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Electronic Supplementary Information

Palladium-Catalyzed Double Bond Migration of Unsaturated Hydrocarbons Accelerated by Tantalum Chloride

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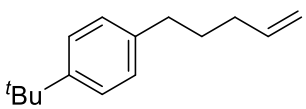
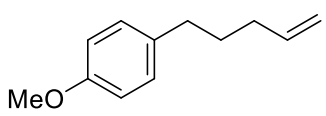
1. General Methods. All reactions were conducted in dry solvent under an argon atmosphere. Unless otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. THF and 2-MeTHF were purchased from Wako Pure Chemical Industries, and was dried by the usual methods and degassed with argon for 20 min before use. $PdCl_2$ (99.9% purity) and $FeCl_3$ were purchased from Wako Pure Chemical Industries, $TaCl_5$ (99%) was purchased from Nacalai Tesque, and $CrCl_2$ (99.99% purity, H_2O <100 ppm) was purchased from Sigma-Aldrich, respectively. Alkenes **1h**[1] and **1l**[2] were synthesized according to previously reported methods. ^1H (400 or 300 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using JEOL JNN-LA400 spectrometer. Proton chemical shifts are reported in ppm based on the solvent resonance resulting from incomplete deuteration ($CDCl_3$ at 7.26 ppm) as the internal standard. ^{13}C NMR spectra were recorded with complete proton decoupling and the chemical shifts were reported relative to $CDCl_3$ at 77.00 ppm. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sext: sextet, m: multiplet. Column chromatography was performed with silica gel 60N (neutral, 40-50 μm) purchased from Kanto Chemical. High-resolution mass spectra (HRMS) were obtained using JEOL JMS-700 MStation FAB-MS.

2. Preparation of 1-(*tert*-Butyl)-4-(4-penten-1-yl)benzene (1a). A mixture of magnesium turnings (534 mg, 22 mmol) in THF (4.0 mL) was added 4-bromo-1-butene (2.0 mL, 20 mmol) in THF (15 mL) dropwise over a period of 1 h at 25 °C. After stirring for 1 h, CuI (760 mg, 4.0 mmol) and 2,2'-bipyridyl (624 mg, 4.0 mmol) were added at 0 °C, and further stirred for 15 min. 4-(*tert*-Butyl)benzyl bromide (3.40 g, 15 mmol) in THF (15 mL) was slowly added, and the resulting mixture was stirred overnight at 25 °C. The reaction mixture was quenched with 1 N HCl *aq*. (20 mL), and organic solvent was removed under reduced pressure.

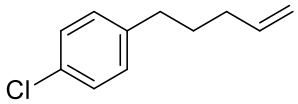


Extraction with EtOAc for three times (20 mL×3), and the combined organic extracts were dried over $MgSO_4$. After filtration, the organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel with hexane as the eluent afforded 1-(*tert*-butyl)-4-(4-penten-1-yl)benzene (**1a**) as a colorless oil (2.94 g, 15 mmol, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 1.72 (quint, J = 8.0 Hz, 2H), 2.11 (dt, J = 6.8, 8.0 Hz, 2H), 2.60 (t, J = 7.2 Hz, 2H), 4.98 (d, J = 10.4 Hz, 1H), 5.04 (dd, J = 1.6, 17.2 Hz, 1H), 5.85 (ddt, J = 7.2, 10.4, 17.2 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.6, 31.4, 33.4, 34.3, 34.8, 114.6, 125.1, 128.1, 138.7, 139.4, 148.4. HRMS (FAB^+): calcd for $C_{15}H_{22}$ ($[M]^+$) 202.1721; found. 202.1720.

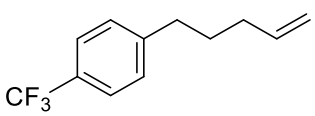


1-Methoxy-4-(4-penten-1-yl)benzene (1b): A mixture of magnesium turnings (534 mg, 22 mmol) in THF (4.0 mL) was added 4-bromo-1-butene (2.0 mL, 20 mmol) in THF (15 mL) dropwise over a period of 1 h at 25 °C, and stirred for 1 h. 4-Anisaldehyde (2.34 g, 17 mmol) was added slowly at 0 °C, and stirred at 25 °C for 30 min. The reaction mixture was quenched with 1 N HCl *aq*. (20 mL), and organic solvent was removed under reduced pressure. Extraction with EtOAc for three times (20 mL×3), and the combined organic extracts were dried over $MgSO_4$. After filtration, the organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1 ~ 5 / 1) afforded 1-(4-methoxyphenyl)-4-penten-1-ol as a colorless oil (3.11 g, 16 mmol, 94% yield). The analytical data matched those reported in the literature (Shi, L.; Horn, M.; Kobayashi, S.; Mayr, H. *Chem. Eur. J.* **2009**. *15*, 8533). A solution of 1-(4-methoxyphenyl)-4-penten- 1-ol (1.34 g, 7.0 mmol) in CH_2Cl_2 (20 mL) was added triethylsilane (2.2 mL, 14 mmol) at 0 °C. BF_3-Et_2O (1.7 mL, 14 mmol) was added dropwise, and stirred at 25 °C for 30 min. The reaction mixture was quenched with 1 N NaOH *aq*. (10 mL), and organic solvent was

removed under reduced pressure. Extraction with EtOAc for three times (15 mL × 3), and the combined organic extracts were dried over $MgSO_4$. After filtration, the organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (eluent: hexane / EtOAc = 50 / 1) afforded 1-methoxy-4-(4-penten-1-yl)benzene (**1b**) as a colorless oil (1.14 g, 6.4 mmol, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69 (quint, J = 7.6 Hz, 2H), 2.10 (dt, J = 7.2, 7.6 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 3.79 (s, 3H), 4.97 (d, J = 10.0 Hz, 1H), 5.03 (dd, J = 1.2, 16.8 Hz, 1H), 5.84 (ddt, J = 7.2, 10.0, 16.8 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.8, 33.2, 34.4, 55.2, 113.7, 114.6, 129.3, 134.5, 138.7, 157.7. The analytical data matched those reported in the literature ((a) C. Martín-Santos, C. Jarava-Barrera, S. del Pozo, A. Parra, S. Díaz-Tendero, R. Mas-Ballesté, S. Cabrera, J. Alemán, *Angew. Chem. Int. Ed.* 2014, **53**, 8184; (b) H. Shigehisa, T. Ano, H. Honma, K. Ebisawa, K. Hiroya, *Org. Lett.* 2016, **18**, 3622).

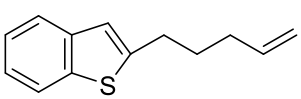


1-Chloro-4-(4-penten-1-yl)benzene (1c): Following the procedure for the synthesis of **1b** using 4-chlorobenzaldehyde (1.11 g, 7.9 mmol), 1.25 g (6.9 mmol, 88% yield (over 2 steps)) of **1c** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (quint, J = 7.6 Hz, 2H), 2.01 (q, J = 7.2 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 4.98 (d, J = 10.0 Hz, 1H), 5.03 (dd, J = 2.0, 17.6 Hz, 1H), 5.83 (ddt, J = 6.8, 10.0, 17.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.5, 33.1, 34.6, 114.9, 128.3, 129.8, 131.4, 138.3, 140.8. HRMS (FAB^+): calcd for $C_{11}H_{13}Cl$ ($[M]^+$) 180.0706; found. 180.0696.

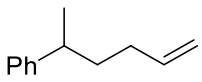


1-(4-Penten-1-yl)-4-(trifluoromethyl)benzene (1d): Following the procedure for the synthesis of **1b** using 4-trifluoromethyl benzaldehyde (1.46 g, 8.4 mmol), 1.65 g (7.7 mmol, 92% yield (over 2 steps)) of **1d** was

obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (quint, J = 7.6 Hz, 2H), 2.10 (q, J = 7.6 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 5.00 (d, J = 10.8 Hz, 1H), 5.03 (dd, J = 1.2, 16.8 Hz, 1H), 5.83 (ddt, J = 7.2, 10.8, 16.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.3, 33.1, 35.1, 115.1, 124.4 (q, J = 268.8 Hz), 125.2 (q, J = 3.8 Hz), 128.7, 128.1 (q, J = 32.4 Hz), 138.2, 146.5. HRMS (FAB$^+$): calcd for $C_{12}H_{14}F_3$ ($[M+H]^+$) 215.1048; found. 215.1053.



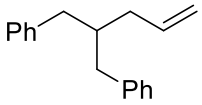
2-(4-Penten-1-yl)benzo[*b*]thiophene (1e): Following the procedure for the synthesis of **1b** using benzo[*b*]thiophen-2-carbaldehyde (1.49 g, 9.2 mmol), 1.47 g (7.3 mmol, 79% yield (over 2 steps)) of **1e** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (quint, J = 7.6 Hz, 2H), 2.17 (q, J = 7.2 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 4.99-5.03 (m, 1H), 5.03-5.08 (m, 1H), 5.84 (ddt, J = 6.8, 10.0, 16.8 Hz, 1H), 7.01 (s, 1H), 7.25 (dt, J = 1.2, 7.2 Hz, 2H), 7.30 (dt, J = 1.2, 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.0, 30.2, 33.0, 115.2, 120.6, 122.1, 122.7, 123.4, 124.0, 138.0, 139.3, 140.2, 146.3. HRMS (FAB$^+$): calcd for $C_{13}H_{14}S$ ($[M+H]^+$) 202.0816; found. 202.0816.



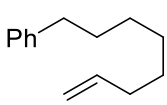
5-Hexen-2-ylbenzene (1f): A mixture of 2-phenylpropanal (3.40 g, 25.4 mmol) in benzene (50 mL) was added [(ethoxycarbonyl)methylene] triphenylphosphorane (8.46 g, 24 mmol), and stirred at 100 °C for 12 h. After cooling to 25 °C, the resulting mixture was diluted with Et_2O (100 mL), and silica gel (200 mg) was added. After stirring for 1 h, the reaction mixture was filtered, and the organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1) afforded ethyl (*E*)-4-phenylpent-2-enoate as a colorless oil (3.37 g, 17 mmol, 68% yield). The analytical data matched those reported in the literature (S. Kojima, J. Arimura, K. Kajiyama, *Chem. Lett.* 2010, **39**, 1138). A solution

of ethyl (*E*)-4-phenylpent-2-enoate (3.37 g, 17 mmol) in MeOH (50 mL) was added Pd/C (10 wt% on carbon, 529 mg, 0.50 mmol), and stirred under an H_2 atmosphere (1 atm) at 25 °C for 3 h. Filtration through a short silica gel pad followed by removal of organic solvent under reduced pressure afforded ethyl 4-phenylpentanoate as a colorless oil (3.40 g, 17 mmol, quant.). The analytical data matched those reported in the literature (J. Inagawa, S. Sakai, Y. Handa, M. Yamaguchi, Y. Yokoyama, *Chem. Lett*. 1991, **20**, 2117). To a solution of ethyl 4-phenylpentanoate (3.34 g, 16 mmol) in Et_2O (30 mL) was added a suspension of $LiAlH_4$ (672 mg, 18 mmol) in Et_2O (30 mL) at 0 °C. The resulting mixture was stirred at 25 °C for 30 min, and then quenched with H_2O (0.7 mL), aq. NaOH (15 wt%, 0.7 mL), and H_2O (2.1 mL). Filtration through a pad of Celite, and the solvent was removed under reduced pressure to afford 4-phenylpentan-1-ol as a colorless oil (2.61 g, 16 mmol, 98% yield). The analytical data matched those reported in the literature (A. C. Atesin, N. A. Ray, P. C. Stair, T. J. Marks, *J. Am .Chem. Soc*. 2012, **134**, 14682). To a mixture of 4-phenylpentan-1-ol (2.59 g, 16 mmol) and MS5A (2.0 g) in CH_2Cl_2 (30 mL) was added pyridinium chlorochromate (3.66 g, 17 mmol), and stirred at 25 °C for 2 h. Filtration through a short pad of basic alumina, and the solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1) afforded 4-phenylpentanal as a colorless oil (1.31 g, 8.1 mmol, 51% yield). The analytical data matched those reported in the literature (E. Larionov, L. Lin, L. Guénée, C. Mazet, *J. Am. Chem. Soc*. 2014, **136**, 16882). To a stirred mixture of methyltriphenylphosphonium bromide (5.81 g, 16 mmol) in toluene (30 mL) was added a solution of ^{t}BuOK (1.99 g, 16 mmol) in THF (20 mL) at 25 °C, and stirred for 3 h. A solution of 4-phenylpentanal (1.30 g, 8.0 mmol) in THF (3.0 mL) was added dropwise at 0 °C, and stirred at 25 °C for an additional 2 h. The resulting mixture was diluted with Et_2O (60 mL), and silica gel (120 mg) was added. After stirring for 1 h, the reaction mixture was filtered, and organic solvent was removed under reduced pressure.

Purification by flash column chromatography on silica gel with hexane as the eluent to afford 5-hexen-2-ylbenzene (**1f**) as a colorless oil (884 mg, 5.5 mmol, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (d, J = 6.8 Hz, 3H), 1.64-1.71 (m, 2H), 1.97 (dt, J = 7.6 Hz, 2H), 2.72 (sext, J = 7.2 Hz, 1H), 4.92-5.00 (m, 2H), 5.80 (ddt, J = 6.4, 10.4, 17.2 Hz, 1H), 7.17-7.20 (m, 3H), 7.30 (t, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 31.8, 37.5, 39.3, 114.4, 125.9, 127.0, 128.3, 138.8, 147.4. HRMS (FAB^+): calcd for $C_{12}H_{16}$ ($[M]^+$) 160.1250; found. 160.1252.

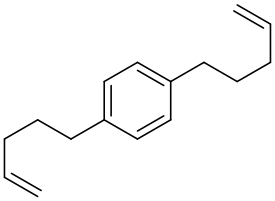


(2-Allyl-1,3-diphenyl)propane (1g): Following the procedure for the synthesis of **1f** (Wittig olefination of diphenylacetone with [(ethoxycarbonyl)methylene]triphenylphosphorane (43% yield), hydrogenation (quant.), reduction with $LiAlH_4$ (quant.), oxidation with TEMPO (67% yield), Wittig olefination with methyltriphenylphosphonium bromide (82% yield)), **1g** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (q, J = 6.4 Hz, 2H), 2.07 (sext, J = 6.4 Hz, 1H), 2.57 (d, J = 7.6 Hz, 2H), 2.58 (d, J = 7.6 Hz, 2H), 5.03 (d, J = 16.8 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H), 5.76-5.87 (ddt, J = 6.4, 10.0, 16.8 Hz, 1H), 7.14 (d, J = 7.2 Hz, 4H), 7.19 (t, J = 7.2 Hz, 2H), 7.28 (t, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.0, 39.7, 41.8, 116.7, 125.8, 128.2, 129.2, 136.7, 140.0. HRMS (FAB^+): calcd for $C_{18}H_{20}$ ($[M]^+$) 236.1565; found. 236.1567.

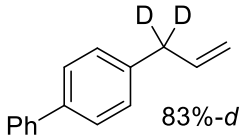


8-Phenyl-1-octene (1i): Following the procedure for the synthesis of **1a** using 1-bromo-5-phenylpentane (2.03 g, 9.1 mmol), allylmagnesium bromide (prepared from the reaction of allyl bromide (2.16 g, 18 mmol) with magnesium turnings (500 mg, 21 mmol) in THF (20 mL) at 25 °C), CuI (285 mg, 1.5 mmol), and 2,2'-bipyridine (234 mg, 1.5 mmol), 1.37 g (7.2 mmol, 80% yield) of **1i** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36-1.43 (m, 6H), 1.63 (quint, J = 7.6 Hz,

2H), 2.05 (q, J = 6.8 Hz, 2H), 2.61 (t, J = 7.6 Hz, 2H), 4.94 (dd, J = 1.2, 10.0 Hz, 1H), 4.99 (dd, J = 1.2, 17.4 Hz, 1H), 5.82 (ddt, J = 6.8, 10.0, 18.8 Hz, 1H), 7.16-7.19 (m, 3H), 7.27-7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 29.0, 29.1, 31.4, 33.8, 35.9, 114.2, 125.6, 128.2, 128.4, 139.1, 142.9. The analytical data matched those reported in the literature (M. Uemura, H. Yorimitsu, K. Oshima, *Chem. Commun.* 2006, 4726; (b) A. J. Kennedy, T. P. Mathews, Y. Kharel, S. D. Field, M. L. Moyer, J. E. East, J. D. Houck, K. R. Lynch, T. L. Macdonald, *J. Med. Chem.* 2011, **54**, 3524).



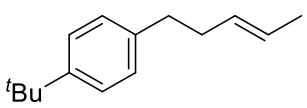
1,4-Di(4-penten-1-yl)benzene (1j): Following the procedure for the synthesis of **1b** using terephthalaldehyde (1.34 g, 10 mmol), 1.74 g (8.1 mmol, 81% yield of **1j** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71 (quint, J = 7.6 Hz, 2H), 2.10 (q, J = 7.6 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 5.14 (dd, J = 1.2, 10.0 Hz, 1H), 5.19 (dd, J = 1.2, 17.2 Hz, 1H), 5.84 (ddt, J = 7.6, 10.0, 17.2 Hz, 1H), 7.10 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.7, 33.3, 34.9, 114.6, 128.3, 138.7, 139.7. The analytical data matched those reported in the literature ((a) N. F. Sauty, L. C. da Silva, C. Gallagher, R. Graf, K. B. Wagener, *Polym. Chem.* 2015, **6**, 6073; (b) S. Huang, J. M. Tour, *J. Org. Chem.* 1999, **64**, 8898).



4-Allyl-1,1'-biphenyl-d_2 (1k-*d*): A mixture of NaOH (1.2 g, 30 mmol) in D_2O (20 mL) was treated with 2-([1,1'-biphenyl]-4-yl)acetic acid (4.24 g, 20 mmol), and stirred at 120 °C for 12 h. The reaction mixture was quenched with 1 N HCl *aq*. (30 mL), and extracted with EtOAc for three times (30 mL×3). The combined organic extracts were dried over $MgSO_4$, and filtered. Removal of the organic solvent afforded 2-([1,1'-biphenyl]-4-yl)acetic acid-d_2 as a colorless oil (4.24 g, 20 mmol, quant. (95%-*d* content)). A mixture of NaOH (1.2 g, 30 mmol) in D_2O (20 mL) was treated with 2-([1,1'-biphenyl]-4-yl)acetic acid (4.24 g, 20

mmol), and stirred at 120 °C for 12 h. The reaction mixture was quenched with 1 N HCl *aq*. (30 mL), and extracted with EtOAc for three times (30 mL × 3). The combined organic extracts were dried over $MgSO_4$, and filtered. Removal of the organic solvent afforded 2-([1,1'-biphenyl]-4-yl)acetic acid-d_2 as a colorless oil (4.16 g, 20 mmol, 98% yield (98%-*d* content)). To a solution of 2-([1,1'-biphenyl]-4-yl)acetic acid-d_2 (4.16 g, 20 mmol) in Et_2O (30 mL) was added a suspension of $LiAlH_4$ (759 mg, 20 mmol) in Et_2O (30 mL) at 0 °C. The resulting mixture was stirred at 25 °C for 30 min, and then quenched with H_2O (0.8 mL), aq. NaOH (15 wt%, 0.8 mL), and H_2O (2.4 mL). Filtration through a pad of Celite, and the solvent was removed under reduced pressure to afford 2-([1,1'-biphenyl]-4-yl)ethanol-d_2 as a colorless oil (3.89 g, 20 mmol, 98% yield, 98%-*d* content). To a mixture of 2-([1,1'-biphenyl]-4-yl)ethanol-d_2 (991 mg, 5.0 mmol) in DMSO (30 mL) was added IBX (2.80 g, 13 mmol), and stirred at 25 °C for 3 h. Filtration through a short pad of silica gel, and the solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1) afforded 2-([1,1'-biphenyl]-4-yl)acetaldehyde-d_2 as a colorless oil (442 mg, 2.3 mmol, 45% yield, 98%-*d* content). To a stirred mixture of methyltriphenylphosphonium bromide (2.36 g, 6.6 mmol) in THF (30 mL) was added a solution of ^{n}BuLi (1.66 M in hexane, 1.3 mL, 2.2 mmol) at -78 °C, and stirred for 3 h. A solution of 2-([1,1'-biphenyl]-4-yl)acetaldehyde-d_2 (431 mg, 2.2 mmol) in THF (3.0 mL) was added dropwise at 0 °C, and stirred for 30 min. The resulting mixture was diluted with Et_2O (20 mL), and silica gel (100 mg) was added. After stirring for 30 min, the reaction mixture was filtered, and organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel with hexane as the eluent to afford 4-allyl-1,1'-biphenyl-d_2 (**1k**-*d*) as a colorless oil (302 mg, 1.5 mmol, 70% yield, 83%-*d* content). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.44 (d, J = 6.4 Hz, 0.34H), 5.10 (d, J = 10.0 Hz, 1H), 5.14 (d, J = 16.8 Hz, 1H), 6.09 (ddt, J = 6.4, 10.0, 16.8 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz,

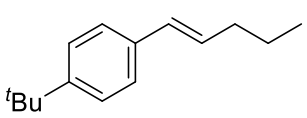
2H), 7.54 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ39.5 (quint, J = 19.1 Hz), 115.9, 127.0 (two peaks overlapped), 127.2, 128.7, 129.0, 137.2, 139.1 (two peaks overlapped), 141.0. The analytical data matched those reported in the literature (S. M. M. Knapp, S. E. Shaner, D. Kim, D. Y. Shopov, J. A. Tendler, D. M. Pudalov, A. R. Chiamese, *Organometallics* 2014, **33**, 473).



(*E*)-1-(*tert*-Butyl)-4-(3-penten-1-yl)benzene (*E*-4a)): Following the procedure of Wittig olefination, hydrogenation, and reduction with $LiAlH_4$ for the synthesis of **1f** using 4-*tert*-butylbenzaldehyde (6.48 g, 40 mmol), 4.76 g (24.8 mmol, 62% yield (over 3 steps) of 3-(4-(*tert*-butyl)phenyl)propan-1-ol was obtained as a colorless oil. The analytical data matched those reported in the literature (K. Muñiz, H. Zhang, *ACS Catal*. 2017, **7**, 4122). To a mixture of 3-(4-(*tert*-butyl)-phenyl)propan-1-ol (4.76 g, 25.0 mmol), TEMPO (780 mg, 5.0 mmol) in CH_2Cl_2 (30 mL) was added iodobenzene diacetate (9.66 g, 30 mmol), and stirred at 25 °C for 30 min. The resulting mixture was quenched with *sat.* sodium thiosulfate *aq*. (200 mL), and extracted with EtOAc for three times (30 mL×3). The combined organic extracts were dried over $MgSO_4$, filtered, and the organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (eluent: hexane / EtOAc = 20 / 1) afforded 3-(4-(*tert*-butyl)phenyl)propanal as a colorless oil (4.23 g, 23 mmol, 89% yield). The analytical data matched those reported in the literature (E. Larionov, L. Lin, L. Guénée, C. Mazet, *J. Am. Chem. Soc*. 2014, **136**, 16882). To a stirred mixture of ethyltriphen ylphosphonium bromide (7.43 g, 20 mmol) in THF (60 mL) was added ^{n}BuLi (1.66 M in hexane, 24.1 mL, 40 mmol) at -78 °C, and stirred for 3 h. A solution of 3-(4-(*tert*-butyl)phenyl)propanal (3.61 g, 19 mmol) in THF (5.0 mL) was added dropwise, and the resulting mixture was stirred for and additional 1 h. The reaction mixture was diluted with Et_2O (200 mL), and silica gel (200 mg) was added. After stirring for 1 h, the

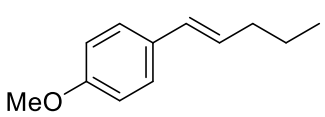
reaction mixture was filtered, and organic solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel with hexane as the eluent gave 1-(*tert*-butyl)-4-(3-penten-1-yl)benzene as a mixture of two stereoisomers (2.89 g, 14 mmol, 75% yield). Further purification by silver ion chromatography[3] afforded (*E*)-1-(*tert*-butyl)-4-(3-penten-1-yl)benzene (*E*-**4a**) as a colorless oil (1.33 g, 6.6 mmol, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 1.60 (d, J = 4.8 Hz, 3H), 2.38 (dt, J = 5.2, 9.2 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 5.48-5.49 (m, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.7, 28.7, 31.4, 34.3, 35.2, 124.4, 125.1, 128.0, 129.9, 139.1, 148.5. HRMS (FAB^+): calcd for $C_{15}H_{22}$ ($[M]^+$) 202.1722; found. 202.1721.

3. General Procedure for Palladium-Catalyzed Double Bond Migration of Olefins. A flame-dried Schlenk tube was charged with $PdCl_2$ (1.1 mg, 6.0 μmol), $TaCl_5$ (4.3 mg, 12 μmol) and THF (0.60 mL). After stirring for 5 min, terminal alkene **1** (0.30 mmol) was added, and the mixture was stirred at the temperature specified in the text for 12 or 24 h. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexane / EtOAc as eluents to afford the corresponding internal alkenes **2** as a mixture of their constitutional isomers.

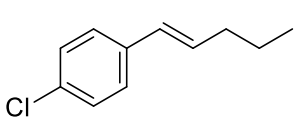


(*E*)-1-(*tert*-Butyl)-4-(1-penten-1-yl)benzene (2a): Following the general procedure using **1a** (60.6 mg, 0.30 mmol) at 60 °C for 24 h, 59.4 mg of a mixture of **2a** (0.28 mmol, 94% yield) and its constitutional isomer, 1-(*tert*-butyl)-4-(3-penten-1-yl)benzene (**4a**) (0.012 mmol, 4% yield) was obtained. The stereoselectivity of **4a** was determined to be E / Z = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, J = 7.6 Hz, 3H), 1.32 (s, 9H), 1.49 (sext, J = 7.2 Hz, 2H), 2.18 (q, J = 7.2 Hz, 2H), 6.19 (dt, J = 7.2, 15.2 Hz, 1H), 6.36 (d, J = 15.6 Hz, 1H), 7.28-7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 22.6, 31.3, 34.5,

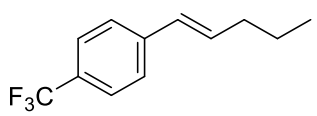
35.1, 125.0, 125.6, 129.6, 130.2, 135.2, 149.7. The analytical data matched those reported in the literature (N. Zhu, J. Zhao, H. Bao, *Chem. Sci.* 2017, **8**, 2081).



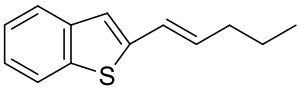
(*E*)-1-Methoxy-4-(1-penten-1-yl)benzene (2b): Following the general procedure using **1b** (52.8 mg, 0.30 mmol) at 100 °C for 24 h, 52.3 mg of mixture of **2b** (0.20 mmol, 65% yield) and its constitutional isomer, 1-methoxy-4-(3-penten-1-yl)benzene (**4b**) (0.10 mmol, 34% yield) was obtained. The stereoselectivity of **2b** was determined to be *E* / *Z* = >99 / 1, **4b** was determined to be *E* / *Z* = 74 / 26 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.48 (sext, *J* = 7.2 Hz, 2H), 2.16 (dt, *J* = 6.8, 7.2 Hz, 2H), 3.80 (s, 3H), 6.08 (dt, *J* = 6.8 Hz, 15.6 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 22.7, 35.1, 55.3, 113.9, 126.9, 128.8, 129.2, 130.8, 158.6. The analytical data matched those reported in the literature (S. M. Stevenson, M. P. Shores, E. M. Ferreira, *Angew. Chem. Int. Ed.* 2015, **54**, 6506).



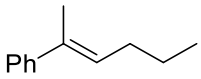
(*E*)-1-Chloro-4-(1-penten-1-yl)benzene (2c): Following the general procedure using **1c** (54.0 mg, 0.30 mmol) at 60 °C for 12 h, 50.7 mg of mixture of **2c** (0.27 mmol, 89% yield) and its constitutional isomer, 1-chloro-4-(3-penten-1-yl)benzene (**4c**) (0.015 mmol, 5% yield) was obtained. The stereoselectivity of **2c** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.50 (sext, *J* = 7.2 Hz, 2H), 2.19 (q, *J* = 6.4 Hz, 2H), 6.21 (dt, *J* = 7.6, 15.6 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 7.23-7.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 22.4, 35.1, 127.1, 128.6, 128.7, 131.7, 132.3, 136.4. The analytical data matched those reported in the literature (Z.-Y. Peng, F.-F. Ma, L.-F. Zhu, X.-M. Xie, Z. Zhang, *J. Org. Chem.* 2009, **74**, 6855).



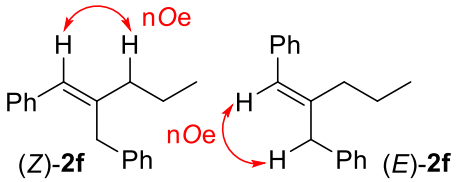
(*E*)-1-(1-Penten-1-yl)-4-(trifluoromethyl)benzene (2d): Following the general procedure using **1d** (64.2 mg, 0.30 mmol) at 60 °C for 12 h, 61.6 mg of mixture of **2d** (0.28 mmol, 92% yield) and its constitutional isomer, 1-(3-penten-1- yl)-4-(trifluoromethyl)benzene (0.012 mmol, 4% yield) was obtained. The stereoselectivity of **2d** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.6 Hz, 3H), 1.52 (quint, *J* = 7.6 Hz, 2H), 2.22 (q, *J* = 7.2 Hz, 2H), 6.33 (dt, *J* = 7.2, 16.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz), 7.42 (d, *J* = 8.4 Hz, 2), 7.54 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.4, 35.2, 124.2 (q, *J* = 276.5 Hz), 125.4 (q, *J* = 3.8 Hz), 126.0, 128.6 (q, *J* = 31.5 Hz), 128.7, 133.8, 141.4. The analytical data matched those reported in the literature (G. W. Kabalka, D. Tejedor, N.-S. Li, R. R. Malladi, S. Trotman, *Tetrahedron* 1998, **54**, 15525).



(*E*)-2-(1-Penten-1-yl)benzo[*b*]thiophene (2e): Following the general procedure using **1e** (60.6 mg, 0.30 mmol) at 60 °C for 12 h, 58.2 mg of mixture of **2e** (0.28 mmol, 94% yield) and its constitutional isomer, 2-(3-penten-1-yl)benzo[*b*]thiophene (0.0060 mmol, 2% yield) was obtained. The stereoselectivity of **2e** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.74 (q, *J* = 7.6 Hz, 2H), 2.43 (q, *J* = 7.6 Hz, 2H), 6.39 (dt, *J* = 6.8, 15.6 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 7.26 (s, 1H), 7.47 (dt, *J* = 1.6, 7.2 Hz, 1H), 7.51 (dt, *J* = 1.6, 7.2 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 22.3, 35.0, 121.1, 122.1, 123.1, 123.9, 124.2, 124.3, 133.9, 138.5, 140.3, 143.3. The analytical data matched those reported in the literature ((a) B. Gabriele, R. Mancuso, E. Lupinacci, L. Veltri, G. Salerno, C. Carfagna, *J. Org. Chem.* 2011, **76**, 8277; (b) A. J. Eberhart, H. Shrives, Y. Zhang, A. Carrër, A. V. S. Parry, D. J. Tate, M. L. Turner, D. J. Procter, *Chem. Sci.* 2016, **7**, 1281).

