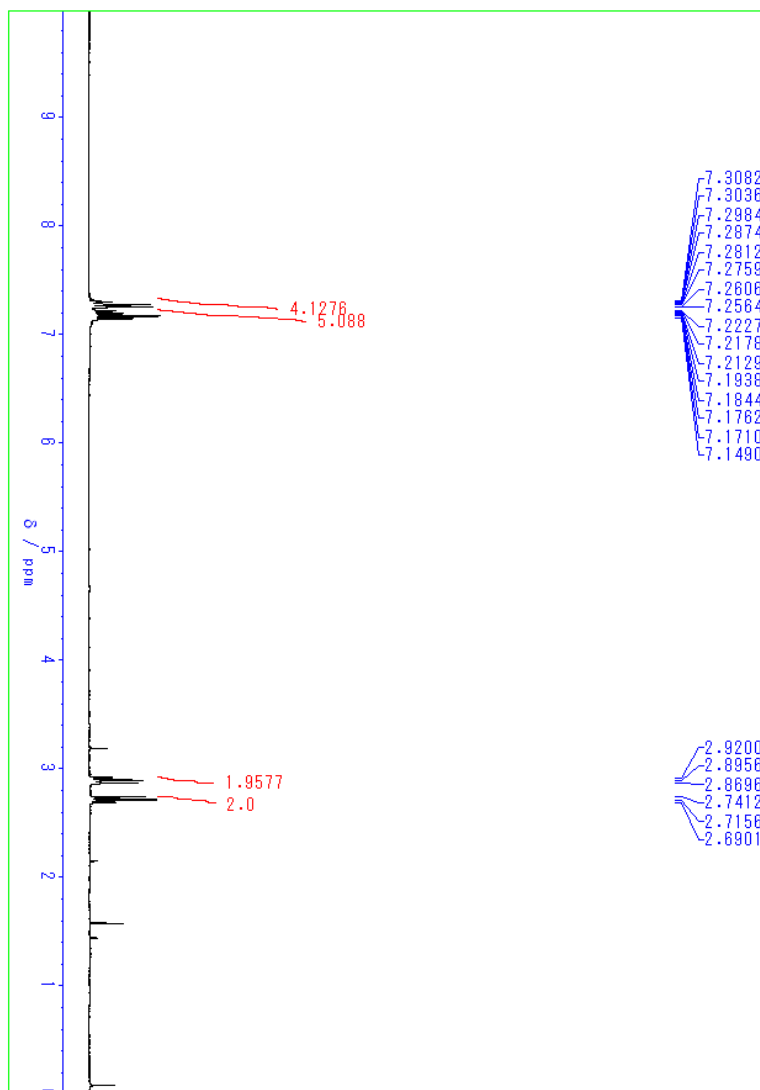


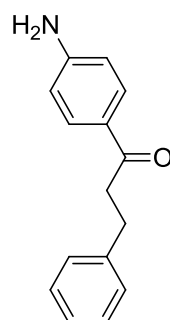
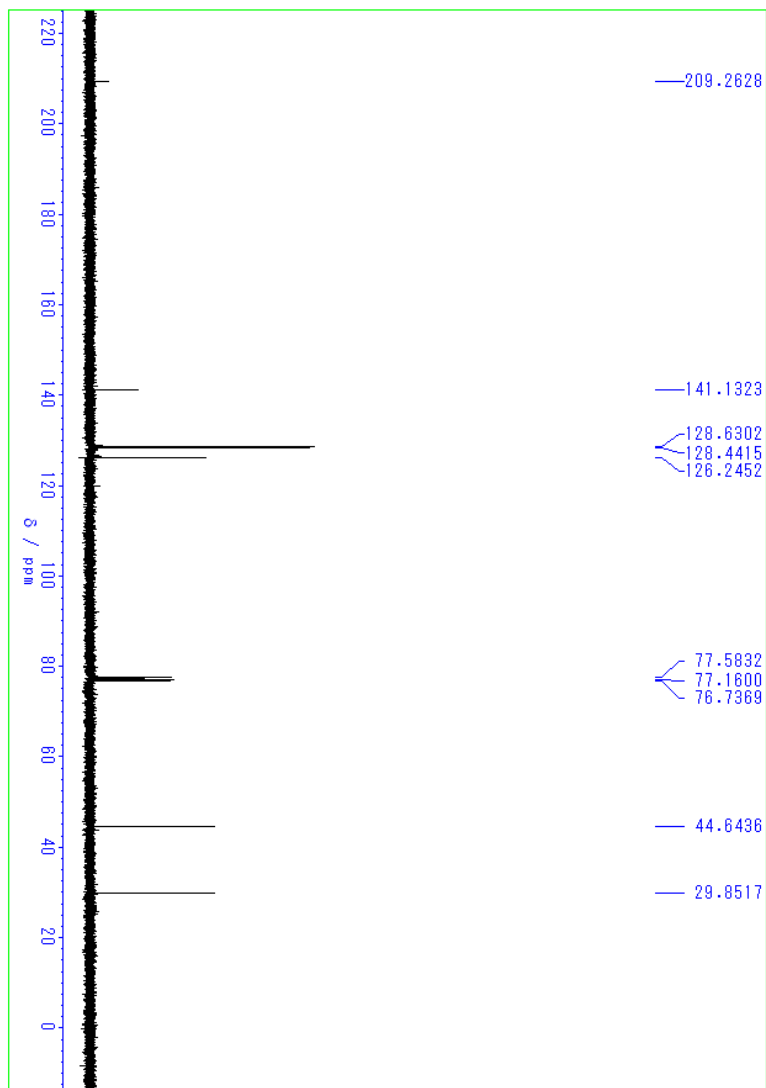


