- Supporting Information -

Arylative Desulfonation of Diarylmethyl Phenyl Sulfones with Arenes Catalyzed by Scandium Triflate

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1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. $Sc(OTf)_3$ was purchased from Tokyo Chemical Industry Co. Diarylmethanols were prepared according to procedures reported in the literature.[1] Diarylmethyl phenyl sulfones **1a**, **1b**, **1c**, **1d**[2], and **1f**[3] were prepared according to procedures reported in the literature. 1-Tosylpyrrole[4], and 1-tosylindole[5] were prepared according to procedures reported in the literature.

Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard vacuum-line techniques. 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 F_{254} precoated plates (0.25 mm) visualizing with UV light (254 nm) and ethanolic phosphomolybdic acid. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling HPLC was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Gas chromatographic (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with an HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with an HP-5 column (30 m × 0.25 mm, Hewlett-Packard).

High-resolution mass spectra (HRMS) were obtained from a JEOL JMS700 (fast atom bombardment mass spectrometry, FAB-MS) and a JMS-T100TD instrument (DART). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz), and JEOL A-400, JEOL ECS-400 (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometers. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration

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1 a) Zhang, S.; Wang, Y.; Feng, X.; Bao, M. *J. Am. Chem. Soc.* **2012**, *134*, 5492–5495. b) Hillard, E.; Vessières, A.; Bideau, F. L.; Plazuk, D.; Spera, D.; Huchè, Jaouen, G. *ChemMedChem* **2006**, *1*, 551–559. c) Kodama, S.; Hashidate, S.; Nomoto, A.; Yano, S.; Ueshima, M.; Ogawa, A. *Chem. Lett.* **2011**, *40*, 495–497.

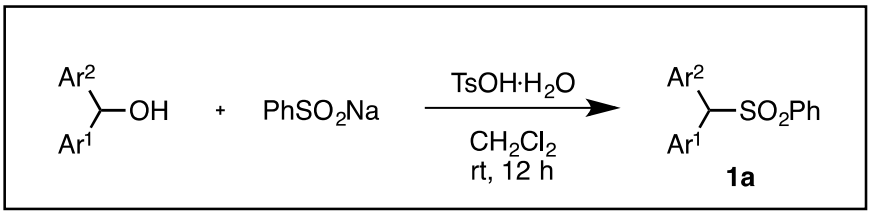
2 Nambo, M.; Crruden, C. M. *Angew. Chem. Int. Ed.* **2014**, *53*, 742–746.

3 Liu, C.-R.; Li, M.-B.; Cheng, D.-J.; Yang, C.-F.; Tian, S.-K. *Org. Lett.* **2009**, *11*, 2543–2545.

4 Farwaha, H. S.; Bucher, G.; Murphy, J. A. *Org. Biomol. Chem.,* **2013**, *11*, 8073–8081.

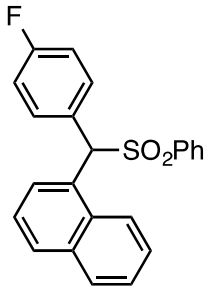
5 Voloshchuk, R.; Gatezowski, M.; Gryko, D. T. *Synthesis,* **2009**, *7*, 1147–1152.

2. Preparation of Diarylmethyl Phenyl Sulfones



A 30-mL flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added $PhSO_2Na$ (189 mg, 1.15 mmol), $TsOH{\cdot}H_2O$ (333 mg, 1.75 mmol), and dry CH_2Cl_2 (4 mL) under a stream of argon. After stirring for 5 min, a solution of diarylmethanol (1 mmol) in CH_2Cl_2 (3 mL) was added at room temperature and the mixture was stirred at room temperature for 12 h. The mixture was treated with sat. $NaHCO_3$ (~5 mL) and extracted with CH_2Cl_2 (3 times). The combined extracts were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by silica-gel flash column chromatography or recrystallization (CH_2Cl_2/hexane) to afford the desired product.

Compound Data for Diarylmethyl Phenyl Sulfones

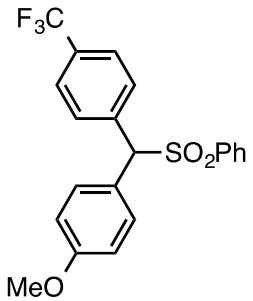


(4-Fluorophenyl)(1-naphthyl)methyl phenyl sulfone (1e)

Purification by recrystallization

223 mg, 59% isolated yield; colorless crystals

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (s, 1H), 6.97 (t, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.37-7.43 (m, 2H), 7.45-7.51 (m, 3H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.73-7.76 (m, 1H), 7.80-7.85 (m, 2H), 8.44 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.9, 115.6 (d, *J* = 22 Hz), 121.8, 125.3, 125.7, 126.8, 127.15, 127.16, 128.7, 128.9, 129.0, 129.3, 129.4, 131.3, 132.1 (d, *J* = 8.7 Hz), 133.6, 134.0, 138.3, 162.8 (d, *J* = 250 Hz). HRMS (FAB) *m/z* calcd for $C_{23}H_{17}O_2FSNa$ [M+Na]$^+$: 399.0825, found 399.0811.



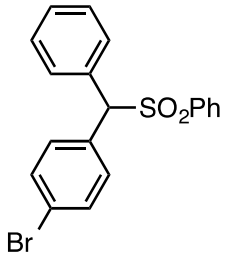
(4-Methoxyphenyl)(4-trifluoromethylphenyl)methyl phenyl sulfone (1g)

Purification by column chromatography (EtOAc/hexane = 1:4).

216 mg, 53% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 5.30 (s, 1H), 6.83 (dm, *J* = 9.2 Hz, 2H), 7.36-7.41 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.58-7.64 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 75.3, 114.3, 123.8 (q, *J* = 274 Hz), 124.0, 125.6 (q, *J* = 3.8 Hz), 128.8, 129.0, 130.2, 130.7 (q, *J* = 33 Hz), 131.1, 133.7, 137.3, 137.9, 160.1.

HRMS (FAB) *m/z* calcd for $C_{21}H_{17}O_3F_3SNa$ [M+Na]$^+$: 429.0743, found 429.0756.

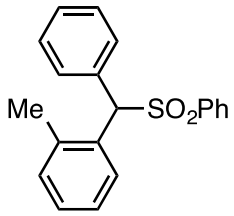


(4-Bromophenyl)phenylmethyl phenyl sulfone (1h)

Purification by column chromatography (CH_2Cl_2/hexane = 1:10).

186 mg, 48% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (s, 1H), 7.30-7.56 (m, 12H), 7.62 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.7, 123.1, 127.74, 128.78, 128.84, 129.0, 129.8, 131.5, 131.85, 131.92, 132.4, 133.7, 137.9. HRMS (FAB) *m/z* calcd for $C_{19}H_{15}O_2SBrNa$ [M+Na]$^+$: 408.9868, found 408.9870.

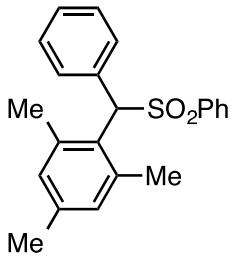


(2-Methylphenyl)phenylmethyl phenyl sulfone (1i)

Purification by column chromatography (EtOAc/hexane = 15:85).

212 mg, 66% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 5.59 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.20 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.28-7.32 (m, 4H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.45-7.49 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 8.0, 0.8 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 71.3, 126.5, 128.47, 128.54, 128.62, 128.63, 128.89, 128.95, 130.2, 130.7, 131.8, 132.7, 133.5, 136.8, 138.6. HRMS (FAB) *m/z* calcd for $C_{20}H_{18}O_2SNa$ [M+Na]$^+$: 345.0920, found 345.0926.

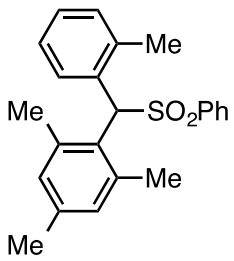


Phenyl(2,4,6-trimethylphenyl)methyl phenyl sulfone (1j)

Purification by recrystallization

155 mg, 44% isolated yield; colorless crystals

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.18 (s, 3H), 2.23 (s, 3H), 6.08 (s, 1H), 6.67 (s, 1H), 6.83 (s, 1H) 7.23-7.32 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.51-7.57 (m, 3H), 7.67 (dd, *J* = 8.4, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.0, 21.8, 70.8, 127.2, 128.1, 128.37, 128.38, 128.5, 128.8, 129.0, 131.8, 133.4, 134.5, 138.5, 138.8, 139.7, 140.0. HRMS (FAB) *m/z* calcd for $C_{22}H_{22}O_2SNa$ [M+Na]$^+$: 373.1233, found 373.1241.



(2-Methylphenyl)(2,4,6-trimethylphenyl)methyl phenyl sulfone (1k)

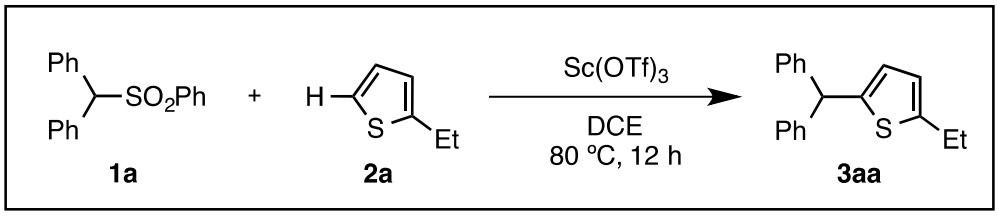
Purification by recrystallization

223 mg, 61% isolated yield; colorless crystals

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H), 1.99 (br.s, 3H), 2.13 (br.s, 3H), 2.23 (s, 3H), 5.83 (s, 1H), 6.74 (br.s, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H),

7.24 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H) 7.55 (t, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.51 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.7, 20.8, 22.4, 69.6, 125.1, 125.5, 127.6, 128.6, 129.2, 129.3, 130.5, 131.0, 132.1, 132.4, 132.6, 133.5, 136.8, 138.6, 139.4. 140.3. HRMS (FAB) *m/z* calcd for $C_{23}H_{24}O_2SNa$ $[M+Na]^+$: 387.1389, found 387.1392.

3. Typical Procedure for Sc-catalyzed Arylative Desulfonation of Diarylmethyl Phenyl Sulfones with Arenes



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added diphenylmethyl phenyl sulfone **1a** (92.4 mg, 0.3 mmol), $Sc(OTf)_3$ (14.7 mg, 30 μmol), and dry DCE (1.2 mL) at room temperature under a stream of argon. Then 2-ethylthiophene **2a** (102 μL, 0.9 mmol) was added, and then the vessel was sealed. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel and washed with copious EtOAc (~20 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane) to afford 2-benzhydryl-5-ethylthiophene **3aa** (66.0 mg, 79%) as a pale yellow oil.

Compound Data for Triarylmethanes (3)

Unless otherwise noted, triarylmethanes described in this section were prepared following the typical procedure. All products were purified by PTLC or preparative recycling HPLC equipped with JAIGEL-1H/JAIGEL-2H column (eluent: $CHCl_3$). All spectral data of **3ak**[6] and **3al**[2] matched those of the known compounds. Ratios of *p*- and *o*- isomers[6] were calculated using integrations of Ar_3C–H in ^{1}H NMR.

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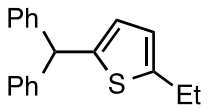
6 Aoyama, T.; Hayakawa, M.; Ogawa, S.; Nakajima, E.; Mitsuyama, E.; Iwabushi, T.; Takido, T.; Kodomari, M. *Synlett* **2014**, *25*, 2493–2497.

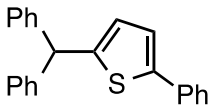


2-Benzhydryl-5-ethylthiophene (3aa)

Purification by PTLC (hexane).

66.0 mg, 79% isolated yield; pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.8 Hz, 3H), 2.75 (q, *J* = 7.8 Hz, 2H), 5.58 (s, 1H), 6.46 (d, *J* = 3.6 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 7.16-7.22 (m, 6H), 7.26-7.28 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7, 23.4, 52.3, 122.5, 125.9, 126.6, 128.3, 128.8, 143.8, 144.9, 146.6. HRMS (DART) *m/z* calcd for $C_{19}H_{17}S$ $[M-H]^+$: 277.1051, found 277.1048.

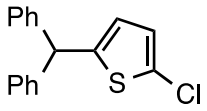


5-Benzhydryl-2-phenylthiophene (3ab)

Purification by PTLC (hexane).

57.8 mg, 59% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (s, 1H), 6.64 (d, *J* = 4.0 Hz, 1H), 7.13 (d, *J* = 4.0 Hz, 1H), 7.19-7.32 (m, 13H), 7.52 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 122.4, 125.5, 126.8, 127.2, 127.4, 128.4, 128.75, 128.85, 134.4, 143.4, 143.5, 147.5. HRMS (DART) *m/z* calcd for $C_{23}H_{17}S$ $[M-H]^+$: 325.1051, found 325.1058.

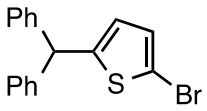


5-Benzhydryl-2-chlorothiophene (3ac)

Purification by PTLC (hexane).

67.0 mg, 75% isolated yield; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 6.44 (d, *J* = 3.6 Hz, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 7.13-7.32 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 125.58, 125.62, 126.95, 126.96, 128.5, 128.8, 142.9, 146.7. HRMS (DART) *m/z* calcd for $C_{17}H_{12}ClS$ $[M-H]^+$: 283.0348, found 283.0351.

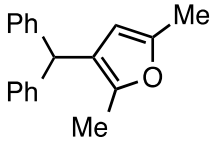


5-Benzhydryl-2-bromothiophene (3ad)[6]

Purification by PTLC (hexane).

70.0 mg, 71% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (s, 1H), 6.43 (dd, *J* = 4.0, 0.8 Hz, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 7.19-7.23 (m, 4H), 7.24-7.27 (m, 2H), 7.29-7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 111.0, 126.7, 127.0, 128.5, 128.8, 129.4, 142.9, 149.6. HRMS (DART) *m/z* calcd for $C_{17}H_{12}SBr$ $[M-H]^+$: 326.9843, found 326.9846.



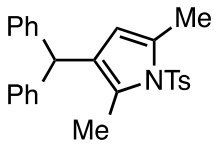
3-Benzhydryl-2,5-dimethylfuran (3ae)[7]

Purification by PTLC (hexane).

7 Maity, A. K.; Chatterjee, P. N.; Roy, S. *Tetrahedron*, **2013**, *69*, 942–956.

45.0 mg, 54% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.19 (s, 3H), 5.20 (s, 1H), 5.66 (s, 1H), 7.14-7.21 (m, 6H), 7.25-7.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 13.5, 47.4, 107.7, 121.8, 126.1, 128.2, 128.8, 144.1, 145.8, 149.2. HRMS (DART) *m/z* calcd for $C_{19}H_{19}O$ [M-H]$^+$: 263.1436, found 263.1426.

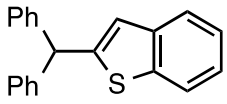


1-Tosyl-3-benzhydryl-2,5-dimethylpyrrole (3af)

Purification by PTLC (hexane:EtOAc = 20:1).

14.2 mg, 34% isolated yield (0.1 mmol scale); white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.34 (s, 3H), 2.42 (s, 3H), 5.25 (s, 1H), 5.57 (s, 1H), 7.04 (d, *J* = 6.8 Hz, 4H), 7.12-7.28 (m, 8H), 7.52 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 15.7, 21.6, 47.9, 114.0, 126.1, 126.2, 126.3, 127.9, 128.2, 128.9, 129.8, 131.4, 137.5, 143.7, 144.3. HRMS (DART) *m/z* calcd for $C_{26}H_{26}NO_2S$ [M+H]$^+$: 416.1684, found 416.1674.

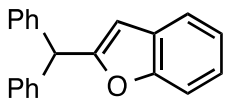


2-Benzhydrylbenzo[*b*]thiophene (3ag) [6]

Purification by PTLC (hexane).

59.4 mg, 66% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (s, 1H), 6.71 (s, 1H), 7.16-7.30 (m, 12H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 122.70, 122.75, 123.9, 124.2, 125.1, 126.6, 128.5, 129.1, 138.5, 139.1, 140.7, 142.6. HRMS (DART) *m/z* calcd for $C_{21}H_{15}S$ [M-H]$^+$: 299.0895, found 299.0895.

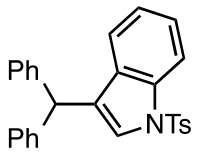


2-Benzhydrylbenzofuran (3ah)[8]

Purification by PTLC (hexane).

60.5 mg, 71% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 1H), 6.27 (s, 1H), 7.16-7.34 (m, 12H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 105.6, 111.1, 120.6, 120.7, 122.6, 123.7, 127.0, 128.5, 128.9, 141.0, 155.1, 159.9. HRMS (DART) *m/z* calcd for $C_{21}H_{15}O$ [M-H]$^+$: 283.1123, found 283.1126.



1-Tosyl-3-benzhydrylindole (3ai)[9]

Purification by GPC.

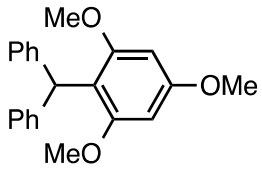
31.8 mg, 74% isolated yield (0.1 mmol scale); white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.51 (s, 1H), 6.93 (d, *J* = 1.2 Hz, 1H), 7.05-7.09 (m, 2H),

8 Liu, J.; Liu, Z.; Liao, P.; Bi, X. *Org. Lett.* **2014**, *16*, 6204–6207.

9 Jana, U.; Maiti, S.; Biswas, S. *Tetrahedron Lett.* **2007**, *48*, 7160–7163.

7.12-7.14 (m, 4H), 7.20-7.30 (m, 9H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 48.5, 113.9, 120.5, 123.2, 124.7, 125.8, 126.7, 126.8, 128.5, 128.8, 129.75, 129.76, 130.5, 135.1, 135.8, 142.1, 144.8. HRMS (DART) *m/z* calcd for $C_{28}H_{22}NO_2S$ [M-H]$^+$: 436.1371, found 436.1379.

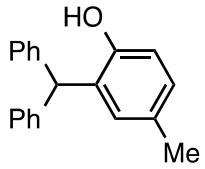


2-Benzhydryl-1,3,5-trimethoxybenzene (3aj) [6]

Purification by PTLC (hexane:EtOAc = 20:1).

26.9 mg, 80% isolated yield (0.1 mmol scale); white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 6H), 3.79 (s, 3H), 6.05 (s, 1H), 6.14 (s, 2H), 7.32-7.40 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.1, 55.2, 55.7, 91.6, 113.6, 125.3, 127.5, 129.1, 144.1, 159.1, 160.0. HRMS (DART) *m/z* calcd for $C_{22}H_{23}O_3$ [M+H]$^+$: 335.1647, found 335.1643.

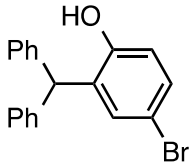


2-Benzhydryl-4-methylphenol (3am) [6]

Purification by GPC.

17.0 mg, 62% isolated yield (0.1 mmol scale); white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 4.49 (br.s, 1H), 5.70 (s, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 4H), 7.21-7.25 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 51.0, 116.0, 126.6, 128.3, 128.5, 129.4, 129.9, 130.0, 130.9, 142.6, 151.1. HRMS (DART) *m/z* calcd for $C_{20}H_{17}O$ [M-H]$^+$: 273.1279, found 273.1285.

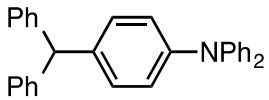


2-Benzhydryl-4-bromophenol (3an)

Purification by GPC.

95.4 mg, 94% isolated yield; white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (s, 1H), 5.66 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 2.8 Hz, 1H), 7.11-7.14 (m, 4H), 7.23-7.28 (m, 3H), 7.31-7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.9, 113.1, 117.9, 127.0, 128.7, 129.3, 130.8, 132.7, 133.0, 141.6, 152.6. HRMS (DART) *m/z* calcd for $C_{19}H_{14}OBr$ [M-H]$^+$: 337.0228, found 337.0222.



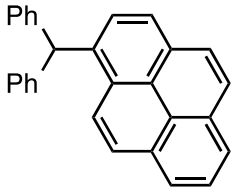
4-Benzhydryltriphenylamine (3ao)

Purification by PTLC (hexane).

16.3 mg, 40% isolated yield (0.1 mmol scale) ; gray solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H), 6.96-7.00 (m, 6H), 7.08 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.19-7.24 (m, 6H), 7.29 (t, *J* = 8.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 122.6, 123.7, 124.1, 126.3, 128.3, 129.2, 129.4, 130.1, 138.0, 144.1, 145.9, 147.8. HRMS (DART) *m/z* calcd for

$C_{31}H_{26}N$ [M+H]$^+$: 412.2065, found 412.2075.

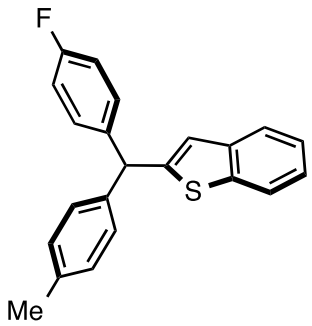


1-Benzhydrylpyrene (3ap)

Purification by PTLC (hexane).

10.1 mg, 27% isolated yield (0.1 mmol scale); white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (s, 1H), 7.15-7.17 (m, 4H), 7.20-7.31 (m, 7H), 7.97 (t, *J* = 8.0 Hz, 1H), 8.00-8.02 (m, 3H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.3, 123.5, 124.5, 124.8, 125.0, 125.1, 125.2, 125.9, 126.4, 127.1, 127.5, 127.6, 127.7, 128.4, 128.9, 129.9, 130.1, 130.7, 131.4, 137.7, 144.1. HRMS (DART) *m/z* calcd for $C_{29}H_{21}$ [M+H]$^+$: 369.1643, found 369.1636.

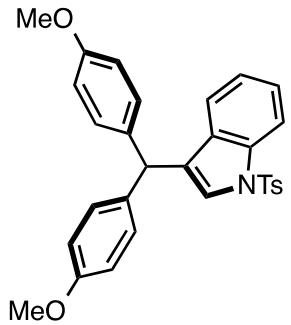


(2-Benzo[b]thienyl)(4-fluorophenyl)(4-methylphenyl)methane (3bg)

Purification by PTLC (hexane:EtOAc = 50:1).

24.6 mg, 74% isolated yield (0.1 mmol scale); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 5.68 (s, 1H), 6.70 (d, *J* = 0.8 Hz, 1H), 6.96 (t, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.07-7.13 (m, 4H), 7.21-7.25 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 50.2, 115.3 (d, *J* = 21 Hz), 122.7, 122.8, 123.9, 124.3, 125.0, 128.8, 129.3, 130.4 (d, *J* = 7.6 Hz), 136.3, 138.3, 138.6 (d, *J* = 3 Hz), 139.2, 139.5, 140.7, 161.6 (d, *J* = 246 Hz). HRMS (DART) *m/z* calcd for $C_{22}H_{16}FS$ [M-H]$^+$: 331.0957, found 331.0952.

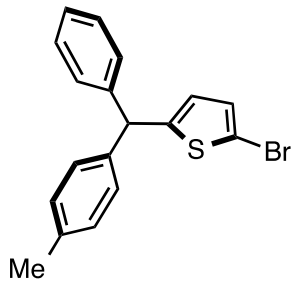


Bis(4-methoxyphenyl)[3-(1-tosyl)indolyl]methane (3ci)

Purification by PTLC (hexane:EtOAc = 19:1).

39.7 mg, 80% isolated yield (0.1 mmol scale); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.79 (s, 6H), 5.40 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.90 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 4H), 7.07-7.08 (m, 2H), 7.20-7.25 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 46.8, 55.2, 113.8, 113.9, 120.6, 123.1, 124.7, 125.6, 126.8, 127.5, 129.6, 129.7, 130.5, 134.6, 135.1, 135.8, 144.7, 158.2. HRMS (DART) *m/z* calcd for $C_{30}H_{26}NO_4S$ [M-H]$^+$: 496.1583, found 496.1574.



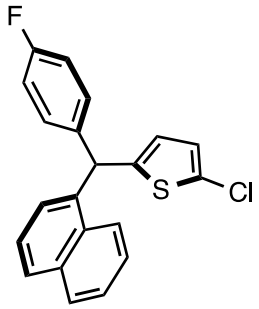
[5-(2-Bromothienyl)]phenyl(4-methylphenyl)methane (3dd)

Purification by PTLC (hexane:EtOAc = 50:1).

27.0 mg, 78% isolated yield (0.1 mmol scale); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 5.53 (s, 1H), 6.43 (d, *J* = 3.6 Hz,

1H), 6.86 (d, *J* = 3.6 Hz, 1H), 7.07-7.12 (m, 4H), 7.19-7.24 (m, 3H), 7.29-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 52.0, 110.9, 126.5, 126.9, 128.5, 128.6, 128.7, 129.2, 129.3, 136.6, 140.0, 143.1, 149.9. HRMS (DART) *m/z* calcd for $C_{18}H_{14}SBr$ $[M-H]^+$: 341.0000, found 340.9999.

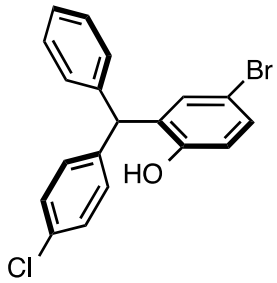


[5-(2-Chlorothienyl)](4-fluorophenyl)(1-naphthyl)methane (3ec)

Purification by PTLC (hexane:EtOAc = 50:1).

31.2 mg, 88% isolated yield (0.1 mmol scale); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (s, 1H), 6.40 (d, *J* = 4.4 Hz, 1H), 6.73 (dd, *J* = 3.6, 2.0 Hz, 1H), 6.97-7.02 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.15-7.19 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.43-7.49 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.86-7.88 (m, 1H), 7.95 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.5, 115.5 (d, *J* = 22 Hz), 123.6, 125.3, 125.7, 125.8, 126.2, 126.5, 126.8, 128.1, 128.9, 129.0, 130.4 (d, *J* = 8.6 Hz), 131.3, 133.9, 138.4 (d, *J* = 2.9 Hz), 138.7, 146.2, 161.8 (d, *J* = 247 Hz). HRMS (DART) *m/z* calcd for $C_{21}H_{13}FClS$ $[M-H]^+$: 351.0411, found 351.0413.

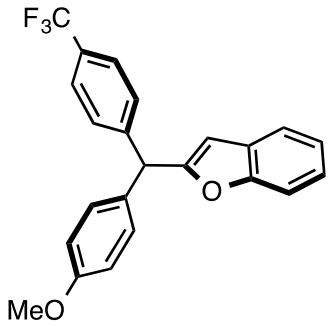


[2-(4-Bromo-1-hydroxyphenyl)](4-chlorophenyl)phenylmethane (3fn)

Purification by PTLC (hexane:EtOAc = 10:1).

98.2 mg, 87% isolated yield; pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (s, 1H), 5.67 (s, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.08-7.11 (m, 2H), 7.24-7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.9, 113.1, 117.7, 127.1, 128.76, 128.78, 129.2, 130.6, 130.9, 132.3, 132.7, 132.9, 140.5, 141.3, 152.4. HRMS (DART) *m/z* calcd for $C_{19}H_{13}OClBr$ $[M-H]^+$: 370.9838, found 370.9841.

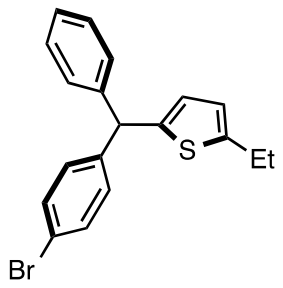


(2-Benzofuryl)(4-methoxyphenyl)(4-trifluoromethyphenyl)methane (3gh)

Purification by PTLC (hexane:EtOAc = 19:1).

29.3 mg, 76% isolated yield (0.1 mmol scale); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 5.58 (s, 1H), 6.28 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.17-7.26 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.46-7.48 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.3, 55.3, 105.8, 111.2, 114.1, 120.7, 121.8 (q, *J* = 339 Hz), 122.8, 124.0, 125.5 (q, *J* = 4.8 Hz), 128.3, 129.1, 129.3 (q, *J* = 32 Hz), 129.8, 132.2, 145.4, 155.1, 158.8, 159.1. HRMS (DART) *m/z* calcd for $C_{23}H_{16}O_2F_3$ $[M-H]^+$: 381.1102, found 381.1098.

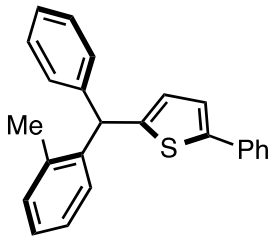


(4-Bromophenyl)[5-(2-ethylthienyl)]phenylmethane (3ha)

Purification by PTLC (hexane).

75.8 mg, 71% isolated yield; pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.6 Hz, 3H), 2.78 (q, *J* = 7.6 Hz, 2H), 5.54 (s, 1H), 6.45 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.09 (dm, *J* = 8.0 Hz, 2H), 7.17-7.20 (m, 2H), 7.23-7.25 (m, 1H) 7.28-7.31 (m, 2H), (dm, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 23.4, 51.7, 120.5, 122.6, 126.0, 126.8, 128.4, 128.7, 130.6, 131.4, 142.9, 143.2, 144.2, 146.9. HRMS (DART) *m/z* calcd for $C_{19}H_{16}SBr$ $[M-H]^+$: 355.0156, found 355.0155.

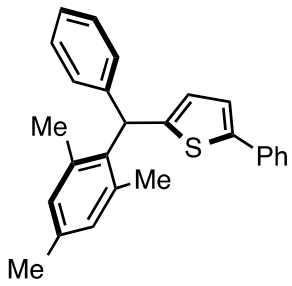


(2-Methylphenyl)[5-(2-phenylthienyl)]phenylmethane (3ib)

Purification by PTLC (hexane:EtOAc = 50:1).

27.0 mg, 78% isolated yield (0.1 mmol scale); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 5.81 (s, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 7.04-7.06 (m, 1H), 7.12-7.26 (m, 8H), 7.28-7.33 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 48.7, 122.4, 125.5, 126.0, 126.7, 126.8, 127.2, 127.6, 128.4, 128.7, 128.8, 129.0, 130.4, 134.4, 136.2, 141.9, 143.0, 143.3, 147.1. HRMS (DART) *m/z* calcd for $C_{24}H_{19}S$ $[M-H]^+$: 339.1208, found 339.1214.

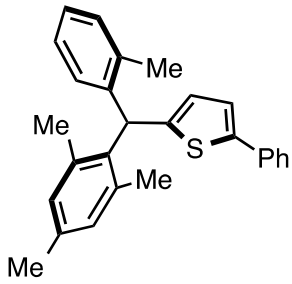


[5-(2-Phenylthienyl)]phenyl(2,4,6-trimethylphenyl)methane (3jb)

Purification by PTLC (hexane).

21.7 mg, 59% isolated yield (0.1 mmol scale); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 6H), 2.28 (s, 3H), 6.11 (s, 1H), 6.70 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.86 (s, 2H), 7.15 (d, *J* = 3.6 Hz, 1H), 7.19-7.33 (m, 8H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.7, 46.7, 122.3, 125.4, 126.2, 127.1, 127.2, 128.2, 128.5, 128.8, 130.2, 134.5, 136.4, 137.0, 137.2, 142.4, 142.9, 146.1. HRMS (DART) *m/z* calcd for $C_{26}H_{23}S$ $[M-H]^+$: 367.1521, found 367.1523.



(2-Methylphenyl)[5-(2-phenylthienyl)](2,4,6-trimethylphenyl)methane (3kb)

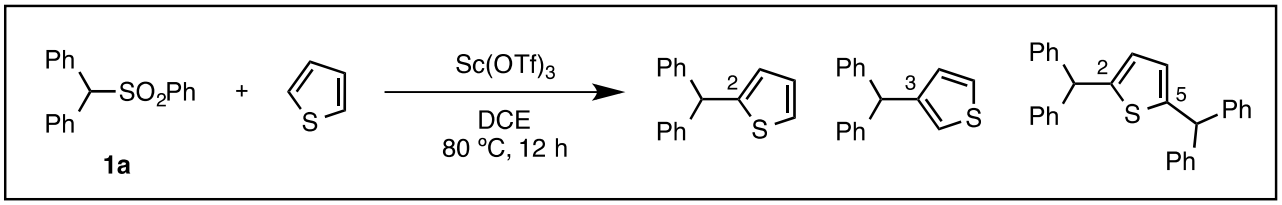
Purification by PTLC (hexane).

14.1 mg, 36% isolated yield (0.1 mmol scale); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 6H), 2.14 (s, 3H), 2.27 (s, 3H), 5.96 (s, 1H), 6.55 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.83 (s, 2H), 7.09-7.11 (m, 2H), 7.13 (d, *J* = 4.0 Hz, 1H), 7.14-7.17 (m, 2H), 7.19-7.23 (m, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.52-7.55 (m, 2H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 19.5, 20.8, 21.6, 45.6, 122.4, 125.4, 125.8, 126.6, 127.1, 127.3, 128.8, 129.0, 130.3, 130.4, 134.5, 136.2, 136.3, 136.8, 137.1, 140.9, 143.0, 146.6. HRMS (DART) *m/z* calcd for $C_{27}H_{25}S$ $[M-H]^+$: 381.1677, found 381.1679.

4. Sc-catalyzed Arylative Desulfonation of Diphenylmethyl Phenyl Sulfone with Thiophene

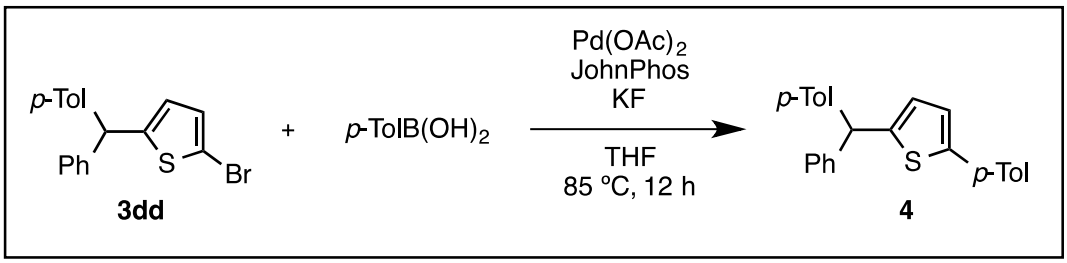


A 5-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added diphenylmethyl phenyl sulfone **1a** (30.8 mg, 0.1 mmol), $Sc(OTf)_3$ (4.9 mg, 10 μmol), and dry DCE (0.4 mL) at room temperature under a stream of argon. Then thiophene (24 μL, 0.3 mmol) was added, and then the vessel was sealed. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel and washed with copious EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The yield of 2-benzhydrylthiophene (5.67 ppm, Ar_3C–H), 3-benzhydrylthiophene (5.50 ppm, Ar_3C–H), and 2,5-dibenzhydrylthiophene (5.55 ppm, Ar_3C–H) were determined to be 16%[10], 3%[2], and 18%[10] respectively, by ^1H NMR analysis of crude mixture using 1,4-dimethoxybenzene (0.1 mmol) as an internal standard. And the yield of **1a** (5.28 ppm, $Ph_2(SO_2Ph)$ C–H) was determined to be 36% yield.

5. Derivatization of 3dd

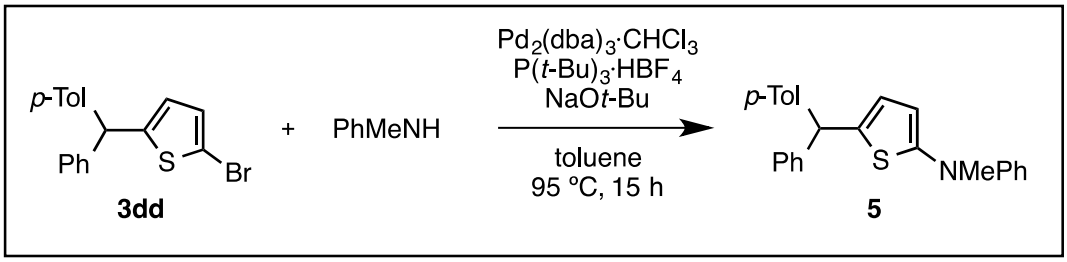
A) Pd-catalyzed Suzuki-Miyaura Cross-Coupling

[10] Watanabe, N.; Matsugi, A.; Nakano, K.; Ichikawa, Y.; Kotsuki, H. *SynLett.* **2014**, *25*, 438–442.



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel was added **3dd** (50 mg, 0.145 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), JohnPhos (9.6 mg, 0.032 mmol), *p*-tolylboronic acid (29.7 mg, 0.219 mmol), and potassium fluoride (25.4 mg, 0.437 mmol). The vessel was evacuated and backfilled with argon. Then dry THF (290 μL) was added at room temperature and the vessel was capped and sealed under a stream of argon. The mixture was stirred at 85 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washing with EtOAc (~5 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane/EtOAc = 20/1) to afford the product **4** as a white solid (42.5 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 5.61 (s, 1H), 6.62 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 7.10-7.16 (m, 6H), 7.21-7.32 (m, 5H), 7.41 (dd, *J* = 8.4, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.1, 52.0, 121.9, 125.4, 126.7, 127.2, 128.4, 128.7, 128.8, 129.1, 129.4, 131.7, 136.3, 137.0, 140.7, 143.5, 143.8, 147.2. HRMS (DART) *m/z* calcd for $C_{25}H_{21}S$ $[M-H]^+$: 353.1364, found 353.1357.

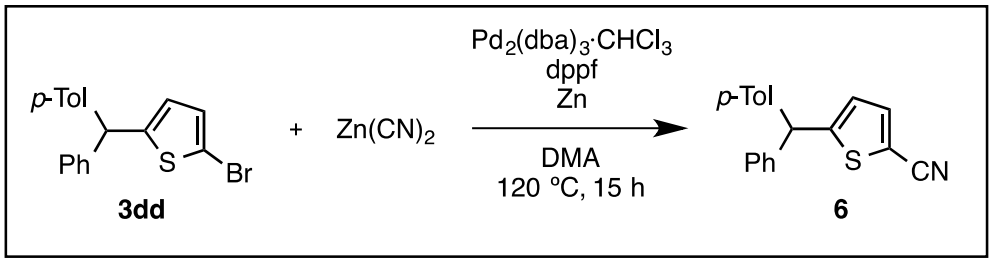
B) Pd-catalyzed Buchwald-Hartwig Amination



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel was added **3dd** (50 mg, 0.145 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.5 mg, 0.0015 mmol), $P(t\text{-}Bu)_3{\cdot}HBF_4$ (8.4 mg, 0.0029 mmol), and NaO*t*-Bu (15.6 mg, 0.163 mmol). The vessel was evacuated and backfilled with argon. Then dry toluene (290 μL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then, *N*-methylaniline (15.6 mg, 0.145 mmol) was added and the vessel was capped and sealed under a stream of argon. The mixture was stirred at 95 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washing with

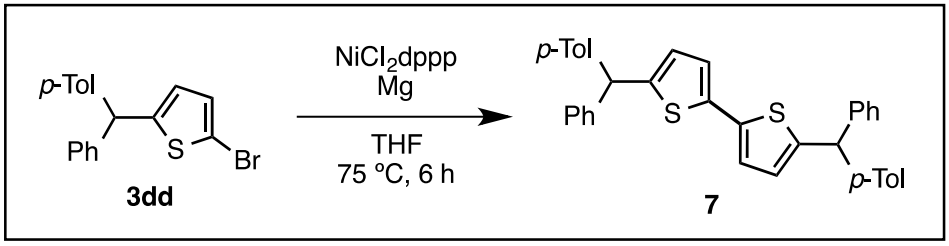
EtOAc (~5 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane/EtOAc = 20/1) to afford the product **5** as a dark red oil (28.7 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.27 (s, 3H), 5.51 (s, 1H), 6.41 (d, *J* = 3.6 Hz, 1H), 6.45 (d, *J* = 3.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 7.10-7.15 (m, 4H), 7.20-7.25 (m, 5H), 7.30 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 41.8, 52.4, 116.1, 118.2, 119.7, 124.5, 126.6, 128.3, 128.7, 128.8, 128.9, 129.1, 136.2, 140.6, 141.7, 143.7, 149.1, 152.3. HRMS (DART) *m/z* calcd for $C_{25}H_{24}NS$ $[M+H]^+$: 370.1629, found 370.1629.

C) Pd-catalyzed Cyanation



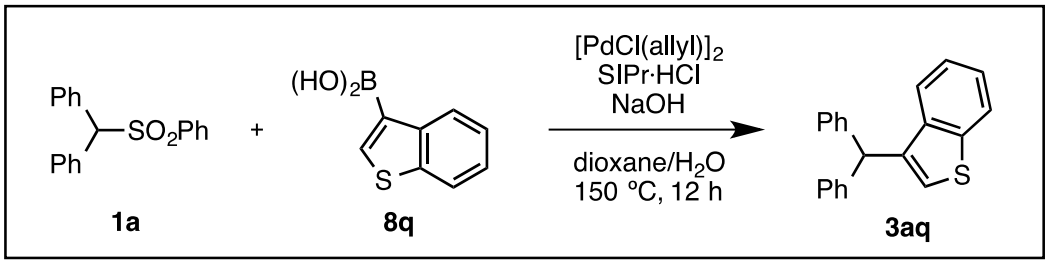
A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel was added **3dd** (50 mg, 0.145 mmol), $Pd_2(dba)_3$·$CHCl_3$ (4.5 mg, 0.0044 mmol), dppf (4.8 mg, 0.0087 mmol), $Zn(CN)_2$ (14.7 mg, 0.125 mmol), and Zn (1.6 mg, 0.025 mmol). The vessel was evacuated and backfilled with argon. Then dry DMA (290 μL) was added at room temperature and the vessel was capped and sealed under a stream of argon. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washing with EtOAc (~5 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane/EtOAc = 20/1) to afford the product **6** as a white solid (40.5 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 5.62 (s, 1H), 6.72 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.17-7.19 (m, 2H), 7.24-7.34 (m, 3H), 7.46 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 51.9, 108.5, 114.4, 126.7, 127.3, 128.5, 128.6, 128.7, 129.4, 137.1, 137.4, 139.2, 142.4, 157.1. HRMS (DART) *m/z* calcd for $C_{19}H_{16}NS$ $[M+H]^+$: 290.1003, found 290.1014.

D) Ni-catalyzed Dimerization



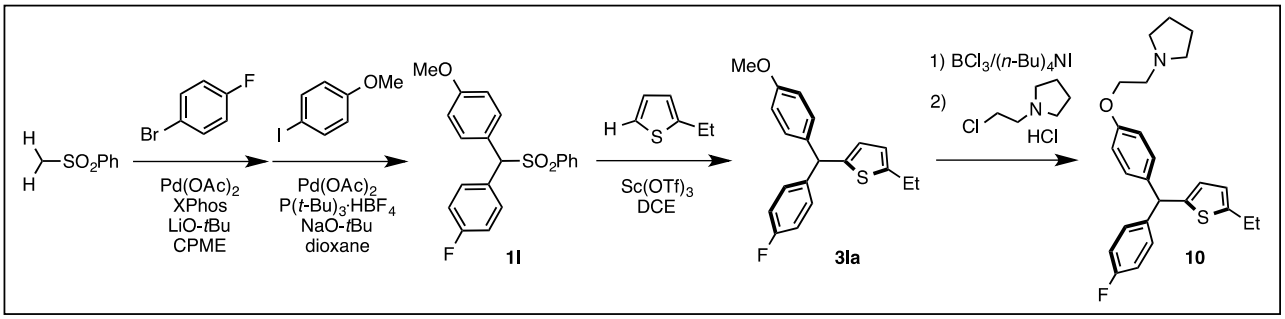
A 50-mL two-necked flask equipped with a reflux condenser was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel was added magnesium turnings (15.5 mg, 0.639 mmol). A solution of **3dd** (366 mg, 1.07 mmol) in THF (1.5 mL) was added dropwise followed by $NiCl_2$dppp (14.4 mg, 0.027 mmol). The mixture was stirred at 75 °C for 6 h. After cooling to room temperature, the mixture was poured onto cold 2N HCl (20 mL). The organic phase was extracted with EtOAc (3x20 mL), washed with brine, and dried over Na_2SO_4. The crude product was purified by PTLC (hexane/EtOAc = 20/1) to afford the product **7** as a red-brown oil (148 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 5.56 (s, 2H), 6.52 (dd, *J* = 3.6, 0.8 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 7.10 (s, 8H), 7.20-7.24 (m, 6H), 7.27-7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 51.9, 122.6, 126.7, 126.9, 128.4, 128.7, 128.8, 129.1, 136.4, 136.7, 140.5, 143.6, 147.1. HRMS (DART) *m/z* calcd for $C_{36}H_{31}S_2$ $[M+H]^+$: 527.1867, found 527.1864.

