Copper-Catalyzed Intermolecular Amidation of 8-Methylquinolines with *N*-Fluoroarylsulfonimides *via* Csp^3-H Activation

Xiaolei Zhang,[†] Rui Wu,[†] Wanyi Liu,[†] Dang-Wei Qian,[†] Jinhui Yang,[†] Pengjv Jiang,[†] and Qing-Zhong Zheng[†‡]

[†] Department of Chemistry and State Key Laboratory Cultivation Base of Natural Gas Conversion, School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China.

[‡] State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Rd. 38, Beijing 100191, China.

E-mail: qzzheng@nxu.edu.cn

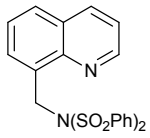
Supporting Information

Table of Contents

General remarks

All manipulations were conducted with sealed tubes. ^{1}H-NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with $CDCl_3$. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification

Experimental procedure and characterization data

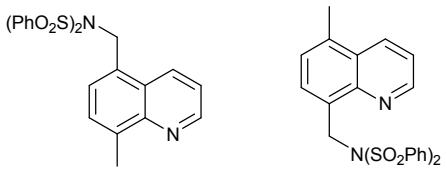


3a

1) *N*-(Phenylsulfonyl)-*N*-(quinolin-8-ylmethyl)benzenesulfonamide (3a) [1]

Typical procedure:

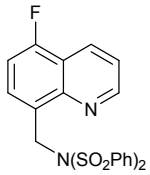
The reaction of 8-methyl-quinoline (**1a**) (1.0 mmol, 143.2 mg), *N*-Fluorobenzenesulfonimide (**2a**) (1.3 mmol, 410.0 mg), CuBr (10 mol %, 14.3 mg), 1,10-phenanthroline (5 mol %, 9.0 mg), Na_2CO_3 (50 mol %, 53.0 mg), in 3 mL DCE at 110 ^oC under air for 15 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 355.1 mg (81%) of **3a** as solid: MP: 144-145 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 2.8 Hz, 1H), 8.14 (dd, J = 8.4, 1.4 Hz, 1H), 7.90-7.88 (m, 4H), 7.67 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.51 (d, J = 7.2 Hz, 1H), 7.47-7.41 (m, 5H), 7.28 (d, J = 8.0 Hz, 1H), 5.82 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 145.5, 139.5, 136.2, 133.7, 132.9, 128.7, 128.3, 127.9, 127.8, 127.2, 125.9, 121.1, 49.0 ppm. MS (70 eV): m/z (%): 439.1 (100) $[M]^+$, 440.1 (20).



3b **3b'**

2) *N*-((8-Methylquinolin-5-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3b) and *N*-((5-Methylquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3b') [1]

The reaction of 5,8-dimethylquinoline (**1b**) (0.3 mmol, 47.1 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 15 h as monitored by TLC. The resulting mixture were concentrated and purified by flash chromatography on silica gel to afford 74.2 mg (55%) of **3b** as solid**,** and 25.2 mg (18%) of **3b'** as solid. The total yield of **3b** and **3b'** is 73% (2.9:1). **3b**: MP: 198-199 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.50 (dd, J = 8.4, 0.8 Hz, 1H), 7.71 (dd, J = 8.4, 1.0 Hz, 4H), 7.46 (t, J = 7.6, Hz, 2H), 7.41-7.33 (m, 3H), 7.30 (t, J = 8.0 Hz, 4H), 5.45 (s, 2H), 2.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 146.9, 139.7, 138.1, 133.4, 131.4, 129.3, 128.5, 127.6, 127.2, 126.4, 120.9, 50.8, 18.2 ppm. HRMS m/z (ESI): Calcd. for $C_{23}H_{21}N_2O_4S_2$ $[M+H]^+$ 453.0943, Found: 453.0937. **3b'**: MP: 199-200 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.0, 1.6 Hz, 1H), 8.31 (dd, J = 8.4, 1.2 Hz, 1H), 7.90 (dd, J = 8.8, 1.2 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.47-7.39 (m, 6H), 7.11 (d, J = 7.2 Hz, 1H), 5.78 (s, 2H), 2.63 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 145.9, 139.7, 134.0, 133.7, 132.6, 130.9, 128.8, 128.4, 127.5, 127.3, 126.3, 120.7, 49.3 , 18.5 ppm. MS (70 eV): m/z (%): 453.1 (100) $[M]^+$, 454.1 (25).

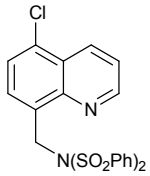


3c

3) *N*-((5-Fluoroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3c) [1]

The reaction of 5-fluoro-8-methyl-quinoline (**1c**) (0.3 mmol, 48.3 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 15 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 126.3 mg (92%) of **3c** as solid: MP: 143-144 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J =

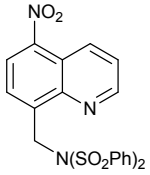
4.0, 1.6 Hz, 1H), 8.42 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.89 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.63-7.59 (m, 2H), 7.51 (t, *J* = 4.4, Hz, 1H), 7.48-7.44 (m, 5H), 6.97 (t, *J* = 8.8 Hz, 1H), 5.75 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (d, *J* = 253.7 Hz), 150.2, 145.8 (d, *J* = 3.2 Hz), 139.4, 133.7, 129.2 (d, *J* = 5.3 Hz), 128.9 (d, *J* = 4.2 Hz), 128.7, 128.1, 127.7 (d, *J* = 8.6 Hz), 121.3 (d, *J* = 3.3 Hz), 118.4 (d, *J* = 16.3 Hz), 109.6 (d, *J* = 18.3 Hz), 48.6 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -123.5. MS (70 eV): m/z (%): 457.1 (100) $[M]^+$, 458.1 (20).



3d

4) *N*-((5-Chloroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3d)

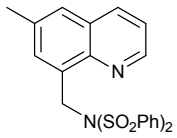
The reaction of 5-chloro-8-methyl-quinoline (**1d**) (0.3 mmol, 53.2 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^{o}C under air for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 112.0 mg (79%) of **3d** as solid: MP: 205-206 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.58 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.90 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.64 (t, *J* = 1.2 Hz, 2H), 7.55 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.49-7.42 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 1H), 5.76 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 145.9, 139.5, 133.9, 133.2, 132.5, 130.7, 128.9, 128.3, 128.0, 126.0, 125.9, 122.0, 48.9 ppm. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}ClN_2O_4S_2$ $[M+H]^+$ 473.0397, Found: 473.0391.



3e

5) *N*-((5-Nitroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3e) [1]

The reaction of 8-methyl-5-nitro-quinoline (**1e**) (0.3 mmol, 56.4 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.6 mmol, 189.2 mg), $Cu(OAc)_2$ (2 equiv, 109 mg), Li_2CO_3 (50 mol %, 11.0 mg), in 0.75 mL DCE and 0.75mL MeCN at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 73.1 mg (50%) of **3e** as solid: MP: 197-199 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (dd, J = 8.8, 1.6 Hz, 1H), 9.05 (dd, J = 4.0, 1.6 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 1.2 Hz, 4H), 7.72 (dd, J = 8.8, 4.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.9 Hz, 4H), 5.84 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.2, 144.6, 141.5, 139.2, 134.2, 132.3, 129.1, 128.4, 125.8, 124.0, 123.9, 120.7, 49.5 ppm. MS (70 eV): m/z (%): 484.1 (50) $[M]^+$.



3f

6) *N*-((6-Methylquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3f)

The reaction of 6,8-dimethyl-quinoline (**1f**) (0.3 mmol, 47.1 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 15 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 66.5 mg (49%) of **3f** as solid: MP: 168-170 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (dd, J = 4.0, 1.6 Hz, 1H), 8.04 (dd, J = 8.2, 1.7 Hz, 1H), 7.93 (dd, J = 8.4, 1.2 Hz, 4H), 7.62 (t, J = 7.6 Hz, 2H), 7.49-7.45 (m, 4H), 7.42 (s, 1H), 7.38 (q, J = 4.0 Hz, 1H), 7.19 (s, 1H), 5.80 (s, 2H), 2.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 144.2, 139.7, 135.7, 135.5, 133.7, 132.2, 130.1, 128.8, 128.3, 128.0, 126.0, 121.2, 49.2, 21.5 ppm. HRMS m/z (ESI): Calcd. for $C_{23}H_{21}N_2O_4S_2$ $[M+H]^+$ 453.0943, Found: 453.0937.

Additionally, the stucture of compound **3f** was also corroborated by x-ray diffraction (CCDC 1476725) as shown in Fig. 1.

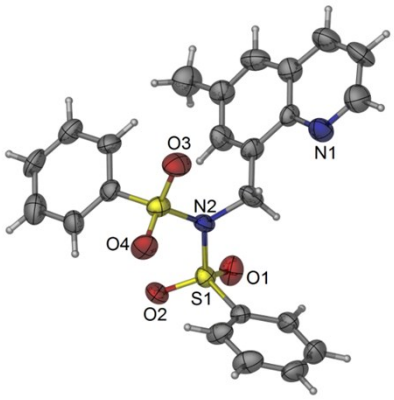
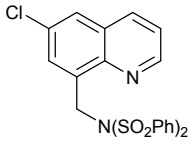


Fig. 1. ORTEP view of the crystal structure of compound **3f**.

3g

7) *N*-((6-Fluoroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3g)

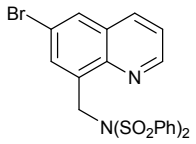
The reaction of 6-fluoro-8-methyl-quinoline (**1g**) (0.3 mmol, 48.3 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.6 mmol, 189.2 mg), $Cu(OAc)_2$ (2 equiv, 109 mg), Li_2CO_3 (50 mol %, 11.0 mg), in 0.75 mL DCE and 0.75mL MeCN at 110 ^oC under Ar for 22h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 84.7 mg (62%) of **3g** as solid: MP: 167-168 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 2.8 Hz, 1H), 8.18 (d, J = 7.6 Hz, 1H), 7.93 (dd, J = 8.8, 1.2 Hz, 4H), 7.65 (t, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 5H), 7.32 (d, J = 8.0 Hz, 2H), 5.81 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, J = 246.9 Hz), 148.6 (d, J = 3.4 Hz), 142.6, 139.4, 136.6 (d, J = 8.5 Hz), 135.7 (d, J = 5.0 Hz), 134.0, 128.9, 128.8 (d, J = 10.5 Hz), 128.3, 122.0, 118.3 (d, J = 17.8 Hz), 109.9 (d, J = 22.1 Hz), 48.8 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -112.5. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}FN_2O_4S_2$ $[M+H]^+$ 457.0692, Found: 457.0687.



3h

8) *N*-((6-Chloroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3h)

The reaction of 6-chloro-8-methyl-quinoline (**1h**) (0.3 mmol, 53.2 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.6 mmol, 189.2 mg), $Cu(OAc)_2$ (2 equiv, 109 mg), Li_2CO_3 (50 mol %, 11.0 mg), in 0.75 mL DCE and 0.75mL MeCN at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 92.1 mg (65%) of **3h** as solid: MP: 193-195 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 2.8 Hz, 1H), 8.09 (d, J = 5.2 Hz, 1H), 7.95 (d, J = 7.2 Hz, 4H), 7.68-7.64 (m, 3H), 7.51 (t, J = 8.0 Hz, 5H), 7.33 (s, 1H), 5.77 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 143.8, 139.4, 135.6, 135.2, 134.1, 132.1, 129.0, 128.9, 128.7, 128.4, 125.8, 122.2, 48.8 ppm. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}ClN_2O_4S_2$ $[M+H]^+$ 473.0397, Found: 473.0391.



3i

9) *N*-((6-Bromoquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3i)

The reaction of 6-bromo-8-methyl-quinoline (**1i**) (0.3 mmol, 66.6 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.6 mmol, 189.2 mg), $Cu(OAc)_2$ (2 equiv, 109 mg), Li_2CO_3 (50 mol %, 11.0 mg), in 0.75 mL DCE and 0.75mL MeCN at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 83.0 mg (53%) of **3i** as solid: MP: 211-213 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.0, 1.6 Hz, 1H), 8.06 (dd, J = 8.0, 1.6 Hz, 1H), 7.96 (dd, J = 8.0, 1.2 Hz, 4H), 7.84 (d, J = 2.0 Hz, 1H), 7.66 (t, J = 7.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 4H), 7.46 (q, J = 4.0 Hz, 1H), 7.42 (t, J = 1.2 Hz, 1H), 5.76 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 144.1, 139.5, 135.3, 134.0, 131.3, 129.7, 129.2, 129.0, 128.3, 126.4, 122.1, 120.2, 48.6 ppm. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}BrN_2O_4S_2$ $[M+H]^+$ 516.9891, Found: 516.9886.

3j

10) *N*-((7-Methylquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3j)

The reaction of 7,8-dimethyl-quinoline (**1j**) (0.3 mmol, 47.1 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 82.6 mg (61%) of **3j** as solid: MP: 158-159 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.0, 2.0 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.61 (dd, J = 8.0, 1.1 Hz, 4H), 7.55 (d, J = 8.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 8.4 Hz, 5H), 7.07 (d, J = 8.0 Hz, 1H), 5.99 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 146.9, 140.8, 140.3, 135.6, 132.9, 129.8, 128.3, 128.1, 127.6, 127.4, 126.2, 120.3, 46.3, 20.2 ppm. HRMS m/z (ESI): Calcd. for $C_{23}H_{21}N_2O_4S_2$ $[M+H]^+$ 453.0943, Found: 453.0937.

3k

11) *N*-((7-Methoxyquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3k)

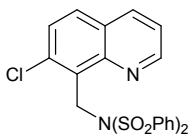
The reaction of 7-methoxy-8-methylquinoline (**1k**) (0.3 mmol, 51.9 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 15 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 53.6 mg (38%) of **3k** as solid: MP: 155-156 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.0, 1.6 Hz, 1H), 8.02 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 (dd, J = 8.0, 1.0 Hz, 4H), 7.63 (d,

J = 9.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.32-7.27 (m, 4H), 7.25 (d, *J* = 4.4 Hz, 1H), 6.85 (d, *J* = 9.2 Hz, 1H), 6.00 (s, 2H), 3.63 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 150.4, 147.3, 141.1, 135.9, 132.7, 132.6, 129.6, 128.2, 127.5, 126.3, 122.8, 118.8, 115.1, 112.6, 55.3, 44.0 ppm. HRMS m/z (ESI): Calcd. for $C_{23}H_{21}N_2O_5S_2$ $[M+H]^+$ 469.0892, Found: 469.0886.

3l

12) *N*-((7-Fluoroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3l)

The reaction of 7-fluoro-8-methyl-quinoline (**1l**) (0.3 mmol, 48.3 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^{o}C under air for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 75.3 mg (55%) of **3l** as solid: MP: 158-159 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.4, 1.2 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 4H), 7.65 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 5H), 7.09 (t, *J* = 9.2 Hz, 1H), 5.88 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 252.6 Hz), 150.4, 146.9 (d, *J* = 8.8 Hz), 140.1, 135.9, 133.2, 130.0 (d, *J* = 11.1 Hz), 128.4, 127.7, 124.7, 120.4 (d, *J* = 2.2 Hz), 116.7 (d, *J* = 25.7 Hz), 116.4, 42.7 (d, *J* = 2.7 Hz) ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -108.2. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}FN_2O_4S_2$ $[M+H]^+$ 457.0692, Found: 457.0687.

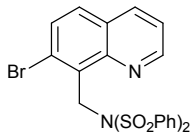


3m

13) *N*-((7-Chloroquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide

(3m)

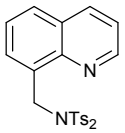
The reaction of 7-chloro-8-methyl-quinoline (**1m**) (0.3 mmol, 53.2 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0 mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 36 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 58.3 mg (41%) of **3m** as solid: MP: 171-173 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.4, 2.0 Hz, 1H), 7.98 (dd, J = 8.4, 1.2 Hz, 1H), 7.71 (dd, J = 8.4, 1.2 Hz, 4H), 7.56 (d, J = 8.8 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (q, J = 4.0 Hz, 1H), 7.31-7.26 (m, 5H), 6.02 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 147.0, 140.4, 137.0, 135.7, 132.9, 129.3, 128.3, 128.2, 128.1, 127.4, 126.3, 121.3, 46.5 ppm. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}ClN_2O_4S_2$ $[M+H]^+$ 473.0397, Found: 473.0391.



3n

14) *N*-((7-Bromoquinolin-8-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3n)

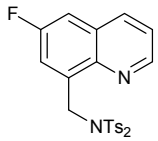
The reaction of 7-bromo-8-methyl-quinoline (**1n**) (0.3 mmol, 66.6 mg), *N*-Fluorobenzenesulfonimide (**2a**) (0.39 mmol, 123.0mg), CuBr (10 mol %, 4.3 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 15.9 mg), in 3 mL DCE at 110 ^oC under air for 15 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 57.3 mg (37%) of **3n** as solid: MP: 169-171 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, J = 4.0, 1.2 Hz, 1H), 7.91-7.89 (m, 1H), 7.69 (d, J = 7.6 Hz, 4H), 7.46 (t, J = 5.6 Hz, 2H), 7.43-7.38 (m, 2H), 7.32 (dd, J = 8.0, 4.4 Hz, 1H), 7.25 (t, J = 7.6 Hz, 4H), 6.00 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 147.1, 140.6, 135.6, 132.8, 131.0, 130.2, 129.4, 128.2, 127.6, 127.4, 126.7, 121.4, 49.4 ppm. HRMS m/z (ESI): Calcd. for $C_{22}H_{18}BrN_2O_4S_2$ $[M+H]^+$ 516.9891, Found: 516.9886.



3o

15) 4-Methyl-*N*-(quinolin-8-ylmethyl)-*N*-tosylbenzenesulfonamide (3o) [1]

The reaction of 8-methyl-quinoline (**1o**) (0.1 mmol, 14.3 mg), *N*-fluoro-4-methyl-*N*-tosylbenzenesulfonamide (**2b**) (0.2 mmol, 68.7 mg), $Cu(OAc)_2$ (2 equiv, 36.3 mg), Li_2CO_3 (50 mol %, 3.7 mg), in 0.5 mL DCE and 0.5mL MeCN at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 37.1mg (80%) of **3o** as solid: MP: 134-136 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 2.8 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 4H), 7.71 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.46 (dd, J = 8.0, 3.6 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.4 Hz, 4H), 5.78 (s, 2H), 2.43 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 144.8, 136.6, 133.2, 129.4, 128.5, 128.2, 128.0, 127.2, 126.1, 121.2, 49.0, 21.6 ppm. MS (70 eV): m/z (%): 439.1 (20), 467.1 (100) $[M]^+$, 468.1 (25).

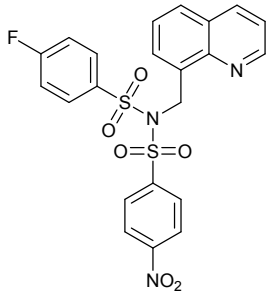


3p

16) *N*-((6-Fluoroquinolin-8-yl)methyl)-4-methyl-*N*-tosylbenzenesulfonamide (3p)

The reaction of 6-fluoro-8-methyl-quinoline (**1g**) (0.1 mmol, 16.1 mg), *N*-fluoro-4-methyl-*N*-tosylbenzenesulfonamide (**2b**) (0.2 mmol, 68.7 mg), $Cu(OAc)_2$ (2 equiv, 36.3 mg), Li_2CO_3 (50 mol %, 3.7 mg), in 0.5 mL DCE and 0.5mL MeCN at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 24.5 mg (51%) of **3p** as solid: MP: 156-158 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, J = 4.4, 1.2 Hz, 1H), 8.10 (dd, J = 8.4, 1.6 Hz, 1H), 7.81 (d, J = 8.4 Hz, 4H), 7.45 (dd, J = 8.4, 4.0 Hz, 1H), 7.28-7.22 (m, 6H), 5.73 (s, 2H), 2.44 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ

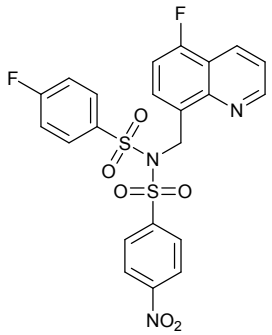
160.0 (d, J = 246.9 Hz), 148.6 (d, J = 2.0 Hz), 145.1, 142.6, 136.9 (d, J = 8.1 Hz), 136.5, 135.7 (d, J = 5.8 Hz), 129.5, 129.0, 128.8 (d, J = 9.5 Hz), 128.4, 122.0, 118.4 (d, J = 27.6 Hz), 109.8 (d, J = 20.8 Hz), 48.7, 21.6 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -112.1. HRMS m/z (ESI): Calcd. for $C_{24}H_{22}FN_2O_4S_2$ $[M+H]^+$ 485.1005, Found: 485.1000.



3q

17) 4-Fluoro-*N*-((4-nitrophenyl)sulfonyl)-*N*-(quinolin-8-ylmethyl)benzenesulfonamide (3q)

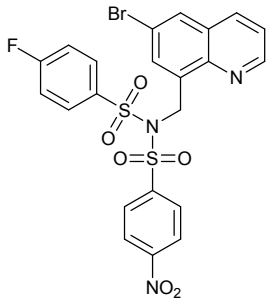
The reaction of 8-methyl-quinoline (**1a**) (0.15 mmol, 21.5 mg), *N*,4-difluoro-*N*-((4-nitrophenyl)sulfonyl)benzenesulfonamide (**2c**) (1.3 equvi, 73.5 mg), CuBr (10 mol %, 2.1 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 8.0 mg), in 1.5 mL DCE at 110 ^{o}C under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 37.8 mg (50%) of **3q** as solid: MP: 175-177 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 2.4 Hz, 1H), 8.23 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.92 (dd, J = 8.8, 5.2 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 4.9 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 8.5 Hz, 2H), 5.86 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, J = 255.9 Hz), 150.1 (d, J = 55.3 Hz), 145.6, 145.2, 136.2, 135.3 (d, J = 3.6 Hz), 132.0, 131.3 (d, J = 9.8 Hz), 129.6, 128.5, 128.0 (d, J = 4.3 Hz), 125.8, 123.8, 121.5, 116.2 (d, J = 22.5 Hz), 49.2 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -102.0. HRMS m/z (ESI): Calcd. for $C_{22}H_{17}FN_3O_6S_2$ $[M+H]^+$ 502.0543, Found: 502.0537.



3r

18) 4-Fluoro-*N*-((5-fluoroquinolin-8-yl)methyl)-*N*-((4-nitrophenyl)sulfonyl)benze-nesulfonamide (3r)

The reaction of 5-fluoro-8-methyl-quinoline (**1c**) (0.15 mmol, 24 mg), *N*,4-difluoro-*N*-((4-nitrophenyl)sulfonyl)benzenesulfonamide (**2c**) (1.3 equvi, 73.5 mg), CuBr (10 mol %, 2.1 mg), 1,10-phenanthroline (5 mol %, 2.7 mg), Na_2CO_3 (50 mol %, 8.0 mg), in 1.5 mL DCE at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 52.0 mg (72%) of **3r** as solid: MP: 165-167 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.46 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.28 (dd, *J* = 7.2, 2.0 Hz, 2H), 8.06 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.92-7.89 (m, 2H), 7.55 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.47 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.12 (t, *J* = 8.8 Hz, 2H), 7.06-7.04 (m, 1H), 5.80 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.8 (d, *J* = 256.6 Hz), 157.5 (d, *J* = 255.5 Hz), 150.5 (d, *J* = 21.6 Hz), 146.0 (d, *J* = 3.0 Hz), 145.1, 135.1 (d, *J* = 3.4 Hz), 131.3 (d, *J* = 9.9 Hz), 129.6, 128.4 (d, *J* = 9.0 Hz), 128.1 (d, *J* = 4.9 Hz), 123.9, 121.6 (d, *J* = 3.4 Hz), 118.7 (d, *J* = 16.8 Hz), 116.2 (d, *J* = 22.8 Hz), 109.3 (d, *J* = 20.1 Hz), 48.8 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) *δ* = -101.9, -121.9. HRMS m/z (ESI): Calcd. for $C_{22}H_{16}F_2N_3O_6S_2$ $[M+H]^+$ 520.0449, Found: 520.0443.



3s

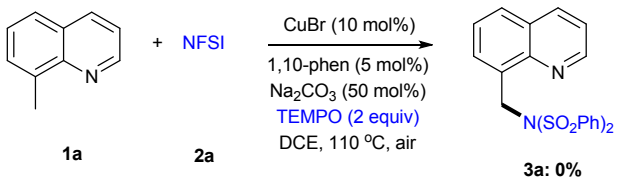
19) *N*-((6-Bromoquinolin-8-yl)methyl)-4-fluoro-*N*-((4-nitrophenyl)sulfonyl)benzenesulfonamide (3s)

The reaction of 6-bromo-8-methyl-quinoline (**1i**) (0.15 mmol, 33.3 mg), *N*,4-difluoro-*N*-((4-nitrophenyl)sulfonyl)benzenesulfonamide (**2c**) (0.3 mmol, 113.5 mg), $Cu(OAc)_2$ (2 equiv, 36.3 mg), Li_2CO_3 (50 mol %, 3.7 mg), in 0.5 mL DCE and 0.5 mL MeCN at 110 ^oC under Ar for 22 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 72.4 mg (83%) of **3s** as solid: MP: 172-173 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.0, 1.6 Hz, 1H), 8.32 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 9.2 Hz, 2H), 8.06 (dd, J = 8.4, 1.6 Hz, 1H), 7.99 (dd, J = 8.8, 4.8 Hz, 2H), 7.86 (d, J = 2.0 Hz, 1H), 7.47 (dd, J = 8.0, 4.4 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.20 (t, J = 8.8 Hz, 2H), 5.80 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (d, J = 256.5 Hz), 150.6, 150.0, 144.5 (d, J = 81.9 Hz), 135.2, 135.0 (d, J =3.0 Hz), 134.4, 131.4, 131.3 (d, J = 5.8 Hz), 129.6, 129.1, 124.1, 122.4, 119.8, 116.5 (d, J = 22.9 Hz), 48.9 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -101.5. HRMS m/z (ESI): Calcd. for $C_{22}H_{16}BrFN_3O_6S_2$ [M+H]+ 579.9648, Found: 579.9642.

The radical-trapping experiment

The radical-trapping experiment was carried out. When 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) was added (2 equiv) in the model reaction under the present reaction conditions, the reaction was completely inhibited (we did not get the **3a**). It is

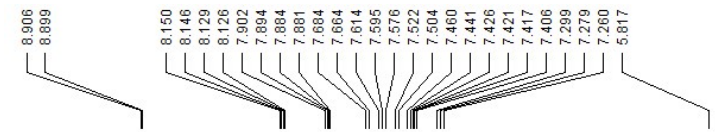
suggested that the reaction may involve a radical process.



1a **2a** **3a: 0%**

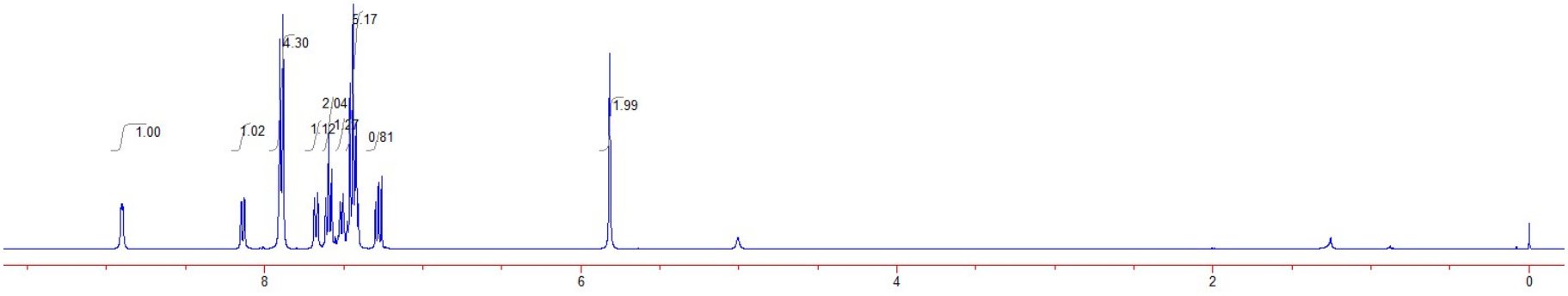
Reference

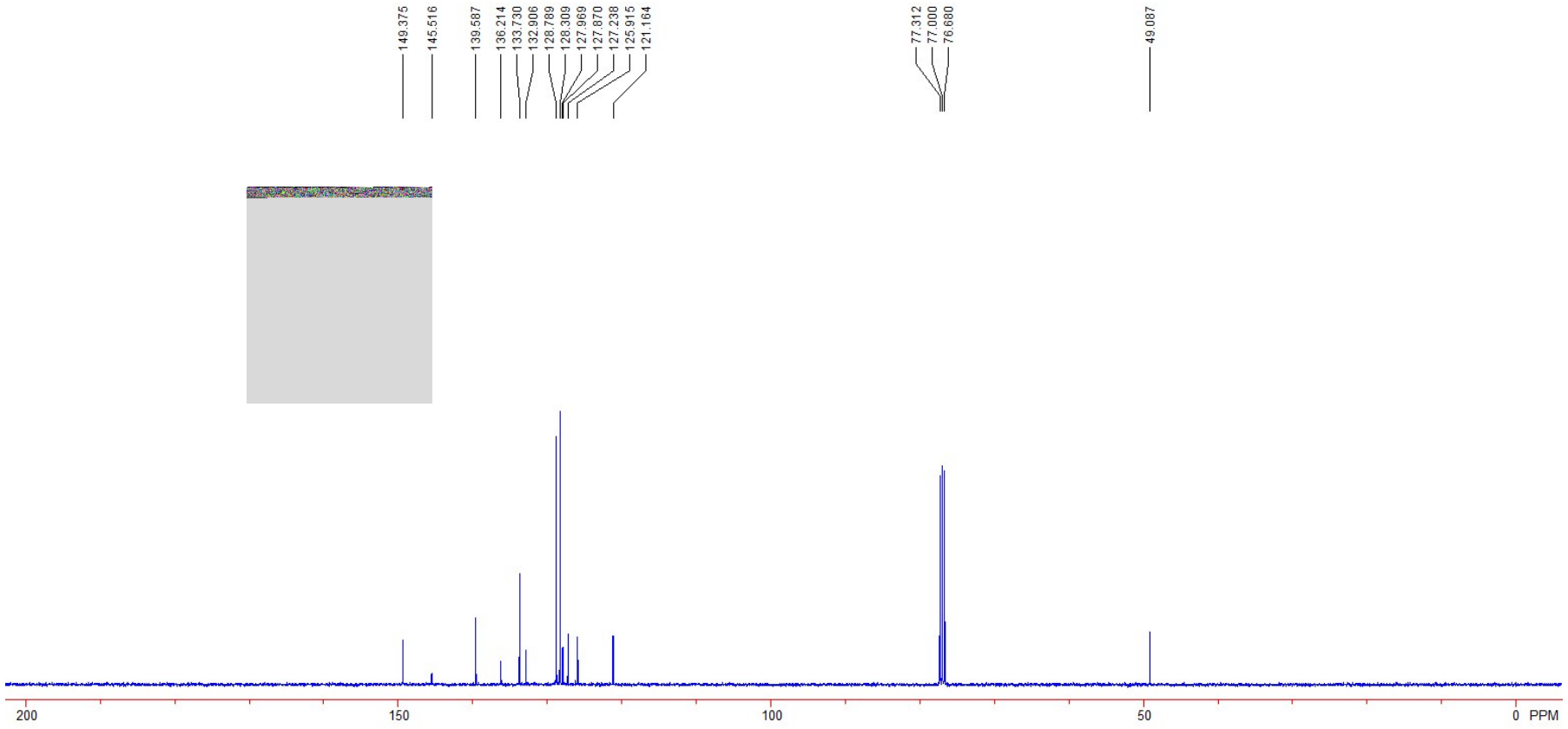
1. Á. Iglesias, R.Álvarez, Á. R. de Lera, Muñiz, K. *Angew. Chem., Int. Ed.*, 2012, **51**, 2225.


8.906
8.899
8.150
8.146
8.129
8.126
7.902
7.894
7.884
7.881
7.684
7.664
7.614
7.595
7.576
7.522
7.504
7.460
7.441
7.426
7.421
7.417
7.406
7.299
7.279
7.260
5.817

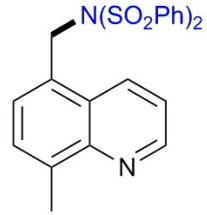

N
N(SO2Ph)2

3a

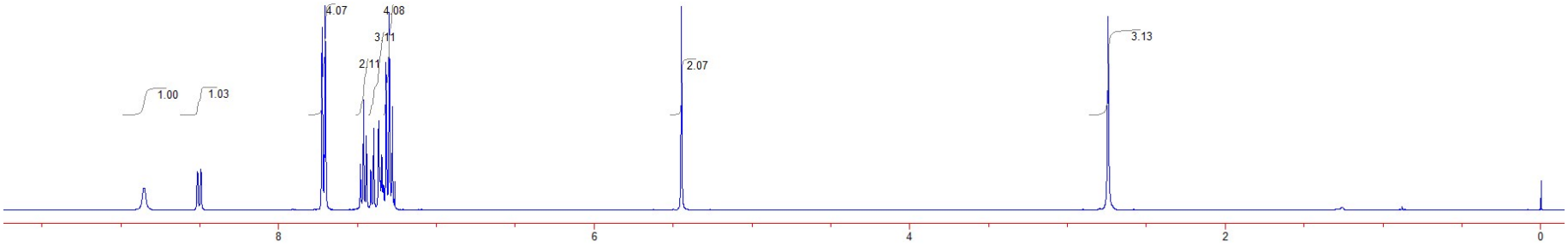

6.17
4.30
2.04
1.99
1.00
1.02
1.12
1.27
0.81
8
6
4
2
0

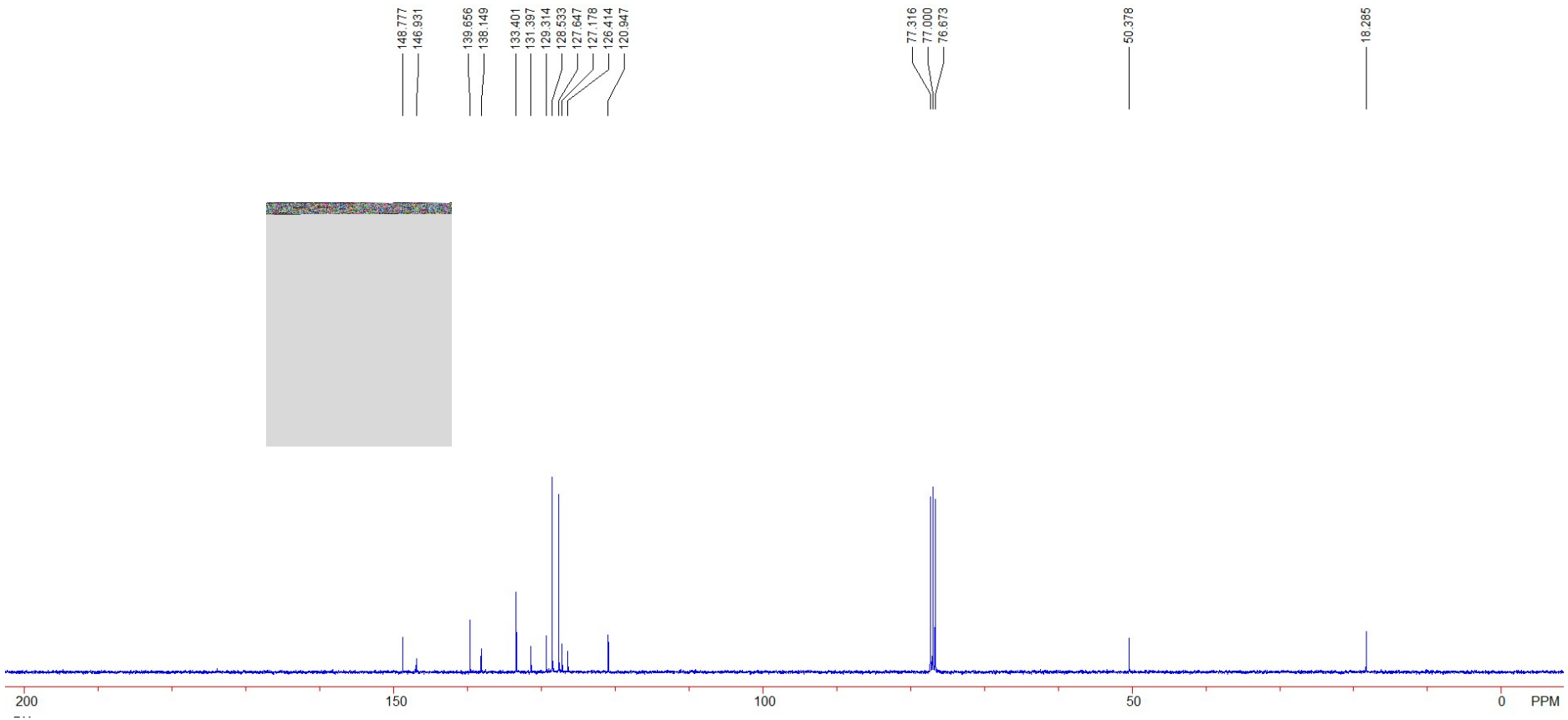

149.375
145.516
139.587
136.214
133.730
132.906
128.789
128.309
127.969
127.870
127.238
125.915
121.164
77.312
77.000
76.680
49.087
200
150
100
50
0 PPM

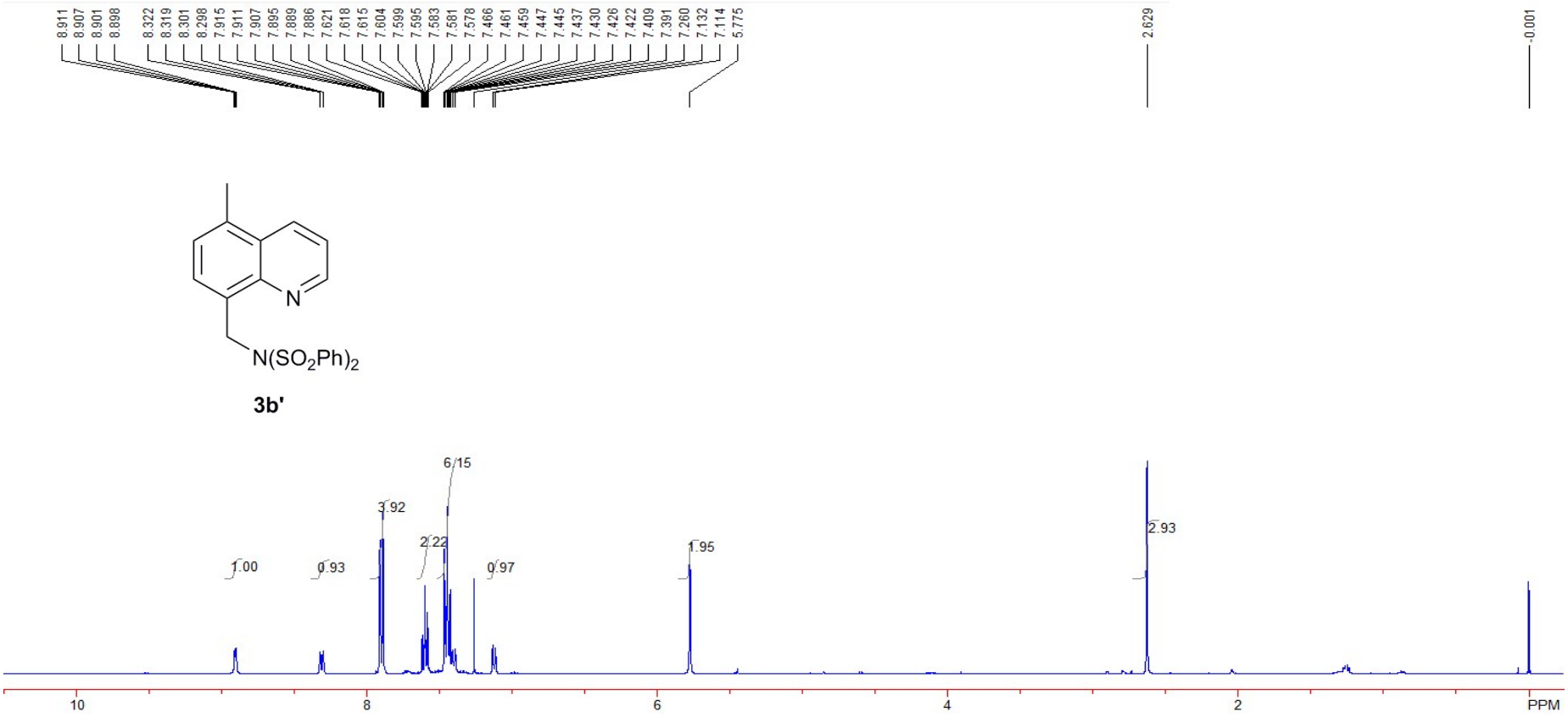

8.852
8.515
8.513
8.494
8.492
7.726
7.724
7.710
7.705
7.702
7.483
7.480
7.478
7.461
7.445
7.443
7.440
7.415
7.397
7.366
7.357
7.346
7.335
7.319
7.315
7.300
7.298
7.284
7.279
7.263
5.447
2.742
0.000

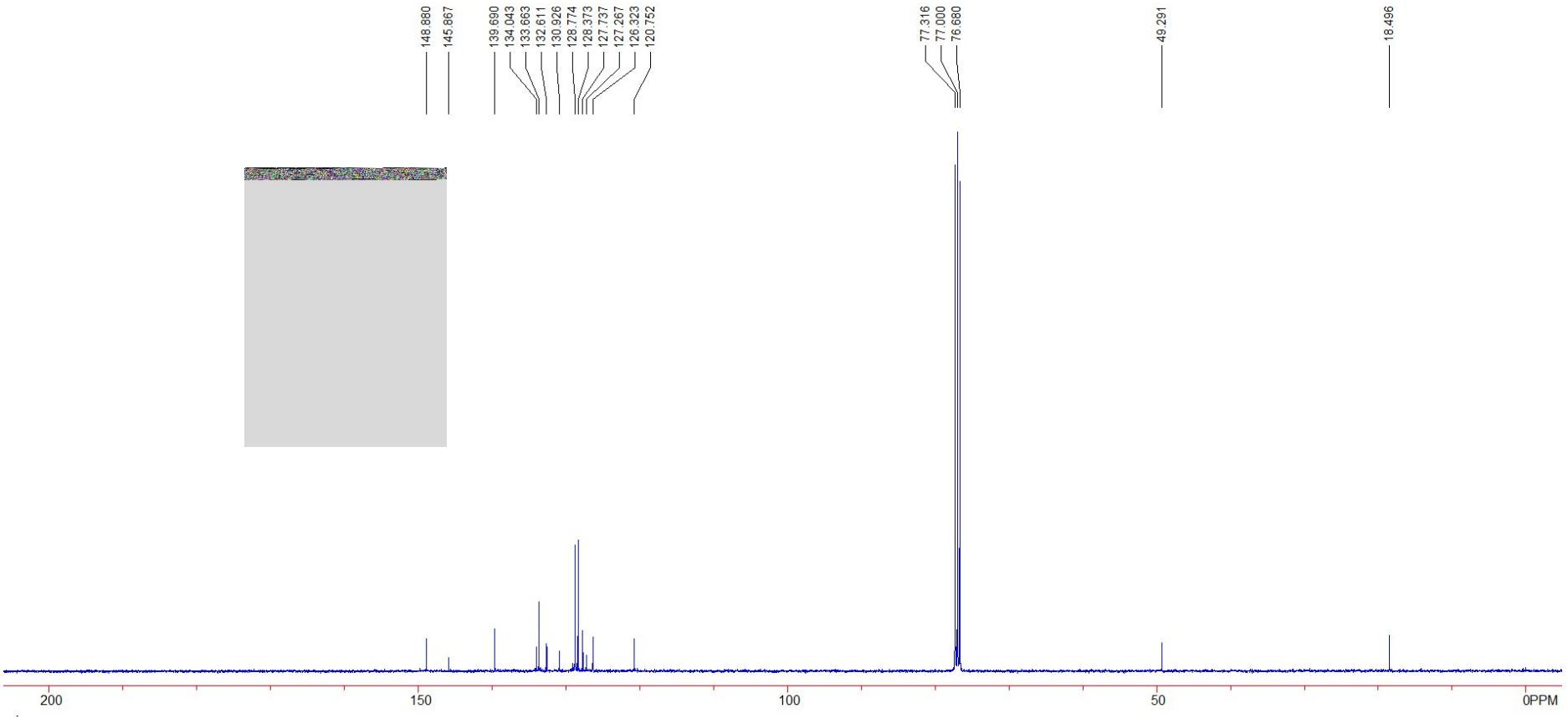

N(SO2Ph)2
N

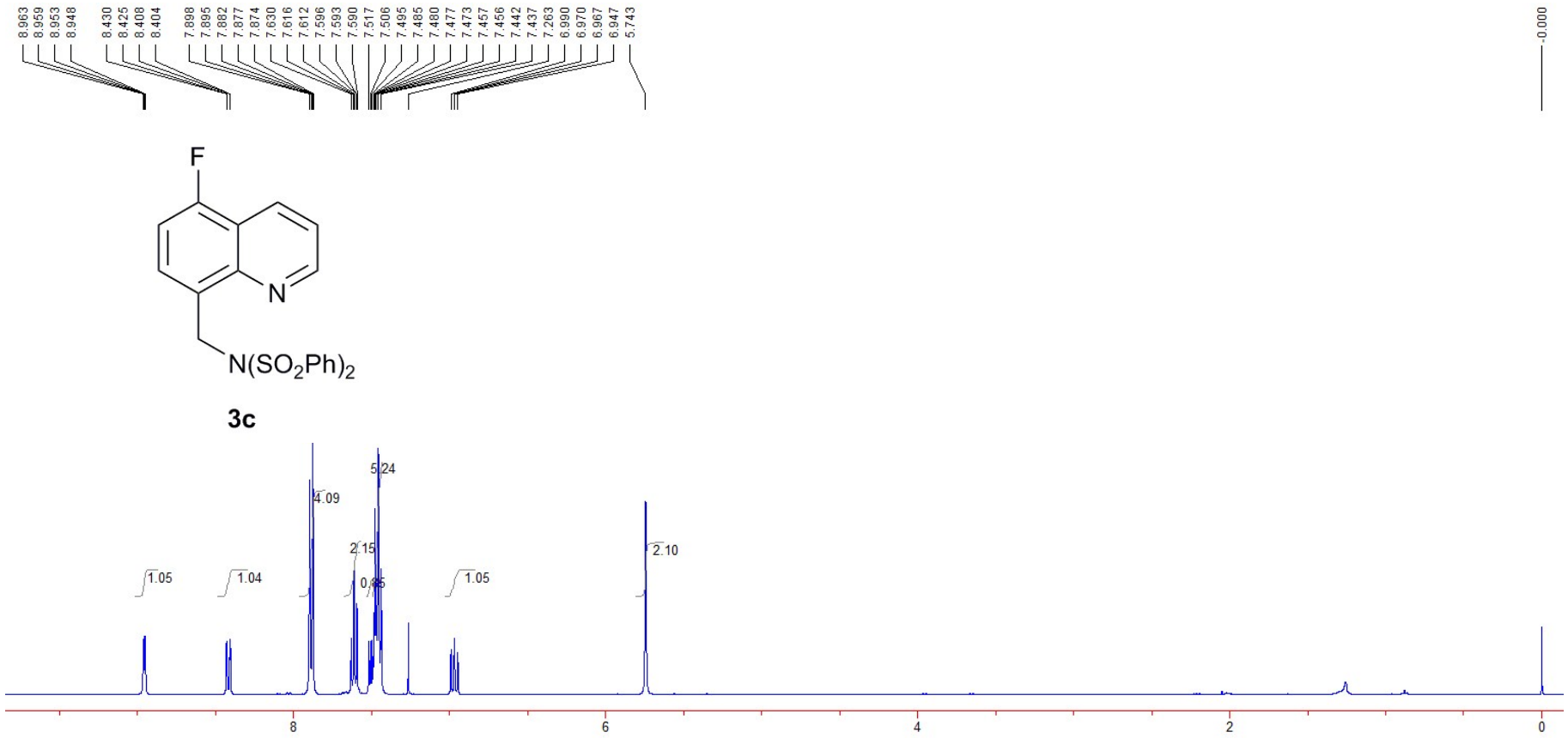
3b

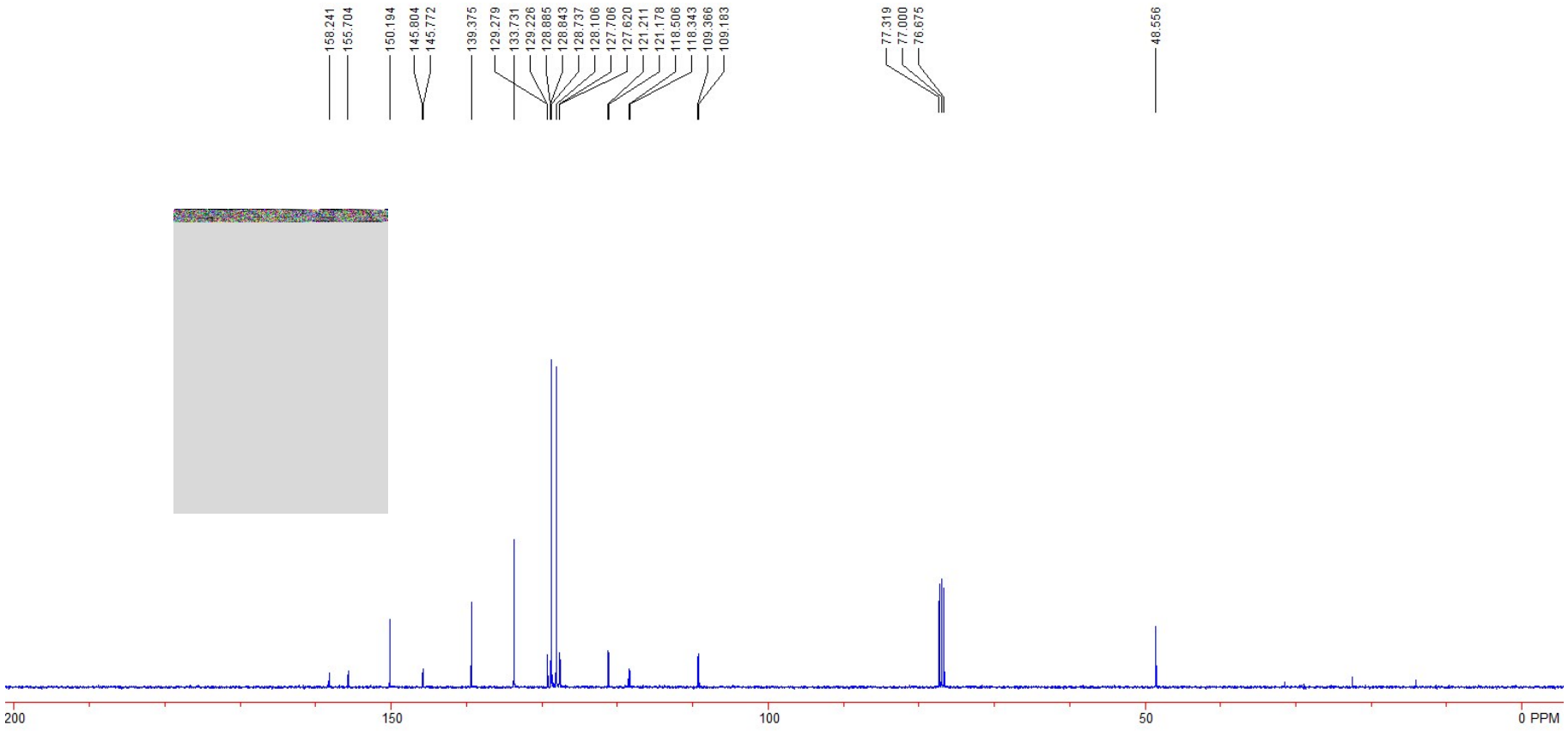

4.07
4.08
3.11
2.11
1.00
1.03
2.07
3.13
8
6
4
2
0

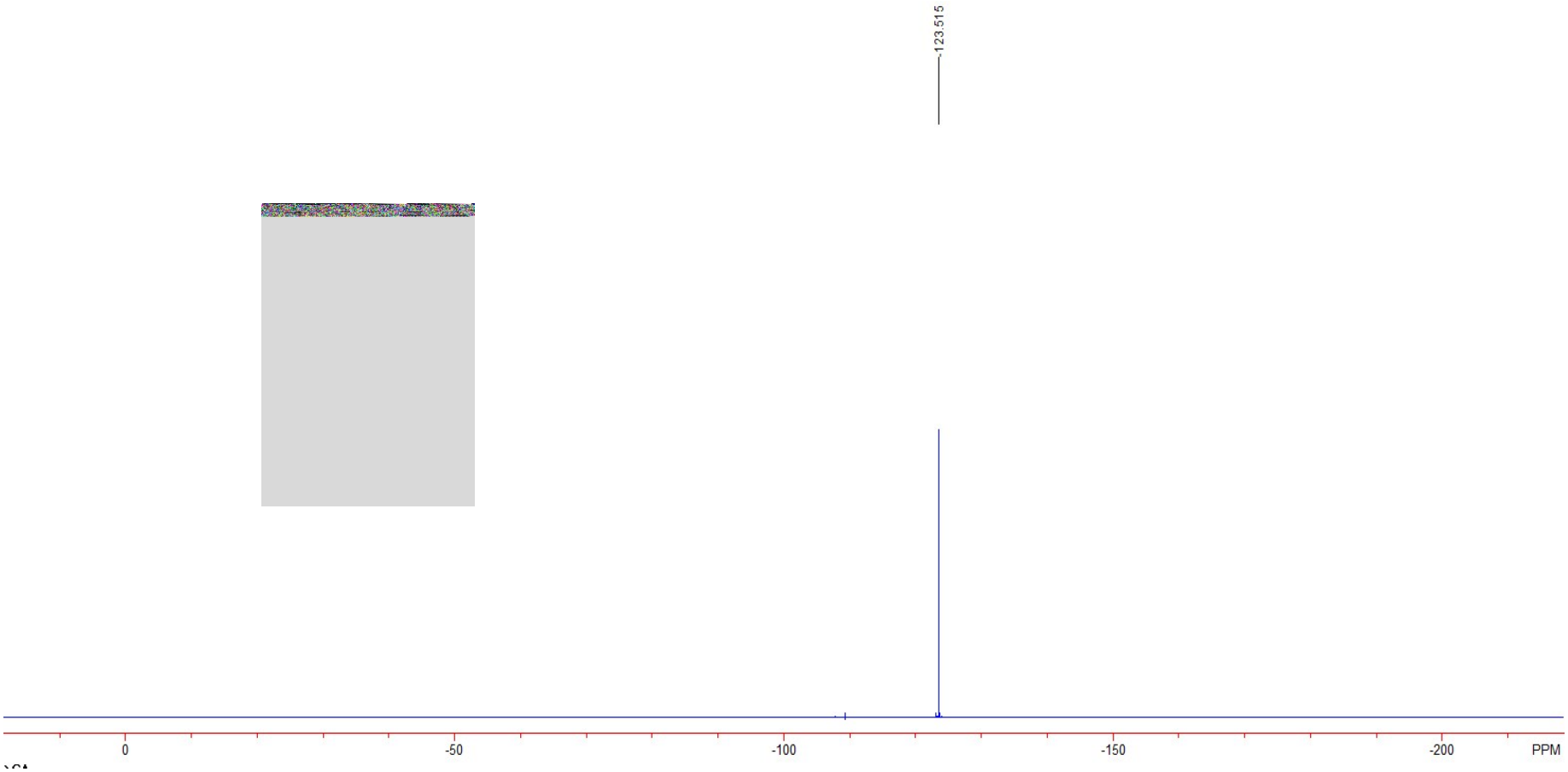

148.777
146.931
139.656
138.149
133.401
131.397
129.314
128.533
127.647
127.178
126.414
120.947
77.316
77.000
76.673
50.378
18.285
200
150
100
50
0
PPM

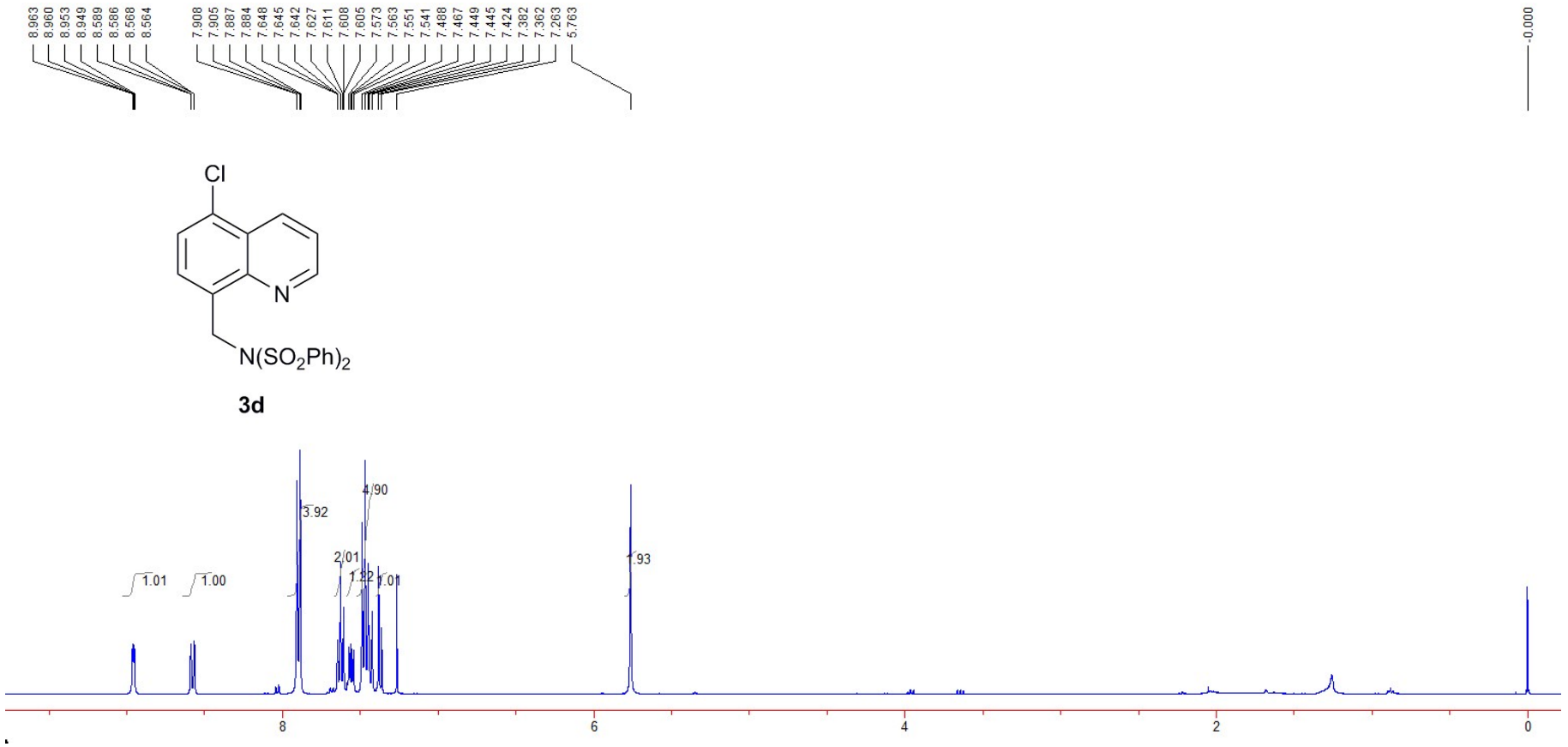

8.911
8.907
8.901
8.898
8.322
8.319
8.301
8.298
7.915
7.911
7.907
7.895
7.889
7.886
7.621
7.618
7.615
7.604
7.599
7.595
7.583
7.581
7.578
7.466
7.461
7.459
7.447
7.445
7.437
7.430
7.426
7.422
7.409
7.391
7.260
7.132
7.114
5.775
2.629
-0.001
N
N(SO2Ph)2
3b'
6.15
3.92
2.22
1.00
0.93
0.97
1.95
2.93
10
8
6
4
2
PPM

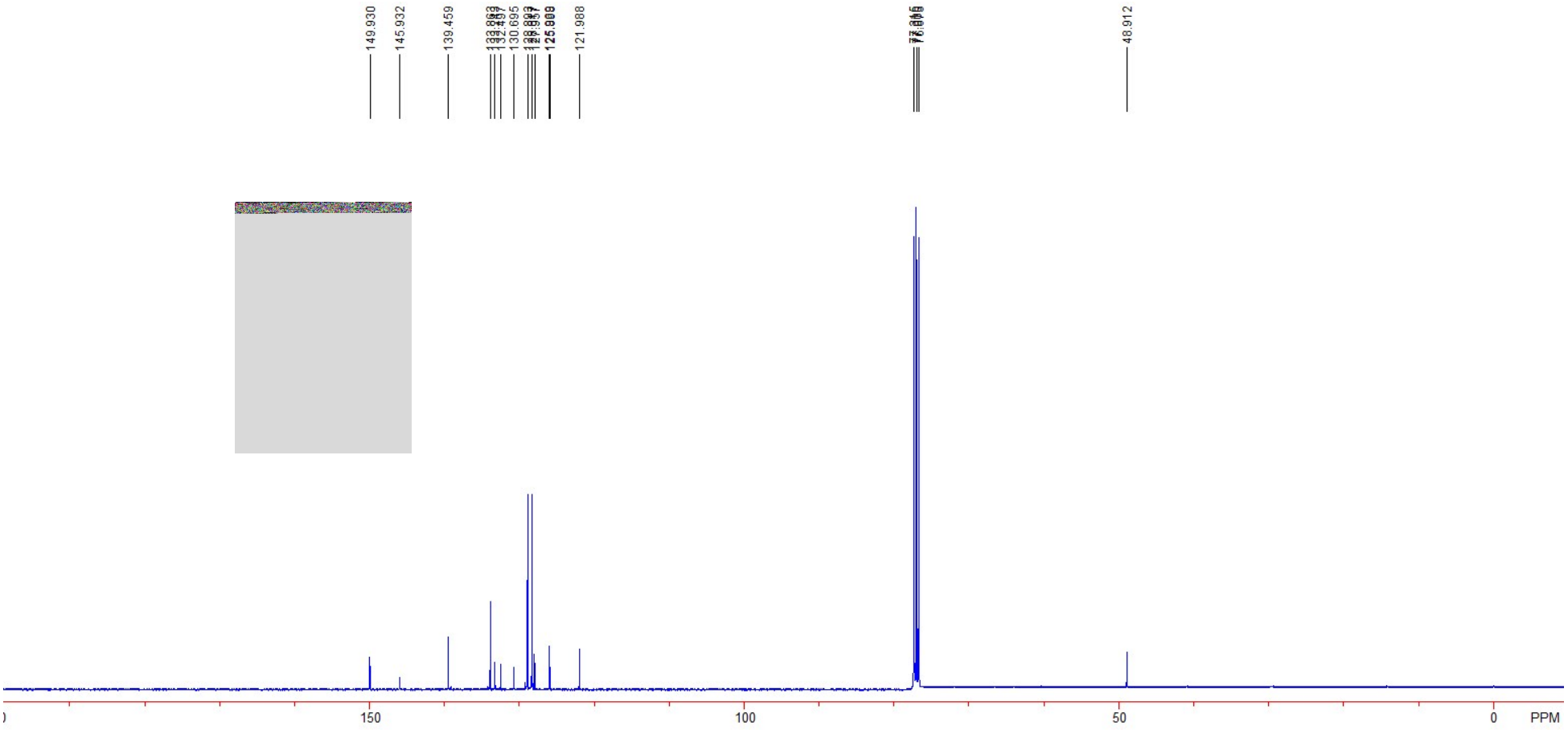

148.880
145.867
139.690
134.043
133.663
132.611
130.926
128.774
128.373
127.737
127.267
126.323
120.752
77.316
77.000
76.680
49.291
18.496
200
150
100
50
0PPM

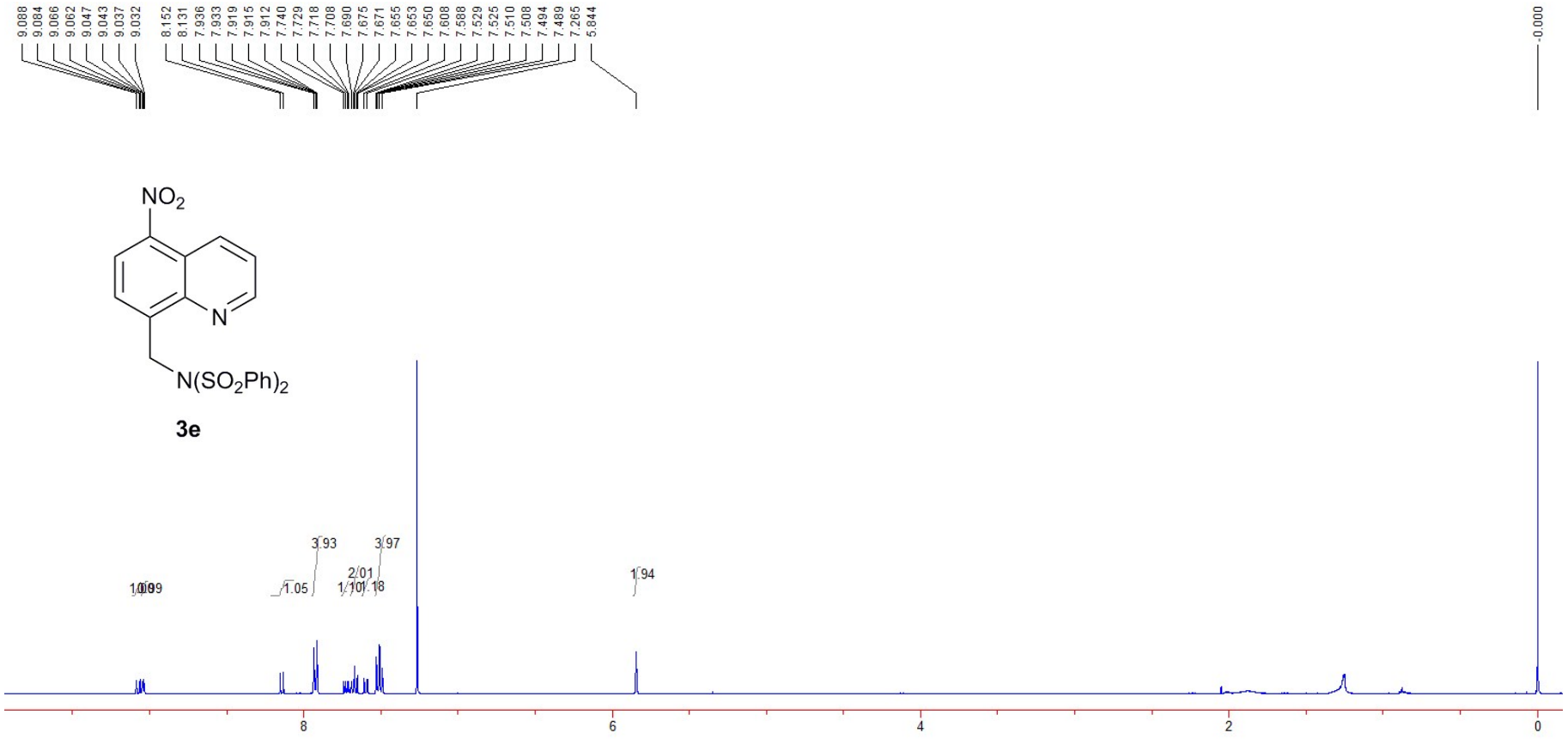

8.963
8.959
8.953
8.948
8.430
8.425
8.408
8.404
7.898
7.895
7.882
7.877
7.874
7.630
7.616
7.612
7.596
7.593
7.590
7.517
7.506
7.495
7.485
7.480
7.477
7.473
7.457
7.456
7.442
7.437
7.263
6.990
6.970
6.967
6.947
5.743
-0.000
F
N
N(SO2Ph)2
3c
5.24
4.09
2.15
2.10
1.05
1.04
1.05
8
6
4
2
0

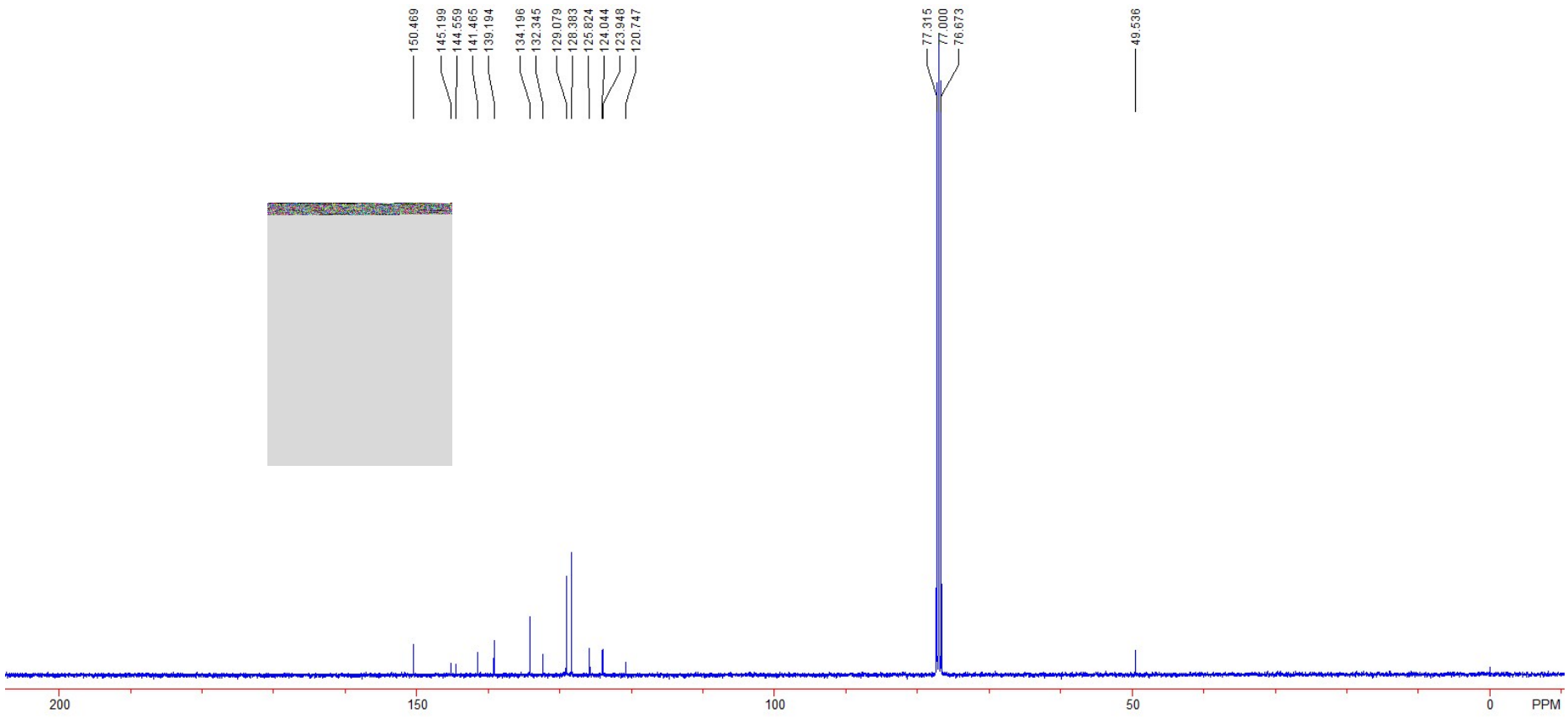

158.241
155.704
150.194
145.804
145.772
139.375
129.279
133.731
129.226
128.885
128.843
128.737
128.106
127.706
127.620
121.211
121.178
118.506
118.343
109.366
109.183
77.319
77.000
76.675
48.556
200
150
100
50
0 PPM


-123.515
0
-50
-100
-150
-200
PPM


8.963
8.960
8.953
8.949
8.589
8.586
8.568
8.564
7.908
7.905
7.887
7.884
7.648
7.645
7.642
7.627
7.611
7.608
7.605
7.573
7.563
7.551
7.541
7.488
7.467
7.449
7.445
7.424
7.382
7.362
7.263
5.763
-0.000
Cl
N
N(SO2Ph)2
3d
1.01
1.00
3.92
4.90
2.01
1.22
1.01
1.93
8
6
4
2
0


149.930
145.932
139.459
121.988
48.912
150
100
50
0
PPM

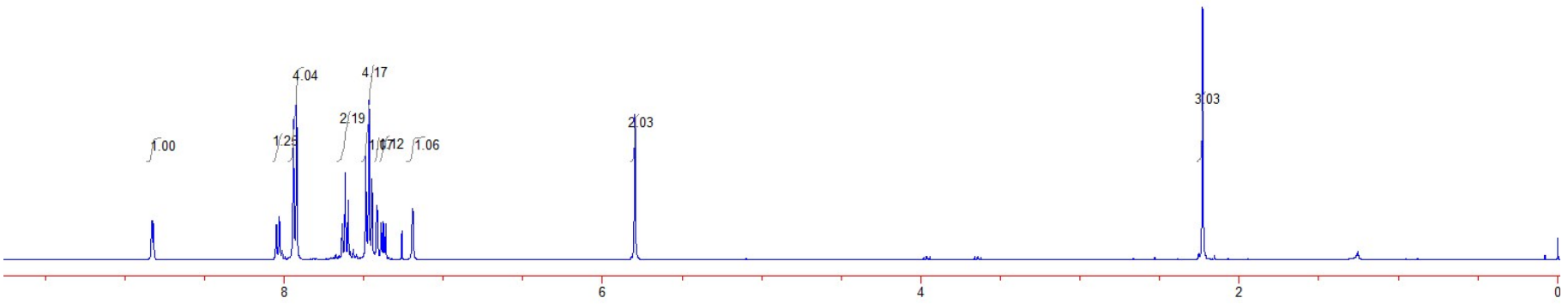

9.088
9.084
9.066
9.062
9.047
9.043
9.037
9.032
8.152
8.131
7.936
7.933
7.919
7.915
7.912
7.740
7.729
7.718
7.708
7.690
7.675
7.671
7.655
7.653
7.650
7.608
7.588
7.529
7.525
7.510
7.508
7.494
7.489
7.265
5.844
0.000
NO2
N
N(SO2Ph)2
3e
3.93
3.97
2.01
1.94
1.05
1.18
8
6
4
2
0

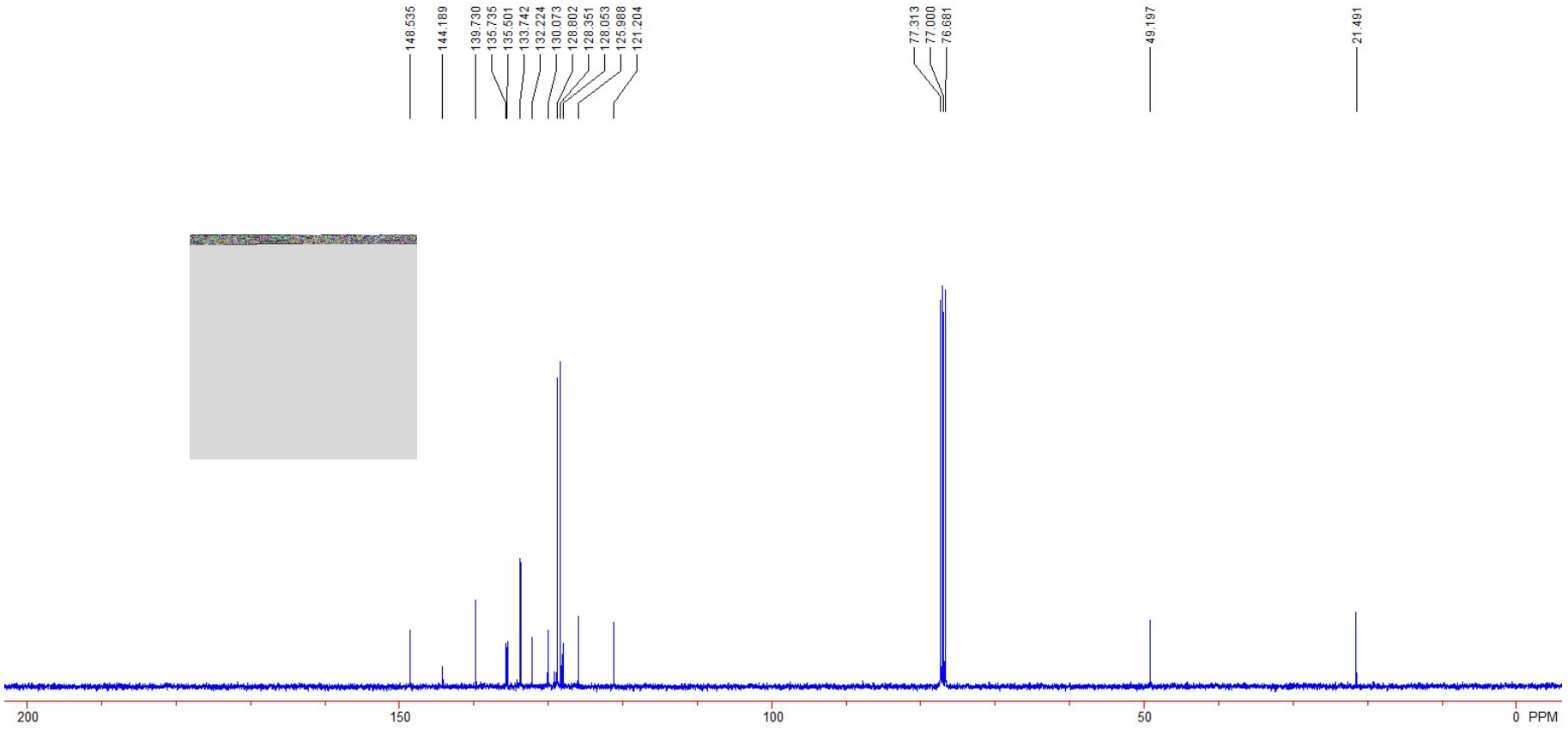

150.469
145.199
144.559
141.465
139.194
134.196
132.345
129.079
128.383
125.824
124.044
123.948
120.747
77.315
77.000
76.673
49.536
200
150
100
50
0
PPM

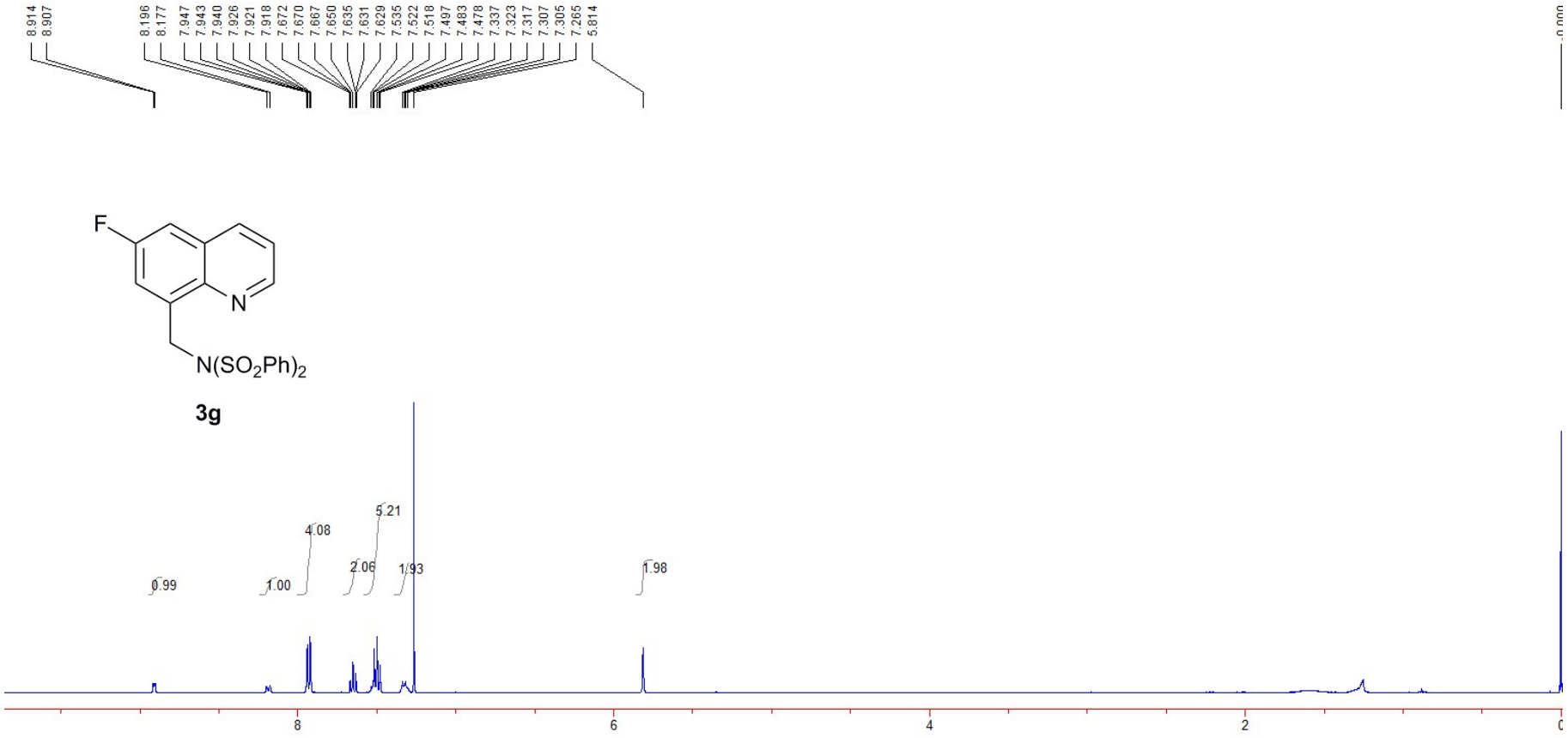

8.833
8.829
8.823
8.818
8.051
8.047
8.031
8.026
7.943
7.940
7.927
7.922
7.919
7.638
7.635
7.633
7.616
7.600
7.598
7.594
7.486
7.465
7.451
7.447
7.416
7.391
7.381
7.371
7.360
7.260
7.193
5.796
2.231

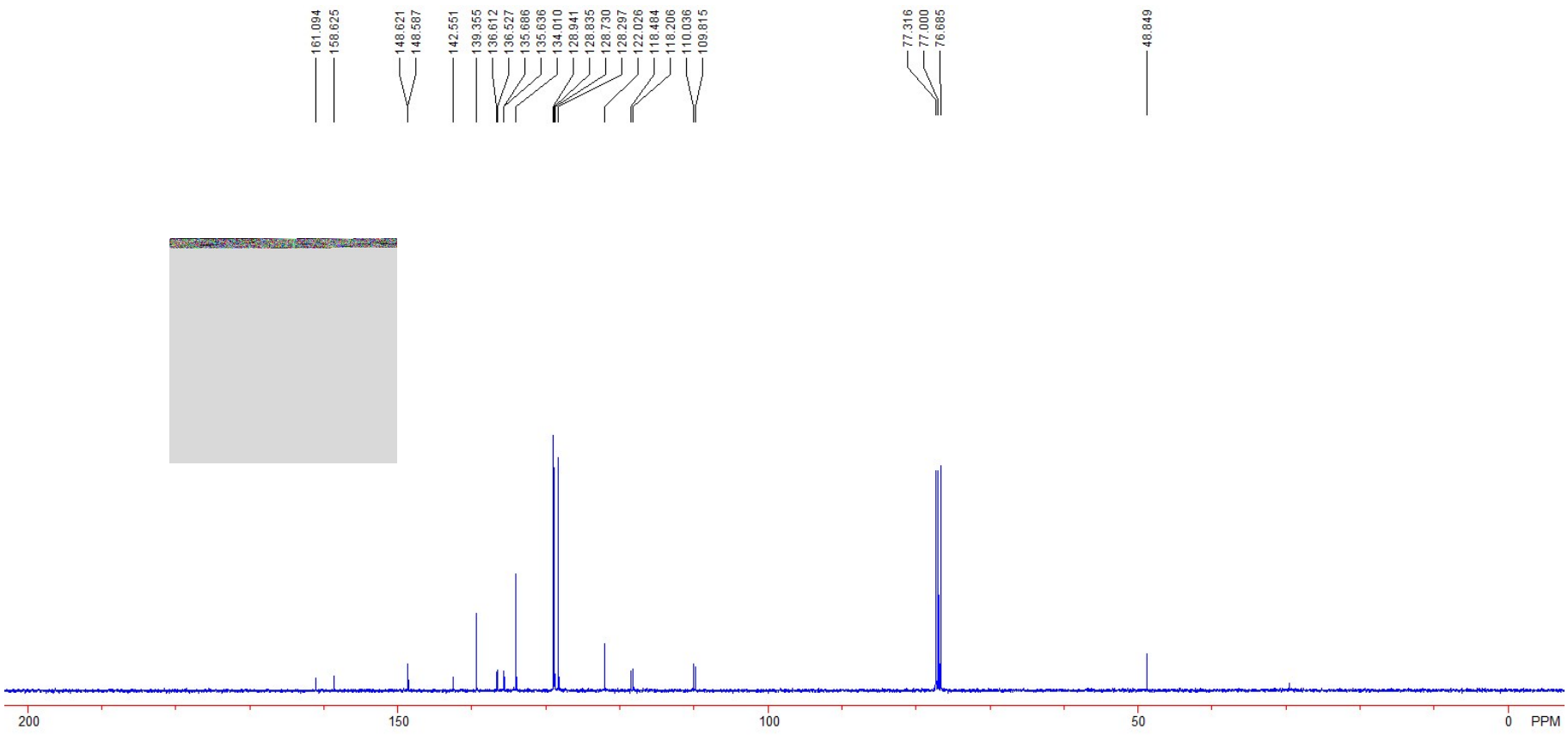

N
N(SO2Ph)2

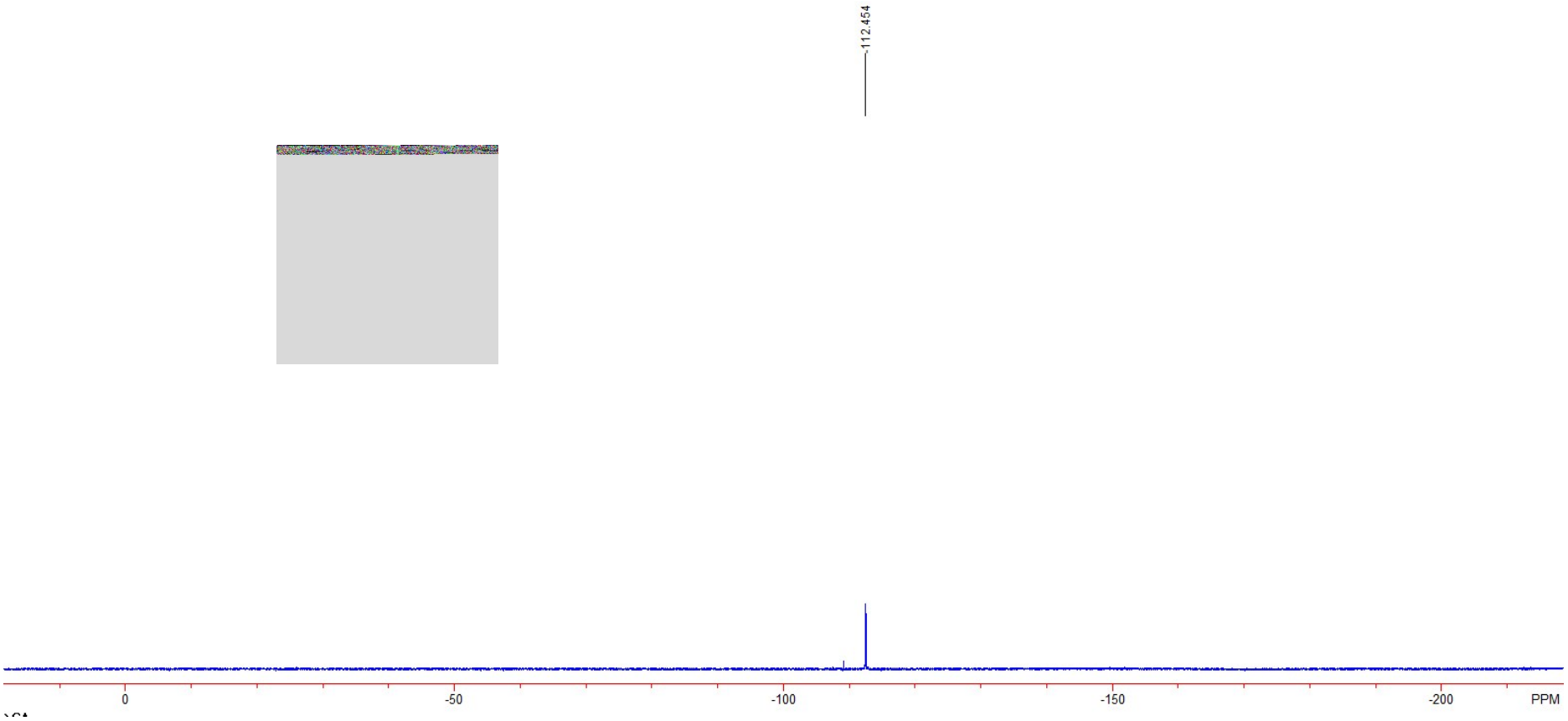
3f

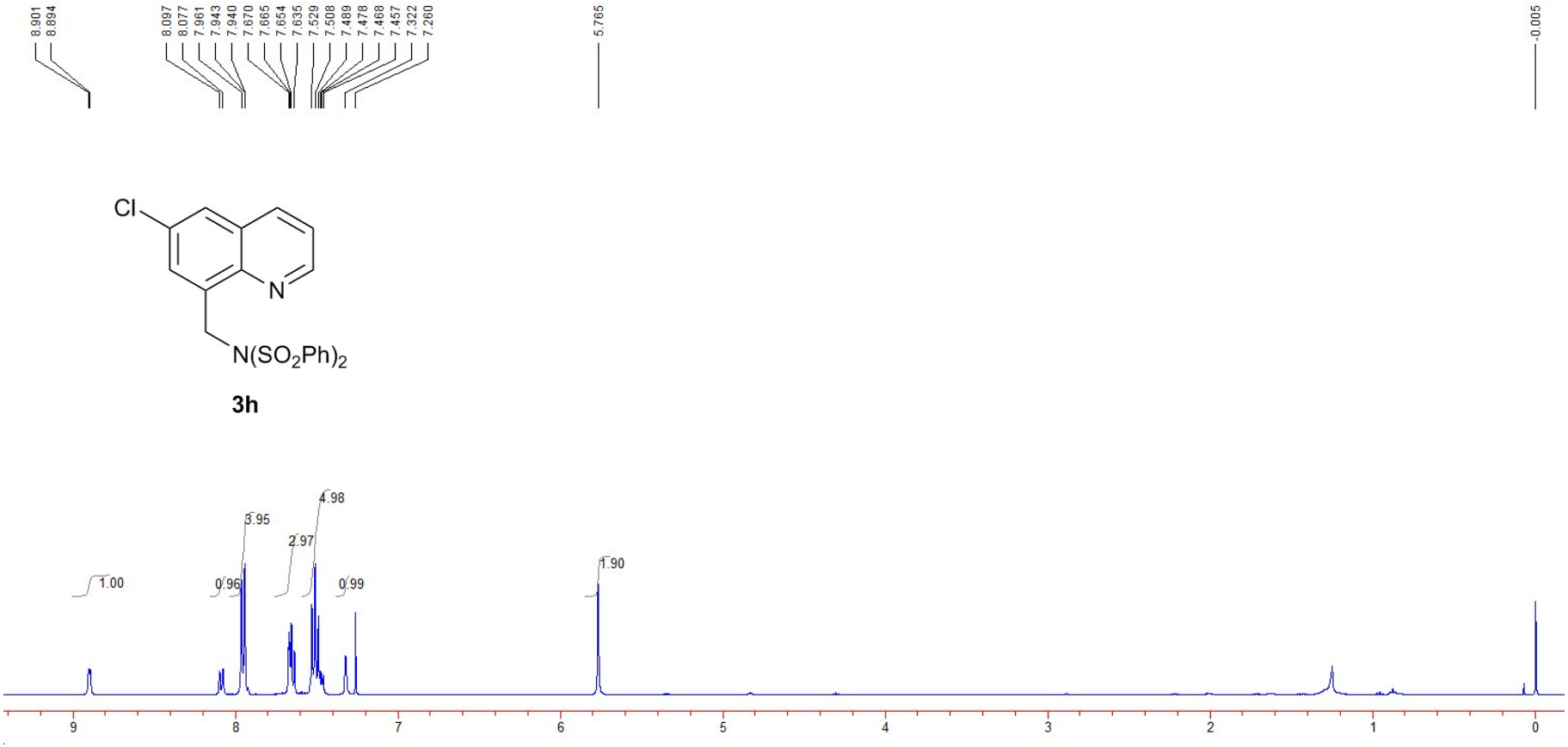

1.00
4.04
1.25
4.17
2.19
1.07
1.12
1.06
2.03
3.03
8
6
4
2
0


148.535
144.189
139.730
135.735
135.501
133.742
132.224
130.073
128.802
128.351
128.053
125.988
121.204
77.313
77.000
76.681
49.197
21.491
200
150
100
50
0 PPM

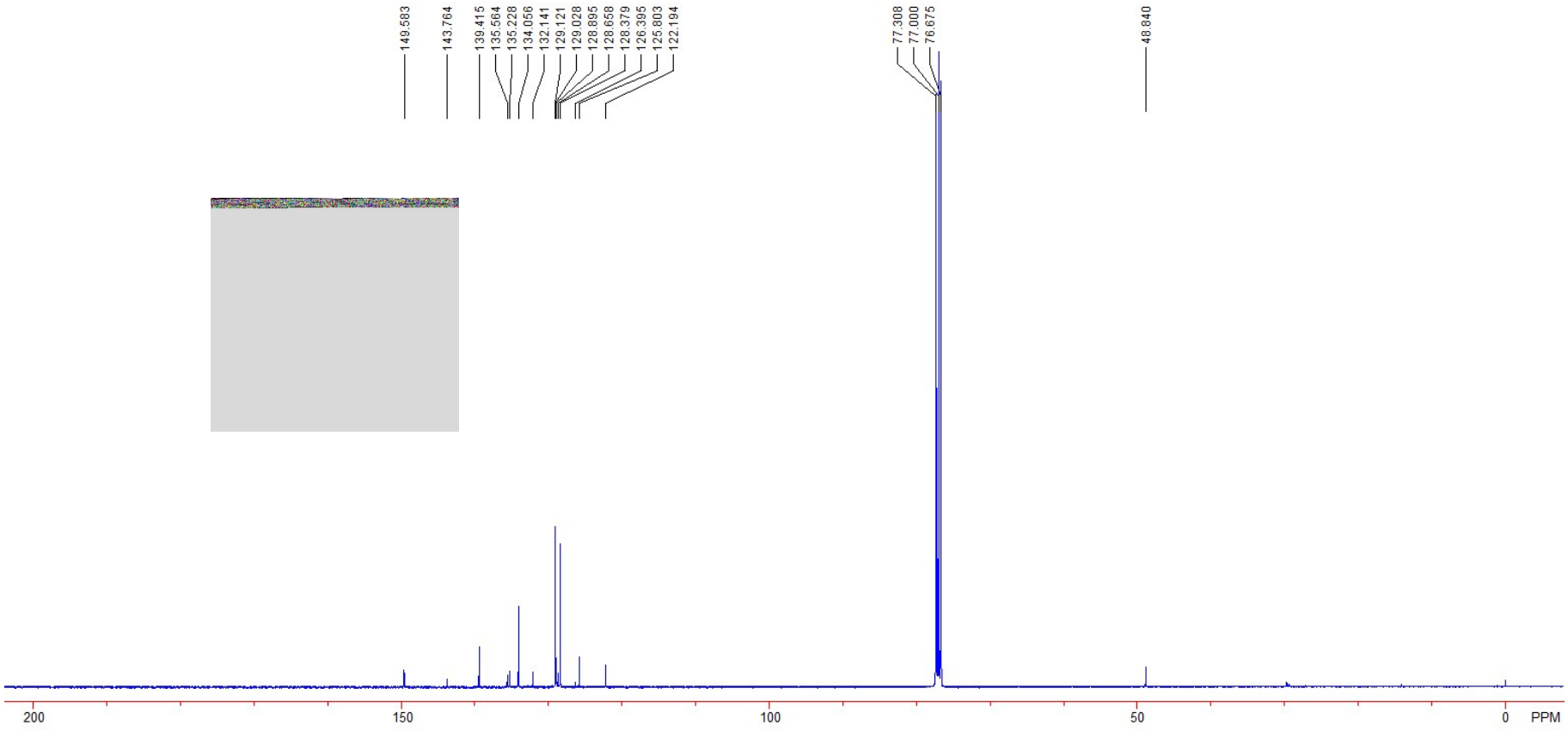

8.914
8.907
8.196
8.177
7.947
7.943
7.940
7.926
7.921
7.918
7.672
7.670
7.667
7.650
7.635
7.631
7.629
7.535
7.522
7.518
7.497
7.483
7.478
7.337
7.323
7.317
7.307
7.305
7.265
5.814
F
N
N(SO2Ph)2
3g
0.99
1.00
4.08
2.06
5.21
1.93
1.98
8
6
4
2

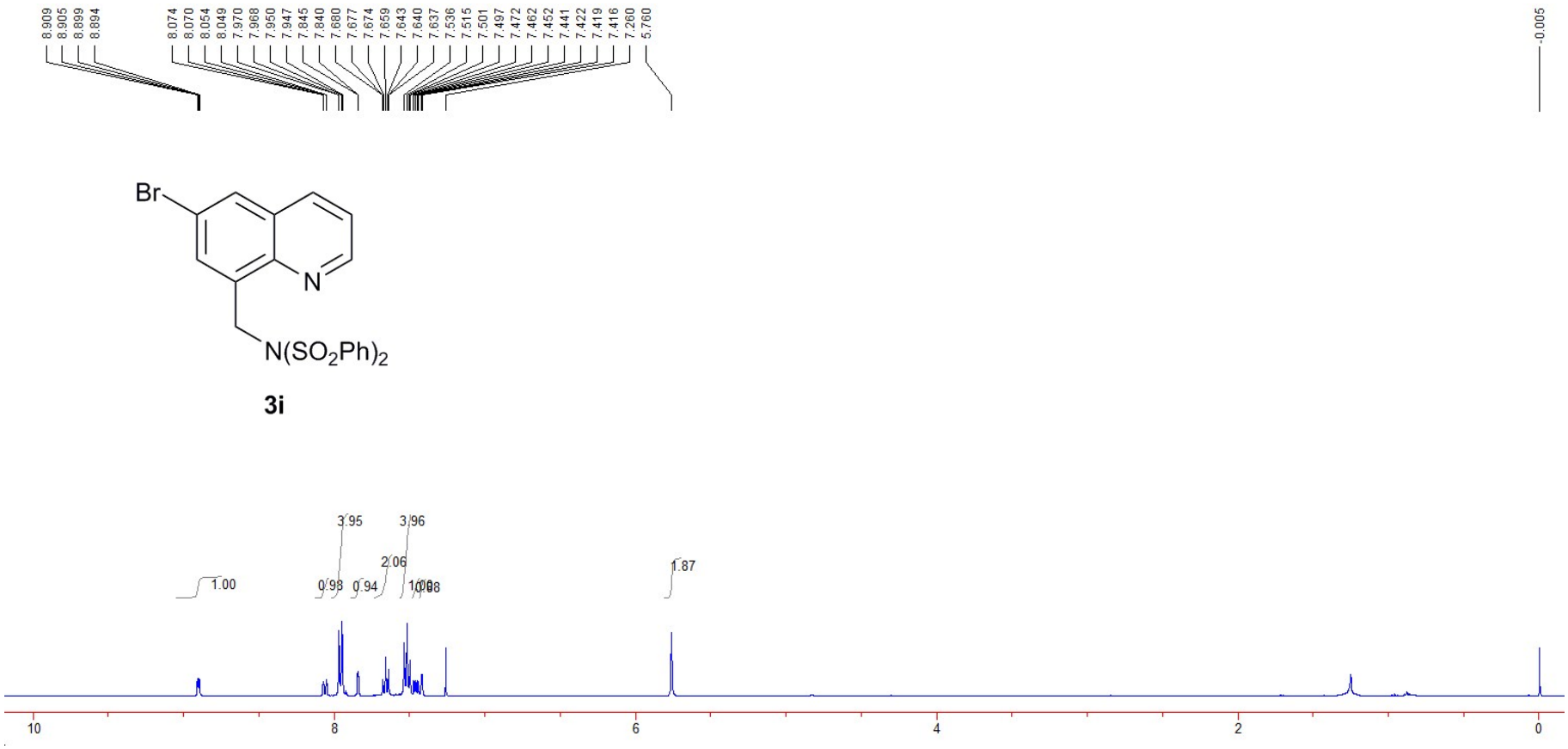

161.094
158.625
148.621
148.587
142.551
139.355
136.612
136.527
135.686
135.636
134.010
128.941
128.835
128.730
128.297
122.026
118.484
118.206
110.036
109.815
77.316
77.000
76.685
48.849
200
150
100
50
0
PPM

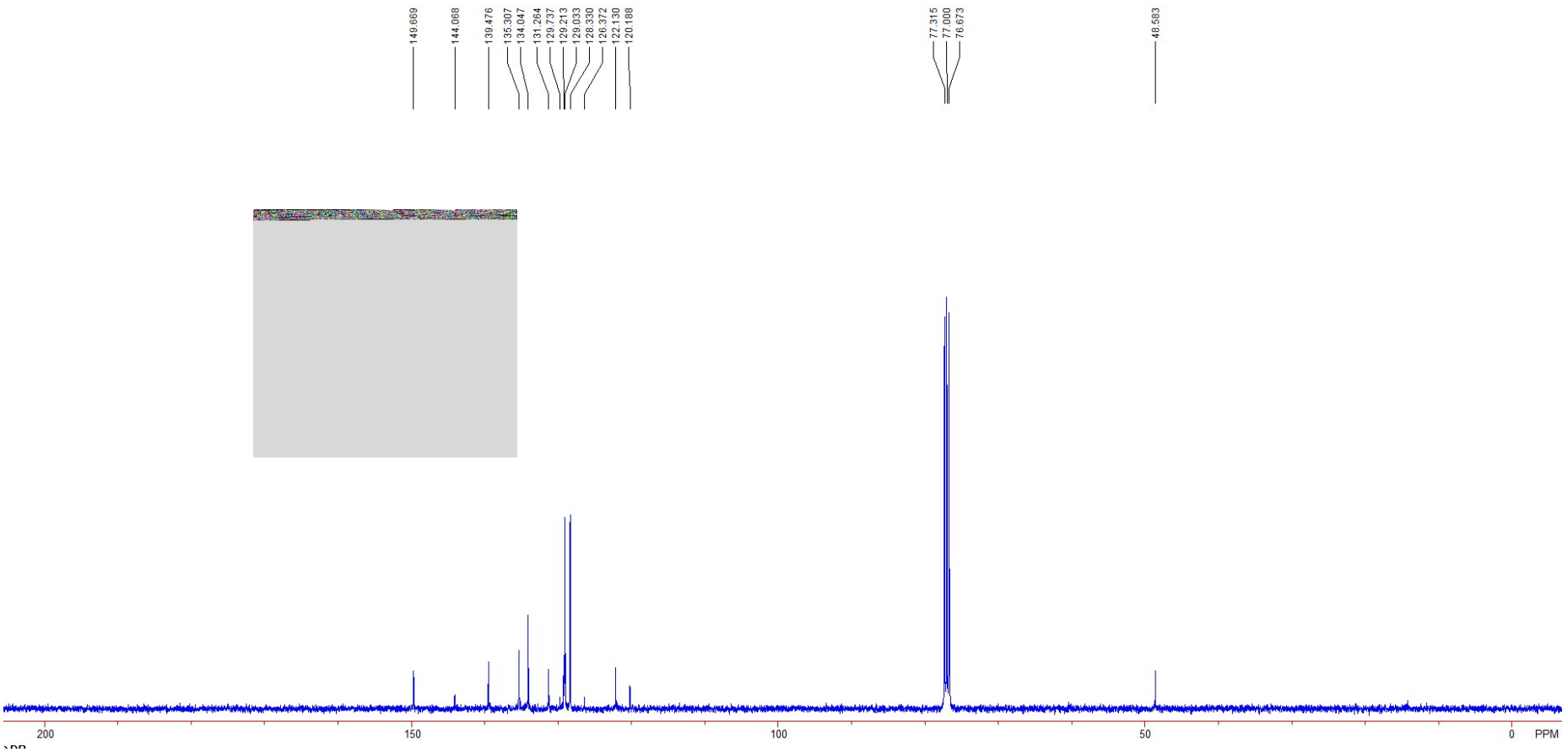

-112.454
0
-50
-100
-150
-200
PPM

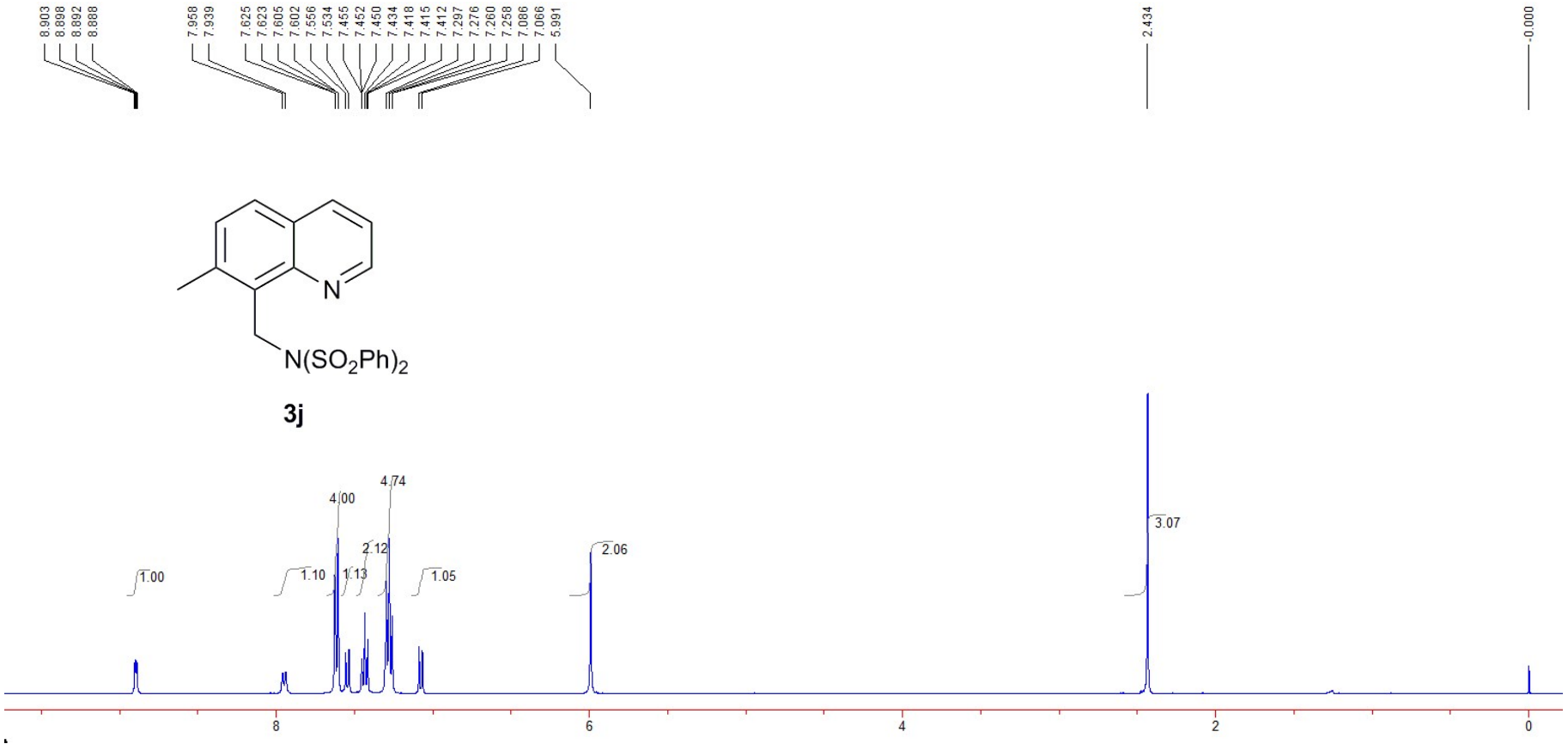

8.901
8.894
8.097
8.077
7.961
7.943
7.940
7.670
7.665
7.654
7.635
7.529
7.508
7.489
7.478
7.468
7.457
7.322
7.260
5.765
-0.005
Cl
N
N(SO2Ph)2
1.00
0.96
3.95
2.97
4.98
0.99
1.90
9
8
7
6
5
4
3
2
1
0

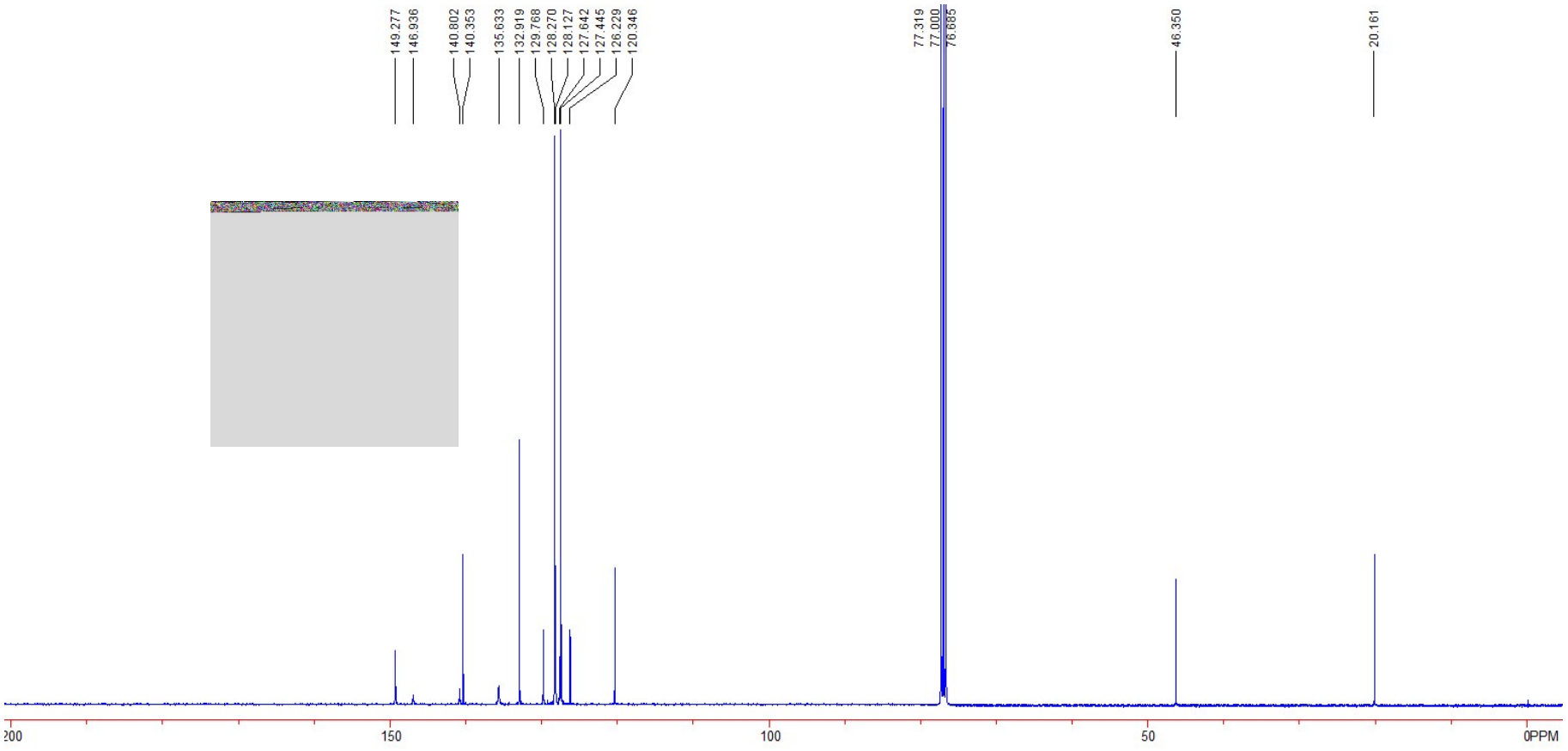
3h

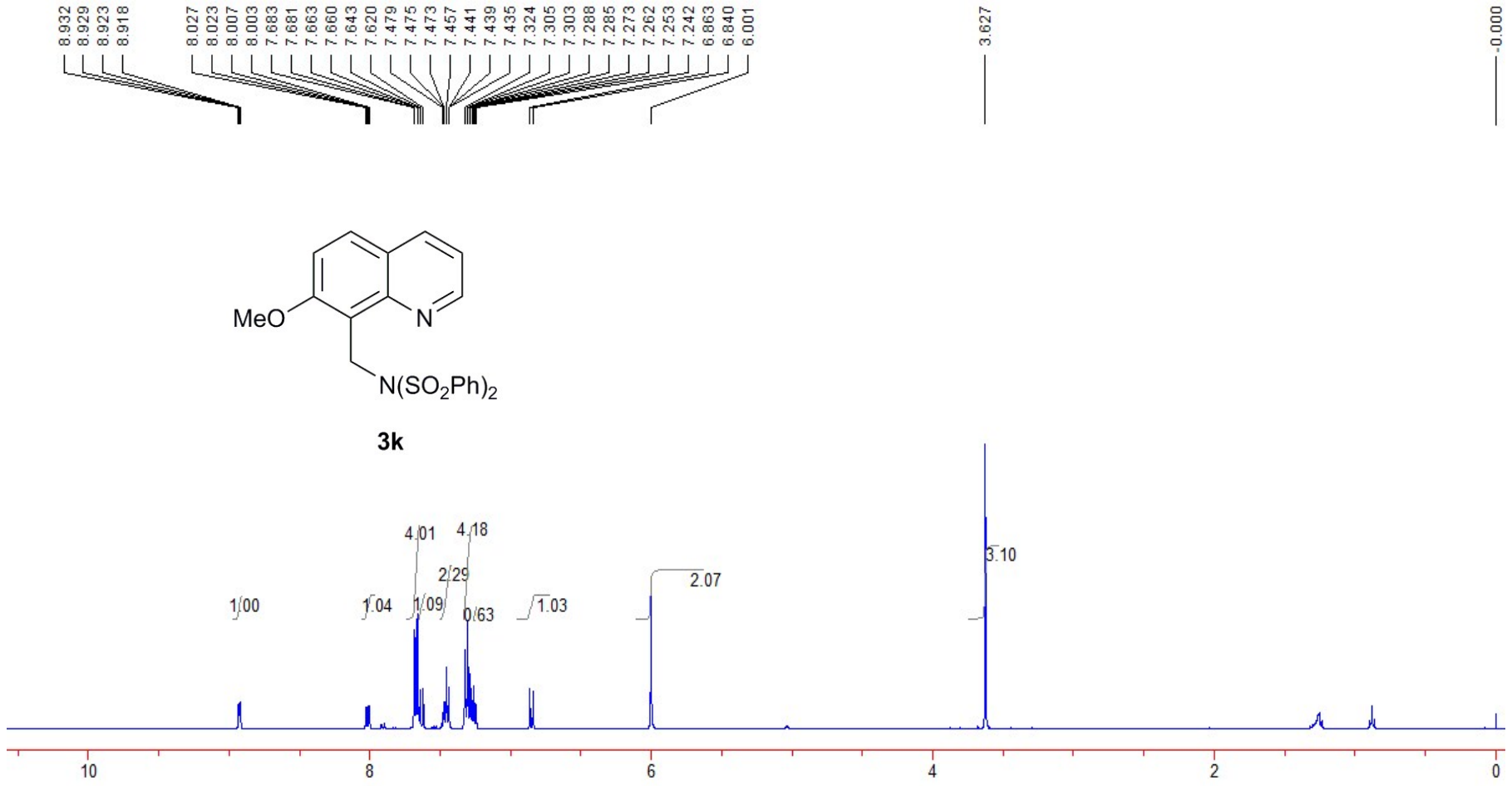

149.583
143.764
139.415
135.564
135.228
134.056
132.141
129.121
129.028
128.895
128.658
128.379
126.395
125.803
122.194
77.308
77.000
76.675
48.840
200
150
100
50
0
PPM

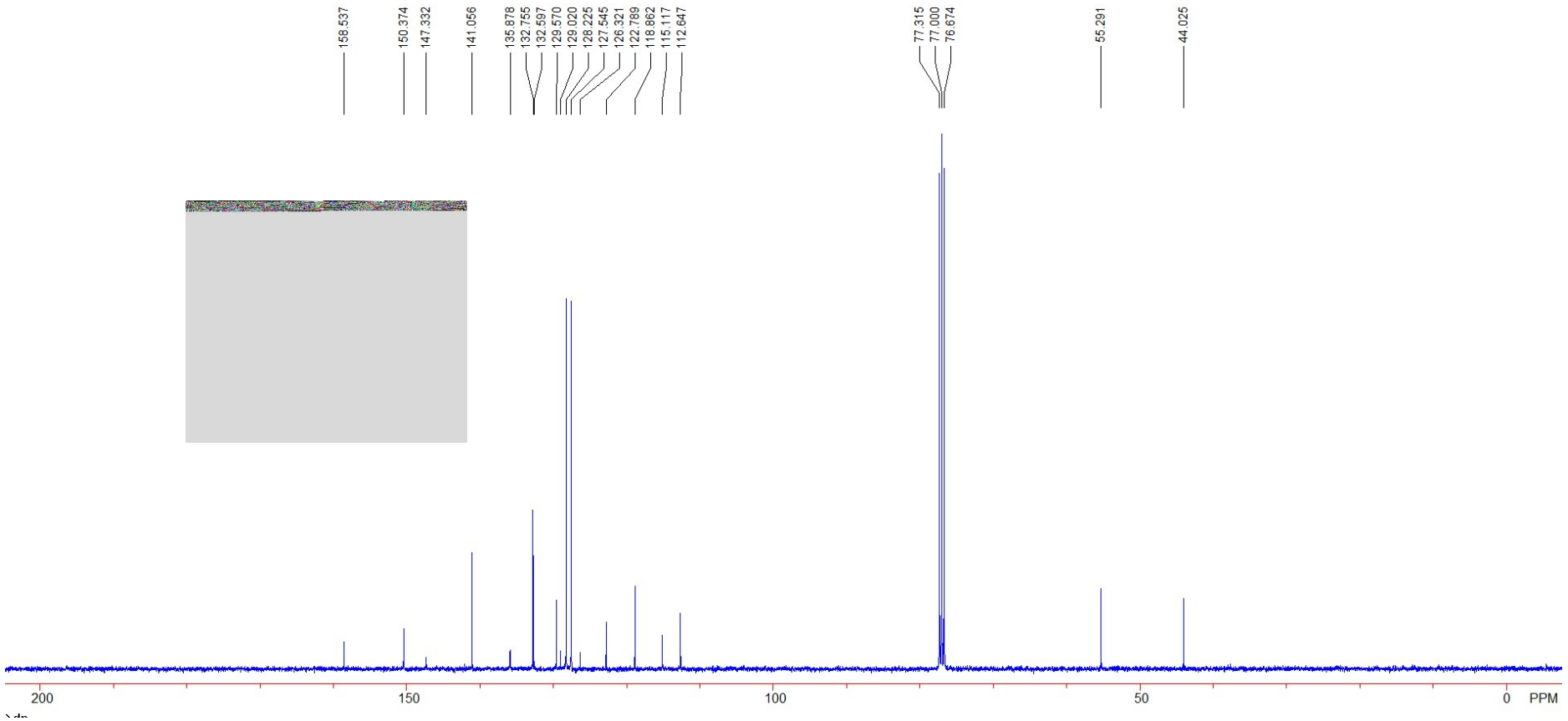

8.909
8.905
8.899
8.894
8.074
8.070
8.054
8.049
7.970
7.968
7.950
7.947
7.845
7.840
7.680
7.677
7.674
7.659
7.643
7.640
7.637
7.536
7.515
7.501
7.497
7.472
7.462
7.452
7.441
7.422
7.419
7.416
7.260
5.760
-0.005
Br
N
N(SO2Ph)2
3i
3.95
3.96
2.06
1.87
1.00
0.98
0.94
10
8
6
4
2
0

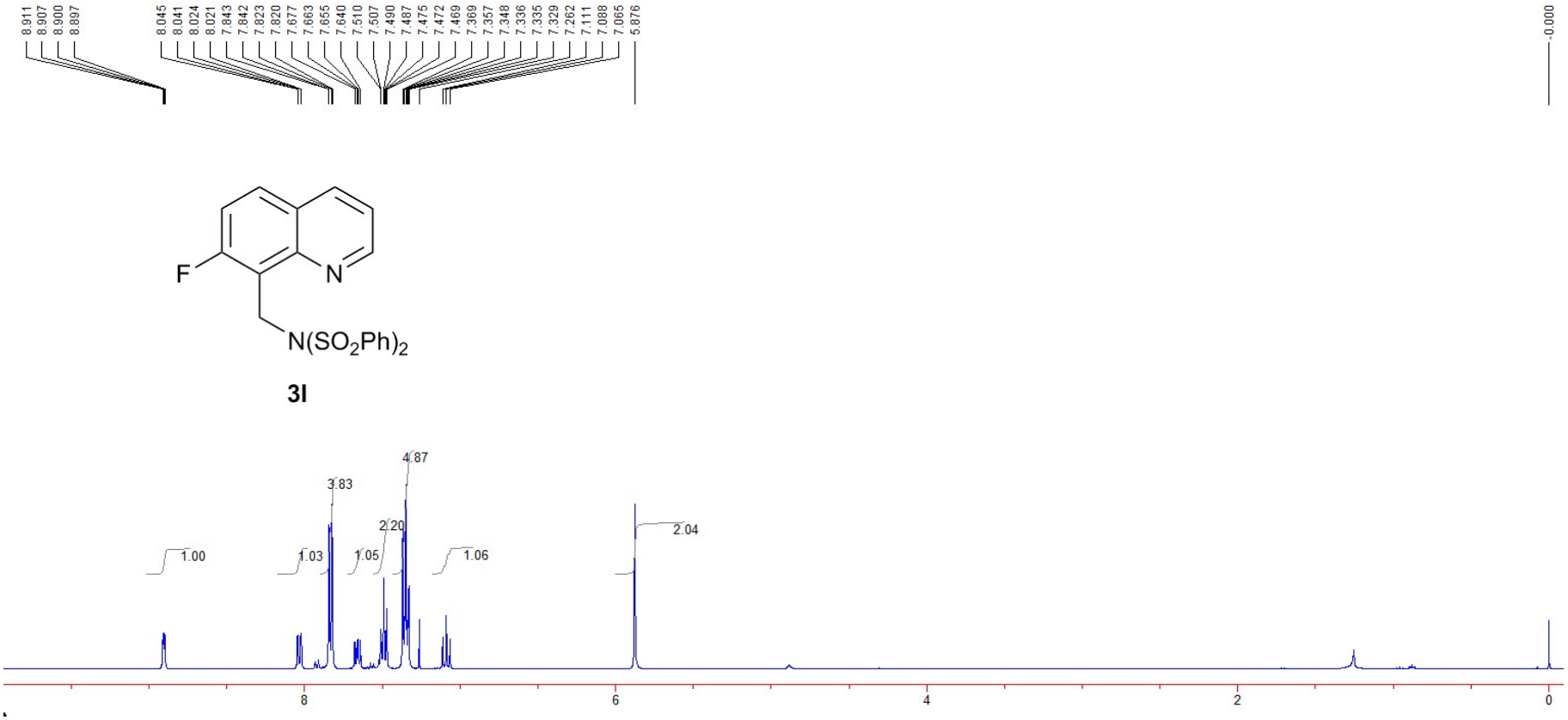

149.669
144.068
139.476
135.307
134.047
131.264
129.737
129.213
129.033
128.330
126.372
122.130
120.188
77.315
77.000
76.673
48.583
200
150
100
50
0
PPM

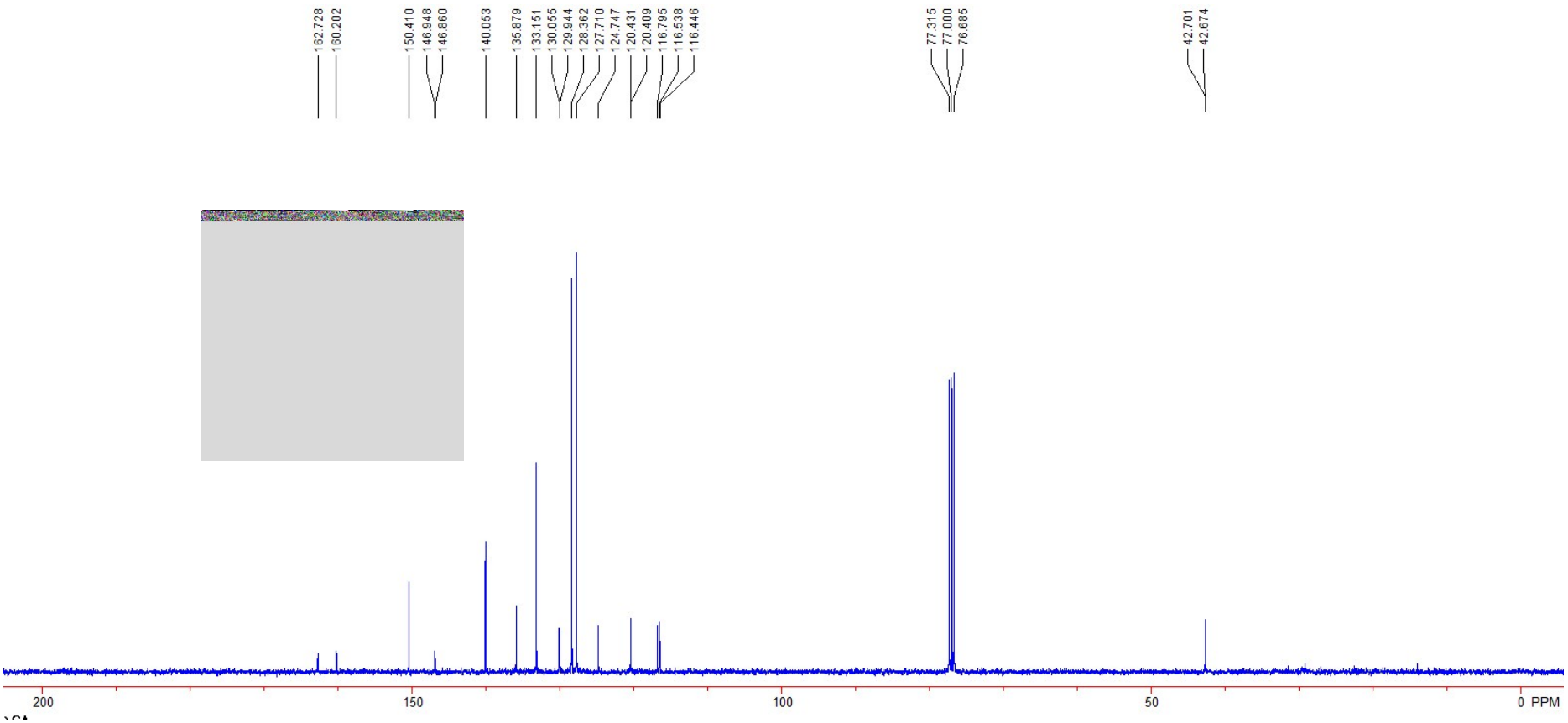

8.903
8.898
8.892
8.888
7.958
7.939
7.625
7.623
7.605
7.602
7.556
7.534
7.455
7.452
7.450
7.434
7.418
7.415
7.412
7.297
7.276
7.260
7.258
7.086
7.066
5.991
2.434
-0.000
N
N(SO2Ph)2
3j
4.74
4.00
2.12
1.00
1.10
1.13
1.05
2.06
3.07
8
6
4
2
0

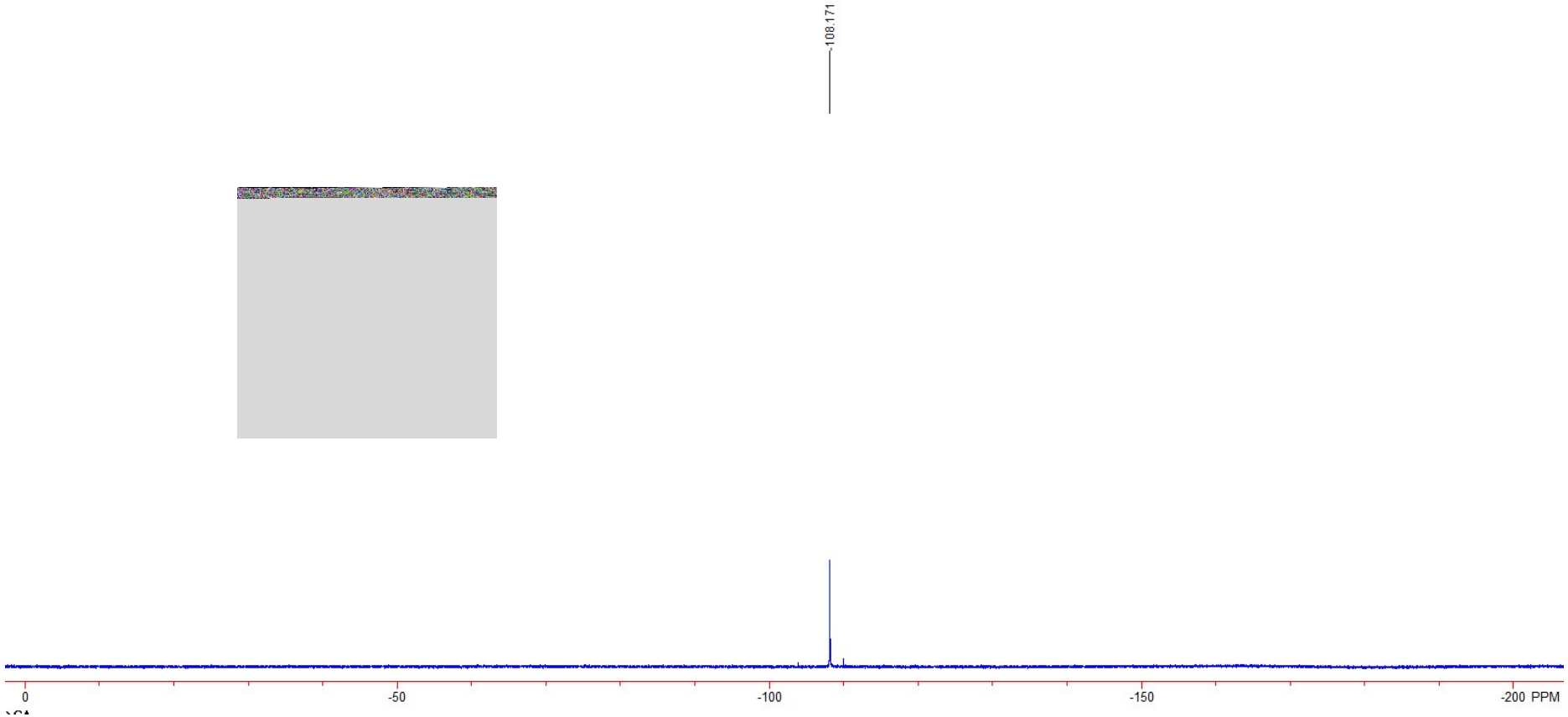

149.277
146.936
140.802
140.353
135.633
132.919
129.768
128.270
128.127
127.642
127.445
126.229
120.346
77.319
77.000
76.685
46.350
20.161
200
150
100
50
0PPM

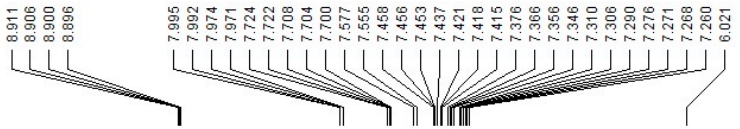

8.932
8.929
8.923
8.918
8.027
8.023
8.007
8.003
7.683
7.681
7.663
7.660
7.643
7.620
7.479
7.475
7.473
7.457
7.441
7.439
7.435
7.324
7.305
7.303
7.288
7.285
7.273
7.262
7.253
7.242
6.863
6.840
6.001
3.627
-0.000
MeO
N
N(SO2Ph)2
3k
1.00
1.04
4.01
1.09
2.29
4.18
0.63
1.03
2.07
3.10
10
8
6
4
2
0


158.537
150.374
147.332
141.056
135.878
132.755
132.597
129.570
129.020
128.225
127.545
126.321
122.789
118.862
115.117
112.647
77.315
77.000
76.674
55.291
44.025
200
150
100
50
0
PPM


8.911
8.907
8.900
8.897
8.045
8.041
8.024
8.021
7.843
7.842
7.823
7.820
7.677
7.663
7.655
7.640
7.510
7.507
7.490
7.487
7.475
7.472
7.469
7.369
7.357
7.348
7.336
7.335
7.329
7.262
7.111
7.088
7.065
5.876
-0.000
F
N
N(SO2Ph)2
3I
4.87
3.83
2.20
2.04
1.00
1.03
1.05
1.06
8
6
4
2
0

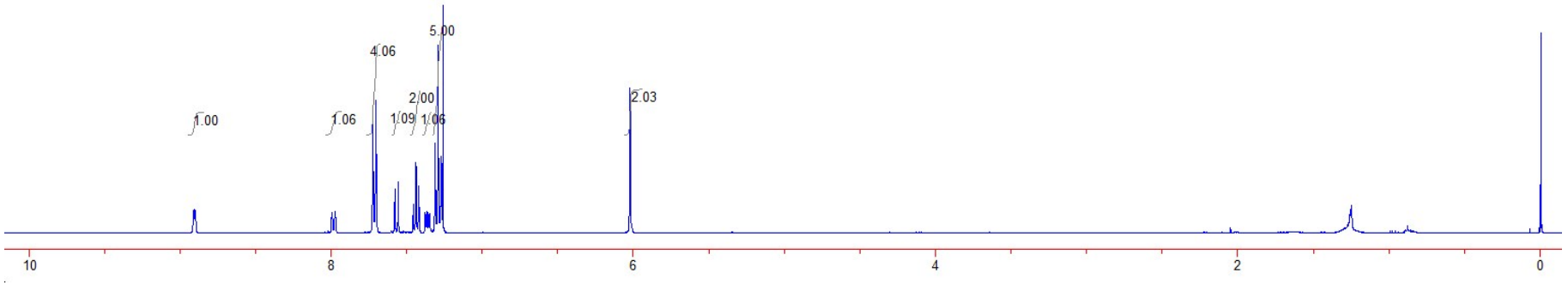

162.728
160.202
150.410
146.948
146.860
140.053
135.879
133.151
130.055
129.944
128.362
127.710
124.747
120.431
120.409
116.795
116.538
116.446
77.315
77.000
76.685
42.701
42.674
200
150
100
50
0 PPM

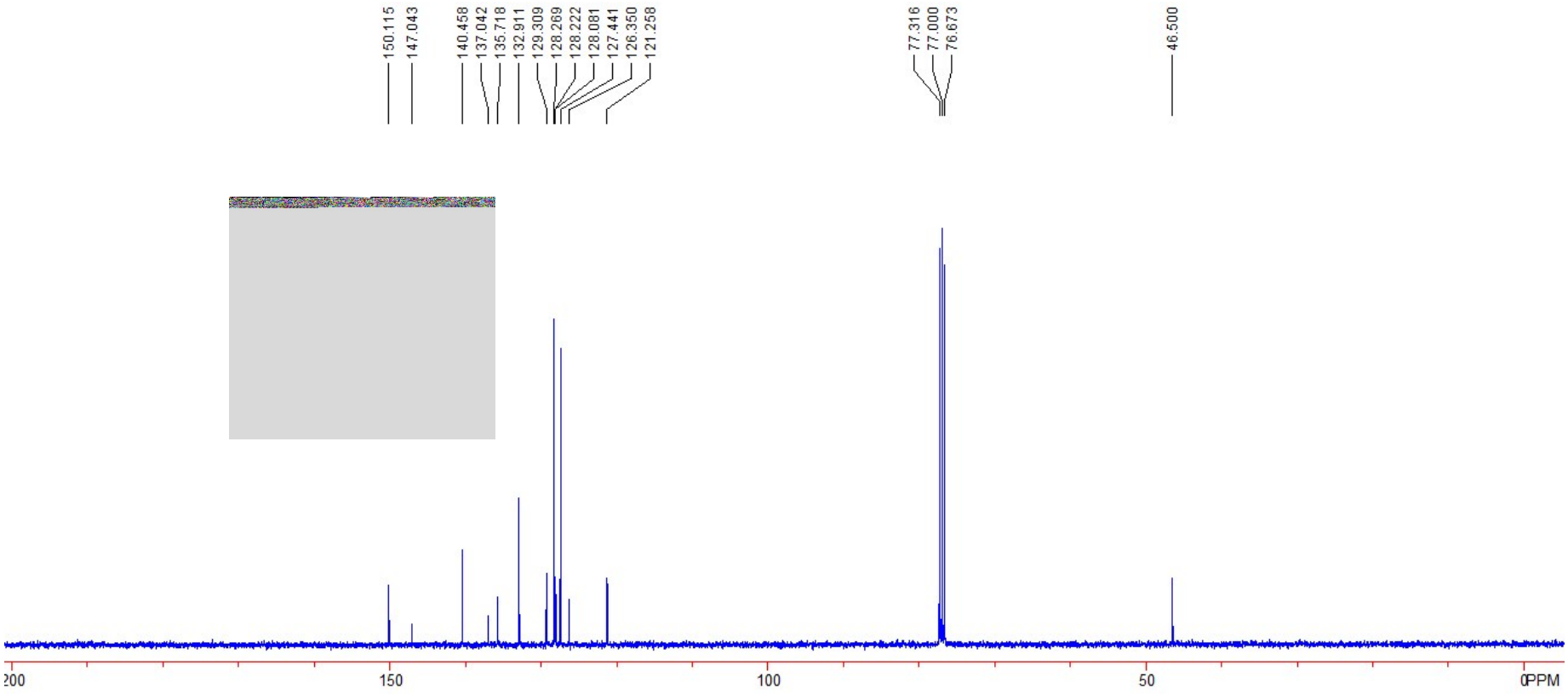

-108.171
0
-50
-100
-150
-200 PPM

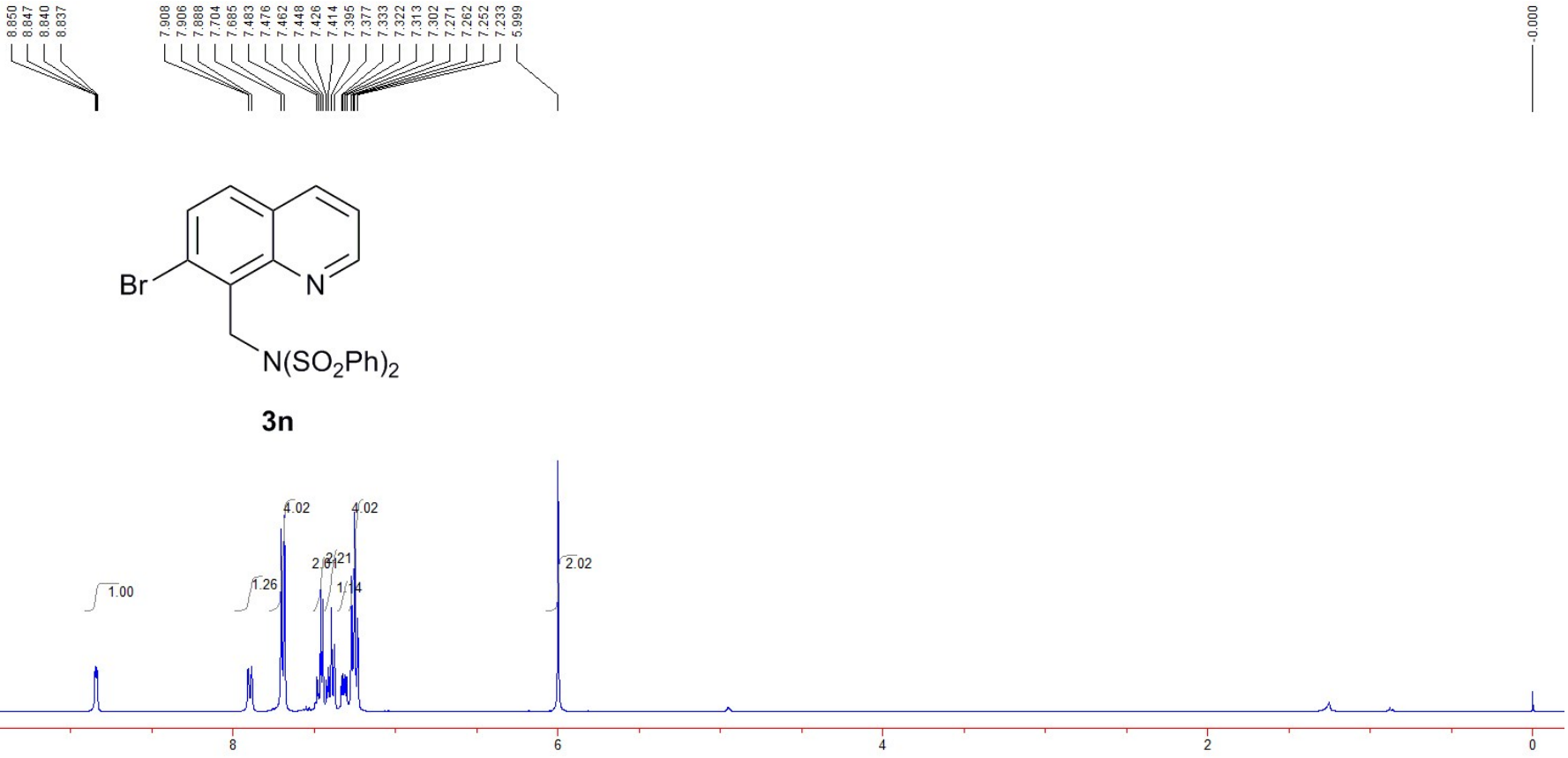

8.911
8.906
8.900
8.896
7.995
7.992
7.974
7.971
7.724
7.722
7.708
7.704
7.700
7.577
7.555
7.458
7.456
7.453
7.437
7.421
7.418
7.415
7.376
7.366
7.356
7.346
7.310
7.306
7.290
7.276
7.271
7.268
7.260
6.021
-0.005

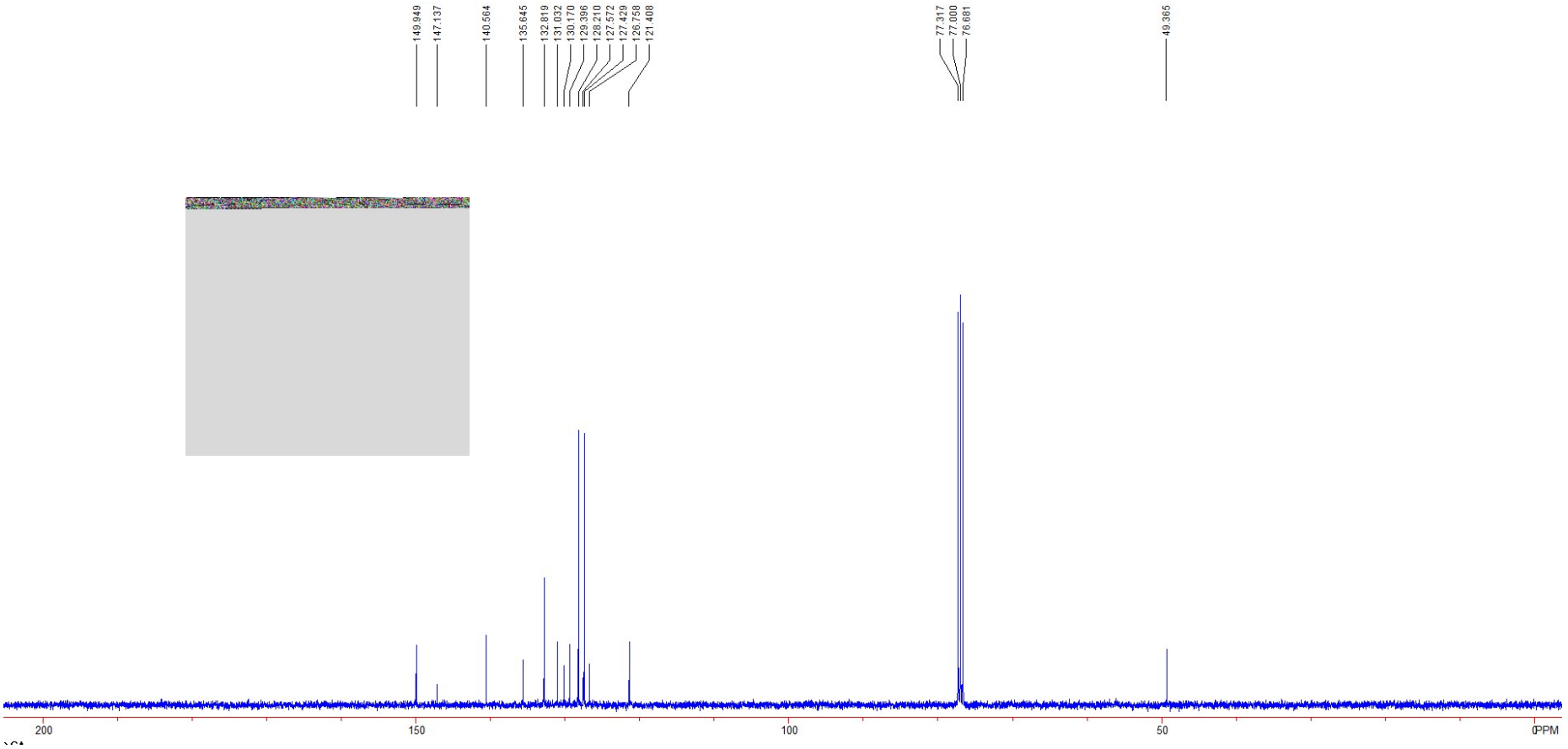

Cl
N
N(SO2Ph)2

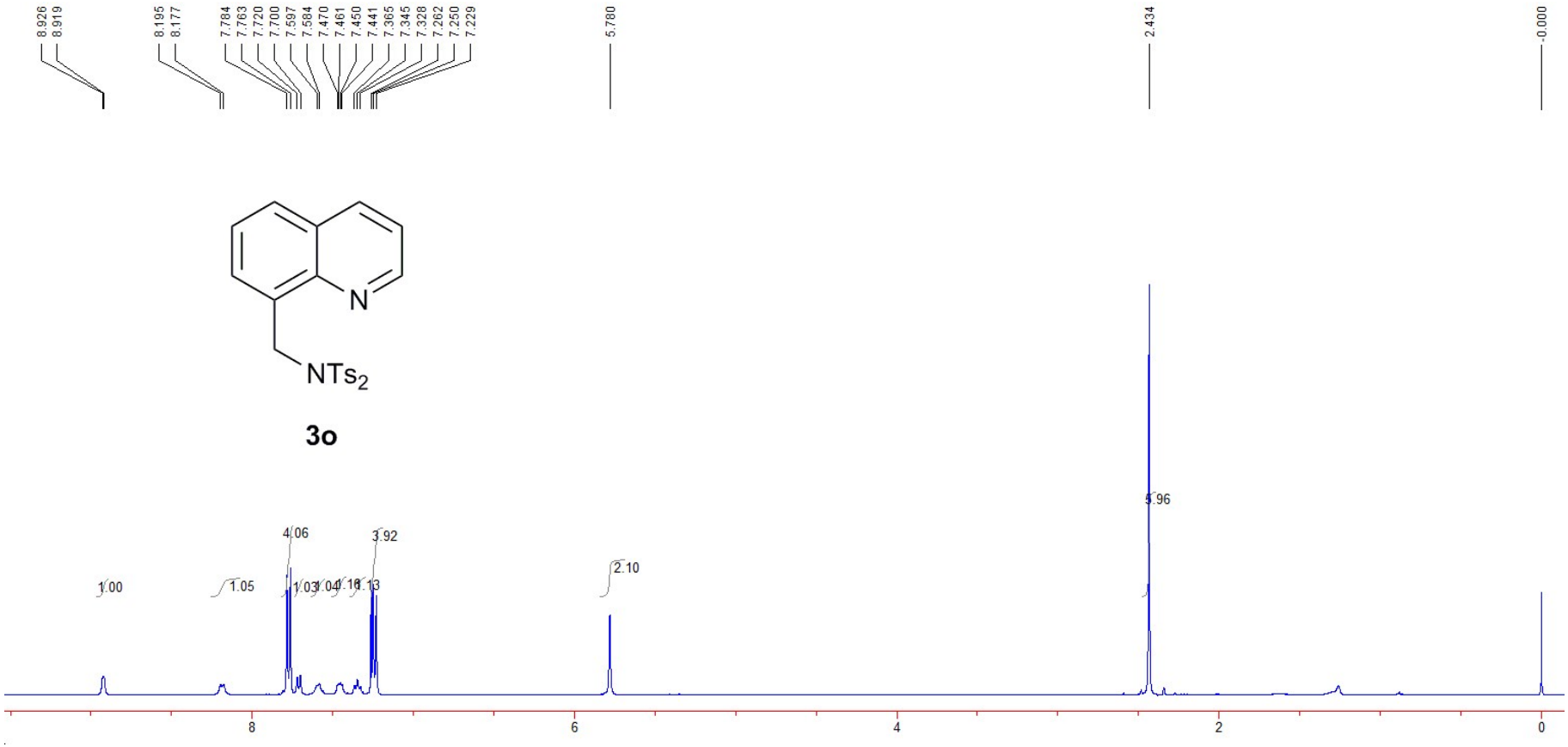
3m

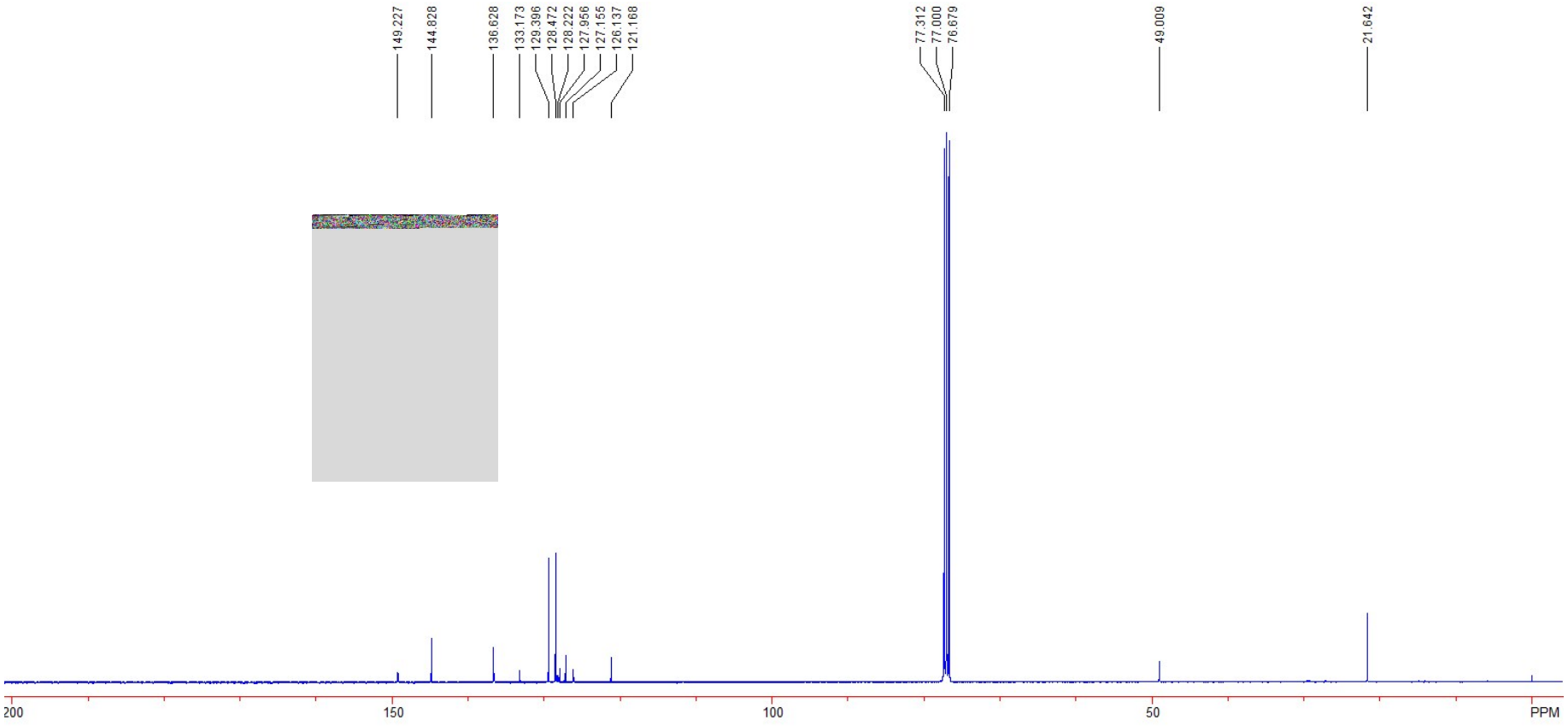

1.00
1.06
4.06
2.00
1.09
1.06
5.00
2.03
10
8
6
4
2
0

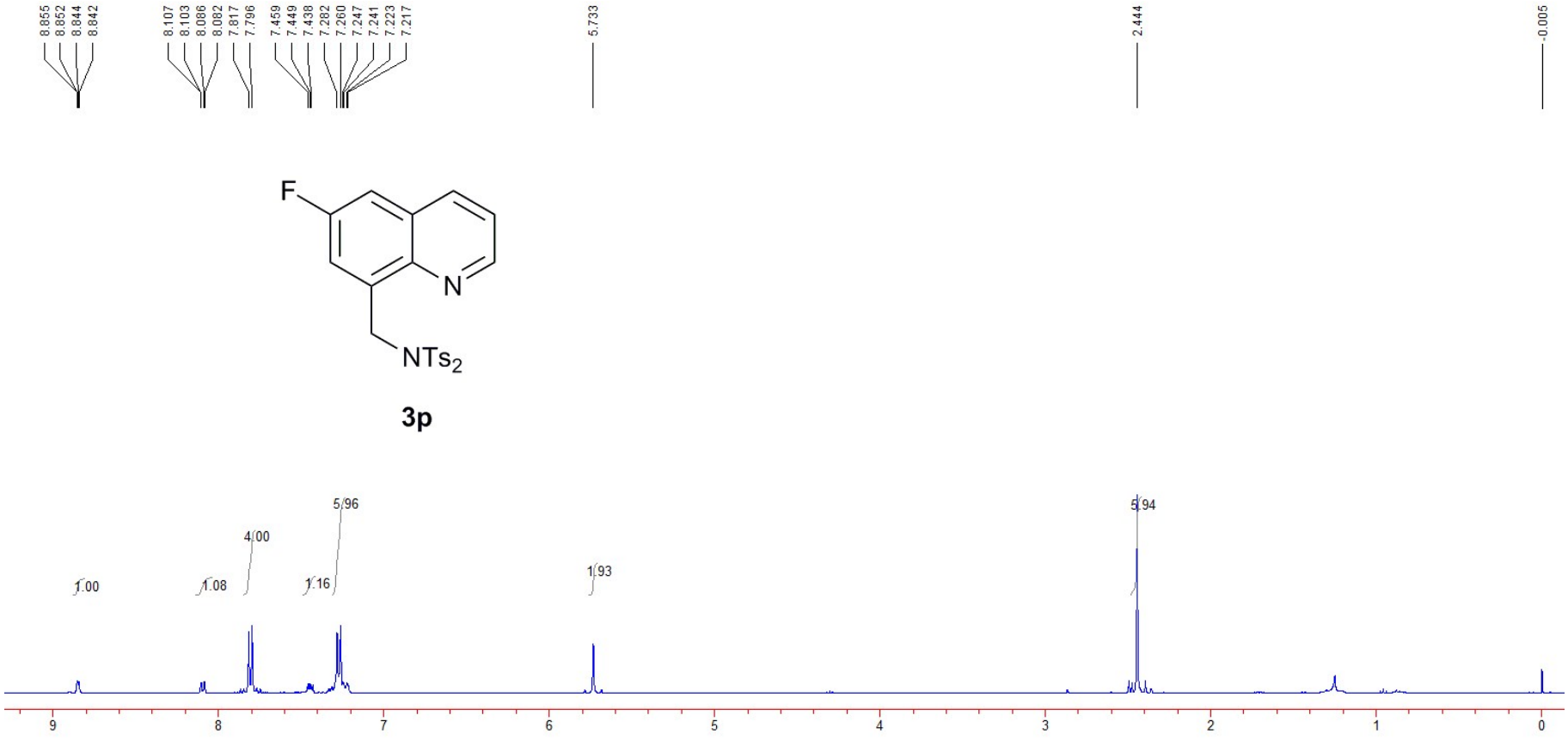

150.115
147.043
140.458
137.042
135.718
132.911
129.309
128.269
128.222
128.081
127.441
126.350
121.258
77.316
77.000
76.673
46.500
200
150
100
50
0PPM

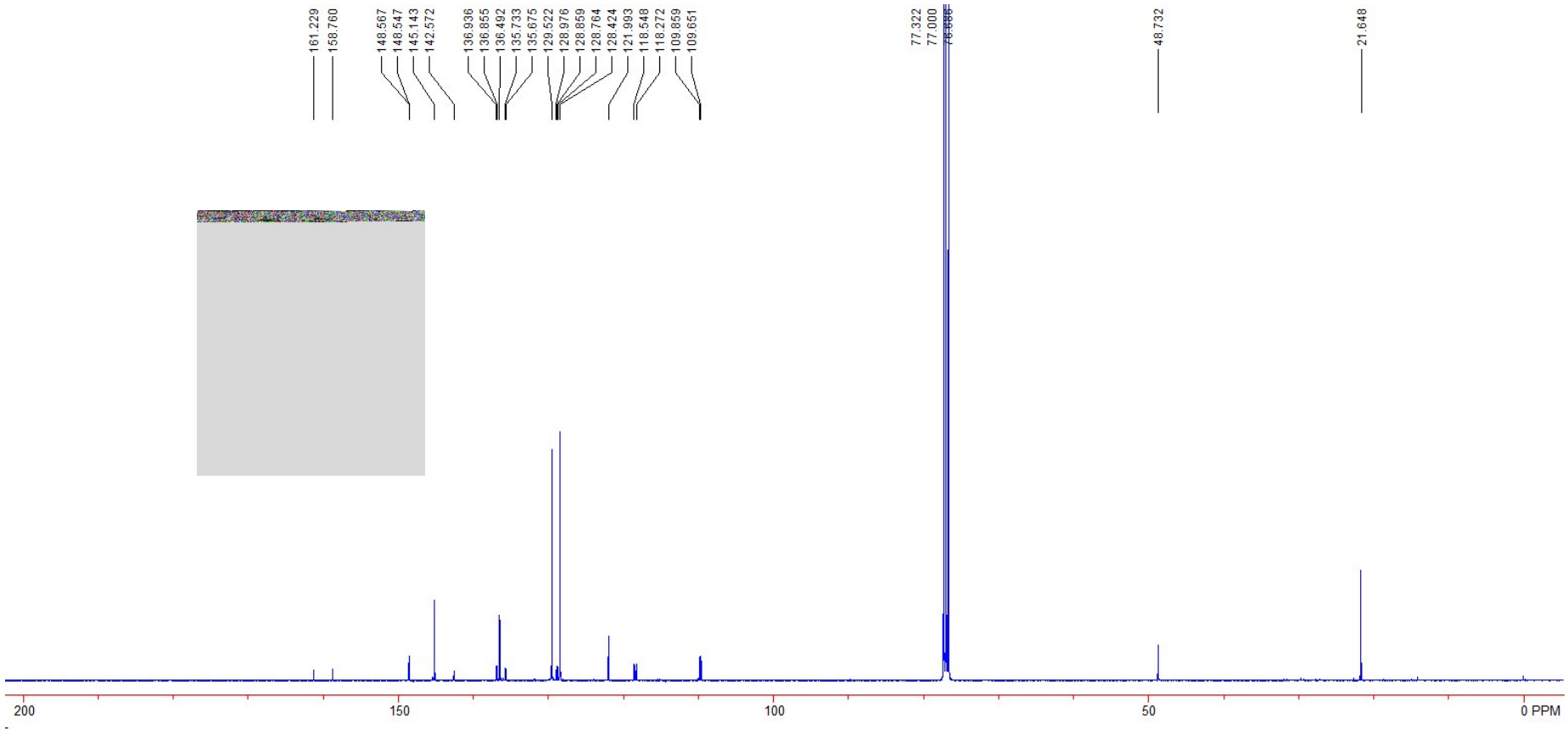

8.850
8.847
8.840
8.837
7.908
7.906
7.888
7.704
7.685
7.483
7.476
7.462
7.448
7.426
7.414
7.395
7.377
7.333
7.322
7.313
7.302
7.271
7.262
7.252
7.233
5.999
-0.000
Br
N
N(SO2Ph)2
3n
1.00
1.26
4.02
2.61
2.21
1.14
4.02
2.02
8
6
4
2
0

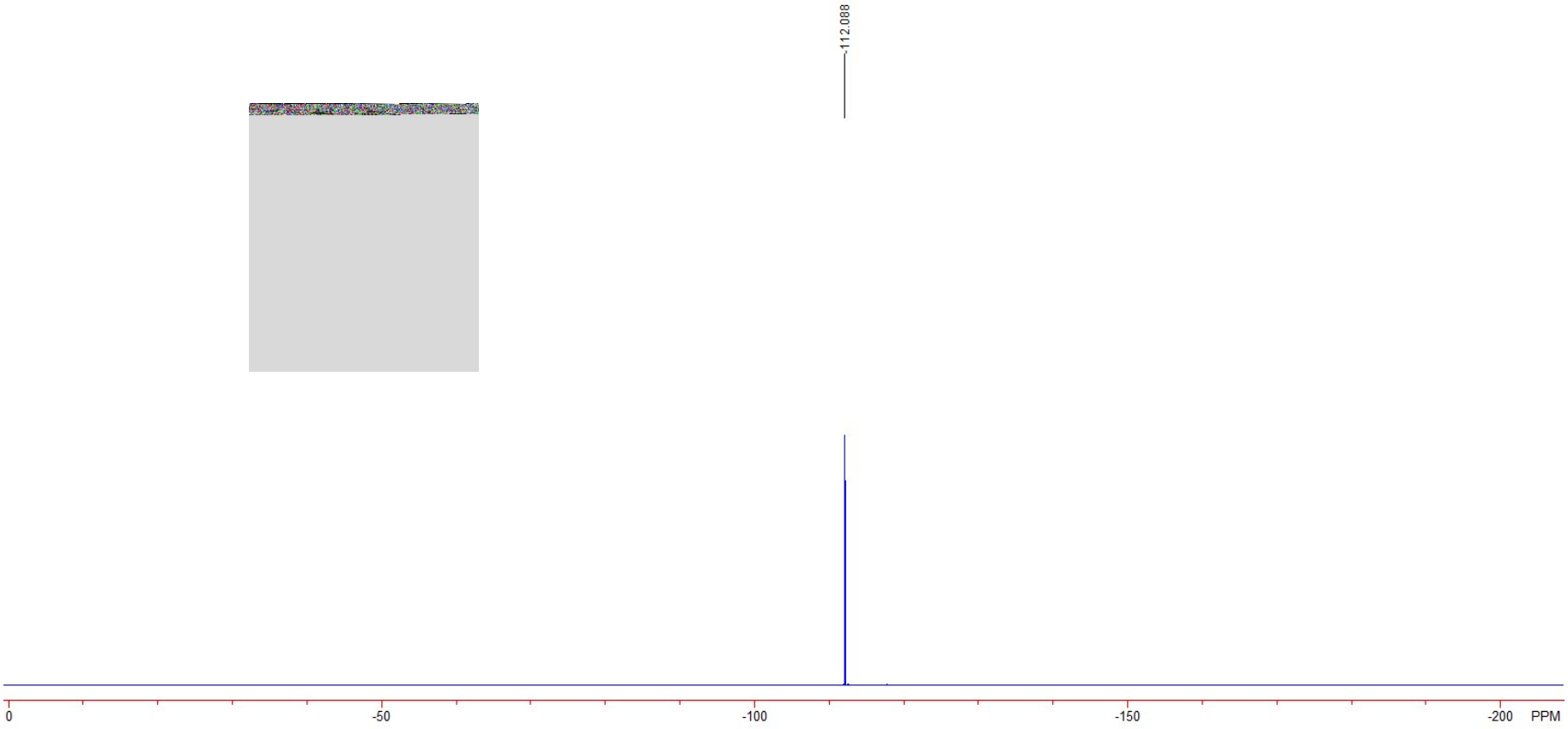

149.949
147.137
140.564
135.645
132.819
131.032
130.170
129.396
128.210
127.572
127.429
126.758
121.408
77.317
77.000
76.681
49.365
200
150
100
50
0
PPM

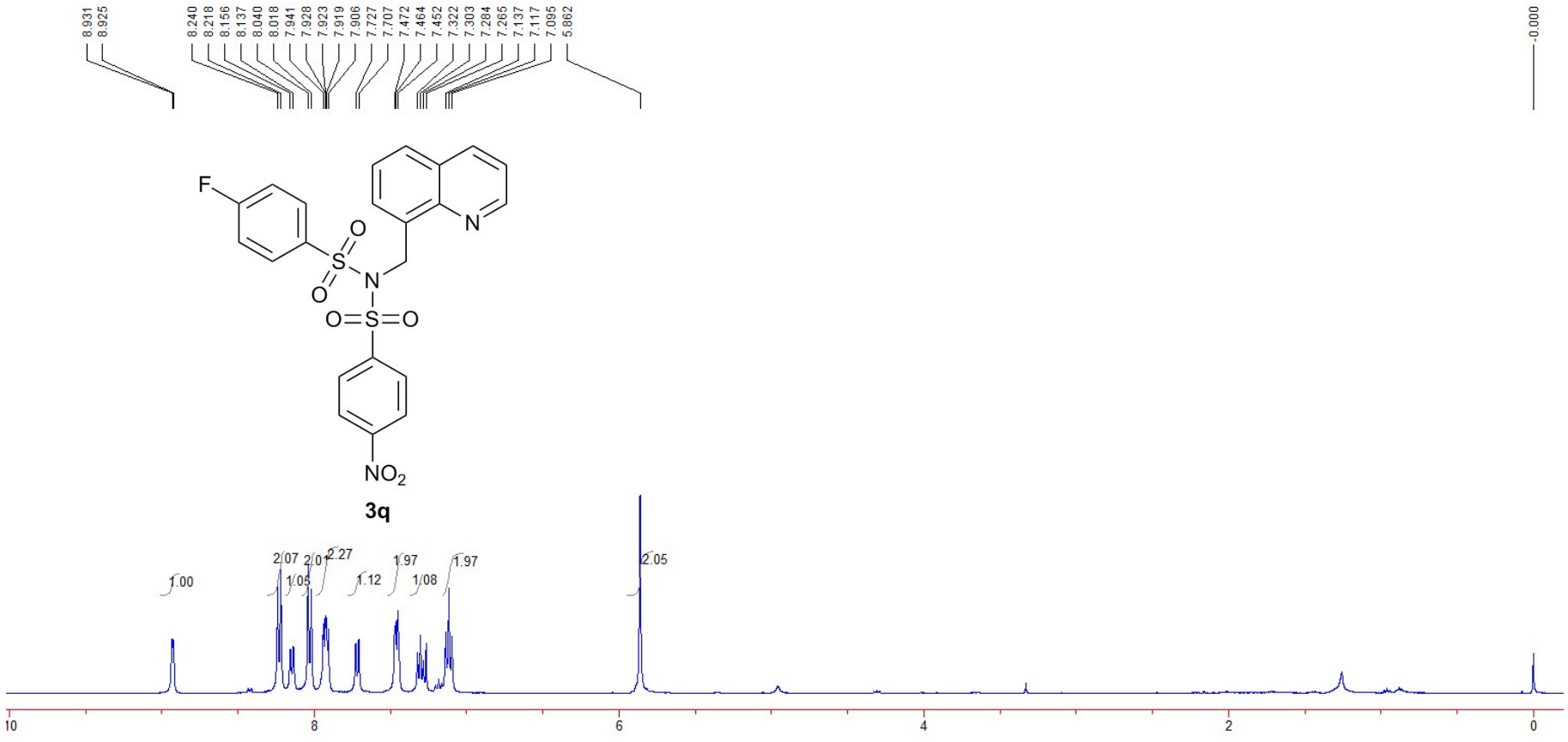

8.926
8.919
8.195
8.177
7.784
7.763
7.720
7.700
7.597
7.584
7.470
7.461
7.450
7.441
7.365
7.345
7.328
7.262
7.250
7.229
5.780
2.434
0.000
N
NTs2
3o
1.00
1.05
4.06
1.03
1.04
1.16
3.92
1.13
2.10
5.96
8
6
4
2
0

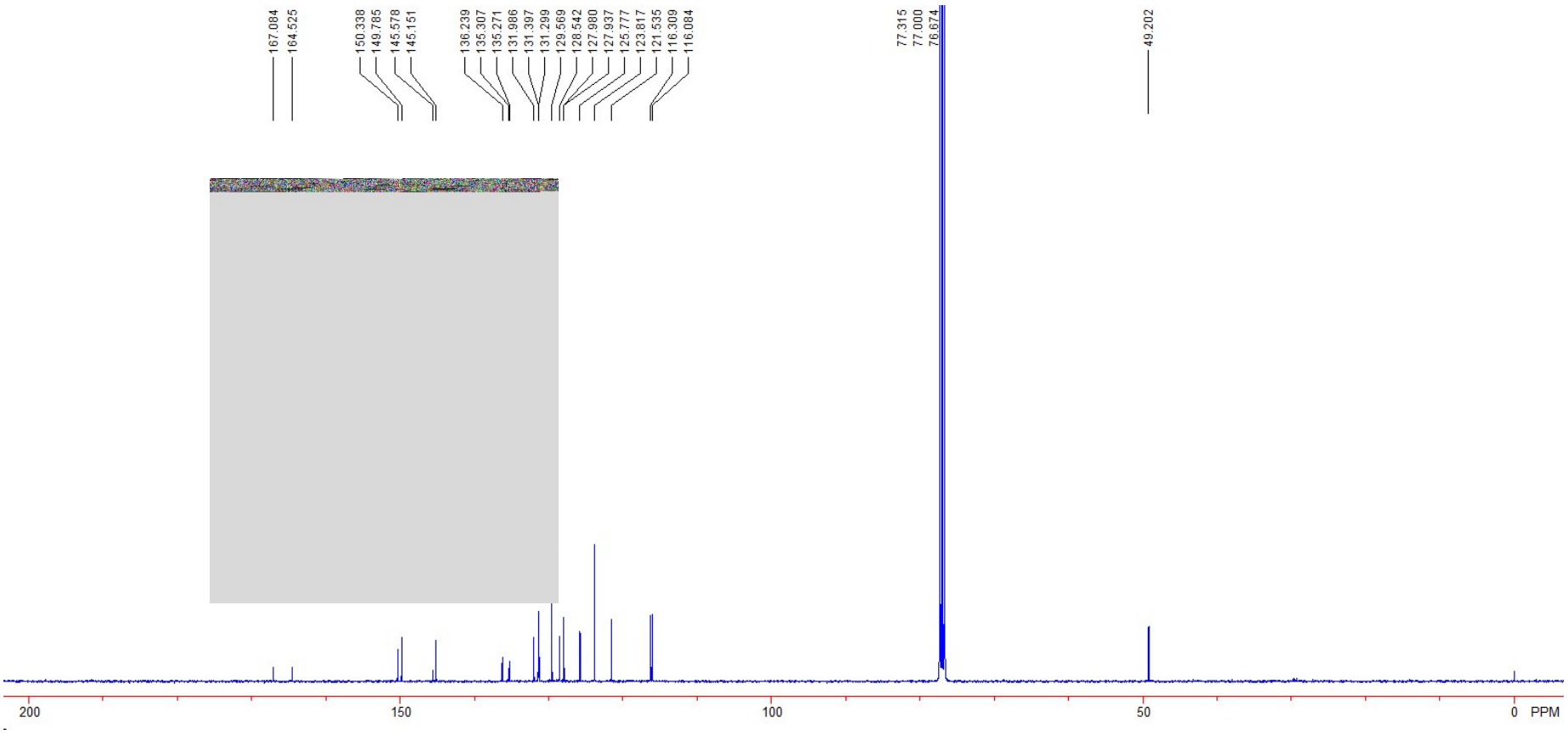

149.227
144.828
136.628
133.173
129.396
128.472
128.222
127.956
127.155
126.137
121.168
77.312
77.000
76.679
49.009
21.642
200
150
100
50
PPM

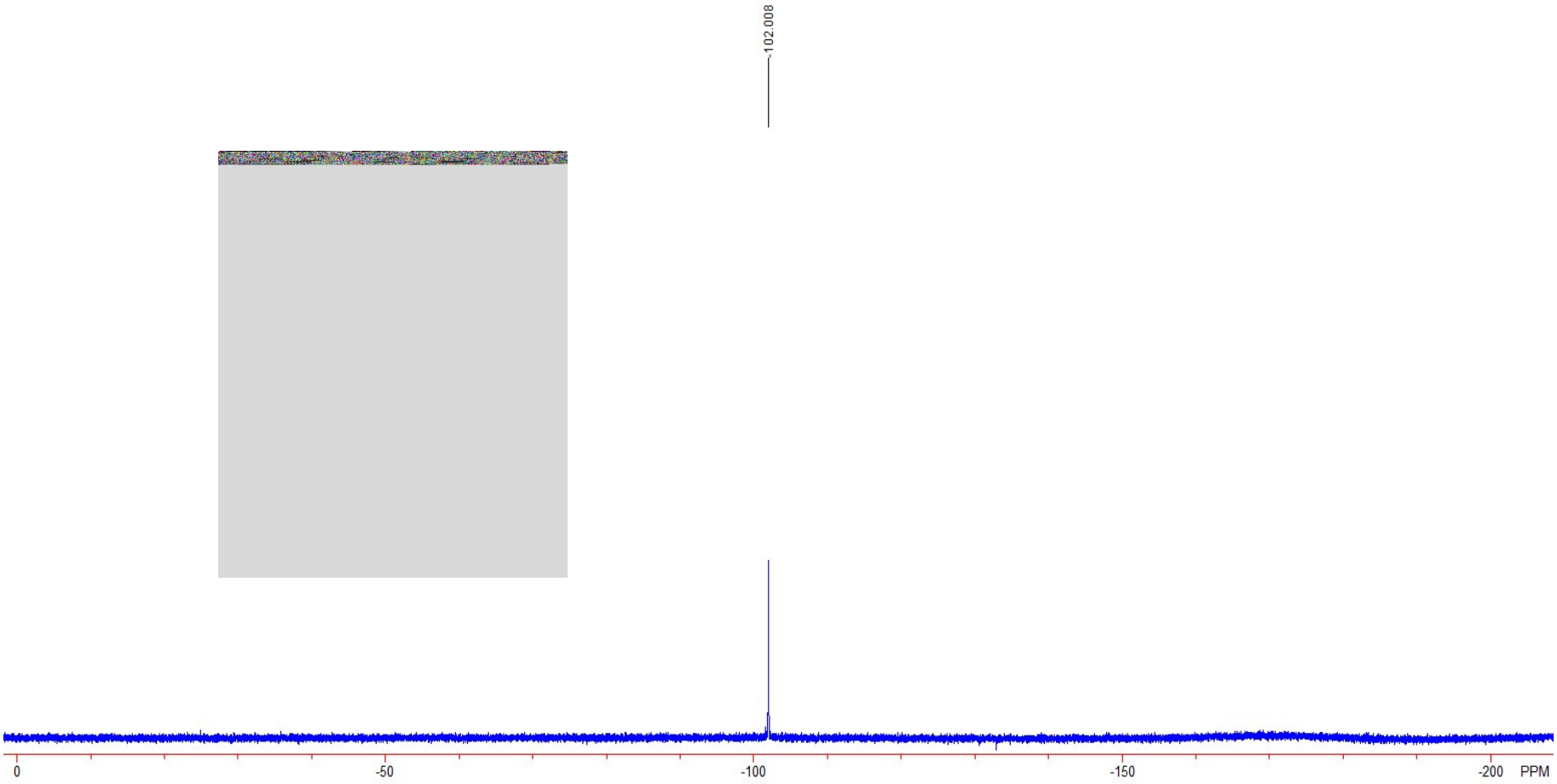

8.855
8.852
8.844
8.842
8.107
8.103
8.086
8.082
7.817
7.796
7.459
7.449
7.438
7.282
7.260
7.247
7.241
7.223
7.217
5.733
2.444
-0.005
F
N
NTs2
3p
1.00
1.08
4.00
5.96
1.16
1.93
5.94
9
8
7
6
5
4
3
2
1
0

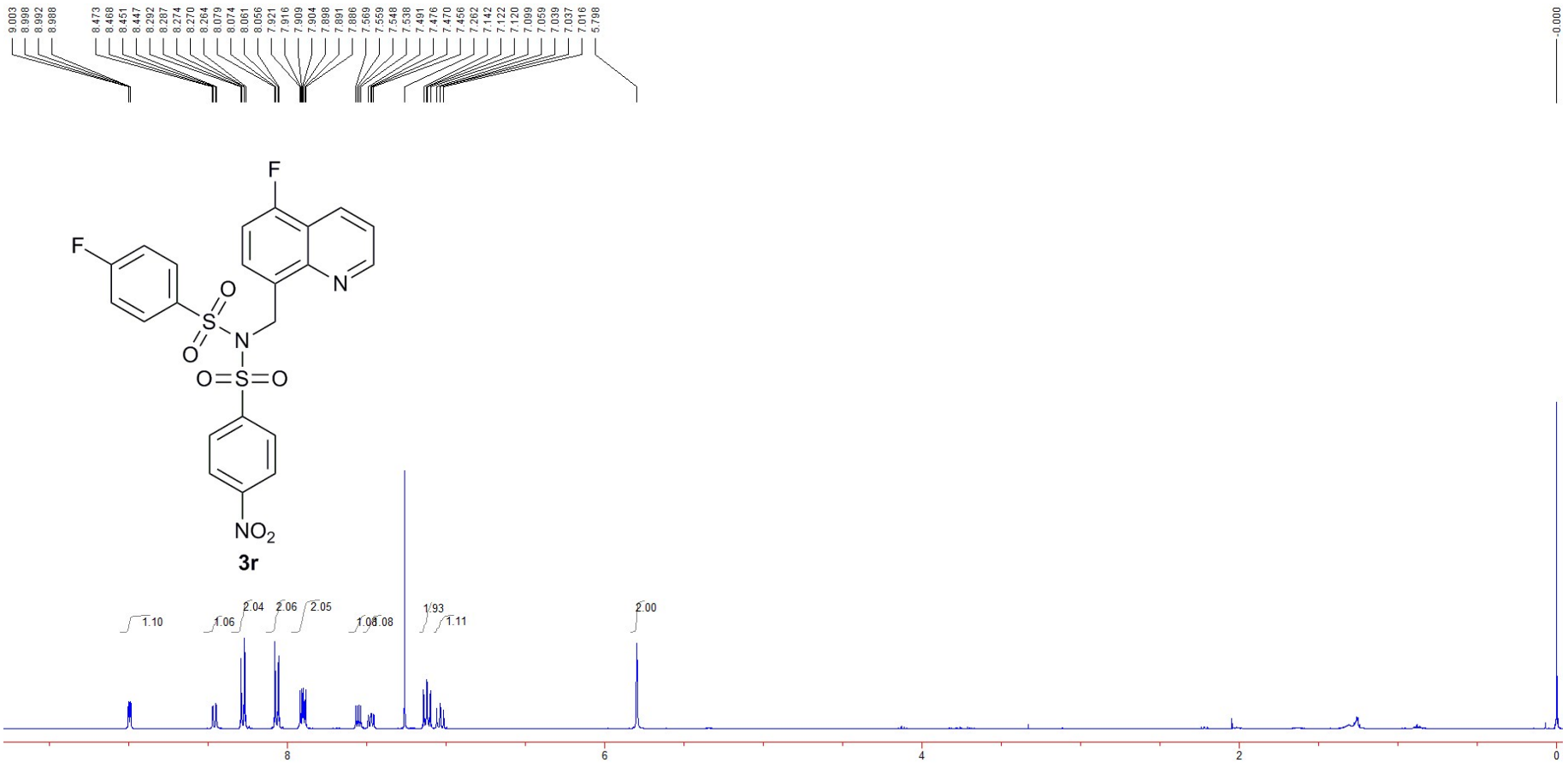

161.229
158.760
148.567
148.547
145.143
142.572
136.936
136.855
136.492
135.733
135.675
129.522
128.976
128.859
128.764
128.424
121.993
118.548
118.272
109.859
109.651
77.322
77.000
48.732
21.648
200
150
100
50
0 PPM

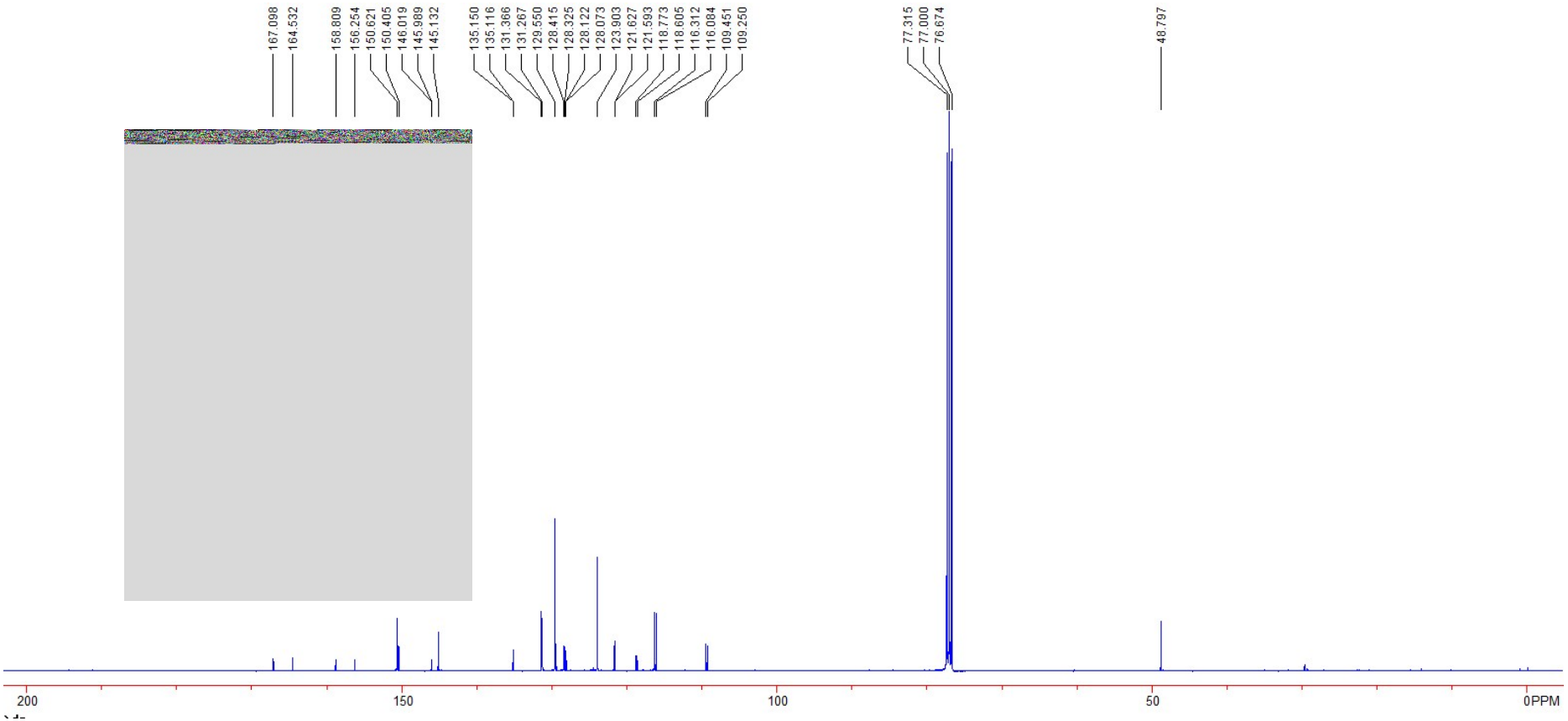

-112.088
0
-50
-100
-150
-200
PPM

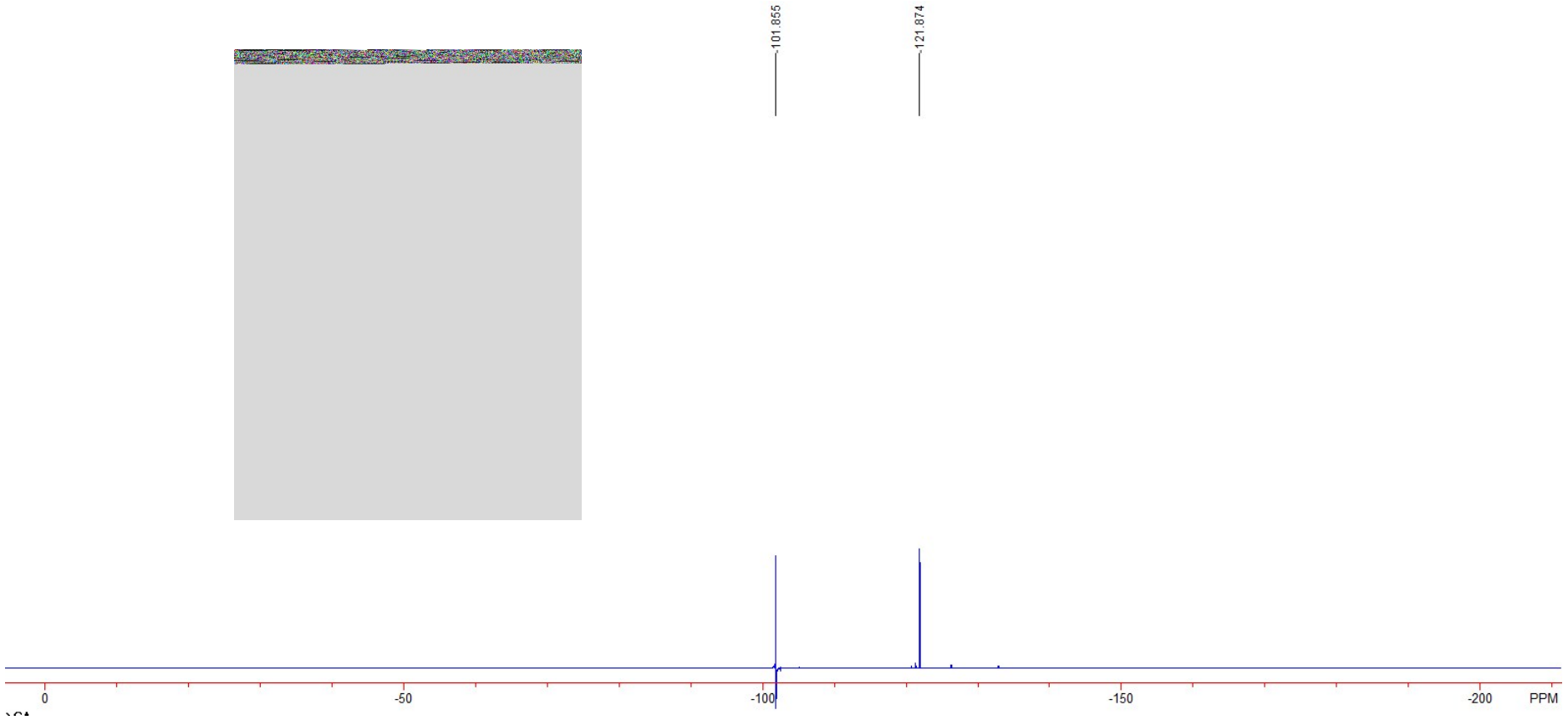

8.931
8.925
8.240
8.218
8.156
8.137
8.040
8.018
7.941
7.928
7.923
7.919
7.906
7.727
7.707
7.472
7.464
7.452
7.322
7.303
7.284
7.265
7.137
7.117
7.095
5.862
-0.000
F
O
S
O
N
O=S=O
N
NO2
3q
1.00
2.07
2.01
2.27
1.05
1.12
1.97
1.08
1.97
2.05
10
8
6
4
2
0

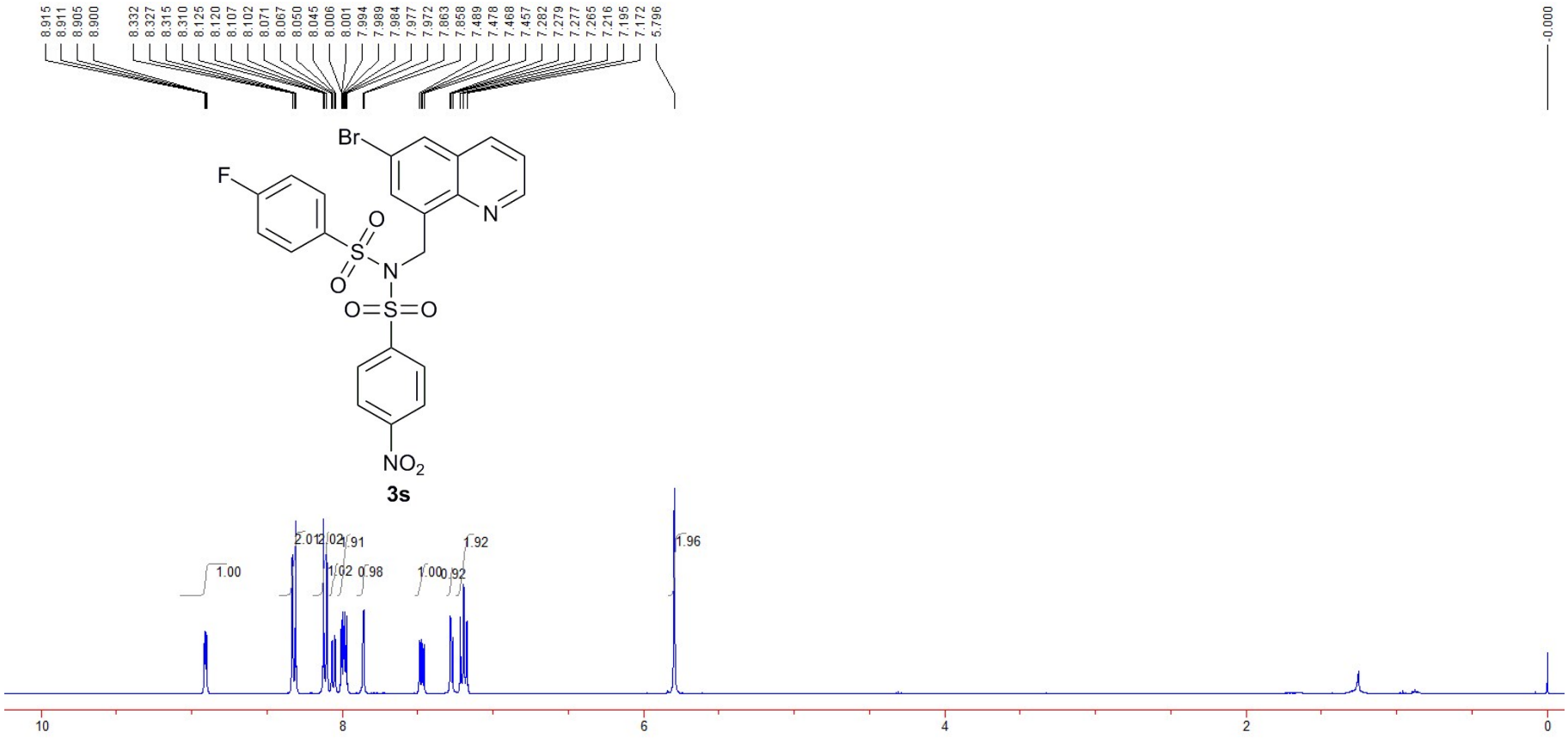

167.084
164.525
150.338
149.785
145.578
145.151
136.239
135.307
135.271
131.986
131.397
131.299
129.569
128.542
127.980
127.937
125.777
123.817
121.535
116.309
116.084
77.315
77.000
76.674
49.202
200
150
100
50
0
PPM

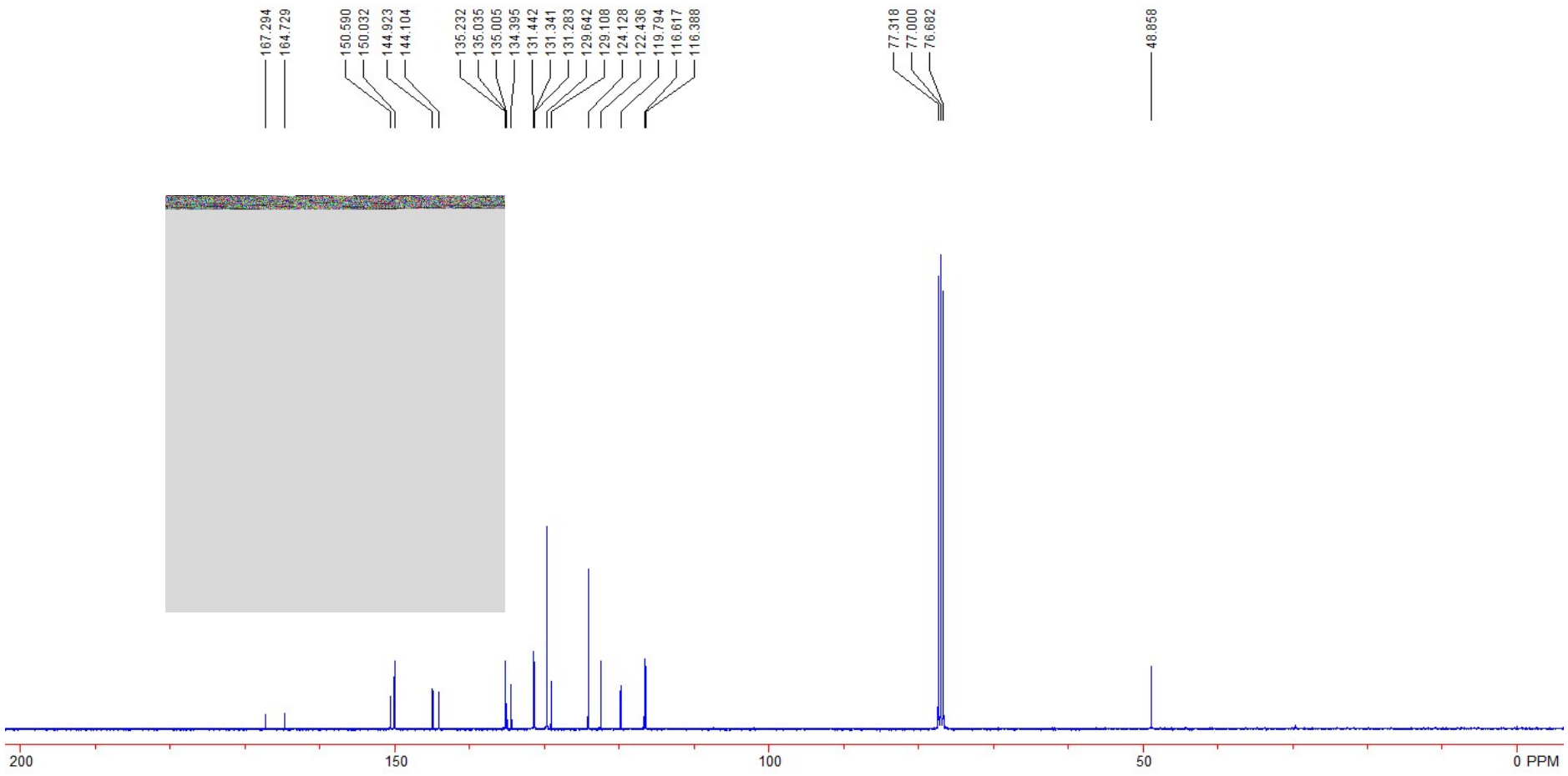

-102.008
0
-50
-100
-150
-200
PPM

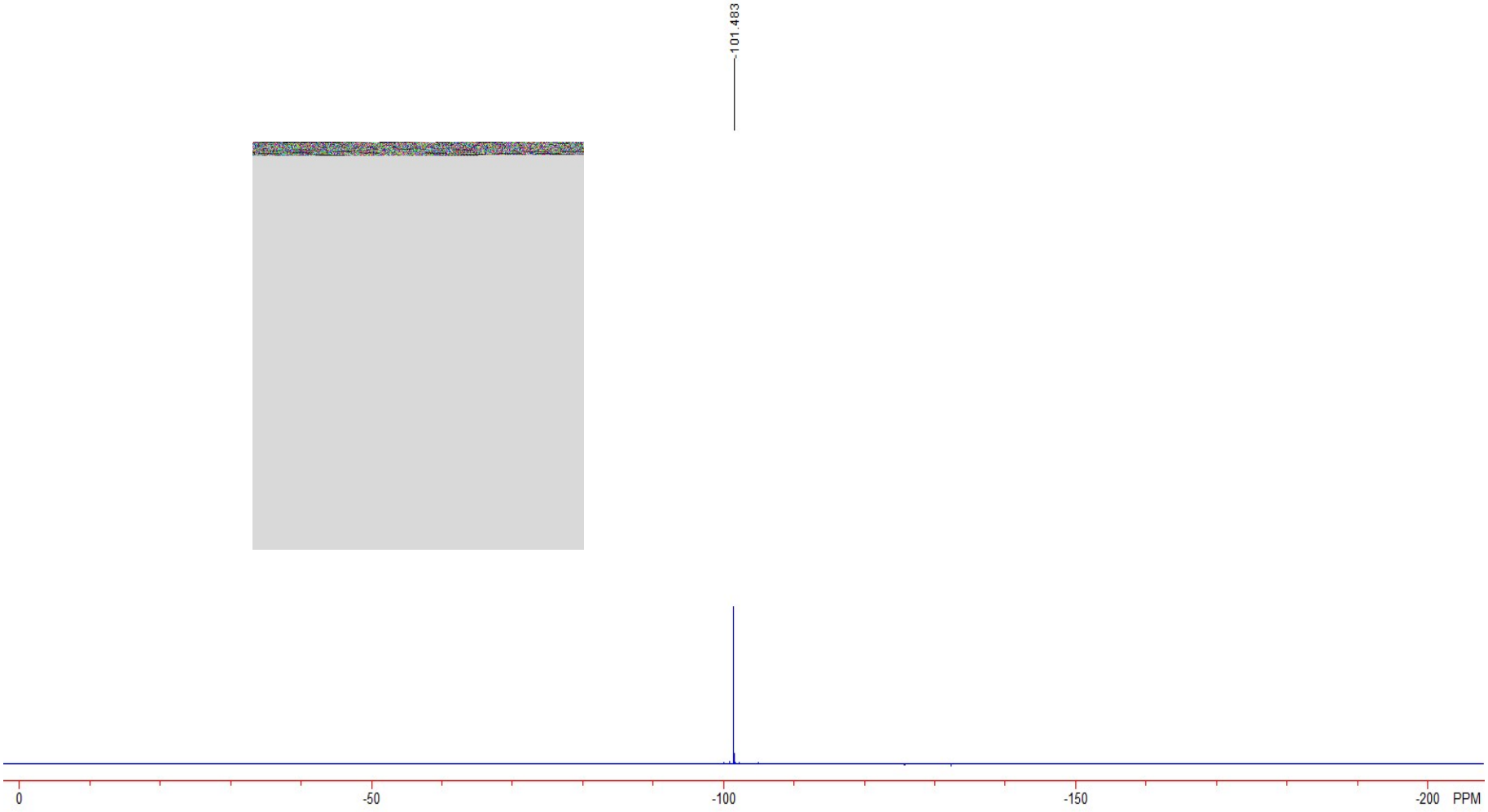

9.003
8.998
8.992
8.988
8.473
8.468
8.451
8.447
8.292
8.287
8.274
8.270
8.264
8.079
8.074
8.061
8.056
7.921
7.916
7.909
7.904
7.898
7.891
7.886
7.569
7.559
7.548
7.538
7.491
7.476
7.470
7.456
7.262
7.142
7.122
7.120
7.099
7.059
7.039
7.037
7.016
5.798
0.000
F
F
O
S
O
N
O=S=O
N
NO2
3r
1.10
1.06
2.04
2.06
2.05
1.08
1.08
1.93
1.11
2.00
8
6
4
2
0


167.098
164.532
158.809
156.254
150.621
150.405
146.019
145.989
145.132
135.150
135.116
131.366
131.267
129.550
128.415
128.325
128.122
128.073
123.903
121.627
121.593
118.773
118.605
116.312
116.084
109.451
109.250
77.315
77.000
76.674
48.797
200
150
100
50
0PPM


-101.855
-121.874
0
-50
-100
-150
-200
PPM


8.915
8.911
8.905
8.900
8.332
8.327
8.315
8.310
8.125
8.120
8.107
8.102
8.071
8.067
8.050
8.045
8.006
8.001
7.994
7.989
7.984
7.977
7.972
7.863
7.858
7.489
7.478
7.468
7.457
7.282
7.279
7.277
7.265
7.216
7.195
7.172
5.796
-0.000
Br
F
N
O
S
N
O
O=S=O
NO2
3s
1.00
2.01
2.02
1.91
1.02
0.98
1.00
0.92
1.92
1.96
10
8
6
4
2
0


167.294
164.729
150.590
150.032
144.923
144.104
135.232
135.035
135.005
134.395
131.442
131.341
131.283
129.642
129.108
124.128
122.436
119.794
116.617
116.388
77.318
77.000
76.682
48.858
200
150
100
50
0 PPM


-101.483
0
-50
-100
-150
-200
PPM