

Electronic Supplementary Information (ESI)

Copper-Catalyzed Coupling Reaction of Unactivated Secondary Alkyl Iodides with Alkyl Grignard Reagents in the Presence of 1,3-Butadiene as an Effective Additive

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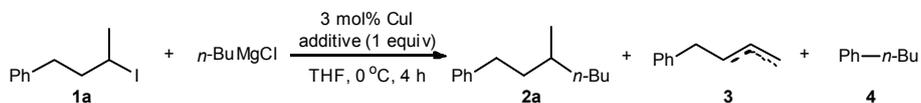
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Additional Data

Condition screening

Table S1. Screening of conditions



Entry	Additive (1 equiv)	2a (%) ^b	3 (%) ^{b,c}	4 (%) ^b
1	1,3-Butadiene	90	1	<1
2	None	56	15	8
3 ^d	1,3-Butadiene	89	1	<1
4	1,3-Butadiene ^e	81	2	2
5	Isoprene	85	2	<1
6	1,3-Pentadiene	74	3	1
7 ^f	2,3-Dimethyl-1,3-butadiene	69	5	2
8	1-Phenyl-1-propyne	69	12	6
9	1,5-Cyclooctadiene	56	15	7
10	2,5-Norbornadiene	57	13	6
11 ^g	1,3-Butadiene	N.R.	–	–
12 ^g	None	N.R.	–	–
13 ^h	1,3-Butadiene	N.D.	2	1

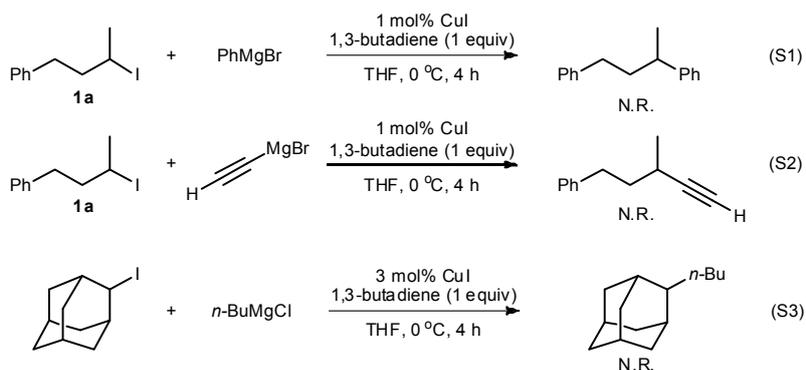
^a To a mixture of **1a** (0.5 mmol), *n*-BuMgCl (0.75 mmol, 0.61 M in THF) was added 1,3-butadiene (0.5 mmol, 11.2 mL) and CuI (0.015 mmol) at -78 °C. The reaction was then stirred at 0 °C. In each case, ca. 9-13% yield of *n*-octane resulted from homocoupling of *n*-BuMgCl was detected as byproduct. ^b GC yield based on **1a** (*n*-decane as internal standard). ^c Combined GC yields of the olefin byproducts from **1a**. ^d 1 mol% CuI. ^e 0.5 equiv. of 1,3-butadiene was used. ^f ca. 10% of **1a** was recovered. ^g No CuI; N.R.: no reaction. ^h Et₂O as solvent; N.D.: not detected; **1a** was recovered.

Additional results on condition screening are shown in Table S1. When a catalytic amount of copper(I) iodide was added to a solution of 4-phenylbutan-2-yl iodide (**1a**), *n*-BuMgCl (1.5 equiv) and 1,3-butadiene (1 equiv) in THF at -78 °C and then stirred at 0 °C for 4 h, the cross-coupled product **2a** was obtained in 90% yield along with a small amount of the elimination products **3** (1%) and the hydrodehalided product **4** (<1%) (Table S1, entry 1). In contrast, the reaction catalyzed by CuI without 1,3-butadiene gave a mixture of **2a** (56%), **3** (15%) and **4** (8%) (entry 2), clearly indicating that the presence of 1,3-butadiene is crucial on improving the yield and selectivity. Decreasing the catalytic CuI from 3 mol% to 1 mol% did not affect the reaction giving a good yield of product (entry 3). However, when the reaction was run with 0.5 equiv of 1,3-butadiene, the yield dropped to 81% (entry 4). We also examined other additives. As shown in Table S1, the use of isoprene gave **2a** in 85% yield (entry 5), however, somewhat lower yields were observed when 2,3-dimethylbuta-1,3-diene or penta-1,3-diene was employed (entries 6 and 7). Although we have reported that an alkyne is effective additive in the Cu-catalyzed coupling reaction of primary alkyl halides,^{11c} the use of 3-phenyl 2-propyne in the present reaction gave a moderate yield of **2a** but with significant amount of byproducts **3** and **4** (entry 8). Neither 1,5-cyclooctadiene nor 2,5-norbornadiene was effective (entries 9 and 10). In addition, the use of other ligands or additives including

TMEDA, PPh₃, NMP and PhCN did not improve the yields nor selectivity, and no reaction took place without a copper catalyst (entry 12). This coupling reaction did not proceed in Et₂O as the solvent resulting in a dark blue mixture, and most of the starting material **1a** was recovered (entry 13).

Additional screening of substrates

It has been extremely reported that secondary alkyl halides couple with aryl Grignard reagents employing Fe^{S1} and Co^{S2} as a catalyst. We thus examined such sp³-sp² cross-coupling reaction though phenyl Grignard reagent retired the present catalyst and **1a** was recovered (eq S1). In addition, sp³-sp coupling also resulted in no reaction (eq S2).^{S3} In the previous report, radical mechanism, namely SET from Fe or Co to secondary alkyl halides to generate alkyl radical intermediates and subsequent recombination with catalyst, was proposed.^{S1,S2} Based on experimental results (see also: eq 1 and Scheme 2), our Cu/butadiene system should proceed through a different mechanism, which is probably S_N2 type mechanism as our previous report.^{11c} No reaction took place when 2-adamantyl iodide was used (eq S3). This result may consistent with proposed mechanism.



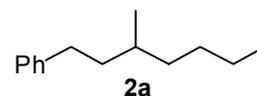
General

^1H NMR and ^{13}C NMR spectra were recorded with a JEOL ECS-400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts were reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a JASCO Corporation FT/IR-4200 instrument. Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. GC analysis was performed on a Shimadzu GC-2014 instrument equipped with a GL Sciences InertCap 5 capillary column. GC yields were determined using *n*-decane as an internal standard. Grignard reagents were purchased from Aldrich Chemical Company or Kanto Chemical Company and used after titration by a method reported by Knochel,^{S4} except for (2-(1,3-dioxolan-2-yl)ethyl) magnesium bromide,^{S5a} pent-4-enyl magnesium bromide^{S5b} and hex-5-enylmagnesium bromide^{S5b} which were prepared from the corresponding alkyl bromides and magnesium in THF. Secondary alkyl iodides were prepared from the corresponding alcohols according to the literature.^{S6}

Experimental Procedures and Analytical Data of Products

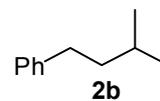
(3-Methylheptyl)benzene (**2a**)^{S7}

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and butylmagnesium chloride (0.75 mmol, $C = 0.61$ M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 77.8 mg of **2a** (82%). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.25 (m, 2H), 7.19-7.14 (m, 3H), 2.68-2.52 (m, 2H), 1.68-1.54 (m, 1H), 1.47-1.12 (m, 8H), 0.93-0.87 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 128.3, 128.2, 125.5, 39.0, 36.6, 33.5, 32.5, 29.2, 23.0, 19.6, 14.2.



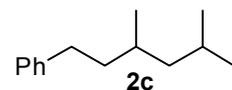
(3-Methylbutyl)benzene (**2b**)^{S8}

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg), methylmagnesium chloride (0.75 mmol, $C = 2.69$ M in THF) and 0.5 mL of THF cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq. Yield of **2b** was determined by GC using *n*-decane as internal standard due to its volatile.



(3,5-Dimethylhexyl)benzene (**2c**)

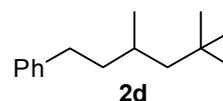
To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and isobutylmagnesium chloride (0.75 mmol, $C = 2.0$ M in THF) and 0.5 mL of THF cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I)



iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 78.5 mg of **2c** (82%). ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.21-7.14 (m, 3H), 2.68-2.51 (m, 2H), 1.70-1.44 (m, 3H), 1.43-1.36 (m, 1H), 1.26-1.14 (m, 1H), 1.06-0.99 (m, 1H), 0.92-0.82 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 128.3, 128.2, 125.5, 46.6, 39.3, 33.4, 30.1, 25.2, 23.4, 22.3, 19.7; IR (neat NaCl, ν/cm⁻¹) 3086, 3063, 3027, 2954, 1939, 1798, 1604, 1496, 1455, 1384, 1366, 1169, 1075, 1031, 969, 911, 744, 697; MS (EI) *m/z* (%) 190 (M⁺, 22), 105 (73), 92 (100); HRMS (EI) *m/z* calcd for C₁₄H₂₂ 190.1722, found 190.1730.

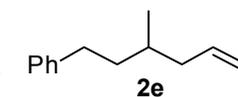
(3,5,5-Trimethylhexyl)benzene (**2d**)^{S9}

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and neopentylmagnesium chloride (0.75 mmol, *C* = 2.0 M in THF) and 0.5 mL of THF cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 80.2 mg of **2d** (79%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.23 (m, 2H), 7.19-7.14 (m, 3H), 2.66-2.52 (m, 2H), 1.64-1.41 (m, 3H), 1.30-1.26 (m, 1H), 1.11-1.06 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 143.1, 128.3, 128.2, 125.5, 51.2, 41.5, 33.7, 31.1, 30.0, 29.1, 22.6; MS (EI) *m/z* (%) 190 (M⁺, 22), 105 (73), 92 (100); HRMS (EI) *m/z* calcd for C₁₄H₂₂ 190.1722, found 190.1730.



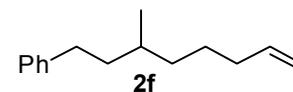
(3-Methylhex-5-enyl)benzene (**2e**)^{S10}

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and allylmagnesium chloride (0.75 mmol, *C* = 0.66 M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 76.6 mg of **2e** (88%). ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.26 (m, 2H), 7.21-7.18 (m, 3H), 5.86-5.76 (m, 1H), 5.05-5.01 (m, 2H), 2.73-2.56 (m, 2H), 2.18-2.12 (m, 1H), 2.11-1.96 (m, 1H), 1.73-1.42 (m, 3H), 0.97 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 137.4, 128.3, 128.2, 125.6, 115.7, 41.2, 38.4, 33.4, 32.4, 19.3.



(3-Methyloct-7-enyl)benzene (**2f**)

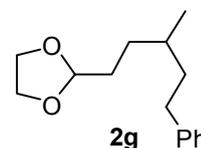
To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and pent-4-enylmagnesium bromide (0.75 mmol, *C* = 0.66 M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas)



through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 86.8 mg of **2f** (86%). ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.21-7.14 (m, 3H), 5.86-5.75 (m, 1H), 5.01-4.92 (m, 1H), 2.68-2.52 (m, 2H), 2.05-2.00 (m, 2H), 1.68-1.58 (m, 1H), 1.50-1.31 (m, 5H), 1.20-1.13 (m, 1H), 0.93 (d, *J* = 6.0 Hz, 6H); ¹³C NMR (100 Hz, CDCl₃) δ 143.1, 139.1, 128.3, 128.2, 125.5, 114.2, 38.9, 36.3, 34.1, 33.4, 32.3, 26.3, 19.6; IR (neat NaCl, ν/cm⁻¹) 3063, 3026 2927, 1940, 1820, 1802, 1640, 1603, 1496, 1455, 1377, 1065, 1031, 995, 909, 744, 697, 638, 516; MS (EI) *m/z* (%) 202 (M⁺, 18), 131 (44), 91 (100); HRMS (EI) *m/z* calcd for C₁₅H₂₂ 202.1722, found 202.1726.

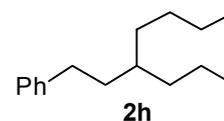
2-(3-Methyl-5-phenylpentyl)-1,3-dioxolane (**2g**)

To a mixture of (3-iodobutyl)benzene (0.5 mmol, 130.0 mg) and (2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide (1.0 mmol, *C* = 1.0 M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (3 mol %, 3.0 mg), the system was closed, and the reaction was stirred at 0 °C for 4 h and 25 °C for another 20 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 70.9 mg of **2g** (61%). 19.2 mg of the starting material (3-iodobutyl)benzene was recovered. ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.25 (m, 2H), 7.18-7.14 (m, 3H), 4.83 (t, *J* = 4.6 Hz, 1H), 3.98-3.82 (m, 4H), 2.69-2.53 (m, 2H), 1.75-1.26 (m, 8H), 0.95 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 128.3, 128.2, 125.5, 104.9, 64.82, 64.8, 38.7, 33.3, 32.3, 31.4, 30.8, 19.4; IR (neat NaCl, ν/cm⁻¹) 3061, 3026 2952, 2876, 1728, 1604, 1496, 1455, 1409, 1378, 1211, 1140, 1033, 973, 944, 876, 746, 699, 578, 514; MS (CI) *m/z* (%) 235 (M+H⁺, 100); HRMS (CI) *m/z* calcd for C₁₅H₂₃O₂ (M+H) 235.1698, found 235.1695.



(3-Propylheptyl)benzene (**2h**)

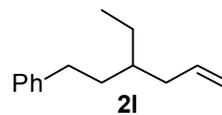
To a mixture of (3-iodohexyl)benzene (0.5 mmol, 114.1 mg) and butylmagnesium chloride (0.75 mmol, *C* = 0.60 M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL×3). The combined organic layers were dried over Na₂SO₄ and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 98.2 mg of **2h** (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.23 (m, 2H), 7.19-7.14 (m, 3H), 2.59-2.55 (m, 2H), 1.59-1.53 (m, 2H), 1.35-1.26 (m, 11H), 0.90 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 128.3, 128.2, 125.5, 37.1, 35.7, 33.2, 33.1, 28.9, 23.1, 14.2; IR (neat NaCl, ν/cm⁻¹) 3063, 3027, 2925, 2858, 1604, 1496, 1455, 1378, 1031, 902, 744,



697; MS (EI) m/z (%) 218 (M^+ , 12), 91 (100); HRMS (EI) m/z calcd for $C_{16}H_{26}$ 218.2035, found 218.2032.

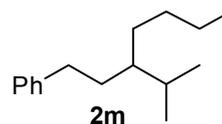
(3-Ethylhex-5-enyl)benzene (**2l**)^{S11}

To a mixture of (3-iodohex-5-enyl)benzene (0.5 mmol, 143.1 mg) and ethylmagnesium bromide (0.75 mmol, $C = 0.56$ M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1.0 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 65.8 mg of **2l** (70%). 1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 5.83-5.73 (m, 1H), 5.04-4.99 (m, 1H), 2.61-2.57 (m, 2H), 2.12-2.05 (m, 2H), 1.60-1.54 (m, 2H), 1.42-1.32 (m, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.3, 128.3, 128.2, 125.6, 115.7, 38.5, 37.5, 34.9, 33.1, 25.6, 10.8.



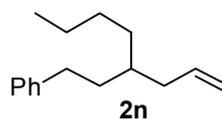
(3-Isopropylheptyl)benzene (**2m**)

To a mixture of (3-iodo-4-methylpentyl)benzene (0.35 mmol, 100.8 mg) and butylmagnesium chloride (0.52 mmol, $C = 0.60$ M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 8.0 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (3 mol %, 2.1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 6 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 60.4 mg of **2m** (80%). 1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 2.65-2.51 (m, 2H), 1.80-1.72 (m, 1H), 1.64-1.55 (m, 1H), 1.52-1.42 (m, 1H), 1.34-1.14 (m, 7H), 0.90 (t, $J = 6.2$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.4, 128.3, 128.2, 125.5, 43.4, 34.2, 32.7, 30.1, 29.9, 29.1, 23.1, 19.2, 19.1; IR (neat $NaCl$, ν/cm^{-1}) 3087, 3063, 3027, 2963, 2927, 2866, 1938, 1867, 1796, 1604, 1496, 1455, 1385, 1367, 1030, 968, 909, 747, 697, 588; MS (EI) m/z (%) 218 (M^+ , 12), 92 (100); HRMS (EI) m/z calcd for $C_{16}H_{26}$ 218.2135, found 218.2133.



(3-Allylheptyl)benzene (**2n**)

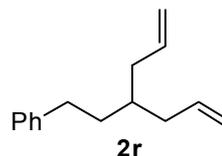
To a mixture of (3-iodohex-5-enyl)benzene (0.5 mmol, 143.1 mg) and butylmagnesium chloride (0.75 mmol, $C = 0.60$ M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 105.8 mg of **2n** (89%). 1H NMR (400 MHz,



CDCl_3) δ 7.29-7.24 (m, 2H), 7.18-7.15 (m, 3H), 5.83-5.73 (m, 1H), 5.05-4.99 (m, 1H), 2.61-2.57 (m, 2H), 2.11-2.08 (m, 2H), 1.60-1.54 (m, 2H), 1.49-1.43 (m, 1H), 1.34-1.28 (m, 6H), 0.89 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 137.3, 128.3, 128.2, 125.6, 115.8, 37.9, 37.0, 35.3, 33.1, 32.9, 28.9, 23.0, 14.1; IR (neat NaCl, ν/cm^{-1}) 3063, 3026, 2925, 2857, 1939, 1821, 1638, 1603, 1496, 1455, 1378, 1031, 994, 910, 745, 698, 575, 512; MS (EI) m/z (%) 216 (M^+ , 7), 104 (23), 91 (100); HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{24}$ 216.1878, found 216.1883.

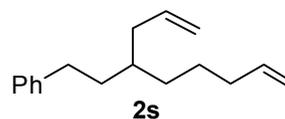
(3-Allylhex-5-enyl)benzene (2r)

To a mixture of (3-iodohex-5-enyl)benzene (0.5 mmol, 143.1 mg) and allylmagnesium chloride (0.75 mmol, $C = 0.65$ M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 86.0 mg of **2s** (86%). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.25 (m, 2H), 7.18-7.16 (m, 3H), 5.83-5.73 (m, 2H), 5.05-5.01 (m, 4H), 2.62 (t, $J = 7.3$ Hz, 3H), 2.12-2.09 (m, 4H), 1.62-1.55 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 136.9, 128.32, 128.27, 125.6, 116.2, 37.6, 36.9, 34.9, 33.0; IR (neat NaCl, ν/cm^{-1}) 3074, 3027, 3001, 2975, 2919, 2859, 1941, 1826, 1639, 1604, 1496, 1454, 1415, 1349, 1029, 994, 911, 745; MS (EI) m/z (%) 200 (M^+ , 2), 117 (26), 104 (15), 91 (100); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{20}$ 200.1565, found 200.1567.



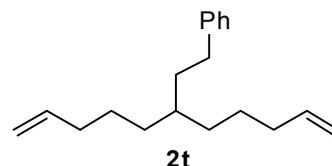
(3-Allyloct-7-enyl)benzene (2s)

To a mixture of (3-iodooct-7-enyl)benzene (0.5 mmol, 157.1 mg) and allylmagnesium chloride (0.75 mmol, $C = 0.65$ M in THF) cooled to -78 °C, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to 0 °C and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 91.2 mg of **2t** (80%). ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.27 (m, 3H), 7.22-7.19 (m, 3H), 5.89-5.76 (m, 2H), 5.01-4.96 (m, 4H), 2.65-2.61 (m, 2H), 2.14-2.04 (m, 4H), 1.65-1.33 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 139.0, 137.1, 128.31, 128.26, 125.6, 115.9, 114.3, 37.9, 36.9, 35.3, 34.1, 33.0, 32.7, 25.9; IR (neat NaCl, ν/cm^{-1}) 3075, 3027, 2976, 2926, 2858, 1940, 1822, 1639, 1604, 1496, 1455, 1415, 1361, 1031, 993, 910, 745, 698; MS (EI) m/z (%) 228 (M^+ , 4), 91 (100); HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{24}$ 228.1878, found 228.1879.



(3-(Pent-4-enyl)oct-7-enyl)benzene (2t)

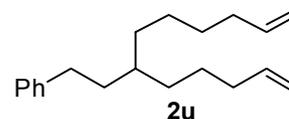
To a mixture of (3-iodooct-7-enyl)benzene (0.5 mmol, 157.1 mg) and pent-4-enylmagnesium bromide (1.0 mmol, $C =$



0.66 M in THF) cooled to $-78\text{ }^{\circ}\text{C}$, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 103.8 mg of **2t** (81%). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.26 (m, 3H), 7.19-7.15 (m, 3H), 5.87-5.77 (m, 2H), 5.02-4.93 (m, 4H), 2.58 (t, $J = 8.2$ Hz, 2H), 2.06-2.01 (m, 4H), 1.59-1.54 (m, 2H), 1.40-1.31 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 139.1, 128.3, 128.2, 125.5, 114.3, 36.9, 35.6, 34.2, 33.1, 32.9, 25.9; IR (neat NaCl, ν/cm^{-1}) 3076, 3026, 2975, 2927, 2856, 1939, 1820, 1640, 1604, 1496, 1455, 1415, 1369, 1031, 992, 909, 745, 698, 638; MS (EI) m/z (%) 256 (M^+ , 7), 185 (17), 91 (100); HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{28}$ 256.2191, found 256.2197.

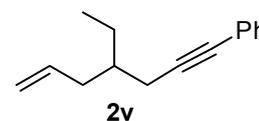
(3-(Pent-4-enyl)non-8-enyl)benzene (**2u**)

To a mixture of (3-iodooct-7-enyl)benzene (1.0 mmol, 314.2 mg) and hex-5-enylmagnesium bromide (2 mmol, $C = 0.66$ M in THF) cooled to $-78\text{ }^{\circ}\text{C}$, was introduced 1 equiv. of 1,3-butadiene (1 mmol, 22.4 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 2.0 mg), the system was closed, and the reaction was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 6 h. The reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 195.8 mg of **2u** (73%). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.24 (m, 3H), 7.18-7.15 (m, 3H), 5.86-5.76 (m, 2H), 5.02-4.93 (m, 4H), 2.59-2.55 (m, 2H), 2.08-2.00 (m, 4H), 1.59-1.53 (m, 2H), 1.40-1.30 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 139.1, 128.3, 128.2, 125.5, 114.3, 114.2, 37.0, 35.6, 34.2, 33.8, 33.2, 33.1, 32.9, 29.3, 26.0, 25.9; IR (neat NaCl, ν/cm^{-1}) 3076, 3026, 2976, 2927, 2857, 1940, 1821, 1640, 1604, 1496, 1455, 1415, 1369, 1031, 993, 909, 745, 698, 641; MS (EI) m/z (%) 270 (M^+ , 10), 91 (100); HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{30}$ 270.2348, found 270.2349.



(4-Ethylhept-6-en-1-ynyl)benzene (**2v**)

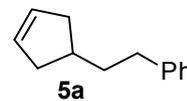
To a mixture of (4-iodohex-1-ynyl)benzene (0.5 mmol, 142.1 mg) and allylmagnesium chloride (0.75 mmol, $C = 0.66$ M in THF) cooled to $-78\text{ }^{\circ}\text{C}$, was introduced 1 equiv. of 1,3-butadiene (0.5 mmol, 11.2 mL as gas) through a septum using a syringe. After adding a catalytic amount of copper(I) iodide (1 mol %, 1 mg), the system was closed, and the reaction was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 4 h. After completion as monitored by GC analysis, the reaction was quenched by 1 M HCl aq., and the product was extracted with ether (10 mL \times 3). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 55.6 mg of **2v** (56%). ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.39 (m, 2H), 7.29-7.25 (m, 3H), 5.86-5.75 (m, 1H), 5.10-5.03 (m, 2H), 2.40 (d, $J = 6.0$ Hz, 2H), 2.20 (t, $J = 6.9$ Hz, 2H), 1.67-1.58 (m, 1H), 1.53-1.43 (m, 2H), 0.94 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.7, 131.5, 128.1, 127.4, 124.1, 116.4, 88.7, 81.6, 38.9, 37.5, 25.8, 22.9, 11.3; IR (neat



NaCl, ν/cm^{-1}) 3019, 2966, 2924, 2400, 1711, 1490, 1428, 1363, 1216, 928, 956, 670; MS (EI) m/z (%) 198 (M^+ , 15), 169 (83), 142 (68), 115 (100); HRMS (EI) m/z calcd for $C_{15}H_{18}$ 198.1409, found 198.1410.

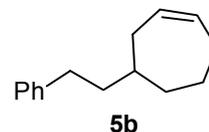
(2-(Cyclopent-3-enyl)ethyl)benzene (5a)^{S12}

To a solution of (3-allylhex-5-enyl)benzene (0.35 mmol, 70.0 mg) in 1 mL of CH_2Cl_2 , was added the Grubbs 1st catalyst (5 mol%, 14.3 mg) under N_2 . After the reaction was stirred at 40 °C for 24 h, the mixture was concentrated under reduced pressure. Purification by silica gel column chromatography with hexane afforded 55.4 mg of **5a** (92%). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 5.67 (s, 2H), 2.63 (t, $J = 7.8$ Hz, 2H), 2.53-2.48 (m, 2H), 2.31-2.20 (m, 1H), 2.05-1.99 (m, 2H), 1.75-1.69 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 129.9, 128.4, 128.2, 125.6, 38.9, 38.4, 37.1, 34.7.



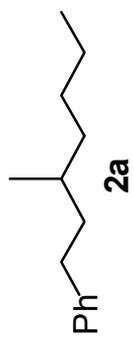
4-Phenethylcyclohept-1-ene (5b)

Following a similar procedure as described above from **2s** (0.41 mmol, 92.5 mg) afforded 70.6 mg of **5b** (87%). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.25 (m, 2H), 7.18-7.15 (m, 3H), 5.84-5.71 (m, 2H), 2.65-2.59 (m, 2H), 2.21-1.93 (m, 4H), 1.82-1.15 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 132.7, 130.4, 128.3, 128.2, 125.5, 38.8, 38.0, 36.9, 34.4, 33.6, 28.8, 25.5. IR (neat NaCl, ν/cm^{-1}): 3085, 3062, 3022, 2918, 1940, 1865, 1799, 1653, 1604, 1496, 1453, 1348, 1280, 1178, 1053, 1117, 1078, 1031, 903, 835, 748, 698, 639, 573; MS (EI) m/z (%) 200 (M^+ , 65), 129 (13), 104 (100), 91 (88), 67 (29); HRMS (EI) m/z calcd for $C_{15}H_{20}$ 200.1565, found 200.1571.