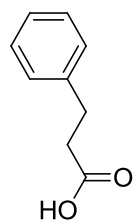
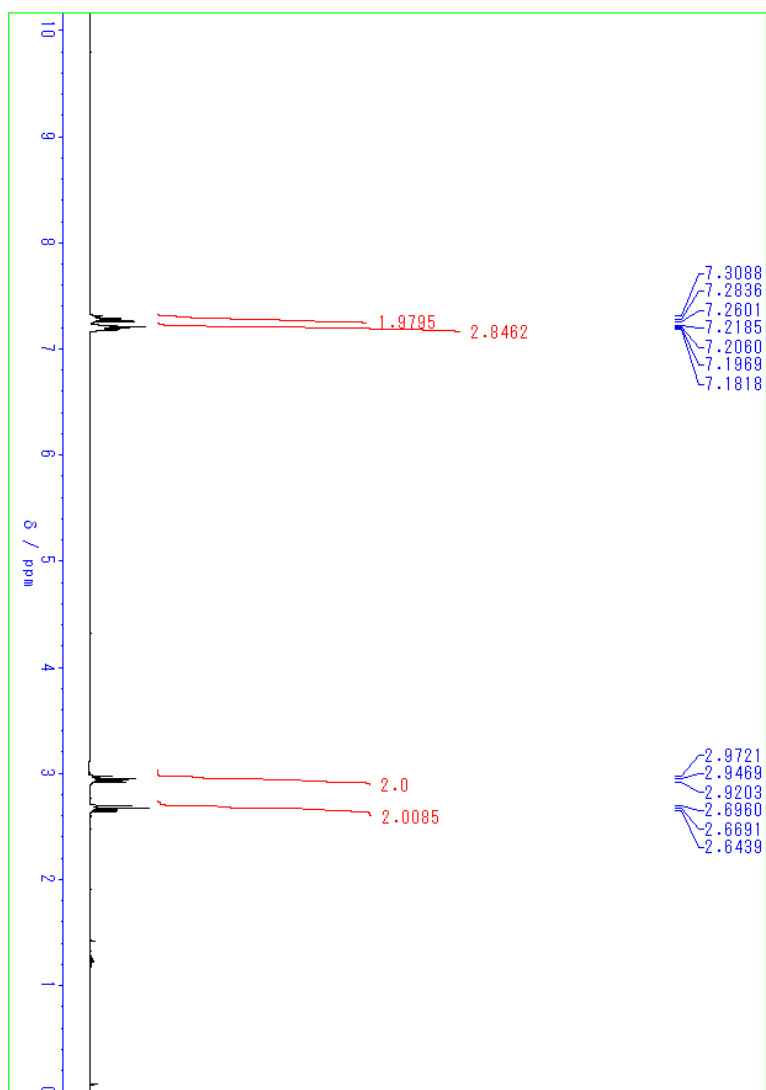


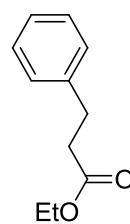
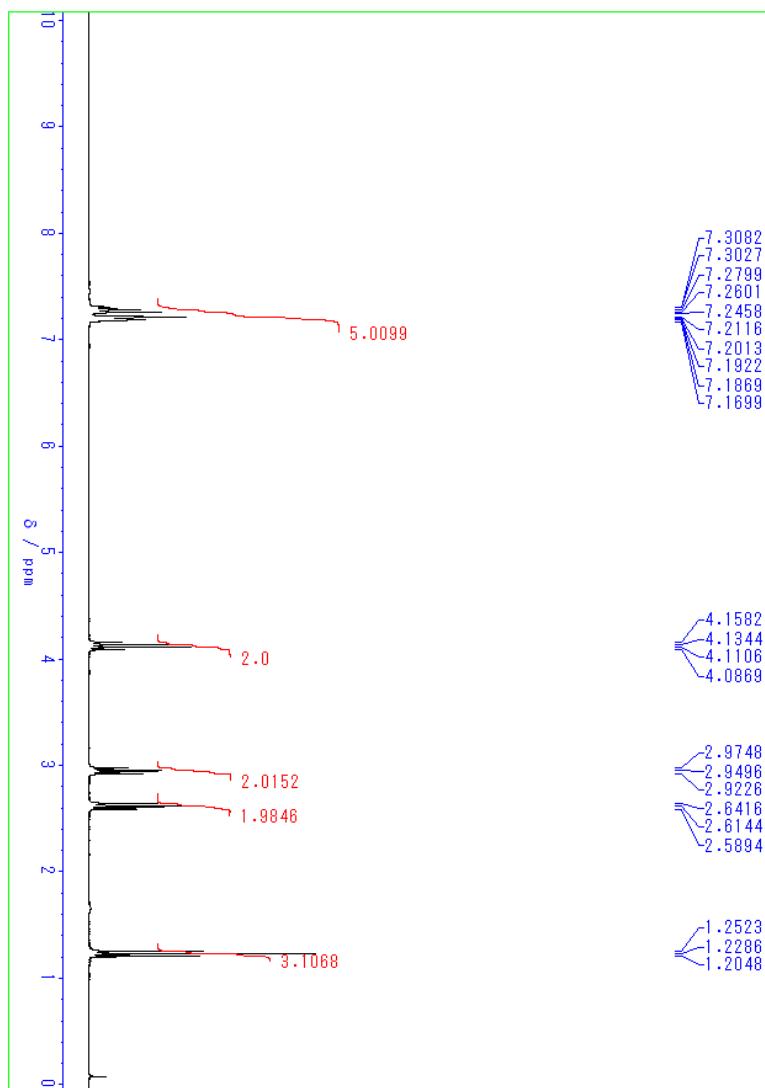


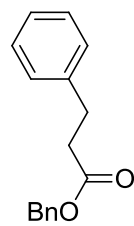
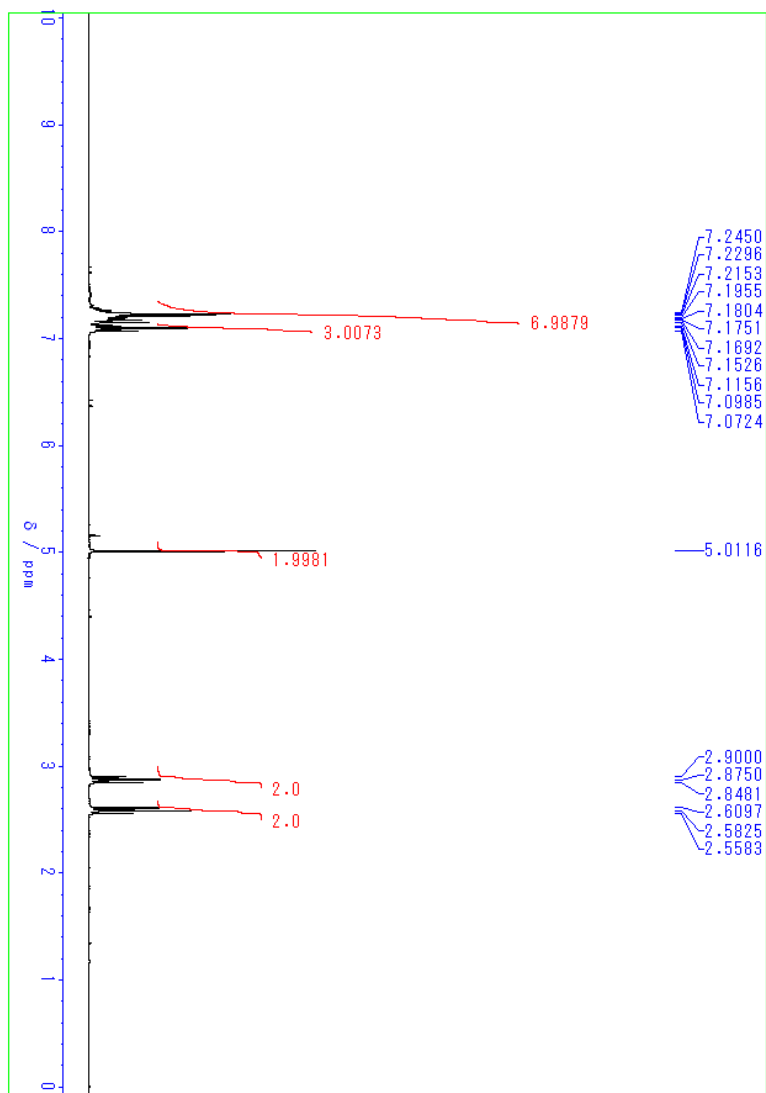


