Supporting Information For:

Iron-Catalyzed Suzuki-Miyaura Coupling of Alkyl Halides

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General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). TLC plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at *ca*. 30–400 mmHg. Flash column chromatography was performed on Kanto silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still et al.[1]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR) phosphorus nuclear magnetic resonance (^{31}P NMR) and boron nuclear magnetic resonance (^{11}B NMR) spectra were recorded on JEOL EX-270 (270 MHz) NMR, VARIAN MercuryVX (300 MHz) NMR, JEOL JNM-AL400 (400 MHz) NMR or JEOL ECS400NR (400 MHz) spectrometers. Proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual proton signal of $CDCl_3$ (δ 7.26). ^{13}C NMR spectra were recorded at 67.8, or 75.5, 99.5 or 98.5 MHz: carbon chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). ^{31}P NMR spectra were recorded at 109.3 or 121.4 MHz: Phosphorus chemical shift values are reported in parts per million (ppm, δ scale) and are

(1) W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

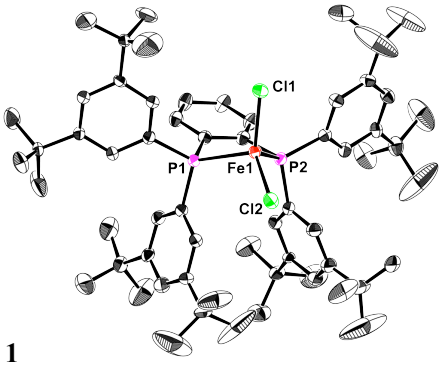
referenced to the external standard phosphorus signal of $(PhO)_3P{=}O$ ($CDCl_3$, δ −16.4). ^{11}B NMR spectra were recorded at 96.3 MHz: Chemical shifts for boron are reported in parts per million (ppm, δ scale) and are referenced to the external standard boron signal of $BF_3{\cdot}OEt_2$ (THF-d_8, δ 0.00). Data are presented as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (*italic*). IR spectra were recorded on a JASCO FT/IR-460 Plus. Characteristic IR absorptions are reported in cm^{-1}. Melting points were recorded on a Yanaco MP-500D. High-resolution mass spectra (HRMS) were obtained using the electron impact (EI) method or fast atom bombardment (FAB) method with JEOL JMS-700. NMR yield was determined for a crude product by ^1H NMR analyses by using 1,1,2,2-tetrachloroethane or pyrazine as an internal standard and GC yield was determined upon calibration by using undecane as an internal standard. Purity of isolated compounds was determined by GC analysis on Shimadzu GC-17A instrument equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m × 0.25 mm i.d., 0.25 μm film thickness) and/or ^1H NMR analyses.

Solvent. Anhydrous tetrahydrofuran (THF) was purchased from Wako Chemical Co. and distilled from benzophenone ketyl at an ambient pressure under argon immediately before use. Water content of the solvent was determined with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 15 ppm.

Materials. Materials were purchased from Wako Pure Chemical Industries, Ltd. (Wako), Tokyo Chemical Industry Co., Ltd. (TCI), Acros Organics Co. (ACROS), and other commercial suppliers, and were used after appropriate purification, unless otherwise noted. Florisil® (100–200 mesh) was purchased from Wako Pure Chemical Industries, Ltd. (Wako), Inc. Anhydrous $FeCl_3$ (powder, 99.99%) was purchased from Aldrich Inc. and dissolved in THF at 0 °C prior to use.

GC analyses. Yield (using undecane as an internal standard) was determined for a crude product by GC analysis on a Shimadzu GC-17A instrument equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m × 0.25 mm i.d., 0.25 μm film thickness). Purity of an isolated compound was determined by GC analysis.

Crystallographic Data Collection and Structure Determination. A crystal of **1** were mounted on a Rigaku Mercury CCD diffractometer with AFC-10R for data collection using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71070 Å). Crystal data and data statistics are summarized in Table 1. The structure was solved by direct methods (SHELXS-97)[2] using Fourier techniques (DIRDIF-99)[3]. In the subsequent refinement, the function $\sum w(|F_o|^2-|F_c|^2)2$, in which $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes were minimized. The positions of all non-hydrogen atoms were determined from difference Fourier electron density maps and refined anisotropically. All hydrogen atoms were placed at calculated positions (C–H = 0.95 Å) and kept fixed. The agreement indices are defined as R1 = $\sum(||F_o|-|F_c||)/\sum|F_o|$ and wR2 = $[\sum w(F_o^2-F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$. All calculations were performedby using the Crystal Structure crystallographic software packages and illustrations were drawn by using ORTEP.



1

Selected bond lengths
Fe–Cl1 2.2190(14) Å
Fe–Cl2 2.2172(18) Å
Fe–P1 2.4623(14) Å
Fe–P2 2.4404(13) Å

Selected angles
Cl1–Fe–Cl2 122.16(6)°
P1–Fe–P2 80.63(4)°

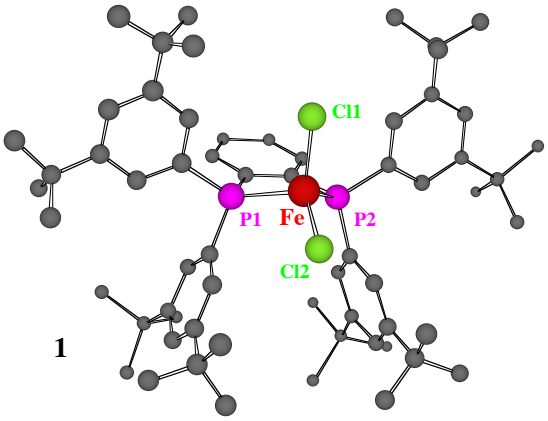
Formula	C62H88Cl2FeP2	Abs. Coefficient, mm^{-1}	0.397
Formula Weight	1022.08	F(000)	4400
Temperature, K	123.1 (2)	Crystal Size, mm^3	0.2, 0.2, 0.2
Wavelength, Å	0.71073	$2\theta_{min}$, $2\theta_{max}$, deg	3.1, 27.5
Crystal System	monoclinic	Index Ranges	-35≤h≤35
Space Group	C 2/c (No. 15)		-16≤k≤25
a, Å	27.612 (7)		-32≤l≤32
b, Å	19.743 (4)	Reflections (unique)	11938
c, Å	24.692(6)	Reflections (I>2.0σ(I))	7528
α, deg	90	Parameters	605
β, deg	105.9441 (16)	GOF on F^2	1.093
γ, deg	90	$R1$ (I>2.0σ(I))	0.931
Volume, $Å^3$	12943 (5)	R, w$R2$ (all data)	0.1376, 0.3023
Z	8	Largest diff peak and hole, e, $Å^{-3}$	2.78, -0.86
$Density_{calcd}$, $g·cm^{-3}$	1.049		

Figure 1. X-ray crystal structure of iron complexe **1** (left) and crystal data and structure refinement (right). Thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity.

(2) Sheldrick, G. M. Program for the Solution of Crystal Structures; University of Göttingen, Germany, 1997.
Sheldrick, G. M. Program for the Solution of Crystal Structures; University of Göttingen, Germany, 1997.

(3) Beurskens, P. T.; Beuskens, G.; de Gelder, R.; Garcîa-Grana, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. The DIRDIF-99 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1999.

Computational Study on Complex 1. Structure optimization of complex **1** in high spin state (S = 2) was performed with Gaussian 03[4] packages using the B3LYP hybrid functional[5] with the 6-31G(d)[6]. No imaginary frequency was observed. Bond lengths and bond angles at the iron center are consistent with X-ray crystal structure.



	UB3LYP/ 6-31G(d)	X-ray crystal structure
Fe–Cl1	2.259 Å	2.2190(14) Å
Fe–Cl2	2.238 Å	2.2172(17) Å
Fe–P1	2.495 Å	2.4623(14) Å
Fe–P2	2.484 Å	2.4404(13) Å
Cl1–Fe–Cl	123.507°	122.16(6)°
P1–Fe–P2	81.557°	80.63(4)°

Figure 2. Optimized structure of iron complex **1** at the UB3LYP/6-31G(d) level.

E (UB+HF-LYP) = –5282.54779273 hartrees, E + ZPE = –5281.191447 hartrees,

H = –5281.112573 hartrees, G = –5281.311959 hartrees

S**2 = 6.0175 (S = 2), S**2 after annihilation = 6.0001

Selected Mulliken atomic spin densities:

Fe 3.737174, Cl1 0.098164, Cl2 0.095337, P1 0.012349, P2 0.012349

(4) Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. stin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gssian, Inc., Wallingford CT, 2004.

(5) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(6) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986 and references cited therein.

Cartesian Coordinate of Complex 1

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Fe	0.457550	1.165451	1.832352
Cl	0.675812	3.332733	2.430100
Cl	0.902344	-0.545288	3.204575
P	-1.678131	0.994186	0.553589
P	1.414688	0.969025	-0.451355
H	-3.262344	2.258850	-1.606705
C	-2.237686	2.196228	-1.961365
C	0.399658	2.114746	-2.845596
C	-1.255112	1.636261	-1.130661
C	-1.913528	2.691010	-3.223709
C	-0.591812	2.647003	-3.668304
C	0.087814	1.599000	-1.578308
H	-2.689056	3.121613	-3.851410
H	-0.329132	3.041336	-4.646194
H	1.432510	2.115616	-3.180939
C	-3.142059	1.981888	1.076111
C	-5.267929	3.546371	1.940186
C	-2.916351	3.287415	1.533020
C	-4.442978	1.466949	1.065231
C	-5.528397	2.241364	1.499390
C	-3.975647	4.092728	1.968704
H	-1.900909	3.668396	1.568527
H	-4.607971	0.451691	0.722351
C	-6.946671	1.637329	1.481339
C	-3.684631	5.517380	2.479095
H	-6.095123	4.153702	2.281342
C	-2.325577	-0.705032	0.272339
C	-3.402985	-3.247300	0.019897
C	-2.958969	-1.085037	-0.914017
C	-2.231476	-1.617462	1.336731
C	-2.768234	-2.903076	1.226593
C	-3.515350	-2.366425	-1.060349
H	-3.024780	-0.376114	-1.732605
H	-1.720505	-1.315964	2.243576
C	-2.674103	-3.940872	2.361328
C	-4.239120	-2.738739	-2.370010
H	-3.818253	-4.243759	-0.073334
C	1.776703	-0.751495	-0.985214
C	2.560928	-3.303589	-1.713120
C	1.445251	-1.249832	-2.251648
C	2.496033	-1.549103	-0.083740
C	2.903381	-2.841858	-0.434235
C	1.838364	-2.537582	-2.638870
H	0.883713	-0.623642	-2.933700
H	2.724609	-1.156219	0.899948
C	3.684189	-3.753677	0.531647
C	1.530151	-3.116821	-4.033188
H	2.867416	-4.305267	-1.999573
C	2.916382	1.919388	-0.932907
C	5.153793	3.427490	-1.589279
C	3.902649	1.385971	-1.770691
C	3.067032	3.214050	-0.419922
C	4.186584	3.991425	-0.743515
C	5.039673	2.131088	-2.111359
H	3.784149	0.377716	-2.152145
H	2.312057	3.608566	0.252686
C	4.320206	5.408066	-0.152298
C	6.107178	1.506363	-3.031250
H	6.027313	4.013397	-1.840668
C	2.860000	-3.418381	-4.764664
C	0.721024	-4.427063	-3.885971
C	0.714828	-2.144028	-4.905960
H	1.254196	-1.207596	-5.088623
H	0.515182	-2.602951	-5.880875
H	-0.251587	-1.898880	-4.451996
H	3.451431	-2.504761	-4.895508
H	3.474777	-4.137238	-4.213196
H	2.662766	-3.840195	-5.757904
H	1.274750	-5.190414	-3.329529
H	-0.221527	-4.248000	-3.356354
H	0.484741	-4.842133	-4.873322
C	5.003326	-4.211014	-0.135223
C	4.036667	-3.040222	1.851135
C	2.821060	-4.994064	0.864594
H	2.559600	-5.562302	-0.034821
H	3.365524	-5.665604	1.539307
H	1.888687	-4.699081	1.359268
H	5.632843	-3.350433	-0.389679
H	5.569290	-4.852890	0.550522
H	4.828674	-4.782394	-1.053268
H	4.670364	-2.162200	1.680405
H	3.145325	-2.714691	2.397522
H	4.593063	-3.725906	2.500351
C	7.281570	2.463943	-3.308136
C	6.675232	0.229767	-2.365800
C	5.464066	1.132660	-4.388092
H	7.433900	-0.231064	-3.010452
H	7.144806	0.466385	-1.404297
H	5.895920	-0.517227	-2.181320
H	6.210220	0.680298	-5.052795
H	4.647186	0.413193	-4.267426
H	5.059006	2.020309	-4.888016
H	8.006424	1.975662	-3.969116
H	6.951630	3.384521	-3.803100
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C	5.595291	6.128845	-0.628876
C	3.098694	6.257858	-0.577744
C	4.363663	5.313843	1.392166
H	3.039139	6.342926	-1.669357
H	2.158615	5.826400	-0.220169
H	3.178665	7.269684	-0.162384
H	6.504791	5.599304	-0.322495
H	5.617538	6.248520	-1.718613
H	5.635544	7.130707	-0.186996
H	5.225662	4.722763	1.722870
H	4.452286	6.316100	1.829315

H	3.461000	4.849121	1.800507
C	-6.981018	0.379211	2.381470
C	-8.014297	2.621872	1.995728
C	-7.319153	1.241150	0.032883
H	-6.622726	0.503632	-0.379349
H	-8.324417	0.803040	0.003098
H	-7.311234	2.116226	-0.627579
H	-7.830093	2.918930	3.034302
H	-8.064438	3.529724	1.383575
H	-9.000549	2.145554	1.959625
C	-2.777420	5.431061	3.730804
C	-2.957993	6.323669	1.376511
C	-4.967102	6.279633	2.862045
H	-2.007019	5.862183	1.092926
H	-3.577255	6.406097	0.475327
H	-2.740204	7.337906	1.732346
H	-3.273117	4.872208	4.533127
H	-1.825836	4.935684	3.514709
H	-2.555069	6.437485	4.106583
H	-5.507980	5.788773	3.679291
H	-4.705383	7.287537	3.203018
H	-5.651306	6.385971	2.011795
H	-6.273071	-0.384689	2.043488
H	-6.729172	0.632675	3.417465
H	-7.983139	-0.067154	2.374359
C	-2.005310	-3.367172	3.624863
C	-4.093124	-4.423477	2.745438
C	-1.837418	-5.148270	1.874069
H	-0.819397	-4.837616	1.612625
H	-1.769287	-5.906052	2.664000
H	-2.280243	-5.623810	0.991745
H	-2.568848	-2.521133	4.034714
H	-1.963974	-4.141403	4.399429
H	-0.980896	-3.029083	3.438171
H	-4.713150	-3.586792	3.087357
H	-4.609741	-4.903931	1.907547
H	-4.034088	-5.155365	3.559982
C	-3.278702	-2.562241	-3.568848
C	-4.741760	-4.195038	-2.372269
C	-5.461411	-1.808334	-2.557861
H	-2.909073	-1.534729	-3.651291
H	-2.410950	-3.224533	-3.475174
H	-3.791702	-2.806488	-4.506882
H	-5.165649	-0.755280	-2.616028
H	-5.992584	-2.057037	-3.484818
H	-6.166321	-1.913773	-1.725128
H	-3.920181	-4.910858	-2.254181
H	-5.472580	-4.378021	-1.576462
H	-5.234955	-4.412491	-3.326324

Magnetic Moment Measurement. Solid-state magnetic moments of complex **1** were measured by a Quantum Design MPMS-XL-5 SQUID magnetometer. Magnetization versus temperature data were recorded in a 500 Oe applied field from 10 to 300 K. Solution-state magnetic moments were measured by Evans method[7] from 303 to 338K. A solution of the compound in a mixture of THF-d^8/benzene (9/1 v/v) placed in a NMR tube (5-mm diameter), while THF-d^8/benzene (9/1 v/v) mixture was sealed in a capillary tube and placed in the NMR tube. Calculations of magnetic moments were based on the difference in the chemical shift observed for the residual benzene signals in the solution containing the paramagnetic species and in the solution sealed in the capillary.

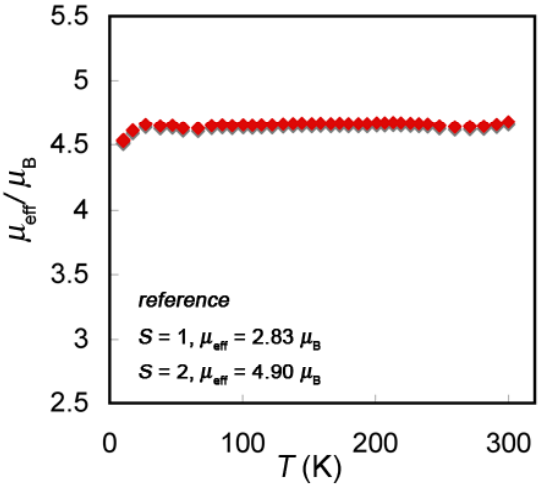


Figure 3. Magnetic moment of complex **1** versus temperature (10 to 300 K) in solid state.

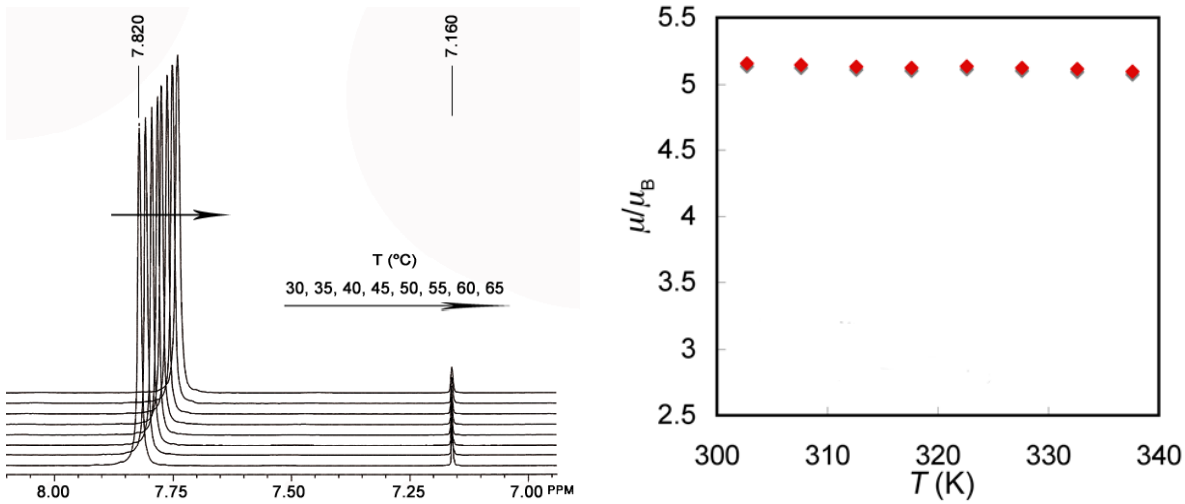
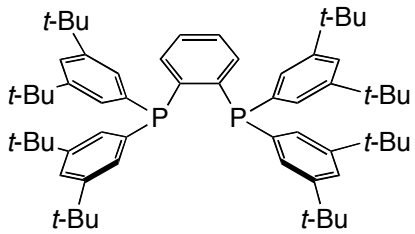


Figure 4. ^{1}H NMR spectra of **1** in THF-d^8/benzene (9/1 v/v) (left) and calculated magnetic moment versus temperature (right, 303 to 338K) in solution state.

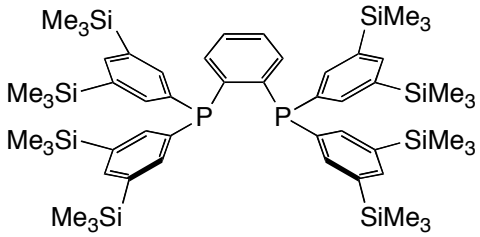
(7) (a) Evans, D. F. *J. Chem. Soc.*, **1959**, 2003–2005. (b) Evans, D. F.; Fazakerley, G. V.; Phillips, P. R. F. *J. Chem. Soc. A*, **1971**, 1931–1934. (c) Crawford, H. D.; Swanson, J. *J. Chem. Educ.*, **1971**, *48*, 382–386. (d) Grant, D. H. *J. Chem. Educ.*, **1995**, *72*, 39–40. (e) Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellmann, K. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.*, **2002**, 1159–1171.

Synthesis of 1,2-{bis[3,5-di(*tert*-butyl)pheny]phosphino}benzene (*t*-Bu-diphosphine)



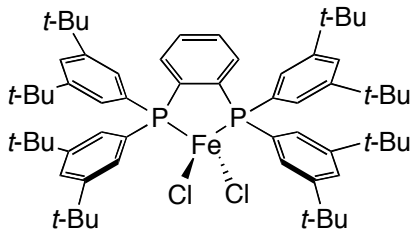
A THF solution (130 mL) of arylmagnesium bromide was prepared from magnesium (5.50 g, 0.23 mol) and 1-bromo-3,5-di-*t*-butylbenzene (33.7 g, 0.13 mol). The Grignard reagent was added slowly to a THF (60 mL) solution of 1,2-bis(dichlorophosphino)benzene (5.60 g, 20 mmol) at –78 ºC. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and then stirred for 4 h. The solvent was removed *in vacuo* to give a brown oily residue. The residue was dissolved in dichloromethane (150 mL) and washed with aqueous NH_4Cl (saturated, 50 mL). The aqueous layer was separated and extracted with dichloromethane (100 mL, three times). The organic layers were combined and washed with brine (200 mL). The organic layer was dried over $MgSO_4$ and then condensed *in vacuo*. The resultant yellow residue was washed by using MeOH with sonication to give a colorless solid (72% yield, 12.9 g). IR (KBr) 3391, 2952, 2865, 1577, 1558, 1541, 1474, 1457, 1418, 1361, 1247, 1130, 874, 710.; mp : 208.6–209.4 ºC.; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.18 (s, 72H), 7.00–7.06 (m, 10H), 7.22 (dd, J = 3.3 Hz, J = 5.6 Hz, 2H), 7.27–7.30 (m, 4H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 31.4, 34.8, 121.9, 127.9 (dd, J = 9.5 Hz, J = 10.4 Hz), 128.5, 133.7, 137.0, 144.7 (dd = 9.4 Hz, J = 10.4 Hz), 150.0 (dd, J = 2.8 Hz, J = 2.8 Hz); ^{31}P NMR (109.3 MHz, $CDCl_3$) δ –9.5; Anal. calcd for $C_{62}H_{88}P_2$ C, 83.17; H, 9.91, found C, 83.17; H, 9.92.:

Synthesis of 1,2-{bis[3,5-bis(trimethylsilyl)pheny]phosphino}benzene (TMS-diphosphine)



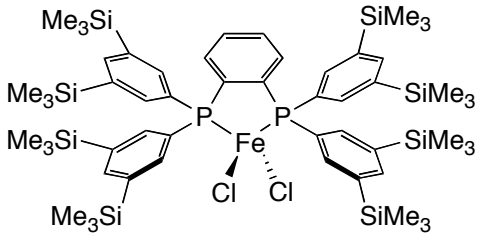
The reaction was carried out by using a THF solution of arylmagnesium bromide was prepared from magnesium (2.70 g, 0.11 mol) and 1-bromo-3,5-bis(trimethylsilyl)benzene (19.1 g, 63.4 mmol) and 1,2-bis(dichlorophosphino)benzene (2.57 g, 9.2 mmol). The title compound was obtained as a colorless solid (73%, 6.90 g). IR (KBr) 3445, 3004, 2953, 2896, 1653, 1636, 1558, 1372, 1247, 1140, 858, 833, 752, 689, 620.; mp : 178.0–178.4 ºC.; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 72 H), 7.03–7.09 (m 2H), 7.25–7.29 (m, 10 H), 7.54 (brs, 4H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ −1.1, 128.8, 133.9, 136.0 (dd, J = 2.8 Hz, J = 3.8 Hz), 137.8, 138.9, 139.1 (dd, J = 9.5 Hz, J = 9.5 Hz), 144.0 (dd, J = 9.5 Hz, J = 10.4 Hz); ^{31}P NMR (109.3 MHz, $CDCl_3$) δ −11.9; Anal. calcd for $C_{54}H_{88}P_2Si_8$ C, 63.34; H, 8.66, found C, 63.50; H, 8.71.:

Synthesis of iron complex 1: dichloro{1,2-[bis(3,5-di-*tert*-butylpheny)phosphino-κ*P*]benzene}iron(II)



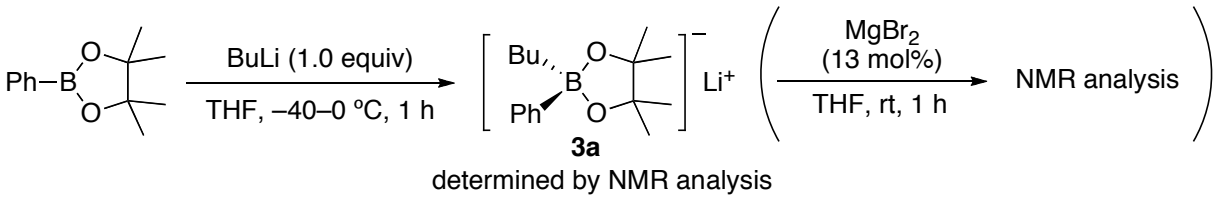
To an EtOH solution (50 mL) of $FeCl_2{\cdot}4H_2O$ (0.500 g, 2.5 mmol) was added *t*-Bu-diphosphine (2.40 g, 2.7 mmol) at room temperature. After the mixture was stirred at 90 ºC for 6 h, the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (50 mL). The solution was filtered through a pad of Celite and condensed. The residue was washed with hexane to give iron complex **1** as a white solid (82%, 2.10 g). IR (KBr) 3057, 2964, 2904, 2870, 1592, 1578, 1477, 1423, 1363, 1250, 1136, 875, 761, 707, 590.; mp : 227.0–229.0 ºC.; ^{1}H NMR (THF-d_8, 300 MHz) δ −5.83, −1.19–2.56, 4.54, 7.08–7.76, 15.3.; HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{62}H_{88}Cl_2FeP_2$ 1020.5088; found 1020.5090; Anal. calcd for $C_{62}H_{88}Cl_2FeP_2$ C, 72.86; H, 8.68, found C, 73.01; H, 8.68.:

Synthesis of iron complex 2: dichloro(1,2-{bis[3,5-bis(trimethylsilyl)pheny]phosphino-κ*P*}benzene)iron(II)



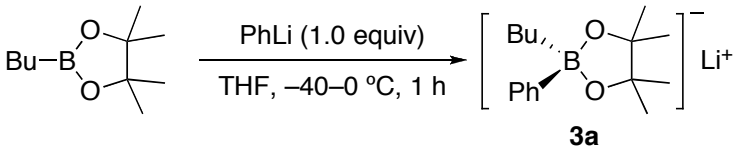
To an EtOH solution (150 mL) of $FeCl_2{\cdot}4H_2O$ (0.64 g, 3.2 mmol) was added TMS-diphosphine (3.00 g, 2.9 mmol) at room temperature. After the mixture was stirred overnight at 90 ºC, the solvent was removed *in vacuo*. A small amount of EtOH was added and the liquid phase was separated by decantation. The residue was washed three times with hexane (10 mL). The solvent was removed *in vacuo* to give iron complex **2** as a white solid. Additionally the solvent of the mother liquor was removed *in vacuo*. Purification by the same method described above was conducted repeatedly to give iron complex **2** as a white solid (total: 74%, 2.50 g). IR (KBr) 3122, 3003, 2954, 2895, 2828, 1941, 1869, 1562, 1404, 1375, 1250, 1145, 858, 755, 690, 620, 549.; mp : 190.4–191.2 ºC.; ^{1}H NMR (THF-d_8, 300 MHz) δ −5.93, −1.47, −0.67–0.52, 0.11–0.27, 0.87, 0.89, 1.11, 1.72, 4.70, 6.03–7.86, 15.1.; Anal. calcd for $C_{54}H_{88}Cl_2FeP_2Si_8$ C, 56.37; H, 7.71; Cl, 6.16, found C, 56.08; H, 7.91; Cl, 6.01.

Preparation of lithium phenylborate 3a from 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane and butyllithium.



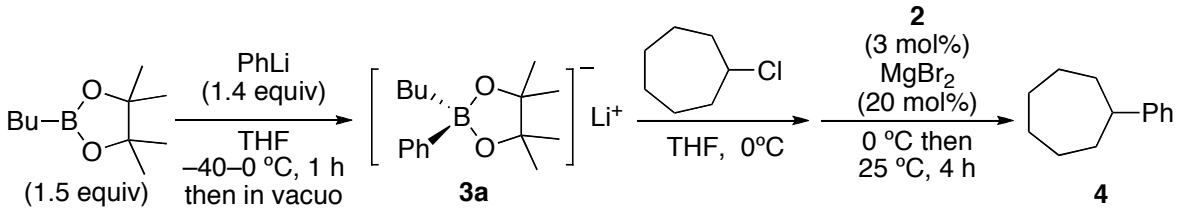
To a THF solution (3.3 mL) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.204 g, 1.0 mmol) was added BuLi (0.650 mL, 1.53 M in hexane, 1.0 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. Formation of borate **3a** was determined by ^{1}H and ^{13}C NMR spectra of the residual solid in THF-d_8 (> 97% conversion). Note that PhMgBr was not observed in NMR analysis after addition of 13 mol% of $MgBr_2$. ^{1}H NMR (THF-d_8, 300 MHz) δ 0.33 (t, J = 7.4 Hz, 2H), 0.73 (t, J = 7.1 Hz, 3H), 0.89–1.31 (m, 14H), 6.82 (dt, J = 0.8 Hz, J = 8.0 Hz, 1H), 6.98 (t, J = 7.4 Hz, 2H), 7.44 (dd, J = 1.4 Hz, J = 7.7 Hz, 2H).; ^{13}C NMR (THF-d_8, 75.5 MHz) δ 14.9, 26.9, 27.1, 28.1, 30.3, 78.3, 123.6, 126.6, 132.4.; ^{11}B NMR (THF-d_8, 96.3 MHz) δ 7.26.