6. Procedure for Pd-catalyzed Arylation of Diphenylmethyl Phenyl Sulfone (1a) with Benzo[b]thiophene-3-boronic acid (8q)



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added $[PdCl(allyl)]_2$ (1.8 mg, 5 μmol), SIPr·HCl (4.3 mg, 10 μmol), dry dioxane (0.25 mL), and 1M NaOH*aq* (0.3 mL, 0.3 mmol) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, diphenylmethyl phenyl sulfone **1a** (30.8 mg, 0.1 mmol), Benzo[b]thiophene-3-boronic acid **8q** (35.6 mg, 0.2 mmol), and dry dioxane (0.25 mL) were added, and then the vessel was sealed. The mixture was stirred at 150 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~20 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane) to afford 3-benzhydrylbenzofuran **3aq** (14.9 mg, 50%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (s, 1H), 6.72 (d, *J* = 1.2 Hz, 1H), 7.17-7.19 (m, 4H), 7.21-7.31 (m, 8H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 122.7, 122.8, 123.9, 124.2, 125.1, 126.6, 128.5, 129.1, 138.5, 139.1, 140.7, 142.6. HRMS (DART) *m/z* calcd for $C_{21}H_{15}S$ $[M-H]^+$: 299.0895, found 299.0904.

7. Synthesis of Bactericidal Agent Analog 10



(4-Fluorophenyl)methyl phenyl sulfone was prepared according to procedures reported in the literature.[2]

A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added $Pd(OAc)_2$ (4.4 mg, 20 μmol), P(*t*-Bu)$_3$·HBF_4 (11.6 mg, 40 μmol), NaO*t*-Bu (57.7 mg, 0.6 mmol), and dry dioxane (250 μL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, (4-fluorophenyl)methyl phenyl sulfone (50.0 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol), and dry dioxane (250 μL) were added, and then the vessel was sealed. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was passed through a pad of celite with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:10) to afford (4-fluorophenyl)(4-methoxyphenyl)methyl phenyl sulfone **1l** (48.5 mg, 68%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 3H), 5.23 (s, 1H), 6.84 (dm, *J* = 8.8 Hz, 2H), 7.01 (tm, *J* = 8.8 Hz, 2H), 7.36-7.42 (m, 4H), 7.48-7.55 (m, 3H), 7.61-7.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 74.9, 114.2, 115.7 (d, *J* = 22 Hz), 124.5, 128.7, 128.9, 129.0 (d, *J* = 2.9 Hz), 131.1, 131.7 (d, *J* = 8.6 Hz), 133.5, 138.1, 159.9, 162.8 (d, *J* = 250 Hz). HRMS (DART) *m/z* calcd for $C_{20}H_{17}O_3FSNa$ $[M+Na]^+$: 379.0775, found 379.0766.

A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added **1l** (107.0 mg, 0.3 mmol), and $Sc(OTf)_3$ (14.7 mg, 30 μmol), and dry DCE (1.2 mL) at room temperature under a stream of argon. Then 2-ethylthiophene **2a** (102 μL, 0.9 mmol) was added, and then the

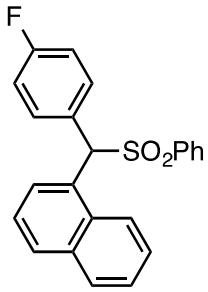
vessel was sealed. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~20 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:15) to afford (2-ethylthienyl)(4-fluorophenyl)(4-methoxylphenyl)methane **3la** (67.5 mg, 69%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.6 Hz, 3H), 2.77 (q, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 5.52 (s, 1H), 6.43 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.58-6.59 (m, 1H), 6.83 (dm, *J* = 8.8 Hz, 2H), 6.97 (tm, *J* = 8.8 Hz, 2H), 7.11 (dm, *J* = 8.8 Hz, 2H), 7.14-7.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 23.4, 50.8, 55.2, 113.7, 115.1 (d, *J* = 21 Hz), 122.6, 125.7, 129.7, 130.2 (d, *J* = 8.6 Hz), 135.9, 140.0 (d, *J* = 3.8 Hz), 145.3, 146.7, 158.3, 161.5 (d, *J* = 246 Hz). HRMS (DART) *m/z* calcd for $C_{20}H_{18}OFS$ $[M-H]^+$: 325.1062, found 325.1058.

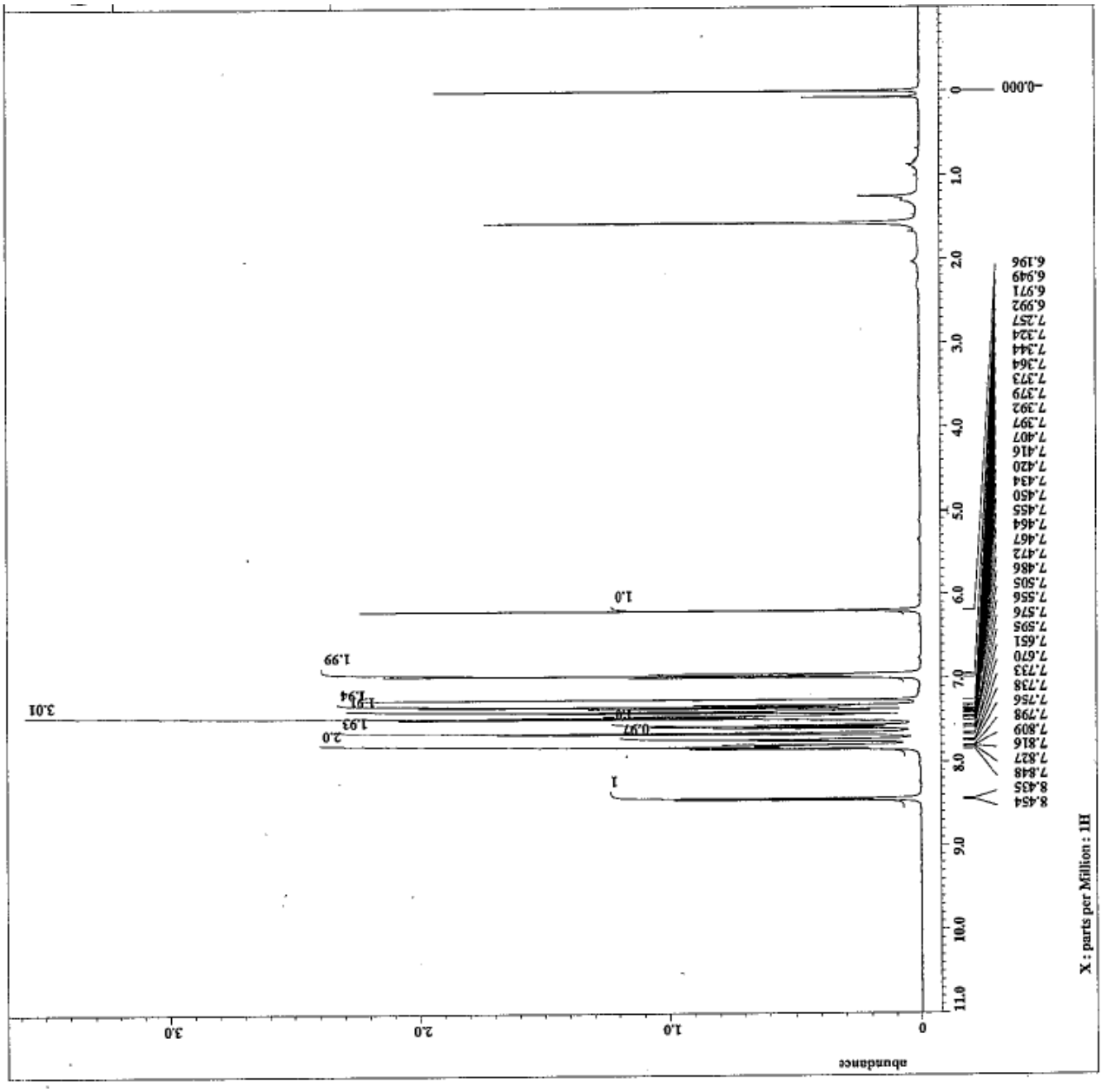
A 10 mL flask was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask was added **3la** (20.7 mg, 0.06 mmol) and tetrabutylammonium iodide (46.8 mg, 0.13 mmol) followed by dry DCM (0.6 mL). The reaction mixture was cooled to -78 °C and then BCl_3 (0.13 mL, 0.13 mmol, 1M solution in hexane) was added dropwise. The reaction was stirred at -78 °C for 1 h and then warmed to 0 °C and stirred for 2 h. Water (10 mL) was added and the organic layer was extracted with EtOAc (3 x 10 mL), washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The crude material was passed through a plug of silica and transferred to a clean dry 10 mL flask. Cs_2CO_3 (112 mg, 0.32 mmol) and 1-(2-chloroethyl)pyrrolidine hydrochloride (24.2 mg, 0.14 mmol) were added followed by dry DMF (0.6 mL). The reaction was stirred at 50 °C for 16 h before water (10 mL) was added. The organic phase was extracted with EtOAc (3 x 10 mL), washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The crude material was purified by PTLC (Hexane/EtOAc/Et_3N = 1:2:0.15) to give the product **10** as a clear oil (18.1 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.6 Hz, 3H), 1.79-1.83 (m, 4H), 2.61-2.64 (m, 4H), 2.77 (q, *J* = 8.0 Hz, 2H), 2.90 (t, *J* = 6.2 Hz, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 5.52 (s, 1H), 6.43 (d, *J* = 3.6 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 6.83-6.87 (m, 2H), 6.95-6.99 (m, 2H), 7.07-7.11 (m, 2H), 7.13-7.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 23.4, 50.7, 54.7, 55.0, 66.9, 77.2, 114.4, 115.0 (d, *J* = 21.9 Hz), 122.5, 125.7, 129.6, 130.2 (d, *J* = 8.6 Hz), 135.9, 139.9 (d, *J* = 2.8 Hz), 145.3, 146.7, 157.6, 161.5 (d, *J* = 248 Hz). HRMS (DART) *m/z* calcd for $C_{25}H_{29}NOFS$ $[M+H]^+$: 410.1954, found 410.1961.

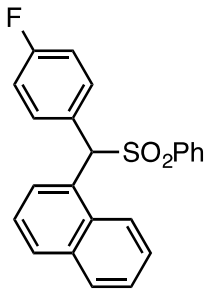
8. ^{1}H and ^{13}C NMR Spectra of Products