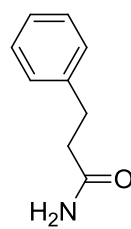
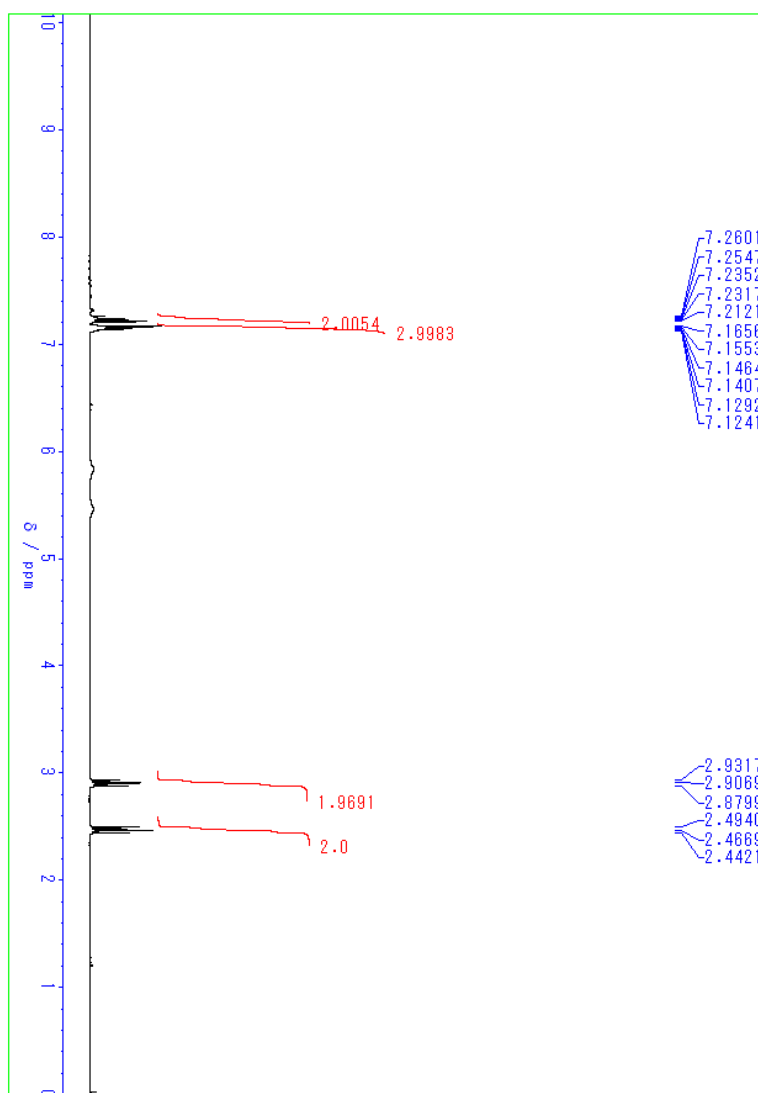


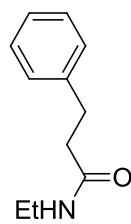
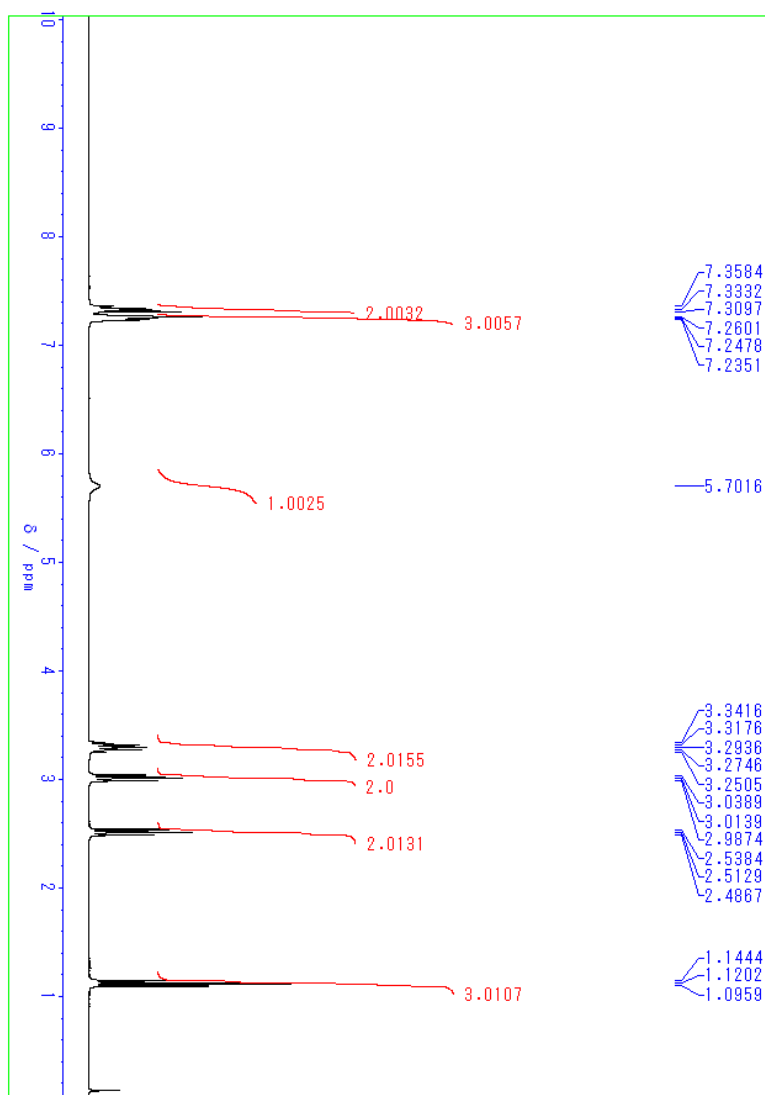


