Iodine-catalyzed three-component oxysulfenylation of alkenes with sulfonyl hydrazides and alcohols

Fu-Lai Yang,[a] Fu-Xiang Wang,[a] Ting-Ting Wang,[a] Yi-Jie Wang[a] and Shi-Kai Tian*[a,b]

[a] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China*
[b] *Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Supporting information

Table of contents

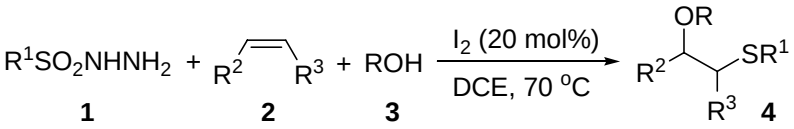
General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High-resolution mass spectrometry (HRMS) was performed on an LC-TOF spectrometer (Micromass). Electron spray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software.

Alkenes **2c** and **2e**,[1] sulfonyl hydrazides (**1b-j**),[2] compound **6a**,[3] disulfide **7a**, sulfonothioate **8a**,[4] sulfinic acid **9a**,[5] and sulfinate ester **10a**[6] were prepared according to literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI, and used as received.

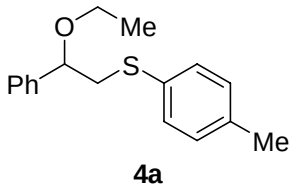
Abbreviations: DCE = 1,2-dichloroethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, NBS = *N*-bromosuccinimide, NIS = *N*-iodosuccinimide, Ts = *p*-toluenesulfonyl.

General procedure for the three-component oxysulfenylation of alkenes with sulfonyl hydrazides and alcohols



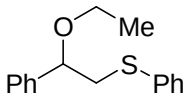
To a solution of sulfonyl hydrazide **1** (0.20 mmol) in 1,2-dichloroethane (0.50 mL) were added alkene **2** (0.24 mmol), alcohol **3** (0.050 mL), and iodine (10.2 mg, 20 mol%). The resulting mixture was stirred at 70 °C for 16 h, cooled to room temperature, and purified by silica gel chromatography, eluting with petroleum ether/ethyl acetate (20:1 to 3:1), to give compound **4**.

Analytical data for the products



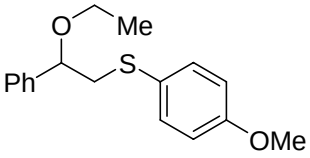
4a

Compound **4a**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.25 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.37 (dd, J = 8.0, 5.2 Hz, 1H), 3.44–3.24 (m, 3H), 3.07 (dd, J = 13.2, 5.2 Hz, 1H), 2.31 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 136.1, 132.9, 130.1, 129.7, 128.5, 128.0, 126.7, 80.7, 64.7, 42.3, 21.0, 15.3; HRMS (EI) calcd for $C_{17}H_{20}OS$ (M) 272.1235, found 272.1236.



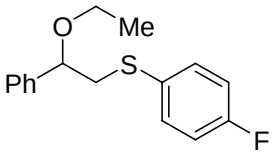
4b

Compound **4b**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 9H), 7.20–7.12 (m, 1H), 4.40 (dd, J = 8.0, 5.2 Hz, 1H), 3.45–3.28 (m, 3H), 3.12 (dd, J = 13.2, 5.2 Hz, 1H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 136.8, 129.3, 128.9, 128.5, 128.0, 126.7, 125.9, 80.7, 64.7, 41.6, 15.2; HRMS (EI) calcd for $C_{16}H_{18}OS$ (M) 258.1078, found 258.1070.



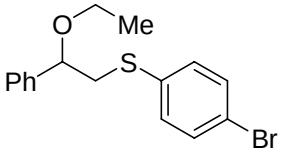
4c

Compound **4c**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 7H), 6.83 (d, J = 8.8 Hz, 2H), 4.33 (dd, J = 8.0, 5.2 Hz, 1H), 3.79 (s, 3H), 3.41–3.32 (m, 2H), 3.23 (dd, J = 13.2, 8.0 Hz, 1H), 3.01 (dd, J = 13.2, 5.2 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 141.4, 133.2, 128.4, 127.9, 126.8, 126.7, 114.5, 80.8, 64.6, 55.3, 43.7, 15.3; HRMS (EI) calcd for $C_{17}H_{20}O_2S$ (M) 288.1184, found 288.1172.



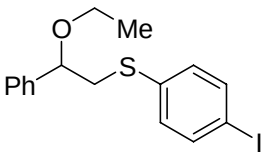
4d

Compound **4d**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 7H), 6.99–6.93 (m, 2H), 4.37 (dd, J = 8.0, 5.2 Hz, 1H), 3.42–3.22 (m, 3H), 3.06 (dd, J = 13.2, 5.2 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J = 245 Hz), 141.1, 132.4 (d, J = 7.9 Hz), 131.6 (d, J = 3.0 Hz), 128.5, 128.0, 126.7, 115.9 (d, J = 22 Hz), 80.8, 64.7, 42.9, 15.2; HRMS (EI) calcd for $C_{16}H_{17}FOS$ (M) 276.0984, found 276.0989.



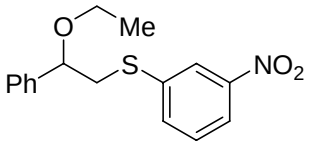
4e

Compound **4e**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 7H), 7.22–7.15 (m, 2H), 4.14 (dd, J = 8.0, 5.2 Hz, 1H), 3.43–3.25 (m, 3H), 3.09 (dd, J = 13.2, 5.2 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 136.1, 131.8, 130.8, 128.6, 128.1, 126.6, 119.7, 80.7, 64.7, 41.7, 15.2; HRMS (EI) calcd for $C_{16}H_{17}BrOS$ (M) 336.0183, found 336.0181.



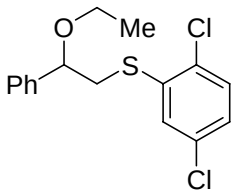
4f

Compound **4f**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 2H), 7.37–7.26 (m, 5H), 7.09–7.02 (m, 2H), 4.39 (dd, J = 8.0, 4.8 Hz, 1H), 3.42–3.24 (m, 3H), 3.09 (dd, J = 13.2, 4.8 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 137.7, 137.1, 130.8, 128.6, 128.1, 126.7, 90.5, 80.7, 64.7, 41.4, 15.3; HRMS (EI) calcd for $C_{16}H_{17}IOS$ (M) 384.0045, found 384.0040.



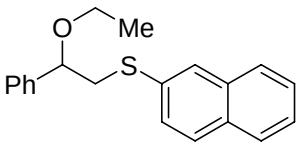
4g

Compound **4g**, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.13 (m, 1H), 7.98–7.93 (m, 1H), 7.61–7.55 (m, 1H), 7.43–7.27 (m, 6H), 4.48 (dd, J = 8.0, 4.8 Hz, 1H), 3.44–3.33 (m, 3H), 3.21 (dd, J = 13.2, 4.8 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 140.6, 140.3, 134.1, 129.3, 128.7, 128.3, 126.6, 122.6, 120.3, 80.9, 64.8, 41.0, 15.2; HRMS (EI) calcd for $C_{16}H_{17}NO_3S$ (M) 303.0929, found 303.0934.



4h

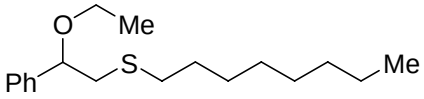
Compound **4h**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.29 (m, 5H), 7.27–7.21 (m, 2H), 7.07–7.00 (m, 1H), 4.49 (dd, J = 8.0, 4.8 Hz, 1H), 3.45–3.27 (m, 3H), 3.11 (dd, J = 13.2, 4.8 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.5, 132.8, 131.2, 130.3, 128.7, 128.3, 127.7, 126.6, 126.1, 80.6, 64.8, 40.4, 15.2; HRMS (EI) calcd for $C_{16}H_{16}Cl_2OS$ (M) 326.0299, found 326.0292.



4i

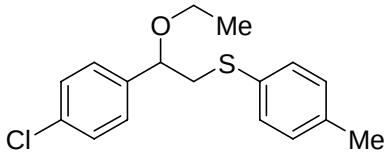
Compound **4i**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.67 (m, 4H), 7.49–7.26 (m, 8H), 4.46 (dd, J = 8.0, 5.2 Hz, 1H), 3.47–3.34 (m, 3H), 3.22 (dd, J = 13.2, 5.2 Hz, 1H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 134.4, 133.8, 131.7, 128.6, 128.4, 128.1, 127.7, 127.4, 127.1, 126.8, 126.7, 126.5,

125.6, 80.7, 64.7, 41.5, 15.3; HRMS (EI) calcd for $C_{20}H_{20}OS$ (M) 308.1235, found 308.1211.



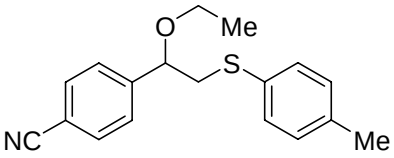
4j

Compound **4j**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5H), 4.38 (dd, J = 8.0, 5.2 Hz, 1H), 3.43–3.35 (m, 2H), 2.93 (dd, J = 13.2, 8.0 Hz, 1H), 2.69 (dd, J = 13.2, 5.2 Hz, 1H), 2.47 (t, J = 7.6 Hz, 2H), 1.60–1.47 (m, 2H), 1.35–1.14 (m, 13H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 128.4, 127.9, 126.7, 82.4, 64.5, 39.8, 33.1, 31.8, 29.7, 29.2, 28.9, 22.7, 15.3, 14.1; HRMS (EI) calcd for $C_{18}H_{30}OS$ (M) 294.2017, found 294.2020.



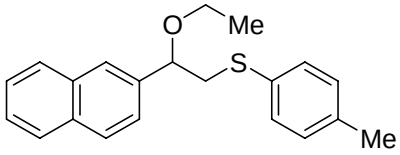
4k

Compound **4k**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.26–7.20 (m, 4H), 7.08 (d, J = 7.6 Hz, 2H), 4.33 (dd, J = 7.6, 5.6 Hz, 1H), 3.38–3.32 (m, 2H), 3.27 (dd, J = 13.6, 7.6 Hz, 1H), 3.02 (dd, J = 13.6, 5.6 Hz, 1H), 2.31 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 136.3, 133.6, 132.5, 130.3, 129.7, 128.6, 128.1, 80.1, 64.8, 42.1, 21.0, 15.2; HRMS (EI) calcd for $C_{17}H_{19}ClOS$ (M) 306.0845, found 306.0833.



4l

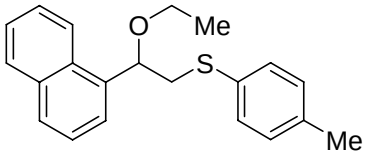
Compound **4l**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 4.43–4.36 (m, 1H), 3.41–3.33 (m, 2H), 3.27 (dd, J = 13.2, 7.2 Hz, 1H), 3.03 (dd, J = 13.2, 5.6 Hz, 1H), 2.32 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 136.7, 132.3, 132.1, 130.4, 129.8, 127.5, 118.8, 111.7, 80.2, 65.2, 41.9, 21.0, 15.2; HRMS (EI) calcd for $C_{18}H_{19}NOS$ (M) 297.1187, found 297.1183.



4m

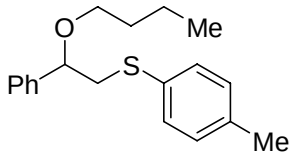
Compound **4m**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.81 (m, 3H),

7.75–7.73 (m, 1H), 7.50–7.42 (m, 3H), 7.30–7.25 (m, 2H), 7.07 (d, J = 7.6 Hz, 2H), 4.57–4.51 (m, 1H), 3.45–3.32 (m, 3H), 3.16 (dd, J = 13.2, 4.8 Hz, 1H), 2.31 (s, 3H), 1.20 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.4, 133.9, 132.7, 130.9, 130.8, 129.7, 129.0, 128.3, 126.0, 125.5, 124.2, 123.0, 78.6, 65.0, 42.2, 21.1, 15.4; HRMS (EI) calcd for $C_{21}H_{22}OS$ (M) 322.1391, found 322.1377.



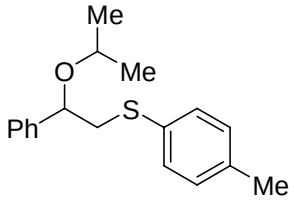
4n

Compound **4n**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.50–7.39 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.10 (dd, J = 8.4, 4.0 Hz, 1H), 3.50–3.40 (m, 2H), 3.39–3.24 (m, 2H), 2.33 (s, 3H), 1.23 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.2, 133.3, 133.2, 132.8, 130.2, 129.6, 128.4, 127.9, 127.7, 126.2, 126.1, 126.0, 124.3, 80.9, 64.7, 42.1, 21.0, 15.3; HRMS (EI) calcd for $C_{21}H_{22}OS$ (M) 322.1391, found 322.1387.



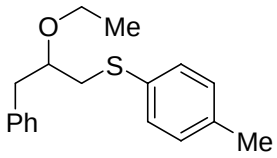
4o

Compound **4o**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.21 (m, 7H), 7.07 (d, J = 8.0 Hz, 2H), 4.35 (dd, J = 8.0, 5.2 Hz, 1H), 3.37–3.24 (m, 3H), 3.06 (dd, J = 13.2, 5.2 Hz, 1H), 2.31 (s, 3H), 1.57–1.49 (m, 2H), 1.39–1.31 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 136.0, 133.1, 130.0, 129.7, 128.5, 127.9, 126.7, 80.9, 69.1, 42.4, 31.9, 21.0, 19.4, 13.9; HRMS (EI) calcd for $C_{19}H_{24}OS$ (M) 300.1548, found 300.1538.

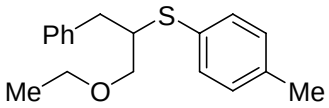


4p

Compound **4p**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.21 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.48 (dd, J = 8.4, 4.8 Hz, 1H), 3.53–3.45 (m, 1H), 3.24 (dd, J = 13.2, 8.4 Hz, 1H), 3.06 (dd, J = 13.2, 4.8 Hz, 1H), 2.31 (s, 3H), 1.15 (d, J = 6.0 Hz, 3H), 1.08 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 135.9, 133.1, 129.8, 129.6, 128.4, 127.8, 126.7, 78.0, 69.8, 42.6, 23.3, 21.3, 21.0; HRMS (EI) calcd for $C_{18}H_{22}OS$ (M) 286.1391, found 286.1387.



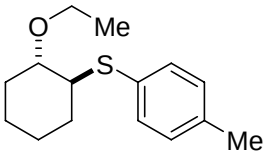
4q



4q'

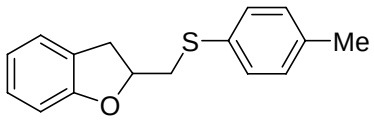
4q:**4q'** = 64:36

Compounds **4q** and **4q'**, obtained as a 64:36 mixture of regioisomers, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.18 (m, 7H), 7.06 (d, J = 8.0 Hz, 2H), 3.64–3.56 (m, 1H), 3.55–3.32 (m, 2H), 3.11–3.01 (m, 1H), 3.01–2.80 (m, 3H), 2.30 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{1}H NMR for minor regioisomer **4q'** δ 7.31–7.18 (m, 7H), 7.08 (d, J = 8.4 Hz, 2H), 3.55–3.32 (m, 5H), 3.01–2.80 (m, 2H), 2.31 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); HRMS (EI) calcd for $C_{18}H_{22}OS$ (M) 286.1391, found 286.1385.



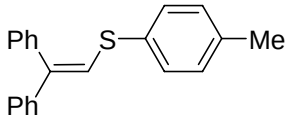
4r

Compound **4r**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 3.68–3.57 (m, 1H), 3.54–3.44 (m, 1H), 3.18 (dt, J = 8.4, 4.0 Hz, 1H), 3.08 (dt, J = 9.2, 4.0 Hz, 1H), 2.31 (s, 3H), 2.14–1.96 (m, 2H), 1.76–1.59 (m, 2H), 1.43–1.21 (m, 4H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.9, 131.5, 129.5, 80.2, 64.5, 51.8, 31.5, 30.8, 24.8, 23.5, 21.1, 15.6; HRMS (EI) calcd for $C_{15}H_{22}OS$ (M) 250.1391, found 250.1382.



4s

Compound **4s**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.16–7.05 (m, 4H), 6.85–6.80 (m, 1H), 6.75 (d, J = 8.0 Hz, 1H), 4.90–4.82 (m, 1H), 3.38–3.31 (m, 2H), 3.08–3.00 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 136.8, 131.5, 130.8, 129.8, 128.1, 126.1, 125.0, 120.6, 109.5, 81.2, 39.6, 34.8, 21.0; HRMS (EI) calcd for $C_{16}H_{16}OS$ (M) 256.0922, found 256.0920.

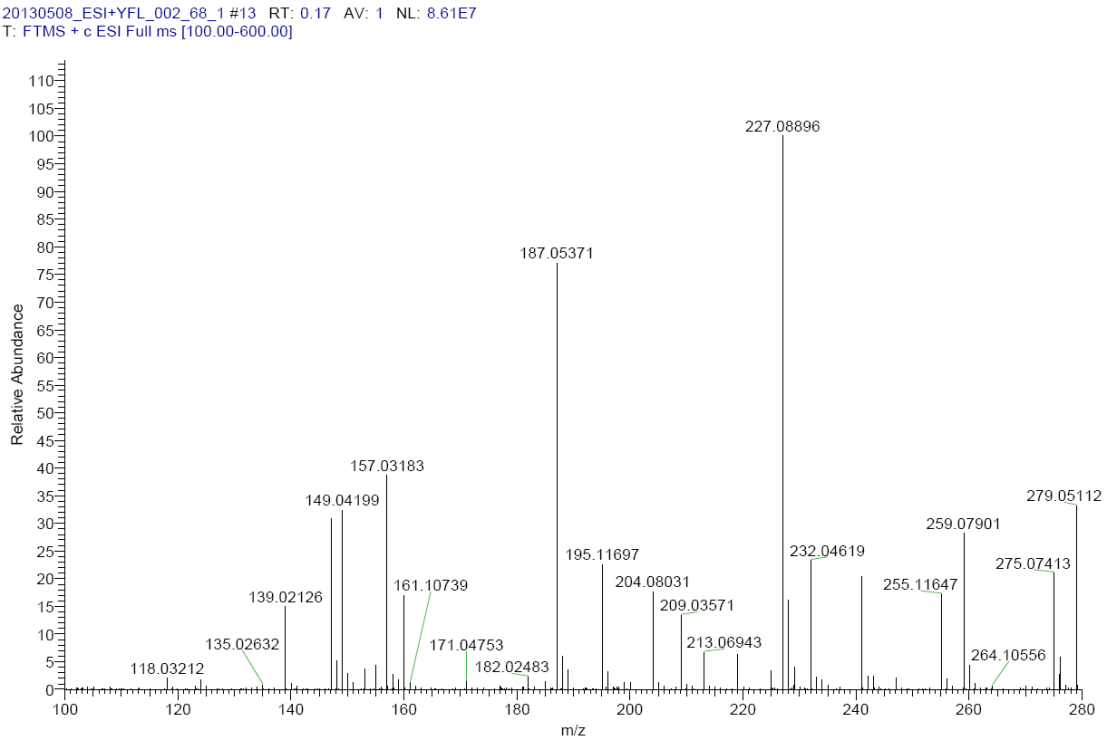


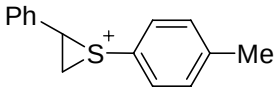
5a

Compound **5a**,[7] white solid, m.p. 86–88°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.19 (m, 12H), 7.11 (d, J = 8.0 Hz, 2H), 6.81 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.3, 139.4, 137.1, 132.9, 130.2, 130.0, 129.9, 128.5, 128.4, 127.9, 127.3, 125.4, 21.2.

