Supplementary Information

Modular Synthesis of Heptaarylindole

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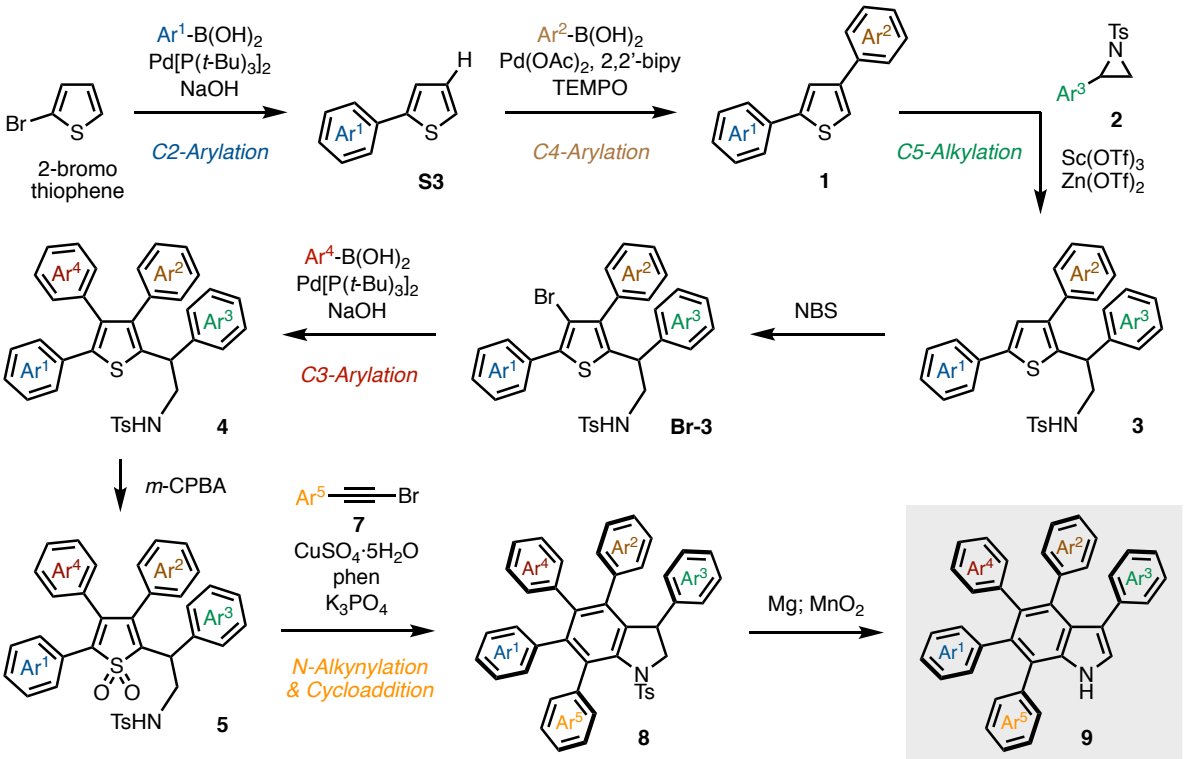
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used as received. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct[1] and was synthesized according to procedures reported in the literature. *N*-Bromosuccinimide (NBS) was freshly recrystallized by water before coupling reaction. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in flame-dried glassware using 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). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) and Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil columns and hexane/EtOAc as an eluent. 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. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. GC/MS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). High-resolution mass spectra (HRMS) were obtained from a JMS-T100TD instrument (DART) and Thermo Fisher Scientific Exactive (ESI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-400 (^{1}H 400 MHz, ^{13}C 101 MHz), a JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) and a JEOL JNM-ECA-600II with Ultra COOL™ probe (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual peak of $C_2D_2Cl_4$ (δ 5.98 ppm) and DMSO-*d*$_6$ (δ 2.50 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm), $C_2D_2Cl_4$ (δ 73.79 ppm) or DMSO-*d*$_6$ (δ 39.52 ppm). Data are reported as follows: chemical shift, multiplicity (brs = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, qd = quartet of doublets, quin = quintet, sext = sextet, m = multiplet), coupling constant (Hz), and integration.

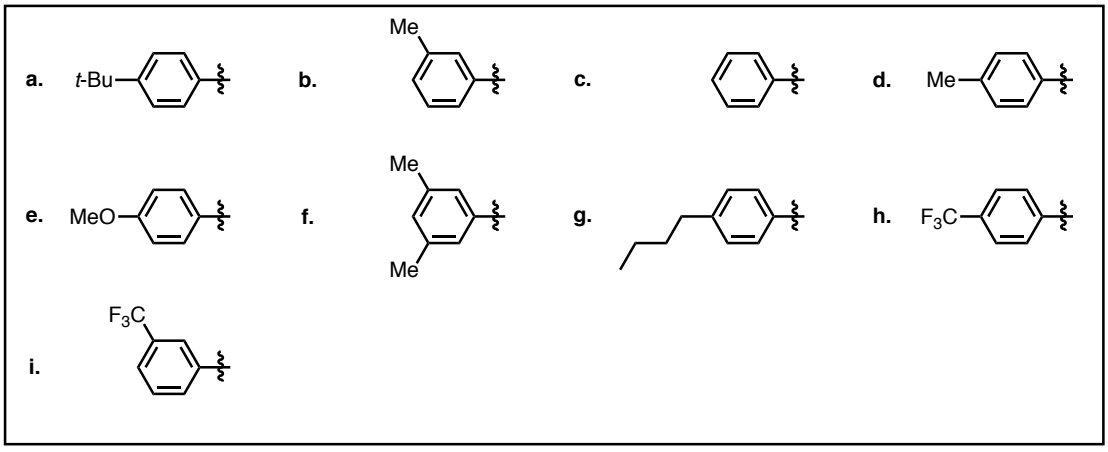
[1] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet and J. A. Ibers, *J. Organometallic Chem.,* 1974, **65**, 253.

2. Overview: Synthesis of Pentaarylindoles 9



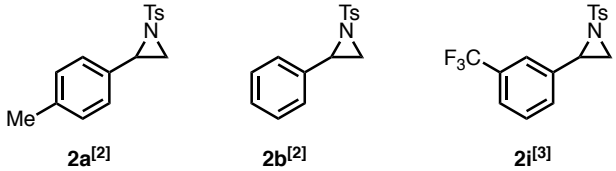
Scheme S1. Overview of the synthesis of pentaarylindoles **9**.

Note: Structure and numbering of installed aryl groups



3. Preparation of Arylaziridines 2

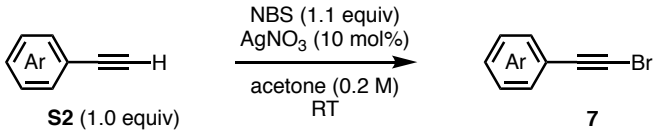
Note: 2-(*p*-Tolyl)-1-tosylaziridine (**2a**),[2] 2-phenyl-1-tosylaziridine (**2b**)[2] and 1-tosyl-2-(3-(trifluoromethyl)phenyl)aziridine (**2i**)[3] were synthesized according to the procedure reported in the literature.



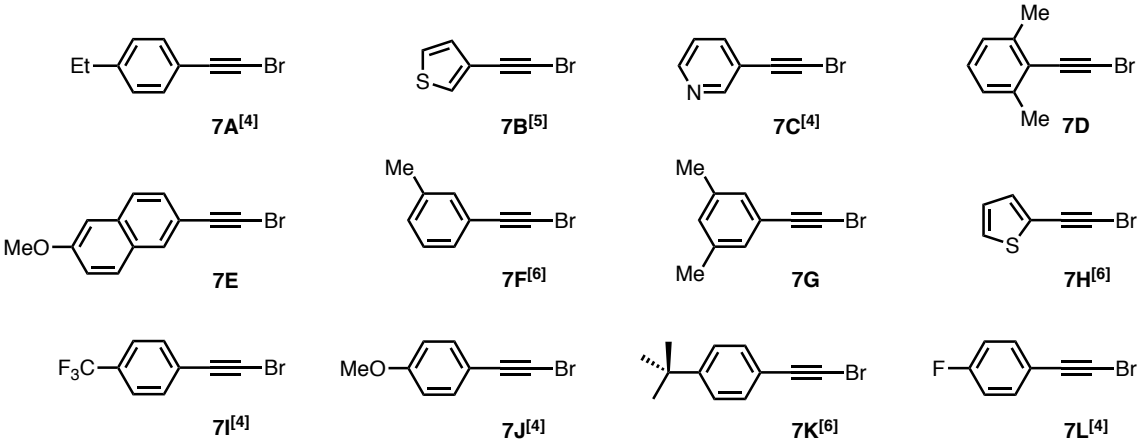
2a[2] **2b**[2] **2i**[3]

4. Preparation of Bromoalkynes 7

Note: Bromoalkynes **7A–7L** were prepared according to reported methods (Scheme S2).[4] Bromoalkynes **7A**,[4] **7B**,[5] **7C**,[4] **7F**,[6] **7H**,[6] **7I**,[4] **7J**,[4] **7K**,[6] and **7L**[4] were reported in the literature. The NMR data obtained for those products were in agreement with the ones previously described in the literature.



S2 (1.0 equiv) **7**



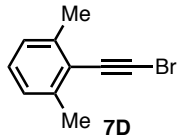
7A[4] **7B**[5] **7C**[4] **7D** **7E** **7F**[6] **7G** **7H**[6] **7I**[4] **7J**[4] **7K**[6] **7L**[4]

Scheme S2. Preparation of bromoalkynes **7**.

A 18-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added terminal alkyne **S2** (2.0 mmol, 1.0 equiv), $AgNO_3$ (34.0 mg, 0.2 mmol, 10 mol%) and acetone (10 mL) under a stream of

[2] T. Ando, D. Kano, S. Minakata, I. Ryu and M. Komatsu, *Tetrahedron*, 1998, **54**, 13485.
[3] I. A. Wani, M. Sayyad and M. K. Ghorai, *Chem. Commun.*, 2017, **53**, 4386.
[4] Y, Feng, Z. Xu, L. Mao, F. Zhang and H. Xu, *Org. Lett.*, 2013, **15**, 1472.
[5] Z. Zeng, H. Jin, J. Xie, B. Tian, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Org. Lett.*, 2017, **19**, 1020.
[6] M. Li, Y. Li, B. Zhao, F. Liang and L. Jin, *RSC Adv.*, 2014, **4**, 30046.

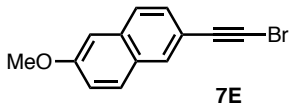
nitrogen. The contents were stirred for 5 min, and *N*-bromosuccinimide (373.8 mg, 2.2 mmol, 1.1 equiv) was added. After stirring at room temperature and monitoring reaction by TLC, the mixture was filtrated with acetone. The filtrate was concentrated *in vacuo* and the residue was purified by Isolera® (hexane/EtOAc) to afford the corresponding bromoalkyne **7**.



7D

2-(Bromoethynyl)-1,3-dimethylbenzene (7D): Purification by Isolera® (hexane) afforded **7D** (243.1 mg, 58% yield) as a yellowish liquid from **S2D** (260.4 mg, 2.0 mmol).

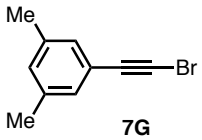
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.1, 128.0, 126.6, 122.5, 78.0, 56.4, 20.9; HRMS (DART) *m/z* calcd for $C_{10}H_{10}Br$ $[MH]^+$: 208.99659, found 208.99640.



7E

2-(Bromoethynyl)-6-methoxynaphthalene (7E): Purification by Isolera® (hexane/EtOAc = 20:1 to 10:1) afforded **7E** (473.0 mg, 91% yield) as a greenish solid from **S2E** (364.8 mg, 2.0 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.70–7.63 (m, 2H), 7.44 (dd, *J* = 1.2 Hz, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.5, 134.3, 131.9, 129.3, 129.0, 128.3, 126.8, 119.5, 117.5, 105.8, 80.5, 55.3, 49.0; HRMS (DART) *m/z* calcd for $C_{13}H_{10}OBr$ $[MH]^+$: 260.99150, found 260.99104.



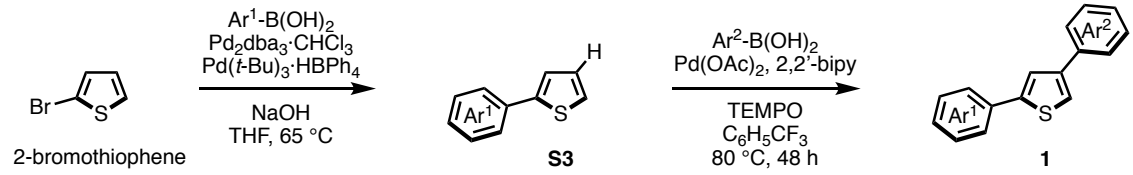
7G

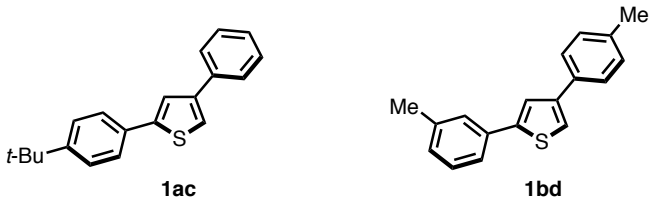
1-(Bromoethynyl)-3,5-dimethylbenzene (7G): Purification by Isolera® (hexane) afforded **7G** (384.7 mg, 92% yield) as a yellowish liquid from **S2G** (260.4 mg, 2.0 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.07 (s, 2H), 6.97 (s, 1H), 2.28 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.9, 130.6, 129.6, 122.3, 80.3, 48.7, 21.0; HRMS (DART) *m/z* calcd for $C_{10}H_{10}Br$ $[MH]^+$: 208.99659, found 208.99659.

5. Synthesis of 2,4-Diarylated Thiophenes 1

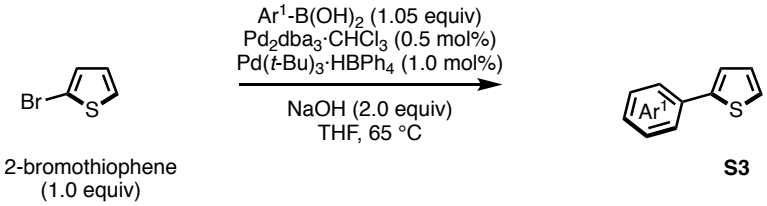
Note: 2,4-Diarylthiophenes **1ac** and **1bd** were prepared according to Scheme S3. 2-Arylthiophene **S3a**[7] and **S3b**[8] were reported in the literature. The NMR data obtained for those products were in agreement with the ones previously described in the literature.



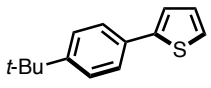


Scheme S3. Synthesis of 2,4-diarylated thiophenes **1**.

5-1. Preparation of C2-Arylthiophene S3



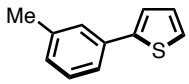
A 500-mL three-necked flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (517.6 mg, 0.5 mmol, 0.5 mol%), tri-*tert*-butylphosphonium tetraphenylborate (522.6 mg, 1 mmol, 1 mol%), arylboronic acid (105 mmol, 1.05 equiv), 2-bromothiophene (9.6 mL, 100 mmol, 1.0 equiv) and THF (200 mL). After stirring for 5 min, NaOH (aq. 3 M, 67 mL, 200 mmol, 2.0 equiv) was slowly added, and then the mixture was stirred at 65 °C for 24 h. After evaporating solvents, water (200 mL) and CH_2Cl_2 (200 mL) were added to the mixture. After extraction with CH_2Cl_2, the organic layer was dried over Na_2SO_4 and the volatiles were removed under reduced pressure. Purification by flash column chromatography afforded 2-arylthiophene **S3**.



S3a: 93% yield

[7] C. C. C. J. Seechurn, S. L. Parisel and T. J. Colacot, *J. Org. Chem.*, 2011, **76**, 7918.
[8] M. N. Rao, D. Banerjee and R. R. Dhanorkar, *Synlett*, 2011, **9**, 1324.

2-(4-(*tert*-Butyl)phenyl)thiophene (S3a): Purification by flash column chromatography (hexane/CH_2Cl_2 = 20:1) afforded **S3a** (20.1 g, 93% yield) as a colorless oil from 4-*tert*-butylphenylboronic acid (18.7 g, 105 mmol).

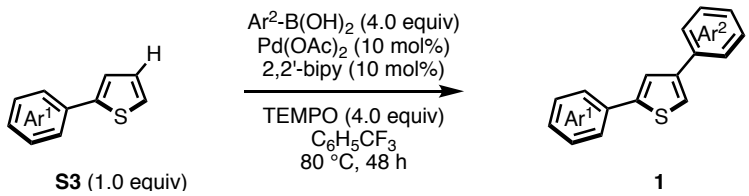


S3b: 98% yield

2-(*m*-Tolyl)thiophene (S3b): Purification by flash column chromatography (hexane/CH_2Cl_2 = 20:1) afforded **S3b** (17.1 g, 98% yield) as a colorless oil from 3-tolylboronic acid (14.3 g, 105 mmol).

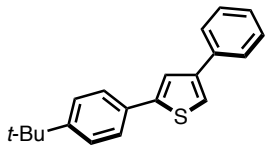
5-2. C4-Arylation of S3

Note: C4-Arylation of 2-arylthiophenes **S3** was conducted according to the procedure reported in the literature.[9]



S3 (1.0 equiv) **1**

A 100-mL two-necked flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added $Pd(OAc)_2$ (1.12 g, 5.0 mmol, 10 mol%), 2,2'-bipyridyl (2,2'-bipy: 780.9 mg, 5.0 mmol, 10 mol%), arylboronic acid (200 mmol, 4.0 equiv), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO: 31.3 g, 200 mmol, 4.0 equiv), 2-arylthiophene **S3** (50 mmol, 1.0 equiv) and *α,α,α*-trifluorotoluene (15 mL) under a stream of nitrogen. The vessel was heated at 80 °C for 48 h. The reaction mixture was filtrated over silica gel (eluent: $CHCl_3$, 100 mL) and the volatiles were removed *in vacuo*. The precipitate was filtrated and washed with hexane to afford 2,4-diarylthiophene **1** as a white solid.

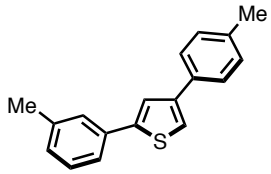


1ac: 49% yield

2-(4-(*tert*-Butyl)phenyl)-4-phenylthiophene (1ac): Purification by filtration with hexane afforded **1ac** (7.16 g, 49%) as a white solid from **S3a** (10.8 g, 50 mmol) and phenylboronic acid (24.4 g, 200 mmol).

[9] S. Kirchberg, S. Tani, K. Ueda, J. Yamaguchi, A. Studer and K. Itami, *Angew. Chem., Int. Ed.*, 2011, **50**, 2387.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.44–7.39 (m, 4H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8, 145.1, 143.0, 135.9, 131.6, 128.8, 127.2, 126.3, 125.8, 125.6, 121.9, 119.3, 34.6, 31.3; HRMS (DART) *m/z* calcd for $C_{20}H_{21}S$ $[MH]^+$: 293.13640, found 293.13500.

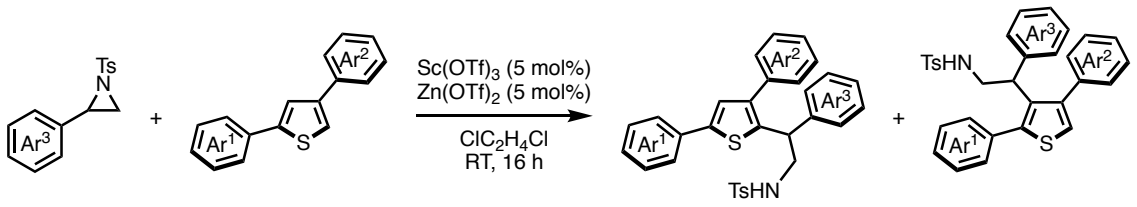


1bd: 45% yield

2-(*m*-Tolyl)-4-(*p*-tolyl)thiophene (1bd): Purification by filtration with hexane afforded **1bd** (5.93 g, 45%) as a white solid from **S3b** (8.7 g, 50 mmol) and *p*-tolylboronic acid (27.2 g, 200 mmol)

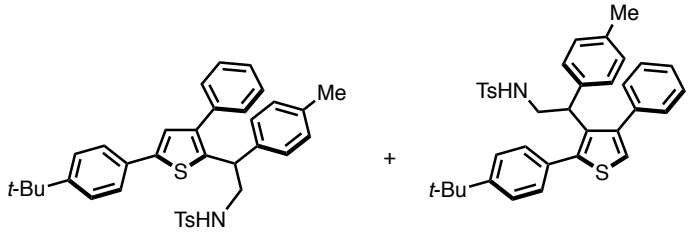
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 1.2 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.47–7.43 (m, 2H), 7.32 (d, *J* = 1.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.0, 143.0, 138.5, 137.0, 134.3, 133.1, 129.5, 128.8, 128.4, 126.5, 126.2, 123.0, 122.2, 118.9, 21.4, 21.1; HRMS (DART) *m/z* calcd for $C_{18}H_{17}S$ $[MH]^+$: 265.10510, found 265.10514.

6. C5-alkylation of 2,4-Diarylated Thiophenes 1



2 (1.0 equiv) **1** (1.5 equiv) **3** (major) **3'** (minor)

A 100-mL two-necked flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added arylaziridine **2** (5.0 mmol, 1.0 equiv), 2,4-diarylthiophene **1** (7.5 mmol, 1.5 equiv) and dichloroethane (27 mL) under a stream of nitrogen. The contents were stirred for 5 min,and scandium trifluoromethanesulfonate (123.0 mg, 0.25 mmol, 5 mol%) and zinc trifluoromethanesulfonate (90.0 mg, 0.25 mmol, 5 mol%) were added. After stirring at room temperature for 24 h, the mixture was passed through a short silica gel pad (EtOAc). The filtrate was concentrated *in vacuo* and the residue was purified by Isolera® (hexane/EtOAc) to afford the corresponding C5-alkylated thiophene **3** (desired regioisomer) and C3-alkylated thiophene **3'** (undesired regioisomer).



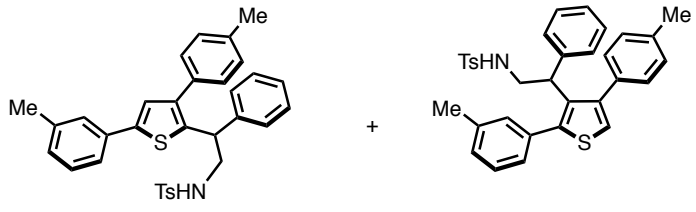
3acd 79% yield (**3acd**:**3acd'** = 9:1) **3acd'**

From **2a** (1.44 g, 5.0 mmol), **1ac** (2.19 g, 7.5 mmol): Purification by Isolera® (hexane/EtOAc = 10:1 to 5:1) afforded the mixture of **3acd** and **3acd'** as a white solid (2.30 g, 79% yield (mixture), **3acd**:**3acd'** = 9/1). To characterize regioisomers, analytical amount of the mixture was separated by preparative recycling gel permeation chromatography (GPC).

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (3acd):** ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41–7.33 (m, 5H), 7.28–7.21 (m, 2H), 7.18–7.13 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 4.44 (brs, 1H), 4.34 (t, *J* = 7.8 Hz, 1H), 3.56–3.48 (m, 1H), 3.46–3.38 (m, 1H), 2.37 (s, 3H), 2.30 (s, 3H) 1.33 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8, 143.3, 142.2, 141.9, 137.6, 137.5, 137.0, 136.6, 136.1, 131.0, 129.60, 129.58, 128.8, 128.5, 127.5, 127.3, 127.0, 125.8, 125.3, 124.9, 49.3, 44.2, 34.6, 31.2, 21.5, 21.0; HRMS (ESI) *m/z* calcd for $C_{36}H_{37}NO_2S_2Na$ $[MNa]^+$: 602.2158, found 602.2159.

***N*-(2-(2-(4-(*tert*-Butyl)phenyl)-4-phenylthiophen-3-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (3acd'):** ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.24–7.16 (m, 5H), 7.12–7.07 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 6.6 Hz, 2H), 6.68 (d, *J* = 8.4

Hz, 2H), 4.44 (brs, 1H), 4.34 (t, *J* = 7.8 Hz, 1H), 3.56–3.48 (m, 1H), 3.46–3.38 (m, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.2, 143.8, 143.1, 142.1, 137.9, 137.1, 136.6, 135.9, 134.3, 131.1, 129.7, 129.6, 129.4, 128.9, 127.8, 127.3, 127.2, 127.0, 125.3, 123.5, 44.5, 42.6, 34.6, 31.3, 21.5, 20.9; HRMS (ESI) *m/z* calcd for $C_{36}H_{37}NO_2S_2Na$ $[MNa]^+$: 602.2158, found 602.2161.

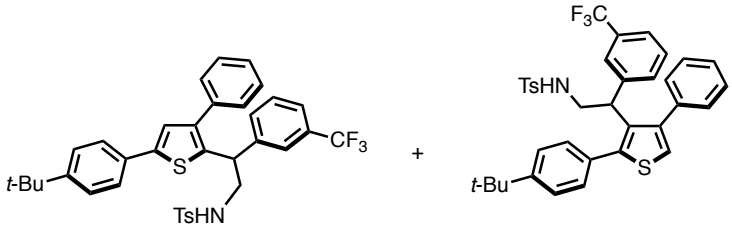


3bdc 62% yield (**3bdc**:**3bdc'** = 7:1) **3bdc'**

From **2b** (1.44 g, 5.0 mmol), **1bd** (2.19 g, 7.5 mmol): Purification by Isolera® (hexane/EtOAc = 10:1 to 3:1) afforded **3bdc** (1.47g, 55% yield) as a white solid and **3bdc'** (206.6 mg, 8% yield) as a white solid.

4-Methyl-*N*-(2-phenyl-2-(5-(*m*-tolyl)-3-(*p*-tolyl)thiophen-2-yl)ethyl)benzenesulfonamide (3bdc): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.37–7.32 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.21 (m, 2H), 7.20–7.14 (m, 7H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 4.43 (brs, 1H), 4.38 (t, *J* = 7.8 Hz, 1H), 3.58–3.50 (m, 1H), 3.48–3.41 (m, 1H), 2.41 (s, 3H), 2.39–2.36 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.3, 142.3, 142.1, 140.7, 138.5, 137.2, 137.1, 136.6, 133.7, 133.1, 129.6, 129.2, 128.9, 128.8, 128.7, 128.5, 127.7, 127.3, 127.0, 126.3, 125.4, 122.7, 49.3, 44.7, 21.5, 21.4, 21.2; HRMS (ESI) *m/z* calcd for $C_{33}H_{31}NO_2S_2Na$ $[MNa]^+$: 560.1688, found 560.1692.

4-Methyl-*N*-(2-phenyl-2-(2-(*m*-tolyl)-4-(*p*-tolyl)thiophen-3-yl)ethyl)benzenesulfonamide (3bdc'): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.19–7.09 (m, 7H), 7.07 (s, 1H), 7.05 (d, *J* = 6.6 Hz, 1H), 7.01 (s, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.83–6.77 (m, 4H), 4.42 (t, *J* = 8.1 Hz, 1H), 4.19–4.12 (m, 1H), 3.48–3.41 (m, 1H), 3.12–3.05 (m, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.8, 143.0, 141.9, 141.2, 137.9, 136.9, 136.5, 134.4, 134.1, 133.9, 130.9, 129.5, 129.2, 128.9, 128.6, 128.2, 128.1, 127.4, 127.0, 126.9, 126.3, 123.3, 44.4, 42.8, 21.5, 21.3, 21.1; HRMS (ESI) *m/z* calcd for $C_{33}H_{31}NO_2S_2Na$ $[MNa]^+$: 560.1688, found 560.1691.



3aci 67% yield (**3aci**:**3aci'** = 8:3) **3aci'**

From **2i** (241.3 mg, 0.71 mmol), **1ac** (313.0 mg, 1.1 mmol): Purification by PTLC (hexane/EtOAc = 4:1) afforded **3aci** (219.7 mg, 49% yield) as a white solid and **3aci'** (80.6 mg, 18% yield) as a white solid.

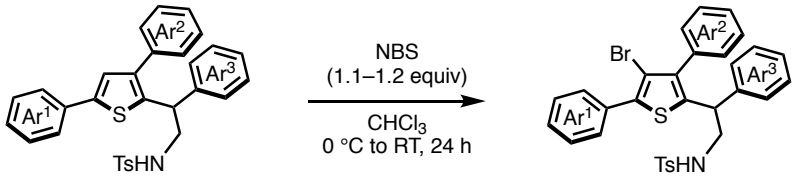
***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-3-phenylthiophen-2-yl)-2-(3-(trifluoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (3aci):**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.51–7.46 (m, 3H), 7.45–7.33 (m, 7H), 7.26 (s, 1H), 7.21–7.13 (m, 5H), 4.56 (q, *J* = 5.6 Hz, 1H), 4.41 (t, *J* = 8.0 Hz, 1H), 3.59–3.44 (m, 2H), 2.39 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 143.6, 142.7, 142.6, 141.7, 136.5, 135.9, 135.8, 131.1 (q, $^{2}J_{CF}$ = 32.6 Hz), 131.0, 130.7, 129.8, 129.4, 128.8, 128.6, 127.6, 127.0, 125.9, 125.4, 125.2, 123.8 ($^{1}J_{CF}$ = 273 Hz), 124.5 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.2 (q, $^{3}J_{CF}$ = 3.8 Hz), 49.0, 44.6, 34.6, 31.2, 21.5; HRMS (ESI) *m/z* calcd for $C_{36}H_{34}F_3NO_2S_2Na$ [MNa]$^{+}$: 656.1875, found 656.1878.

***N*-(2-(2-(4-(*tert*-Butyl)phenyl)-4-phenylthiophen-3-yl)-2-(3-(trifluoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (3aci'):**

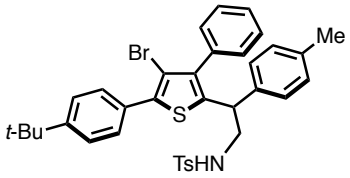
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.24–7.15 (m, 6H), 7.13 (t, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.84 (m, 3H), 4.46 (t, *J* = 8.0 Hz, 1H), 4.24 (dd, *J* = 8.0 Hz, *J* = 4.4 Hz, 1H), 3.46 (ddd, *J* = 12.4 Hz, 8.0 Hz, 8.0 Hz, 1H), 3.20 (ddd, *J* = 12.4 Hz, 8.4 Hz, 4.4 Hz, 1H), 2.43 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): 151.5, 143.4, 142.3, 141.7, 136.8, 136.4, 134.0, 131.3, 130.6, 130.3 (q, $^{2}J_{CF}$ = 31.7 Hz), 129.8, 129.7, 129.4, 128.6, 127.9, 127.5, 127.0, 125.4, 123.9 ($^{1}J_{CF}$ = 274 Hz), 123.66 (q, $^{3}J_{CF}$ = 3.8 Hz), 123.63, 123.2 (q, $^{3}J_{CF}$ = 3.8 Hz), 44.5, 42.6, 34.6, 31.2, 21.5; HRMS (ESI) *m/z* calcd for $C_{36}H_{34}F_3NO_2S_2Na$ [MNa]$^{+}$: 656.1875, found 656.1877.

7. Bromination of 2,3,5-Trisubstituted Thiophenes 3



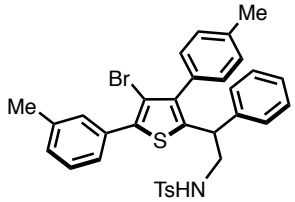
3 (1.0 equiv) **Br-3**

A 100-mL flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added 2-alkyl-3,5-diarylthiophene **3** (1.0 equiv) in chloroform (0.1 M) and *N*-bromosuccinimide (1.1–1.2 equiv) at 0 °C. After warming the reaction mixture to room temperature and stirring at room temperature for 24 h, water (20 mL), saturated $NaHCO_3$ aqueous solution (20 mL) and CH_2Cl_2 (20mL) were added to the mixture. After extraction with CH_2Cl_2, the organic layer was dried over Na_2SO_4 and the volatiles were removed under *in vacuo*. The crude product was purified by Isolera® (hexane/EtOAc) to afford the corresponding bromothiophene **Br-3**.



Br-3acd: 89% yield

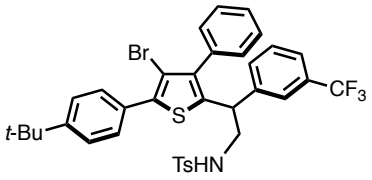
***N*-(2-(4-Bromo-5-(4-(*tert*-butyl)phenyl)-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzene sulfonamide (Br-3acd):** Purification by Isolera® (hexane/EtOAc = 10:1 to 3:1) afforded **Br-3acd** (1.06 g, 89% yield, single isomer) as a white solid from the mixture of **3acd** and **3acd'** (1.16 g, 2.0 mmol (mixture), **3acd**:**3acd'** = 9/1), *N*-bromosuccinimide (391.6 mg, 2.2 mmol) and chloroform (20 mL). The yield of **Br-3acd** was calculated based on the amount of the corresponding isomer **3acd**.
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.68–7.58 (m, 4H), 7.50–7.42 (m, 5H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.23–7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 6.6 Hz, 2H), 4.28–4.21 (m, 2H), 3.59–3.50 (m, 2H), 2.44 (s, 3H), 2.36 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$): δ 151.4, 143.7, 141.1, 139.3, 137.3, 136.38, 136.35, 136.1, 135.0, 130.2, 129.72, 129.66, 128.5, 128.3, 128.0, 127.4, 126.8, 125.4, 109.2, 48.1, 44.7, 34.5, 31.2, 21.5, 21.0; HRMS (ESI) *m/z* calcd for $C_{36}H_{36}BrNO_2S_2Na$ $[MNa]^+$: 680.1263, found 680.1235.



Br-3bdc: 95% yield

***N*-(2-(4-Bromo-5-(*m*-tolyl)-3-(*p*-tolyl)thiophen-2-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (4a):** Purification by Isolera® (hexane/EtOAc = 10:1 to 3:1) afforded **Br-3bdc** (1.52 g, 95% yield) as a white solid from **3bdc** (1.40 g, 2.6 mmol), *N*-bromosuccinimide (556.0 mg, 3.1 mmol) and chloroform (26 mL).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.68–7.61 (m, 2H), 7.54–7.37 (m, 2H), 7.36–7.20 (m, 9H), 7.18–7.05 (m, 4H), 4.59–4.27 (m, 2H), 3.68–3.55 (m, 2H), 2.57–2.48 (m, 3H), 2.48–2.38 (m, 6H) (Several rotamers were detected even in $C_2D_2Cl_4$ at 140 °C.); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 143.0, 141.6, 140.0, 139.3, 137.9, 137.6, 137.5, 136.6, 133.0, 132.4, 130.0, 129.6, 129.3, 128.81, 128.77, 128.6, 128.1, 127.5, 127.2, 126.8, 126.1, 110.1, 48.1, 45.6, 20.95, 20.91, 20.88 (The major rotamer was only assigned.); HRMS (ESI) *m/z* calcd for $C_{33}H_{30}BrNO_2S_2Na$ $[MNa]^+$: 638.0794, found 638.0795.

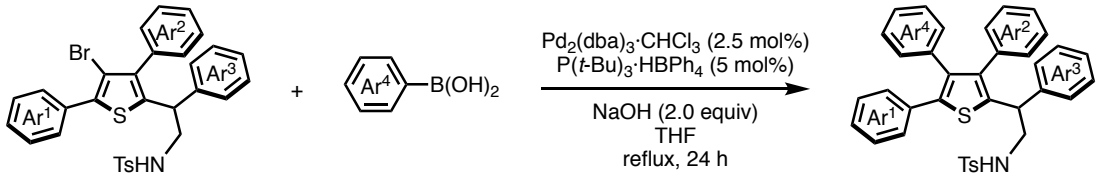


Br-3aci: 74% yield

***N*-(2-(4-Bromo-5-(4-(*tert*-butyl)phenyl)-3-phenylthiophen-2-yl)-2-(3-(trifluoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (Br-3aci):** Purification by PTLC (hexane/EtOAc = 4:1) afforded **Br-3aci** (178.4 mg, 74% yield) as a white solid from **3aci** (214.5 mg, 0.34 mmol), *N*-bromosuccinimide (74.0 mg, 0.41 mmol) and chloroform (3.4 mL).

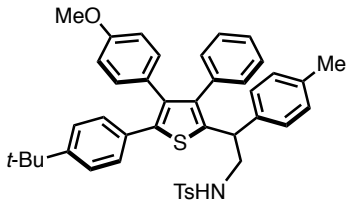
^{1}H NMR (400 MHz, DMSO-d_6, 140 °C): δ 7.59–7.52 (m, 4H), 7.52–7.46 (m, 3H), 7.46–7.41 (m, 3H), 7.37–7.25 (m, 4H), 7.19 (s, 1H), 7.16–7.08 (m, 2H), 4.44 (t, J = 7.6 Hz, 1H), 3.49–3.42 (m, 2H), 2.85–2.80 (m, 1H), 2.38 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6, 140 °C): δ 150.8, 141.8, 141.3, 140.3, 139.1, 137.6, 135.4, 134.4, 130.9, 129.3, 128.9 (q, $^2J_{CF}$ = 34.5 Hz), 128.71, 128.67, 128.6, 127.8, 127.5, 127.2, 125.7, 124.6, 123.7 (q, $^3J_{CF}$ = 3.9 Hz), 123.3 (q, $^1J_{CF}$ = 274 Hz), 122.9 (q, $^3J_{CF}$ = 3.9 Hz), 108.5, 46.7, 44.5, 33.7, 30.3, 20.0; HRMS (ESI) *m/z* calcd for $C_{36}H_{33}F_3NO_2S_2BrNa$ $[MNa]^+$: 734.0980, found 734.0983.

8. Cross-coupling of Bromothiophenes Br-3



Br-3 (1.0 equiv) (3.0 equiv) **4**

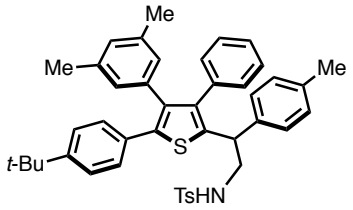
A 50-mL Schlenk tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (25.9 mg, 0.025 mmol, 2.5 mol%), tri-*tert*-butylphosphonium tetraphenylborate (26.1 mg, 0.05 mmol, 5 mol%), bromothiophene **Br-3** (1 mmol, 1.0 equiv), arylboronic acid (3 mmol, 3.0 equiv), NaOH (aq. 3 M, 670 μL, 2 mmol, 2.0 equiv) and THF (5 mL) were added, and then heated at 65 °C for 24 h. After cooling the reaction mixture to room temperature, water (10 mL) and EtOAc (10 mL) were added to the mixture. After extraction with EtOAc, the organic layer was dried over Na_2SO_4 and the volatiles were removed *in vacuo*. The crude product was purified by Isolera® (hexane/EtOAc) to afford the corresponding tetrasubstituted thiophene **4**.



4acde: 82% yield

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (4acde):** Purification by Isolera® (hexane/EtOAc = 10:1 to 5:1) afforded **4acde** (562.3 mg, 82% yield) as a white solid from **Br-3acd** (658.7 mg, 1.0 mmol) and 4-methoxyphenylboronic acid (456.0 mg, 3.0 mmol).

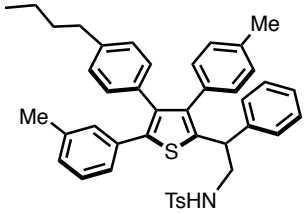
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.27–7.20 (m, 7H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.00–6.96 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 4.34–4.26 (m, 2H), 3.75 (s, 3H), 3.63–3.54 (m, 2H), 2.45 (s, 3H), 2.36 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 158.4, 150.2, 142.9, 142.3, 138.4, 138.0, 137.72, 137.69, 137.6, 136.6, 136.4, 131.6, 131.3, 130.3, 129.3, 129.2, 128.9, 128.4, 127.6, 127.5, 126.8, 126.6, 124.8, 113.5, 55.1, 48.6, 44.9, 34.2, 31.0, 20.9, 20.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}NO_3S_2Na$ $[MNa]^+$: 708.2577, found 708.2573.



4acdf: quant

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(3,5-dimethylphenyl)-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (4acdf):** Purification by Isolera® (hexane/EtOAc = 10:1 to 5:1) afforded **4acdf** (688.8 mg, quant) as a white solid from **Br-3acd** (658.7 mg, 1.0 mmol) and 3,5-dimethylphenylboronic acid (449.9 mg, 3.0 mmol).

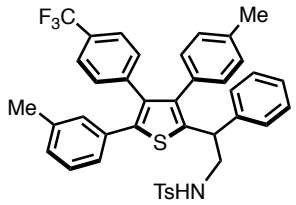
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.29–7.15 (m, 9H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.01–6.93 (m, 2H), 6.72 (s, 1H), 6.56 (s, 2H), 4.39–4.24 (m, 2H), 3.63–3.51 (m, 2H), 2.44 (s, 3H), 2.36 (s, 3H), 2.09 (s, 6H), 1.34 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 150.2, 142.8, 142.3, 138.7, 138.3, 137.7, 137.5, 136.6, 136.4, 136.0, 131.4, 130.3, 129.3, 129.2, 128.5, 128.4, 127.7, 127.5, 127.4, 126.8, 126.6, 124.6, 48.6, 44.9, 34.2, 31.0, 20.9, 20.5; HRMS (ESI) *m/z* calcd for $C_{44}H_{45}NO_2S_2Na$ $[MNa]^+$: 706.2784, found 706.2780.



4bdcg: 97% yield

***N*-(2-(4-(4-Butylphenyl)-5-(*m*-tolyl)-3-(*p*-tolyl)thiophen-2-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (4bdcg):** Purification by Isolera® (hexane/EtOAc = 10:1 to 4:1) afforded **4bdcg** (648.8 mg, 97% yield) as a white solid from **Br-3bdc** (619.6 mg, 1.0 mmol) and 4-*n*-butylphenylboronic acid (536.5 mg, 3.0 mmol).

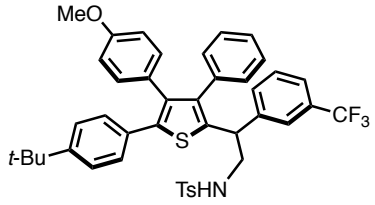
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.35–7.29 (m, 2H), 7.29–7.23 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.11–6.99 (m, 6H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.91–6.86 (m, 4H), 4.42–4.35 (m, 2H), 3.68–3.59 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.48 (s, 3H), 2.37 (s, 3H), 2.25 (s, 3H), 1.60 (quin, *J* = 7.5 Hz, 2H), 1.36 (sext, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 142.9, 142.4, 140.8, 138.9, 138.2, 137.7, 137.3, 136.2, 134.3, 133.6, 133.2, 130.4, 130.1, 129.6, 129.3, 128.5, 128.3, 127.7, 127.62, 127.56, 127.4, 126.9, 126.8, 126.0, 48.6, 45.2, 34.9, 32.8, 21.7, 20.9, 20.8, 20.7, 13.3; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}NO_2S_2Na$ $[MNa]^+$: 692.2627, found 692.2622.



4bdch: 93% yield

4-Methyl-*N*-(2-phenyl-2-(5-(*m*-tolyl)-3-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)thiophen-2-yl)ethyl) benzenesulfonamide (4bdch): Purification by Isolera® (hexane/EtOAc = 10:1 to 4:1) afforded **4bdch** (631.1 mg, 93% yield) as a white solid from **Br-3bdc** (616.5 mg, 1.0 mmol) and 4-trifluoromethylphenylboronic acid (594.5 mg, 3.0 mmol). The reaction was performed for 48 h.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.35–7.30 (m, 2H), 7.30–7.25 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.14–6.98 (m, 8H), 6.88 (d, *J* = 7.8 Hz, 2H), 4.44–4.35 (m, 2H), 3.70–3.60 (m, 2H), 2.46 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 143.0, 141.8, 140.6, 140.3, 139.2, 139.1, 137.7, 137.1, 136.8, 133.6, 132.6, 130.9, 130.0, 129.7, 129.3, 128.59, 128.56 (q, $^2J_{CF}$ = 31.7 Hz), 128.1, 128.0, 127.6, 127.0, 126.8, 126.2, 124.2 (q, $^3J_{CF}$ = 2.85 Hz), 124.1 (q, $^1J_{CF}$ = 270 Hz), 48.6, 45.3, 20.9, 20.7; HRMS (ESI) *m/z* calcd for $C_{40}H_{34}NO_2S_2F_3Na$ [MNa]$^+$: 704.1875, found 704.1870.

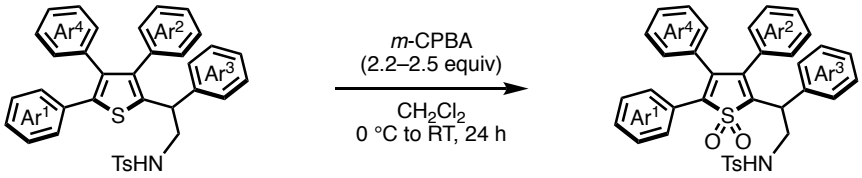


4acie: 71% yield

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)-3-phenylthiophen-2-yl)-2-(3-(trifluoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (4acie):** Purification by PTLC (hexane/EtOAc = 5:1) afforded **4acie** (94.4 mg, 71% yield) as a white solid from **Br-3aci** (128.0 mg, 0.18 mmol) and 4-methoxyphenylboronic acid (83.4 mg, 0.54 mmol).

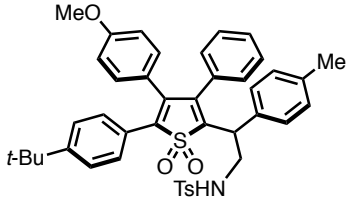
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.26–7.16 (m, 7H), 7.14 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.87 (brs, 2H), 6.80 (d, *J* = 9.2 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.52 (t, *J* = 6.0 Hz, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.58–3.47 (m, 2H), 2.42 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 150.3, 143.6, 143.0, 141.7, 137.9, 136.6, 136.5, 135.9, 131.7, 130.99 (q, $^2J_{CF}$ = 32.9 Hz), 130.97, 130.2, 129.8, 129.3, 128.5, 128.1, 128.0, 127.2, 127.0, 125.3, 124.7 (q, $^3J_{CF}$ = 3.9 Hz), 124.1 (q, $^3J_{CF}$ = 3.9 Hz), 123.8 (q, $^1J_{CF}$ = 274 Hz), 113.3, 55.0, 48.5, 44.9, 34.5, 31.2, 21.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{40}F_3NO_3S_2Na$ [MNa]$^+$: 762.2294, found 762.2295.

9. Oxidation of Tetrasubstituted Thiophene 4



4 (1.0 equiv) **5**

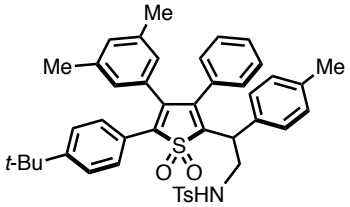
A 50-mL two-necked flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added tetrasubstituted thiophene **4** (0.8 mmol, 1.0 equiv) and CH_2Cl_2 (8 mL) under a stream of nitrogen. The contents were cooled at 0 °C, and *m*-CPBA (1.8–2.0 mmol, 2.2–2.5 equiv) was added. After warming the reaction mixture to room temperature and stirring at room temperature for 24 h, the reaction was quenched by adding saturated $Na_2S_2O_3$ aqueous solution and saturated $NaHCO_3$ aqueous solution. The mixture was extracted with CH_2Cl_2, dried over with Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by Isolera® (hexane/EtOAc) to afford the corresponding thiophene *S,S*-dioxide **5**.



5acde: 85% yield

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)-1,1-dioxido-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (5acde):** Purification by Isolera® (hexane/EtOAc = 5:1 to 3:1) afforded **5acde** (488.1 mg, 85% yield) as a yellow solid from **4acde** (548.8 mg, 0.80 mmol) and *m*-CPBA (413.6 mg, 2.2 equiv, 1.76 mmol).

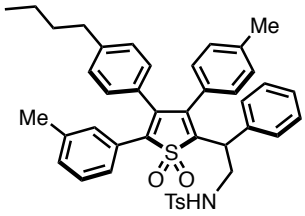
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.34–7.18 (m, 10H), 7.07–7.01 (m, 4H), 6.76 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 9.0 Hz, 2H), 5.63 (dd, J = 9.0 Hz, 4.8 Hz, 1H), 4.33 (dd, J = 10.8 Hz, 5.4 Hz, 1H), 3.80–3.73 (m, 1H), 3.72 (s, 3H), 3.47–3.41 (m, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.8, 152.8, 143.9, 143.3, 137.3, 137.1, 136.9, 135.9, 135.3, 134.8, 131.3, 131.2, 129.7, 129.4, 129.0, 128.9, 128.8, 128.3, 128.0, 127.0, 125.8, 124.0, 123.4, 113.7, 55.1, 45.8, 45.0, 34.8, 31.1, 21.5, 21.0; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}NO_5S_2Na$ $[MNa]^+$: 740.2475, found 740.2466.



5acdf: 74% yield

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(3,5-dimethylphenyl)-1,1-dioxido-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-4-methylbenzenesulfonamide (5acdf):** Purification by Isolera® (hexane/EtOAc = 5:1 to 3:1) afforded **5acdf** (424.1 mg, 74% yield) as a yellow solid from **4acdf** (551.7 mg, 0.80 mmol) and *m*-CPBA (413.6 mg, 2.2 equiv, 1.76 mmol).

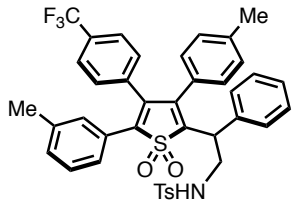
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.31–7.25 (m, 3H), 7.24–7.19 (m, 2H), 7.11–7.05 (m, 4H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.80 (s, 1H), 6.52 (s, 2H), 5.29 (t, *J* = 6.6 Hz, 1H), 4.29 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 3.91–3.83 (m, 1H), 3.62–3.55 (m, 1H), 2.46 (s, 3H), 2.34 (s, 3H), 2.09 (s, 6H), 1.35 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 153.0, 143.6, 142.9, 138.1, 137.6, 137.3, 136.9, 136.5, 135.6, 135.1, 131.6, 131.5, 129.8, 129.4, 129.1, 128.80, 128.76, 128.3, 127.9, 127.7, 127.0, 126.7, 125.2, 124.1, 45.3, 45.0, 34.5, 30.8, 20.9, 20.5, 20.4; HRMS (ESI) *m/z* calcd for $C_{44}H_{45}NO_4S_2Na$ $[MNa]^+$: 738.2682, found 738.2676.



5bdcg: 74% yield

***N*-(2-(4-(4-Butylphenyl)-1,1-dioxido-5-(*m*-tolyl)-3-(*p*-tolyl)thiophen-2-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (5bdcg):** Purification by Isolera® (hexane/EtOAc = 5:1 to 3:1) afforded **5bdcg** (417.7 mg, 74% yield) as a yellow solid from **4bdcg** (536.0 mg, 0.80 mmol) and *m*-CPBA (470.0 mg, 2.5 equiv, 2.0 mmol).

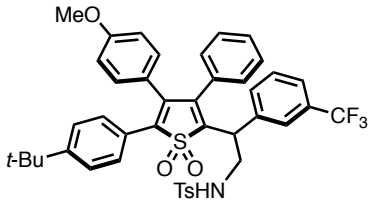
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.29–7.18 (m, 8H), 7.16–7.09 (m, 3H), 7.02 (d, *J* = 6.6 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.80–6.66 (m, 4H), 5.63 (dd, *J* = 9.0 Hz, 4.8 Hz, 1H), 4.38 (dd, *J* = 10.8 Hz, 5.4 Hz, 1H), 3.82–3.74 (m, 1H), 3.50–3.42 (m, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 2.22 (s, 3H), 1.49 (quin, *J* = 7.5 Hz, 2H), 1.24 (sext, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.2, 143.8, 143.3, 139.0, 138.6, 138.4, 138.2, 137.1, 135.5, 135.2, 130.4, 129.7, 129.6, 129.5, 128.9, 128.7, 128.5, 128.3, 128.14, 128.08, 127.5, 126.94, 126.90, 126.5, 46.2, 45.0, 35.2, 33.0, 22.0, 21.5, 21.4, 21.3, 13.9; HRMS (ESI) *m/z* calcd for $C_{43}H_{43}NO_4S_2Na$ $[MNa]^+$: 724.2526, found 724.2517.



5bdch: 72% yield

***N*-(2-(1,1-Dioxido-5-(*m*-tolyl)-3-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)thiophen-2-yl)-2-phenyleth yl)-4-methylbenzenesulfonamide (5bdch):** Purification by Isolera® (hexane/EtOAc = 5:1 to 3:1) afforded **5bdch** (412.6 mg, 72% yield) as a yellow solid from **4bdch** (545.5 mg, 0.80 mmol) and *m*-CPBA (470.0 mg, 2.5 equiv, 2.0 mmol).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32–7.17 (m, 11H), 7.06 (d, *J* = 8.4 Hz, 4H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.24 (t, *J* = 6.9 Hz, 1H), 4.37 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 3.96–3.87 (m, 1H), 3.65–3.58 (m, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 143.0, 142.7, 139.1, 138.5, 138.0, 137.9, 137.7, 136.9, 136.5, 135.7, 130.7 (q, $^2J_{CF}$ = 33.0 Hz), 130.6, 129.8, 129.6, 129.4, 128.9, 128.5, 128.1, 127.8, 127.3, 126.7, 126.4, 126.3, 124.8 (q, $^3J_{CF}$ = 4.4 Hz), 123.5 (q, $^1J_{CF}$ = 272 Hz), 45.8, 44.9, 21.0, 20.8 ; HRMS (ESI) *m/z* calcd for $C_{40}H_{34}NO_4S_2Na$ $[MNa]^+$: 736.1774, found 736.1767.



5acie: 70% yield

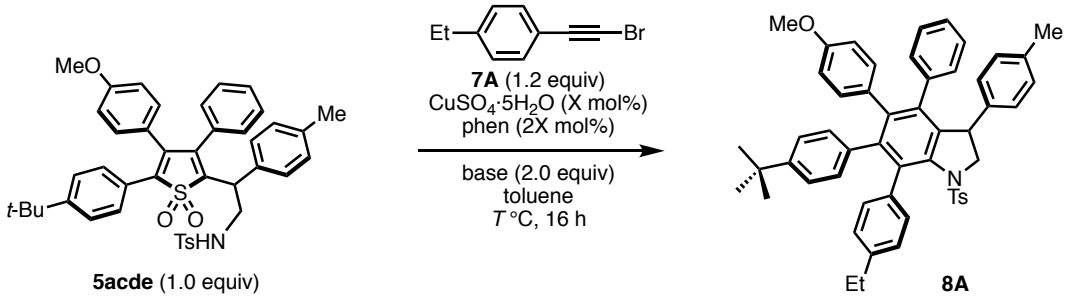
***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)-1,1-dioxido-3-phenylthiophen-2-yl)-2-(3-(trif luoromethyl)phenyl)ethyl)-4-methylbenzenesulfonamide (5acie):** Purification by PTLC (hexane/EtOAc = 3:1) afforded **5acie** (69.0 mg, 70% yield) as a yellow solid from **4acie** (94.4 mg, 0.13 mmol) and *m*-CPBA (56.3 mg, 2.5 equiv, 0.32 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.48–7.41 (m, 2H), 7.40–7.33 (m, 3H), 7.33–7.17 (m, 10H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.72 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 4.41 (dd, *J* = 10.8 Hz, 4.4 Hz, 1H), 3.88–3.79 (m, 1H), 3.72 (s, 3H), 3.47–3.39 (m, 1H), 2.42 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 153.0, 145.0, 143.5, 139.3, 136.9, 136.8, 134.9, 134.8, 131.4, 131.2, 131.0, 130.8 (q, $^2J_{CF}$ = 31.6 Hz), 129.8, 129.20, 129.17, 128.7, 128.5, 126. 9, 125.9, 125.1 (q, $^3J_{CF}$ = 3.8 Hz), 124.4 (q, $^3J_{CF}$ = 3.8 Hz), 123.8, 123.7 (q, $^1J_{CF}$ = 272 Hz), 123.1, 113.8, 55.1, 46.0, 44.5, 34.8, 31.0, 29.7, 21.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{40}F_3NO_5S_2Na$ $[MNa]^+$: 794.2192, found 794.2192.

10. Synthesis of Pentaarylindolines 8

10-1. Screening of Reaction Conditions

Table 1. Condition Screening

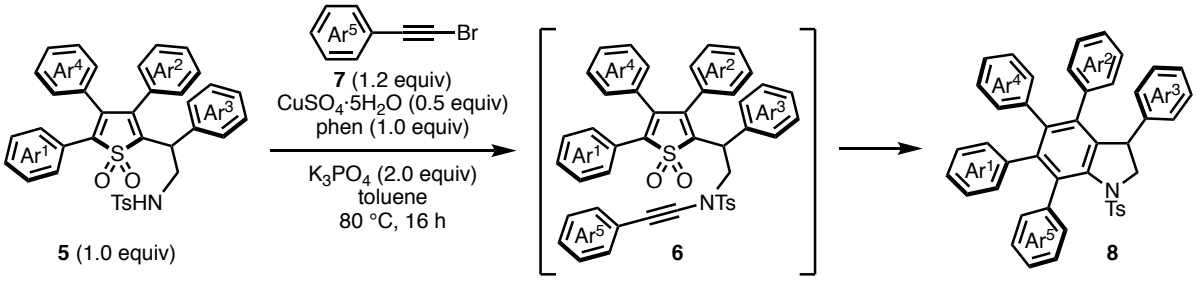


entry	base	X	conc. (M)	*T* (°C)	yield of **8A** (%)[a]	recovery of **5acde** (%)
1	K_2CO_3	50	0.5	65	28 (52)[b]	46[b]
2	K_3PO_4	50	0.5	65	42 (56)[b]	25[b]
3	K_3PO_4	50	0.5	80	41 (52)[b]	21[b]
4	K_3PO_4	50	1.0	80	51 (80)[c]	36[c]
5	K_3PO_4	10	1.0	80	30 (81)[c]	53[c]
6	K_3PO_4	100	1.0	80	40[c]	recovered

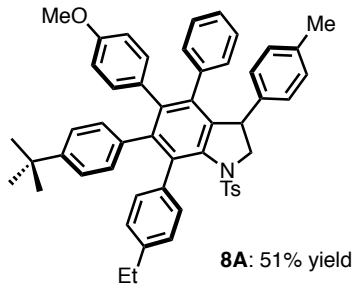
[a] Yields based on brsm in parentheses, [b] Yields determined by ^{1}H NMR analysis of the crude product using $C_2H_2Cl_4$ as an internal standard. [c] Isolated yields.

A 7-mL screw cap tube, containing a magnetic stirring bar and K_2CO_3 or K_3PO_4 (0.20 mmol, 2.0 equiv), was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added thiophene *S,S*-dioxide **5acde** (71.8 mg, 0.1 mmol, 1.0 equiv), bromoalkyne **7** (25.1 mg, 0.12 mmol, 1.2 equiv), $CuSO_4 \cdot 5H_2O$ (0.01 to 0.1 mmol), phenanthroline (phen: 0.02 to 0.2 mmol) and toluene (100 μL or 200 μL) under a stream of nitrogen. The flask was heated at 65 °C or 80 °C for 16 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated *in vacuo*, and the crude product was analyzed by ^{1}H NMR using $C_2H_2Cl_4$ as an internal standard or purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc = 5:1) to afford indoline **8A** and unreacted thiophene *S,S*-dioxide **5acde**.

10-2. Substrate Scope



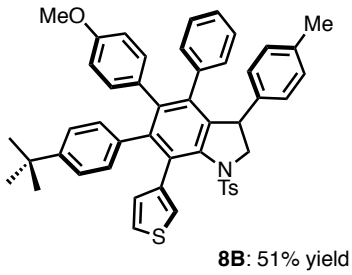
A 7-mL screw cap tube, containing a magnetic stirring bar and K_3PO_4 (42.4 mg, 0.20 mmol, 2.0 equiv), was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added thiophene *S,S*-dioxide **5** (0.1 mmol, 1.0 equiv), bromoalkyne **7** (0.12 mmol, 1.2 equiv), $CuSO_4 \cdot 5H_2O$ (12.5 mg, 0.05 mmol, 0.5 equiv), phenanthroline (phen: 18.0 mg, 0.1 mmol, 1.0 equiv) and toluene (100 μL) under a stream of nitrogen. The flask was heated at 80 °C for 16 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc) to afford the corresponding indoline **8** and unreacted thiophene *S,S*-dioxide **5**.



8A: 51% yield

6-(4-(*tert*-Butyl)phenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-3-(*p*-tolyl)-1-tosylindoline (8A): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8A** (39.9 mg, 51% yield) as a pale yellow solid and unreacted **5acde** (26.0 mg, 36% recovery).

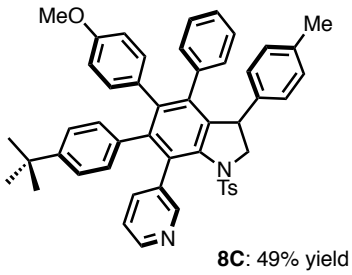
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.05–6.83 (m, 8H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.2 Hz, 2H), 6.63–6.49 (m, 6H), 6.42 (t, *J* = 6.9 Hz, 1H), 6.34 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.29 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.94 (d, *J* = 7.2 Hz, 1H), 4.47 (dd, *J* = 12.6 Hz, 7.8 Hz, 1H), 4.23 (dd, *J* = 9.6 Hz, 7.8 Hz, 1H), 3.82 (dd, *J* = 12.6 Hz, 10.2 Hz, 1H), 3.55 (s, 3H), 2.56 (qd, *J* = 7.2 Hz, 3.6 Hz, 2H), 2.45 (s, 3H), 2.13 (s, 3H), 1.19 (t, *J* = 7.5 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.9, 147.9, 143.2, 141.9, 141.6, 140.5, 139.9, 139.1, 139.0, 138.4, 138.3, 137.0, 136.5, 136.2, 135.4, 134.0, 132.33, 132.30, 132.1, 131.3, 131.2, 130.8, 130.2, 129.2, 129.1, 128.3, 128.1, 127.5, 126.8, 126.7, 126.2, 125.5, 123.4, 123.3, 111.90, 111.86, 61.3, 54.9, 48.7, 34.1, 31.2, 28.5, 21.6, 20.9, 15.5; HRMS (ESI) *m/z* calcd for $C_{53}H_{51}NO_3SNa$ $[MNa]^+$: 804.3482, found 804.3478.



8B: 51% yield

6-(4-(*tert*-Butyl)phenyl)-5-(4-methoxyphenyl)-4-phenyl-7-(thiophen-3-yl)-3-(*p*-tolyl)-1-tosylindoline (8B): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8B** (38.6 mg, 51% yield) as a pale yellow solid and unreacted **5acde** (29.0 mg, 40% recovery).

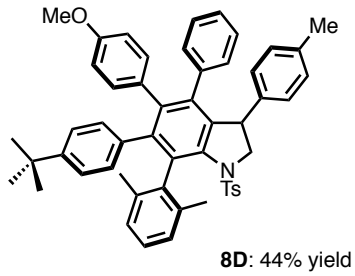
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.01–6.92 (m, 5H), 6.80–6.64 (m, 7H), 6.54–6.47 (m, 4H), 6.40 (t, *J* = 6.9 Hz, 1H), 6.34 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 6.29 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.89 (d, *J* = 6.6 Hz, 1H), 4.44 (dd, *J* = 12.6 Hz, 7.8 Hz, 1H), 4.01 (dd, *J* = 9.6 Hz, 7.8 Hz, 1H), 3.80 (dd, *J* = 12.6 Hz, 10.2 Hz, 1H), 3.55 (s, 3H), 2.50 (s, 3H), 2.11 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.0, 148.5, 143.7, 141.8, 140.8, 140.3, 139.4, 138.8, 138.7, 138.5, 138.1, 137.0, 135.8, 135.4, 132.2, 131.9, 130.9, 130.5, 130.4, 130.1, 129.3, 128.99, 128.96, 128.3, 128.0, 127.8, 126.7, 125.5, 124.5, 123.7, 123.6, 122.5, 112.0, 111.8, 61.3, 54.9, 48.4, 34.2, 31.3, 21.6, 20.8; HRMS (ESI) *m/z* calcd for $C_{49}H_{45}NO_3S_2Na$ $[MNa]^+$: 782.2733, found 782.2733.



8C: 49% yield

6-(4-(*tert*-Butyl)phenyl)-5-(4-methoxyphenyl)-4-phenyl-7-(pyridin-3-yl)-3-(*p*-tolyl)-1-tosylindoline (8C): Purification by PTLC (hexane/EtOAc = 3:1, developed twice) afforded **8C** (36.7 mg, 49% yield) as a pale yellow solid and unreacted **5acde** (20.6 mg, 29% recovery).

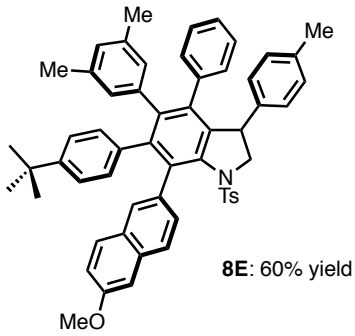
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 8.47 (s, 1H), 8.29 (d, *J* = 4.2 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.99–6.94 (m, 3H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.82–6.74 (m, 4H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.61–6.55 (m, 4H), 6.47 (brs, 2H), 6.37 (d, *J* = 7.8 Hz, 2H), 4.53 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 4.21 (t, *J* = 8.7 Hz, 1H), 3.93 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 3.59 (s, 3H), 2.51 (s, 3H), 2.20 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$): δ 156.7, 148.7, 144.3, 141.8, 140.6, 140.0, 139.8, 139.6, 138.1, 137.4, 135.6, 135.4, 134.7, 132.2, 132.1, 131.3, 131.1, 130.9, 129.7, 129.4, 128.6, 128.4, 127.9, 127.4, 126.7, 125.6, 123.8, 123.6, 122.2, 112.2, 111.6, 61.1, 55.0, 48.0, 34.0, 31.1, 21.6, 20.9; HRMS (ESI) *m/z* calcd for $C_{50}H_{47}N_2O_3S$ $[MH]^+$: 755.3302, found 755.3292.



8D: 44% yield

6-(4-(*tert*-Butyl)phenyl)-7-(2,6-dimethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-3-(*p*-tolyl)-1-tosyl indoline (8D): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8D** (34.7 mg, 44% yield) as a pale yellow solid and unreacted **5acde** (26.8 mg, 37% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.28 (d, *J* = 6.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.95–6.87 (m, 2H), 6.86–6.73 (m, 7H), 6.66 (d, *J* = 7.2 Hz, 1H), 6.62–6.40 (m, 8H), 6.35 (d, *J* = 7.2 Hz, 2H), 4.53 (dd, *J* = 11.1 Hz, 6.9 Hz, 1H), 4.26 (t, *J* = 7.8 Hz, 1H), 3.93 (dd, *J* = 10.8 Hz, 7.8 Hz, 1H), 3.60 (s, 3H), 2.47 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.00 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 157.3, 148.2, 142.5, 141.9, 141.8, 140.2, 139.0, 138.8, 138.4, 137.72, 137.67, 136.6, 136.3, 135.3, 132.5, 132.4, 131.2, 130.4, 129.9, 128.8, 128.3, 127.8, 126.8, 126.7, 126.5, 126.2, 125.3, 122.5, 112.3, 61.3, 55.1, 48.3, 33.8, 30.9, 20.9, 20.5, 20.4; HRMS (ESI) *m/z* calcd for $C_{53}H_{51}NO_3SNa$ $[MNa]^+$: 804.3482, found 804.3480.

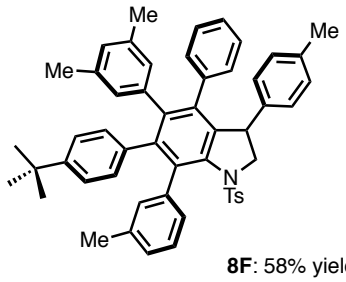


8E: 60% yield

6-(4-(*tert*-Butyl)phenyl)-5-(3,5-dimethylphenyl)-7-(6-methoxynaphthalen-2-yl)-4-phenyl-3-(*p*-tolyl)-1-tosylindoline (8E): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8E** (50.1 mg, 60% yield) as a pale yellow solid and unreacted **5acdf** (25.6 mg, 36% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.48 (s, 1H), 7.42 (d, *J* = 9.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 10.2 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.07–7.03 (m, 2H), 6.90–6.77 (m, 9H), 6.73–6.67 (m, 4H), 6.64–6.50 (m, 2H), 6.40 (s, 1H), 6.31 (s, 2H), 4.64 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 4.37 (t, *J* = 8.1 Hz, 1H), 4.07 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 3.98 (s, 3H), 2.31 (s, 3H), 2.24 (s, 3H), 1.92 (s, 6H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 157.5, 148.1, 142.3, 142.0, 140.7, 140.6, 139.1, 138.9, 138.7, 138.3, 138.1, 137.7, 136.8, 135.3, 135.1, 134.3, 133.0, 132.8, 131.1, 130.6, 130.0, 129.8, 129.4, 129.3, 128.4, 128.3, 127.9, 126.35, 126.31, 126.2, 125.3, 124.6, 122.8, 117.0, 106.6,

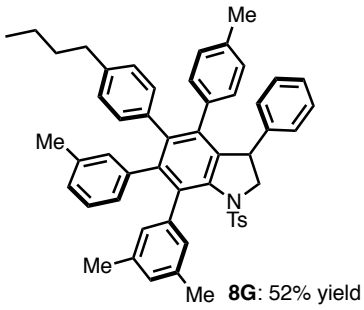
61.6, 55.3, 48.6, 33.8, 30.9, 20.8, 20.4, 20.3; HRMS (ESI) *m/z* calcd for $C_{57}H_{53}NO_3SNa$ $[MNa]^+$: 854.3638, found 854.3636.