Synthesis of lithium phenylborate 3a from 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and phenyllithium.



To a THF solution (3.3 mL) of 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.184 g, 1.0 mmol) was added PhLi (0.520 mL, 1.89 M in cyclohexane/Et_2O, 1.0 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. ^{1}H, ^{13}C and ^{11}B NMR spectra of the residual solid agree with that of borate **3a** described above (> 95% conversion).

A procedure for the iron-catalyzed reaction using the lithium phenylborate 3a prepared from 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and phenyllithium.

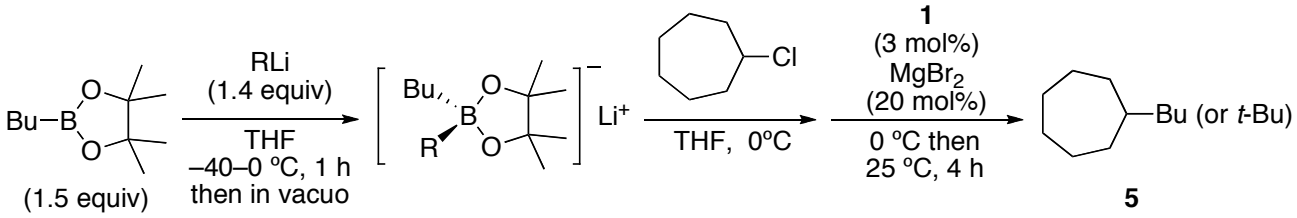


entry	yield (%)[a]			recovery of SM (%)[a]
	4	alkene	alkane	
1	87	0	3	<1

[a] The yield and the recovery of chlorocycloheptane were determined by GC analysis using undecane as an internal standard.

To a THF solution (2.5 mL) of 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.139 g, 0.75 mmol) was added PhLi (0.640 mL, 1.10 M in cyclohexane/Et_2O, 0.70 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To residual borate were added THF (1.5 mL), undecane (37.8 mg, 0.24 mmol), chlorocycloheptane (67.4 mg, 0.51 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol), and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%) at 0 ºC. The coupling reaction was carried out at 25 °C for 4 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.00 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). Product yields and recovery of chlorocycloheptane were determined by GC analysis of the crude product using undecane as an internal standard.

Reaction of chlorocycloheptane with lithium dibutyl- or butyl(*t*-butyl)borate prepared from 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and butyllithium or *t*-butyllithium.

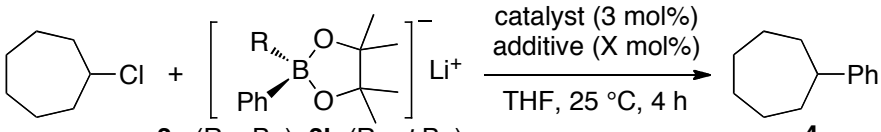


entry	RLi	yield (%)[a]			recovery of SM (%)[a]
		5	alkene	alkane	
1	BuLi	0	9	<1	88
2	*t*-BuLi	0	0	0	98

[a] The yield and the recovery of chlorocycloheptane were determined by GC analysis using undecane as an internal standard.

To a THF solution (2.5 mL) of 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.138 g, 0.75 mmol) was added RLi (0.70 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To residual borate were added THF (1.5 mL), undecane (35.8 mg, 0.23 mmol), chlorocycloheptane (67.3 mg, 0.51 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol), and iron complex **1** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%) at 0 ºC. The coupling reaction was carried out at 25 °C for 4 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.00 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). Product yields and recovery of chlorocycloheptane were determined by GC analysis of the crude product using undecane as an internal standard.

A representative procedure for the iron-catalyzed reaction shown in Table 1 and additional data



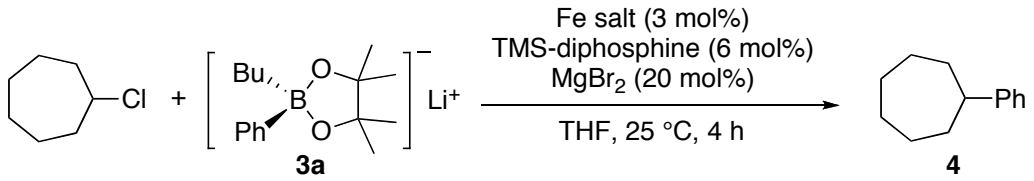
3a (R = Bu), **3b** (R = *t*-Bu) **4**

entry[a]	catalyst (3 mol%)	additive (mol%)	yield (%)[b]	recovery (%)[b]
1	$FeCl_3$	TMEDA (200)	0	> 99
2	$FeCl_3$	TMEDA (200) + $MgBr_2$ (20)	0	> 99
3	$FeCl_2(dppbz)_2$	none	0	> 98
4	$FeCl_2(dppbz)_2$	$MgBr_2$ (20)	14	83
5	complex **1**	$MgBr_2$ (20)	**93**	0
6	complex **2**	$MgBr_2$ (20)	**91**	0
7	complex **2**	none	0	> 99
8[c]	complex **2**	$MgBr_2$ (20)	84	7
9	complex **2**	$MgCl_2$ (20)	80	11
10	complex **2**	$ZnBr_2$ (20)	0	96
11	complex **2**	LiBr (20)	0	95

[a] Reactions were carried out by using 1.4 equiv of phenylborate **3a** on a 0.5 mmol scale. [b] The yield of **4** and the recovery of chlorocycloheptane were determined by GC analysis using undecane as an internal standard. [c] **3b** was used instead of **3a**.

To a THF solution (2.5 mL) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.153 g, 0.75 mmol) was added BuLi (0.480 mL, 1.55 M in hexane, 0.75 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To the residual borate were added THF (1.5 mL), undecane (39.1 mg, 0.25 mmol), chlorocycloheptane (66.3 mg, 0.50 mmol), an additive and an iron catalyst (15 μmol, 3.0 mol%) at 0 ºC. The coupling reaction was carried out at 25 °C for 4 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). Product yields and recovery of chlorocycloheptane were determined by GC analysis of the crude product using undecane as an internal standard.

Effect of counter anion on iron catalyst in the Suzuki-Miyaura coupling reaction

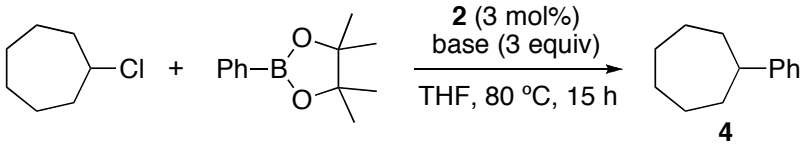


entry[a]	Fe salt	yield (%)[b]			recovery of SM (%)[b]
		4	alkene	alkane	
1	$FeCl_2$	88	3	0	2
2	$FeCl_3$	51	3	0	39
3	FeF_2	1	0	0	95
4[c]	$Fe(OEt)_2$	0	0	0	96

[a] Reactions were carried out by using 1.4 equiv of phenylborate **3a** on a 0.5 mmol scale. [b] The yield of **4** and the recovery of chlorocycloheptane were determined by GC analysis using undecane as an internal standard. [c] $Fe(OEt)_2$ was prepared from $FeCl_2$ and 2 equivalents of NaOEt at 0 ºC.

To a THF solution (2.5 mL) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.153 g, 0.75 mmol) was added BuLi (0.460 mL, 1.53 M in hexane, 0.70 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To the residual borate were added THF (1.5 mL), undecane (38.1 mg, 0.24 mmol), chlorocycloheptane (67.1 mg, 0.51 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol), and a THF solution (0.300 ml) of an iron salt (15 μmol, 3.0 mol%) and TMS-diphosphine (30.7 mg, 30 μmol, 6.0 mol%) at 0 ºC. The coupling reaction was carried out at 25 °C for 4 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). Product yields and recovery of chlorocycloheptane were determined by GC analysis of the crude product using undecane as an internal standard.

Suzuki-Miyaura coupling reaction under conventional conditions: activation of phenyl boronic acid pinacol ester with inorganic bases

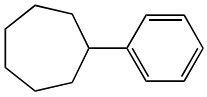


entry	base	yield (%)[a]			recovery of SM (%)[a]
		4	alkene	alkane	
1	Na_2CO_3	0	0	0	97
2	NaOEt	0	0	0	95
3	KO*t*-Bu	0	92	0	0
4	Cs_2CO_3	0	0	0	96
5	K_3PO_4	0	0	0	99
6	KF	0	0	0	98

[a] The yield and the recovery of chlorocycloheptane were determined by GC analysis using undecane as an internal standard.

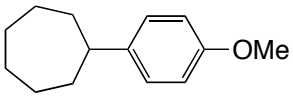
To a THF solution (2.5 mL) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.153 g, 0.75 mmol) was added undecane (34.3 mg, 0.22 mmol), chlorocycloheptane (67.2 mg, 0.51 mmol), base (1.5 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%) at 0 ºC. The coupling reaction was carried out at 80 °C for 15 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). Product yields and recovery of chlorocycloheptane were determined by GC analysis of the crude product using undecane as an internal standard.

Procedure A; A representative procedure for the iron-catalyzed reaction shown in Tables 2
Synthesis of phenylcycloheptane (4)



To a THF solution (2.5 ml) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.153 g, 0.75 mmol) was added *t*-BuLi (0.430 mL, 1.62 M in pentane, 0.70 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To the residual borate were added THF (1.5 mL), undecane (48.5 mg, 0.31 mmol), bromocycloheptane (89.4 mg, 0.50 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol), and iron complex **2** (0.100 mL, 50.0 mM in THF, 5.0 μmol, 1.0 mol%) at 0 ºC. The coupling reaction was carried out at 40 °C for 3 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). The title compound (87.1 mg, 99% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% pentane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[8]

Synthesis of 4-methoxyphenylcycloheptane (S1)

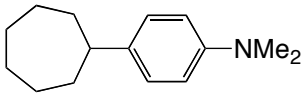


The reaction was carried out according to Procedure A on a 1.0 mmol scale by bromocycloheptane (0.178 g, 1.0 mmol), 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.351 g, 1.5 mmol) using *t*-BuLi (0.780 mL, 1.80 M in pentane, 1.4 mmol), $MgBr_2$ (2.00 mL, 0.100 M in THF,

(8) Nakamura, M.; matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686–3687.

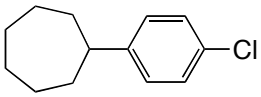
0.20 mmol) and iron complex **2** (0.600 mL, 50.0 mM in THF, 30.0 μmol, 3.0 mol%). Conditions: 40 °C, 3 h. The title compound (0.200 g, 98% yield, > 98% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% hexane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[9]

Synthesis of 4-dimethylaminophenylcycloheptane (S2)



The reaction was carried out according to Procedure A on a 1.0 mmol scale by bromocycloheptane (0.179 g, 1.0 mmol), 2-[4-(dimethylamino)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.371 g, 1.5 mmol) using *t*-BuLi (0.780 mL, 1.80 M in pentane, 1.4 mmol), $MgBr_2$ (2.00 mL, 0.100 M in THF, 0.20 mmol) and iron complex **2** (0.600 mL, 50.0 mM in THF, 30.0 μmol, 3.0 mol%). Conditions: 40 °C, 3 h. The title compound (0.206 g, 94% yield, 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 20:1). R_f = 0.38 (hexane:AcOEt = 10:1); IR (neat) 2923, 2852, 2797, 1615, 1520, 1458, 1343, 1163, 1060, 948, 909, 807, 733.; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.45–1.93 (m, 12H), 2.53–2.65 (m, 1H), 2.90 (s, 6H), 6.69 (dd, *J* = 3.0 Hz, *J* = 8.9 Hz, 2H), 7.07 (dd, *J* = 3.3 Hz, *J* = 9.6 Hz, 2H).; ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 27.1, 28.0, 37.0, 40.9, 46.0, 113.0, 127.2, 138.5, 148.8.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{15}H_{23}N$ 217.1830.; found 217.1825.

Synthesis of 4-chlorophenylcycloheptane (S3)

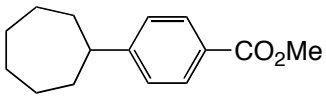


The reaction was carried out according to Procedure A on a 0.50 mmol scale by bromocycloheptane (89.2 mg, 0.50 mmol), 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.179 g, 0.75 mmol) using *t*-BuLi (0.390 mL, 1.80 M in pentane, 0.70 mmol) , $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.00 mol%). Conditions: 40 °C, 3 h. The title compound (80.4 mg, 77% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% pentane). R_f = 0.55 (hexane); IR (neat) 2925, 2854, 1492, 1459, 1409, 1093, 1013, 812, 733.; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.49–1.91 (m, 12H), 2.58–2.67 (m, 1H), 7.08–7.13 (m, 2H), 7.20–7.26 (m, 2H).; ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.1, 27.9, 36.8, 46.4, 128.0, 128.3, 131.0, 148.4.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{13}H_{17}Cl$ 208.1019.; found 208.1018.

(9) Xiao, Y.-P.; Liu, X.-Y.; Che, C.-M. *J. Organomet. Chem.* **2009**, *694*, 494–501.

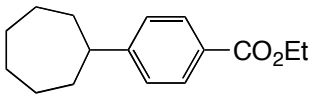
Procedure B; A representative procedure for the iron-catalyzed reaction shown in Tables 2

Synthesis of methyl 4-cyclohepthylbenzoate (S4)



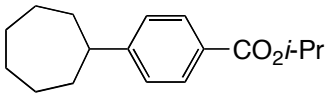
To a THF solution (1.5 mL) of 2-(4-methoxycarbonylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.262 g, 1.0 mmol) was added EtMgBr (1.01 ml, 0.94 M in THF, 0.95 mmol) at –78 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. To the solution (2.0 mL) of the borate were added undecane (37.8 mg, 0.24 mmol), bromocycloheptane (89.5 mg, 0.51 mmol), and iron complex **2** (0.500 mL, 50.0 mM in THF, 25.0 μmol, 5.0 mol%) at 0 ºC. The coupling reaction was carried out at 25 °C for 3 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with Et_2O. The title compound (0.106 g, 90% yield, > 99% pure on GC analysis) was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). R_f = 0.67 (hexane:AcOEt = 5:1); IR (KBr) 2927, 2852, 1716, 1457, 1436, 1416, 1278, 1181, 1111, 1099, 962, 830, 769, 705.; mp : 37.5–38.8 ºC.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50–1.93 (m, 12H), 2.71 (tt, *J* = 3.7 Hz, *J* = 10.5 Hz, 1H), 3.89 (s, 3H), 7.23–7.26 (m, 2H), 7.92–7.96 (m, 2H).; ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 27.2, 27.9, 36.5, 47.0, 51.9, 126.7, 127.5, 129.7, 155.4, 167.2.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{15}H_{20}O_2$ 232.1463.; found 232.1464.

Synthesis of ethyl 4-cyclohepthylbenzoate (S5)



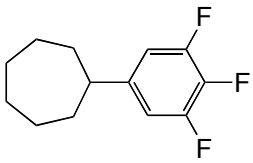
The reaction was carried out according to Procedure B on a 0.50 mmol scale by bromocycloheptane (88.9 mg, 0.50 mmol), 2-(4-ethoxycarbonylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.276 g, 1.0 mmol) using EtMgBr (1.01 mL, 0.94 M in THF, 0.95 mmol) and iron complex **2** (0.500 mL, 50.0 mM in THF, 25.0 μmol, 5.0 mol%). Conditions: 25 °C, 3 h. The title compound (0.100 g, 81% yield, > 99% pure on GC analysis) was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). R_f = 0.68 (hexane:AcOEt = 5:1); IR (KBr) 3902, 3853, 3839, 2988, 2925, 2854, 1710, 1541, 1457, 1275, 1109, 1098, 1021, 842, 769, 706.; mp : 34.7–35.4 ºC.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38 (t, *J* = 7.1 Hz, 3H), 1.50–1.93 (m, 12H), 2.71 (tt, *J* = 3.6 Hz, *J* = 10.5 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.23–7.26 (m, 2H), 7.93–7.96 (m, 2H).; ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 14.3, 27.2, 27.8, 36.5, 47.1, 60.7, 126.6, 127.8, 129.7, 155.2, 166.7.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{16}H_{22}O_2$ 246.1620.; found 246.1622.

Synthesis of isopropyl 4-cyclohepthylbenzoate (S6)



The reaction was carried out according to Procedure B on a 0.50 mmol scale by bromocycloheptane (88.6 mg, 0.50 mmol), 2-(4-isopropoxycarbonylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.290 g, 1.0 mmol) using EtMgBr (1.10 ml, 0.85 M in THF, 0.94 mmol) and iron complex **2** (0.500 mL, 50.0 mM in THF, 25.0 μmol, 5.0 mol%). Conditions: 25 °C, 3 h. The title compound (97.1 mg, 74% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 50:1). R_f = 0.47 (hexane:AcOEt = 10:1); IR (neat) 2979, 2925, 2855, 1714, 1609, 1458, 1373, 1275, 1178, 1097, 1018, 921, 770, 707.; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.35 (d, *J* = 6.3 Hz, 6H), 1.48–1.94 (m, 12H), 2.71 (m, 1H), 5.24 (sept, *J* = 6.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.94 (dd, *J* = 2.0 Hz, *J* = 8.6 Hz, 2H).; ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 22.0, 27.2, 27.9, 36.5, 47.1, 68.0, 126.6, 128.3, 129.7, 155.1, 166.2.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{17}H_{24}O_2$ 260.1776.; found 260.1774.

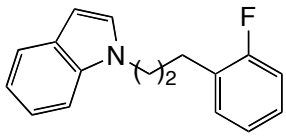
Procedure C; A representative procedure for the iron-catalyzed reaction shown in Tables 2
Synthesis of 3,4,5-trifluorophenylcycloheptane (S7)



To a THF solution (2.5 ml) of 2-(3,4.5-trifluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.194 g, 0.75 mmol) was added *t*-BuLi (0.390 mL, 1.80 M in pentane, 0.70 mmol) at –78 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To the residual borate were added THF (1.5 mL), undecane (30.9 mg, 0.20 mmol), bromocycloheptane (89.2 mg, 0.50 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol), and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%). The coupling reaction was carried out at 40 °C for 3 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with Et_2O. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). The title compound (95.8 mg, 83% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (100% pentane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[10]

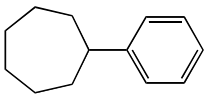
(10) Hatakeyama, T.; Kondo, Y.; Fujiwara, Y.; Takaya, H.; Ito, S.; Nakamura, E.; Nakamura, M. *Chem. Commun.* **2009**, 1216–1218.

Synthesis of *N*-[3-(2-fluorophenyl)propyl]indole (S8)



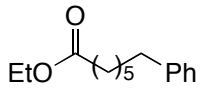
The reaction was carried out according to Procedure C on a 0.44 mmol scale by *N*-[3-iodopropyl]indole (0.126 g, 0.44 mmol), 2-(2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.222 g, 1.0 mmol) using *t*-BuLi (0.530 mL, 1.80 M in pentane, 0.95 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15 μmol, 3.4 mol%). Conditions: 40 °C, 3 h. The title compound (88.2 mg, 79% yield, 98% pure on GC analysis) was obtained as an yellow oil after silica gel column chromatography (hexane:AcOEt = 20:1). R_f = 0.39 (hexane:AcOEt = 10:1); IR (neat) 3056, 2929, 2866, 1510, 1491, 1463, 1316, 1228, 1106, 1014, 757, 741, 716.; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.18 (tt, *J* = 7.3 Hz, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 4.16 (t, *J* = 7.2 Hz, 2H), 6.50 (dd, *J* = 0.6 Hz, *J* = 3.0 Hz, 1H), 6.99–7.31 (m, 8H), 7.63 (dd, *J* = 1.0 Hz, *J* = 8.9 Hz, 1H).; ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 26.4, 30.3, 45.7, 101.2, 109.3, 115.3 (d, *J* = 22.3 Hz), 119.3, 121.0, 121.4, 124.1 (d, *J* = 3.3 Hz), 127.7 (d, *J* = 5.0 Hz), 127.7 (d, *J* = 13.4 Hz), 127.9, 128.6, 130.5 (d, *J* = 5.0 Hz), 136.0, 161.2 (d, *J* = 244.2 Hz).; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{17}H_{16}NF$ 253.1267.; found 253.1266.

Procedure D; A representative procedure for the iron-catalyzed reaction shown in Tables 2. Synthesis of phenylcycloheptane (4)



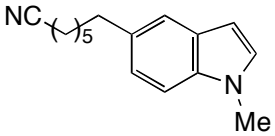
To a THF solution (2.5 mL) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.154 g, 0.75 mmol) was added BuLi (0.480 mL, 1.55 M in hexane, 0.75 mmol) at –40 ºC. The reaction mixture was stirred at the same temperature for 30 min, and then at 0 ºC for 30 min. The solvent was removed *in vacuo* at 0 ºC. To the residual borate were added THF (1.5 mL), undecane (37.5 mg, 0.24 mmol), chlorocycloheptane (66.8 mg, 0.50 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol), and iron complex **1** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%) at 0 ºC. The coupling reaction was carried out at 25 °C for 4 h. After cooling to ambient temperature, aqueous NH_4Cl (saturated, 2.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered with a pad of Florisil (100-200 mesh, Wako Pure Chemical Industries, Ltd.). Product yield (93%) was determined by GC analysis of the crude product using undecane as an internal standard.

Synthesis of ethyl 6-phenyl-hexanoate (S9)



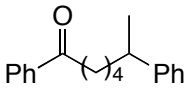
The reaction was carried out according to Procedure A on a 0.51 mmol scale by ethyl 7-bromoheptanoate (0.120 g, 0.51 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.153 g, 0.75 mmol) using *t*-BuLi (0.430 mL, 1.62 M in pentane, 0.70 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%). Conditions: 40 °C, 3 h. The title compound (0.107 g, 90% yield, > 98% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 10:1). R_f = 0.33 (hexane:AcOEt = 10:1); IR (neat) 3027, 2980, 2931, 2857, 1736, 1454, 1372, 1252, 1182, 1093, 1032, 910, 734, 699.; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.25 (t, *J* = 7.2 Hz, 3H), 1.32–1.40 (m, 4H), 1.56–1.67 (m, 4H), 2.28 (t, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 7.14–7.19 (m, 3H), 7.24–7.29 (m, 2H).; ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 14.2, 24.9, 28.8, 28.9, 31.2, 34.3, 35.8, 60.1, 125.6, 128.2, 128.3, 142.7, 173.8.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{15}H_{22}O_2$ 234.1620.; found 234.1623.

Synthesis of 5-(6-cyanohexyl)-1-methyl-1H-indole (S10)



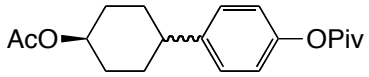
The reaction was carried out according to Procedure D on a 0.50 mmol scale by 7-bromoheptanenitrile (95.9 mg, 0.50 mmol), 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (0.259 g, 1.0 mmol) using BuLi (0.620 mL, 1.53 M in hexane, 0.95 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%). Conditions: 40 °C, 3 h. The title compound (0.117 g, 96% yield, > 98% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 10:1). R_f = 0.31 (hexane:AcOEt = 5:1); IR (neat) 3100, 3019, 2923, 2853, 2247, 1514, 1335, 1247, 1087, 801, 765, 723.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33–1.52 (m, 4H), 1.61–1.71 (m, 4H), 2.31 (t, *J* = 7.3 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 3.77 (s, 3H), 6.41 (d, *J* = 3.2 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 7.05 (dd, *J* = 1.8 Hz, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.40 (brs, 1H).; ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 17.1, 25.3, 28.3, 28.6, 31.8, 32.8, 35.8, 100.4, 108.9, 119.8, 119.9, 122.4, 128.6, 128.9, 133.1, 135.3.; HRMS (FAB) *m/z* $[M+H]^+$ calcd for $C_{16}H_{21}N_2$ 241.1705.; found 241.1706.

Synthesis of 1,6-diphenylheptan-1-one (S11)



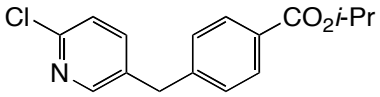
The reaction was carried out according to Procedure A on a 0.50 mmol scale by 6-bromo1-phenylheptan-1-one (0.135 g, 0.50 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.204 g, 1.0 mmol) using *t*-BuLi (0.575 mL, 1.65 M in pentane, 0.95 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol) and iron complex **2** (0.500 mL, 50.0 mM in THF, 25.0 μmol, 5.0 mol%). Conditions: 40 °C, 4 h. The title compound (87.1 mg, 65% yield, > 98% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 50:1). R_f = 0.59 (hexane:AcOEt = 5:1); IR (neat) 3060, 3027, 2929, 2866, 1686, 1598, 1494, 1449, 1223, 1208, 762, 700.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18–1.40 (m, 5H), 1.58–1.80 (m, 4H), 2.70 (tq, *J* = 6.9 Hz, *J* = 7.3 Hz, 1H), 2.91 (t, *J* = 7.8 Hz, 2H), 7.16–7.19 (m, 3H), 7.25–7.30 (m, 2H), 7.42–7.46 (m, 2H), 7.52–7.56 (m, 1H), 7.91–7.93 (m, 2H).; ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 22.3, 24.3, 27.5, 38.2, 38.5, 39.8, 125.8, 127.0, 128.0, 128.3, 128.5, 132.8, 137.0, 147.6, 200.4.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{19}H_{22}O$ 266.1671.; found 266.1672.

Synthesis of 4-(4-acetoxycyclohexyl)phenyl pivalate (S12)



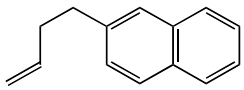
The reaction was carried out according to Procedure B on a 0.50 mmol scale by *trans*-4-bromocyclohexylacetate (0.111 g, 0.50 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pahenyl pivalate (0.380 g, 1.2 mmol) using EtMgBr (1.28 mL, 0.94 M in THF, 1.2 mmol) and iron complex **2** (0.500 mL, 50.0 mM in THF, 25.0 μmol, 5.0 mol%). Conditions: 40 °C, 3 h. The title compound (0.132 g, 83% yield, > 99% pure on GC analysis, *cis*:*trans* = 42:58) was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). R_f = 0.47 (hexane:AcOEt = 5:1); *cis trans* mixture:IR (KBr) 2965, 2930, 2859, 1751, 1732, 1507, 1366, 1248, 1201, 1168, 1117, 893, 842, 793.; mp : 56.9–57.1 ºC.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 9H), 1.44–1.82 (m, 4H), 1.93–2.11 (m, 7H), 2.48–2.61 (m, 1H), 4.77 (tt, *J* = 11.0 Hz, 1H), [5.10 (t, *J* = 2.8 Hz, 1H)], 6.96–7.00 (m, 2H), 7.18–7.24 (m, 2H).; ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 21.4 (21.5), 27.1, 30.2 (28.4), 31.9 (32.2), 39.0, 42.7 (42.8), 72.8 (68.8), 121.3 (121.2), 127.5 (127.6), 143.4 (144.3), 149.3 (149.2), 170.6, 177.2.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{19}H_{26}O_4$ 318.1831.; found 318.1828. The values in parentheses are referred to the minor (*cis*) isomer.

Synthesis of isopropyl 4-[(6-chloropyridin-3-yl)methyl]benzoate (S13)



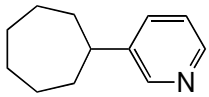
The reaction was carried out according to Procedure B on a 0.51 mmol scale by 2-chloro-5-chloromethylpyridine (82.0 mg, 0.51 mmol), 2-(4-isopropoxycarbonylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.290 g, 1.0 mmol) using EtMgBr (1.01 mL, 0.94 M in THF, 0.95 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%). Conditions: 25 °C, 8 h. The title compound (0.127 mg, 86% yield, > 99% pure on GC analysis) was obtained as a white solid after silica gel column chromatography (hexane:AcOEt = 20:1). R_f = 0.53 (hexane:AcOEt = 2:1); IR (KBr) 3039, 2982, 2945, 1703, 1607, 1566, 1458, 1370, 1279, 1182, 1107, 1018, 919, 768, 741.; mp : 73.2–73.8 ºC.; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.36 (d, *J* = 6.3 Hz, 6H), 4.00 (s, 2H), 5.24 (sept, *J* = 6.3 Hz, 1H), 7.23 (dd, *J* = 2.0 Hz, *J* = 8.2 Hz, 3H), 7.41 (dd, *J* = 2.3 Hz, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 8.26 (d, *J* = 2.0 Hz, 1H).; ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 21.8, 38.0, 68.2, 124.0, 128.6, 129.4, 129.9, 134.5, 139.0, 144.1, 149.5, 149.6, 165.6.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{16}H_{16}O_2NCl$ 289.0870.; found 289.0869.