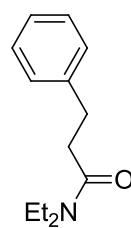
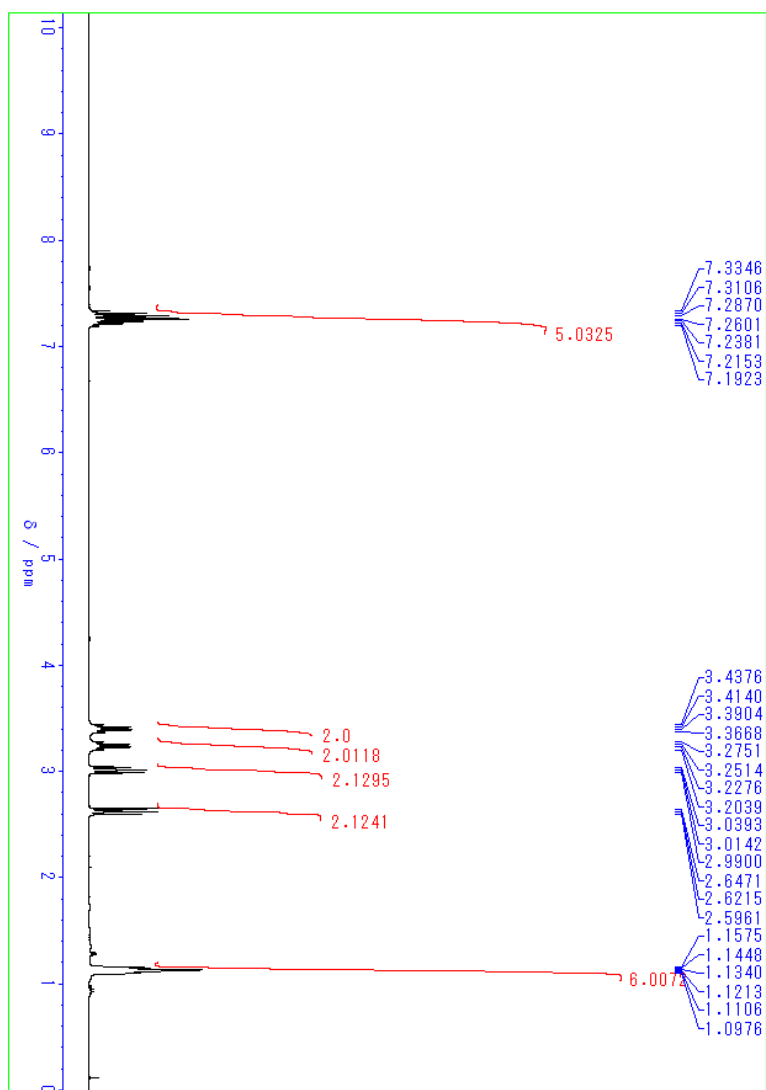


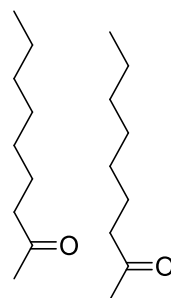
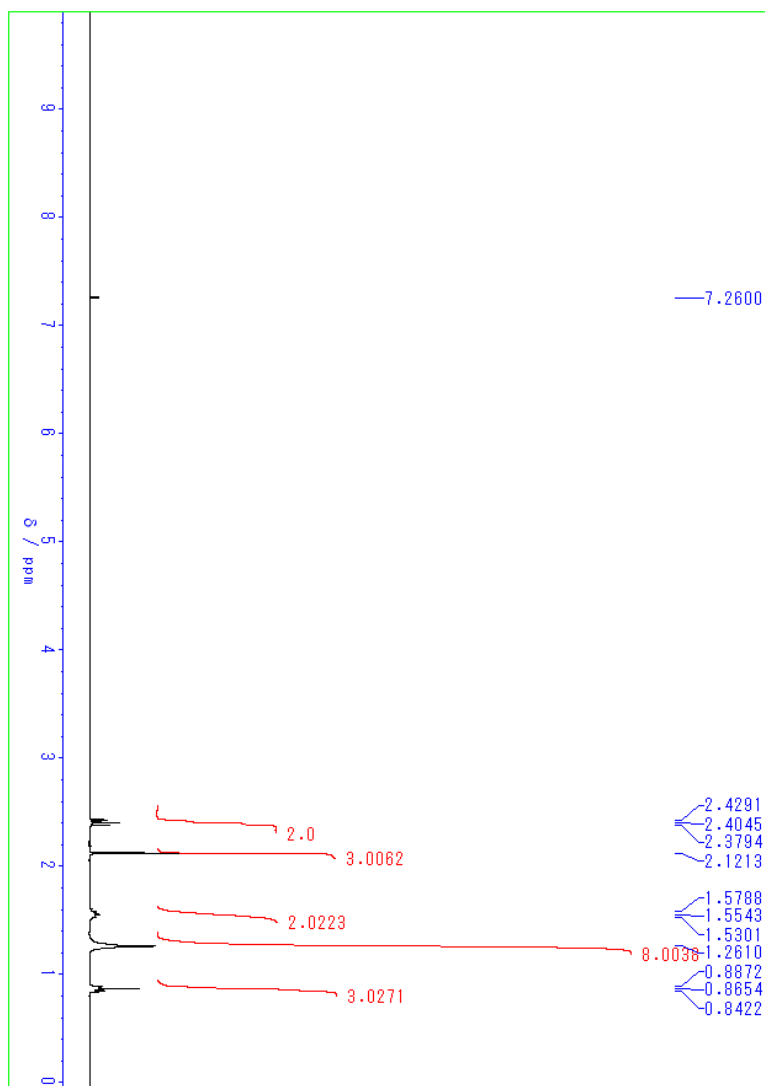


