

## - Supporting Information -

### Development of Versatile Sulfone Electrophiles for Suzuki-Miyaura Cross-Coupling Reactions

Masakazu Nambo<sup>\*1</sup>, Eric C. Keske<sup>2</sup>, Jason P. G. Rygus<sup>2</sup>, Jacky C.-H. Yim<sup>1</sup>,  
and Cathleen M. Crudden<sup>\*1,2</sup>

*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Nagoya 464-8602, Japan, and  
Queen's University, Department of Chemistry, Chernoff Hall, Kingston, Ontario, Canada*

E-mail: mnambo@itbm.nagoya-u.ac.jp, cruddenc@chem.queensu.ca

#### Table of Contents

1.	General	S2
2.	Preparation of 3,5-Bis(trifluoromethyl)phenyl Methyl Sulfone <b>6</b>	S3
3.	Preparation of Benzyl Sulfones <b>1</b>	S3–S5
4.	Preparation of 4-Benzyloxy-2,6-dimethylphenylboronic Acid <b>4v</b>	S5
5.	Typical Procedure for Pd-catalyzed $\alpha$ -Arylation of <b>6</b> with Bromoarenes <b>7</b>	S5-S10
6.	Typical Procedure for Pd-catalyzed Desulfonative Arylation of Arylmethyl Sulfones with Arylboronic Acids	S10-S17
7.	Pd-catalyzed One-pot Synthesis of Unsymmetric Diarylmethane <b>5nu</b>	S18
8.	Pd-catalyzed $\alpha$ C–H/Desulfonative Arylation for the Synthesis of Triarylmethane <b>8</b>	S18-S19
9.	Pd-catalyzed Synthesis of Deuterated Diarylmethane <b>9</b>	S19-S20
10.	Pd-catalyzed Sequential Arylation for the Synthesis of <b>10</b>	S20
11.	Competitive Reaction of Desulfonative Arylation with 4-Methylbenzyl Bromide	S21
12.	Pd-catalyzed Sequential Arylation for the Synthesis of <b>11</b>	S21-S22
13.	The Synthesis of GC-24	S22-S25
14.	References	S26
15.	<sup>1</sup> H, <sup>13</sup> C, and <sup>19</sup> F NMR Spectra of Products	S27-S159

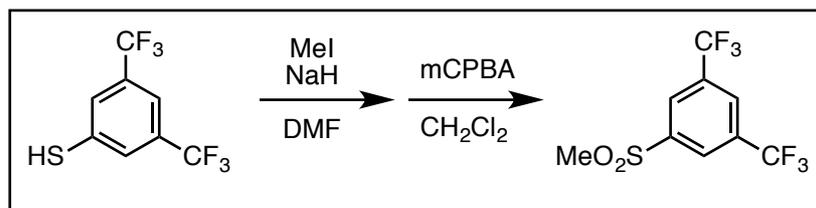
## 1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Benzyl trifluoromethyl sulfone **3a**<sup>1</sup>, benzyl phenyl sulfone **1a**<sup>2</sup>, benzyl 2-pyridyl sulfone **1c**, and benzyl 4-nitrophenyl sulfone **1e**<sup>3</sup> were prepared according to procedures reported in the literature. 1-Bromo-4-(methoxymethoxy)benzene **7d**<sup>4</sup>, *tert*-butyl 4-bromobenzoate **7i**<sup>5</sup>, *N,N*-diethyl-4-bromobenzamide **7j**<sup>6</sup>, 1-methoxymethyl-5-bromoindole **7n**<sup>7</sup>, 4-benzyloxy-2,6-dimethyl-1-bromobenzene<sup>8</sup> were prepared according to procedures reported in the literature. [PdCl(NHC)(allyl)]<sup>9</sup> and PEPPSI<sup>10</sup> catalysts were prepared according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F<sub>254</sub> precoated plates (0.25 mm) visualizing with UV light (254 nm) and ethanolic phosphomolybdic acid. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling HPLC was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Reverse phase HPLC was performed with Biotage Isolera instrument equipped with a Biotage SNAP Ultra C18 Cartridge (12g) using MeCN/H<sub>2</sub>O as eluent. Gas chromatographic (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with an HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with an HP-5 column (30 m × 0.25 mm, Hewlett-Packard). Column chromatography was performed using flash grade silica (Silicycle, 40-63 μm particle size, 60 Å porosity).

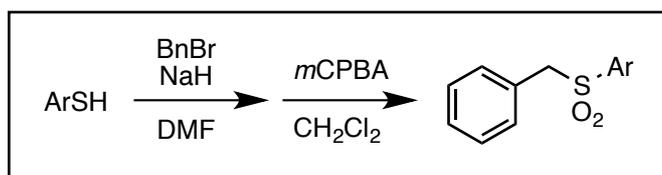
High-resolution mass spectra (HRMS) were obtained from a Thermo Fisher Scientific Exactive (ESI), a JMS-T100TD instrument (DART) or an Applied Biosystems/MDS Sciex QStar XL QqTOF instrument (EI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA600II (<sup>1</sup>H 600 MHz, <sup>13</sup>C 150 MHz), a JEOL ECA-500 (<sup>1</sup>H 500 MHz, <sup>13</sup>C 125 MHz), and a JEOL ECS-400 (<sup>1</sup>H 400 MHz, <sup>13</sup>C 100 MHz, <sup>19</sup>F 376 MHz) spectrometers. Chemical shifts for <sup>1</sup>H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual proton signal in CD<sub>3</sub>OD (δ 3.31 ppm). Chemical shifts for <sup>13</sup>C NMR are expressed in ppm relative to CDCl<sub>3</sub> (δ 77.0 ppm) or residual proton signal in CD<sub>3</sub>OD (δ 49.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quartet, quin = quintet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

## 2. Preparation of 3,5-Bis(trifluoromethyl)phenyl Methyl Sulfone 6<sup>11</sup>



A 50-mL flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added 3,5-bis(trifluoromethyl)benzenethiol (1.69 mL, 10 mmol) and dry DMF (14 mL) under a stream of argon. NaH (60% dispersion in mineral oil, 480 mg, 12 mmol) was added to this mixture at 0 °C. After stirring at 0 °C for 10 min, MeI (750  $\mu$ L, 12 mmol) was slowly added at this temperature and the mixture was stirred at room temperature for 2 h. The mixture was quenched with cold water and extracted with ether (3 times). The combined extracts were dried over MgSO<sub>4</sub> and passed through a pad of silica gel with copious washings with ether. The solvent was evaporated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). *m*CPBA (>77%, 5.6 g, 25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (35 mL) was slowly added to this solution at 0 °C and the mixture was stirred at room temperature for 12 h. The mixture was quenched with sat. Na<sub>2</sub>SO<sub>3</sub> solution (~10 mL) and was washed with 1N NaOH<sub>aq</sub> (3 times). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was dissolved in small amount of CH<sub>2</sub>Cl<sub>2</sub> and excess hexane was added to precipitate out a white solid. The solid was filtered off, washed with hexane, and dried under vacuum to afford **6** (2.69 g, 92%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.16 (s, 3H), 8.18 (s, 1H), 8.42 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  44.3, 122.3 (q, *J* = 275 Hz), 127.4 (br.t, *J* = 2.8 Hz), 128.0 (br.s), 133.4 (q, *J* = 34.5 Hz), 143.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.9. HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>F<sub>6</sub>SNa [M+Na]<sup>+</sup>: 314.9885, found 314.9888.

## 3. Preparation of Benzyl Sulfones 1

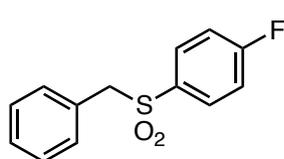


A 30-mL flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added benzenethiol (3 mmol) and dry DMF (3 mL) under a stream of argon. NaH (60% dispersion in mineral oil, 144 mg, 3.3 mmol) was added to this mixture at 0 °C. After stirring at 0 °C for 10 min, benzyl bromide (390  $\mu$ L, 3.3 mmol) was slowly added at this temperature and the mixture was stirred at room temperature for 2 h. The mixture was quenched with cold water and extracted with ether (3 times). The combined extracts were dried over MgSO<sub>4</sub> and passed through a pad of silica gel with copious washings with ether. The solvent was evaporated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL). *m*CPBA (>77%, 1.68 g, 7.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was slowly added to this solution at 0 °C

and the mixture was stirred at room temperature for 12 h. The mixture was quenched with sat. Na<sub>2</sub>SO<sub>3</sub> solution (~3 mL) and was washed with 1N NaOH<sub>aq</sub> (3 times). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was dissolved in small amount of CH<sub>2</sub>Cl<sub>2</sub> and excess hexane was added to precipitate out a white solid. The solid was filtered off, washed with hexane, and dried under vacuum to afford benzyl sulfone 1.

### Compound Data for Benzyl Sulfone 1

Unless otherwise noted, benzyl sulfones described in this section were prepared following the typical procedure.

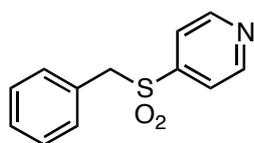


#### Benzyl 4-fluorophenyl sulfone (1b)

571 mg, 76% isolated yield; white solid

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.31 (s, 2H), 7.06-7.12 (m, 4H), 7.24-7.34 (m, 3H), 7.59-7.62 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 62.9, 116.1 (d, *J* = 22

Hz), 127.9, 128.6, 128.8, 130.7, 131.4 (d, *J* = 9.6 Hz), 133.7 (d, *J* = 2.9 Hz), 165.7 (d, *J* = 258 Hz). HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>FSNa [M+Na]<sup>+</sup>: 273.0356, found 273.0357.

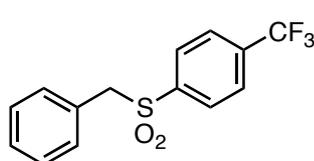


#### Benzyl 4-pyridyl sulfone (1d)

*Note:* 2 equiv *m*CPBA was used, purified by column chromatography (EtOAc/hexane = 1:2)

273 mg, 39% isolated yield; white solid

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.35 (s, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.46 (dd, *J* = 4.8, 1.6 Hz, 2H), 8.79 (dd, *J* = 4.8, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 62.4, 121.7, 127.1, 128.8, 129.2, 130.8, 145.7, 150.9. HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup>: 256.0403, found 256.0403.

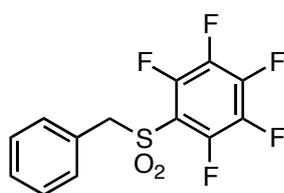


#### Benzyl 4-trifluoromethylphenyl sulfone (1f)

730 mg, 81% isolated yield; white solid

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.35 (s, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* =

8.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 62.7, 123.0 (q, *J* = 277 Hz), 125.9 (br.d, *J* = 3.8 Hz), 127.4, 128.7, 129.0, 129.2, 130.7, 135.3 (q, *J* = 33.4 Hz), 141.3. HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>F<sub>3</sub>SNa [M+Na]<sup>+</sup>: 323.0324, found 323.0323.



#### Benzyl pentafluorophenyl sulfone (1g)

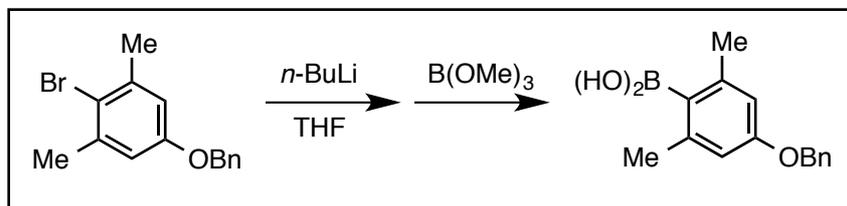
*Note:* NaH was slowly added to the mixture of ArSH and benzyl bromide in DMF at 0 °C

570 mg, 59% isolated yield; white solid

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.56 (s, 2H), 7.25-7.28 (m, 2H), 7.32-7.40 (m,

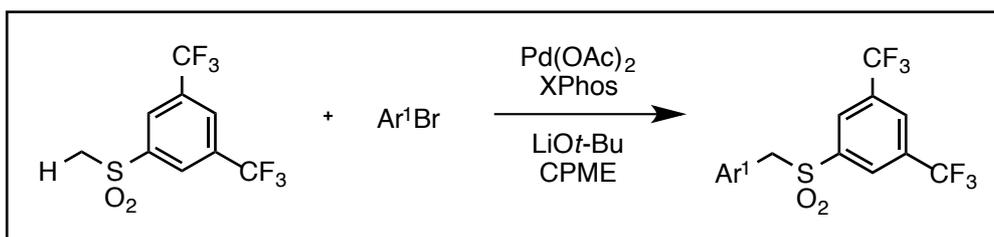
3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  63.9, 113.6 (t,  $J = 9.6$  Hz), 126.1, 129.0, 129.7, 130.6, 137.7 (dm,  $J = 257$  Hz), 144.8 (dtm,  $J = 263, 12.9$  Hz), 144.8 (ddm,  $J = 260, 11.6$  Hz). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_7\text{O}_2\text{F}_5\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 344.9979, found 344.9978.

#### 4. Preparation of 4-Benzyloxy-2,6-dimethylphenylboronic Acid 4v



A 50-mL two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added 4-benzyloxy-2,6-dimethyl-1-bromobenzene (2.15 g, 2 mmol) and dry THF (5 mL) under a stream of argon. 1.6 M  $n\text{-BuLi}$  in hexane (1.4 mL, 2.2 mmol) was slowly added to this mixture at  $-78$  °C. After stirring at this temperature for 1 h,  $\text{B}(\text{OMe})_3$  (445  $\mu\text{L}$ , 4 mmol) was added. The mixture was stirred at room temperature for 12 h, the mixture was quenched with 1 N  $\text{HCl}_{\text{aq}}$  (~5 mL) and then organic solvent was evaporated under reduced pressure. The residue was extracted with EtOAc (3 times), washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated under reduced pressure. The crude material was dissolved in small amount of ether and excess hexane was added to precipitate out a white solid. The solid was filtered off, washed with hexane, and dried under vacuum to afford 4-benzyloxy-2,6-dimethylphenylboronic acid **4v** as a white solid (411 mg, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  2.24 (s, 6H), 5.00 (s, 2H), 6.59 (s, 2H), 7.28 (t,  $J = 8.0$  Hz, 1H), 7.35 (t,  $J = 8.0$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  21.5, 70.8, 113.6, 123.6, 128.5, 129.4, 139.0, 140.2, 160.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{BO}_3$   $[\text{M}-\text{H}]^-$ : 255.1187, found 255.1191.

#### 5. Typical Procedure for Pd-catalyzed C–H Arylation of 1 with Bromoarenes 7

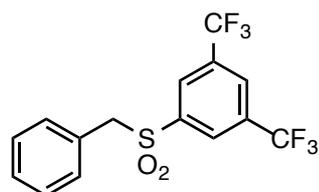


A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added  $\text{Pd}(\text{OAc})_2$  (2.2 mg, 10  $\mu\text{mol}$ ), XPhos (9.3 mg, 20  $\mu\text{mol}$ ), and dry CPME (500  $\mu\text{L}$ ) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, **6** (146 mg, 0.5 mmol), bromobenzene **7a** (20.0  $\mu\text{L}$ , 0.2 mmol),  $\text{LiOt-Bu}$  (40.0 mg, 0.5 mmol), dry CPME (500  $\mu\text{L}$ ) were added, and then the vessel was sealed. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious

washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:20) to afford benzyl 3,5-bis(trifluoromethyl)phenyl sulfone **2a** (65.4 mg, 89%) as a white solid.

### Compound Data for Arylmethyl Sulfone 2

Unless otherwise noted, diarylmethanes described in this section were prepared following the typical procedure. All products were purified by PTLC or preparative recycling HPLC equipped with JAIGEL-1H/JAIGEL-2H column (eluent: CHCl<sub>3</sub>).

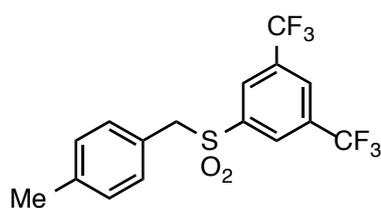


#### Benzyl 3,5-bis(trifluoromethyl)phenyl sulfone **2a**

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

65.4 mg, 89% isolated yield; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.39 (s, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.97 (s, 2H), 8.07 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 62.9, 122.2 (q, *J* = 275 Hz), 127.08, 127.14 (br.t, *J* = 3.8 Hz), 128.9, 129.1 (br.d, *J* = 2.9 Hz), 129.4, 130.7, 132.6 (q, *J* = 34.5 Hz), 140.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.9. HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>F<sub>6</sub>SNa [M+Na]<sup>+</sup>: 391.0198, found 391.0196.

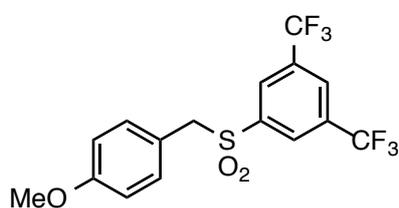


#### 3,5-Bis(trifluoromethyl)phenyl 4-methylbenzyl sulfone **2b**

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

68.2 mg, 89% isolated yield; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.33 (s, 3H), 4.35 (s, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 2H), 8.06 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.0, 62.8, 122.3 (q, *J* = 275 Hz), 123.9, 127.1 (br.t, *J* = 3.8 Hz), 129.2 (br.d, *J* = 2.9 Hz), 129.6, 130.6, 132.5 (q, *J* = 34.5 Hz), 139.8, 140.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.0. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>F<sub>6</sub>SNa [M+Na]<sup>+</sup>: 405.0354, found 405.0353.

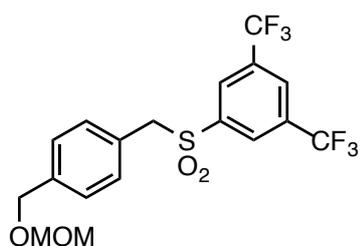


#### 3,5-Bis(trifluoromethyl)phenyl 4-methoxybenzyl sulfone **2c**

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

65.1 mg, 82% isolated yield; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.79 (s, 3H), 4.33 (s, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.96 (s, 2H), 8.07 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 55.3, 62.4, 114.4, 118.7, 122.3 (q, *J* = 275 Hz), 127.1 (br.t, *J* = 3.9 Hz), 129.2 (br.s), 132.0, 132.6 (q, *J* = 35.5 Hz), 140.3, 160.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.9. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>F<sub>6</sub>SNa [M+Na]<sup>+</sup>: 421.0304, found 421.0304.

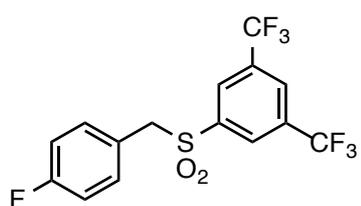


**3,5-Bis(trifluoromethyl)phenyl 4-(methoxymethoxymethyl)benzyl sulfone 2d**

Purification by GPC.

63.6 mg, 72% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (s, 3H), 4.39 (s, 2H), 4.58 (s, 2H), 4.69 (s, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 8.0$  Hz, 2H), 7.97 (s, 2H), 8.08 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.3, 62.7, 68.2, 95.7, 122.2 (q,  $J = 278$  Hz), 126.2, 127.2 (br.t,  $J = 3.8$  Hz), 128.1, 129.2 (br.d,  $J = 2.9$  Hz), 130.8, 132.7 (q,  $J = 35.3$  Hz), 139.8, 140.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{F}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 465.0566, found 465.0559.



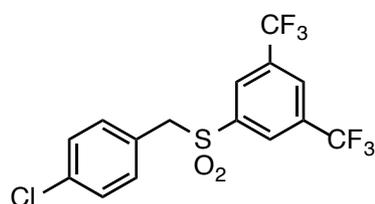
**3,5-Bis(trifluoromethyl)phenyl 4-fluorobenzyl sulfone 2e**

Reaction was conducted at 70 °C.

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

69.0 mg, 89% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.36 (s, 2H), 6.99-7.11 (m, 4H), 8.01 (s, 2H), 8.11 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  62.1, 116.2 (d,  $J = 22$  Hz), 122.2 (q,  $J = 275$  Hz), 122.9 (d,  $J = 3.8$  Hz), 127.3 (br.t,  $J = 3.8$  Hz), 129.1 (br.d,  $J = 1.9$  Hz), 132.6 (d,  $J = 8.6$  Hz), 132.9 (q,  $J = 34.5$  Hz), 140.3, 163.4 (d,  $J = 252$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9, 110.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_8\text{O}_2\text{F}_7\text{S}$   $[\text{M}-\text{H}]^-$ : 385.0128, found 385.0128.



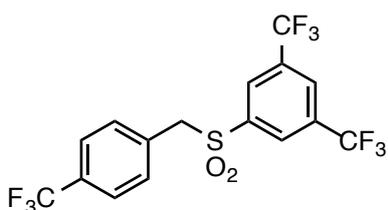
**3,5-Bis(trifluoromethyl)phenyl 4-chlorobenzyl sulfone 2f**

Reaction was conducted at 70 °C.

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

53.0 mg, 66% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.35 (s, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 8.02 (s, 2H), 8.11 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  62.2, 122.2 (q,  $J = 278$  Hz), 125.4, 127.4 (br.t,  $J = 3.8$  Hz), 129.1 (br.d,  $J = 2.9$  Hz), 129.3, 132.0, 132.9 (q,  $J = 35.3$  Hz), 136.0, 140.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_8\text{O}_2\text{F}_6\text{SCl}$   $[\text{M}-\text{H}]^-$ : 400.9832, found 400.9834.



**3,5-Bis(trifluoromethyl)phenyl 4-trifluoromethylbenzyl sulfone 2g**

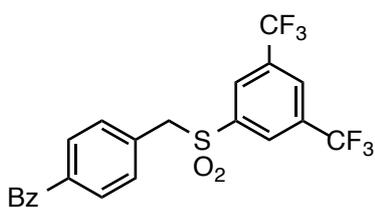
Reaction was conducted at 70 °C.

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

65.4 mg, 75% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.44 (s, 2H), 7.26 (d,  $J = 8.0$  Hz, 2H), 7.59 (d,  $J = 8.0$  Hz, 2H), 8.00 (s, 2H), 8.11 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  62.4, 122.1 (q,  $J = 275$  Hz), 123.5 (q,  $J = 274$  Hz), 125.4 (br.d,  $J = 3.8$  Hz), 127.5 (br.t,  $J = 3.8$  Hz), 129.0 (br.d,  $J = 2.9$  Hz), 131.0, 131.2, 131.9 (q,  $J = 33.6$  Hz),

133.0 (q,  $J = 34.5$  Hz), 140.1.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.00, -63.03. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_8\text{O}_2\text{F}_9\text{S}$   $[\text{M}-\text{H}]^-$ : 435.0101, found 435.0098.



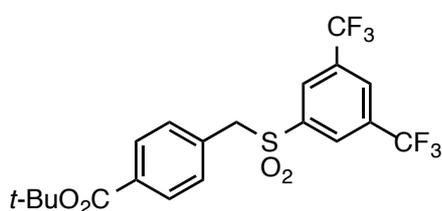
### 3,5-Bis(trifluoromethyl)phenyl 4-benzoylbenzyl sulfone 2h

Purification by GPC.

68.2 mg, 72% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.47 (s, 2H), 7.25 (d,  $J = 7.6$  Hz, 2H), 7.50 (t,  $J = 7.6$  Hz, 2H), 7.62 (t,  $J = 7.6$  Hz, 1H), 7.74–7.77 (m, 4H), 8.09

(s, 2H), 8.13 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  62.6, 122.2 (q,  $J = 275$  Hz), 127.5 (br.t,  $J = 3.8$  Hz), 128.4, 129.1 (br.d,  $J = 2.9$  Hz), 129.9, 130.4, 130.7, 131.0, 132.8, 132.9 (q,  $J = 34.5$  Hz), 136.9, 138.5, 140.3, 195.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{14}\text{O}_3\text{F}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 495.0466, found 495.0458.



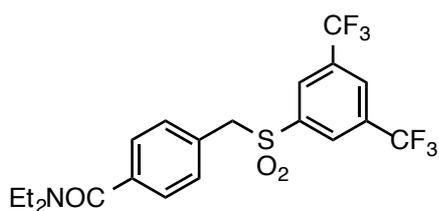
### 3,5-Bis(trifluoromethyl)phenyl 4-(tert-butoxycarbonyl)benzyl sulfone 2i

Purification by GPC.

71.8 mg, 77% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.59 (s, 9H), 4.44 (s, 2H), 7.15 (d,  $J$

= 8.4 Hz, 2H), 7.92 (d,  $J = 8.4$  Hz, 2H), 7.99 (s, 2H), 8.10 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  28.1, 62.7, 81.6, 122.2 (q,  $J = 278$  Hz), 127.4 (br.t,  $J = 3.8$  Hz), 129.1 (br.d,  $J = 3.9$  Hz), 129.9, 130.6, 131.1, 132.8 (q,  $J = 35.3$  Hz), 133.1, 140.2, 164.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_4\text{F}_6\text{S}$   $[\text{M}-\text{H}]^-$ : 467.0757, found 467.0749.



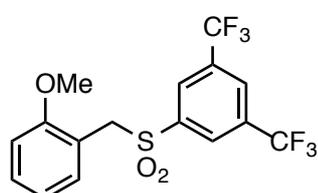
### 3,5-Bis(trifluoromethyl)phenyl 4-(diethylaminocarbonyl)benzyl sulfone 2j

Reaction was conducted at 110 °C.

Purification by PTLC (EtOAc/hexane = 1:2).

62.6 mg, 67% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.12 (br.s, 3H), 1.24 (br.s, 3H), 3.22 (br.s, 2H), 3.54 (br.s, 2H), 4.43 (s, 2H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H), 8.09 (s, 2H), 8.12 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.8, 14.0, 39.2, 43.1, 62.4, 122.2 (q,  $J = 275$  Hz), 127.0, 127.4 (br.t,  $J = 3.8$  Hz), 127.8, 129.1 (br.d,  $J = 2.9$  Hz), 130.8, 132.8 (q,  $J = 34.5$  Hz), 138.5, 140.5, 169.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{18}\text{NO}_3\text{F}_6\text{S}$   $[\text{M}-\text{H}]^-$ : 466.0917, found 466.0907.



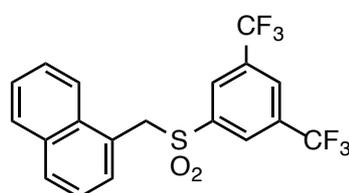
### 3,5-Bis(trifluoromethyl)phenyl 2-methoxybenzyl sulfone 2k

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

68.5 mg, 93% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.26 (s, 3H), 4.51 (s, 2H), 6.58 (d,  $J = 8.0$  Hz,

1H), 7.01 (t,  $J = 8.0$  Hz, 1H), 7.31 (dt,  $J = 8.0, 2.0$  Hz, 1H), 7.41 (dd,  $J = 8.0, 2.0$  Hz, 1H), 7.97 (s, 2H), 8.03 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  54.6, 56.6, 110.1, 115.6, 121.2, 122.3 (q,  $J = 278$  Hz), 126.6 (br.t,  $J = 3.8$  Hz), 129.3 (br.d,  $J = 2.8$  Hz), 131.2, 132.0 (q,  $J = 35.3$  Hz), 132.4, 140.9, 156.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_3\text{F}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 421.0304, found 421.0302.



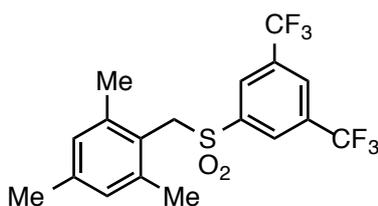
### 3,5-Bis(trifluoromethyl)phenyl 1-naphthylmethyl sulfone 2l

Reaction was conducted at 70 °C.

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

59.6 mg, 71% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.91 (s, 2H), 7.29-7.44 (m, 4H), 7.54 (d,  $J = 8.4$  Hz, 1H), 7.80 (d,  $J = 8.4$  Hz, 1H), 7.84 (s, 2H), 7.85-7.87 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  59.8, 122.1 (q,  $J = 278$  Hz), 122.4, 123.4, 125.2, 126.1, 126.8, 127.0 (br.t,  $J = 3.8$  Hz), 129.0, 129.1 (br.d,  $J = 3.8$  Hz), 130.4, 130.7, 131.3, 132.4 (q,  $J = 35.3$  Hz), 133.7, 139.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{11}\text{O}_2\text{F}_6\text{S}$   $[\text{M}-\text{H}]^-$ : 417.0378, found 417.0388.



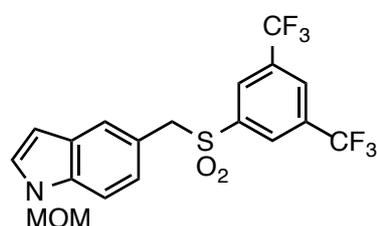
### 3,5-Bis(trifluoromethyl)phenyl 2,4,6-trimethylbenzyl sulfone 2m

Reaction was conducted at 80 °C.

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

69.8 mg, 85% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.13 (s, 6H), 2.26 (s, 3H), 4.56 (s, 2H), 6.84 (s, 2H), 8.05 (s, 2H), 8.10 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.1, 20.8, 57.4, 121.1, 122.3 (q,  $J = 278$  Hz), 127.1 (br.t,  $J = 3.8$  Hz), 129.0 (br.d,  $J = 2.9$  Hz), 129.8, 132.6 (q,  $J = 35.3$  Hz), 138.6, 139.5, 141.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{F}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 433.0667, found 433.0667.

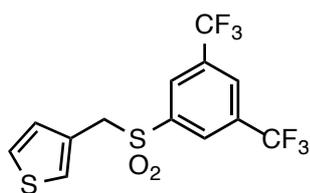


### 3,5-Bis(trifluoromethyl)phenyl 1'-(methoxymethyl)indolylmethyl sulfone 2n

Purification by GPC.

71.4 mg, 79% isolated yield; pale yellow solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.21 (s, 3H), 4.48 (s, 2H), 5.43 (s, 2H), 6.45 (d,  $J = 3.2$  Hz, 1H), 6.89 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.21 (d,  $J = 3.2$  Hz, 1H), 7.32 (d,  $J = 1.6$  Hz, 1H), 7.39 (d,  $J = 8.4$  Hz, 1H), 7.91 (s, 2H), 8.02 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.7, 63.5, 77.5, 102.7, 110.5, 118.4, 122.2 (q,  $J = 275$  Hz), 123.7, 124.3, 127.0 (br.t,  $J = 3.8$  Hz), 129.2 (br.d,  $J = 2.9$  Hz), 129.4, 129.5, 132.4 (q,  $J = 34.5$  Hz), 136.5, 140.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{F}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 474.0569, found 474.0565.



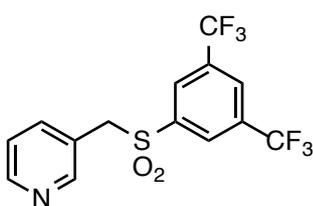
### 3,5-Bis(trifluoromethyl)phenyl 3-thienylmethyl sulfone 2o

Reaction was conducted at 80 °C.

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

49.4 mg, 66% isolated yield; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.46 (s, 2H), 6.92 (d, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 7.32 (dd, *J* = 4.8, 2.8 Hz, 1H), 8.01 (s, 2H), 8.09 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 57.6, 122.2 (q, *J* = 275 Hz), 126.9, 127.18, 127.24 (br.t, *J* = 3.8 Hz), 127.4, 128.6, 129.0 (br.d, *J* = 2.9 Hz), 132.7 (q, *J* = 34.5 Hz), 140.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.9. HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>8</sub>O<sub>2</sub>F<sub>6</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>: 396.9762, found 396.9764.



### 3,5-Bis(trifluoromethyl)phenyl 3-pyridylmethyl sulfone 2p

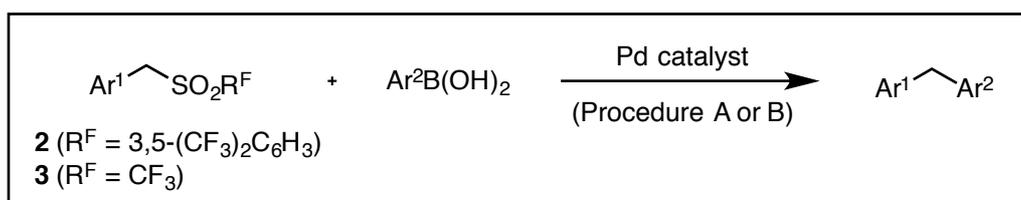
10 mol % Pd(OAc)<sub>2</sub> and 20 mol % XPhos were used. Reaction was conducted at 110 °C.

Purification by PTLC (EtOAc/hexane = 1:2).

36.0 mg, 49% isolated yield; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.42 (s, 2H), 7.33 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 2H), 8.14 (s, 1H), 8.25 (s, 1H), 8.63 (d, *J* = 5.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 59.9, 122.1 (q, *J* = 275 Hz), 123.3, 123.7, 127.7 (br.t, *J* = 3.9 Hz), 129.0 (br.d, *J* = 2.9 Hz), 133.1 (q, *J* = 35.4 Hz), 138.0, 140.1, 150.6, 151.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.9. HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>8</sub>NO<sub>2</sub>F<sub>6</sub>S [M-H]<sup>-</sup>: 368.0185, found 368.0185.

## 6. Typical Procedure for Pd-catalyzed Desulfonative Arylation of Arylmethyl Sulfones with Arylboronic Acids



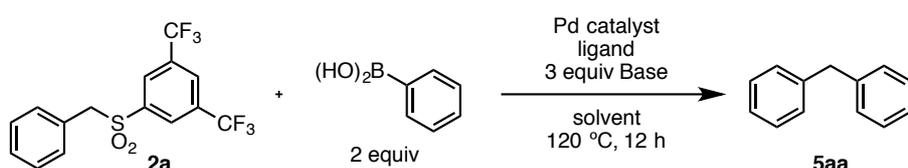
### Procedure A for 2

A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added [Pd(allyl)Cl]<sub>2</sub> (1.8 mg, 5 μmol), SIPr·HCl (8.5 mg, 20 μmol), K<sub>3</sub>PO<sub>4</sub> (127.4 mg, 0.6 mmol), and dry EtOH (500 μL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, benzyl 3,5-bis(trifluoromethyl)phenyl sulfone **2a** (73.8 mg, 0.2 mmol), phenylboronic acid **4a** (48.8 mg, 0.4 mmol), and dry EtOH (500 μL) were added, and then the vessel was sealed. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane) to afford diphenylmethane **5aa** (30.3 mg, 90%) as a colorless oil.

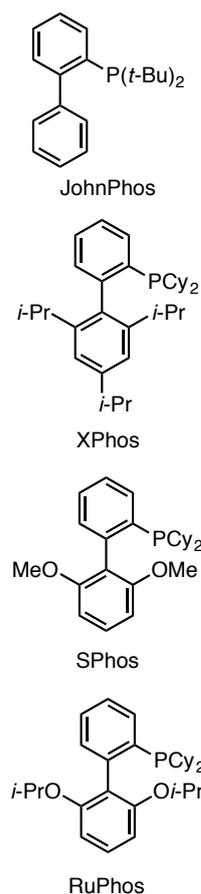
### Procedure B for 3

In a nitrogen filled glovebox, a 20 mL scintillation vial containing a magnetic stir bar was charged with [PdCl(SIPr)(allyl)] (12.0 mg, 21  $\mu$ mol), benzyl trifluoromethyl sulfone **3a** (93.8 mg, 0.42 mmol), phenylboronic acid **4a** (102.4 mg, 0.84 mmol), cesium carbonate (204.8 mg, 0.63 mmol) and dry toluene (3.2 mL). The vial was sealed with a Teflon cap and electrical tape, removed from the glovebox and submerged in an oil bath pre-heated to 100 °C for 18 h with stirring. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc. The filtrate was concentrated under reduced pressure, and the crude product purified by flash chromatography (hexanes) to afford diphenylmethane **5aa** (61.0 mg, 87%) as a colorless oil.

### Reaction optimization for 2a

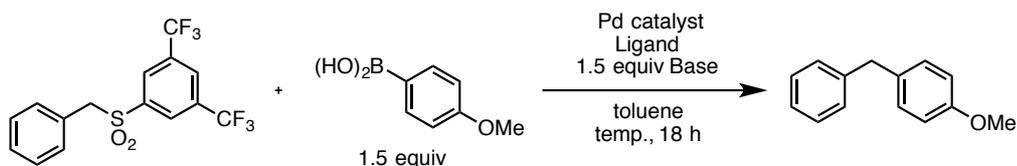


Pd catalyst (mol %)	Ligand (mol %)	Base	solvent	Yield of <b>5aa/2a</b> <sup>a</sup>
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	dioxane:H <sub>2</sub> O = 5:3	85% / 10% <sup>b</sup>
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	EtOH	93% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (10)	NaOH	EtOH	82% / 8%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	EtOH	78% / 18% <sup>c</sup>
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	<i>n</i> -BuOH	85% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	dioxane	71% / 26%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	toluene	71% / 6%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	DME	65% / 11%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	NaOH	DMF	15% / 26%
[PdCl(allyl)] <sub>2</sub> (5)	PCy <sub>3</sub> -HBF <sub>4</sub> (20)	NaOH	EtOH	6% / 43%
[PdCl(allyl)] <sub>2</sub> (5)	P( <i>t</i> -Bu) <sub>3</sub> -HBF <sub>4</sub> (20)	NaOH	EtOH	<1% / 68%
[PdCl(allyl)] <sub>2</sub> (5)	2,2'-bipyridyl	NaOH	EtOH	<1% / 52%
[PdCl(allyl)] <sub>2</sub> (5)	JohnPhos	NaOH	EtOH	62% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	XPhos	NaOH	EtOH	75% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	SPhos	NaOH	EtOH	83% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	RuPhos	NaOH	EtOH	88% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	Na <sub>2</sub> CO <sub>3</sub>	EtOH	21% / 21%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	KOH	EtOH	84% / 2%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (10)	Cs <sub>2</sub> CO <sub>3</sub>	EtOH	79% / <1%
[PdCl(allyl)] <sub>2</sub> (5)	SIPr-HCl (20)	K <sub>3</sub> PO <sub>4</sub>	EtOH	92% / <1%
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	NaOH	EtOH	91% / 2%
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	K <sub>3</sub> PO <sub>4</sub>	EtOH	93% / <1%
[PdCl(allyl)] <sub>2</sub> (1.5)	SIPr-HCl (6)	K <sub>3</sub> PO <sub>4</sub>	EtOH	73% / 17%
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	K <sub>3</sub> PO <sub>4</sub>	EtOH	84% / <1% <sup>d</sup>
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	K <sub>3</sub> PO <sub>4</sub>	EtOH	80% / <1% <sup>e</sup>
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	K <sub>3</sub> PO <sub>4</sub>	EtOH	83% / 12% <sup>f</sup>
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	NaOH	EtOH	92% / <1% <sup>f</sup>
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	K <sub>3</sub> PO <sub>4</sub>	EtOH	67% / 4% <sup>g</sup>
[PdCl(allyl)] <sub>2</sub> (2.5)	SIPr-HCl (10)	NaOH	EtOH	78% / <1% <sup>g</sup>
[PdCl(SIPr)(allyl)] (5)	-	K <sub>3</sub> PO <sub>4</sub>	EtOH	85% / 6%
[PdCl(SIPr)(allyl)] (5)	SIPr-HCl (5)	K <sub>3</sub> PO <sub>4</sub>	EtOH	94% / <1%



<sup>a</sup> Yields were determined by GC using dodecane as an internal standard. <sup>b</sup> 24 h. <sup>c</sup> Reaction temperature was 100 °C. <sup>d</sup> 1.5 equivalent of PhB(OH)<sub>2</sub> was used. <sup>e</sup> 2 equivalent of K<sub>3</sub>PO<sub>4</sub> was used. <sup>f</sup> PhB(neo) was used instead of PhB(OH)<sub>2</sub>. <sup>g</sup> PhB(pin) was used instead of PhB(OH)<sub>2</sub>.

## Reaction optimization for 3a

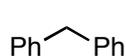


Pd catalyst (mol %)	Ligand (mol %)	Base	Temp. (°C)	Yield (%) <sup>a</sup>
[PdCl(SIPr)(allyl)] (5)	-	KOt-Bu	40	N.D.
[PdCl(SIPr)(allyl)] (5)	-	KOt-Bu	80	78
[PdCl(SIPr)(allyl)] (5)	-	KOt-Bu	100	87
[PdCl(SIPr)(allyl)] (5)	-	K <sub>2</sub> CO <sub>3</sub>	100	42
[PdCl(SIPr)(allyl)] (5)	-	K <sub>3</sub> PO <sub>4</sub>	100	61
[PdCl(SIPr)(allyl)] (5)	-	CS <sub>2</sub> CO <sub>3</sub>	100	99
[PdCl(SIPr)(allyl)] (5)	-	CS <sub>2</sub> CO <sub>3</sub>	80	87
SIPr-PEPPSI (5)	-	CS <sub>2</sub> CO <sub>3</sub>	100	96
[PdCl(IMes)(allyl)] (5)	-	CS <sub>2</sub> CO <sub>3</sub>	100	55
Pd <sub>2</sub> (dba) <sub>3</sub> (2.5)	PCy <sub>3</sub> (5)	CS <sub>2</sub> CO <sub>3</sub>	100	7
Pd <sub>2</sub> (dba) <sub>3</sub> (2.5)	P( <i>t</i> -Bu) <sub>3</sub> HBF <sub>4</sub> (10)	CS <sub>2</sub> CO <sub>3</sub>	100	trace

<sup>a</sup> Yields were determined by <sup>1</sup>H NMR relative to 1,3,5-trimethoxybenzene as an internal standard.

## Compound Data for Diarylmethanes 5

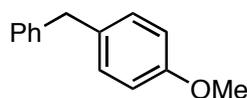
Unless otherwise noted, diarylmethanes described in this section were prepared following the typical procedure. All products were purified by PTLC, column chromatography, or preparative recycling HPLC equipped with JAIGEL-1H/JAIGEL-2H column (eluent: CHCl<sub>3</sub>).



### Diphenylmethane (5aa)

*Procedure A.* Purification by PTLC (hexane). 30.3 mg, 90% isolated yield. *Procedure B.* Purification by flash chromatography (hexane). 61.0 mg, 87% isolated yield; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.98 (s, 2H), 7.18-7.21 (m, 6H), 7.26-7.30 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 41.9, 126.1, 128.4, 128.9, 141.1. HRMS (DART) *m/z* calcd for C<sub>13</sub>H<sub>11</sub> [M-H]<sup>+</sup>: 167.0861, found 167.0865.



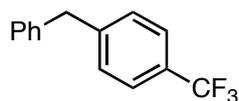
### 4-Benzylanisole (5ab)

*Procedure A.* Purification by PTLC (EtOAc/hexane = 1:60).

34.4 mg, 87% isolated yield; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.76 (s, 3H), 3.91 (s, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.16-7.21 (m, 3H), 7.26 (t, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 41.0, 55.2, 113.8, 125.9, 128.4, 128.8, 129.8, 133.2, 141.5, 157.9. HRMS (DART) *m/z* calcd for C<sub>14</sub>H<sub>15</sub>O [M+H]<sup>+</sup>: 199.1122, found 199.1120.

#### 4-Benzyl-1-trifluoromethylbenzene (5ac)

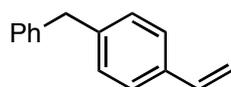


*Procedure A.* Purification by PTLC (hexane). 41.6 mg, 88% isolated yield.

*Procedure B.* Purification by flash chromatography (hexane). 73.2 mg, 75% isolated yield; colorless oil.

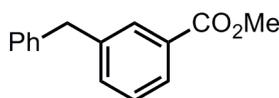
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.03 (s, 2H), 7.17 (d,  $J = 8.0$  Hz, 2H), 7.22 (t,  $J = 7.2$  Hz, 1H), 7.28-7.32 (m, 4H), 7.53 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  41.7, 124.3 (q,  $J = 276$  Hz), 125.4 (br.d,  $J = 3.8$  Hz), 126.5, 128.58 (q,  $J = 33.4$  Hz), 128.64, 128.9, 129.2, 140.0, 145.2. HRMS (DART)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_3$   $[\text{M}-\text{H}]^+$ : 235.0735, found 235.0728.

#### 4-Benzyl-1-vinylbenzene (5ad)



*Procedure A.* 5 mol %  $[\text{PdCl}(\text{allyl})]_2$  and 20 mol %  $\text{SIPr}\cdot\text{HCl}$  were used. Purification by PTLC (hexane). 66.0 mg, 79% isolated yield; pale yellow oil.

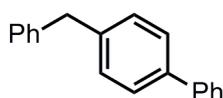
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.97 (s, 2H), 5.19 (d,  $J = 10.8$  Hz, 1H), 5.70 (d,  $J = 17.4$  Hz, 1H), 6.69 (dd,  $J = 17.4, 10.8$  Hz, 1H), 7.15 (d,  $J = 7.8$  Hz, 2H), 7.18 (d,  $J = 7.8$  Hz, 2H), 7.19 (t,  $J = 7.8$  Hz, 1H), 7.28 (t,  $J = 7.8$  Hz, 2H), 7.33 (d,  $J = 7.8$  Hz, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  41.7, 113.2, 126.1, 126.3, 128.5, 128.9, 129.1, 135.5, 136.6, 140.8, 141.0. HRMS (DART)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}$   $[\text{M}+\text{H}]^+$ : 195.1174, found 195.1177.



#### Methyl 3-benzylbenzoate (5ae)

*Procedure B.* Purification by flash chromatography (gradient: hexane to 20:1 hexane/ethyl acetate). 70.0 mg, 74% isolated yield; colorless oil.

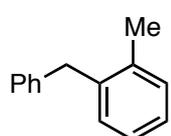
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.90 (s, 3H), 4.03 (s, 2H), 7.17-7.21 (m, 3H), 7.26-7.30 (m, 2H), 7.35-7.38 (m, 2H), 7.87-7.91 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  41.9, 52.2, 126.4, 127.6, 128.69, 128.73, 129.0, 130.2, 130.5, 133.7, 140.6, 141.6, 167.3. HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2$   $[\text{M}]^+$ : 226.0994, found 226.0990.



#### 4-Benzyl-1,1'-biphenyl (5af)

*Procedure B.* Purification by flash chromatography (gradient: hexane to 20:1 hexane/ethyl acetate). 85.2 mg, 83% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09 (s, 3H), 7.28-7.41 (m, 8H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.58 (d,  $J = 8.3$  Hz, 2H), 7.64 (dd,  $J = 1.4$  Hz, 8.3 Hz, 2H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  41.7, 126.3, 127.1, 127.2, 127.4, 128.7, 128.9, 129.1, 129.5, 139.2, 140.4, 141.130, 141.134. HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}$   $[\text{M}]^+$ : 244.1252, found 244.1248.

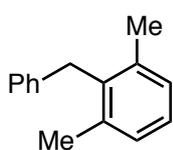


#### 2-Benzyltoluene (5ag)

*Procedure B.* Purification by flash chromatography (hexane). 62.3 mg, 82% isolated yield; colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.31 (s, 3H), 4.06 (s, 2H), 7.17-7.27 (m, 7H), 7.32-7.36 (m, 2H).  $^{13}\text{C}$

NMR (100 MHz, CDCl<sub>3</sub>) δ 19.1, 39.58, 126.0, 126.1, 126.6, 128.9, 130.1, 130.4, 136.8, 139.1, 140.5.  
HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>14</sub> [M]<sup>+</sup>: 182.1096, found 182.1099.

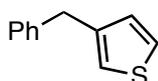


### 1-Benzyl-2,6-dimethylbenzene (5ah)

*Procedure A.* Purification by PTLC (hexane).

30.2 mg, 77% isolated yield; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.24 (s, 6H), 5.58 (s, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 7.04-7.11 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 20.2, 35.0, 125.7, 126.3, 127.8, 128.1, 128.3, 136.8, 137.2, 139.8. HRMS (DART) *m/z* calcd for C<sub>15</sub>H<sub>15</sub> [M-H]<sup>+</sup>: 195.1174, found 195.1168.



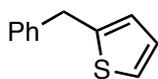
### 3-Benzylthiophene (5ai)

*Procedure A.* 5 mol % [PdCl(allyl)]<sub>2</sub> and 20 mol % SIPr·HCl were used.

Purification by PTLC (hexane).

31.2 mg, 90% isolated yield; pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.97 (s, 2H), 6.89-6.91 (m, 2H), 7.19-7.24 (m, 4H), 7.29 (t, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 36.5, 121.2, 125.6, 126.1, 128.42, 128.44, 128.7, 140.6, 141.4. HRMS (DART) *m/z* calcd for C<sub>11</sub>H<sub>9</sub>S [M-H]<sup>+</sup>: 173.0425, found 173.0420.

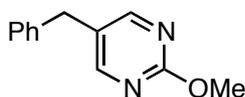


### 2-Benzylthiophene (5aj)

*Procedure A.* 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene was used instead of 2-thiopheneboronic acid. 5 mol % [PdCl(allyl)]<sub>2</sub> and 20 mol % SIPr·HCl

were used. Purification by PTLC (hexane). 25.8 mg, 74% isolated yield; pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.15 (s, 2H), 6.79 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.92 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.14 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.20-7.25 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 36.0, 123.9, 125.1, 126.5, 126.8, 128.5, 128.6, 140.4, 144.0. HRMS (DART) *m/z* calcd for C<sub>11</sub>H<sub>11</sub>S [M+H]<sup>+</sup>: 175.0582, found 175.0582.



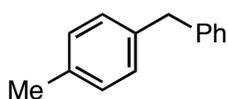
### 5-Benzyl-2-methoxypyrimidine (5ak)

*Procedure A.* 5 mol % [PdCl(allyl)]<sub>2</sub> and 20 mol % SIPr·HCl were used.

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

32.4 mg, 81% isolated yield; colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 3.90 (s, 2H), 3.99 (s, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 8.35 (s, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 35.5, 54.8, 126.7, 127.3, 128.6, 128.8, 139.1, 159.2, 164.5. HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>ONa [M+Na]<sup>+</sup>: 223.0842, found 223.0846.

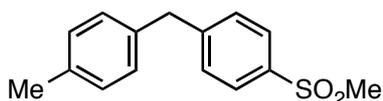


#### 4-Benzyltoluene (5ba)

Procedure A. Purification by PTLC (hexane).

32.0 mg, 88% isolated yield; colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.31 (s, 3H), 3.94 (s, 2H), 7.06-7.11 (m, 4H), 7.17-7.19 (m, 3H), 7.27 (t,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.0, 41.5, 126.0, 128.4, 128.79, 128.85, 129.1, 135.5, 138.0, 141.4. HRMS (DART)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{13}$   $[\text{M}-\text{H}]^+$ : 181.1017, found 181.1025.

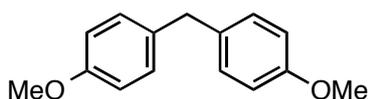


#### 4-(4'-Methylsulfonylbenzyl)toluene (5bl)

Procedure A. Purification by GPC.

37.8 mg, 73% isolated yield; white solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H), 3.02 (s, 3H), 4.02 (s, 2H), 7.06 (d,  $J = 7.8$  Hz, 2H), 7.12 (d,  $J = 7.8$  Hz, 2H), 7.37 (d,  $J = 8.4$  Hz, 2H), 7.84 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  21.0, 41.4, 44.6, 127.6, 128.8, 129.4, 129.7, 136.3, 136.4, 138.3, 148.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 283.0763, found 283.0761.

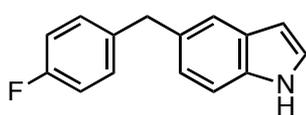


#### Bis(4-dimethoxyphenyl)methane (5cb)

Procedure A. Purification by PTLC (EtOAc/hexane = 1:15).

41.2 mg, 90% isolated yield; white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.77 (s, 6H), 3.86 (s, 2H), 6.82 (dm,  $J = 8.8$  Hz, 4H), 7.09 (dm,  $J = 8.8$  Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  40.1, 55.2, 113.8, 129.7, 133.7, 157.8. HRMS (DART)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_2$   $[\text{M}-\text{H}]^+$ : 227.1072, found 227.1078.

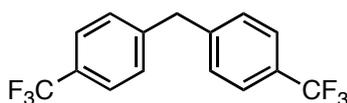


#### 5-(4'-Fluorobenzyl)indole (5em)

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

36.4 mg, 81% isolated yield; white solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.04 (s, 2H), 6.48 (s, 1H), 6.92-6.96 (m, 2H), 7.00 (d,  $J = 8.4$  Hz, 1H), 7.14-7.18 (m, 3H), 7.30 (d,  $J = 8.4$  Hz, 1H), 7.42 (s, 1H), 8.06 (br.s, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  41.2, 102.4, 111.0, 115.0 (d,  $J = 20.1$  Hz), 120.5, 123.3, 124.4, 128.1, 130.2 (d,  $J = 7.2$  Hz), 132.4, 134.5, 137.9 (d,  $J = 2.9$  Hz), 161.3 (d,  $J = 243$  Hz). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{11}\text{NF}$   $[\text{M}-\text{H}]^+$ : 224.0881, found 224.0873.

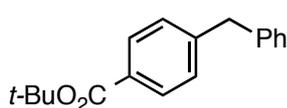


#### Bis(4-trifluoromethylphenyl)methane (5gc)

Procedure A. Purification by PTLC (hexane).

52.2 mg, 86% isolated yield; colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09 (s, 2H), 7.28 (d,  $J = 8.0$  Hz, 4H), 7.56 (d,  $J = 8.0$  Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  41.4, 124.2 (q,  $J = 277$  Hz), 125.6 (q,  $J = 3.8$  Hz), 128.9 (q,  $J = 33.4$  Hz), 129.2, 144.0. HRMS (DART)  $m/z$  calcd for  $\text{C}_{15}\text{H}_9\text{F}_6$   $[\text{M}-\text{H}]^+$ : 303.0608, found 303.0610.

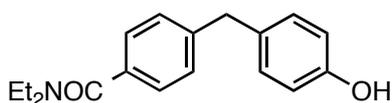


**tert-Butyl 4-benzylbenzoate (5ia)**

*Procedure A.* Purification by PTLC (EtOAc/hexane = 1:20).

41.6 mg, 78% isolated yield; colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.58 (s, 9H), 4.02 (s, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.20-7.30 (m, 5H), 7.91 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  28.2, 41.9, 80.8, 126.3, 128.5, 128.8, 128.9, 129.6, 129.9, 140.3, 145.9, 165.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 291.1356, found 291.1353.

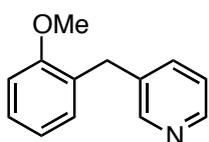


**4-(4'-Diethylaminocarbonylbenzyl)phenol (5jn)**

*Procedure A.* 4-TBSOC<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub> was used. After removal of solvent, 1M TBAF in THF (500  $\mu\text{L}$ ) was added. This mixture was

stirred at room temperature for 1 h, and then passed through a pad of silica gel. Purification by PTLC (EtOAc/hexane = 1:2). 44.6 mg, 79% isolated yield; white solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  1.10 (br.s, 3H), 1.24 (br.s, 3H), 3.27 (br.s, 2H), 3.54 (br.s, 2H), 3.88 (s, 2H), 6.63 (d,  $J = 8.4$  Hz, 2H), 6.92 (d,  $J = 8.4$  Hz, 2H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  12.8, 14.2, 39.5, 40.8, 43.5, 115.5, 126.4, 128.8, 129.8, 131.5, 134.3, 143.2, 154.9, 171.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 306.1465, found 306.1465.

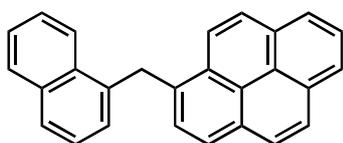


**3-(2'-Methoxybenzyl)pyridine (5ko)**

*Procedure A.* Purification by PTLC (EtOAc/hexane = 1:5).

24.6 mg, 62% isolated yield; colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.80 (s, 3H), 3.95 (s, 2H), 6.86 (d,  $J = 7.8$  Hz, 1H), 6.89 (t,  $J = 7.8$  Hz, 1H), 7.10 (d,  $J = 7.8$  Hz, 1H), 7.16 (d,  $J = 3.6, 7.2$  Hz, 1H), 7.22 (t,  $J = 7.8$  Hz, 1H), 7.48 (d,  $J = 7.2$  Hz, 1H), 8.41 (d,  $J = 3.6$  Hz, 1H), 8.52 (s, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  33.4, 55.2, 110.5, 120.6, 123.2, 127.9, 128.4, 130.2, 136.2, 136.5, 147.2, 150.3, 157.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$ : 200.1070, found 200.1068.

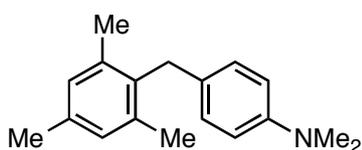


**1-(1'-Naphthylmethyl)pyrene (5lp)**

*Procedure A.* Purification by PTLC (hexane).

60.2 mg, 88% isolated yield; white solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.11 (s, 2H), 6.95 (d,  $J = 7.2$  Hz, 1H), 7.26 (t,  $J = 7.8$  Hz, 1H), 7.47-7.52 (m, 2H), 7.68 (d,  $J = 8.4$  Hz, 1H), 7.74 (d,  $J = 7.8$  Hz, 1H), 7.90 (d,  $J = 7.2$  Hz, 1H), 7.97 (t,  $J = 7.2$  Hz, 1H), 8.00-8.03 (m, 3H), 8.04 (d,  $J = 8.4$  Hz, 1H), 8.11 (d,  $J = 7.8$  Hz, 1H), 8.14 (d,  $J = 7.2$  Hz, 1H), 8.16 (d,  $J = 7.2$  Hz, 1H), 8.21 (d,  $J = 9.6$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  36.0, 123.5, 123.8, 124.91, 124.93, 125.05, 125.07, 125.66, 125.69, 125.9, 126.1, 126.87, 126.99, 127.02, 127.5, 127.6, 127.9, 128.8, 129.3, 130.2, 130.88, 130.92, 131.4, 132.1, 133.8, 133.9, 136.6. HRMS (DART)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{19}$   $[\text{M}+\text{H}]^+$ : 343.1487, found 343.1481.

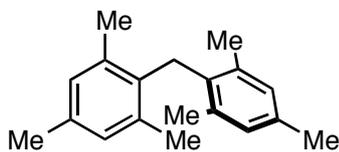


**1-(4'-dimethylaminobenzyl)-2,4,6-trimethylbenzene (5mq)**

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

37.2 mg, 73% isolated yield; colorless crystal.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.21 (s, 6H), 2.28 (s, 3H), 2.88 (s, 6H), 3.91 (s, 2H), 6.63 (d,  $J = 7.8$  Hz, 2H), 6.87-6.88 (m, 4H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  20.1, 20.9, 33.6, 40.9, 113.0, 128.1, 128.4, 128.8, 134.5, 135.3, 136.9, 148.9. HRMS (DART)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{24}\text{N}$   $[\text{M}+\text{H}]^+$ : 254.1903, found 254.1897.

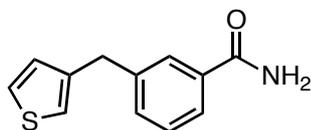


### Bis(mesityl)methane (5mr)

Procedure A. Purification by PTLC (hexane).

13.8 mg, 27% isolated yield; white solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.08 (s, 12H), 2.24 (s, 6H), 3.99 (s, 2H), 6.78 (s, 4H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7, 20.8, 31.0, 129.3, 134.8, 134.9, 136.7. HRMS (DART)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{23}$   $[\text{M}-\text{H}]^+$ : 251.1800, found 251.1797.

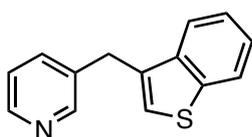


### 3-(3'-aminocarbonylbenzyl)thiophene (5os)

Procedure A. Purification by GPC.

27.1 mg, 62% isolated yield; pale yellow solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.03 (s, 2H), 5.96 (br.s, 1H), 6.09 (br.s, 1H), 6.89 (d,  $J = 6.4$  Hz, 1H), 6.93 (d,  $J = 1.2$  Hz, 1H), 7.25-7.27 (m, 1H), 7.36-7.39 (m, 2H), 7.63-7.64 (m, 1H), 7.68 (s, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  36.3, 121.5, 125.1, 125.9, 127.8, 128.2, 128.8, 132.4, 133.6, 140.6, 141.3, 169.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{11}\text{NOSNa}$   $[\text{M}+\text{Na}]^+$ : 240.0454, found 240.0452.



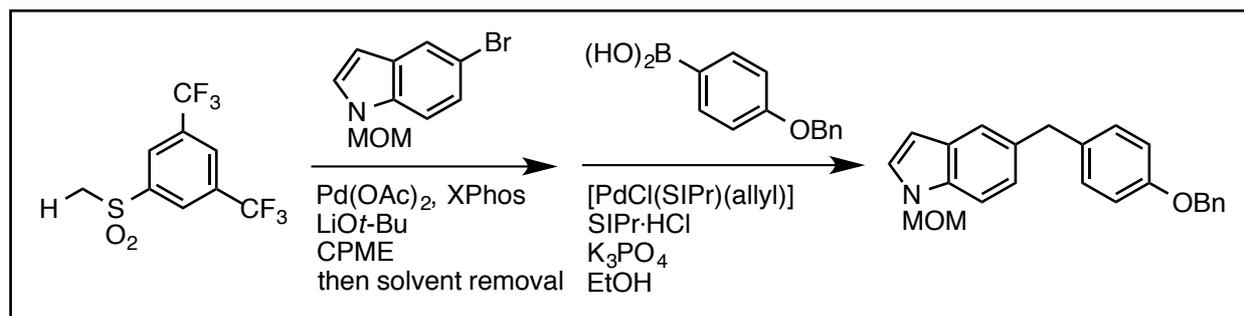
### 3-(3'-pyridylmethyl)benzothiophene (5pt)

Procedure A. 5 mol %  $[\text{PdCl}(\text{allyl})]_2$  and 20 mol % SIPr·HCl were used.

Purification by PTLC (EtOAc/hexane = 1:5). 21.2 mg, 47% isolated yield; colorless oil.

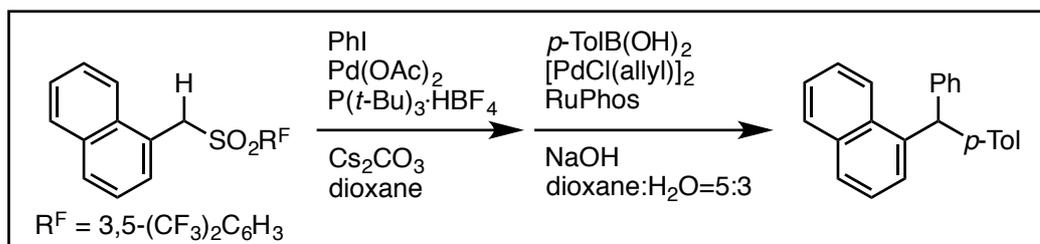
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.19 (s, 2H), 7.03 (s, 1H), 7.21 (dd,  $J = 7.8, 4.8$  Hz, 1H), 7.34-7.37 (m, 2H), 7.51 (d,  $J = 7.8$  Hz, 1H), 7.65-7.68 (m, 1H), 7.85-7.88 (m, 1H), 8.49 (dd,  $J = 4.8, 1.2$  Hz, 1H), 8.60 (d,  $J = 1.2$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  32.1, 121.7, 122.9, 123.4, 123.5, 124.1, 124.5, 134.2, 134.8, 136.2, 138.4, 140.6, 147.9, 150.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{NS}$   $[\text{M}+\text{H}]^+$ : 226.0685, found 226.0686.

## 7. Pd-catalyzed One-pot Synthesis of Unsymmetric Diarylmethane 5nu



A 100-mL glass vessel equipped with J. Young® O-ring tap, containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added Pd(OAc)<sub>2</sub> (56 mg, 0.25 mmol), XPhos (238 mg, 0.5 mmol), and dry CPME (12.5 mL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, **6** (3.65 g, 12.5 mmol), 1-methoxymethyl-5-bromoindole **7n** (1.20 g, 5 mmol), LiOt-Bu (1.01 g, 12.5 mmol), dry CPME (12.5 mL) were added, and then the vessel was sealed with O-ring tap. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, O-ring tap was removed and then solvent was removed in *vacuo*. To this vessel were added [PdCl(allyl)(SIPr)] (135 mg, 0.25 mmol), SIPr·HCl (107 mg, 0.25 mmol), 4-benzyloxyphenylboronic acid **4u** (2.28 g, 10 mmol), K<sub>3</sub>PO<sub>4</sub> (1.59 g, 7.5 mmol), and dry EtOH (25 mL) under a stream of argon, and then the vessel was sealed with O-ring tap. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, O-ring tap was removed and the mixture was passed through a pad of silica gel with copious washings with EtOAc (~70 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/hexane = 1:20) and then GPC to give the 5-(4'-benzyloxybenzyl)-1-methoxymethylindole **5nu** as a pale yellow solid (1.27 g, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.20 (s, 3H), 4.01 (s, 2H), 5.00 (s, 2H), 5.37 (s, 2H), 6.45 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.10-7.13 (m, 3H), 7.27-7.41 (m, 7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 41.0, 55.8, 70.0, 77.4, 102.3, 110.0, 114.7, 120.7, 123.5, 127.4, 127.8, 128.2, 128.5, 129.3, 129.8, 133.4, 134.6, 135.0, 137.2, 157.0. HRMS (ESI) *m/z* calcd for C<sub>24</sub>H<sub>23</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup>: 380.1621, found 380.1621.

## 8. Pd-catalyzed α C–H/Desulfonative Arylation for the Synthesis of Triarylmethane 8

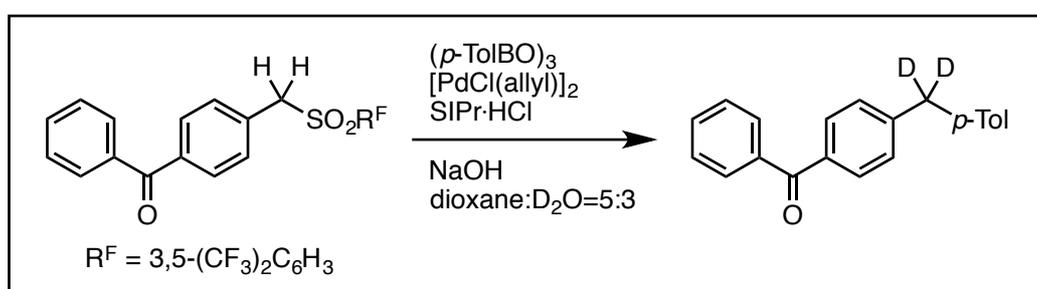


A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. The tube was charged with Pd(OAc)<sub>2</sub> (6.7 mg, 0.03 mmol), P(*t*-Bu)<sub>3</sub>·HBF<sub>4</sub> (26 mg, 0.09 mmol), Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6

mmol). The mixture was evacuated under vacuum and refilled with Ar. This cycle was repeated two additional times. Under an Ar atmosphere, CPME (0.9 mL) was added and the reaction was stirred at room temperature for 30 min. 3,5-Bis(trifluoromethyl)phenyl 1-naphthylmethyl sulfone **21** (125.4 mg, 0.3 mmol) and iodobenzene (50.4  $\mu$ L, 0.45 mmol) was then added, the reaction was sealed and stirred at 125 °C for 12 h. The reaction was then allowed to cool to room temperature, quenched with 3-4 drops of sat.  $\text{NH}_4\text{Cl}$  aq and filtered through a short pad of silica using EtOAc. The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane/ $\text{CH}_2\text{Cl}_2$  = 1:10:1) to afford 3,5-bis(trifluoromethyl)phenyl 1-naphthylphenylmethyl sulfone (112.2 mg, 76%) as a off-white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.25 (s, 1H), 7.34-7.43 (m, 5H), 7.58-7.62 (m, 3H), 7.70 (d,  $J$  = 9.2 Hz, 1H), 7.80-7.82 (m, 1H), 7.86 (s, 1H), 7.87 (d,  $J$  = 6.8 Hz, 1H), 7.95 (s, 2H), 8.37 (d,  $J$  = 6.8 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  70.8, 121.3, 122.1 (q,  $J$  = 275 Hz), 125.3, 125.9, 126.8 (q,  $J$  = 3.8 Hz), 127.0, 127.8, 127.9, 129.0, 129.27, 129.32, 129.4, 129.9, 130.2, 131.2, 131.9, 132.3 (q,  $J$  = 34.5 Hz), 133.9, 140.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{16}\text{O}_2\text{F}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 517.0667, found 517.0668.

A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  (1.8 mg, 5  $\mu$ mol), RuPhos (4.6 mg, 10  $\mu$ mol), NaOH (24 mg, 0.6 mmol), dry dioxane (500  $\mu$ L), and  $\text{H}_2\text{O}$  (600  $\mu$ L) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, 3,5-Bis(trifluoromethyl)phenyl 1-naphthylphenylmethyl sulfone (98.9 mg, 0.2 mmol), *p*-tolylboronic acid (54.4 mg, 0.4 mmol), and dry dioxane (500  $\mu$ L) were added, and then the vessel was sealed. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane) to afford **9** (56.8 mg, 92%) as a white solid. All spectral data of **8** matched those of the known compounds.<sup>2</sup>

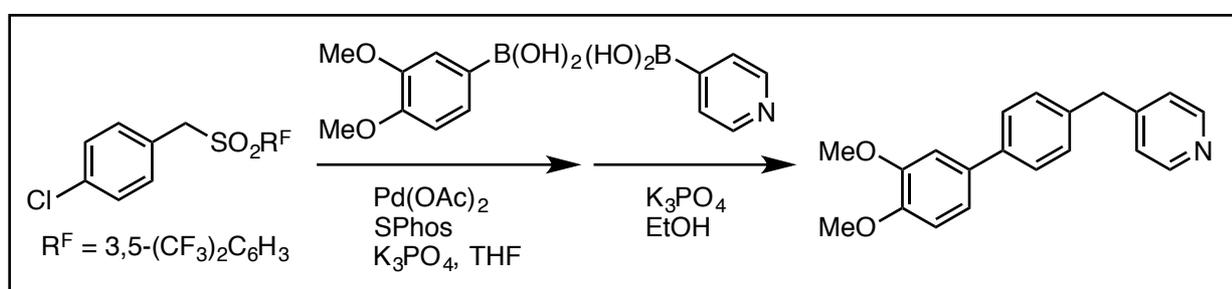
### 9. Pd-catalyzed Synthesis of Deuterated Diarylmethane **9**



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  (1.8 mg, 5  $\mu$ mol), SIPr-HCl (8.5 mg, 20  $\mu$ mol), NaOH (12 mg, 0.3 mmol), dry dioxane (250  $\mu$ L), and  $\text{D}_2\text{O}$  (300  $\mu$ L) at room temperature under a stream of argon. After

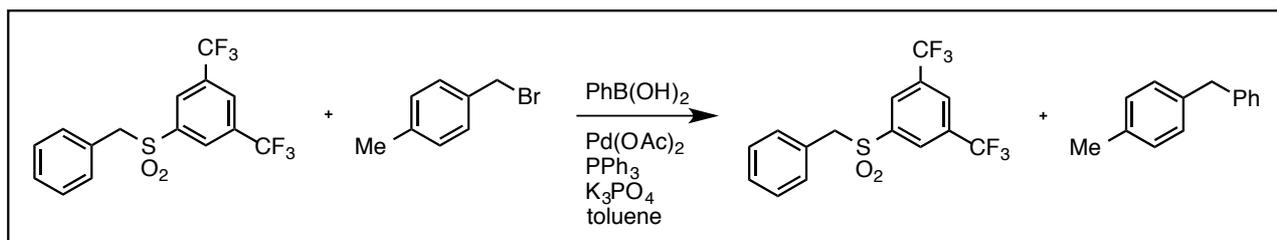
stirring the mixture at this temperature for 30 min, 3,5-bis(trifluoromethyl)phenyl 4-benzoylbenzyl sulfone **2h** (47.2 mg, 0.1 mmol), *p*-tolylboroxine (23.4 mg, 0.066 mmol), and dry dioxane (250  $\mu$ L) were added, and then the vessel was sealed. The mixture was stirred at 120  $^{\circ}$ C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:20) to afford **9** (25.4 mg, 88%) as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.32 (s, 3H), 7.08-7.13 (m, 4H), 7.29 (dm,  $J$  = 8.8 Hz, 2H), 7.46 (t,  $J$  = 7.2 Hz, 2H), 7.56 (t,  $J$  = 7.2 Hz, 1H), 7.73 (dm,  $J$  = 8.8 Hz, 2H), 7.78 (d,  $J$  = 7.2 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.0, 40.8 (quin,  $J$  = 20 Hz), 128.2, 128.7, 128.8, 129.3, 129.9, 130.4, 132.2, 135.4, 135.9, 137.0, 137.8, 146.4, 196.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{D}_2\text{ONa}$   $[\text{M}+\text{Na}]^+$ : 311.1375, found 311.1377.

## 10. Pd-catalyzed Sequential Arylation for the Synthesis of **10**



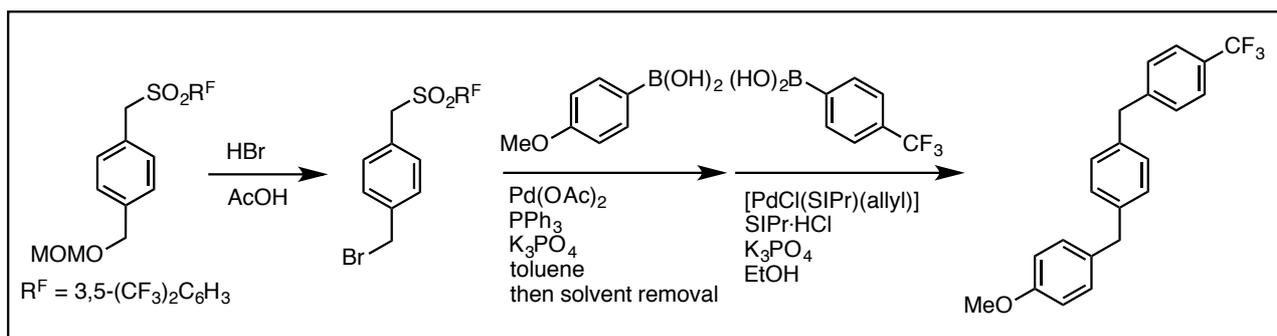
A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added  $\text{Pd}(\text{OAc})_2$  (2.2 mg, 10  $\mu\text{mol}$ ), SPhos (8.2 mg, 20  $\mu\text{mol}$ ),  $\text{K}_3\text{PO}_4$  (127 mg, 0.6 mmol), and dry THF (400  $\mu\text{L}$ ) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, 3,5-bis(trifluoromethyl)phenyl 4-chlorobenzyl sulfone **2f** (80.6 mg, 0.2 mmol), 3,4-dimethoxyphenylboronic acid (54.6 mg, 0.3 mmol), and dry THF (400  $\mu\text{L}$ ) were added, and then the vessel was sealed. The mixture was stirred at 50  $^{\circ}$ C for 12 h. After cooling to room temperature, solvent was removed in *vacuo*. To this vessel were added 4-pyridineboronic acid (49.3 mg, 0.4 mmol),  $\text{K}_3\text{PO}_4$  (63.5 mg, 0.3 mmol), and dry EtOH (1 mL) under a stream of argon, and then the vessel was sealed. The mixture was stirred at 120  $^{\circ}$ C for 12 h. After cooling to room temperature, O-ring tap was removed and the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:2) to afford **10** (26.5 mg, 43%, 2 steps) as a white solid.  $^{12}\text{C}$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.92 (s, 3H), 3.94 (s, 3H), 4.00 (s, 2H), 6.94 (d,  $J$  = 8.8 Hz, 1H), 7.09 (d,  $J$  = 2.4 Hz, 1H), 7.12-7.15 (m, 3H), 7.23 (d,  $J$  = 8.0 Hz, 2H), 7.51 (d,  $J$  = 8.0 Hz, 2H), 8.51 (d,  $J$  = 6.0 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  40.8, 55.90, 55.94, 110.3, 111.4, 119.2, 124.2, 127.1, 129.4, 133.7, 137.5, 139.5, 148.6, 149.1, 149.8, 149.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 306.1489, found 306.1487.

## 11. Competitive Reaction of Desulfonative Arylation with 4-Methylbenzyl Bromide



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added Pd(OAc)<sub>2</sub> (1.1 mg, 5 μmol), PPh<sub>3</sub> (2.6 mg, 10 μmol), K<sub>3</sub>PO<sub>4</sub> (63.5 mg, 0.3 mmol), **2a** (36.9 mg, 0.1 mmol), 4-methylbenzyl bromide (18.5 mg, 0.1 mmol), phenylboronic acid **4a** (18.3 mg, 0.15 mmol) and dry toluene (400 μL) at room temperature under a stream of argon. The vessel was sealed and this mixture was stirred at 80 °C for 12 h. The yield of 4-benzyltoluene **5ba** and unreacted **2a** were determined to be 98% and >99%, respectively, by GC analysis of crude mixture using dodecane as an internal standard.