8F: 58% yield

6-(4-(*tert*-Butyl)phenyl)-5-(3,5-dimethylphenyl)-4-phenyl-7-(*m*-tolyl)-3-(*p*-tolyl)-1-tosylindoline (8F): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8F** (44.6 mg, 58% yield) as a pale yellow solid and unreacted **5acdf** (30.4 mg, 42% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.94–6.88 (m, 4H), 6.86–6.73 (m, 6H), 6.69–6.62 (m, 4H), 6.51 (brs, 2H), 6.40 (s, 1H), 6.29 (s, 2H), 4.56 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 4.31 (t, *J* = 8.4 Hz, 1H), 3.95 (dd, *J* = 12.0 Hz, 9.0 Hz, 1H), 2.48 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H), 1.92 (s, 6H), 1.22 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 148.1, 142.6, 141.9, 140.6, 140.3, 139.2, 138.9, 138.7, 138.6, 138.2, 138.1, 137.5, 137.0, 135.6, 135.2, 135.1, 133.4, 132.4, 131.1, 129.7, 129.4, 128.7, 128.6, 128.3, 127.9, 127.1, 126.35, 126.26, 126.21, 126.15, 125.2, 122.6, 61.1, 48.5, 33.8, 31.0, 20.9, 20.7, 20.4, 20.3; HRMS (ESI) *m/z* calcd for $C_{53}H_{51}NO_2SNa$ $[MNa]^+$: 788.3533, found 788.3528.

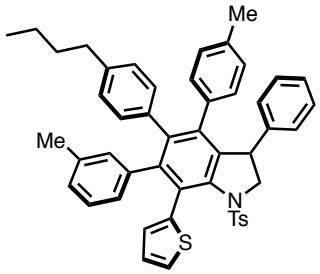


8G: 52% yield

5-(4-Butylphenyl)-7-(3,5-dimethylphenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-1-tosylindoline (8G): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8G** (40.2 mg, 52% yield) as a pale yellow solid and unreacted **5bdcg** (26.6 mg, 38% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.29 (d, *J* = 6.6 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.05–6.96 (m, 3H), 6.83–6.78 (m, 2H), 6.77–6.71 (m, 3H), 6.69–6.52 (m, 10H), 6.41 (brs, 2H), 4.61 (dd, *J* = 11.4 Hz, 8.4 Hz, 1H), 4.39 (t, *J* = 8.1 Hz, 1H), 4.00 (dd, *J* = 11.4 Hz, 9.3 Hz, 1H), 2.46 (s, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.16–2.07 (m, 9H), 2.03 (s, 3H), 1.42 (quin, *J* = 7.2 Hz, 2H), 1.17 (sext, *J* = 7.2 Hz, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 142.4, 142.1, 141.8, 140.4, 140.3, 139.9, 139.2, 138.34, 138.31, 138.0, 137.9, 137.1, 135.8, 135.5, 135.2, 134.6, 133.1, 132.3, 131.1,

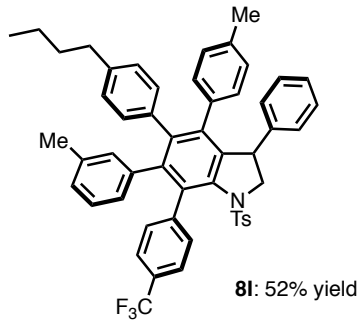
129.6, 129.5, 128.6, 128.4, 128.1, 127.4, 127.1, 126.8, 126.1, 125.8, 125.7, 125.4, 61.1, 49.0, 34.7, 32.8, 21.3, 20.9, 20.6, 20.43, 20.37, 13.3; HRMS (ESI) *m/z* calcd for $C_{53}H_{51}NO_2SNa$ $[MNa]^+$: 788.3533, found 788.3522.



8H: 48% yield

5-(4-Butylphenyl)-3-phenyl-7-(thiophen-2-yl)-6-(*m*-tolyl)-4-(*p*-tolyl)-1-tosylindoline (8H): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8H** (35.5 mg, 48% yield) as a pale yellow solid and unreacted **5bdcg** (30.5 mg, 43% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 4.8 Hz, 1H), 7.00–6.93 (m, 3H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.81–6.74 (m, 3H), 6.73–6.67 (m, 4H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 6.0 Hz, 2H), 6.30 (brs, 2H), 4.56 (dd, *J* = 12.6 Hz, 7.2 Hz, 1H), 4.20 (t, *J* = 8.4 Hz, 1H), 3.93 (dd, *J* = 12.0 Hz, 9.6 Hz, 1H), 2.52 (s, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.14–2.06 (m, 6H), 1.42 (quin, *J* = 7.2 Hz, 2H), 1.17 (sext, *J* = 7.2 Hz, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 143.1, 142.8, 141.5, 141.4, 141.0, 139.8, 139.7, 139.4, 139.2, 138.8, 136.9, 136.7, 135.7, 135.4, 134.8, 130.9, 129.4, 129.3, 128.9, 128.0, 127.5, 127.4, 127.1, 126.3, 126.23, 126.16, 126.1, 125.8, 125.3, 125.2, 61.1, 48.8, 34.7, 32.8, 21.3, 21.0, 20.6, 20.3, 13.3; HRMS (ESI) *m/z* calcd for $C_{49}H_{45}NO_2S_2Na$ $[MNa]^+$: 766.2784, found 766.2781.

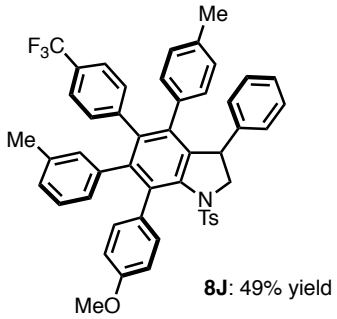


8I: 52% yield

5-(4-Butylphenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-1-tosyl-7-(4-(trifluoromethyl)phenyl)indoline (8I): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8I** (42.2 mg, 52% yield) as a pale yellow solid and unreacted **5bdcg** (26.6 mg, 38% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.32–7.24 (m, 6H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.02–6.96 (m, 3H), 6.80–6.74 (m, 3H), 6.71 (d, *J* = 6.6 Hz, 1H), 6.67–6.50 (m, 8H), 6.39 (brs, 2H), 4.61 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 4.35 (t, *J* = 8.4 Hz, 1H), 4.00 (dd, *J* = 12.6 Hz, 8.4 Hz, 1H), 2.48 (s, 3H), 2.38 (t, *J* =

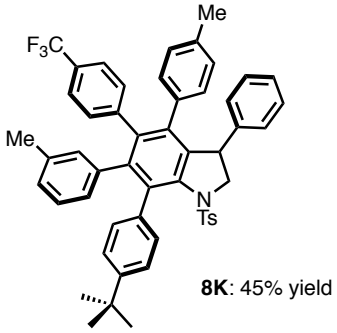
7.2 Hz, 2H), 2.11 (s, 3H), 2.02 (s, 3H), 1.43 (quin, J = 7.2 Hz, 2H), 1.17 (sext, J = 7.2 Hz, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 143.1, 142.7, 141.8, 141.5, 140.8, 140.3, 139.5, 139.4, 139.2, 138.5, 137.3, 136.6, 135.8, 135.4, 134.9, 132.2, 131.8, 131.5, 131.0, 129.4, 128.9, 128.4, 128.0, 127.5, 127.2, 126.8, 126.2, 125.94, 125.86, 124.3 (q, $^1J_{CF}$ = 270 Hz), 123.3 (q, $^3J_{CF}$ = 2.85 Hz), 61.1, 48.9, 34.7, 32.8, 21.3, 20.9, 20.4, 13.3 ($^2J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{52}H_{46}F_3NO_2SNa$ $[MNa]^+$: 828.3094, found 828.3087.



8J: 49% yield

7-(4-Methoxyphenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-1-tosyl-5-(4-(trifluoromethyl)phenyl)indoline (8J): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8J** (37.9 mg, 49% yield) as a pale yellow solid and unreacted **5bdch** (31.8 mg, 45% recovery). A single crystal of **8J** was obtained from a chloroform solution by slow evaporation at room temperature, and the structure was confirmed by X-ray crystallography.

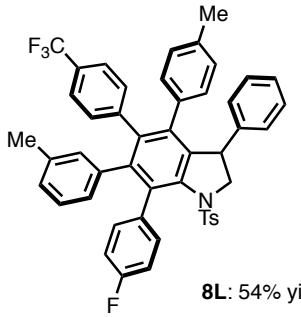
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.35 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.2 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 7.02–6.96 (m, 3H), 6.85 (d, J = 8.4 Hz, 2H), 6.83–6.71 (m, 4H), 6.65–6.52 (m, 6H), 6.37 (brs, 2H), 4.61 (dd, J = 12.0 Hz, 7.5 Hz, 1H), 4.35 (t, J = 8.4 Hz, 1H), 3.99 (dd, J = 12.0 Hz, 8.4 Hz, 1H), 3.78 (s, 3H), 2.49 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 158.3, 143.9, 142.8, 142.0, 141.5, 139.2, 138.8, 138.7, 138.1, 137.5, 135.9, 135.3, 135.0, 133.1, 132.4, 132.2, 131.5, 131.0, 129.4, 128.8, 128.3, 128.0, 127.5, 127.4, 127.0, 126.4, 126.0, 125.9, 124.1 (q, $^1J_{CF}$ = 270 Hz), 122.9 (q, $^3J_{CF}$ = 3.0 Hz), 112.7, 61.1, 55.0, 48.9, 21.0, 20.42, 20.35 ($^2J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{49}H_{40}F_3NO_3SNa$ $[MNa]^+$: 802.2573, found 802.2556.



8K: 45% yield

7-(4-(*tert*-Butyl)phenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-1-tosyl-5-(4-(trifluoromethyl)phenyl)indoline (8K): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8K** (36.3 mg, 45% yield) as a pale yellow solid and unreacted **5bdch** (24.2 mg, 34% recovery).

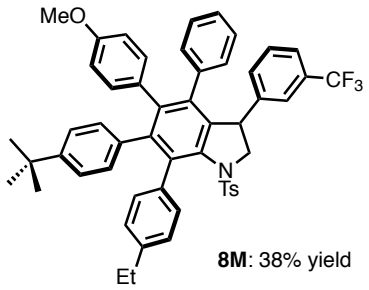
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.10–7.07 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.02–6.97 (m, 3H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.82–6.69 (m, 4H), 6.59 (brs, 2H), 6.50 (d, *J* = 6.0 Hz, 2H), 6.39 (brs, 2H), 4.60 (dd, *J* = 12.3 Hz, 7.5 Hz, 1H), 4.45 (t, *J* = 8.1 Hz, 1H), 3.96 (dd, *J* = 12.4 Hz, 9.3 Hz, 1H), 2.46 (s, 3H), 2.12 (s, 3H), 2.00 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 148.9, 144.0, 142.7, 142.0, 141.5, 141.1, 139.2, 138.6, 138.1, 137.5, 135.7, 135.4, 135.3, 135.0, 133.6, 132.1, 131.6, 131.1, 129.4, 128.8, 128.4, 128.1, 127.5, 127.4, 127.09 (q, $^{2}J_{CF}$ = 31.7 Hz), 127.06, 126.2, 125.92, 125.91 (q, $^{1}J_{CF}$ = 270 Hz), 125.8, 123.2, 122.9 (q, $^{3}J_{CF}$ = 2.85 Hz), 61.1, 49.0, 34.0, 31.1, 21.0, 20.4; HRMS (ESI) *m/z* calcd for $C_{52}H_{46}F_3NO_2SNa$ $[MNa]^+$: 828.3094, found 828.3091.



8L: 54% yield

7-(4-Fluorophenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-1-tosyl-5-(4-(trifluoromethyl)phenyl)indoline (8L): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8L** (41.2 mg, 54% yield) as a pale yellow solid and unreacted **5bdch** (26.0 mg, 36% recovery).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C): δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.13–7.07 (m, 4H), 7.03–6.96 (m, 3H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.83–6.70 (m, 6H), 6.68–6.51 (m, 4H), 6.36 (brs, 2H), 4.61 (dd, *J* = 12.3 Hz, 7.5 Hz, 1H), 4.35 (t, *J* = 8.4 Hz, 1H), 4.00 (dd, *J* = 12.6 Hz, 9.0 Hz, 1H), 2.50 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C): δ 161.5 (d, $^{1}J_{CF}$ = 244 Hz), 143.7, 143.1, 141.9, 141.34, 141.31, 138.94, 138.85, 138.6, 137.4, 136.1, 135.5, 134.8, 134.3 (d, $^{4}J_{CF}$ = 2.85 Hz), 133.0 (d, $^{3}J_{CF}$ = 8.55 Hz), 132.3, 132.1, 131.5, 129.3, 128.9, 128.3, 128.0, 127.6, 127.5, 126.9, 126.5, 126.3, 126.0, 124.1 (q, $^{1}J_{CF}$ = 270 Hz), 123.0 (q, $^{3}J_{CF}$ = 3.0 Hz), 113.5 (d, $^{2}J_{CF}$ = 21.6 Hz), 61.1, 48.9, 21.0, 20.40, 20.36 (q, $^{2}J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{48}H_{37}F_4NO_2SNa$ $[MNa]^+$: 790.2373, found 790.2366.

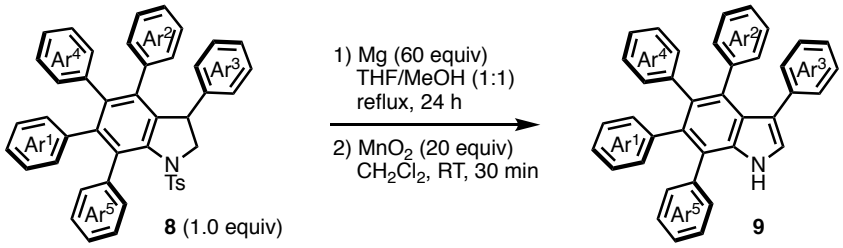


8M: 38% yield

6-(4-(*tert*-Butyl)phenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-1-tosyl-3-(3-(trifluoromethyl)phenyl)indoline (8M): Purification by PTLC (hexane/EtOAc = 5:1) afforded **8M** (28.2 mg, 38% yield) as a pale yellow solid and unreacted **5acde** (13.6 mg, 20% recovery) from **5acde** (69.0 mg, 0.09 mmol) and **7A** (26.3 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.8 Hz, 2H), 7.20–7.14 (m, 3H), 7.10–6.98 (m, 5H), 6.97–6.85 (m, 6H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.59–6.64 (m, 2H), 6.56–6.51 (m, 2H), 6.41 (t, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 6.30 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 5.91 (d, *J* = 8.0 Hz, 1H), 4.54–4.47 (m, 2H), 3.81–3.73 (m, 1H), 3.56 (s, 3H), 2.59 (q, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.20 (t, *J* = 8.0 Hz, 3H), 1.16 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 148.3, 143.3, 142.7, 142.6, 141.8, 140.9, 140.3, 138.9, 138.4, 138.0, 137.0, 136.1, 134.4, 132.4, 132.1, 131.6, 131.5, 131.3, 131.0, 130.2 (q, $^{2}J_{CF}$ = 32.6 Hz), 129.1, 128.3, 127.6, 127.1, 126.3, 126.0, 125.3 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.0 (q, $^{1}J_{CF}$ = 265 Hz), 123.44, 123.37, 123.0 (q, $^{3}J_{CF}$ = 3.8 Hz), 112.2, 61.3, 55.0, 49.5, 34.2, 31.3, 28.6, 21.5, 15.4; HRMS (ESI) *m/z* calcd for $C_{53}H_{48}NO_3SNa$ $[MNa]^+$: 858.3199, found 858.3198.

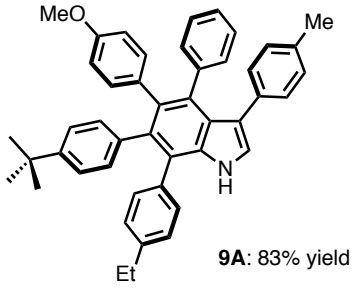
11. Synthesis of Pentaarylindoles 9



8 (1.0 equiv) **9**

A 7-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added indoline **8** (0.02 mmol, 1.0 equiv), magnesium tunings (29.2 mg, 1.2 mmol, 60 equiv), THF (200 μL) and methanol (200 μL) under a stream of nitrogen. The reaction mixture was refluxed for 24 h. After cooling the reaction mixture to room temperature, the reaction was quenched by adding saturated NH_4Cl aqueous solution. The mixture was extracted with Et_2O, dried over with $MgSO_4$, and concentrated *in vacuo*. The volatiles was concentrated *in vacuo*, and used for the next step without further purification.

A 20-mL vial, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vial were added the material obtained above, CH_2Cl_2 (400 μL) and MnO_2 (34.2 mg, 0.4 mmol, 20 equiv). The reaction mixture was stirred at room temperature for 30 min, and the mixture was passed through Celite® (CH_2Cl_2). The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc or hexane/CH_2Cl_2) to afford the corresponding indole **9**.

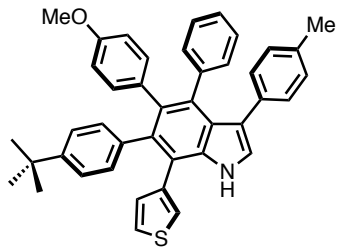


9A: 83% yield

6-(4-(*tert*-Butyl)phenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-3-(*p*-tolyl)-1*H*-indole (9A): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9A** (10.4 mg, 83% yield) as a white solid. A single crystal of **9A** was obtained from a chloroform solution through vapor diffusion of pentane at room temperature, and the structure was confirmed by X-ray crystallography.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 3.0 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.84–6.79 (m, 3H), 6.75–6.65 (m, 10H), 6.37 (d, J = 9.0 Hz, 2H), 3.59 (s, 3H), 2.61 (q, J = 7.5 Hz, 2H), 2.21 (s, 3H), 1.21 (t, J = 7.5 Hz, 3H), 1.14 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.7, 147.6, 142.5, 139.3, 137.6, 135.5, 135.0, 134.8, 134.2, 133.6, 133.50, 133.47, 133.3, 132.8, 131.5, 131.2, 130.4, 129.1, 127.7, 127.6, 126.3, 125.1, 124.2, 124.0,

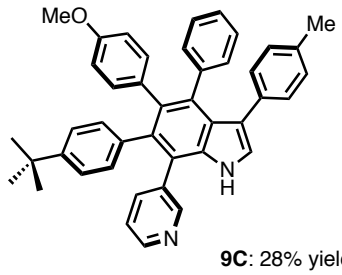
123.32, 123.28, 120.3, 111.8, 54.9, 34.1, 31.2, 28.5, 21.0, 15.5; HRMS (ESI) *m/z* calcd for $C_{46}H_{43}NONa$ $[MNa]^+$: 648.3242, found 648.3234.



9B: 46% yield

6-(4-(*tert*-Butyl)phenyl)-5-(4-methoxyphenyl)-4-phenyl-7-(thiophen-3-yl)-3-(*p*-tolyl)-1*H*-indole (9B): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9B** (5.6 mg, 46% yield) as a white solid.

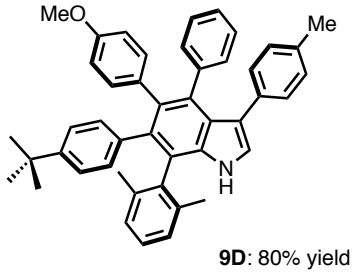
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.21–7.17 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.87 (dd, *J* = 4.2 Hz, 1.8 Hz, 1H), 6.83–6.79 (m, 3H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.75–6.68 (m, 6H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 8.4 Hz, 2H), 3.58 (s, 3H), 2.21 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.7, 148.0, 139.2, 138.0, 137.7, 135.7, 134.8, 134.3, 133.9, 133.6, 133.3, 133.2, 132.7, 131.2, 131.1, 129.6, 129.1, 127.6, 127.3, 125.1, 125.0, 124.0, 123.8, 123.5, 123.4, 120.5, 119.2, 111.8, 54.9, 34.2, 31.3, 21.0; HRMS (ESI) *m/z* calcd for $C_{42}H_{37}NOSNa$ $[MNa]^+$: 626.2488, found 626.2486.



9C: 28% yield

6-(4-(*tert*-Butyl)phenyl)-5-(4-methoxyphenyl)-4-phenyl-7-(pyridin-3-yl)-3-(*p*-tolyl)-1*H*-indole (C): Purification by PTLC (hexane/EtOAc = 3:1) afforded **9C** (3.2 mg, 28% yield) as a pale yellow solid.

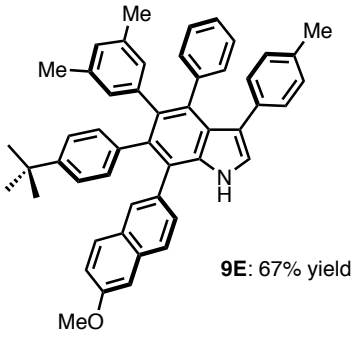
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.44–8.32 (m, 2H), 7.51 (dd, *J* = 6.3 Hz, 2.1 Hz, 1H), 7.20 (d, *J* = 3.0 Hz, 1H), 7.15 (dd, *J* = 5.1 Hz, 2.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.84–6.80 (m, 3H), 6.78–6.68 (m, 9H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 8.4 Hz, 2H), 3.59 (s, 3H), 2.22 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.8, 150.9, 148.2, 147.9, 139.0, 138.2, 136.8, 136.1, 134.7, 134.6, 134.4, 134.1, 133.8, 133.2, 133.0, 132.5, 131.5, 131.1, 129.1, 127.7, 126.4, 125.3, 124.4, 123.7, 123.2, 120.61, 120.57, 120.3, 111.9, 54.9, 34.2, 31.2, 21.0; HRMS (ESI) *m/z* calcd for $C_{43}H_{38}N_2ONa$ $[MNa]^+$: 621.2876, found 621.2870.



9D: 80% yield

6-(4-(*tert*-butyl)phenyl)-7-(2,6-dimethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-3-(*p*-tolyl)-1*H*-indole (9D): Purification by PTLC (hexane/EtOAc = 5:1) afforded **9D** (10.0 mg, 80% yield) as a white solid.

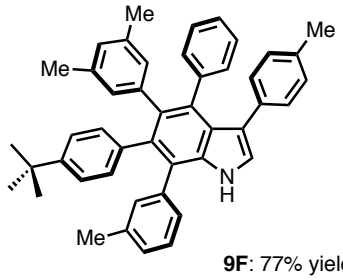
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.10–7.06 (m, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.85–6.81 (m, 5H), 6.76–6.68 (m, 8H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.35 (d, *J* = 9.0 Hz, 2H), 3.59 (s, 3H), 2.22 (s, 3H), 2.07 (s, 6H), 1.21 (t, *J* = 7.5 Hz, 3H), 1.11 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.6, 147.6, 139.7, 137.8, 137.3, 136.6, 135.1, 134.4, 134.1, 133.8, 133.5, 133.0, 131.4, 130.1, 129.0, 127.6, 127.3, 127.2, 126.3, 124.9, 123.6, 123.1, 122.2, 120.1, 111.7, 54.9, 34.1, 31.2, 21.0, 20.7; HRMS (ESI) *m/z* calcd for $C_{46}H_{43}NONa$ $[MNa]^+$: 648.3242, found 648.3239.



9E: 67% yield

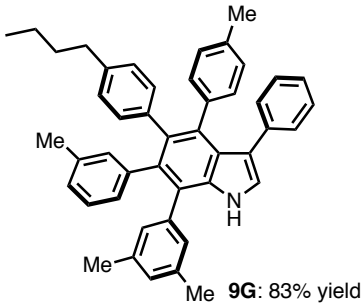
6-(4-(*tert*-Butyl)phenyl)-5-(3,5-dimethylphenyl)-7-(6-methoxynaphthalen-2-yl)-4-phenyl-3-(*p*-tolyl)-1*H*-indole (9E): Purification by PTLC (hexane/EtOAc = 5:1) afforded **9E** (9.0 mg, 67% yield) as a pale yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 8.18 (s, 1H), 7.81 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.13–7.08 (m, 3H), 6.86–6.67 (m, 13H), 6.39 (s, 1H), 6.35 (s, 2H), 3.91 (s, 3H), 2.20 (s, 3H), 1.89 (s, 6H), 1.09 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.0, 147.8, 140.5, 139.6, 137.7, 135.5, 135.1, 134.6, 134.3, 133.7, 133.6, 133.4, 133.1, 131.7, 131.4, 130.7, 129.5, 129.4, 129.3, 129.1, 129.0, 127.7, 126.7, 126.2, 126.0, 125.1, 124.0, 123.9, 123.7, 123.3, 120.8, 118.7, 106.0, 55.4, 34.2, 31.2, 20.92, 20.85; HRMS (ESI) *m/z* calcd for $C_{50}H_{45}NONa$ $[MNa]^+$: 698.3393, found 698.3392.



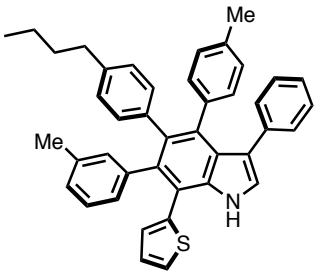
9F: 77% yield

6-(4-(*tert*-Butyl)phenyl)-5-(3,5-dimethylphenyl)-4-phenyl-7-(*m*-tolyl)-3-(*p*-tolyl)-1*H*-indole (9F): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9F** (9.4 mg, 77% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.19–7.12 (m, 3H), 7.09 (s, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.83–6.78 (m, 3H), 6.76–6.68 (m, 8H), 6.40 (s, 1H), 6.33 (s, 2H), 2.23 (s, 3H), 2.21 (s, 3H), 1.89 (s, 6H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.6, 140.3, 139.4, 137.8, 137.7, 137.6, 135.1, 135.0, 134.6, 134.2, 133.4, 132.9, 131.5, 131.3, 131.2, 130.6, 129.1, 128.1, 127.6, 127.5, 127.3, 126.1, 125.9, 125.1, 124.1, 123.9, 123.3, 123.1, 120.4, 34.2, 31.2, 21.3, 21.0, 20.9; HRMS (ESI) *m/z* calcd for $C_{46}H_{43}NNa$ $[MNa]^+$: 632.3288, found 632.3286.



9G: 83% yield

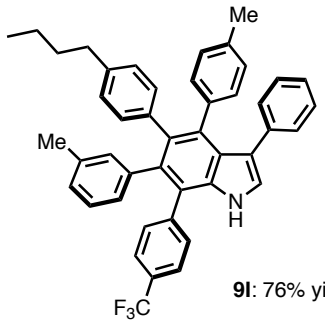
5-(4-Butylphenyl)-7-(3,5-dimethylphenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-1*H*-indole (9G): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9G** (10.1 mg, 83% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 8.16 (s, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.96–6.89 (m, 3H), 6.89–6.80 (m, 5H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.71–6.60 (m, 9H), 6.48 (d, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.21 (s, 6H), 2.07 (s, 3H), 1.99 (s, 3H), 1.39 (quin, *J* = 7.5 Hz, 2H), 1.12 (sext, *J* = 7.5 Hz, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.7, 138.9, 138.5, 137.8, 137.6, 136.5, 136.2, 135.6, 135.50, 134.96, 134.6, 134.2, 133.5, 133.0, 132.2, 131.1, 129.5, 129.1, 128.4, 128.3, 127.0, 126.8, 126.4, 126.2, 125.6, 124.5, 124.2, 123.9, 123.7, 120.8, 35.1, 33.4, 21.7, 21.2, 21.0, 20.9, 13.8; HRMS (ESI) *m/z* calcd for $C_{46}H_{43}NNa$ $[MNa]^+$: 632.3288, found 632.3288.



9H: 76% yield

5-(4-Butylphenyl)-3-phenyl-7-(thiophen-2-yl)-6-(*m*-tolyl)-4-(*p*-tolyl)-1*H*-indole (9H): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9H** (8.9 mg, 76% yield) as a pale yellow solid.

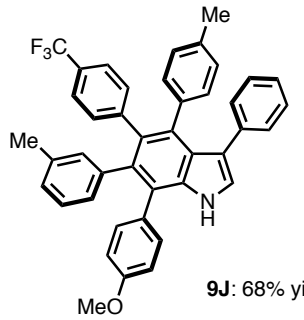
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.26 (d, J = 4.8 Hz, 1H), 7.21 (d, J = 3.0 Hz, 1H), 7.02–6.94 (m, 3H), 6.88 (t, J = 7.8 Hz, 2H), 6.86–6.81 (m, 3H), 6.76–6.60 (m, 9H), 6.52–6.45 (m, 2H), 2.36 (t, J = 7.5 Hz, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 1.38 (quin, J = 7.2 Hz, 2H), 1.10 (sext, J = 7.2 Hz, 2H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.4, 138.99, 138.96, 137.9, 136.6, 135.89, 135.87, 135.8, 135.1, 134.7, 134.5, 134.1, 132.6, 132.1, 131.9, 130.9, 130.8, 129.4, 128.6, 127.9, 127.02, 126.96, 126.85, 126.75, 126.5, 126.4, 126.3, 126.0, 124.6, 124.1, 123.6, 120.7, 116.4, 35.0, 33.3, 21.7, 21.1, 20.9, 13.9; HRMS (ESI) *m/z* calcd for $C_{42}H_{37}NSNa$ $[MNa]^+$: 610.2539, found 610.2537.



9I: 76% yield

5-(4-Butylphenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-7-(4-(trifluoromethyl)phenyl)-1*H*-indole (9I): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9I** (9.9 mg, 76% yield) as a white solid.

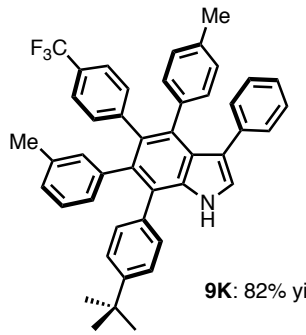
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.58–7.36 (m, 4H), 7.18 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.8 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 6.76 (t, J = 8.1 Hz, 1H), 6.72–6.60 (m, 9H), 6.54–6.46 (m, 2H), 2.36 (t, J = 7.2 Hz, 2H), 2.09 (s, 3H), 1.98 (s, 3H), 1.39 (quin, J = 7.2 Hz, 2H), 1.11 (sext, J = 7.2 Hz, 2H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.0, 139.8, 139.1, 137.8, 126.0, 135.9, 135.7, 135.5, 134.8, 134.4, 134.3, 134.2, 132.8, 132.1, 131.9, 130.9, 130.8, 129.4, 128.9, 128.83 (q, $^2J_{CF}$ = 38.9 Hz), 127.1, 127.0, 126.9, 126.52, 126.46, 126.0, 125.29, 125.26, 124.7, 124.3, 124.2 (q, $^1J_{CF}$ = 270 Hz), 123.8, 122.3, 120.8, 35.0, 33.3, 21.7, 21.0, 20.9, 13.9 ($^3J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{45}H_{38}F_3NNa$ $[MNa]^+$: 672.2849, found 672.2845.



9J: 68% yield

7-(4-Methoxyphenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-5-(4-(trifluoromethyl)phenyl)-1*H*-indole (9J): Purification by PTLC (hexane/EtOAc = 5:1) afforded **9J** (8.5 mg, 68% yield) as a white solid.

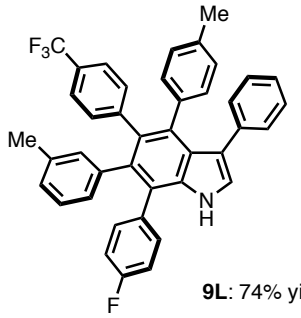
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 8.18 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 3.0 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.98–6.80 (m, 9H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.70–6.64 (m, 3H), 6.64–6.59 (m, 2H), 6.50 (d, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 60 °C): δ 158.7, 145.5, 140.1, 136.1, 135.85, 135.75, 135.5, 135.2, 133.5, 132.9, 132.7, 132.6, 131.5, 131.0, 129.9, 129.5, 129.0, 127.3, 126.9, 126.7, 126.1, 124.7, 124.5 (q, $^1J_{CF}$ = 270 Hz), 124.3, 123.9, 123.8, 123.2, 121.0, 114.1, 55.3, 21.0, 20.9 ($^2J_{CF}$ and $^3J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{42}H_{32}F_3NONa$ $[MNa]^+$: 646.2328, found 646.2340.



9K: 82% yield

7-(4-(*tert*-Butyl)phenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-5-(4-(trifluoromethyl)phenyl)-1*H*-indole (9K): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9K** (10.6 mg, 82% yield) as a white solid.

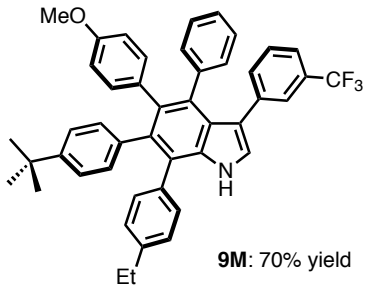
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 8.24 (s, 1H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.98–6.80 (m, 7H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.68–6.64 (m, 3H), 6.60 (d, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.96 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$, 60 °C): δ 149.9, 145.6, 140.0, 136.0, 135.9, 135.8, 135.4, 135.2, 135.1, 134.6, 133.6, 132.9, 132.7, 132.6, 131.0, 130.2, 129.6, 129.1, 127.3, 126.9, 126.5, 126.0, 125.2, 124.7, 124.5 (q, $^1J_{CF}$ = 270 Hz), 124.3, 123.8, 123.2, 120.9, 34.6, 31.3, 20.88, 20.85 ($^2J_{CF}$ and $^3J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{45}H_{37}F_3N$ $[M–H]^–$: 648.2873, found 648.2884.



9L: 74% yield

7-(4-Fluorophenyl)-3-phenyl-6-(*m*-tolyl)-4-(*p*-tolyl)-5-(4-(trifluoromethyl)phenyl)-1*H*-indole (9L): Purification by PTLC (hexane/EtOAc = 10:1) afforded **9L** (9.0 mg, 74% yield) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 8.11 (s, 1H), 7.26 (dd, *J* = 7.5 Hz, 6.0 Hz, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 5.4 Hz, 2H), 6.99–6.86 (m, 7H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 7.8 Hz, 2H), 2.08 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 60 °C): δ 161.9 (d, $^{1}J_{CF}$ = 246 Hz), 145.3, 139.8, 136.3, 135.7, 135.6, 135.33, 135.25, 124.0, 133.6 (d, $^{4}J_{CF}$ = 4.35 Hz), 132.7, 132.6, 132.1 (d, $^{3}J_{CF}$ = 8.55 Hz), 130.9, 129.5, 129.0, 127.4, 127.1 (q, $^{2}J_{CF}$ =31.7 Hz), 127.0, 126.9, 126.8, 126.3, 124.8, 124.5 (q, $^{1}J_{CF}$ = 270 Hz), 124.4, 124.0, 123.22, 123.15, 121.1, 115.4 (d, $^{2}J_{CF}$ = 21.6 Hz), 20.94, 20.85 (q, $^{3}J_{CF}$: not detected); HRMS (ESI) *m/z* calcd for $C_{41}H_{28}F_4N$ $[M–H]^-$: 610.2152, found 610.2150.



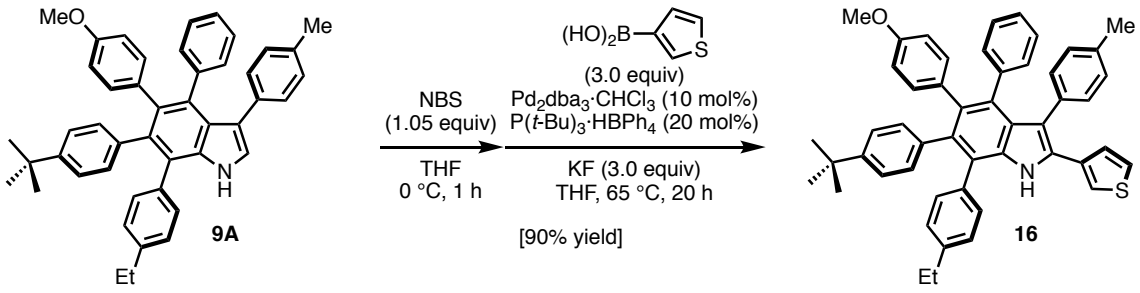
9M: 70% yield

6-(4-(*tert*-Butyl)phenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-3-(3-(trifluoromethyl)phenyl)-1*H*-indole (9M): Purification by PTLC (hexane/CH_2Cl_2 = 1:1) afforded **9M** (15.7 mg, 70% yield) as a white solid from **8M** (27.4 mg, 0.03 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.23–7.17 (m, 4H), 7.12–7.00 (m, 5H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.84–6.77 (m, 3H), 6.76–6.70 (m, 4H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 8.8 Hz, 2H), 3.60 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 147.7, 142.7, 138.8, 137.3, 136.7, 135.9, 134.8, 133.9, 133.19, 133.13, 133.10, 132.1, 131.4, 131.0, 130.3, 129.2 (q, $^{2}J_{CF}$ = 32.0 Hz), 127.8, 127.4, 126.6, 126.0 (q, $^{3}J_{CF}$ = 4.8 Hz), 125.6, 124.40, 124.37, 124.1 (q, $^{1}J_{CF}$ = 274 Hz), 123.4, 123.0, 121.8 (q, $^{3}J_{CF}$ = 2.9 Hz), 119.0, 111.8, 54.9, 34.1, 31.2, 28.5, 15.5; HRMS (ESI) *m/z* calcd for $C_{46}H_{40}F_3NONa$ $[MNa]^+$: 702.2954, found 702.2958.

12. Synthesis of Fully Arylated Indoles 17

12-1. C2-Arylation of Indole 9A

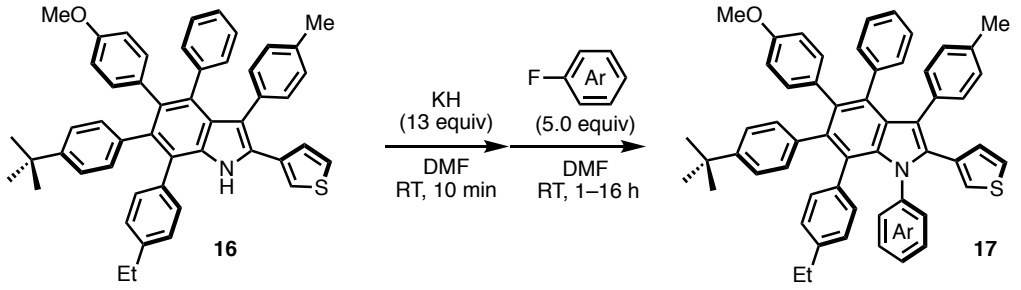


A 7-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added a solution of pentaarylindole **9A** (12.5 mg, 20 μmol, 1.0 equiv) in THF (400 μL) and *N*-bromosuccinimide (3.9 mg, 22 μmol, 1.05 equiv) at 0 °C. After stirring the mixture at 0 °C for 1 h, tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (2.1 mg, 2 μmol, 10 mol%), tri-*tert*-butylphosphonium tetraphenylborate (2.1 mg, 4 μmol, 20 mol%), thiophen-3-ylboronic acid (7.7 mg, 60 μmol, 3.0 equiv) and potassium fluoride (3.5 mg, 60 μmol, 3.0 equiv) were added and the mixture was further stirred at 65 °C for 20 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc = 10/1) to afford C2-arylated indole **16** (12.7 mg, 90% yield) as a white solid.

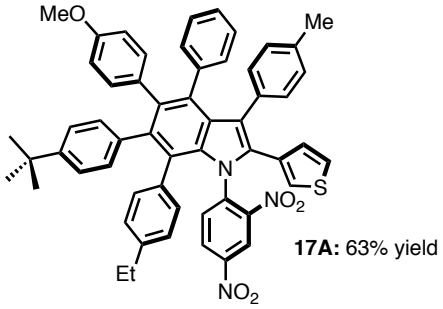
6-(4-(*tert*-Butyl)phenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-2-(thiophen-3-yl)-3-(*p*-tolyl)-1*H*-indole (16):

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.14 (dd, *J* = 4.8 Hz, 3.0 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 4.8 Hz, 1H), 6.78–6.62 (m, 14H), 6.35 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 3H), 2.63 (q, *J* = 7.2 Hz, 2H), 2.22 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.14 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.6, 147.6, 142.5, 138.6, 137.6, 135.6, 135.0, 134.8, 134.0, 133.9, 133.8, 133.7, 133.4, 133.2, 132.5, 131.5, 131.2, 131.1, 130.6, 130.3, 128.0, 127.8, 126.9, 126.1, 125.6, 125.3, 124.7, 123.7, 123.3, 121.6, 116.6, 111.8, 54.9, 34.1, 31.2, 28.5, 21.1, 15.4; HRMS (ESI) *m/z* calcd for $C_{50}H_{45}NOSNa$ $[MNa]^+$: 730.3114, found 730.3112.

12-2. *N*-Arylation of Indole 13



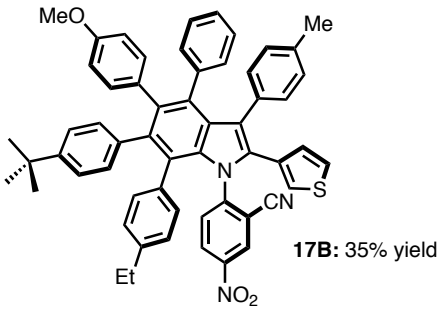
A 7-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added potassium hydride (16.8 mg, 30wt%, 0.13 mmol, 13 equiv), DMF (100 μL) and indole **16** (7.2 mg, 10 μmol, 1.0 equiv) was added under a stream of nitrogen. The contents were stirred for 5 minutes, and fluoroarene (50 μmol, 5.0 equiv) was added. The mixture was further stirred at room temperature for 1 h or 16 h. The reaction was quenched by adding saturated NH_4Cl aqueous solution. The mixture was extracted with EtOAc, dried over with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc = 5/1) to afford heptaarylindole **17**.



17A: 63% yield

6-(4-(*tert*-Butyl)phenyl)-1-(2,4-dinitrophenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-2-(thiophen-3-yl)-3-(*p*-tolyl)-1*H*-indole (17A): Purification by PTLC (hexane/EtOAc = 5:1) afforded **14A** (5.5 mg, 63% yield) as a red solid. A single crystal of **17A** was obtained from a chloroform solution through vapor diffusion of pentane at room temperature, and the structure was confirmed by X-ray crystallography.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (d, *J* = 3.0 Hz, 1H), 7.84 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 6.94 (dd, *J* = 4.8 Hz, 3.0 Hz, 1H), 6.85–6.71 (m, 7H), 6.69–6.47 (m, 12H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 9.0 Hz, 2H), 6.30 (d, *J* = 6.0 Hz, 1H), 3.57 (s, 3H), 2.30 (q, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.08 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.7, 147.6, 145.4, 145.1, 142.6, 139.7, 138.39, 138.37, 137.3, 135.2, 134.9, 134.6, 134.3, 134.2, 133.9, 133.1, 133.0, 132.9, 131.5, 131.4, 131.3, 131.2, 130.5, 130.2, 128.9, 127.6, 127.1, 126.6, 126.4, 126.0, 125.7, 125.1, 124.9, 124.5, 123.2, 123.1, 121.3, 119.6, 111.9, 111.8, 54.9, 34.0, 31.1, 28.2, 21.0, 15.6; HRMS (ESI) *m/z* calcd for $C_{56}H_{47}N_3O_5SNa$ $[MNa]^+$: 896.3129, found 896.3129.



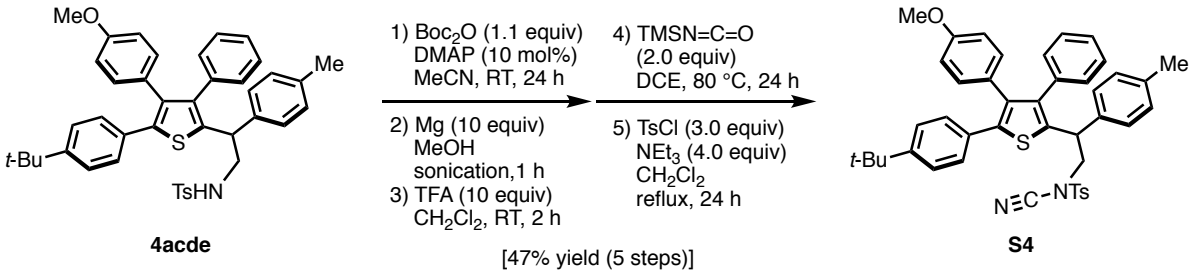
17B: 35% yield

2-(6-(4-(*tert*-Butyl)phenyl)-7-(4-ethylphenyl)-5-(4-methoxyphenyl)-4-phenyl-2-(thiophen-3-yl)-3-(*p*-tolyl)-1*H*-indol-1-yl)-5-nitrobenzonitrile(17B): Purification by PTLC (hexane/EtOAc = 5:1) afforded **17B** (3.2 mg, 35% yield) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 7.95 (s, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 6.93 (dd, *J* = 4.8 Hz, 3.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 6.79–6.58 (m, 13H), 6.57 (d, *J* = 7.8 Hz, 2H), 6.52–6.46 (m, 2H), 6.33 (d, *J* = 7.8 Hz, 2H), 3.55 (s, 3H), 2.31 (q, *J* = 7.8 Hz, 2H), 2.14 (s, 3H), 1.07 (s. 9H), 0.97 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 60 °C): δ 157.1, 149.0, 147.8, 145.8, 142.5, 138.8, 138.6, 137.5, 135.7, 135.6, 135.3, 134.9, 134.7, 134.6, 133.3, 133.1, 133.0, 132.4, 131.7, 131.6, 131.5, 131.4, 131.3, 131.0, 130.6, 129.4, 127.7, 127.00, 126.97, 126.6, 126.5, 126.4, 126.3, 126.1, 126.0, 125.0, 124.9, 124.7, 123.2, 123.1, 121.5, 115.6, 114.6, 112.14, 112.07, 55.0, 34.1, 31.2, 28.3, 21.0, 15.5; HRMS (ESI) *m/z* calcd for $C_{57}H_{47}N_3O_3SK$ $[MK]^+$: 892.2966, found 892.2970.

13. Synthesis of Pentaaryl-7-azaindoles 12

13-1. Synthesis of cyanamide 10



A 18-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added tetrasubstituted thiophene **4acde** (225.7 mg, 0.33 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP: 4.0 mg, 0.03 mmol, 10 mol%), MeCN (1.6 mL), and di-*tert*-butyl dicarbonate (78.6 μL, 0.36 mmol, 1.1 equiv) under a stream of nitrogen. The reaction mixture was stirred at room temperature for 24 h. The mixture was concentrated *in vacuo*, and directly used for the next step without further purification.

A 30-mL vial, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vial were added the material obtained above, magnesium tunings (80.2 mg, 3.3 mmol, 10 equiv), and MeOH (3.3 mL) u nder a stream of nitrogen. The contents were sonicated for 1 h. The reaction was quenched by adding 1N HCl aqueous solution, and the mixture was extracted with Et_2O, dried over with $MgSO_4$. The residue was concentrated *in vacuo*, and directly used for the next step without further purification.

A 30-mL vial, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vial were added the material obtained above, CH_2Cl_2 (1.6 mL) and trifluoroacetic acid (0.3 mL, 3.3 mmol, 10 equiv) under a stream of nitrogen. The reaction mixture was stirred at room temperature for 2 h. The reaction was carefully quenched by adding saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with CH_2Cl_2, dried over with Na_2SO_4. The residue was passed through a short silica gel pad with hexane/EtOAc = 1:1 (to remove unreacted materials) and $CHCl_3$/MeOH = 10:1 (to flow out the desired amine). The filtrate was concentrated *in vacuo*, and directly used for the next step without further purification.

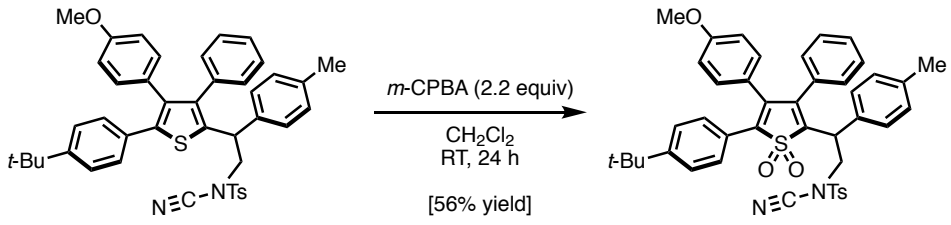
A 18-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added the material obtained above, dichloroethane (330 μL) and trimethylsilyl isocyanate (88 μL, 0.66 mmol, 2.0 equiv) under a stream of nitrogen. The reaction mixture was heated at 80 °C for 24 h. After cooling the reaction mixture to room temperature, the mixture was quenched with MeOH, concentrated *in vacuo*, and directly used for the next step without further purification.

A 18-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added the material obtained above, CH_2Cl_2 (3.3 mL), *p*-toluenesulfonyl chloride (190.7 mg, 0.99 mmol, 3.0 equiv), and

triethylamine (184 μL, 1.32 mmol, 4.0 equiv) under a stream of nitrogen. The reaction mixture was refluxed for 24 h. After cooling the reaction mixture to room temperature, the mixture was extracted with saturated $NaHCO_3$ aqueous solution and CH_2Cl_2, dried over with $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by Isolera® (hexane/EtOAc = 5:1 to 3:1) to afford cyanamide **S4** (111.0 mg, 47% yield in 5 steps) as a colorless oil.

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-*N*-cyano-4-methylbenzenesulfonamide (S4)**

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.28–7.23 (m, 5H), 7.19 (d, *J* = 9.0 Hz, 2H), 7.10–7.05 (m, 4H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.00–6.95 (m, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 4.51 (t, *J* = 8.4 Hz, 1H), 3.92 (d, *J* = 7.8 Hz, 2H), 3.70 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.1, 150.1, 146.0, 142.3, 137.9, 137.6, 137.4, 137.1, 136.01, 135.96, 133.7, 131.7, 131.2, 130.3, 130.2, 129.6, 128.6, 128.3, 128.1, 127.82, 127.79, 127.1, 125.2, 113.2, 108.1, 55.0, 54.8, 43.7, 34.5, 31.2, 21.7, 21.1; HRMS (ESI) *m/z* calcd for $C_{44}H_{42}N_2O_3S_2Na$ $[MNa]^+$: 733.2529, found 733.2522.



S4 **10**

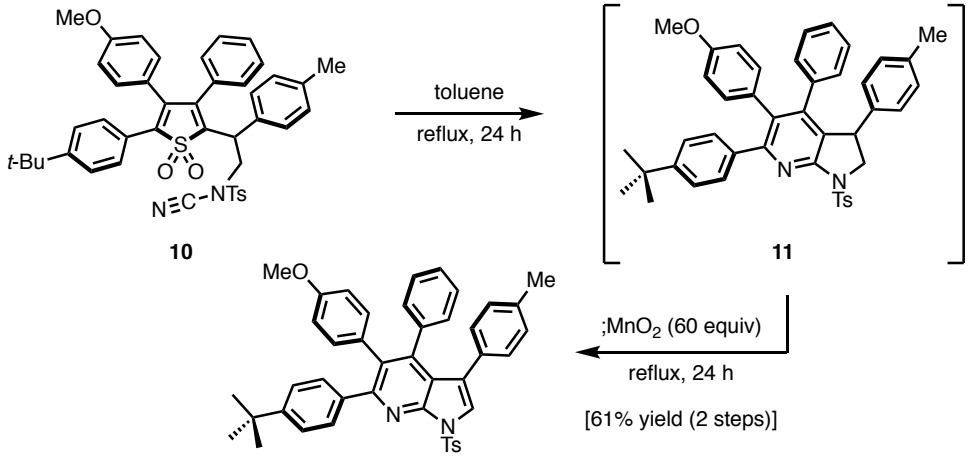
A 18-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this flask were added thiophene **S4** (41.5 mg, 58 μmol, 1.0 equiv) and CH_2Cl_2 (580 μL) under a stream of nitrogen. The contents were cooled at 0 °C, and *m*-CPBA (30.2 mg, 0.13 mmol, 2.2 equiv) was added. After warming the reaction mixture to room temperature and stirring at room temperature for 24 h, the reaction was quenched by adding saturated $Na_2S_2O_3$ aqueous solution and saturated $NaHCO_3$ aqueous solution. The mixture was extracted with CH_2Cl_2, dried over with Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc = 2:1 then $CHCl_3$) to afford the corresponding thiophene *S,S*-dioxide **10** (24.2 mg, 56% yield) as a pale yellow solid.

***N*-(2-(5-(4-(*tert*-Butyl)phenyl)-4-(4-methoxyphenyl)-1,1-dioxido-3-phenylthiophen-2-yl)-2-(*p*-tolyl)ethyl)-*N*-cyano-4-methylbenzenesulfonamide (10):**

^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.33–7.22 (m, 9H), 7.09–6.99 (m, 4H), 6.91 (brs, 2H), 6.75 (d, *J* = 7.8 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.39 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 4.27 (dd, *J* = 13.2 Hz, 6.0 Hz, 1H), 4.17 (dd, *J* = 13.2 Hz, 10.2 Hz, 1H), 3.69 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.8, 152.8, 146.2, 143.2, 137.9, 136.4, 135.3, 134.7, 133.4, 132.1, 131.2, 131.0, 130.3, 129.4, 129.0, 128.85, 128.77, 128.6, 128.4, 127.9,

125.7, 124.1, 123.5, 113.8, 108.1, 55.1, 51.3, 43.2, 34.8, 31.0, 21.7, 21.1; HRMS (ESI) *m/z* calcd for $C_{44}H_{42}N_2O_5S_2Na$ $[MNa]^+$: 765.2427, found 765.2422.

13-2. Synthesis of Tetraarylazaindole 12



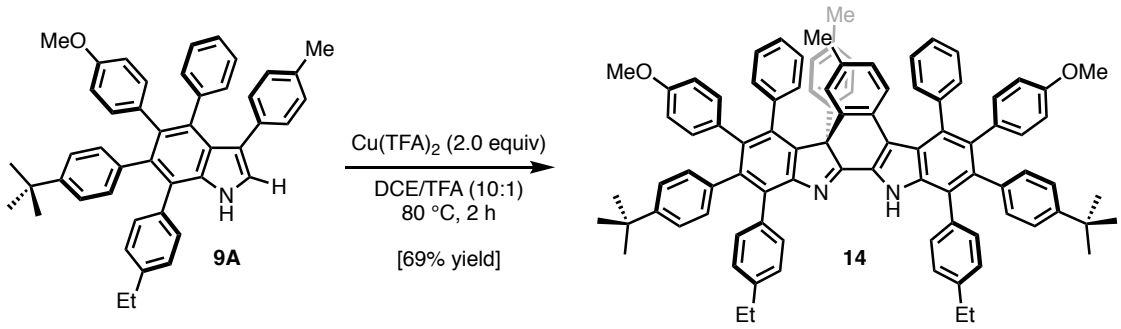
A 7-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added thiophene *S,S*-dioxide **10** (14.8 mg, 20 μmol, 1.0 equiv) and toluene (400 μL) under a stream of nitrogen. The reaction mixture was refluxed for 24 h. To this mixture was added MnO_2 (34.2 mg, 0.4 mmol, 20 equiv, 3 times every 3 hours), and the resultant mixture was further heated at 110 °C for 15 h. After cooling the reaction mixture to room temperature the mixture was passed through Celite® (CH_2Cl_2). The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (PTLC: hexane/EtOAc = 5:1) to afford the corresponding 7-azaindole **12** (8.3 mg, 61% yield) as a white solid. A single crystal of **12** was obtained from a chloroform solution through vapor diffusion of pentane at room temperature, and the structure was confirmed by X-ray crystallography.

6-(4-(*tert*-Butyl)phenyl)-5-(4-methoxyphenyl)-4-phenyl-3-(*p*-tolyl)-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (12):

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.23–7.18 (m, 4H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 2H), 6.68–6.61 (m, 6H), 6.51 (d, *J* = 7.8 Hz, 2H), 3.67 (s, 3H), 2.45 (s, 3H), 2.21 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 153.5, 149.9, 146.2, 145.1, 144.2, 138.1, 136.2, 135.8, 135.5, 132.9, 130.5, 130.4, 130.19, 130.15, 130.1, 129.4, 129.2, 128.7, 127.9, 126.8, 126.4, 124.2, 124.1, 121.5, 118.6, 112.8, 55.0, 34.5, 31.3, 21.8, 21.0; HRMS (ESI) *m/z* calcd for $C_{44}H_{41}N_2O_3S$ $[MH]^+$: 677.2832, found 677.2828.

14. Dimerization of Pentaarylindole 9

14-1. Dimerization of Pentaarylindole 9A

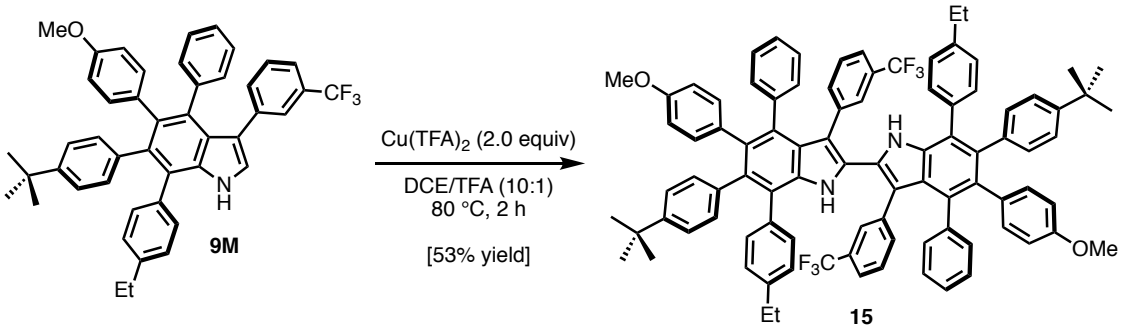


A 7-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added pentaarylindole **9A** (12.6 mg, 0.02 mmol, 0.5 equiv), copper(II) trifluoroacetate (5.8 mg, 0.02 mmol, 1.0 equiv), dichloroethane (DCE: 200 μL), and trifluoroacetate (TFA: 20 μL) under a stream of nitrogen. The reaction mixture was heated at 80 °C for 2 h. The reaction was quenched by adding saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with CH_2Cl_2, dried over with Na_2SO_4. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (hexane/CH_2Cl_2 = 2:1) to afford the corresponding indole dimer **14** (8.6 mg, 69% yield) as a yellow solid. A single crystal of **14** was obtained from a toluene solution through vapor diffusion of pentane at room temperature, and the structure was confirmed by X-ray crystallography.

2,11-Bis(4-(*tert*-butyl)phenyl)-1,12-bis(4-ethylphenyl)-3,10-bis(4-methoxyphenyl)-6-methyl-4,9-diphenyl-4b-(*p*-tolyl)-4b,13-dihydrobenzo[*c*]indolo[2,3-*a*]carbazole (14):

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.22–6.68 (m, 26H), 6.67–6.54 (m, 5H), 6.50–6.40 (m, 3H), 6.38–6.32 (m, 3H), 6.27–6.23 (m, 2H), 5.91 (d, *J* = 7.8 Hz, 1H), 5.61 (d, *J* = 7.2 Hz, 1H), 3.62 (s, 3H), 3.57 (s, 3H), 2.62–2.50 (m, 4H), 2.33 (s, 3H), 1.90 (s, 3H), 1.20–1.10 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.0, 156.9, 156.8, 155.1, 147.9, 147.7, 142.6, 142.4, 141.9, 141.3, 141.1, 140.1, 139.91, 139.88, 138.6, 137.9, 137.8, 137.32, 137.25, 136.7, 135.5, 135.3, 134.11, 134.07, 134.0, 133.6, 133.5, 133.2, 133.1, 132.91, 132.87, 132.8, 132.4, 132.0, 131.5, 131.13, 131.07, 131.0, 130.9, 130.2, 129.0, 128.8, 128.7, 127.5, 127.2, 127.1, 126.7, 126.61, 126.58, 126.4, 126.0, 125.9, 125.2, 123.43, 123.40, 123.31, 123.27, 122.5, 121.2, 112.1, 111.9, 111.6, 70.7, 55.01, 54.96, 34.13, 34.11, 31.2, 28.6, 28.5, 21.1, 20.4, 15.5, 15.4; HRMS (ESI) *m/z* calcd for $C_{92}H_{81}N_2O_2$ $[M–H]^-$: 1245.6293, found 1245.6325.

14-2. Dimerization of Pentaarylindole 9M



A 7-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this tube were added pentaarylindole **9M** (7.3 mg, 0.01 mmol, 0.5 equiv), copper(II) trifluoroacetate (3.4 mg, 0.01 mmol, 1.0 equiv), dichloroethane (DCE: 100 μL), and trifluoroacetate (TFA: 10 μL) under a stream of nitrogen. The reaction mixture was heated at 80 °C for 2 h. The reaction was quenched by adding saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with CH_2Cl_2, dried over with Na_2SO_4. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (hexane/EtOAc 10:1 then hexane/CH_2Cl_2 = 1:1) to afford the corresponding indole dimer **15** (3.9 mg, 53% yield) as a yellow solid.

6,6'-Bis(4-(*tert*-butyl)phenyl)-7,7'-bis(4-ethylphenyl)-5,5'-bis(4-methoxyphenyl)-4,4'-diphenyl-3,3'-bis(3-(trifluoromethyl)phenyl)-1*H*,1'*H*-2,2'-biindole (15):

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (s, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.09 (s, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.84–6.50 (m, 32H), 6.30 (d, *J* = 8.4 Hz, 2H), 3.54 (s, 6H), 2.57 (q, *J* = 7.8 Hz, 4H), 1.19 (t, *J* = 7.8 Hz, 6H), 1.09 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.7, 147.7, 141.9, 138.1, 137.2, 136.5, 135.7, 134.5, 134.1, 133.9, 133.6, 133.1, 132.9, 131.3, 130.7, 129.9 (q, $^2J_{CF}$ = 31.5 Hz), 129.4, 128.2, 127.8, 127.5, 127.3, 126.7 (q, $^3J_{CF}$ = 5.7 Hz), 126.1 (q, $^3J_{CF}$ = 5.7 Hz), 125.3, 124.1, 123.8, 123.7 (q, $^1J_{CF}$ = 271 Hz), 123.4, 123.2, 115.2, 111.8, 54.9, 34.1, 31.2, 28.3, 15.1; HRMS (ESI) *m/z* calcd for $C_{92}H_{78}F_6N_2O_2Na$ $[MNa]^+$: 1379.5860, found 1379.5852.

15. DFT Calculations

The Gaussian 09 program[10] running on a SGI Altix4700 system was used for geometry optimization (B3LYP/6-31G(d)).[11] All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase unless otherwise noted. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency). Visualization of the results was performed by use of GaussView 5.0 software.

To make the calculation easier, the structure of ynamide **S5** and **S6**, in which aryl groups were simplified as phenyl group, was optimized. As a result of DFT calculations, HOMOs of **S5** are delocalized over the ynamide moiety. On the other hand, LUMO are delocalized over the thiophene *S*,*S*-dioxide moiety, indicating that the reaction proceeded via inverse electron-demand Diels–Alder reaction.

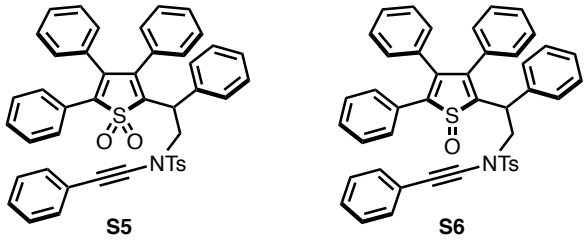


Table S2. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

structure	*E*	*E* + *ZPE*	*H*	*G*
S5	-2887.669680	-2886.986664	-2886.939924	-2887.075134
S6	-2812.515081	-2811.792227	-2811.746246	-2811.879140

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and thermal enthalpies; *G* (= $H - TS$): sum of electronic and thermal free energies.

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

[11] a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

Table S3. Cartesian coordinates of optimized **S5**.

S	0.699328	1.436375	-1.175555	C	-2.498274	-2.778806	3.452320
O	0.941850	1.702094	-2.610798	C	-3.515831	-2.011634	4.036301
O	-0.522552	1.987922	-0.566808	C	-4.432009	-1.365092	3.193703
C	1.909977	-0.488361	0.017404	C	-4.337193	-1.466233	1.808260
C	2.631114	0.775191	0.402737	C	-3.618996	-1.871370	5.536005
C	2.126579	1.898025	-0.159593	S	-3.160129	-2.372588	-0.519158
C	0.875024	-0.331123	-0.835329	O	-2.199189	-3.436478	-0.834831
C	2.422450	3.325228	0.020837	O	-4.509717	-2.386623	-1.083309
C	2.349588	4.207791	-1.073355	H	2.088717	3.824368	-2.054398
C	2.615758	5.565204	-0.903170	H	2.558690	6.232575	-1.758624
C	2.952306	6.065099	0.355428	H	3.157487	7.124205	0.485777
C	3.016091	5.198584	1.449911	H	3.264033	5.582392	2.435787
C	2.751407	3.841854	1.288187	H	2.786241	3.177471	2.144768
C	2.362522	-1.820476	0.503541	H	0.599008	-2.163432	1.694147
C	1.552428	-2.571279	1.368771	H	1.335298	-4.394153	2.493488
C	1.969914	-3.824115	1.819983	H	3.522530	-5.319725	1.758231
C	3.198623	-4.343064	1.409220	H	4.966982	-4.000436	0.222815
C	4.010338	-3.601565	0.548622	H	4.232329	-1.775810	-0.570243
C	3.598590	-2.347023	0.101389	H	2.827489	-0.257411	2.924034
C	3.819641	0.751234	1.293084	H	4.811066	-0.258379	4.396390
C	3.757188	0.180747	2.574742	H	6.954398	0.727475	3.608173
C	4.877829	0.180053	3.404420	H	7.088292	1.727318	1.333356
C	6.080310	0.734992	2.962707	H	5.092832	1.747783	-0.131972
C	6.155235	1.297018	1.686764	H	-0.084172	-2.200495	-0.813404
C	5.033507	1.308961	0.859494	H	-1.316943	-0.034217	-2.557021
C	0.080511	-1.410256	-1.548777	H	-1.653528	-1.747099	-2.778241
C	-1.327785	-1.000687	-2.049922	H	0.321183	-4.044747	-2.061928
C	0.861329	-2.059098	-2.701489	H	1.497027	-5.181933	-3.918829
C	0.854098	-3.457455	-2.805019	H	2.698155	-3.842427	-5.640651
C	1.511132	-4.096863	-3.856455	H	2.705420	-1.359707	-5.478901
C	2.184131	-3.346115	-4.821570	H	1.540101	-0.226809	-3.621006
C	2.189439	-1.953694	-4.728775	H	-2.665248	3.624036	-0.430147
C	1.531806	-1.310801	-3.677947	H	-3.862550	5.796051	-0.216906
C	-3.103937	0.220857	-0.874063	H	-6.347685	5.861433	-0.298502
C	-3.766615	1.233579	-0.785672	H	-7.629149	3.753623	-0.613026
C	-4.468759	2.468129	-0.654164	H	-6.430695	1.595019	-0.862282
C	-3.749197	3.666625	-0.470795	H	-1.603295	-3.494901	1.616517
C	-4.427077	4.876998	-0.351780	H	-1.793968	-3.307011	4.090343
C	-5.823454	4.914517	-0.397136	H	-5.237604	-0.778672	3.628258
C	-6.543175	3.730233	-0.572610	H	-5.059839	-0.978369	1.164653
C	-5.875138	2.515545	-0.708858	H	-3.164818	-0.930349	5.873191
N	-2.346977	-0.895287	-0.964362	H	-4.663166	-1.862534	5.866261
C	-3.297263	-2.218144	1.256435	H	-3.105000	-2.687973	6.052576
C	-2.379338	-2.885890	2.067749				

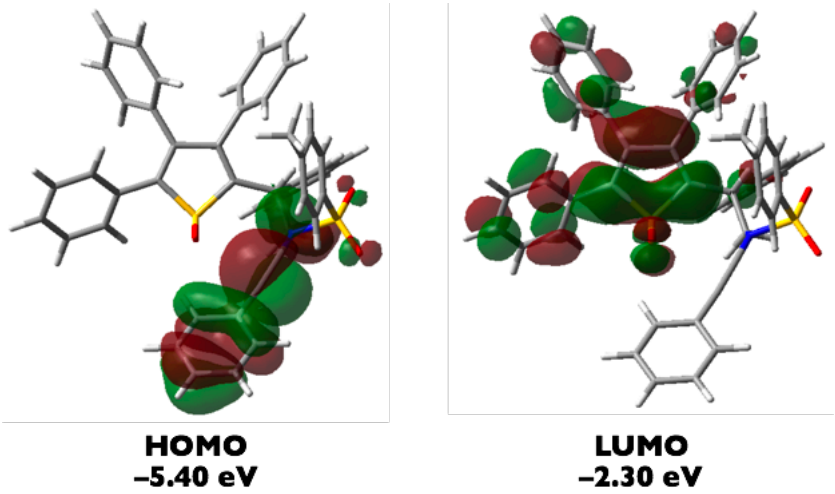


Figure S1. Pictorial frontier molecular orbitals and calculated energy levels of **S5**.

Table S4. Cartesian coordinates of optimized **S6**.