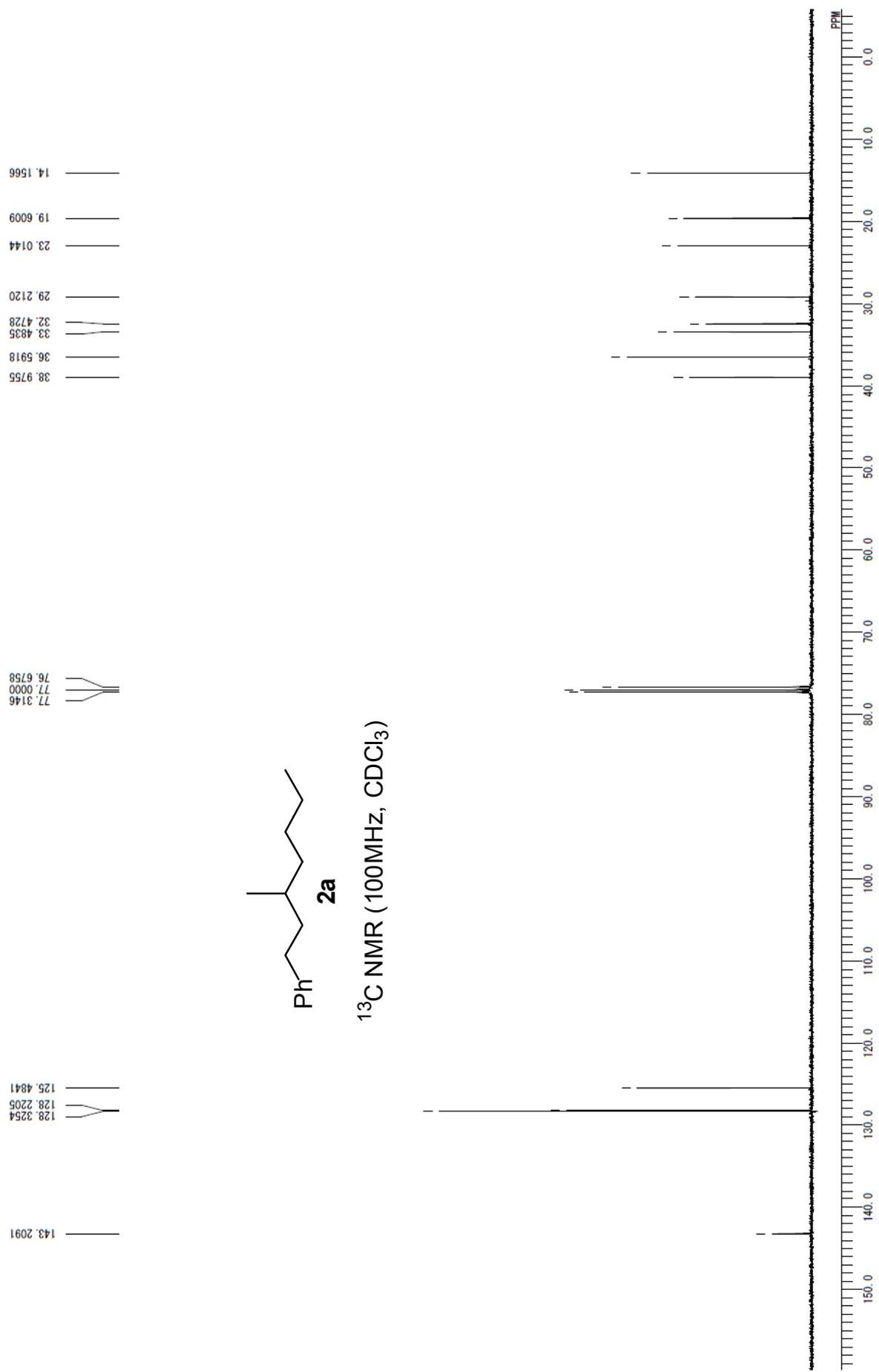


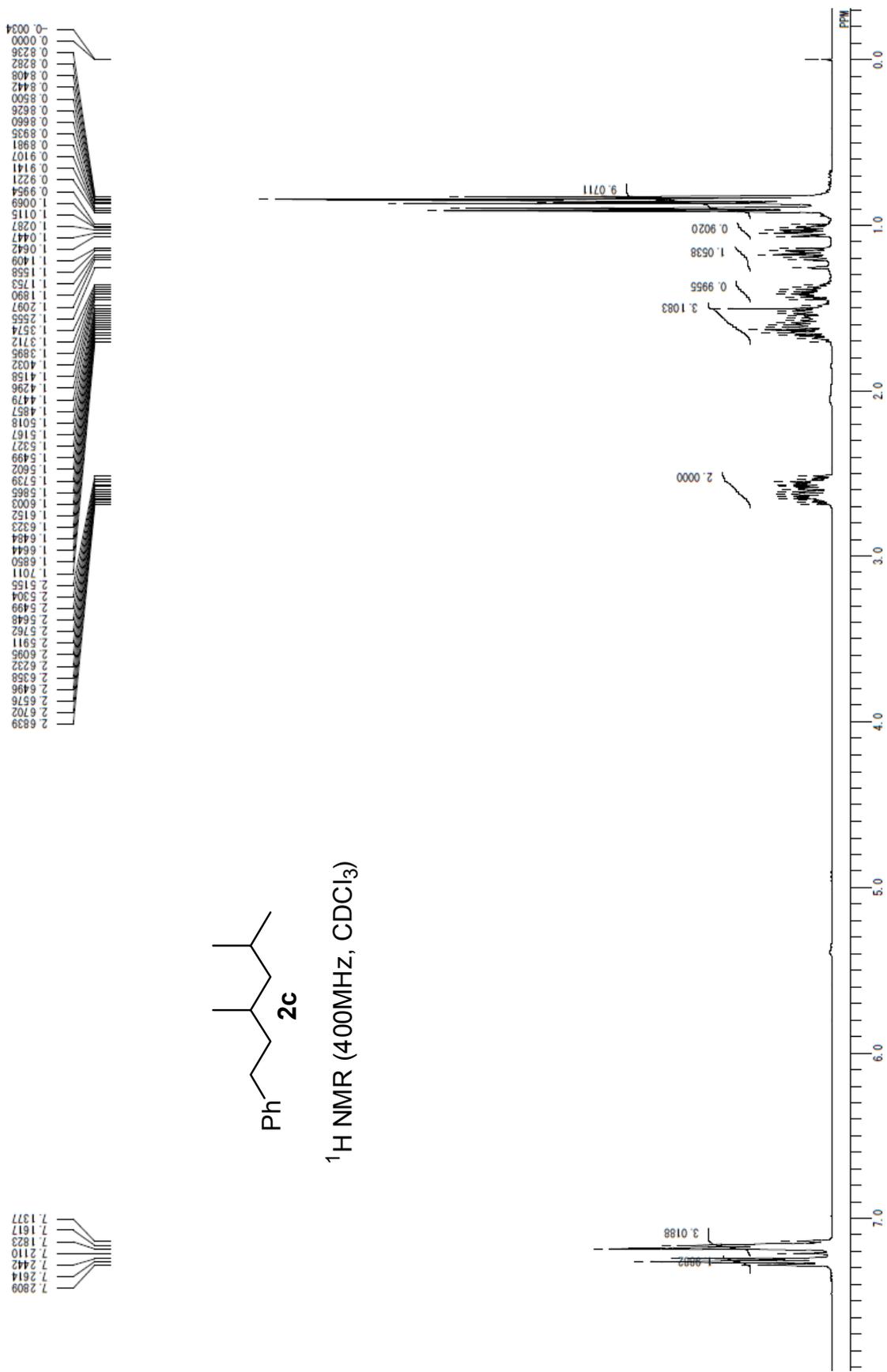
References

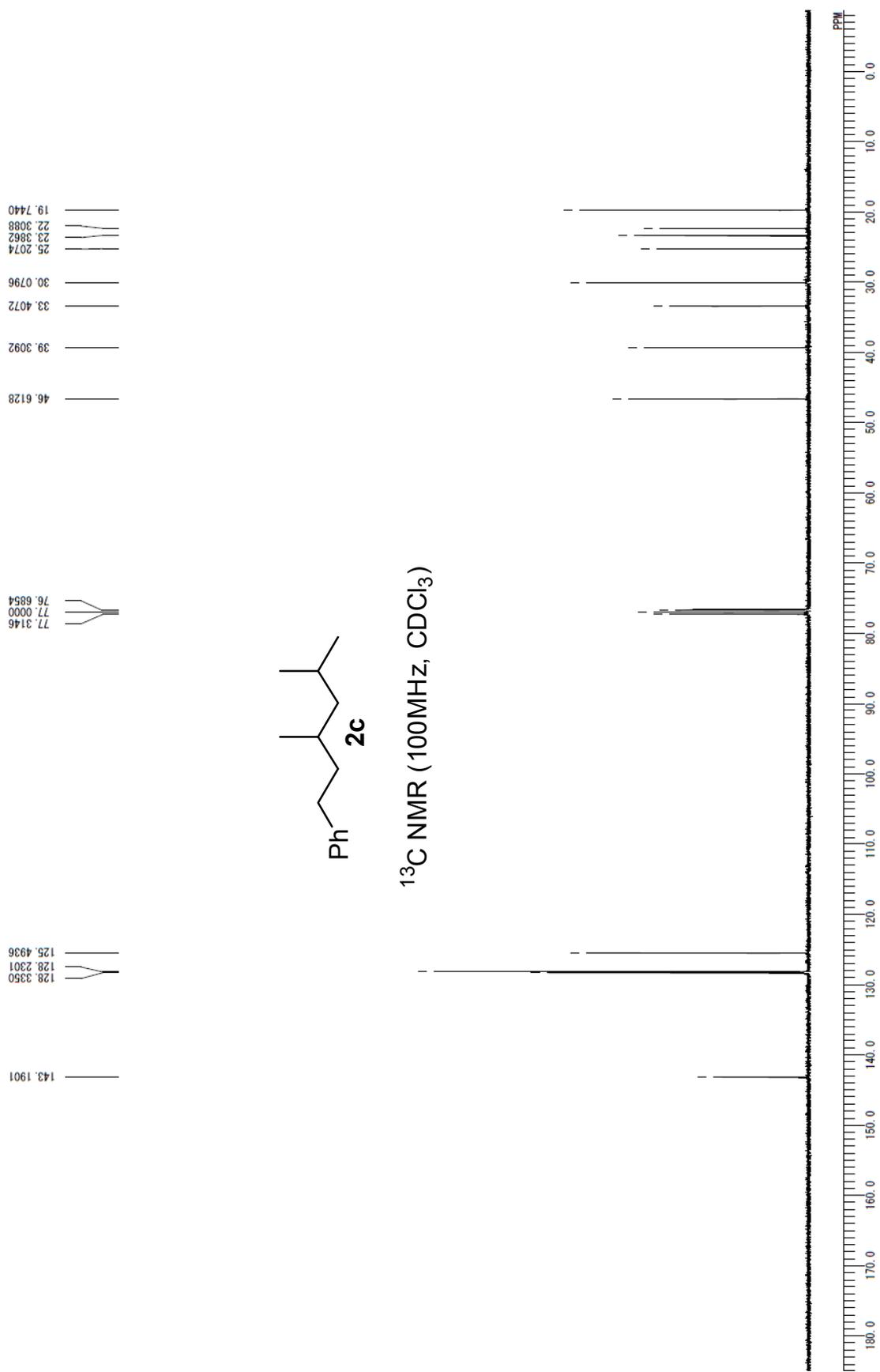
- S1 Cross-coupling of unactivated secondary alkyl halides with aryl Grignard reagents has been well established, for reviews, see: (a) W. M. Czaplik, M. Mayer, J. Cvengroš and A. J. von Wangelin, *ChemSusChem*, 2009, **2**, 396; (b) E. Nakamura and N. Yoshikai, *J. Org. Chem.*, 2010, **75**, 6061; For recent examples, see: (c) L. Dieu and O. Dauguils, *Org. Lett.*, 2010, **12**, 4277; (d) H.-h. Gao, C.-h. Yan, X.-P. Tao, Y. Xia, H.-M. Sun, Q. Shen and Y. Zhang, *Organometallics*, 2010, **29**, 4189; (e) T. Hatakeyama, Y.-I. Fujiwara, Y. Okada, T. Itoh, T. Hashimoto, S. Kawamura, K. Ogata, H. Takaya and M. Makamura, *Chem. Lett.*, 2011, **40**, 1030; (f) X. Qian, L. N. Dawe and C. M. Kozak, *Dalton Trans.*, 2011, **40**, 933;
- S2 (a) H. Ohmiya, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2006, **128**, 1886; (b) G. Cahiez, C. Chaboche, C. Duplais and A. Moyeux, *Org. Lett.*, 2009, **11**, 277; Ni: (c) O. Vechorkin, V. Proust and X. Hu, *J. Am. Chem. Soc.*, 2009, **131**, 9756.
- S3 The coupling reaction of unactivated secondary alkyl halides with alkynyl Grignard reagents is less explored. For the reported examples, see: (a) H. Ohmiya, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2006, **8**, 3093; (b) T. Hatakeyama, Y. Okada, Y. Yoshimoto and M. Nakamura, *Angew. Chem., Int. Ed.*, 2011, **50**, 10973; For examples on coupling of primary alkyl halides with alkynyl Grignard reagents, see: (c) L. M. Yang, L. F. Huang and T. Y. Luh, *Org. Lett.*, 2004, **6**, 1461; (d) H. Someya, H. Ohmiya, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2007, **9**, 1565; (e) O. Vechorkin, A. Godinat, R. Scopelliti and X. Hu, *Angew. Chem., Int. Ed.*, 2011, **50**, 11777.
- S4 A. Krasovskiy and P. Knochel, *Synthesis*, 2006, **5**, 890-891.
- S5 (a) K. Fukumoto, K. Suzuki, H. Nemoto, T. Kametani and H. Furuyama, *Tetrahedron*, 1982, **38**, 3701-3704; (b) L. Ebersson and L. Greci, *J. Org. Chem.*, 1984, **49**, 2135-2139.
- S6 G. L. Lange and C. Gottardo, C., *Synth. Commun.*, 1990, **20**, 1473-1479.
- S7 M. Akita, H. Yasuda and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 480-487.
- S8 D. H. R. Barton, L. Bohe and X. Lusinch, *Tetrahedron*, 1990, **46**, 5273.
- S9 3M Innovative Properties Company, Patent: US6974877 B2, 2005.
- S10 M. Sai, H. Yorimitsu and K. Oshima, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 1194-1196.
- S11 T. Mukaiyama, et al. *Chem. Lett.*, 1977, 1257-1260.
- S12 R. L. Danheiser, J. J. Bronson and K. Okano, *J. Am. Chem. Soc.*, 1985, **107**, 4579-4581.

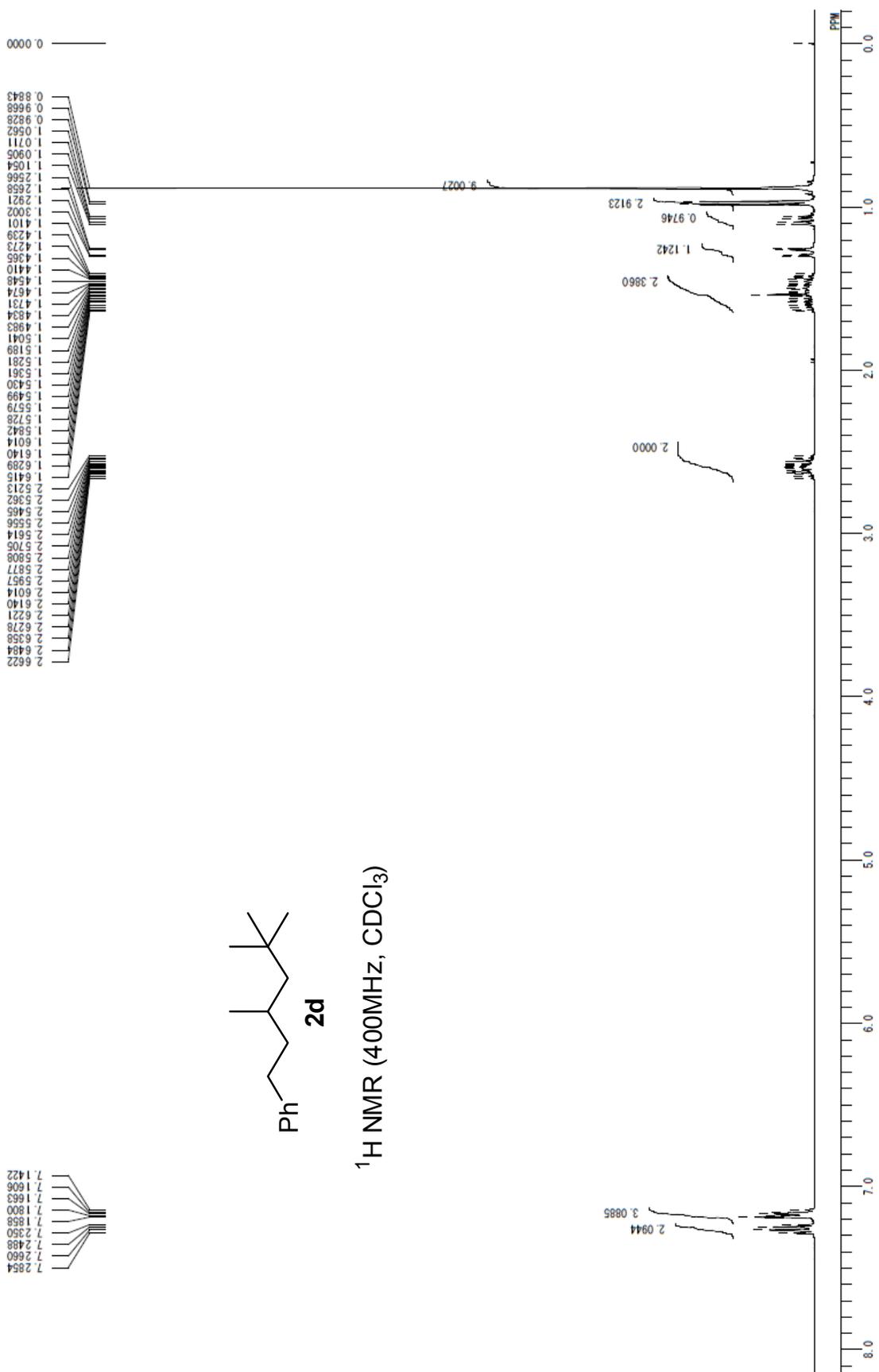


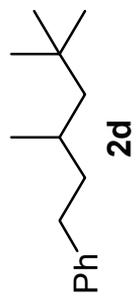
^{13}C NMR (100MHz, CDCl_3)



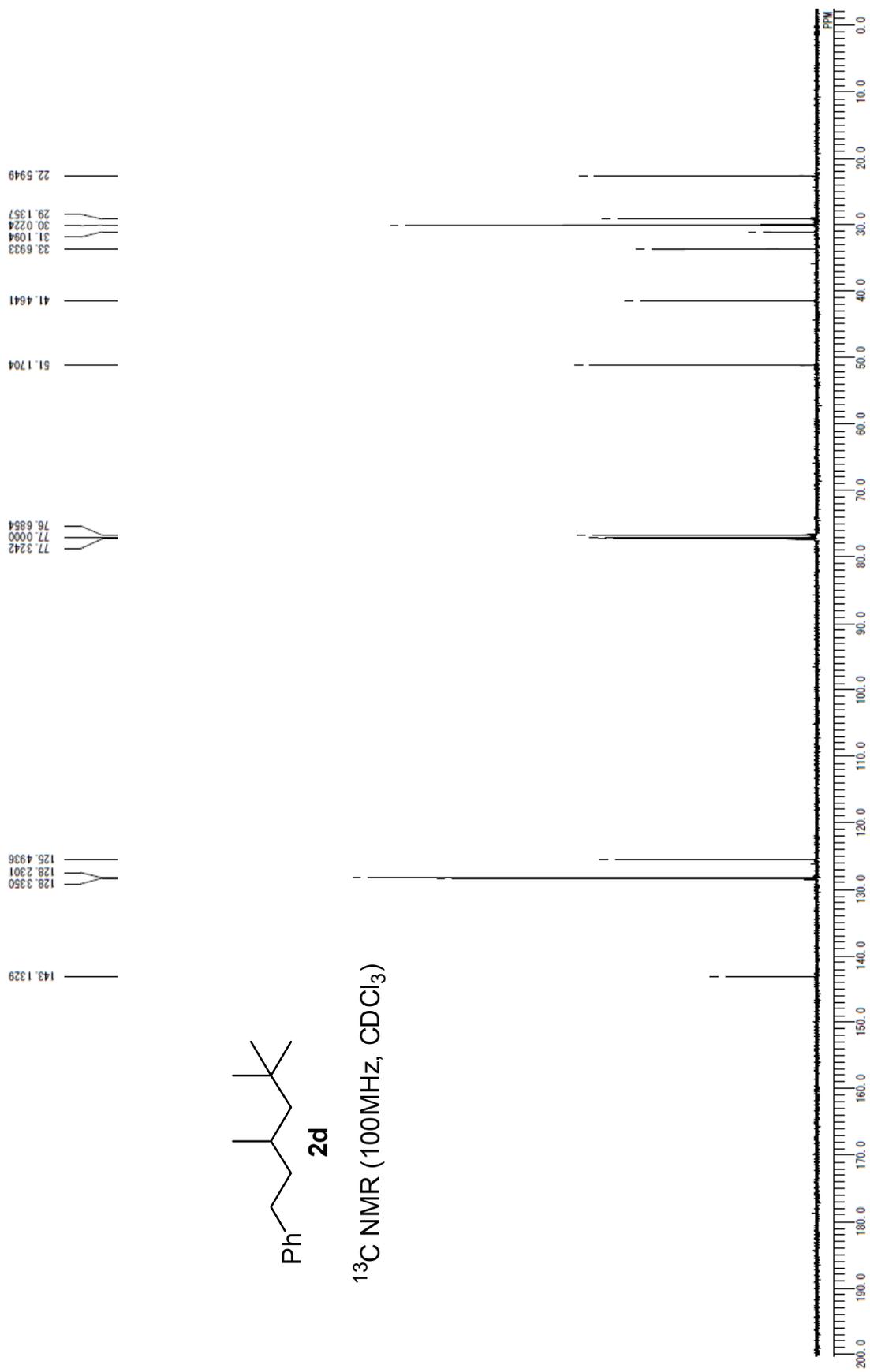


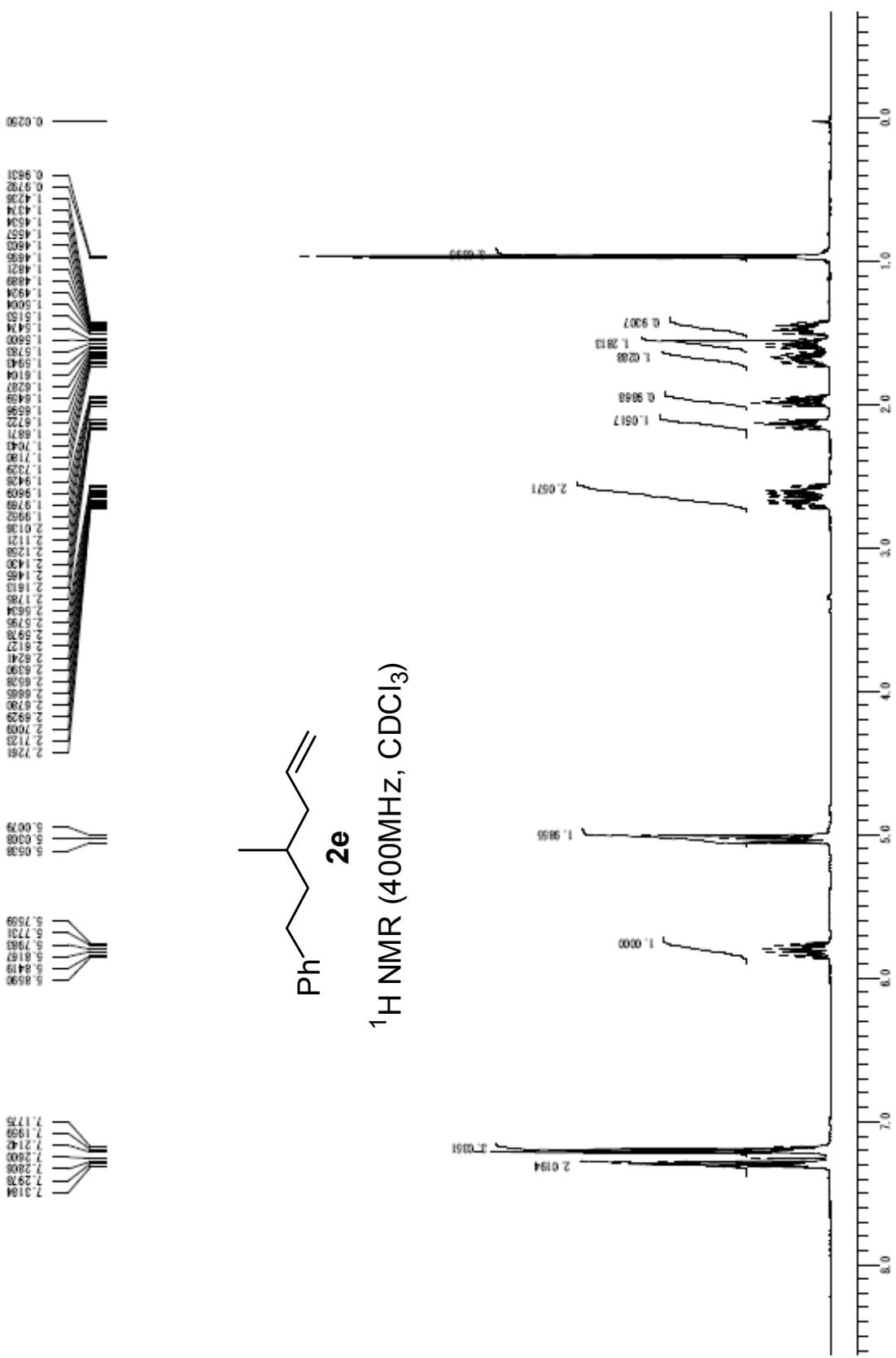


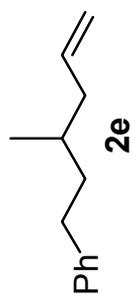




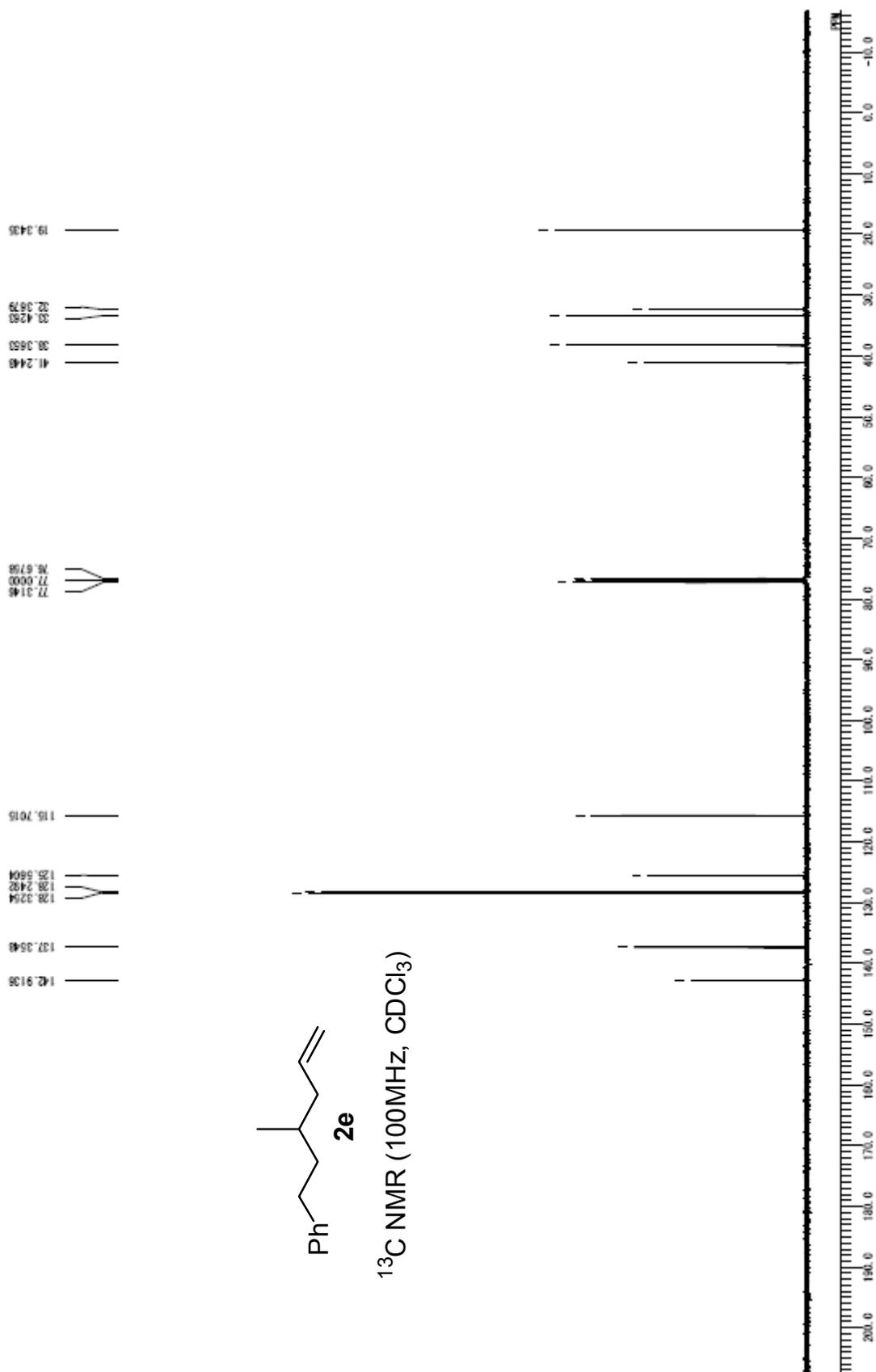
^{13}C NMR (100MHz, CDCl_3)