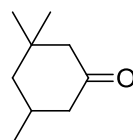
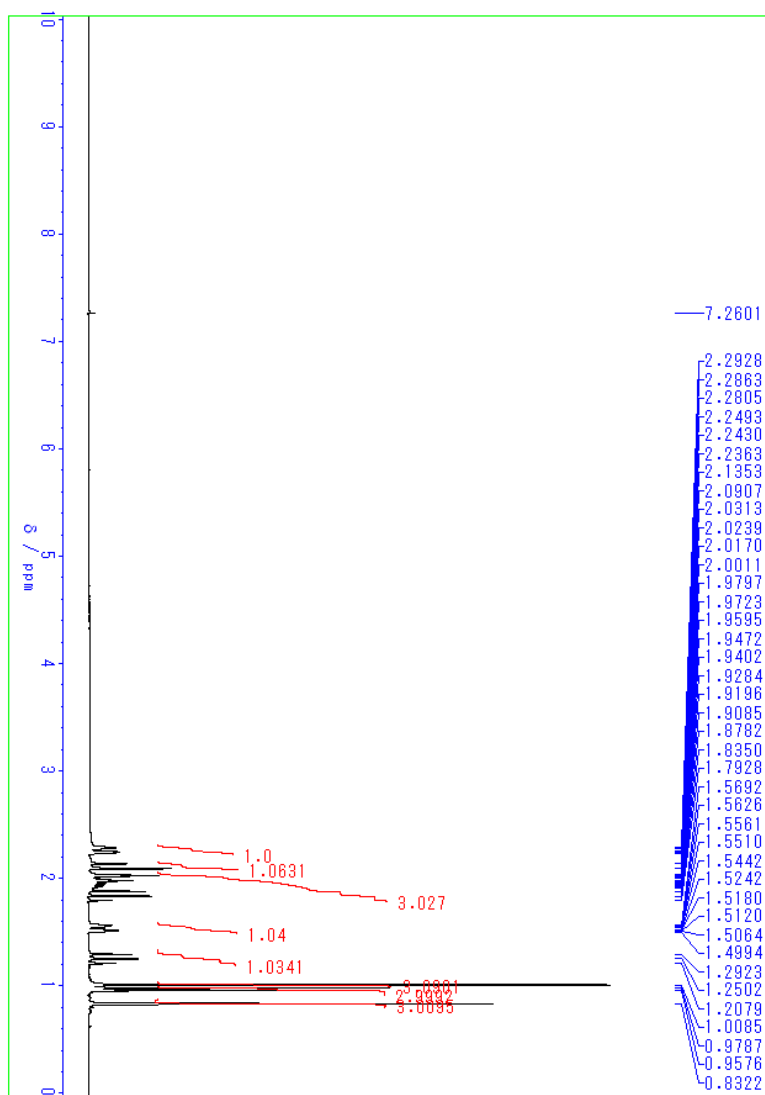


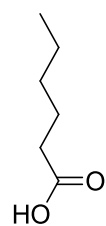
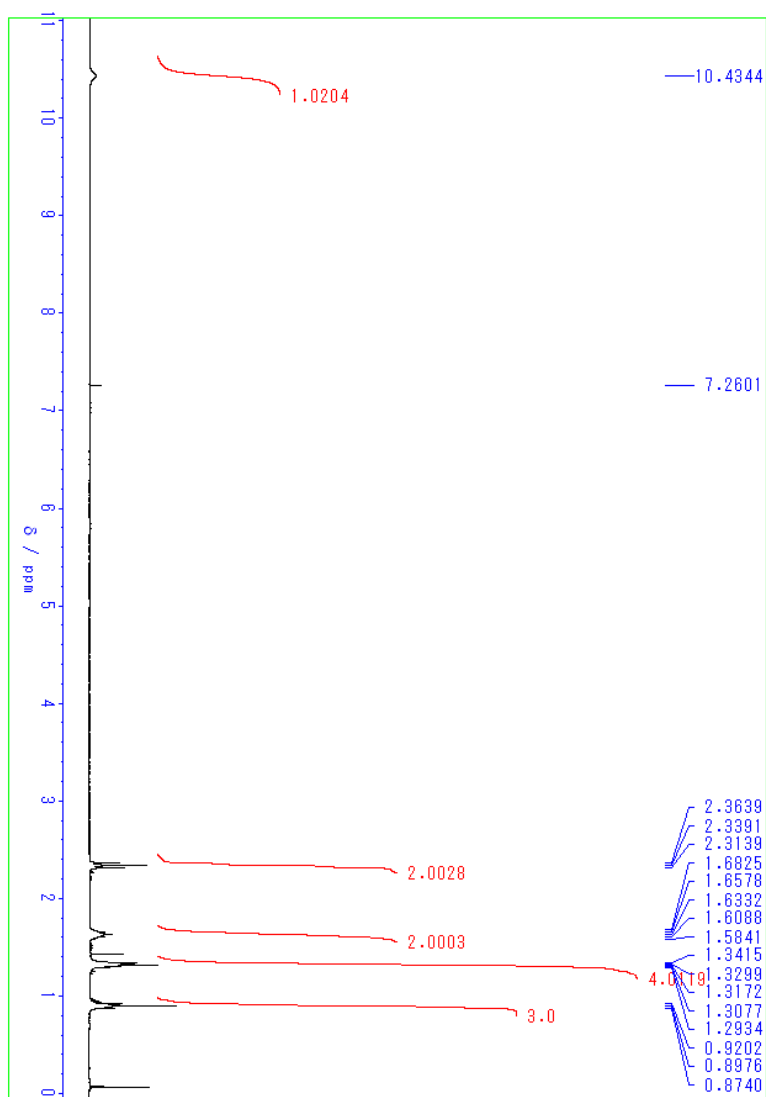