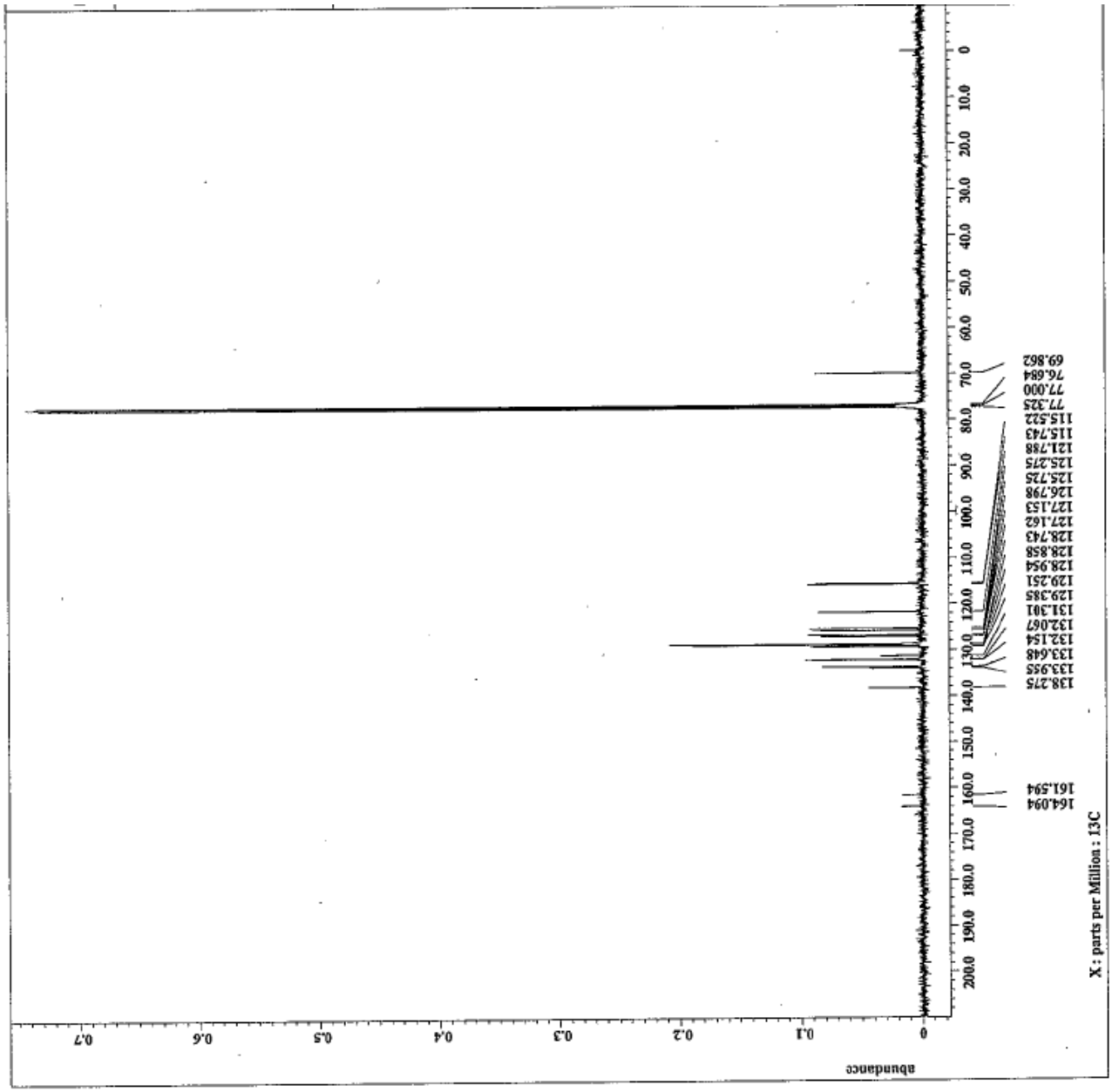
^{1}H-NMR (400 MHz, $CDCl_3$) of 1e



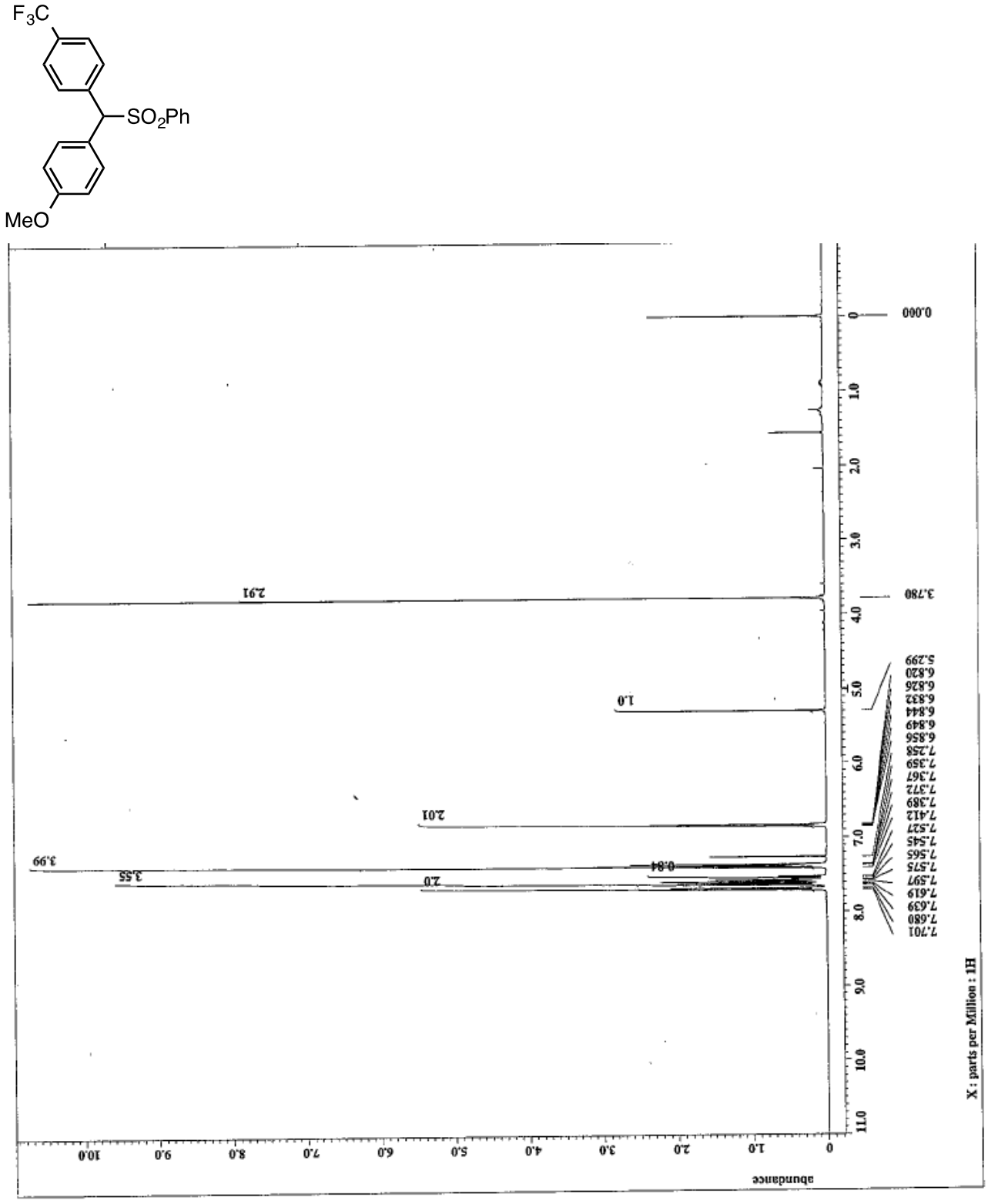


^{13}C-NMR (100 MHz, $CDCl_3$) of 1e

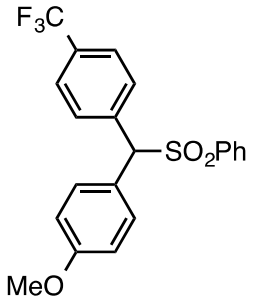


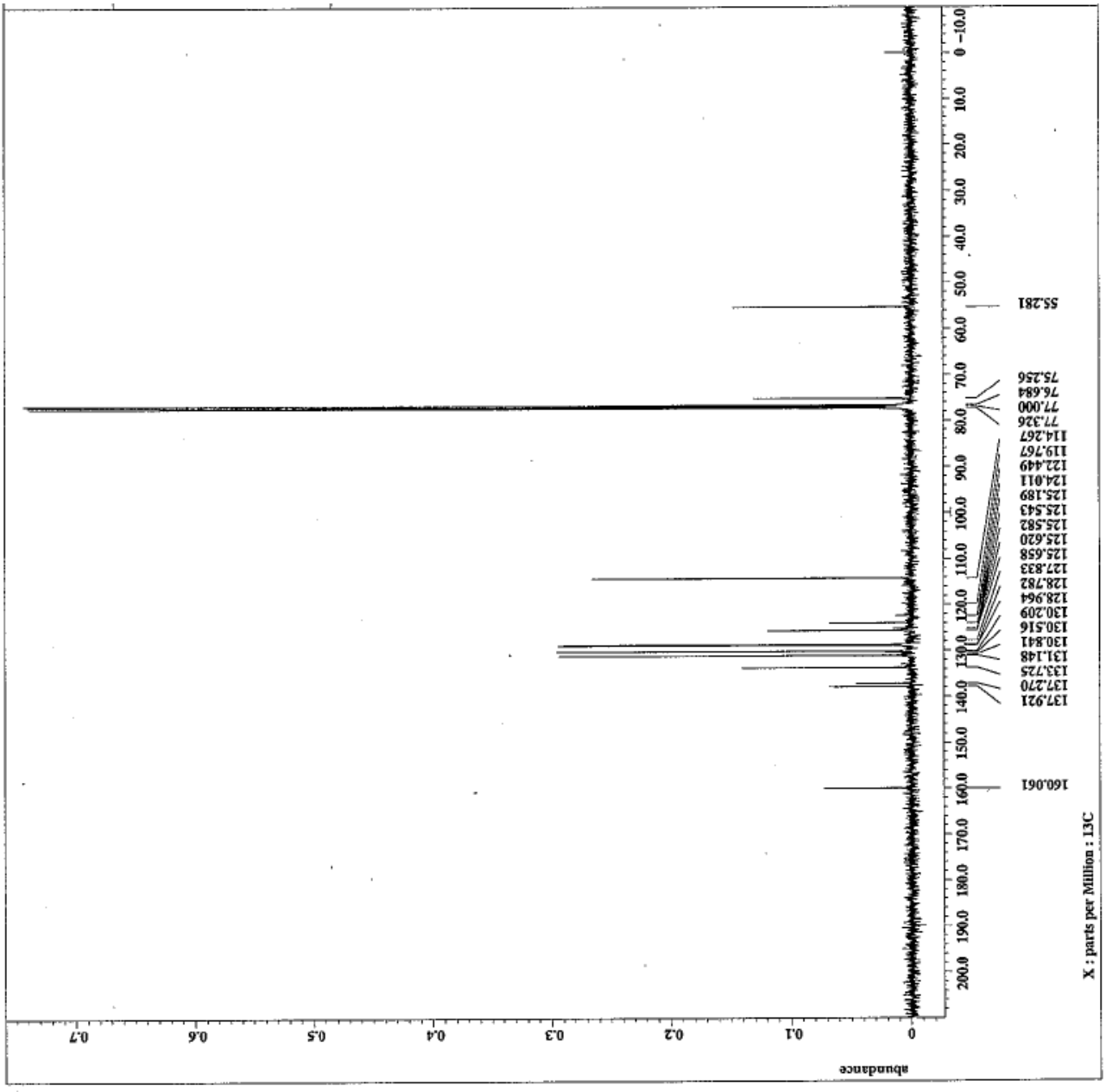


^{1}H-NMR (400 MHz, $CDCl_3$) of 1g

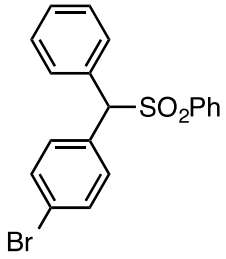


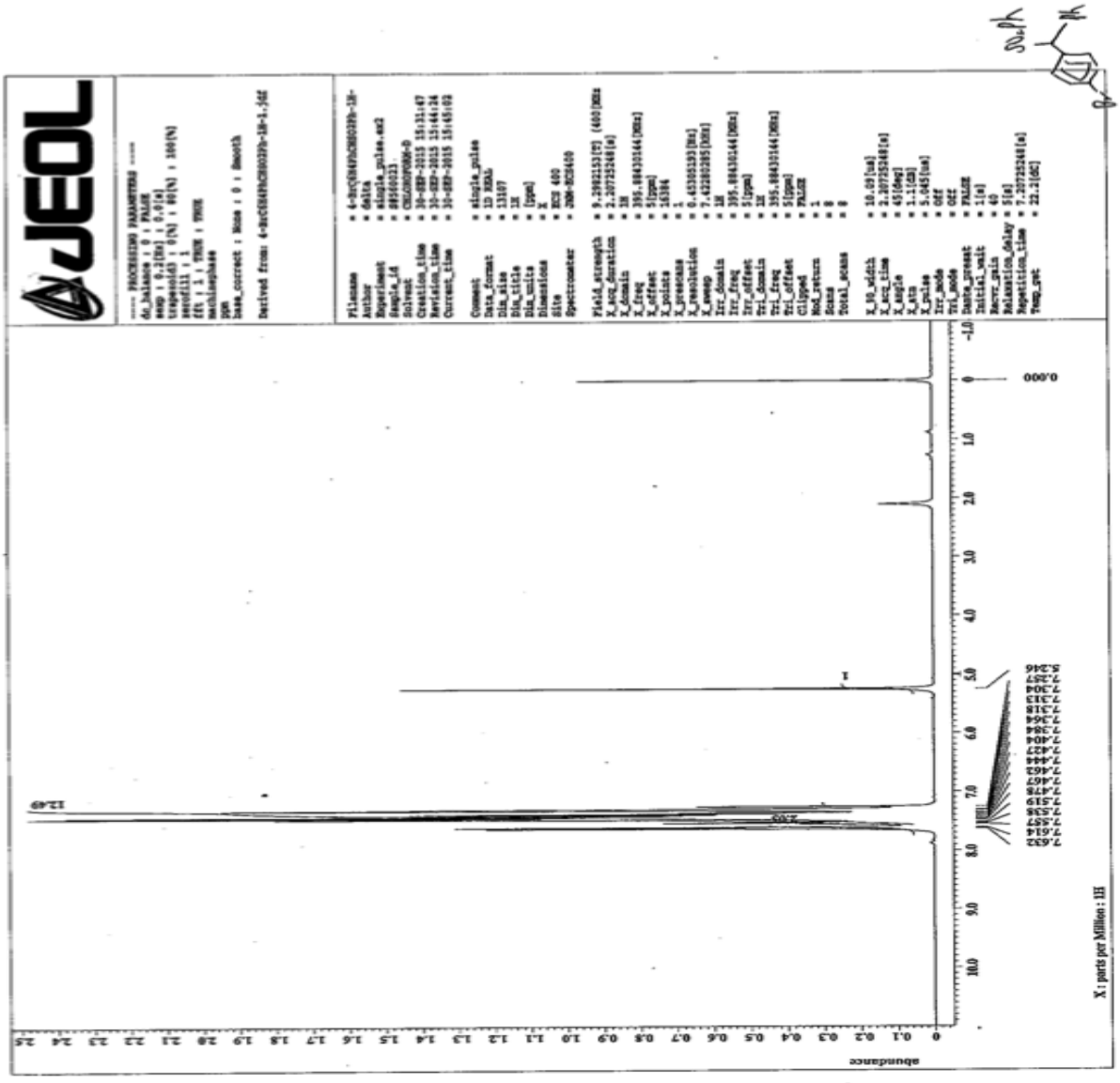
^{13}C-NMR (100 MHz, $CDCl_3$) of 1g



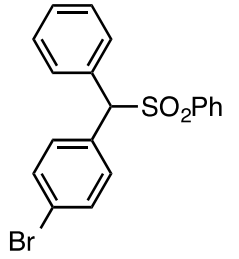


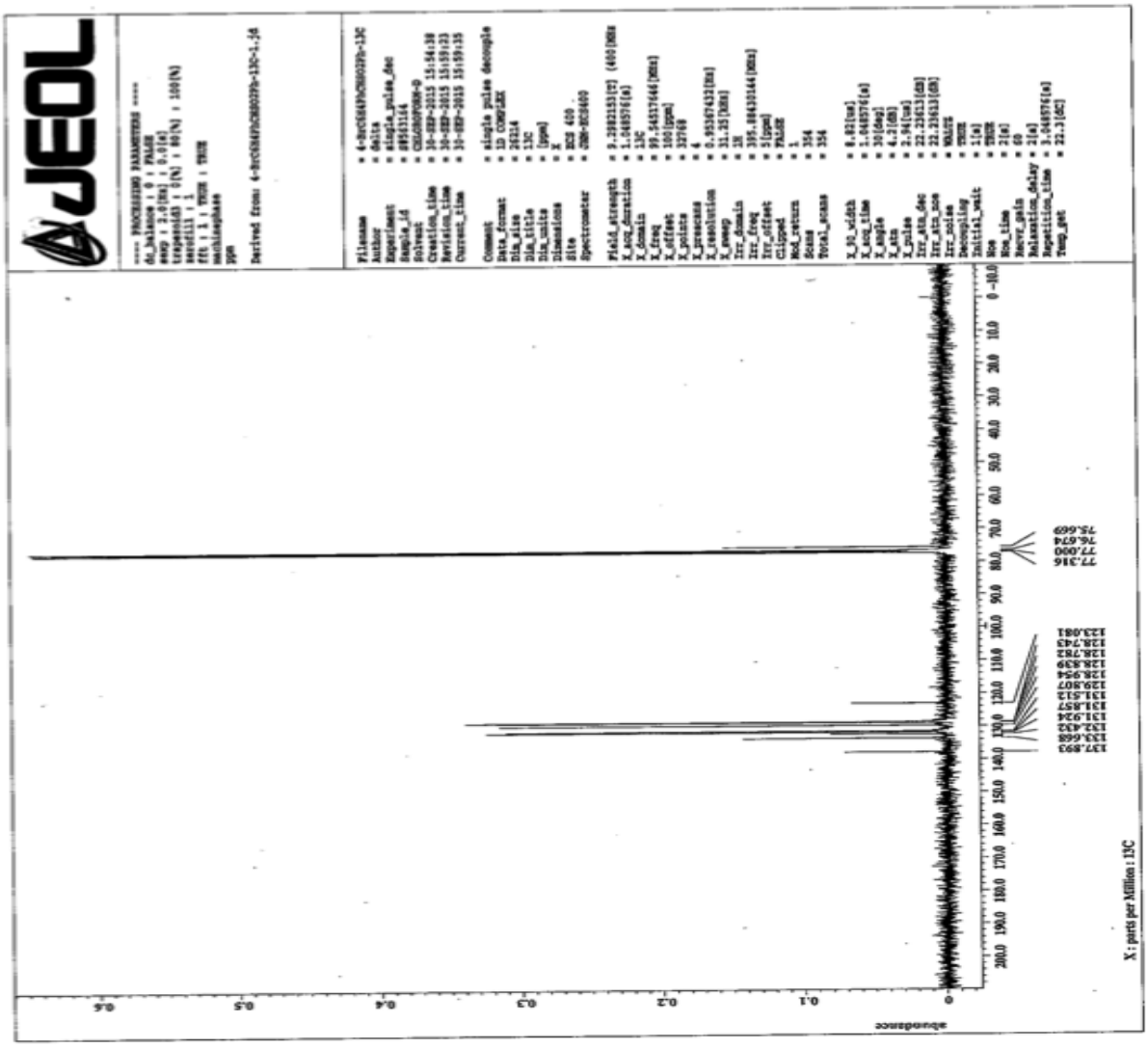
^{1}H-NMR (400 MHz, $CDCl_3$) of 1h



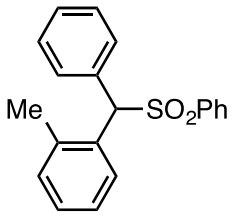


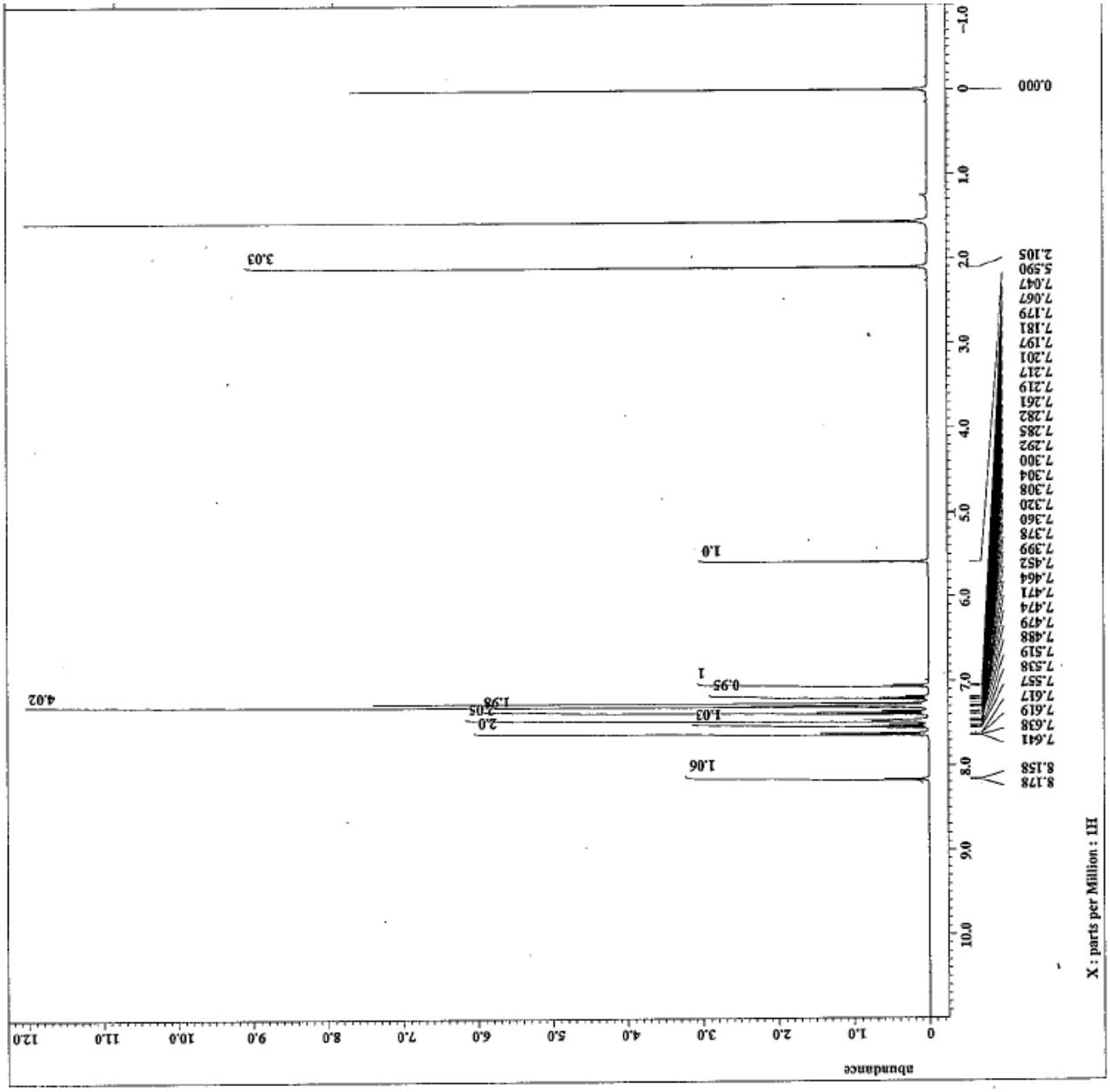
^{13}C-NMR (100 MHz, $CDCl_3$) of 1h



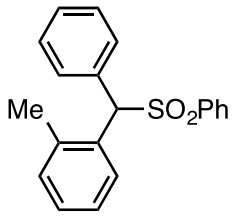


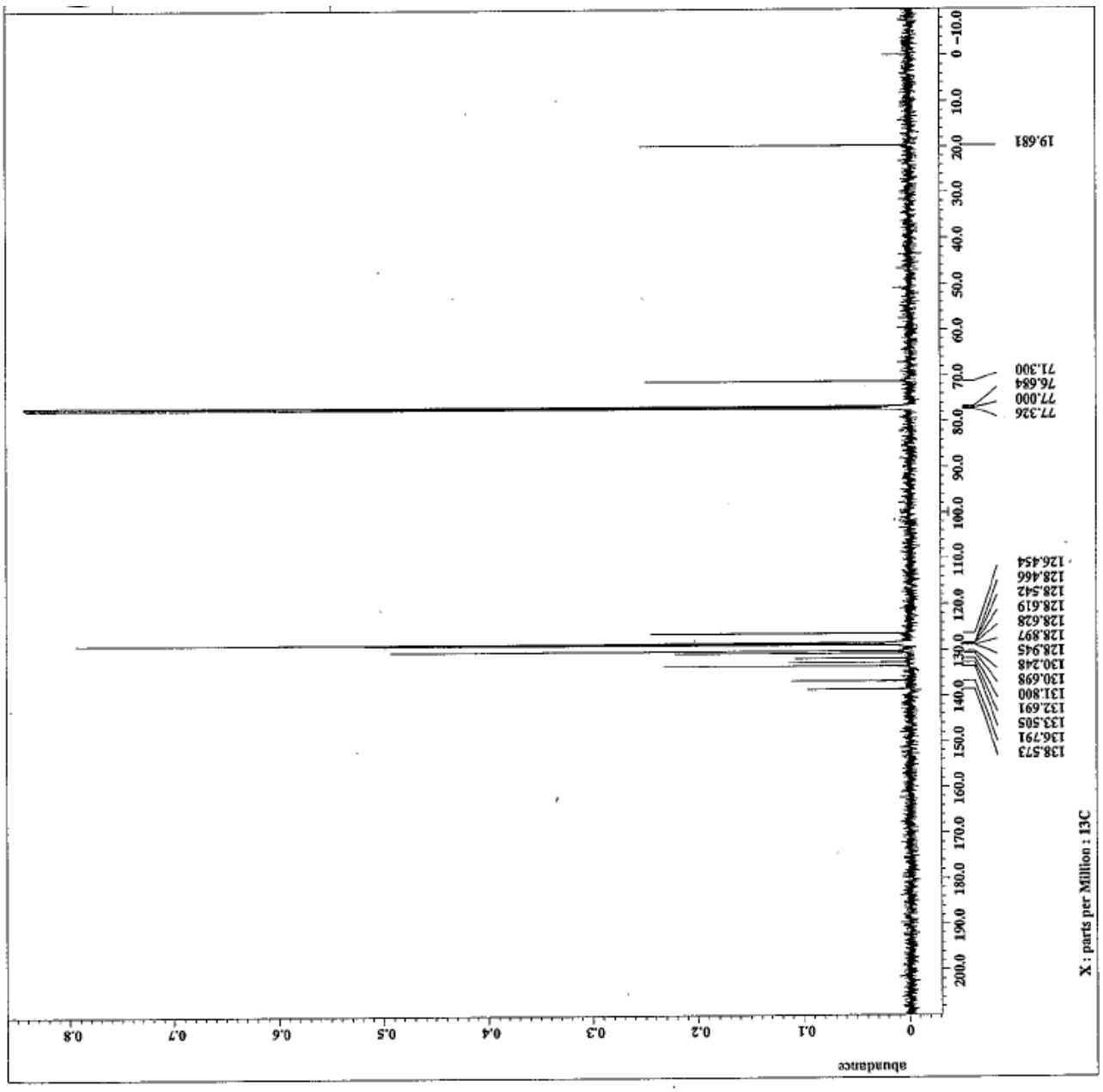
^{1}H-NMR (400 MHz, $CDCl_3$) of 1i



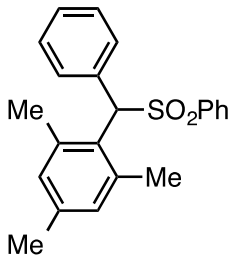


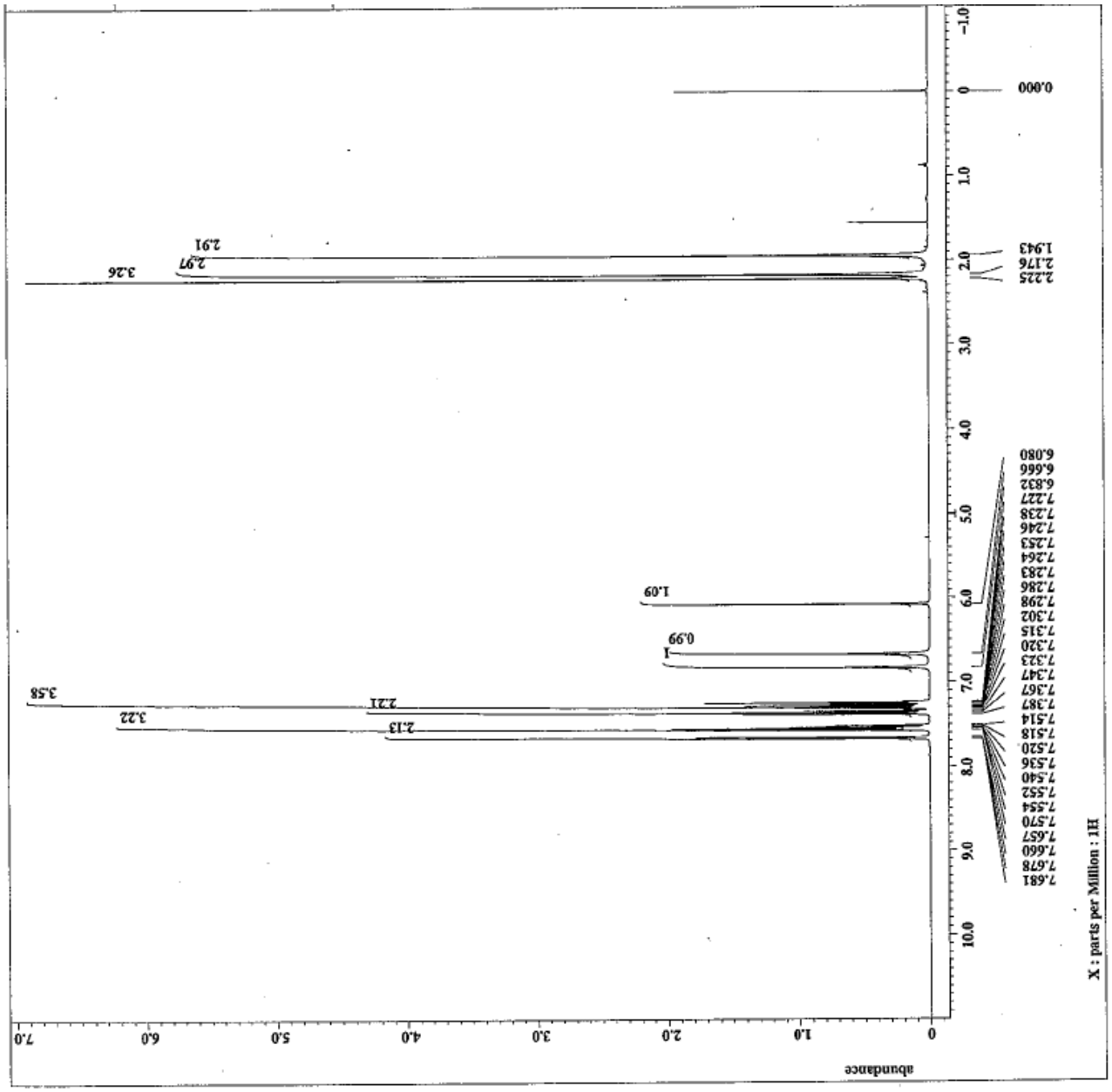
^{13}C-NMR (100 MHz, $CDCl_3$) of 1i



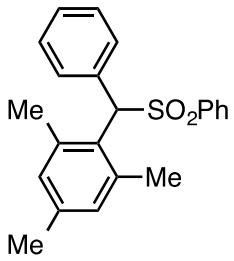


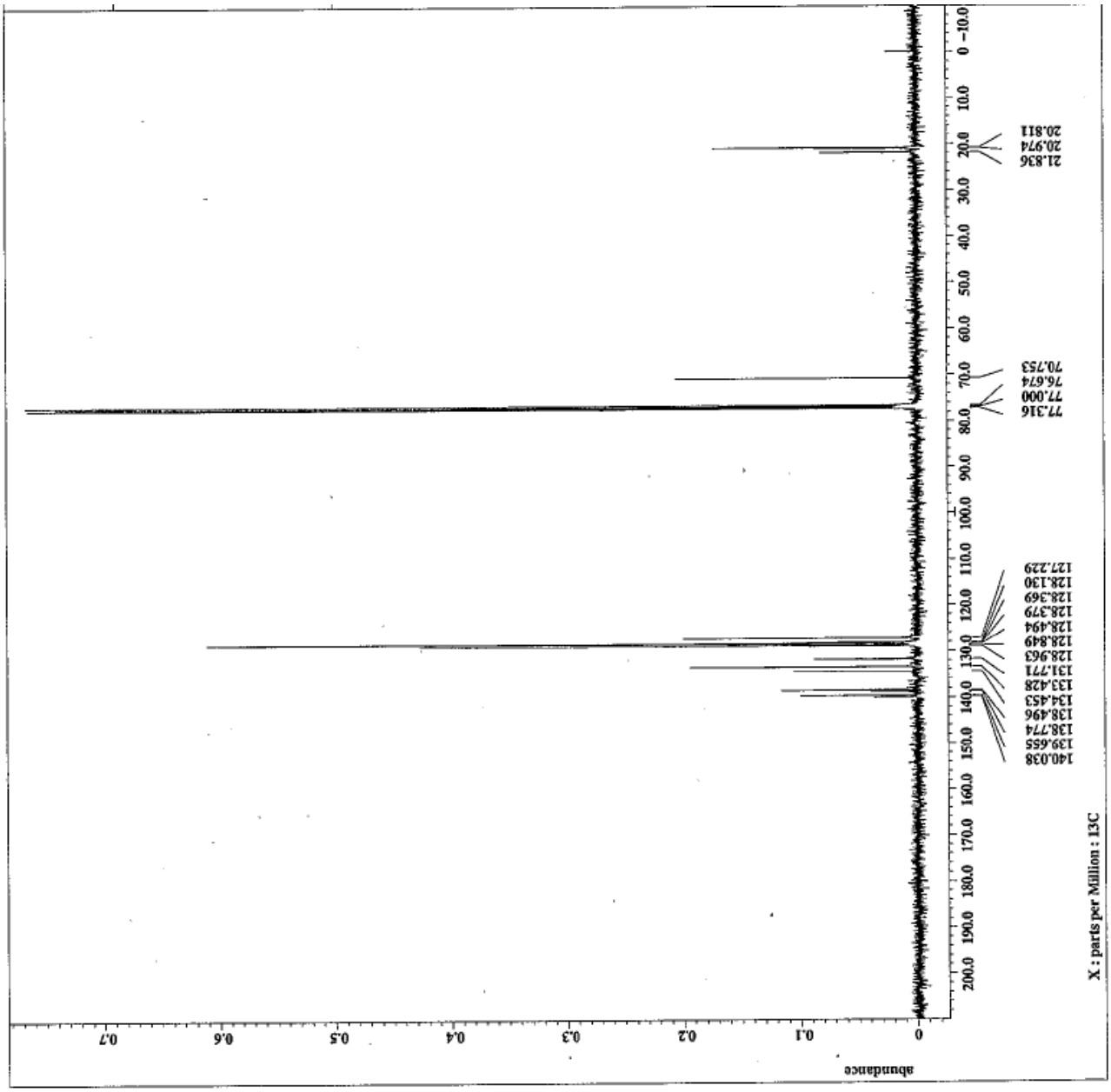
^{1}H-NMR (400 MHz, $CDCl_3$) of 1j



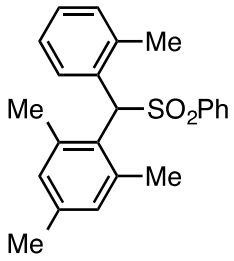


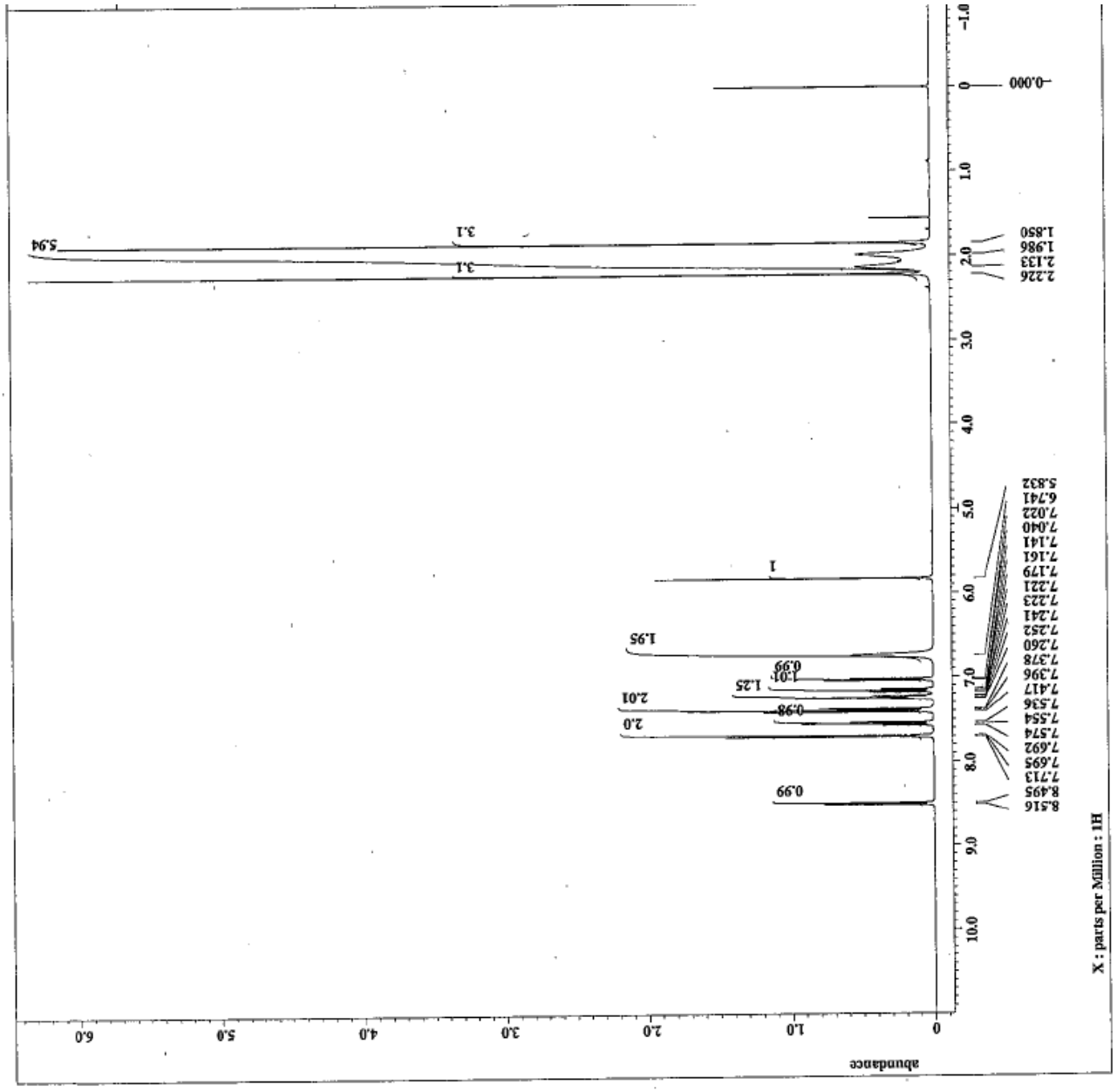
^{13}C-NMR (100 MHz, $CDCl_3$) of 1j



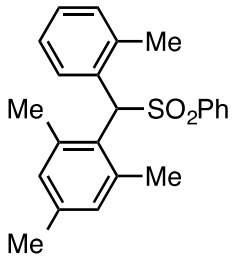


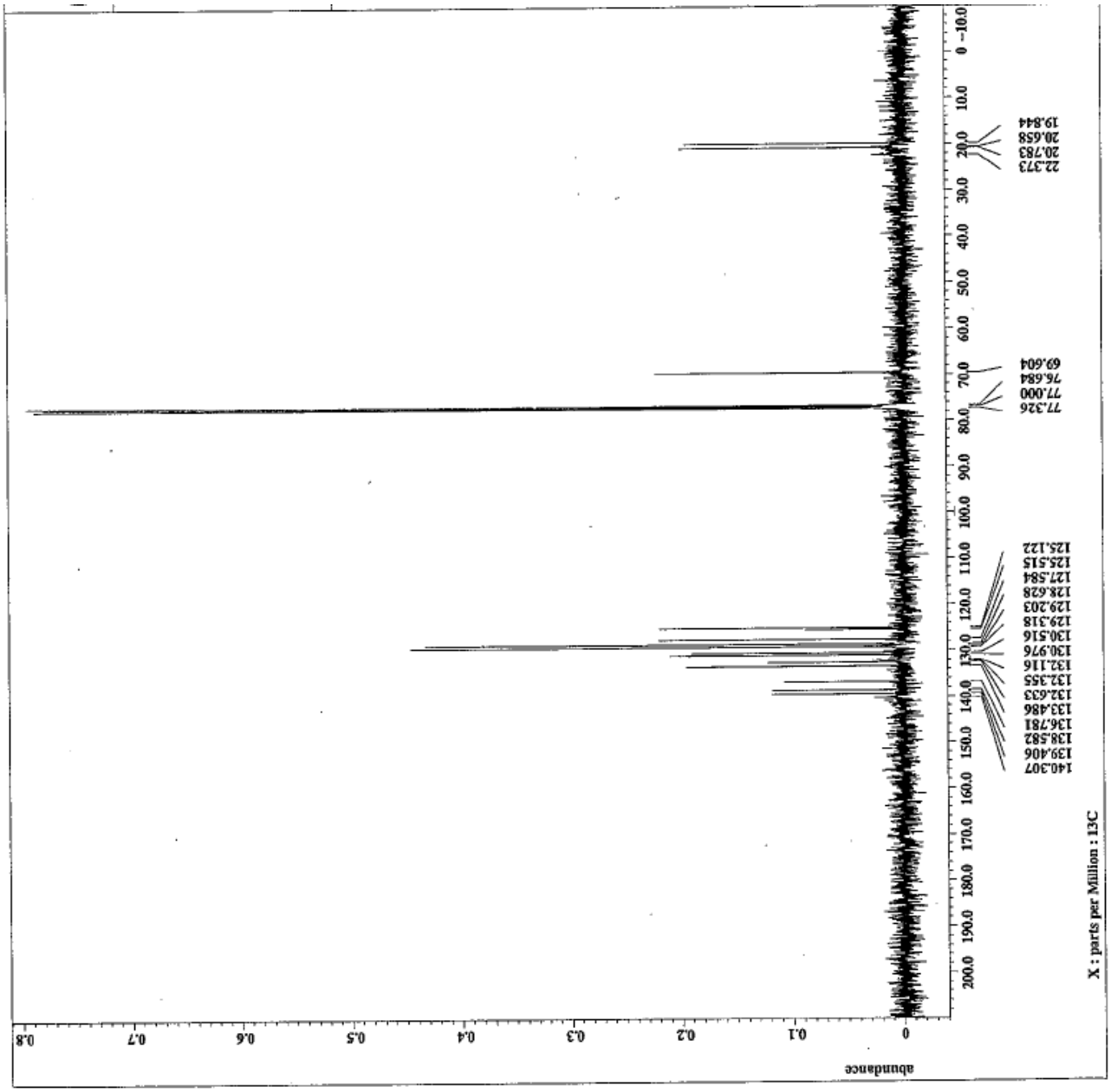
^{1}H-NMR (400 MHz, $CDCl_3$) of 1k



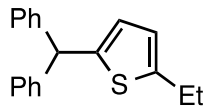


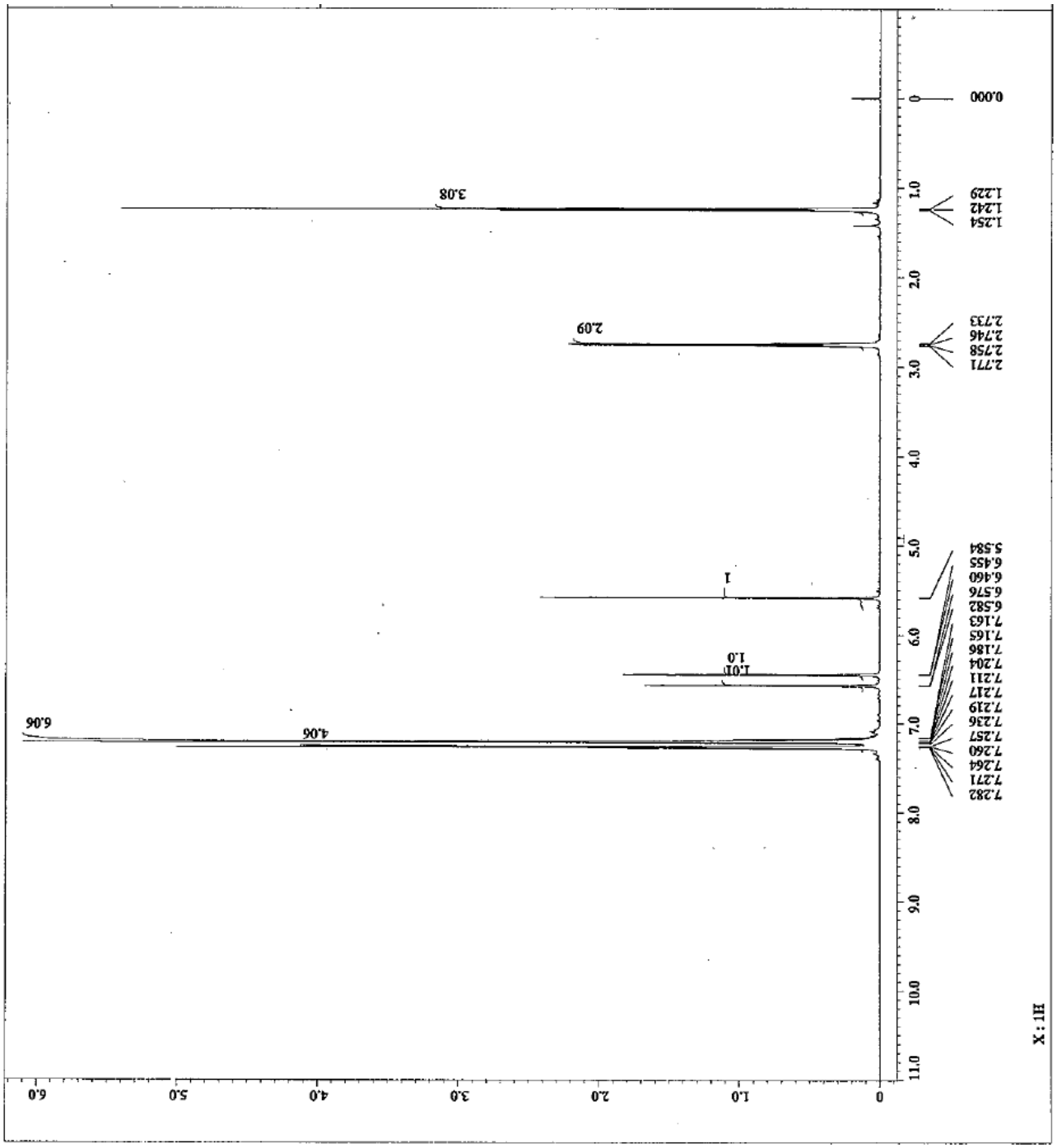
^{13}C-NMR (100 MHz, $CDCl_3$) of 1k



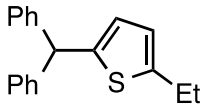


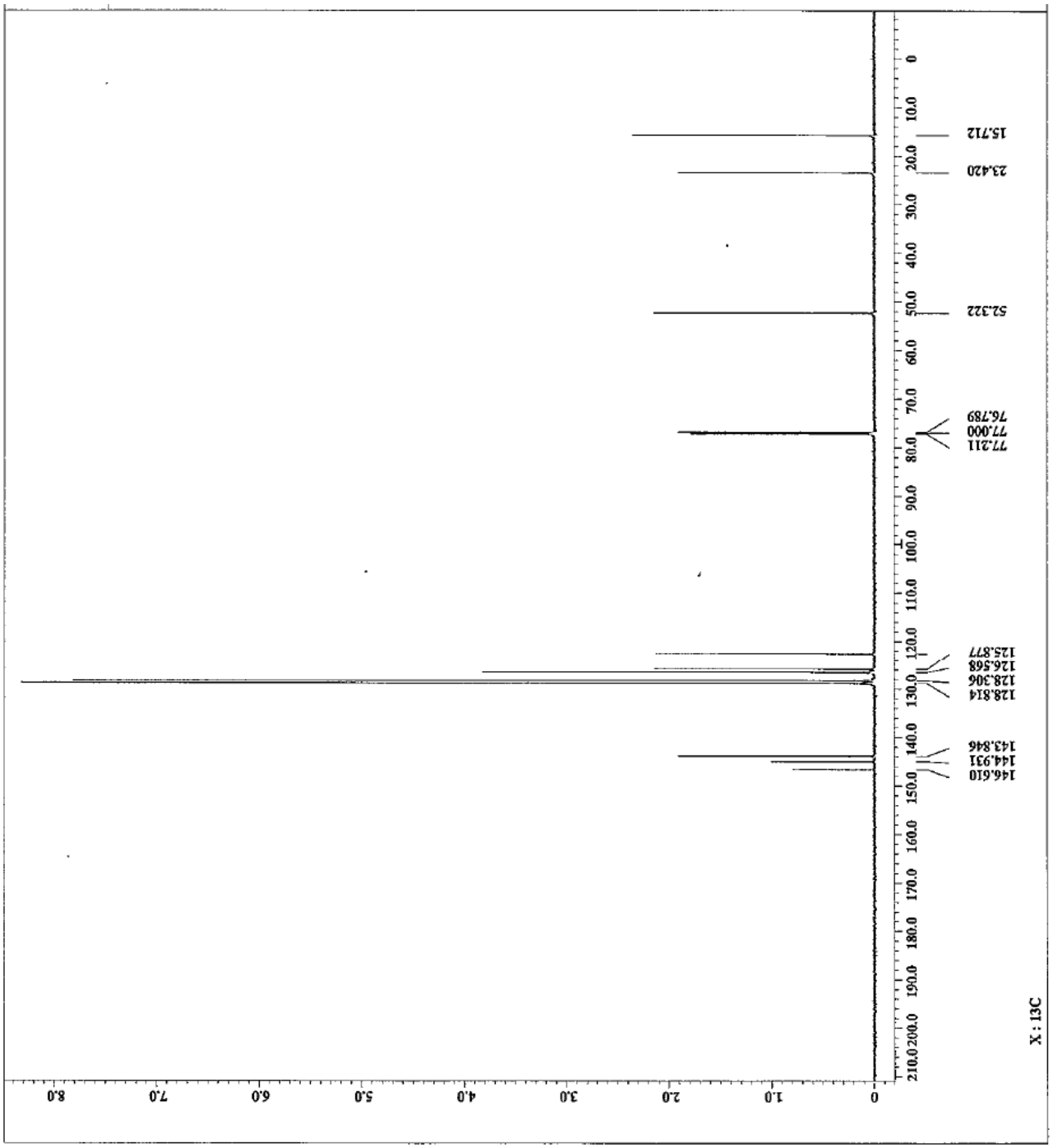
^{1}H-NMR (600 MHz, $CDCl_3$) of 3aa



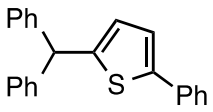


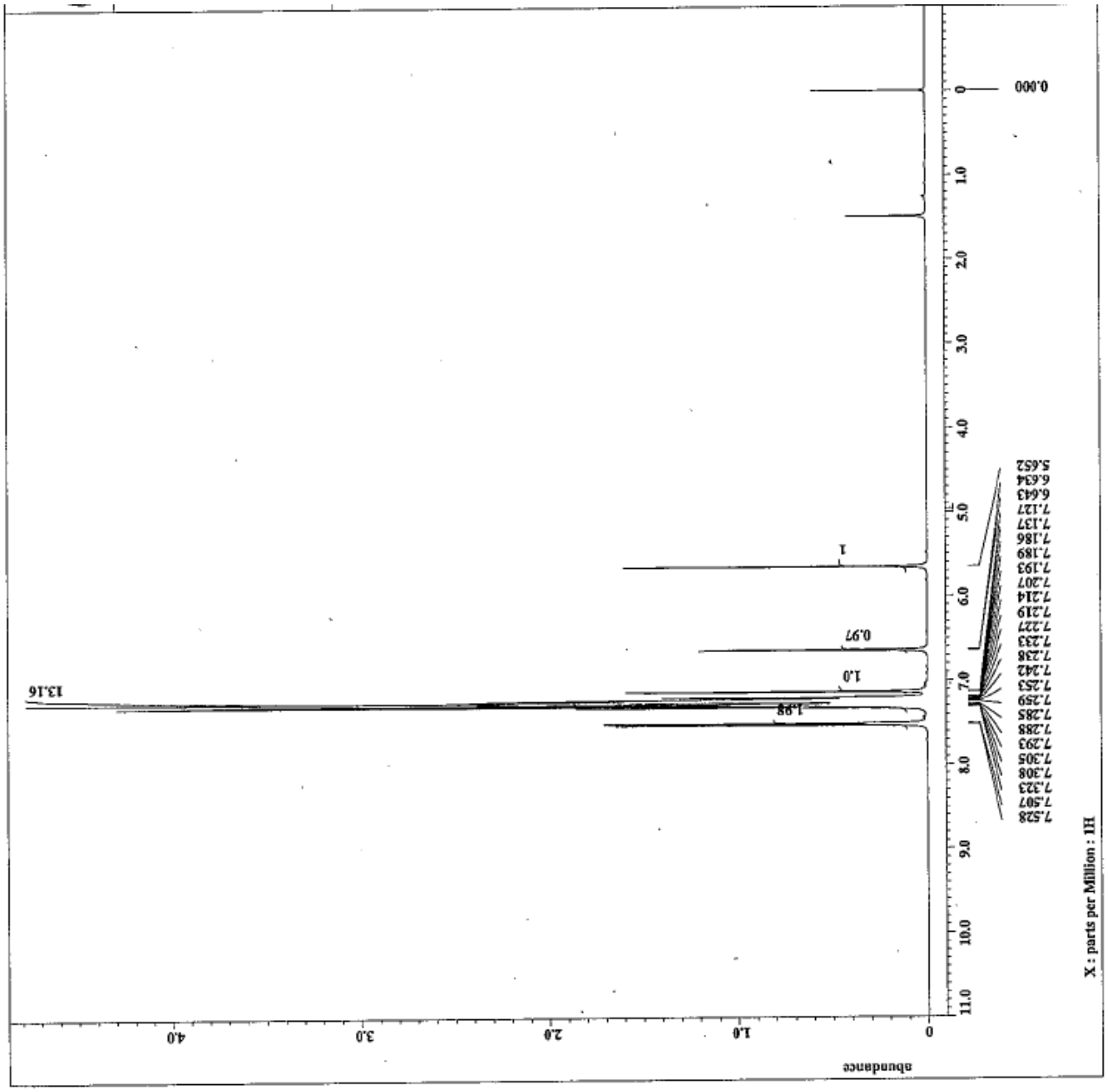
^{13}C-NMR (150 MHz, $CDCl_3$) of 3aa



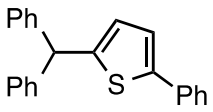


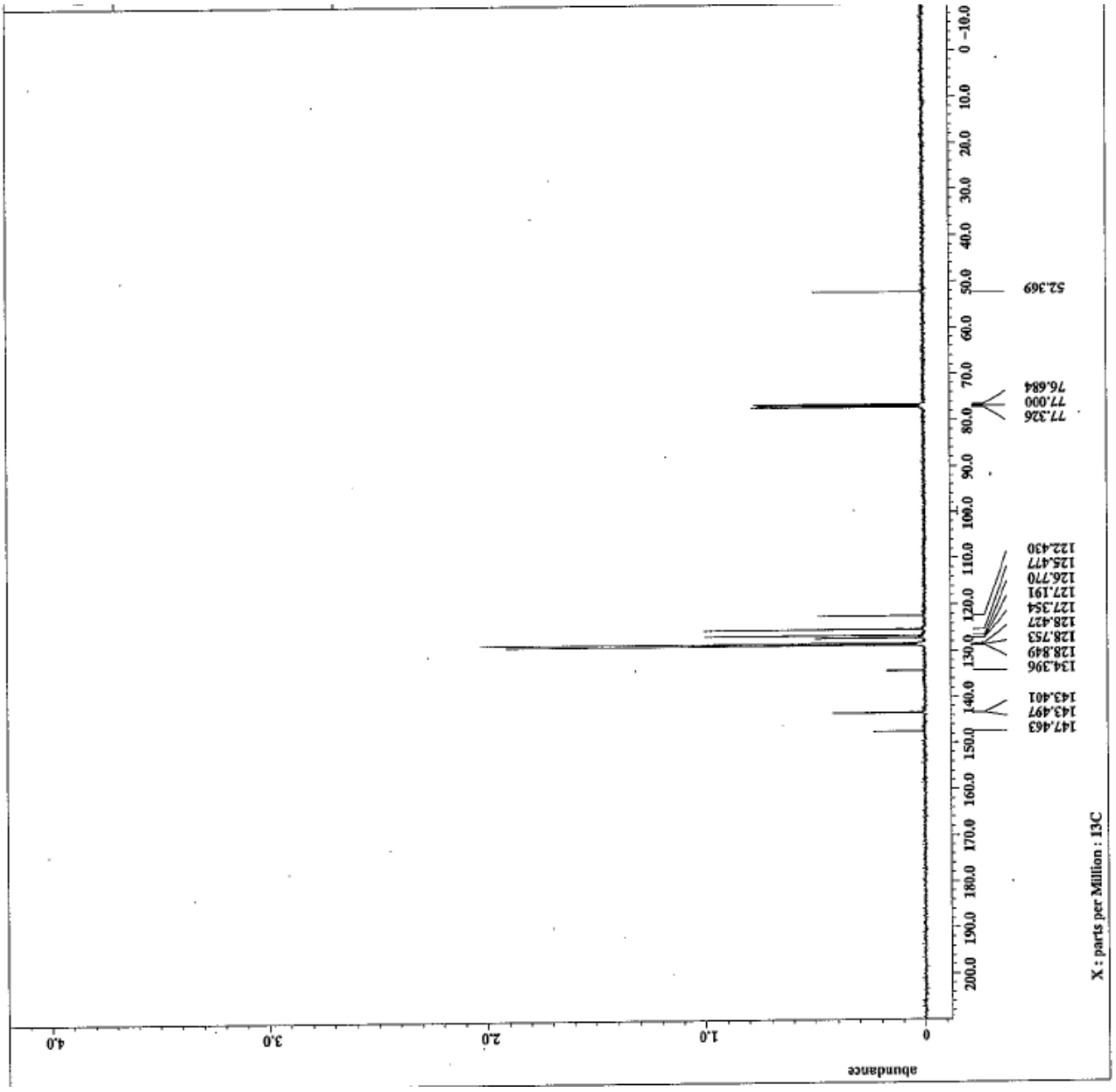
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ab



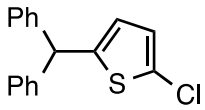


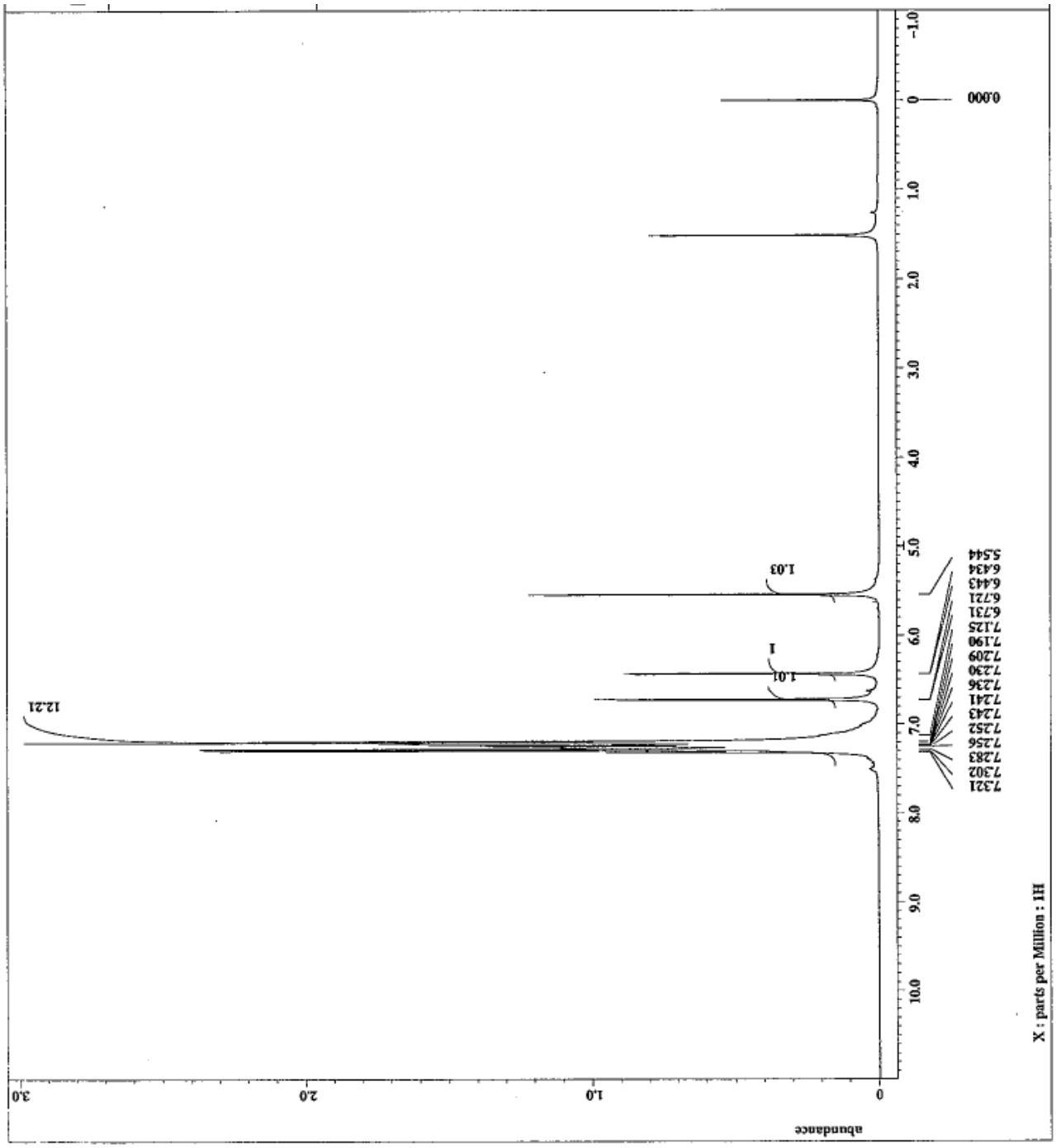
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ab



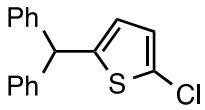


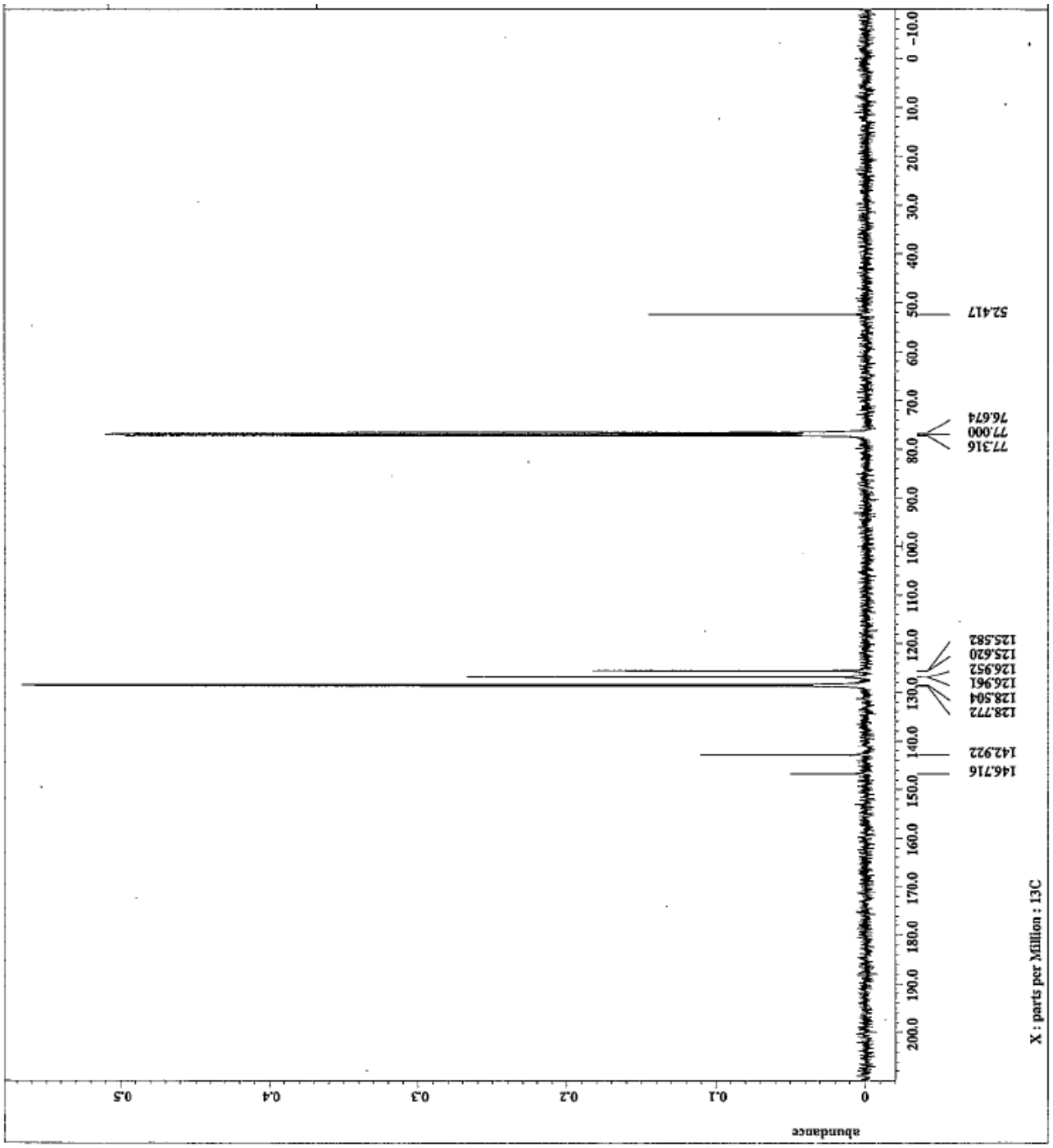
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ac



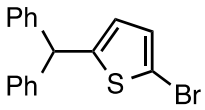


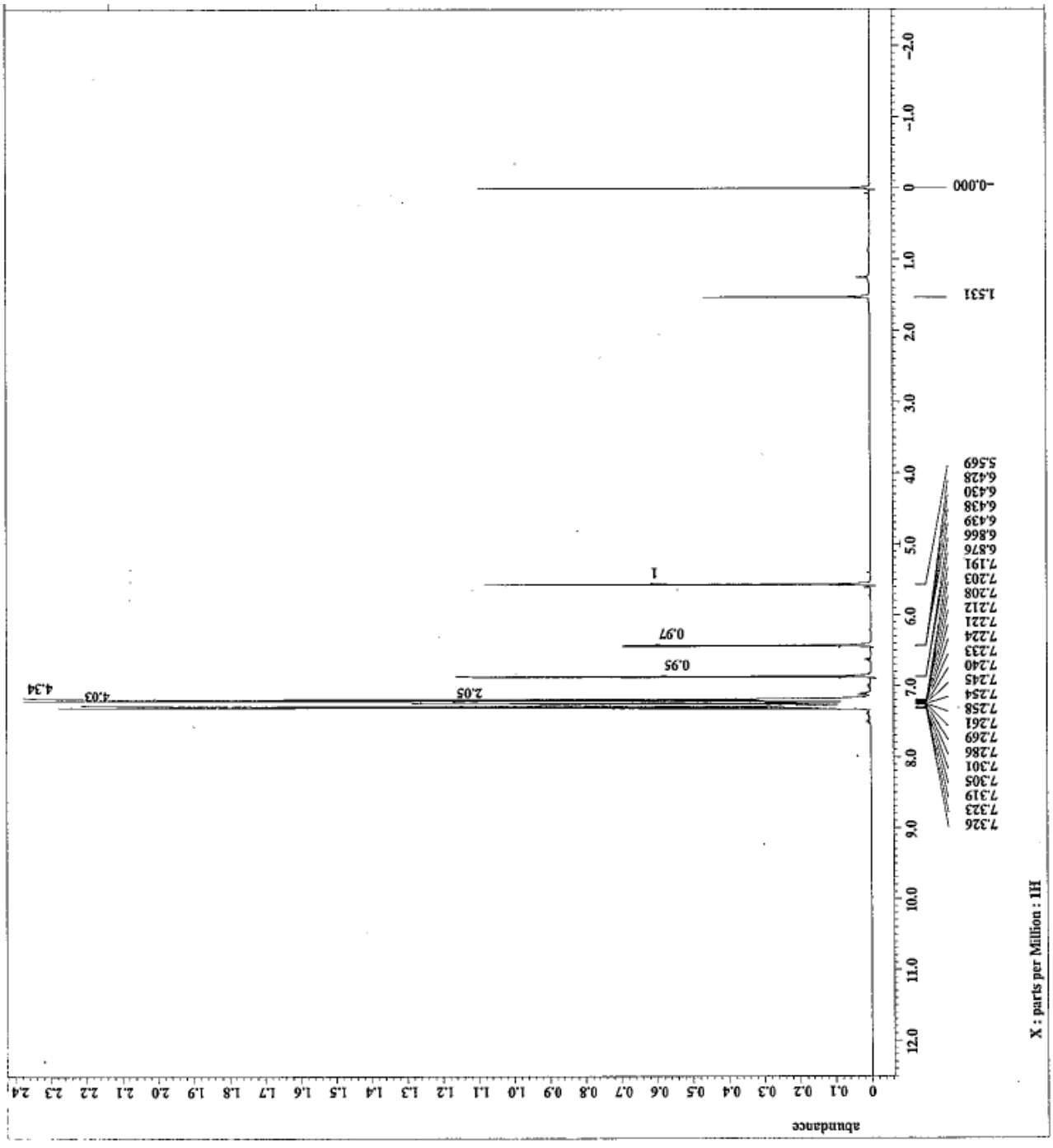
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ac



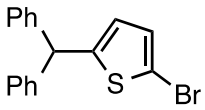


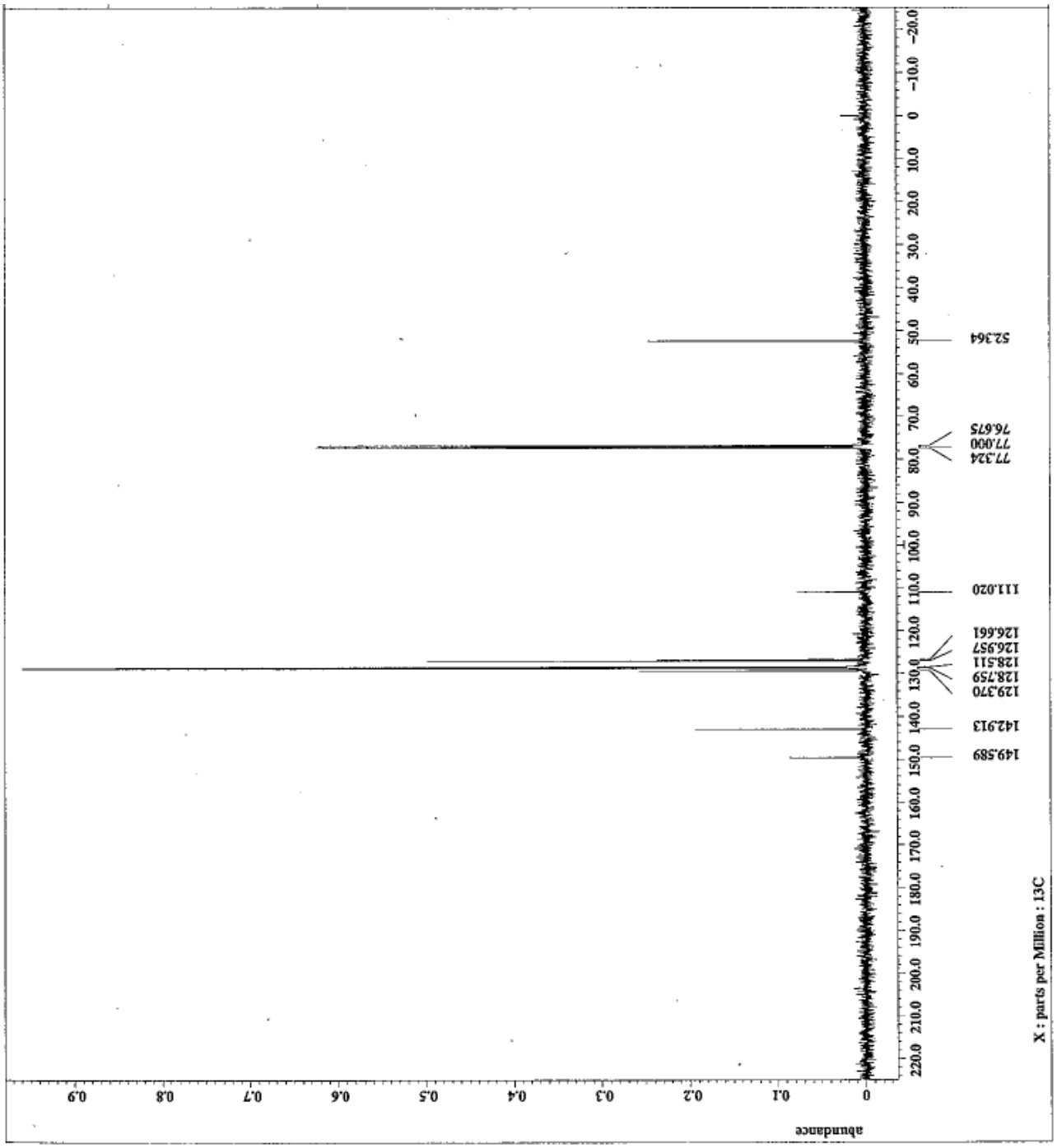
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ad



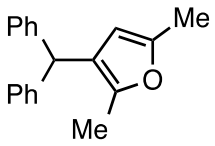


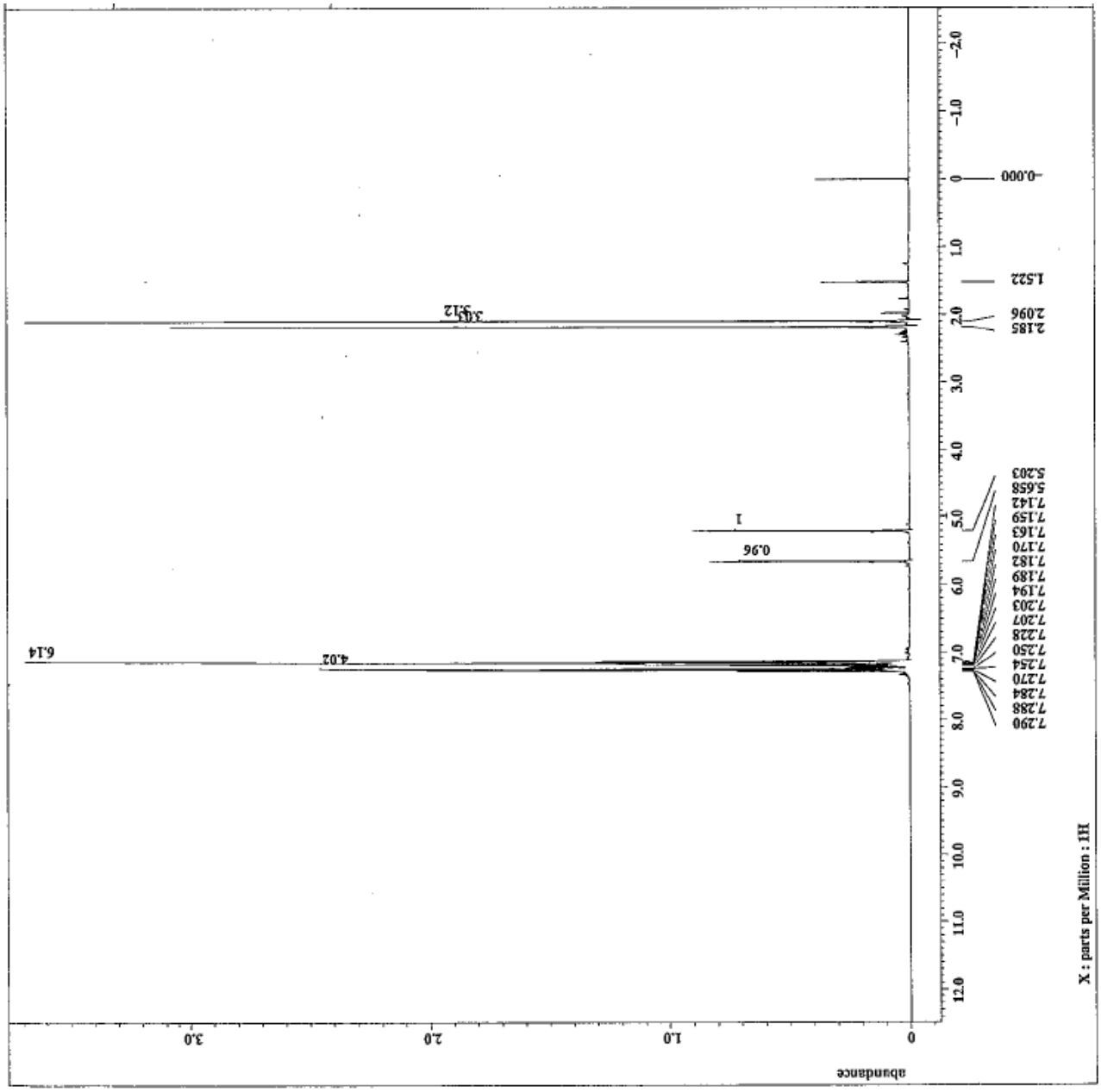
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ad