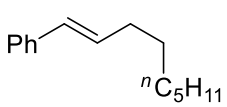


(*E*)-2-Hexene-2-ylbenzene (2f): Following the general procedure using **1f** (48.0 mg, 0.30 mmol) at 120 °C in 2-MeTHF for 12 h, 44.2 mg of mixture of **2f** (0.26 mmol, 85% yield) and its constitutional isomer, 1-hexene-2-ylbenzene **2f'** (0.021 mmol, 7% yield) and 4-hexene-2-ylbenzene (0.021 mmol, 7% yield) was obtained. The stereoselectivity of **2f** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.48 (quint, *J* = 7.2 Hz, 2H), 2.03 (s, 3H), 2.18 (q, *J* = 7.2 Hz, 2H), 5.79 (t, *J* = 7.2 Hz, 1H), 7.19-7.23 (m, 1H), 7.28-7.32 (m, 2H), 7.37-7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 15.8, 22.8, 30.8, 125.6, 126.4, 128.1, 128.6, 134.3, 143.7. The analytical data matched those reported in the literature ((a) Q. Sha, Y. Ling, W. Wang, Y. Wei, *Adv. Synth. Catal.* 2013, **355**, 2145; (b) M. Brown, R. Kumar, J. Rehbein, T. Wirth, *Chem. Eur. J.* 2016, **22**, 4030).

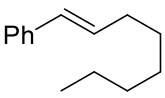


1,3-Diphenyl-2-propylpropene (2g): Following the general procedure using **1g** (70.8 mg, 0.30 mmol) at 60 °C for 12 h, 63.0 mg of mixture of **2g** (0.26 mmol, 85% yield) and its constitutional isomer, 1,3-diphenyl-2-(propylidene)propane (0.012 mmol, 4% yield) was obtained. The stereoselectivity of **2g** was determined to be *E* / *Z* = 57 / 43 by ^{1}H NMR analysis of the crude product. Stereoisomers of **2g** can be separable by flash column chromatography on silica gel with hexane as the eluent. ^{1}H NMR for (*E*)-**2g** (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.52 (sext, *J* = 7.6 Hz, 2H), 2.06 (t, *J* = 7.2 Hz, 2H), 3.62 (s, 2H), 6.53 (s, 1H), 7.19-7.22 (m, 5H), 7.28-7.31 (m, 5H). ^{13}C NMR for (*E*)-**2g** (100 MHz, $CDCl_3$): δ 14.6, 21.5, 35.2, 42.9, 125.8, 125.9, 128.2, 128.3, 128.7, 129.1, 130.4, 136.6, 140.0, 140.3. ^{1}H NMR for (*Z*)-**2g** (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.6 Hz, 3H), 1.51 (sext, *J* = 7.6 Hz, 2H), 2.16 (t, *J* = 7.6 Hz, 2H), 3.50 (s, 2H), 6.33 (s, 1H), 7.18-7.26 (m, 5H), 7.27-7.34 (m, 5H). ^{13}C NMR for (*Z*)-**2g** (100 MHz, $CDCl_3$): δ 14.1,

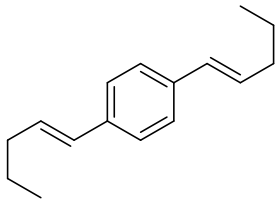
21.5, 32.4, 43.8, 126.06, 126.09, 127.3, 128.1, 128.3, 128.7, 129.1, 138.3, 140.0, 142.6. HRMS (FAB^+): calcd for $C_{18}H_{20}$ ($[M]^+$) 236.1565; found. 236.1565.



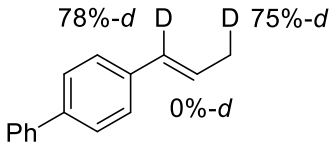
(*E*)-1-Phenyl-1-nonene (2h): Following the general procedure using **1h** (56.4 mg, 0.30 mmol) at 100 °C for 24 h, 38.4 mg of **2h** (0.20 mmol, 68% yield) was obtained as a colorless oil after purification by HPLC with hexane as an eluent. The stereoselectivity of **2h** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.27-1.39 (m, 8H), 1.47 (quint, *J* = 7.2 Hz, 2H), 2.21 (q, *J* = 6.8 Hz, 2H), 6.23 (dt, *J* = 6.8, 15.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 28.9, 29.3, 31.7, 33.0, 125.9, 126.7, 128.4, 129.6, 131.3, 137.9. The analytical data matched those reported in the literature ((a) A. Rimkus, N. Sewald, *Org. Lett.* 2002, **4**, 3289. (b) C. Thiot, M. Schmutz, A. Wagner, C. Mioskowski, *Chem. Eur. J.* 2007, **13**, 8971).



(*E*)-1-Phenyl-1-octene (2i): Following the general procedure using **1i** (60.6 mg, 0.30 mmol), $PdCl_2$ (2.7 mg, 15 μmol), and $TaCl_5$ (10.7 mg, 30 μmol) at 100 °C for 24 h, 44.8 mg of **2i** (0.22 mmol, 74% yield) was obtained as a colorless oil after purification by HPLC with hexane as an eluent. The stereoselectivity of **2i** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.6 Hz, 3H), 1.29-1.34 (m, 6H), 1.47 (quint, *J* = 7.6 Hz, 2H), 2.21 (q, *J* = 6.8 Hz, 2H), 6.23 (dt, *J* = 6.4, 15.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 7.19 (t, *J* = 6.8 Hz, 1H), 7.28 (t, *J* = 6.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 29.2, 29.4, 31.8, 33.0, 125.9, 126.7, 128.4, 129.6, 131.3, 137.9. The analytical data matched those reported in the literature (G. Cahiez, O. Gager, F. Lecomte, *Org. Lett.* 2008, **10**, 5255).



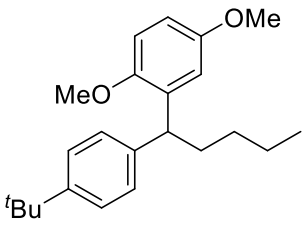
1,4-Di((*E*)-1-penten-1-yl)benzene (2j): Following the general procedure using **1j** (64.2 mg, 0.30 mmol) at 60 °C for 12 h, 53.9 mg of **2j** (0.25 mmol, 84% yield) was obtained as a colorless oil after purification by HPLC with hexane as an eluent. The stereoselectivity of **2j** was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.49 (q, *J* = 7.6 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 6.21 (dt, *J* = 6.8, 15.6 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 7.20-7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 22.5, 35.1, 126.0, 129.6, 130.4, 136.5. HRMS (FAB^+): calcd for $C_{16}H_{22}$ ($[M]^+$) 214.1722; found. 214.1711.



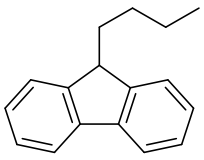
(*E*)-4-(1-Propen-1-yl)-1,1'-biphenyl-*d* (2k-*d*): Following the general procedure using **1k**-*d* (58.9 mg, 0.30 mmol) at 60 °C for 12 h, 57.1 mg of **2k**-*d* (0.29 mmol, 97% yield) was obtained as a colorless oil. The stereoselectivity of **2k**-*d* was determined to be *E* / *Z* = >99 / 1 by ^{1}H NMR analysis of the crude product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87-1.92 (m, 2.2H), 6.26-6.32 (m, 1H), 6.44 (d, *J* = 15.6 Hz, 0.22H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.39-7.45 (m, 4H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H). The analytical data matched those reported in the literature (S. M. M. Knapp, S. E. Shaner, D. Kim, D. Y. Shopov, J. A. Tendler, D. M. Pudalov, A. R. Chiamese, *Organometallics* 2014, **33**, 473).

4. General Procedure for Palladium-Catalyzed Sequential Migration and Hydroarylation of Terminal Alkynes

2-(1-(4-*tert*-Butylphenyl)pentyl)-1,4-dimethoxybenzene (5a): A flame-dried Schlenk tube was charged with $PdCl_2$ (2.7 mg, 15 μmol) and $FeCl_3$ (4.9 mg, 30 μmol), and THF (2.0 mL). After stirring for 10 min, 5-(4-*tert*-butylphenyl)-1-pentene (**1a**) (60.7 mg, 0.30 mmol) was added, and further stirred at 100 °C for 24 h. The reaction mixture was cooling



to 25 °C, and the solvent was removed under reduced pressure. 1,4-Dimethoxybenzene (414 mg, 3.0 mmol) was added, and stirred at 100 °C for 24 h. The residue was directly subjected to flash column chromatography on silica gel (eluent: hexane / EtOAc = 50 / 1 to 20 / 1) to afford **5a** as a colorless oil (86.0 mg, 0.25 mmol, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, J = 7.2 Hz, 3H), 1.22-1.36 (m, 4H), 1.28 (s, 9H), 1.97 (q, J =7.2 Hz, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.35 (t, J = 8.0 Hz, 1H), 6.66 (dd, J = 2.8, 8.4 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 2.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.7, 30.2, 31.4, 34.3, 34.9, 42.5, 55.6, 56.3, 110.2, 111.8, 114.8, 125.0, 127.6, 135.6, 141.9, 148.3, 151.5, 153.6. HRMS (FAB$^+$): calcd for $C_{23}H_{32}O_2$ ([M]$^+$) 340.2402; found. 340.2402.



9-Butyl-9*H*-fluorene (5b): A flame-dried Schlenk tube was charged with $PdCl_2$ (2.7 mg, 15 μmol) and $FeCl_3$ (4.9 mg, 30 μmol), and THF (2.0 mL). After stirring for 10 min, 2-(4-penten-1-yl)-1,1'-biphenyl (66.6 mg, 0.30 mmol) was added, and further stirred at 100 °C for 24 h. The reaction mixture was cooling to 25 °C, and the solvent was removed under reduced pressure. 1,2-Dichloroethane (1.0 mL) was added, and further stirred at 80 °C for 24 h. The residue was directly subjected to flash column chromatography on silica gel (eluent: hexane / EtOAc = 50 / 1 ~ 20 / 1) to afford **5b** as a colorless oil (86.0 mg, 0.25 mmol, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, J = 7.2 Hz, 3H), 1.14-1.20 (m, 2H), 1.24-1.31 (m, 2H), 1.98-2.03 (m, 2H), 3.98 (t, J = 6.4 Hz, 1H), 7.28-7.22 (m, 2H), 7.33-7.39 (m, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 23.0, 27.8, 32.8, 47.5, 119.7, 124.3, 126.75, 126.80, 141.1, 147.6. The analytical data matched those reported in the literature (J. Chen, Y. Li, S. Li, J. Liu, F. Zheng, Z. Zhang, Q. Xu, *Green Chem.* 2017, **19**, 623).

5. References

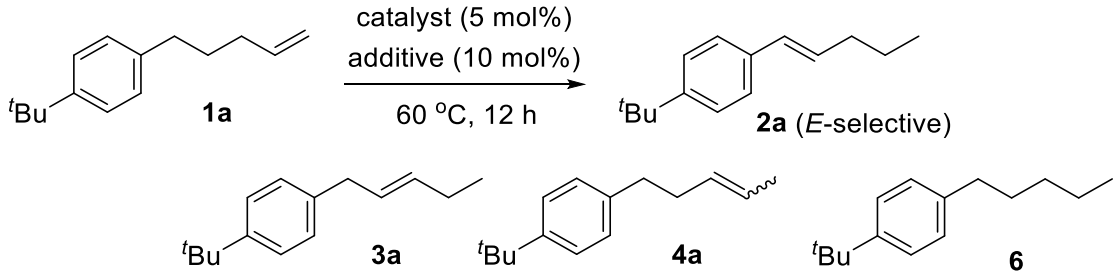
1. C. M. Williams, L. N. Mander, *Tetrahedron* 2001, **57**, 425.

2. J. Waser, B. Gaspar, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* 2006, **128**, 11693.

3. C. M. Williams, L. N. Mander, *Tetrahedron* 2001, **57**, 425.

6. Optimization of Reaction Conditions

Table S1. Effect of additives and solvents



entry	catalyst	additive	Yield / % (*E* / *Z*)[a] 2a	3a	4a	6
1	$PdCl_2$	——	76	<1	22 (78 / 22)	0
2	$PdBr_2$	——	48	11 (81 / 19)	26 (65 / 35)	0
3	$Pd(OAc)_2$	——	0	0	0	0
4	$PdCl_2(PPh_3)_2$	——	0	0	0	0
5	$NiCl_2$	——	0	0	0	0
6	$TaCl_5$	——	0	0	0	0
7	$PdCl_2$	$TaCl_5$	96	<1	4	0
8	$PdCl_2$	WCl_6	69	<1	27 (60 / 40)	0
9	$PdCl_2$	$ReCl_5$	46	4	36 (76 / 24)	0
10	$PdCl_2$	$FeCl_3$	89	<1	11 (71 / 29)	0
11	$PdCl_2$	$Fe(OTf)_3$	84	<1	12 (74 / 26)	0
12	$PdCl_2$	$NiCl_2$	33	<1	26 (71 / 29)	0
13	$PdCl_2$	$ZnCl_2$	65	<1	35 (70 / 30)	0
14[b]	$PdCl_2$	$TaCl_5$	87	<1	12 (72 / 28)	0
15[c]	$PdCl_2$	$TaCl_5$	96	<1	4	0
16[d]	$PdCl_2$	$TaCl_5$	94	<1	5	0

[a]Determined by ^{1}H NMR. [b]5 mol% or [c]20 mol% of $TaCl_5$ was used. [d]$PdCl_2$ (2 mol%), $TaCl_5$ (4 mol%) for 24 h.

7. Possible Alternative Reaction Mechanism

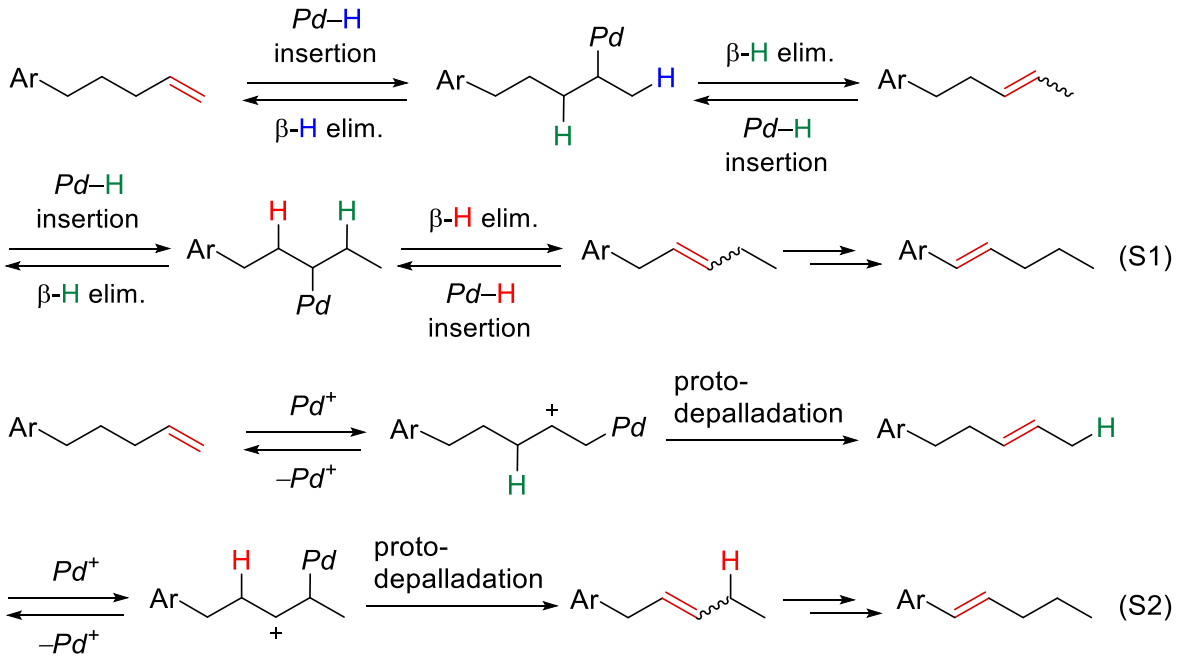
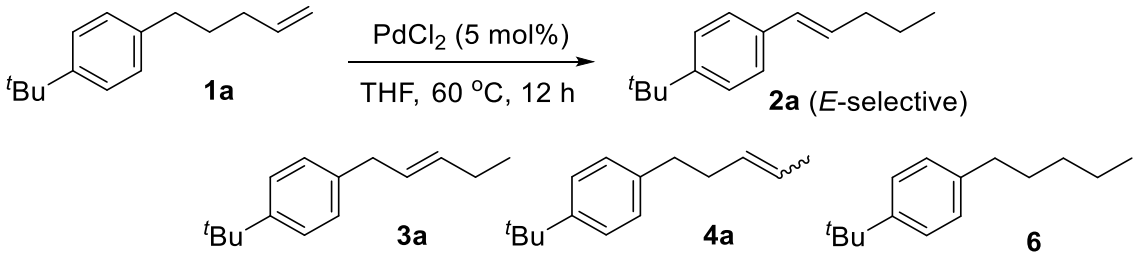


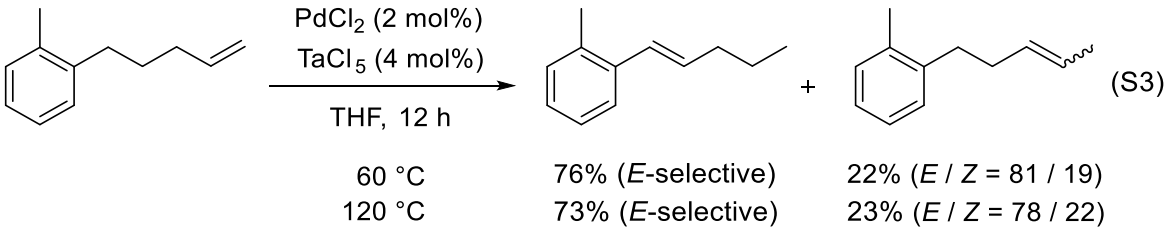
Table S2. Migration of olefinic double bond of **1a** using $PdCl_2$ from various commercial suppliers



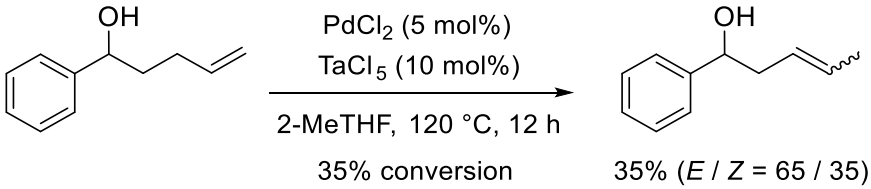
entry	$PdCl_2$	Yield / % (*E* / *Z*)[a]			
		2a	**3a**	**4a**	**6**
1	99.9% (Wako, 168-13561)	76	<1	22 (78 / 22)	0
2	>99.9% (Aldrich, 520659)	76	<1	21 (75 / 25)	0
3	99% (Aldrich, 205885)	80	<1	16 (75 / 25)	0
4	99.9% (STREM, 46-1850)	79	<1	21 (70 / 30)	0
5	>98% (TCI, P1489)	70	<1	24 (75 / 25)	0
6[b]	>59%-Pd/$PdCl_2$ (Nacalai Tesque)	80	<1	19 (76 / 24)	0

[a]Determined by ^{1}H NMR. [b]Manufactured in March, 1989, and the bottle was freshly opened in June, 2018. ">59%-Pd/$PdCl_2$" means ">98% $PdCl_2$ content".

8. Double Bond Migration of Other Olefins



(S3)



(S4)

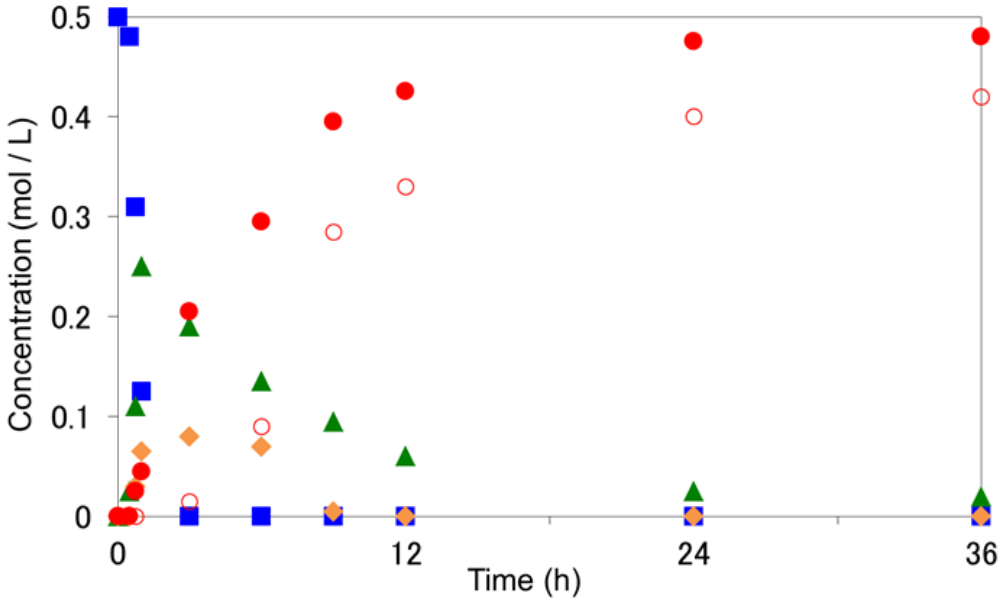
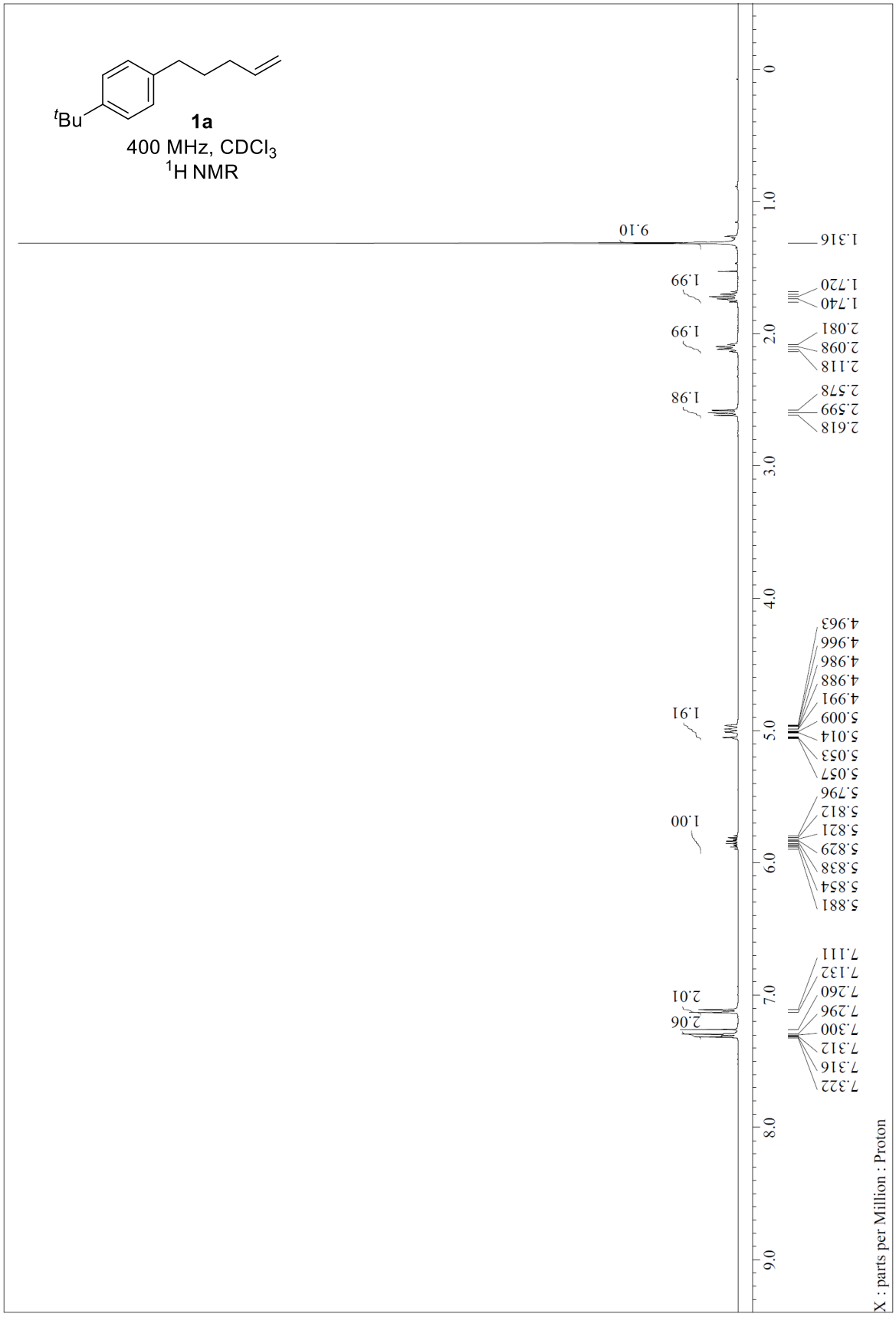
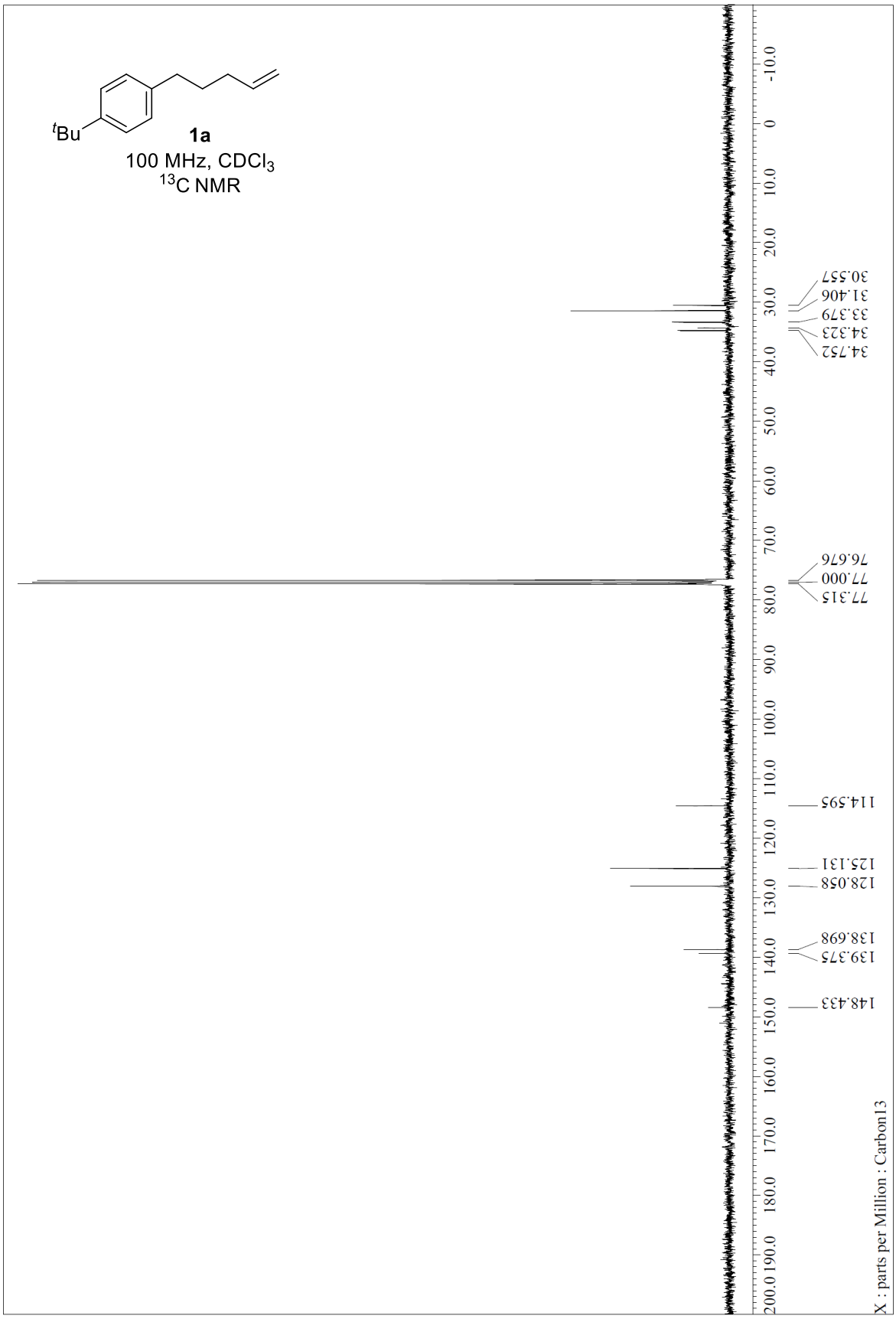


Figure S1. Reaction profile for migration of **1a** under the conditions in Table 2, entry 1 (**1a** (■), **2a** (●), **3a** (◆), **4a** (▲)). Time change curve for the formation of **2a** using only $PdCl_2$ is shown with ○.

9. Copies of ^{1}H NMR and ^{13}C NMR Spectra

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34.323
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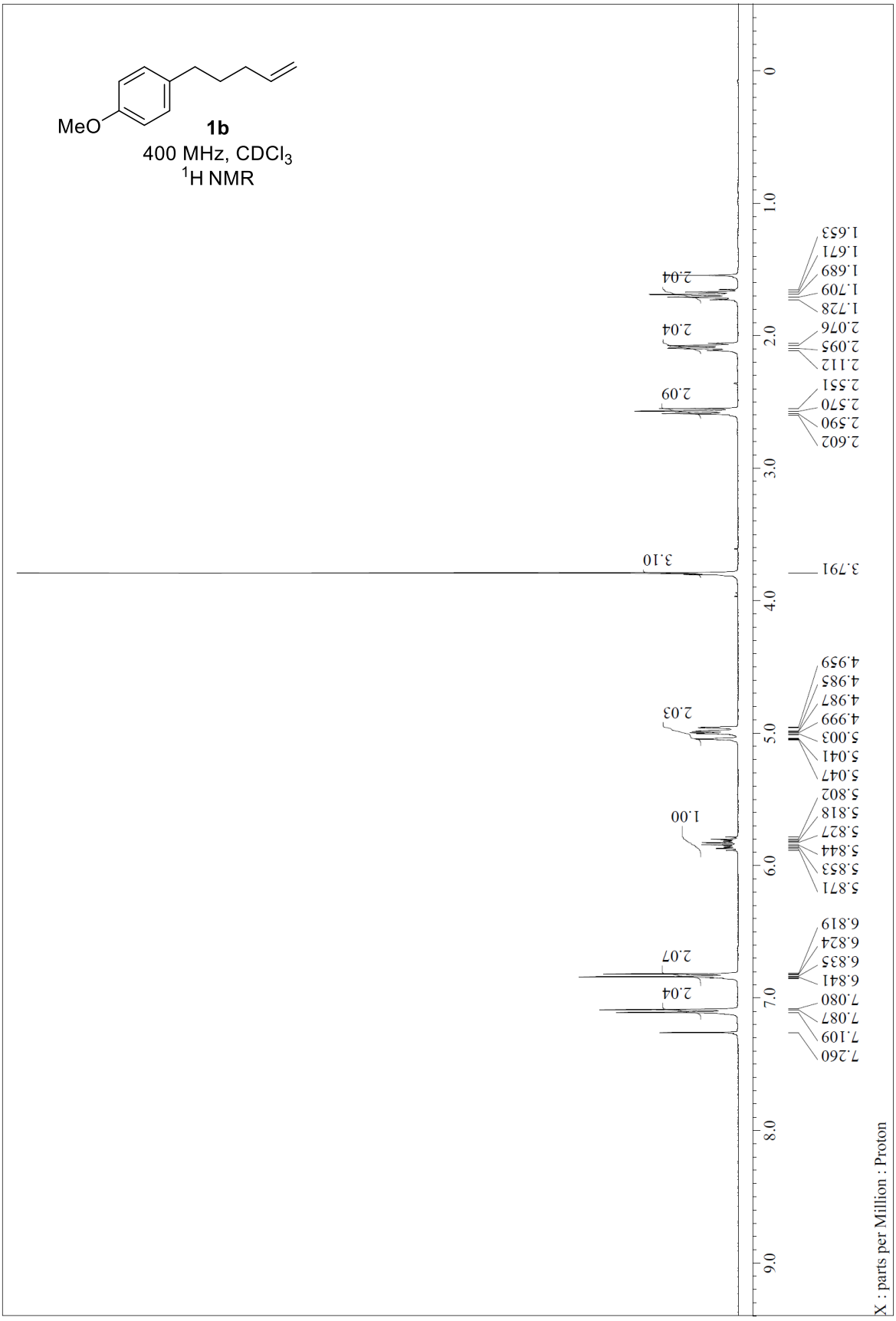
114.595
125.131
128.058
138.698
139.375
148.433
X : parts per Million : Carbon13


MeO
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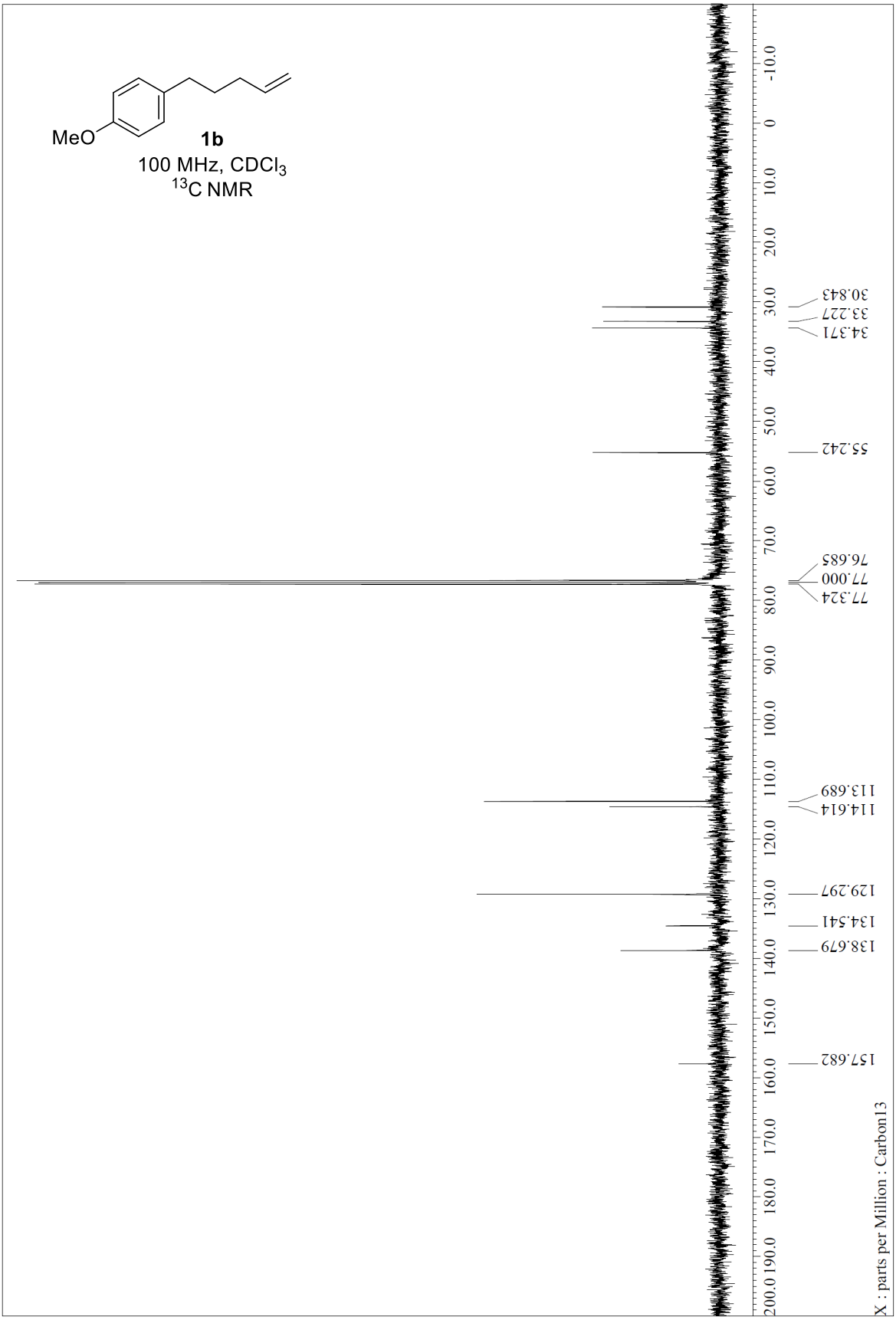
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton


MeO
1b
100 MHz, CDCl3
13C NMR
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34.371
55.242
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77.000
77.324
113.689
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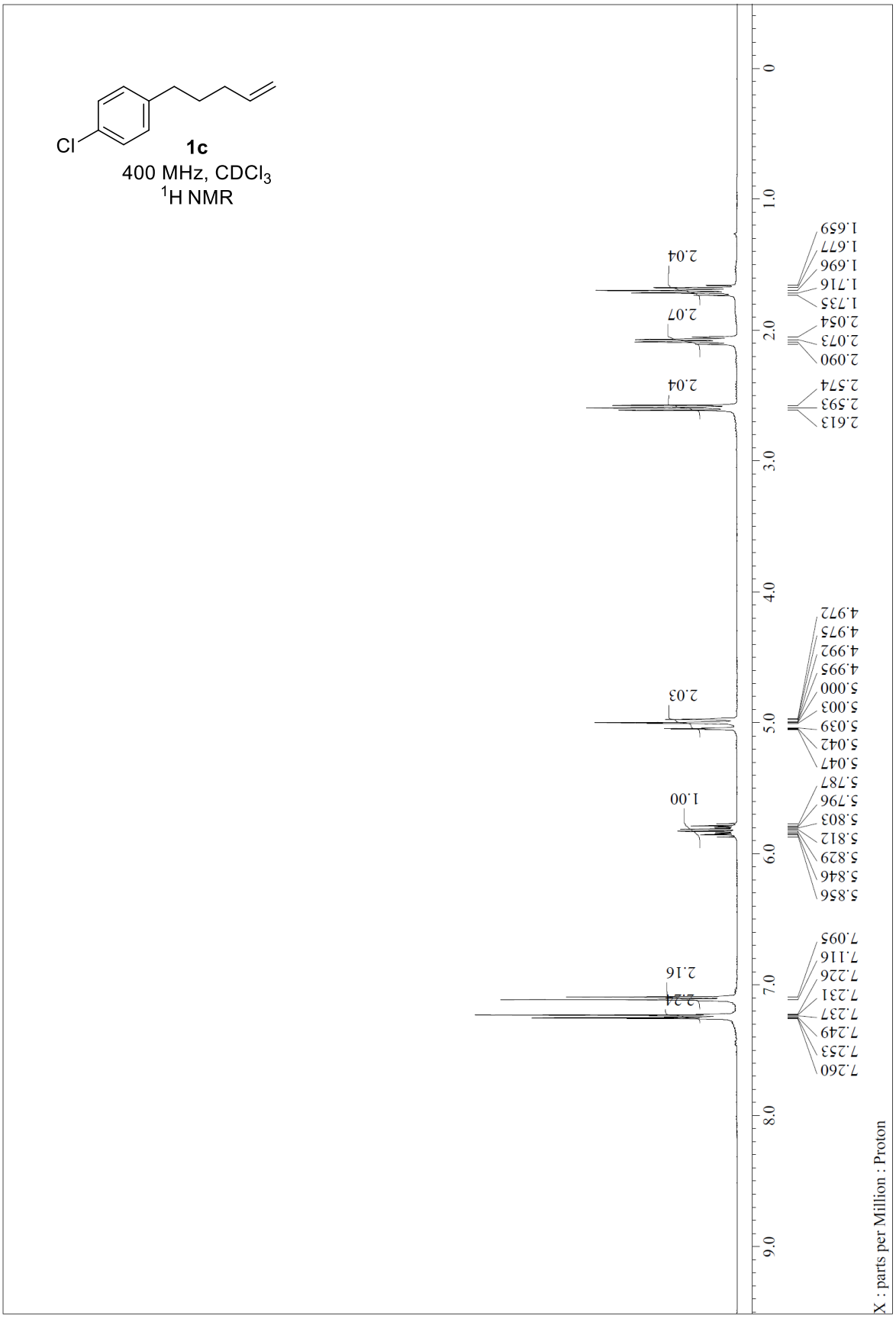
138.679
157.682
X : parts per Million : Carbon13


Cl
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400 MHz, CDCl3
1H NMR
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2.07
2.04
2.03
1.00
2.16
2.24
1.659
1.677
1.696
1.716
1.735
2.054
2.073
2.090
2.574
2.593
2.613
4.972
4.975
4.992
4.995
5.000
5.003
5.039
5.042
5.047
5.787
5.796
5.803
5.812
5.829
5.846
5.856
7.095
7.116
7.226
7.231
7.237
7.249
7.253
7.260
0
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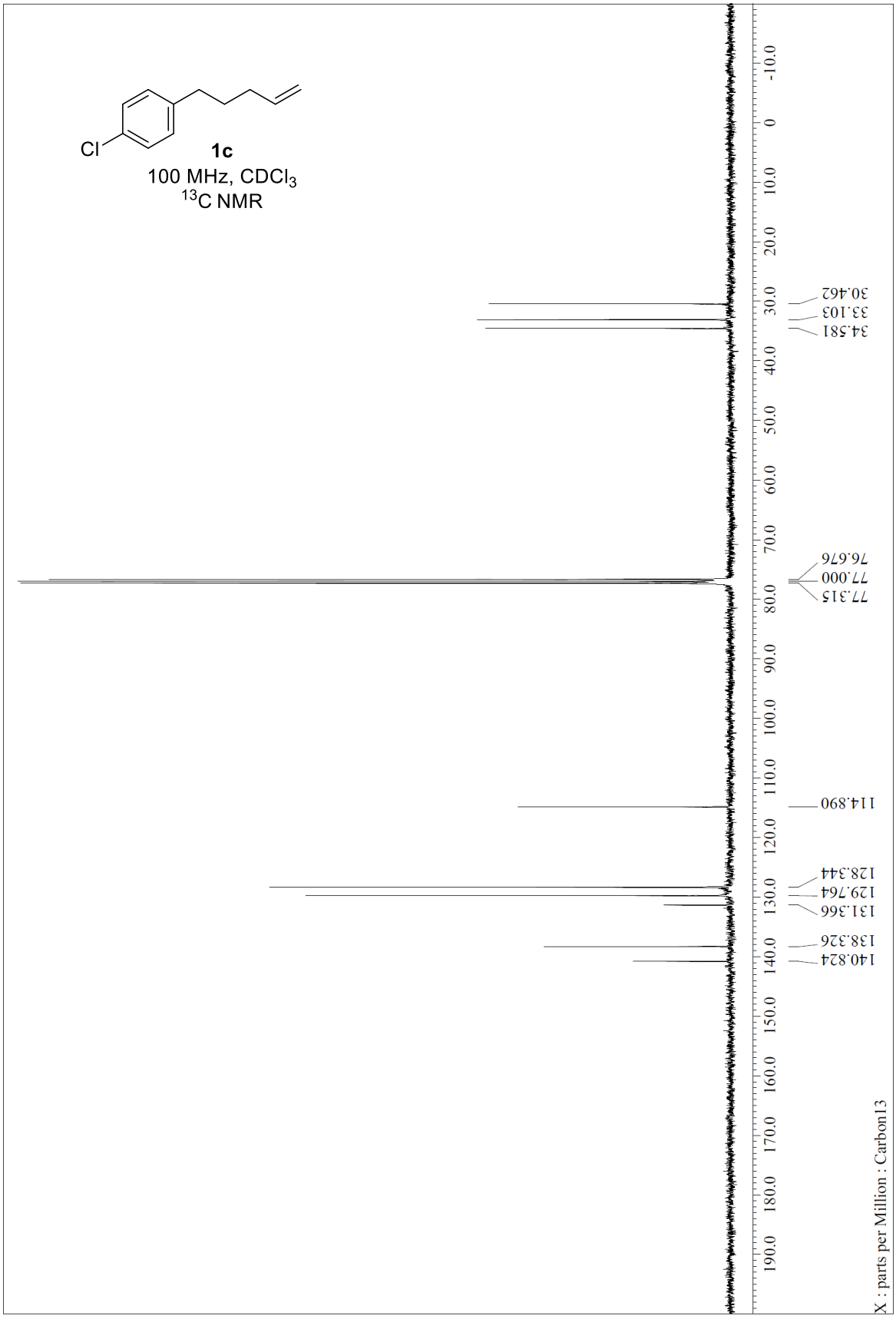
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton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100 MHz, CDCl3
13C NMR
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76.676
77.000
77.315
114.890
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129.764
131.366
138.326
140.824
-10.0
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
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130.0
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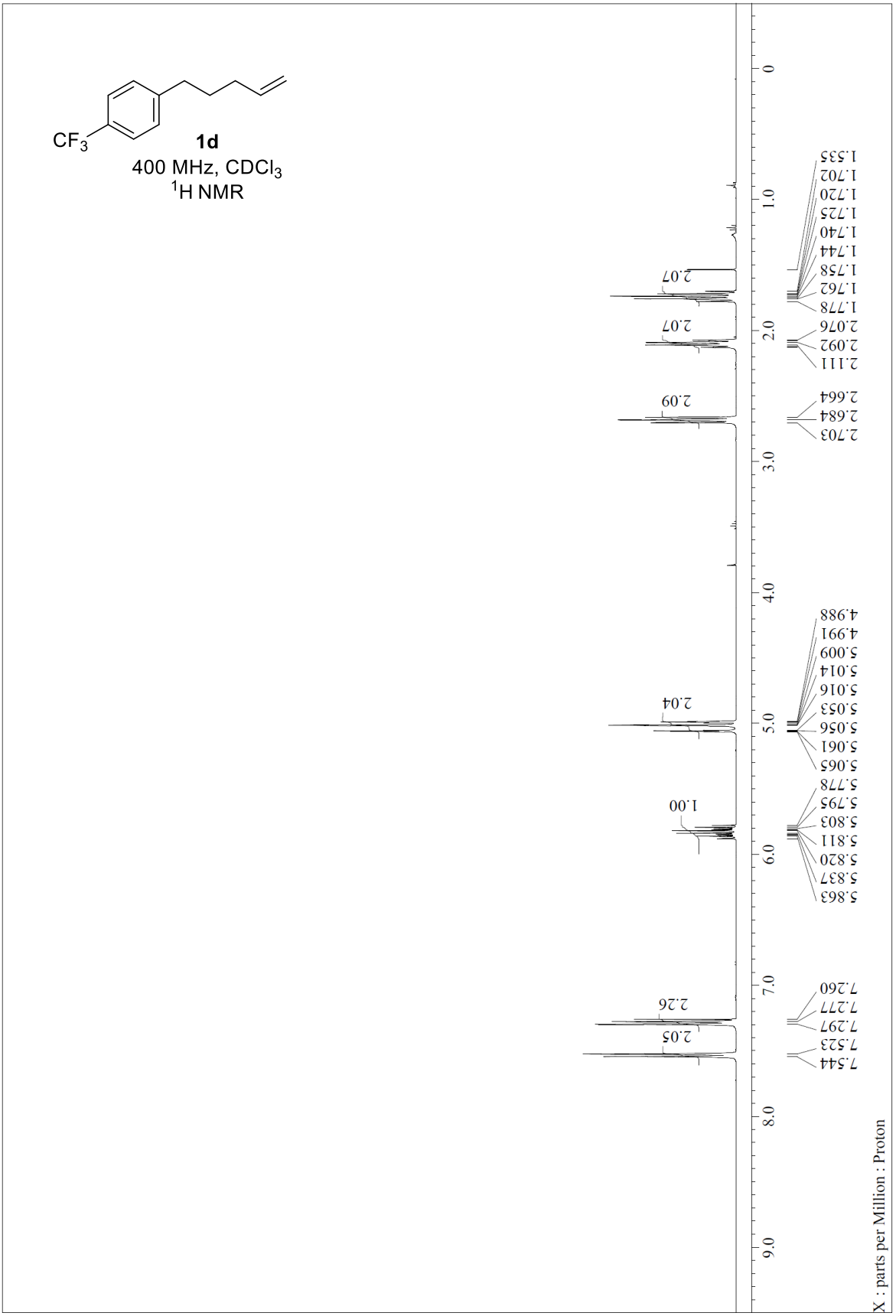
170.0
180.0
190.0
X : parts per Million : Carbon13


CF3
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400 MHz, CDCl3
1H NMR
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2.07
2.09
2.04
1.00
2.26
2.05
7.544
7.523
7.297
7.277
7.260
5.863
5.837
5.820
5.811
5.803
5.795
5.778
5.065
5.061
5.056
5.053
5.016
5.014
5.009
4.991
4.988
2.703
2.684
2.664
2.111
2.092
2.076
1.778
1.762
1.758
1.744
1.740
1.725
1.720
1.702
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5.0
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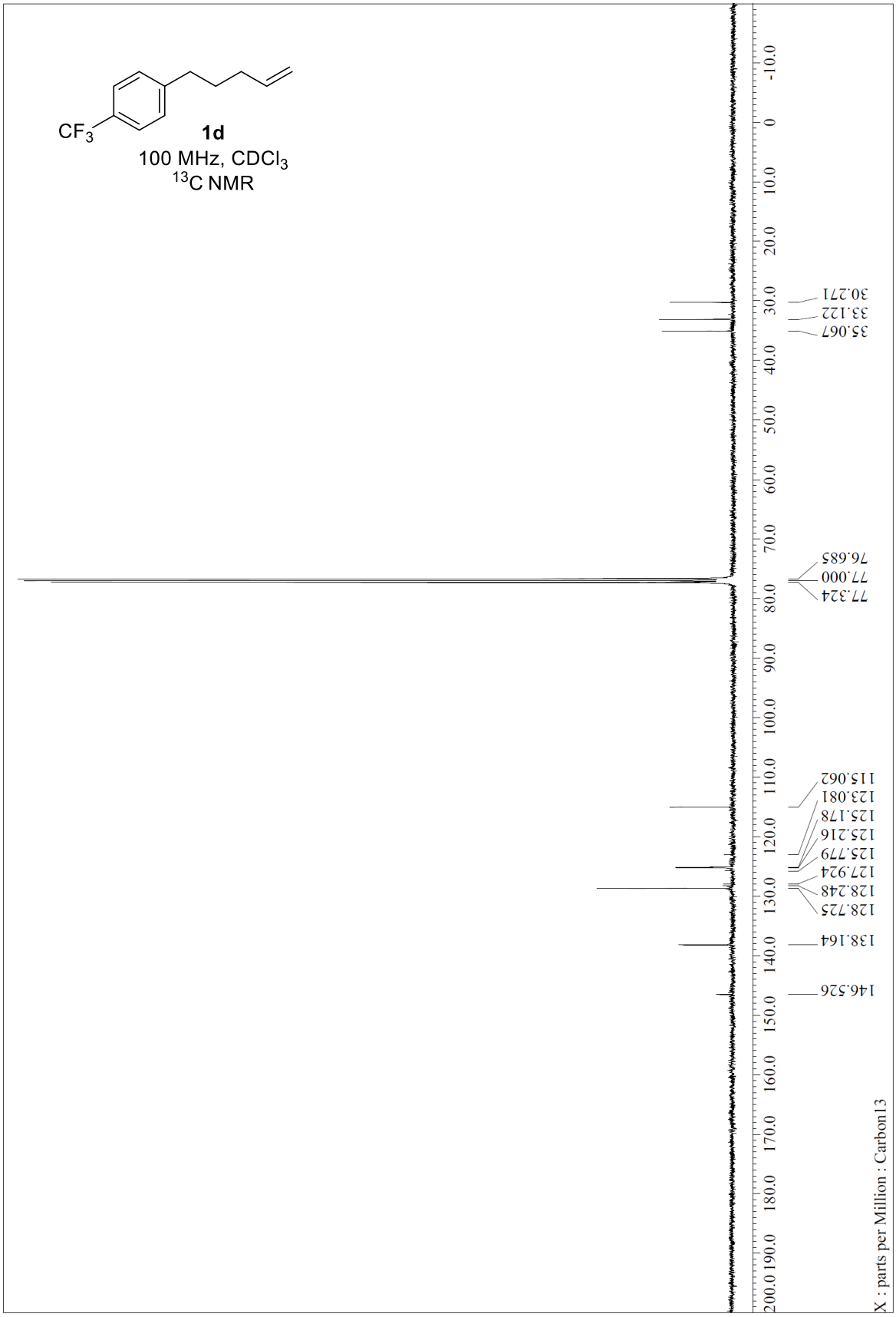
7.0
8.0
9.0
X : parts per Million : Proton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128.725
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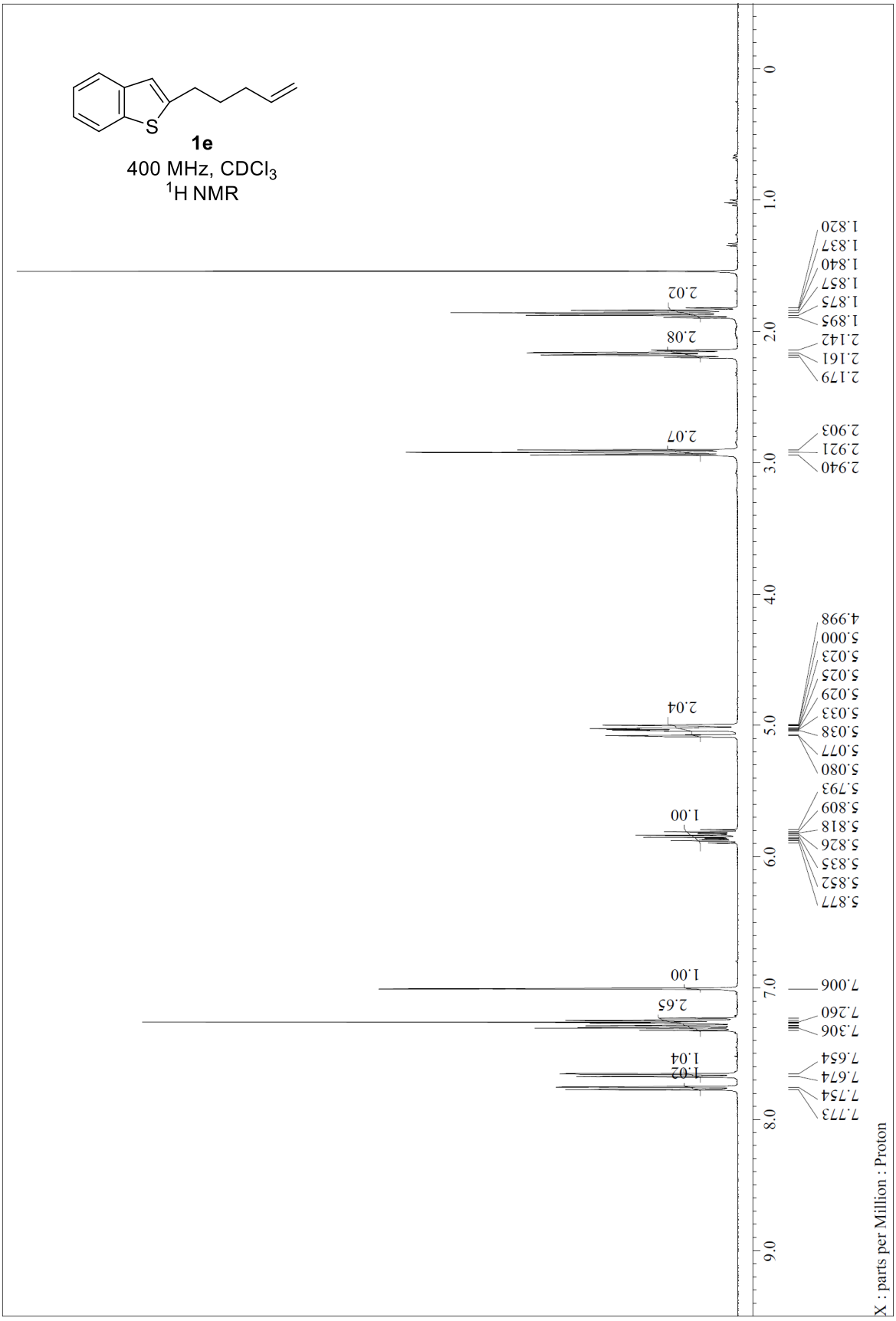
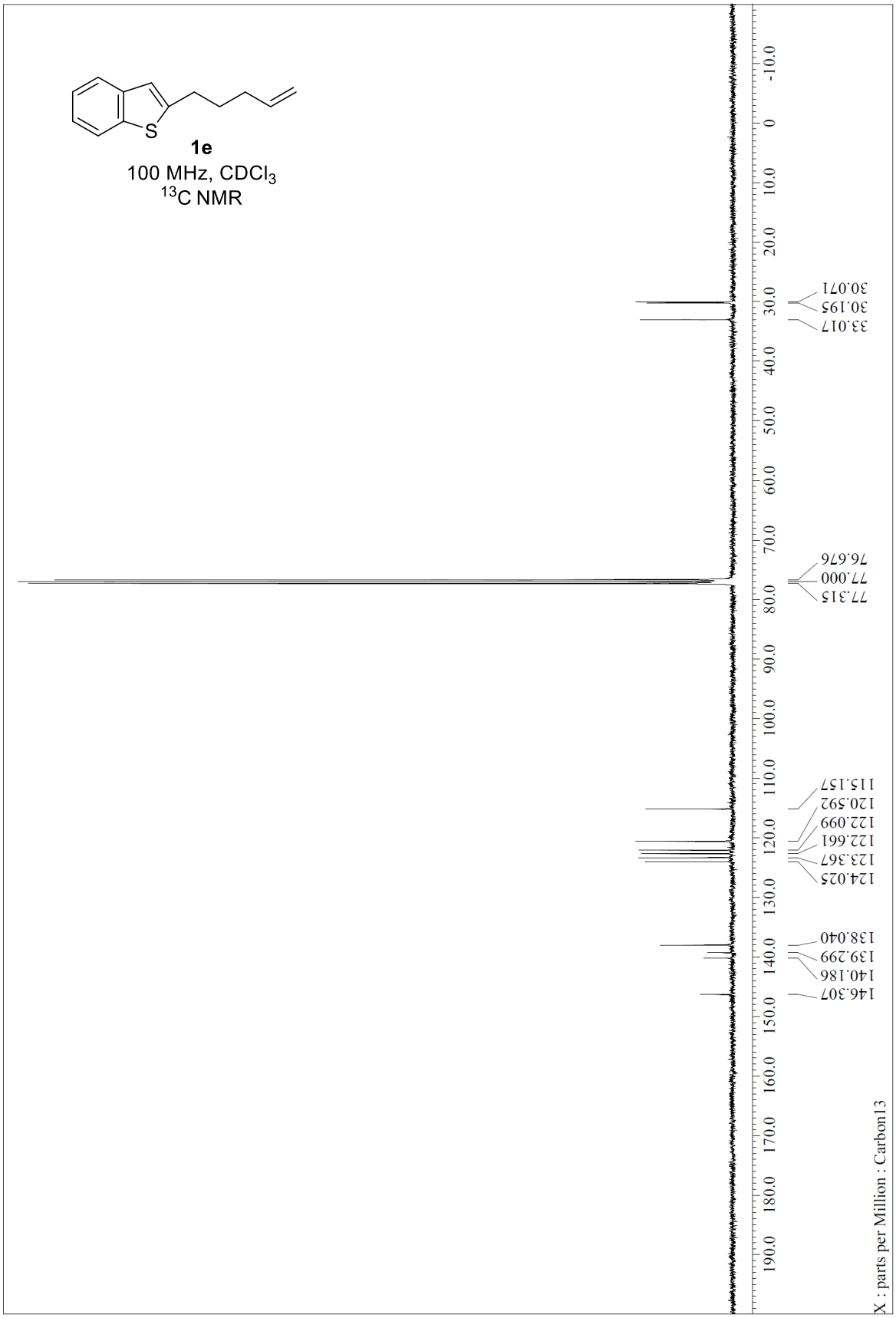
X : parts per Million : Carbon13