Synthesis of 2-(3-butenyl)naphthalene (S14)

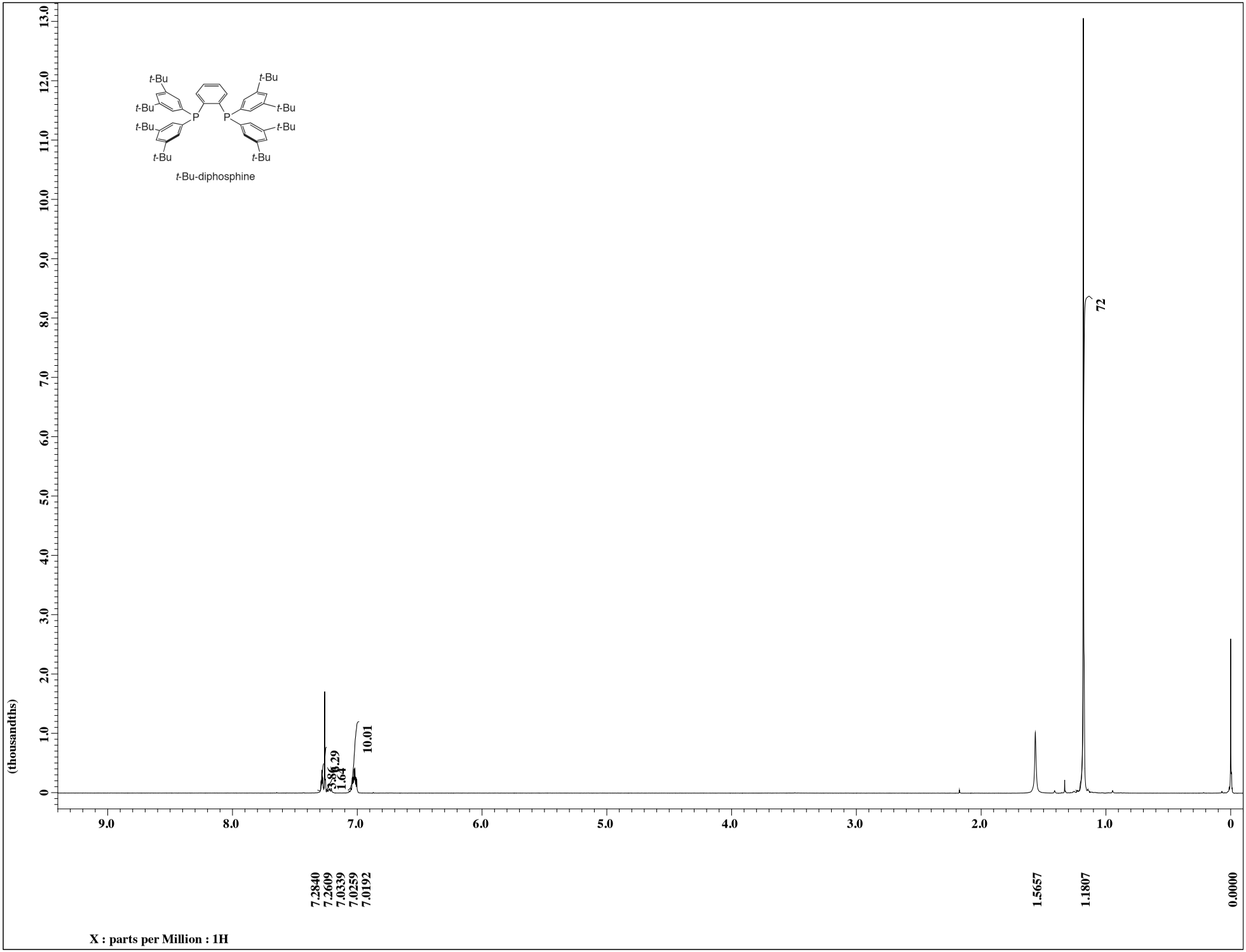


The reaction was carried out according to Procedure C on a 0.50 mmol scale by bromomethylcyclopropane (67.9 mg, 0.50 mmol), 2-(2-napthyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.254 g, 1.0 mmol) using *t*-BuLi (0.530 mL, 1.80 M in pentane, 0.95 mmol), $MgBr_2$ (1.00 mL, 0.100 M in THF, 0.10 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%). Conditions: 40 °C, 3 h. The title compound (90.7 mg, 99% yield, > 93% pure on GC analysis, including 6% of *trans* and *cis* isomers of 2-(2-butenyl)naphthalene) was obtained as a colorless oil after silica gel column chromatography (100% pentane). Major compound; R_f = 0.45 (hexane); IR (neat) 3054, 3019, 2977, 2925, 2853, 1638, 1601, 1508, 1438, 996, 911, 853, 815, 745.; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44–2.50 (m, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 4.97–5.00 (m, 1H), 5.06 (ddt, *J* = 1.4 Hz, *J* = 1.8 Hz, *J* = 17.9 Hz, 1H), 5.90 (ddt, *J* = 6.4 Hz , *J* = 10.5 Hz , *J* = 17.4 Hz, 1H) 7.34 (dd, *J* = 1.8 Hz, *J* = 8.7 Hz, 1H), 7.43 (m, 2H), 7.63 (brs, 1H), 7.76–7.81 (m, 3H).; ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 35.4, 35.5, 115.0, 125.1, 125.9, 126.4, 127.3, 127.4, 127.6, 127.8, 132.0, 133.6, 138.0, 139.4.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{14}H_{14}$ 182.1096.; found 182.1099.

Synthesis of 3-cycloheptylpyridine (S15)



The reaction was carried out according to Procedure B on a 0.50 mmol scale by bromocycloheptane (88.7 mg, 0.50 mmol), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (0.205 g, 1.0 mmol) using EtMgBr (0.90 mL, 1.05 M in THF, 0.95 mmol) and iron complex **2** (0.300 mL, 50.0 mM in THF, 15.0 μmol, 3.0 mol%). Conditions: 40 °C, 3 h. The title compound (64.3 mg, 73% yield, > 99% pure on GC analysis) was obtained as a colorless oil after silica gel column chromatography (hexane:AcOEt = 10:1). R_f = 0.30 (hexane:AcOEt = 2:1); IR (neat) 2924, 2854, 1574, 1458, 1422, 1024, 798, 715.; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.49–1.94 (m, 12H), 2.64–2.72 (m, 1H), 7.19 (dd, *J* = 4.9, *J* = 7.6 Hz, 1H), 7.49 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 7.9 Hz, 1H), 8.41 (dd, *J* = 1.6 Hz, *J* = 4.9 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H).; ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 27.1, 27.8, 36.5, 44.4, 123.3, 133.9, 144.7, 147.1, 148.7.; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{12}H_{17}N$ 175.1361.; found 175.1362.


t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
P
P
t-Bu-diphosphine
(thousandths)
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
72
10.01
1.64
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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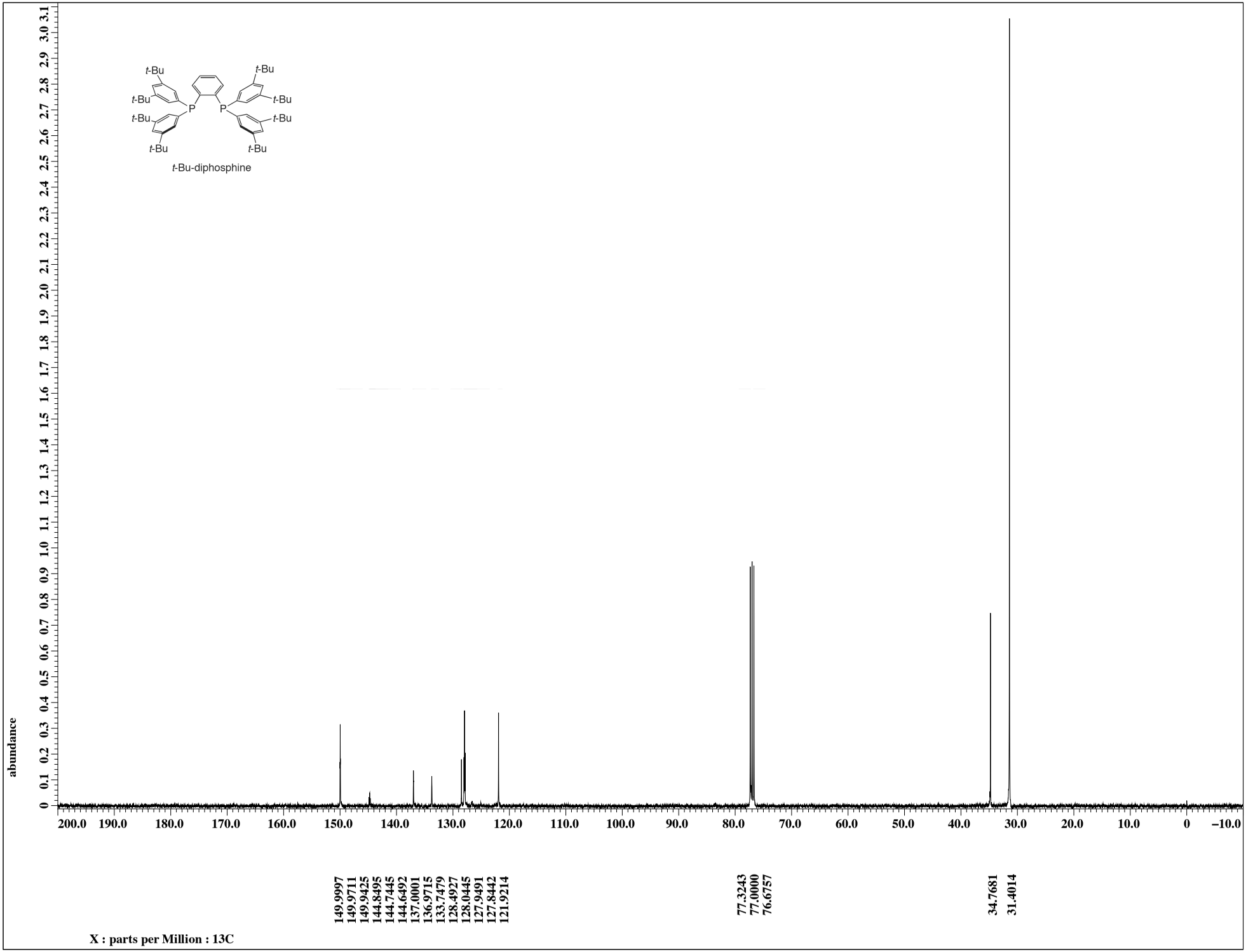
7.0339
7.0259
7.0192
1.5657
1.1807
0.0000
X : parts per Million : 1H


t-Bu
t-Bu
t-Bu
t-Bu
P
P
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu-diphosphine
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
149.9997
149.9711
149.9425
144.8495
144.7445
144.6492
137.0001
136.9715
133.7479
128.4927
128.0445
127.9491
127.8442
121.9214
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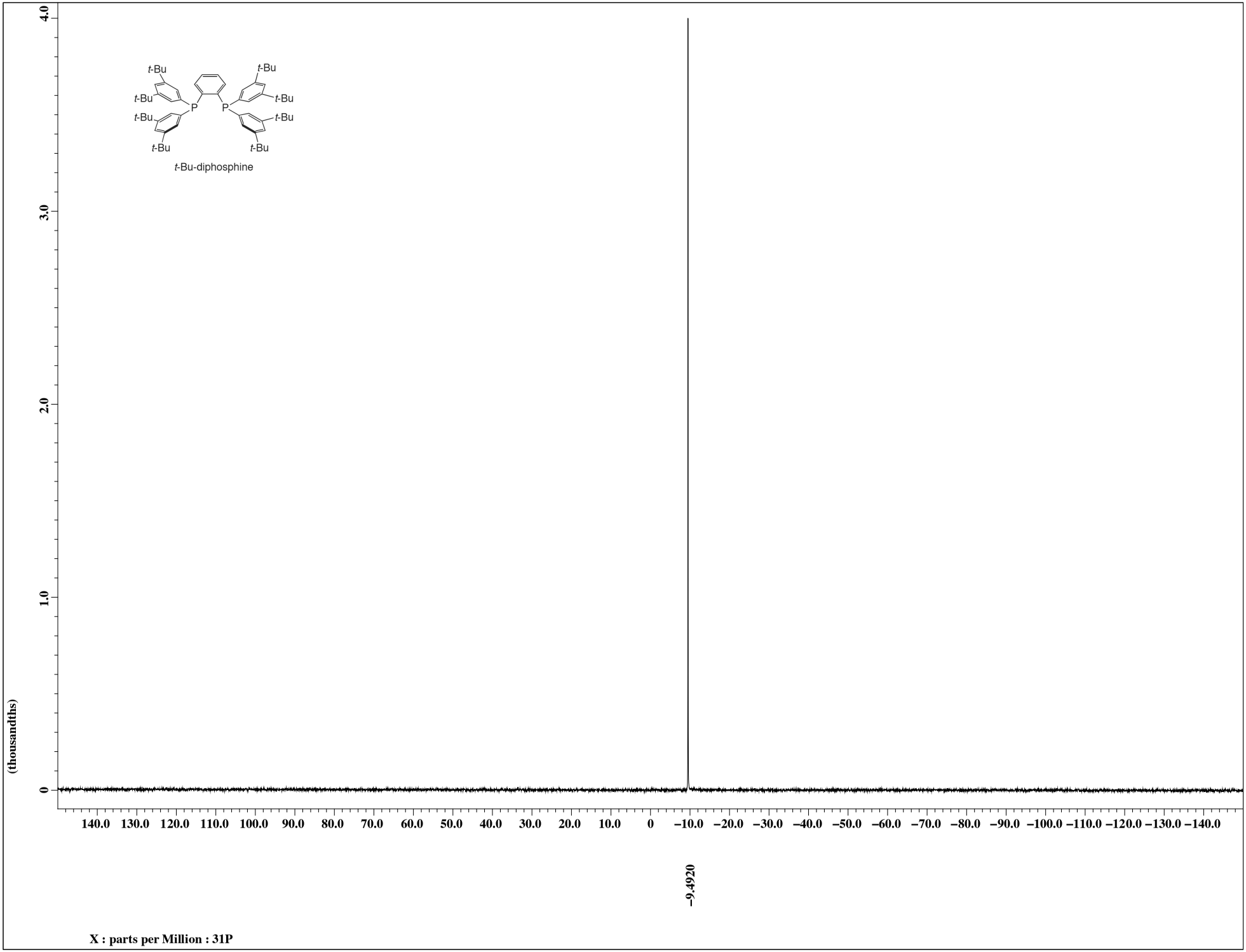
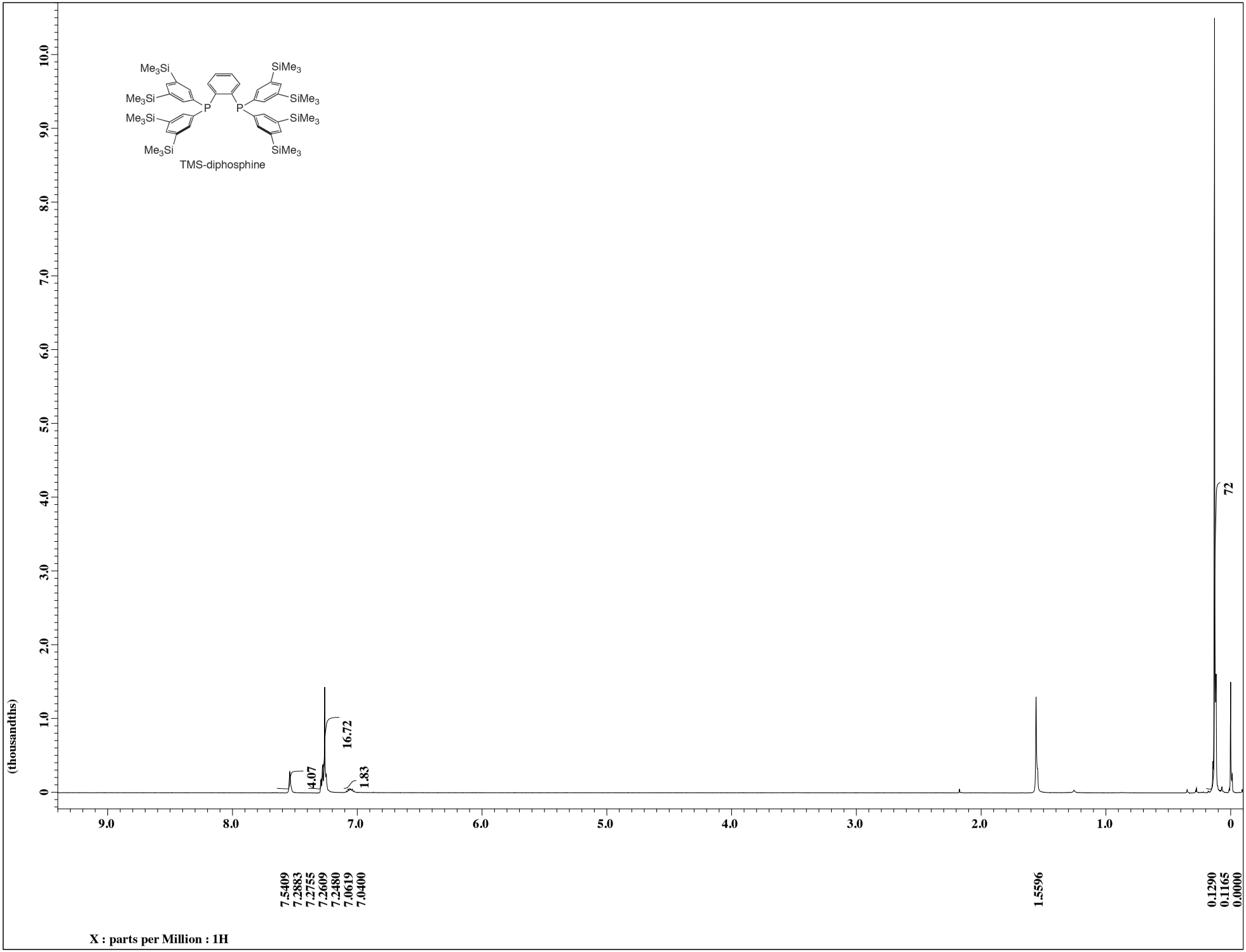
77.0000
76.6757
34.7681
31.4014
X : parts per Million : 13C


t-Bu
t-Bu
t-Bu
t-Bu
P
P
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu-diphosphine
(thousandths)
4.0
3.0
2.0
1.0
0
140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 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
−9.4920
X : parts per Million : 31P


Me3Si
SiMe3
Me3Si
SiMe3
Me3Si
SiMe3
Me3Si
SiMe3
P
P
TMS-diphosphine
(thousandths)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.07
16.72
1.83
72
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5409
7.2883
7.2755
7.2609
7.2480
7.0619
7.0400
1.5596
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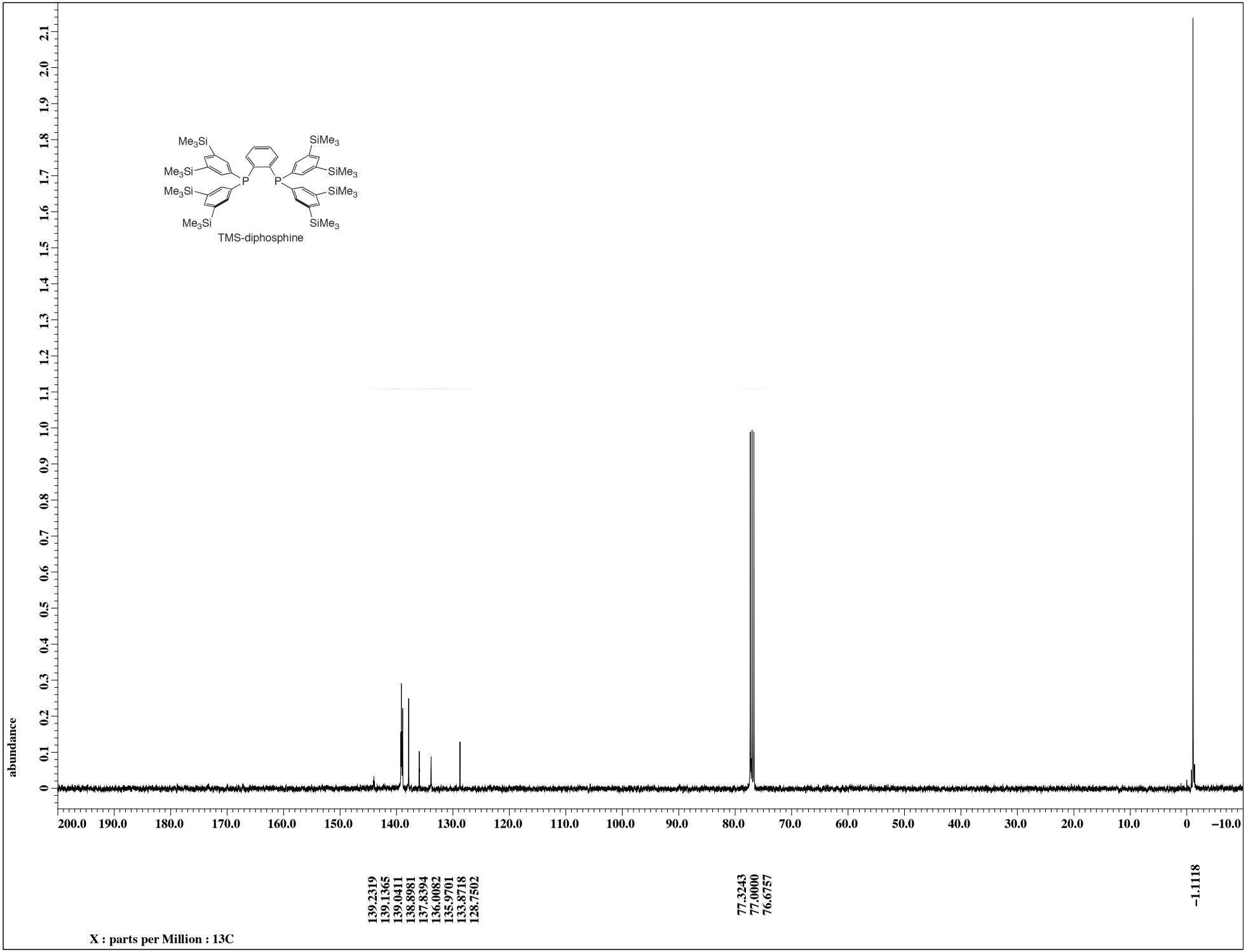
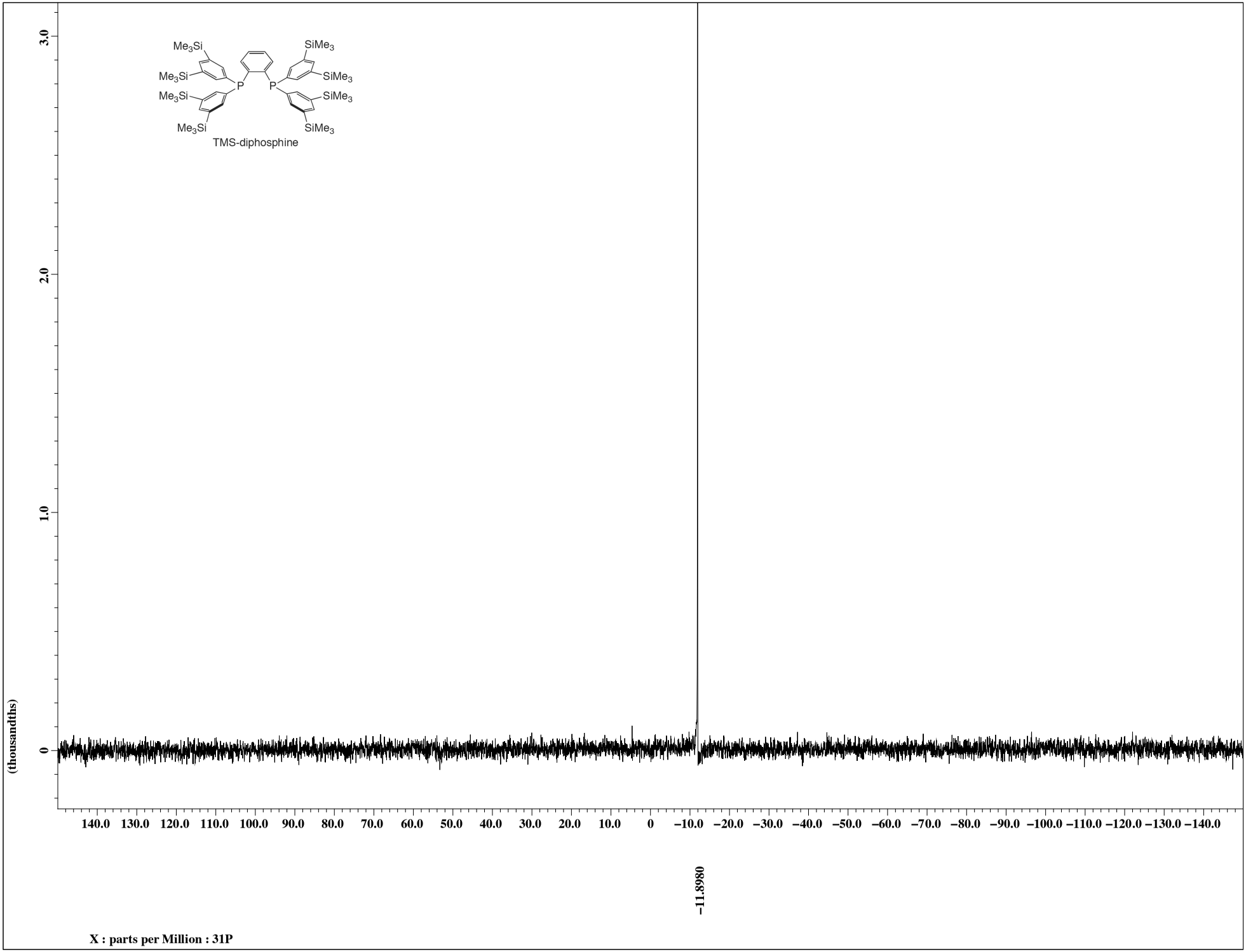
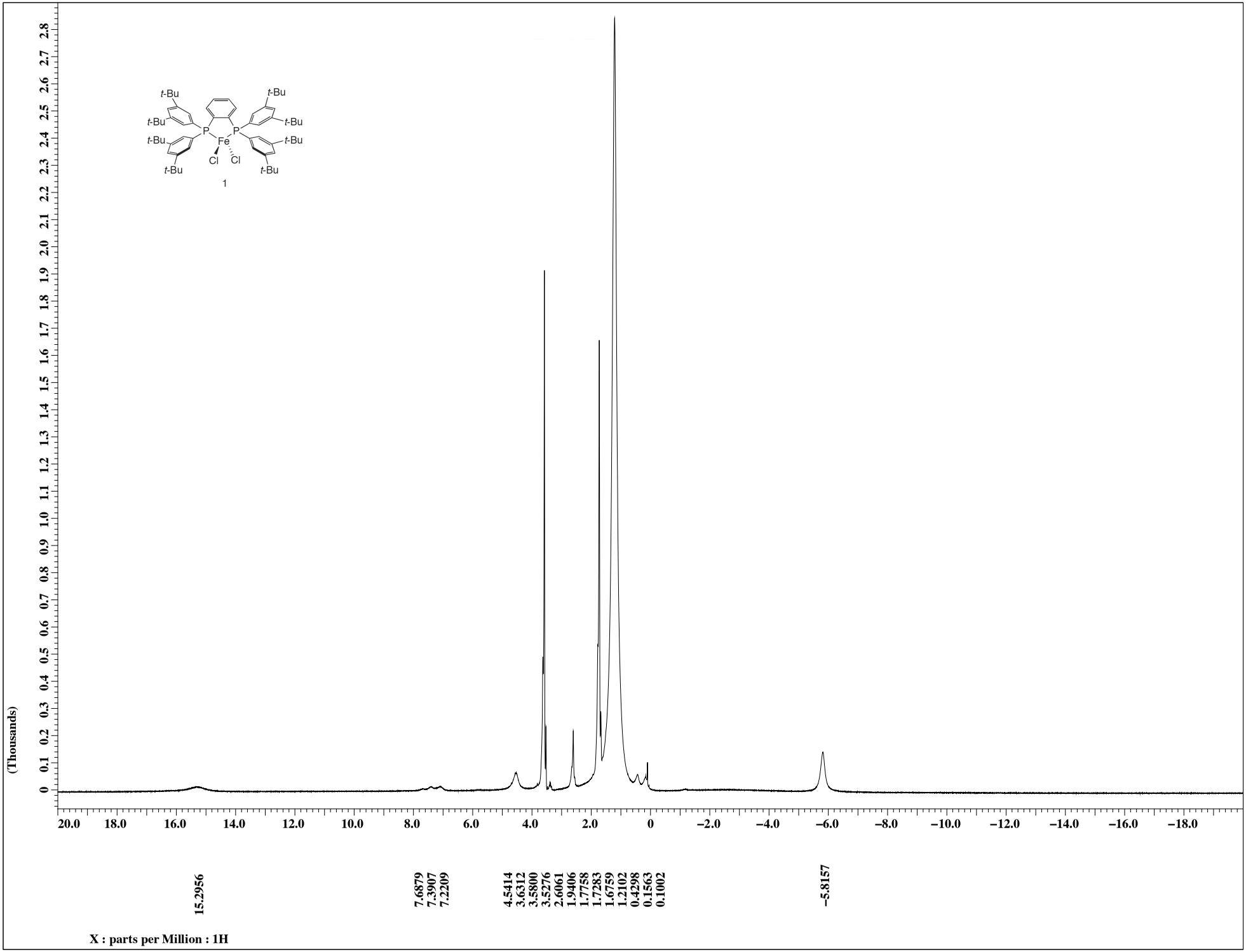
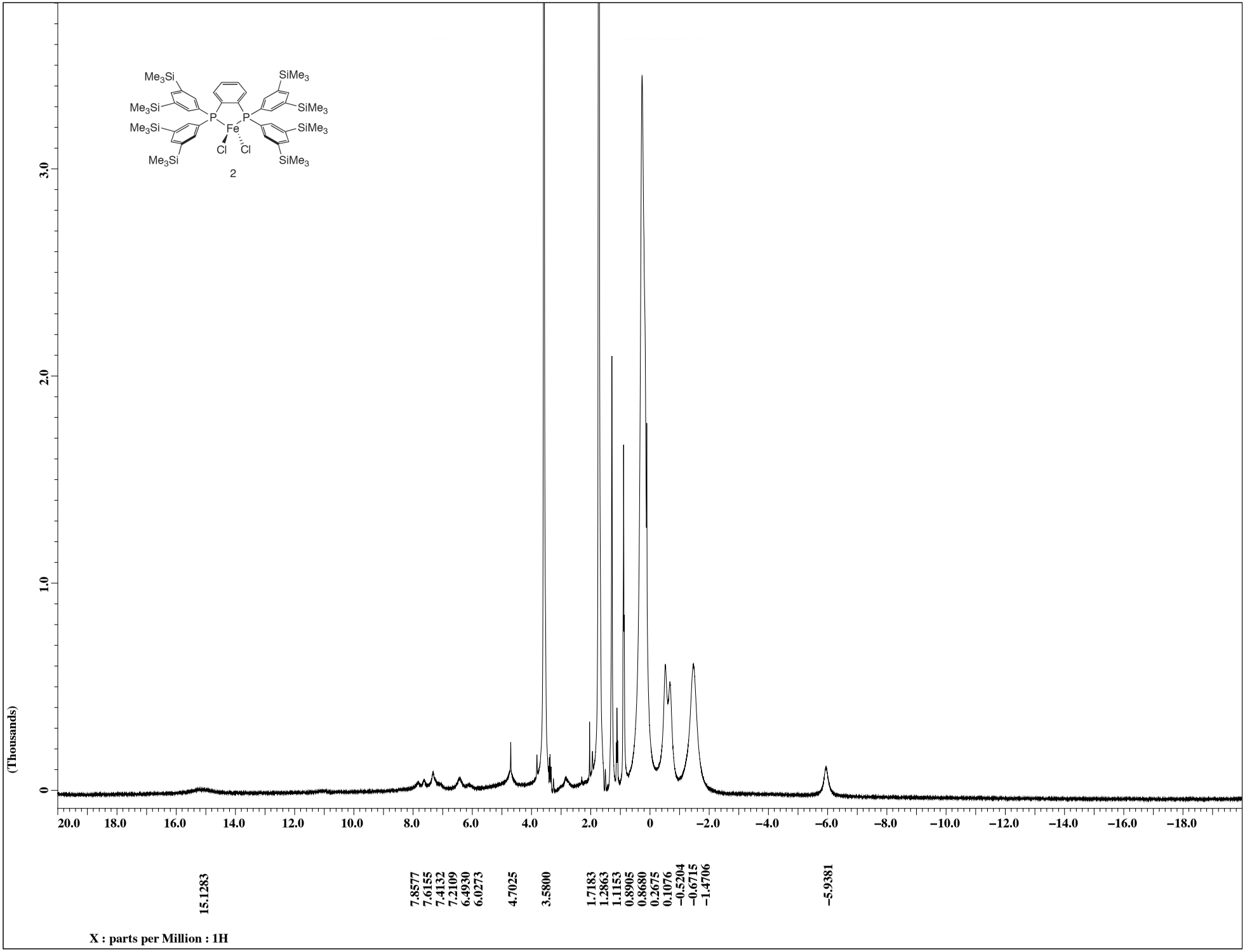
0.1165
0.0000
X : parts per Million : 1H