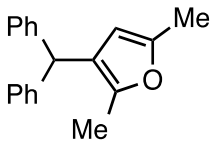


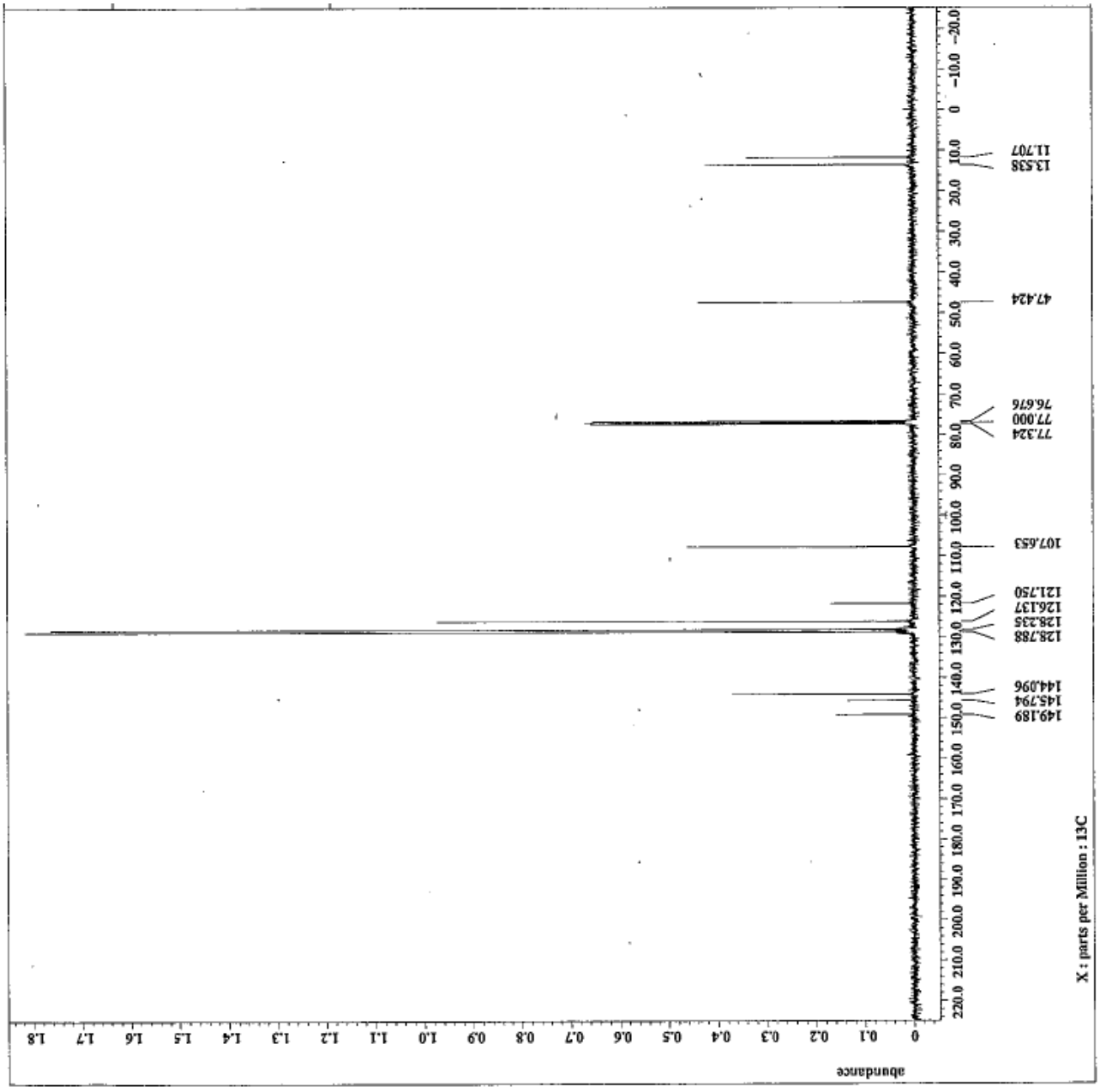
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ae



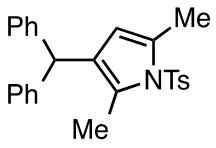


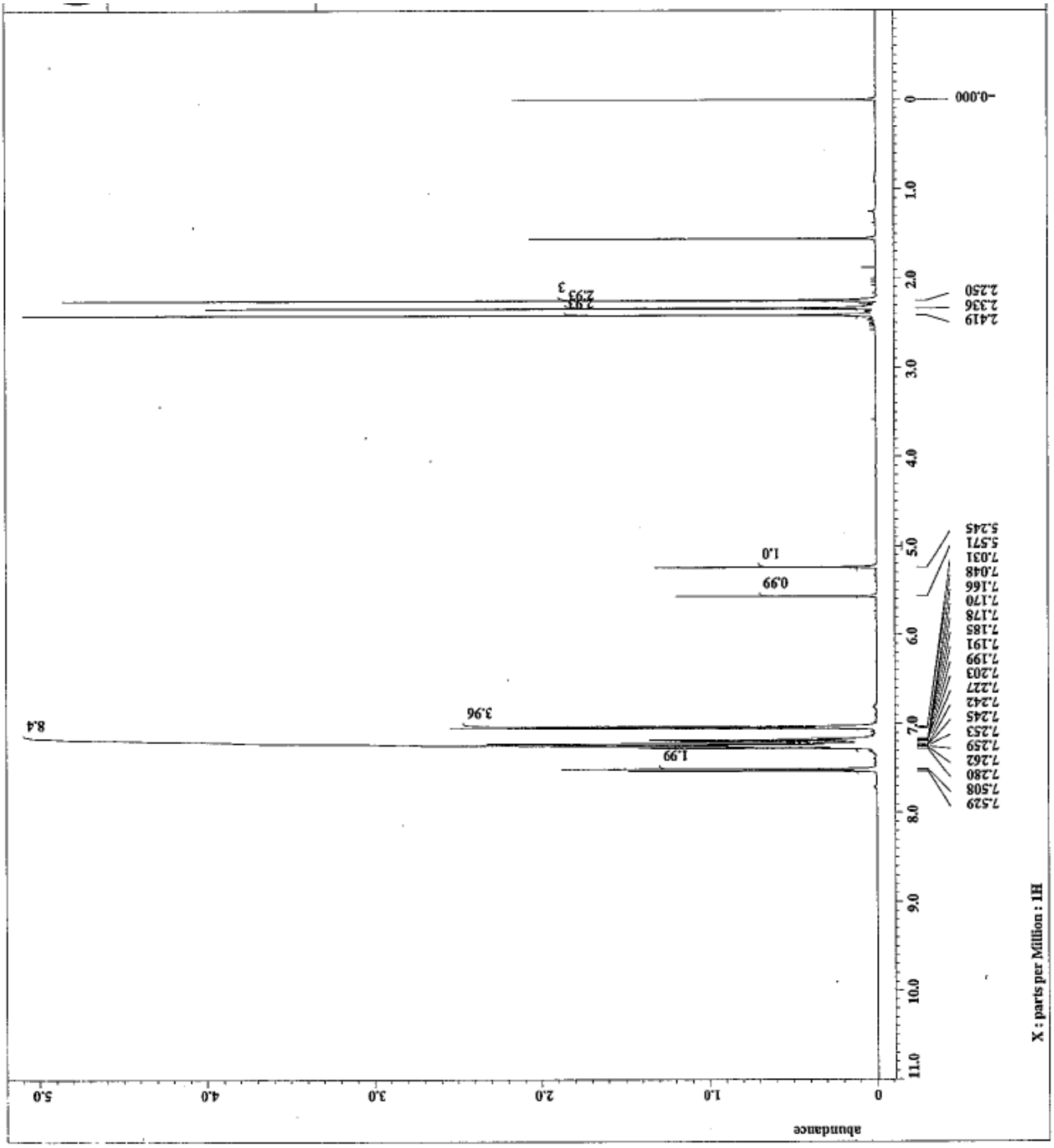
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ae



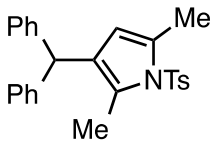


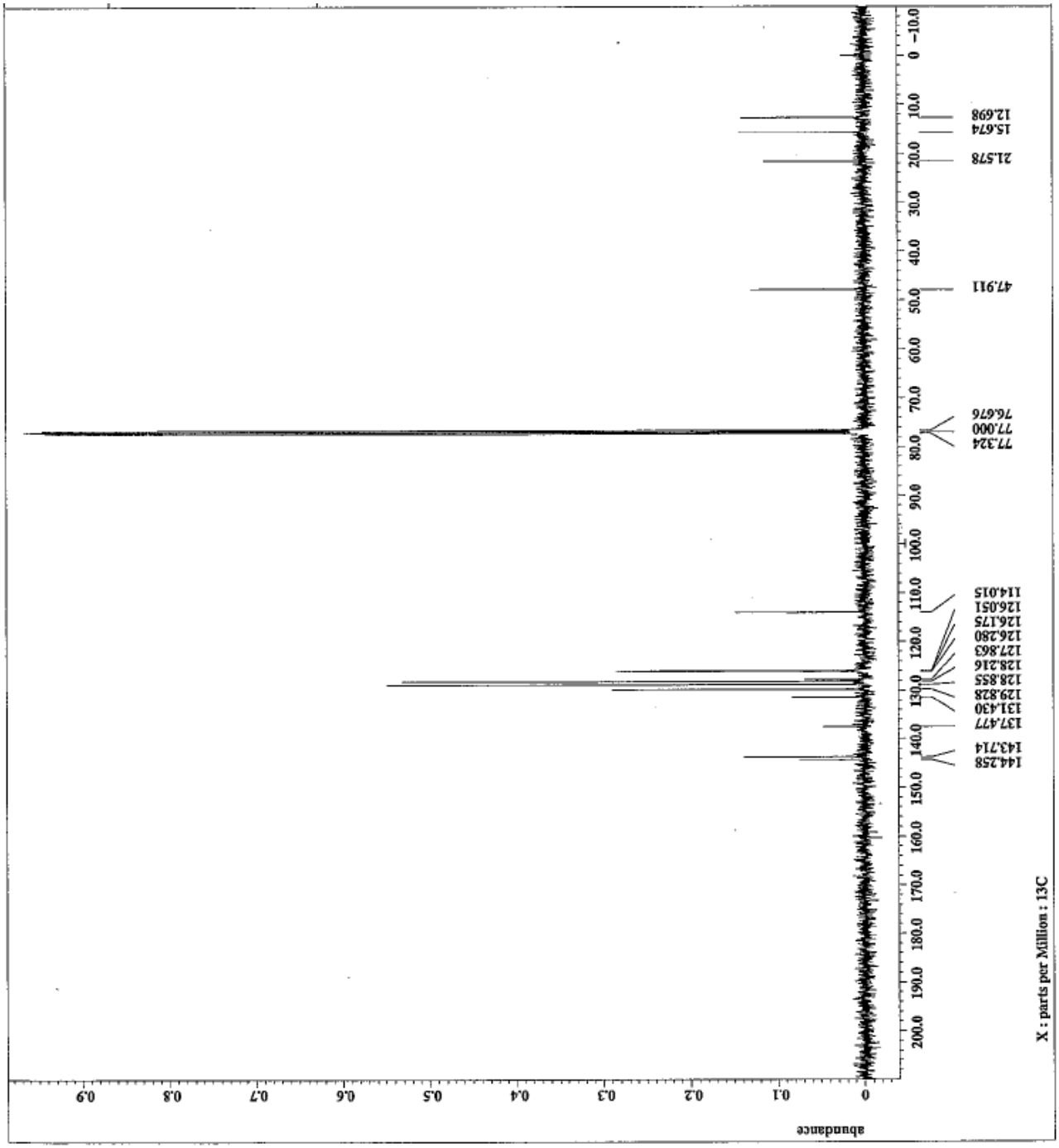
^{1}H-NMR (400 MHz, $CDCl_3$) of 3af



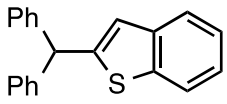


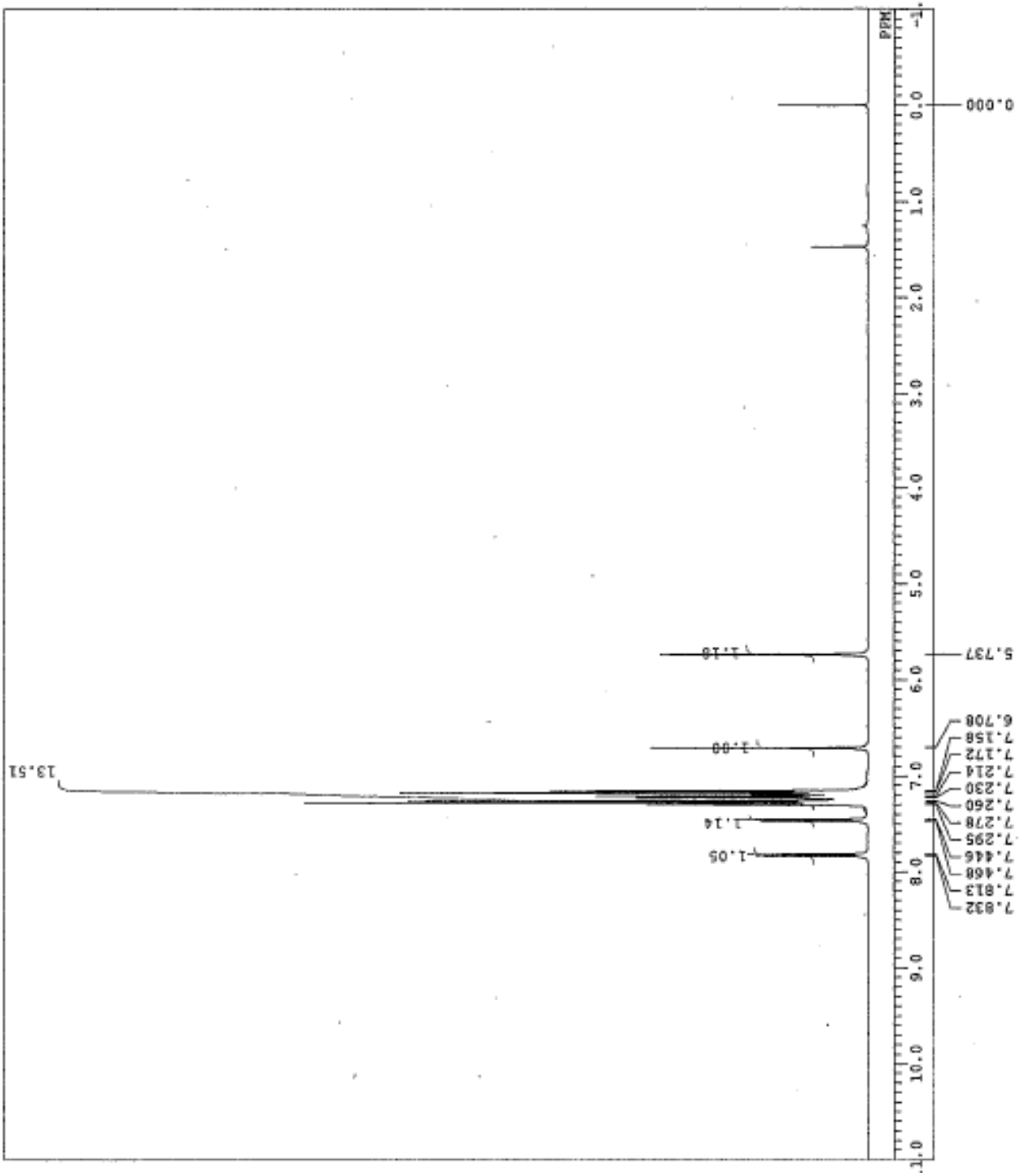
^{13}C-NMR (100 MHz, $CDCl_3$) of 3af



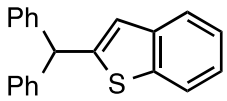


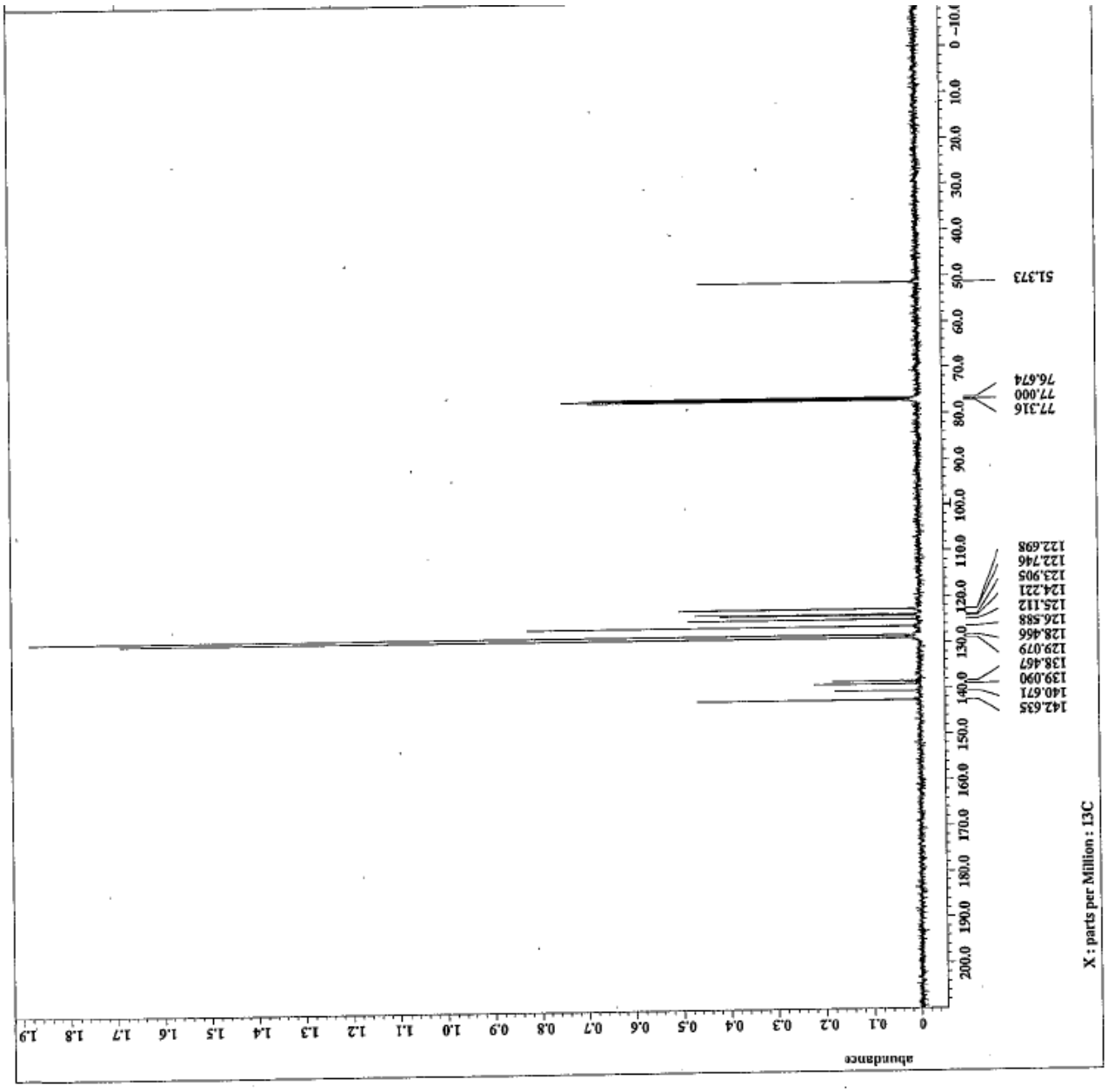
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ag



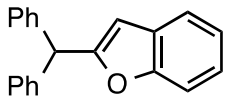


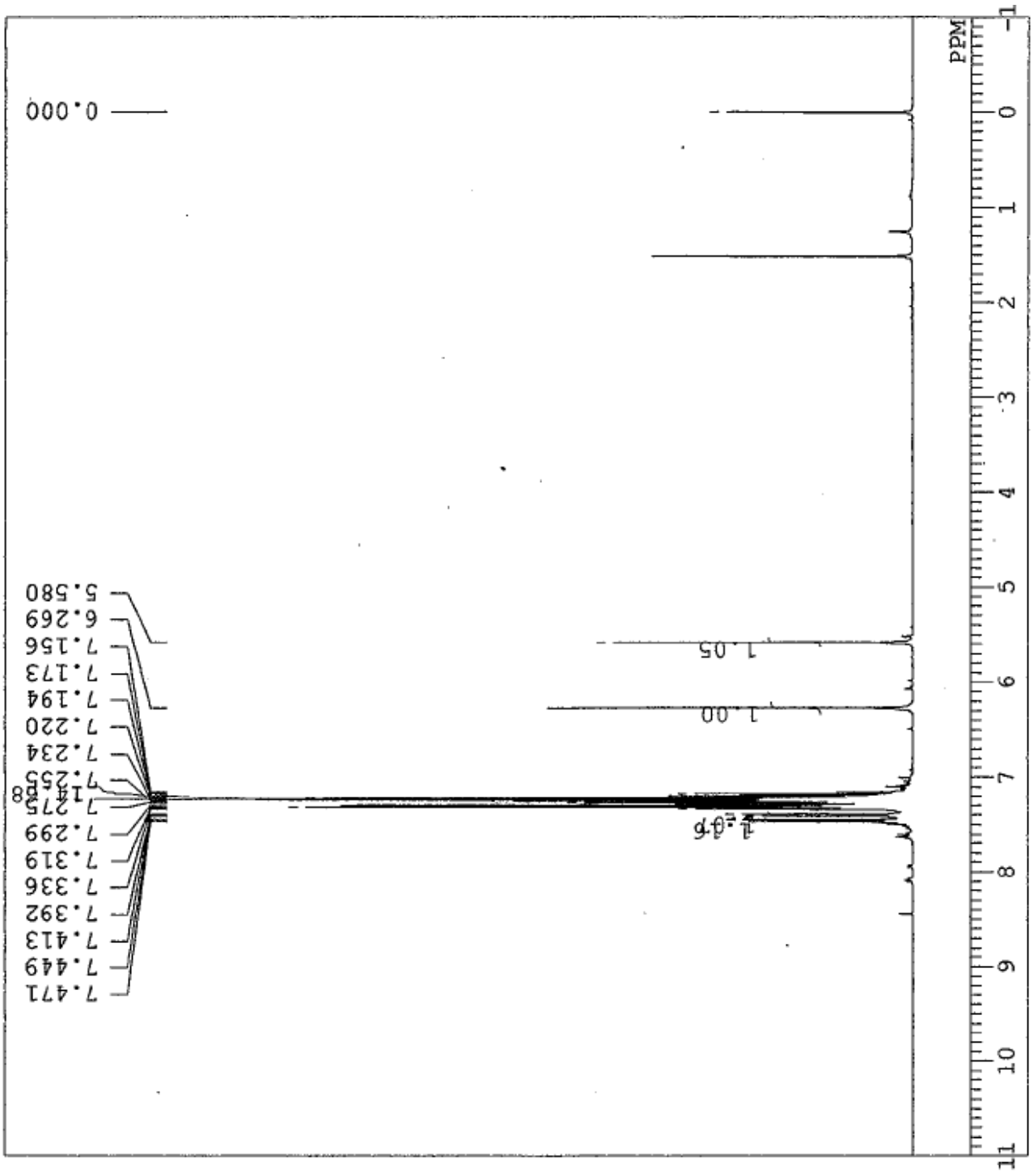
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ag



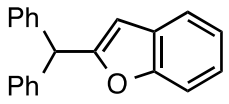


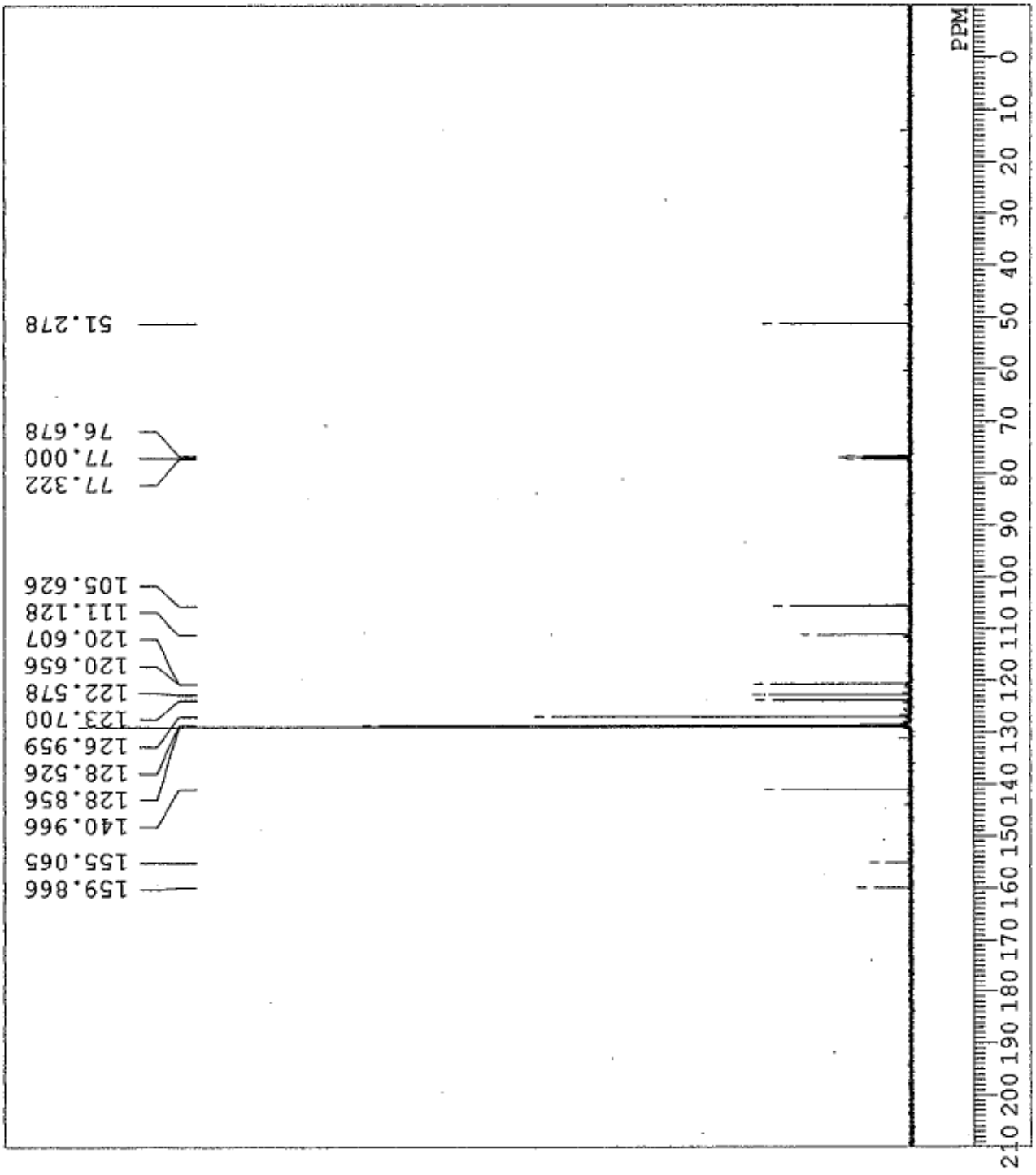
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ah



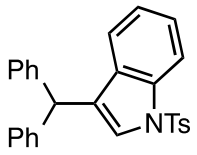


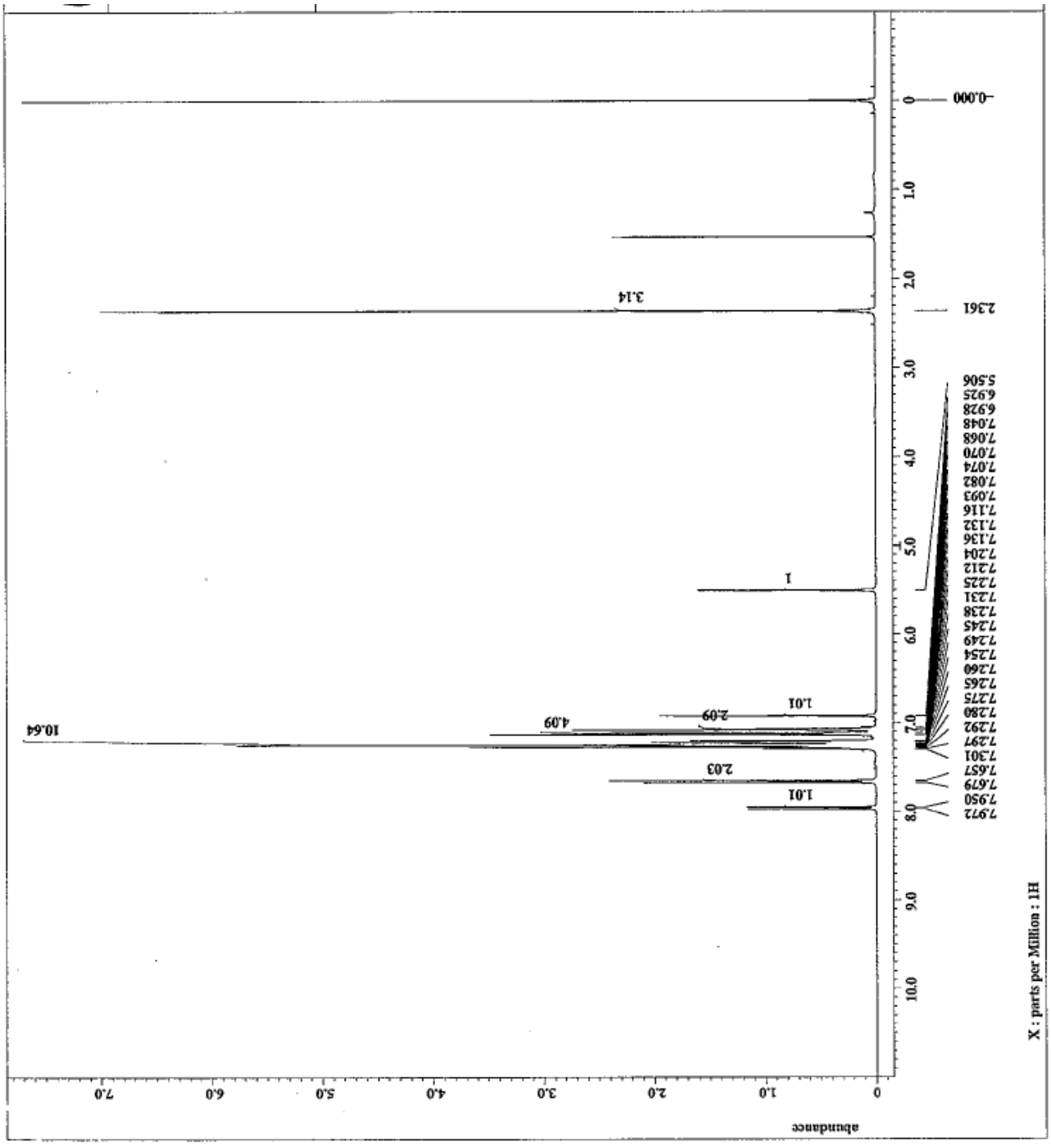
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ah



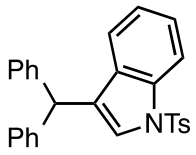


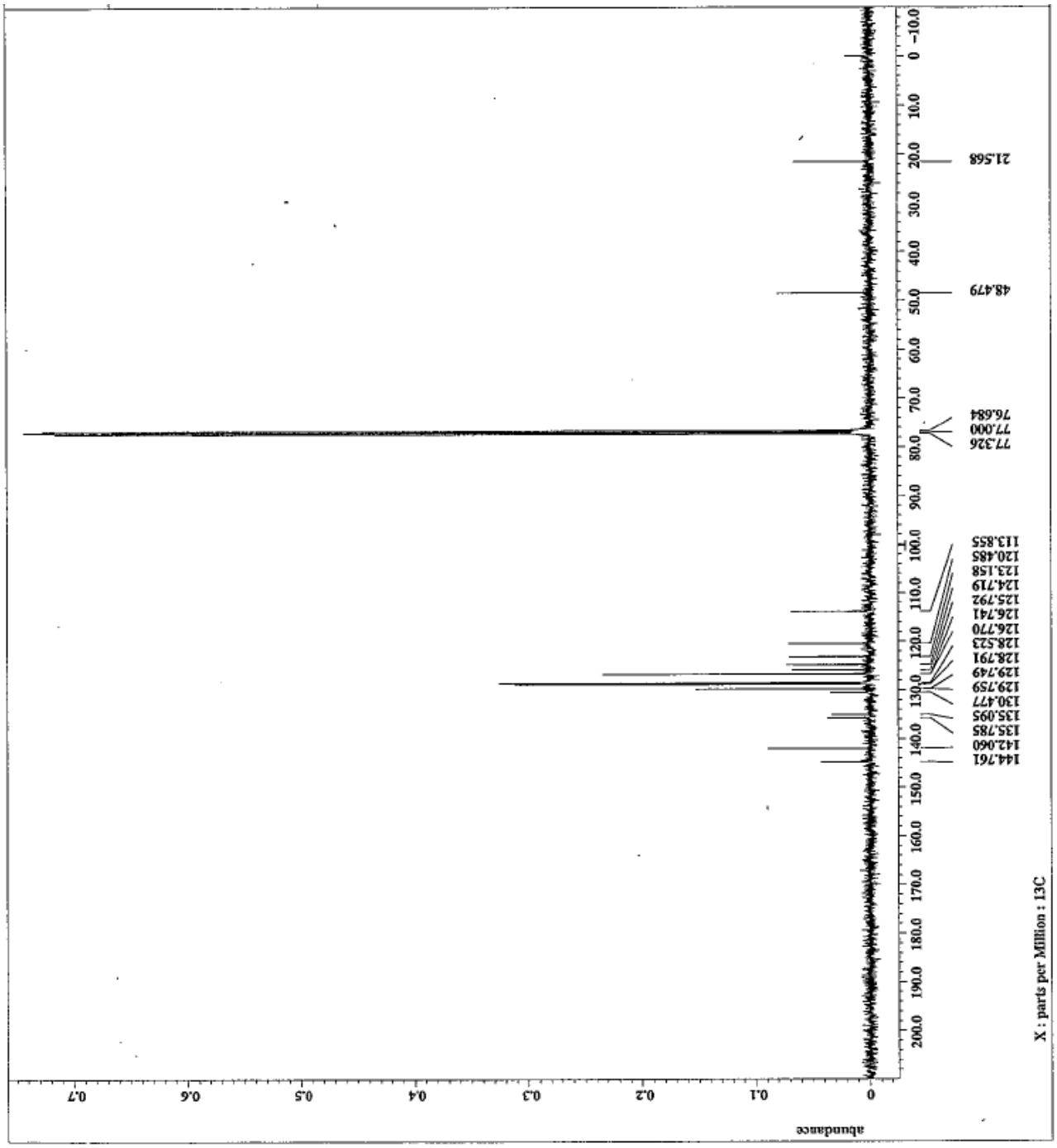
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ai



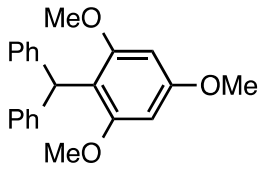


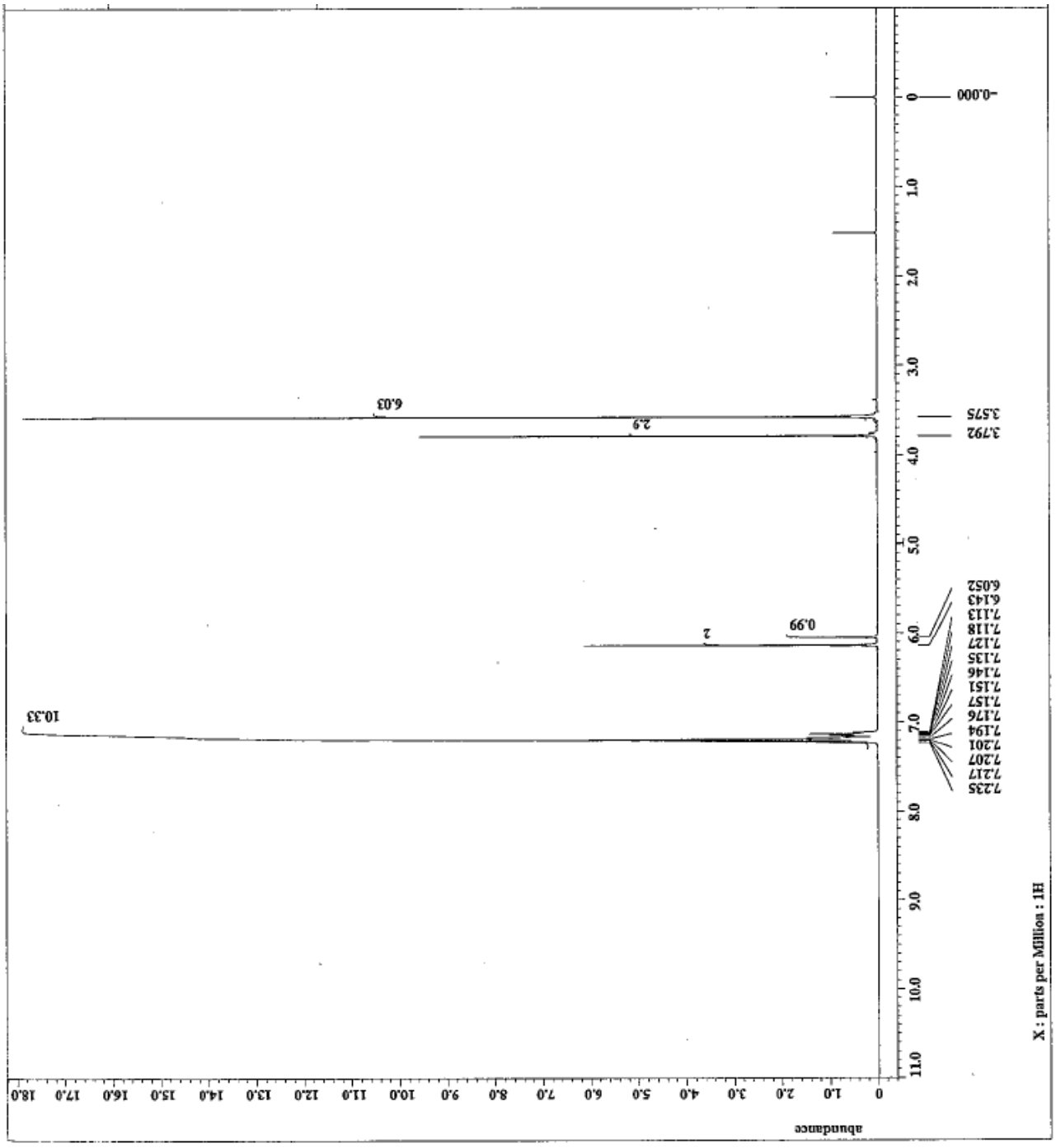
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ai



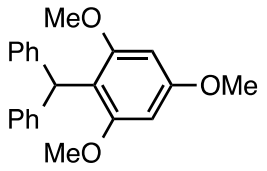


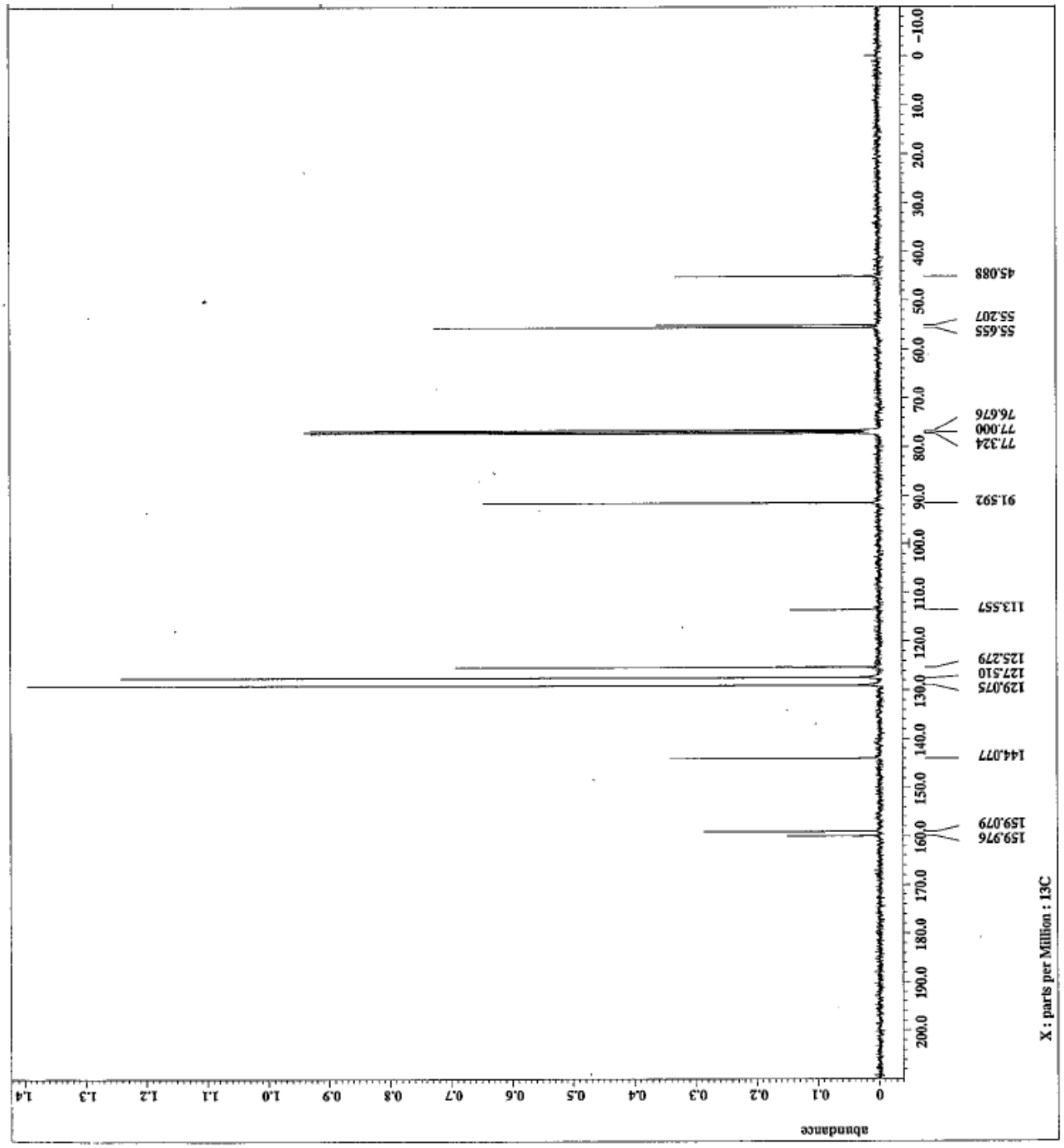
^{1}H-NMR (400 MHz, $CDCl_3$) of 3aj



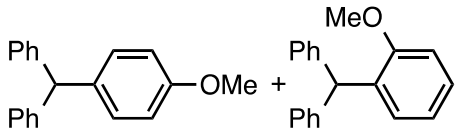


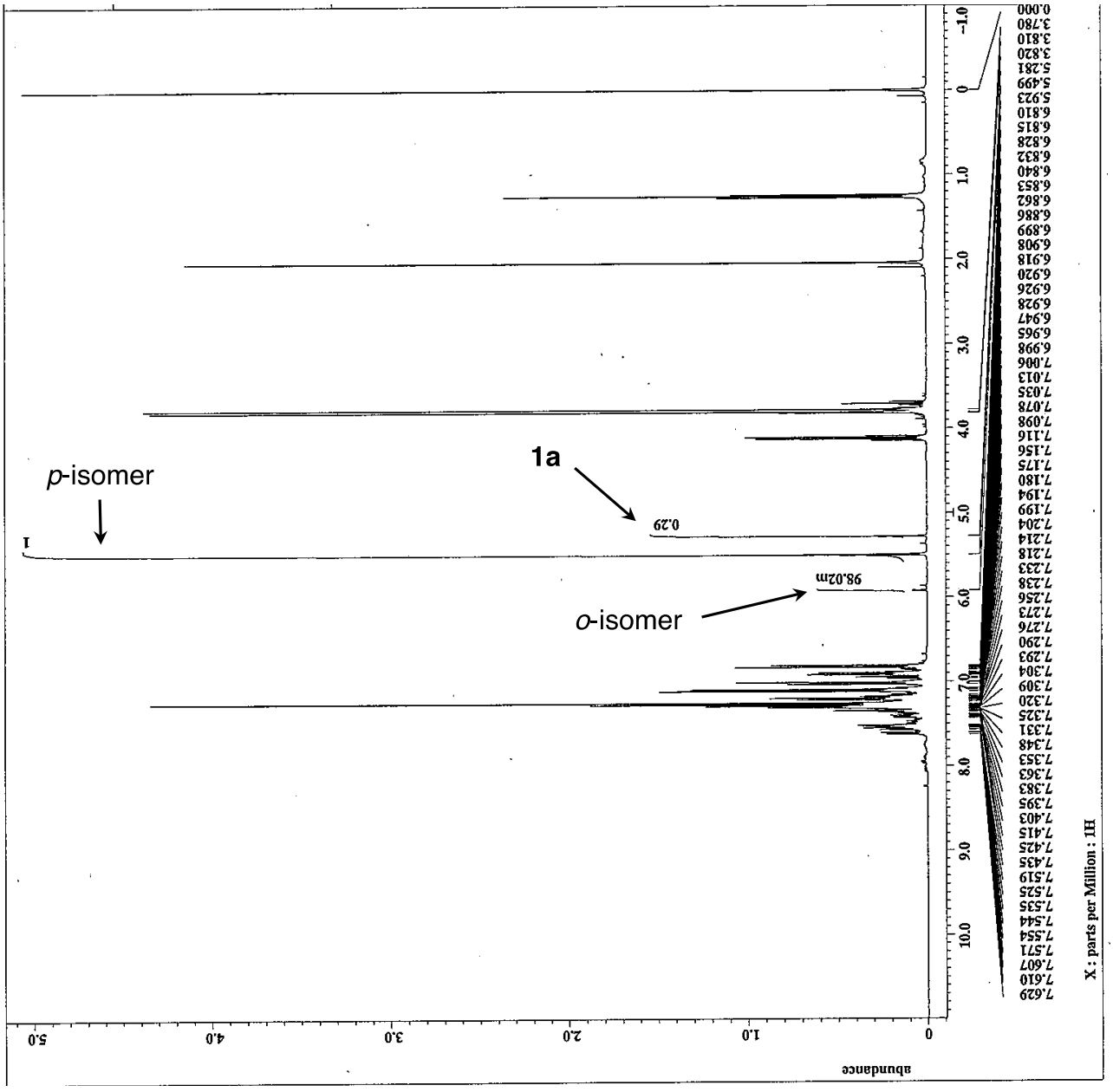
^{13}C-NMR (100 MHz, $CDCl_3$) of 3aj



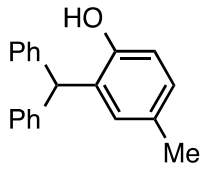


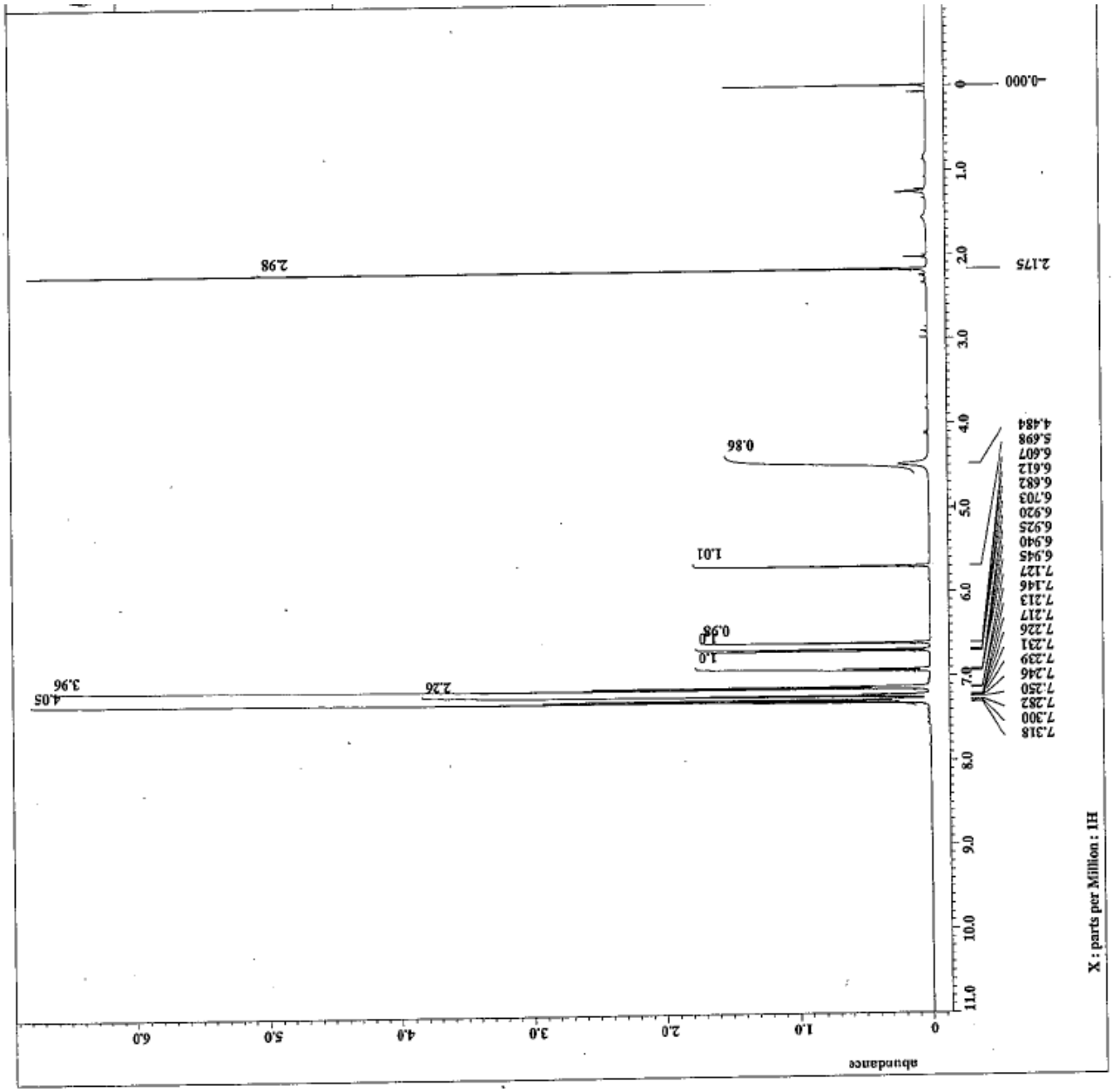
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ak (*p*- and *o*-isomer, crude)



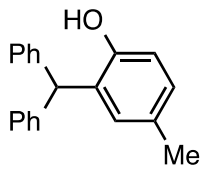


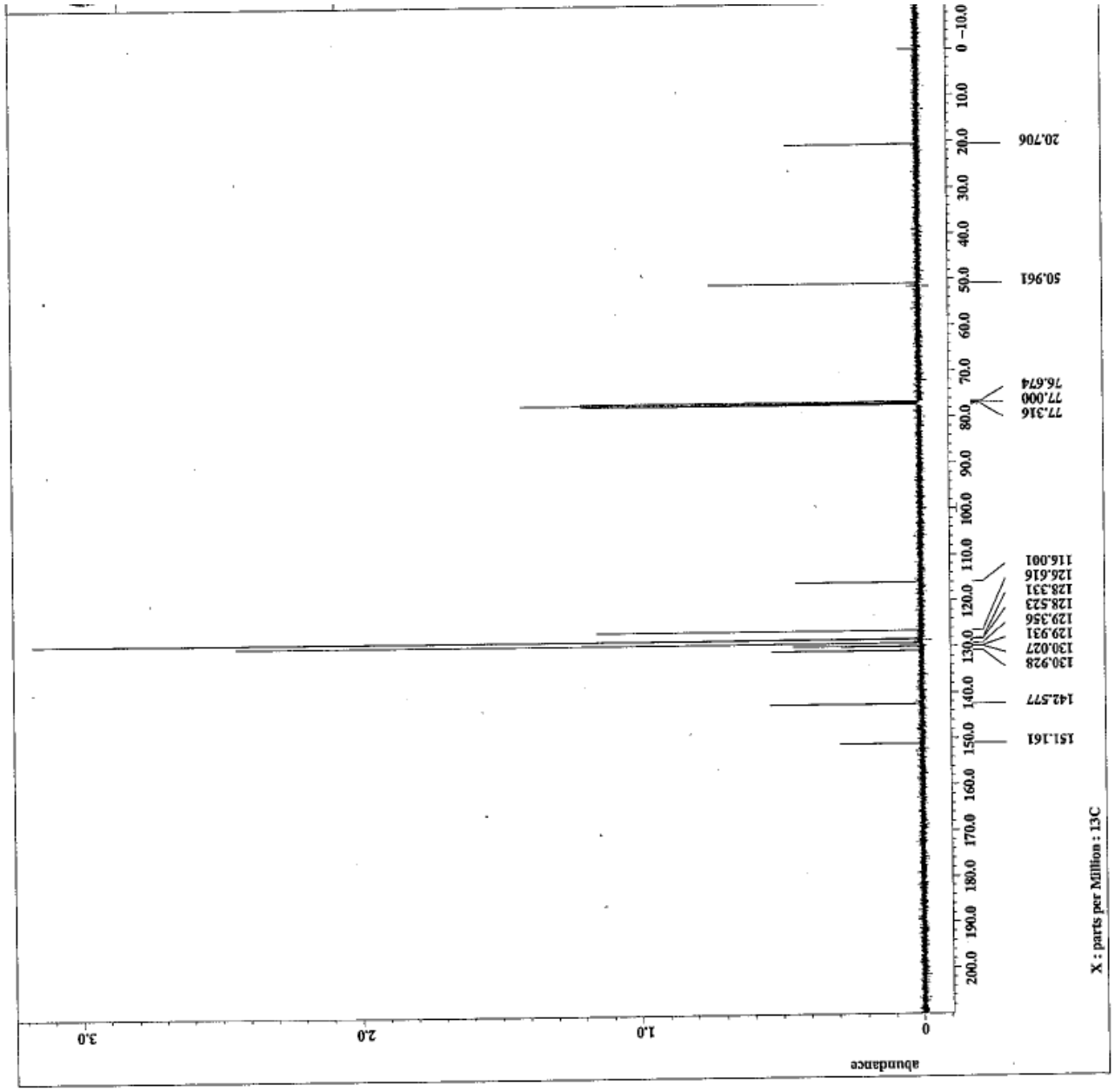
^{1}H-NMR (400 MHz, $CDCl_3$) of 3am



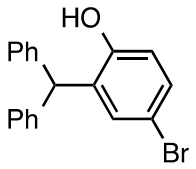


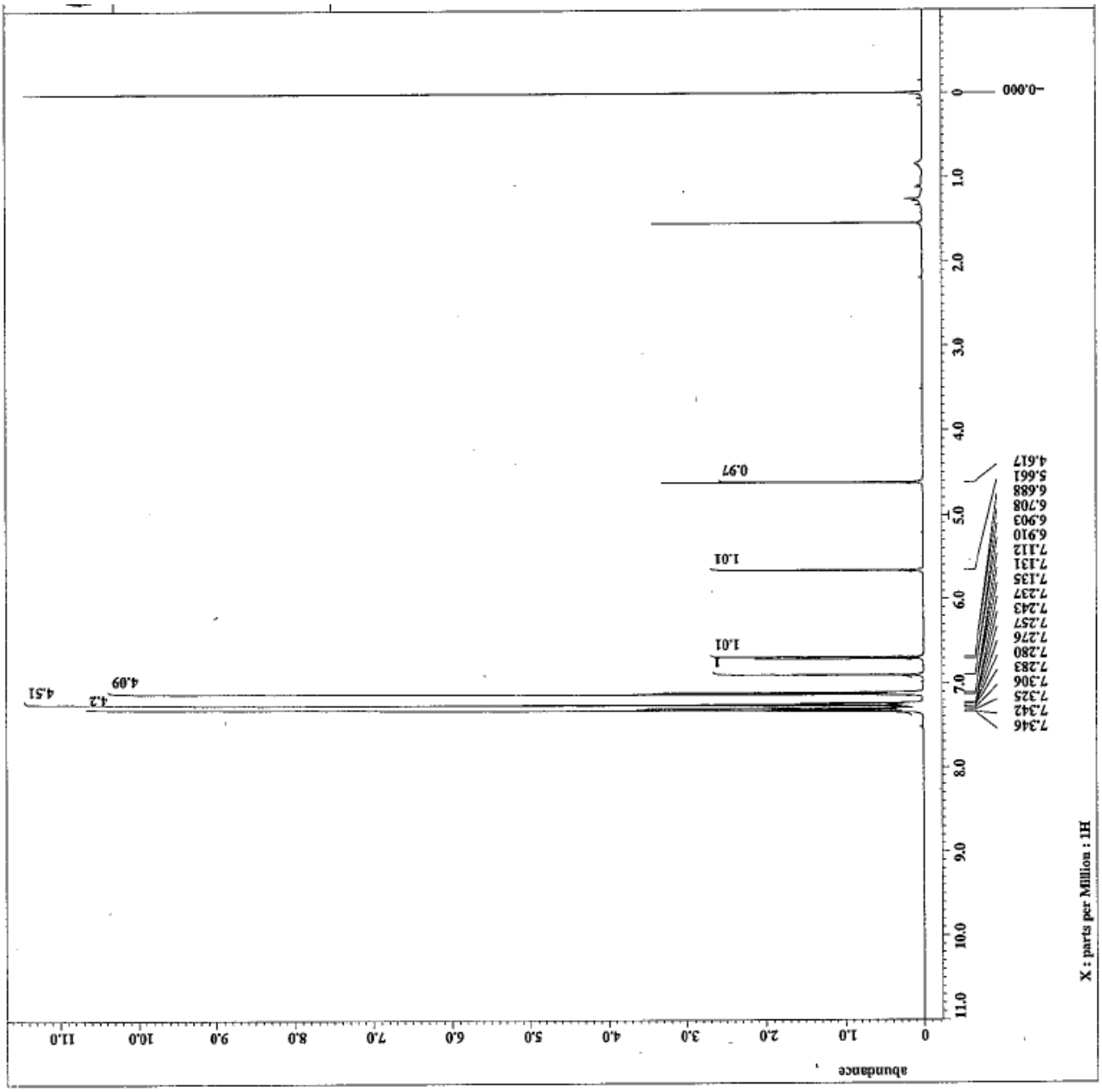
^{13}C-NMR (100 MHz, $CDCl_3$) of 3am



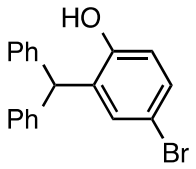


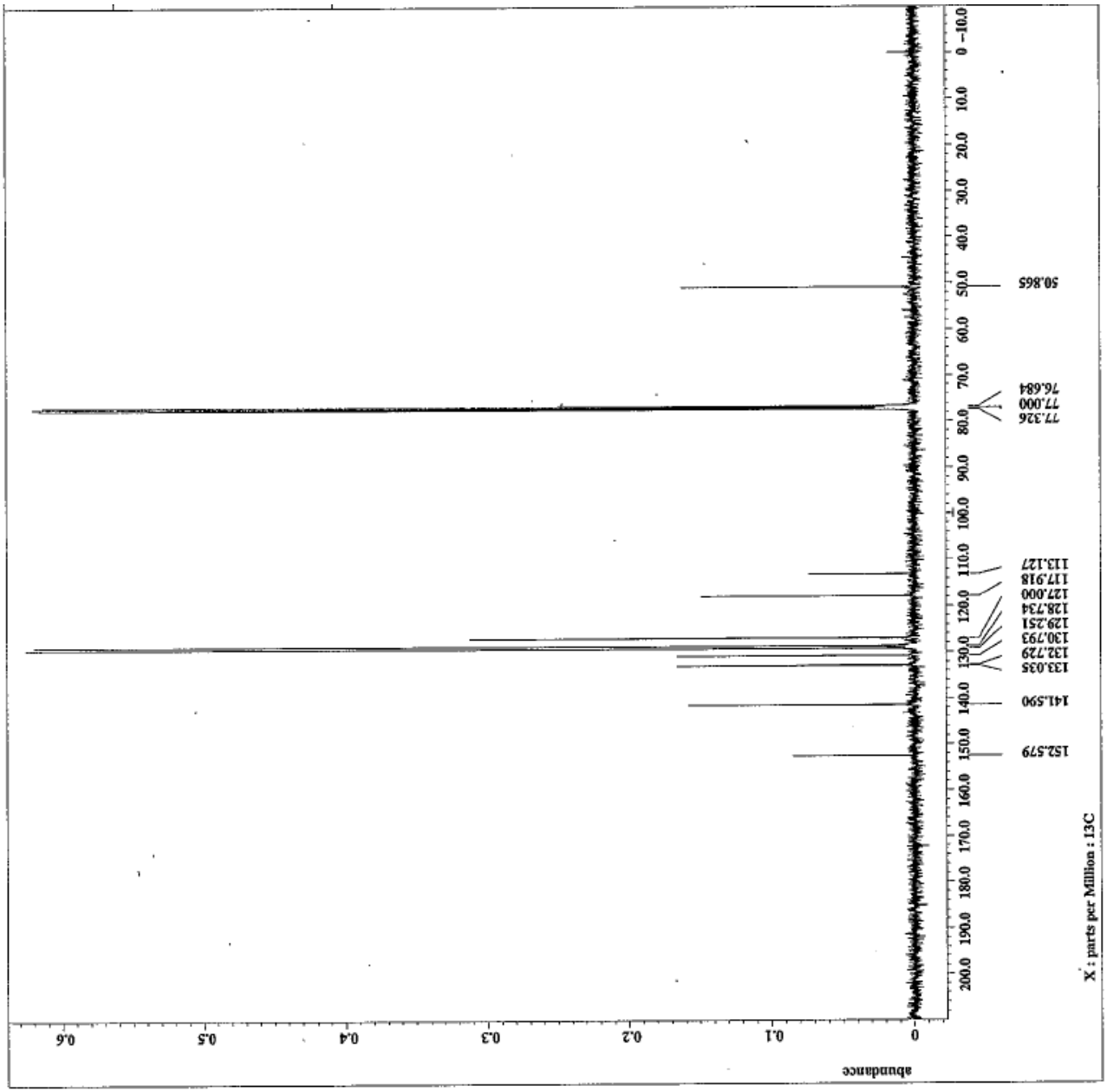
^{1}H-NMR (400 MHz, $CDCl_3$) of 3an



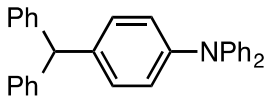


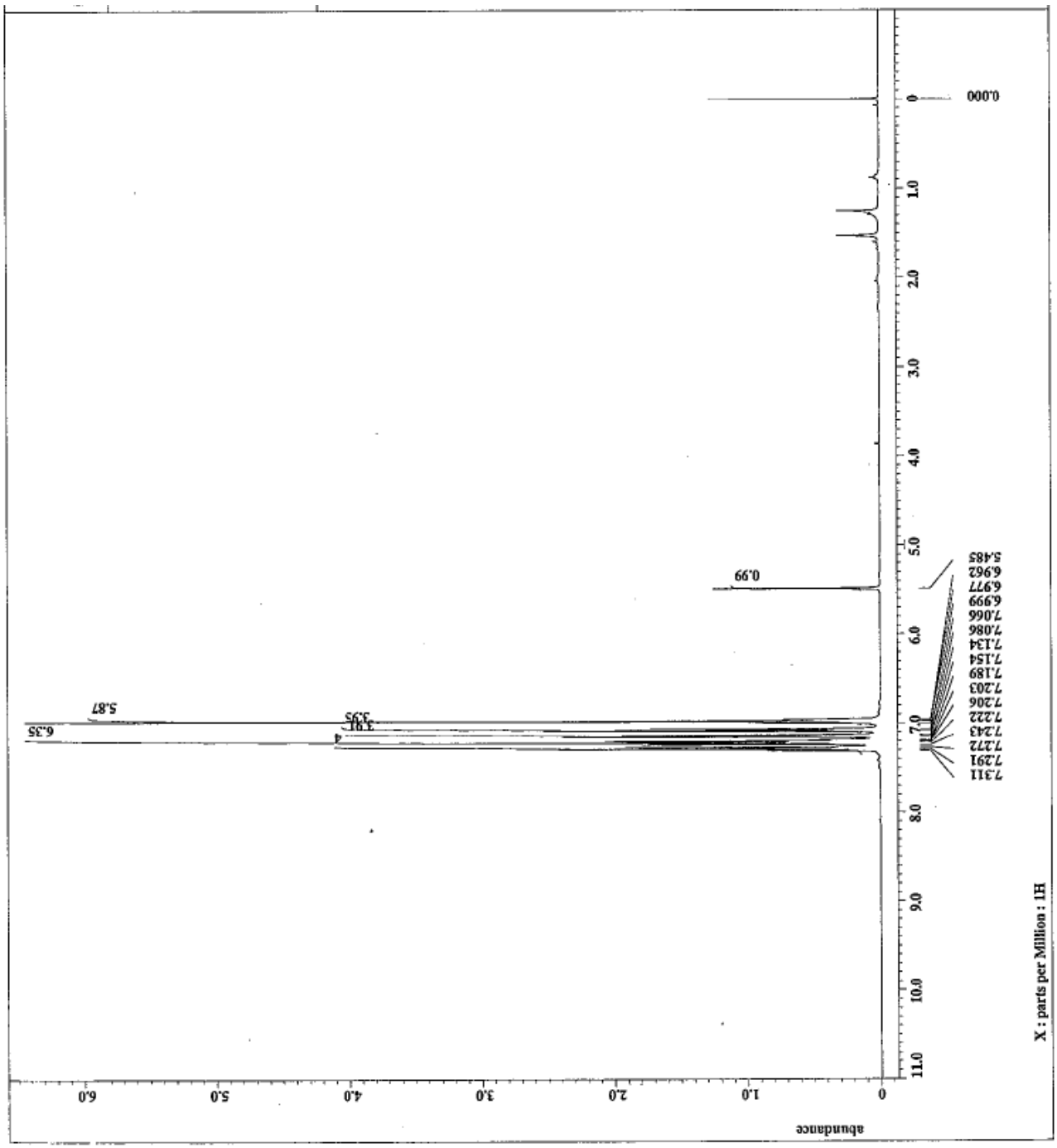
^{13}C-NMR (100 MHz, $CDCl_3$) of 3an



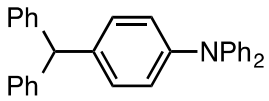


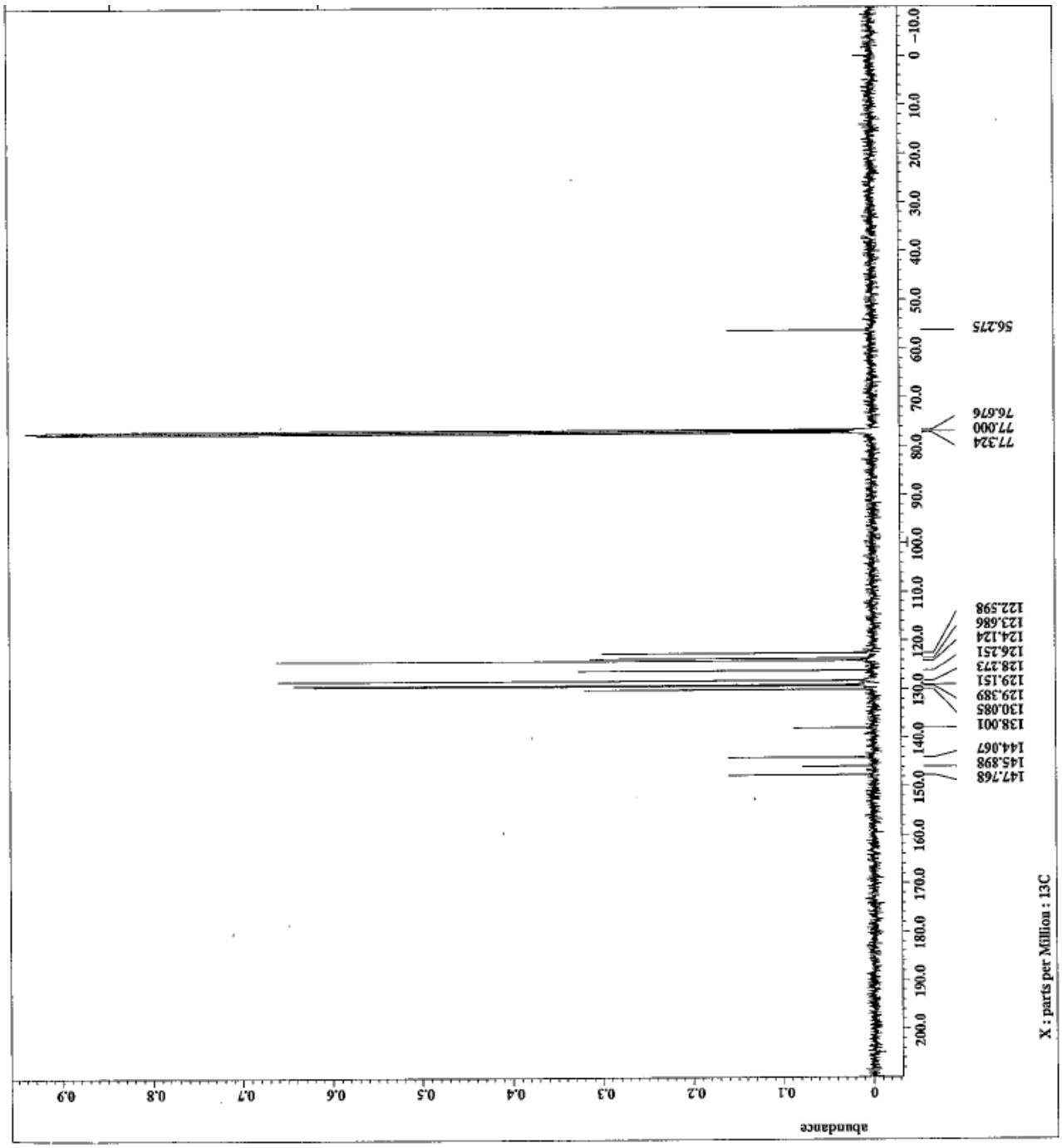
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ao



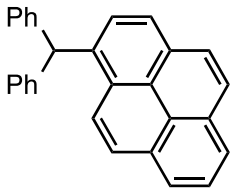


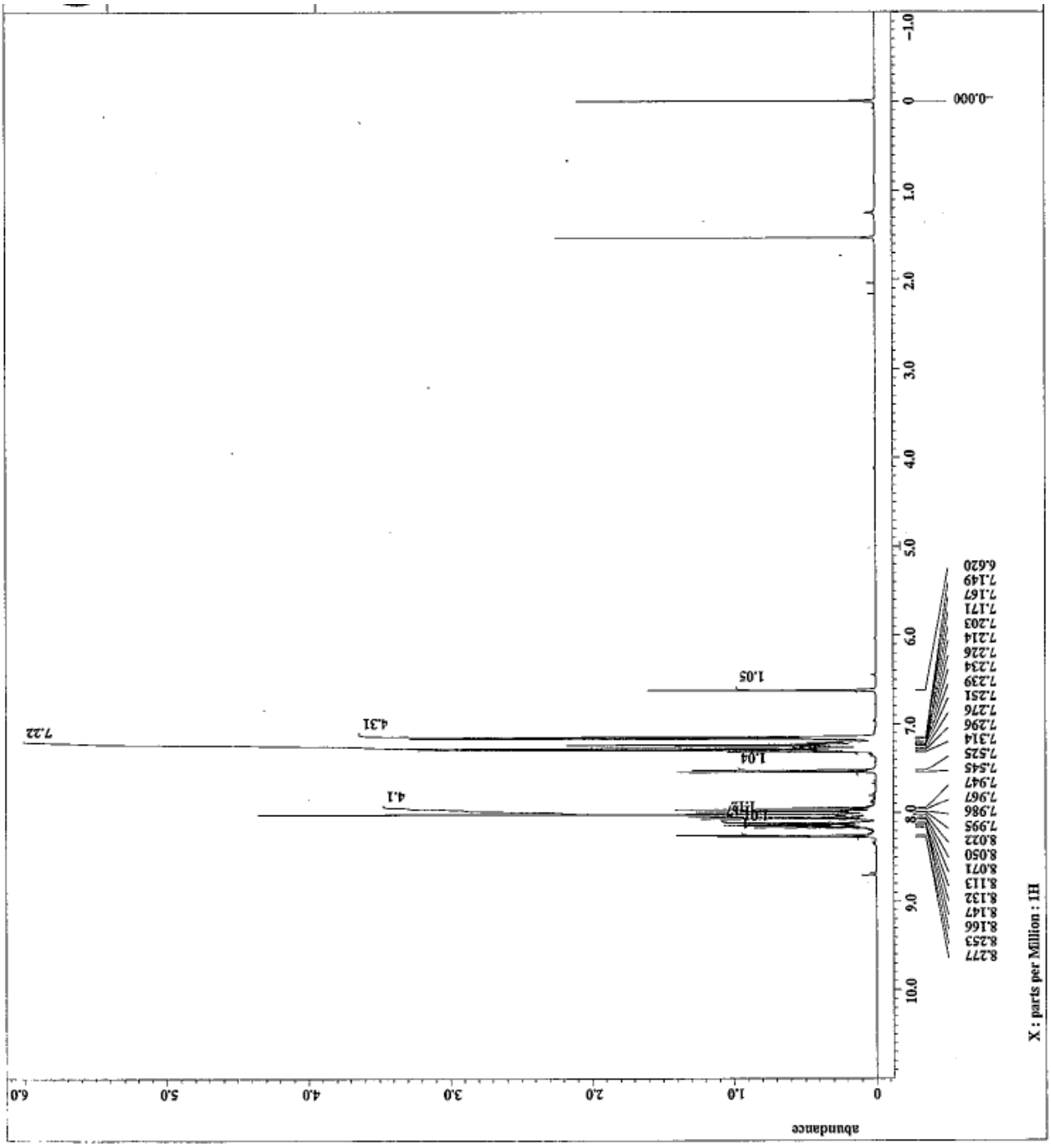
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ao



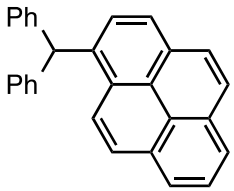


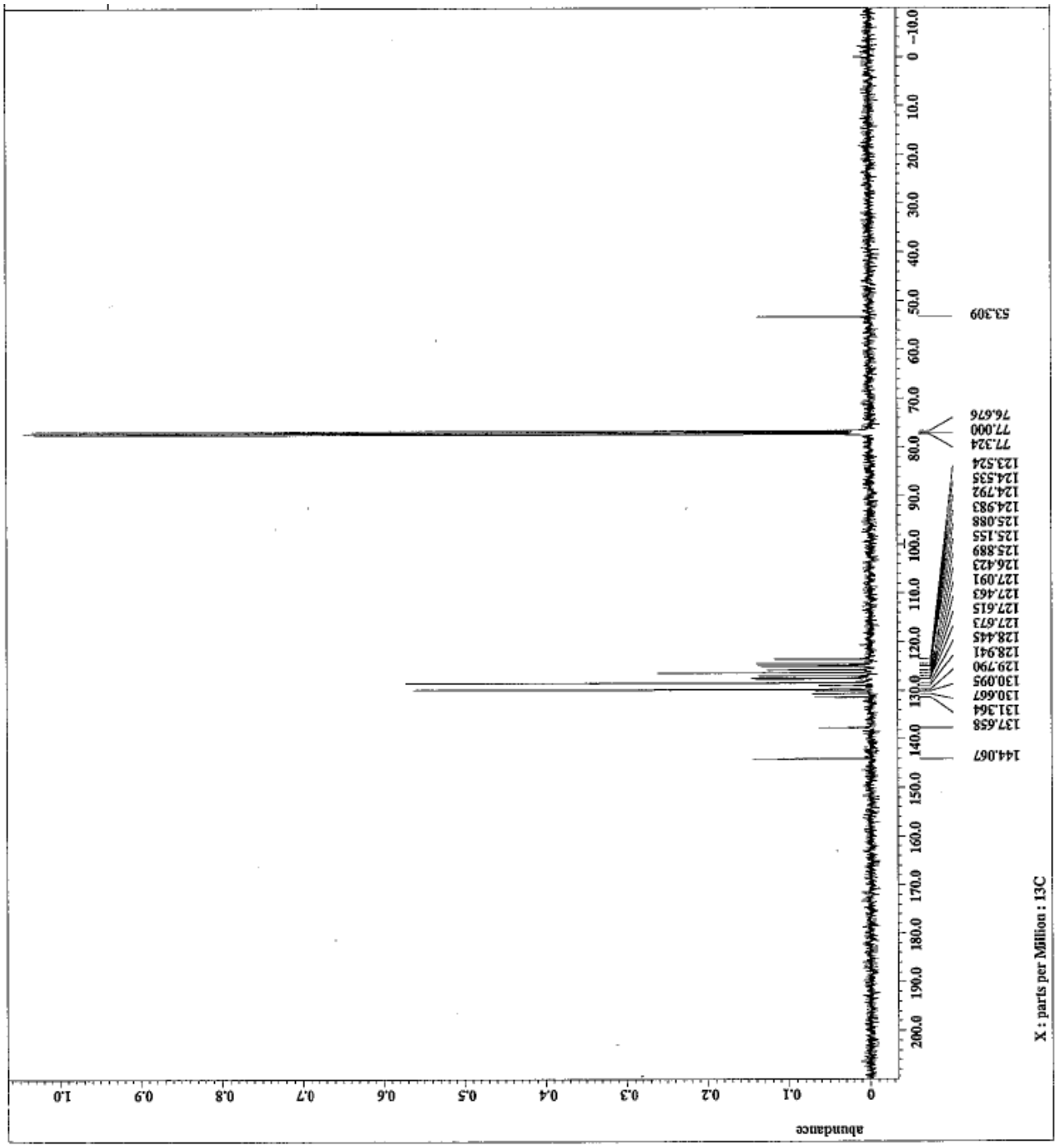
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ap



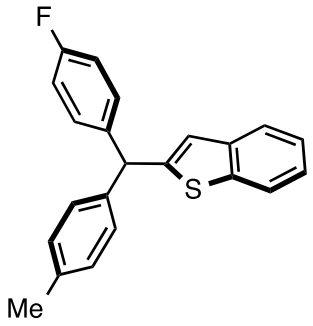


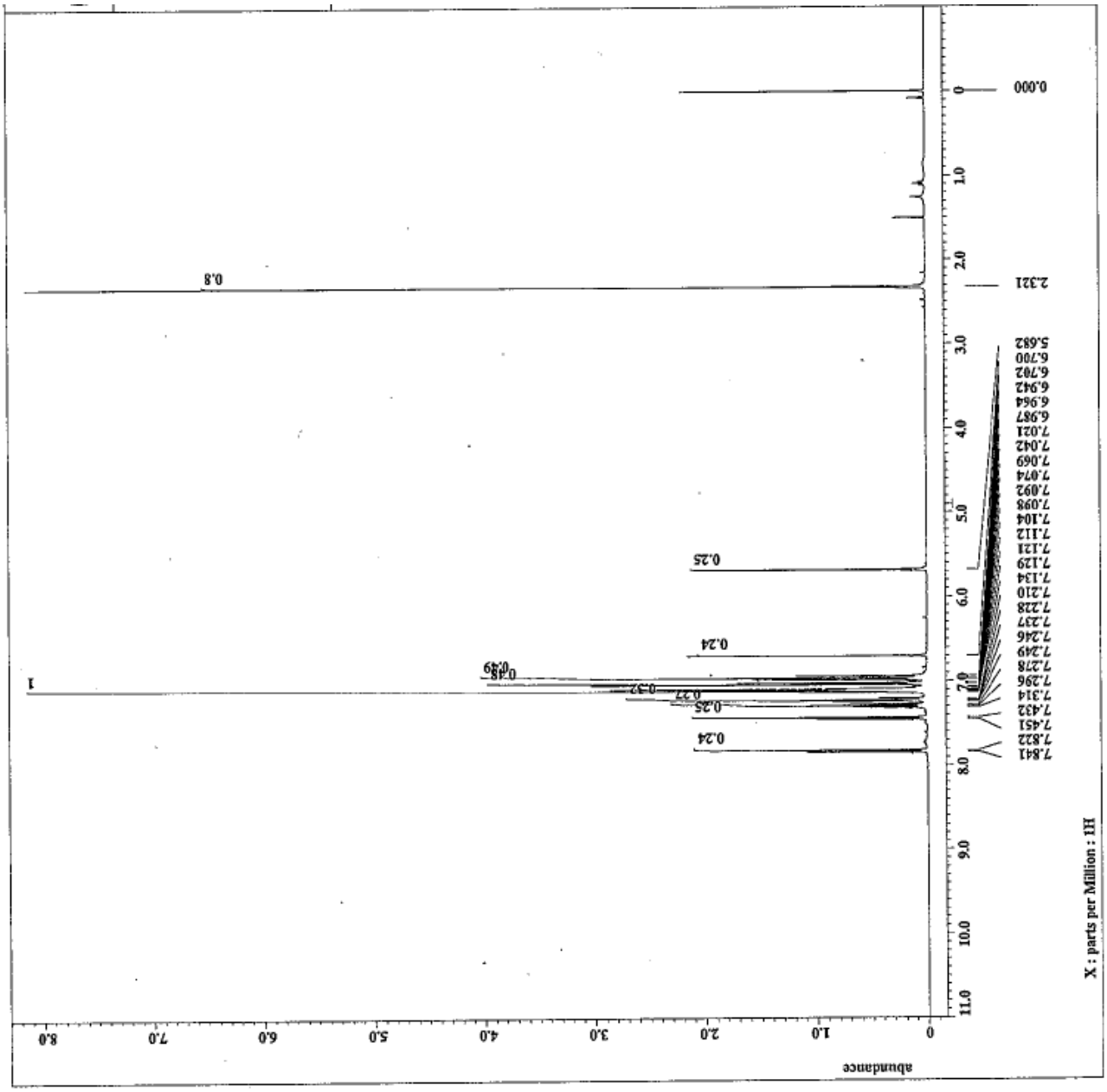
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ap



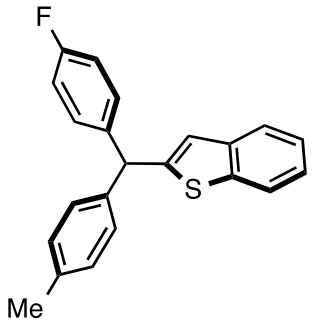


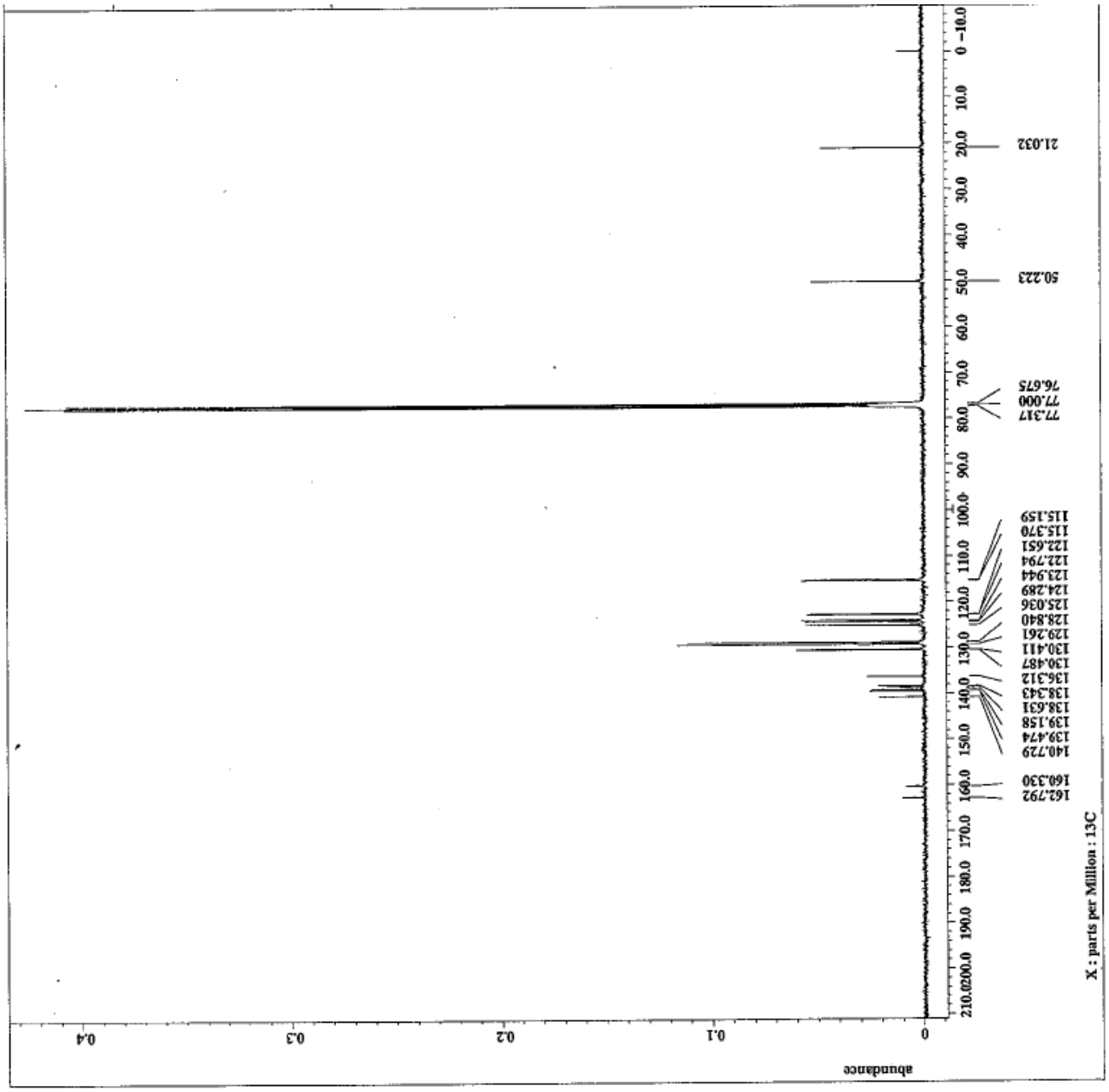
^{1}H-NMR (400 MHz, $CDCl_3$) of 3bg



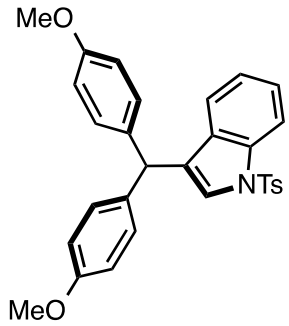


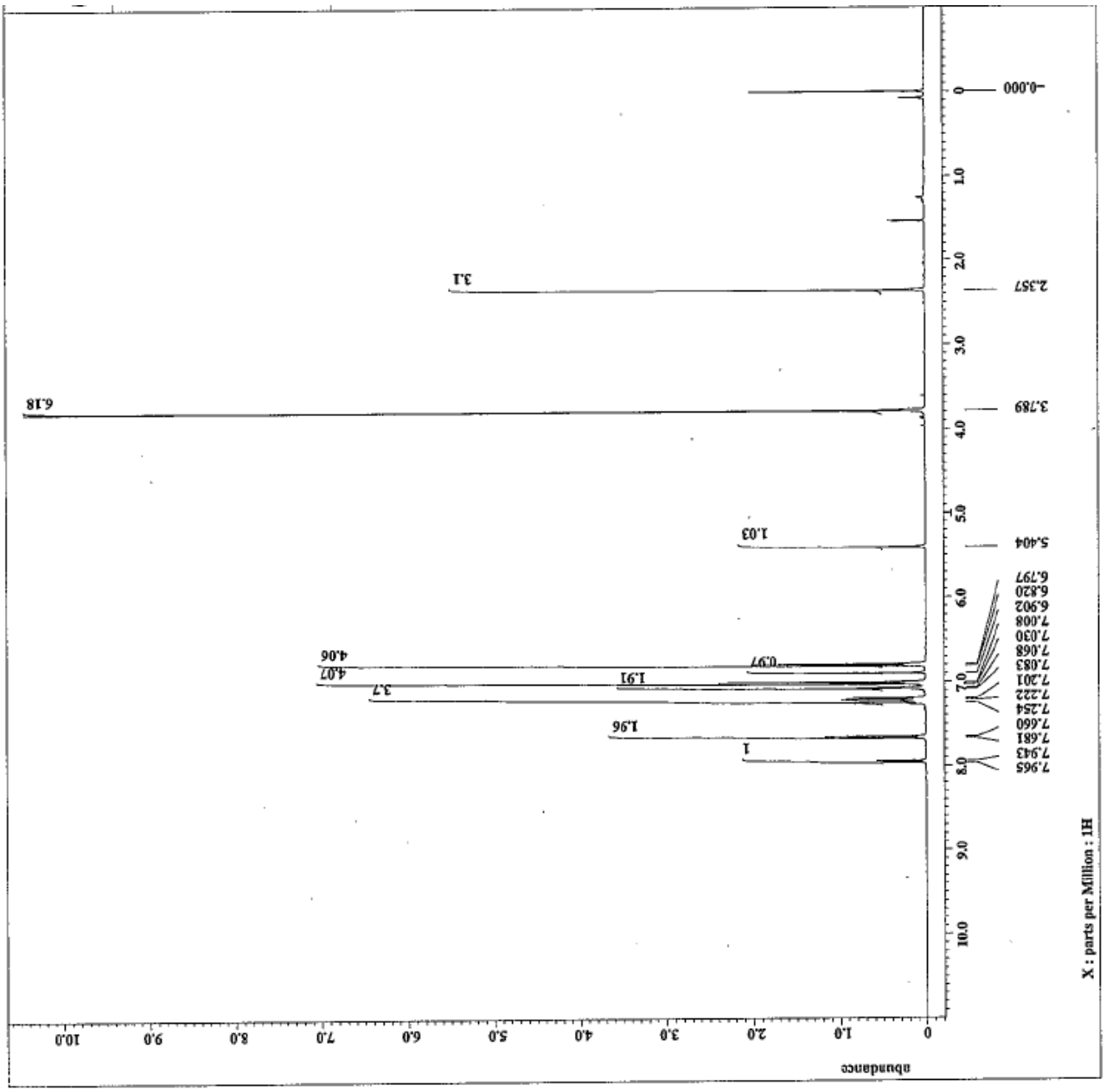
^{13}C-NMR (100 MHz, $CDCl_3$) of 3bg



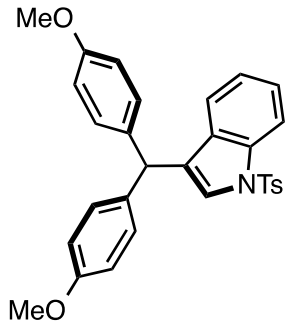


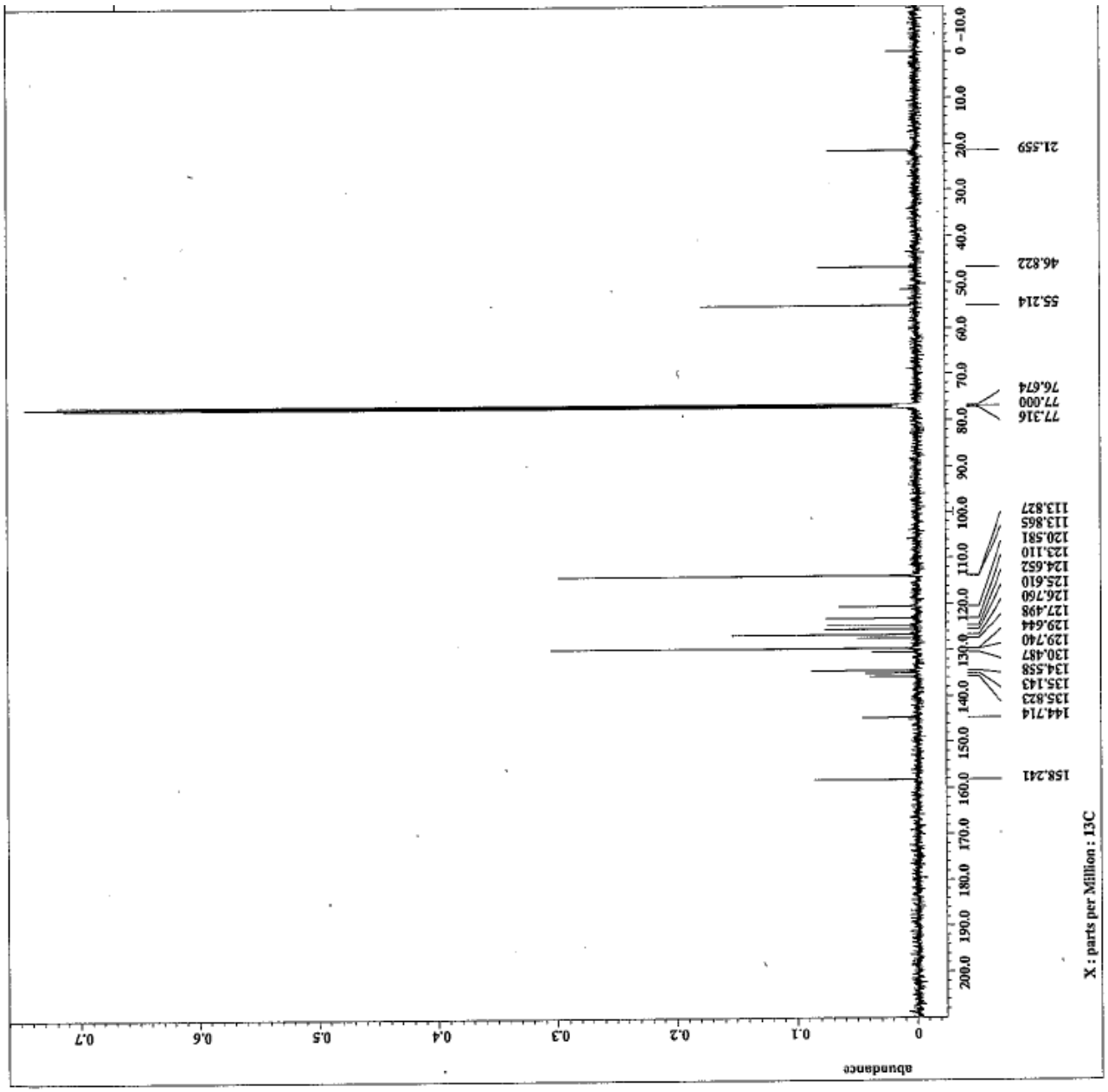
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ci



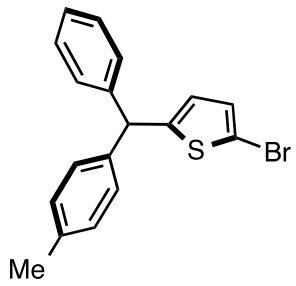


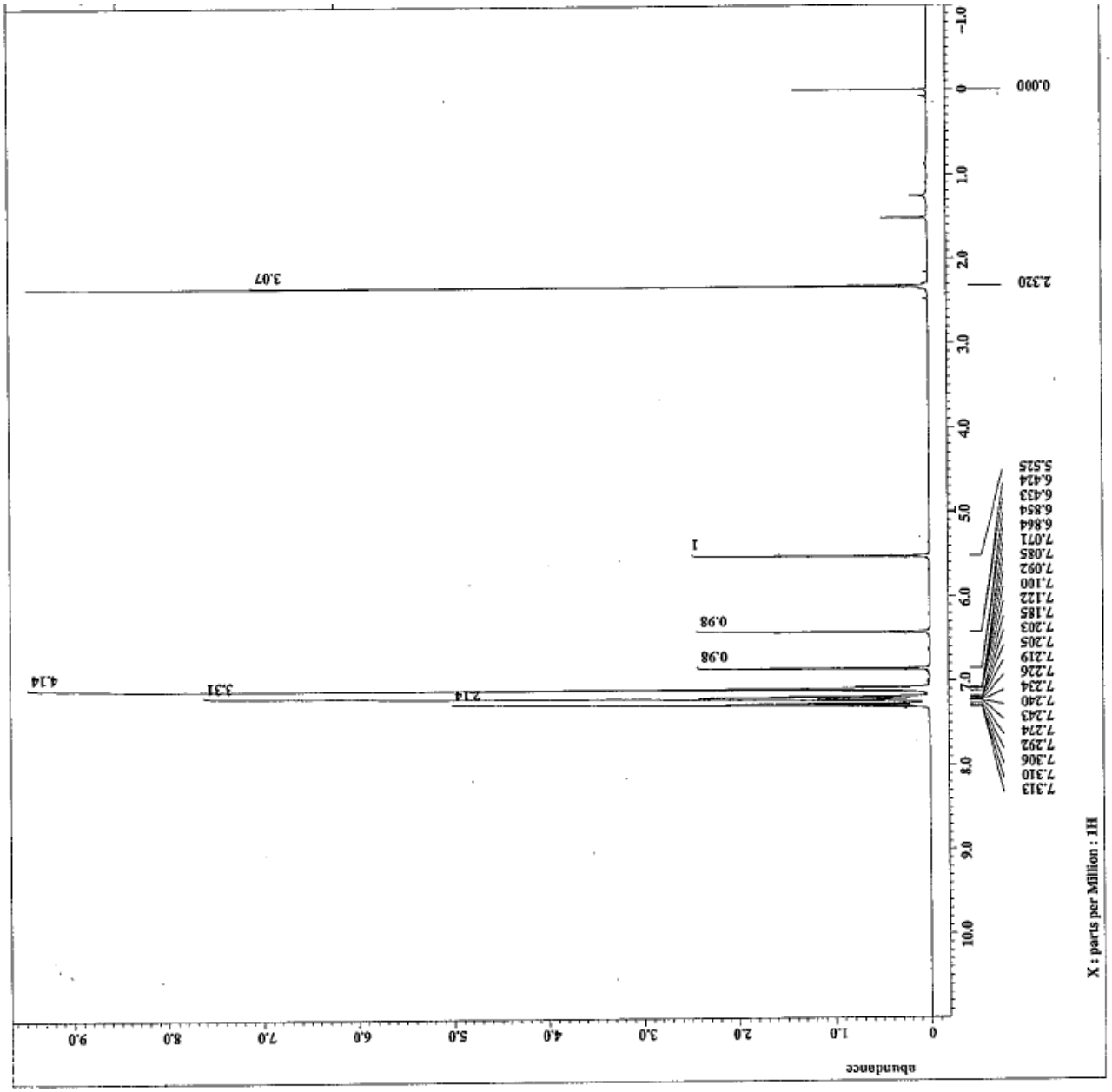
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ci



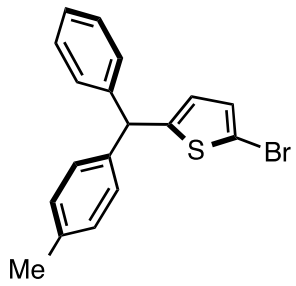


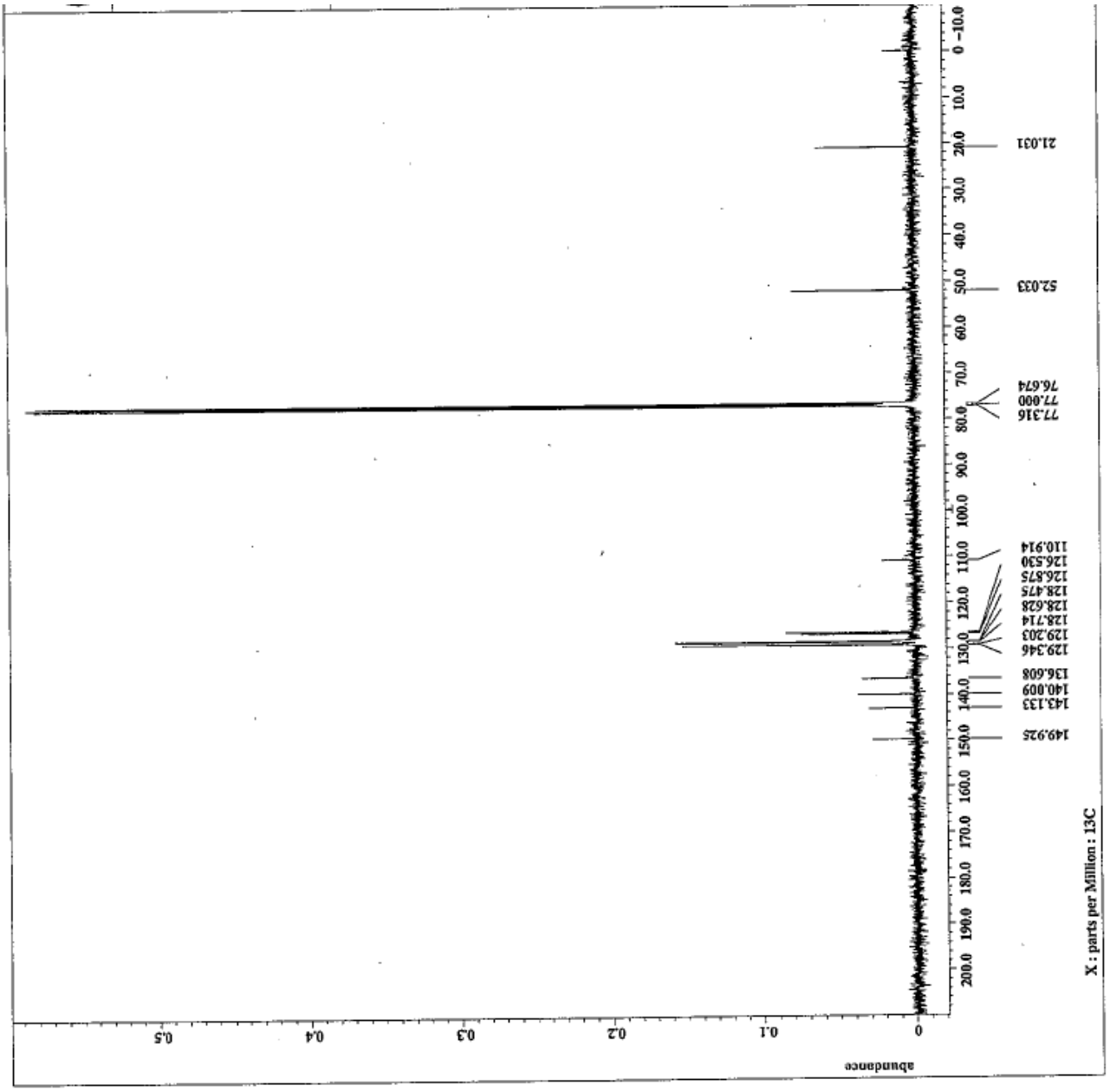
^{1}H-NMR (400 MHz, $CDCl_3$) of 3dd



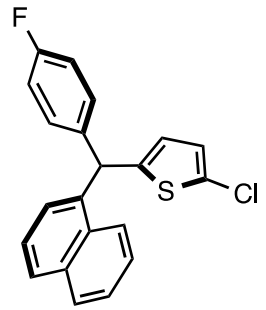


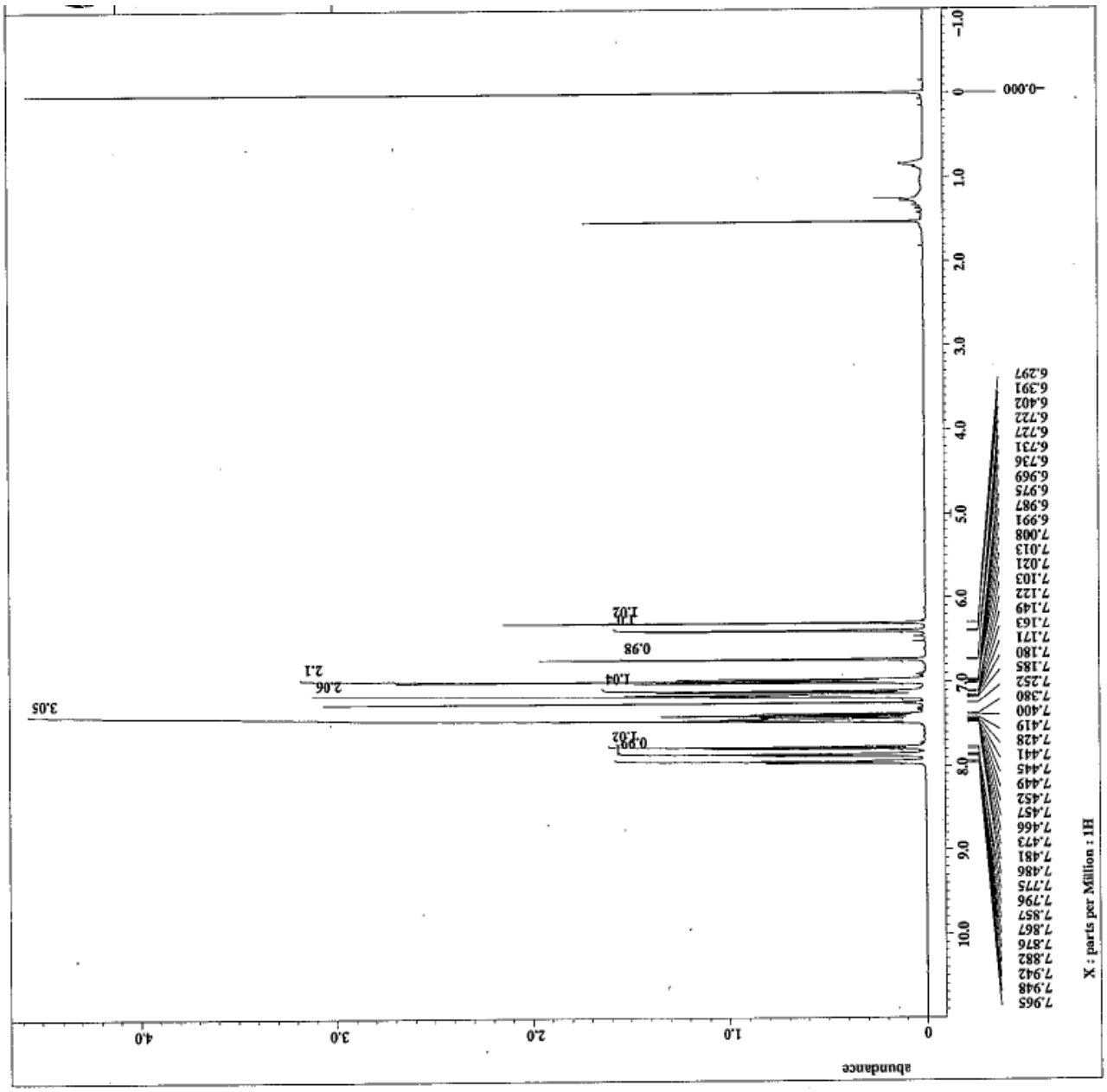
^{13}C-NMR (100 MHz, $CDCl_3$) of 3dd



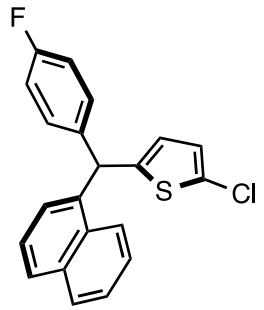


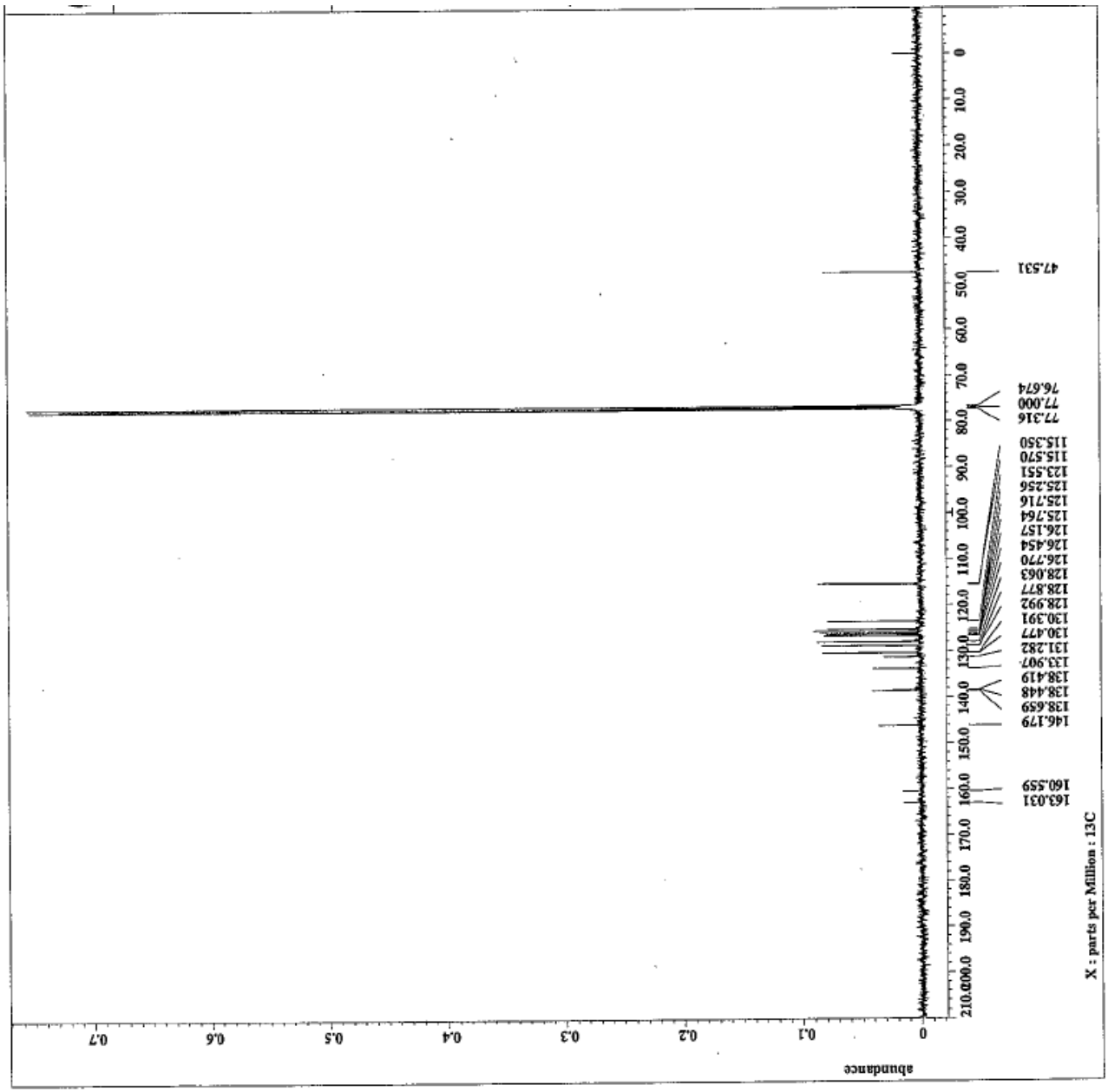
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ec



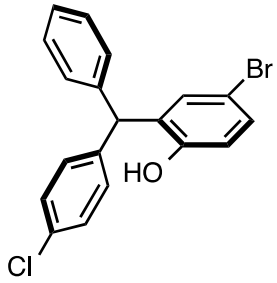


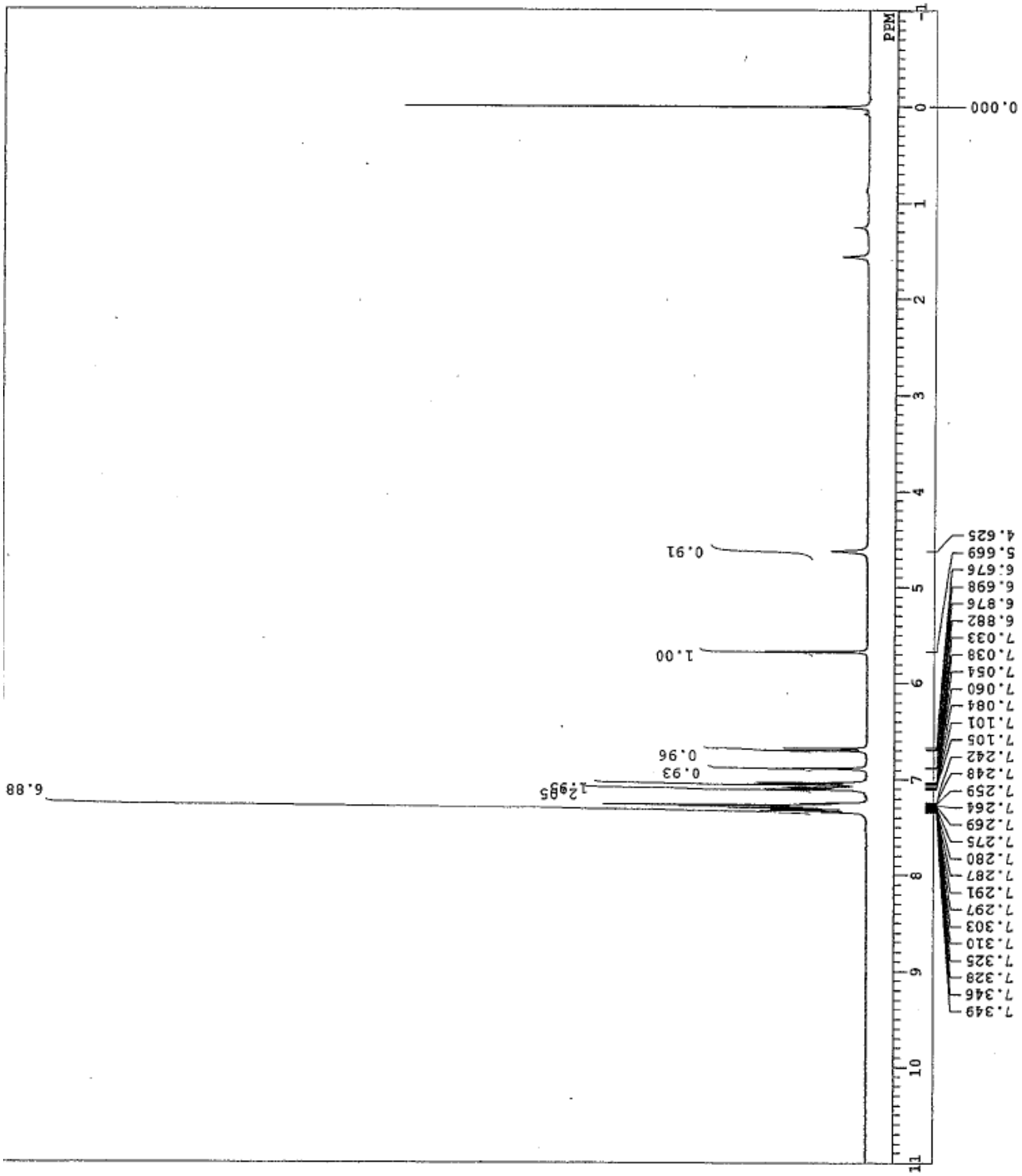
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ec



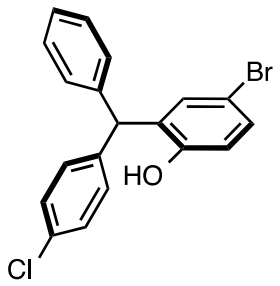


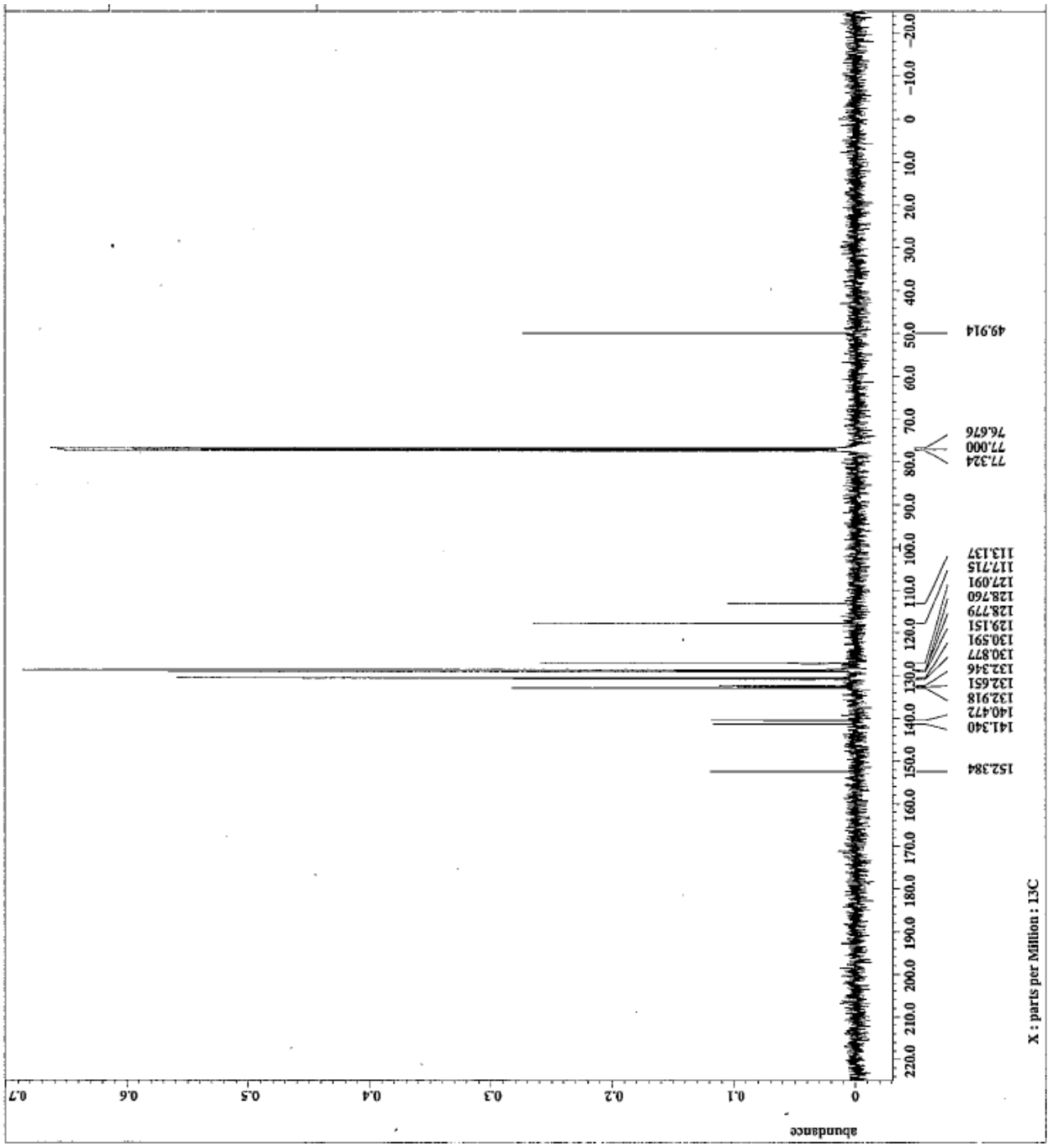
^{1}H-NMR (400 MHz, $CDCl_3$) of 3fn



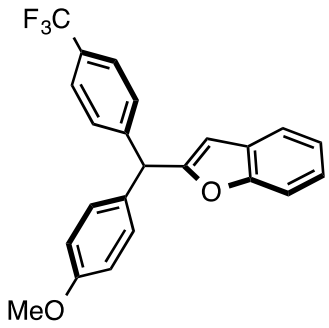


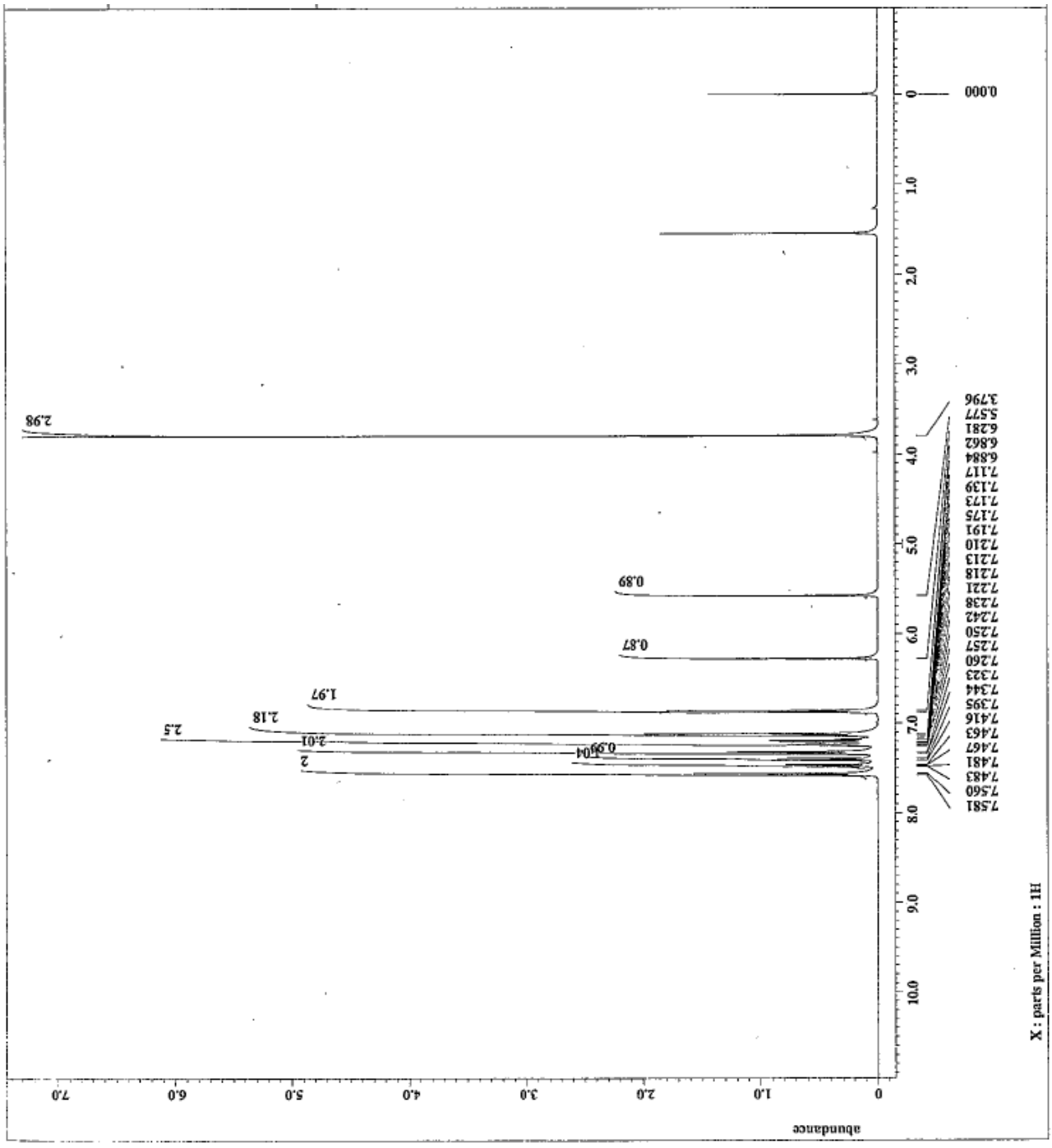
^{13}C-NMR (100 MHz, $CDCl_3$) of 3fn



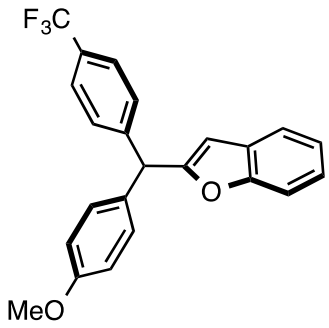


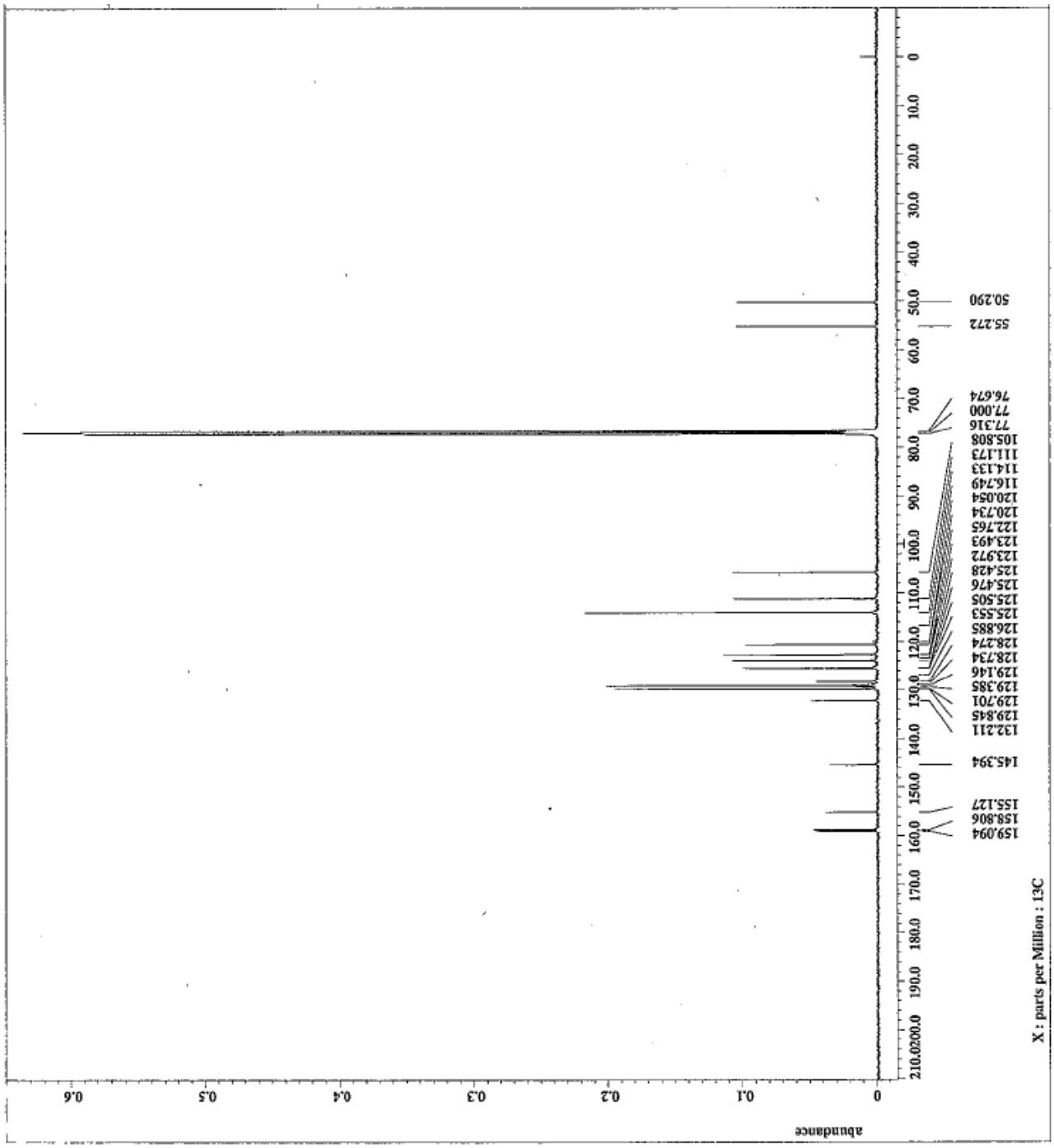
^{1}H-NMR (400 MHz, $CDCl_3$) of 3gh



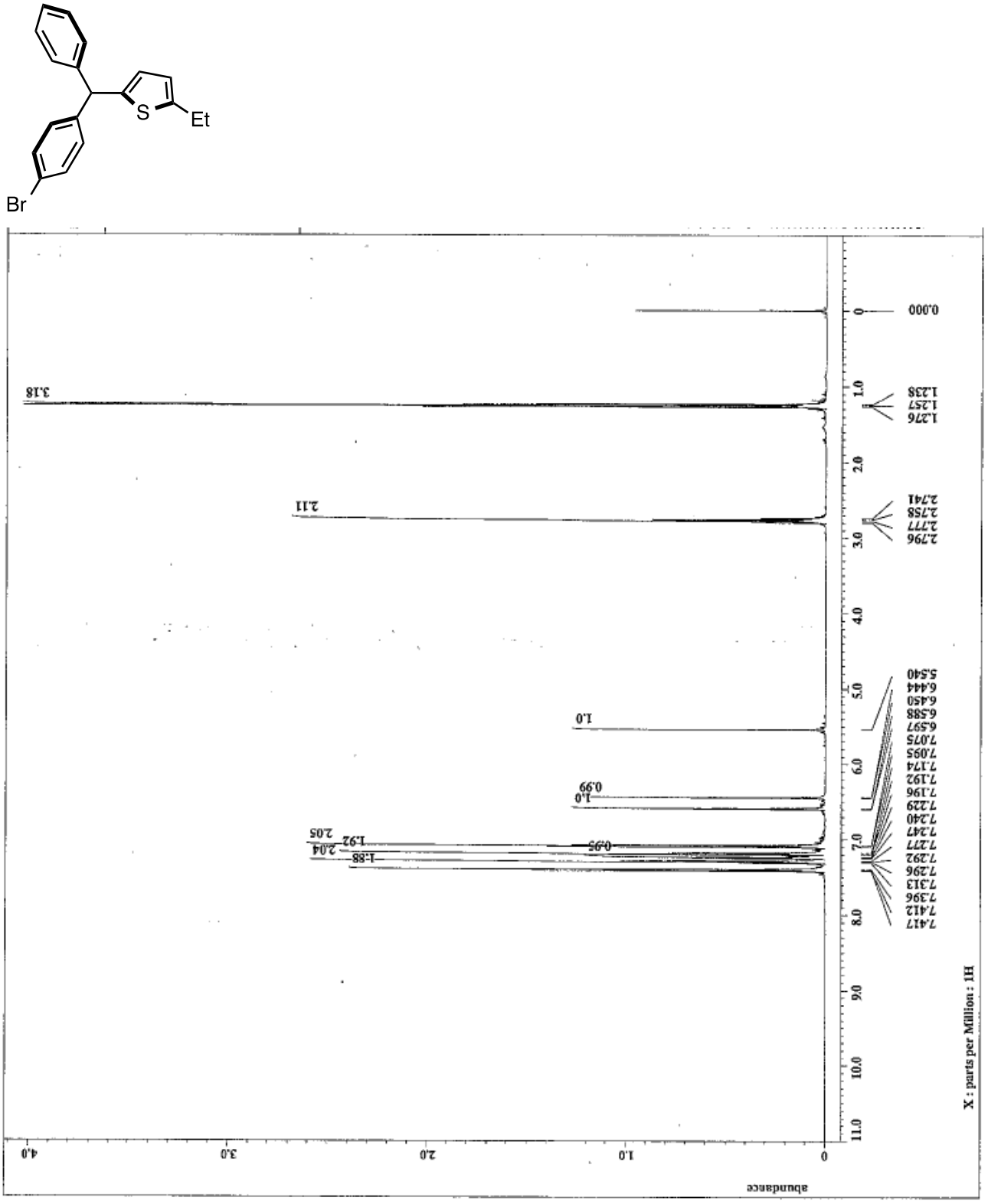


^{13}C-NMR (100 MHz, $CDCl_3$) of 3gh

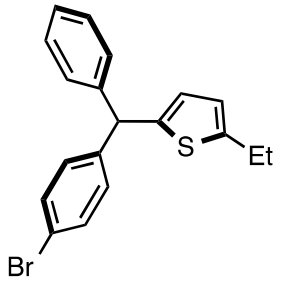


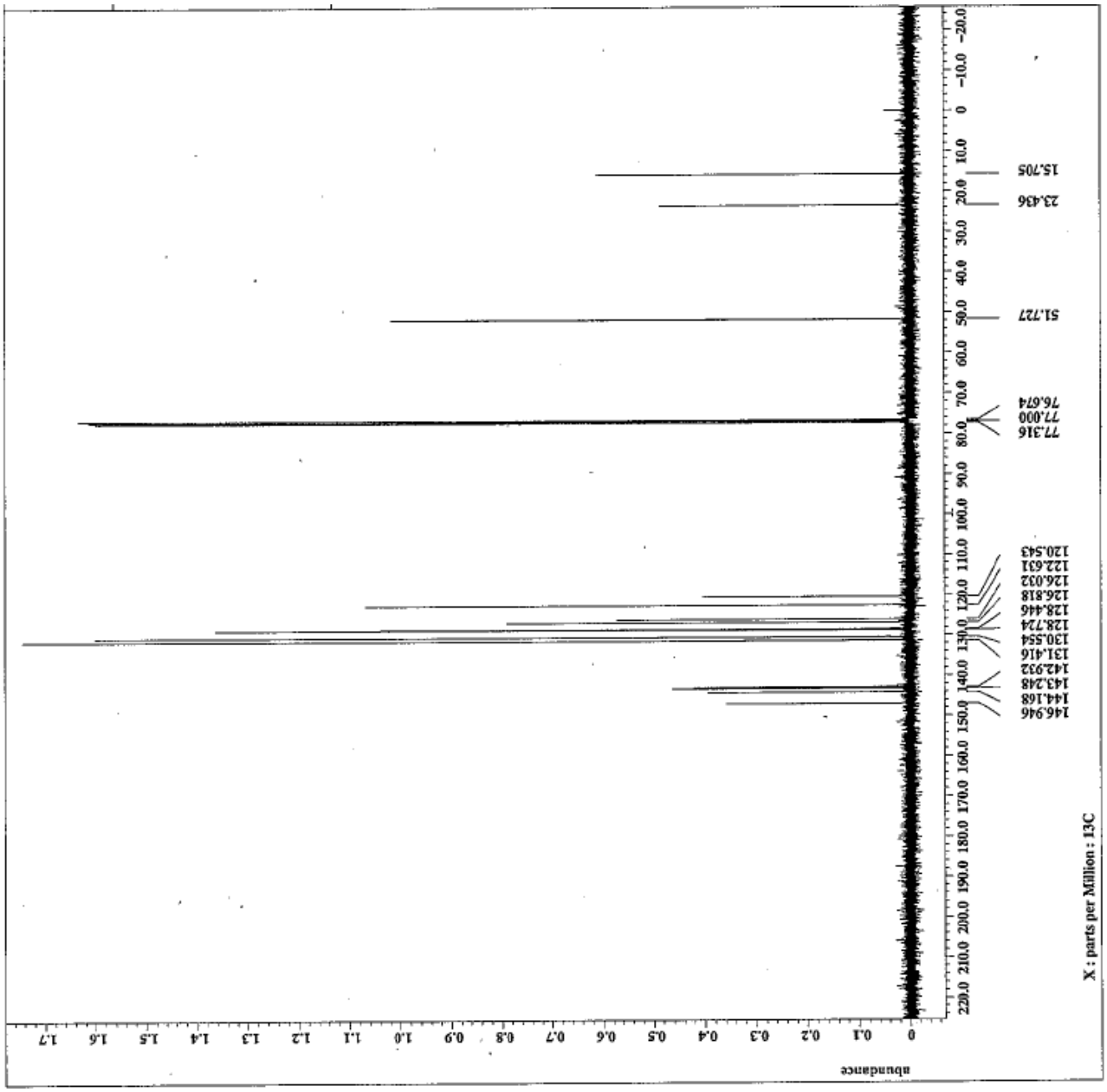


^{1}H-NMR (400 MHz, $CDCl_3$) of 3ha

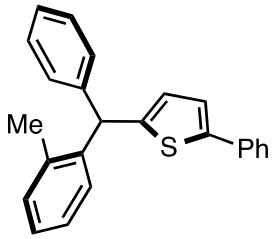


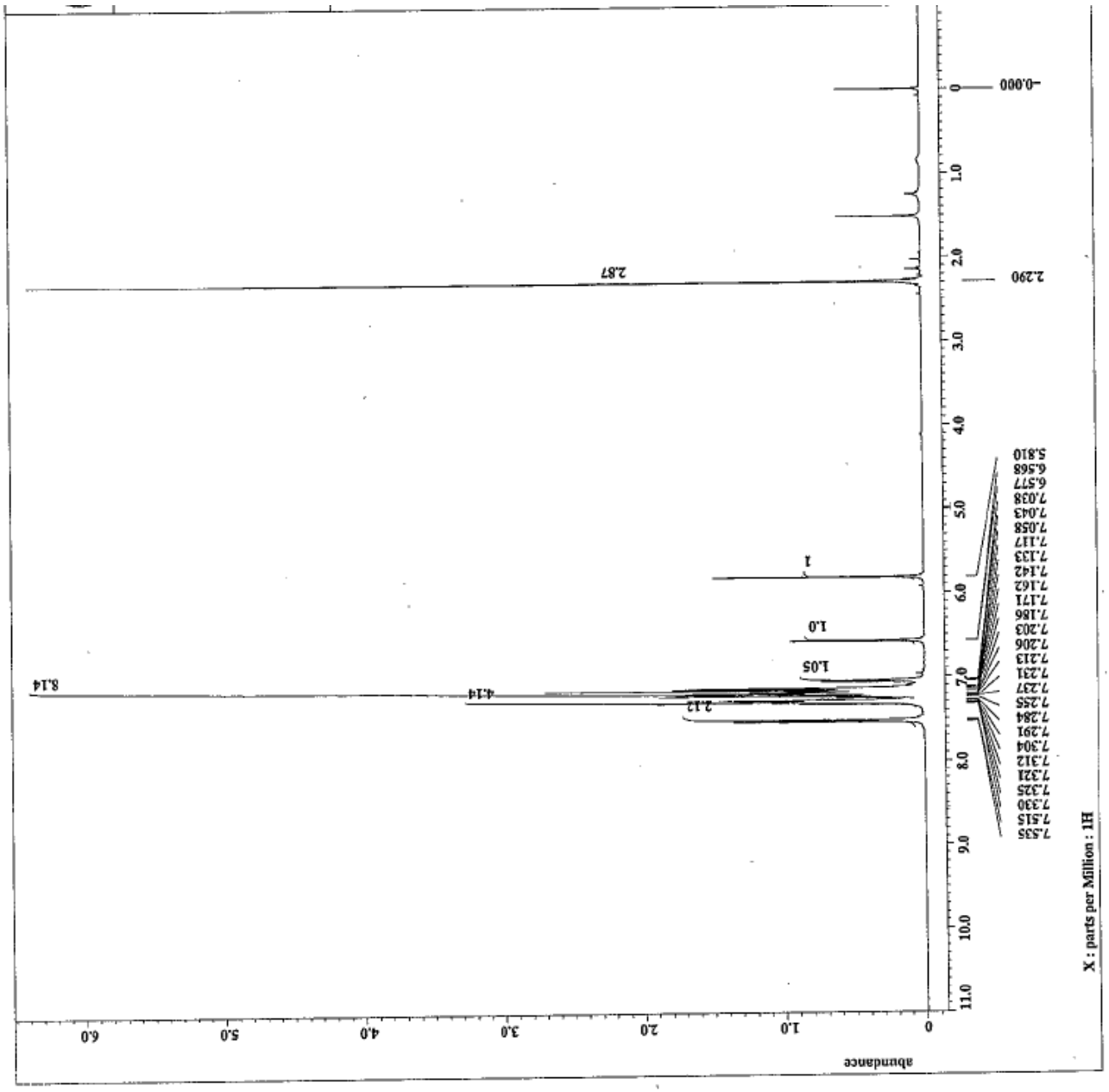
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ha



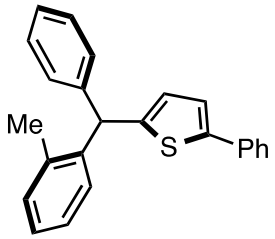


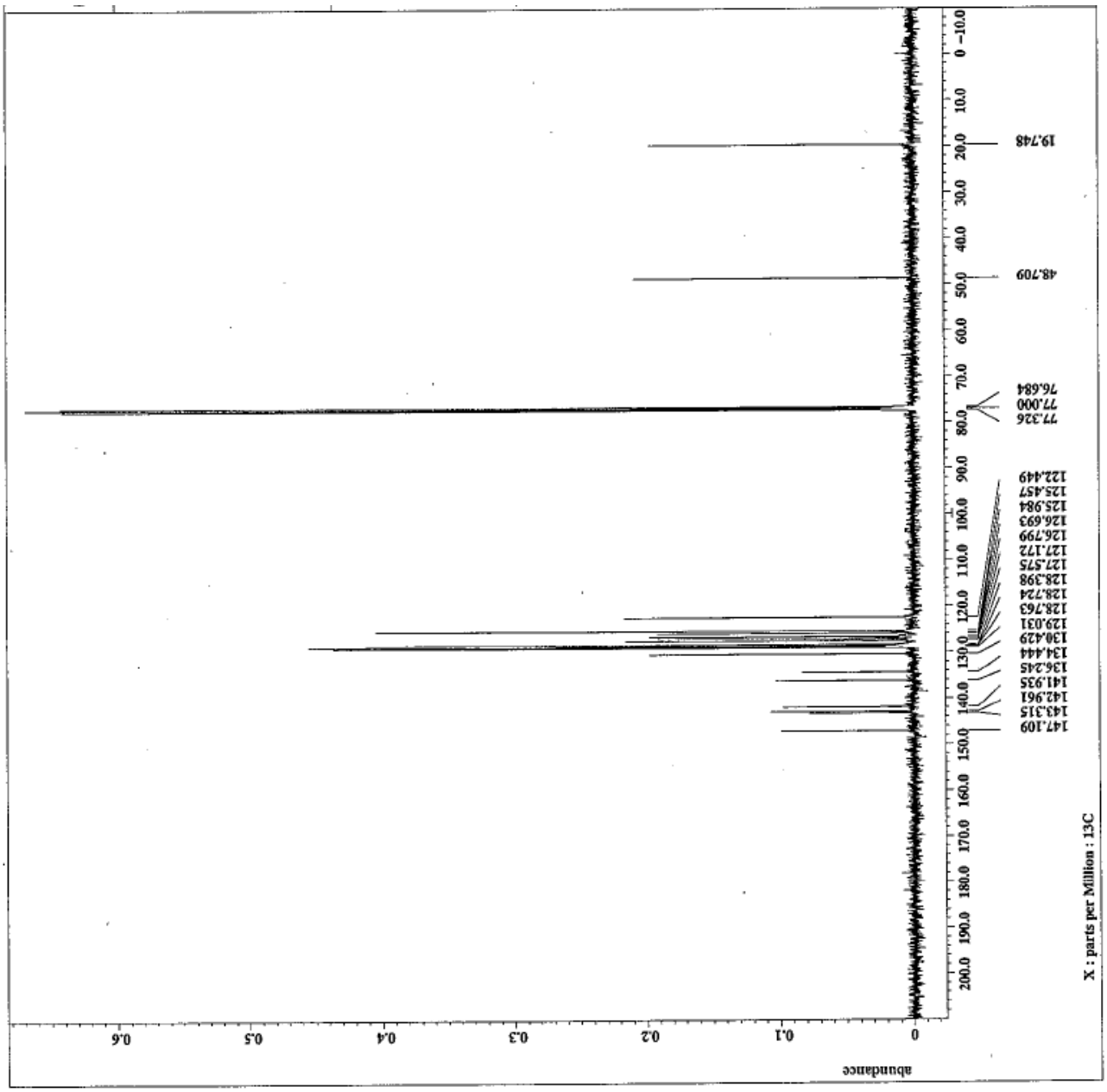
^{1}H-NMR (400 MHz, $CDCl_3$) of 3ib



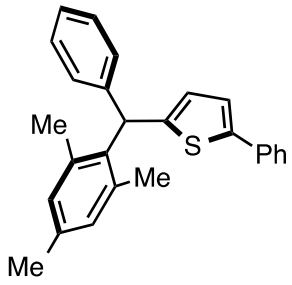


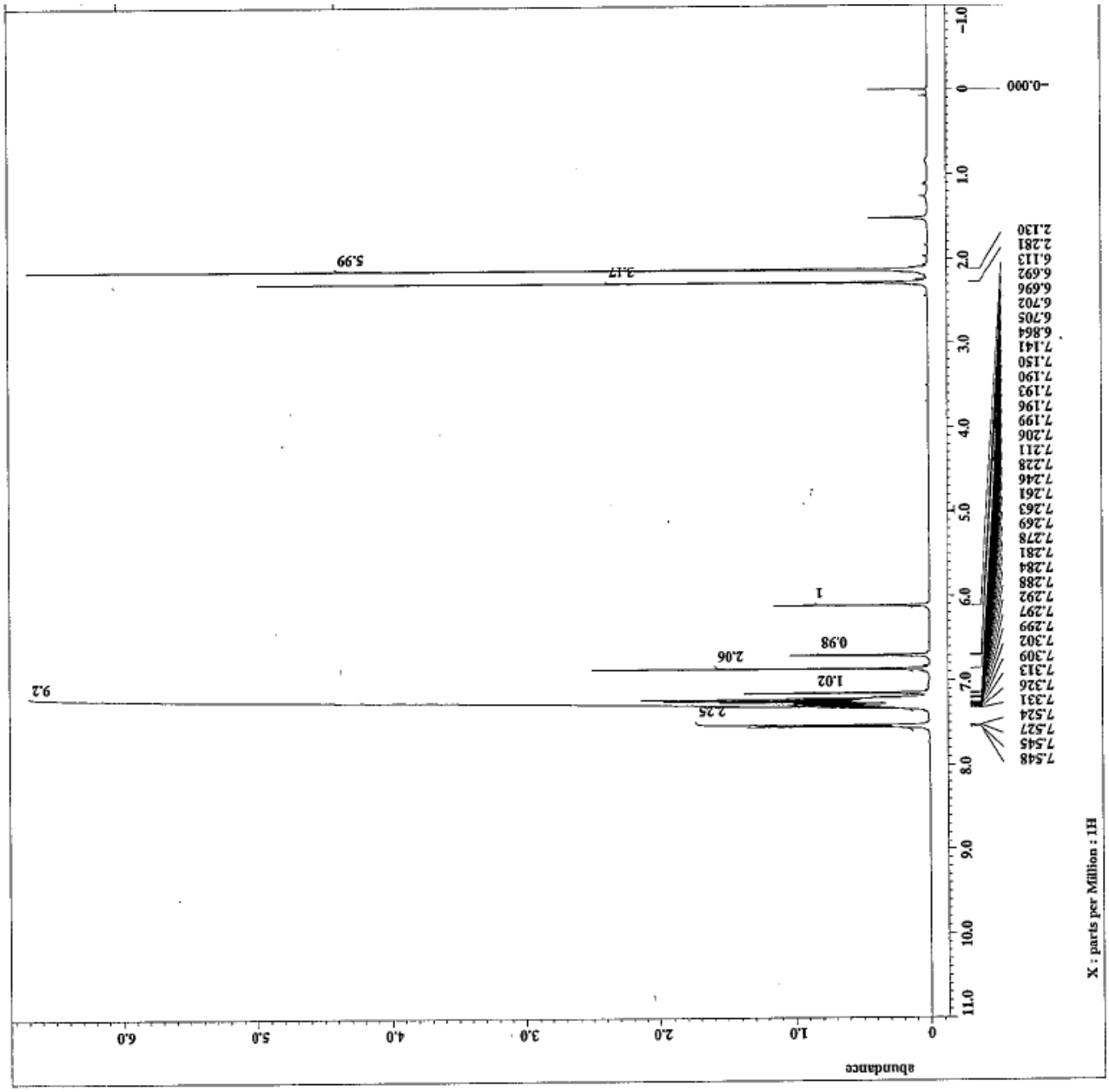
^{13}C-NMR (100 MHz, $CDCl_3$) of 3ib



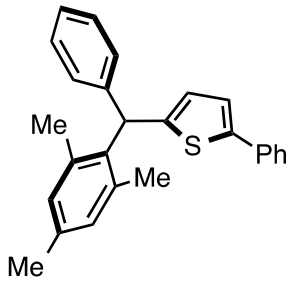


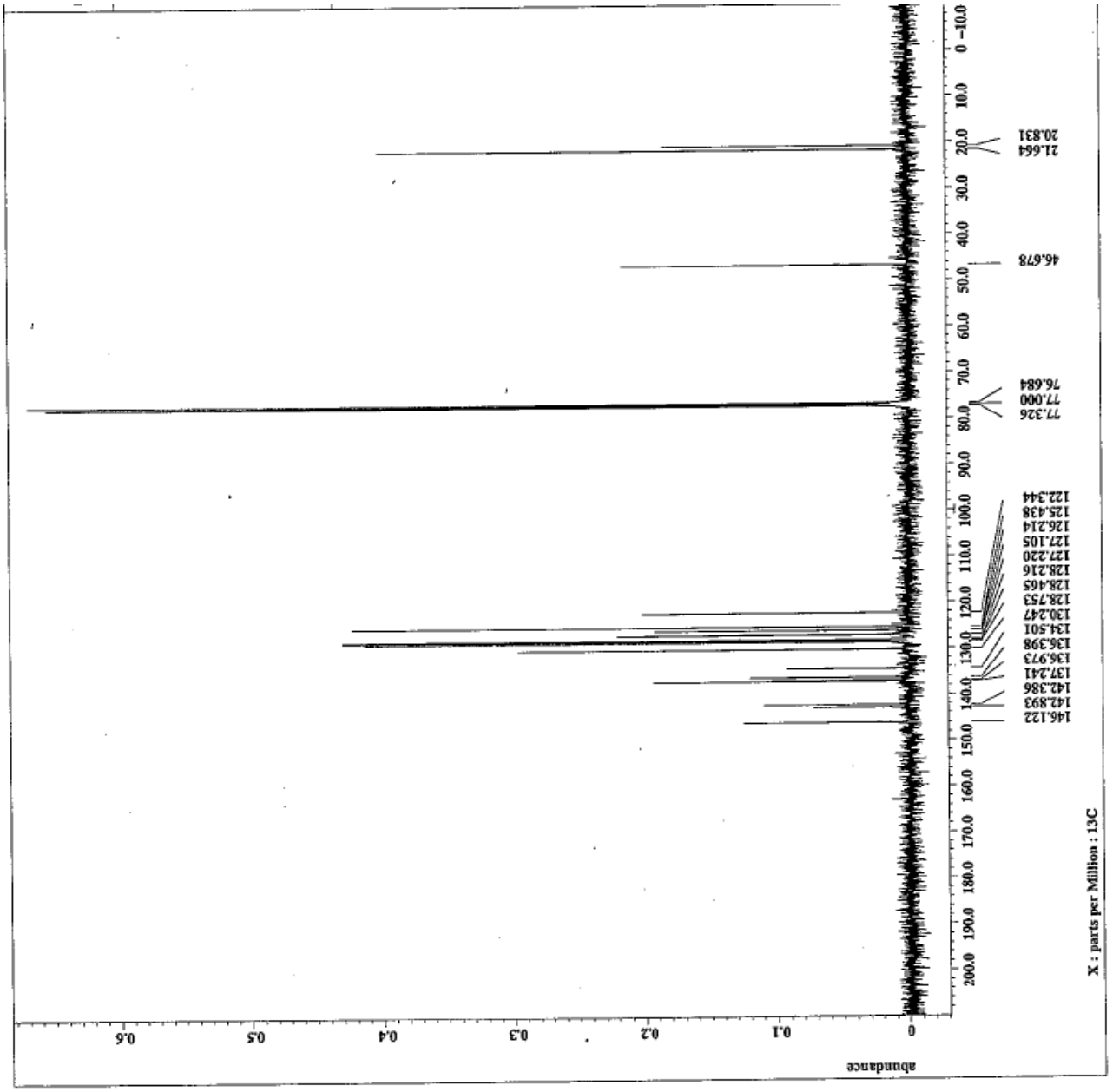
^{1}H-NMR (400 MHz, $CDCl_3$) of 3jb



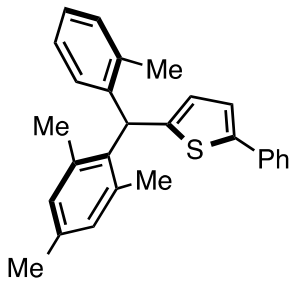


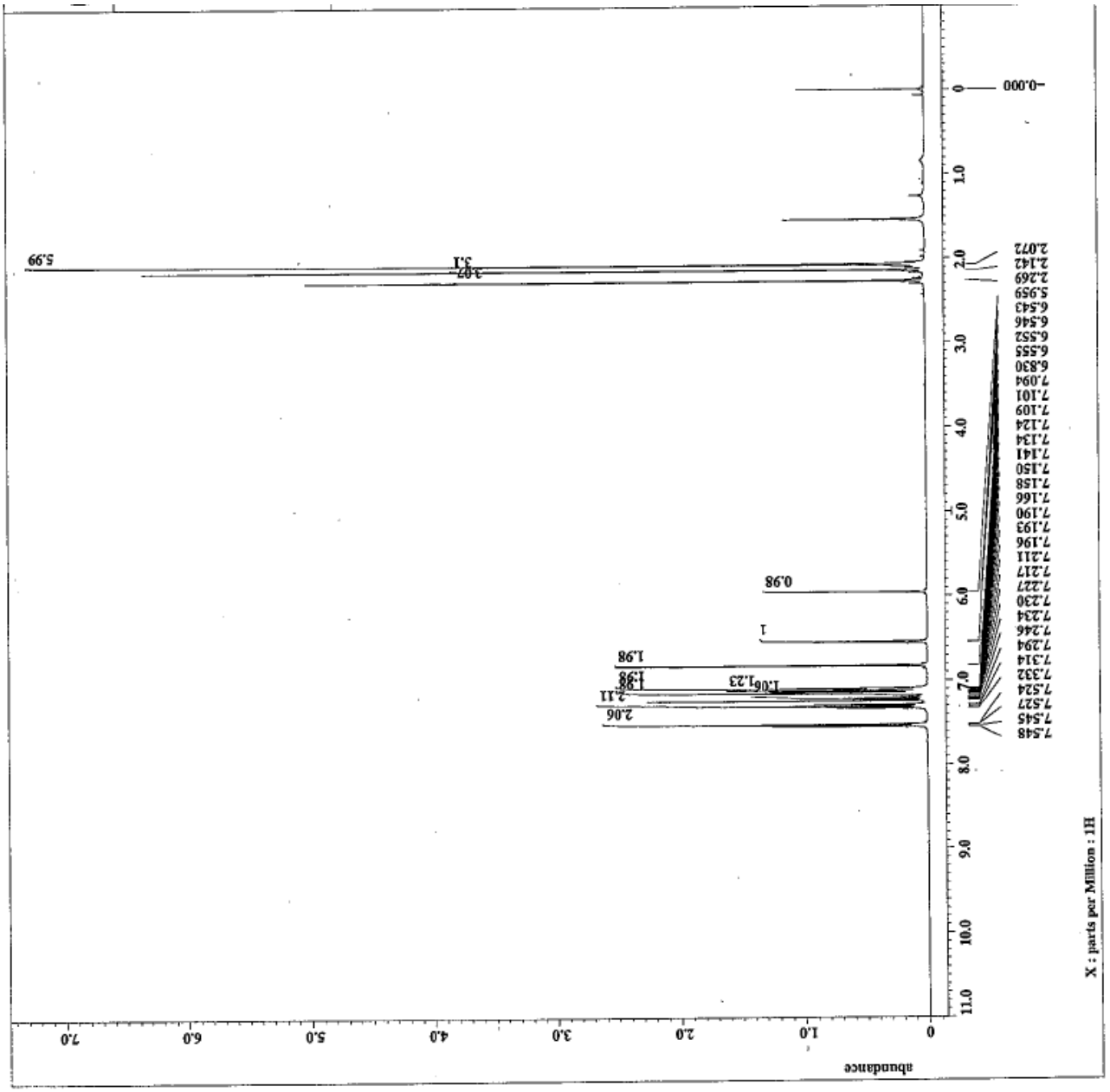
^{13}C-NMR (100 MHz, $CDCl_3$) of 3jb



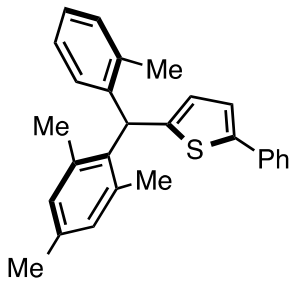


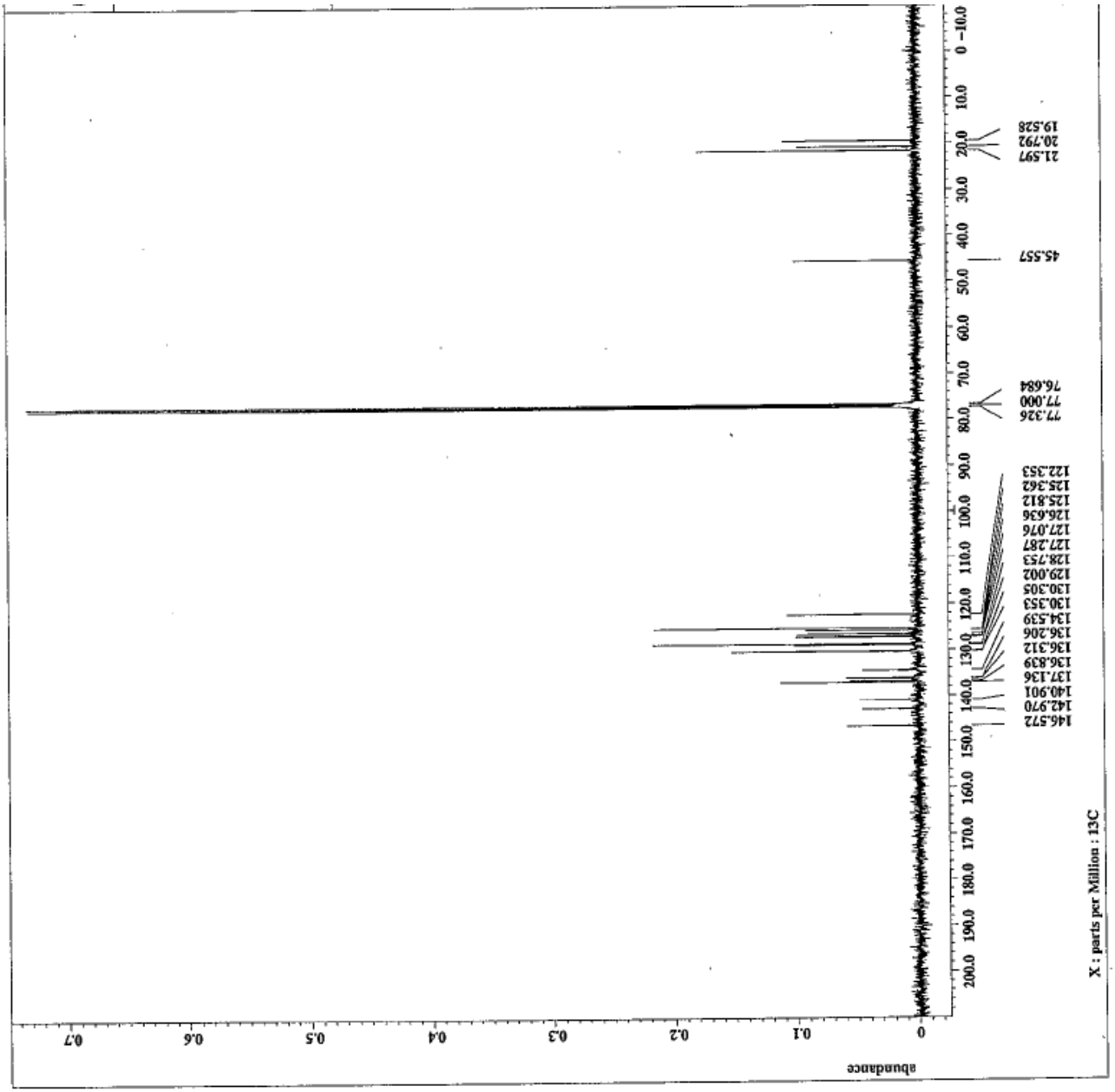
^{1}H-NMR (400 MHz, $CDCl_3$) of 3kb



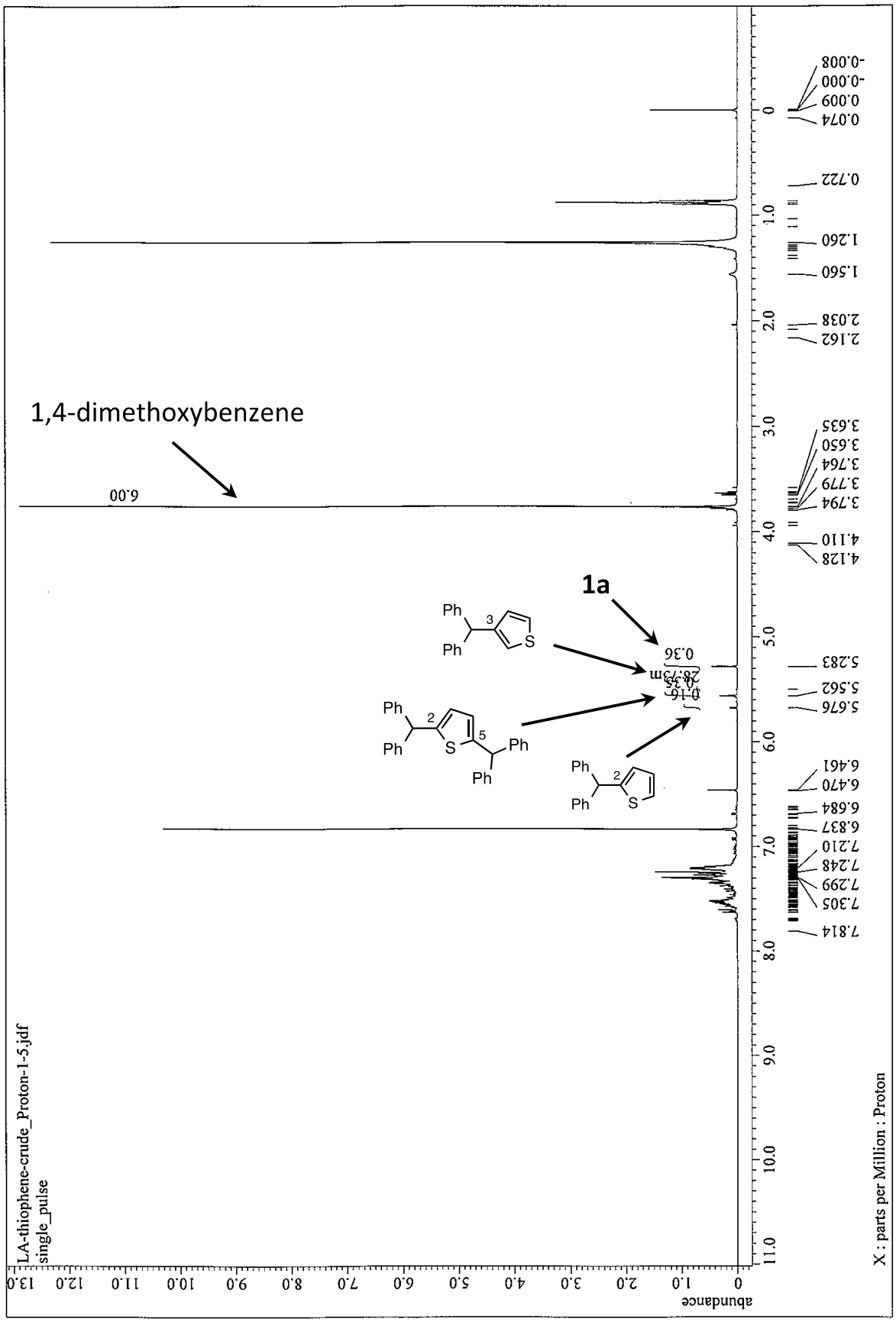


^{13}C-NMR (100 MHz, $CDCl_3$) of 3kb

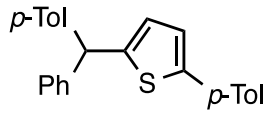


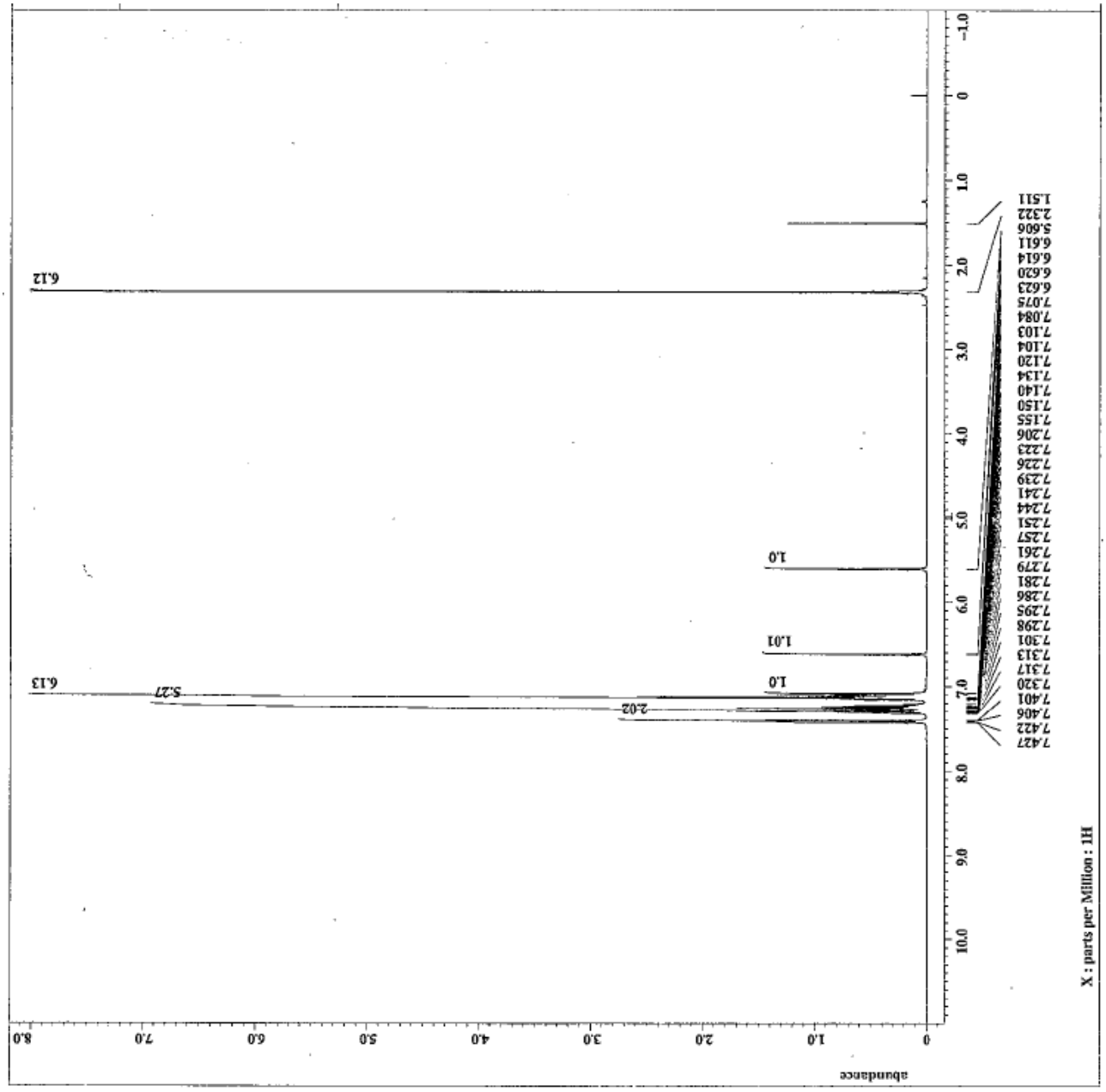


^{1}H-NMR (400 MHz, $CDCl_3$) of crude of reaction with thiophene

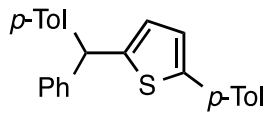


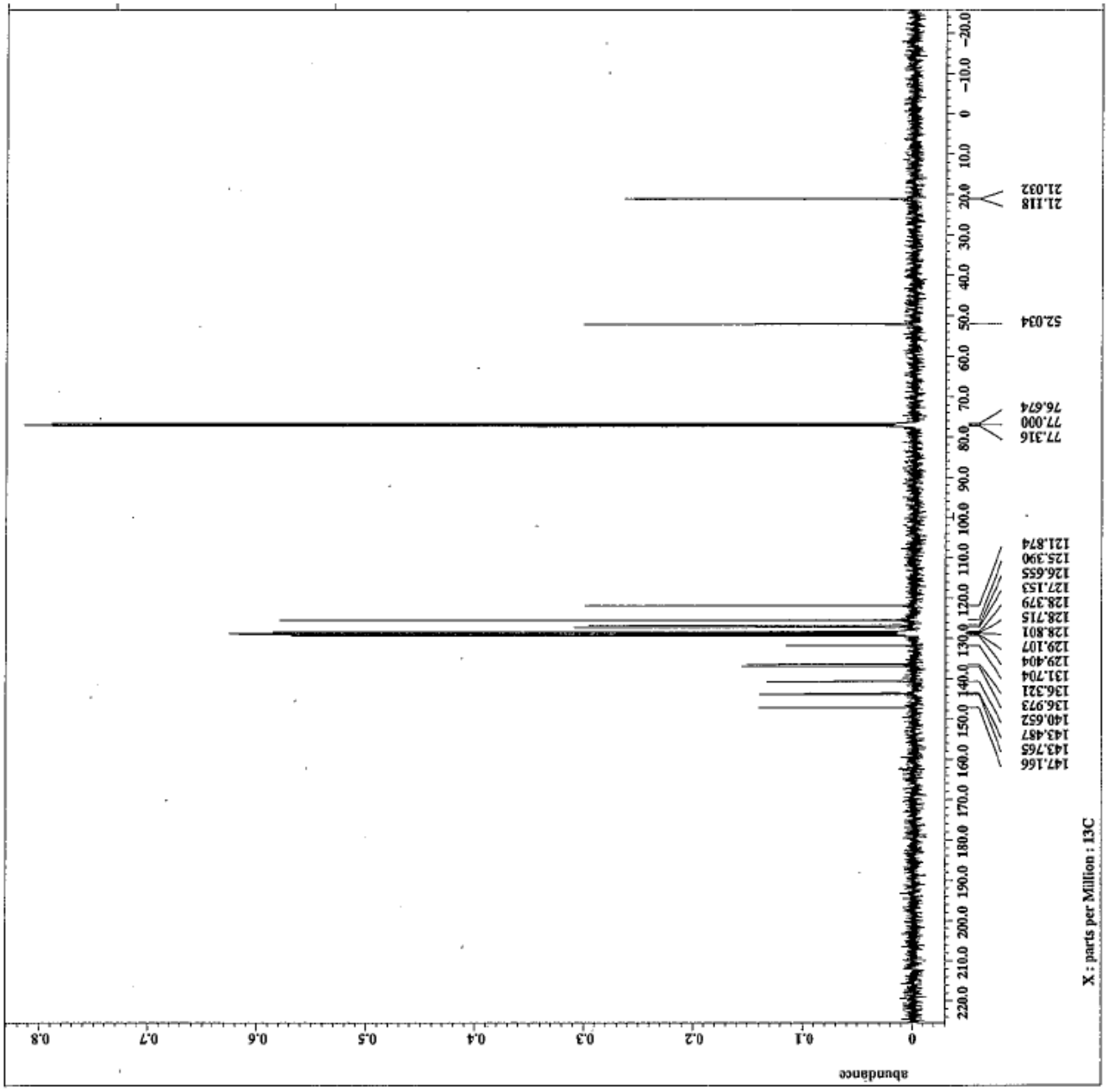
^{1}H-NMR (400 MHz, $CDCl_3$) of 4



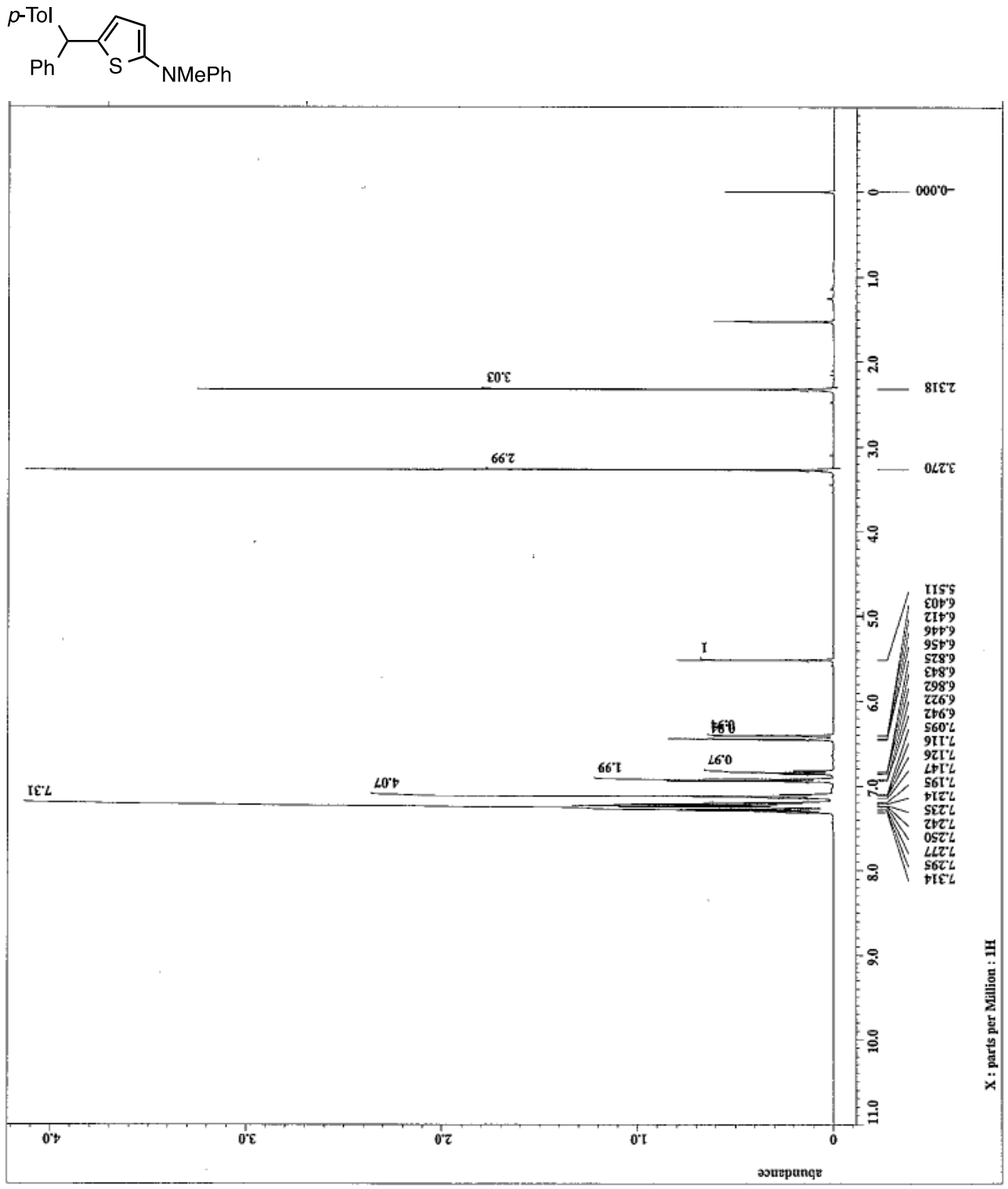


^{13}C-NMR (100 MHz, $CDCl_3$) of 4

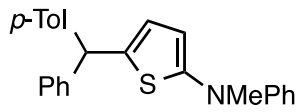


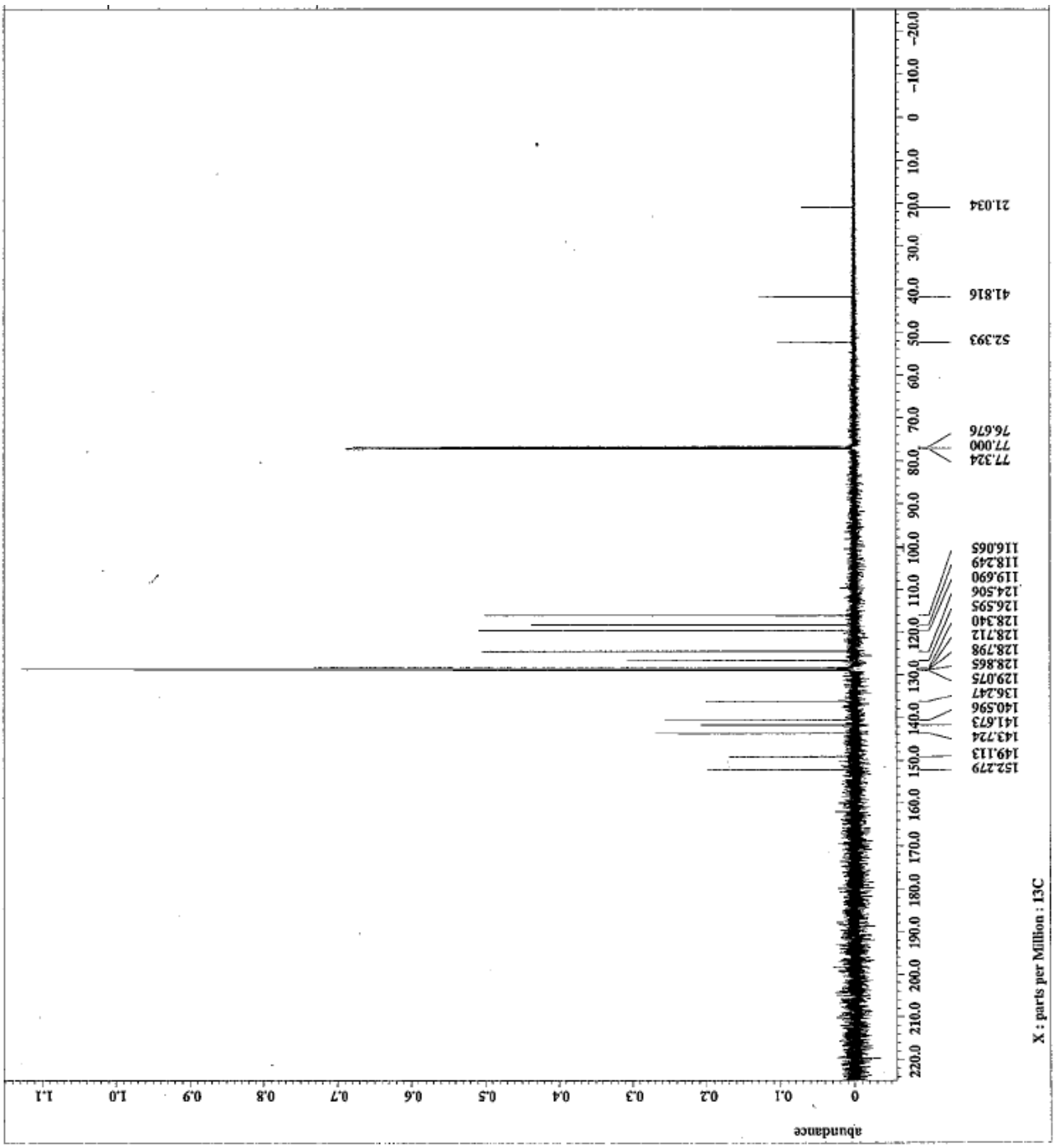


^{1}H-NMR (400 MHz, $CDCl_3$) of 5

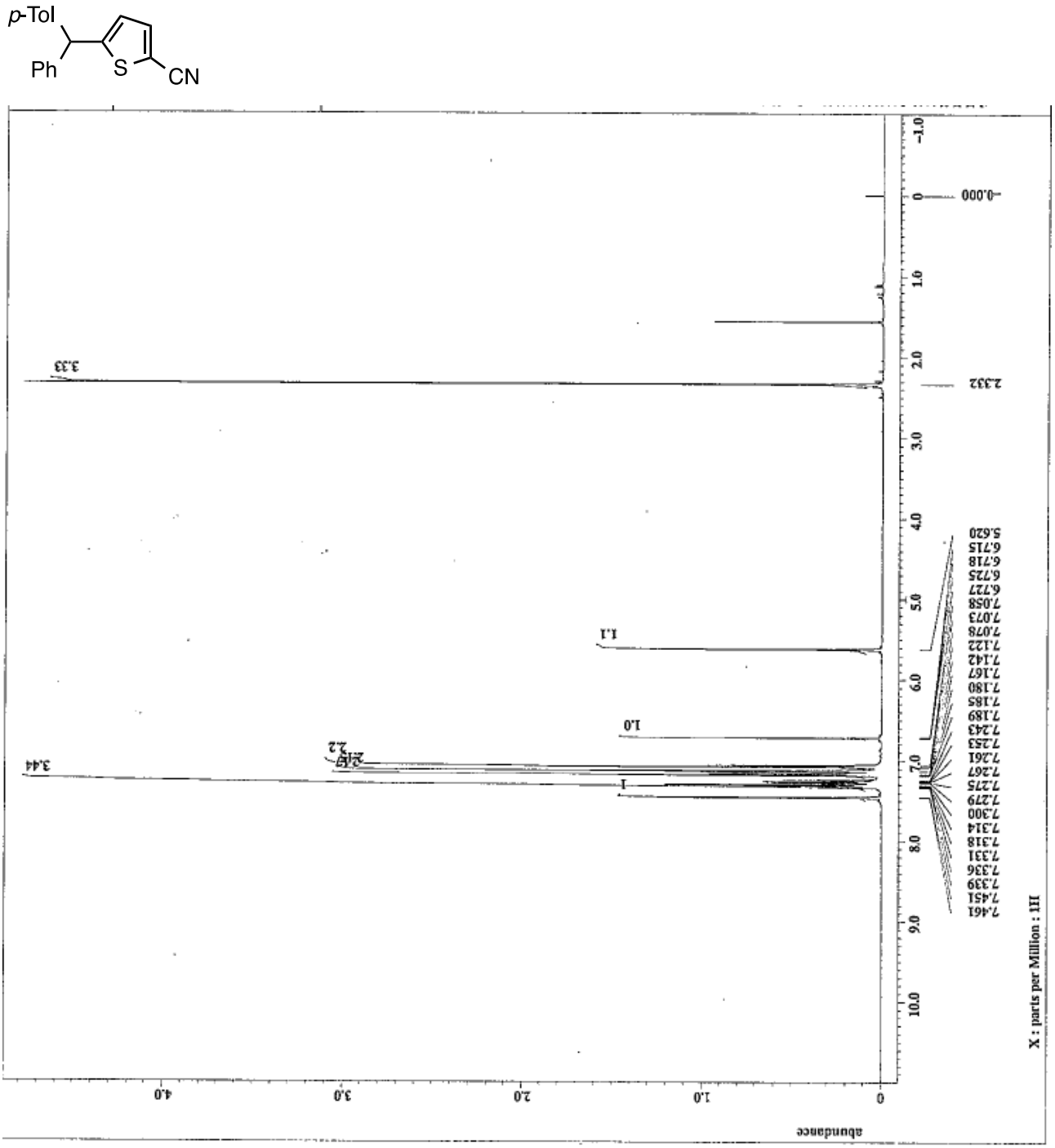


^{13}C-NMR (100 MHz, $CDCl_3$) of 5