1e
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton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10.0
20.0
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60.0
70.0
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90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
30.071
30.195
33.017
76.676
77.000
77.315
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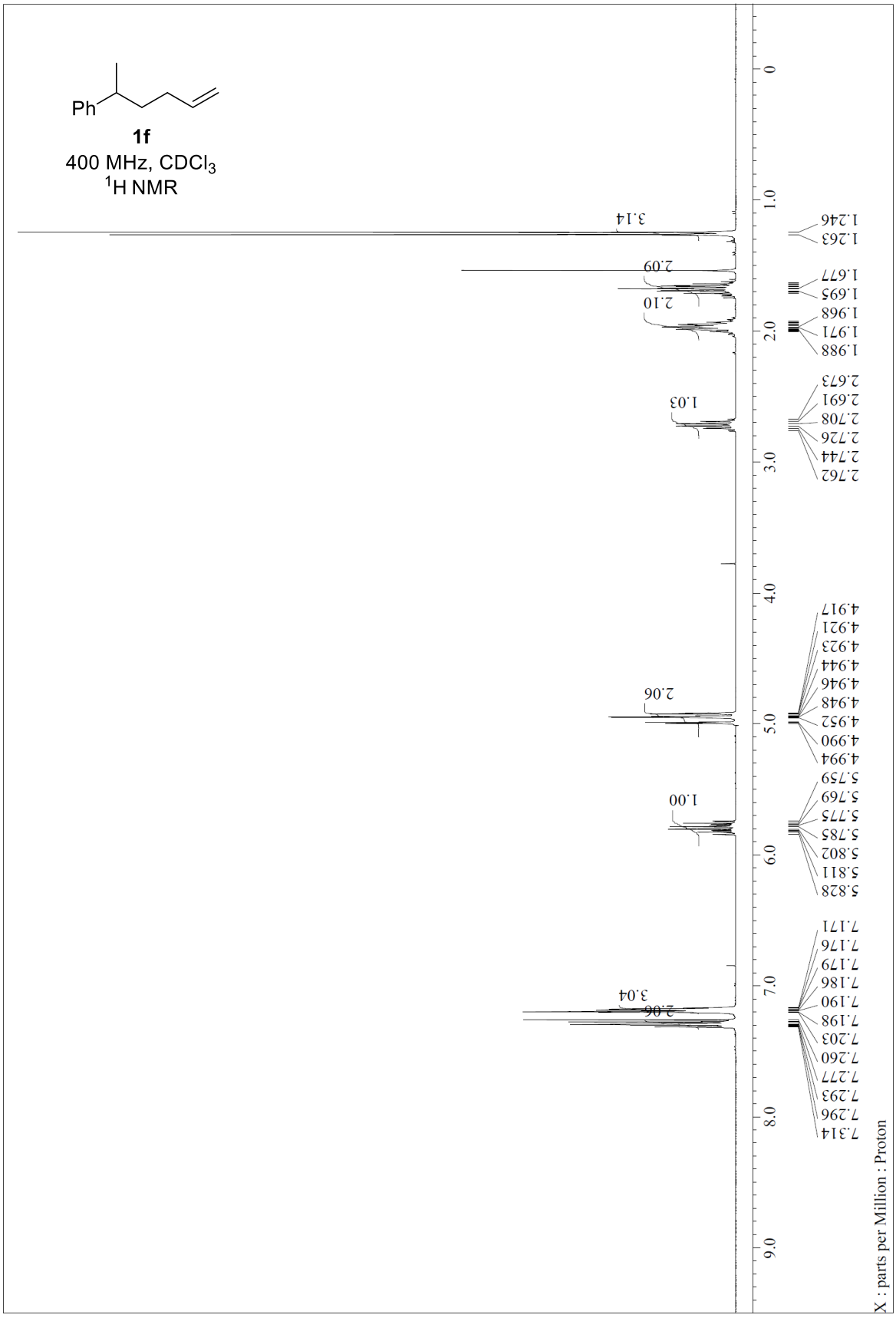
139.299
140.186
146.307
X : parts per Million : Carbon13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1.968
1.971
1.988
2.673
2.691
2.708
2.726
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2.762
4.917
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4.923
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4.946
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4.952
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5.769
5.775
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7.198
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7.260
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7.293
7.296
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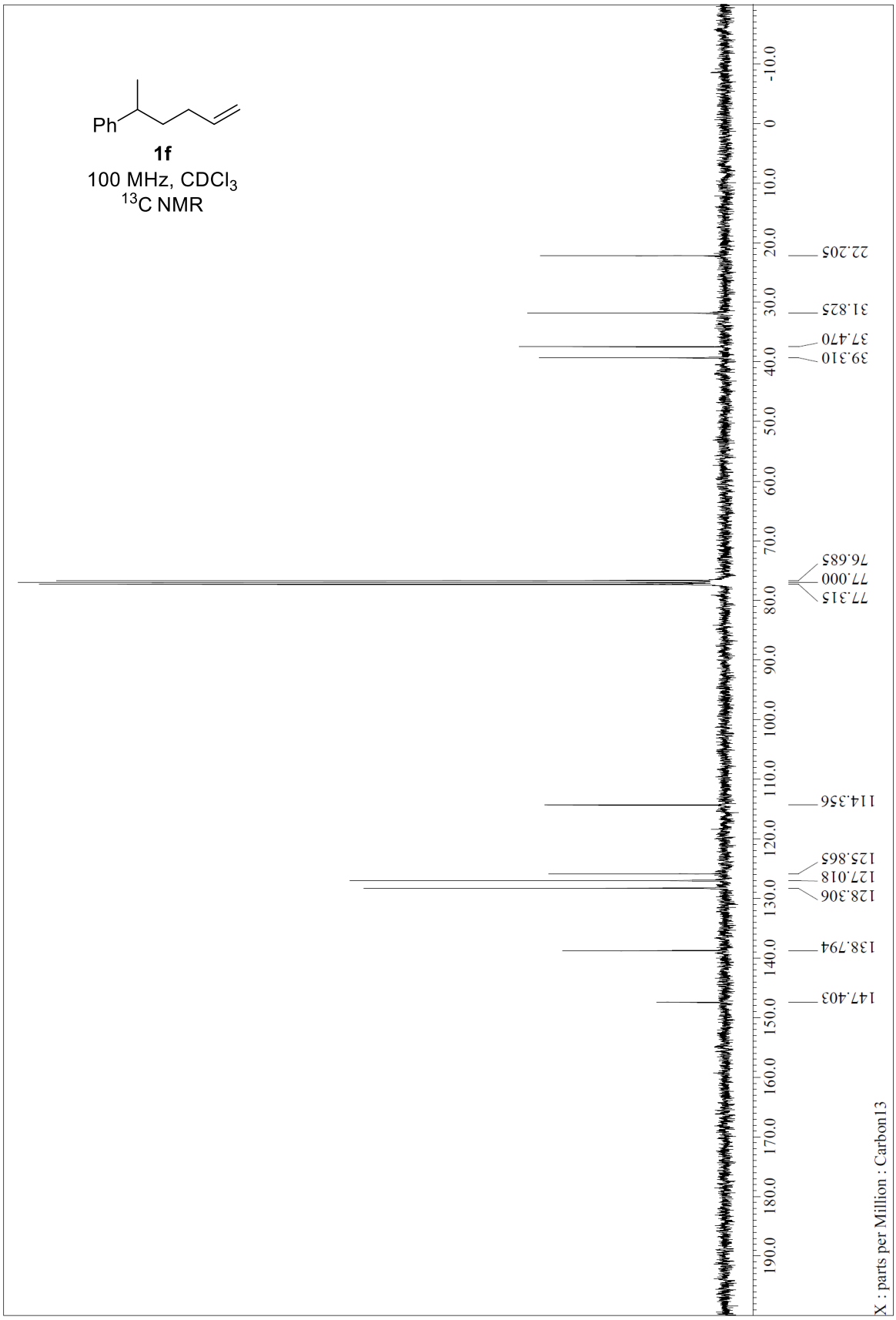
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton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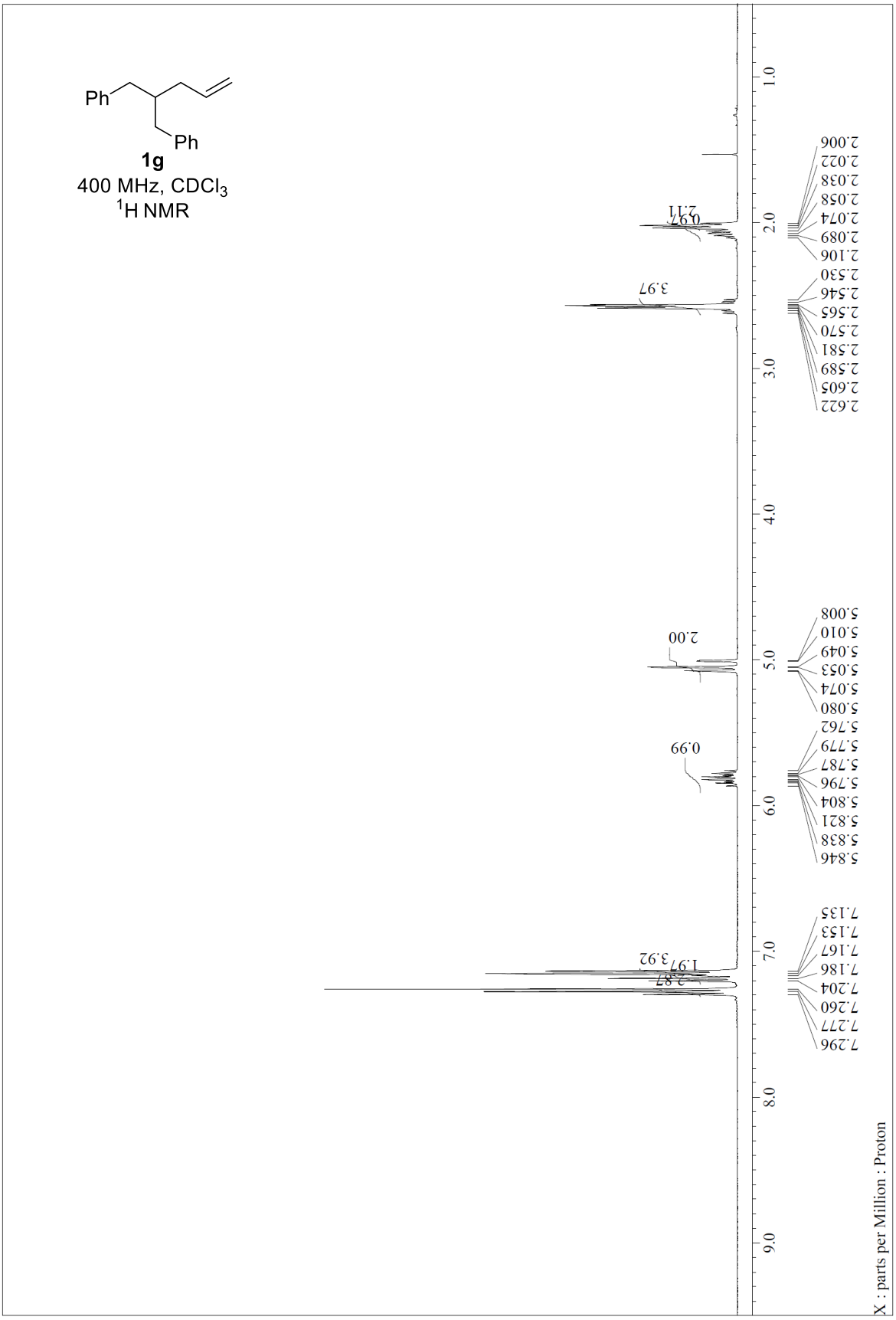
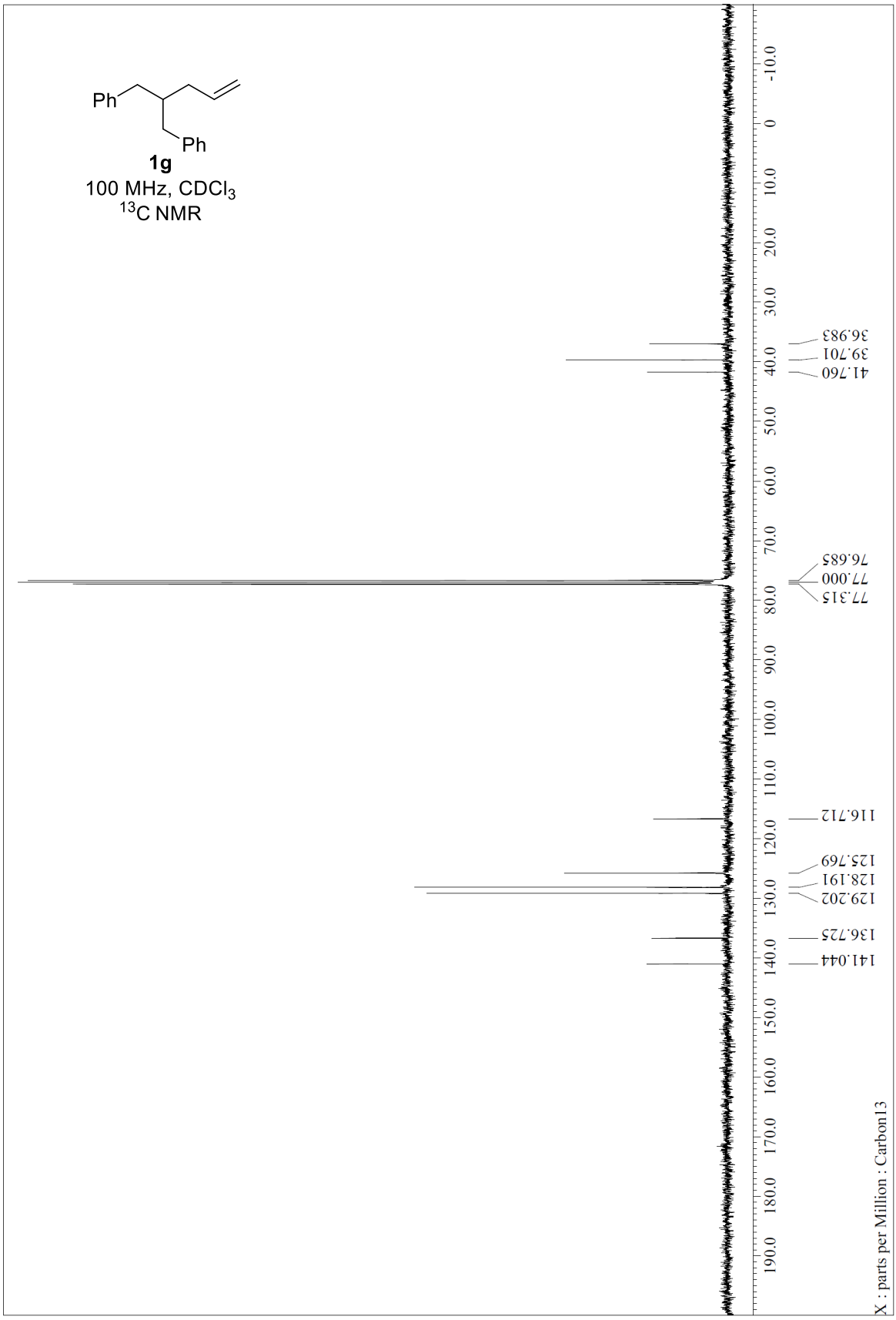
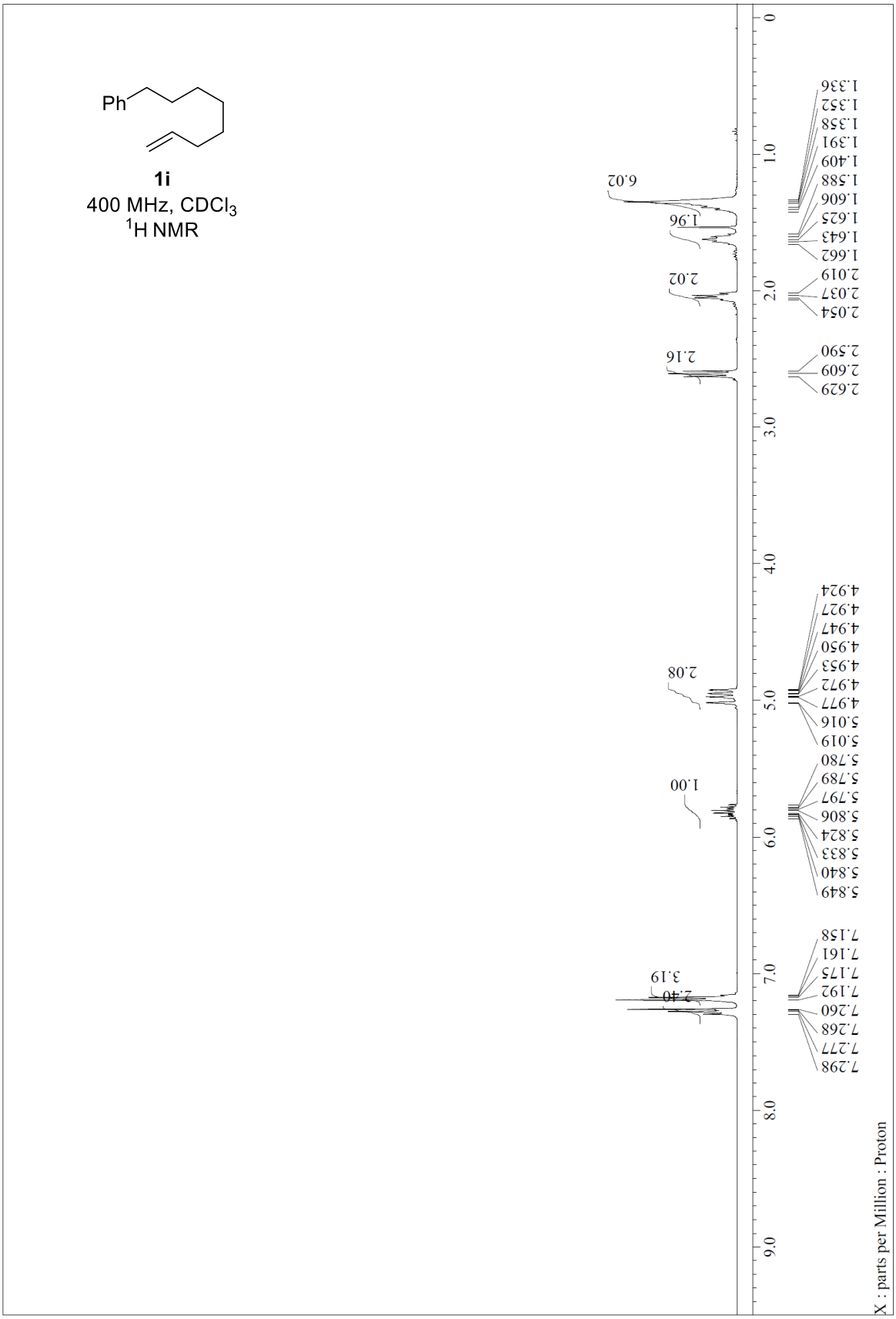
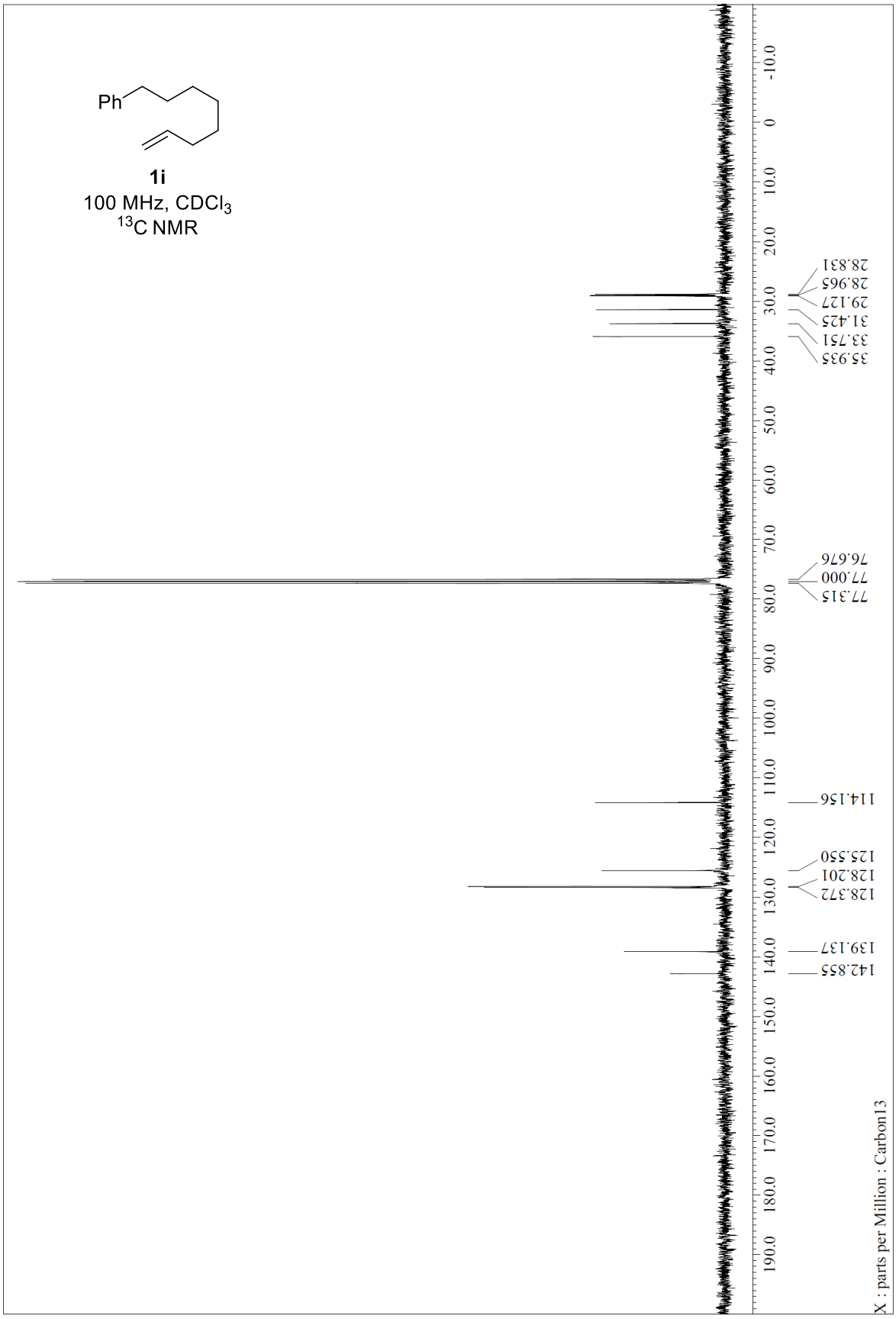
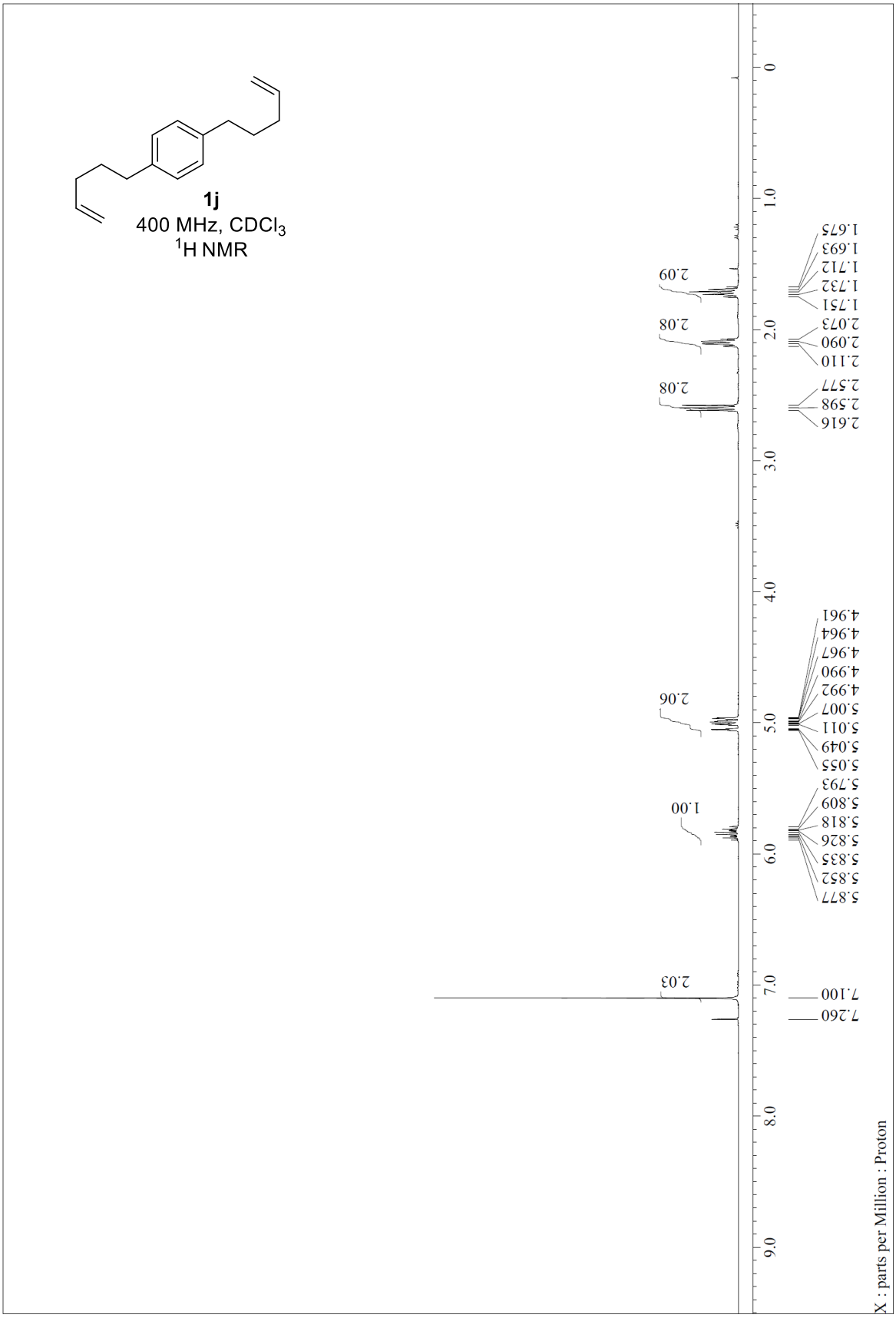
X : parts per Million : Carbon13

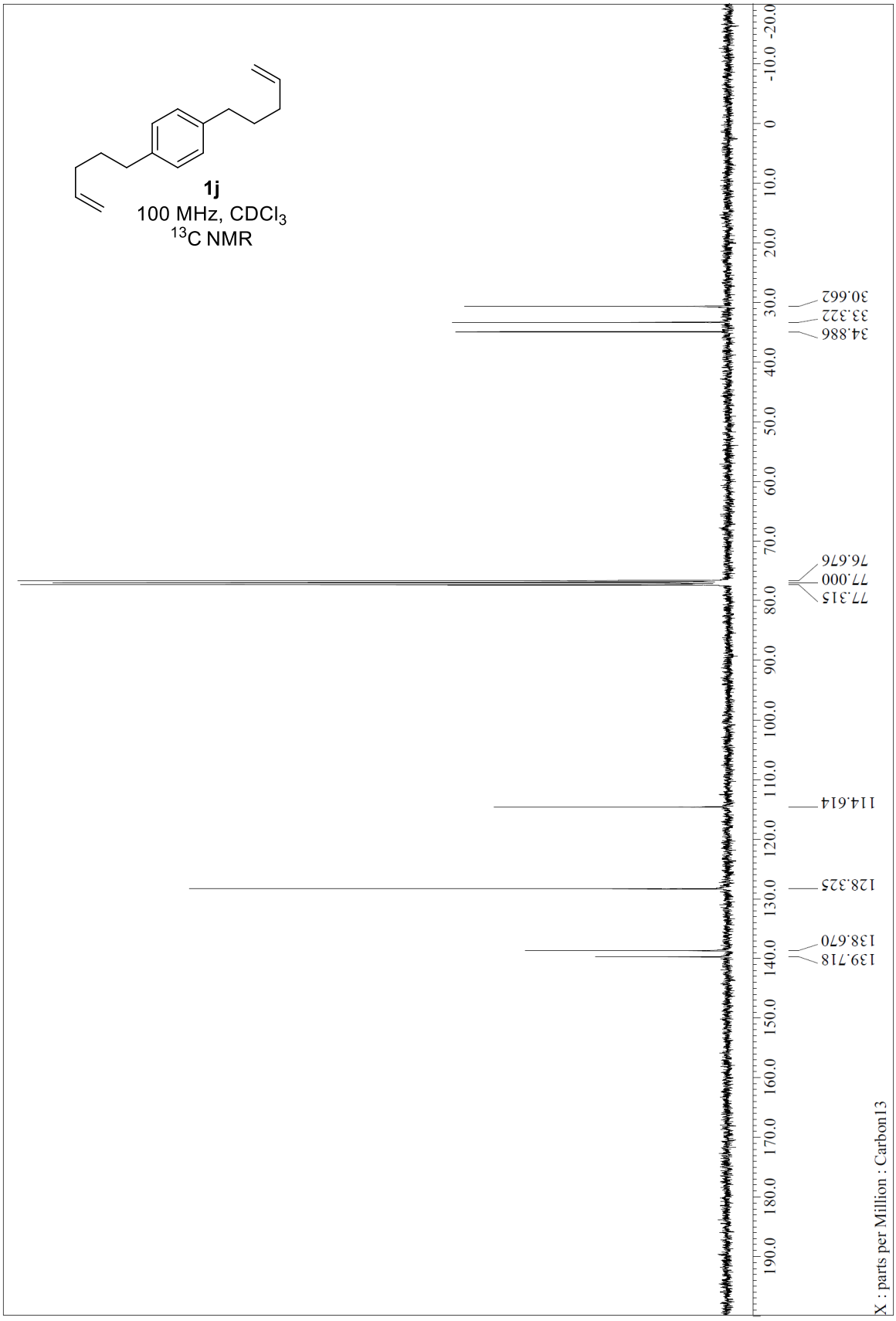

Ph
Ph
1g
400 MHz, CDCl3
1H NMR
2.11
3.97
2.00
0.99
1.97
3.92
3.87
X : parts per Million : Proton

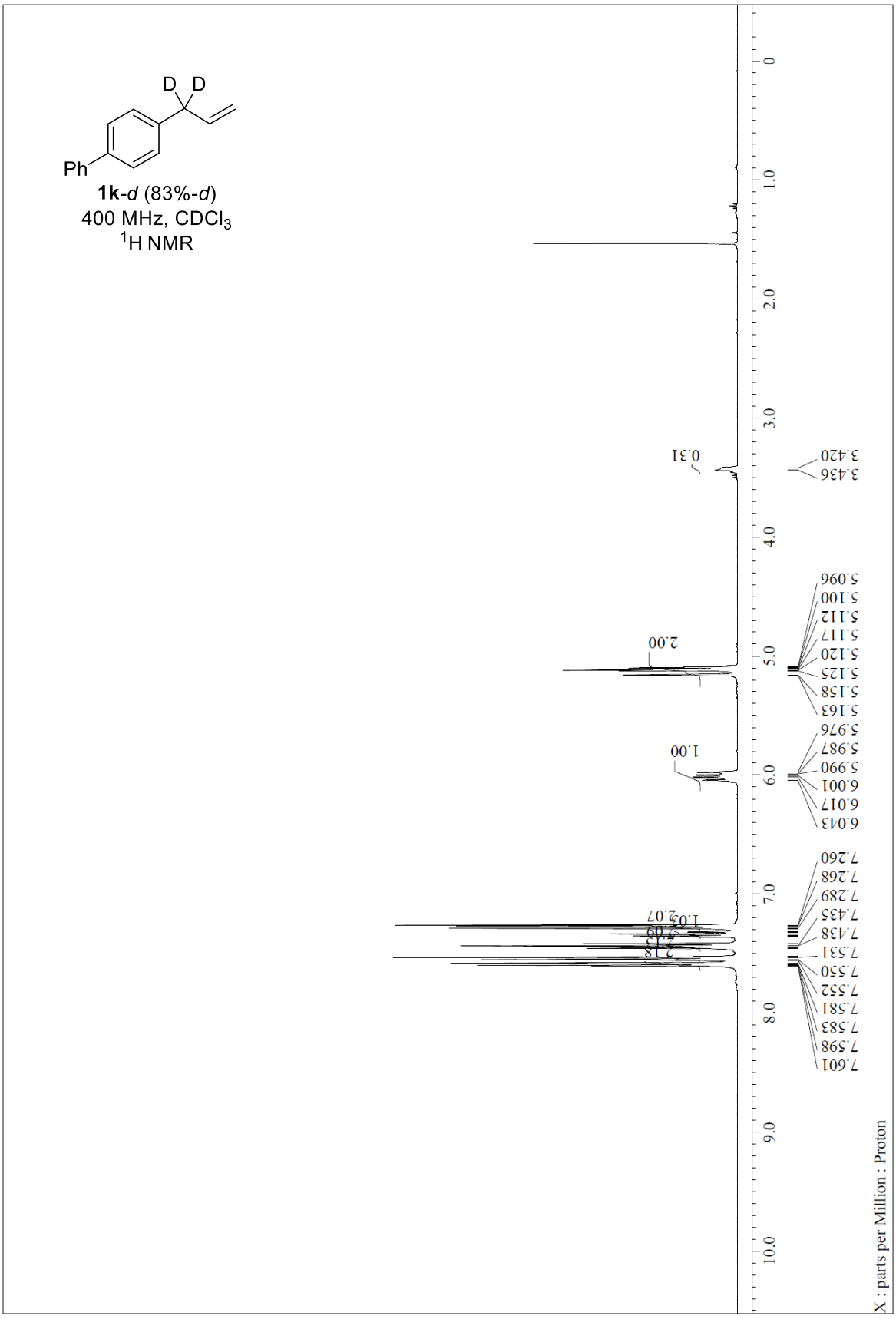

Ph
Ph
1g
100 MHz, CDCl3
13C NMR
36.983
39.701
41.760
76.685
77.000
77.315
116.712
125.769
128.191
129.202
136.725
141.044
X : parts per Million : Carbon13