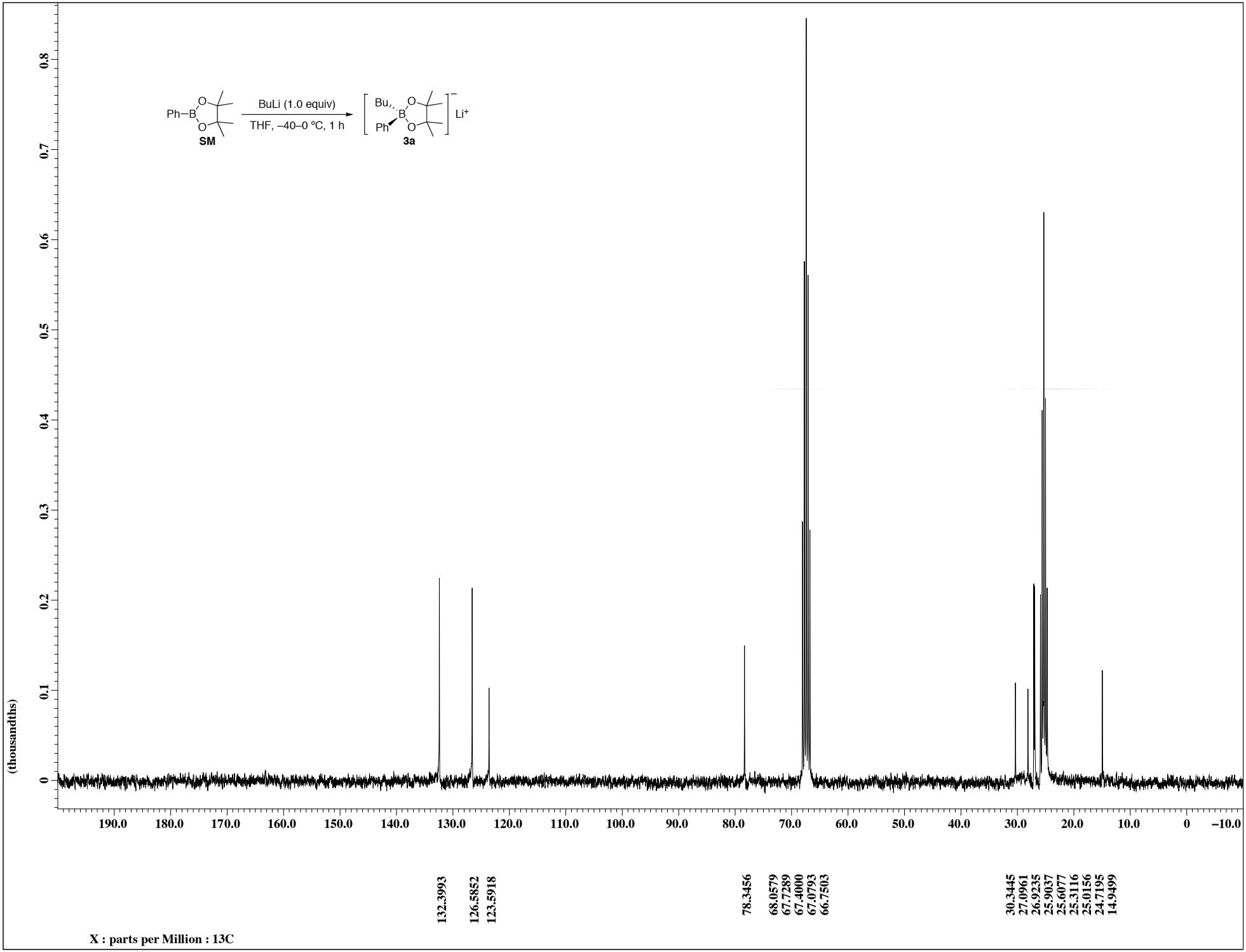

Me3Si
Me3Si
Me3Si
Me3Si
P
P
SiMe3
SiMe3
SiMe3
SiMe3
TMS-diphosphine
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
139.2319
139.1365
139.0411
138.8981
137.8394
136.0082
135.9701
133.8718
128.7502
77.3243
77.0000
76.6757
−1.1118
X : parts per Million : 13C

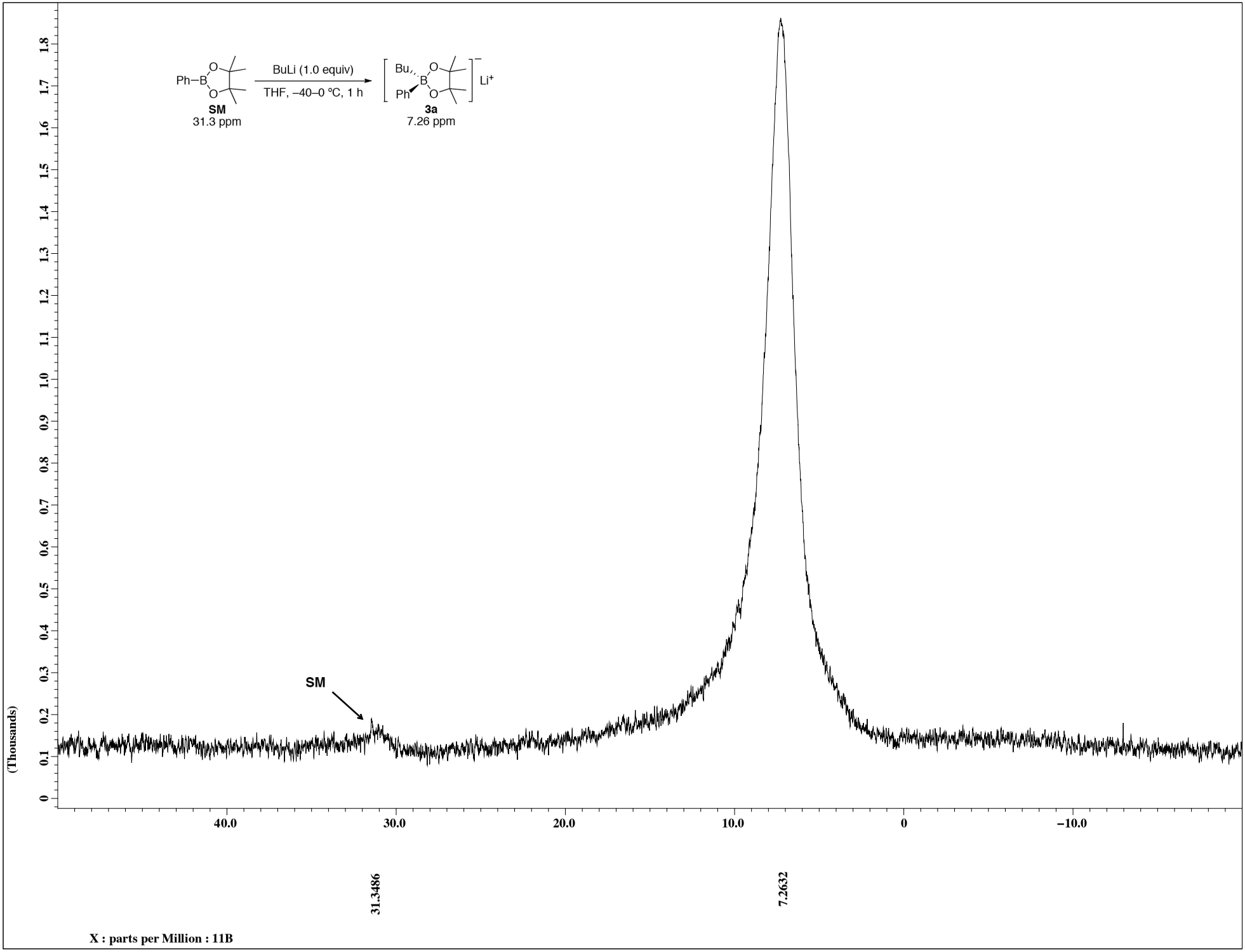

Me3Si
SiMe3
Me3Si
SiMe3
Me3Si
SiMe3
Me3Si
SiMe3
P
P
TMS-diphosphine
3.0
2.0
1.0
0
(thousandths)
140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0 −110.0 −120.0 −130.0 −140.0
−11.8980
X : parts per Million : 31P


t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
P
P
Fe
Cl
Cl
1
(Thousands)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8
20.0 18.0 16.0 14.0 12.0 10.0 8.0 6.0 4.0 2.0 0 −2.0 −4.0 −6.0 −8.0 −10.0 −12.0 −14.0 −16.0 −18.0
15.2956
7.6879
7.3907
7.2209
4.5414
3.6312
3.5800
3.5276
2.6061
1.9406
1.7758
1.7283
1.6759
1.2102
0.4298
0.1563
0.1002
−5.8157
X : parts per Million : 1H

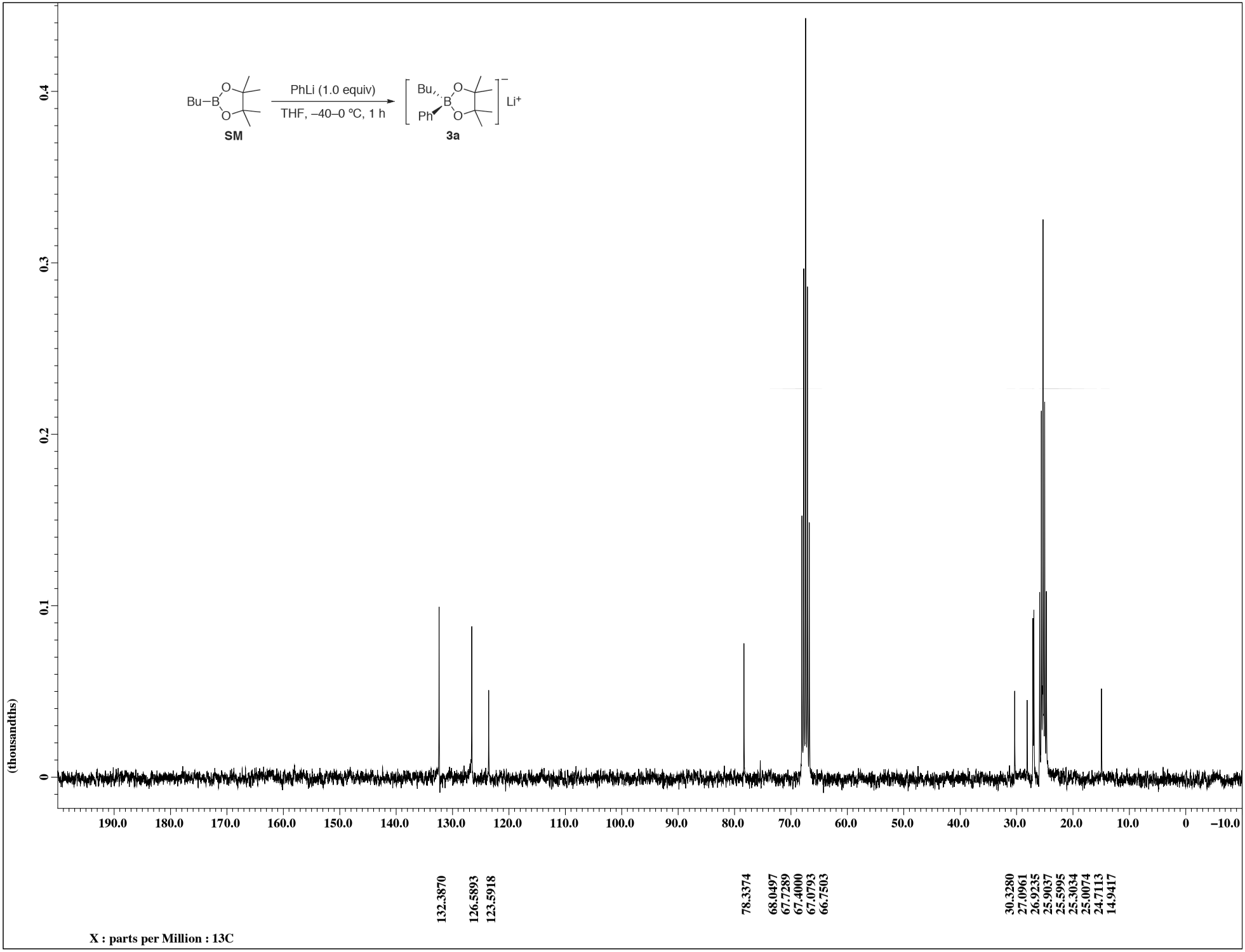

Me3Si
SiMe3
Me3Si
SiMe3
Me3Si
SiMe3
Me3Si
SiMe3
P
P
Fe
Cl
Cl
2
(Thousands)
3.0
2.0
1.0
0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
−2.0
−4.0
−6.0
−8.0
−10.0
−12.0
−14.0
−16.0
−18.0
15.1283
7.8577
7.6155
7.4132
7.2109
6.4930
6.0273
4.7025
3.5800
1.7183
1.2863
1.1153
0.8905
0.8680
0.2675
0.1076
−0.5204
−0.6715
−1.4706
−5.9381
X : parts per Million : 1H

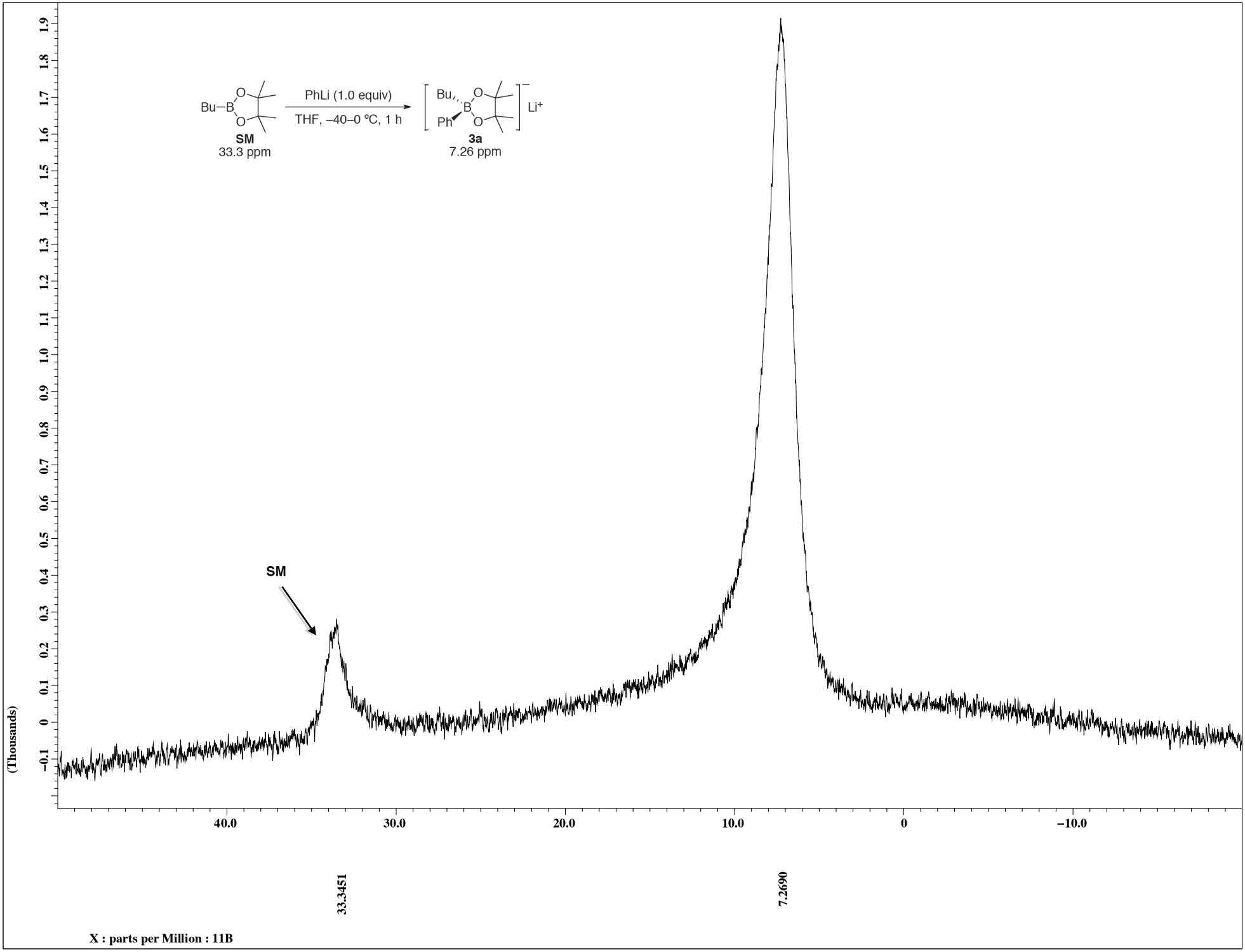
Ph–B
SM
BuLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
3a
Li+
(Thousands)
SM
7.4606
7.4558
7.4349
7.0066
6.9818
6.9571
6.8229
3.5800
1.7277
1.1633
1.1386
1.1205
0.9606
0.9234
0.7550
0.7312
0.7074
0.3609
0.3324
0.3076
2.08
1.9
0.8
17.32
3
1.93
X : parts per Million : 1H


Ph–B
O
O
SM
BuLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
B
O
O
Li+
3a
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
–10.0
132.3993
126.5852
123.5918
78.3456
68.0579
67.7289
67.4000
67.0793
66.7503
30.3445
27.0961
26.9235
25.9037
25.6077
25.3116
25.0156
24.7195
14.9499
X : parts per Million : 13C

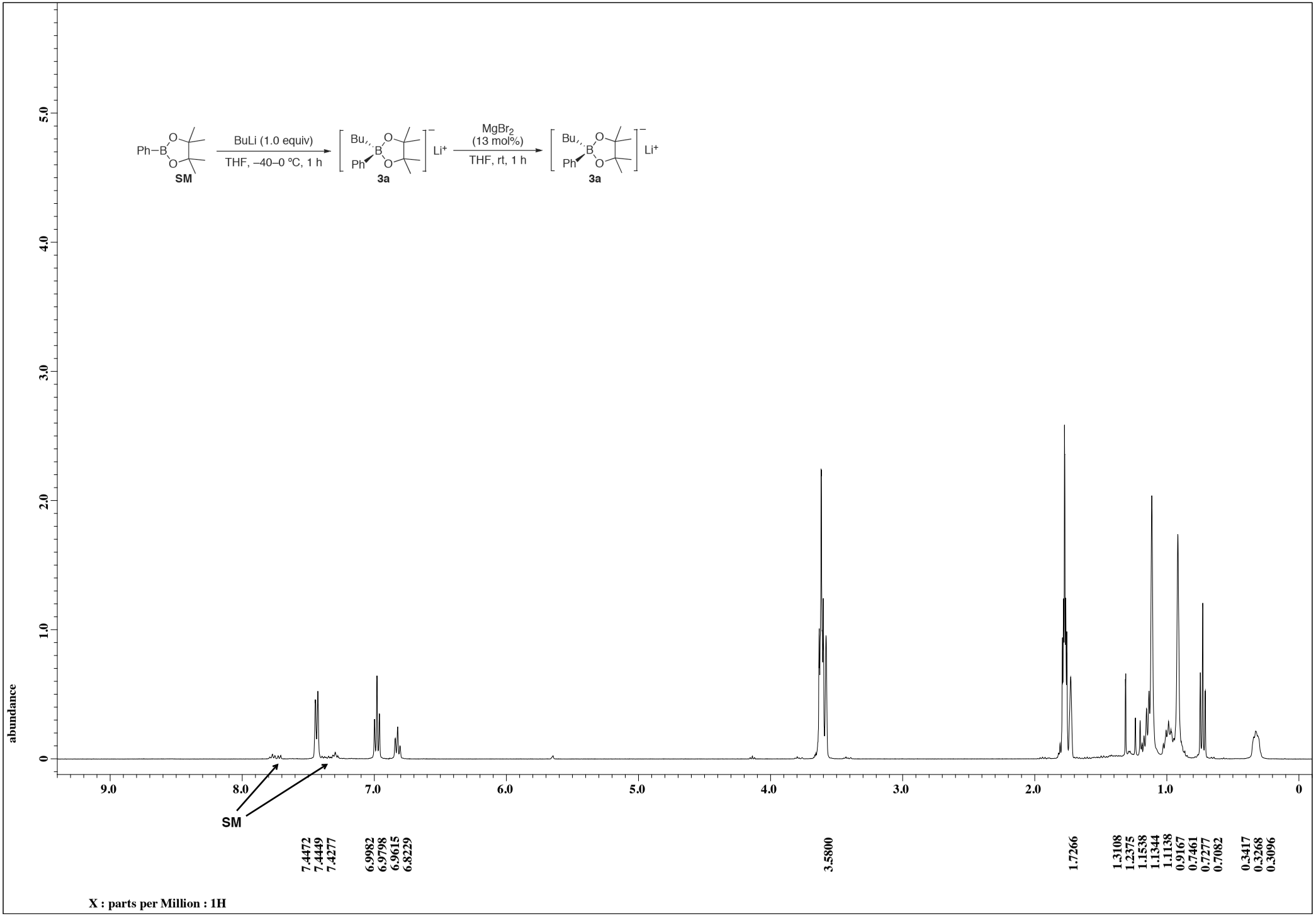

Ph–B
O
O
SM
31.3 ppm
BuLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
B
O
O
Li+
3a
7.26 ppm
SM
(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
40.0
30.0
20.0
10.0
0
−10.0
31.3486
7.2632
X : parts per Million : 11B

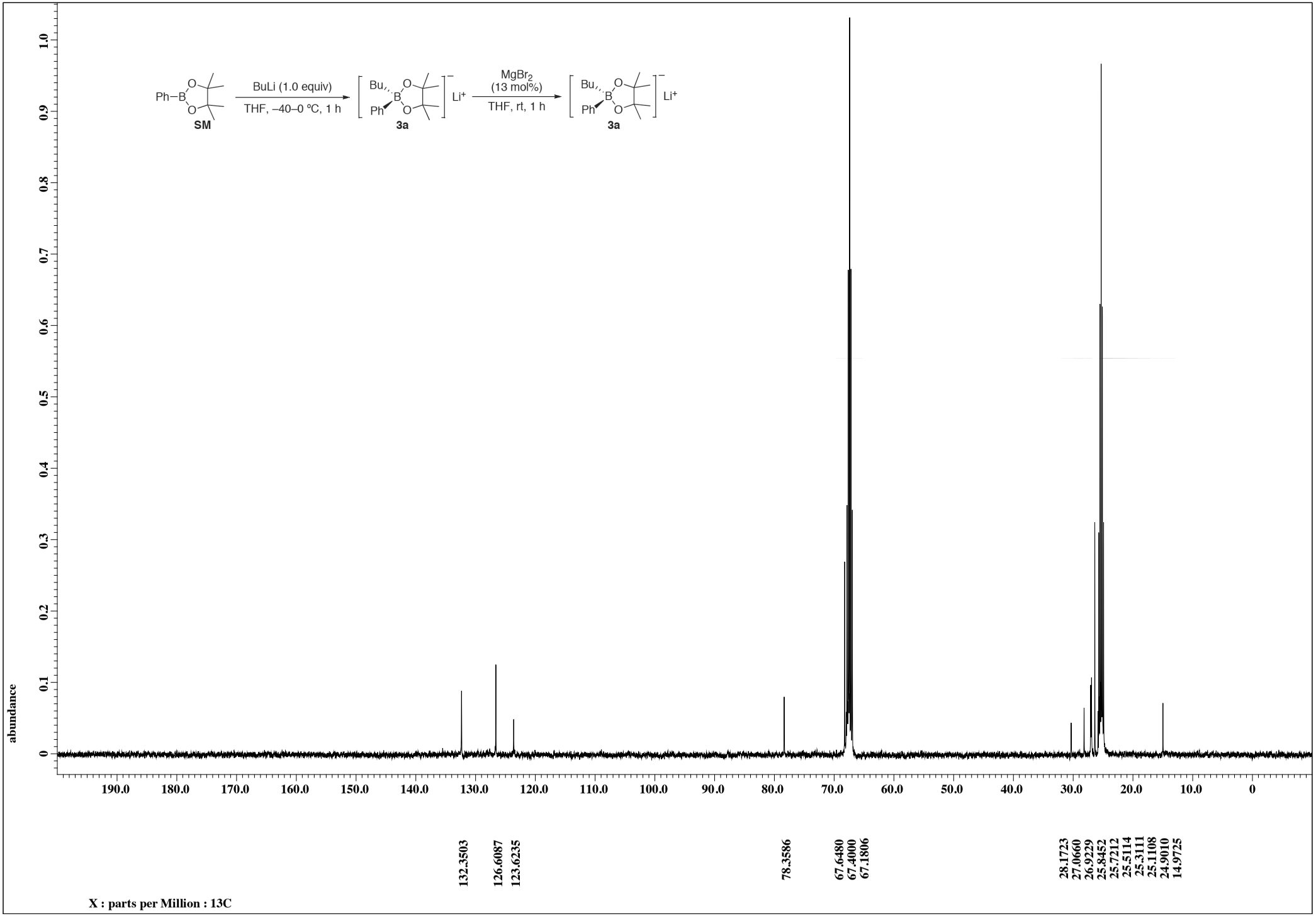
Bu–B
O
O
SM
PhLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
B
Ph
O
O
Li+
3a
(thousandths)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.4568
7.4336
7.4287
7.0004
6.9748
6.9467
6.8162
3.5763
1.7240
1.2139
1.1883
1.1602
1.1151
1.0125
0.9845
0.9528
0.9174
0.7551
0.7282
0.7014
0.3560
0.3231
0.2962
2.44
2.12
0.93
21.95
3
2.26
X : parts per Million : 1H