ESI-MS analysis of the reaction mixture

To a solution of sulfonyl hydrazide **1a** (37.2 mg, 0.20 mmol) in 1,2-dichloroethane (0.50 mL) were added alkene **2a** (25.0 mg, 27.4 μL, 0.24 mmol), ethanol (**3a**) (0.050 mL) and iodine (10.2 mg, 20 mol%). The mixture was stirred at 70 ^{o}C for 1 h, cooled to room temperature, and subjected to ESI-MS (positive mode) analysis. Copied below is the ESI mass spectrometry we obtained.



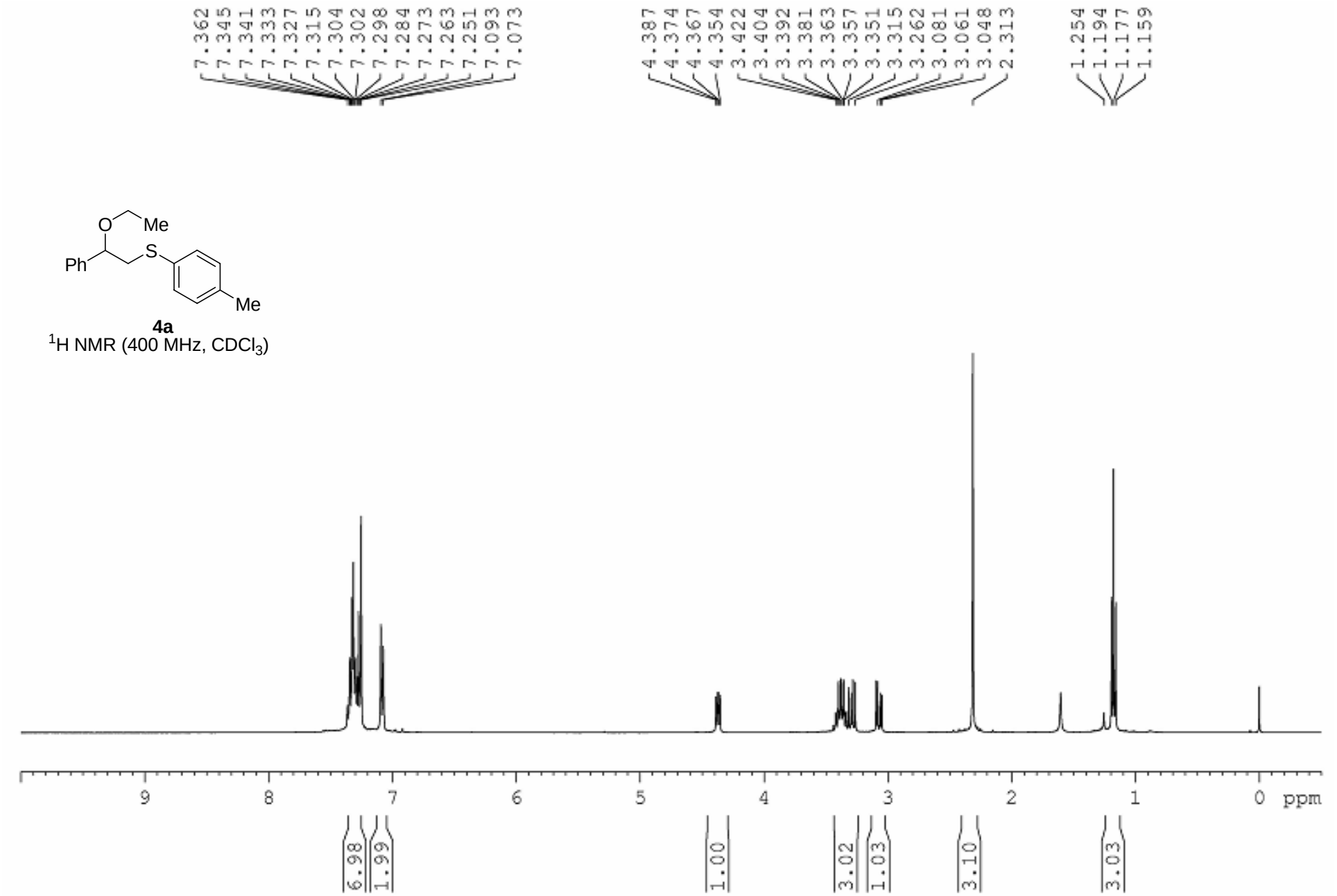


11a

Thiiranium ion **11a**: HRMS (ESI) calcd for $C_{15}H_{15}S^{+}$ 227.0889, found 227.0890.

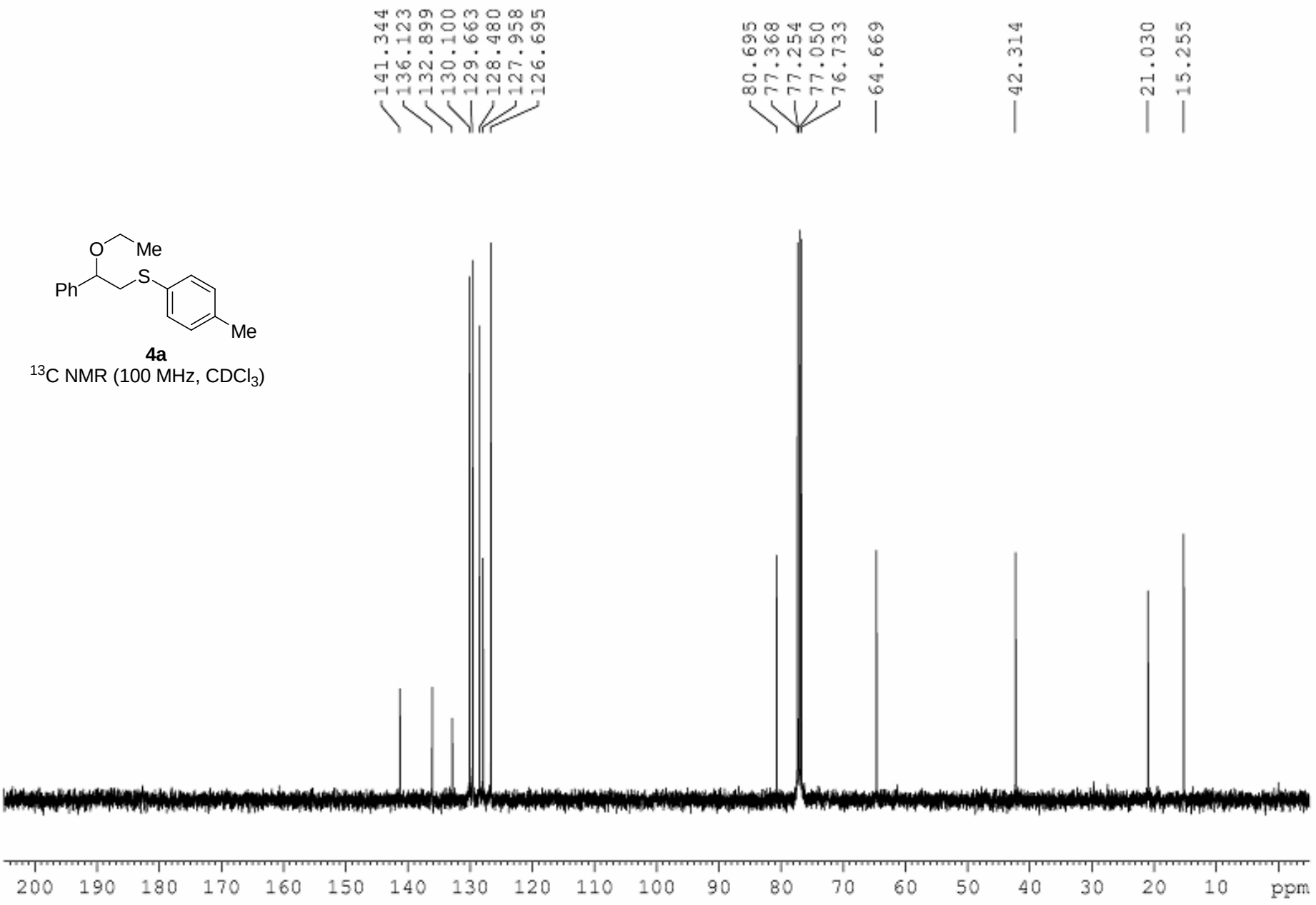
References

1 S. I. Cho, N. H. Jensen, T. Kurome, S. Kadari, M. L. Manzano, J. E. Malberg, B. Caldarone, B. L. Roth and A. P. Kozikowski, *J. Med. Chem.*, 2009, **52**, 1885.
2 A. G. Myers, B. Zheng and M. Movassaghi, *J. Org. Chem.*, 1997, **62**, 7507.
3 Y. Li, Y. Wang, J. Li and J. Wang, *J. Sulphur Chem.*, 2007, **28**, 177.
4 F.-L. Yang and S.-K. Tian, *Angew. Chem., Int. Ed.*, 2013, 52, 4929.
5 G.-W. Wang and T. Miao, *Chem. Eur. J.*, 2011, **17**, 5787.
6 T. Yoshino, S. Imoria and H. Togo, *Tetrahedron*, 2006, **62**, 1309.
7 M. Watanabe, M. Nakamura and T. Satoh, *Tetrahedron*, 2005, **61**, 4409.



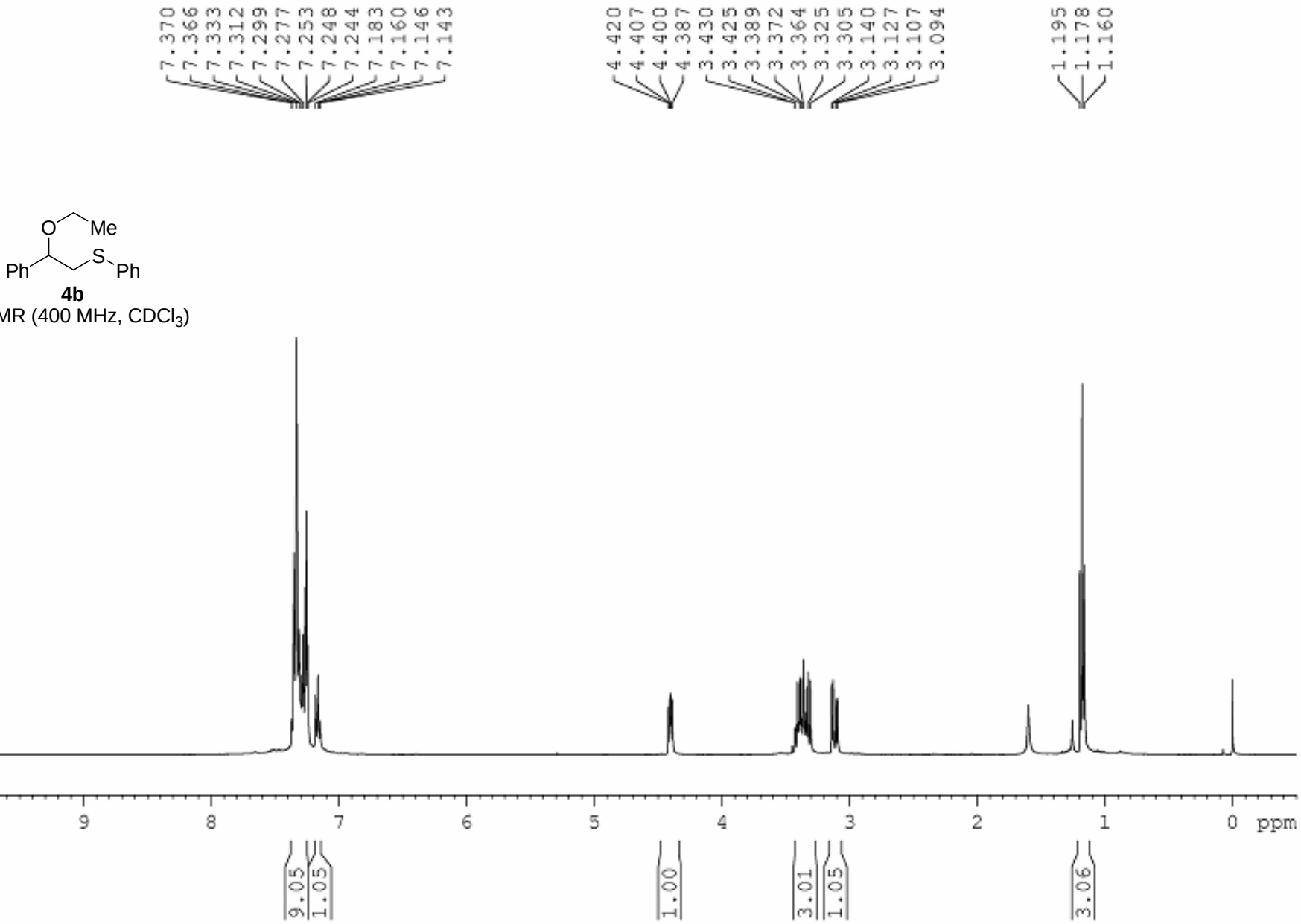
4a

^{1}H NMR (400 MHz, $CDCl_3$)



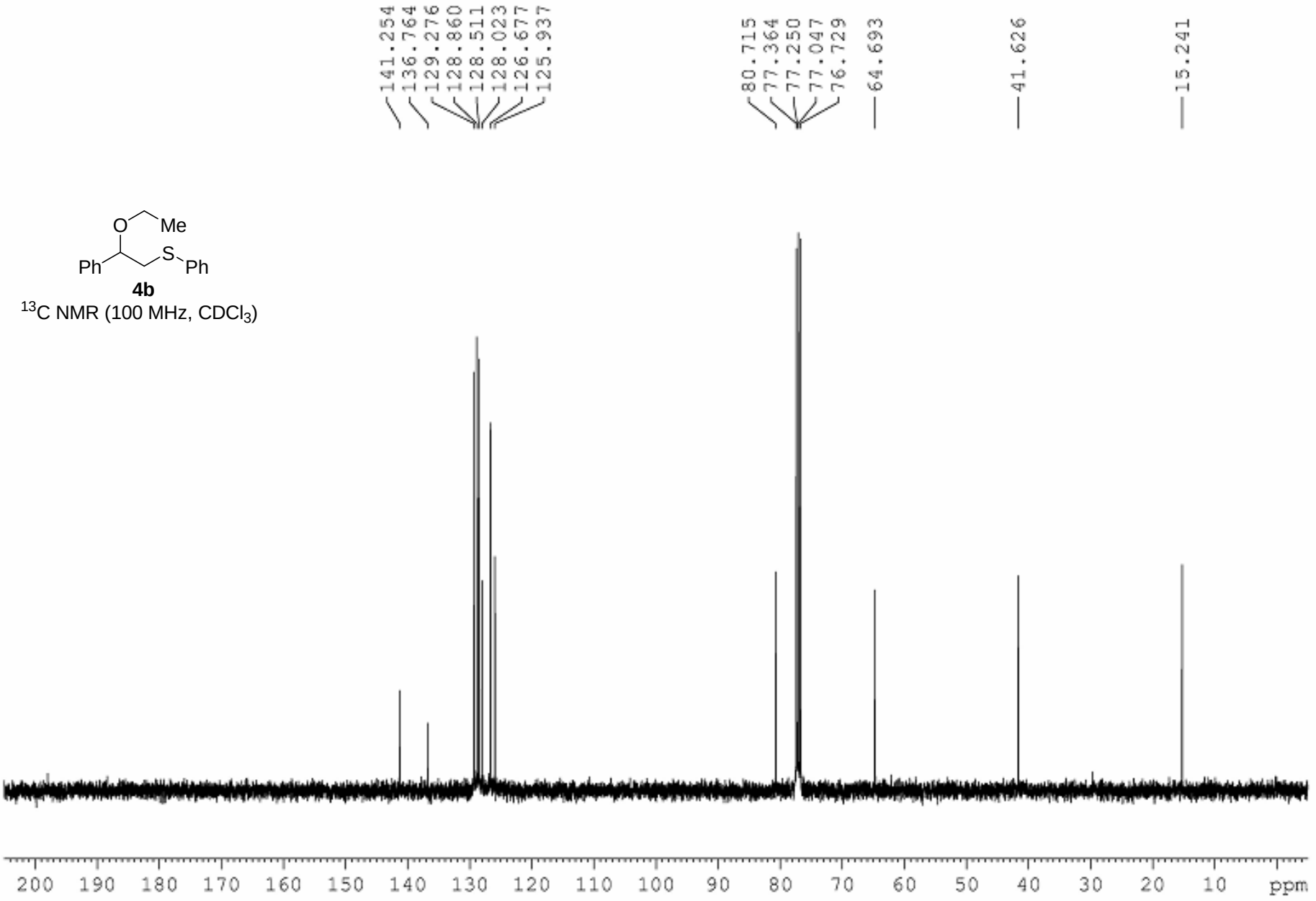
4a

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



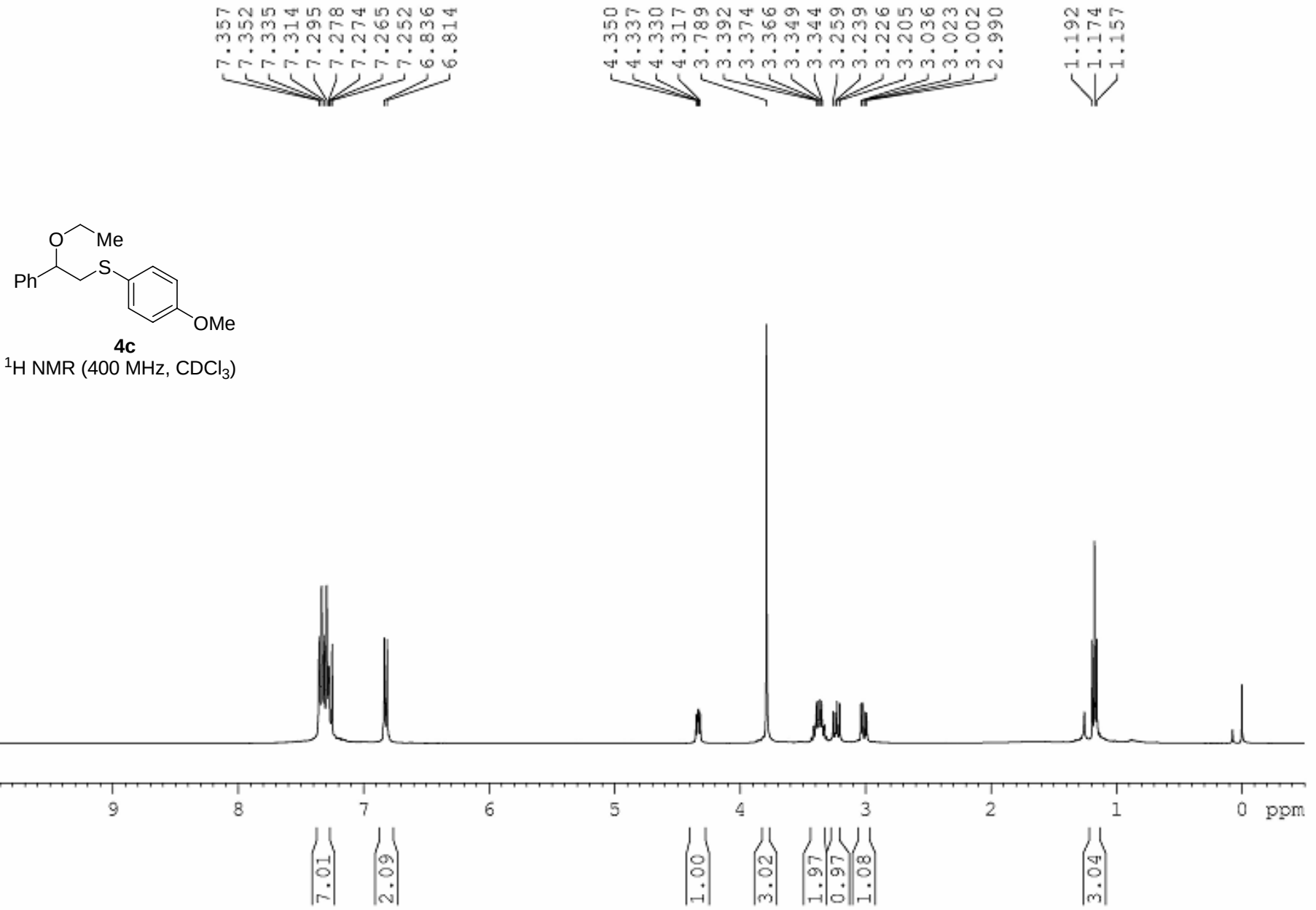
4b

^{1}H NMR (400 MHz, $CDCl_3$)