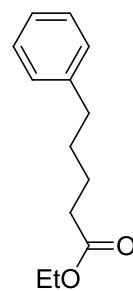
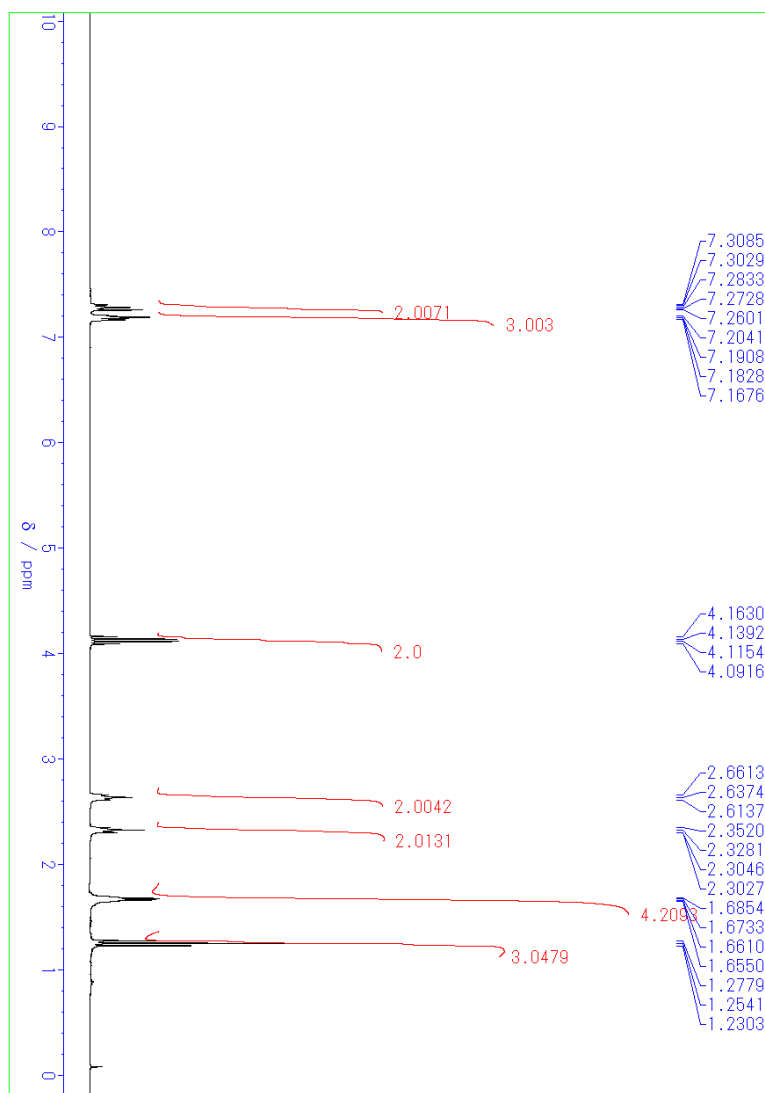


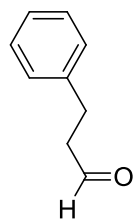
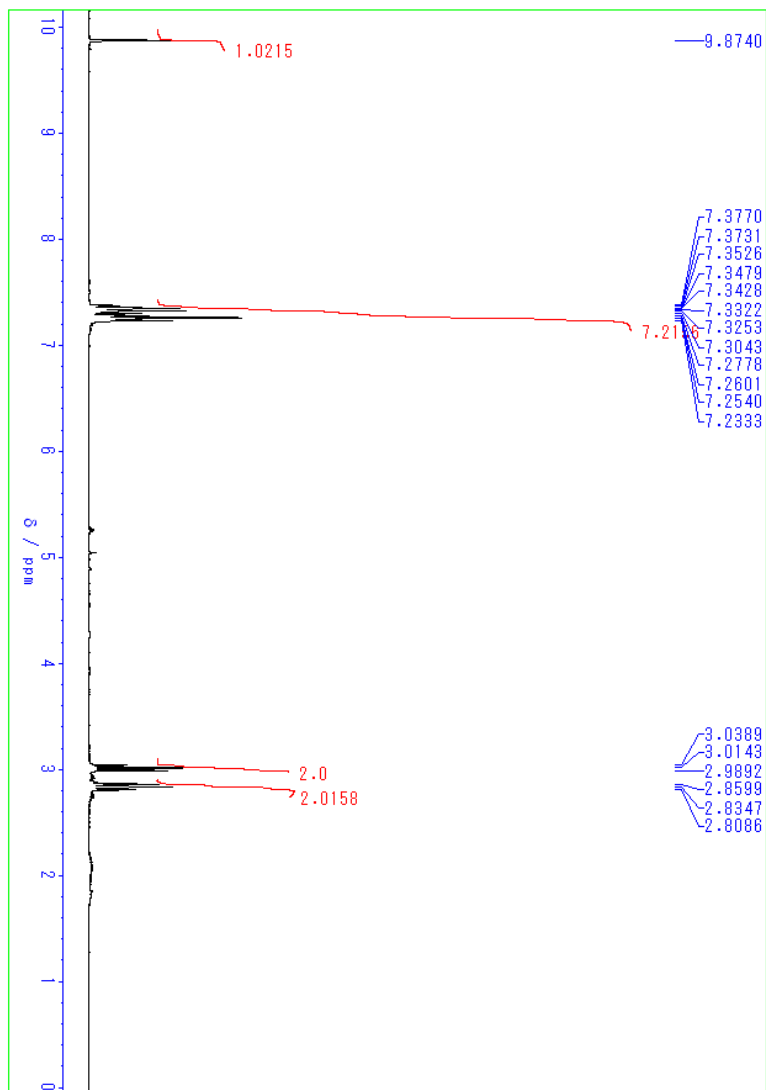


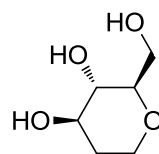
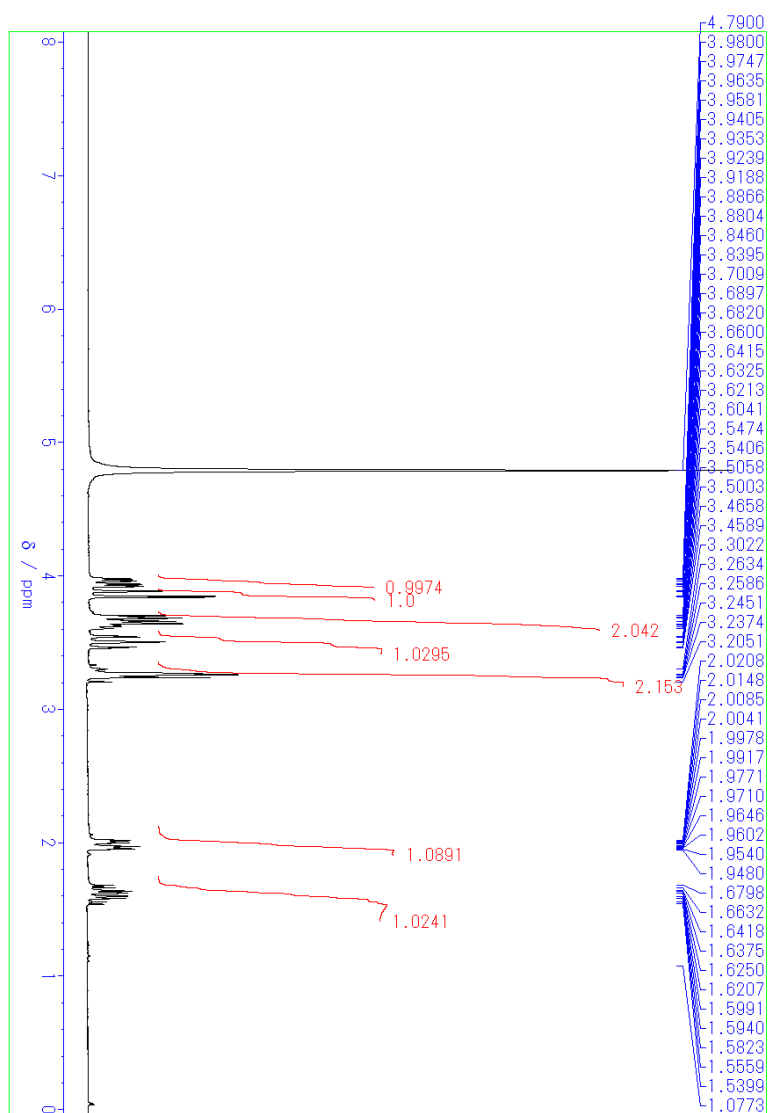