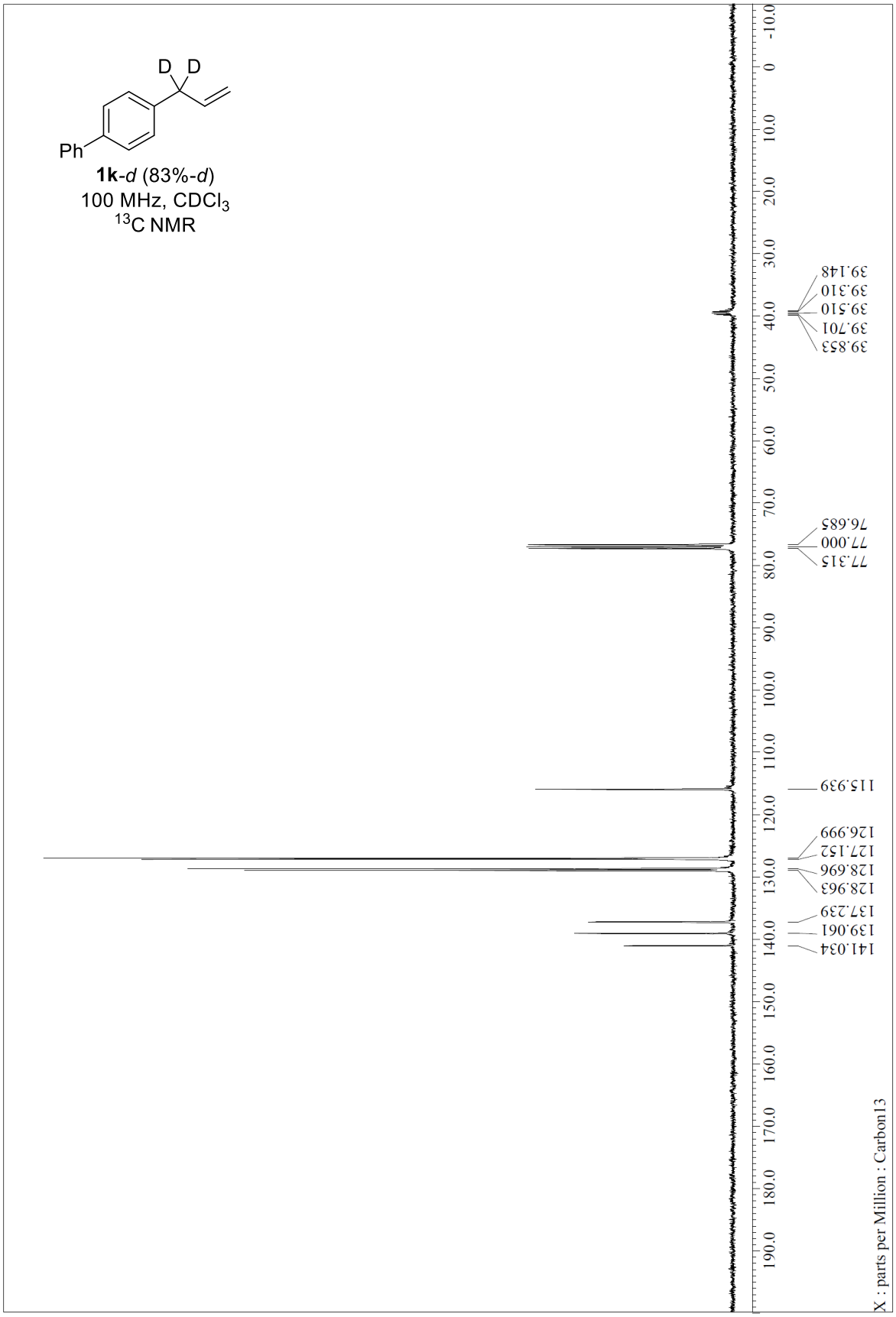

Ph
1i
400 MHz, CDCl3
1H NMR
6.02
1.96
2.02
2.16
2.08
1.00
3.19
2.40
1.336
1.352
1.358
1.391
1.409
1.588
1.606
1.625
1.643
1.662
2.019
2.037
2.054
2.590
2.609
2.629
4.924
4.927
4.947
4.950
4.953
4.972
4.977
5.016
5.019
5.780
5.789
5.797
5.806
5.824
5.833
5.840
5.849
7.158
7.161
7.175
7.192
7.260
7.268
7.277
7.298
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

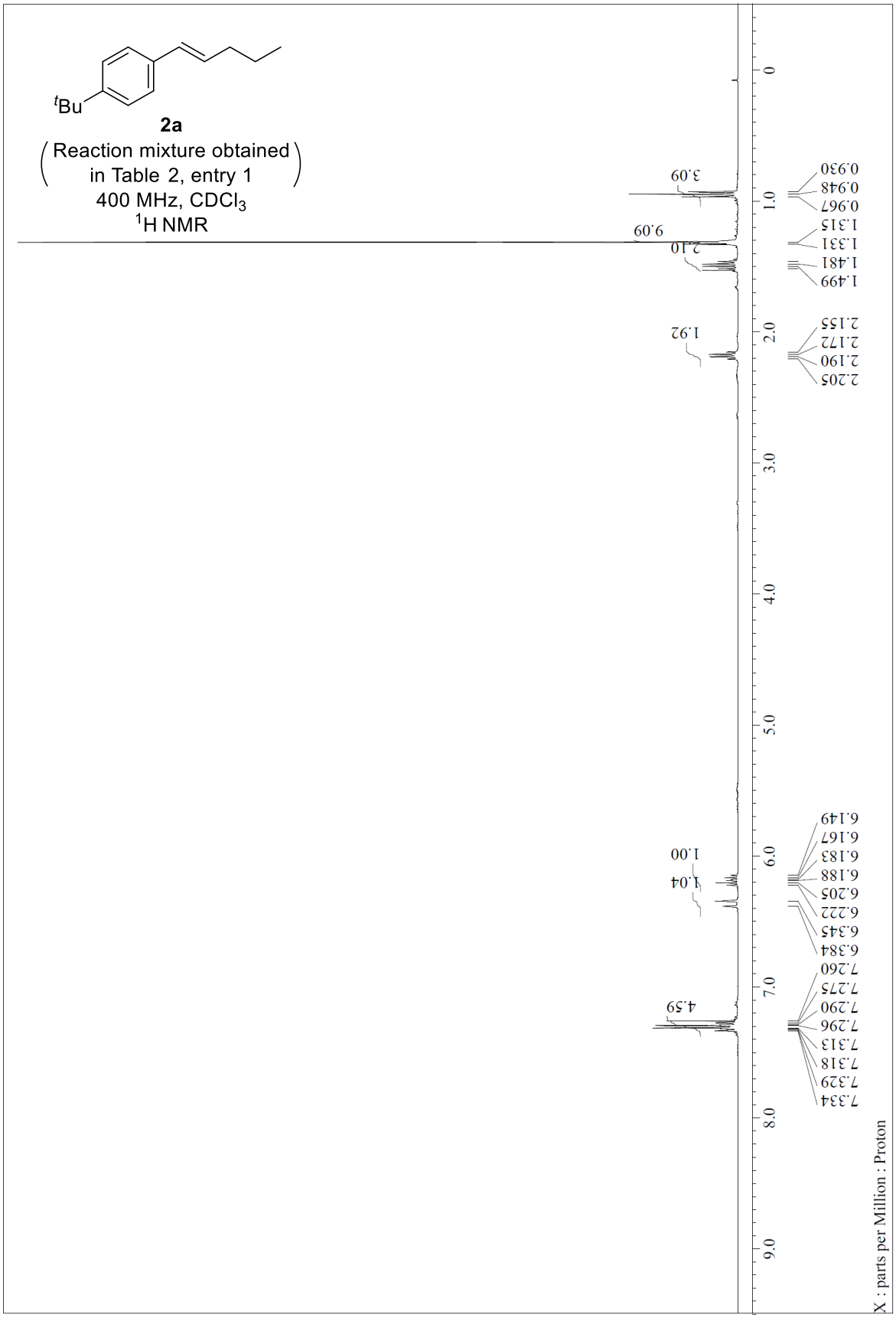

Ph
1i
100 MHz, CDCl3
13C NMR
-10.0
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
X : parts per Million : Carbon13
28.831
28.965
29.127
31.425
33.751
35.935
76.676
77.000
77.315
114.156
125.550
128.201
128.372
139.137
142.855

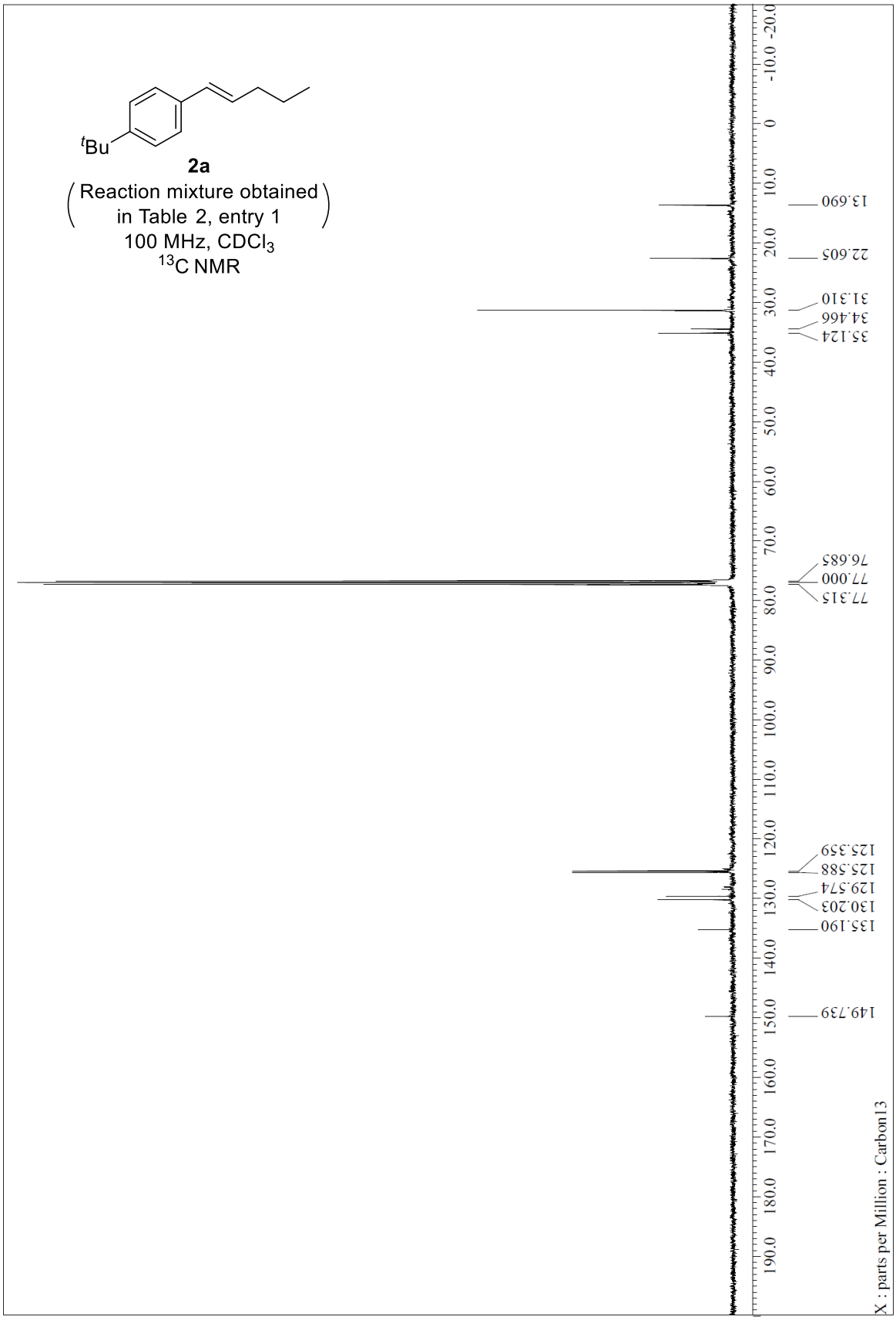

1j
400 MHz, CDCl3
1H NMR
2.09
2.08
2.08
2.06
1.00
2.03
1.675
1.693
1.712
1.732
1.751
2.073
2.090
2.110
2.577
2.598
2.616
4.961
4.964
4.967
4.990
4.992
5.007
5.011
5.049
5.055
5.793
5.809
5.818
5.826
5.835
5.852
5.877
7.100
7.260
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

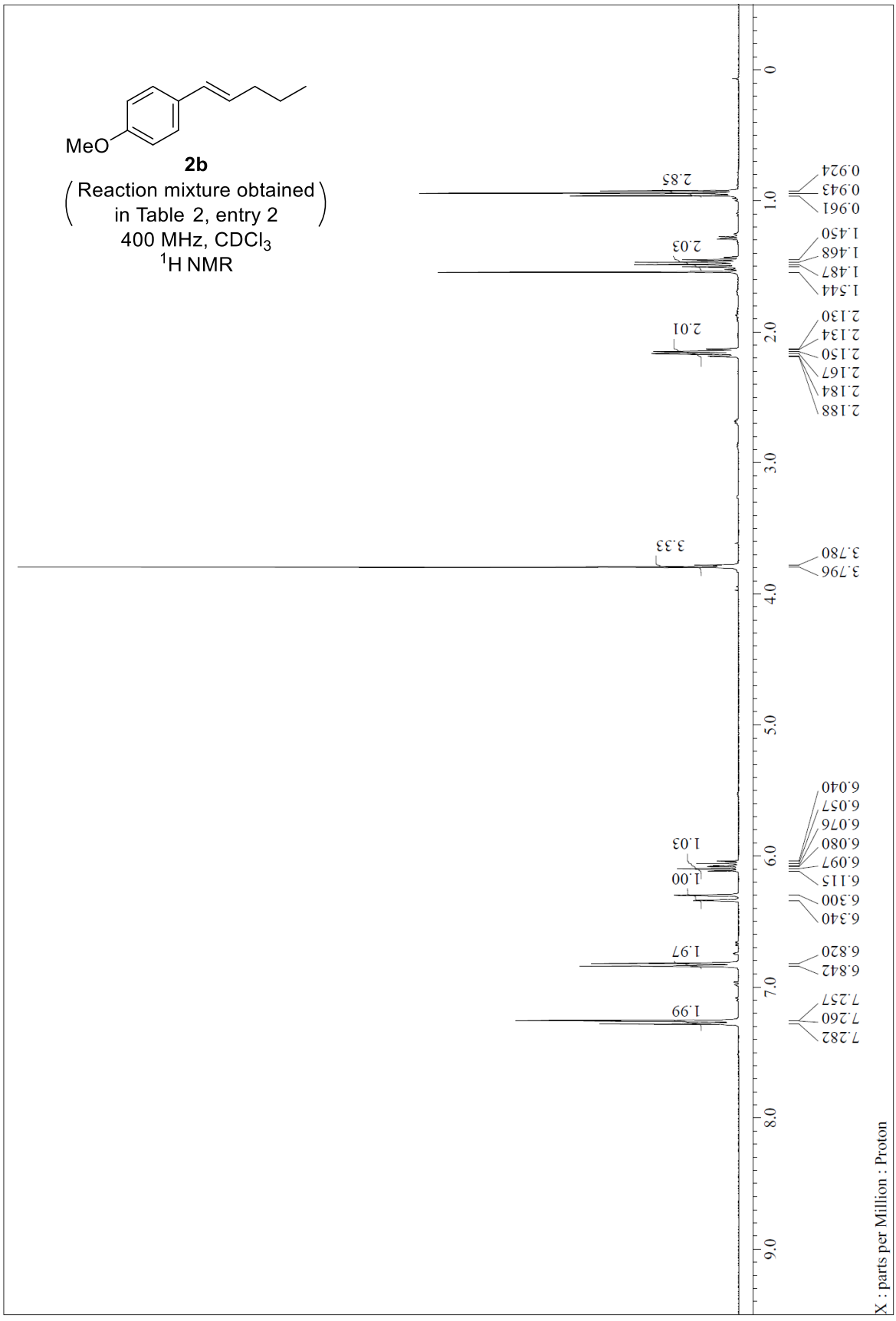

1j
100 MHz, CDCl3
13C NMR
30.662
33.322
34.886
76.676
77.000
77.315
114.614
128.325
138.670
139.718
X : parts per Million : Carbon13

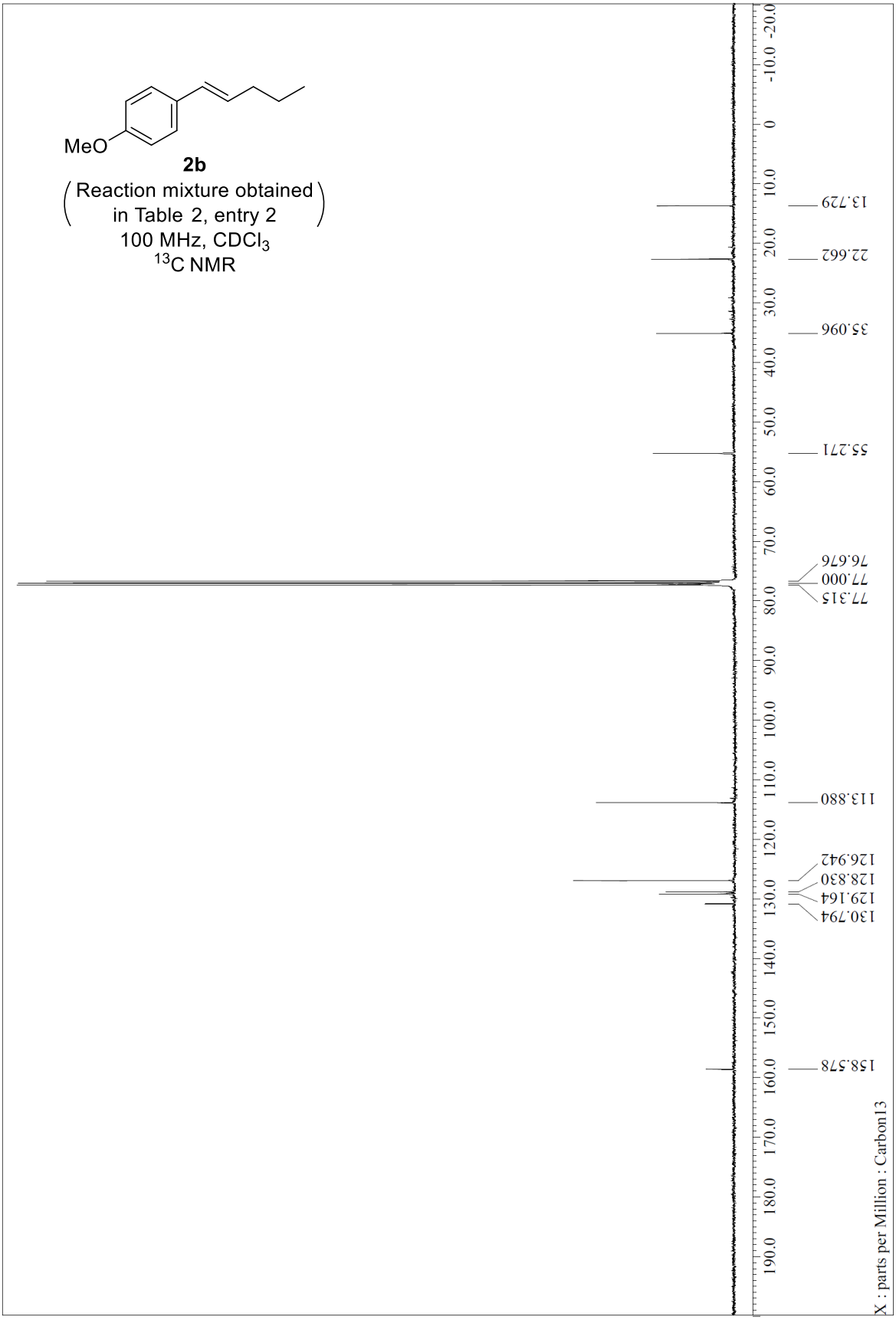

D D
Ph
1k-d (83%-d)
400 MHz, CDCl3
1H NMR
0.31
2.00
1.00
2.07
3.420
3.436
5.096
5.100
5.112
5.117
5.120
5.125
5.158
5.163
5.976
5.987
5.990
6.001
6.017
6.043
7.260
7.268
7.289
7.435
7.438
7.531
7.550
7.552
7.581
7.583
7.598
7.601
X : parts per Million : Proton

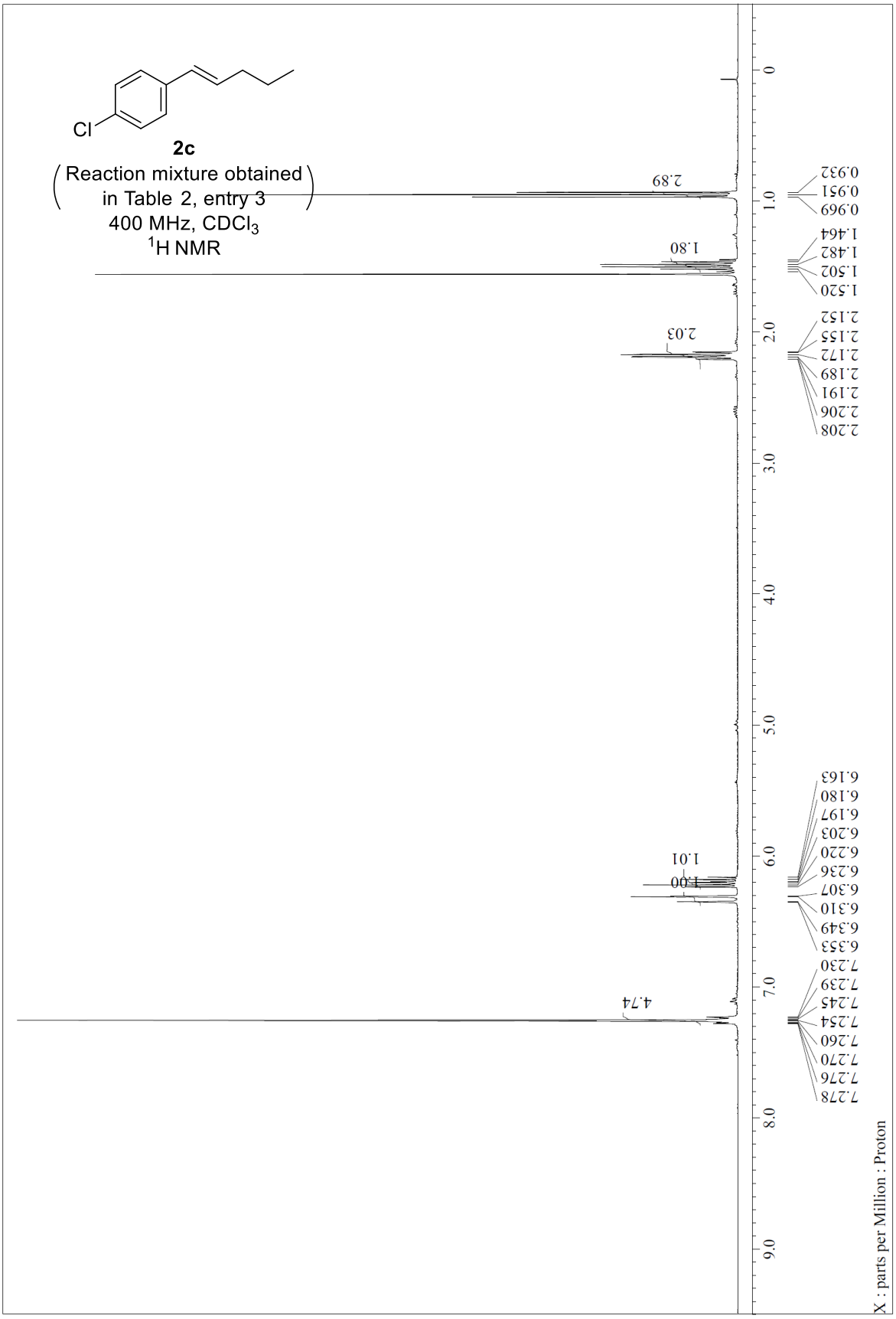

D D
Ph
1k-d (83%-d)
100 MHz, CDCl3
13C NMR
39.853
39.701
39.510
39.310
39.148
77.315
77.000
76.685
115.939
126.999
127.152
128.696
128.963
137.239
139.061
141.034
X : parts per Million : Carbon13

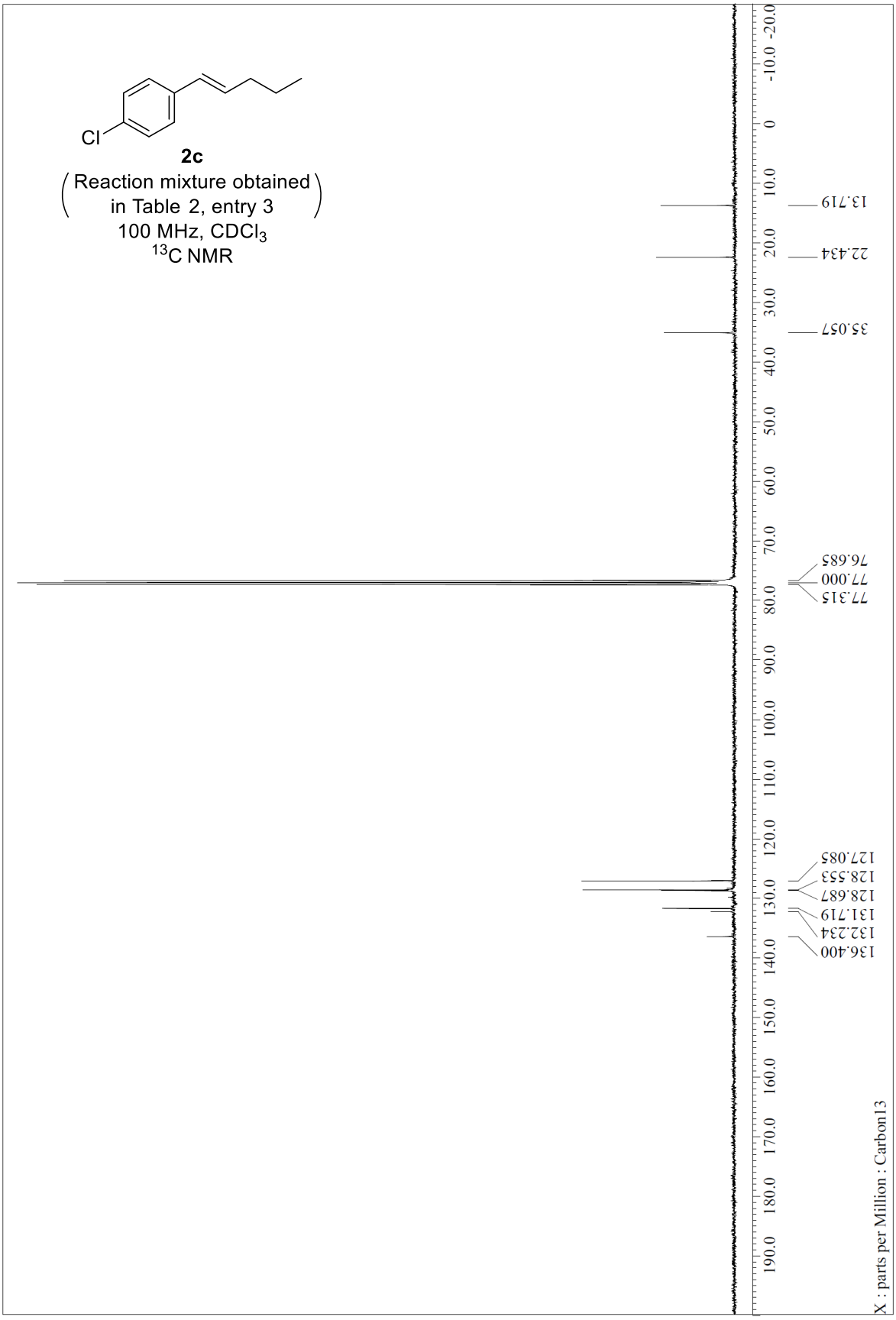

tBu
2a
Reaction mixture obtained
in Table 2, entry 1
400 MHz, CDCl3
1H NMR
3.09
9.09
2.10
1.92
1.04
1.00
4.59
0.930
0.948
0.967
1.315
1.331
1.481
1.499
2.155
2.172
2.190
2.205
6.149
6.167
6.183
6.188
6.205
6.222
6.345
6.384
7.260
7.275
7.290
7.296
7.313
7.318
7.329
7.334
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