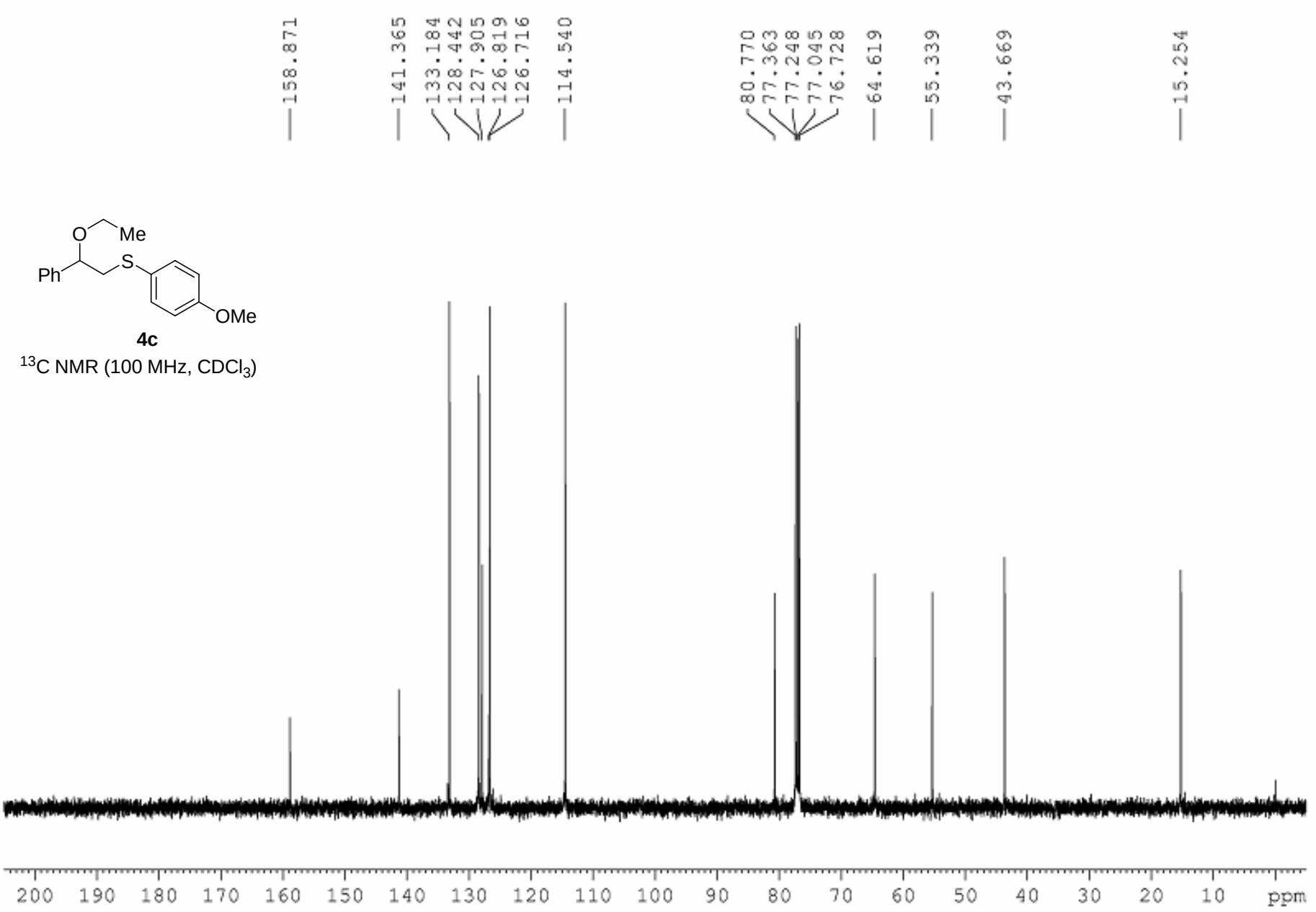
4b

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



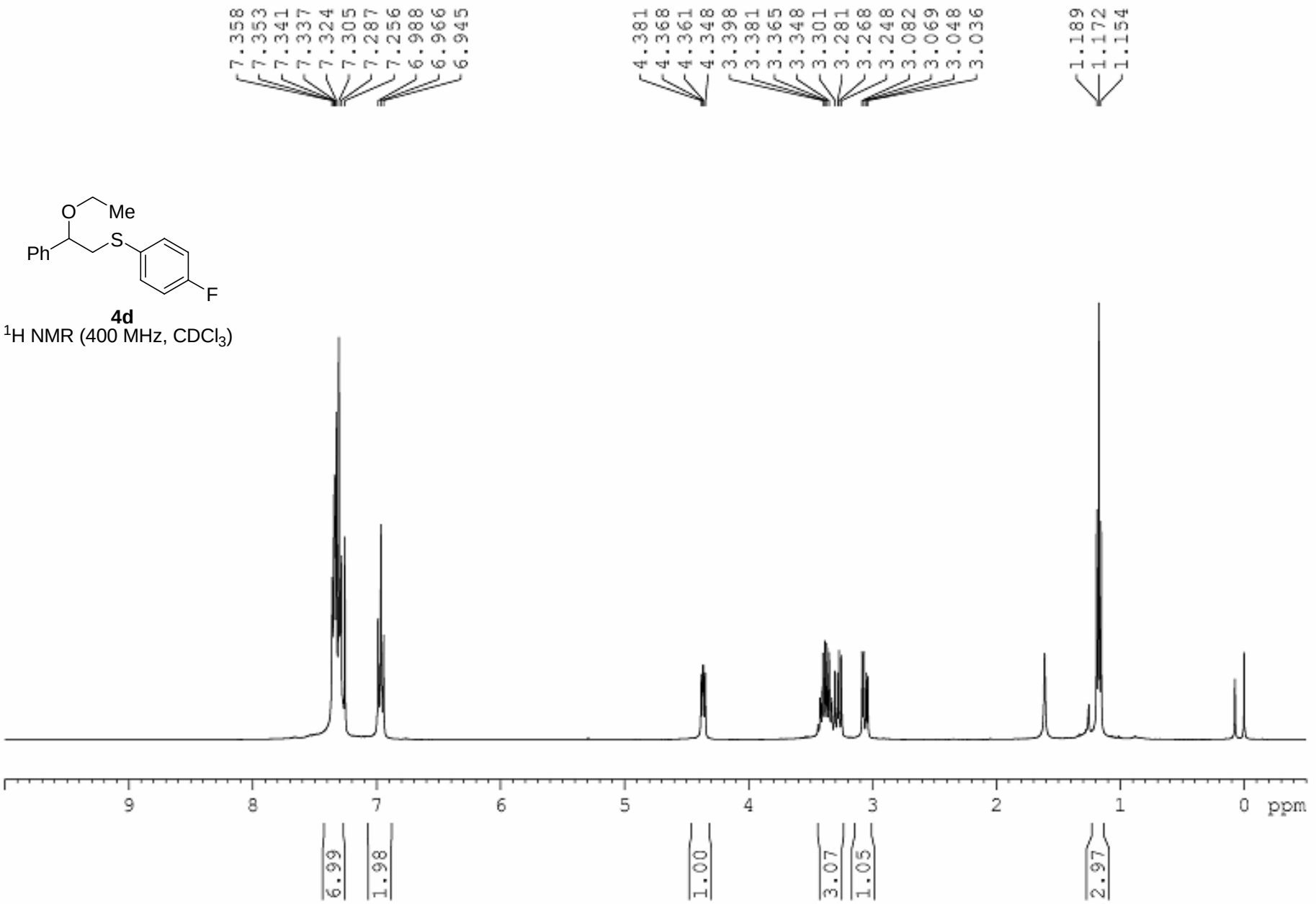
4c

^{1}H NMR (400 MHz, $CDCl_3$)



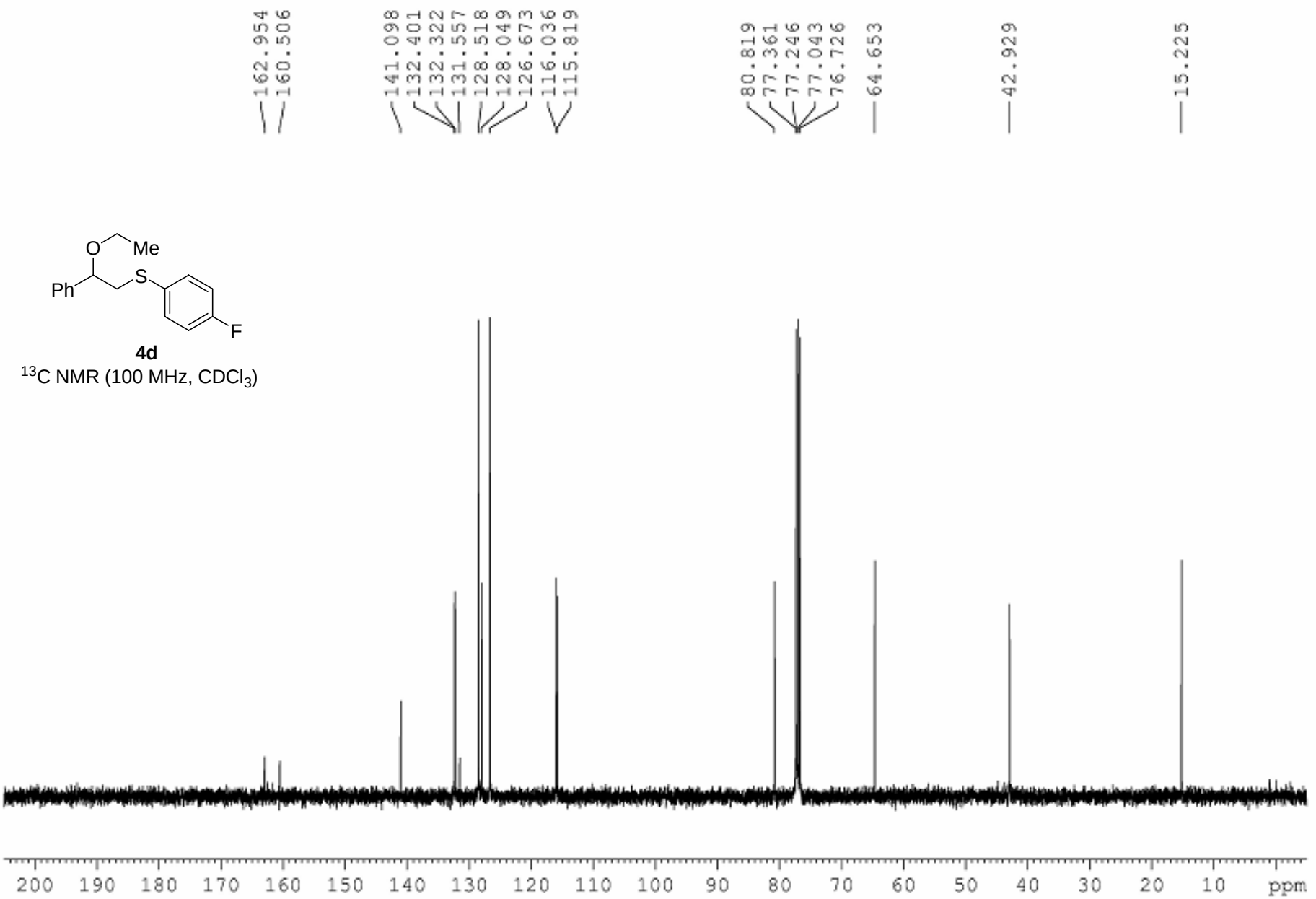
4c

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



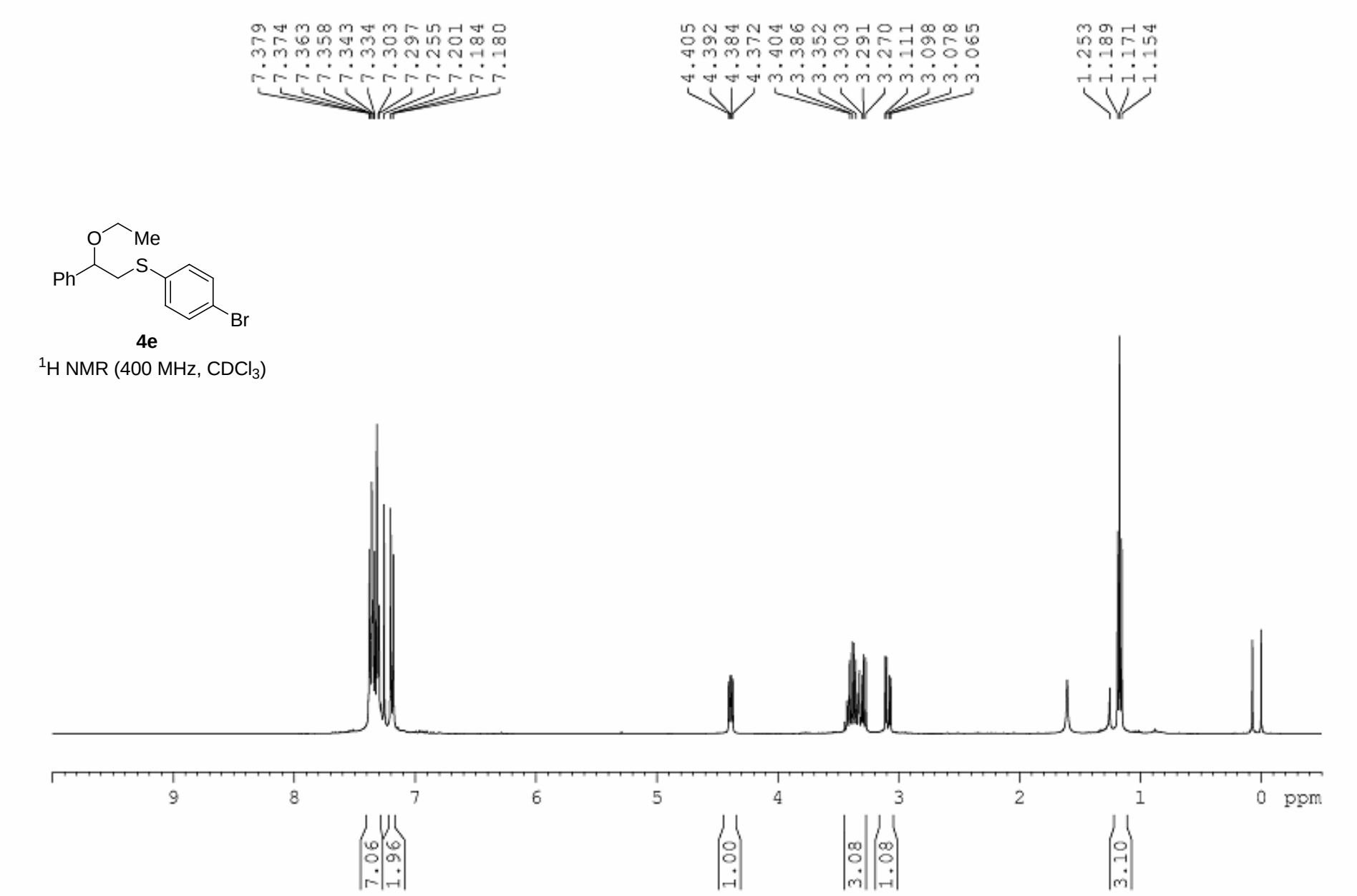
4d

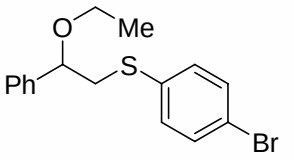
^{1}H NMR (400 MHz, $CDCl_3$)



4d

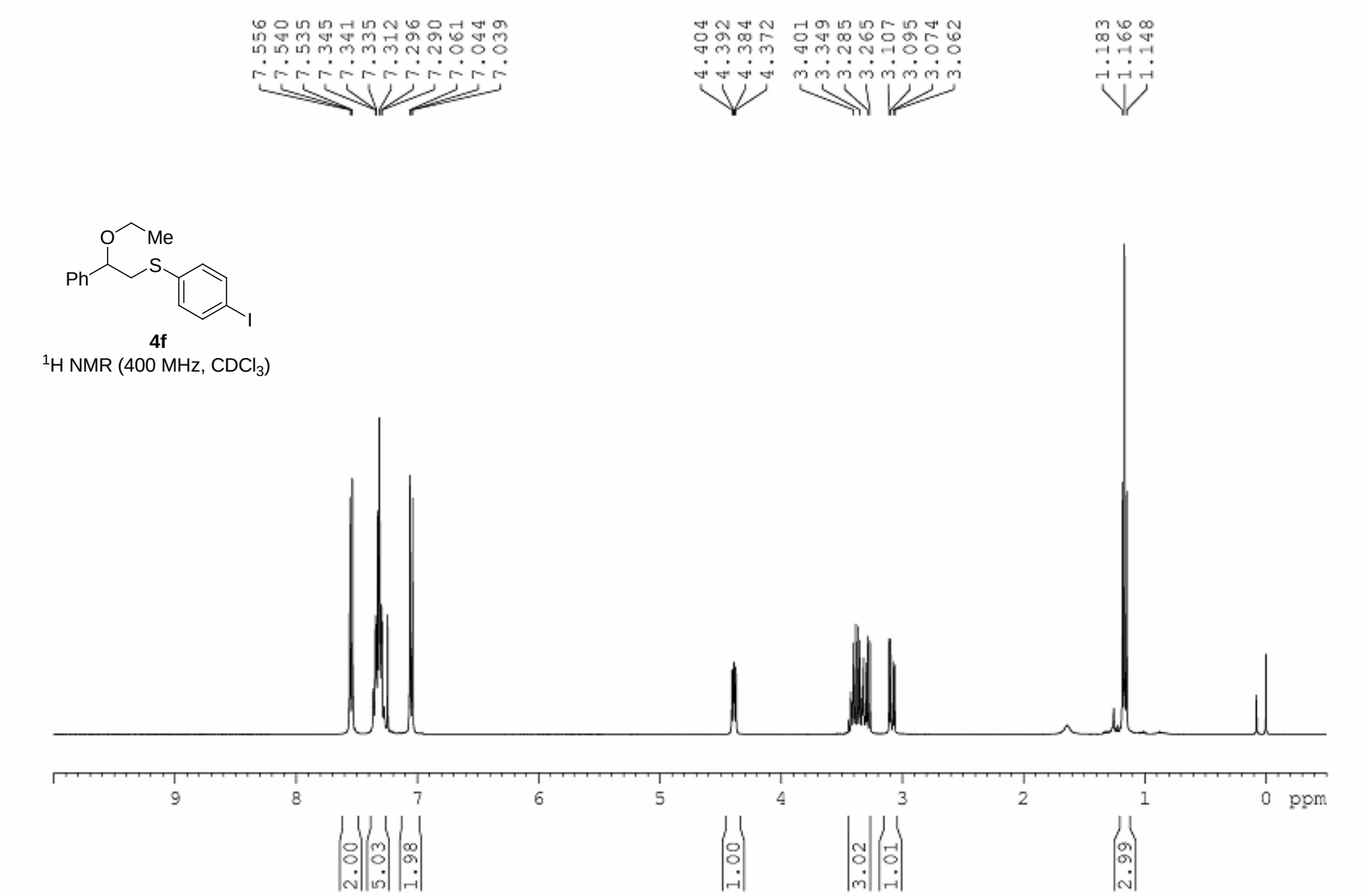
^{13}C NMR (100 MHz, $CDCl_3$)





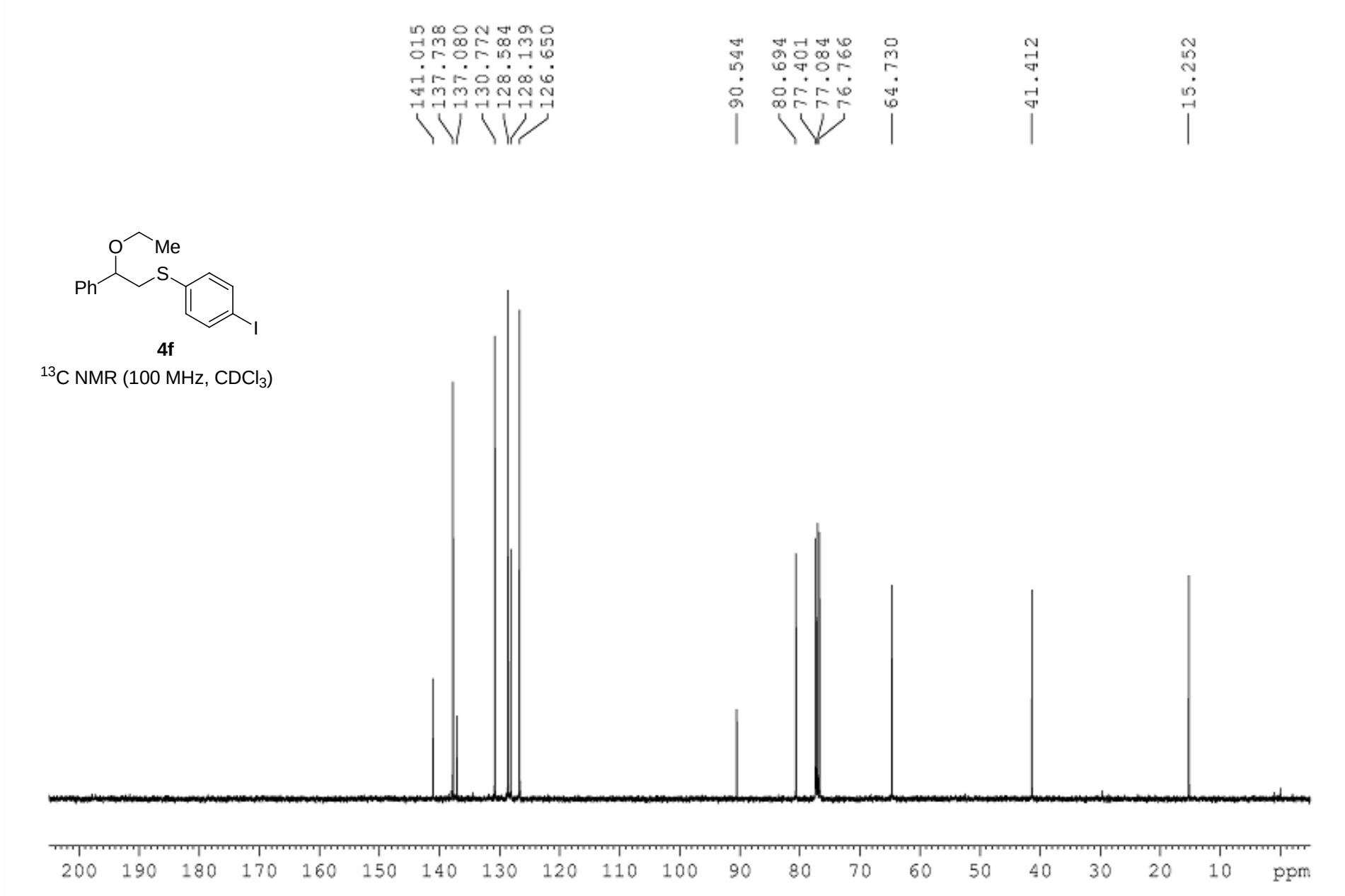
4e

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



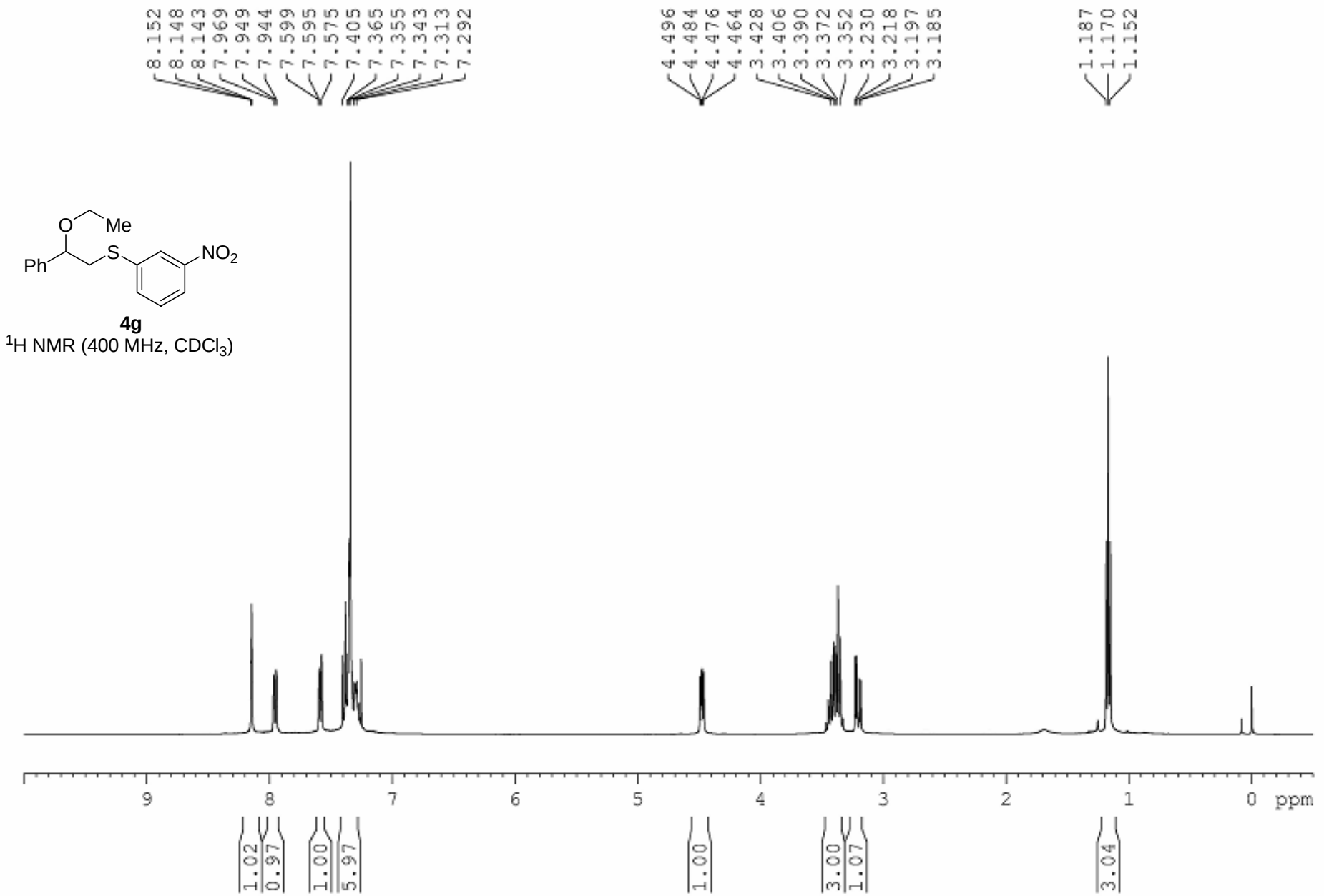
4f

^{1}H NMR (400 MHz, $CDCl_3$)



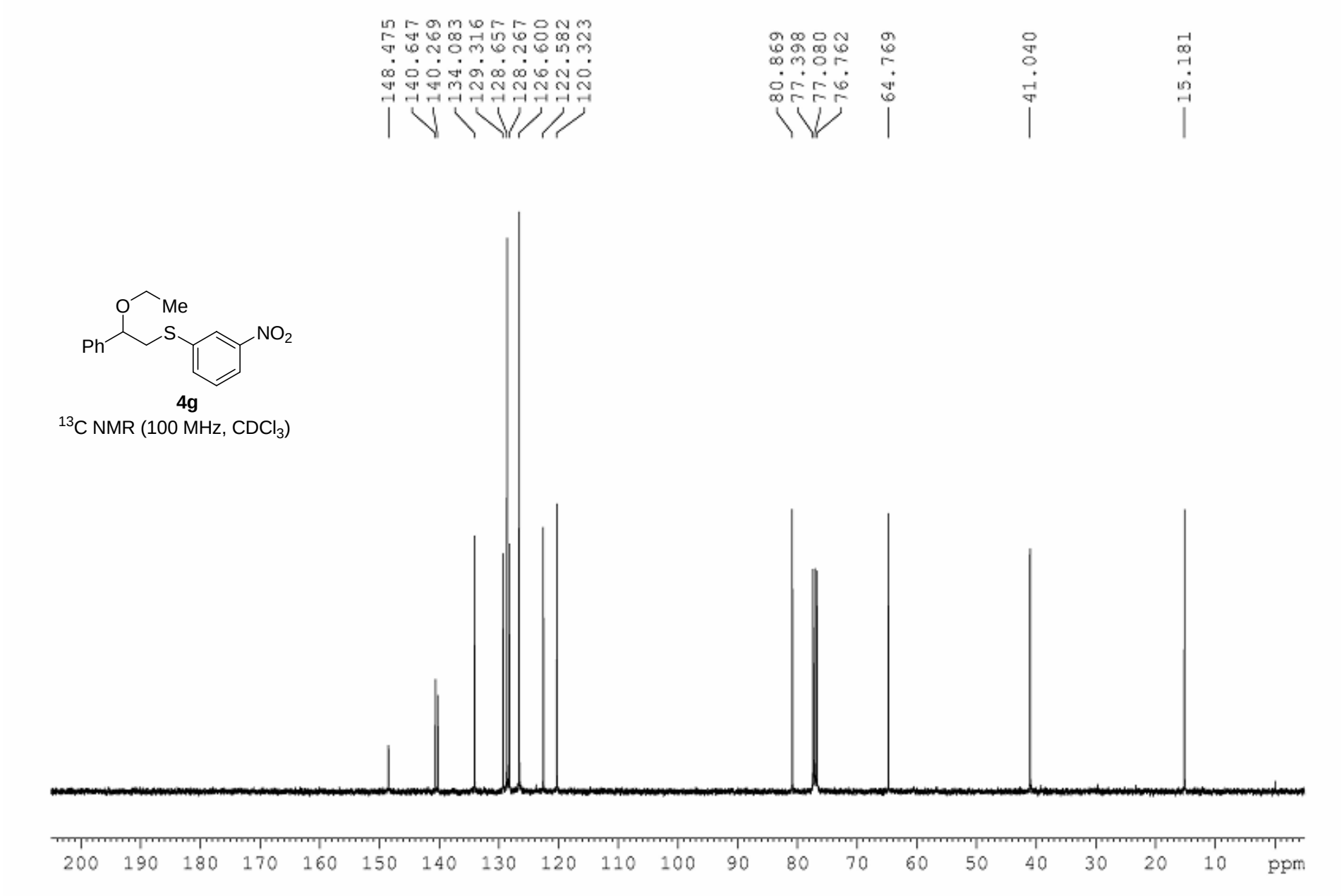
4f

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



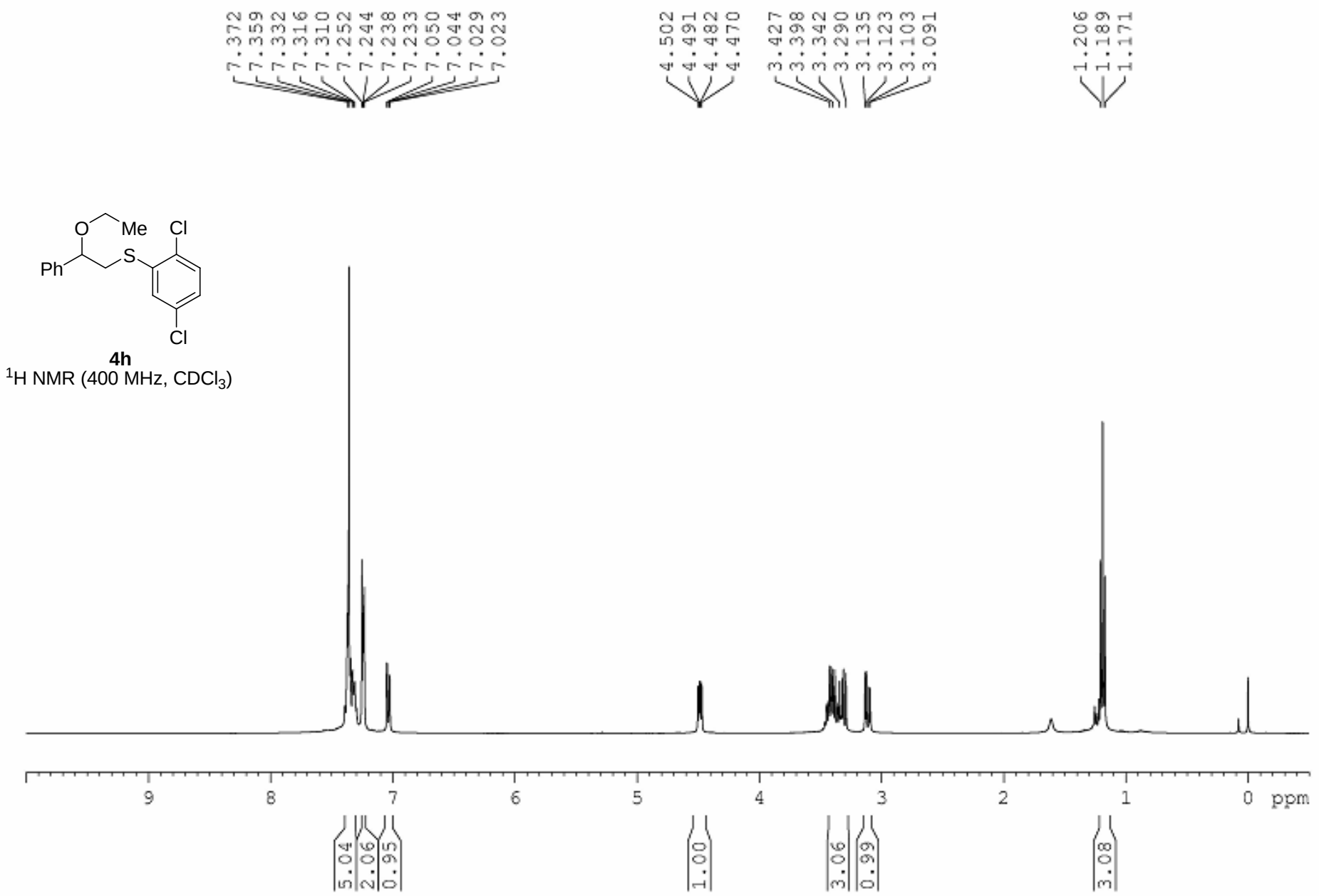
4g

^{1}H NMR (400 MHz, $CDCl_3$)



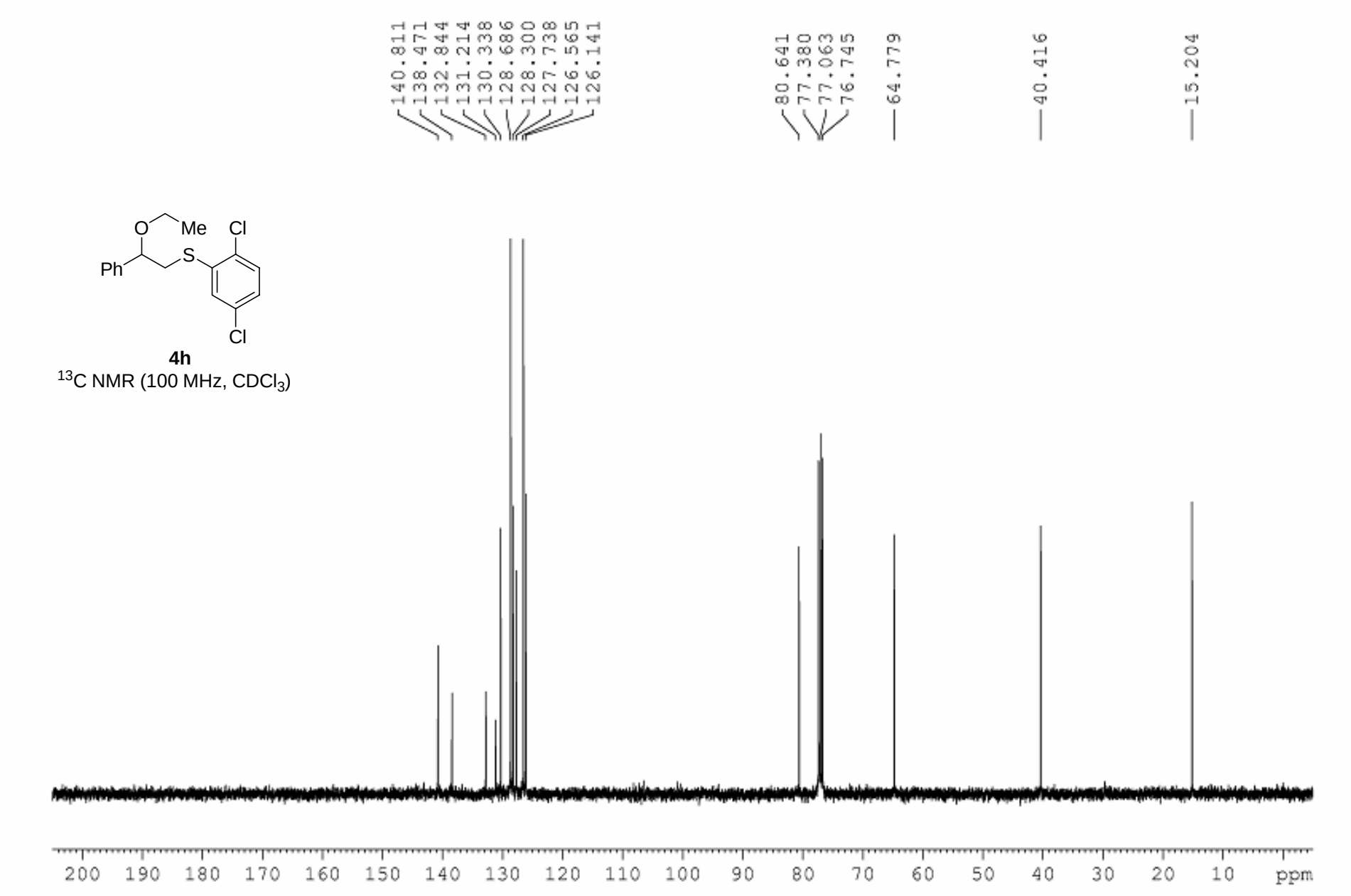
4g

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



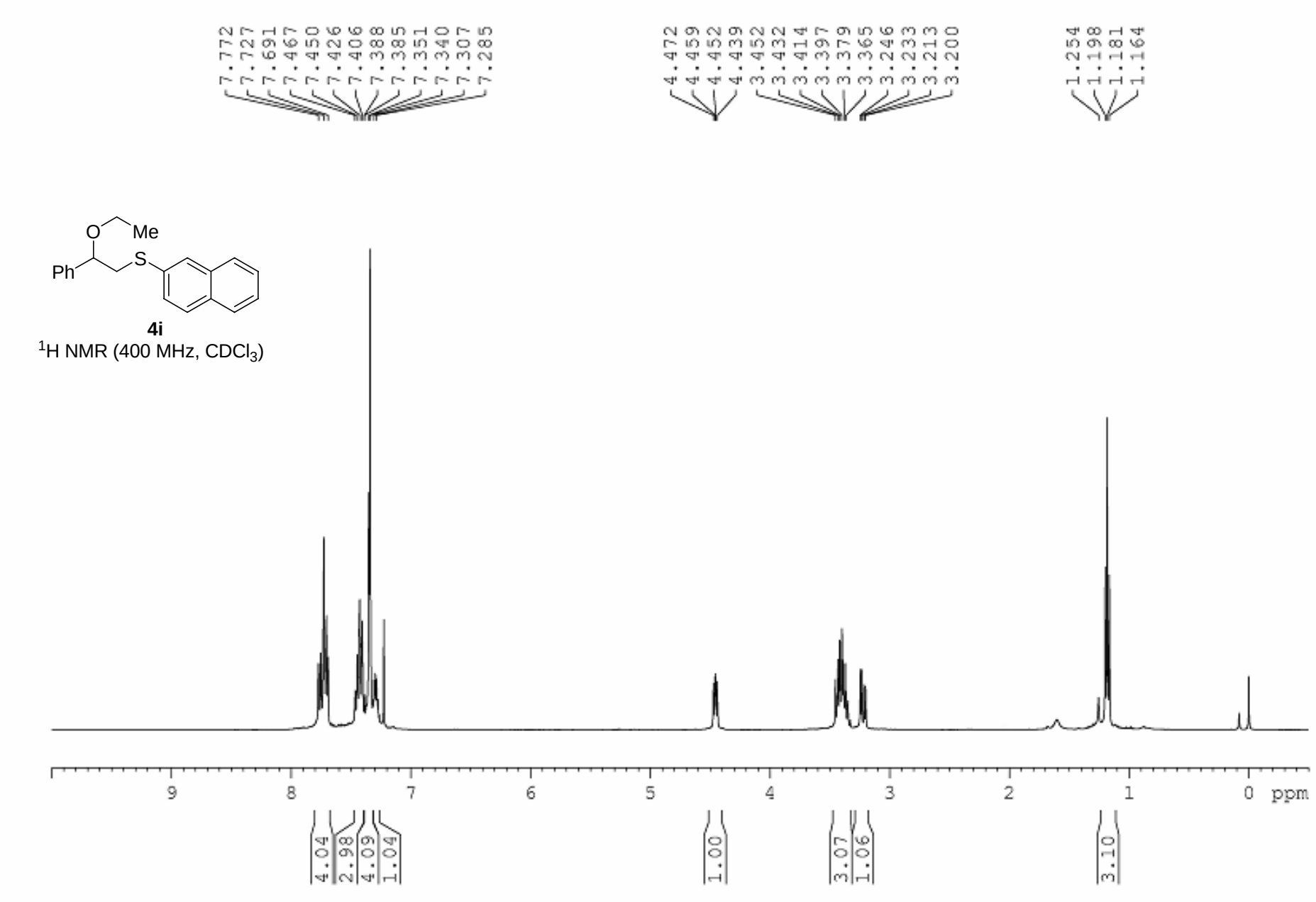
4h

^{1}H NMR (400 MHz, $CDCl_3$)



