

Supporting Information

for

Copper-mediated Reaction of Zirconacyclopentadienes with Azides: A One-pot Three-component Synthesis of Multiply-substituted Pyrroles from Azide and Two Alkynes

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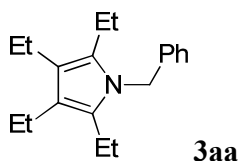
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General Considerations:

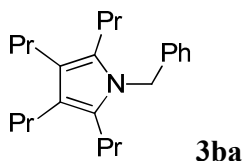
All reactions were carried out with standard Schlenk techniques under nitrogen atmosphere. THF and toluene were distilled and stored over sodium. Most materials without special note were commercially available and were used without further purification. Azides were prepared in accordance with literature procedures^[1]. Thin-layer chromatography (TLC) was carried out on silica gel purchased from commercial sources, and components were located by observation under UV light. ¹H NMR and ¹³C NMR spectra were recorded on NMR spectrometer at ambient temperature with CDCl₃ as the solvent and TMS as internal standard. GC-MS spectra were recorded on Hewlett Packard GC-MS system. The reaction progress was monitored by GC.

Experimental Procedures

To a solution of Cp_2ZrCl_2 (176 mg, 0.6 mmol) in THF (3 mL) was added *n*-BuLi (1.6 M *n*-Hexane solution, 1.2 mmol) at -78°C , and the mixture was stirred for 1 h at -78°C . 3-Hexyne (112 μL , 1 mmol) was added and the mixture was warmed to room temperature and stirred for 1 h. Then the mixture was warmed to 50°C , and stirred for 1 h. CuCl (99 mg, 1 mmol) was added at 0°C and was stirred at the same temperature for 10 min. Benzyl azide (120 μL , 0.6 mmol) was added and warmed to 50°C and stirred for 3 h. Then distilled water was added to quench the reaction. Ethyl acetate was used to extract and evaporated in vacuo and the residue was purified by column chromatography on alumina (petroleum ether) to afford product **3aa**.

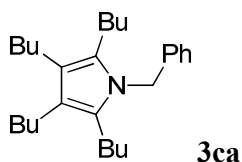


1-Benzyl-2,3,4,5-tetraethylpyrrole (3aa): As light yellow oil in 65% isolated yield. ^1H NMR (CDCl_3 , 300 MHz) δ 7.16-7.29 (m, 3H), 6.83 (d, $J = 6.9$ Hz, 2H), 5.00 (s, 2H), 2.40-2.47 (m, 8H), 1.31 (t, $J = 7.5$ Hz, 6H), 0.97 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 140.2, 128.8, 128.6, 126.8, 125.8, 119.6, 46.6, 18.0, 17.9, 17.4, 16.0. GC-MS (EI, m/z): 269. HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{N}+\text{H}^+$ 270.2222, found 270.2226.

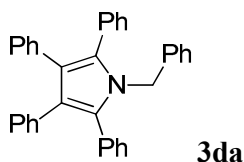


1-Benzyl-2,3,4,5-tetrapropylpyrrole (3ba): As light yellow oil in 62% isolated yield. ^1H NMR (CDCl_3 , 300 MHz) δ 7.19-7.27 (m, 3H), 6.79 (d, $J = 6.9$ Hz, 2H), 4.98 (s, 2H), 2.32-2.37 (m, 8H), 1.48 (q, $J = 8.8$ Hz, 4H), 1.32 (q, $J = 7.8$ Hz, 4H), 0.96 (t, $J = 6.9$ Hz, 6H), 0.84 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 140.3, 128.5,

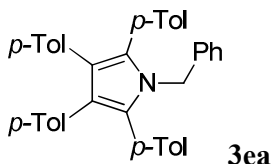
127.8, 126.7, 125.6, 118.5, 46.7, 27.4, 27.1, 25.5, 24.5, 14.6, 14.3. GC-MS (EI, m/z): 325. HRMS calcd for C₂₃H₃₅N+H⁺ 326.2848, found 326.2850.



1-Benzyl-2,3,4,5-tetrabutylpyrrole (3ca): As light yellow oil in 60% isolated yield. ¹H NMR (CDCl₃, 300 MHz) δ 7.19-7.27 (m, 3H), 6.80 (d, *J* = 7.3 Hz, 2H), 4.98 (s, 2H), 2.34-2.38 (m, 8H), 1.36-1.50 (m, 8H), 1.23-1.33 (m, 8H), 0.95 (t, *J* = 7.3 Hz, 6H), 0.82 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 140.3, 128.5, 127.7, 126.7, 125.6, 118.5, 46.7, 34.7, 33.4, 24.8, 24.6, 23.2, 22.8, 14.2, 13.9. GC-MS (EI, m/z): 381. HRMS calcd for C₂₇H₄₃N+H⁺ 382.3474, found 382.3478.

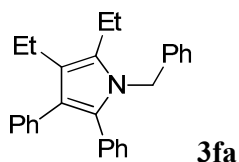


1-Benzyl-2,3,4,5-tetraphenylpyrrole (3da):^[2] As yellow solid in 41% isolated yield. M.P. 215-217 °C. ¹H NMR (CDCl₃, 300 MHz) δ 6.87-7.21 (m, 25H), 5.10 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 139.2, 135.6, 132.8, 132.0, 131.6, 130.9, 128.2, 128.0, 127.4, 127.3, 126.7, 126.0, 125.1, 122.6, 48.2. GC-MS (EI, m/z): 461. HRMS calcd for C₃₅H₂₇N+H⁺ 462.2222, found 462.2216.

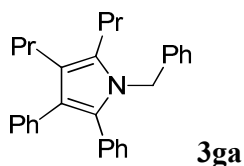


1-Benzyl-2,3,4,5-tetra-*p*-tolylpyrrole (3ea): As yellow solid in 51% isolated yield. M.p. 233-234 °C. ¹H NMR (CDCl₃, 300 MHz) δ 6.76-7.17 (m, 20H), 5.05 (s, 2H), 2.28 (s, 6H), 2.23 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 139.7, 136.9, 134.3, 133.0, 131.8, 131.5, 130.8, 130.1, 128.8, 128.3, 128.2, 126.7, 126.2, 122.4, 48.2, 21.4, 21.3.

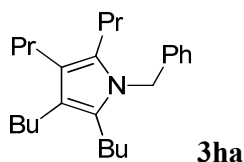
GC-MS (EI, m/z): 517. HRMS calcd for $C_{39}H_{35}N+H^+$ 518.2848, found 518.2850.



1-Benzyl-2,3-diethyl-4,5-diphenylpyrrole (3fa): As light yellow oil in 62% isolated yield. 1H NMR ($CDCl_3$, 300 MHz) δ 7.06-7.28 (m, 13H), 6.88 (d, J = 6.9 Hz, 2H), 5.07 (s, 2H), 2.54 (t, J = 7.6 Hz, 4H), 1.02-1.11 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.8, 137.0, 133.1, 131.4, 131.1, 130.4, 130.3, 128.5, 127.9, 127.7, 126.8, 126.6, 125.8, 125.1, 122.7, 121.0, 47.6, 18.1, 17.9, 16.8, 15.5. GC-MS (EI, m/z): 365. HRMS calcd for $C_{27}H_{27}N+H^+$ 366.2222, found 366.2218



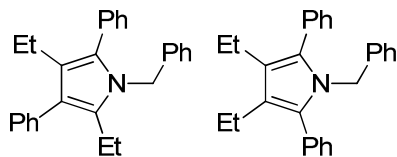
1-Benzyl-2,3-diphenyl-4,5-dipropylpyrrole (3ga): As light yellow oil in 67% isolated yield. 1H NMR ($CDCl_3$, 300 MHz) δ 7.02-7.29 (m, 13H), 6.88 (d, J = 6.9 Hz, 2H), 5.06 (s, 2H), 2.48 (q, J = 7.9 Hz, 4H), 1.34-1.51 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H), 0.83 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.8, 137.2, 133.2, 131.1, 130.4, 130.3, 128.5, 127.9, 127.7, 126.8, 126.6, 125.7, 125.1, 122.9, 119.7, 47.7, 27.3, 27.1, 24.9, 24.2, 14.4, 14.3. GC-MS (EI, m/z): 393. HRMS calcd for $C_{29}H_{31}N+H^+$ 394.2535, found 394.2538.



1-Benzyl-2,3-dibutyl-4,5-dipropylpyrrole (3ha): As light yellow oil in 53% isolated yield. 1H NMR ($CDCl_3$, 300 MHz) δ 7.18-7.27 (m, 3H), 6.79 (d, J = 6.9 Hz, 2H), 4.97 (s, 2H), 2.32-2.37 (m, 8H), 1.25-1.50 (m, 12H), 0.92-0.97 (m, 6H), 0.78-0.86 (m, 6H);

^{13}C NMR (CDCl_3 , 75 MHz) δ 140.3, 128.5, 127.7, 127.6, 126.7, 125.6, 118.6, 118.4, 46.7, 34.7, 33.4, 27.4, 27.1, 25.5, 24.8, 24.6, 24.5, 23.2, 22.8, 14.6, 14.3, 14.2, 13.9.

GC-MS (EI, m/z): 353. HRMS calcd for $\text{C}_{25}\text{H}_{39}\text{N}+\text{H}^+$ 354.3161, found 354.3164.



(3ia)

As light yellow oil in 75% isolated yield. The ratio of the two isomers:

1-benzyl-3,5-diethyl-2,4-diphenylpyrrole and

1-benzyl-2,5-diethyl-3,4-diphenylpyrrole is 4:1. ^1H NMR (CDCl_3 , 300 MHz) δ

6.50-7.41 (m, 21H), 5.05(s, 2H), 4.90 (s, 0.5H), 2.23-2.52 (m, 6H), 1.10 (t, $J = 7.8$ Hz,

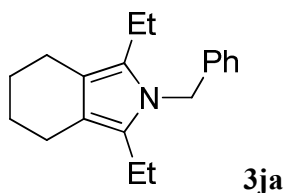
1.5H), 1.03 (t, $J = 7.8$ Hz, 3H), 0.84 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ

139.8, 137.6, 133.7, 133.5, 131.7, 131.5, 131.0, 130.9, 130.4, 130.1, 128.6, 128.19,

128.15, 128.1, 128.0, 127.1, 127.0, 126.9, 126.5, 126.2, 126.8, 123.0, 122.3, 122.2,

48.4, 47.7, 18.3, 18.2, 18.1, 16.7, 16.4, 15.7. GC-MS (EI, m/z): 365. HRMS calcd for

$\text{C}_{27}\text{H}_{27}\text{N}+\text{H}^+$ 366.2222, found 366.2225.



3ja

2-Benzyl-1,3-diethyl-4,5,6,7-tetrahydro-isoindole (3ja): As light yellow oil in 64%

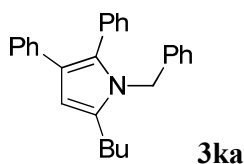
isolated yield. ^1H NMR (CDCl_3 , 300 MHz) δ 7.18-7.29 (m, 3H), 6.90 (d, $J = 7.3$ Hz,

2H), 5.01 (s, 2H), 2.51 (br, 4H), 2.43 (q, $J = 7.3$ Hz, 4H), 1.73-1.78 (m, 4H), 0.97 (t, J

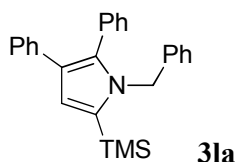
$= 7.8$ Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 139.9, 128.5, 127.2, 126.8, 125.8, 114.8,

46.4, 24.4, 21.8, 18.0, 14.8. GC-MS (EI, m/z): 267. HRMS calcd for $\text{C}_{19}\text{H}_{25}\text{N}+\text{H}^+$

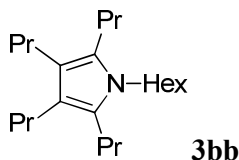
268.2065, found 268.2067.



1-Benzyl-5-butyl-2,3-diphenylpyrrole (3ka): As light yellow oil in 48% isolated yield. ^1H NMR (CDCl_3 , 300 MHz) 7.13-7.28 (m, 13H), 6.90 (d, $J = 6.9$ Hz, 2H), 6.32 (s, 1H), 5.00 (s, 2H), 2.47 (t, $J = 7.6$ Hz, 2H), 1.66 (quint, $J = 7.6$ Hz, 2H), 1.40 (s, 4H), 0.91 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 139.2, 136.8, 134.3, 133.5, 131.4, 130.3, 128.7, 128.5, 128.1, 127.7, 127.6, 127.0, 125.6, 124.9, 121.9, 106.1, 47.4, 30.7, 26.4, 22.7, 14.1. GC-MS (EI, m/z): 365. HRMS calcd for $\text{C}_{27}\text{H}_{27}\text{N}+\text{H}^+$ 366.2222, found 366.2227.

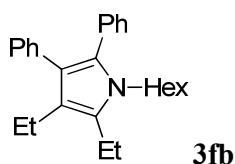


1-Benzyl-2,3-diphenyl-5-(trimethylsilyl)pyrrole (3la): As light yellow oil in 40% isolated yield. ^1H NMR (CDCl_3 , 300 MHz) 7.14-7.25 (m, 13H), 6.78 (d, $J = 6.8$ Hz, 2H), 6.74 (s, 1H), 5.13 (s, 2H), 0.14 (s, 9H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 139.7, 136.5, 136.0, 133.2, 131.1, 128.8, 128.5, 128.2, 128.0, 127.8, 127.6, 127.0, 125.9, 125.1, 123.6, 119.5, 50.7, 0.02. GC-MS (EI, m/z): 381. HRMS calcd for $\text{C}_{26}\text{H}_{27}\text{NSi}+\text{H}^+$ 382.1991, found 382.1993..

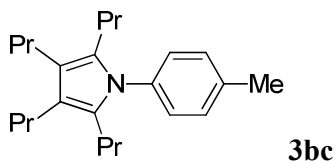


1-Hexyl-2,3,4,5-tetrapropylpyrrole (3bb): As light yellow oil in 60% isolated yield. ^1H NMR (CDCl_3 , 300 MHz) δ 3.61-3.67 (m, 2H), 2.41-2.47 (m, 4H), 2.27-2.33 (m, 4H), 1.31-1.55 (m, 16H), 0.88-0.99 (m, 15H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 127.1,

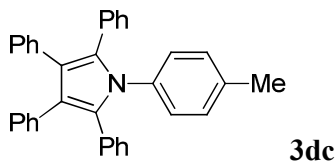
118.1, 43.8, 32.3, 31.6, 27.6, 27.3, 27.0, 25.7, 24.8, 22.7, 14.9, 14.6, 14.1. GC-MS (EI, m/z): 319. HRMS calcd for $C_{22}H_{41}N+H^+$ 320.3317, found 320.3315.



2,3-Diethyl-1-hexyl-4,5-diphenyl-pyrrole (3fb): As light yellow oil in 57% isolated yield. 1H NMR ($CDCl_3$, 300 MHz) δ 7.08-7.26 (m, 12H), 3.79 (t, $J = 7.8$ Hz, 2H), 2.70 (q, $J = 7.3$ Hz, 2H), 2.70 (q, $J = 7.3$ Hz, 2H), 1.47 (quint, $J = 7.3$ Hz, 2H), 1.27 (t, $J = 7.3$ Hz, 3H), 1.07-1.19 (m, 6H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.80 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.1, 133.8, 131.3, 130.9, 130.5, 129.6, 128.1, 127.7, 126.6, 125.0, 122.4, 120.1, 44.3, 31.6, 31.3, 26.6, 22.5, 18.2, 18.0, 16.8, 15.9, 14.1. GC-MS (EI, m/z): 359. HRMS calcd for $C_{26}H_{33}N+Na^+$ 386.2511, found 382.2505

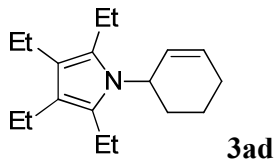


2,3,4,5-Tetrapropyl-1-(p-tolyl) -pyrrole (3bc):^[3] As yellow oil in 81% isolated yield. 1H NMR ($CDCl_3$, 300 MHz) δ 7.07-7.21 (m, 4H), 2.41 (s, 3H), 2.26-2.40 (m, 8H), 1.50-1.59 (m, 4H), 1.14-1.27 (m, 4H), 0.99 (t, $J = 7.2$ Hz, 6H), 0.71 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.2, 137.0, 129.3, 129.0, 128.8, 118.3, 27.5, 27.2, 25.5, 24.1, 21.2, 14.8, 14.3. GC-MS (EI, m/z): 325. HRMS calcd for $C_{23}H_{35}N+H^+$ 326.2848, found 326.2851.

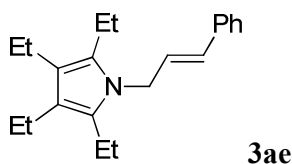


2,3,4,5-Tetraphenyl-1-(p-tolyl) -pyrrole (3dc):^[3] As yellow solid in 58% isolated yield. M.p. 246-248 °C. 1H NMR ($CDCl_3$, 300 MHz) δ 7.82-7.31 (m, 24H), 2.28 (s,

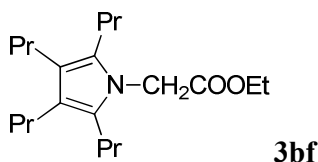
3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 136.6, 136.1, 135.5, 132.5, 131.8, 131.6, 131.3, 129.1, 129.0, 127.7, 127.6, 126.5, 125.5, 122.9, 21.2. GC-MS (EI, m/z): 461. HRMS calcd for $\text{C}_{35}\text{H}_{27}\text{N}+\text{H}^+$ 462.2222, found 462.2220.



1-(Cyclohex-2-en-1-yl)-2,3,4,5-tetraethylpyrrole (3ad): As yellow oil in 43% isolated yield. ^1H NMR (CDCl_3 , 400 MHz) δ 5.79 (s, 2H), 4.68-4.73 (m, 1H), 2.60 (br, 4H), 2.40 (q, $J = 7.8$ Hz, 4H), 1.70-2.14 (m, 6H), 1.13 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 131.1, 128.6, 128.0, 52.4, 31.4, 24.7, 22.9, 18.3, 17.9, 17.0, 16.4. GC-MS (EI, m/z): 259. HRMS calcd for $\text{C}_{18}\text{H}_{29}\text{N}+\text{H}^+$ 260.2378, found 260.2373.

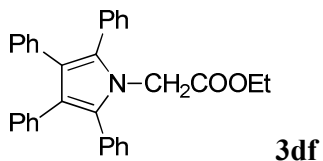


1-Cinnamyl-2,3,4,5-tetraethylpyrrole (3ae): As yellow oil in 52% isolated yield. ^1H NMR (CDCl_3 , 400 MHz) δ 7.20-7.30 (m, 5H), 6.10-6.28 (m, 2H), 4.55 (d, $J = 4.8$ Hz, 2H), 2.55 (q, $J = 7.2$ Hz, 4H), 2.42 (q, $J = 7.2$ Hz, 4H), 1.13 (t, $J = 7.6$ Hz, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 136.9, 130.5, 128.7, 128.6, 127.8, 127.6, 126.5, 119.4, 45.3, 17.9, 17.3, 16.1. GC-MS (EI, m/z): 295. HRMS calcd for $\text{C}_{21}\text{H}_{29}\text{N}+\text{H}^+$ 296.2378, found 296.2384.

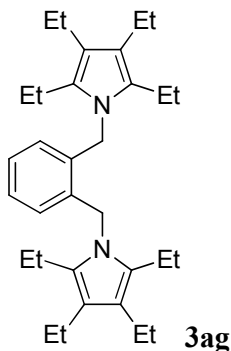


Ethyl 2-(2,3,4,5-tetrapropyl-1H-pyrrol-1-yl)acetate (3bf): As yellow oil in 74% isolated yield. ^1H NMR (CDCl_3 , 400 MHz) δ 4.47 (s, 2H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.40 (t, $J = 8.0$ Hz, 4H), 2.31 (t, $J = 8.0$ Hz, 4H), 1.38-1.51 (m, 8H), 1.26 (t, $J = 7.1$

Hz, 3H), 0.87-0.97 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.1, 127.8, 118.9, 61.4, 45.4, 27.5, 27.1, 25.5, 24.2, 14.7, 14.4, 14.3. GC-MS (EI, m/z): 321. HRMS calcd for $\text{C}_{16}\text{H}_{27}\text{NO}_2 + \text{H}^+$ 322.2746, found 322.2750.



Ethyl 2-(2,3,4,5-tetraphenyl-1H-pyrrol-1-yl)acetate (3df): As light yellow solid in 62% isolated yield. M.p. 168-170 °C. ^1H NMR (CDCl_3 , 300 MHz) 6.97-7.34 (m, 20 H), 4.50 (s, 2H), 4.04 (q, $J = 7.2$ Hz, 2H), 1.09 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 169.5, 135.4, 132.5, 132.0, 131.6, 130.9, 128.4, 127.8, 127.5, 125.3, 122.6, 61.4, 47.0, 14.2. GC-MS (EI, m/z): 457. HRMS calcd for $\text{C}_{32}\text{H}_{27}\text{NO}_2 + \text{H}^+$ 458.2120, found 458.2124.



1,2-Bis((2,3,4,5-tetraethyl-pyrrol-1-yl)methyl)benzene (3ag): As light yellow oil in 39% isolated yield. ^1H NMR (CDCl_3 , 400 MHz) δ 7.06-7.08 (m, 2H), 6.26-6.29 (m, 2H), 4.95 (s, 4H), 2.38-2.47 (m, 16H), 1.14 (t, $J = 7.3$ Hz, 12H), 0.99 (t, $J = 7.8$ Hz, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 136.0, 128.8, 127.4, 125.9, 119.9, 43.9, 18.0, 17.4, 16.1. GC-MS (EI, m/z): 460. HRMS calcd for $\text{C}_{32}\text{H}_{48}\text{N}_2 + \text{H}^+$ 461.3896, found 461.3893.

XPS Measurement

X-ray photoelectron spectra(XPS) were measured with a Quantum 2000 spectrometer with monochromatized Al K α X-rays ($h\nu=1486.7$ eV) operating at 150 W. The original peak of the sample was calibrated by the BE (284.8 eV) of the C_{1s} to correct the binding energies of the other elements.

XPS Analysis The XPS spectrum (Figure 1) displays a single Cu 2p_{3/2} at 932.9 eV. So the presence of Cu²⁺ can be discarded. It is, however, difficult to differentiate between Cu⁰ and Cu^I on the basis of only binding energy of Cu 2p_{3/2} due to the close proximity of their binding energies (ca. 932.0-933.0 eV)^[4]. It can be clearly observed from the Cu LMM Auger spectra (Figure 2) that shows a Cu LMM peak at 568.4 eV. According to the literature, kinetic energy of Cu LMM equals $h\nu$ (1486.7) minus binding energy, so the results is 918.3 eV. Considering binding energy of Cu 2p_{3/2} and kinetic energy of Cu LMM together, the brown solid we got after the reaction must be metallic copper.^[5]

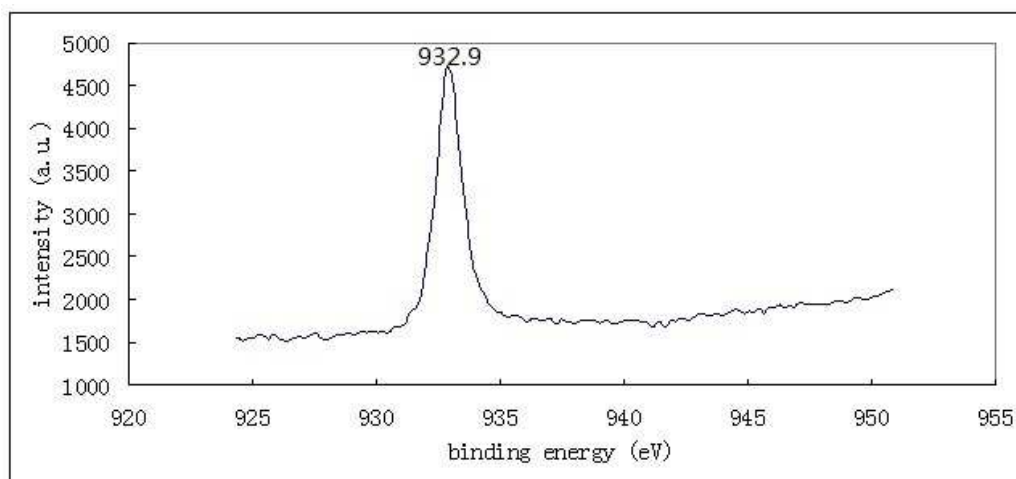


Figure 1. XPS of Cu 2p_{3/2}

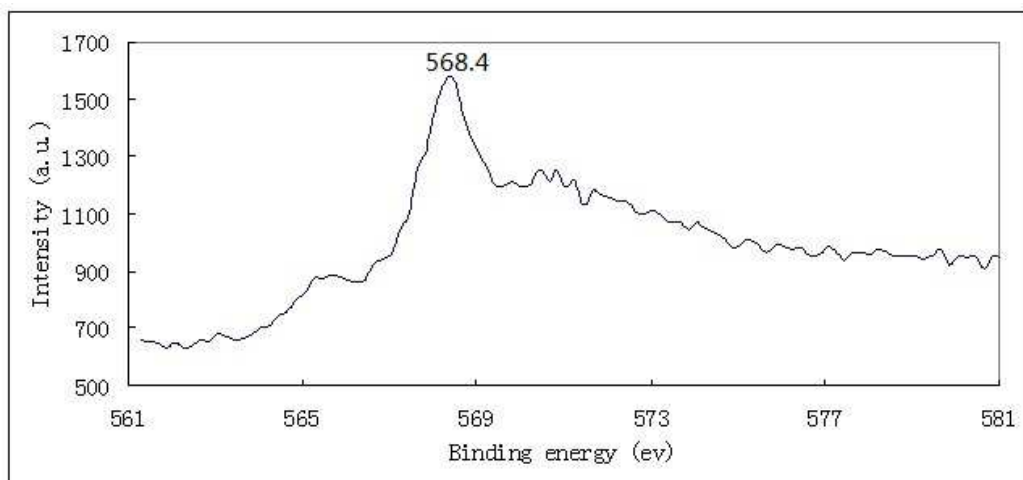
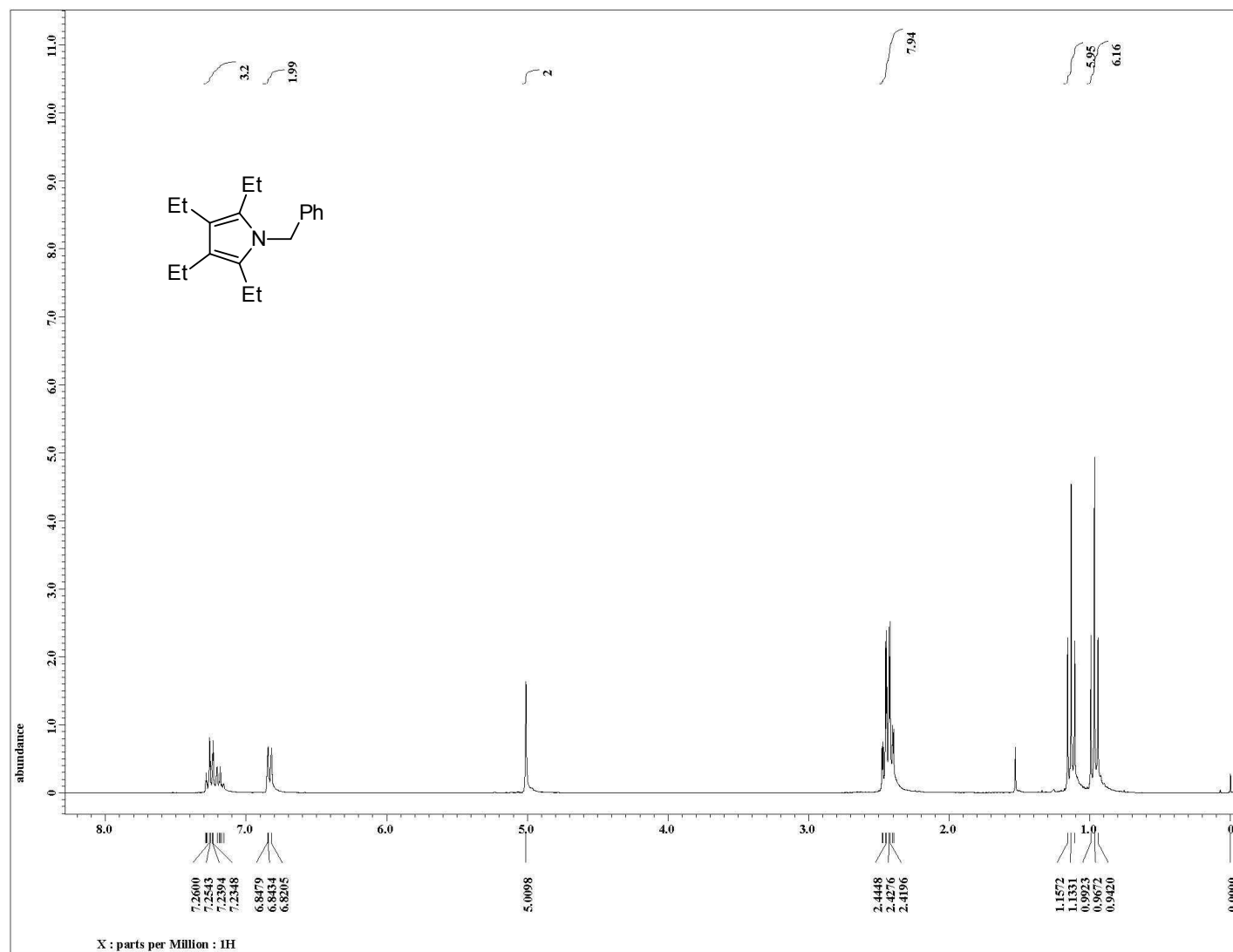


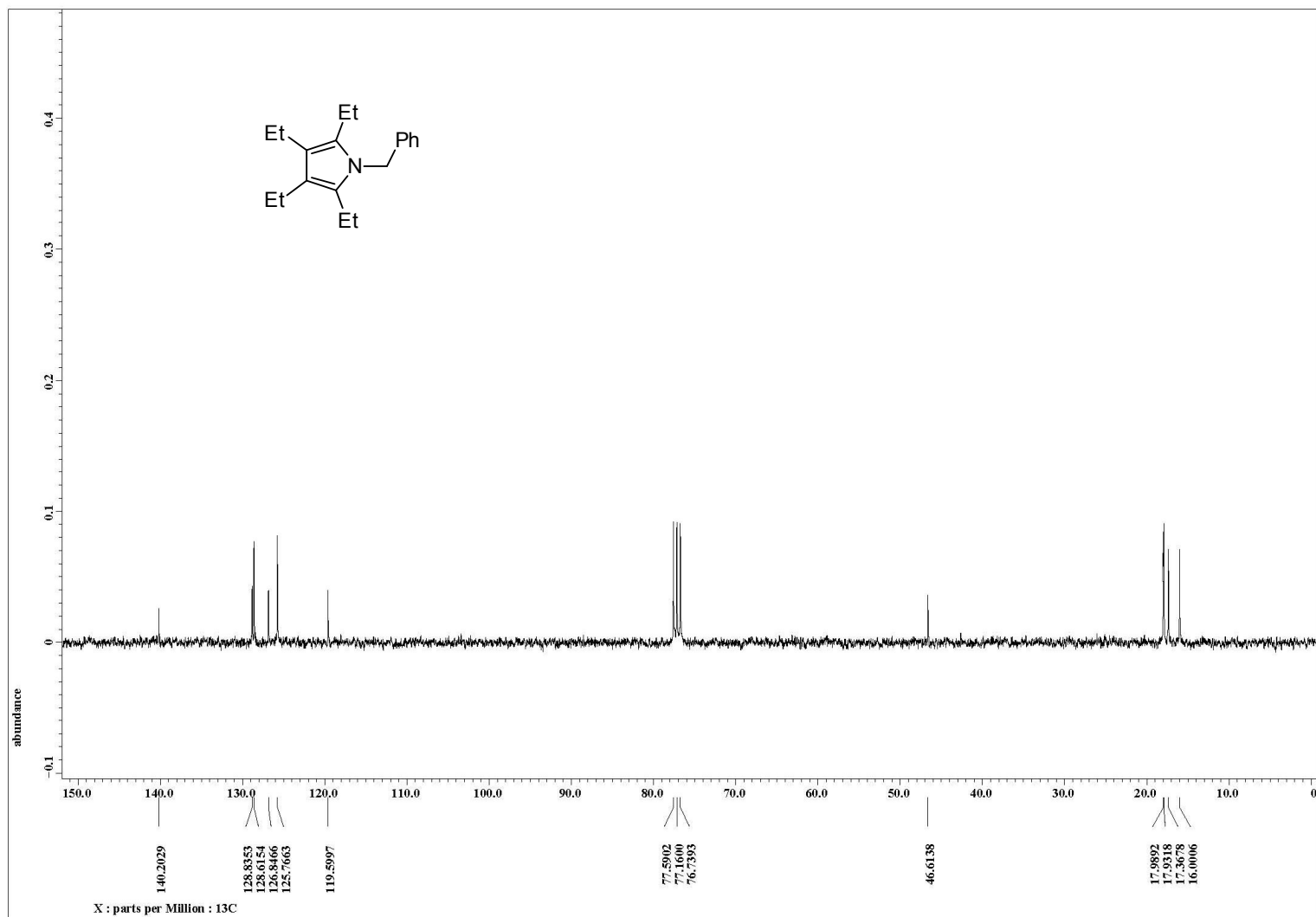
Figure 2. XPS of Cu LMM

References:

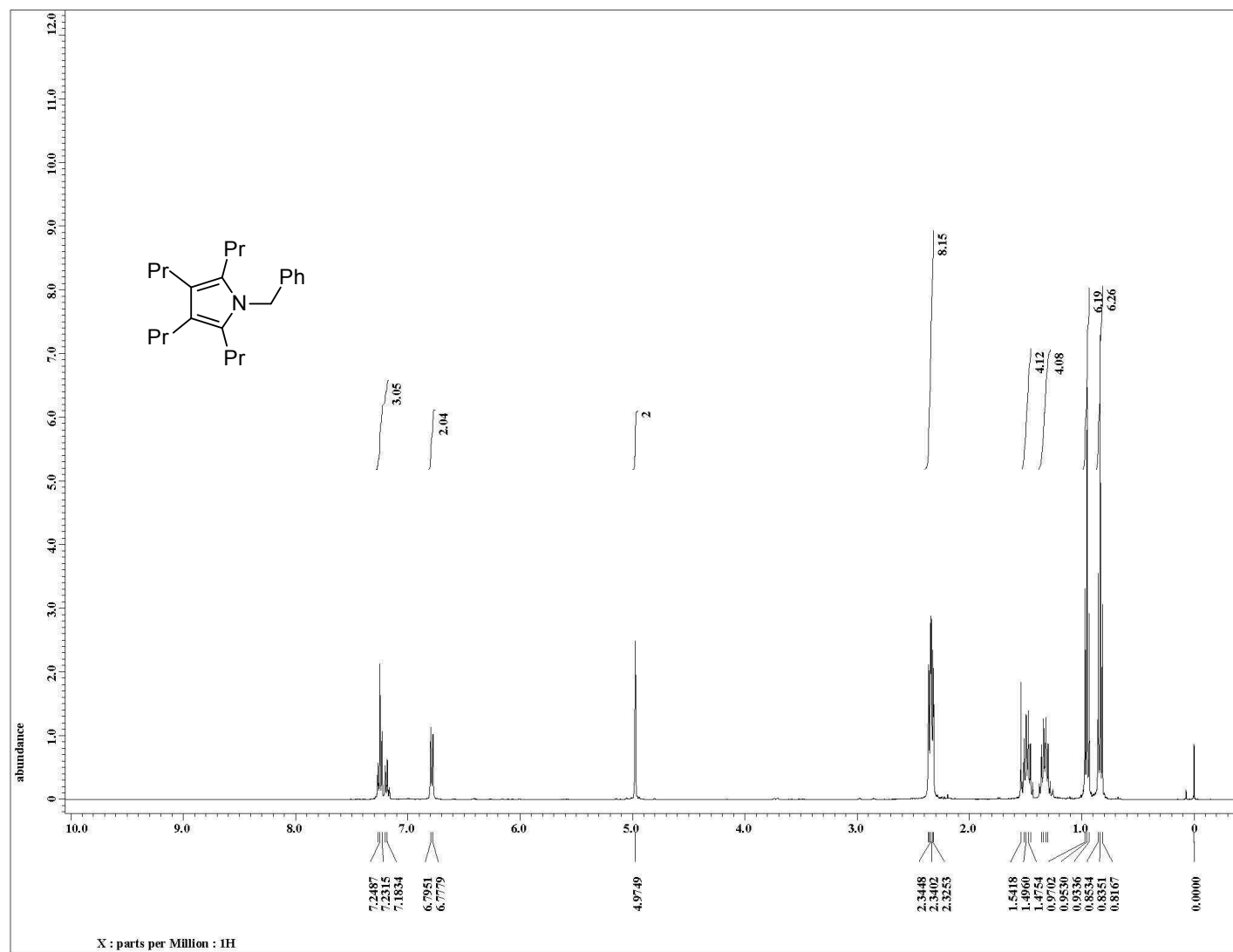
- [1] (a) Ju, Y. H.; Kumar, D.; Varma, R. S. *J. Org. Chem.* **2006**, *71*, 6697; (b) Asano, K.; Matsubara, S. *Org. Lett.* **2010**, *12*, 4988.
- [2] Liliane, V. Q.; Yen, V. Q. *Tetrahedron Lett.* **1978**, *47*, 4679
- [3] Liao, Q.; Zhang, L.; Wang, F.; Xi, C. *Eur. J. Org. Chem.* **2010**, 5426
- [4] Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-Ray Photoelectron Spectroscopy ; Physical Electronics Division, 1979, P. 82.
- [5] Briggs, D.; Seah, M. P. Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy: John Wiley & Son Ltd, 1983, P. 496.