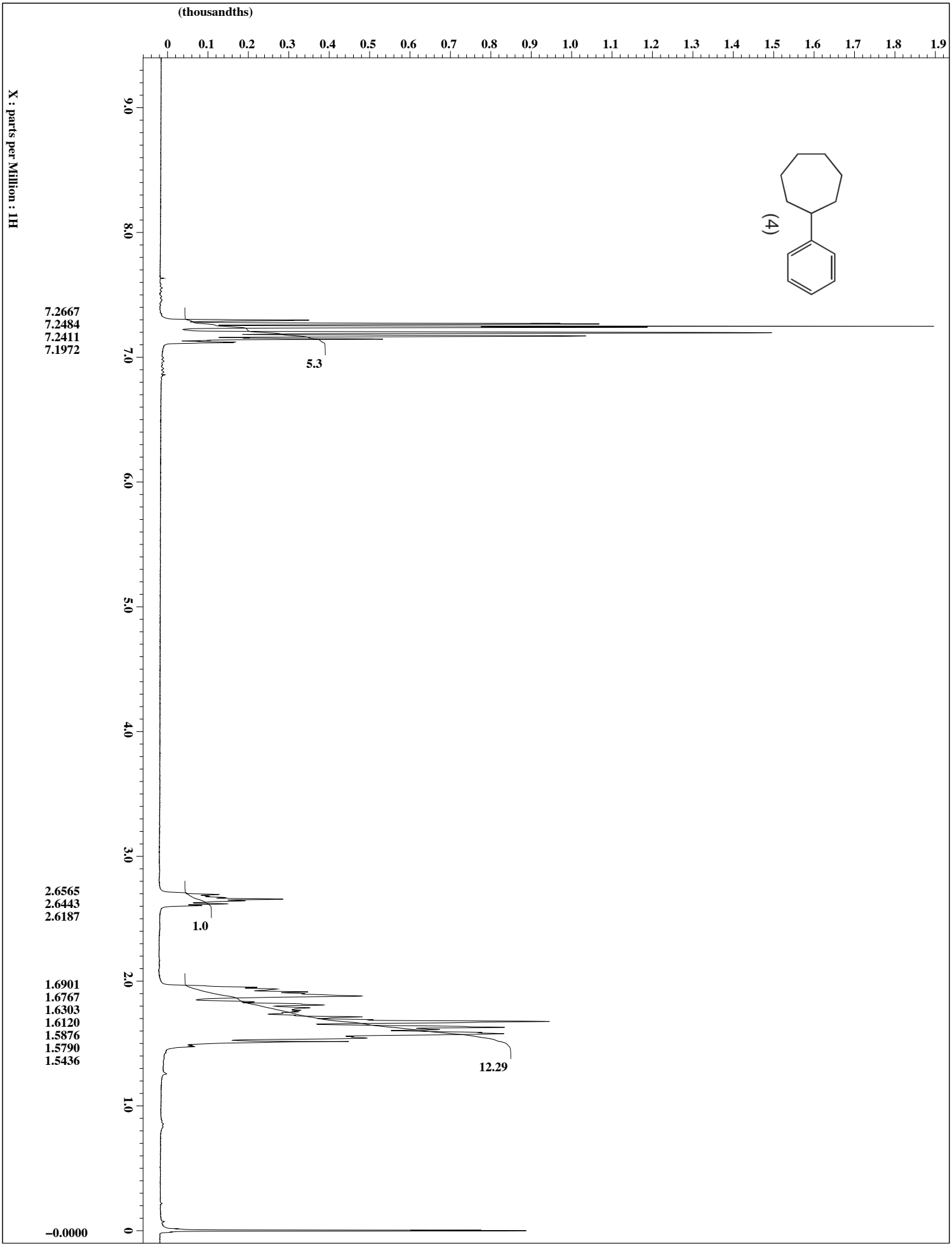

Bu–B
O
O
SM
PhLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
B
O
O
Li+
3a
(thousandths)
0
0.1
0.2
0.3
0.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
–10.0
132.3870
126.5893
123.5918
78.3374
68.0497
67.7289
67.4000
67.0793
66.7503
30.3280
27.0961
26.9235
25.9037
25.5995
25.3034
25.0074
24.7113
14.9417
X : parts per Million : 13C

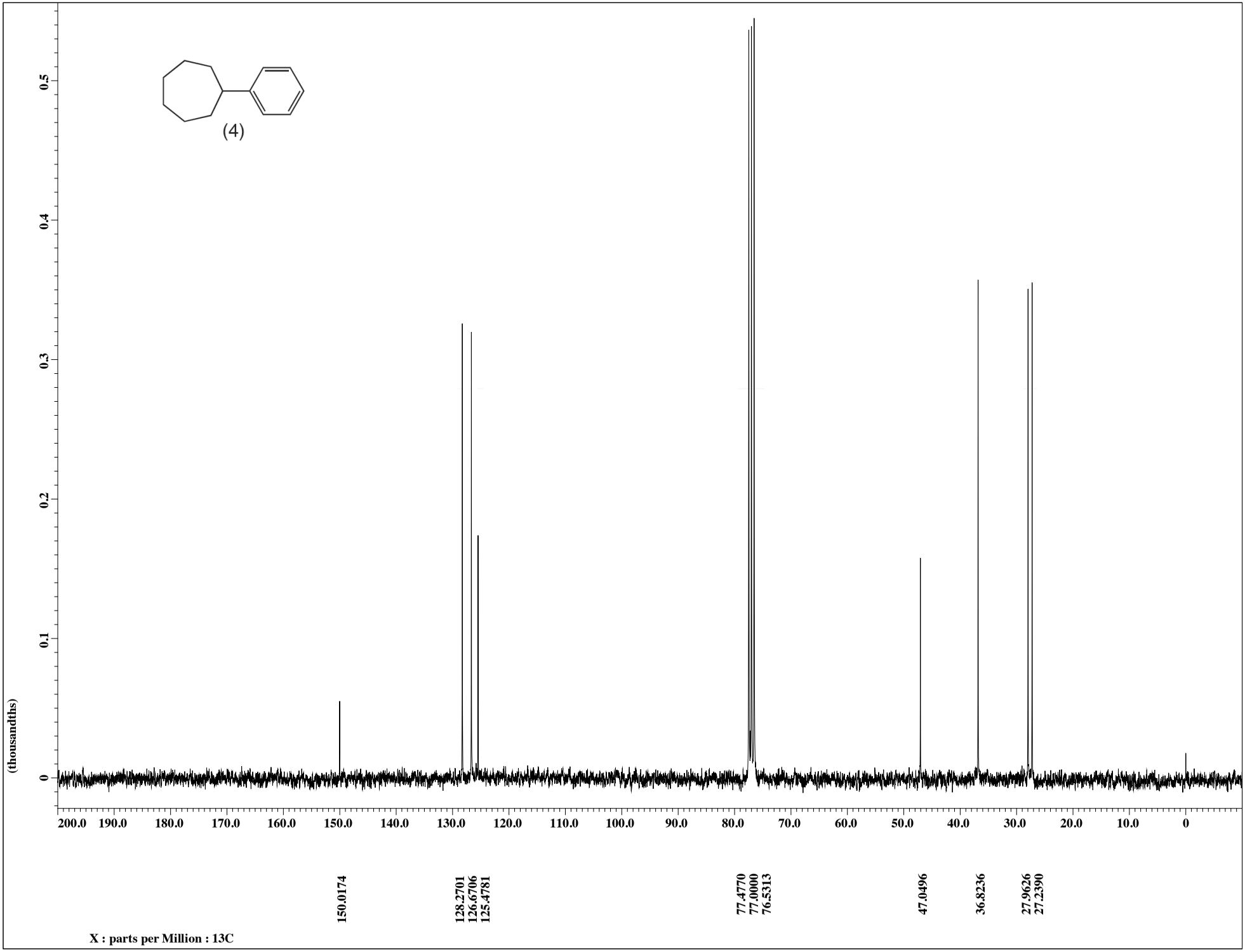

Bu–B
O
O
SM
33.3 ppm
PhLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
B
O
O
Li+
3a
7.26 ppm
SM
(Thousands)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
40.0
30.0
20.0
10.0
0
−10.0
33.3451
7.2690
X : parts per Million : 11B

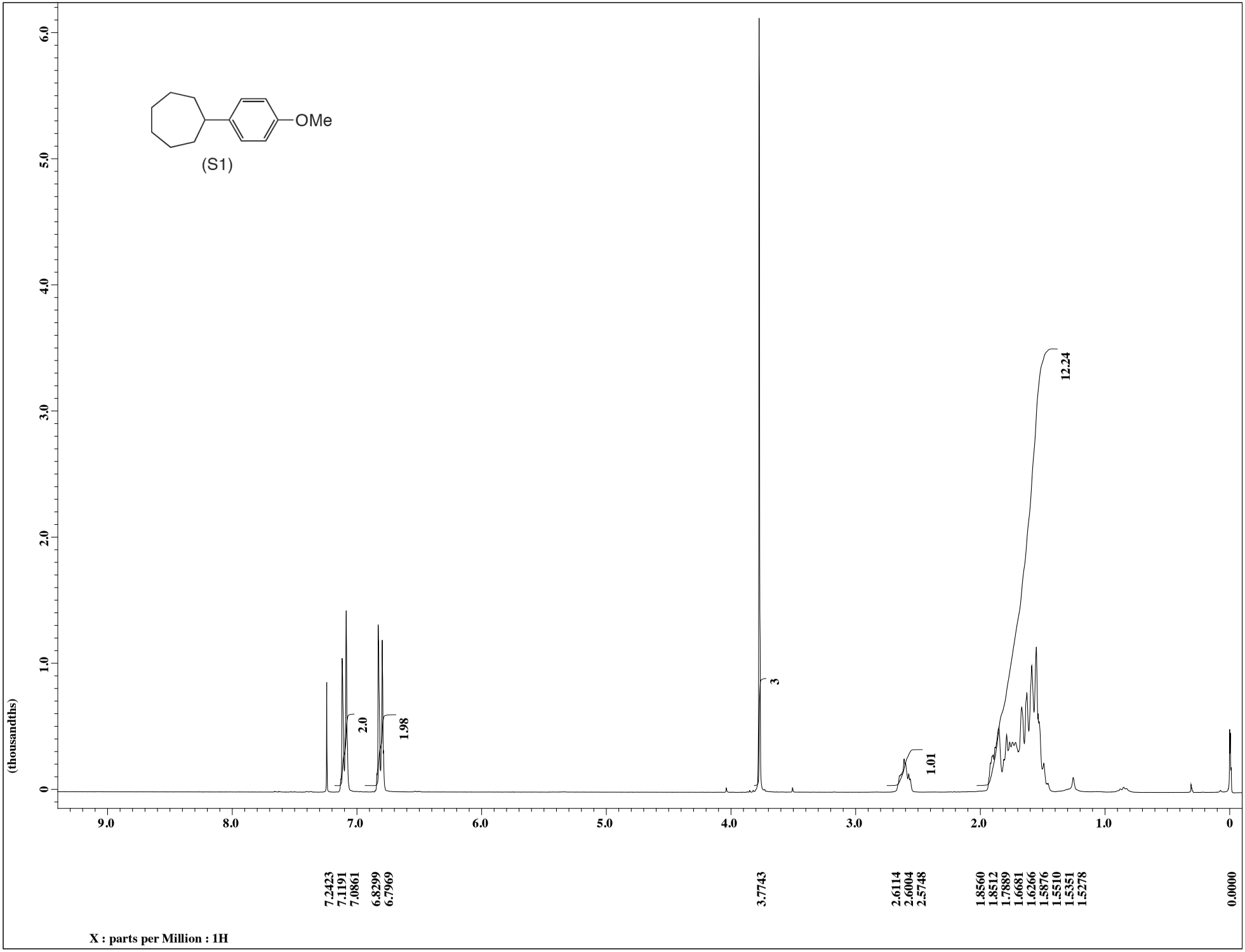
Ph–B
O
O
SM
BuLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
B
O
O
Li+
3a
MgBr2
(13 mol%)
THF, rt, 1 h
Bu
Ph
B
O
O
Li+
3a

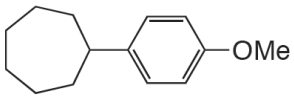

abundance
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
SM
7.4472
7.4449
7.4277
6.9982
6.9798
6.9615
6.8229
3.5800
1.7266
1.3108
1.2375
1.1538
1.1344
1.1138
0.9167
0.7461
0.7277
0.7082
0.3417
0.3268
0.3096
X : parts per Million : 1H


Ph–B
O
O
SM
BuLi (1.0 equiv)
THF, –40–0 °C, 1 h
Bu
Ph
B
O
O
Li+
3a
MgBr2
(13 mol%)
THF, rt, 1 h
Bu
Ph
B
O
O
Li+
3a
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
132.3503
126.6087
123.6235
78.3586
67.6480
67.4000
67.1806
28.1723
27.0660
26.9229
25.8452
25.7212
25.5114
25.3111
25.1108
24.9010
14.9725
X : parts per Million : 13C


(thousandths)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2667
7.2484
7.2411
7.1972
5.3
2.6565
2.6443
2.6187
1.0
1.6901
1.6767
1.6303
1.6120
1.5876
1.5790
1.5436
12.29
−0.0000
(4)


(4)
(thousandths)
0.5
0.4
0.3
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
150.0174
128.2701
126.6706
125.4781
77.4770
77.0000
76.5313
47.0496
36.8236
27.9626
27.2390
X : parts per Million : 13C


OMe
(S1)
(thousandths)
6.0
5.0
4.0
3.0
2.0
1.0
0
2.0
1.98
3
1.01
12.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2423
7.1191
7.0861
6.8299
6.7969
3.7743
2.6114
2.6004
2.5748
1.8560
1.8512
1.7889
1.6681
1.6266
1.5876
1.5510
1.5351
1.5278
0.0000
X : parts per Million : 1H



(S1)

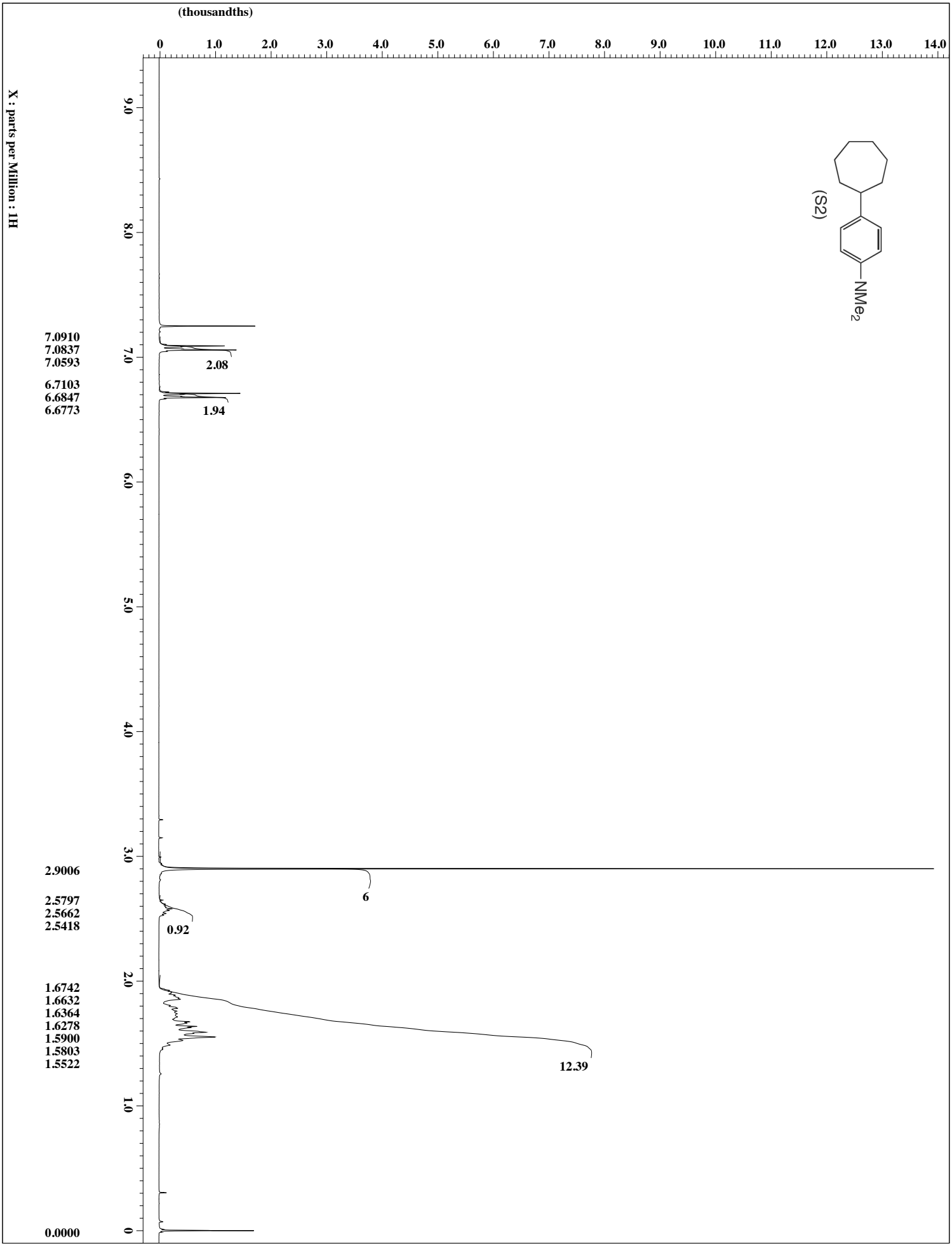
(thousandths)

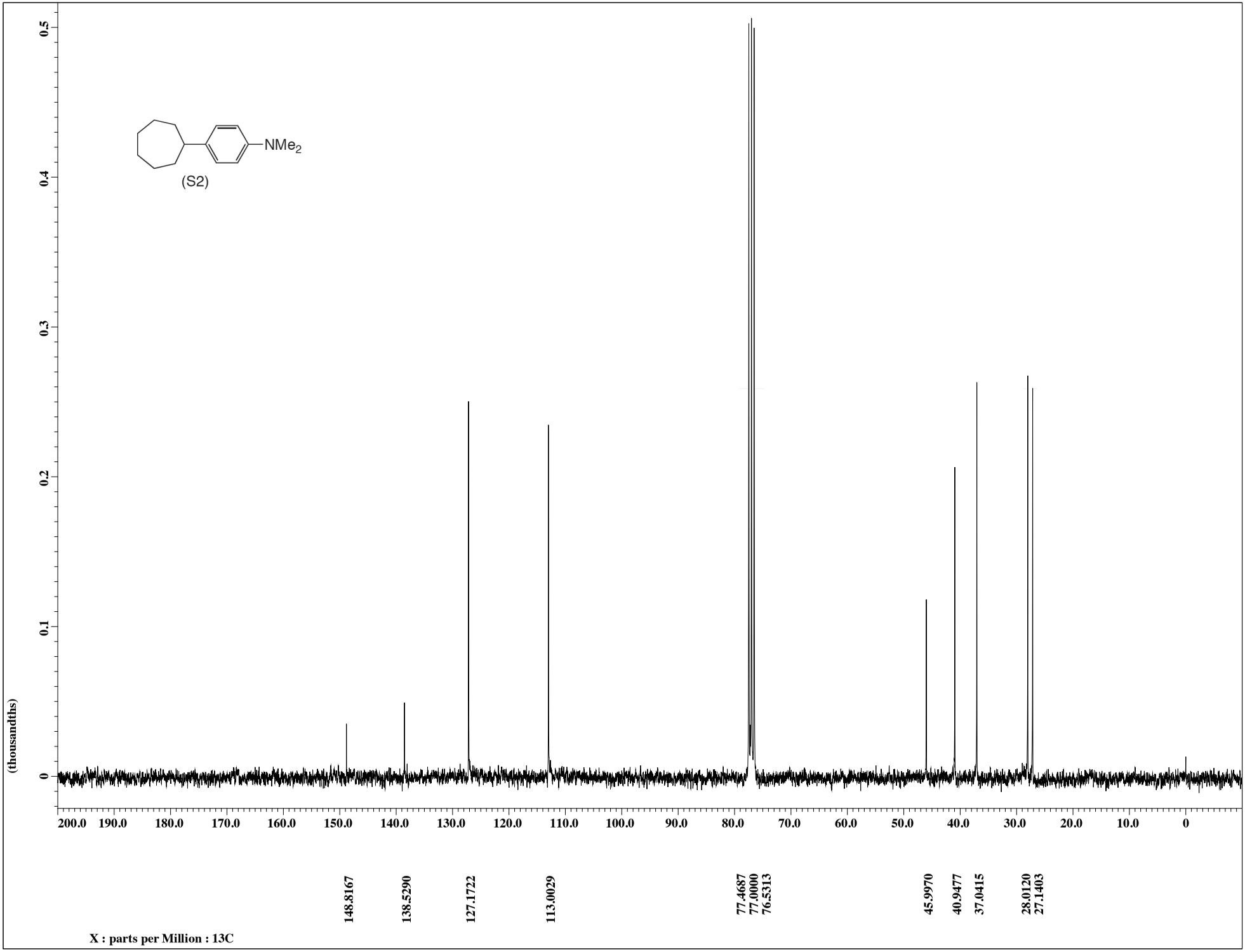
0.5
0.4
0.3
0.2
0.1
0

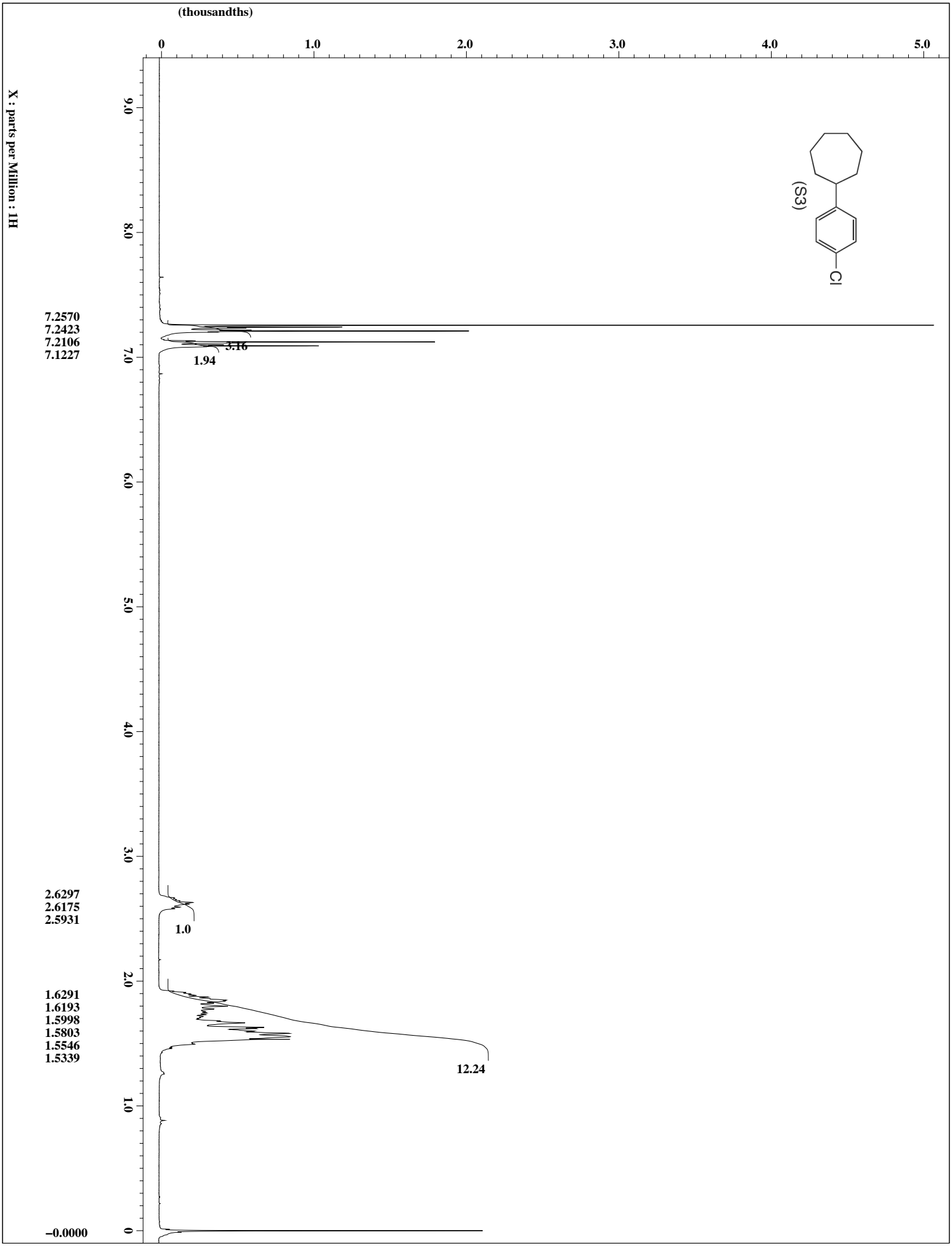
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

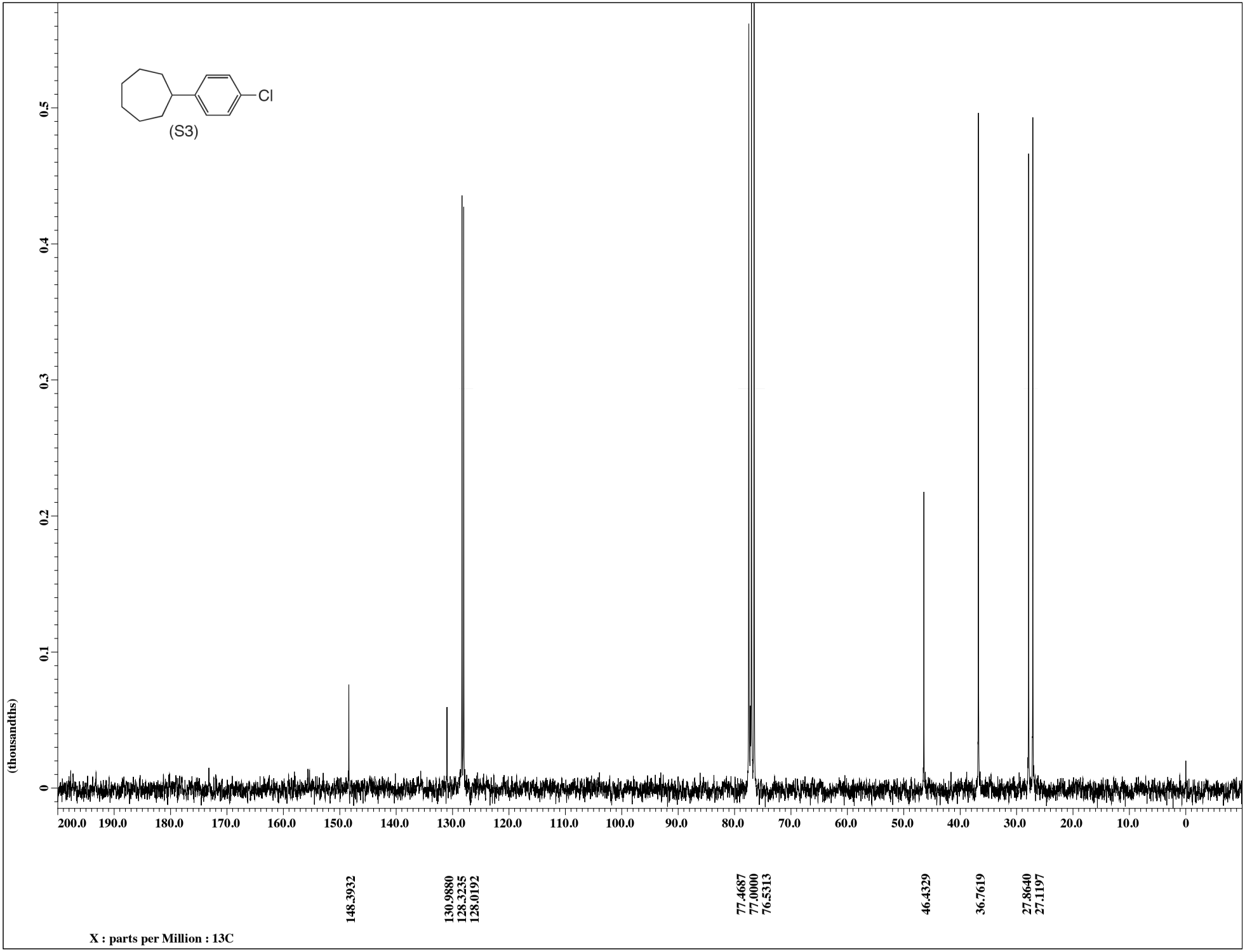
157.4186
142.2831
127.4559
113.6238
77.4687
77.0000
76.5230
55.2157
46.1779
37.0497
27.9462
27.1321

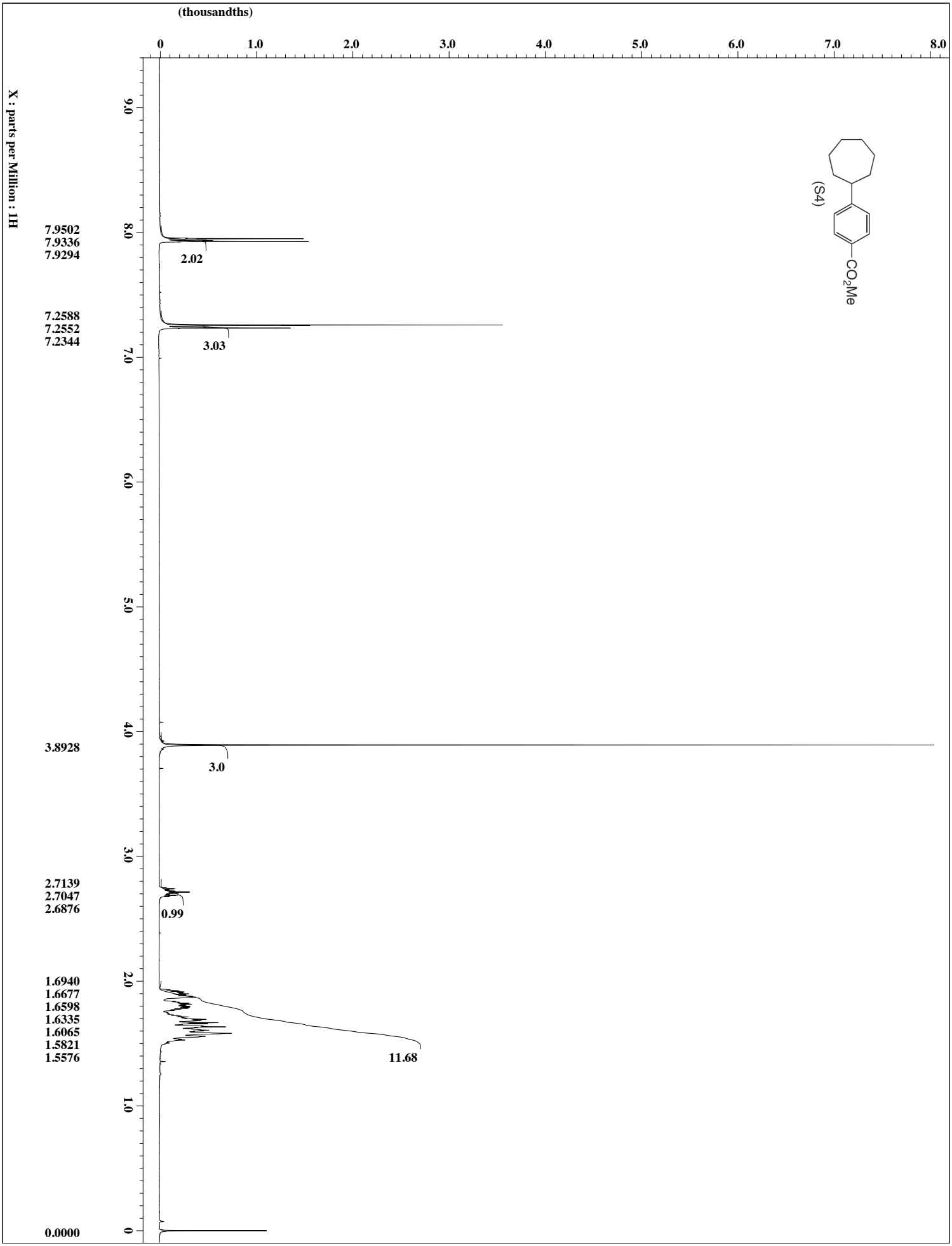
X : parts per Million : 13C

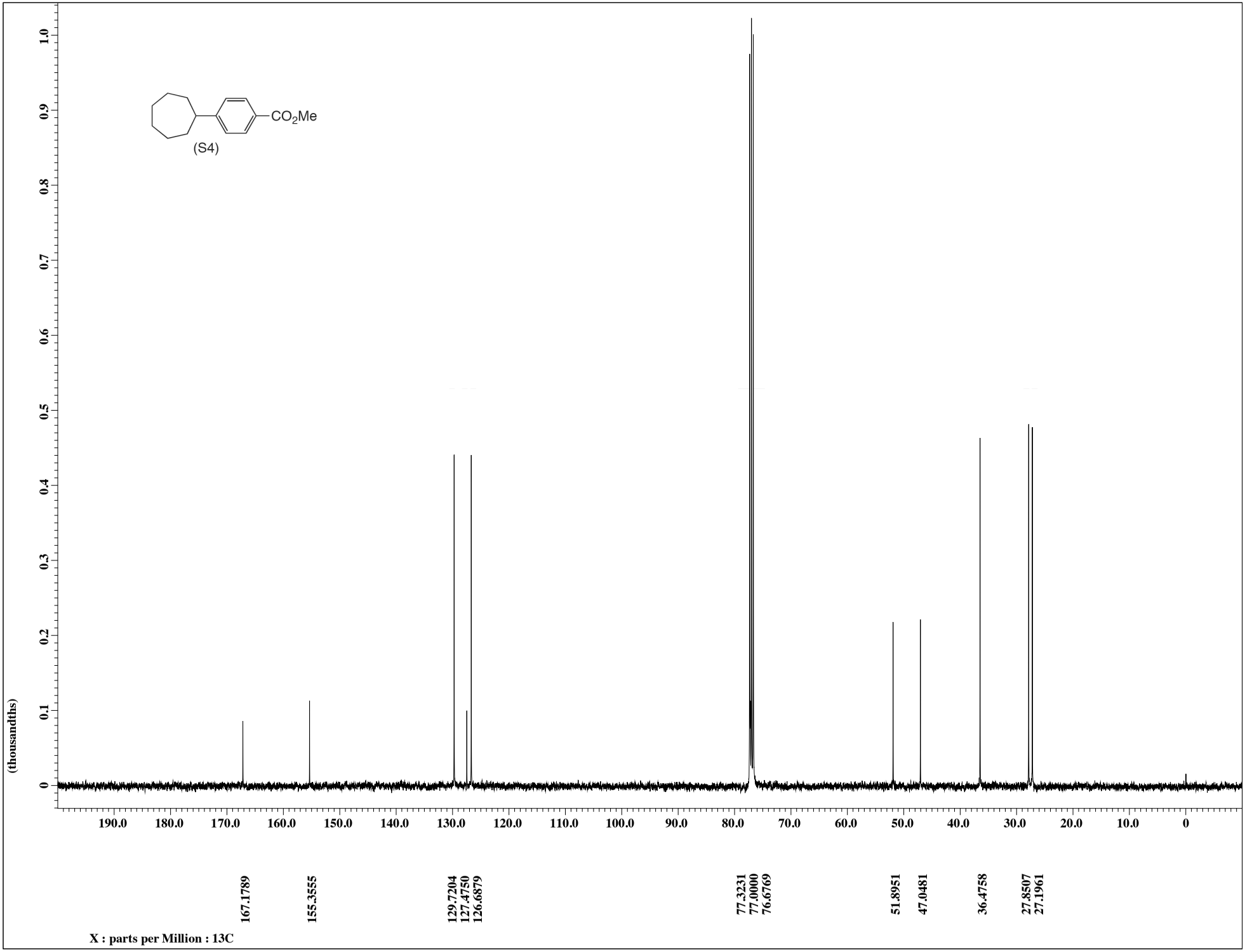

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.0910
7.0837
7.0593
6.7103
6.6847
6.6773
2.9006
2.5797
2.5662
2.5418
1.6742
1.6632
1.6364
1.6278
1.5900
1.5803
1.5522
0.0000
2.08
1.94
6
0.92
12.39
(S2)
NMe2

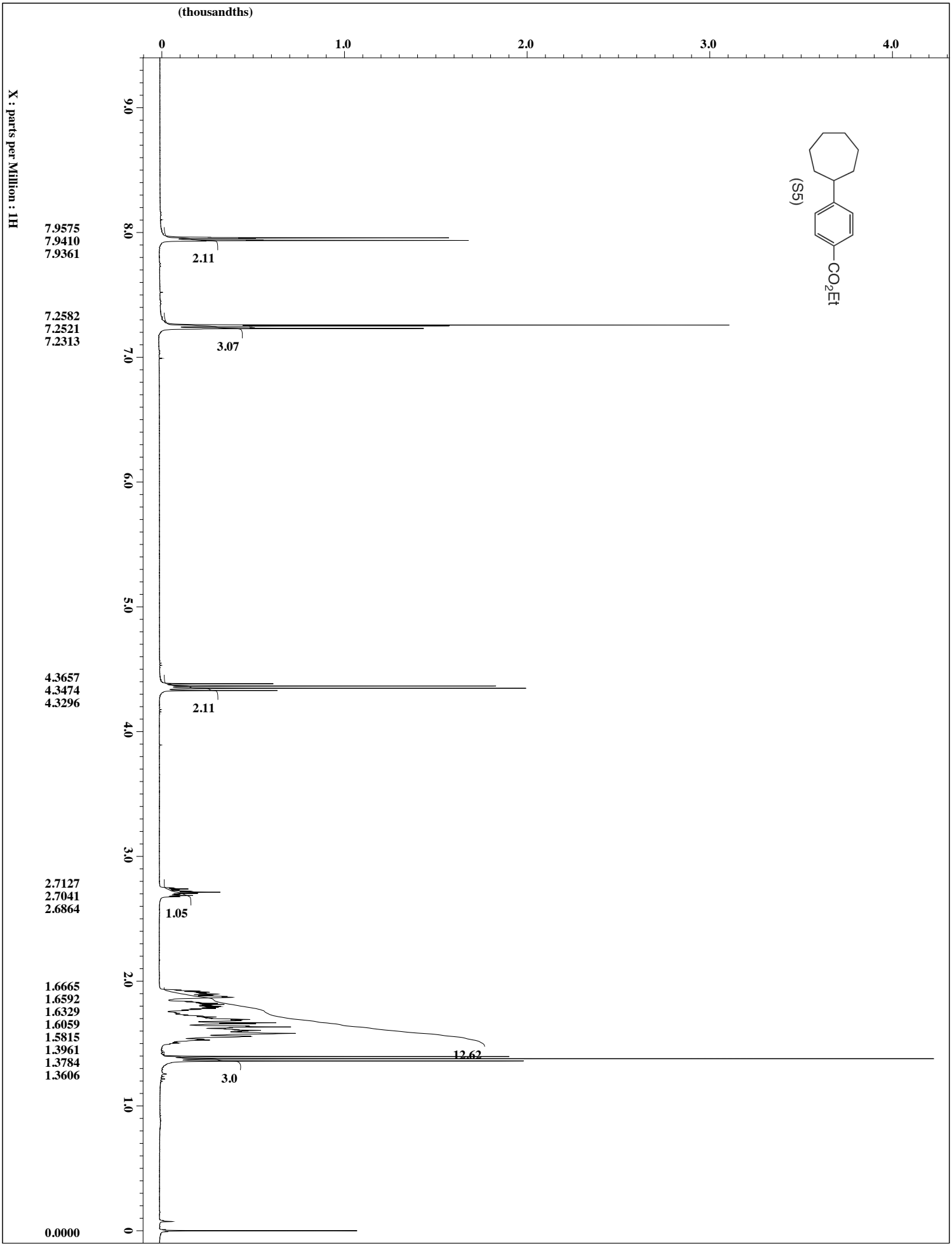

NMe2
(S2)
(thousandths)
0.5
0.4
0.3
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
148.8167
138.5290
127.1722
113.0029
77.4687
77.0000
76.5313
45.9970
40.9477
37.0415
28.0120
27.1403
X : parts per Million : 13C

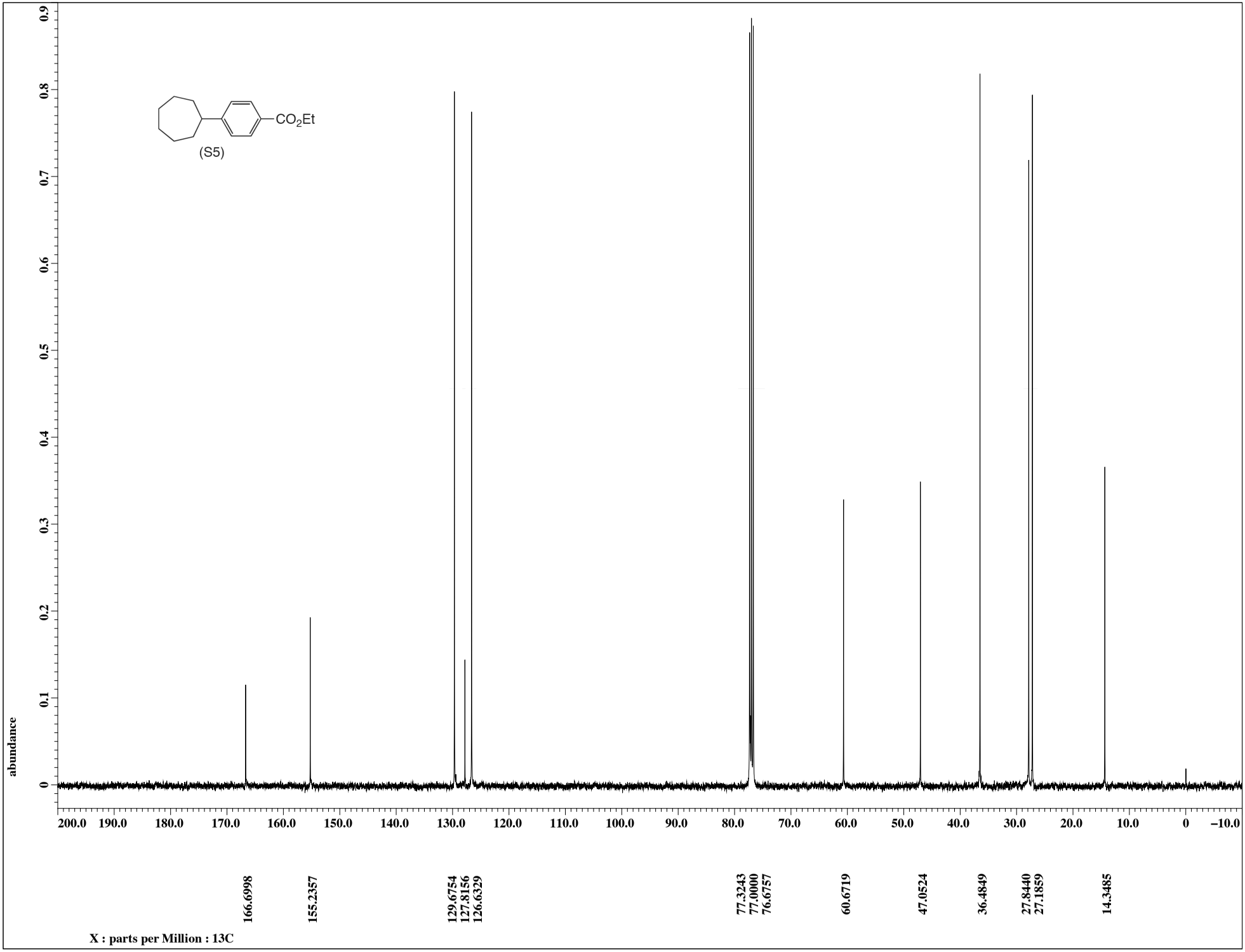

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2570
7.2423
7.2106
7.1227
3.16
1.94
2.6297
2.6175
2.5931
1.0
1.6291
1.6193
1.5998
1.5803
1.5546
1.5339
12.24
−0.0000
(S3)
Cl

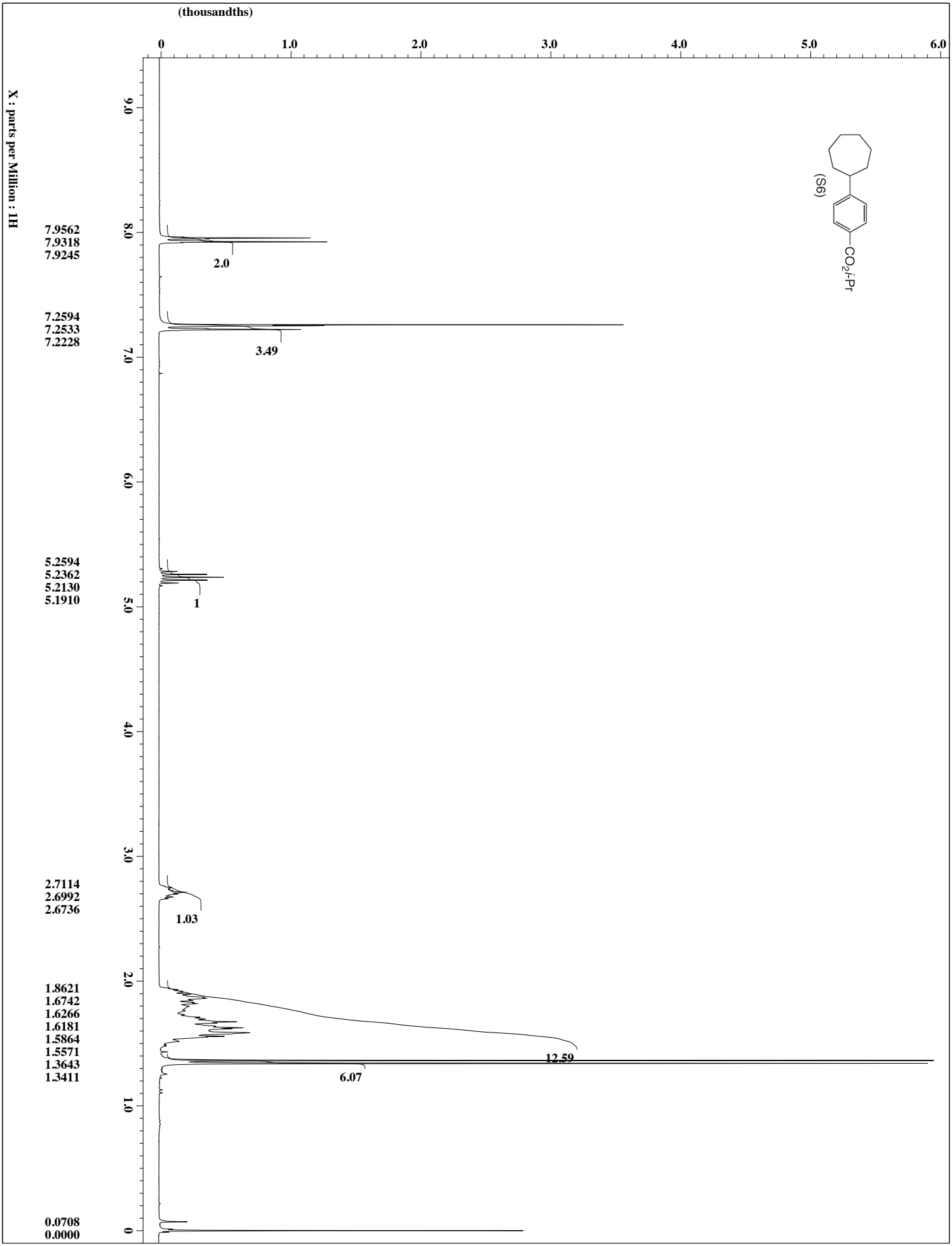

Cl
(S3)
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
148.3932
130.9880
128.3235
128.0192
77.4687
77.0000
76.5313
46.4329
36.7619
27.8640
27.1197
X : parts per Million : 13C

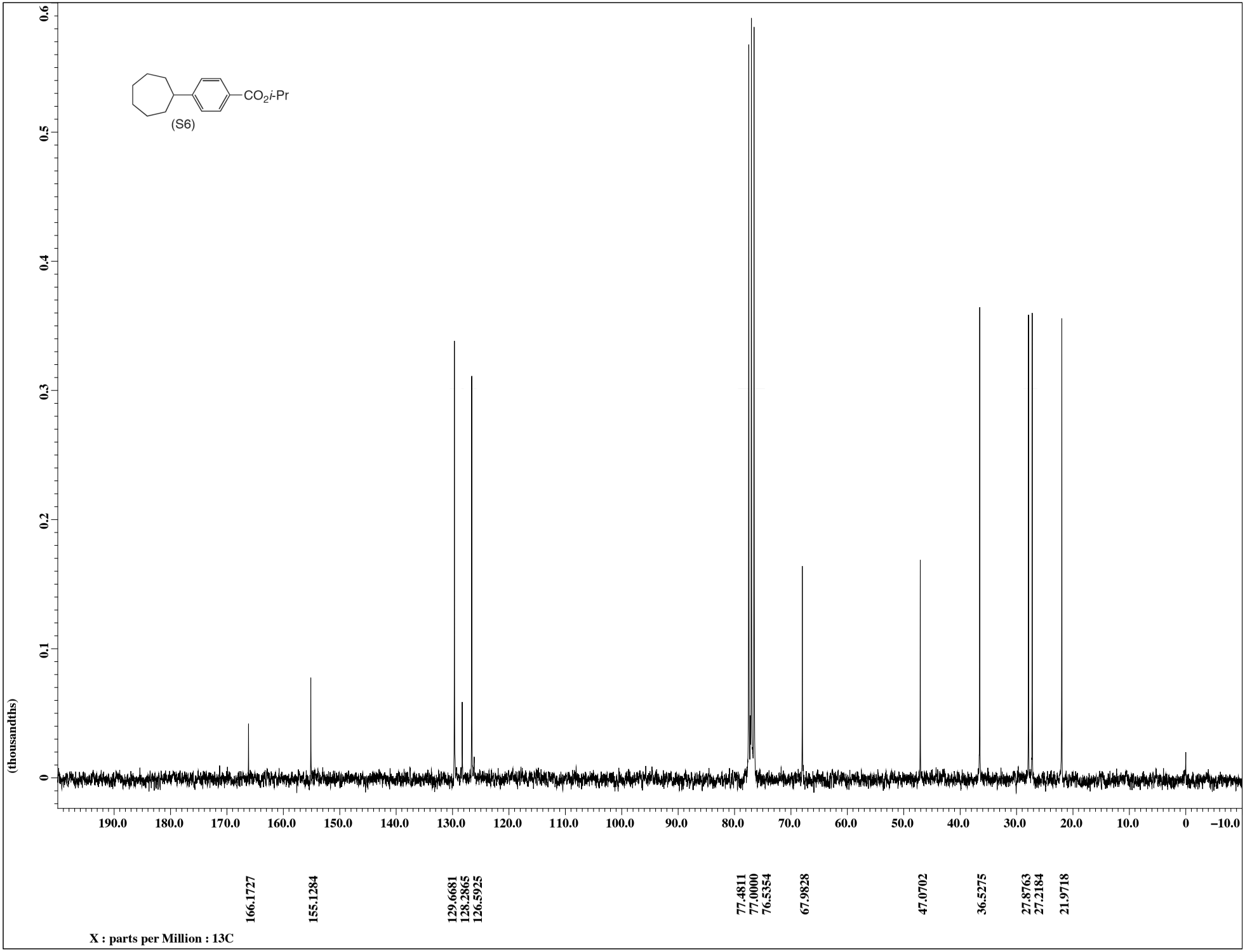

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
7.9502
7.9336
7.9294
2.02
7.2588
7.2552
7.2344
3.03
3.8928
3.0
2.7139
2.7047
2.6876
0.99
1.6940
1.6677
1.6598
1.6335
1.6065
1.5821
1.5576
11.68
0.0000
(S4)
CO2Me

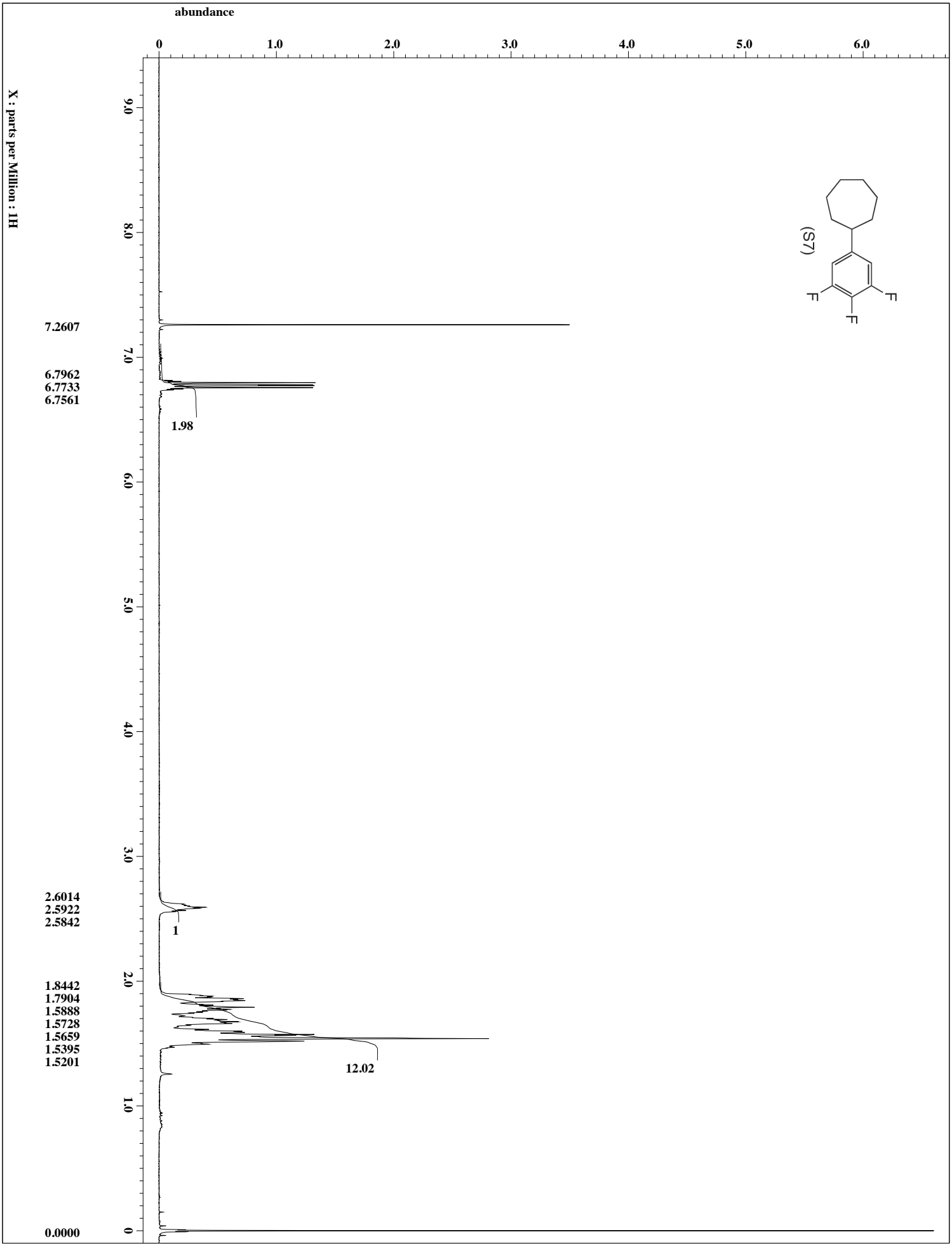

CO2Me
(S4)
(thousandths)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.1789
155.3555
129.7204
127.4750
126.6879
77.3231
77.0000
76.6769
51.8951
47.0481
36.4758
27.8507
27.1961
X : parts per Million : 13C

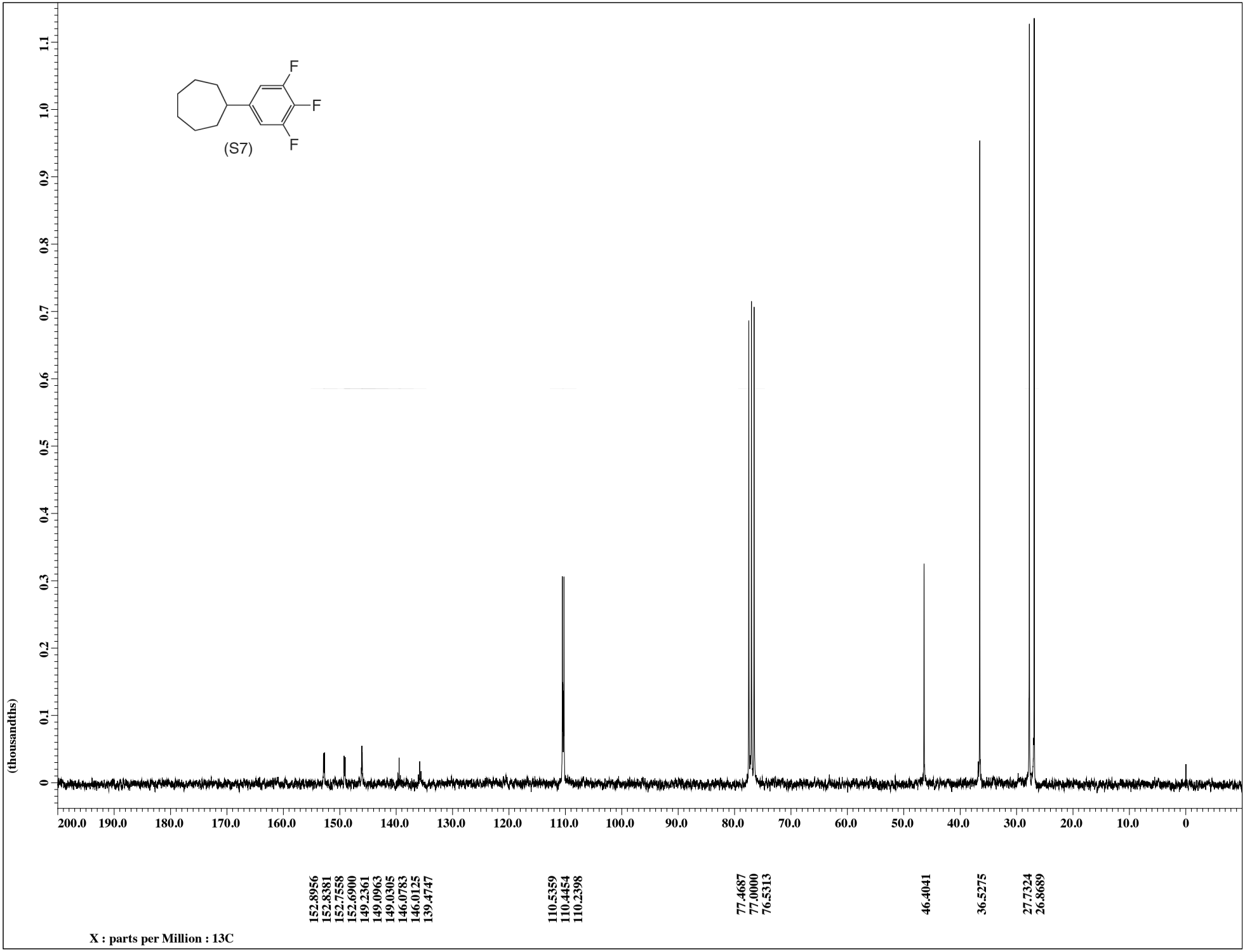

(thousandths)
0
1.0
2.0
3.0
4.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.9575
7.9410
7.9361
2.11
7.2582
7.2521
7.2313
3.07
4.3657
4.3474
4.3296
2.11
2.7127
2.7041
2.6864
1.05
1.6665
1.6592
1.6329
1.6059
1.5815
1.3961
1.3784
1.3606
12.62
3.0
0.0000
(S5)
CO2Et

