Supporting Information

Room Temperature Activation of Aryloxysulfonyl Azides by [Co(II)(TPP)] for Selective Radical Aziridination of Alkenes via Metalloradical Catalysis

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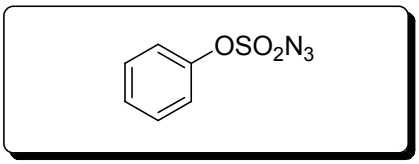
General Considerations. All reactions were carried out under nitrogen atmosphere in an oven-dried glassware following Schlenk techniques. 4 A molecular sieves were dried in a vaccum oven prior to use. Chlorobenzene were dried over calcium hydride under nitrogen and freshly distilled before use. Toluene and tetrahydrofuran were dried by refluxing over sodium benzophenone. All olefins were purchased from Acros or Aldrich Chemicals and used without further purification. All other solvents were dried by refluxing over calcium hydride. Cobalt tetraphenylporphyrin was purchased from Strem. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 spectrometer and referenced with respect to residual solvent. Thin layer chromatography was carried out on E. Merck Silica Gel 60 F-254 TLC plates.

Synthesis of Phenoxysulfonyl Azide. The phenol (10 mmol) was dissolved in DCM (20 mL). Pyridine (10 mL) was added in one portion at 0^{o} C, and the resulting solution was stirred for 15-20 minutes. Sulfuryl chloride (1.78 mL, 22 mmol in 20 mL DCM) was added dropwise over 20-30 minutes. The reaction mixture was allowed to warm up to room temperature and stirred overnight. After the reaction was complete, the flask underwent rotary evaporation until the DCM was removed. The residue was dissolved in 10 mL CH_3CN and the solution was stirred at 0 °C for 15-20 minutes. Sodium azide (1.95 g, 1.5 eq) was added in one portion to the sufuryl chloride mixture and the reaction mixture was allowed to

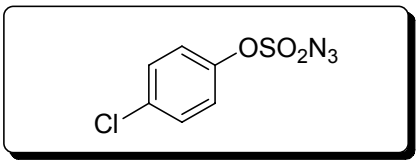
warm up to room temperature and stirred overnight. After the reaction was complete, the flask underwent rotary evaporation until the acetonitrile was removed. The crude product was extracted from the water using ethyl acetate (3 x 50 mL). It was then washed with brine (20 mL), dried over sodium sulfate, and concentrated by rotary evaporation. The resulting oil was then purified by flash column chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford a colorless oily liquid.



Compound **2a:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.40 (m, 5H).

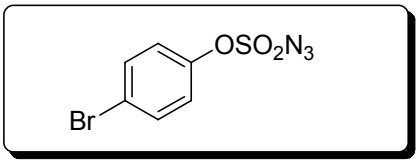
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.68, 130.83, 129.37, 122.26.



Compound **2b:**

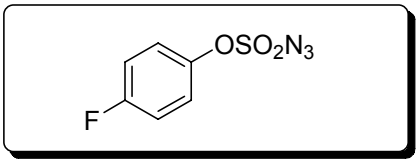
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 2H, *J* = 7.2 Hz), 7.23 (d, 2H, *J* = 7.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.33, 134.37, 130.59, 123.19.

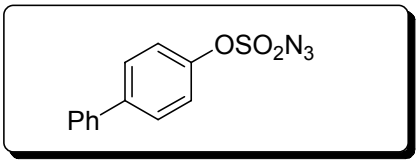


Compound **2c:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 2H, *J* = 8.8 Hz), 7.24 (d, 2H, *J* = 8.8 Hz).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.91, 133.62, 123.53, 122.15.



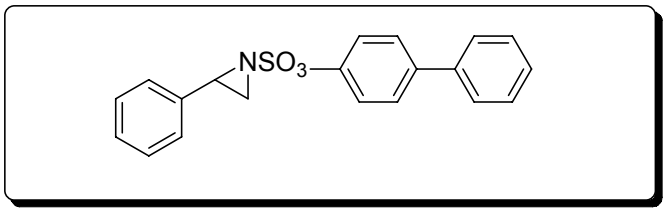
Compound **2d:**
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.41 (m, 2 H), 7.26-7.22 (m, 2 H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.89 (d, *J* = 248 Hz), 145.74, 123.62 (d, *J* = 9 Hz), 117.30 (d, *J* = 23 Hz).



Compound **2e:**
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.39 (m, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.33, 141.81, 139.64, 129.19, 129.11, 128.23, 127.41, 122.05.

General Procedure for the Aziridination of Styrene with Aryloxysulfonyl azides. An oven dried schlenk tube was equipped with a stir bar, degassed on a vacuum line, and purged with nitrogen. The tube was charged with cobalt tetraphenyl porphyrin (5 mol%), and 5 angstrom molecular sieves (100 mg). The tube was fitted with a Teflon screw cap and evacuated for 30 min, and then the tube was backfilled with nitrogen. The Teflon screw cap was replaced with a rubber septum. Styrene (0.5 mmol) was added followed by the azide **2** (0.1 mmol) and 1mL of PhCl. The tube was then purged with nitrogen for 1 min and

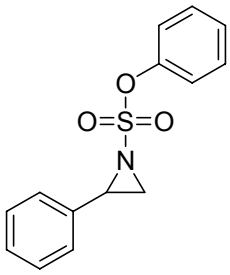
the Teflon screw cap was replaced. The reaction was stirred at room temperature overnight for 20 h. After completion, the reaction was concentrated under vacuum. The concentrated was purified by flash chromatography to afford pure product.



Compound **4ea**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 - 7.45 (m, 14H), 3.73 (dd, 1H, J = 7.2, 4.8 Hz), 2.98 (d, 1H, J = 7.2 Hz), 2.548 (d, 1H, J = 4.4 Hz).

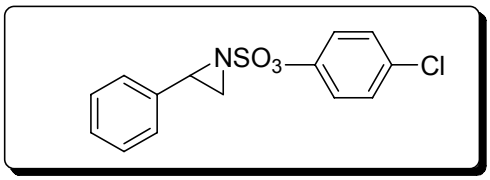
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.898, 140.723, 140.048, 134.234, 129.08, 129.02, 128.95, 128.58, 127.90, 127.351, 126.75, 122.42, 43.26, 37.73.



Compound **4aa:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 10H), 3.81 (dd, 1H, *J* = 7.2, 4.5 Hz), 3.06 (d, 1H, *J* = *7.*2 H), 2.57 (d, 1H, *J* = 4.5 Hz).

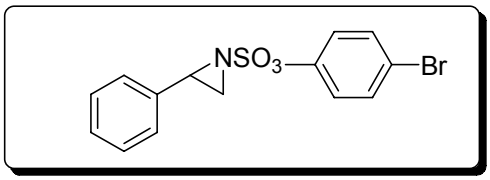
^{13}C (100 MHz, $CDCl_3$): δ 150.34, 134.04, 129.67, 128.74, 128.69, 127.28, 126.51, 121.89, 42.89, 37.48.



Compound **4ba:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.42-7.22 (m, 9H), 3.86 (dd, 1H, J_1 = 7.2, 4.8 Hz), 3.12 (d, 1H, *J* = 7.2 Hz), 2.64 (d, 1H, *J* = 4.8 Hz).

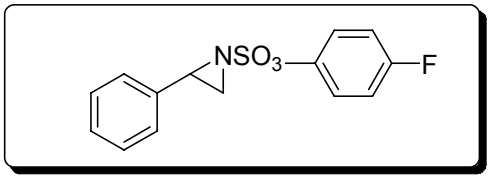
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.93, 134.02, 133.23, 129.99, 129.14, 126.71, 123.57, 43.36, 37.77.



Compound **4ca:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.26 - 7.23 (m, 3H), 7.14 - 7.09 (m, 4H), 6.90 - 6.86 (m, 2H), 3.70 (dd, 1H, J_1 = 7.2, 4.4 Hz), 2.96 (d, 1H, *J* = 7.2 Hz), 2.48 (d, 1H, *J* = 4.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.91, 146.63, 134.42, 129.43, 129.32, 127.03, 124.21, 124.12, 43.61, 38.07.



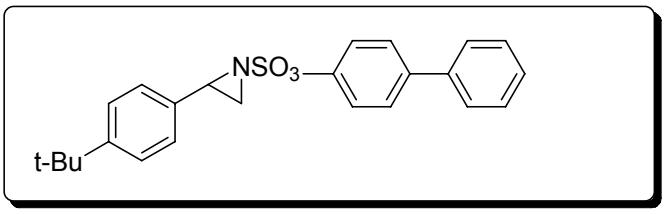
Compound **4da:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.26 - 7.23 (m, 3 H), 7.14 - 7.09 (m, 4 H), 6.90 - 6.86 (m, 2 H), 3.70 (dd, 1 H, *J* = 7.2, 4.4 Hz), 2.96 (d, 1 H, *J* = 7.2 Hz), 2.48 (d, 1 H, *J* = 4.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.68 (d, J = 246 Hz), 146.63, 134.42, 129.38 (d, J = 11 Hz), 127.03, 124.17 (d, J = 9 Hz), 117.00, 43.61, 38.07.

General Procedure for the Aziridination of olefins with Aryloxysulfonyl azides. An oven dried schlenk tube was equipped with a stir bar, degassed on a vacuum line, and purged with nitrogen. The tube was charged with cobalt tetraphenyl porphyrin (5 mol%), and 5 angstrom molecular sieves (100 mg). The

tube was fitted with a Teflon screw cap and evacuated for 30 min, and then the tube was backfilled with nitrogen. The Teflon screw cap was replaced with a rubber septum. Olefin **3** (0.5 mmol) was added followed by the azide **2** (0.1 mmol) and 1mL of PhCl. The tube was then purged with nitrogen for 1 min and the Teflon screw cap was replaced. The reaction was stirred at room temperature overnight for 20 h. After completion, the reaction was concentrated under vacuum. The concentrated was purified by flash chromatography to afford pure product.



Compound **4eb:**

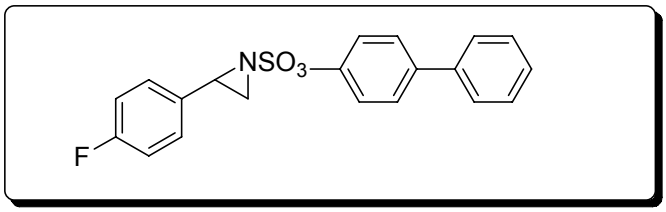
^{1}H NMR (400MHz, $CDCl_3$): δ 7.48 - 7.11 (m, 13 H), 3.73 (dd, 1 H, *J* = 7.2, 4.4 Hz), 2.99 (d, 1 H, *J* = 7.2 Hz), 2.44 (d, 1 H, *J* = 4.4 Hz), 1.20 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.00, 149.92, 140.73, 139.89, 129.14, 128.66, 128.01, 127.34, 127.13, 126.96, 122.29, 42.36, 37.88, 34.00, 31.00.

Compound **4ec:**

^{1}H NMR (400MHz, $CDCl_3$): 6.97 - 7.44 (m, 13 H), 3.74 (dd, 1 H, *J* = 7.2, 4.8 Hz), 2.98 (d, 1 H, *J* = 7.2 Hz), 2.50 (d, 1 H, *J* = 4.8 Hz), 2.24 (s, 3 H).

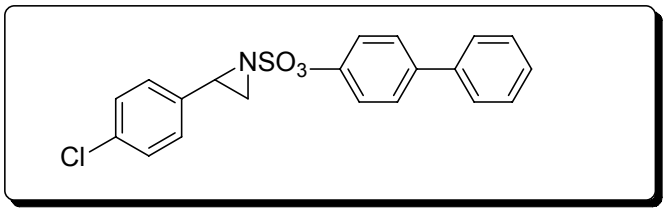
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.92, 140.73, 140.08, 138.77, 134.14, 129.79, 129.09, 128.86, 128.58, 127.90, 127.36, 123.88, 122.47, 43.32, 37.68, 21.56.



Compound **4ed:**

^{1}H NMR (400MHz, $CDCl_3$): δ 6.94 - 7.54 (m, 13 H), 3.74 (dd, 1 H, *J* = 7.2, 4.8 Hz), 3.01 (d, 1 H, *J* = 6.8 Hz), 2.49 (d, 1 H, *J* = 4.8 Hz).

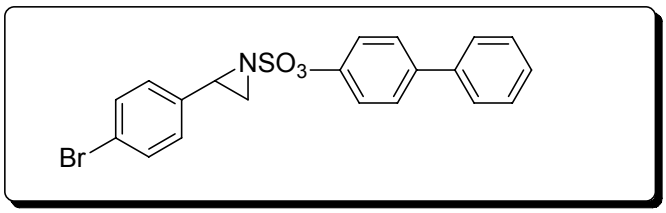
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.19 (d, *J* = 247 Hz), 149.86, 140.82, 139.98, 130.07, 128.12. 128.62. 128.50, 127.97, 127.35, 122.37, 116.03 (d, *J* = 22 Hz), 42.60, 37.76.



Compound **4ee:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.09 - 7.53 (m, 13 H), 3.72 (dd, 1 H, *J* = 7.2, 4.4 Hz), 3.01 (d, 1 H, *J* = 7.2 Hz), 2.48 (d, 1 H, *J* = 4.4 Hz).

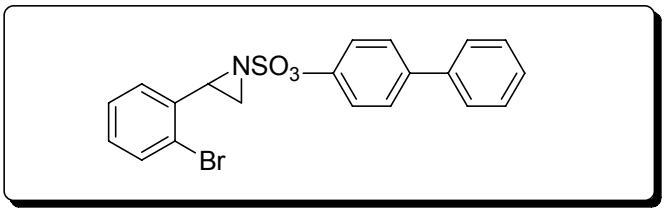
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.85, 140.85, 139.95, 134.99, 132.85, 129.21, 129.13, 128.63, 128.11, 127.97, 127.36, 122.35, 42.54, 37.75.



Compound **4ef:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.03- 7.47 (m, 13 H), 3.70 (dd, 1 H, *J* = 7.2, 4.4 Hz), 3.01 (d, 1 H, *J* = 7.2 Hz), 2.48 (d, 1 H, *J* = 4.8 Hz).

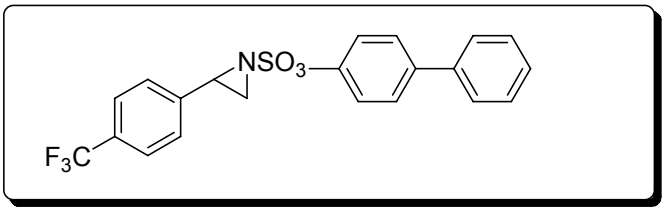
^{13}C NMR (100 MHz, $CDCl_3$): 149.83, 140.84, 139.94, 133.38, 132.15, 129.13, 128.62, 128.39, 127.97, 127.35, 123.09, 122.34, 42.59, 37.70.



Compound **4eg:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.48 - 7.11 (m, 13 H), 3.73 (dd, 1 H, J = 7.2, 4.4 Hz), 2.99 (d, 1 H, J = 7.2 Hz), 2.44 (d, 1 H, J = 4.4 Hz).

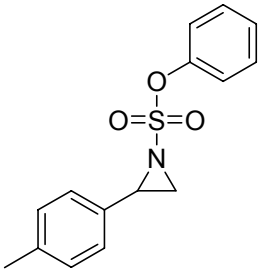
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.92, 140.73, 139.89, 128.43, 131.42, 131.09, 129.14, 128.66, 128.02, 127.34, 127.13, 126.96, 122.29, 42.36, 37.88.



Compound **4eh:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.48 - 7.11 (m, 13 H), 3.73 (dd, 1 H, *J* = 7.2, 4.4 Hz), 2.99 (d, 1 H, *J* = 7.2 Hz), 2.44 (d, 1 H, *J* = 4.4 Hz).

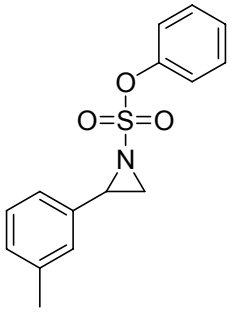
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.92, 140.73, 139.89, 138.00, 129.14, 128.66, 128.015, 127.34, 127.13, 126.96, 122.29, 42.36, 37.88.



Compound **4ai:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 5 H), 7.15 (m, 4 H), 3.780 (dd, 1 H, *J* = 7.2, 4.8 Hz), 3.04 (1 H, *J* = 7.2 Hz), 2.56 (1 H, *J* = 4.8 Hz).

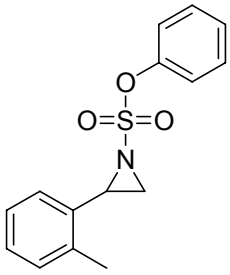
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.37, 138.67, 130.99, 129.67, 129.37, 127.24, 126.45, 121.93, 42.93, 37.40, 21.18.



Compound **4ac:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.30 – 6.8 (m, 9 H), 3.70 (dd, 1 H, *J* = 7.2, 4.8 Hz), 2.90 (1 H, *J* = 7.2 Hz), 2.49 (1 H, *J* = 4.8 Hz), 2.24 (s, 3 H).

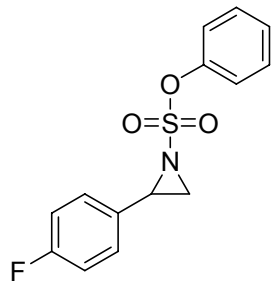
^{13}C NMR (100 MHz, $CDCl_3$ δ 150.27, 139.50, 131.10, 129.80, 127. 50, 126.60, 121.75, 43.10, 37.60, 21.00.



Compound **4aj:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.33 (m, 9 H), 3.94 (dd, 1 H, J_1 = 7.2, 4.5 Hz), 3.07 (d, 1 H, *J* = 7.2 Hz), 2.53 (d, 1 H, *J* = 4.5 Hz), 2.40 (s, 3 H).

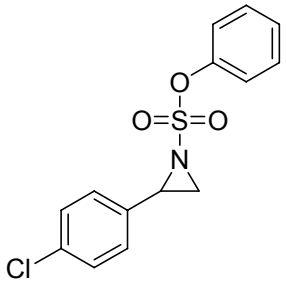
^{13}C NMR (100 MHz, $CDCl_3$): 151.10, 138.00, 132.50, 130.00, 128.50, 127.50, 126.50, 126.00, 122.00, 41.00, 38.00, 19.00.



Compound **4ad:**

^{1}H NMR (400MHz, $CDCl_3$): δ 7.40 -6.90 (m, 9 H), 3.78 (dd, 1 H, *J* = 7.2, 4.5 Hz), 3.04 (d, 1 H, *J* = 7.2 Hz), 2.53 (d, 1 H, *J* = 4.5 Hz).

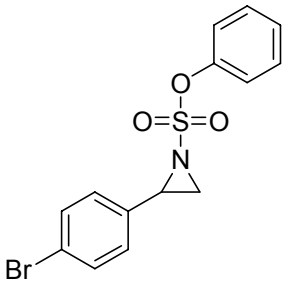
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.41 (d, *J* = 228 Hz), 150.28, 138.10, 129.71, 128.27 (d, *J* = 11 Hz), 127.34, 121.82, 115.74 (d, *J* = 29 Hz), 42.22, 37.48.



Compound **4ae:**

^{1}H NMR (400MHz, $CDCl_3$): 7.25 (m, 9 H), 3.76 (dd, 1 H, *J* = 7.2, 4.5 Hz), 3.05 (d, 1 H, *J* = 7.2 Hz), 2.52 (d, 1 H, *J* = 4.5 Hz).

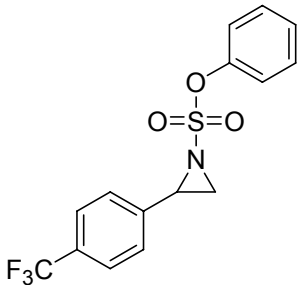
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.28, 138.69, 135.63, 133.00, 130.10, 129.74, 128.92, 121.80, 42.14, 37.49.