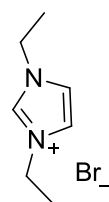
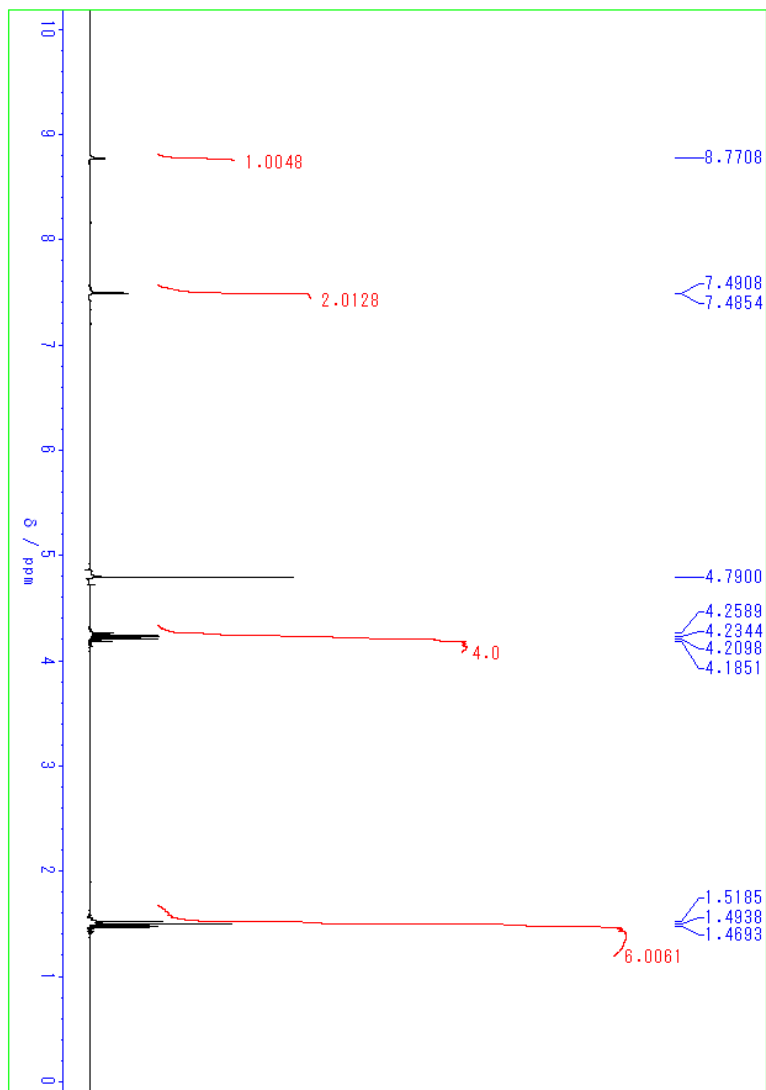


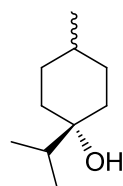
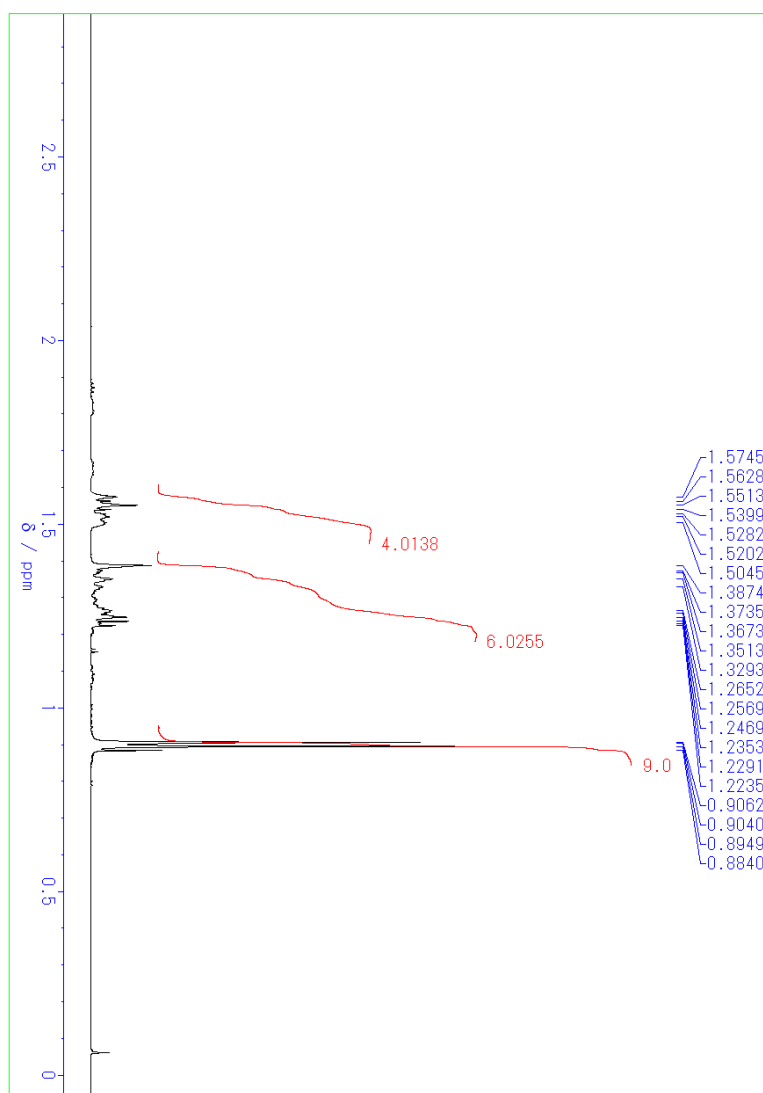