## 12. Pd-catalyzed Sequential Arylation for the Synthesis of 11



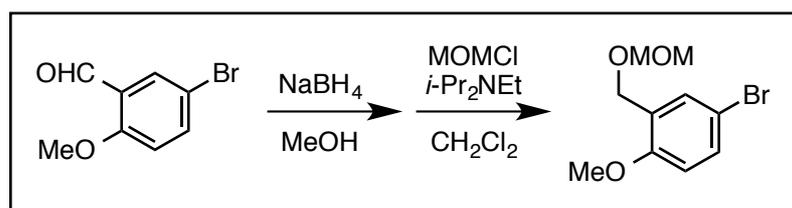
A 50-mL two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added 3,5-bis(trifluoromethyl)phenyl 4-(methoxymethoxymethyl)benzyl sulfone **2d** (221 mg, 0.5 mmol) and HBr (5 mL, 30% in AcOH) at room temperature. After stirring at this temperature for 2 h, the mixture was quenched with sat. Na<sub>2</sub>CO<sub>3</sub> aq, extracted with EtOAc (3 times), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc/hexane = 1:10) to give the 3,5-bis(trifluoromethyl)phenyl 4-(bromomethyl)benzyl sulfone **2q** as a white solid (204.2 mg, 89% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.38 (s, 2H), 4.44 (s, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.99 (s, 2H), 8.09 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 31.9, 62.5, 122.2 (q, *J* = 278 Hz), 127.0, 127.3 (br.t, *J* = 3.8 Hz), 129.1 (br.d, *J* = 3.8 Hz), 129.6, 131.2, 132.8 (q, *J* = 35.3 Hz), 139.5, 140.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.9. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>F<sub>6</sub>SBrNa [M+Na]<sup>+</sup>: 482.9460, found 482.9460.

A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added Pd(OAc)<sub>2</sub> (2.2 mg, 10 μmol), PPh<sub>3</sub> (5.2 mg, 20 μmol), K<sub>3</sub>PO<sub>4</sub> (127 mg, 0.6 mmol), **2q** (92.1 mg, 0.2

mmol), 4-methoxyphenylboronic acid **4b** (45.6 mg, 0.3 mmol) and dry toluene (800  $\mu$ L) at room temperature under a stream of argon. The vessel was sealed and this mixture was stirred at 80  $^{\circ}$ C for 12 h. After cooling to room temperature, solvent was removed in *vacuo*. To this vessel were added [PdCl(allyl)(SIPr)] (11.5 mg, 20  $\mu$ mol), SIPr-HCl (8.5 mg, 20  $\mu$ mol), 4-trifluoromethylphenylboronic acid **4c** (76.0 mg, 0.4 mmol), K<sub>3</sub>PO<sub>4</sub> (63.5 mg, 0.3 mmol), and dry EtOH (1 mL) under a stream of argon, and then the vessel was sealed. The mixture was stirred at 120  $^{\circ}$ C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:50) to afford **11** (53.8 mg, 75%, 2 steps) as a white solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  3.77 (s, 3H), 3.89 (s, 2H), 3.98 (s, 2H), 6.82 (dm, *J* = 8.4 Hz, 2H), 7.07-7.11 (m, 6H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  40.6, 41.3, 55.2, 113.9, 124.3 (q, *J* = 270 Hz), 125.3 (br.d, *J* = 4.4 Hz), 128.4 (q, *J* = 31.7 Hz), 128.95, 129.04, 129.1, 129.8, 133.2, 137.6, 139.8, 145.3, 158.0. HRMS (DART) *m/z* calcd for C<sub>22</sub>H<sub>18</sub>OF<sub>3</sub> [M-H]<sup>+</sup>: 355.1310, found 355.1302.

### 13. The Synthesis of GC-24

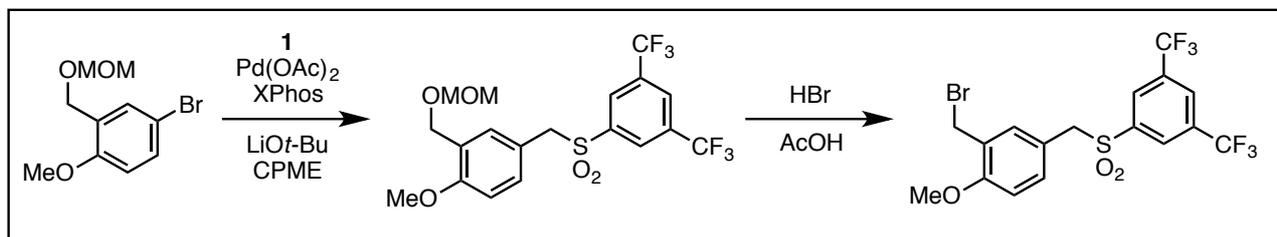
#### A) Preparation of 4-Bromo-2-(methoxymethoxymethyl)anisole **7r**



A 100-mL two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added 5-bromo-2-methoxybenzaldehyde (2.15 g, 10 mmol) and dry MeOH (20 mL) under a stream of argon. NaBH<sub>4</sub> (757 mg, 20 mmol) was slowly added to this mixture at 0  $^{\circ}$ C. After stirring at room temperature for 1 h, the mixture was quenched with water at 0  $^{\circ}$ C and then organic solvent was evaporated under reduced pressure. The residue was extracted with EtOAc (3 times) and washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and passed through a pad of silica gel with copious washings with EtOAc. The solvent was evaporated under reduced pressure to afford benzyl alcohol as a white solid (2.17 g, >99% yield). To this flask were added dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and *i*-Pr<sub>2</sub>NEt (2 mL, 12 mmol) under a stream of argon. Chloromethyl methyl ether (900  $\mu$ L, 12 mmol) was slowly added to this mixture at room temperature. After stirring at room temperature for 12 h, the mixture was quenched with water at 0  $^{\circ}$ C and then organic solvent was evaporated under reduced pressure. The residue was extracted with ether (3 times), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude material was purified by column chromatography (EtOAc/hexane = 1:20) to give the 4-bromo-2-(methoxymethoxymethyl)anisole **7r** as a colorless oil (2.56 g, 98% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.42 (s, 3H), 3.81 (s, 3H), 4.59 (s, 2H), 4.73 (s, 2H), 6.74 (d, *J* = 9.2 Hz, 1H), 7.36 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>) δ 55.3, 55.6, 63.7, 96.0, 111.8, 112.7, 128.7, 131.2, 131.4, 156.1. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>13</sub>O<sub>3</sub>BrNa [M+Na]<sup>+</sup>: 282.9940, found 282.9943.

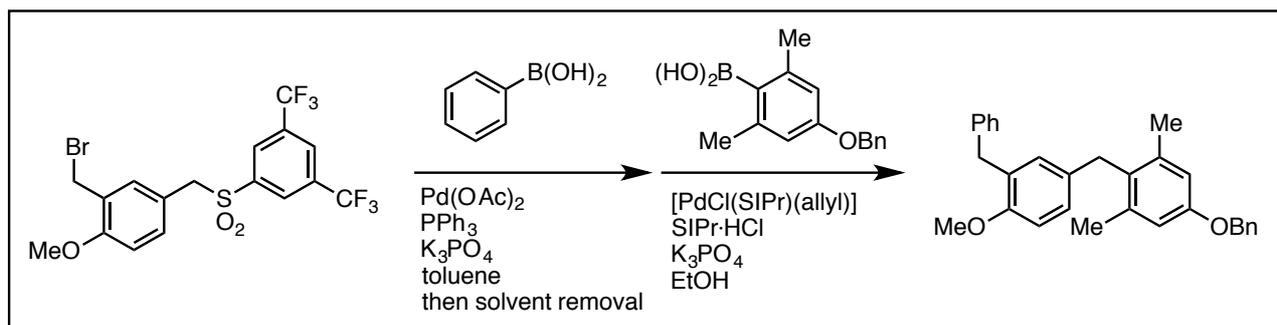
## B) Preparation of 4s



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added Pd(OAc)<sub>2</sub> (3.3 mg, 15 μmol), XPhos (14.1 mg, 30 μmol), and dry CPME (750 μL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, **6** (219 mg, 0.75 mmol), **7r** (78.3 mg, 0.3 mmol), LiOt-Bu (59.9 mg, 0.75 mmol), dry CPME (750 μL) were added, and then the vessel was sealed. The mixture was stirred at 70 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:10) to afford **2r** (127.5 mg, 90%) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.35 (s, 3H), 3.82 (s, 3H), 4.34 (s, 2H), 4.51 (s, 2H), 4.64 (s, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 7.04 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.98 (s, 2H), 8.06 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 55.2, 55.5, 62.5, 63.6, 95.9, 110.5, 118.5, 122.3 (q, *J* = 272 Hz), 127.0 (br.t, *J* = 3.5 Hz), 127.5, 129.2 (br.d, *J* = 2.4 Hz), 130.8, 131.0, 132.6 (q, *J* = 34.6 Hz), 140.4, 157.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.9. HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>18</sub>O<sub>5</sub>F<sub>6</sub>SNa [M+Na]<sup>+</sup>: 495.0671, found 495.0670.

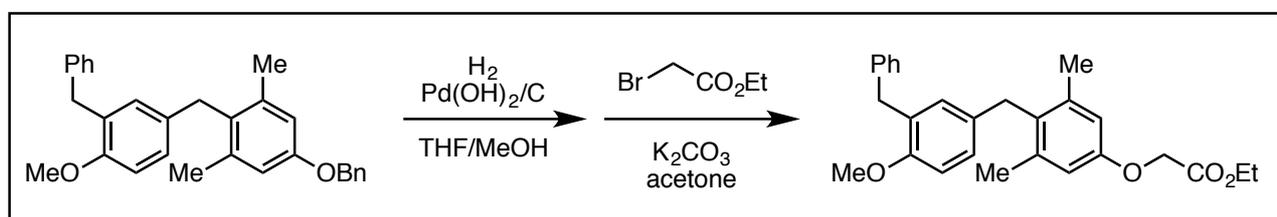
A 50-mL two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added **2r** (236 mg, 0.5 mmol) and HBr (5 mL, 30% in AcOH) at room temperature. After stirring at this temperature for 2 h, the mixture was quenched with sat. Na<sub>2</sub>CO<sub>3</sub>aq, extracted with EtOAc (3 times), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc/hexane = 1:10) to give **2s** as a white solid (239.2 mg, 97% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.88 (s, 3H), 4.32 (s, 2H), 4.42 (s, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 7.02-7.05 (m, 2H), 7.98 (s, 2H), 8.08 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 27.4, 55.8, 62.1, 111.3, 118.8, 122.2 (q, *J* = 274 Hz), 127.2, 127.3 (br.t, *J* = 3.8 Hz), 129.1 (br.d, *J* = 2.9 Hz), 132.4, 132.7 (q, *J* = 34.5 Hz), 133.1, 140.2, 158.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.8. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>12</sub>O<sub>3</sub>F<sub>6</sub>SBr [M-H]<sup>-</sup>: 488.9600, found 488.9601.

### C) Preparation of 12



A 10-mL sealable glass vessel containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the glass vessel were added Pd(OAc)<sub>2</sub> (2.2 mg, 10 μmol), PPh<sub>3</sub> (5.2 mg, 20 μmol), K<sub>3</sub>PO<sub>4</sub> (127 mg, 0.6 mmol), **2s** (98.2 mg, 0.2 mmol), phenylboronic acid **4a** (36.6 mg, 0.3 mmol) and dry toluene (800 μL) at room temperature under a stream of argon. The vessel was sealed and this mixture was stirred at 80 °C for 12 h. After cooling to room temperature, solvent was removed in *vacuo*. To this vessel were added [PdCl(allyl)(SIPr)] (11.6 mg, 20 μmol), SIPr-HCl (8.5 mg, 20 μmol), 4-benzyloxy-2,6-dimethylphenylboronic acid **4v** (102.4 mg, 0.4 mmol), K<sub>3</sub>PO<sub>4</sub> (63.5 mg, 0.3 mmol), and dry EtOH (1 mL) under a stream of argon, and then the vessel was sealed. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~15 mL). The filtrate was concentrated under reduced pressure. The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:50) to afford **12** (56.2 mg, 66%, 2 steps) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.18 (s, 6H), 3.74 (s, 3H), 3.86 (s, 2H), 3.91 (s, 2H), 5.04 (s, 2H), 6.69 (s, 2H), 6.71-6.72 (m, 2H), 6.80 (s, 1H), 7.14-7.17 (m, 3H), 7.23-7.26 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 20.5, 33.5, 36.0, 55.4, 69.8, 110.4, 114.2, 125.6, 126.1, 127.5, 127.8, 128.2, 128.5, 128.8, 129.3, 129.9, 130.2, 131.9, 137.4, 138.4, 141.1, 155.5, 156.8. HRMS (ESI) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>: 445.2138, found 445.2135.

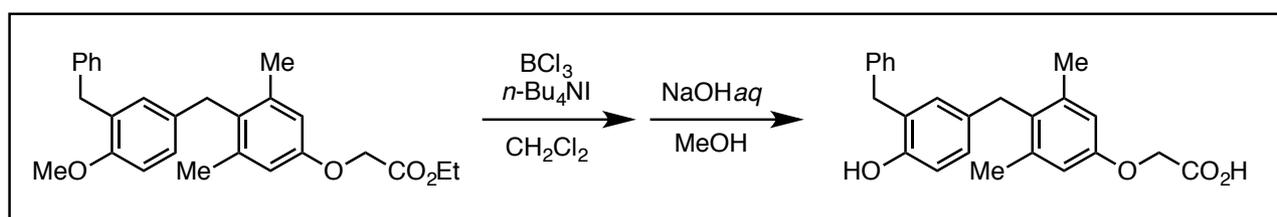
### D) Preparation of 13



To 10-mL flask were added **12** (84.5 mg, 0.2 mmol), Pd(OH)<sub>2</sub>/C (23 mg, Pd 20%, wetted with ca. 50% water), THF (400 μL), and MeOH (400 μL) at room temperature. This mixture was vigorously stirred at room temperature under hydrogen pressure (1 atm, balloon) for 4 h. The mixture was passed through Celite with copious washings with EtOAc (~10 mL), and evaporated under reduced pressure. The residue was dissolved in dry acetone (5 mL), and K<sub>2</sub>CO<sub>3</sub> (83 mg, 0.6

mmol) and ethyl bromoacetate (26.5  $\mu$ L, 0.24 mmol) was added. The mixture was heated under reflux for 12 h. After cooling to room temperature, the mixture was quenched with H<sub>2</sub>O and then organic solvent was evaporated under reduced pressure. The residue was extracted with EtOAc (3 times), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude product was purified by PTLC (EtOAc/hexane = 1:10) to afford **13** (74.9 mg, 89%, 2 steps) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.31 (t, *J* = 7.2 Hz, 3H), 2.17 (s, 6H), 3.75 (s, 3H), 3.85 (s, 2H), 3.90 (s, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.60 (s, 2H), 6.61 (s, 2H), 6.70 (s, 2H), 6.79 (s, 2H), 7.15-7.18 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.1, 20.4, 33.4, 35.9, 55.4, 61.2, 65.4, 110.3, 114.1, 125.6, 126.1, 128.1, 128.8, 129.3, 130.1, 130.6, 131.6, 138.4, 141.1, 155.5, 155.8, 169.2. HRMS (ESI) *m/z* calcd for C<sub>27</sub>H<sub>30</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup>: 441.2036, found 441.2034.

#### E) Preparation of GC-24



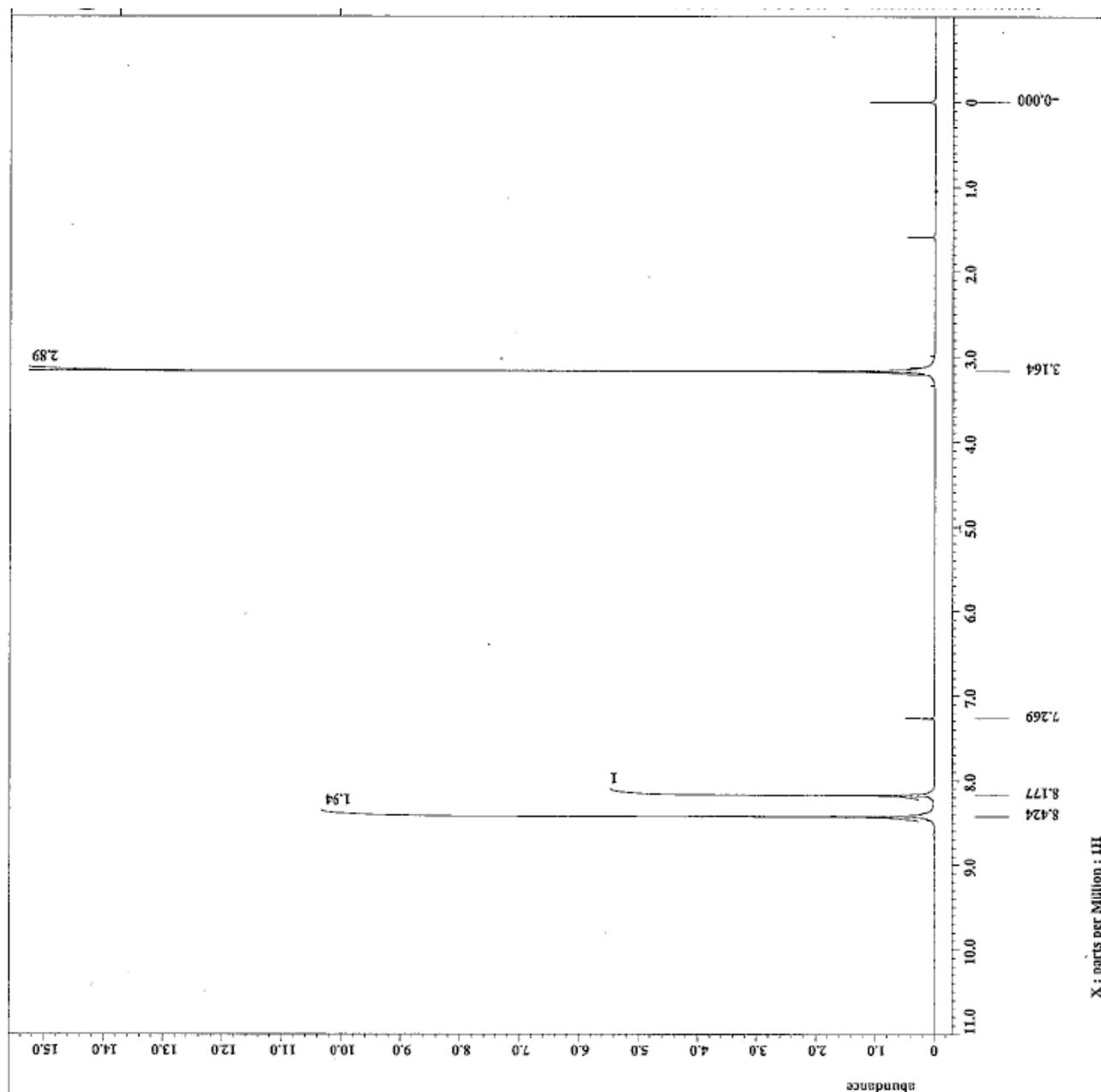
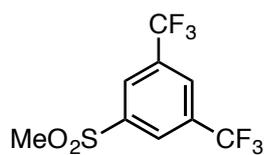
A 10-mL two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added **13** (62.9 mg, 0.15 mmol), *n*-Bu<sub>4</sub>NI (140 mg, 0.375 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at room temperature under a stream of argon. 1.0 M BCl<sub>3</sub> in hexane (375  $\mu$ L, 0.375 mmol) was slowly added to this mixture at -78 °C. The reaction was stirred at -78 °C for 5 min and then warmed to 0 °C and stirred for 2 h. The mixture was quenched with water at 0 °C and extracted with EtOAc (3 times), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The residue was dissolved in MeOH (4 mL), and 2M NaOH aq (2 mL) was added. After stirring at room temperature for 1 h, then organic solvent was evaporated under reduced pressure. 2M HCl aq (4 mL) was added, and mixture was extracted with EtOAc (3 times), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude material was purified via reverse-phase HPLC to give GC-24 as a white solid (47.1 mg, 83%, 2 steps). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  2.22 (s, 6H), 3.80 (s, 2H), 3.83 (s, 2H), 4.57 (s, 2H), 6.57-6.60 (m, 1H), 6.59 (s, 2H), 6.62-6.64 (m, 2H), 7.07-7.12 (m, 3H), 7.16-7.20 (m, 2H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  20.5, 34.2, 36.6, 65.8, 115.0, 115.9, 126.6, 127.3, 128.9, 129.1, 129.8, 131.1, 131.97, 131.99, 139.4, 142.7, 154.1, 157.3, 173.1. HRMS (ESI) *m/z* calcd for C<sub>24</sub>H<sub>23</sub>O<sub>4</sub> [M-H]<sup>-</sup>: 375.1602, found 375.1594.

#### 14. References

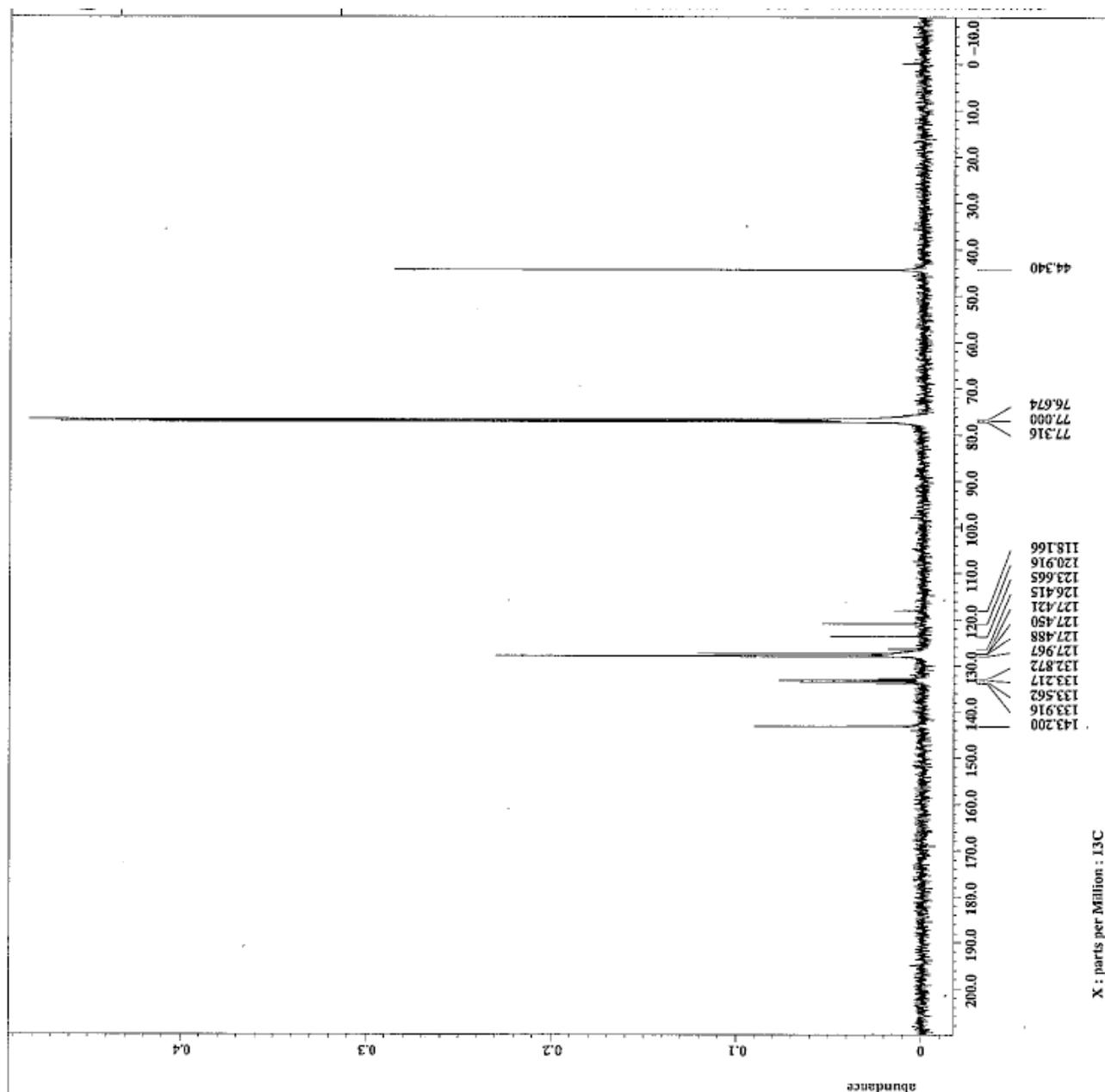
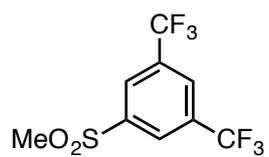
- (1) Hasegawa, A.; Ishikawa, T.; Ishihara, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1401–1410.
- (2) Nambo, M.; Crudden, C. M. *Angew. Chem. Int. Ed.* **2014**, *53*, 742–746.
- (3) Jiang, F.; Zhao, Y.; Hu, J. *Org. Chem. Front.* **2014**, *1*, 625–629.
- (4) Kinzel, O.; Fattori, D.; Muraglia, E.; Gallinari, P.; Nardi, M. C.; Paolini, C.; Roscilli, G.; Toniatti, C.; Paz, O. G.; Laufer, R.; Lahm, A.; Tramontano, A.; Cortese, R.; Francesco, R. D.; Ciliberto, G.; Koch, U. *J. Med. Chem.* **2006**, *49*, 5404–5407.
- (5) Egawa, T.; Hirabayashi, K.; Koide, Y.; Kobayashi, C.; Takahashi, N.; Mineno, T.; Terai, T.; Ueno, T.; Komatsu, T.; Ikegaya, Y.; Matsuki, N.; Nagano, T.; Hanaoka, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 3874–3877.
- (6) Crisenza, G. E. M.; McCreanor, N. G.; Bower, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 10258–10261.
- (7) Goto, T.; Natori, Y.; Takeda, K.; Nambu, H.; Hashimoto, S. *Tetrahedron: Asymmetry* **2011**, *22*, 907–915.
- (8) Rechenmacher, F.; Neubauer, S.; Polleux, J.; Mas-Moruno, C.; Simone, M. D.; Cavalcanti-Adam, E. A.; Spatz, J. P.; Fässler, R.; Kessler, H. *Angew. Chem. Int. Ed.* **2013**, *52*, 1572–1575.
- (9) Viciu, M.S.; Navarro, O.; Germaneau, R.F.; Kelly, R.A., III; Sommer, W.; Marion, N.; Stevens, E.D.; Cavallo, L.; Nolan, S.P. *Organometallics* **2004**, *23*, 1629–1635.
- (10) Pompeo, M.; Farmer, J.L.; Froese, R.D.J.; Organ, M.G. *Angew. Chem. Int. Ed.* **2014**, *53*, 3223–3226.
- (11) Alonso, D. A.; Fuensanta, M.; Nájera, C.; Varea, M. *J. Org. Chem.*, **2005**, *70*, 6404–6416.
- (12) Hu, Q.; Jagusch, C.; Hille, U. E.; Hauptenthal, J.; Hartmann, R. W. *J. Med. Chem.* **2010**, *53*, 5749–5758.

# 15. $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR Spectra of Products

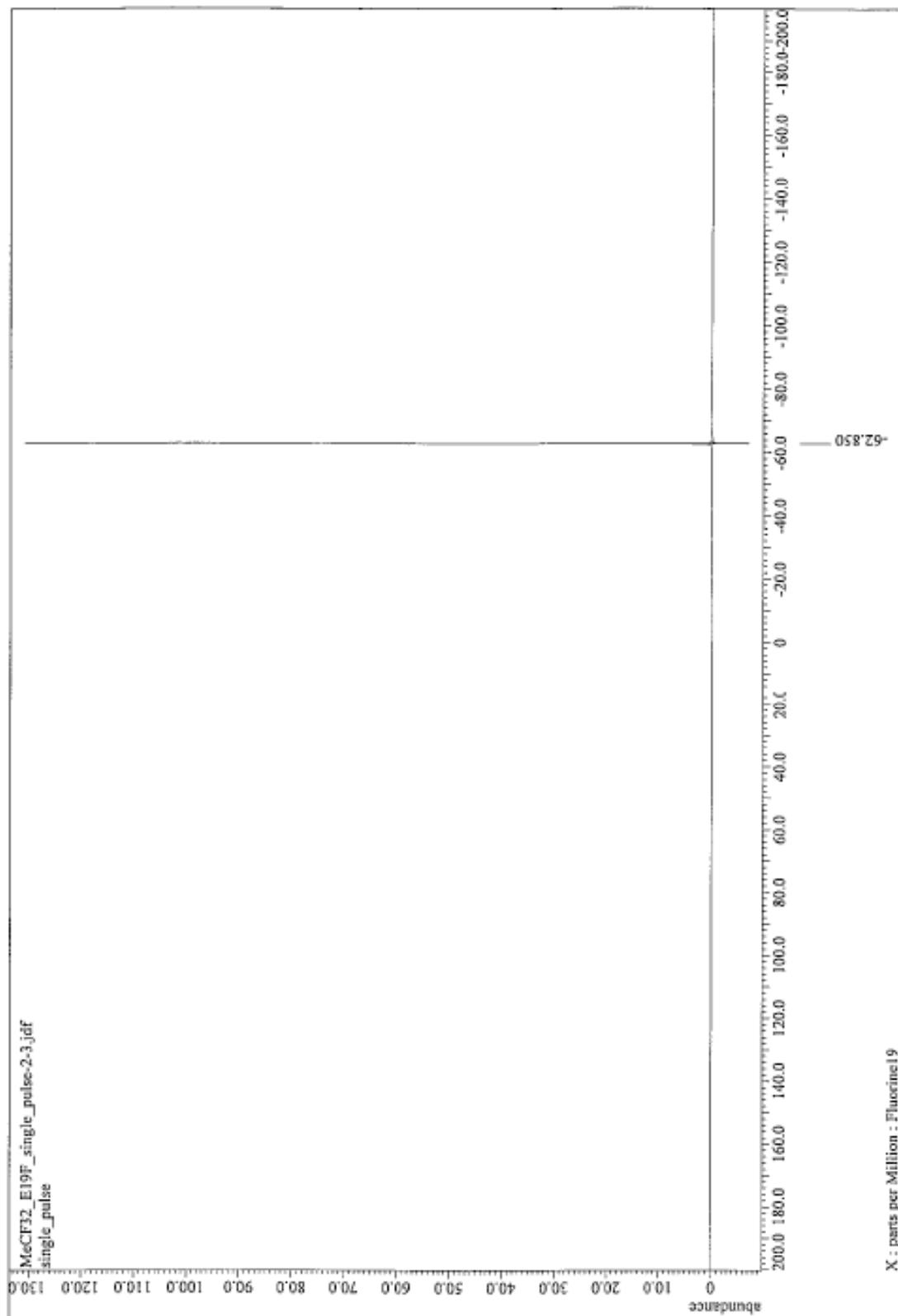
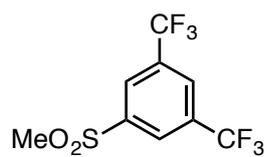
$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) of 6



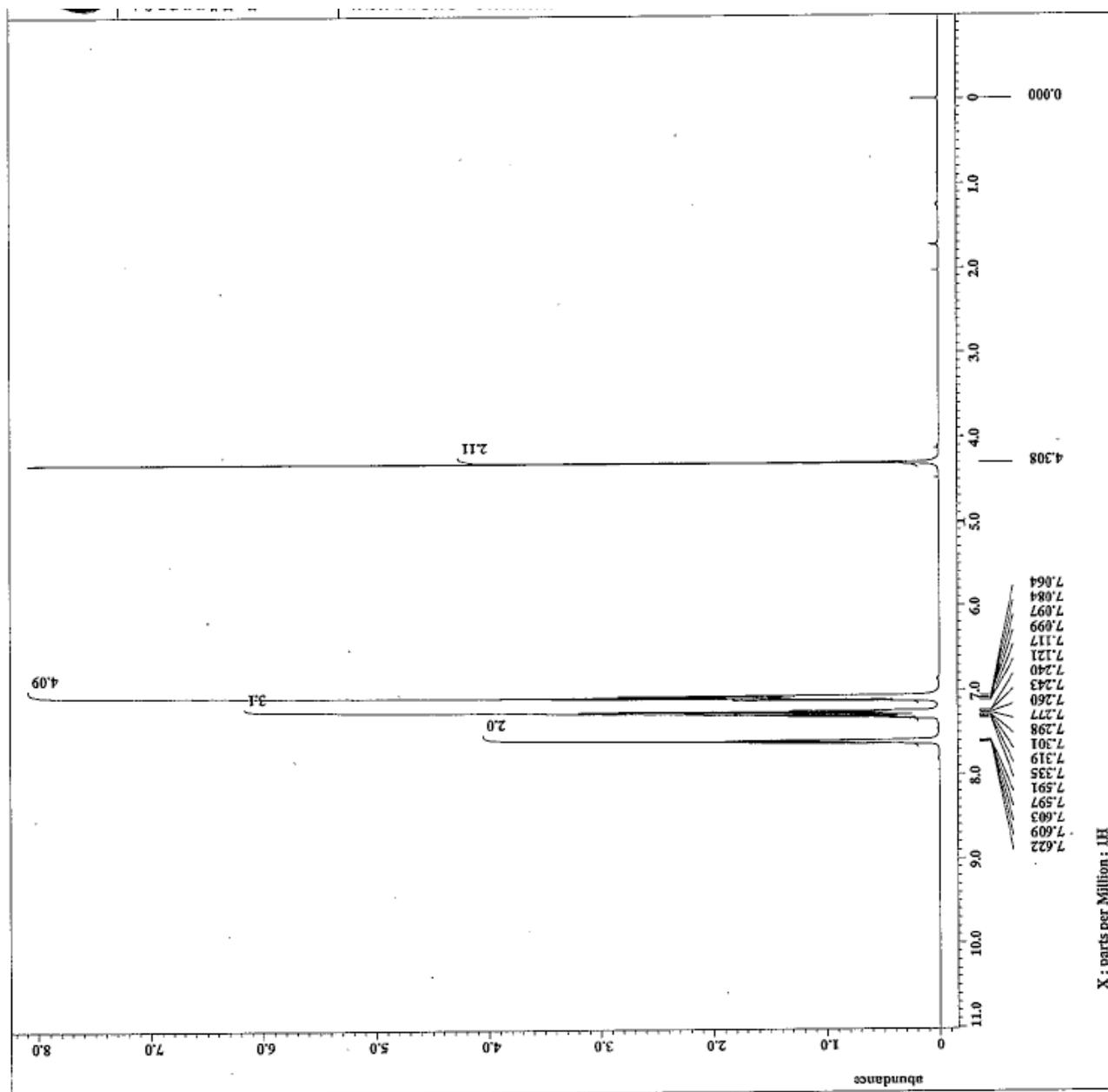
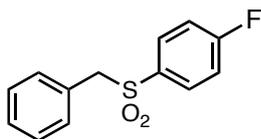
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 6



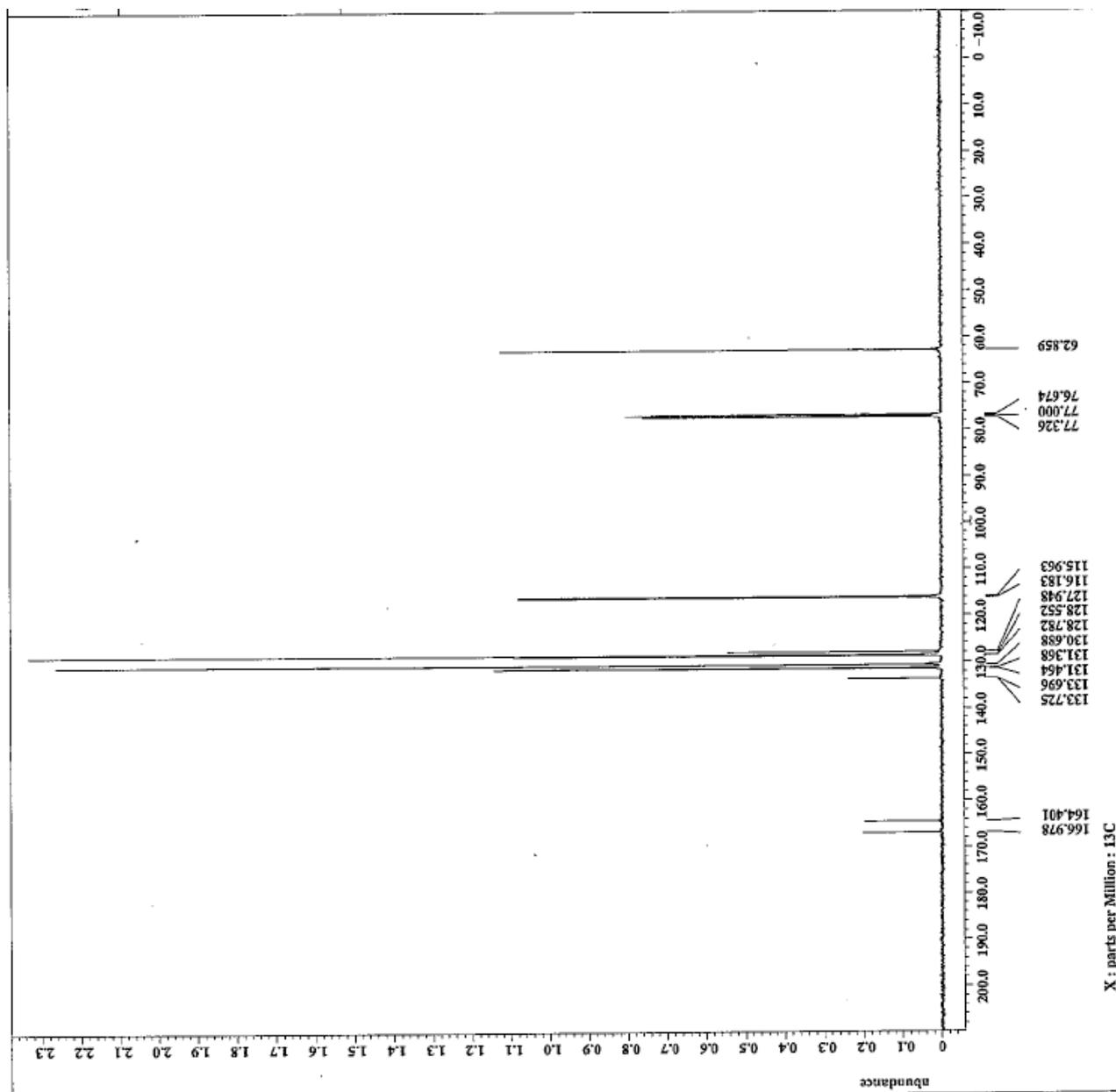
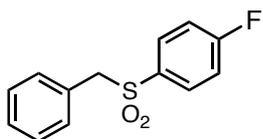
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 6



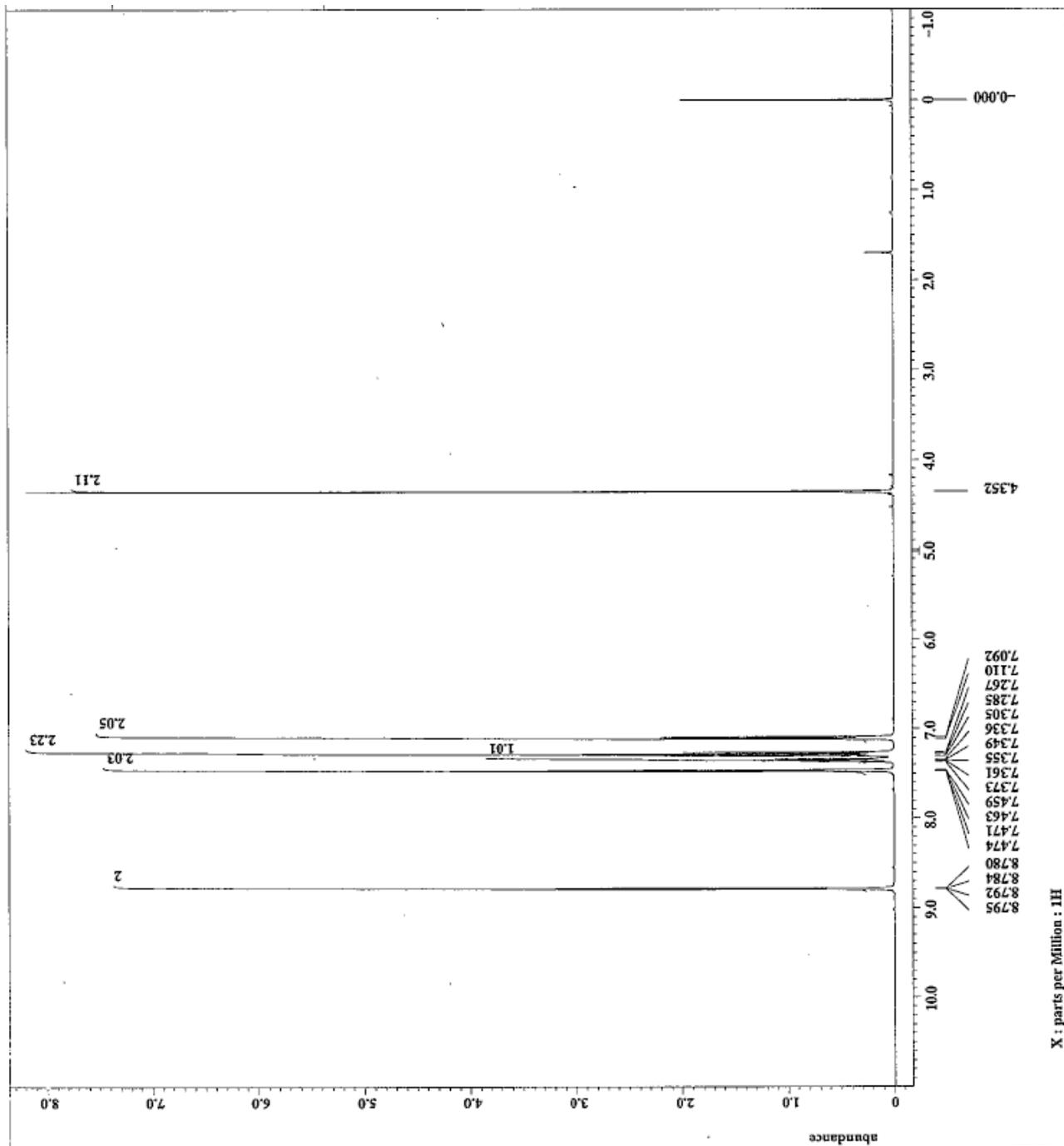
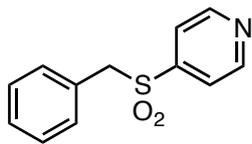
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 1b



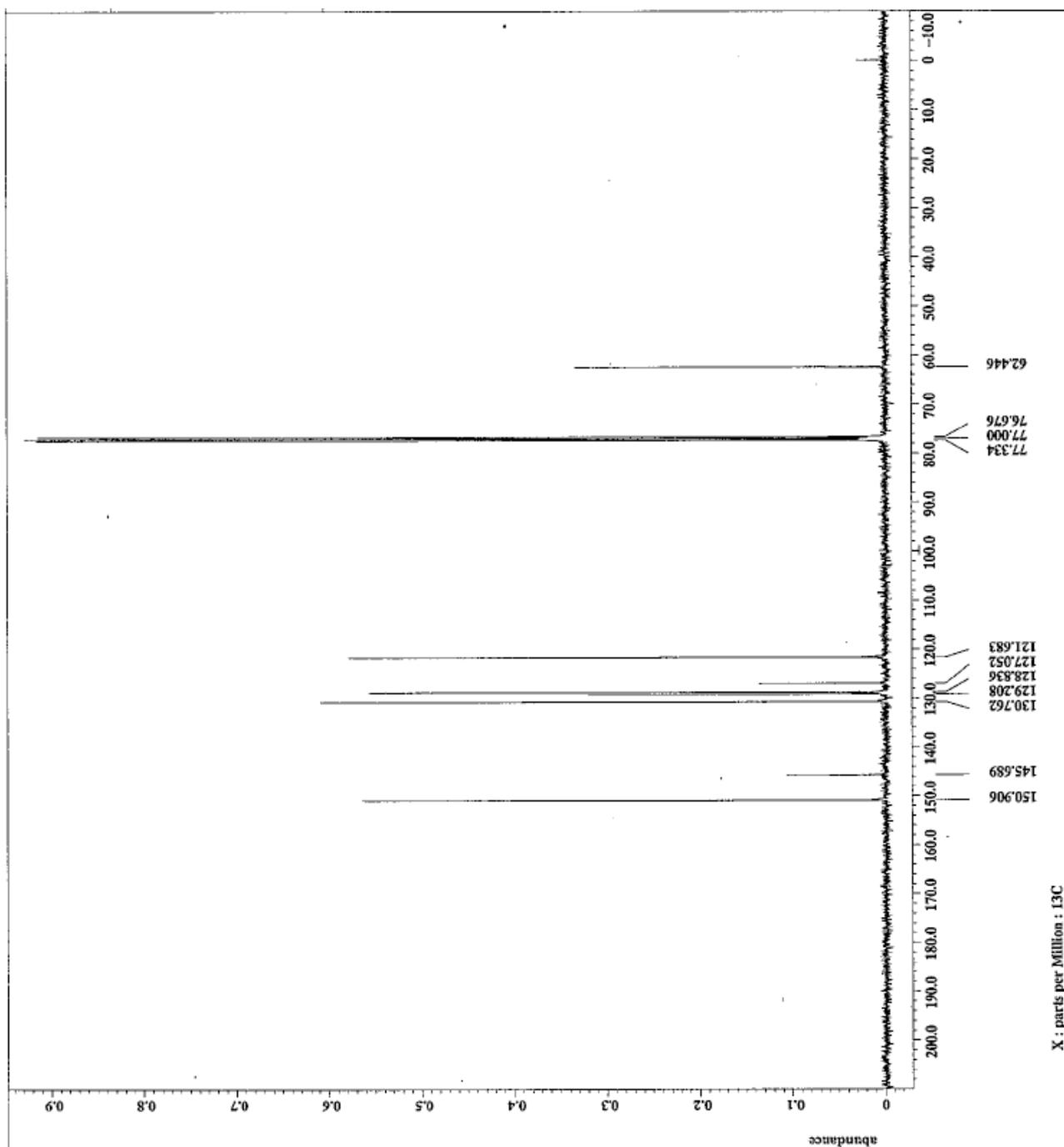
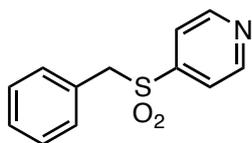
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 1b



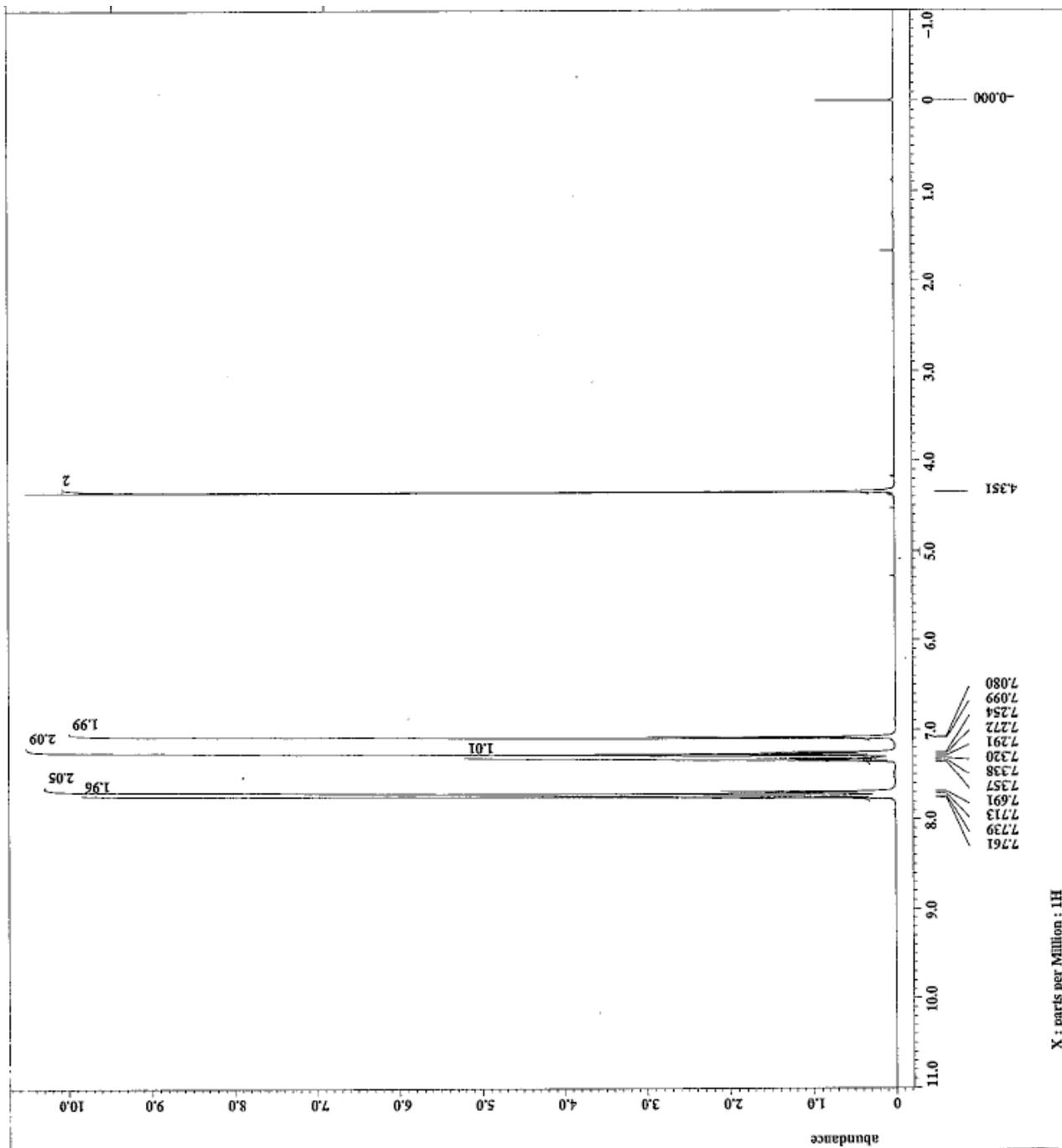
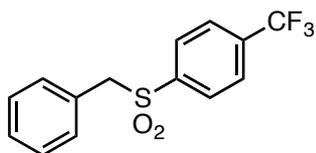
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 1d



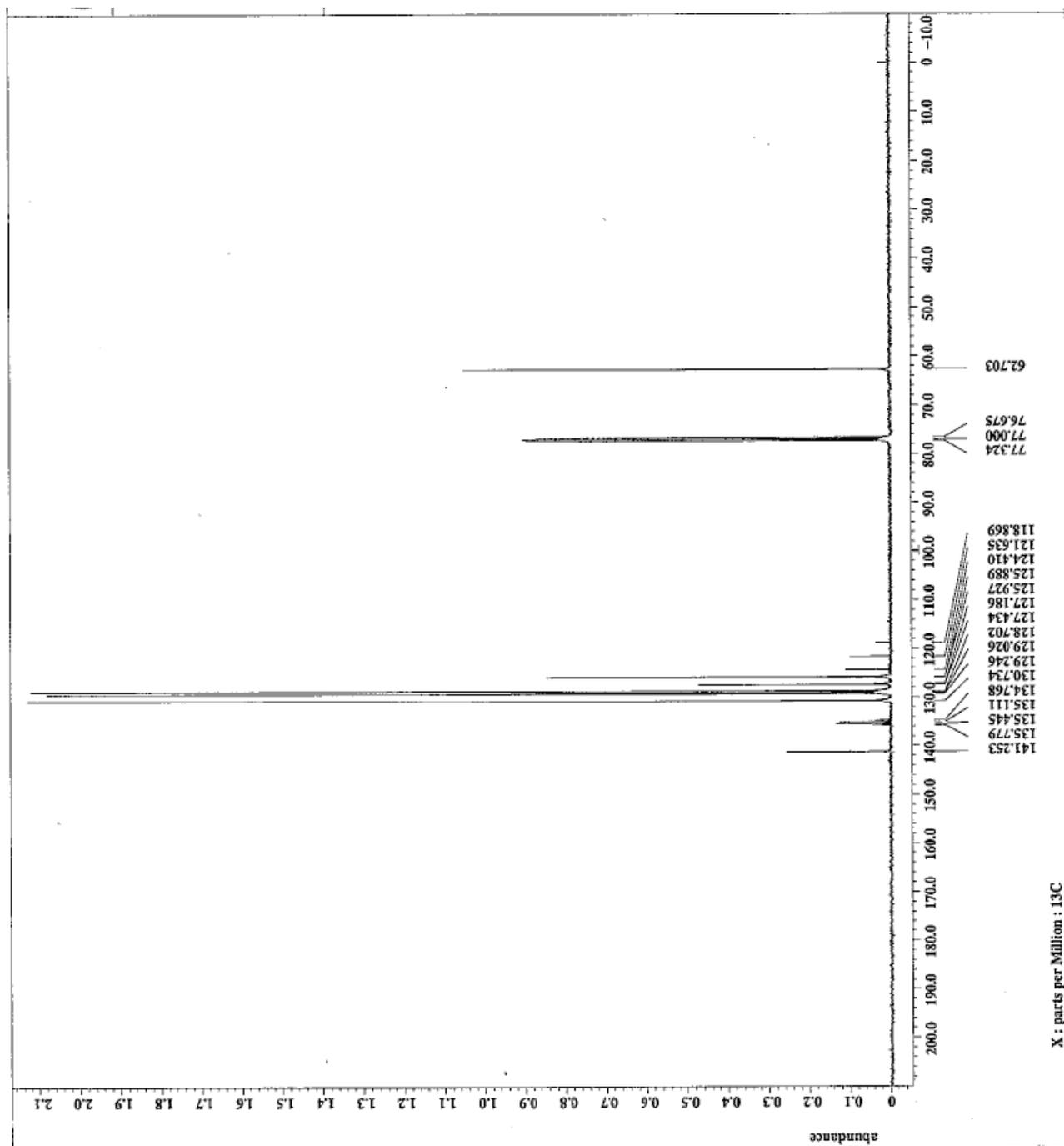
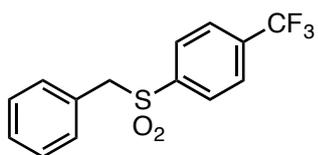
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 1d



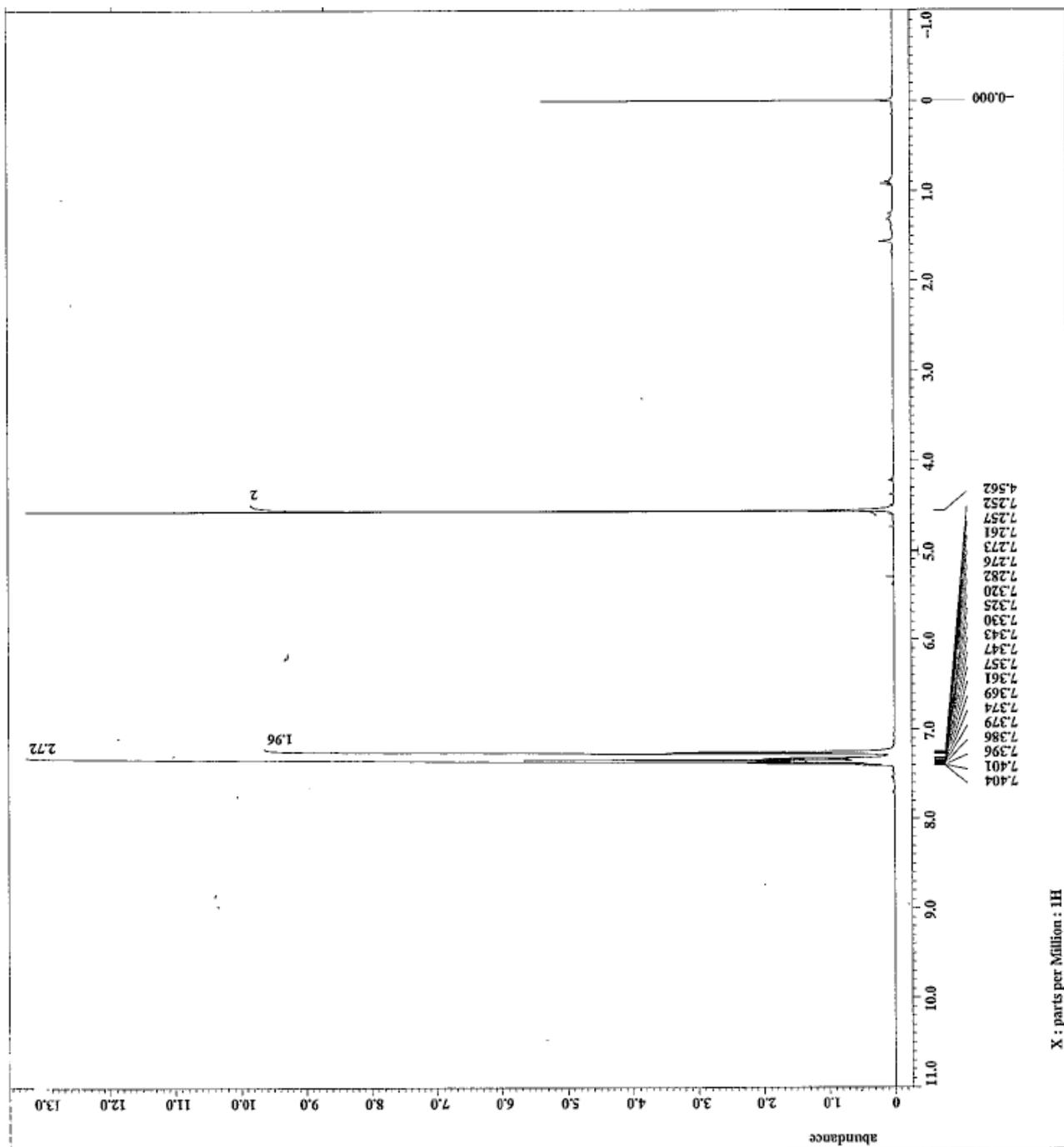
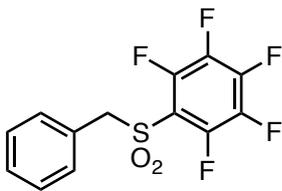
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 1f



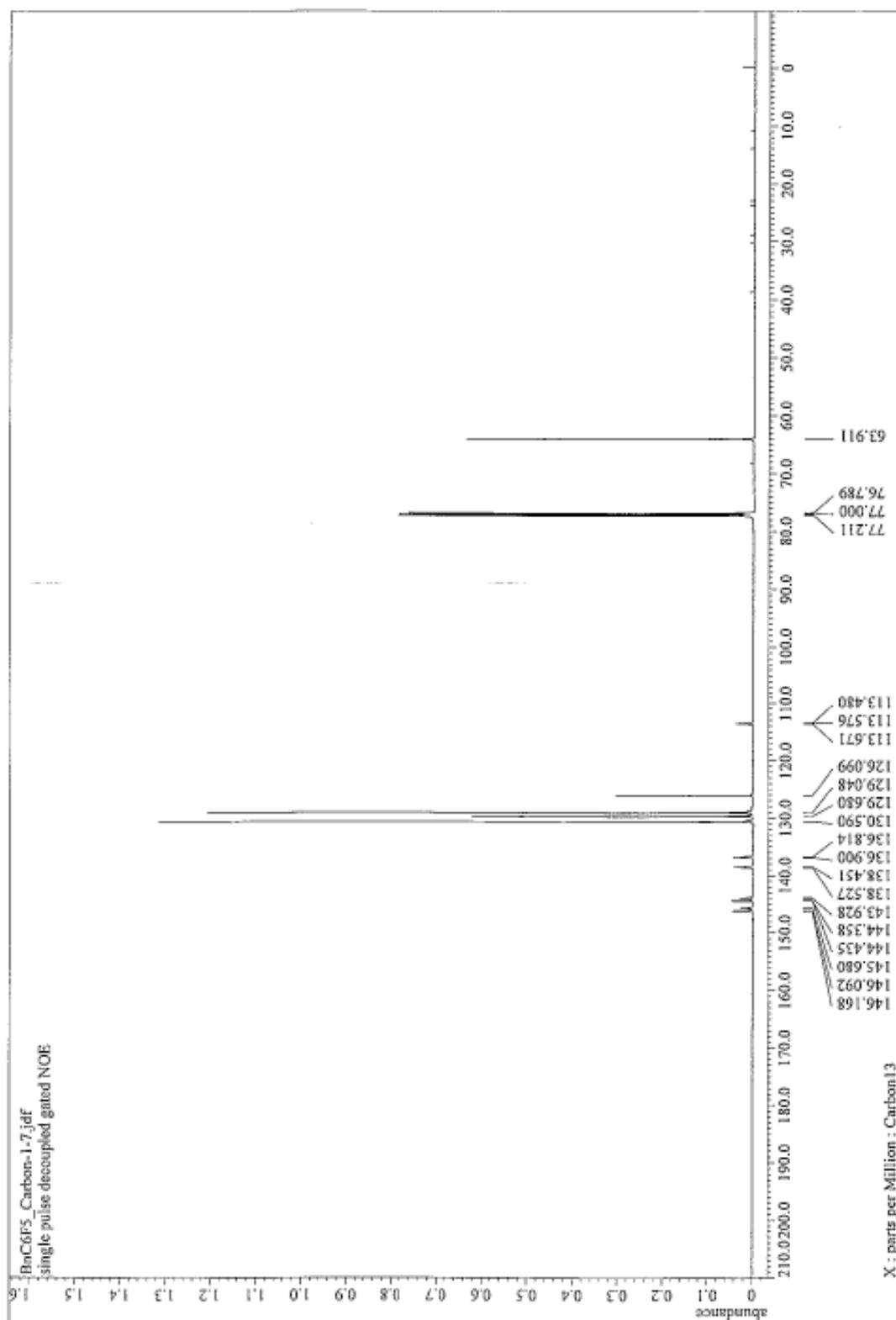
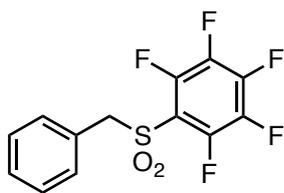
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 1f



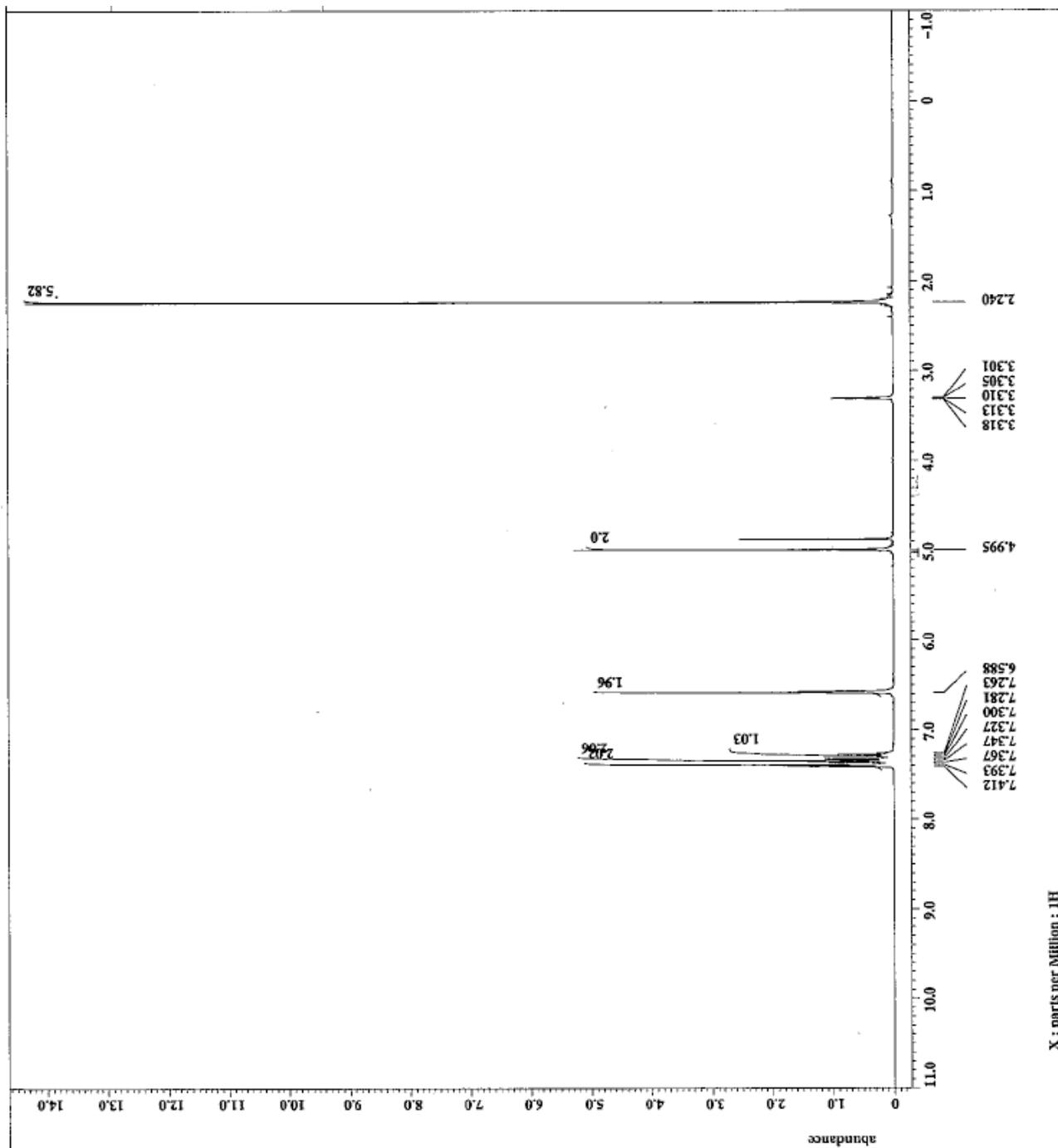
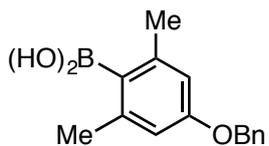
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 1g



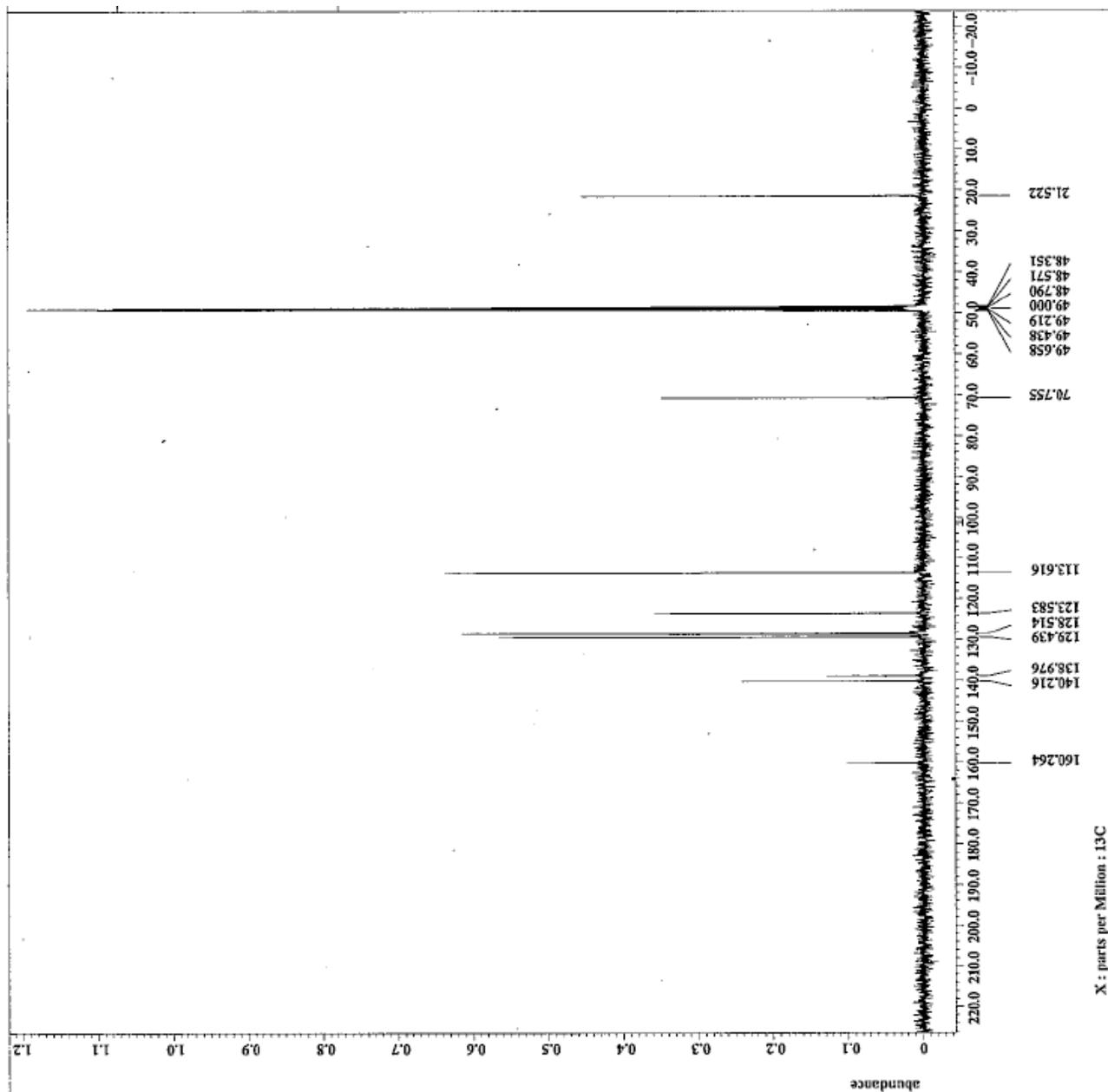
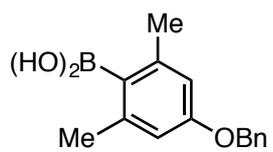
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 1g



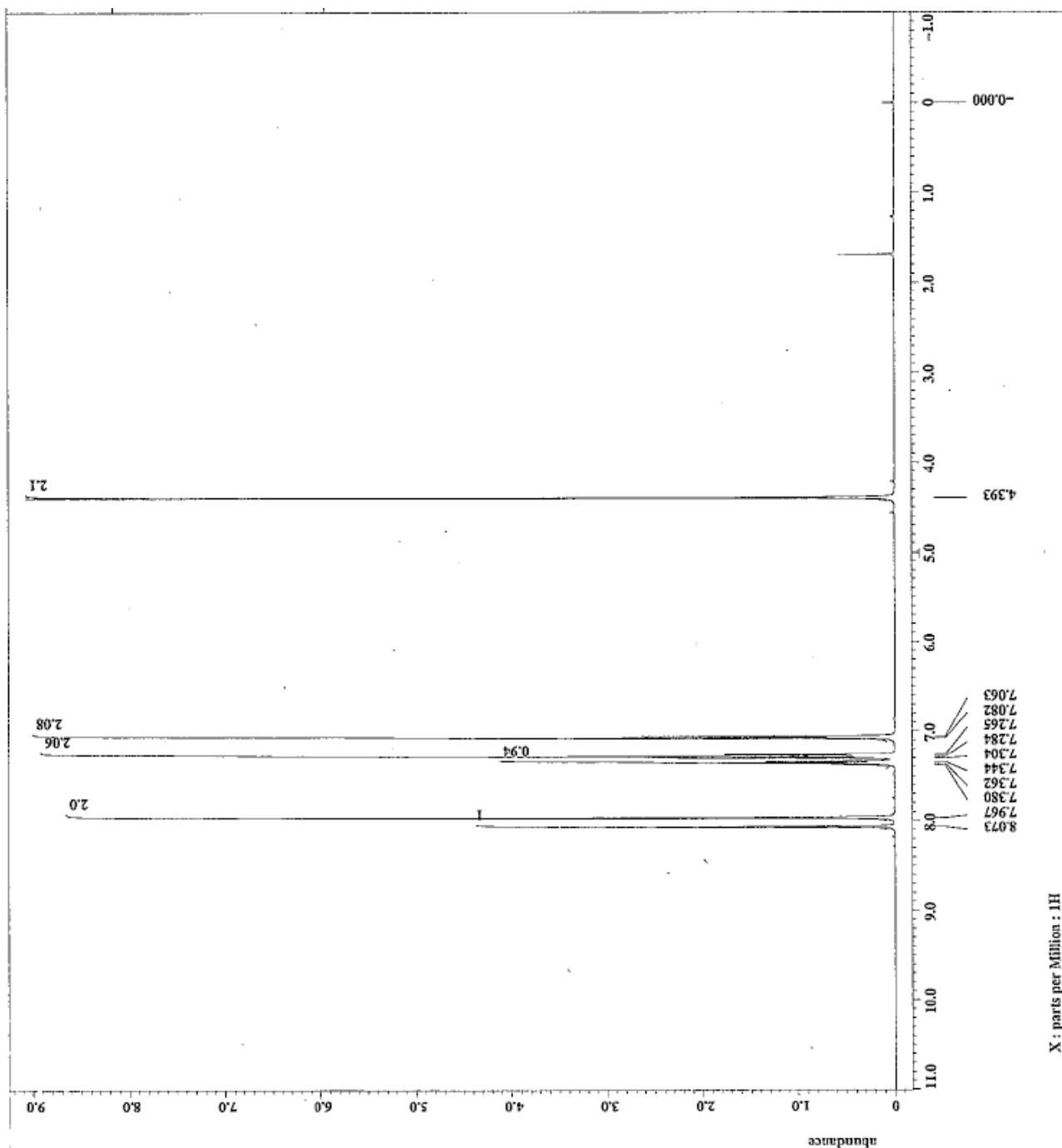
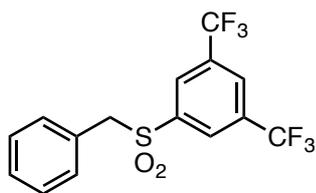
<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD) of 4v



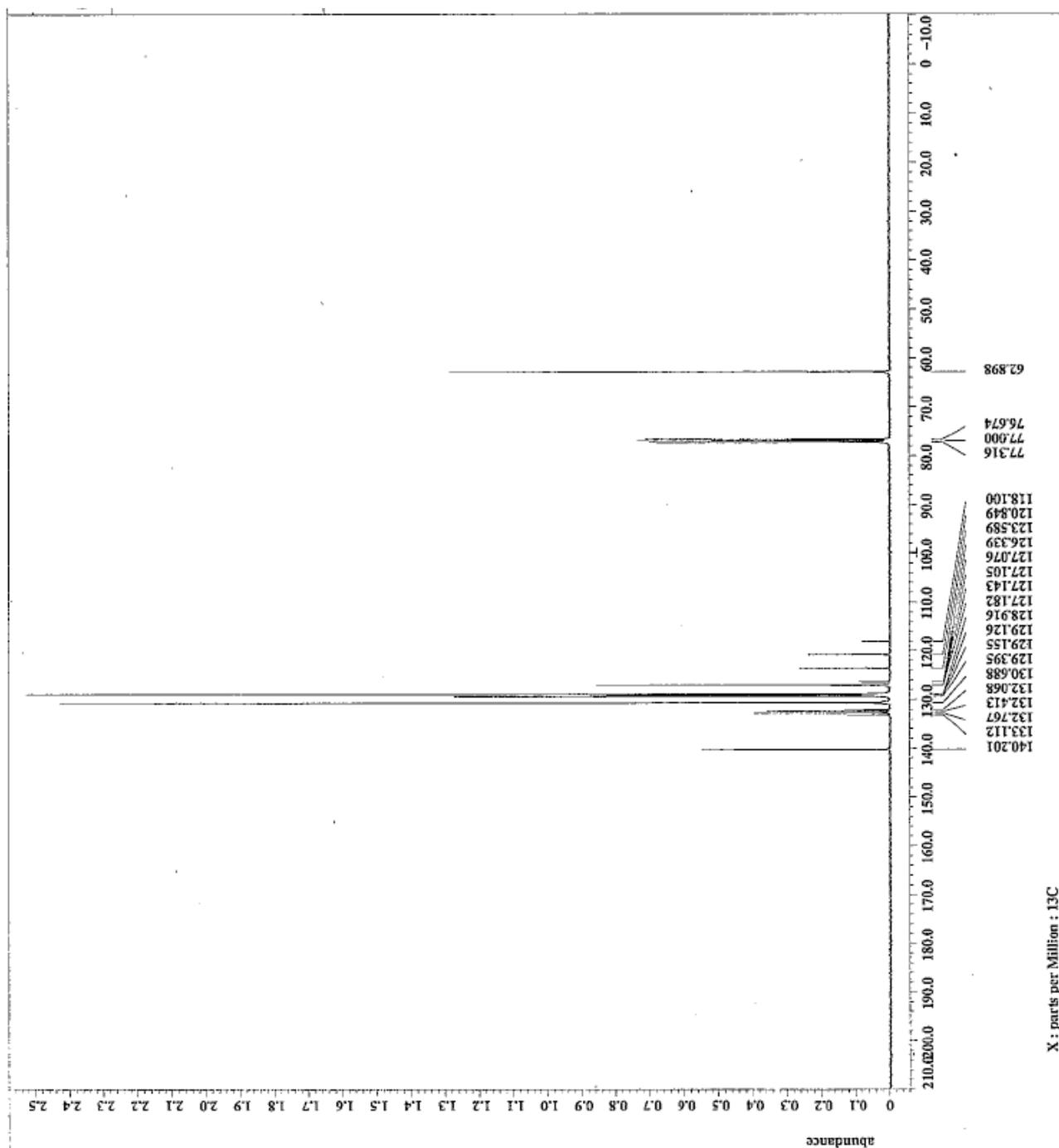
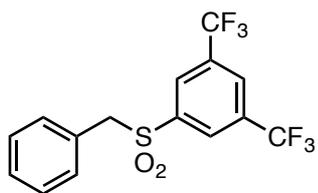
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_3\text{OD}$ ) of 4v



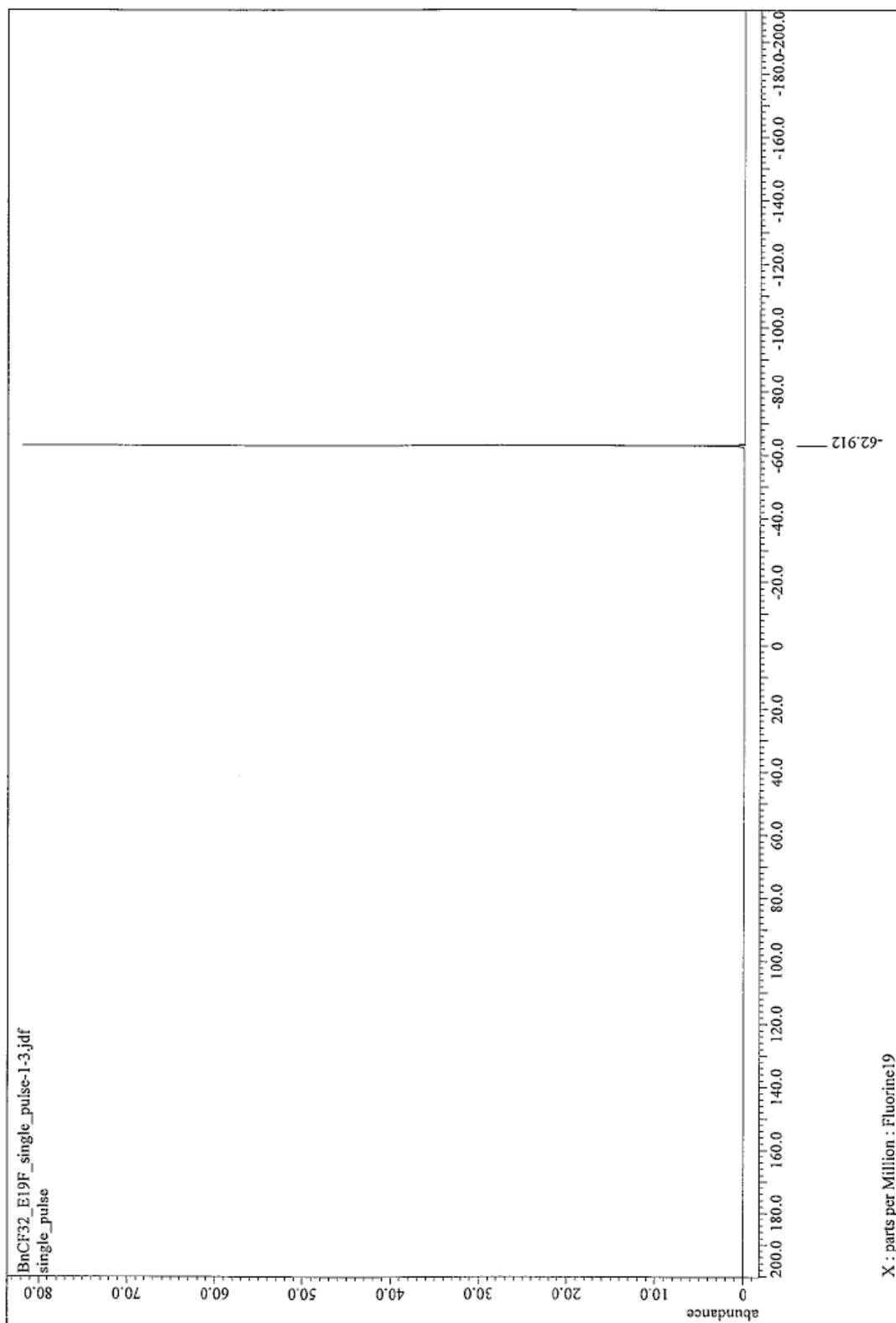
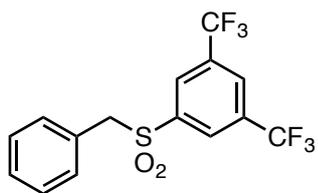
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2a



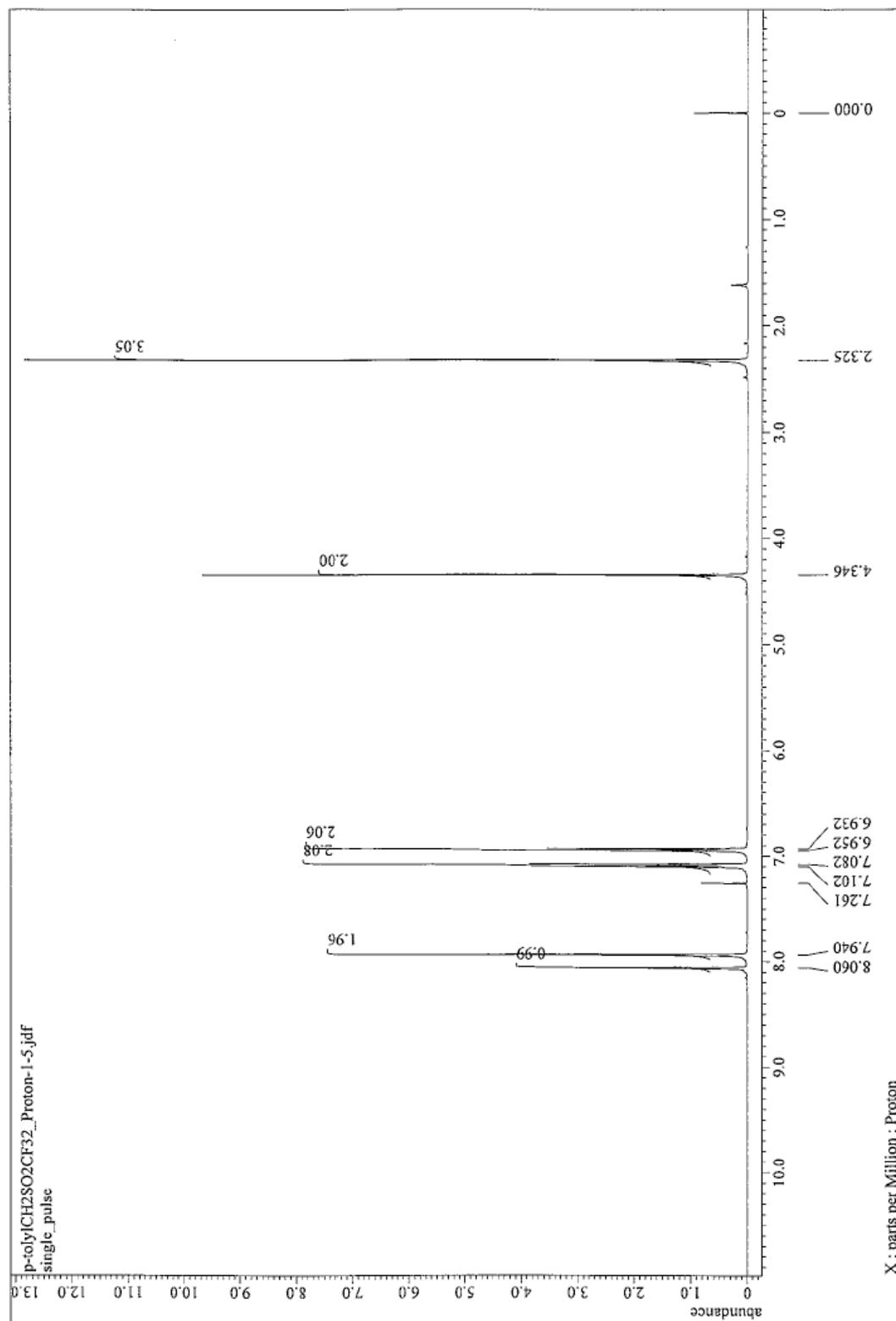
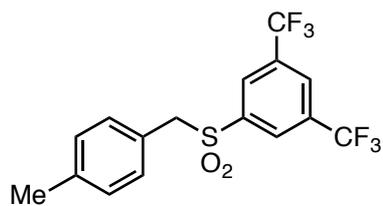
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2a



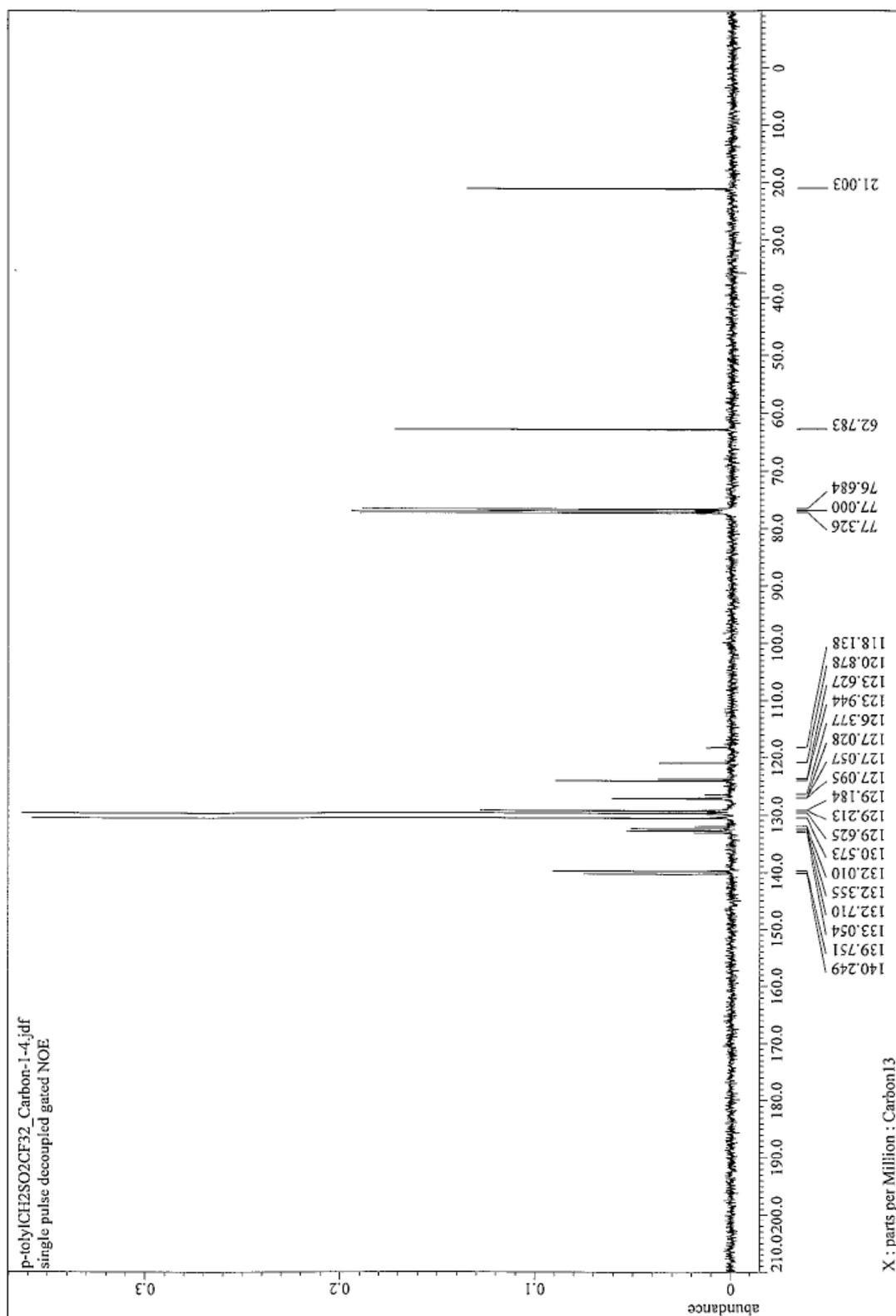
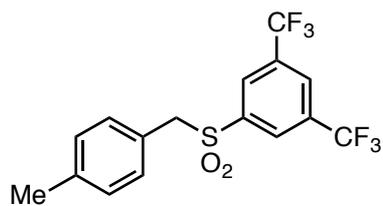
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2a



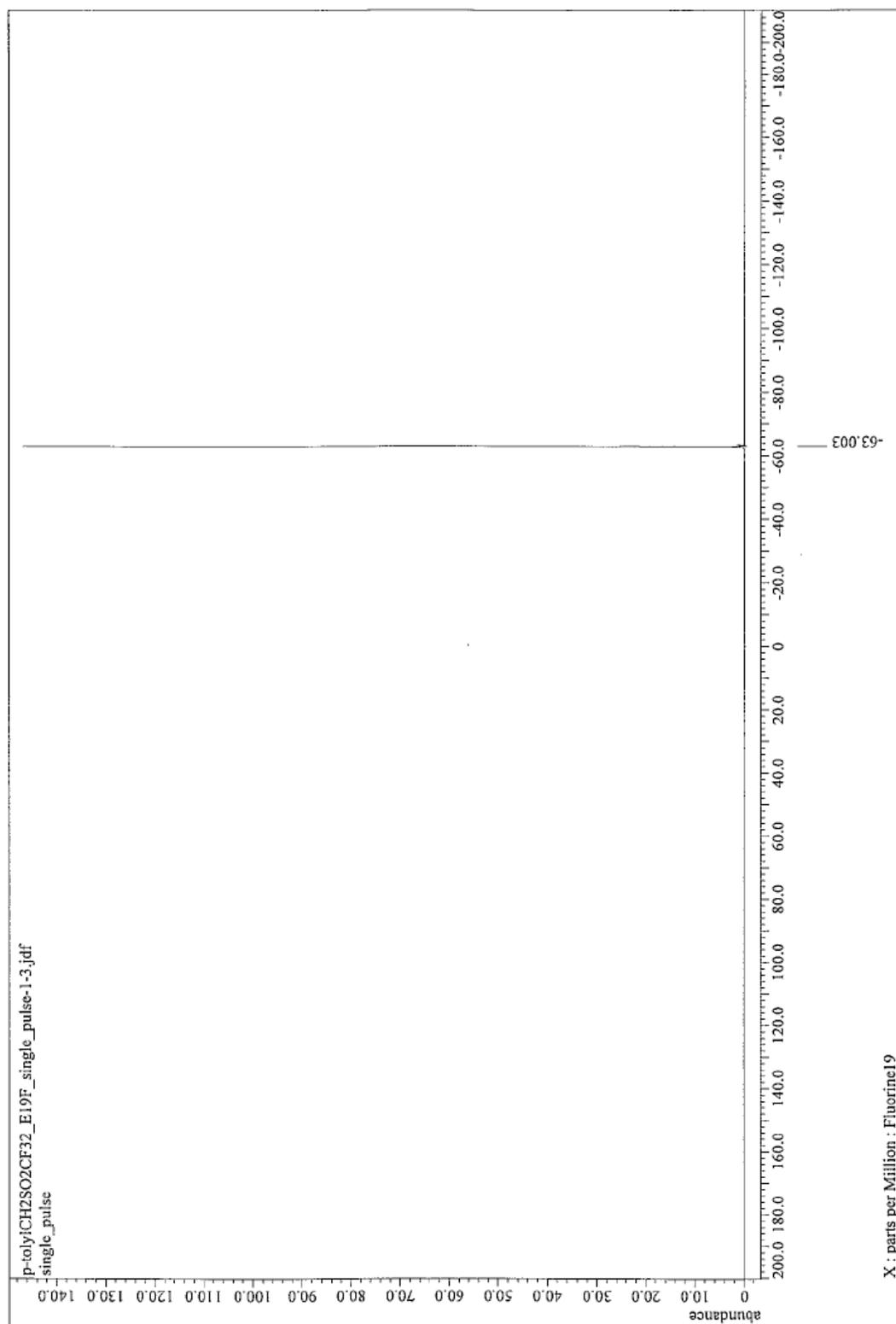
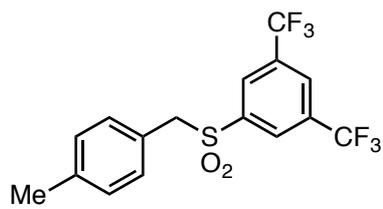
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2b



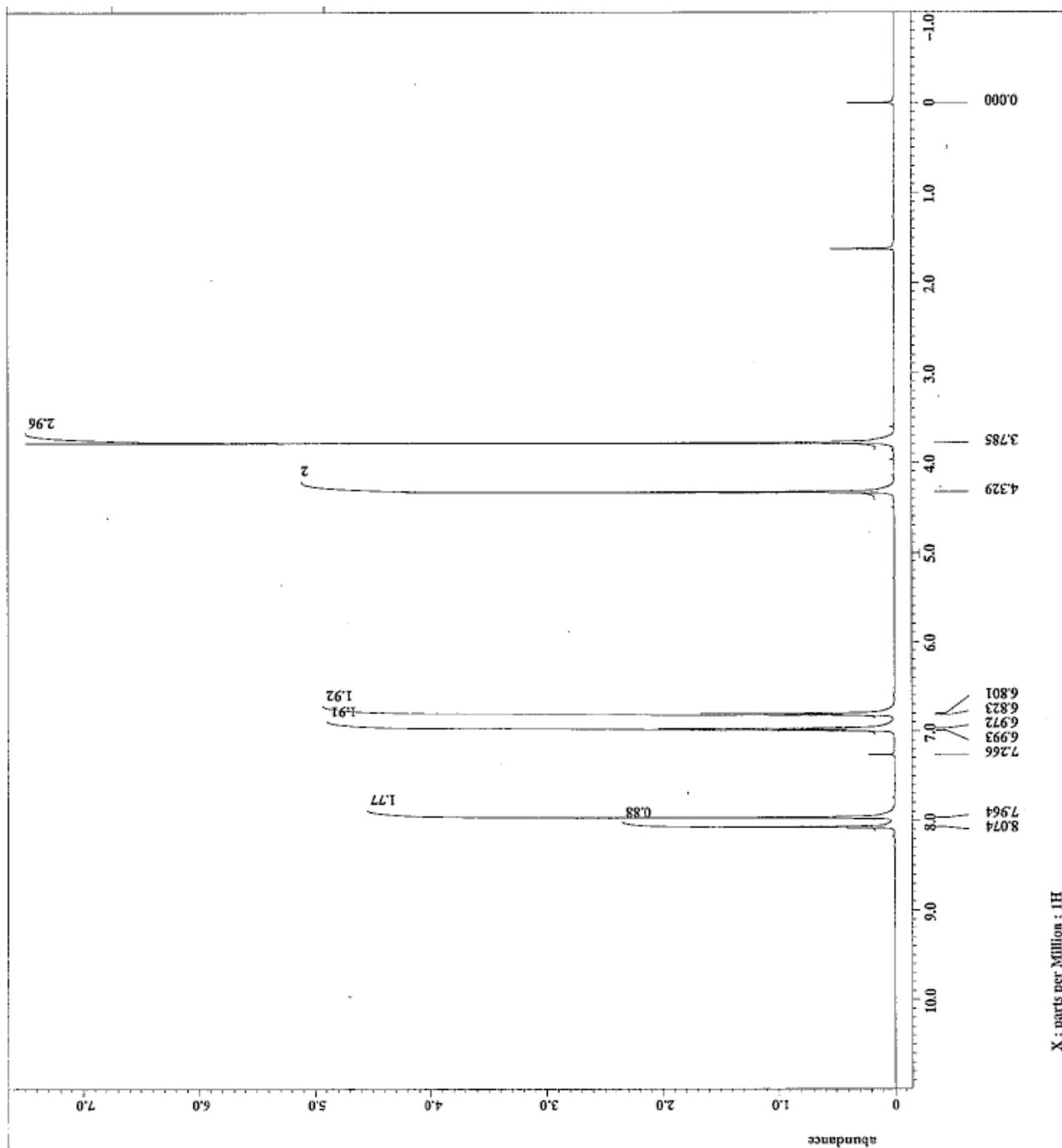
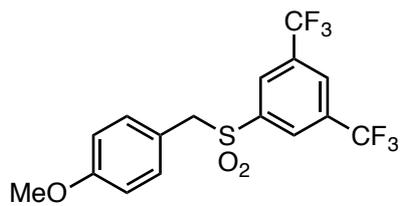
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2b



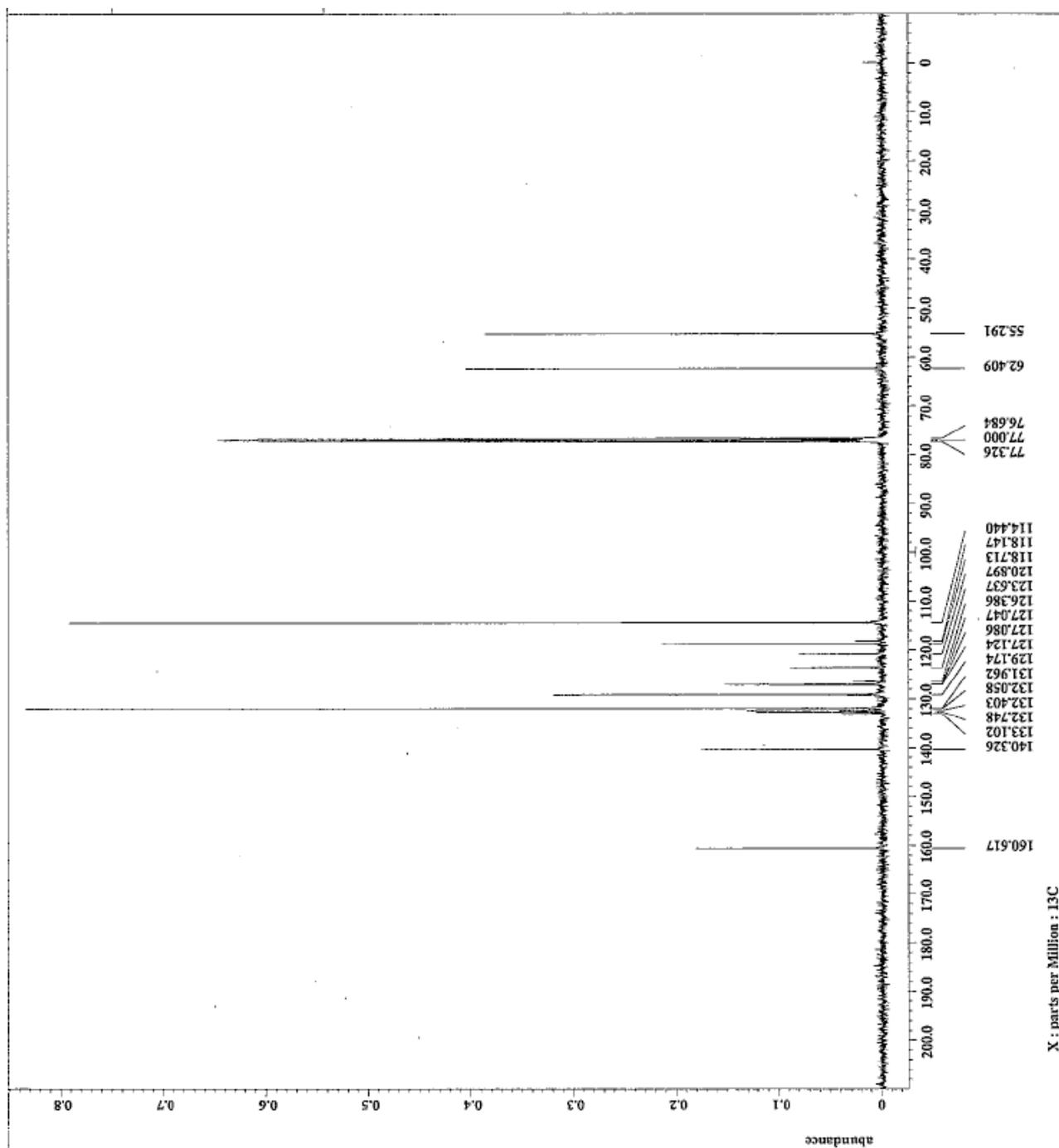
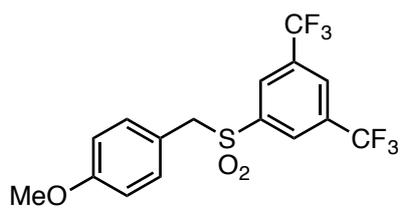
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2b



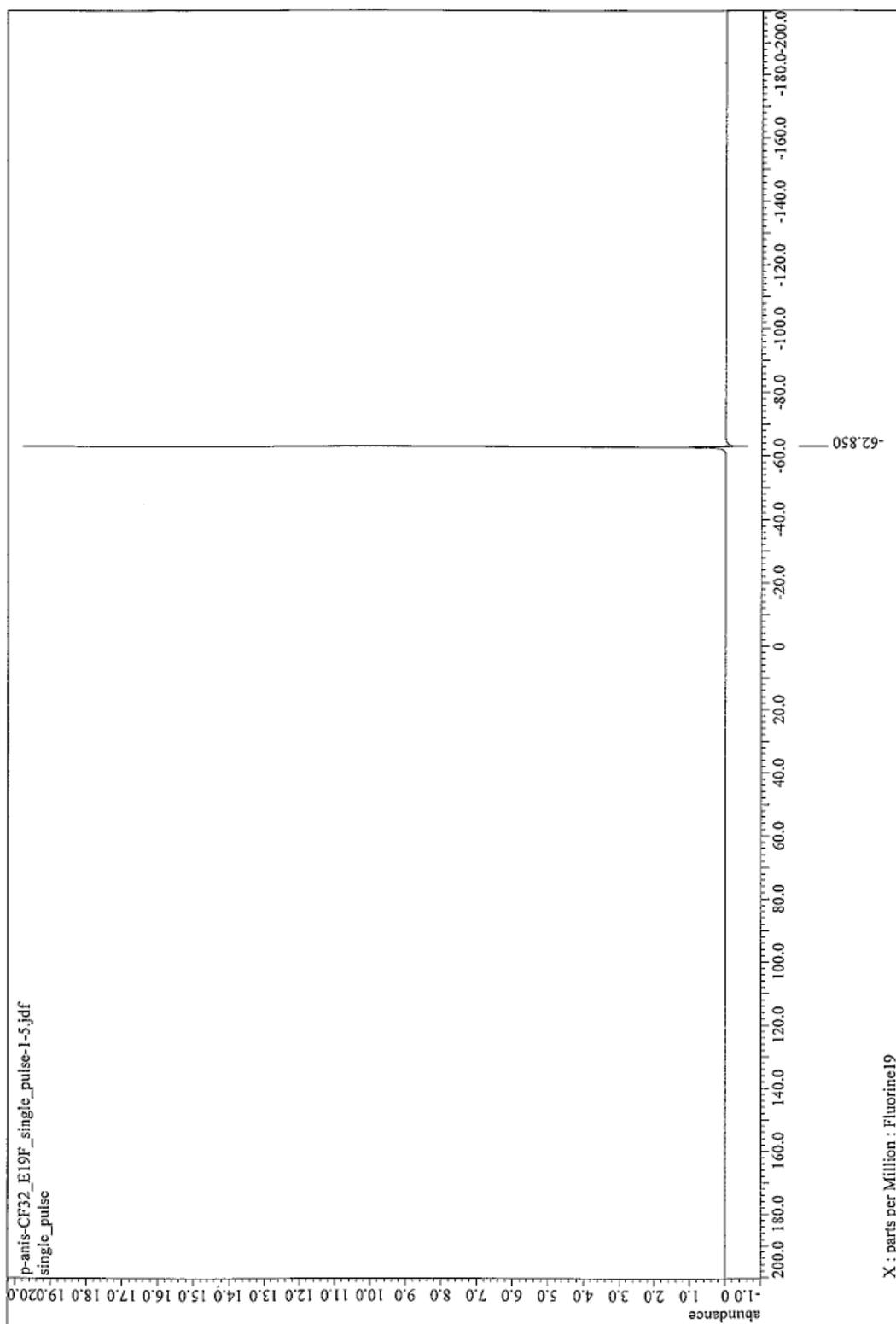
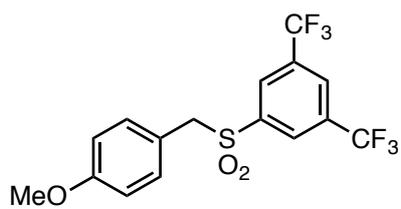
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2c



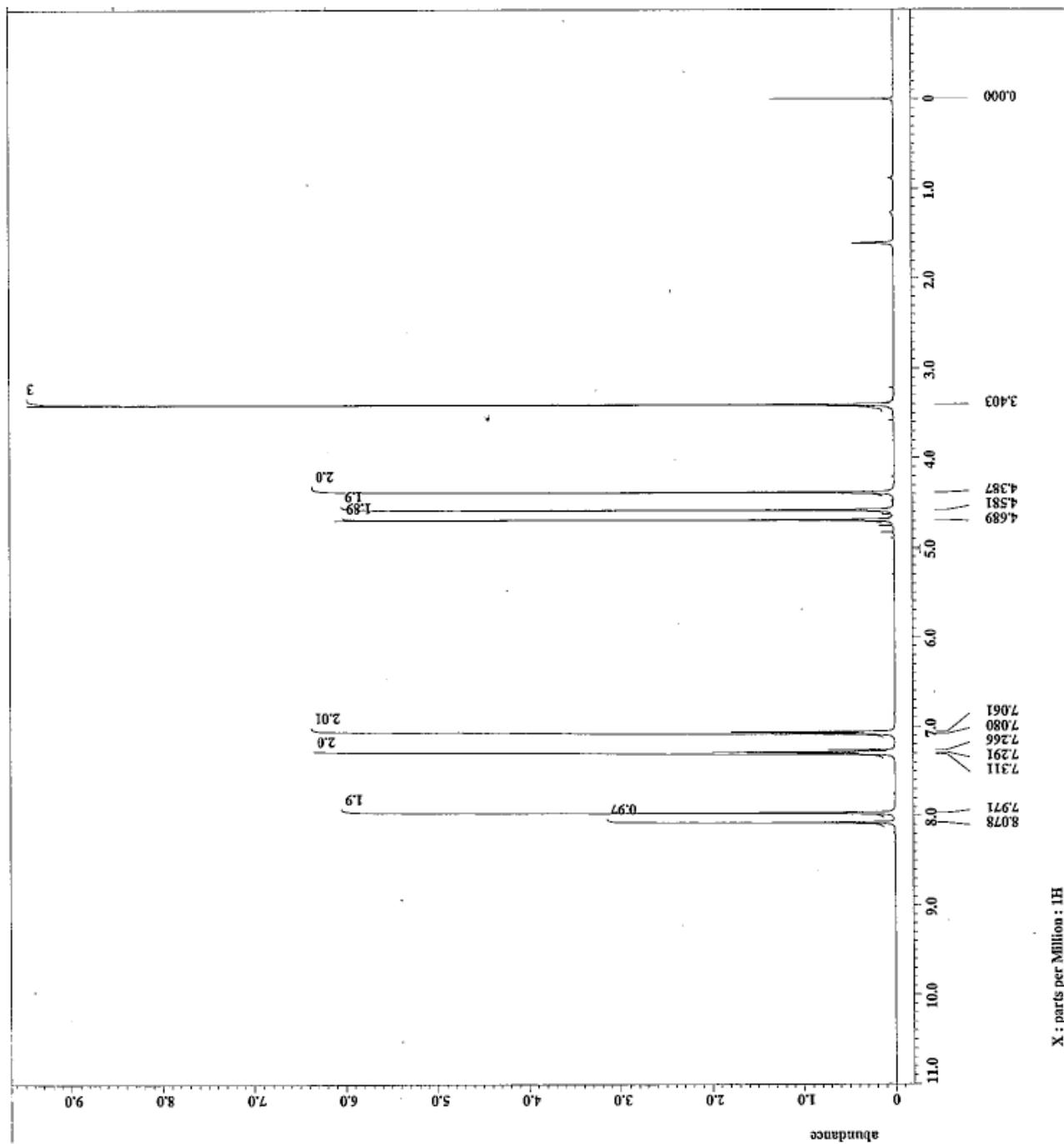
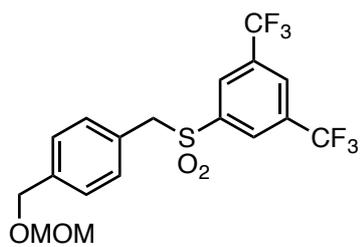
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2c



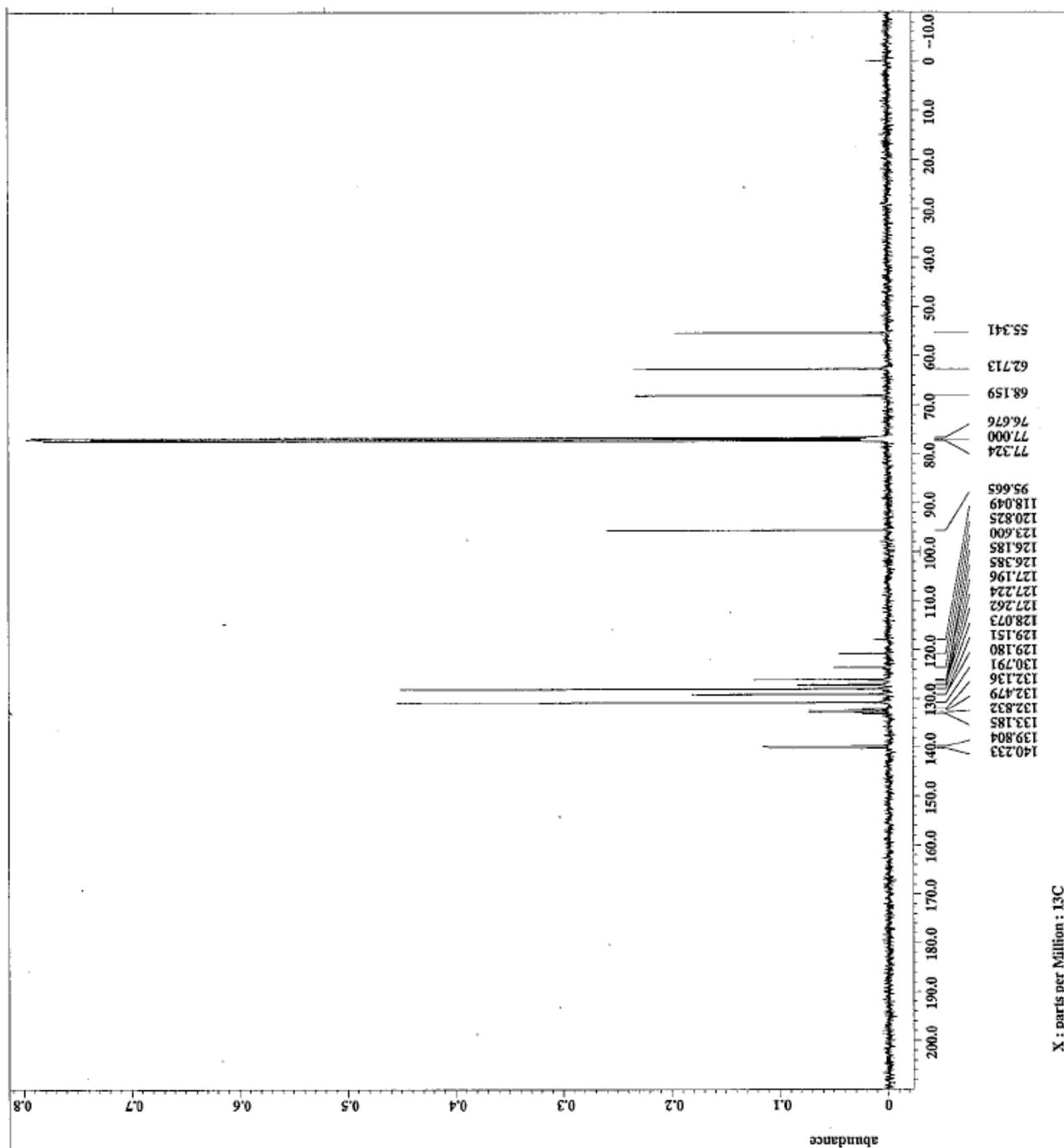
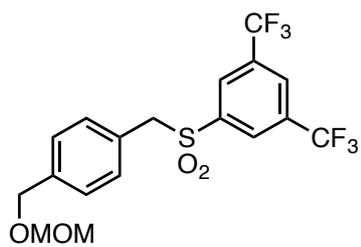
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2c



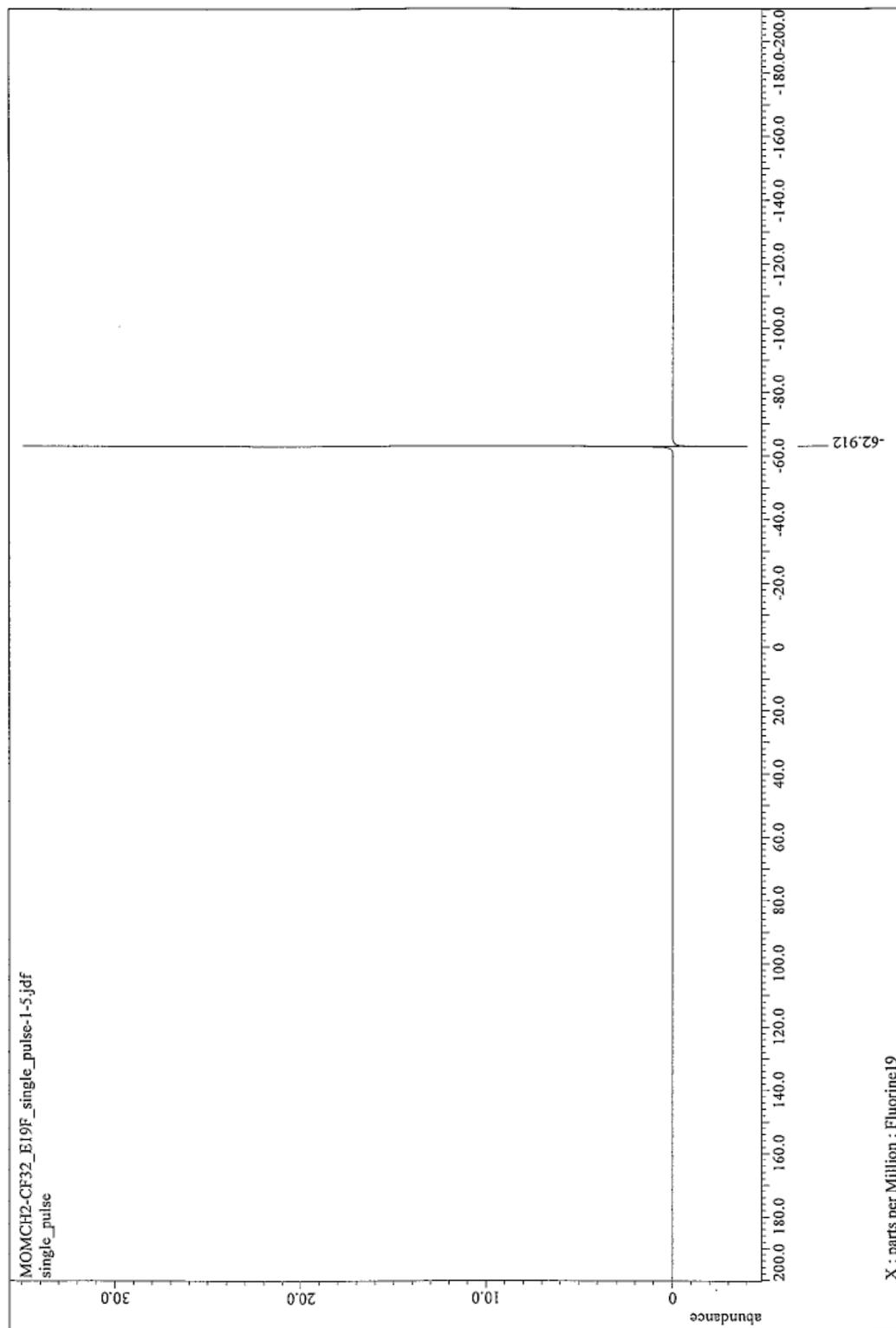
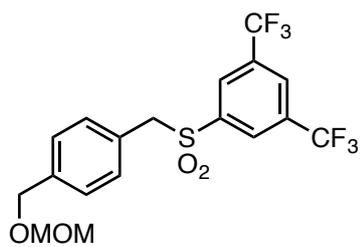
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2d



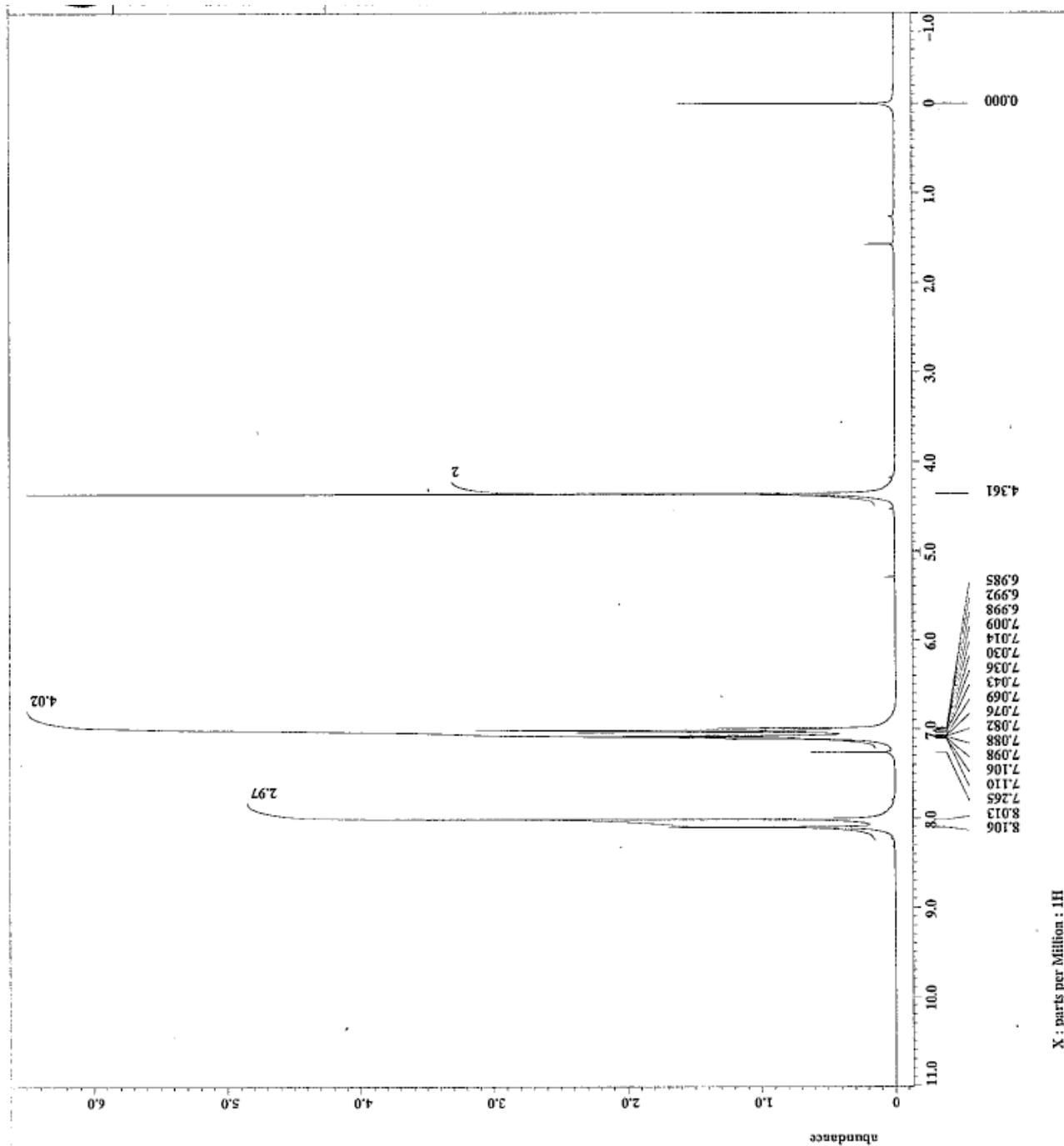
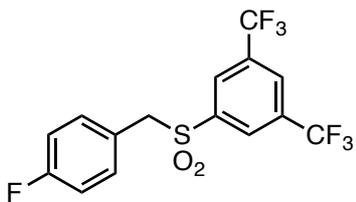
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2d



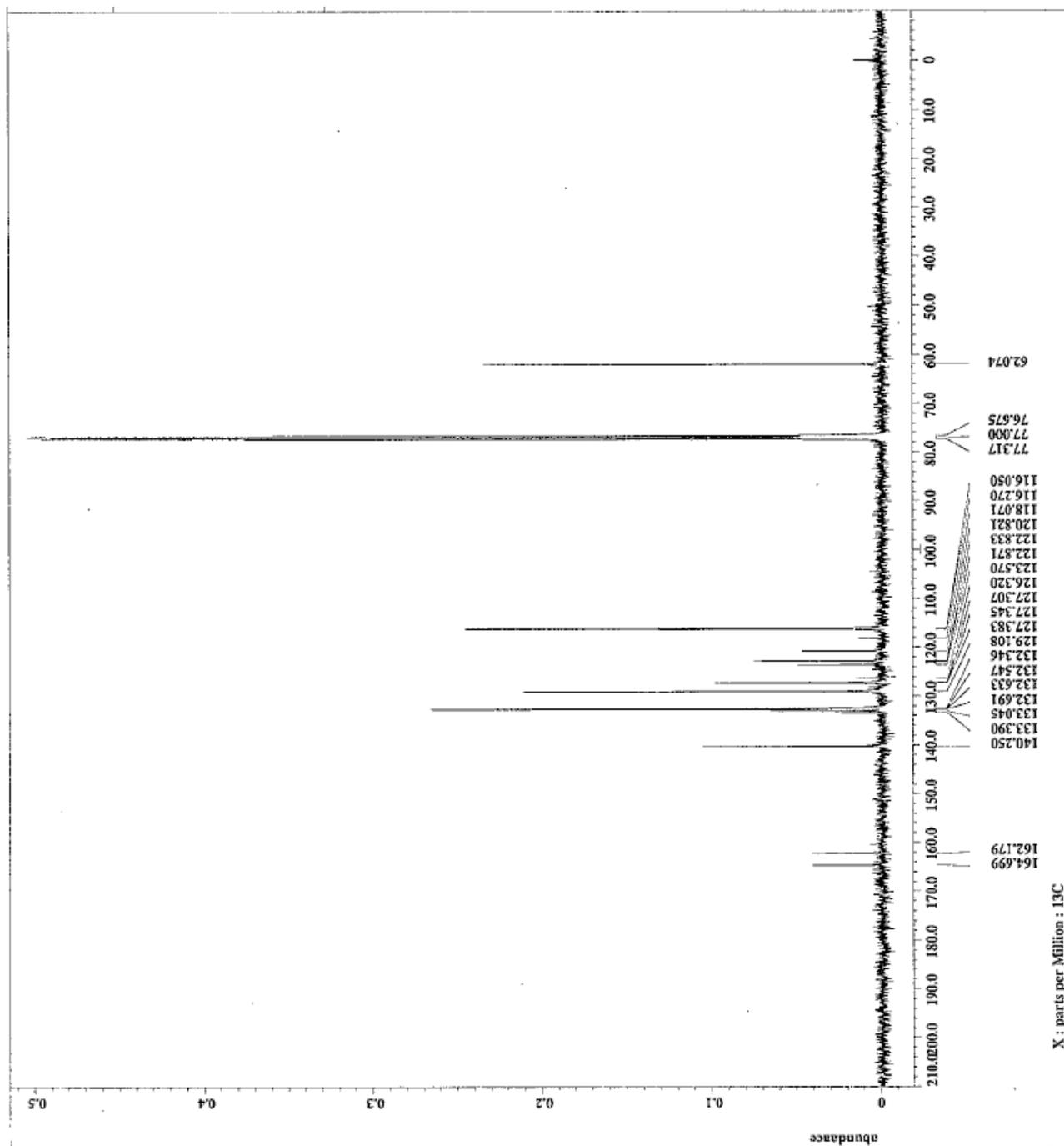
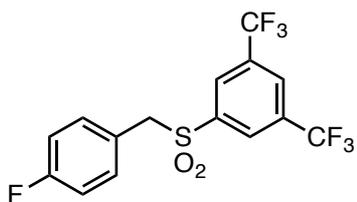
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2d



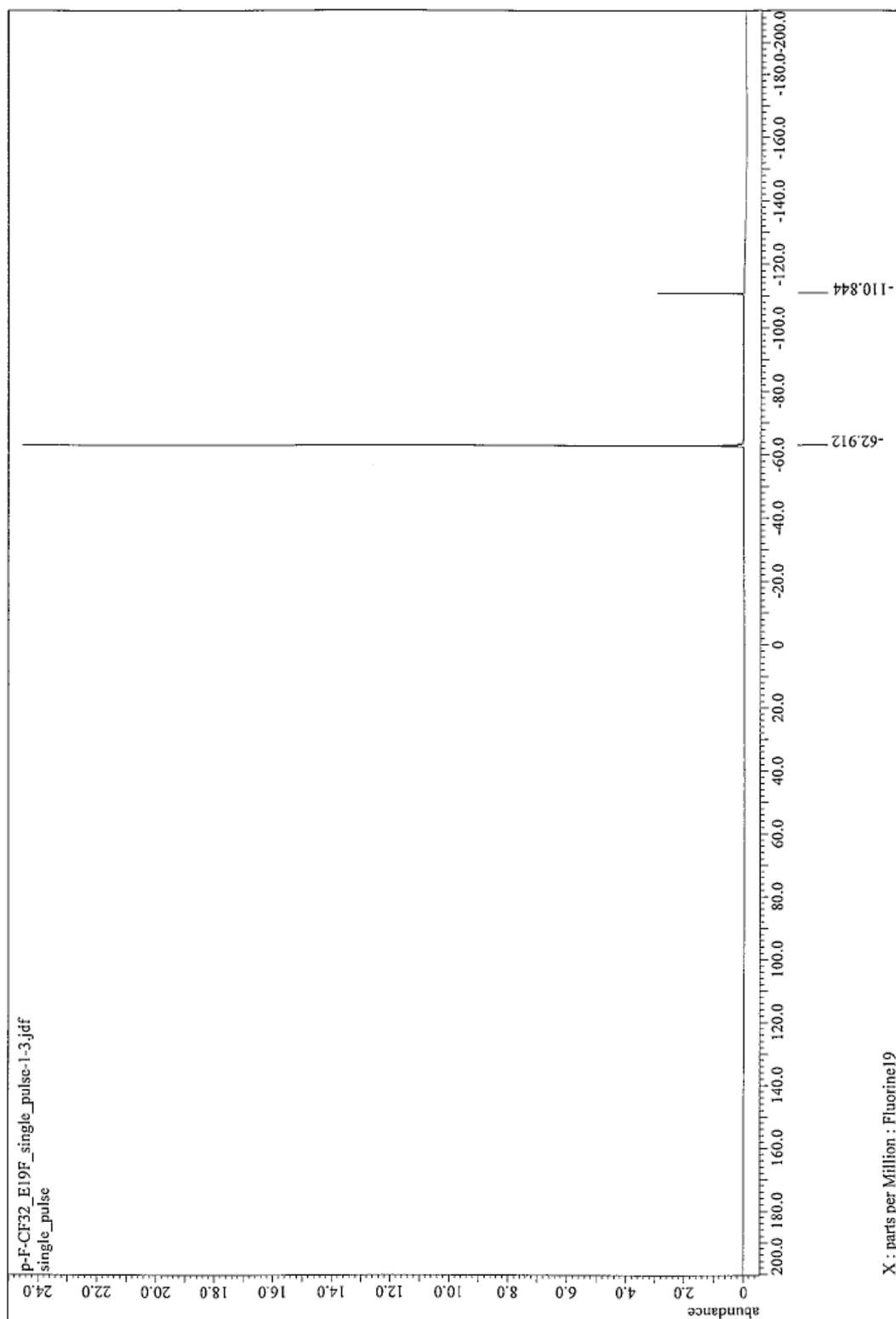
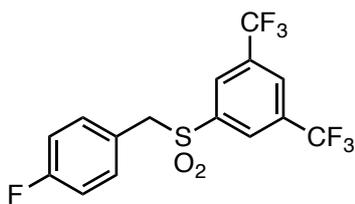
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2e



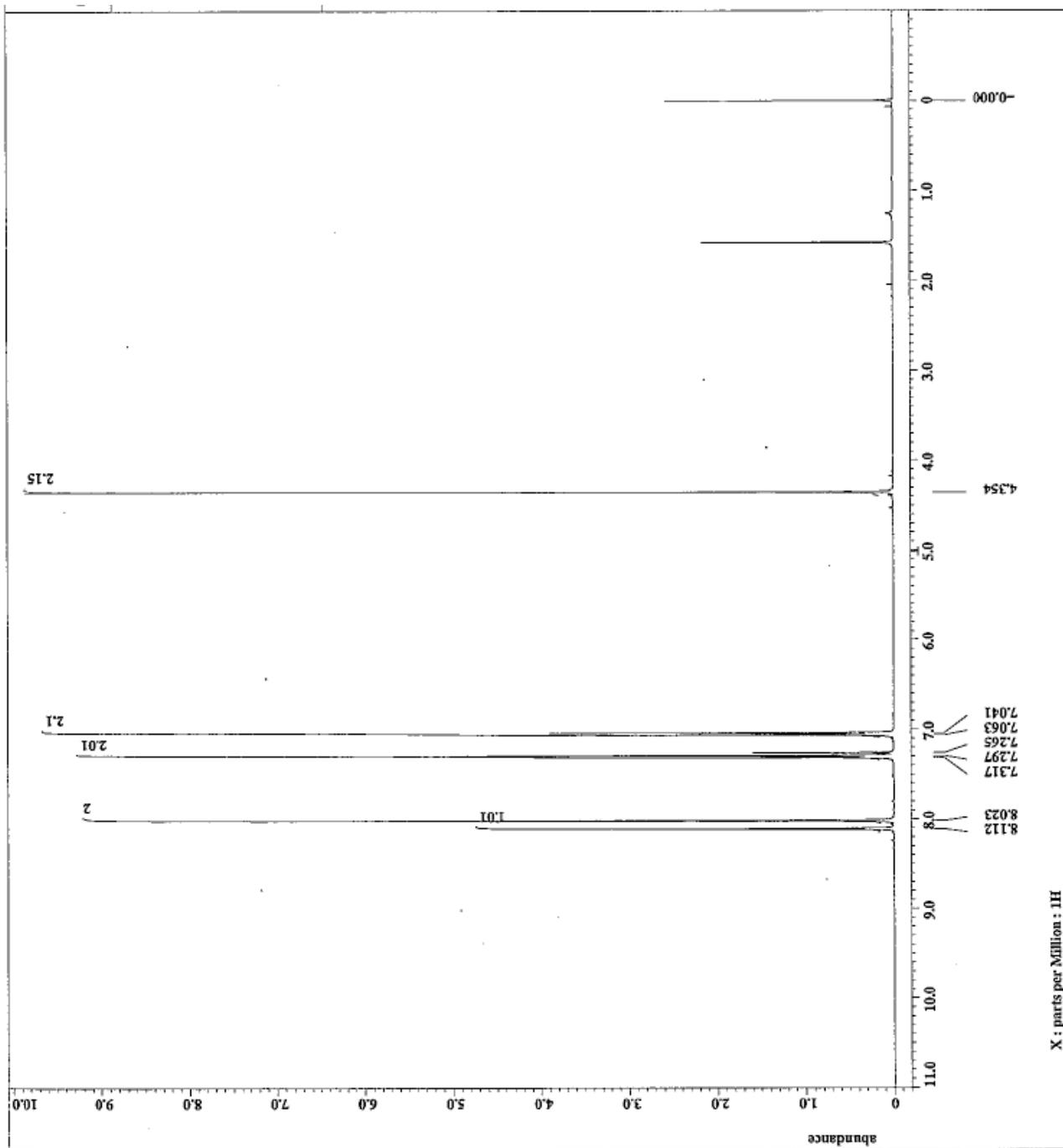
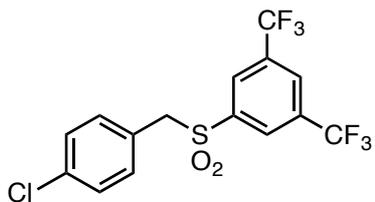
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2e



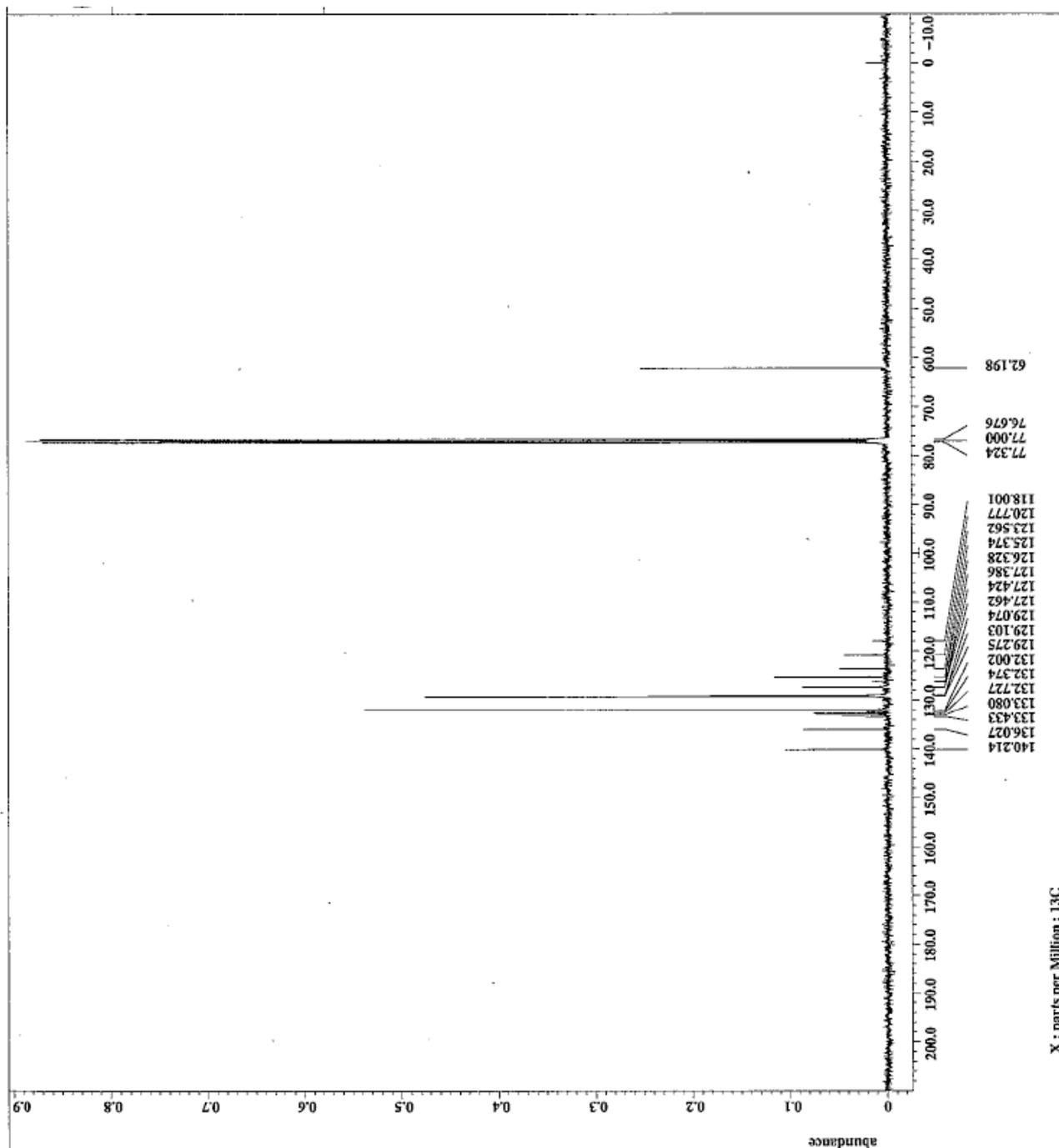
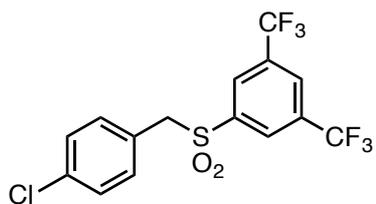
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2e



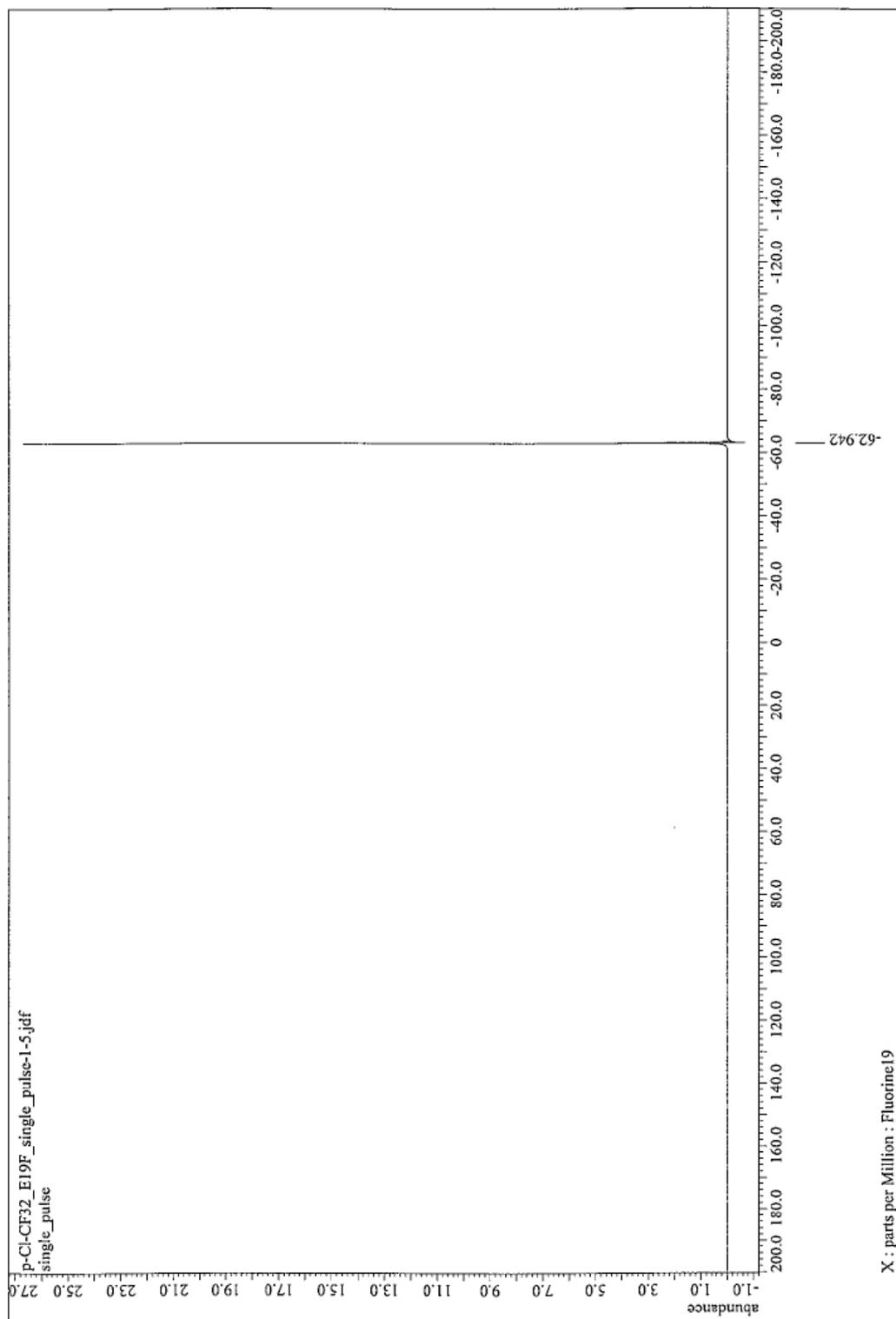
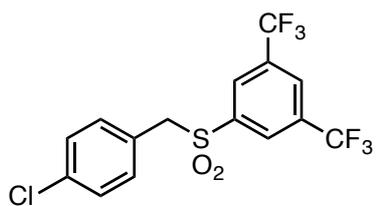
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2f



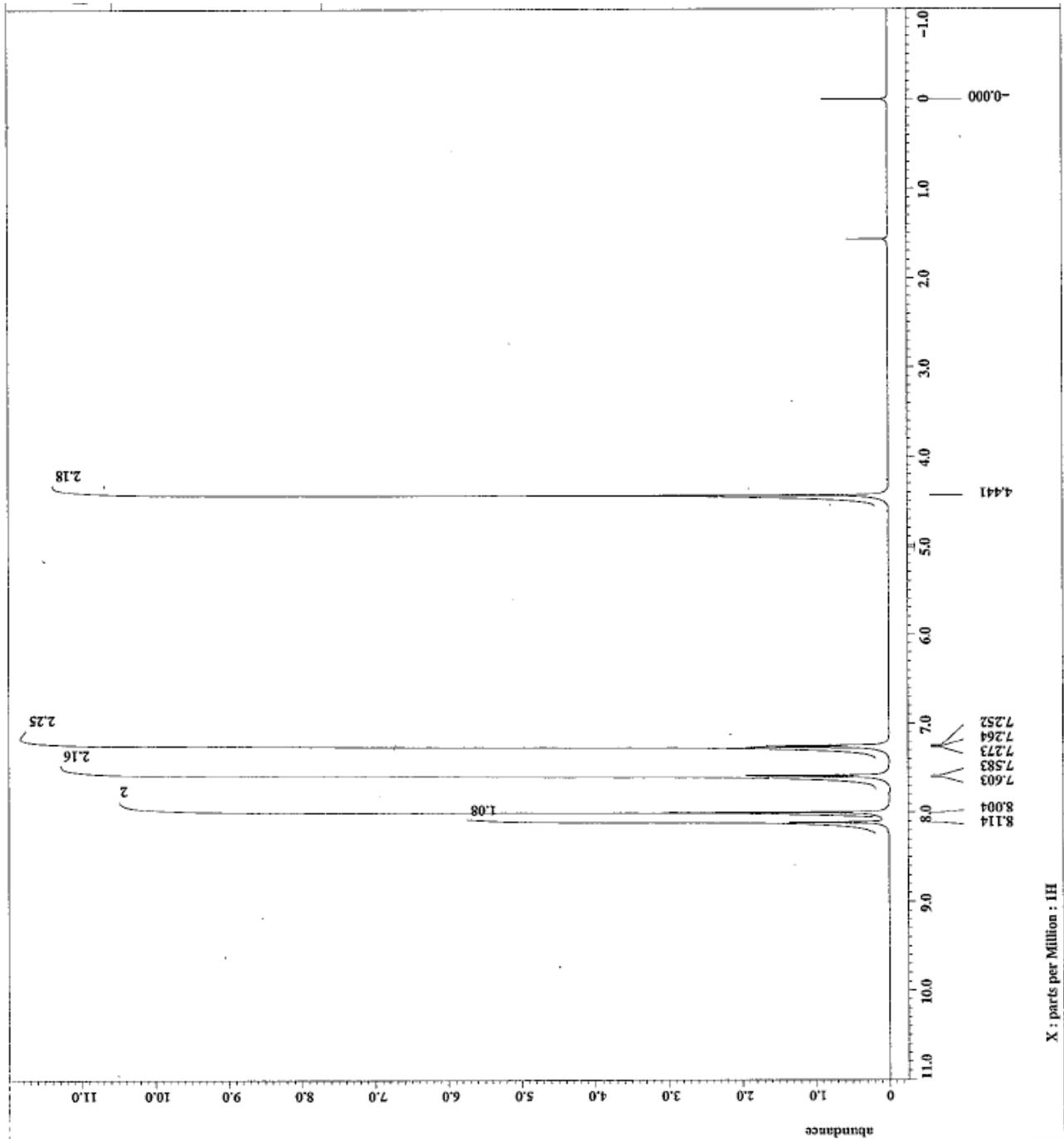
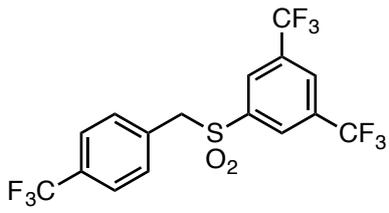
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2f



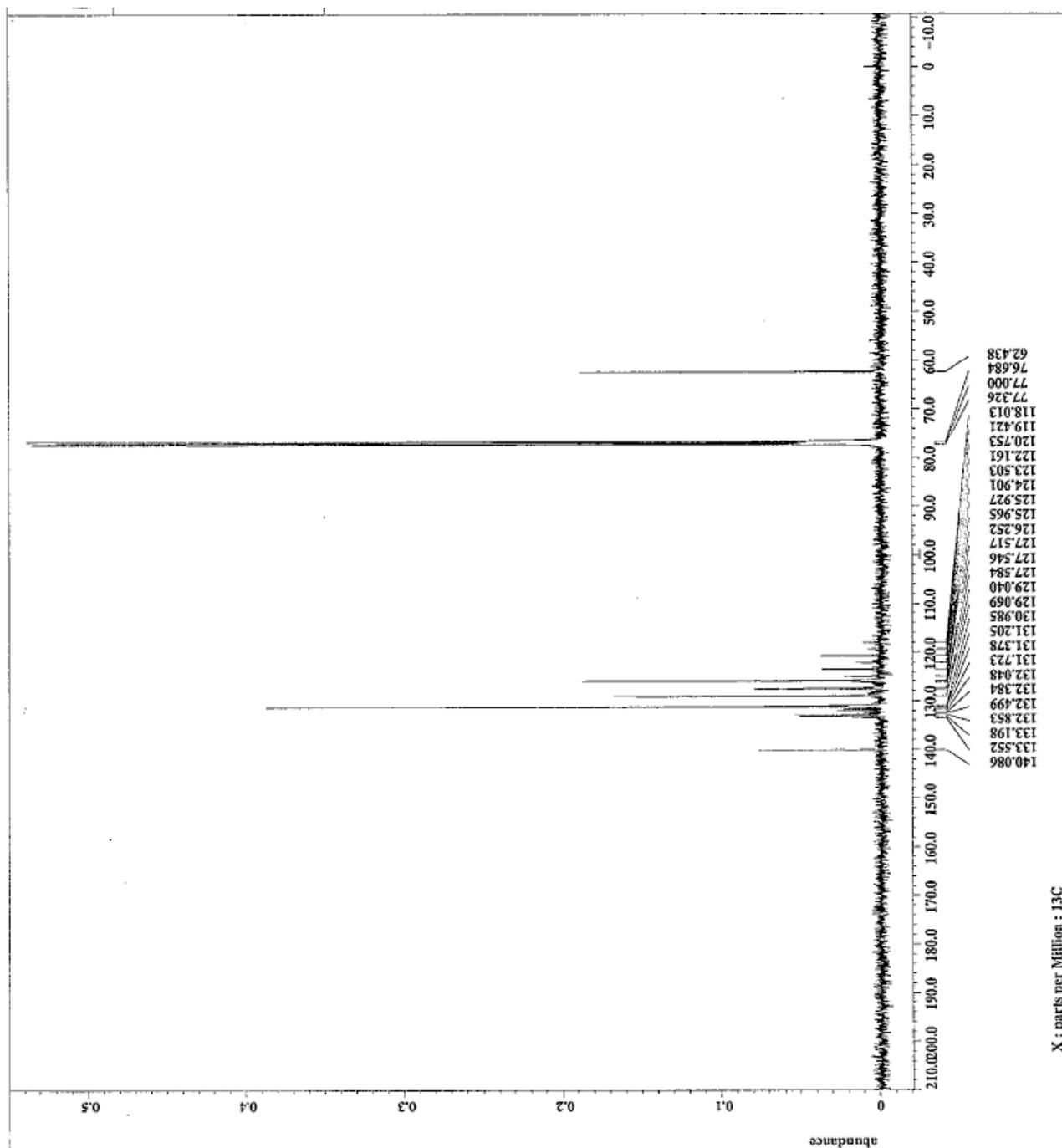
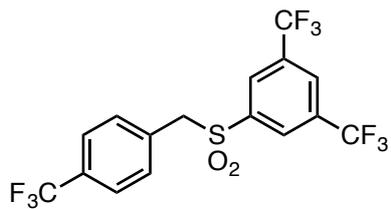
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2f



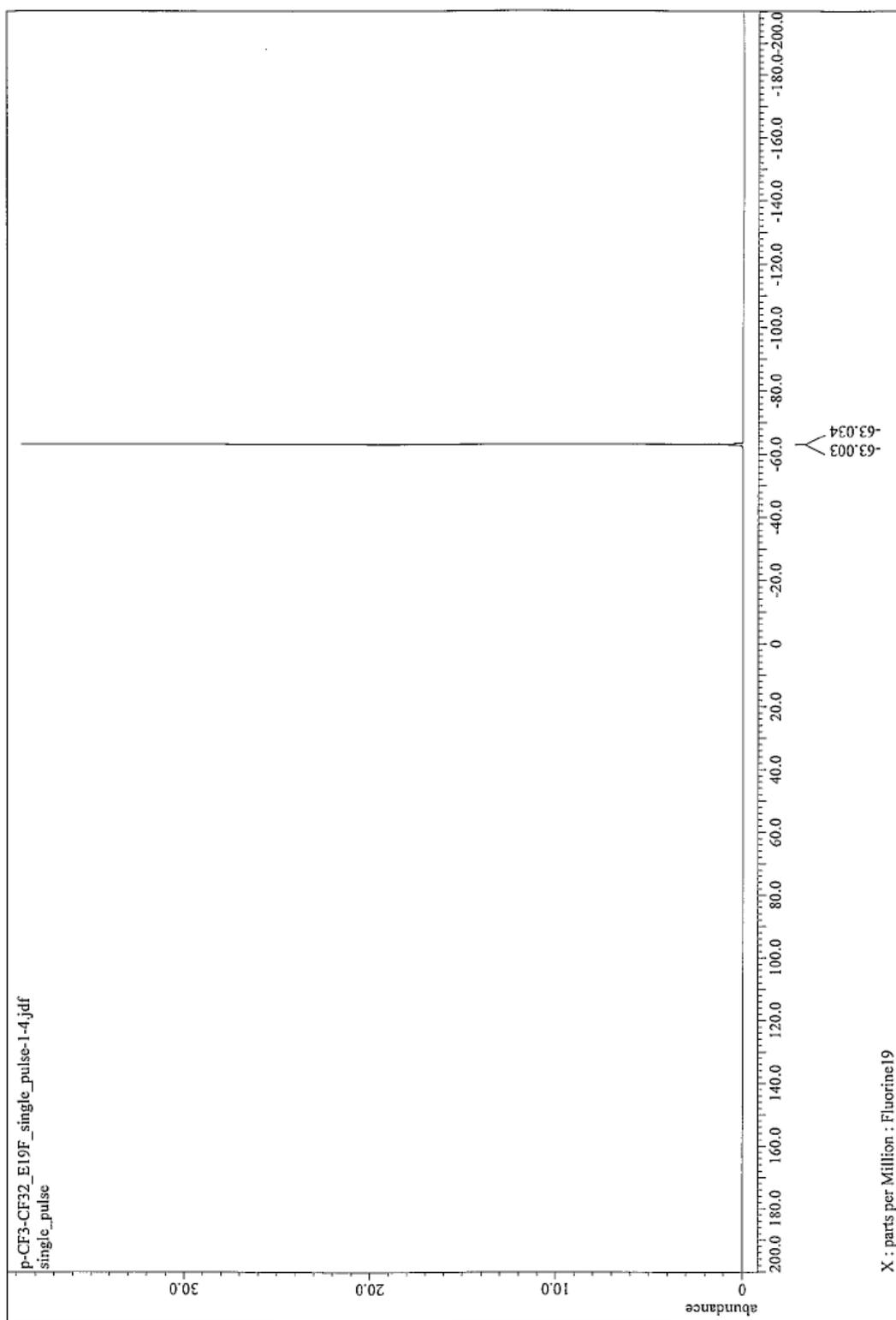
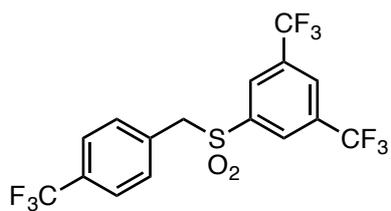
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2g



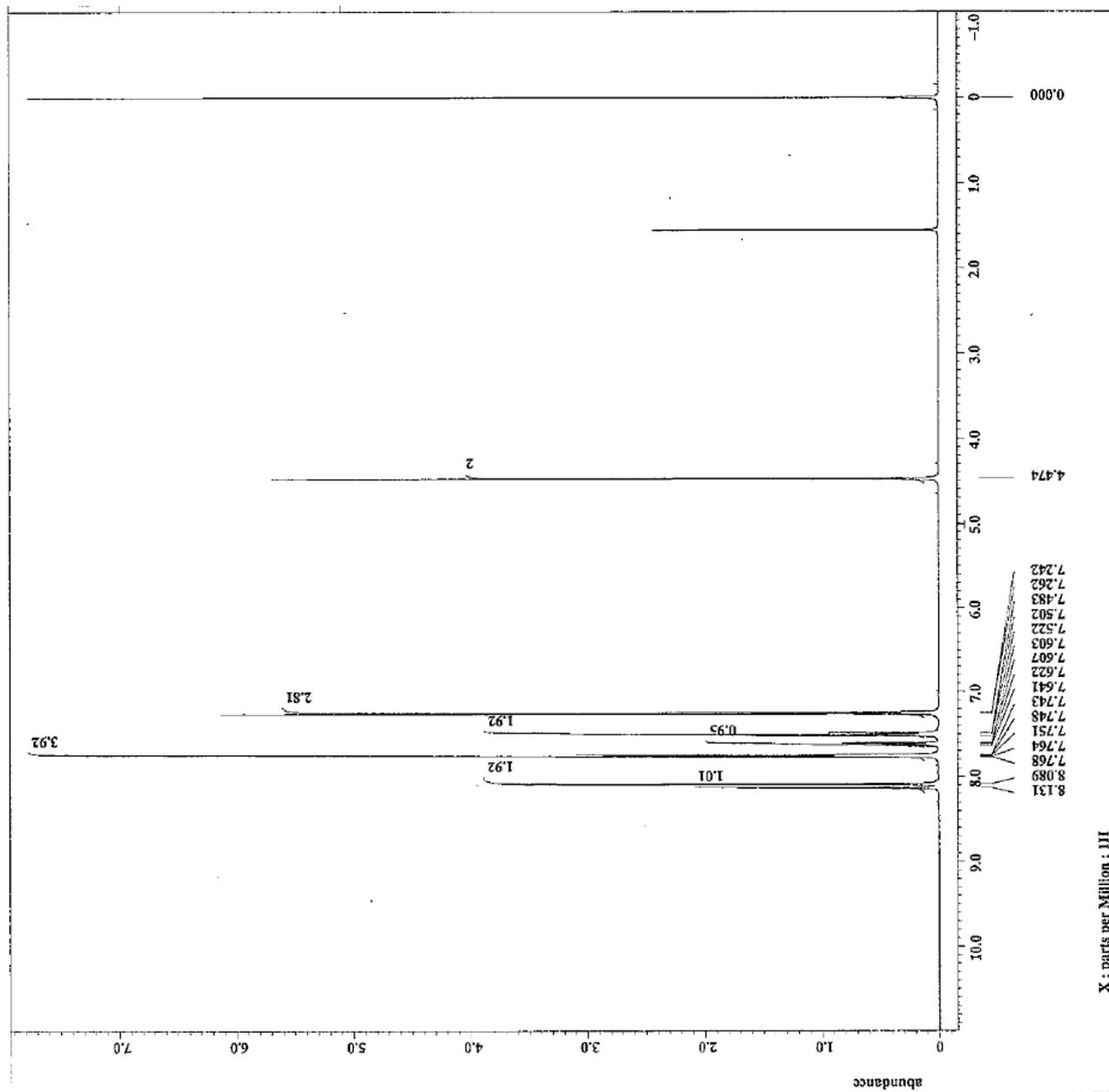
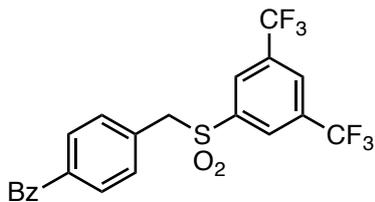
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 2g



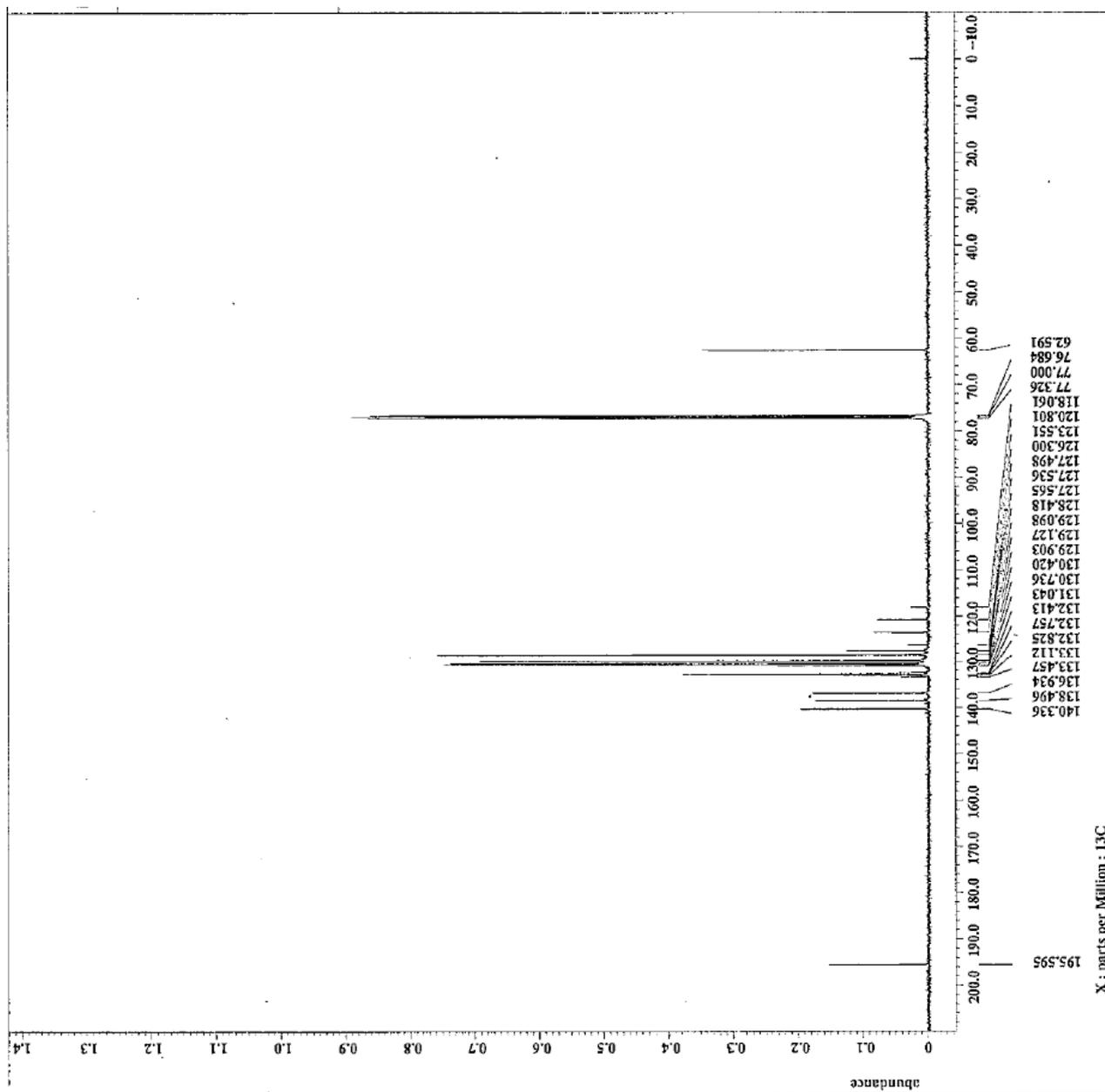
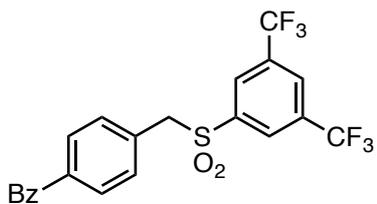
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2g



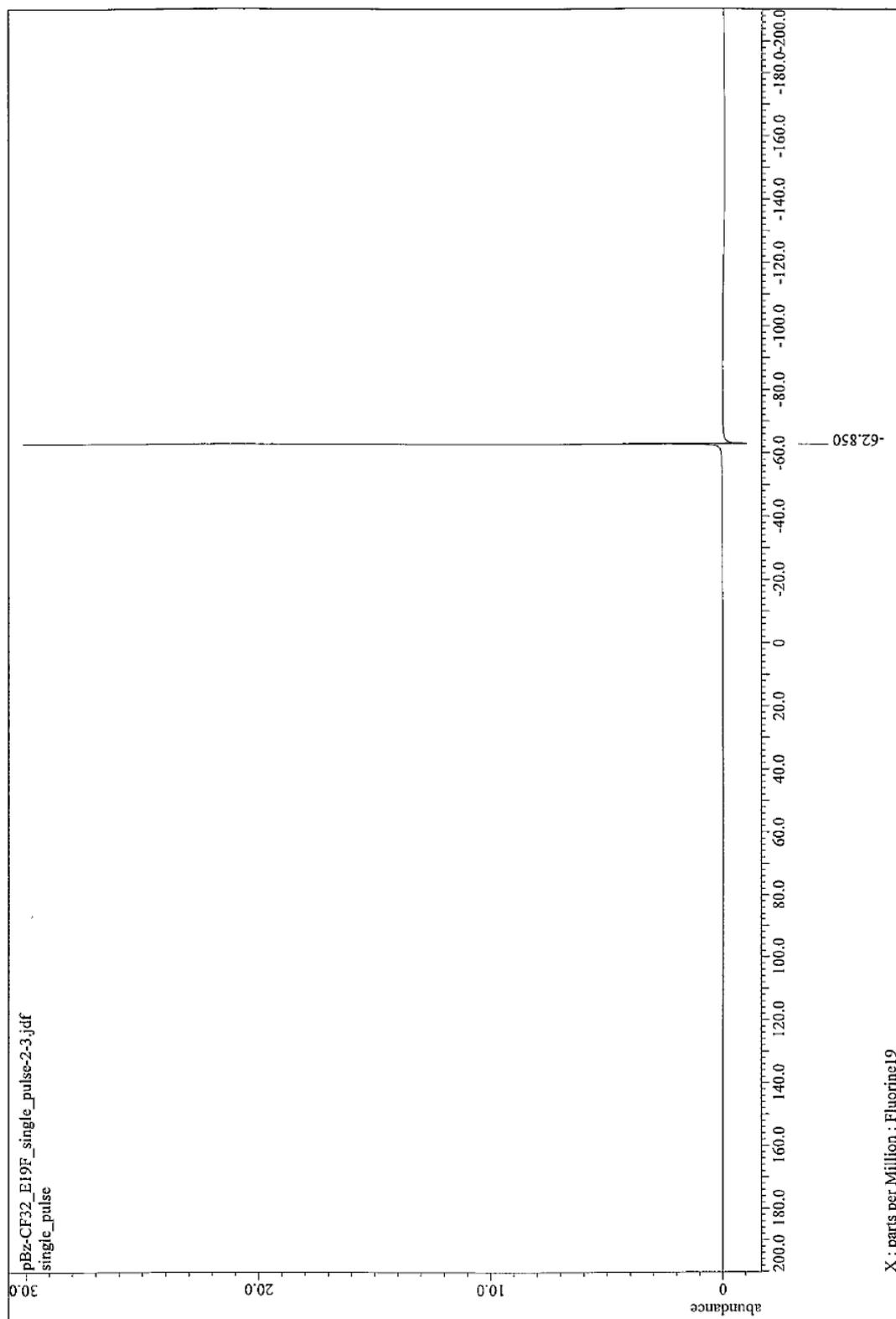
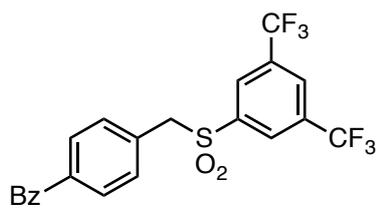
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2h



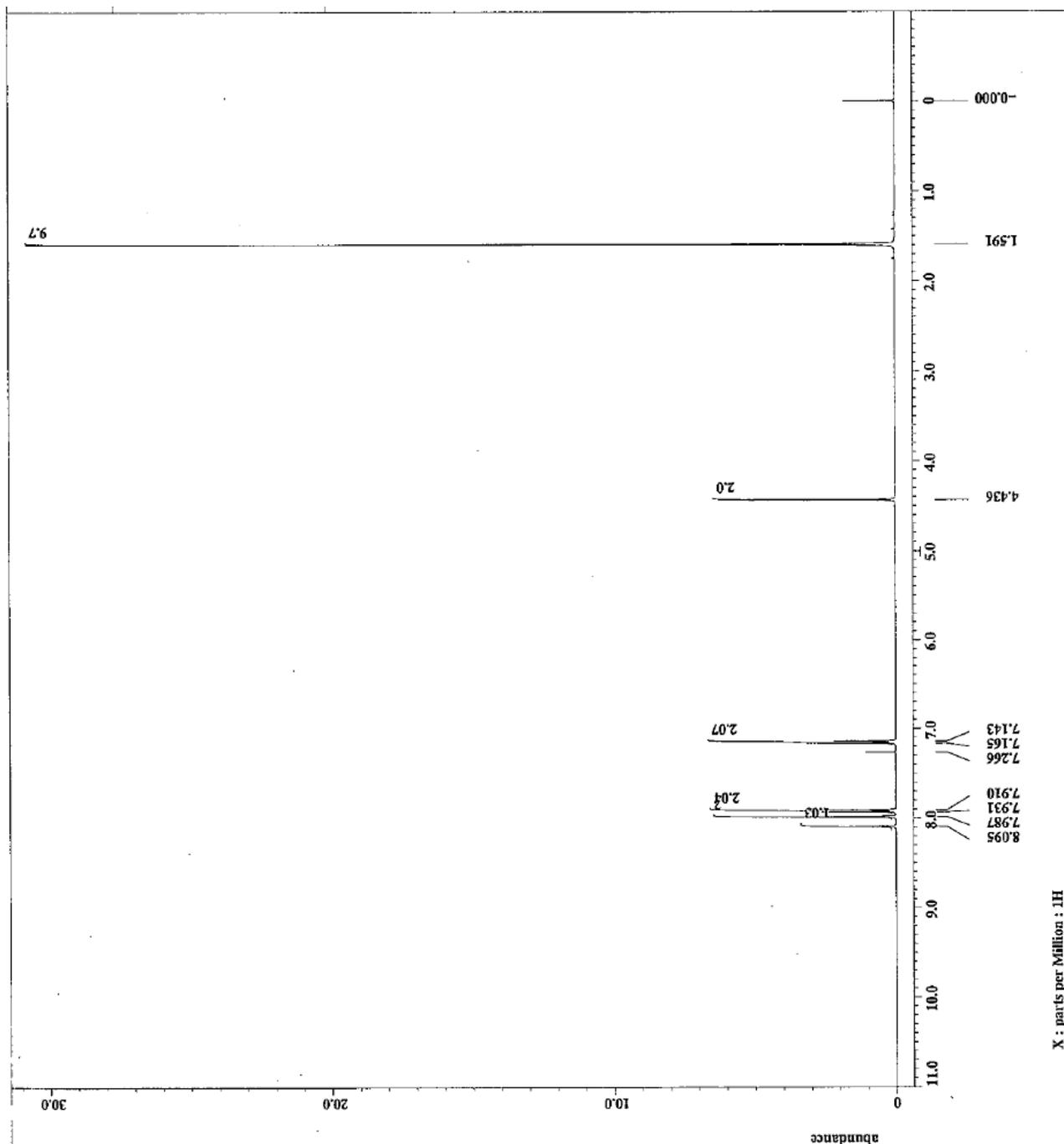
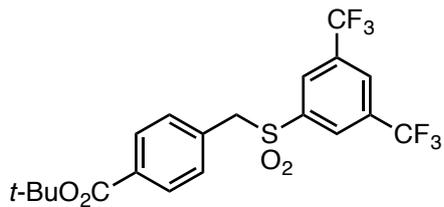
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2h



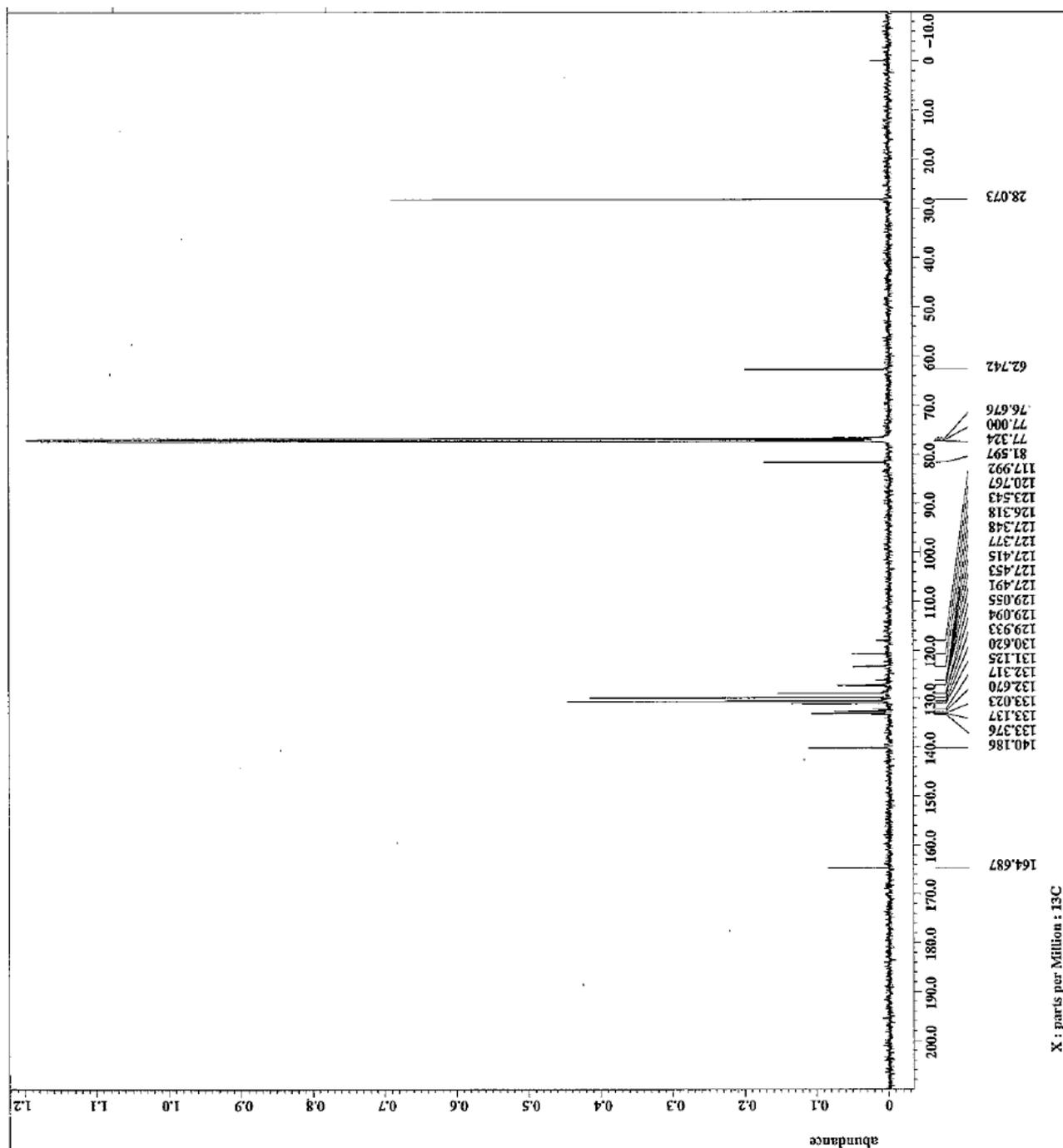
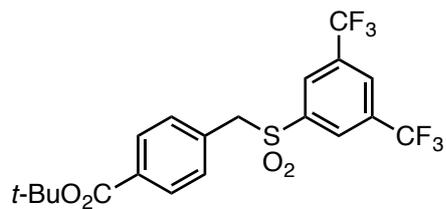
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2h



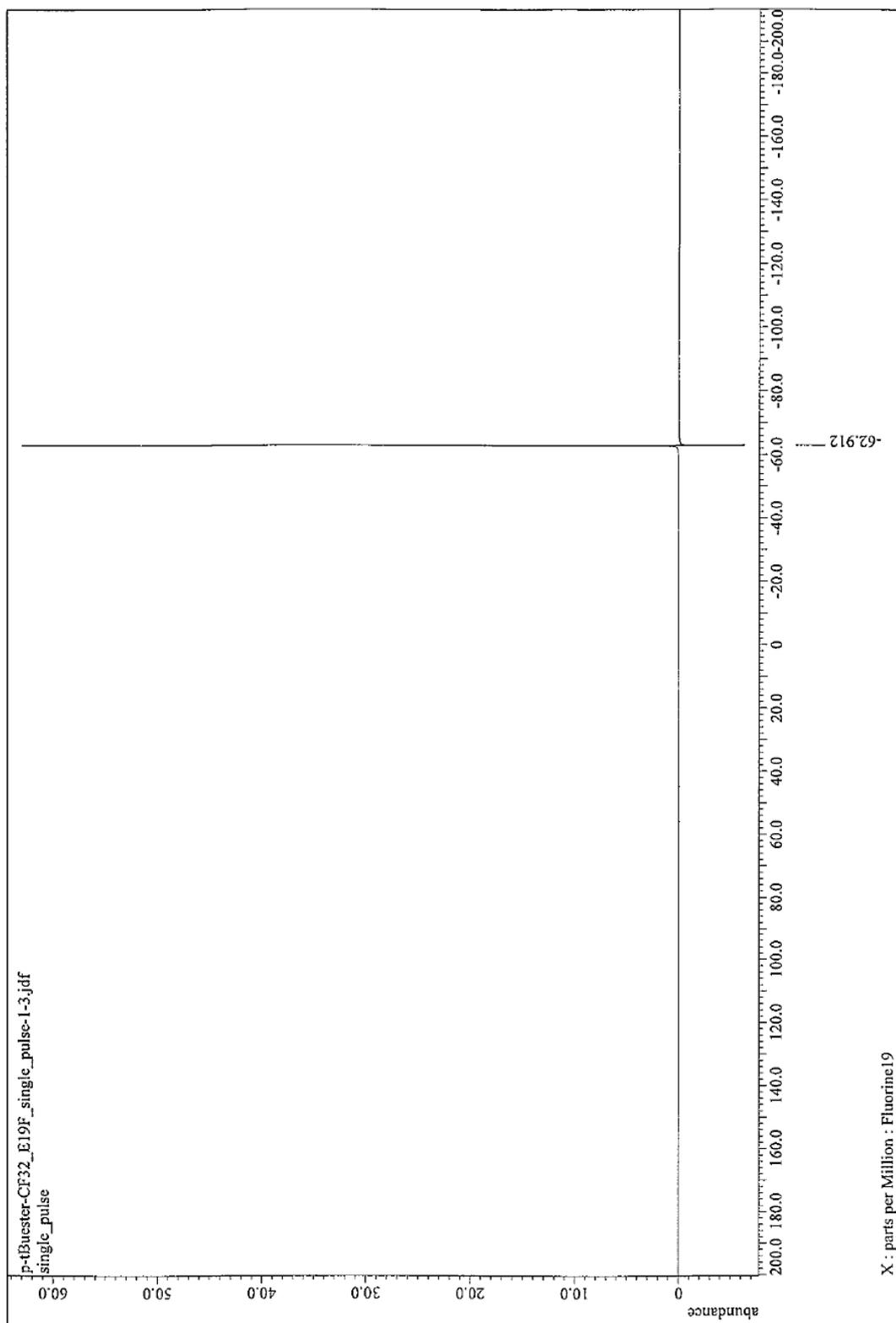
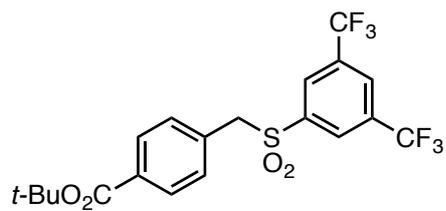
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2i



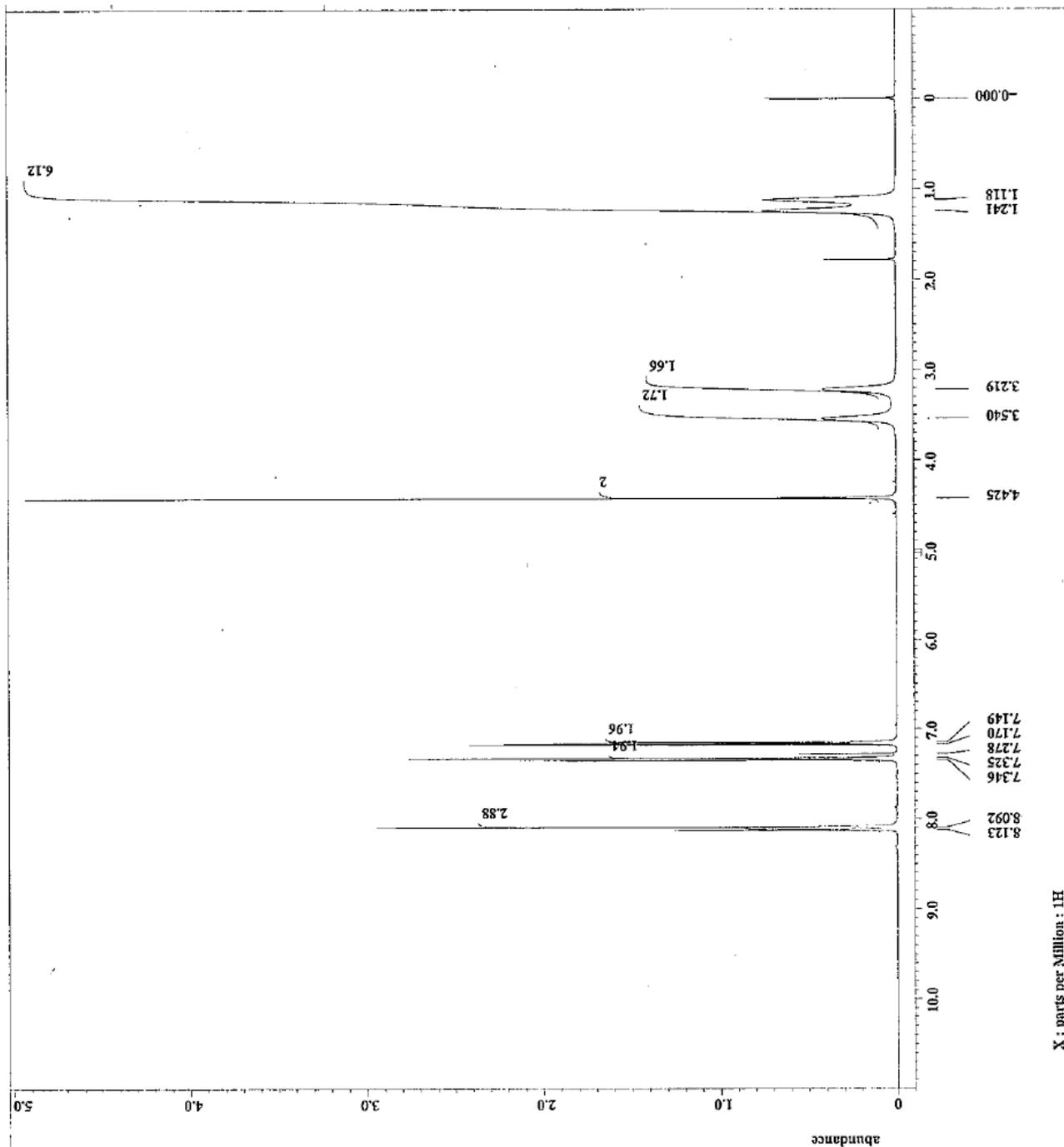
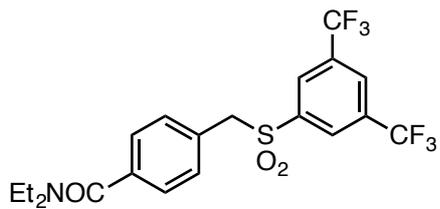
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 2i



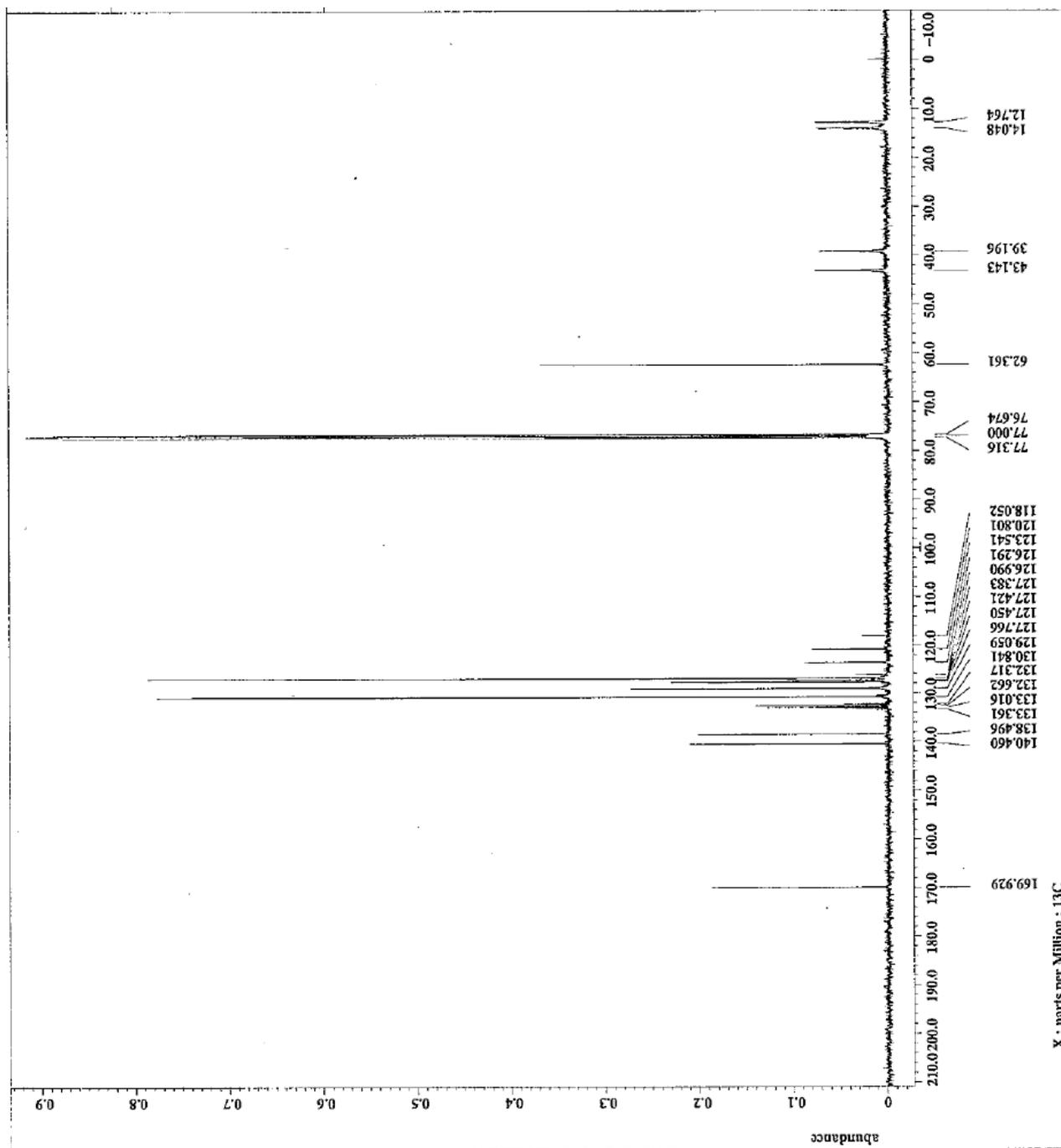
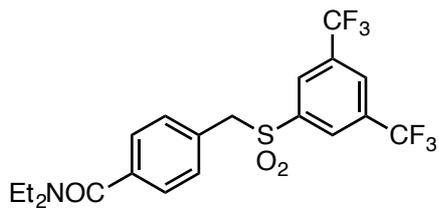
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2i



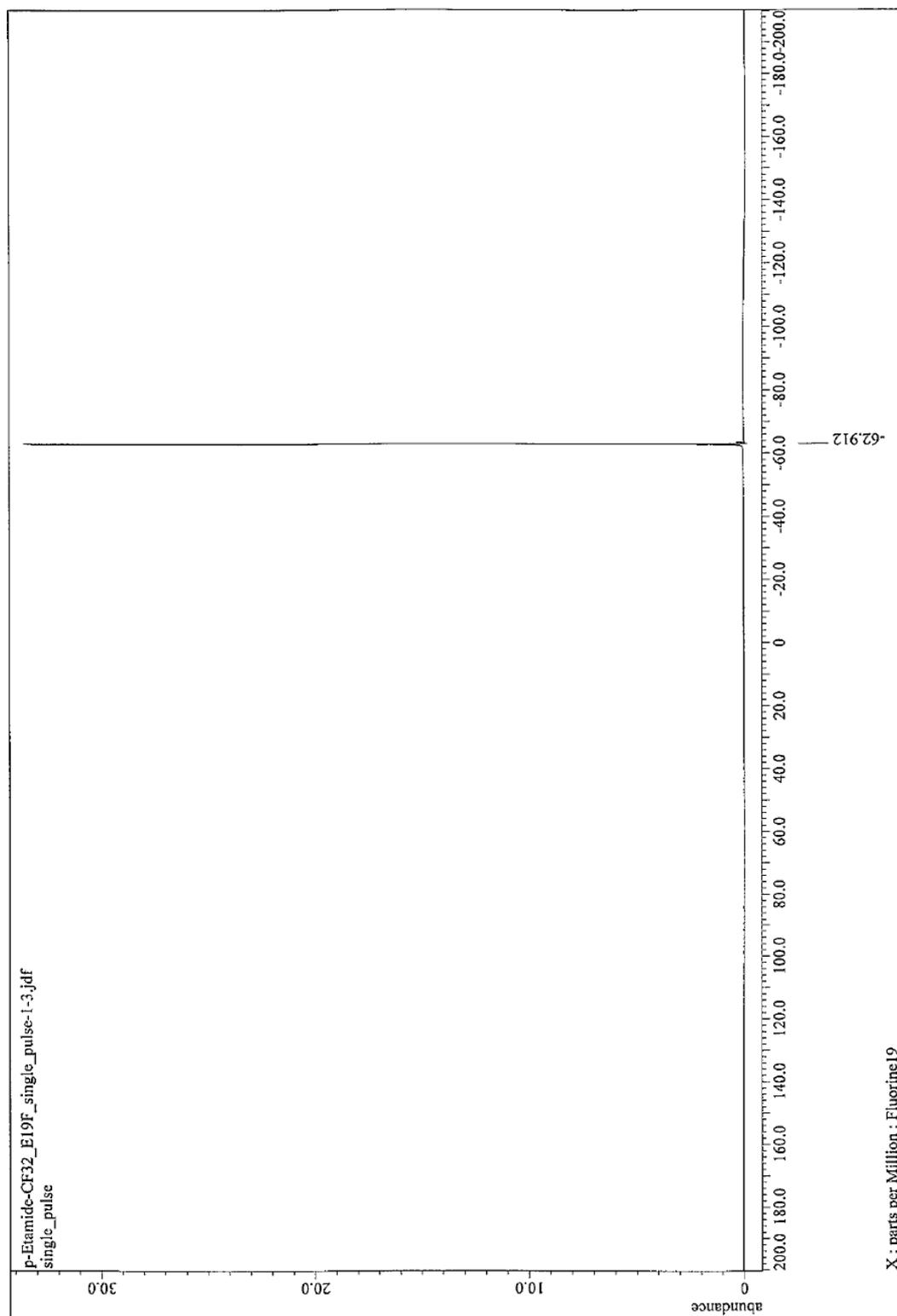
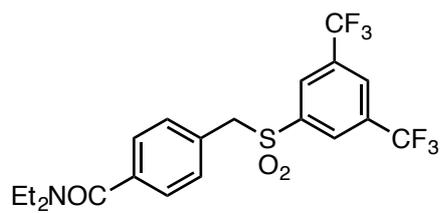
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2j



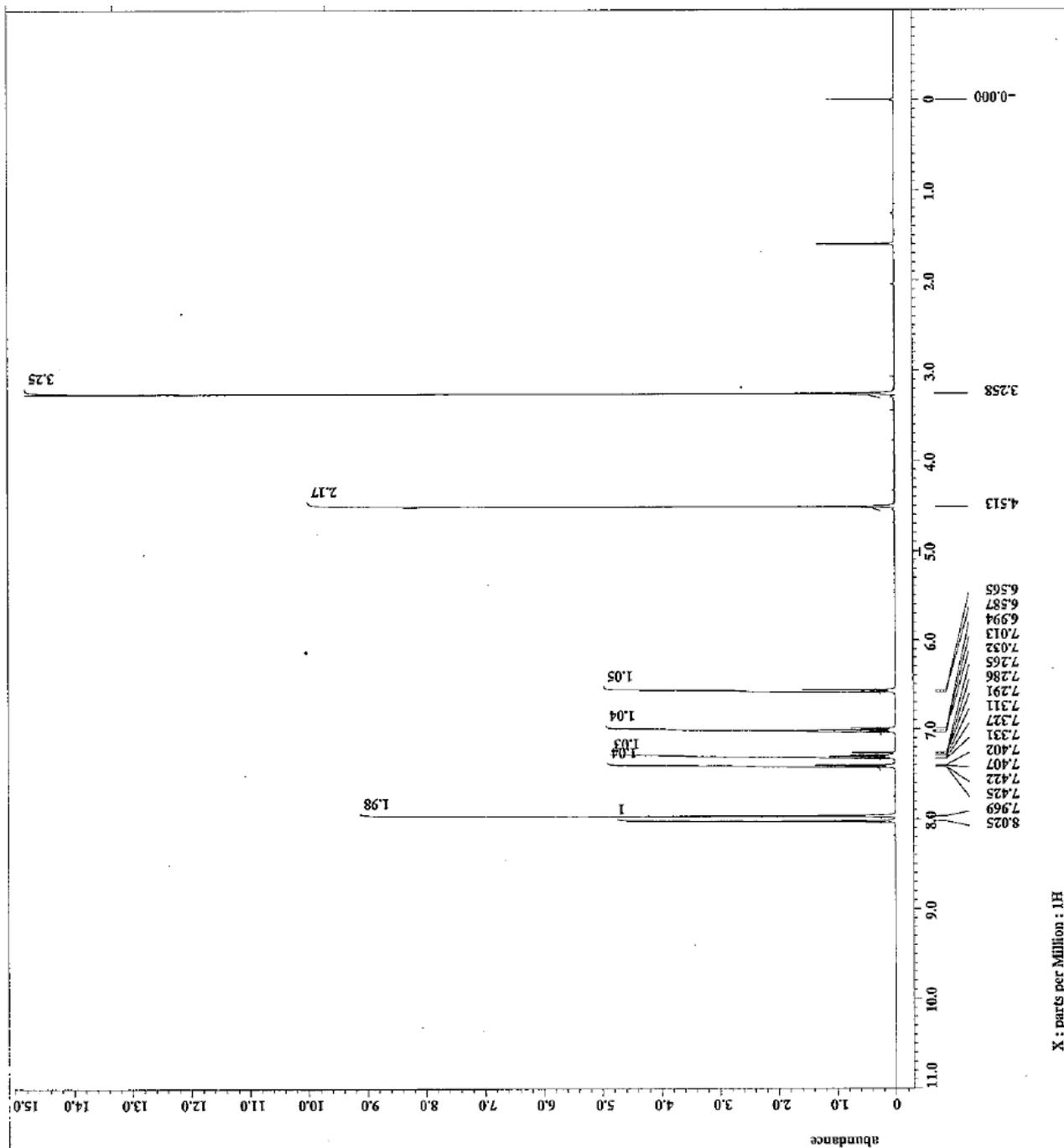
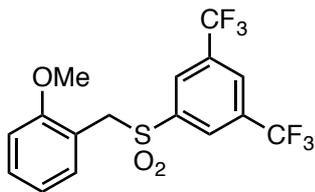
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2j



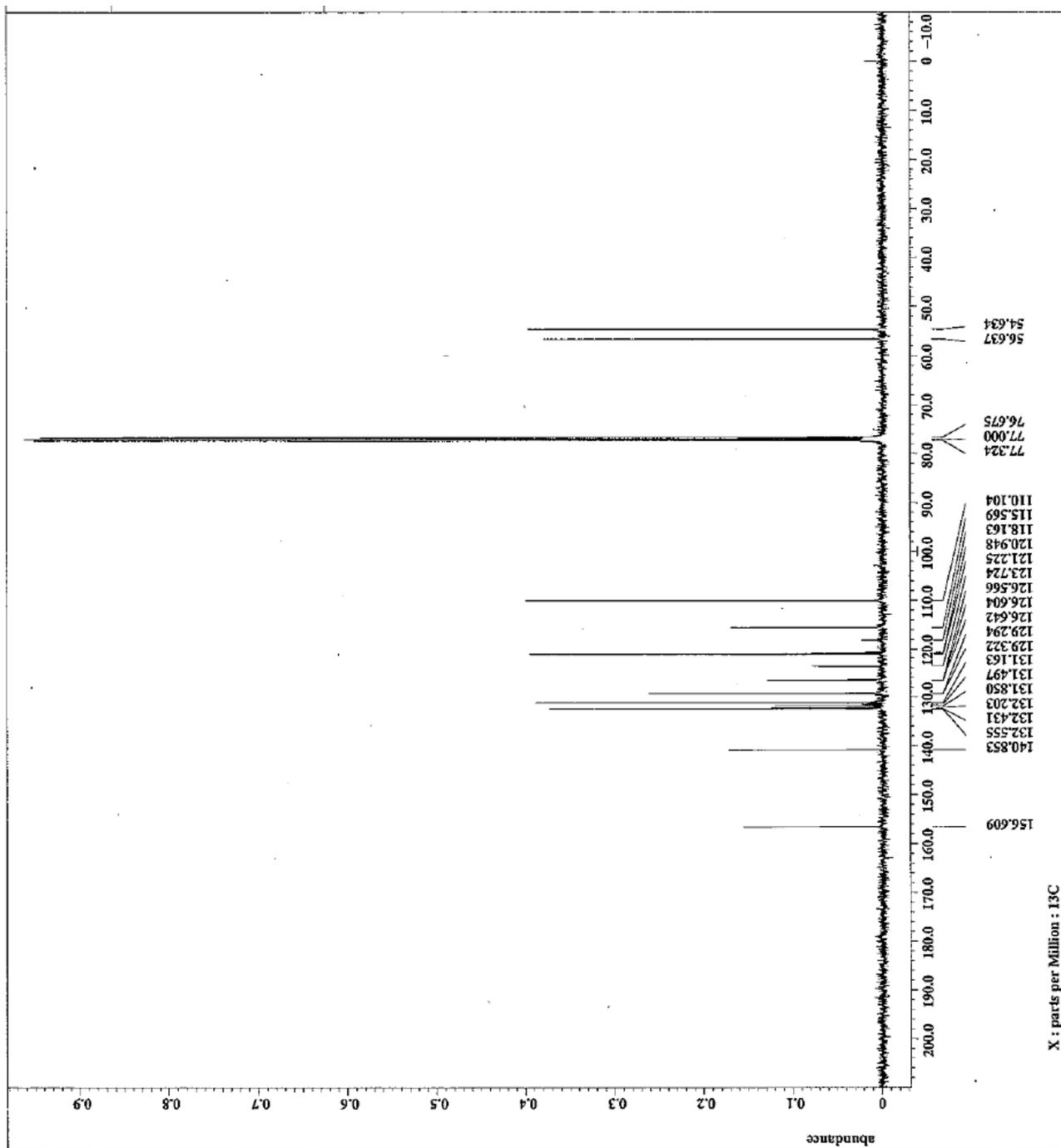
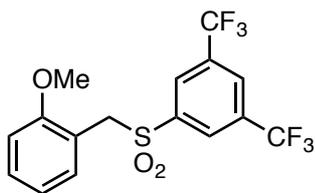
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2j



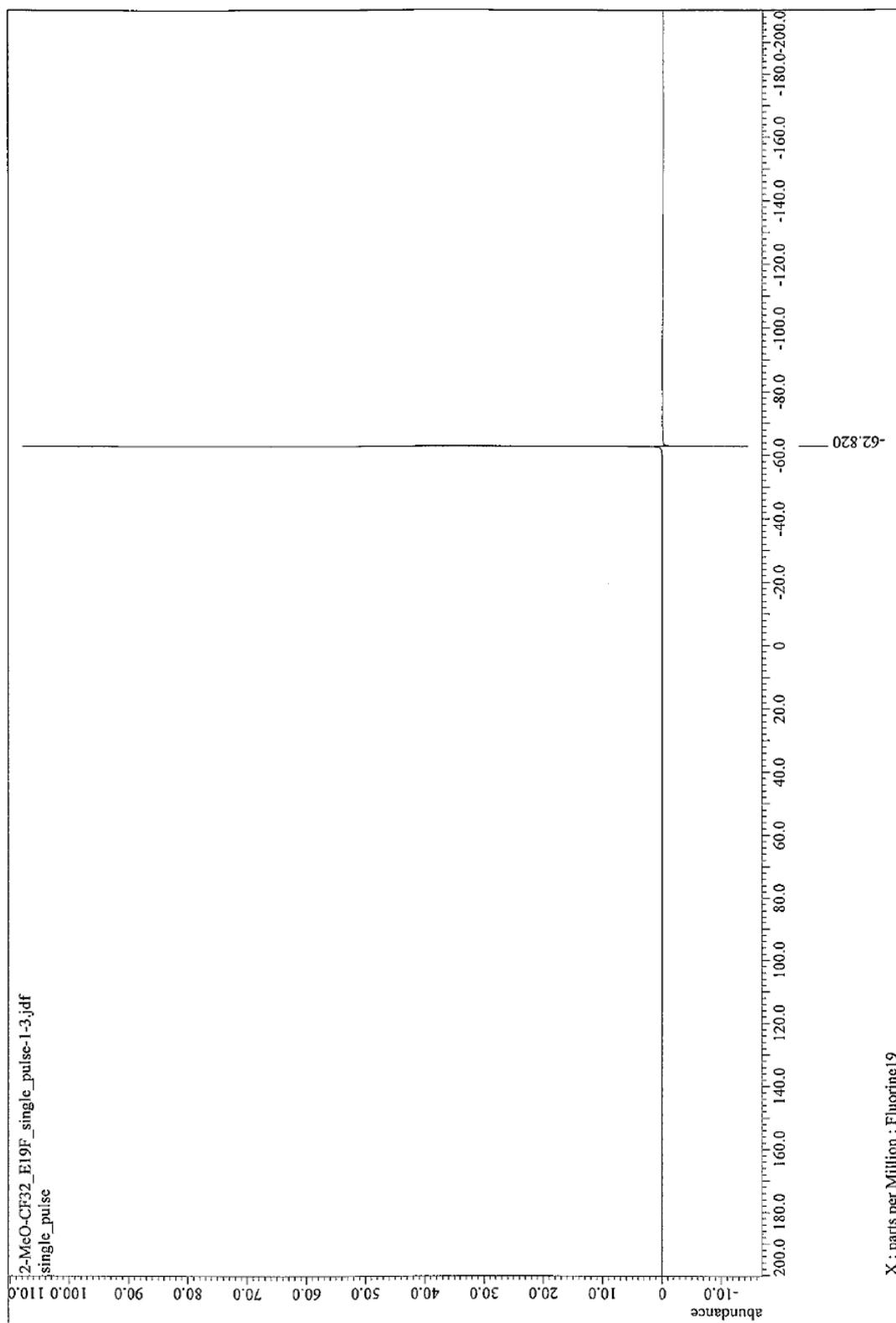
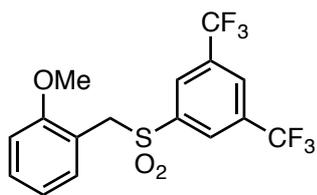
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2k



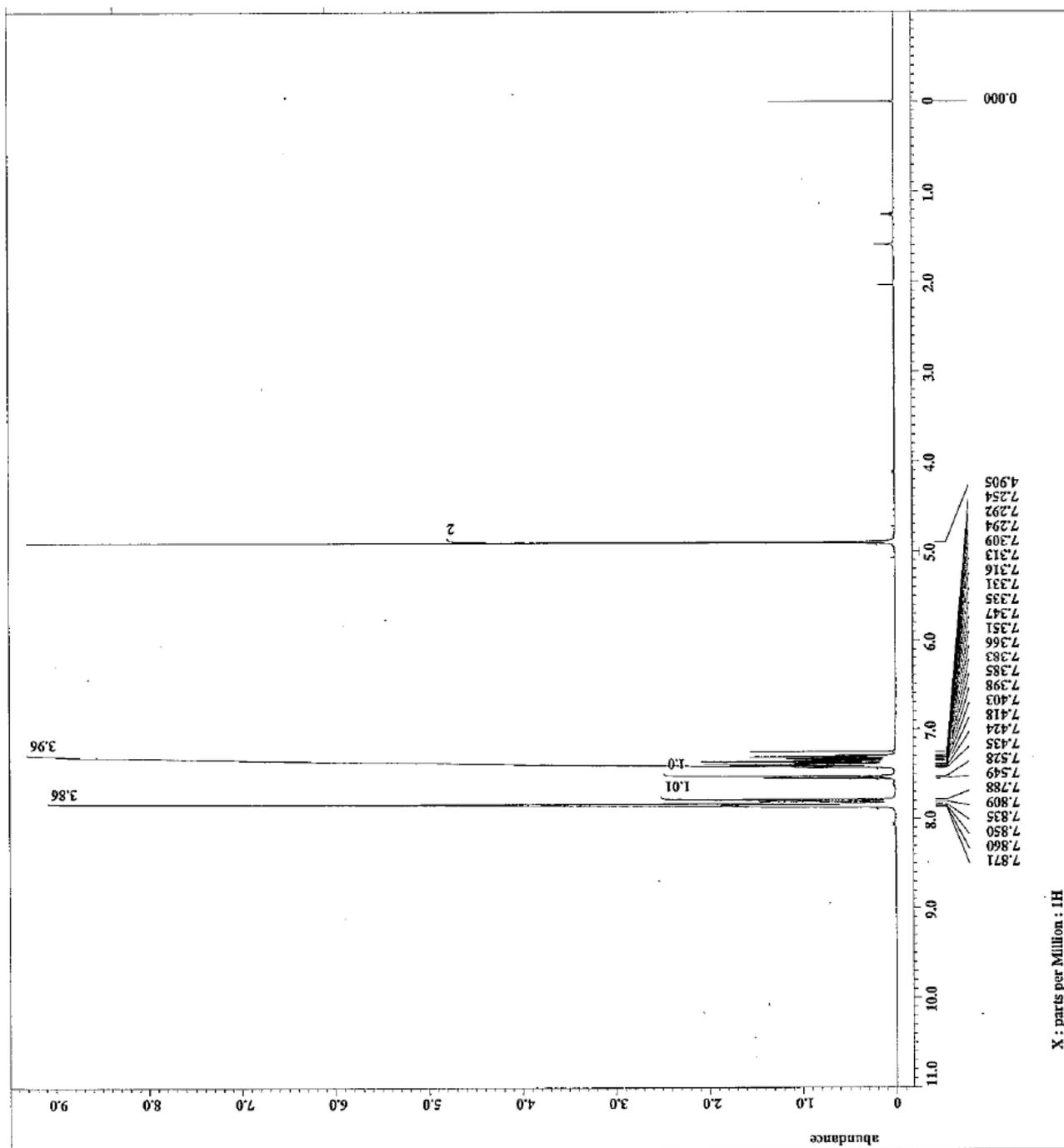
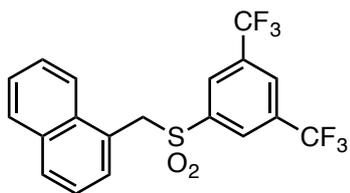
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2k



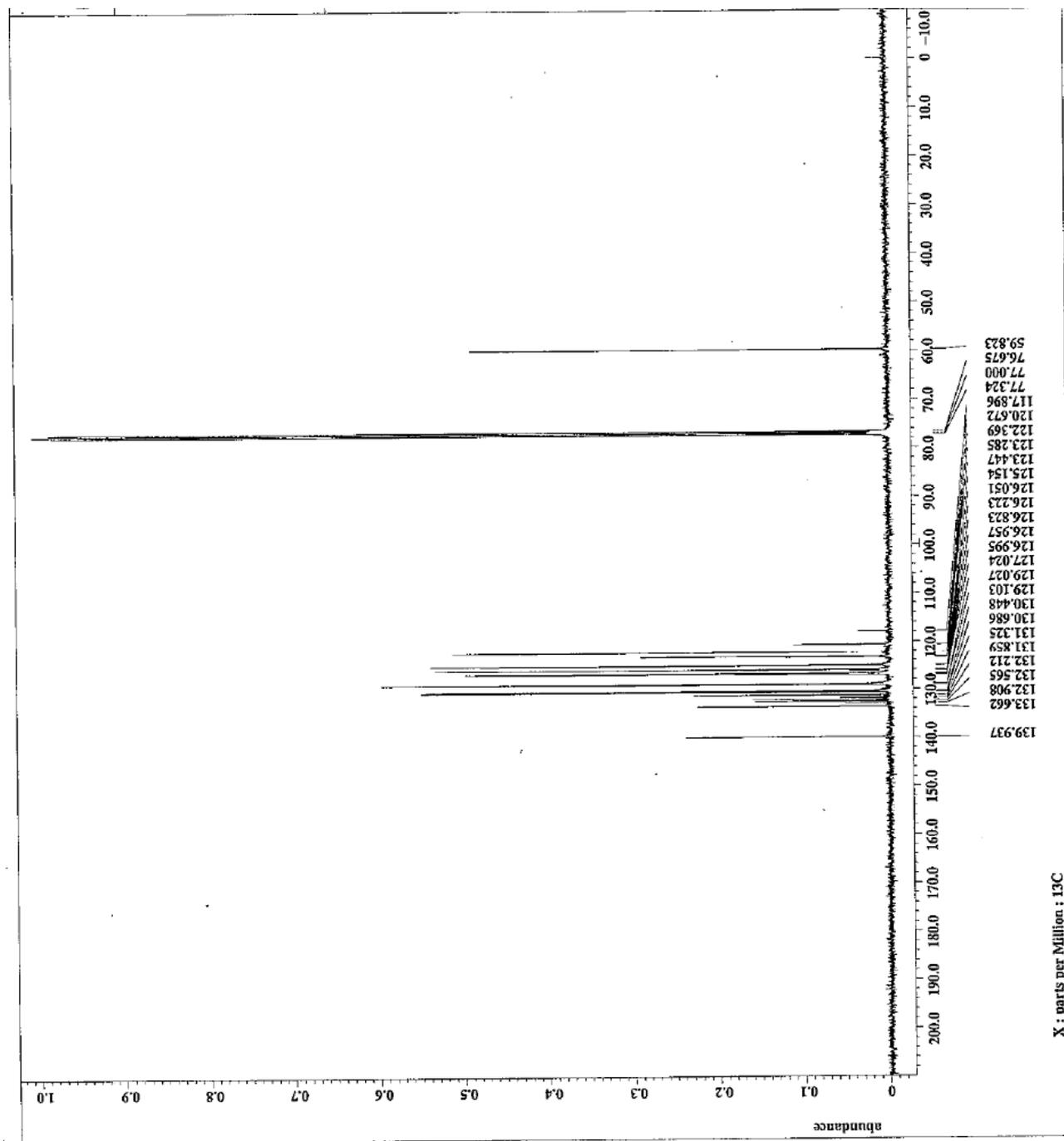
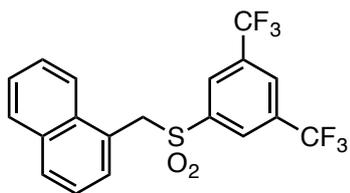
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2k



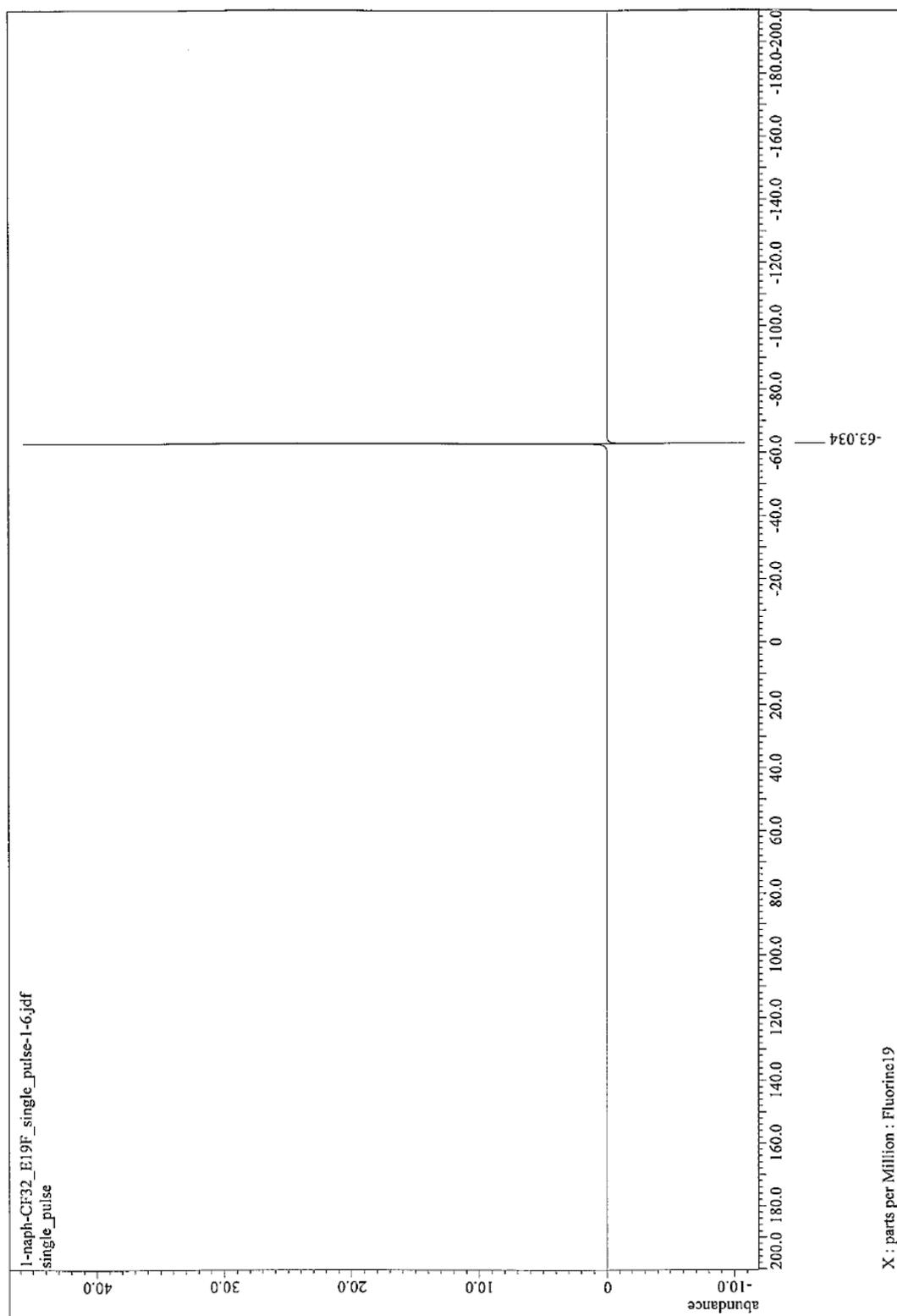
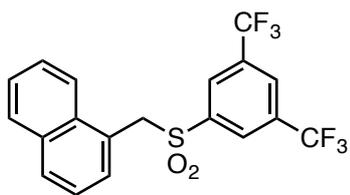
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2l



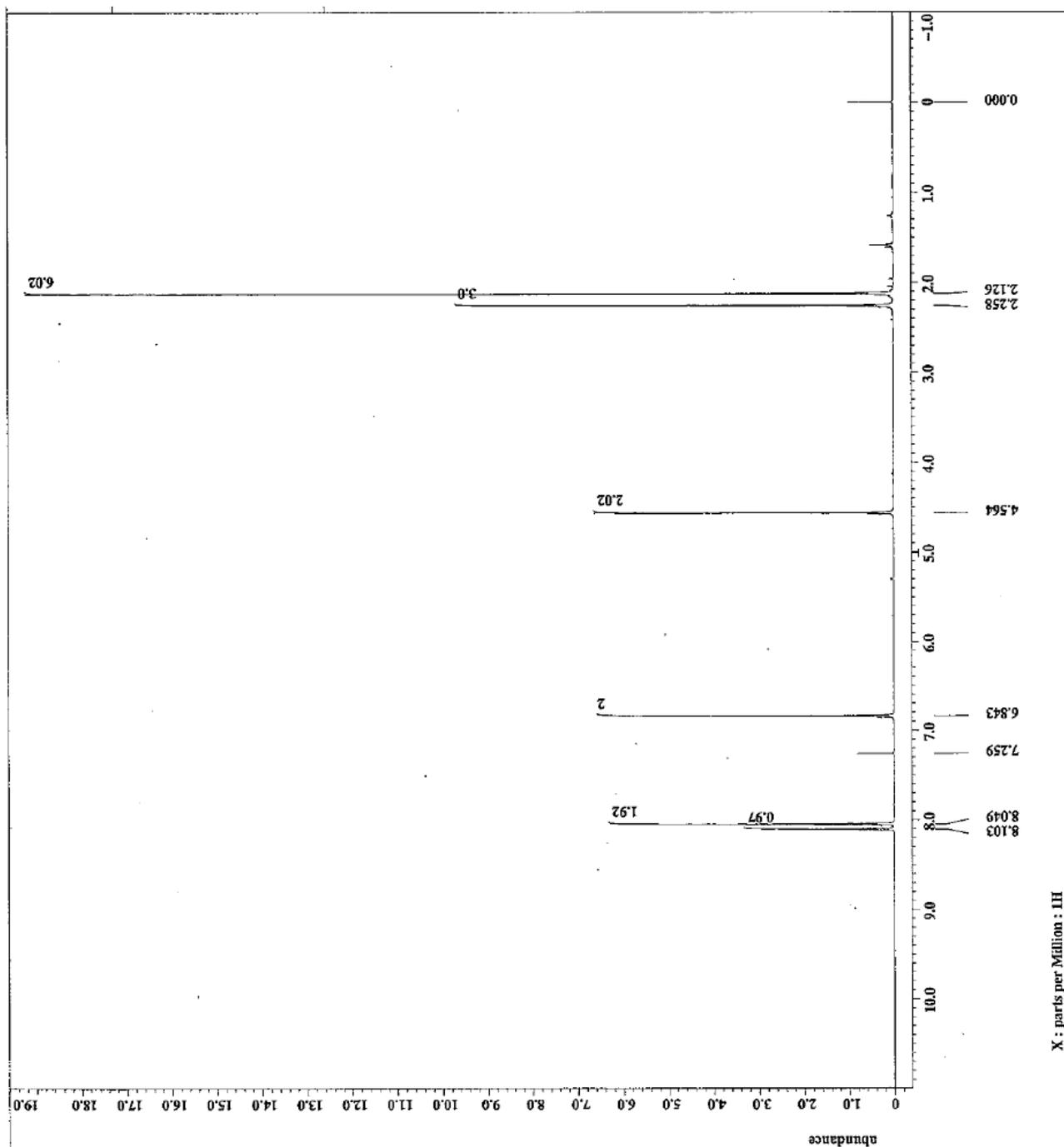
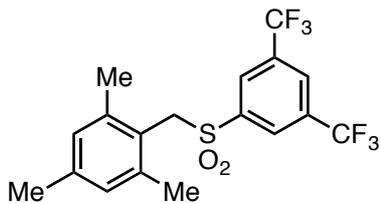
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2l



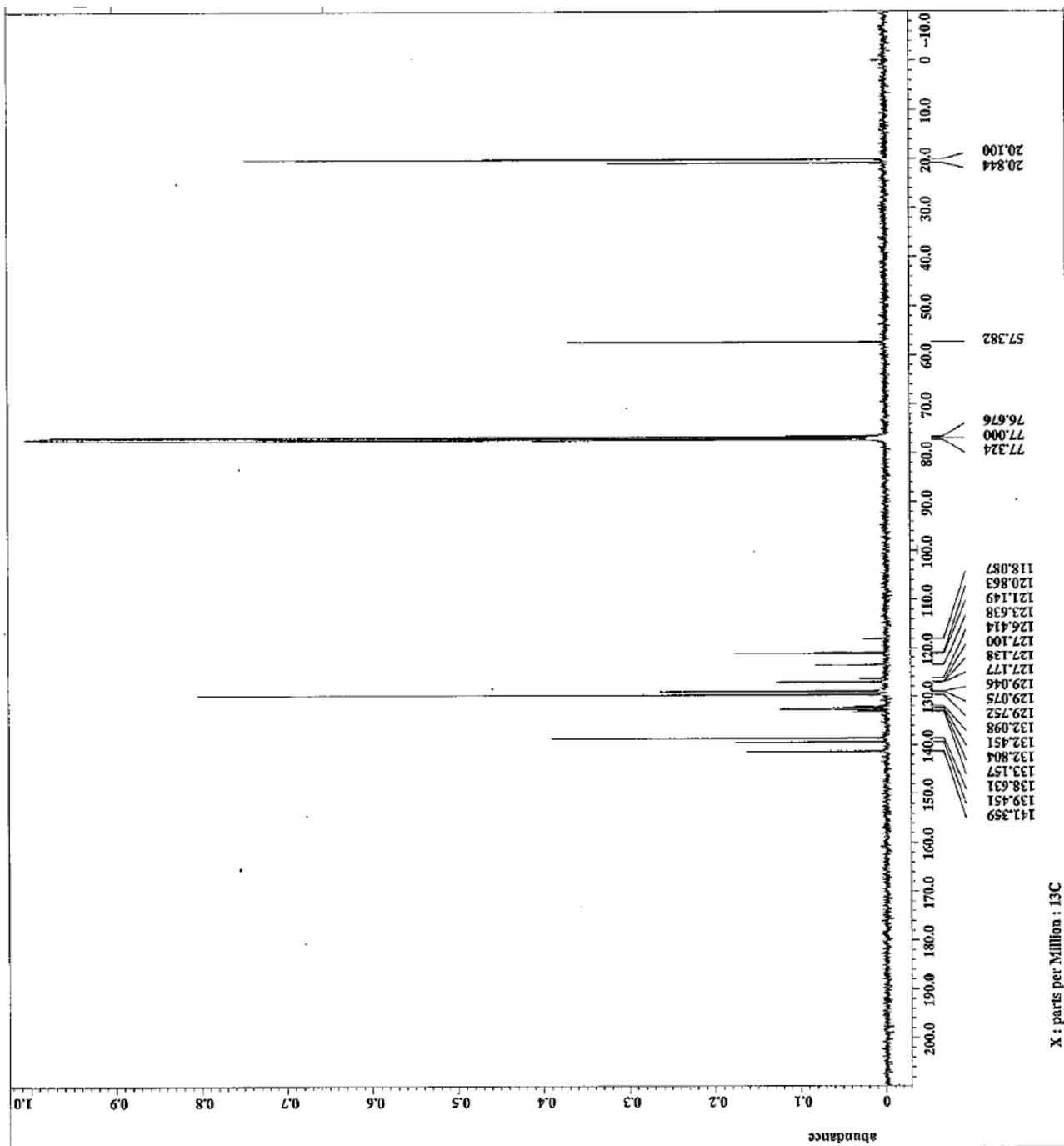
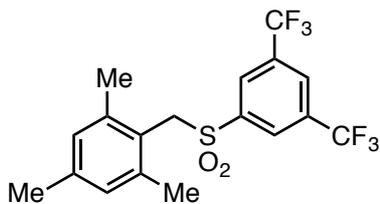
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2I



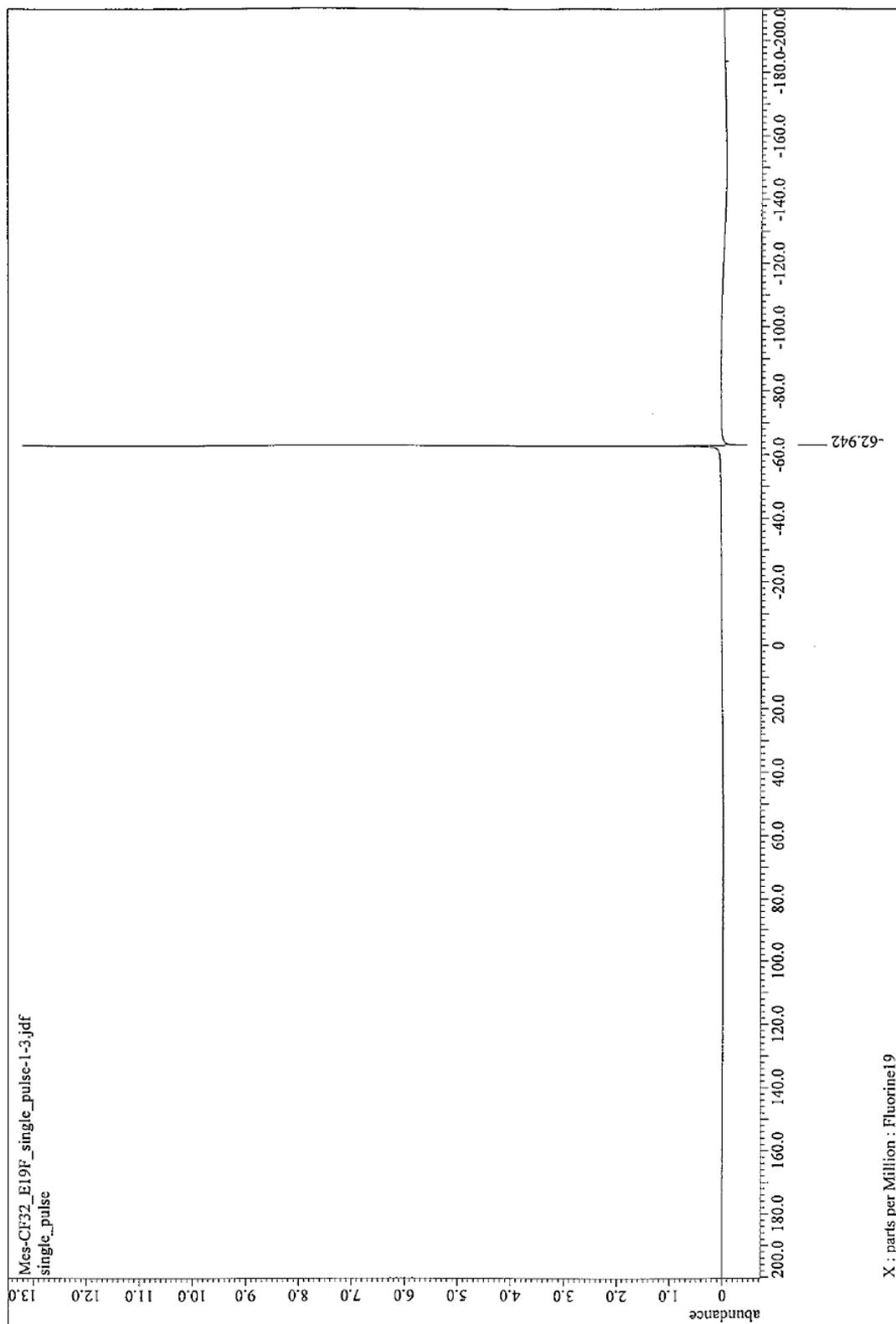
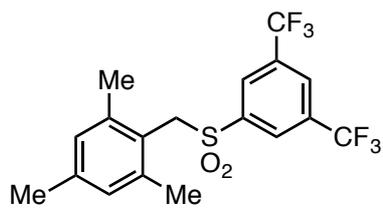
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2m



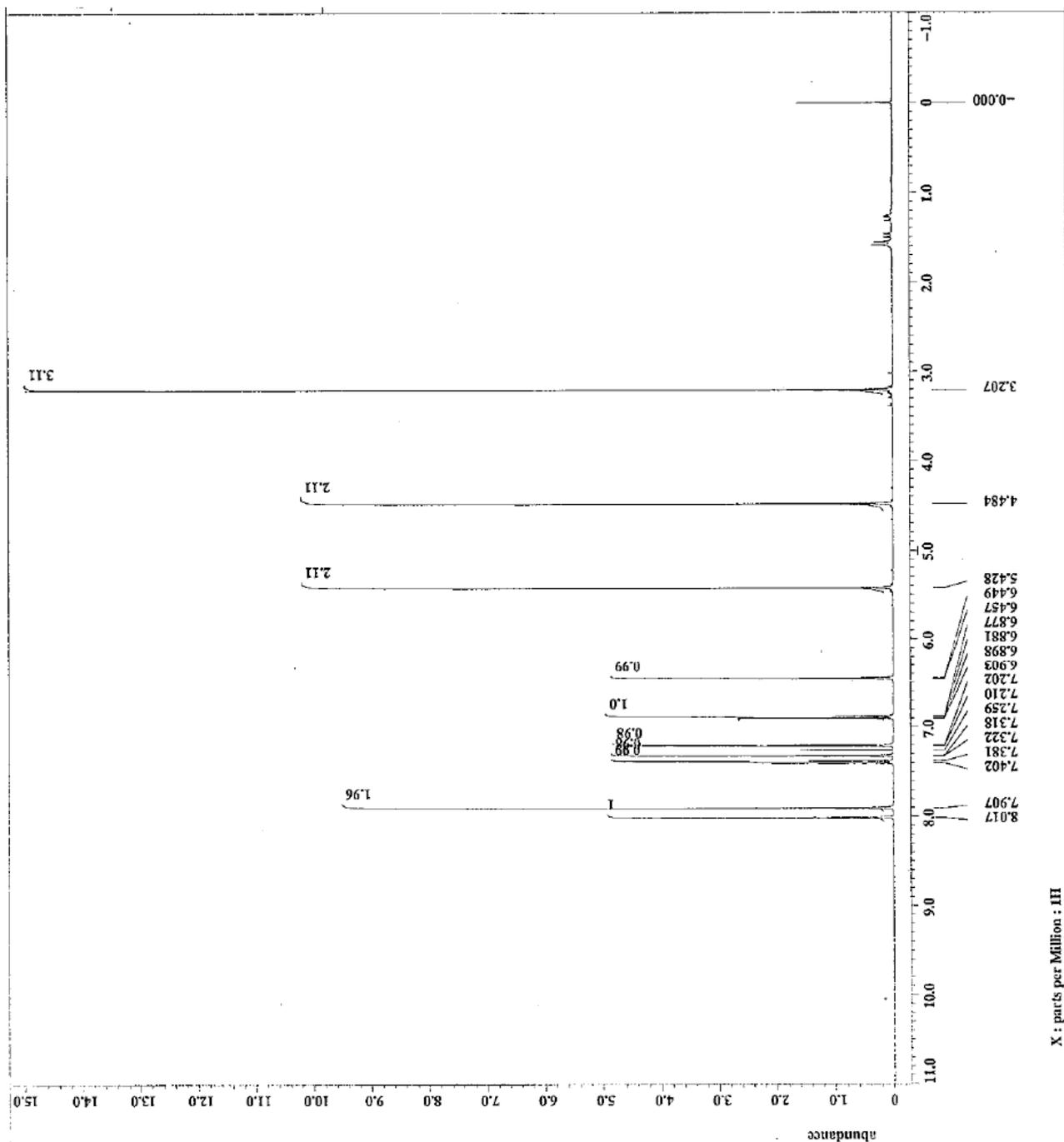
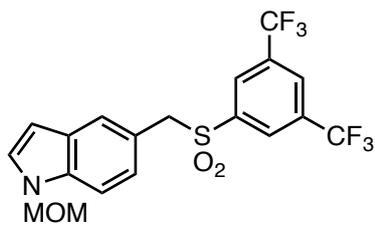
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2m



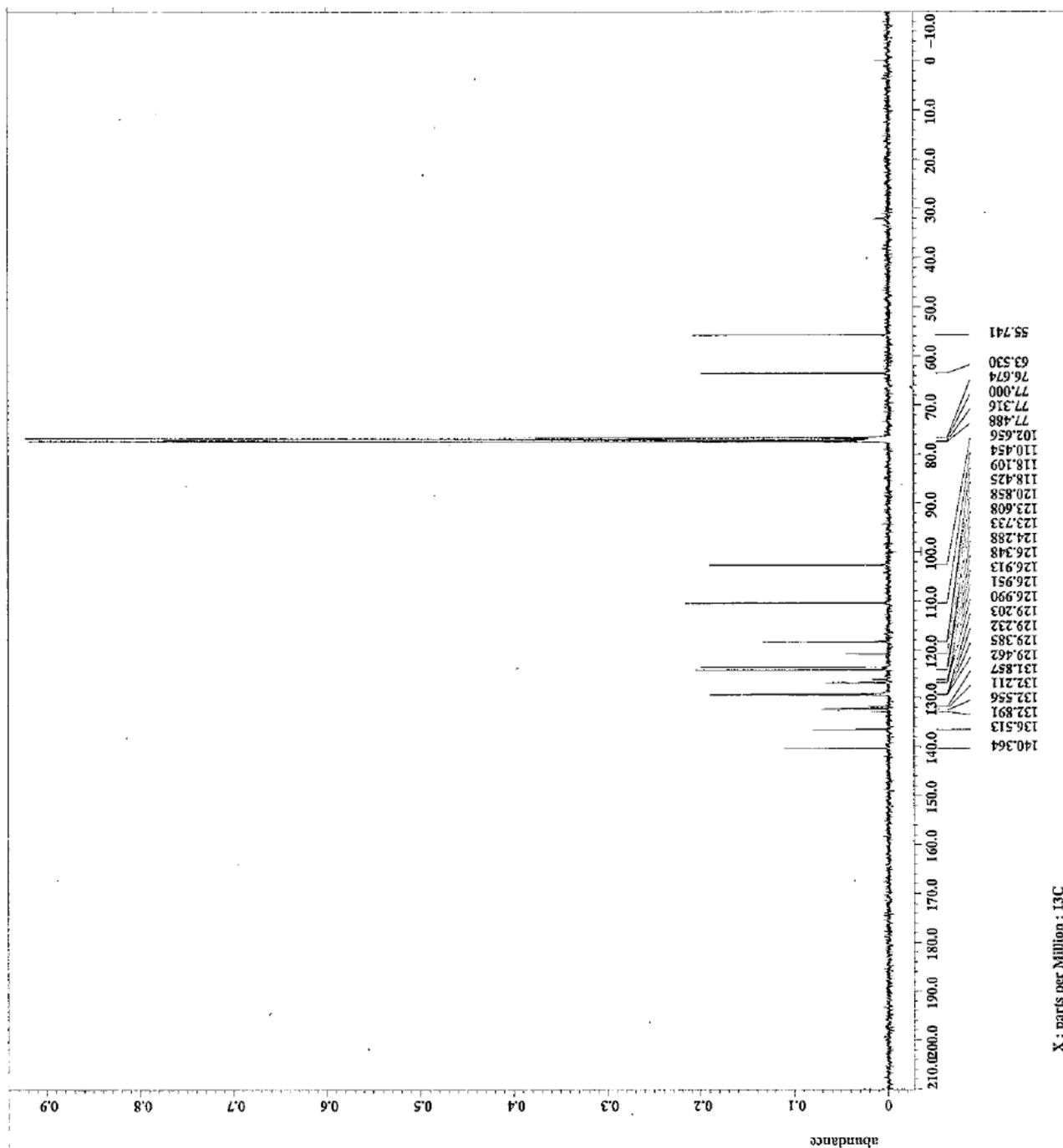
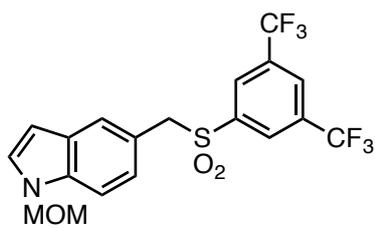
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2m



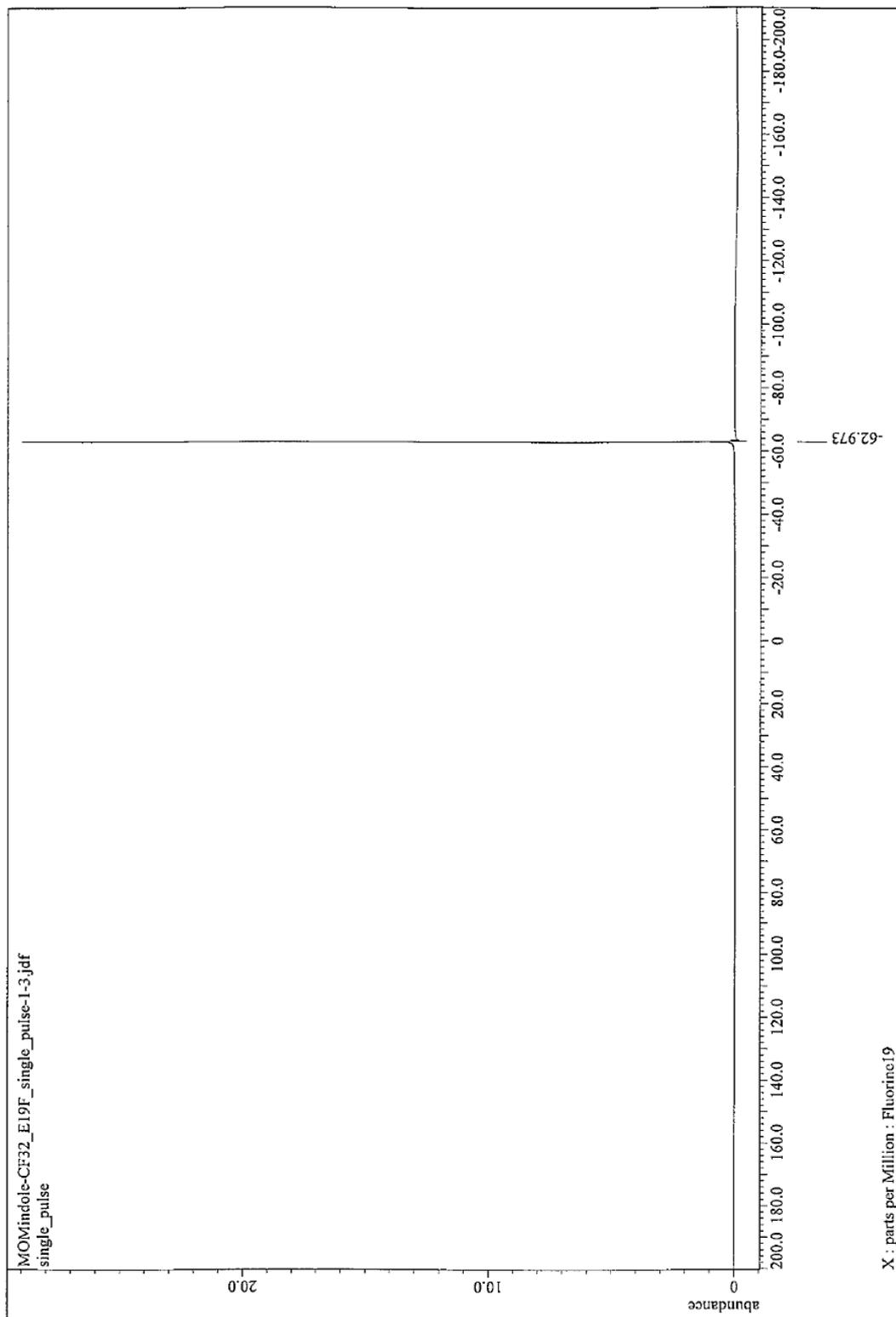
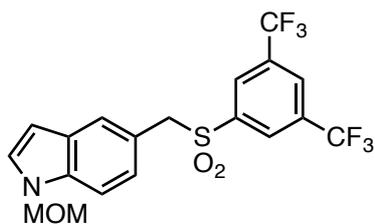
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2n



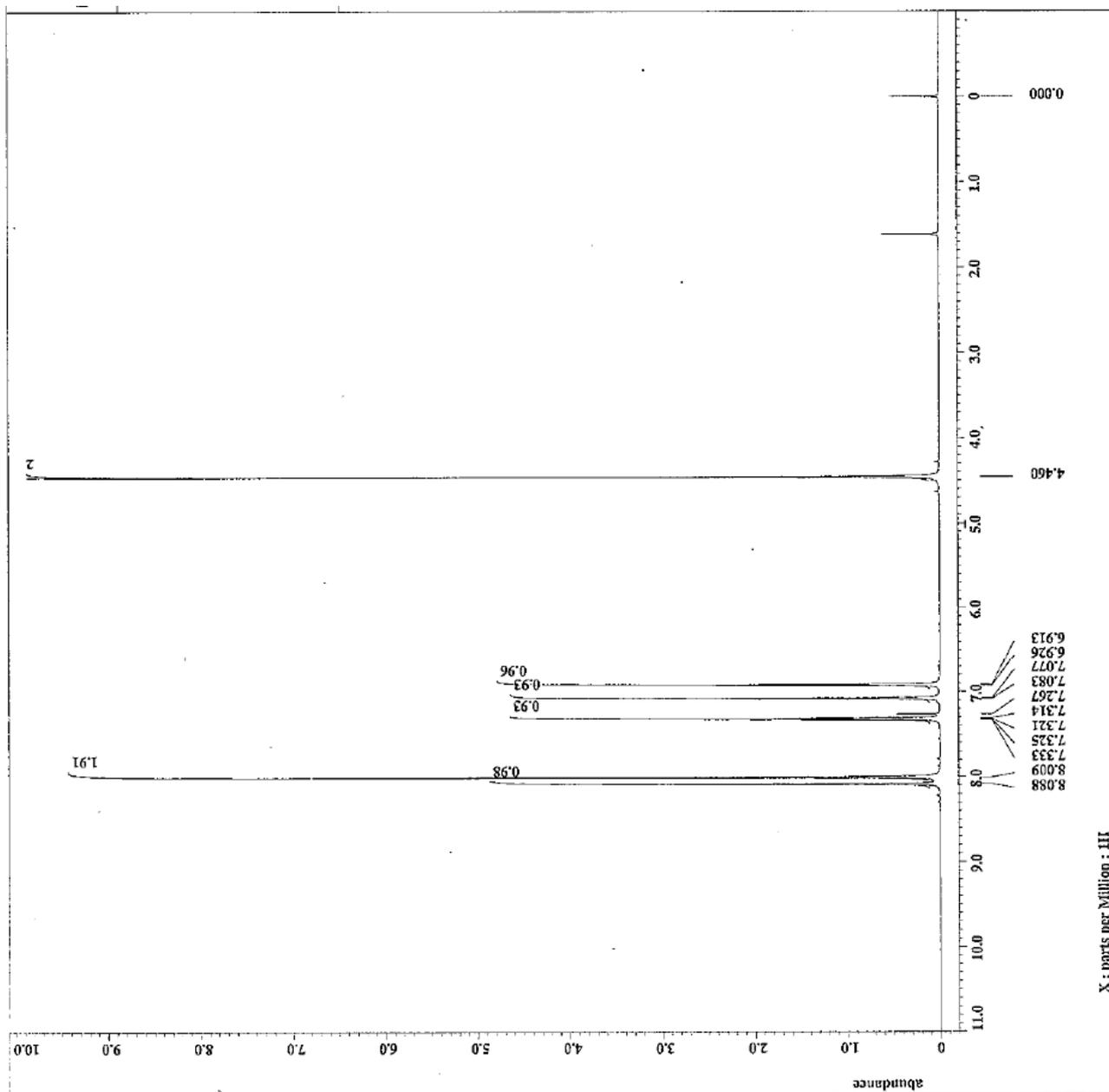
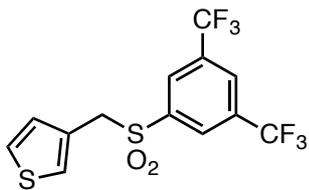
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2n



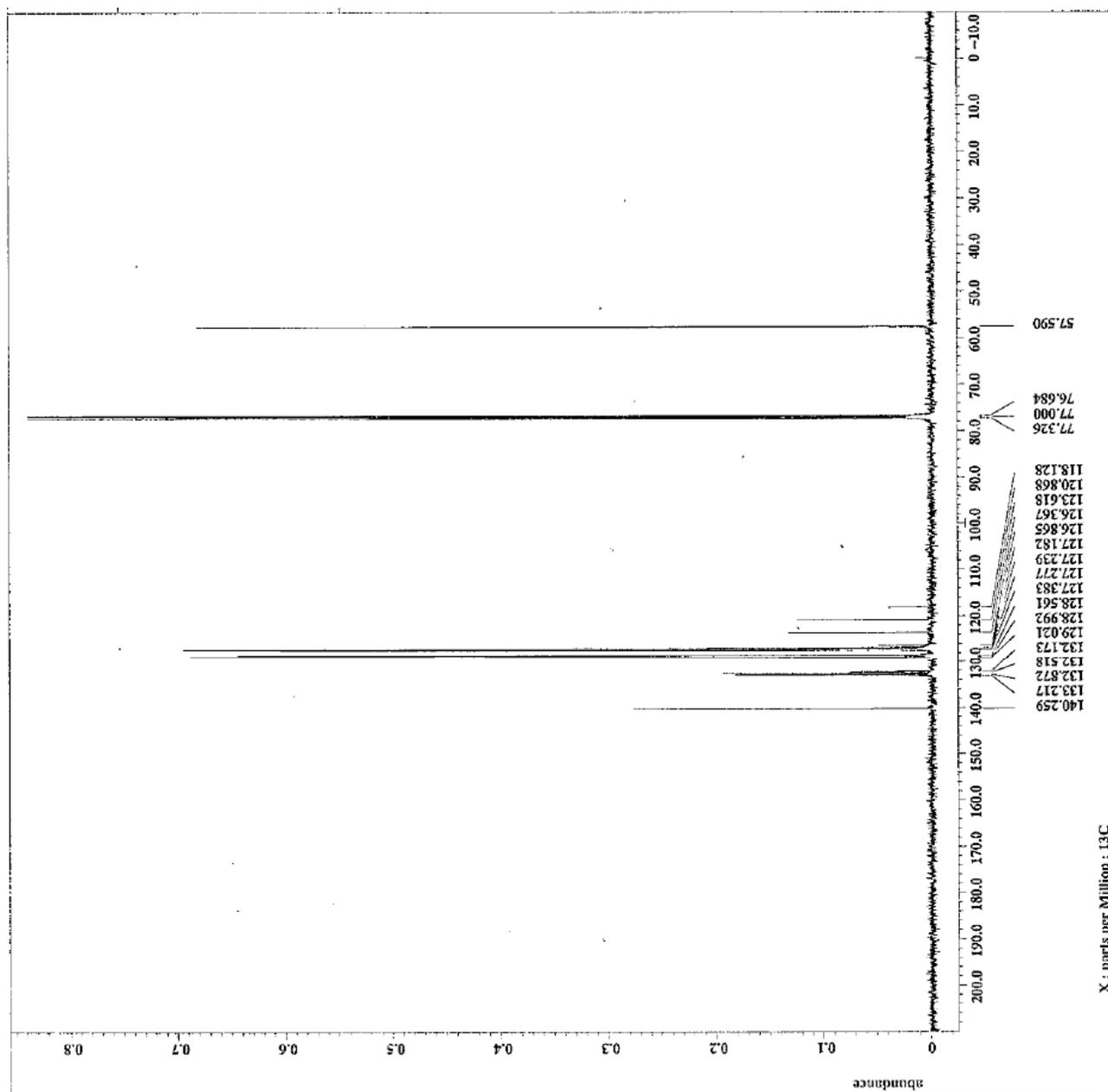
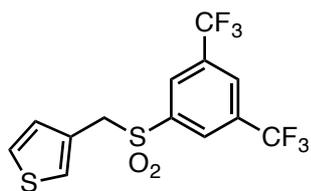
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2n



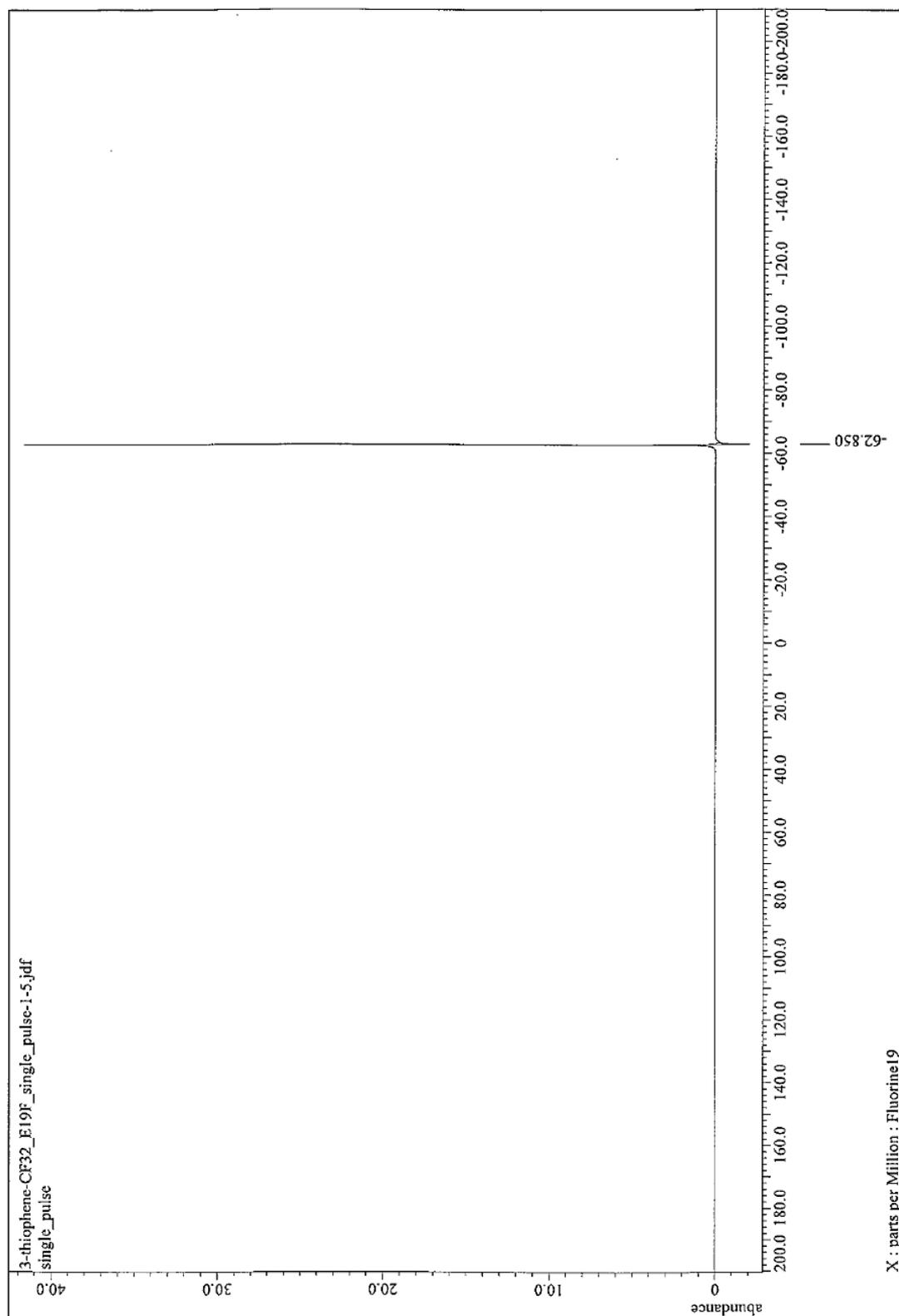
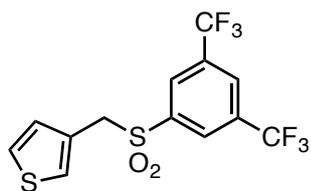
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2o



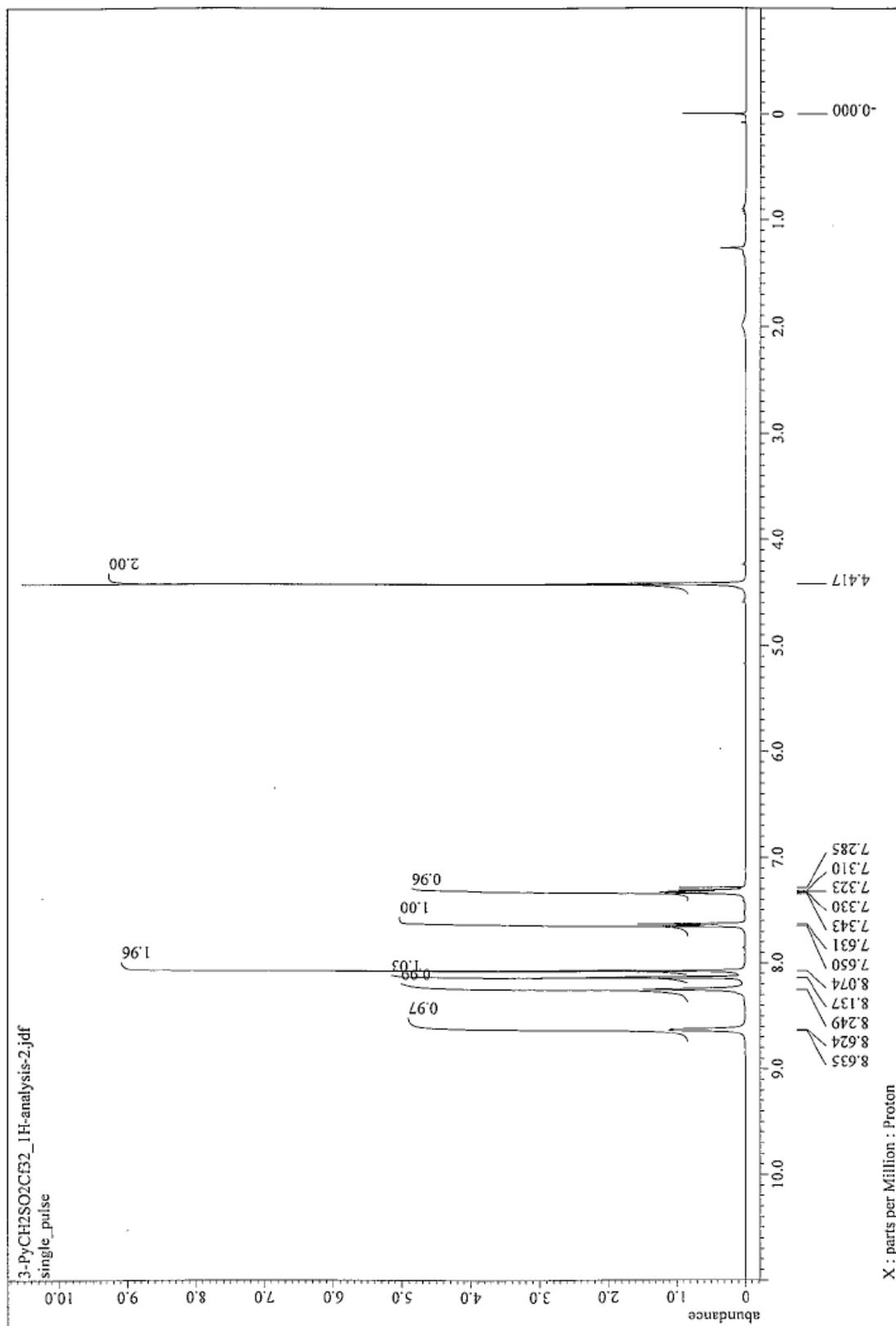
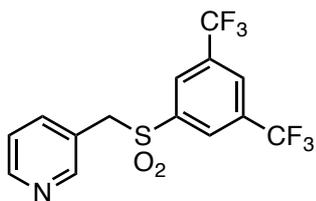
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2o



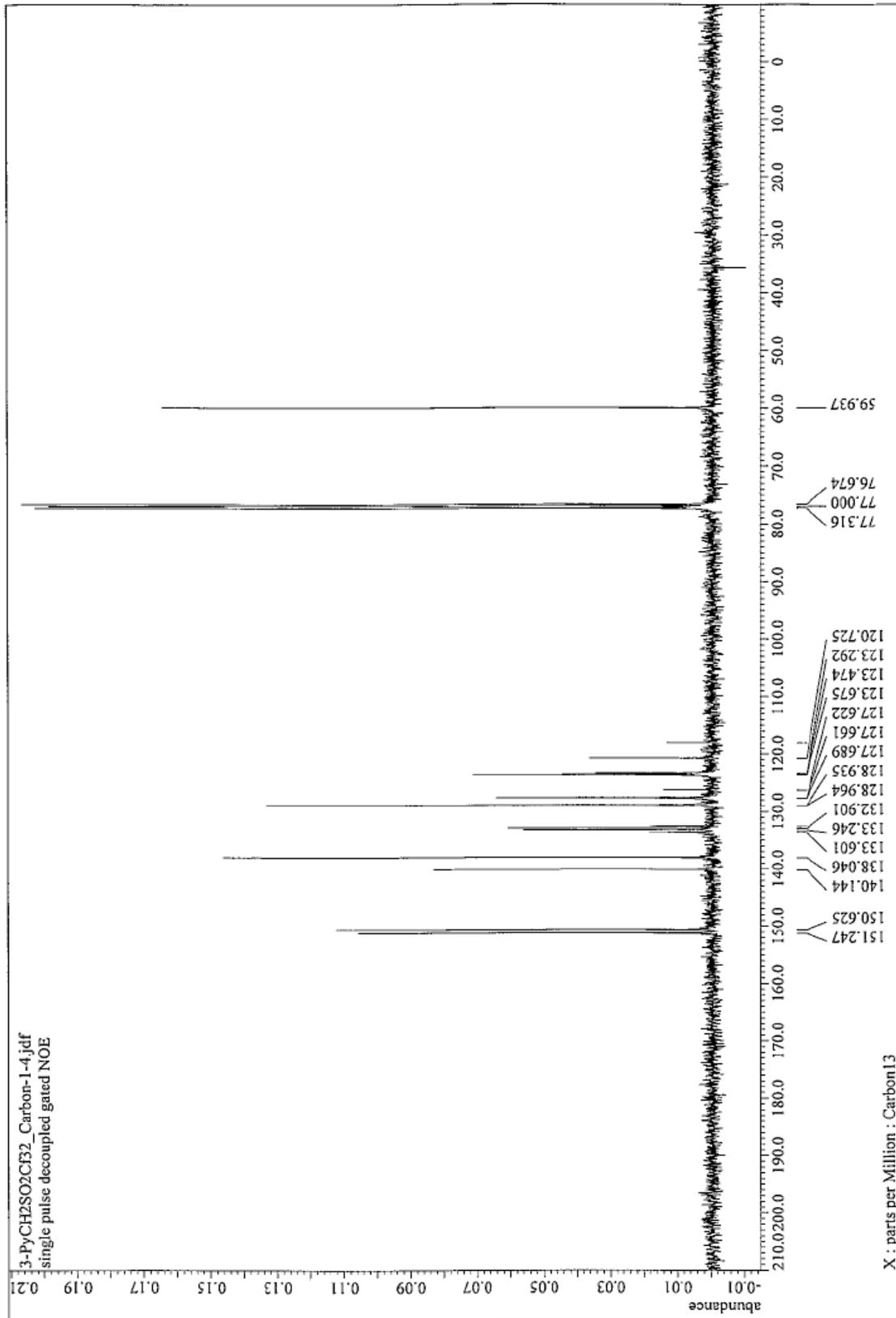
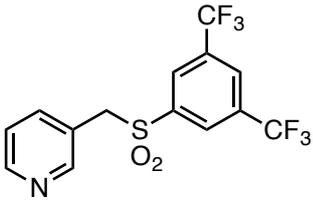
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2o



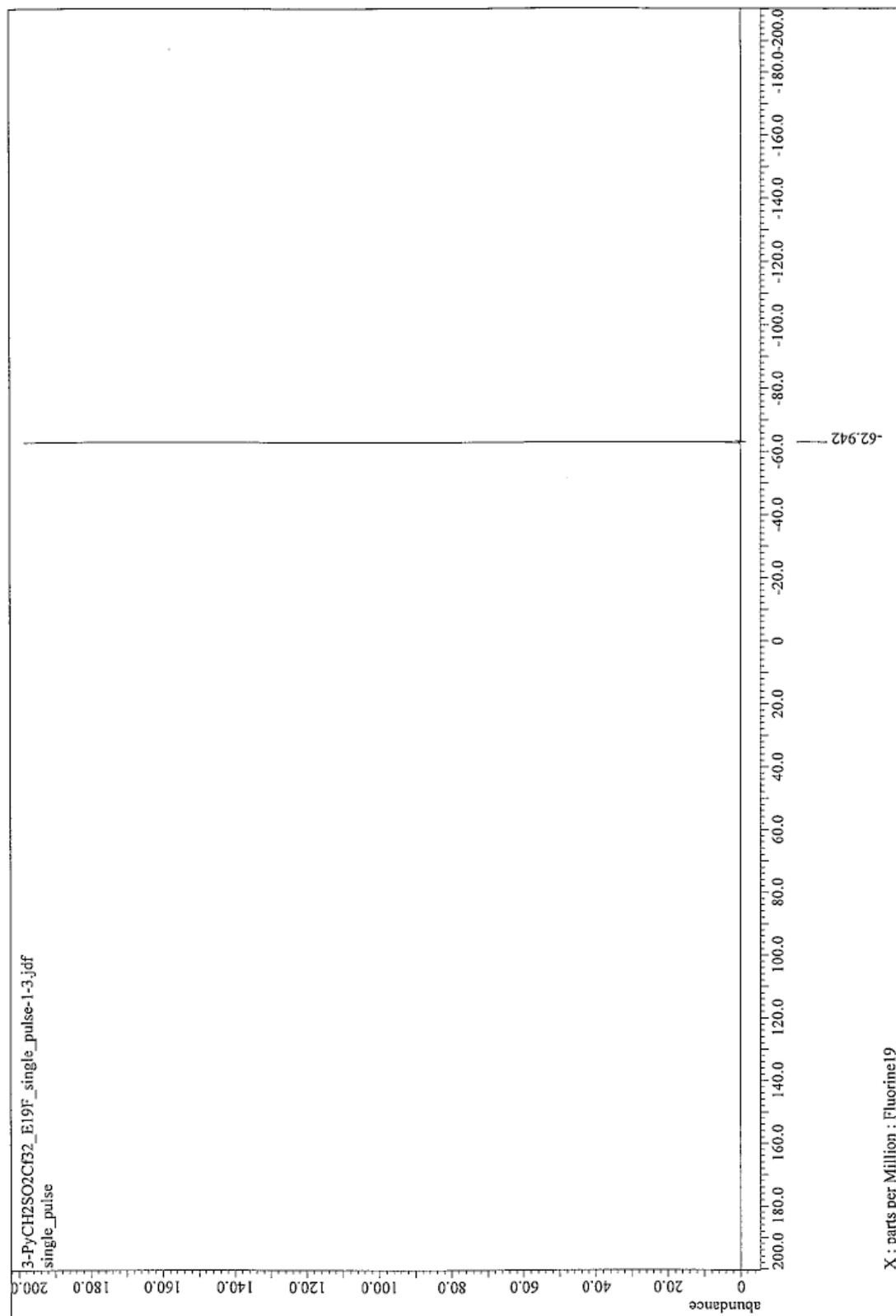
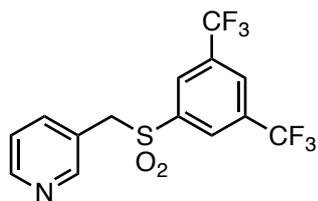
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2p



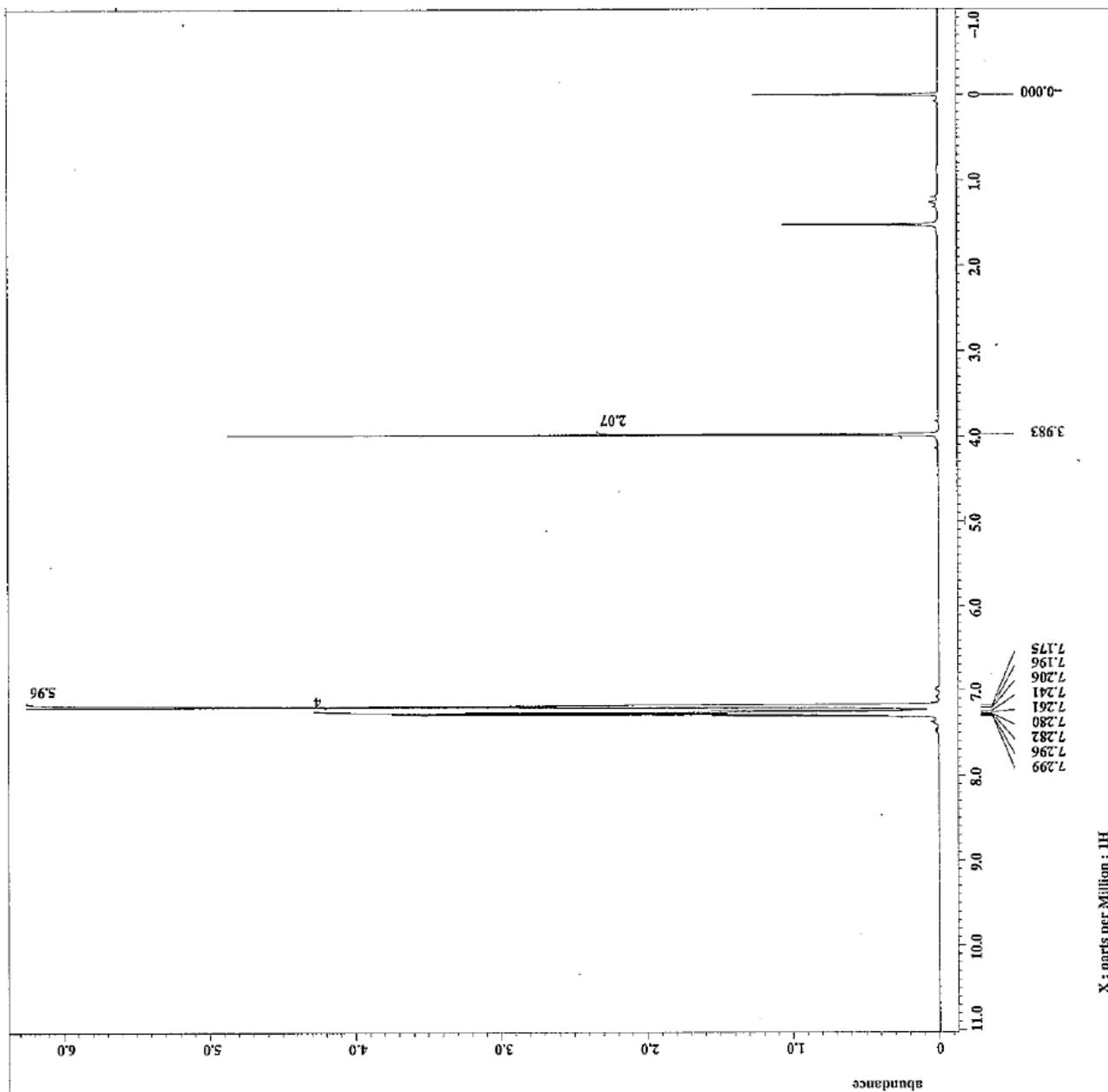
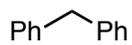
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2p



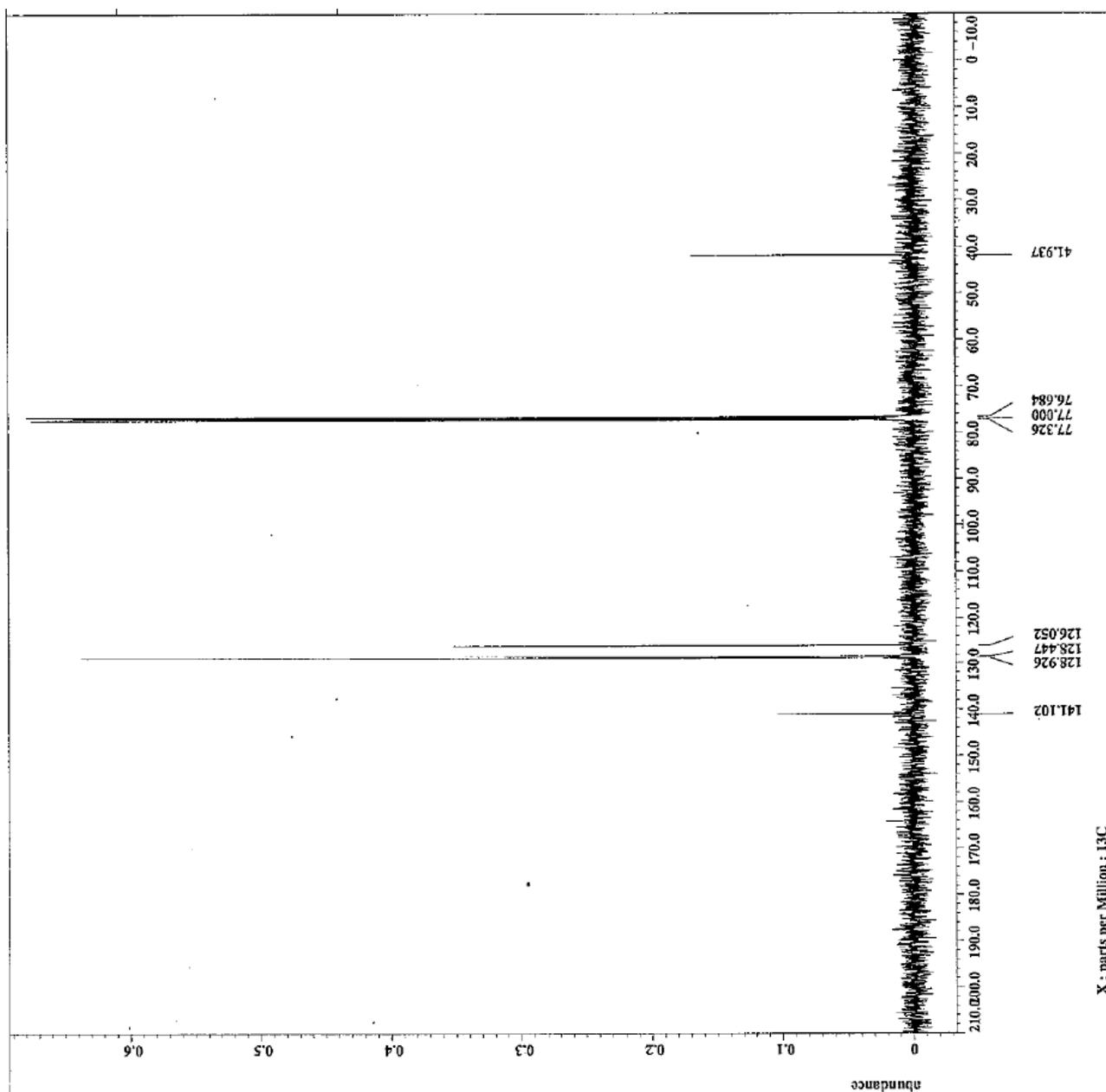
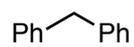
<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) of 2p



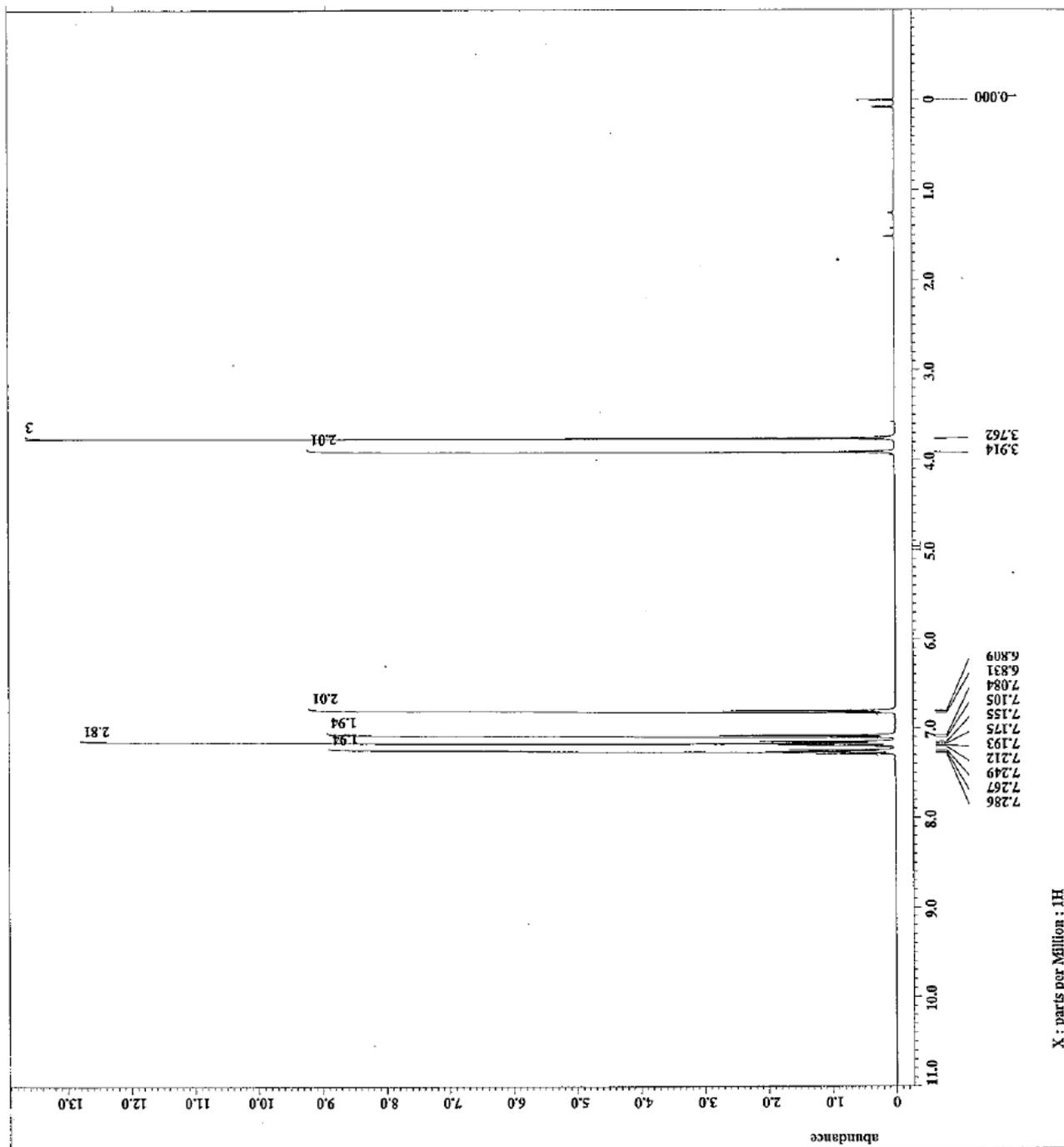
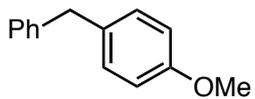
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5aa



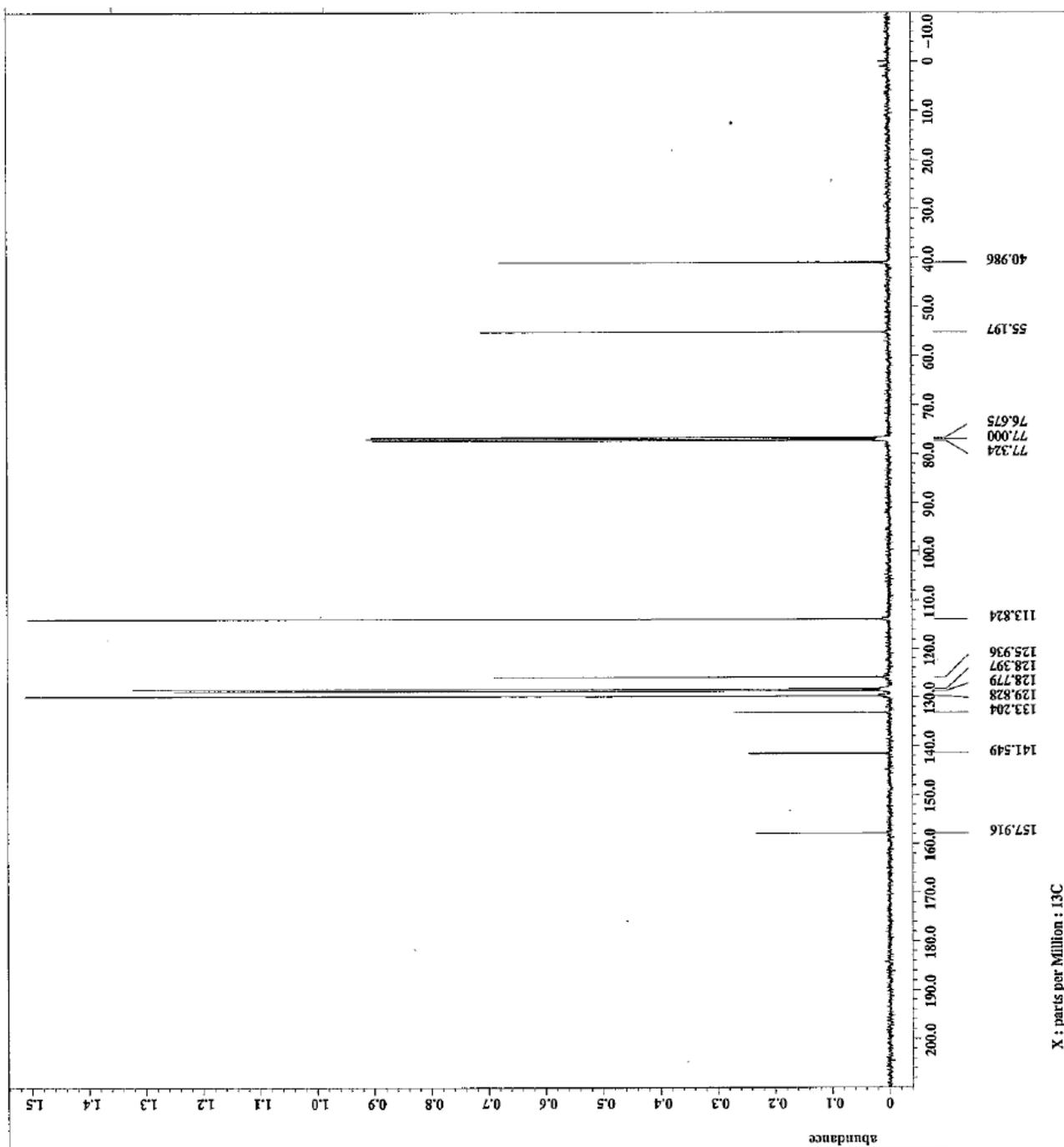
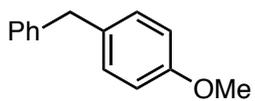
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 5aa



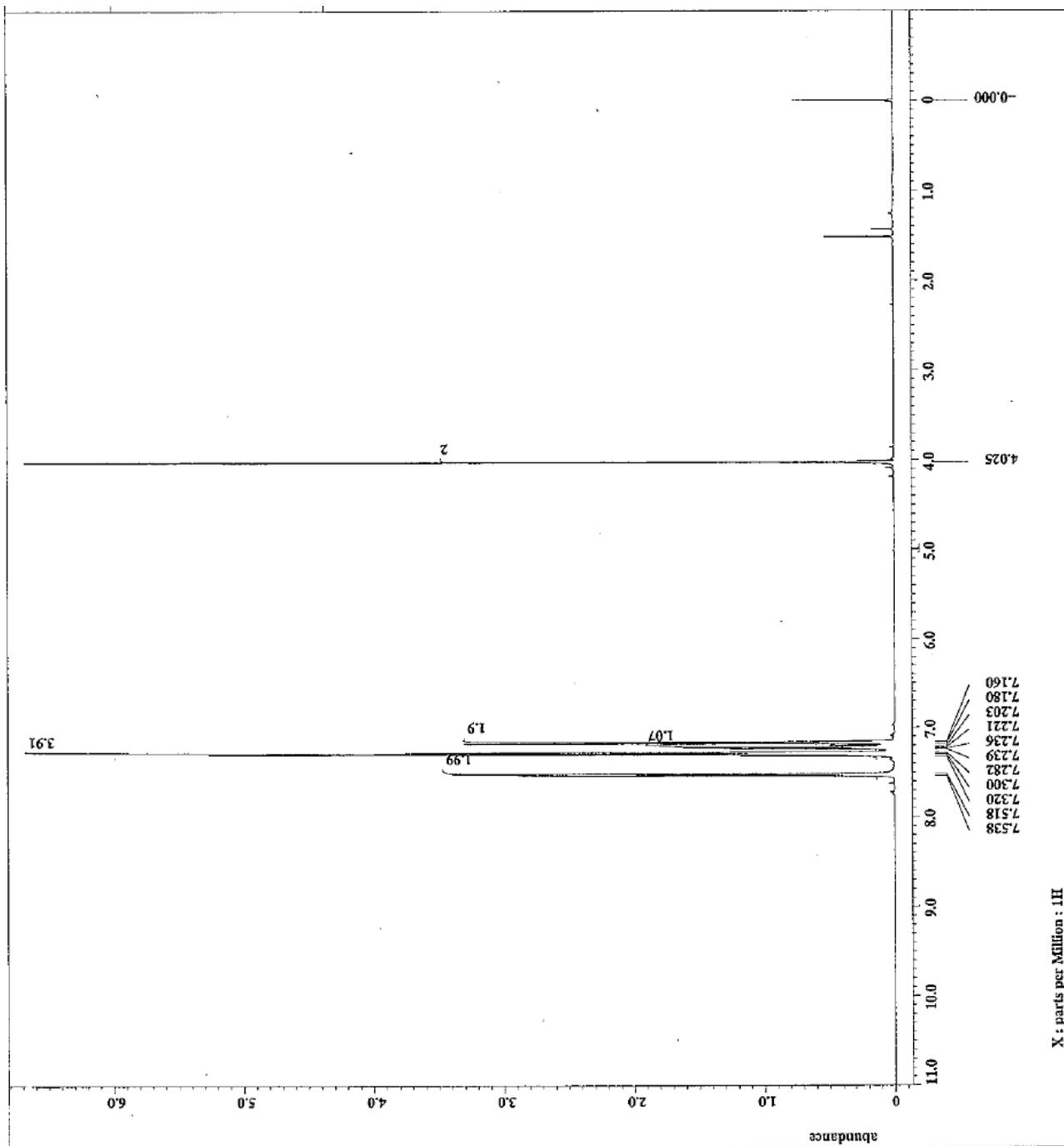
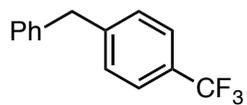
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ab



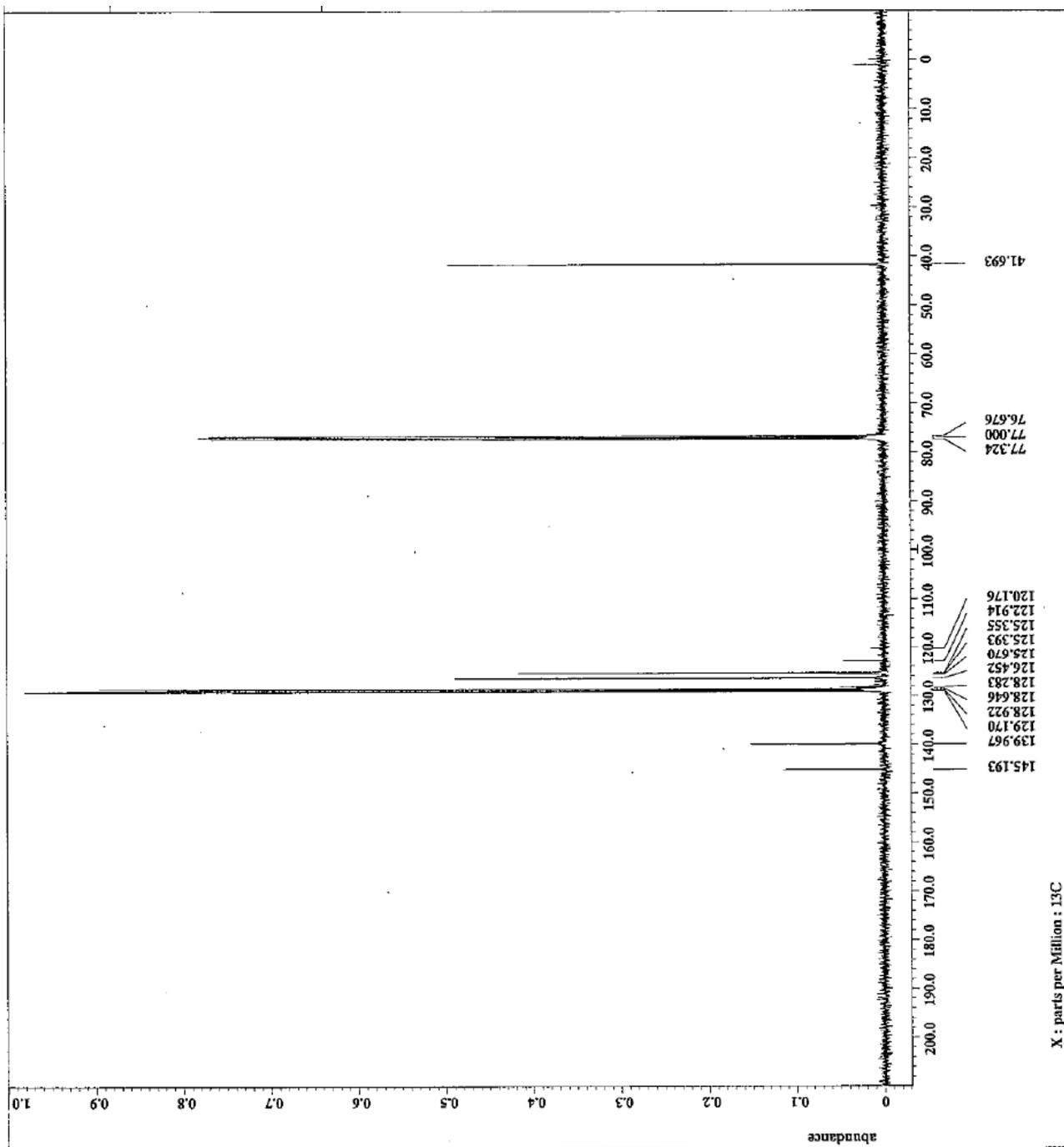
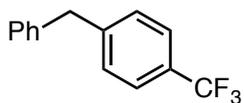
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 5ab



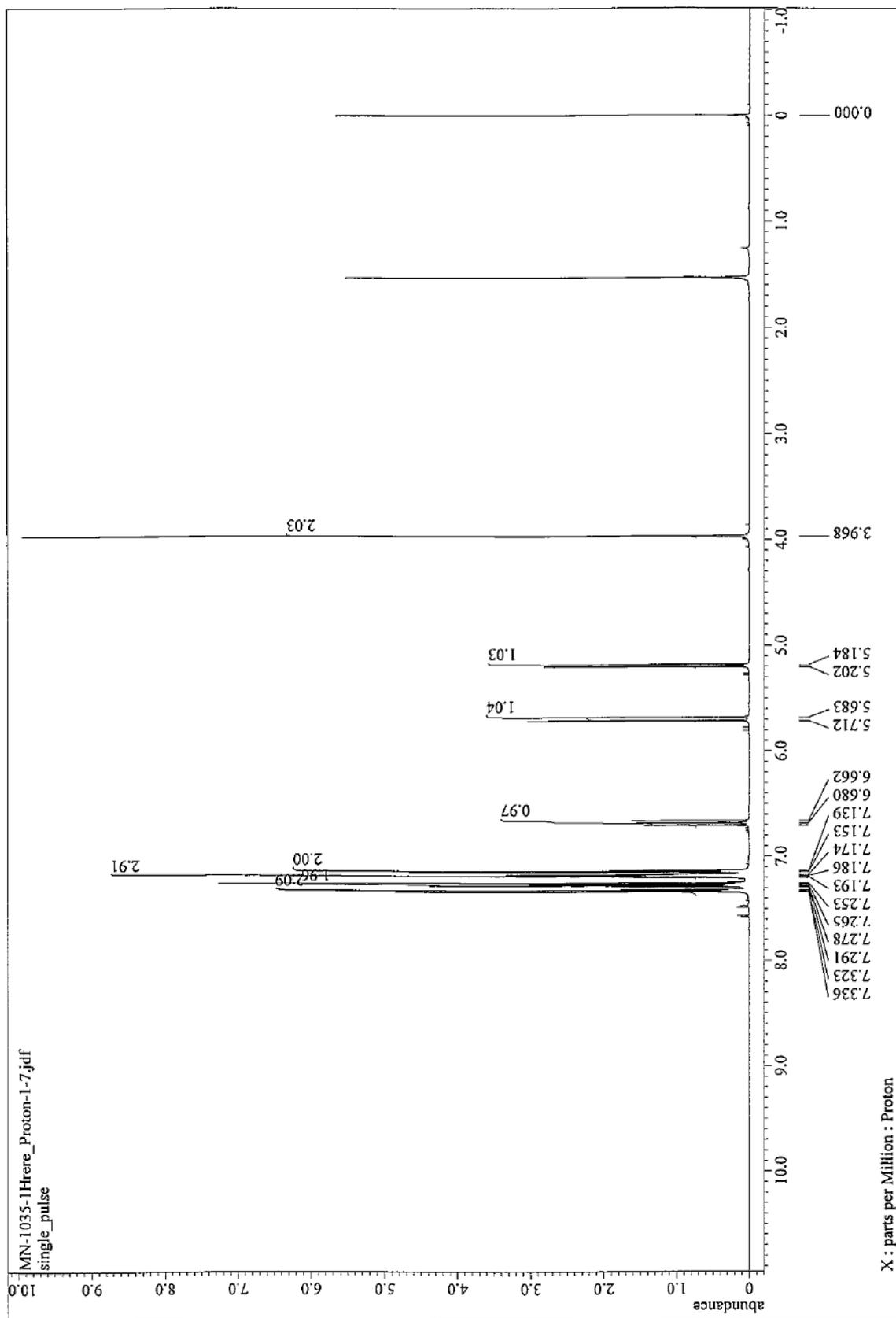
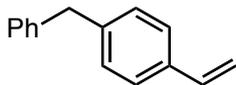
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ac



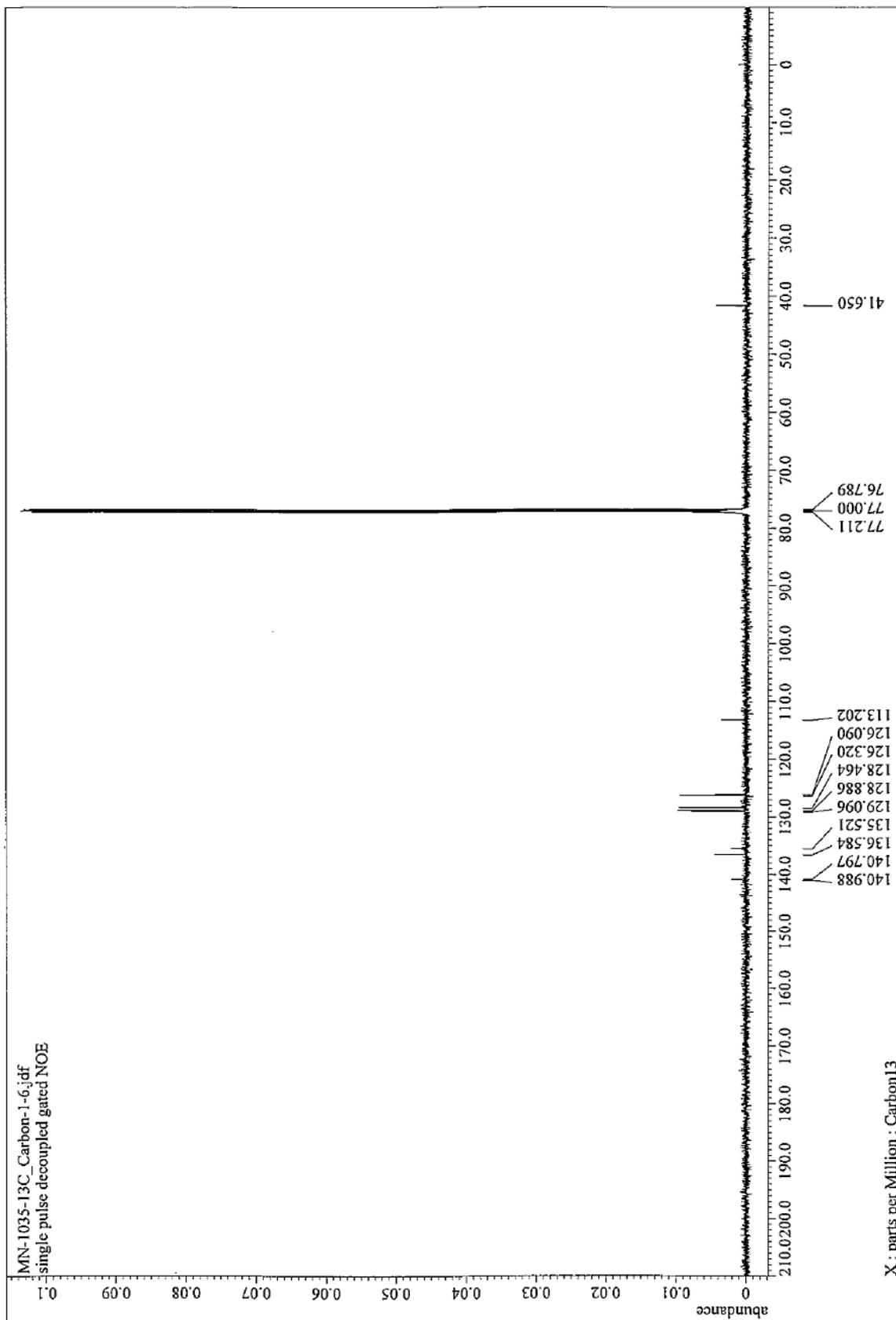
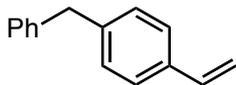
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 5ac



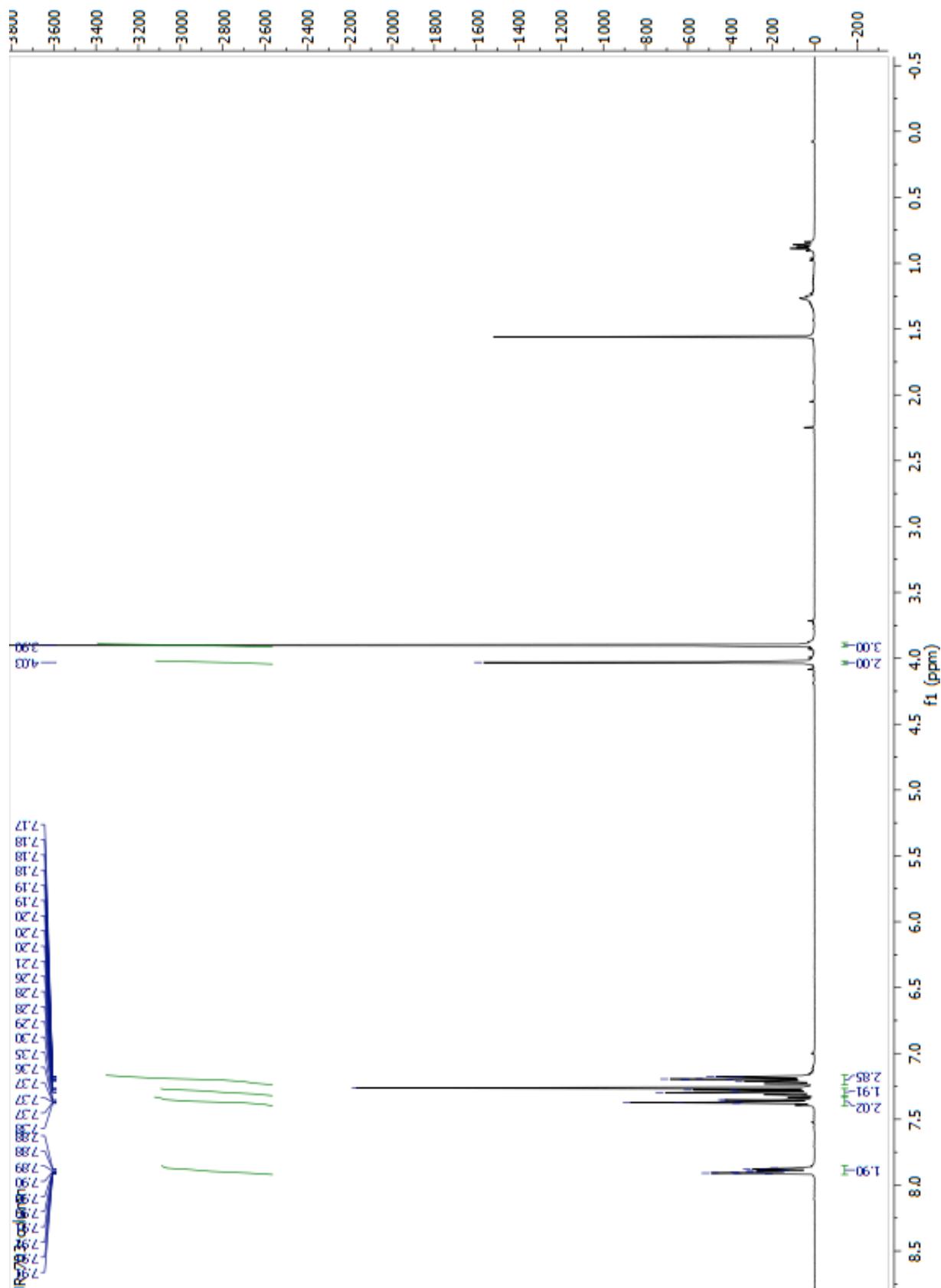
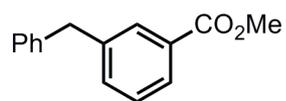
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5ad



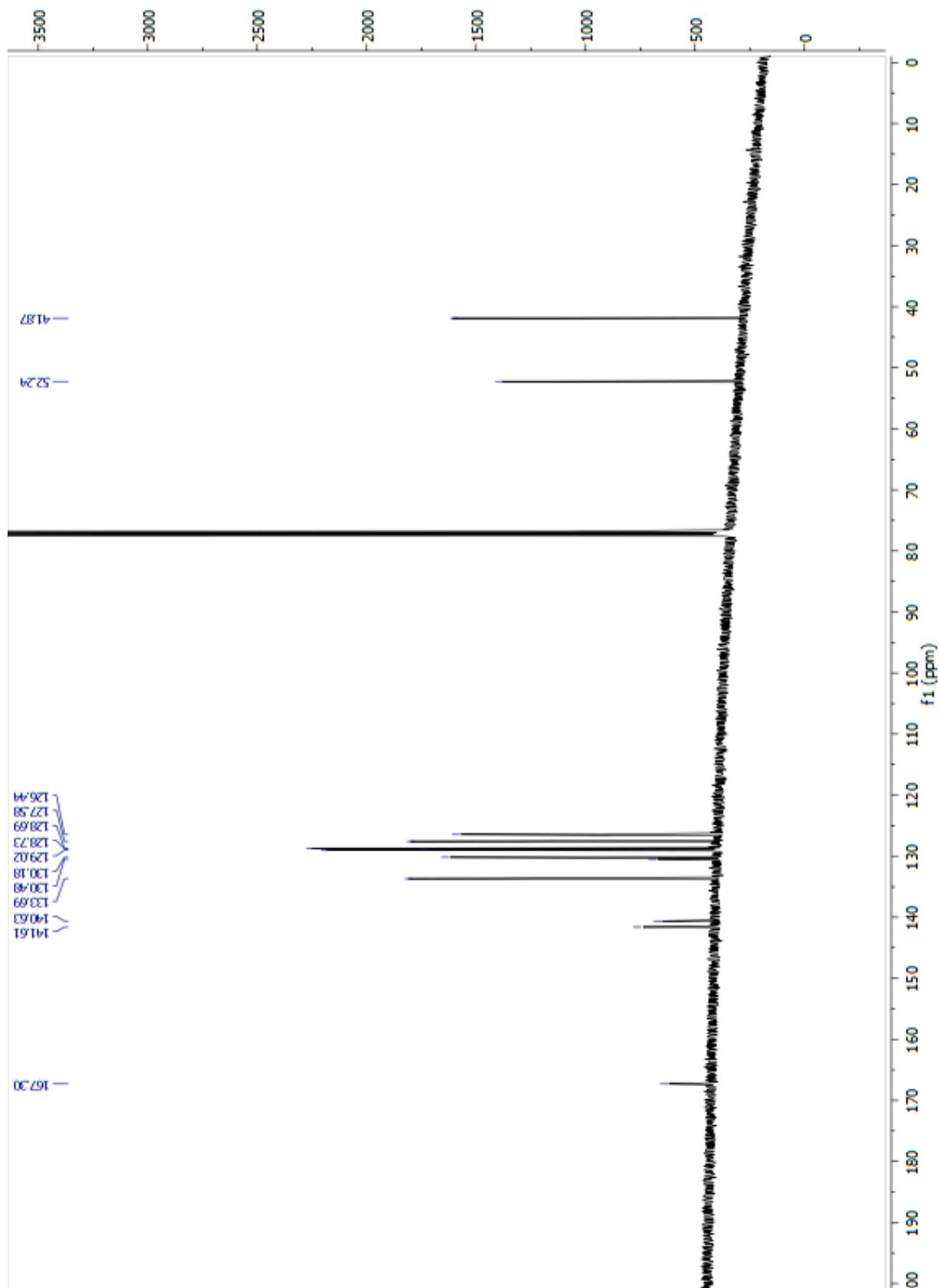
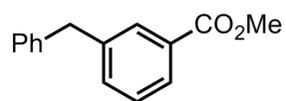
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5ad



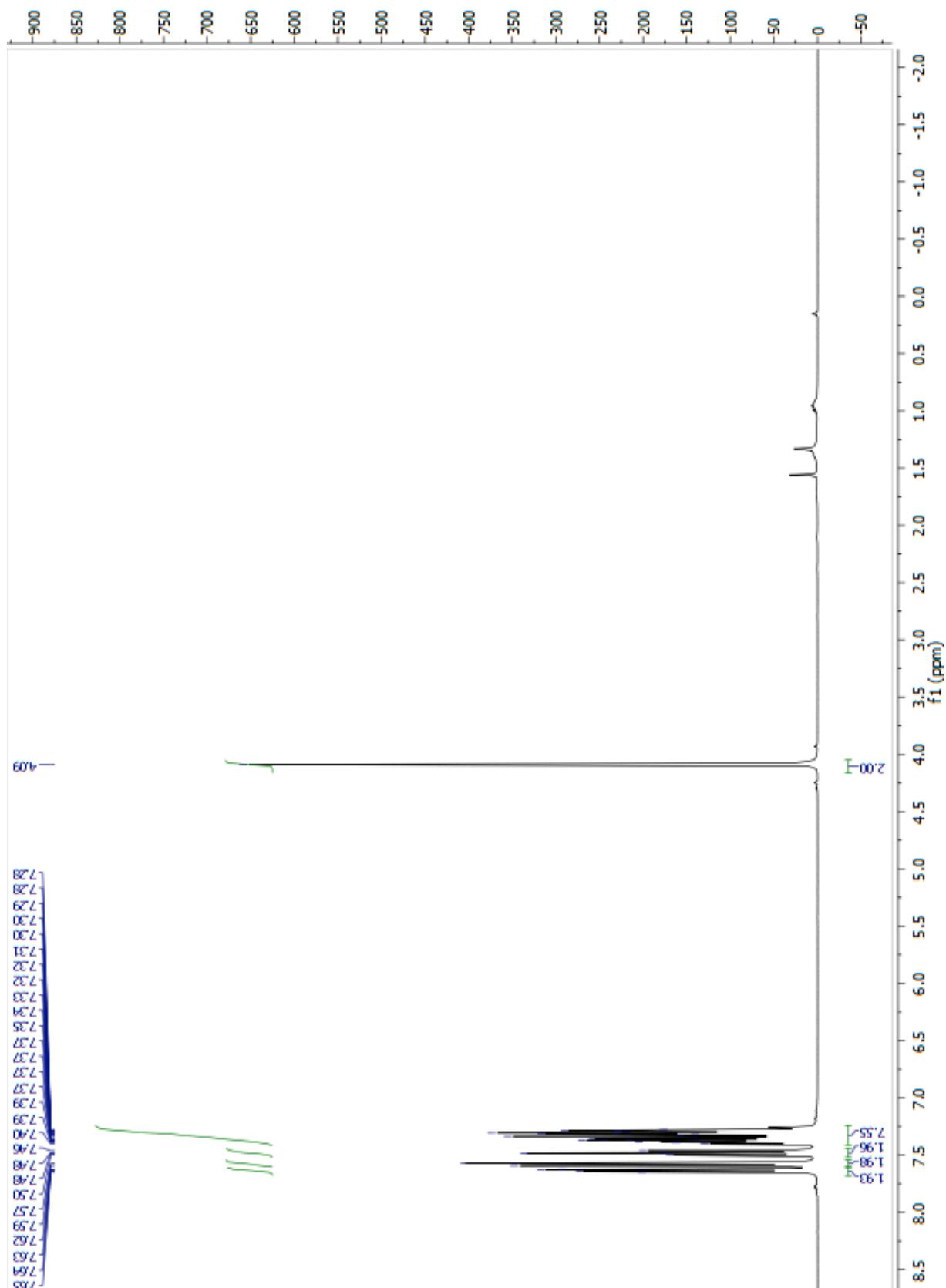
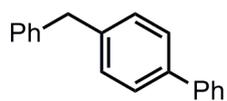
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ae



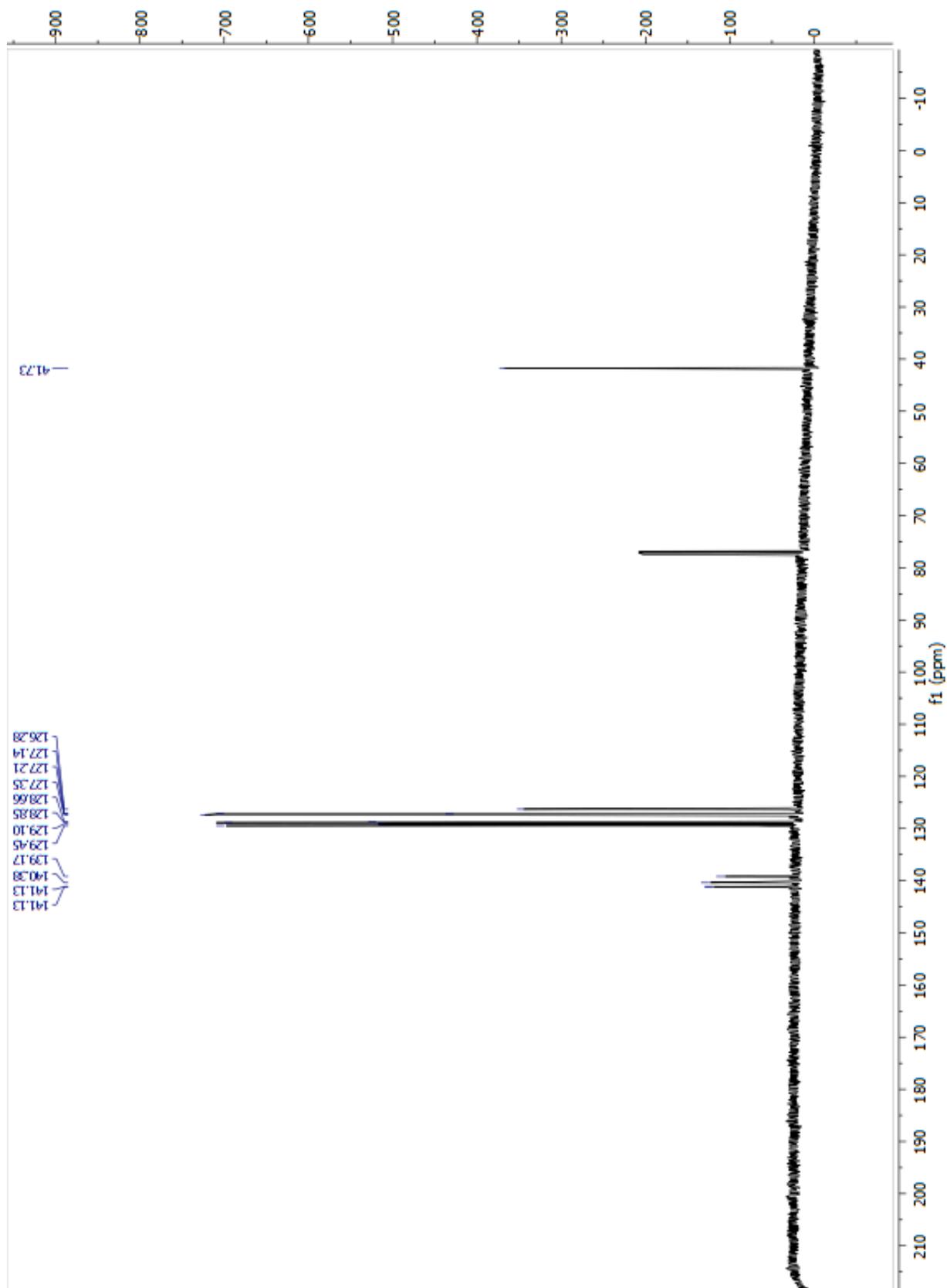
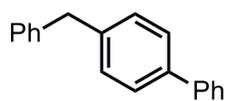
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 5ae



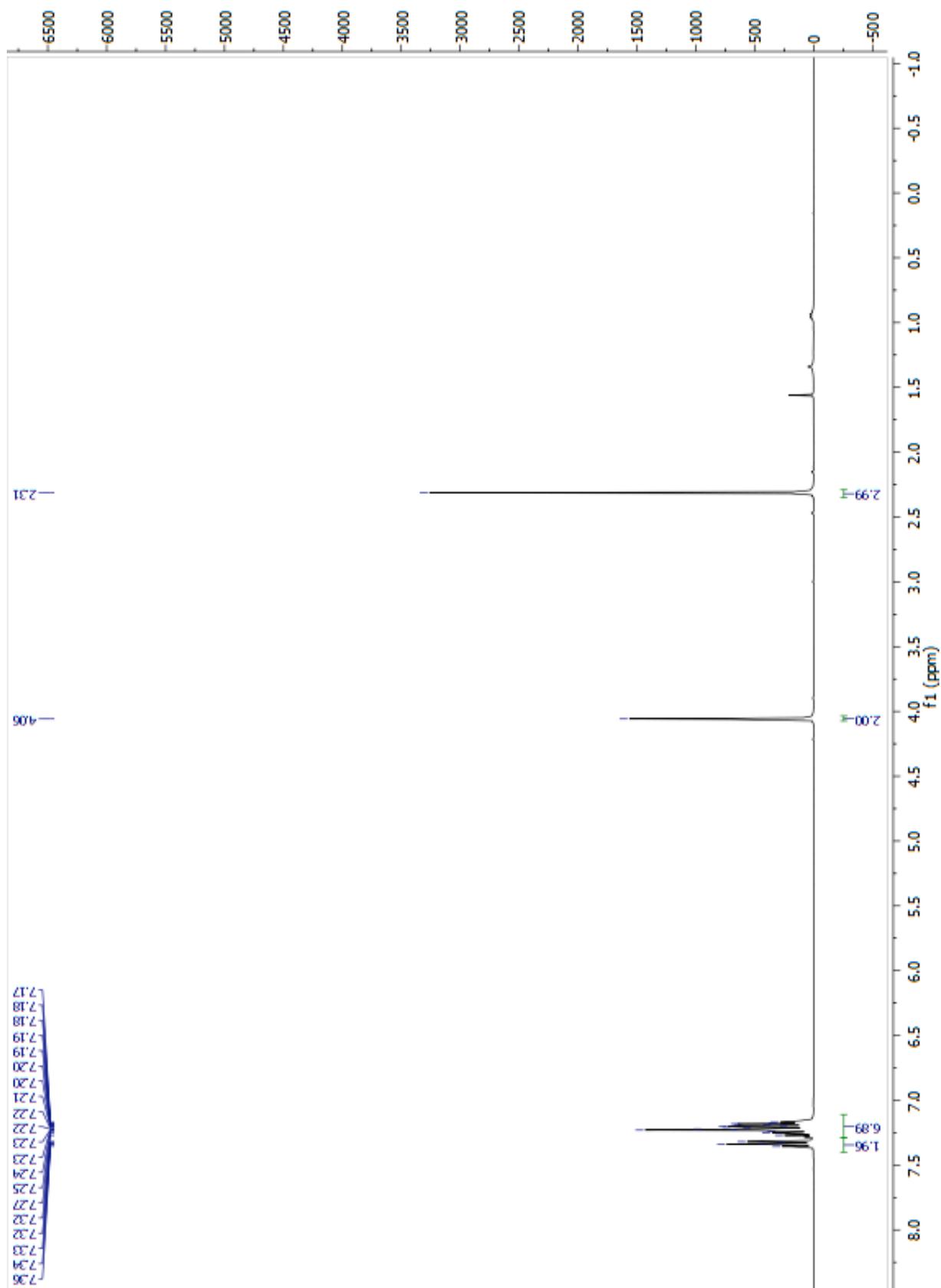
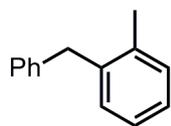
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5af



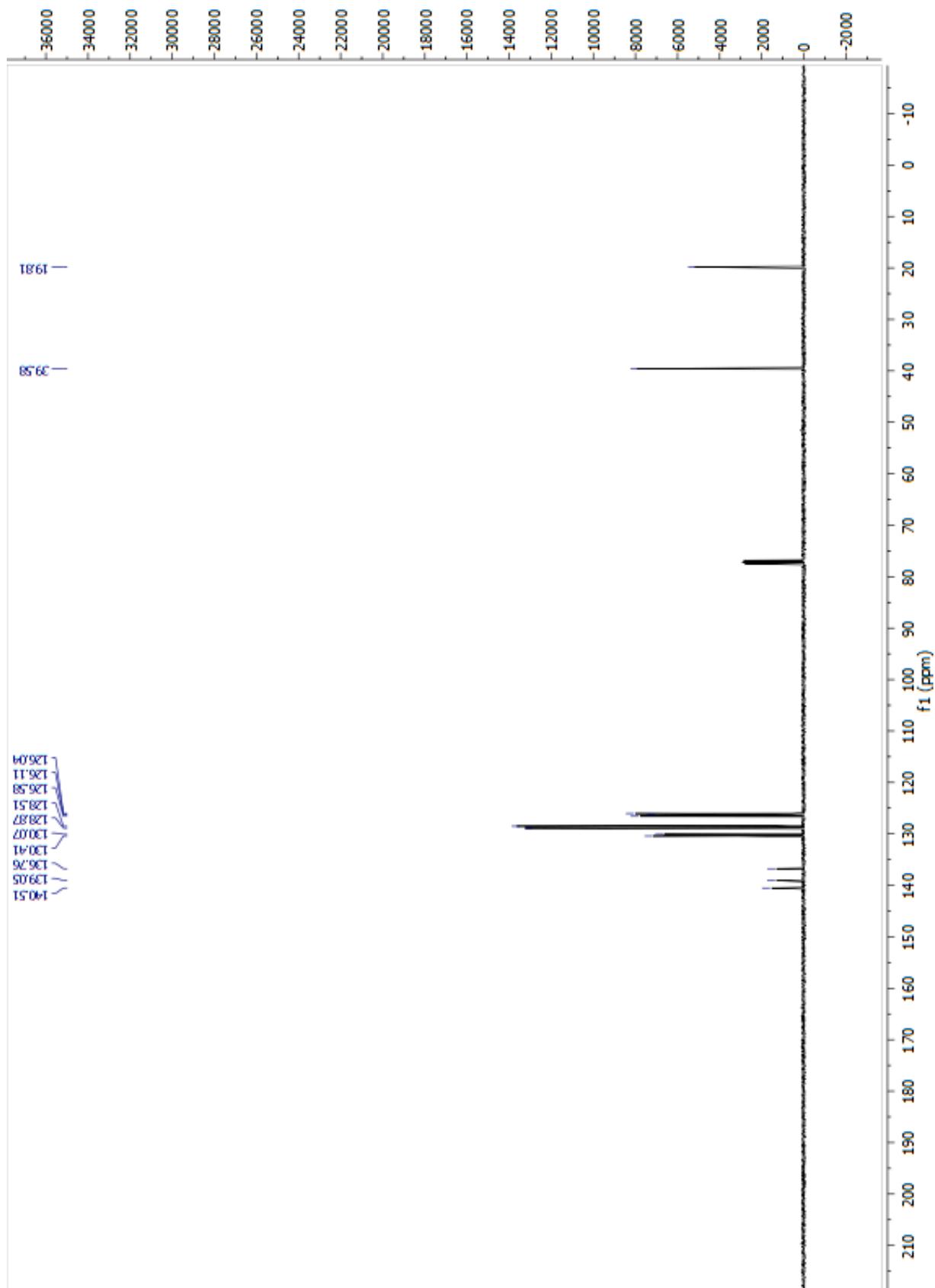
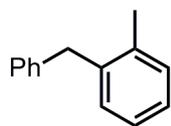
$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) of 5af



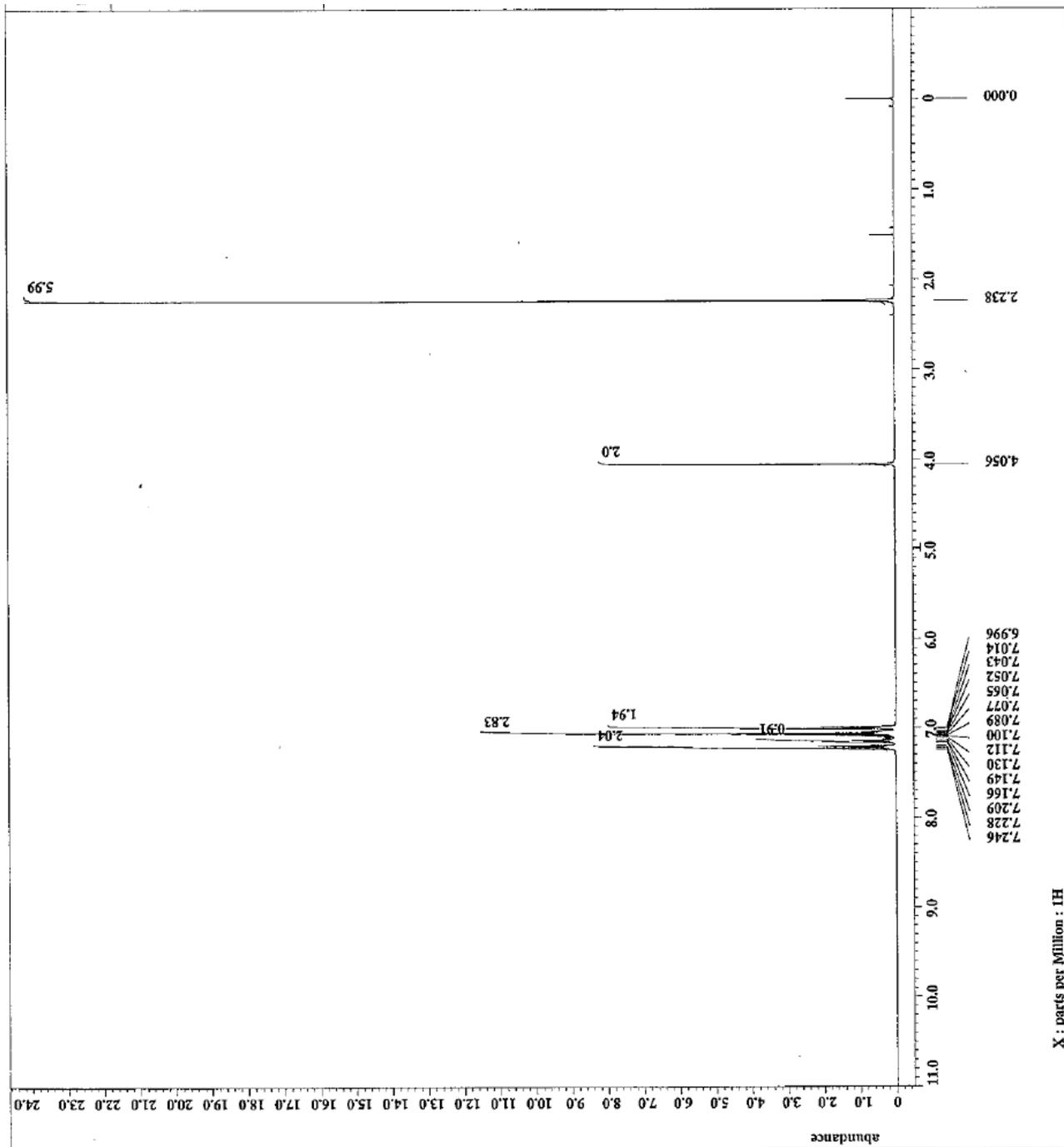
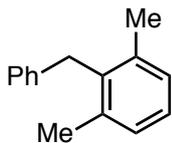
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ag



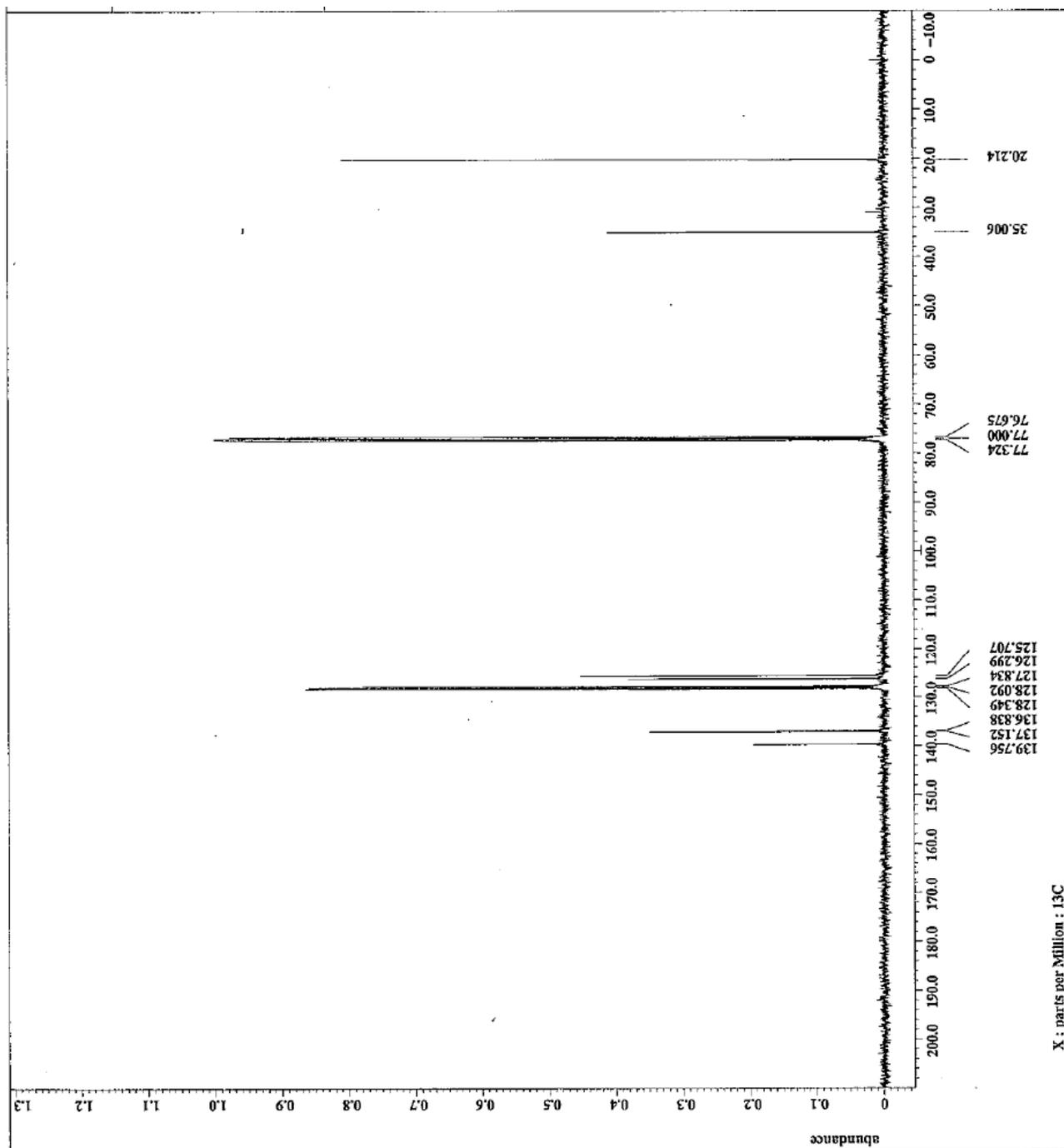
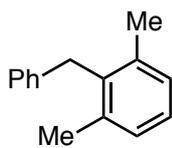
$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) of 5ag



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ah

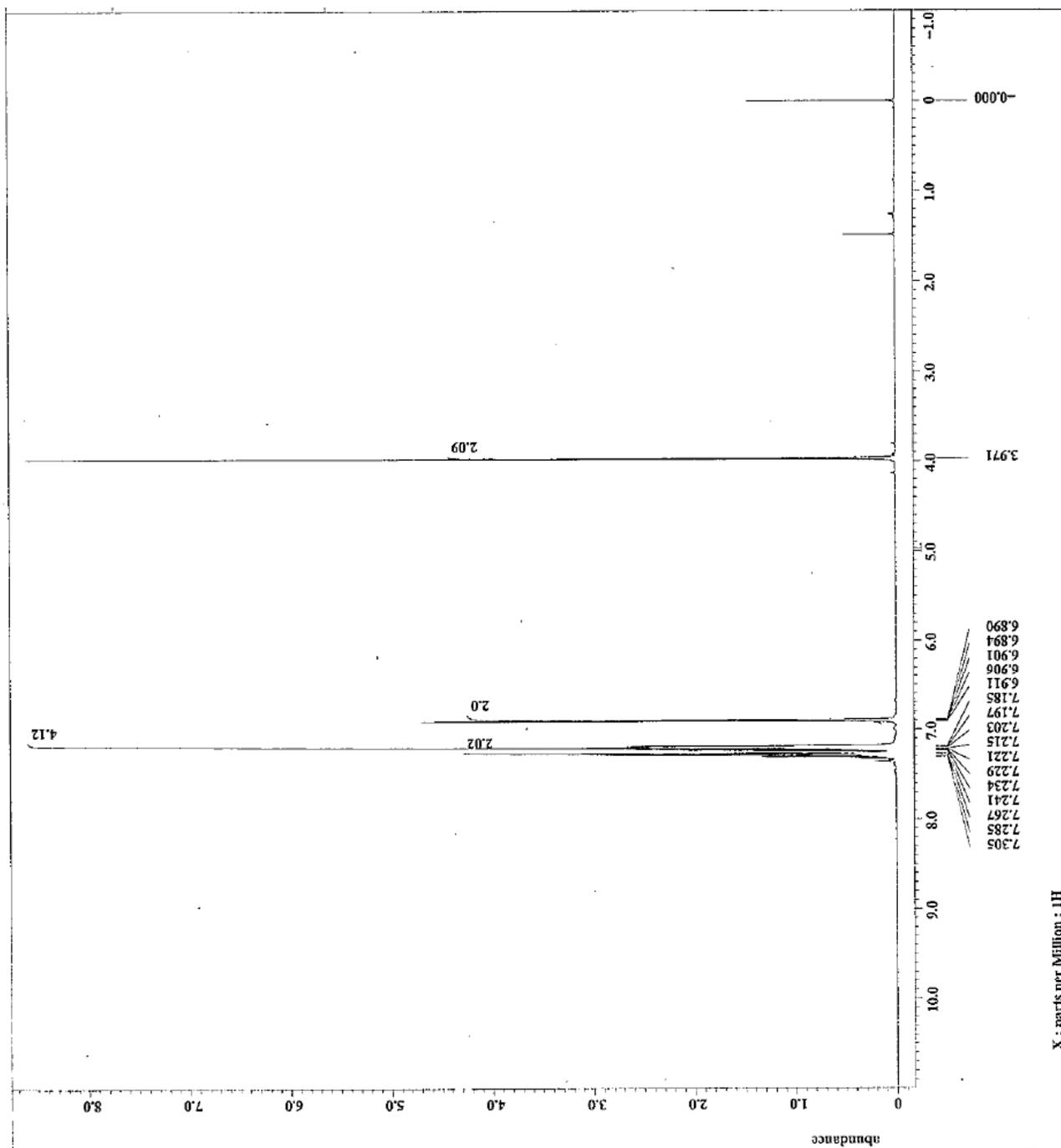
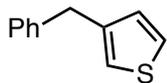


$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 5ah

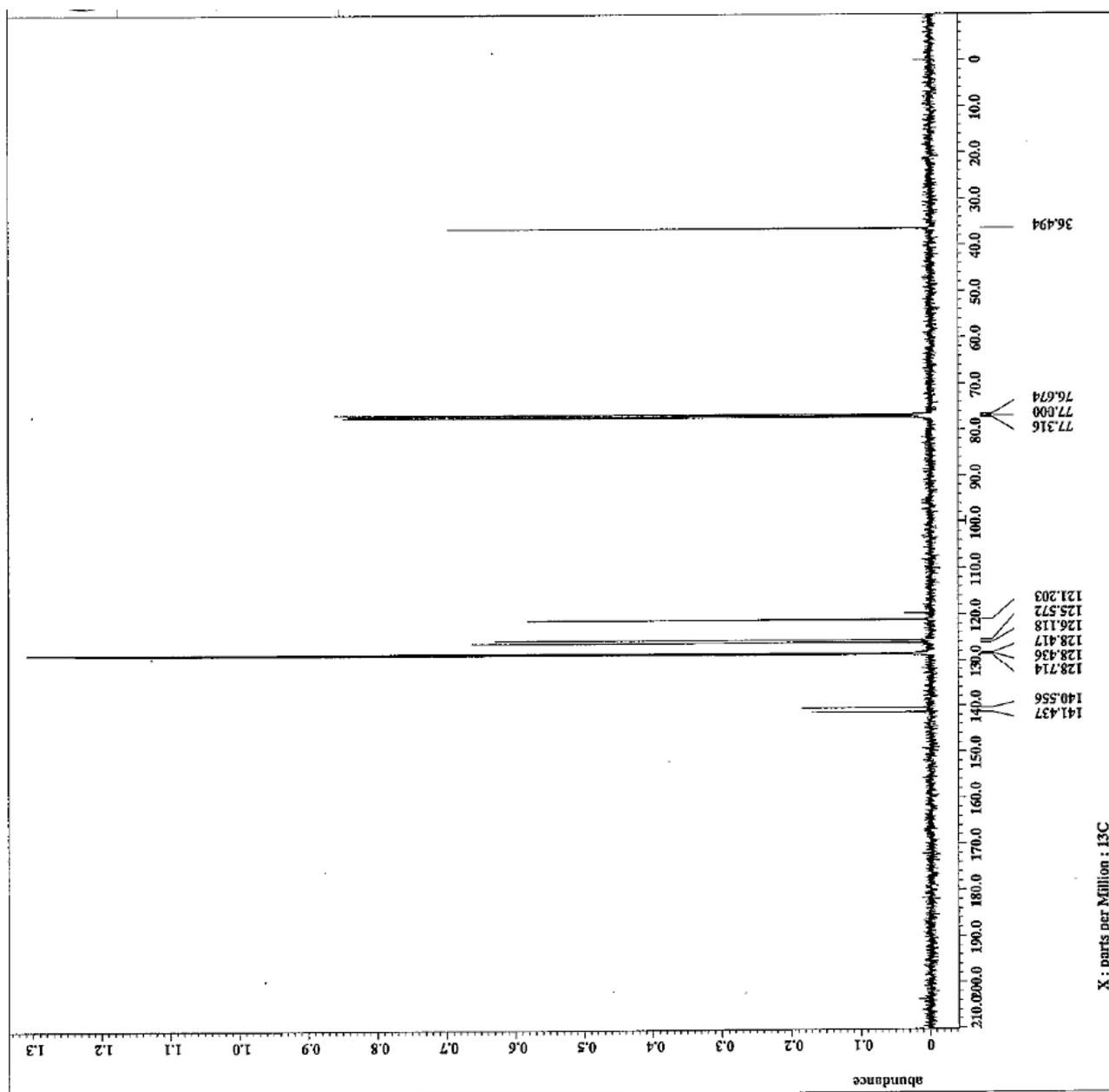
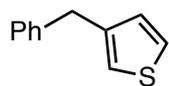


X : parts per Million : 13C

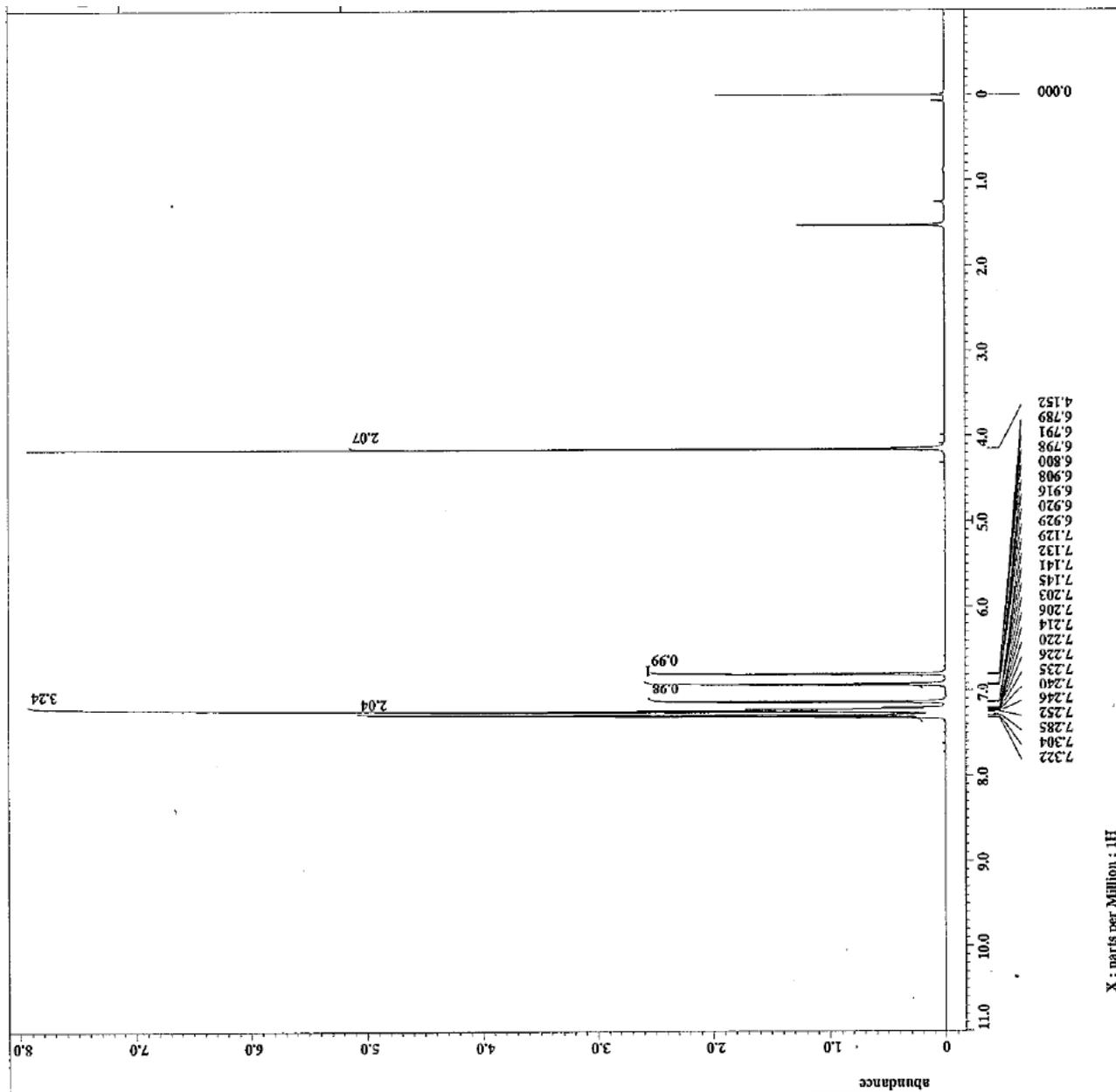
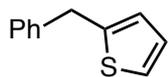
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ai



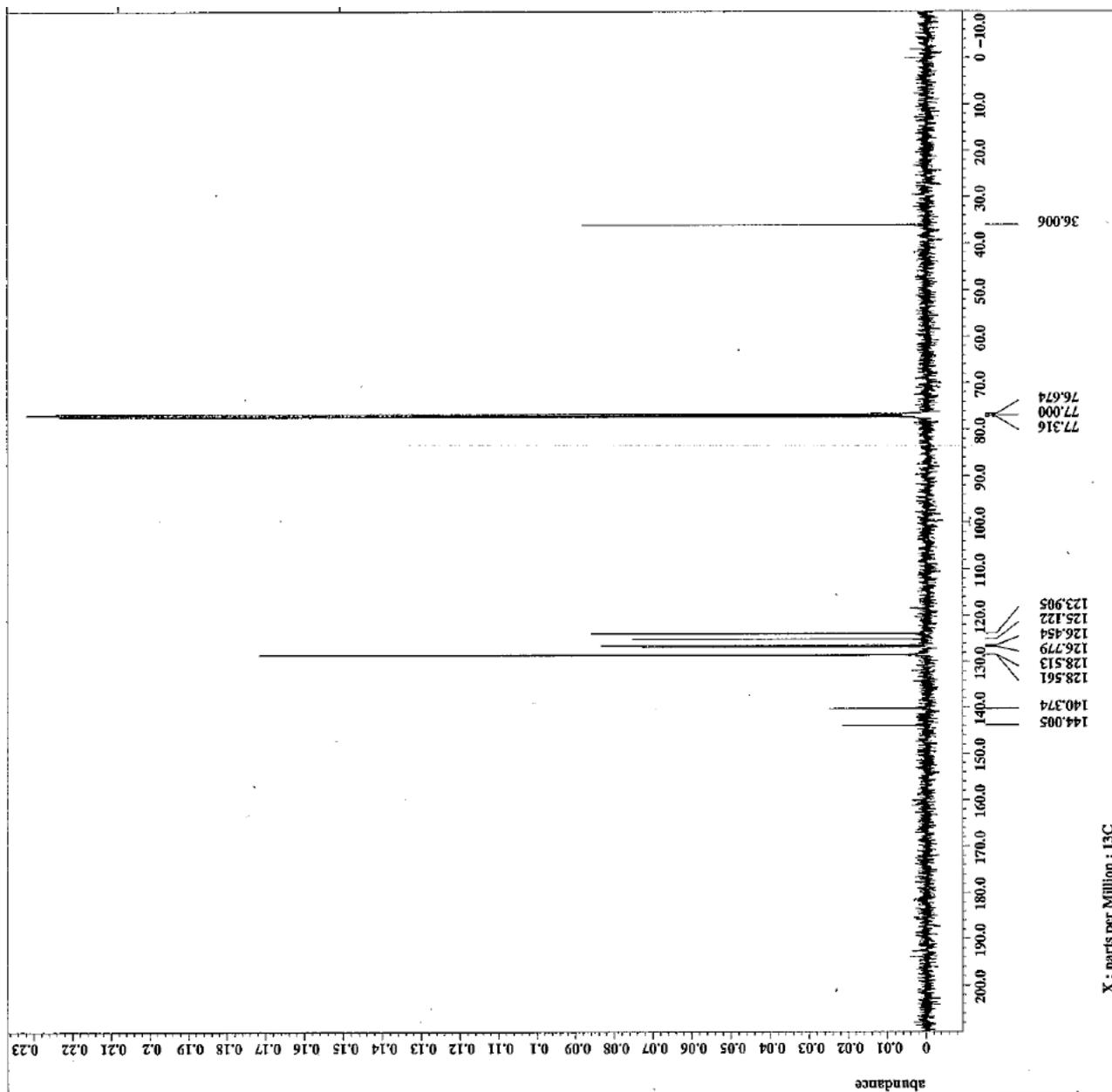
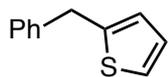
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 5ai



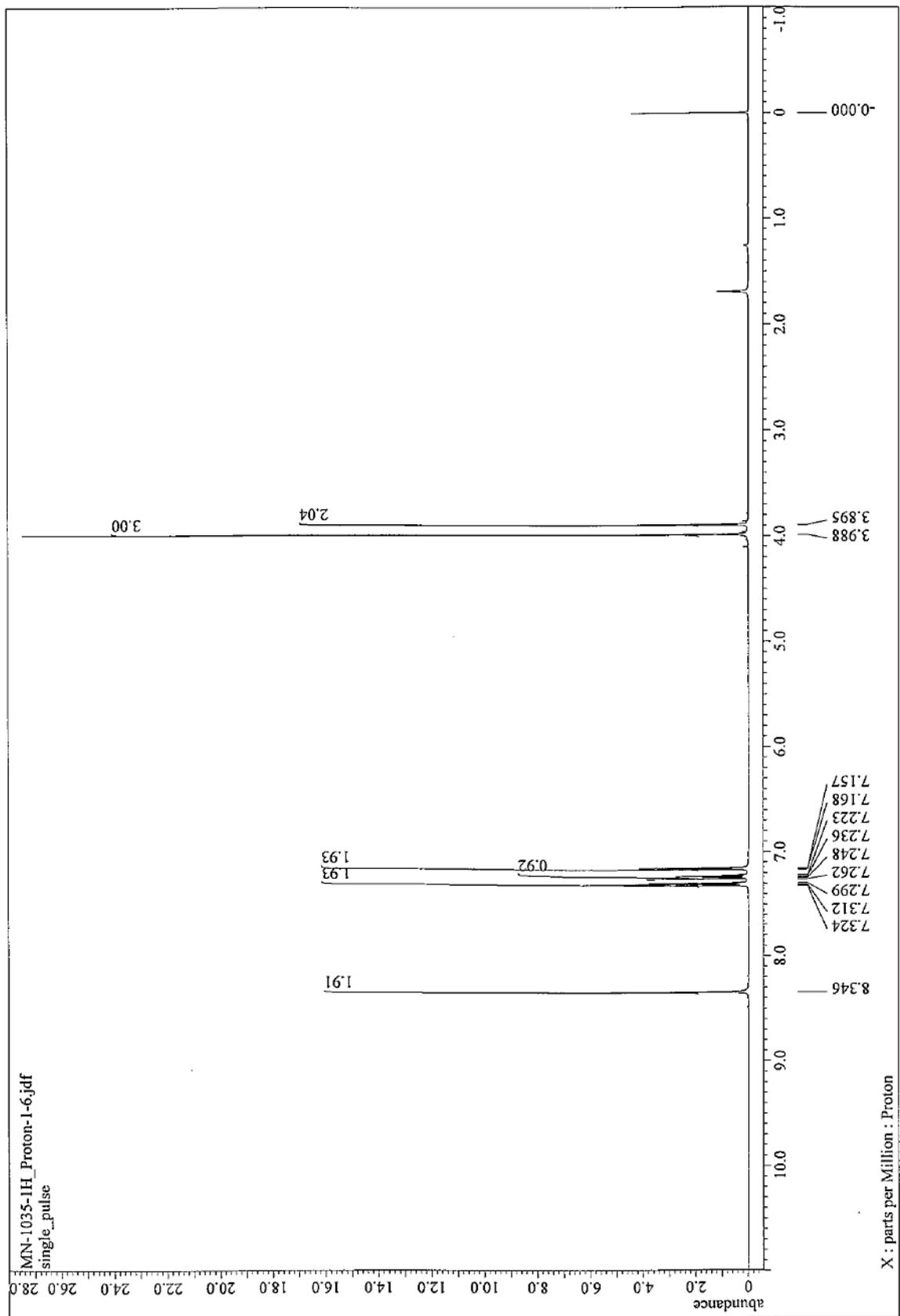
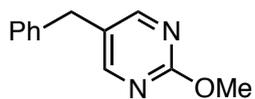
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5aj



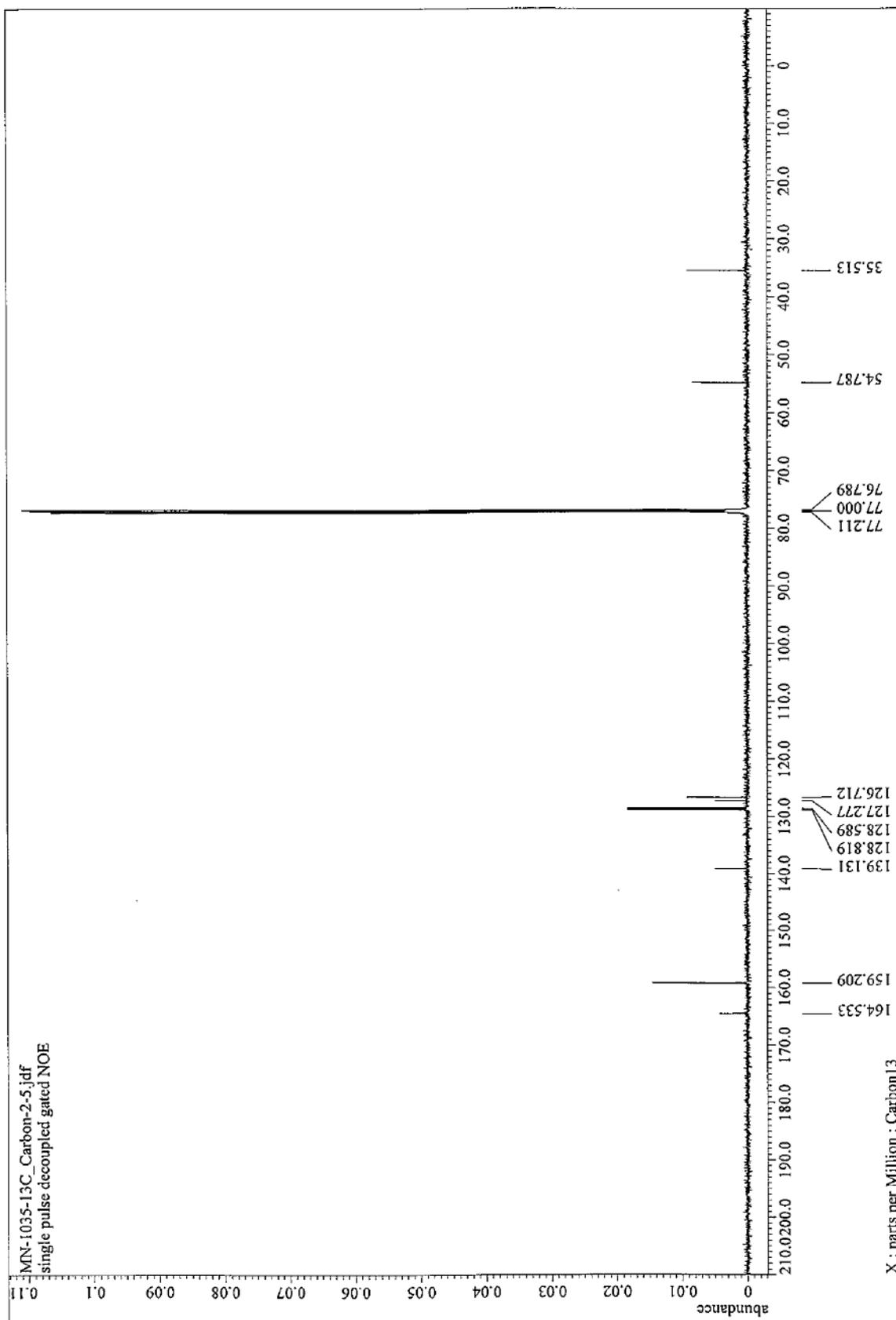
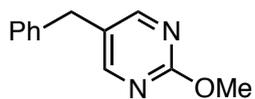
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 5aj



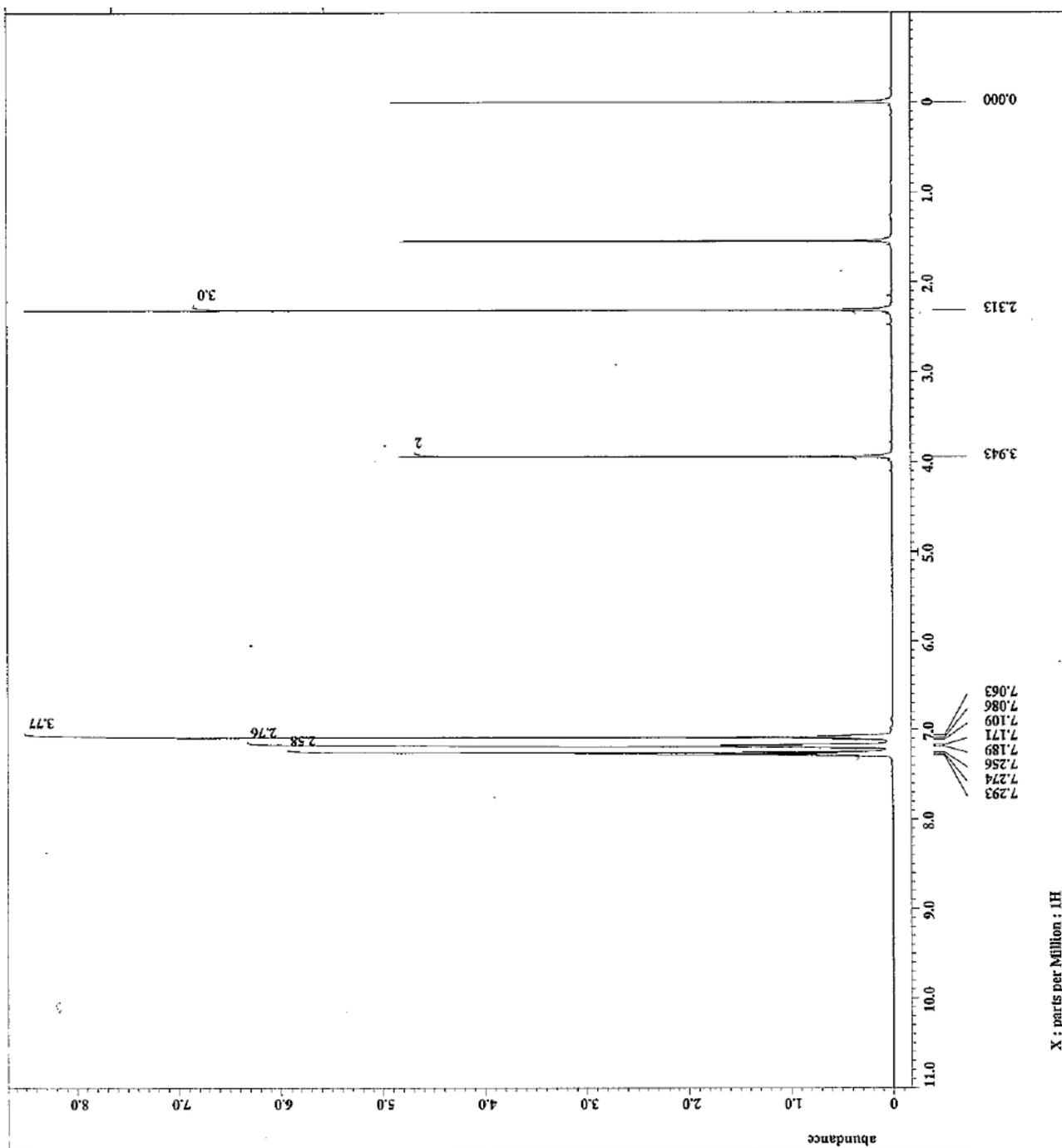
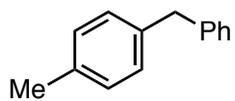
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5ak



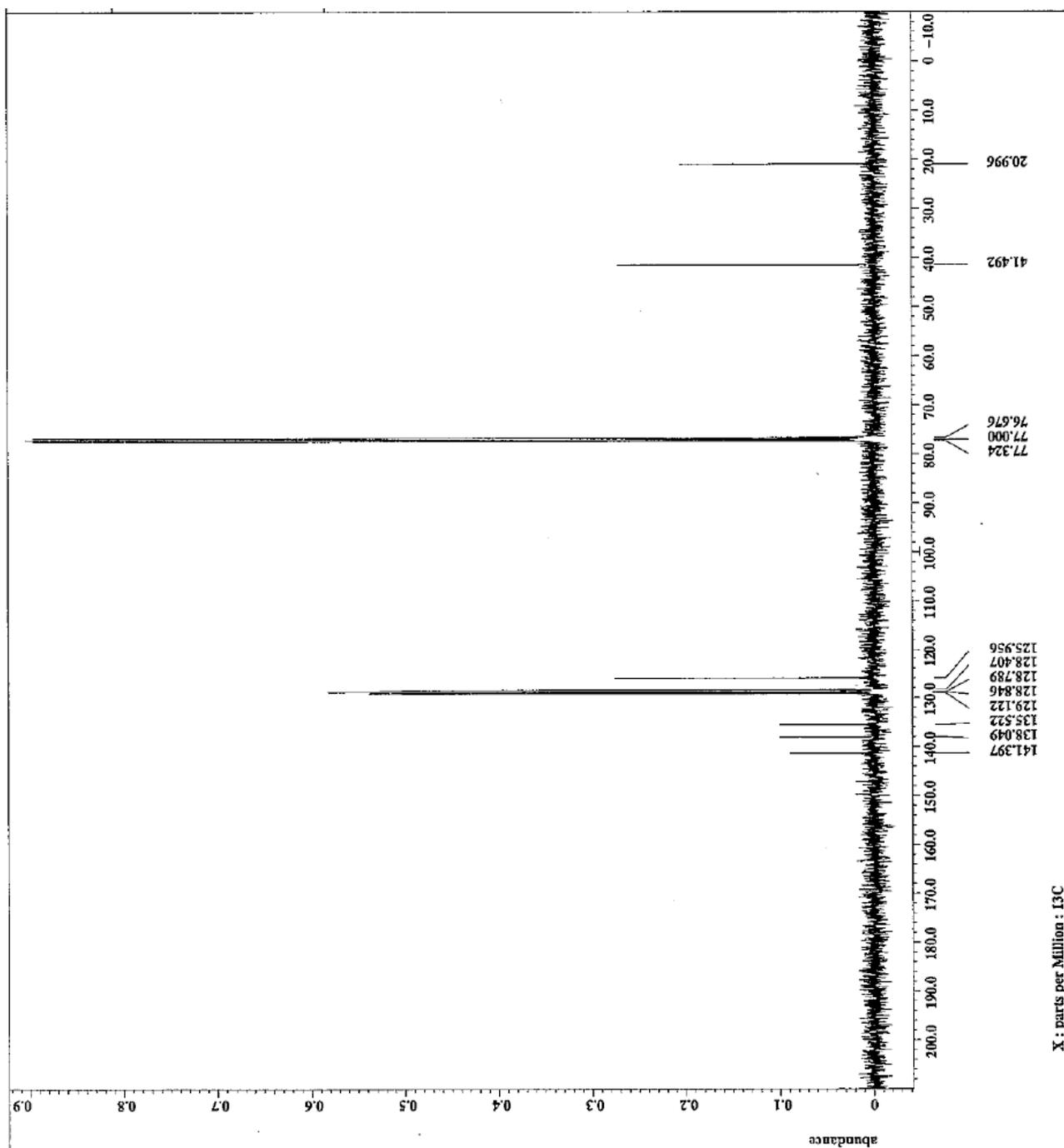
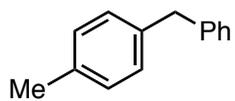
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5ak



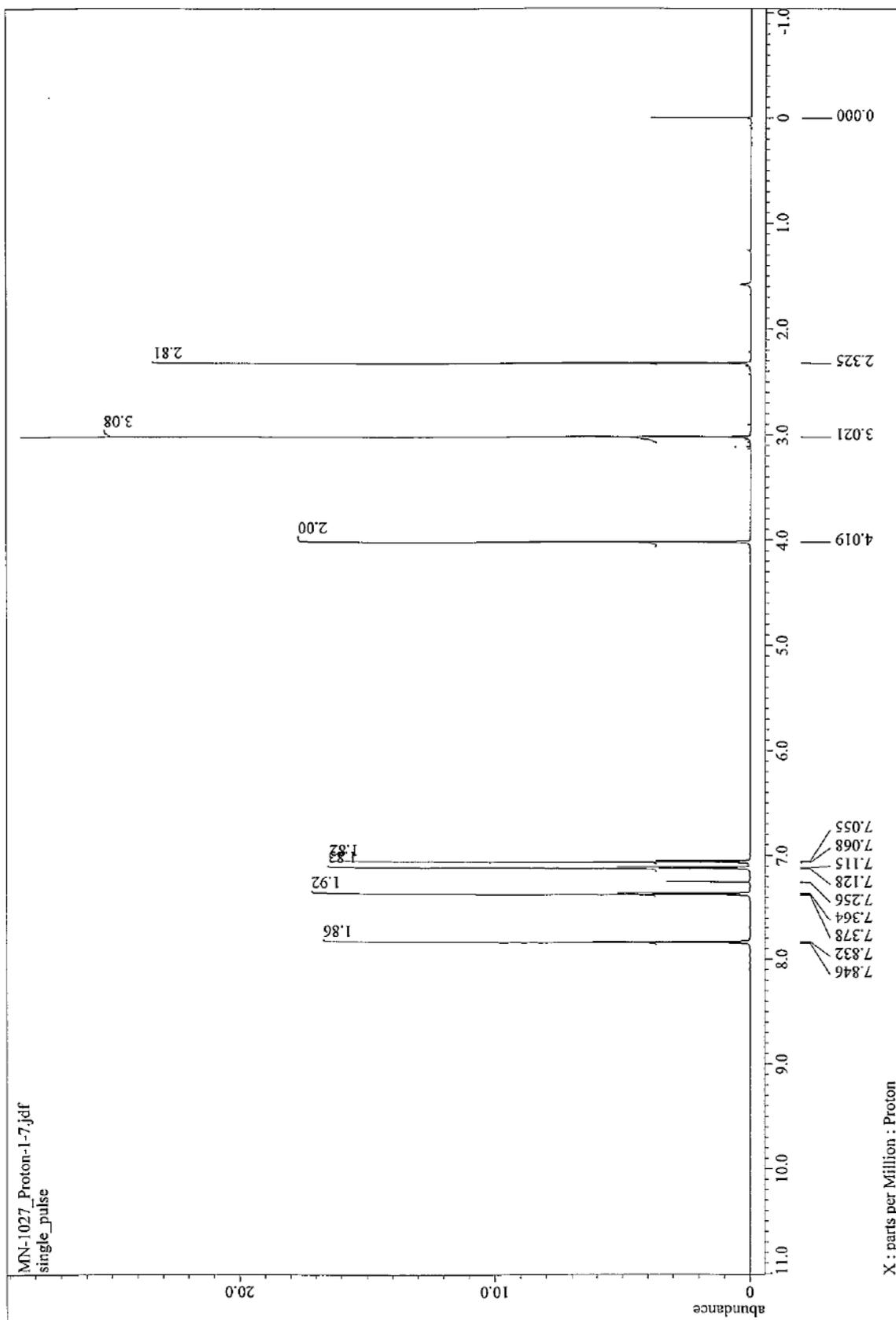
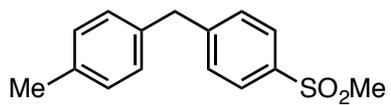
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ba



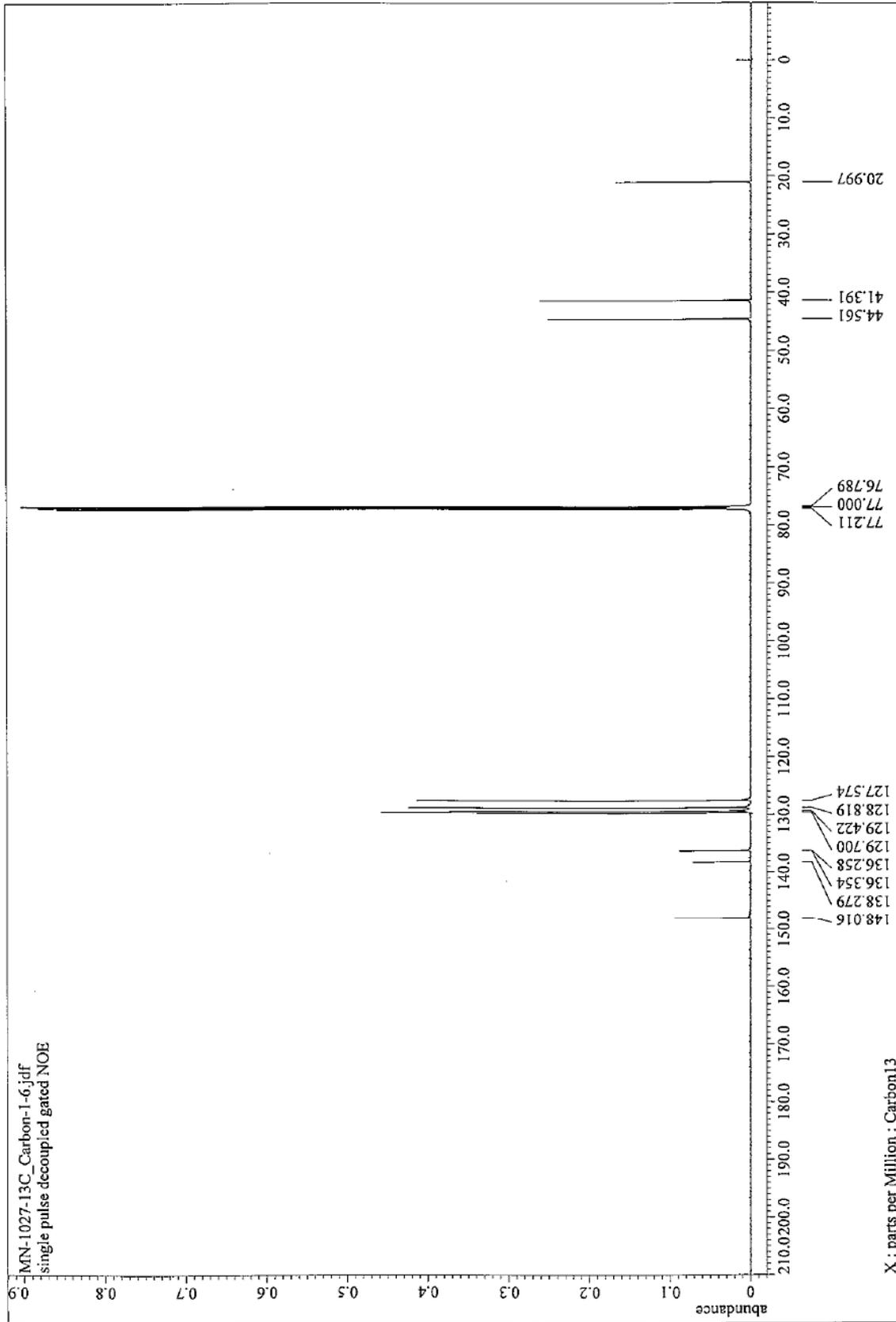
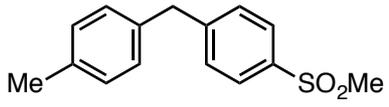
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 5ba



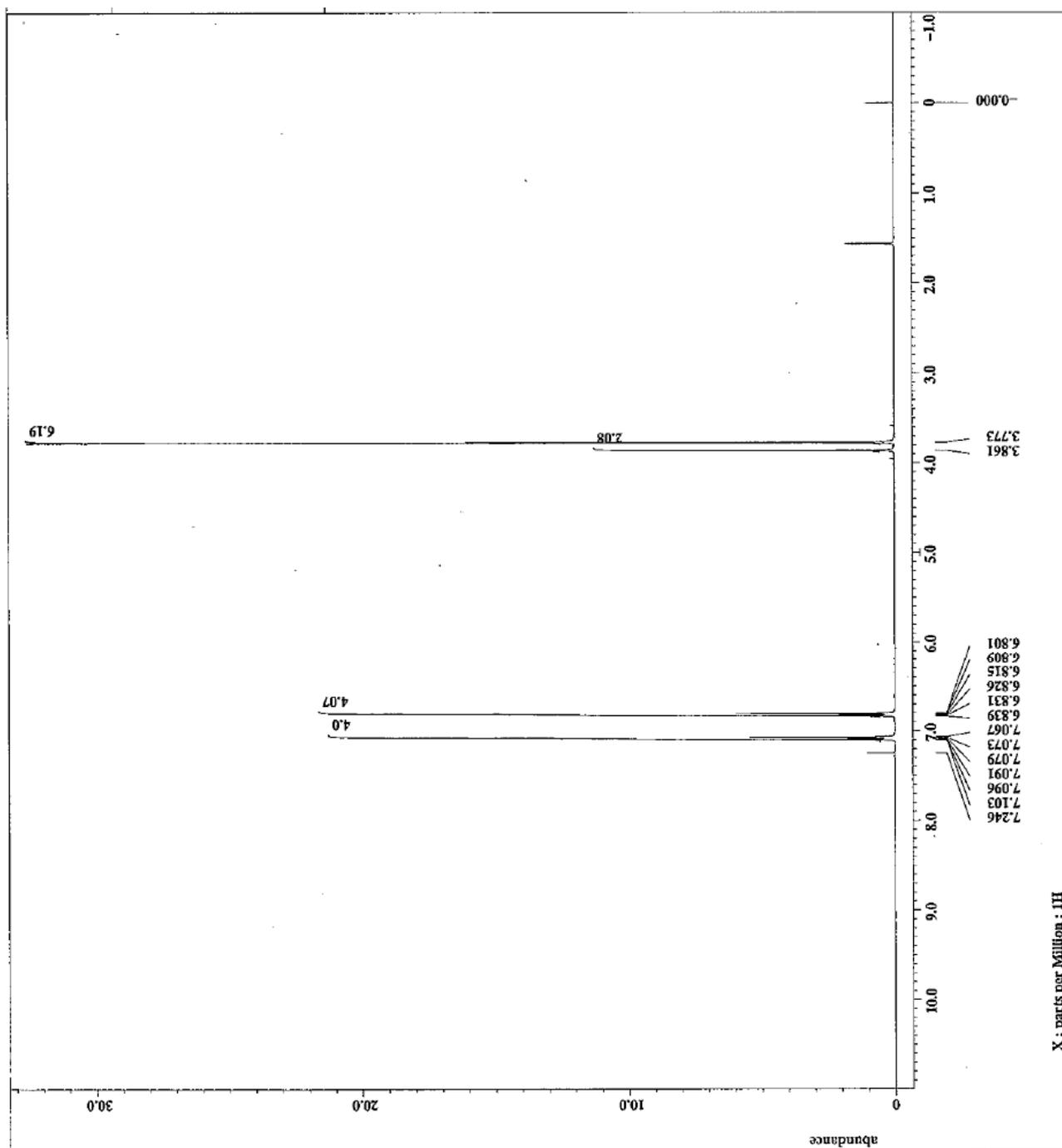
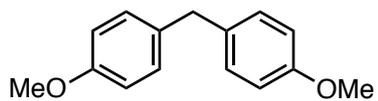
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5b1



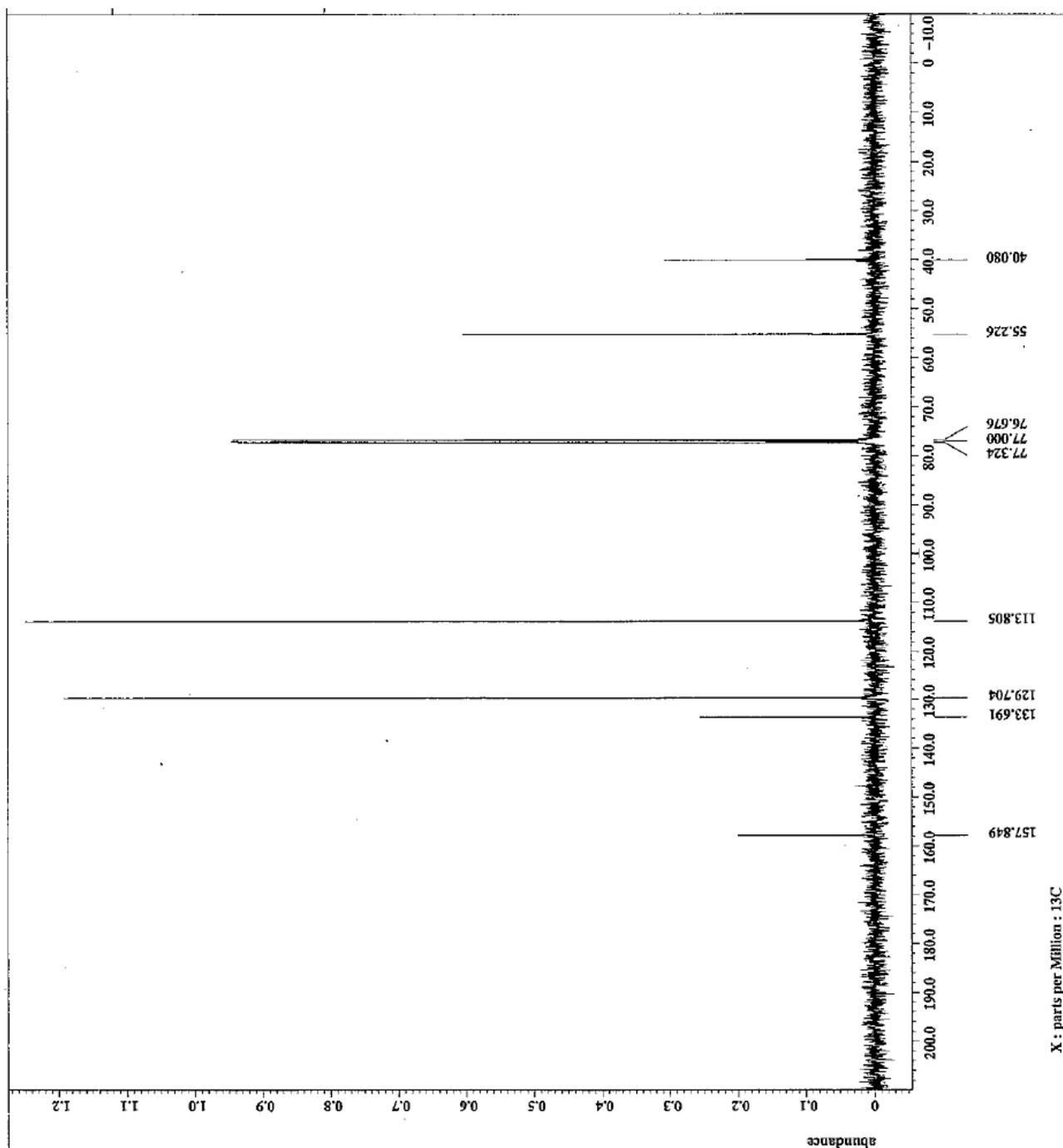
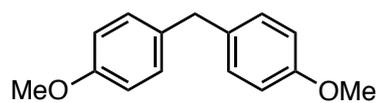
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5bl



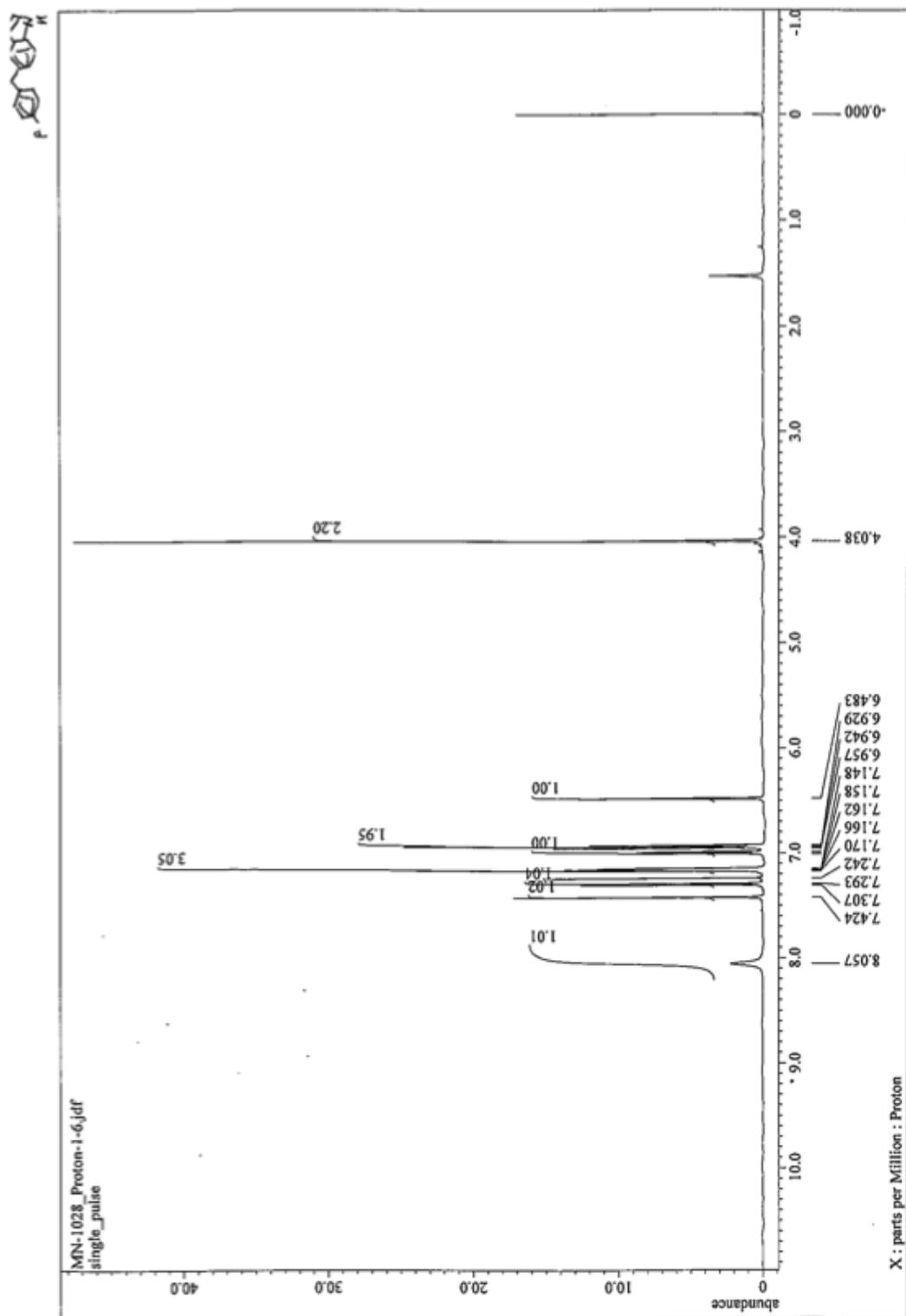
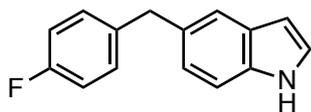
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5cb



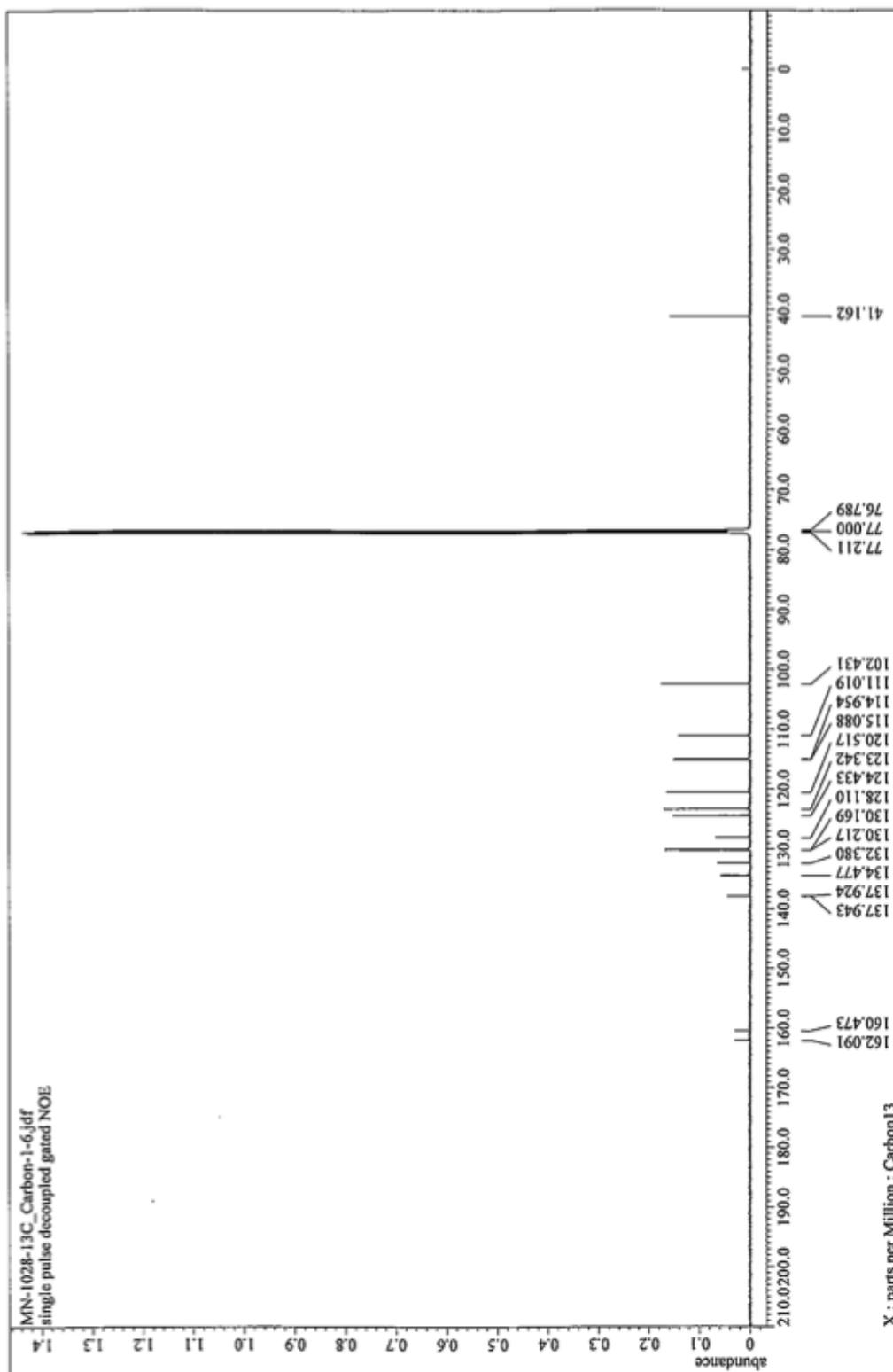
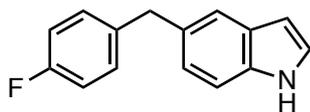
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 5cb



<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5em

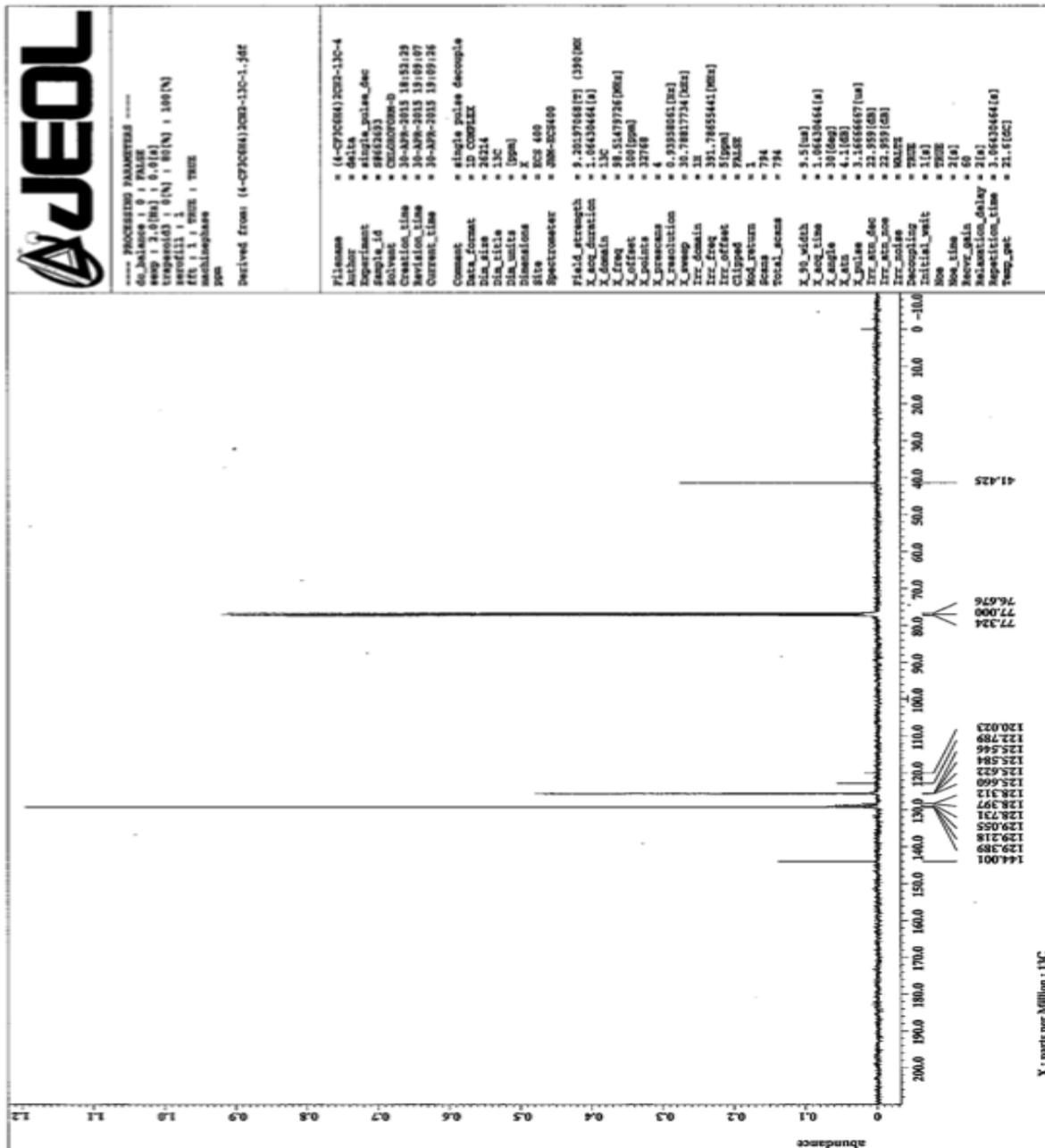
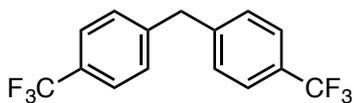


<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5em

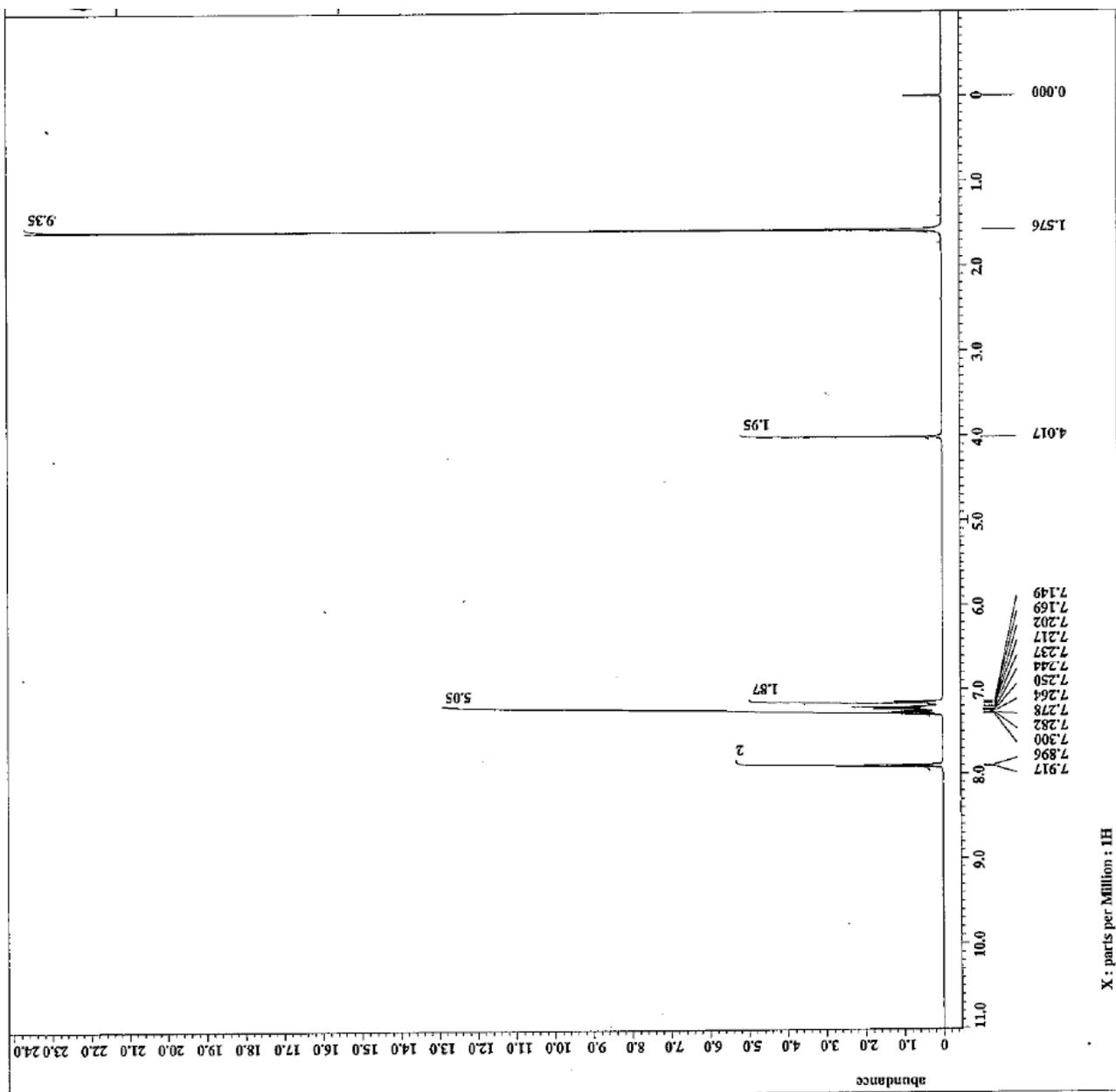
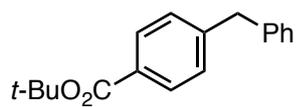




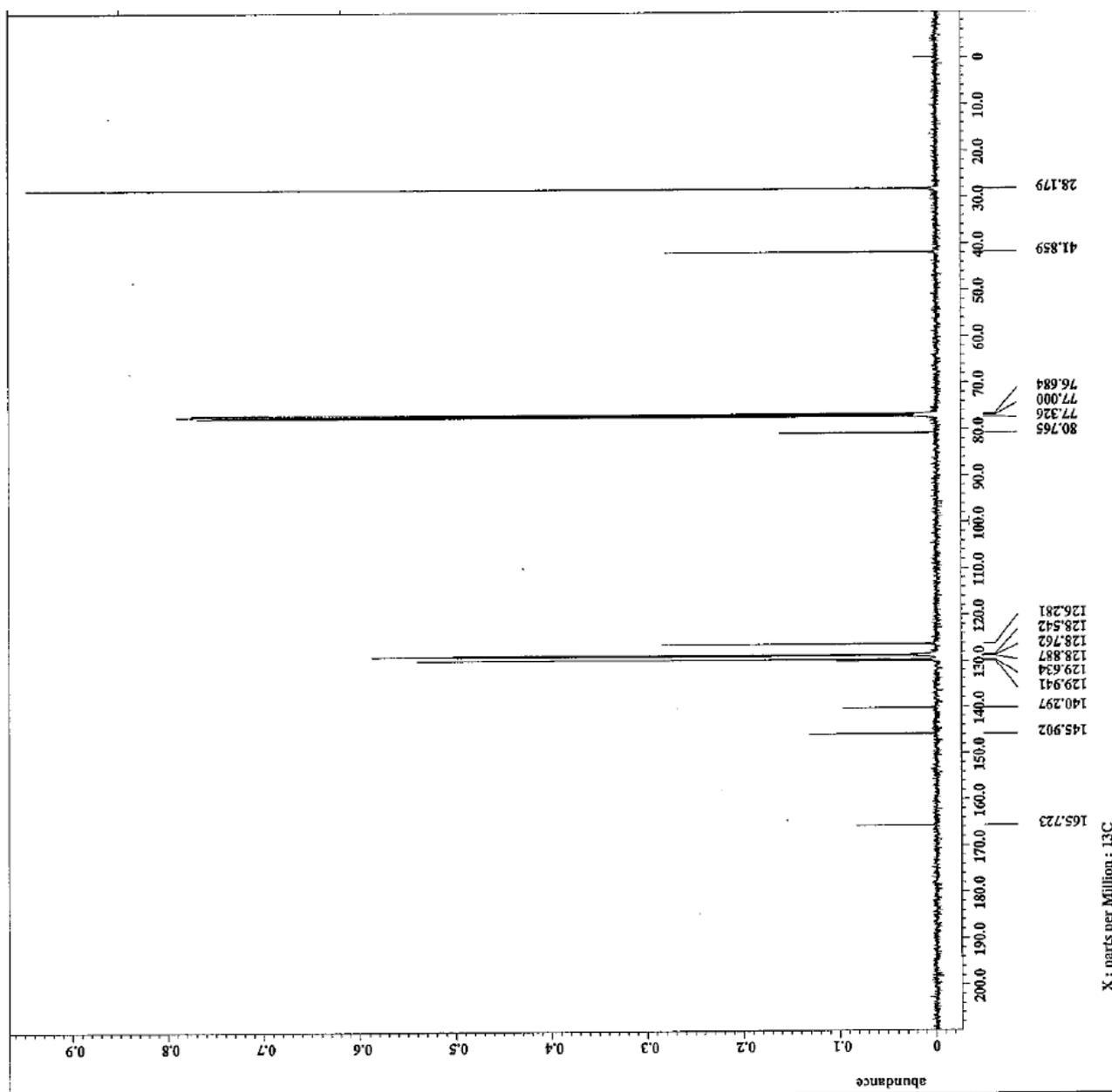
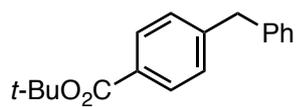
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 5gc



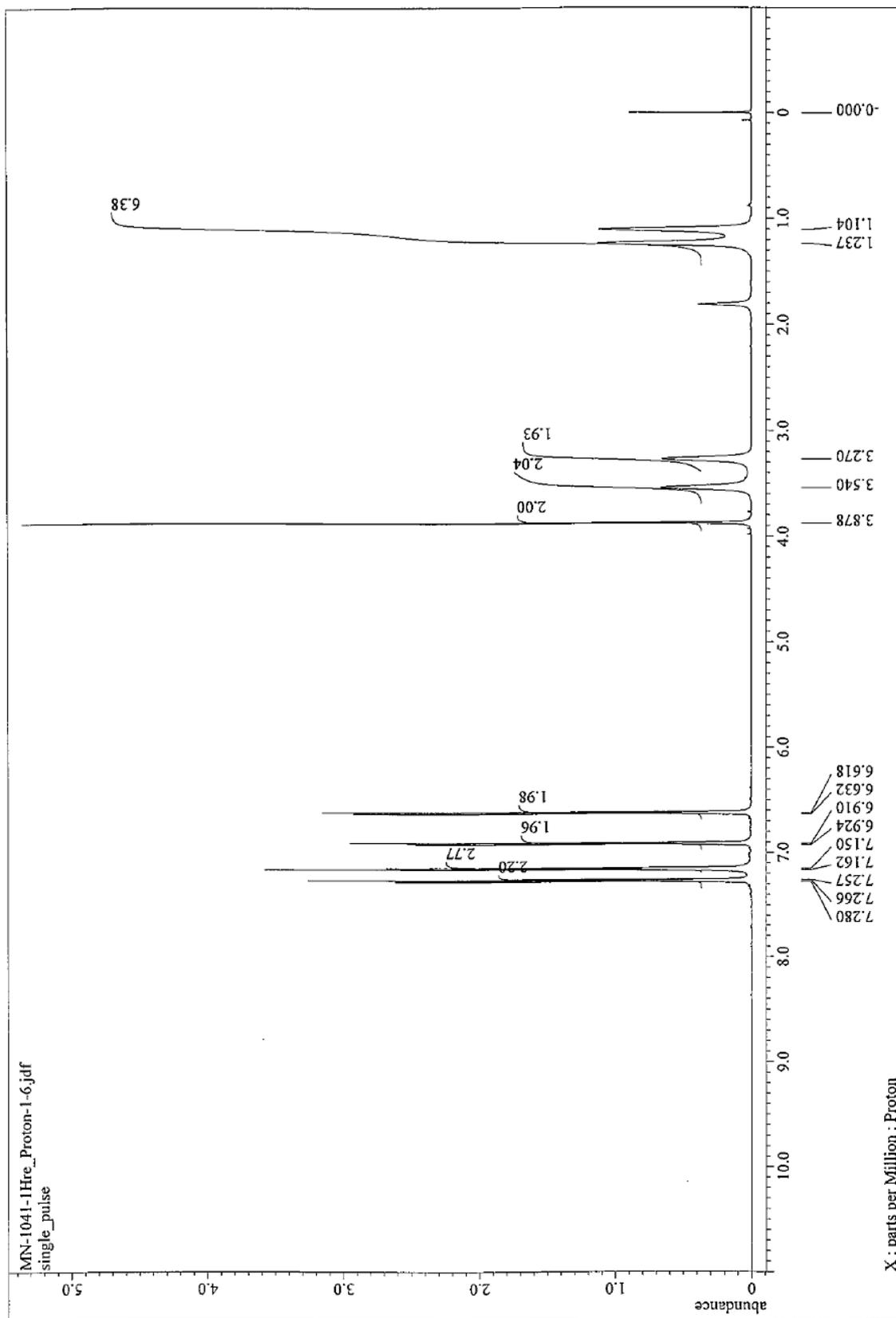
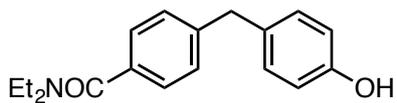
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5ia



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 5ia



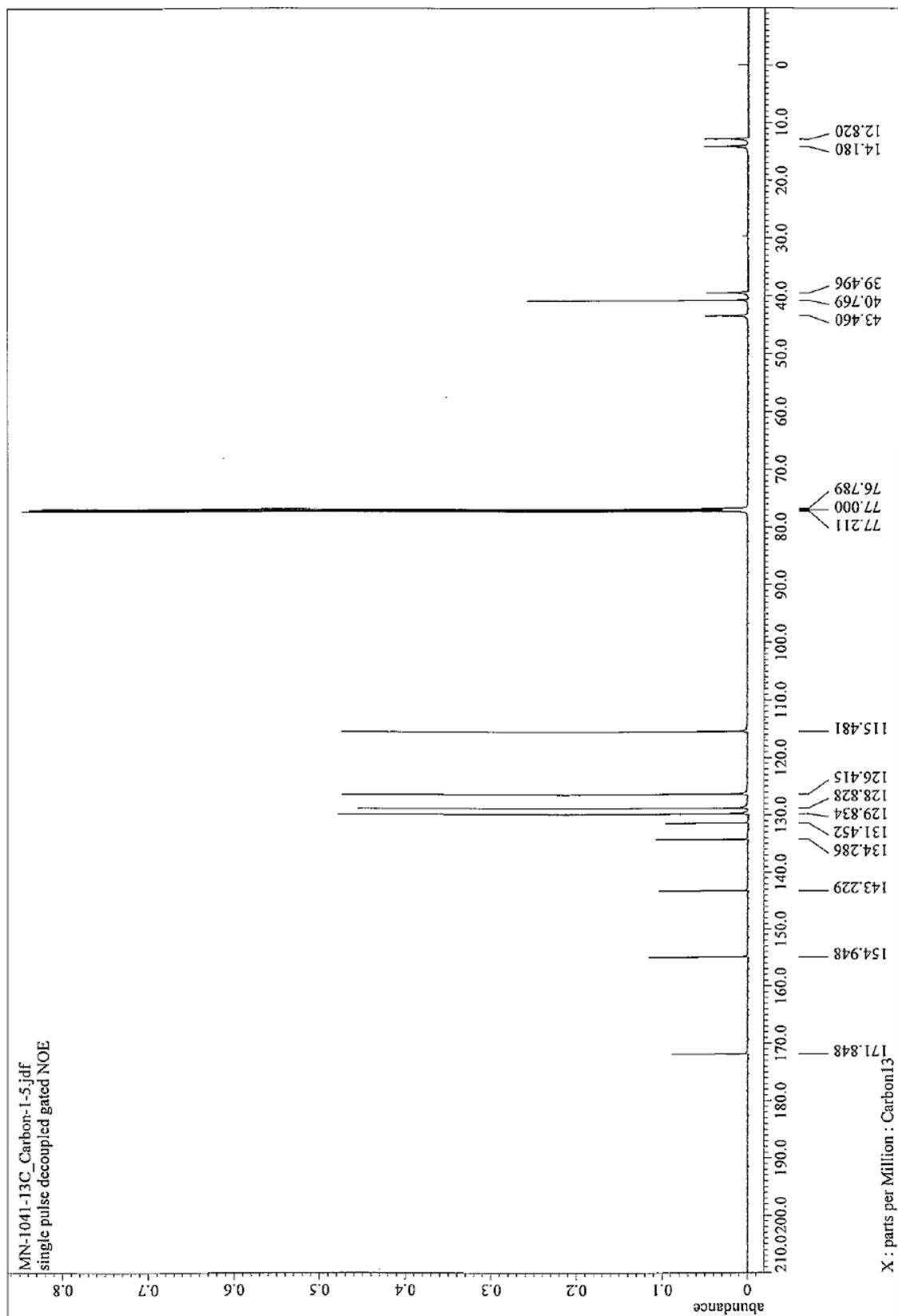
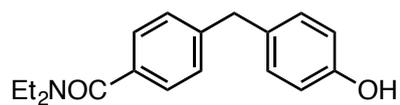
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5jn



MN-1041-1Hre\_Proton-1-6.jdf  
single\_pulse

X : parts per Million : Proton

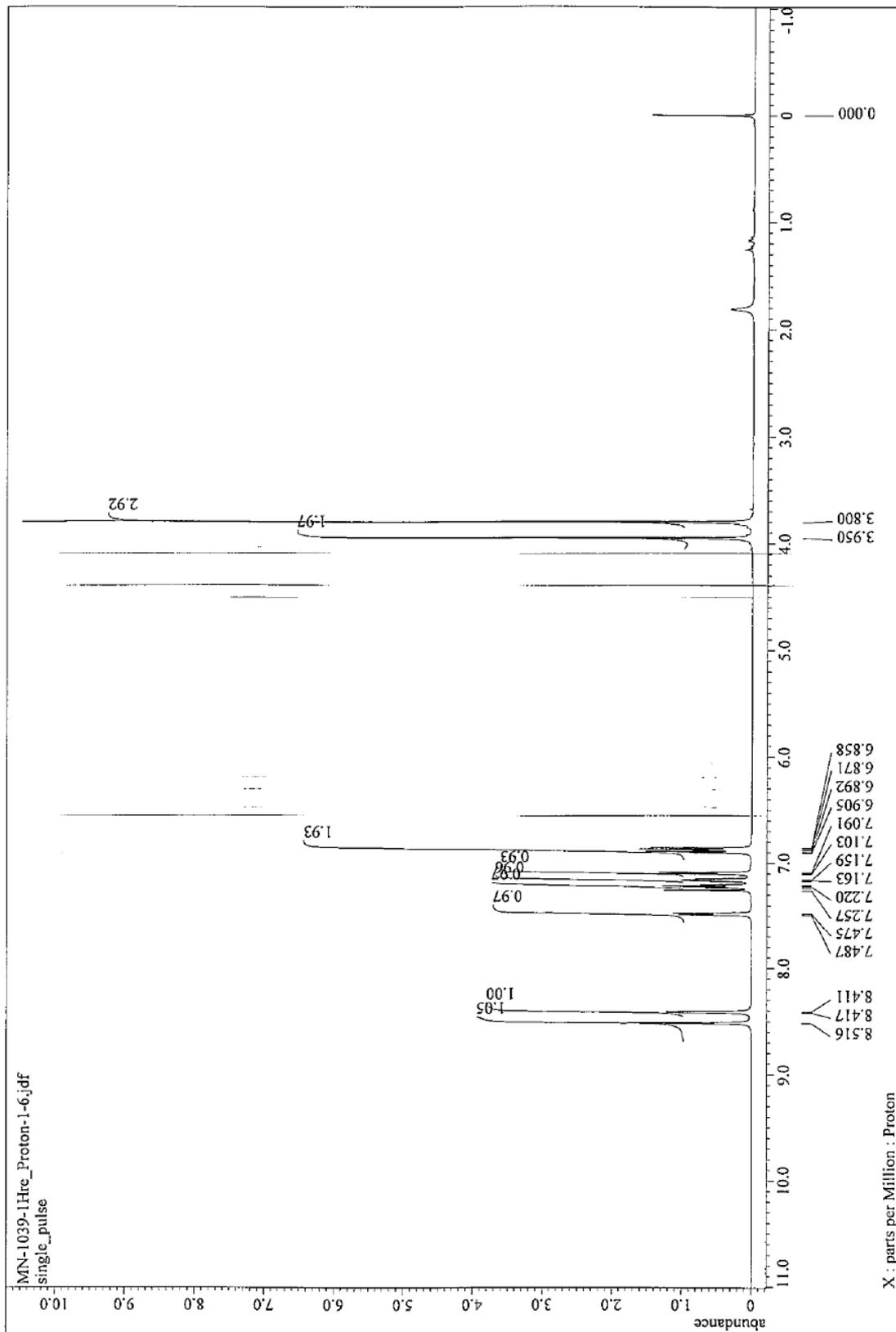
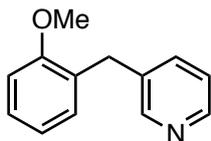
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5jn



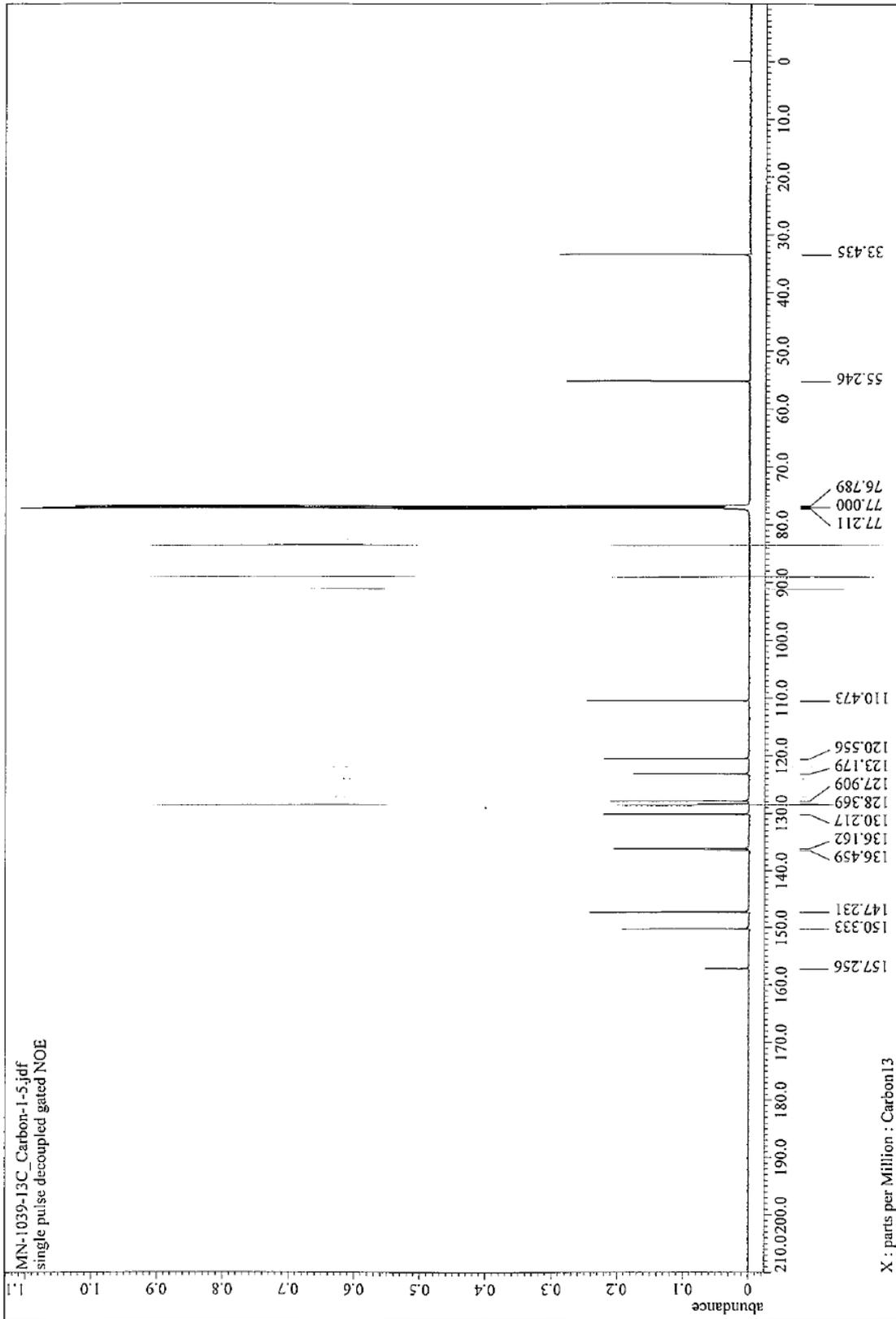
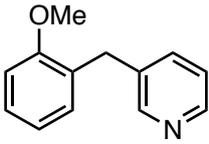
MN-1041-13C\_Carbon-1-5.jdf  
single pulse decoupled gated NOE

X : parts per Million : Carbon13

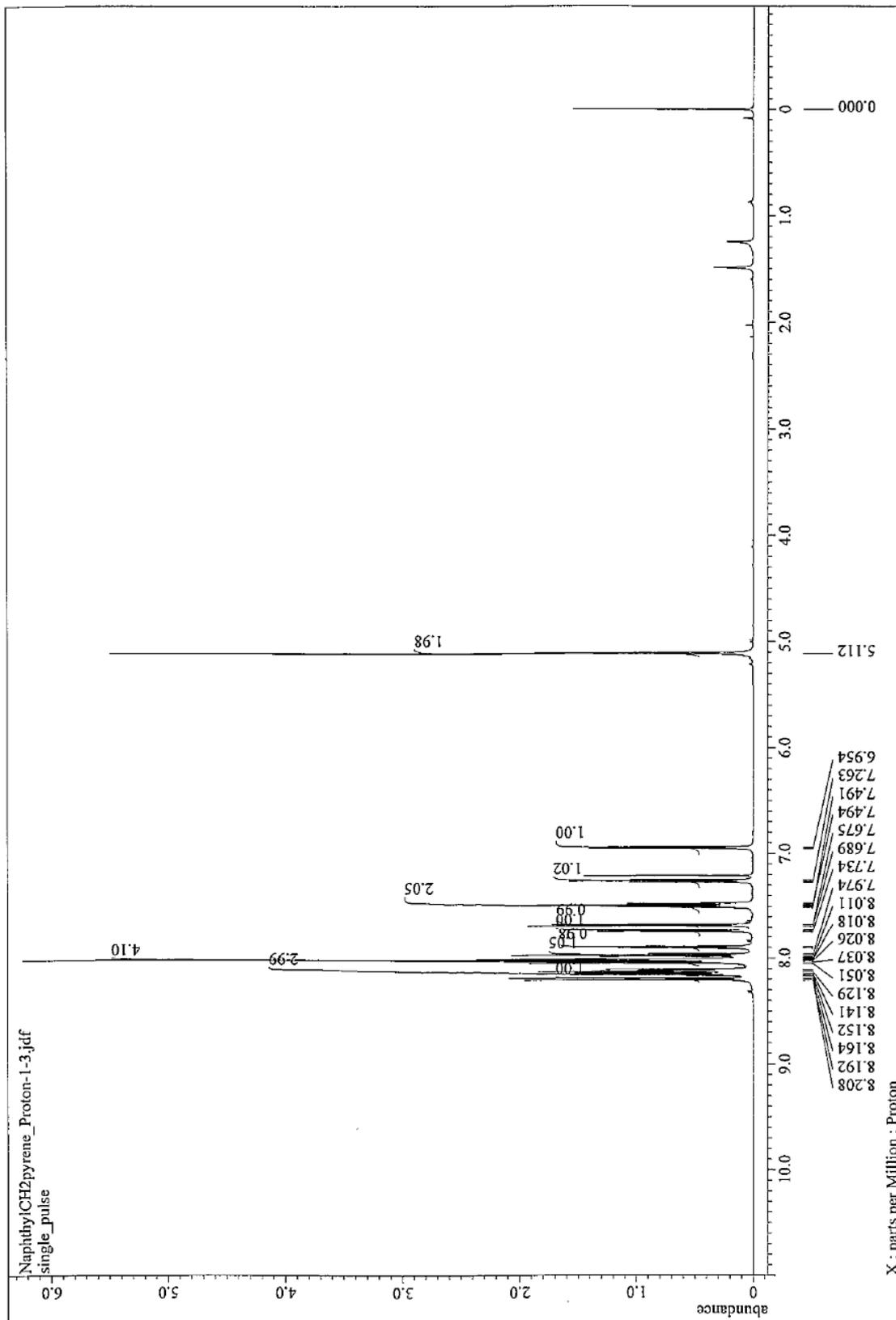
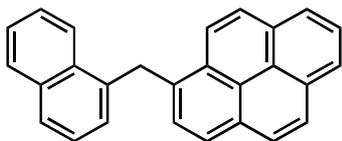
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5ko



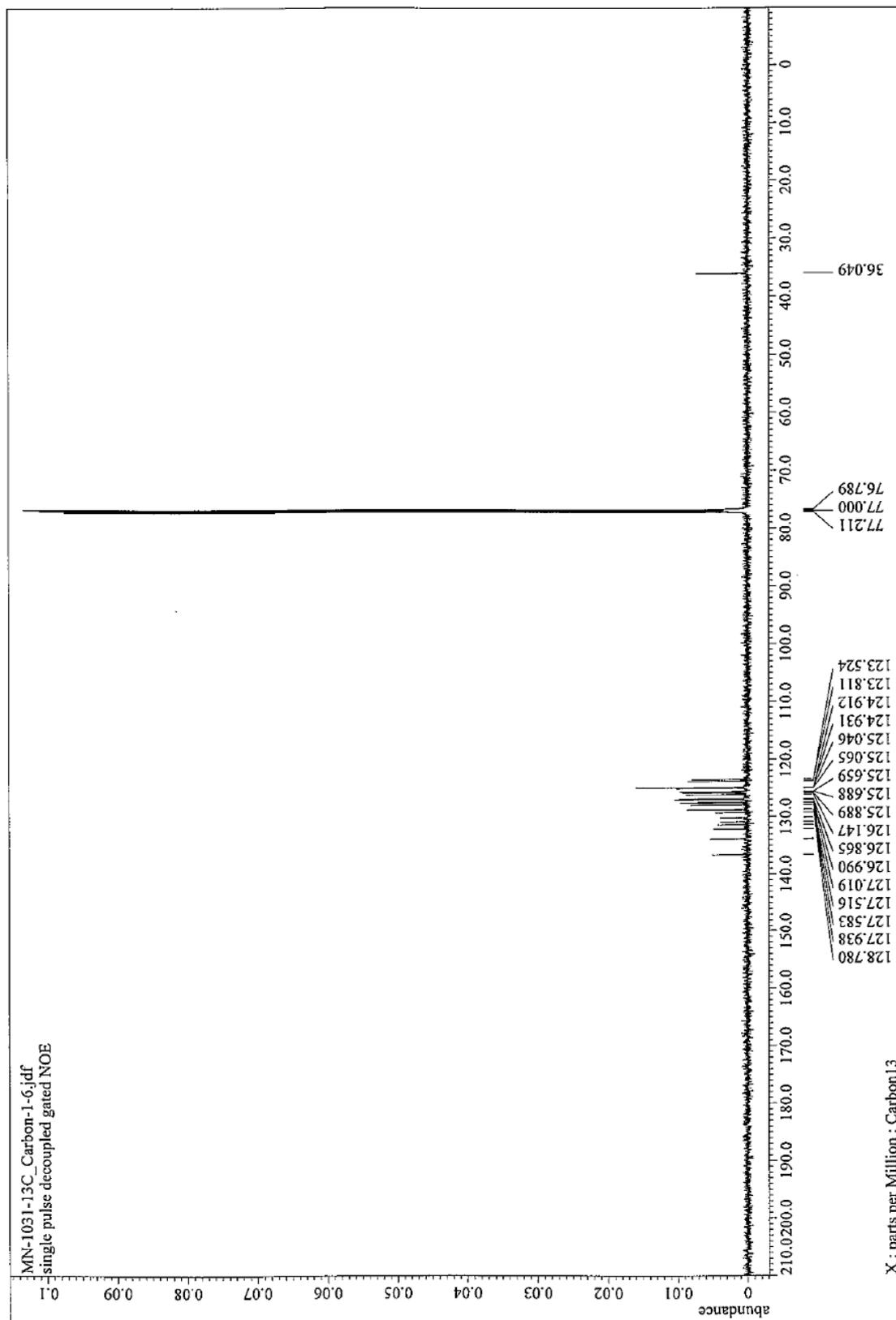
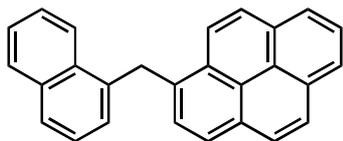
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5ko



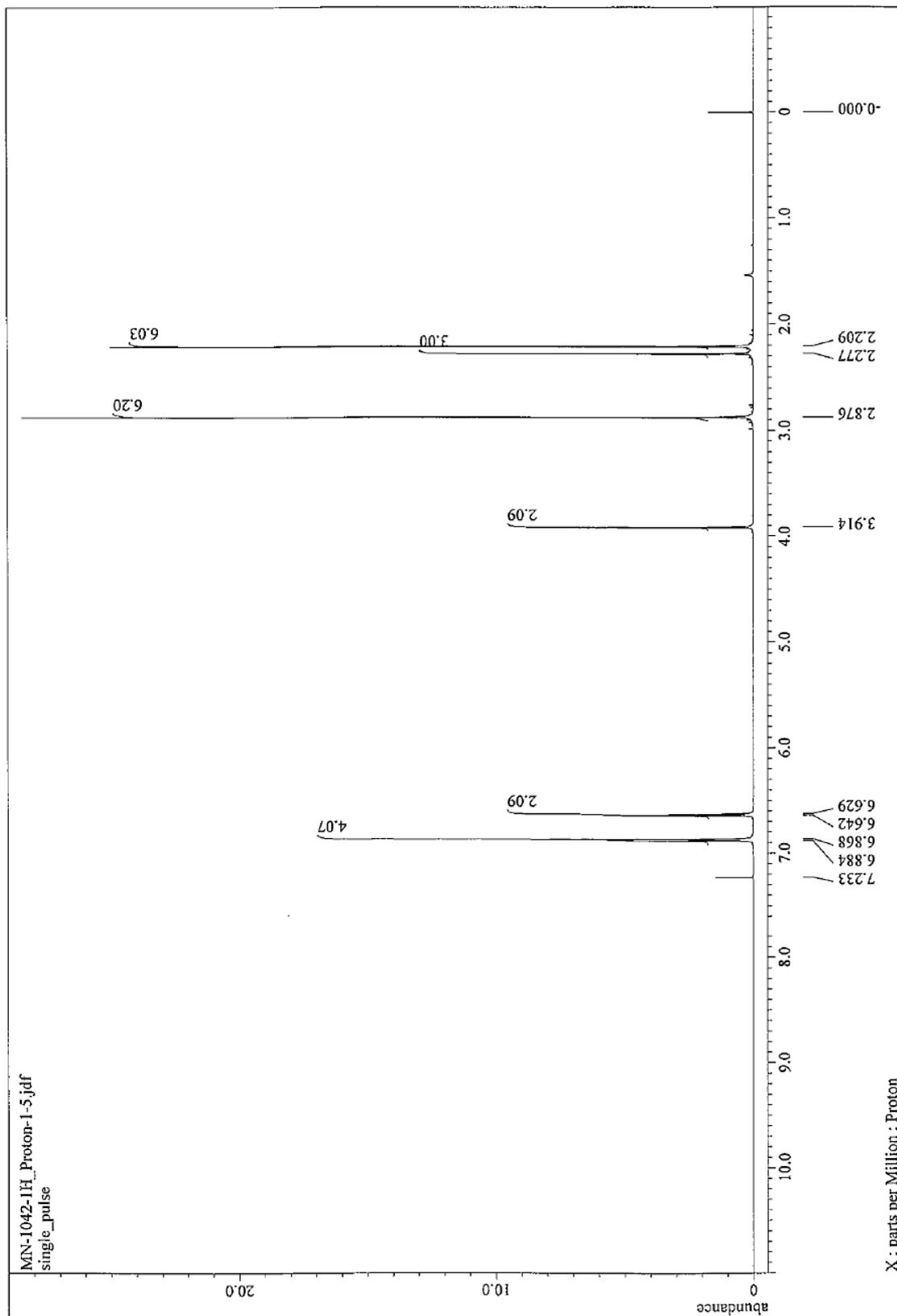
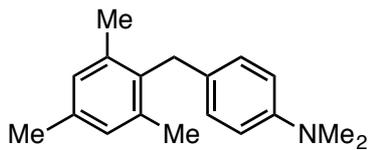
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5lp



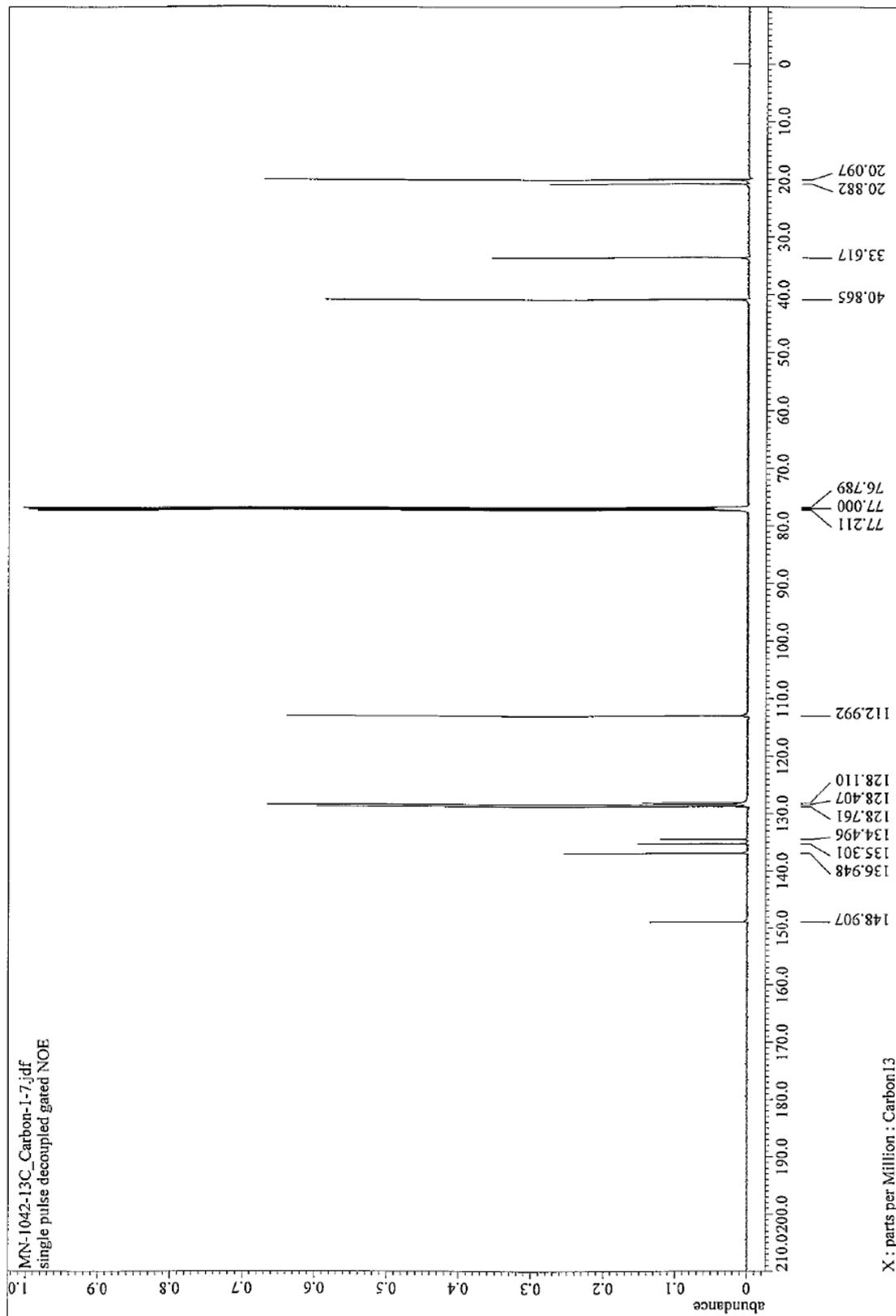
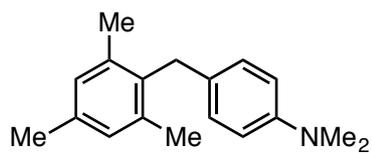
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ) of 5lp



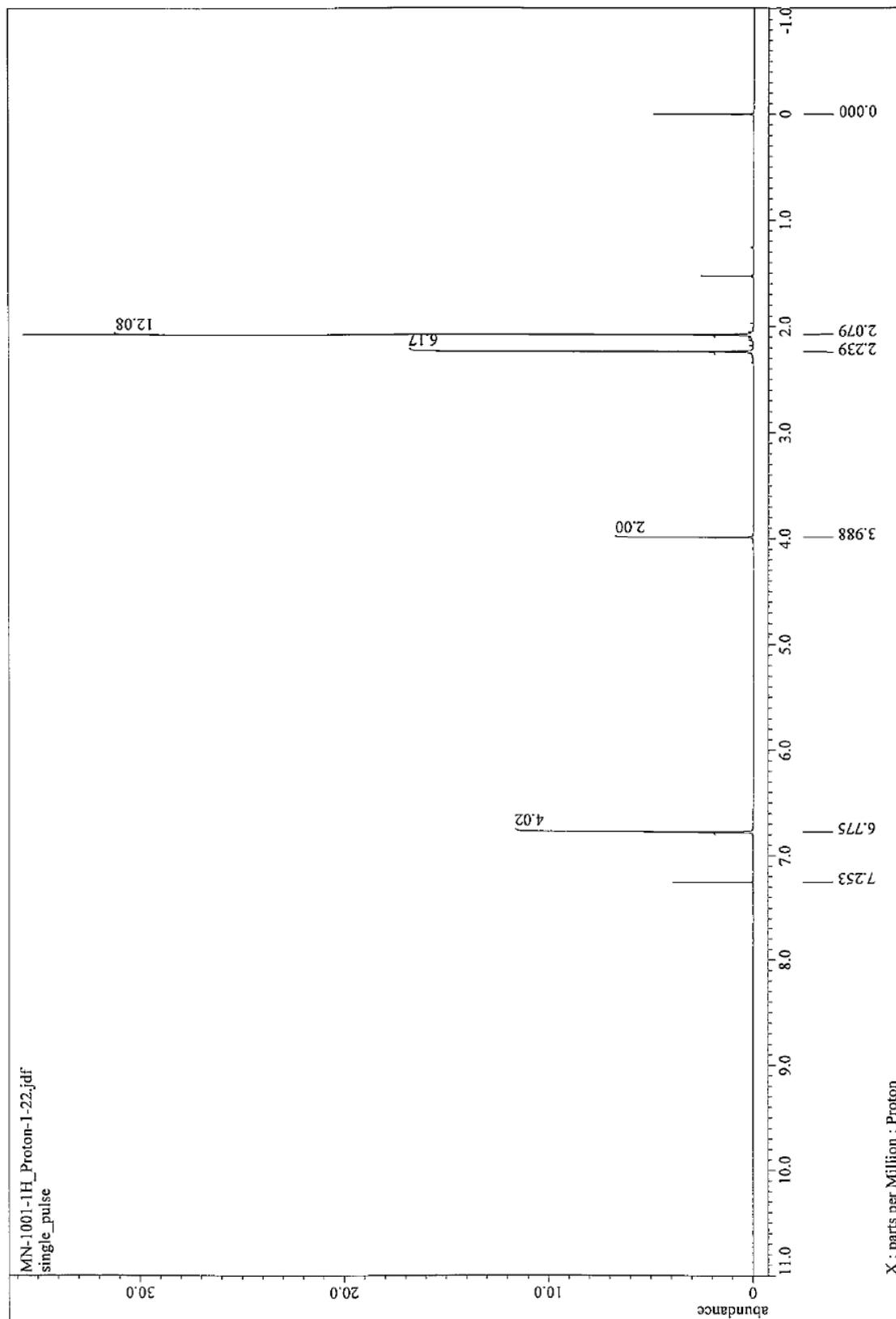
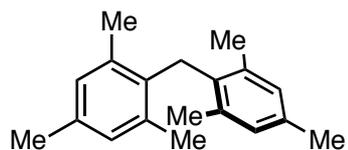
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5mq



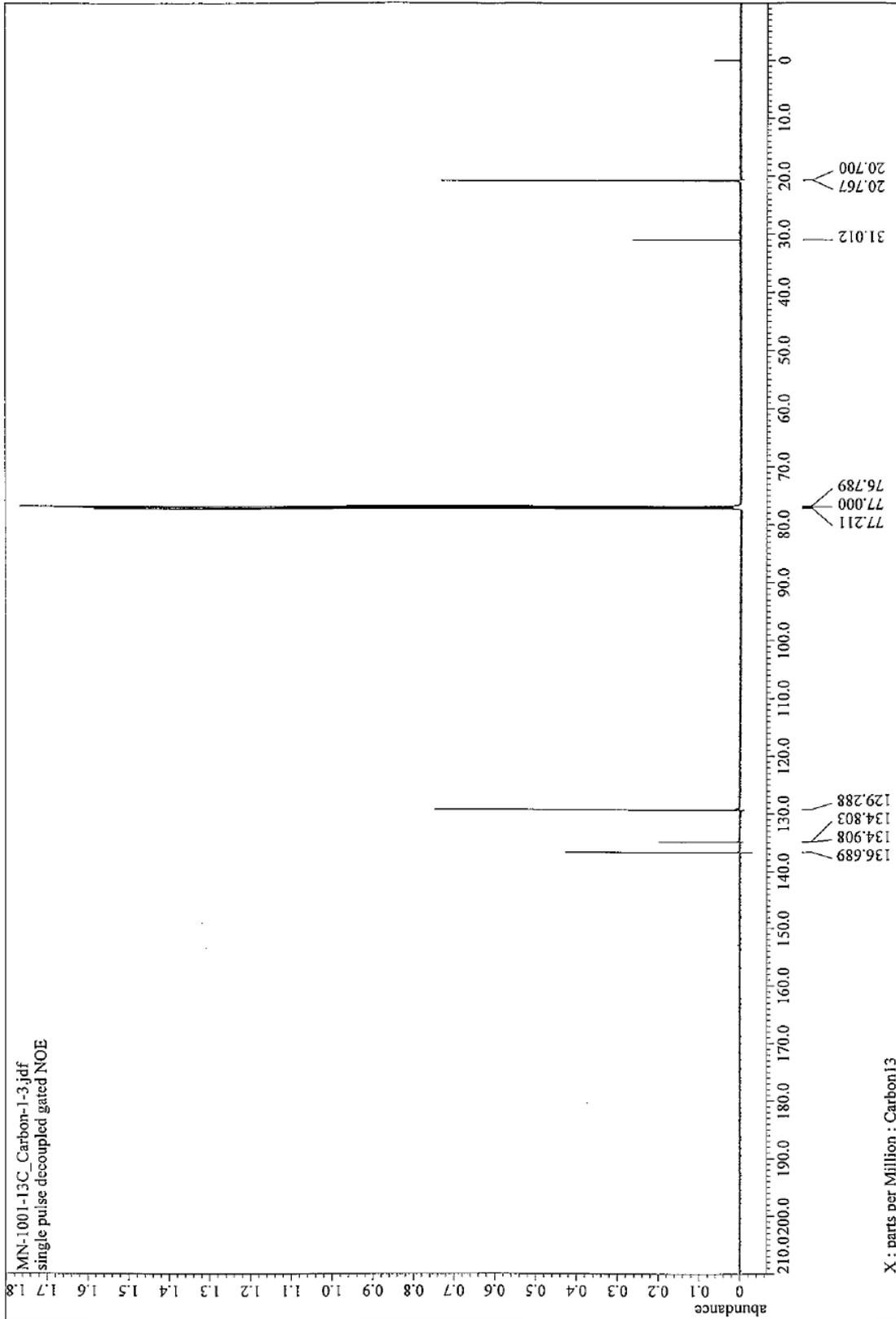
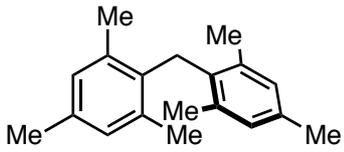
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5mq



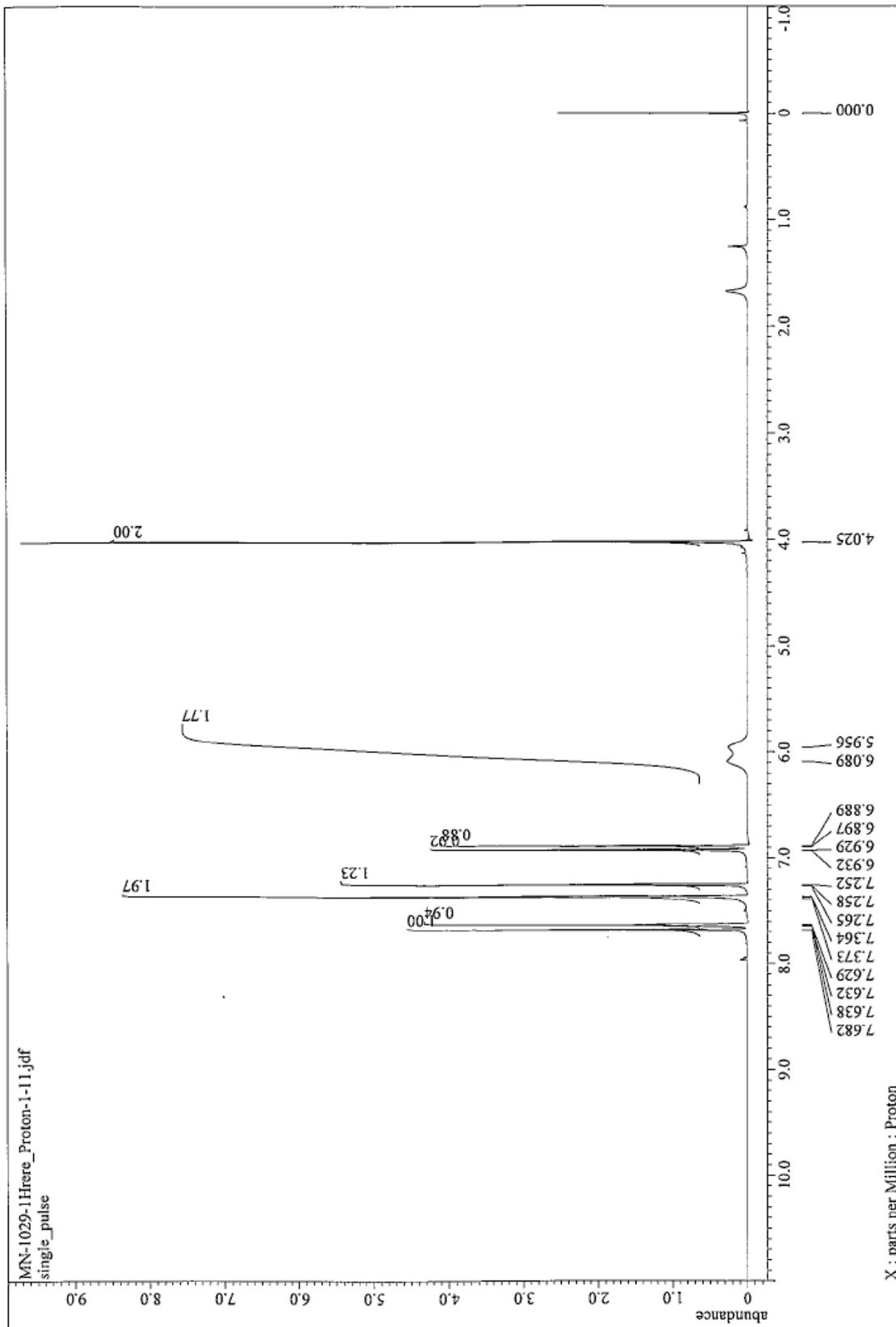
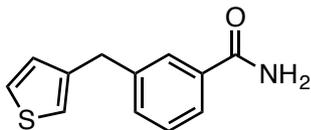
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5mr



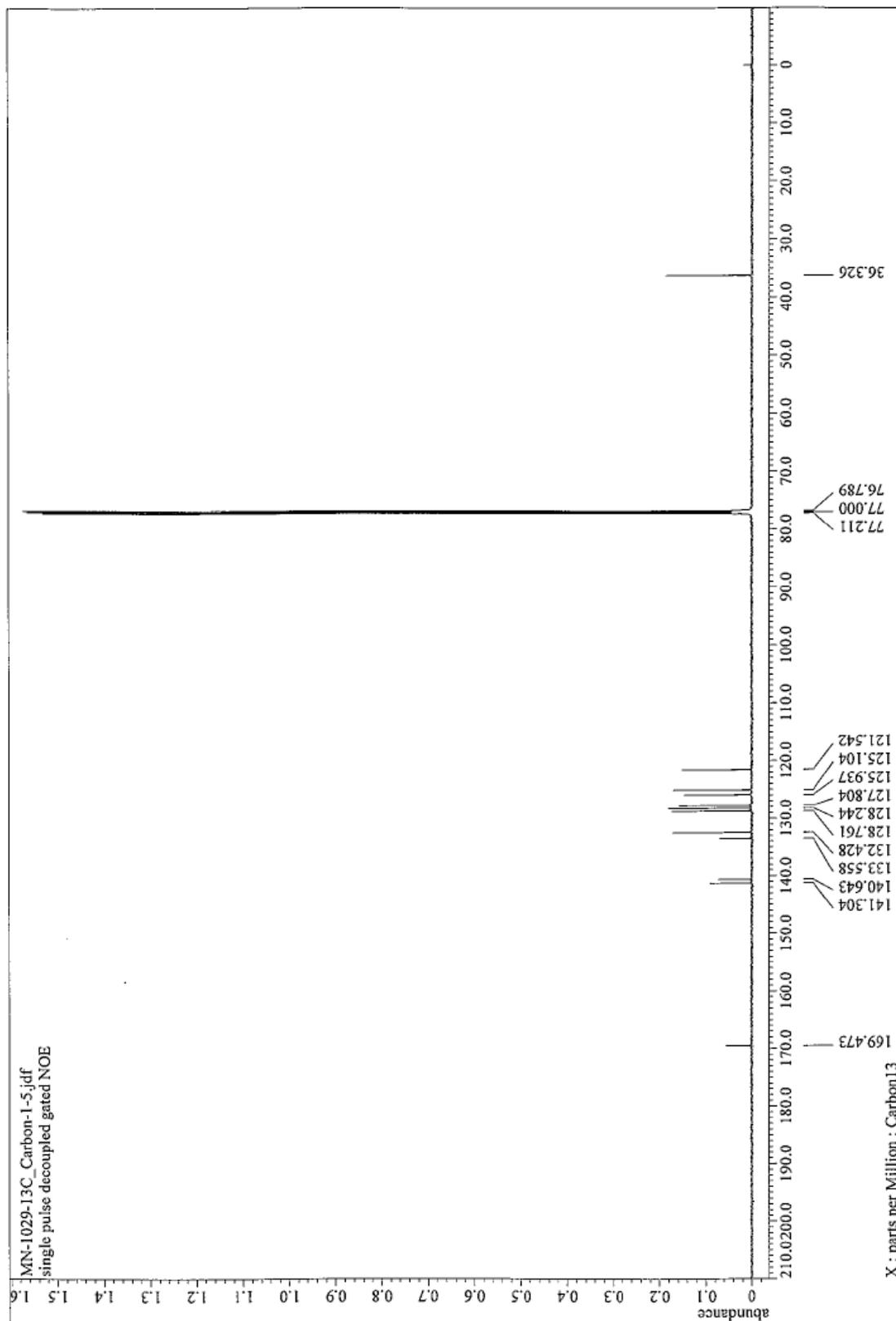
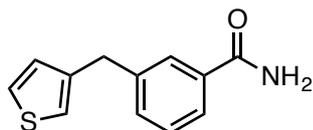
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5mr



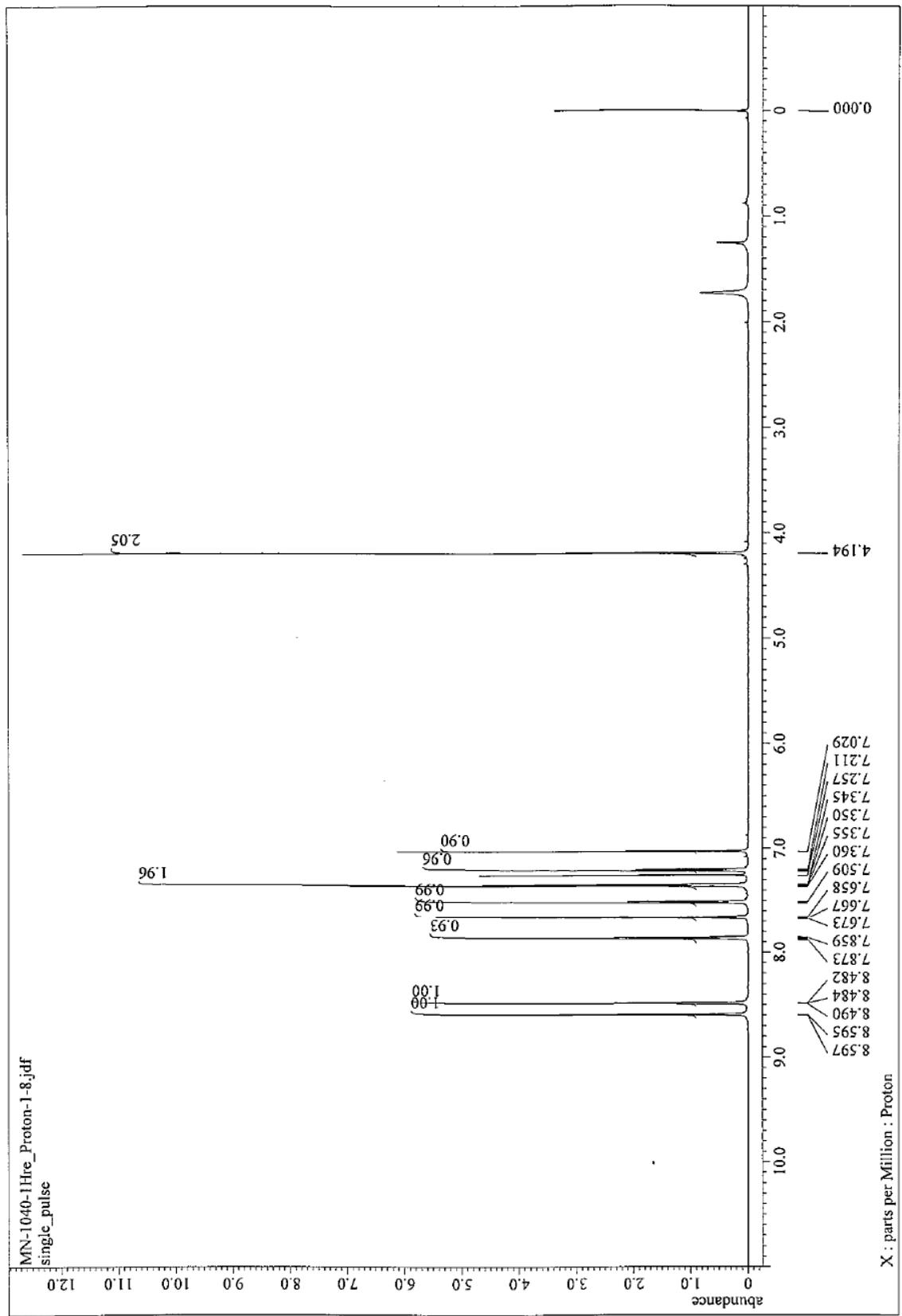
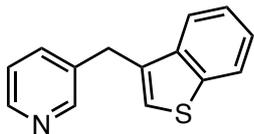
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5os



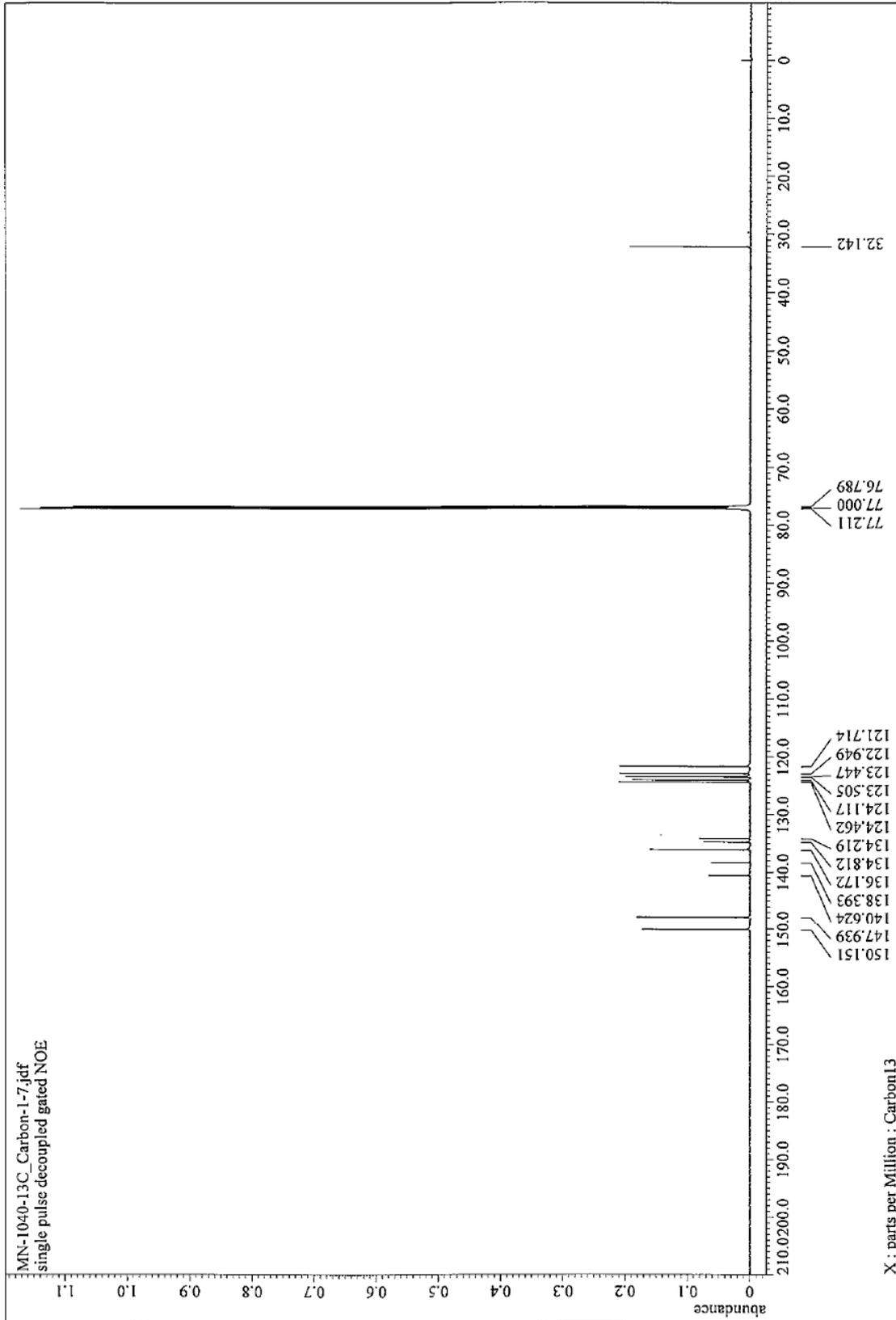
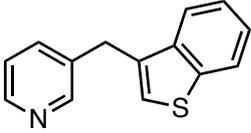
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5os



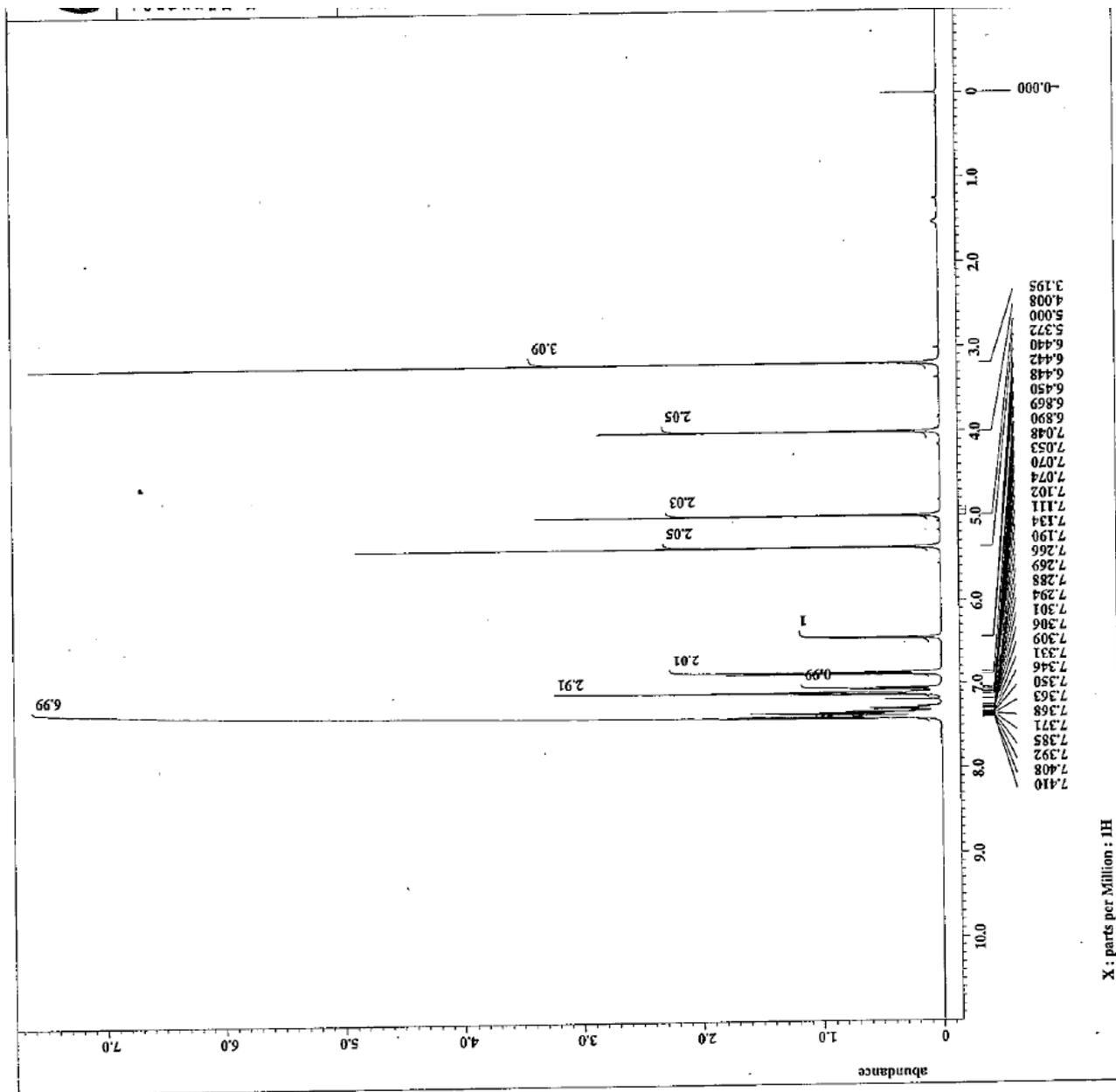
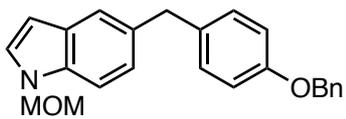
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 5pt



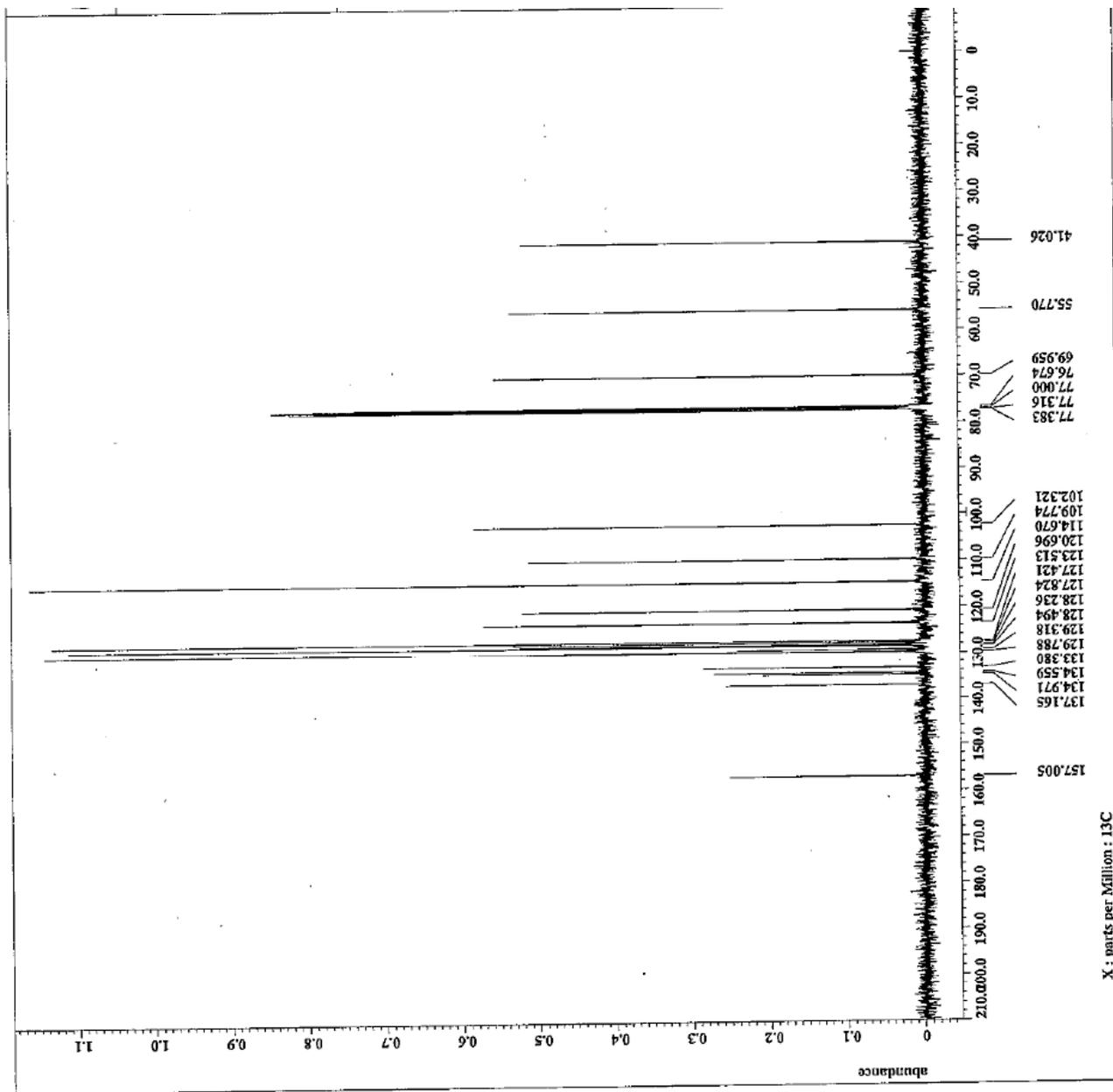
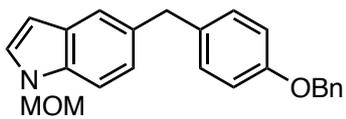
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 5pt



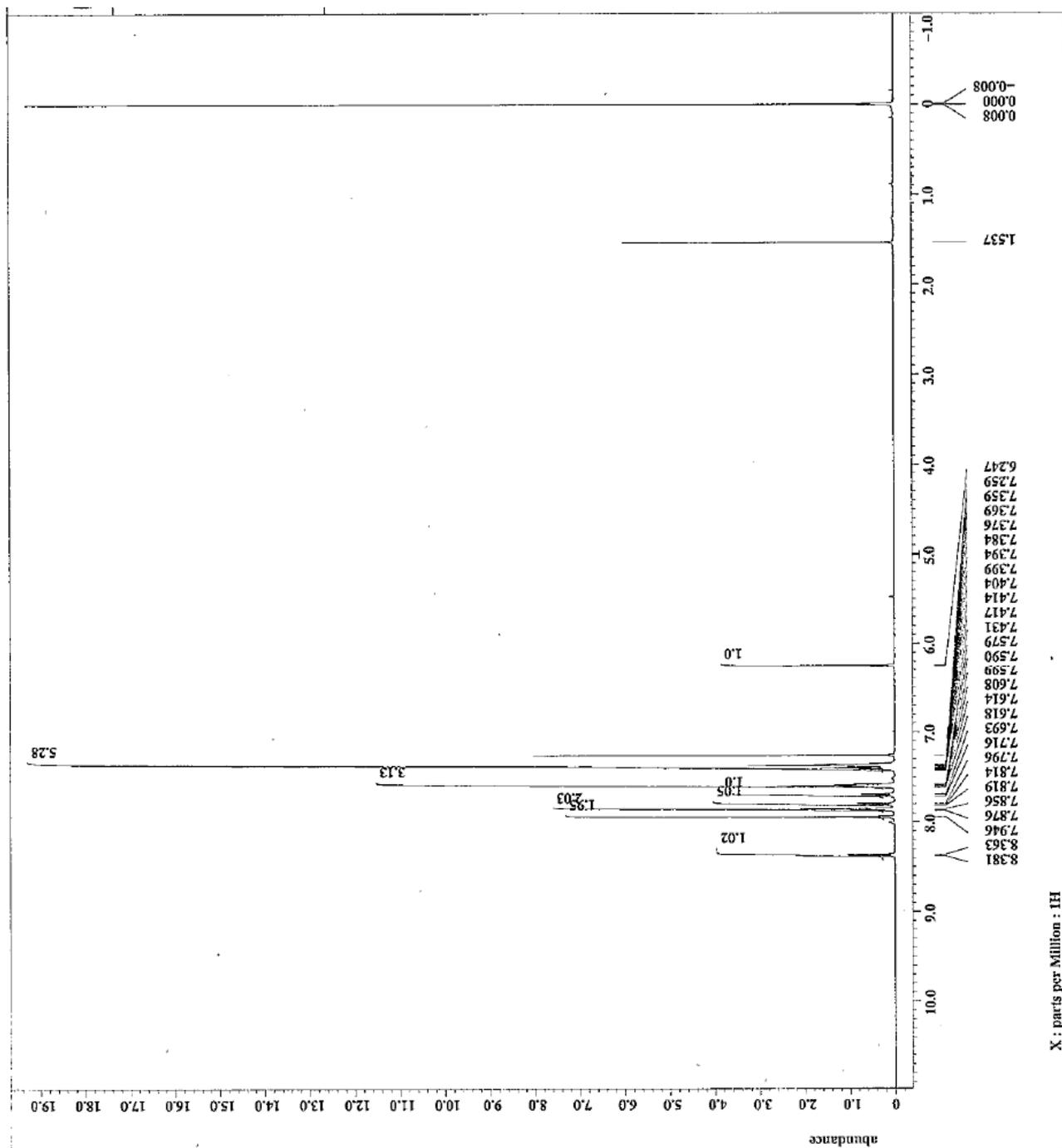
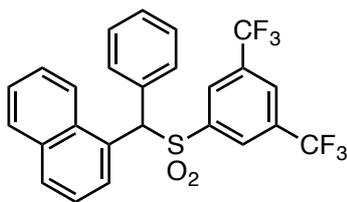
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 5nu



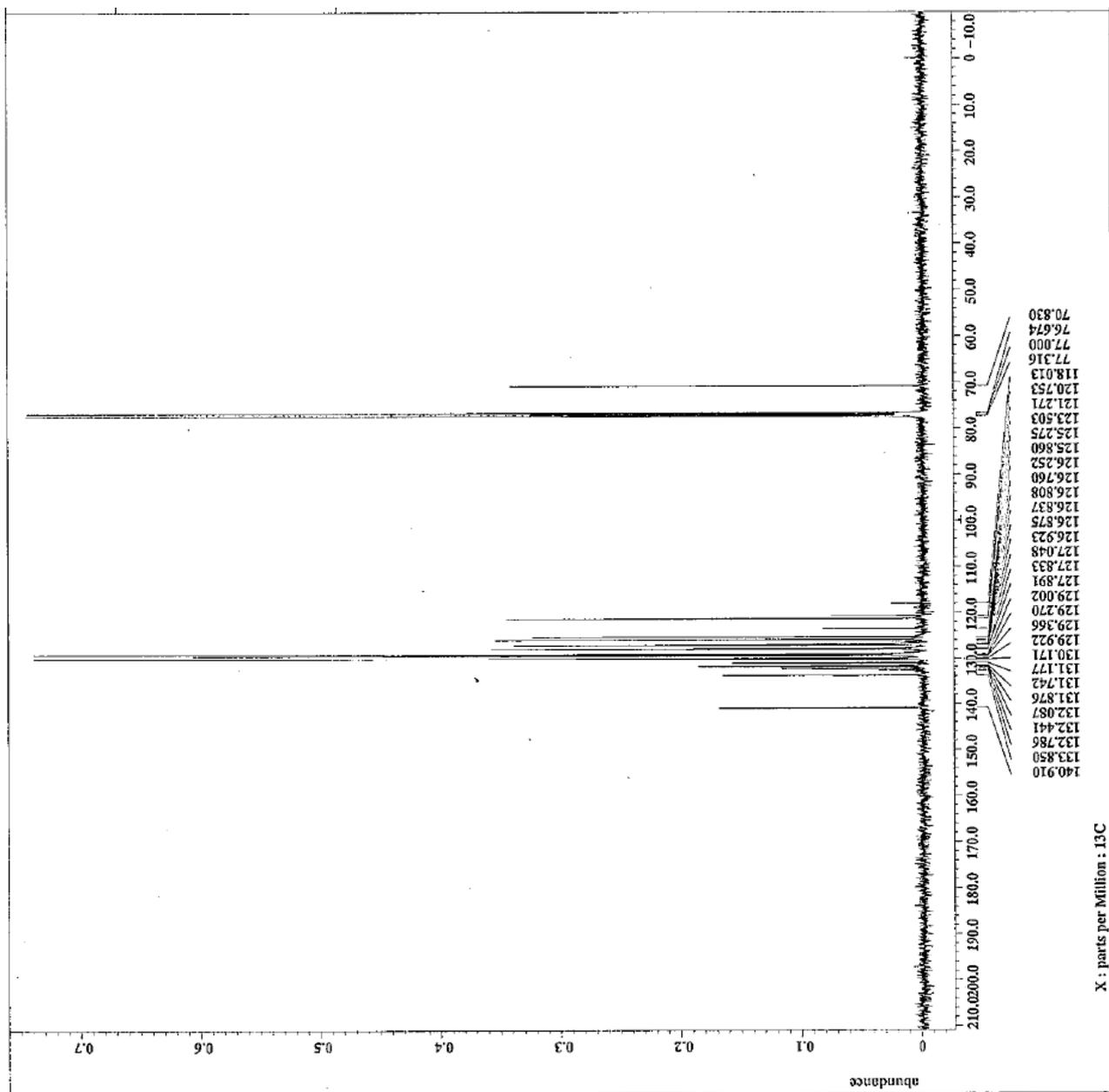
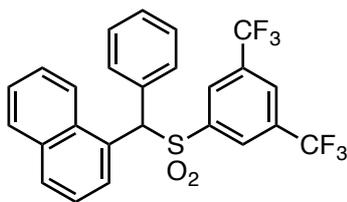
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 5nu



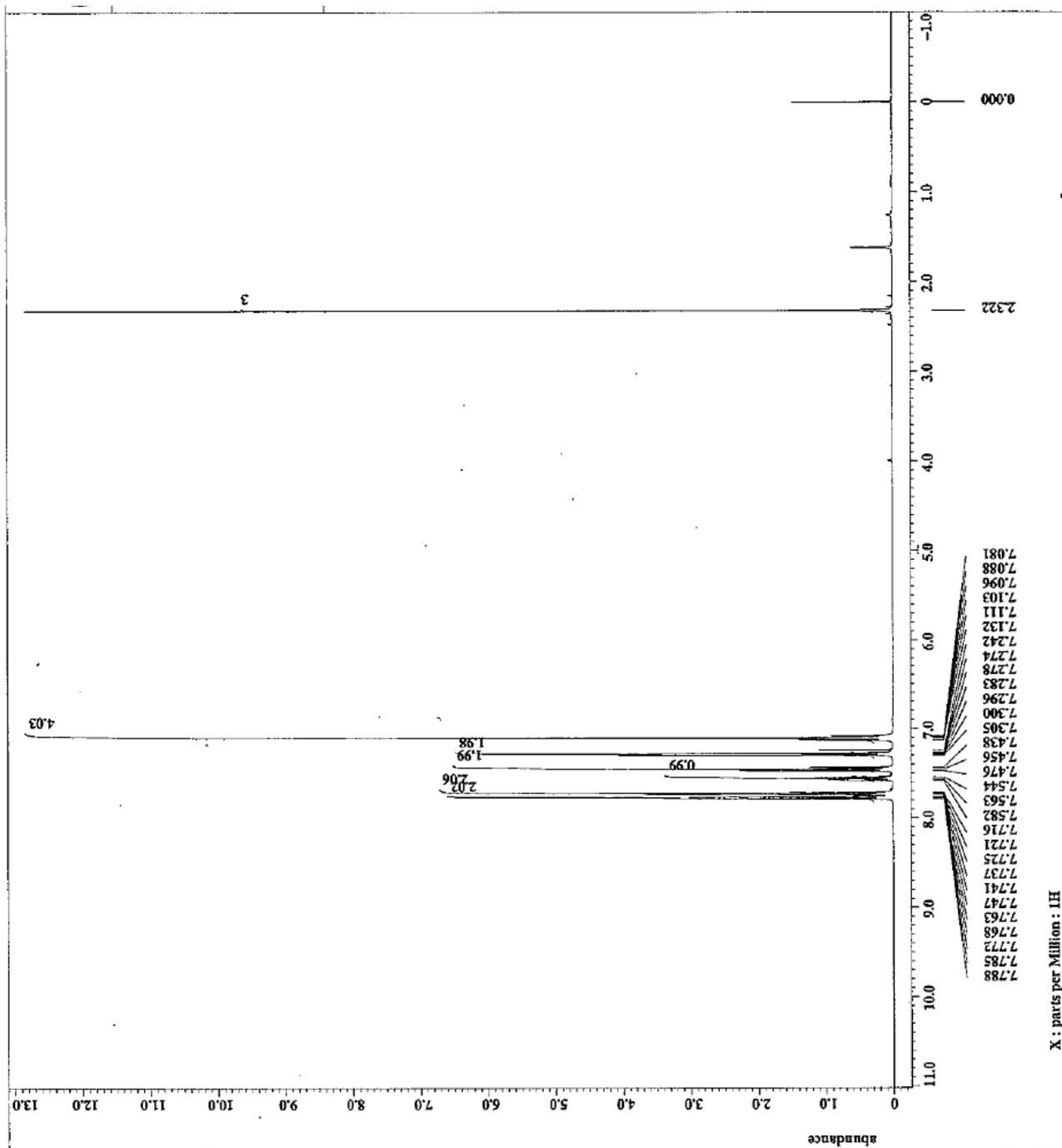
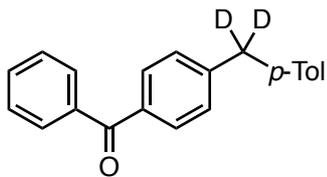
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 3,5-bis(trifluoromethyl)phenyl 1-naphthylphenylmethyl sulfone



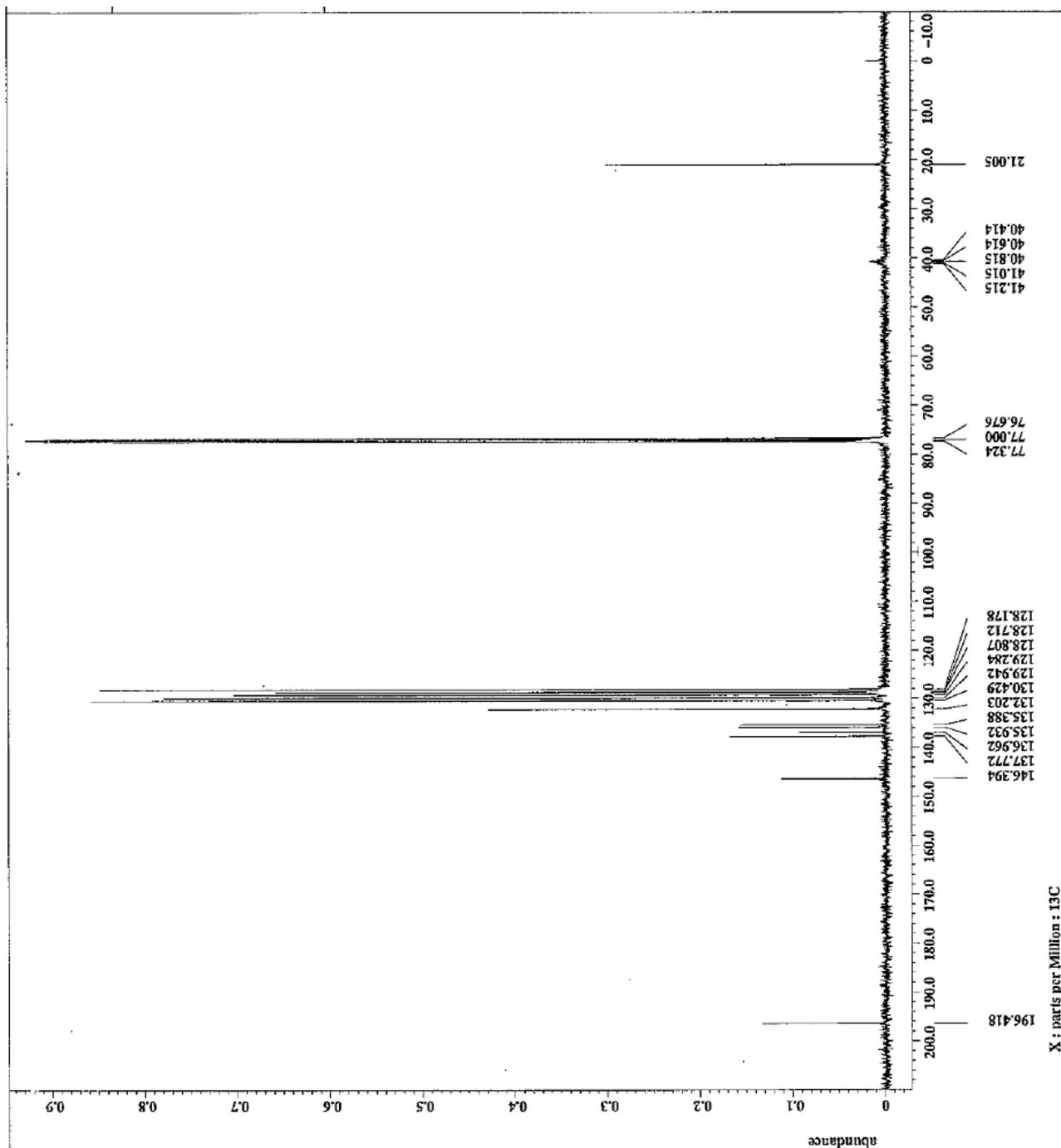
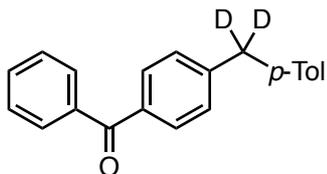
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 3,5-bis(trifluoromethyl)phenyl 1-naphthylphenylmethyl sulfone



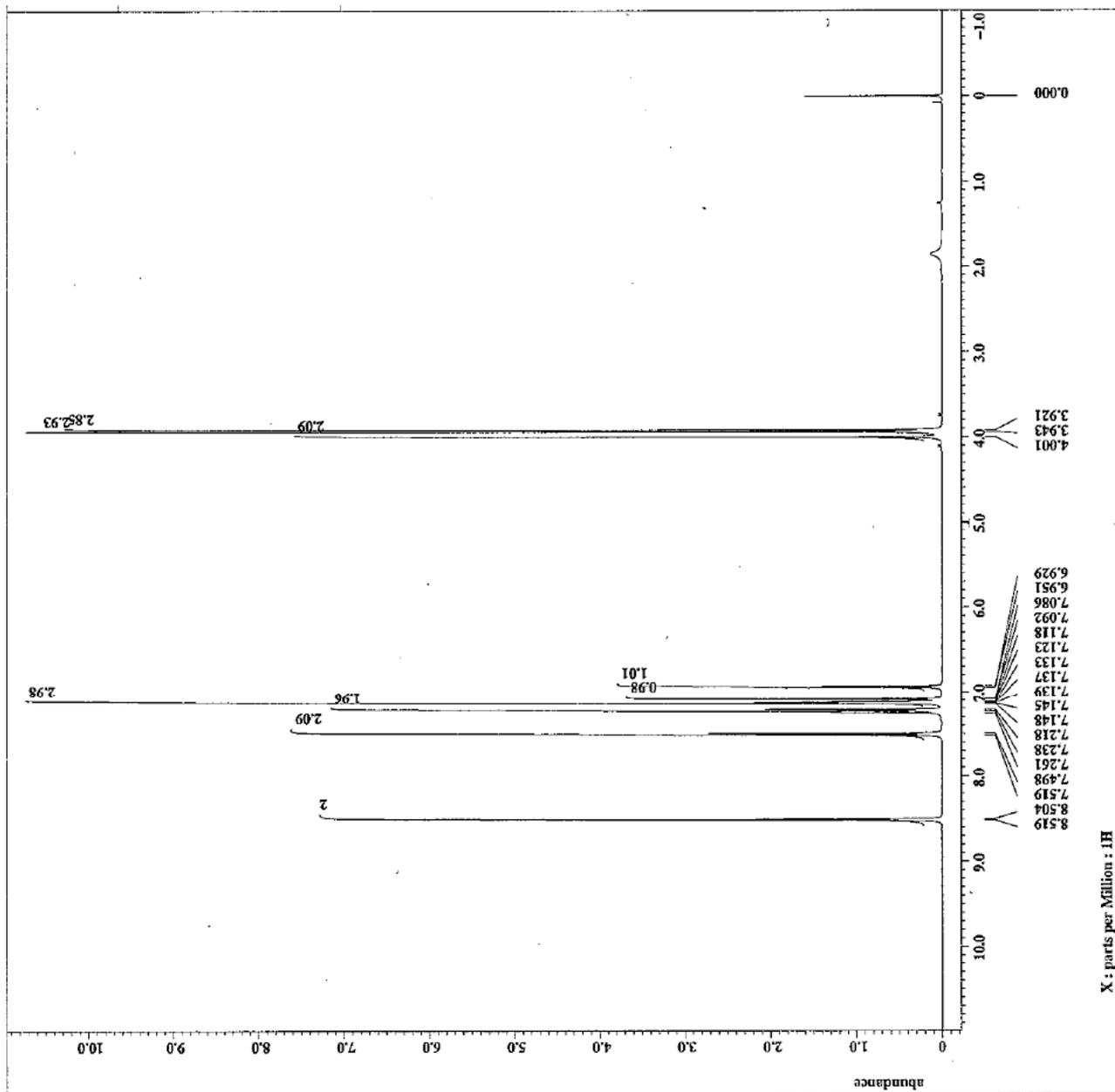
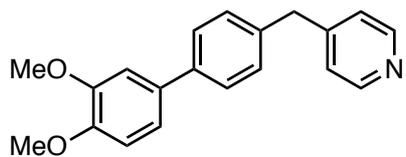
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 9



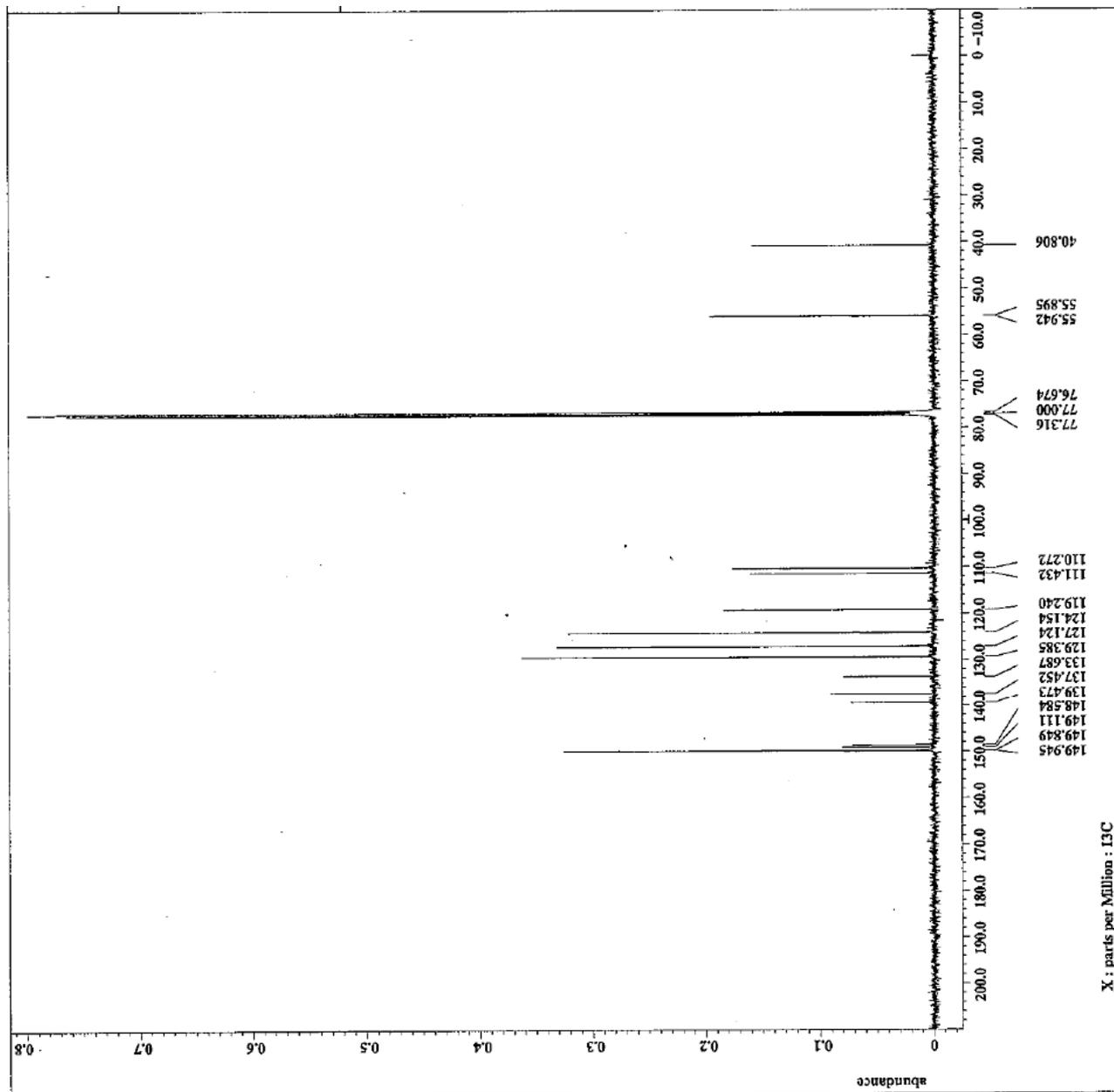
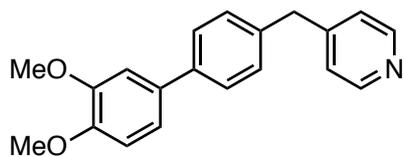
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 9



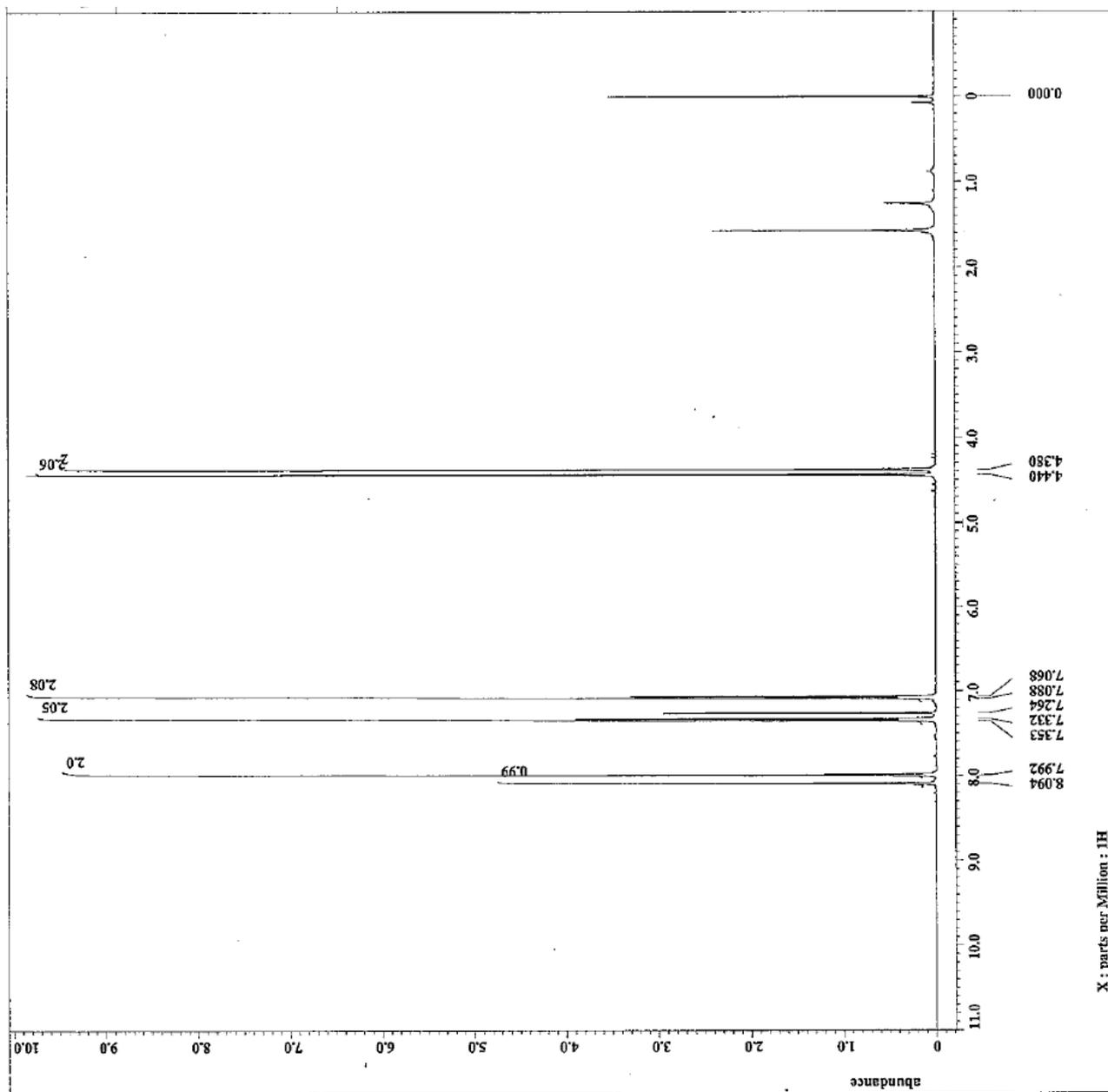
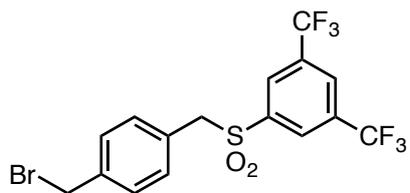
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 10



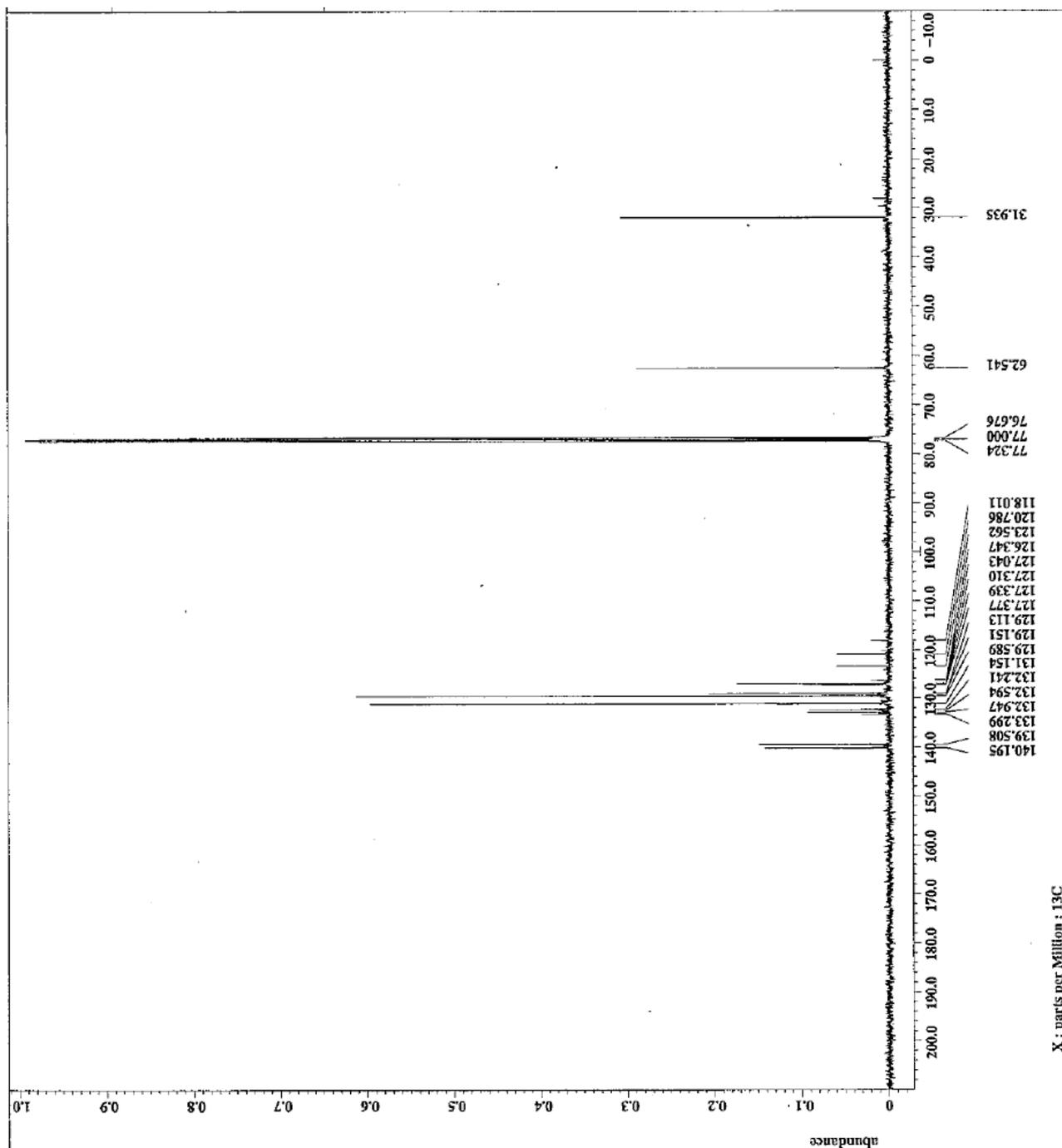
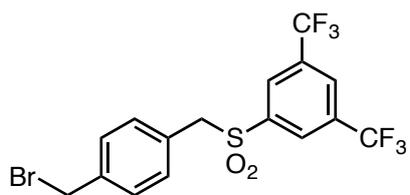
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 10



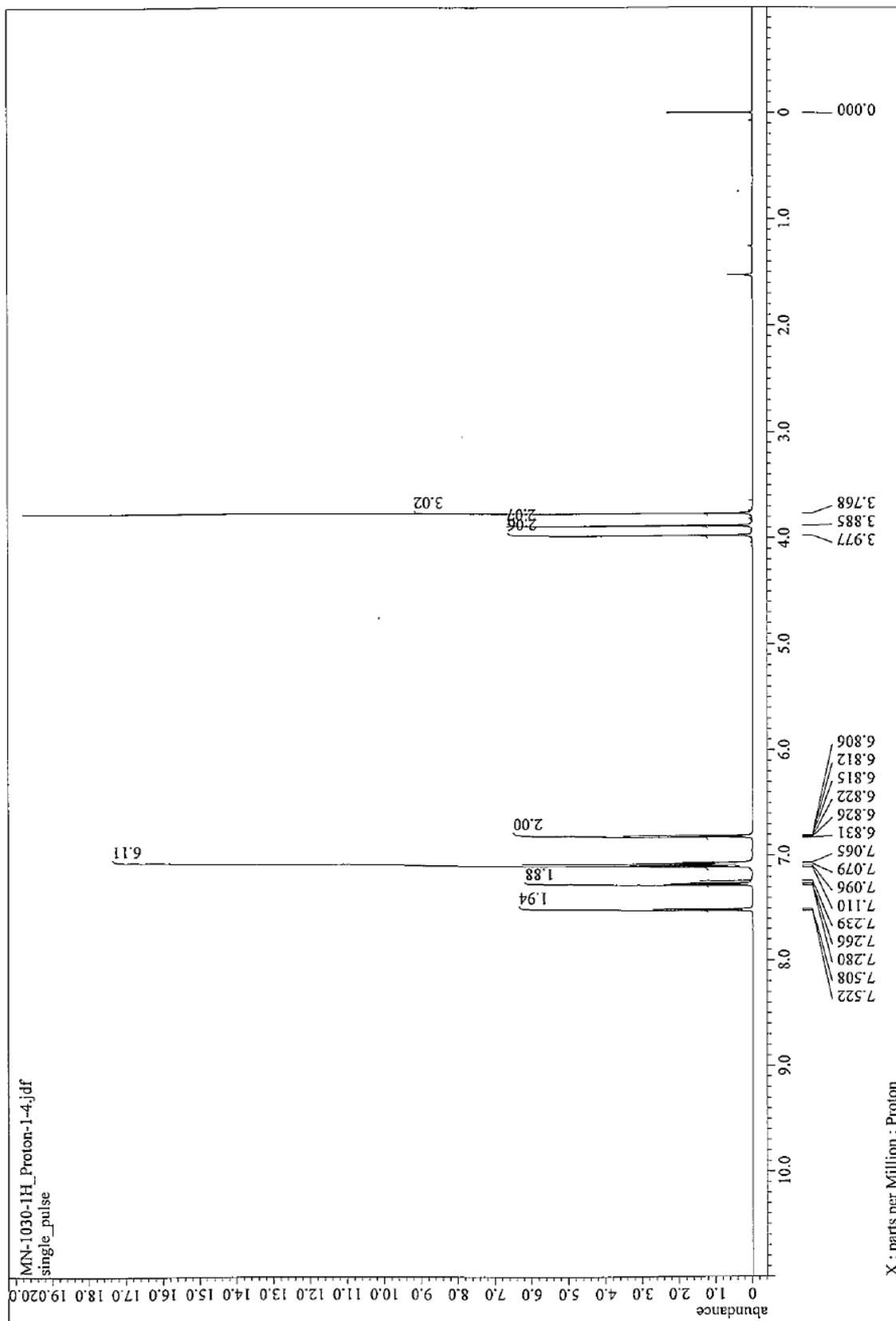
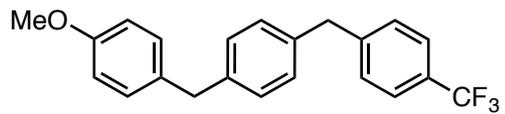
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2q



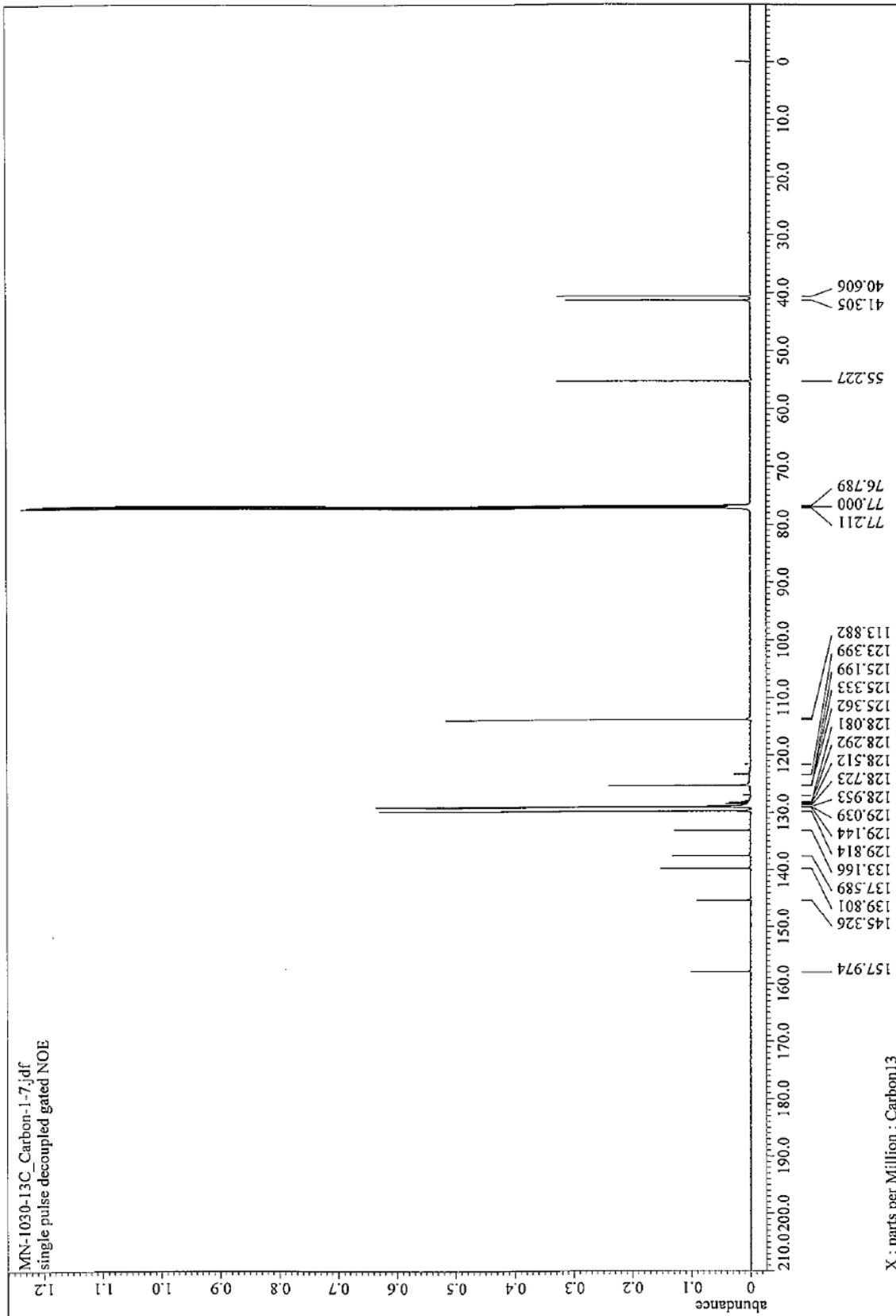
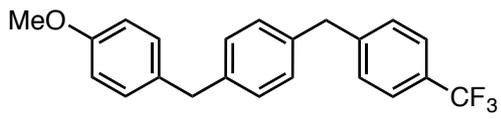
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2q



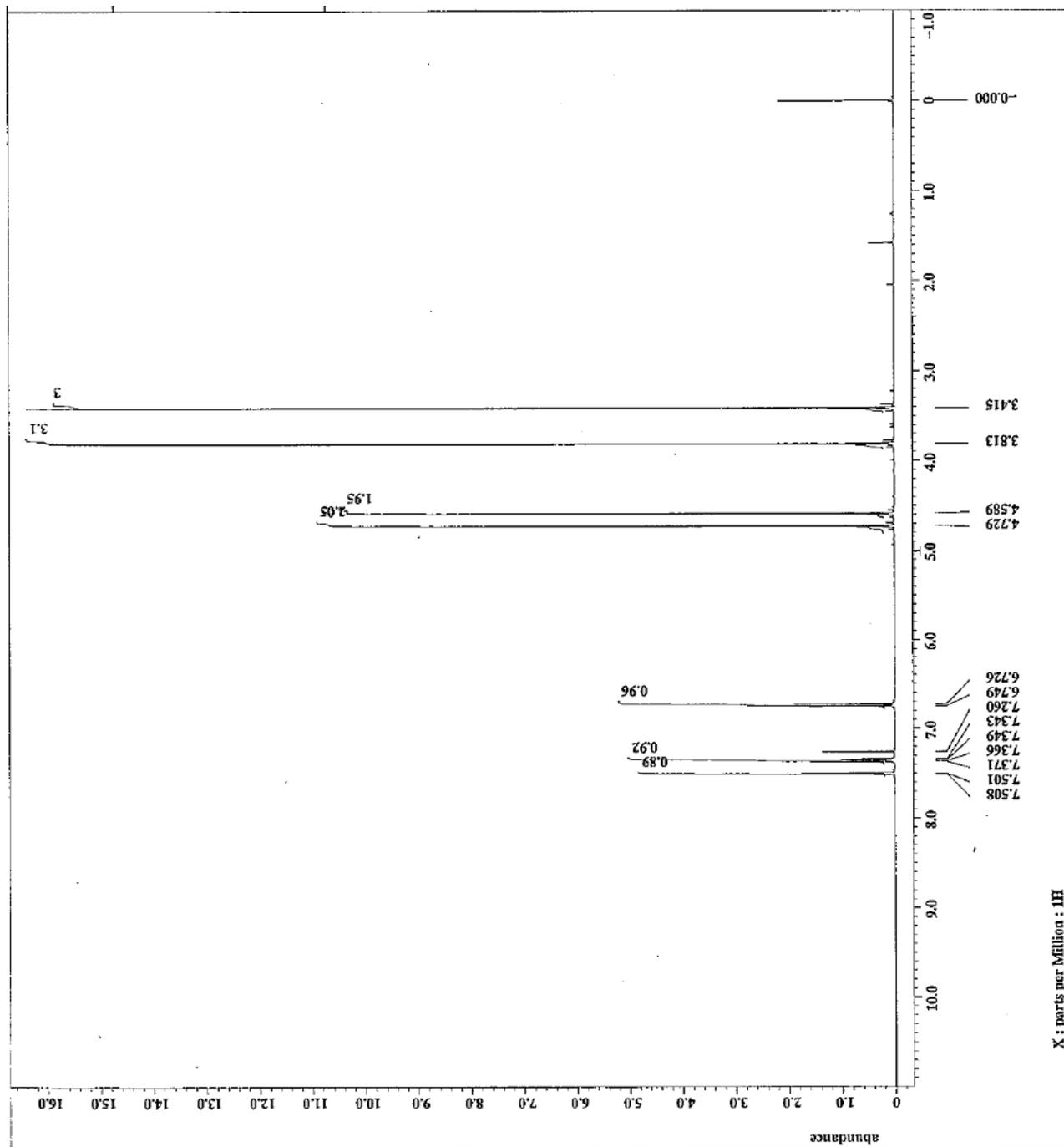
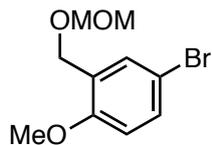
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) of 11



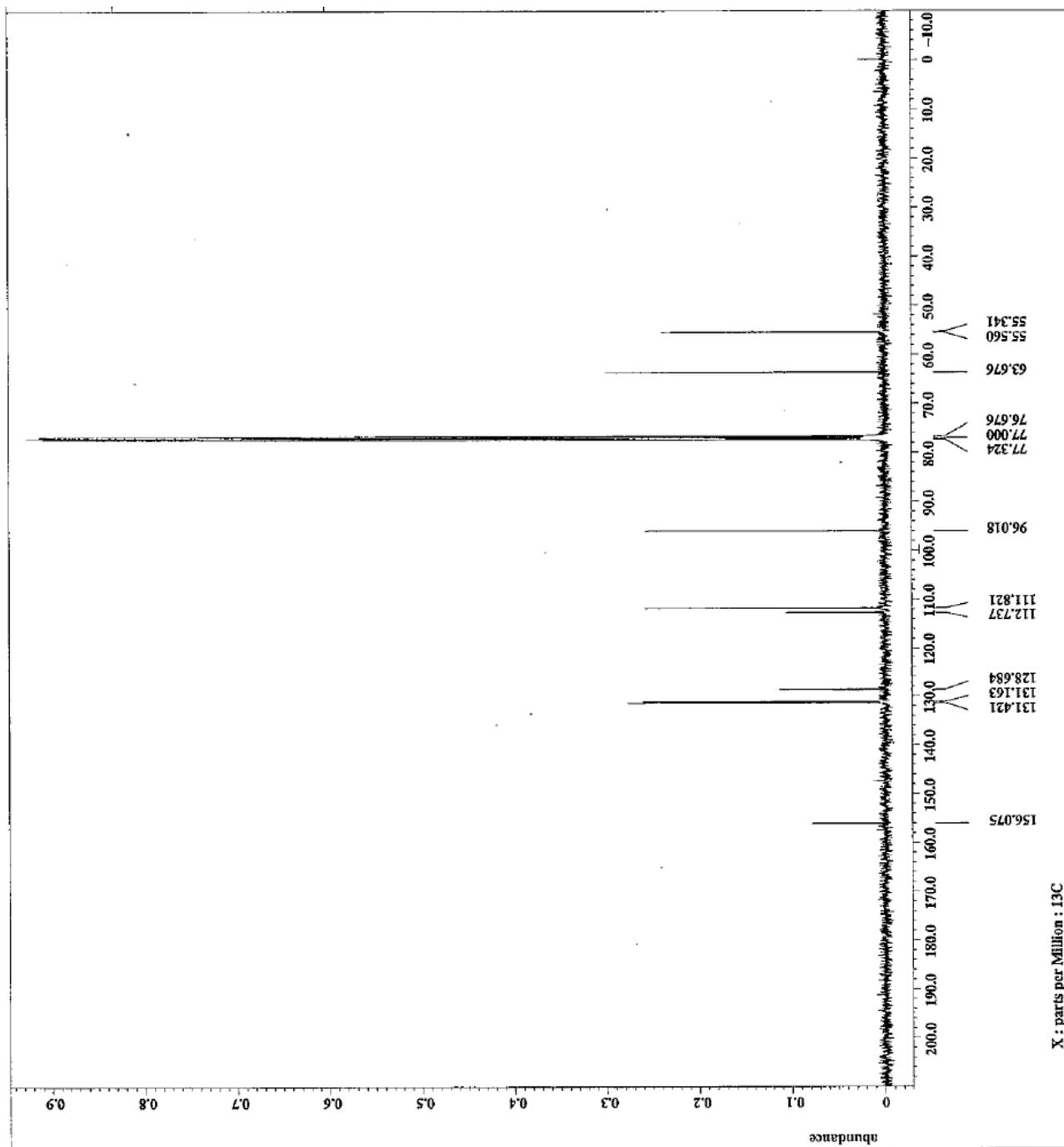
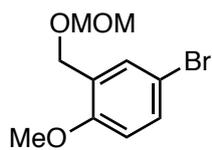
<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) of 11



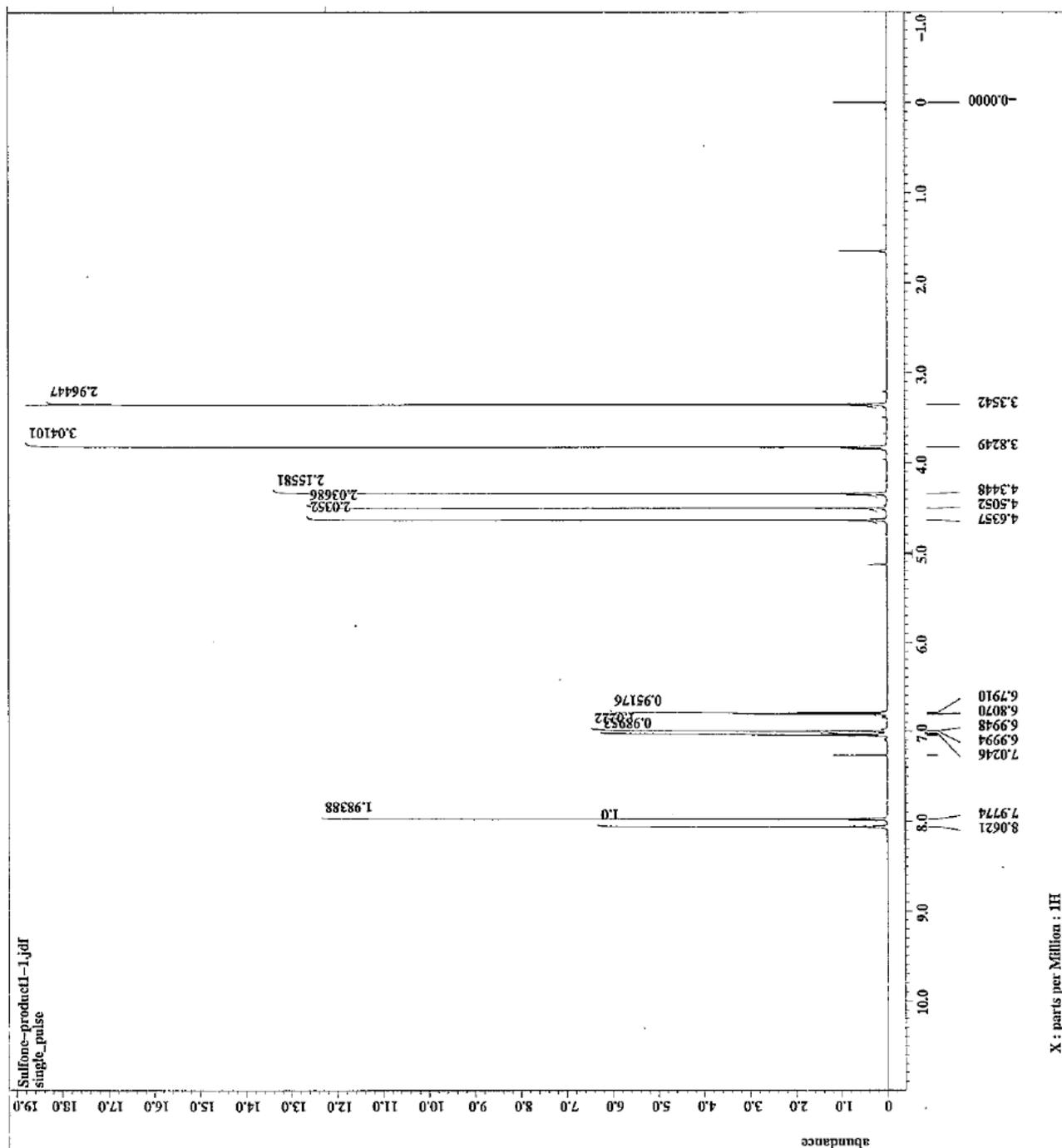
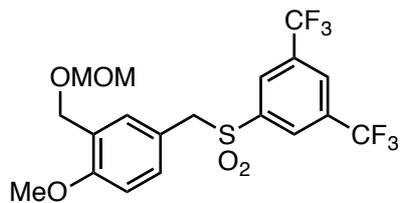
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 7r



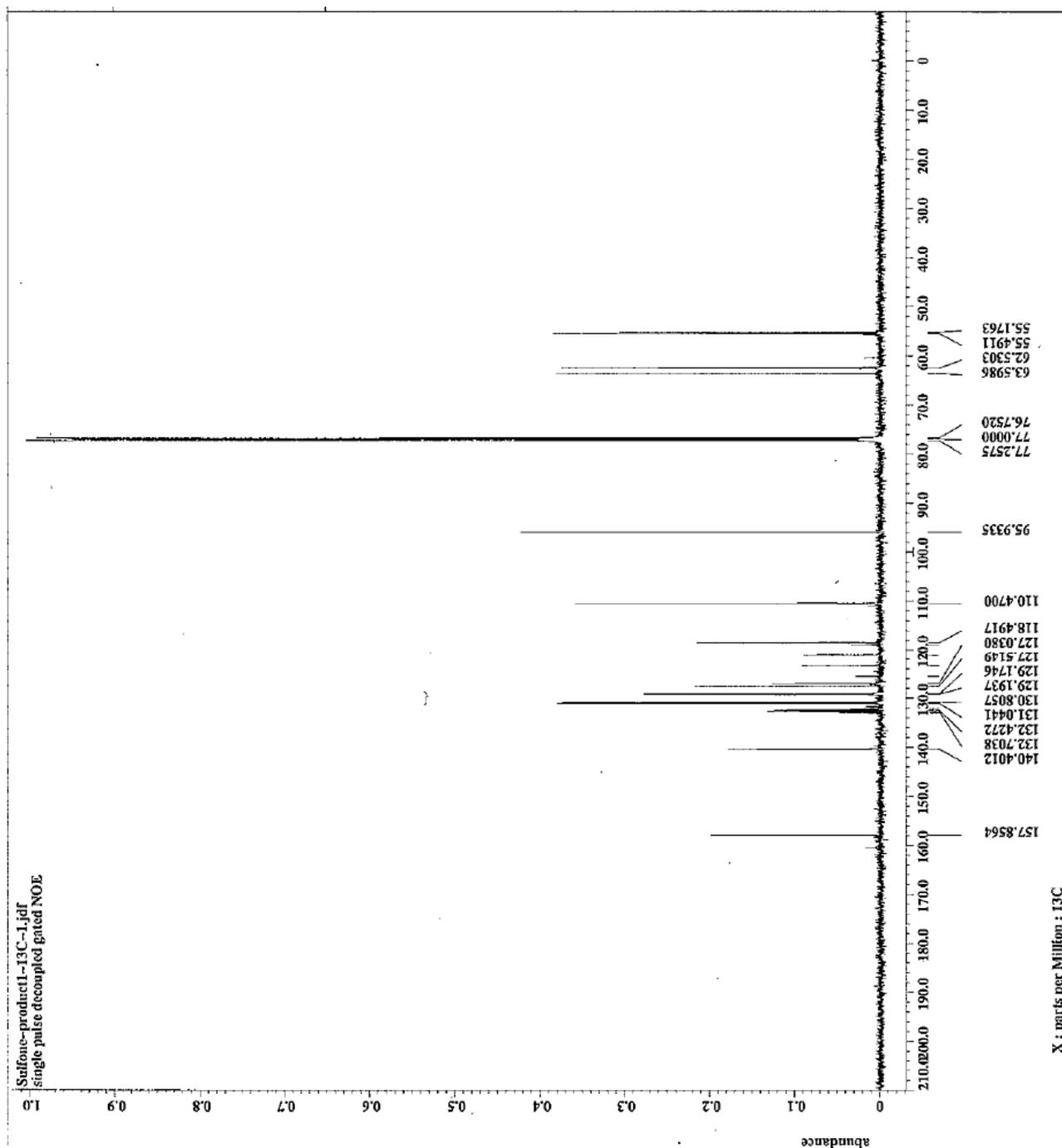
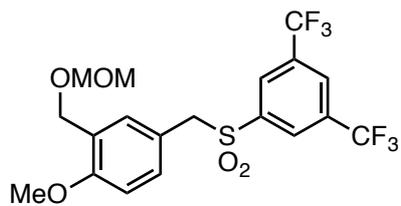
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) of 7r



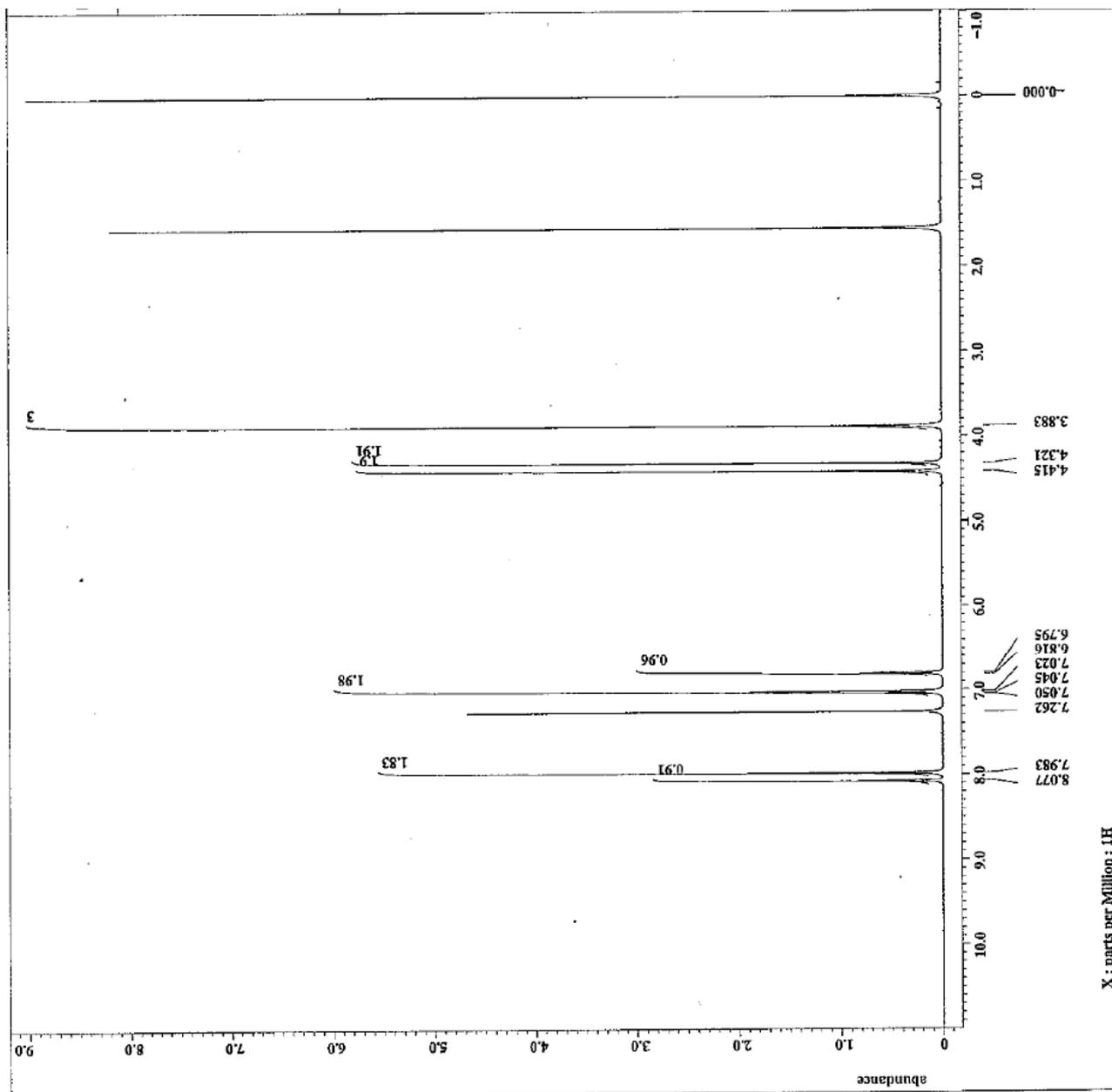
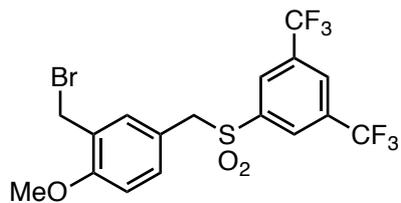
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) of 2r



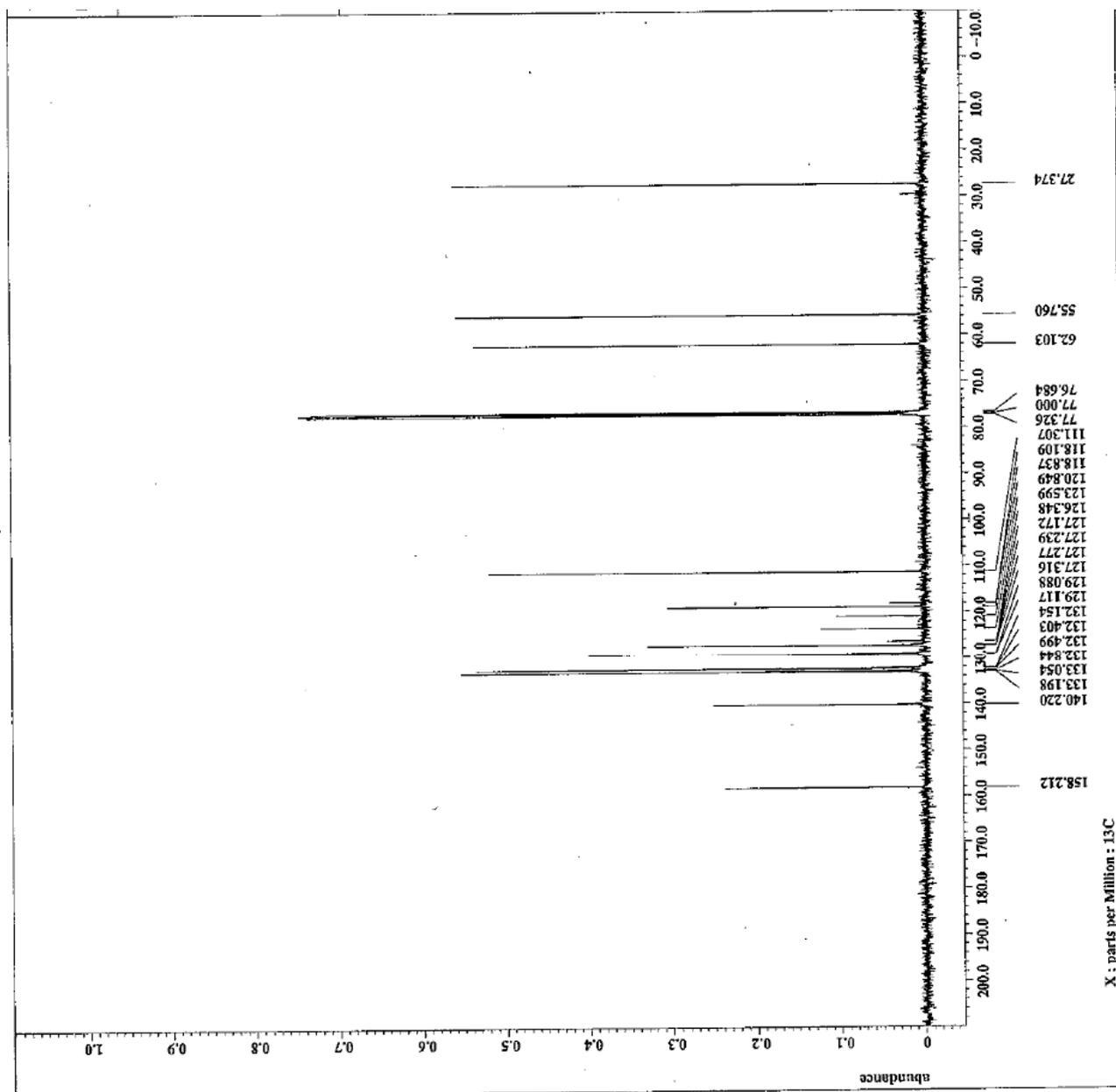
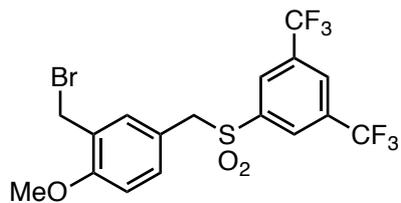
<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) of 2r



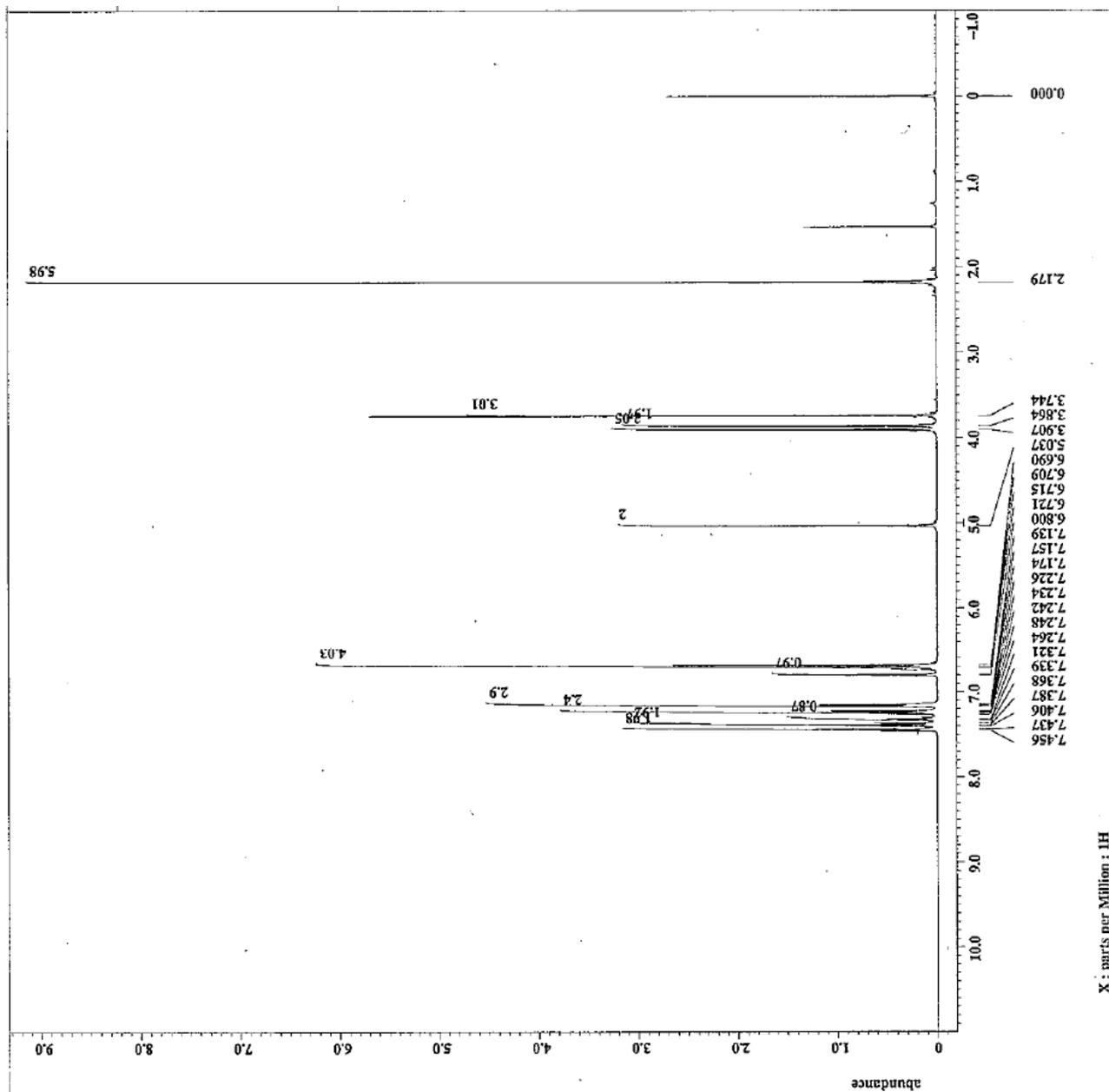
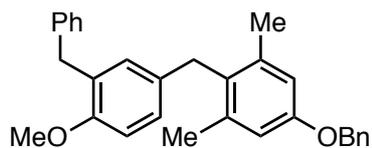
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 2s



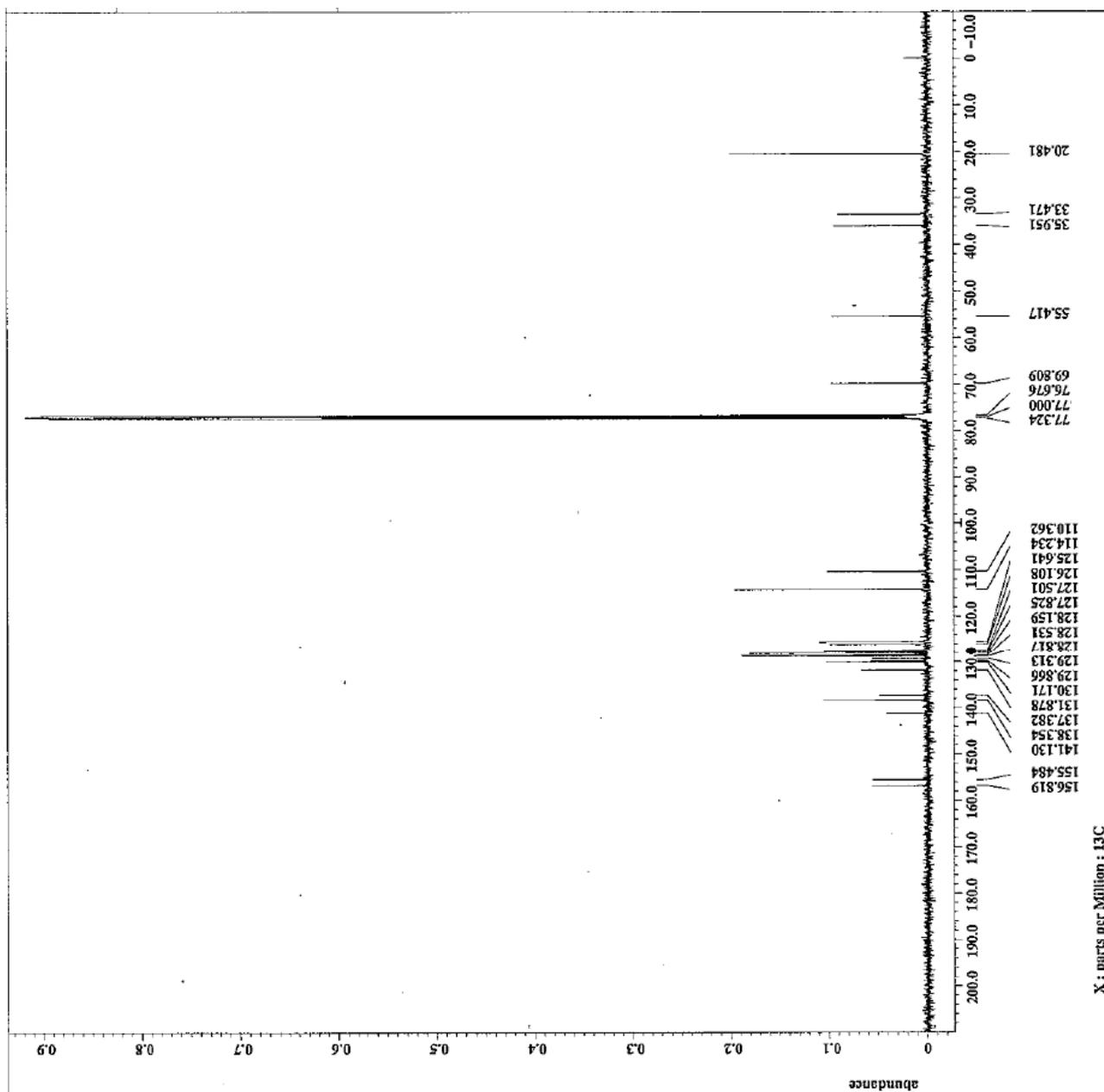
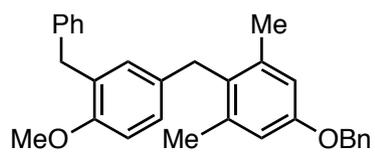
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 2s



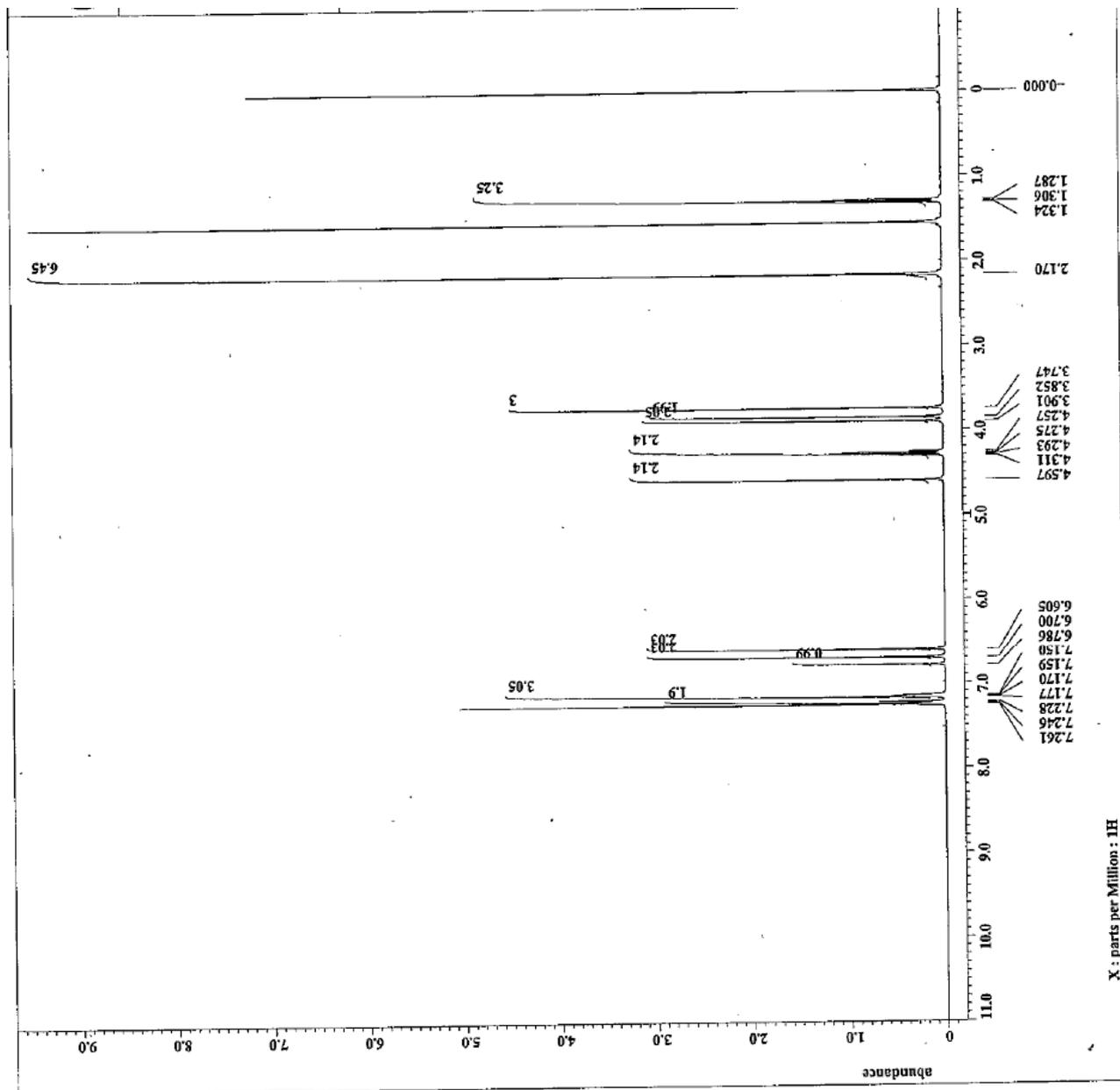
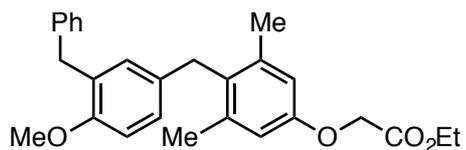
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 12



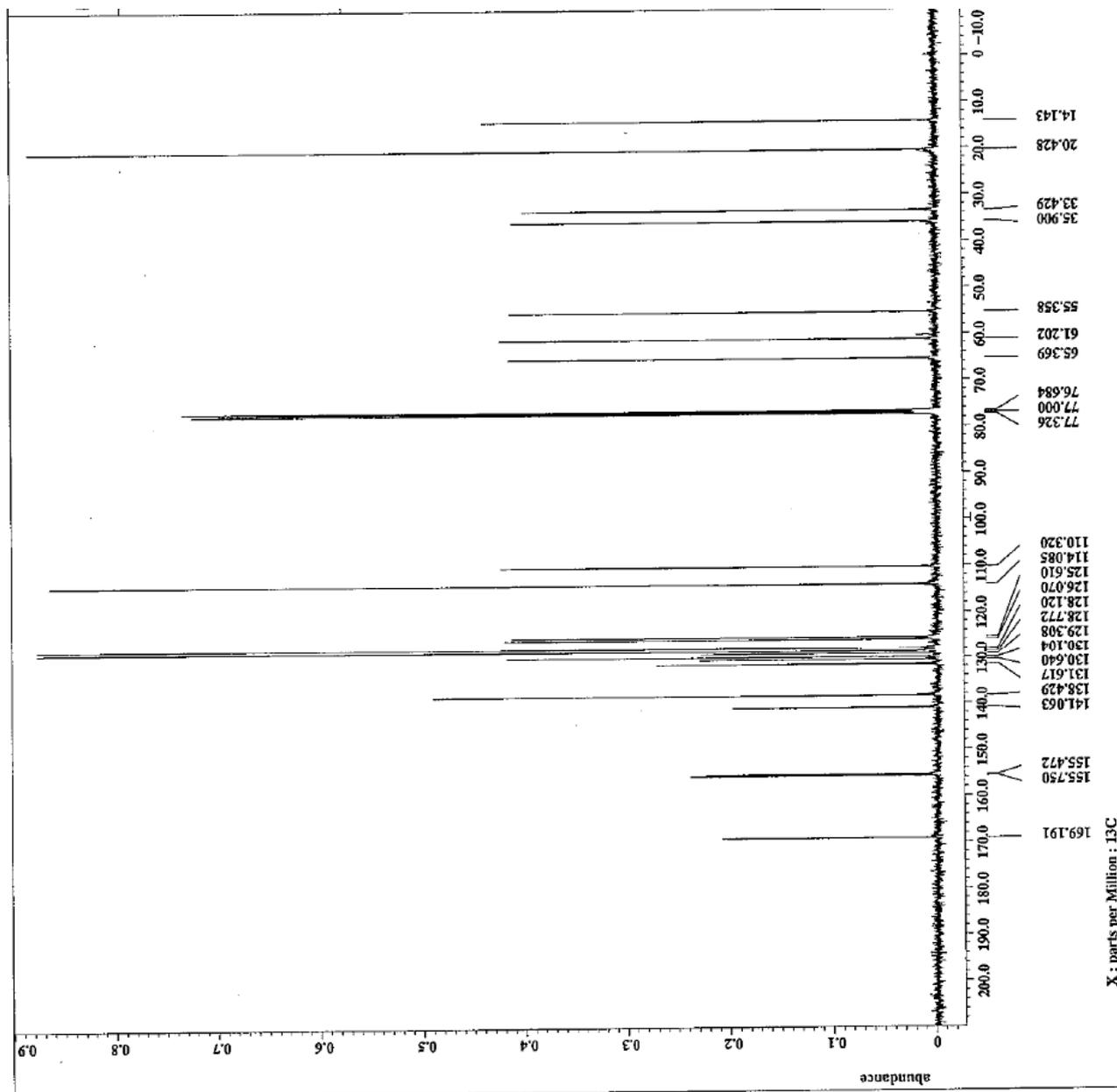
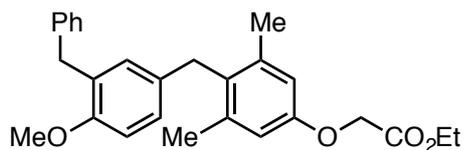
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 12



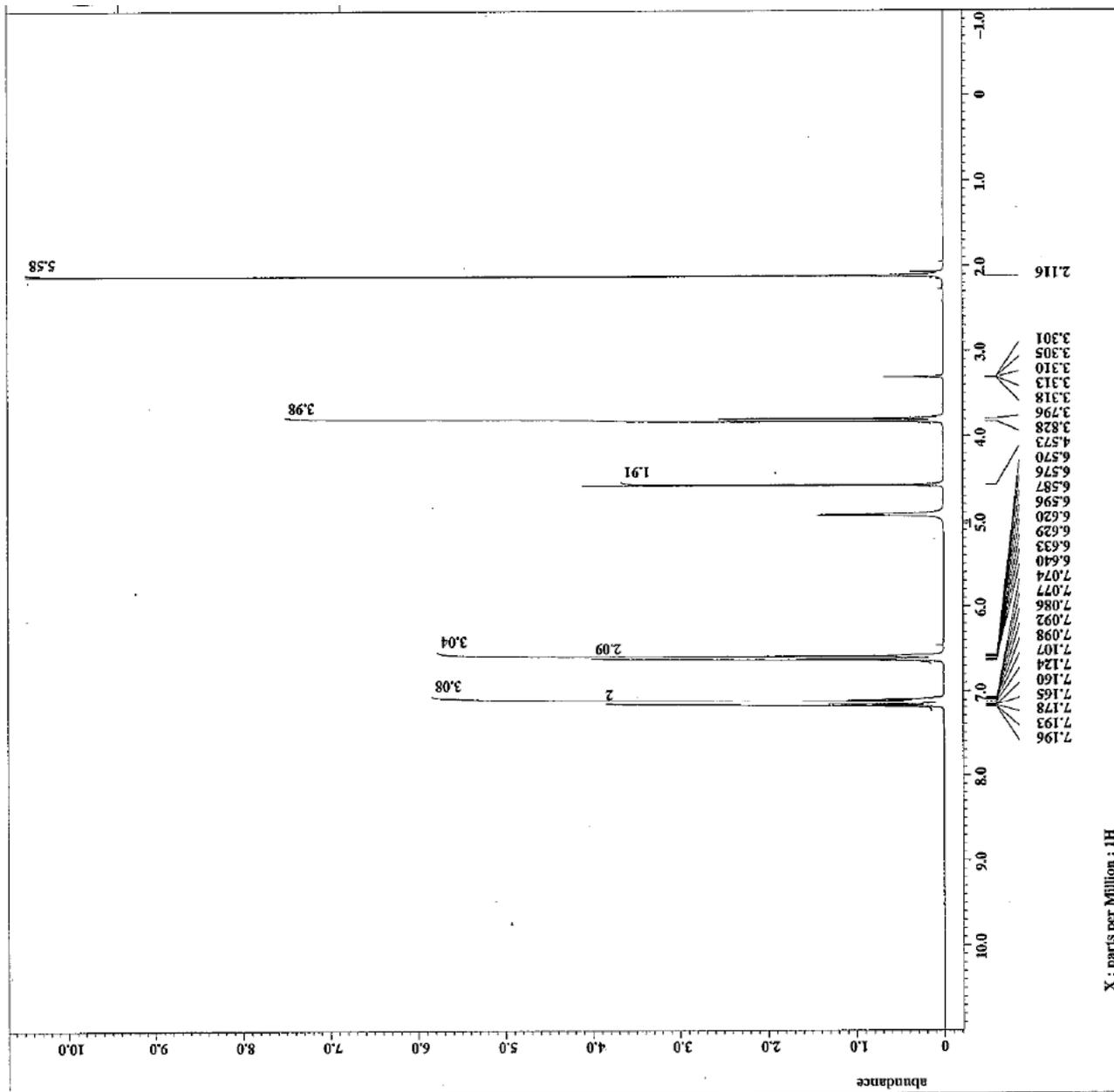
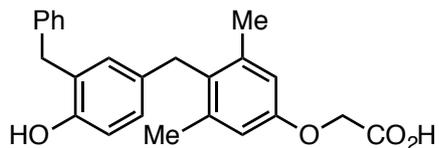
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) of 13



<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of 13



<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD) of GC-24



<sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD) of GC-24