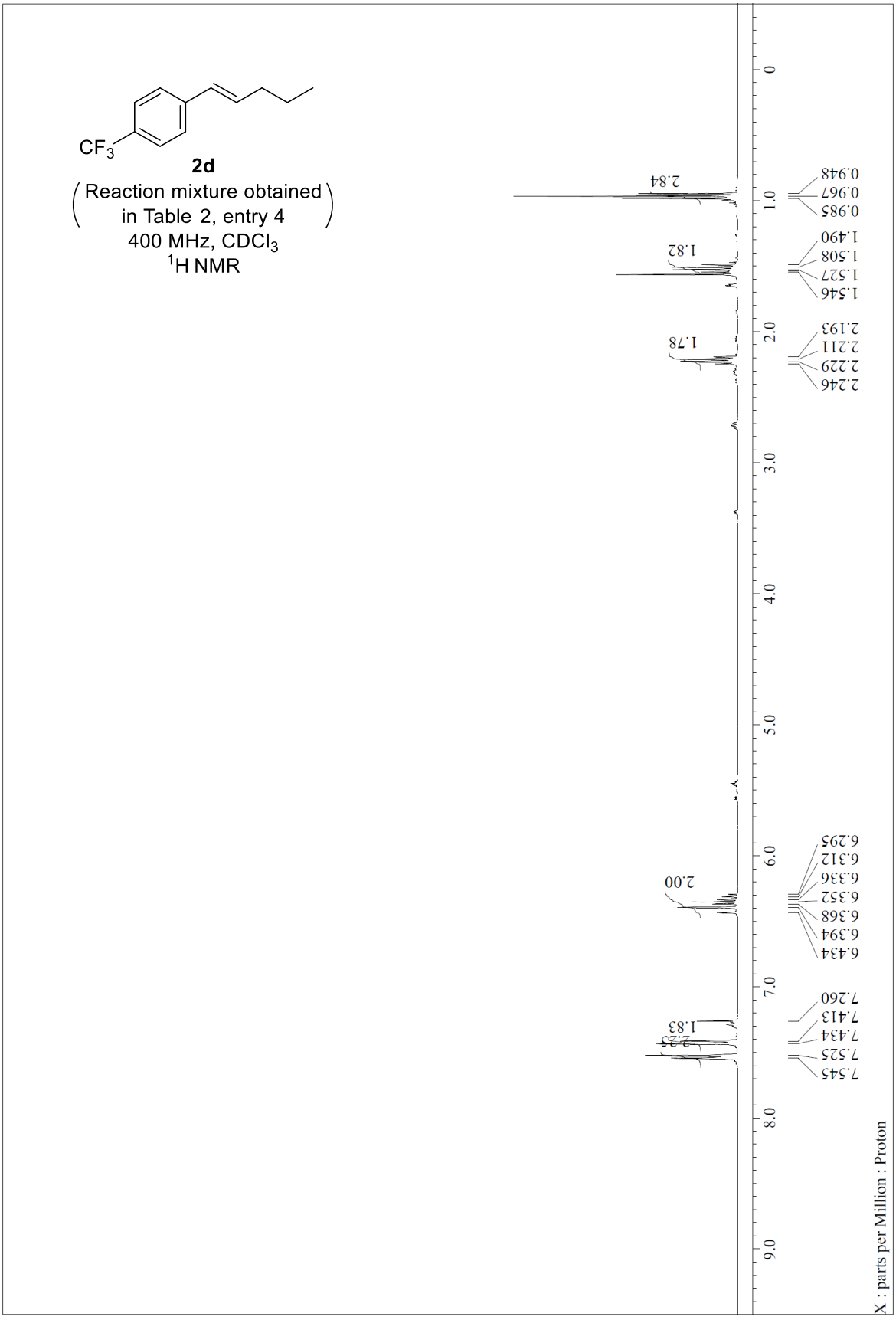

tBu
2a
Reaction mixture obtained
in Table 2, entry 1
100 MHz, CDCl3
13C NMR
13.690
22.605
31.310
34.466
35.124
76.685
77.000
77.315
125.359
125.588
129.574
130.203
135.190
149.739
X : parts per Million : Carbon13

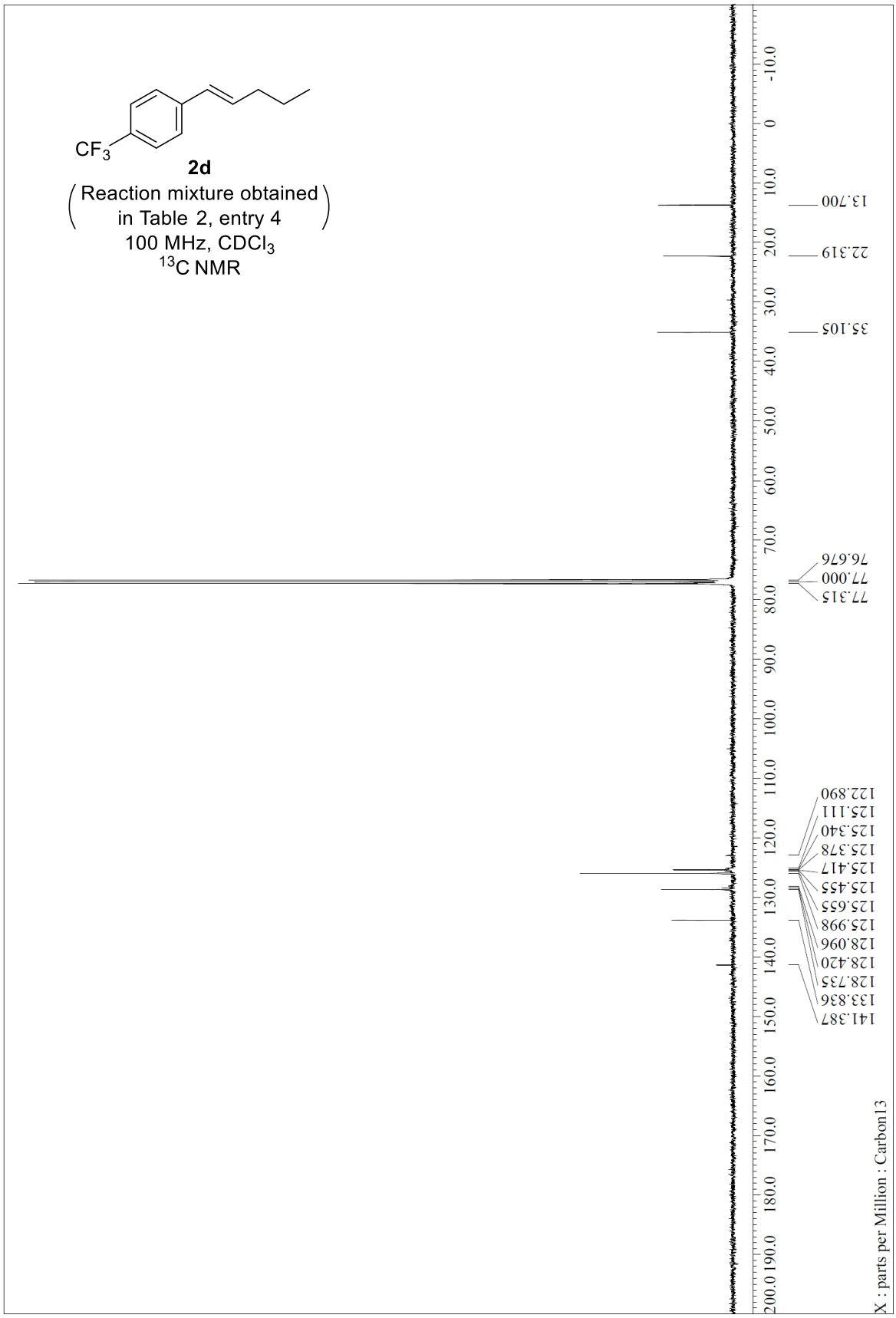

MeO
2b
(Reaction mixture obtained in Table 2, entry 2)
400 MHz, CDCl3
1H NMR
2.85
2.03
2.01
3.33
1.03
1.00
1.97
1.99
0.924
0.943
0.961
1.450
1.468
1.487
1.544
2.130
2.134
2.150
2.167
2.184
2.188
3.780
3.796
6.040
6.057
6.076
6.080
6.097
6.115
6.300
6.340
6.820
6.842
7.257
7.260
7.282
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

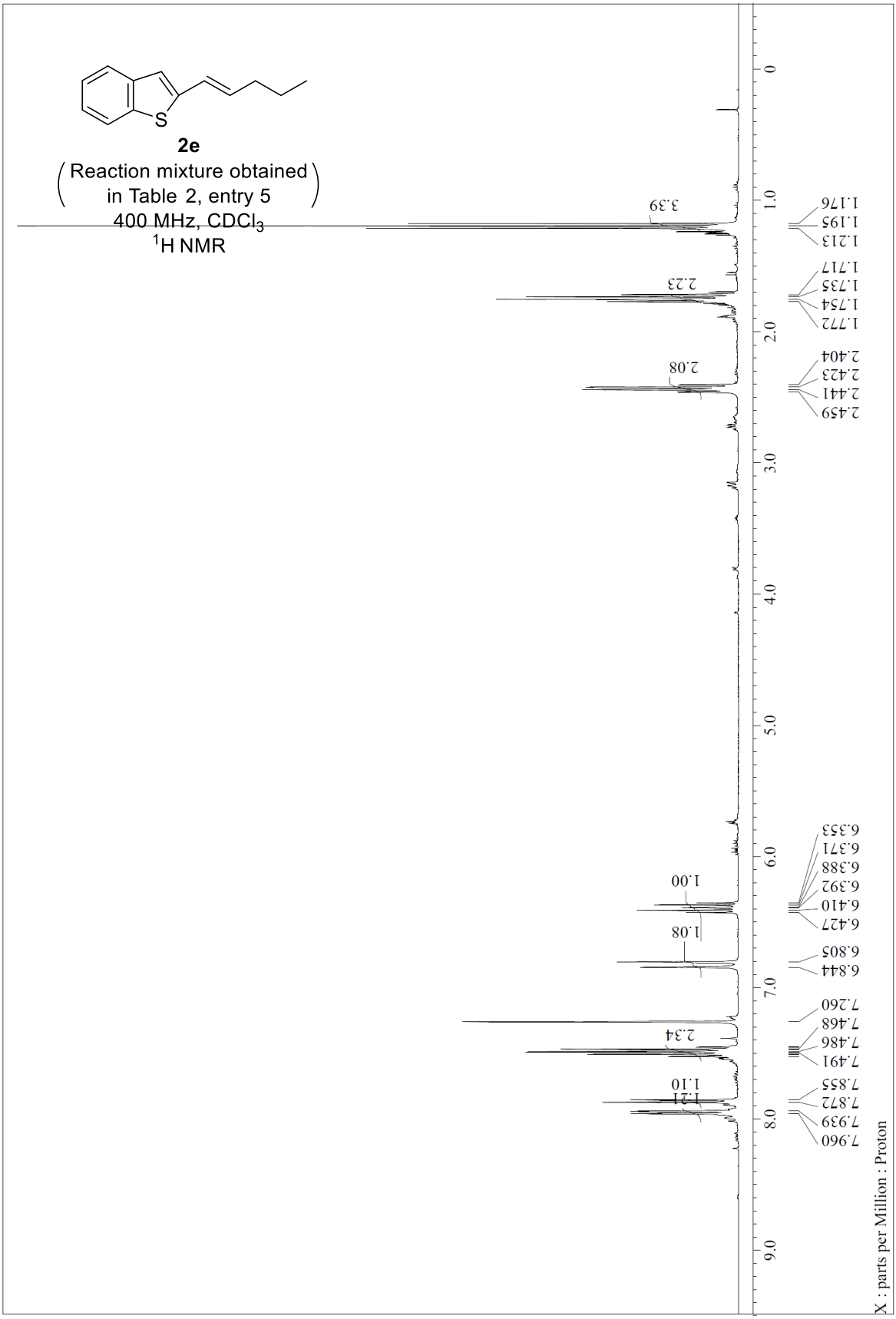

MeO
2b
Reaction mixture obtained
in Table 2, entry 2
100 MHz, CDCl3
13C NMR
13.729
22.662
35.096
55.271
76.676
77.000
77.315
113.880
126.942
128.830
129.164
130.794
158.578
X : parts per Million : Carbon13

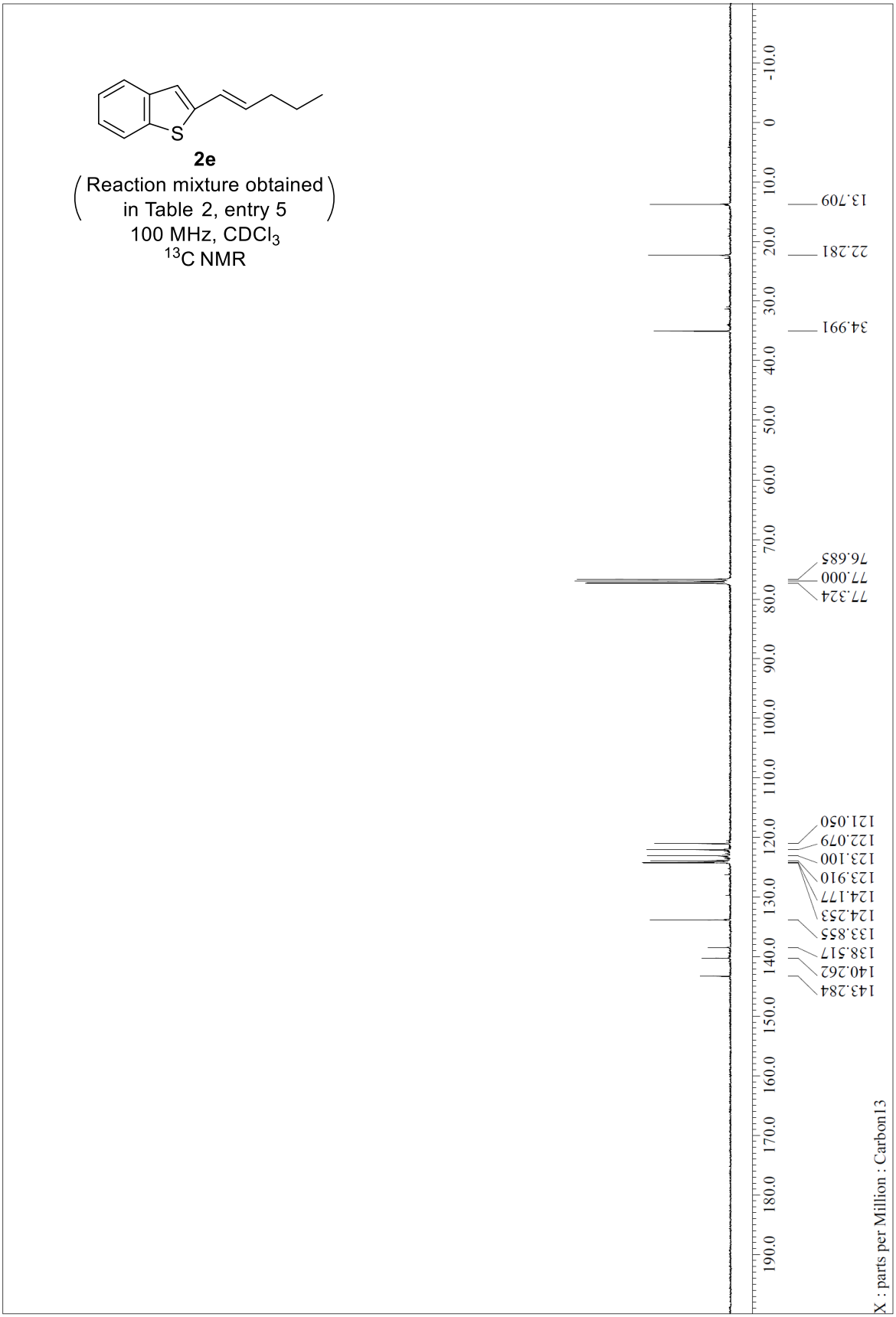

Cl
2c
Reaction mixture obtained
in Table 2, entry 3
400 MHz, CDCl3
1H NMR
2.89
1.80
2.03
1.01
1.00
4.74
0.932
0.951
0.969
1.464
1.482
1.502
1.520
2.152
2.155
2.172
2.189
2.191
2.206
2.208
6.163
6.180
6.197
6.203
6.220
6.236
6.307
6.310
6.349
6.353
7.230
7.239
7.245
7.254
7.260
7.270
7.276
7.278
X : parts per Million : Proton

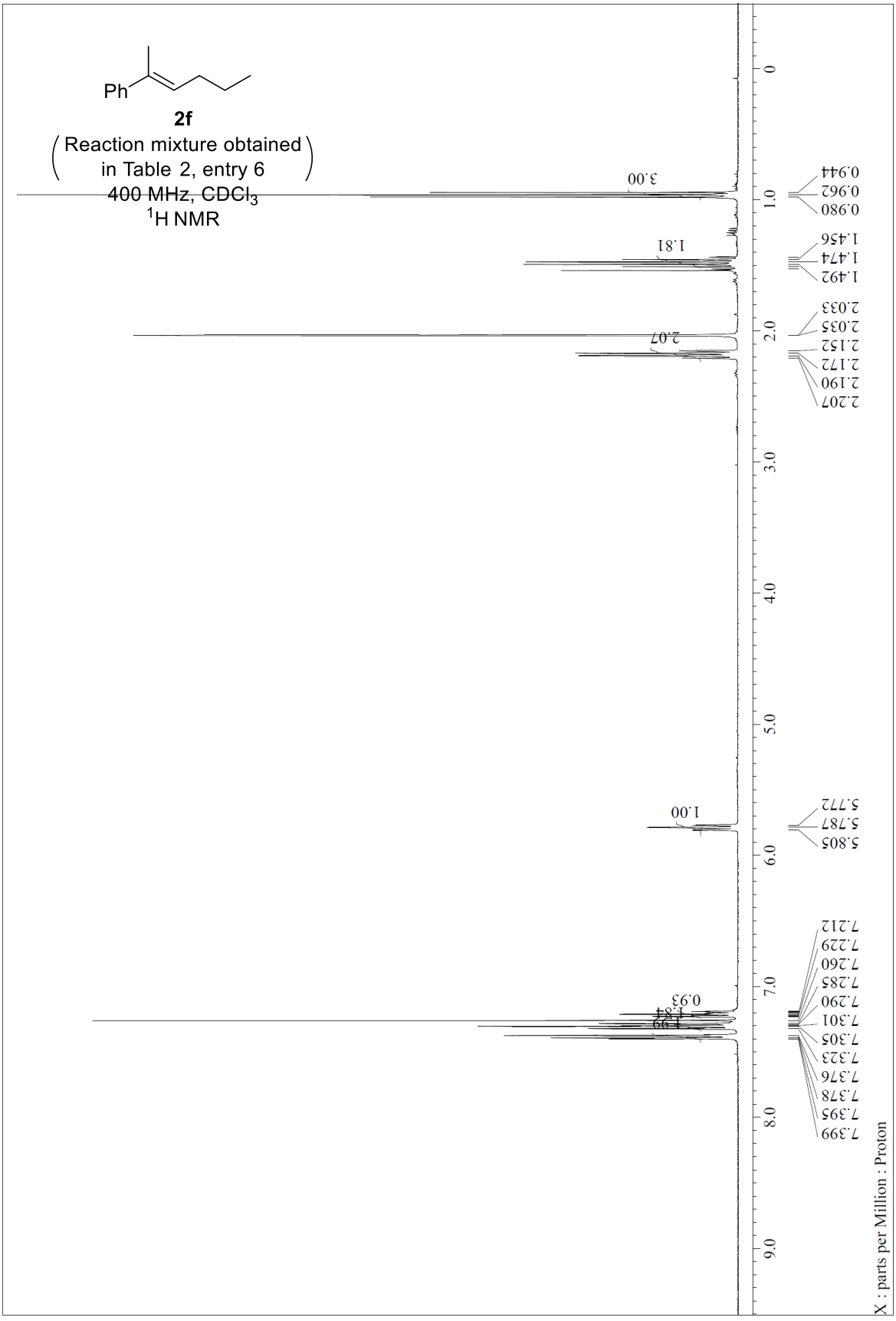

Cl
2c
(Reaction mixture obtained in Table 2, entry 3)
100 MHz, CDCl3
13C NMR
13.719
22.434
35.057
76.685
77.000
77.315
127.085
128.553
128.687
131.719
132.234
136.400
X : parts per Million : Carbon13

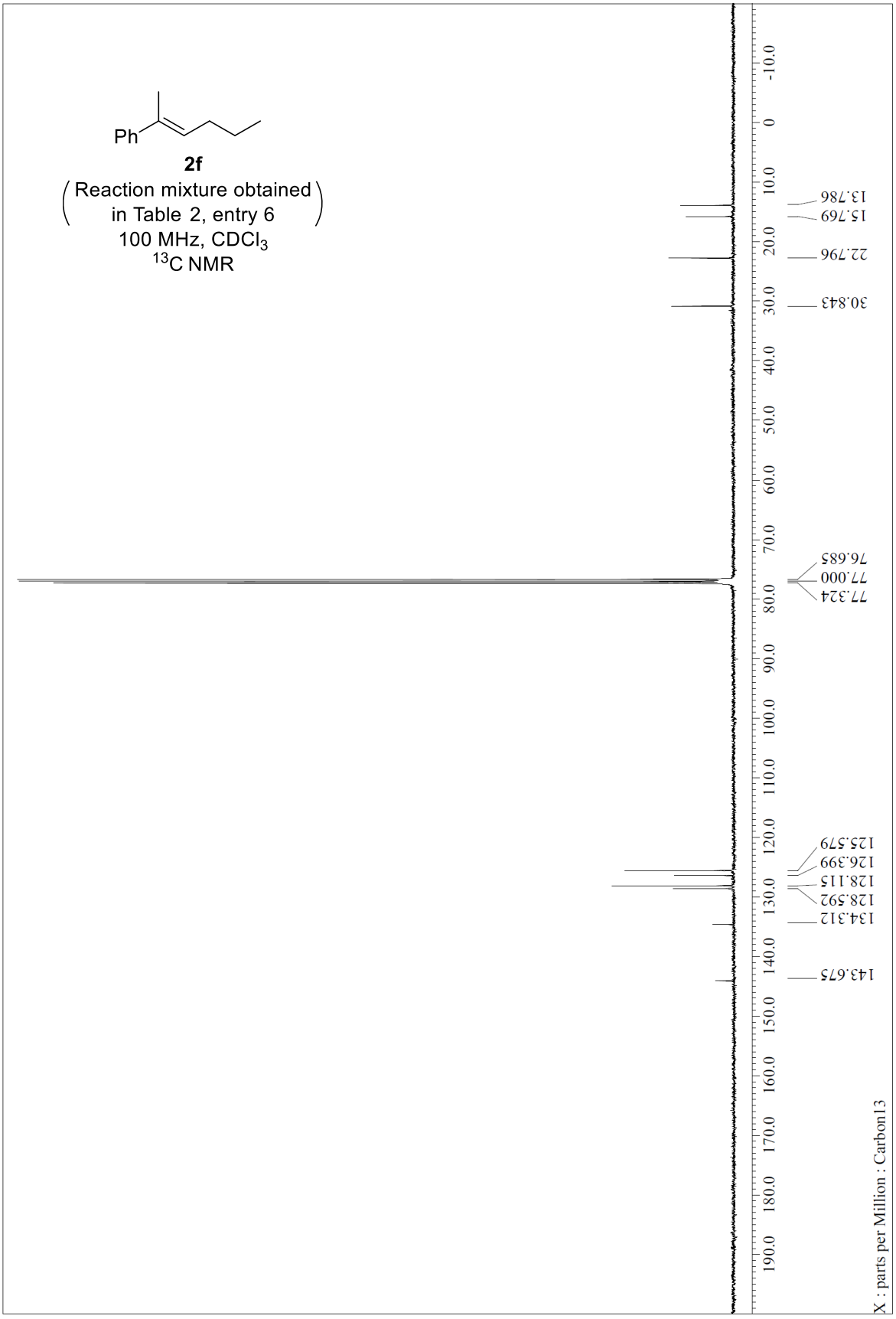

CF3
2d
Reaction mixture obtained
in Table 2, entry 4
400 MHz, CDCl3
1H NMR
2.84
1.82
1.78
2.00
1.83
2.25
0.985
0.967
0.948
1.546
1.527
1.508
1.490
2.246
2.229
2.211
2.193
6.434
6.394
6.368
6.352
6.336
6.312
6.295
7.545
7.525
7.434
7.413
7.260
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

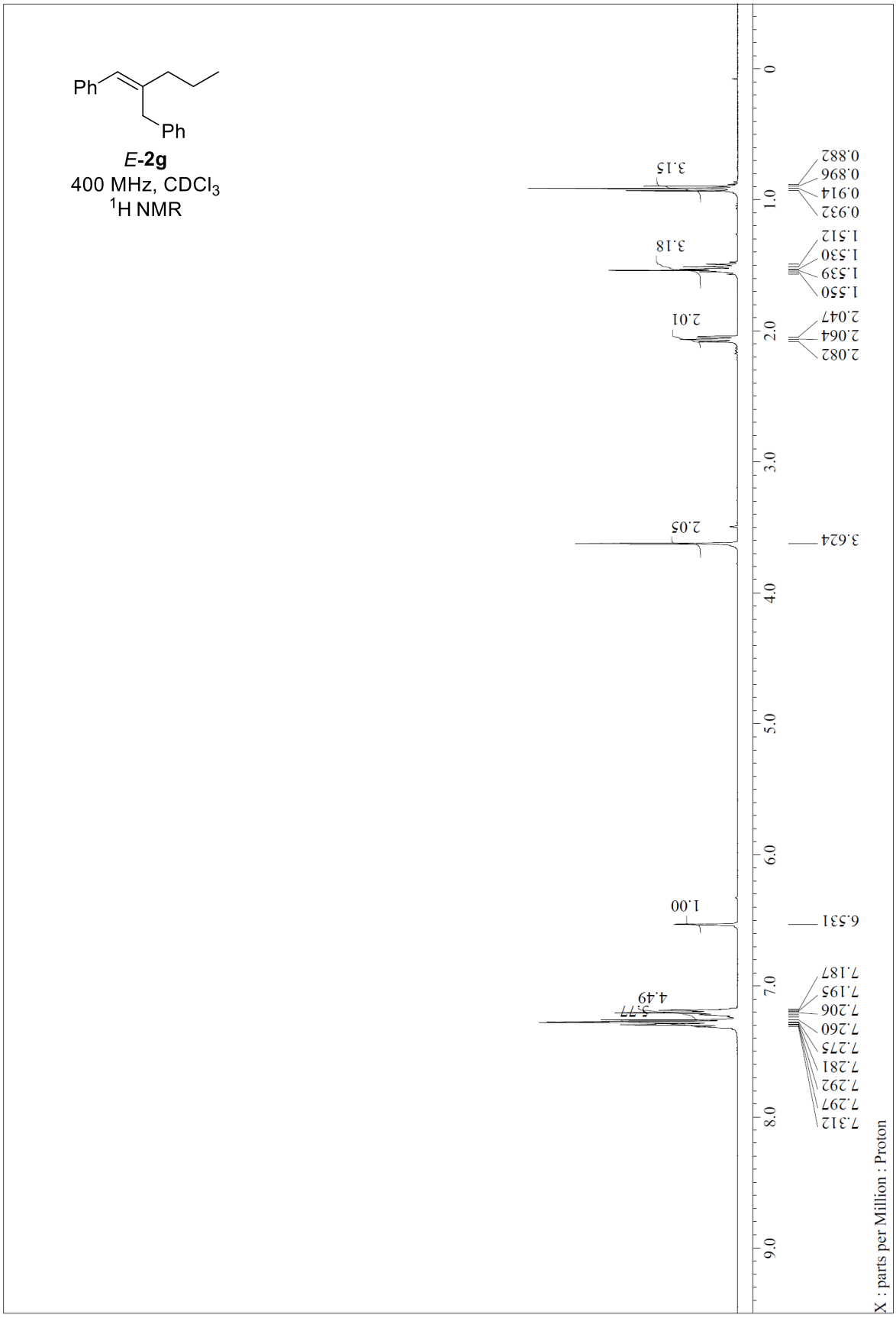

CF3
2d
Reaction mixture obtained
in Table 2, entry 4
100 MHz, CDCl3
13C NMR
13.700
22.319
35.105
76.676
77.000
77.315
122.890
125.111
125.340
125.378
125.417
125.455
125.655
125.998
128.096
128.420
128.735
133.836
141.387
X : parts per Million : Carbon13

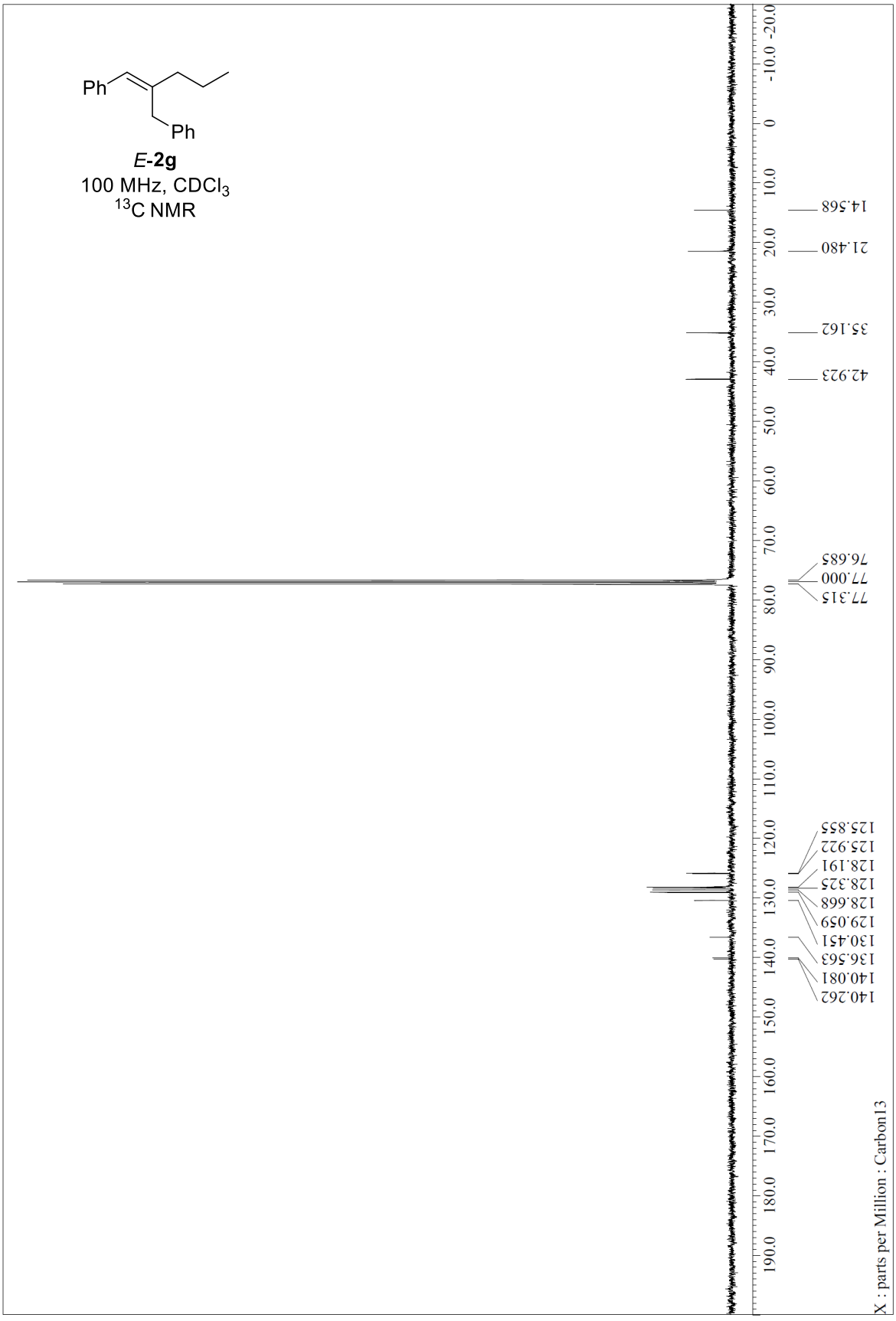

2e
Reaction mixture obtained
in Table 2, entry 5
400 MHz, CDCl3
1H NMR
3.39
2.23
2.08
1.00
1.08
2.34
1.10
1.21
1.176
1.195
1.213
1.717
1.735
1.754
1.772
2.404
2.423
2.441
2.459
6.353
6.371
6.388
6.392
6.410
6.427
6.805
6.844
7.260
7.468
7.486
7.491
7.855
7.872
7.939
7.960
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