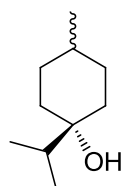
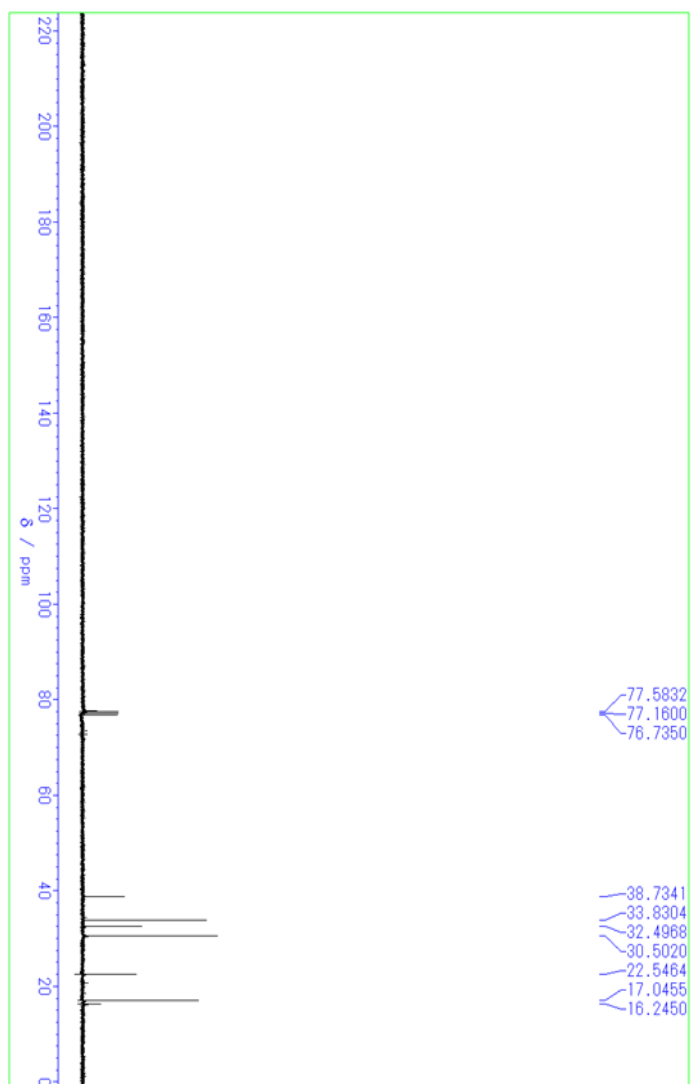












8. Reference

1. A. Wilhelm, L. A. Lopez-Garcia, K. Busschots, W. Fröhner, F. Maurer, S., Boettcher, H. Zhang, J. O. Schulze, R. M. Biondi and M. Engel, *J. Med. Chem.*, 2012, **55**, 9817-9830
2. S. Alcaro, A. Bolasco, R. Cirilli, R. Ferretti, R. Fioravanti and F. Ortuso, *J. Chem. Inf. Model*, 2012, **52**, 649-654
3. W. M. Weber, L. A. Hunsaker, S. F. Abcouwer, L. M. Deck and D. L. V. Jagt, *Bioorg. Med. Chem.*, 2005, **13**, 3811-3820
4. V. Tomar, G. Bhattacharjee, Kamaluddin, S. Rajakumar, K. Srivastava and S. K. Puri, *Eur. J. Med. Chem.*, 2010, **45**, 745-751
5. A. R. Katritzky, S. Zhang, A. Soares and M. Wang, *ARKIVOC*, 2001, **10**, 54-57
6. G. Merey and O. Anac, *Helv. Chim. Acta.*, 2011, **94**, 1053-1054
7. K. Ando and K. Yamada, *Tetrahedron Lett.*, 2010, **51**, 3297-3299
8. M. Teijeira, L. Suárez, G. Gómez, C. Terán and Y. Fall, *Tetrahedron Lett.*, 2005, **46**, 5889-5892
9. C. Zhao, H. Wang, N. Yan, C. Xiao, Z. Mu, P. J. Dyson and Y. Kou, *J. Catal.*, 2007, **250**, 33-40
10. T. Ikawa, H. Sajiki and K. Hirota, *Tetrahedron*, 2005, **61**, 2217
11. Z. Ji, S. Natarajan, N. S. Choon, K. O. Lian and S. K. Yeow, *J. Chem. Res. (S)*, 1994, **3**, 98-99
12. P. Colbon, J. Ruan, M. Purdle and J. Xlao, *Org. Lett.*, 2010, **12**, 3670-3673
13. K. Y. Koltunov, S. Walspurger and J Sommer, *Eur. J. Org. Chem.*, 2004, **19**, 4039-4047
14. S. Hanada, E. Tatsumi, Y. Motoyama and H. Nagashima, *J. Am. Chem. Soc.*, 2009, **131**, 15032-15040
15. M. Kunishima, K. Yamamoto, Y. Watanabe, K. Hioki and S. Tani, *Chem. Commun.*, 2005, 2698-2700
16. A. Arase, M. Hoshi and Y. Masuda, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 209-213
17. M. M. Aghayan, R. Boukherroub, M. Bolourtchian and M. Rahimifard, *J. Organomet. Chem.*, 2007, **692**, 5113-5116
18. A. T. Murr-ray, P. Matton, N. W. G. Fairhurst, M. P. John and D. R. Carbery, *Org. Lett.*, 2012, **14**, 3656-3659
19. A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard and C. W.

- Lehmann, *J. Am. Chem. Soc.*, 2008, **130**, 8773-8787
20. M. K. Kantam, T. Parsharamulu and S. V. Manorama, *J. Mol. Catal. A-Chem.*, 2012, **365**, 1125-119
21. K. Shigetomi, K. Shoji, S. Mitsuhashi and M. Ubukata, *Phytochemistry*, 2010, **71**, 312-324
22. (a) J. L. Hickey, R. A. Ruhayel, P. J. Barard, M. V. Baker, S. J. Berners-Price and A. Filipovska, *J. Am. Chem. Soc.*, 2008, **130**, 12570-12571
23. R. H. Crabtree and M. W. Davis, *J. Org. Chem.*, 1986, **51**, 2655-2661; (b) D. Dauzonne, N. Goasdoue and N. Platzner, *Org. Magn. Reson.*, 1981, **17**, 18-25
24. W. S. Hummers and R. E. Offman, *J. Am. Chem. Soc.*, 1957, **80**, 1339