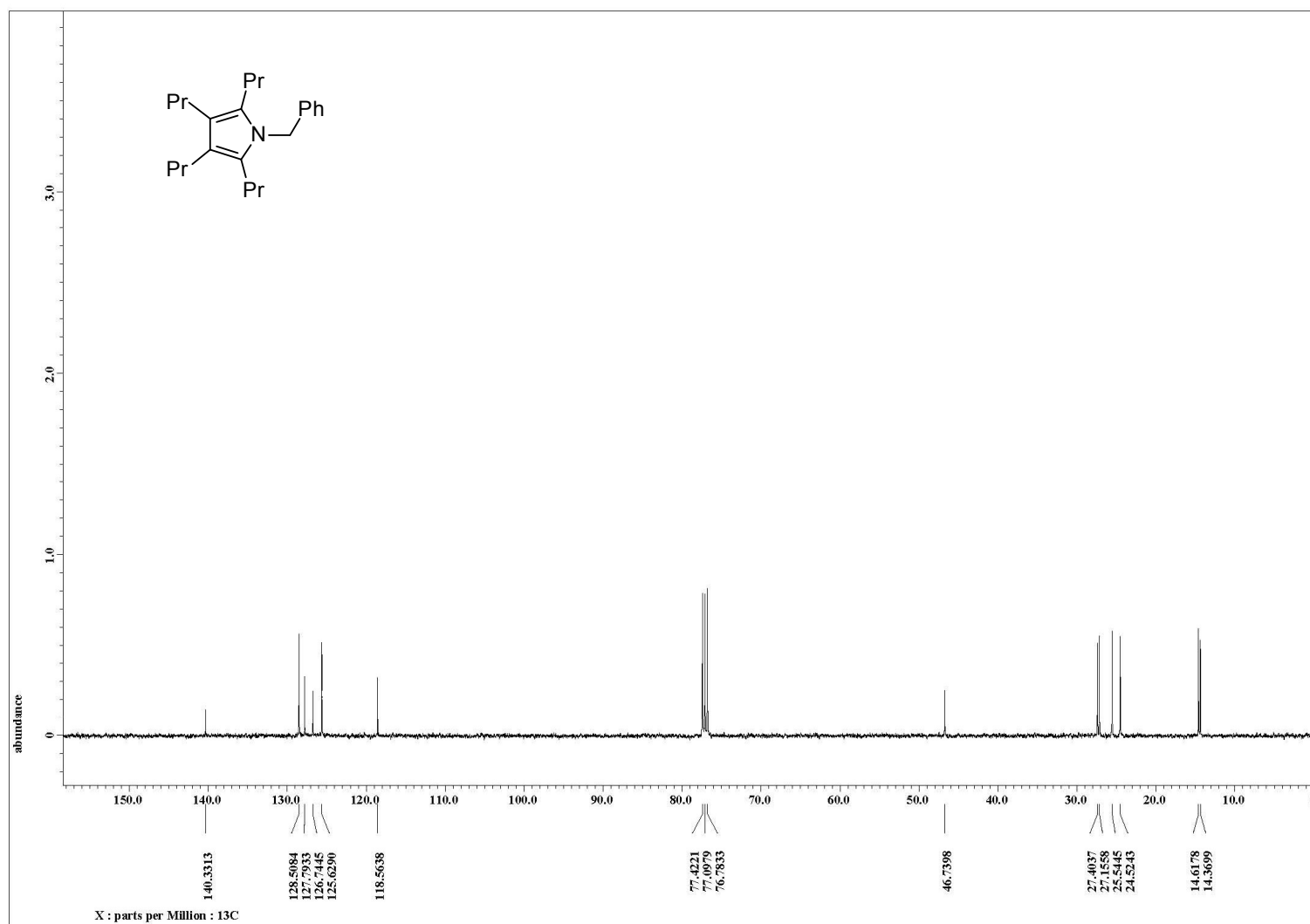
¹H NMR of Compound **3aa**



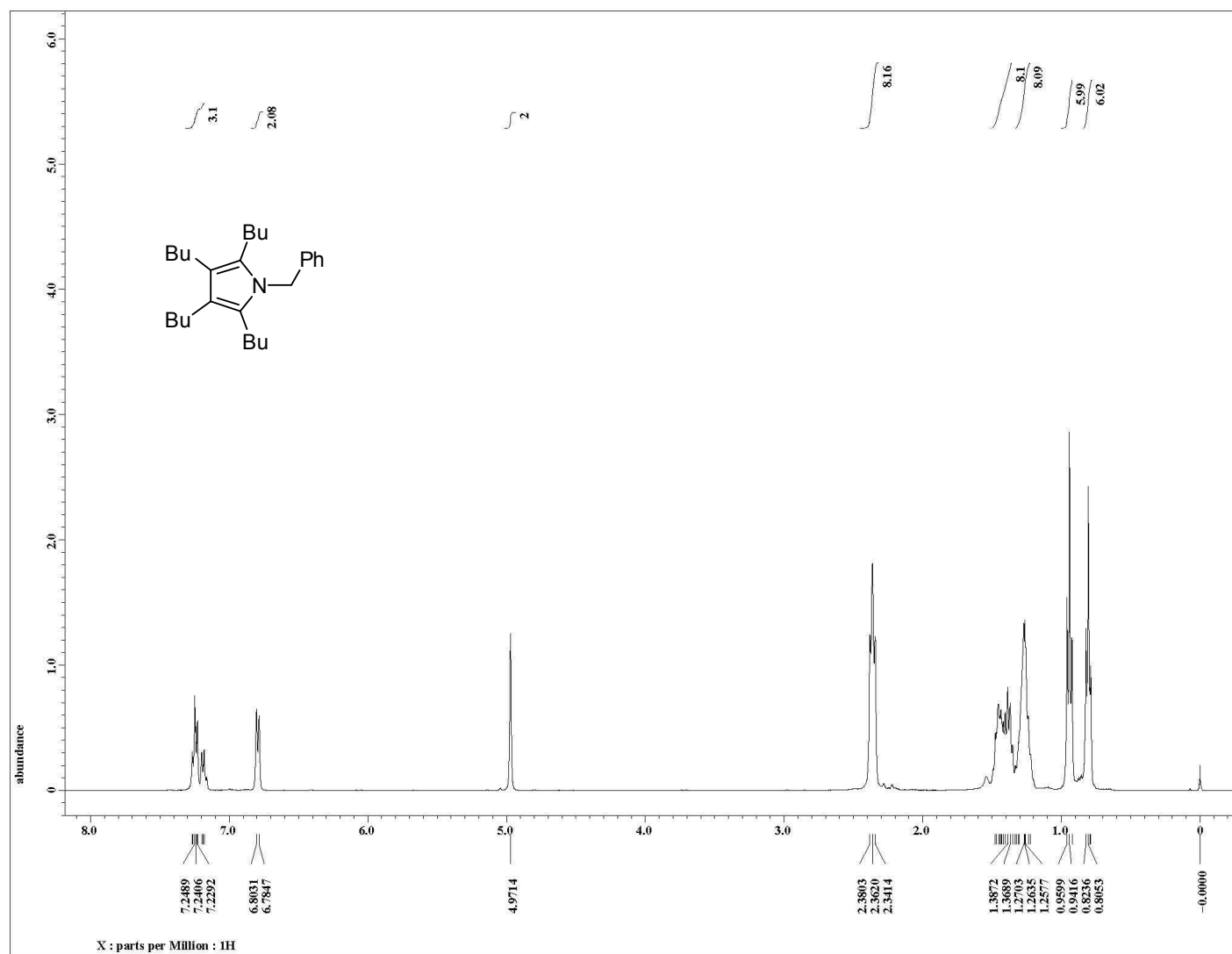
^{13}C NMR of Compound **3aa**



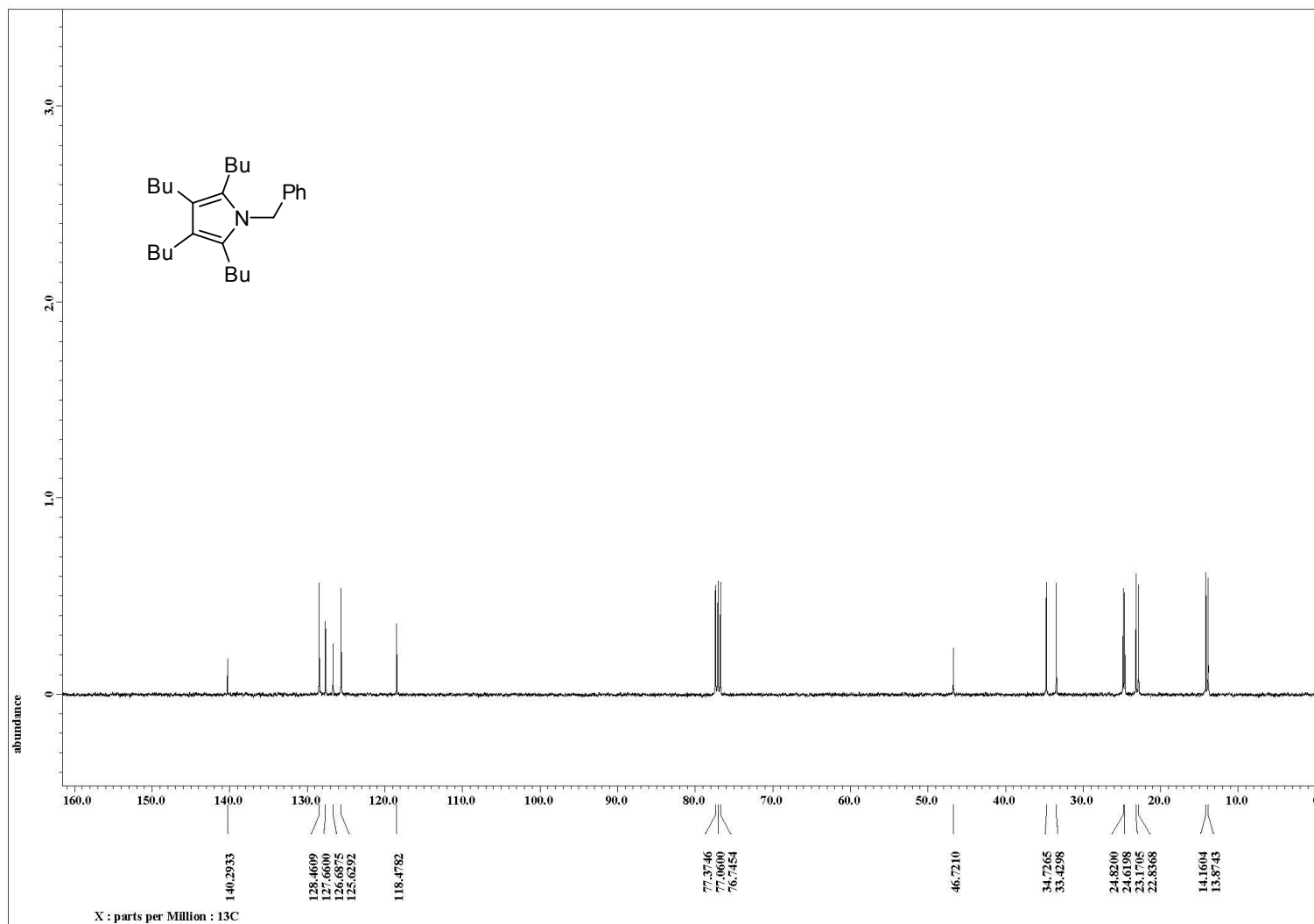
¹H NMR of compound **3ba**



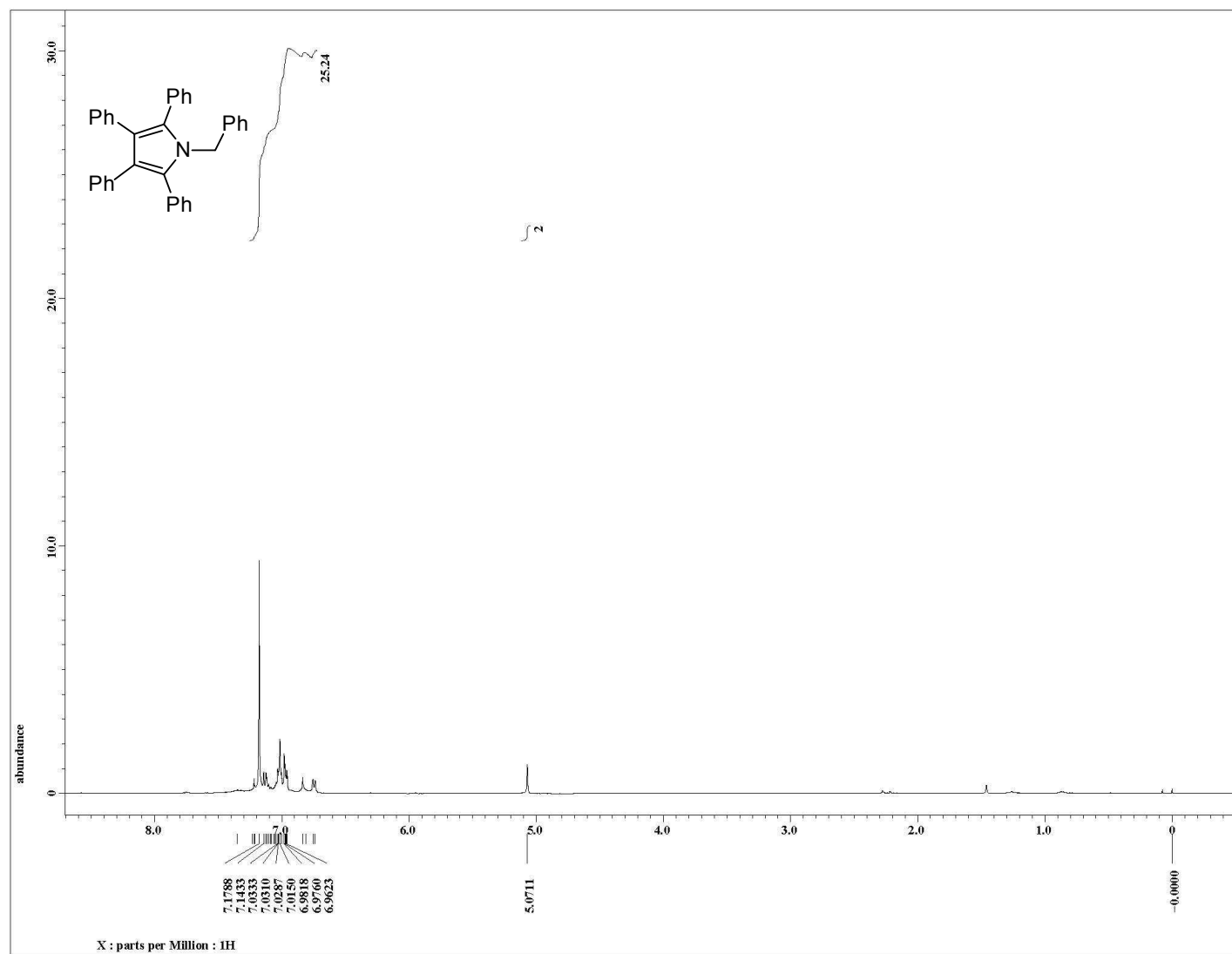
^{13}C NMR of compound **3ba**



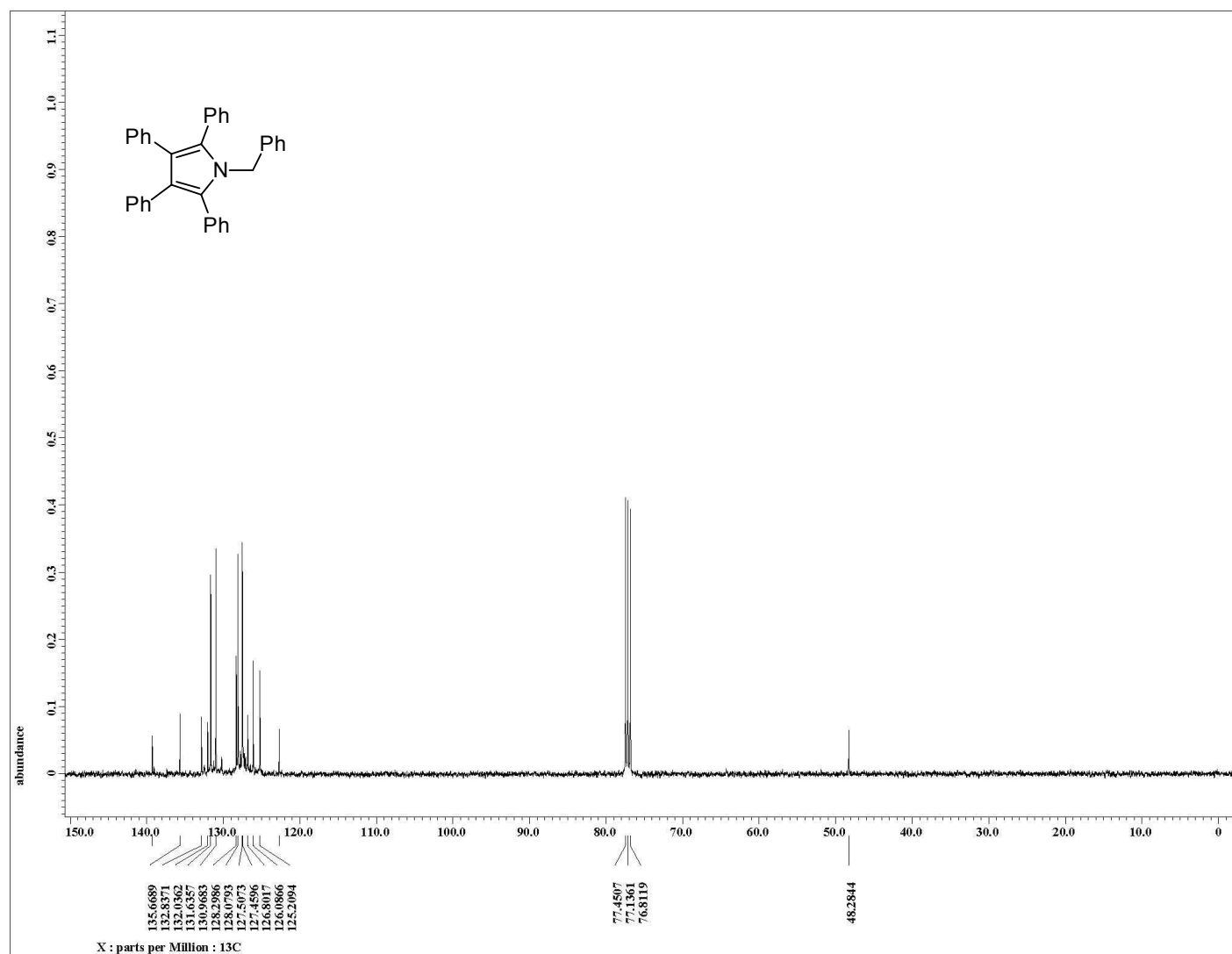
¹H NMR of compound **3ca**



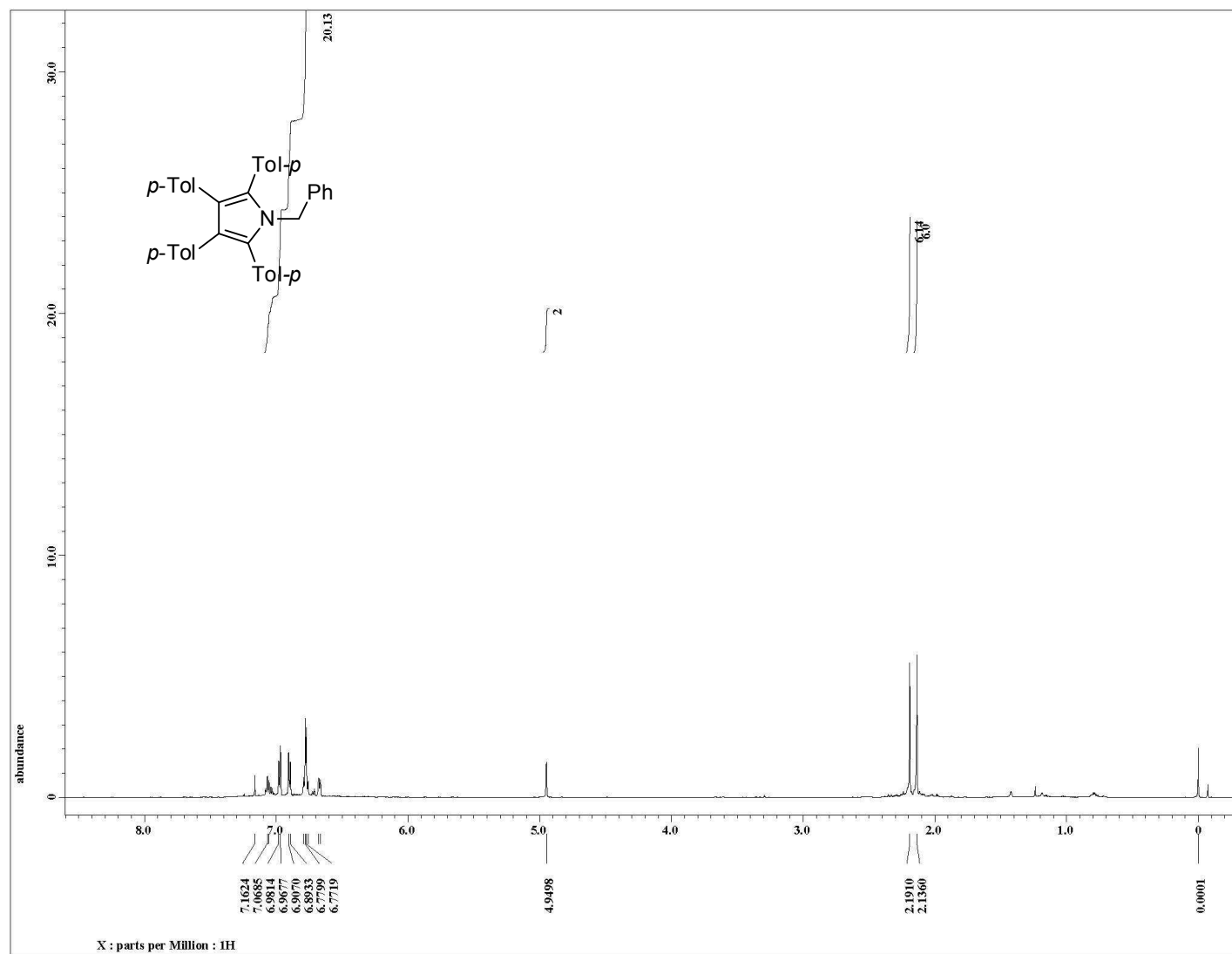
^{13}C NMR of compound **3ca**



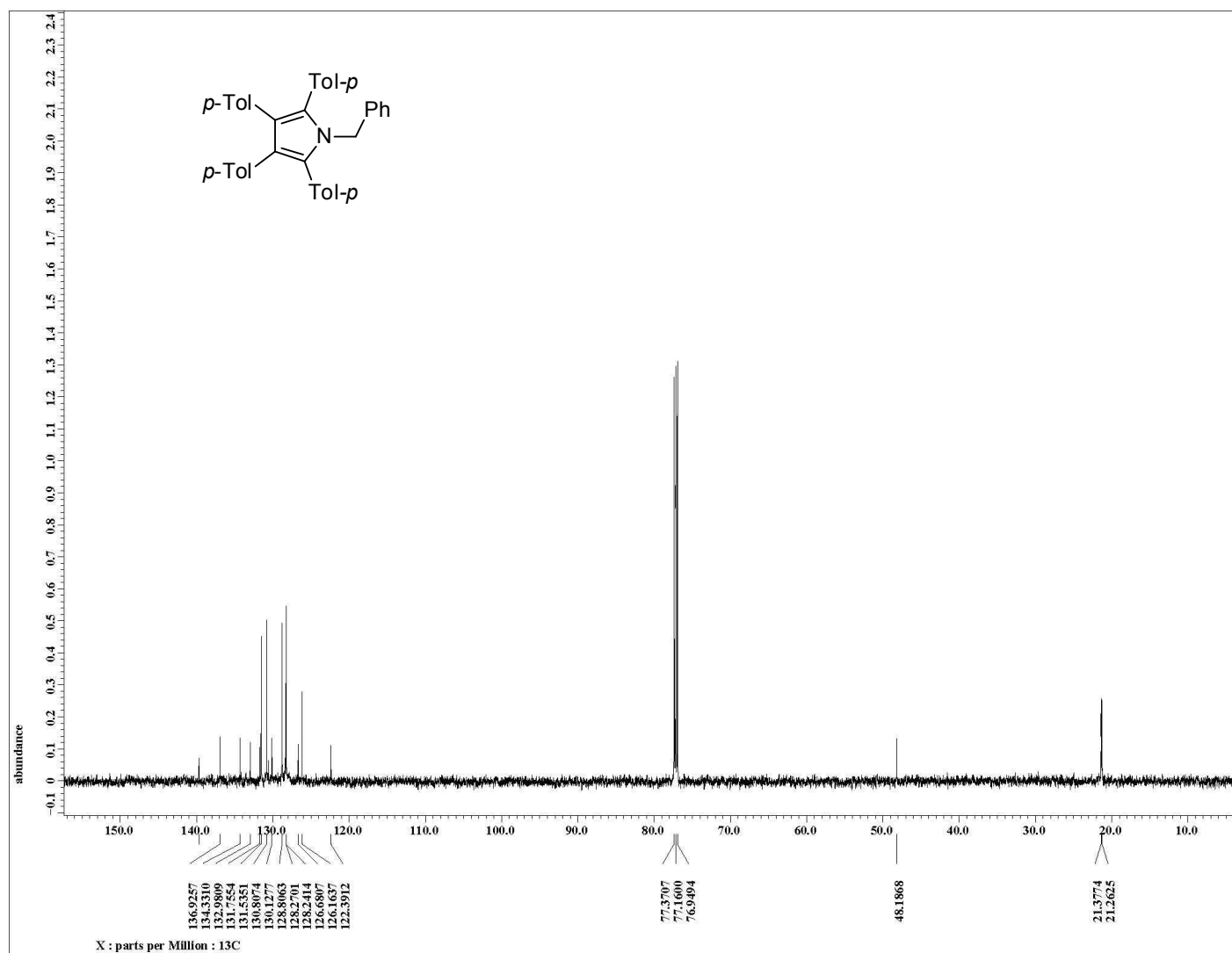
¹H NMR of compound **3da**
S20



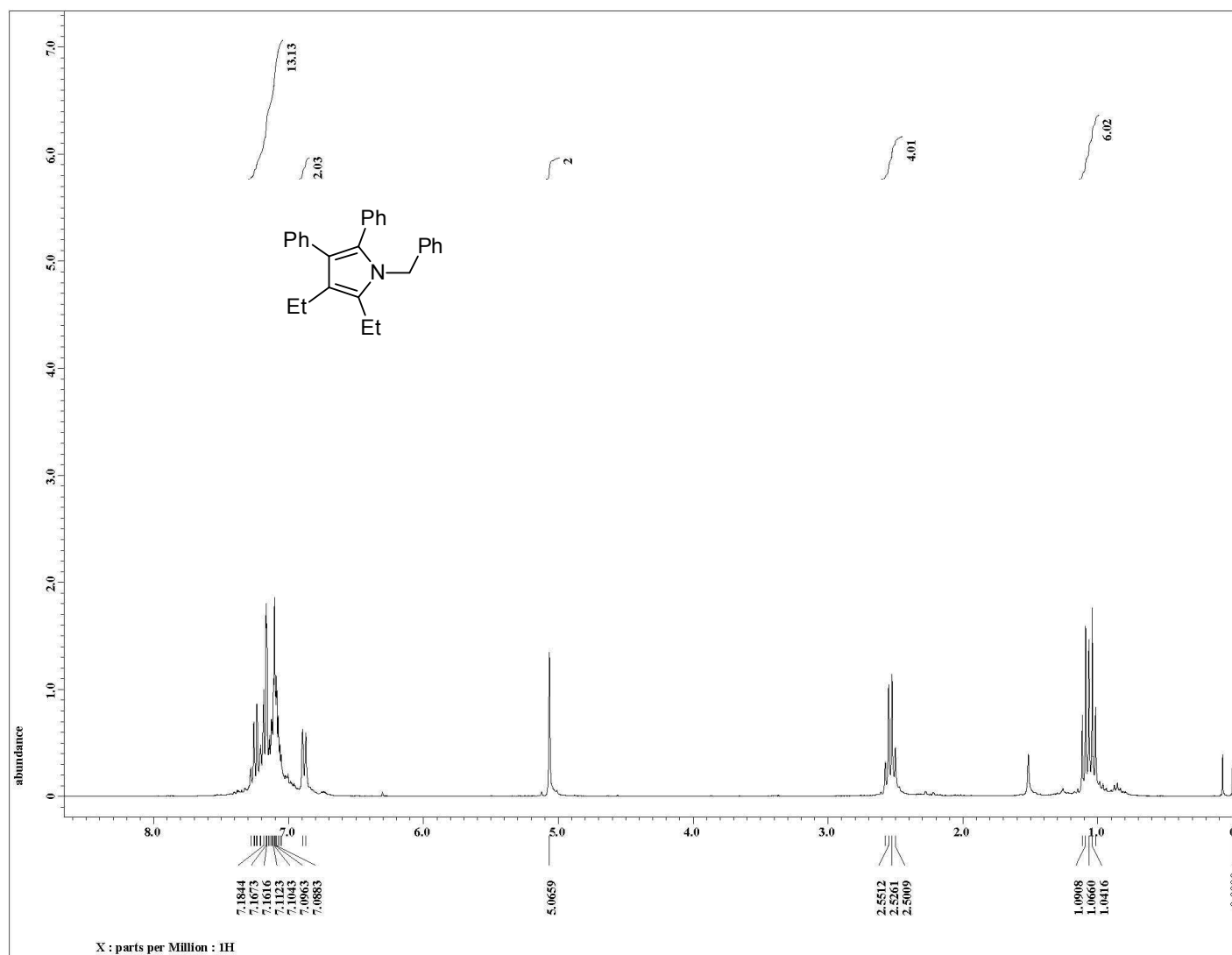
^{13}C NMR of compound **3da**



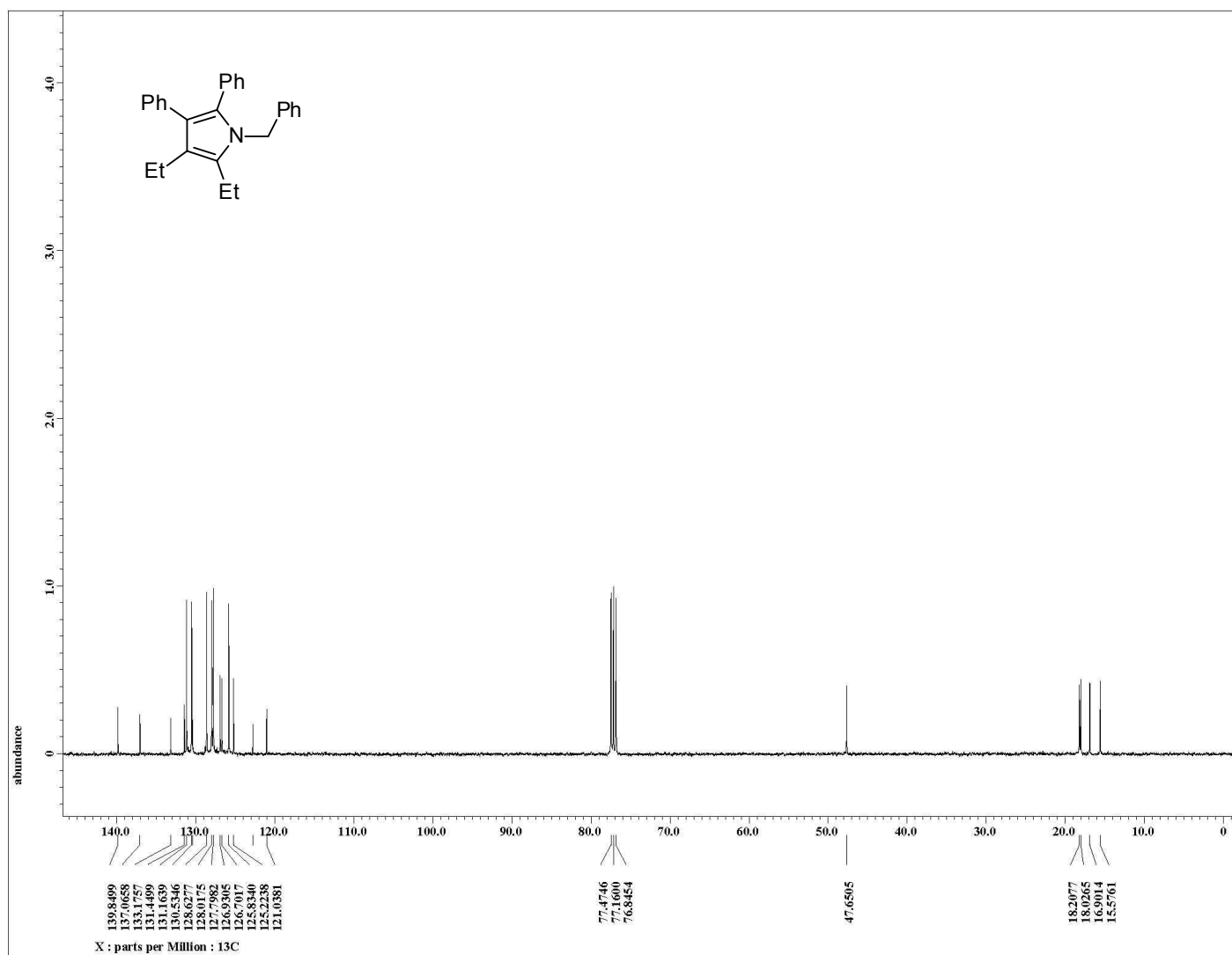
¹H NMR of compound **3ea**
S22



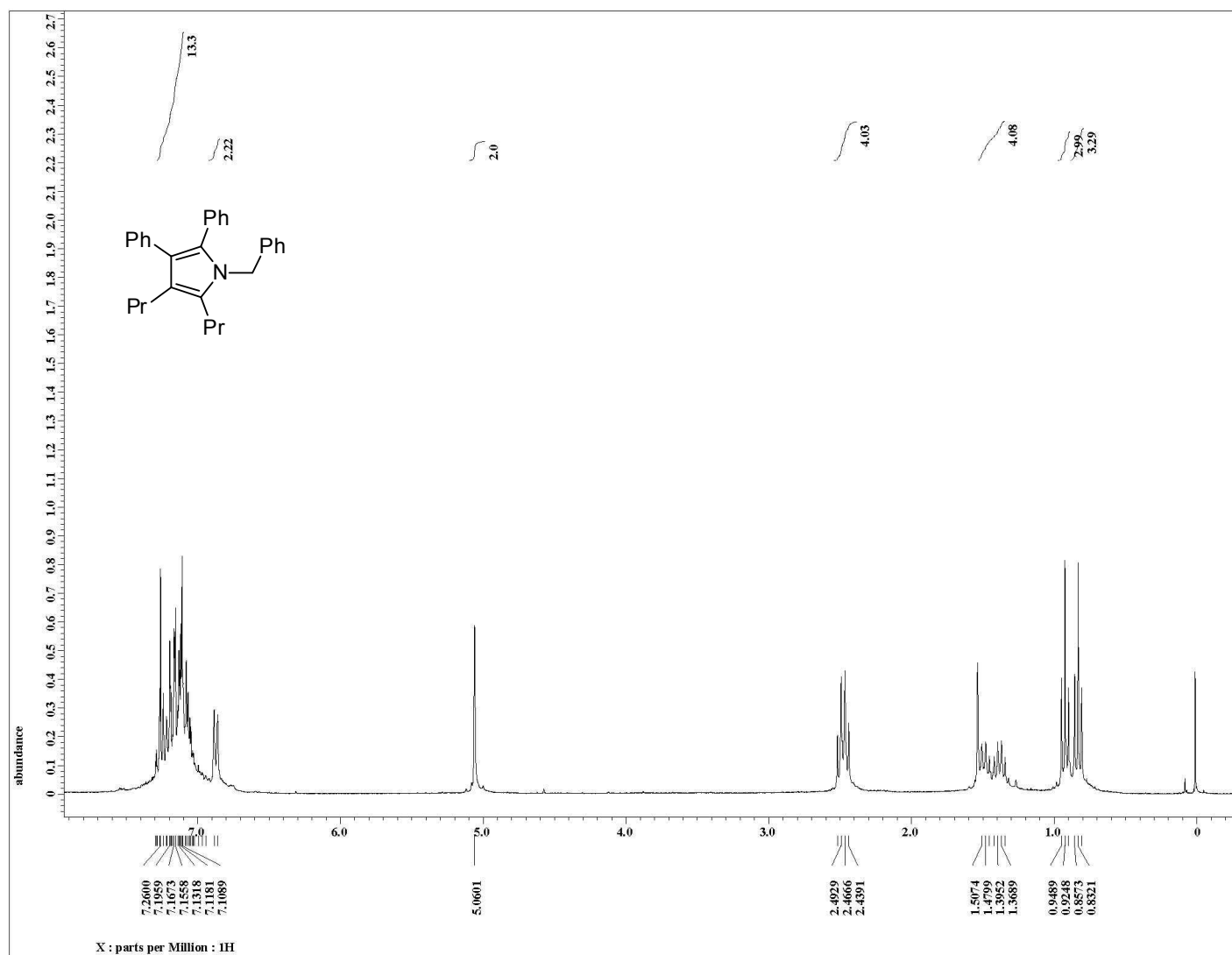
¹³C NMR of compound **3ea**



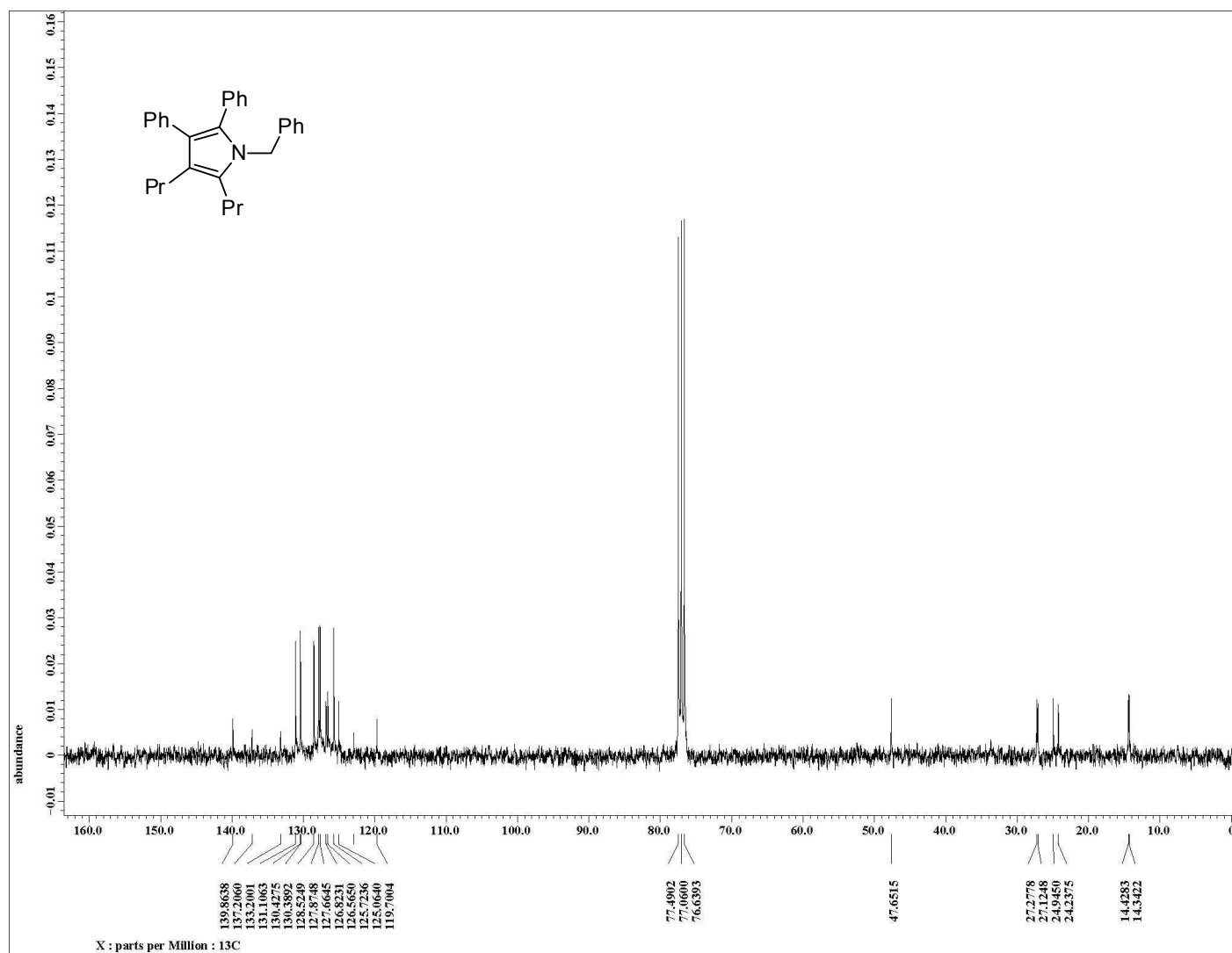
¹H NMR of compound **3fa**



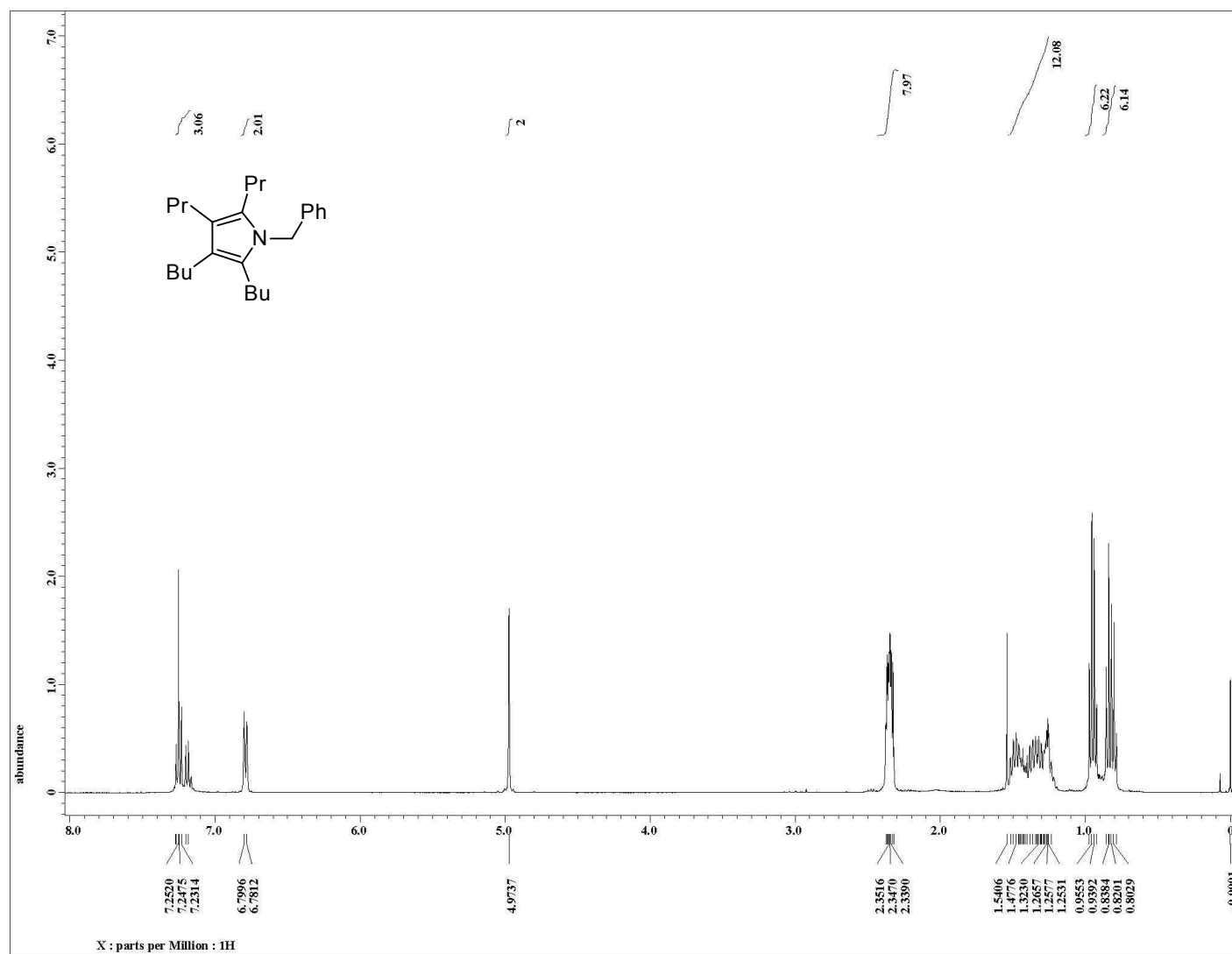
^{13}C NMR of compound **3fa**



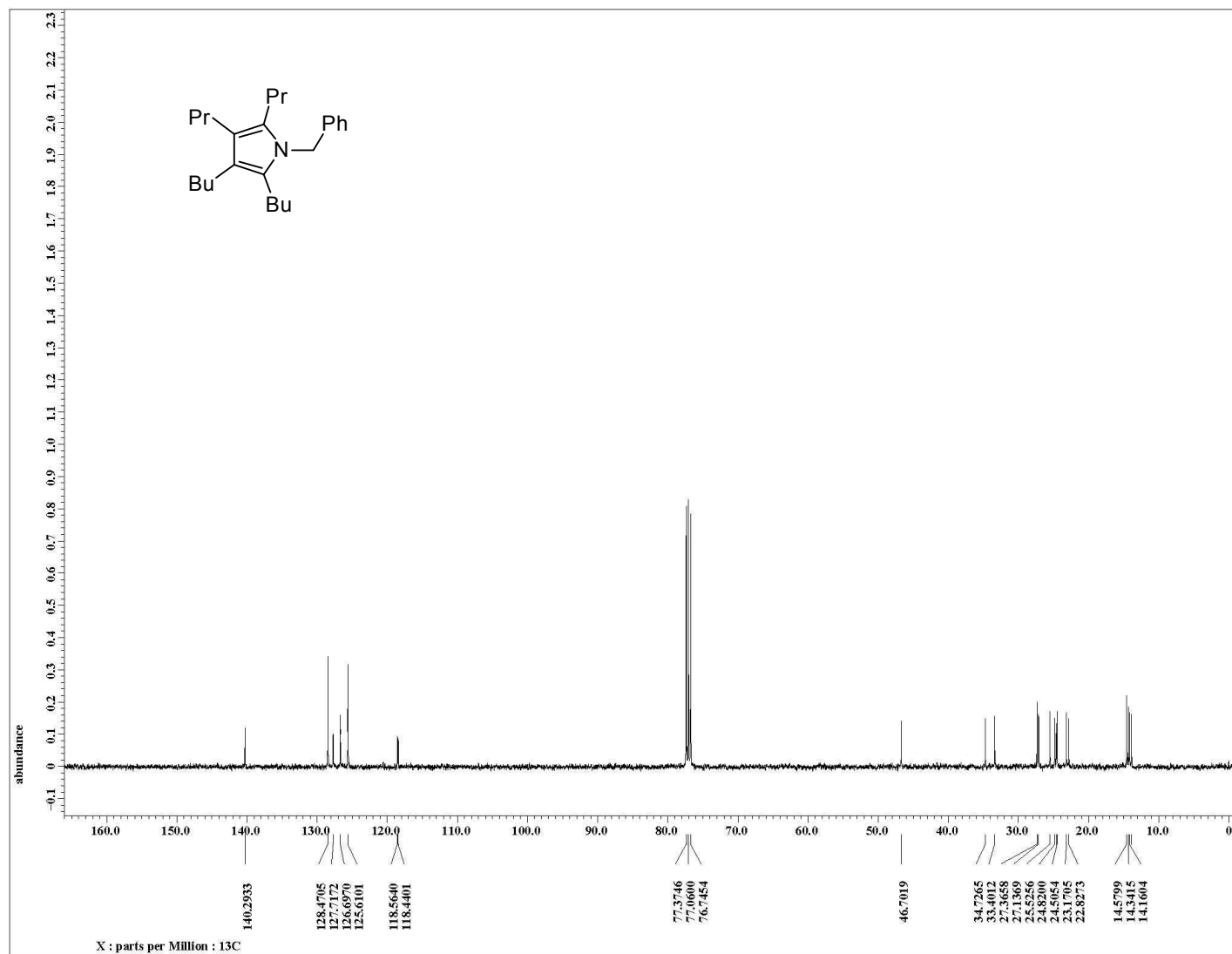
¹H NMR of compound **3ga**



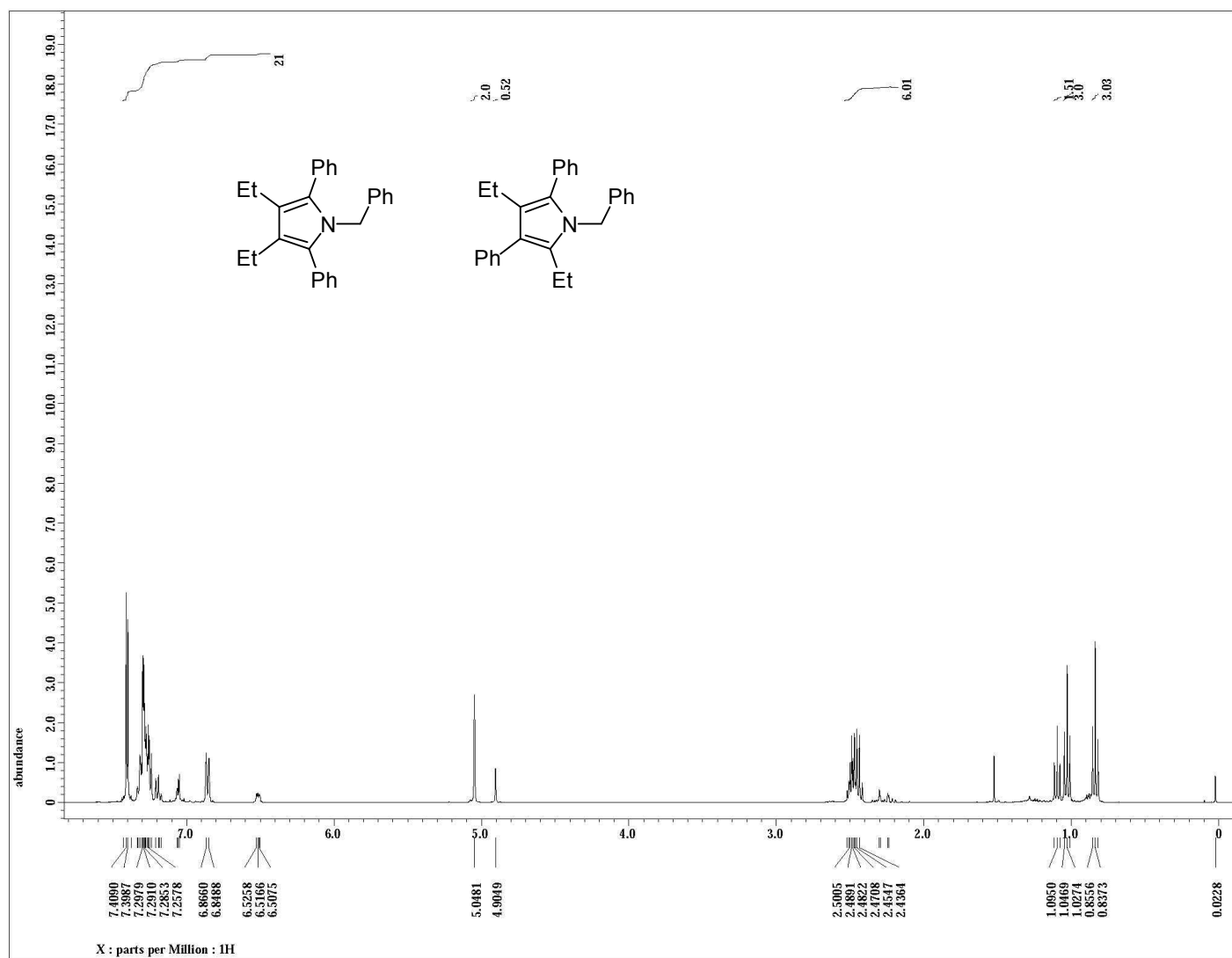
^{13}C NMR of compound **3ga**



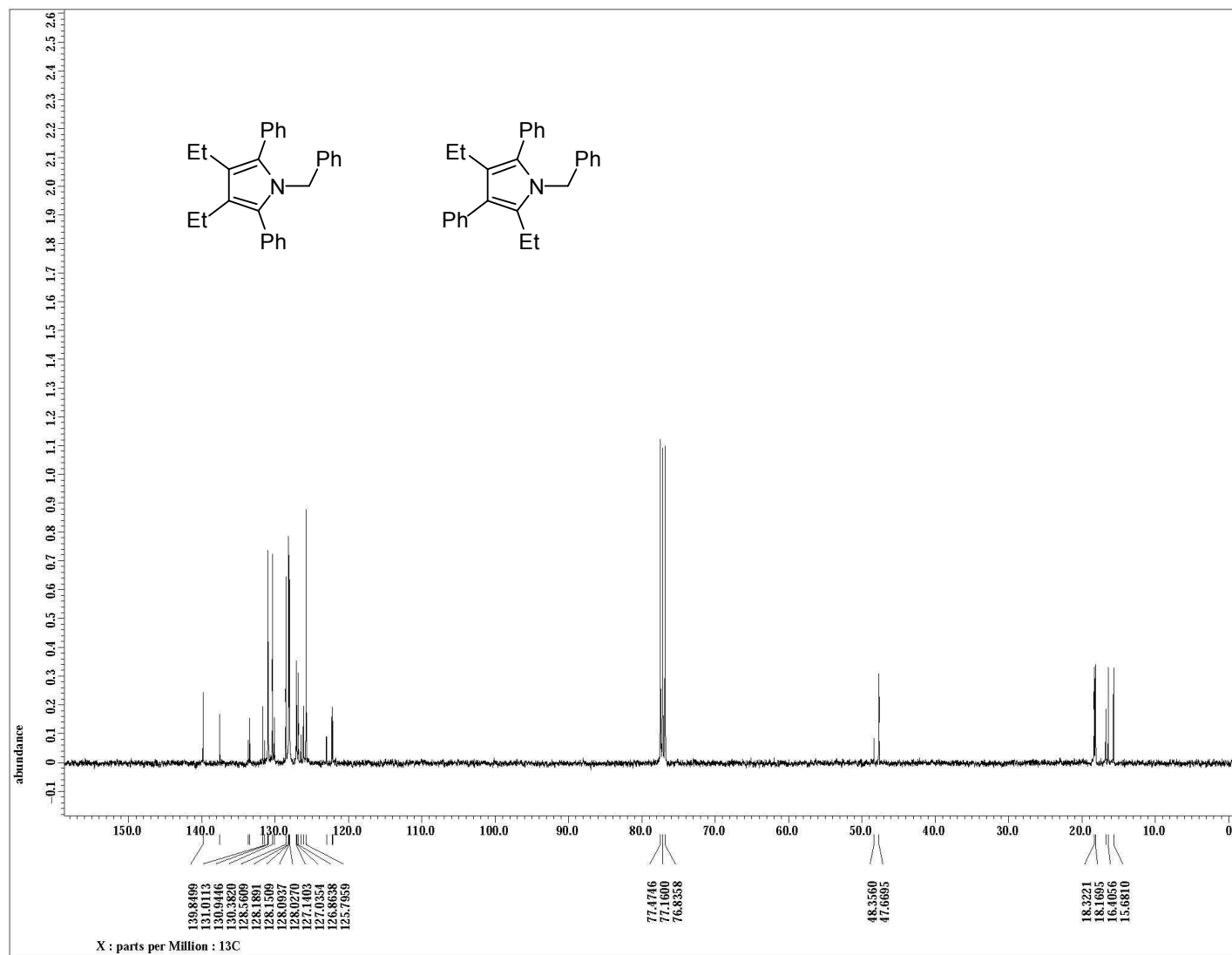
¹H NMR of compound **3ha**



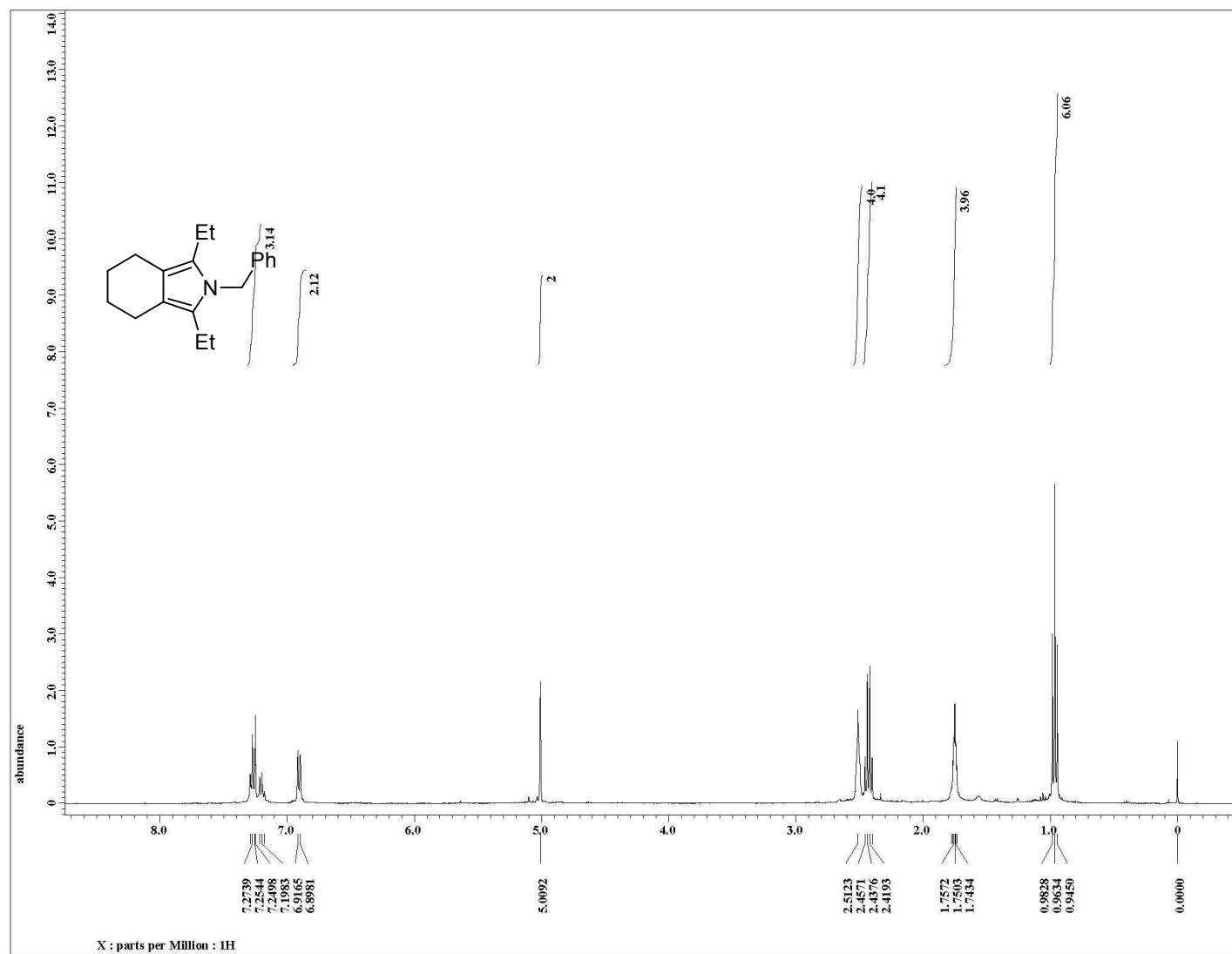
^{13}C NMR of compound **3ha**
S29



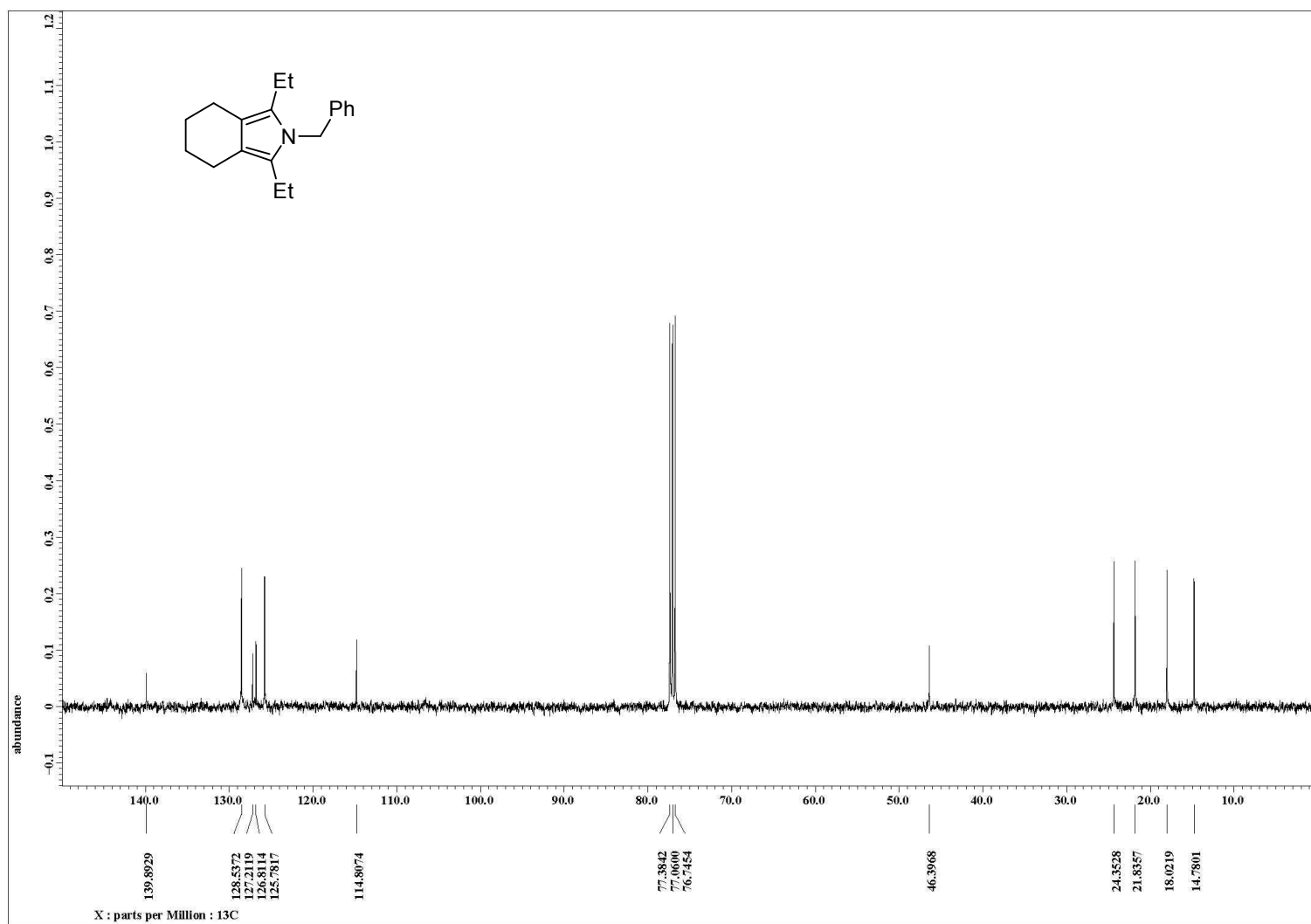
¹H NMR of compound **3ia**



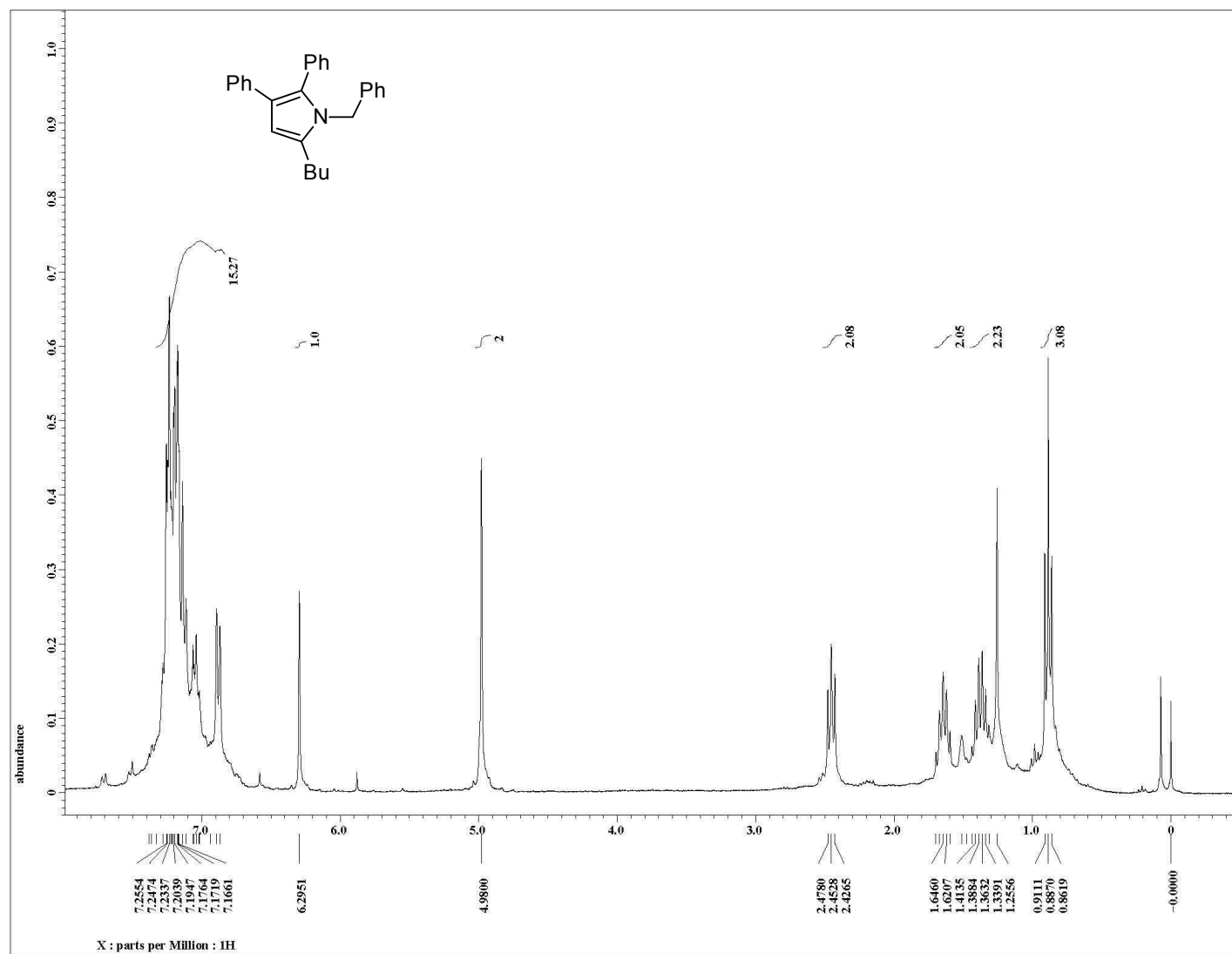
¹³C NMR of compound **3ia**
S31



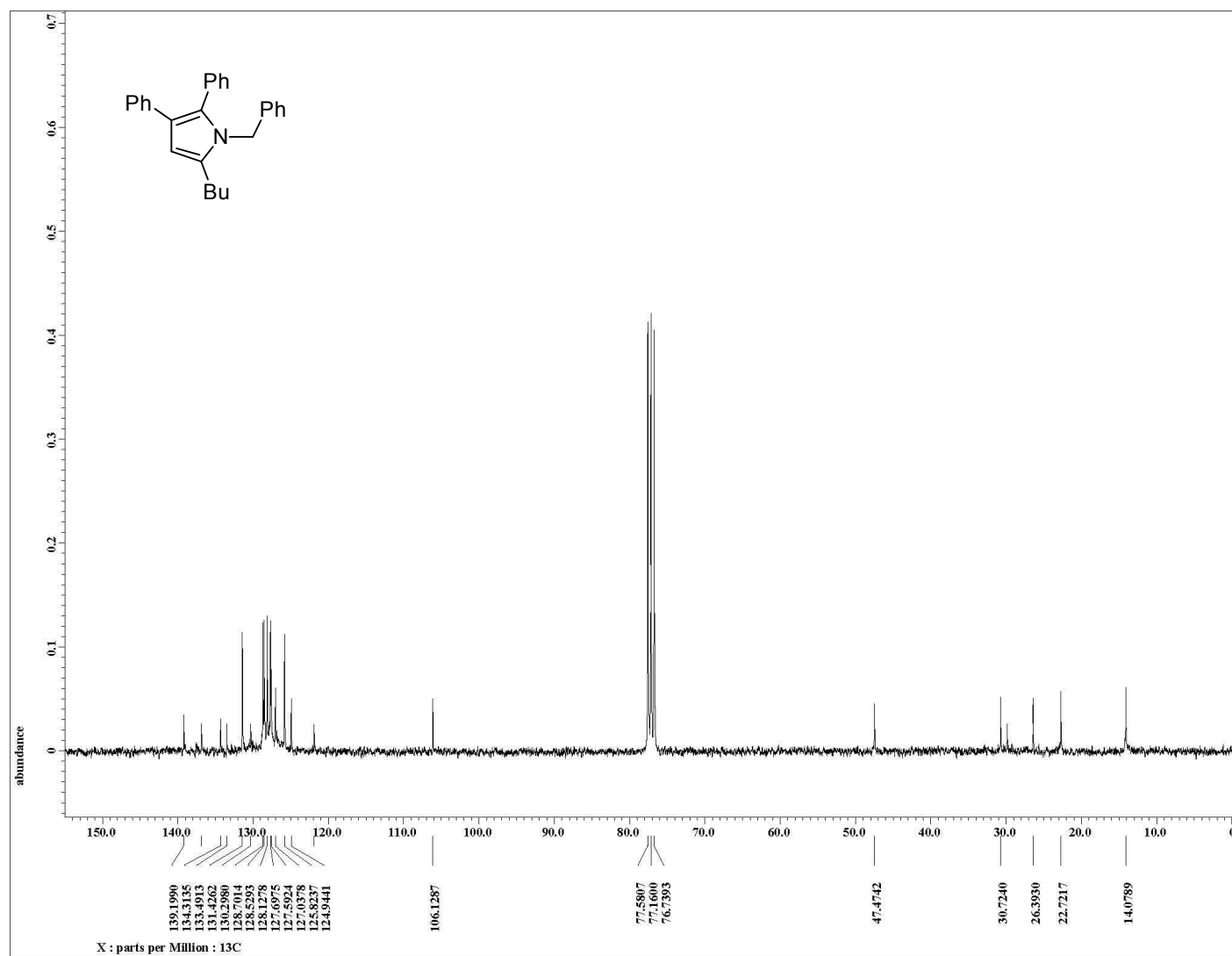
¹H NMR of compound **3ja**



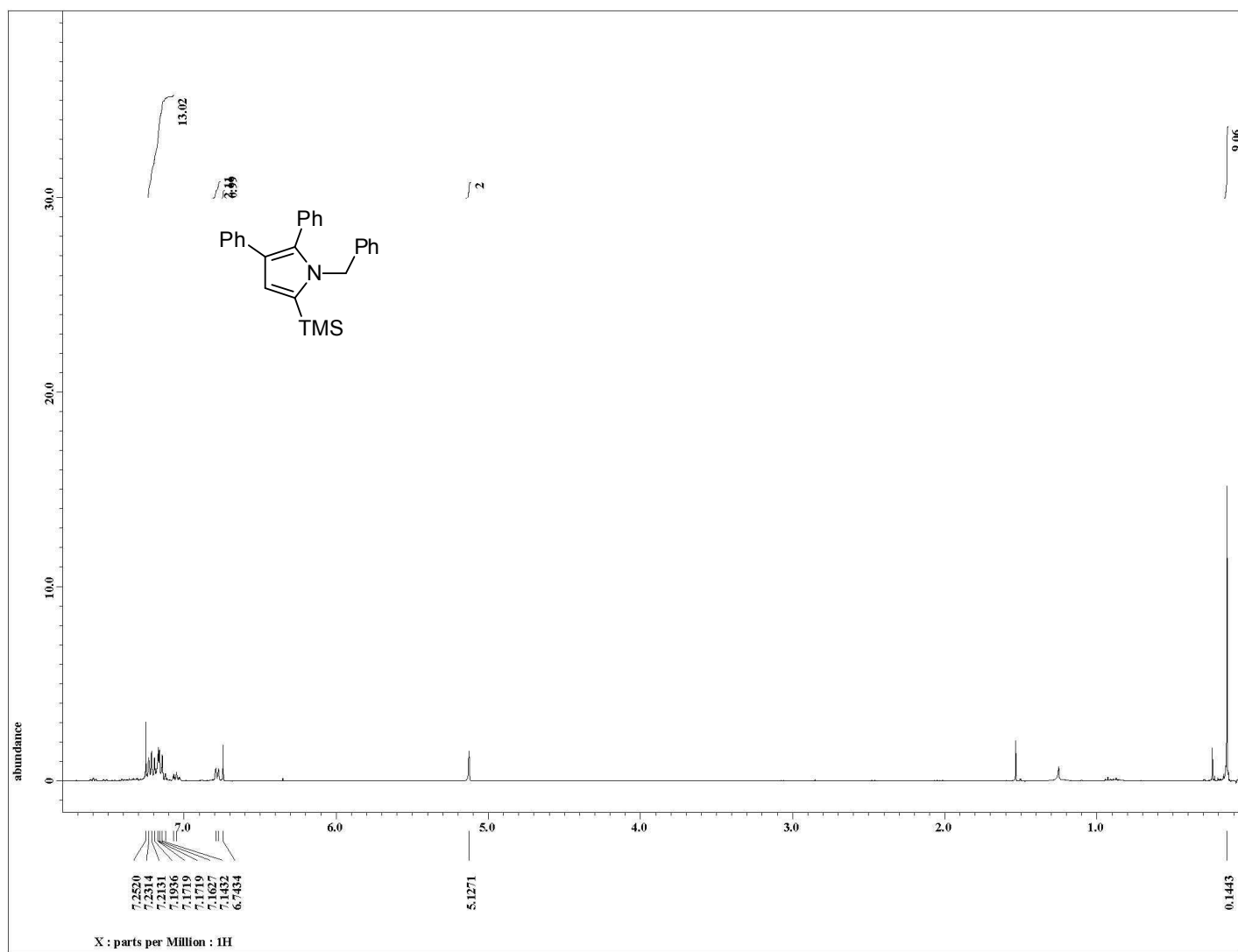
^{13}C NMR of compound **3ja**



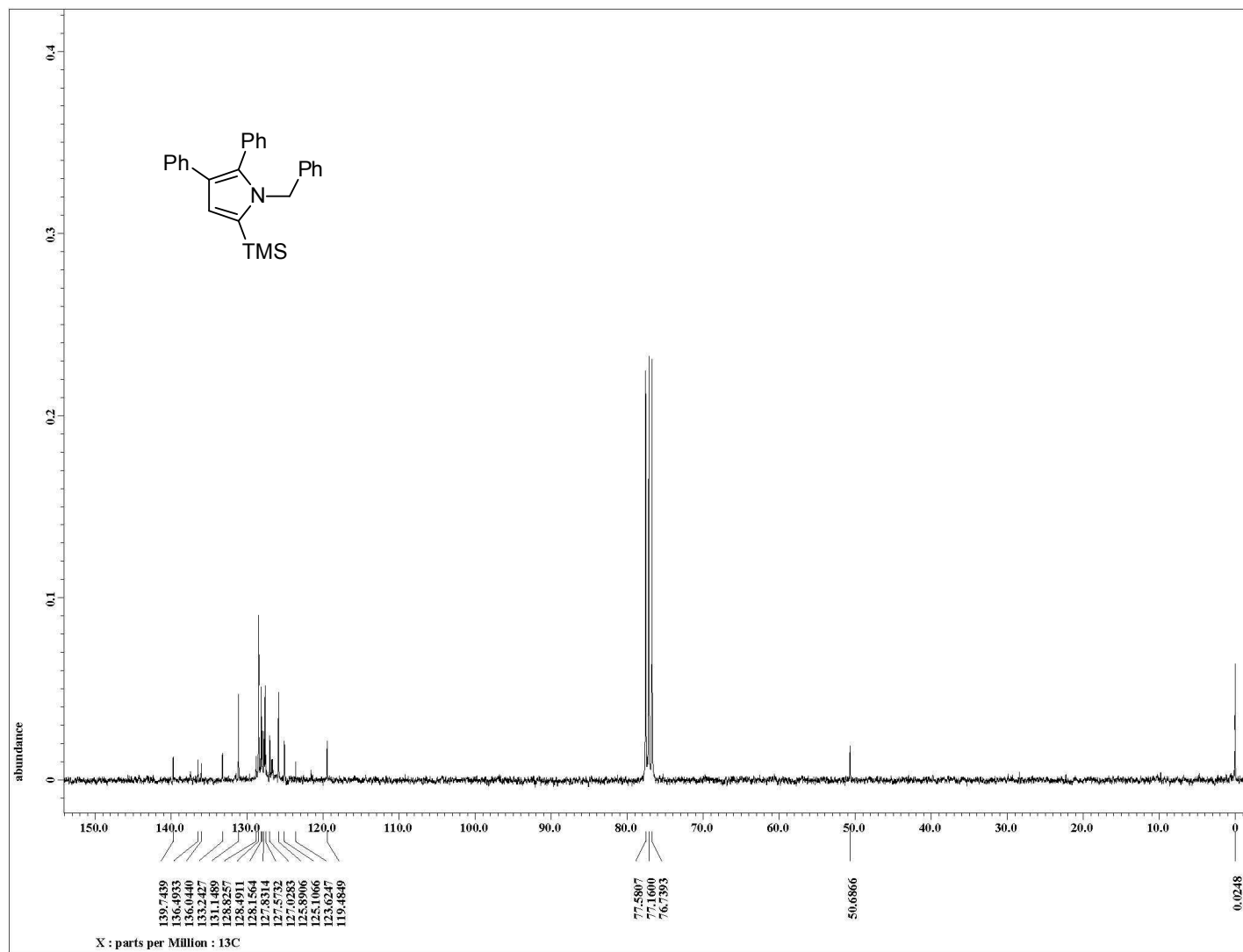
¹H NMR of compound **3ka**



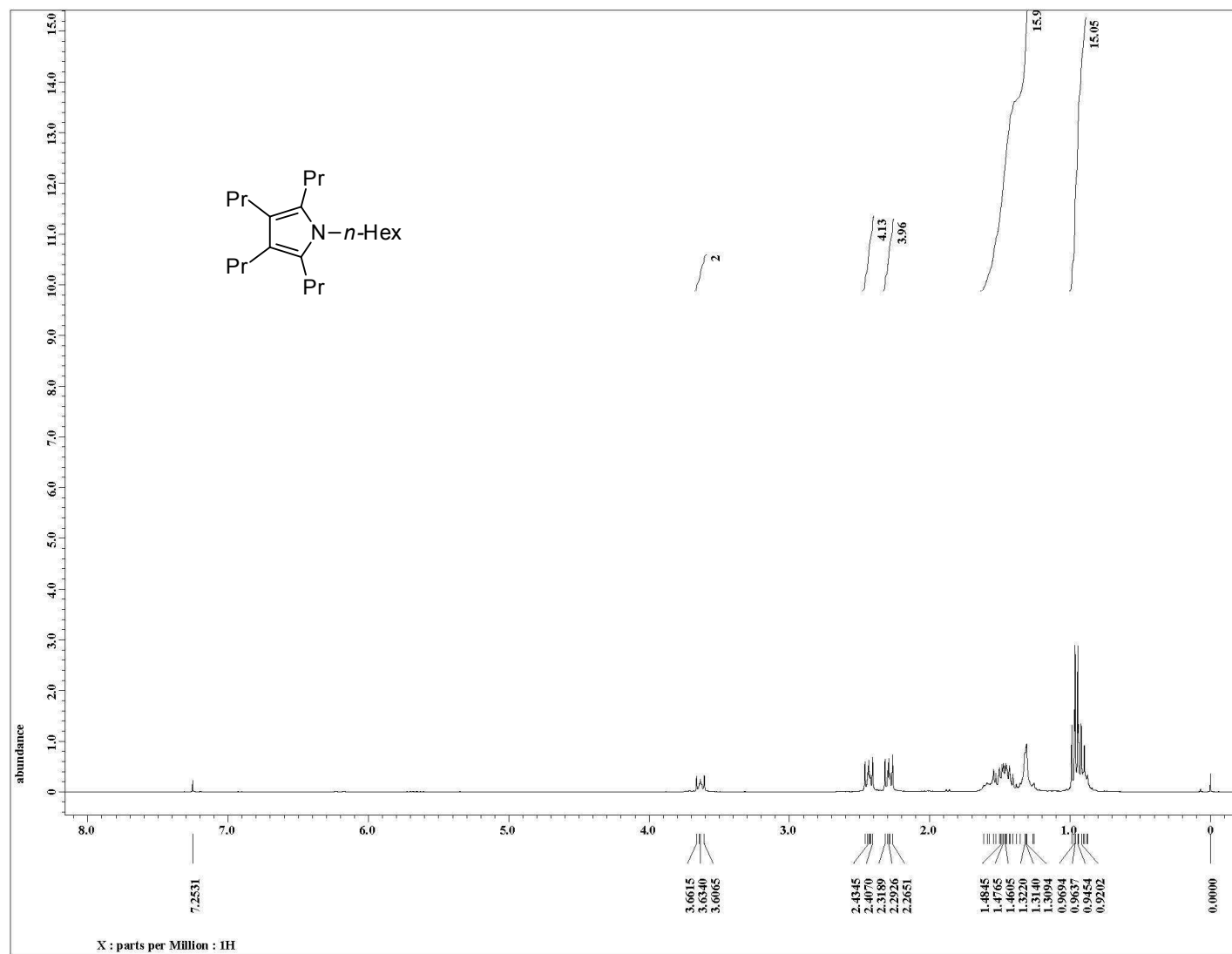
^{13}C NMR of compound **3ka**



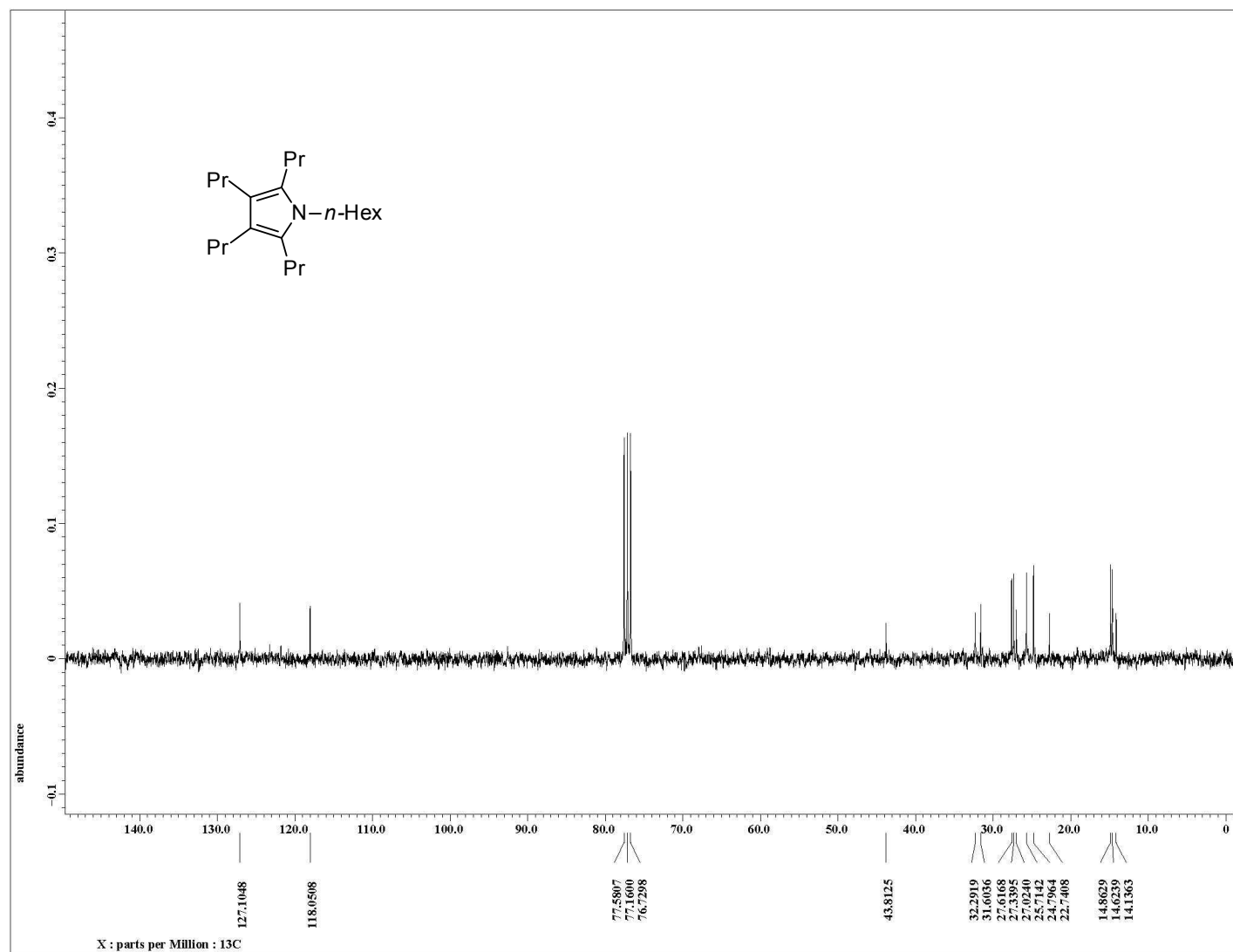
¹H NMR of compound **3la**



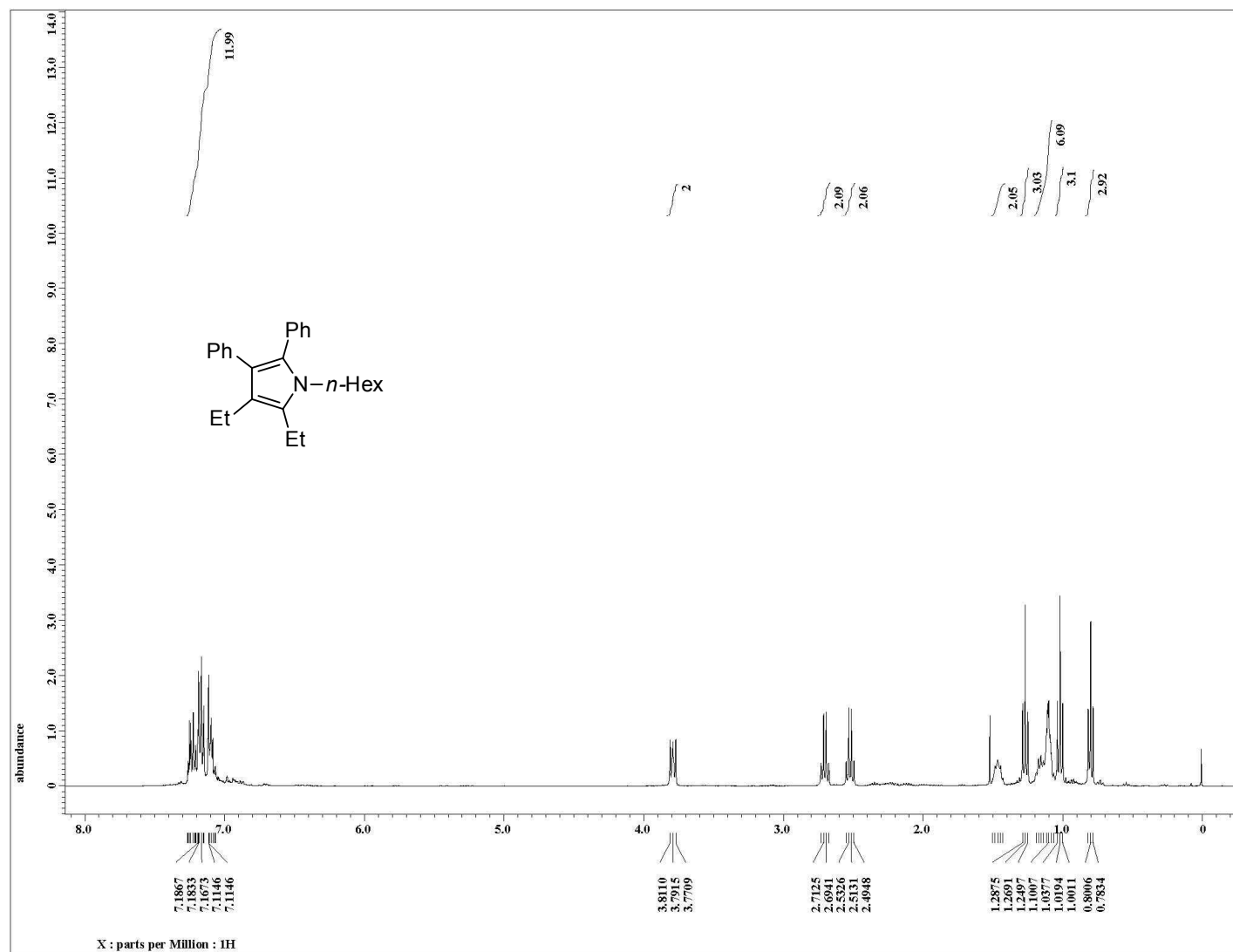
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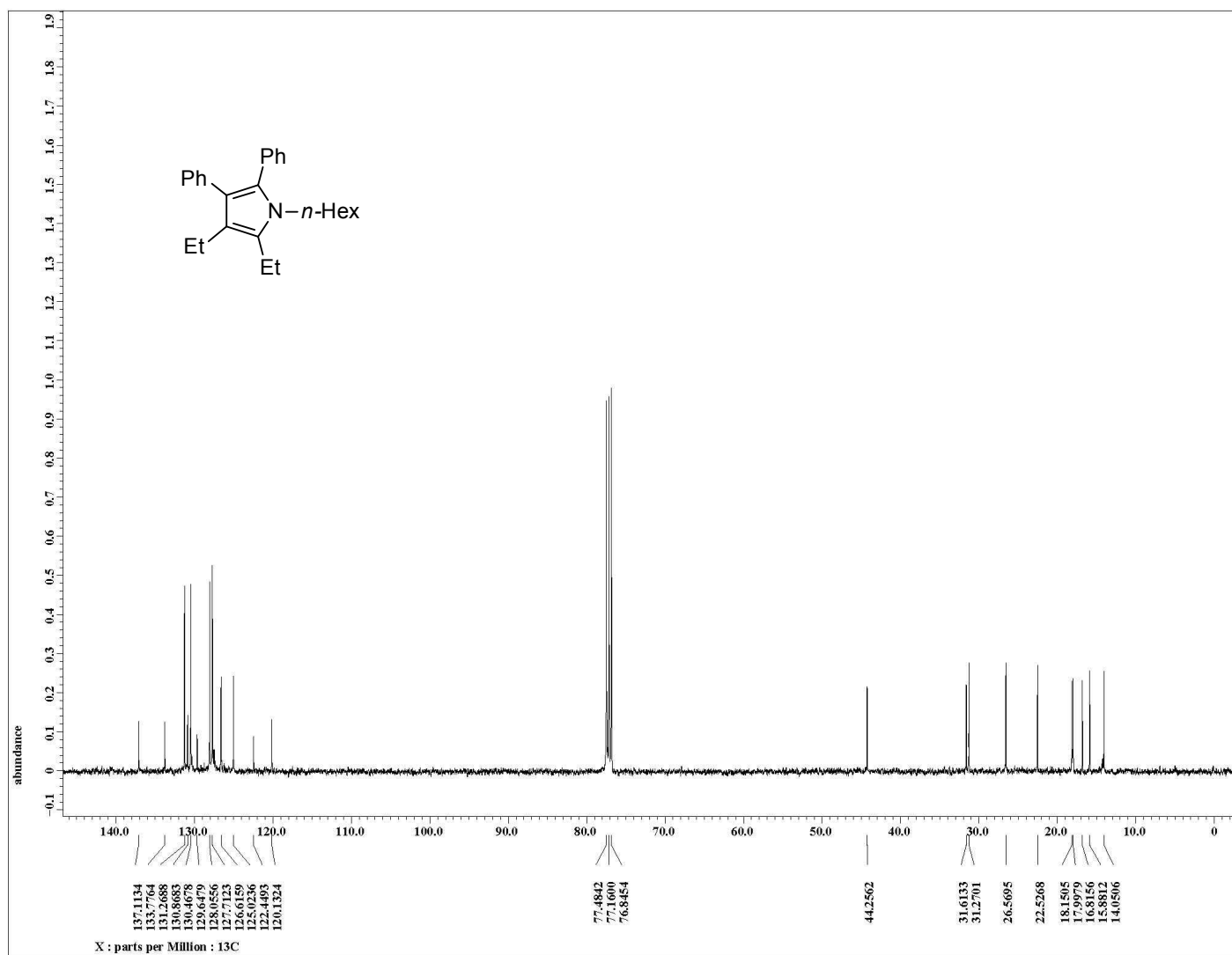
¹H NMR of compound **3bb**
S38



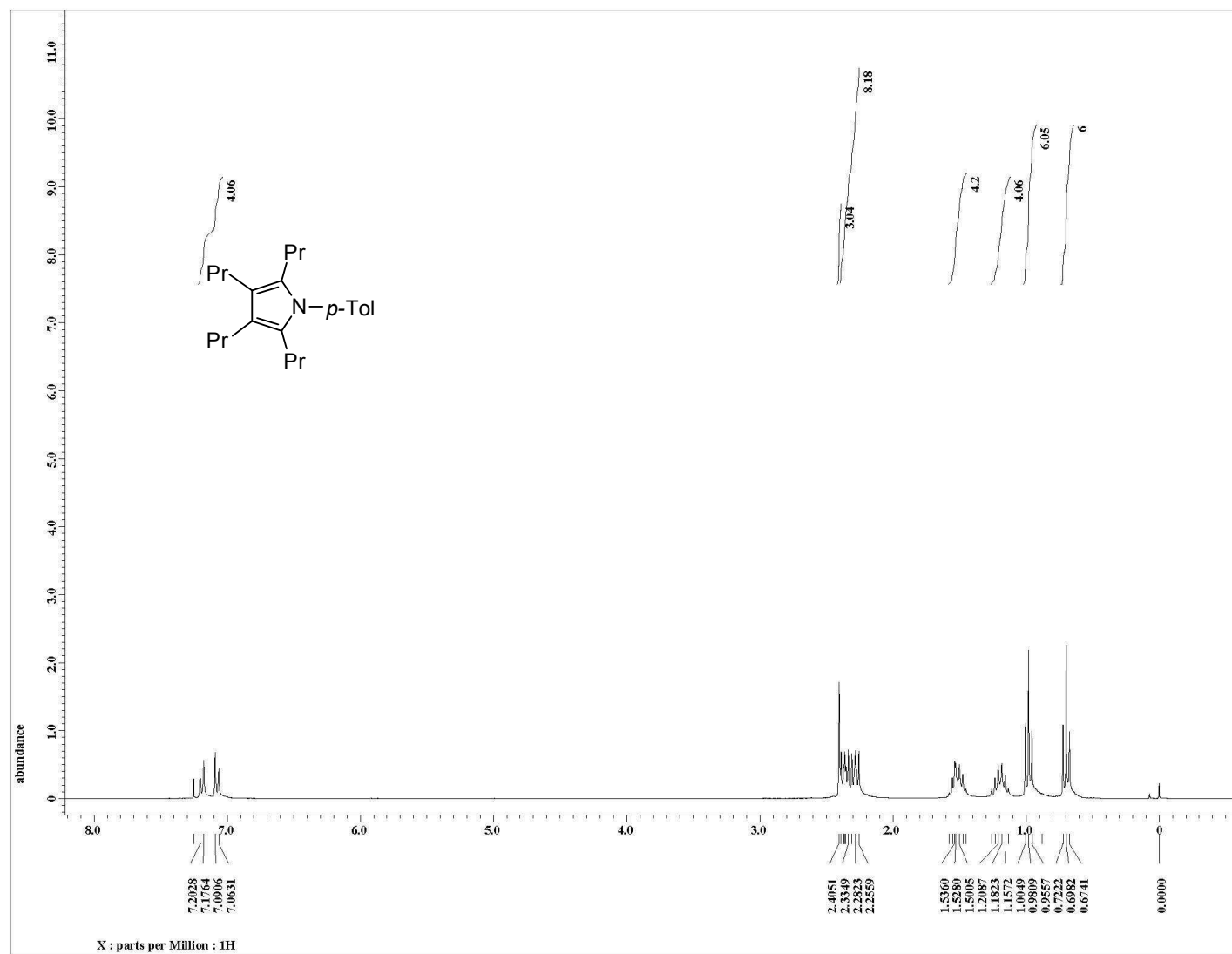
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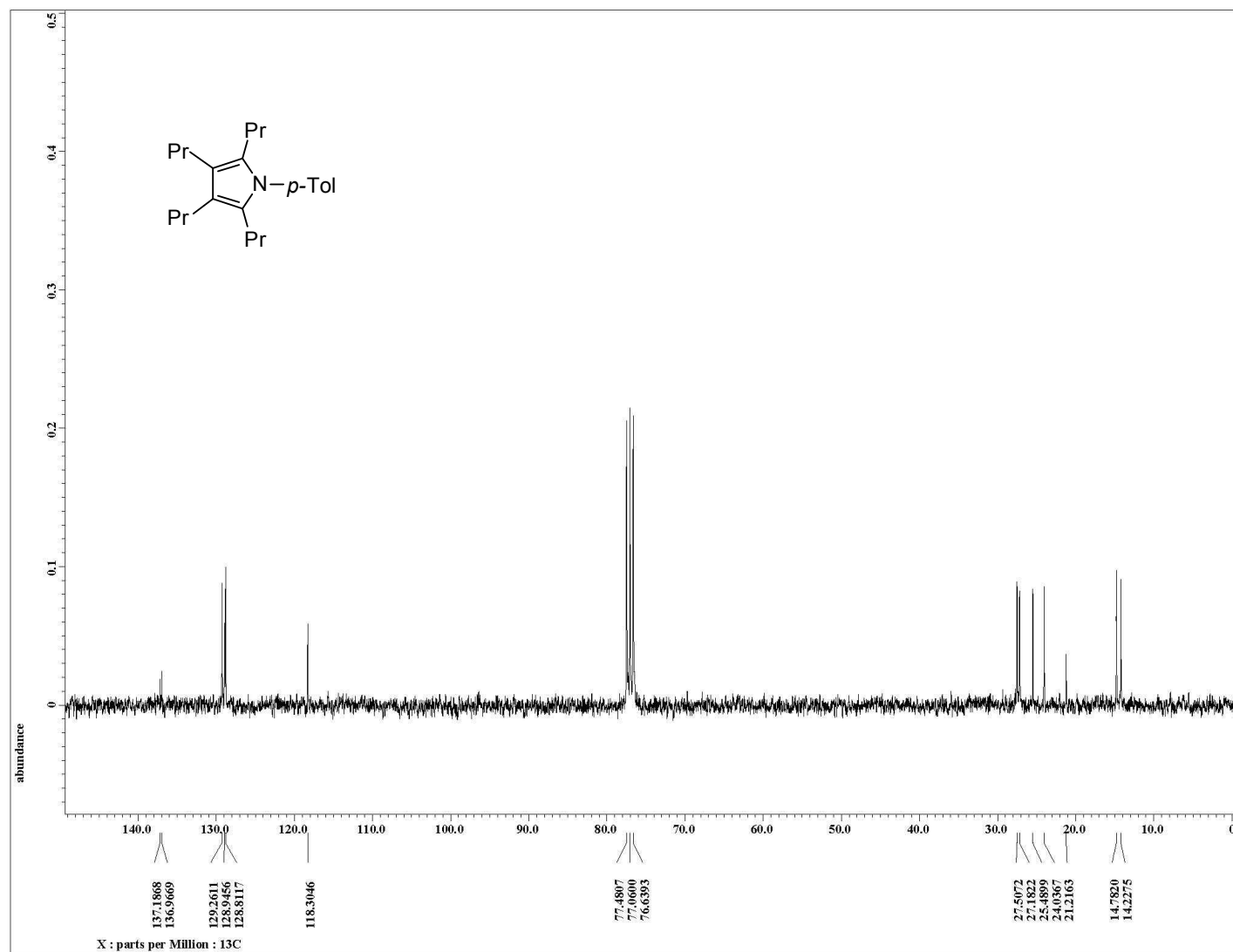
¹H NMR of compound **3fb**



^{13}C NMR of compound **3fb**

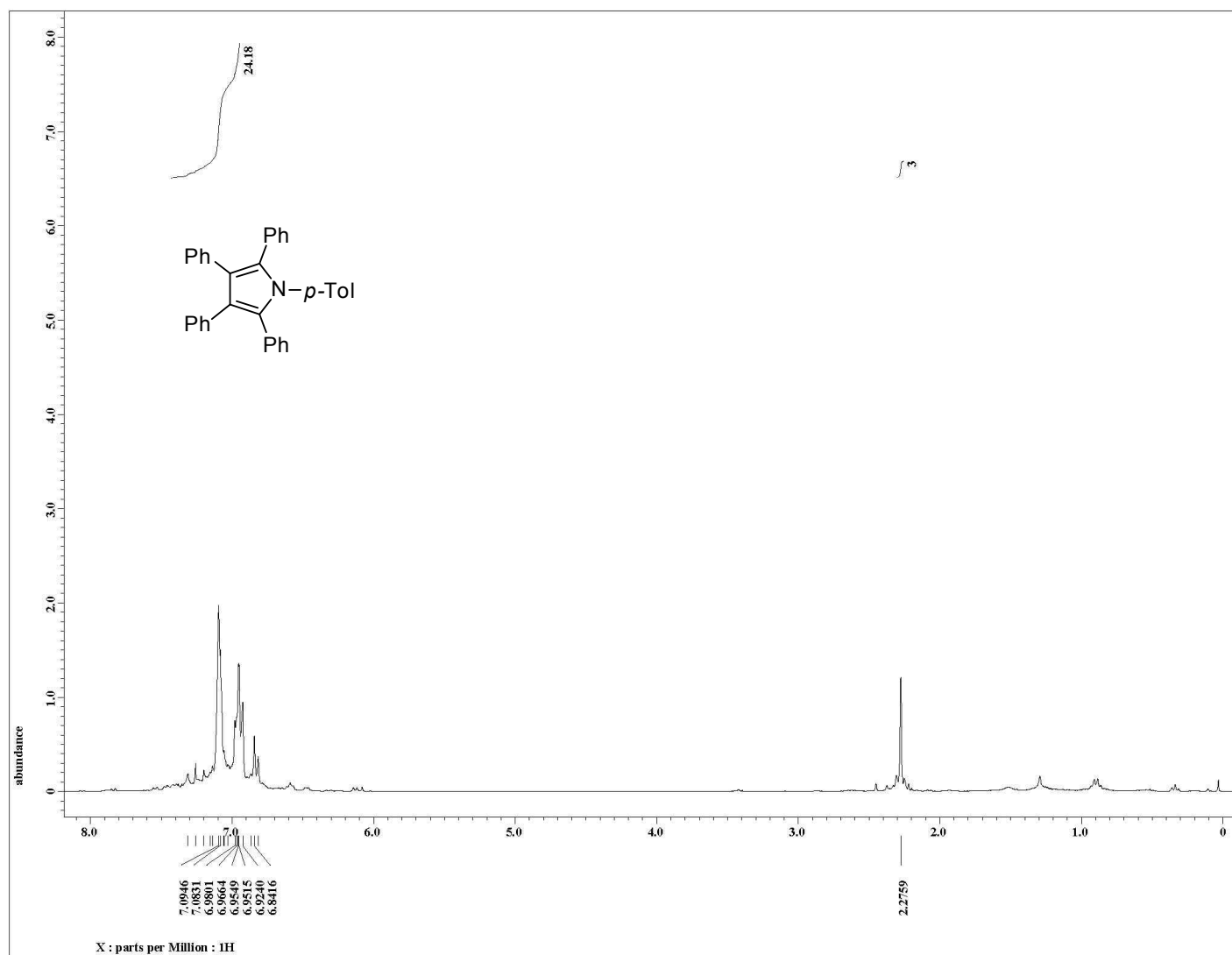


¹H NMR of compound **3bc**
S42

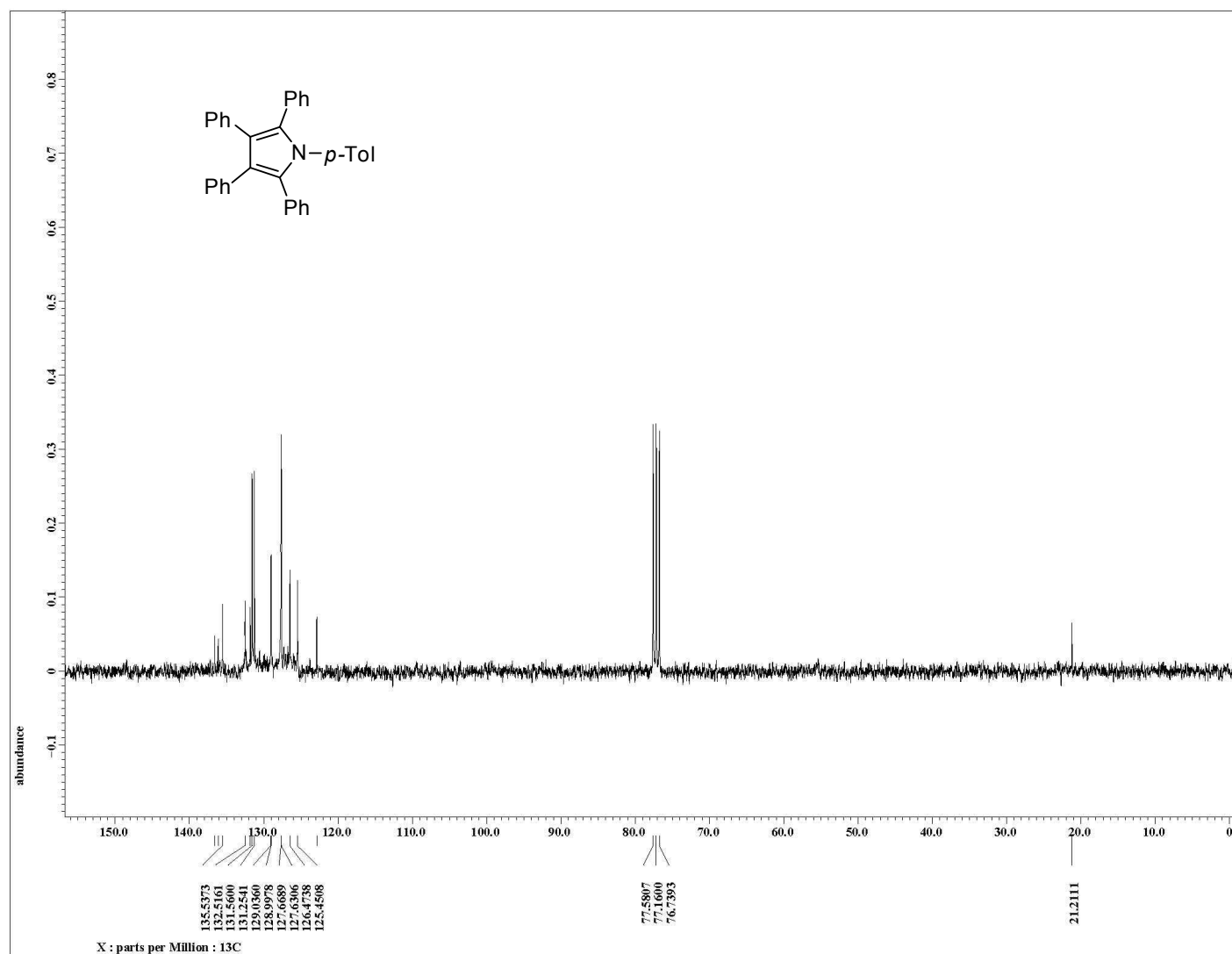


^{13}C NMR of compound **3bc**

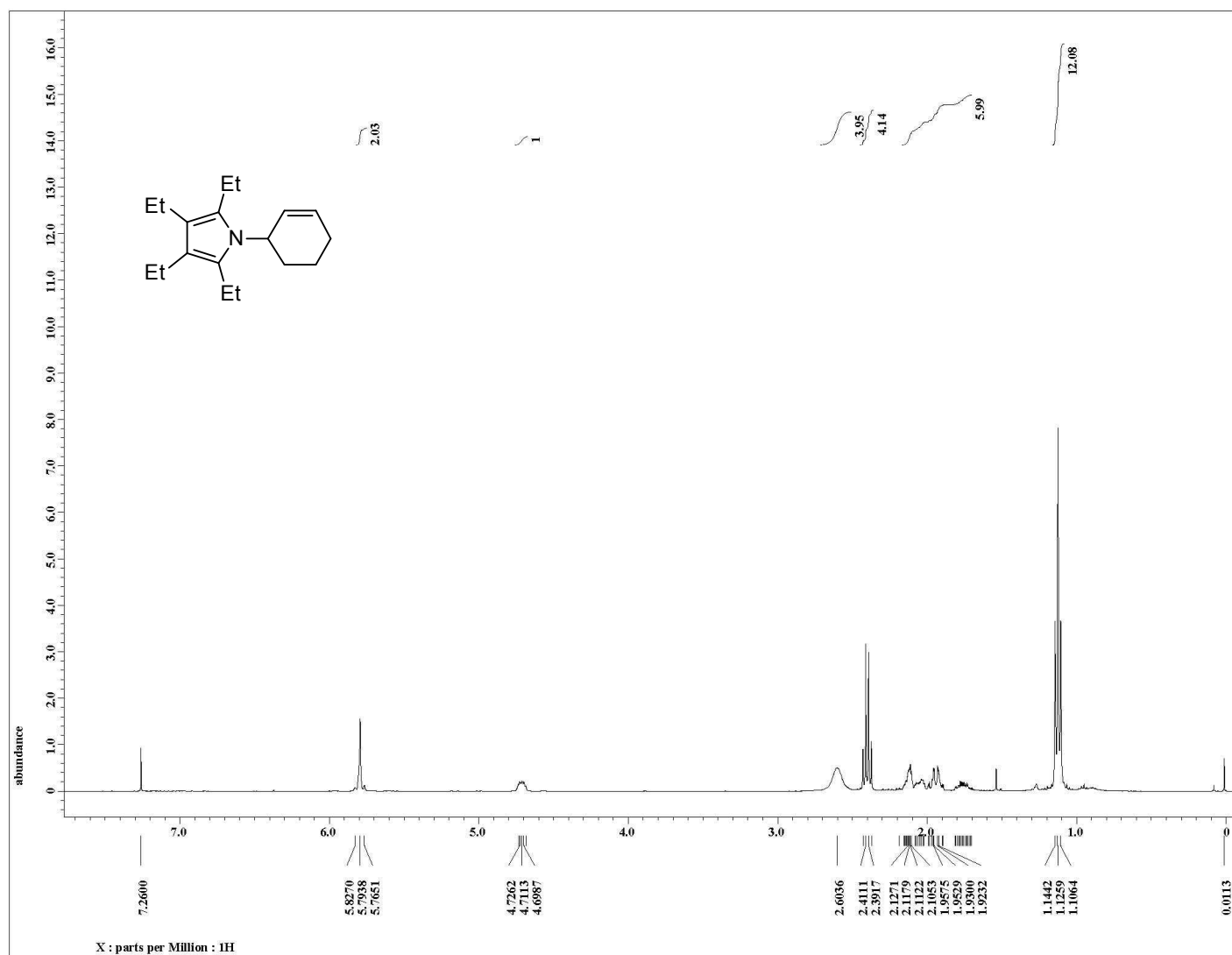
S43



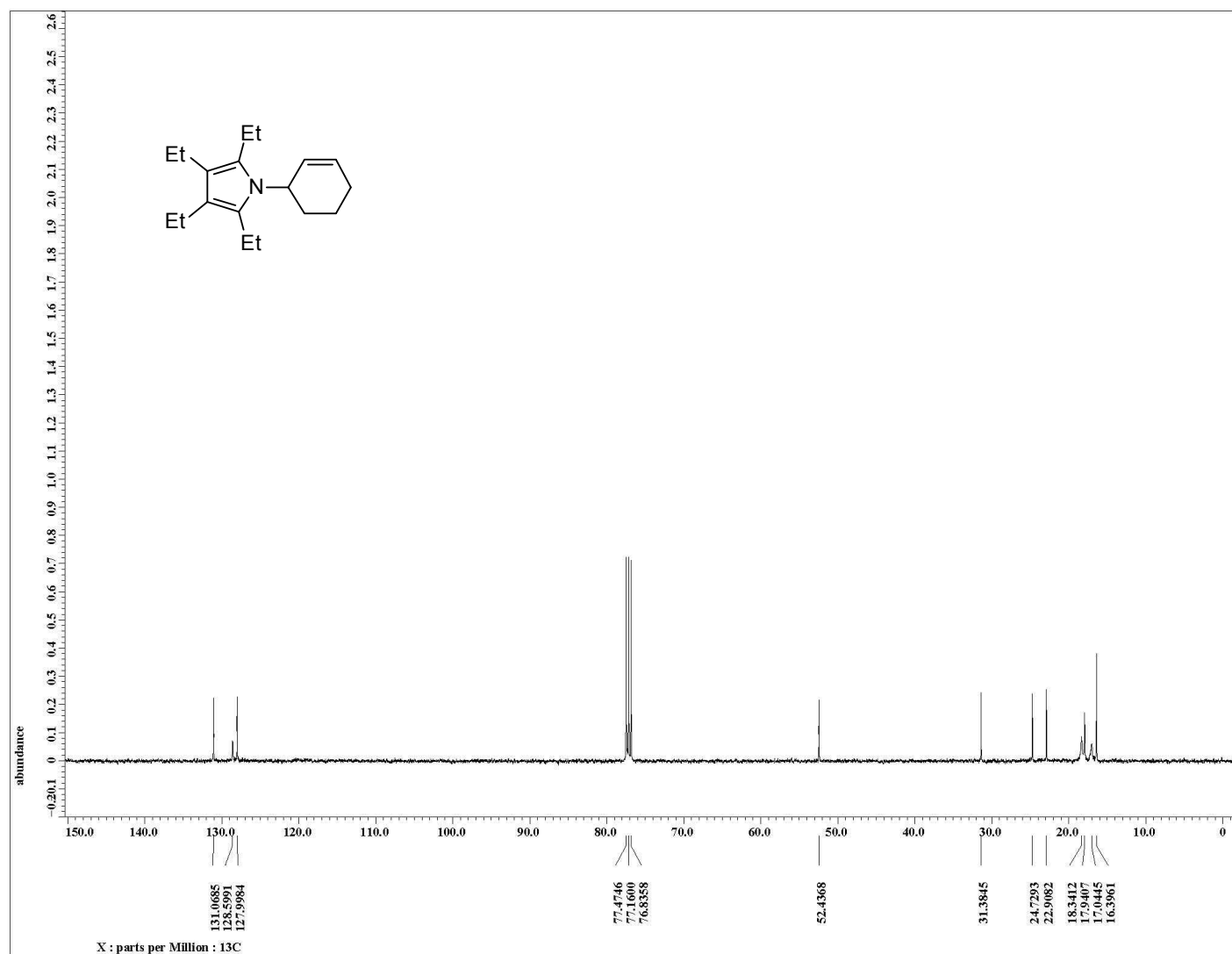
^1H NMR of compound **3dc**



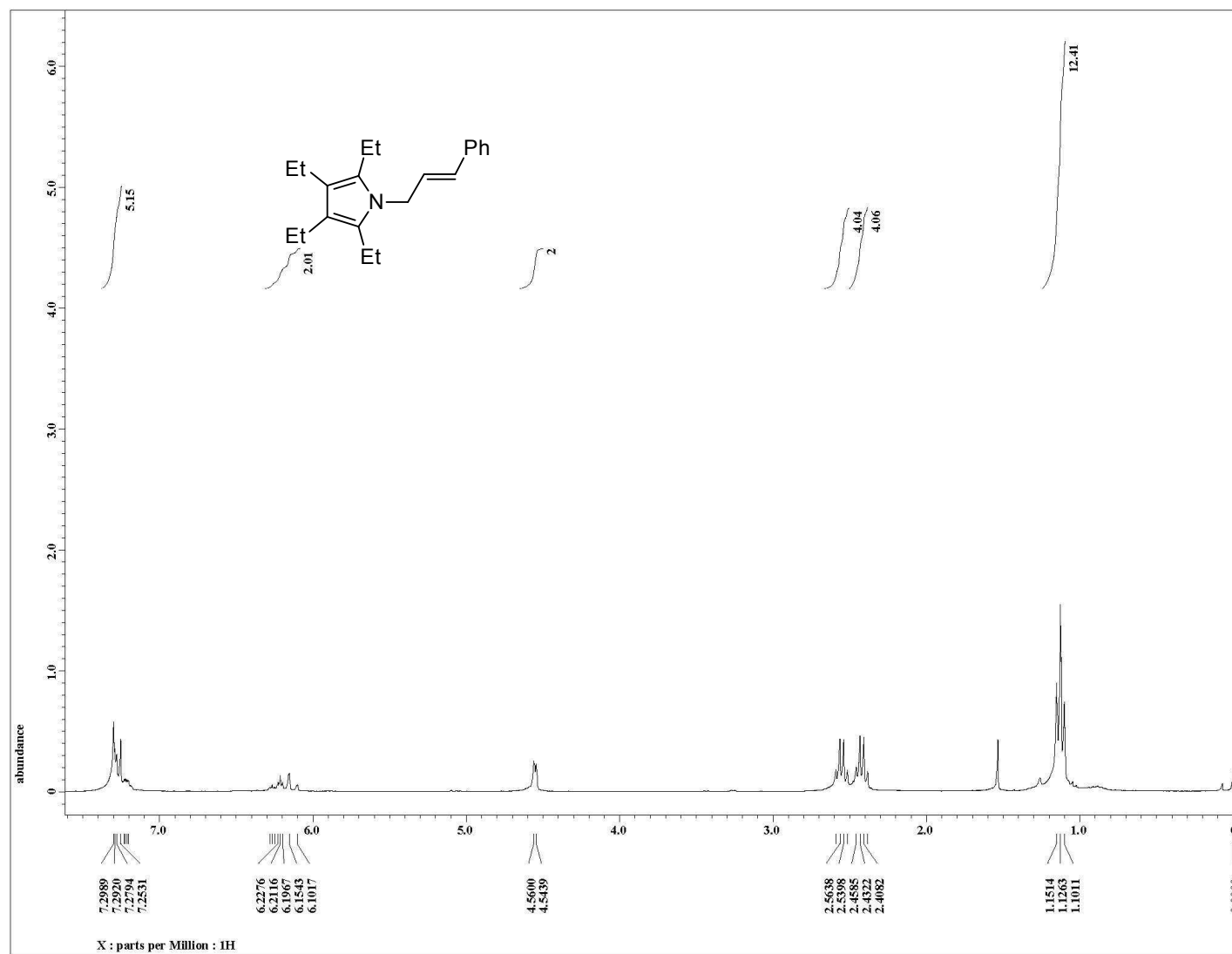
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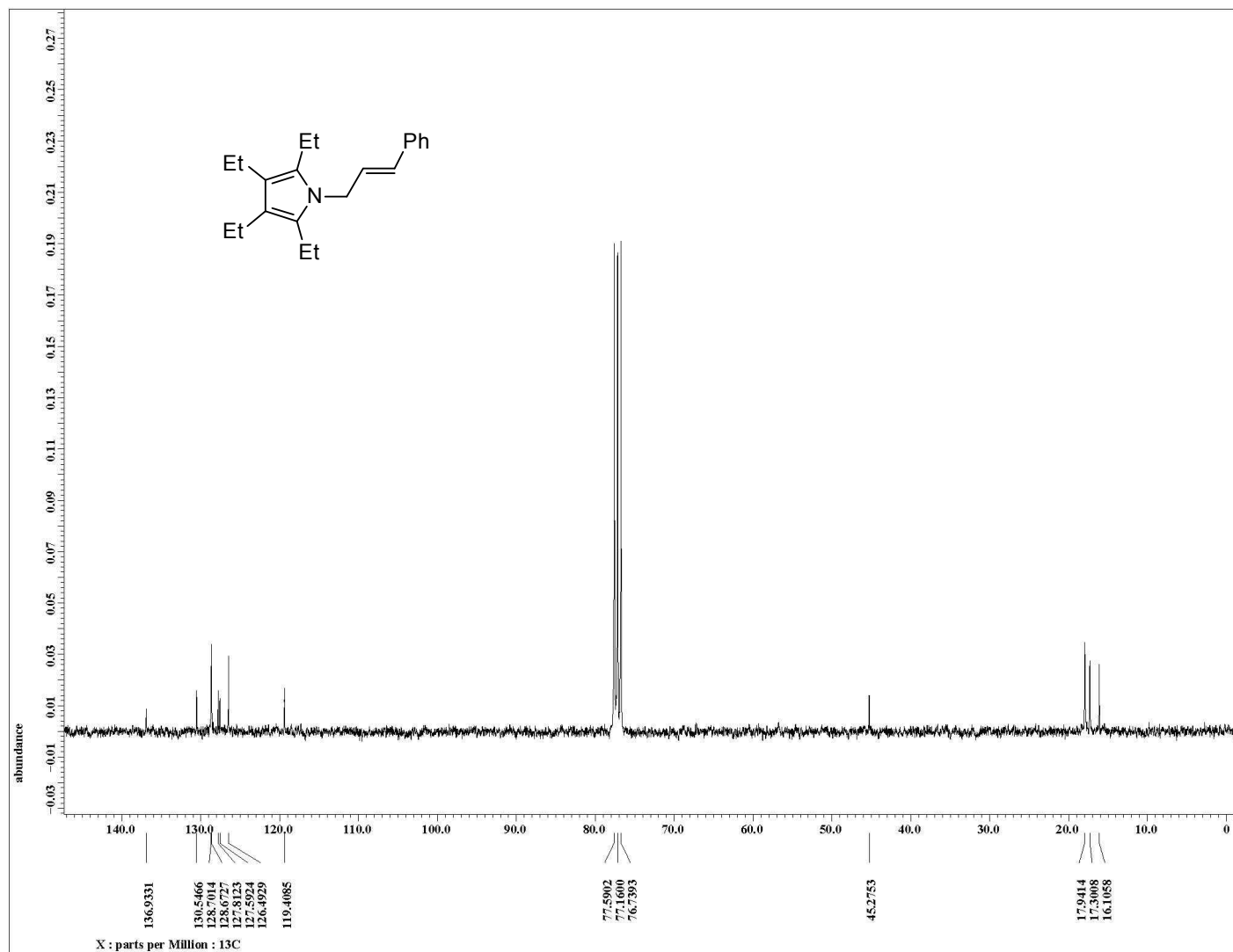
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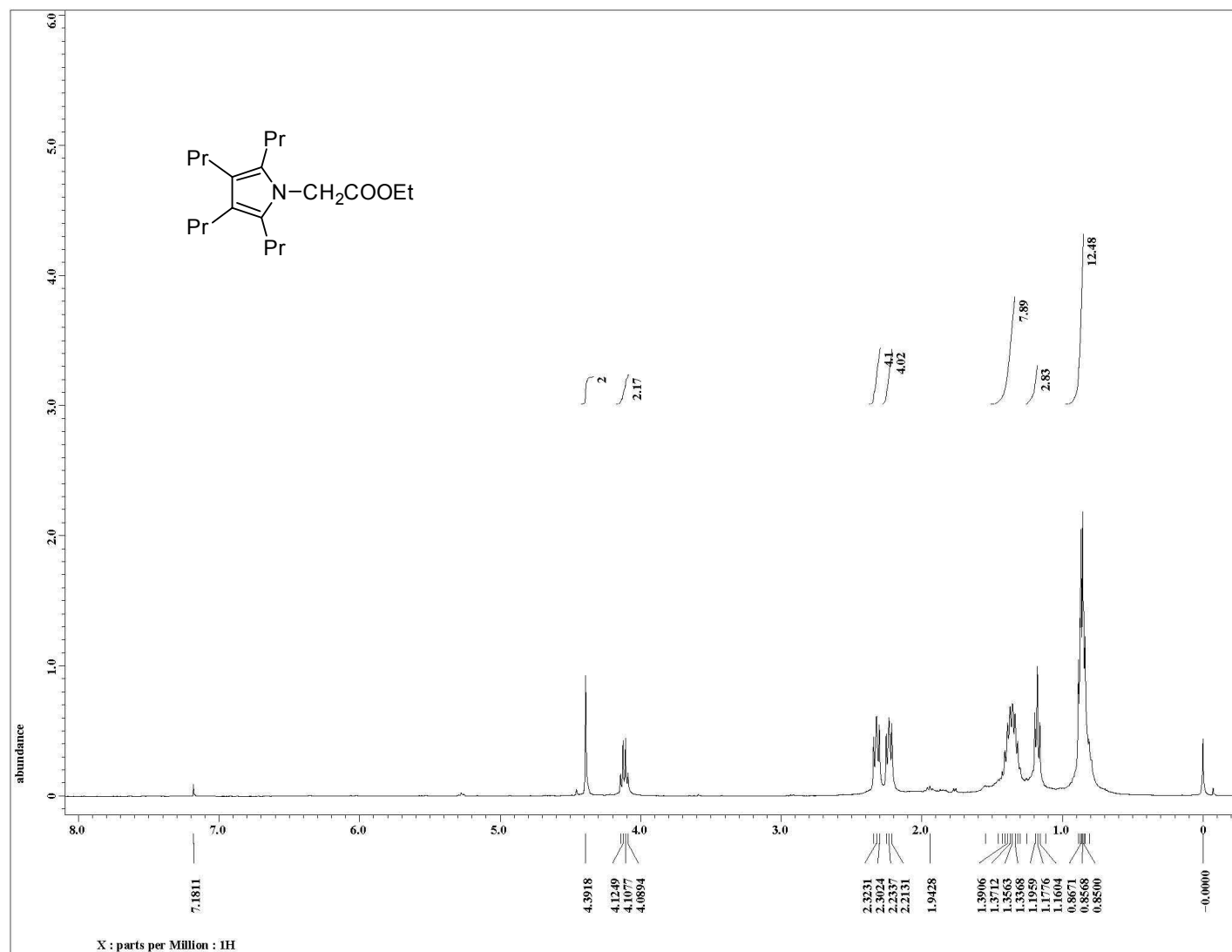
^{13}C NMR of compound **3ad**



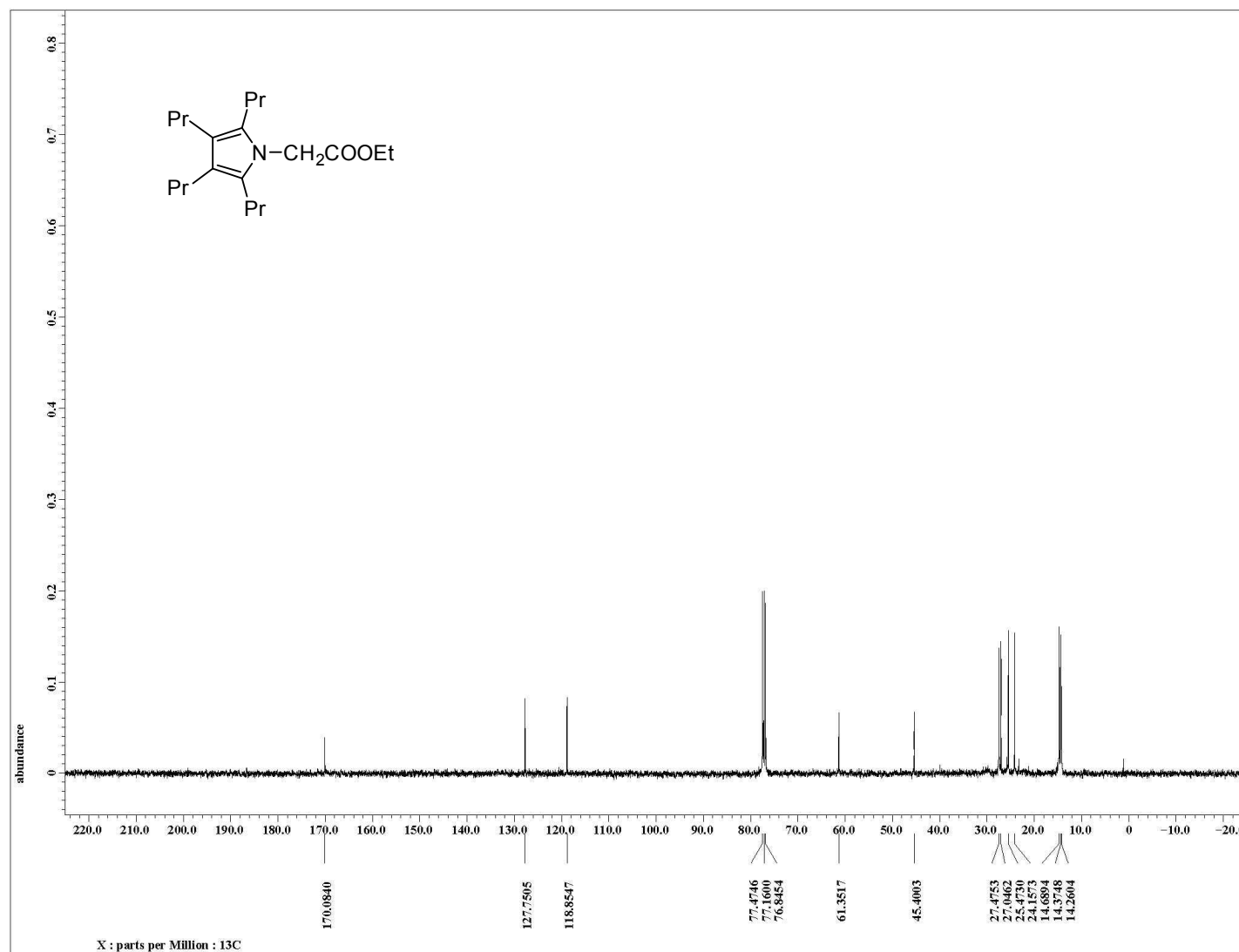
¹³C NMR of compound **3ae**
S48



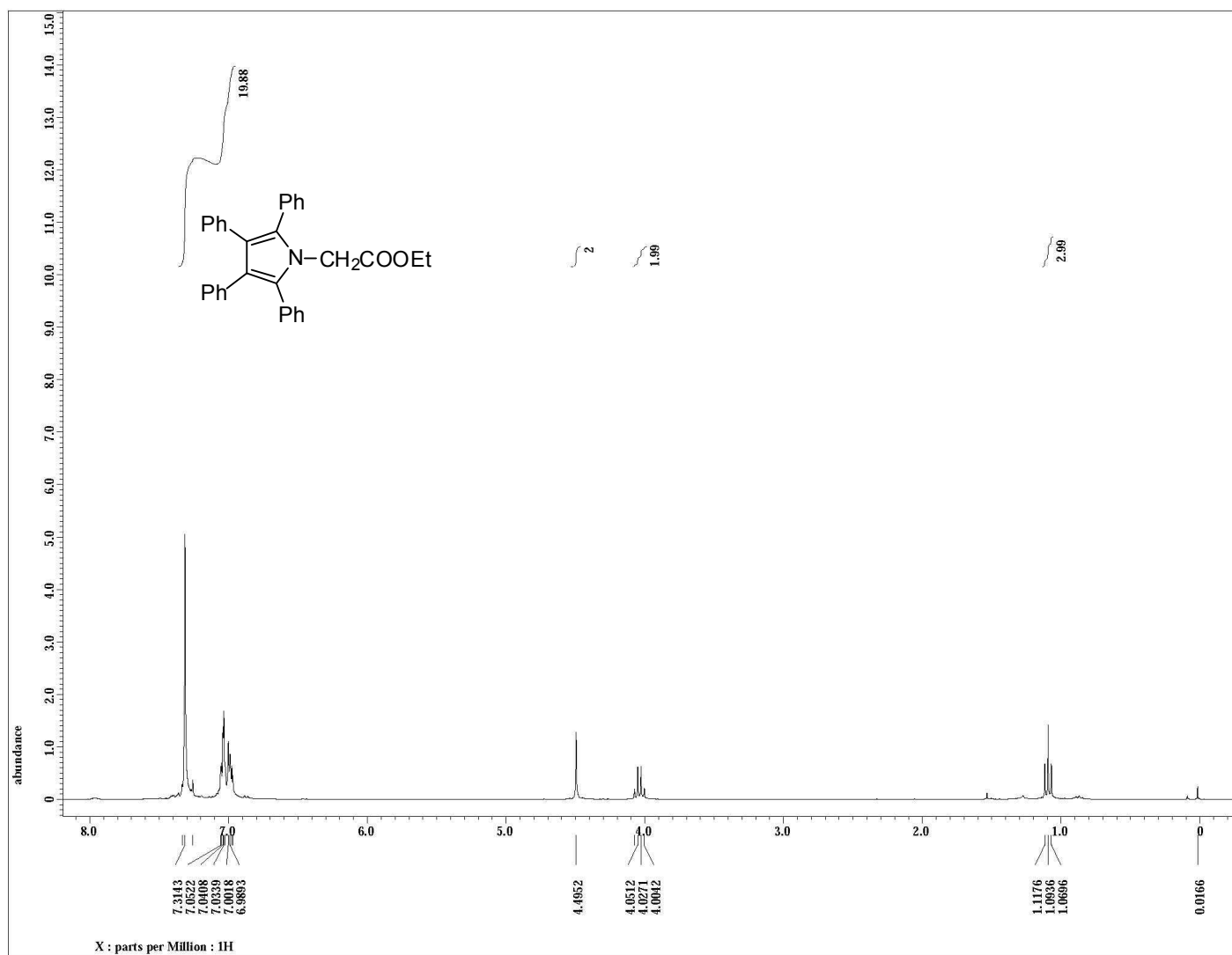
^{13}C NMR of compound **3ae**



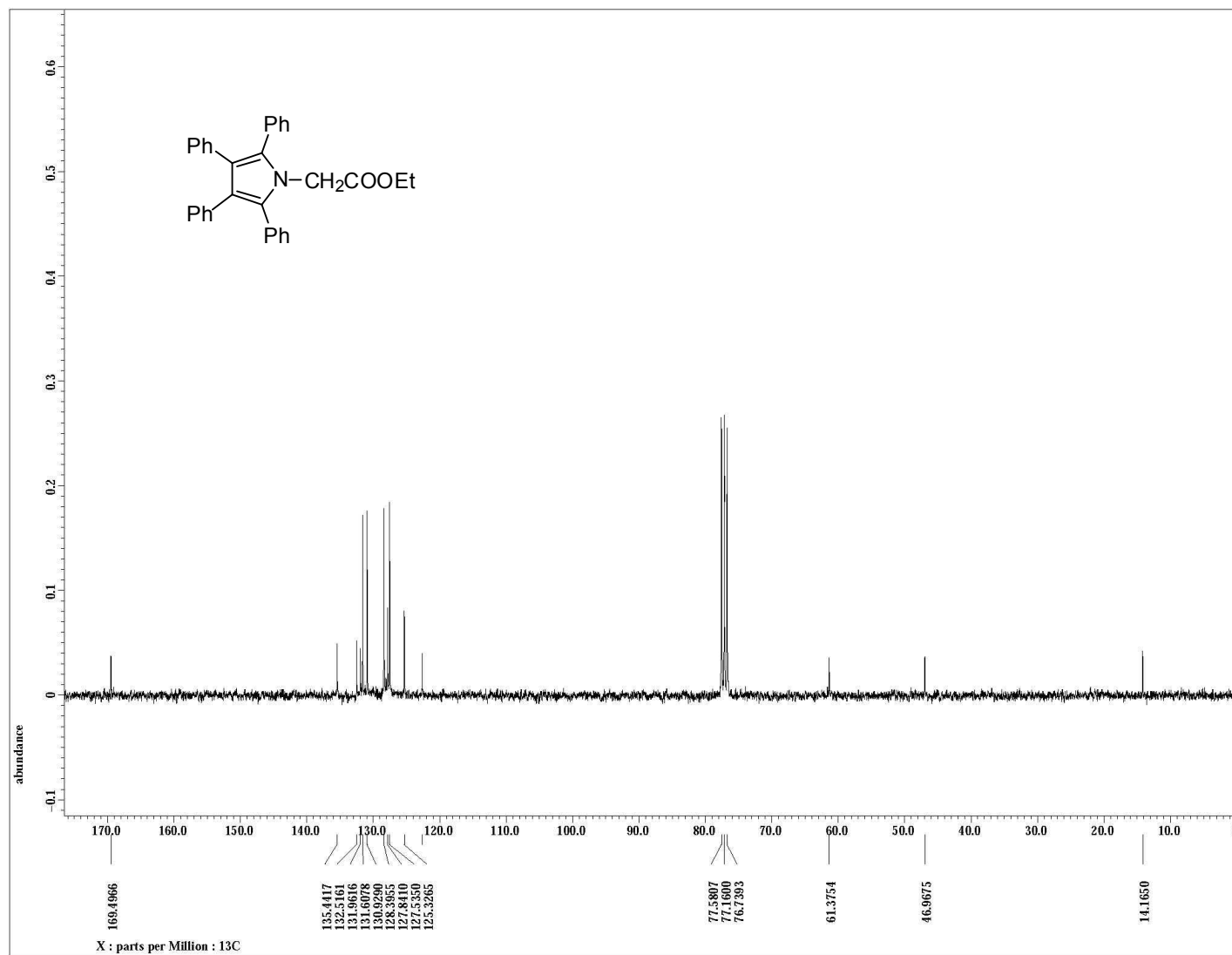
¹H NMR of compound **3bf**
S50



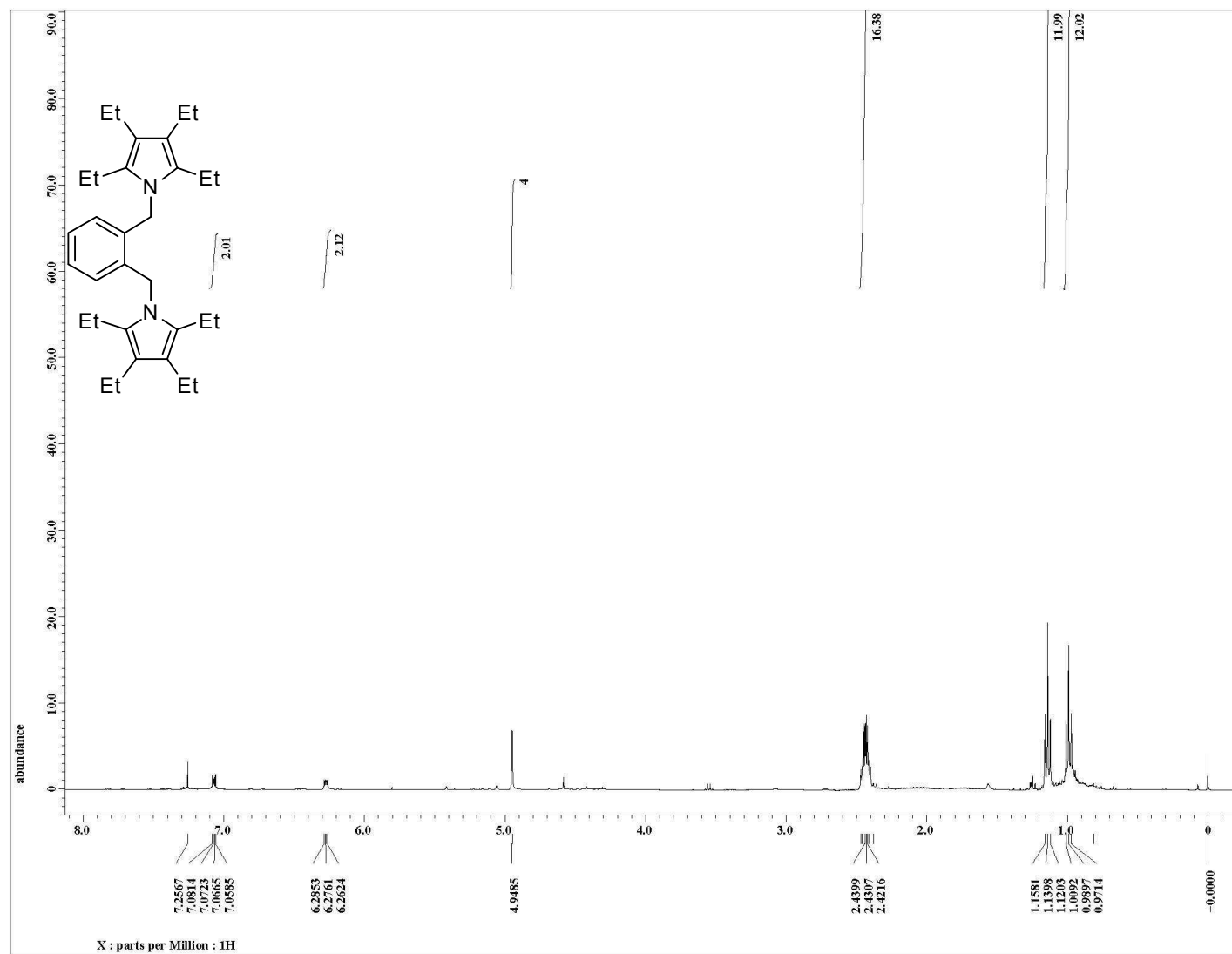
^{13}C NMR of compound **3bf**
S51



¹H NMR of compound **3df**

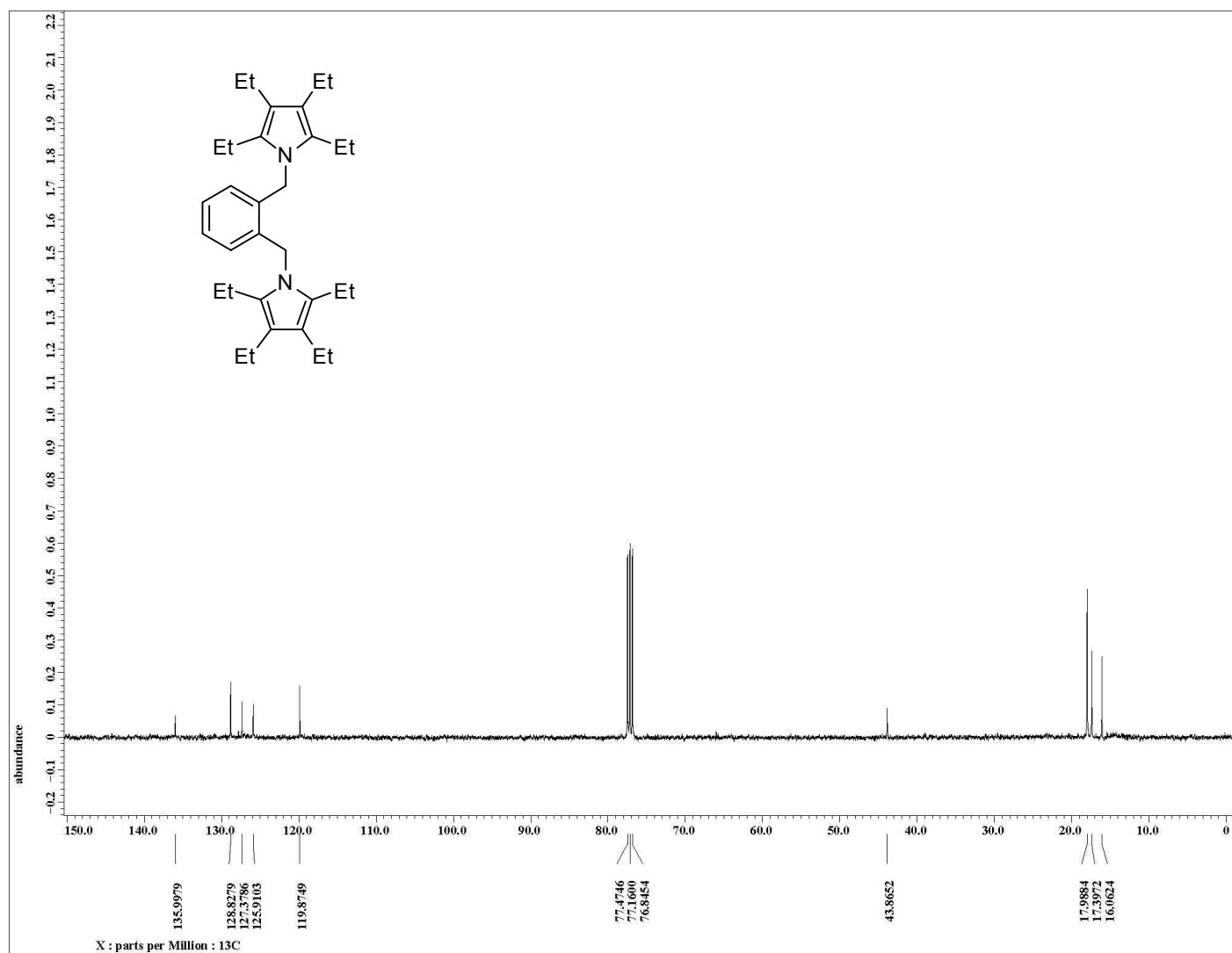


¹H NMR of compound **3df**
S53



^{13}C NMR of compound **3ag**

S54



^{13}C NMR of compound **3ag**