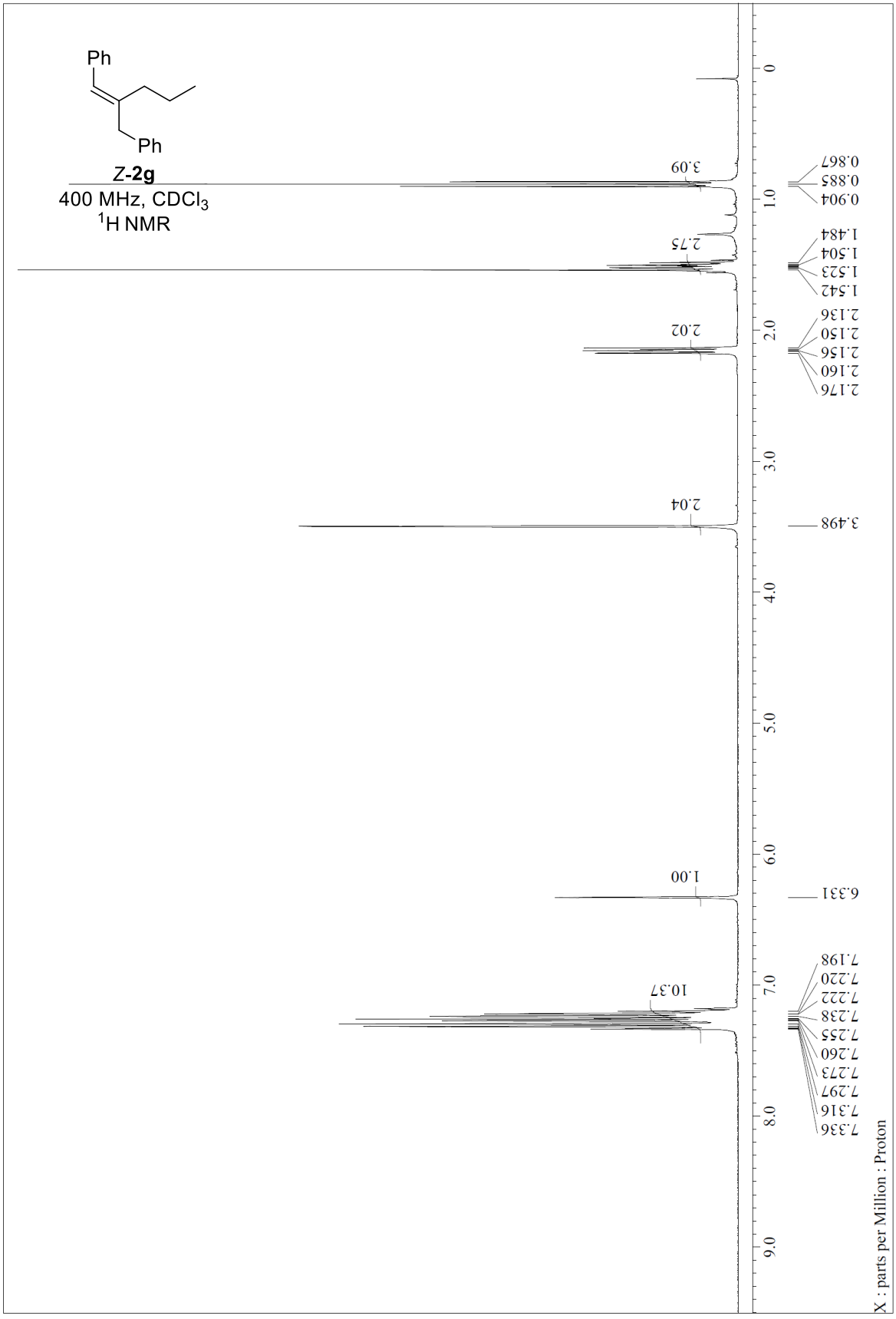

2e
Reaction mixture obtained
in Table 2, entry 5
100 MHz, CDCl3
13C NMR
13.709
22.281
34.991
76.685
77.000
77.324
121.050
122.079
123.100
123.910
124.177
124.253
133.855
138.517
140.262
143.284
X : parts per Million : Carbon13

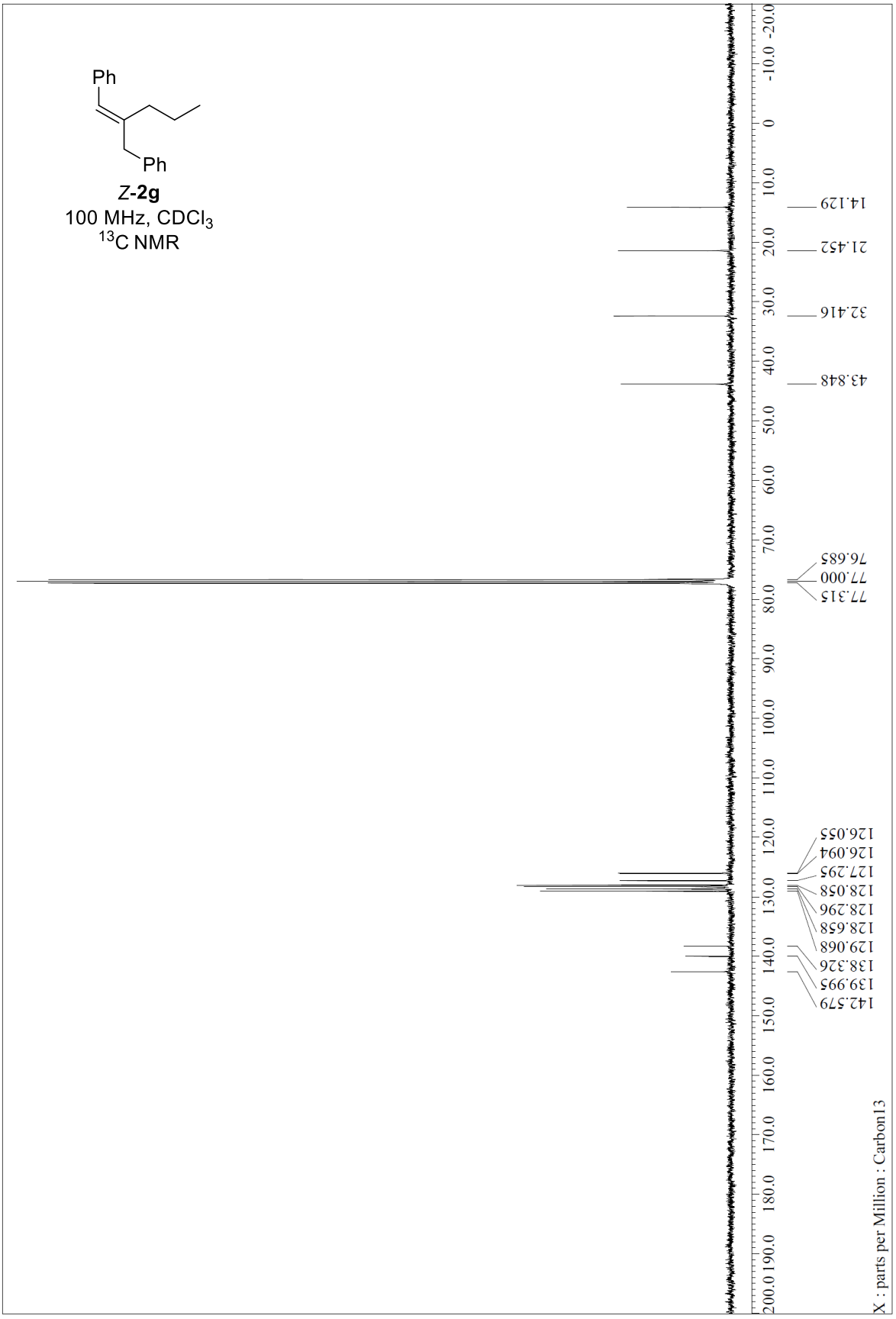

Ph
2f
Reaction mixture obtained
in Table 2, entry 6
400 MHz, CDCl3
1H NMR
3.00
1.81
2.07
1.00
0.93
1.84
1.99
0.944
0.962
0.980
1.456
1.474
1.492
2.033
2.035
2.152
2.172
2.190
2.207
5.772
5.787
5.805
7.212
7.229
7.260
7.285
7.290
7.301
7.305
7.323
7.376
7.378
7.395
7.399
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

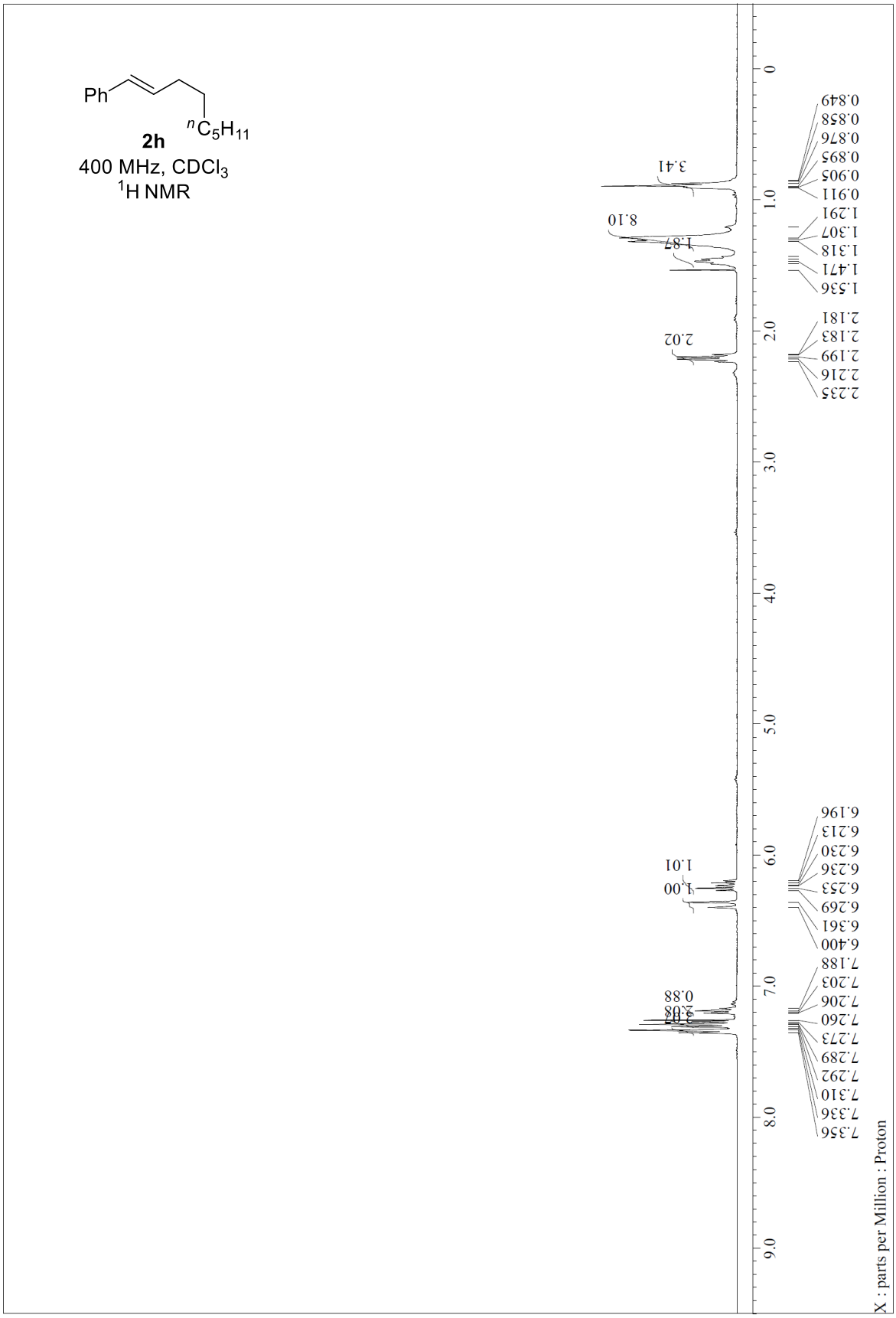

Ph
2f
(Reaction mixture obtained in Table 2, entry 6)
100 MHz, CDCl3
13C NMR
13.786
15.769
22.796
30.843
76.685
77.000
77.324
125.579
126.399
128.115
128.592
134.312
143.675
X : parts per Million : Carbon13

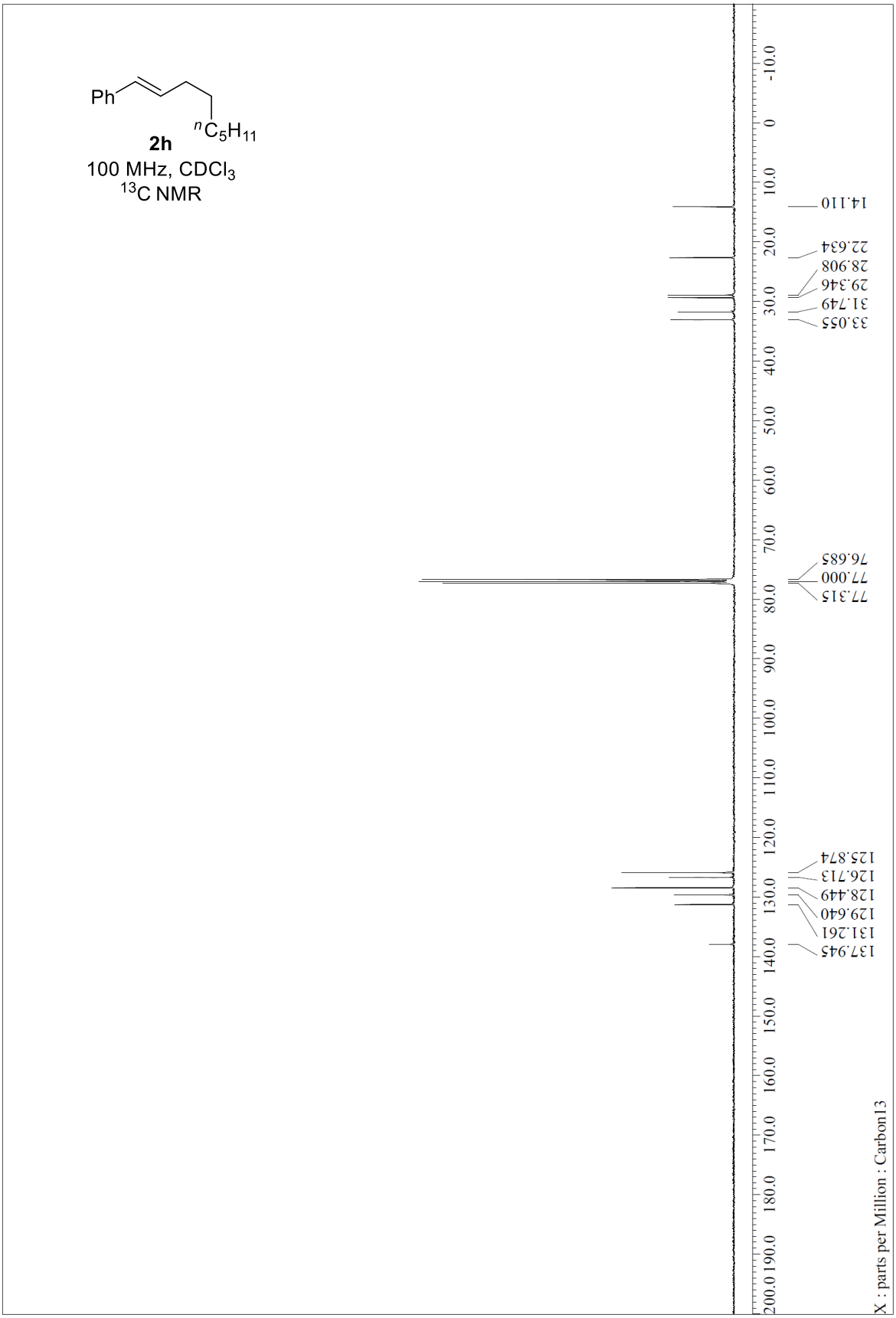

Ph
Ph
E-2g
400 MHz, CDCl3
1H NMR
3.15
3.18
2.01
2.05
1.00
4.49
5.77
0.882
0.896
0.914
0.932
1.512
1.530
1.539
1.550
2.047
2.064
2.082
3.624
6.531
7.187
7.195
7.206
7.260
7.275
7.281
7.292
7.297
7.312
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

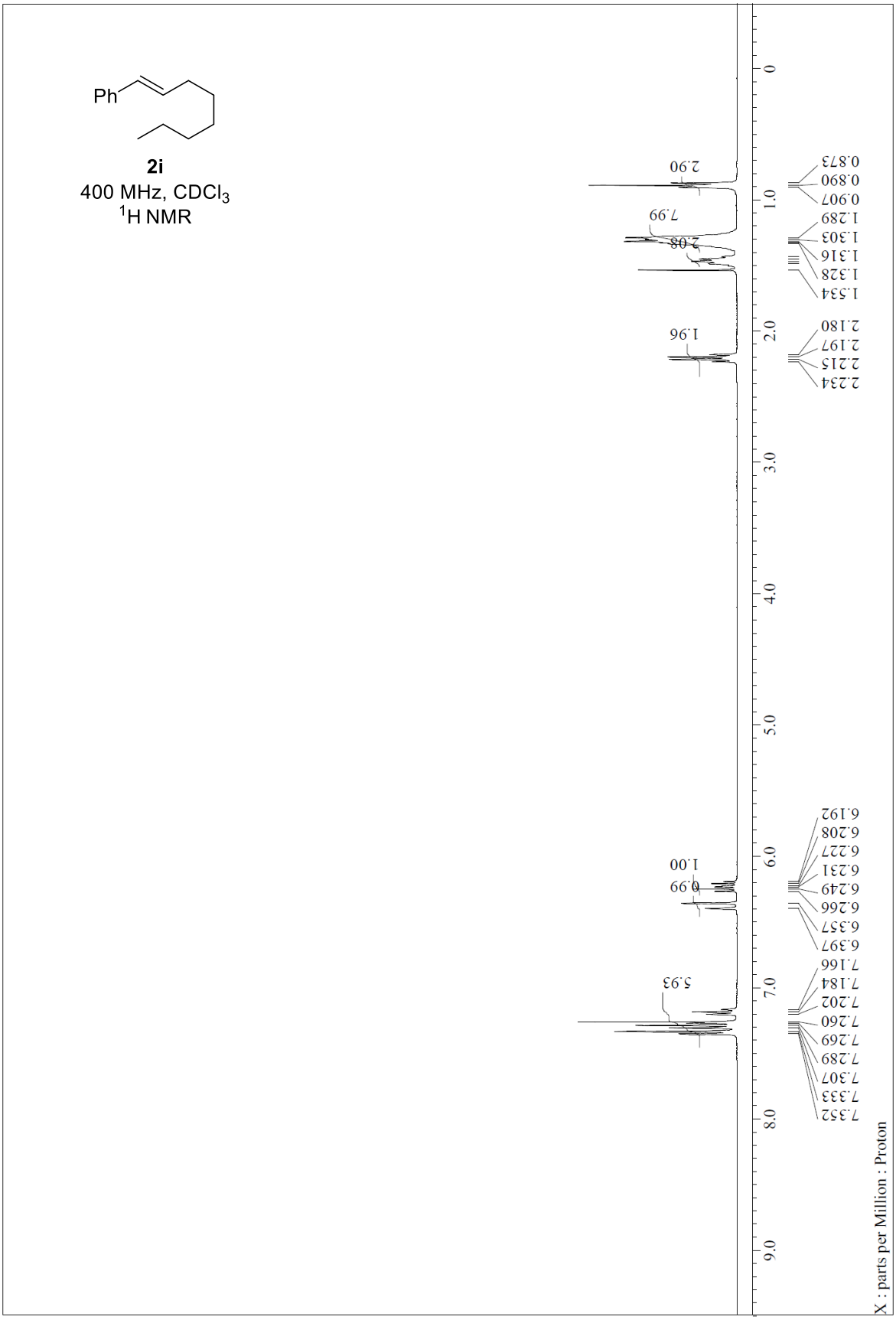

Ph
Ph
E-2g
100 MHz, CDCl3
13C NMR
14.568
21.480
35.162
42.923
76.685
77.000
77.315
125.855
125.922
128.191
128.325
128.668
129.059
130.451
136.563
140.081
140.262
X : parts per Million : Carbon13

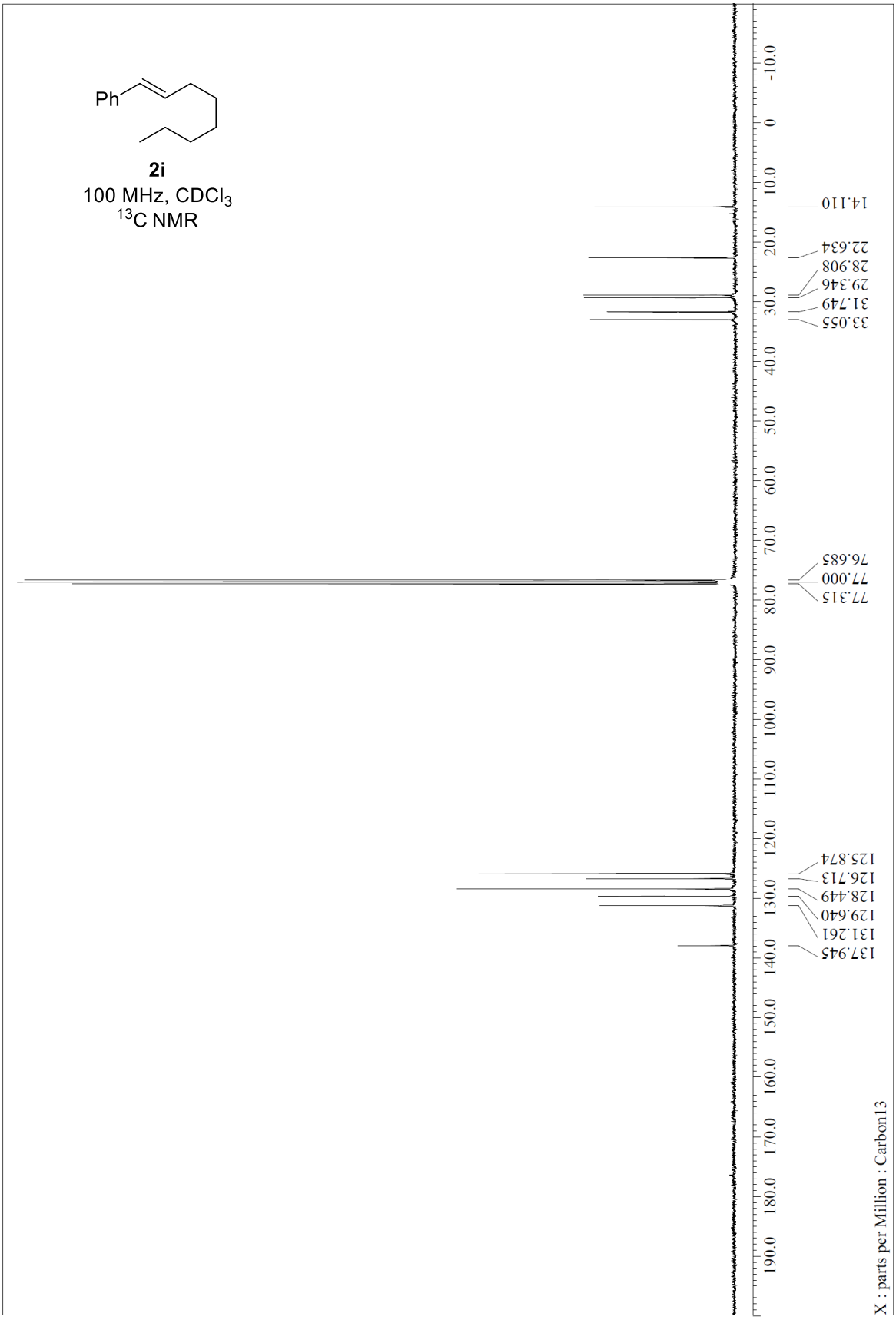

Ph
Ph
Z-2g
400 MHz, CDCl3
1H NMR
3.09
2.75
2.02
2.04
1.00
10.37
0.867
0.885
0.904
1.484
1.504
1.523
1.542
2.136
2.150
2.156
2.160
2.176
3.498
6.331
7.198
7.220
7.222
7.238
7.255
7.260
7.273
7.297
7.316
7.336
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

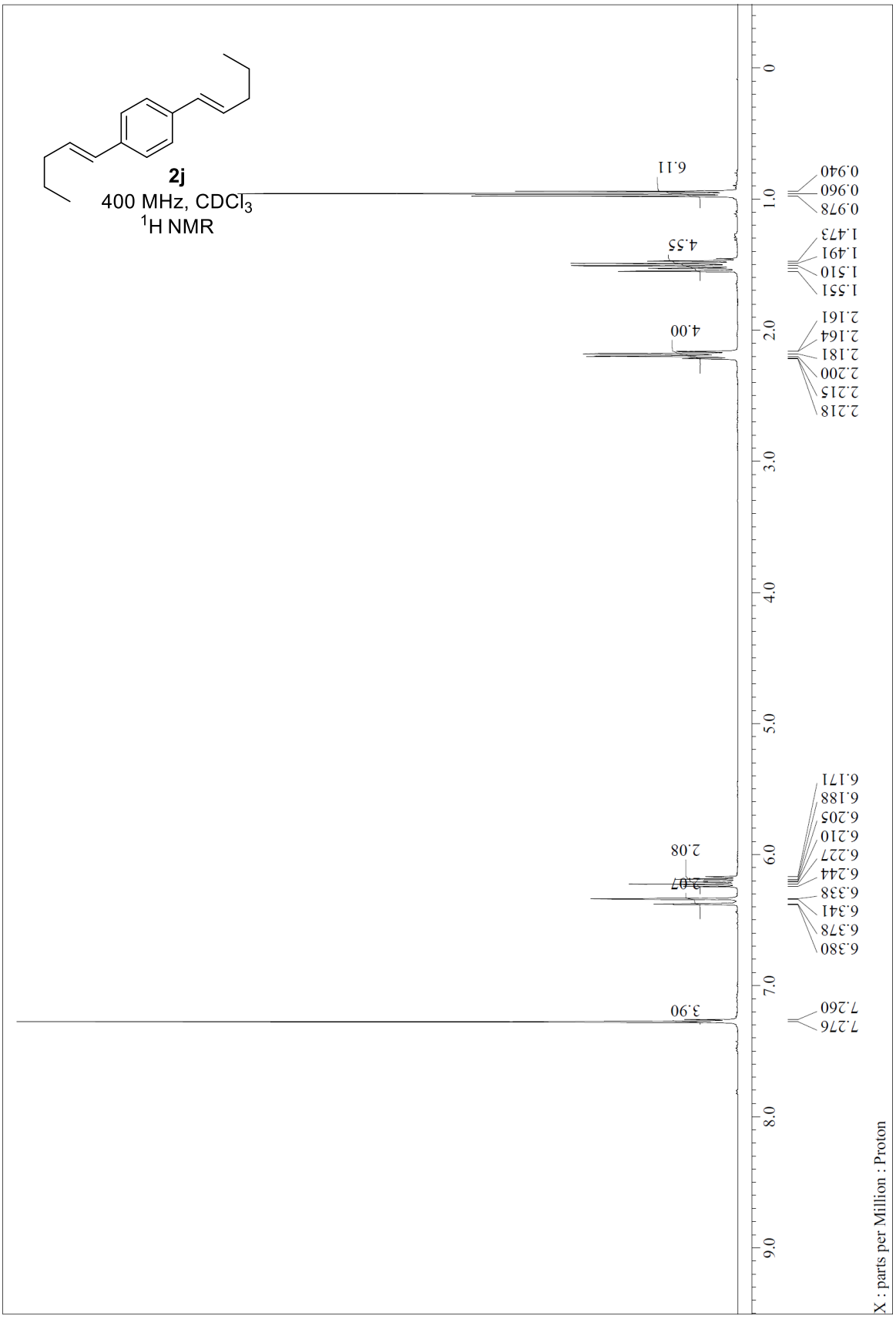

Ph
Ph
Z-2g
100 MHz, CDCl3
13C NMR
14.129
21.452
32.416
43.848
76.685
77.000
77.315
126.055
126.094
127.295
128.058
128.296
128.658
129.068
138.326
139.995
142.579
X : parts per Million : Carbon13

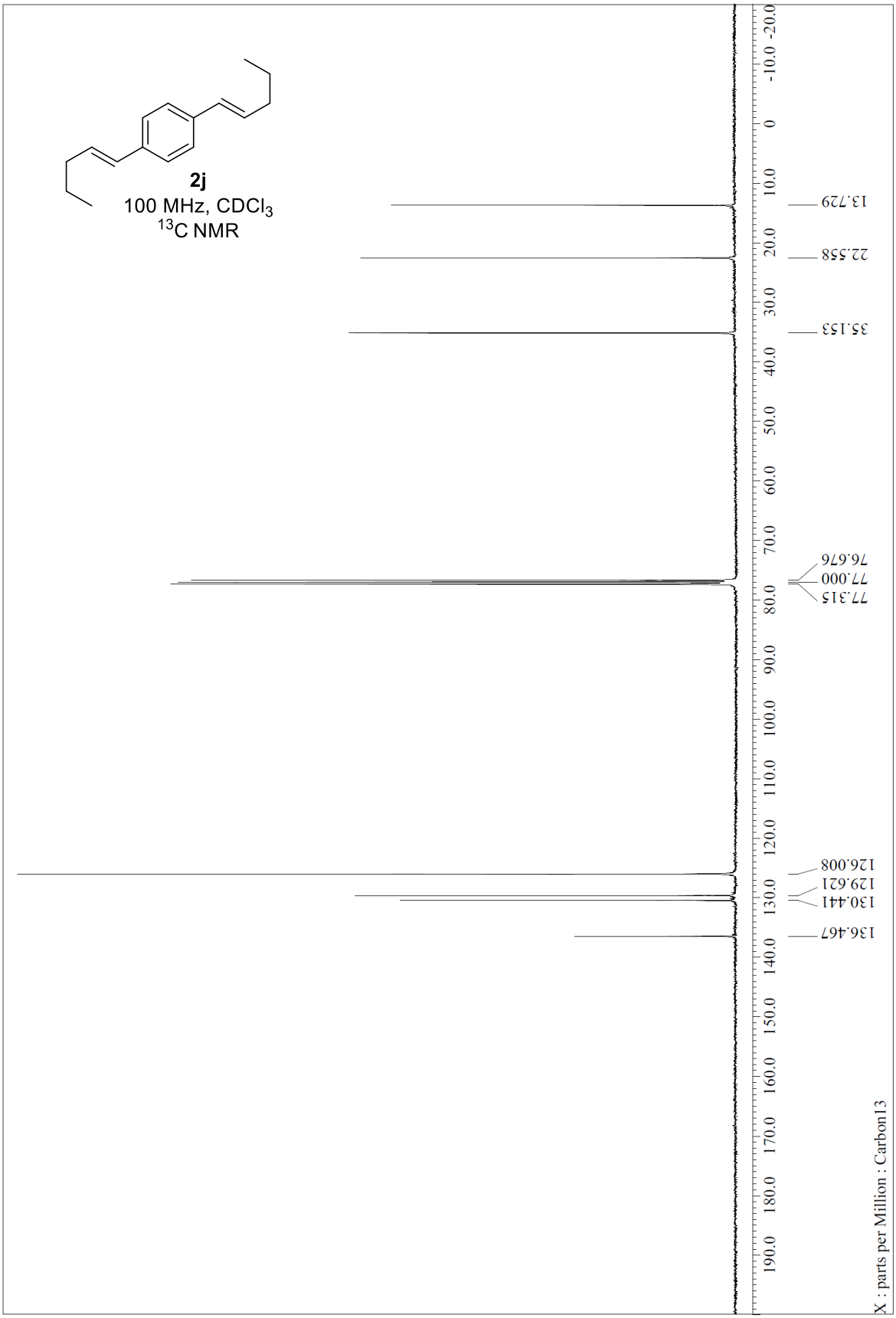

Ph
$^{n}C_5H_{11}$
2h
400 MHz, CDCl3
1H NMR
3.41
8.10
1.87
2.02
1.00
1.01
3.08
0.88
0.849
0.858
0.876
0.895
0.905
0.911
1.291
1.307
1.318
1.471
1.536
2.181
2.183
2.199
2.216
2.235
6.196
6.213
6.230
6.236
6.253
6.269
6.361
6.400
7.188
7.203
7.206
7.260
7.273
7.289
7.292
7.310
7.336
7.356
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