Compound **4af:**

^{1}H NMR (400MHz, $CDCl_3$): 7.48 (d, 2 H, *J* = 8.7 Hz), 7.25 (m, 5 H), 7.10 (d, 2 H, *J* = 8.7 Hz), 3.75 (dd, 1 H, *J* = 7.2, 4.8 Hz), 3.05 (d, 1 H, *J* = 7.2 Hz), 2.52 (d, 1 H, *J* = 4.8 Hz).

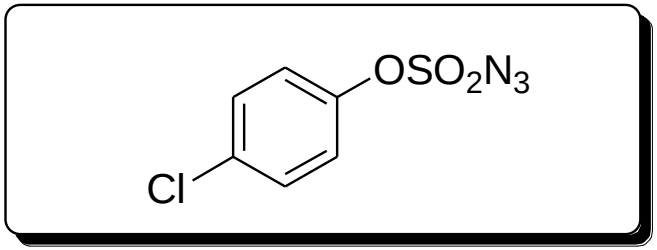
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.26, 136.77, 133.16, 131.86, 129.73, 128.13, 127.37, 121.79, 42.17, 37.44.



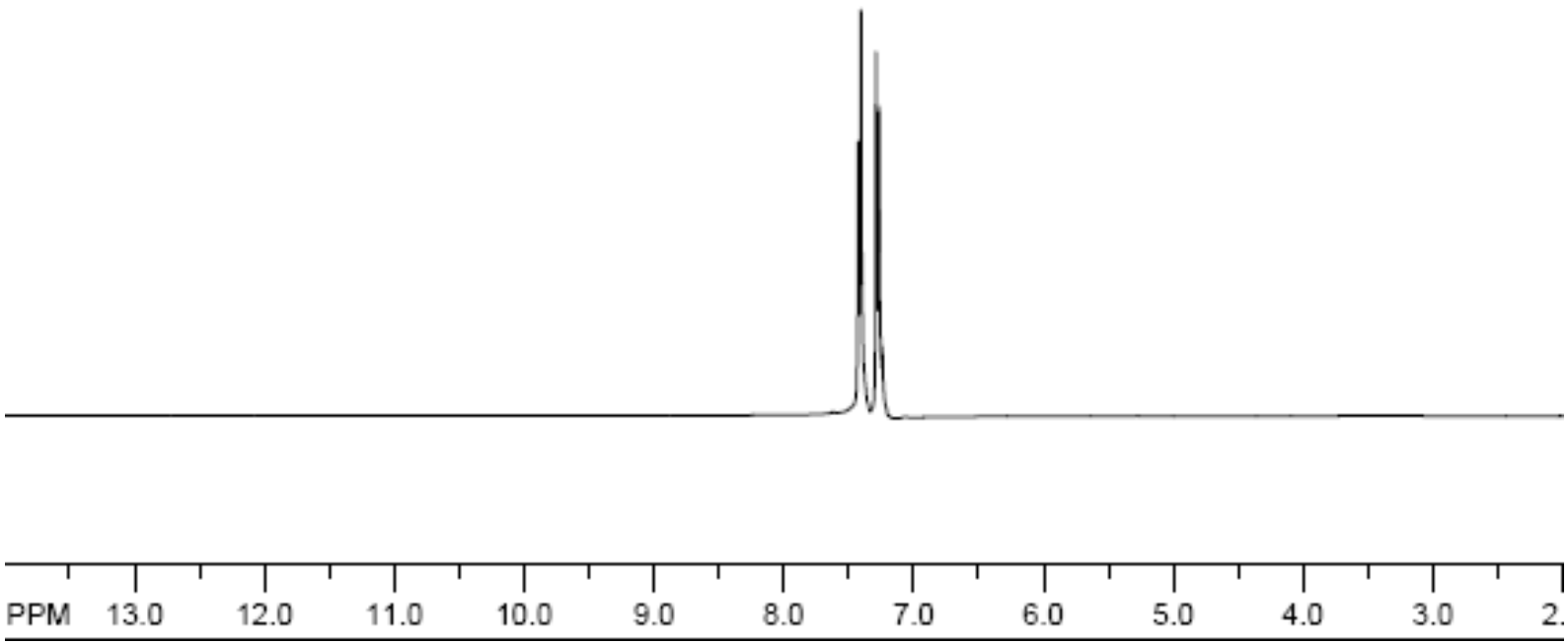
Compound **4ah:**

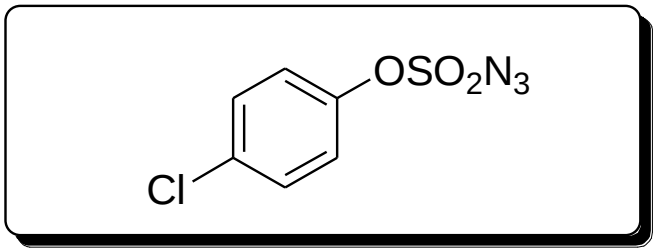
^{1}H NMR (400MHz, $CDCl_3$): δ 7.61 (d, 2 H, *J* = 8.1 Hz), 7.38 (m, 7 H), 3.84 (dd, 1 H, *J* = 7.2, 4.5 Hz), 3.093 (d, 1 H, *J* = 7.2 Hz), 2.55 (d, 1 H, *J* = 4.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.27, 138.23, 136.79, 129.78, 127.45, 126.88, 125.69, 121.75, 41.96, 37.64.

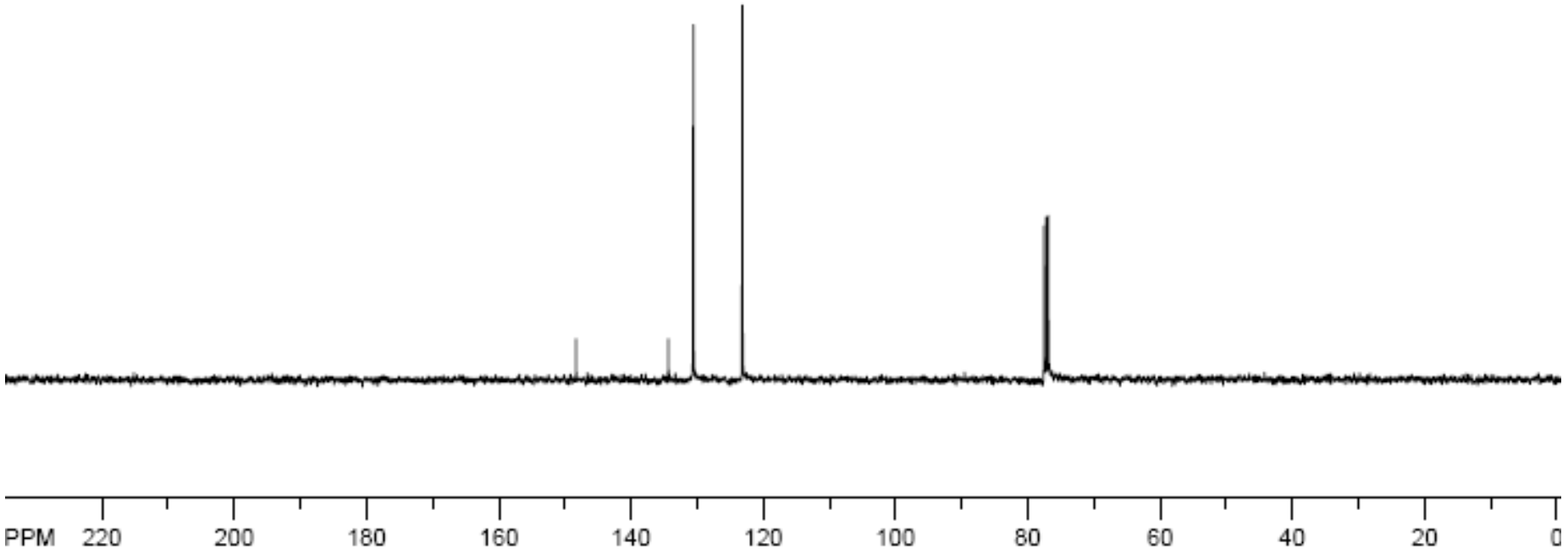


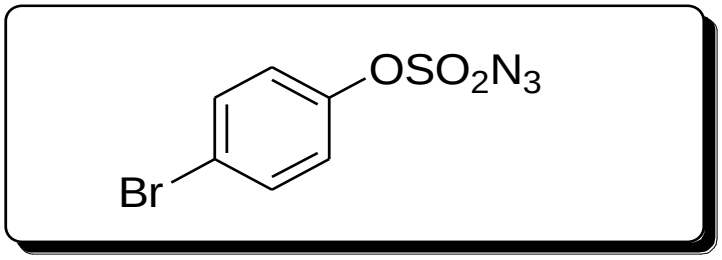
Compound **2b**



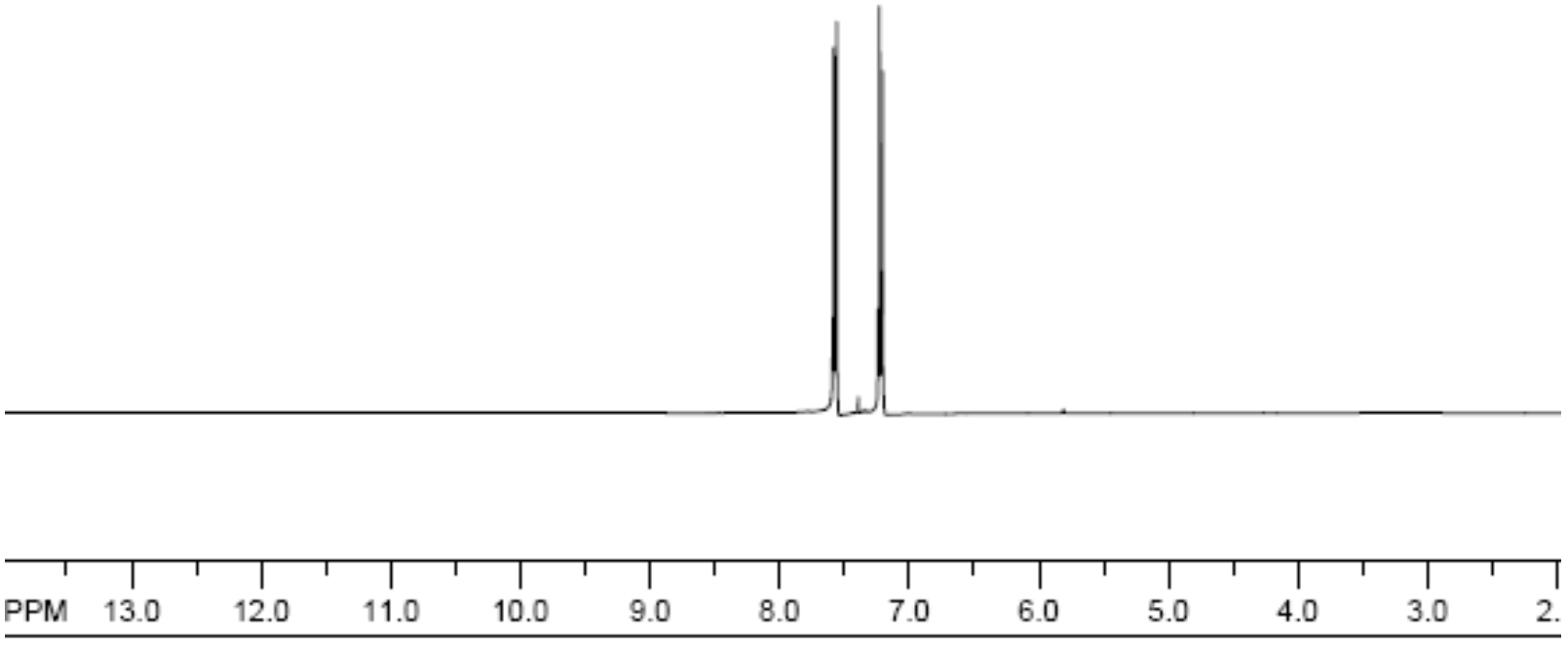


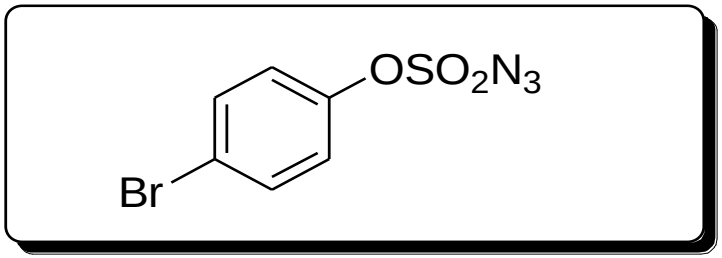
Compound **2b**



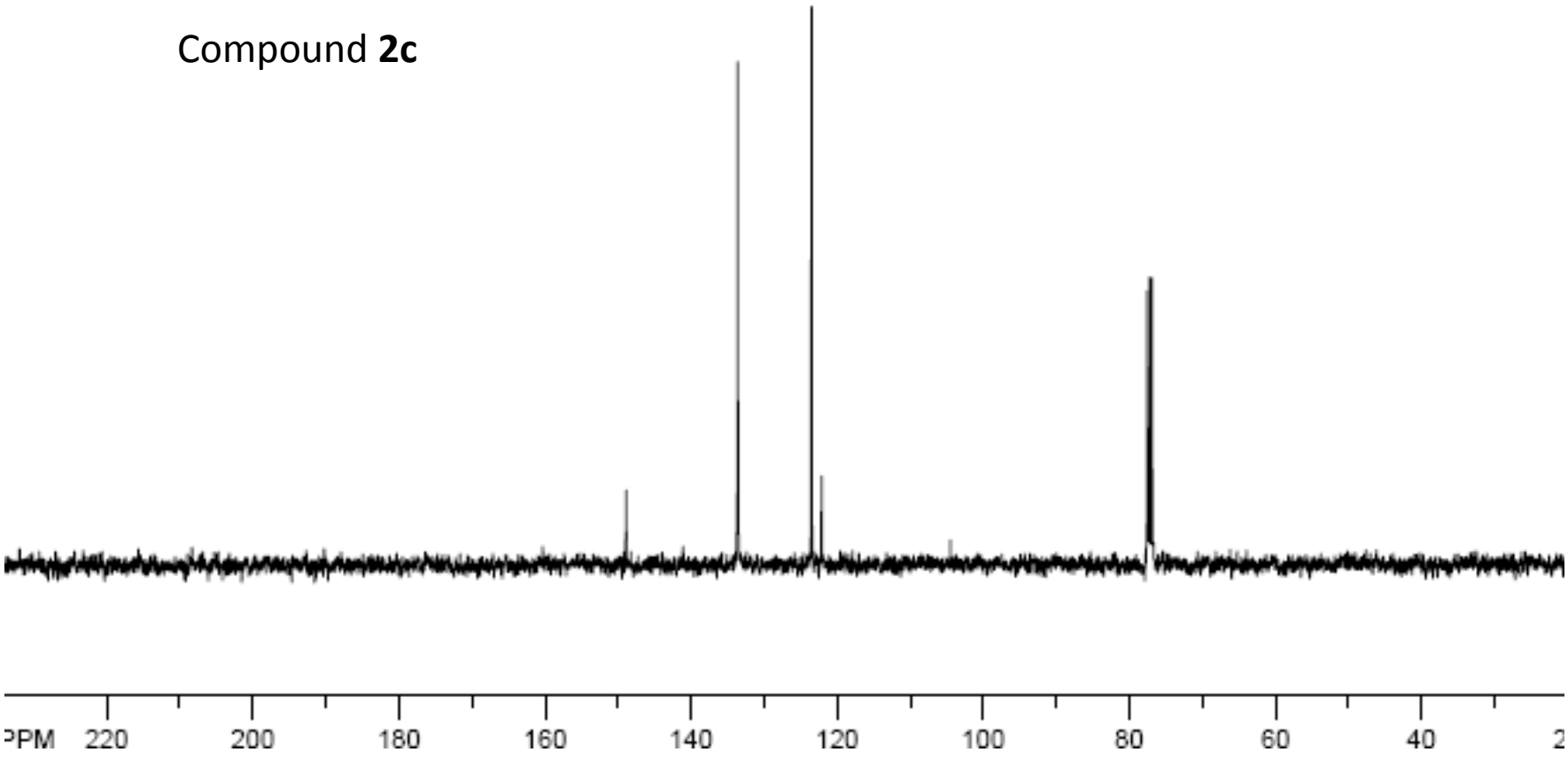


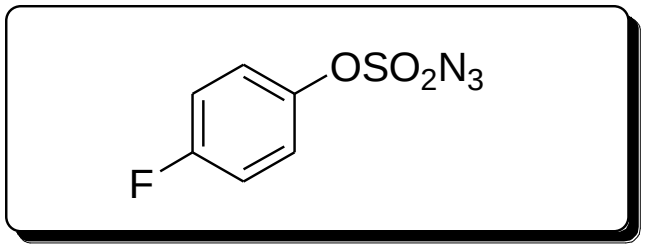
Compound **2c**



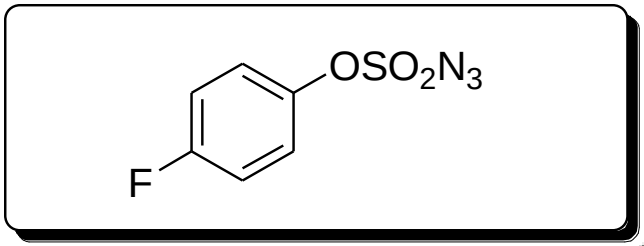


Compound **2c**

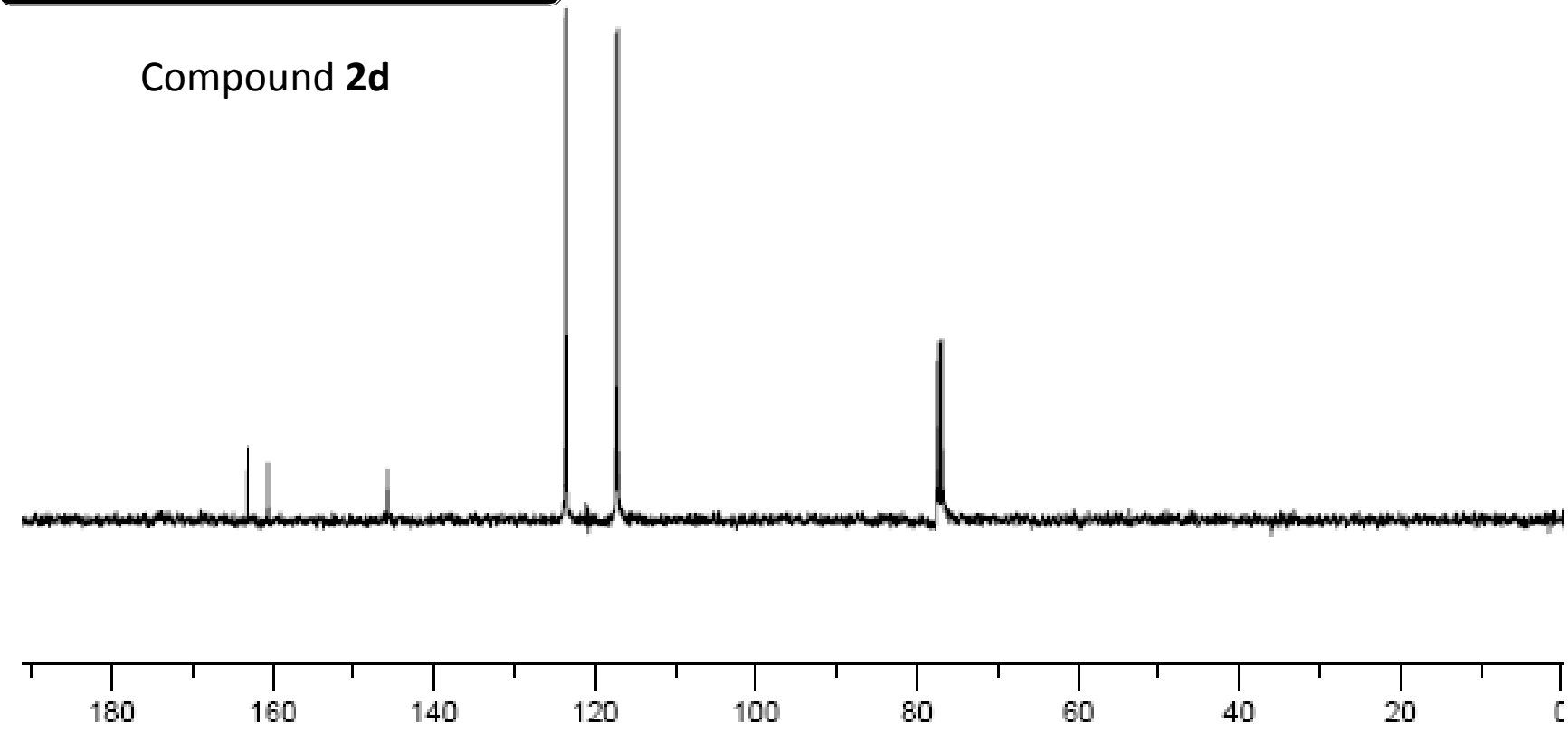


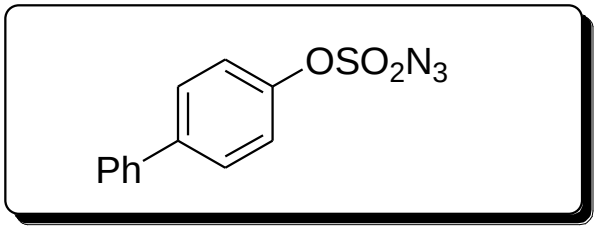


Compound **2d**

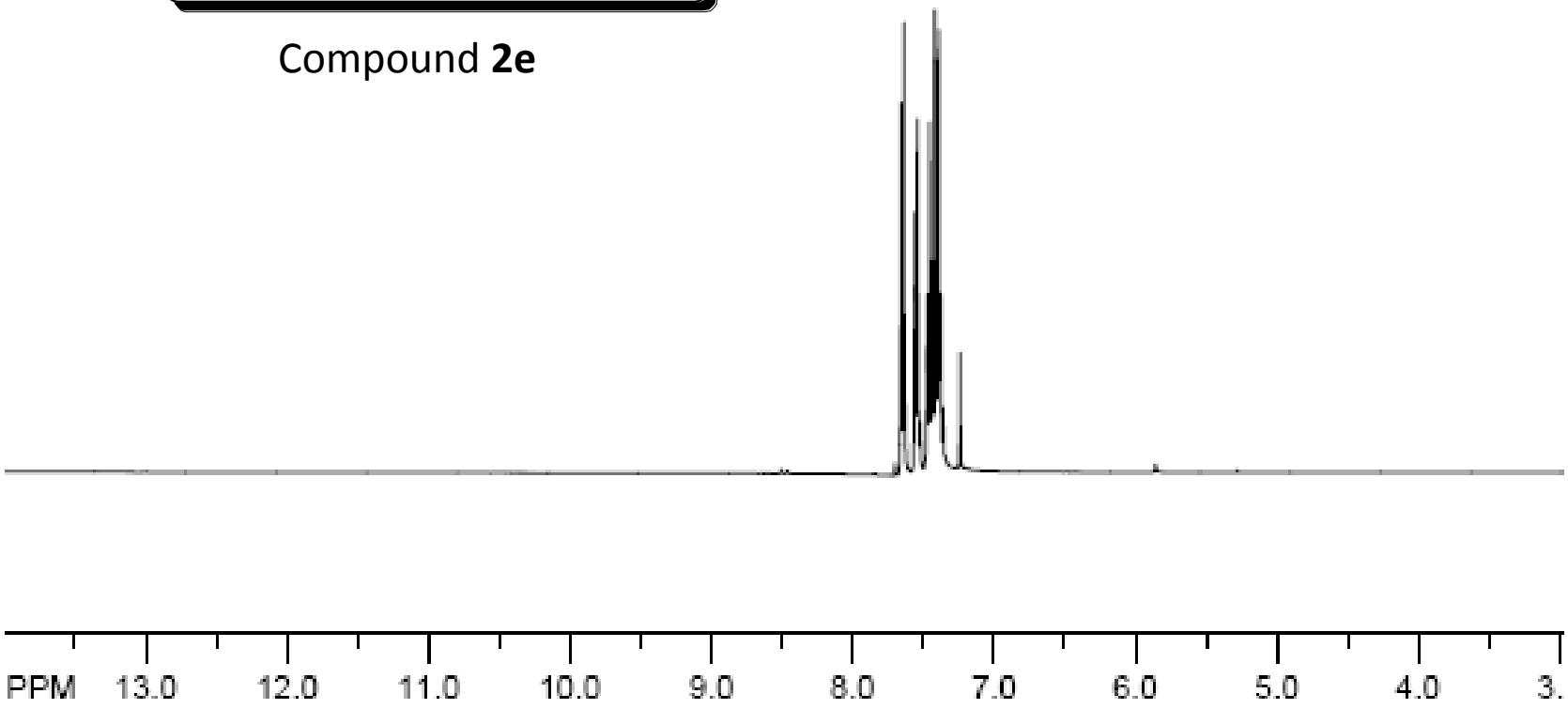


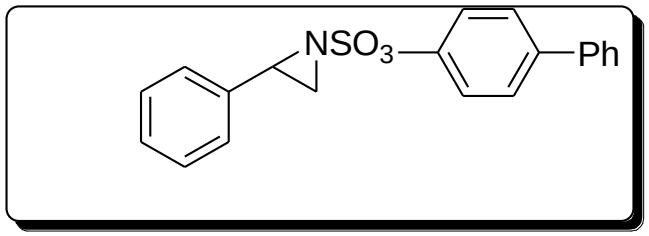
Compound **2d**



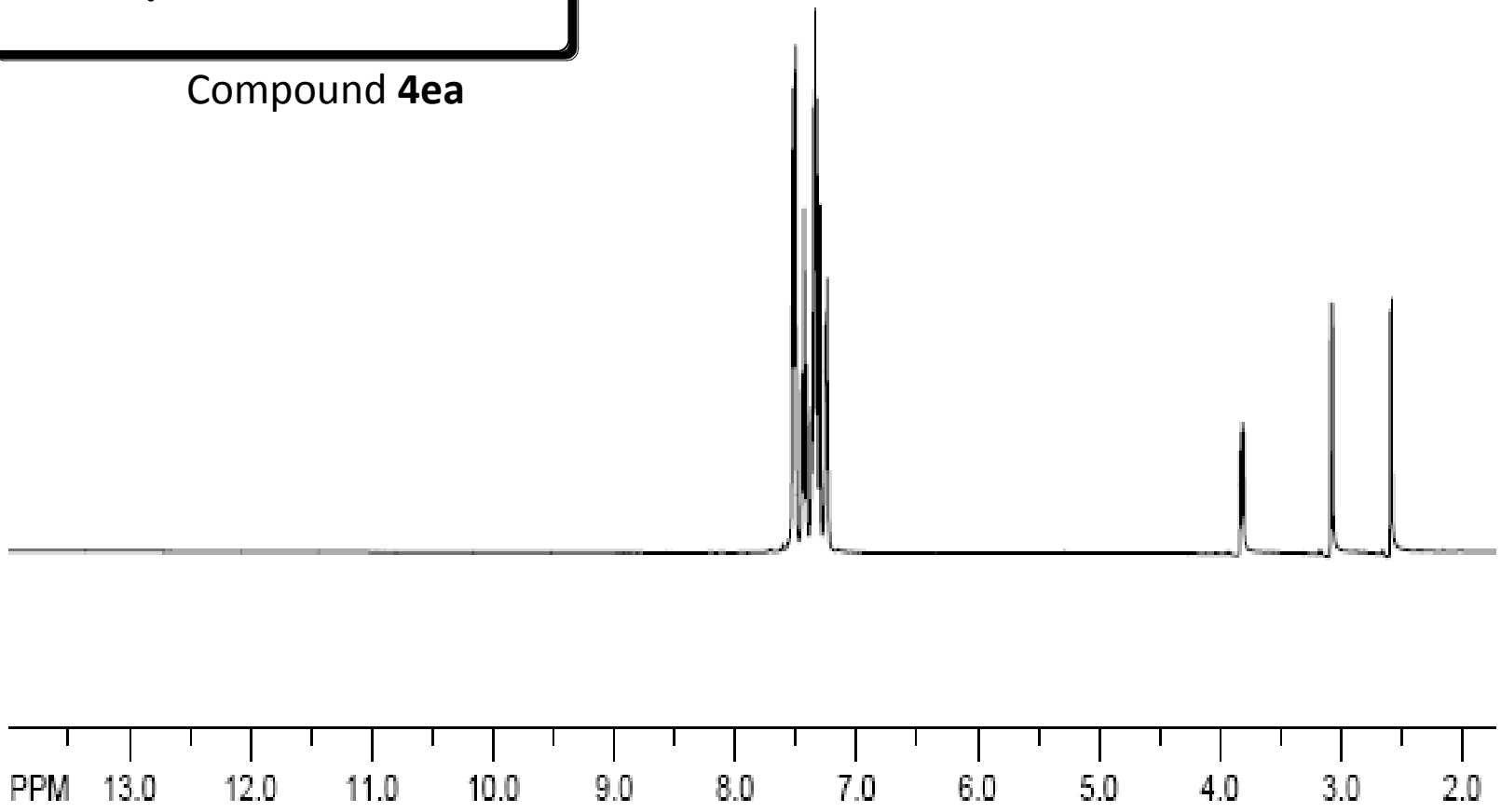


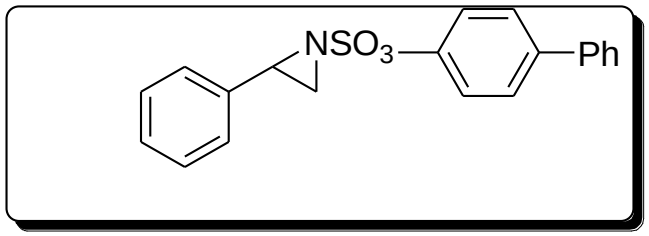
Compound **2e**





Compound **4ea**





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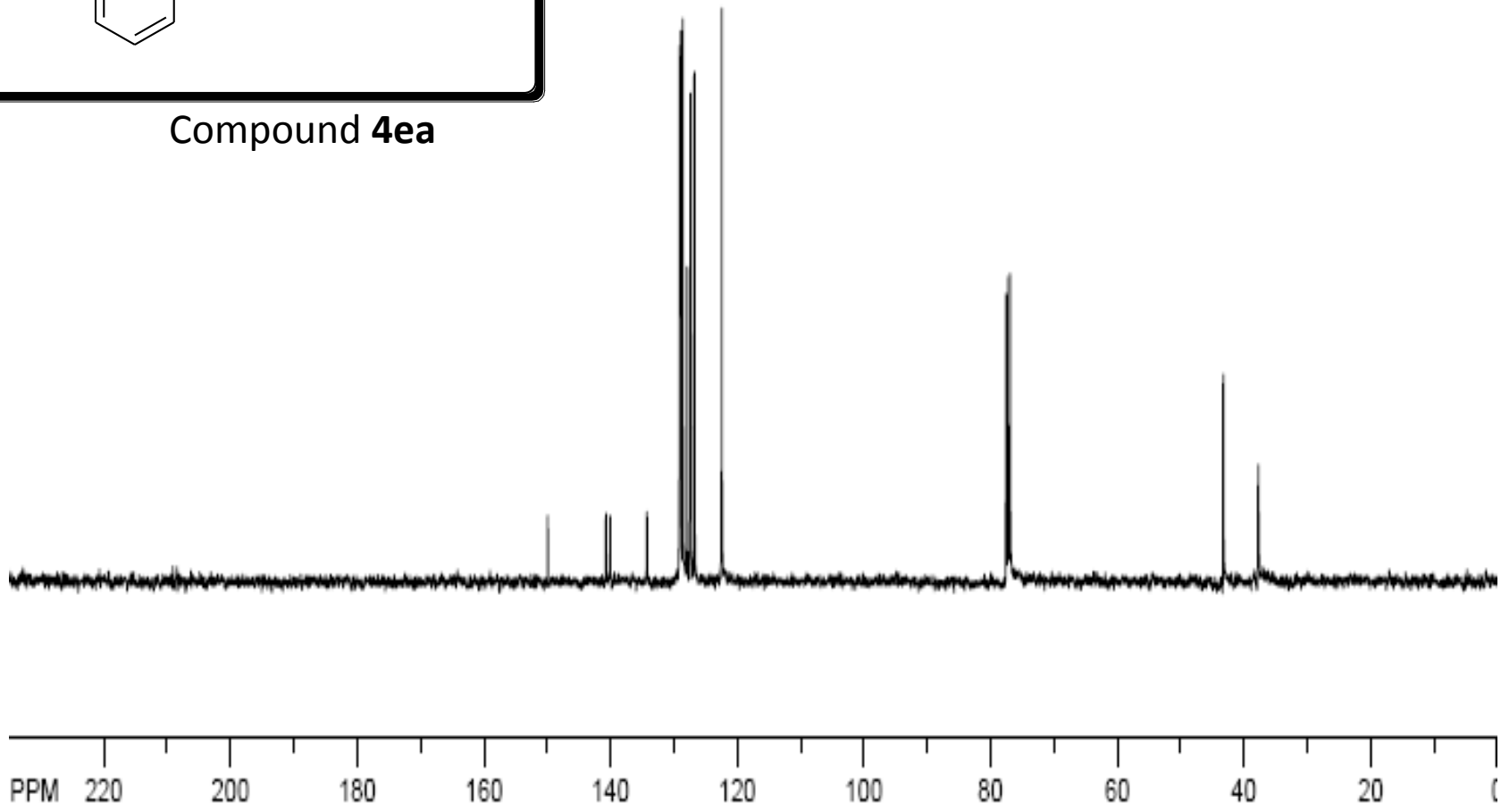
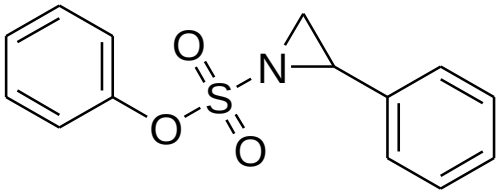
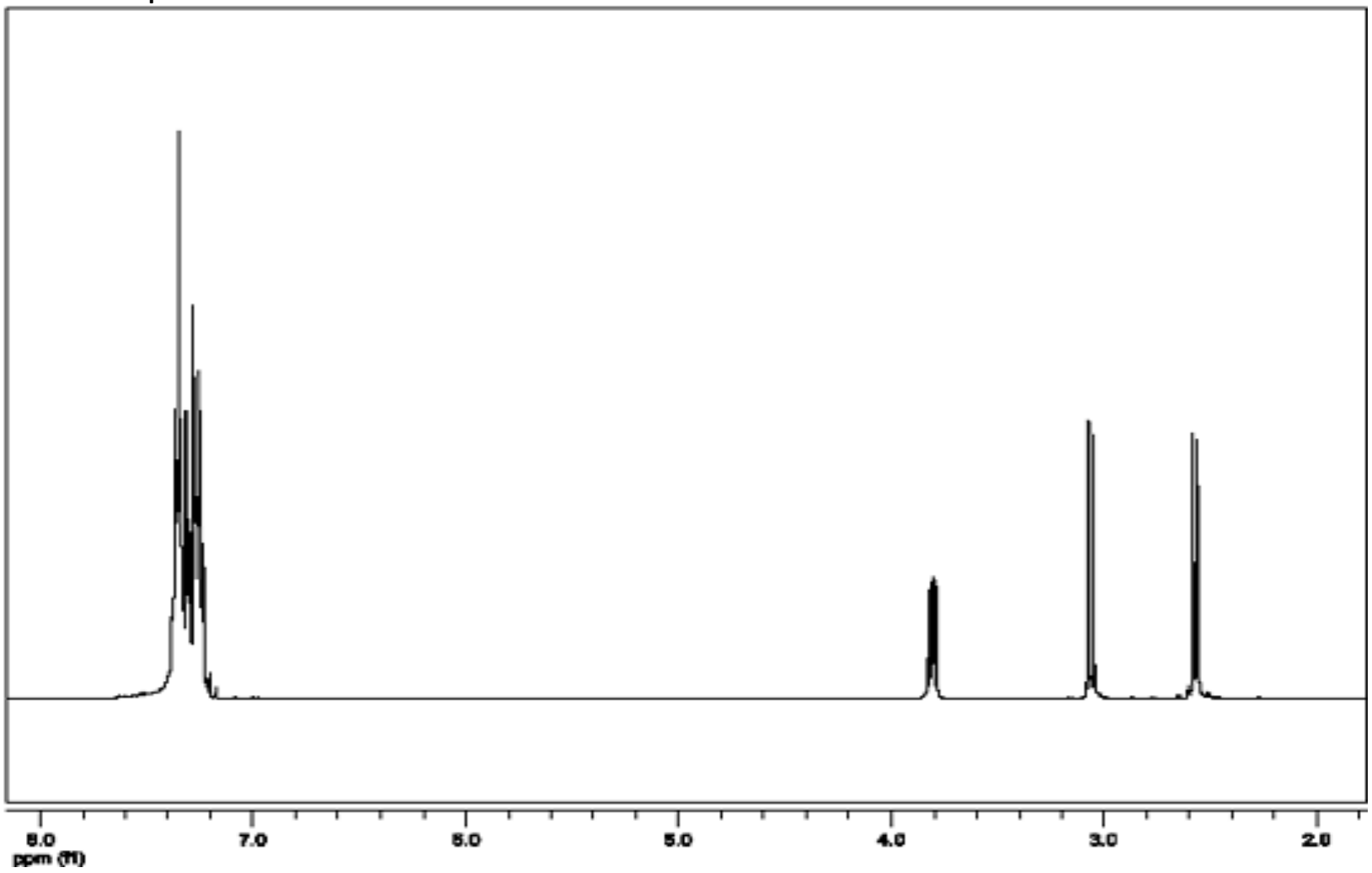
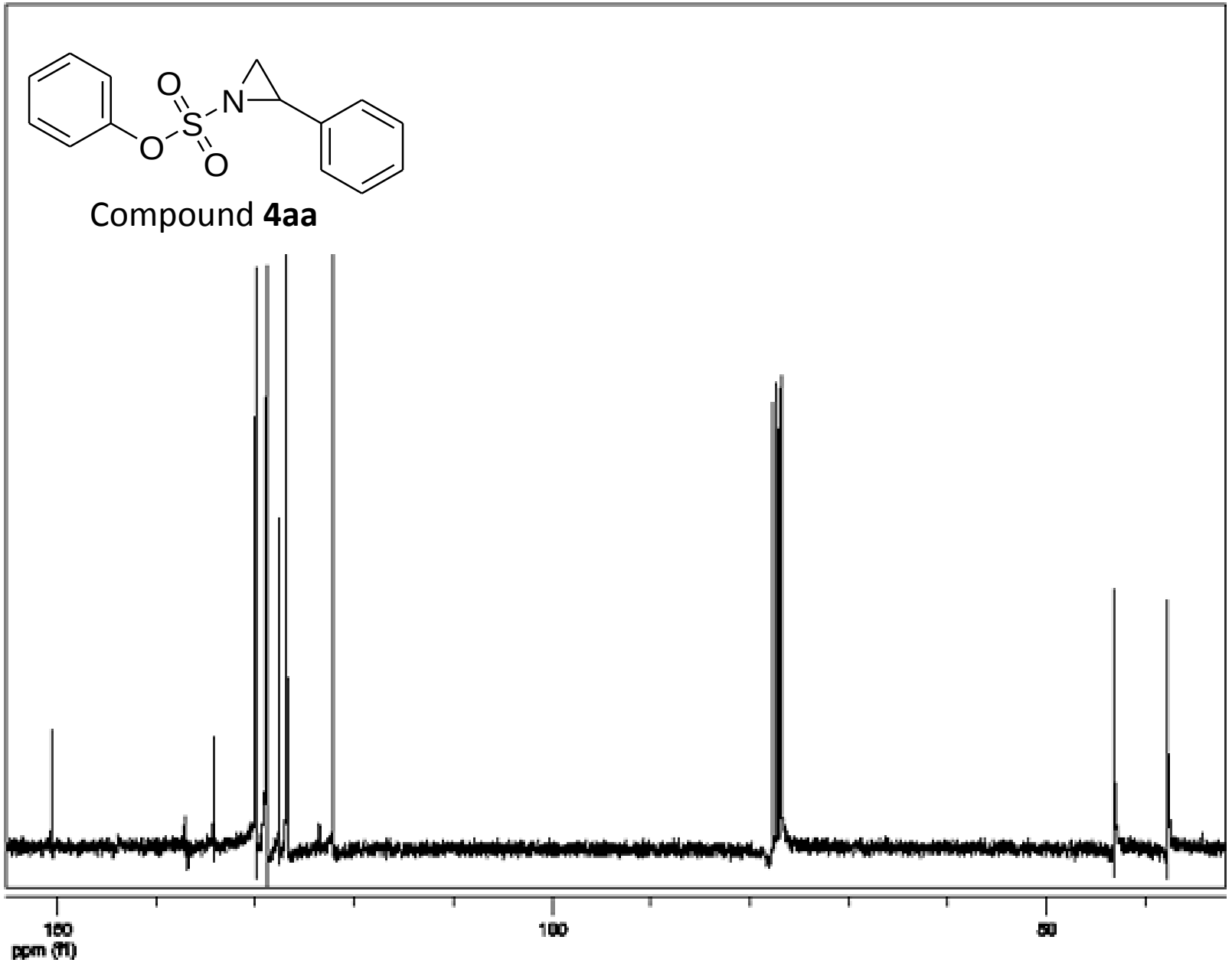
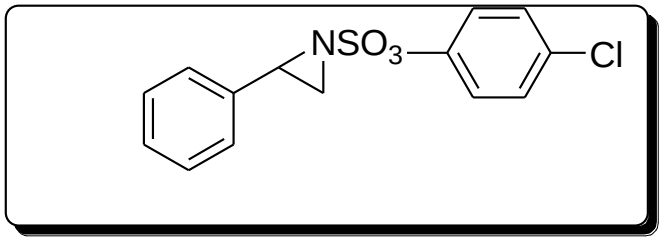




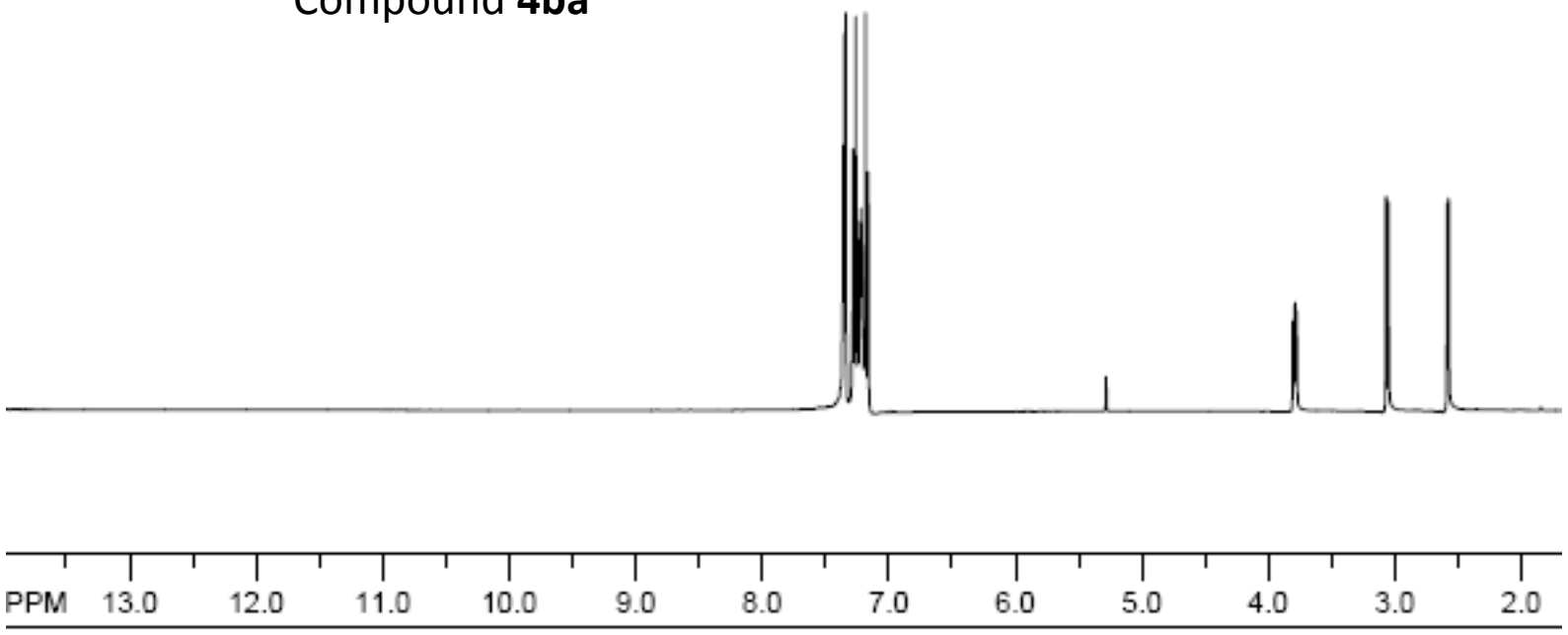
Compound **4aa**

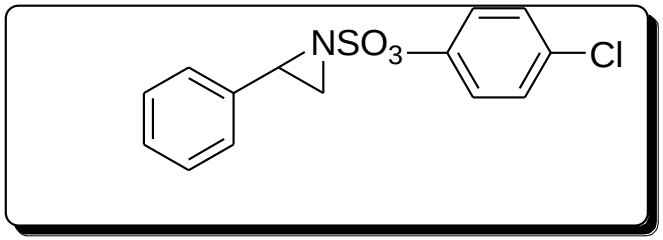



O
S
N
O
O
Compound **4aa**
150
ppm (f1)
100
50

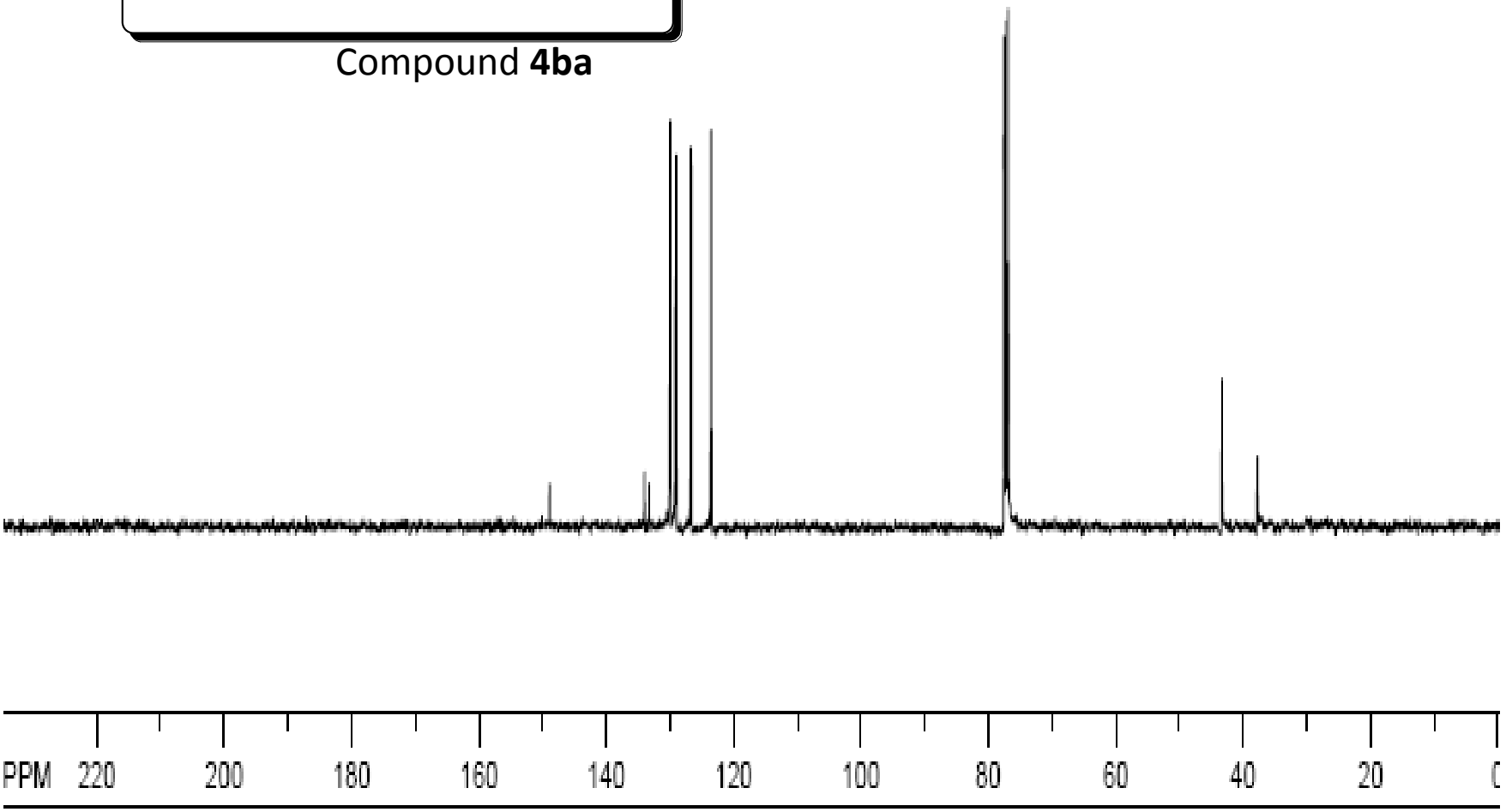


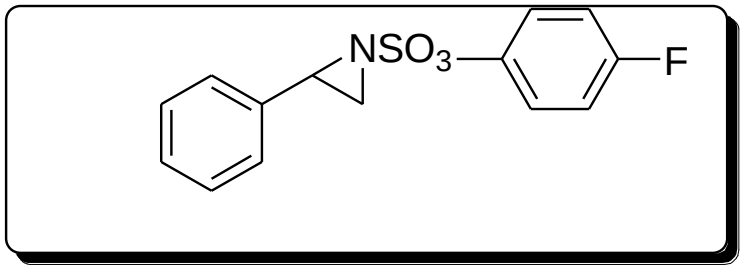
Compound **4ba**



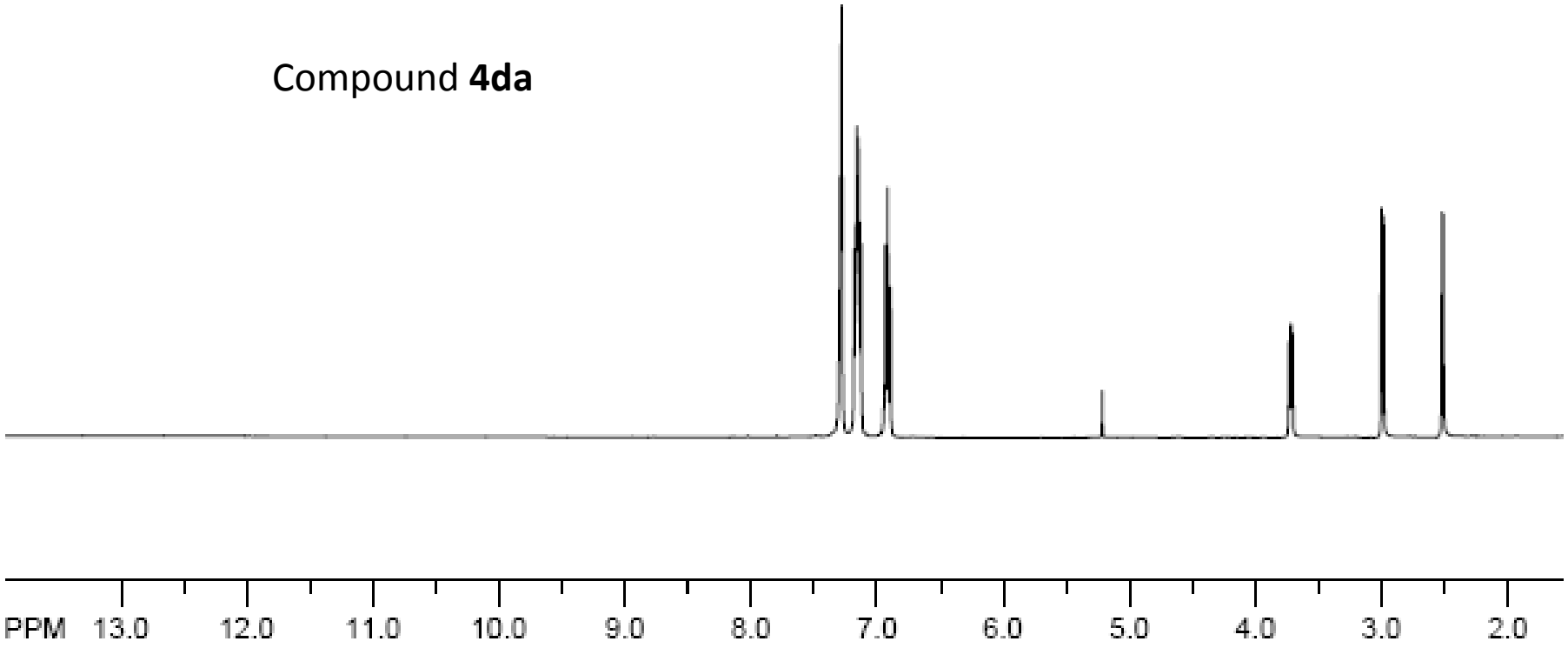


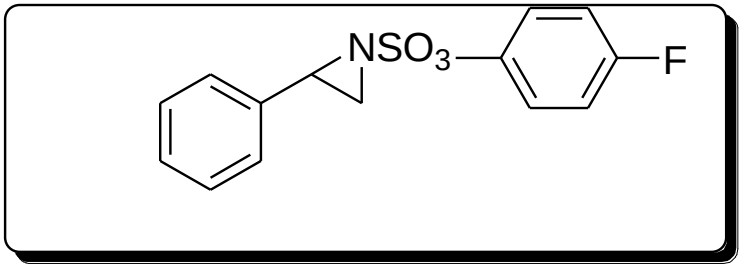
Compound **4ba**



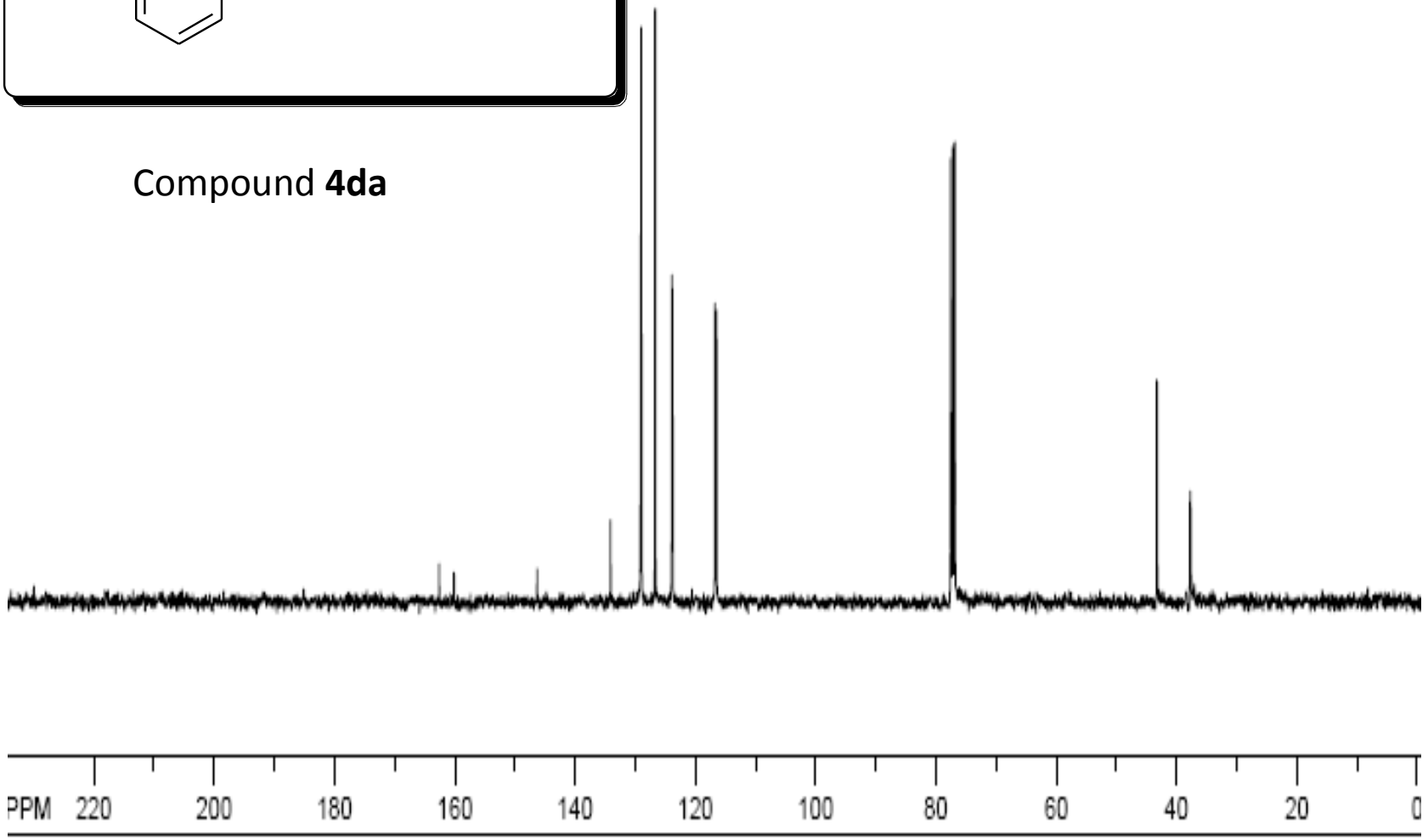


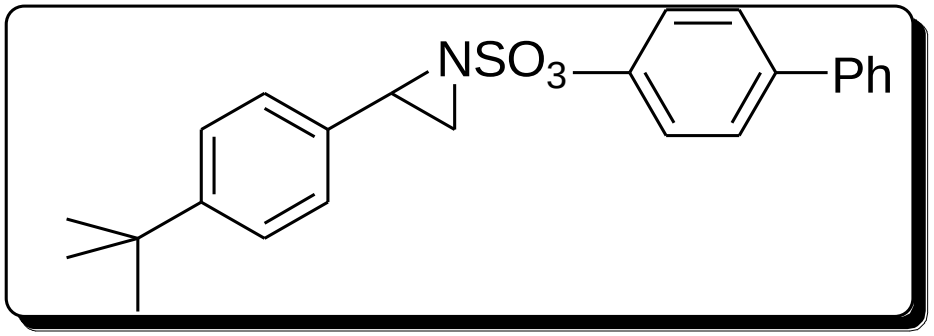