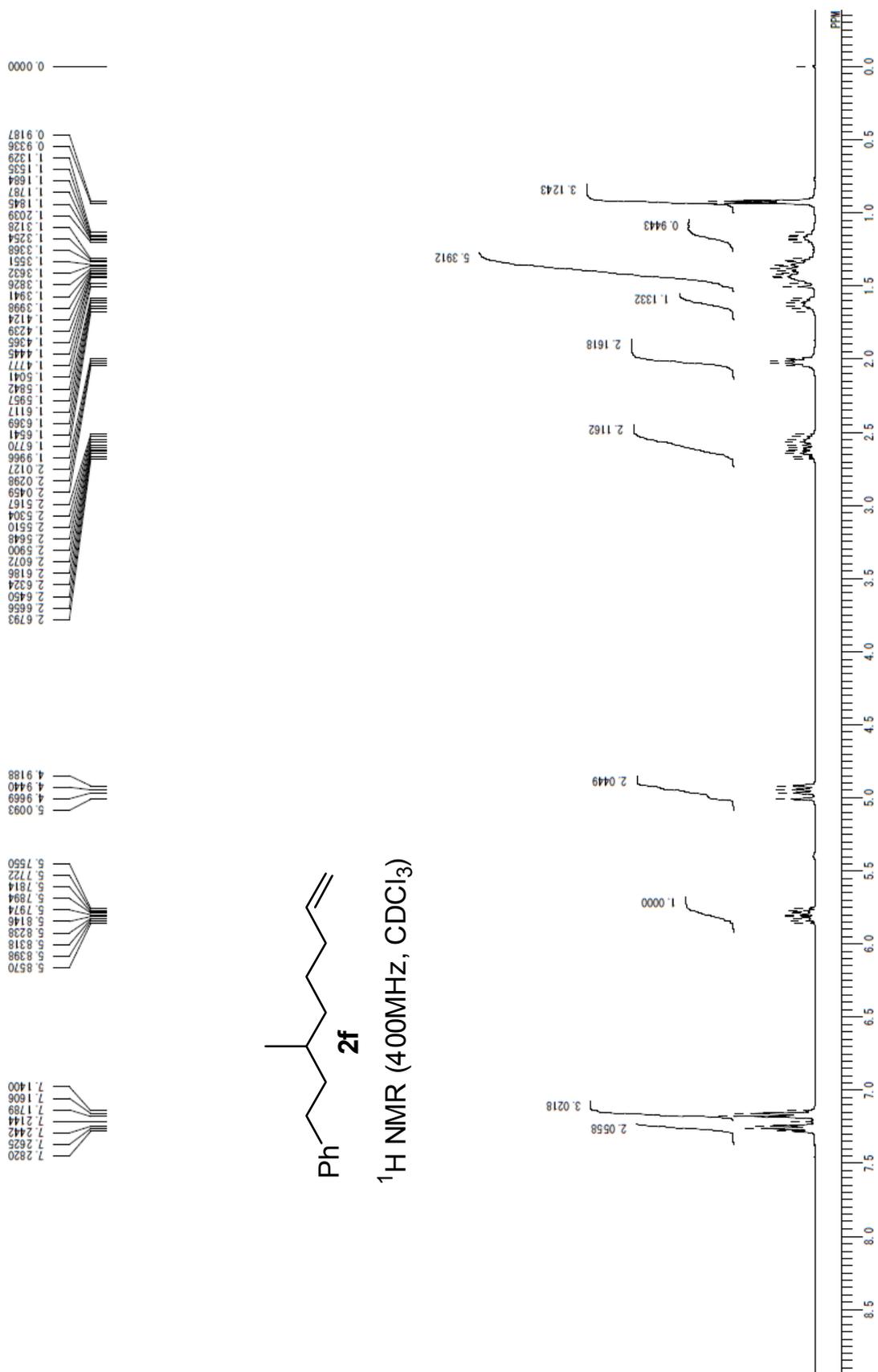


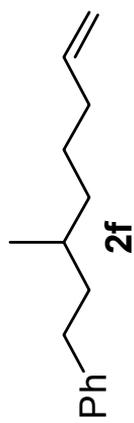




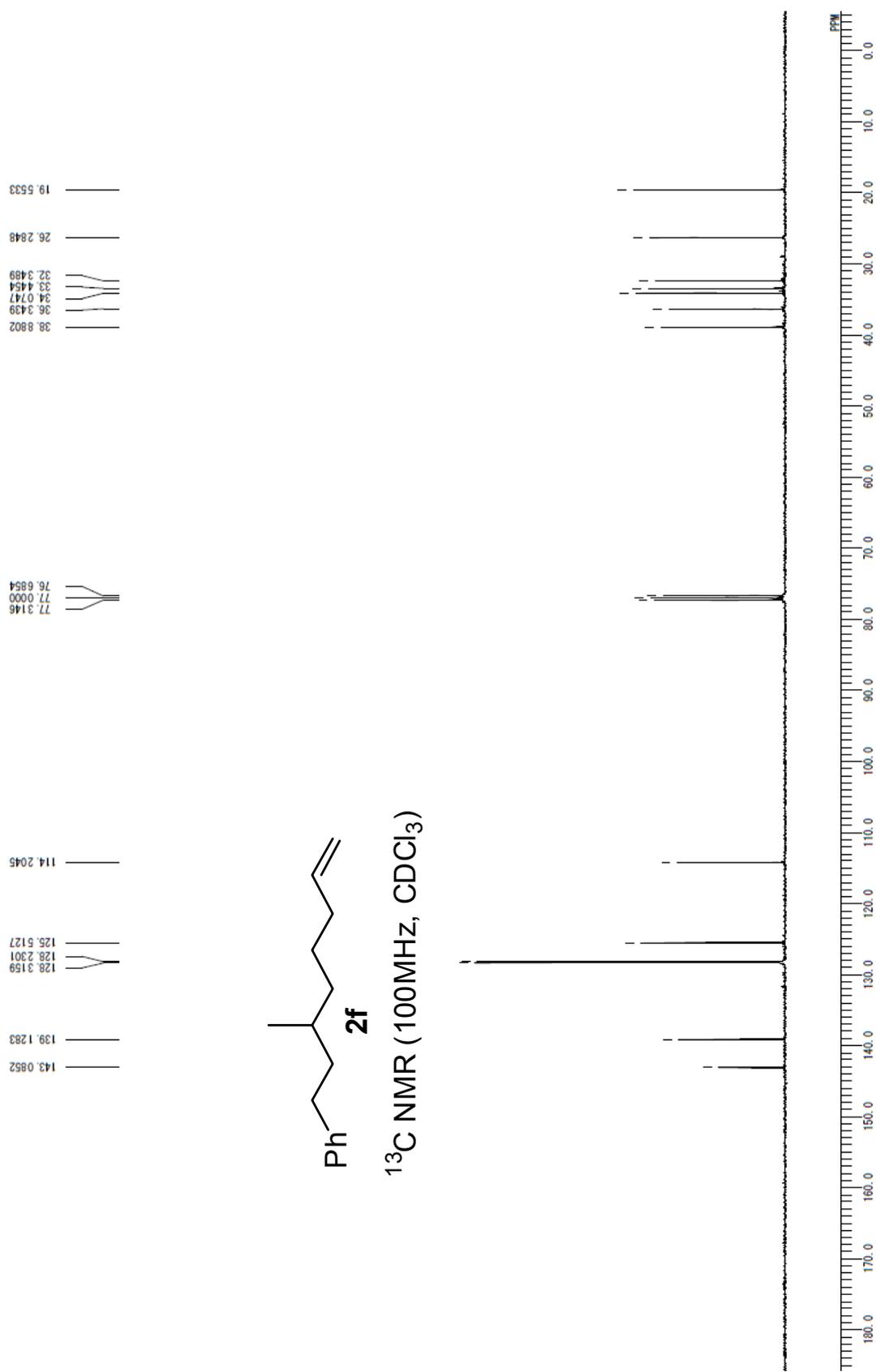
^{13}C NMR (100MHz, CDCl_3)

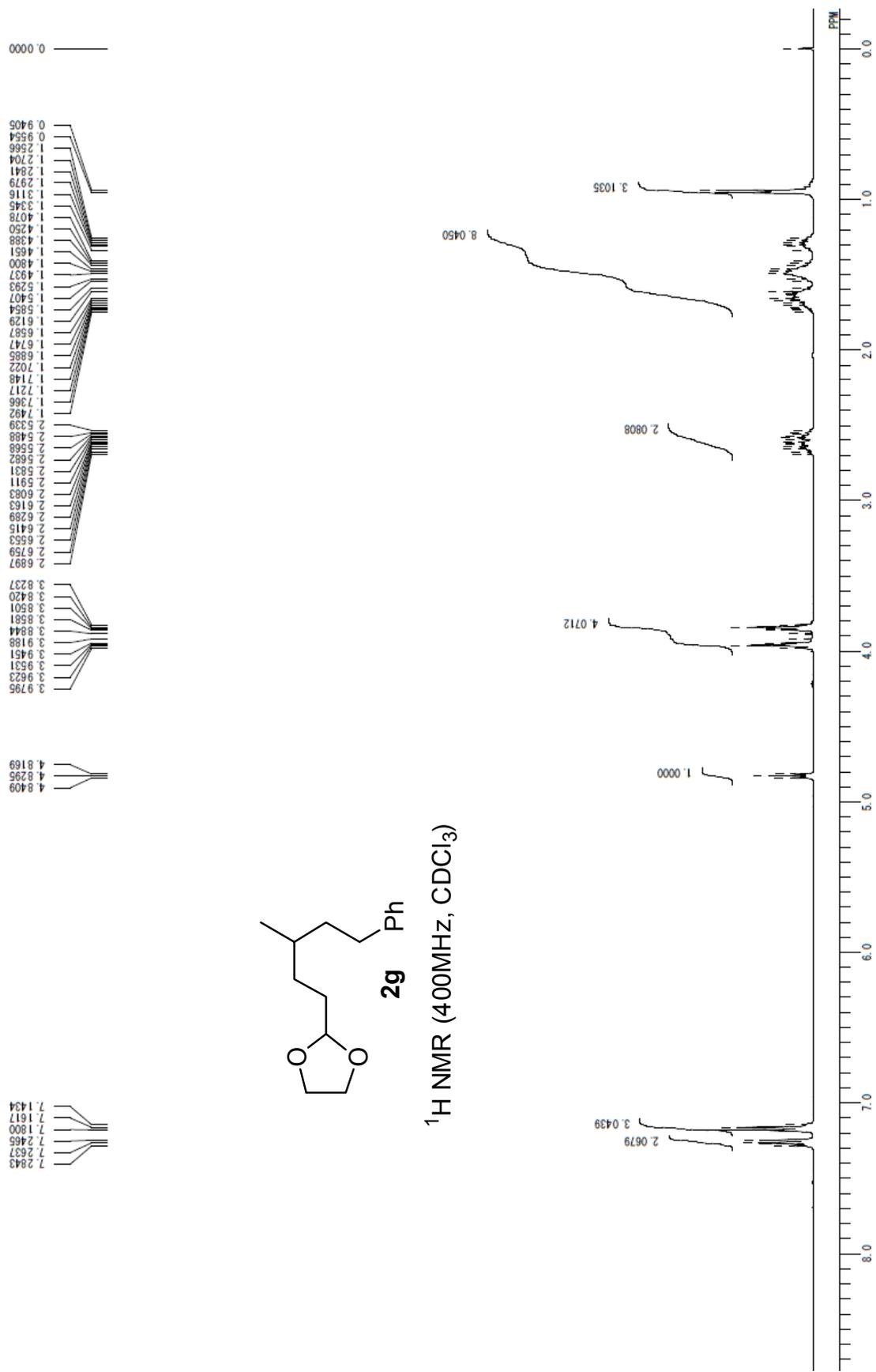


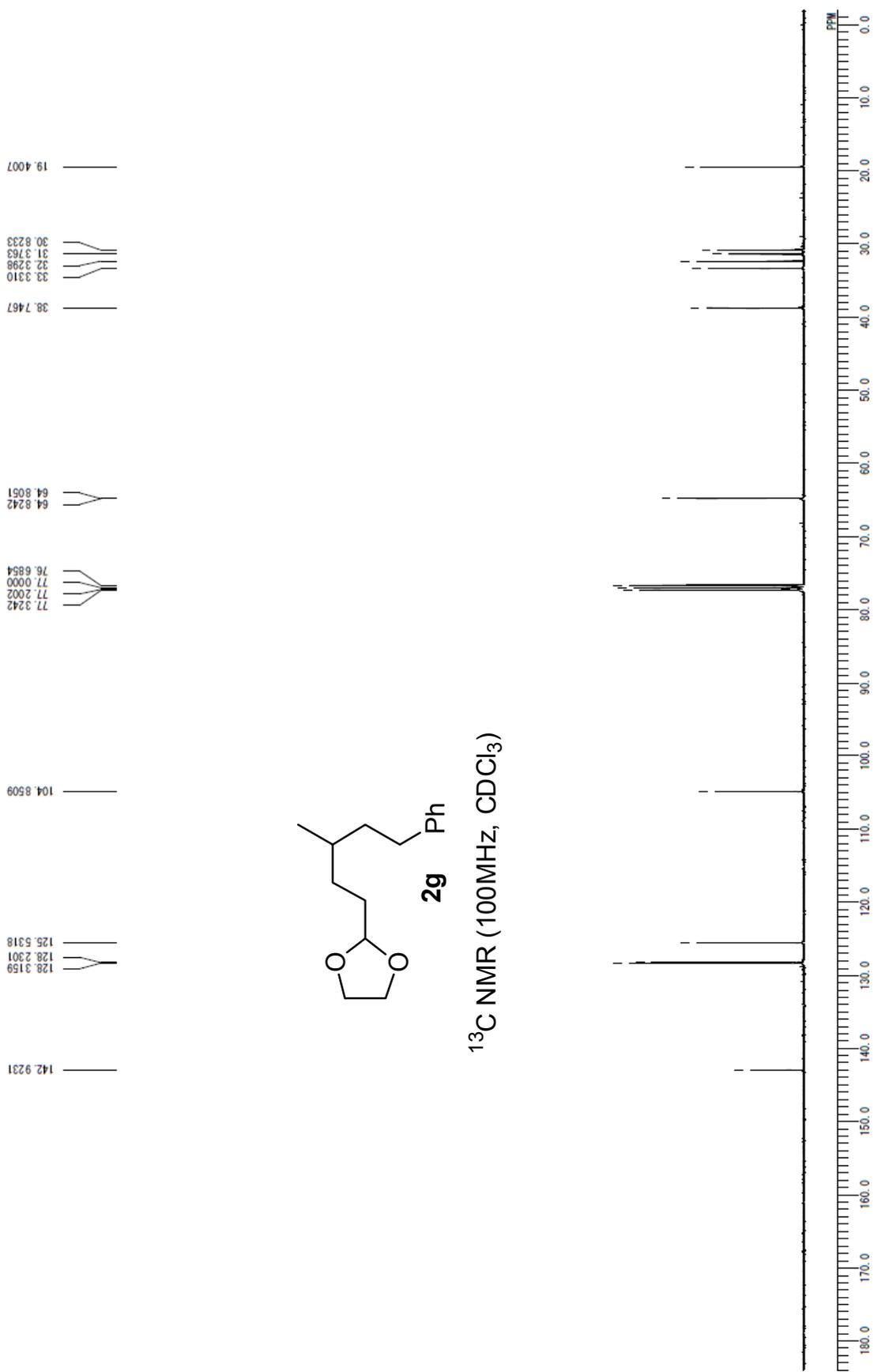


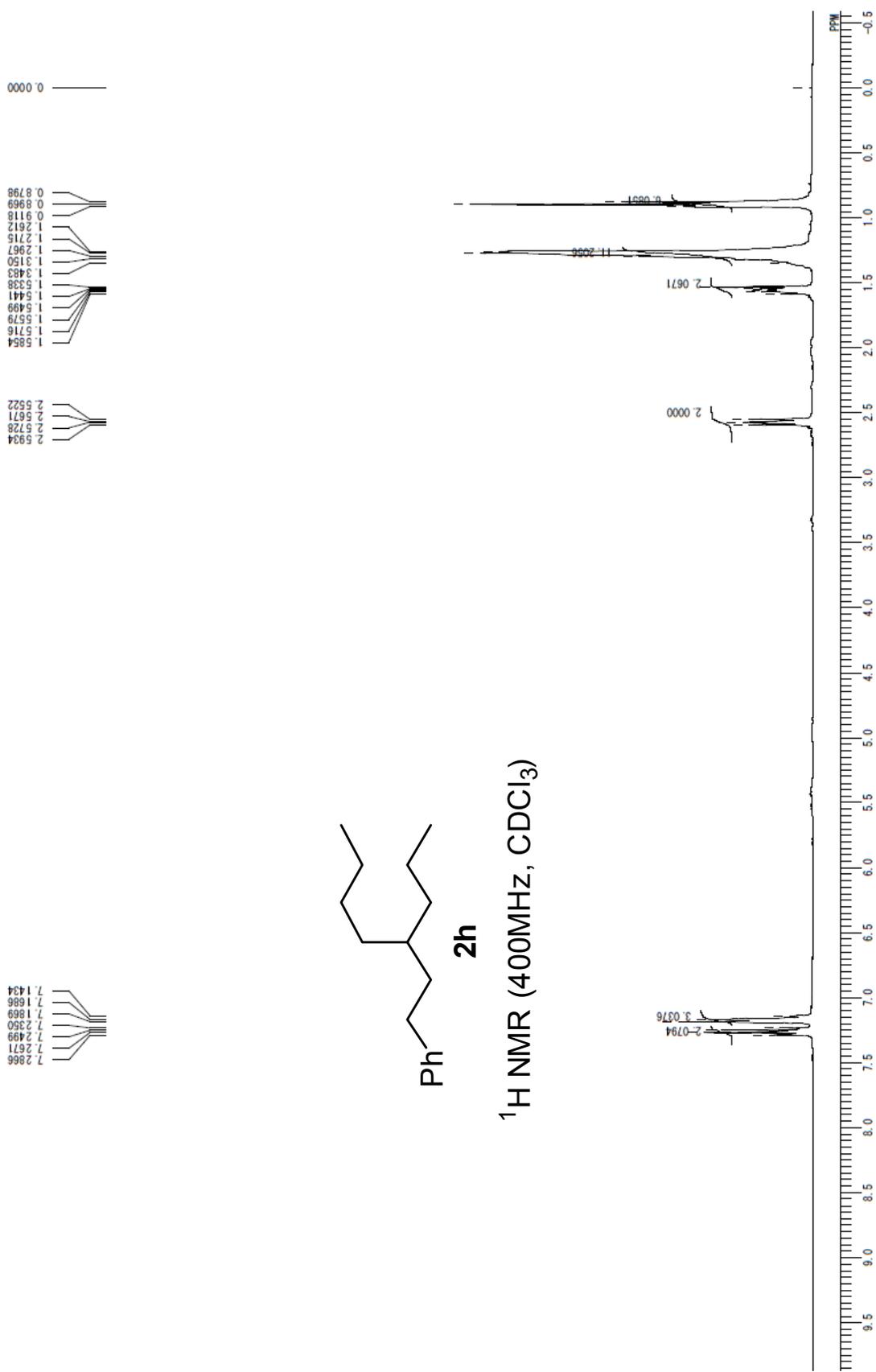


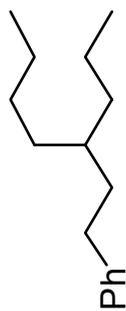
^{13}C NMR (100MHz, CDCl_3)





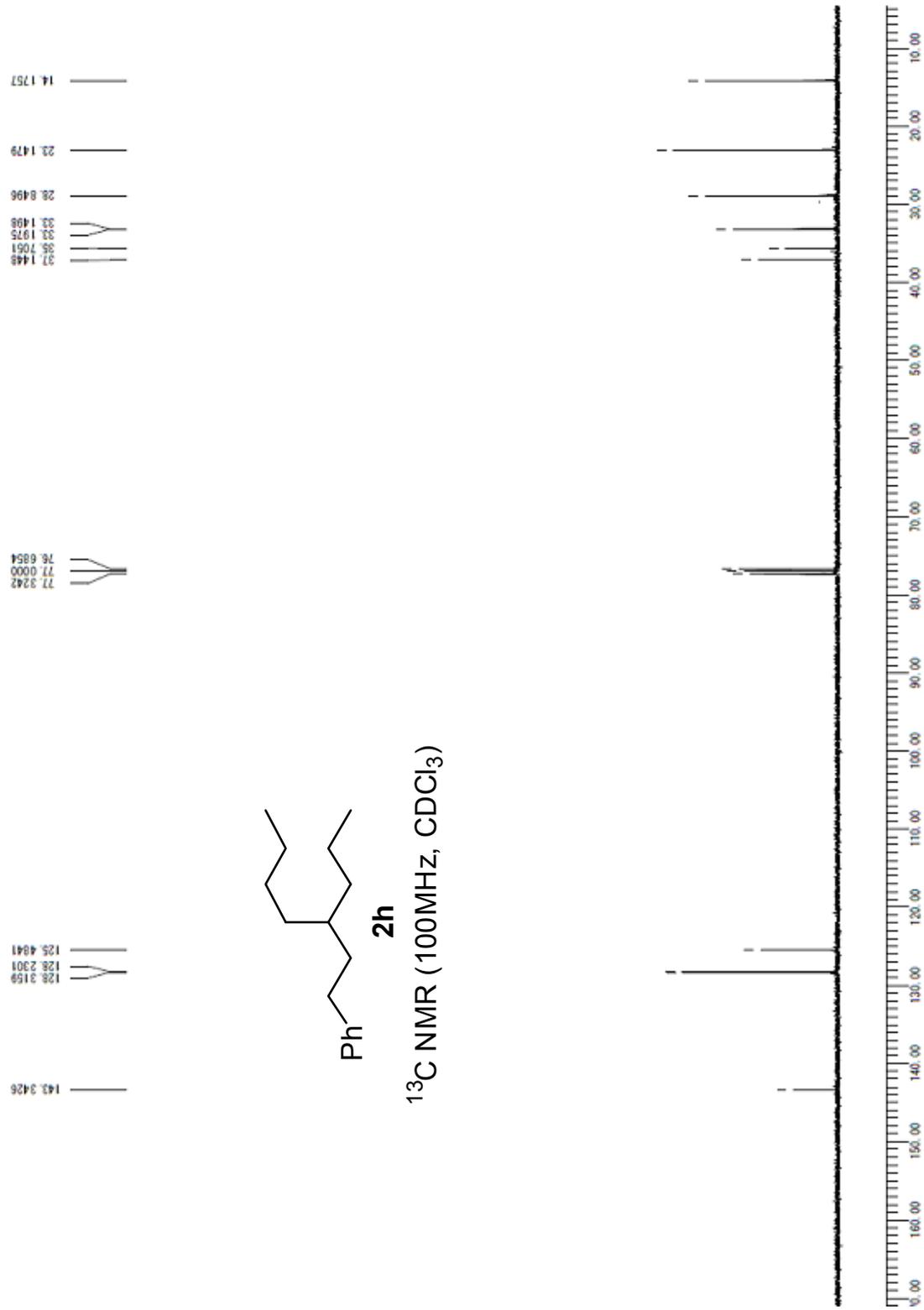


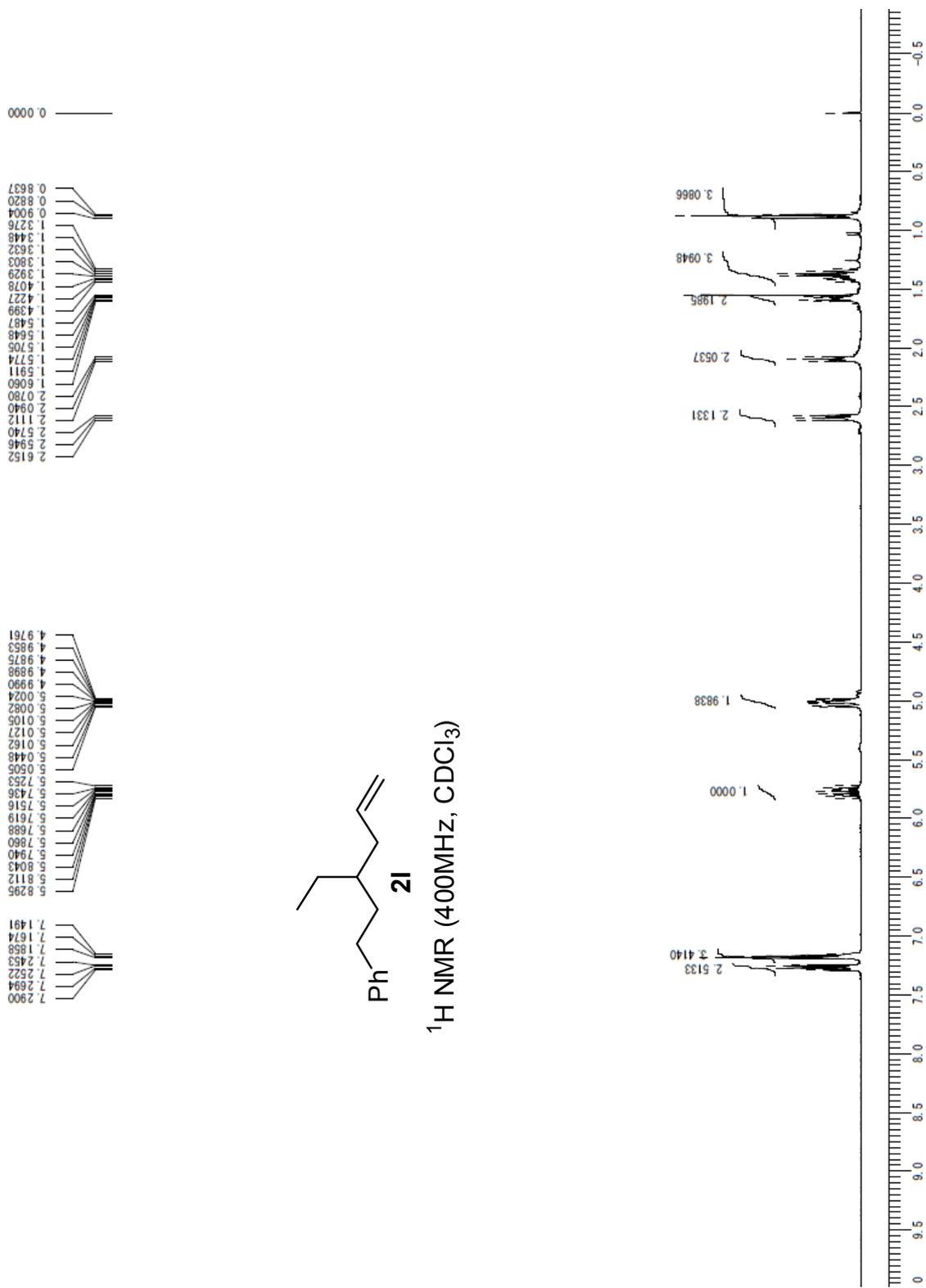


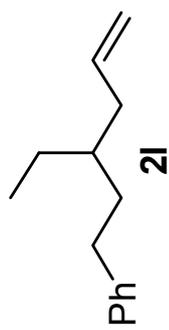


2h

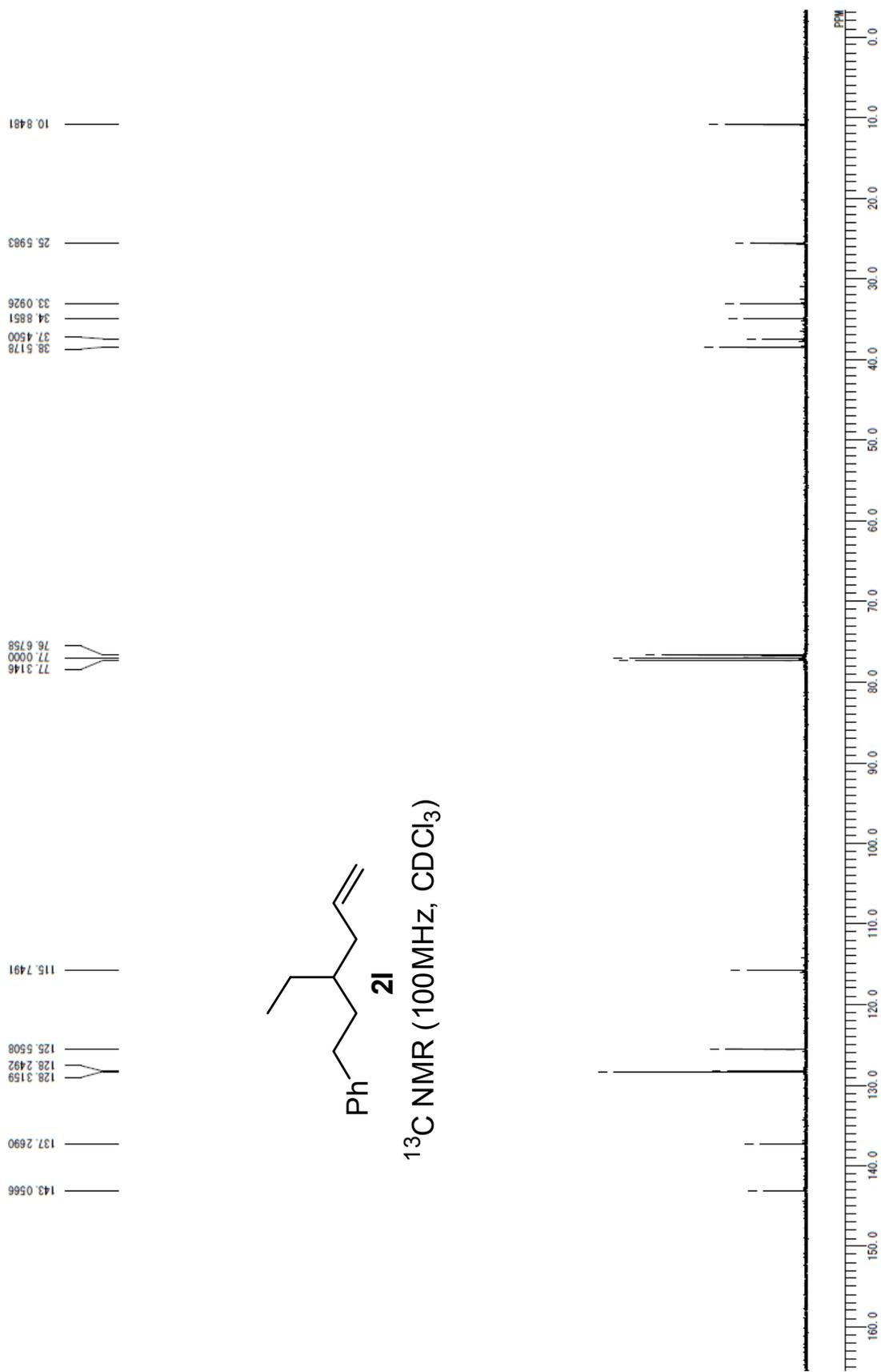
^{13}C NMR (100MHz, CDCl_3)