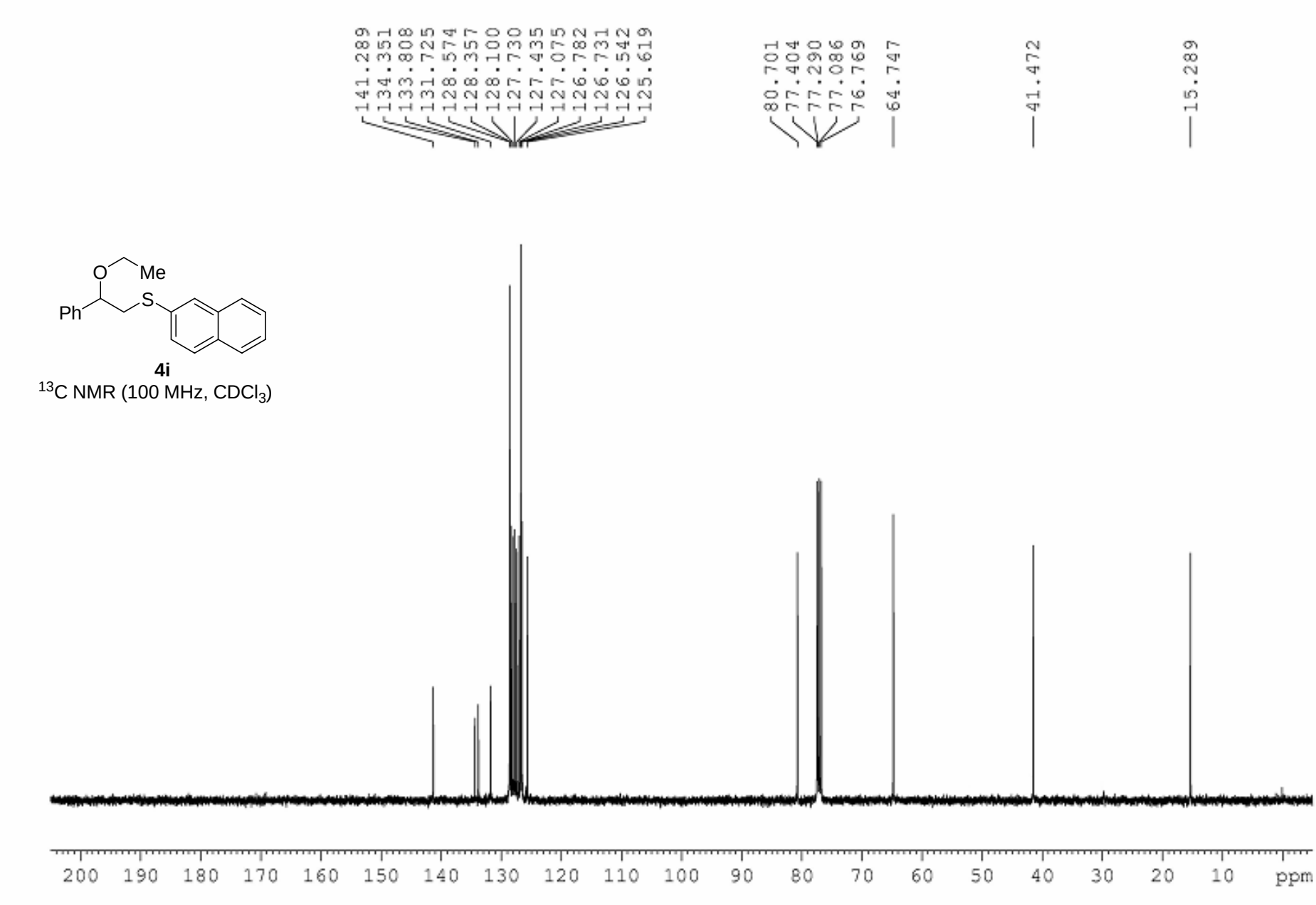
4h

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



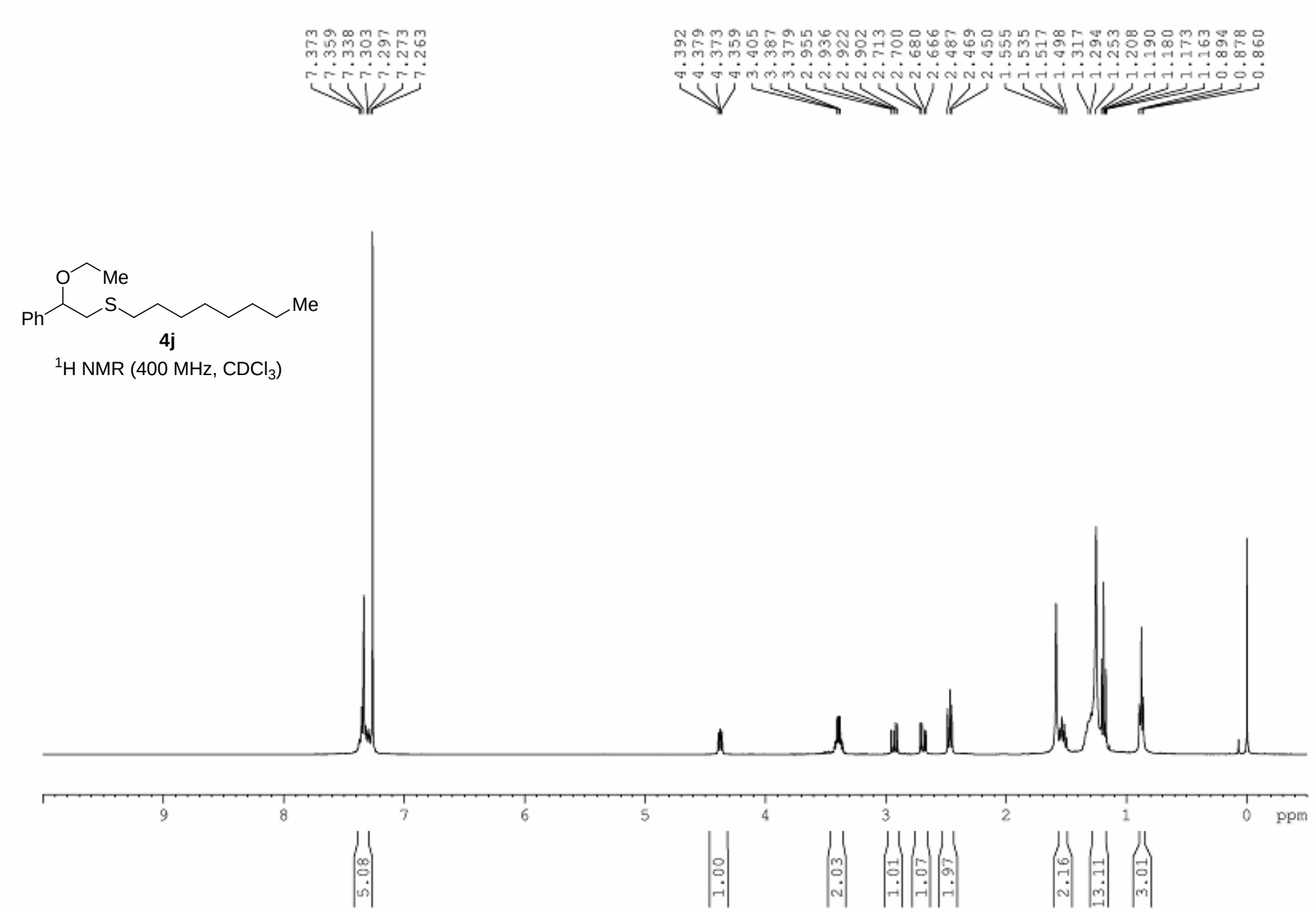
4i

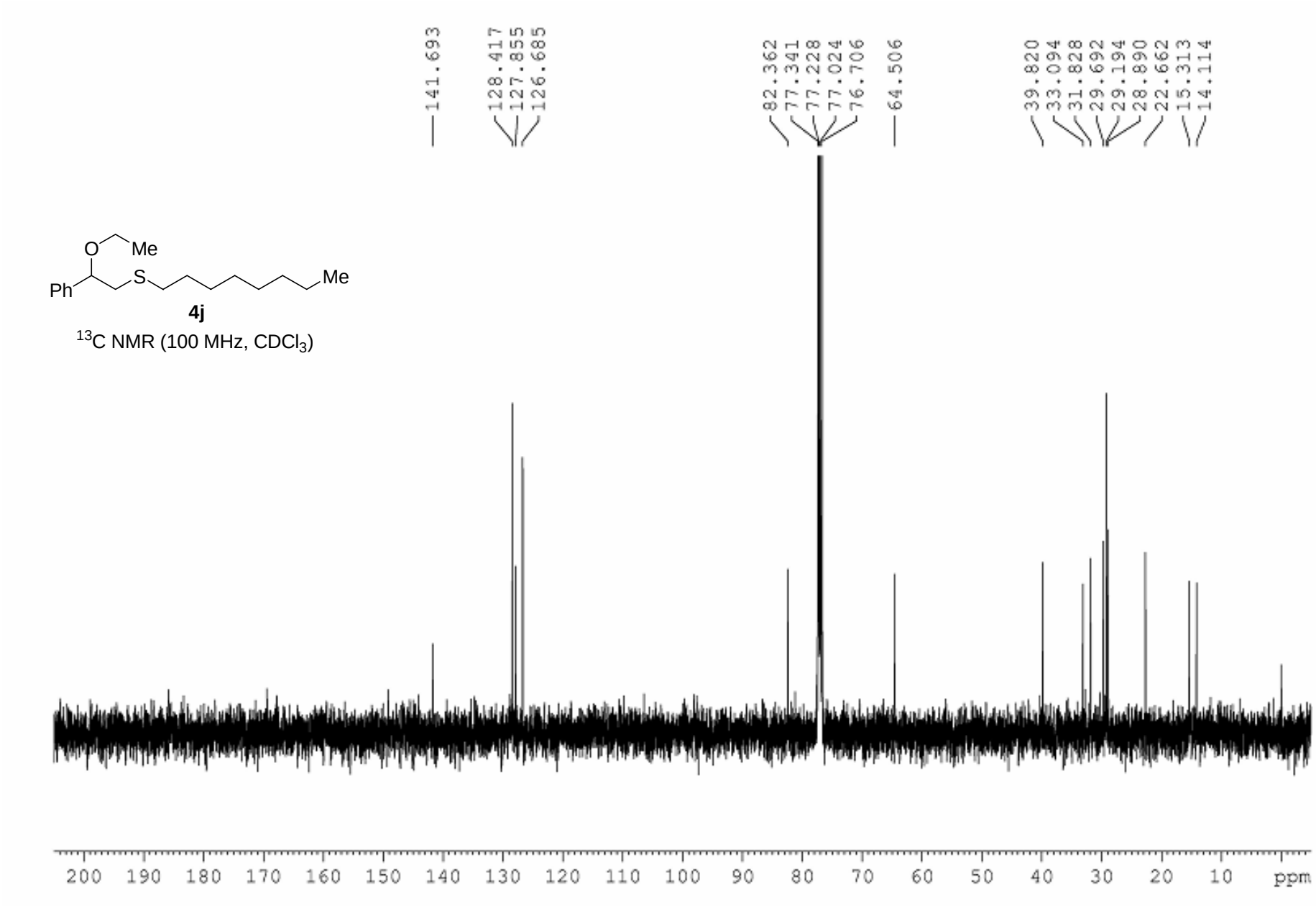
^{1}H NMR (400 MHz, $CDCl_3$)



4i

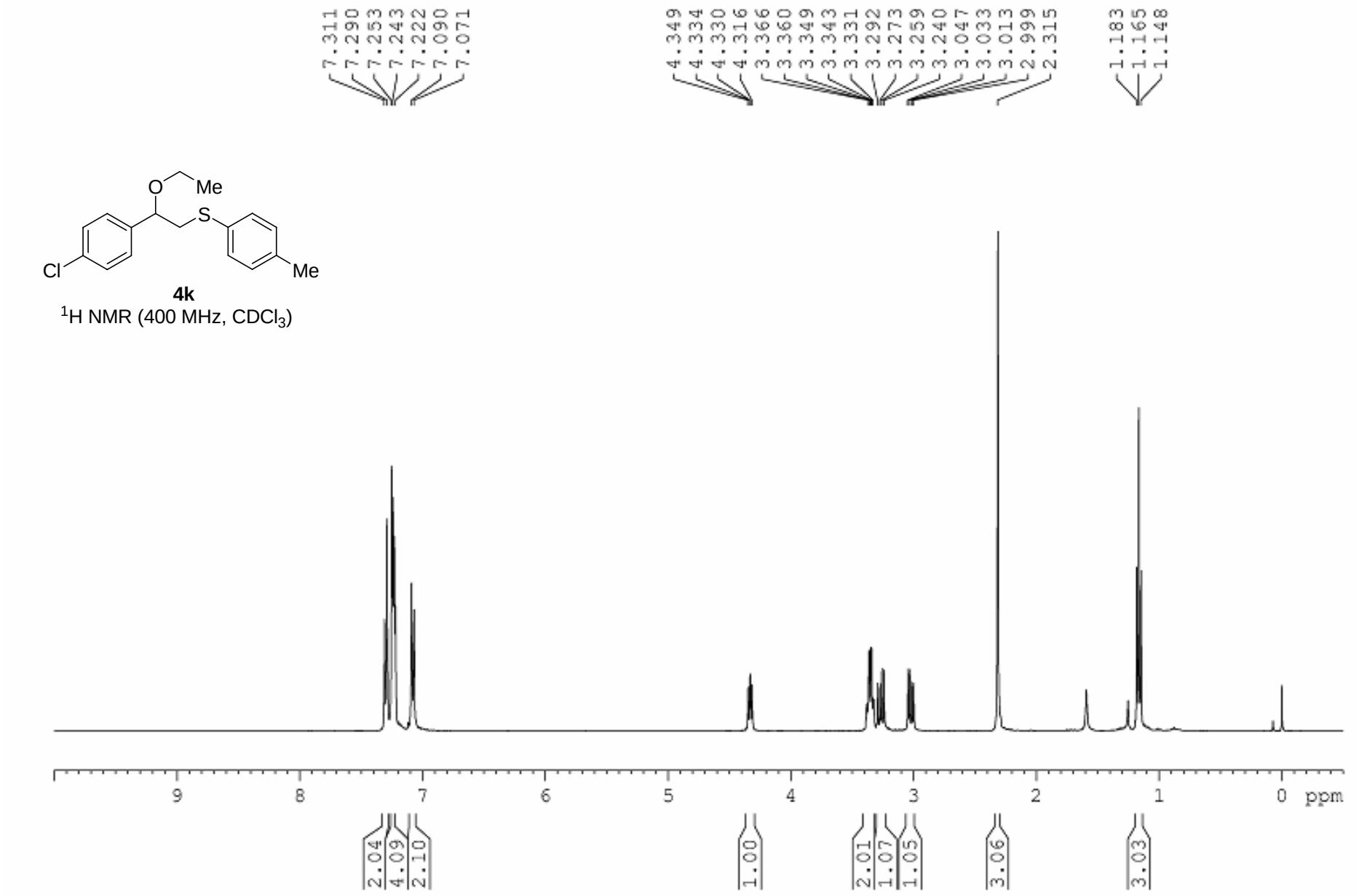
^{13}C NMR (100 MHz, $CDCl_3$)