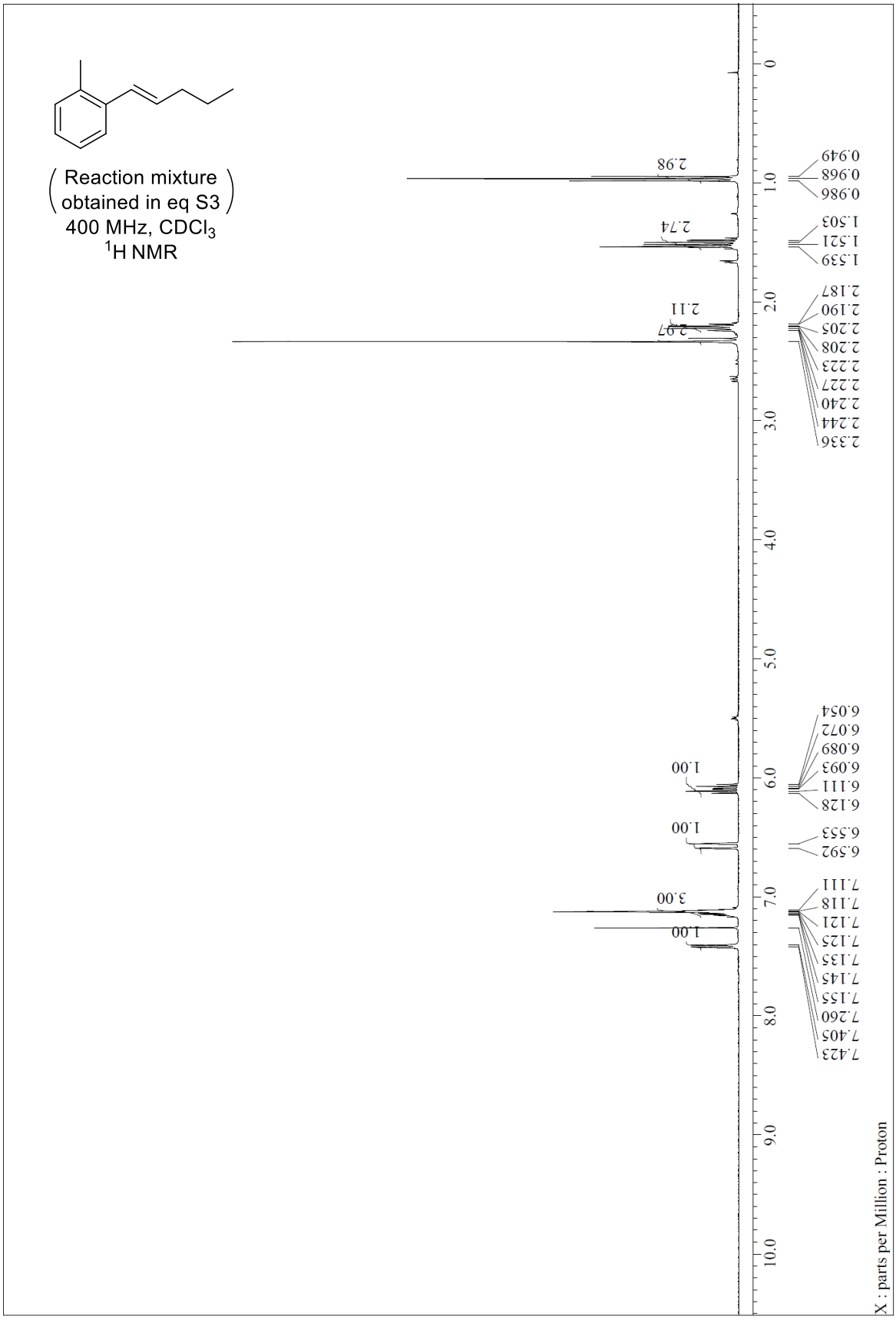

Ph
$^{n}C_5H_{11}$
2h
100 MHz, $CDCl_3$
^{13}C NMR
14.110
22.634
28.908
29.346
31.749
33.055
76.685
77.000
77.315
125.874
126.713
128.449
129.640
131.261
137.945
X : parts per Million : Carbon13

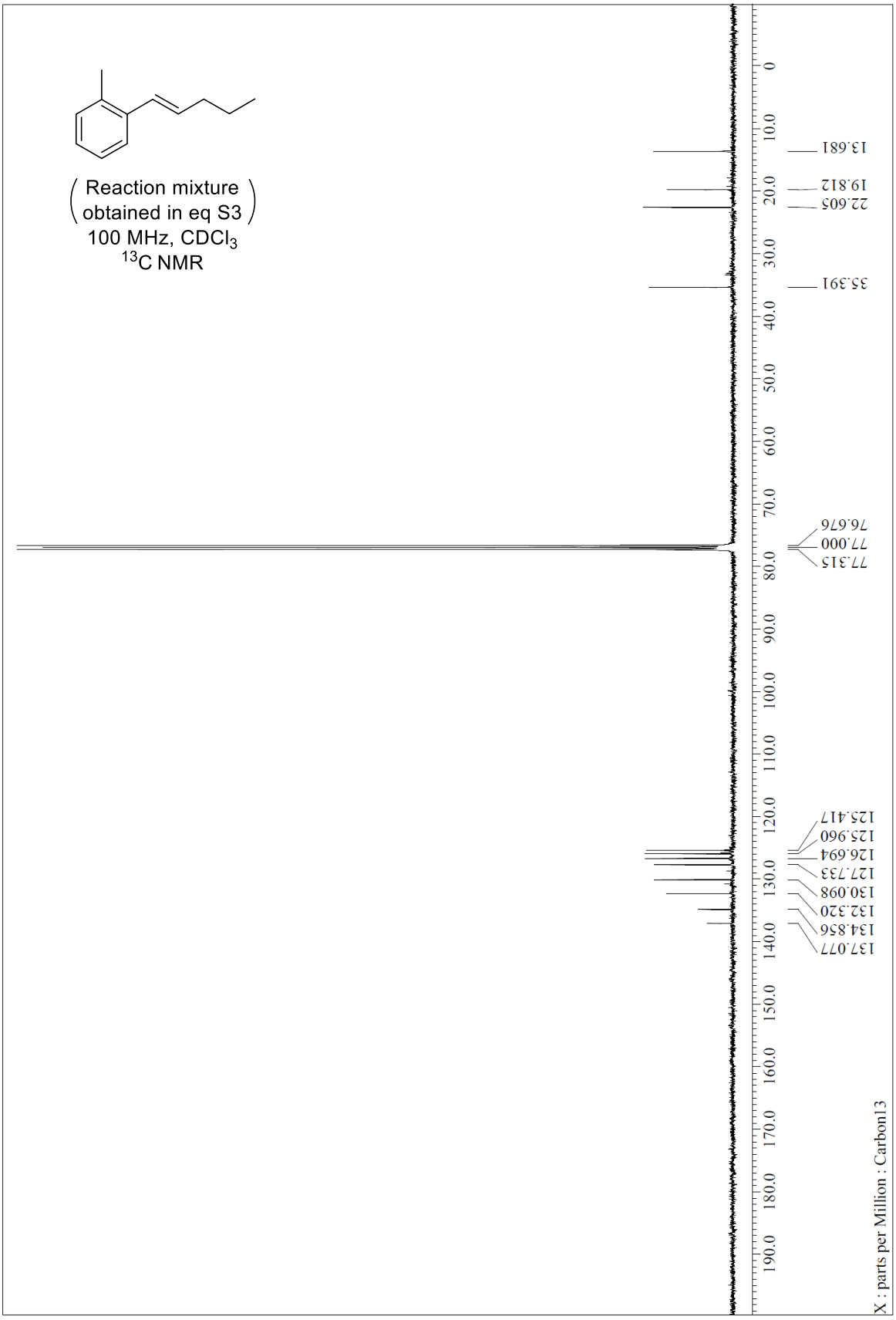

Ph
2i
400 MHz, CDCl3
1H NMR
2.90
7.99
2.08
1.96
1.00
0.99
5.93
0.873
0.890
0.907
1.289
1.303
1.316
1.328
1.534
2.180
2.197
2.215
2.234
6.192
6.208
6.227
6.231
6.249
6.266
6.357
6.397
7.166
7.184
7.202
7.260
7.269
7.289
7.307
7.333
7.352
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

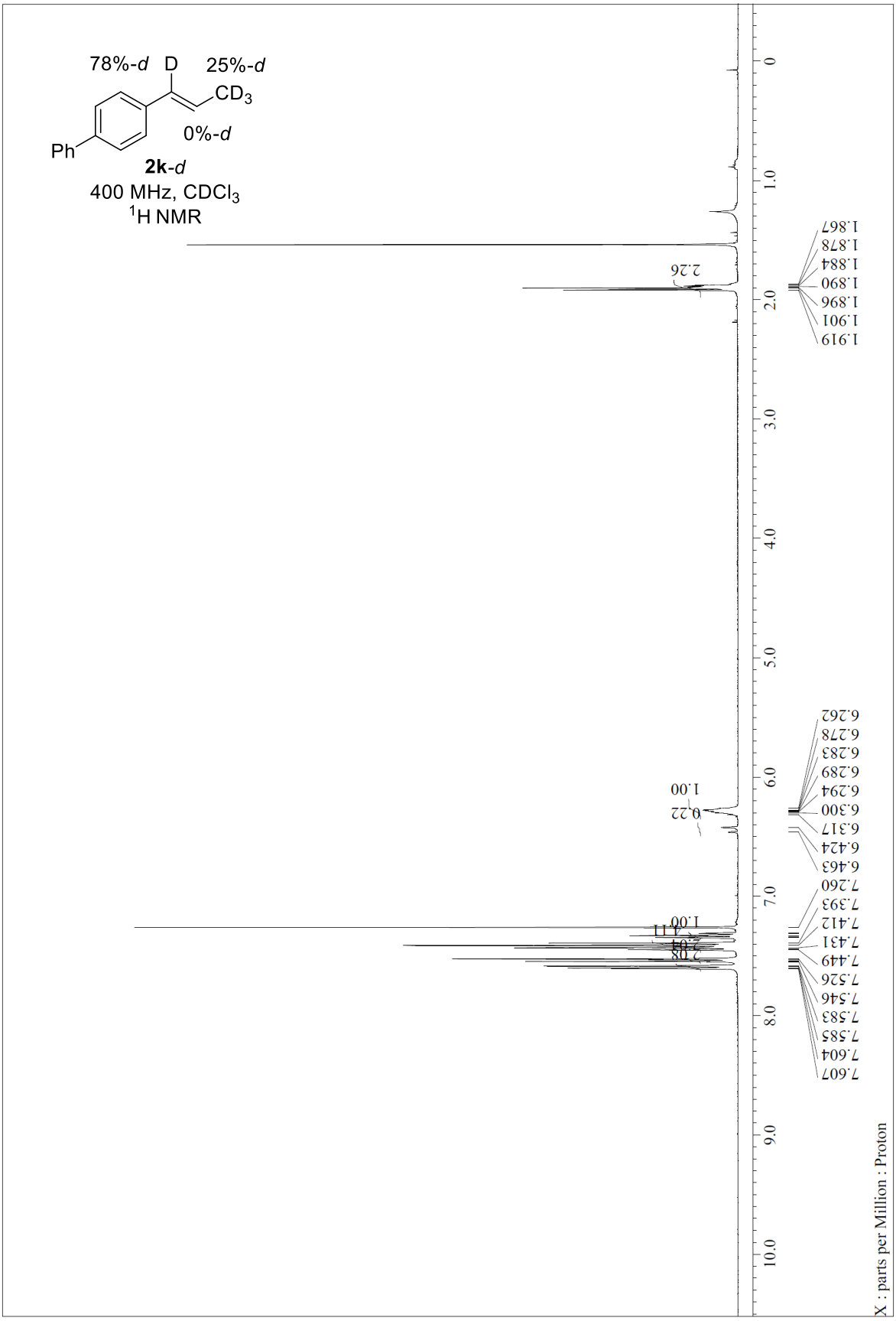

Ph
2i
100 MHz, CDCl3
13C NMR
14.110
22.634
28.908
29.346
31.749
33.055
76.685
77.000
77.315
125.874
126.713
128.449
129.640
131.261
137.945
X : parts per Million : Carbon13

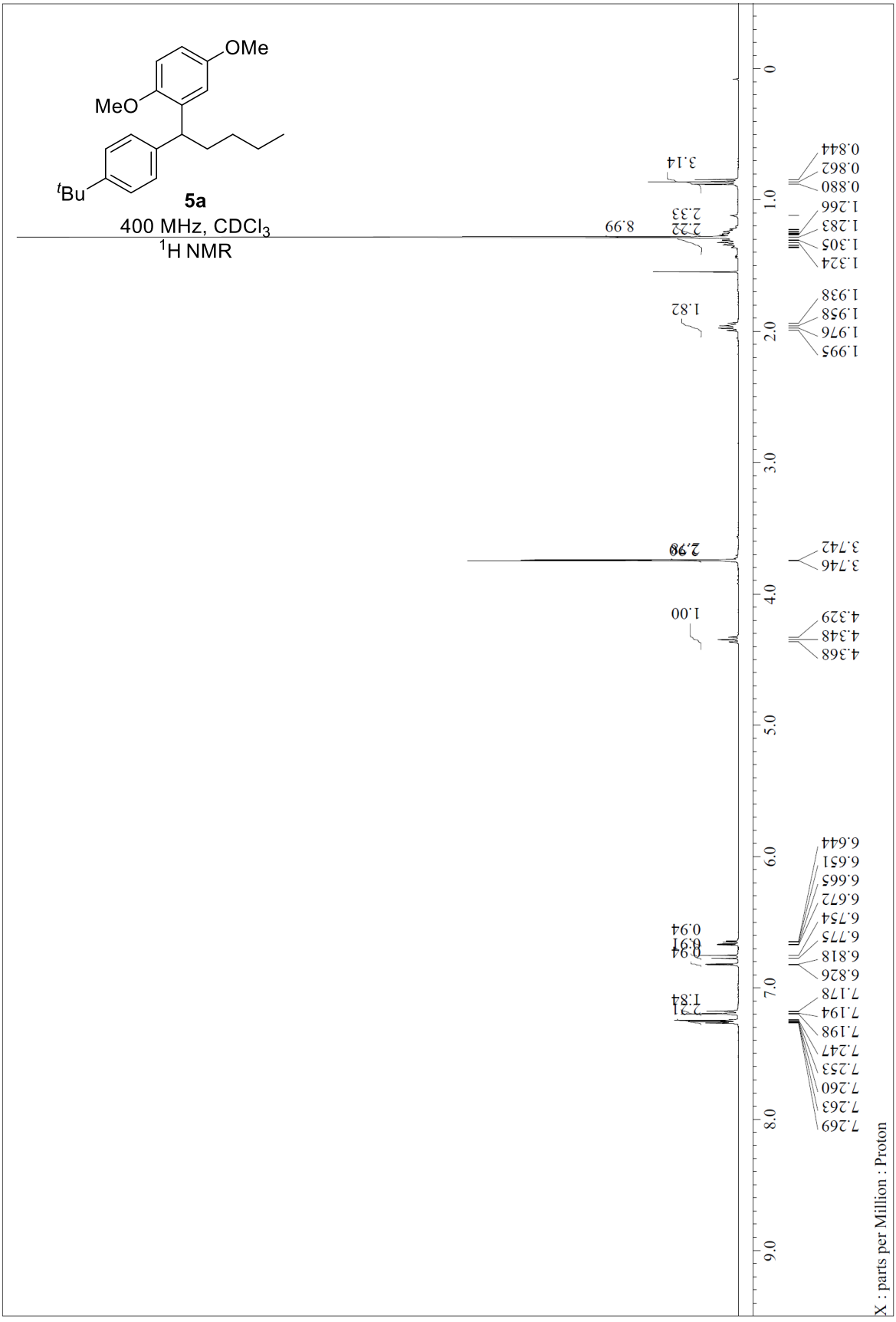

2j
400 MHz, CDCl3
1H NMR
6.11
4.55
4.00
2.08
3.07
3.90
0.940
0.960
0.978
1.473
1.491
1.510
1.551
2.161
2.164
2.181
2.200
2.215
2.218
6.171
6.188
6.205
6.210
6.227
6.244
6.338
6.341
6.378
6.380
7.260
7.276
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : Proton

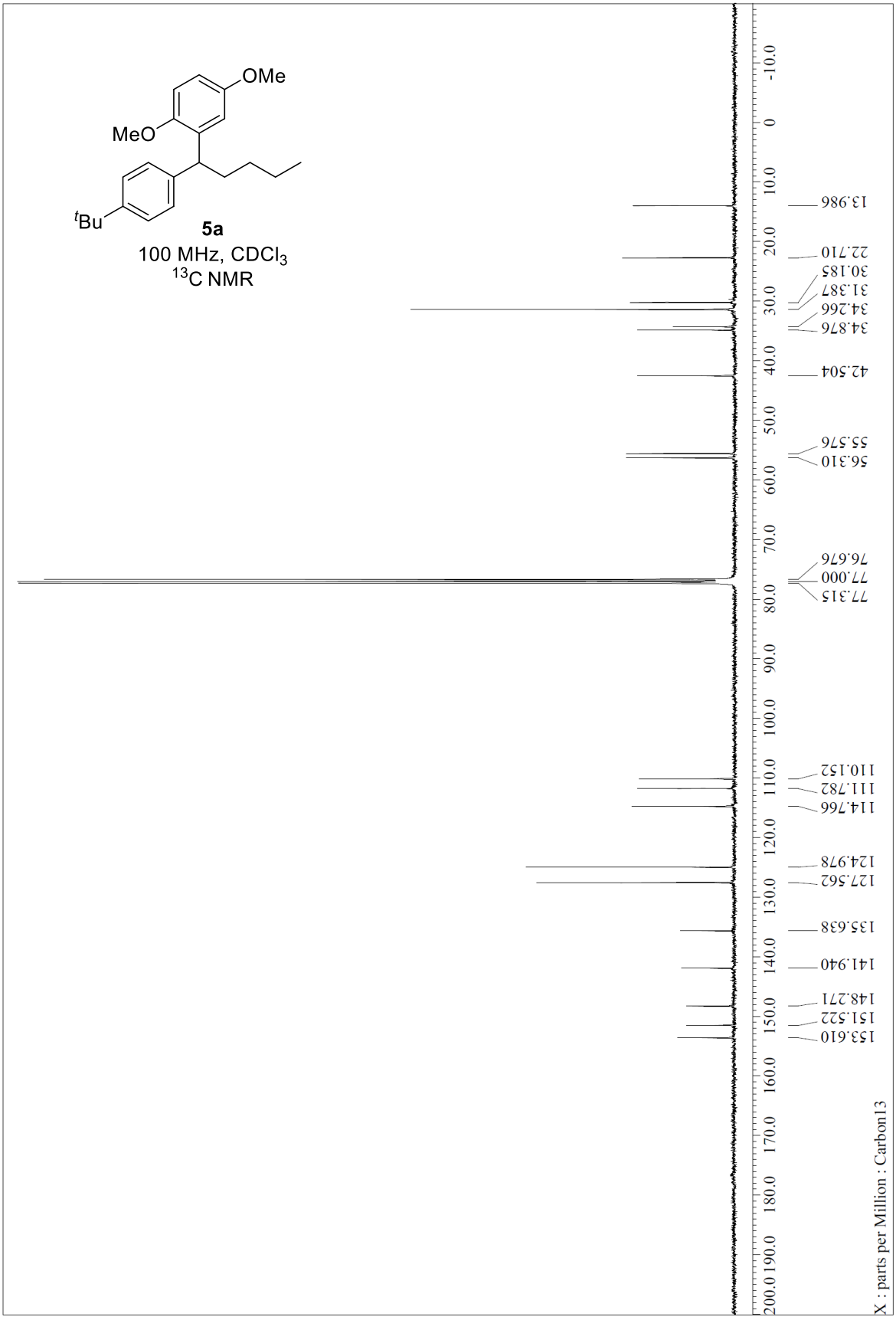

2j
100 MHz, CDCl3
13C NMR
13.729
22.558
35.153
76.676
77.000
77.315
126.008
129.621
130.441
136.467
X : parts per Million : Carbon13

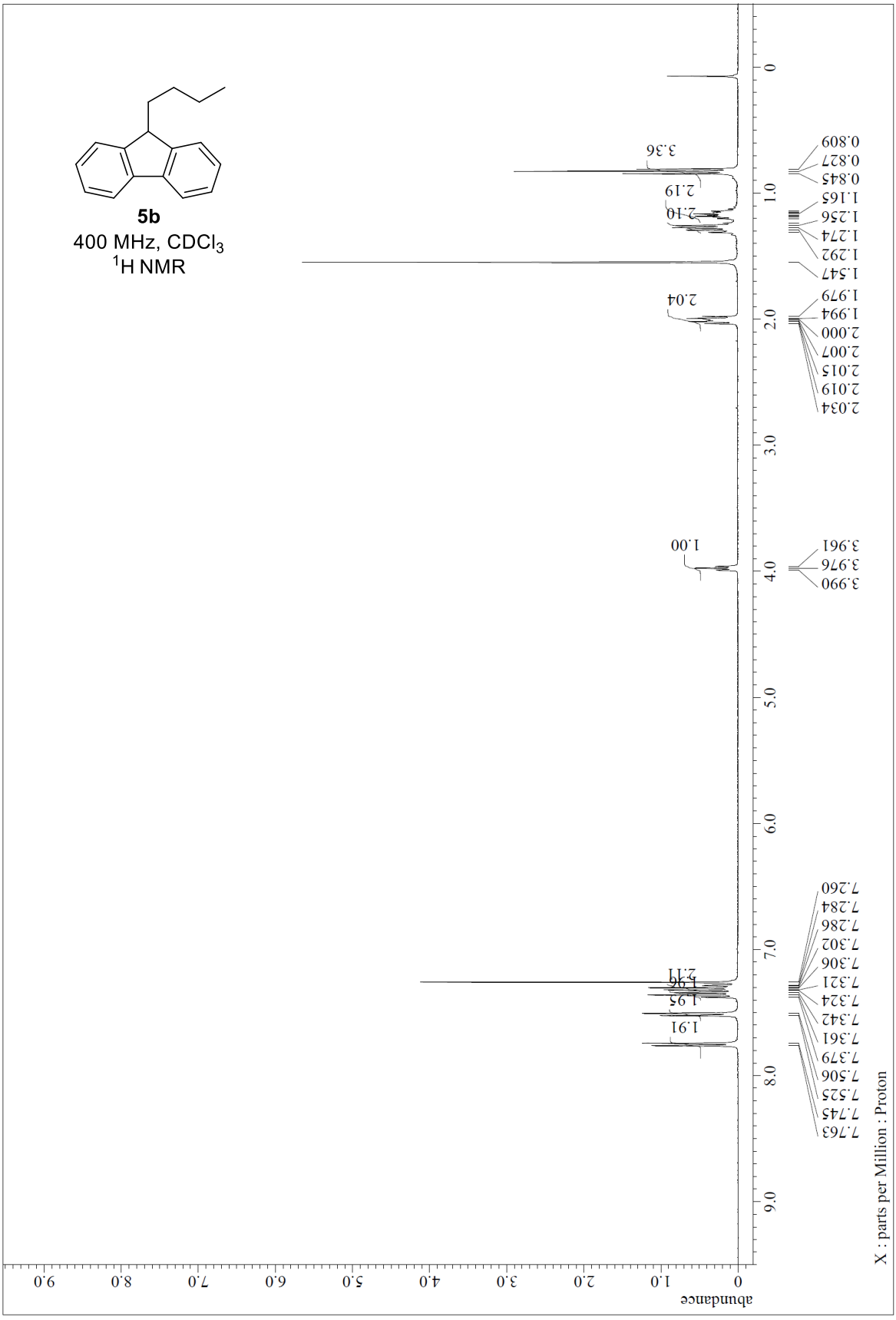

Reaction mixture
obtained in eq S3
400 MHz, CDCl3
1H NMR
2.98
2.74
2.11
2.07
1.00
1.00
3.00
1.00
0.949
0.968
0.986
1.503
1.521
1.539
2.187
2.190
2.205
2.208
2.223
2.227
2.240
2.244
2.336
6.054
6.072
6.089
6.093
6.111
6.128
6.553
6.592
7.111
7.118
7.121
7.125
7.135
7.145
7.155
7.260
7.405
7.423
X : parts per Million : Proton

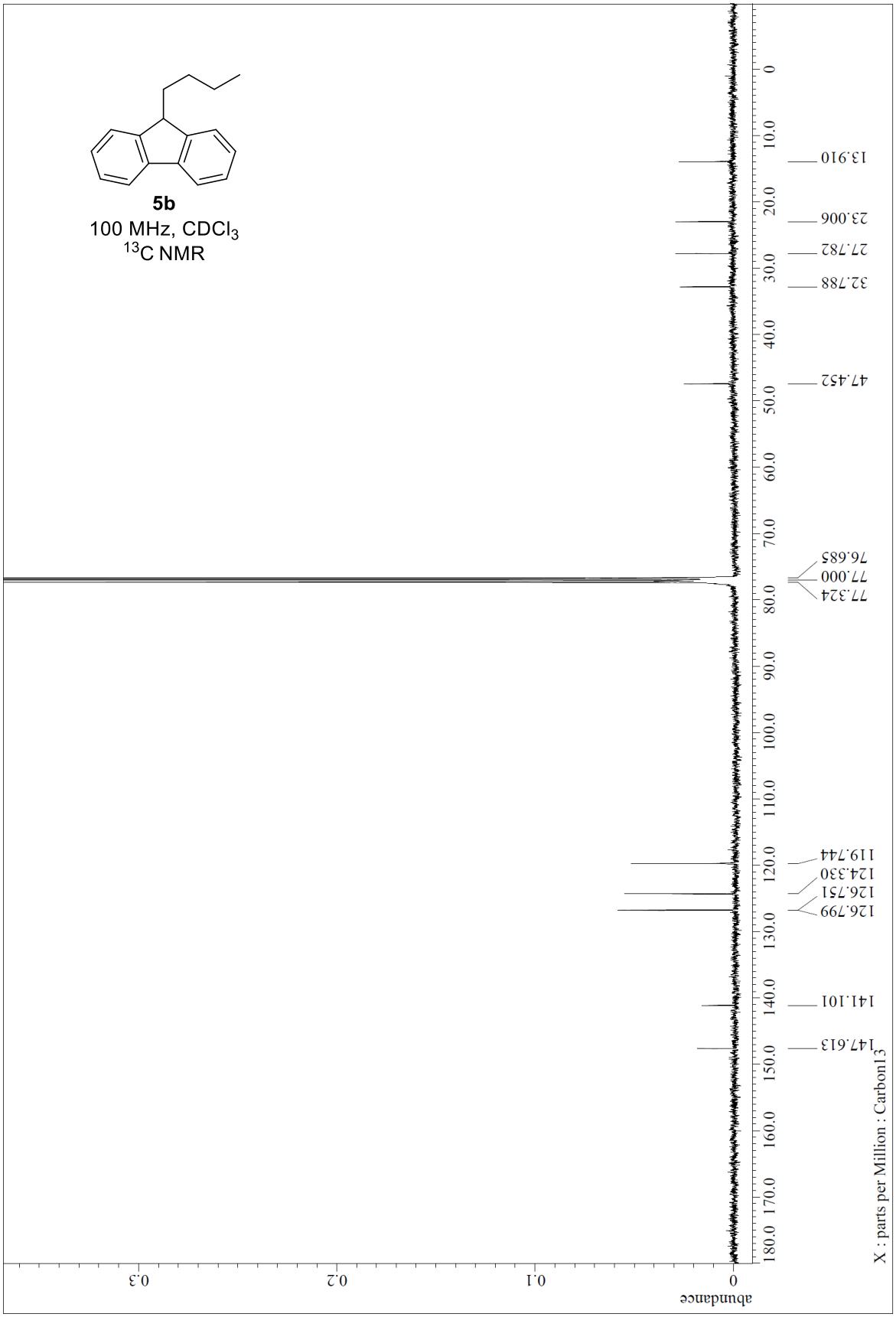

Reaction mixture
obtained in eq S3
100 MHz, CDCl3
13C NMR
13.681
19.812
22.605
33.391
76.676
77.000
77.315
125.417
125.960
126.694
127.733
130.098
132.320
134.856
137.077
X : parts per Million : Carbon13


78%-d
D
25%-d
CD3
0%-d
Ph
2k-d
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton


OMe
MeO
tBu
5a
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton


OMe
MeO
tBu
5a
100 MHz, CDCl3
13C NMR
13.986
22.710
30.185
31.387
34.266
34.876
42.504
55.576
56.310
76.676
77.000
77.315
110.152
111.782
114.766
124.978
127.562
135.638
141.940
148.271
151.522
153.610
X : parts per Million : Carbon13


5b
400 MHz, CDCl3
1H NMR
X : parts per Million : Proton
abundance


5b
100 MHz, CDCl3
13C NMR
13.910
23.006
27.782
32.788
47.452
76.685
77.000
77.324
119.744
124.330
126.751
126.799
141.101
147.613
X : parts per Million : Carbon13
abundance