S	0.69933	1.43638	-1.17556	C	-2.49827	-2.77881	3.45232
O	-0.52255	1.98792	-0.56681	C	-3.51583	-2.01163	4.03630
C	1.90998	-0.48836	0.01740	C	-4.43201	-1.36509	3.19370
C	2.63111	0.77519	0.40274	C	-4.33719	-1.46623	1.80826
C	2.12658	1.89803	-0.15959	C	-3.61900	-1.87137	5.53601
C	0.87502	-0.33112	-0.83533	S	-3.16013	-2.37259	-0.51916
C	2.42245	3.32523	0.02084	O	-2.19919	-3.43648	-0.83483
C	2.34959	4.20779	-1.07336	O	-4.50972	-2.38662	-1.08331
C	2.61576	5.56520	-0.90317	H	2.08872	3.82437	-2.05440
C	2.95231	6.06510	0.35543	H	2.55869	6.23257	-1.75862
C	3.01609	5.19858	1.44991	H	3.15749	7.12420	0.48578
C	2.75141	3.84185	1.28819	H	3.26403	5.58239	2.43579
C	2.36252	-1.82048	0.50354	H	2.78624	3.17747	2.14477
C	1.55243	-2.57128	1.36877	H	0.59901	-2.16343	1.69415
C	1.96991	-3.82412	1.81998	H	1.33530	-4.39415	2.49349
C	3.19862	-4.34306	1.40922	H	3.52253	-5.31973	1.75823
C	4.01034	-3.60157	0.54862	H	4.96698	-4.00044	0.22282
C	3.59859	-2.34702	0.10139	H	4.23233	-1.77581	-0.57024
C	3.81964	0.75123	1.29308	H	2.82749	-0.25741	2.92403
C	3.75719	0.18075	2.57474	H	4.81107	-0.25838	4.39639
C	4.87783	0.18005	3.40442	H	6.95440	0.72748	3.60817
C	6.08031	0.73499	2.96271	H	7.08829	1.72732	1.33336
C	6.15524	1.29702	1.68676	H	5.09283	1.74778	-0.13197
C	5.03351	1.30896	0.85949	H	-0.08417	-2.20050	-0.81340
C	0.08051	-1.41026	-1.54878	H	-1.31694	-0.03422	-2.55702
C	-1.32779	-1.00069	-2.04992	H	-1.65353	-1.74710	-2.77824
C	0.86133	-2.05910	-2.70149	H	0.32118	-4.04475	-2.06193
C	0.85410	-3.45746	-2.80502	H	1.49703	-5.18193	-3.91883
C	1.51113	-4.09686	-3.85646	H	2.69816	-3.84243	-5.64065
C	2.18413	-3.34612	-4.82157	H	2.70542	-1.35971	-5.47890
C	2.18944	-1.95369	-4.72878	H	1.54010	-0.22681	-3.62101
C	1.53181	-1.31080	-3.67795	H	-2.66525	3.62404	-0.43015
C	-3.10394	0.22086	-0.87406	H	-3.86255	5.79605	-0.21691
C	-3.76662	1.23358	-0.78567	H	-6.34769	5.86143	-0.29850
C	-4.46876	2.46813	-0.65416	H	-7.62915	3.75362	-0.61303
C	-3.74920	3.66663	-0.47080	H	-6.43070	1.59502	-0.86228
C	-4.42708	4.87700	-0.35178	H	-1.60330	-3.49490	1.61652
C	-5.82345	4.91452	-0.39714	H	-1.79397	-3.30701	4.09034
C	-6.54318	3.73023	-0.57261	H	-5.23760	-0.77867	3.62826
C	-5.87514	2.51555	-0.70886	H	-5.05984	-0.97837	1.16465
N	-2.34698	-0.89529	-0.96436	H	-3.16482	-0.93035	5.87319
C	-3.29726	-2.21814	1.25644	H	-4.66317	-1.86253	5.86626
C	-2.37934	-2.88589	2.06775	H	-3.10500	-2.68797	6.05258

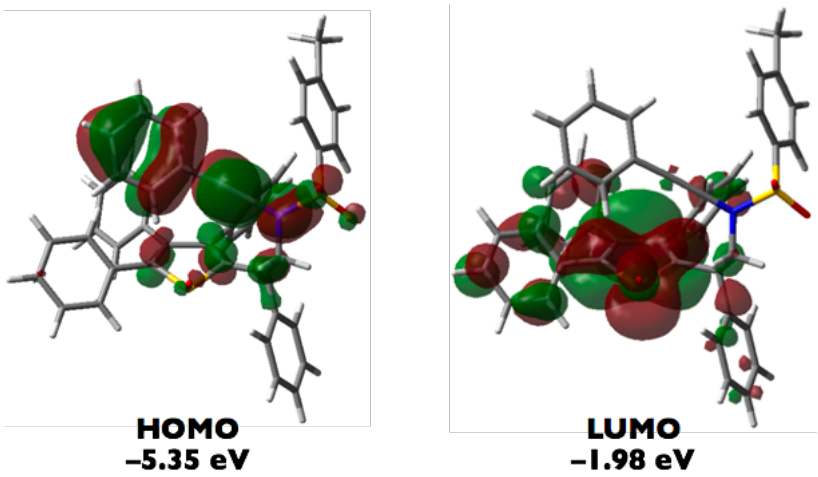


Figure S2. Pictorial frontier molecular orbitals and calculated energy levels of **S6**.

16. X-ray Crystal Structure Analysis

Details of the crystal data and a summary of the intensity data collection parameters for **8J**, **9A**, **12**, **17A** and **14** are listed in Table S5. Suitable crystals of **8J**, **9A**, **12**, **17A** and **14** was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) was used. The structures were solved by direct methods with (SIR-97)[12] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2016)[13] with Yadokari-XG program.[14] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 1580596–1580599 and 1832929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S5. Crystallographic data and structure refinement details for **8J**, **9A**, **12, 17A** and **14**

	8J·$CHCl_3$	**9A**·$CHCl_3$	**12**	**17A**	**14**·EtOH·C_5H_{12}
formula	$C_{50}H_{41}F_3Cl_3NO_3S$	$C_{47}H_{44}Cl_3NO$	$C_{44}H_{40}N_2O_3S$	$C_{56}H_{47}N_3O_5S$	$C_{99}H_{100}N_2O_3$
fw	899.25	745.18	676.84	874.02	1365.80
T (K)	123(2)	143(2)	123(2)	123(2)	123(2)
λ (Å)	0.71075	0.71075	0.71075	0.71075	0.71075
cryst syst	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	P-1	P21/c	P21/n	P21/c	P-1
a, (Å)	9.7851(11)	11.365(2)	14.744(3)	14.816(5)	13.339(5)
b, (Å)	10.7442(14)	13.805(2)	9.8309(15)	28.030(8)	18.203(6)
c, (Å)	22.106(3)	25.674(4)	25.091(4)	12.060(4)	18.304(7)
α, (deg)	103.099(7)	90	90	90	106.445(4)
β, (deg)	95.707(7)	92.439 (4)	94.077(5)	113.633(7)	110.829(6)
γ, (deg)	98.173(7)	90	90	90	95.262(6)
V, (Å^3)	2219.6(5)	4024.4(11)	3627.7(11)	4588(3)	3891(2)
Z	2	4	4	4	2
D_{calc}, (g / cm^3)	1.345	1.230	1.239	1.265	1.166
m (mm^{-1})	0.310	0.264	0.132	0.124	0.069
F(000)	932	1568	1432	1840	1464
cryst size (mm)	0.15 × 0.15 × 0.10	0.25 × 0.10 × 0.02	0.20 × 0.15 × 0.15	0.20 × 0.15 × 0.10	0.08 × 0.08 × 0.02
2θ range, (deg)	3.044–24.999	3.056-24.999	3.03–25.00	3.002–24.996	3.024–25.00
reflns collected	20535	42923	38207	48650	43494
indep reflns/R_{int}	7672/0.0225	7079/0.0558	6376/0.0340	8068/0.0373	13591/0.1612
params	619	503	457	708	957
GOF on F^2	1.063	1.046	1.037	1.014	1.019
R_1, wR_2 [I>2σ(I)]	0.0614, 0.1657	0.0671, 0.1681	0.0466, 0.1175	0.0360, 0.0871	0.0936, 0.2036
R_1, wR_2 (all data)	0.0712, 0.1725	0.1071, 0.1940	0.0618, 0.1255	0.0503, 0.0952	0.2317, 0.2860

[12] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
[13] G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.
[14] a) K. Wakita, Yadokari-XG, Software for crystal structure analyses, 2001; b) C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.

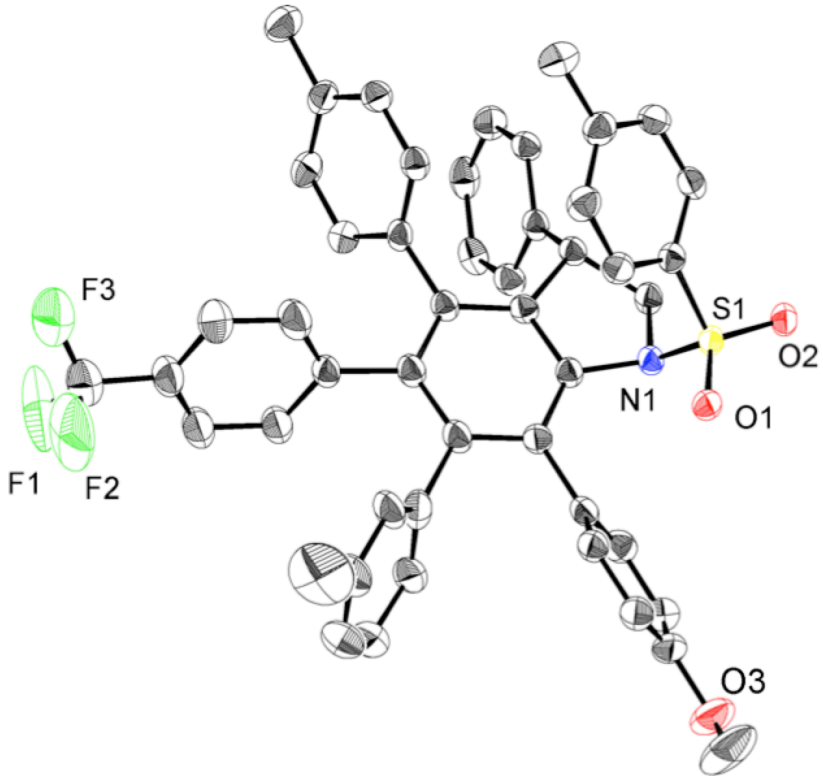


Figure S3. ORTEP drawing of **8J** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

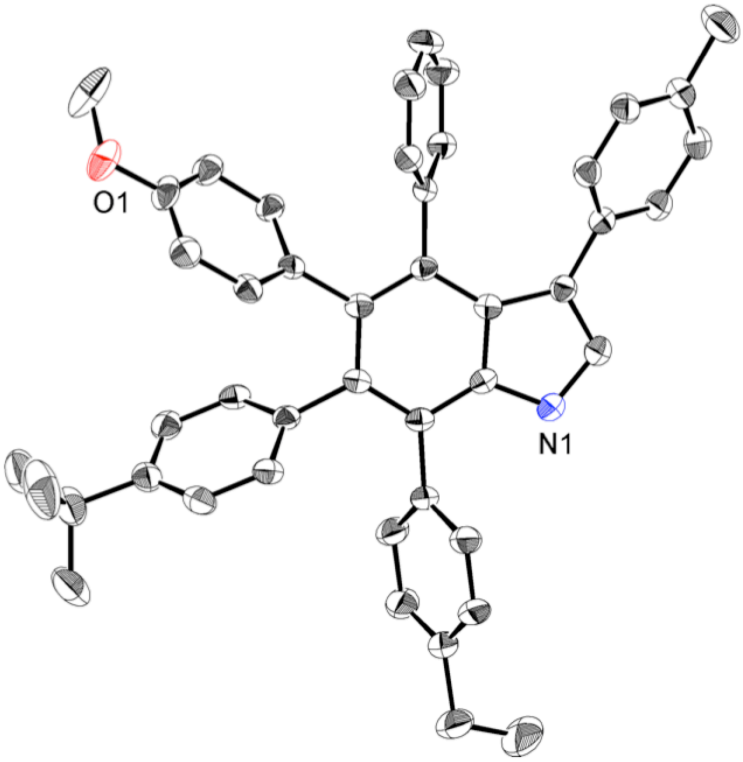


Figure S4. ORTEP drawing of **9A** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

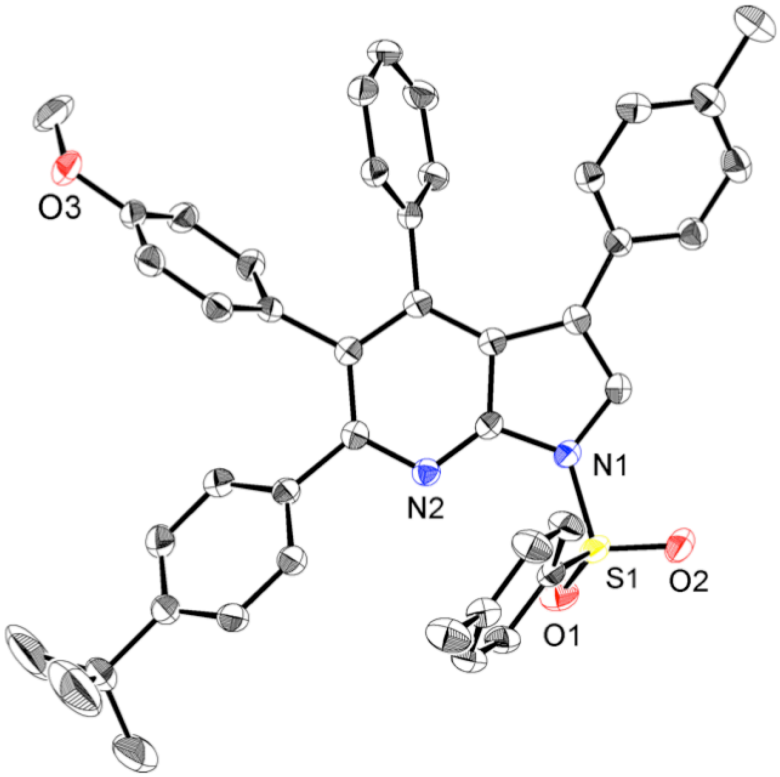


Figure S5. ORTEP drawing of **12** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

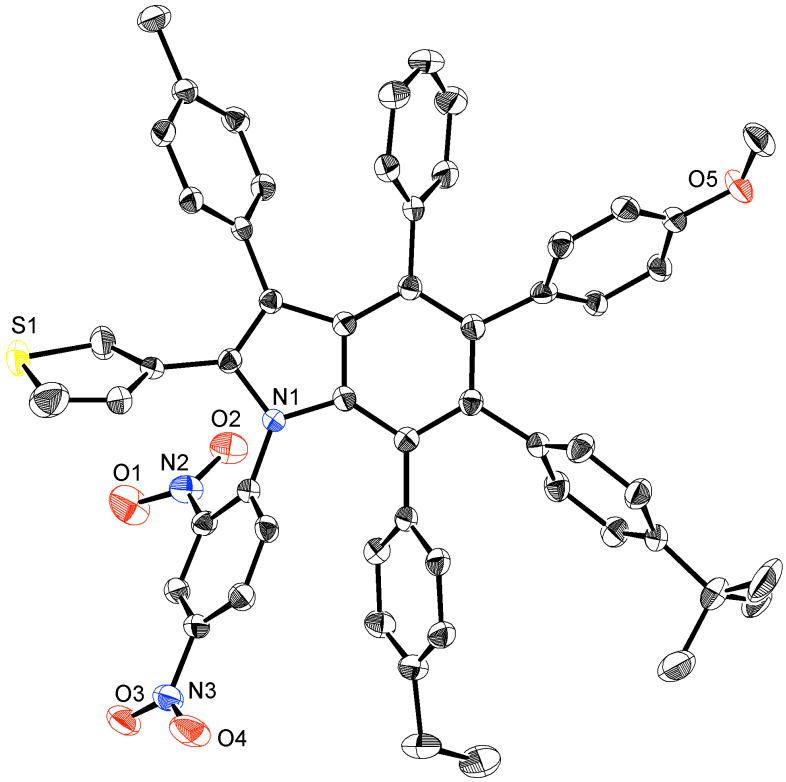


Figure S6. ORTEP drawing of **17A** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

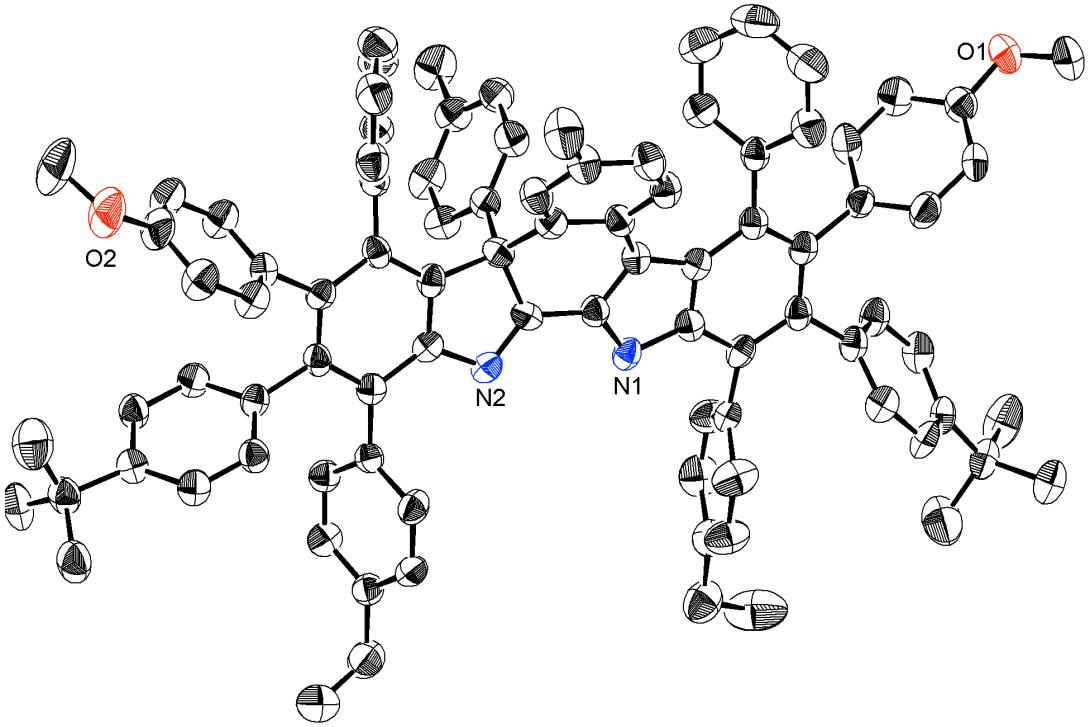
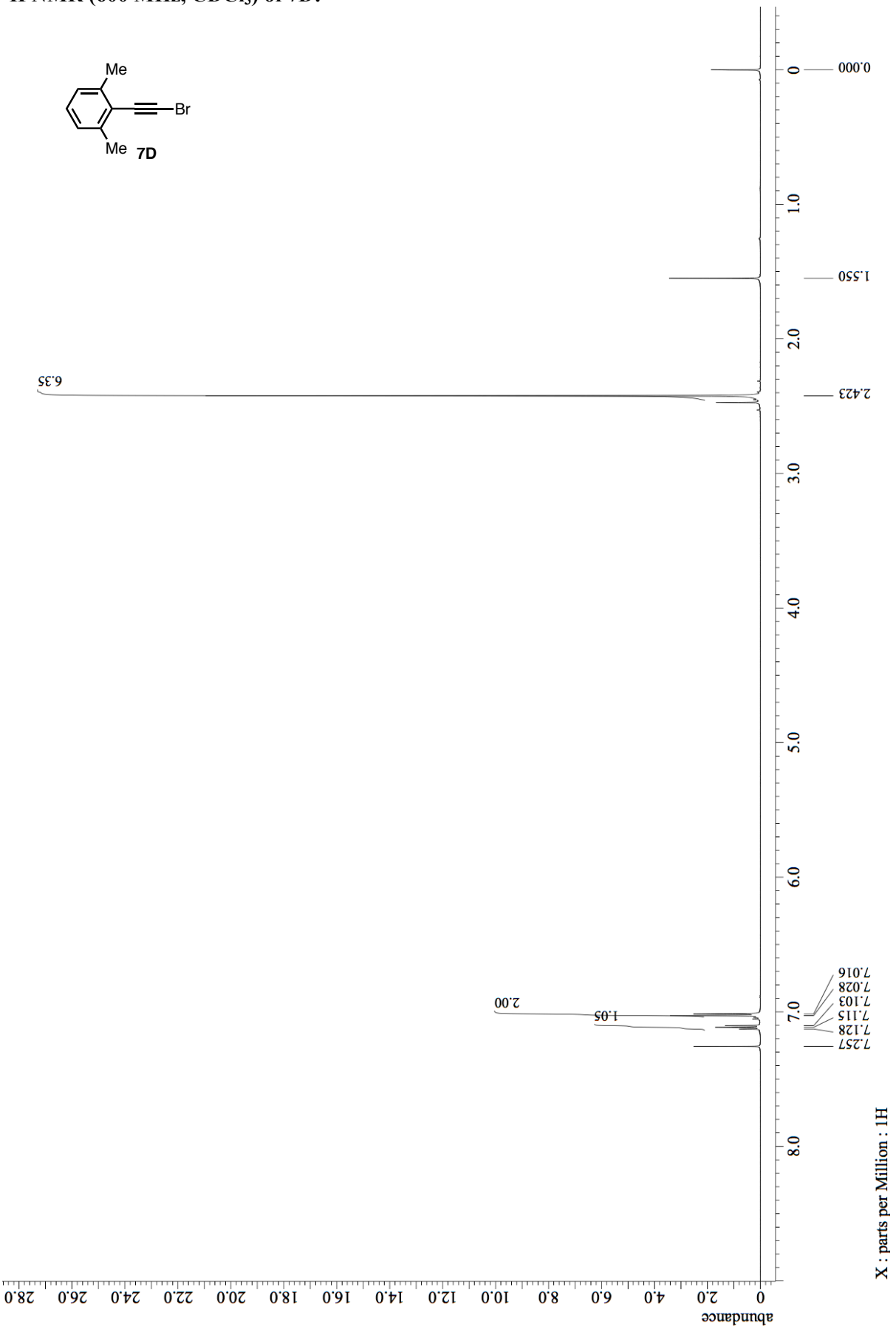


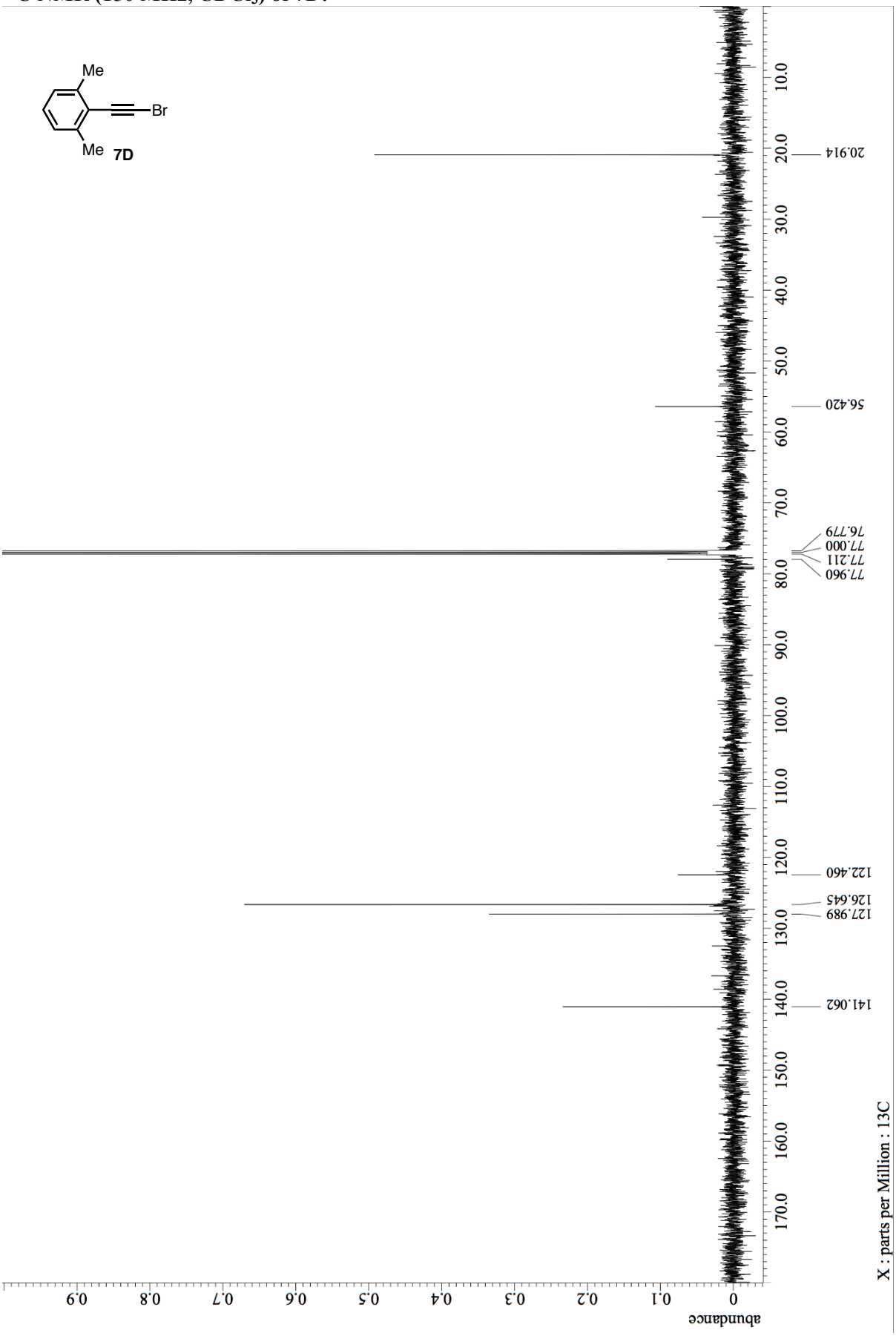
Figure S7. ORTEP drawing of **14** with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

17. ^{1}H NMR and ^{13}C NMR Spectra

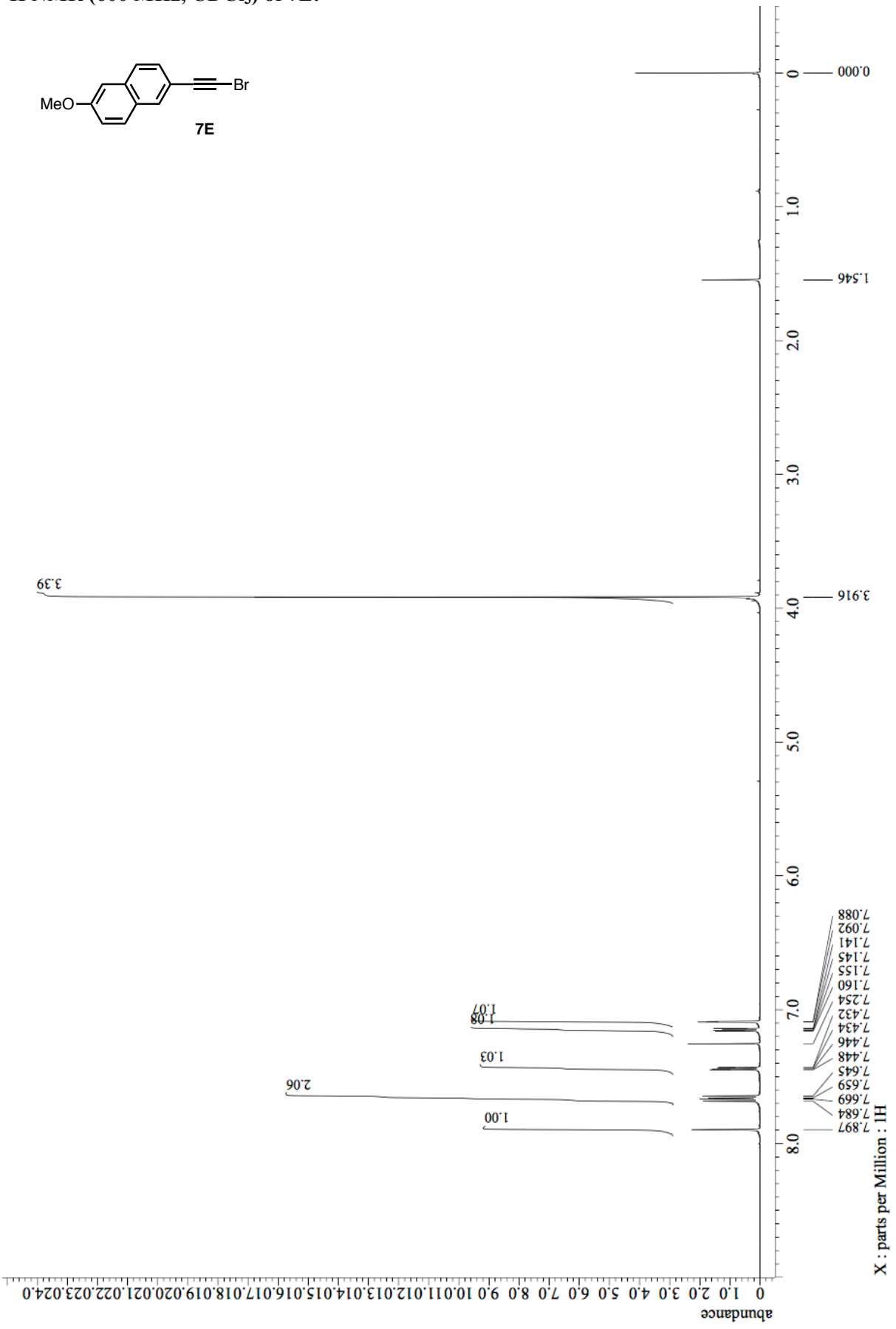
^{1}H NMR (600 MHz, $CDCl_3$) of 7D:



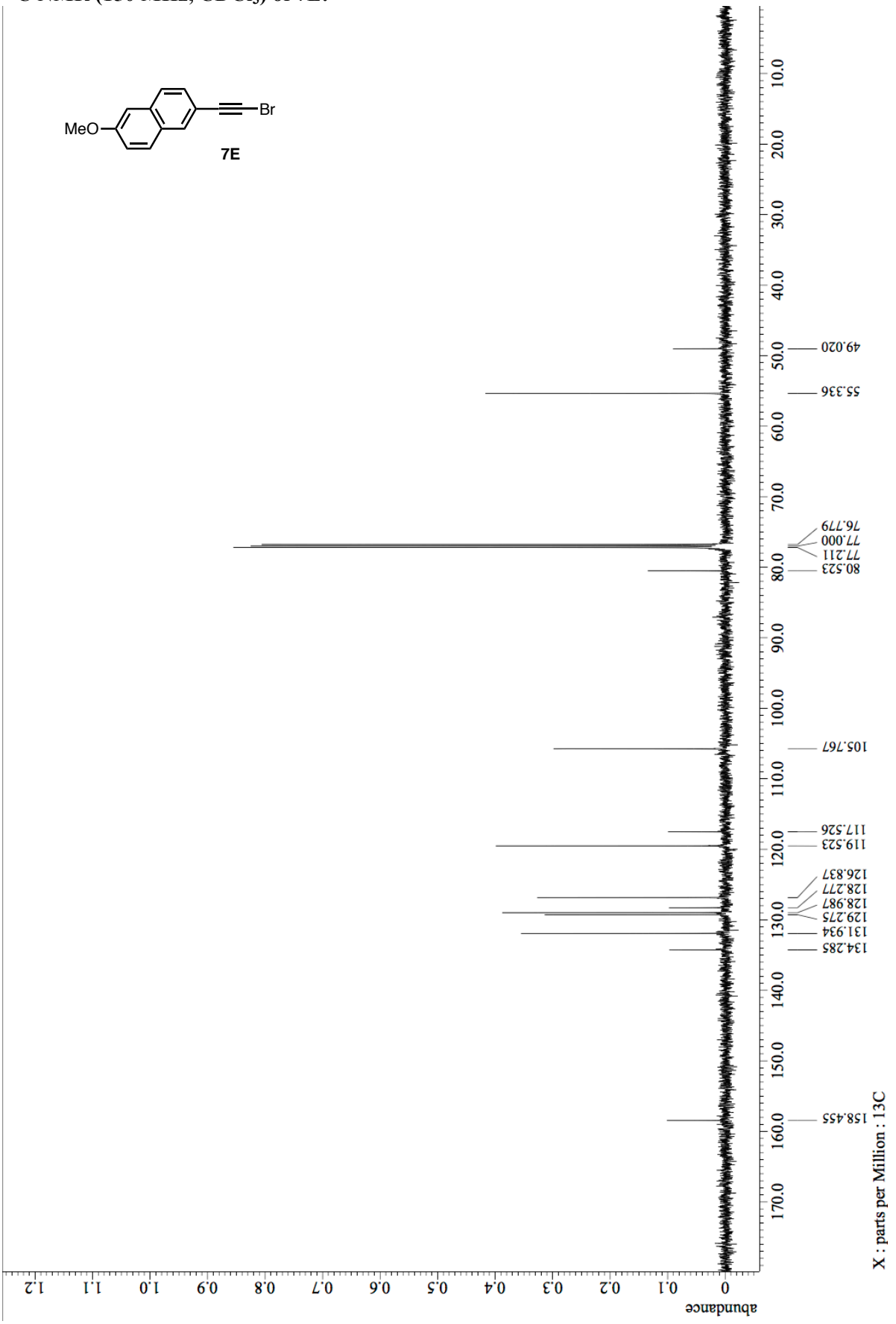
^{13}C NMR (150 MHz, $CDCl_3$) of 7D:



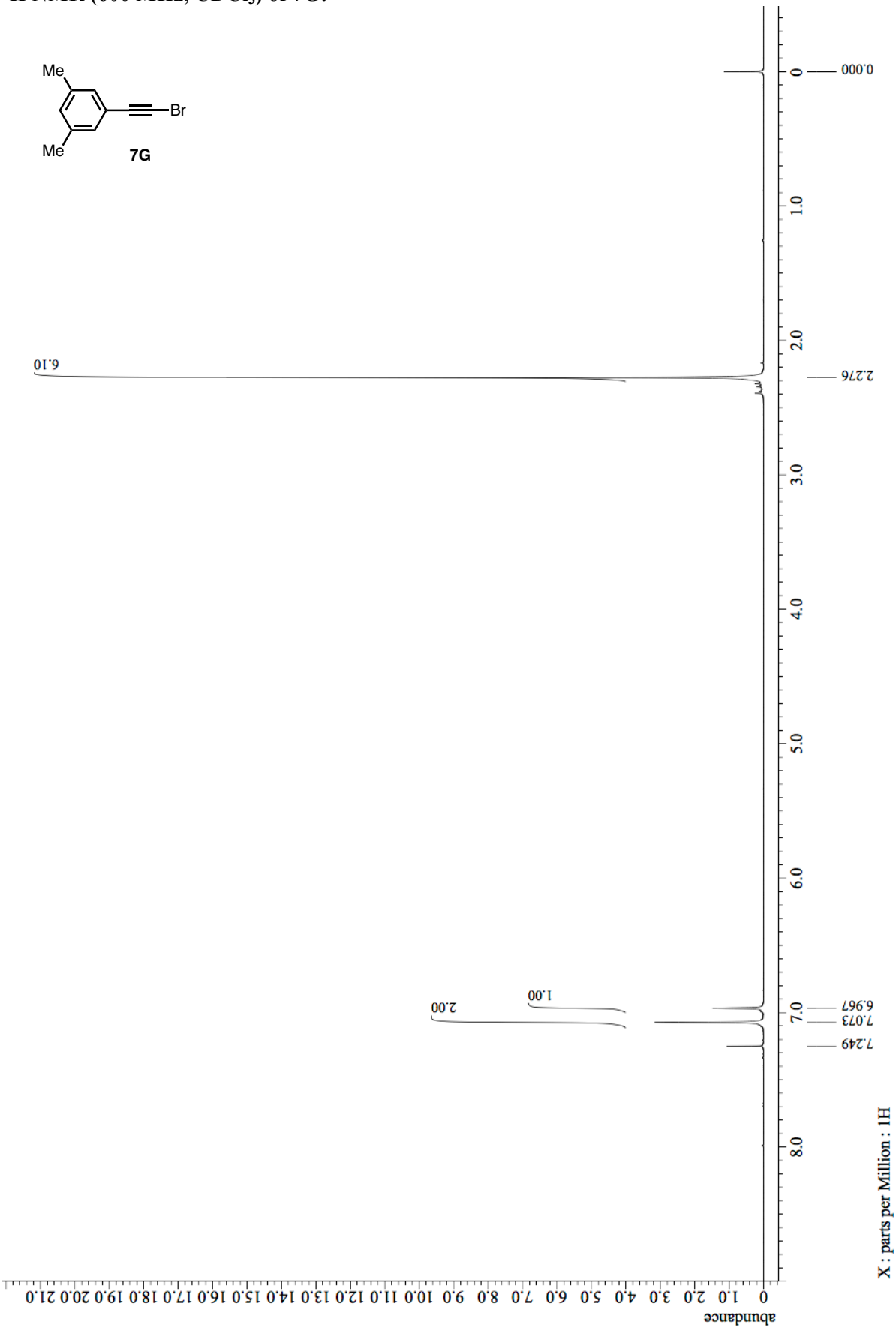
^{1}H NMR (600 MHz, $CDCl_3$) of 7E:



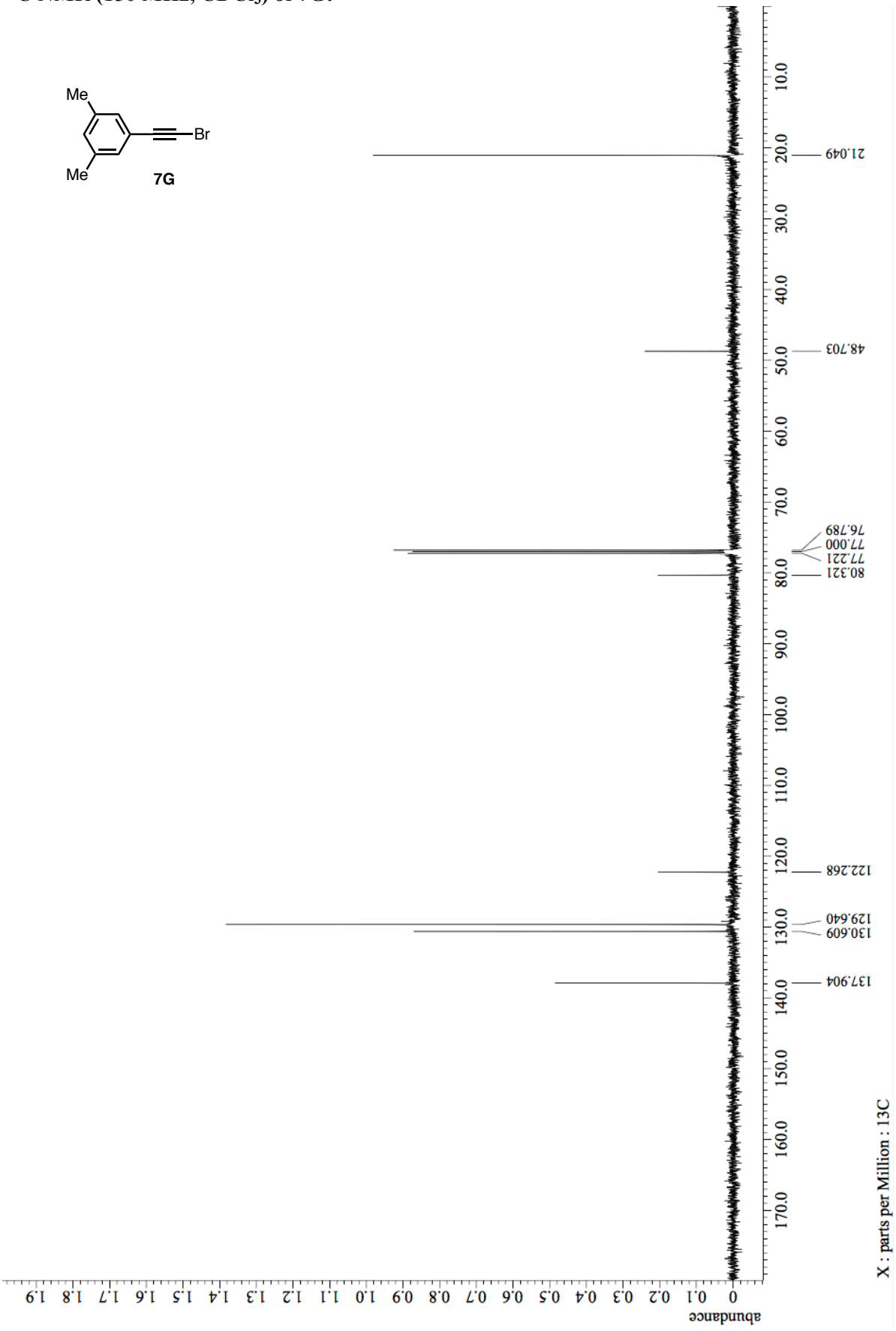
^{13}C NMR (150 MHz, $CDCl_3$) of 7E:



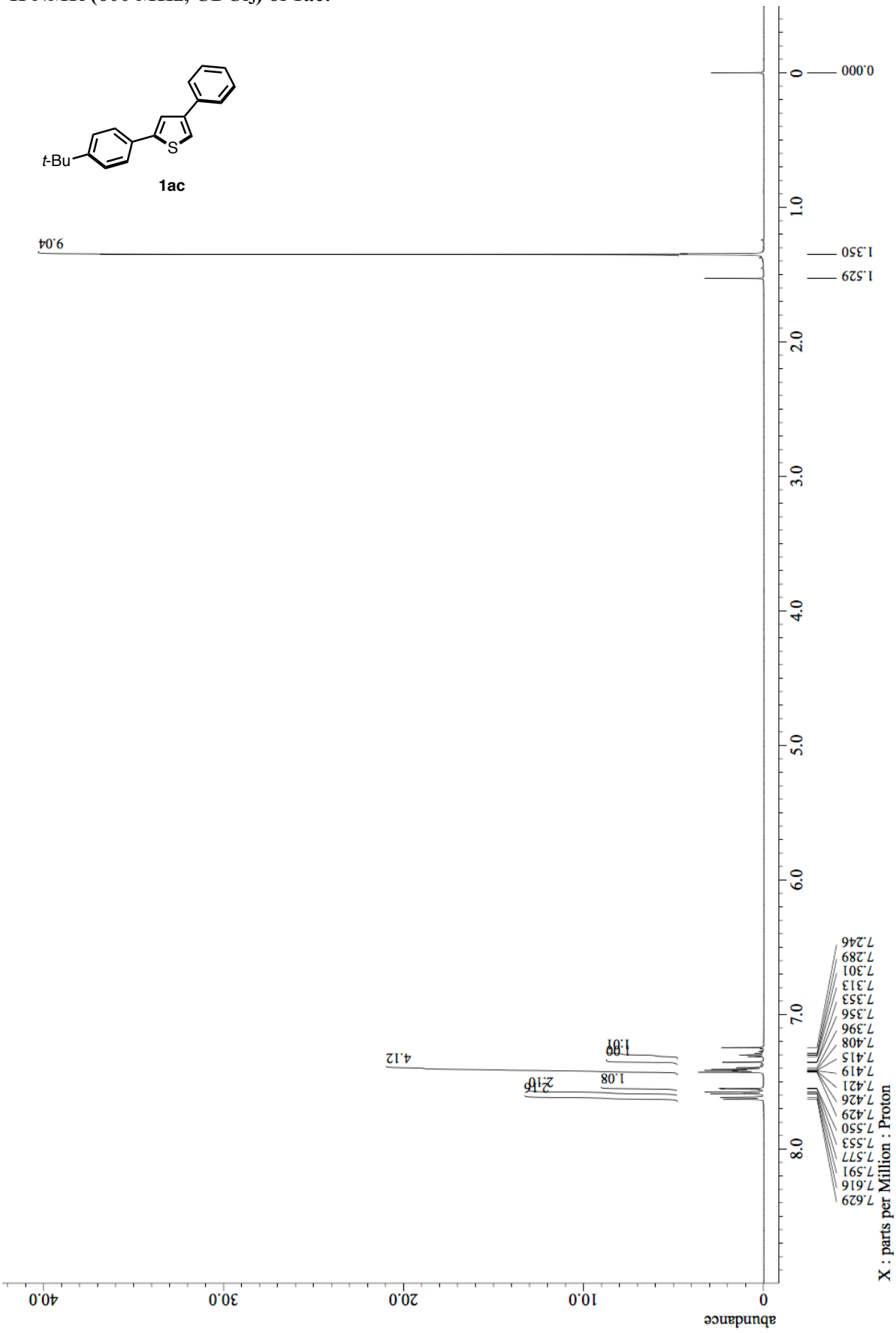
^{1}H NMR (600 MHz, $CDCl_3$) of 7G:



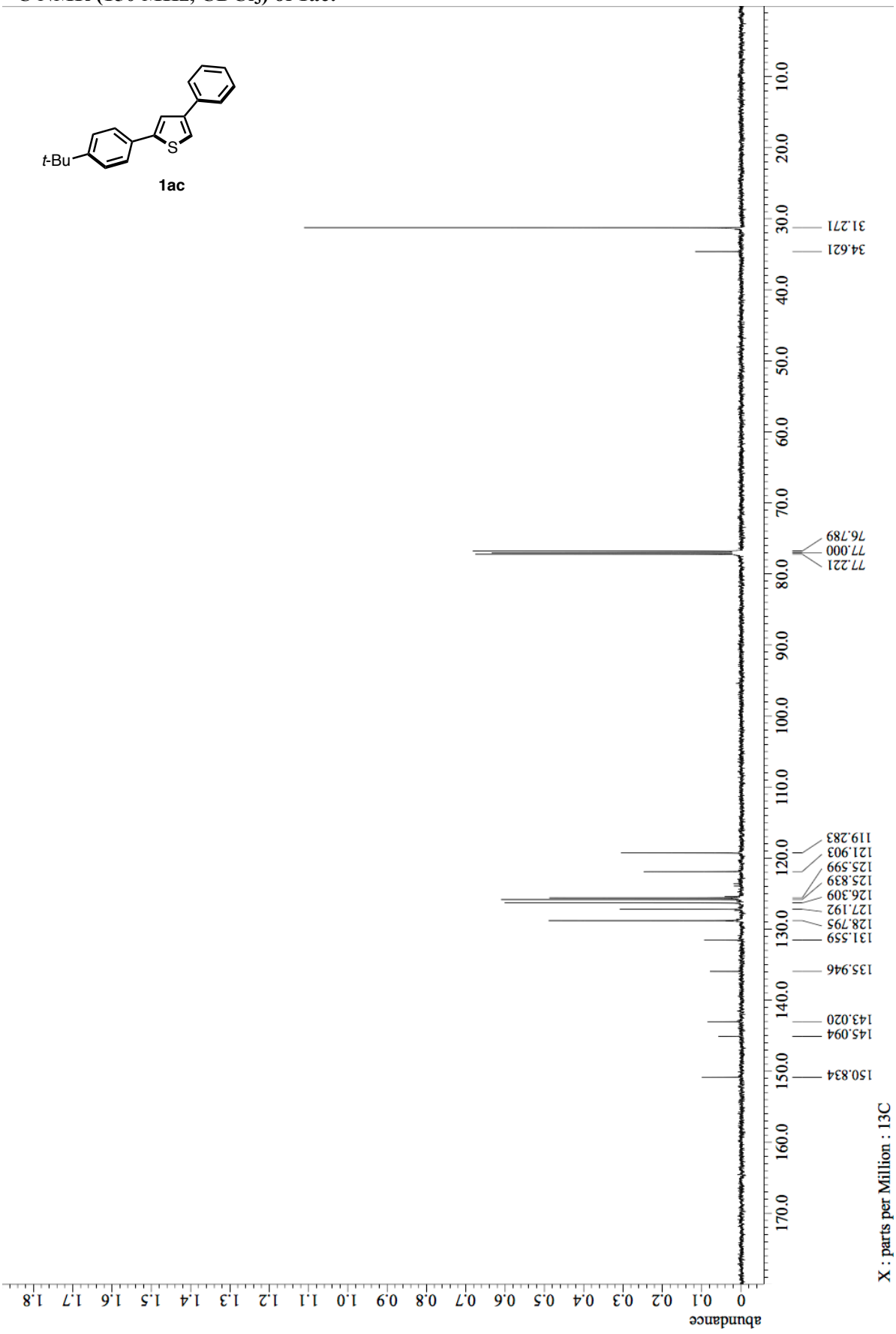
^{13}C NMR (150 MHz, $CDCl_3$) of 7G:



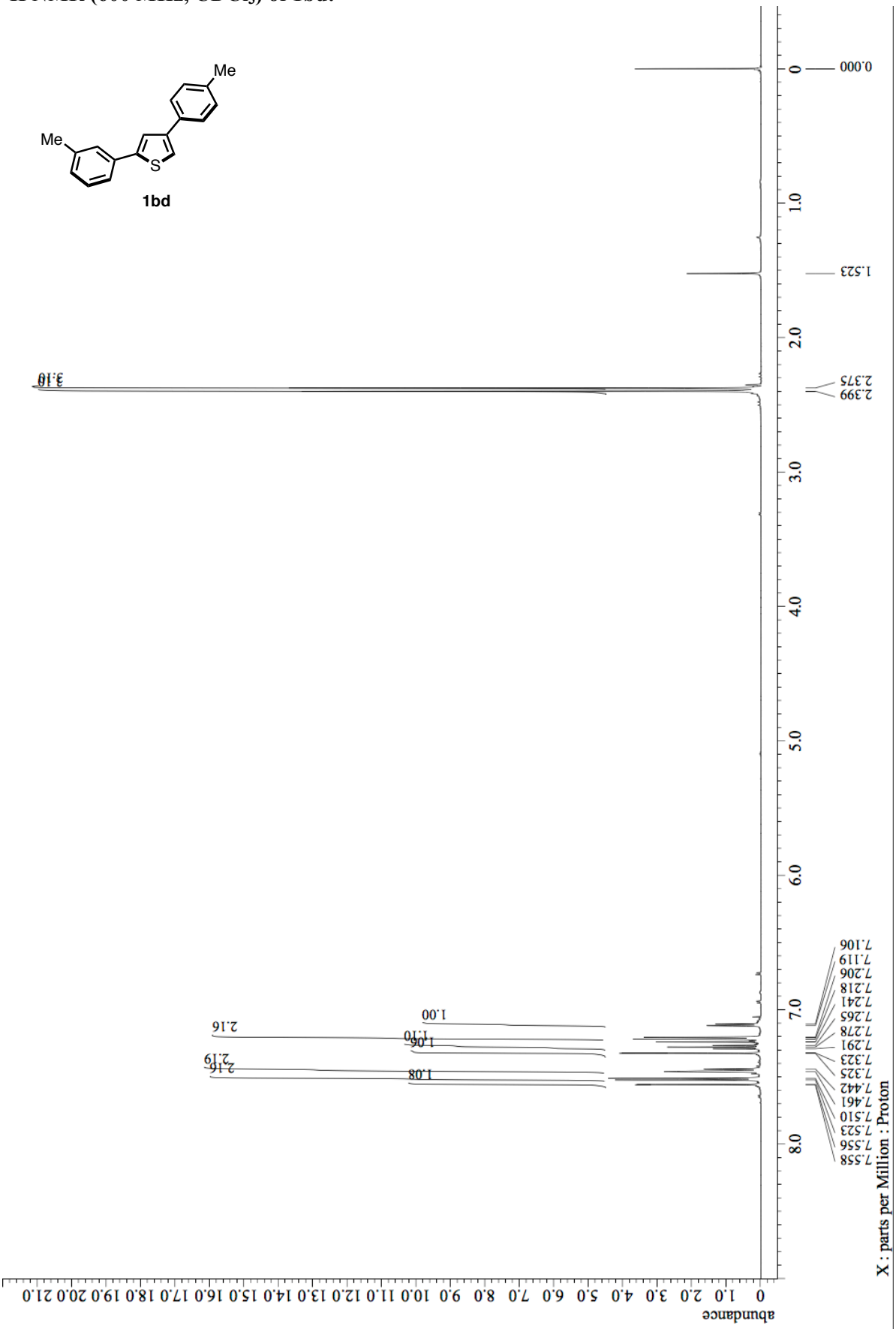
^{1}H NMR (600 MHz, $CDCl_3$) of 1ac:



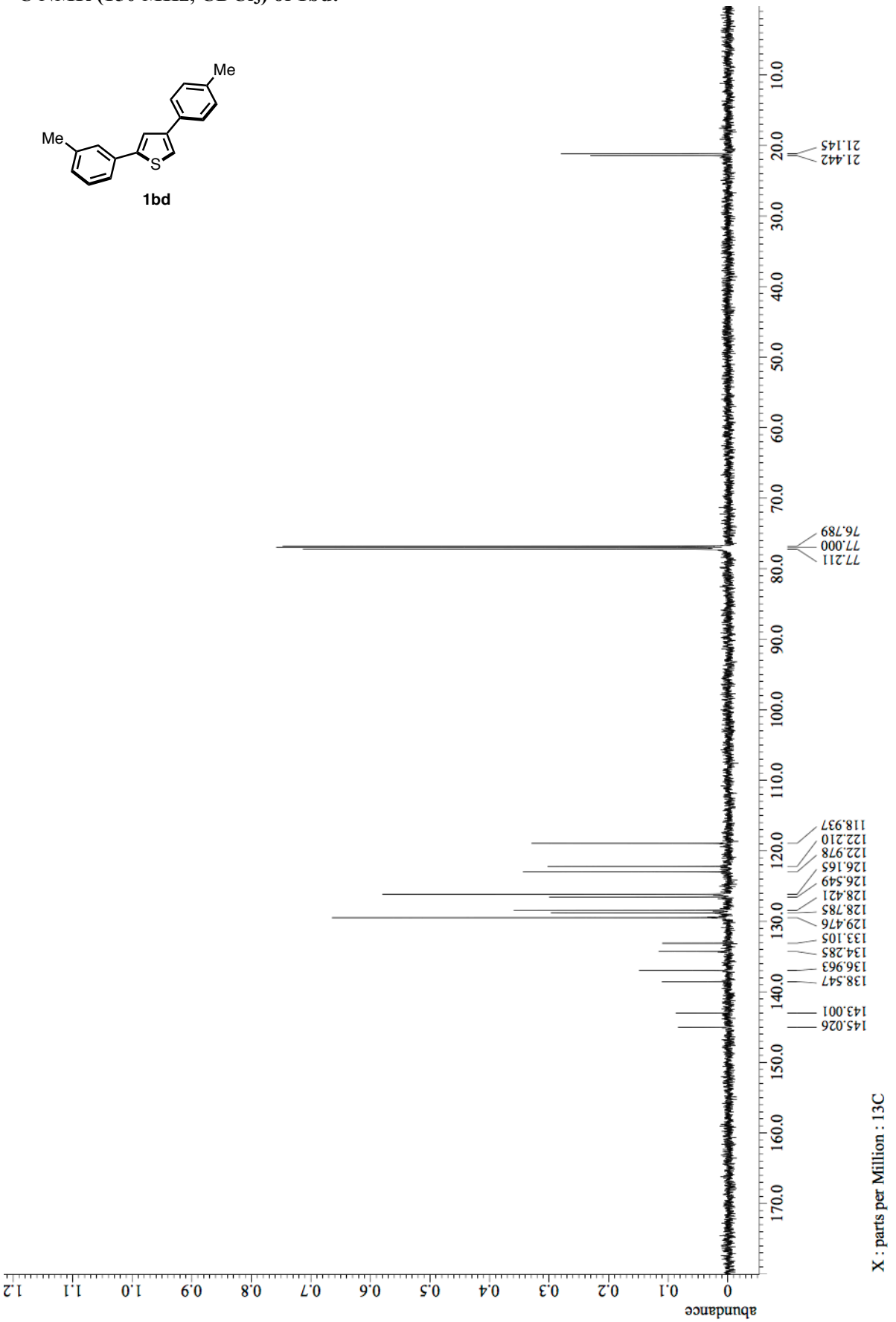
^{13}C NMR (150 MHz, $CDCl_3$) of 1ac:



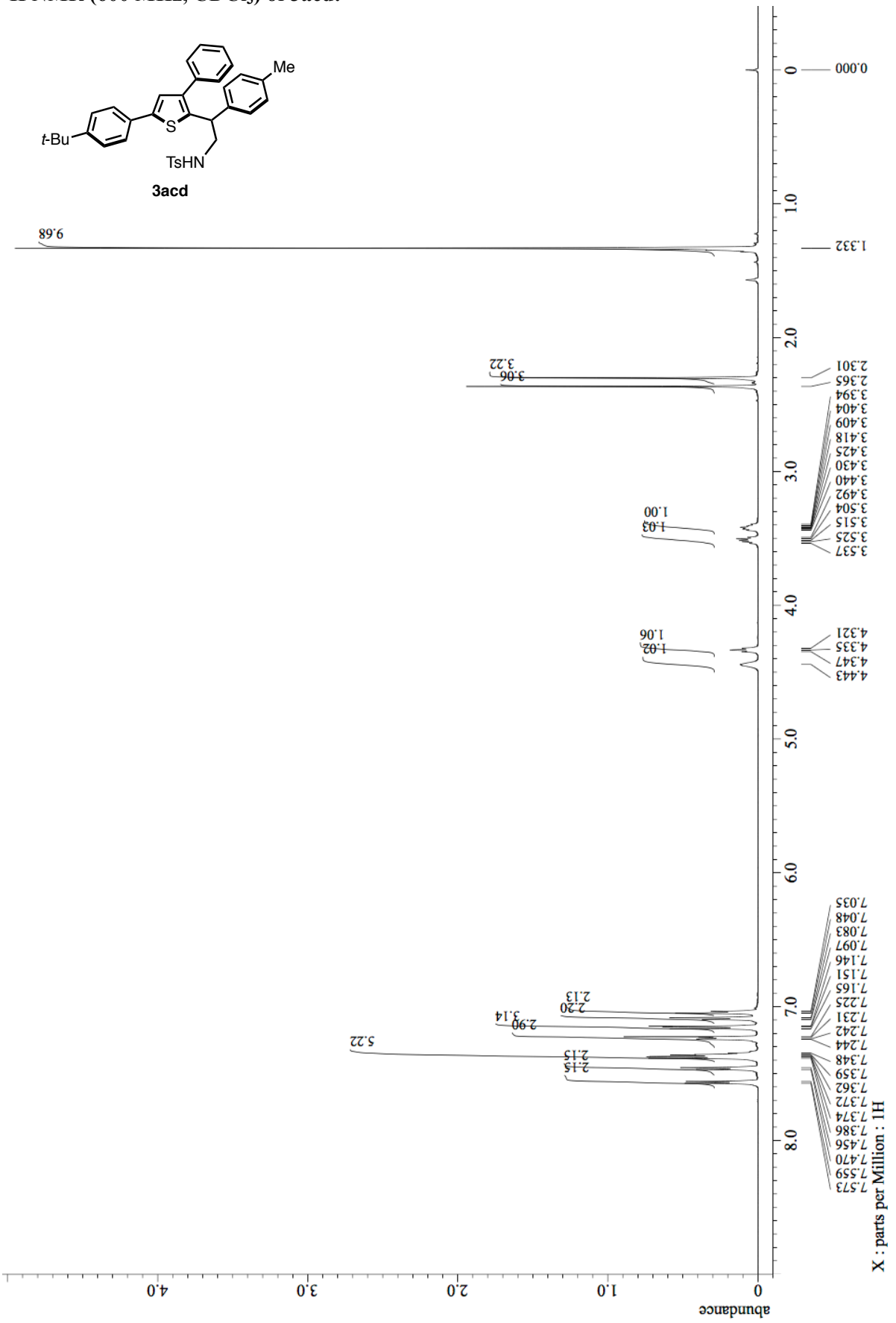
^{1}H NMR (600 MHz, $CDCl_3$) of 1bd:



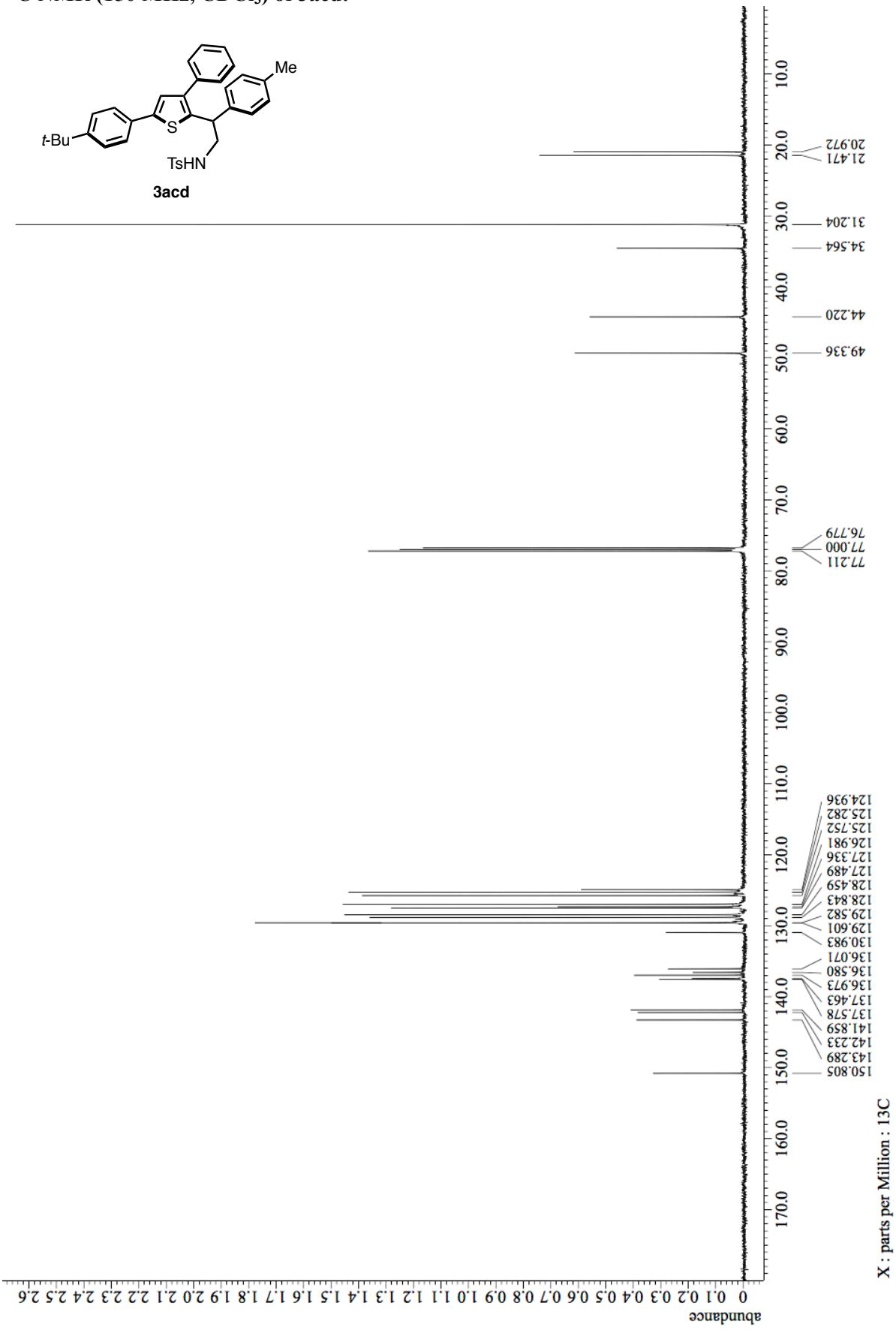
^{13}C NMR (150 MHz, $CDCl_3$) of 1bd:



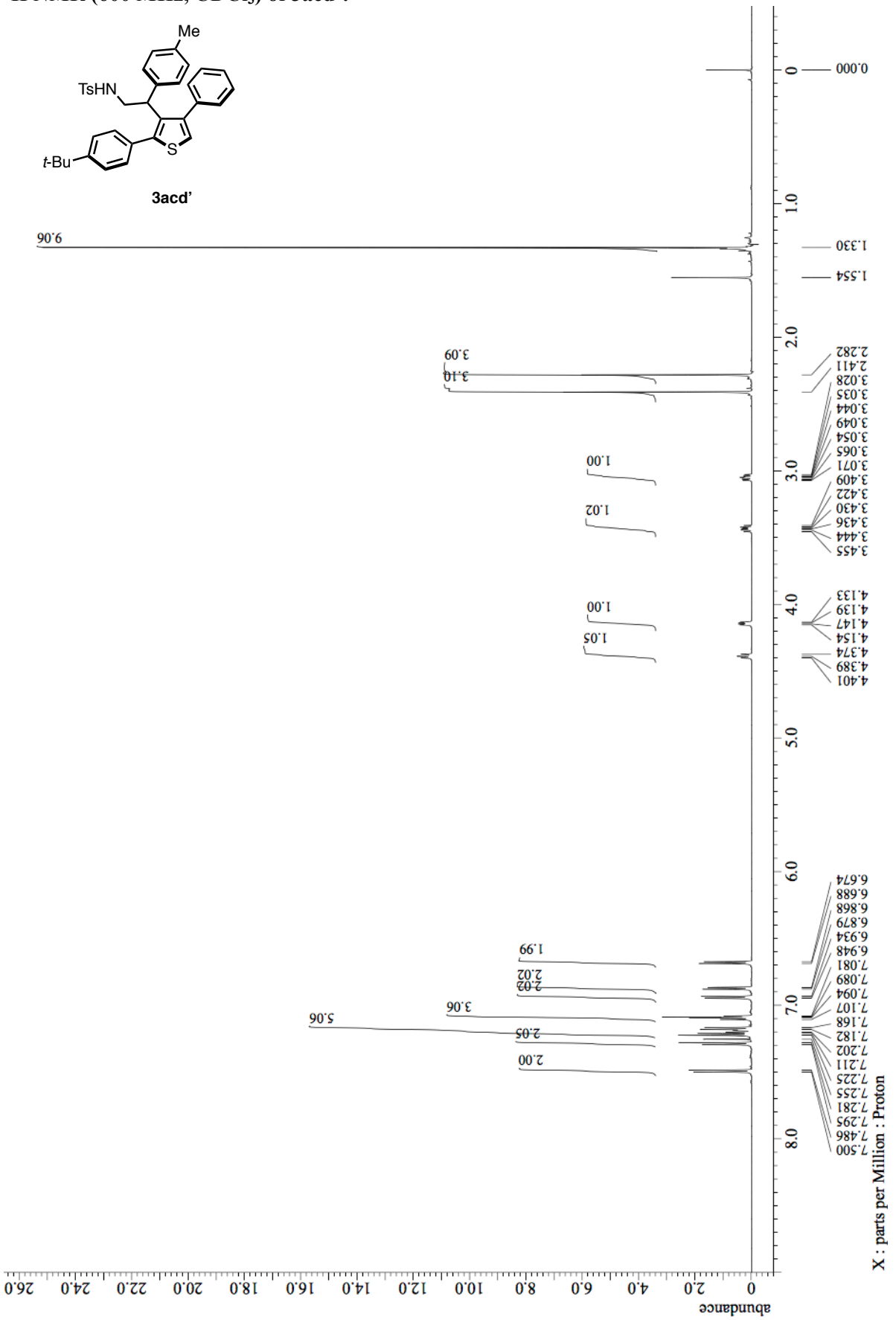
^{1}H NMR (600 MHz, $CDCl_3$) of 3acd:



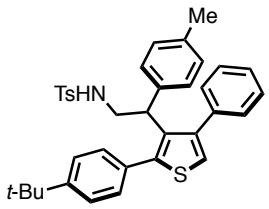
^{13}C NMR (150 MHz, $CDCl_3$) of 3acd:



^{1}H NMR (600 MHz, $CDCl_3$) of 3acd':

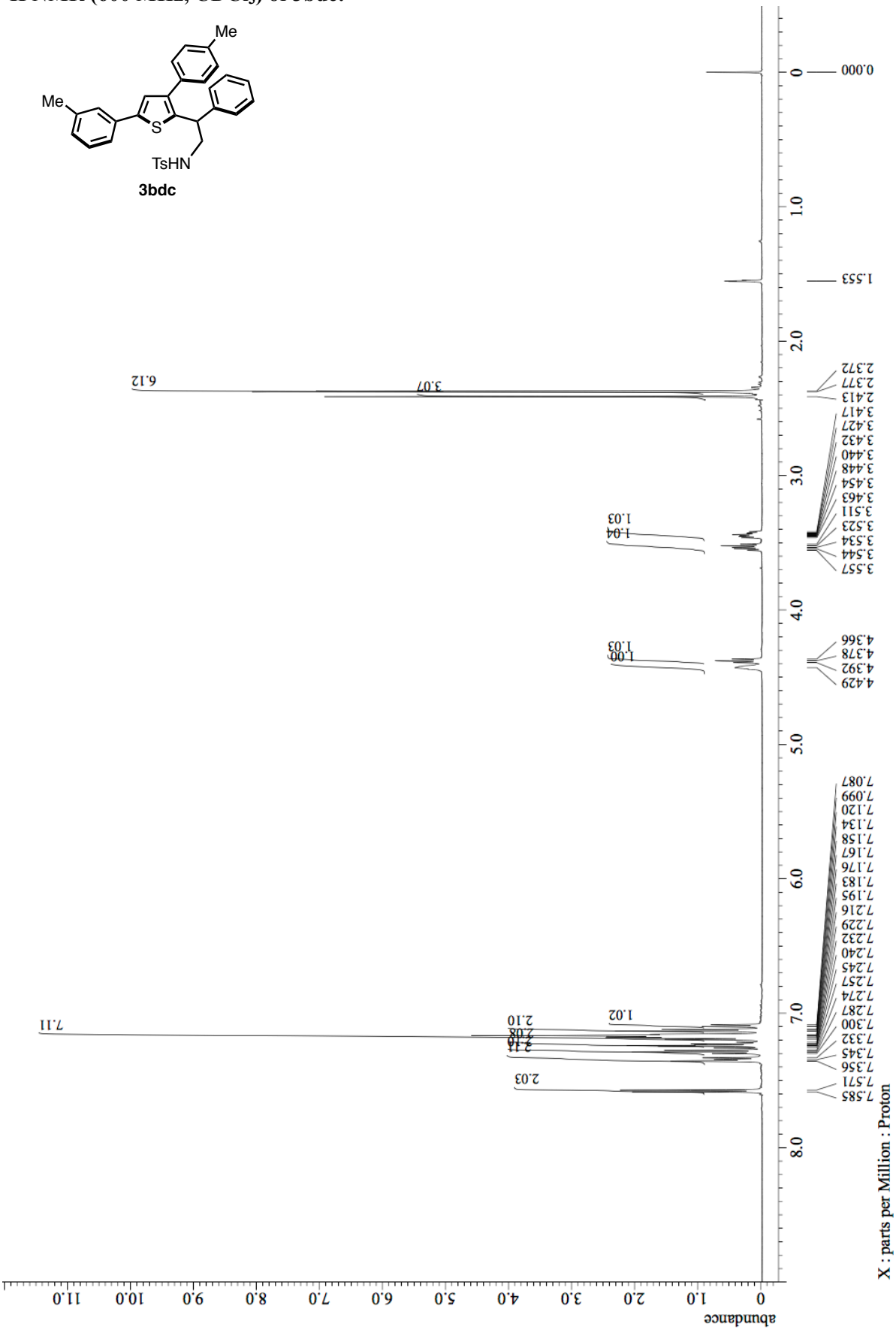


^{13}C NMR (150 MHz, $CDCl_3$) of 3acd'