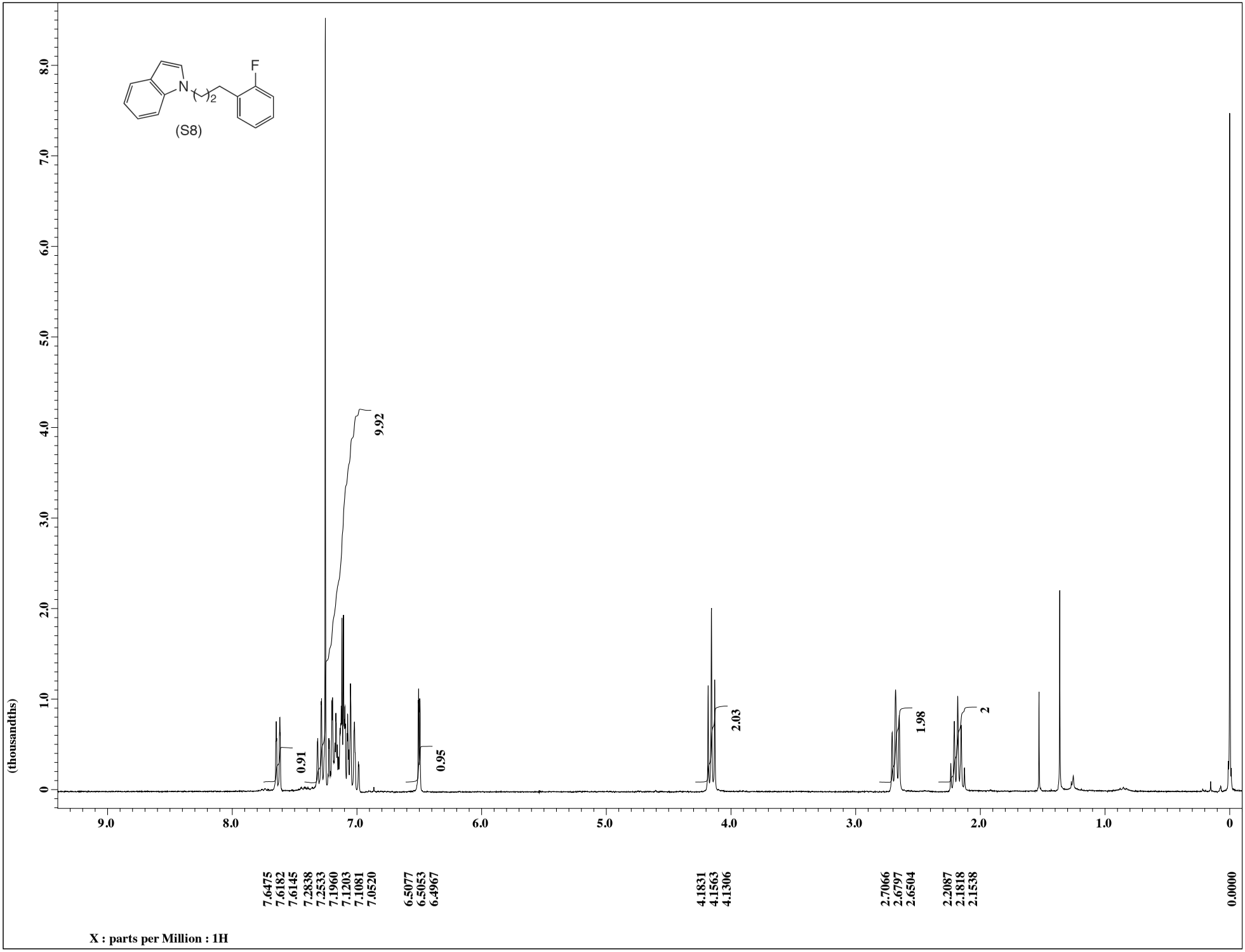

CO2Et
(S5)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
166.6998
155.2357
129.6754
127.8156
126.6329
77.3243
77.0000
76.6757
60.6719
47.0524
36.4849
27.8440
27.1859
14.3485
X : parts per Million : 13C

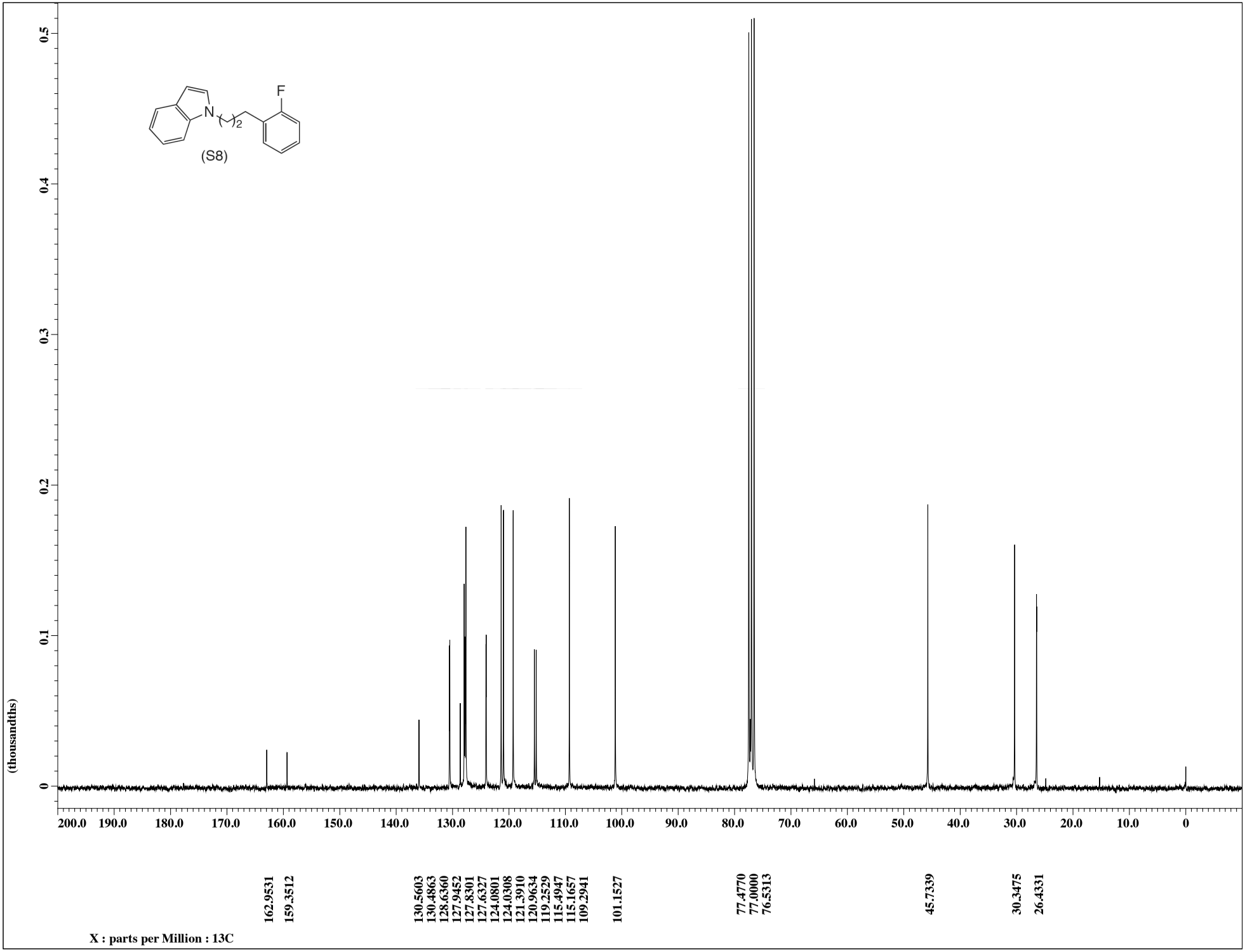

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.9562
7.9318
7.9245
2.0
7.2594
7.2533
7.2228
3.49
5.2594
5.2362
5.2130
5.1910
1
2.7114
2.6992
2.6736
1.03
1.8621
1.6742
1.6266
1.6181
1.5864
1.5571
1.3643
1.3411
12.59
6.07
0.0708
0.0000
(S6)
CO2-i-Pr

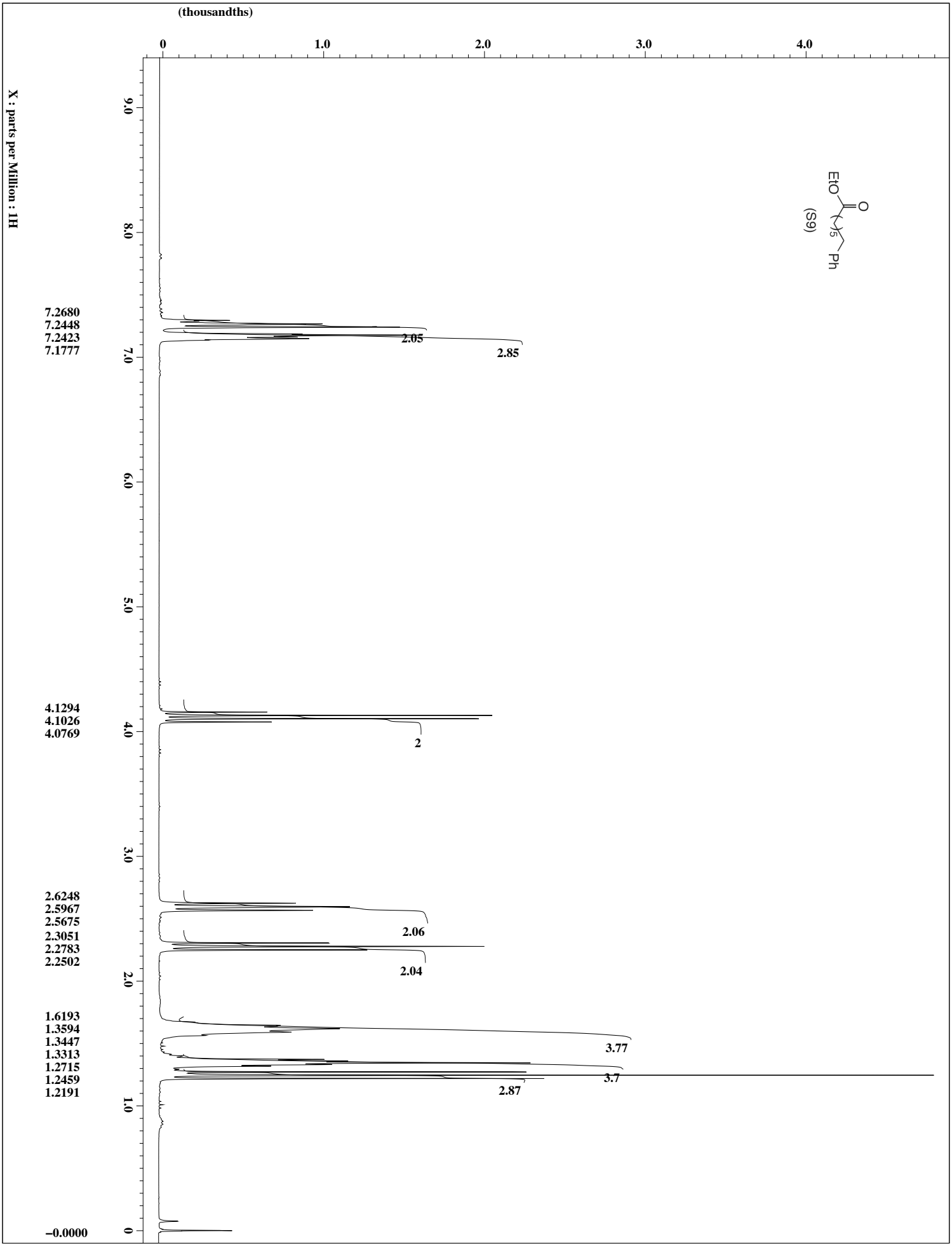

CO2i-Pr
(S6)
(thousandths)
0.6
0.5
0.4
0.3
0.2
0.1
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
166.1727
155.1284
129.6681
128.2865
126.5925
77.4811
77.0000
76.5354
67.9828
47.0702
36.5275
27.8763
27.2184
21.9718
X : parts per Million : 13C

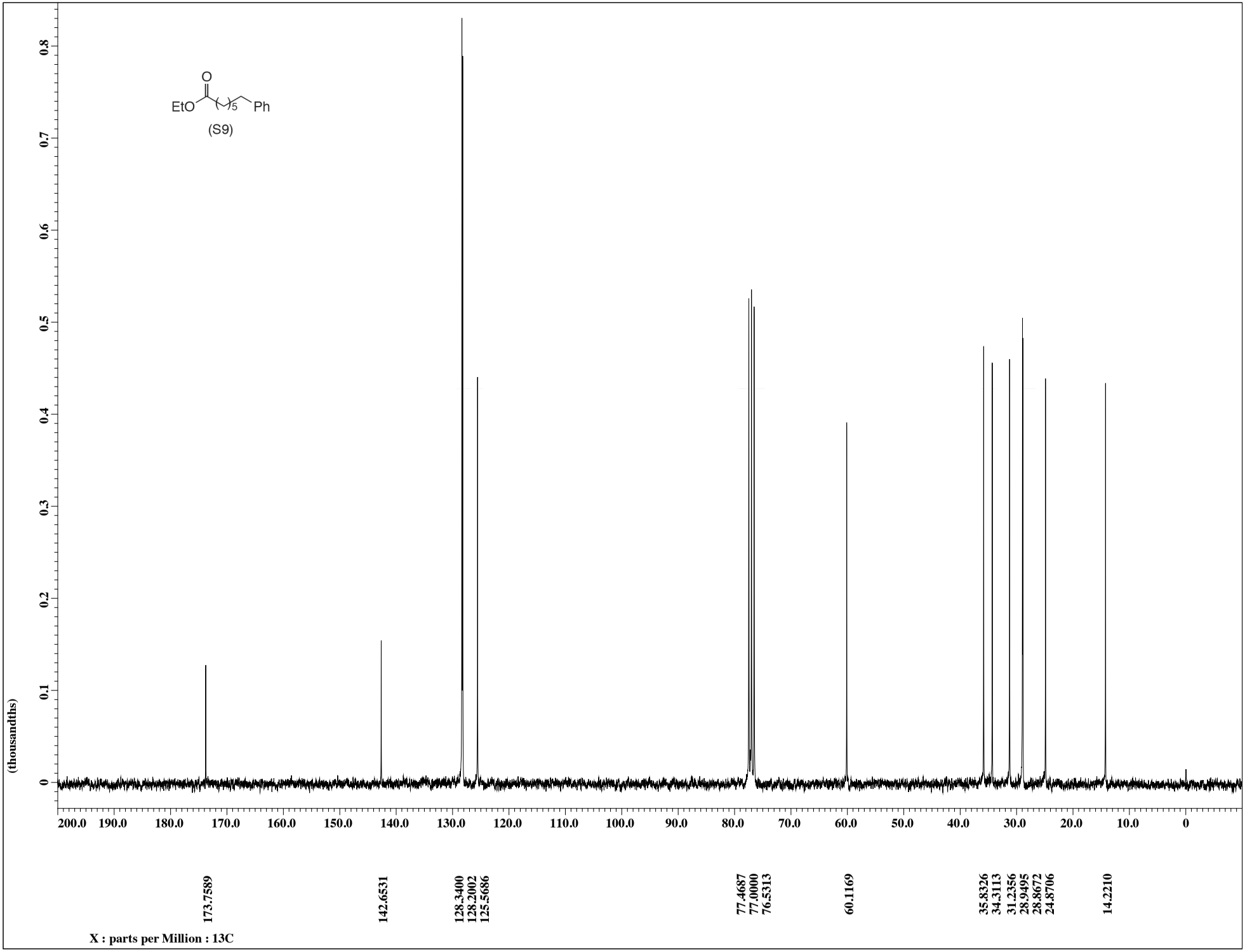

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2607
6.7962
6.7733
6.7561
1.98
2.6014
2.5922
2.5842
1
1.8442
1.7904
1.5888
1.5728
1.5659
1.5395
1.5201
12.02
0.0000
(S7)
F
F
F

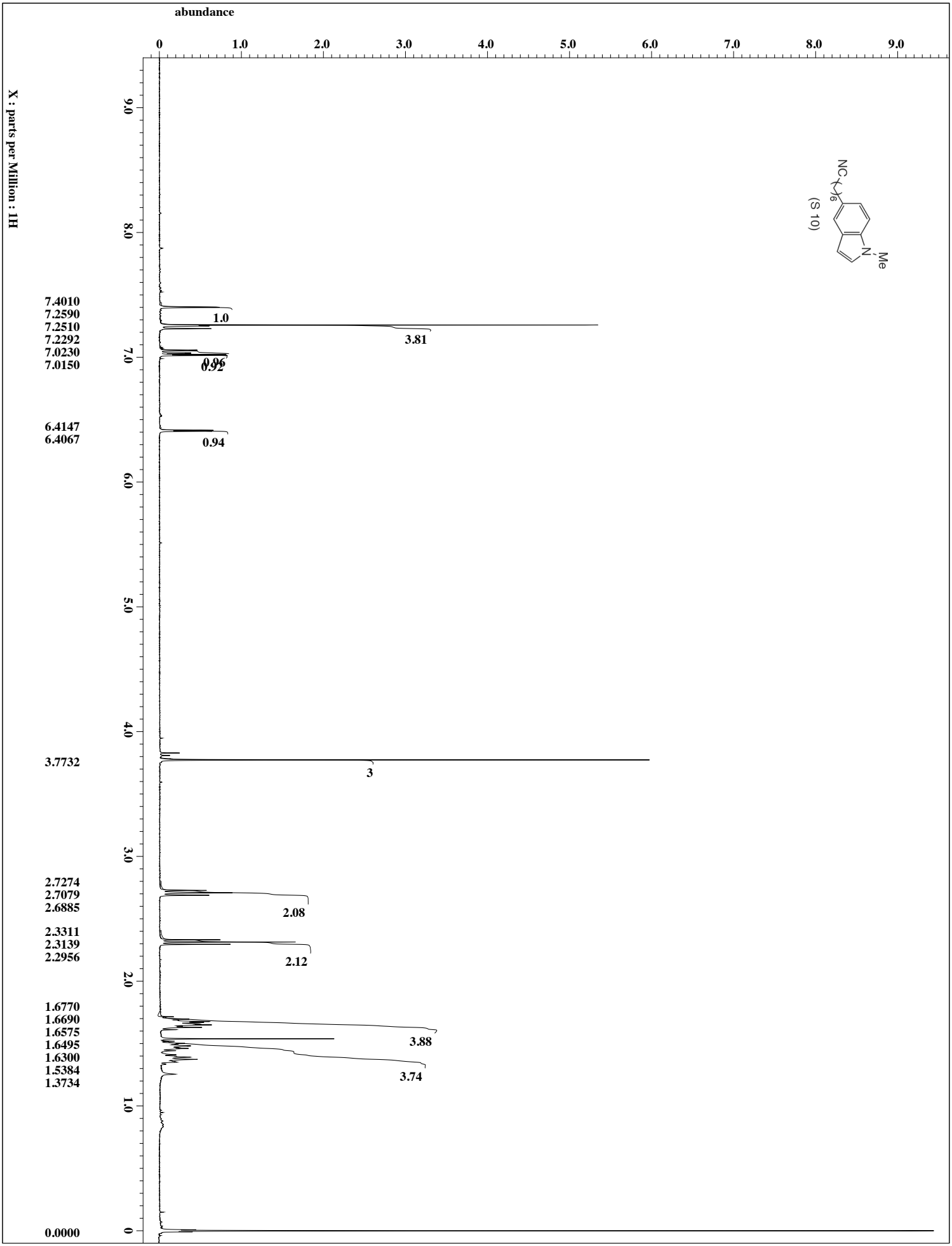

F
F
F
(S7)
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
152.8956
152.8381
152.7558
152.6900
149.2361
149.0963
149.0305
146.0783
146.0125
139.4747
110.5359
110.4454
110.2398
77.4687
77.0000
76.5313
46.4041
36.5275
27.7324
26.8689
X : parts per Million : 13C

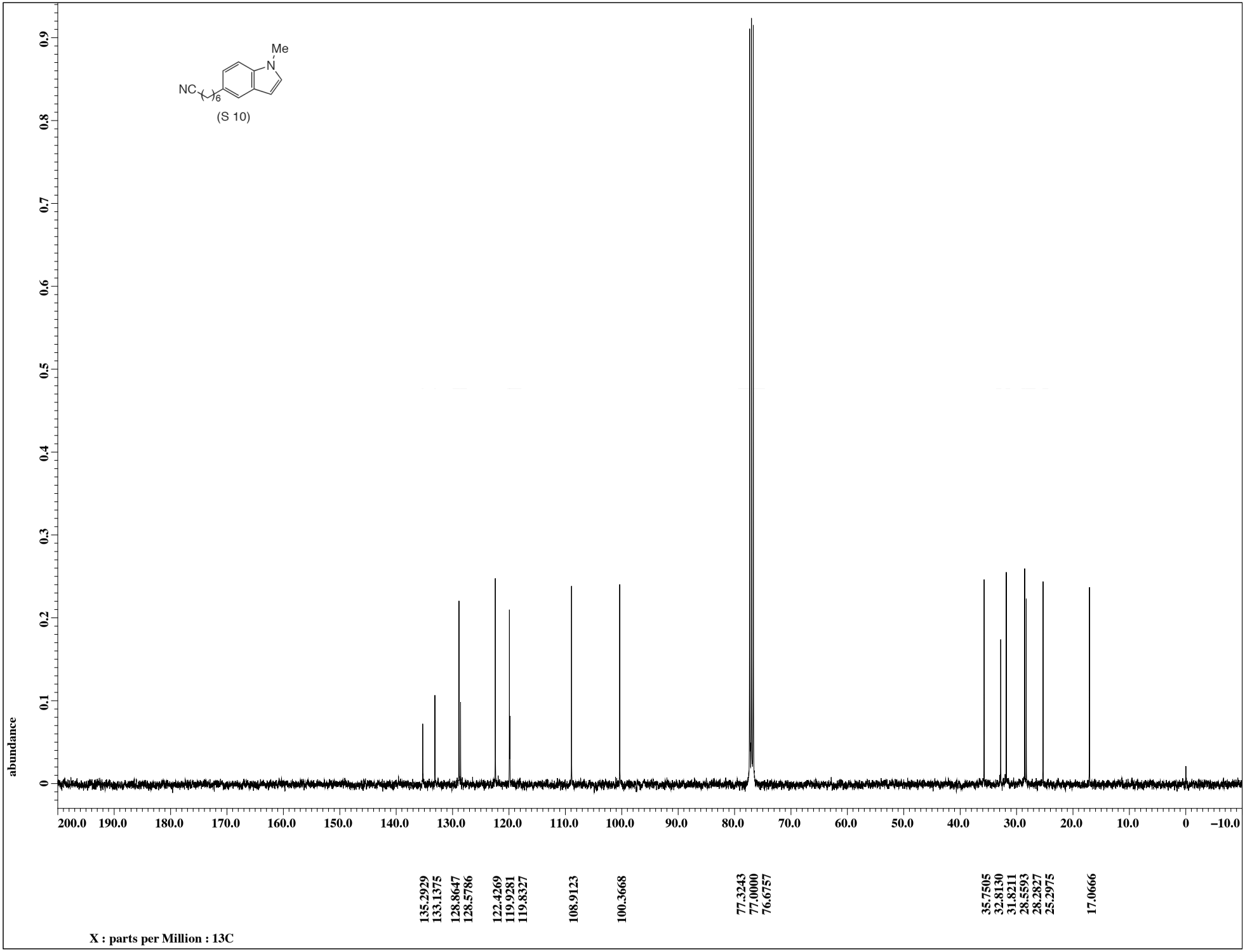

(S8)
F
N
2
(thousandths)
9.92
0.91
0.95
2.03
1.98
2
7.6475
7.6182
7.6145
7.2838
7.2533
7.1960
7.1203
7.1081
7.0520
6.5077
6.5053
6.4967
4.1831
4.1563
4.1306
2.7066
2.6797
2.6504
2.2087
2.1818
2.1538
0.0000
X : parts per Million : 1H

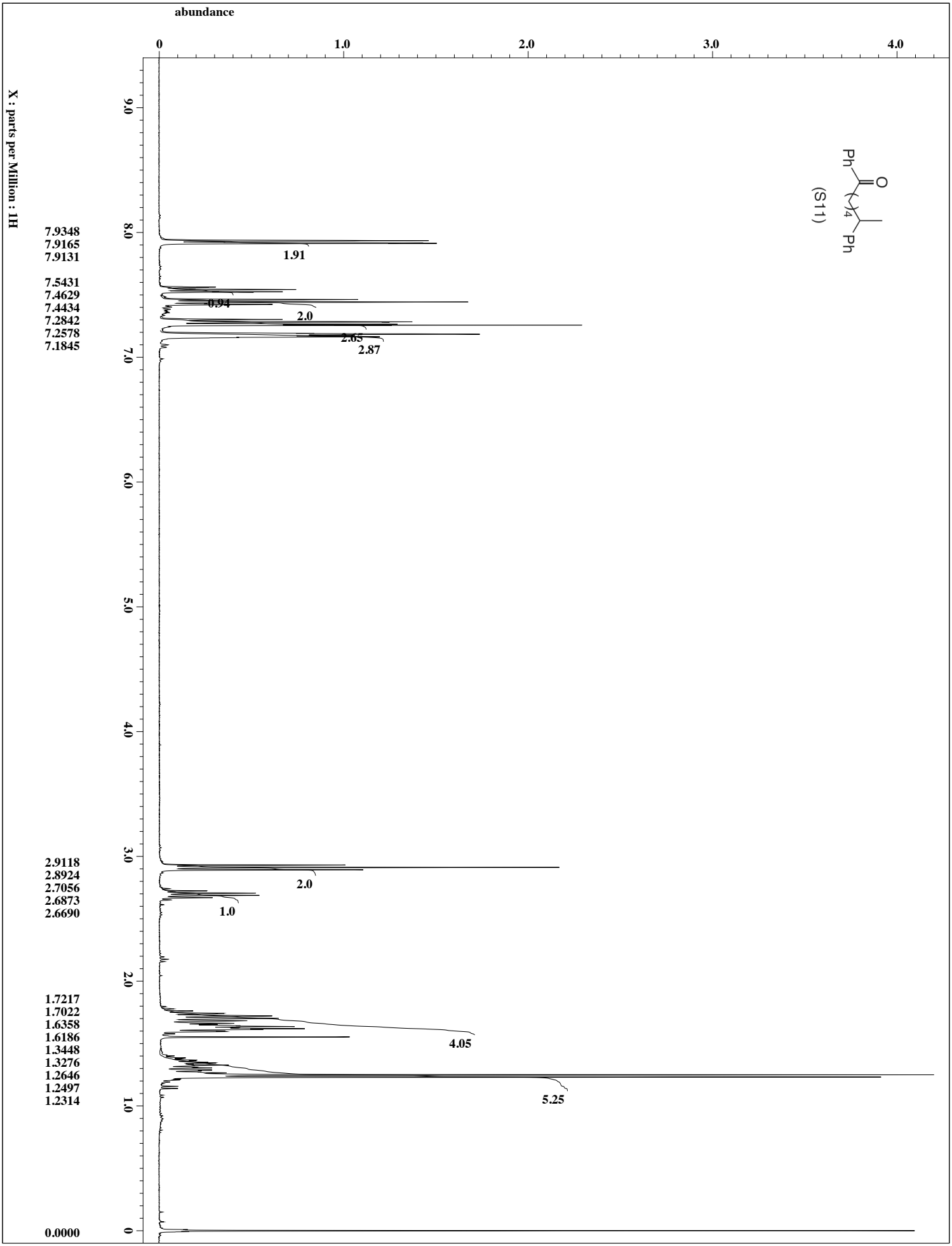

(S8)
F
N
2
(thousandths)
0.5
0.4
0.3
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
162.9531
159.3512
130.5603
130.4863
128.6360
127.9452
127.8301
127.6327
124.0801
124.0308
121.3910
120.9634
119.2529
115.4947
115.1657
109.2941
101.1527
77.4770
77.0000
76.5313
45.7339
30.3475
26.4331
X : parts per Million : 13C

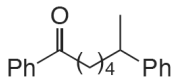

(thousandths)
0
1.0
2.0
3.0
4.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2680
7.2448
7.2423
7.1777
2.05
2.85
4.1294
4.1026
4.0769
2
2.6248
2.5967
2.5675
2.3051
2.2783
2.2502
2.06
2.04
1.6193
1.3594
1.3447
1.3313
1.2715
1.2459
1.2191
3.77
3.7
2.87
−0.0000
O
EtO
5
Ph
(S9)


O
EtO
5
Ph
(S9)
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.7589
142.6531
128.3400
128.2002
125.5686
77.4687
77.0000
76.5313
60.1169
35.8326
34.3113
31.2356
28.9495
28.8672
24.8706
14.2210
X : parts per Million : 13C


abundance
X : parts per Million : 1H
7.4010
7.2590
7.2510
7.2292
7.0230
7.0150
6.4147
6.4067
3.7732
2.7274
2.7079
2.6885
2.3311
2.3139
2.2956
1.6770
1.6690
1.6575
1.6495
1.6300
1.5384
1.3734
0.0000
1.0
3.81
0.96
0.92
0.94
3
2.08
2.12
3.88
3.74
NC
6
N
Me
(S 10)