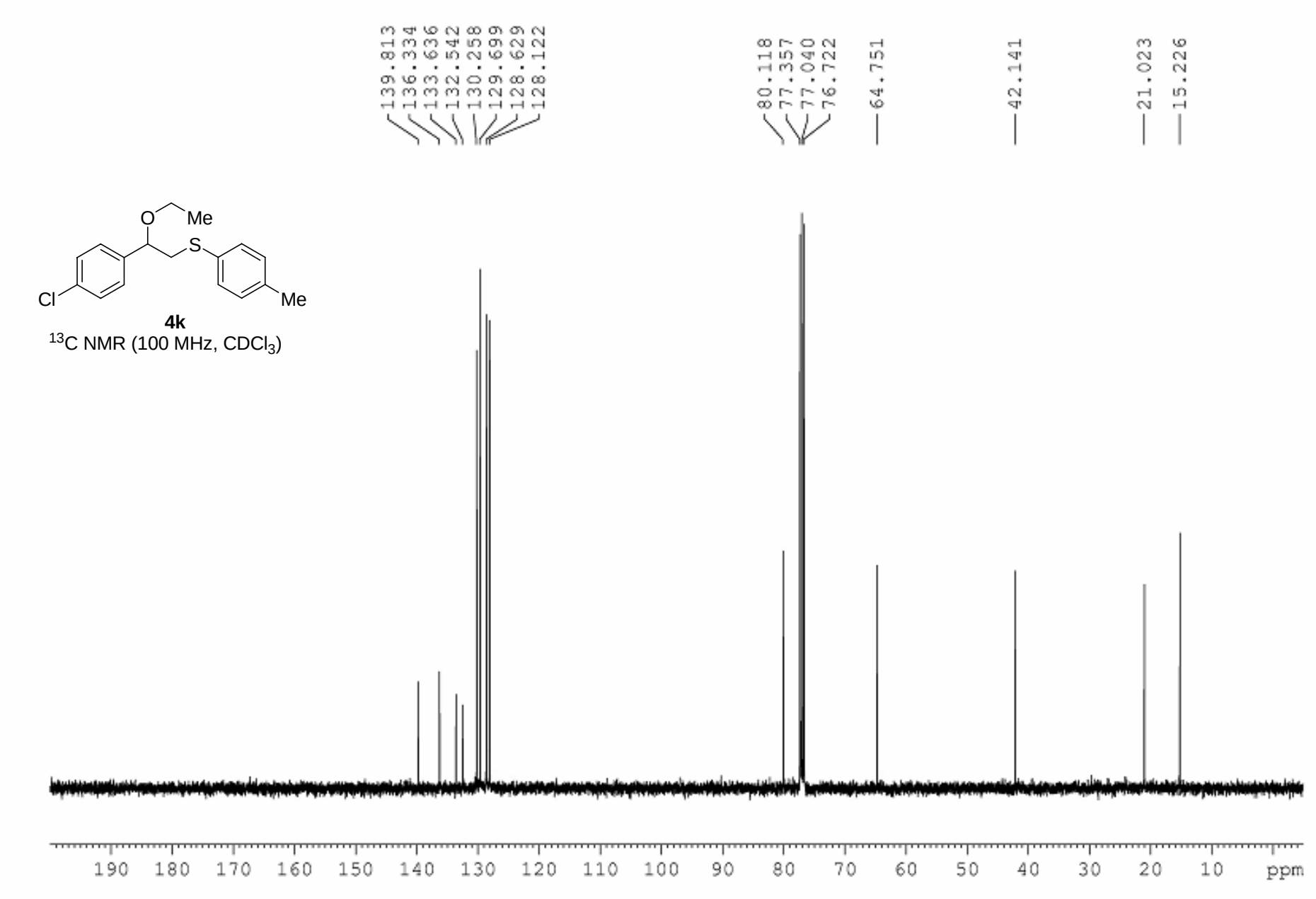
4j

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



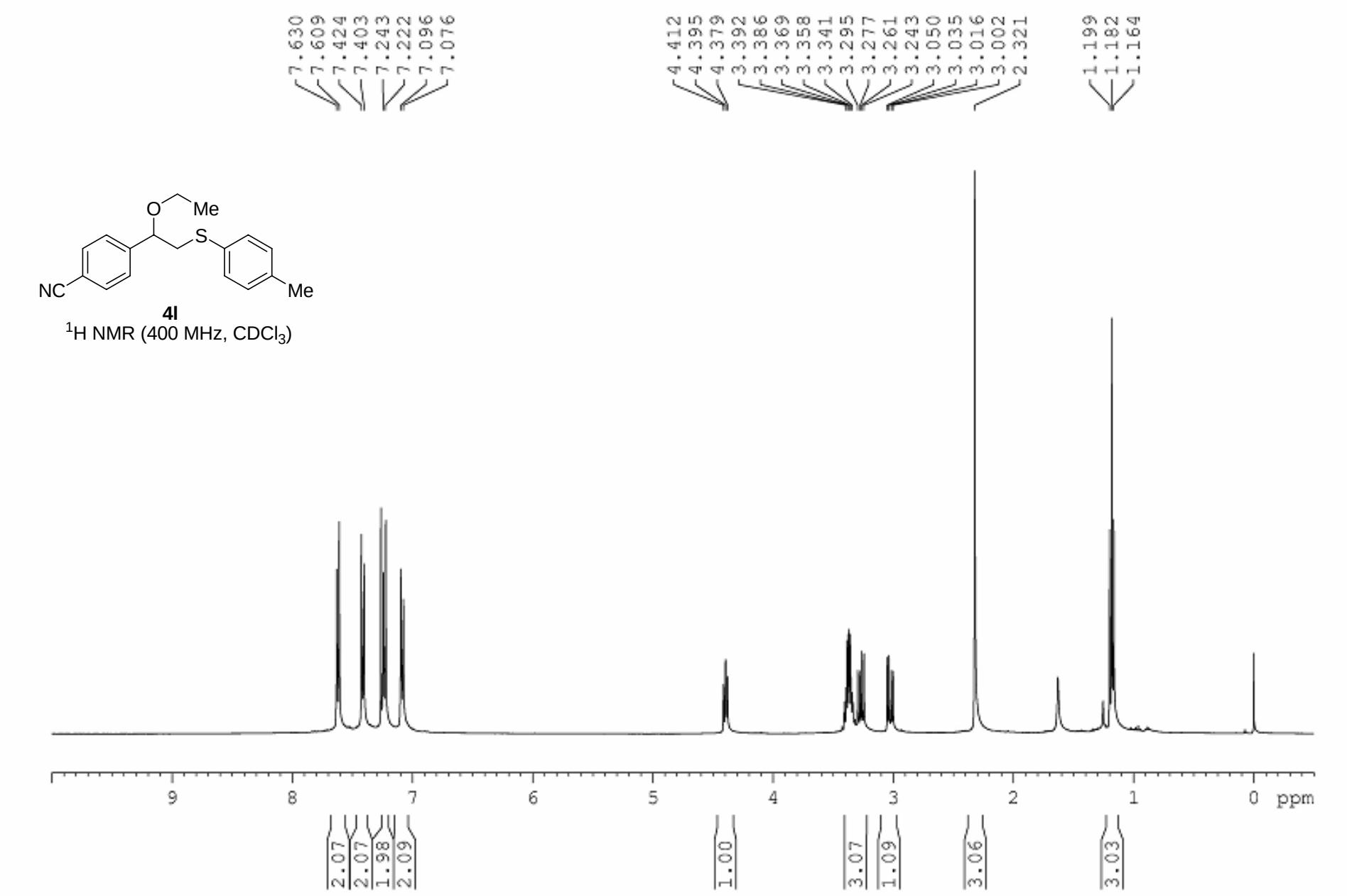
4k

^{1}H NMR (400 MHz, $CDCl_3$)



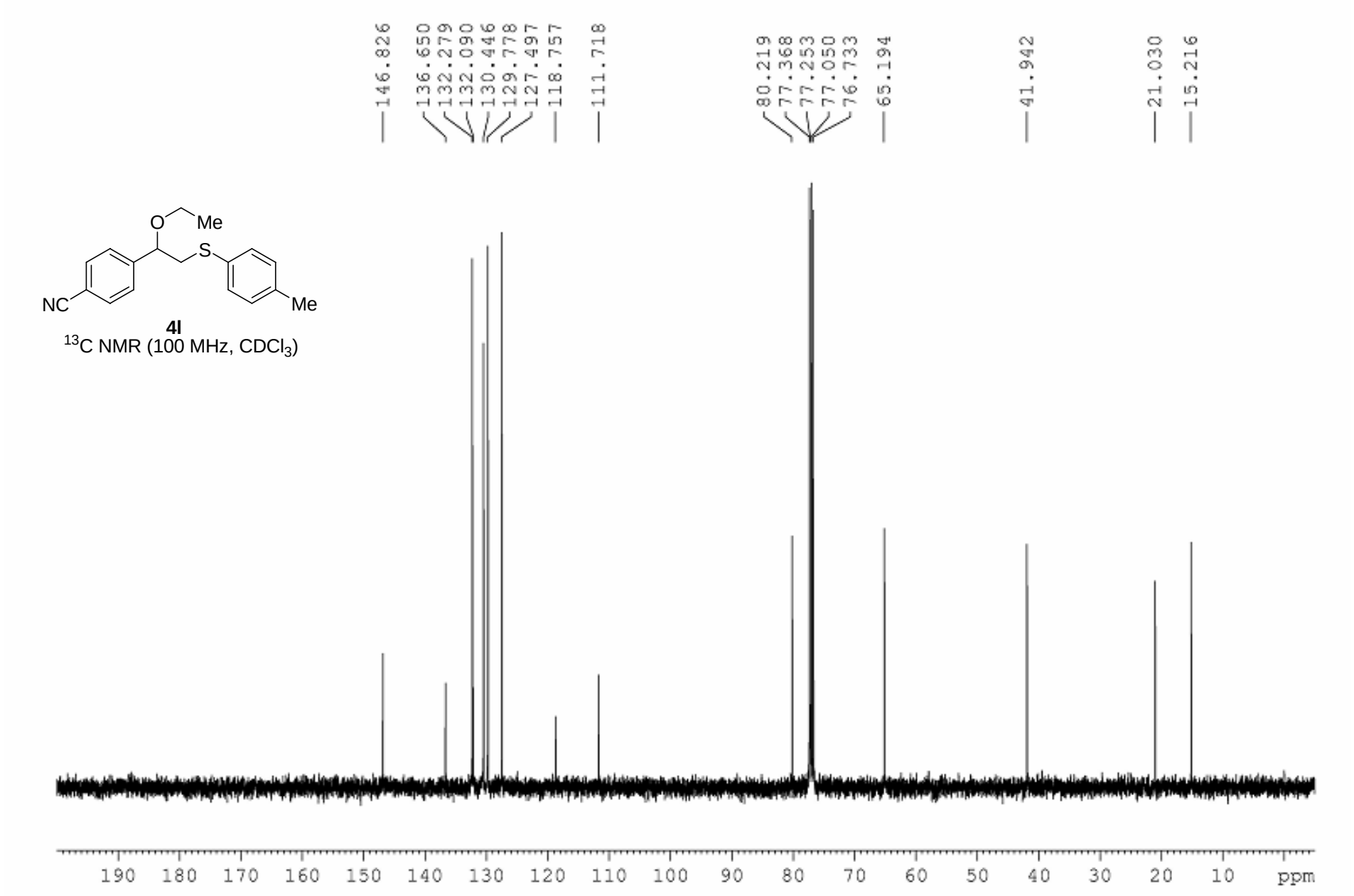
4k

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



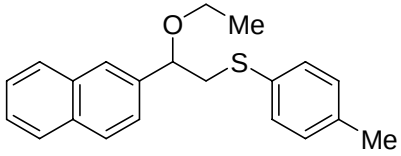
4l

^{1}H NMR (400 MHz, $CDCl_3$)



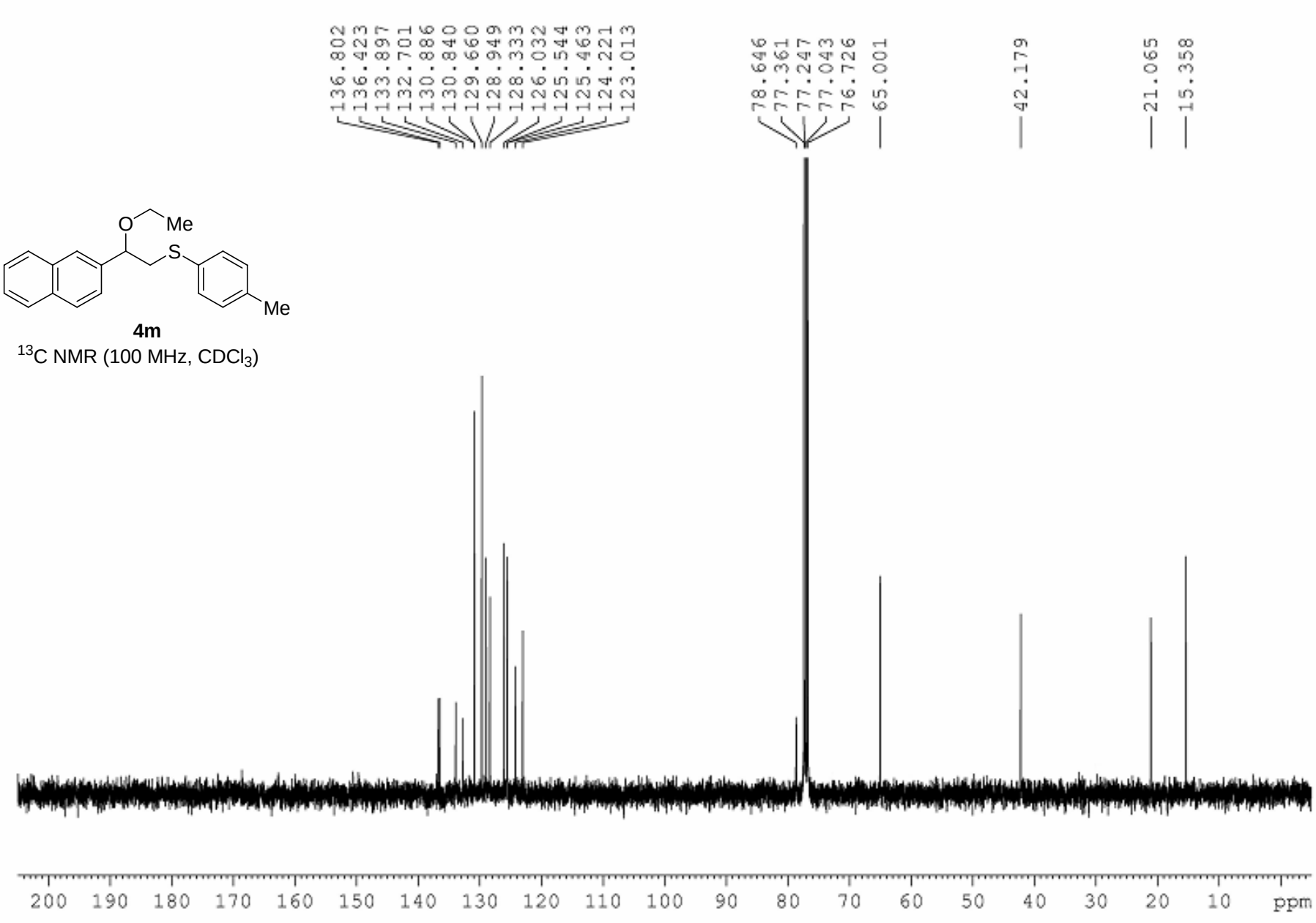
4l

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



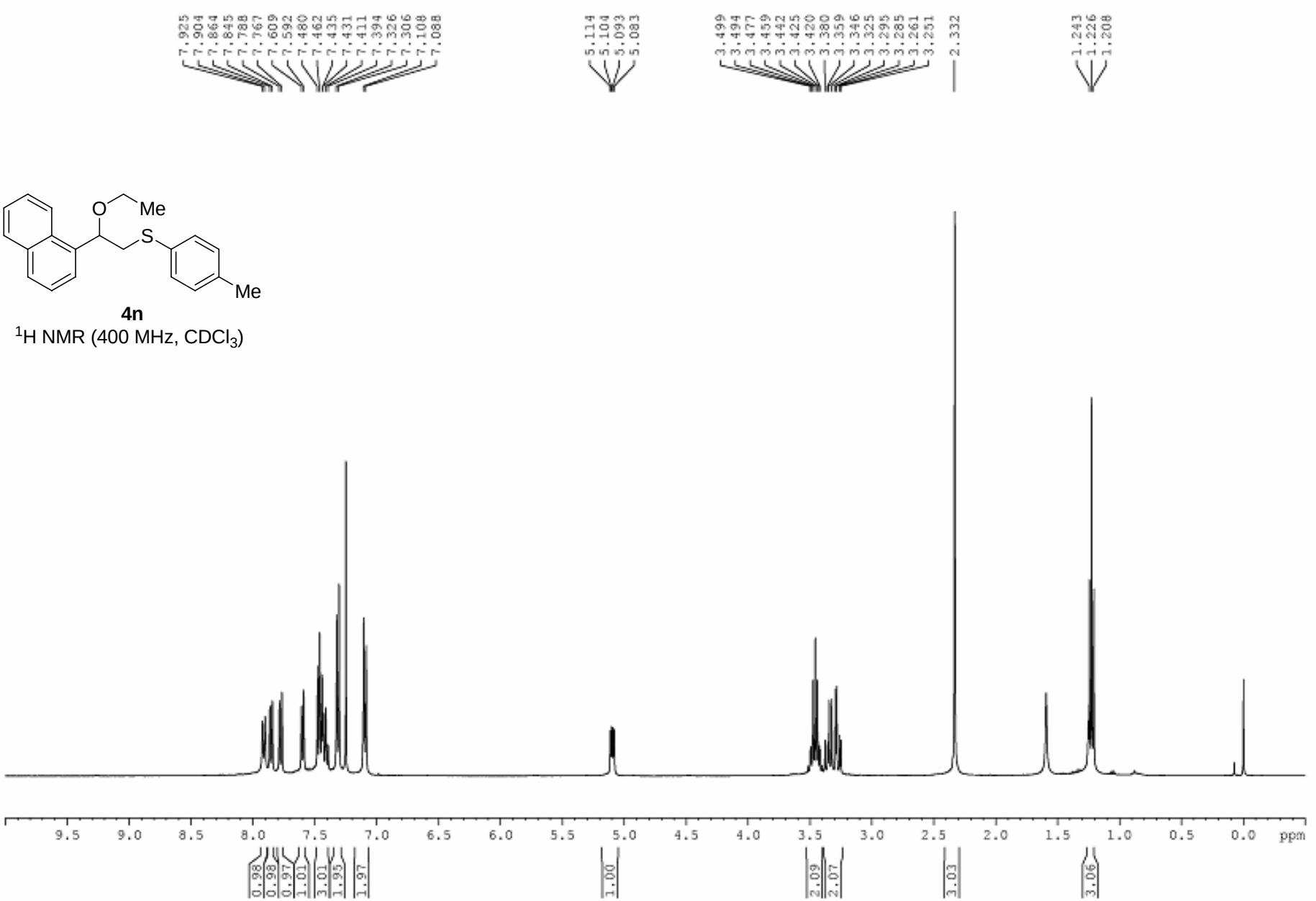
4m

^{1}H NMR (400 MHz, $CDCl_3$)



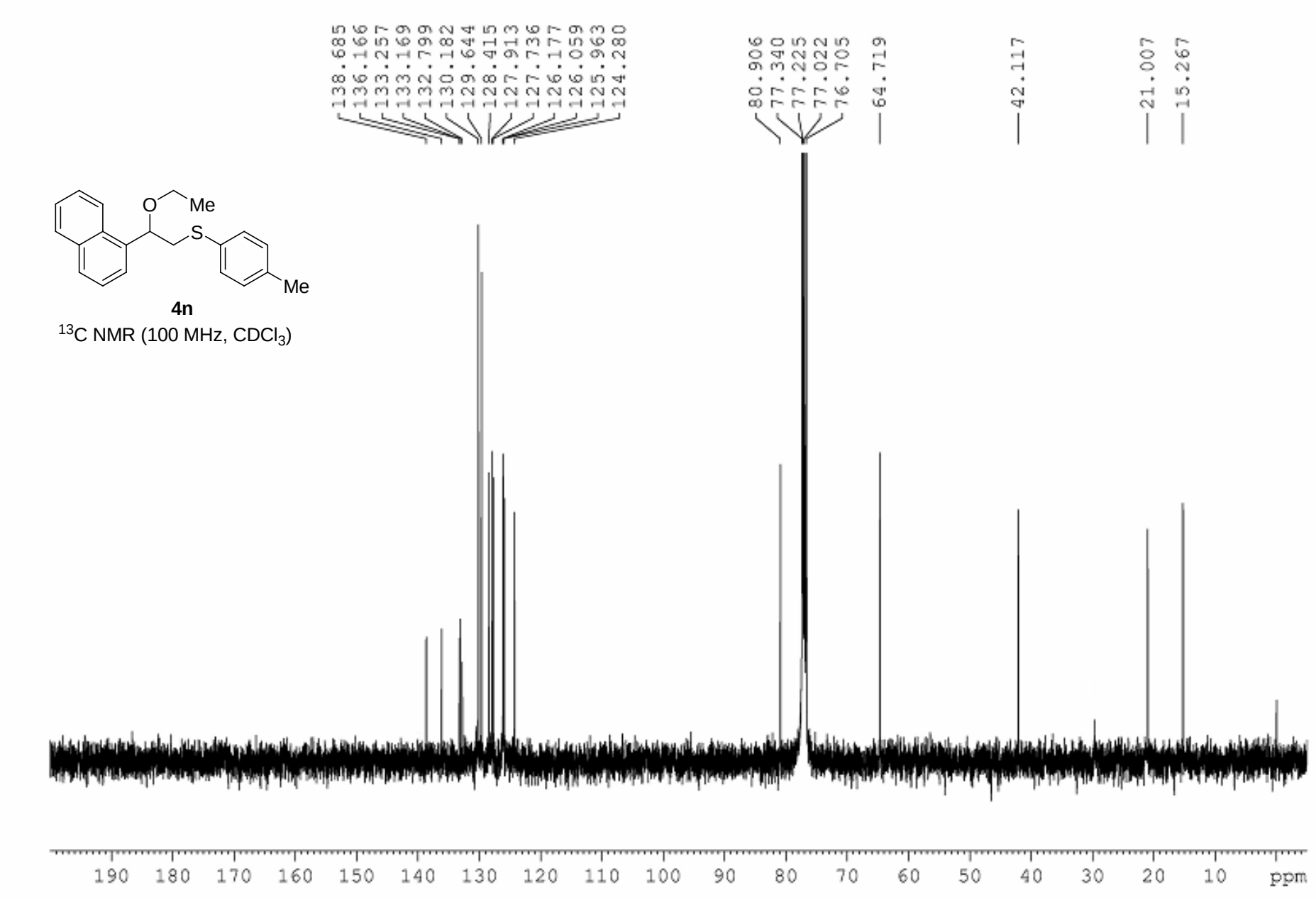
4m

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



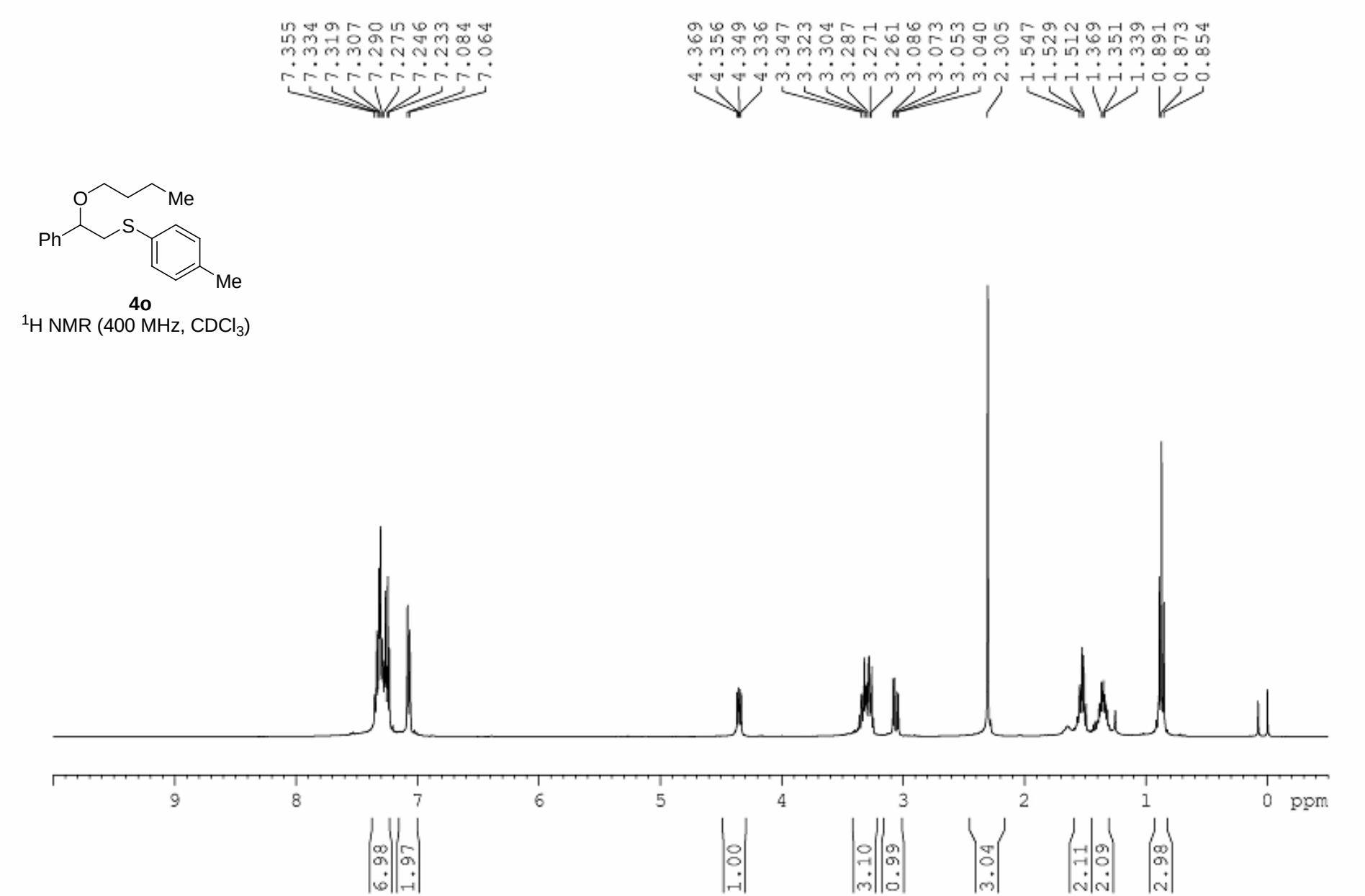
4n

^{1}H NMR (400 MHz, $CDCl_3$)



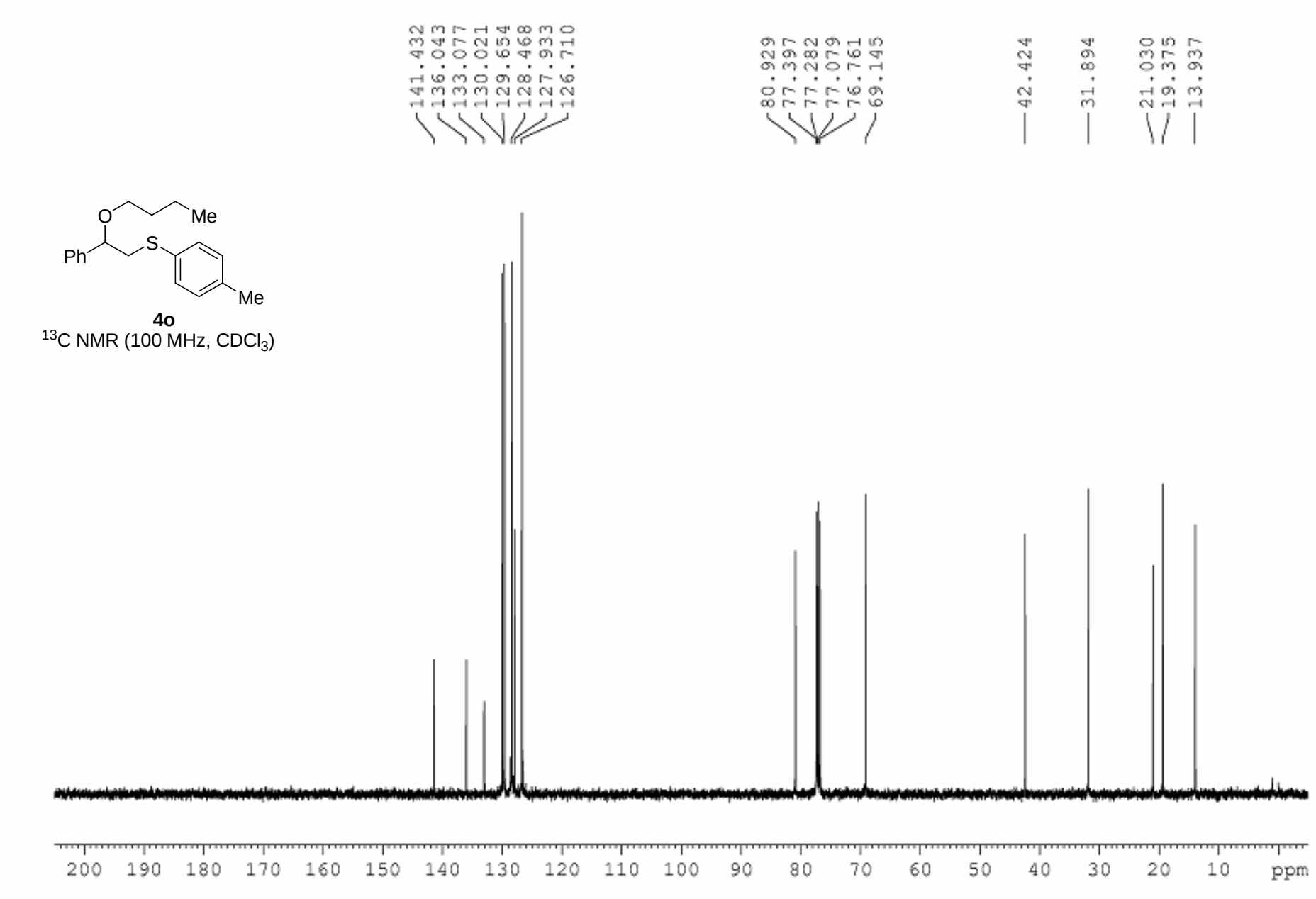
4n

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



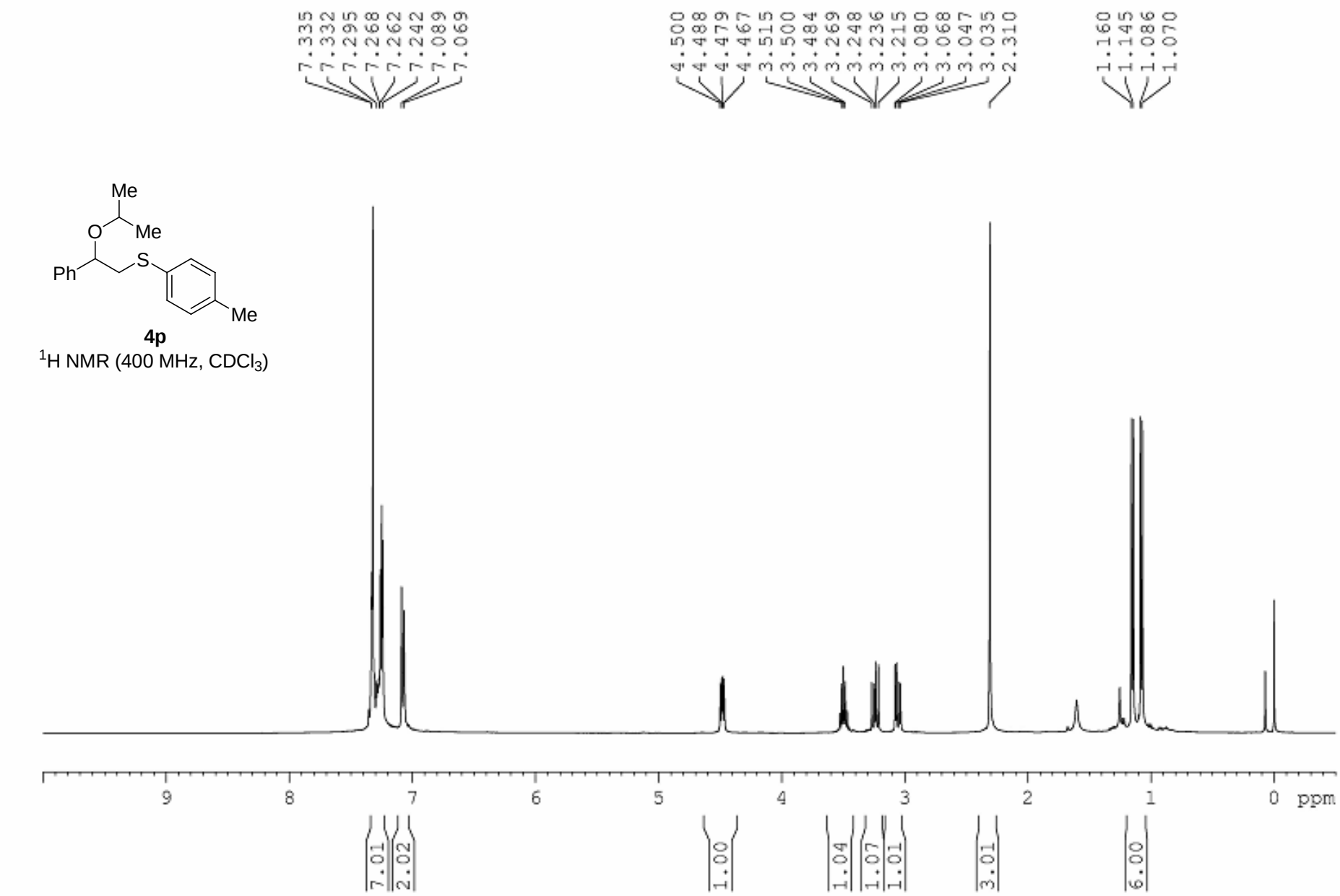
4o

^{1}H NMR (400 MHz, $CDCl_3$)



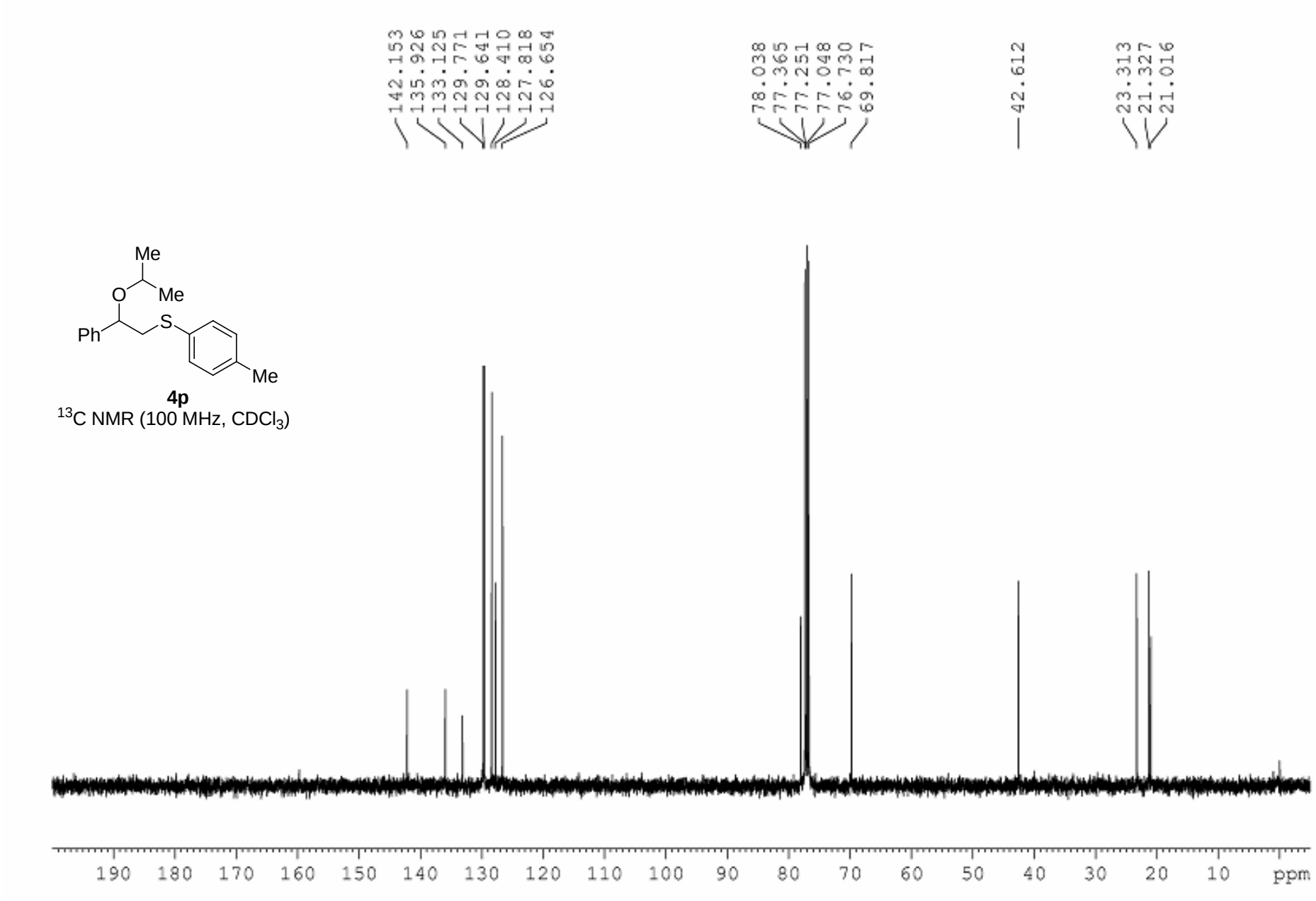
4o

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



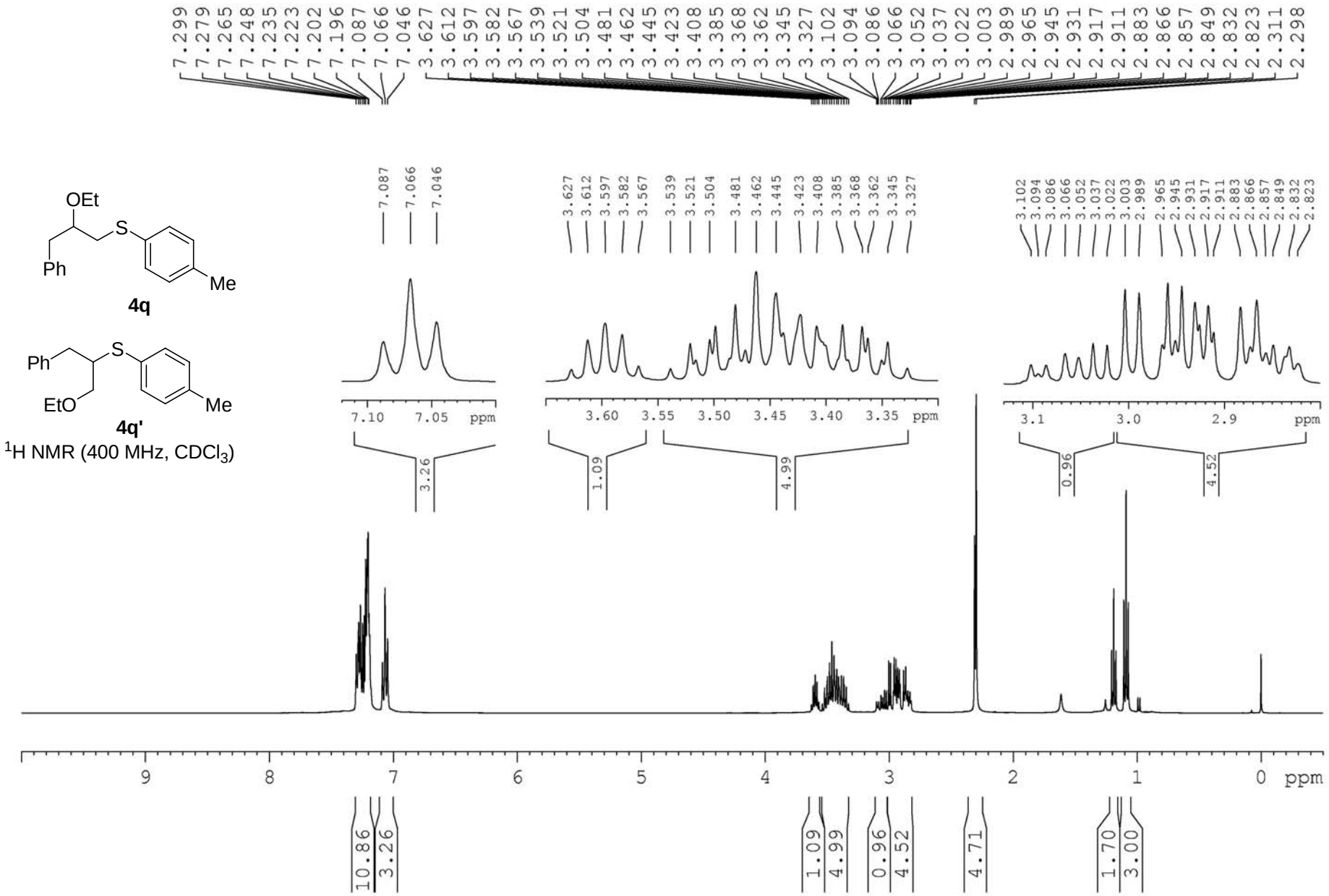
4p

^{1}H NMR (400 MHz, $CDCl_3$)