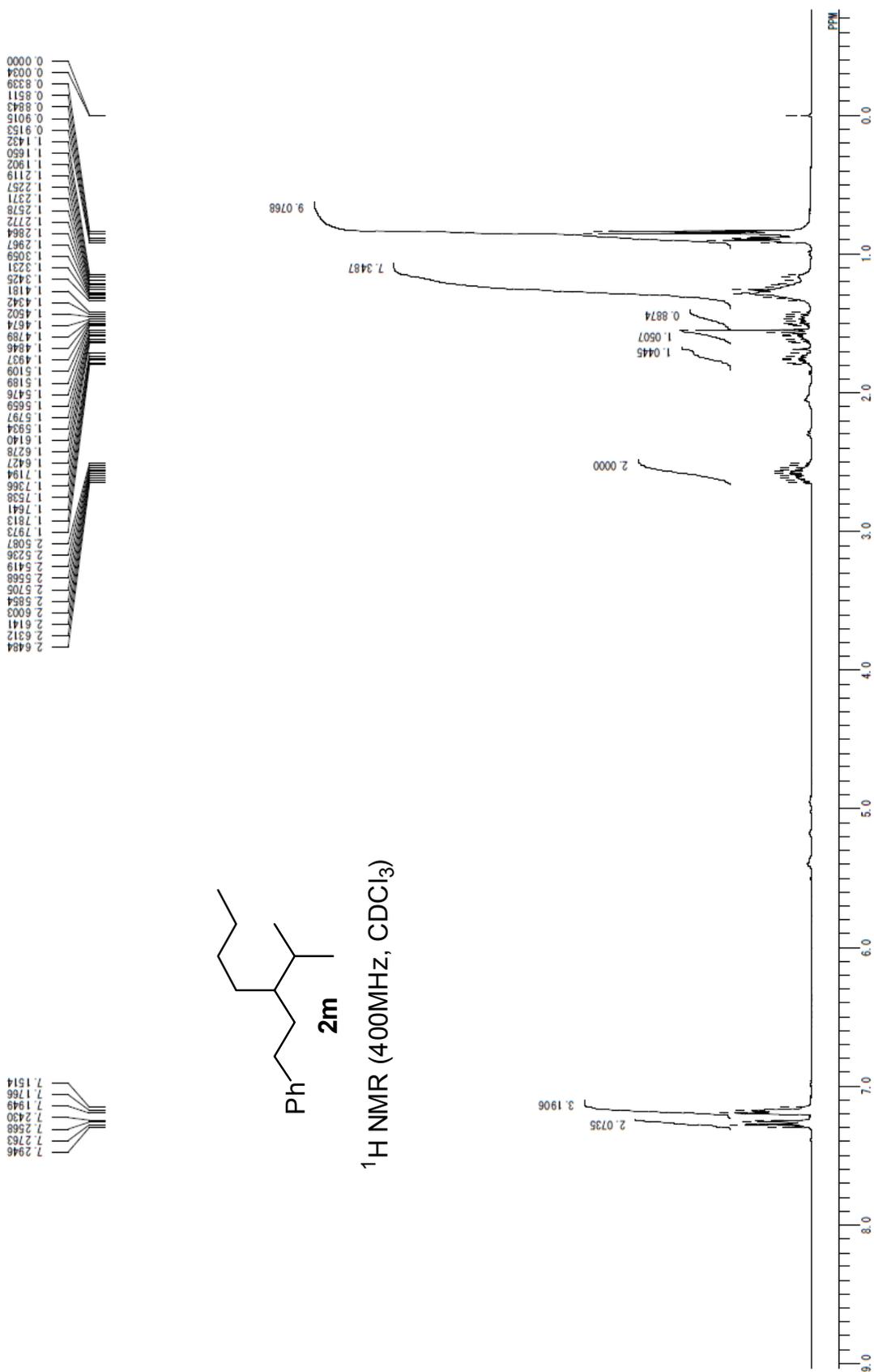


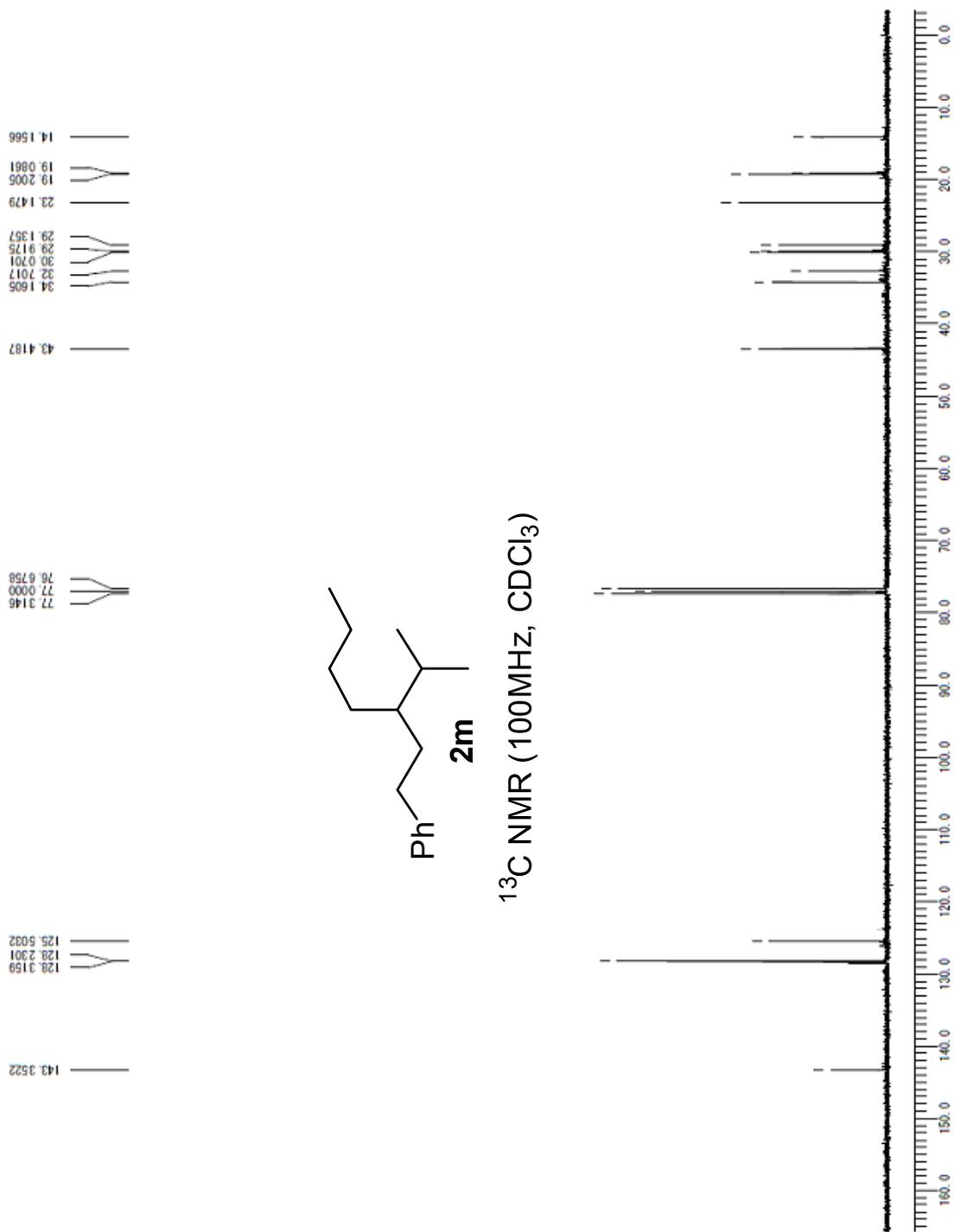


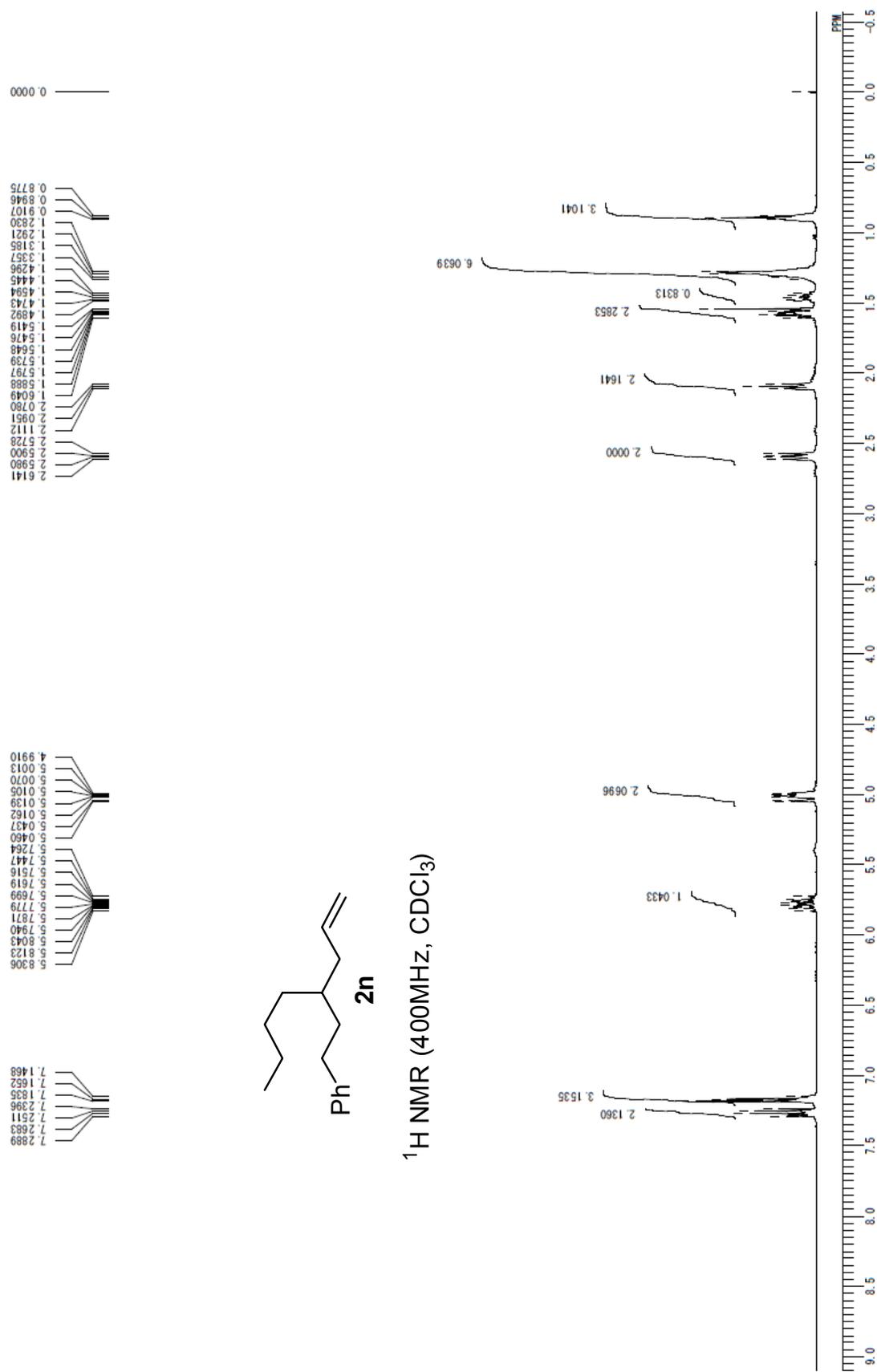


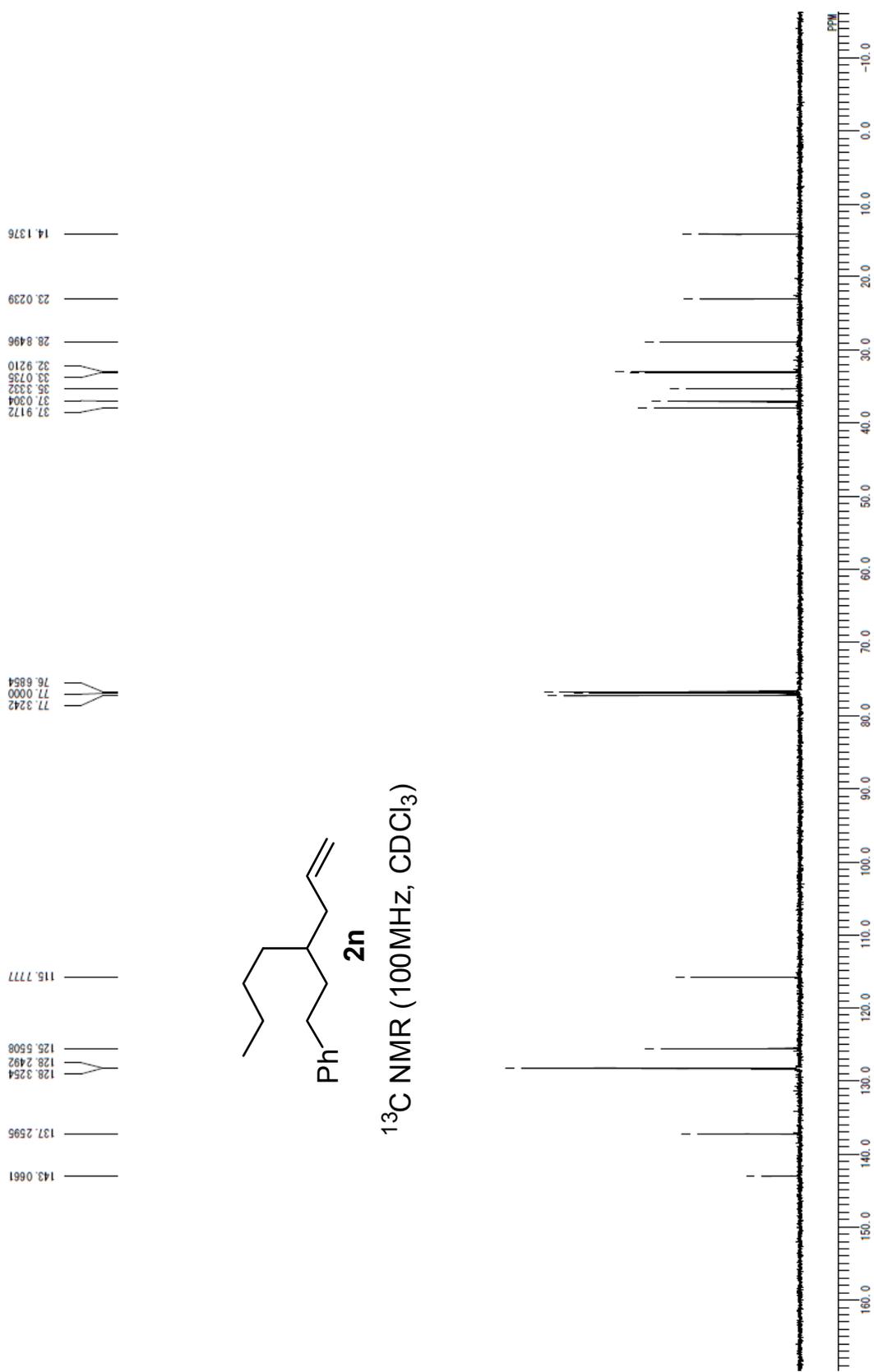
^{13}C NMR (100MHz, CDCl_3)

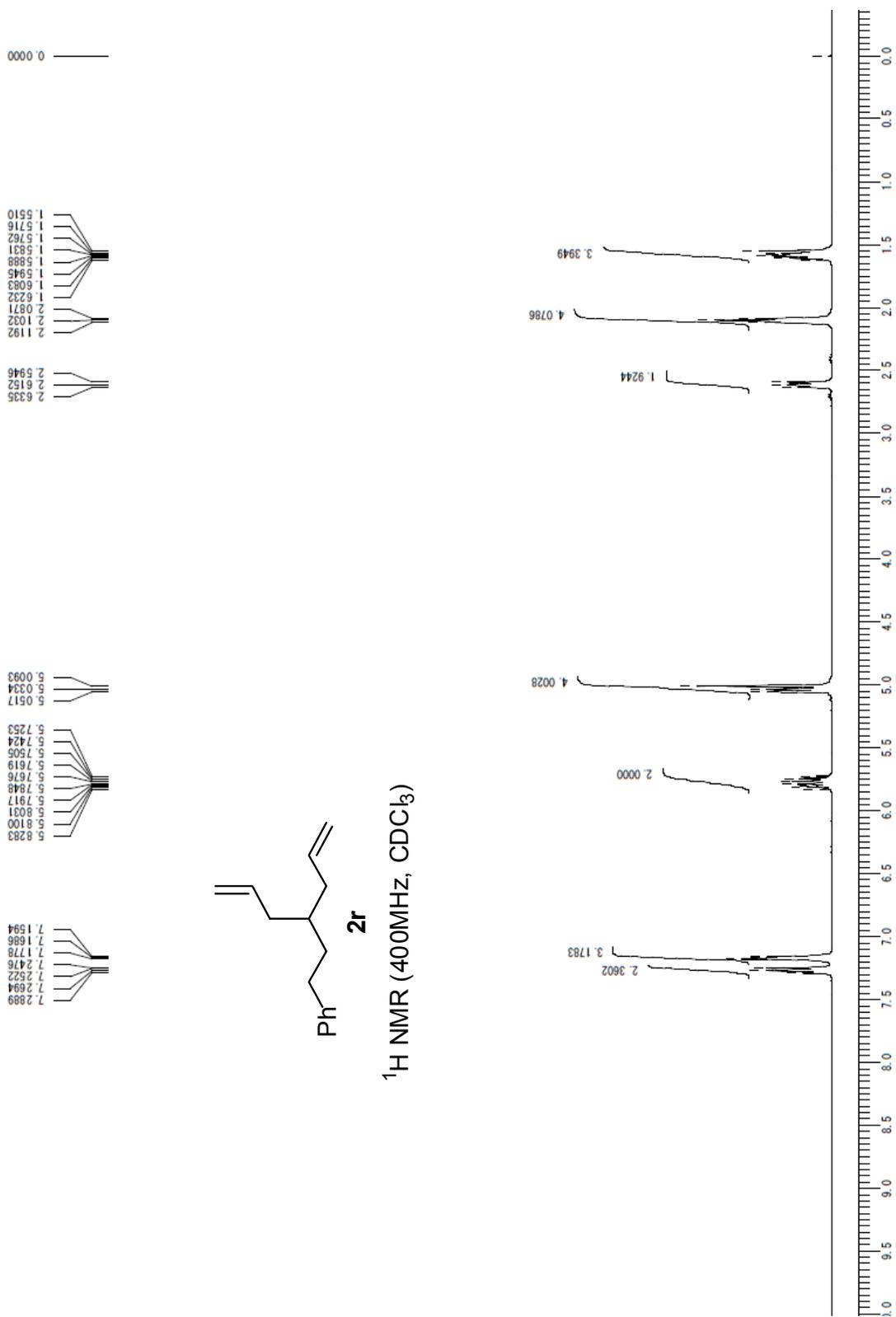








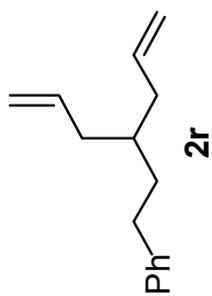




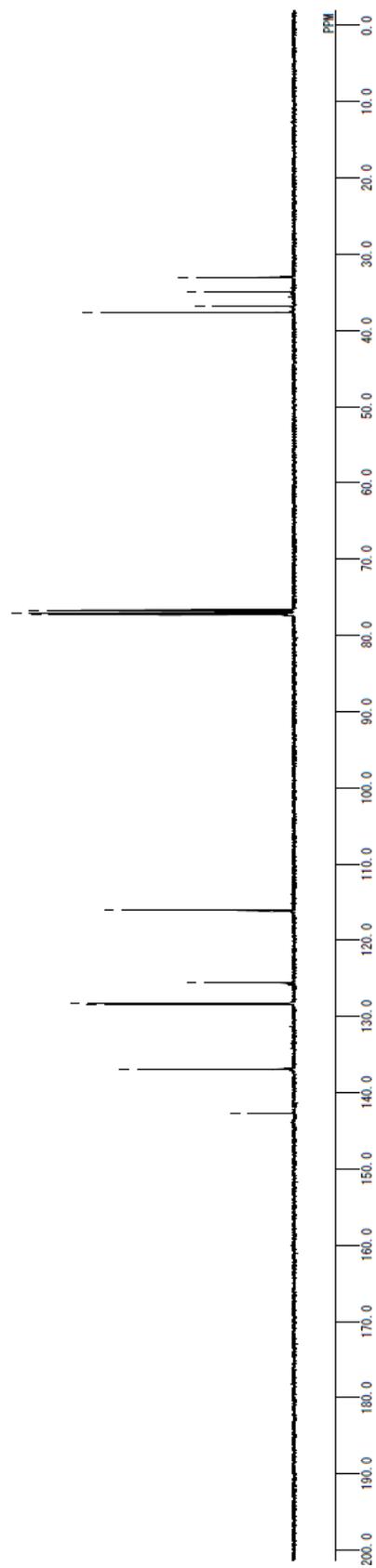
37.6216
36.9065
34.9423
33.0449

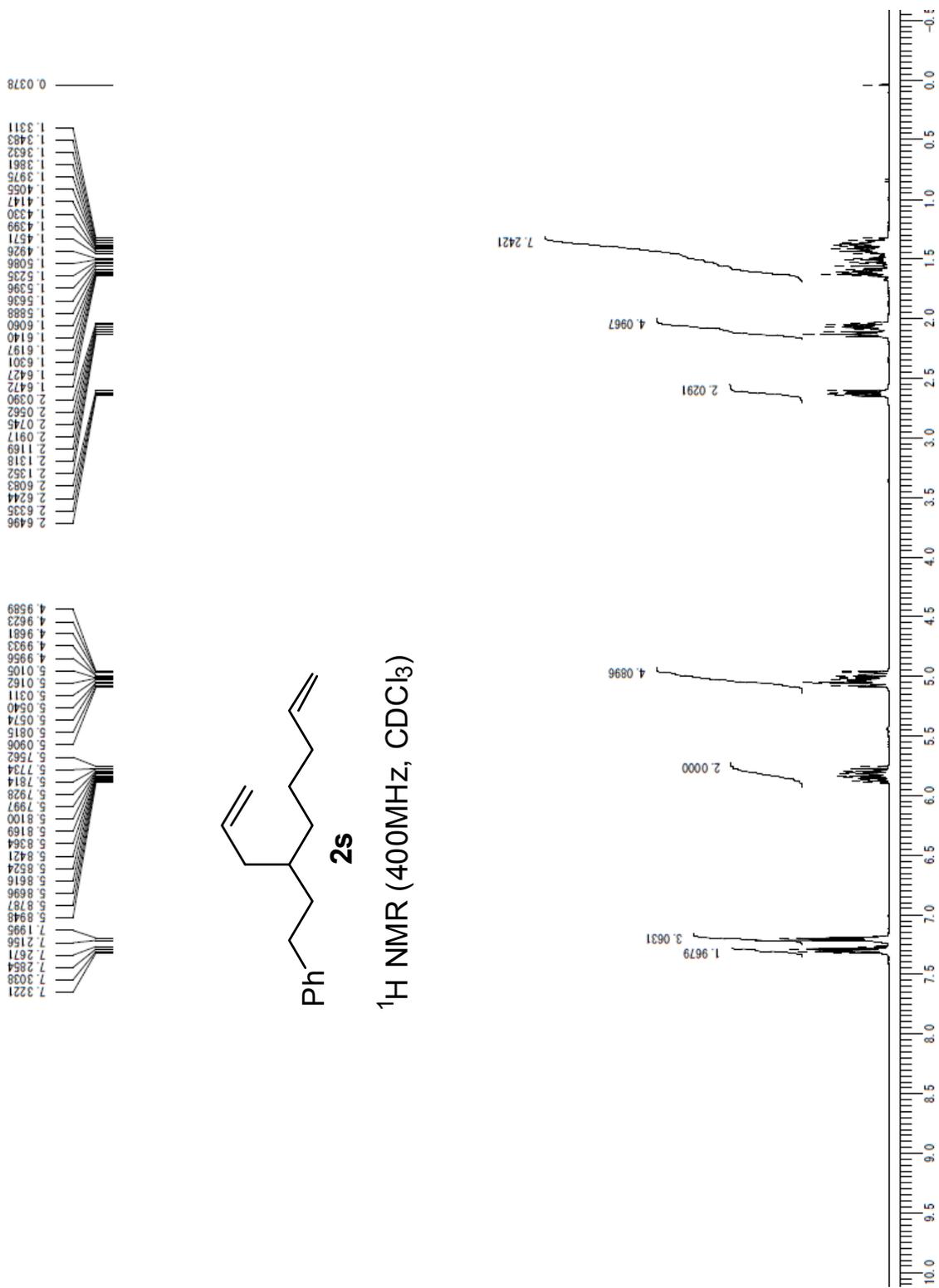
77.3146
77.0000
76.6854

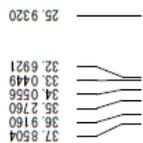
142.7991
136.9162
128.3254
128.2778
125.6080
116.1591



^{13}C NMR (100MHz, CDCl_3)

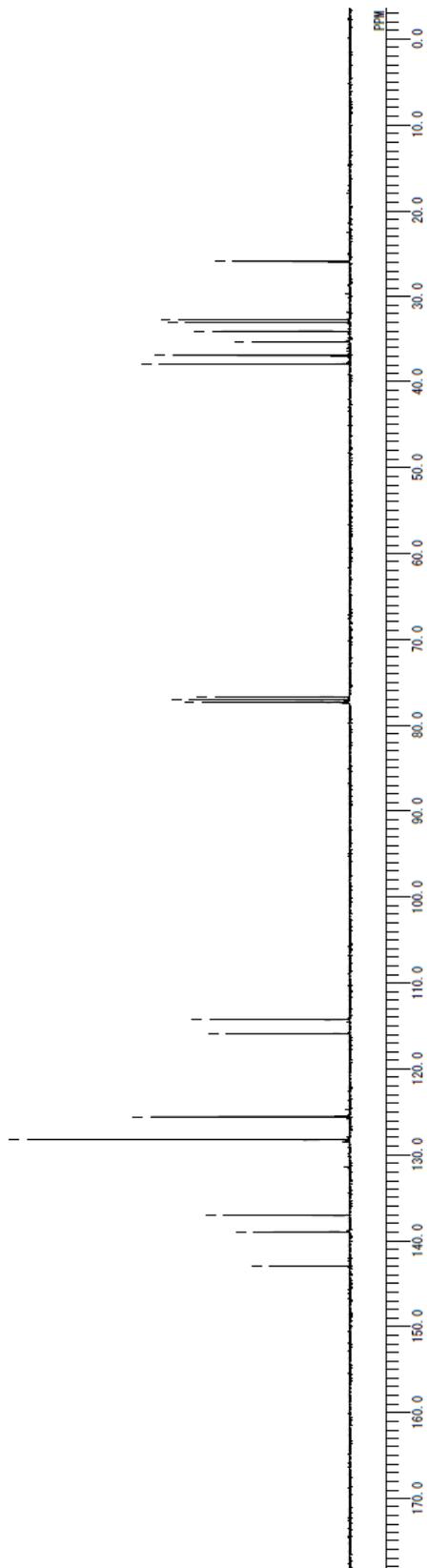
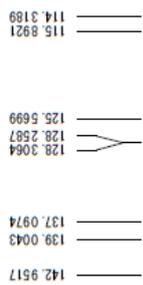


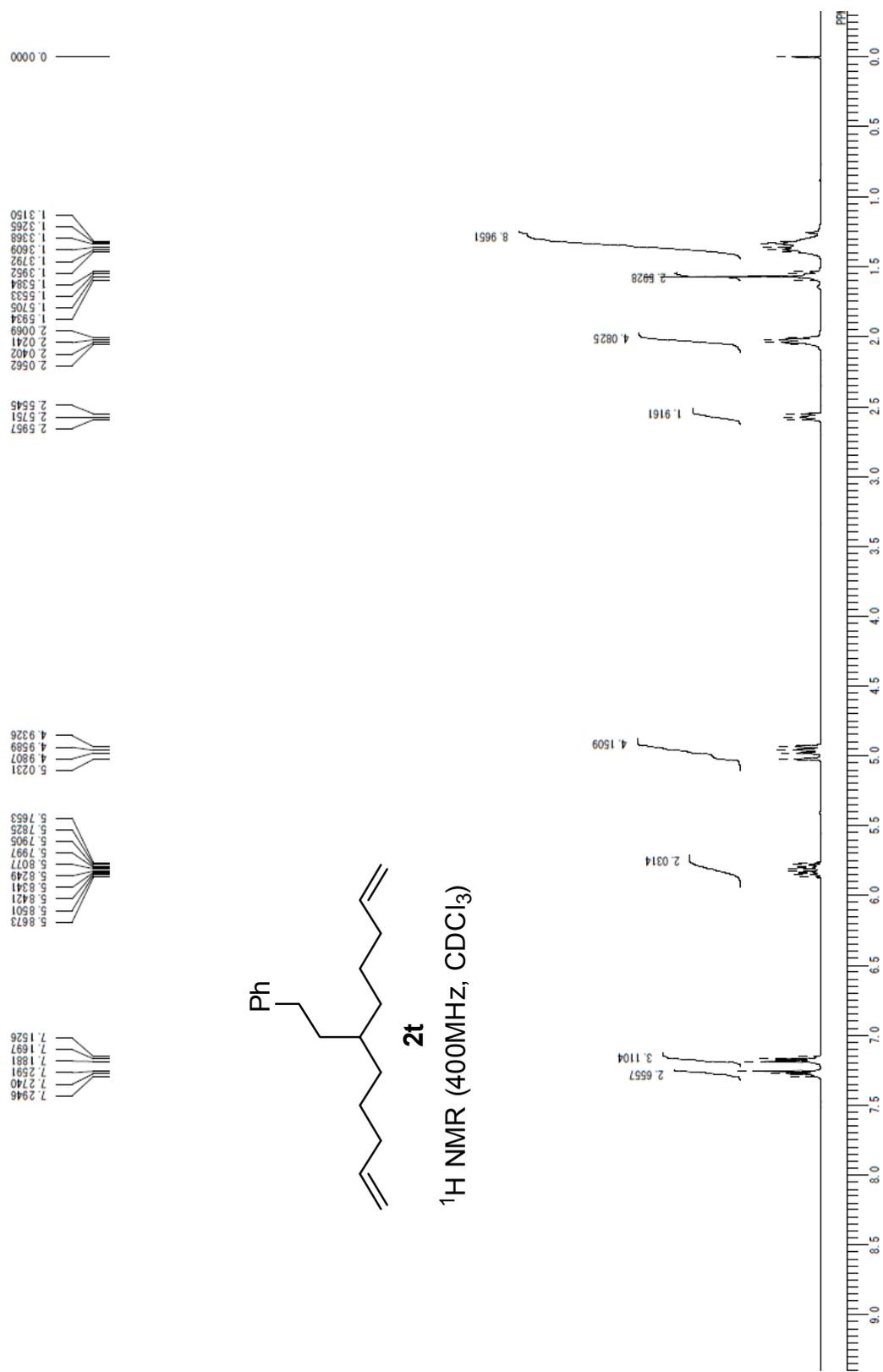


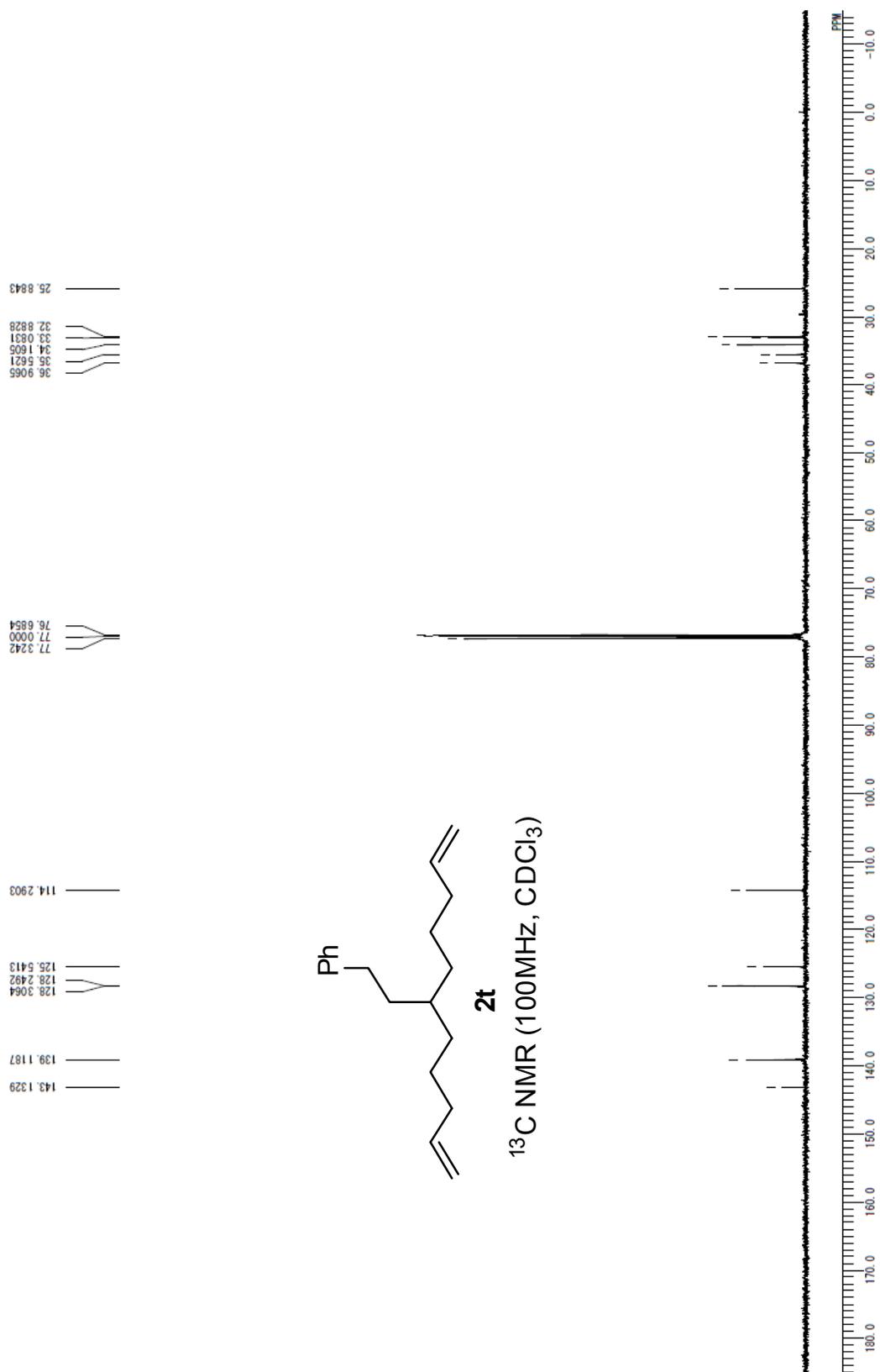


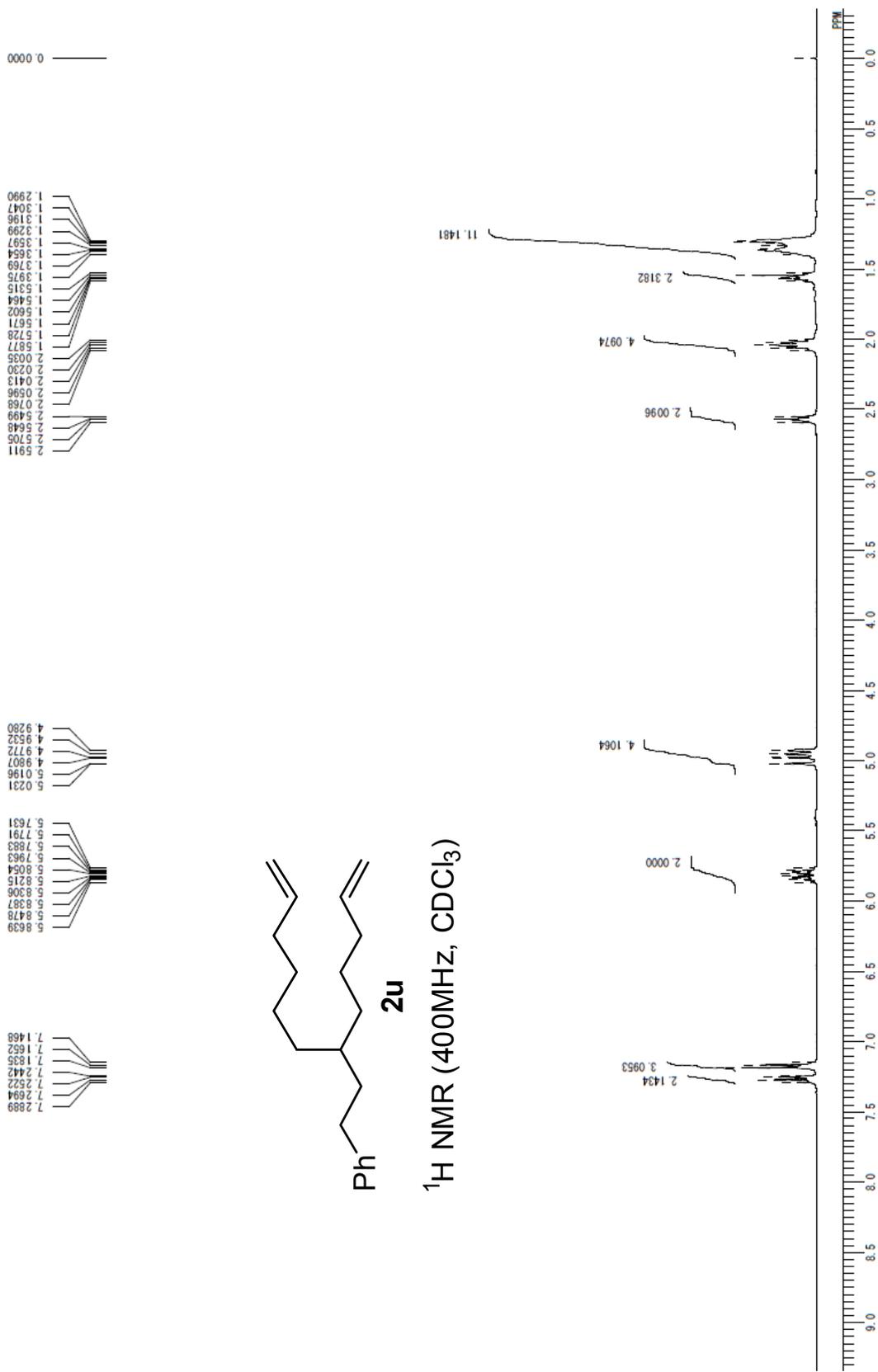
2s

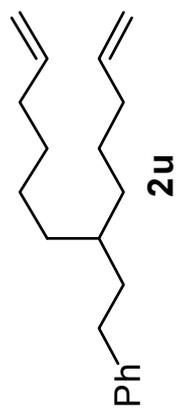
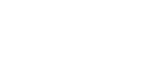
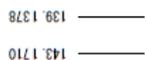
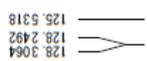
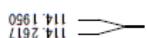
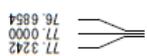
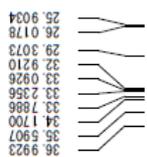
^{13}C NMR (100MHz, CDCl_3)



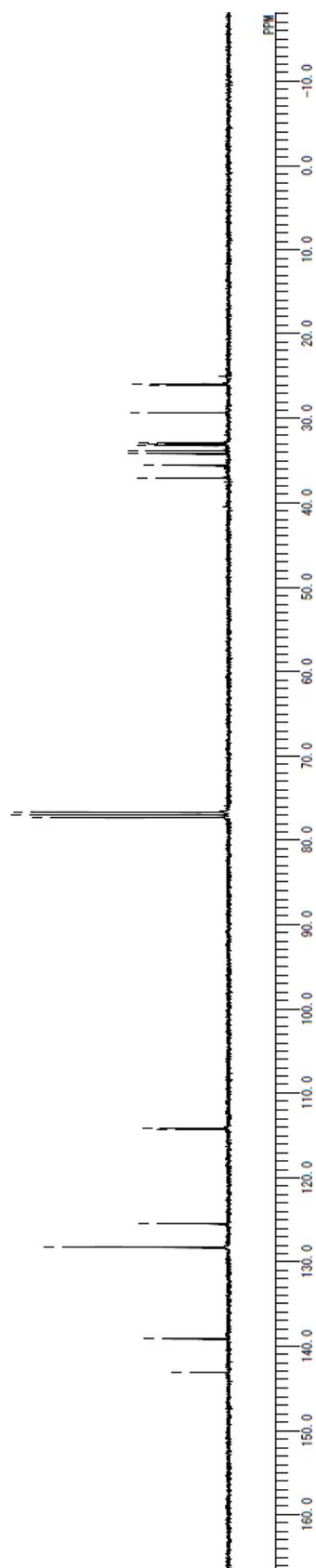


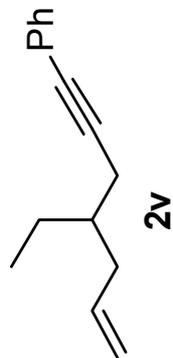
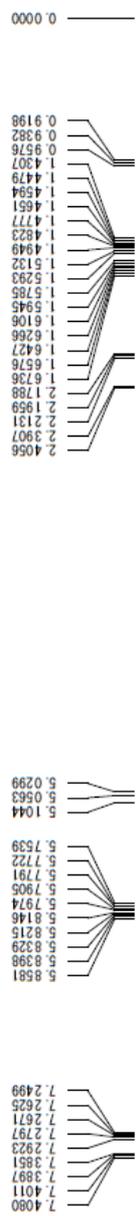




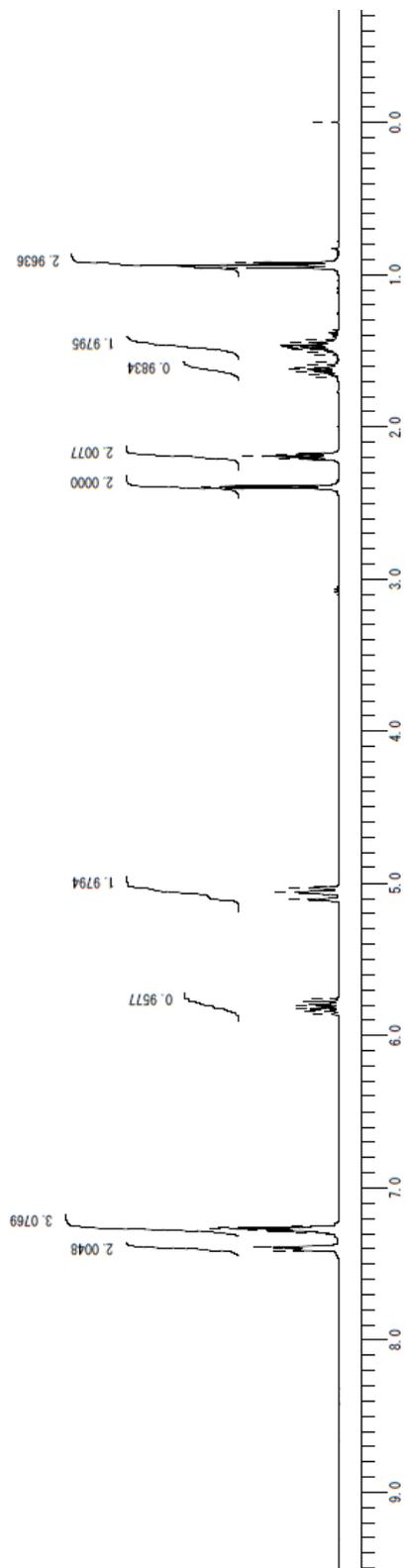


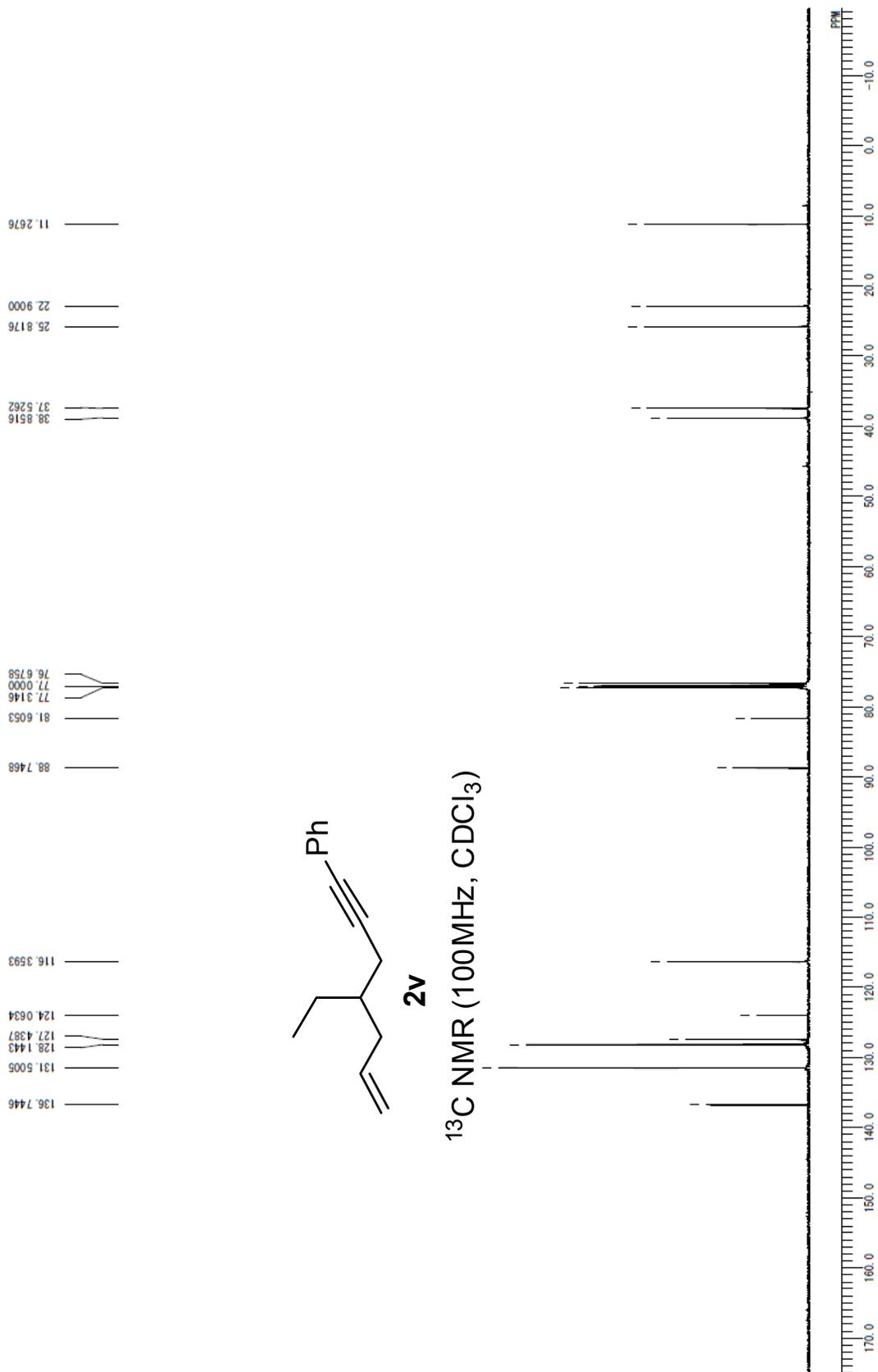
^{13}C NMR (100MHz, CDCl_3)

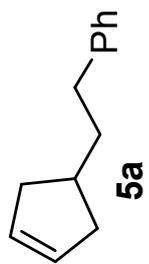




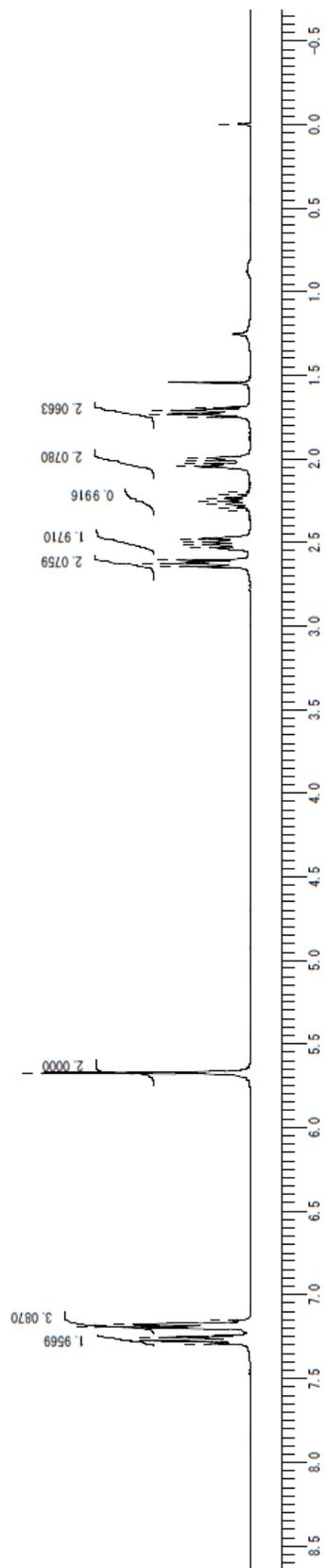
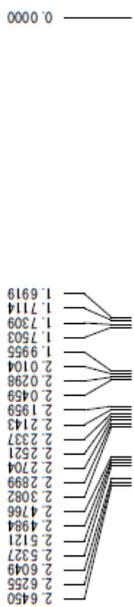
^1H NMR (400MHz, CDCl_3)

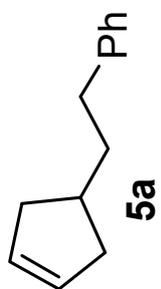




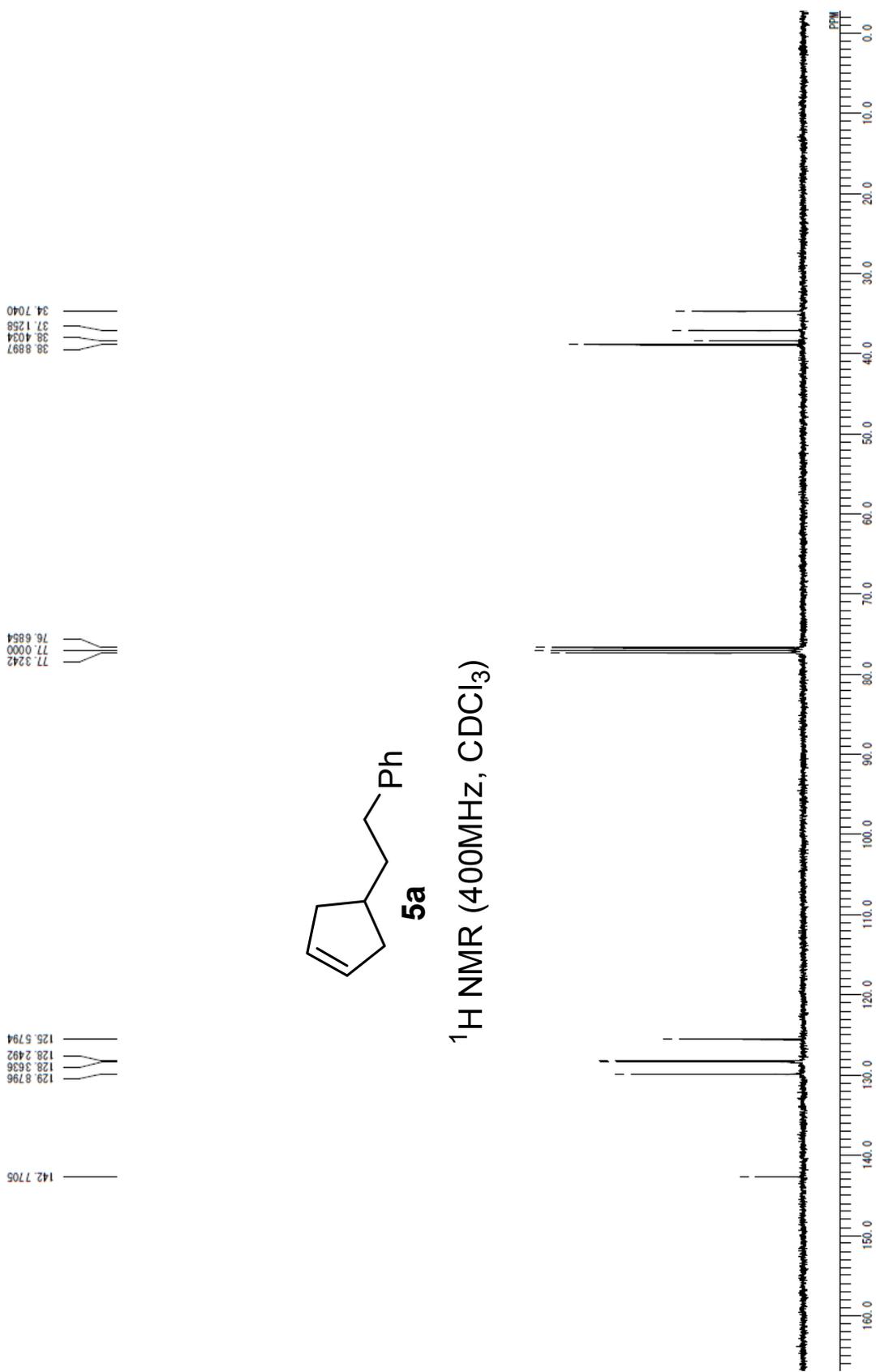


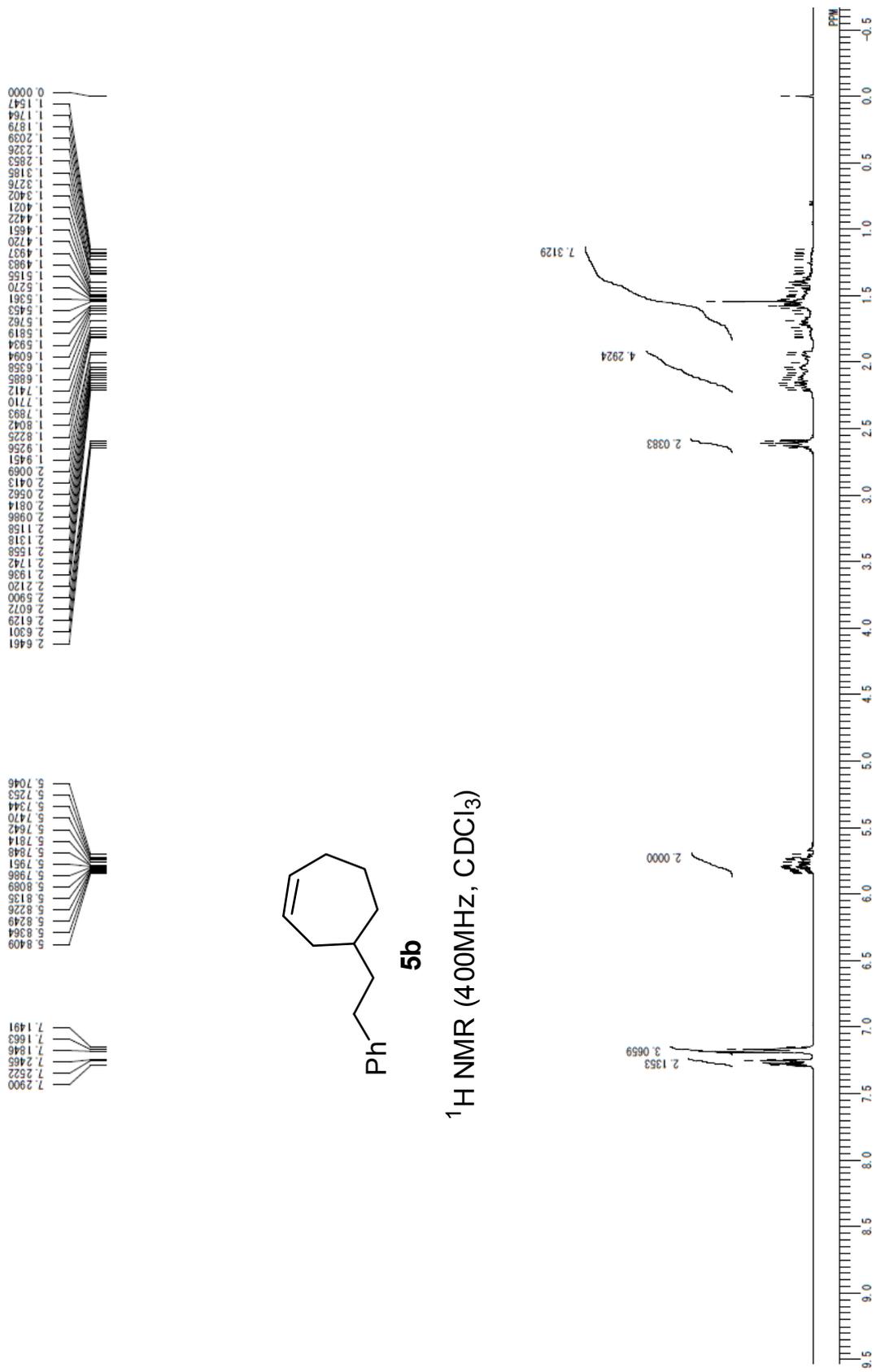
^1H NMR (400MHz, CDCl_3)

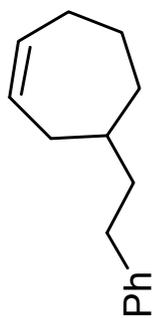




^1H NMR (400MHz, CDCl_3)







5b

^{13}C NMR (100MHz, CDCl_3)