Me
N
NC
6
(S 10)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
135.2929
133.1375
128.8647
128.5786
122.4269
119.9281
119.8327
108.9123
100.3668
77.3243
77.0000
76.6757
35.7505
32.8130
31.8211
28.5593
28.2827
25.2975
17.0666
X : parts per Million : 13C


abundance
0
1.0
2.0
3.0
4.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.9348
7.9165
7.9131
7.5431
7.4629
7.4434
7.2842
7.2578
7.1845
2.9118
2.8924
2.7056
2.6873
2.6690
1.7217
1.7022
1.6358
1.6186
1.3448
1.3276
1.2646
1.2497
1.2314
0.0000
1.91
0.94
2.0
2.65
2.87
2.0
1.0
4.05
5.25
O
Ph
4
Ph
(S11)

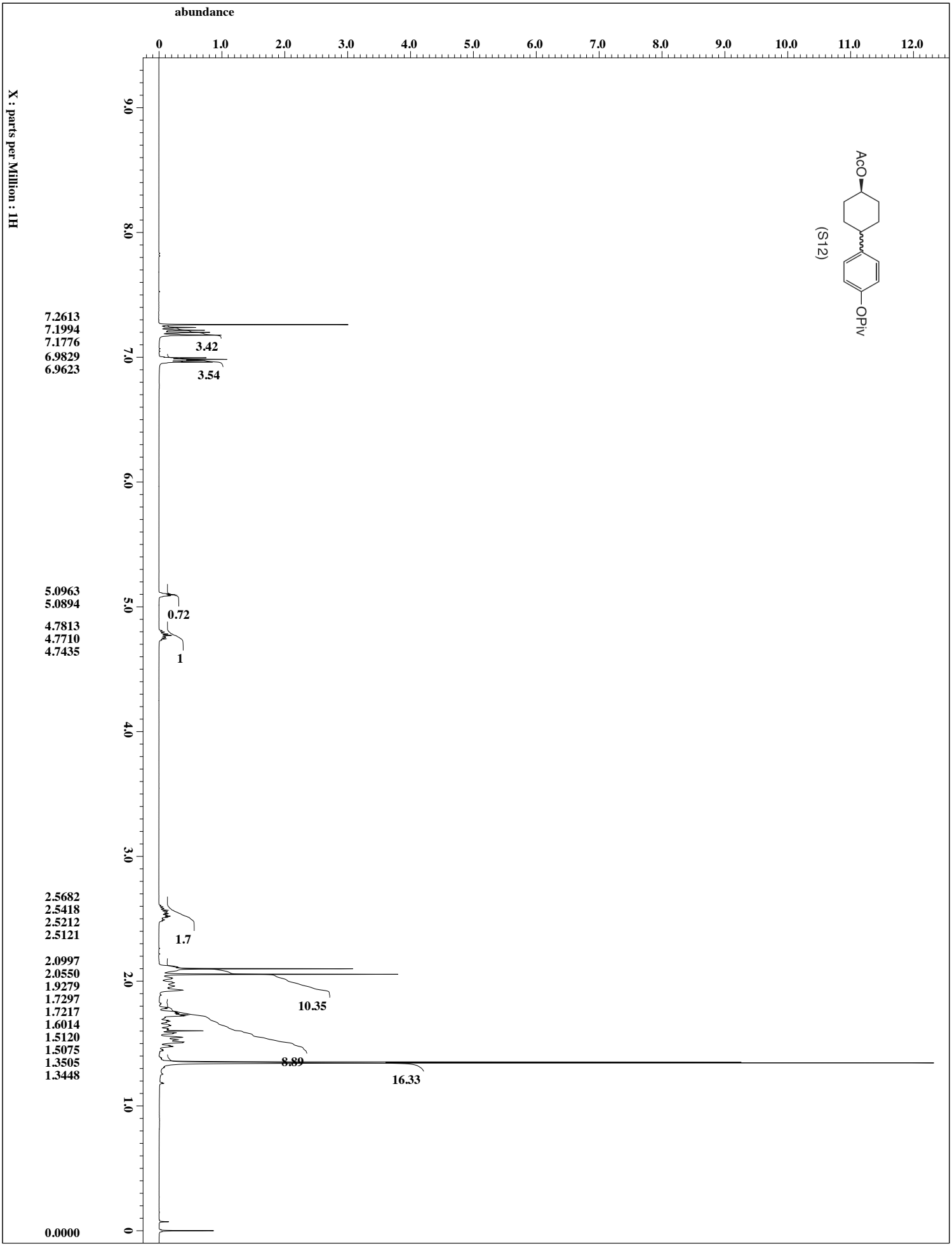


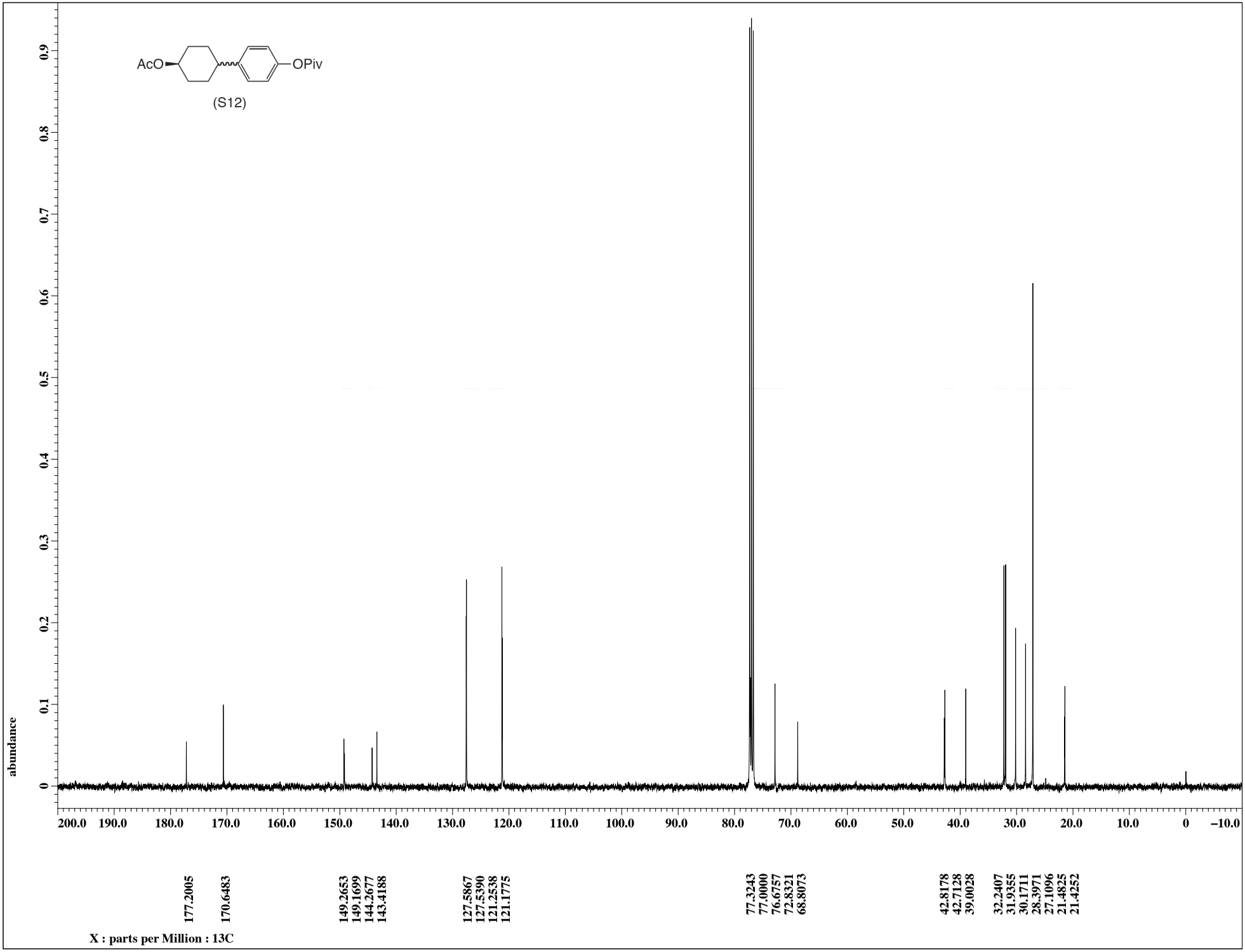
(S11)

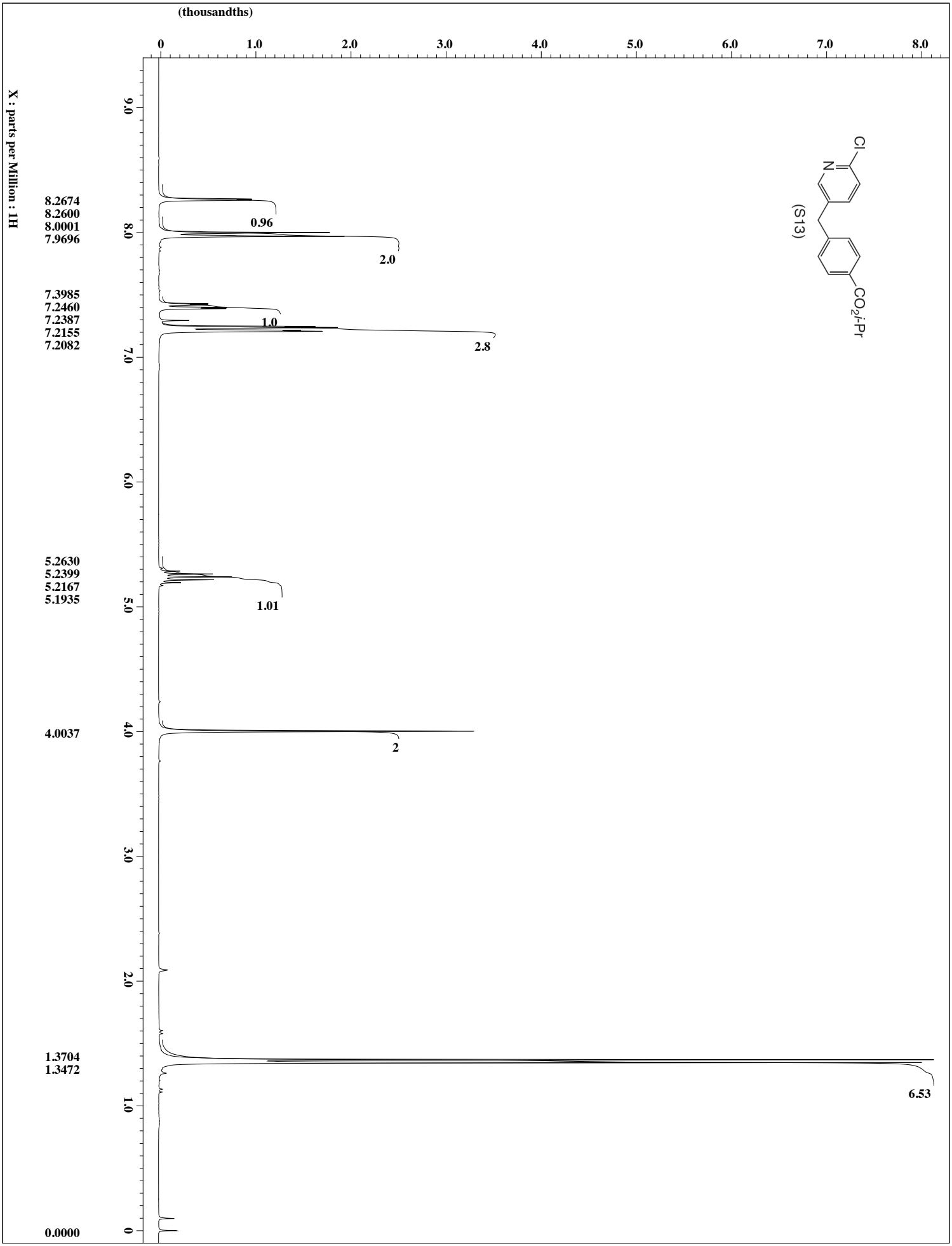
(thousandths)

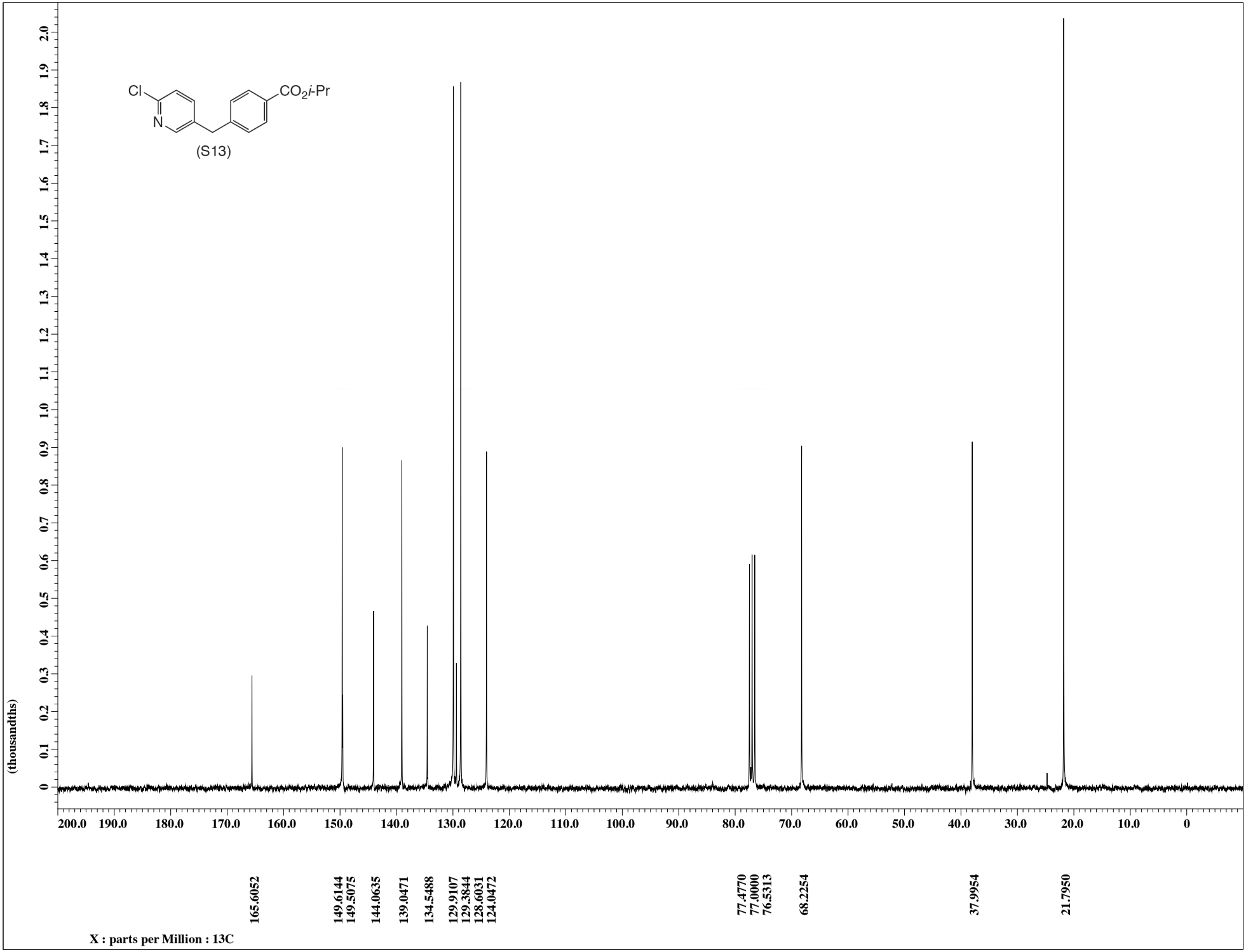
200.3953
147.5838
137.0198
132.8440
128.5107
128.2870
128.0053
126.9530
125.8179
77.3231
77.0000
76.6852
39.7983
38.5306
38.1909
27.4613
24.3294
22.3160

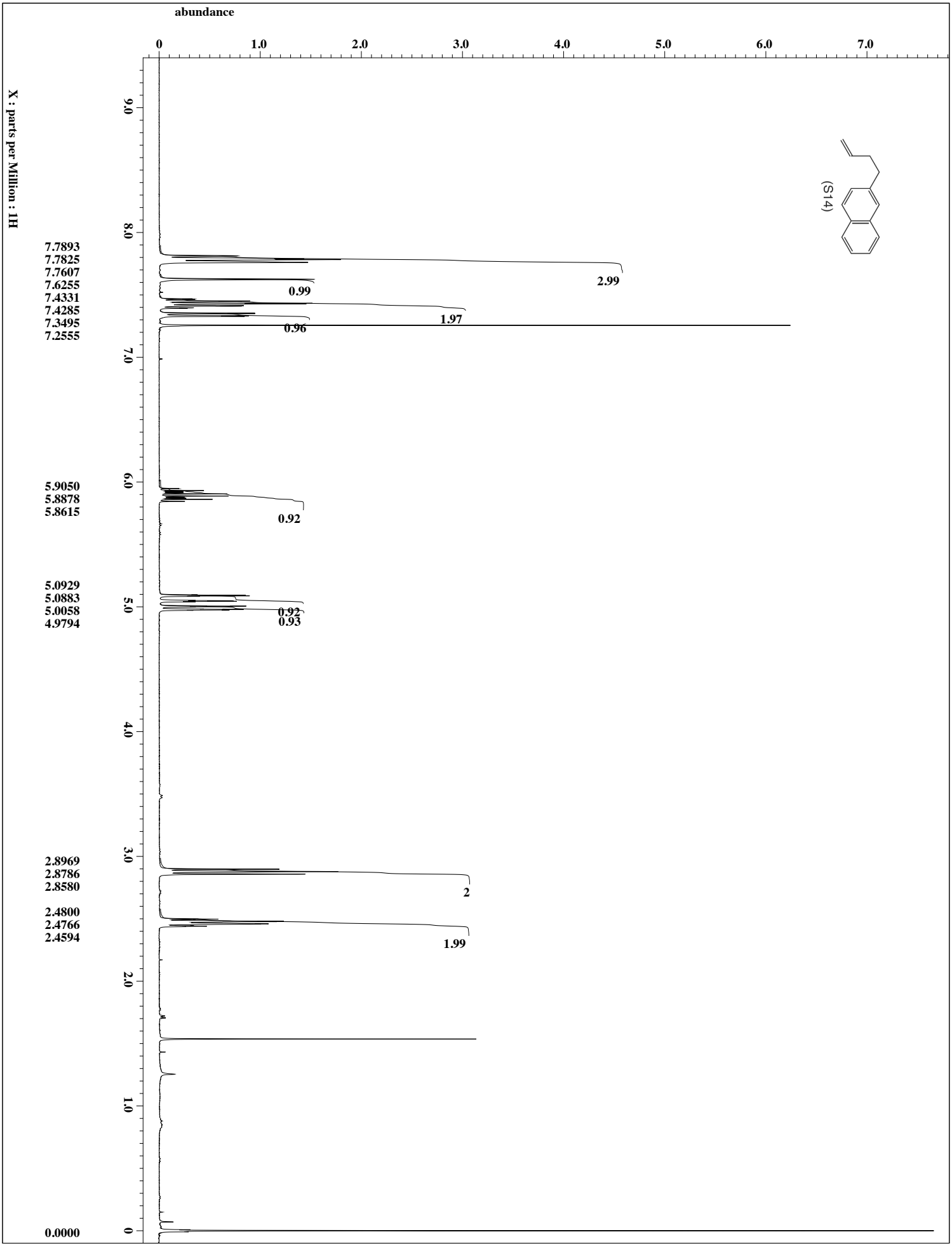
X : parts per Million : 13C


abundance
X : parts per Million : 1H
AcO
OPiv
(S12)
7.2613
7.1994
7.1776
6.9829
6.9623
3.42
3.54
5.0963
5.0894
4.7813
4.7710
4.7435
0.72
1
2.5682
2.5418
2.5212
2.5121
1.7
2.0997
2.0550
1.9279
1.7297
1.7217
1.6014
1.5120
1.5075
1.3505
1.3448
10.35
8.89
16.33
0.0000


AcO
OPiv
(S12)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
177.2005
170.6483
149.2653
149.1699
144.2677
143.4188
127.5867
127.5390
121.2538
121.1775
77.3243
77.0000
76.6757
72.8321
68.8073
42.8178
42.7128
39.0028
32.2407
31.9355
30.1711
28.3971
27.1096
21.4825
21.4252
X : parts per Million : 13C

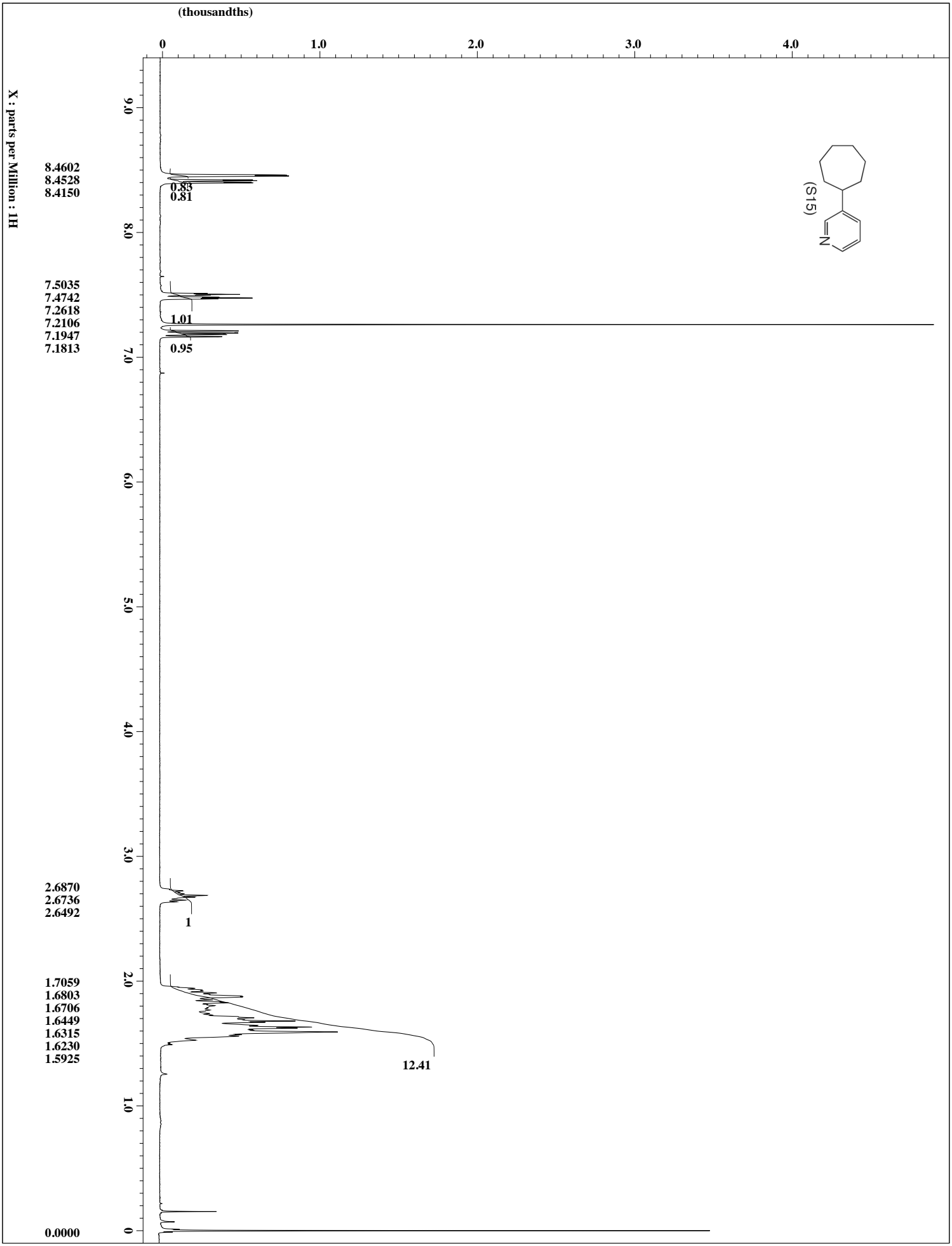

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
8.2674
8.2600
8.0001
7.9696
0.96
2.0
7.3985
7.2460
7.2387
7.2155
7.2082
1.0
2.8
5.2630
5.2399
5.2167
5.1935
1.01
4.0037
2
1.3704
1.3472
6.53
0.0000
Cl
N
CO2i-Pr
(S13)

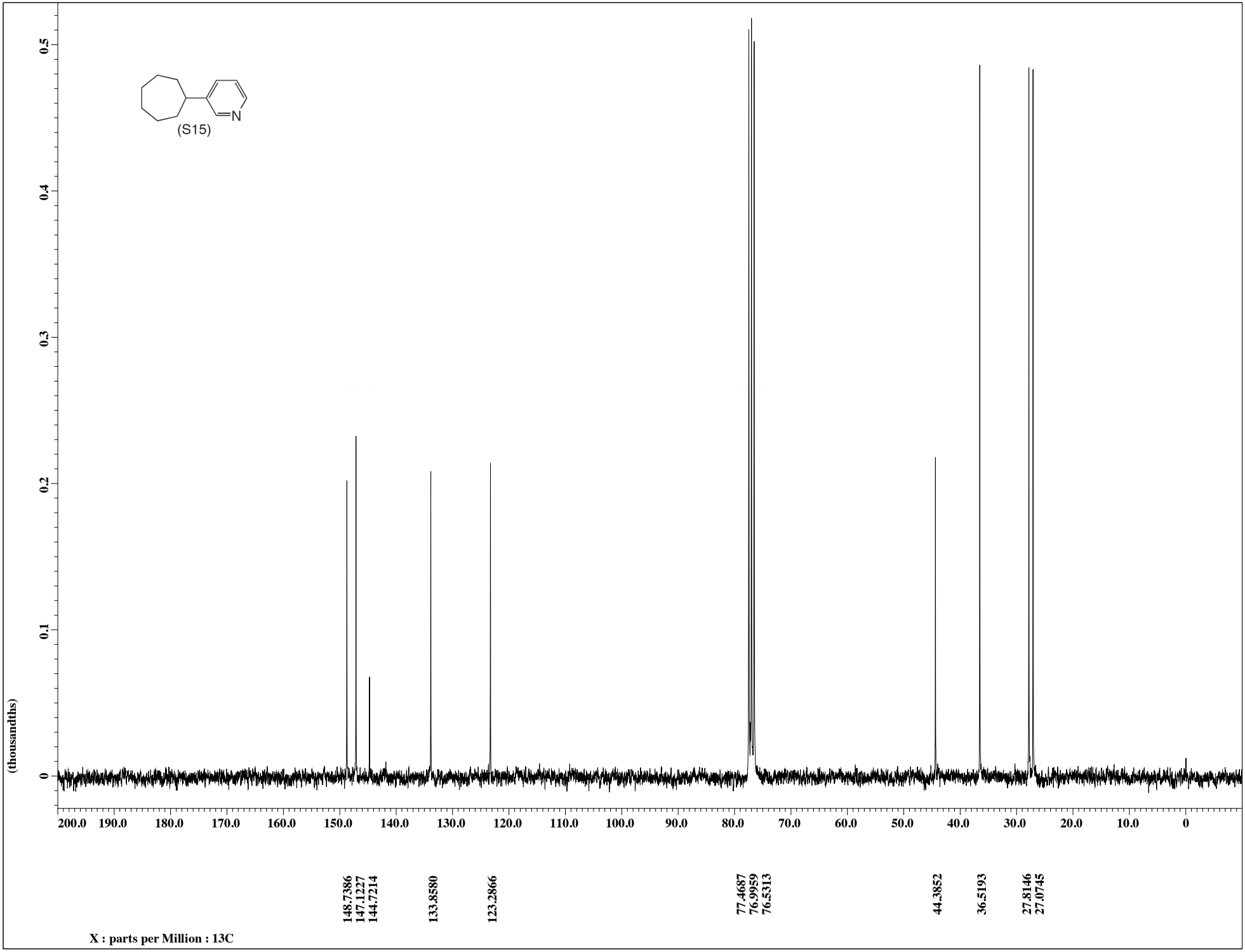

Cl
N
CO2i-Pr
(S13)
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.6052
149.6144
149.5075
144.0635
139.0471
134.5488
129.9107
129.3844
128.6031
124.0472
77.4770
77.0000
76.5313
68.2254
37.9954
21.7950
X : parts per Million : 13C


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.7893
7.7825
7.7607
7.6255
7.4331
7.4285
7.3495
7.2555
2.99
0.99
1.97
0.96
5.9050
5.8878
5.8615
0.92
5.0929
5.0883
5.0058
4.9794
0.92
0.93
2.8969
2.8786
2.8580
2
2.4800
2.4766
2.4594
1.99
0.0000
(S14)

(S14)

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
139.3654
138.0111
133.5762
131.9739
127.7965
127.5867
127.4150
127.3292
126.4040
125.8509
125.0974
115.0258
77.3243
77.0000
76.6757
35.5216
35.4072
X : parts per Million : 13C


(thousandths)
0
1.0
2.0
3.0
4.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.4602
8.4528
8.4150
0.83
0.81
7.5035
7.4742
7.2618
7.2106
7.1947
7.1813
1.01
0.95
2.6870
2.6736
2.6492
1
1.7059
1.6803
1.6706
1.6449
1.6315
1.6230
1.5925
12.41
0.0000
(S15)
N


(S15)
N
(thousandths)
0.5
0.4
0.3
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
148.7386
147.1227
144.7214
133.8580
123.2866
77.4687
76.9959
76.5313
44.3852
36.5193
27.8146
27.0745
X : parts per Million : 13C