Compound **4da**



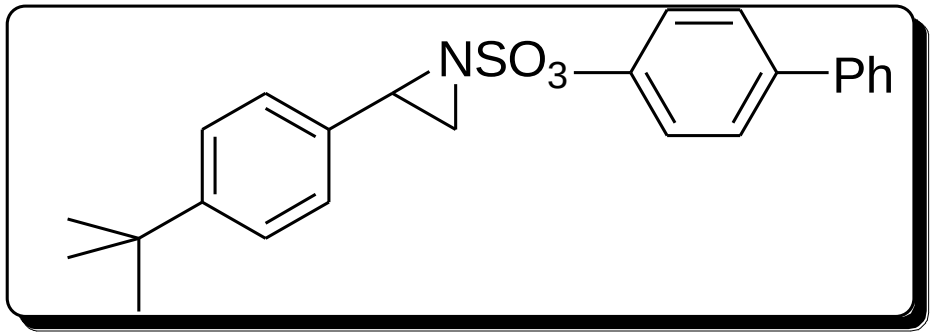


Compound **4da**

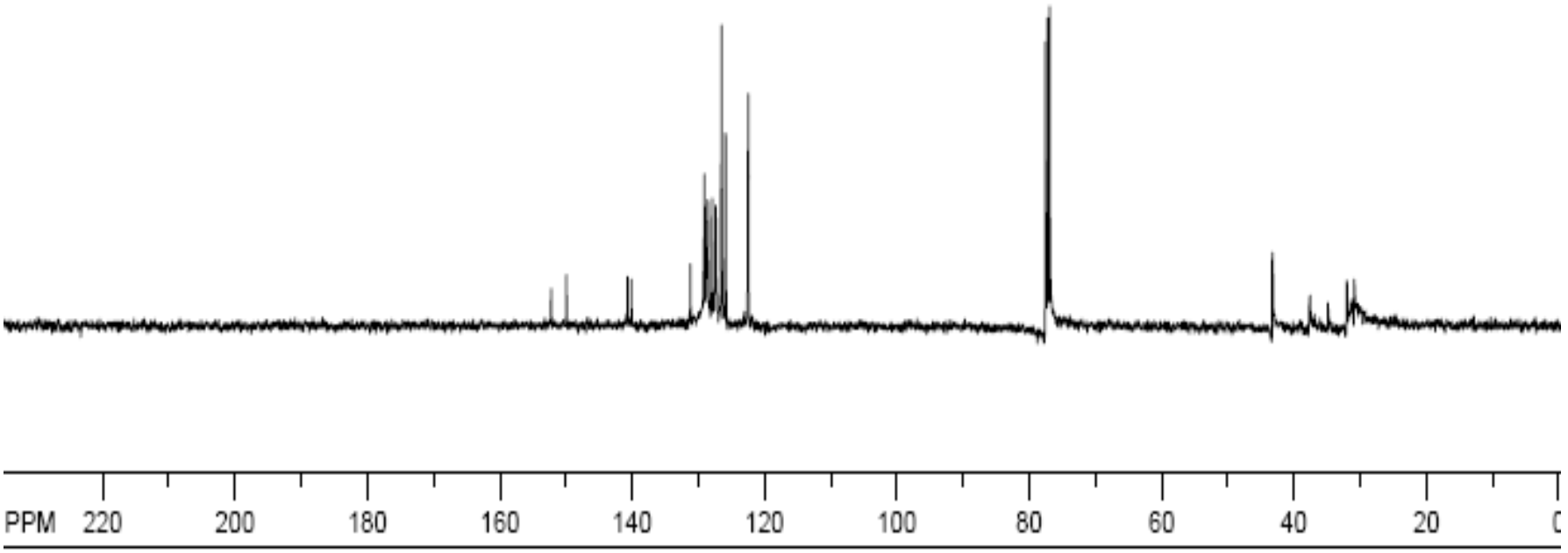




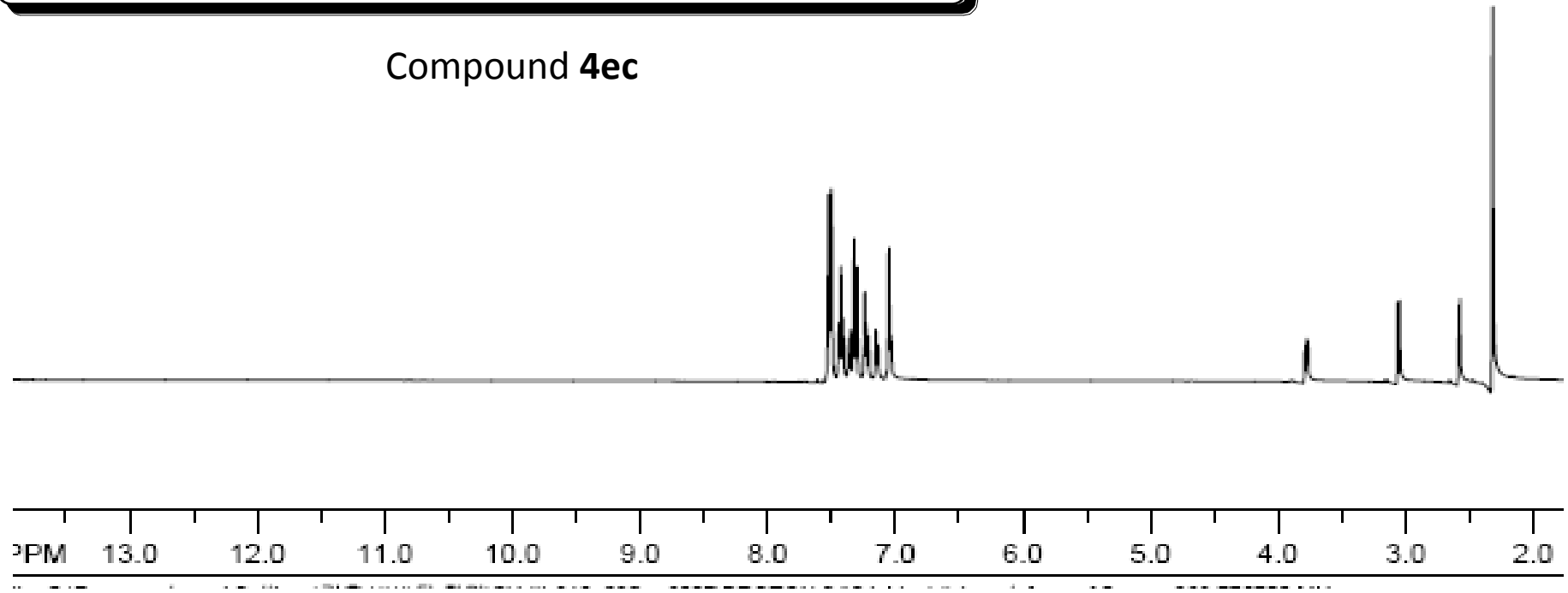
Compound **4eb**



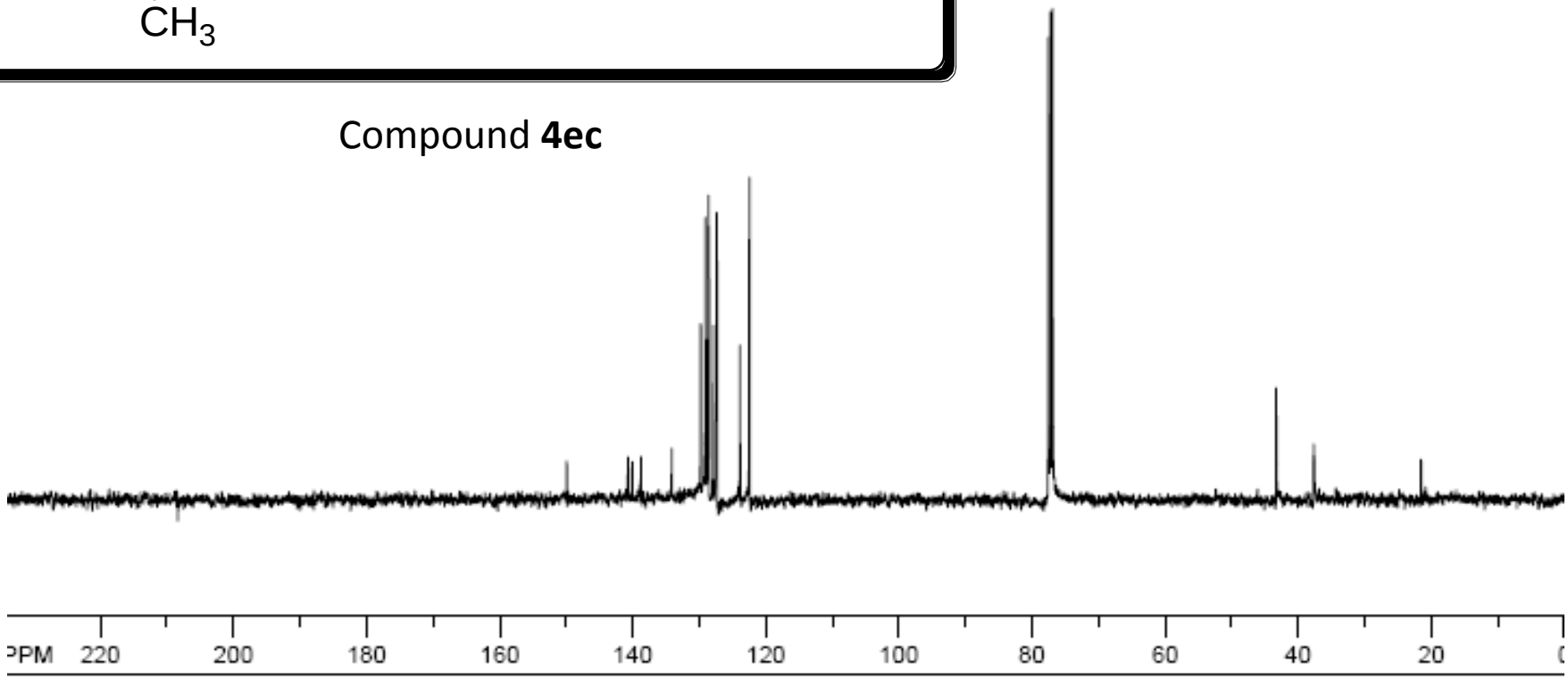
Compound **4eb**



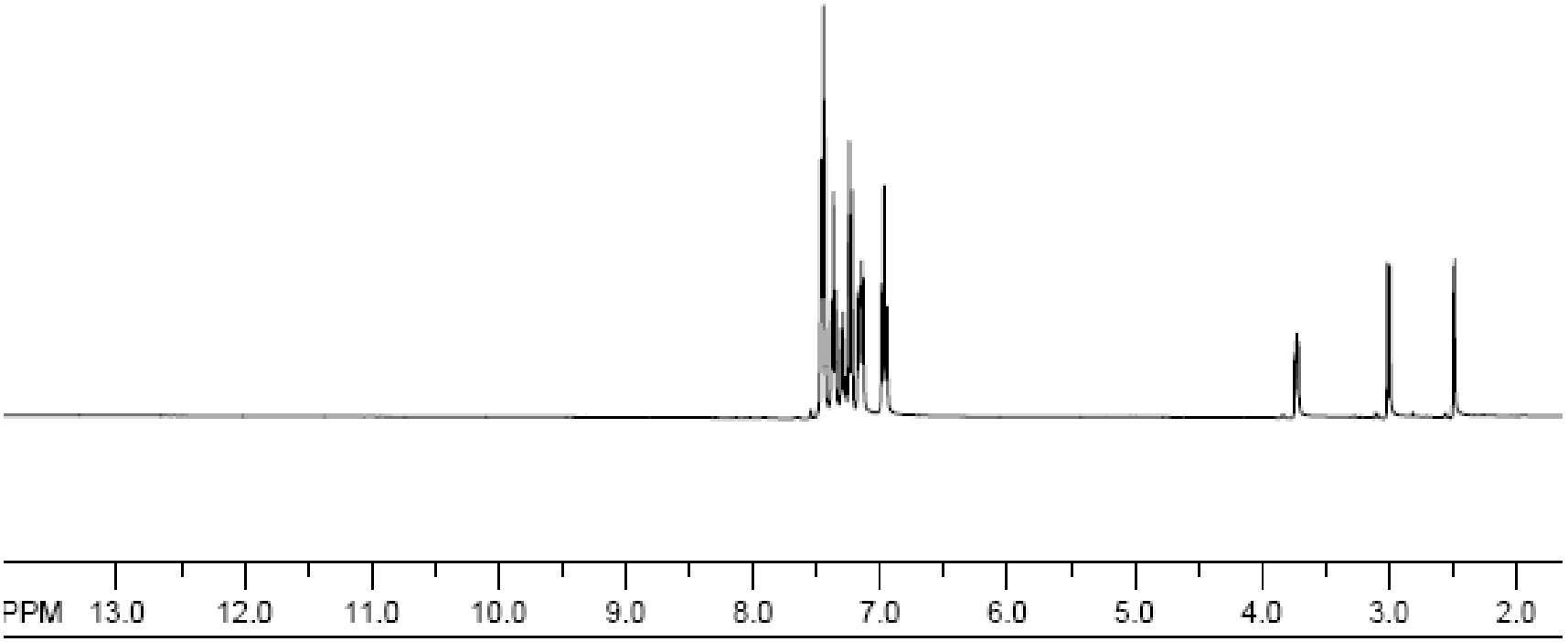
Compound **4ec**



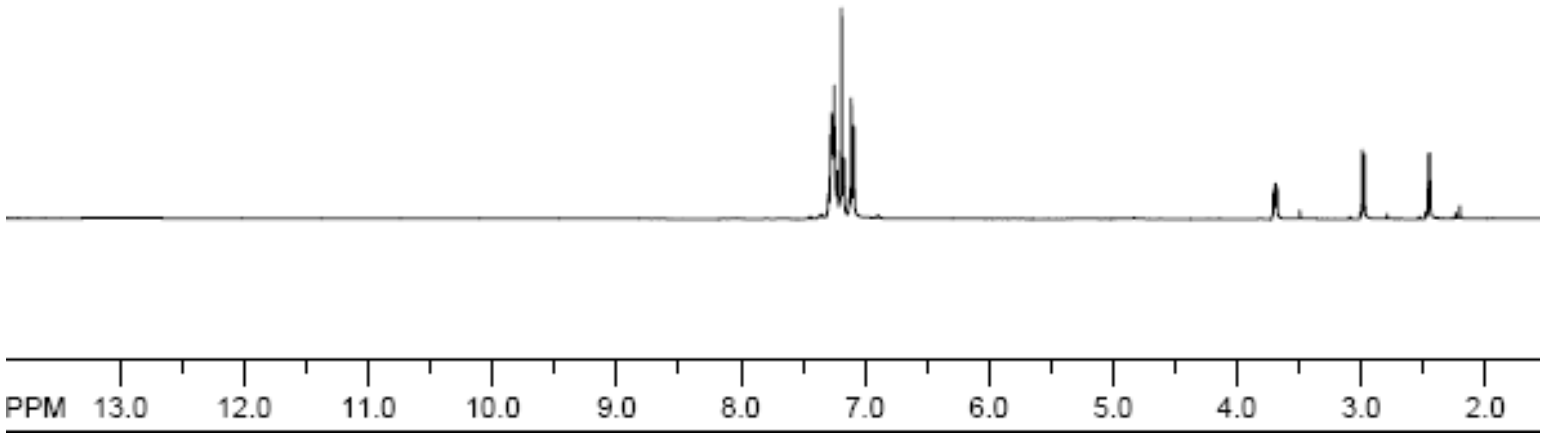
Compound **4ec**

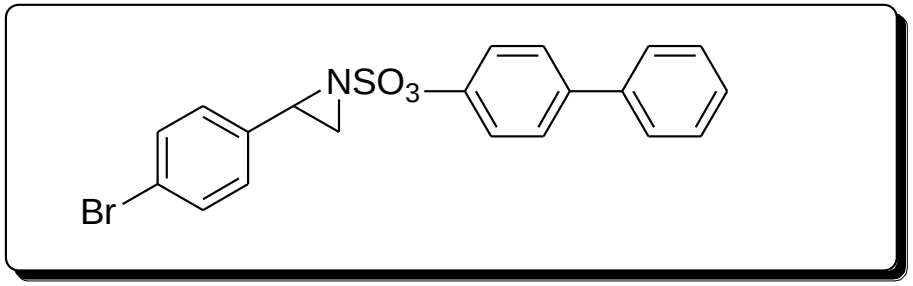


Compound **4ed**

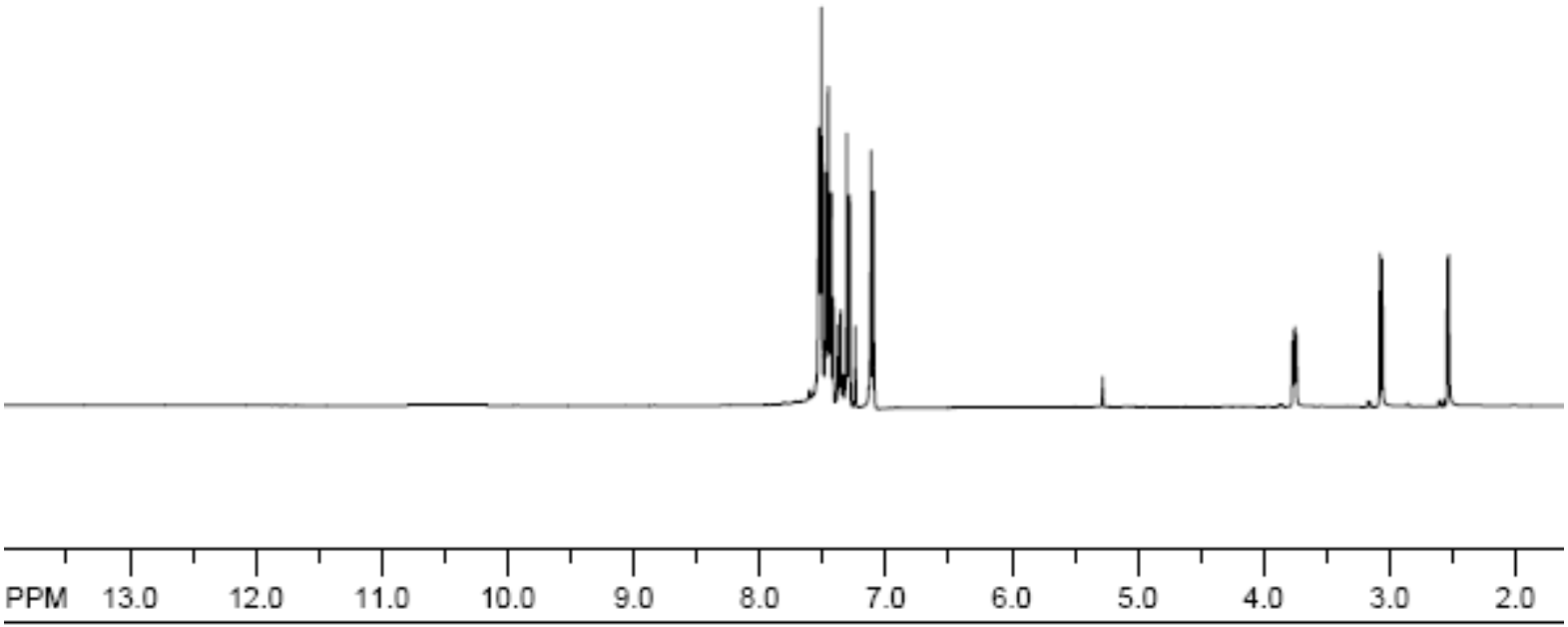


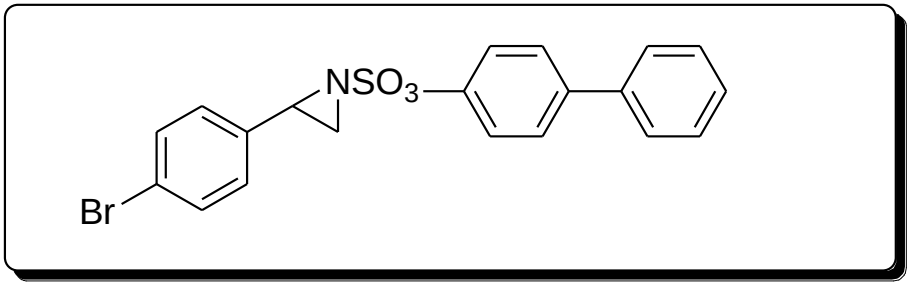
Compound **4ee**



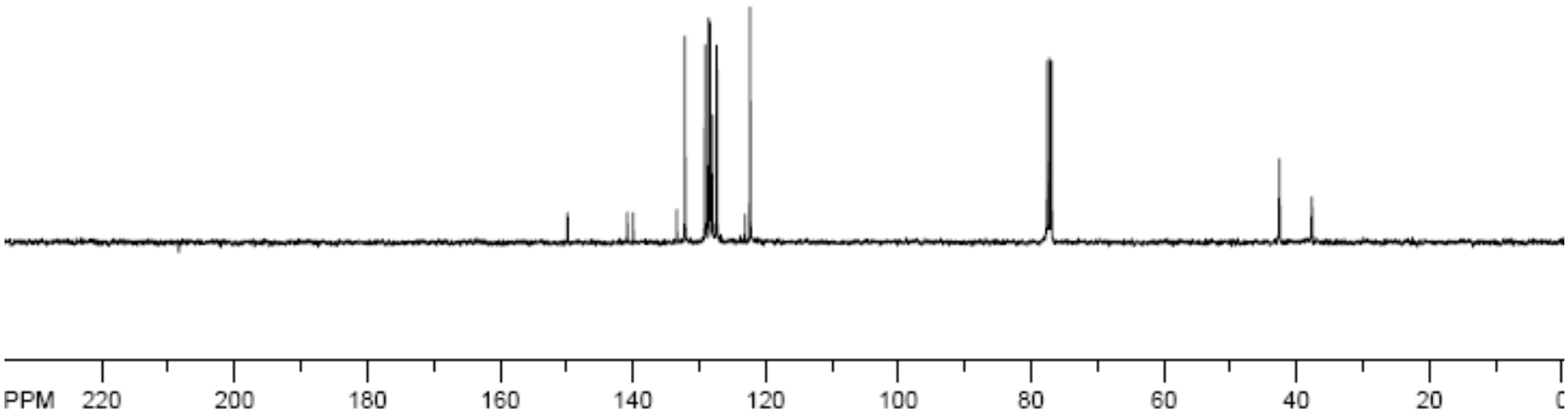


Compound **4ef**

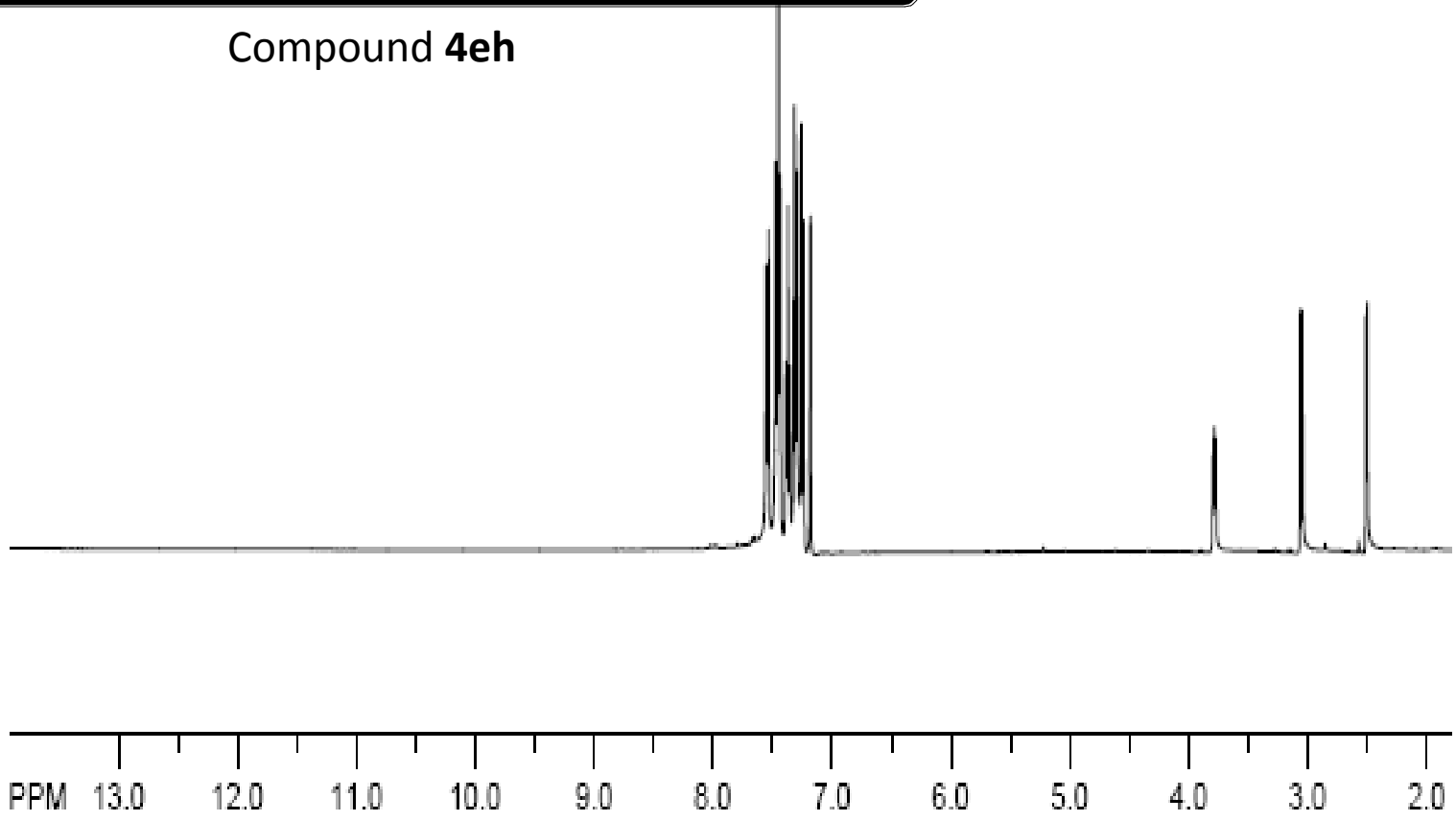




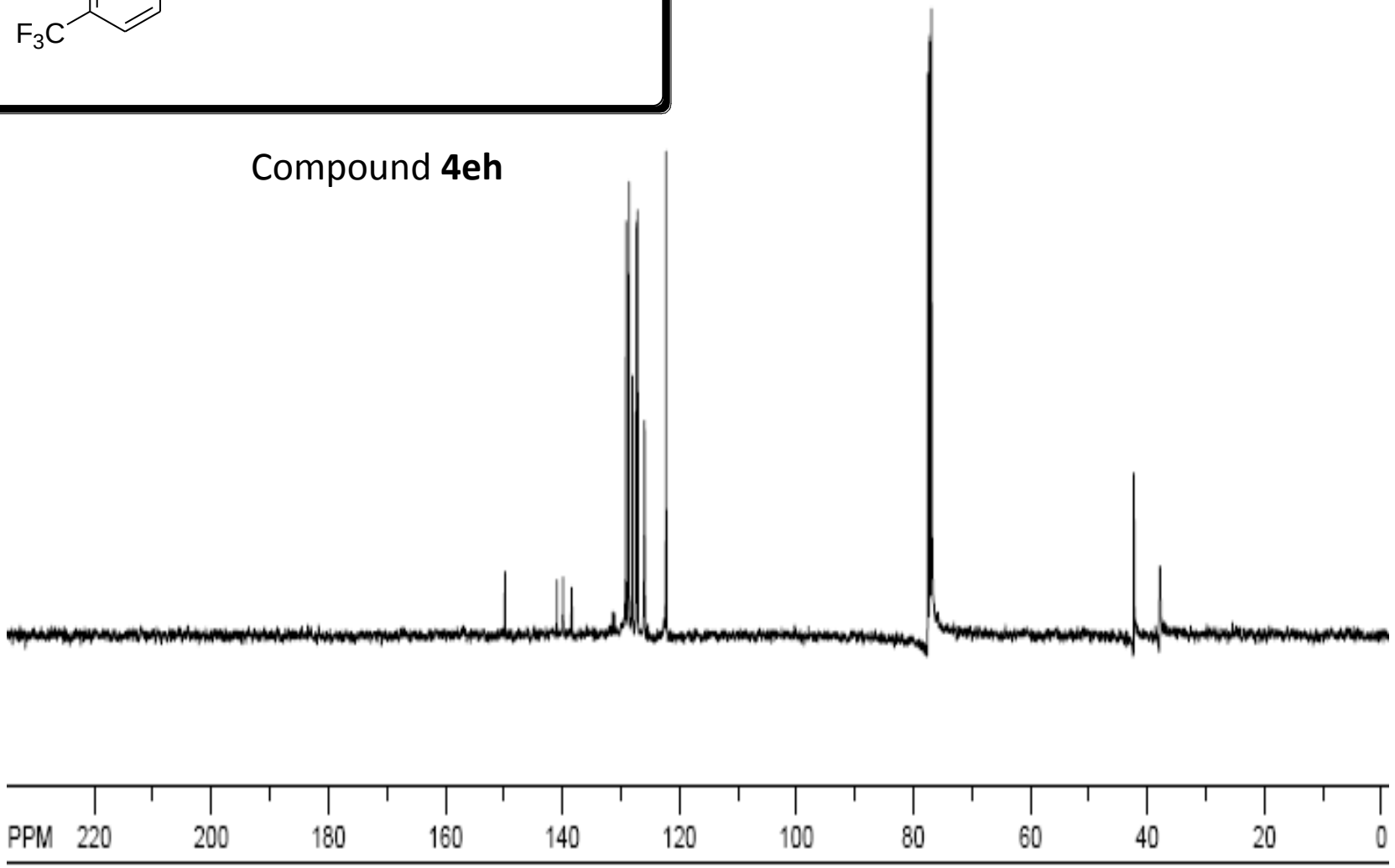
Compound **4ef**

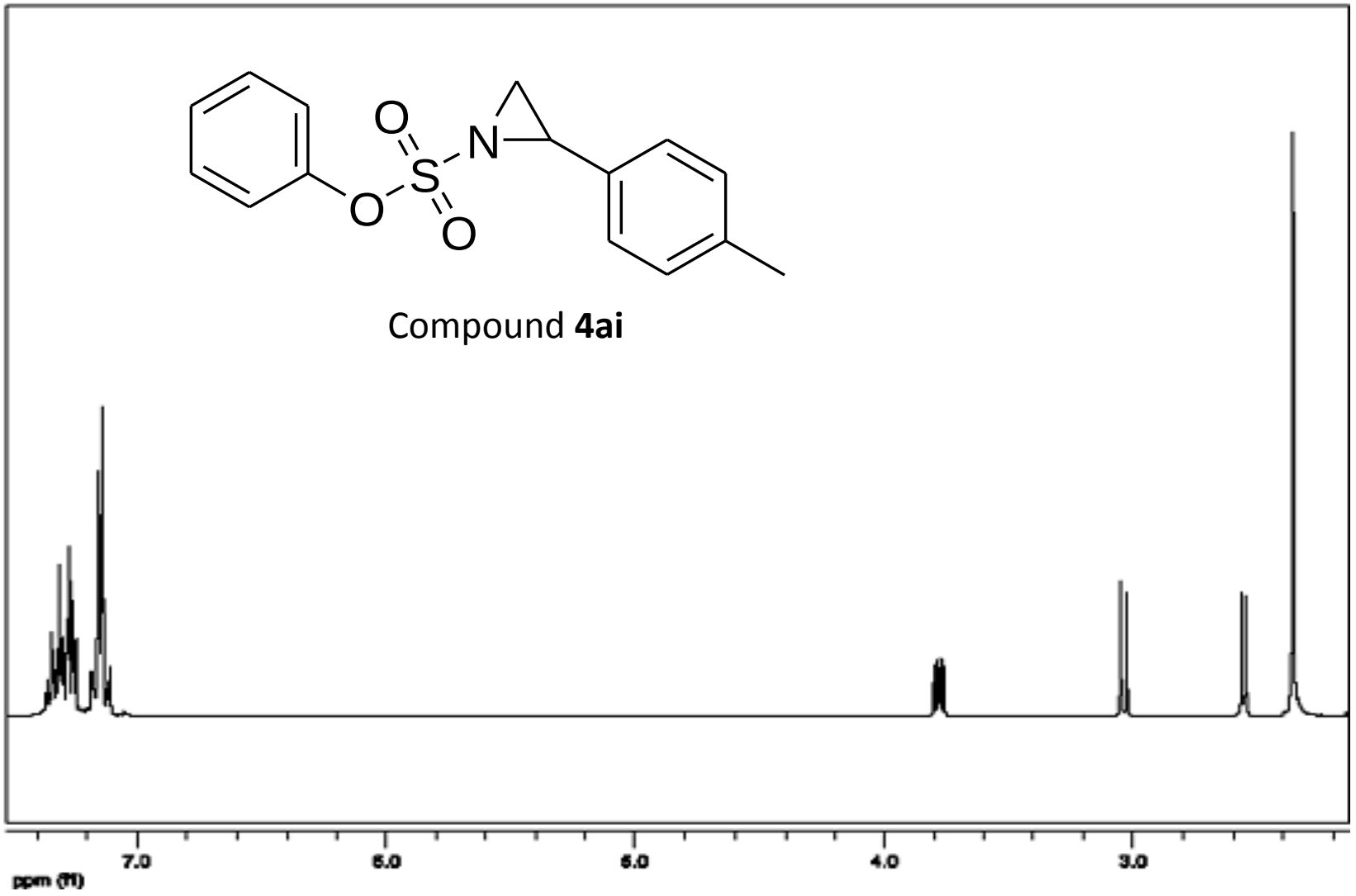


Compound **4eh**

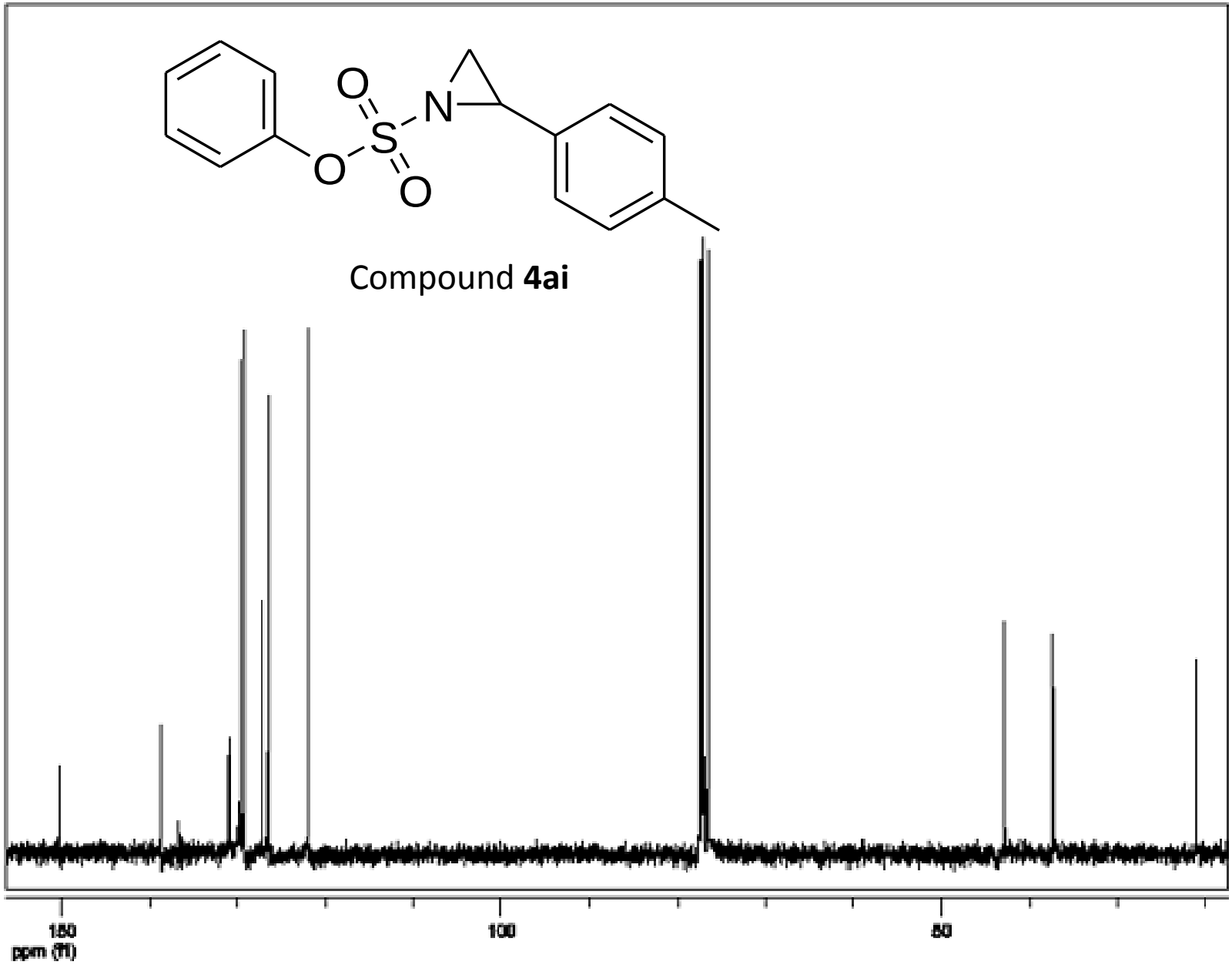


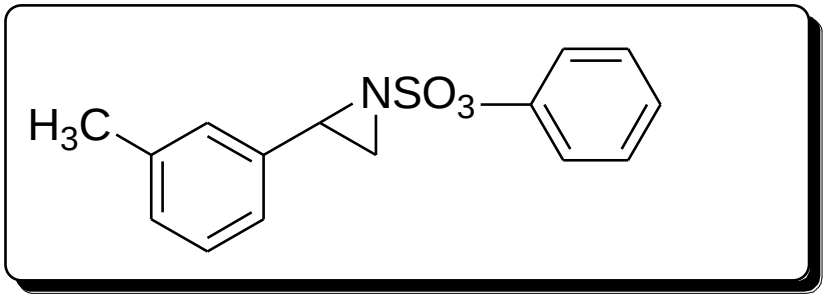
Compound **4eh**



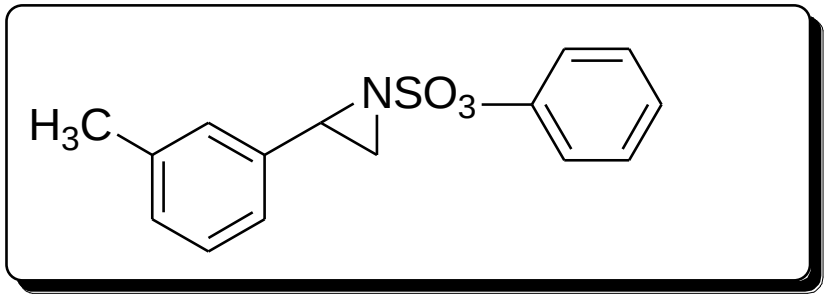


Compound **4ai**

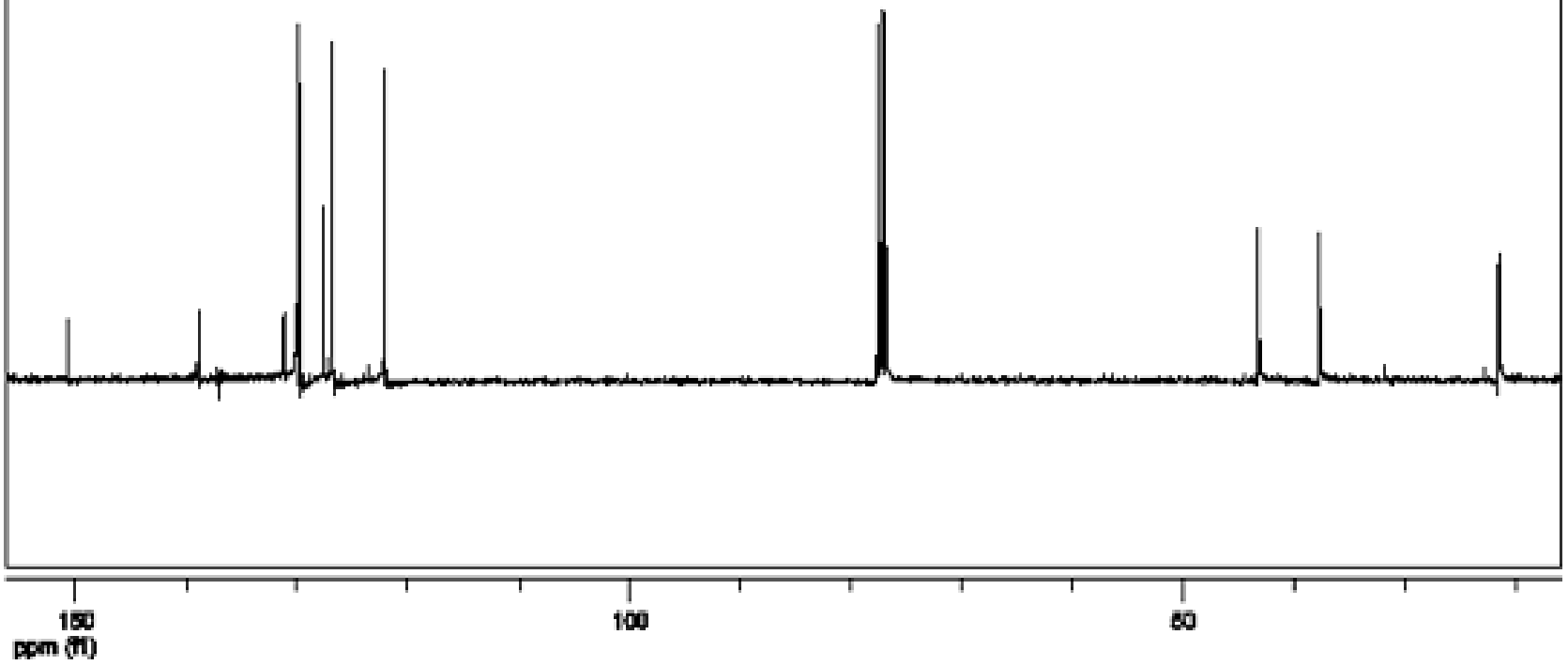

O
S
N
O
O
Compound **4ai**
150
ppm (f1)
100
50

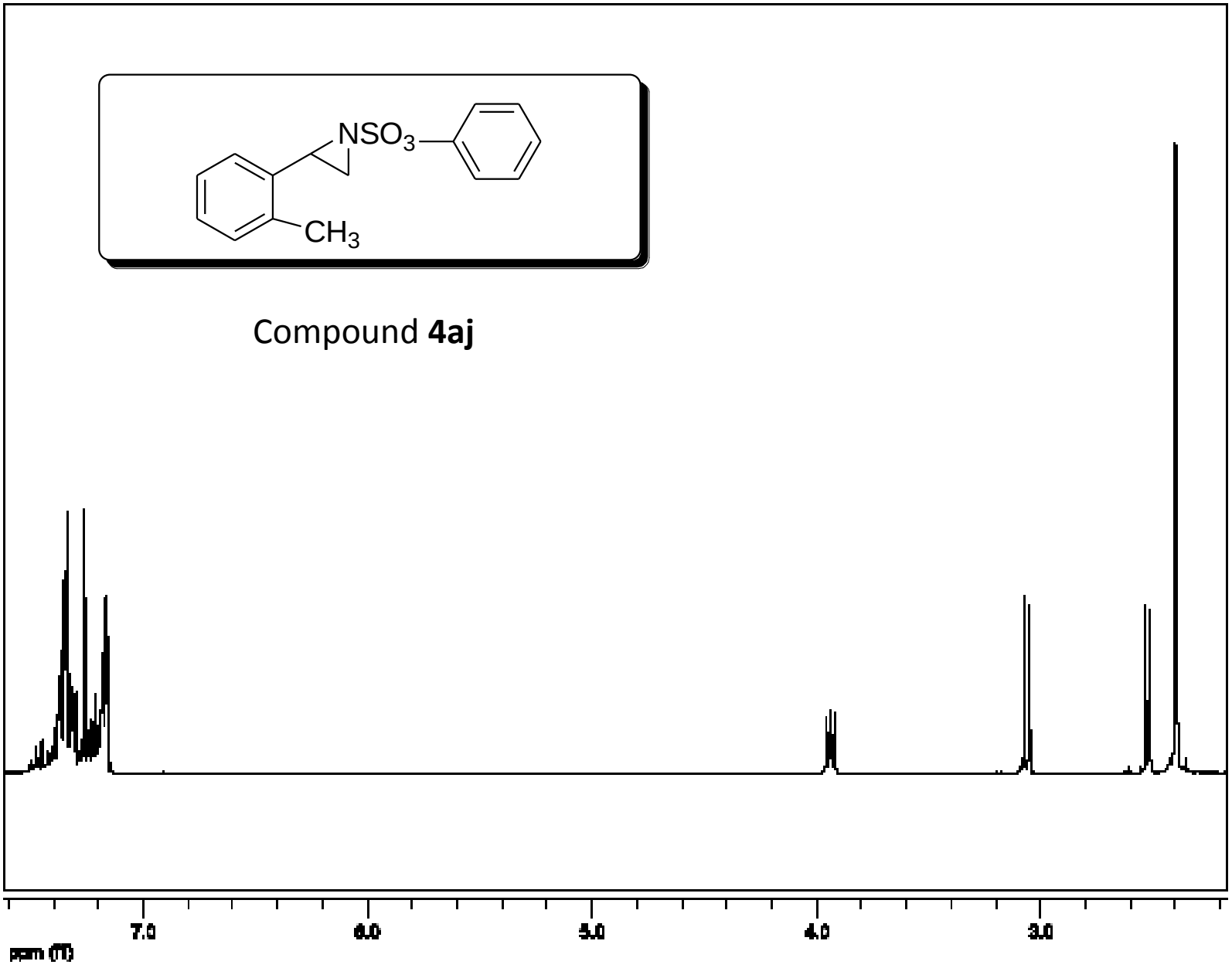


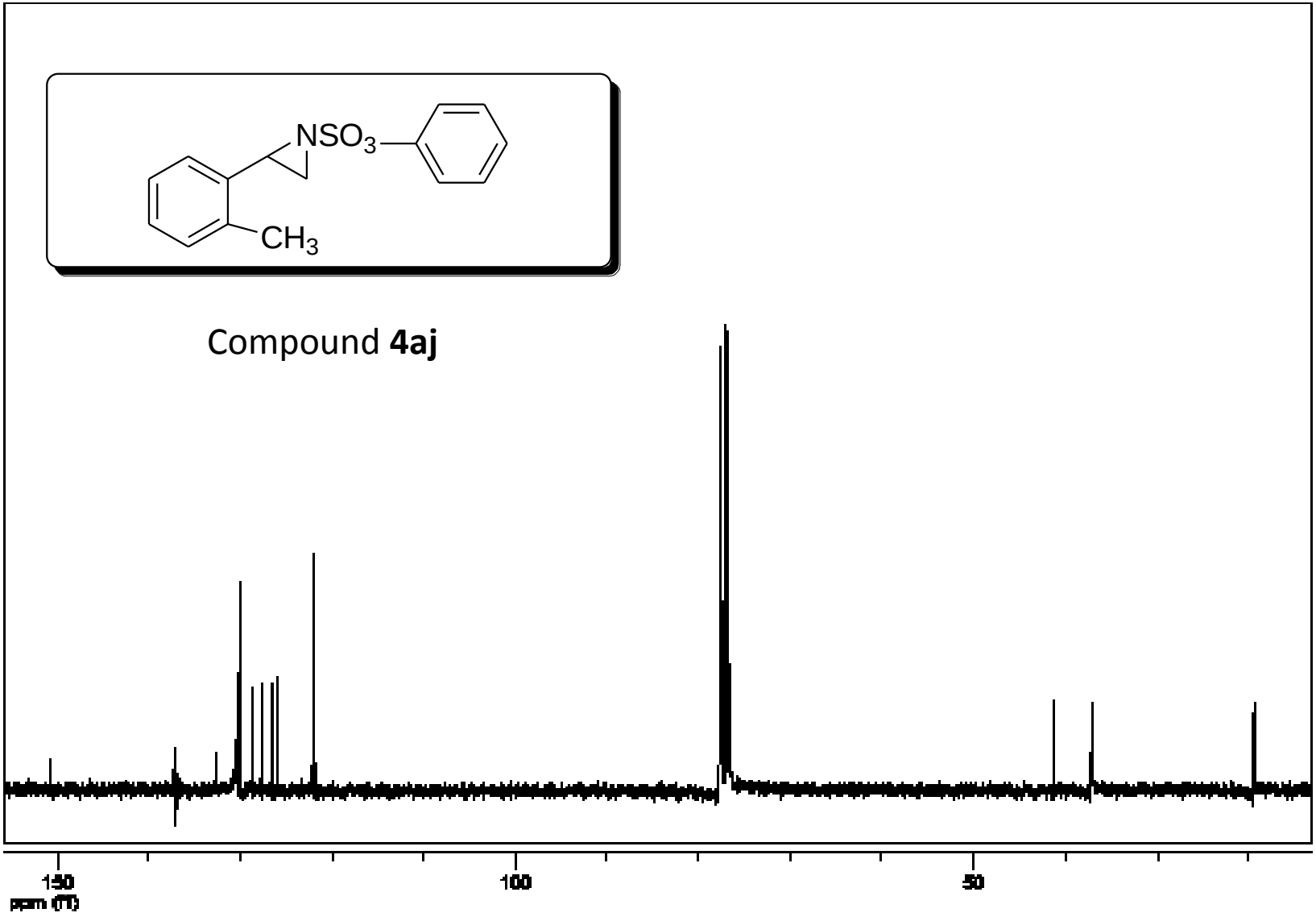
Compound **4ac**

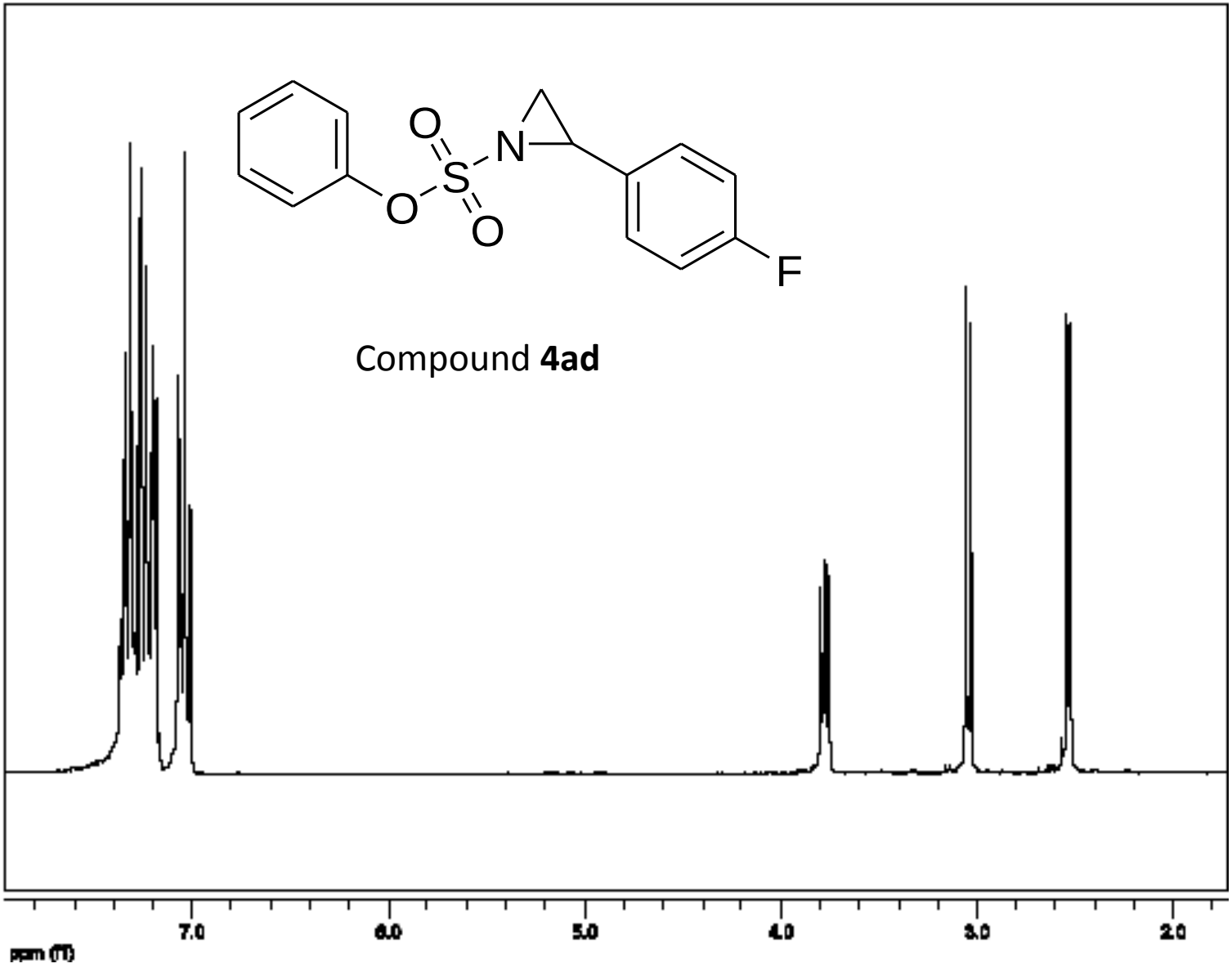


Compound **4ac**

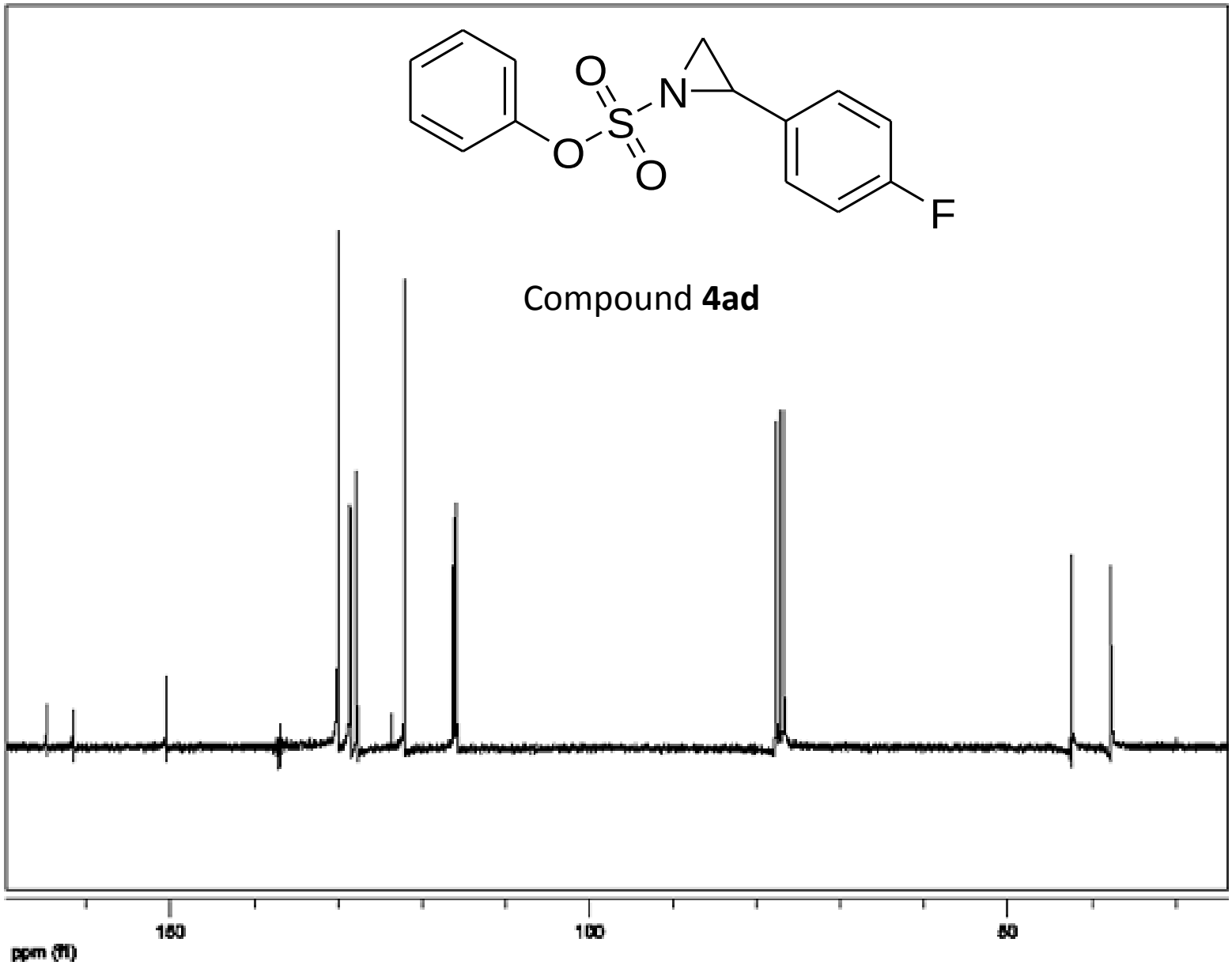


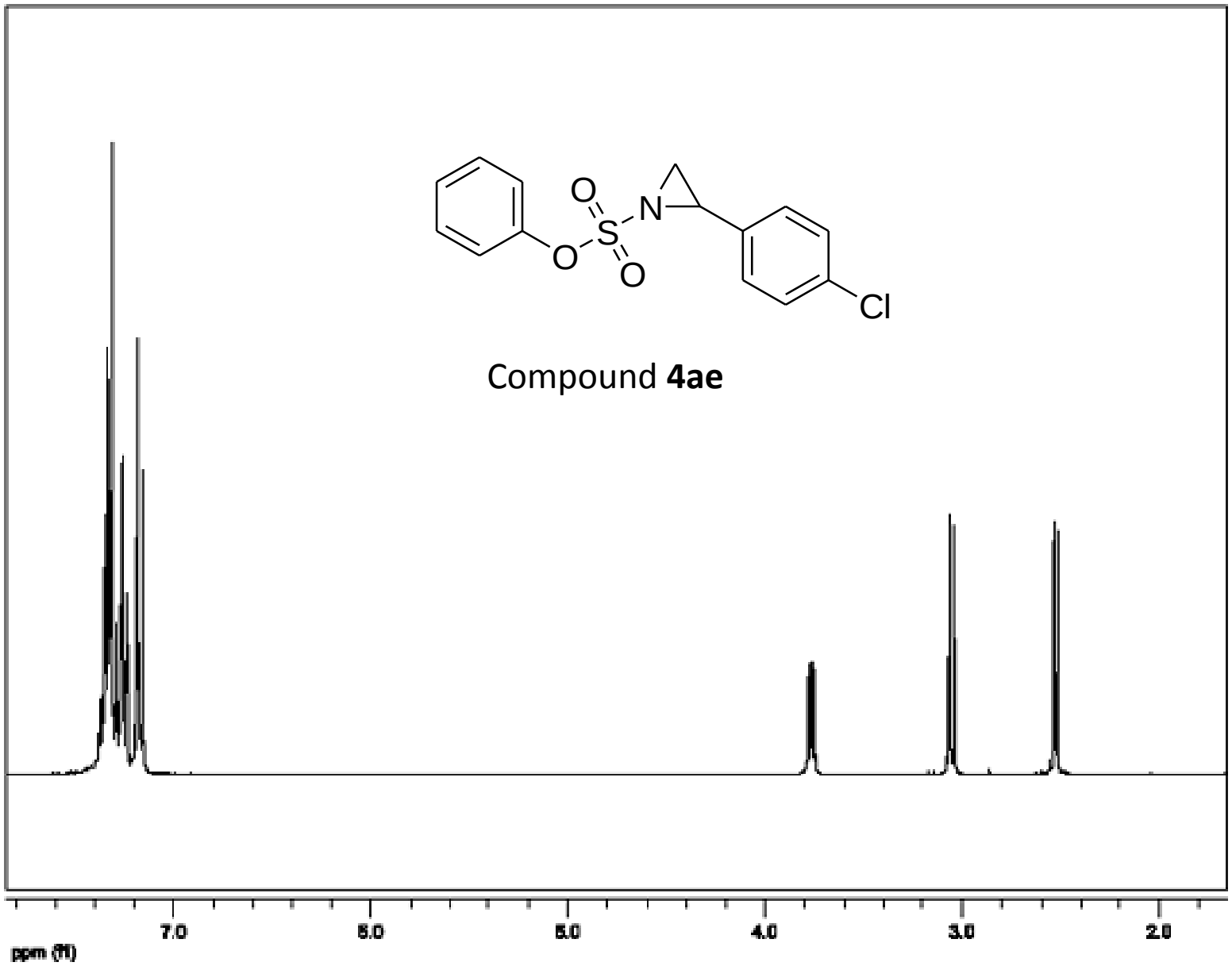

NSO3
CH3
Compound 4aj
7.0
6.0
5.0
4.0
3.0
ppm (f1)


NSO3
CH3
Compound 4aj
150
ppm (f1)
100
50

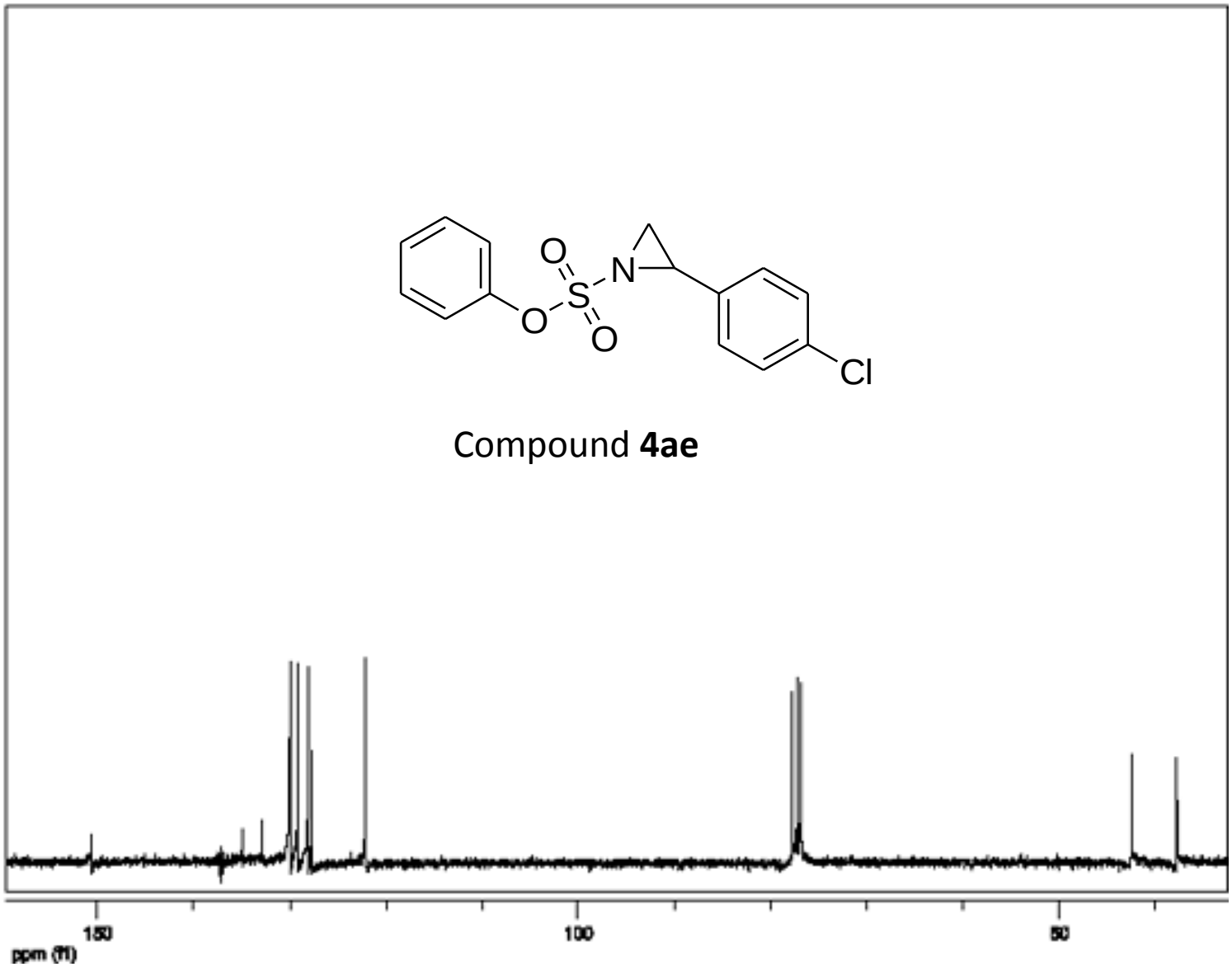


Compound **4ad**

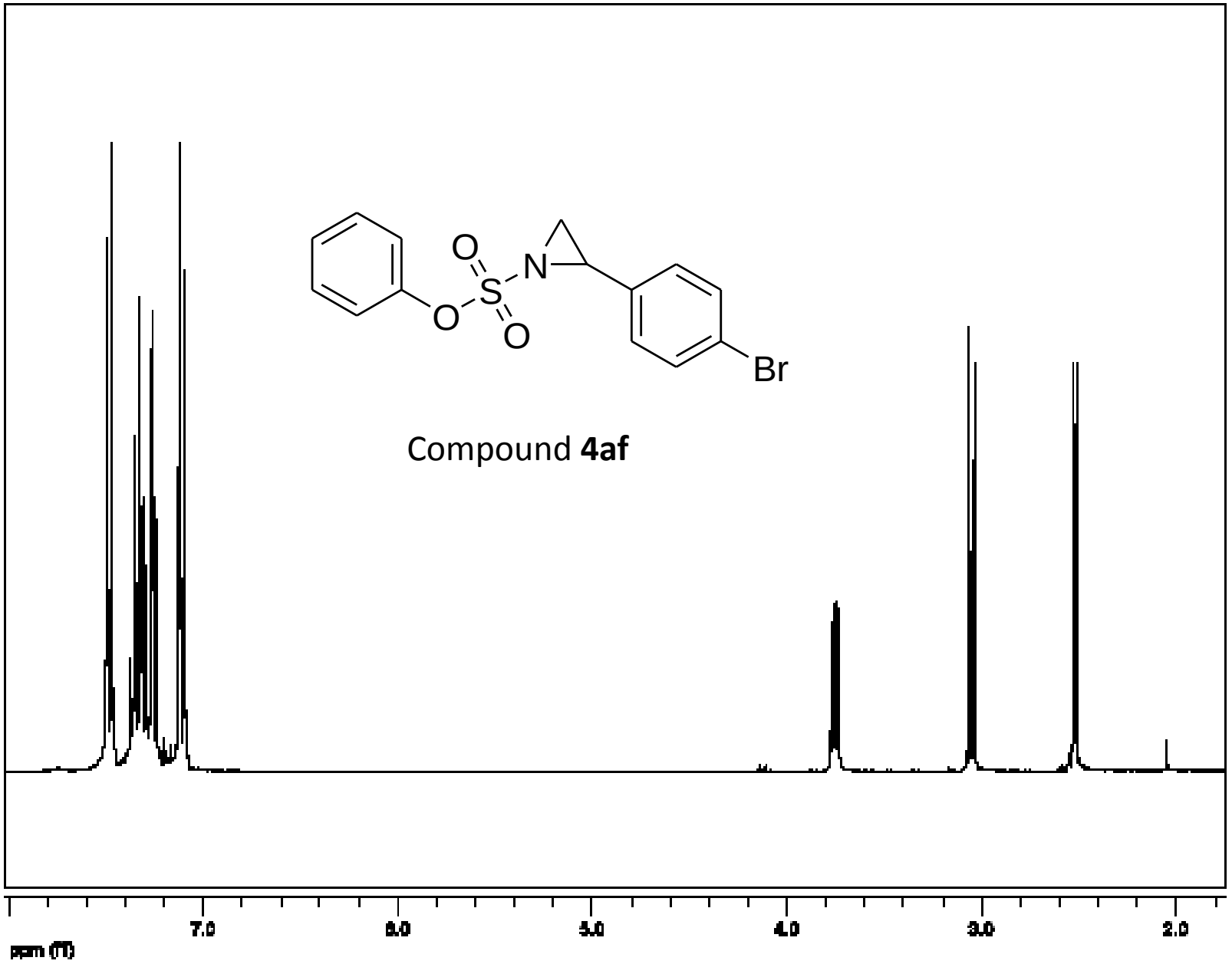

O
S
O
O
N
F
Compound **4ad**
150
100
50
ppm (f1)



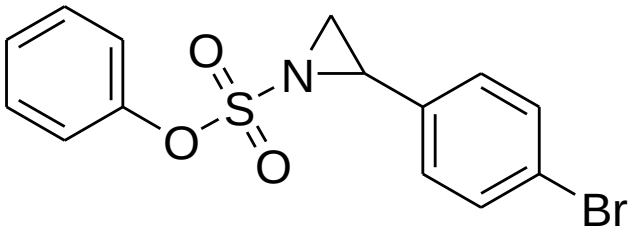
Compound **4ae**



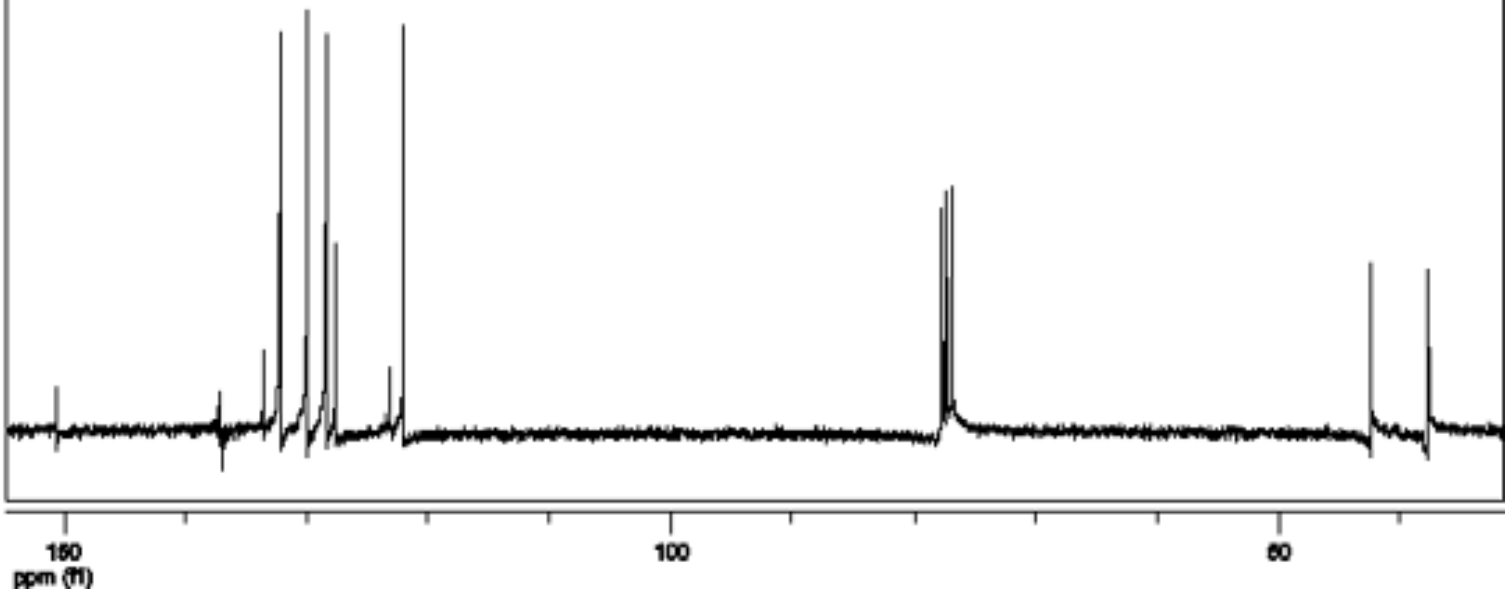
Compound **4ae**

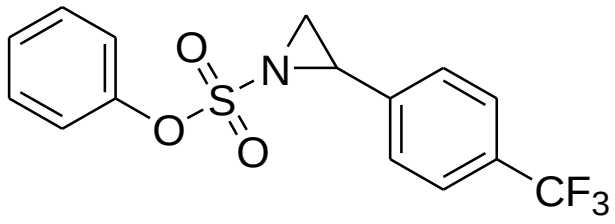


Compound **4af**

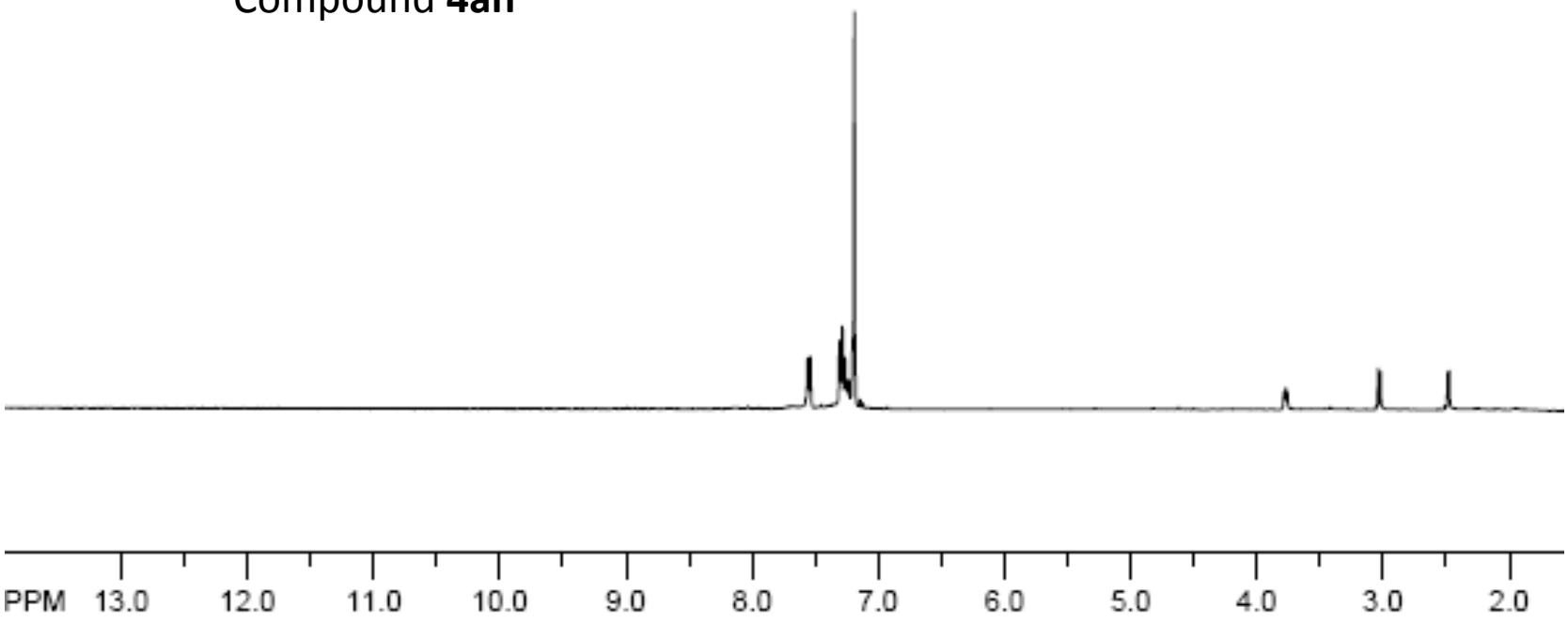


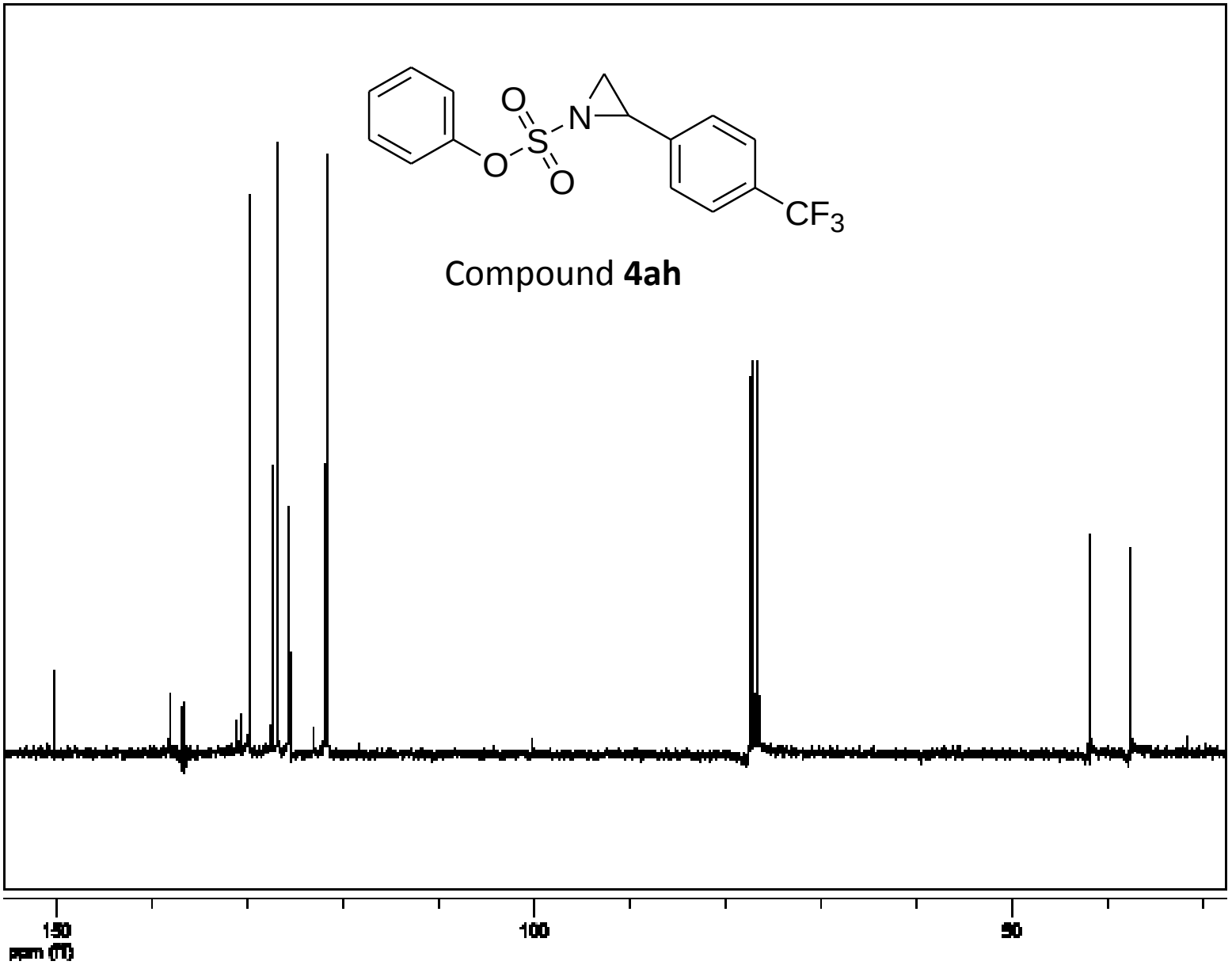
Compound **4af**





Compound **4ah**





Compound **4ah**