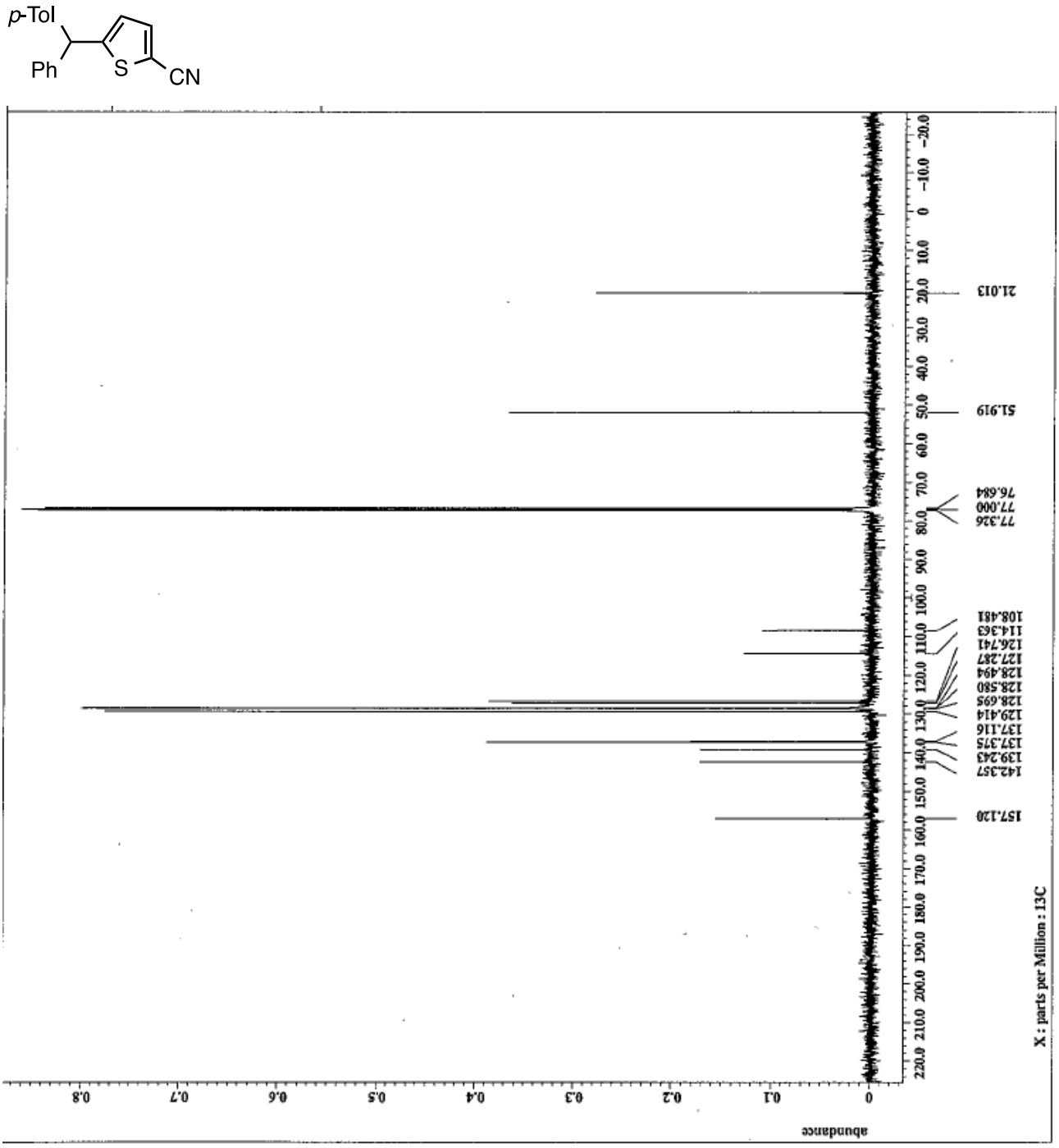




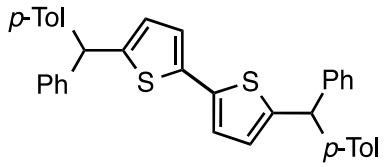
^{1}H-NMR (400 MHz, $CDCl_3$) of 6

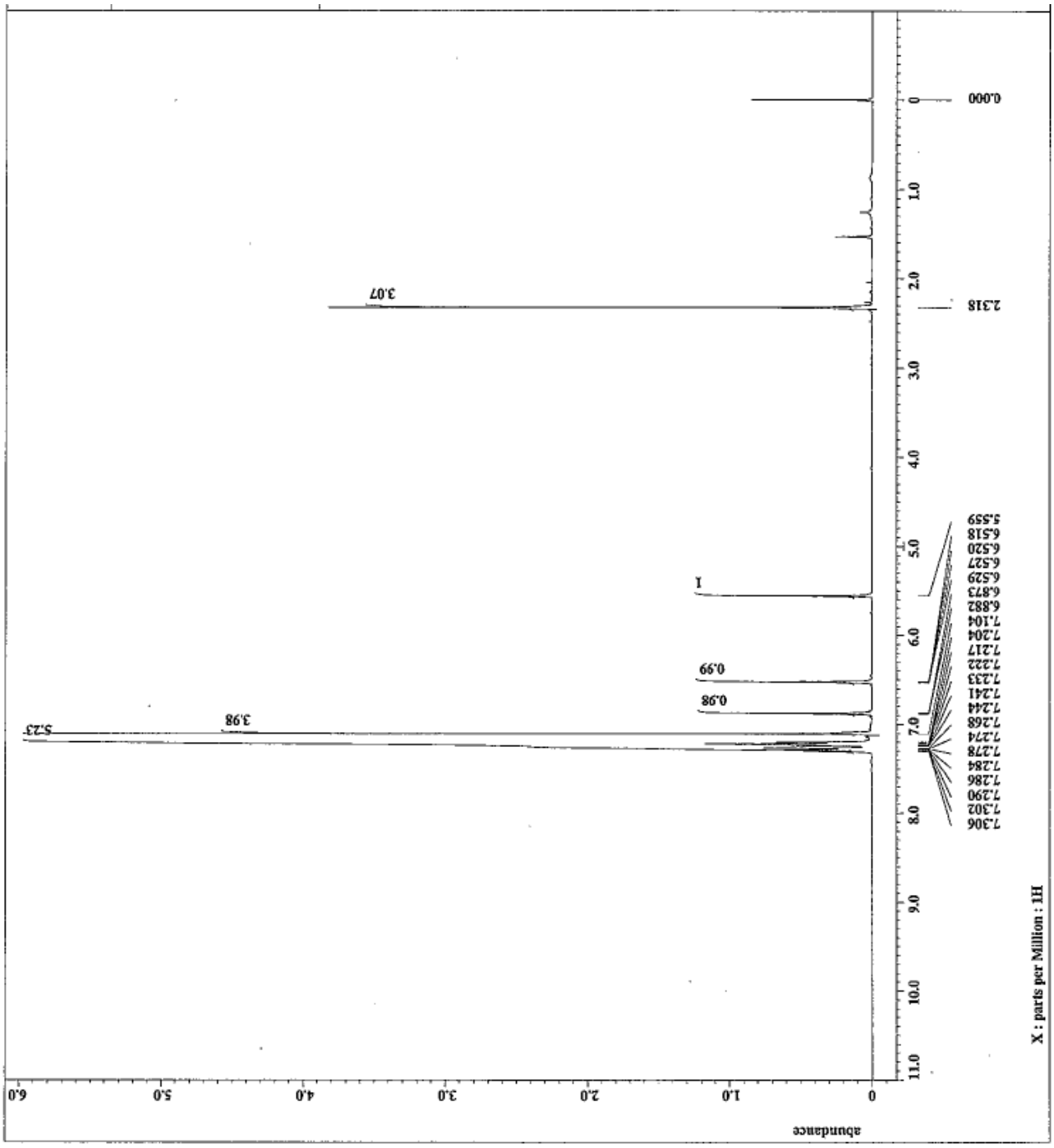


^{13}C-NMR (100 MHz, $CDCl_3$) of 6

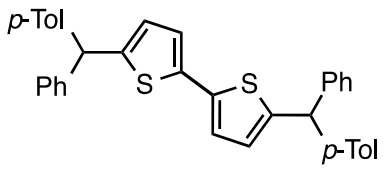


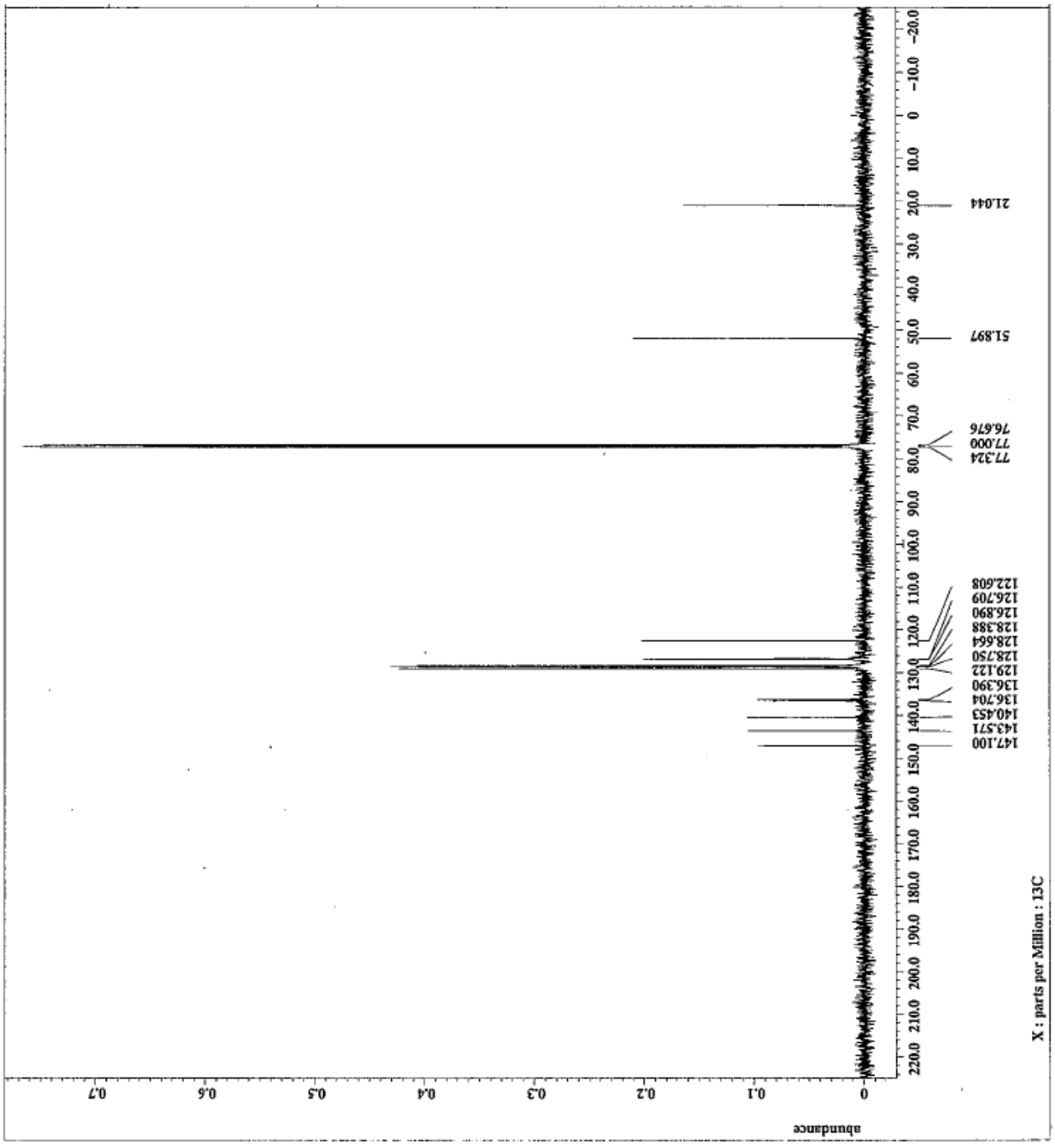
^{1}H-NMR (400 MHz, $CDCl_3$) of 7



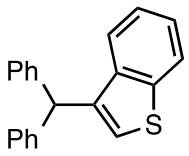


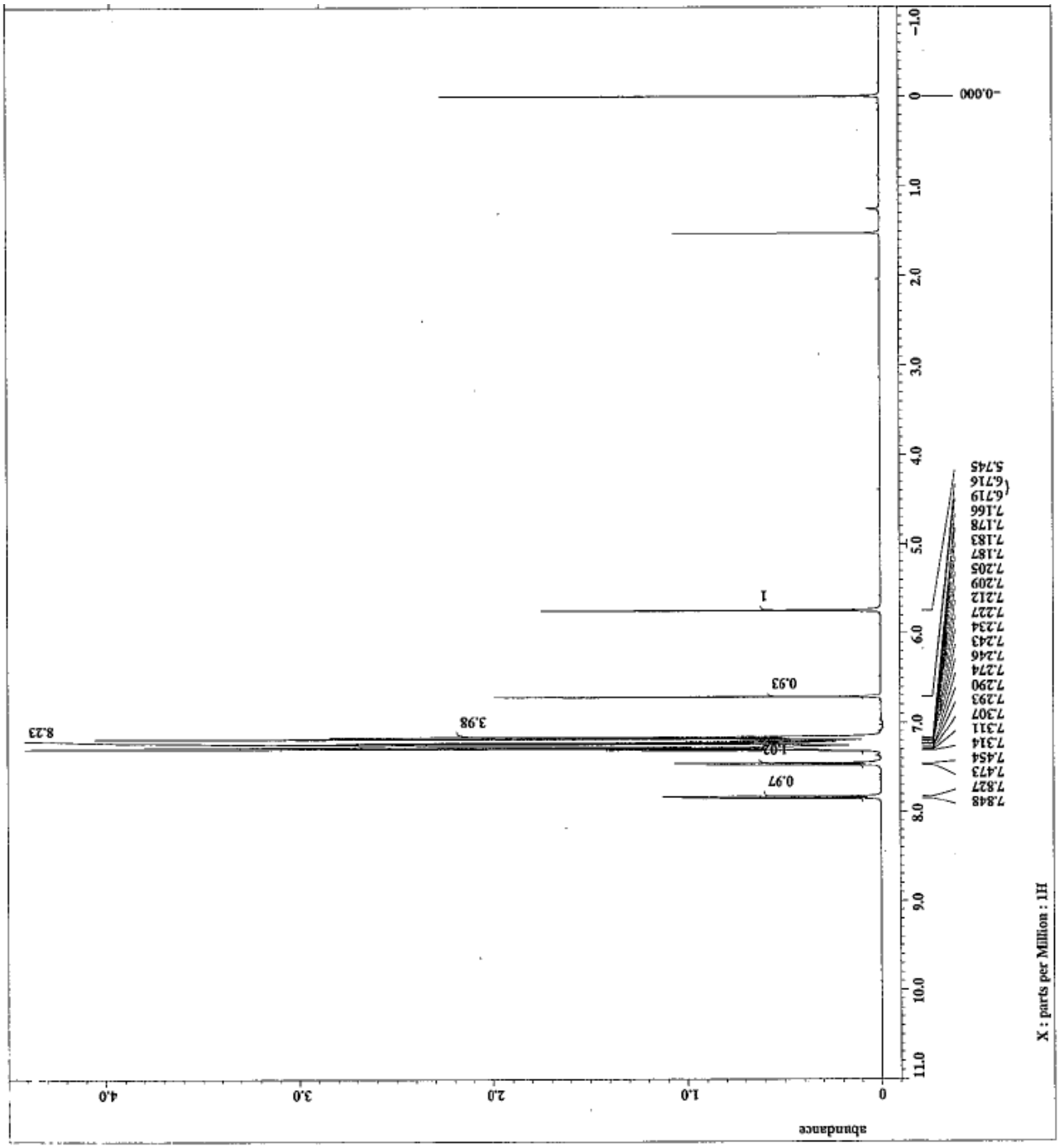
^{13}C-NMR (100 MHz, $CDCl_3$) of 7



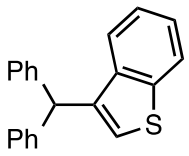


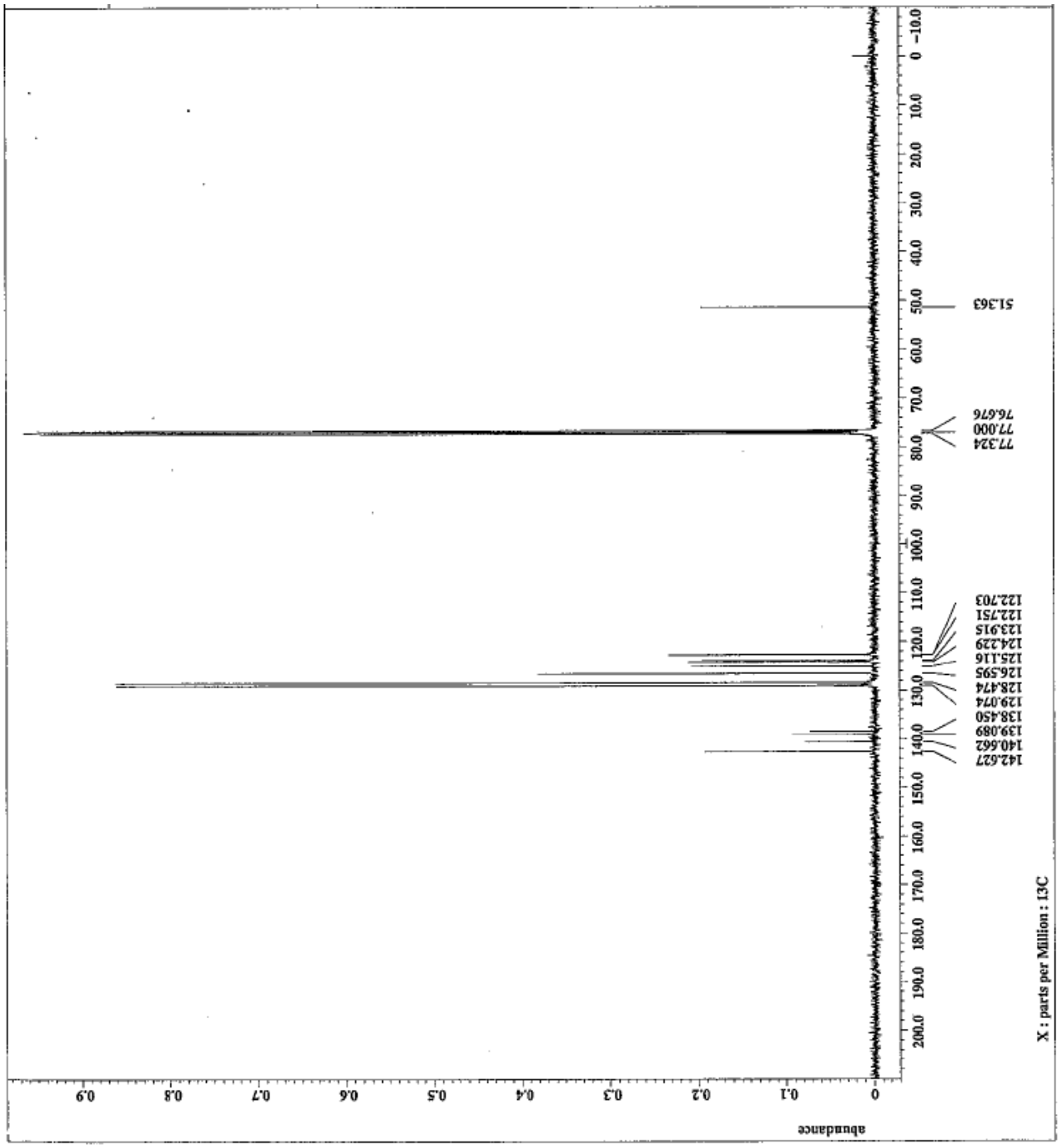
^{1}H-NMR (400 MHz, $CDCl_3$) of 3aq



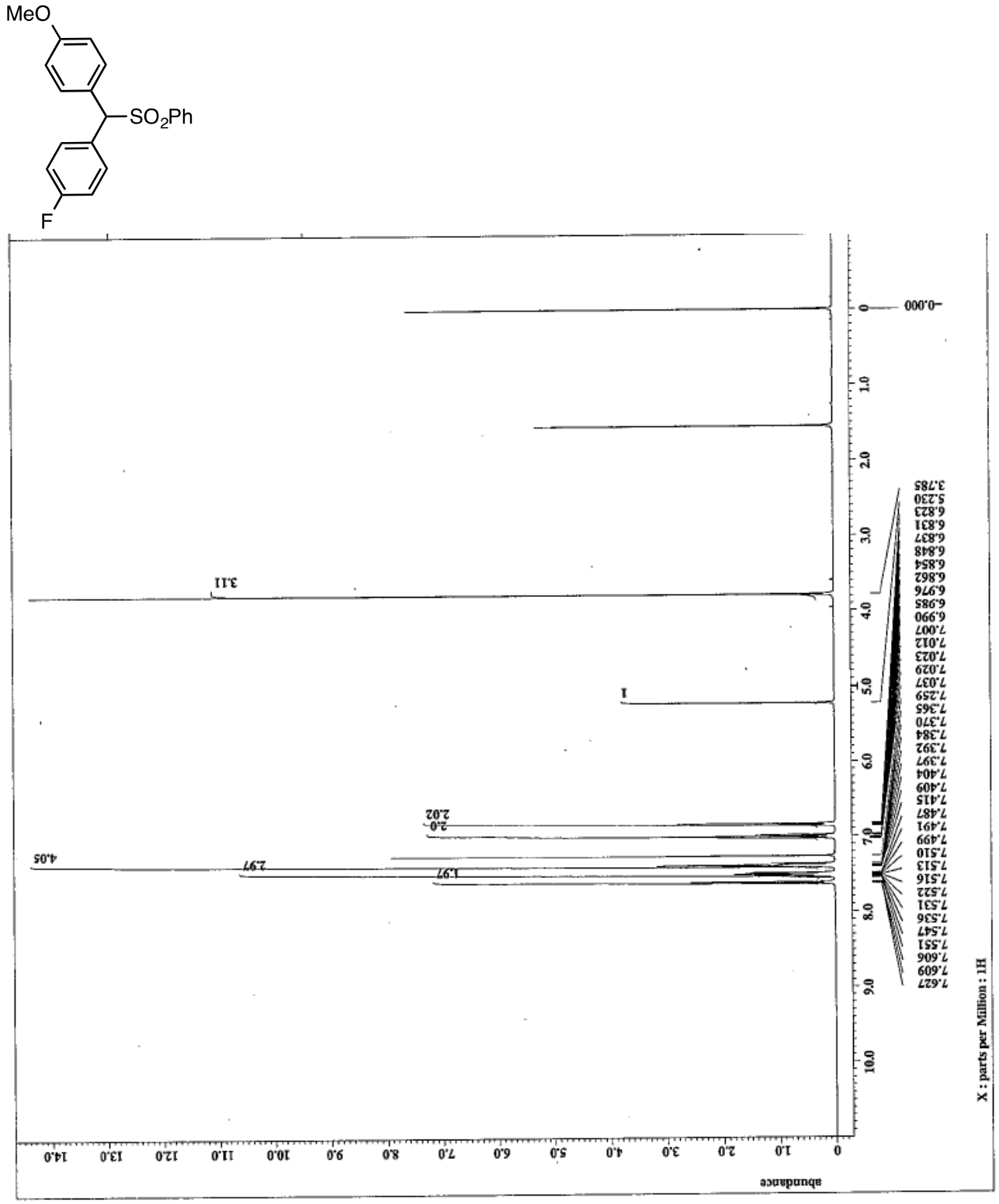


^{13}C-NMR (100 MHz, $CDCl_3$) of 3aq

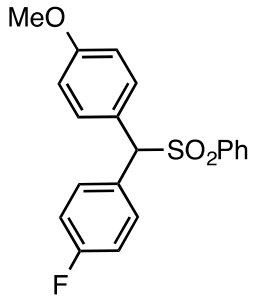


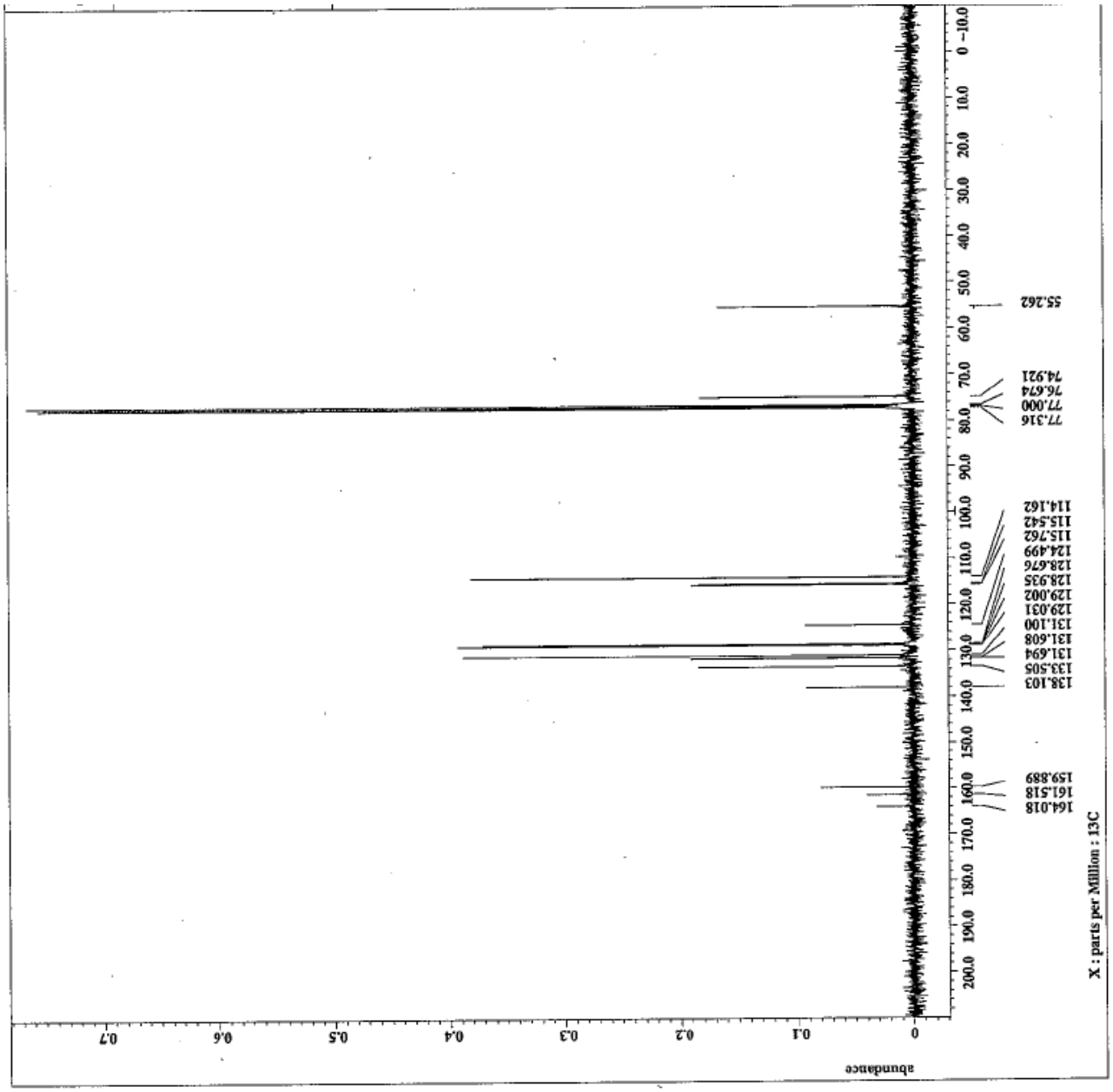


^{1}H-NMR (400 MHz, $CDCl_3$) of 1l

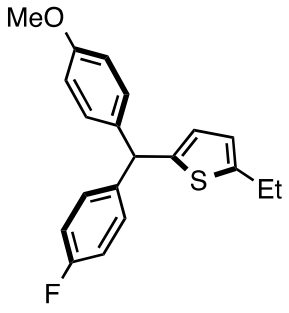


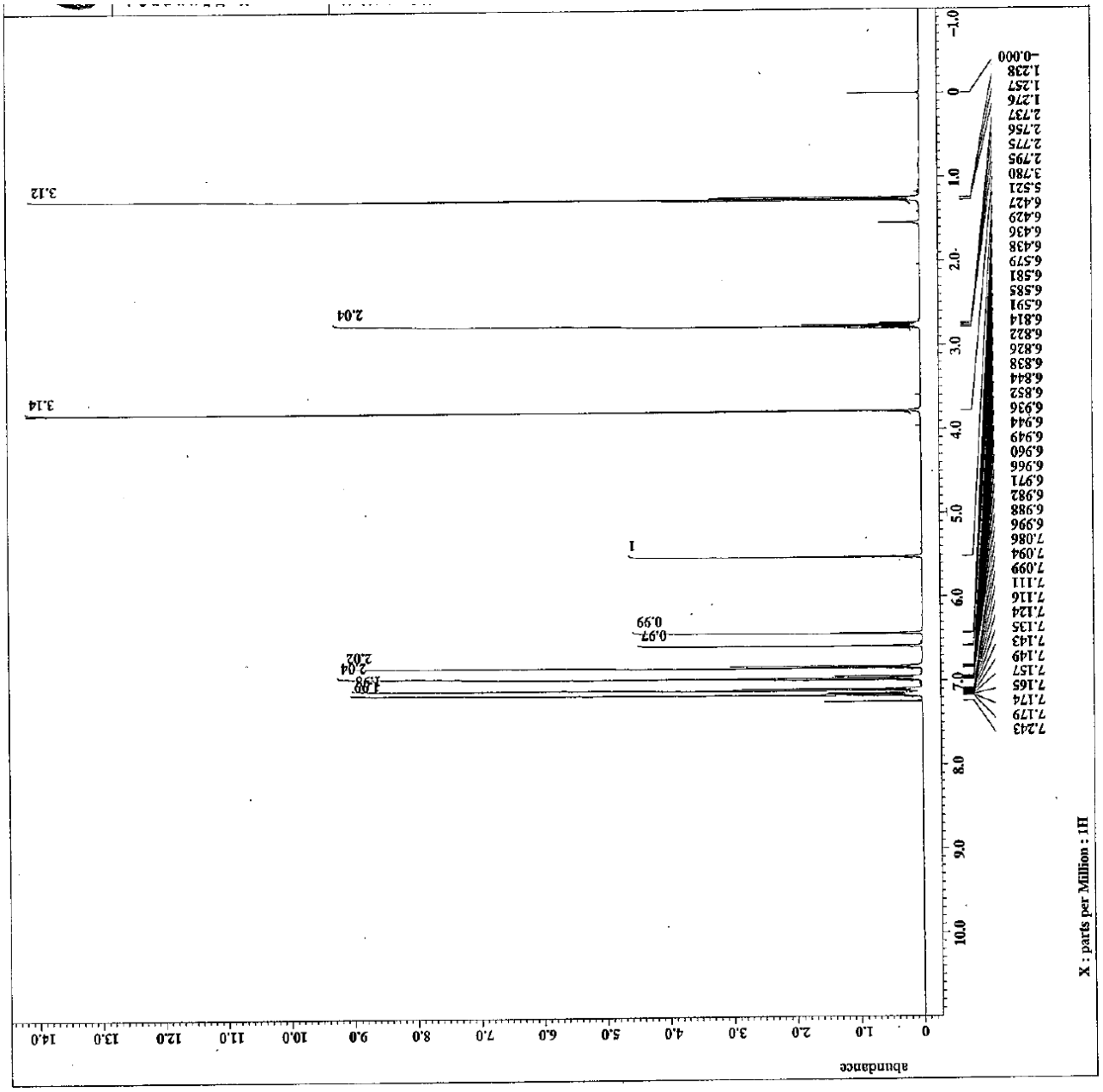
^{13}C-NMR (100 MHz, $CDCl_3$) of 1l



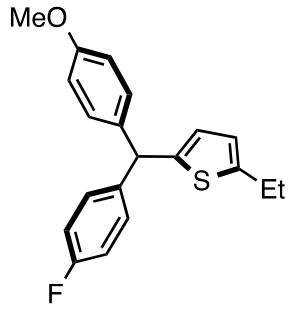


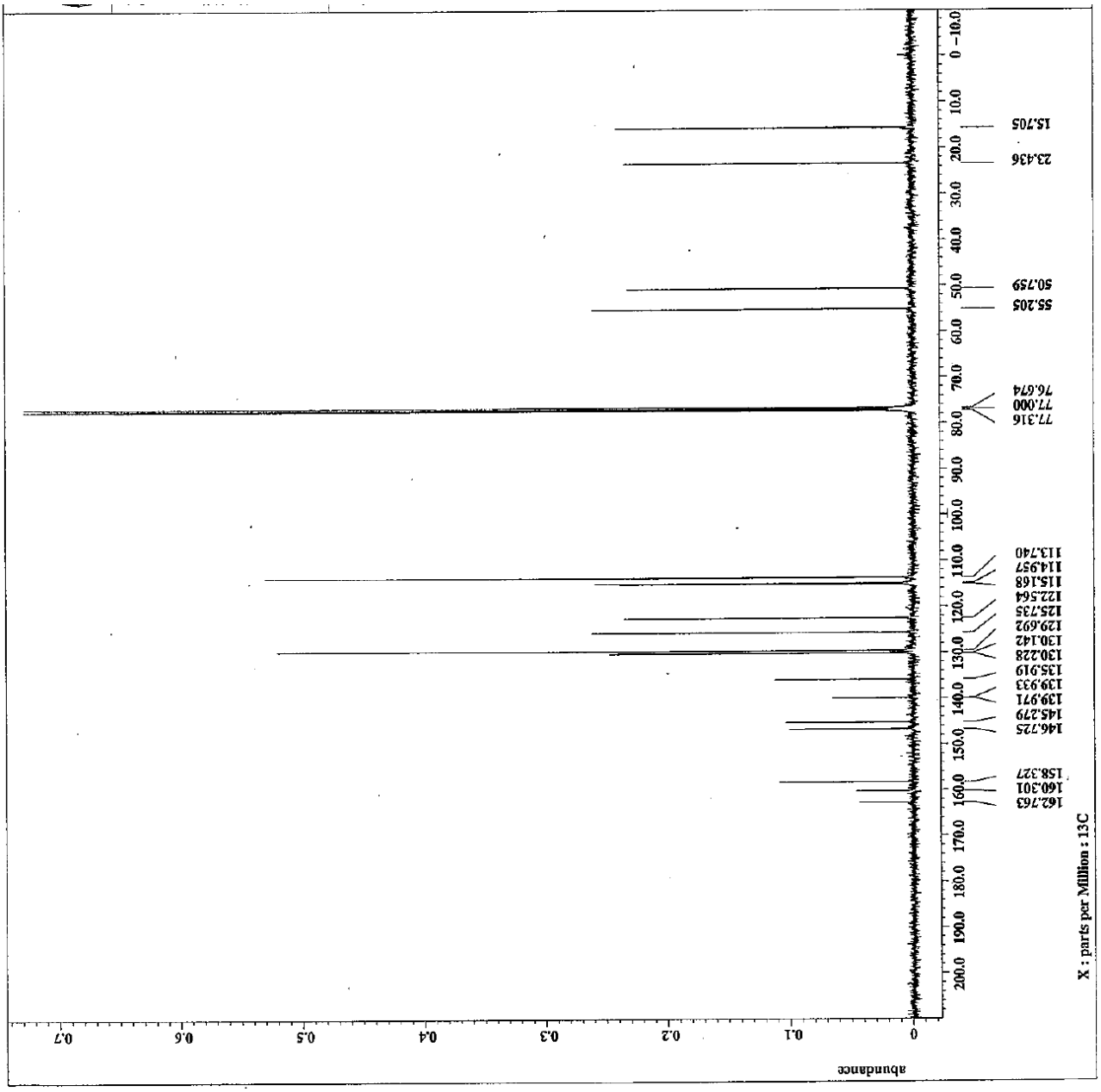
^{1}H-NMR (400 MHz, $CDCl_3$) of 3la



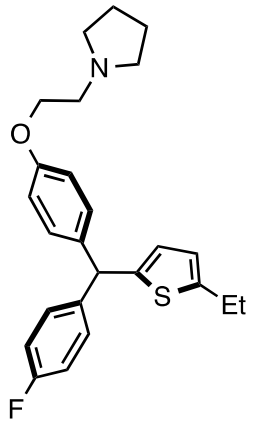


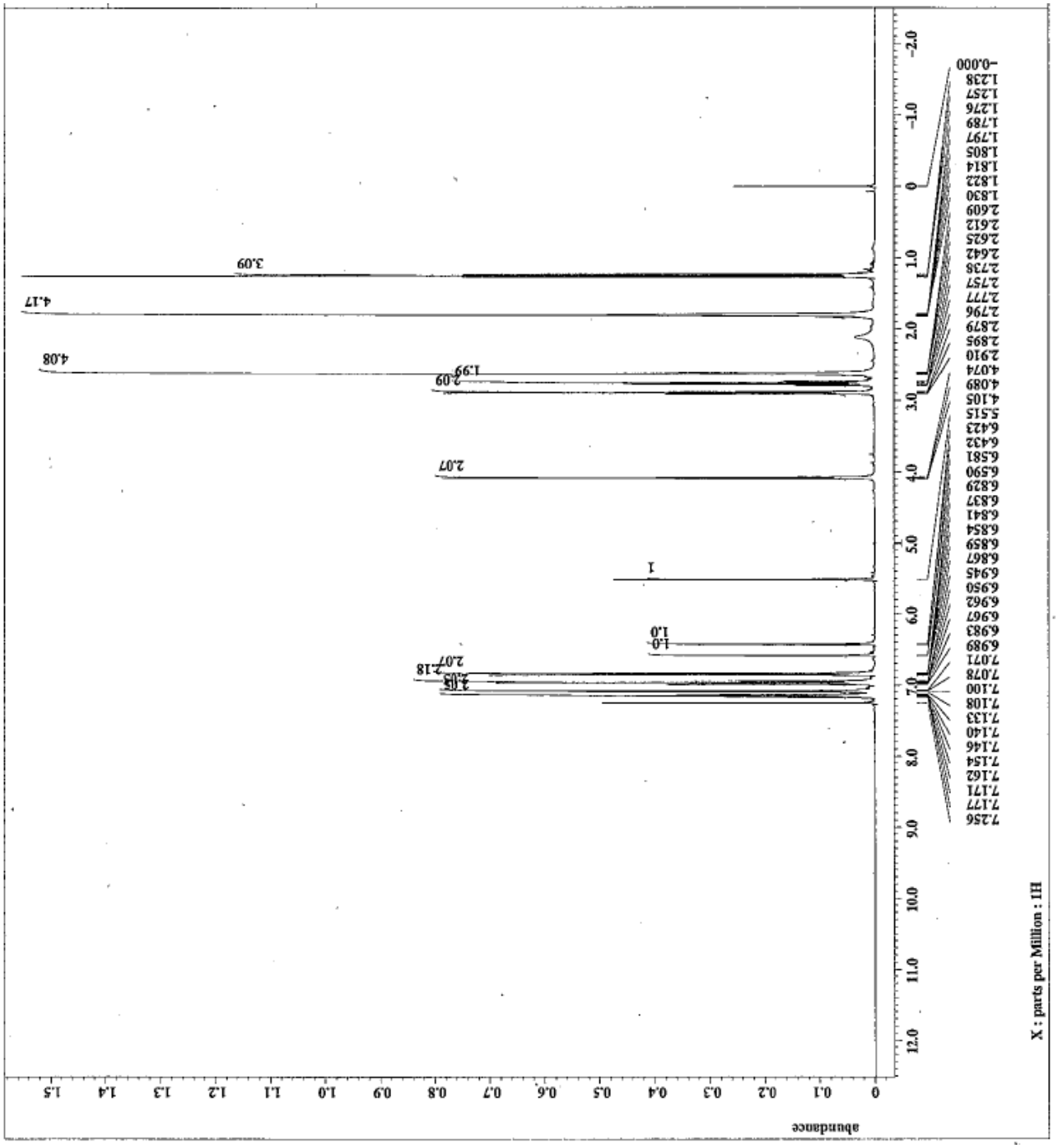
^{13}C-NMR (100 MHz, $CDCl_3$) of 3la





^{1}H-NMR (400 MHz, $CDCl_3$) of 10





^{13}C-NMR (100 MHz, $CDCl_3$) of 10