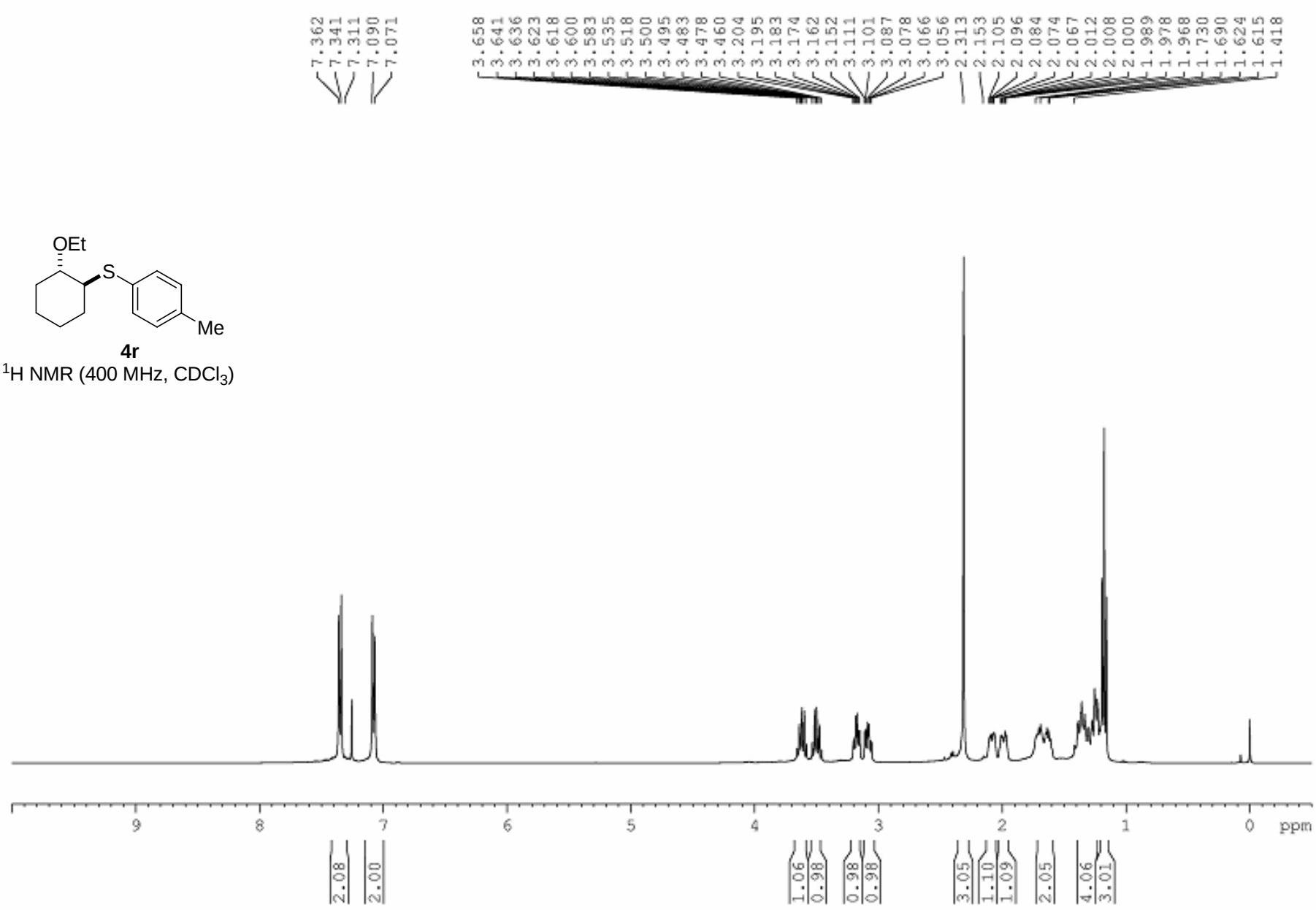


4p

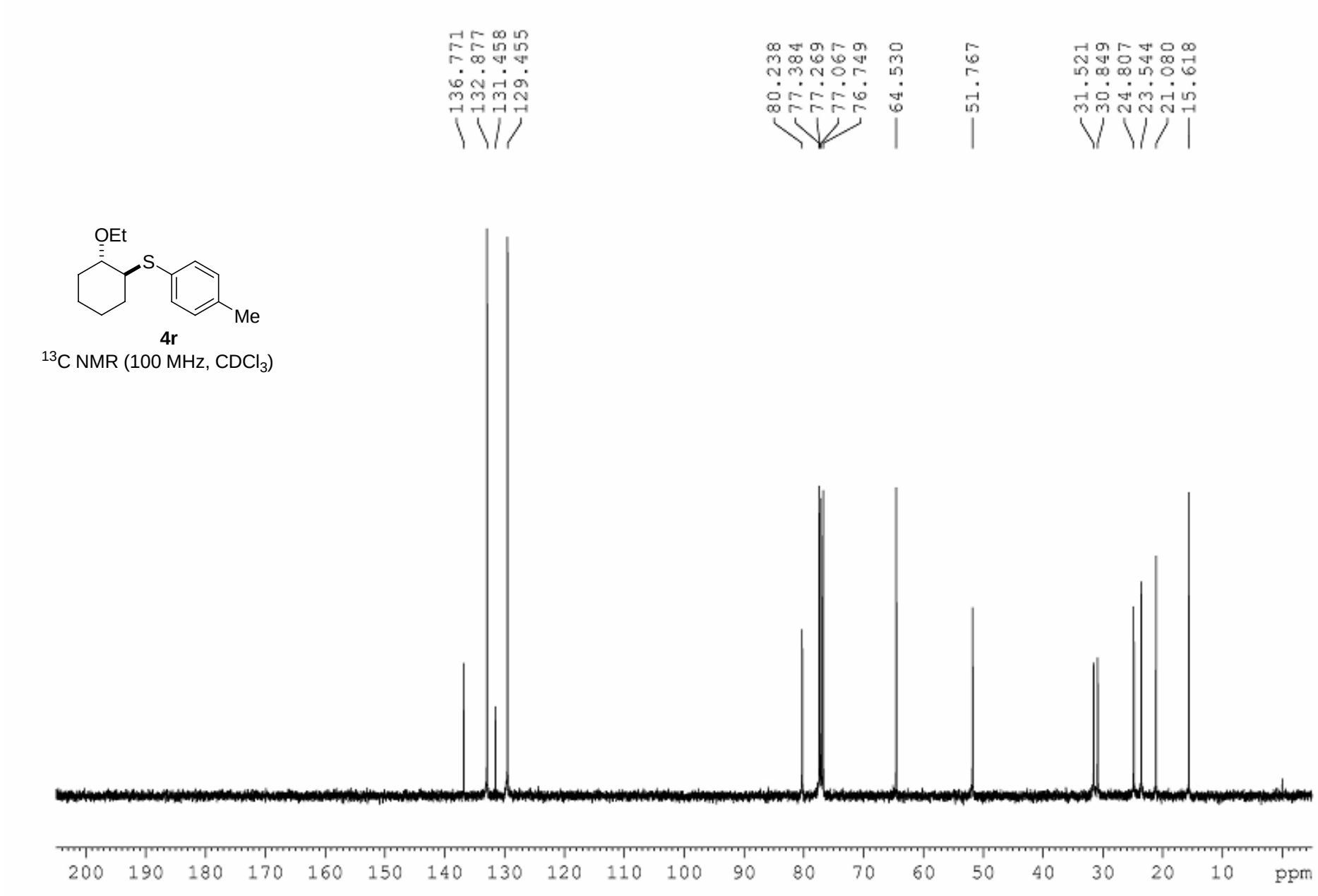
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

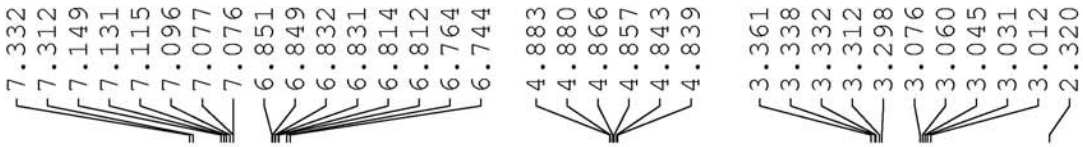


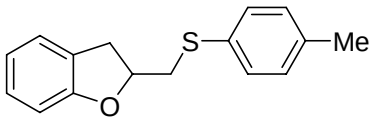
^{1}H NMR (400 MHz, $CDCl_3$)



4r

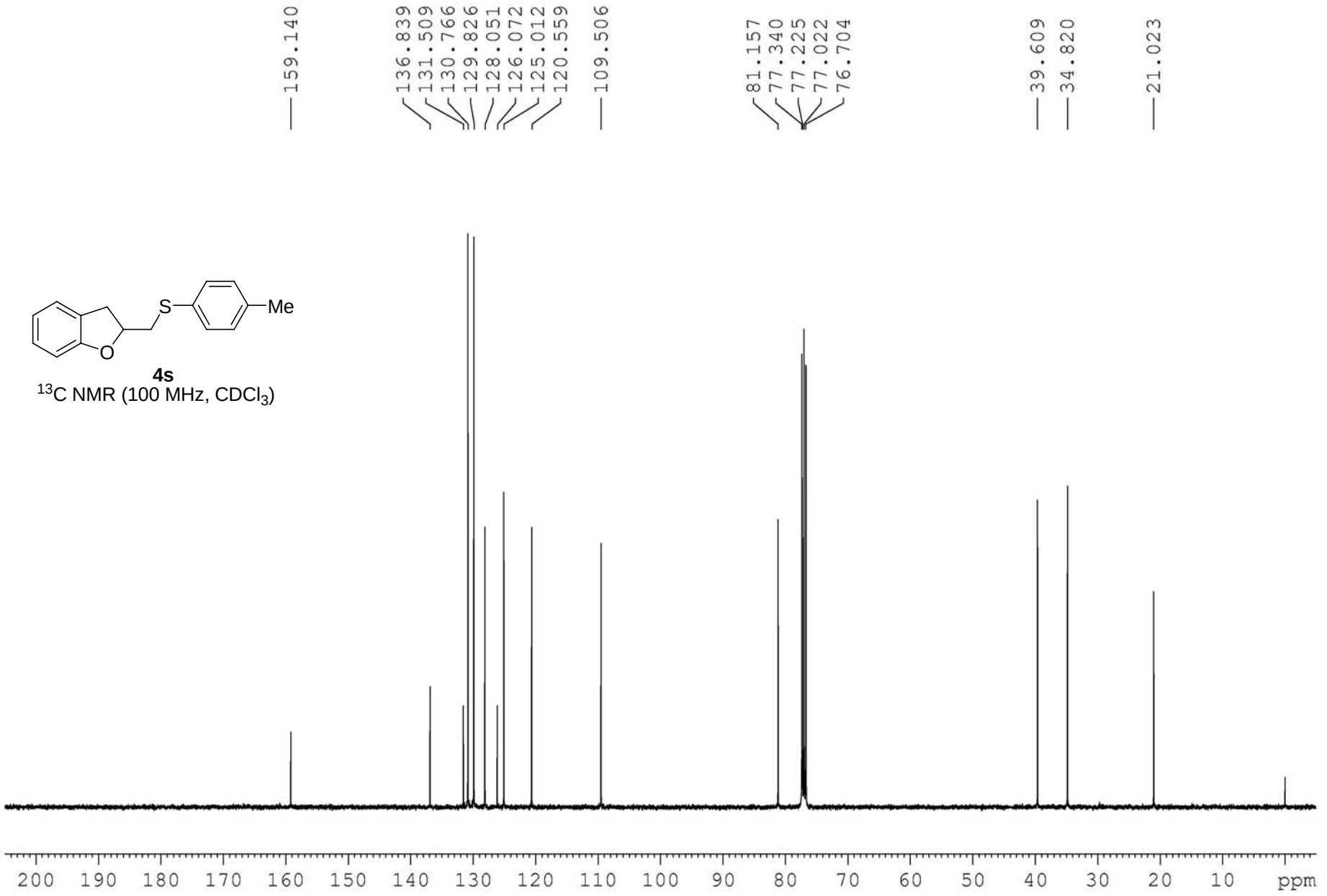
^{13}C NMR (100 MHz, $CDCl_3$)





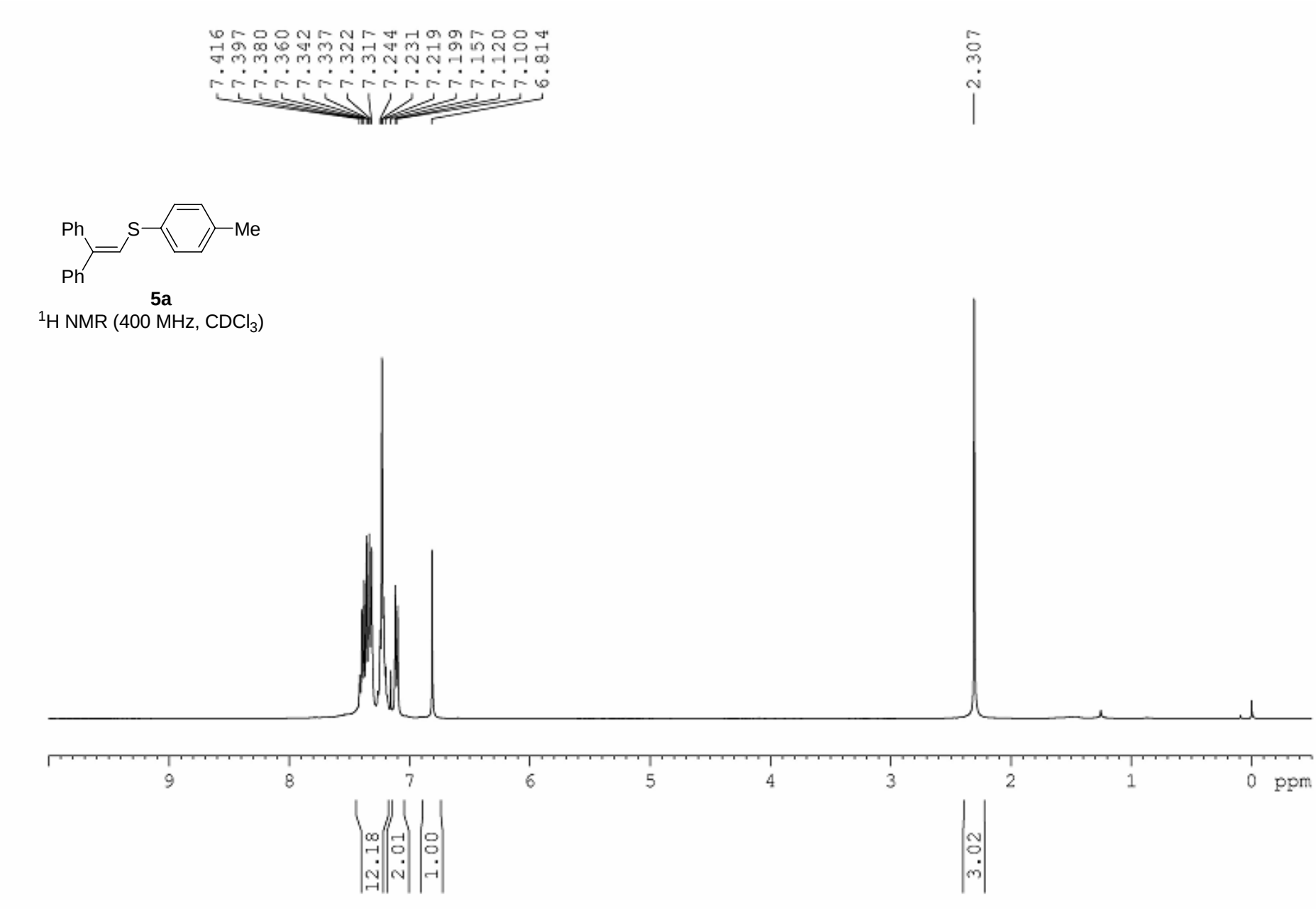
4s

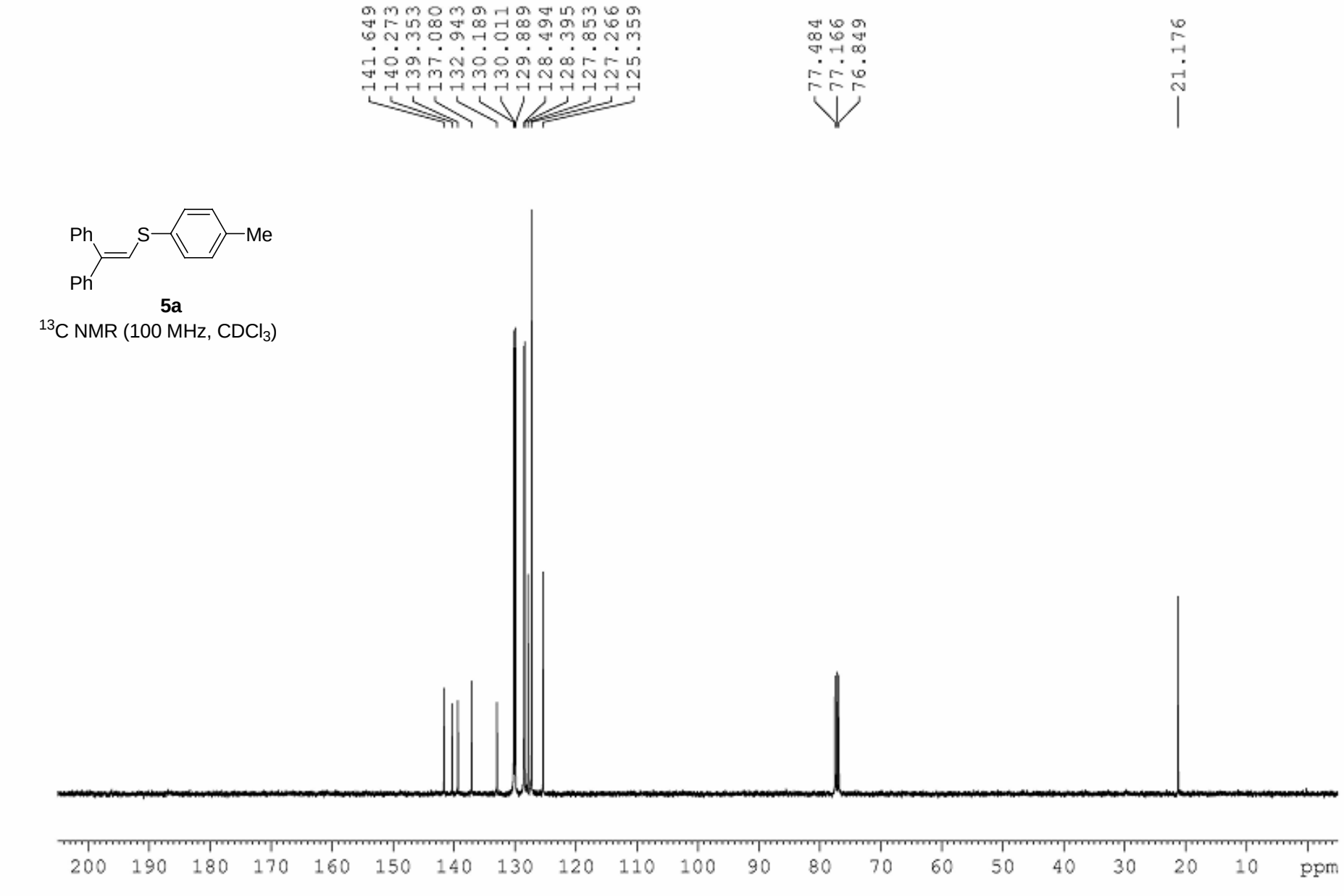
^{1}H NMR (400 MHz, $CDCl_3$)



4s

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





5a

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