

Supporting Information

β -Selective C–H Arylation of Pyrroles Leading to Concise Syntheses of Lamellarins C and I

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1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. The ligand P[OCH(CF₃)₂]₃,¹ RhCl(CO){P[OCH(CF₃)₂]₃}₂,² 2-benzyl-1-methylpyrrole,³ ethyl 3-(1-methylpyrrol-2-yl)propanoate,⁴ ethyl (E)-3-(1-methylpyrrol-2-yl)acrylate,⁵ 3-methyl-1-(triisopropylsilyl)pyrrole,⁶ 1,2-dimethoxy-4-iodobenzene⁷ and 1-isopropoxy-2-methoxy-4-iodobenzene⁸ were prepared according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in heat-gun-dried glassware using standard vacuum-line techniques. All C-H bond arylation reactions were carried out in glass vessels equipped with J. Young® O-ring tap, heated in a 8-well reaction block (heater + magnetic stirrer). All work-up and purification procedures were carried out with reagent-grade solvents in air. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm) and ethanolic phosphomolybdic acid/sulfuric acid. Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m x 0.25 mm, Hewlett-Packard). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a HP-5 column (30 m x 0.25 mm, Hewlett-Packard). High-resolution mass spectroscopy (HRMS) was obtained from a JMS-T100TD instrument (DART). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (¹H 600 MHz, ¹³C 150 MHz) spectrometer. Chemical shifts for ¹H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ¹³C NMR are expressed in ppm relative to CDCl₃ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, hept = heptet, m = multiplet), coupling constant (Hz), and integration.

(1) van Leeuwen, P. W. N. M.; Roobeek, C. F. *Tetrahedron* **1981**, *37*, 1973.

(2) (a) Yanagisawa, S.; Sudo, T.; Noyori, R.; Itami, K. *J. Am. Chem. Soc.* **2006**, *128*, 11748. (b) Yanagisawa, S.; Sudo, T.; Noyori, R.; Itami, K. *Tetrahedron* **2008**, *64*, 6073.

(3) (a) He, F.; Wu, H. Y.; Chen, J. X.; Su, W. K. *Synth. Commun.* **2008**, *38*, 255. (b) Greenhouse, R.; Ramierz, C.; Muchowski, J. M. *J. Org. Chem.* **1985**, *50*, 2961.

(4) Carson, J. R.; Jetter, M. C.; Lee, J. S.; Youngman, M. A. Novel heteroaryl alkylamide derivatives useful as bradykinin receptor modulators and their preparation, use, and pharmaceutical compositions. U. S. Patent Application Publication US 2004/0192720 A1. Sep 30, 2004.

(5) Fleming, C. L.; Ashton, T. D.; Gaur, V.; McGee, S. L.; Pfeffer, F. M. *J. Med. Chem.* **2014**, *57*, 1132.

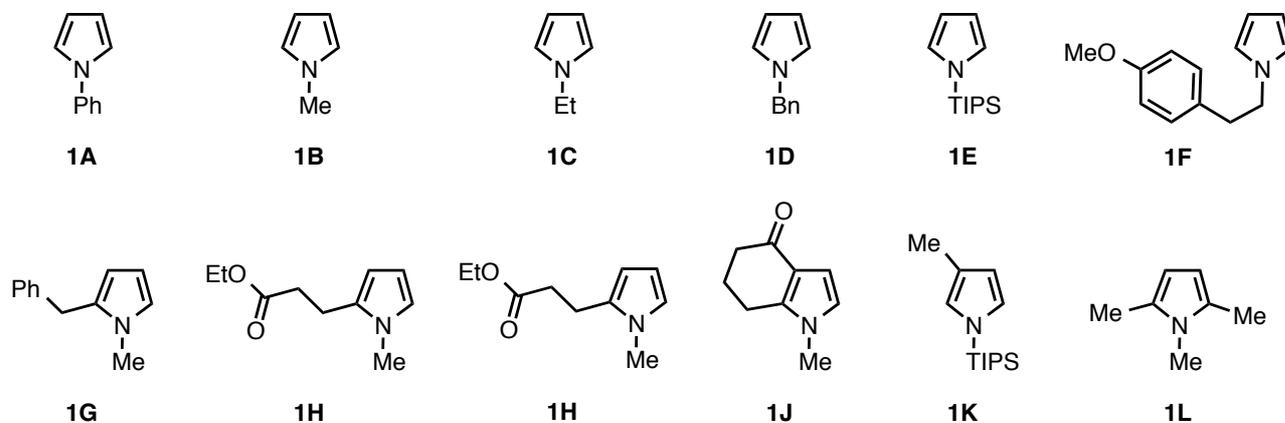
(6) Kozikowski, A. P.; Cheng, X. M. *J. Org. Chem.* **1984**, *49*, 3239.

(7) Castanet, A.-S.; Colobert, F.; Broutin, P.-E. *Tetrahedron Lett.* **2002**, *43*, 5047.

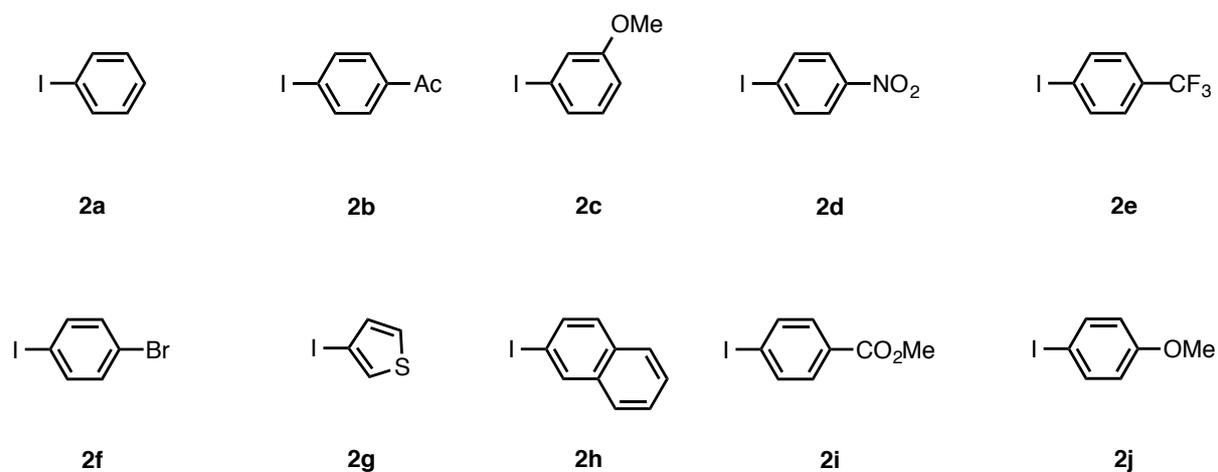
(8) Bushby, R. J.; Lu, Z. *Synthesis* **2001**, *5*, 763.

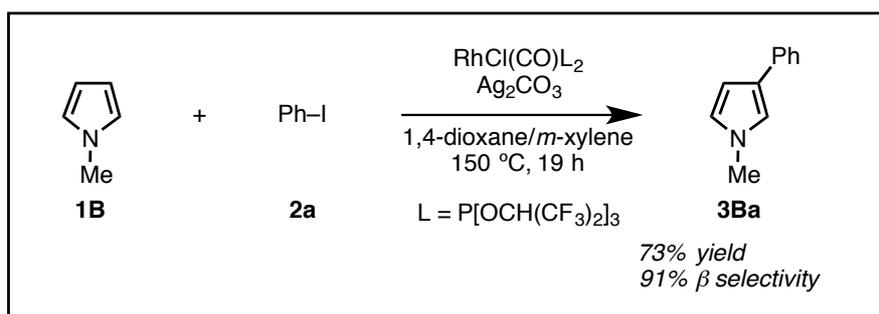
2. Substrates Structures of Pyrroles 1 and Aryl iodides 2

Pyrroles 1



Aryl iodides 2



3. Typical Procedure for β -Selective Arylation of Pyrroles

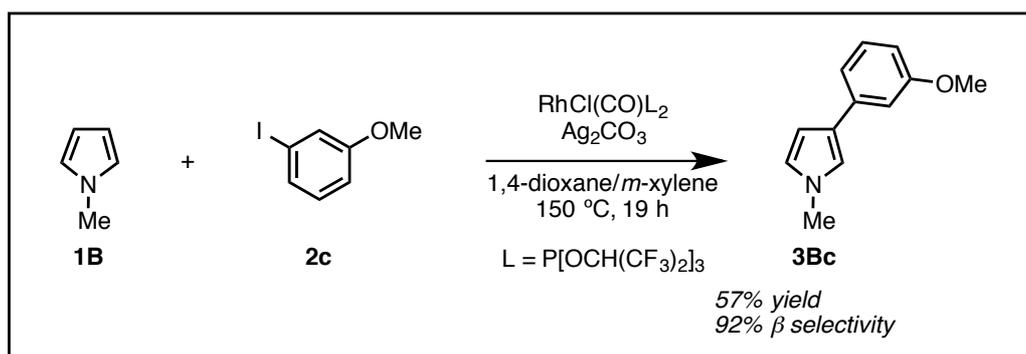
A 20-mL glass vessel equipped with J. Young® O-ring tap, containing a magnetic stirring bar, was heat-gun-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vessel were added $\text{RhCl}(\text{CO})\{\text{P}[\text{OCH}(\text{CF}_3)_2]_3\}_2$ (18.5 mg, 15 μmol , 3 mol%), Ag_2CO_3 (68.0 mg, 0.25 mmol, 0.5 equiv), 1-methylpyrrole (**1A**: 60.8 mg, 0.75 mmol, 1.5 equiv), iodobenzene (**2a**: 102.0 mg, 0.50 mmol, 1.0 equiv), and dry 1,4-dioxane/*m*-xylene (1:1) (1.7 mL) under a stream of nitrogen. The vessel was sealed with the O-ring tap, and then heated at 150 °C for 19 h in a 8-well reaction block with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was analyzed by ^1H NMR, GC, and GCMS showing that the reaction took place at the β -position in 91% regioselectivity ($\alpha:\beta = 9:91$). The residue was then purified by flash column chromatography (hexane/EtOAc = 40:1) to afford 1-methyl-3-phenylpyrrole (**3Ba**: 58.0 mg, 73% yield) as orange solid.

1-Methyl-3-phenylpyrrole (3Ba): ^1H NMR (600 MHz, CDCl_3) δ 7.49 (d, $J = 7.1$ Hz, 2H), 7.32 (t, $J = 7.1$ Hz, 2H), 7.15 (t, $J = 7.1$ Hz, 1H), 6.91 (t, $J = 1.8$ Hz, 1H), 6.63 (t, $J = 2.4$ Hz, 1H), 6.44 (dd, $J = 2.4, 1.8$ Hz, 1H), 3.68 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 135.9, 128.9, 128.6, 125.2, 125.0, 122.7, 118.5, 106.3, 36.3; HRMS (DART) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{N}$ [MH] $^+$: 158.0970, found 158.0971.

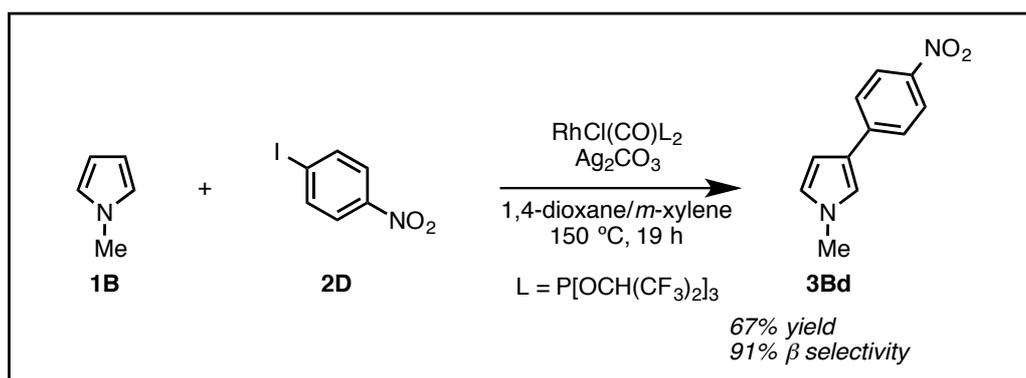
(9) (a) Wang, X.; Lane, B. S.; Sames, D. J. *Am. Chem. Soc.* **2005**, *127*, 4996. For C2-isomer (1-methyl-2-phenylpyrrole), see: (b) Deprez, N. R.; Kalyani, D.; Krause, A.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 4972.

4. Compound Data for Other Arylation Products of Pyrroles

Unless otherwise noted, all arylated pyrroles (**3**) described in this section were prepared following the typical procedure given in Section 2 (Page S3). Compounds were purified either by preparative thin-layer chromatography (PTLC) or flash column chromatography. The regioselectivities of arylation products were determined by the NMR experiments (NOESY, chemical shifts, and coupling constants) and/or by the comparison of NMR spectra of possible regioisomers.



3-(3-Methoxyphenyl)-1-methylpyrrole¹⁰ (**3Bc**): Purification by flash column chromatography (hexane/EtOAc = 20:1); Yield, 57%; Regioselectivity, $\alpha:\beta = 8:92$; White solid. ^1H NMR (600 MHz, CDCl_3) δ 7.24–7.22 (m, 1H), 7.10–7.08 (m, 1H), 7.03 (dd, $J = 2.4, 1.5$ Hz, 1H), 6.89 (t, $J = 1.8$ Hz, 1H), 6.72–6.70 (m, 1H), 6.61 (t, $J = 2.4$ Hz, 1H), 6.42 (dd, $J = 3.0, 1.5$ Hz, 1H), 3.82 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.9, 137.4, 129.5, 124.8, 122.7, 118.7, 117.7, 110.7, 110.6, 106.4, 55.1, 36.3; HRMS (DART) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$ [MH]⁺: 188.1075, found 188.1077.

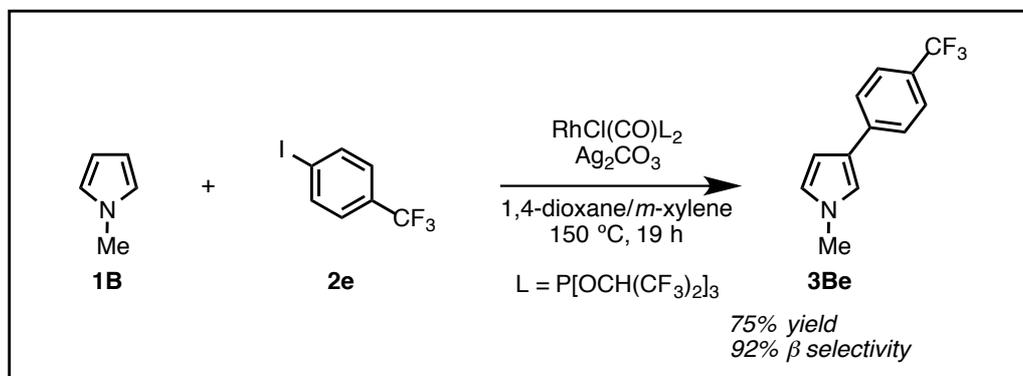


1-Methyl-3-(4-nitrophenyl)pyrrole¹¹ (**3Bd**): Purification by flash column chromatography (hexane/EtOAc = 5:1); Yield, 67%; Regioselectivity, $\alpha:\beta = 9:91$; Yellow solid. ^1H NMR (600 MHz,

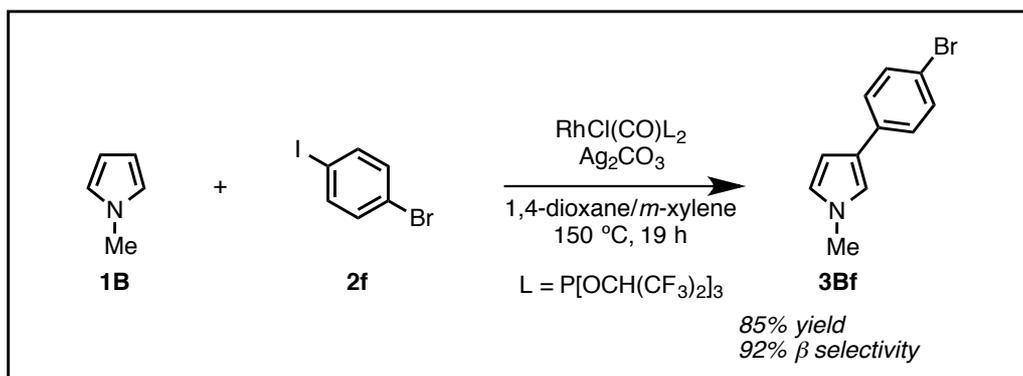
(10) Ogunrombi, M. O.; Malan, S. F.; Terre'Blanche, G.; Castagnoli, N. Jr.; Bergh, J. J.; Petzer, J. P. *Bioorg. Med. Chem.* **2008**, *16*, 2463.

(11) For C2-isomer (1-methyl-2-(4-nitrophenyl)pyrrole), see: (a) Gryko, D. T.; Vakuliuk, O.; Gryko, D.; Koszarna, B. J. *Org. Chem.* **2009**, *74*, 9517. (b) Jafarpour, F.; Rahiminejadan, S.; Hazrati, H. J. *Org. Chem.* **2010**, *75*, 3109.

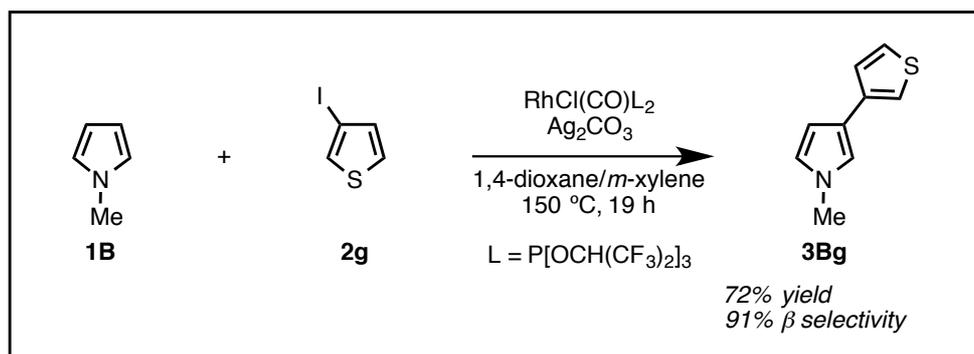
CDCl₃) δ 8.17 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 7.05 (t, J = 1.8 Hz, 1H), 6.68 (t, J = 3.0 Hz, 1H), 6.50 (dd, J = 3.0, 1.8 Hz, 1H), 3.72 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 145.1, 142.8, 124.6, 124.3, 123.8, 122.9, 120.5, 106.9, 36.6; HRMS (DART) m/z calcd for C₁₁H₁₁N₂O₂ [MH]⁺: 203.0821, found 203.0823.



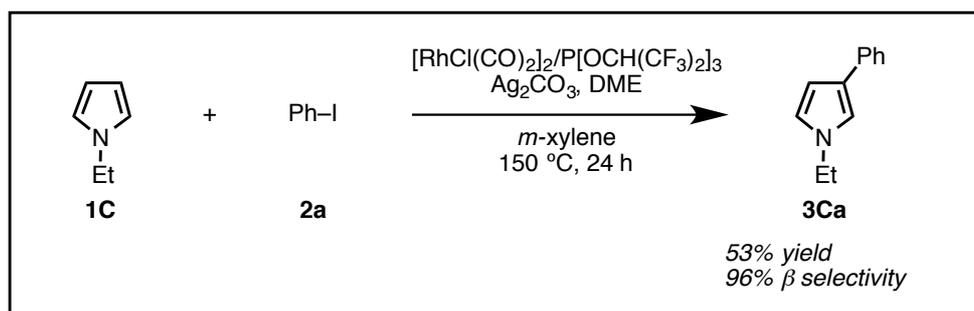
1-Methyl-3-(4-trifluoromethylphenyl)pyrrole (3Be): Purification by flash column chromatography (hexane/EtOAc = 9:1); Yield, 75%; Regioselectivity, α : β = 8:92; White solid. ¹H NMR (600 MHz, CDCl₃) δ 7.56–7.53 (m, 4H), 6.95 (t, J = 1.8 Hz, 1H), 6.64 (t, J = 2.4 Hz, 1H), 6.45 (dd, J = 2.4, 1.8 Hz, 1H), 3.68 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 139.5, 126.9 (q, J_{C-F} = 31.5 Hz), 125.5 (q, J_{C-F} = 4.3 Hz), 124.7, 123.7, 123.6, 119.4, 106.5, 36.4; HRMS (DART) m/z calcd for C₁₂H₁₁F₃N [MH]⁺: 226.0844, found 226.0844.



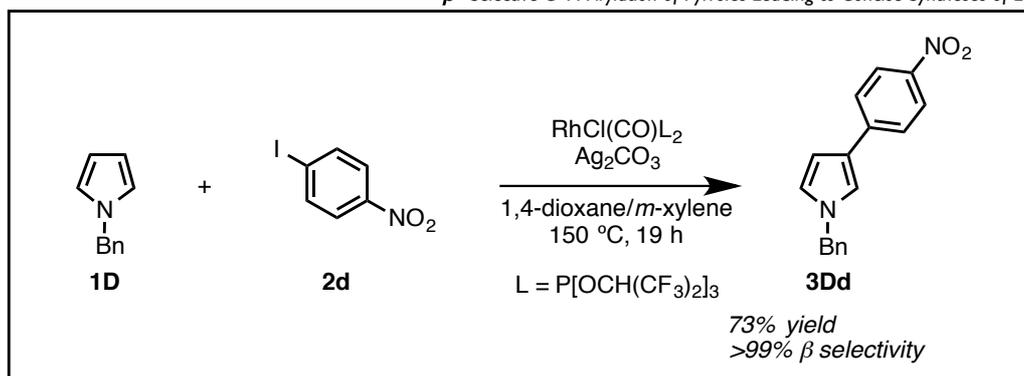
3-(4-Bromophenyl)-1-methylpyrrole (3Bf): Purification by flash column chromatography (hexane/EtOAc = 15:1); Yield, 85%; Regioselectivity, α : β = 8:92; White solid. ¹H NMR (600 MHz, CDCl₃) δ 7.42–7.40 (m, 2H), 7.35–7.32 (m, 2H), 6.87 (t, J = 1.8 Hz, 1H), 6.61 (t, J = 3.0 Hz, 1H), 6.39 (dd, J = 3.0, 1.8 Hz, 1H), 3.66 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 134.9, 131.5, 126.5, 123.8, 122.9, 118.6, 118.6, 106.2, 36.3; HRMS (DART) m/z calcd for C₁₁H₁₁BrN [MH]⁺: 236.0075, found 236.0074.



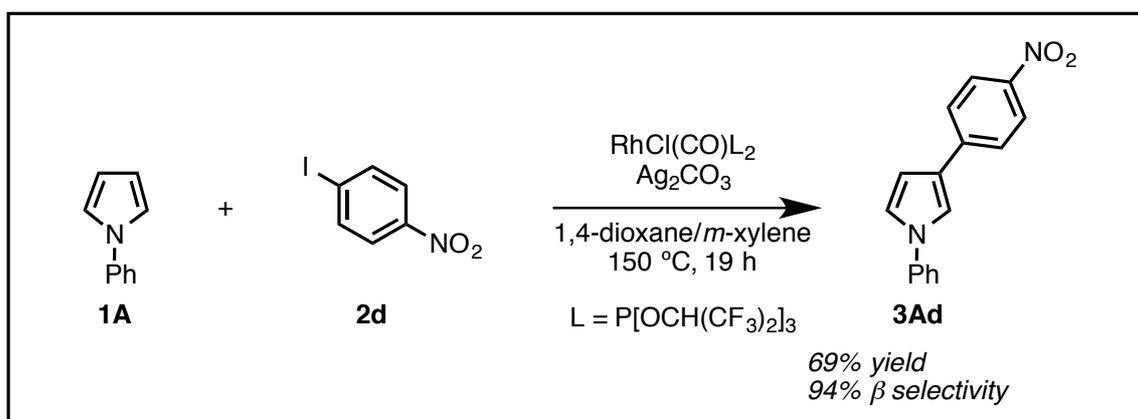
1-Methyl-3-(3-thienyl)pyrrole (3Bg): Purification by flash column chromatography (hexane/EtOAc = 20:1); Yield, 72%; Regioselectivity, $\alpha:\beta = 9:91$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 7.28 (dd, $J = 4.8, 3.0$ Hz, 1H), 7.21 (dd, $J = 4.8, 1.2$ Hz, 1H), 7.15 (dd, $J = 3.0, 1.2$ Hz, 1H), 6.82 (t, $J = 1.8$ Hz, 1H), 6.59 (t, $J = 2.4$ Hz, 1H), 6.34 (dd, $J = 2.4, 1.8$ Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.2, 126.1, 125.3, 122.4, 120.5, 118.6, 116.4, 106.7, 36.2; HRMS (DART) m/z calcd for $\text{C}_8\text{H}_{10}\text{NS}$ [MH] $^+$: 164.0534, found 164.0534.



1-Ethyl-3-phenylpyrrole (3Ca): Reaction conducted with 1.6 mol% of $[\text{RhCl}(\text{CO})_2]_2$, 6.1 mol% of $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$, 1.0 equiv of Ag_2CO_3 , 1.0 equiv of 1,2-dimethoxyethane, and dry *m*-xylene (0.2 M); Purification by PTLC (hexane/EtOAc = 40:1); Yield, 53%; Regioselectivity, $\alpha:\beta = 4:96$; Colorless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.50 (dd, $J = 8.4, 0.9$ Hz, 2H), 7.31 (t, $J = 7.8$ Hz, 2H), 7.15–7.12 (m, 1H), 6.97 (t, $J = 2.4$ Hz, 1H), 6.68 (t, $J = 2.4$ Hz, 1H), 6.44 (dd, $J = 2.7, 1.2$ Hz, 1H), 3.94 (q, $J = 7.2$ Hz, 2H), 1.45 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.0, 128.5, 125.2, 124.9, 124.7, 121.0, 116.9, 106.0, 44.4, 16.6; HRMS (DART) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{N}$ [MH] $^+$: 172.1126, found 172.1167.



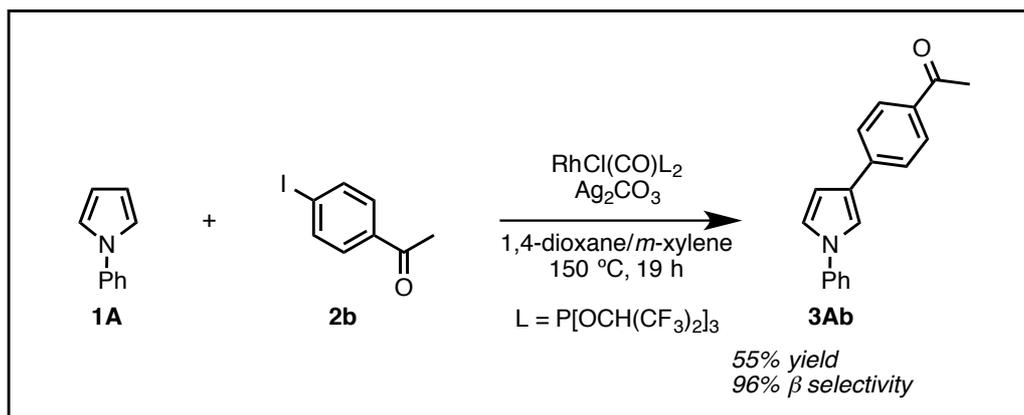
1-Benzyl-3-(4-nitrophenyl)pyrrole ¹³ (**3Dd**): Purification by flash column chromatography (hexane/EtOAc = 10:1); Yield, 69%; Regioselectivity, virtually complete at the β -position; Yellow solid. ¹H NMR (600 MHz, CDCl₃) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.38–7.31 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 1.8 Hz, 1H), 6.76 (t, *J* = 2.4 Hz, 1H), 6.55 (dd, *J* = 2.7, 2.1 Hz, 1H), 5.10 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 145.1, 142.6, 137.0, 128.9, 128.1, 127.2, 124.7, 124.3, 123.3, 123.1, 119.8, 107.1, 53.8; HRMS (DART) *m/z* calcd for C₁₇H₁₅N₂O₂ [MH]⁺: 279.11335, found 279.11350.



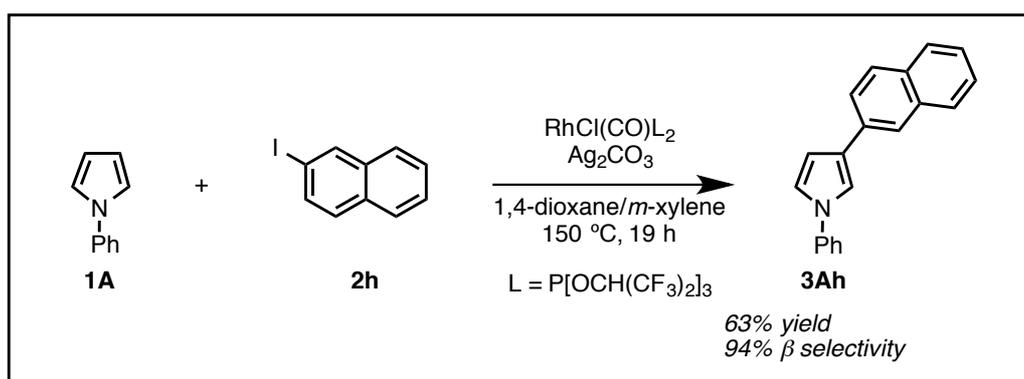
3-(4-Nitrophenyl)-1-phenylpyrrole ¹³ (**3Ad**): Purification by flash column chromatography (hexane/EtOAc = 25:1); Yield, 69%; Regioselectivity, α : β = 6:94; Yellow solid. ¹H NMR (600 MHz, CDCl₃) δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.50–7.43 (m, 5H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.16 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.71 (dd, *J* = 3.0, 1.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 145.5, 142.2, 140.1, 129.8, 126.5, 125.0, 124.7, 124.4, 121.5, 120.7, 117.8. HRMS (DART) *m/z* calcd for C₁₆H₁₃N₂O₂ [MH]⁺: 265.0977, found 265.0977.

(12) For C2-isomer 1-benzyl-2-(4-nitrophenyl)pyrrole, see: Liégault, B.; Petrov, I.; Gorelsky, S. I.; Fagnou, K. *J. Org. Chem.* **2010**, *75*, 1047.

(13) For C2-isomer (1-phenyl-2-(4-nitrophenyl)pyrrole), see reference 7a.

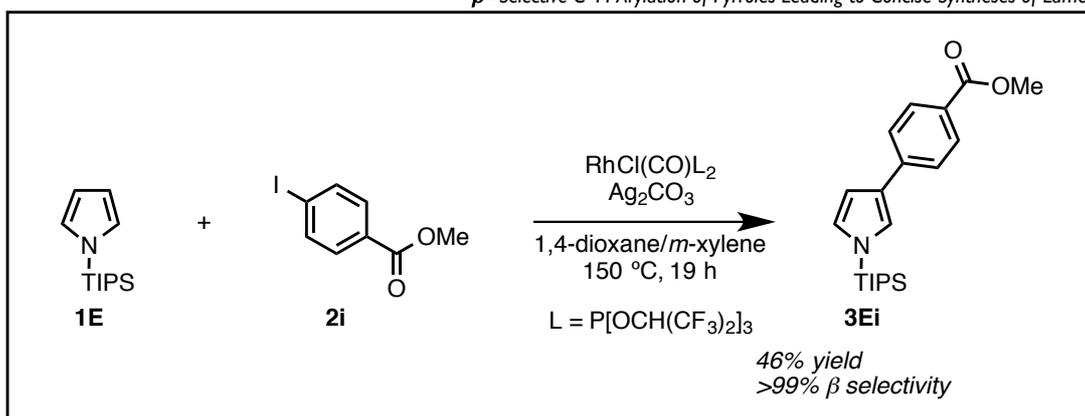


3-(4-Acetylphenyl)-1-phenylpyrrole (**3Ab**): Purification by flash column chromatography (hexane/EtOAc = 6:1); Yield, 55%; Regioselectivity, $\alpha:\beta = 4:96$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 7.96 (d, $J = 8.9$ Hz, 2H), 7.64 (d, $J = 8.3$ Hz, 2H), 7.48–7.43 (m, 5H), 7.31–7.28 (m, 1H), 7.14 (t, $J = 2.4$ Hz, 1H), 6.71 (dd, $J = 3.0, 1.8$ Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 197.5, 140.3, 140.2, 134.5, 129.7, 129.1, 126.2, 125.6, 124.8, 121.0, 120.6, 117.1, 108.8, 26.5; HRMS (DART) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{NO}$ [MH] $^+$: 262.1232, found 262.1231.

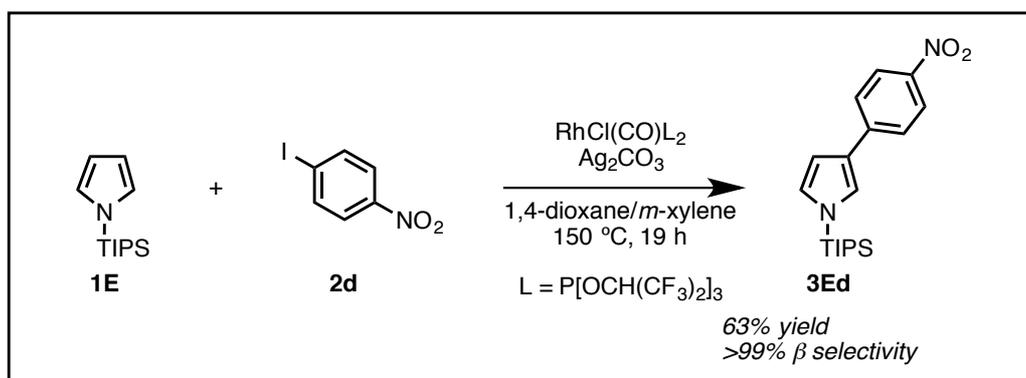


3-(2-Naphthalenyl)-1-phenylpyrrole (**3Ah**): Purification by flash column chromatography (hexane/EtOAc = 100:1); Yield, 63%; Regioselectivity, $\alpha:\beta = 6:94$; White solid. ^1H NMR (600 MHz, CDCl_3) δ 8.00–7.99 (m, 1H), 7.83–7.79 (m, 3H), 7.73 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.50 (t, $J = 2.4$ Hz, 1H), 7.47–7.43 (m, 5H), 7.40 (ddd, $J = 8.3, 6.5, 1.2$ Hz, 1H), 7.28–7.26 (m, 1H), 7.16 (t, $J = 2.4$ Hz, 1H), 6.79 (dd, $J = 3.0, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.5, 134.0, 132.7, 132.1, 129.6, 128.2, 127.7, 126.8, 126.1, 125.8, 125.0, 124.5, 122.7, 120.6, 120.4, 116.2, 108.9; HRMS (DART) m/z calcd for $\text{C}_{20}\text{H}_{15}\text{N}$ [MH] $^+$: 270.1283, found 270.1282.

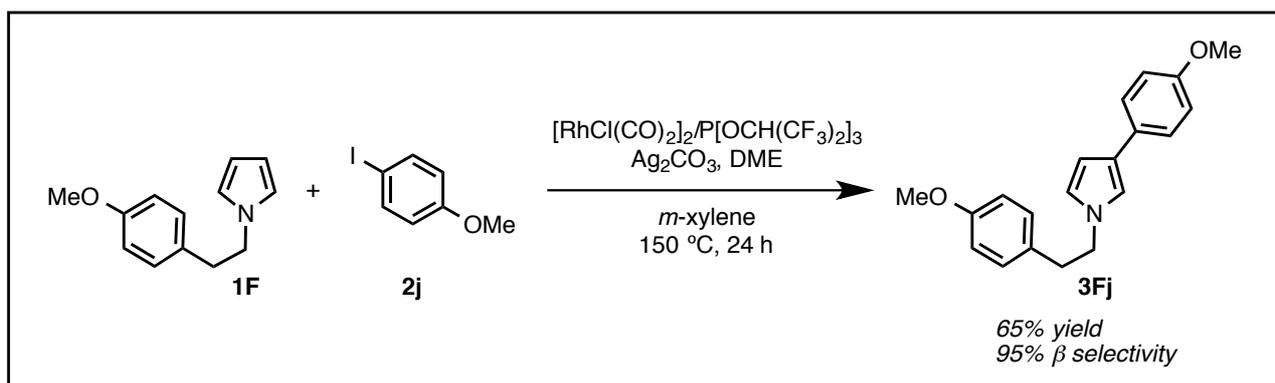
(14) For C2-isomer (2-(4-acetylphenyl)-1-phenylpyrrole), see: Rogera, J.; Doucet, H. *Adv. Synth. Catal.* **2009**, 351, 1977.



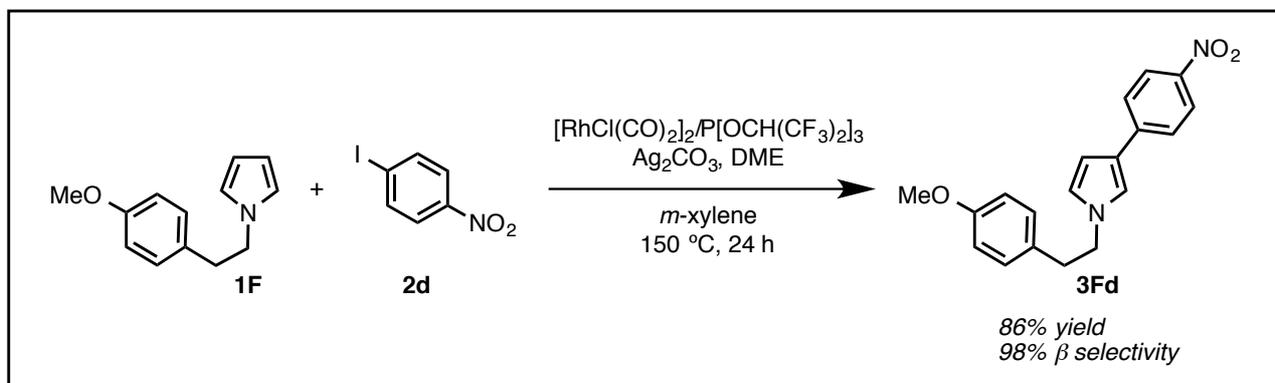
Methyl 4-(1-triisopropylsilyl-3-pyrrolyl)benzoate (3Ei): Purification by flash column chromatography (hexane/EtOAc = 50:1); Yield, 46%; Regioselectivity, virtually complete at the β -position; White solid. ^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.15 (t, $J = 1.8$ Hz, 1H), 6.82 (dd, $J = 3.0, 1.8$ Hz, 1H), 6.66 (dd, $J = 3.0, 1.8$ Hz, 1H), 3.91 (s, 3H), 1.49 (hept, $J = 7.7$ Hz, 3H), 1.13 (d, $J = 7.7$ Hz, 18H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.3, 140.7, 130.1, 126.6, 125.8, 125.7, 124.6, 121.8, 108.8, 51.9, 17.8, 11.6; HRMS (DART) m/z calcd for $\text{C}_{21}\text{H}_{32}\text{NO}_2\text{Si}$ [MH] $^+$: 358.2202, found 358.2201.



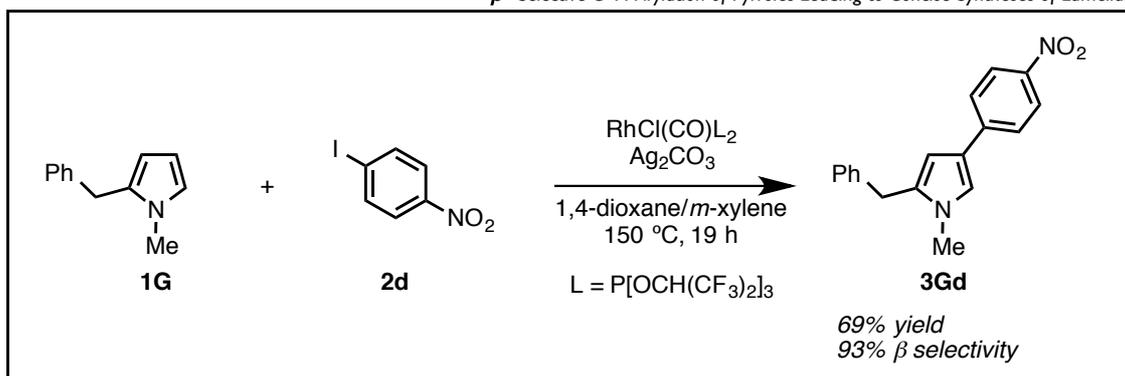
3-(4-Nitrophenyl)-1-triisopropylsilylpyrrole (3Ed): Purification by flash column chromatography (Hexane/EtOAc = 110:1); Yield, 63%; Regioselectivity, virtually complete at the β -position; Orange solid. ^1H NMR (600 MHz, CDCl_3) δ 8.18 (d, $J = 8.9$ Hz, 2H), 7.64 (d, $J = 8.9$ Hz, 2H), 7.19 (s, 1H), 6.85 (t, $J = 2.4$ Hz, 1H), 6.67 (t, $J = 1.2$ Hz, 1H), 1.50 (hept, $J = 7.1$ Hz, 3H), 1.14 (d, $J = 7.1$ Hz, 18H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.1, 142.9, 138.7, 126.3, 125.0, 124.2, 122.7, 108.9, 17.7, 11.6; HRMS (DART) m/z calcd for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_2\text{Si}$ [MH] $^+$: 345.1998, found 345.1997.



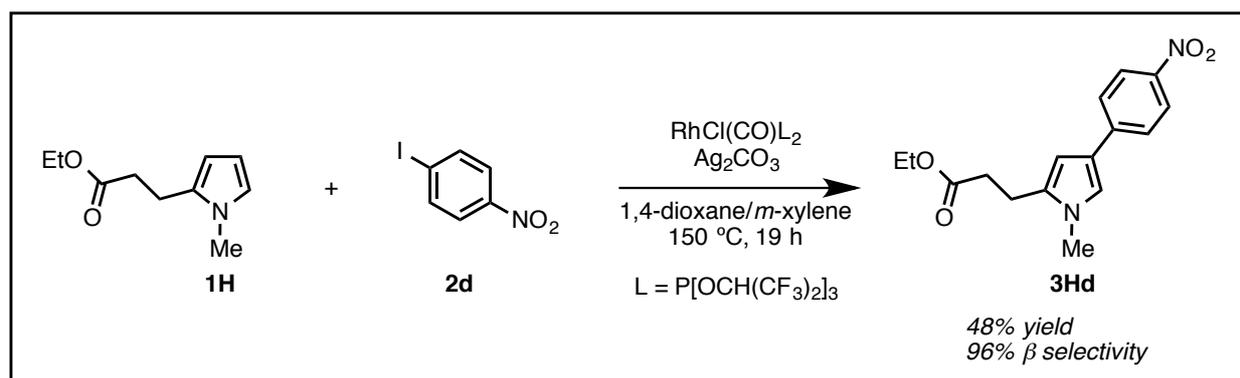
3-(4-Methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]pyrrole (3Fj): Reaction conducted with 1.5 mol% of $[\text{RhCl}(\text{CO})_2]_2$, 6.0 mol% of $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$, 1.0 equiv of Ag_2CO_3 , 1.0 equiv of 1,2-dimethoxyethane, and *m*-xylene (0.15 M); Purification by flash column chromatography (hexane/EtOAc = 6:1); Yield, 65%; Regioselectivity, $\alpha:\beta = 5:95$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 7.40 (d, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 9.1$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 6.80 (dd, $J = 2.3, 1.8$ Hz, 1H), 6.57 (dd, $J = 2.7, 2.3$ Hz, 1H), 6.35 (dd, $J = 2.7, 1.8$ Hz, 1H), 4.05 (dd, $J = 7.7, 7.2$ Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.01 (dd, $J = 7.7, 7.3$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.3, 157.6, 130.4, 129.7, 128.9, 126.0, 124.5, 121.4, 116.6, 114.0, 114.0, 105.9, 55.3, 55.2, 51.6, 37.4; HRMS (DART) m/z calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2$ [MH] $^+$: 308.1651, found 308.1651.



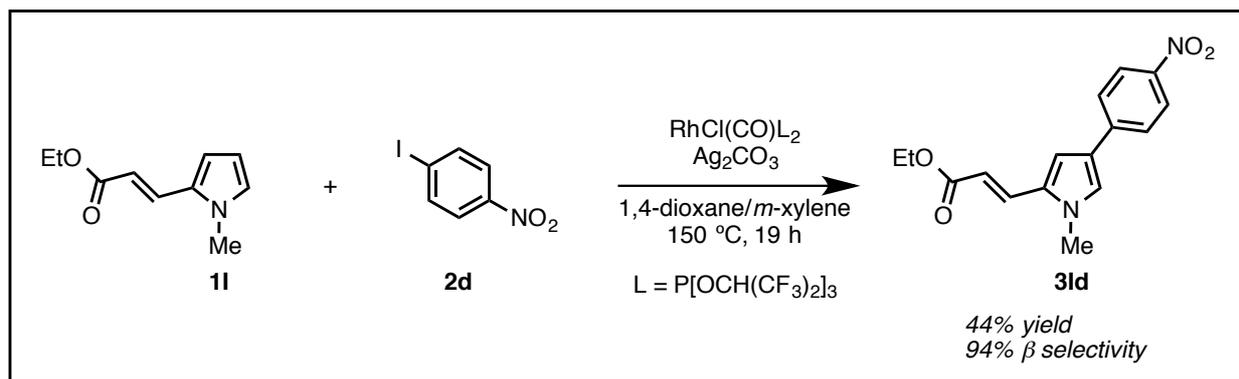
3-(4-Nitrophenyl)-1-[2-(4-methoxyphenyl)ethyl]pyrrole (3Fd): Reaction conducted with 1.5 mol% of $[\text{RhCl}(\text{CO})_2]_2$, 6.0 mol% of $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$, 1.0 equiv of Ag_2CO_3 , 1.0 equiv of 1,2-dimethoxyethane, and dry *m*-xylene (0.2 M); Purification by PTLC (hexane/EtOAc = 3:1); Yield, 86%; Regioselectivity, $\alpha:\beta = 2:98$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.16 (d, $J = 9.1$ Hz, 2H), 7.55 (d, $J = 9.1$ Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 6.98 (dd, $J = 2.3, 1.8$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.63 (dd, $J = 2.7, 2.3$ Hz, 1H), 6.47 (dd, $J = 2.7, 1.8$ Hz, 1H), 4.10 (t, $J = 7.3$ Hz, 2H), 3.79 (s, 3H), 3.03 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.5, 145.0, 142.8, 129.9, 129.6, 124.6, 124.3, 122.7, 122.5, 119.4, 114.1, 106.7, 55.3, 51.9, 37.3; HRMS (DART) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_3$ [MH] $^+$: 323.1396, found 323.1395.



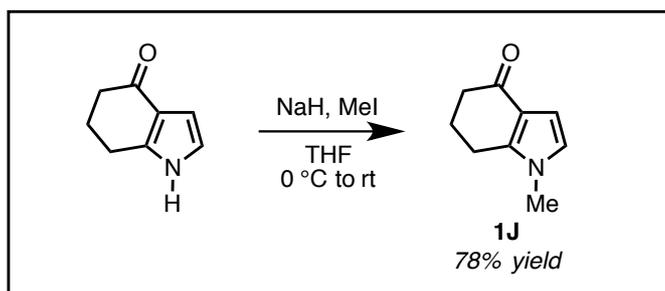
2-Benzyl-1-methyl-4-(4-nitrophenyl)pyrrole (3Gd): Purification by flash column chromatography (hexane/EtOAc = 7:1); Yield, 69%; Regioselectivity, $\alpha:\beta = 7:93$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.15 (d, $J = 9.0$ Hz, 2H), 7.54 (d, $J = 9.0$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.26–7.23 (m, 1H), 7.19 (d, $J = 7.2$ Hz, 2H), 7.03 (d, $J = 2.4$ Hz, 1H), 6.26 (d, $J = 1.8$ Hz, 1H), 3.97 (s, 2H), 3.49 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 144.9, 142.8, 138.4, 133.9, 128.7, 128.4, 126.5, 124.4, 124.3, 121.2, 120.8, 106.4, 34.2, 32.8; HRMS (DART) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_2$ [MH] $^+$: 293.12900, found 293.12894.



Ethyl 3-(1-methyl-4-(4-nitrophenyl)pyrrol-2-yl)propanoate (3Hd): Purification by flash column chromatography (hexane/EtOAc = 3:1); Yield, 48%; Regioselectivity, $\alpha:\beta = 4:96$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.16 (d, $J = 9.0$ Hz, 2H), 7.53 (d, $J = 9.0$ Hz, 2H), 7.00 (d, $J = 1.8$ Hz, 1H), 6.25 (d, $J = 1.8$ Hz, 1H), 4.18 (q, $J = 6.6$ Hz, 2H), 3.62 (s, 3H), 2.91 (t, $J = 7.2$ Hz, 2H), 2.70 (t, $J = 7.8$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.5, 144.8, 142.7, 133.9, 124.3, 124.2, 121.1, 120.4, 104.1, 60.6, 33.9, 33.1, 21.4, 14.2; HRMS (DART) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_4$ [MH] $^+$: 303.13448, found 303.13457.

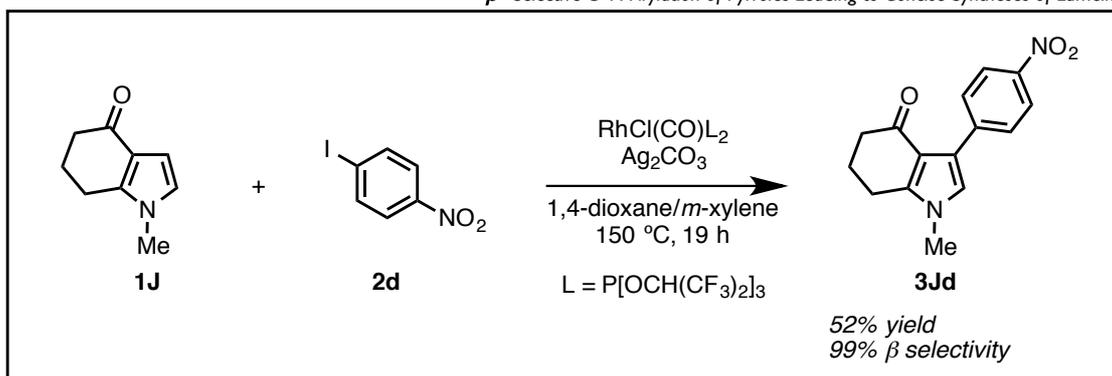


Ethyl (E)-3-(1-methyl-4-(4-nitrophenyl)pyrrol-2-yl)acrylate (3Id): Purification by flash column chromatography (hexane/EtOAc = 3:1); Yield, 44%; Regioselectivity, $\alpha:\beta = 6:94$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 9.0$ Hz, 2H), 7.60–7.57 (m, 3H), 7.17 (d, $J = 1.8$ Hz, 2H), 6.97 (d, $J = 1.8$ Hz, 1H), 6.26 (d, $J = 15.6$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.78 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.4, 145.6, 141.3, 131.3, 131.1, 129.89, 129.86, 124.3, 123.2, 114.9, 108.9, 60.5, 34.8, 14.3; HRMS (DART) m/z calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_4$ [MH] $^+$: 301.11883, found 301.11893.

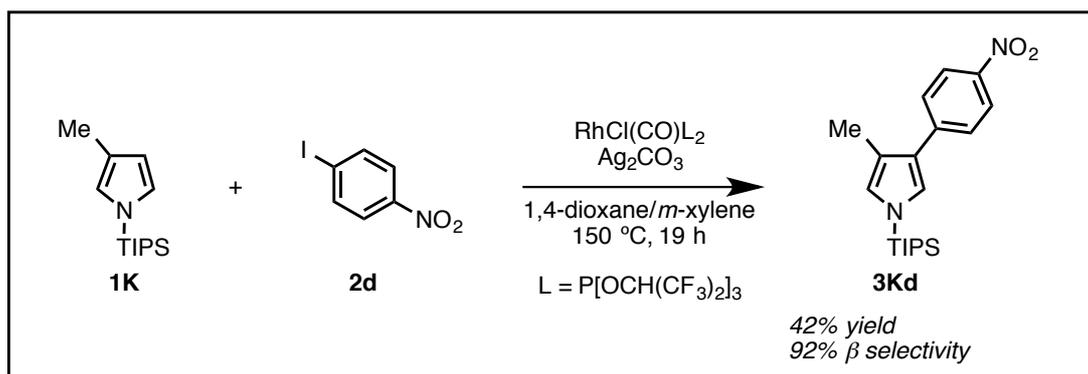


1-Methyl-1,5,6,7-tetrahydroindol-4-one (1J): To a solution of 1,5,6,7-tetrahydroindol-4-one (540.6 mg, 4.0 mmol, 1.0 equiv) in THF (10 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 520.0 mg, 8.0 mmol, 2.0 equiv). After stirring for 30 min, methyl iodide (0.30 mL, 4.8 mmol, 1.2 equiv) was added and then the reaction mixture was warmed to room temperature. After completion of the reaction, it was quenched with H_2O . The reaction mixture was extracted with EtOAc, washed with brine, and dried over Na_2SO_4 . Evaporation of solvent under reduced pressure gave a residue, which was purified by silica gel column chromatography (hexane/EtOAc = 2 : 3) to afford **1J** as white solid (463 mg, 78% yield).

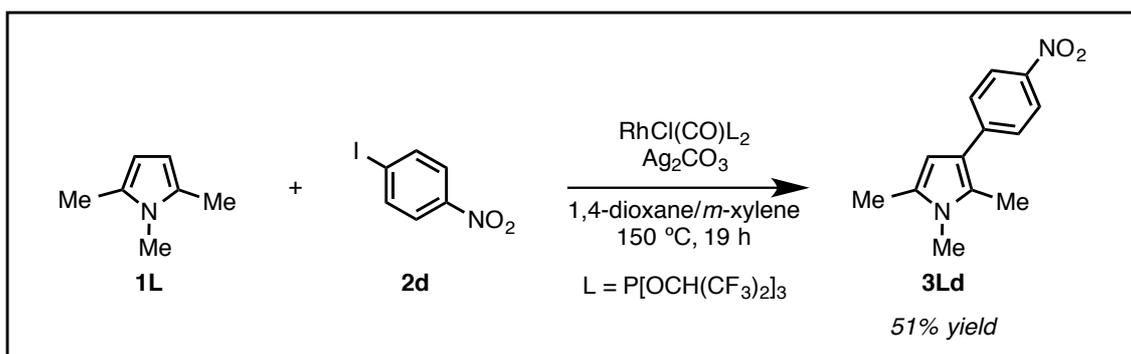
^1H NMR (600 MHz, CDCl_3) δ 6.54 (d, $J = 3.0$ Hz, 1H), 6.51 (d, $J = 3.0$ Hz, 1H), 3.56 (s, 3H), 2.73 (t, $J = 6.0$ Hz, 2H), 2.44 (t, $J = 6.0$ Hz, 2H), 2.15 (quin, $J = 6.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 194.0, 143.6, 123.1, 120.6, 105.1, 37.5, 33.3, 23.5, 21.4; HRMS (DART) m/z calcd for $\text{C}_8\text{H}_{12}\text{NO}$ [MH] $^+$: 150.09189, found 150.09191.



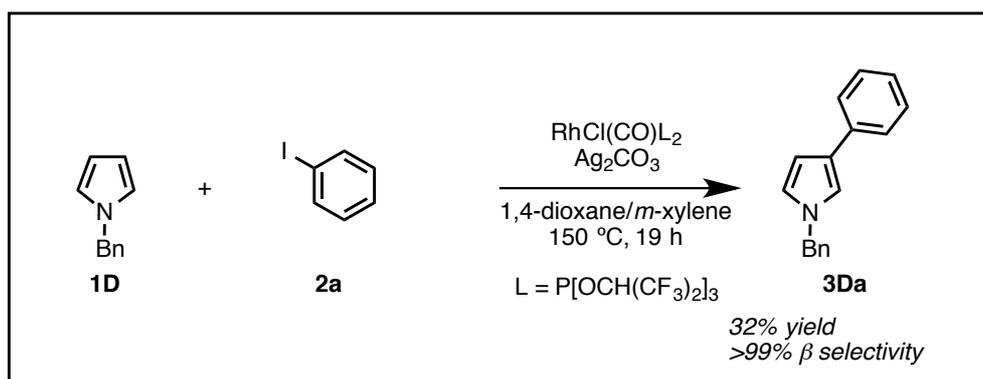
1-Methyl-3-(4-nitrophenyl)-1,5,6,7-tetrahydroindol-4-one (3Jd): Purification by flash column chromatography (hexane/EtOAc = 3:1); Yield, 52%; Regioselectivity, $\alpha:\beta = 1:99$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.17 (d, $J = 9.0$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 6.77 (s, 1H), 3.63 (s, 3H), 2.81 (t, $J = 6.0$ Hz, 2H), 2.52 (t, $J = 6.0$ Hz, 2H), 2.20 (quin, $J = 6.0$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 193.6, 145.9, 145.7, 141.5, 128.8, 123.2, 123.1, 122.2, 117.2, 38.7, 33.6, 23.0, 21.9; HRMS (DART) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_3$ [MH] $^+$: 271.10827, found 271.10818.



3-Methyl-4-(4-nitrophenyl)-1-(triisopropylsilyl)pyrrole (3Kd): Purification by flash column chromatography (hexane/EtOAc = 40:1); Yield, 42%; Regioselectivity, $\alpha:\beta = 8:92$; Yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 9.0$ Hz, 2H), 7.59 (d, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.62–6.61 (m, 1H), 2.28 (s, 3H), 1.47 (hept, $J = 7.8$ Hz, 3H), 1.13 (d, $J = 7.2$ Hz, 18H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.0, 144.0, 126.9, 124.60, 124.56, 124.0, 123.9, 119.0, 17.8, 12.2, 11.6; HRMS (DART) m/z calcd for $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}_2\text{Si}$ [MH] $^+$: 359.21548, found 359.21539.



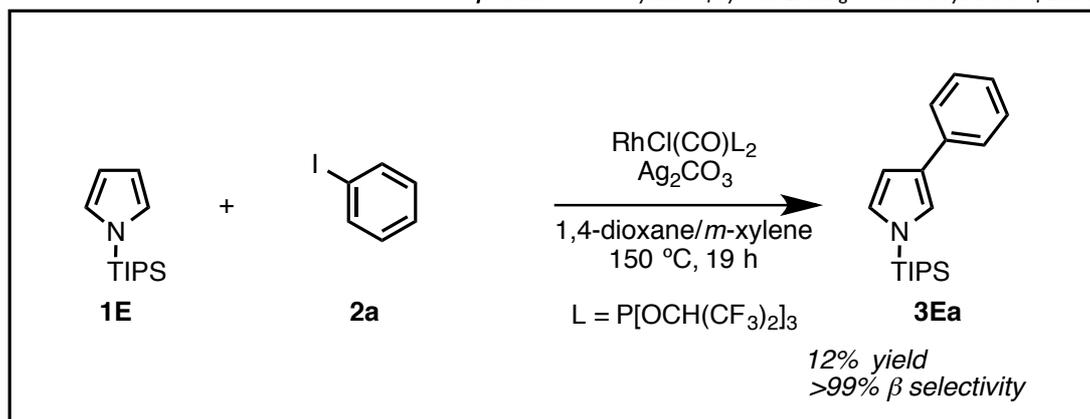
3-(4-Nitrophenyl)-1,2,5-trimethylpyrrole¹⁵ (3Ld): Purification by flash column chromatography (hexane/EtOAc = 10:1); Yield, 51%; Orange solid. ^1H NMR (600 MHz, CDCl_3) δ 8.19 (d, $J = 8.9$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 6.07 (s, 1H), 3.46 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 144.7, 128.9, 127.4, 126.4, 123.8, 118.7, 105.6, 30.5, 12.4, 11.6; HRMS (DART) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2$ [MH] $^+$: 231.1134, found 231.1137.



1-Benzyl-3-phenylpyrrole¹⁶ (3Da): Purification by gel permeation chromatography (GPC); Yield, 32%; Regioselectivity, $\alpha/\beta = 1:>99$; Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.50–7.49 (m, 2H), 7.34–7.28 (m, 5H), 7.17–7.12 (m, 3H), 6.98 (t, $J = 2.4$ Hz, 1H), 6.71 (t, $J = 2.4$ Hz, 1H), 6.50 (dd, $J = 2.4$, 1.8 Hz, 1H), 5.08 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.8, 135.8, 128.8, 128.6, 127.8, 127.1, 125.3, 125.2, 124.9, 122.2, 118.0, 106.6, 53.6; HRMS (DART) m/z calcd for $\text{C}_{17}\text{H}_{16}\text{N}$ [MH] $^+$: 234.12827, found 234.12824.

(15) Vakuliuk, O.; Gryko, D. T. *Eur. J. Org. Chem.* **2011**, 2854.

(16) For C2-isomer 1-benzyl-2-phenylpyrrole, see: Aponick, A.; Li, C.-Y.; Malinge, J.; Marques E. F. *Org. Lett.* **2009**, *11*, 4624.

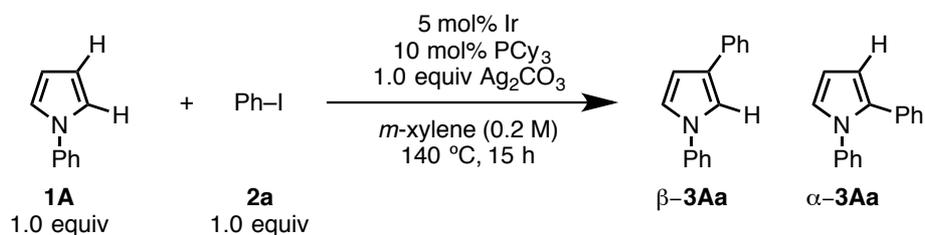


3-Phenyl-1-triisopropylsilylpyrrole⁺ (3Ea): Purification by gel permeation chromatography (GPC); Yield, 12%; Regioselectivity, $\alpha/\beta = 1:>99$; Colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.54 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.14 (t, $J = 7.2$ Hz, 1H), 7.06 (t, $J = 1.8$ Hz, 1H), 6.80 (t, $J = 2.4$ Hz, 1H), 6.61 (dd, $J = 3.0, 1.2$ Hz, 1H), 1.48 (hept, $J = 7.2$ Hz, 3H), 1.13 (d, $J = 7.8$ Hz, 18H); ¹³C NMR (150 MHz, CDCl₃) δ 136.0, 128.5, 126.8, 125.3, 125.22, 125.16, 120.6, 108.6, 17.8, 11.7; HRMS (DART) m/z calcd for C₁₃H₂₀NSi [MH]⁺: 300.21475, found 300.21472.

5. Effects of Reaction Parameters

Effects of reaction parameters (Ir and Rh sources, ligands, additives, solvents, and temperatures) were investigated. Results using the phenylation of *N*-phenylpyrrole (**1A**) or *N*-methylpyrrole (**1B**) with iodobenzene (**2a**) as a model reaction are shown here.

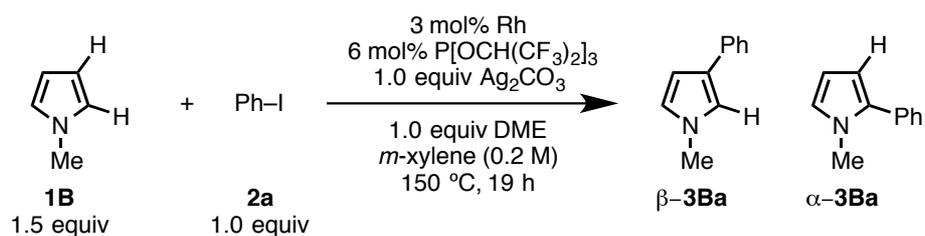
Table S1. Effect of Ir Source.



| entry | Ir | yield (%) ^a | β/α ^a |
|-------|--|------------------------|-----------------------------|
| 1 | Ir(acac)(CO) ₂ | 6 | >99:1 |
| 2 | [Ir(OMe)(cod)] ₂ | 14 | 99:1 |
| 3 | [IrCl(cod)] ₂ | 9 | 98:2 |
| 4 | Ir(acac)(cod) | 7 | >99:1 |
| 5 | Ir(cod)(acac-F ₆) | 9 | >99:1 |
| 6 | Ir(MeCp)(cod) | <1 | >99:1 |
| 7 | IrCl(CO)(PPh ₃) ₂ | 5 | >99:1 |
| 8 | IrH(CO)(PPh ₃) ₃ | 6 | >99:1 |
| 9 | Ir(Ind)(cod) | 12 | >99:1 |

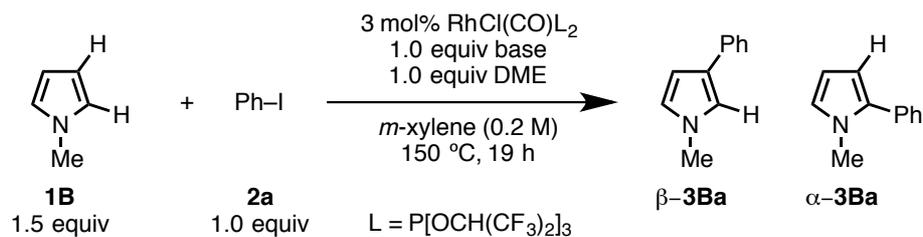
^a Determined by GC analysis.

Table S2. Effect of Rh Source.

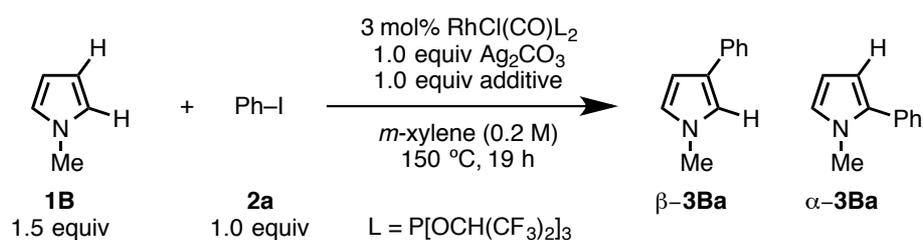


| entry | Rh | yield (%) ^a | β/α ^a |
|-------|---|------------------------|-----------------------------|
| 1 | [RhCl(CO) ₂] ₂ ^b | 76 | 91:9 |
| 2 | Rh(nbd) ₂ BF ₄ | 29 | 50:50 |
| 3 | [Rh(nbd)Cl] ₂ ^b | 52 | 79:21 |
| 4 | Rh(acac)(C ₂ H ₄) ₂ | 24 | 64:36 |
| 5 | Rh(CO) ₂ (acac) | 71 | 88:12 |

^a Determined by GC analysis. ^b Reaction with 1.5 mol% Rh.

Table S3. Effect of Base.

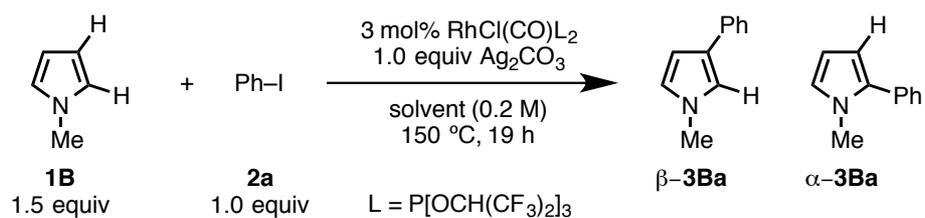
| entry | base | yield (%) ^a | β/α^a |
|-------|---------------------------------|------------------------|------------------|
| 1 | AgNO ₃ | – | – |
| 2 | AgO | 37 | 85:15 |
| 3 | Ag ₂ O | 73 | 92:8 |
| 4 | K ₂ CO ₃ | – | – |
| 5 | Na ₂ CO ₃ | – | – |
| 6 | Cs ₂ CO ₃ | – | – |

^a Determined by GC analysis.**Table S4.** Effect of Additive.

| entry | additive | yield (%) ^a | β/α^a |
|-------|-----------------|------------------------|------------------|
| 1 | none | 66 | 89:11 |
| 2 | diglyme | 74 | 93:7 |
| 3 | 1,4-dioxane | 73 | 91:9 |
| 4 | ethylene glycol | 1 | 22:78 |
| 5 | methanol | 39 | 69:31 |
| 6 | acetonitrile | 67 | 86:14 |
| 7 | NMP | 30 | 74:26 |
| 8 | DMSO | 42 | 42:58 |
| 9 | triethylamine | 1 | 20:80 |
| 10 | pyridine | – | – |

^a Determined by GC analysis.

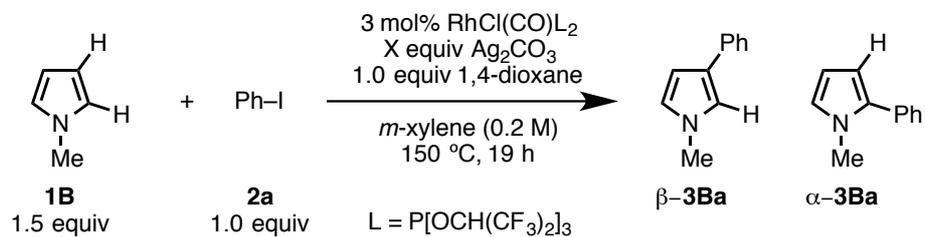
Table S5. Effect of Solvent.



| entry | 1,4-dioxane/ <i>m</i> -xylene | yield (%) ^a | β/α^a |
|-------|-------------------------------|------------------------|------------------|
| 1 | 1,4-dioxane | 74 | 89:11 |
| 2 | <i>m</i> -xylene | 66 | 89:11 |
| 3 | 1:4 | 77 | 90:10 |
| 4 | 2:3 | 76 | 89:11 |
| 5 | 3:2 | 82 | 90:10 |
| 6 | 4:1 | 76 | 87:13 |
| 7 | <i>m</i> -xylene ^b | 73 | 91:9 |
| 8 | octane ^b | 66 | 86:14 |

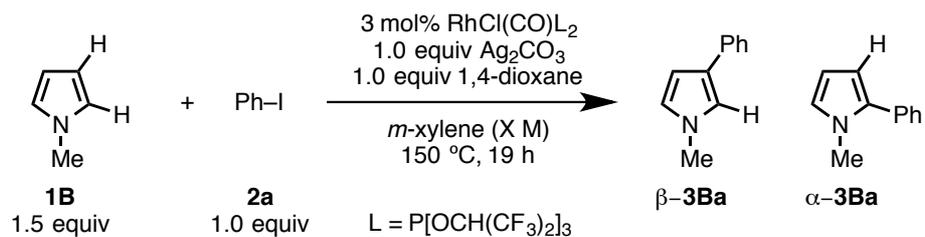
^a Determined by GC analysis. ^b Reaction with 1.0 equiv 1,4-dioxane.

Table S6. Effect of Amount of Base.



| entry | X (equiv) | yield (%) ^a | β/α^a |
|-------|-----------|------------------------|------------------|
| 1 | 0.5 | 77 | 87:13 |
| 2 | 1.0 | 73 | 91:9 |
| 3 | 1.5 | 68 | 93:7 |
| 4 | 2.0 | 45 | 88:12 |

^a Determined by GC analysis.

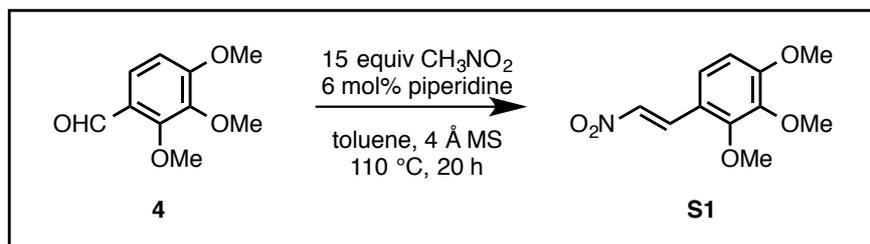
Table S7. Effect of Concentration.

| entry | X (M) | yield (%) ^a | β/α ^a |
|-------|-------|------------------------|-----------------------------|
| 1 | 0.50 | 67 | 91:9 |
| 2 | 0.33 | 81 | 93:7 |
| 3 | 0.17 | 77 | 93:7 |
| 4 | 0.14 | 75 | 93:7 |

^a Determined by GC analysis.

6. Total Synthesis of Lamellarins C and I

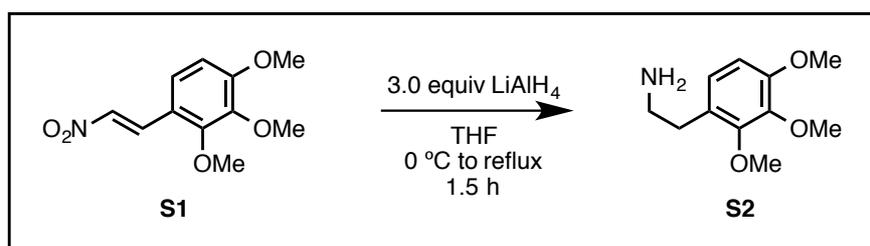
1-((E)-2-Nitrovinyl)-2,3,4-trimethoxybenzene¹⁸ (S1):



This synthesis is based on a procedure reported by Fioravanti, Pellacani, and Tardella *et al.*¹⁹ To a 1-L two-neck flask fitted with a mechanical stirrer and a condenser were added activated 4 Å molecular sieves (100 g), 2,3,4-trimethoxybenzaldehyde (5: 25 g, 127 mmol, 1.0 equiv), piperidine (650 mg, 7.6 mmol, 6 mol%), and nitromethane (117 g, 1.9 mol, 15 equiv). After dry toluene (325 mL) was added, the flask was filled with nitrogen. The reaction mixture was stirred at 110 °C for 20 h in oil bath. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad (hexane/CH₂Cl₂ = 1:1) until the color of eluting solution was disappeared. The volatiles were removed under reduced pressure to afford 1-((E)-2-nitrovinyl)-2,3,4-trimethoxybenzene (S1: 28 g, 92%) as yellow solid. The crude was sufficiently pure, and used for the next step without further purification.

¹H NMR (600 MHz, CDCl₃) δ 8.09 (d, *J* = 13.7 Hz, 1H), 7.77 (d, *J* = 13.7 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 157.3, 154.3, 142.4, 136.5, 135.3, 126.6, 117.0, 107.6, 61.2, 60.9, 56.2; HRMS (DART) *m/z* calcd for C₁₁H₁₁NO₅ [MH]⁺: 240.0872, found 240.0875.

2-(2,3,4-Trimethoxyphenyl)ethylamine²⁰ (S2):



The reaction was an adaption of the conditions reported by Iwao *et al.*²¹ A 1-L flask containing a stirring bar was dried with a heat-gun under vacuum and filled with nitrogen after cooling to room temperature. 1-((E)-2-Nitrovinyl)-2,3,4-trimethoxybenzene (S1: 28 g, 117 mmol, 1.0 equiv) was added portion-wise to a suspension of LiAlH₄ (13.3 g, 351 mmol, 3.0 equiv) in THF (420 mL) at

(18) Chien, C.-W.; Shi, C.; Lin, C.-F.; Ojima, I. *Tetrahedron* **2011**, *67*, 6513.

(19) Fioravanti, S.; Pellacani, L.; Tardella, P. A.; Vergari, M. C. *Org. Lett.* **2008**, *10*, 1449.

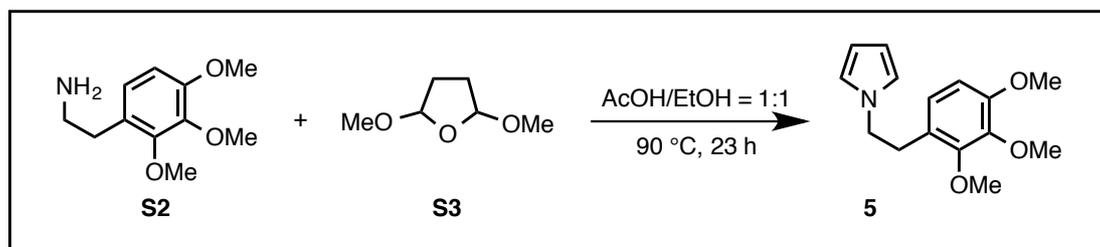
(20) Yoshida, Y.; Mohri, K.; Isobe, K.; Itoh, T.; Yamamoto, K. *J. Org. Chem.* **2009**, *74*, 6010.

(21) Fujikawa, N.; Ohta, T.; Yamaguchi, T.; Fukuda, T.; Ishibashi, F.; Iwao, M. *Tetrahedron* **2006**, *62*, 594.

0 °C. The reaction mixture was stirred at 0 °C for 1 h and, then heated at 75 °C for 0.5 h. After the reaction mixture appeared pale white and no more gas was formed, the mixture was cooled to 0 °C and quenched carefully with water (13 mL), 15% aqueous NaOH (13 mL), and water (39 mL). The slurry was stirred vigorously for 2 h and diluted with THF (300 mL). The white precipitates is filtered off and washed with EtOAc until it appears white. After drying the filtrate over MgSO₄, the volatiles were removed under reduced pressure to give 2-(2,3,4-trimethoxyphenyl)ethylamine (**S2**: 20.4 g, 83%) as yellow liquid. The crude was sufficiently pure and used for the next step without further purification.

¹H NMR (600 MHz, CDCl₃) δ 6.84 (d, J = 8.9 Hz, 1H), 6.62 (d, J = 8.9 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84 (s, 3H), 2.90 (t, J = 7.1 Hz, 2H), 2.70 (t, J = 7.1 Hz, 2H), 1.18 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 152.2, 152.1, 142.3, 125.7, 124.3, 107.1, 60.9, 60.7, 56.0, 43.1, 34.3; HRMS (DART) m/z calcd for C₁₁H₁₆NO₃ [MH]⁺: 212.1287, found 212.1289.

1-[2-(2,3,4-Trimethoxyphenyl)ethyl]pyrrole (**5**):

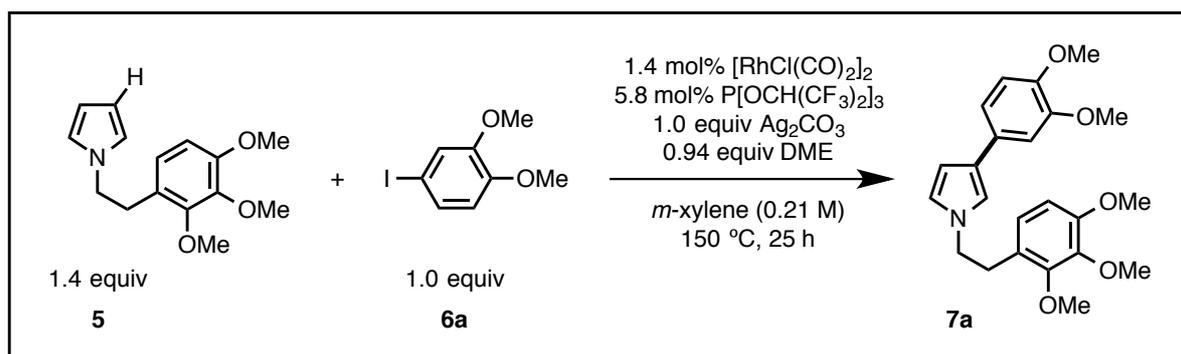


This synthesis is based on a procedure reported by Melander *et al.*²² A 500-mL three-neck flask fitted with a condenser, containing a magnetic stirring bar, was dried with a heat-gun under vacuum and filled with nitrogen after cooling to room temperature. 2,5-Dimethoxytetrahydrofuran (**S3**: 8.99 g, 68.0 mmol, 1.2 equiv) was dissolved in AcOH (110 mL) and EtOH (110 mL) and to this solution was added 2-(2,3,4-trimethoxyphenyl)ethylamine (**S2**: 11.7 g, 55.3 mmol, 1.0 equiv). The reaction was heated at 90 °C for 18 h. After cooling to room temperature, excess AcOH was removed by rotary evaporation. The residue was taken up in EtOAc (450 mL) and sequentially washed with 1N HCl (2 x 217 mL), 10% K₂CO₃ (3 x 325 mL), and brine (2 x 217 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated. The mixture was passed through a short silica gel pad (hexane/EtOAc = 5:1 to 3:1). The filtrate was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc = 5:1) to afford 1-[2-(2,3,4-trimethoxyphenyl)-ethyl] pyrrole (**5**: 8.03 g, 56%) as pale yellow oil.

¹H NMR (600 MHz, CDCl₃) δ 6.68 (d, J = 8.7 Hz, 1H), 6.62 (dd, J = 2.3, 1.8 Hz, 2H), 6.57 (d, J = 8.6 Hz, 1H), 6.11 (dd, J = 2.3, 1.8 Hz, 2H), 4.05 (t, J = 7.5 Hz, 2H), 3.88 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 2.99 (t, J = 7.5 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 152.7, 152.0, 142.3, 124.3, 124.2, 120.5, 107.8, 107.1, 60.9, 60.7, 56.0, 50.4, 32.8; HRMS (DART) m/z calcd for C₁₅H₁₉NO₃ [MH]⁺: 262.1443, found 262.1441.

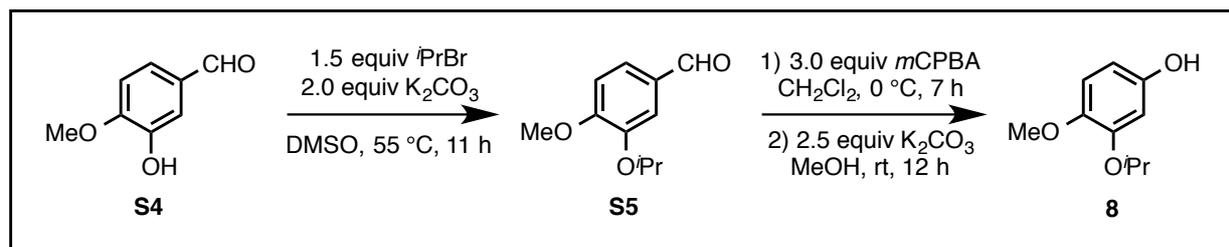
(22) Richards, J. J.; Reed, C. S.; Melander, C. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4325.

3-(3,4-Dimethoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole (7a):



A 200-mL glass vessel equipped with J. Young® O-ring tap, containing a magnetic stirring bar, was dried with a heat gun under vacuum and filled with nitrogen after cooling to room temperature. To this vessel were added $[\text{RhCl}(\text{CO})_2]_2$ (59.5 mg, 0.15 mmol, 1.4 mol%), $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$ (191 μL , 0.61 mmol, 5.8 mol%), Ag_2CO_3 (2.77 g, 10.0 mmol, 0.94 equiv), 1,2-dimethoxyethane (1.04 mL, 9.97 mmol, 1.0 equiv), 1-[2-(2,3,4-Trimethoxyphenyl)ethyl]pyrrole (**5**: 3.96 g, 15.1 mmol, 1.4 equiv), 1,2-dimethoxy-4-iodobenzene (**6a**: 2.80 g, 10.6 mmol, 1.0 equiv), and dry *m*-xylene (50 mL) under a stream of nitrogen. The vessel was sealed with an O-ring tap, and then heated at 150 °C for 25 h in an oil-bath. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was purified by flash column chromatography (FCC) (hexane/EtOAc = 4:1 to 3:1) to afford 3-(3,4-dimethoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole (**7a**: 2.08 g, 49%) as pale yellow oil.

^1H NMR (600 MHz, CDCl_3) δ 7.03 (dd, $J = 2.3, 1.8$ Hz, 1H), 7.00 (d, $J = 1.8$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.84 (dd, $J = 2.3, 1.8$ Hz, 1H), 6.72 (d, $J = 8.6$ Hz, 1H), 6.62 (d, $J = 2.3$ Hz, 1H), 6.58 (d, $J = 8.6$ Hz, 1H), 6.35 (dd, $J = 2.7, 1.8$ Hz, 2H), 4.05 (dd, $J = 7.7, 7.3$ Hz, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.02 (dd, $J = 7.7, 7.3$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.8, 152.0, 149.0, 147.0, 142.3, 129.4, 124.6, 124.4, 124.1, 121.5, 117.2, 116.8, 111.6, 108.8, 107.2, 105.9, 61.0, 60.8, 56.0, 55.8, 50.6, 32.7; HRMS (DART) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_5$ $[\text{MH}]^+$: 398.1967, found 398.1970.

3-Isopropoxy-4-methoxyphenol^{14,23} (8):

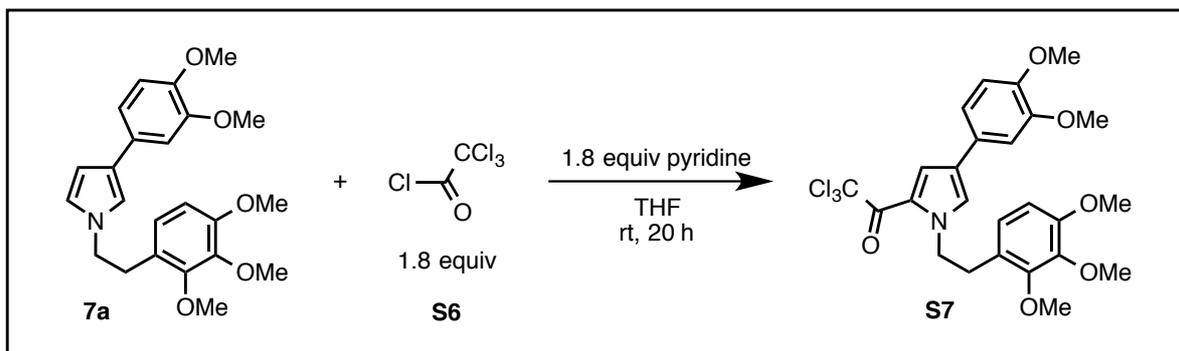
According to a procedure of Jia *et al.*²³ and Iwao *et al.*,¹⁴ to a suspension of 3-hydroxy-4-methoxybenzaldehyde (S4: 6.09 g, 40 mmol, 1.0 equiv) and K_2CO_3 (11.1 g, 80 mmol, 2.0 equiv) in DMSO (116 mL) was added i PrBr (5.6 mL, 60 mmol, 1.5 equiv) at room temperature and the mixture was heated at 55 °C for 11 h. The reaction mixture was cooled to room temperature and diluted with water. The mixture was extracted with diethyl ether (3 x 100 mL) and the extract was washed successively with 10% aqueous NaOH (150 mL), water (150 mL), and brine (100 mL), and dried over Na_2SO_4 . The solvent was evaporated under reduced pressure to give a quantitative yield of 3-isopropoxy-4-methoxybenzaldehyde (S5). This product was used without further purification. Under an nitrogen atmosphere, *m*-chloroperbenzoic acid (18.0 g of 77 wt%, 80 mmol) was added portion wise to a solution of 3-isopropoxy-4-methoxybenzaldehyde (S5: 40 mmol) in dichloromethane (80 mL) at 0 °C. After being stirred for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 x 130 mL). The combined extract was washed with brine (200 mL), dried over Na_2SO_4 , and evaporated under reduced pressure. The residue was dissolved in methanol (146 mL), and K_2CO_3 (13.9 g, 100 mmol) was added portion wise to the solution at room temperature. After being stirred for 1 h, the mixture was evaporated under reduced pressure. Water (170 mL) was added to the residue and the product was extracted with diethyl ether (3 x 150 mL). The extract was washed with brine (150 mL), dried over Na_2SO_4 , evaporated under reduced pressure. The residue was then purified by crystallization from diethyl ether to afford 3-isopropoxy-4-methoxyphenol (8: 4.62 g, 63% yield) as colorless solid.

1H NMR (600 MHz, $CDCl_3$) δ 6.74 (d, J = 8.6 Hz, 1H), 6.48 (d, J = 2.7 Hz, 1H), 6.35 (dd, J = 8.6, 2.7 Hz, 1H), 4.99 (s, 1H), 4.46 (q, J = 6.4 Hz, 1H), 3.79 (s, 3H), 1.34 (d, J = 6.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 148.2, 144.4, 113.4, 106.4, 104.1, 71.3, 56.8, 22.0. HRMS (DART) m/z calcd. for $C_{10}H_{15}O_3$ [MH]⁺: 183.1021, found 183.1020.

(23) Pla, D.; Marchal, A.; Olsen, C. A.; Albericio, F.; Álvarez, M. *J. Org. Chem.* **2005**, *70*, 8231.

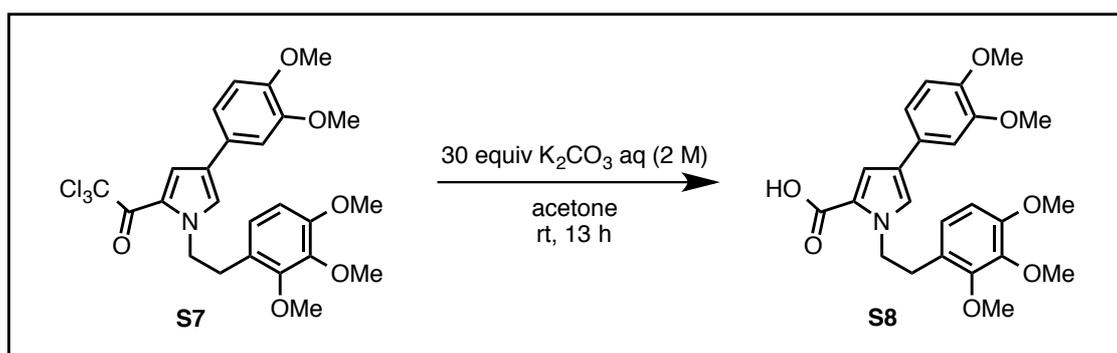
(24) Li, Q.; Jiang, J.; Fan, A.; Cui, Y.; Jia, Y. *Org. Lett.* **2011**, *13*, 312.

4-(3,4-Dimethoxyphenyl)-2-trichloroacetyl-1-[2-(2,3,4-trimethoxyphenyl)ethyl]-pyrrole (S7):



According to a procedure of Itami *et al.*²⁵ and Varvounis *et al.*,²⁶ to a solution of pyrrole (**11**: 2.6 g, 6.54 mmol, 1.0 equiv) in anhydrous THF (32 mL) was added pyridine (955 μ L, 11.8 mmol, 1.8 equiv) dropwise at room temperature. The solution was stirred for 10 min and cooled down to 0 °C. Then trichloroacetyl chloride (**S6**: 1.35 mL, 12.0 mmol, 1.8 equiv) was added dropwise to the reaction mixture over 20 min at 0 °C. The reaction mixture was allowed to warm at room temperature and stirred for 20 h. Then the reaction was quenched with 1 N HCl (1.3 mL), evaporated under reduced pressure, extracted with ether (3 x 20 mL), washed with brine (10 mL) and dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give a brownish solid **S7**. The compound was used in the next reaction without any further purification and characterization.

4-(3,4-Dimethoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole-2-carboxylic acid (S8):



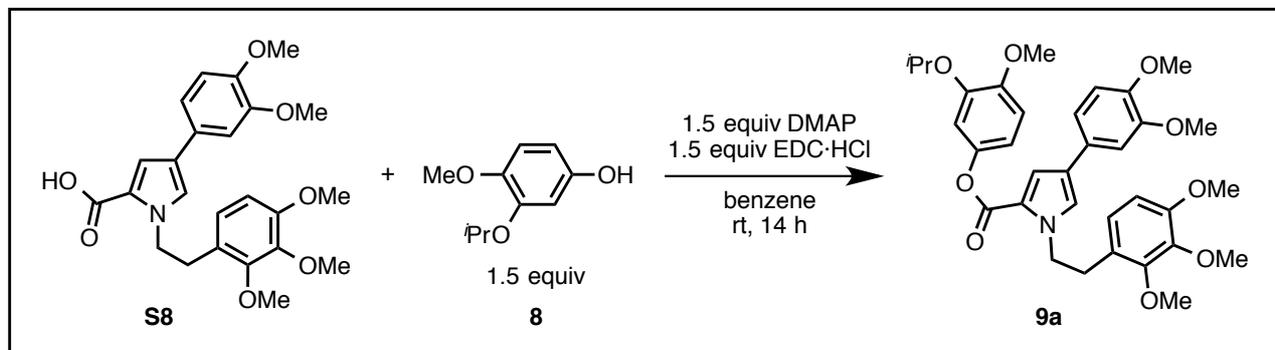
The resulting solid **S7** was then dissolved in acetone (48 mL), and aqueous 2 M K₂CO₃ (120 mL) was added. The reaction mixture was stirred for 13 h at room temperature, and then stirred at ambient temperature for 1 h, followed by concentration under vacuum. Acetone was removed under reduced pressure, the solution was acidified with aqueous 12 N HCl to pH 3 and then extracted with ethyl acetate (3 x 75 mL). The combined organic extracts were washed with brine

(25) Mandal, D.; Yamaguchi, A. D.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.*, **2011**, *133*, 19660.

(26) Koriatopoulou, K.; Karousis, N.; Varvounis, G. *Tetrahedron* **2008**, *64*, 10009.

(75 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to afford a residue **S8**. The compound was used in the next reaction without any further purification and characterization

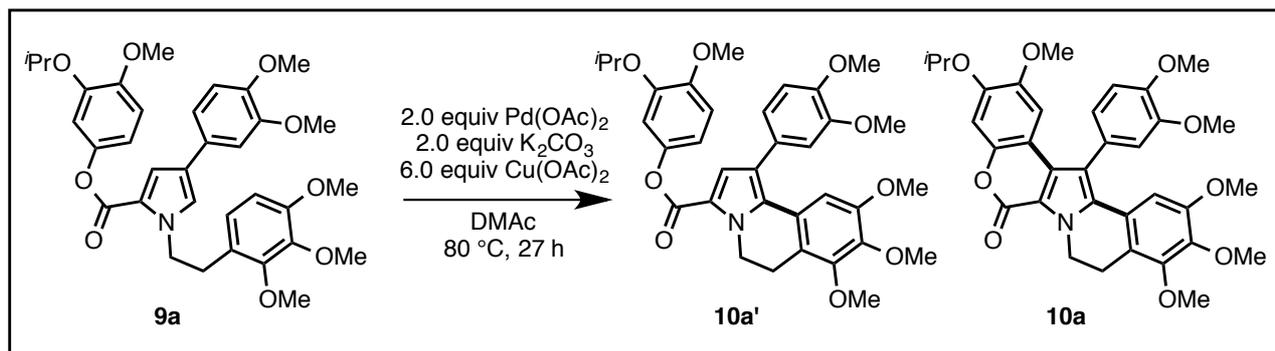
3-Isopropoxy-4-methoxyphenyl 4-(3,4-dimethoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole-2-carboxylate (9a**):**



According to a procedure of Itami *et al.*,²⁷ to a 100-mL round bottom flask containing **S8** were added phenol **8** (2.22 g, 12 mmol, 1.5 equiv), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl: 2.34 g, 12 mmol, 1.5 equiv), *N,N*-dimethyl-4-aminopyridine (DMAP: 1.49 g, 12 mmol, 1.5 equiv), and benzene (81 mL). After stirring the mixture for 14 h, this reaction mixture was quenched with water and extracted with ethyl acetate (3 x 130 mL). The combined organic layer was washed with brine (75 mL), dried over Na_2SO_4 , and then filtered. Following evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (hexane/EtOAc = 2:1 to 1:1) to afford phenyl ester **9a** as colorless viscous oil (2.27 g, 57% over 3 steps).

^1H NMR (600 MHz, CDCl_3) δ 7.38 (d, J = 1.8 Hz, 1H), 7.01 (dd, J = 8.2, 1.8 Hz, 1H), 6.97 (dd, J = 5.4, 1.8 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.77 (dd, J = 5.4, 2.7 Hz, 1H), 6.75 (d, J = 2.7 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 8.6 Hz, 1H), 4.56–4.51 (m, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.05 (t, J = 7.3 Hz, 2H), 1.40 (d, J = 6.4 Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.6, 152.7, 152.0, 149.2, 148.1, 147.8, 147.8, 144.1, 142.2, 127.5, 126.2, 124.8, 124.2, 124.0, 121.3, 117.4, 116.2, 113.6, 112.1, 111.6, 109.8, 108.8, 107.2, 71.5, 61.0, 60.8, 56.4, 56.0, 55.9, 50.1, 32.2, 29.7, 22.0; HRMS (DART) m/z calcd for $\text{C}_{34}\text{H}_{40}\text{NO}_8$ [MH]⁺: 606.2703, found 606.2702.

14-(3,4-Dimethoxyphenyl)-3-isopropoxy-2,10,11,12-tetramethoxy-8,9-dihydro-6H-chromeno[4',3':4,5]pyrrolo[2,1-a]isoquinolin-6-one (10a):



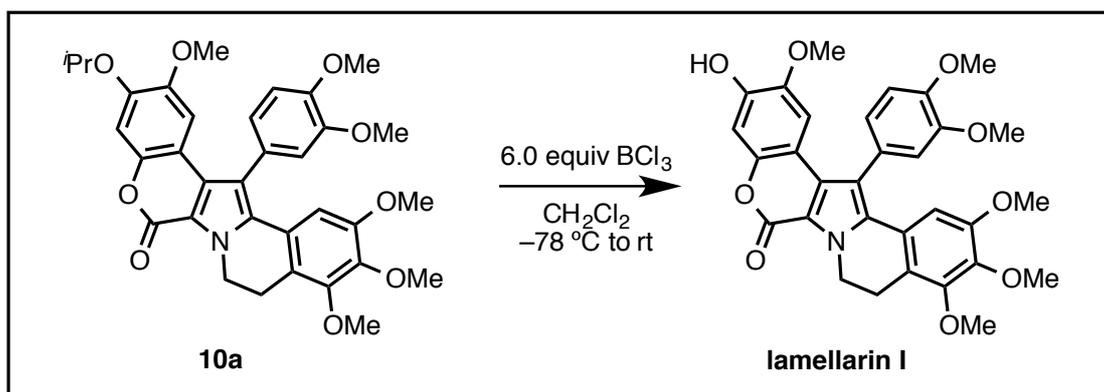
Following the procedure of Greaney *et al.*,²⁸ a screw cap test tube was loaded with compound **9a** (30.4 mg, 0.05 mmol, 1.0 equiv), K₂CO₃ (13.9 mg, 0.1 mmol, 2.0 equiv), Pd(OAc)₂ (22.8 mg, 0.1 mmol, 2.0 equiv) and Cu(OAc)₂ (54.7 mg, 0.3 mmol, 6.0 equiv). Anhydrous DMAc (300 μ L) was then added, and the tube was flushed with nitrogen before being sealed. The reaction mixture was allowed to stir at 80 °C for 27 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad (EtOAc). The residue was then purified by preparative thin-layer chromatography (PTLC). Pure product **10a** was obtained in 39% yield as white solid. The mixture of recovered starting material **9a** and single coupling product **10a'** were also obtained. The yields of each compound were determined by ¹H NMR (**9a**: 15%, **10a'**: 26%). After purification by gel permeation chromatography (GPC), single coupling product **10a'** was isolated as white solid.

10a': ¹H NMR (600 MHz, CDCl₃) δ 7.21 (s, 1H), 7.04 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H), 6.75–6.73 (m, 2H), 4.61 (t, *J* = 6.8 Hz, 2H), 4.52 (q, *J* = 5.9 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.42 (s, 3H), 3.08 (t, *J* = 6.8 Hz, 2H), 1.39 (d, *J* = 5.9 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 155.9, 151.7, 150.5, 148.9, 148.1, 148.0, 147.8, 144.1, 141.7, 132.2, 129.0, 123.7, 122.7, 121.8, 120.4, 119.6, 119.5, 113.5, 112.7, 112.0, 111.3, 109.7, 105.1, 71.5, 61.0, 61.0, 56.4, 56.0, 56.0, 55.5, 42.3, 22.2, 22.0; HRMS (DART) *m/z* calcd for C₃₃H₃₃NO, [MH]⁺: 604.2547, found 604.2546.

10a: ¹H NMR (600 MHz, CDCl₃) δ 7.10 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 1.4 Hz, 1H), 6.92 (s, 1H), 6.62 (s, 1H), 6.57 (s, 1H), 4.81–4.73 (m, 2H), 4.54 (q, *J* = 5.9 Hz, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 3.87 (s, 6H), 3.42 (s, 3H), 3.34 (s, 3H), 3.14 (t, *J* = 6.8 Hz, 2H), 1.39 (dd, *J* = 5.9, 1.4 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 155.6, 151.8, 150.7, 149.8, 148.8, 147.1, 146.6, 146.0, 142.3, 135.4, 128.2, 128.0, 123.5, 123.0, 120.1, 115.5, 114.0, 113.9, 111.9, 110.3, 105.1, 104.9, 103.5, 71.5, 61.0, 60.9, 56.2, 56.2, 55.5, 55.2, 42.2, 21.9, 21.8; HRMS (DART) *m/z* calcd for C₃₄H₃₃NO, [MH]⁺: 602.2390, found 602.2387.

(28) Pintori, D. G.; Greaney, M. F. *J. Am. Chem. Soc.* **2011**, *133*, 1209.

14-(3,4-Dimethoxyphenyl)-3-hydroxy-2,10,11,12-tetramethoxy-8,9-dihydro-6H-chromeno[4',3':4,5]pyrrolo[2,1-a]isoquinolin-6-one³⁰ (lamellarin I):



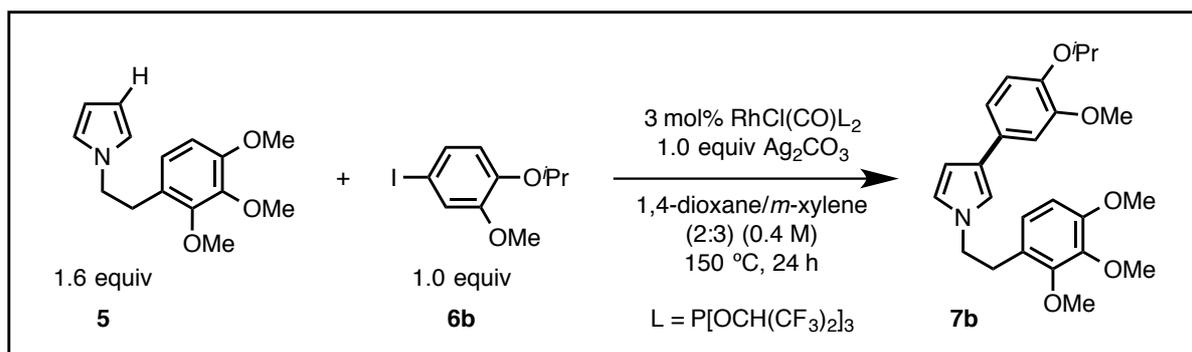
According to a procedure of Iwao et al.,³⁰ a heptane solution of BCl_3 (1.0 M, 680 μL , 0.68 mmol, 6 equiv) was added dropwise to a solution of **10a** (68.3 mg, 0.11 mmol, 1.0 equiv) in dichloromethane (12 mL) at $-78\text{ }^\circ\text{C}$ under a nitrogen atmosphere. After being stirred for 1 h at $-78\text{ }^\circ\text{C}$, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The mixture was quenched with saturated aqueous NaHCO_3 , and the product was extracted with ethyl acetate. The extract was washed with brine, dried over Na_2SO_4 , and evaporated. The residue was then purified by preparative thin-layer chromatography (PTLC) to afford lamellarin I (45.4 mg, 71% yield) as white solid.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.10 (dd, $J = 8.2, 1.4\text{ Hz}$, 1H), 7.08 (d, $J = 8.1\text{ Hz}$, 1H), 7.04 (d, $J = 1.4\text{ Hz}$, 1H), 6.96 (s, 1H), 6.59 (s, 1H), 6.56 (s, 1H), 5.69 (s, 1H), 4.78–4.75 (m, 2H), 3.97 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.48 (s, 3H), 3.34 (s, 3H), 3.14 (t, $J = 6.8\text{ Hz}$, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.6, 151.8, 150.7, 149.8, 148.9, 146.4, 145.5, 143.3, 142.3, 135.3, 128.1, 123.6, 123.0, 120.1, 115.3, 113.9, 111.9, 110.2, 105.1, 104.0, 103.5, 61.0, 60.9, 56.3, 56.2, 55.6, 55.2, 42.2, 21.9; HRMS (DART) m/z calcd for $\text{C}_{31}\text{H}_{30}\text{NO}_8$ [MH]⁺: 560.1921, found 560.1920.

3-(4-Isopropoxy-3-methoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole (7b):

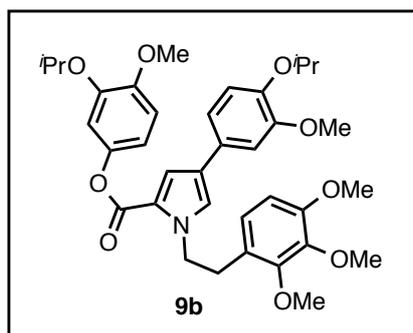
(29) Ploypradith, P.; Petchmance, T.; Sahakitpichan, P.; Litvinas, N. D.; Ruchirawat, S. *J. Org. Chem.* **2006**, *71*, 9440.

(30) Ohta, T.; Fukuda, T.; Ishibashi, F.; Iwao, M. *J. Org. Chem.* **2009**, *74*, 8143.



A 20-mL glass vessel equipped with J. Young® O-ring tap, containing a magnetic stirring bar, was dried with a heat-gun under vacuum and filled with nitrogen after cooling to room temperature. To this vessel were added $\text{RhCl}(\text{CO})\{\text{P}[\text{OCH}(\text{CF}_3)_2]_3\}_2$ (37.5 mg, 30 μmol , 3 mol%), Ag_2CO_3 (276.1 mg, 1.0 mmol, 1.0 equiv), 1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole (**5**: 418.6 mg, 1.6 mmol, 1.6 equiv), 1-isopropoxy-2-methoxy-4-iodobenzene (**6b**: 295.4 mg, 1.0 mmol, 1.0 equiv), and dry 1,4-dioxane/*m*-xylene (2:3) (2.5 mL) under a stream of nitrogen. The vessel was sealed with an O-ring tap, and then heated at 150 °C for 24 h in a 8-well reaction block with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc = 4:1) to afford 3-(4-isopropoxy-3-methoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole (**7b**: 172.4 mg, 40%) as yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.00–6.98 (m, 2H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.84 (dd, $J = 2.3, 1.8$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 1H), 6.61 (dd, $J = 2.7, 2.3$ Hz, 1H), 6.57 (d, $J = 8.2$ Hz, 1H), 6.34 (dd, $J = 2.7, 1.8$ Hz, 1H), 4.49 (q, $J = 5.9$ Hz, 1H), 4.05 (t, $J = 6.8$ Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.01 (t, $J = 7.5$ Hz, 2H), 1.36 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.8, 152.0, 150.7, 145.2, 142.3, 130.0, 124.7, 124.4, 124.1, 121.5, 117.3, 116.9, 116.9, 109.5, 107.2, 105.9, 71.7, 61.0, 60.8, 56.0, 56.0, 50.6, 32.8, 22.2; HRMS (DART) m/z calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_5$ [MH] $^+$: 426.2280, found 426.2280.

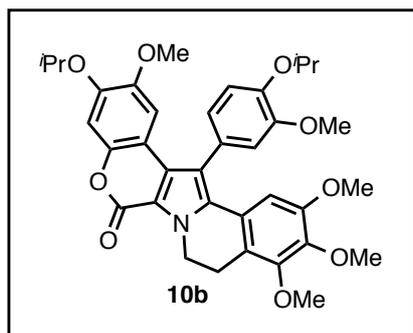
3-Isopropoxy-4-methoxyphenyl 4-(3,4-dimethoxyphenyl)-1-[2-(2,3,4-trimethoxyphenyl)ethyl]pyrrole-2-carboxylate (9b):



Purification by PTLC (hexane/EtOAc = 1:1); Yield, virtually quantitative yield; White solid. ^1H NMR (600 MHz, CDCl_3) δ 7.38 (d, J = 2.3 Hz, 1H), 6.98–6.96 (m, 3H), 6.90 (d, J = 9.1 Hz, 1H), 6.88 (d, J = 9.1 Hz, 1H), 6.77–6.75 (m, 2H), 6.72 (d, J = 8.6 Hz, 1H), 6.53 (d, J = 8.6 Hz, 1H), 4.56–4.50 (m, 4H), 3.90 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.05 (dd, J = 8.5, 7.3 Hz, 2H), 1.40 (d, J = 6.4 Hz, 6H), 1.38 (d, J = 6.4 Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.6, 152.7, 152.0, 150.7, 148.0, 147.8, 146.0, 144.1, 142.2,

128.0, 126.3, 124.8, 124.3, 124.0, 121.2, 117.4, 116.5, 116.2, 113.6, 112.1, 109.8, 109.5, 107.2, 71.7, 71.5, 61.0, 60.8, 56.4, 56.0, 56.0, 50.1, 32.2, 22.1, 22.0; HRMS (DART) m/z calcd for $\text{C}_{36}\text{H}_{44}\text{NO}_8$ [MH] $^+$: 634.3016, found 634.3017.

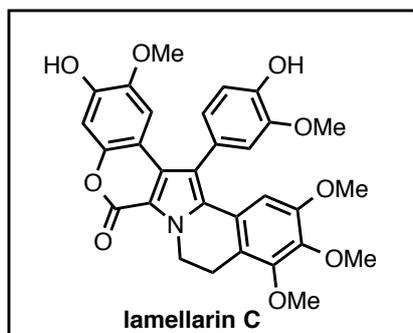
8,9-Dihydro-3-isopropoxy-14-(4-isopropoxy-3-methoxyphenyl)-2,10,11,12-tetramethoxy-6H-[1]benzopyrano-[4',3':4,5]pyrrolo[2,1-a]isoquinolin-6-one (10b):



Purification by PTLC (hexane/EtOAc = 1:1); Yield, 46%; Pale pink solid. ^1H NMR (600 MHz, CDCl_3) δ 7.10 (d, J = 8.1 Hz, 1H), 7.06 (dd, J = 8.2, 1.8 Hz, 1H), 7.03 (d, J = 1.8 Hz, 1H), 6.92 (s, 1H), 6.64 (s, 1H), 6.60 (s, 1H), 4.79–4.75 (m, 2H), 4.60 (q, J = 5.9 Hz, 1H), 4.54 (q, J = 5.9 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.42 (s, 3H), 3.34 (s, 3H), 3.14 (t, J = 7.3 Hz, 2H), 1.41 (dd, J = 5.9, 1.8 Hz, 6H), 1.39 (d, J = 5.9 Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ

155.7, 151.8, 151.3, 150.6, 147.1, 147.0, 146.6, 146.0, 142.2, 135.4, 128.5, 128.2, 123.4, 123.1, 120.1, 117.0, 115.6, 114.6, 114.0, 110.3, 105.2, 104.9, 103.5, 71.8, 71.5, 61.0, 60.9, 56.2, 55.5, 55.2, 42.2, 29.7, 21.9, 21.8; HRMS (DART) m/z calcd for $\text{C}_{32}\text{H}_{38}\text{NO}_8$ [MH] $^+$: 630.2703, found 630.2707.

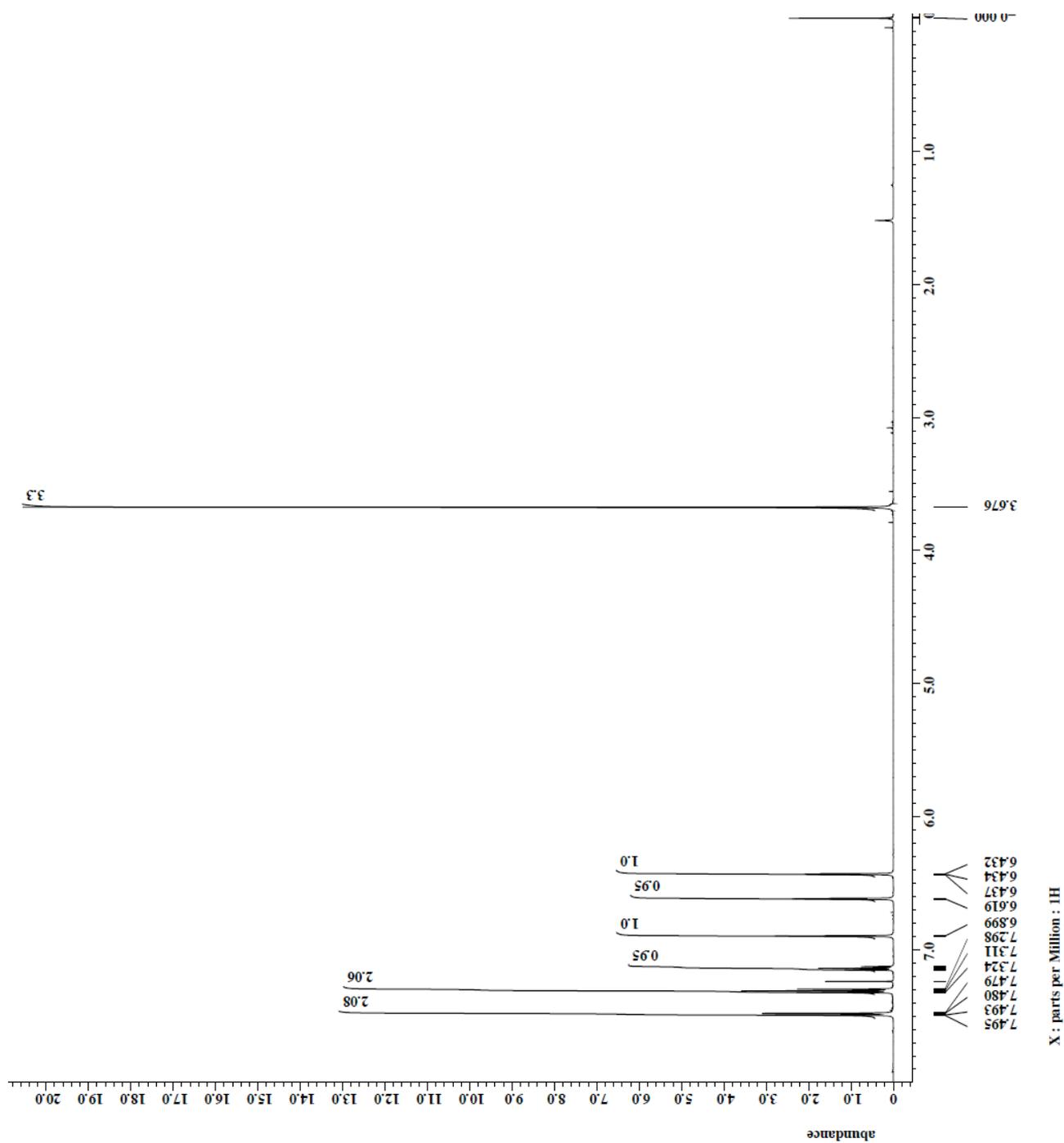
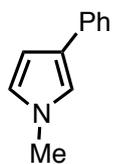
14-(4-Hydroxy-3-methoxyphenyl)-3-hydroxy-2,10,11,12-tetramethoxy-8,9-dihydro-6H-chromeno[4',3':4,5]pyrrolo[2,1-a]isoquinolin-6-one^{22,31} (lamellarin C):



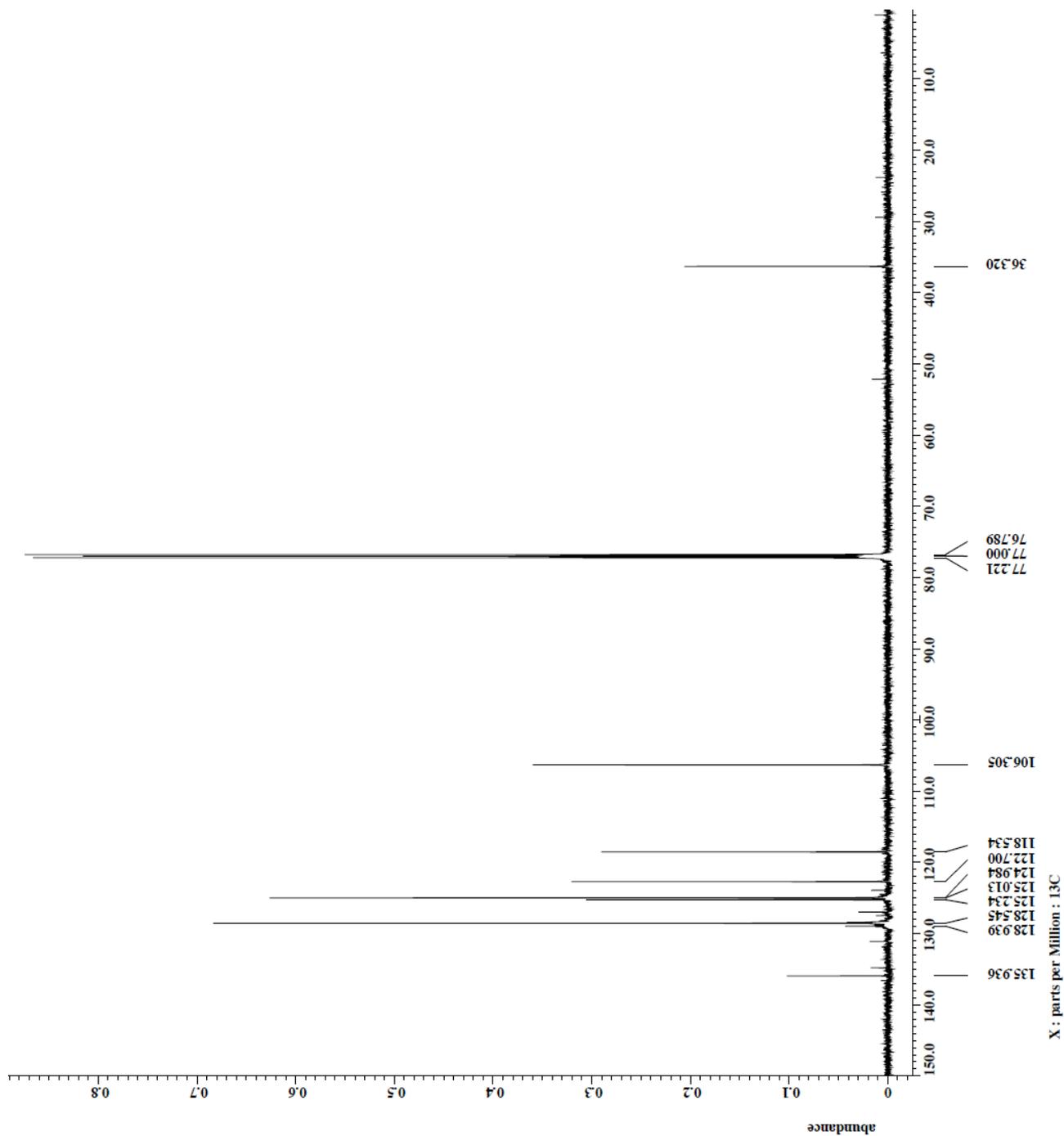
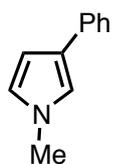
Purification by PTLC (hexane/EtOAc = 1:2); Yield, 39%; White solid. ^1H NMR (600 MHz, CDCl_3) δ 7.13 (d, J = 8.2 Hz, 1H), 7.07 (dd, J = 8.1, 1.8 Hz, 1H), 6.97 (d, J = 1.8 Hz, 1H), 6.96 (s, 1H), 6.60 (s, 1H), 6.57 (s, 1H), 5.74 (s, 1H), 5.69 (s, 1H), 4.92–4.87 (m, 1H), 4.65–4.60 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.50 (s, 3H), 3.36 (s, 3H), 3.20–3.15 (m, 1H), 3.12–3.07 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 155.6, 151.9, 150.7, 147.2, 146.4, 145.5,

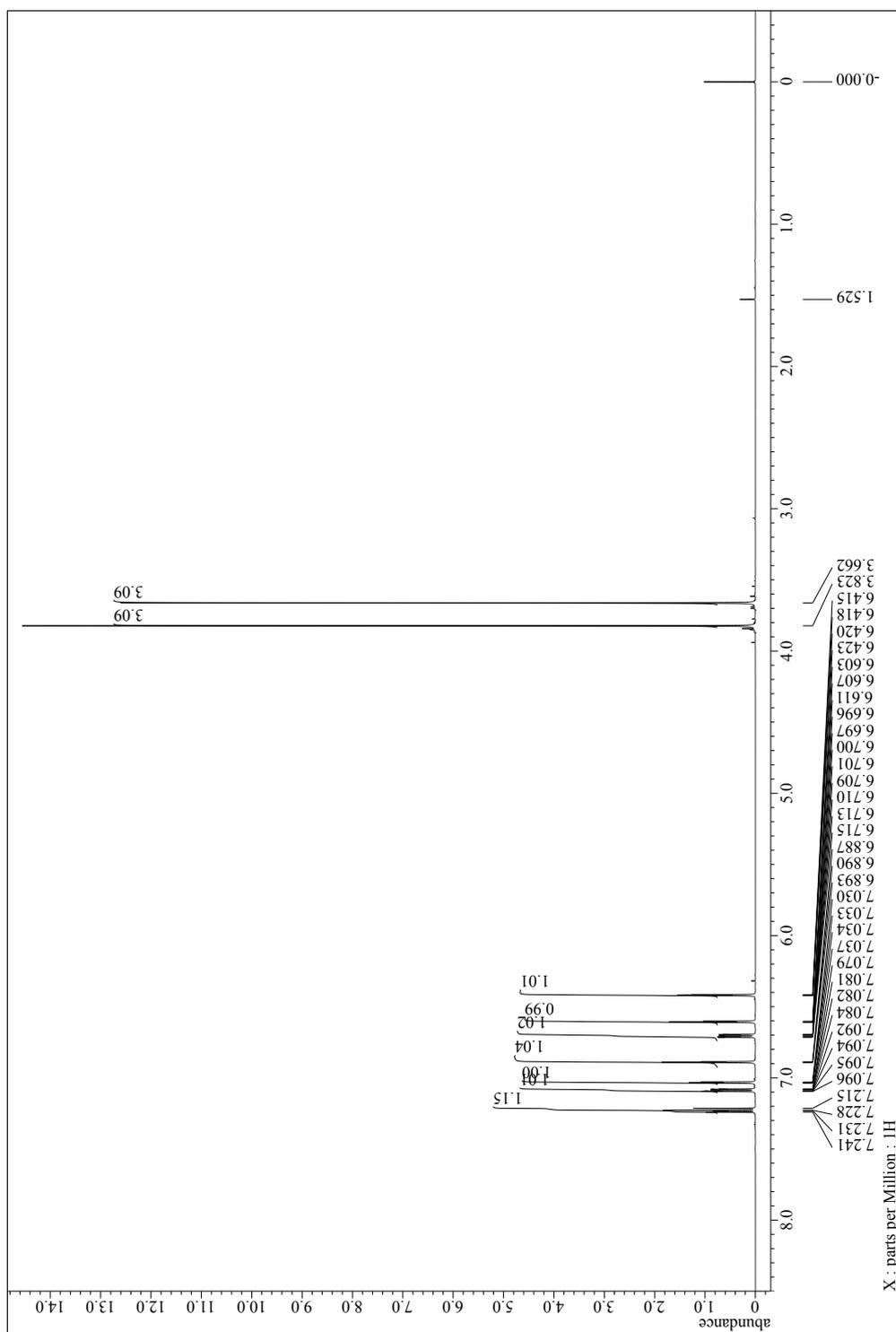
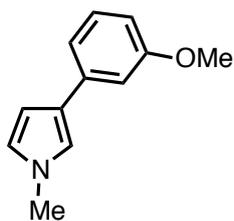
(31) Díaz, M.; Guitián, E.; Castedo, E. *Synlett* **2001**, 1164.

145.5, 143.3, 142.3, 135.3, 128.2, 127.3, 124.2, 123.0, 120.1, 115.5, 115.1, 113.9, 113.3, 110.2, 105.2, 104.0, 103.4, 61.0, 60.9, 56.3, 55.6, 55.2, 42.2, 21.9. HRMS (DART) m/z calcd for $C_{30}H_{28}NO$, [MH]⁺: 546.1764, found 546.1764.

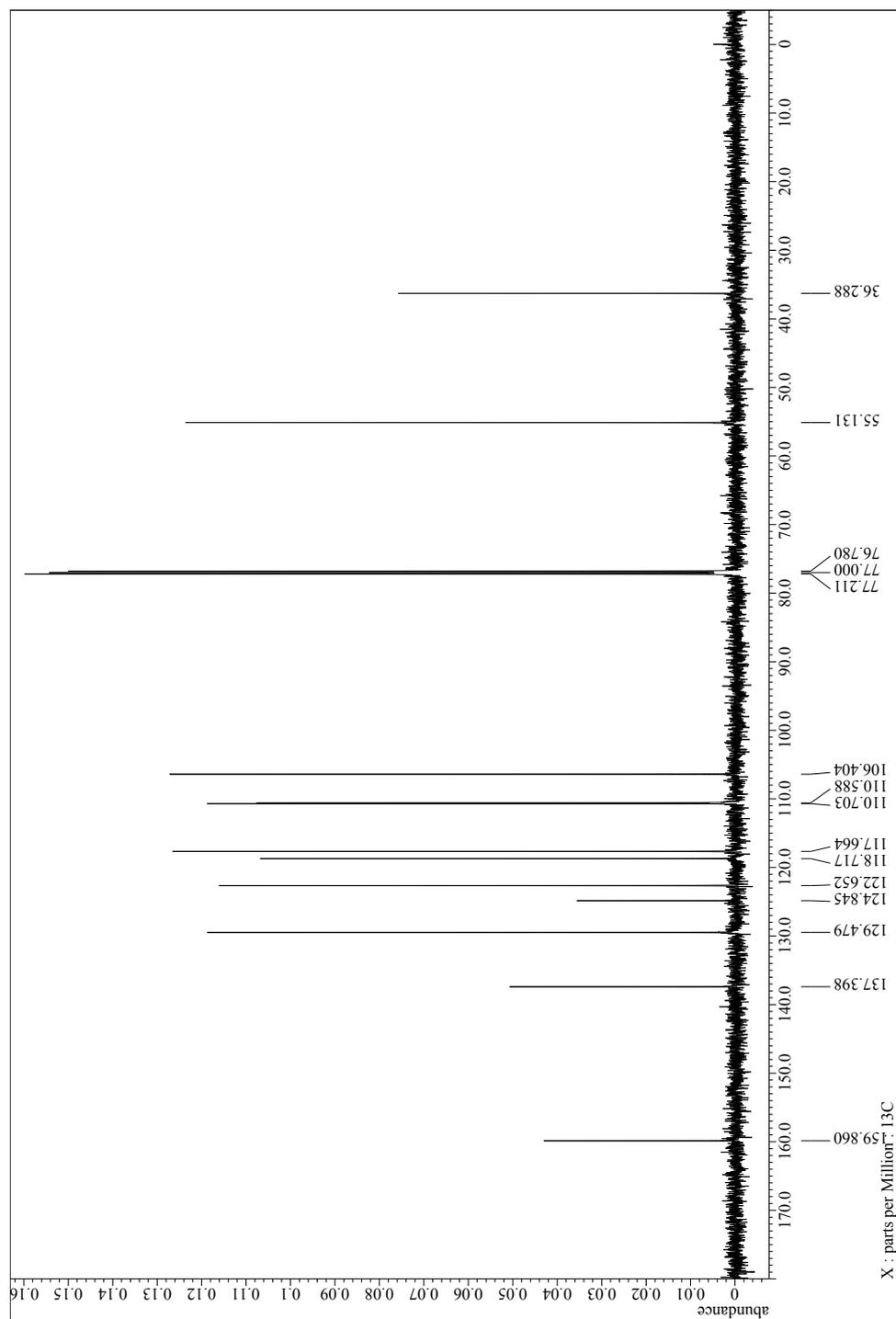
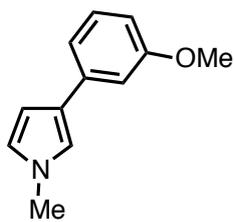
7. ^1H and ^{13}C NMR Spectra of Products ^1H -NMR (600 MHz, CDCl_3) of 3Ba

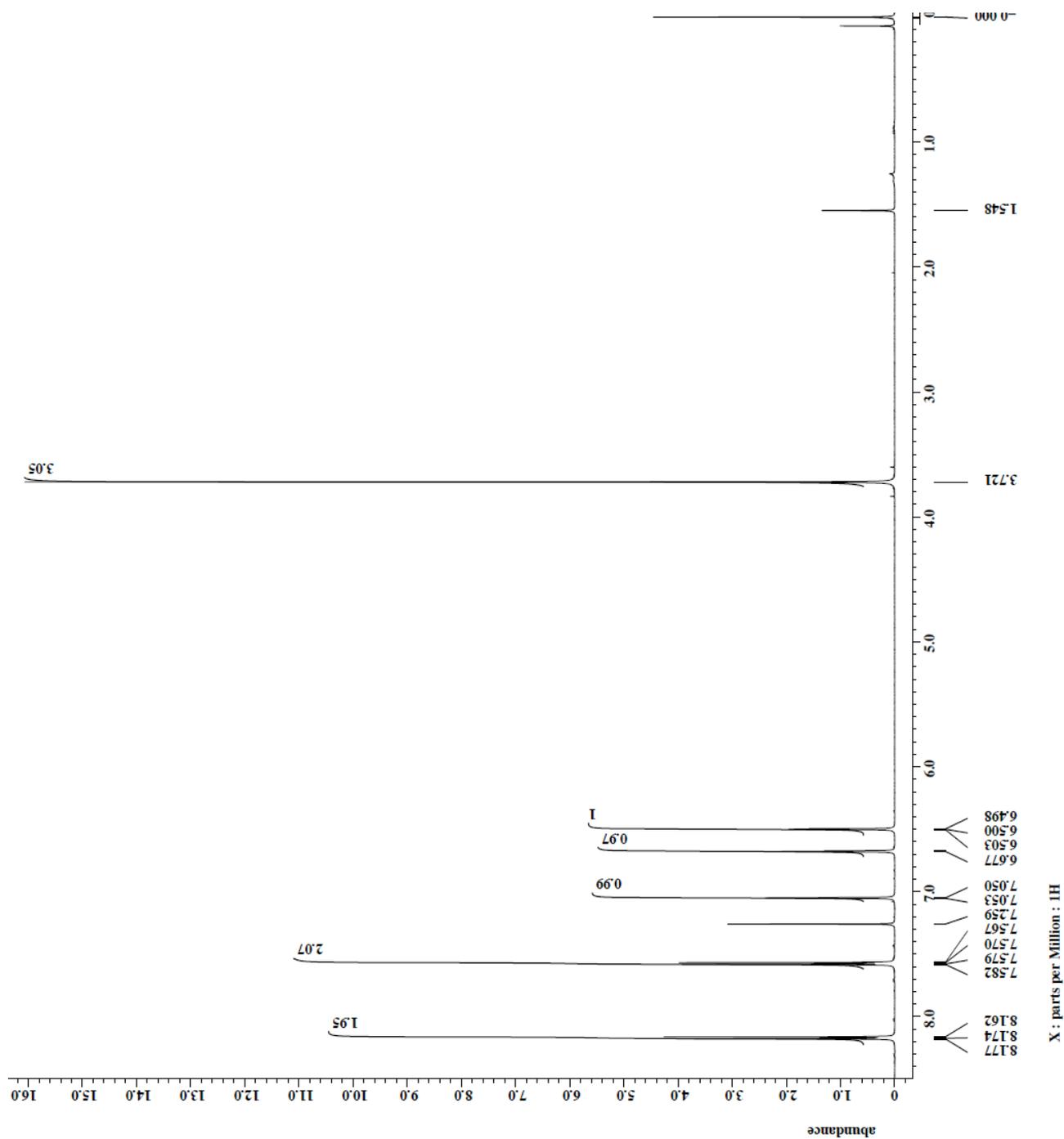
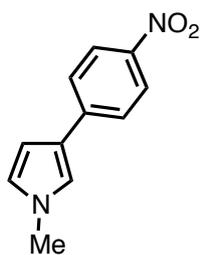
^{13}C -NMR (150 MHz, CDCl_3) of 3Ba



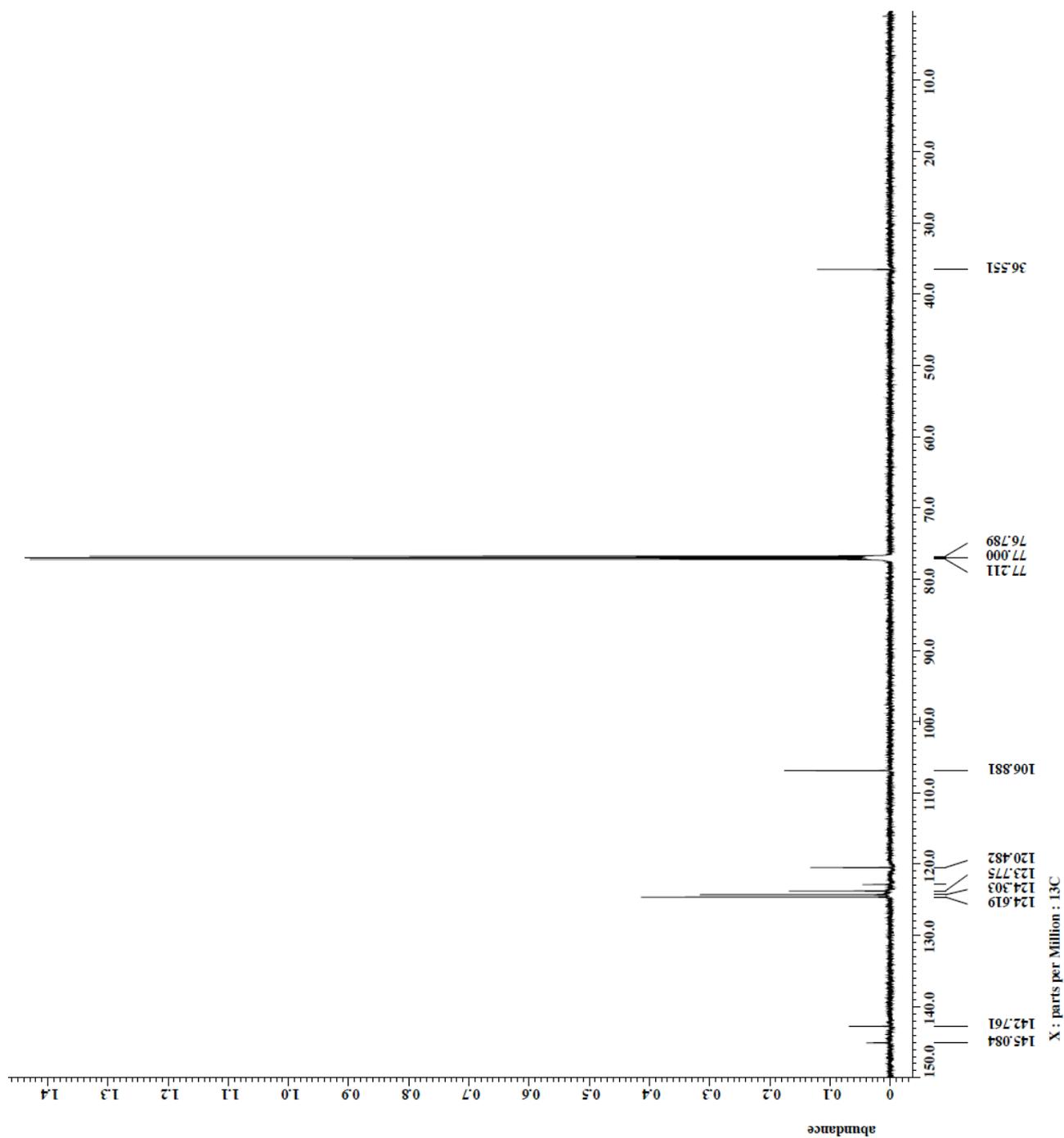
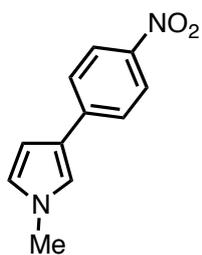
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Bc

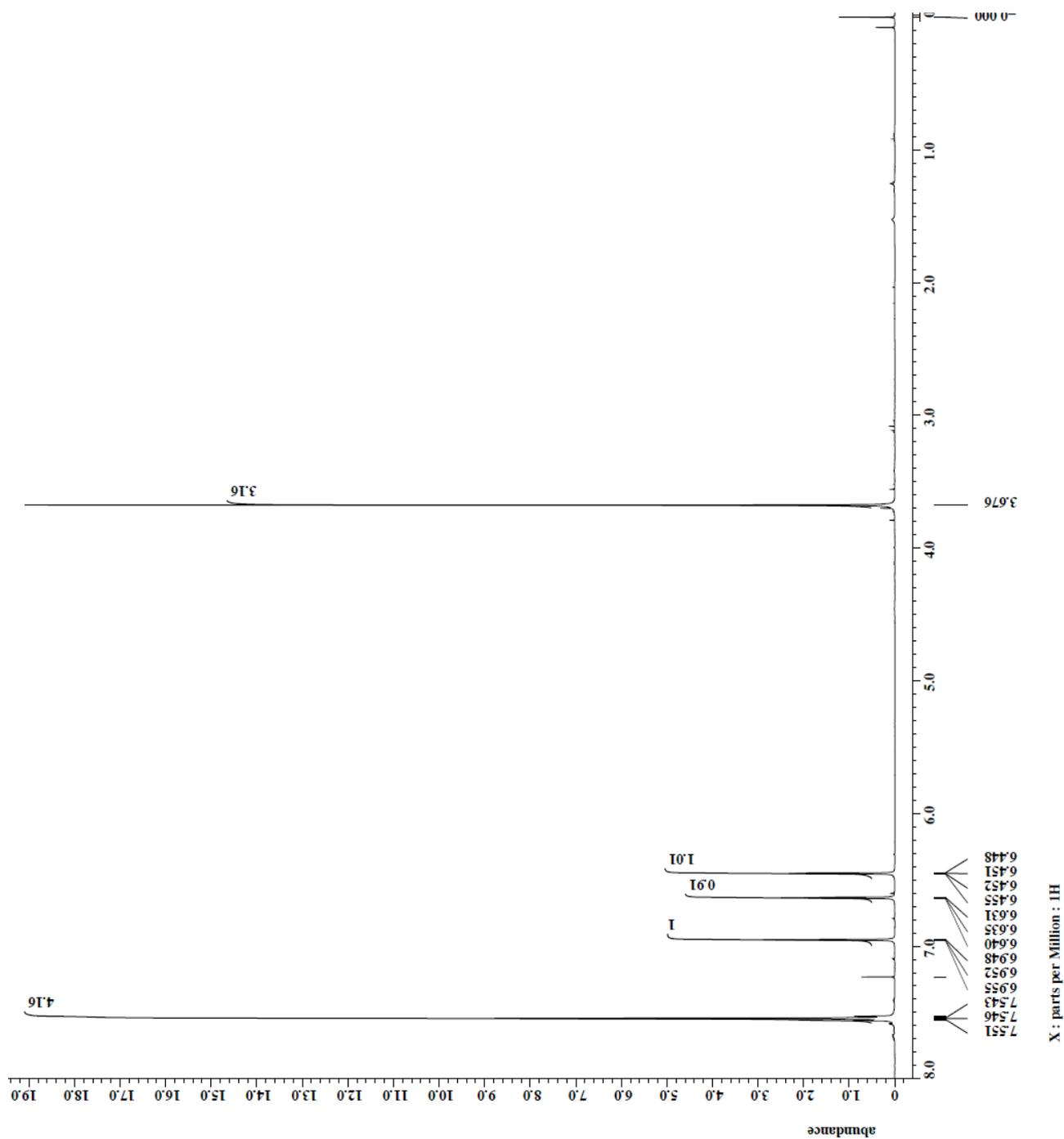
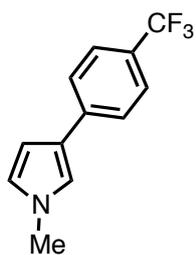
^{13}C -NMR (150 MHz, CDCl_3) of 3Bc



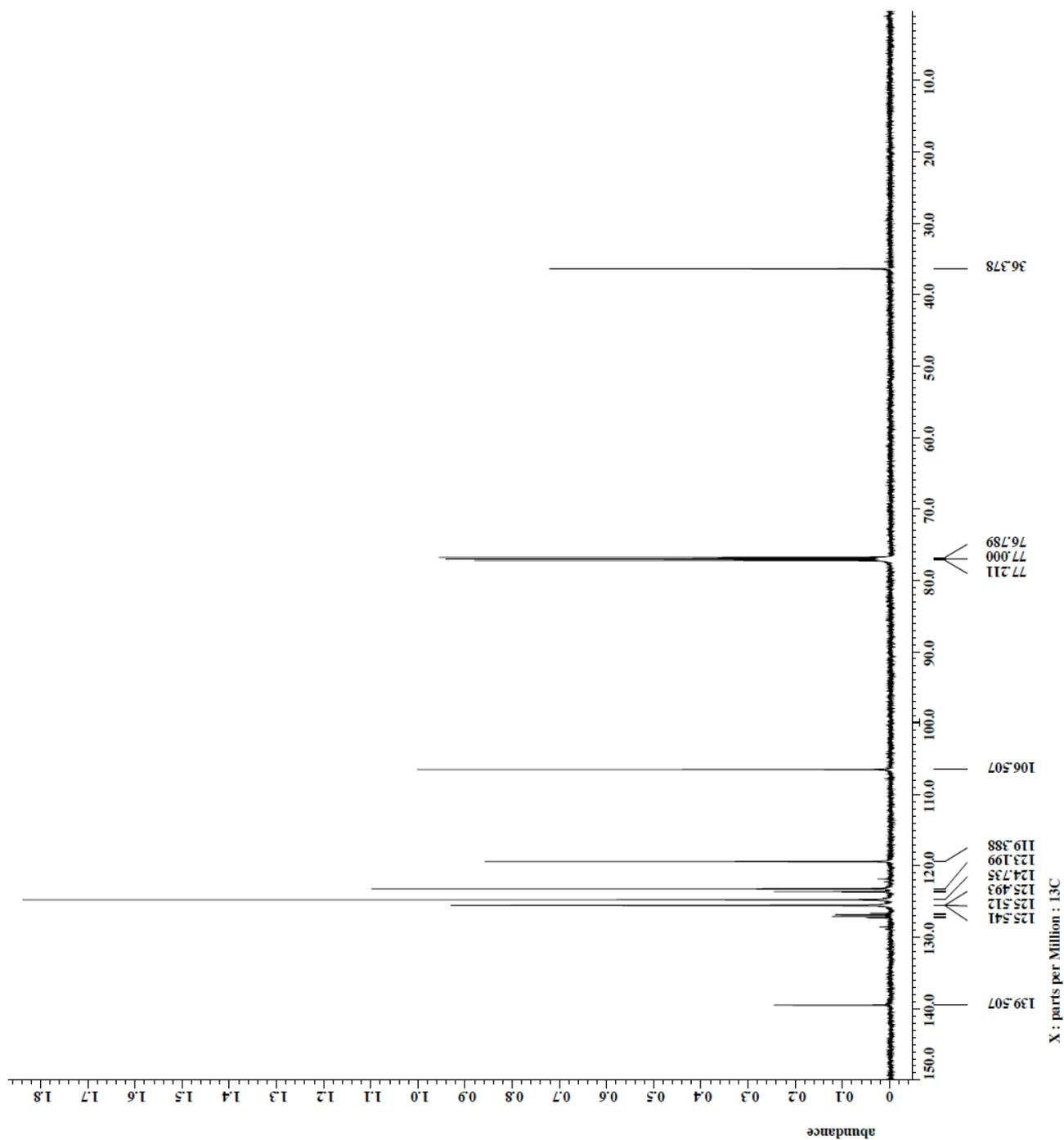
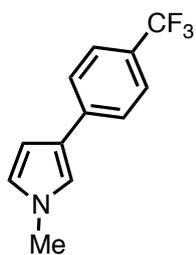
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Bd

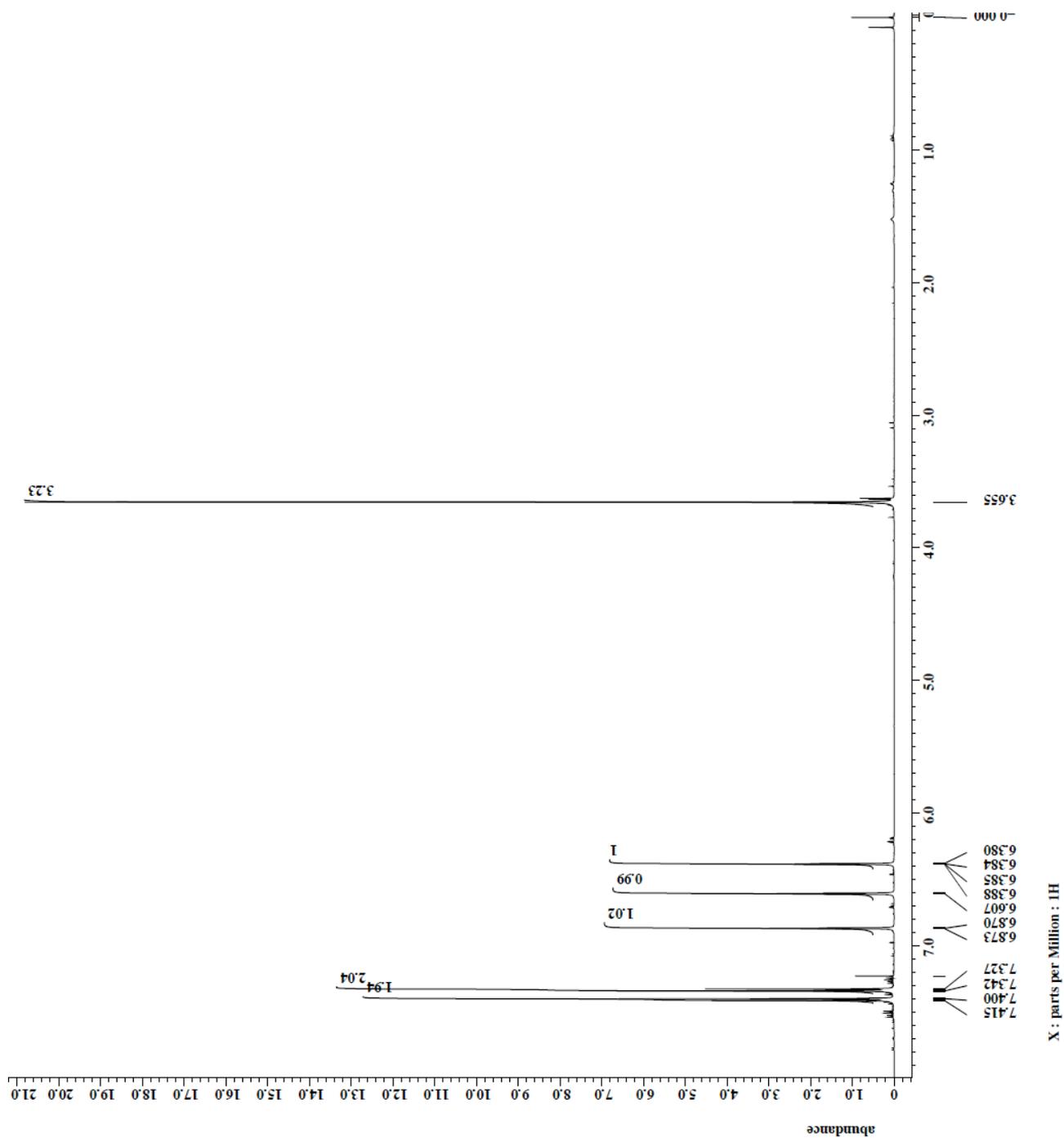
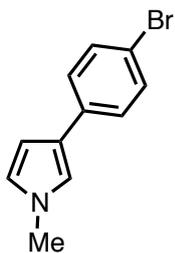
^{13}C -NMR (150 MHz, CDCl_3) of 3Bd



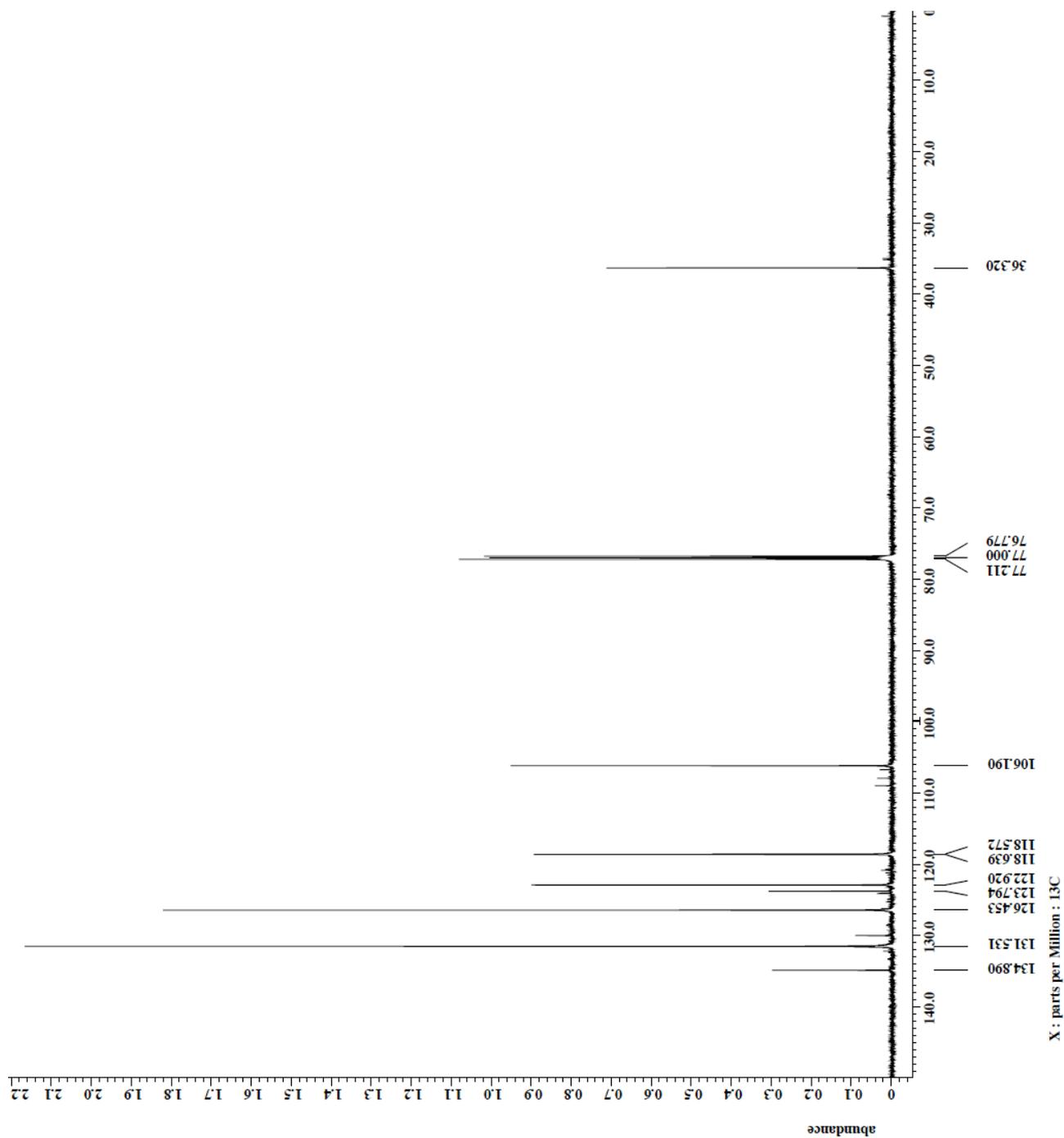
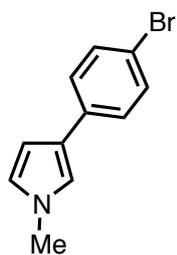
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of **3Be**

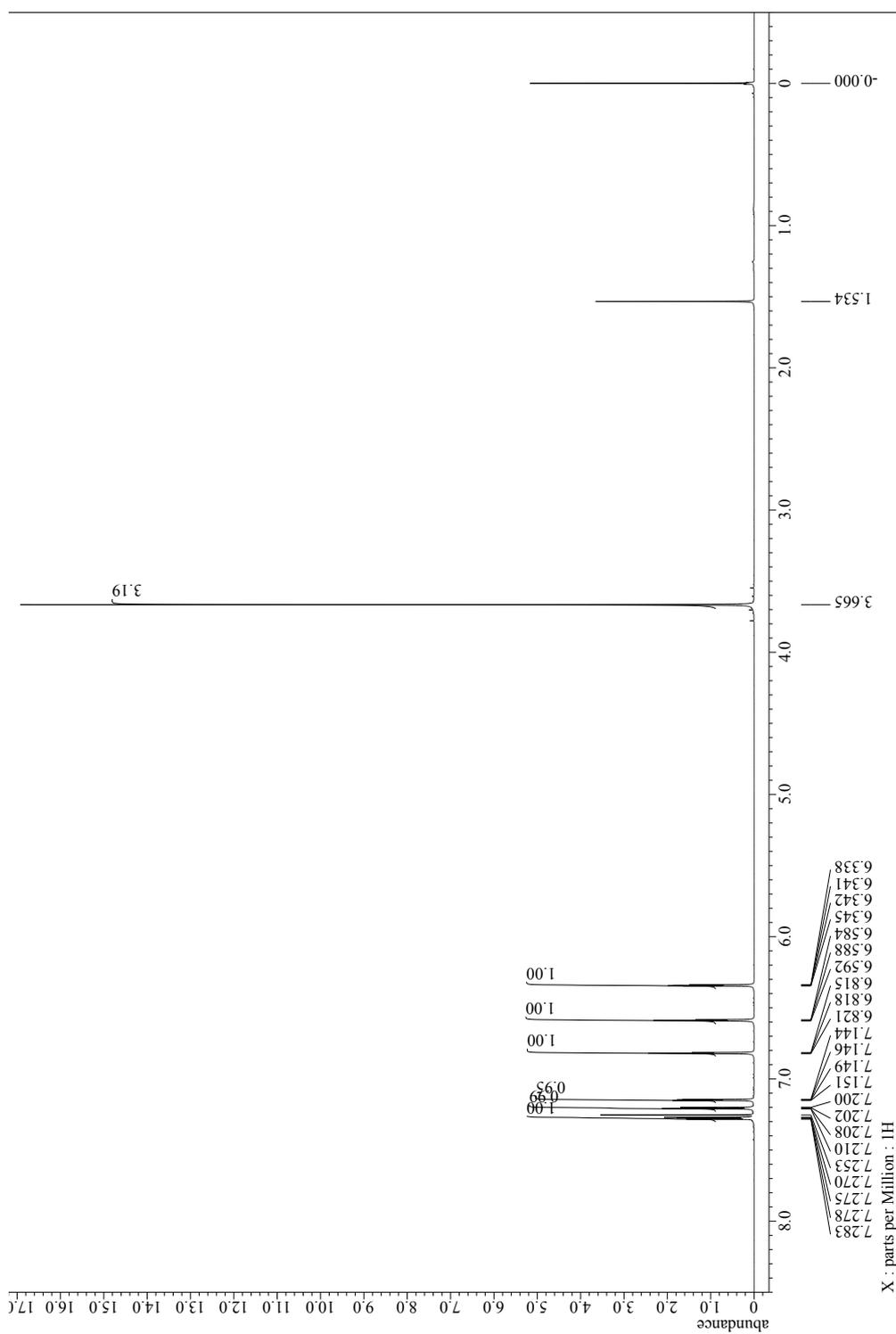
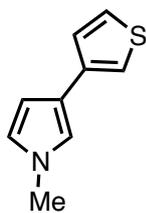
^{13}C -NMR (150 MHz, CDCl_3) of **3Be**



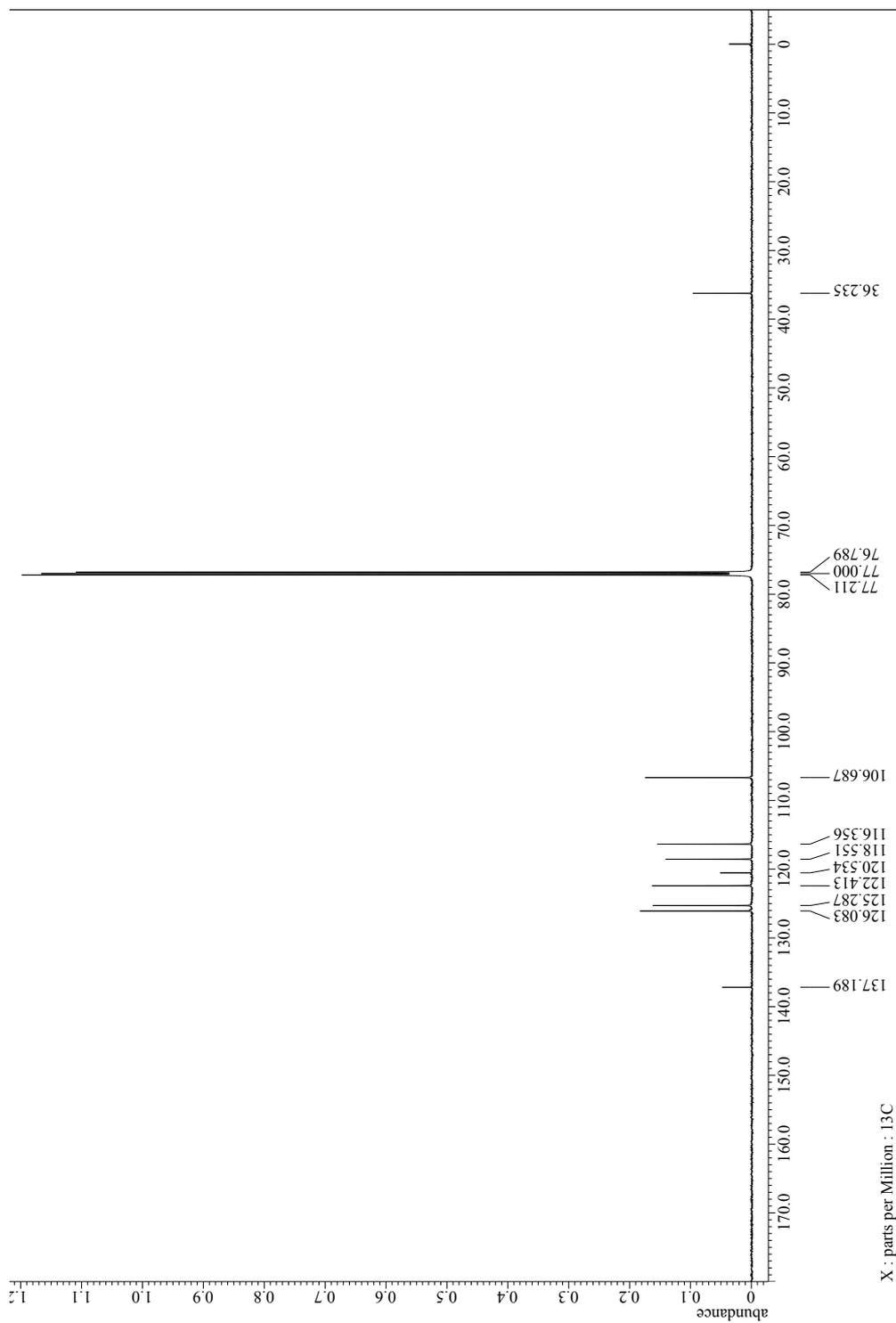
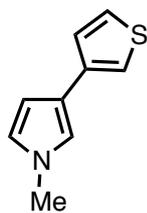
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Bf

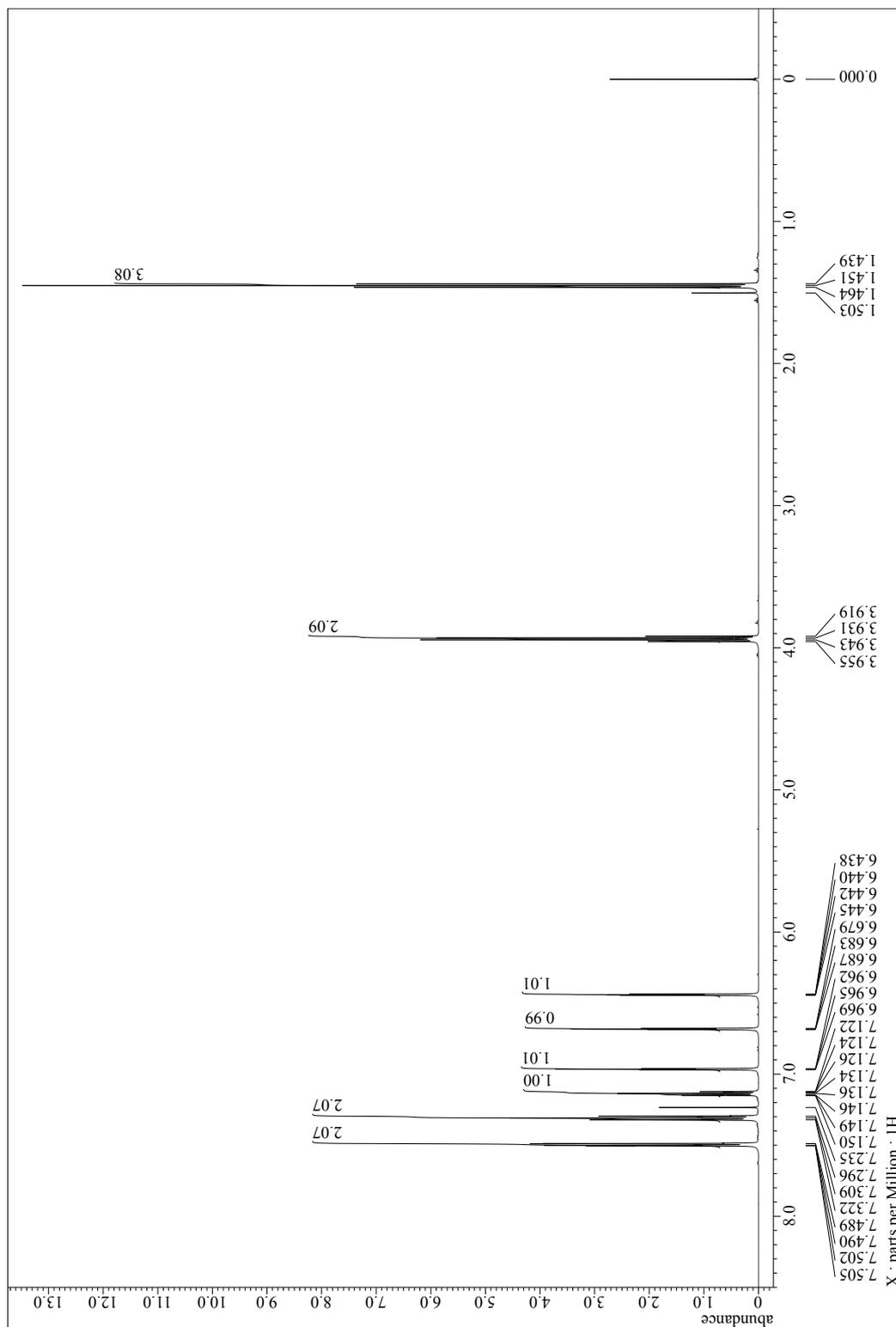
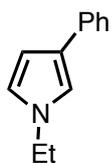
^{13}C -NMR (150 MHz, CDCl_3) of 3Bf



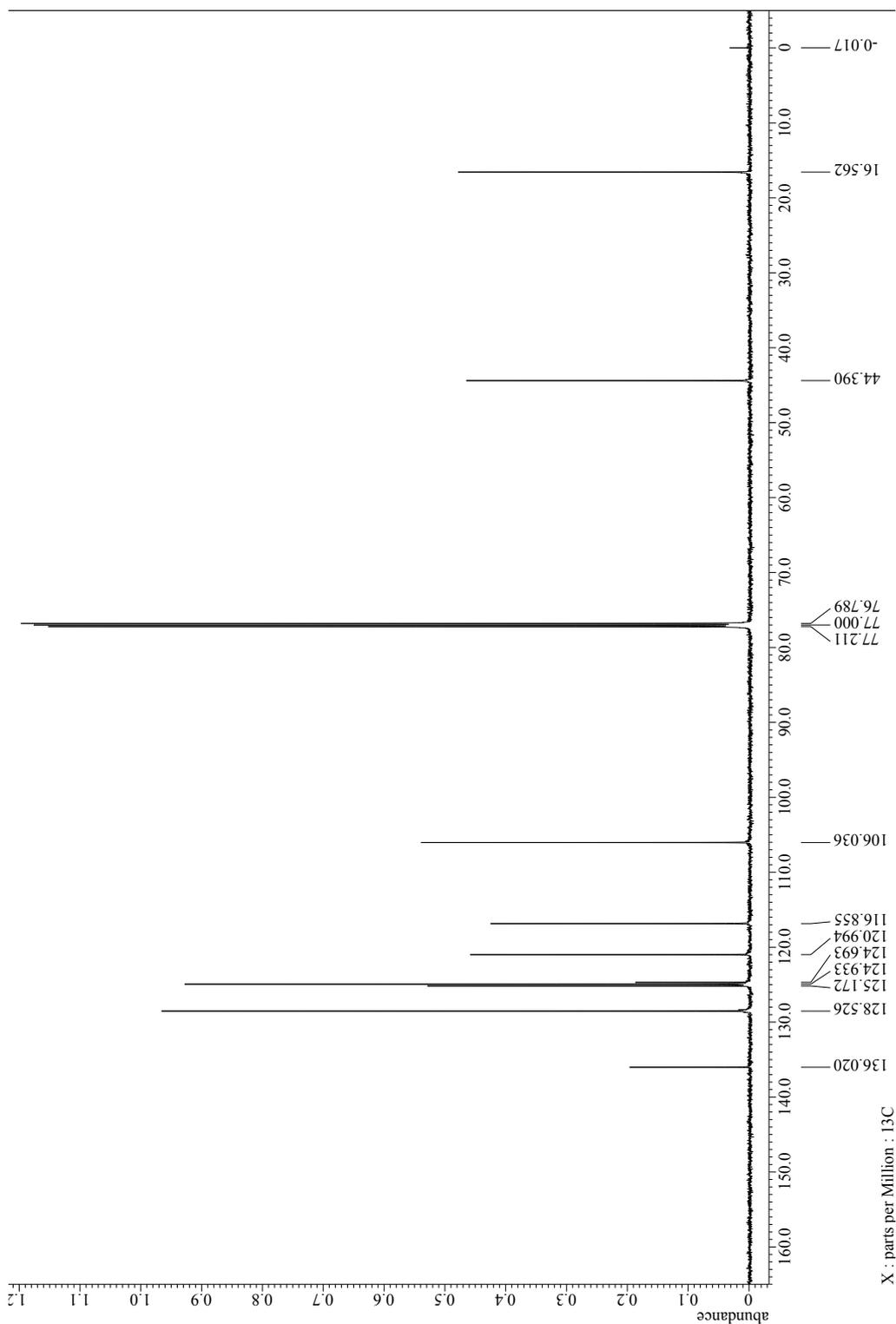
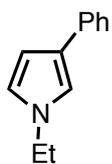
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Bg

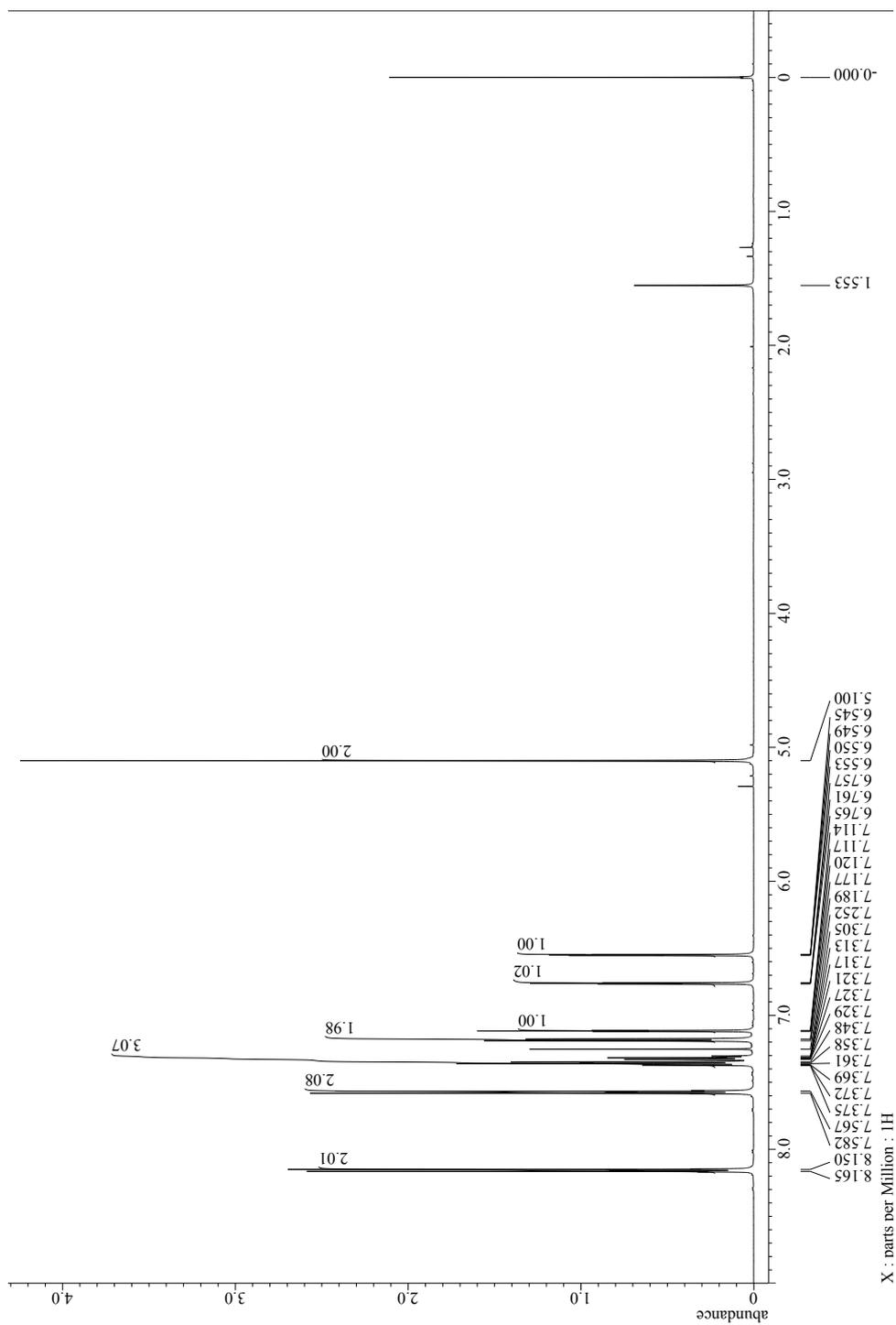
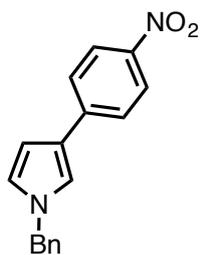
^{13}C -NMR (150 MHz, CDCl_3) of **3Bg**



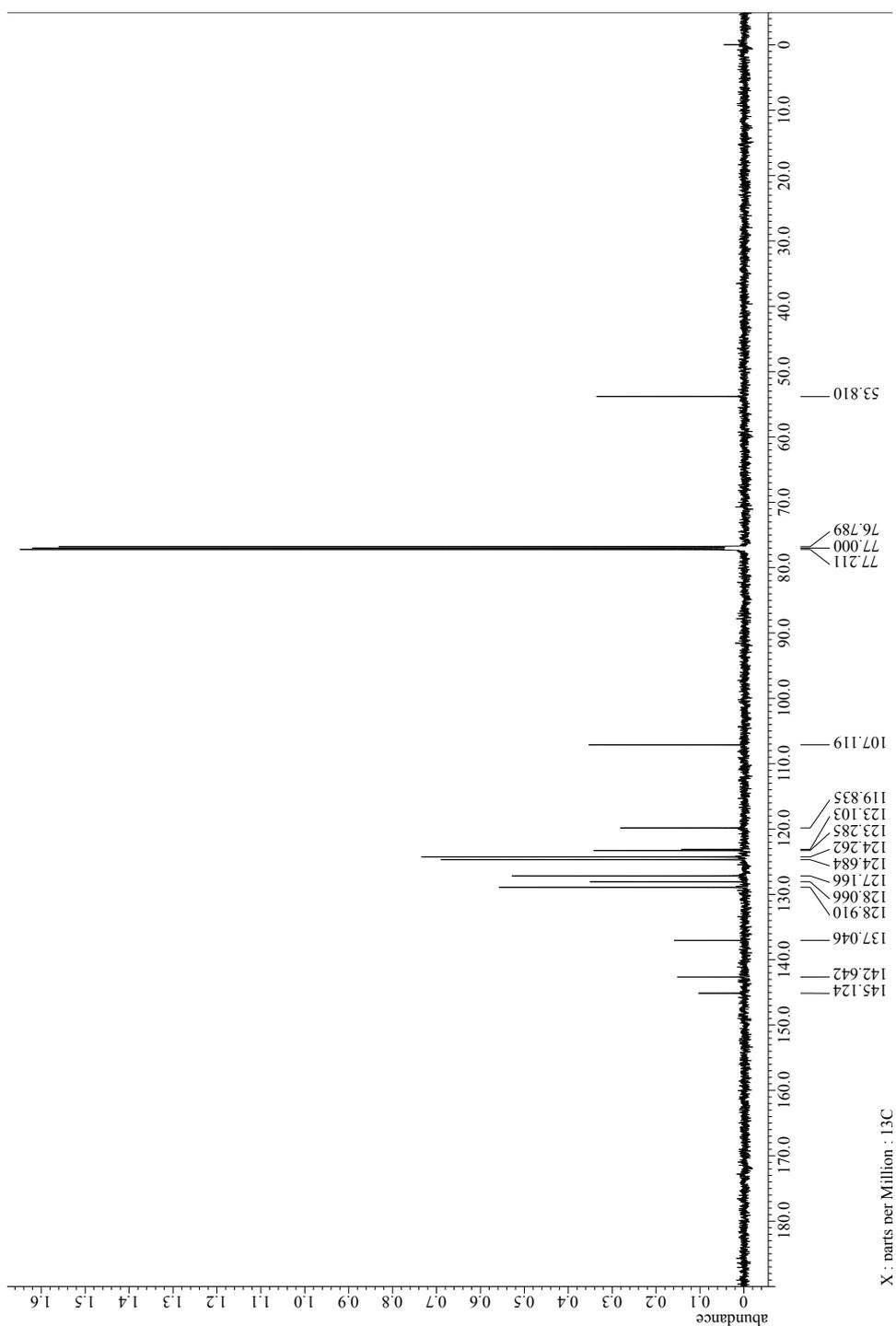
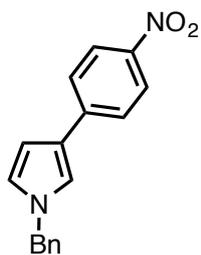
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Ca

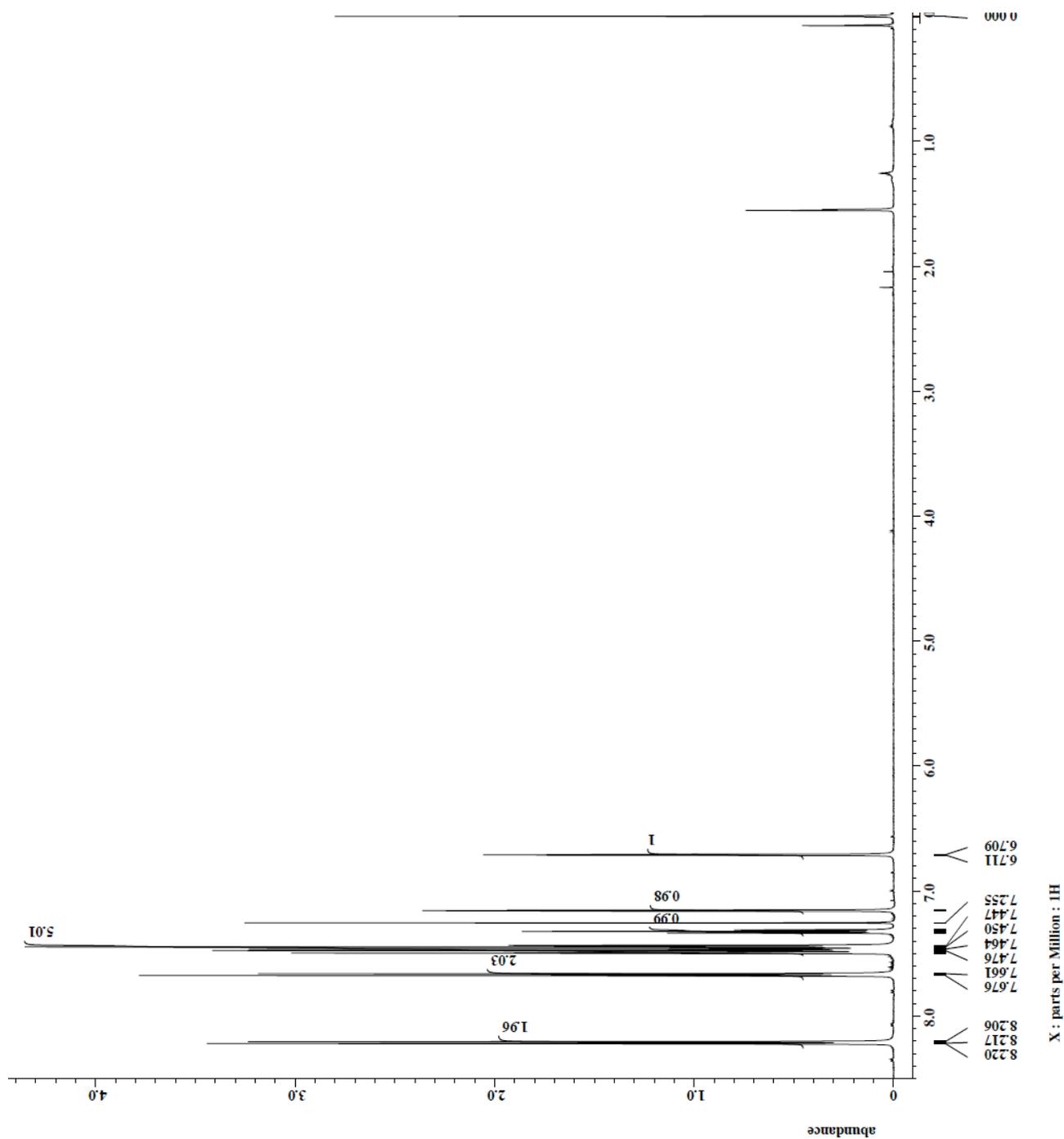
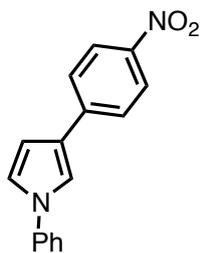
^{13}C -NMR (150 MHz, CDCl_3) of 3Ca



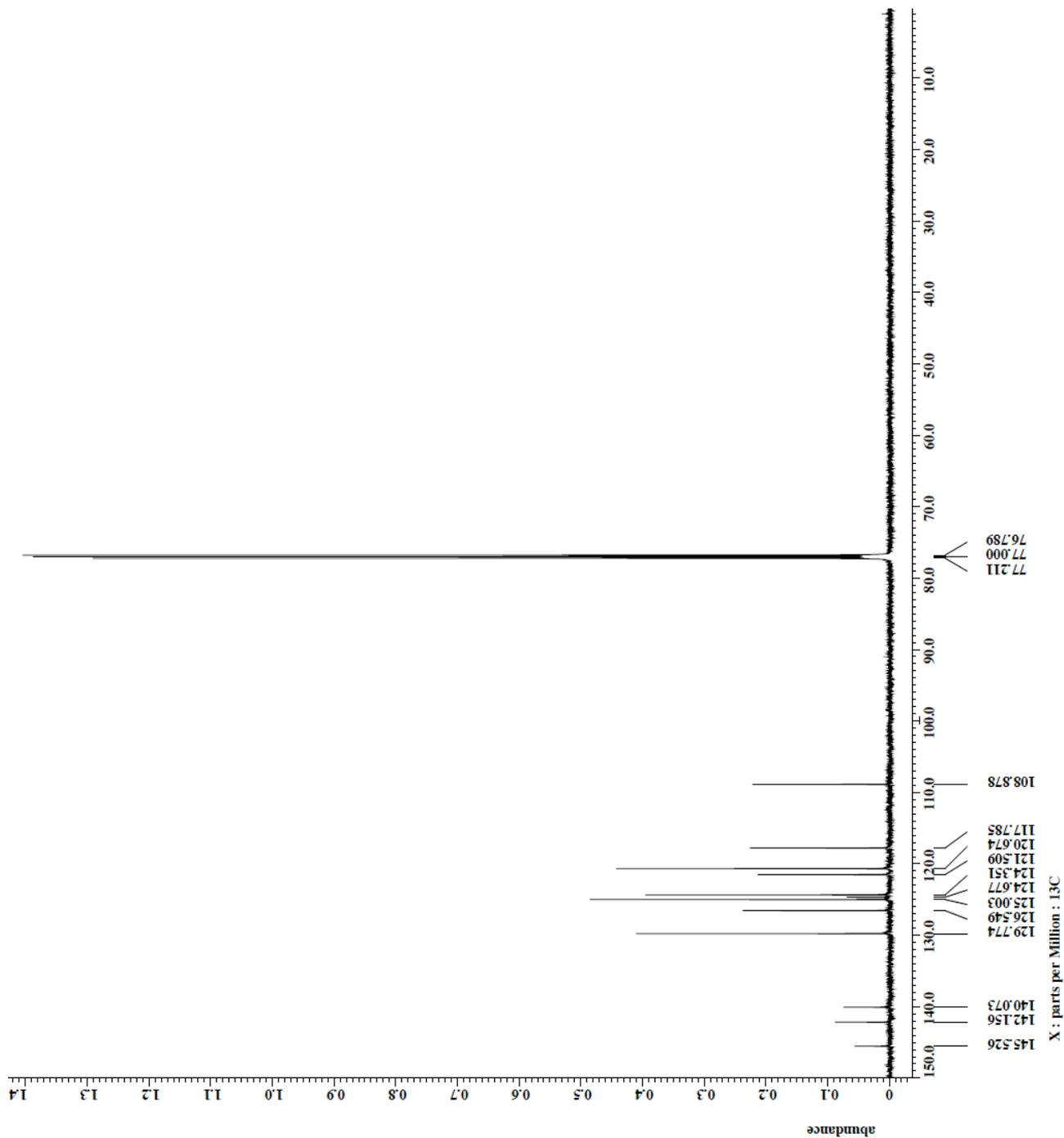
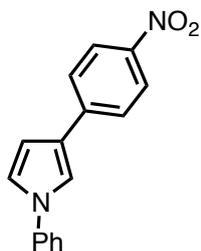
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Dd

^{13}C -NMR (150 MHz, CDCl_3) of 3Dd

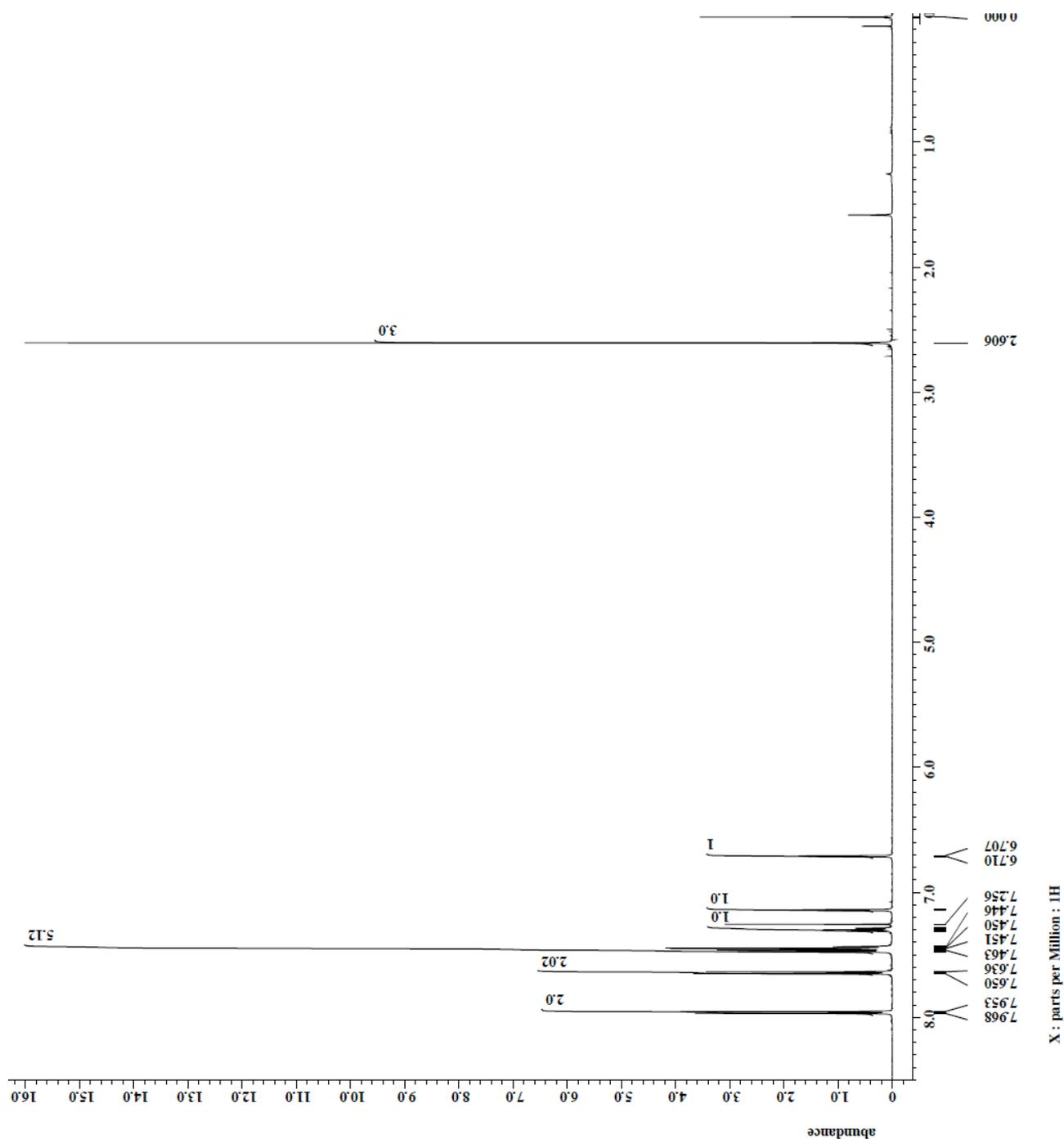
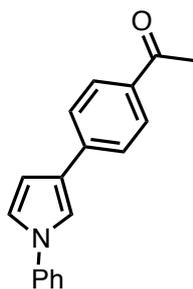


$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Ad

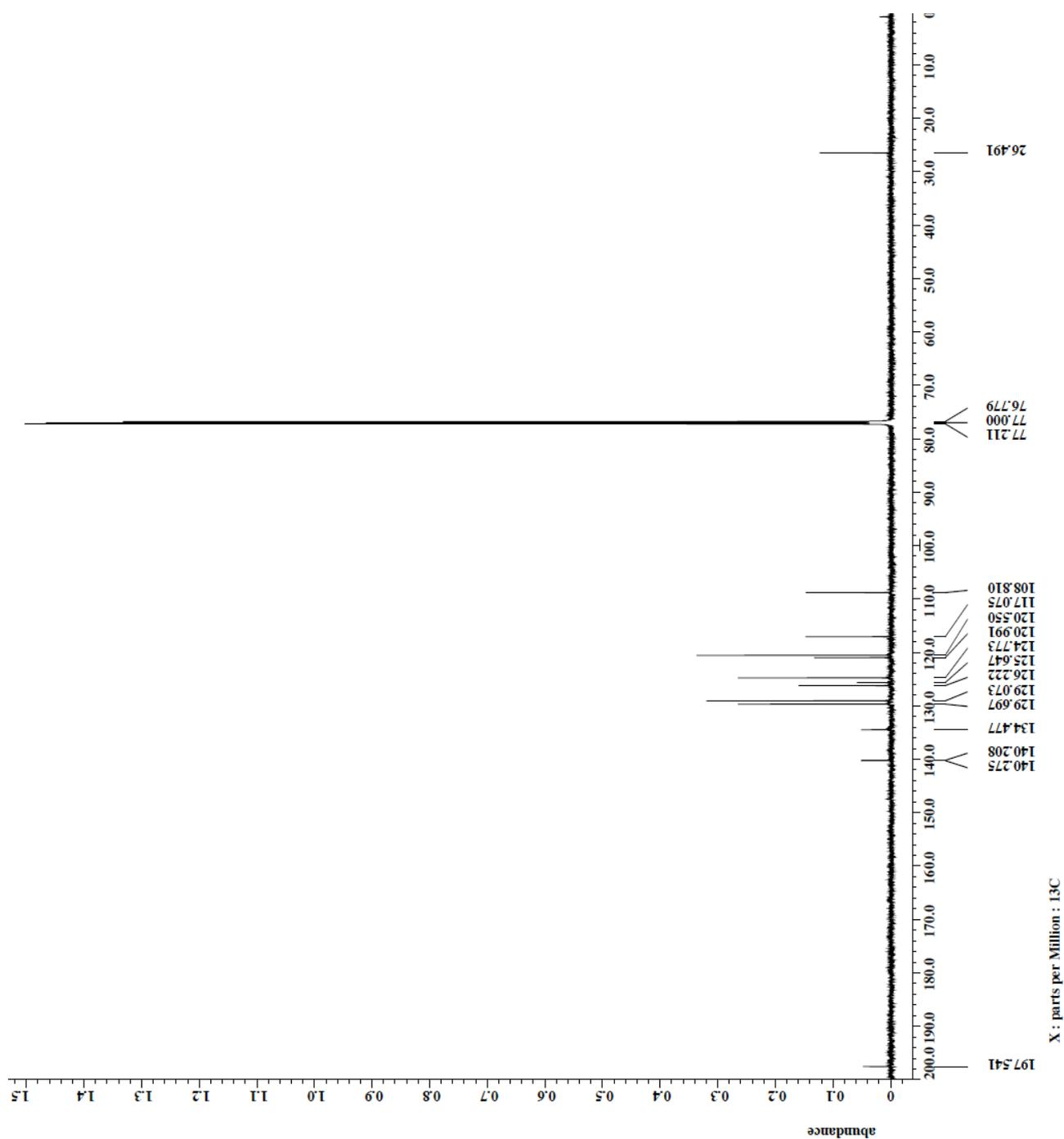
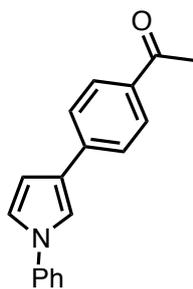
^{13}C -NMR (150 MHz, CDCl_3) of 3Ad

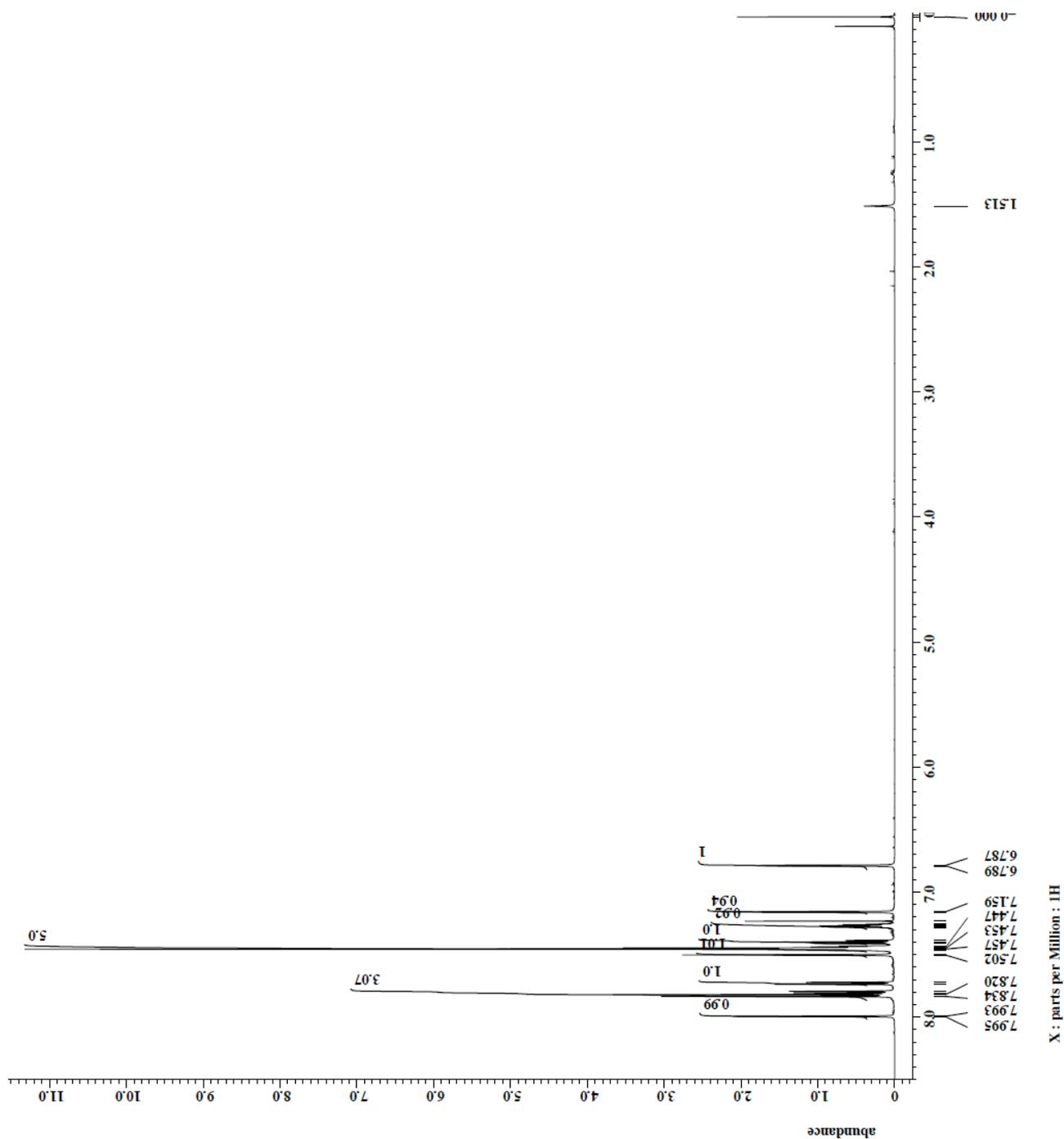
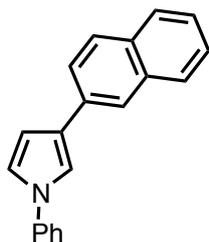


¹H-NMR (600 MHz, CDCl₃) of 3Ab

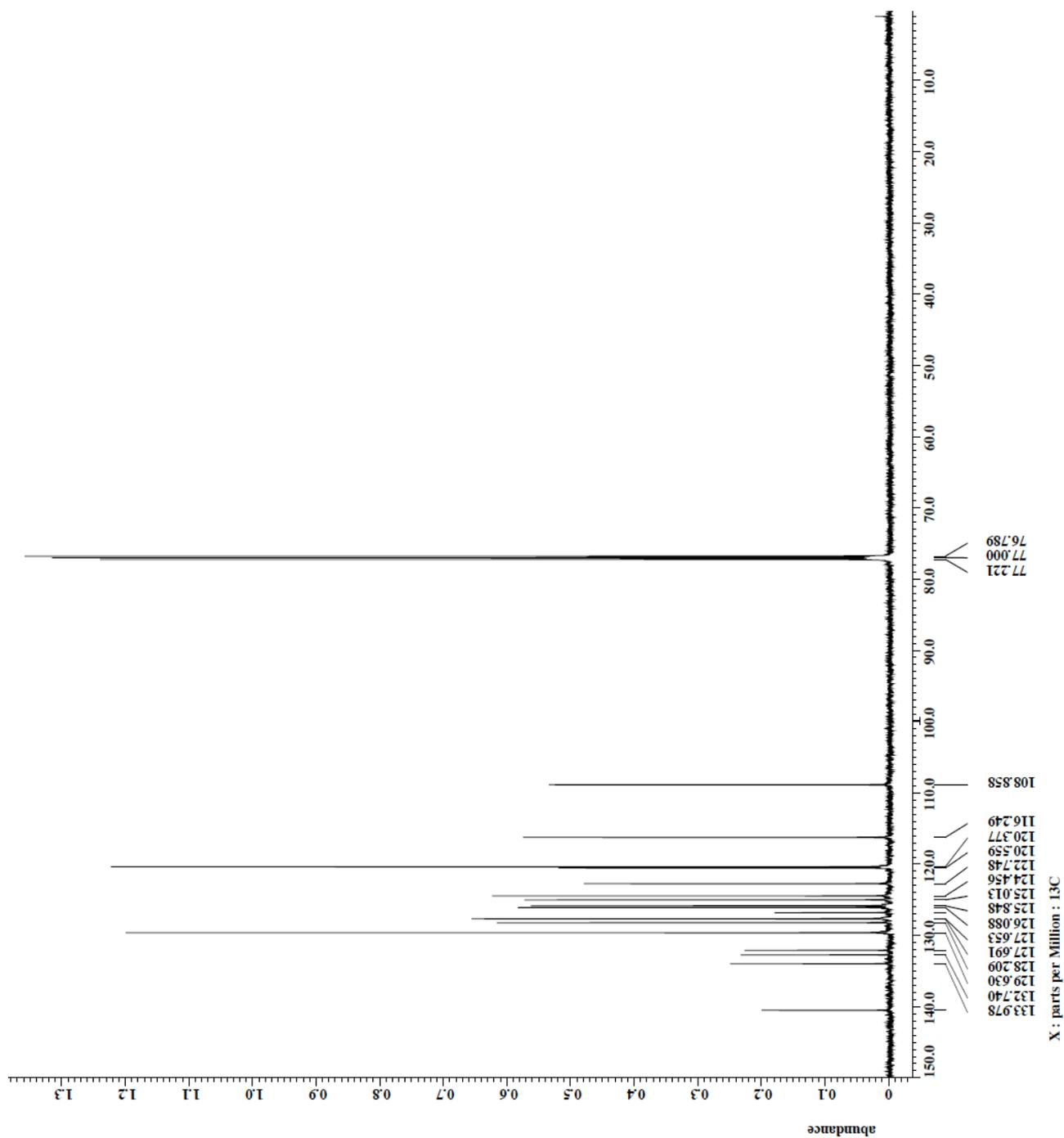
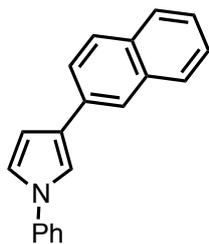


^{13}C -NMR (150 MHz, CDCl_3) of 3Ab

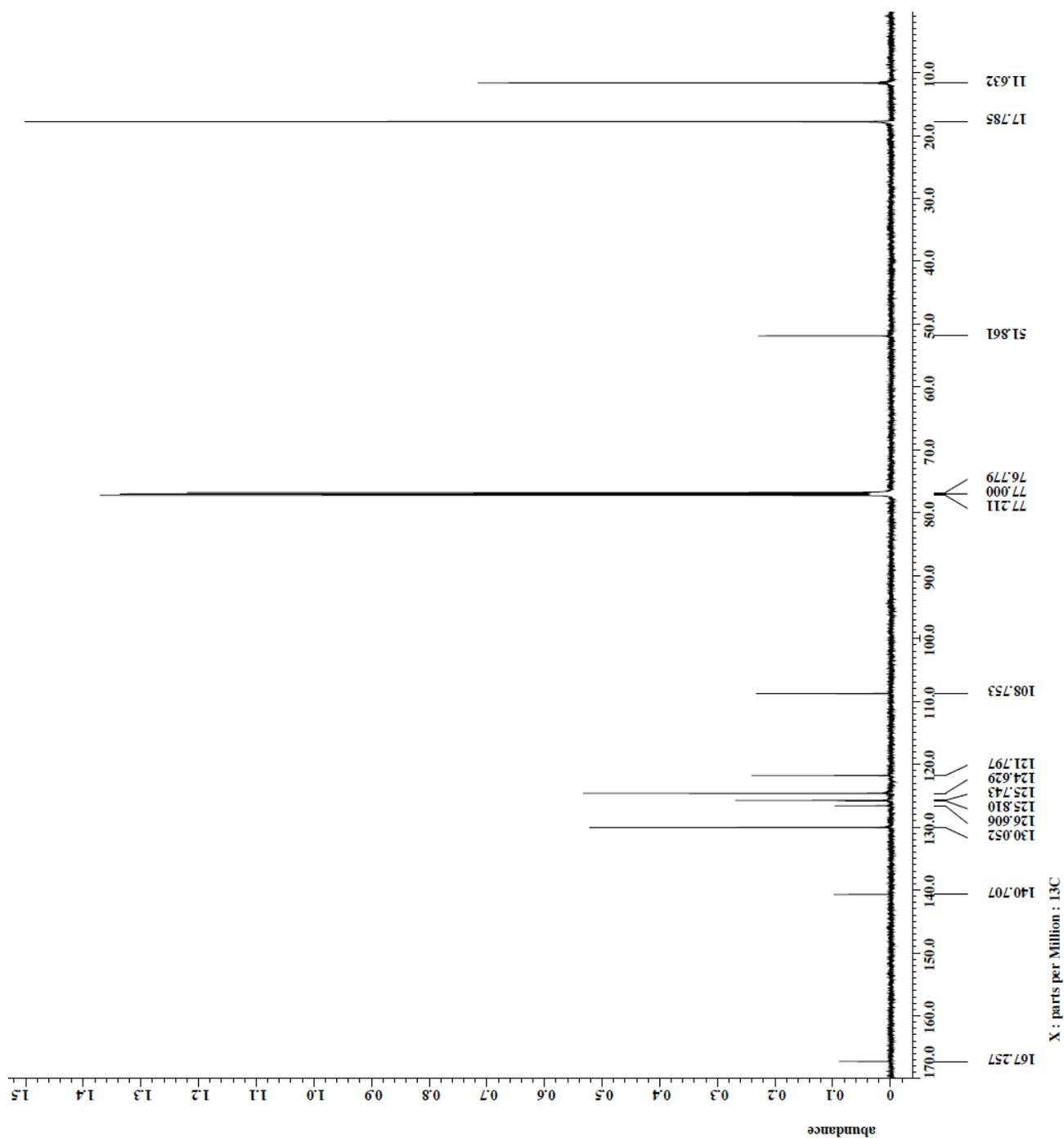
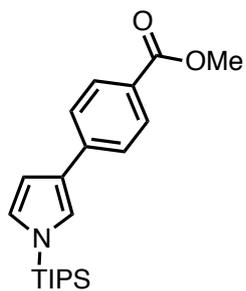


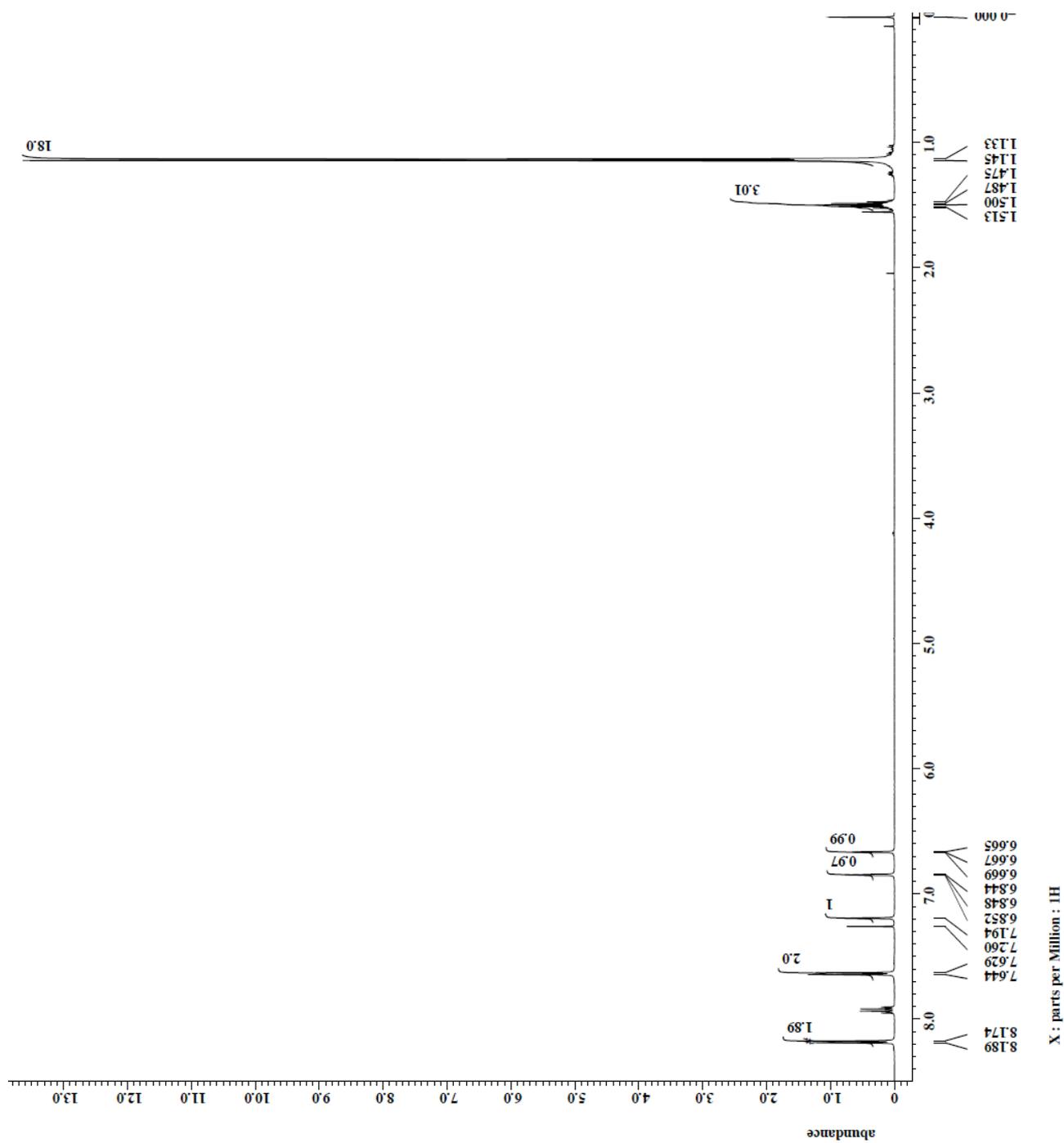
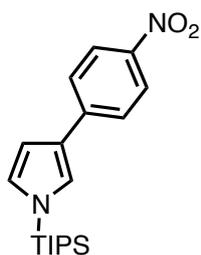
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Ah

^{13}C -NMR (150 MHz, CDCl_3) of 3Ah

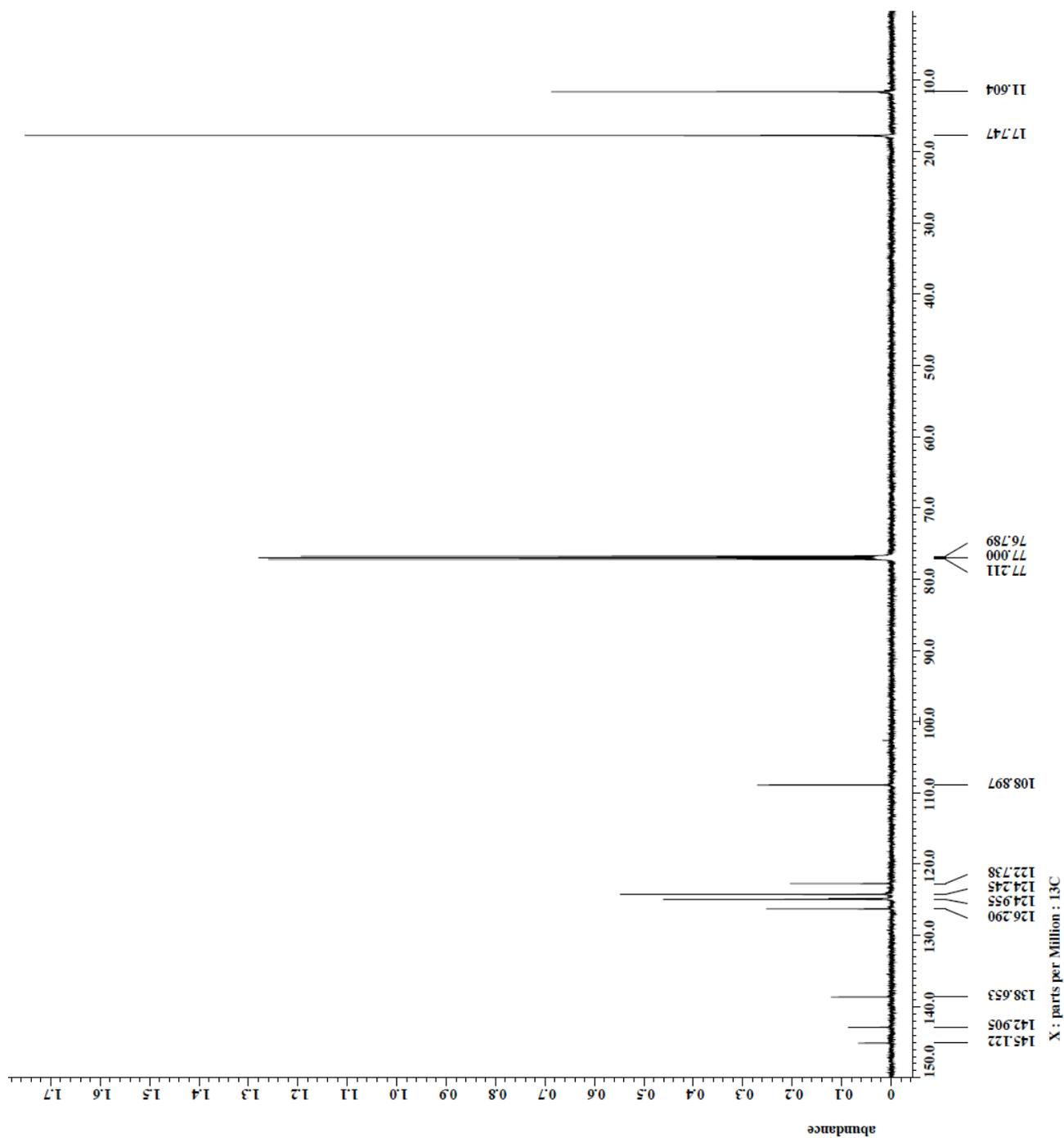
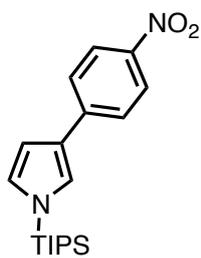


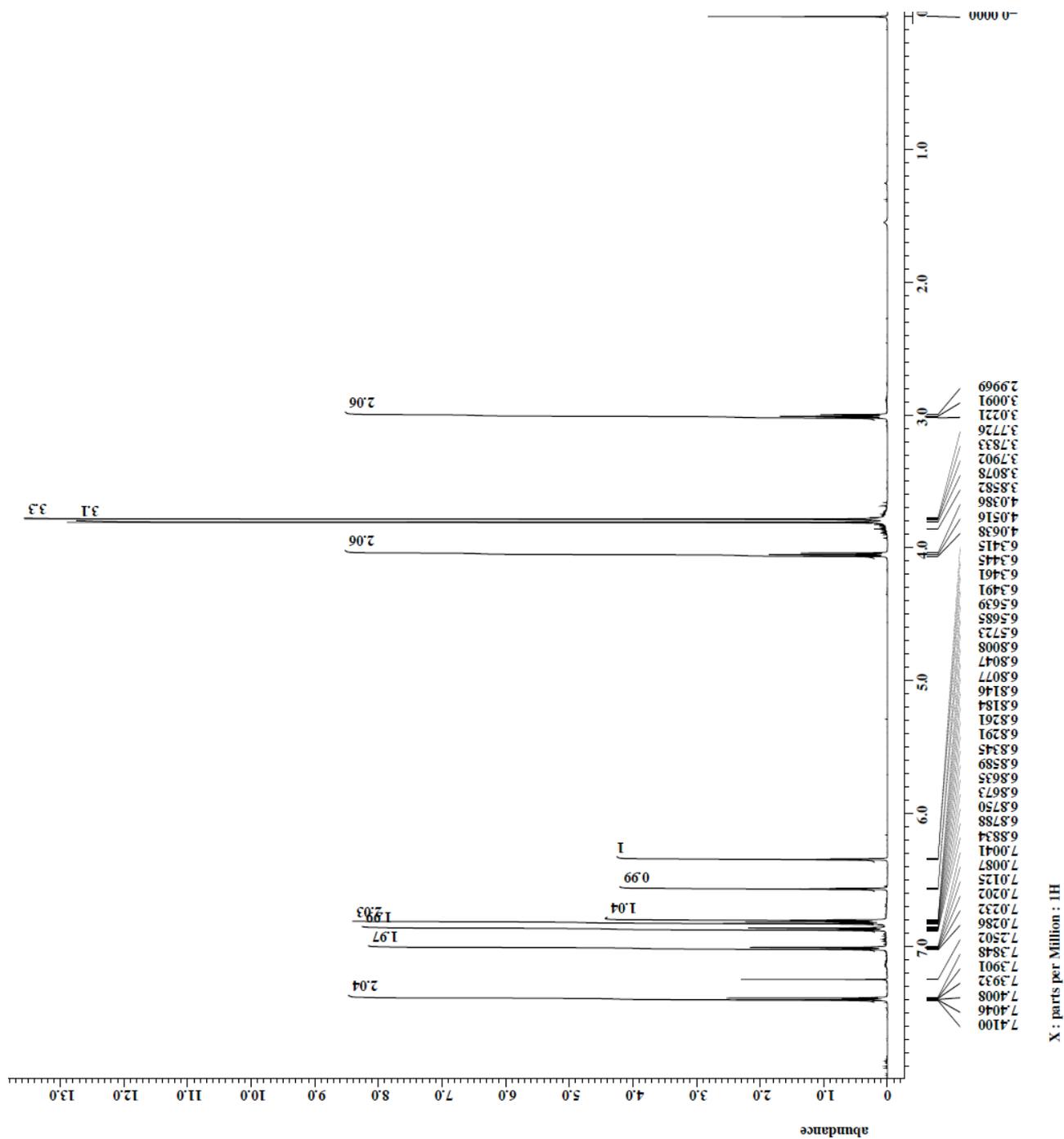
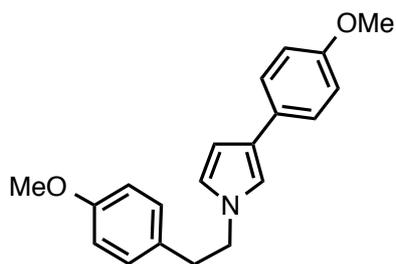
^{13}C -NMR (150 MHz, CDCl_3) of 3Ei



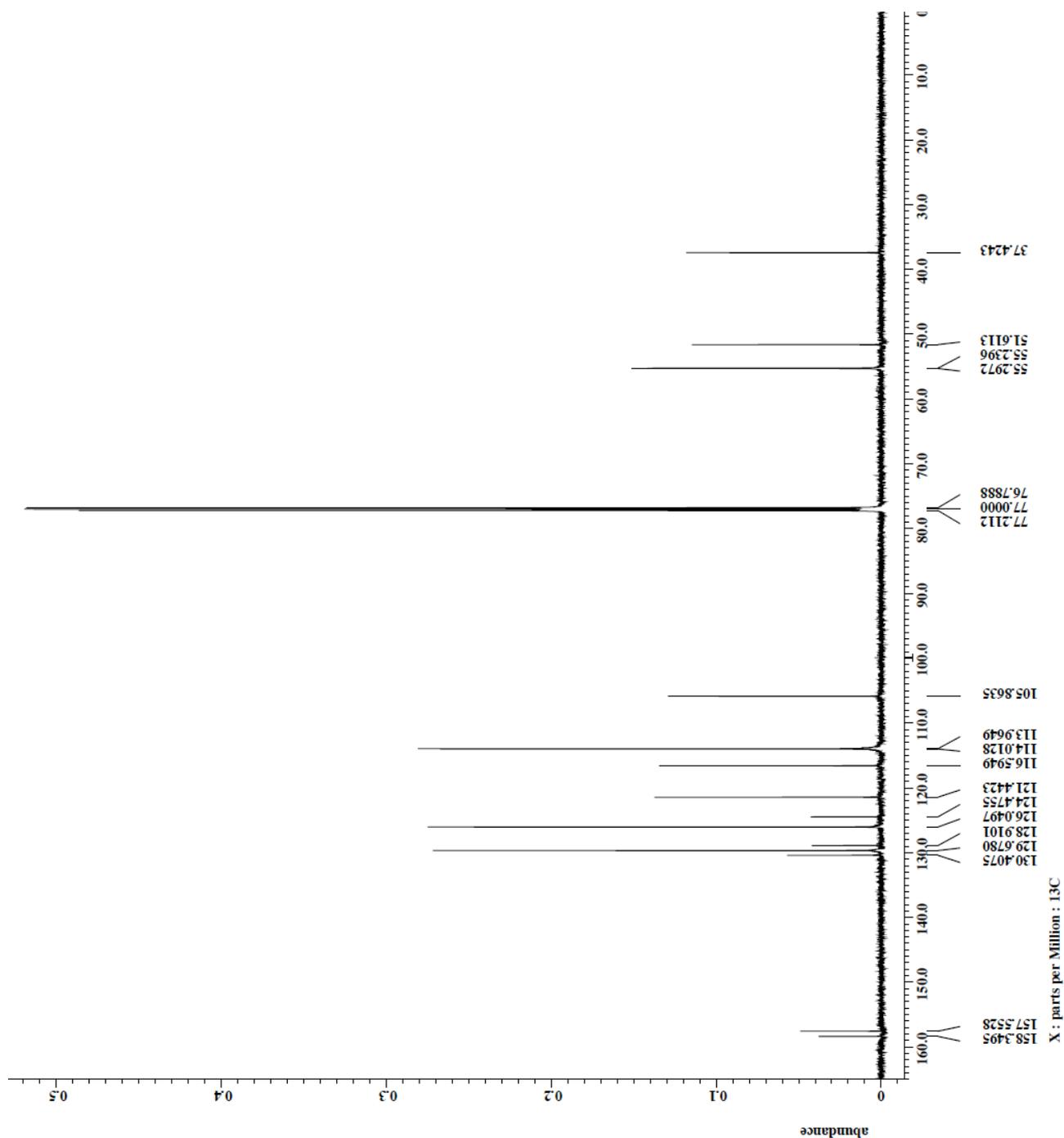
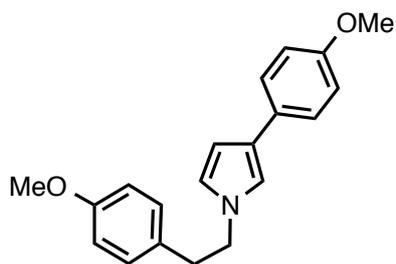
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Ed

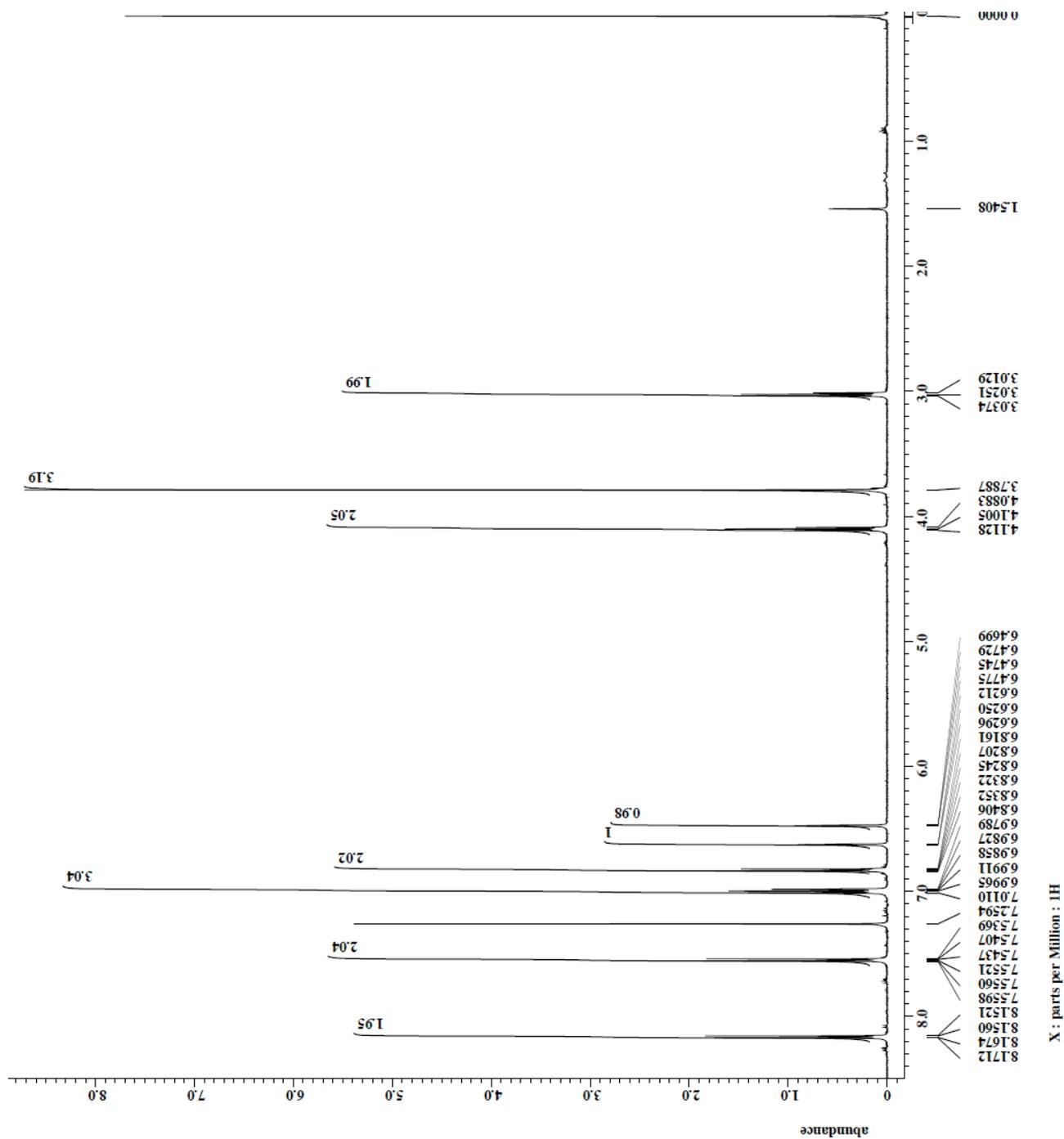
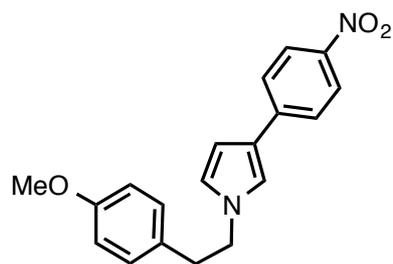
^{13}C -NMR (150 MHz, CDCl_3) of 3Ed



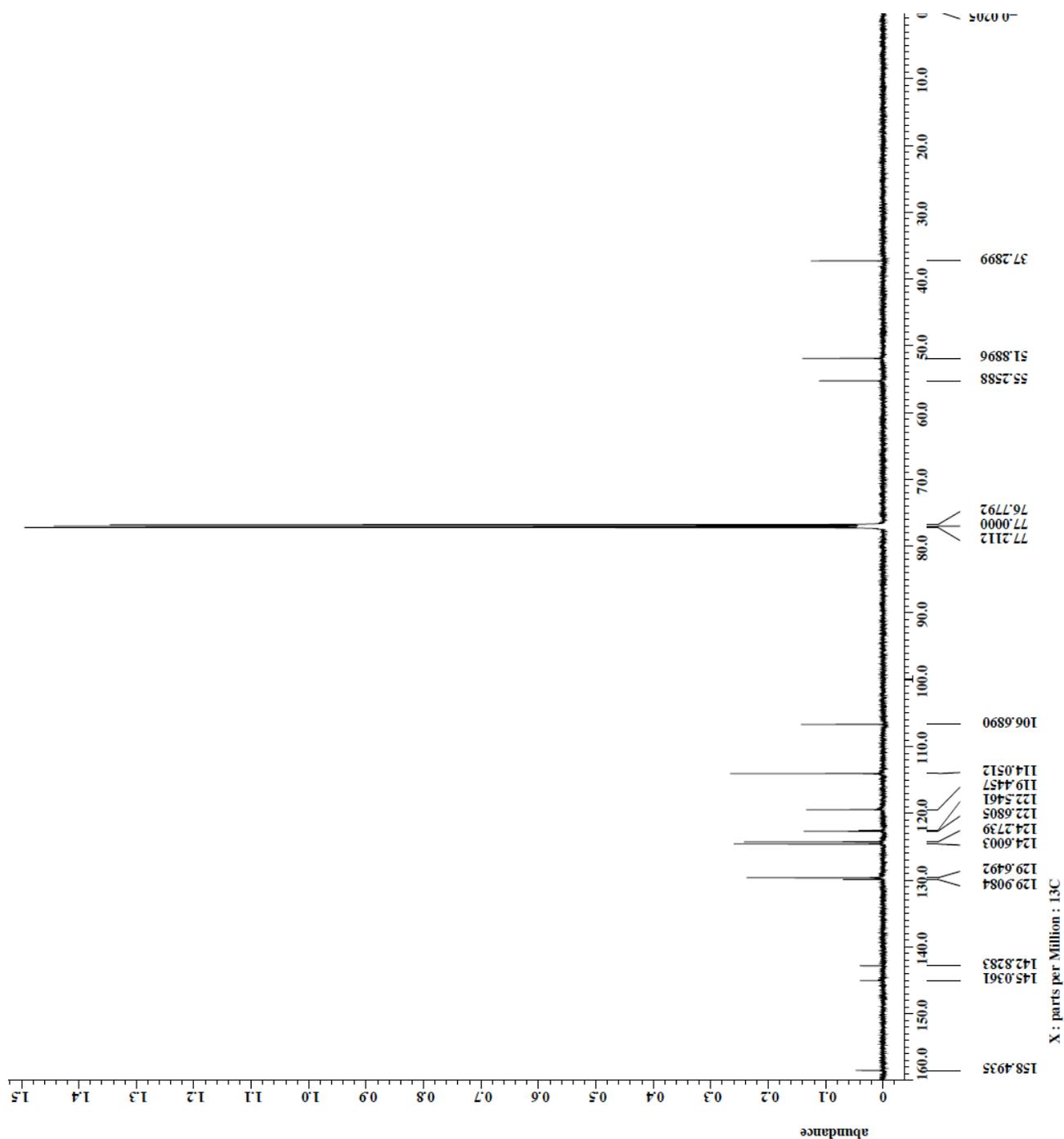
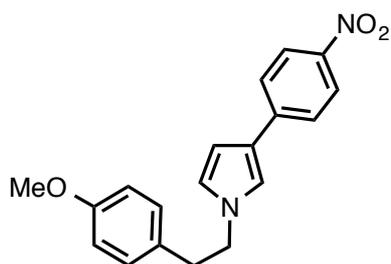
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Fj

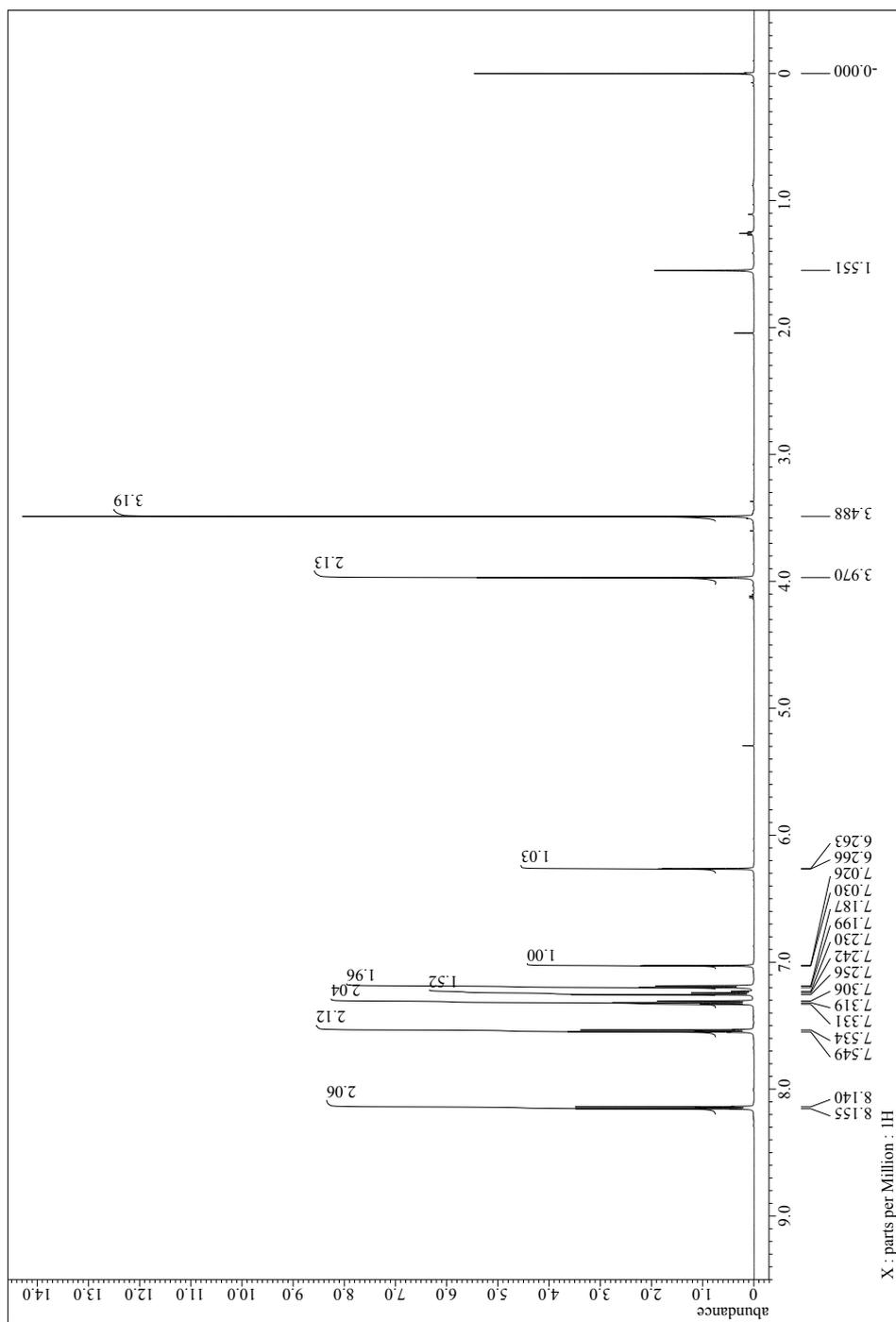
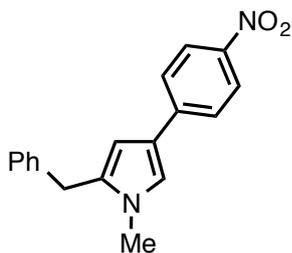
^{13}C -NMR (150 MHz, CDCl_3) of 3Fj



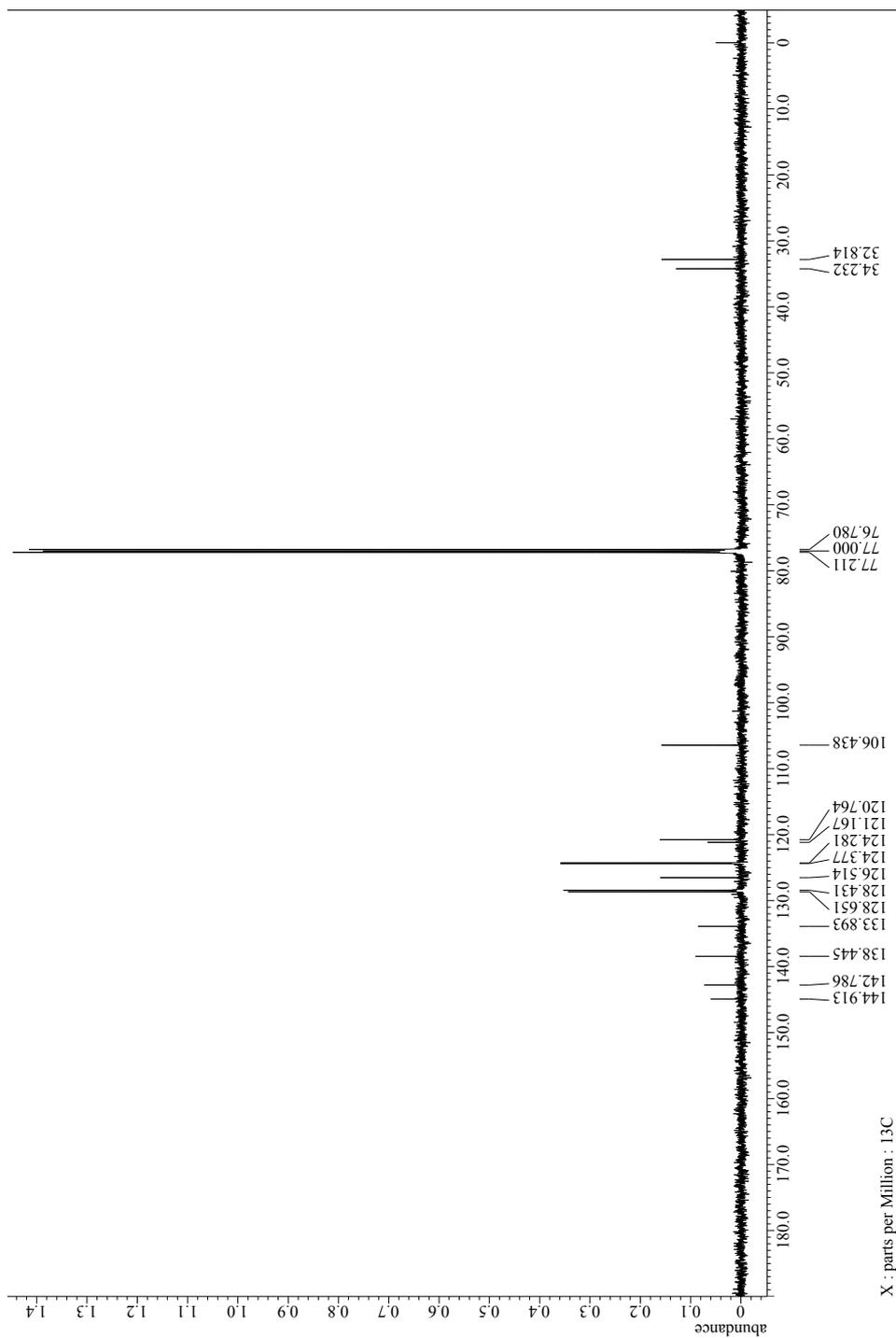
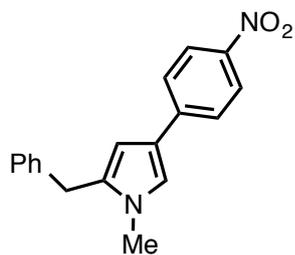
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Fd

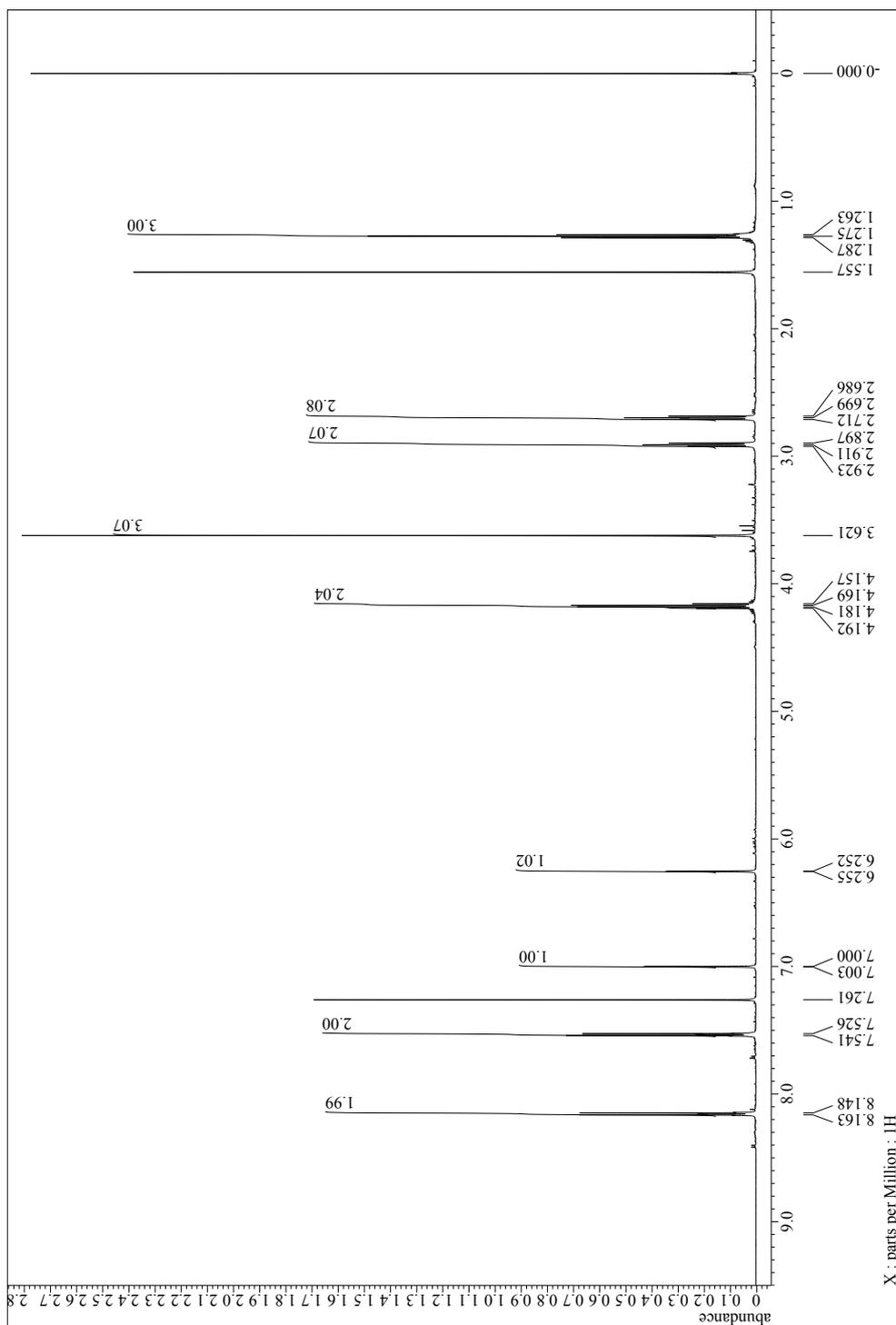
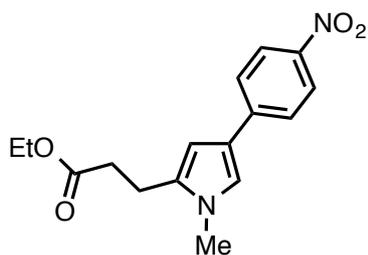
^{13}C -NMR (150 MHz, CDCl_3) of 3Fd



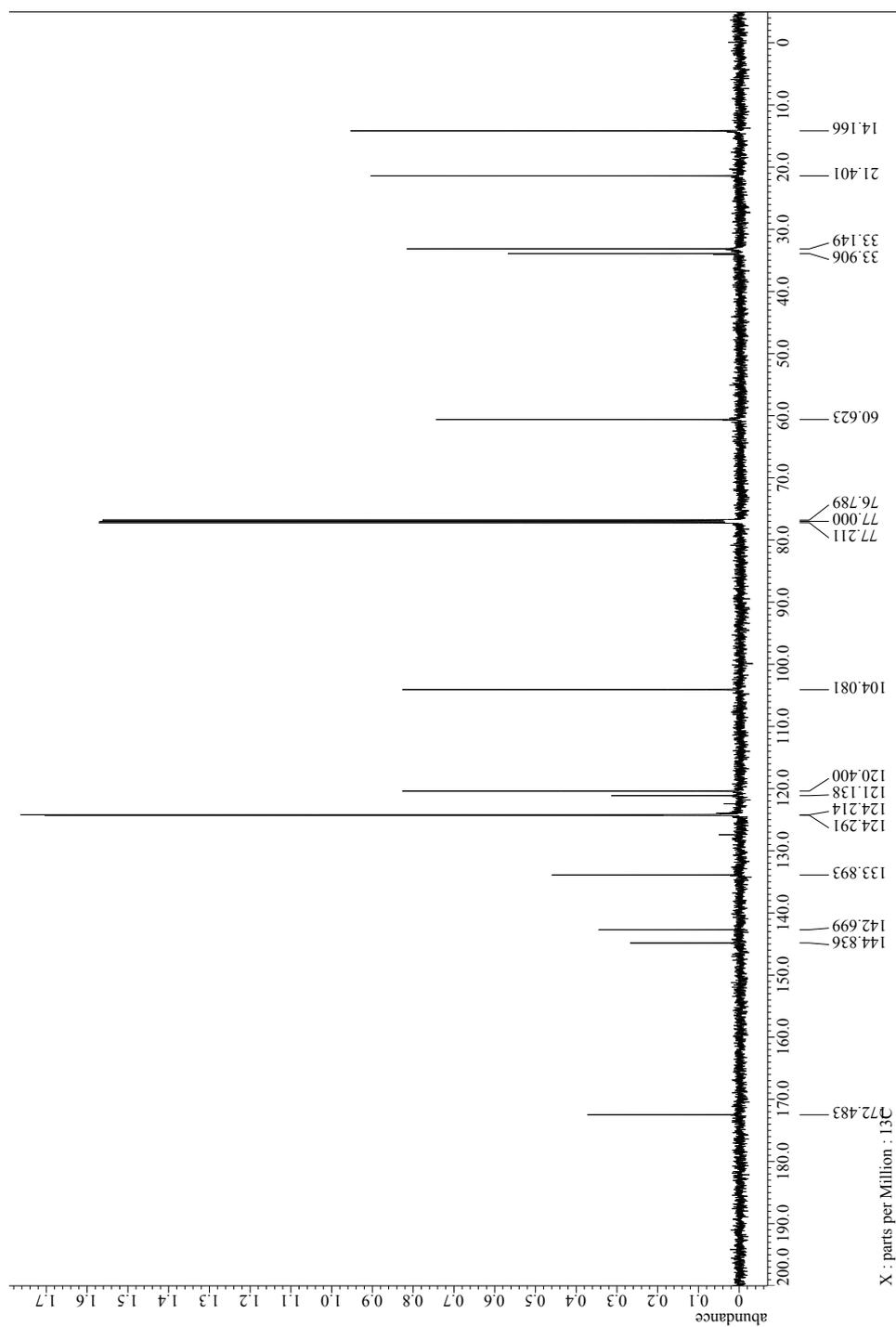
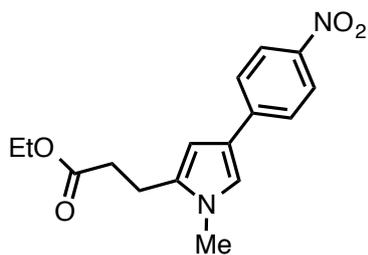
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Gd

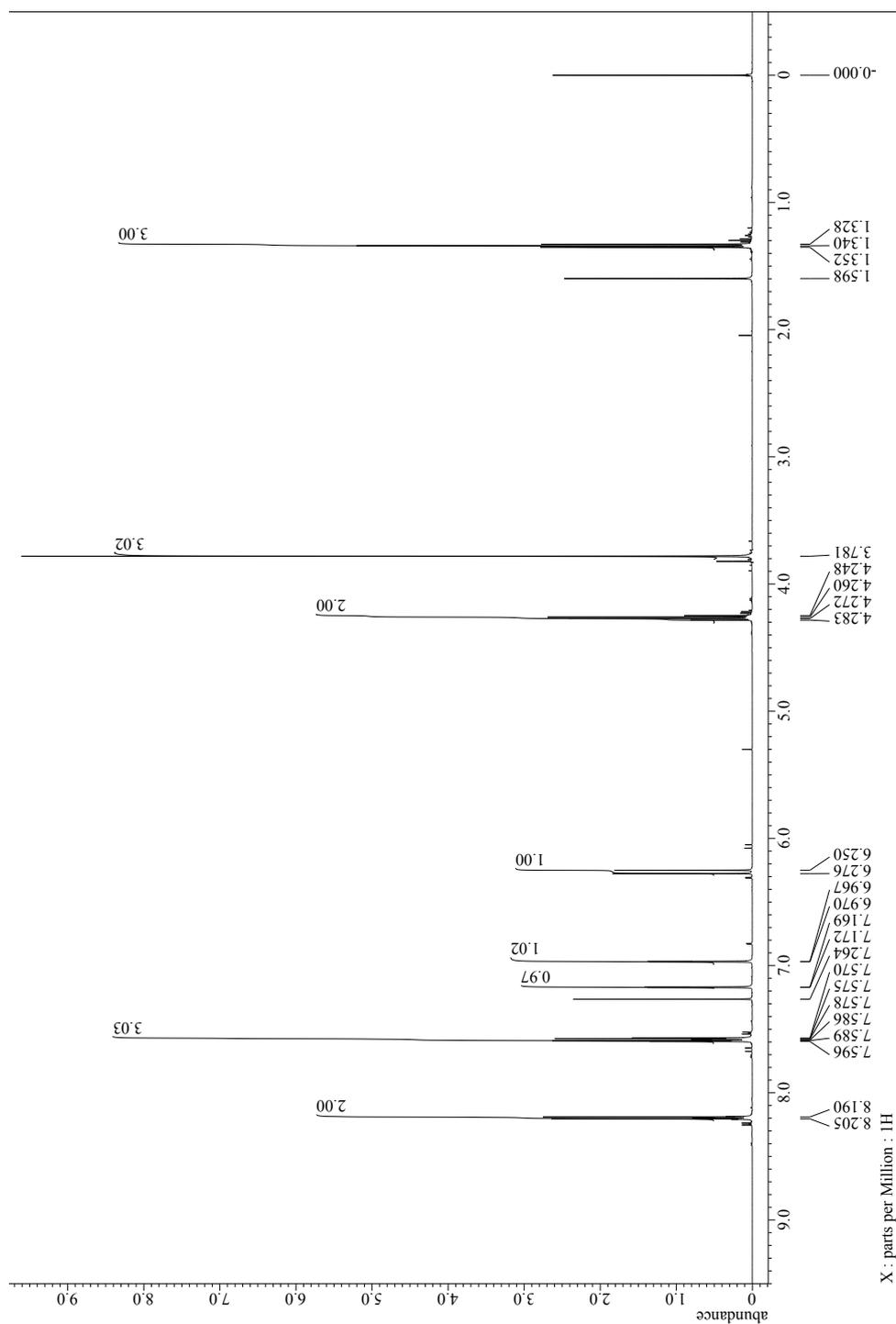
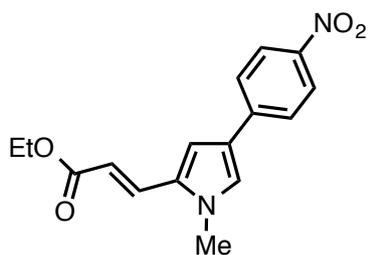
^{13}C -NMR (150 MHz, CDCl_3) of 3Gd



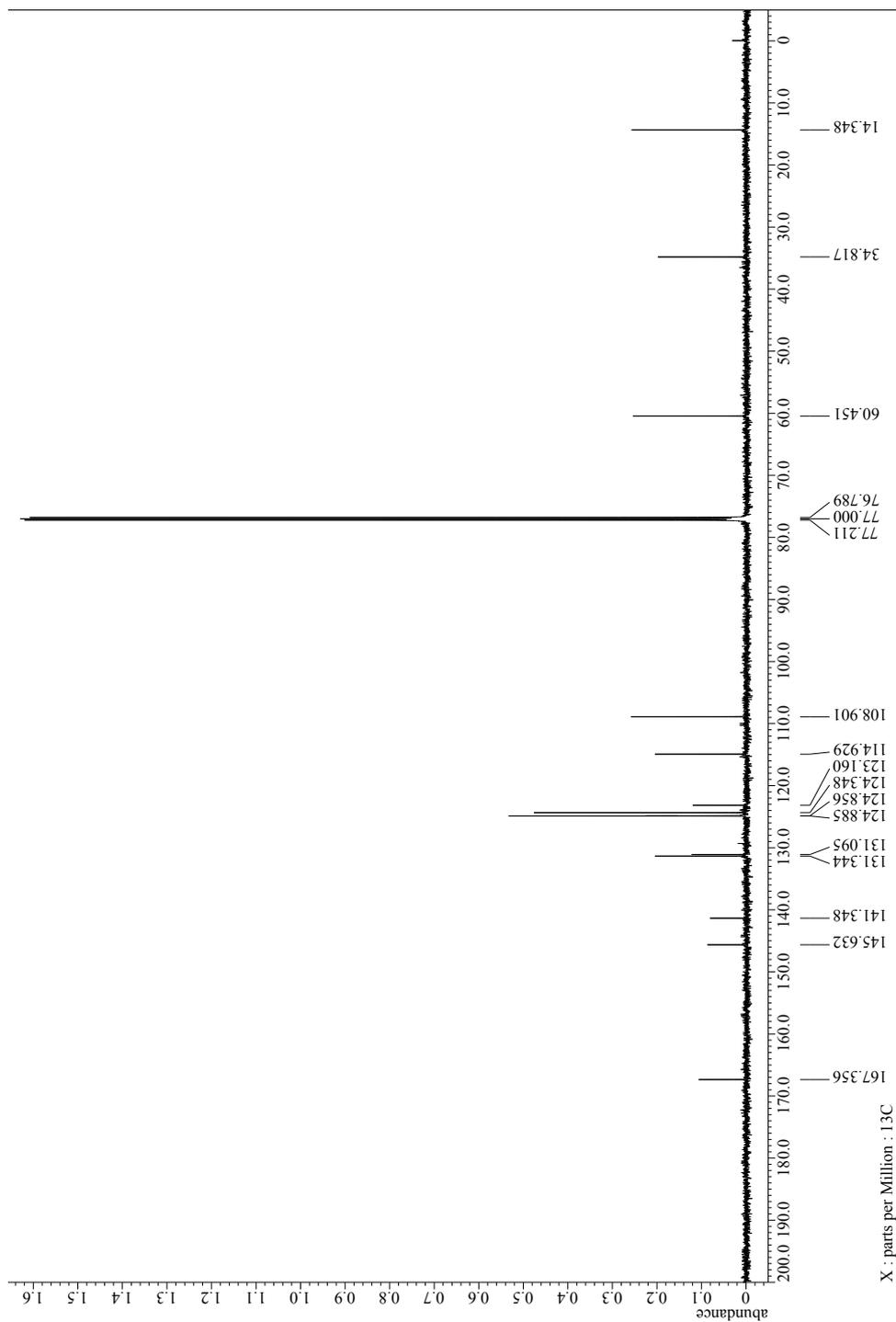
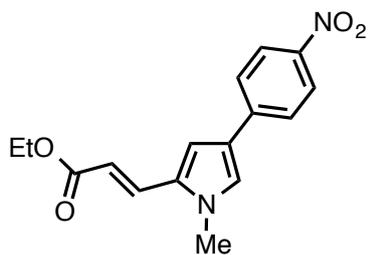
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Hd

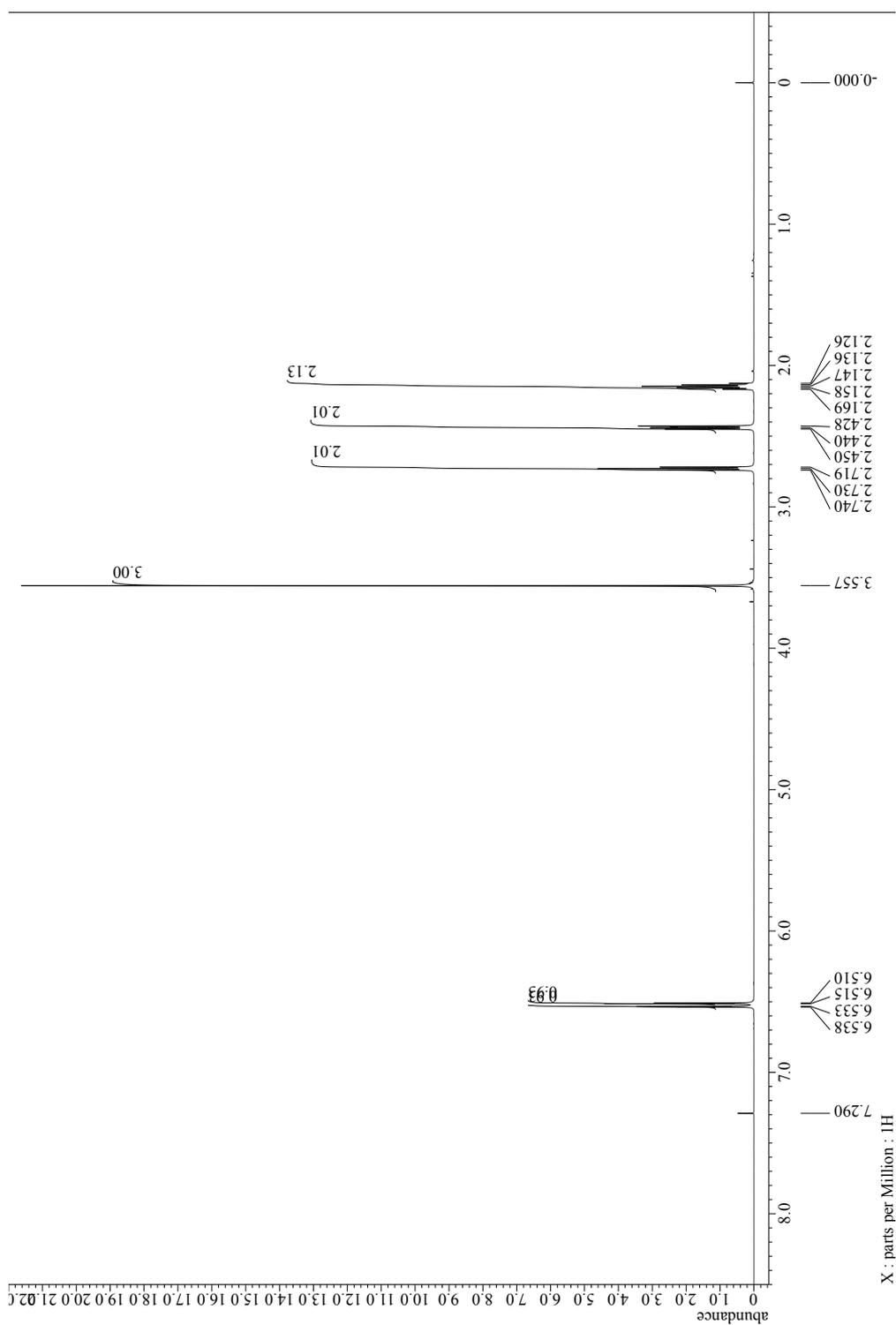
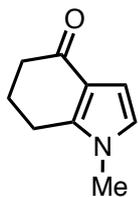
^{13}C -NMR (150 MHz, CDCl_3) of 3Hd



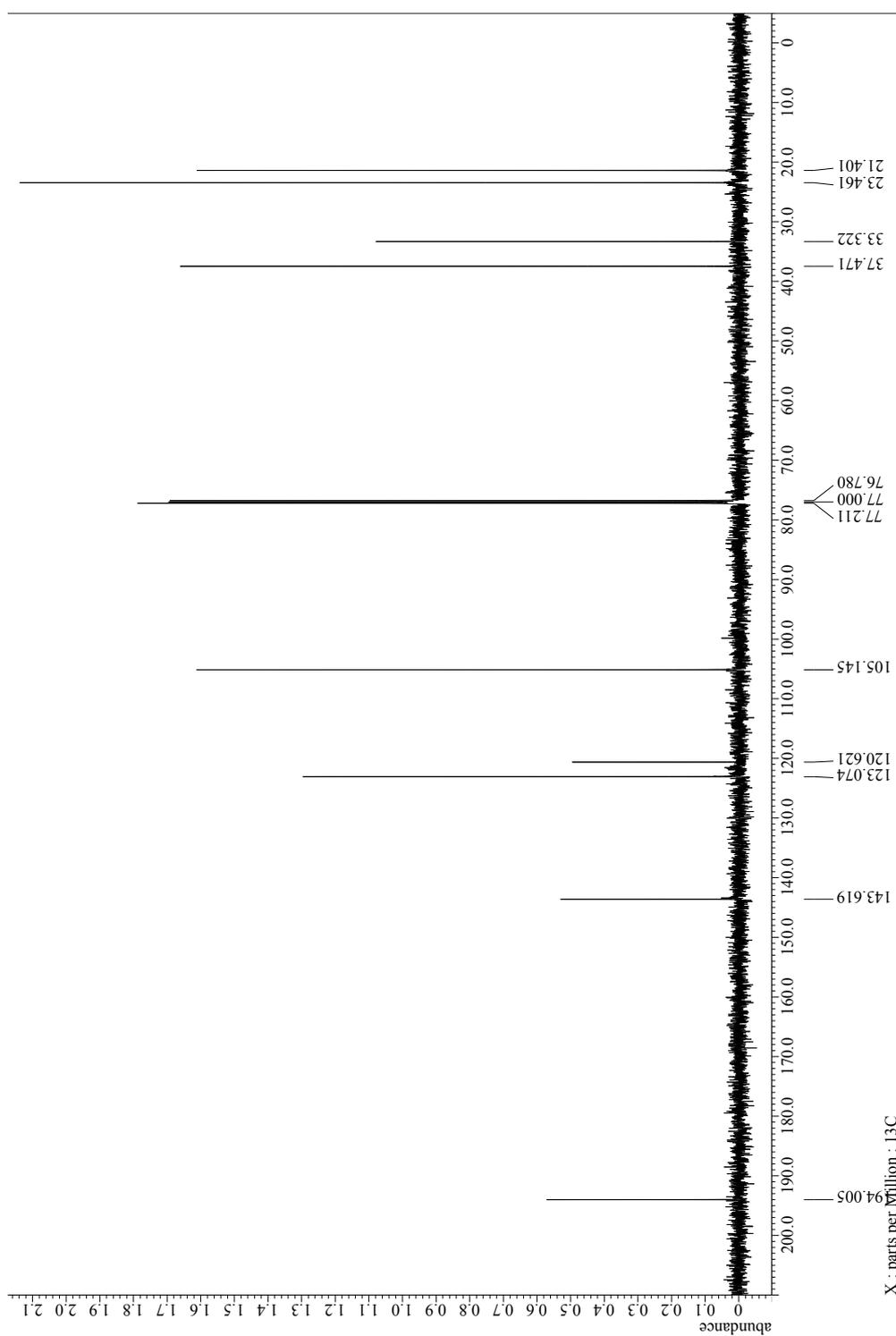
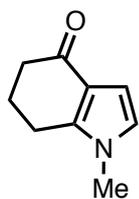
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Id

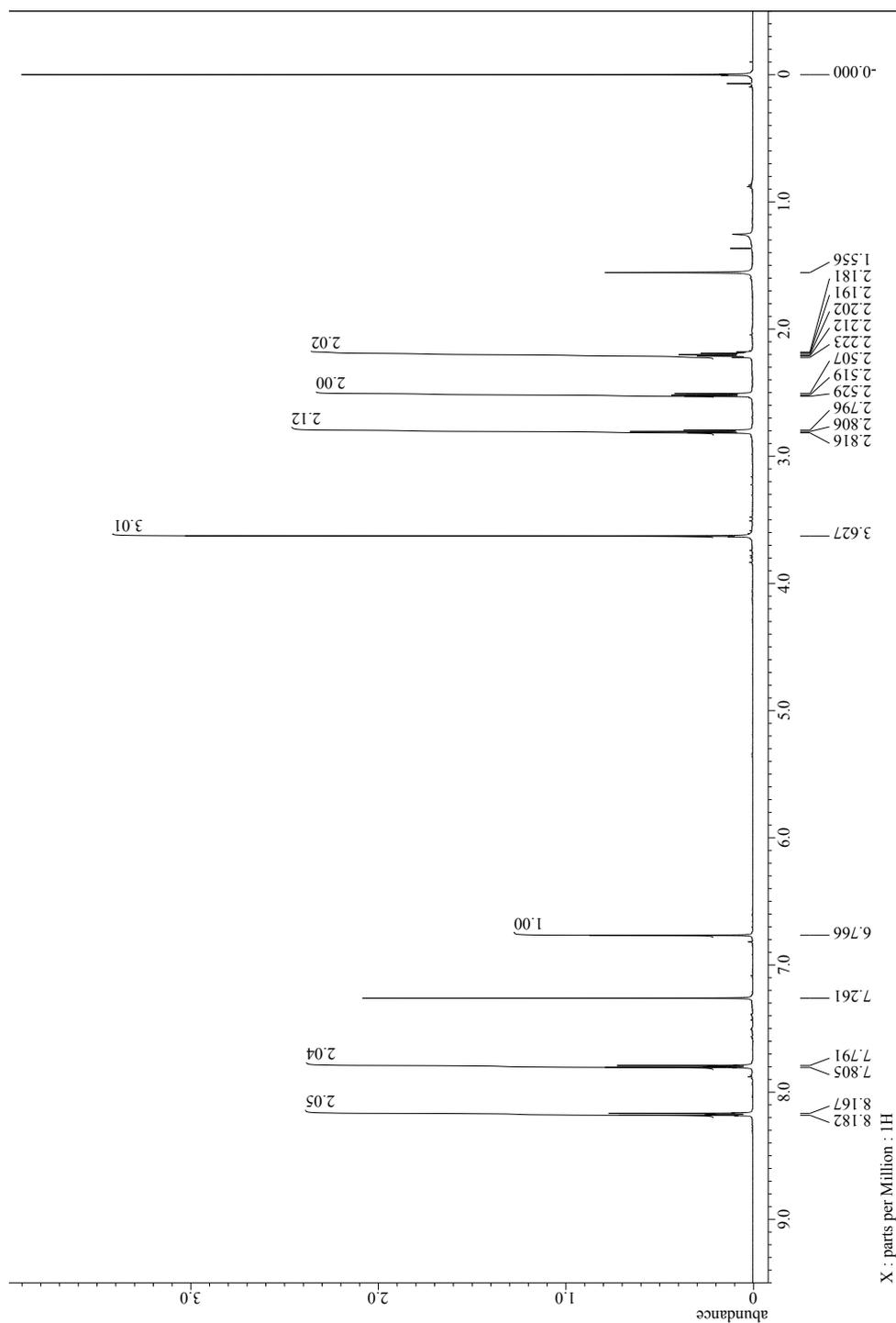
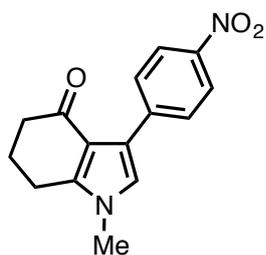
^{13}C -NMR (150 MHz, CDCl_3) of 3Id



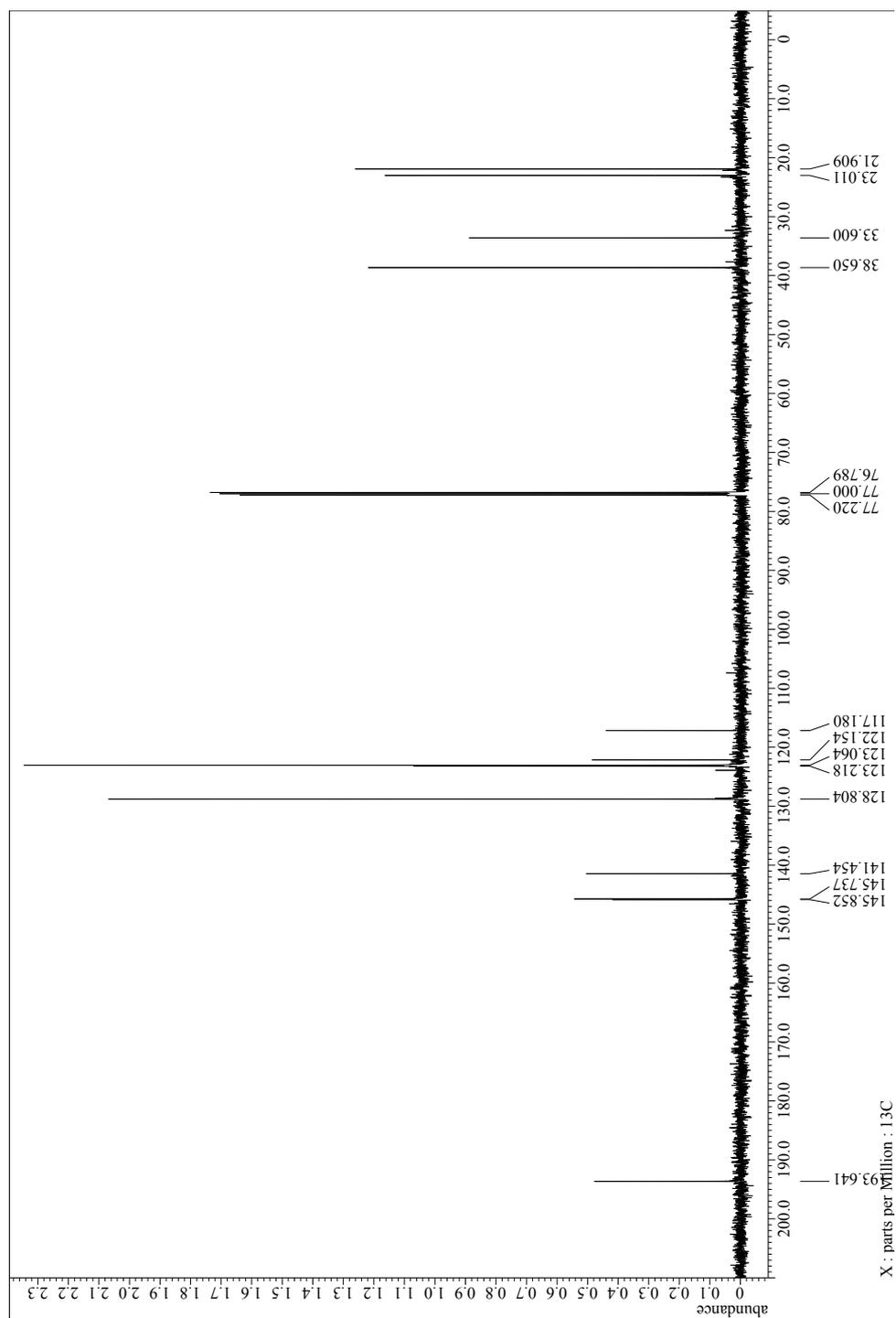
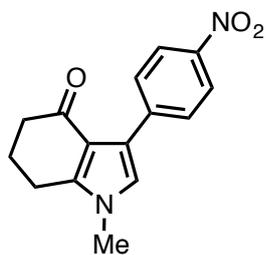
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3J

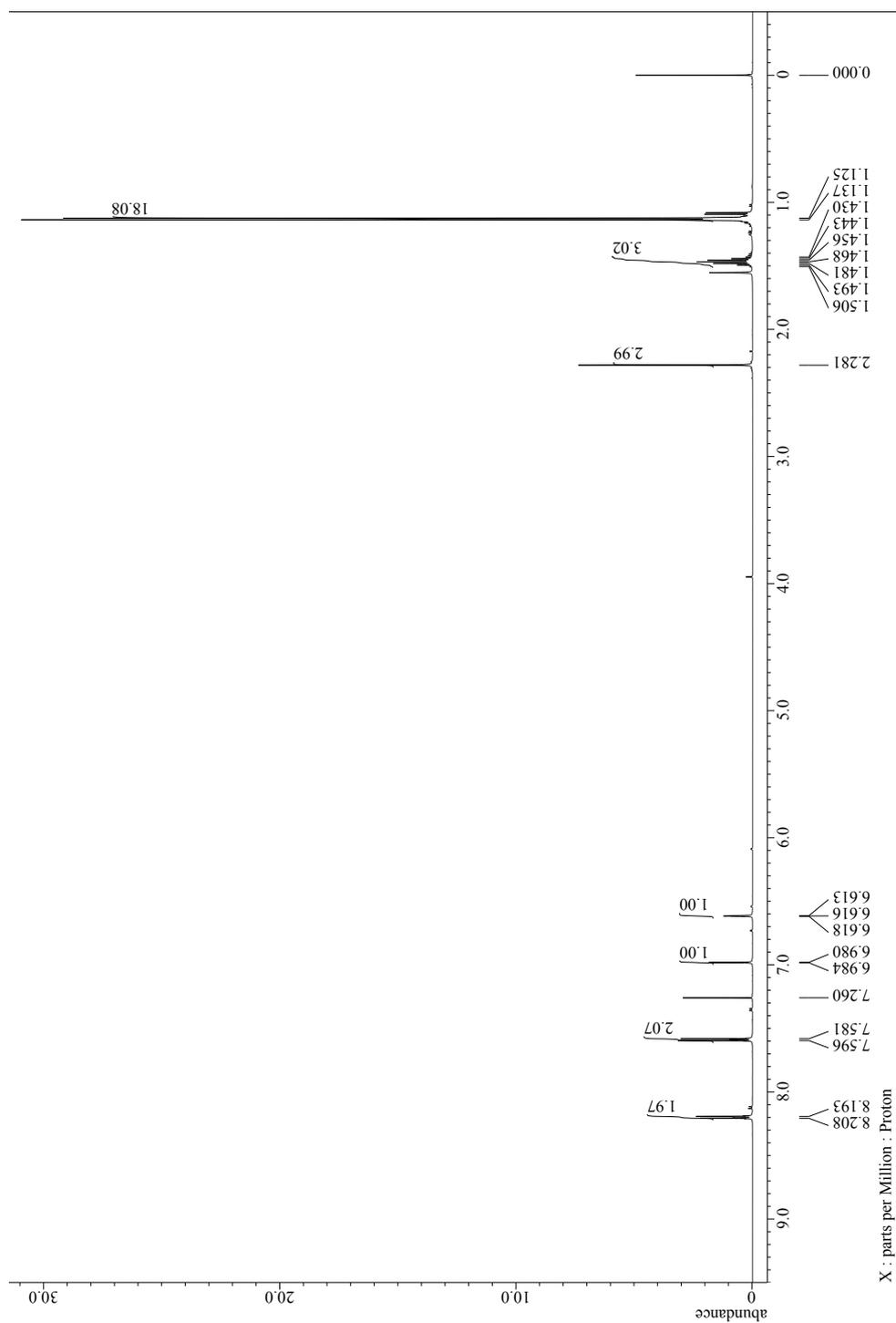
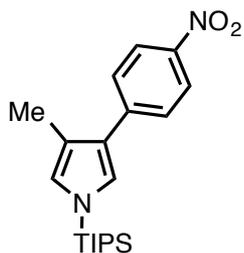
^{13}C -NMR (150 MHz, CDCl_3) of 3J



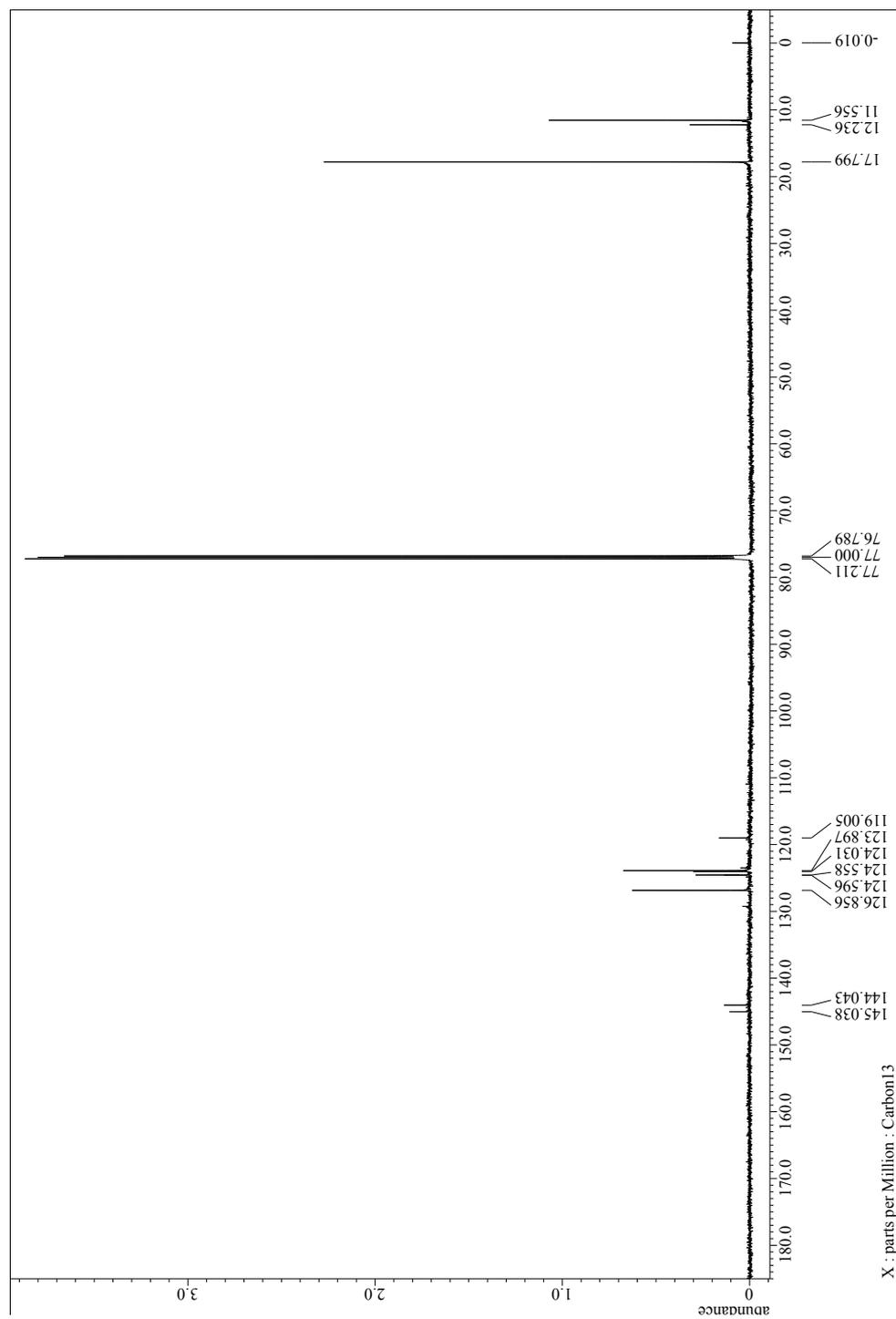
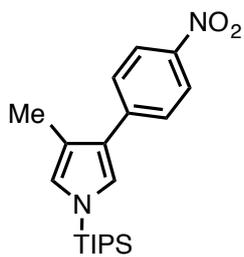
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Jd

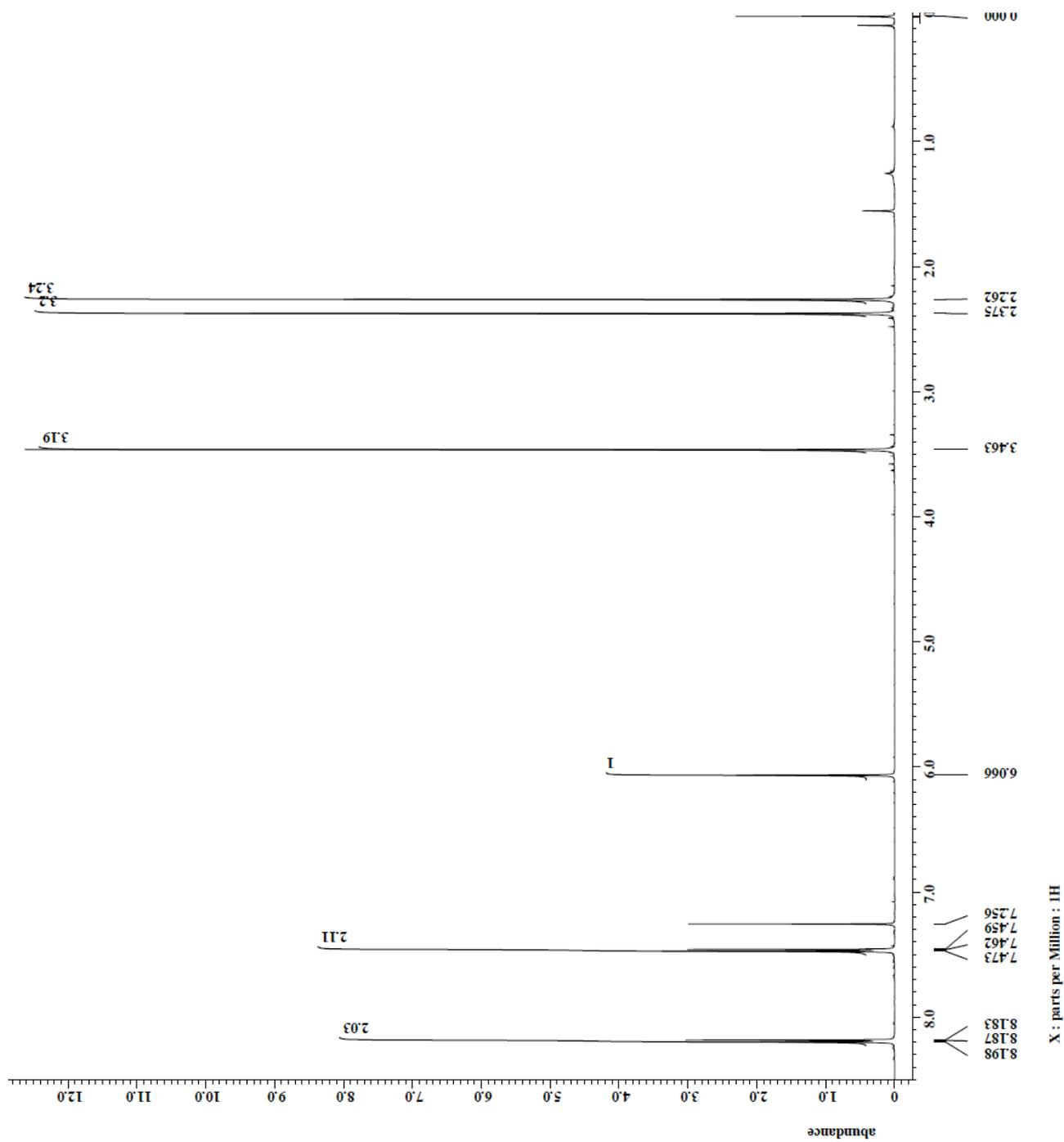
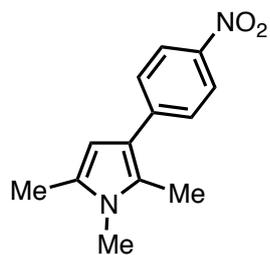
^{13}C -NMR (150 MHz, CDCl_3) of 3Jd



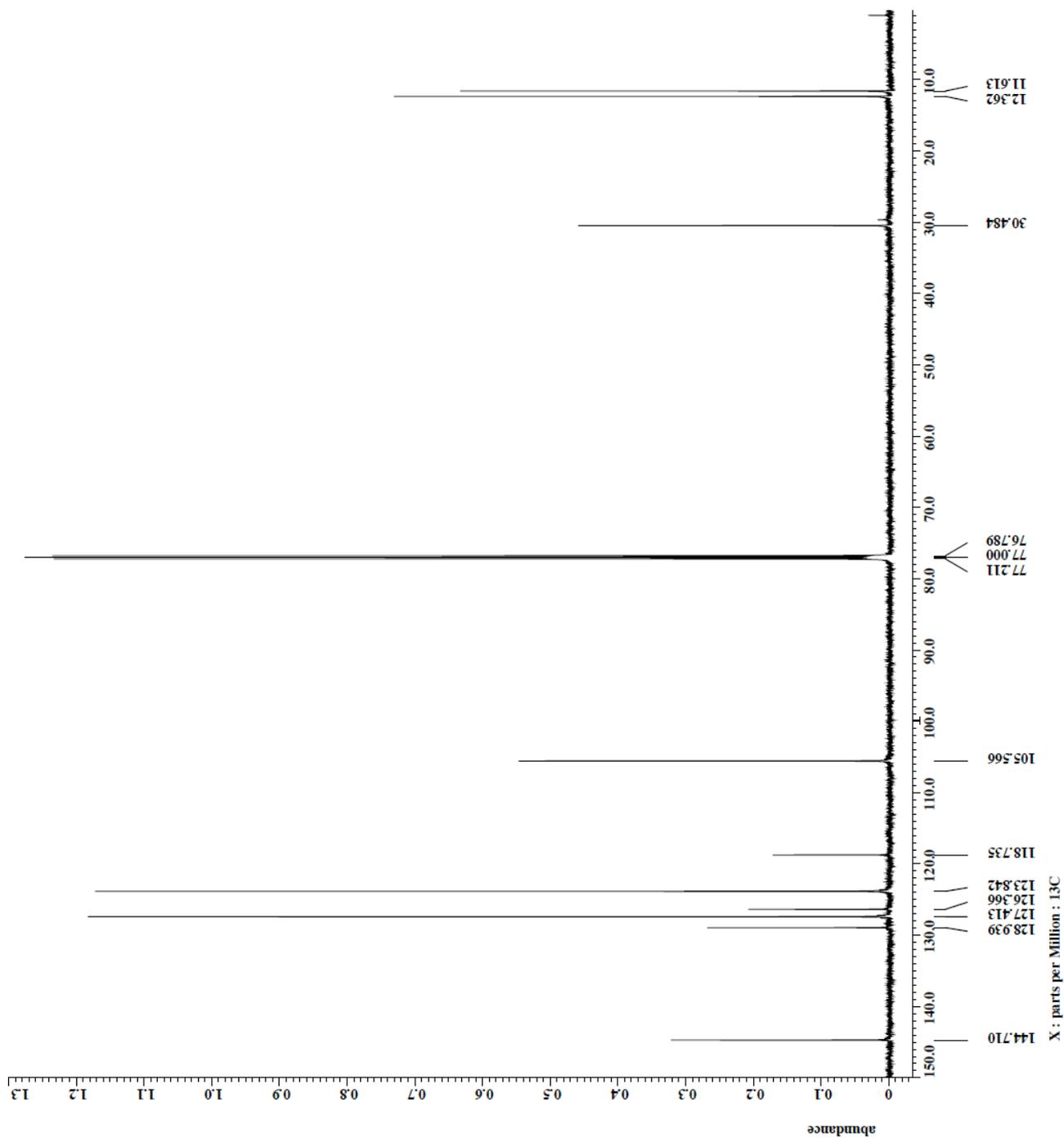
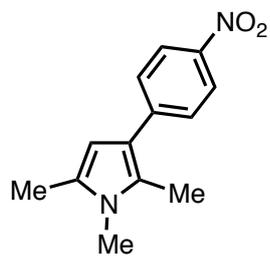
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Kd

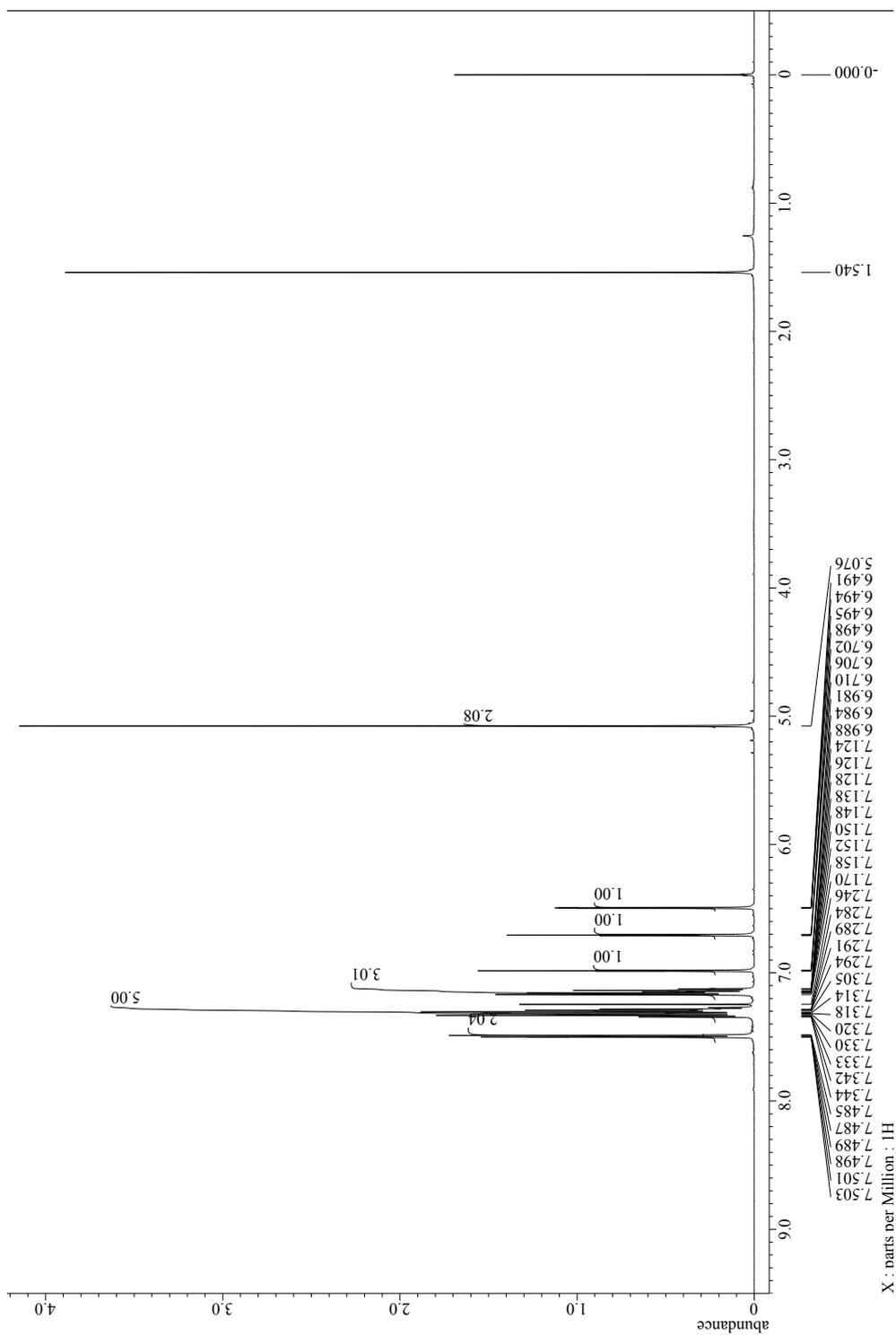
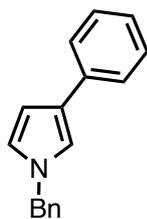
^{13}C -NMR (150 MHz, CDCl_3) of 3Kd



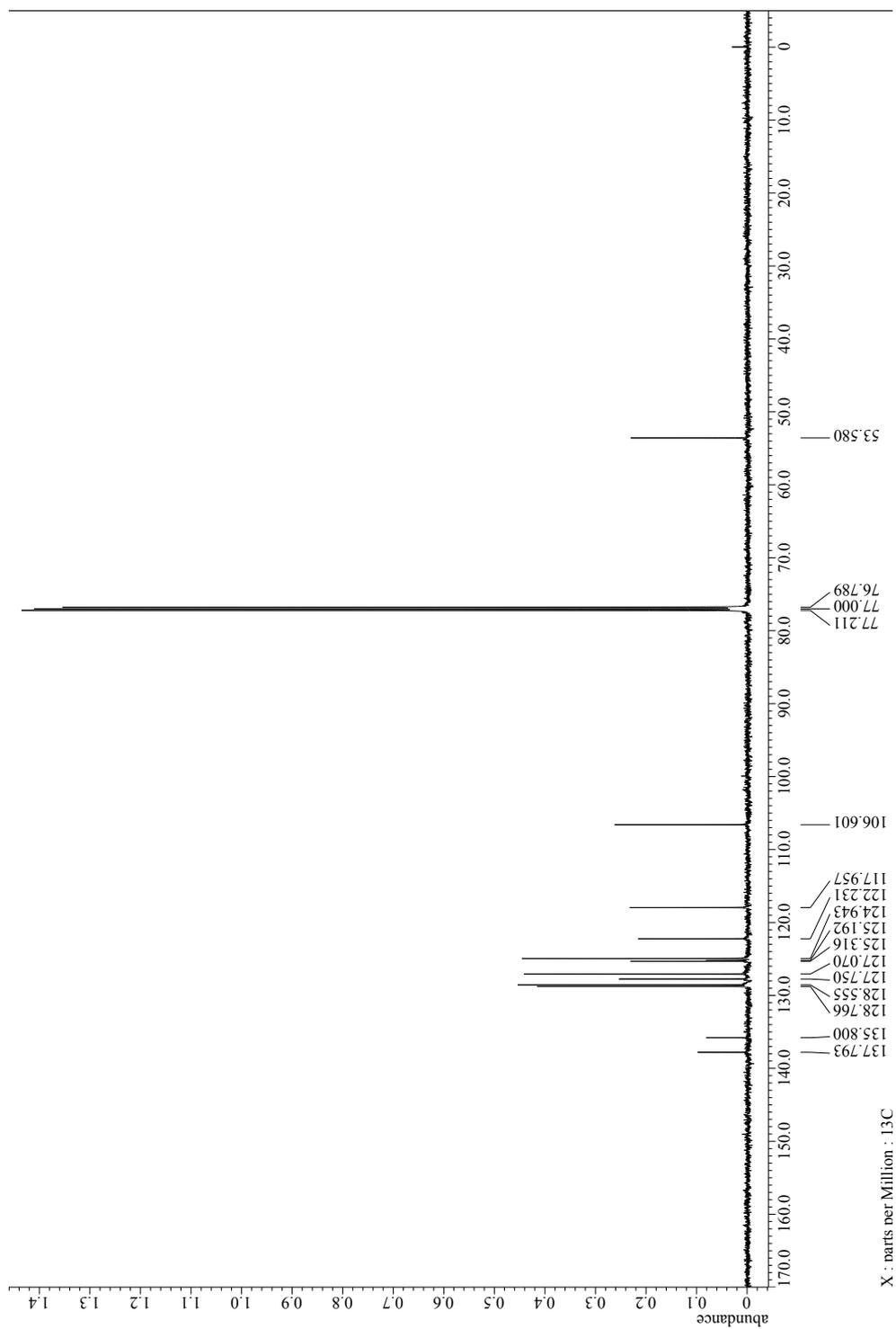
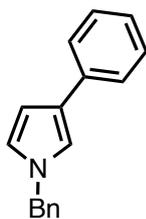
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Ld

^{13}C -NMR (150 MHz, CDCl_3) of 3Ld

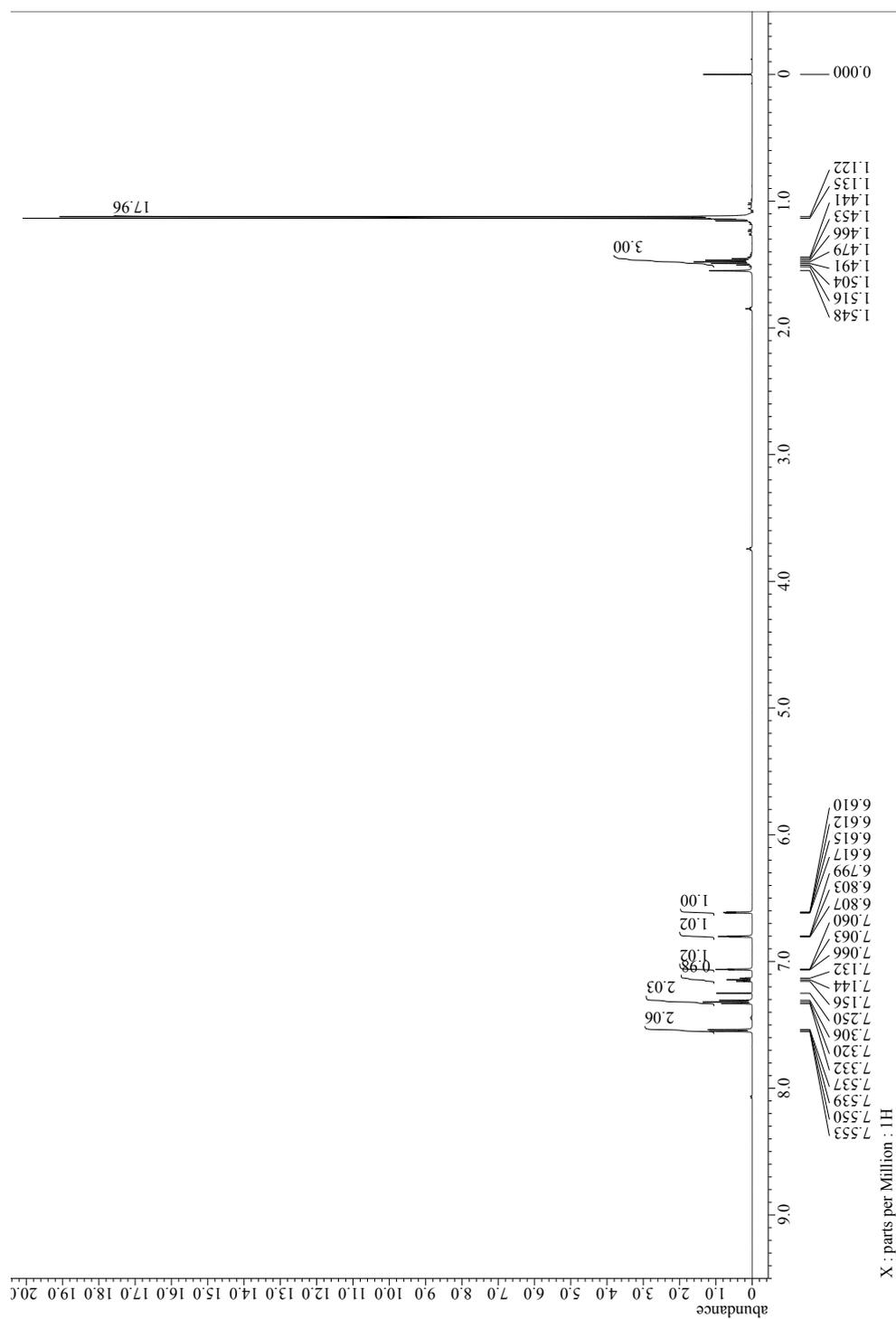
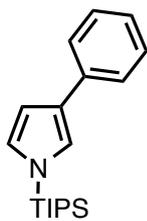


$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Da

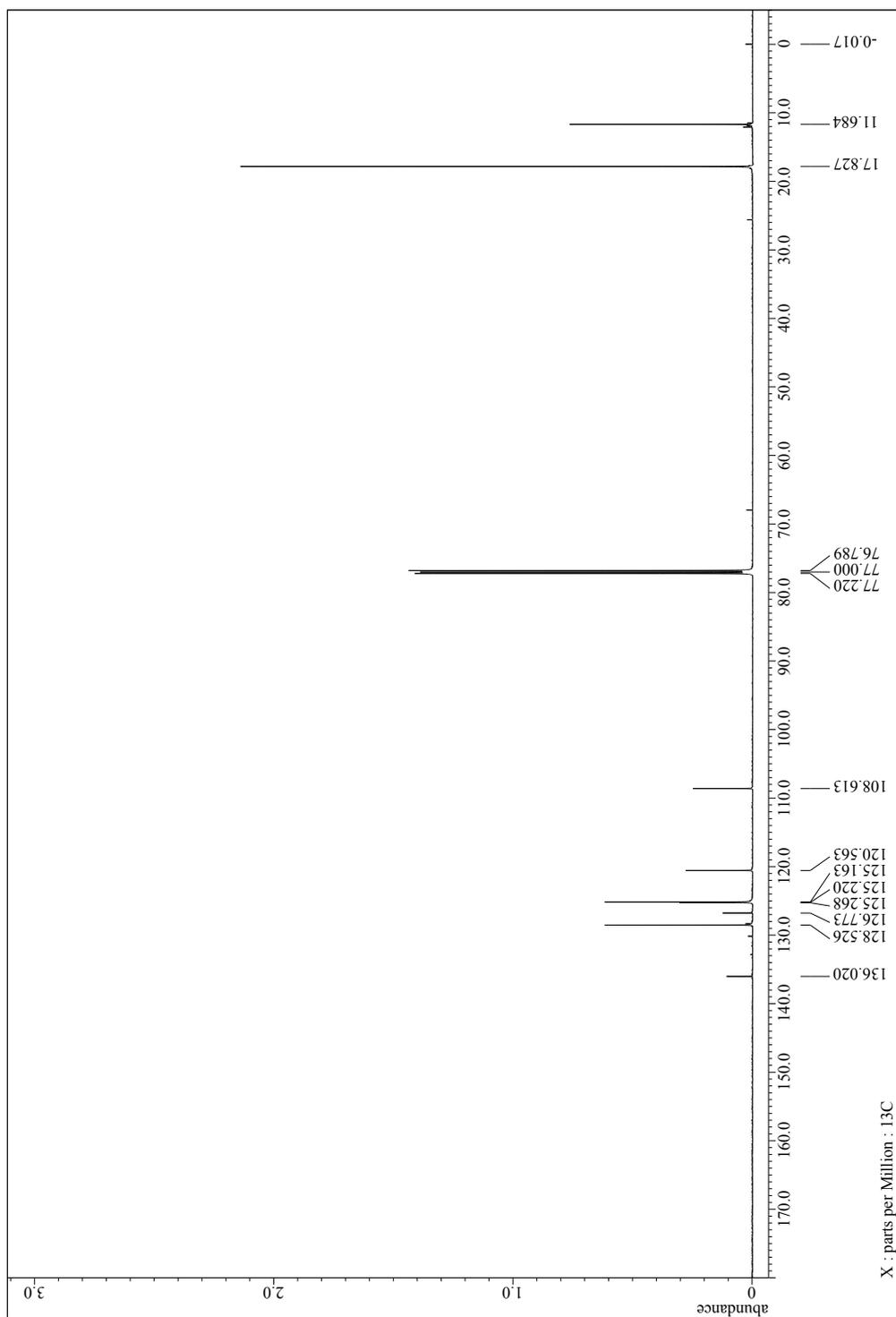
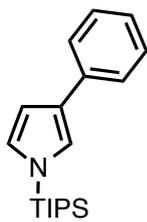
^{13}C -NMR (150 MHz, CDCl_3) of 3Da

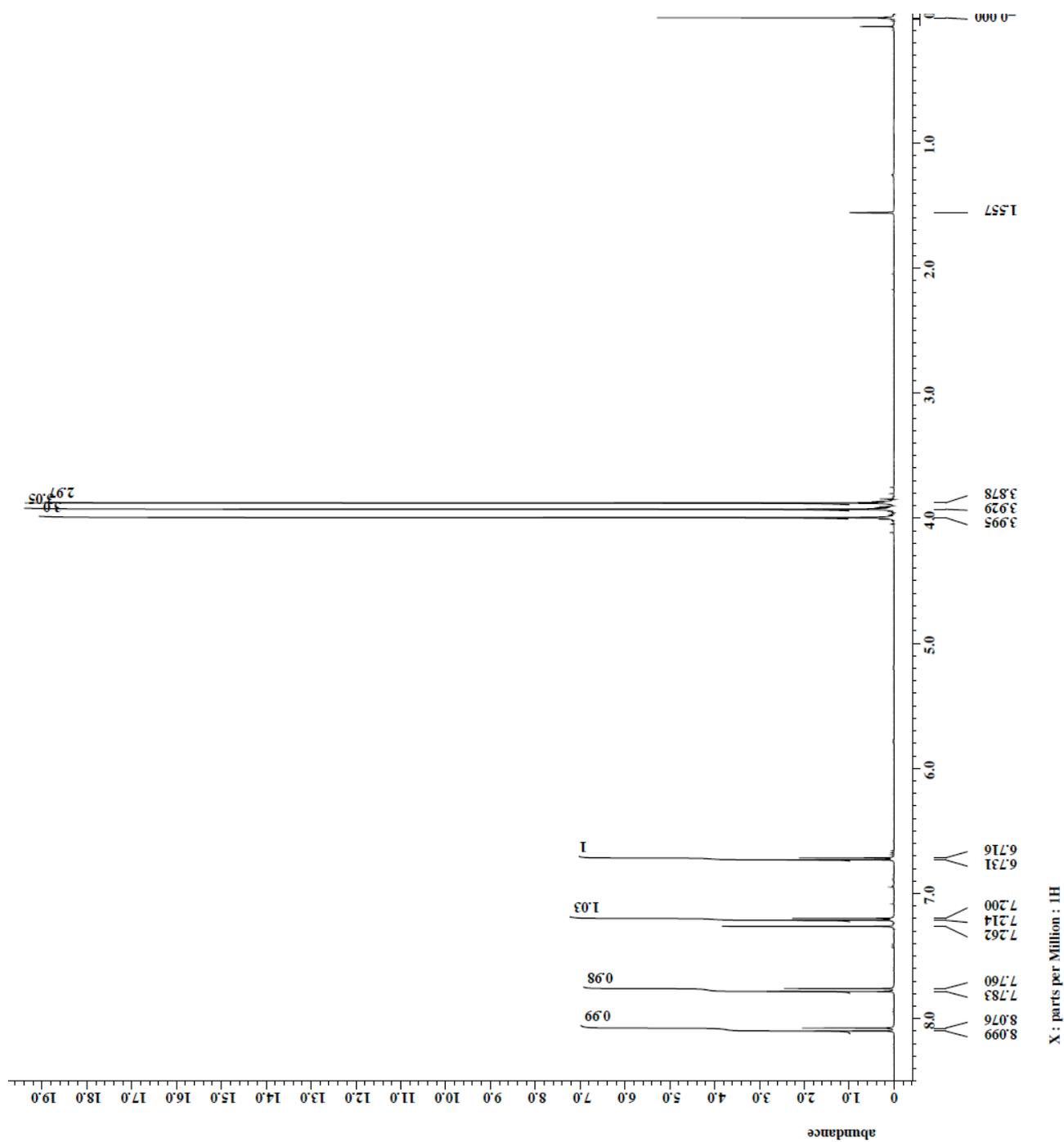
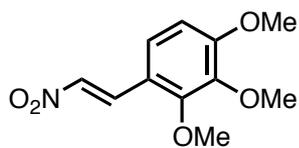


X : parts per Million : 13C

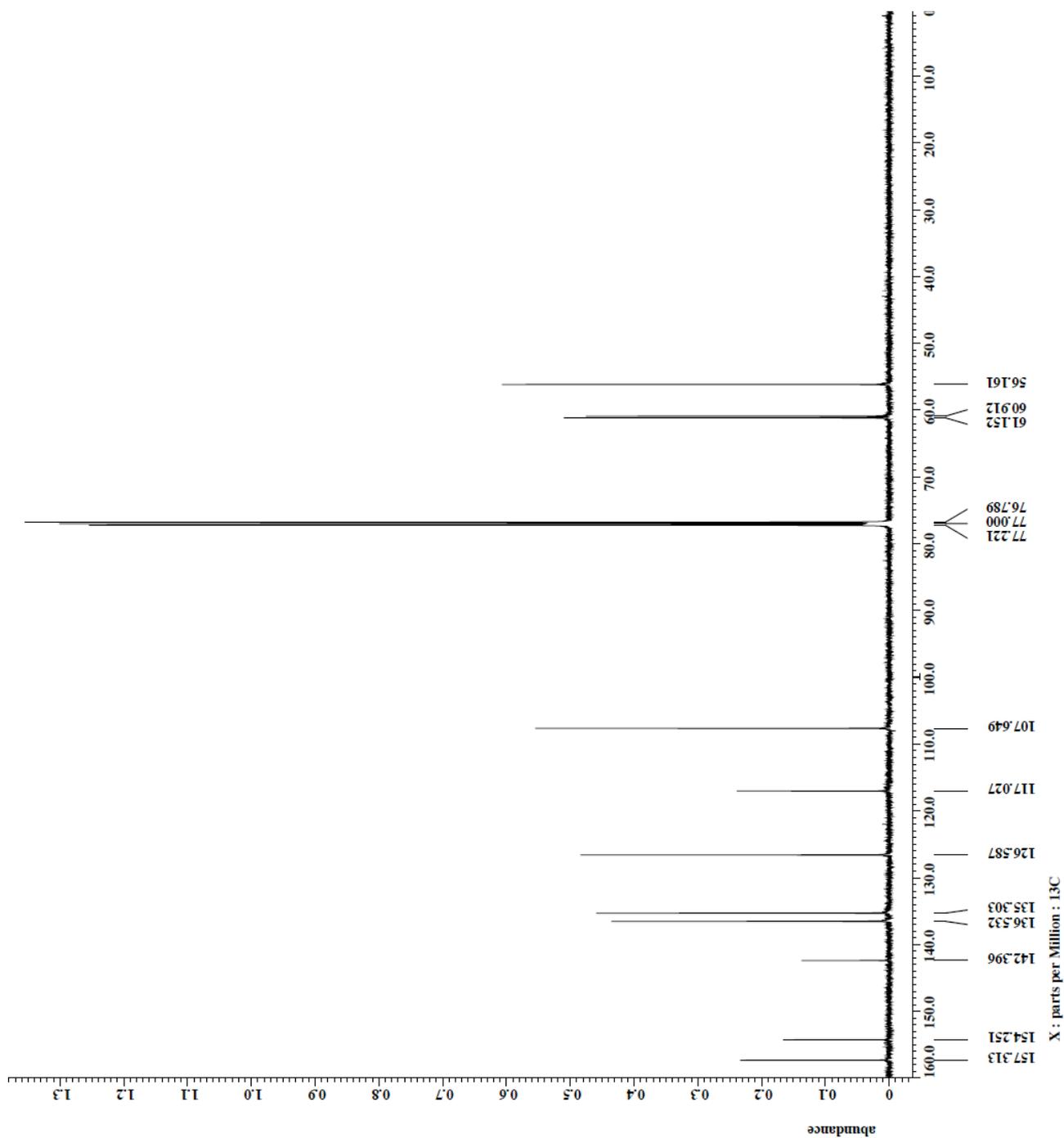
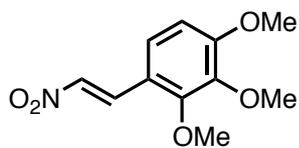
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 3Ea

^{13}C -NMR (150 MHz, CDCl_3) of 3Ea

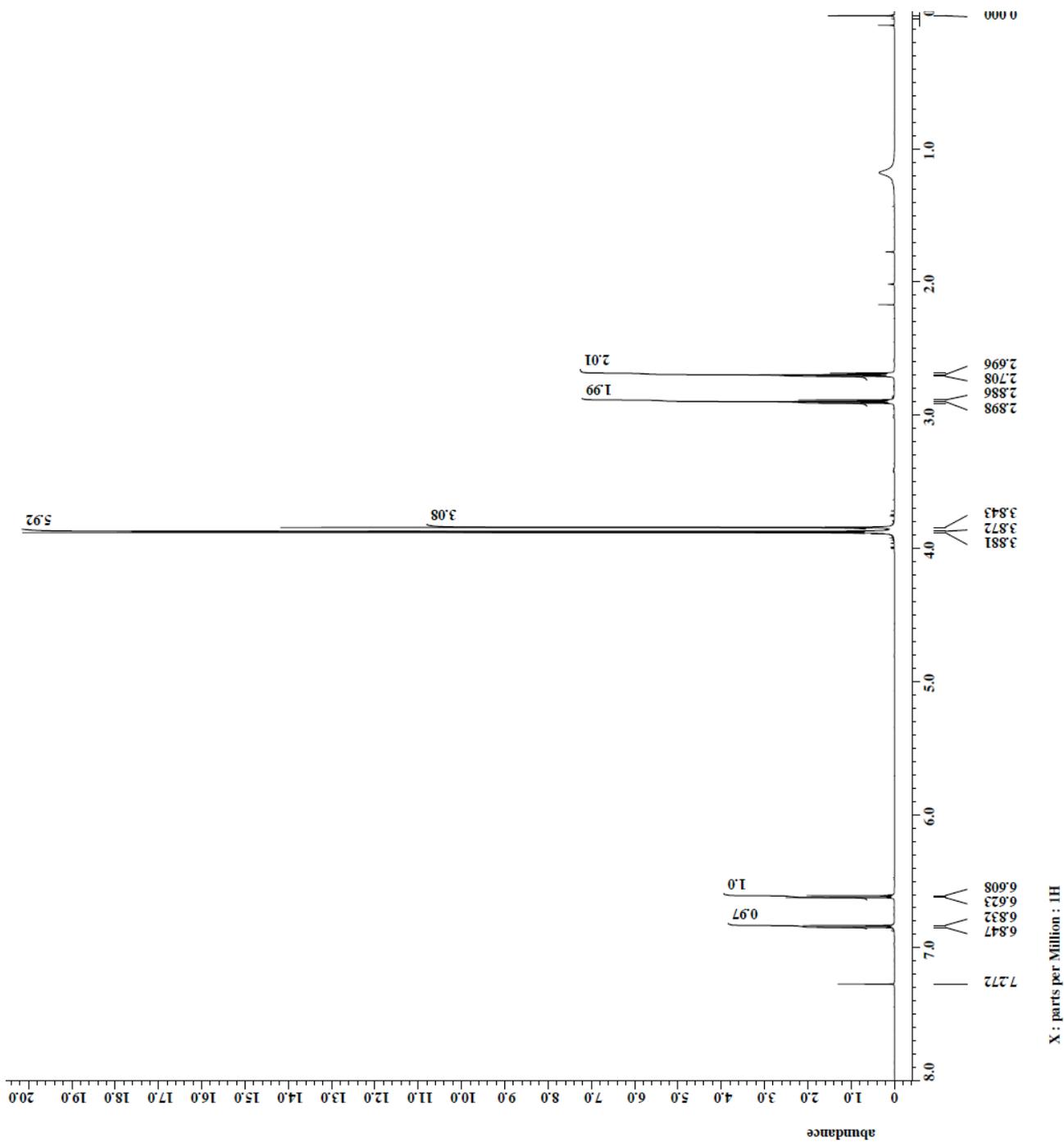
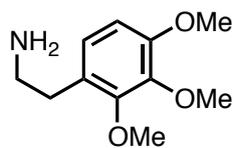


$^1\text{H-NMR}$ (600 MHz, CDCl_3) of S1

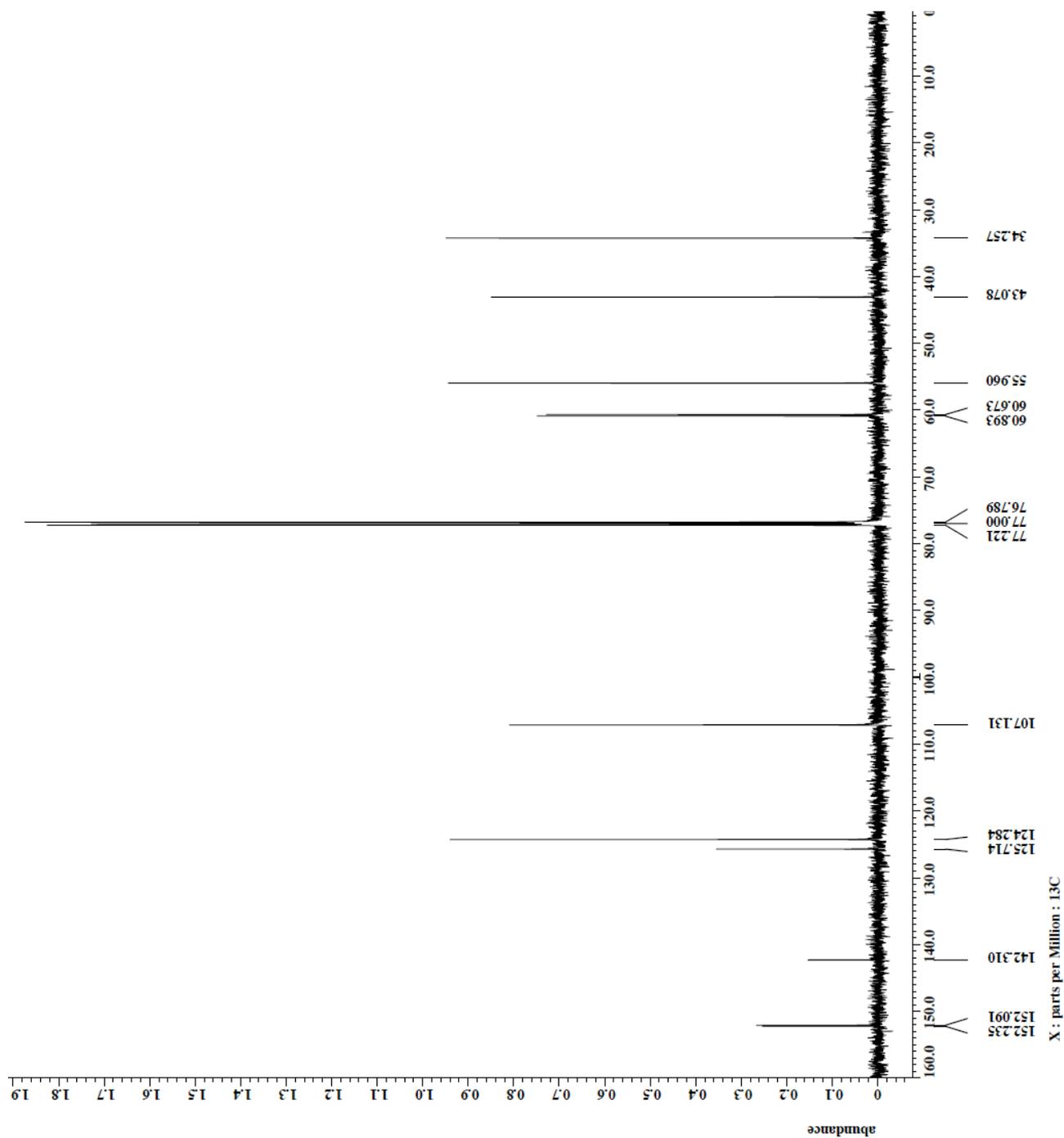
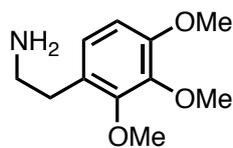
^{13}C -NMR (150 MHz, CDCl_3) of S1

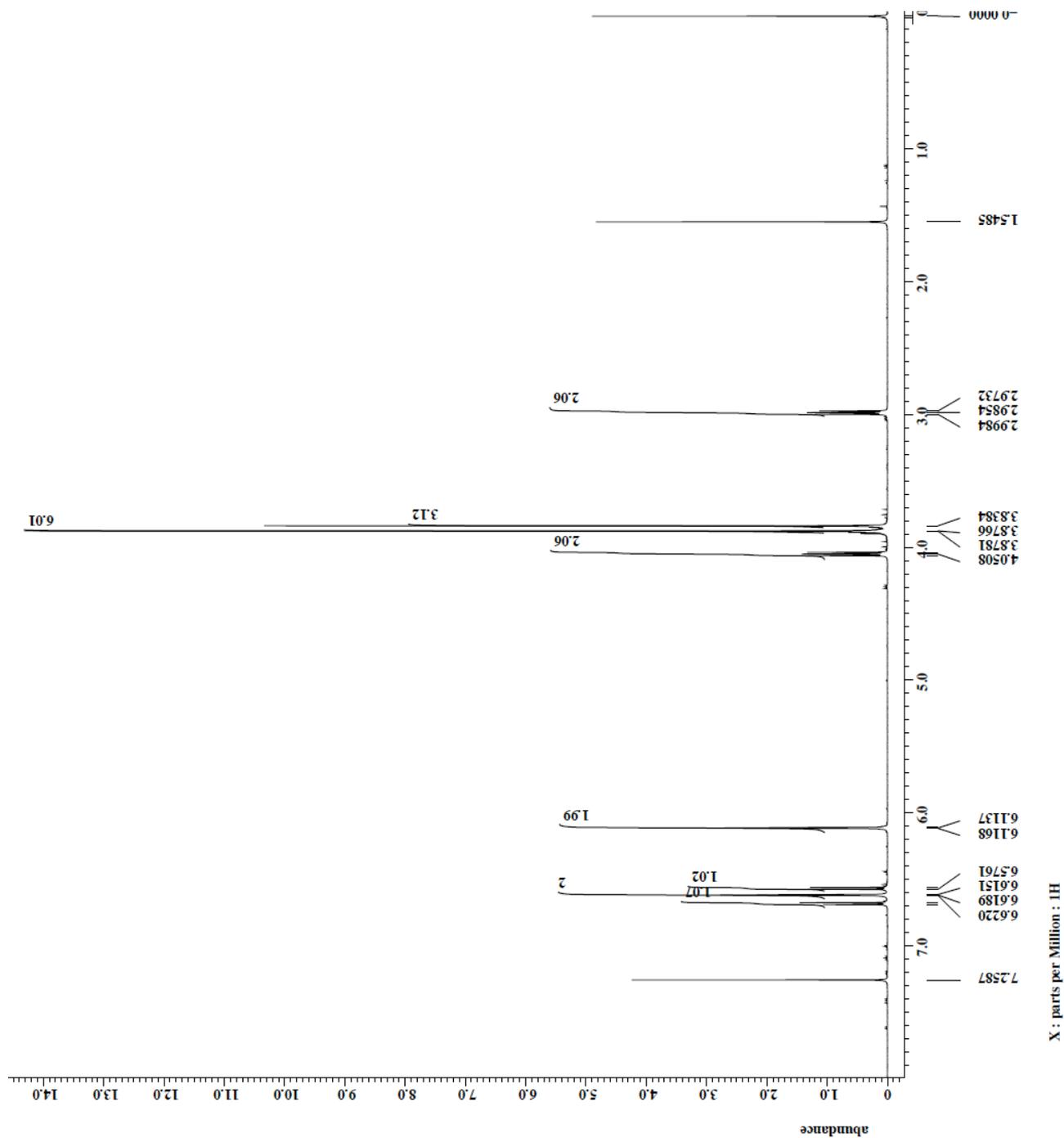
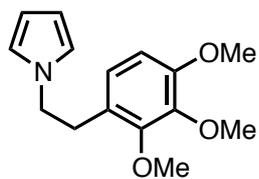


¹H-NMR (600 MHz, CDCl₃) of S2

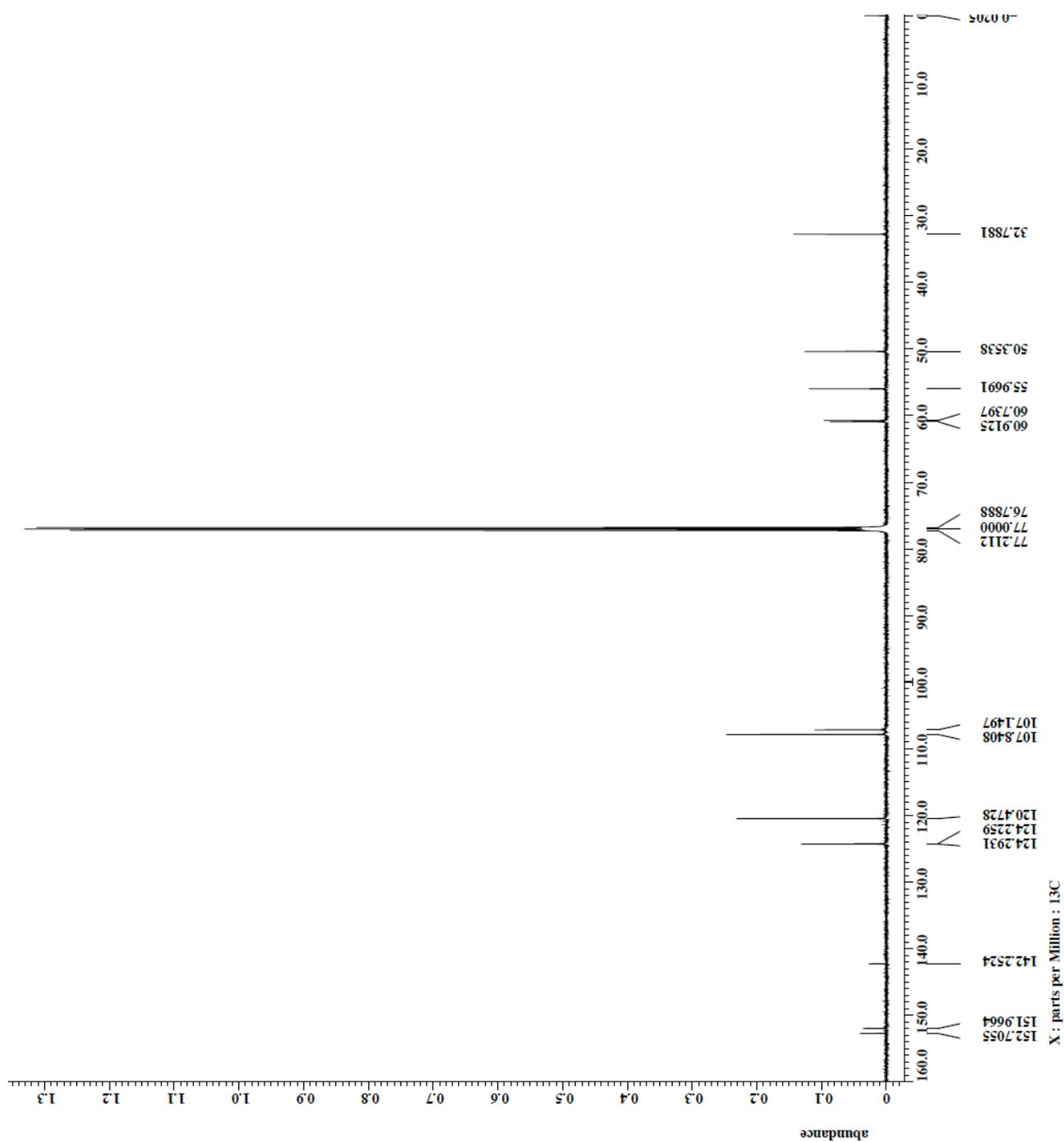
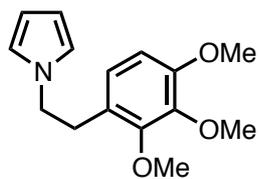


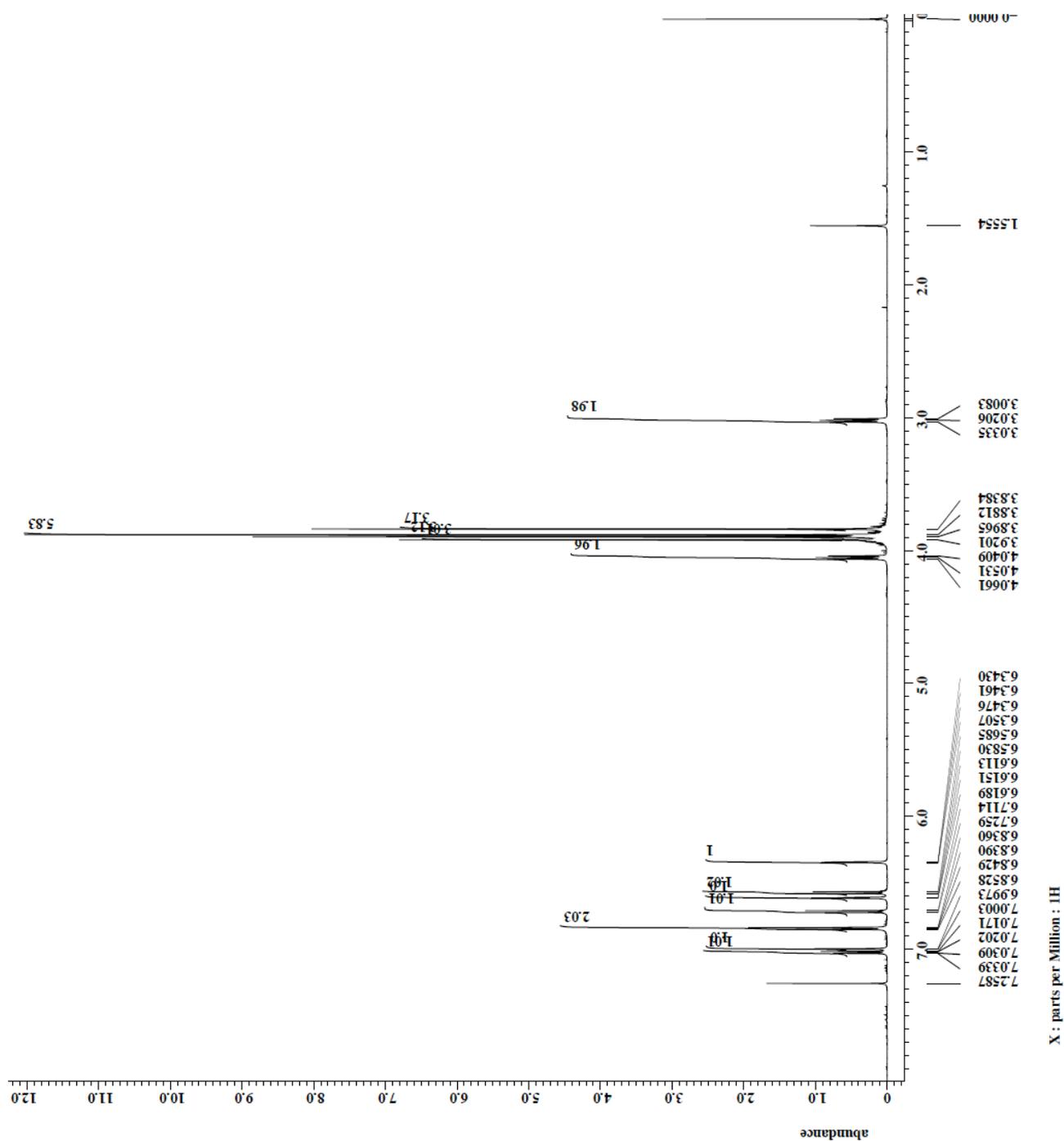
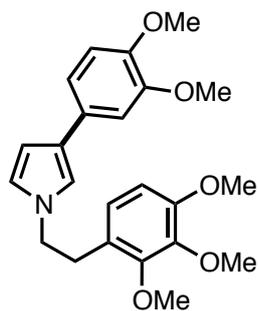
^{13}C -NMR (150 MHz, CDCl_3) of S2



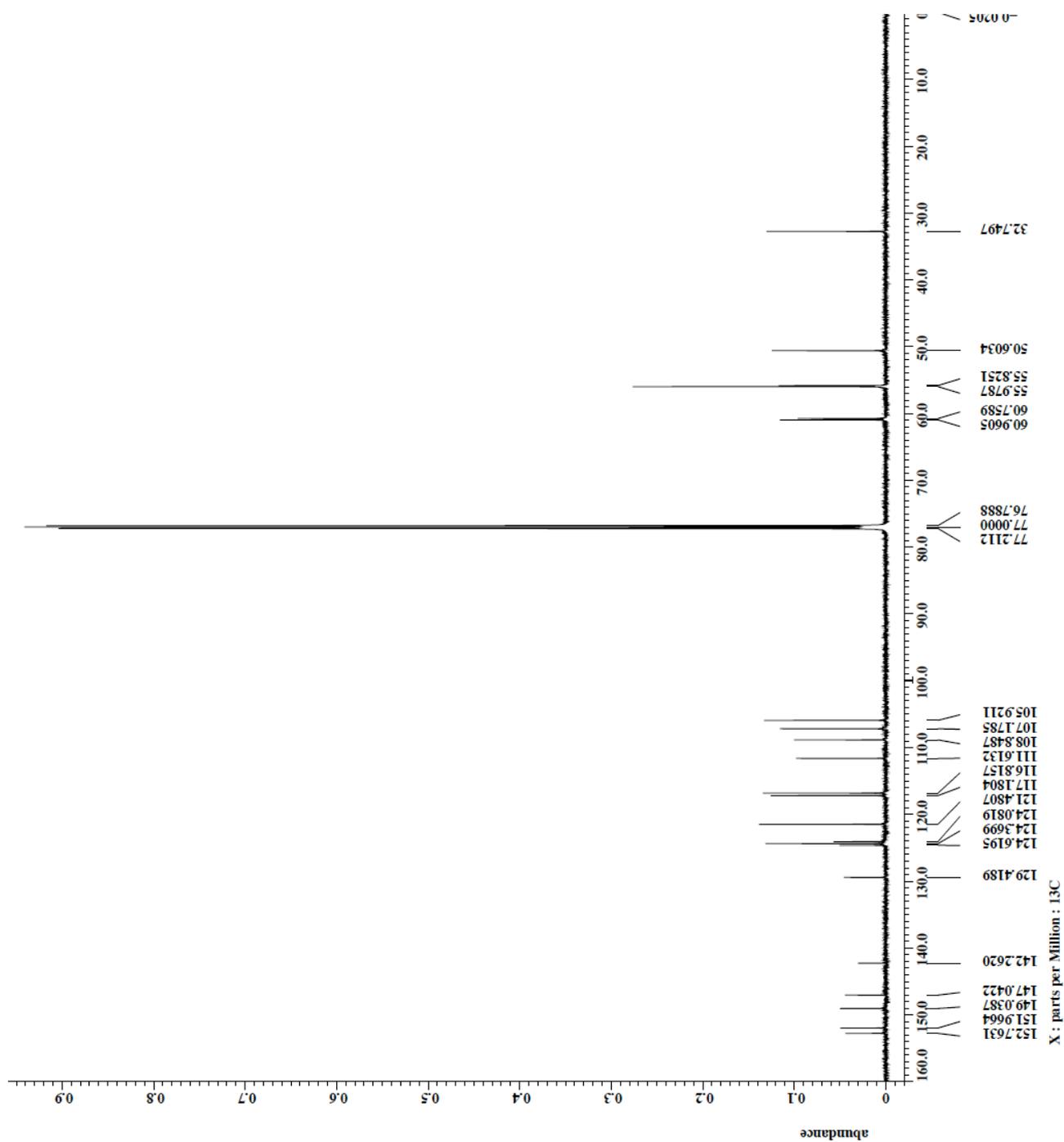
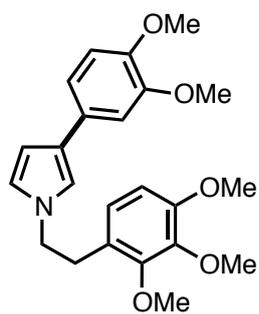
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of **5**

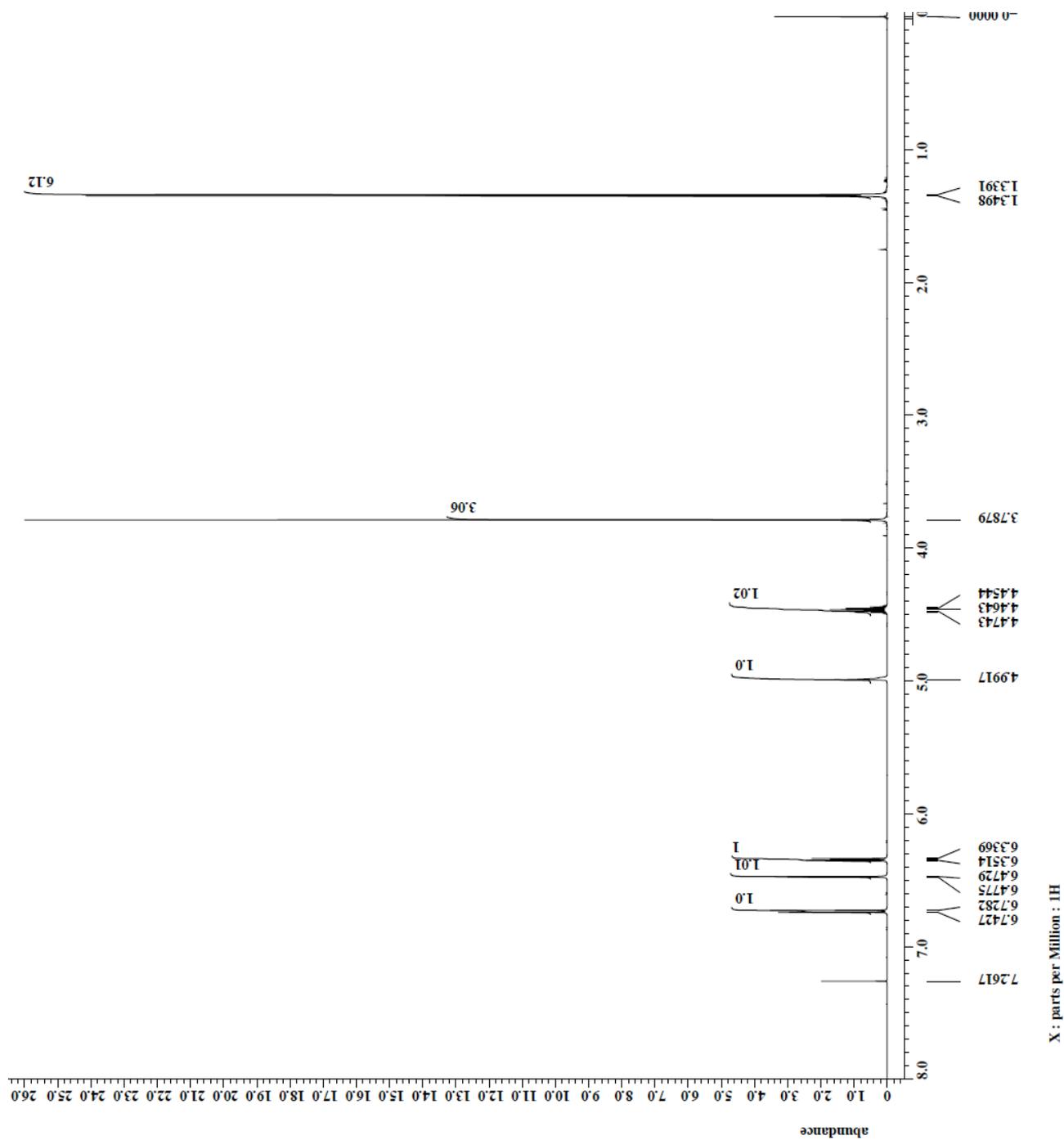
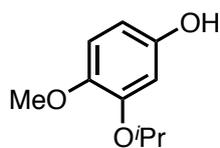
^{13}C -NMR (150 MHz, CDCl_3) of 5



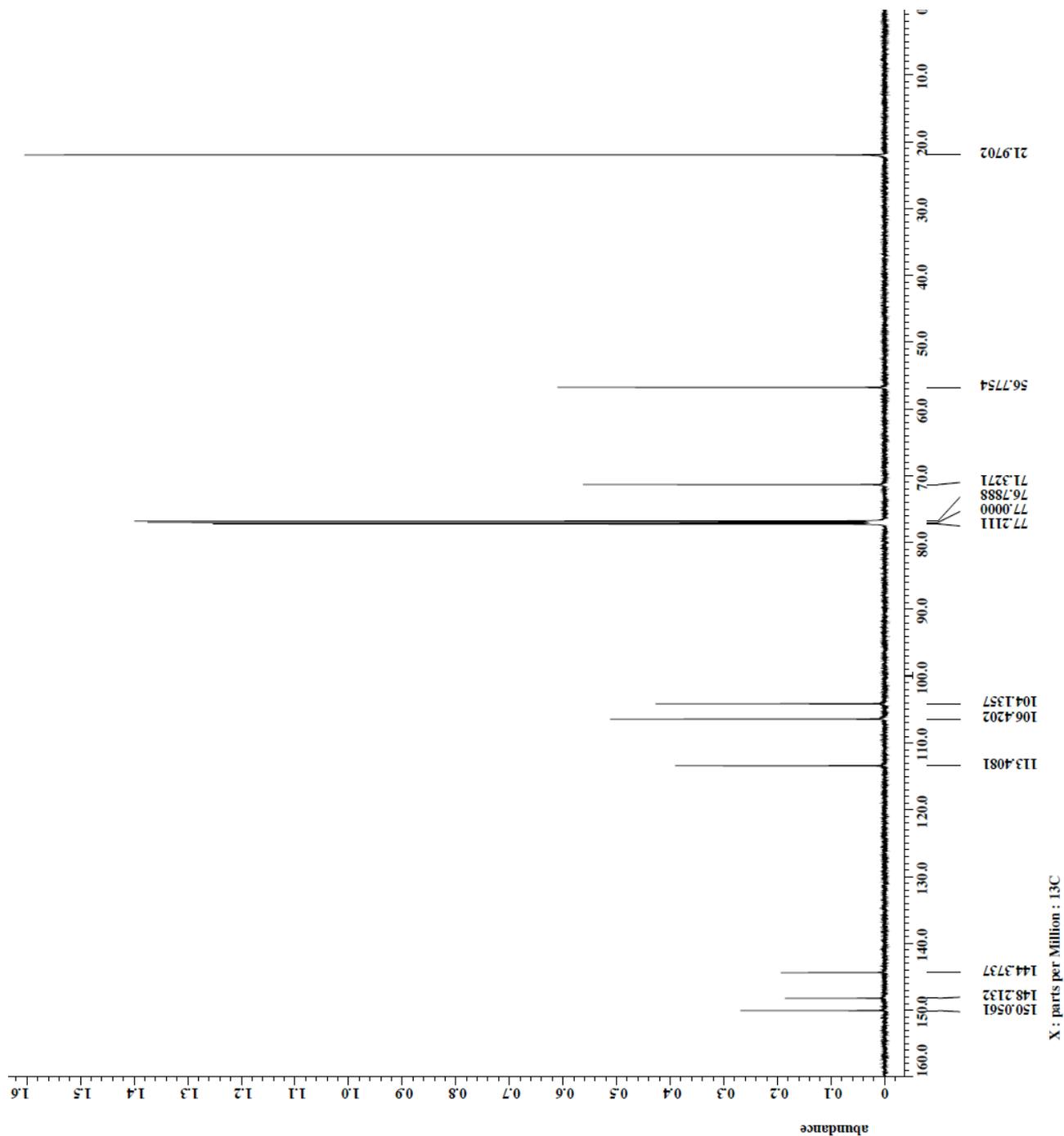
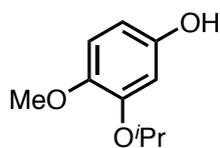
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 7a

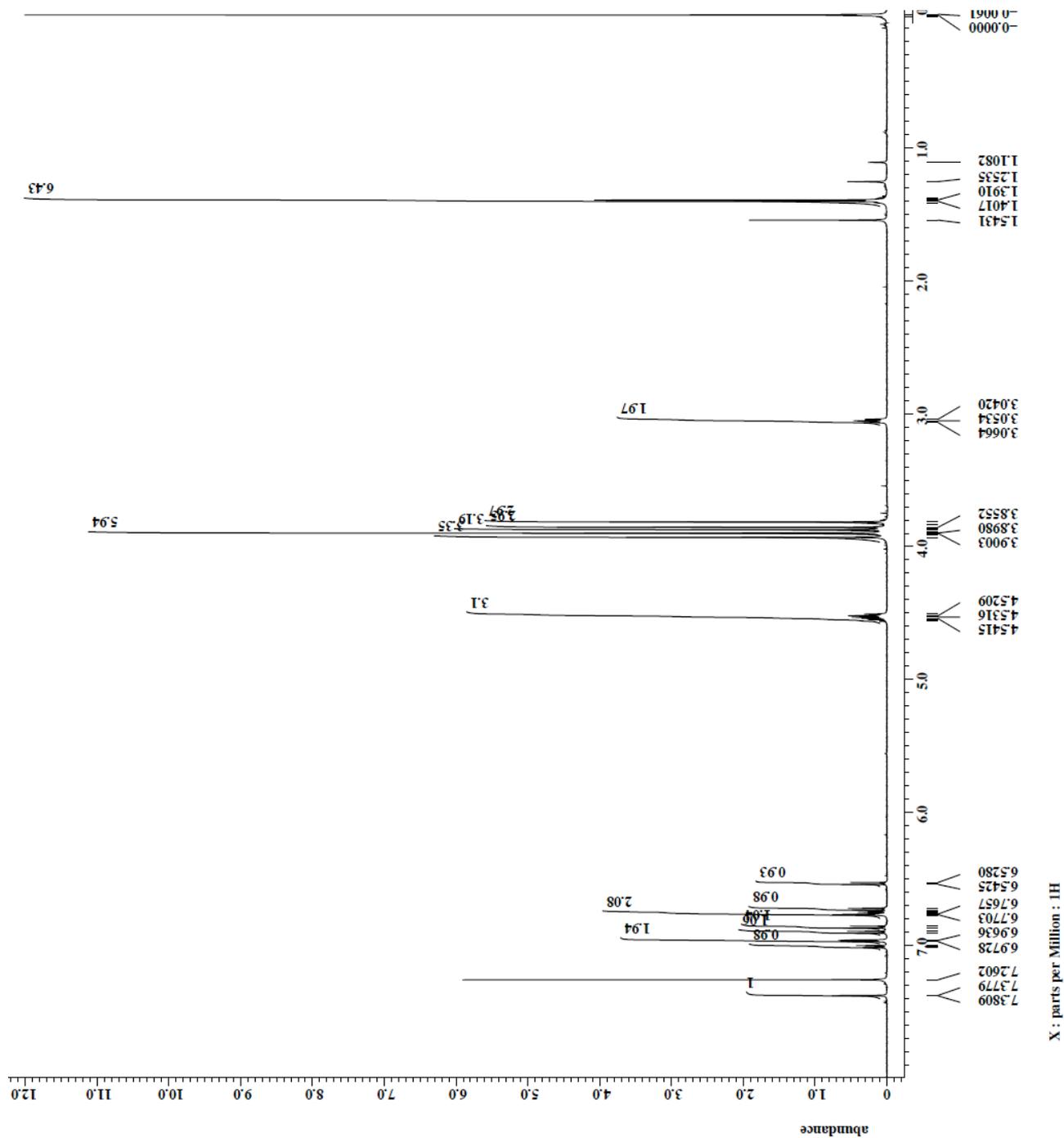
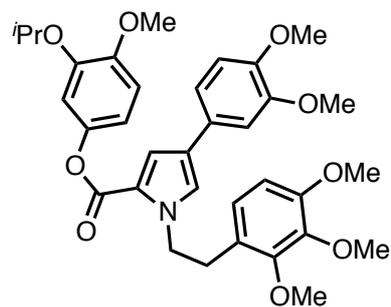
^{13}C -NMR (150 MHz, CDCl_3) of 7a



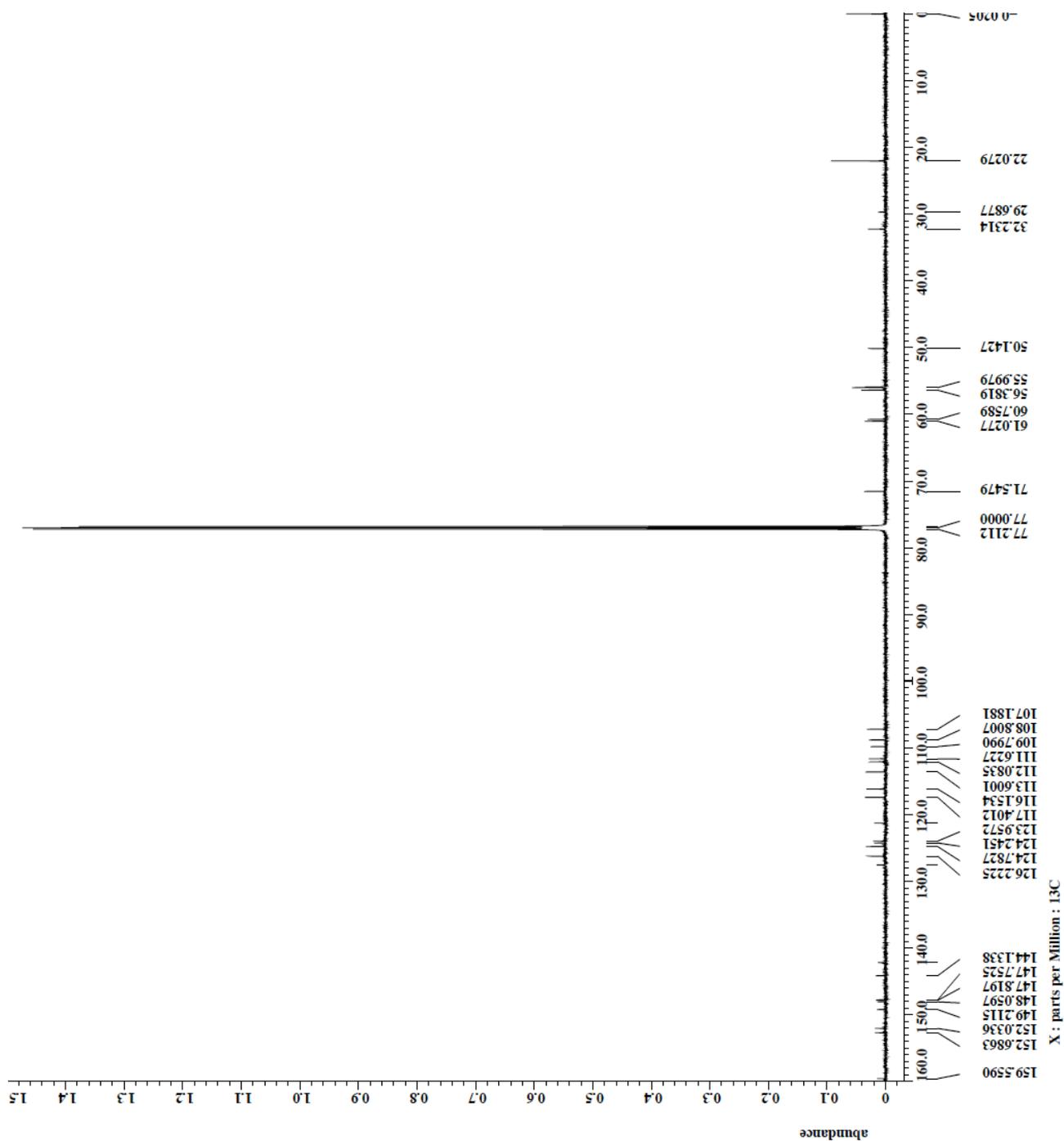
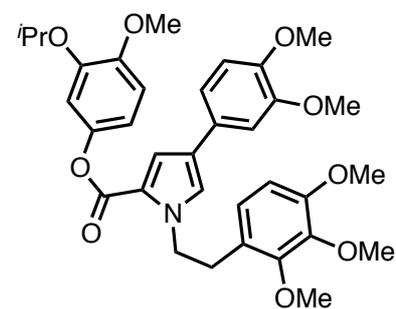
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of **8**

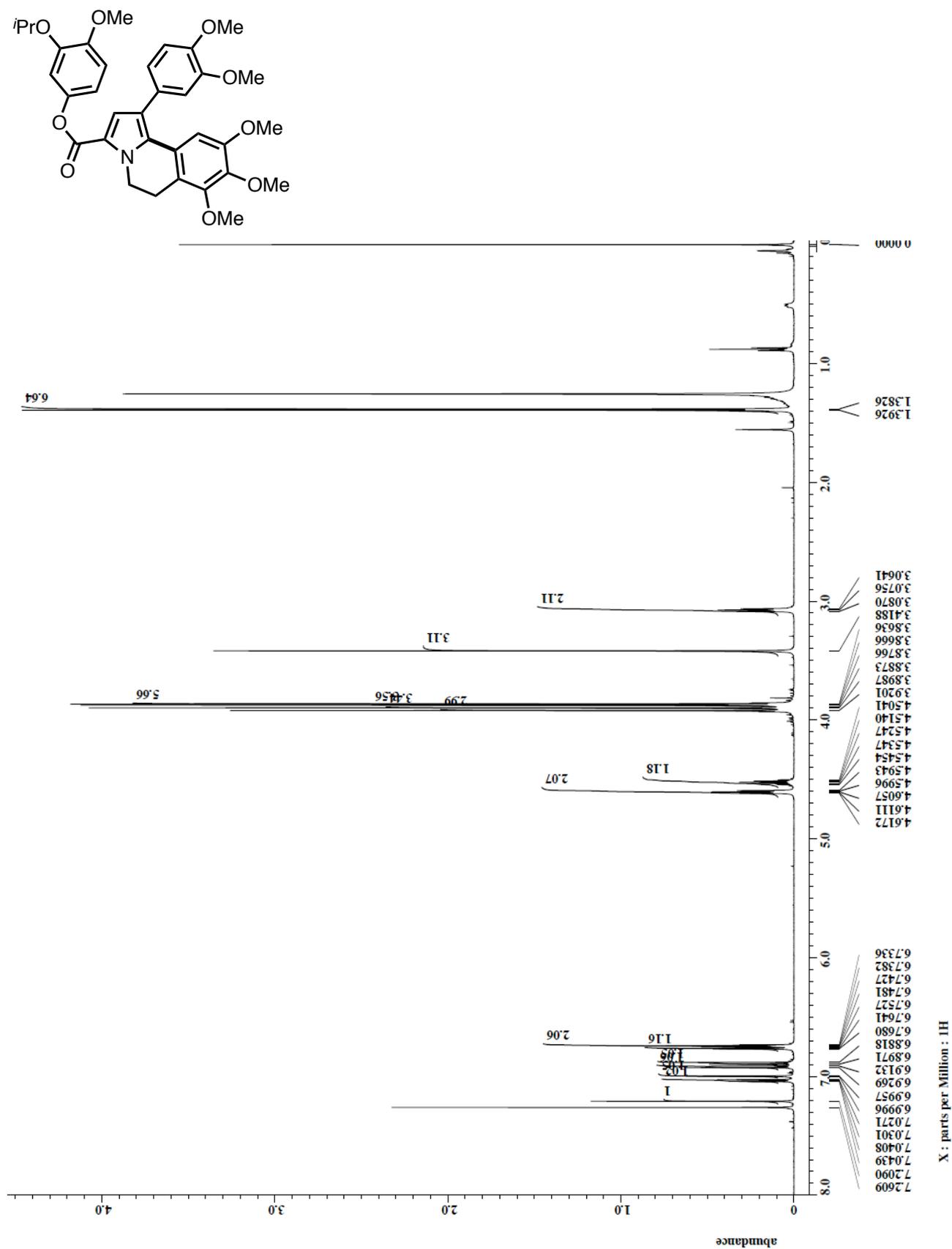
^{13}C -NMR (150 MHz, CDCl_3) of 8



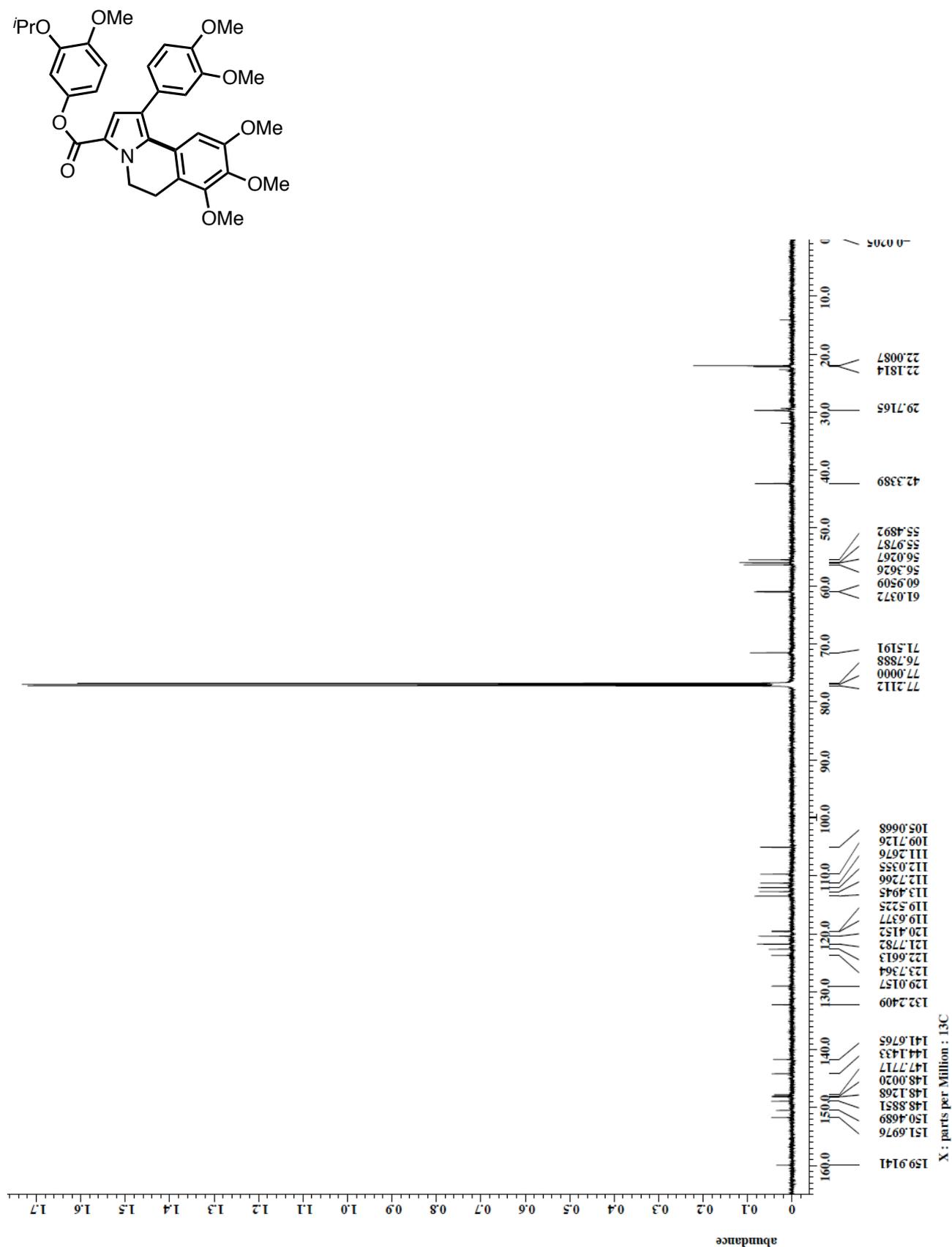
¹H-NMR (600 MHz, CDCl₃) of 9a

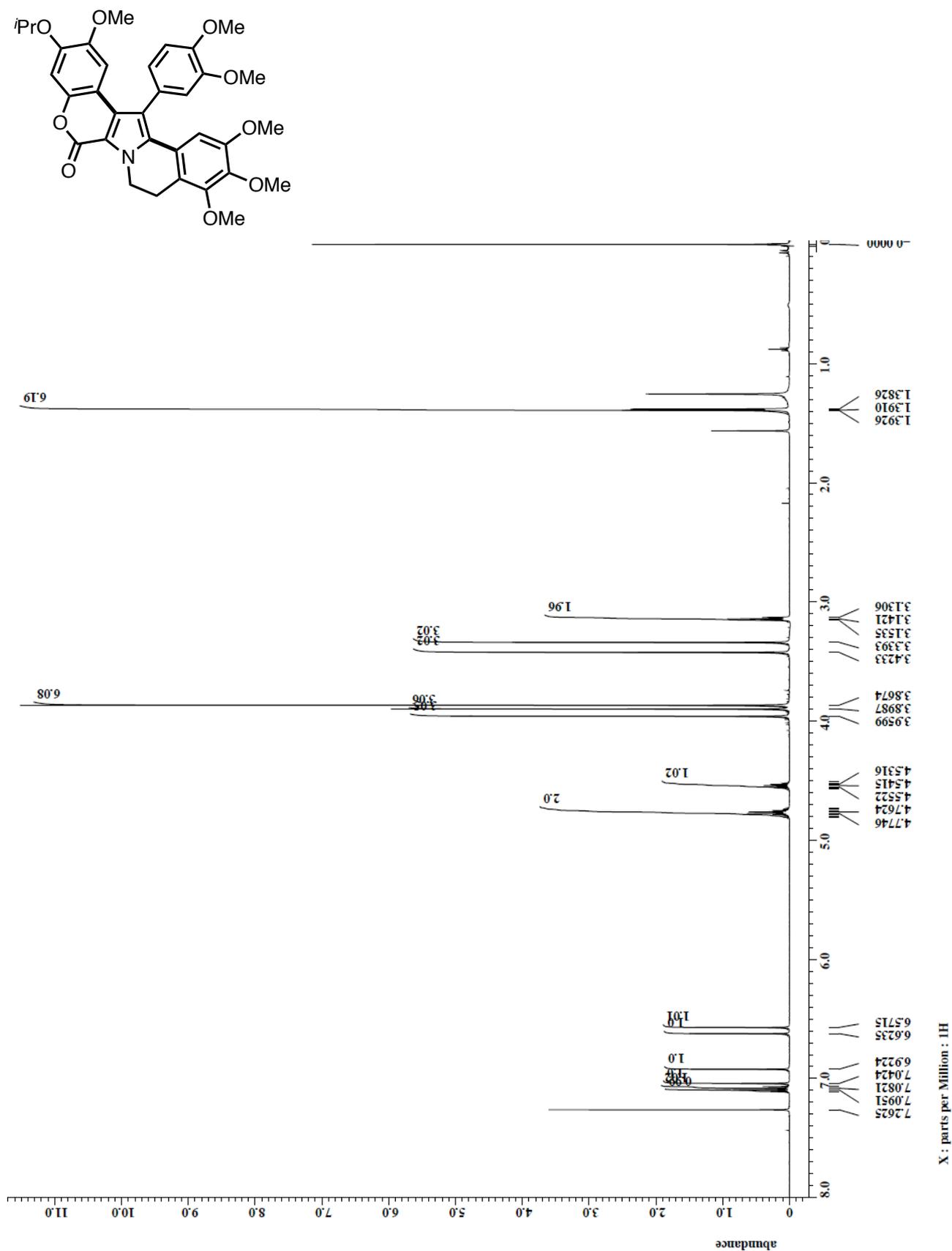
^{13}C -NMR (150 MHz, CDCl_3) of 9a



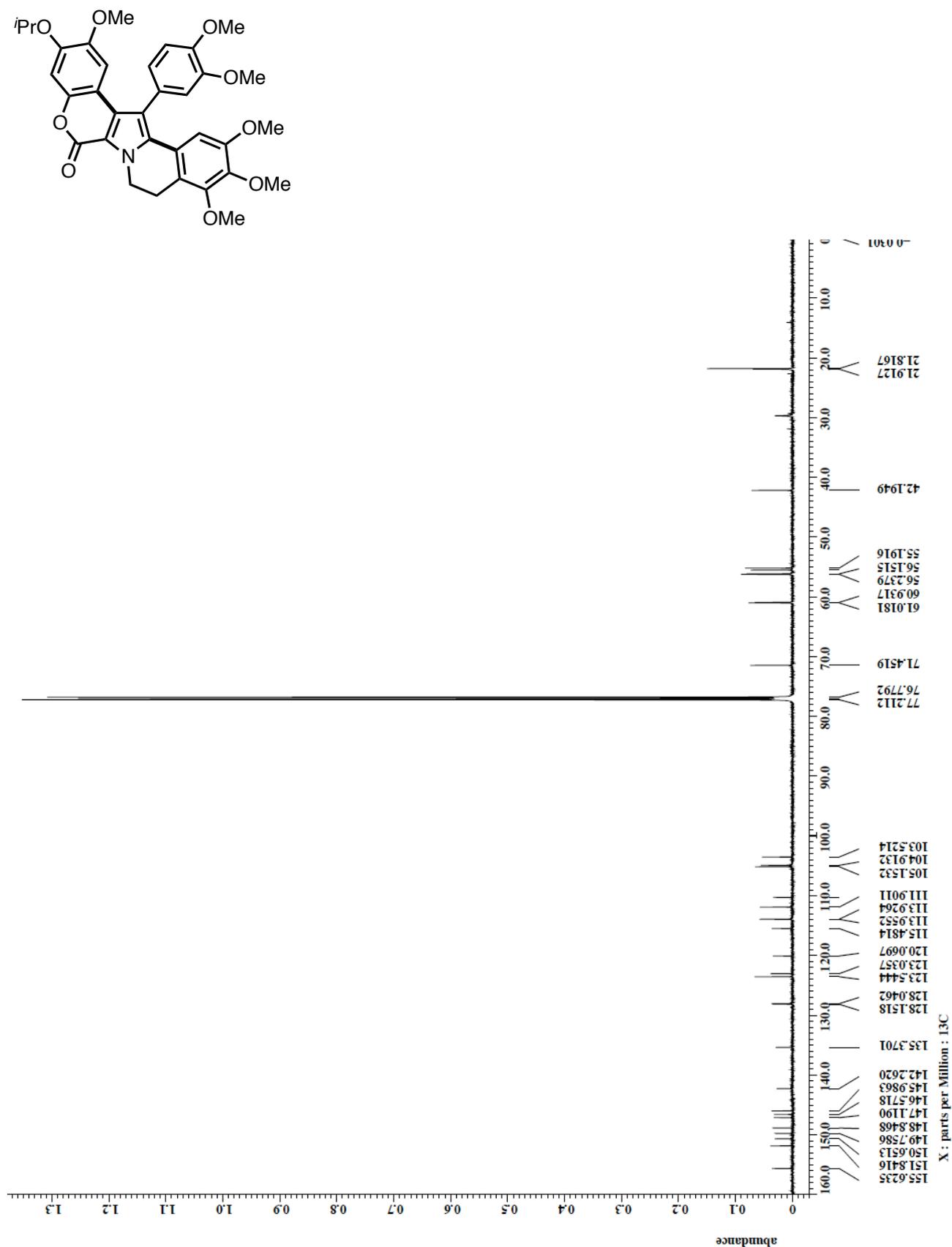
$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 10a'

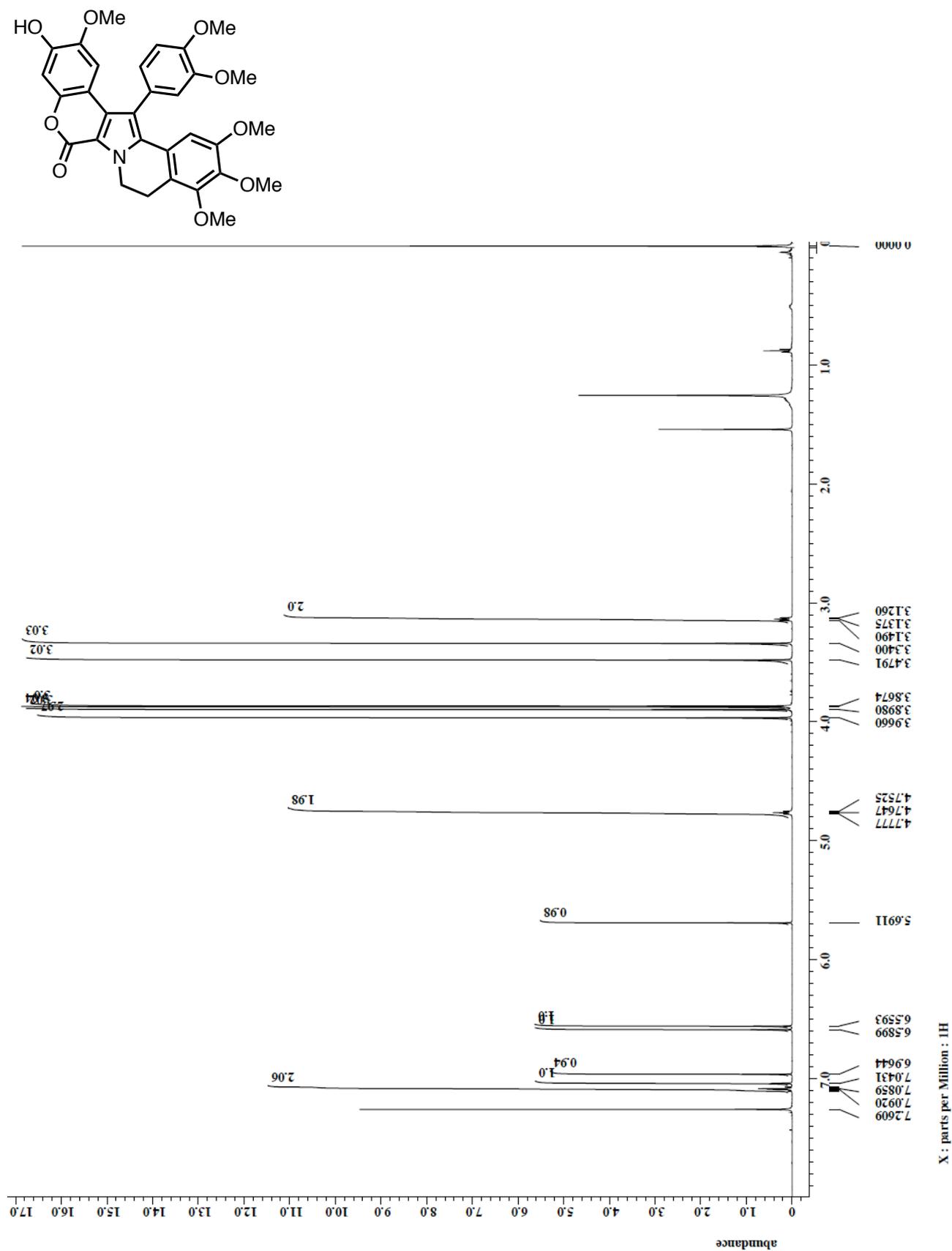
^{13}C -NMR (150 MHz, CDCl_3) of 10a'



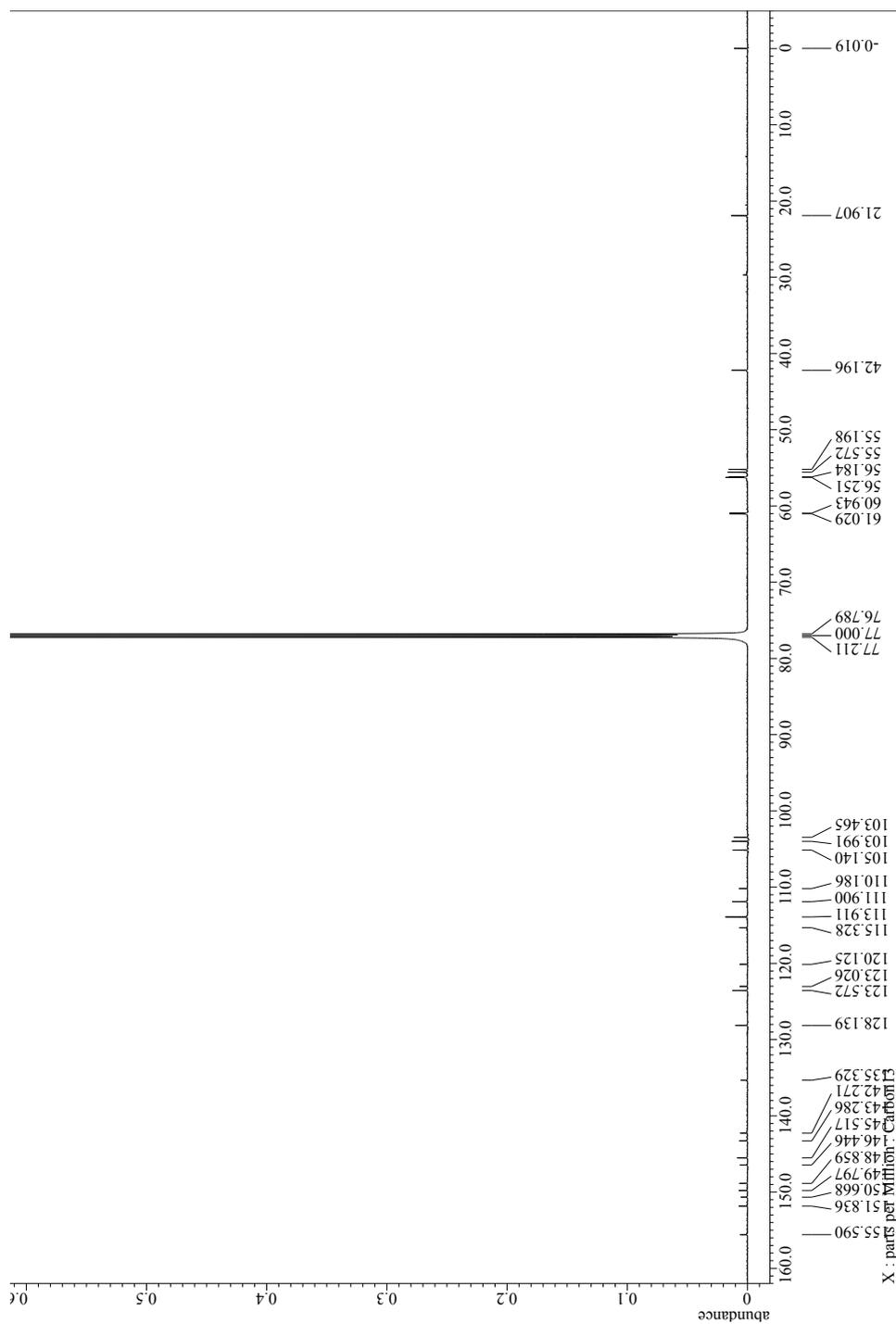
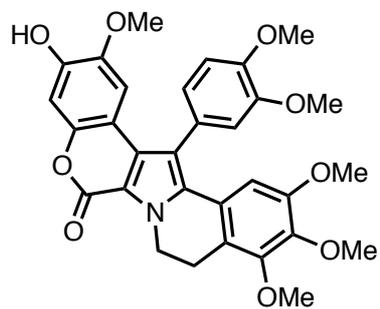
¹H-NMR (600 MHz, CDCl₃) of 10a

^{13}C -NMR (150 MHz, CDCl_3) of 10a

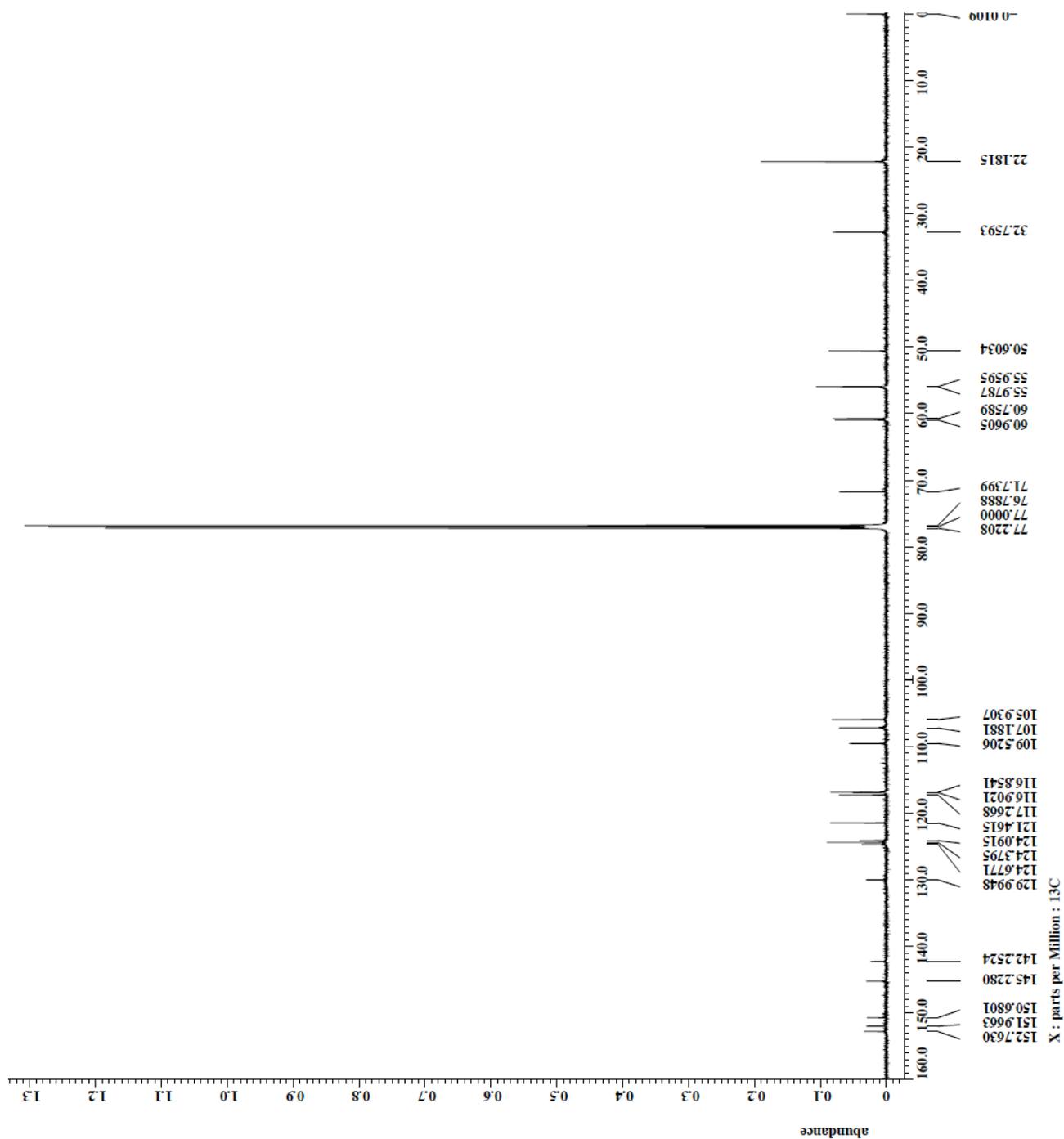
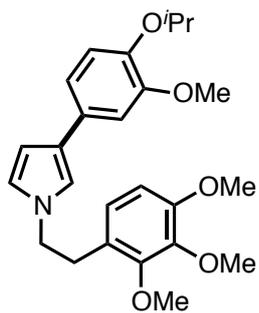


¹H-NMR (600 MHz, CDCl₃) of lamellarin I

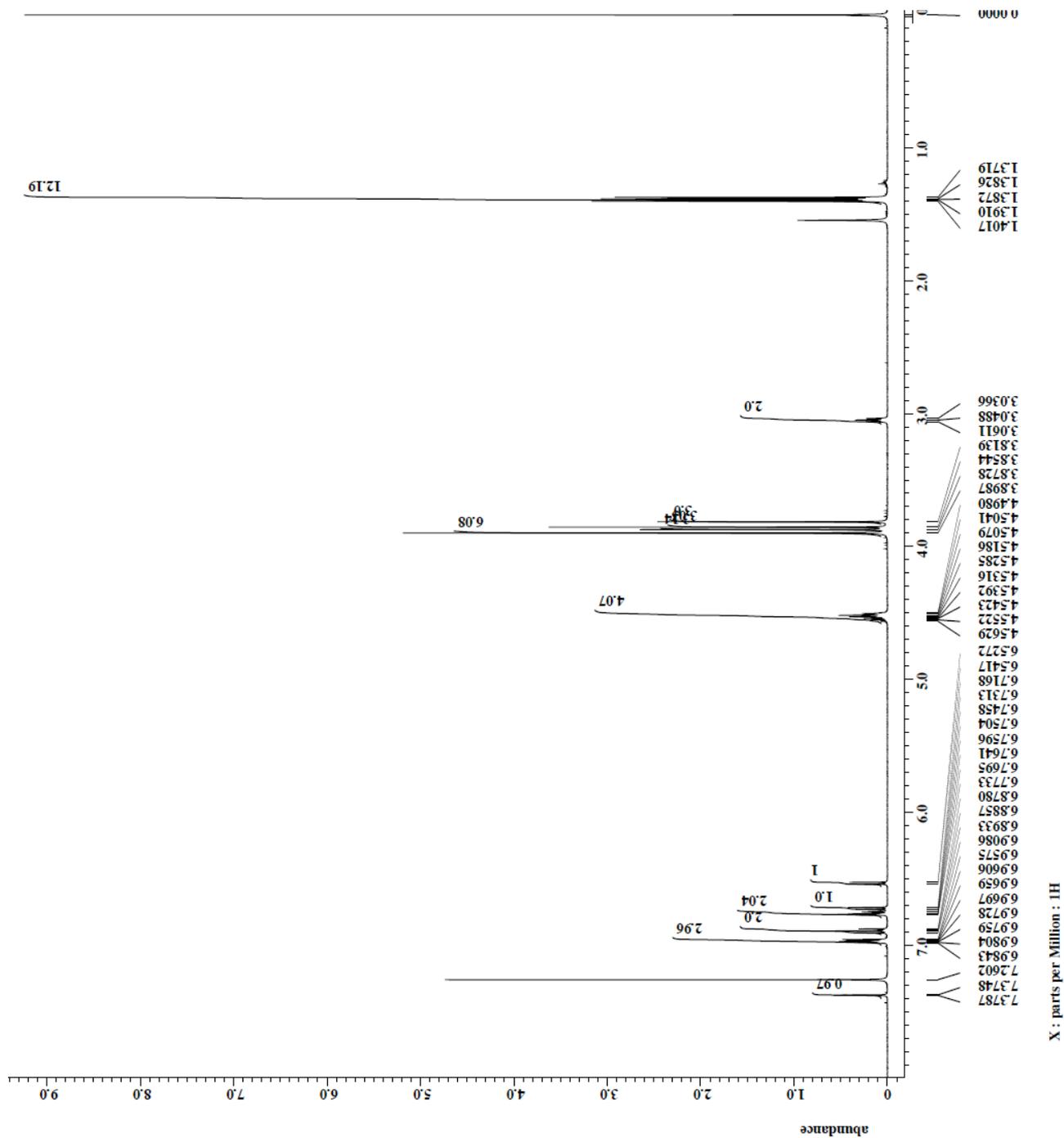
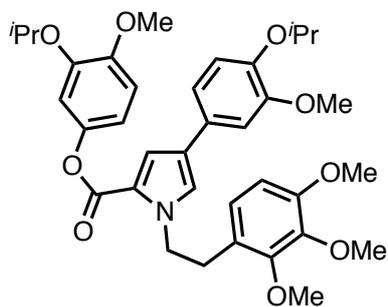
^{13}C -NMR (150 MHz, CDCl_3) of lamellarin I



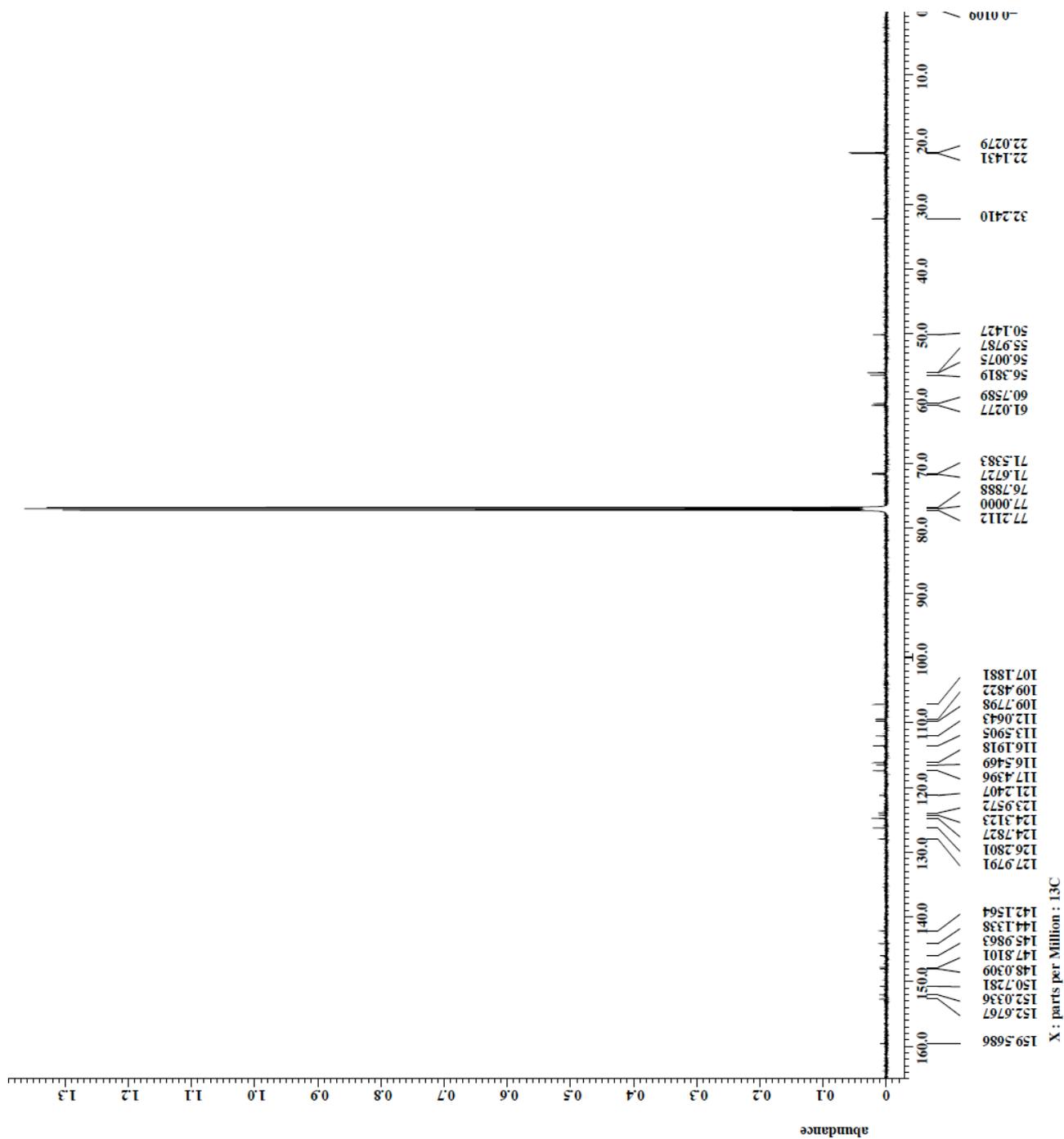
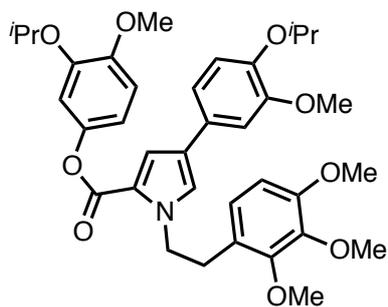
^{13}C -NMR (150 MHz, CDCl_3) of 7b

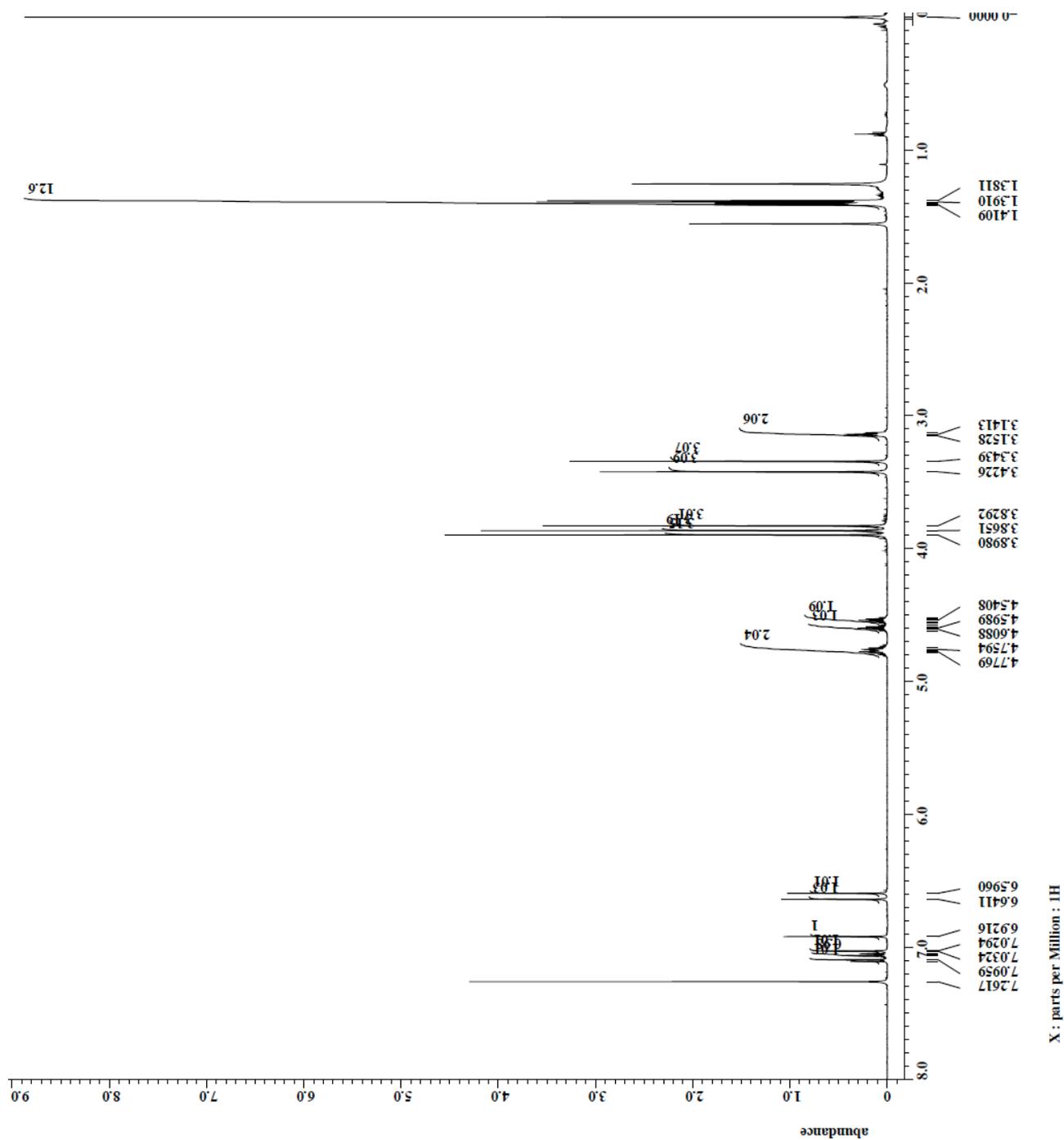
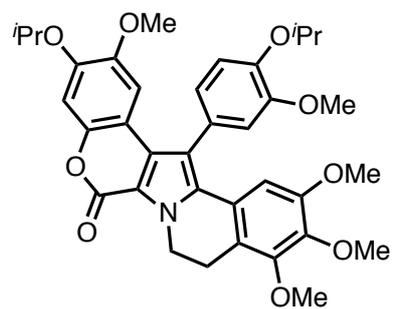


¹H-NMR (600 MHz, CDCl₃) of 9b

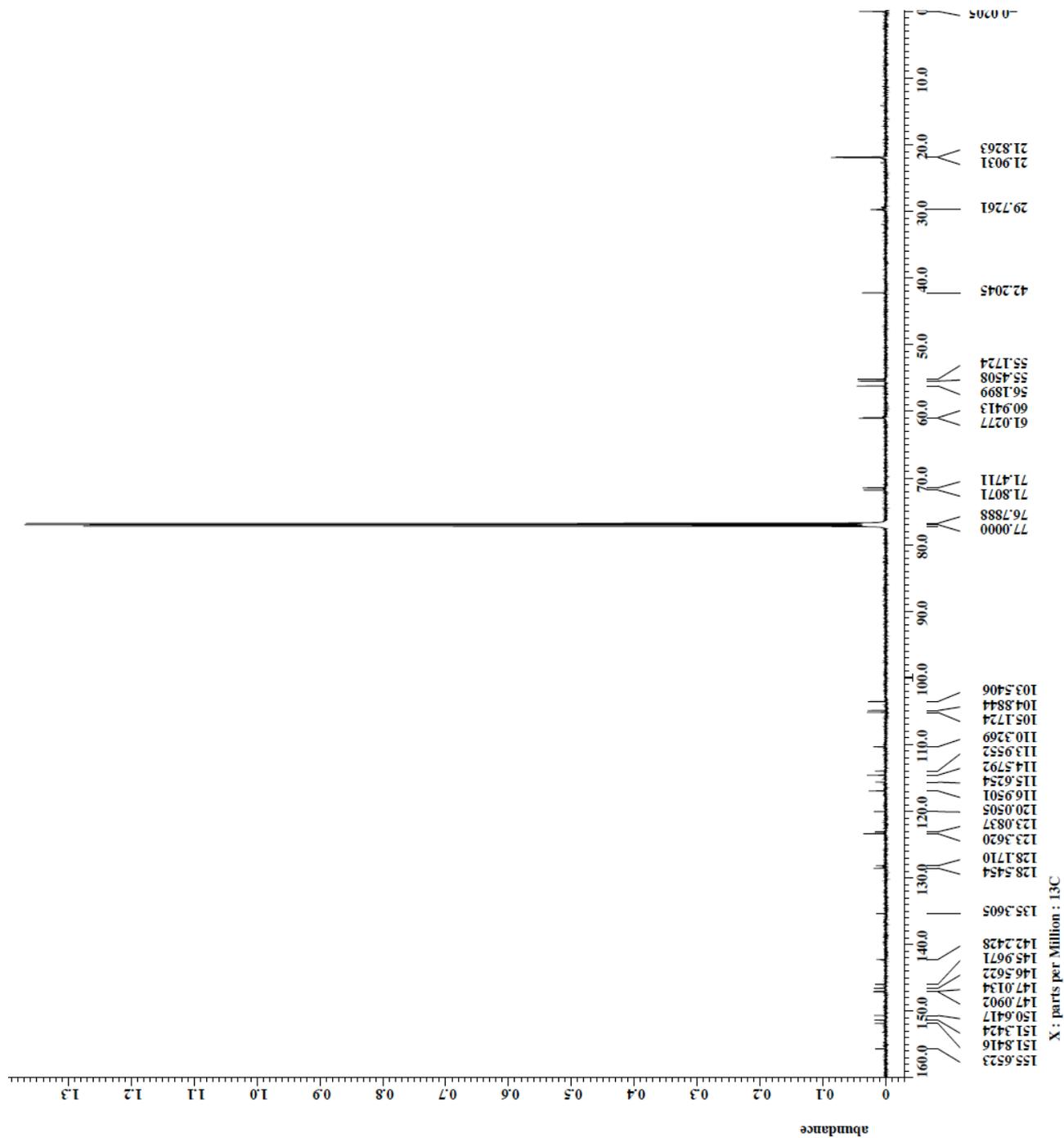
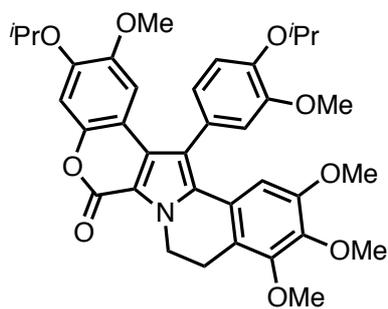


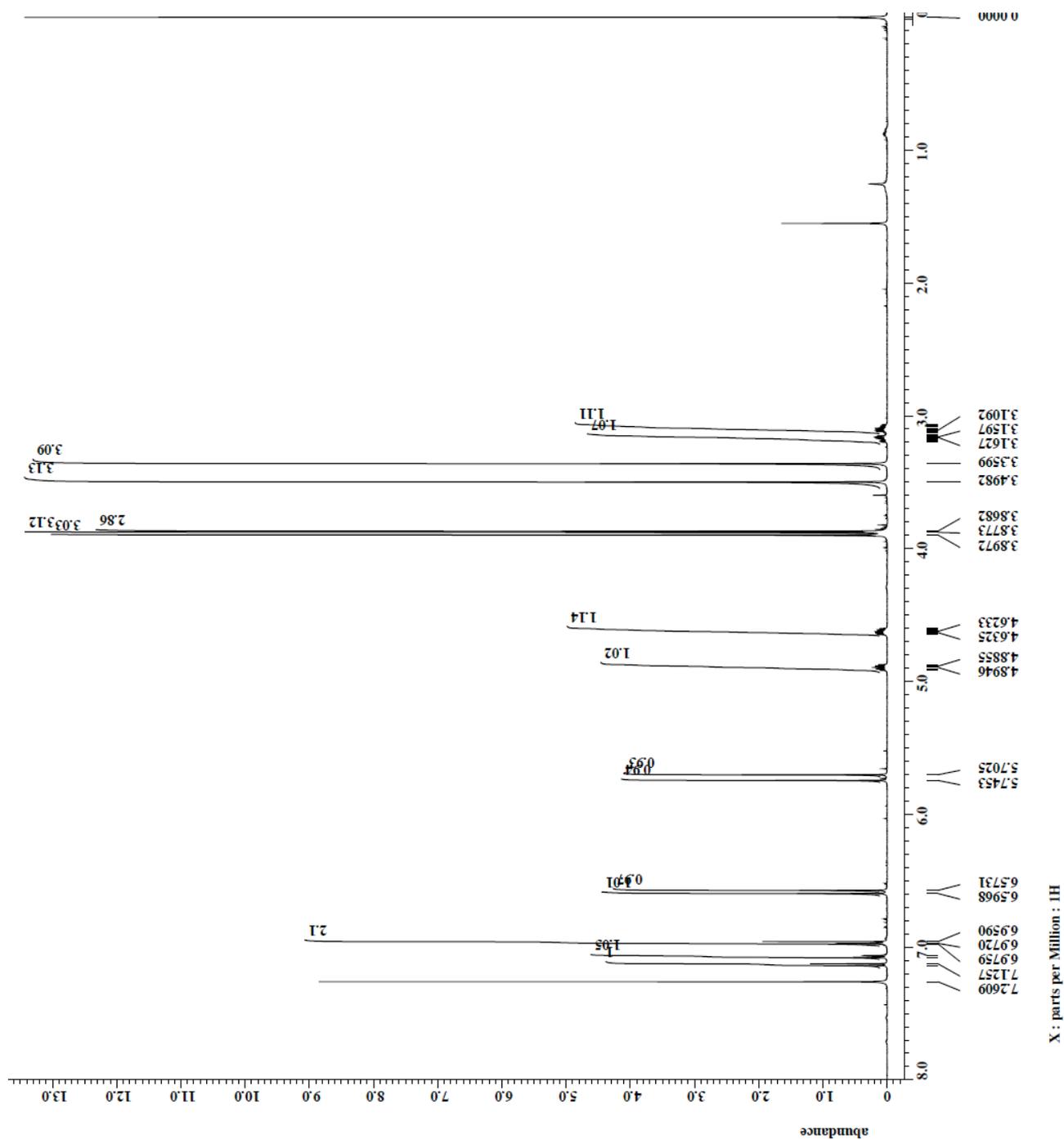
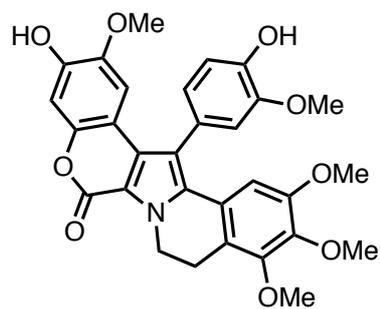
^{13}C -NMR (150 MHz, CDCl_3) of 9b



$^1\text{H-NMR}$ (600 MHz, CDCl_3) of 10b

^{13}C -NMR (150 MHz, CDCl_3) of 10b



¹H-NMR (600 MHz, CDCl₃) of lamellarin C

^{13}C -NMR (150 MHz, CDCl_3) of lamellarin C