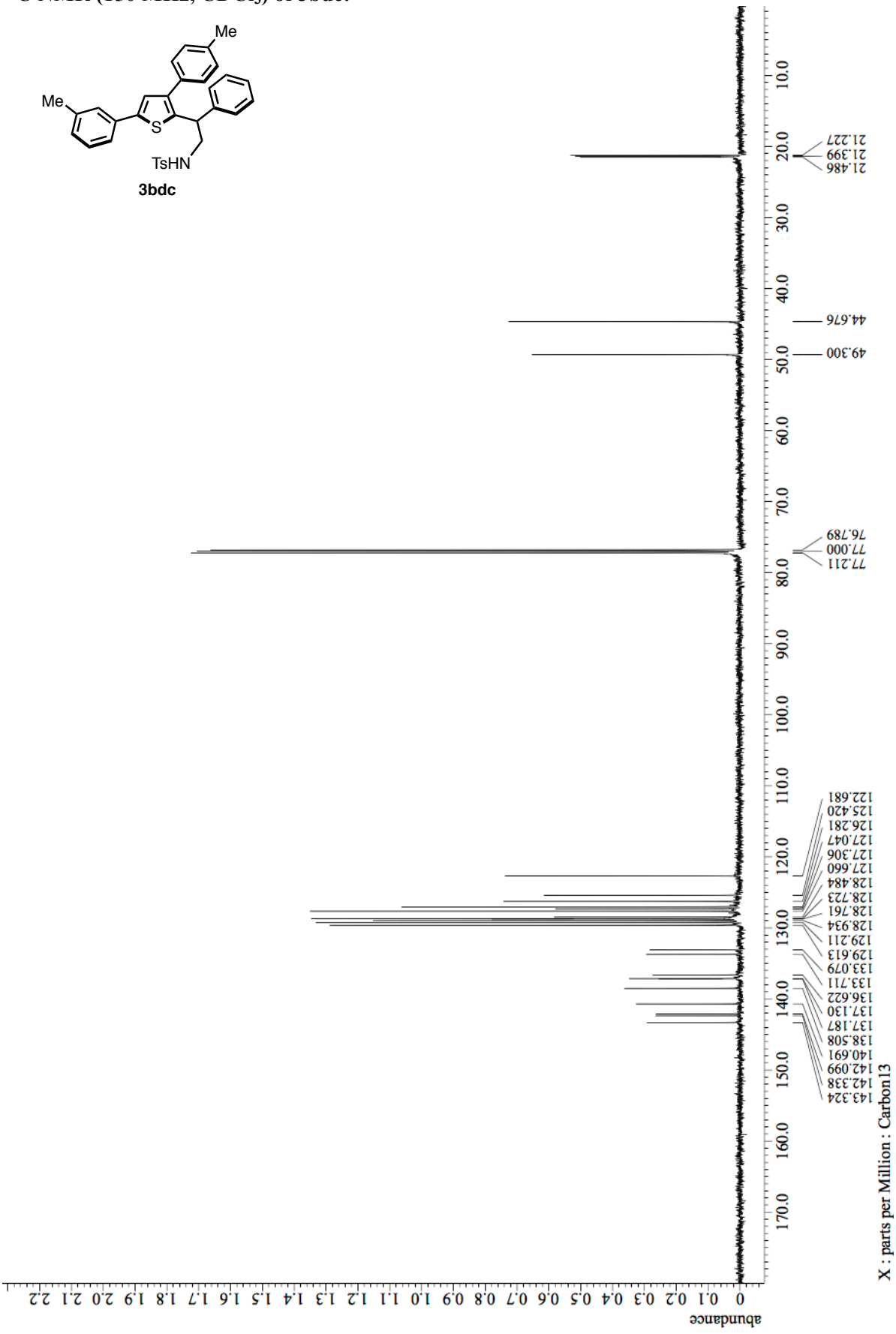


3acd'

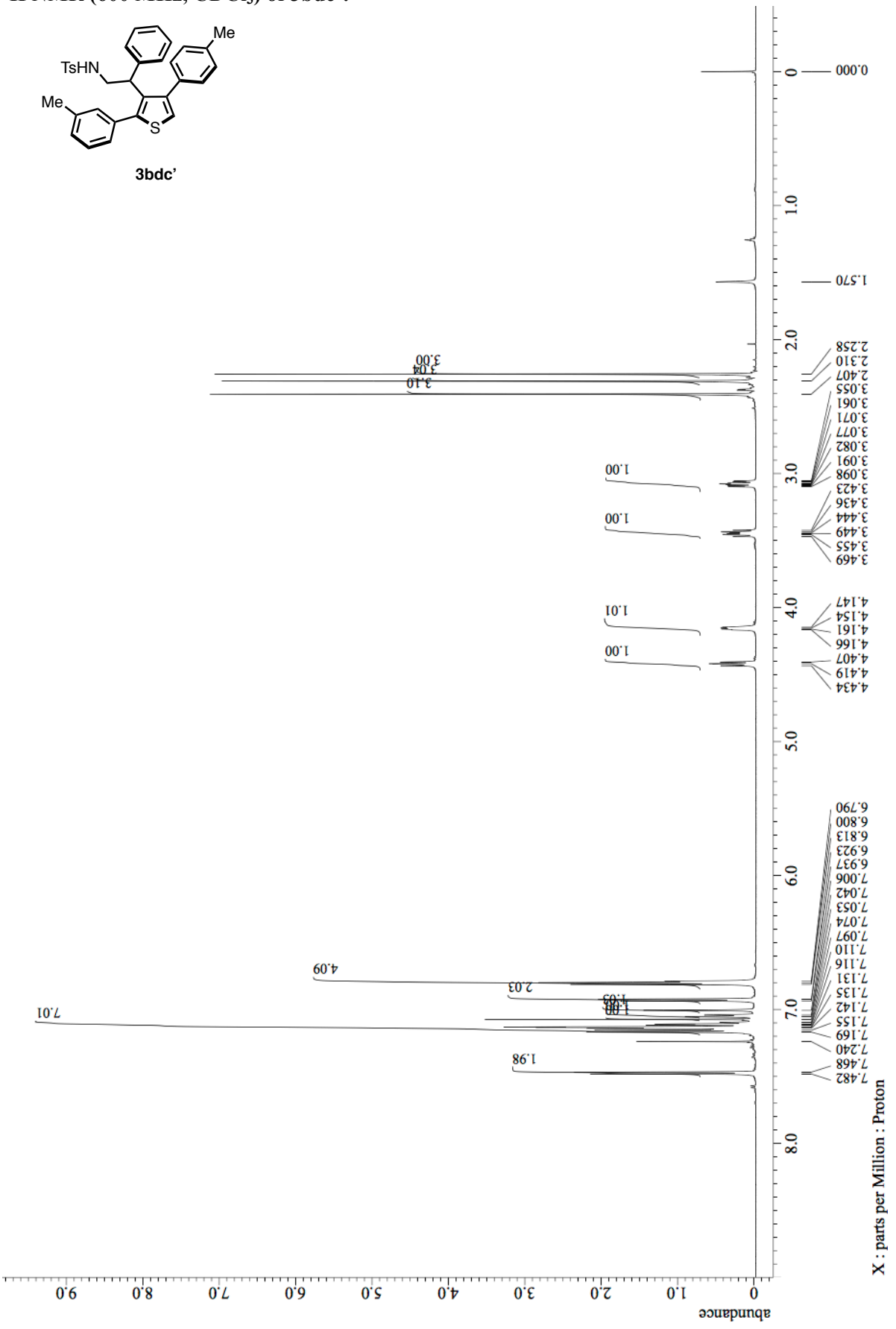
^{1}H NMR (600 MHz, $CDCl_3$) of 3bdc:



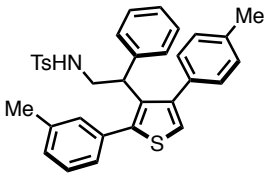
^{13}C NMR (150 MHz, $CDCl_3$) of 3bdc:



^{1}H NMR (600 MHz, $CDCl_3$) of 3bdc':

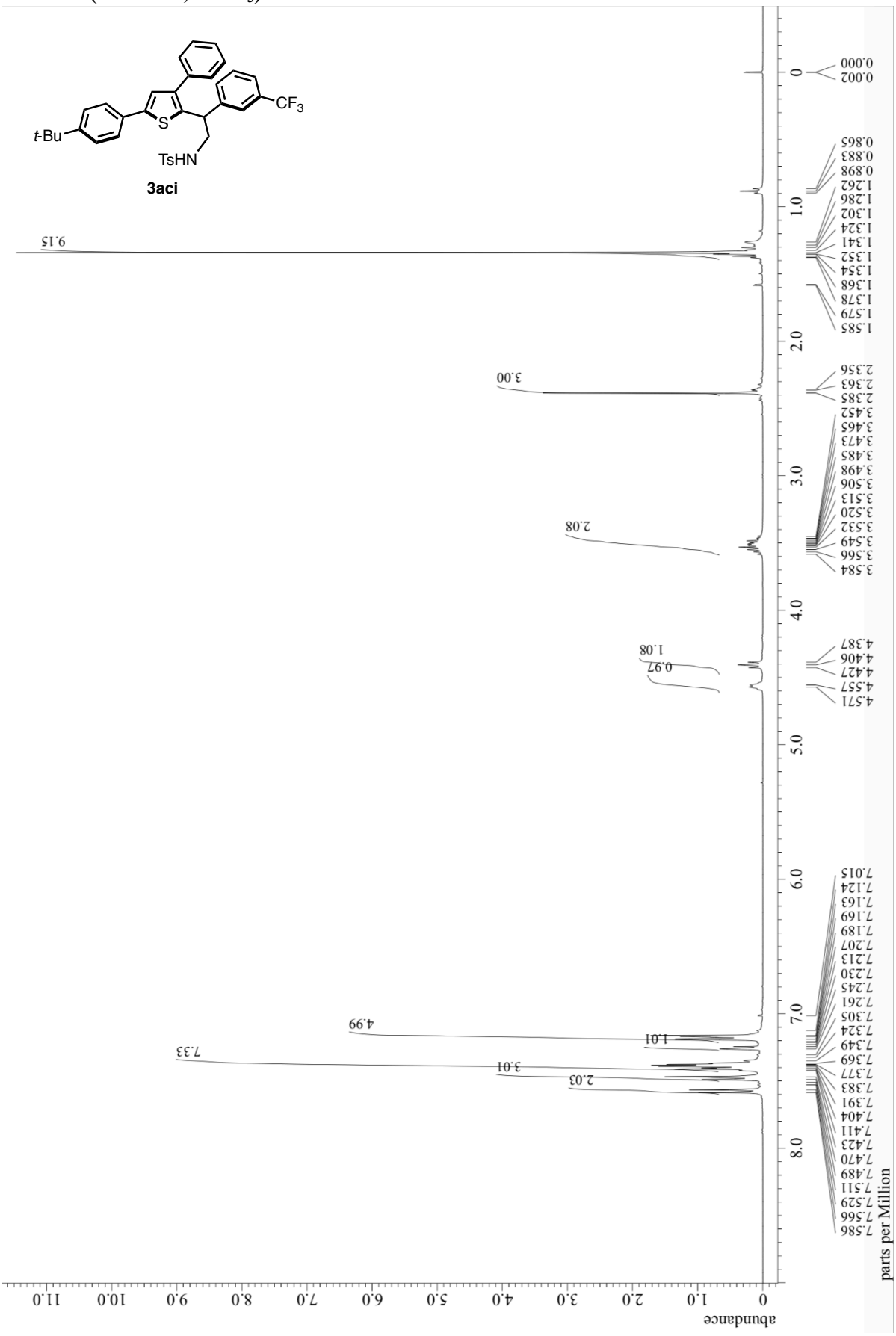


^{13}C NMR (150 MHz, $CDCl_3$) of 3bdc':

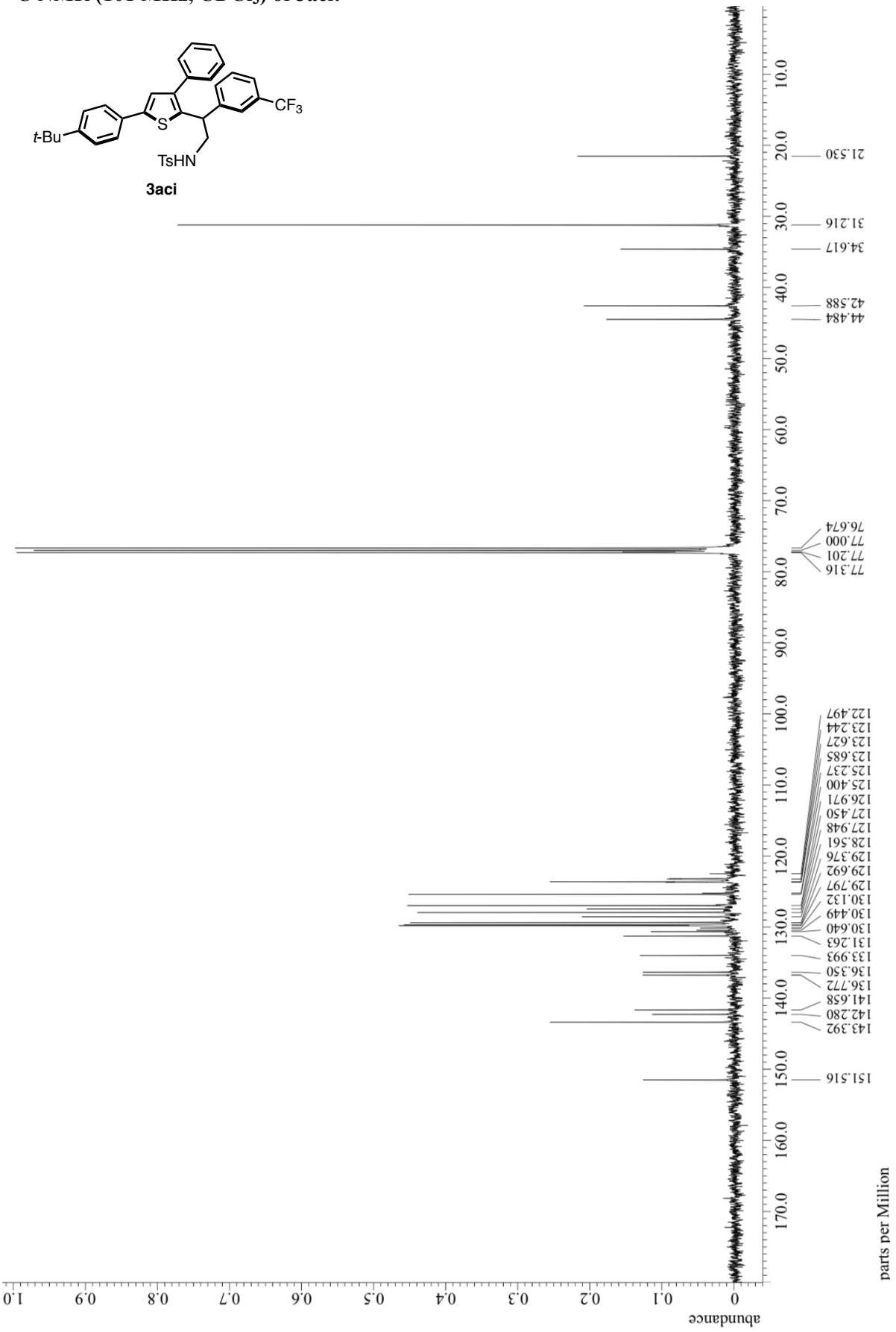


3bdc'

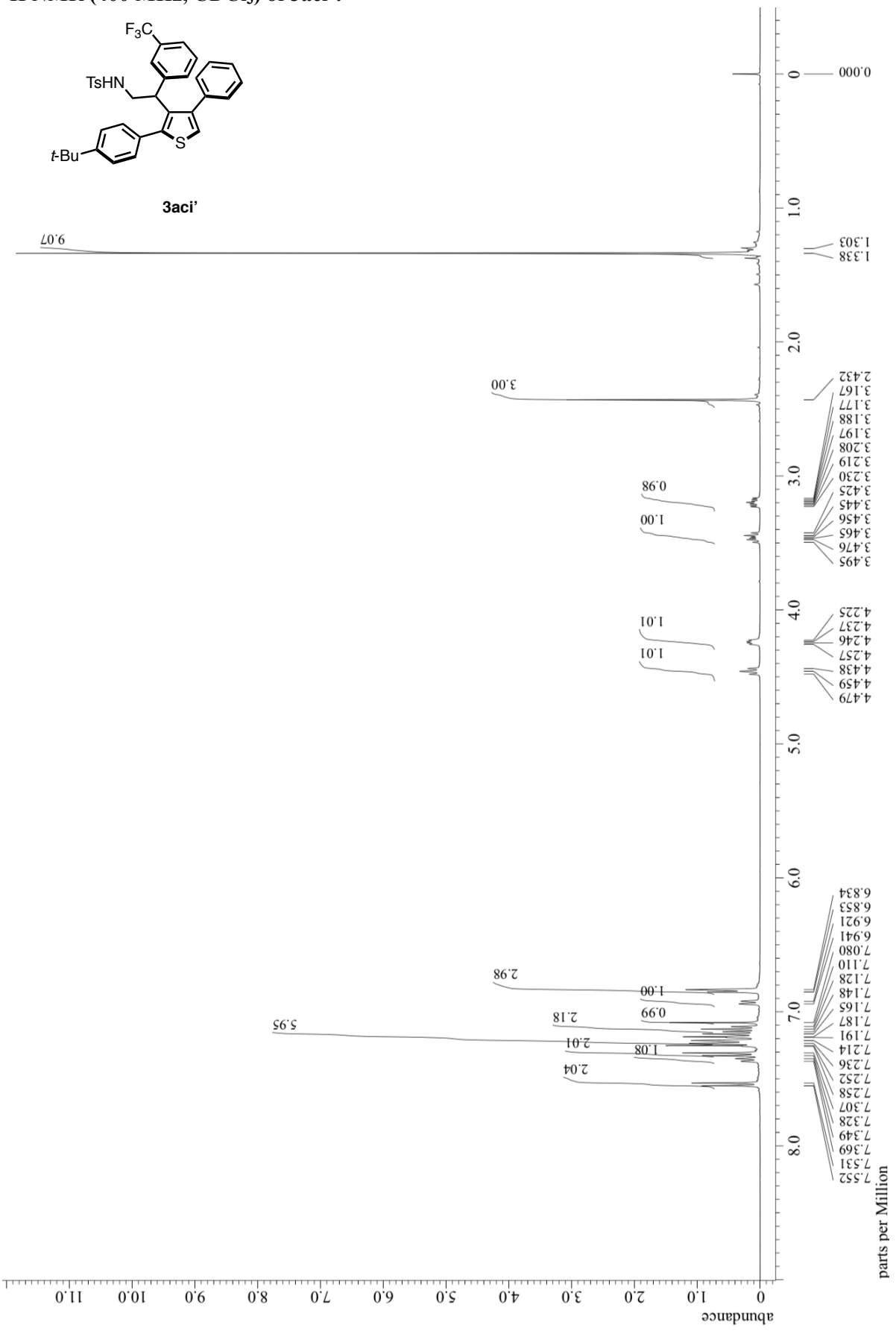
^{1}H NMR (400 MHz, $CDCl_3$) of 3aci:



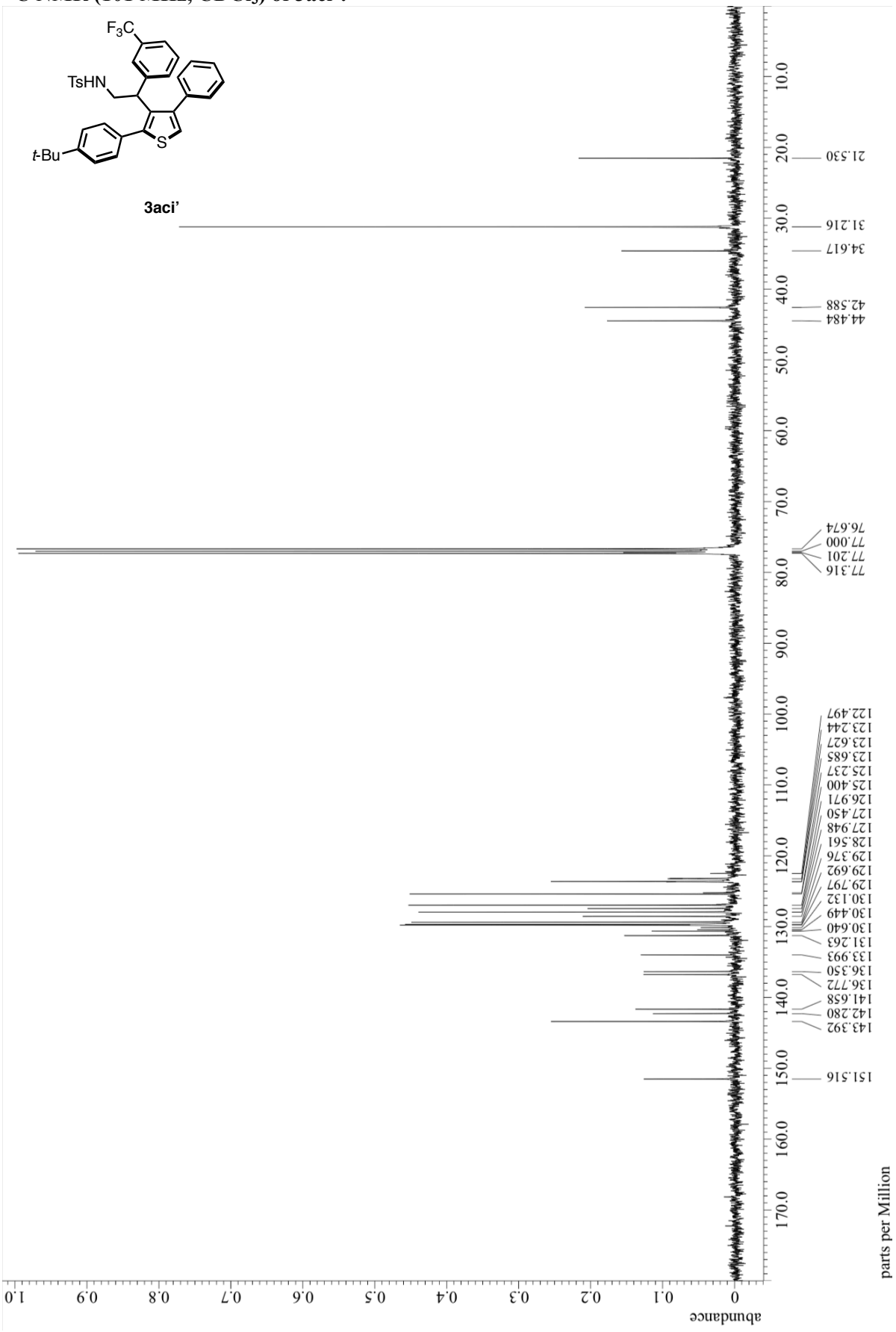
^{13}C NMR (101 MHz, $CDCl_3$) of 3aci:



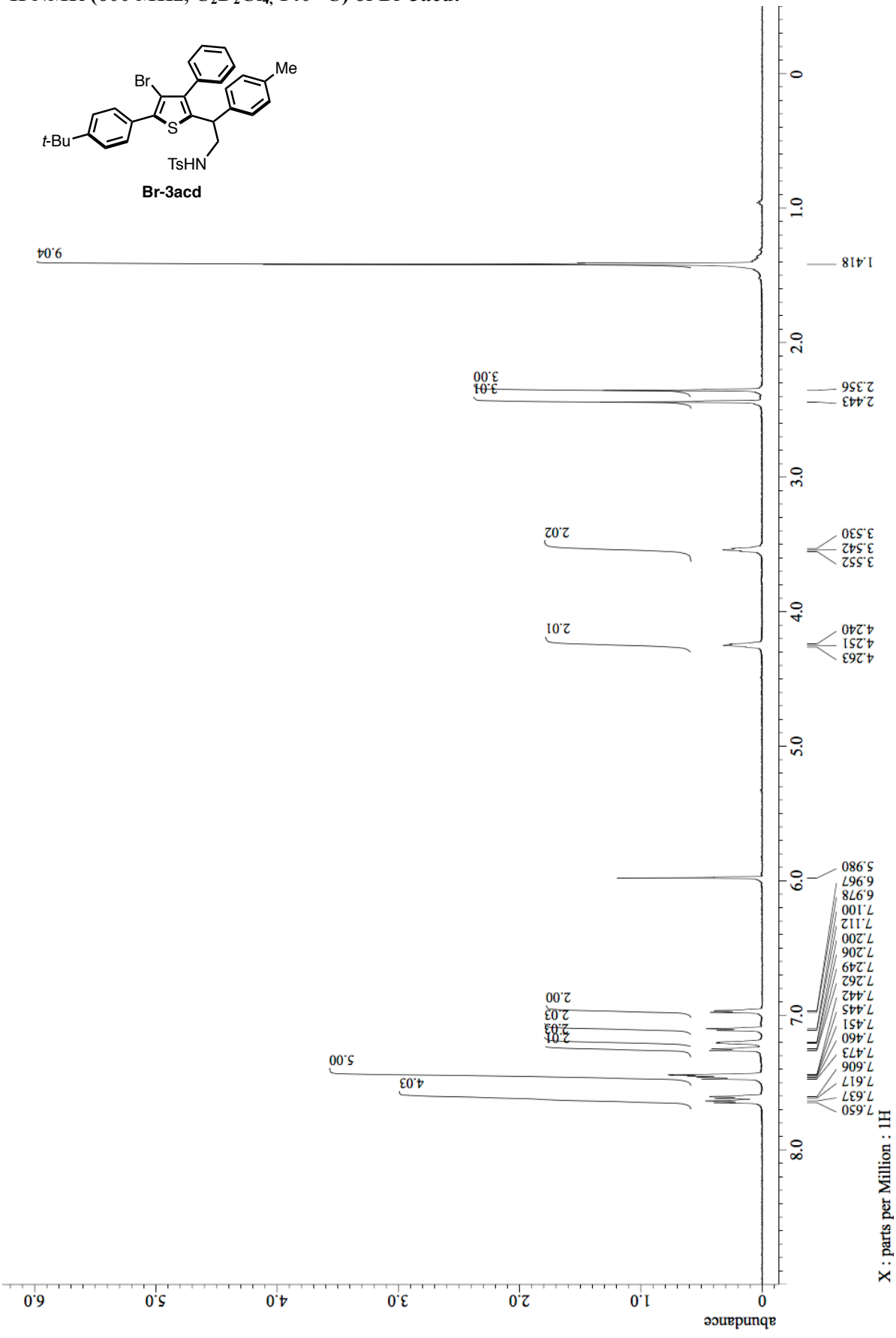
^{1}H NMR (400 MHz, $CDCl_3$) of 3aci':



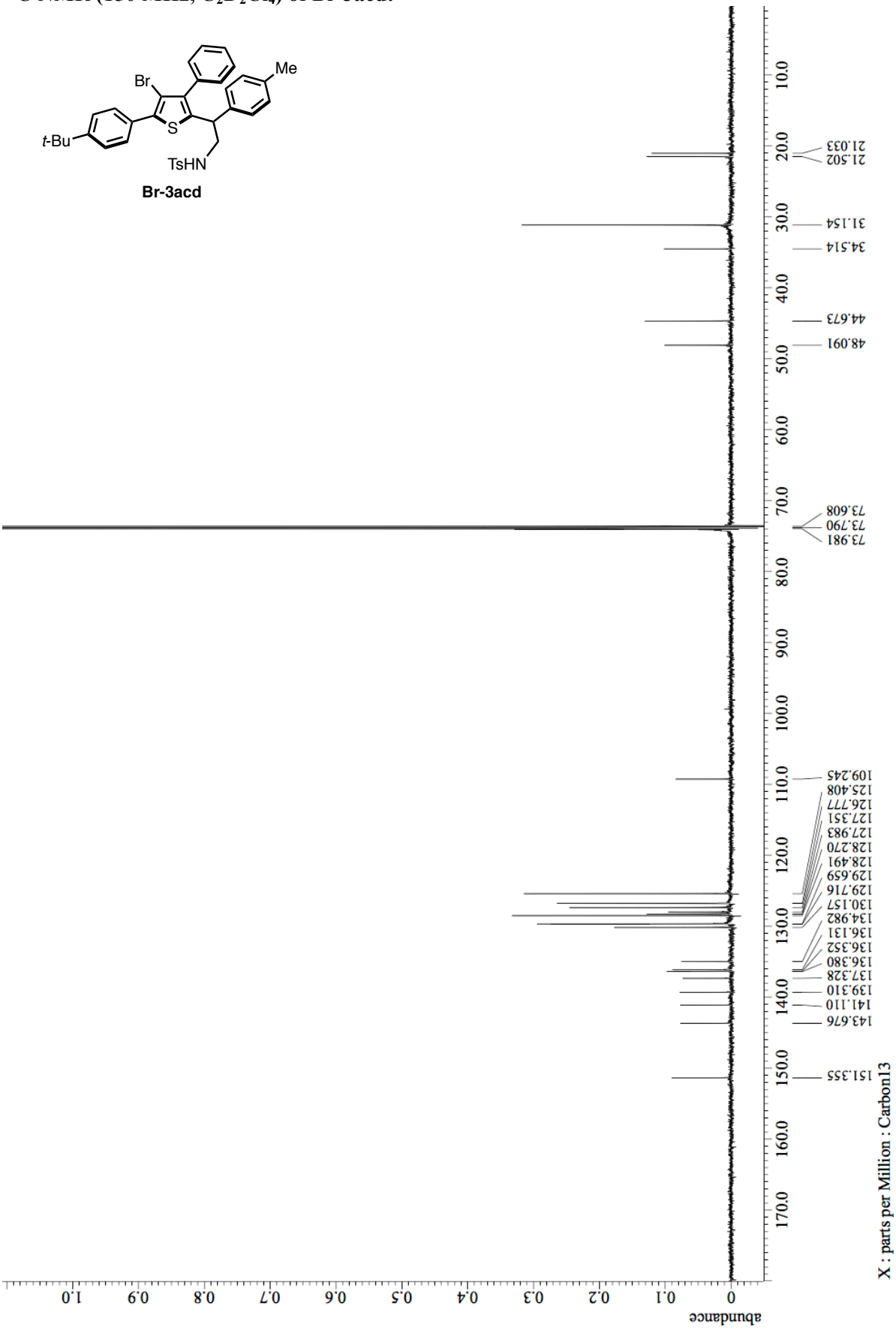
^{13}C NMR (101 MHz, $CDCl_3$) of 3aci':



^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of Br-3acd:

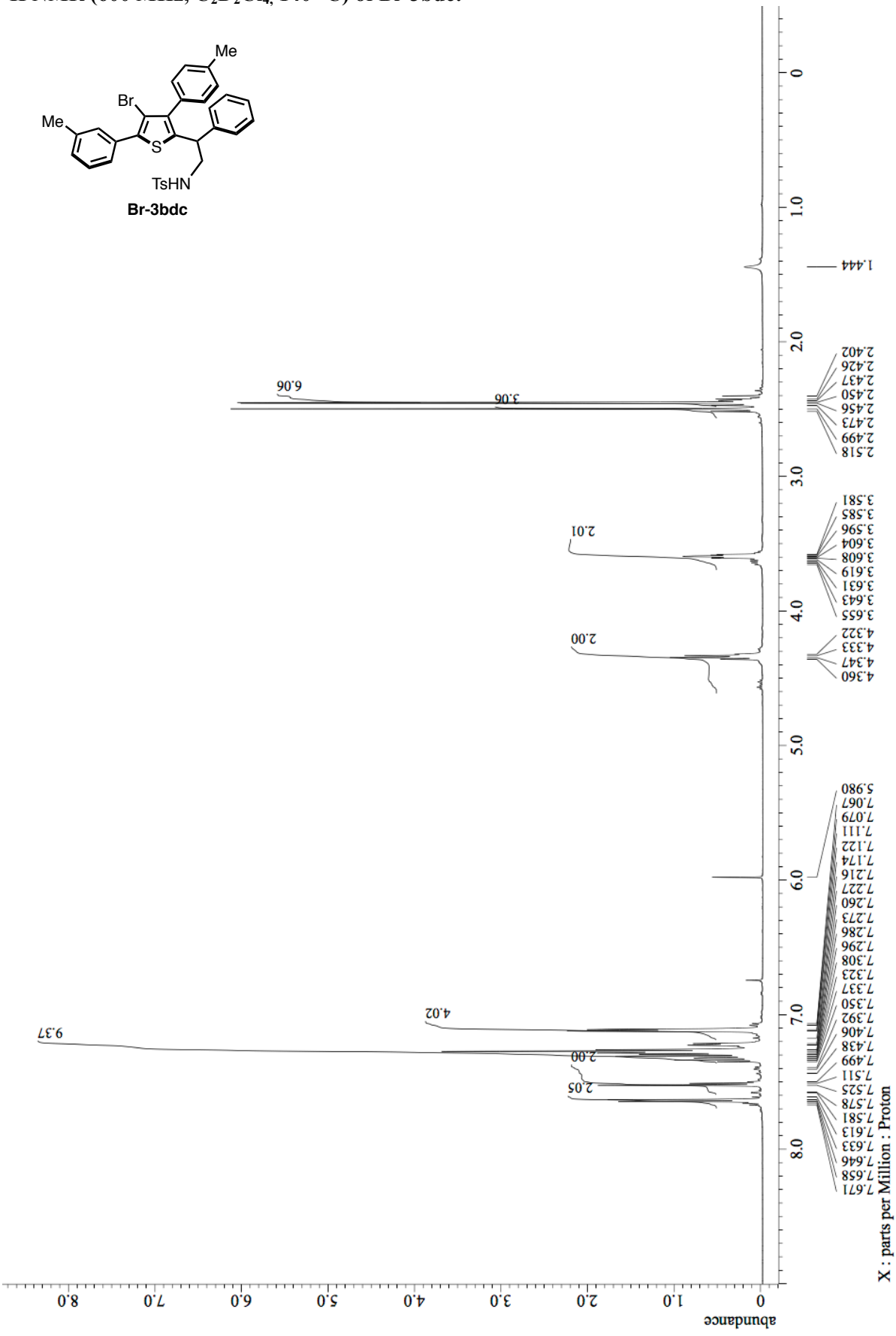


^{13}C NMR (150 MHz, $C_2D_2Cl_4$) of Br-3acd:

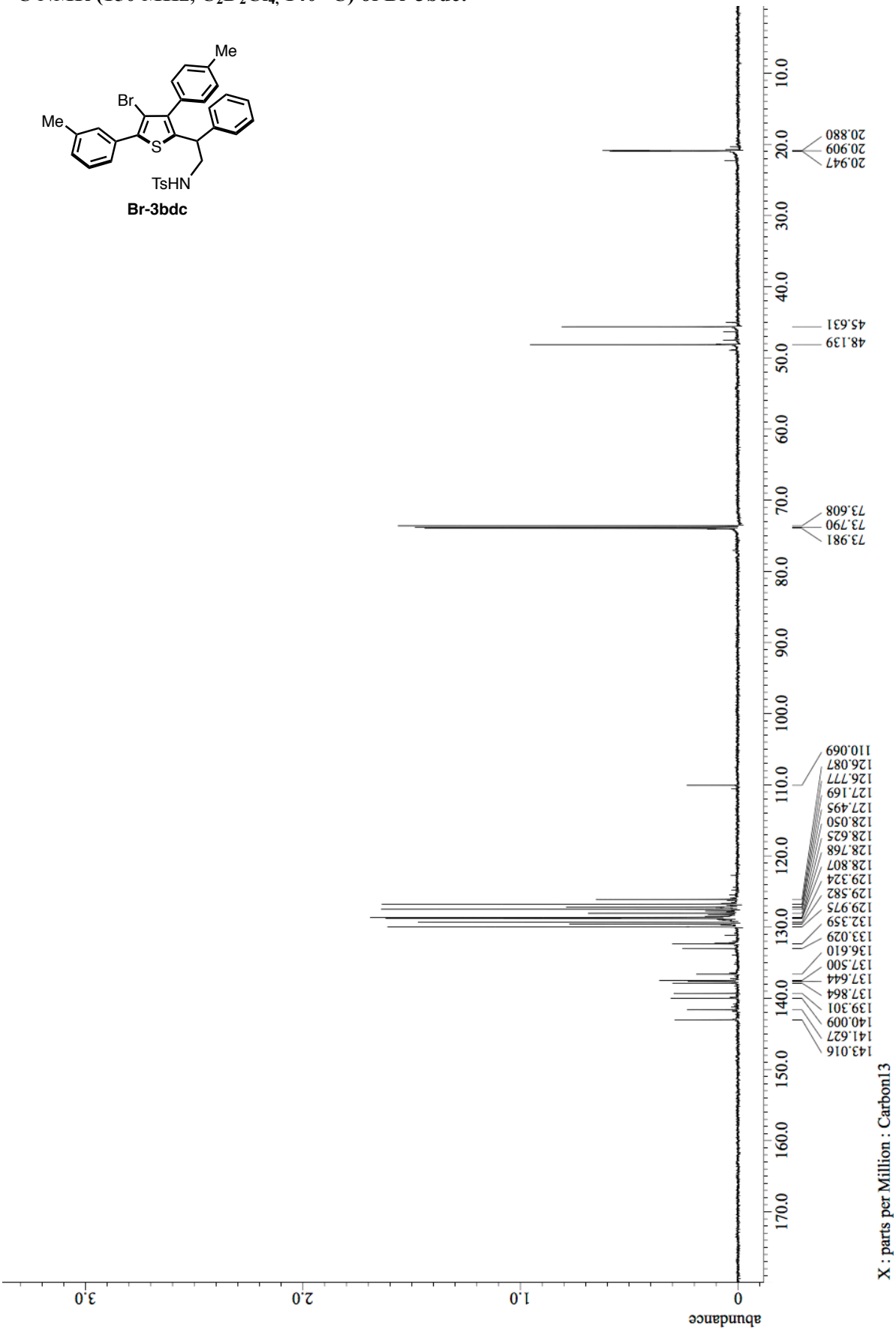


Br-3acd

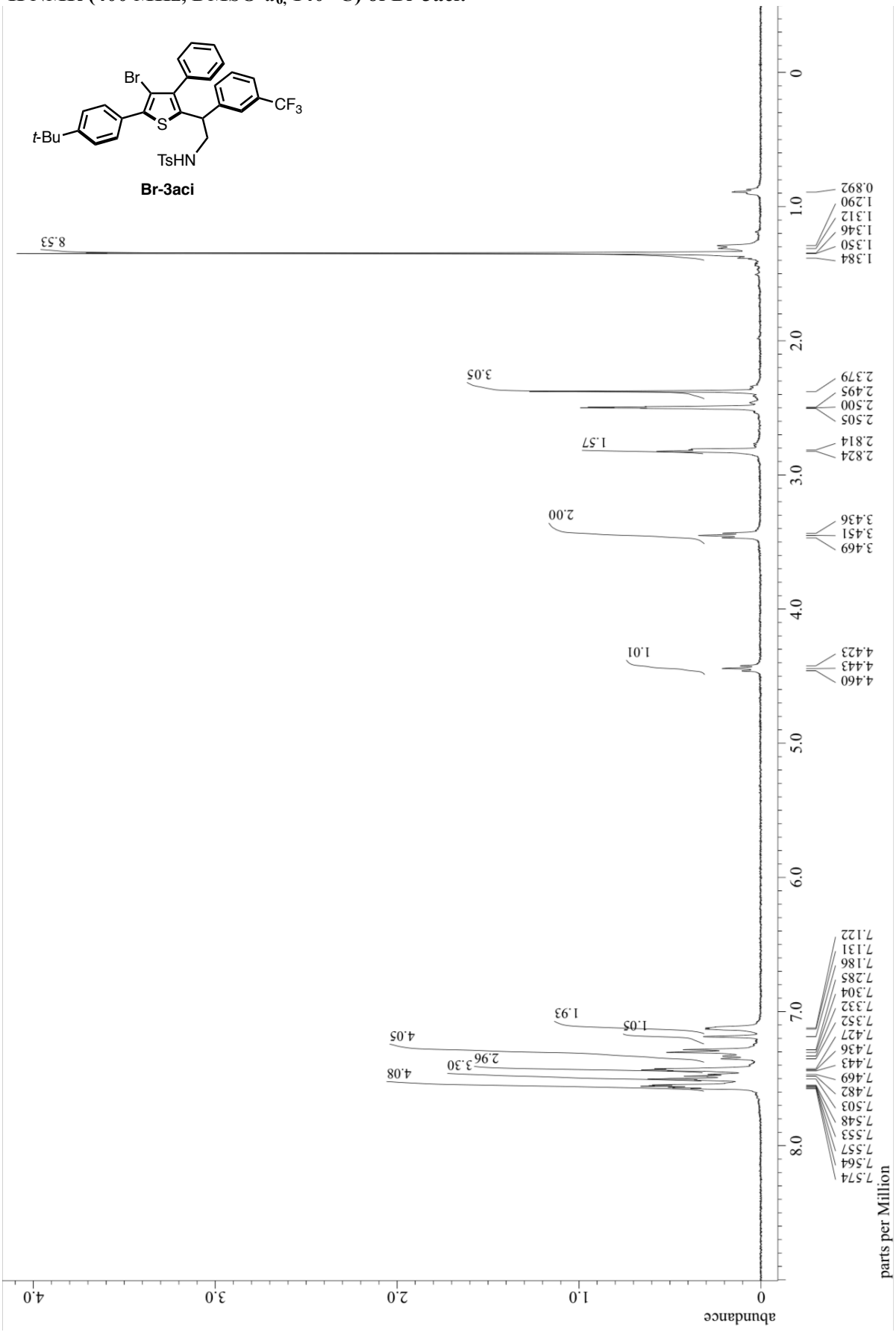
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of Br-3bdc:



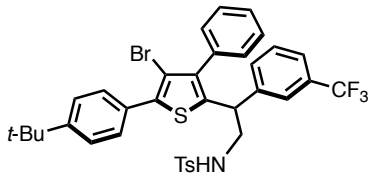
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of Br-3bdc:



^{1}H NMR (400 MHz, DMSO-d_6, 140 °C) of Br-3aci:

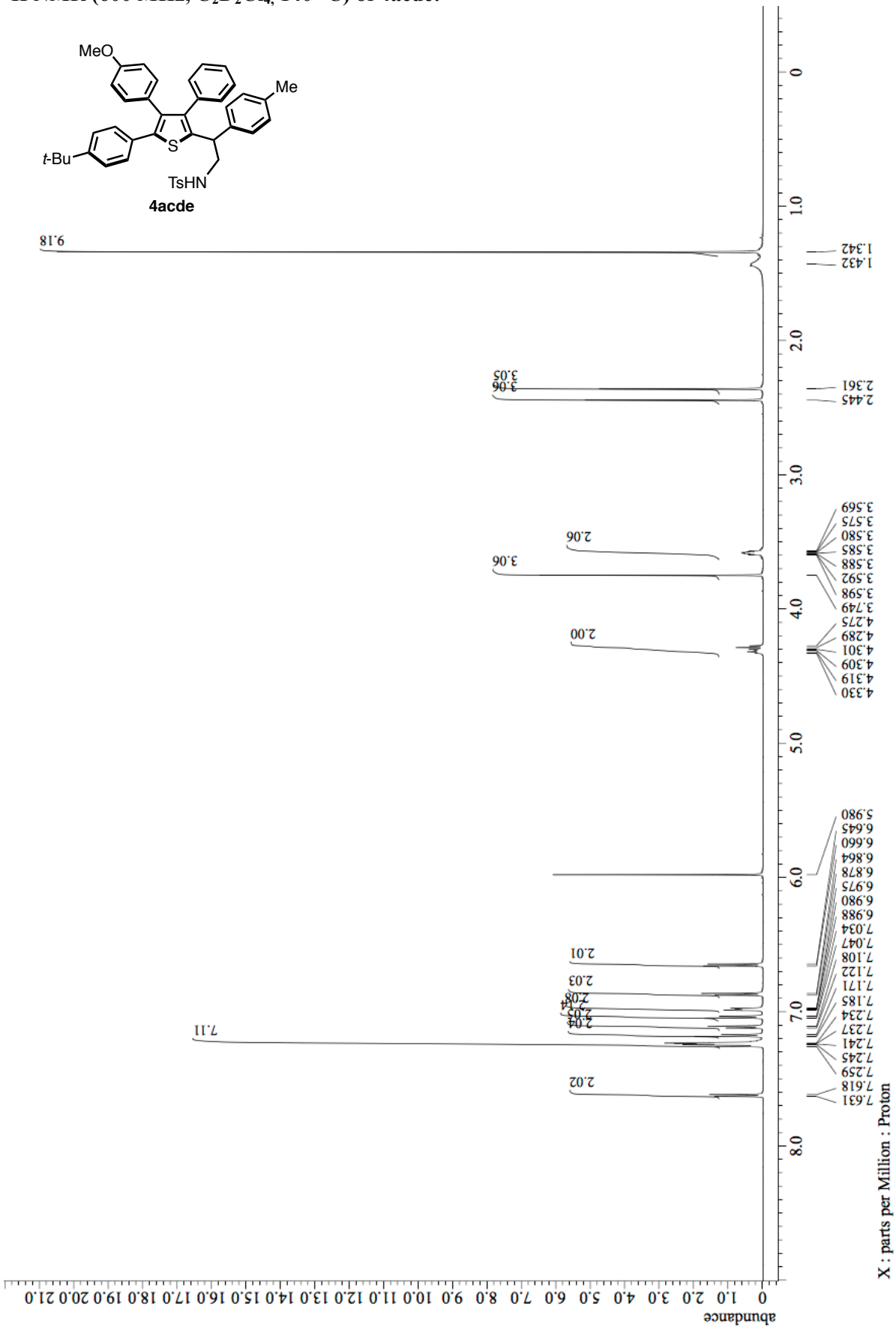


^{13}C NMR (101 MHz, DMSO-d_6, 140 °C) of Br-3aci:

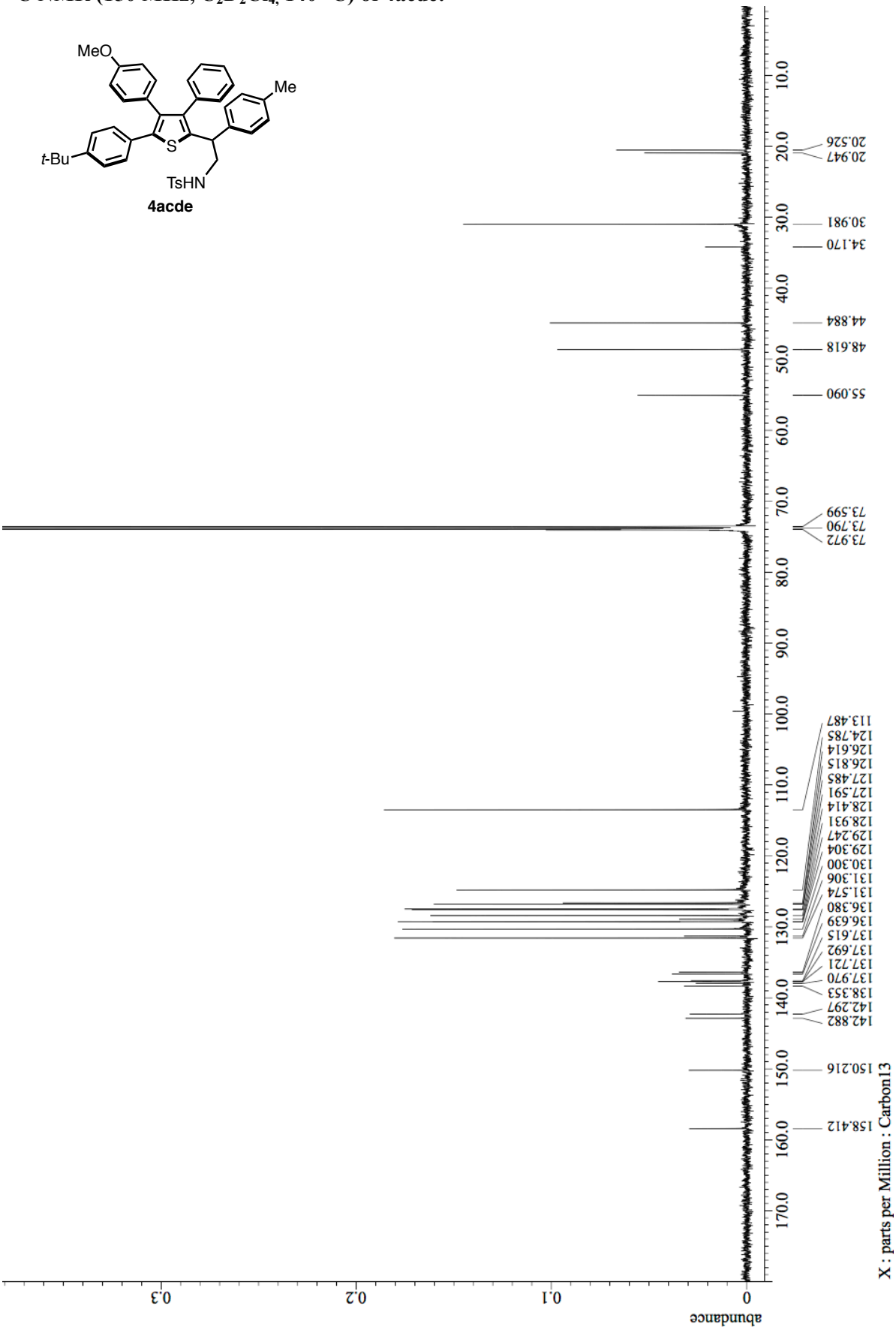


Br-3aci

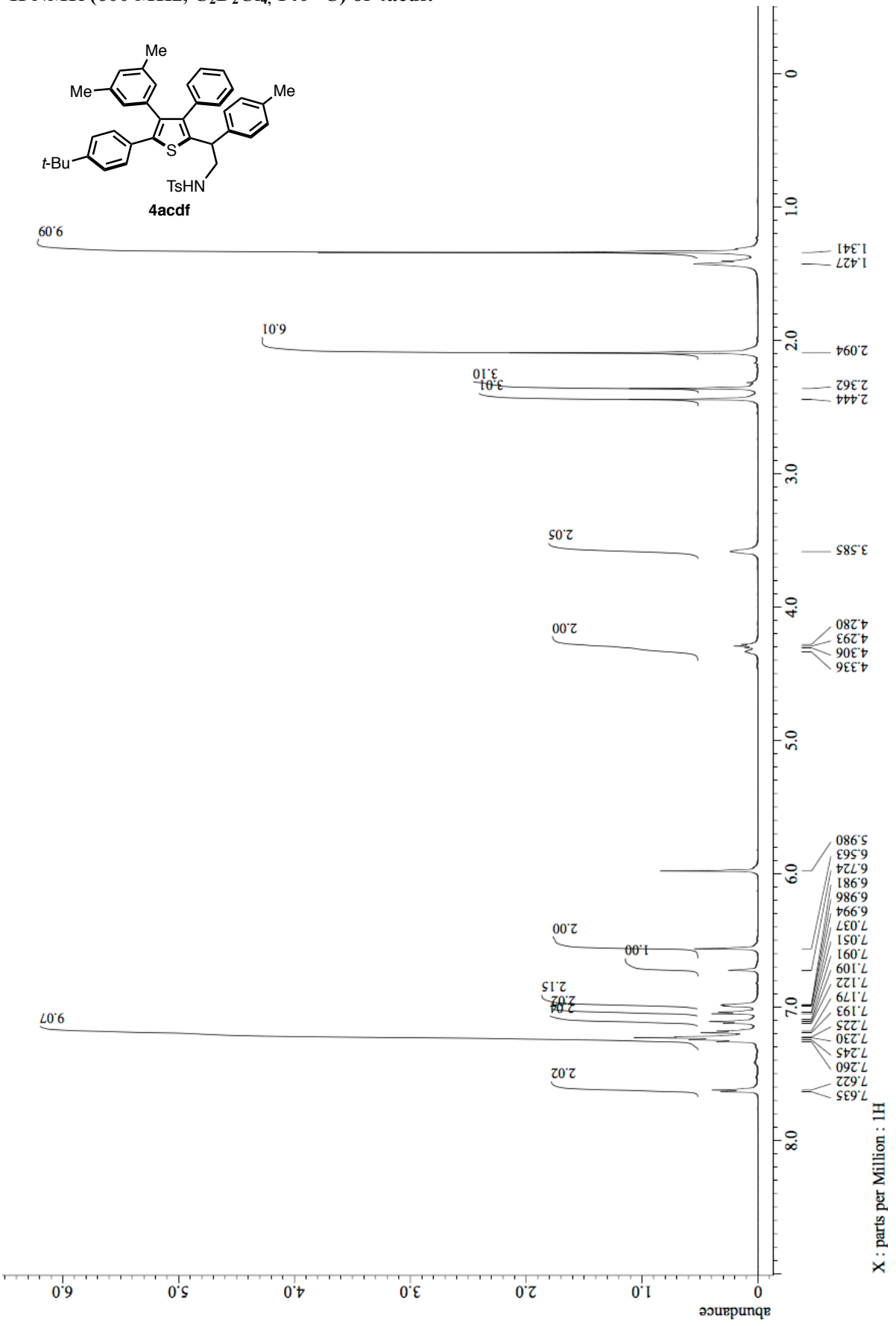
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 4acde:



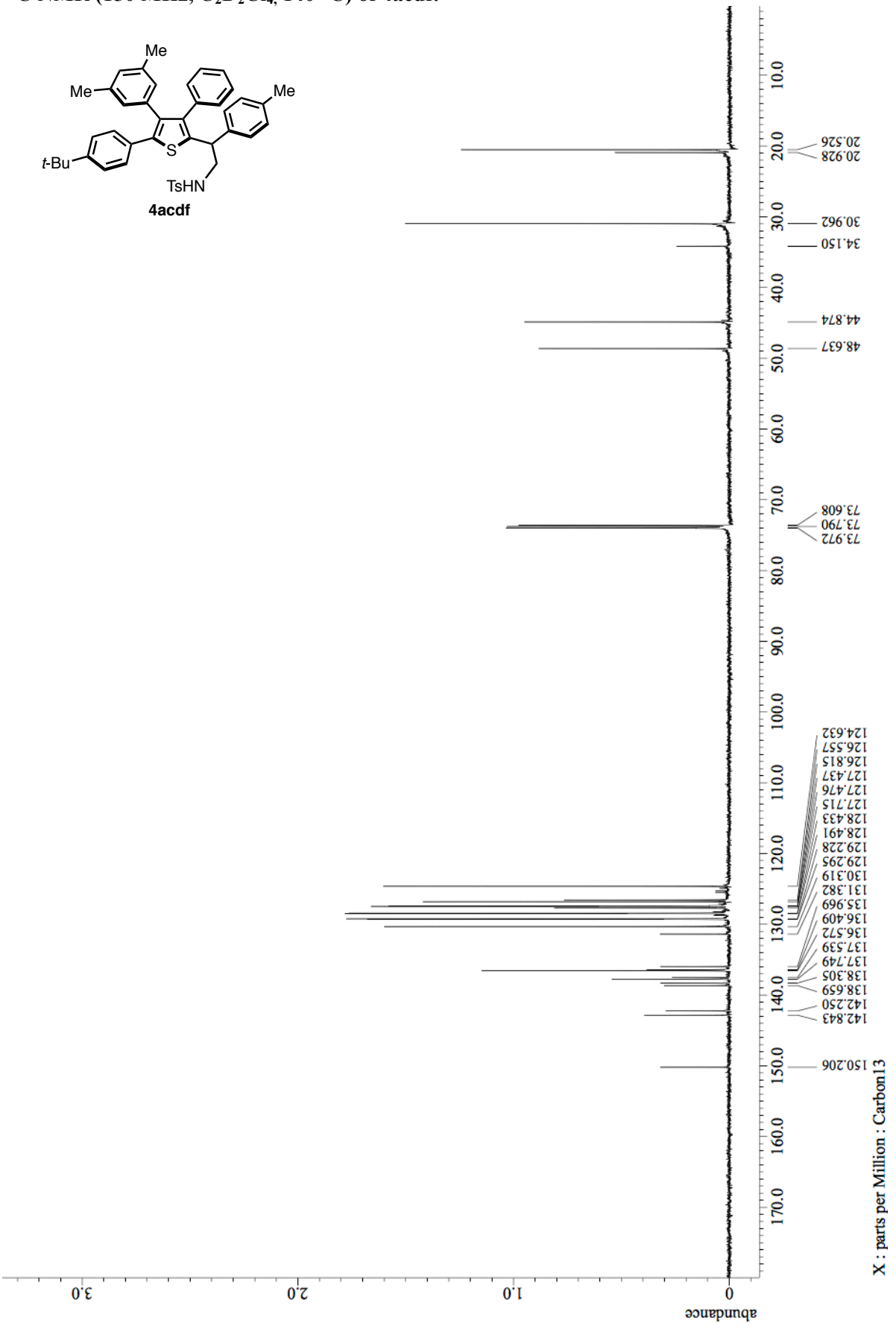
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 4acde:



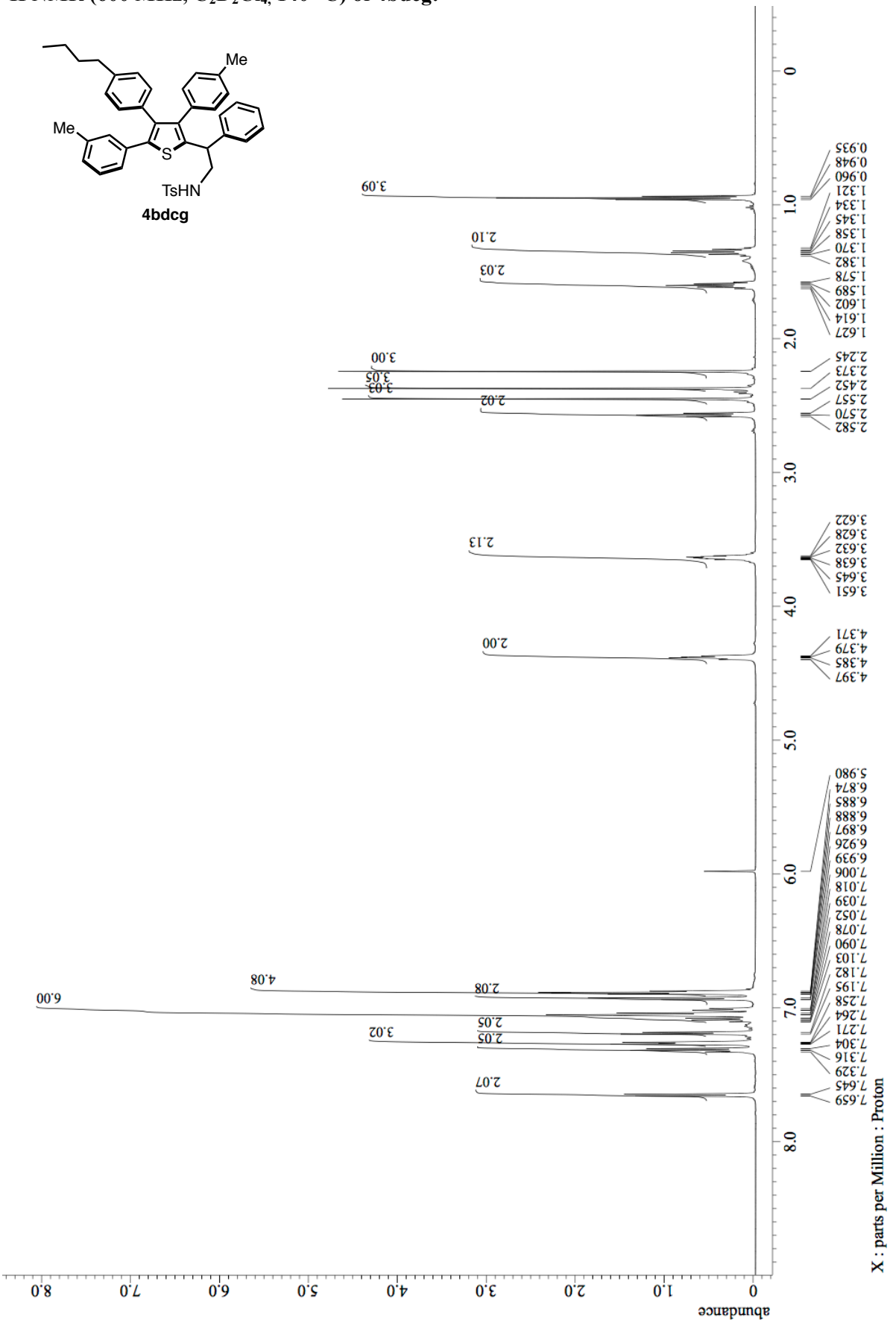
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 4acdf:



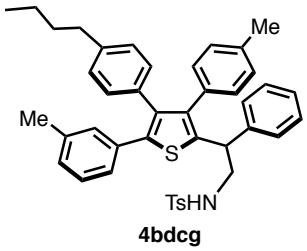
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 4acdf:



^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 4bdcg:

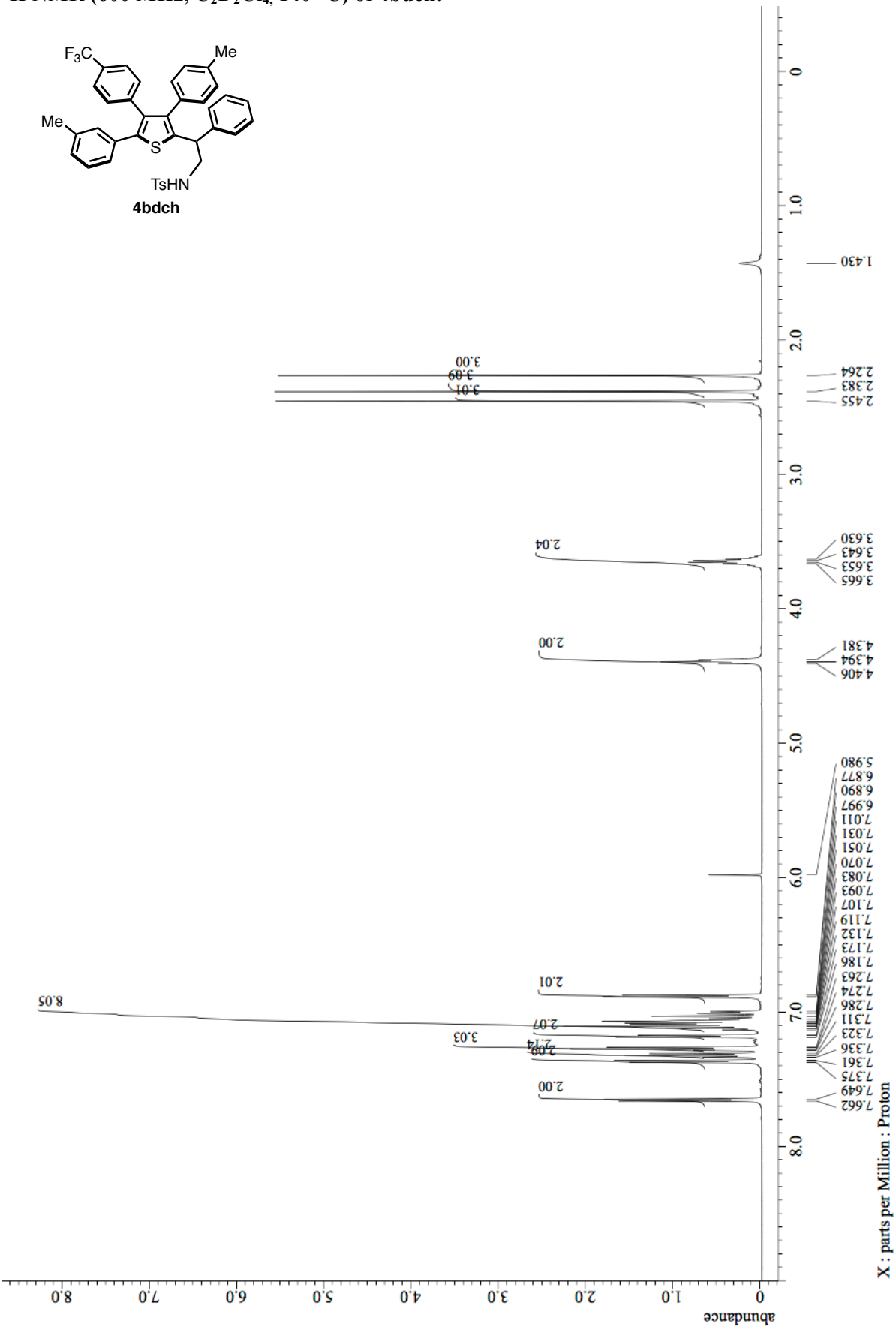


^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 4bdcg:

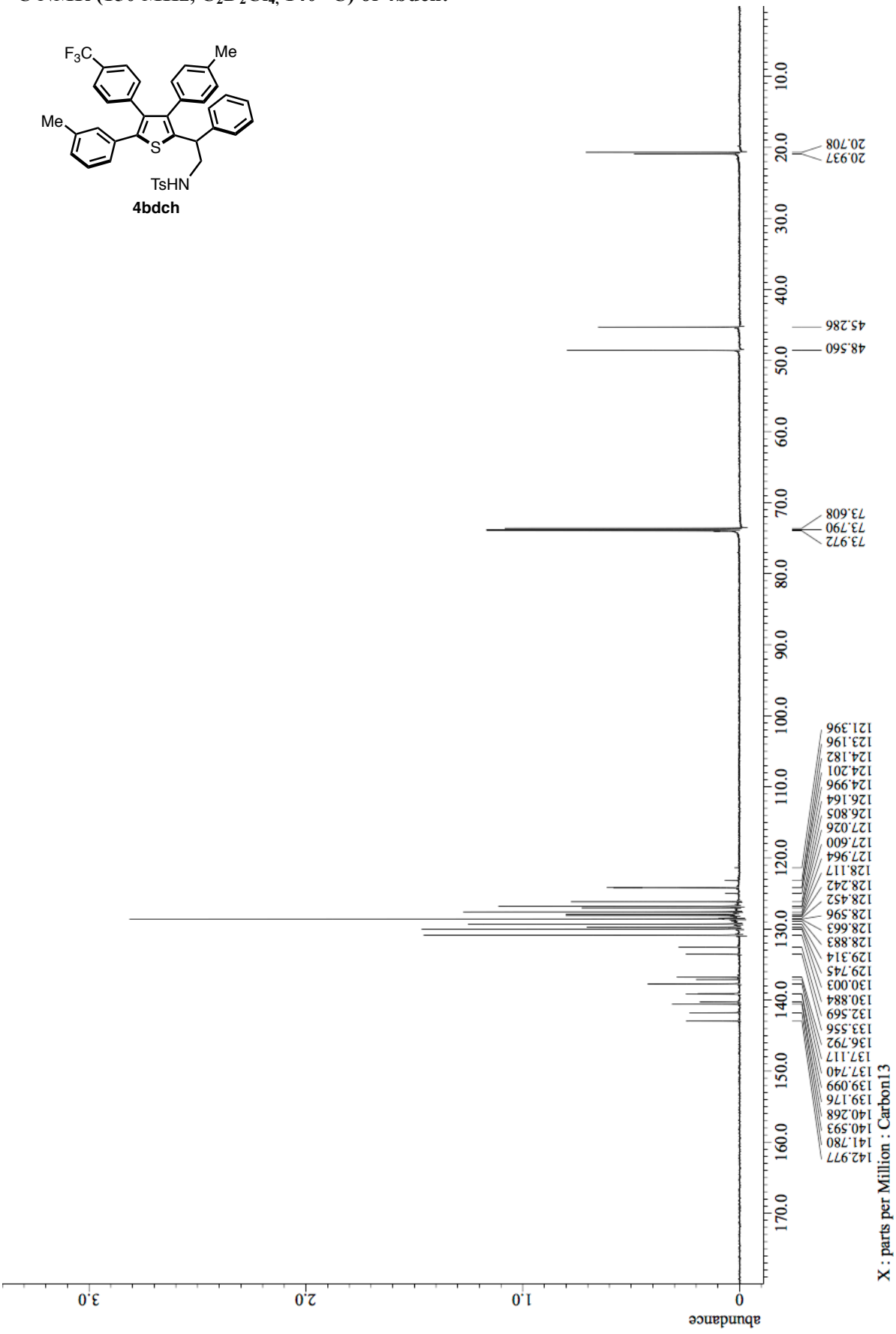


4bdcg

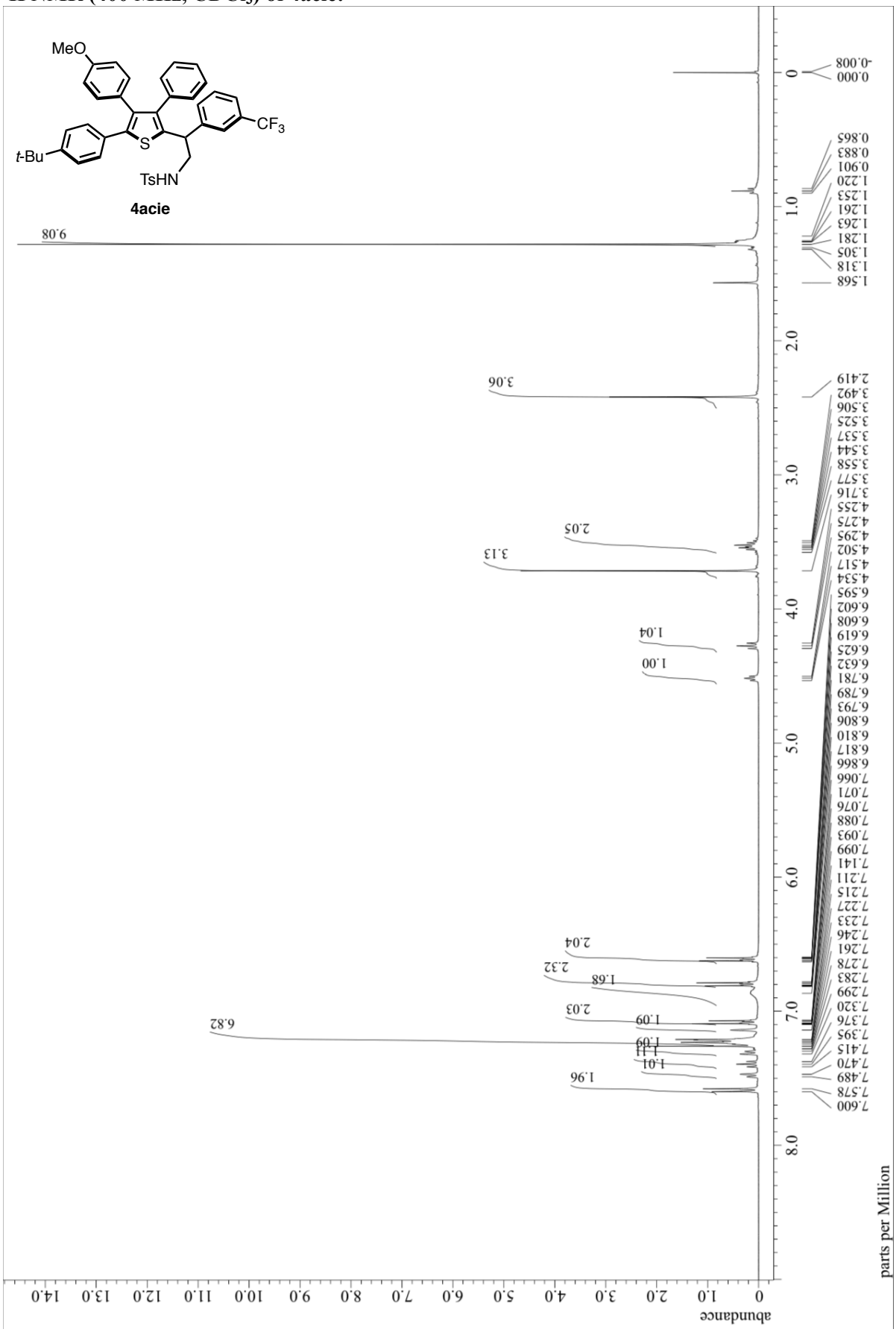
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 4bdch:



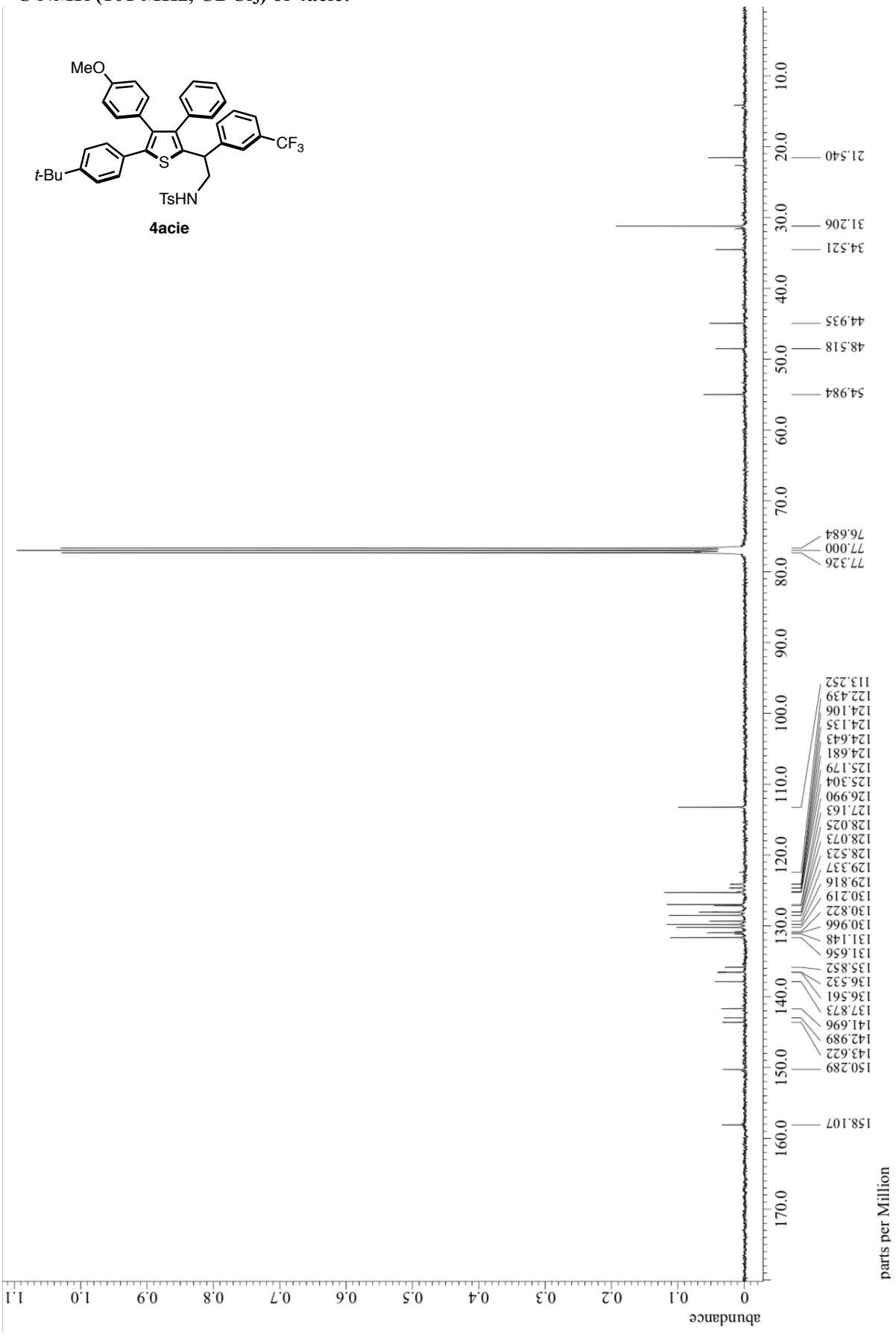
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 4bdch:



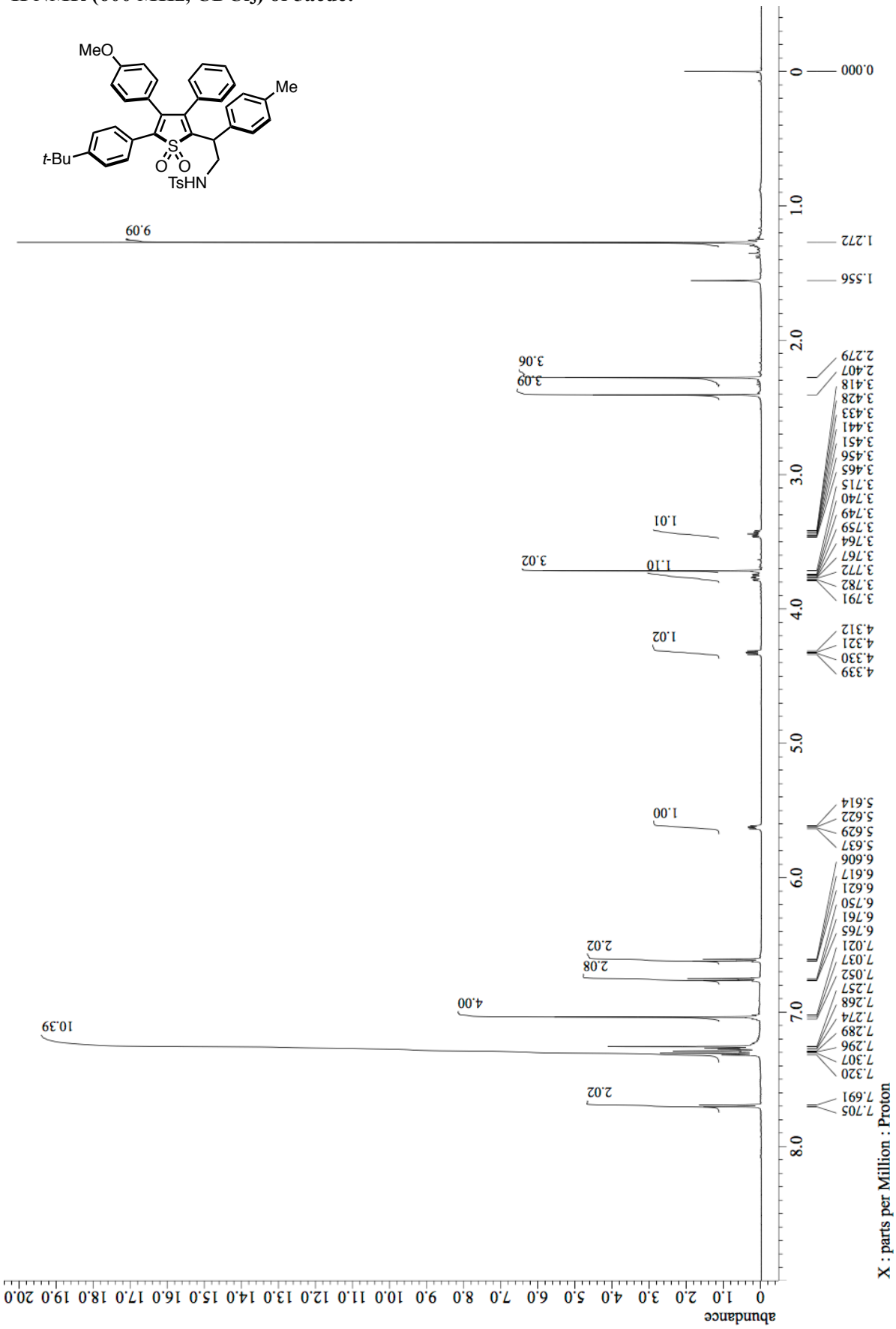
^{1}H NMR (400 MHz, $CDCl_3$) of 4acie:



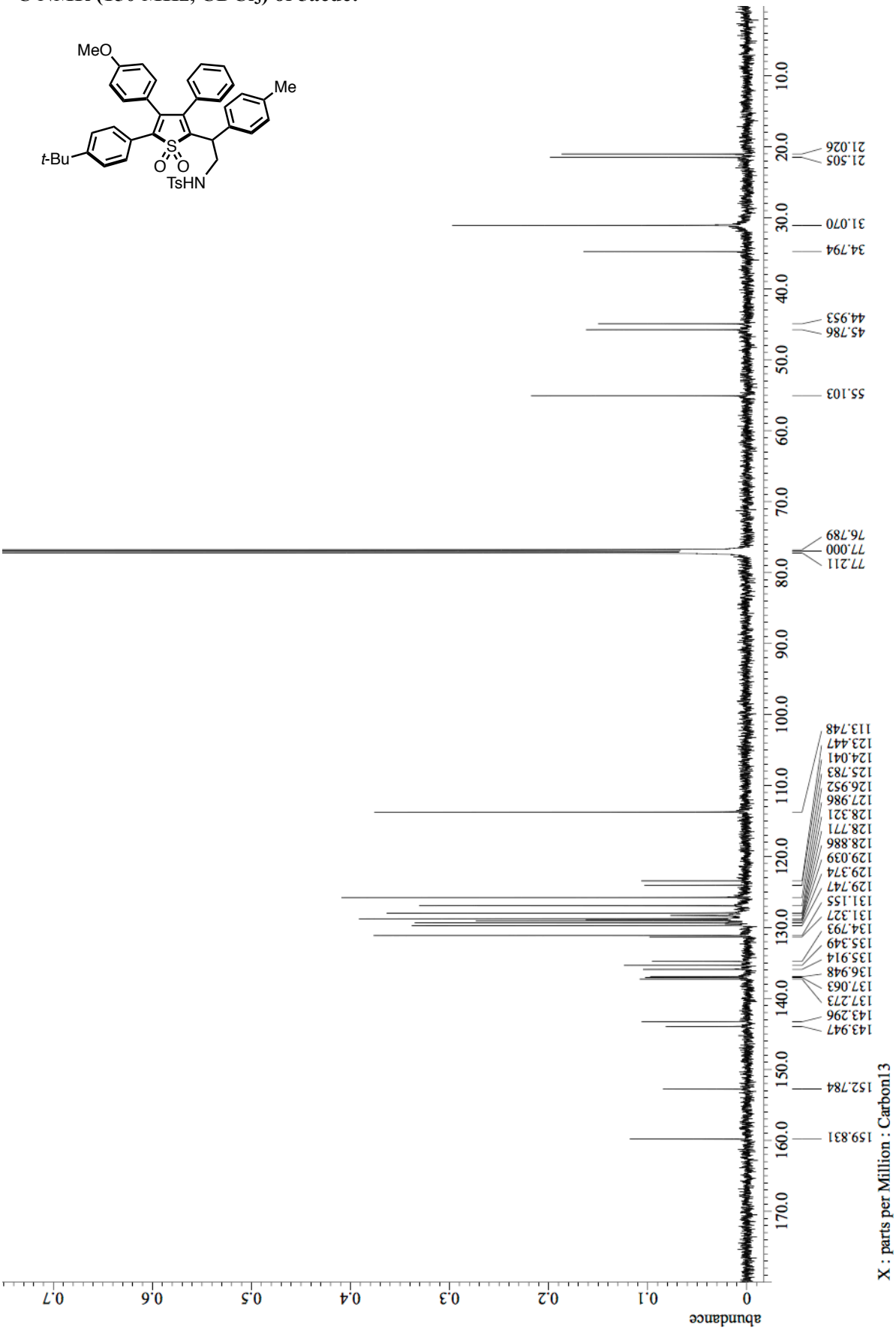
^{13}C NMR (101 MHz, $CDCl_3$) of 4acie:



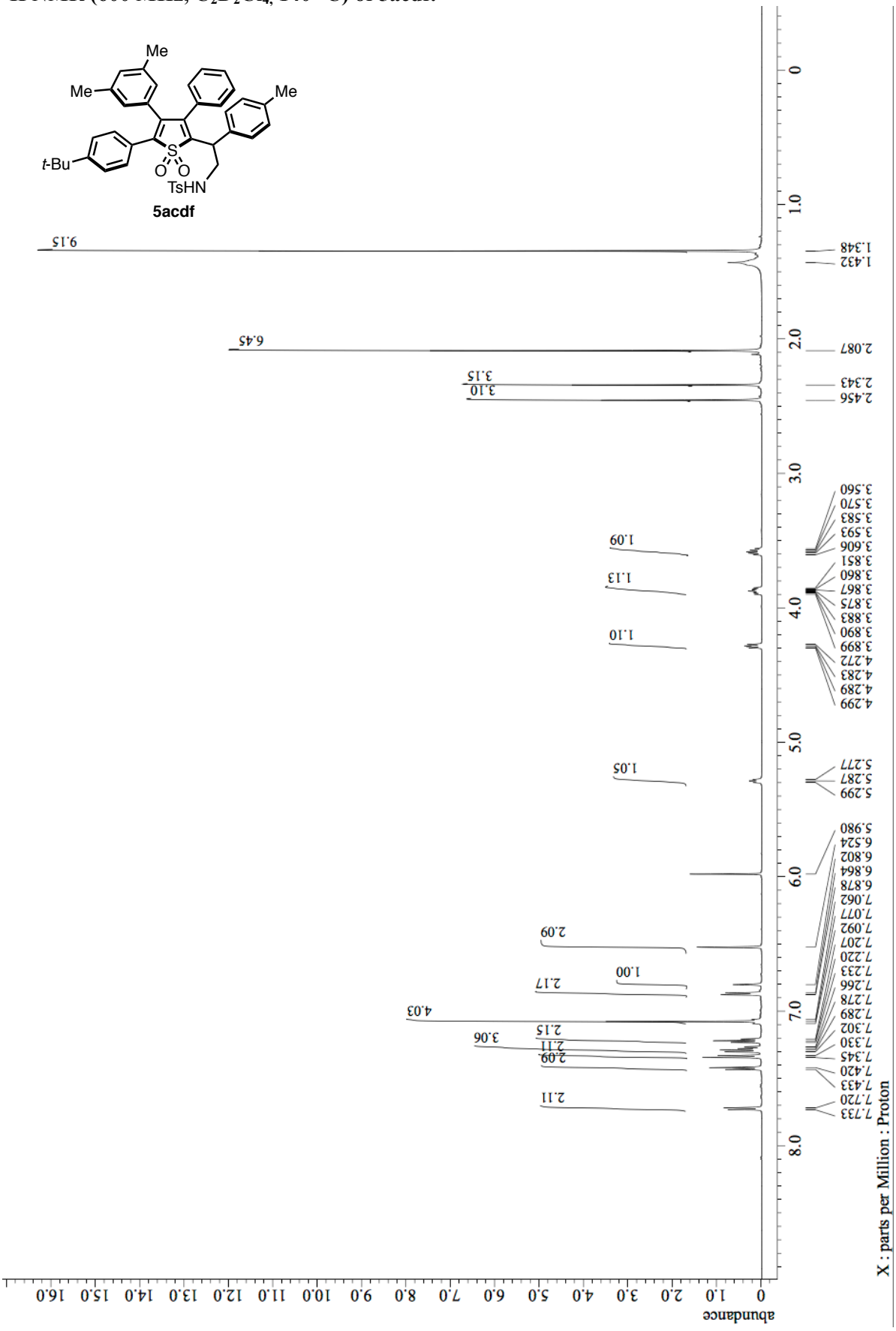
^{1}H NMR (600 MHz, $CDCl_3$) of 5acde:



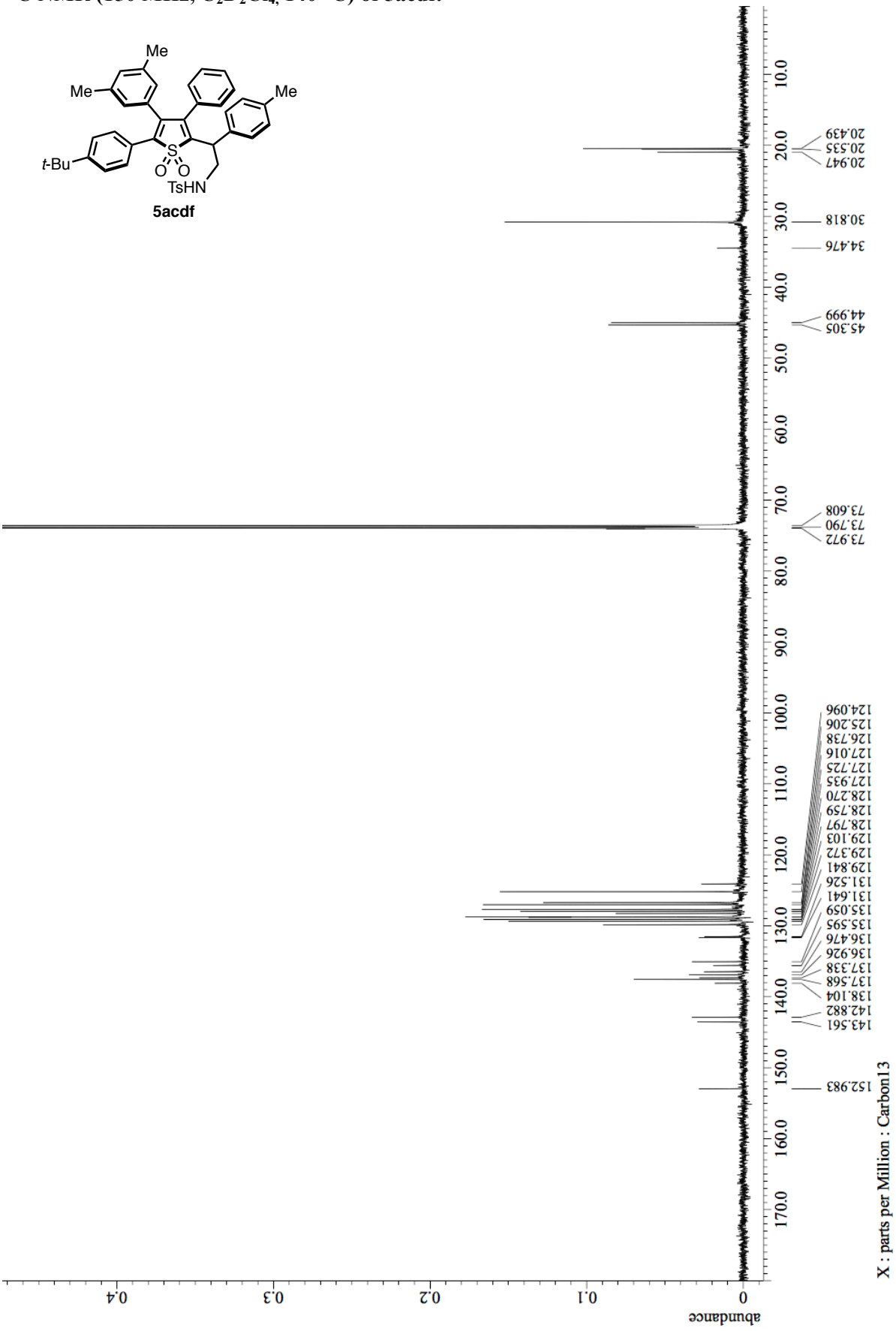
^{13}C NMR (150 MHz, $CDCl_3$) of 5acde:



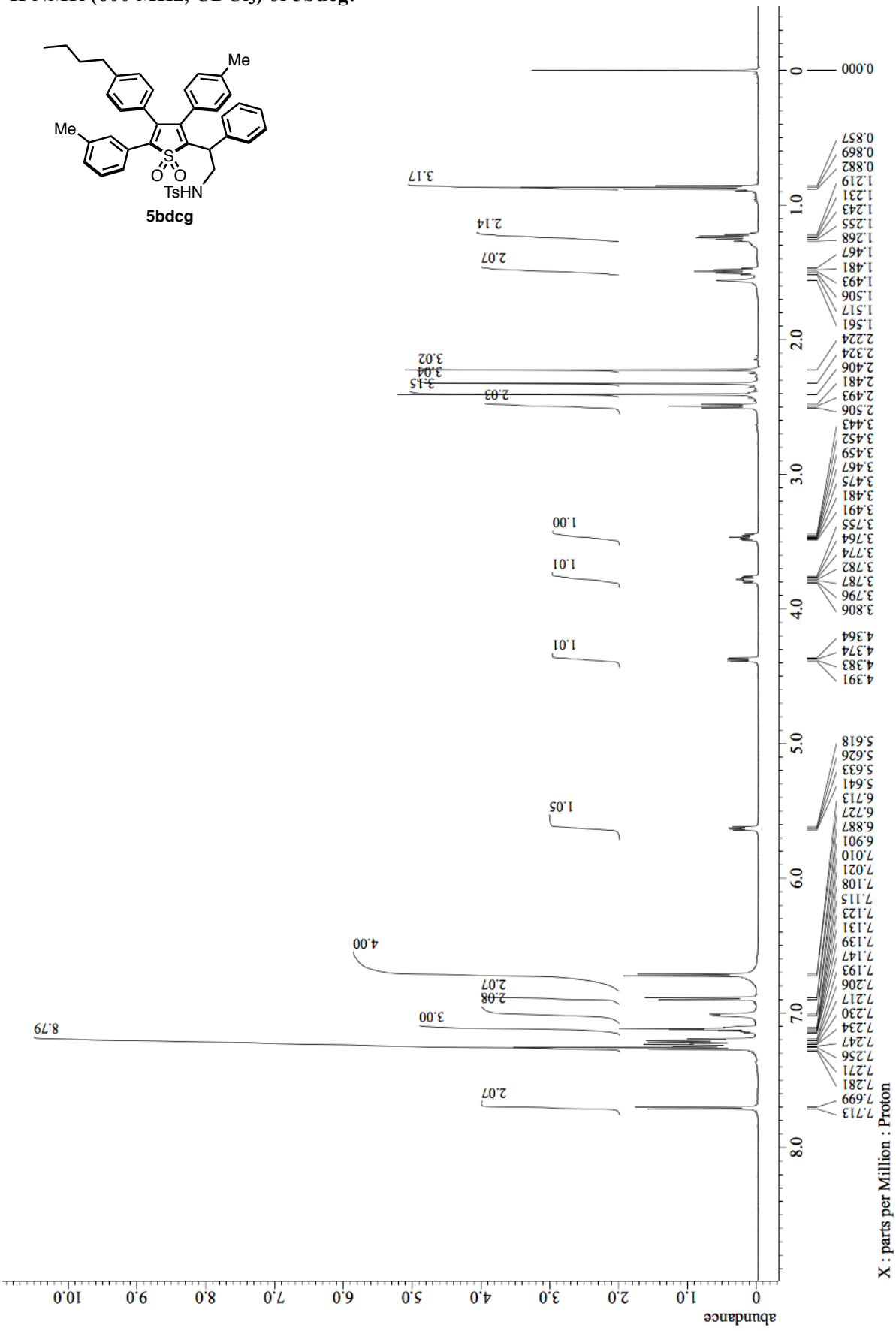
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 5acdf:



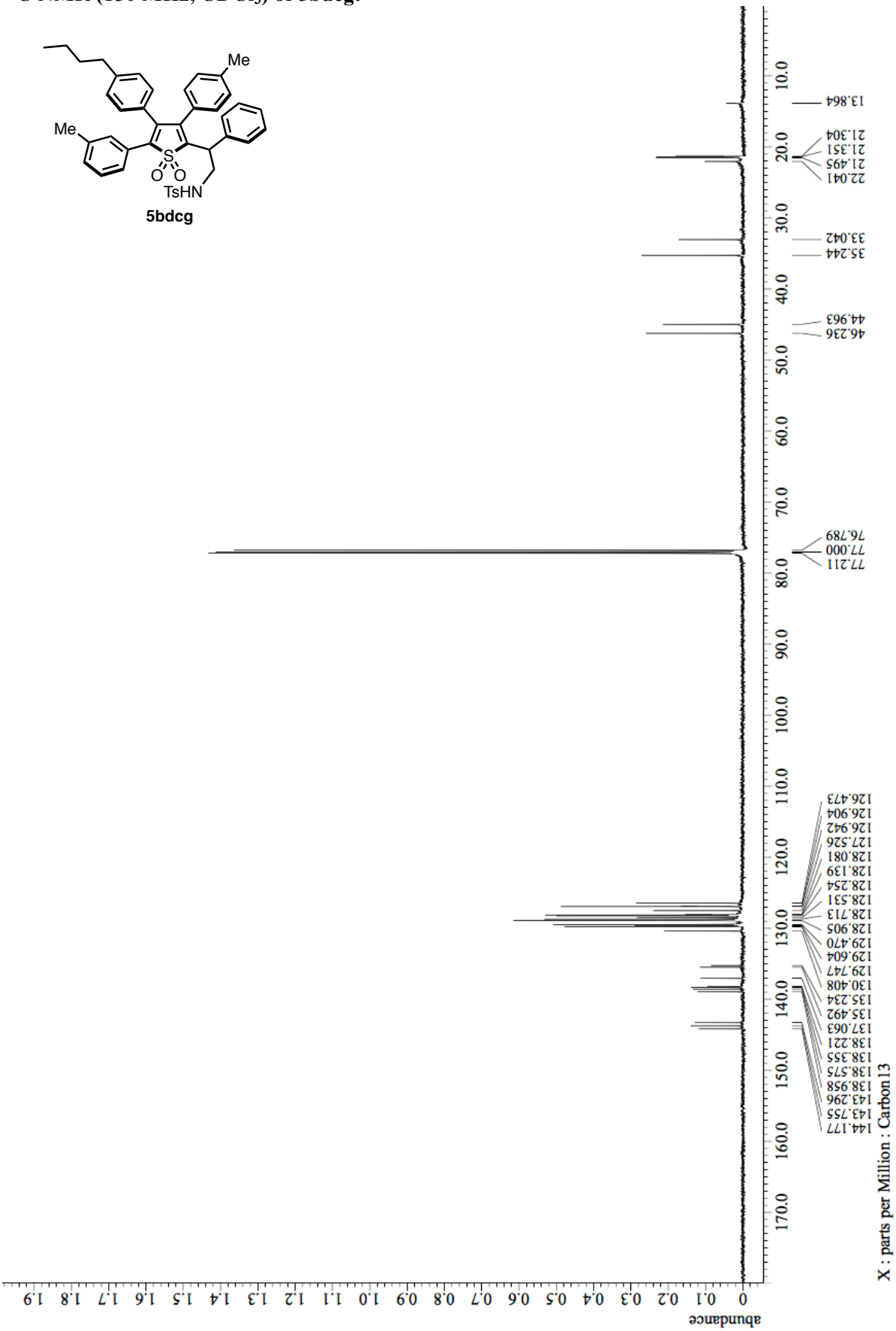
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 5acdf:



^{1}H NMR (600 MHz, $CDCl_3$) of 5bdcg:

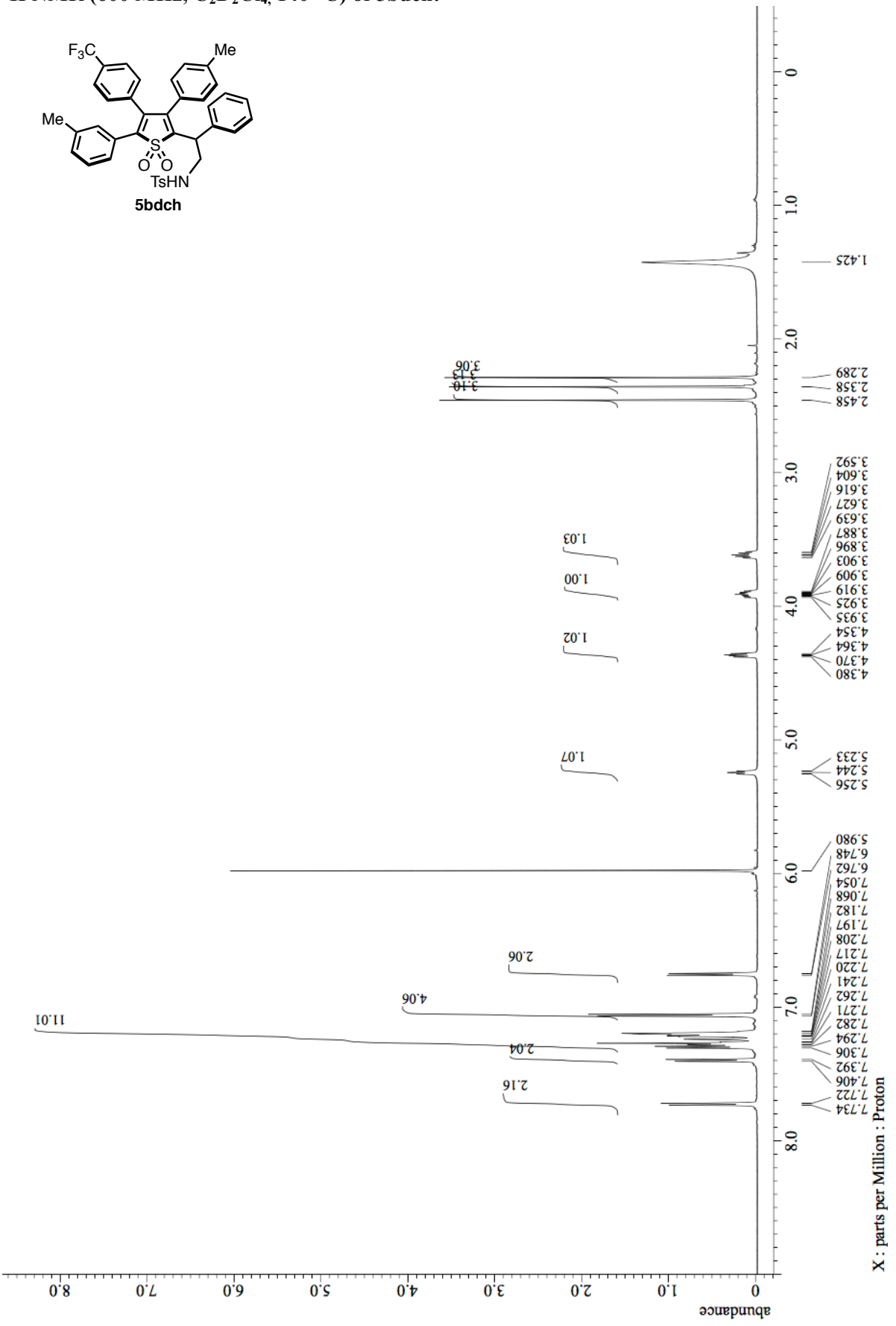


^{13}C NMR (150 MHz, $CDCl_3$) of 5bdcg:

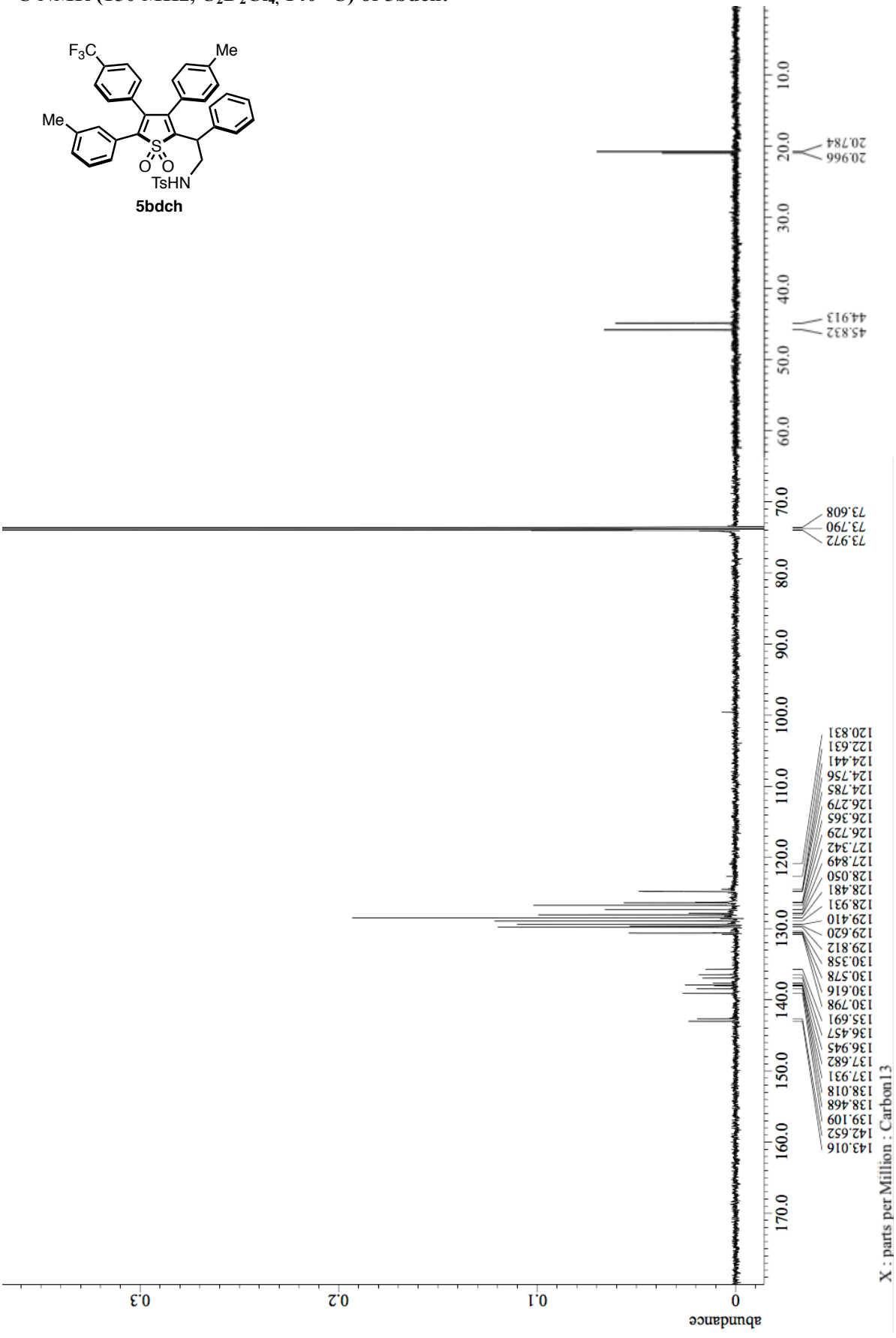


5bdcg

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 5bdch:

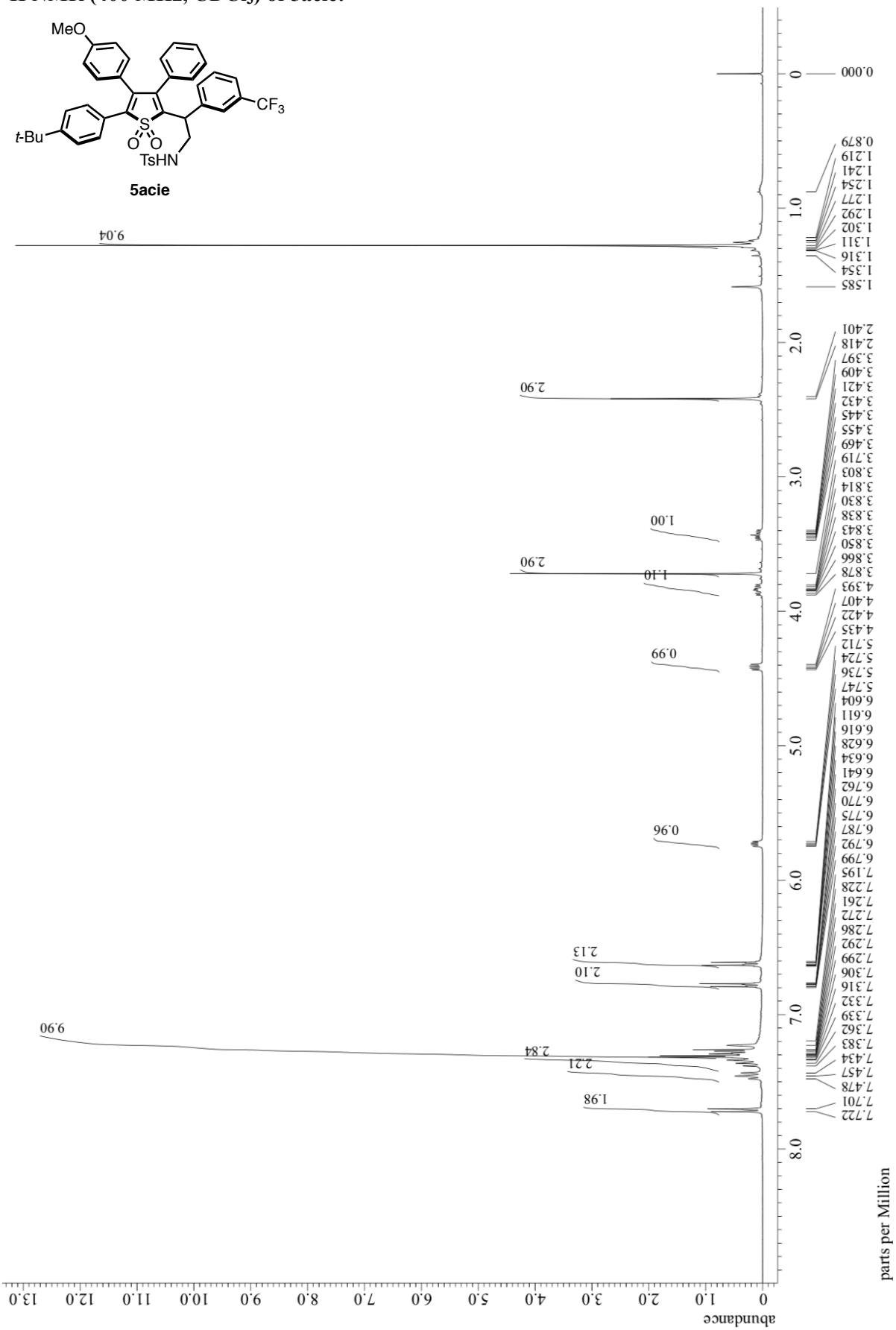


^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 5bdch:

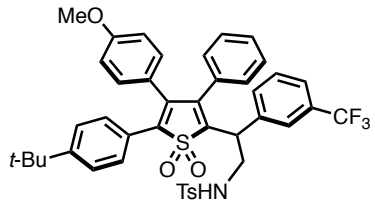


5bdch

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

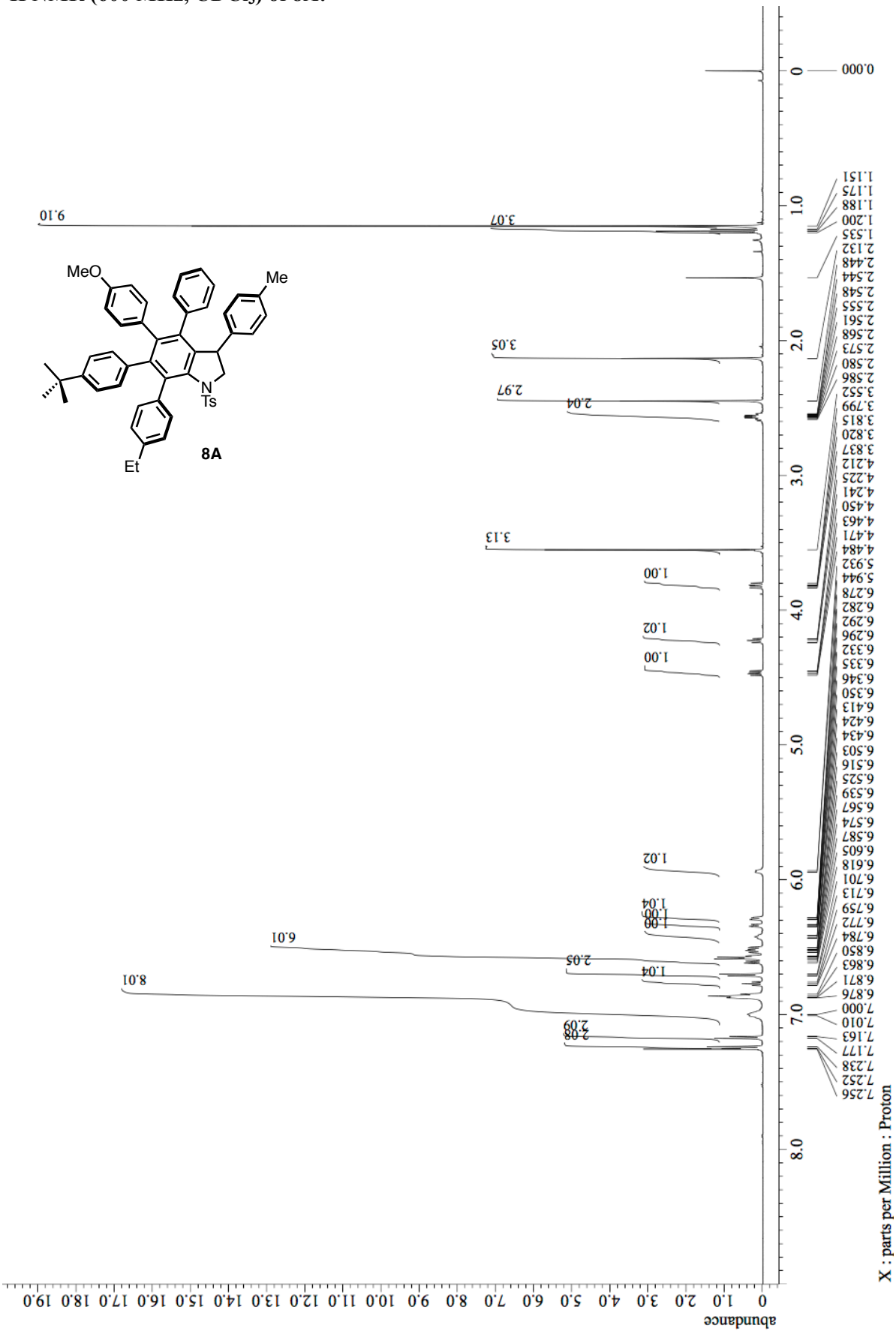


^{13}C NMR (101 MHz, $CDCl_3$) of 5acie:

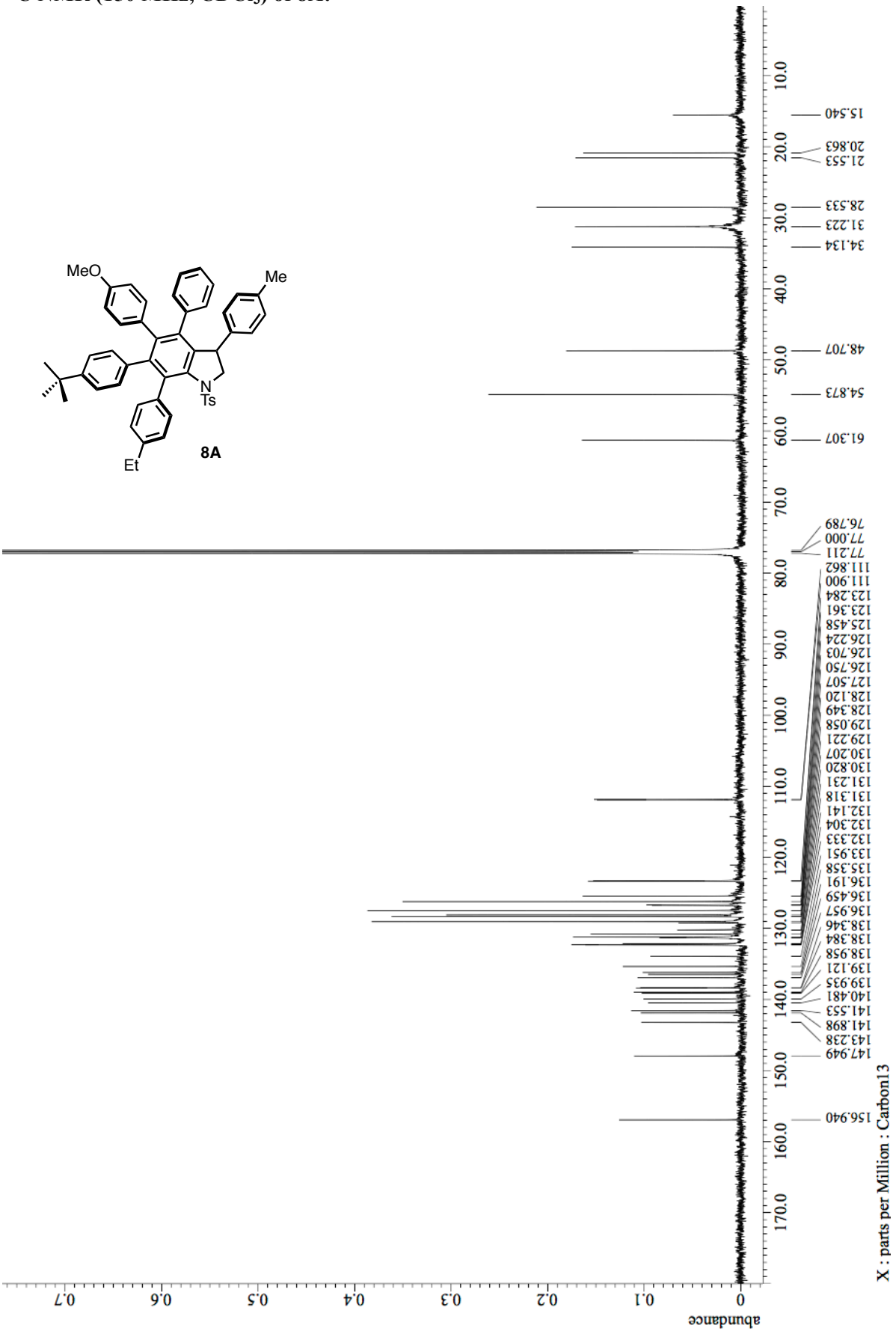


5acie

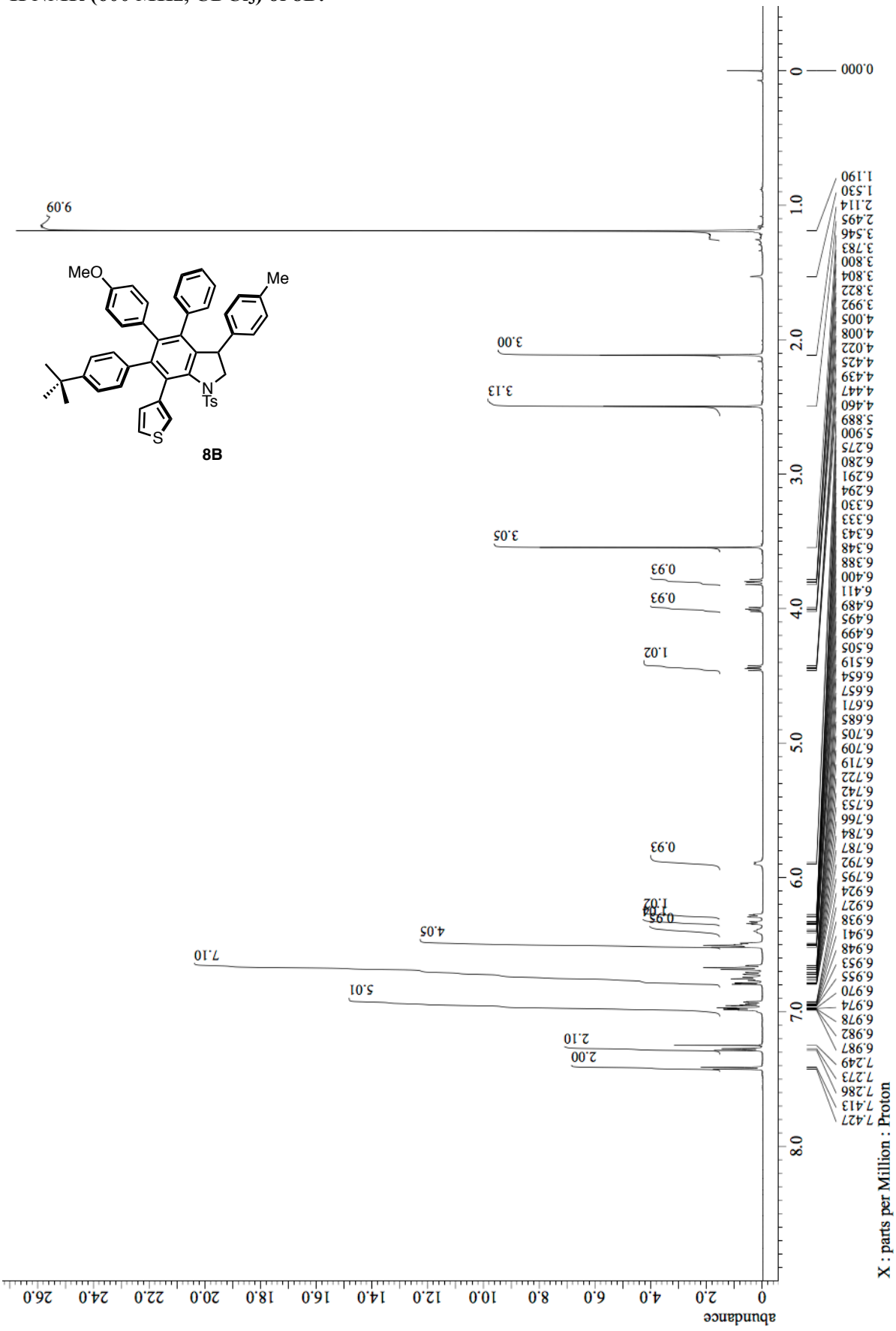
^{1}H NMR (600 MHz, $CDCl_3$) of 8A:



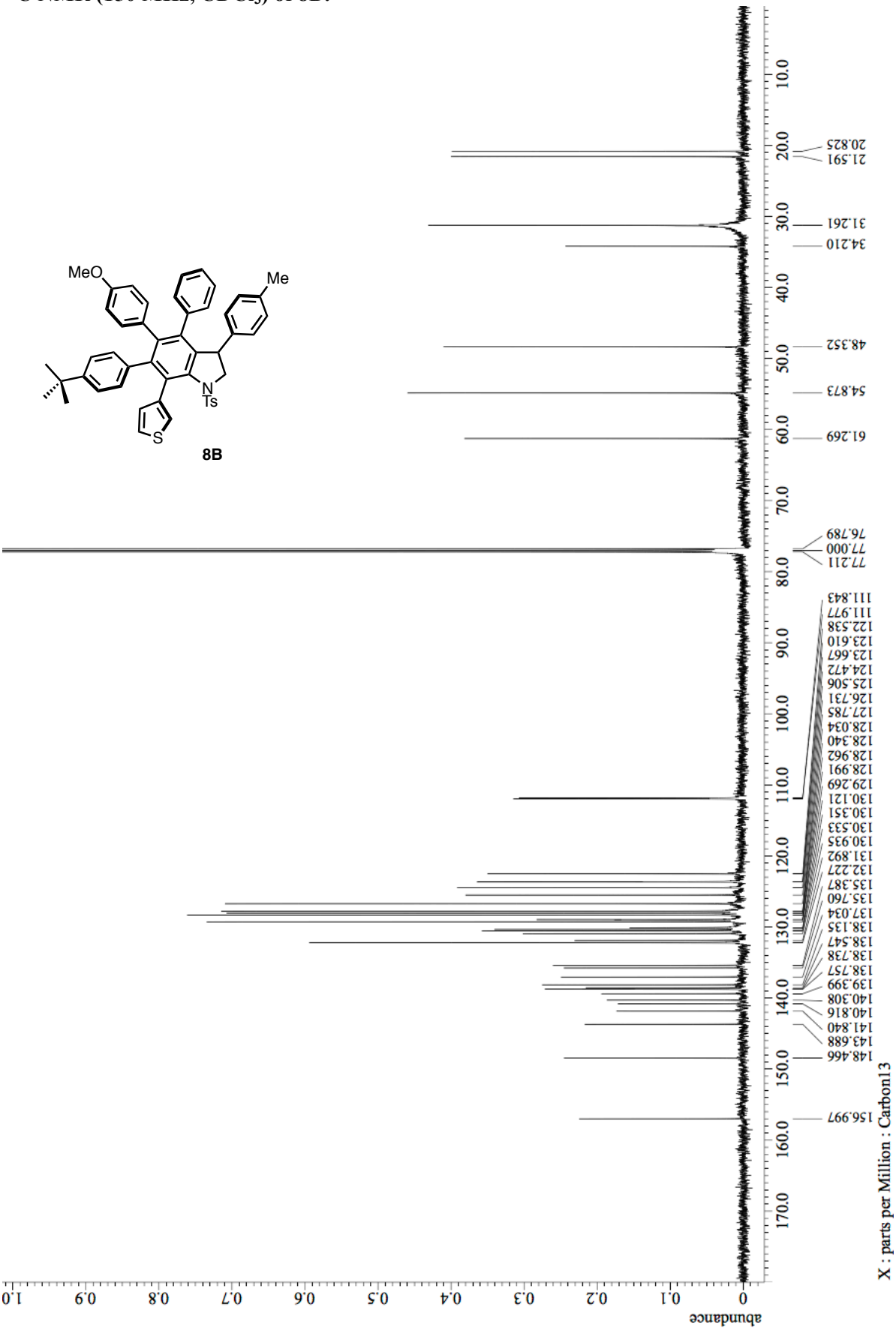
^{13}C NMR (150 MHz, $CDCl_3$) of 8A:



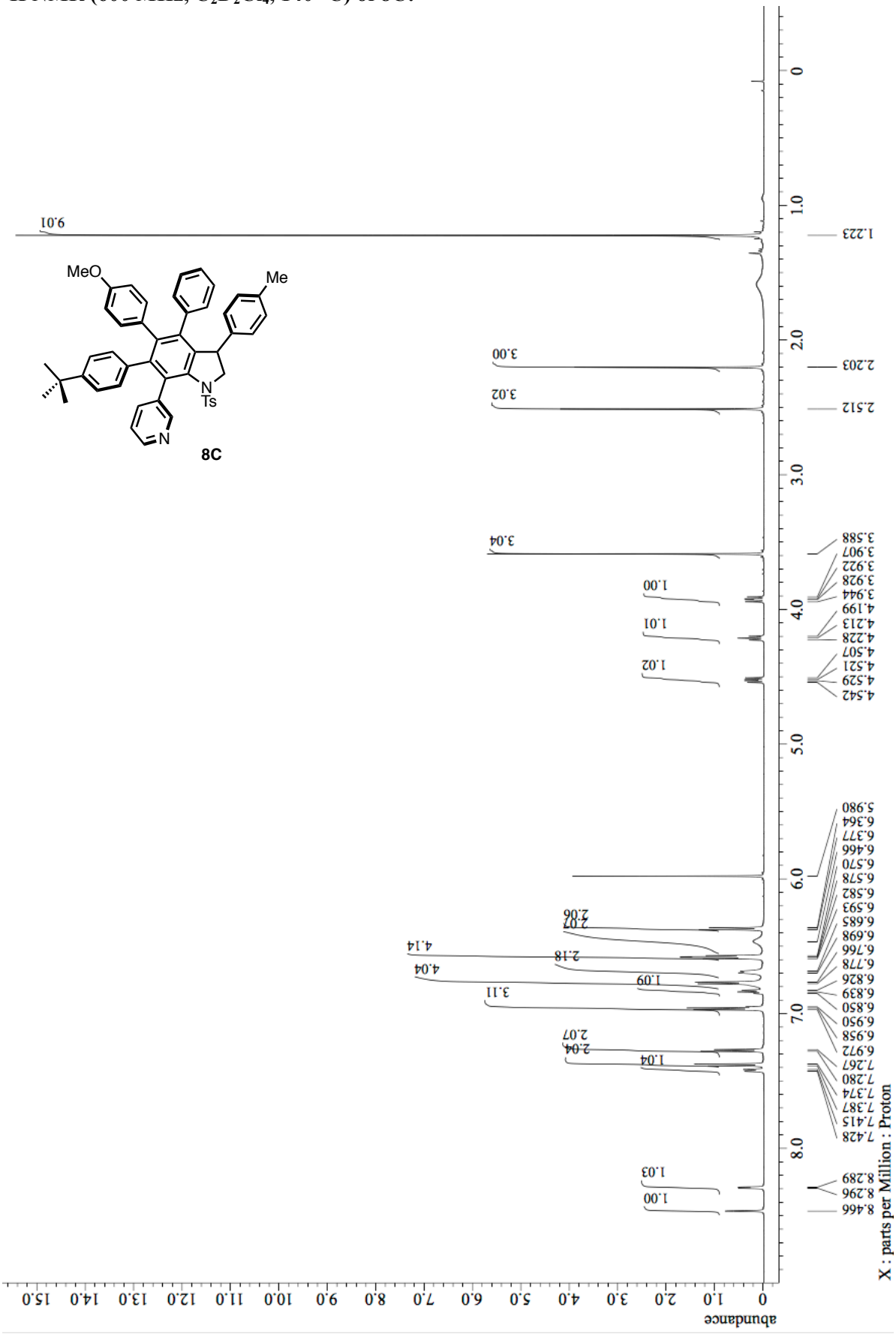
^{1}H NMR (600 MHz, $CDCl_3$) of 8B:



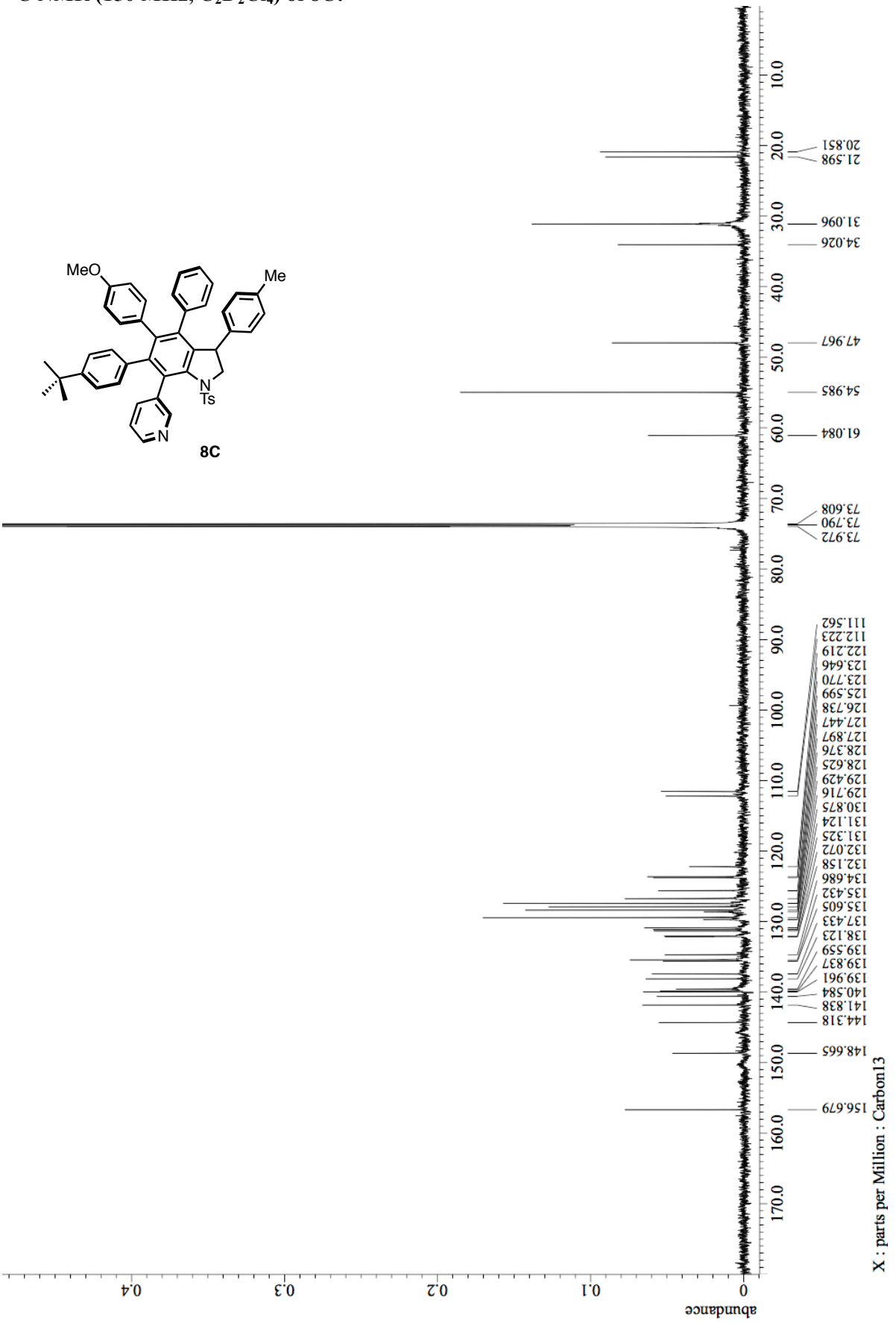
^{13}C NMR (150 MHz, $CDCl_3$) of 8B:



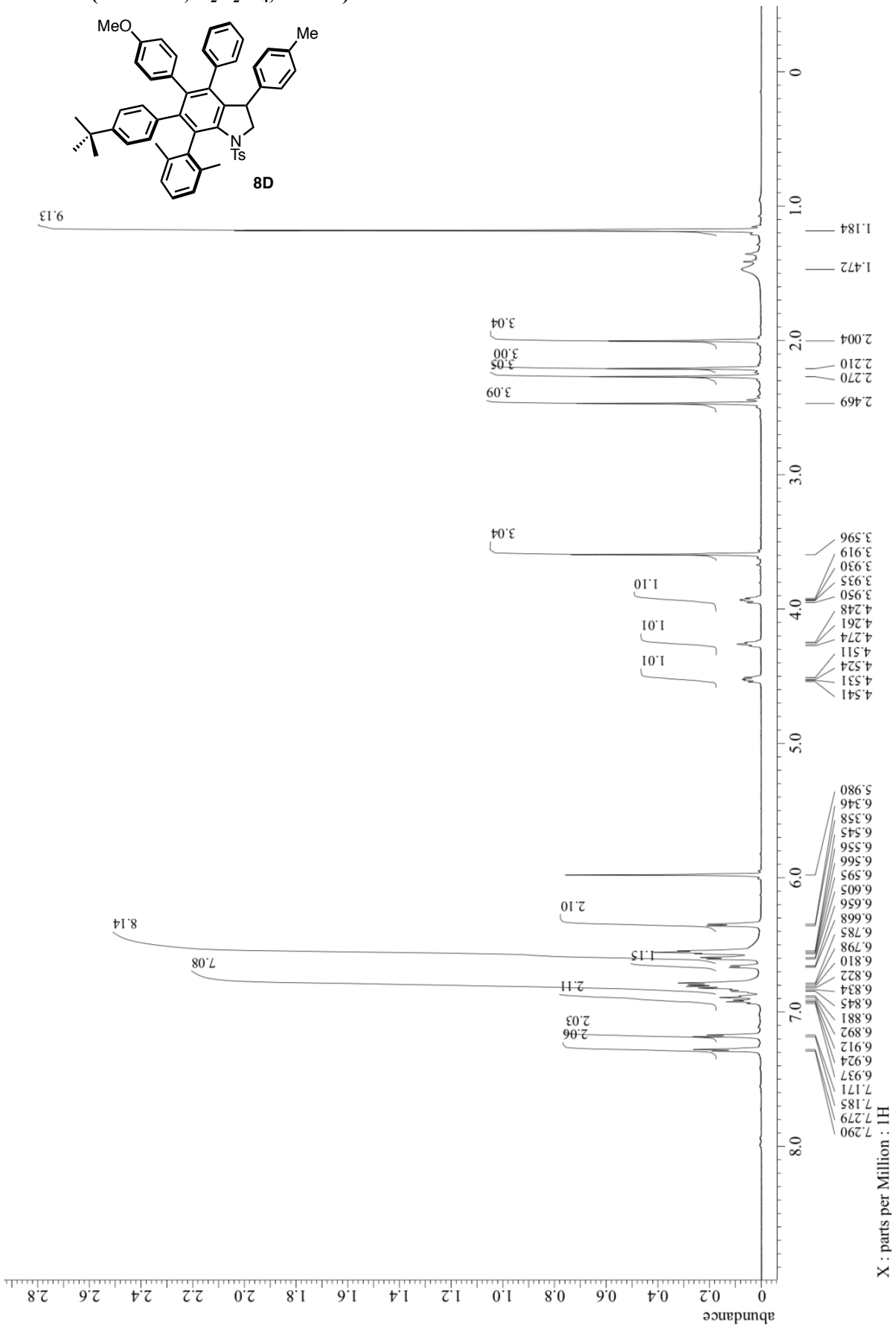
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8C:



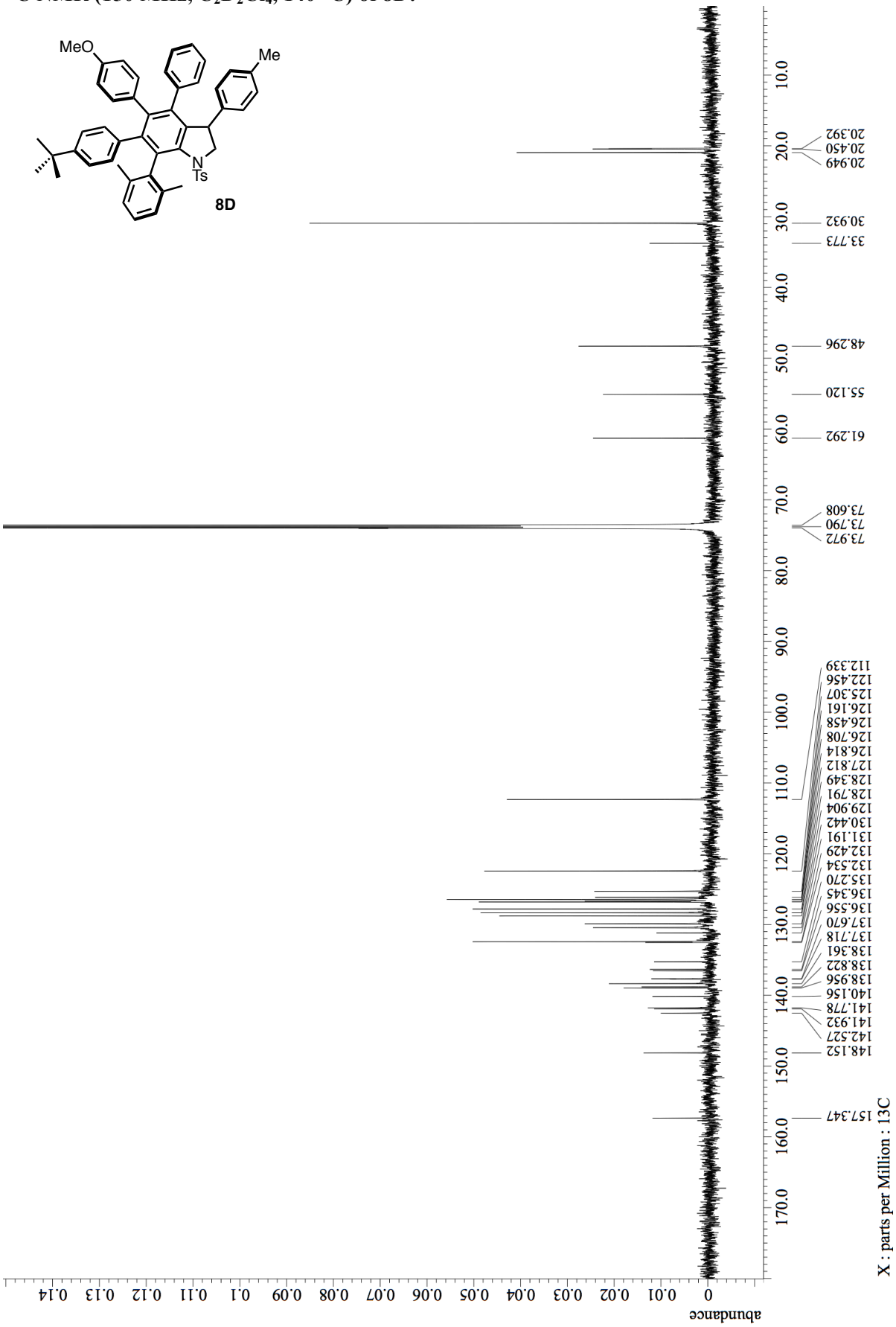
^{13}C NMR (150 MHz, $C_2D_2Cl_4$) of 8C:



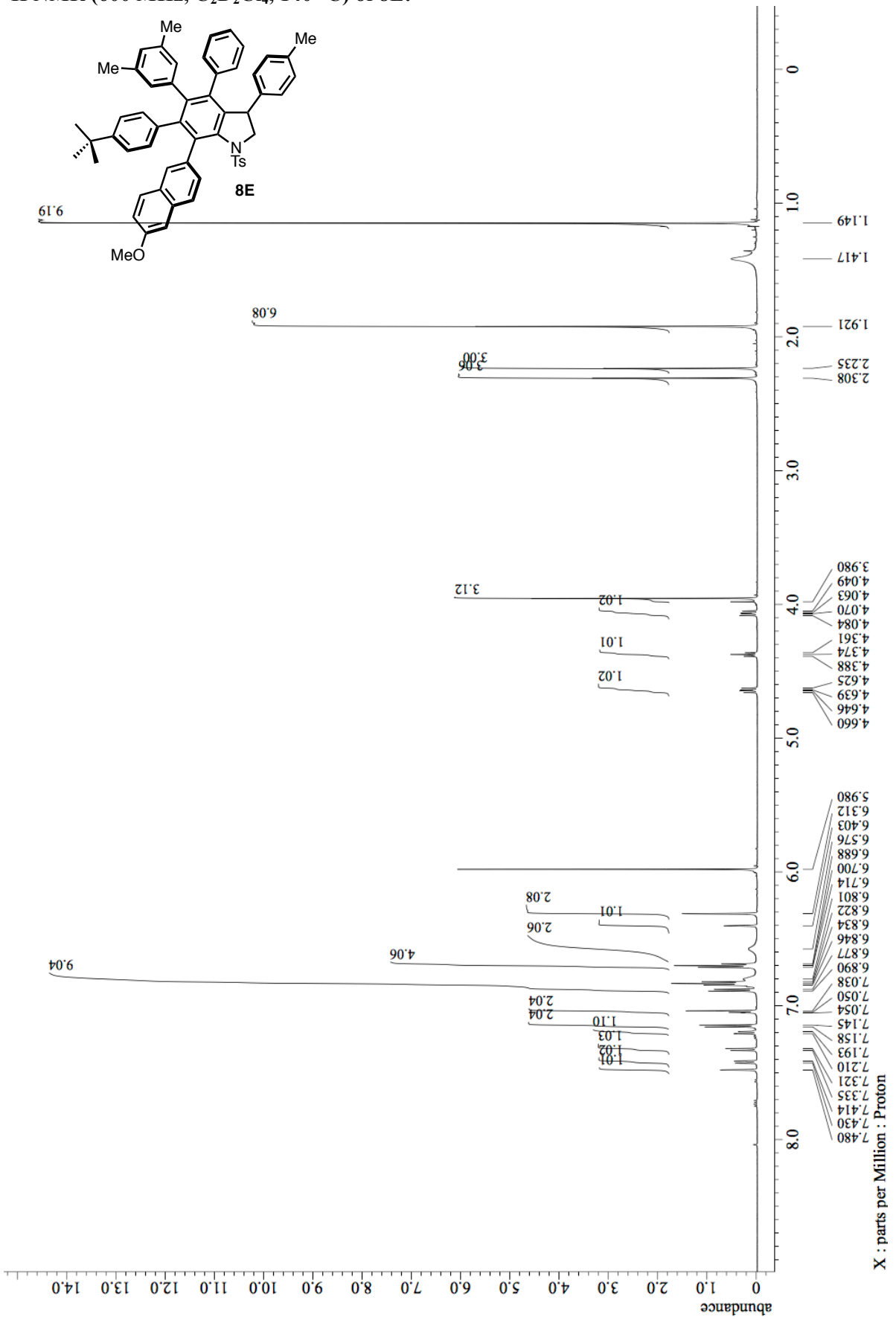
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8D:



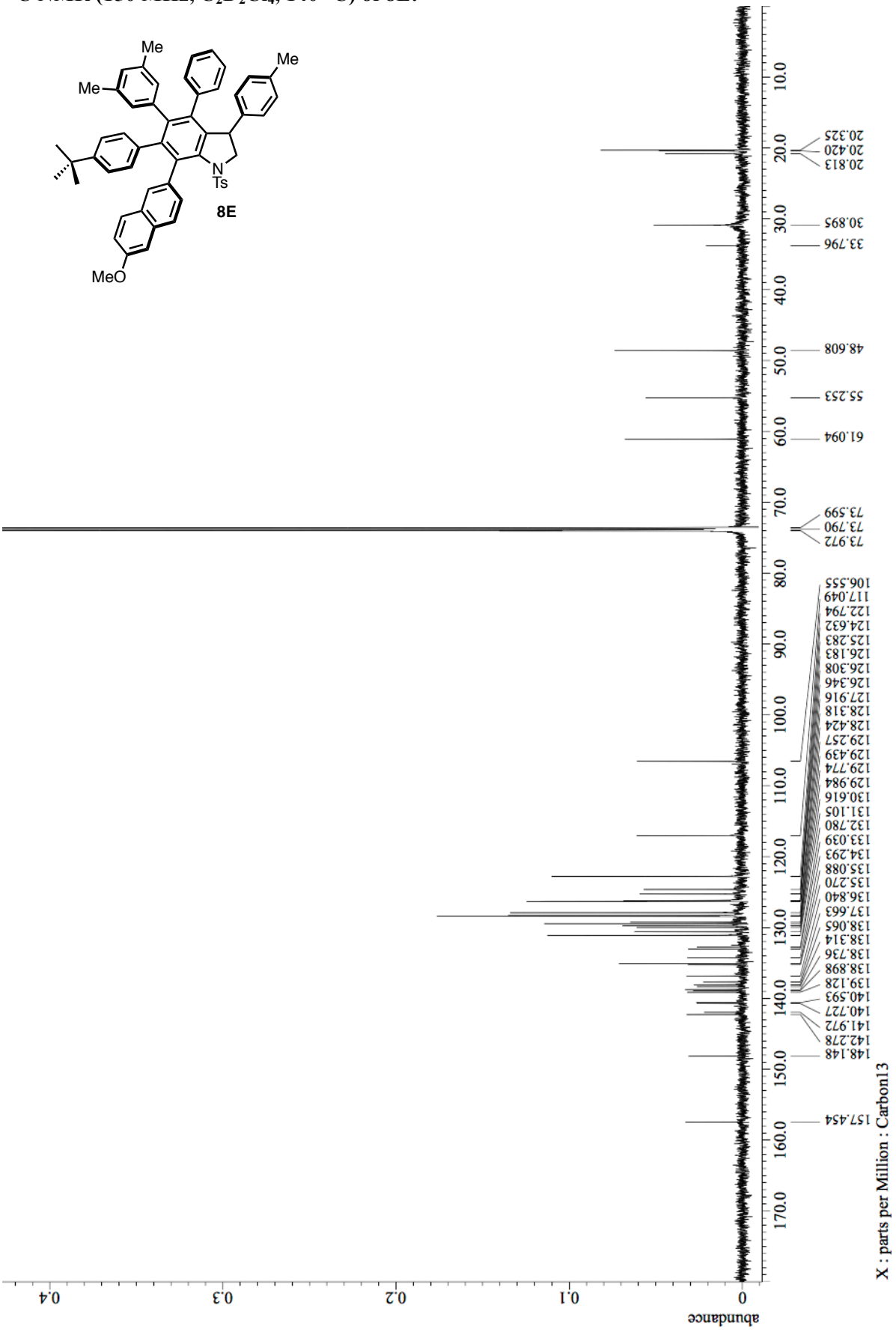
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8D:



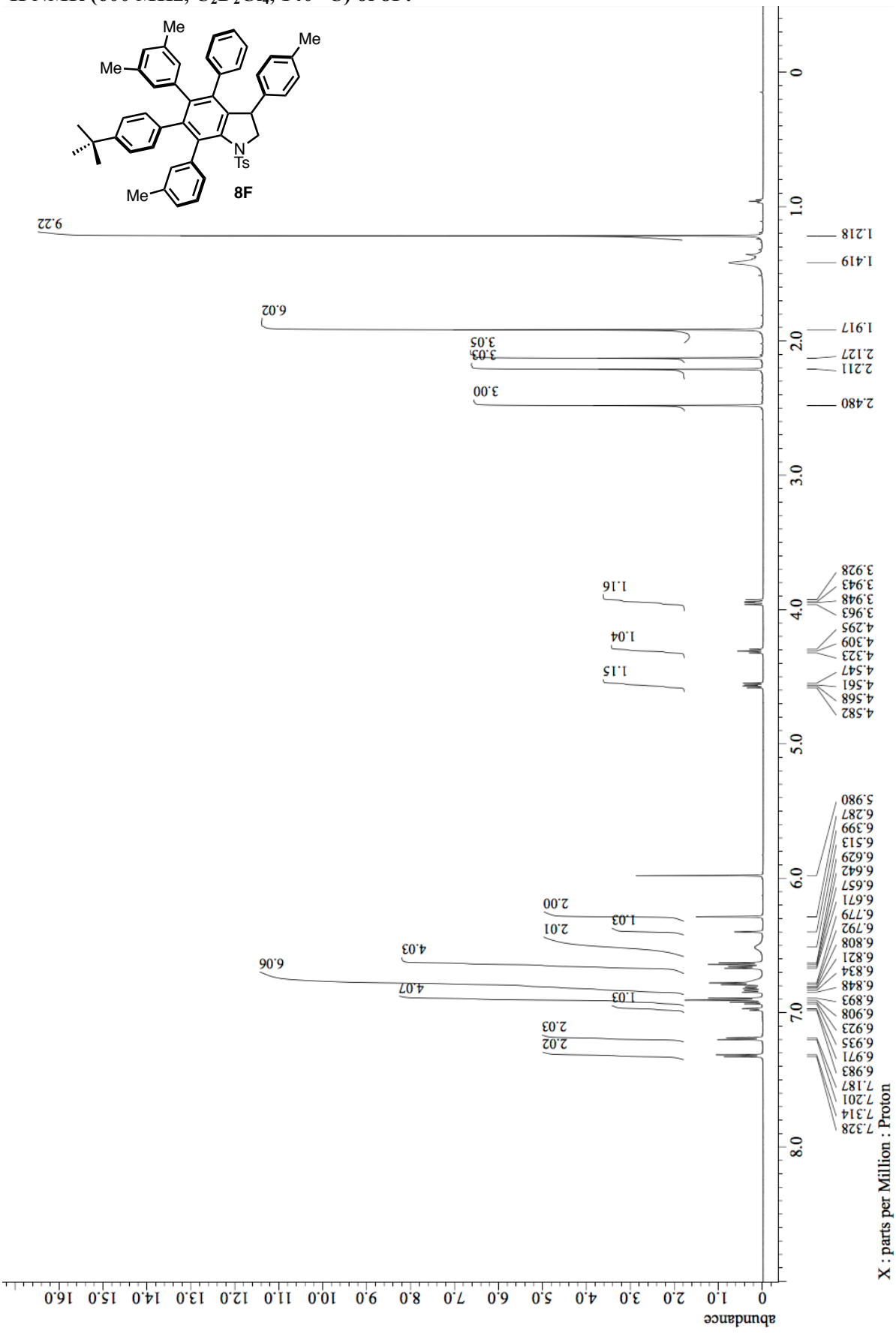
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8E:



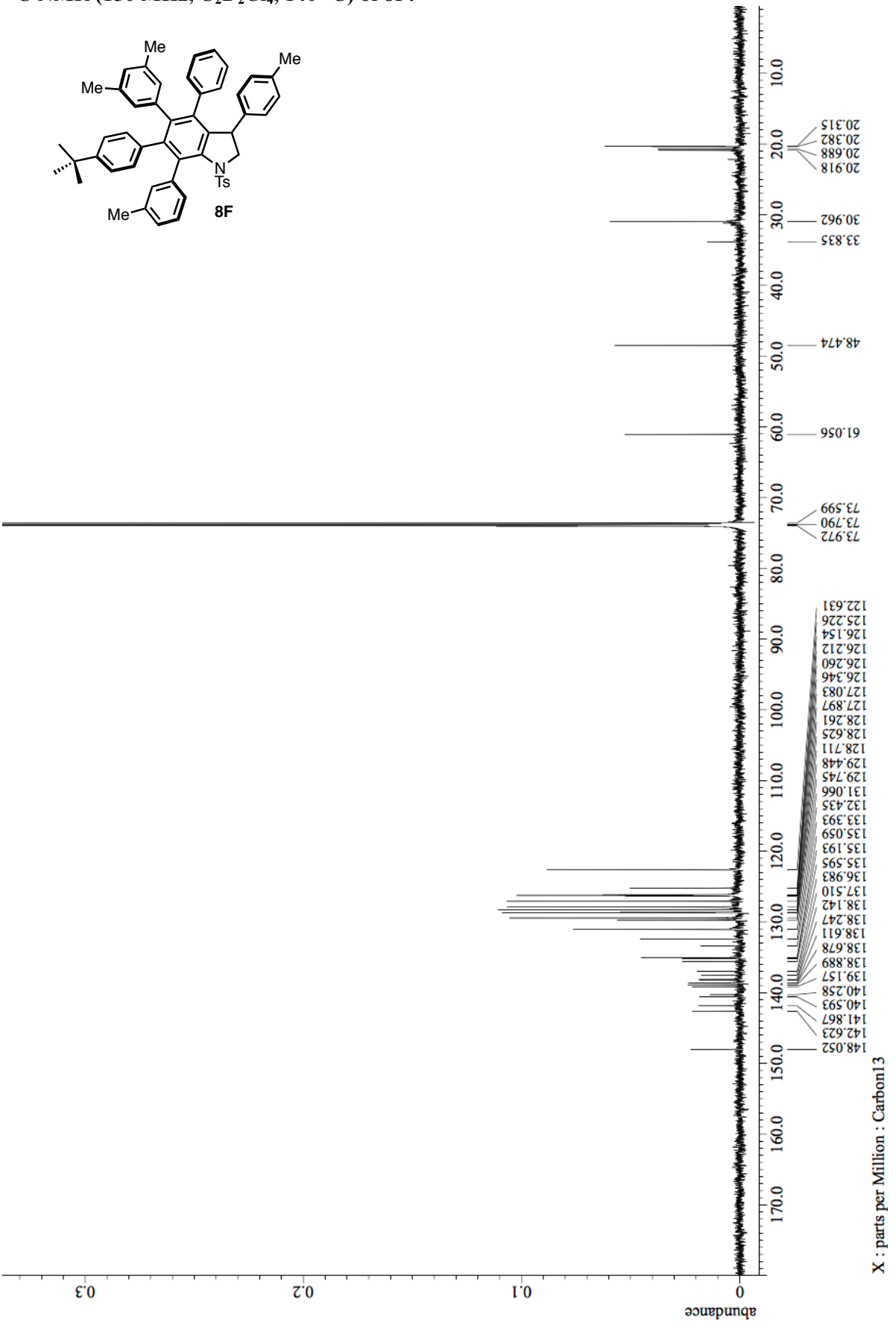
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8E:



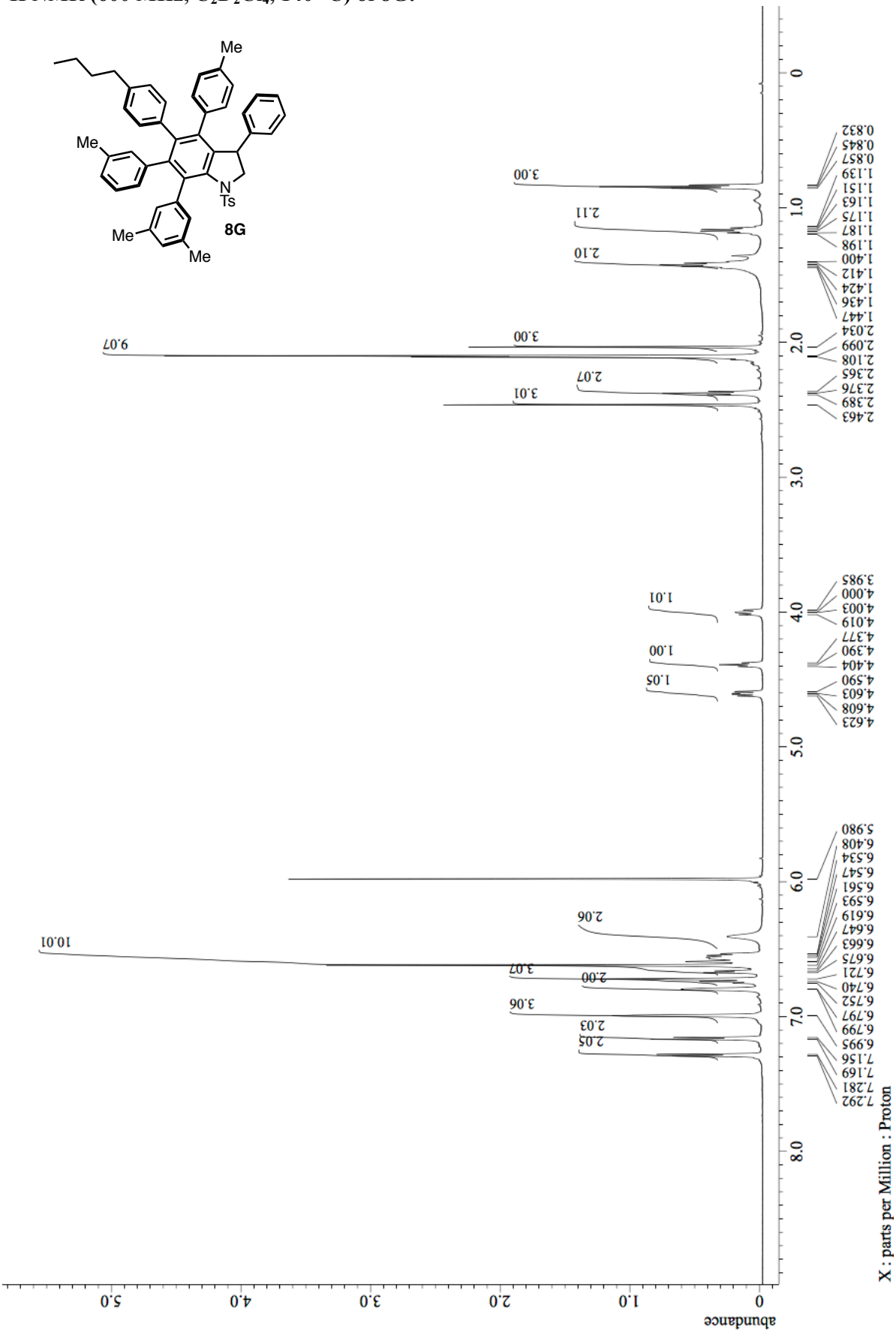
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8F:



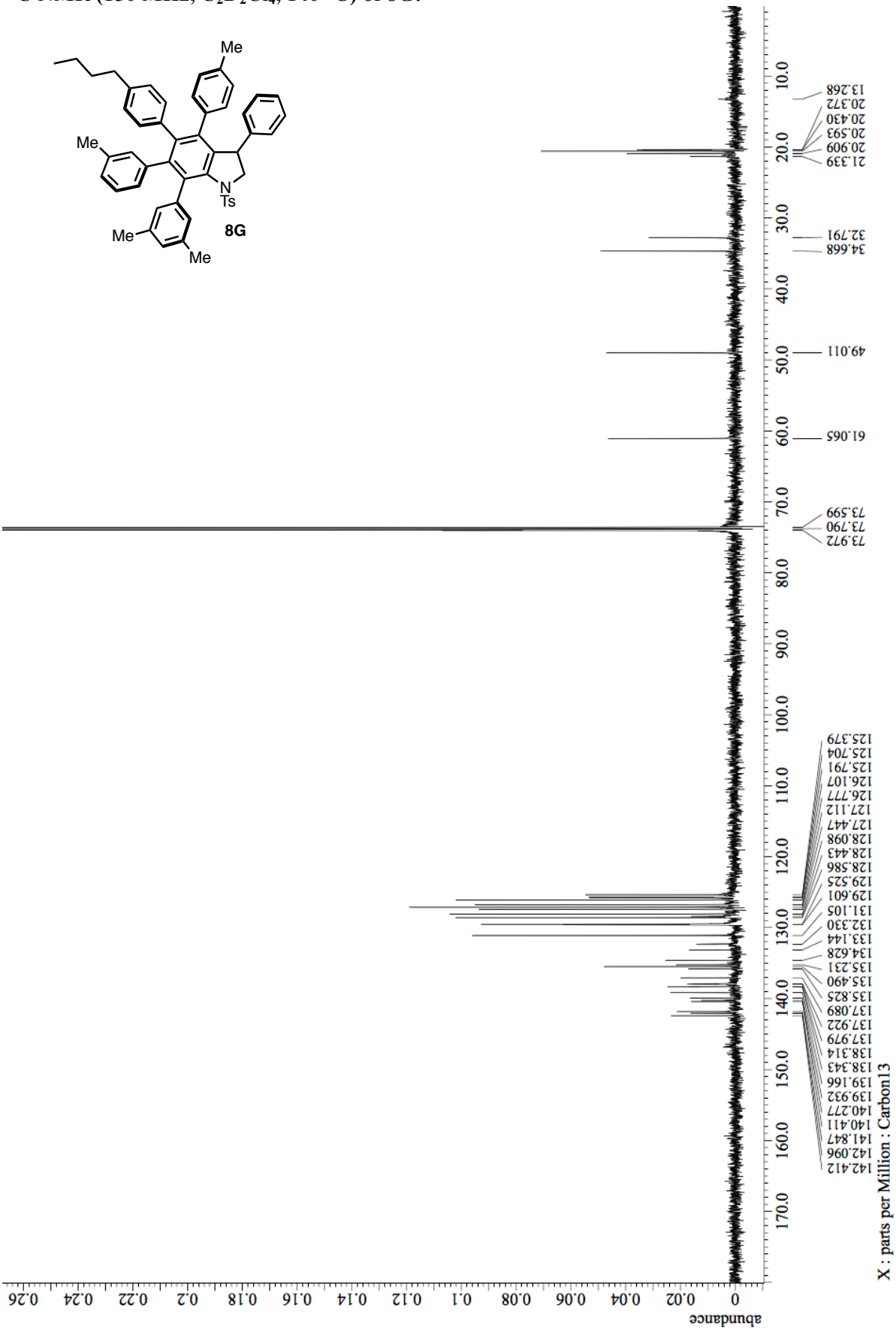
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8F:



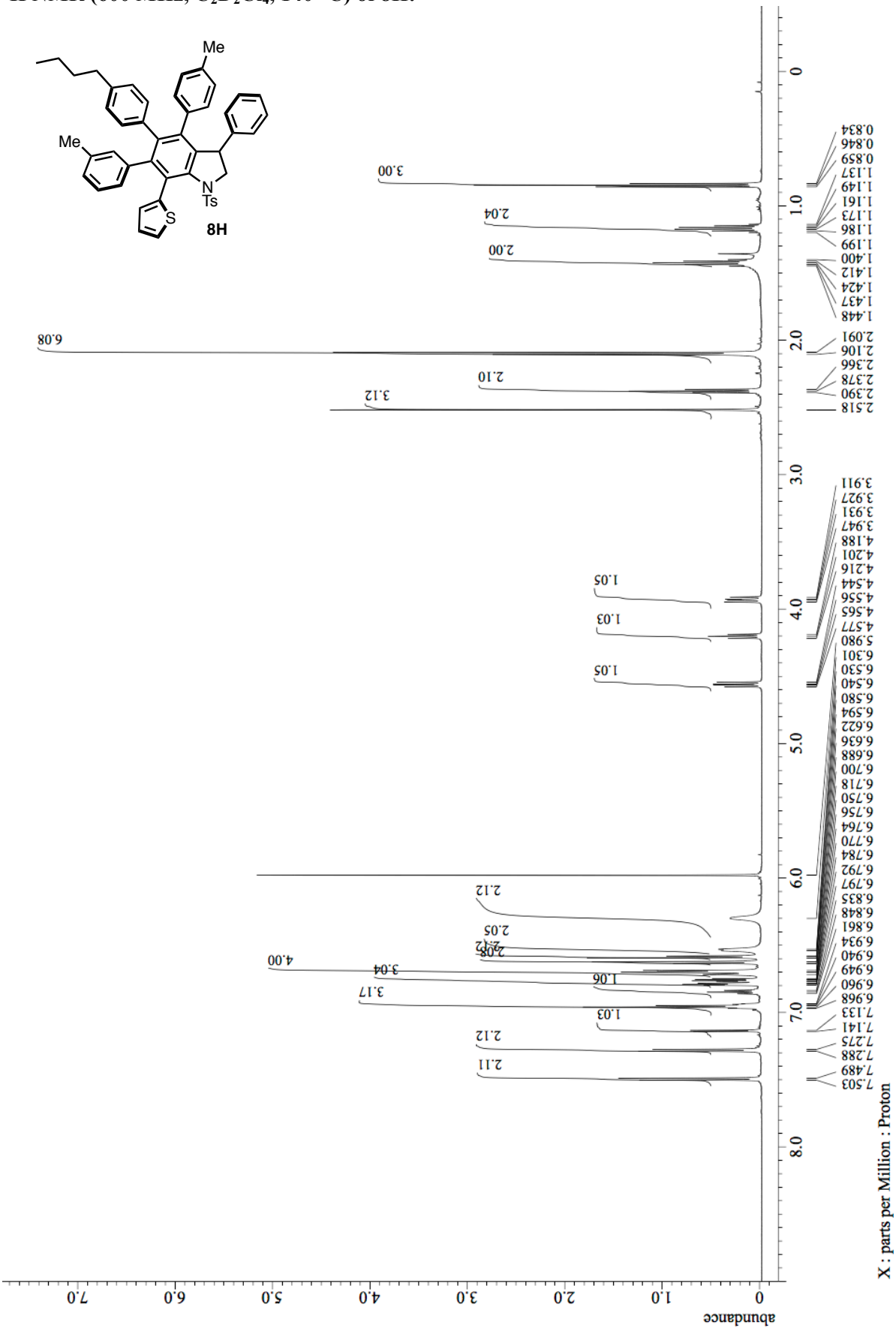
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8G:



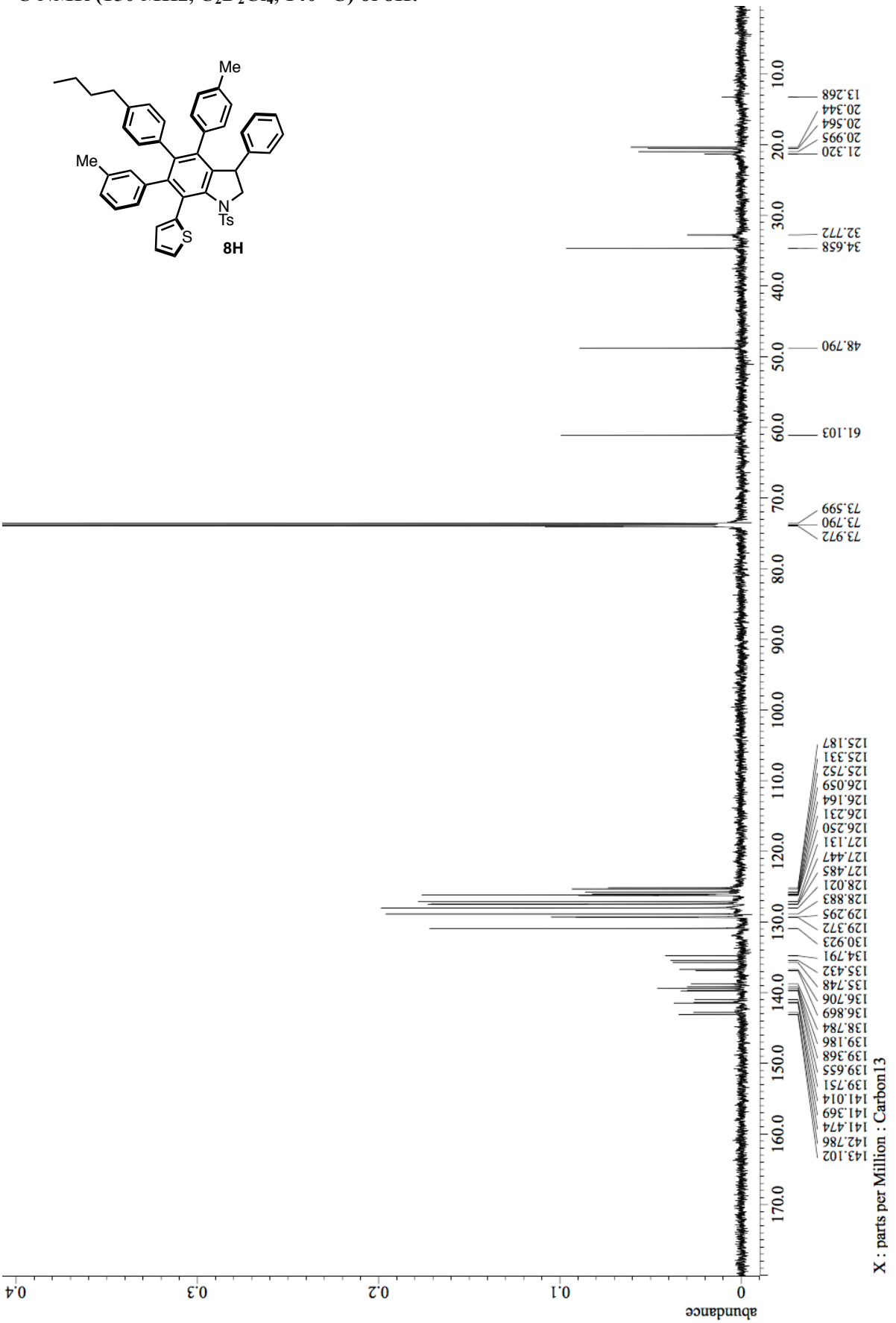
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8G:



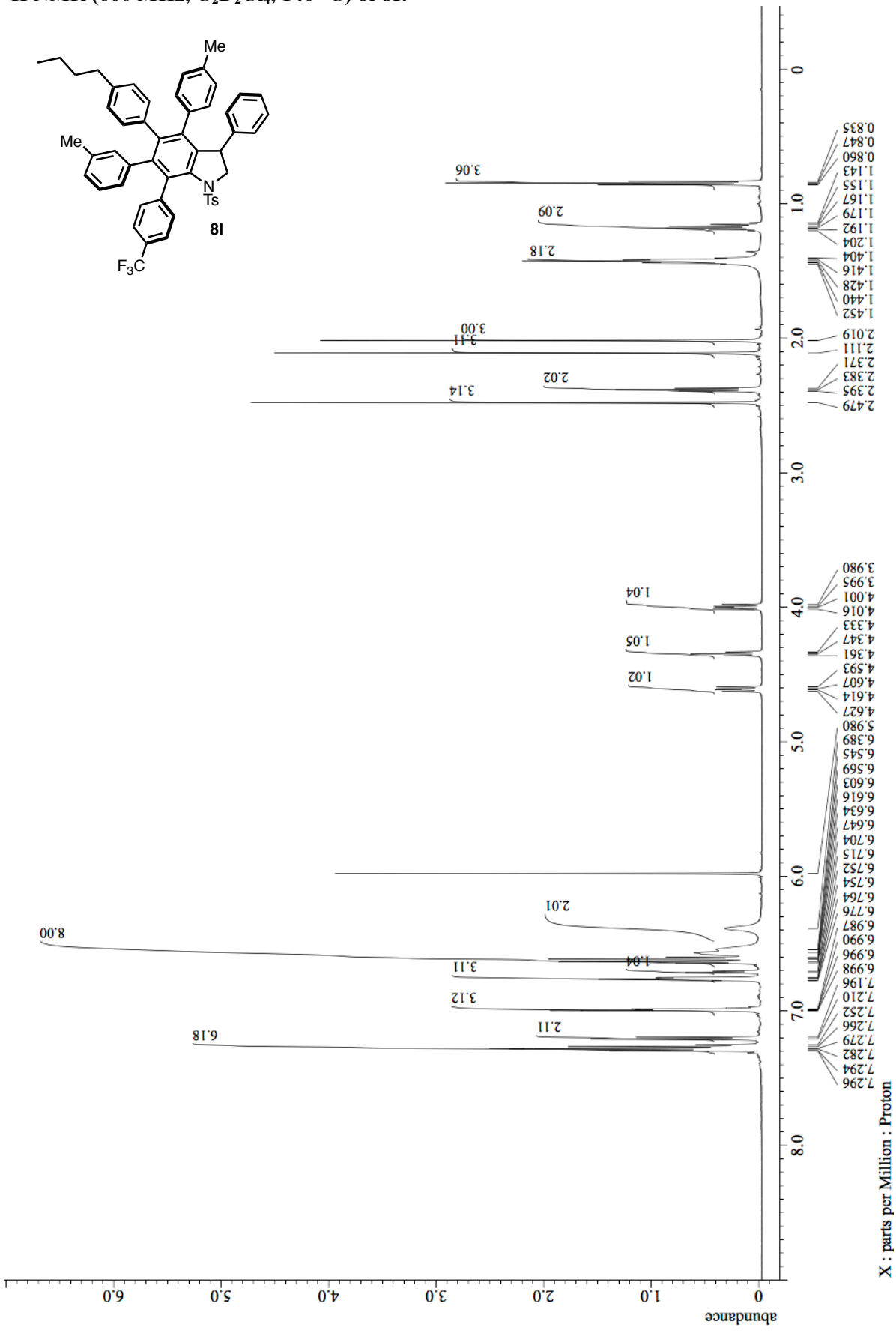
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8H:



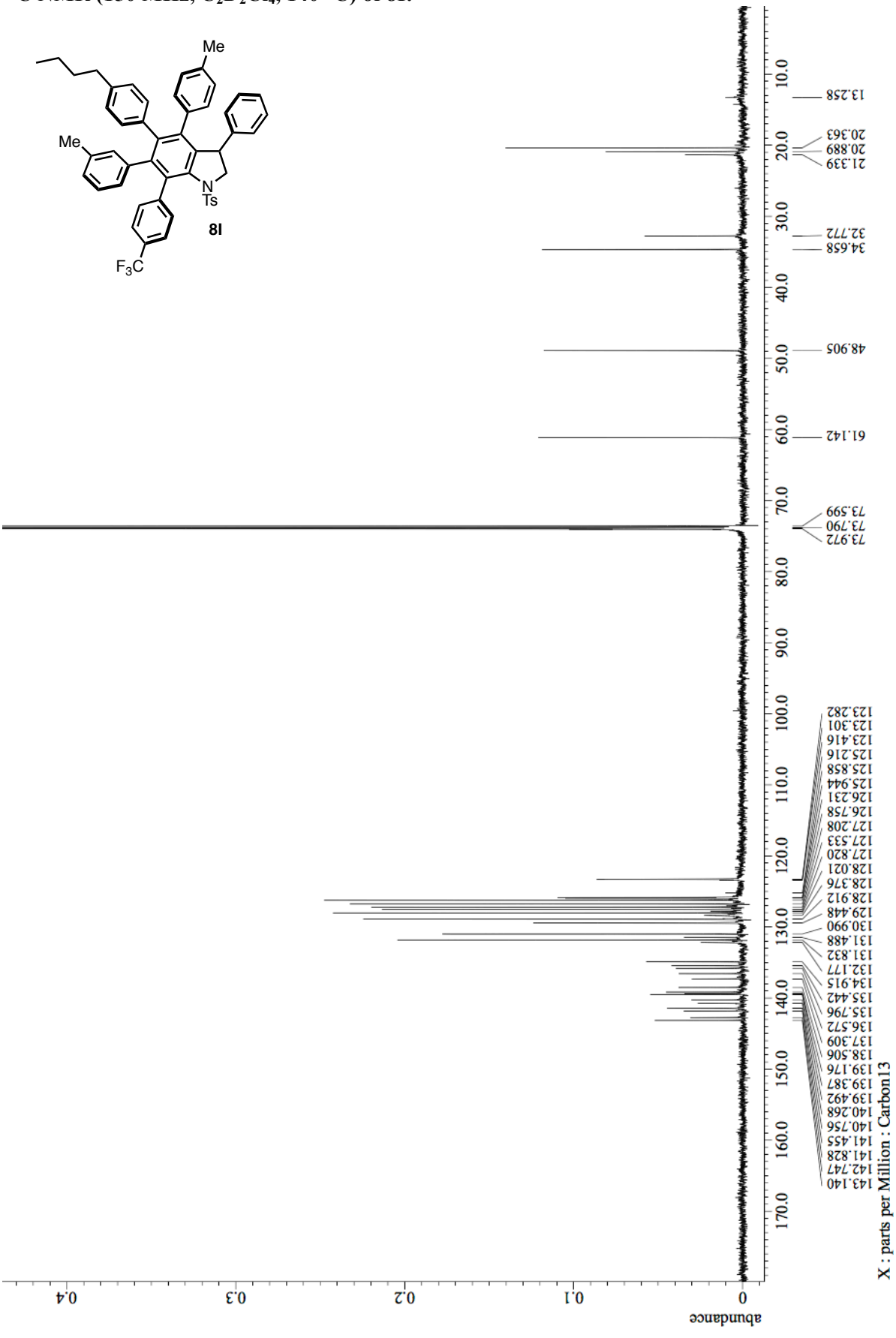
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8H:



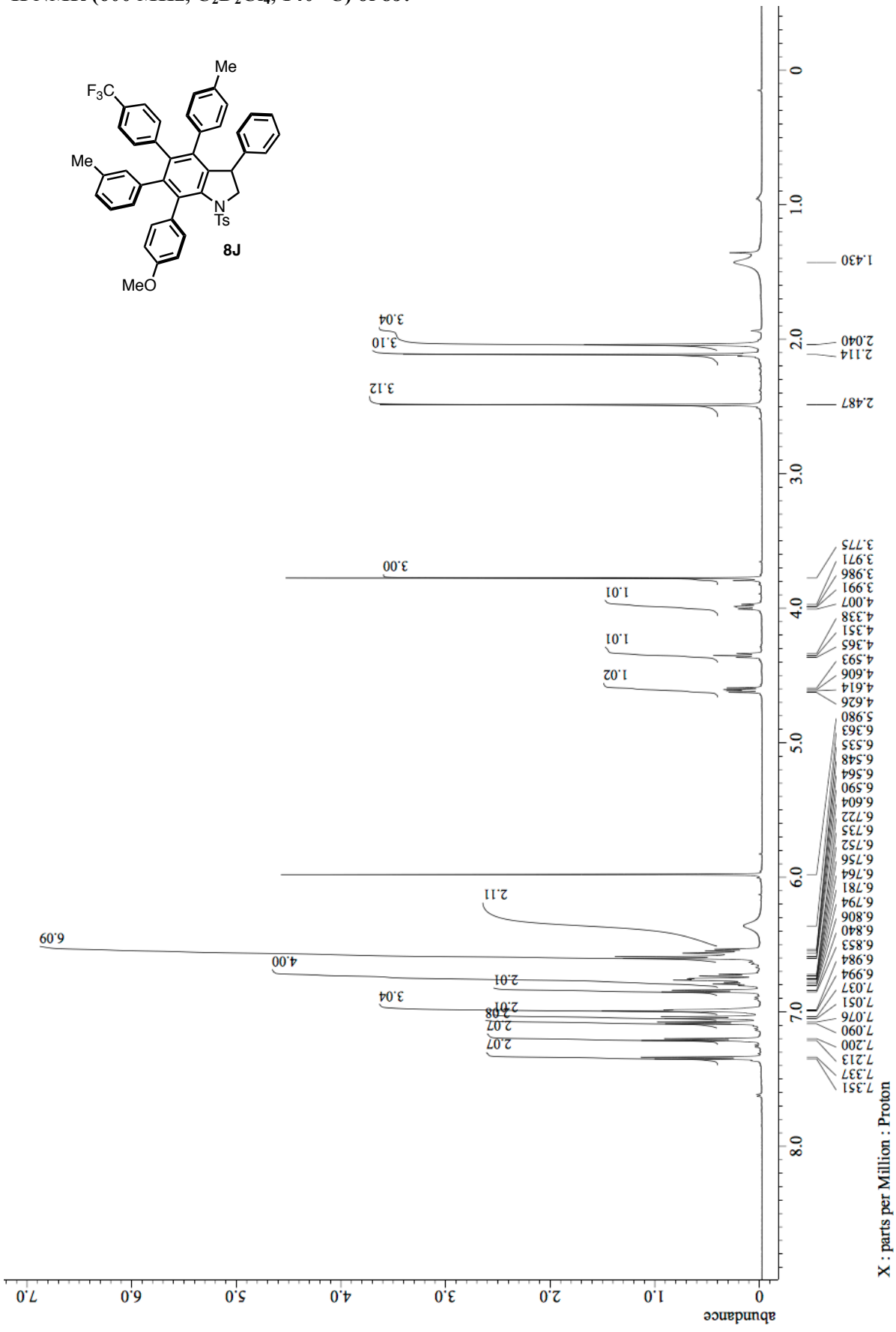
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8I:



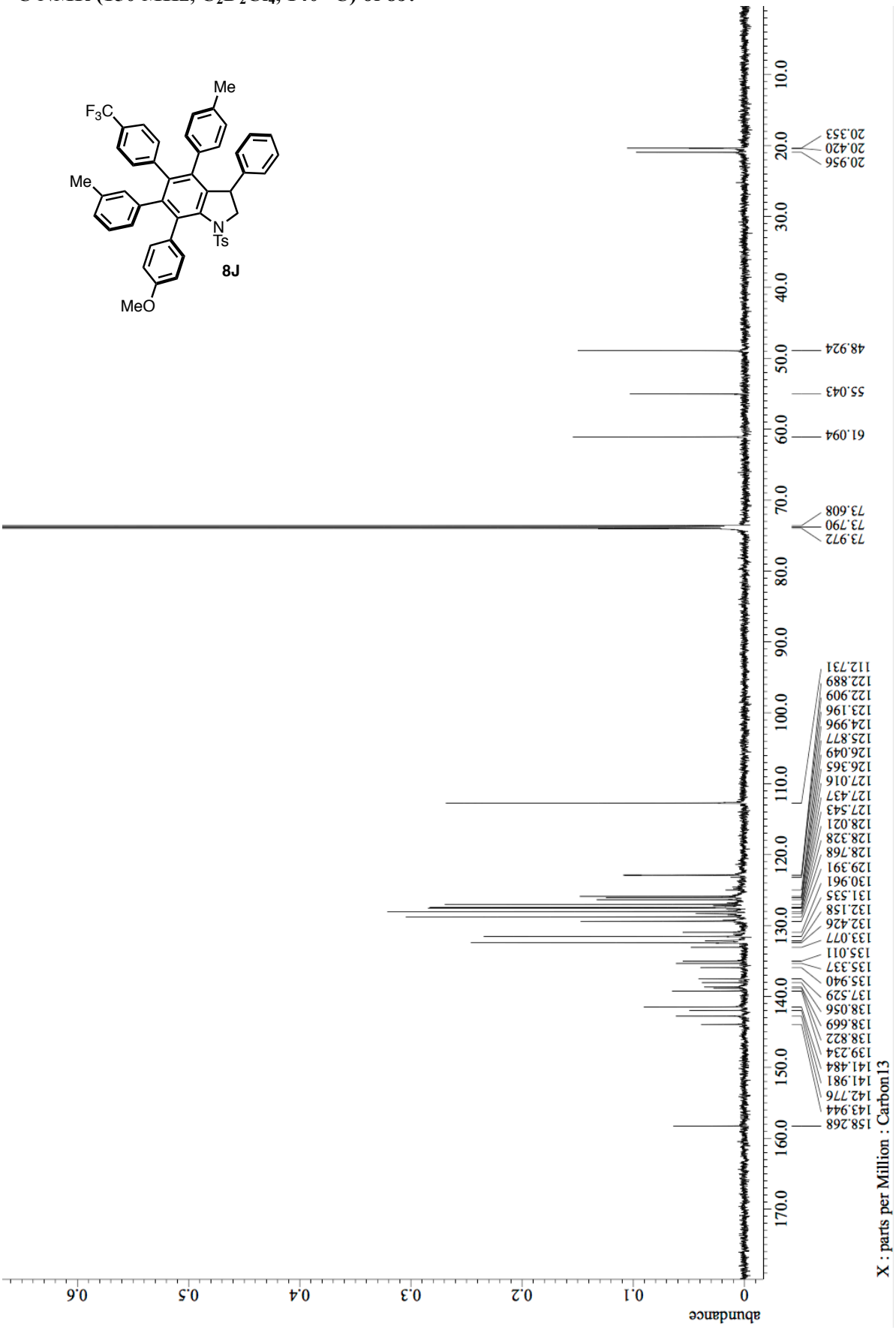
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8I:



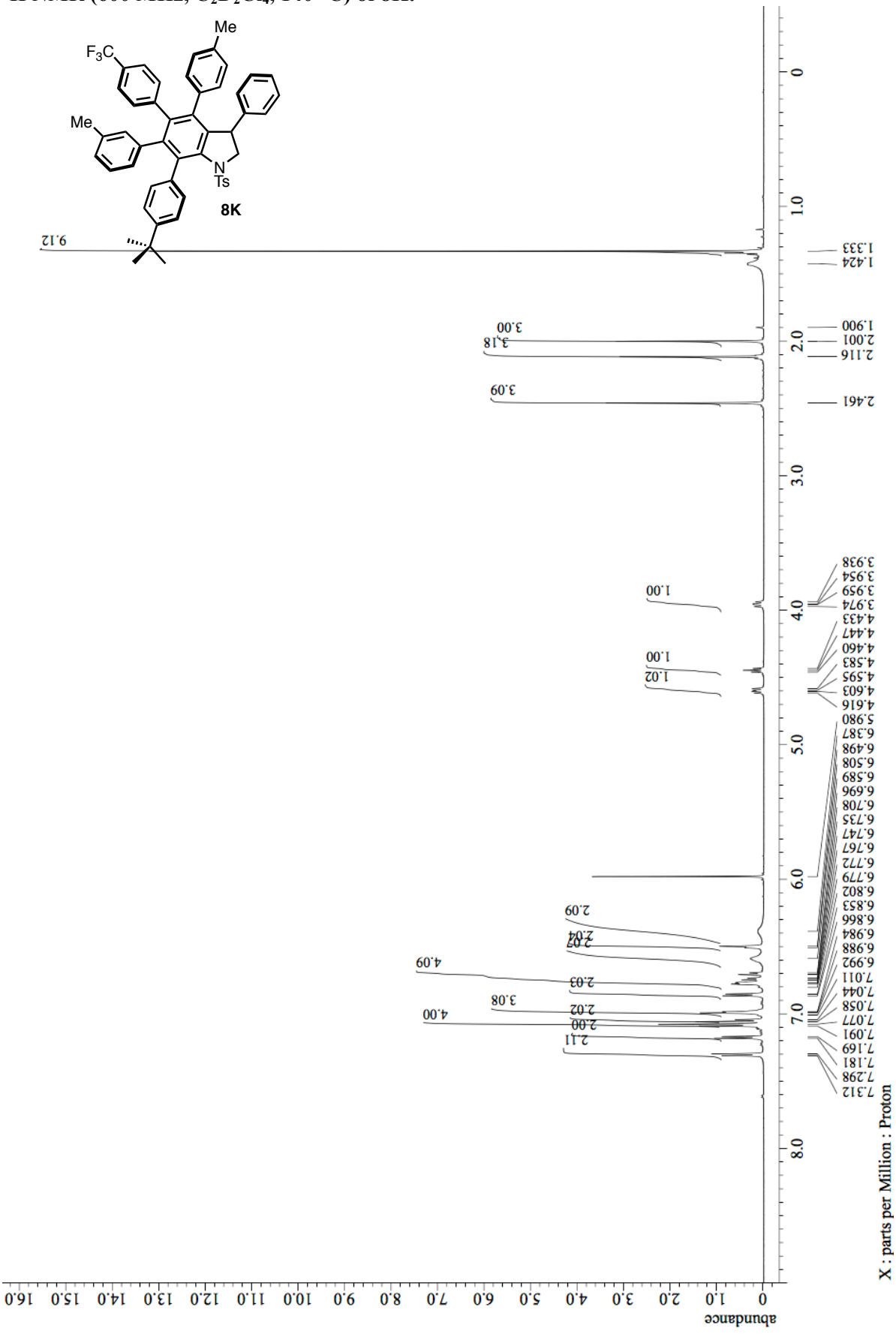
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8J:



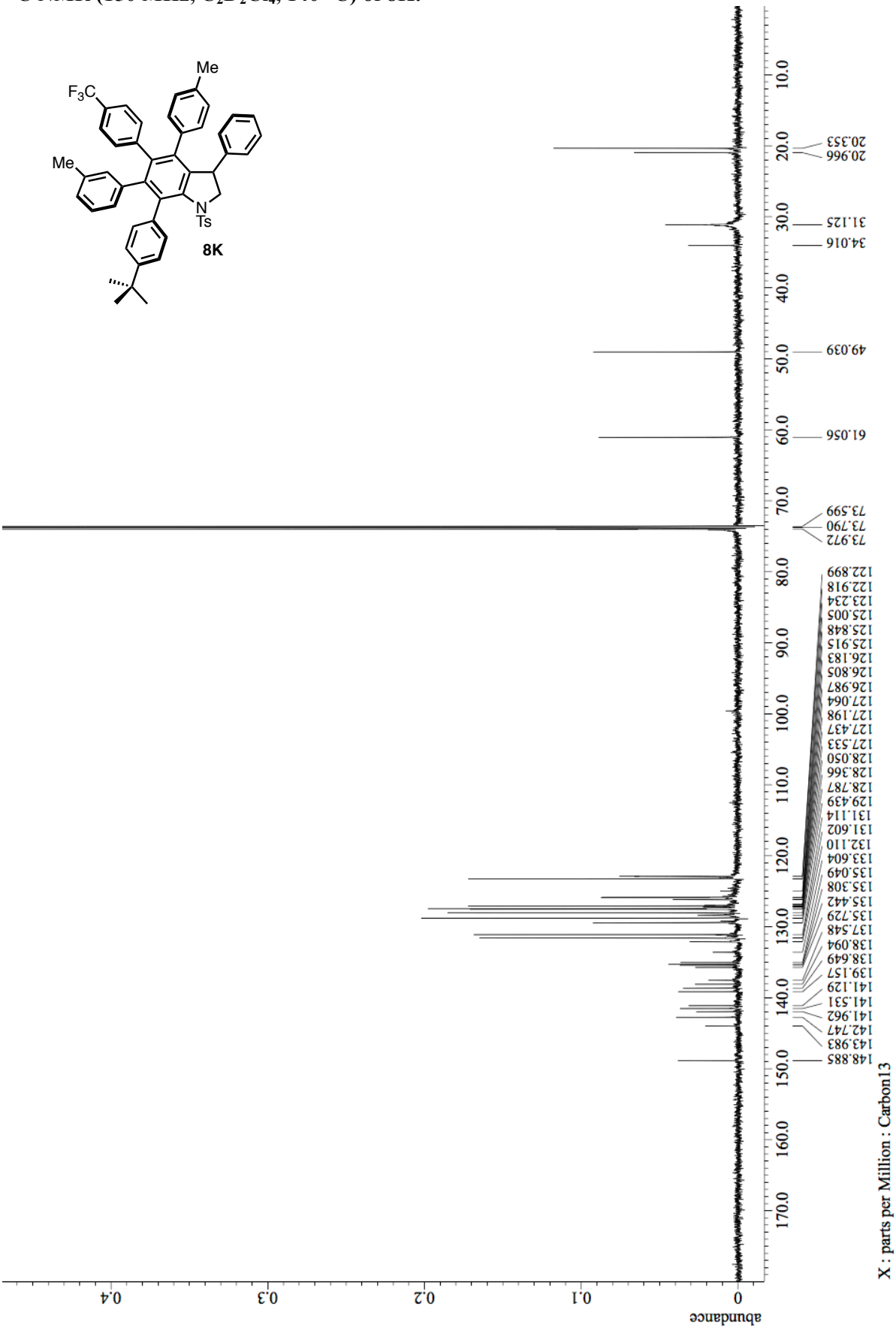
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8J:



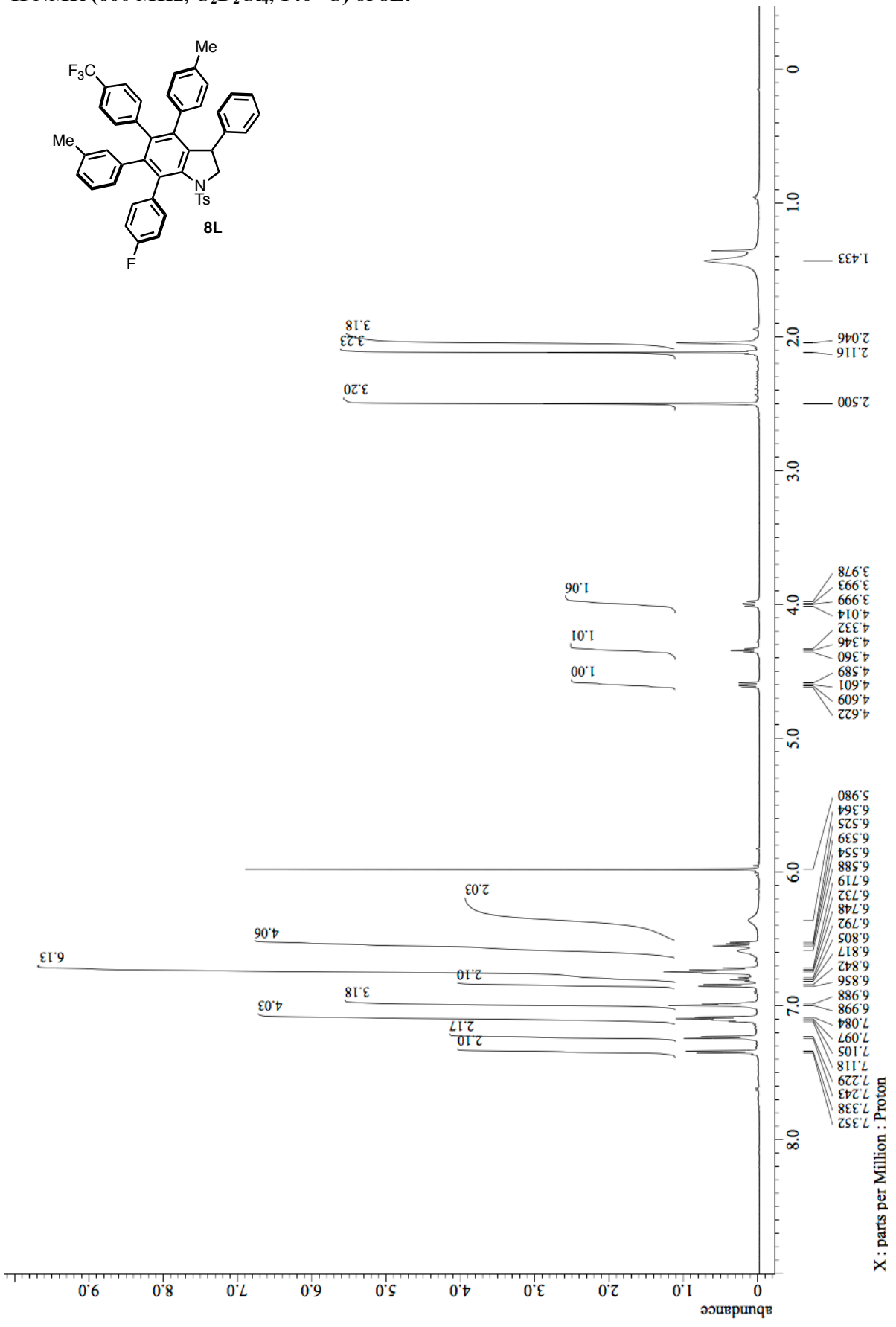
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8K:



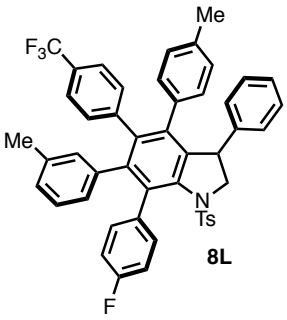
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8K:



^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 140 °C) of 8L:

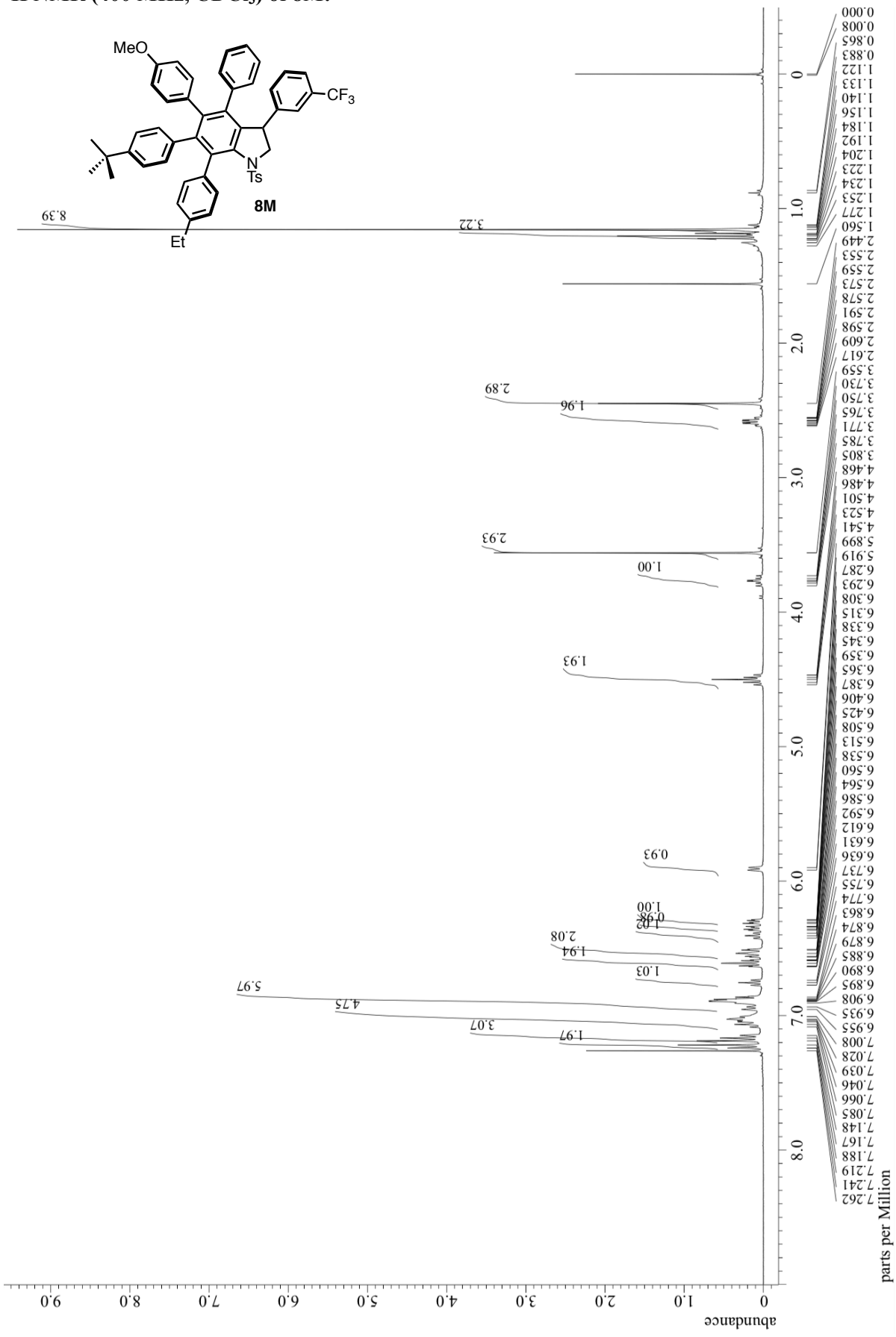


^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 140 °C) of 8L:

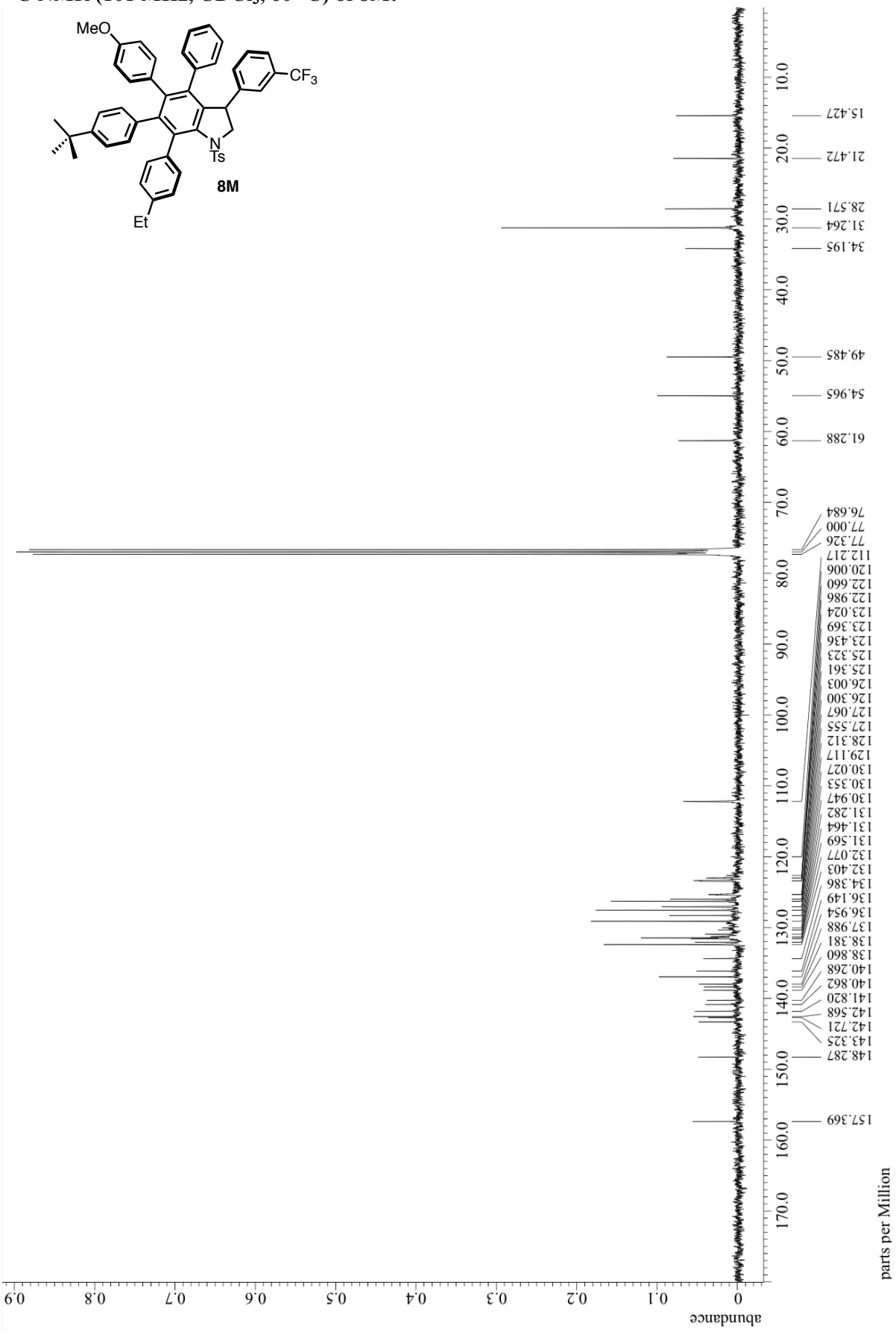


8L

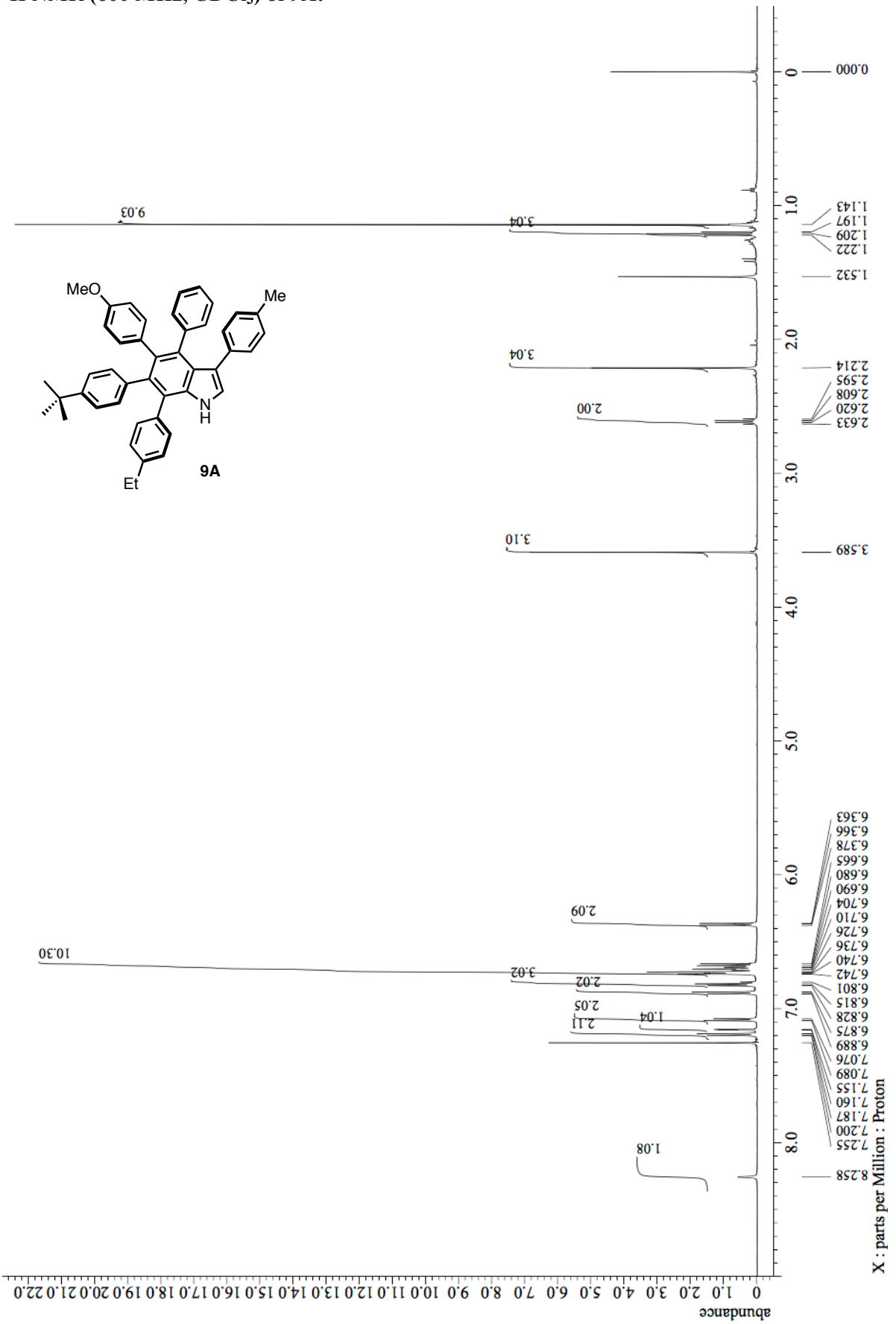
^{1}H NMR (400 MHz, $CDCl_3$) of 8M:



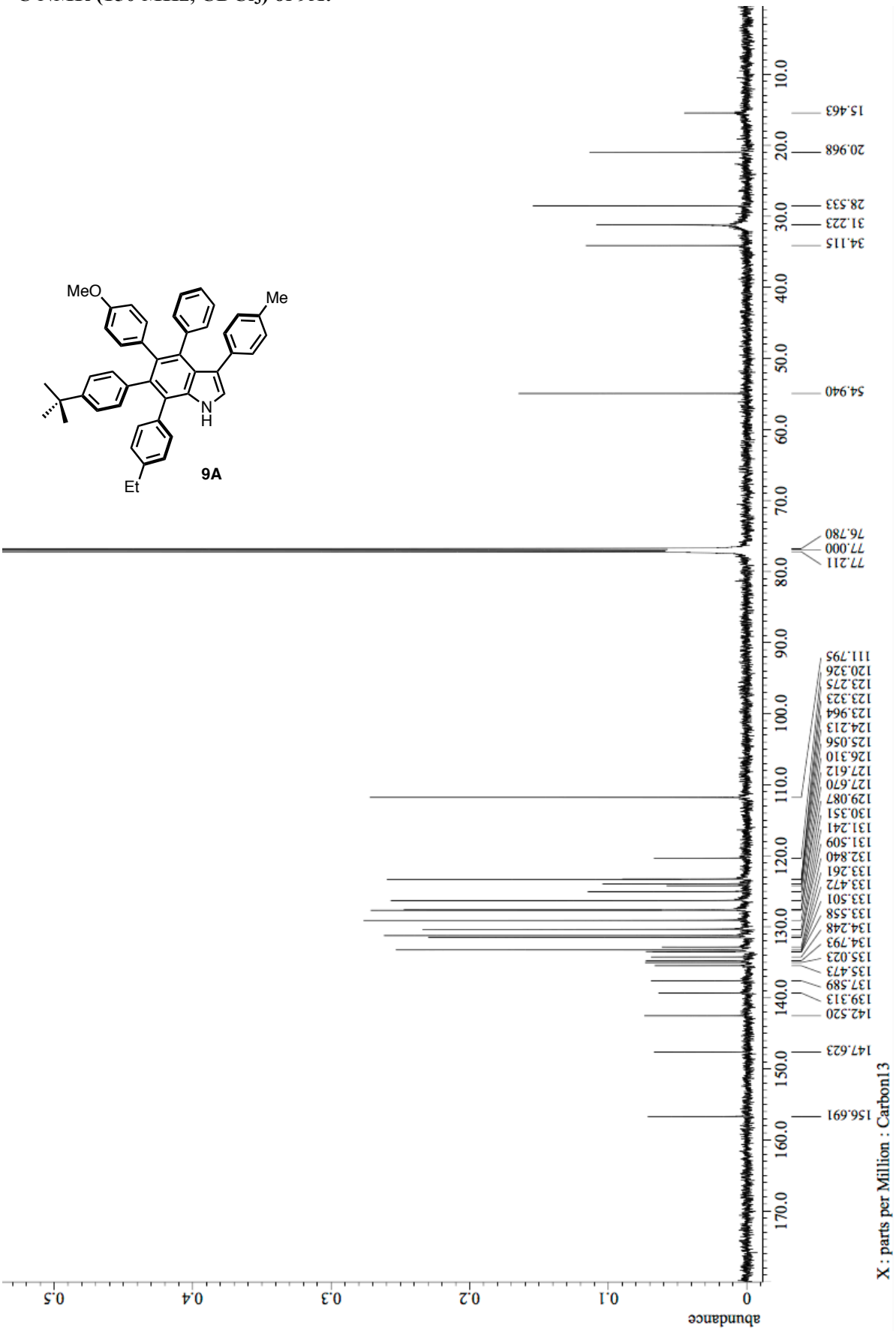
^{13}C NMR (101 MHz, $CDCl_3$, 60 °C) of 8M:



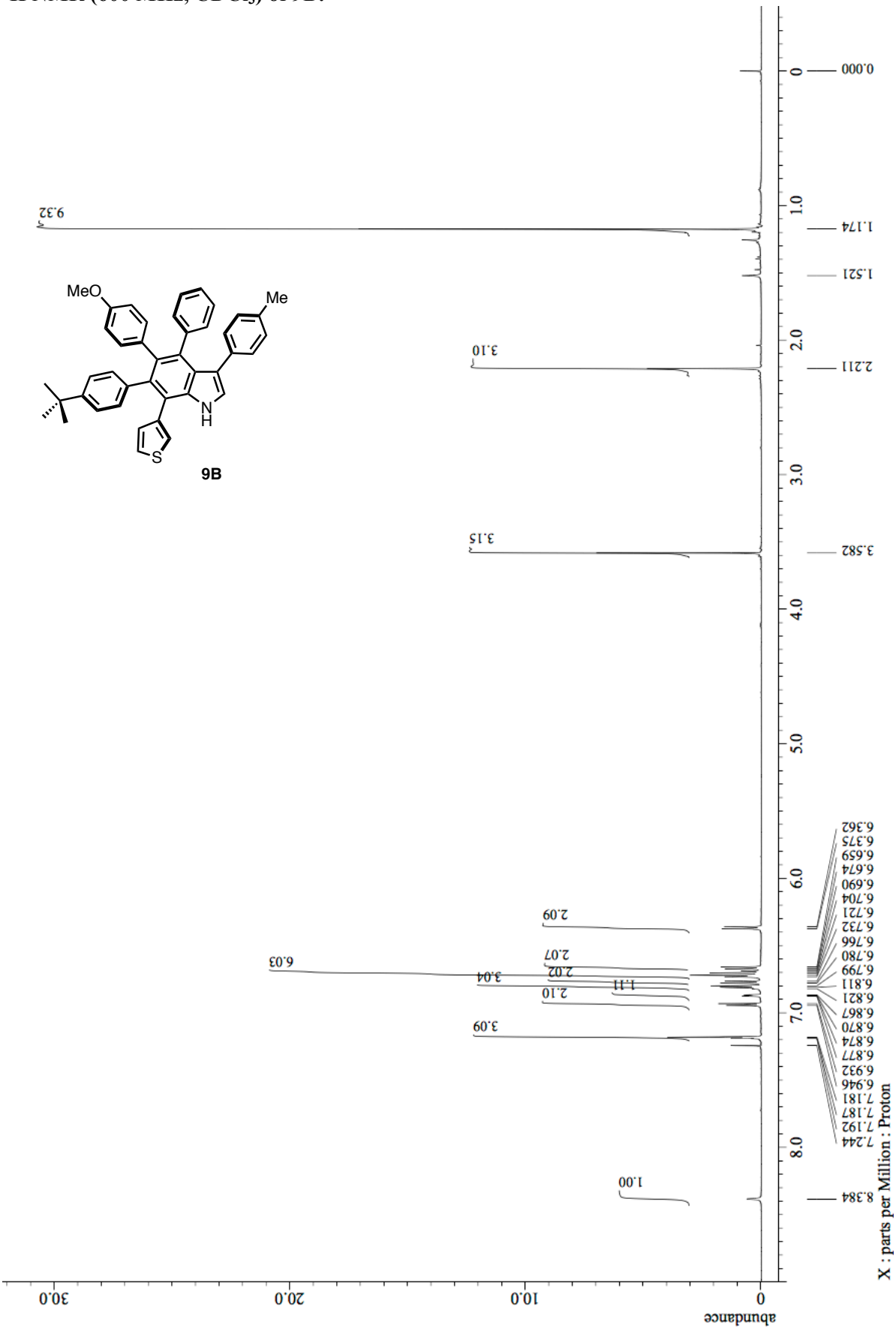
^{1}H NMR (600 MHz, $CDCl_3$) of 9A:



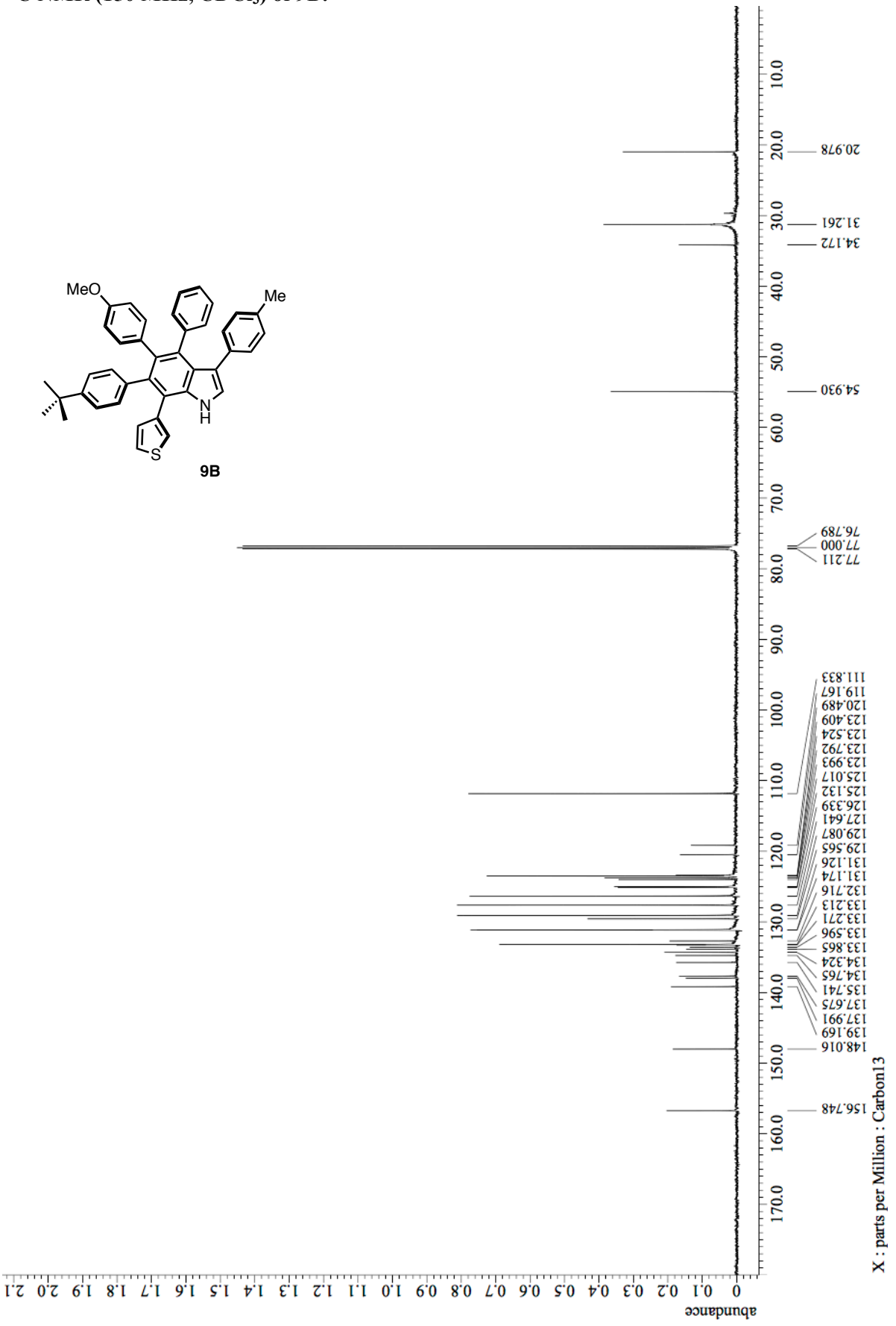
^{13}C NMR (150 MHz, $CDCl_3$) of 9A:



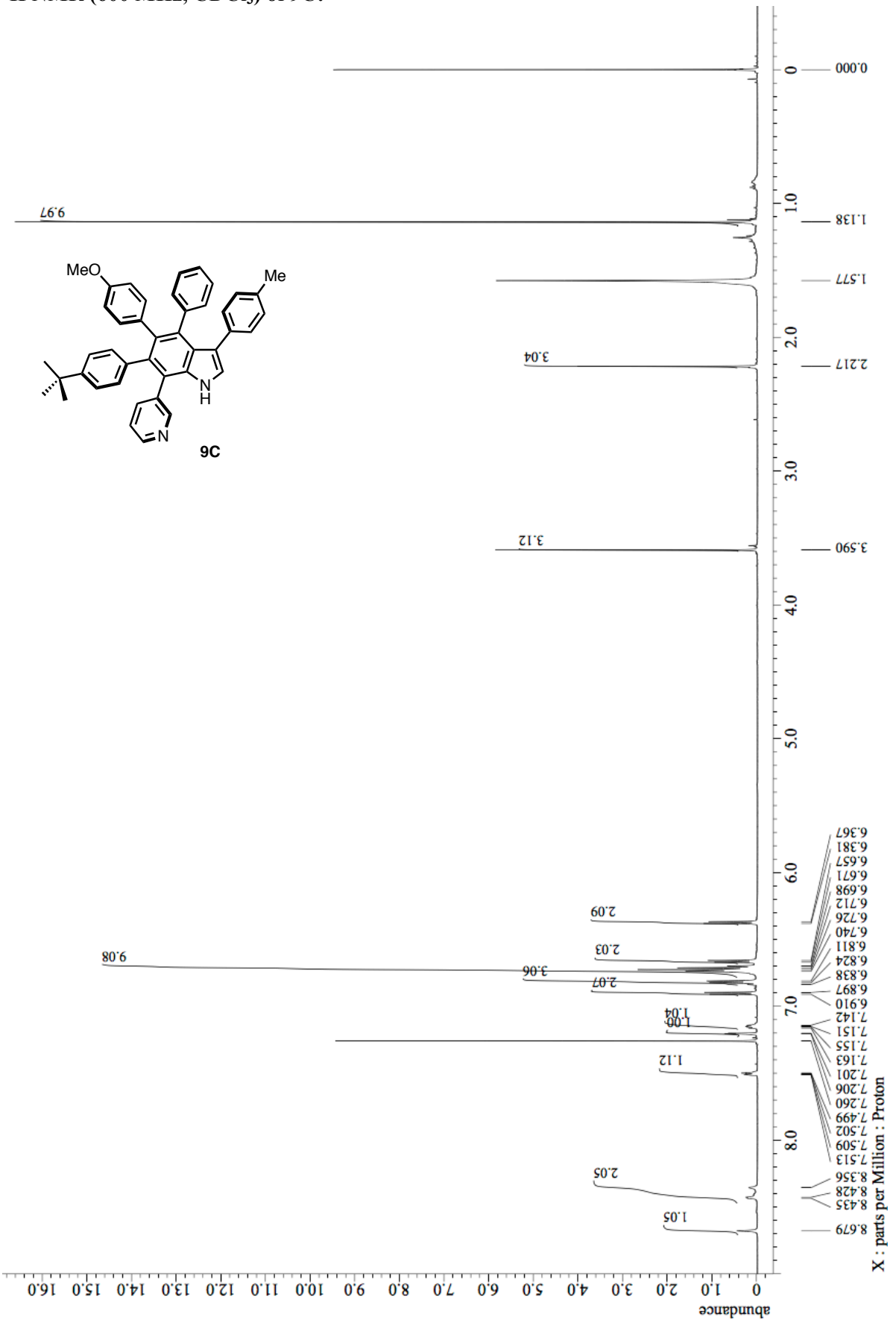
^{1}H NMR (600 MHz, $CDCl_3$) of 9B:



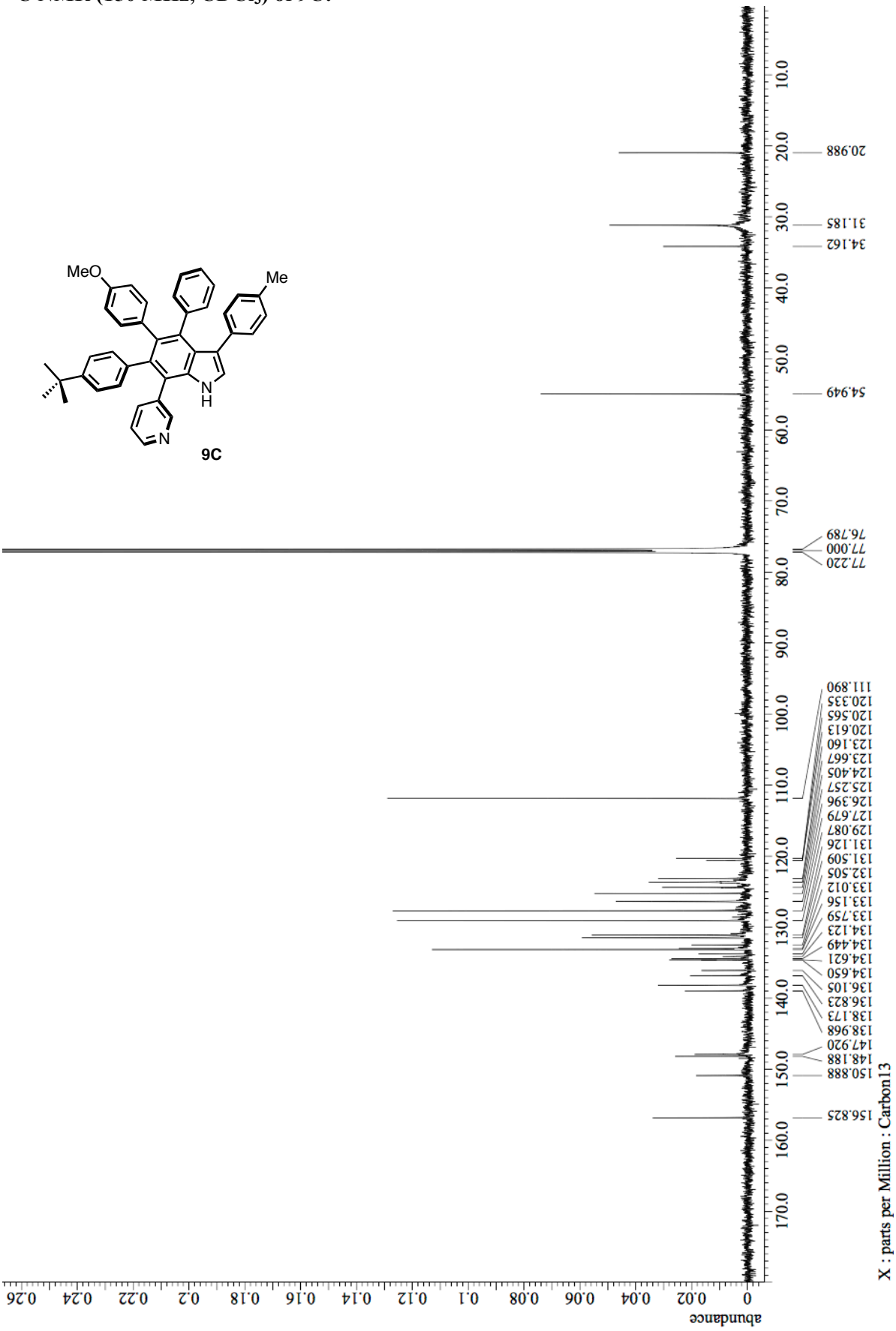
^{13}C NMR (150 MHz, $CDCl_3$) of 9B:



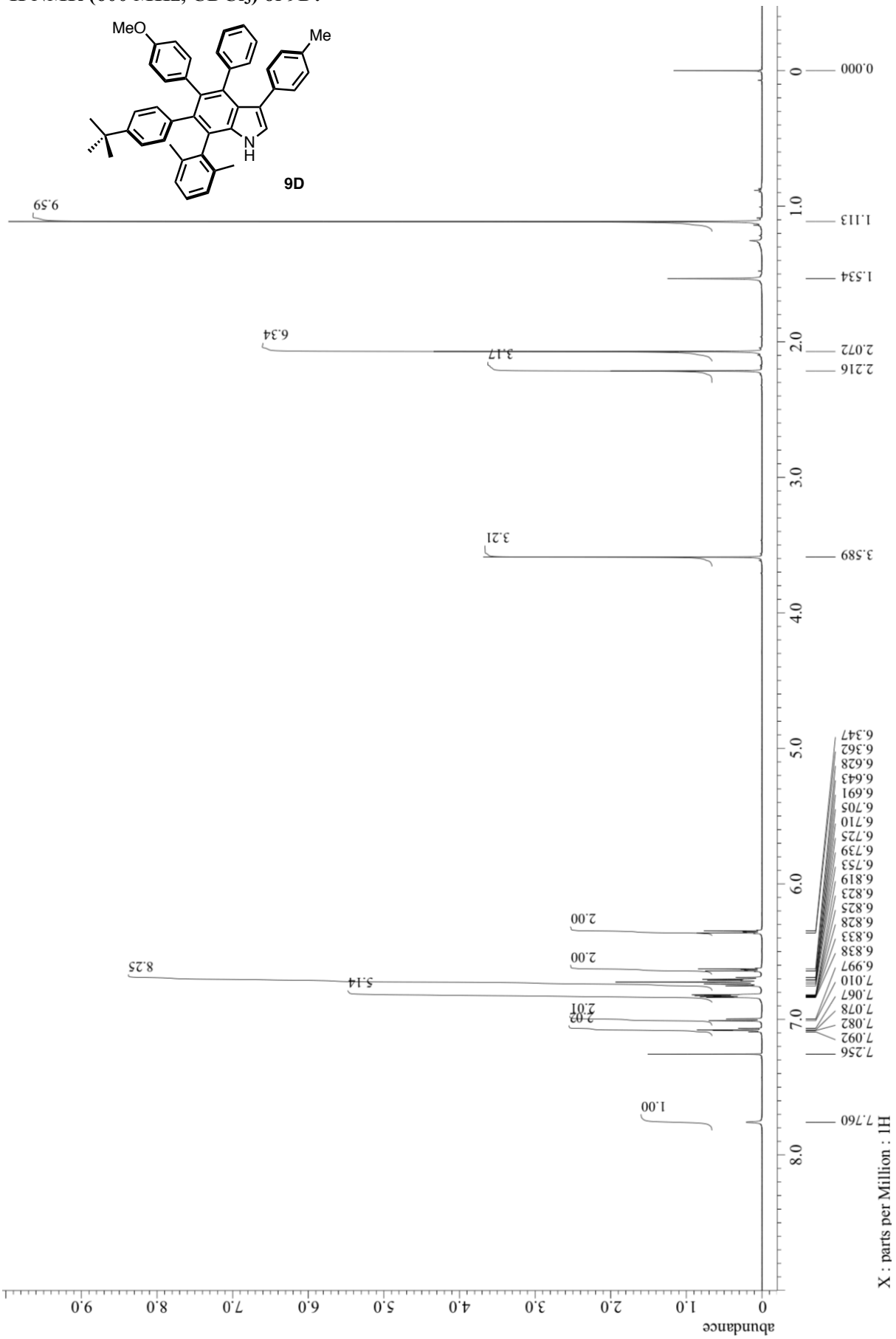
^{1}H NMR (600 MHz, $CDCl_3$) of 9C:



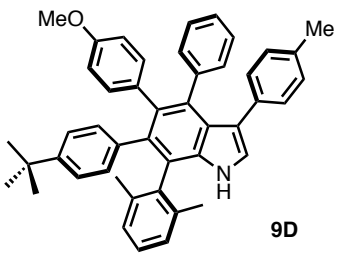
^{13}C NMR (150 MHz, $CDCl_3$) of 9C:



^{1}H NMR (600 MHz, $CDCl_3$) of 9D:

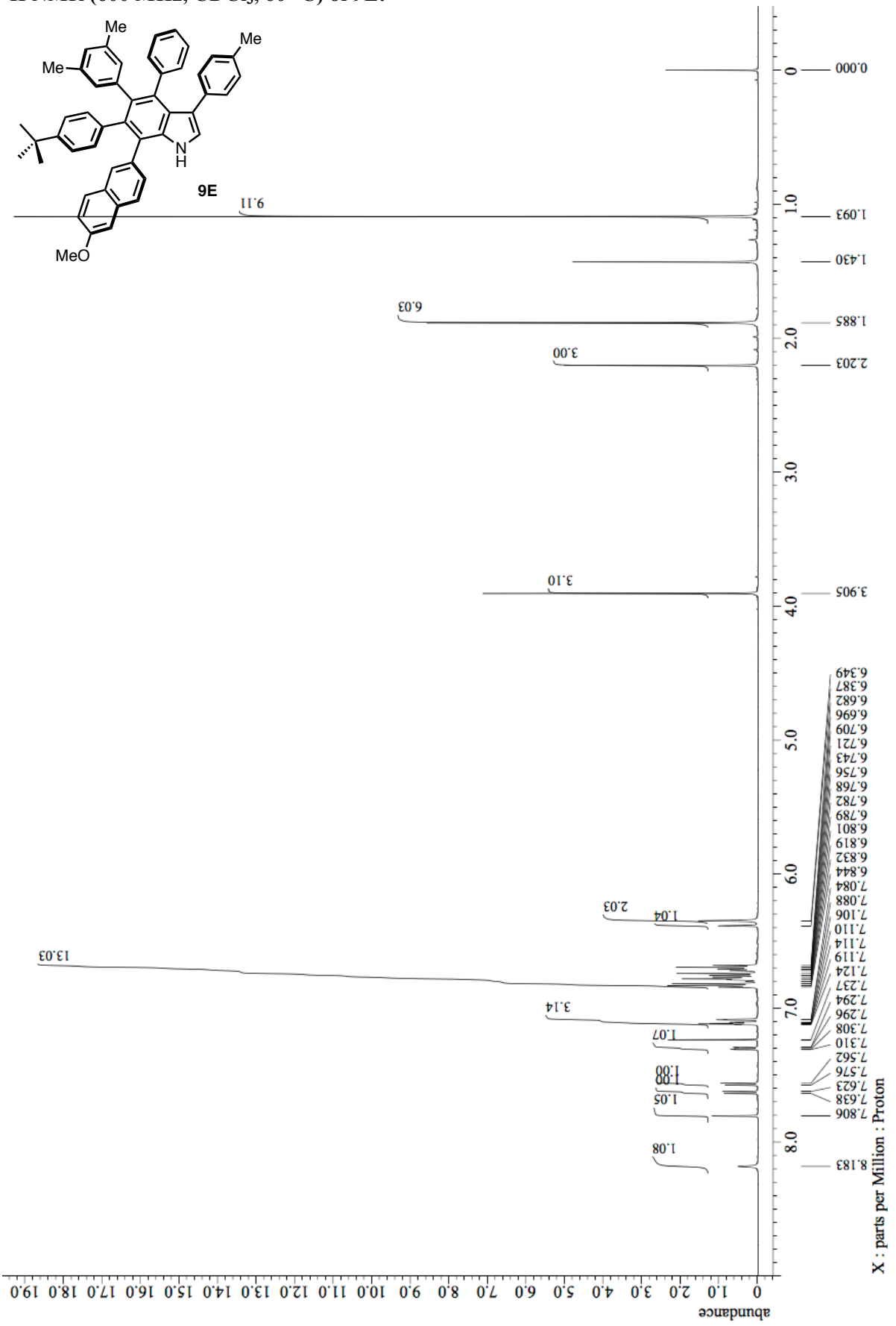


^{13}C NMR (150 MHz, $CDCl_3$) of 9D:

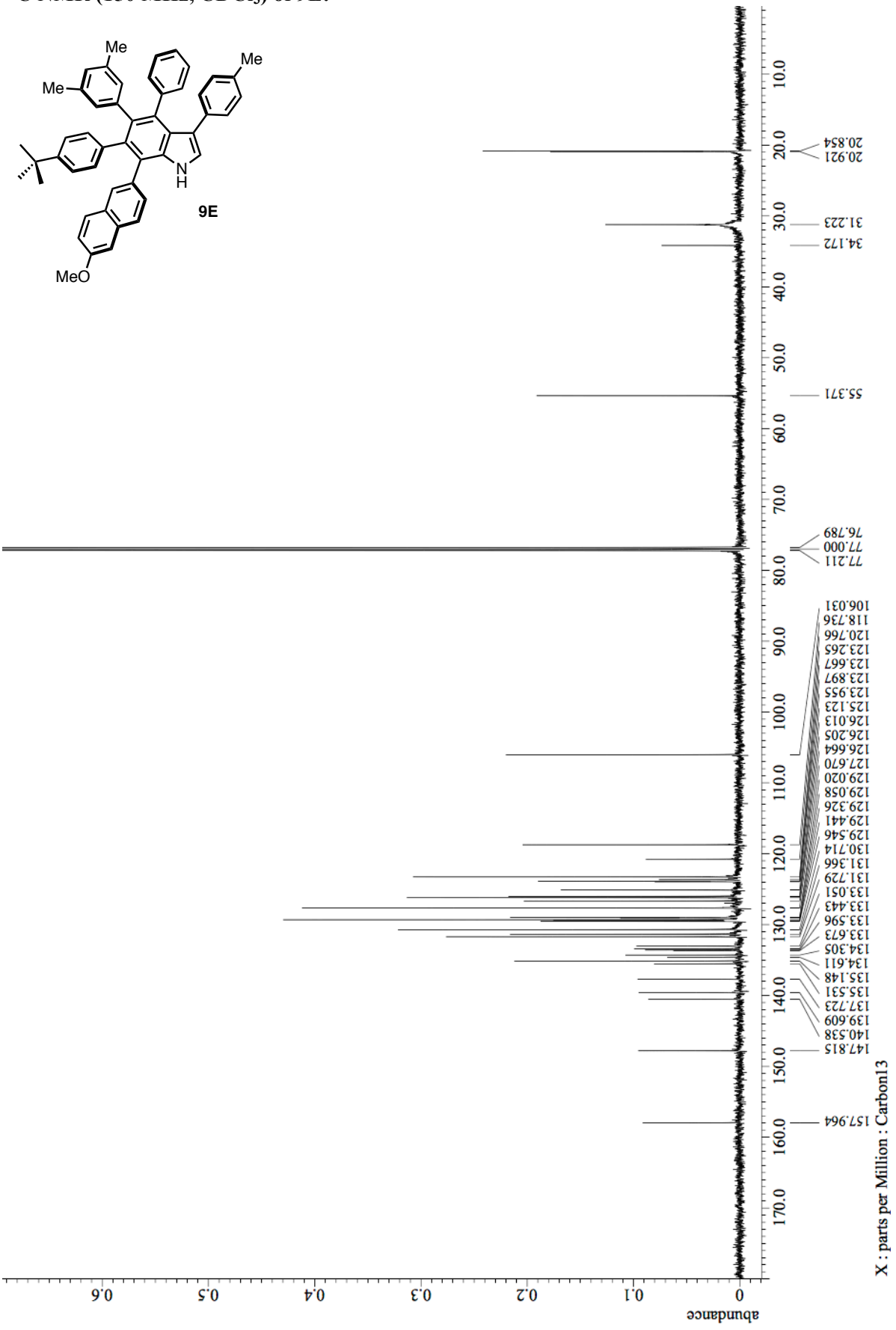


9D

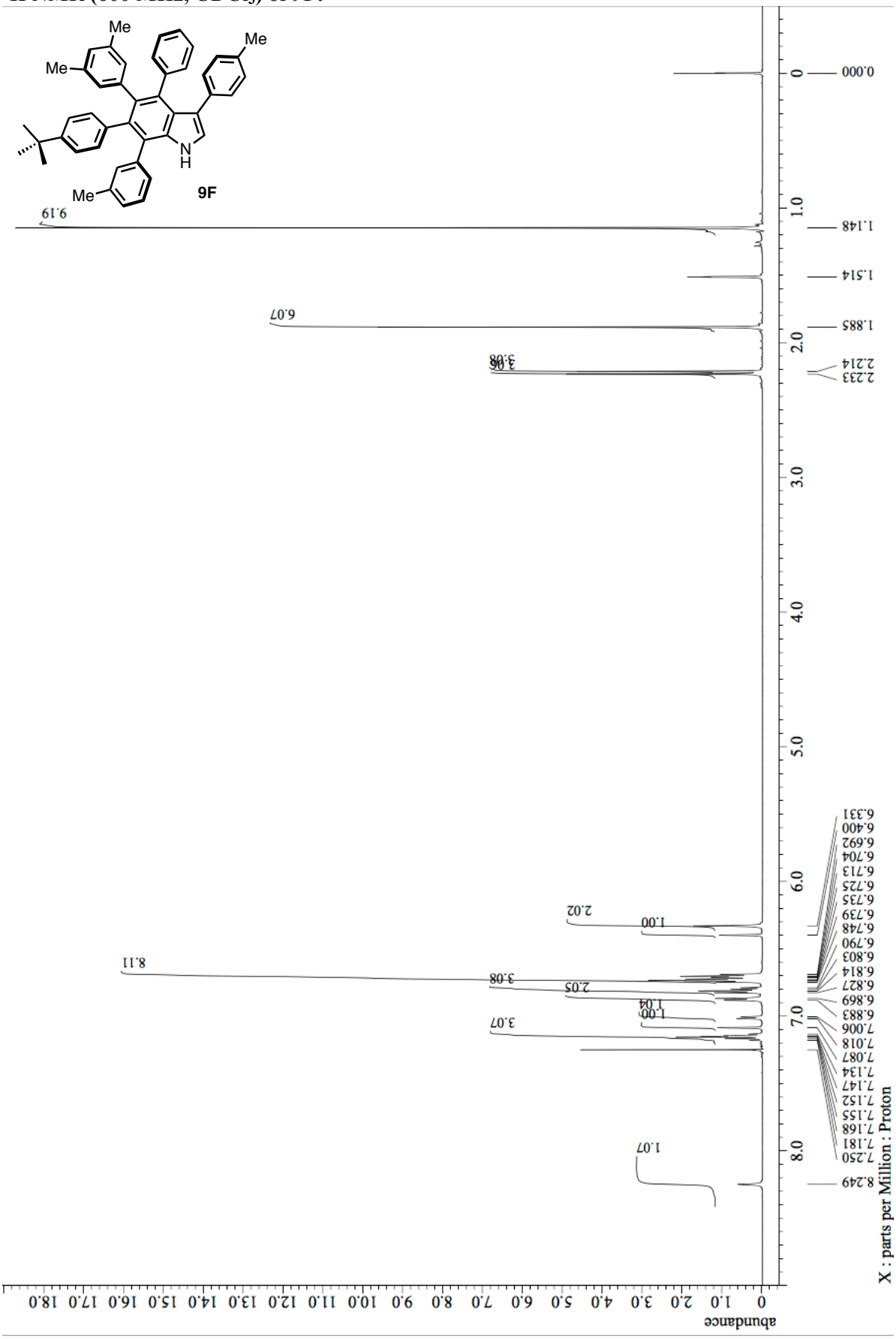
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 9E:



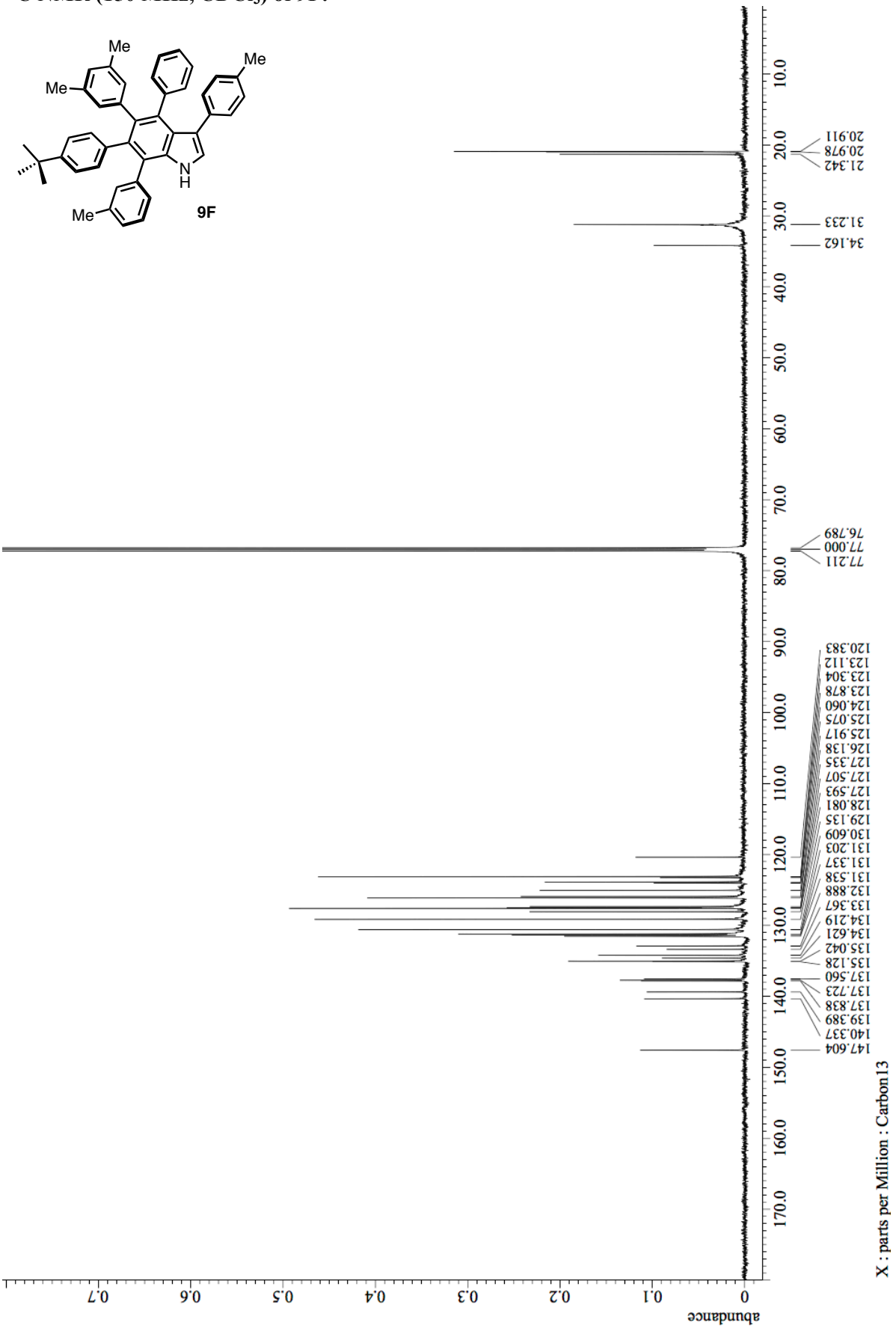
^{13}C NMR (150 MHz, $CDCl_3$) of 9E:



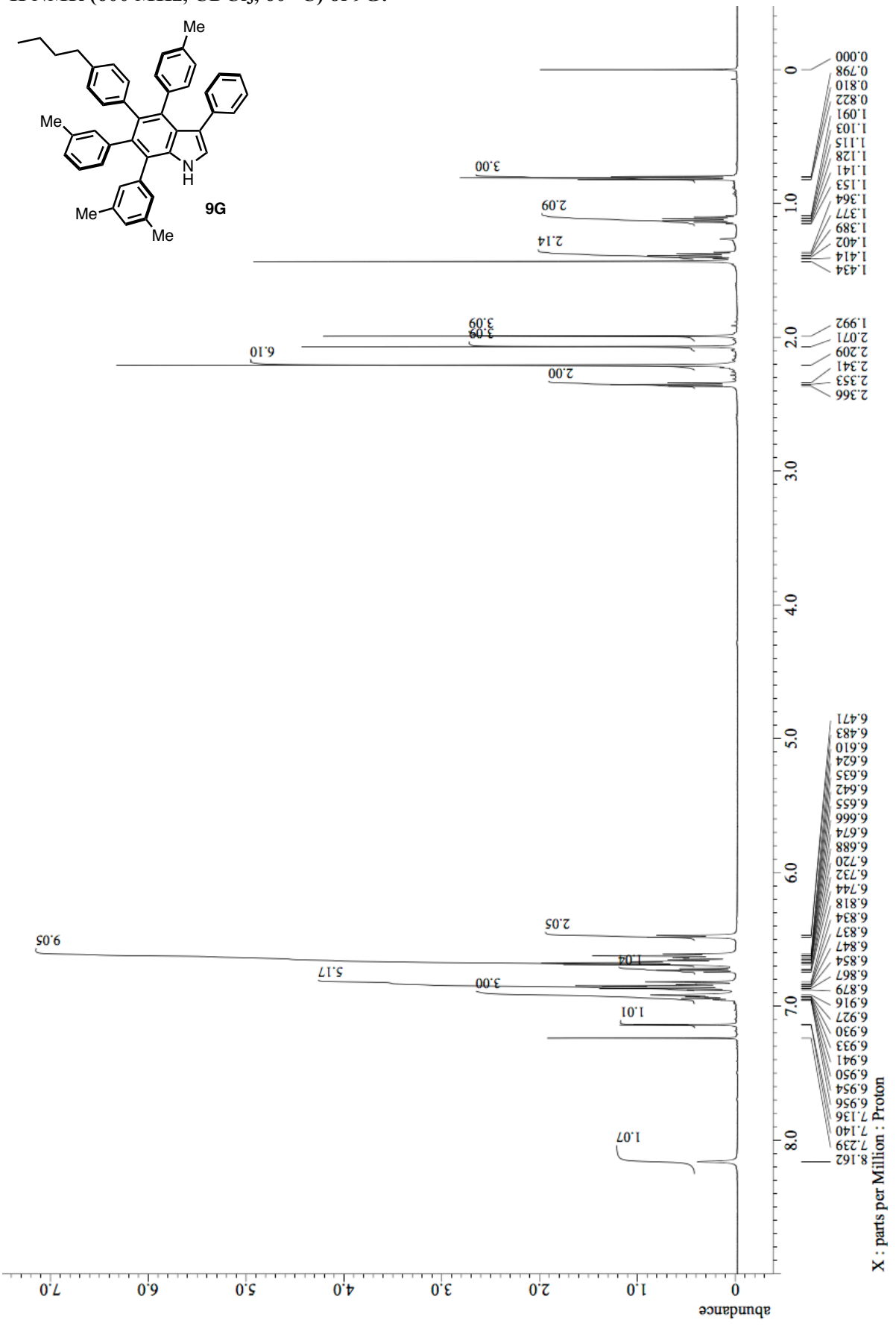
^{1}H NMR (600 MHz, $CDCl_3$) of 9F:



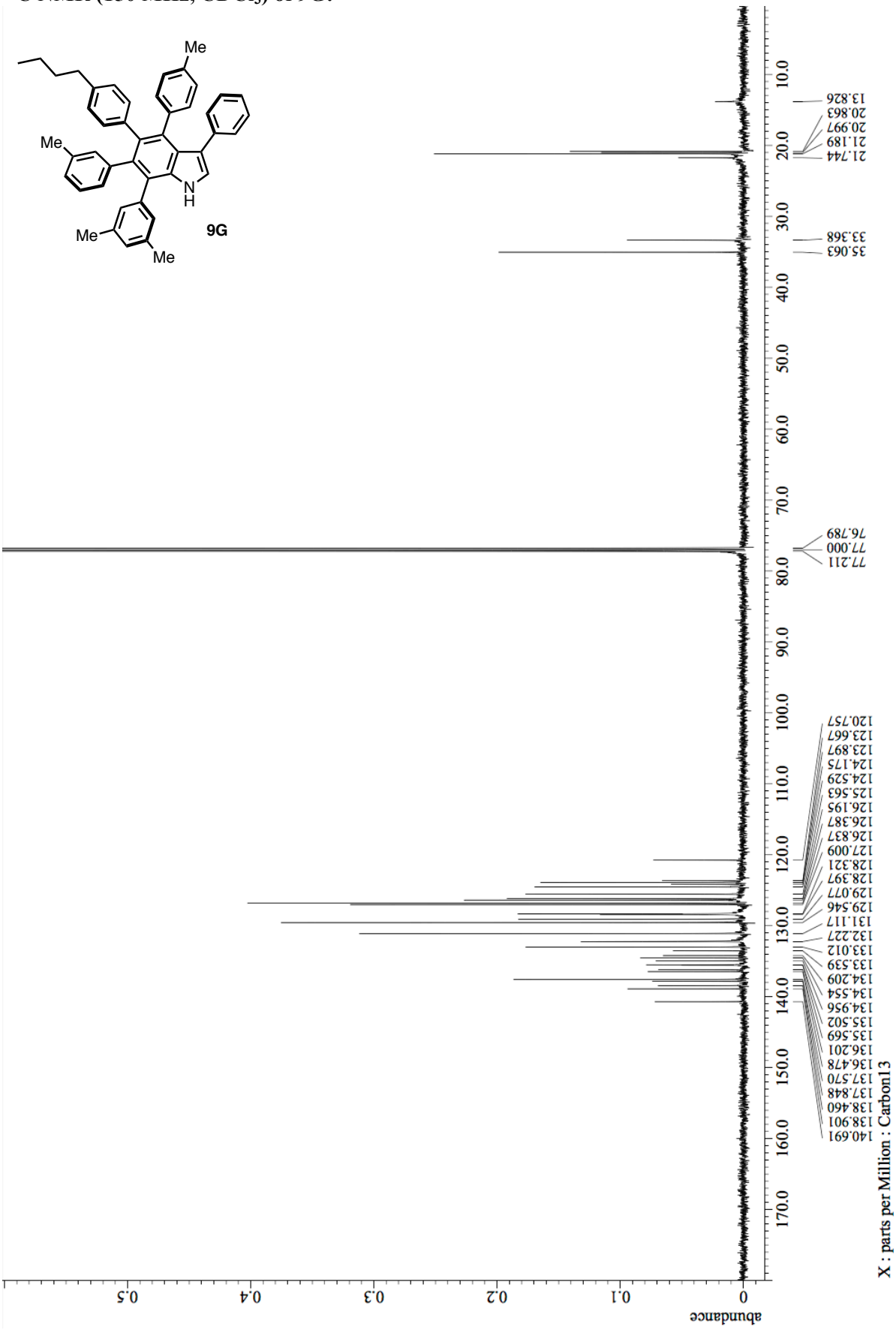
^{13}C NMR (150 MHz, $CDCl_3$) of 9F:



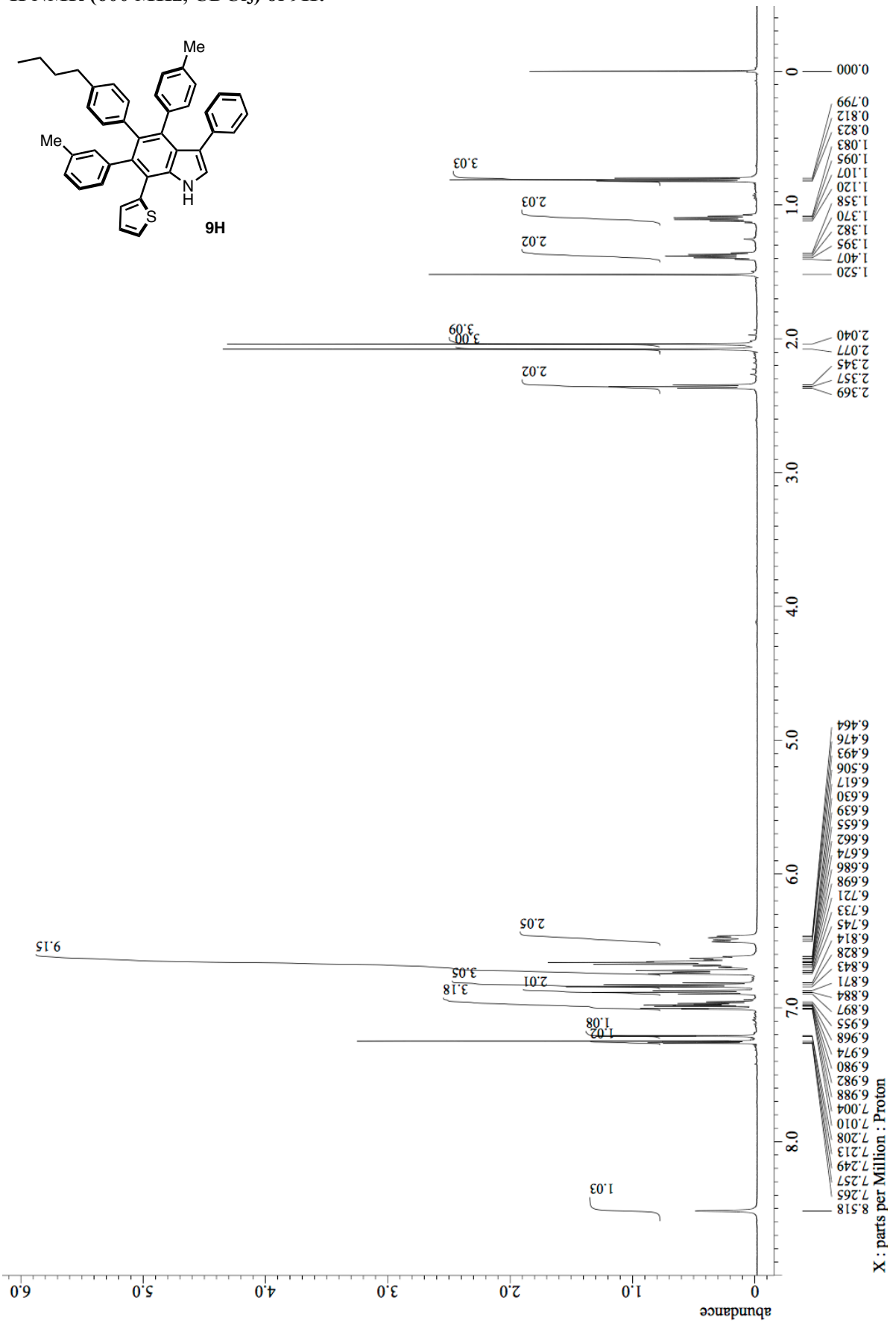
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 9G:



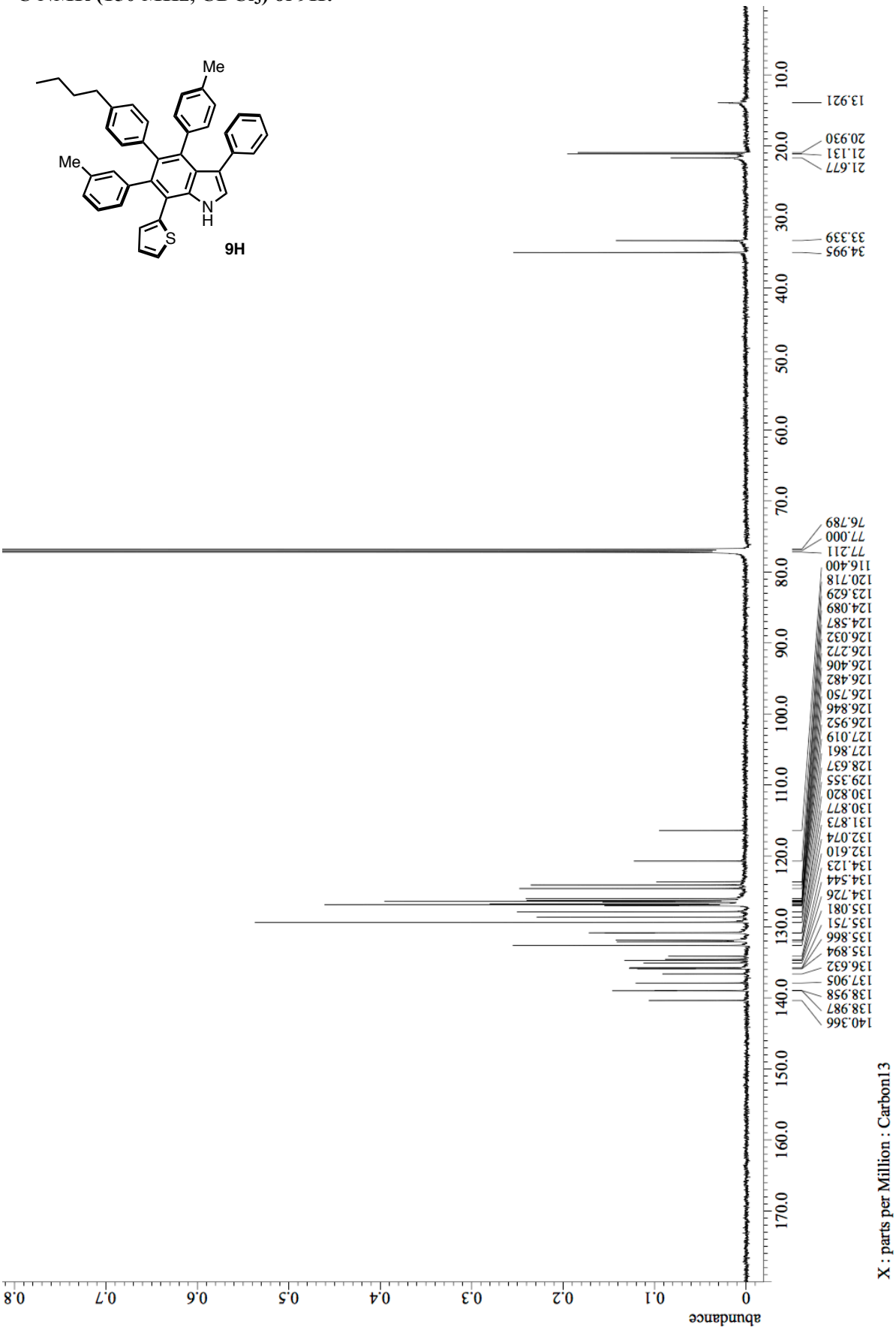
^{13}C NMR (150 MHz, $CDCl_3$) of 9G:



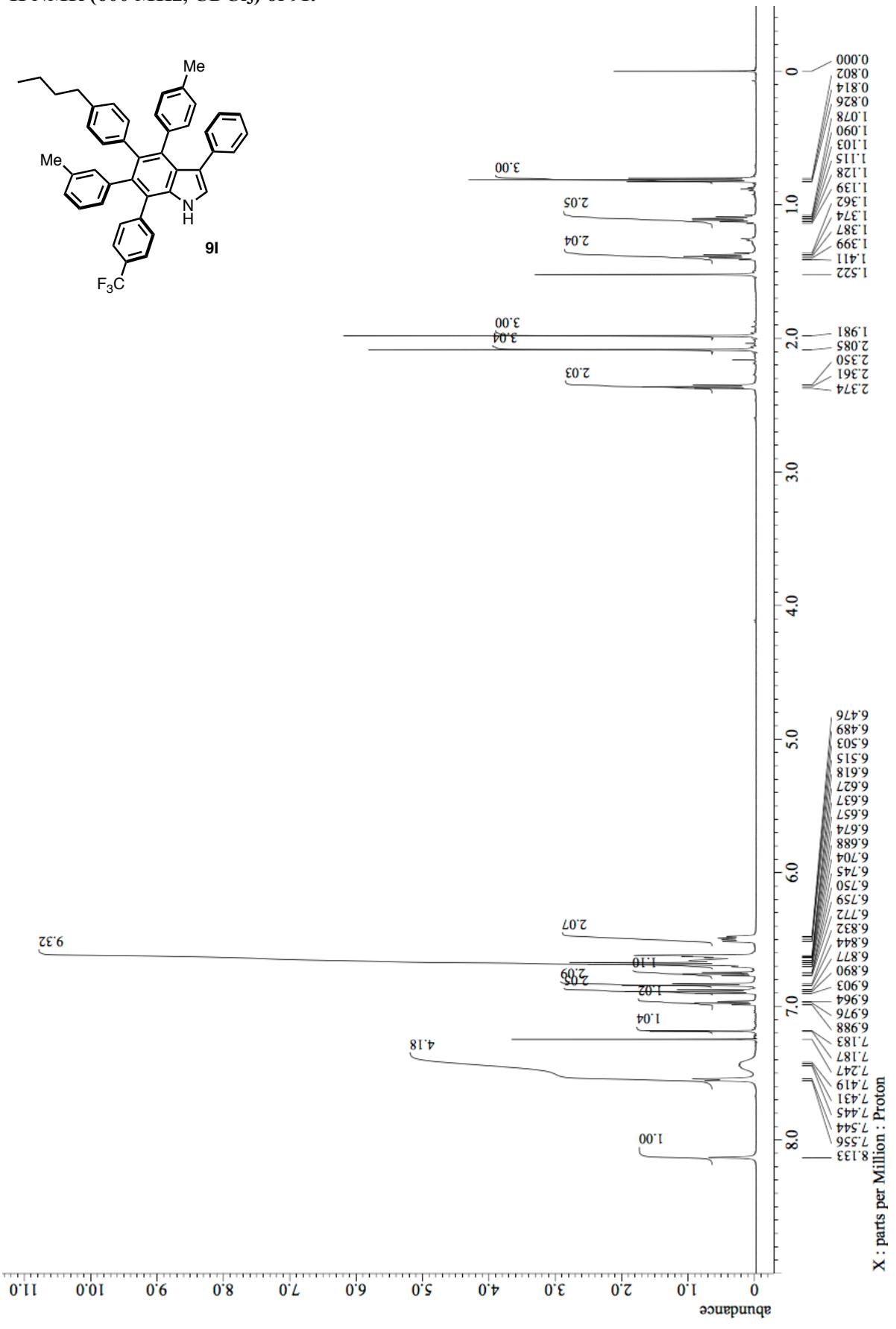
^{1}H NMR (600 MHz, $CDCl_3$) of 9H:



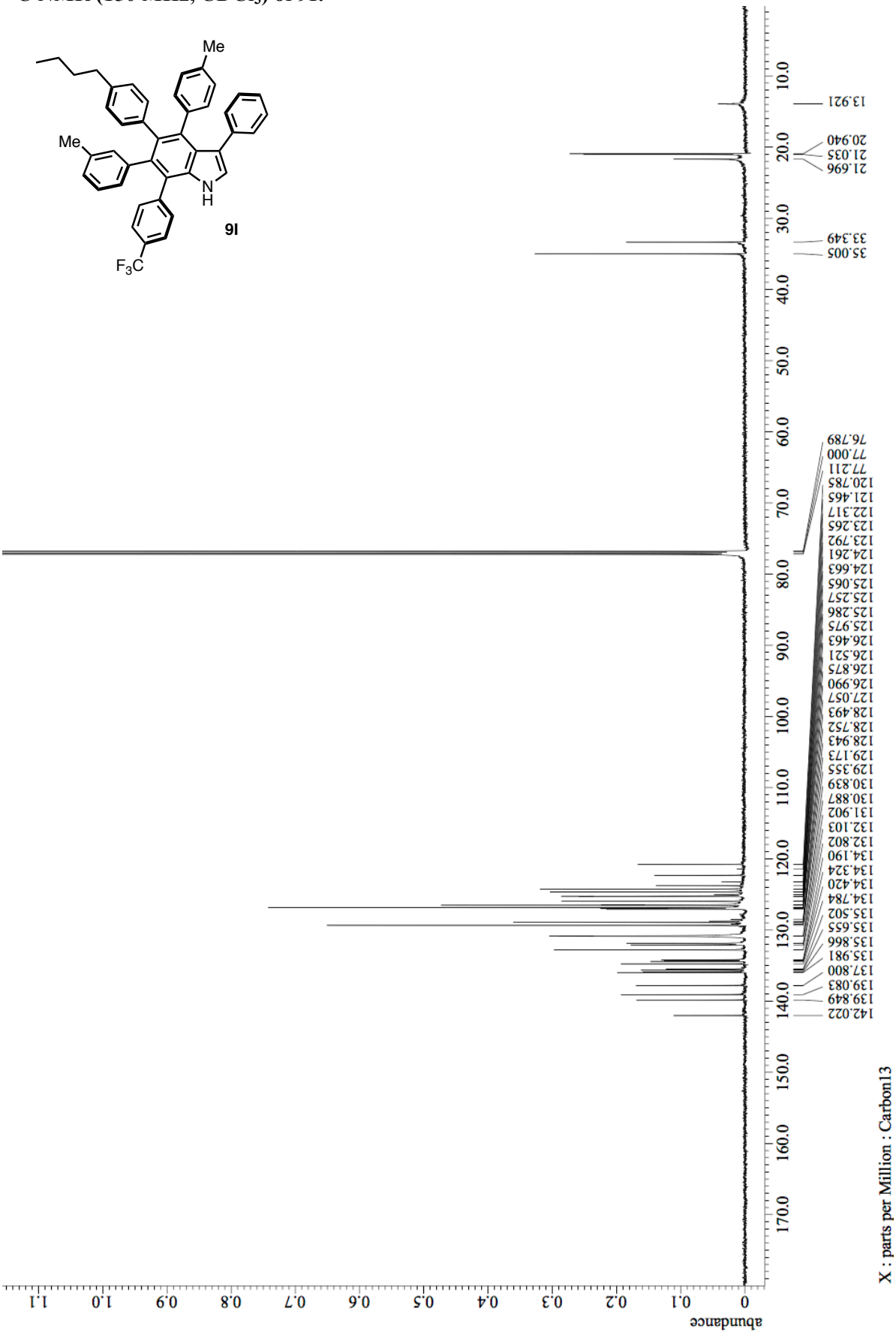
^{13}C NMR (150 MHz, $CDCl_3$) of 9H:



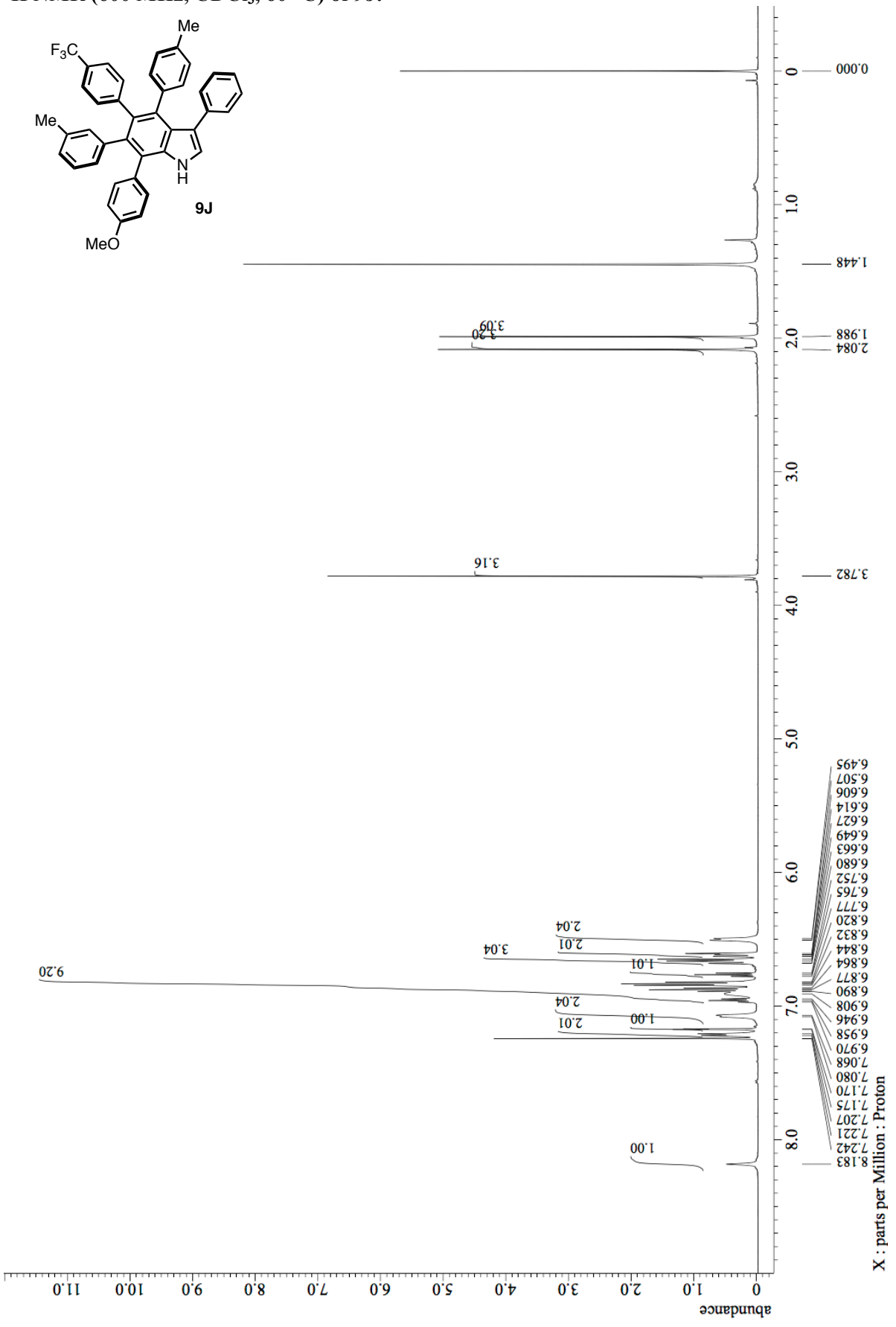
^{1}H NMR (600 MHz, $CDCl_3$) of 9I:



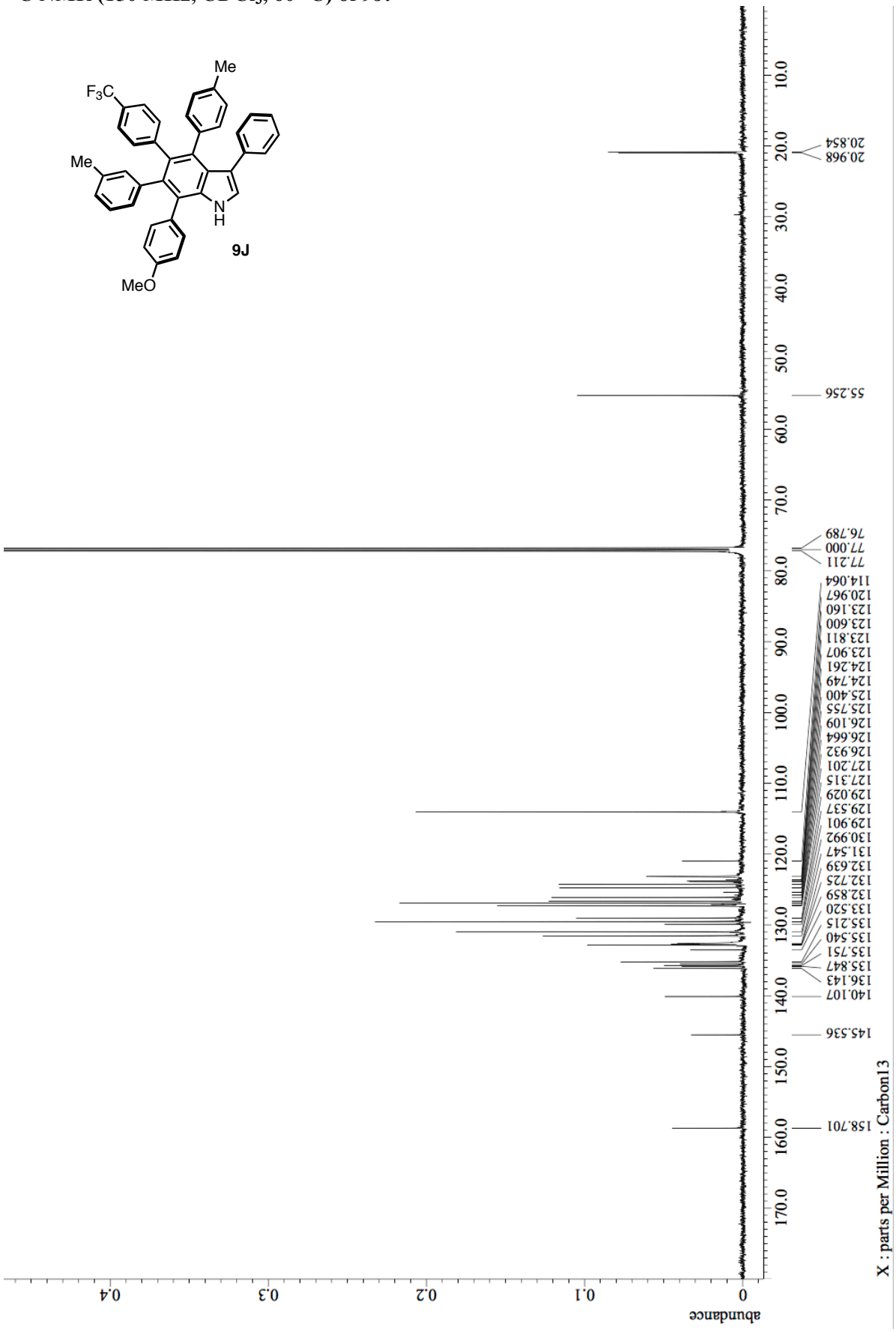
^{13}C NMR (150 MHz, $CDCl_3$) of 9I:



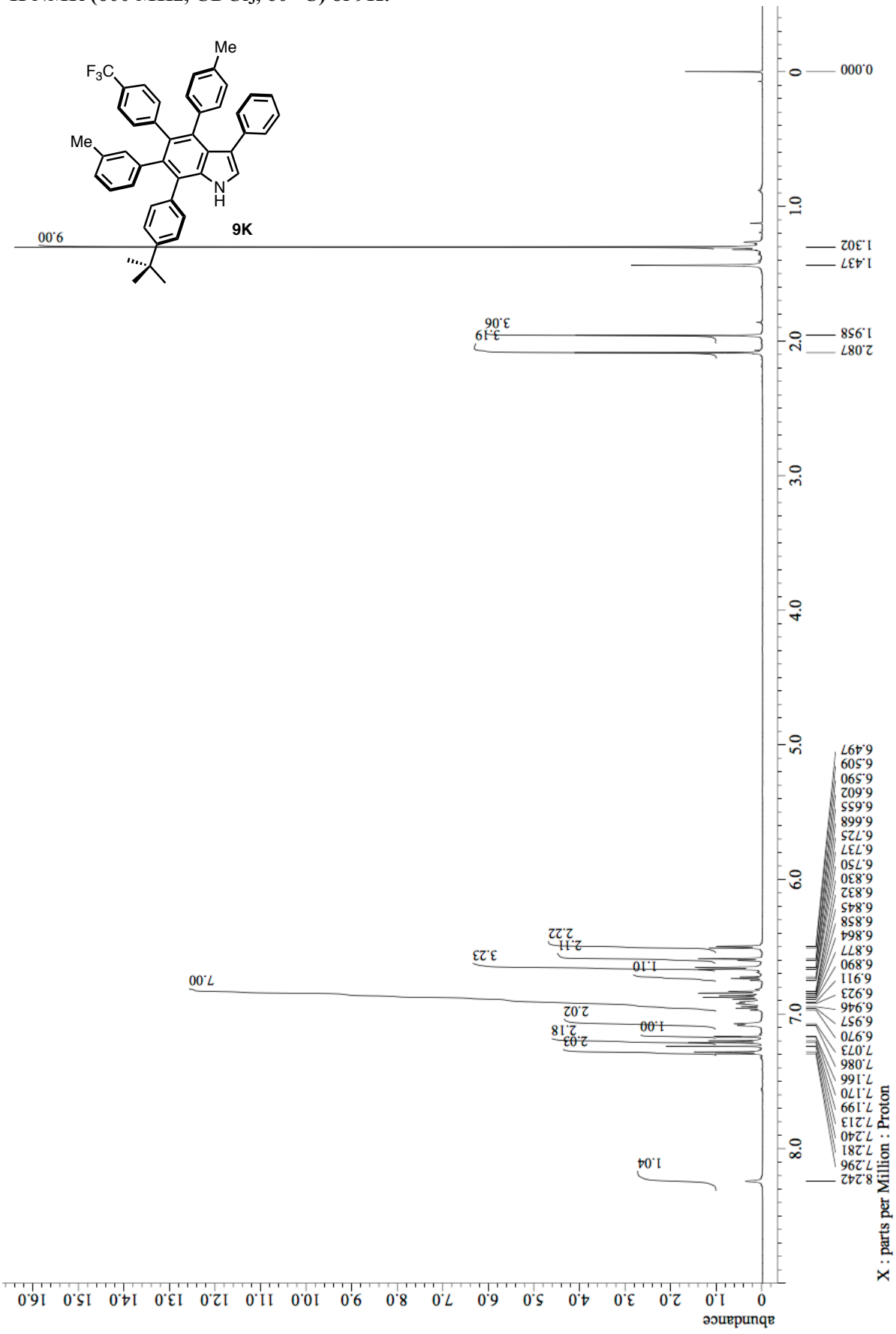
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 9J:



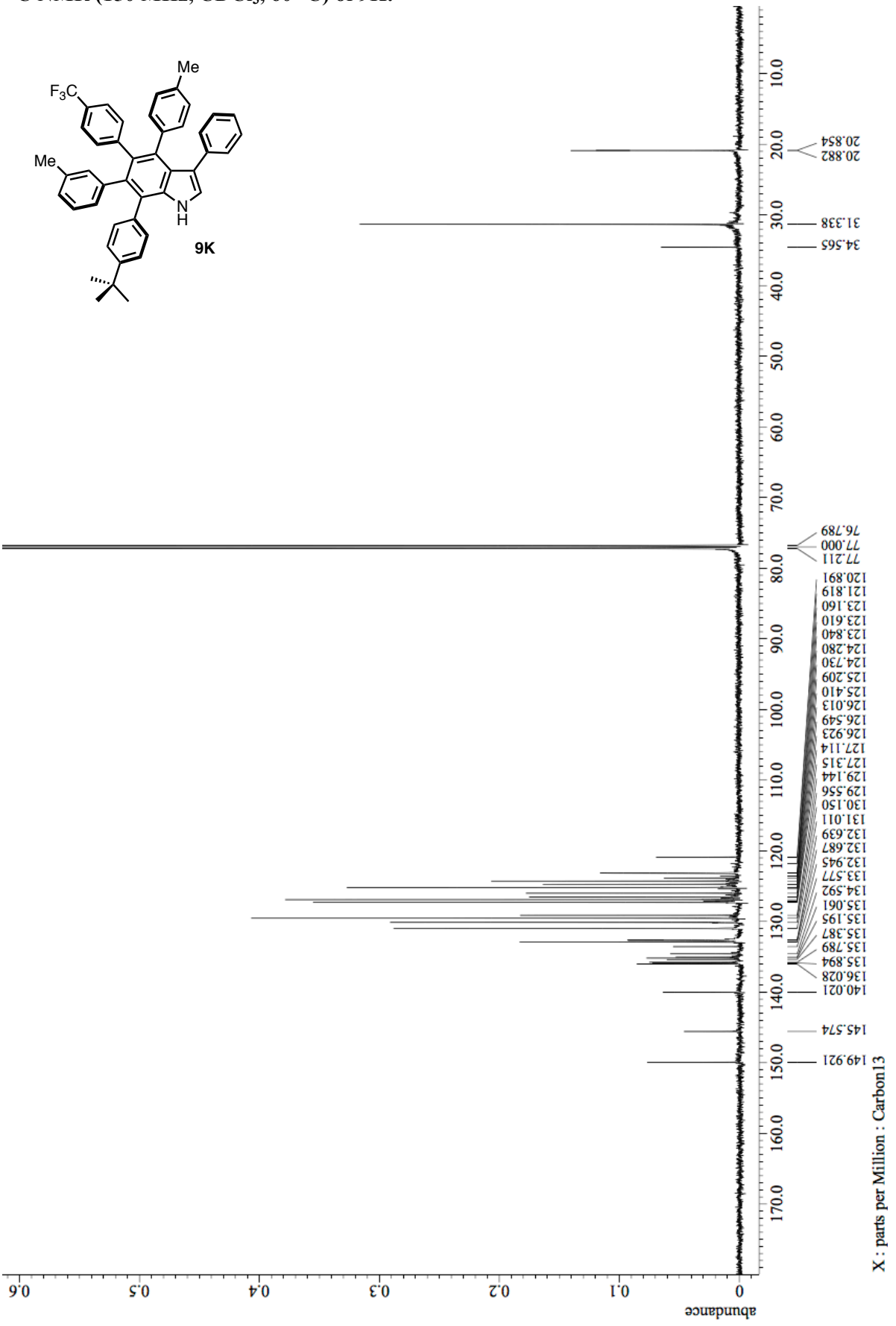
^{13}C NMR (150 MHz, $CDCl_3$, 60 °C) of 9J:



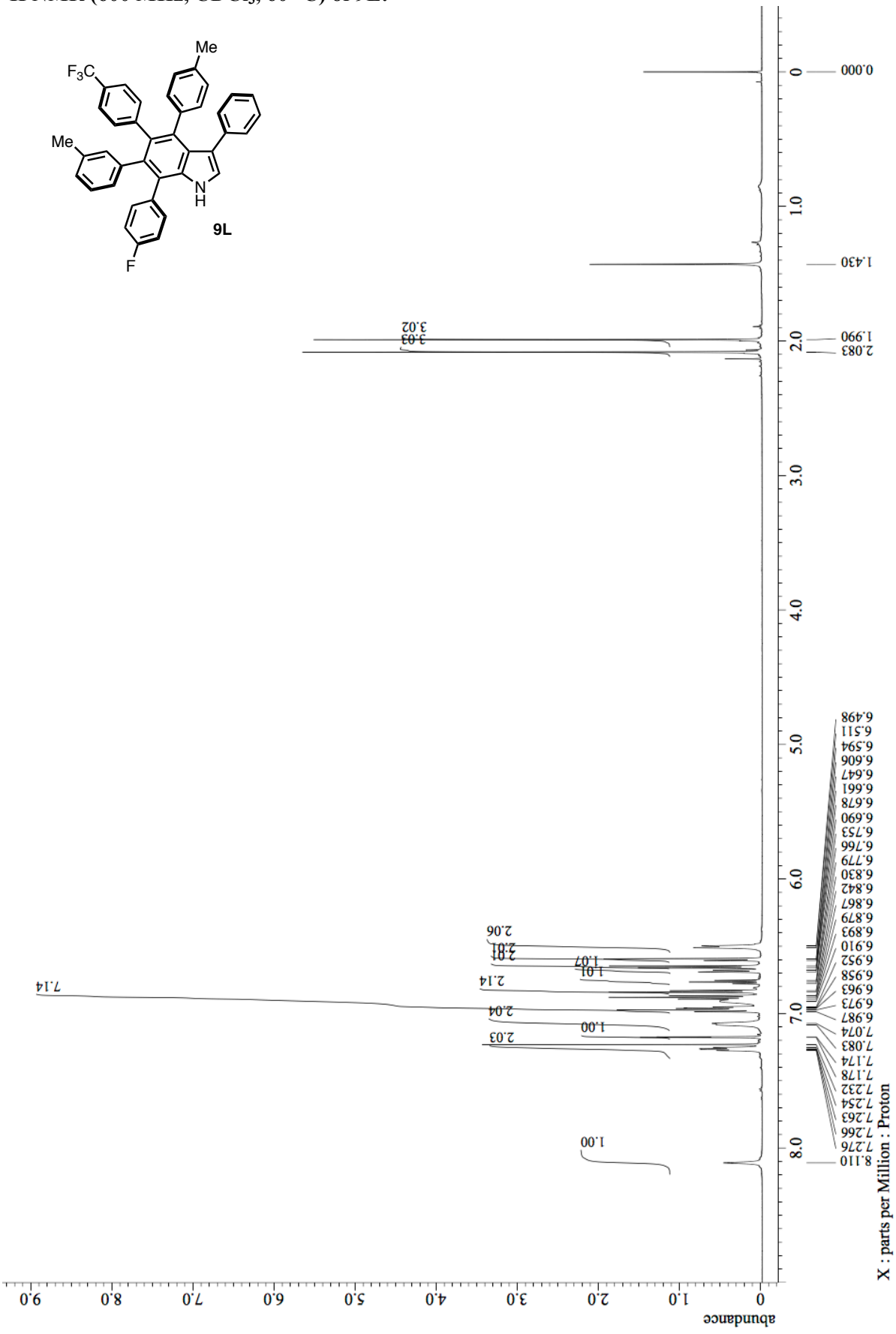
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 9K:



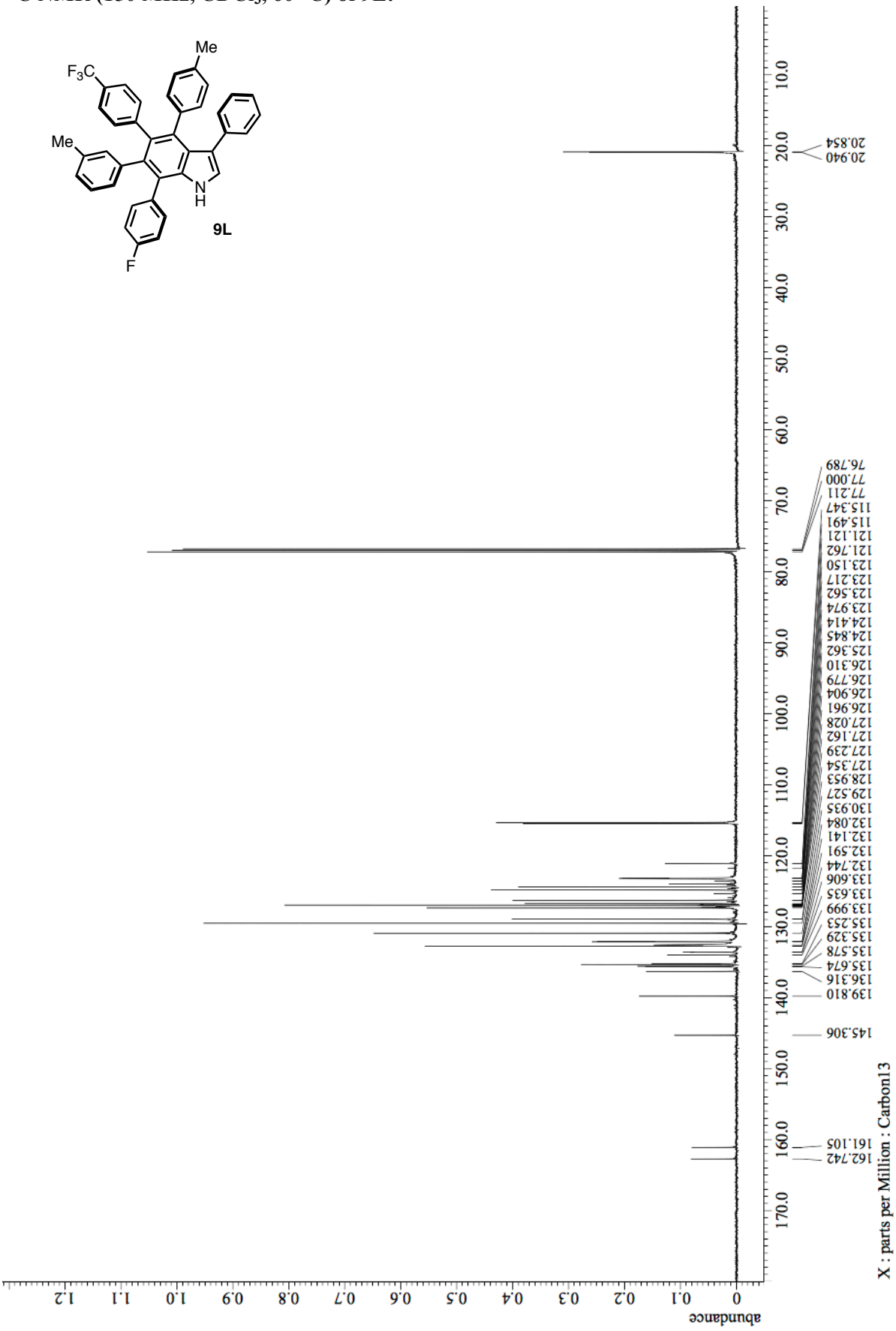
^{13}C NMR (150 MHz, $CDCl_3$, 60 °C) of 9K:



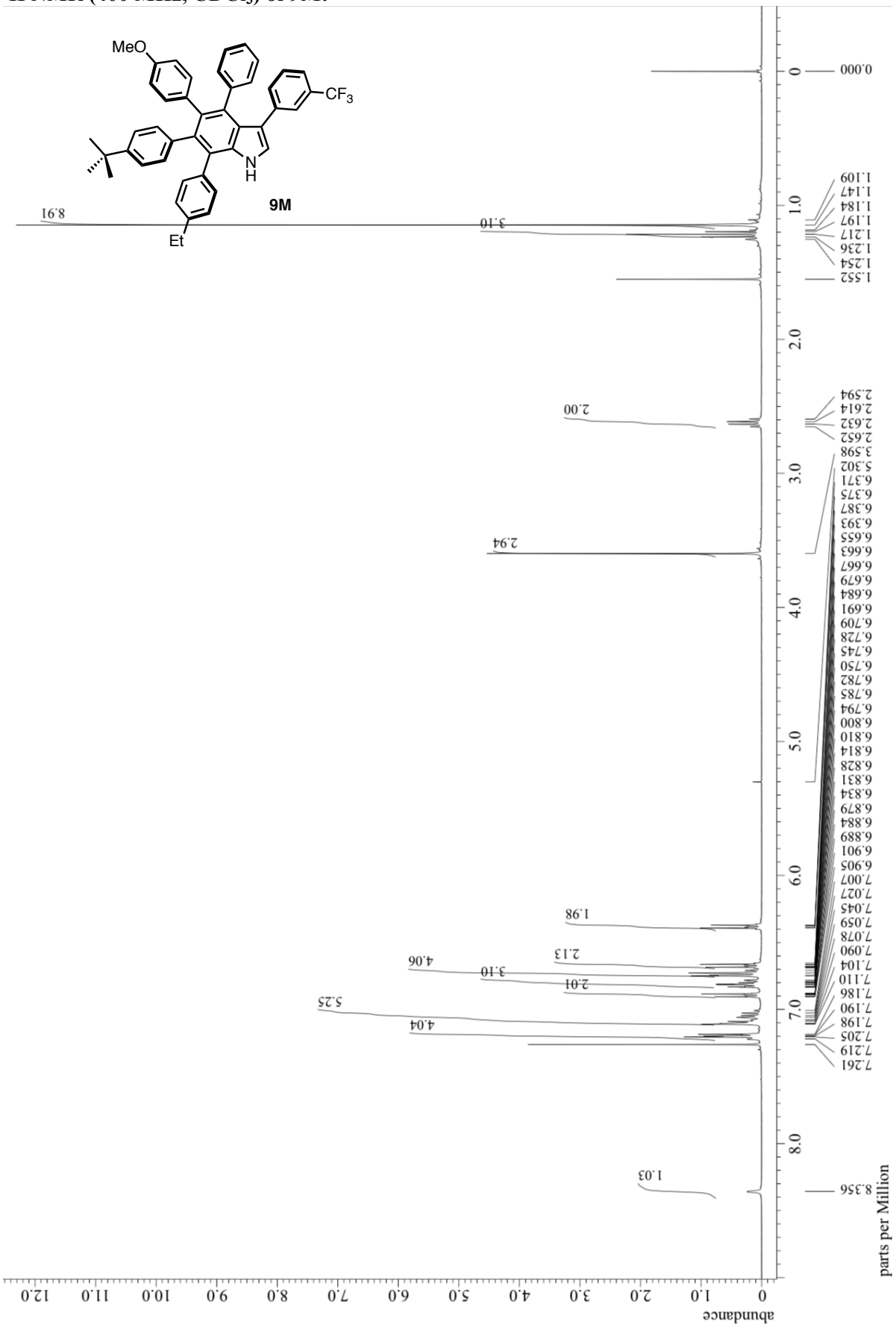
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 9L:



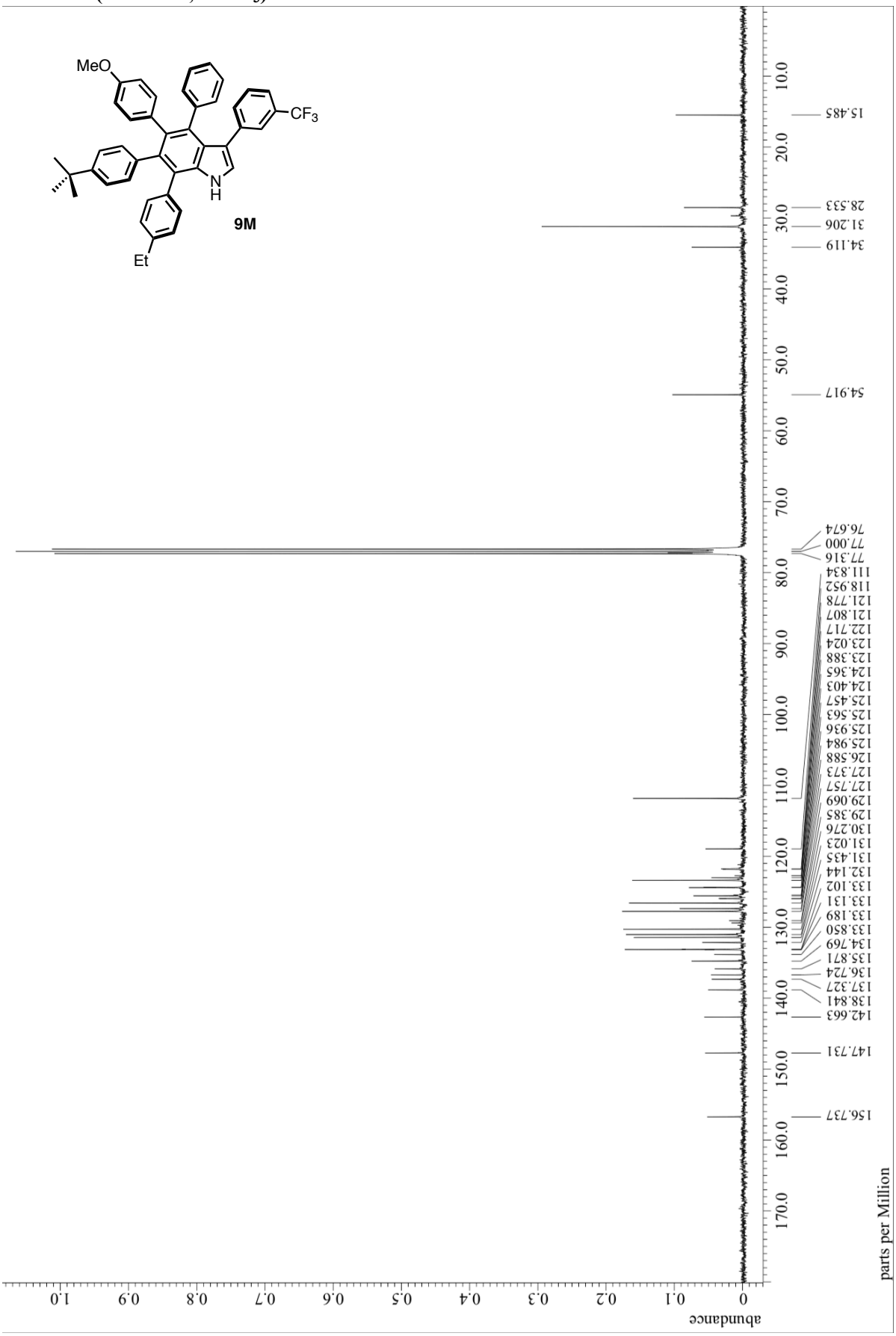
^{13}C NMR (150 MHz, $CDCl_3$, 60 °C) of 9L:



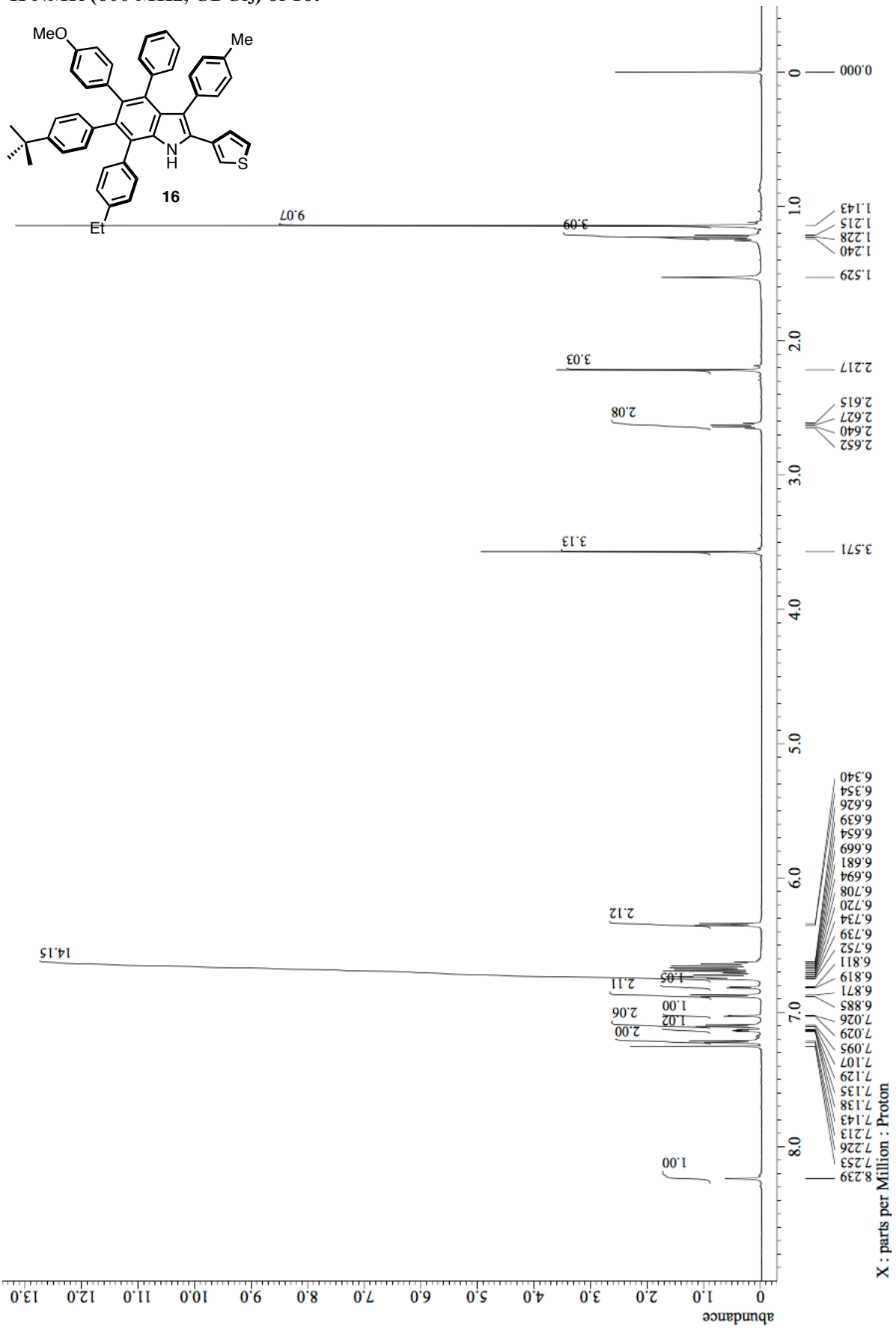
^{1}H NMR (400 MHz, $CDCl_3$) of 9M:



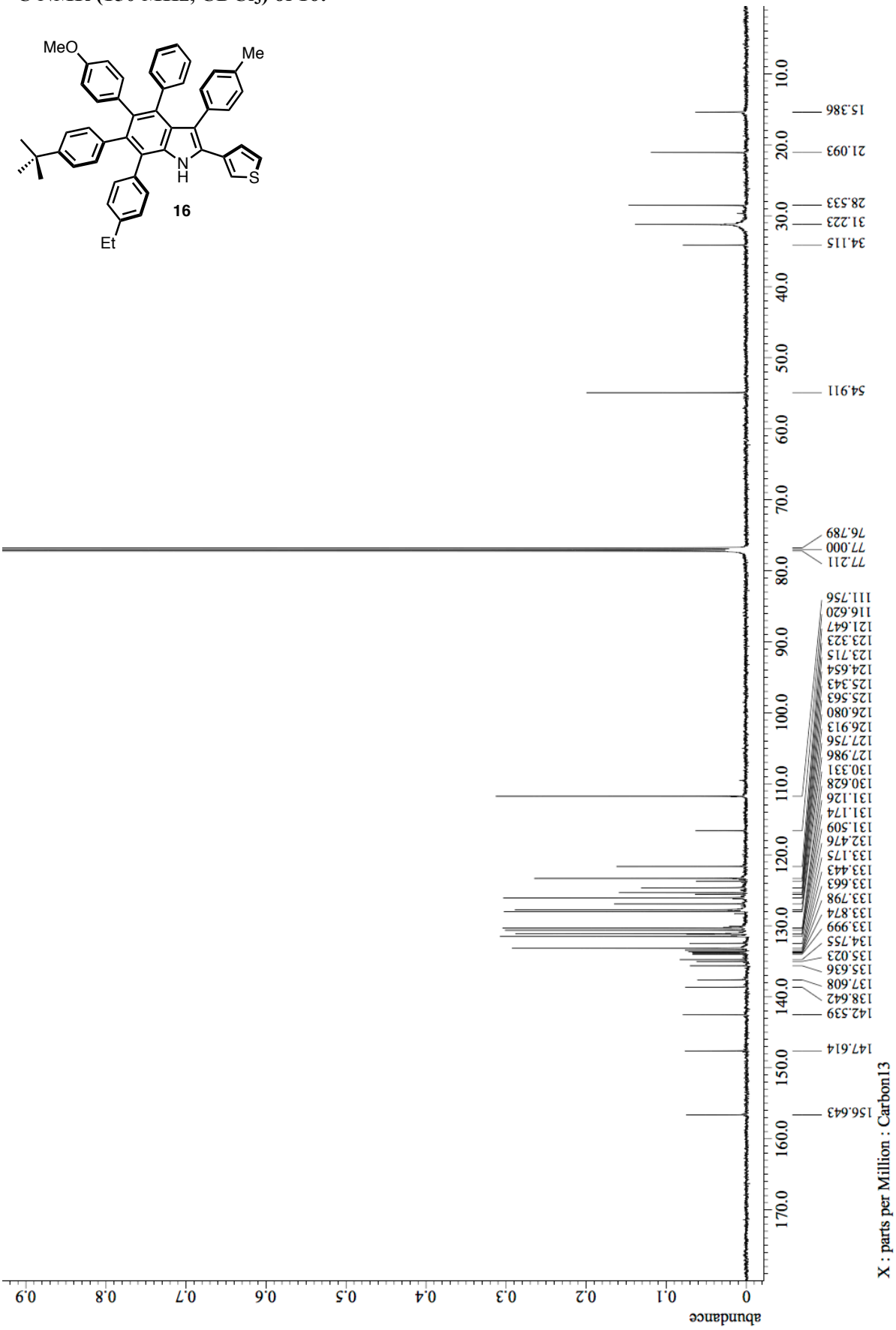
^{13}C NMR (101 MHz, $CDCl_3$) of 9M:



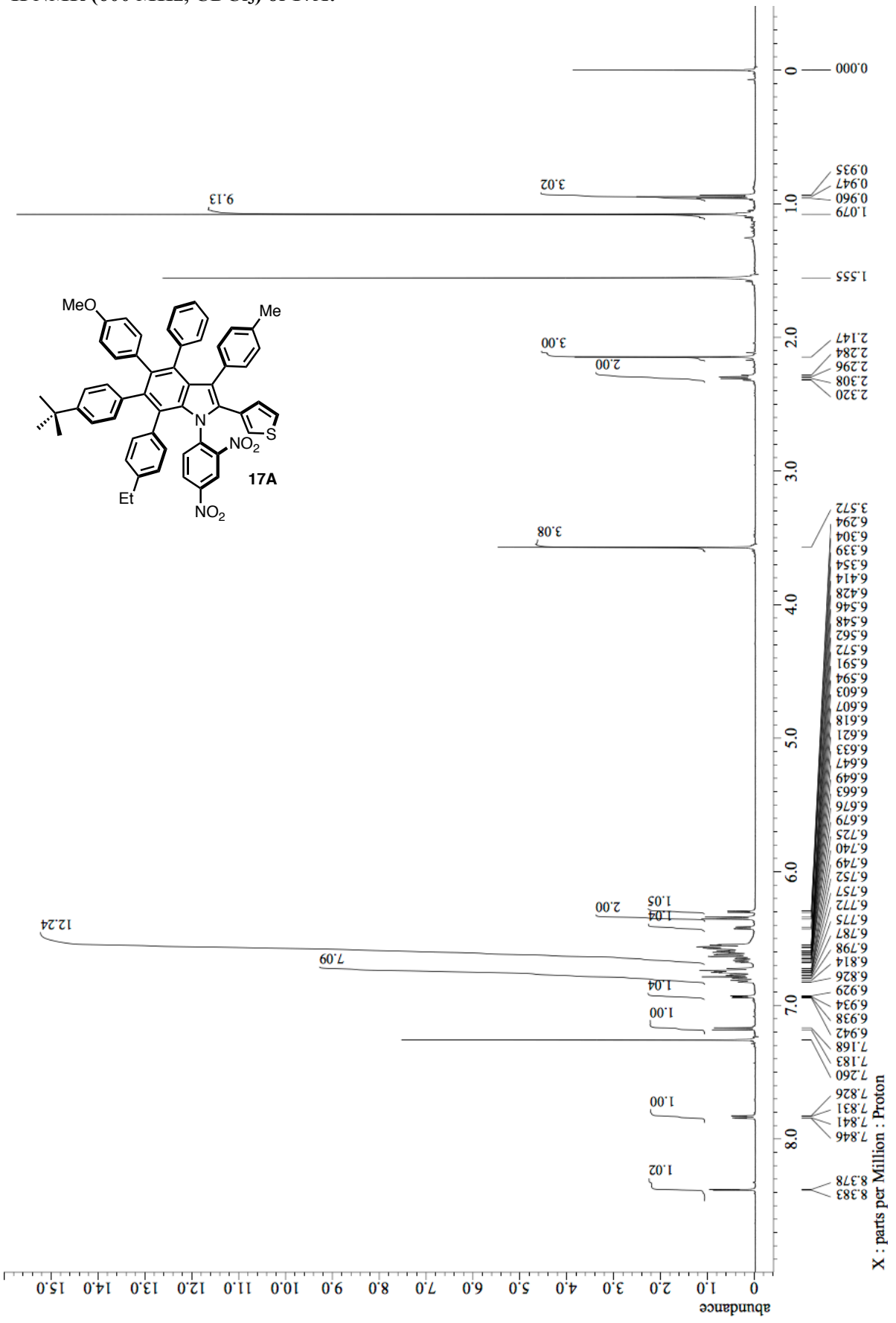
^{1}H NMR (600 MHz, $CDCl_3$) of 16:



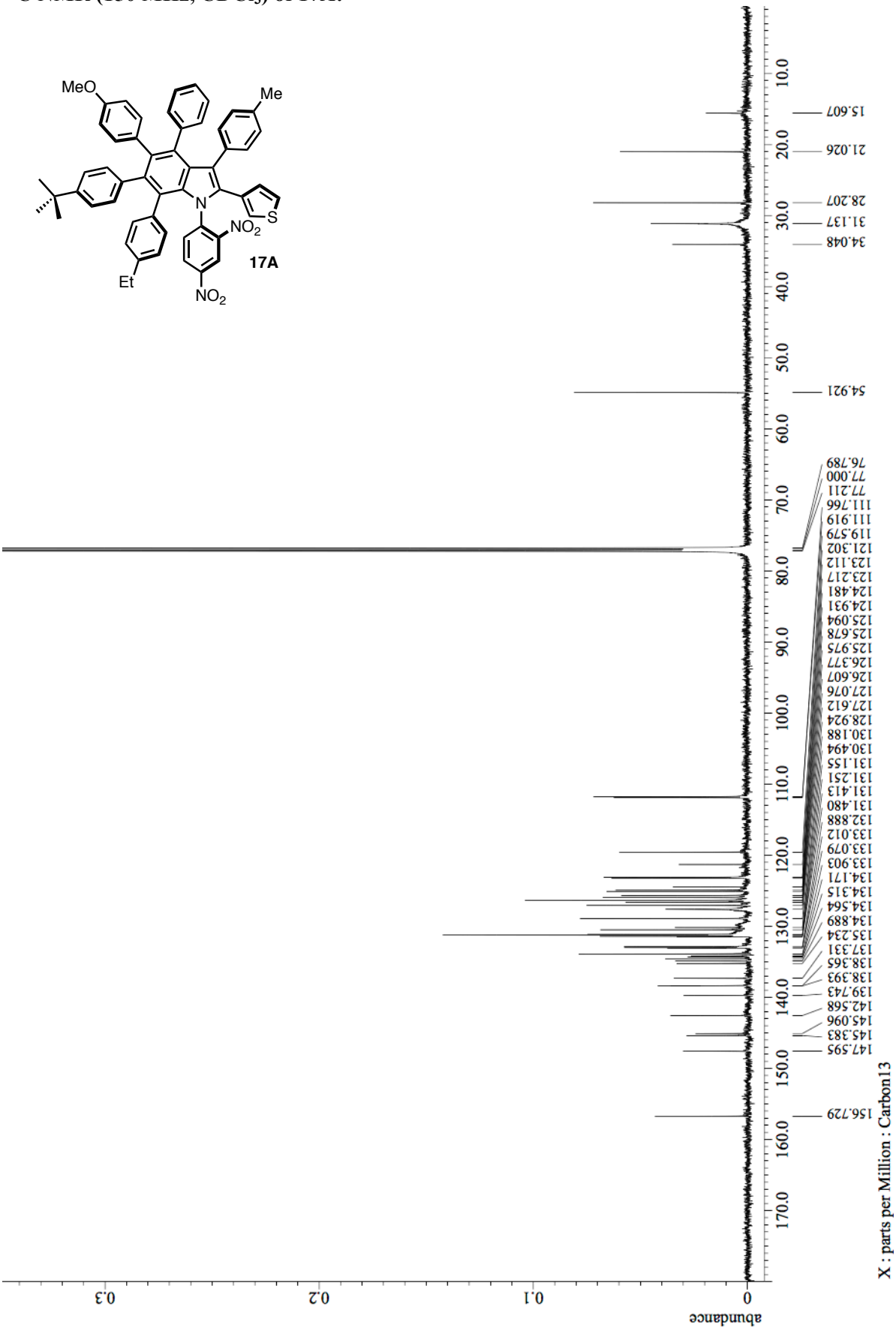
^{13}C NMR (150 MHz, $CDCl_3$) of 16:



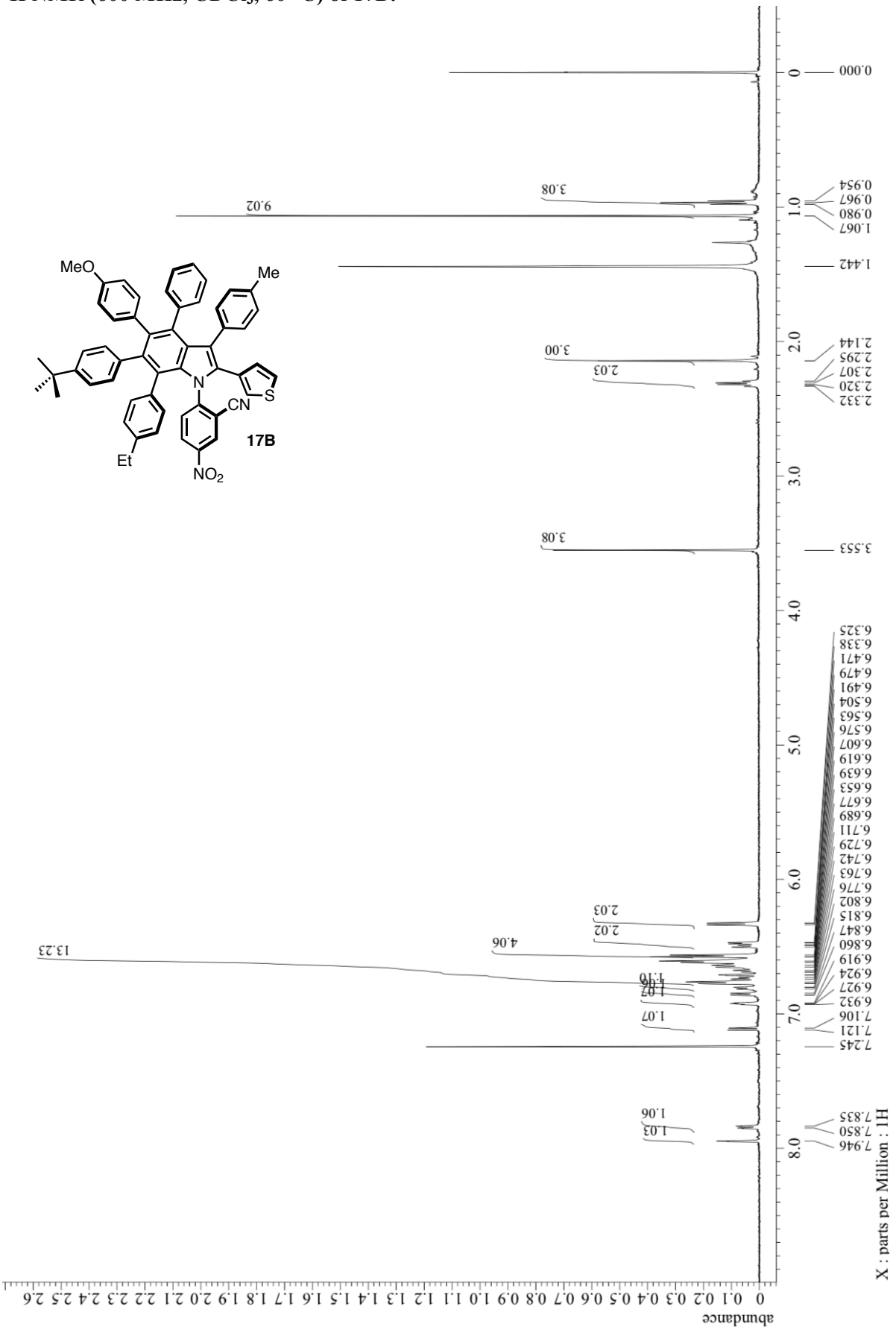
^{1}H NMR (600 MHz, $CDCl_3$) of 17A:



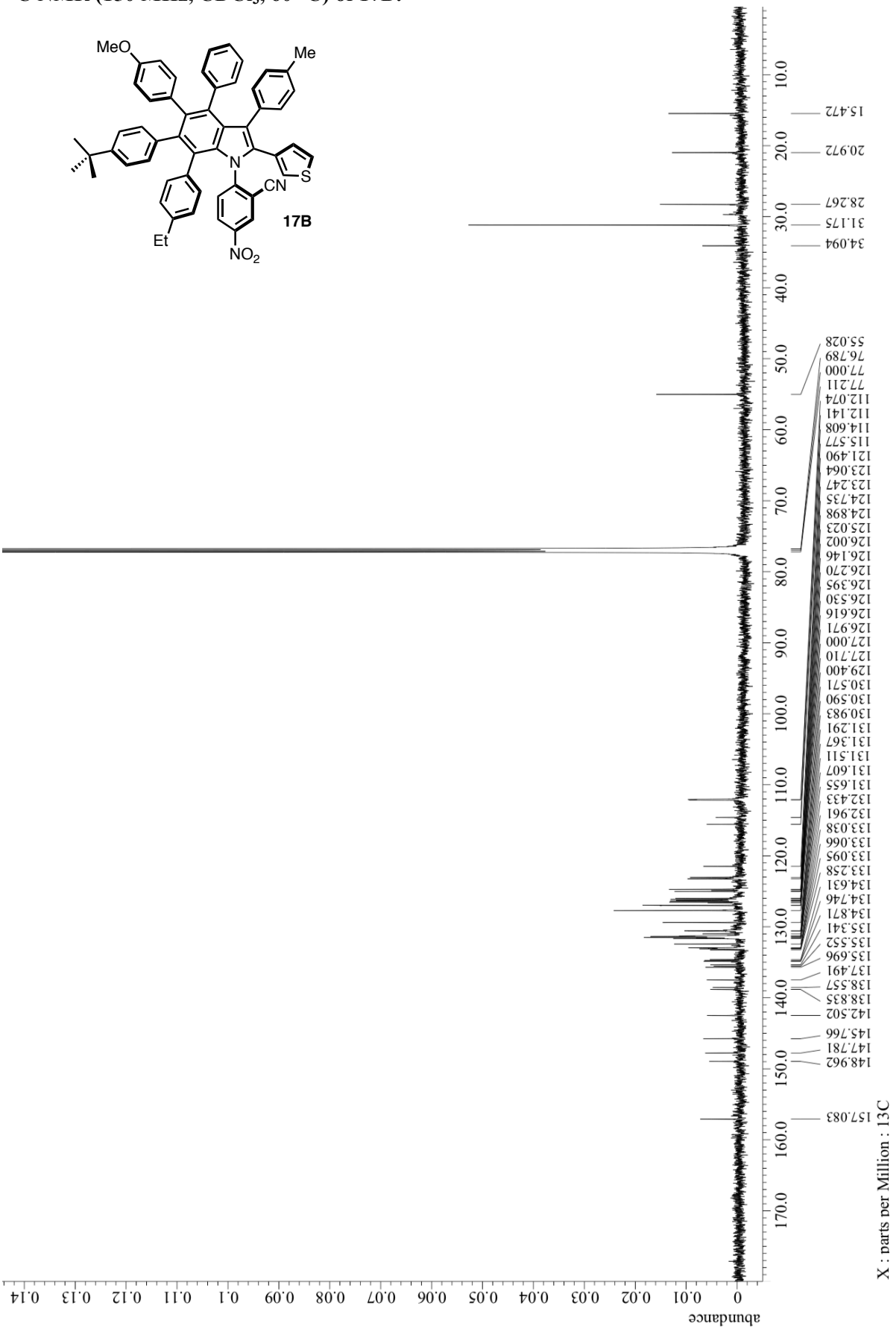
^{13}C NMR (150 MHz, $CDCl_3$) of 17A:



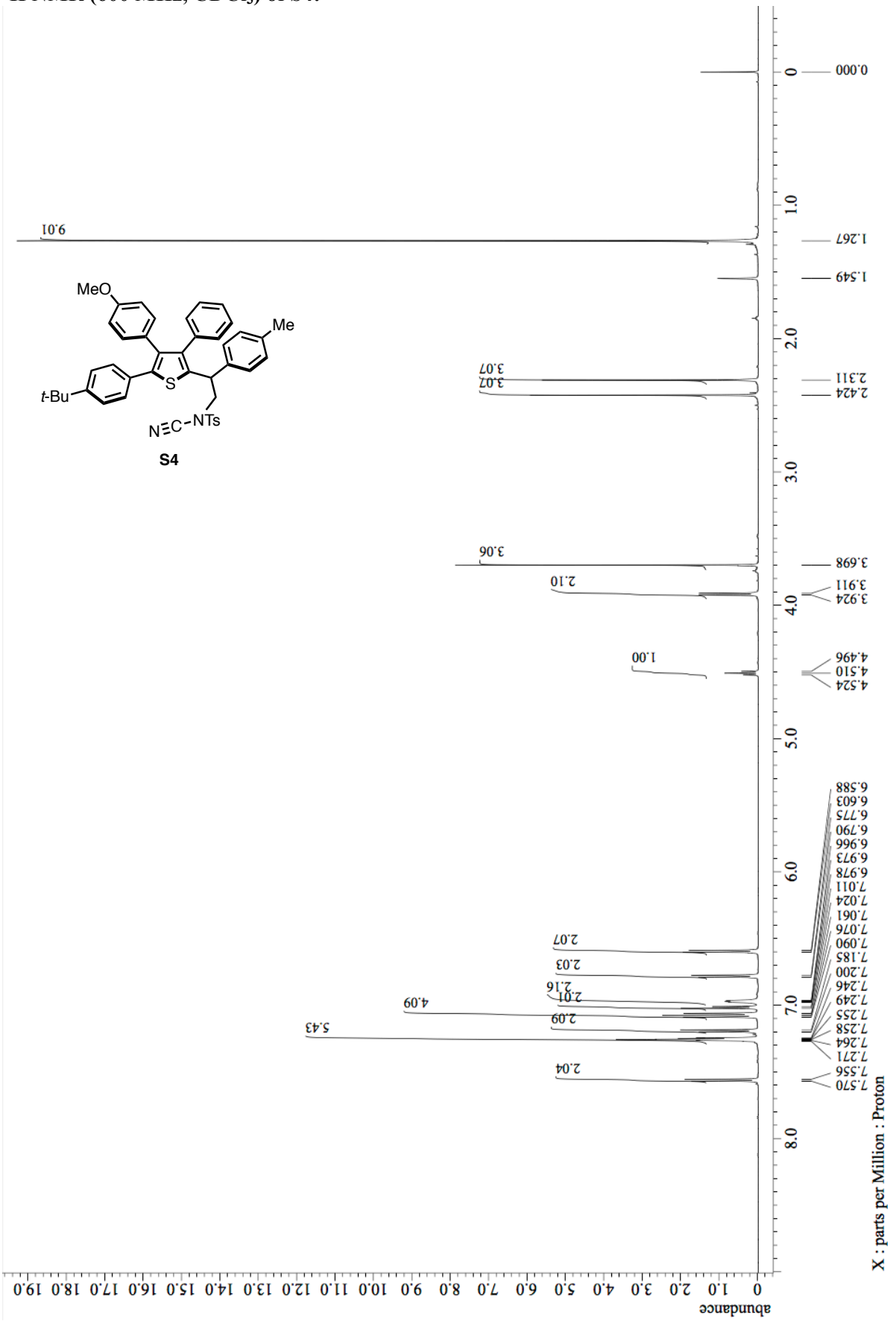
^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 17B:



^{13}C NMR (150 MHz, $CDCl_3$, 60 °C) of 17B:



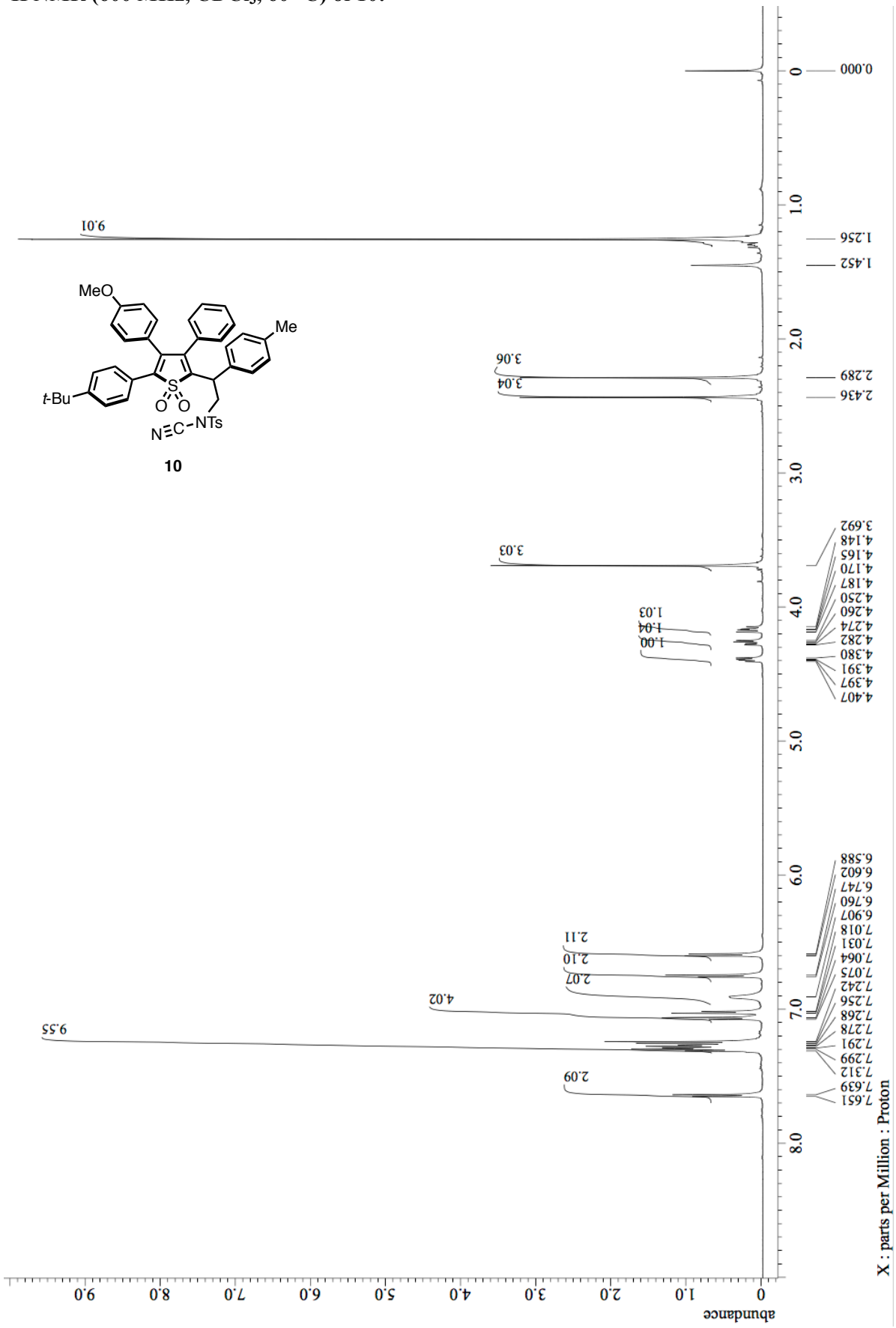
^{1}H NMR (600 MHz, $CDCl_3$) of S4:



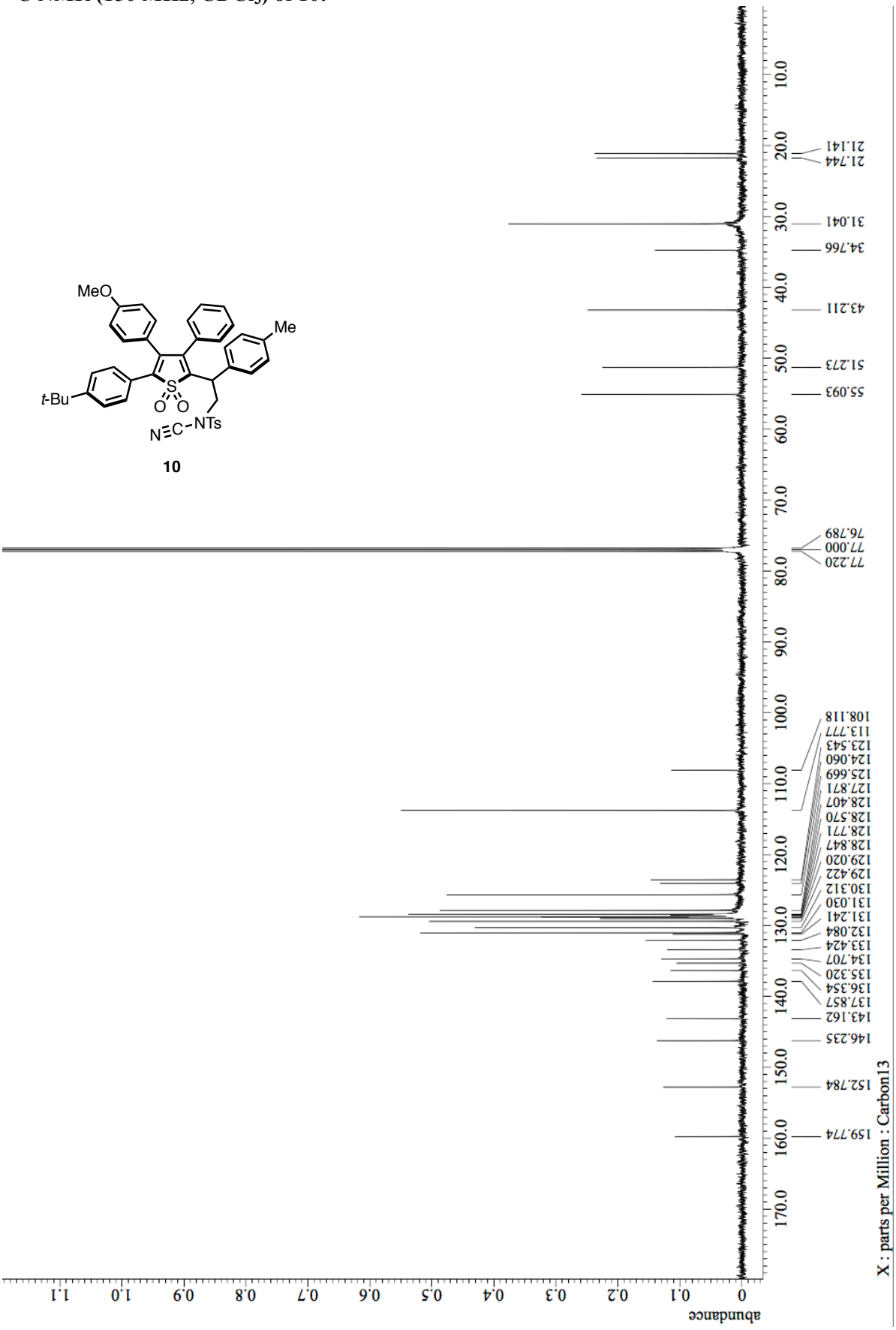
^{13}C NMR (150 MHz, $CDCl_3$) of S4:

S4

^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) of 10:

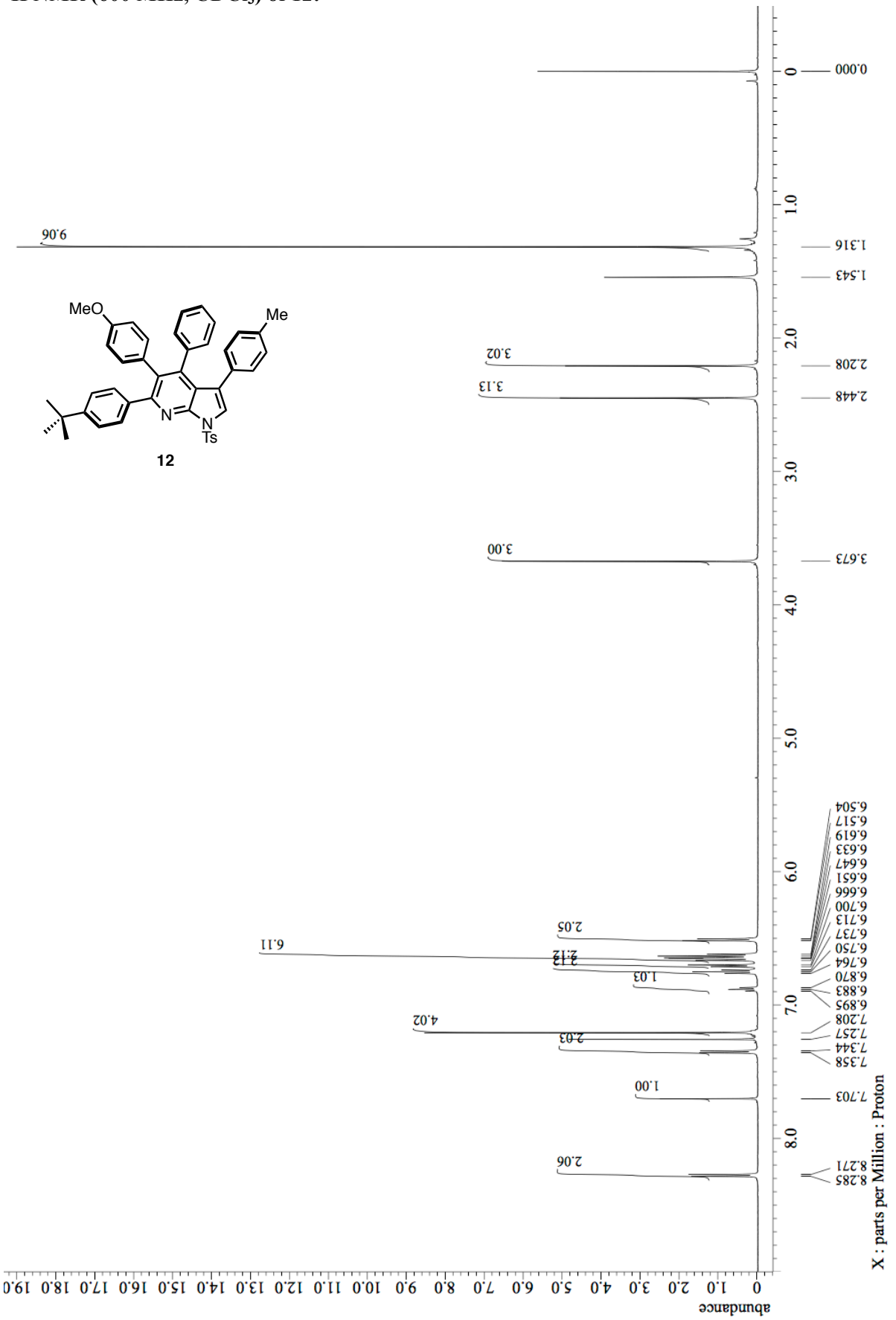


^{13}C NMR (150 MHz, $CDCl_3$) of 10:

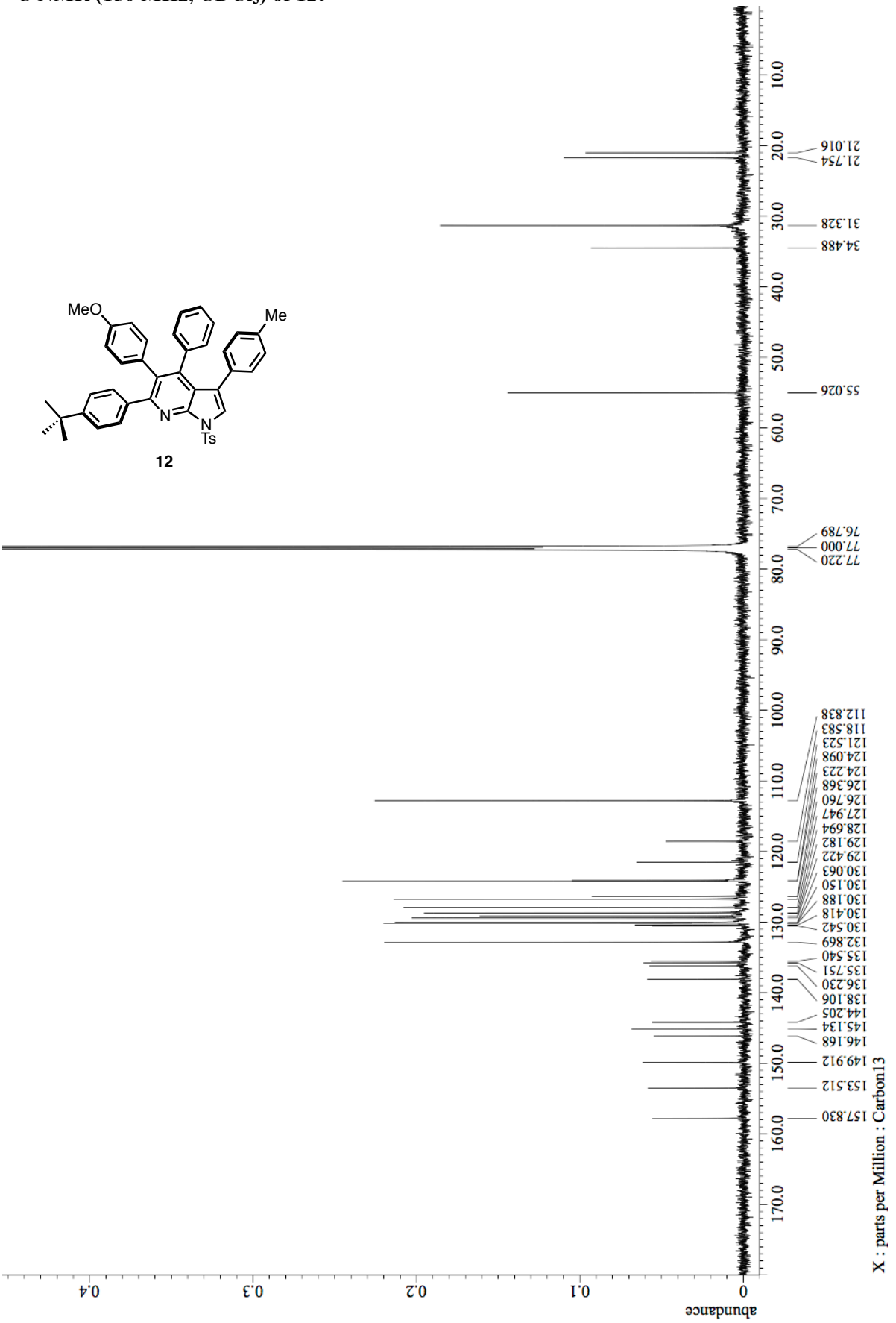


10

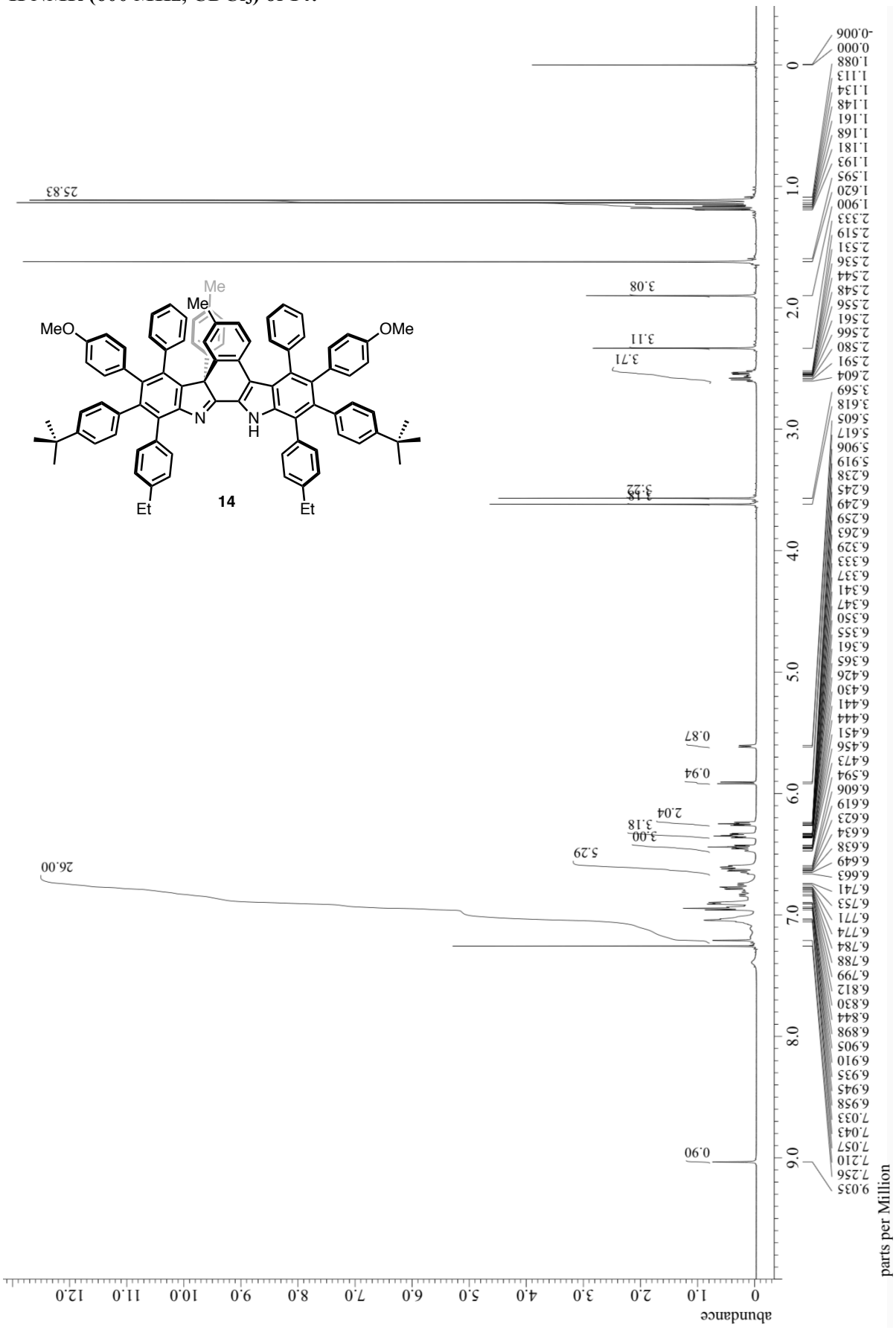
^{1}H NMR (600 MHz, $CDCl_3$) of 12:



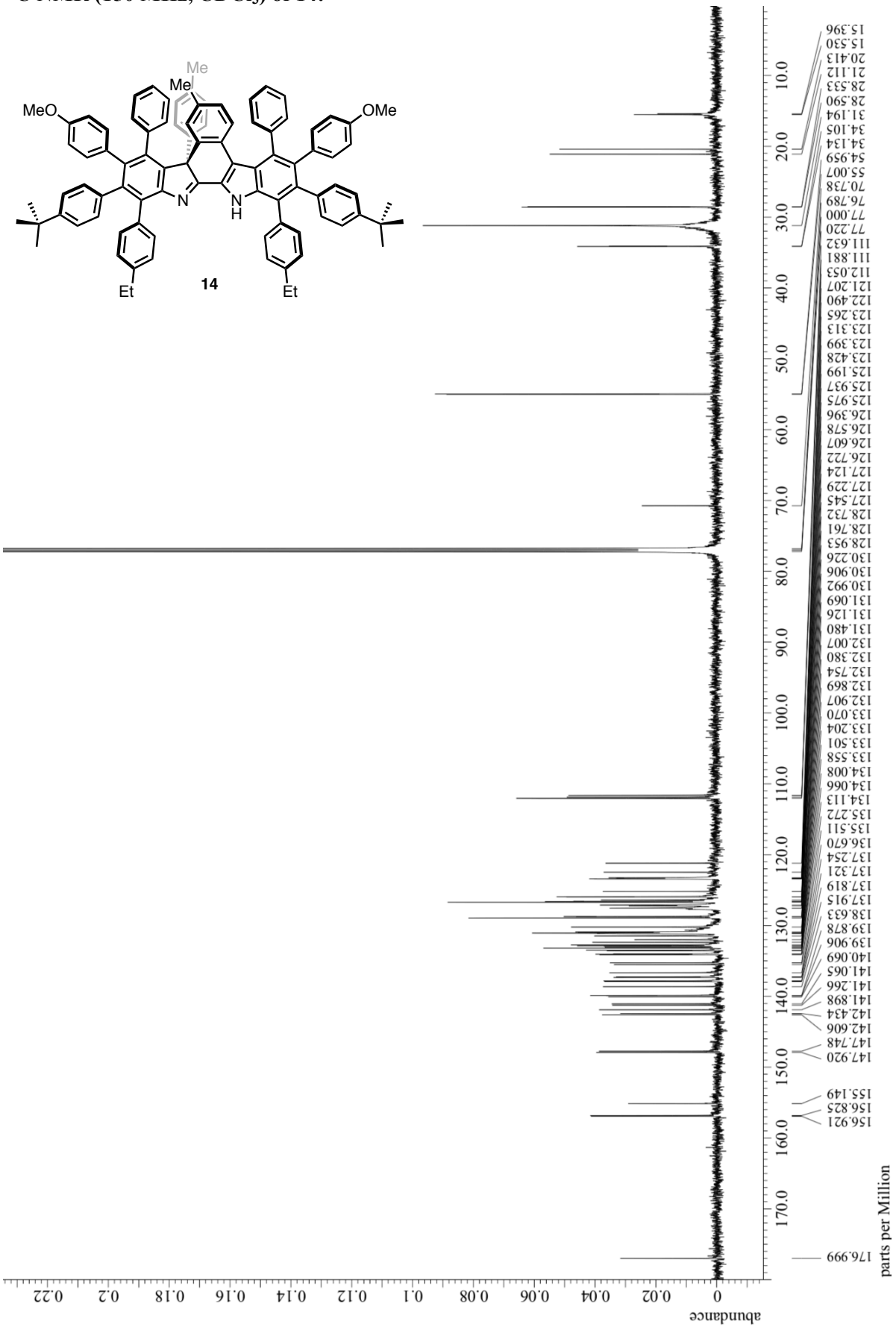
^{13}C NMR (150 MHz, $CDCl_3$) of 12:



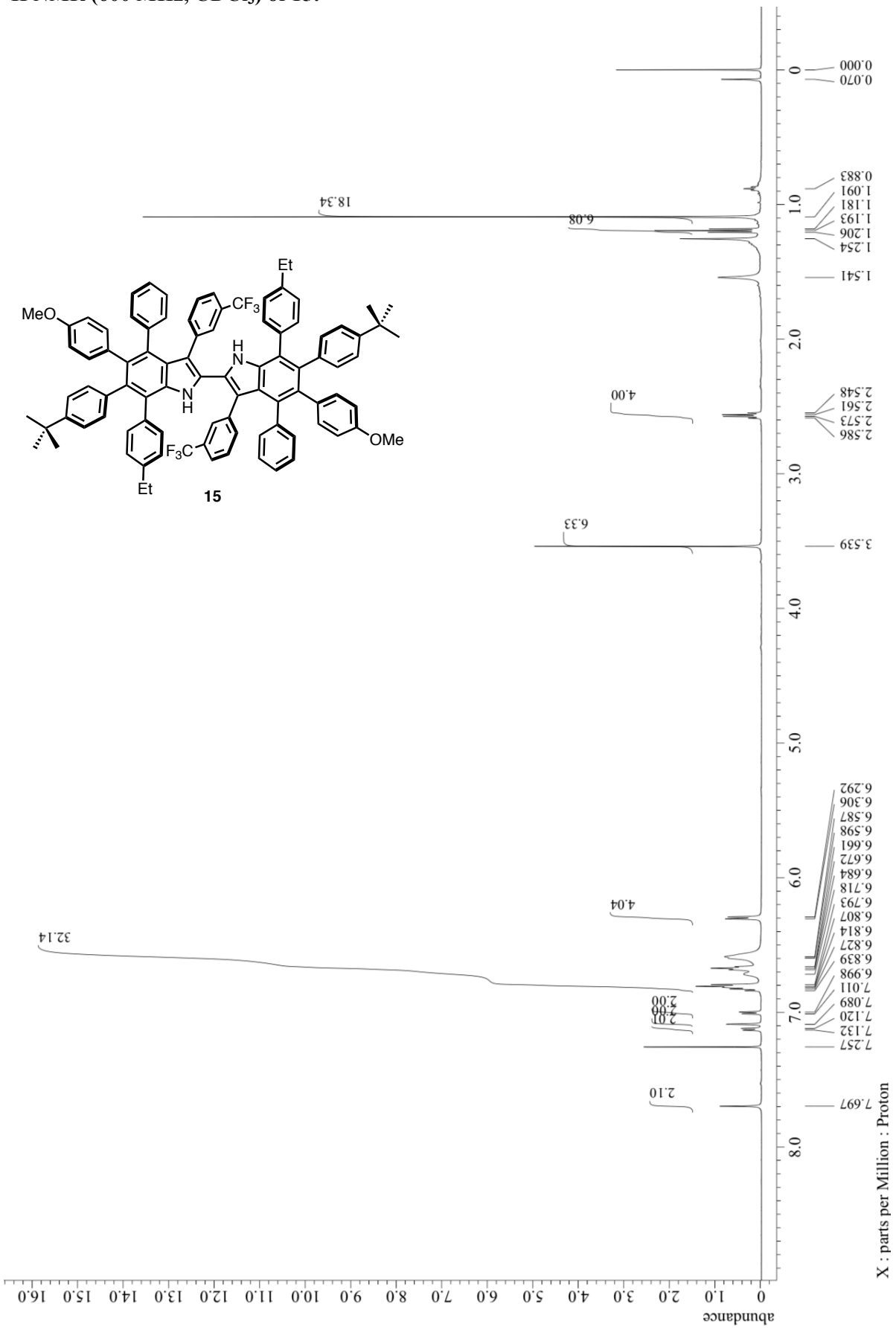
^{1}H NMR (600 MHz, $CDCl_3$) of 14:



^{13}C NMR (150 MHz, $CDCl_3$) of 14:



^{1}H NMR (600 MHz, $CDCl_3$) of 15:



^{13}C NMR (150 MHz, $CDCl_3$) of 15: