Supporting Information

for

Nickel-catalyzed 1,4-aryl rearrangement of aryl *N*-benzylimidates via C–O and C–H bond cleavage

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Note added after first publication: This supplementary information file replaces the version originally published on 17 June 2022, in which the kinetic isotope effect value on page S46 was given as 2.4 in error. The correct value of 4.2 is included in this updated version. This does not affect the conclusions of the paper.

CONTENTS

I. General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$. ^{2}H NMR spectra were recorded in $CHCl_3$. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethylsilane (δ 0.00). The chemical shifts in ^{2}H NMR spectra were recorded relative to $CDCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.0). The chemical shifts in ^{19}F NMR spectra were recorded relative to hexafluorobenzene (δ –163.00). The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silica Gel 60N (spherical, neutral) (40-50 μm, KANTO CHEMIXAL CO., INC.) and NH Silica (Silica Gel 60 (spherical) NH_2 (40-50 μm)). Some of the compounds were purified by LC-908 HPLC (GPC). Microwave synthesis was performed by Biotage® Initiator+.

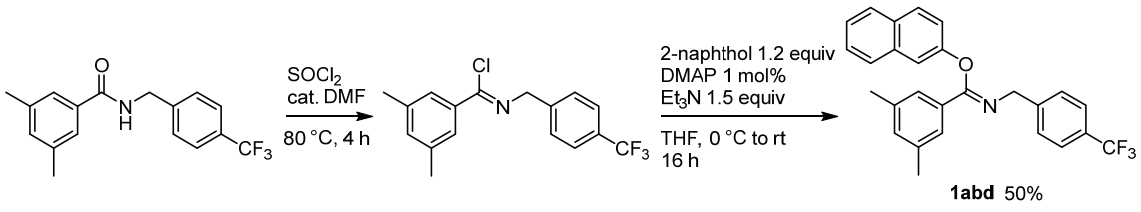
II. Materials

Toluene (deoxygenated) (FUJI FILM Wako Chemicals) and 1,4-dioxane (super dehydrated) (FUJI FILM Wako Chemicals) were used as received. $Ni(cod)_2$ was purchased from Strem Chemicals and used as received. PCy3 (Sigma-Aldrich), dcype (Sigma-Aldrich), dppe (TCI), dcypm (FUJI FILM Wako Chemicals), dcypp (Sigma-Aldrich), IPr·HCl (TCI) and were purchased from commercial suppliers and used as received.

III. Synthesis of Starting Materials

Synthesis of Aryl *N*-Benzylimidates

General procedure A: Synthesis of imidate with $SOCl_2$.[1]

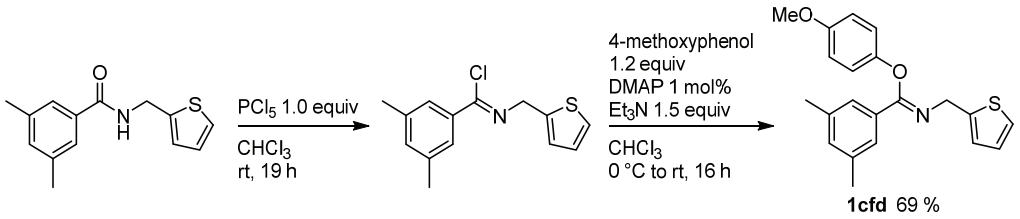


1abd 50%

3,5-Dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzamide (1.56 g, 5.1 mmol), DMF (2 drops) and $SOCl_2$ (5 mL) were added to a 50 mL two-necked flask. After the mixture was stirred at 80 °C for 4 h, the resulting mixture was concentrated to give the corresponding imidoyl chloride, which was used in the

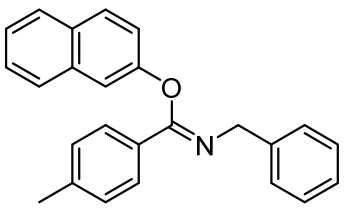
next step without further purification. The imidoyl chloride was added dropwise to a solution of 2-naphthol (893 mg, 6.2 mmol), Et_3N (1.1 mL, 7.9 mmol) and DMAP (15 mg, 0.12 mmol) in THF (10 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred at rt for 16 h. After the precipitate (Et_3N·HCl) was filtered off, the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/EtOAc = 97/3) to give naphthalen-2-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (**1abd)** as a white solid (1.10 g, 50%). Aryl *N*-benzylimidates **1aaa**, **1aab**, **1aac**, **1aad**, **1aae**, **1aaf**, **1bbd**, **1cbd**, **1dbd**, **1ebd**, **1fbd**, **1gbd**, **1hbd**, **1ibd**, **1jbd**, **1kbd, 1lbd, 1add, 1cad, 1cad-*d*$_2$, 1nbd** and **1obd** were prepared in a similar manner.

General Procedure B: Synthesis of imidate with PCl_5.[2]



PCl_5 (1.27 g, 6.1 mmol) was added at 0 °C to a solution of 3,5-dimethyl-*N*-(thiophen-2-ylmethyl)benzamide (1.48 g, 6.0 mmol) in $CHCl_3$ (30 mL) . After the mixture was stirred at rt for 19 h, the resulting mixture was concentrated to give the corresponding imidoyl chloride (brown oil), which was used in the next step without further purification. The imidoyl chloride was added dropwise at 0 °C to a solution of 4-methoxyphenol (910 mg, 7.3 mmol), Et_3N (1.8 mL, 12.9 mmol) and DMAP (16 mg, 0.13 mmol) in $CHCl_3$ (12 mL). After the addition was complete, the reaction mixture was stirred at rt for 16 h. After the precipitate (Et_3N·HCl) was filtered off, the filtrate was concentrated in vacuo.The residue was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 95/5) to give 4-methoxyphenyl 3,5-dimethyl-*N*-(thiophen-2-ylmethyl)benzimidate (**1cfd)** as a pale yellow oil (1.47 g, 69%). Aryl *N*-benzylimidates **1ccd**, **1ced** and **1mag** were prepared in a similar manner.

Naphthalen-2-yl *N*-benzyl-4-methylbenzimidate (1aaa).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:17), which was determined by ^{1}H NMR.

White solid (5.67 g, 87%). R_f 0.58 (SiO_2, Hexane/EtOAc = 3/1). Mp 59.1-61.4 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.30 (s, 3H), 4.76 (s, 2H), 7.10 (s, 1H), 7.12 (s, 1H), 7.14 (d, J = 2.8 Hz, 1H), 7.22-7.42 (m, 8H), 7.59 (d, J = 8.2 Hz, 1H), 7.74-7.86 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.40, 51.82, 110.84, 117.69, 124.46, 126.62, 126.66, 126.92, 127.68, 127.79, 128.32, 128.67, 129.14, 129.59, 129.79, 130.20, 134.17, 139.87, 141.18, 153.20, 153.73.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.41 (s, 3H), 4.63 (s, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 1.8 Hz, 1H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.47, 53.61, 118.42, 122.61, 125.05, 126.10, 126.30, 126.76, 127.48, 127.93, 128.19, 128.78, 130.99, 134.08, 140.38, 140.73, 151.24, 161.18. Other peaks are overlapped with those of a major isomer.

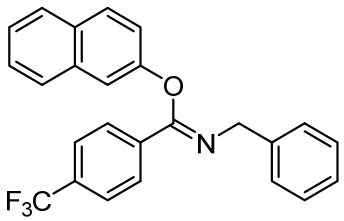
E/Z Mixture

IR (KBr): 3030 m, 2892 m, 1653 s, 1626 s, 1597 s, 1508 s, 1463 m, 1455 m, 1352 s, 1272 s, 1244 s, 1206 m, 1165 s, 1063 s, 1112 s, 993 s, 880 m, 854 s, 813 s, 746 s, 735 s, 601 m.

MS, *m/z* (relative intensity, %): 351 (M^+, 33), 232 (41), 208 (42), 127 (11), 120 (14), 119 (97), 115 (13), 92 (38), 91 (100), 65 (26).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO$: 352.1696. Found: 352.1706.

Naphthalen-2-yl *N*-benzyl-4-(trifluoromethyl)benzimidate (1aab).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:20), which was determined by ^{1}H NMR.

Colorless oil (415 mg, 10%). R_f 0.71 (SiO_2, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.80 (s, 2H), 7.12 (d, J = 2.1 Hz, 1H), 7.24-7.28 (m, 2H), 7.32-7.42 (m, 6H), 7.57 (m, 3H), 7.78-7.84 (m, 2H), 8.05 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 52.15, 110.98, 117.49, 123.76 (q, J = 272.2 Hz), 124.83, 125.41 (q, J = 3.8 Hz), 126.88, 126.92, 126.94, 127.75, 127.83, 128.44, 129.05, 129.80, 130.54, 132.43 (q, J = 32.6 Hz), 134.08, 136.08, 139.31, 152.41, 152.70.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.58 (s, 2H), 7.71-7.72 (m, 7H), 7.87-7.90 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 54.01, 125.24 (q, J = 3.8 Hz), 126.30, 126.69, 127.50, 128.35, 128.74, 129.33, 129.40, 131.60. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

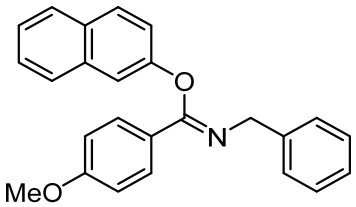
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −64.17, −63.84.

IR (KBr): 3058 m, 3032 m, 1663 s, 1627 s, 1598 s, 1510 s, 1464 s, 1408 s, 1324 s, 1243 m, 1163 s, 1123 s, 1067 s, 1017 s, 984 m, 958 m, 942 m, 843 s, 811 m, 744 s, 697 s, 616 m.

MS, *m/z* (relative intensity, %): 405 (M^+, 3), 262 (11), 91 (100).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{19}F_3NO$: 406.1413. Found: 406.1420.

Naphthalen-2-yl *N*-benzyl-4-methoxybenzimidate (1aac).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:20), which was determined by ^{1}H NMR.

White solid (853 mg, 23%). R_f 0.64 (SiO_2, Hexane/EtOAc = 1/1). Mp 71.5-73.2 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.74 (s, 3H), 4.74 (s, 2H), 6.79-6.83 (m, 2H), 7.15 (d, J = 2.3 Hz, 1H), 7.20-7.25 (m, 2H), 7.29-7.42 (m, 6H), 7.60 (d, J = 7.8 Hz, 1H), 7.75-7.79 (m, 2H), 7.87-7.90 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 51.76, 55.22, 100.77, 113.74, 117.64, 124.46, 124.95, 126.60, 126.67, 126.90, 127.67, 127.79, 128.31, 129.58, 130.20, 130.39, 134.19, 139.93, 153.25, 153.49, 161.72.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.83 (s, 3H), 4.66 (s, 2H), 8.18-8.22 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) Peaks are not clearly observed.

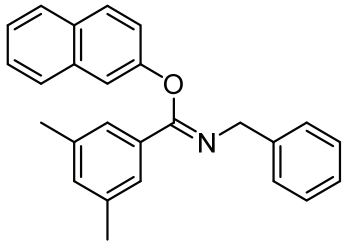
E/Z Mixture

IR (KBr): 2359 w, 1698 m, 1683 m, 1652 s, 1636 m, 1558 s, 1540 s, 1515 m, 1507 s, 1456 s, 1261 m, 1243 s, 1160 m, 1051 m, 1024 m, 837 m, 757 m, 700 m, 607 w, 582 w.

MS, *m/z* (relative intensity, %): 367 (M^+, 18), 232 (14), 135 (100), 107 (10), 92 (10), 91 (48), 77 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO_2$: 368.1645. Found: 368.1647.

Naphthalen-2-yl *N*-benzyl-3,5-dimethylbenzimidate (1aad).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:13), which was determined by ^{1}H NMR.

Colorless oil (638 mg, 54%). R_f 0.68 (SiO_2, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.38 (s, 6H), 4.90 (s, 2H), 7.13 (s, 1H), 7.29-7.55 (m, 9H), 7.73-7.74 (m, 3H), 7.86-7.92 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.16, 51.93, 110.68, 117.63, 124.41, 126.37, 126.62, 126.89, 127.63, 127.81, 128.30, 129.56, 130.19, 132.47, 132.71, 134.16, 137.94, 139.71, 153.18, 154.08.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.50 (s, 6H), 4.75 (s, 2H), 7.23 (s, 1H), 7.58-7.61 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.26, 53.60, 118.42, 122.59, 125.01, 125.84, 126.06, 126.27, 126.81, 127.44, 128.12, 128.74, 130.84, 130.97, 131.70, 134.06, 138.15, 140.75, 151.16, 161.44. Other peaks are overlapped with those of a major isomer.

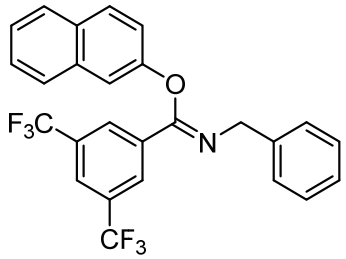
E/Z Mixture

IR (KBr): 3058 w, 3028 w, 2915 w, 1660 s, 1629 s, 1599 s, 1509 m, 1463 m, 1317 m, 1246 m, 1211 s, 1185 s, 1161 s, 1087 s, 1027 m, 962 m, 845 m, 809 m, 746 m, 697 m.

MS, *m/z* (relative intensity, %): 365 (M^+, 24), 232 (25), 222 (21), 133 (81), 105 (31), 92 (10), 91 (100), 79 (12), 77 (11), 65 (10).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{24}NO$: 366.1852. Found: 366.1862.

Naphthalen-2-yl *N*-benzyl-3,5-bis(trifluoromethyl)benzimidate (1aae).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:37), which was determined by ^{1}H NMR.

Yellow oil (118 mg, 8%). R_f 0.72 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.77 (s, 2H), 7.13 (d, J = 2.3 Hz, 1H), 7.28-7.48 (m, 8H), 7.64 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.90 (s, 1H), 8.41 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 52.48, 110.89, 117.27, 122.95 (q, J = 273.2 Hz), 124.41 (m, J = 3.4 Hz), 125.06, 126.98, 127.09, 127.83, 127.89, 128.53, 128.63 (q, J = 2.9 Hz), 130.01, 130.89, 132.01 (q, J = 33.6 Hz), 134.05, 135.22, 138.77, 150.93, 152.30.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.56 (s, 2H), 8.03 (br, 4H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) Peaks were not observed due to low concentration of the minor isomer.

E/Z Mixture

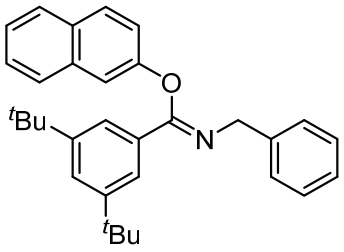
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −64.17.

IR (KBr): 3062 m, 3026 w, 1811 w, 1667 s, 1629 s, 1600 s, 1512 s, 1496 m, 1458 s, 1414 w, 1385 s, 1352 m, 1279 s, 1233 m, 1209 m, 1165 s, 1133 s, 1014 m, 960 m, 909 m, 835 m, 810 m, 729 m, 694 s, 682 s.

MS, *m/z* (relative intensity, %): 473 (M^+, 1), 330 (50), 227 (100), 115 (27).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{18}F_6NO$: 474.1287. Found: 474.1289.

Naphthalen-2-yl *N*-benzyl-3,5-di-*tert*-butylbenzimidate (1aaf).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:7.0), which was determined by ^{1}H NMR.

White solid (499 mg, 12%). R_f 0.70 (NH silica, Hexane/EtOAc = 1/1). Mp 91.8-92.8 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.25 (s, 18H), 4.80 (s, 2H), 7.17-7.45 (m, 10H), 7.61 (d, J = 8.2 Hz, 1H), 7.74-7.78 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 31.29, 34.80, 51.89, 111.37, 117.98, 123.05, 124.42, 125.04, 126.56, 126.79, 126.95, 127.66, 127.79, 128.29, 129.63, 130.09, 131.85, 134.20, 139.97, 150.76, 153.32, 154.65.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.33 (s, 18H), 4.61 (s, 2H), 7.47-7.50 (m, 2H), 7.54-7.55 (m, 1H), 7.71-7.72 (m, 1H), 7.82-7.90 (m, 4H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 31.34, 34.92, 53.67, 118.55, 121.45, 122.38, 122.74, 123.32, 124.21, 125.62, 126.10, 126.28, 127.50, 127.71, 128.78, 129.36, 131.03, 134.12, 140.89, 151.05, 151.27, 162.41.

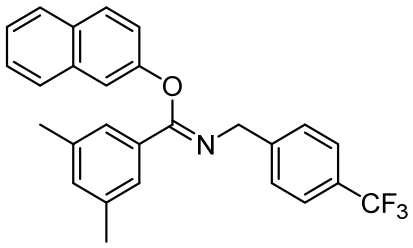
E/Z Mixture

IR (KBr): 2965 s, 2911 s, 2866 m, 1665 s, 1627 s, 1597 s, 1508 s, 1460 s, 1450 m, 1361 s, 1318 m, 1242 s, 1206 s, 1160 s, 1093 s, 1009 m, 963 m, 885 m, 809 m, 750 m, 734 s, 705 m.

MS, *m/z* (relative intensity, %): 449 (M^+, 20), 306 (11), 232 (32), 218 (13), 217 (71), 133 (17), 91 (100), 57 (26).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{32}H_{36}NO$: 450.2791. Found: 450.2792.

Naphthalen-2-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1abd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:9.5), which was determined by ^{1}H NMR.

White solid (1.10 g, 50%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1). Mp 108.2-109.1 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 4.78 (s, 2H), 7.04 (s, 1H), 7.13 (m, 1H), 7.19-7.24 (m, 1H), 7.24-7.27 (m, 1H), 7.35-7.44 (m, 2H), 7.50-7.52 (m, 2H), 7.56-7.58 (m, 4H), 7.62 (d, J = 8.2 Hz, 1H), 7.77-7.82 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 51.43, 110.79, 117.60, 124.62, 124.29 (q, J = 271.3 Hz), 124.62, 125.25 (q, J = 3.8 Hz), 126.41, 126.77, 126.93, 127.71, 128.01, 128.91 (q, J = 32.3 Hz), 129.68, 130.35, 132.23, 133.02, 134.16, 138.14, 143.87, 153.06.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.39 (s, 6H), 4.63 (s, 2H), 7.19 (s, 2H), 7.46 (d, J = 1.8 Hz, 1H), 7.48 (s, 2H), 7.66 (m, 2H), 7.85-7.89 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.33, 53.19, 118.54, 122.52, 125.08 (q, J = 3.8 Hz), 125.80, 126.26, 127.03, 127.50, 127.76, 128.88, 130.68, 131.09, 131.97, 134.08, 138.37, 144.93, 151.07, 154.94, 162.14. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

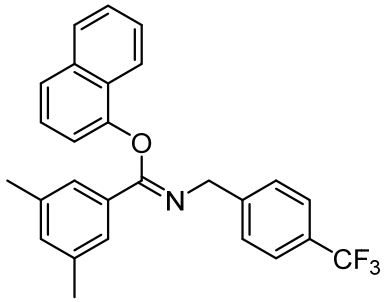
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.62.

IR (KBr): 2898 m, 1663 s, 1628 s, 1598 s, 1511 s, 1464 m, 1418 m, 1324 s, 1247 m, 1159 s, 1118 m, 1087 s, 1066 s, 961 m, 915 m, 840 s, 746 s, 732 s, 691 m.

MS, *m/z* (relative intensity, %): 433 (M^+, 4), 290 (22), 159 (100), 133 (41), 115 (17), 109 (13), 105 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{23}F_3NO$: 434.1726. Found: 434.1729.

Naphthalen-1-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1bbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:10), which was determined by ^{1}H NMR.

Yellow oil (149 mg, 8%). R_f 0.66 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.25 (s, 6H), 4.77 (s, 2H), 6.64 (d, J = 7.8 Hz, 1H), 7.05 (s, 1H), 7.19-7.24 (m, 1H), 7.49-7.62 (m, 9H), 7.87-7.89 (m, 1H), 8.42 (d, J = 7.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.20, 51.30, 109.02, 121.54, 122.47, 124.30 (q, J = 271.9 Hz), 124.52, 125.26 (q, J = 3.8 Hz), 125.66, 126.10, 126.13, 126.88, 127.86, 128.04, 128.91 (q, J = 32.3 Hz), 133.11, 134.90, 138.16, 143.85, 150.77.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.42 (s, 6H), 4.59 (s, 2H), 7.28 (s, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.64 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.38, 52.99, 118.47, 122.07, 124.89 (q, J = 3.8 Hz), 125.48, 125.78, 125.92, 126.44, 126.84, 127.64, 132.06, 132.21, 138.45, 155.28. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

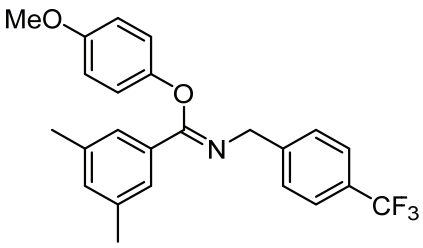
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.56.

IR (KBr): 3053 w, 2918 w, 1738 w, 1661 m, 1618 m, 1577 w, 1507 w, 1461 w, 1392 m, 1324 s, 1233 m, 1162 s, 1123 s, 1094 s, 1066 s, 1018 m, 857 w, 820 m, 791 m, 779 m, 769 m.

MS, *m/z* (relative intensity, %): 433 (M^+, 1), 290 (30), 159 (100), 133 (19), 115 (14), 109 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{23}F_3NO$: 434.1726. Found: 434.1733.

4-Methoxyphenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1cbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.2), which was determined by ^{1}H NMR.

Yellow oil (425 mg, 17%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 3.74 (s, 3H), 4.76 (s, 2H), 6.76-6.85 (m, 4H), 7.03 (s, 1H), 7.45 (s, 2H), 7.51-7.60 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 51.27, 55.57, 114.87, 117.18, 124.31 (q, J = 271.9 Hz), 125.23 (q, J = 3.8 Hz), 126.48, 128.00, 128.81 (q, J = 32.6 Hz), 132.57, 132.65, 137.96, 144.13, 149.23, 155.00, 155.51.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 6H), 3.82 (s, 3H), 4.60 (s, 2H), 6.92-6.95 (m, 2H), 7.12 (s, 3H), 7.14-7.17 (m, 2H), 7.27 (d, J = 7.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 53.11, 55.52, 114.25, 122.97, 125.06 (q, J = 3.8 Hz), 125.69, 126.96, 130.81, 131.81, 138.30, 145.13, 146.71, 156.50, 162.47. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

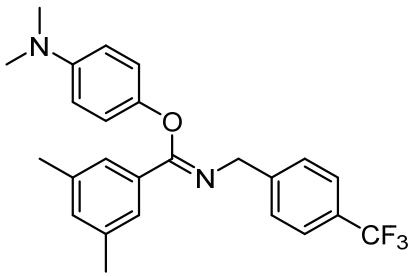
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.56 (s, 1F).

IR (KBr): 2916 w, 1733 w, 1654 m, 1606 w, 1504 s, 1456 w, 1418 w, 1324 s, 1246 w, 1178 s, 1122 m, 1066 m, 1036 w, 1018 w, 821 m, 778 w.

MS, *m/z* (relative intensity, %): 413 (M^+, 1), 291 (11), 290 (55), 160 (28), 159 (100), 123 (28), 109 (29), 95 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{23}F_3NO_2$: 414.1675. Found: 414.1665.

4-(Dimethylamino)phenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1dbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.5), which was determined by ^{1}H NMR.

Yellow oil (397 mg, 12%). R_f 0.76 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 2.87 (s, 6H), 4.76 (s, 2H), 6.62–6.66 (m, 2H), 6.80–6.83 (m, 2H), 7.02 (s, 1H), 7.46 (s, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 41.20, 51.25, 114.09, 117.05, 124.33 (q, J = 271.6 Hz), 125.19 (q, J = 3.8 Hz), 126.49, 128.01, 128.72 (q, J = 32.6 Hz), 132.50, 132.88, 137.85, 144.33, 146.72, 147.00, 155.91.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 2.95 (s, 6H), 4.60 (s, 2H), 6.76–6.79 (m, 2H), 6.91 (s, 1H), 7.06–7.08 (m, 2H), 7.11 (s, 3H), 7.17 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 41.09, 53.14, 113.26, 122.47, 125.01 (q, J = 3.8 Hz), 125.67, 126.98, 131.66, 138.21, 144.11, 148.05. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

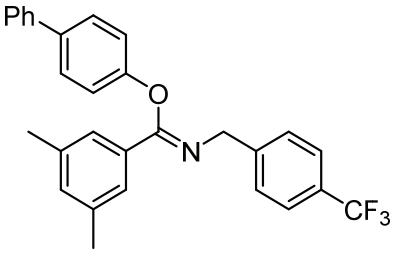
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.53.

IR (KBr): 2918 s, 2802 m, 1733 s, 1669 m, 1653 s, 1616 s, 1608 s, 1516 s, 1508 s, 1324 s, 1202 s, 1162 s, 1123 s, 1066 m, 850 m, 820 m.

MS, *m/z* (relative intensity, %): 426 (M^+, 9), 291 (11), 290 (55), 160 (11), 159 (100), 136 (42), 109 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{26}F_3N_2O$: 427.1992. Found: 427.1997.

[1,1'-Biphenyl]-4-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1ebd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:9.1), which was determined

by ^{1}H NMR.

Yellow oil (188 mg, 10%). R_f 0.67 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.29 (s, 6H), 4.78 (s, 2H), 6.96-7.00 (m, 2H), 7.06 (s, 1H), 7.30-7.33 (m, 1H), 7.38-7.42 (m, 2H), 7.47-7.48 (m, 1H), 7.49-7.50 (m, 2H), 7.51-7.53 (m, 5H), 7.58-7.60 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 51.37, 116.34, 122.48, 124.30 (q, J = 272.0 Hz), 125.25 (q, J = 3.5 Hz), 126.41, 126.74, 127.06, 128.00, 128.59, 128.76, 128.89 (q, J = 32.3 Hz), 132.35, 132.93, 135.73, 138.11, 140.17, 143.91, 154.85.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.38 (s, 6H), 4.64 (s, 2H), 7.14 (s, 1H), 7.16 (s, 2H), 7.27-7.29 (m, 4H), 7.61-7.62 (m, 4H), 7.64 (s, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 53.21, 121.99, 125.10 (q, J = 3.8 Hz), 125.74, 127.10, 127.30, 127.89, 127.94, 130.68, 131.93, 137.83, 138.35, 152.78. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

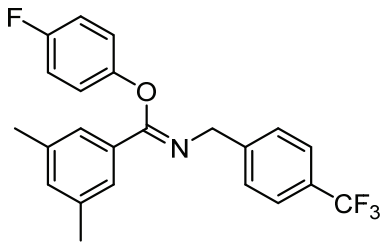
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.53.

IR (KBr): 3057 m, 3032 s, 2918 s, 1661 s, 1605 s, 1513 s, 1485 s, 1450 m, 1417 s, 1325 s, 1216 s, 1169 s, 1123 s, 1066 s, 1018 s, 821 s, 761 s, 697 s.

MS, *m/z* (relative intensity, %): 459 (M^+, 7), 290 (30), 159 (100), 133 (74), 109 (11), 105 (21).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{29}H_{25}F_3NO$: 460.1883. Found: 460.1889.

4-Fluorophenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1fbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.8), which was determined by ^{1}H NMR.

Yellow oil (2.06 g, 85%). R_f 0.74 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 4.75 (s, 2H), 6.83–6.87 (m, 2H), 6.91–6.97 (m, 2H), 7.05 (s, 1H), 7.44 (s, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 51.27, 116.44 (d, J = 23.0 Hz), 117.35 (d, J = 8.6 Hz), 124.28

(q, J = 271.9 Hz), 125.27 (q, J = 3.8 Hz), 126.45, 127.98, 128.94 (q, J = 32.3 Hz), 132.12, 132.88, 138.12, 143.83, 151.33 (d, J = 1.9 Hz), 154.96, 158.20 (d, J = 241.5 Hz).

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.38 (s, 6H), 4.60 (s, 2H), 7.06–7.11 (m, 2H), 7.13 (s, 3H), 7.17–7.20 (m, 2H), 7.26 (d, J = 7.8 Hz, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.29, 53.07, 115.81 (d, J = 23.0 Hz), 123.57 (d, J = 8.6 Hz), 125.11 (q, J = 3.8 Hz), 125.69, 126.97, 130.49, 131.99, 138.37, 143.86, 149.07 (d, J = 2.9 Hz), 159.66 (d, J = 242.5 Hz), 161.98. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

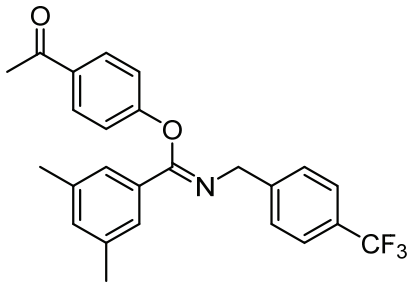
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −122.19 (s, 1F, *major isomer*), −119.64 (s, 1F, *minor isomer*), −63.59 (s, 3F, major/minor isomers overlapped).

IR (KBr): 2916 m, 1666 s, 1618 s, 1606 s, 1505 s, 1419 s, 1331 s, 1318 s, 1288 m, 1186 s, 1159 s, 1120 s, 1067 s, 1038 m, 903 m, 864 s, 830 s, 782 s, 739 m, 696 m, 671 s.

MS, *m/z* (relative intensity, %): 401 (M^+, 1), 291 (16), 290 (76), 160 (18), 159 (100), 133 (16), 116 (11), 109 (35).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{20}F_4NO$: 402.1476. Found: 402.1478.

4-Acetylphenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1gbd).



The product was obtained as a mixture of geometrical isomers (E:Z = 1:13) , which was determined by ^{1}H NMR.

White solid (1.63 g, 63%). R_f 0.60 (NH silica, Hexane/EtOAc = 1/1). Mp 91.1-91.8 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.30 (s, 6H), 2.55 (s, 3H), 4.73 (s, 2H), 6.95–6.98 (m, 2H), 7.08 (s, 1H), 7.47 (s, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.90–7.93 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 26.42, 51.38, 115.77, 124.23 (q, J = 272.2 Hz), 125.31 (q, J = 3.8 Hz), 126.25, 127.94, 129.03 (q, J = 32.3 Hz), 130.93, 131.71, 131.96, 133.24, 138.29, 143.47, 153.82, 159.03, 196.55.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.39 (s, 6H), 2.62 (s, 3H), 4.63 (s, 2H), 7.15 (s, 3H), 7.32–7.34 (m, 2H), 8.03–8.05 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.32, 26.61, 122.30, 125.72, 127.03, 129.87, 132.17, 133.77, 138.46. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

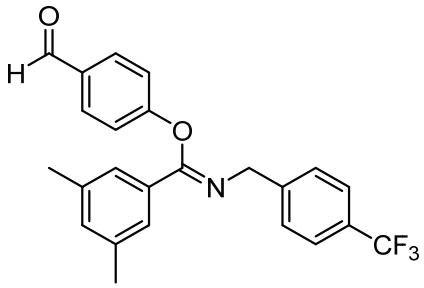
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.62.

IR (KBr): 3002 m, 2918 m, 1659 s, 1649 s, 1599 s, 1584 s, 1504 s, 1418 s, 1358 m, 1327 s, 1227 m, 1160 m, 1121 m, 1088 m, 1019 m, 912 m, 847 s, 828 s, 817 s, 719 m, 686 m, 592 s.

MS, *m/z* (relative intensity, %): 425 (M^+, 9), 134 (10), 133 (100), 105 (24).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{23}F_3NO_2$: 426.1675. Found: 426.1685.

4-Formylphenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1hbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:12), which was determined by ^{1}H NMR.

White solid (1.86 g, 75%). R_f 0.64 (SiO_2, Hexane/EtOAc = 1/1). Mp 99.9-101.0 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.30 (s, 6H), 4.74 (s, 2H), 7.04 (d, J = 8.7 Hz, 2H), 7.09 (s, 1H), 7.48 (s, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.81-7.85 (m, 2H), 9.90 (s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 51.34, 116.41, 122.88, 124.21 (q, J = 271.9 Hz), 125.35 (q, J = 3.8 Hz), 126.29, 127.97, 129.14 (q, J = 32.6 Hz), 131.16, 131.49, 132.27, 133.43, 138.39, 143.25, 160.00, 190.50.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.39 (s, 6H), 4.64 (s, 2H), 7.16 (s, 3H), 7.41 (d, J = 8.2 Hz, 2H), 7.94-7.96 (m, 2H), 10.01 (s, 1H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.32, 53.22, 125.35 (q, J = 3.8 Hz), 125.74, 127.06, 133.13, 138.51, 191.14. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

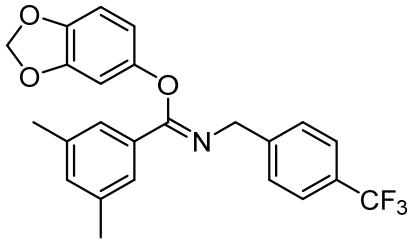
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.65.

IR (KBr): 2918 w, 2839 w, 1698 s, 1668 s, 1599 s, 1505 s, 1419 m, 1324 s, 1239 m, 1156 m, 1115 m, 1082 m, 943 m, 903 m, 824 s, 768 m, 719 m, 597 m, 501 m.

MS, *m/z* (relative intensity, %): 411 (M^+, 11), 134 (17), 133 (100), 105 (40), 79 (15), 77 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{21}F_3NO_2$: 412.1519. Found: 412.1525.

Benzo[*d*][1,3]dioxol-5-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1ibd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.6), which was determined by ^{1}H NMR.

Yellow oil (674 mg, 27%). R_f 0.70 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.29 (s, 6H), 4.77 (s, 2H), 5.93 (s, 2H), 6.30 (dd, J = 8.2, 2.3 Hz, 1H), 6.49 (d, J = 2.3 Hz, 1H), 6.64 (d, J = 8.7 Hz, 1H), 7.05 (s, 1H), 7.45 (s, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.24, 51.27, 99.09, 101.51, 108.05, 108.25, 124.30 (q, J = 272.2 Hz), 125.26 (q, J = 3.8 Hz), 126.42, 127.99, 128.87 (q, J = 32.3 Hz), 132.42, 132.78, 138.03, 143.03, 144.02, 148.52, 150.30, 155.16.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 6H), 4.61 (s, 2H), 5.99 (s, 2H), 6.67 (dd, J = 8.2, 2.3 Hz, 1H), 6.77 (d, J = 2.3 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 7.10-7.13 (m, 3H), 7.29 (d, J = 8.2 Hz, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 53.15, 104.48, 107.91, 114.40, 125.11 (q, J = 3.8 Hz), 125.67, 126.97, 130.61, 131.89, 138.33, 144.60, 144.99, 147.63, 147.86, 162.48. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

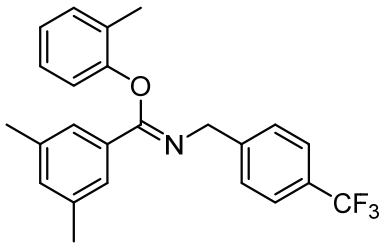
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.59, −63.53.

IR (KBr): 3009 w, 2916 m, 1735 w, 1661 m, 1618 m, 1606 m, 1483 s, 1446 m, 1417 m, 1325 s, 1246 m, 1171 s, 1125 s, 1066 s, 1038 s, 1019 m, 949 m, 932 m, 821 s, 681 w, 595 w.

MS, *m/z* (relative intensity, %): 427 (M^+, 1), 290 (41), 160 (21), 159 (100), 137 (17), 133 (11), 109 (24), 107 (10), 79 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{21}F_3NO_3$: 428.1468. Found: 428.1474.

***o*-Tolyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1jbd).**



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.3), which was determined by ^{1}H NMR.

Pale yellow oil (105 mg, 4%). R_f 0.80 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 2.44 (s, 3H), 4.71 (s, 2H), 6.57 (dd, J = 7.8, 1.4 Hz, 1H), 6.91–7.01 (m, 2H), 7.05 (s, 1H), 7.15 (s, 1H), 7.45 (s, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 16.21, 21.23, 51.23, 114.80, 122.65, 124.31 (q, J = 271.9 Hz), 125.24 (q, J = 3.8 Hz), 125.60, 126.19, 126.92, 127.07, 128.02, 128.86 (q, J = 32.3 Hz), 131.52, 132.84, 138.02, 138.35, 144.02, 153.42.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.29 (s, 3H), 2.39 (s, 6H), 4.58 (s, 2H), 7.27 (d, J = 7.3 Hz, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 16.55, 21.34, 53.06, 122.52, 125.02 (q, J = 3.8 Hz), 126.79, 129.65, 130.69, 130.85, 130.96, 131.85, 132.51, 145.15, 151.74, 155.55, 161.52. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

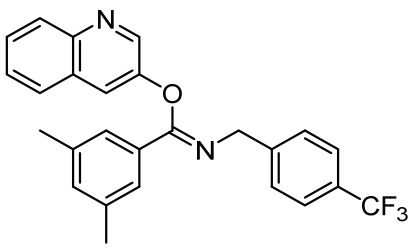
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.59, −63.53.

IR (KBr): 2920 w, 1661 m, 1618 w, 1605 w, 1587 w, 1490 m, 1418 w, 1324 s, 1226 m, 1176 s, 1117 s, 1066 m, 1018 w, 820 w, 751 w.

MS, *m/z* (relative intensity, %): 397 (M^+, 2), 290 (43), 160 (11), 159 (100), 133 (15), 109 (21).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{23}F_3NO$: 398.1726. Found: 398.1729.

Quinolin-3-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1kbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:3.1), which was determined by ^{1}H NMR.

Brown oil (1.06 g, 40%). R_f 0.64 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.29 (s, 6H), 4.80 (s, 2H), 7.07 (s, 1H), 7.32 (d, J = 2.8 Hz, 1H), 7.46-7.64 (m, 9H), 8.08 (d, J = 8.2 Hz, 1H), 8.87 (d, J = 3.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 51.47, 117.58, 124.20 (q, J = 271.3 Hz), 125.31 (q, J = 3.8 Hz), 125.75, 126.38, 126.91, 127.06, 127.52, 127.93, 128.44 (q, J = 31.2 Hz), 129.20, 131.37, 133.32, 138.39, 143.01, 144.39, 147.42, 148.74, 153.77.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.42 (s, 6H), 4.64 (s, 2H), 7.19 (s, 1H), 7.22 (s, 2H), 7.26-7.28 (m, 2H), 7.68-7.72 (m, 1H), 7.82 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 2.3 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 8.91 (d, J = 2.8 Hz, 1H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.32, 53.18, 116.47, 126.06, 127.01, 127.45, 129.98, 132.27, 138.51, 143.39, 144.34, 145.39, 146.74, 161.47. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

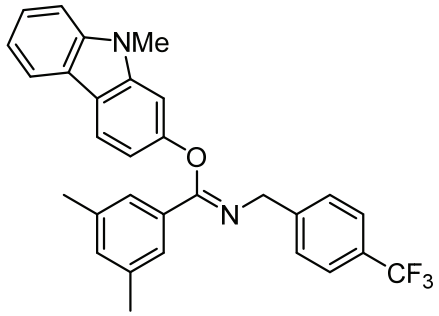
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.62.

IR (KBr): 3055 m, 3010 m, 2919 s, 1737 m, 1668 s, 1603 s, 1497 m, 1464 m, 1418 m, 1324 s, 1269 m, 1162 s, 1123 s, 1066 s, 987 m, 858 s, 820 s, 781 s, 750 s, 612 m.

MS, *m/z* (relative intensity, %): 434 (M^+, 7), 159 (24), 134 (10), 133 (100), 105 (28), 79 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{22}F_3N_2O$: 435.1679. Found: 435.1682.

9-Methyl-9*H*-carbazol-2-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1lbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:8.5), which was determined by ^{1}H NMR.

White solid (1.35 g, 68%). R_f 0.62 (NH silica, Hexane/EtOAc = 1/1). Mp 128.5-132.1 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 3.69 (s, 3H), 4.81 (s, 2H), 6.83–6.87 (m, 2H), 7.04 (s, 1H), 7.19–7.23 (m, 1H), 7.32–7.34 (m, 1H), 7.40-7.42 (m, 1H), 7.51-7.53 (m, 2H), 7.56-7.57 (m, 4H),

7.94 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.24, 29.13, 51.44, 95.83, 108.27, 108.35, 118.23, 119.26, 119.66, 121.42, 122.48, 124.29 (q, J = 272.2 Hz), 125.06, 125.22 (q, J = 3.8 Hz), 126.44, 128.02, 128.84 (q, J = 32.6 Hz), 132.65, 132.84, 138.03, 141.25, 142.02, 144.08, 154.49, 155.22.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.40 (s, 6H), 3.81 (s, 3H), 4.65 (s, 2H), 7.11–7.15 (m, 2H), 7.27-7.30 (m, 3H), 7.48 (s, 1H), 8.06-8.10 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.35, 53.23, 102.24, 113.78, 119.05, 119.89, 120.00, 120.55, 125.84, 127.04, 128.35, 130.84, 131.91, 138.35. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

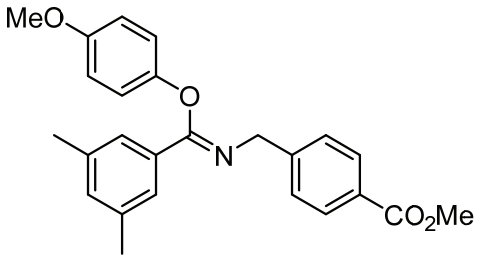
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.56.

IR (KBr): 3052 w, 2940 w, 1662 s, 1631 s, 1600 s, 1497 m, 1468 s, 1458 s, 1418 s, 1360 m, 1328 s, 1233 m, 1203 m, 1181 s, 1113 s, 1067 m, 1017 m, 955 m, 863 m, 808 s, 745 s, 594 m.

MS, *m/z* (relative intensity, %): 486 (M^+, 3), 290 (50), 168 (11), 159 (100).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{30}H_{26}F_3N_2O$: 487.1992. Found: 487.1998.

Methyl 4-((((3,5-dimethylphenyl)(4-methoxyphenoxy)methylene)amino)methyl)benzoate (1ccd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.1), which was determined by ^{1}H NMR. Based on NOSEY spectroscopy of compound **1ccd**, the stereochemistry of the major isomer was determined to have a *Z* configuration.

Colorless oil (545 mg, 55%). R_f 0.54 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 6H), 3.74 (s, 3H), 3.91 (s, 3H), 4.76 (s, 2H), 6.76-6.85 (m, 4H), 7.03 (s, 1H), 7.45-7.49 (m, 4H), 8.00-8.02 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.21, 51.45, 52.00, 55.57, 114.86, 117.18, 126.48, 127.65, 128.42, 129.52, 129.67, 132.61, 137.93, 145.43, 149.26, 154.97, 155.41, 167.13.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 3.82 (s, 3H), 3.89 (s, 3H), 4.60 (s, 2H), 6.92-6.94 (m, 2H), 7.12 (s, 3H), 7.15-7.17 (m, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.93-7.95 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.30, 51.97, 53.35, 55.52, 114.25, 122.96, 125.71, 126.66, 131.78,

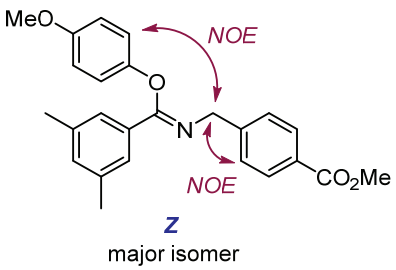
134.30, 138.25. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

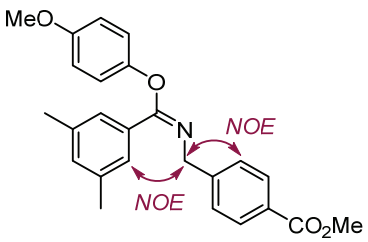
IR (KBr): 3002 m, 2950 m, 1718 s, 1653 s, 1609 m, 1505 s, 1456 m, 1435 m, 1278 s, 1204 s, 1179 s, 1105 m, 1036 m, 823 m, 755 m.

MS, *m/z* (relative intensity, %): 403 (M^+, 5), 281 (11), 280 (48), 150 (15), 149 (100), 133 (21), 123 (19), 121 (33), 90 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{26}NO_4$: 404.1856. Found: 404.1868.

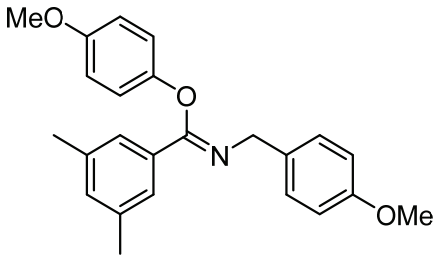


Z
major isomer



E
minor isomer

4-Methoxyphenyl *N*-(4-methoxybenzyl)-3,5-dimethylbenzimidate (1ced).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.1), which was determined by ^{1}H NMR.

Colorless oil (2.37 g, 79%). R_f 0.56 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.26 (s, 6H), 3.74 (s, 3H), 3.80 (s, 3H), 4.65 (s, 2H), 6.76-6.88 (m, 6H), 7.00 (s, 1H), 7.31 (d, J = 8.7 Hz, 2H), 7.44 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.20, 51.24, 55.25, 55.78, 113.72, 114.82, 117.12, 126.47, 129.03, 132.17, 132.39, 132.86, 137.81, 149.45, 154.47, 154.84, 158.35.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 3.78 (s, 3H), 3.81 (s, 3H), 4.49 (s, 2H), 6.90-6.92 (m, 2H), 7.07-7.16 (m, 6H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 52.95, 55.21, 55.51, 113.53, 114.18, 122.97, 125.77, 127.83, 131.56, 133.12, 138.11. Other peaks are overlapped with those of a major isomer.

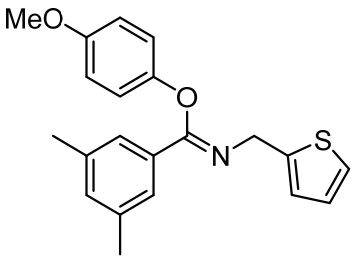
E/Z Mixture

IR (KBr): 2951 w, 2911 w, 1654 m, 1607 m, 1504 s, 1463 m, 1440 w, 1317 m, 1301 m, 1245 s, 1178 s, 1088 m, 1035 m, 821 m, 779 w, 517 w.

MS, *m/z* (relative intensity, %): 375 (M^+, 3), 122 (45), 121 (100), 91 (11), 78 (10), 77 (15).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{26}NO_3$: 376.1907. Found: 376.1910.

4-Methoxyphenyl 3,5-dimethyl-*N*-(thiophen-2-ylmethyl)benzimidate (1cfd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.0), which was determined by ^{1}H NMR.

Pale yellow oil (1,47 g, 69%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.27 (s, 6H), 3.74 (s, 3H), 4.88 (s, 2H), 6.76-6.86 (m, 4H), 6.95 (d, *J* = 3.7 Hz, 2H), 7.01 (s, 1H), 7.21 (t, *J* = 3.2 Hz, 1H), 7.43 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.21, 47.00, 55.57, 114.83, 117.31, 122.99, 124.11, 124.31, 126.57, 126.65, 132.56, 137.85, 143.45, 149.26, 154.99, 155.27.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 6H), 3.81 (s, 3H), 4.70 (s, 2H), 6.91-6.93 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 49.58, 55.51, 114.17, 122.66, 123.50, 125.73, 126.50, 131.75, 138.21, 145.03, 146.60, 156.41, 162.36. Other peaks are overlapped with those of a major isomer.

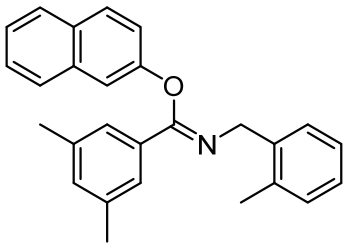
E/Z Mixture

IR (KBr): 2948 w, 2913 w, 1655 m, 1604 w, 1503 s, 1462 w, 1440 w, 1314 m, 1245 m, 1190 m, 1091 m, 1034 m, 822 m, 779 w, 698 m.

MS, *m/z* (relative intensity, %): 351 (M^+, 3), 228 (26), 220 (15), 123 (11), 99 (20), 98 (49), 97 (100), 53 (19), 44 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{21}H_{22}NO_2S$: 352.1366. Found: 352.1368.

Naphthalen-2-yl 3,5-dimethyl-*N*-(2-methylbenzyl)benzimidate (1add).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:13), which was determined by ^{1}H NMR.

White solid (1.05 g, 46%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1). Mp 61.2-62.7 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.26 (s, 6H), 2.32 (s, 3H), 4.71 (s, 2H), 7.02 (s, 1H), 7.14-7.17 (m, 4H), 7.25-7.28 (m, 1H), 7.33-7.37 (m, 1H), 7.39-7.43 (m, 2H), 7.55 (s, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.76-7.81 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.28, 21.22, 50.00, 110.76, 117.72, 124.45, 125.77, 125.91, 126.41, 126.64, 126.79, 126.96, 127.69, 128.18, 129.61, 130.00, 130.21, 132.52, 132.73, 134.21, 136.19, 137.84, 137.98, 153.27.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 6H), 2.41 (s, 3H), 4.51 (s, 2H), 7.08-7.10 (m, 3H), 7.46 (m, 2H), 7.68 (m, 2H), 7.84-7.87 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.02, 21.33, 51.65, 118.49, 122.64, 125.04, 125.65, 126.09, 126.25, 126.51, 127.49, 127.91, 128.78, 129.65, 130.92, 131.01, 131.72, 138.20, 153.99. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

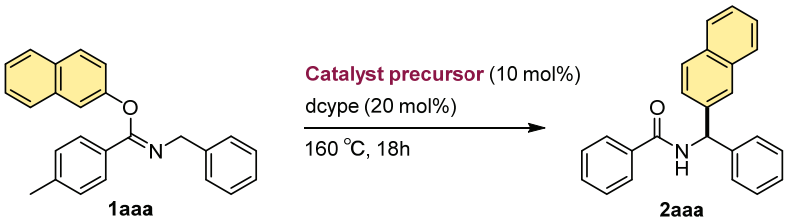
IR (KBr): 3008 m, 2918 m, 2231 s, 1662 s, 1629 m, 1605 s, 1508 s, 1456 s, 1377 m, 1316 s, 1248 s, 1212 s, 1187 s, 1166 s, 1083 m, 1038 m, 960 m, 908 m, 856 s, 746 s.

MS, *m/z* (relative intensity, %): 379 (M^+, 5), 133 (33), 105 (100), 79 (15), 77 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{26}NO$: 380.2009. Found: 380.2009.

IV. Optimization Studies

Table S1. Screening of catalyst precursors[a]



1aaa **2aaa**

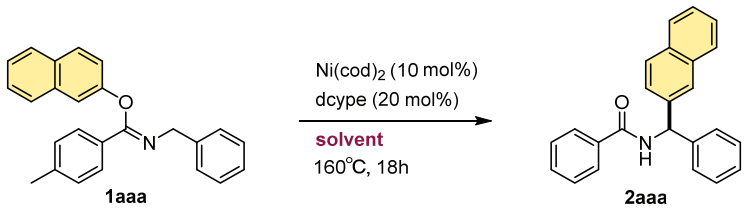
Entry	Catalyst precursor	Yield of **2aaa** [%]	Recovery of **1aaa** [%]
1	$Ni(cod)_2$	51	12
2	$NiCl_2$·DME	0	94
3	$NiBr_2$·DME	0	100
4	$Ni(OAc)_2$	0	71
5	$Ni(OTf)_2$	0	89
7[b]	$Ni(dcype)(CO)_2$	13	50
8	$NiCl_2$·DME/ Mn (1 equiv)	0	91
9	$Ni(acac)_2$/BuLi (20 mol%)	12	42
10	$Ni(acac)_2$/MeMgI (20 mol%)	0	0
11[c]	$Pd_2(dba)_3$ (5 mol%)	0	60
12[c]	$[RhCl(cod)]_2$ (5 mol%)	0	84
13[c]	None	0	100

[a] Reaction conditions: **1aaa** (0.20 mmol), catalyst (0.020 or 0.010 mmol), dcype (0.040 mmol), and dioxane (1.5 mL) in a screw capped vial under N_2 at 160 °C for 18h. Yields were determined by GC using pentadecane as an internal standard.

[b] With dcype 10 mol% instead of 20 mol%

[c] In toluene instead of dioxane

Table S2. Screening of solvent[a]

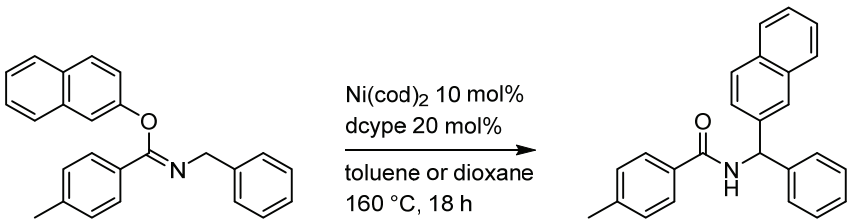


1aaa 2aaa

Entry	Solvent	Yield of **2aaa** [%]	Recovery of **1aaa** [%]
1	toluene	46	13
2	mesitylene	44	2
3	**dioxane**	51	12
4	dibutyl ether	51	7
5	CPME	49	3
6	diglyme	37	9
7	DMF	19	9
8	DMAc	27	3
9	DMI	16	3
10	DMSO	19	n.d.
11	*tert*-amyl alcohol	0.3	30
12	octane	34	22
13	ethylcyclohexane	43	16

[a] Reaction conditions: **1aaa** (0.20 mmol), $Ni(cod)_2$ (0.020 mmol), dcype (0.040 mmol), and solvent (1.5 mL) in a screw capped vial under N_2 at 160 °C for 18 h. Yields were determined by GC using pentadecane as an internal standard.

V. A Typical Procedure

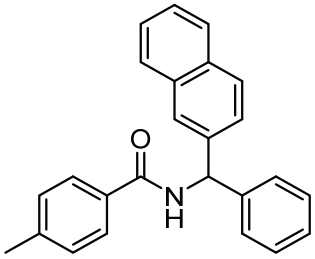


1aaa **2aaa**

In a glovebox filled with nitrogen, aryl *N*-benzylimidate **1aaa** (73.5 mg, 0.21 mmol), $Ni(cod)_2$ (5.5 mg, 0.020 mmol), dcype (16.9 mg, 0.040 mmol) and solvent (1.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 18 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 9/1 to 7/3) to give **2aaa** as a white solid (36.3 mg, 49%).

Spectroscopic Data of Products

4-Methyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aaa).



White solid (36.3 mg, 49%). R_f 0.54 (SiO_2, Hexane/EtOAc = 1/1). Mp 187.2-188.1 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.40 (s, 3H), 6.61 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 7.23 (s, 1H), 7.26 (d, J = 0.9 Hz, 1H), 7.29-7.41 (m, 6H), 7.45-7.49 (m, 2H), 7.73-7.83 (m, 6H).

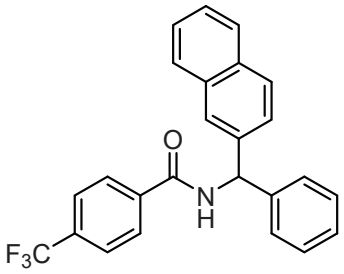
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.47, 57.45, 125.66, 126.05, 126.07, 126.28, 127.06, 127.62, 127.64, 127.99, 128.59, 128.76, 129.28, 131.25, 132.72, 133.24, 138.82, 141.36, 142.21, 166.43.

IR (KBr): 3325 m, 3055 m, 2923 m, 1634 s, 1540 s, 1506 s, 1454 m, 1329 s, 1281 m, 1189 m, 1121 m, 817 s, 754 s, 734 m, 698 s, 655 m, 576 m, 474 s.

MS, *m/z* (relative intensity, %): 352 (10), 351 (M^+, 37), 351 (49), 233 (13), 232 (64), 215 (15), 120 (11), 119 (100), 104 (19), 91 (35).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO$: 352.1696. Found: 352.1694.

***N*-(Naphthalen-2-yl(phenyl)methyl)-4-(trifluoromethyl)benzamide (2aab).**



White solid (36.9 mg, 40%). R_f 0.66 (SiO_2, Hexane/EtOAc = 1/1). Mp 193.1-193.2 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.61 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 7.3 Hz, 1H), 7.30-7.40 (m, 6H), 7.46-7.50 (m, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.74 (s, 1H), 7.77-7.81 (m, 1H), 7.82-7.84 (m, 2H), 7.94 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 57.79, 123.58 (q, J = 273.2 Hz), 125.46, 125.71 (q, J = 3.4 Hz), 126.10, 126.26, 126.45, 127.57, 127.66, 127.86, 127.97, 128.77, 128.89, 132.79, 133.22, 133.43 (q, J = 32.6 Hz), 137.37, 138.28, 140.85, 165.26.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: −64.23.

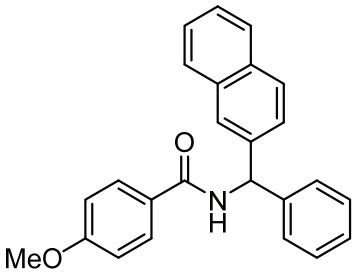
IR (KBr): 3297 m, 1644 s, 1539 s, 1507 m, 1327 s, 1165 s, 1128 s, 1110 m, 1068 m, 1016 m, 860 m,

813 m, 750 m, 719 w, 697 m, 477 m.

MS, *m/z* (relative intensity, %): 406 (18), 405 (M^+, 64), 233 (17), 232 (80), 217 (15), 216 (26), 215 (52), 202 (13), 173 (78), 154 (19), 145 (66), 129 (24), 128 (11), 127 (23), 105 (12), 104 (100), 77 (18).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{19}F_3NO$: 406.1413. Found: 406.1414.

4-Methoxy-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aac).



White solid (26.3 mg, 35%). R_f 0.48 (SiO_2, Hexane/EtOAc = 1/1). Mp 162.7-163.3 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ: 3.84 (s, 3H), 6.60 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 7.27-7.36 (m, 5H), 7.39 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.44-7.49 (m, 2H), 7.74 (s, 1H), 7.76-7.82 (m, 5H).

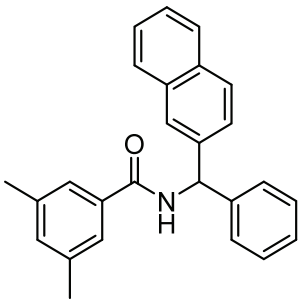
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 55.40, 57.45, 113.77, 125.67, 126.05, 126.27, 126.37, 127.58, 127.60, 127.64, 127.98, 128.55, 128.74, 128.90, 132.71, 133.24, 138.92, 141.44, 162.32, 166.02.

IR (KBr): 3289 m, 3057 w, 1635 s, 1605 s, 1539 s, 1504 s, 1456 w, 1438 w, 1337 m, 1297 m, 1253 s, 1181 m, 1033 m, 847 m, 813 m, 751 m, 698 m, 477 m.

MS, *m/z* (relative intensity, %): 367 (M^+, 20), 233 (11), 232 (56), 215 (10), 136 (10), 135 (100), 107 (10), 77 (18).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO_2$: 368.1645. Found: 368.1644.

3,5-Dimethyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aad).



White solid (37.6 mg, 52%). R_f 0.62 (SiO_2, Hexane/EtOAc = 1/1). Mp 179.5-180.2 °C. The only detectable byproducts were hydrolysis products (*i.e.*, 9% of 2-naphthol and 10% of *N*-benzyl-3,5-dimethylbenzamide was observed, as determined by GC using pentadecane as an internal standard.).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 6.61 (d, J = 7.8 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 7.13 (s, 1H), 7.27-7.35 (m, 5H), 7.39 (dd, J = 8.7 Hz, J = 1.8 Hz, 1H), 7.43 (s, 2H), 7.45-7.48 (m, 2H), 7.74 (s, 1H), 7.76-7.78 (m, 1H), 7.79-7.81 (m, 2H).

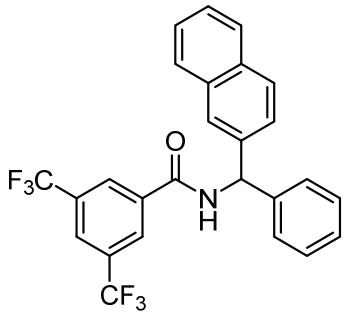
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 57.40, 124.78, 125.68, 126.05, 126.08, 126.26, 127.57, 127.59, 127.64, 127.97, 128.54, 128.72, 132.70, 133.23, 133.27, 134.13, 138.33, 138.83, 141.35, 166.85.

IR (KBr): 3298 s, 3052 m, 1634 s, 1602 s, 1539 s, 1455 m, 1348 m, 1336 m, 1244 s, 892 m, 860 m, 841 m, 816 s, 748 s, 713 s, 699 s, 590 m, 556 m, 478 s.

MS, *m/z* (relative intensity, %): 366 (13), 365 (M^+, 43), 233 (14), 232 (74), 215 (18), 134 (23), 133 (100), 127 (10), 105 (43), 104 (21), 79 (15), 77 (17).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{24}NO$: 366.1852. Found: 366.1850.

_N_-(Naphthalen-2-yl(phenyl)methyl)-3,5-bis(trifluoromethyl)benzamide (2aae).



White solid (29.9 mg, 31%). R_f 0.72 (SiO_2, Hexane/EtOAc = 1/1). Mp 192.9-193.2 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.60 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 6.9 Hz, 1H), 7.31-7.40 (m, 6H), 7.47-7.51 (m, 2H), 7.73 (s, 1H), 7.76-7.81 (m, 1H), 7.82-7.85 (m, 2H), 8.01 (s, 1H), 8.26 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 58.12, 122.82 (q, J = 273.2 Hz), 125.26 (m, J = 3.4 Hz), 125.41, 126.24, 126.37, 126.53, 127.39 (q, J =1.9 Hz), 127.60, 127.68, 127.97, 128.01, 128.86, 128.94, 132.23 (q, J = 33.9 Hz), 132.82, 133.17, 136.06, 137.84, 140.41, 163.63.

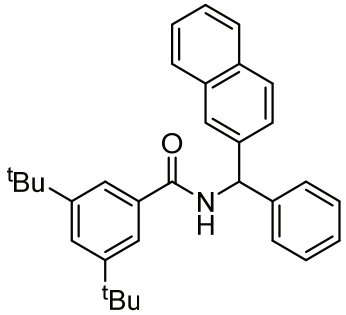
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −64.08.

IR (KBr): 3292 m, 1637 s, 1616 m, 1539 s, 1455 m, 1380 w, 1331 m, 1277 s, 1172 m, 1141 s, 908 m, 845 m, 815 m, 754 m, 700 m, 681 m, 477 m.

MS, *m/z* (relative intensity, %): 474 (16), 473 (M^+, 90), 241 (65), 232 (77), 217 (13), 216 (32), 215 (69), 212 (34), 207 (50), 129 (22), 127 (20), 104 (100), 73 (41).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{18}F_6NO$: 474.1287. Found: 474.1294.

3,5-Di-*tert*-butyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aaf).



White solid (36.9 mg, 41%). R_f 0.70 (SiO_2, Hexane/EtOAc = 1/1). Mp 221.1-221.6 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.34 (s, 18H), 6.64 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 7.29-7.40 (m, 5H), 7.43 (dd, J = 8.7, 1.8 Hz, 1H), 7.46-7.50 (m, 2H), 7.60 (t, J = 1.8 Hz, 1H), 7.65 (d, J = 1.8 Hz, 2H), 7.77-7.85 (m, 4H).

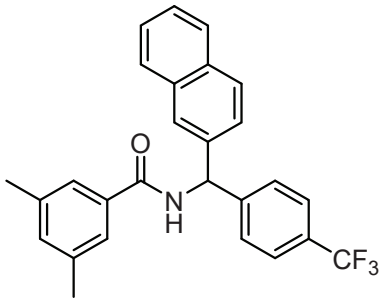
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 31.37, 34.98, 57.52, 121.15, 125.71, 126.01, 126.09, 126.17, 126.31, 127.63, 127.68, 128.01, 128.62, 128.78, 132.73, 133.24, 133.79, 138.86, 141.37, 151.37, 167.59.

IR (KBr): 3256 s, 2961 s, 1634 s, 1592 m, 1539 s, 1522 s, 1363 m, 1275 m, 1249 m, 889 m, 810 m, 748 s, 708 s, 696 s, 477 m.

MS, *m/z* (relative intensity, %): 450 (13), 449 (M^+, 35), 233 (19), 232 (100), 218 (16), 217 (55), 215 (12), 207 (11), 133 (18), 104 (13), 73 (11), 57 (25).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{32}H_{36}NO$: 450.2791. Found: 450.2793.

4-Methyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2abd).



White solid (52.2 mg, 60%). R_f 0.64 (SiO_2, Hexane/EtOAc = 1/1). Mp 199.0-200.0 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.33 (s, 6H), 6.62 (d, J = 7.8 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 7.35 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.42 (s, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.48-7.51 (m, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.69 (s, 1H), 7.75-7.79 (m, 1H), 7.82-7.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 57.27, 124.04 (q, J = 271.9 Hz), 124.81, 125.49, 125.65 (q, J = 3.8 Hz), 126.44, 126.57, 126.61, 127.67, 127.75, 127.98, 128.96, 129.70 (q, J = 32.3 Hz), 132.84, 133.21, 133.53, 133.71, 137.93, 138.44, 145.28, 167.04.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.74.

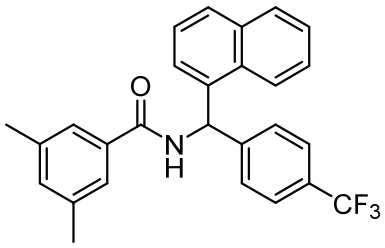
IR (KBr): 3285 s, 1636 s, 1602 s, 1527 s, 1327 s, 1249 m, 1160 s, 1121 s, 1068 m, 1021 m, 862 m,

848 s, 814 m,737 m, 607 m, 473 s.

MS, *m/z* (relative intensity, %): 433 (M^+, 20), 300 (35), 134 (19), 133 (100), 105 (31).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{23}F_3NO$: 434.1726. Found: 434.1722.

3,5-Dimethyl-*N*-(naphthalen-1-yl(4-(trifluoromethyl)phenyl)methyl)benzamide (2bbd).



White solid (62.7 g, 88%). R_f 0.66 (SiO_2, Hexane/EtOAc = 1/1). Mp 228.6-229.7 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.32 (s, 6H), 6.72 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 7.16 (d, J = 6.9 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.39 (s, 2H), 7.42 (d, J = 6.9 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.51-7.55 (m, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.90-7.94 (m, 1H), 8.06-8.09 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 53.89, 123.39, 124.07 (q, J = 272.0 Hz), 124.78, 125.20, 125.63 (q, J = 3.8 Hz), 126.20, 126.23, 127.10, 127.70, 128.95, 129.10, 129.66 (q, J = 31.6 Hz), 131.20, 133.52, 133.56, 134.04, 136.40, 138.45, 145.21, 166.84.

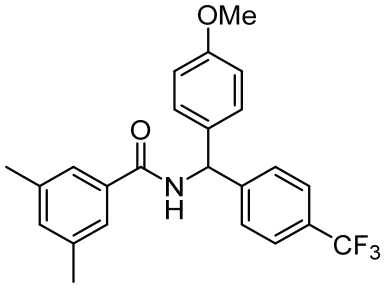
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.71.

IR (KBr): 3302 s, 3042 w, 1628 s, 1598 s, 1527 s, 1421 w, 1324 s, 1244 m, 1157 s, 1125 s, 1071 s, 1019 m, 859 m, 832 w, 803 m, 776 s, 709 m, 692 m, 623 w.

MS, *m/z* (relative intensity, %): 433 (M^+, 19), 300 (24), 134 (120), 133 (100), 105 (32), 79 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{23}F_3NO$: 434.1726. Found: 434.1727.

***N*-((4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2cbd).**



White solid (62.9 mg, 75%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 184.7-184.9 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 3.79 (s, 3H), 6.39 (d, J = 7.3 Hz, 1H), 6.70 (d, J = 7.3 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 7.14 (s, 1H), 7.17 (d, J = 8.7 Hz, 2H), 7.40-7.42 (m, 4H), 7.58 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 55.28, 56.65, 114.28, 124.06 (q, J = 272.2 Hz), 124.76, 125.53 (q, J = 3.8 Hz), 127.46, 128.99, 129.47 (q, J = 32.6 Hz), 132.82, 133.44, 133.78, 138.38, 145.69, 159.24, 166.90.

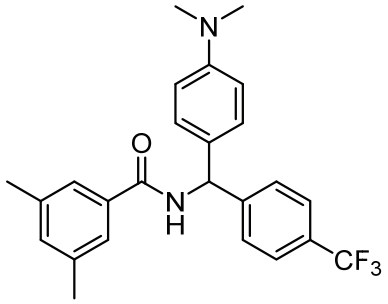
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.71.

IR (KBr): 3301 s, 2954 m, 2912 m, 2837 m, 1633 s, 1604 s, 1532 m, 1512 s, 1328 s, 1247 s, 1167 s, 1120 s, 1071 s, 1035 s, 1021 s, 862 s, 825 s, 768 m, 711 m, 688 m, 604.

MS, *m/z* (relative intensity, %): 414 (10), 413 (M^+, 42), 280 (27), 207 (12), 134 (43), 133 (100), 105 (33), 79 (11), 73 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{23}F_3NO_2$: 414.1675. Found: 414.1678.

_N_-((4-(Dimethylamino)phenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2dbd).



White solid (58.2 mg, 68%). R_f 0.52 (SiO_2, Hexane/EtOAc = 1/1). Mp 217.2-217.8 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 2.95 (s, 6H), 6.34 (d, J = 7.3 Hz, 1H), 6.62 (d, J = 7.3 Hz, 1H), 6.69 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 7.14 (s, 1H), 7.40 (s, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 40.41, 56.88, 112.50, 124.15 (q, J = 272.2 Hz), 124.74, 125.42 (q, J = 3.8 Hz), 127.28, 128.20, 128.77, 129.19 (q, J = 32.6 Hz), 133.33, 133.93, 138.34, 146.06, 150.14, 166.84.

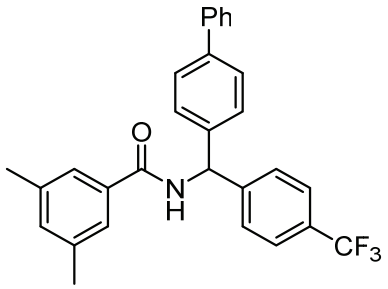
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.65.

IR (KBr): 3289 s, 2916 m, 1633 s, 1604 s, 1522 s, 1324 s, 1247 s, 1163 s, 1119 s, 1069 s, 1019 m, 947 m, 861 s, 809 s, 751 m, 689 m, 603 m.

MS, *m/z* (relative intensity, %): 427 (14), 426 (M^+, 49), 293 (17), 281 (17), 279 (11), 278 (59), 277 (20), 276 (12), 165 (12), 147 (11), 134 (20), 133 (100), 122 (24), 105 (48), 103 (12), 79 (22), 77 (21).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{26}F_3N_2O$: 427.1992. Found: 427.1988.

_N_-([1,1'-Biphenyl]-4-yl(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2ebd).



White solid (45.6 mg, 50%). R_f 0.68 (SiO_2, Hexane/EtOAc = 1/1). Mp 219.4-220.4 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 6.51 (d, J = 7.3 Hz, 1H), 6.70 (d, J = 7.3 Hz, 1H), 7.16 (s, 1H), 7.33-7.38 (m, 3H), 7.43-7.49 (m, 6H), 7.56-7.63 (m, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.23, 56.97, 124.04 (q, J = 272.2 Hz), 124.78, 125.70 (q, J = 3.8 Hz), 127.07, 127.55, 127.68, 127.71, 128.15, 128.84, 129.74 (q, J = 32.6 Hz), 133.55, 133.73, 138.47, 139.61, 140.34, 141.01, 145.34, 166.98.

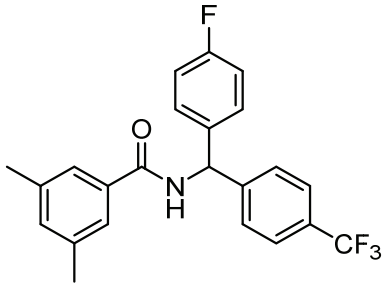
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.74.

IR (KBr): 3278 s, 3031 w, 1637 s, 1605 s, 1527 s, 1486 m, 1329 s, 1247 m, 1165 s, 1122 s, 1072 m, 1018 m, 870 s, 819 s, 763 s, 701 s, 664 m, 620 m.

MS, *m/z* (relative intensity, %): 459 (M^+, 27), 326 (16), 134 (41), 133 (100), 105 (39), 79 (13), 77 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{29}H_{25}F_3NO$: 460.1883. Found: 460.1885.

_N_-((4-Fluorophenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (1fbd).



White solid (46.1 g, 54%). R_f 0.68 (SiO_2, Hexane/EtOAc = 1/1). Mp 198.8-199.1 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.35 (s, 6H), 6.45 (d, J = 7.3 Hz, 1H), 6.65 (br, 1H), 7.05 (t, J = 8.7 Hz, 2H), 7.16 (s, 1H), 7.22-7.26 (m, 2H), 7.40-7.42 (m, 4H), 7.61 (d, J = 7.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.20, 56.47, 115.88 (d, J = 22.0 Hz), 123.96 (q, J = 272.2 Hz), 124.74, 125.73 (q, J = 3.5 Hz), 127.62, 129.39 (d, J = 8.6 Hz), 129.83 (q, J = 32.6 Hz), 133.60, 136.46 (d, J = 3.8 Hz), 138.48, 145.15, 162.29 (d, J = 247.3 Hz), 166.93.

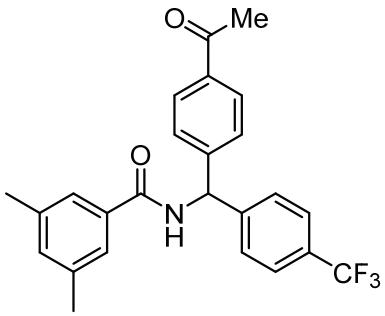
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −115.22 (s, 1F), −63.80 (s, 3F).

IR (KBr): 3332 s, 1635 s, 1604 s, 1539 m, 1511 m, 1333 s, 1248 m, 1226 m, 1162 s, 1119 s, 1072 s, 1017 s, 915 m, 877 m, 864 s, 825 s, 767 s, 751 s, 716 m, 687 m, 634 m, 602 s, 553 m, 531 s.

MS, *m/z* (relative intensity, %): 401 (M^+, 32), 134 (33), 133 (100), 105 (32), 79 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{20}F_4NO$: 402.1476. Found: 402.1479.

***N*-((4-Acetylphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2gbd).**



The general procedure was followed, except that the reaction temperature was 180 °C in dibutyl ether.

White solid (45.7 mg, 56%). R_f 0.50 (SiO_2, Hexane/EtOAc = 1/1). Mp 189.3-190.6 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 2.60 (s, 3H), 6.53 (d, J = 7.8 Hz, 1H), 6.64 (d, J = 7.3 Hz, 1H), 7.17 (s, 1H), 7.39-7.43 (m, 6H), 7.63 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.23, 26.68, 56.93, 123.89 (q, J = 272.2 Hz), 124.75, 125.90 (q, J = 3.8 Hz), 127.72, 127.88, 129.00, 130.15 (q, J = 32.6 Hz), 133.46, 133.71, 136.65, 138.55, 144.64, 145.67, 166.99, 197.48.

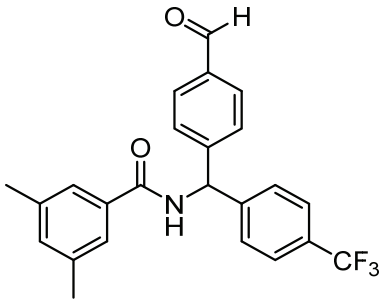
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.87.

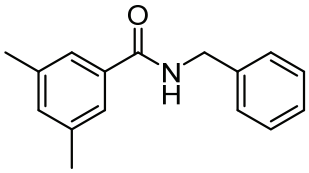
IR (KBr): 3294 s, 1688 s, 1636 s, 1604 s, 1519 s, 1423 m, 1358 m, 1326 s, 1268 s, 1237 m, 1158 s, 1117 s, 1068 s, 1017 s, 962 s, 862 s, 833 s, 815 s, 752 s, 687 s, 613 s, 588 s.

MS, *m/z* (relative intensity, %): 425 (M^+, 22), 292 (13), 134 (17), 133 (100), 105 (27).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{23}F_3NO_2$: 426.1675. Found: 426.1676.

***N*-((4-Formylphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2hbd).**





33 %

White solid (32.5 mg, 38%). R_f 0.52 (SiO_2, Hexane/EtOAc = 1/1). Mp 198.9-200.1 °C. The only detectable byproducts were hydrolysis products (*i.e.*, 33 % of *N*-benzyl-3,5-dimethylbenzamide was formed, as determined by GC using pentadecane as an internal standard).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.35 (s, 6H), 6.54 (d, J = 7.8 Hz, 1H), 6.81 (br, 1H), 7.17 (s, 1H), 7.40-7.41 (m, 4H), 7.46 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 7.8 Hz, 2H), 9.99 (s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.20, 57.01, 123.84 (q, J = 272.2 Hz), 124.79, 125.94 (q, J = 3.8 Hz), 127.95, 128.12, 130.22 (q, J = 32.6 Hz), 130.30, 133.34, 133.76, 135.85, 138.54, 144.41, 147.18, 167.09, 191.62.

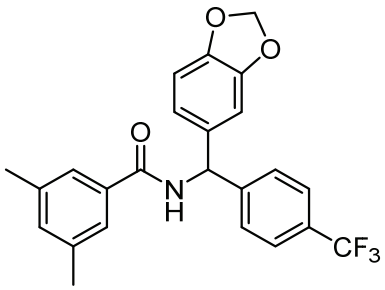
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.87.

IR (KBr): 3286 s, 1698 s, 1635 s, 1605 s, 1530 m, 1327 s, 1212 m, 1164 s, 1121 s, 1068 s, 1017 s, 863 s, 826 s, 807 s, 769 m, 692 m, 611m.

MS, *m/z* (relative intensity, %): 412 (13), 411 (M^+, 43), 134 (19), 133 (100), 105 (23).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{21}F_3NO_2$: 412.1519. Found: 412.1513.

_N_-(Benzo[*d*][1,3]dioxol-5-yl(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2ibd).



White solid (58.1 mg, 67%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 176.0-176.4 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.33 (s, 6H), 5.94 (d, J = 0.9 Hz, 2H), 6.34 (d, J = 7.3 Hz, 1H), 6.71-6.78 (m, 4H), 7.14 (s, 1H), 7.39-7.41 (m, 4H), 7.57 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.16, 56.94, 101.27, 108.09, 108.47, 121.22, 124.02 (q, J = 272.2 Hz), 124.77, 125.56 (q, J = 2.9 Hz), 127.45, 129.57 (q, J = 32.3 Hz), 133.46, 133.68, 134.58, 138.37, 145.46, 147.28, 148.12, 166.92.

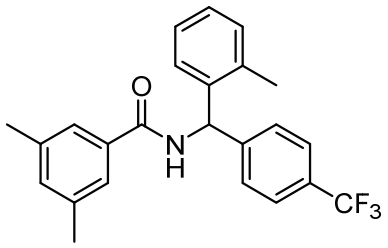
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.74.

IR (KBr): 3289 s, 1634 s, 1603 s, 1526 s, 1504 s, 1487 s, 1328 s, 1251 s, 1164 s, 1124 s, 1072 m, 1039 m, 939 m, 859 s, 798 m, 711 m, 662 w.

MS, *m/z* (relative intensity, %): 428 (12), 427 (M^+, 42), 294 (24), 134 (38), 133 (100), 105 (35), 79 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{21}F_3NO_3$: 428.1468. Found: 428.1469.

3,5-Dimethyl-*N*-(*o*-tolyl(4-(trifluoromethyl)phenyl)methyl)benzamide (2jbd).



White solid (25.6 g, 30%). R_f 0.64 (SiO_2, Hexane/EtOAc = 1/1). Mp 192.7-193.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 2.40 (s, 3H), 6.54 (d, J = 7.3 Hz, 1H), 6.66 (d, J = 7.3 Hz, 1H), 7.03 (d, J = 7.3 Hz, 1H), 7.16 (s, 1H), 7.19 (q, J = 4.1 Hz, 1H), 7.25 (d, J = 5.0 Hz, 2H), 7.38-7.41 (m, 4H), 7.59 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.48, 21.21, 54.03, 124.05 (q, J = 271.3 Hz), 124.73, 125.58 (q, J = 3.8 Hz), 126.45, 127.30, 127.63, 128.08, 129.57 (q, J = 32.3 Hz), 131.06, 133.52, 133.61 136.72, 138.46, 138.80, 145.17, 166.77.

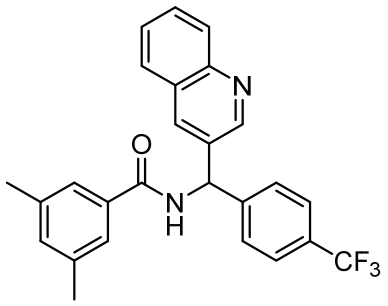
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.74.

IR (KBr): 3294 s, 3043 m, 2917 m, 1637 s, 1527 m, 1325 m, 1244 m, 1170 s, 1126 s, 1068 m,1018 m, 865 s, 835 s, 755 s, 732 s, 613 s, 449 m.

MS, *m/z* (relative intensity, %): 397 (M^+, 32), 179 (47), 134 (17), 133 (100), 105 (39), 79 (15), 77 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{23}F_3NO$: 398.1726. Found: 398.1727.

3,5-Dimethyl-*N*-(quinolin-3-yl(4-(trifluoromethyl)phenyl)methyl)benzamide (2kbd).



White solid (48.6 mg, 57%). R_f 0.32 (SiO_2, Hexane/EtOAc = 1/1). Mp 211.2-211.5 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.32 (s, 6H), 6.67 (d, J = 7.3 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 7.15 (s, 1H), 7.43 (s, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.73 (t, J = 7.8 Hz, 1H), 7.77 (s, 1H), 7.97 (s, 1H), 8.10 (d, J = 8.2 Hz, 1H), 8.91 (br, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.15, 55.22, 123.86 (q, J = 272.2 Hz), 124.85, 125.93 (q, J = 2.9 Hz), 127.26, 127.51, 127.84, 129.09, 129.93, 130.19 (q, J = 32.6 Hz), 133.32, 133.41, 133.70, 134.47, 138.48, 144.11, 147.43, 150.24, 167.15.

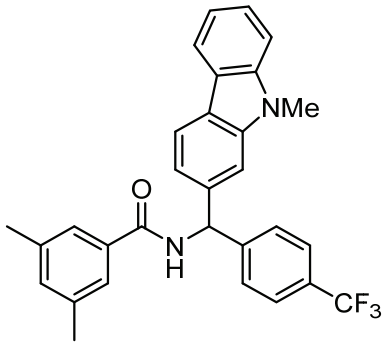
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.84.

IR (KBr): 3268 s, 1642 s, 1603 m, 1524 s, 1495 m, 1329 s, 1242 m, 1166 s, 1119 s, 1071 s, 1018 m, 862 s, 785 m, 754 s, 749 s, 717 m.

MS, *m/z* (relative intensity, %): 434 (M^+, 14), 301 (27), 207 (10), 134 (16), 133 (100), 105 (39), 79 (15), 77 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{22}F_3N_2O$: 435.1679. Found: 435.1686.

3,5-Dimethyl-*N*-((9-methyl-9H-carbazol-2-yl)(4-(trifluoromethyl)phenyl)methyl)benzamide (2lbd).



White solid (65.6 mg, 67%). R_f 0.56 (SiO_2, Hexane/EtOAc = 1/1). Mp 235.8-237.0 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.33 (s, 6H), 3.78 (s, 3H), 6.65 (d, J = 7.3 Hz, 1H), 6.84 (d, J = 7.3 Hz, 1H), 7.10 (dd, J = 8.2, 1.4 Hz, 1H), 7.14 (s, 1H), 7.21-7.25 (m, 1H), 7.29 (s, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.43 (s, 2H), 7.46-7.49 (m, 3H), 7.59 (d, J = 8.2 Hz, 2H), 8.04-8.07 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 29.12, 57.93, 108.11, 108.55, 118.36, 119.18, 120.34, 120.87, 122.23, 122.52, 124.09 (q, J = 272.2 Hz), 124.79, 125.53 (q, J = 3.8 Hz), 126.01, 127.55, 129.49 (q, J = 32.6 Hz), 133.46, 133.83, 138.35, 138.41, 141.07, 141.40, 145.86, 166.96.

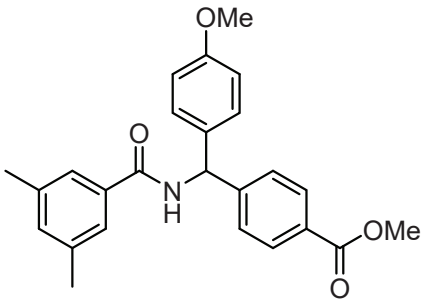
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.65.

IR (KBr): 3263 s, 3061 m, 2919 m, 1634 s, 1604 s, 1539 s, 1497 m, 1468 m, 1454 m, 1420 m, 1323 s, 1254 s, 1165 s, 1123 s, 1069 s, 1017 m, 862 s, 834 m, 818 s, 748 s, 726 s, 684 w, 666 w, 654 m, 618 m, 506 m, 449 m.

MS, *m/z* (relative intensity, %): 487 (20), 486 (M^+, 62), 354 (23), 353 (100), 182 (18), 167 (16), 134 (26), 133 (74), 105 (35), 79 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{30}H_{26}F_3N_2O$: 487.1992. Found: 487.1993.

Methyl 4-((3,5-dimethylbenzamido)(4-methoxyphenyl)methyl)benzoate (2ccd).



White solid (50.2 mg, 62%). R_f 0.48 (SiO_2, Hexane/EtOAc = 1/1). Mp 184.2-184.5 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 3.79 (s, 3H), 3.90 (s, 3H), 6.41 (d, J = 7.3 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 6.86-6.89 (m, 2H), 7.14 (s, 1H), 7.16-7.19 (m, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.40 (s, 2H), 7.99-8.01 (m, 2H).

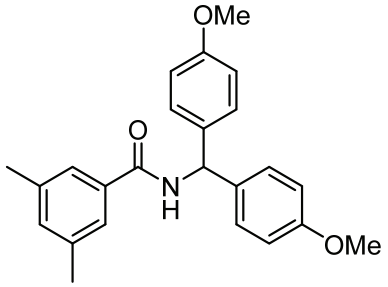
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.20, 52.10, 55.28, 56.71, 114.213, 124.74, 127.15, 128.97, 129.12, 129.90, 133.00, 133.37, 133.90, 138.36, 146.78, 159.16, 166.79, 166.84.

IR (KBr): 3304 s, 2949 w, 1729 s, 1636 s, 1604 m, 1529 s, 1515 s, 1457 w, 1435 m, 1274 s, 1251 s, 1186 m, 1106 m, 1036 w, 1020 m, 864 m, 810 m, 764 m, 736 m, 699 m.

MS, *m/z* (relative intensity, %): 404 (13), 403 (M^+, 45), 270 (30), 134 (30), 133 (100), 105 (30), 79 (10).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{26}NO_4$: 404.1856. Found: 404.1851.

***N*-(Bis(4-methoxyphenyl)methyl)-3,5-dimethylbenzamide (2ced).**



White solid (37.5 mg, 48%). R_f 0.48 (SiO_2, Hexane/EtOAc = 1/1). Mp 180.2-182.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 3.79 (s, 3H), 3.90 (s, 3H), 6.34 (d, J = 7.8 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 6.85-6.89 (m, 4H), 7.13 (s, 1H), 7.19-7.22 (m, 4H), 7.40 (s, 2H).

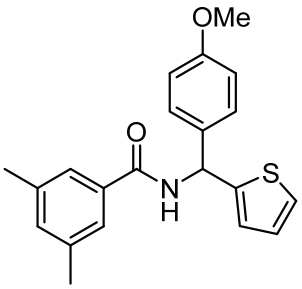
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.21, 55.27, 56.17, 113.98, 124.72, 128.59, 133.18, 133.91, 134.27, 138.28, 158.83, 166.69.

IR (KBr): 3326 s, 3004 m, 2931 m, 2833 s, 1635 s, 1605 s, 1508 s, 1463 m, 1323 m, 1306 m, 1281 m, 1238 s, 1176 s, 1111 m, 1032 s, 862 s, 815 s, 767 m, 687 s, 669 m, 582 s, 569 m.

MS, *m/z* (relative intensity, %): 376 (23), 375 (M^+, 84), 243 (12), 242 (60), 227 (30), 226 (18), 211 (16), 207 (12), 134 (70), 133 (100), 105 (39), 103 (10), 79 (18), 77 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{26}NO_3$: 376.1907. Found: 376.1904.

_N_-((4-Methoxyphenyl)(thiophen-2-yl)methyl)-3,5-dimethylbenzamide (2cfd).



White solid (45.0 mg, 59%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 174.0-175.1 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 3.80 (s, 3H), 6.59 (d, J = 8.2 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.86-6.96 (m, 4H), 7.13 (s, 1H), 7.23-7.25 (m, 1H), 7.31-7.33 (m, 2H), 7.40 (s, 2H).

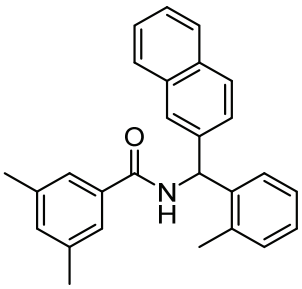
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 52.75, 55.26, 114.01, 124.77, 125.06, 125.73, 126.89, 128.38, 133.28, 133.35, 134.03, 138.30, 146.20, 159.17, 166.57.

IR (KBr): 3287 s, 3042 w, 2999 m, 2964 w, 2833 w, 1639 s, 1604 s, 1535 s, 1512 s, 1462 m, 1379 m, 1342 m, 1284 m, 1244 s, 1183 s, 1029 s, 859 s, 839 m, 801 m, 697 s, 533 w.

MS, *m/z* (relative intensity, %): 352 (17), 351 (M^+, 69), 218 (42), 203 (15), 202 (11), 187 (17), 134 (156), 133 (100), 115 (11), 110 (12), 105 (41), 103 (11), 79 (19), 77 (17).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{21}H_{22}NO_2S$: 352.1366. Found: 352.1359.

3,5-Dimethyl-_N_-(naphthalen-2-yl(o-tolyl)methyl)benzamide (2add).



The general procedure was followed, except that the reaction temperature was 180 °C in dibutyl ether.

White solid (31.2 mg, 42%). R_f 0.58 (SiO_2, Hexane/EtOAc = 1/1). Mp 157.6-158.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.35 (s, 6H), 2.38 (s, 3H), 6.64 (d, J = 7.8 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 7.18-7.24 (m, 4H), 7.39 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.44 (s, 2H), 7.45-7.48 (m, 2H), 7.66 (s, 1H), 7.74-7.76 (m, 1H), 7.80-7.83 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.53, 21.22, 54.48, 124.77, 125.87, 125.97, 126.02, 126.21, 126.23, 127.00, 127.60, 127.68, 127.95, 128.50, 130.90, 132.70, 133.24, 133.32, 133.99, 136.67, 138.37, 138.44, 139.34, 166.61.

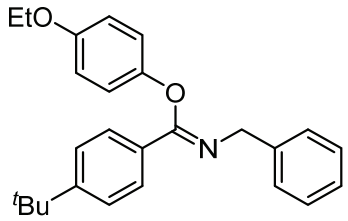
IR (KBr): 3294 s, 3047 m, 2917 m, 1627 s, 1602 s, 1525 s, 1458 m, 1334 m, 1240 m, 1051 m, 912 m, 860 m, 820 m, 770 m, 751 s, 725 w, 696 m, 483 m, 477 m.

MS, *m/z* (relative intensity, %): 379 (M^+, 23), 246 (35), 230 (25), 229 (23), 228 (13), 215 (12), 207 (12), 134 (17), 133 (100), 127 (11), 118 (14), 105 (47), 103 (12), 91 (12), 79 (19), 77 (18), 73 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{26}NO$: 380.2009. Found: 380.2012.

VI. Gram-Scale Reaction

VI-1. Synthesis of the starting imidate 1mag



4-Ethoxyphenyl *N*-benzyl-4-(tert-butyl)benzimidate (1mag). This compound was prepared according to general procedure B. The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.7), which was determined by ^{1}H NMR.

Colorless oil (2.75 g, 71%). R_f 0.60 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.28 (s, 9H), 1.37 (t, J = 7.1 Hz, 3H), 3.94 (q, J = 7.0 Hz, 2H), 4.73 (s, 2H), 6.75-6.86 (m, 4H), 7.30-7.34 (m, 4H), 7.40 (d, J = 7.8 Hz, 2H), 7.48 (s, 1H), 7.76-7.79 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 14.85, 31.12, 34.78, 51.63, 63.80, 115.44, 117.07, 125.26, 126.51, 127.76, 128.28, 128.52, 130.06, 140.14, 149.35, 153.91, 154.23, 154.27.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.35 (s, 9H), 1.41 (t, J = 7.1 Hz, 3H), 3.94 (q, J = 6.9 Hz, 2H), 4.62 (s, 2H), 6.90-6,92 (m, 2H), 7.15-7.23 (m, 9H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 14.90, 31.19, 34.86, 53.48, 63.69, 114.79, 122.97, 125.38, 126.22, 126.69, 128.06, 128.15. Other peaks are overlapped with those of a major isomer.

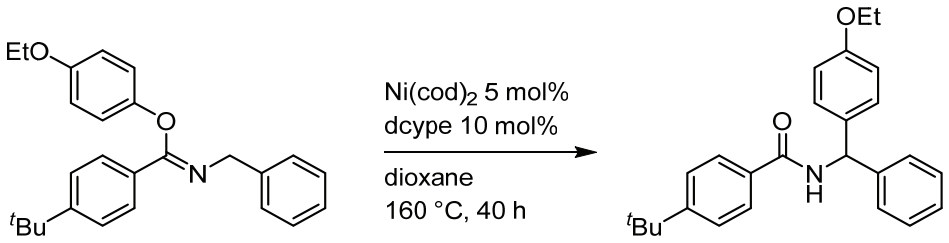
E/Z Mixture

IR (KBr): 2964 m, 2903 m, 1660 s, 1608 w, 1503 m, 1477 m, 1269 m, 1242 m, 1202 s, 1186 s, 1112 m, 1062 s, 1017 w, 823 m, 778 w, 733 m, 697 m.

MS, *m/z* (relative intensity, %): 387 (M^+, 6), 251 (16), 250 (172), 161 (14), 116 (11), 109 (24), 92 (60), 91 (100), 65 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{30}NO_2$: 388.2271. Found: 388.2274.

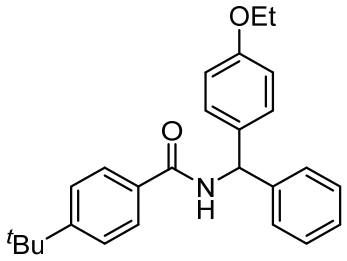
VI-2. Gram-Scale Reaction



1mag **2mag**

In a glovebox filled with nitrogen, aryl *N*-benzylimidate **1mag** (1.96 g, 5.0 mmol), $Ni(cod)_2$ (69.5 mg, 0.25 mmol), dcype (214.2 mg, 0.50 mmol) and 1,4-dioxane (25 mL) were added to a 200 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 40 h. This mixture was then evaporated to dryness, and the residue was purified by flash column chromatography using hexane/EtOAc = 17/3 as the eluent to give **2mag** as a white solid (1.43 g, 73%).

4-(*tert*-Butyl)-*N*-((4-ethoxyphenyl)(phenyl)methyl)benzamide (2mag).



White solid (1.43 g, 73%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 166.1-166.9 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ: 1.32 (s, 9H), 1.40 (t, J = 6.9 Hz, 3H), 4.00 (q, J = 7.0 Hz, 2H), 6.39 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.83-6.86 (m, 2H), 7.17-7.20 (m, 2H), 7.24-7.45 (m, 5H), 7.42-7.45 (m, 2H), 7.74-7.77 (m, 2H).

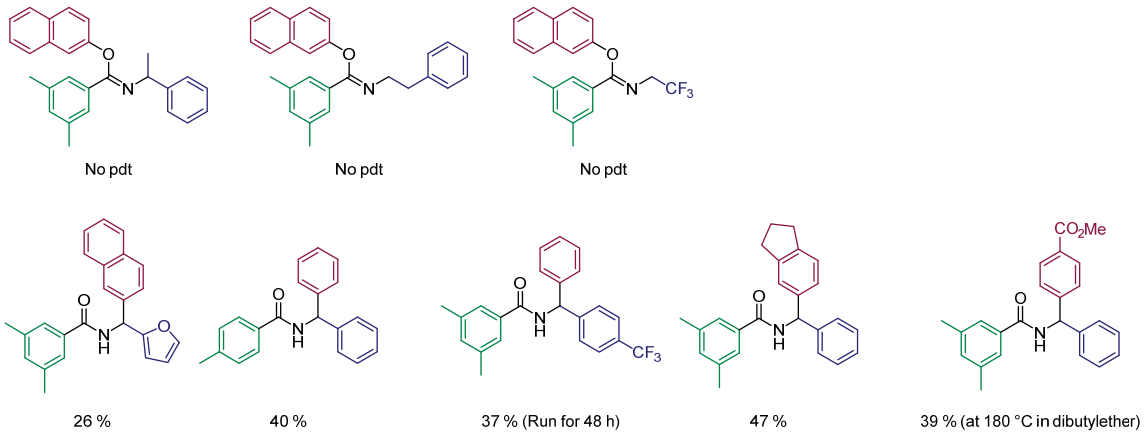
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 14.79, 31.10, 34.88, 56.71, 63.39, 114.53, 125.47, 126.85, 127.32, 128.58, 128.71, 131.33, 133.53, 141.73, 155.09, 158.25, 166.27.

IR (KBr): 3308 s, 2965 s, 2908 m, 2869 m, 1628 s, 1539 s, 1507 s, 1455 m, 1361 m, 1322 m, 1303 m, 1243 s, 1173 s, 1116 m, 1048 s, 923 m, 855 m, 824 m, 747 m, 702 s.

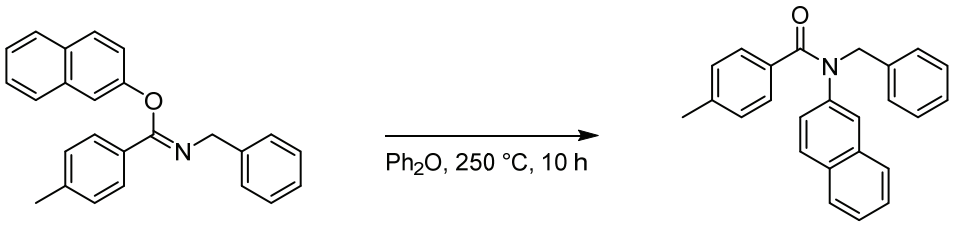
MS, *m/z* (relative intensity, %): 388 (28), 387 (M^+, 97), 310 (10), 227 (10), 226 (57), 211 (15), 181 (10), 162 (14), 161 (100), 146 (14), 123 (11), 118 (25), 105 (16), 104 (27), 91 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{30}NO_2$: 388.2271. Found: 388.2271.

VII. Additional Scope and Limitations



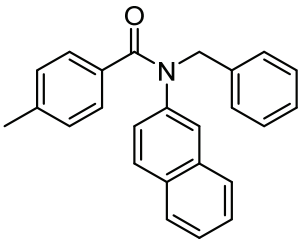
VIII. Chapman Rearrangement of 1aaa



1aaa **3aaa**

In a glovebox filled with nitrogen, imidate **1aaa** (71.1 mg, 0.20 mmol) and Ph_2O (1.5 mL) were added to a 5 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 250 °C for 10 h using a microwave reactor. This mixture was purified by flash column chromatography using hexane/EtOAc (1/9) as the eluent to give **3aaa** as a yellow oil (25.1 mg, 35 %).

***N*-Benzyl-4-methyl-*N*-(naphthalen-2-yl)benzamide (3aaa).**



Yellow oil (25.1 mg, 35%). R_f 0.58 (SiO_2, Hexane/EtOAc = 1/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.20 (s, 3H), 5.22 (s, 2H), 6.91 (d, J = 8.2 Hz, 2H), 7.04 (dd, J = 8.7, 2.3 Hz, 1H), 7.22–7.35 (m, 7H), 7.39 (d, J = 2.3 Hz, 1H), 7.41–7.44 (m, 2H), 7.61–7.63 (m, 2H), 7.72–7.74 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.30, 54.15, 125.45, 126.12, 126.41, 127.30, 127.57, 127.76, 128.35, 128.45, 128.83, 128.96, 131.50, 132.84, 133.28, 137.63, 139.95, 141.31, 170.68.

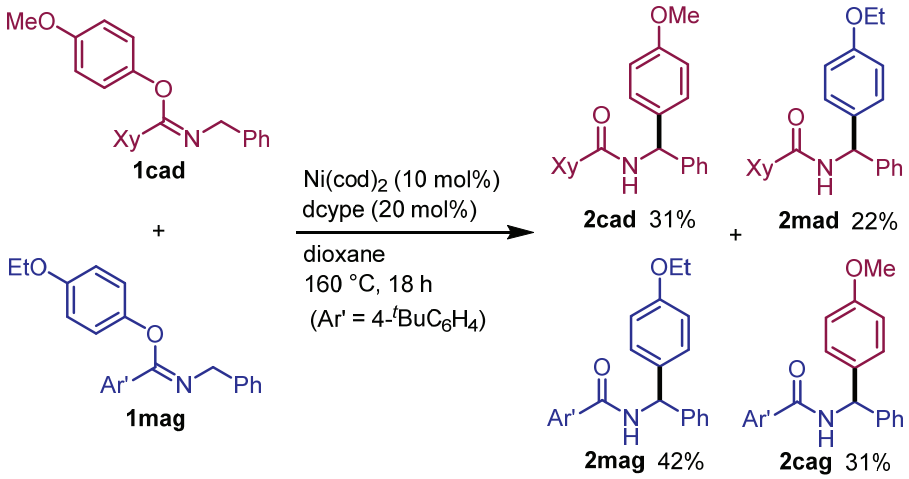
IR (KBr): 3059 m, 2923 m, 1645 s, 1599 s, 1508 s, 1441 m, 1388 m, 1304 m, 1290 m, 1182 m, 832

m, 819 m, 748 s, 700 s.

MS, *m/z* (relative intensity, %): 351 (M^+, 21), 232 (26), 119 (100), 91 (60), 65 (12).

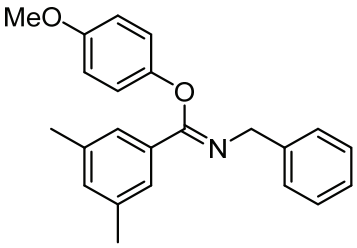
HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO$: 352.1696. Found: 352.1695.

IX. Crossover Experiments



In a glovebox filled with nitrogen, aryl *N*-benzylimidates **1cad** (67.4 mg, 2.0 mmol) and **1mag** (76.2 mg, 2.0 mmol), $Ni(cod)_2$ (12.6 mg, 0.46 mmol), dcype (34.9 mg, 0.83 mmol) and 1,4-dioxane (3 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 18 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 9/1 to 7/3) and GPC to give crossover products **2mad** (22%) and **2cag** (31%) and intramolecular migration products **2cad** (31%) and **2mag** (42%).

4-Methoxyphenyl *N*-benzyl-3,5-dimethylbenzimidate (1cad).



This compound was prepared according to general procedure A. The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.4), which was determined by ^{1}H NMR.

Colorless oil (672 mg, 32%). R_f 0.72 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.27 (s, 6H), 3.81 (s, 3H), 4.72 (s, 2H), 6.76-6.80 (m, 2H), 7.82-7.85

(m, 2H), 7.01 (s, 1H), 7.24-7.26 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.39-7.41 (m, 2H), 7.45 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.22, 51.77, 55.58, 114.83, 117.14, 126.48, 126.58, 127.85, 128.32, 132.43, 132.82, 137.85, 140.01, 149.41, 154.76, 154.86.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 3.81 (s, 3H), 4.56 (s, 2H), 6.91-6.93 (m, 2H), 7.10-7.12 (m, 4H), 7.15-7.18 (m, 5H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.31, 53.52, 55.52, 114.19, 122.99, 125.76, 126.22, 126.77, 128.13, 131.60, 138.14. Other peaks are overlapped with those of a major isomer.

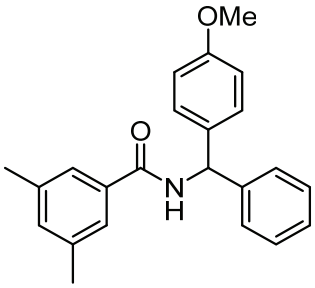
E/Z Mixture

IR (KBr): 3003 w, 2914 m, 1734 w, 1655 s, 1604 m, 1504 s, 1454 m, 1317 m, 1244 m, 1203 s, 1178 s, 1091 m, 1035 m, 824 m, 774 w, 730 m, 698 m.

MS, *m/z* (relative intensity, %): 345 (M^+, 2), 222 (41), 92 (24), 91 (100), 65 (15).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{24}NO_2$: 346.1802. Found: 346.1802.

_N_-((4-Methoxyphenyl)(phenyl)methyl)-3,5-dimethylbenzamide (2cad).



White solid (20.7 mg, 31%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 160.3-160.6 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.33 (s, 6H), 3.78 (d, J = 0.9 Hz, 3H), 6.39 (d, J = 7.7 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 6.86 (d, J = 7.8 Hz, 2H), 7.12 (s, 1H), 7.20 (d, J = 8.7 Hz, 2H), 7.25-7.36 (m, 5H), 7.40 (s, 2H).

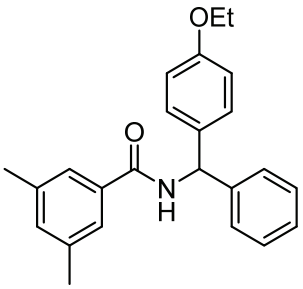
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 55.23, 56.69, 113.99, 124.72, 127.34, 128.59, 128.74, 133.18, 133.70, 134.19, 138.25, 141.68, 158.85, 166.73.

IR (KBr): 3339 s, 2918 m, 1634 s, 1601 s, 1539 s, 1515 s, 1465 m, 1305 m, 1238 s, 1183 s, 1120 m, 1034 s, 911 m, 861 s, 817 s, 789 m, 763 m, 726 s, 700 s, 573 s.

MS, *m/z* (relative intensity, %): 346 (18), 345 (M^+, 70), 212 (46), 197 (12), 134 (38), 133 (100), 105 (39), 104 (19), 79 (16), 77 (18).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{24}NO_2$: 346.1802. Found: 346.1802.

_N_-((4-Ethoxyphenyl)(phenyl)methyl)-3,5-dimethylbenzamide (2mad).



White solid (15.7 mg, 22%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 144.7-144.9 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.40 (t, J = 6.9 Hz, 3H), 2.35 (s, 6H), 4.01 (q, J = 7.0 Hz, 2H), 6.39 (d, J = 8.2 Hz, 1H), 6.60 (d, J = 7.3 Hz, 1H), 6.84-6.88 (m, 2H), 7.13 (s, 1H), 7.17-7.21 (m, 2H), 7.27-7.37 (m, 5H), 7.41 (s, 2H).

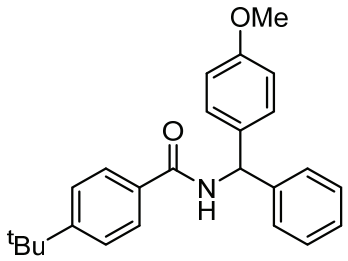
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 14.81, 21.22, 56.71, 63.41, 114.54, 124.72, 127.35, 128.61, 128.74, 133.21, 133.51, 134.20, 138.30, 141.70, 158.27, 166.72.

IR (KBr): 3292 s, 3031 m, 2978 m, 2918 m, 1635 s, 1602 s, 1508 s, 1475 m, 1327 m, 1304 m, 1243 s, 1176 s, 1116 m, 1048 s, 922 m, 861 m, 820 m, 759 m, 699 s, 597 m.

MS, *m/z* (relative intensity, %): 360 (17), 359 (M^+, 64), 226 (44), 134 (25), 133 (100), 105 (38), 104 (17), 79 (14), 77 (14).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{26}NO_2$: 360.1958. Found: 360.1964.

4-(*tert*-Butyl)-*N*-((4-methoxyphenyl)(phenyl)methyl)benzamide (2cag).



White solid (31.8 mg, 31%). R_f 0.60 (SiO_2, Hexane/EtOAc = 1/1). Mp 180.1-181.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.33 (s, 9H), 3.79 (d, 3H), 6.40 (d, J = 7.3 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.85-6.89 (m, 2H), 7.12-7.22 (m, 2H), 7.27-7.36 (m, 5H), 7.43-7.46 (m, 2H), 7.74-7.77 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 31.13, 34.91, 55.29, 56.77, 114.05, 125.54, 126.85, 127.33, 127.41, 128.65, 128.73, 131.33, 133.72, 141.70, 155.18, 158.91, 166.31.

IR (KBr): 3310 s, 2964 s, 2870 m, 1636 s, 1614 m, 1540 s, 1508 s, 1321 m, 1248 s, 1176 s, 1114 m, 1031 s, 853 s, 837 s, 800 m, 744 m, 696 s, 675 s, 621 m, 594 m, 546 m.

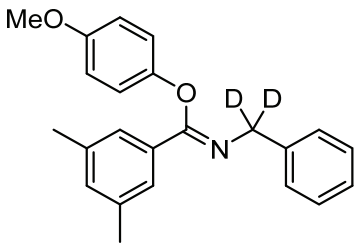
MS, *m/z* (relative intensity, %): 374 (27), 373 (M^+, 100), 212 (58), 197 (20), 196 (10), 162 (14), 161 (97), 153 (12), 146 (14), 134 (13), 118 (25), 109 (14), 105 (17), 104 (29), 91 (19), 77 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{28}NO_2$: 374.2115. Found: 374.2116.

X. Kinetic Studies

X-1. Synthesis of 1cad-d_2.

This compound was prepared according to General Procedure A using amide derived from benzylamine-d_2.



4-Methoxyphenyl 3,5-dimethyl-*N*-(phenylmethyl-d_2)benzimidate (1cad-d_2). The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.2), which was determined by ^{1}H NMR.

Colorless oil (1.02 g, 65%, 97%D). R_f 0.62 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.27 (s, 6H), 3.73 (s, 3H), 6.75-6.79 (m, 2H), 6.82-6.86 (m, 2H), 7.01 (s, 1H), 7.15-7.18 (m, 1H), 7.23-7.26 (m, 1H), 7.31-7.41 (m, 4H), 7.45 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.20, 51.20 (m), 55.57, 114.83, 117.15, 126.49, 126.60, 127.89, 128.31, 132.43, 132.84, 137.83, 139.87, 149.43, 154.80, 154.86.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H), 3.80 (s, 3H), 6.90-6.92 (m, 2H), 7.10-7.12 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.30, 55.51, 114.19, 122.99, 125.76, 126.25, 126.81, 128.13, 131.05, 131.59, 138.14, 140.86, 146.84, 156.34, 161.87.

E/Z Mixture

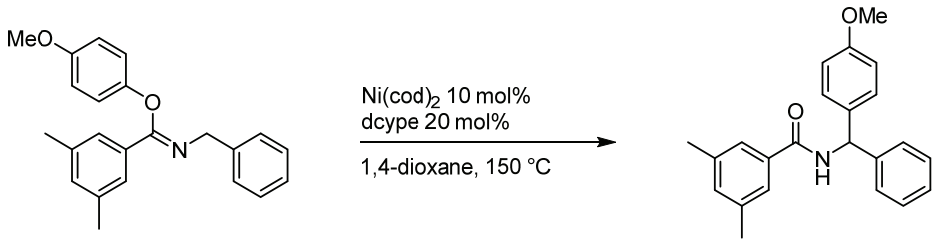
^{2}H-NMR ($CHCl_3$, 61.37 MHz) δ: 4.56 (minor), 4.73 (major).

IR (KBr): 2949 w, 2914 w, 1654 m, 1604 w, 1503 s, 1447 w, 1316 w, 1243 w, 1206 m, 1186 s, 1102 w, 1035 m, 823 w, 714 w.

MS, *m/z* (relative intensity, %): 347 (M^+, 3), 225 (12), 224 (59), 123 (14), 94 (47), 93 (100), 92 (33), 66 (10).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{22}D_2NO_2$: 348.1927. Found: 348.1936.

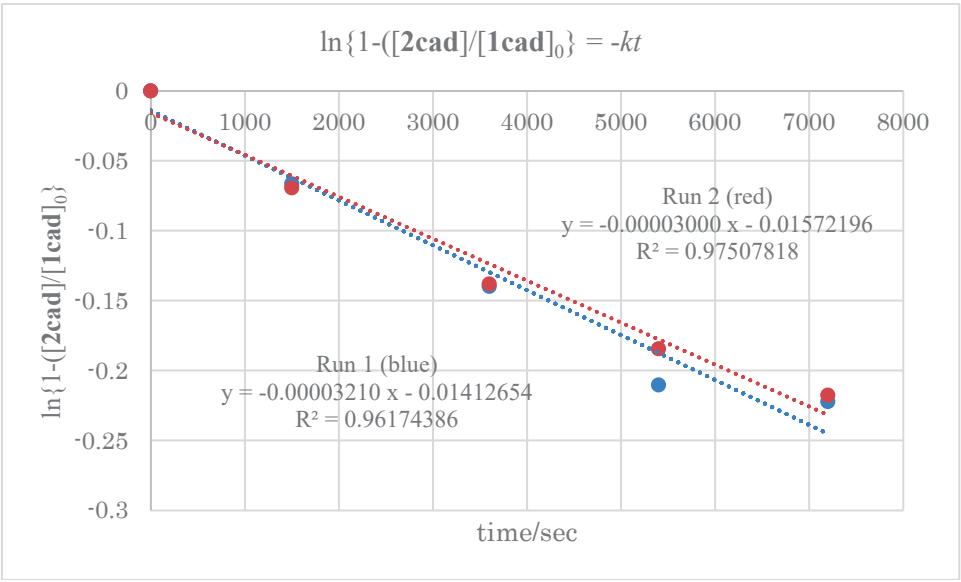
X-2. Kinetic studies



1cad **2cad**

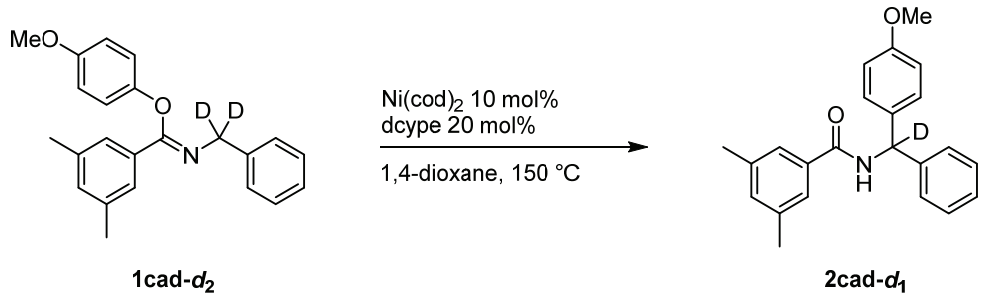
In a glovebox filled with nitrogen, imidate **1cad** (210.4 mg, 0.6 mmol), $Ni(cod)_2$ (16.2 mg, 0.06 mmol), dcype (51.4 mg, 0.12 mmol) and 1,4-dioxane (4.5 mL) were added to a 30 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 150 °C. An aliquot of the crude reaction mixture was taken through the septum using a syringe at the indicated time, was diluted with EtOAc and was analyzed by GC. The yields of **1cad** and **2cad** were determined based on the calibration curves. The same experiment was repeated twice.

	Run 1			**Run 2**		
Time / s	GC yields (%)		ln{**1**-[**2cad**])/[**1cad**]$_0$}	GC yields (%)		ln{**1**-[**2cad**])/[**1cad**]$_0$}
	1cad	**2cad**		**1cad**	**2cad**	
0	98	0	0	96	0	0
1500	74	6	-0.0665	74	6	-0.0694
3600	71	13	-0.140	65	12	-0.138
5400	59	18	-0.210	59	16	-0.184
7200	49	20	-0.222	53	19	-0.218



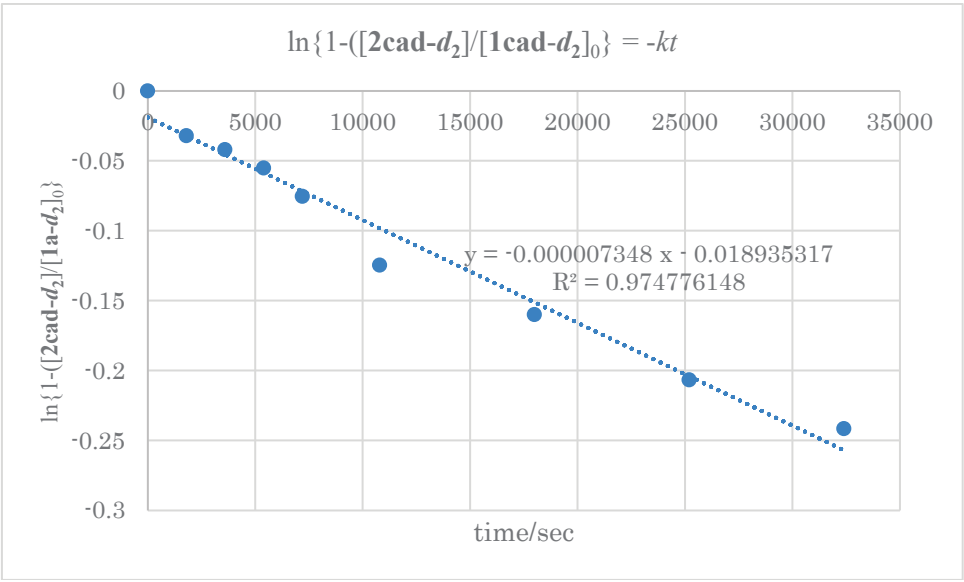
The same experiment was conducted using **1cad-*d*$_2$** (213.2 mg, 0.61 mmol) as the substrate. The results

are summarized below.



1cad-d_2 **2cad-d_1**

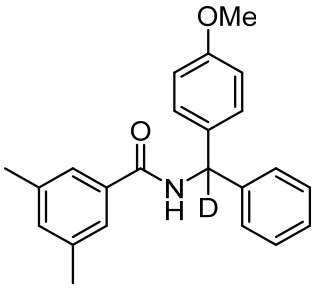
Time / s	GC yields (%)		ln{**1**-[**2cad-d_1**])/[**1cad-d_2**]$_0$}
	1cad-d_2	**2cad-d_1**	
0	97	0	0
1800	82	3	-0.0320
3600	79	4	-0.0421
5400	75	5	-0.0552
7200	71	7	-0.0754
10800	63	11	-0.125
18000	53	14	-0.160
25200	54	18	-0.207
32400	46	21	-0.241



The reaction of **2cad** and **2cad-*d*$_2$** followed first-order kinetics with respect to the concentration of the substrate. Rate constants for these reactions, which were determined by the slopes obtained in the ln(1-([substrate])/[starting material]$_0$) vs time plot shown above, were summarized in the following table. The kinetic isotope effect (k_H/k_D) was determined to be 4.2, indicating that the C–H bond cleavage process is involved in the turnover-limiting step in this catalytic reaction.

	k_{obs} / s^{-1} (Run 1)	k_{obs} / s^{-1} (Run 2)	Average	KIE
1a	3.21×10^{-5}	3.00×10^{-5}	3.11×10^{-5}	4.2
1a-*d*$_2$	7.35×10^{-6}	--	7.35×10^{-6}	

***N*-((4-Methoxyphenyl)(phenyl)methyl-*d*)-3,5-dimethylbenzamide (2cad-*d*).**



White solid (58.6 mg, 94%D). R_f 0.52 (SiO_2, Hexane/EtOAc = 1/1). Mp 161.4-162.0 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.34 (s, 6H), 3.78 (s, 3H), 6.64 (s, 1H), 6.87 (d, J = 7.8 Hz, 2H), 7.12 (s, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.29-7.34 (m, 5H), 7.40 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.19, 55.24, 56.39 (d, J = 20.6 Hz, **2cad-*d*)**, 56.71 (**2cad**), 113.91, 114.01, 124.73, 127.34, 128.61, 128.74, 133.19, 133.66, 134.22, 138.27, 141.64, 158.89, 166.75.

^{2}H-NMR ($CHCl_3$, 61.37 MHz) δ: 6.39.

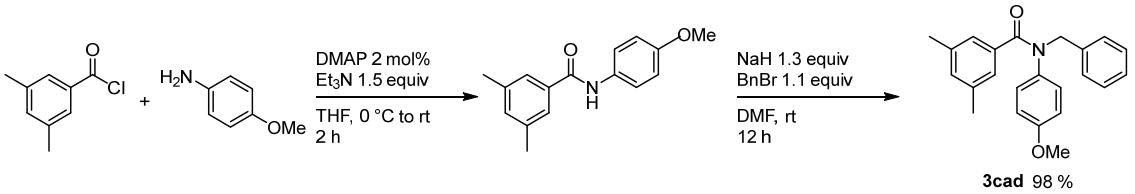
IR (KBr): 3335 s, 3054 w, 3004 w, 2918 m, 2838 w, 1628 s, 1600 s, 1531 s, 1512 s, 1465 m, 1298 m, 1246 s, 1182 m, 1035 s, 911 m, 861 m, 797 w, 764 w, 726 m, 701m, 644 w, 618 w, 582 m, 570 m.

MS, *m/z* (relative intensity, %): 347 (28), 346 (M^+, 51), 214 (13), 213 (32), 198 (10), 134 (38), 133 (100), 105 (42), 104 (14), 79 (16), 77 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{23}DNO_2$: 347.1864. Found: 347.1867.

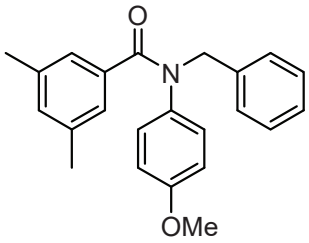
XI. The Reaction of 3cad under Standard Conditions

XI-1. Synthesis of 3cad.[3]



3,5-Dimethylbenzoyl chloride (1.71 g, 10.1 mmol) was added at 0 °C to a solution of 4-methoxyaniline (1.41 g, 11.4 mmol), Et_3N (2.0 mL, 14.3 mmol) and DMAP (24.8 mg, 0.20 mmol) in THF (20 mL). The mixture was then allowed to warm to rt and stirred for 2 h. The mixture was quenched with an aqueous solution of HCl (1 M, 5 mL) and extracted with EtOAc (30 mL x 2). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford corresponding amide (white solid), which was used in the next step without further purification. Benzyl bromide (2.20 g, 12.9 mmol) was added to a solution of NaH (60 % dispersion in paraffin liquid, 0.55 g, 13.3 mmol) and the amide in DMF (40 mL). After the addition was complete, the reaction mixture was stirred at rt for 12 h. The mixture was quenched with saturated aqueous solution of $NaHCO_3$ (100 mL) and extracted with hexane/Et_2O = 1/1 (240 mL). The combined organic layers were washed three times with water (240 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (eluent: hexane/EtOAc = 4/1 to 3/2) to give *N*-benzyl-*N*-(4-methoxyphenyl)-3,5-dimethylbenzamide (**3cad)** as a colorless oil (3.43 g, 98%).

***N*-Benzyl-*N*-(4-methoxyphenyl)-3,5-dimethylbenzamide (3cad).**



Colorless oil. R_f 0.48 (SiO_2, Hexane/EtOAc = 1/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.11 (s, 6H), 3.58 (s, 3H), 5.05 (s, 2H), 6.59 (d, J = 8.7 Hz, 2H), 6.78 (br, 3H), 6.94 (s, 2H), 7.16–7.29 (m, 5H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 20.79, 53.53, 54.86, 113.69, 126.11, 126.96, 128.10, 128.25, 128.60, 130.74, 135.79, 135.92, 136.80, 137.39, 157.59, 170.59.

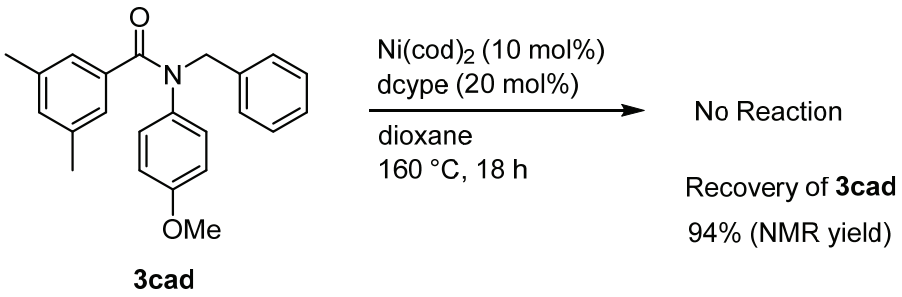
IR (KBr): 3031 m, 3005 m, 2918 m, 2837 w, 1640 s, 1604 s, 1584 m, 1510 s, 1440 s, 1389 s, 1325 s, 1298 m, 1249 s, 1212 m, 1180 m, 1108 w, 1080 w, 1029 m, 979 w, 890 w, 858 m, 837 s, 778 w, 755 s, 728 m, 701 s, 623 m, 553 m, 541 m.

MS, *m/z* (relative intensity, %): 346 (M^+, 25), 345 (82), 344 (15), 212 (59), 196 (10), 134 (30), 133

(100), 105 (78), 103 (17), 91 (56), 79 (29), 77 (27), 65 (10).

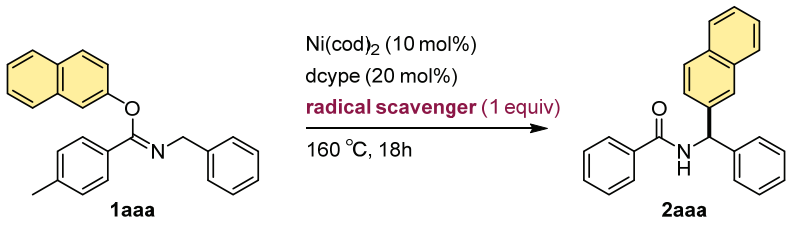
HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{24}NO_2$: 346.1802. Found: 346.1811.

XI-2. The reaction of 3cad under the standard conditions



Yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. This result rules out the intermediacy of a 1,3 aryl shift compound, such as **3cad**, in the 1,4 aryl shift reaction.

XII. The Reaction of 1aaa with Radical Scavengers

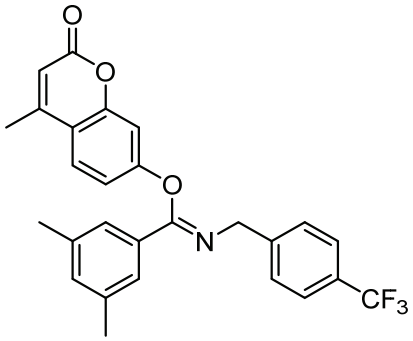


Entry	Solvent	Radical scavenger	Yield of **2aaa** [%]	Recovery of **1aaa** [%]
1	dibutyl ether	none	51	7
2	dibutyl ether	BHT	42	6
3	dioxane	none	51	12
4	dioxane	TEMPO	19	15

To rule out the radical pathway, the reaction was performed with radical scavengers. In a glovebox filled with nitrogen, aryl *N*-benzylimidate **1aaa** (73.5 mg, 0.21 mmol), $Ni(cod)_2$ (5.5 mg, 0.020 mmol), dcype (16.9 mg, 0.040 mmol), radical scavengers (1 equiv) and solvent (1.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 18 h. Yields were determined by GC using pentadecane as an internal standard. In the presence of a radical scavenger, the reaction still proceeded, indicating that a radical pathway is unlikely.

XIII. Synthetic Applications

4-Methyl-2-oxo-2*H*-chromen-7-yl (3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1nbd).



This imidate was synthesized according to the general procedure A using 4-methylumbelliferone (1.06 g, 6.0 mmol), except that the solvent was $CHCl_3$. This compound was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:9.5), which was determined by ^{1}H NMR.

White solid (1.98 g, 85%). R_f 0.72 (NH silica, Hexane/EtOAc = 1/1). Mp 52.2-55.5 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.30 (s, 6H), 2.38 (d, J = 0.92 Hz, 3H), 4.75 (s, 2H), 6.17 (d, J = 1.4 Hz, 1H), 6.86–6.89 (m, 2H), 7.08 (s, 1H), 7.47 (s, 2H), 7.49–7.52 (m, 3H), 7.59 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 18.64, 21.20, 51.35, 104.24, 112.56, 113.07, 115.28, 124.20 (q, J = 272.2 Hz), 125.31 (q, J = 3.8 Hz), 126.23, 127.92, 129.04 (q, J = 32.3 Hz), 131.52, 133.32, 138.35, 143.36, 152.07, 153.54, 154.98, 157.85, 160.61.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.39 (s, 6H), 2.45 (d, J = 1.4 Hz, 3H), 4.63 (s, 2H), 6.26 (d, J = 1.4 Hz, 1H), 7.15 (s, 3H), 7.20–7.23 (m, 1H), 7.27–7.29 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 18.74, 21.29, 53.25, 110.81, 113.92, 116.99, 118.87, 125.05, 125.67, 127.02, 129.92, 132.23, 138.49, 144.35, 152.21, 154.30, 156.03, 160.86, 161.33. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

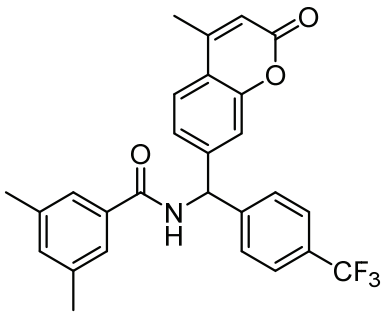
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.62.

IR (KBr): 3058 w, 2920 m, 2868 w, 1734 s, 1666 s, 1610 s, 1564 m, 1505 m, 1418 s, 1387 s, 1325 s, 1267 s, 1133 s, 1066 s, 1016 s, 851 s, 821 s, 685 m.

MS, *m/z* (relative intensity, %): 465 (M^+, 9), 134 (10), 133 (100), 105 (24).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{23}F_3NO_3$: 466.1625. Found: 466.1636.

3,5-Dimethyl-*N*-((4-methyl-2-oxo-2*H*-chromen-7-yl)(4-(trifluoromethyl)phenyl)methyl) benzamide (2nbd).



The typical procedure was followed using **1nbd** (96.8 mg, 0.21 mmol).

White solid (49.5 mg, 51%). R_f 0.32 (SiO_2, Hexane/EtOAc = 1/1). Mp 208.3-210.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.35 (s, 6H), 2.42 (d, J = 0.92 Hz, 3H), 6.25 (d, J = 0.92 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 6.89 (d, J = 7.3 Hz, 1H), 7.16 (s, 1H), 7.24 (dd, J = 8.2, 1.8 Hz, 1H), 7.30 (d, J = 1.4 Hz, 1H), 7.42-7.45 (m, 4H), 7.59 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 18.64, 21.21, 56.73, 115.09, 115.53, 119.39, 123.69, 123.83 (q, J = 272.2 Hz), 124.82, 125.16, 125.96 (q, J = 3.8 Hz), 128.02, 130.29 (q, J = 32.6 Hz), 133.33, 133.73, 138.50, 144.32, 145.13, 152.07, 153.74, 160.52, 167.17.

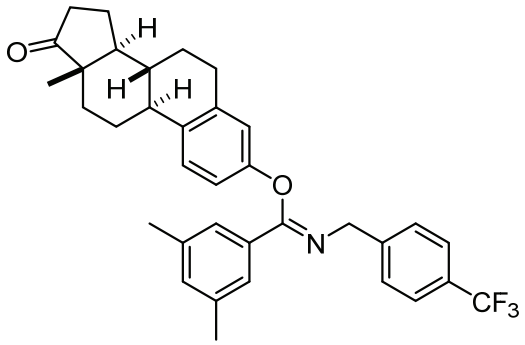
^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.90.

IR (KBr): 3248 s, 3064 m, 1723 s, 1634 s, 1602 s, 1539 s, 1417 m, 1386 m, 1327 s, 1176 m, 1115 s, 1069 m, 1017 m, 888 m, 861 s, 819 m, 750 m, 712 s, 683 m.

MS, *m/z* (relative intensity, %): 465 (M^+, 30), 332 (16), 134 (31), 133 (100), 105 (31).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{23}F_3NO_3$: 466.1625. Found: 466.1619.

13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1obd).



This imidate was synthesized according to the general procedure A using estrone (1.18 g, 4.4 mmol, 1.1 equiv), except that the solvent was $CHCl_3$. The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:8.3), which was determined by ^{1}H NMR.

White solid (1.21 g, 54%). R_f 0.76 (NH silica, Hexane/EtOAc = 1/1). Mp 74.4-78.2 °C.

Major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (s, 3H), 1.37-1.66 (m, 7H), 1.93-2.22 (m, 5H), 2.30 (s, 6H), 2.47-2.54 (m, 1H), 2.79-2.81 (m, 2H), 4.72 (s, 2H), 6.62 (d, J = 2.8 Hz, 1H), 6.72 (dd, J = 8.2, 2.8 Hz, 1H), 7.06 (s, 1H), 7.17 (d, J = 8.7 Hz, 1H), 7.49–7.52 (m, 4H), 7.56–7.58 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 13.81, 21.24, 21.52, 25.74, 26.31, 29.44, 31.48, 35.81, 38.05, 43.93, 47.92, 50.33, 51.36, 113.33, 115.74, 124.28 (q, J = 272.2 Hz), 125.17 (q, J = 3.8 Hz), 126.32, 126.81, 127.96, 128.80 (q, J = 31.6 Hz), 132.64, 132.84, 134.03, 138.00, 138.45, 144.03, 153.31, 155.10, 220.84.

Minor isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.93 (s, 3H), 2.37 (s, 6H), 2.93-2.95 (m, 2H), 4.61 (s, 2H), 6.97–6.98 (m, 1H), 7.11 (s, 3H), 7.29–7.33 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.30, 26.44, 31.53, 44.16, 47.97, 50.41, 53.22, 119.38, 122.06, 125.04 (q, J = 3.8 Hz), 125.68, 126.16, 127.00, 130.81, 131.81, 136.17, 137.62, 138.28, 145.14, 151.07, 162.43. Other peaks are overlapped with those of a major isomer.

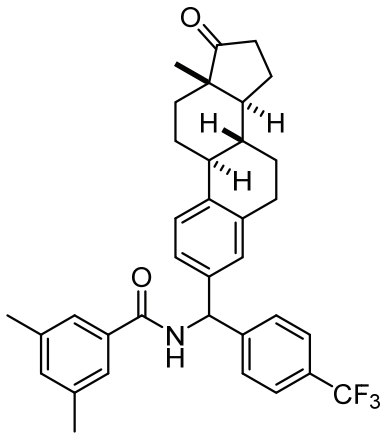
E/Z Mixture

^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.56.

IR (KBr): 2929 m, 2865 m, 1740 s, 1659 m, 1605 m, 1493 m, 1455 w, 1417 m, 1324 s, 1229 m, 1161 s, 1122 s, 1066 s, 1018 m, 820 m.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{35}H_{37}F_3NO_2$: 560.2771. Found: 560.2781.

3,5-Dimethyl-*N*-((14-methyl-15-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)(4-(trifluoromethyl)phenyl)methyl)benzamide (2obd).



The typical procedure was followed using **1nbd** (111.8 mg, 0.20 mmol).

White solid (66.1 mg, 59%). R_f 0.48 (SiO_2, Hexane/EtOAc = 1/1). M.p. 142.7-144.4 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (s, 3H), 1.41-1.68 (m, 6H), 1.95-2.18 (m, 4H), 2.26-2.54 (m, 8H), 2.47-2.54 (m, 1H), 2.87-2.90 (m, 2H), 6.39 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 7.3 Hz, 1H), 7.00-7.01 (m, 1H), 7.03-7.05 (m, 1H), 7.15 (s, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.41 (s, 2H), 7.44 (d, J = 8.2 Hz, 2H),

7.59 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 13.77, 21.20, 21.51, 25.61, 26.33, 29.39, 31.48, 35.78, 37.96, 44.28, 47.89, 50.39, 56.96, 124.05 (q, J = 271.9 Hz), 124.74, 124.94, 125.03, 125.56 (q, J = 4.2 Hz), 126.01, 127.48, 128.34, 128.43, 129.48 (q, J = 32.5 Hz), 133.44, 133.76, 137.26, 138.14, 138.37, 139.65, 145.53, 166.87, 220.77.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: −63.71.

IR (KBr): 3311 m, 2929 m, 2863 m, 1737 s, 1639 s, 1603 s, 1522 s, 1472 m, 1455 m, 1411w, 1324 s, 1240 m, 1163 s, 1123 s, 1068 s, 1017 m, 862 m, 822 m, 757 s.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{35}H_{37}F_3NO_2$: 560.2771. Found: 560.2762.

XIV. References

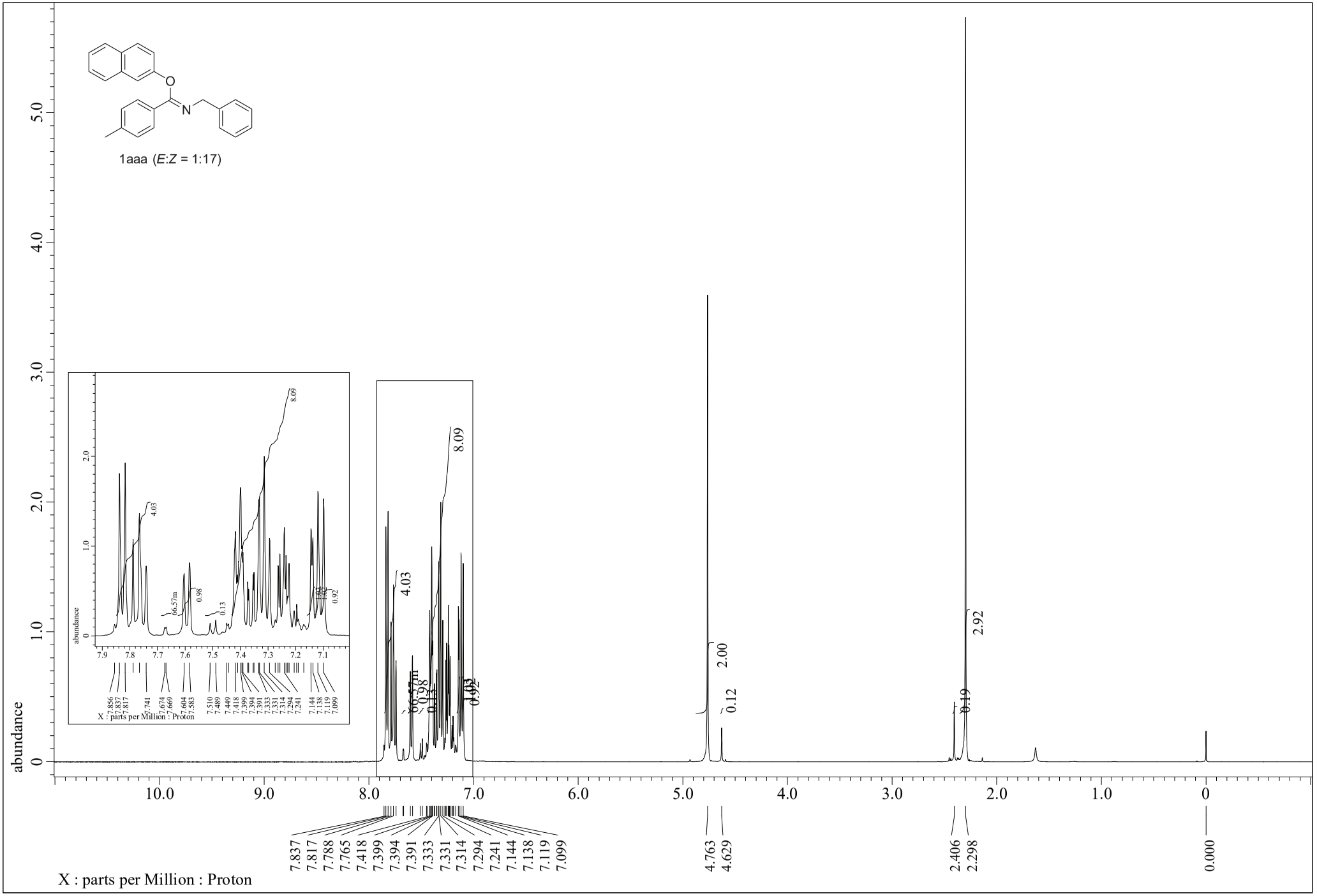
[1] J. E. Rowe, Synthesis, 1980, 114.

[2] P. W. Groundwater, I. Garnett, A. J. Morton, T. Sharif, S. J. Coles, M. B. Hursthouse, M. Nyerges, R. J. Anderson, D. Bendell, A. McKillop, W. Zhanga, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2781.

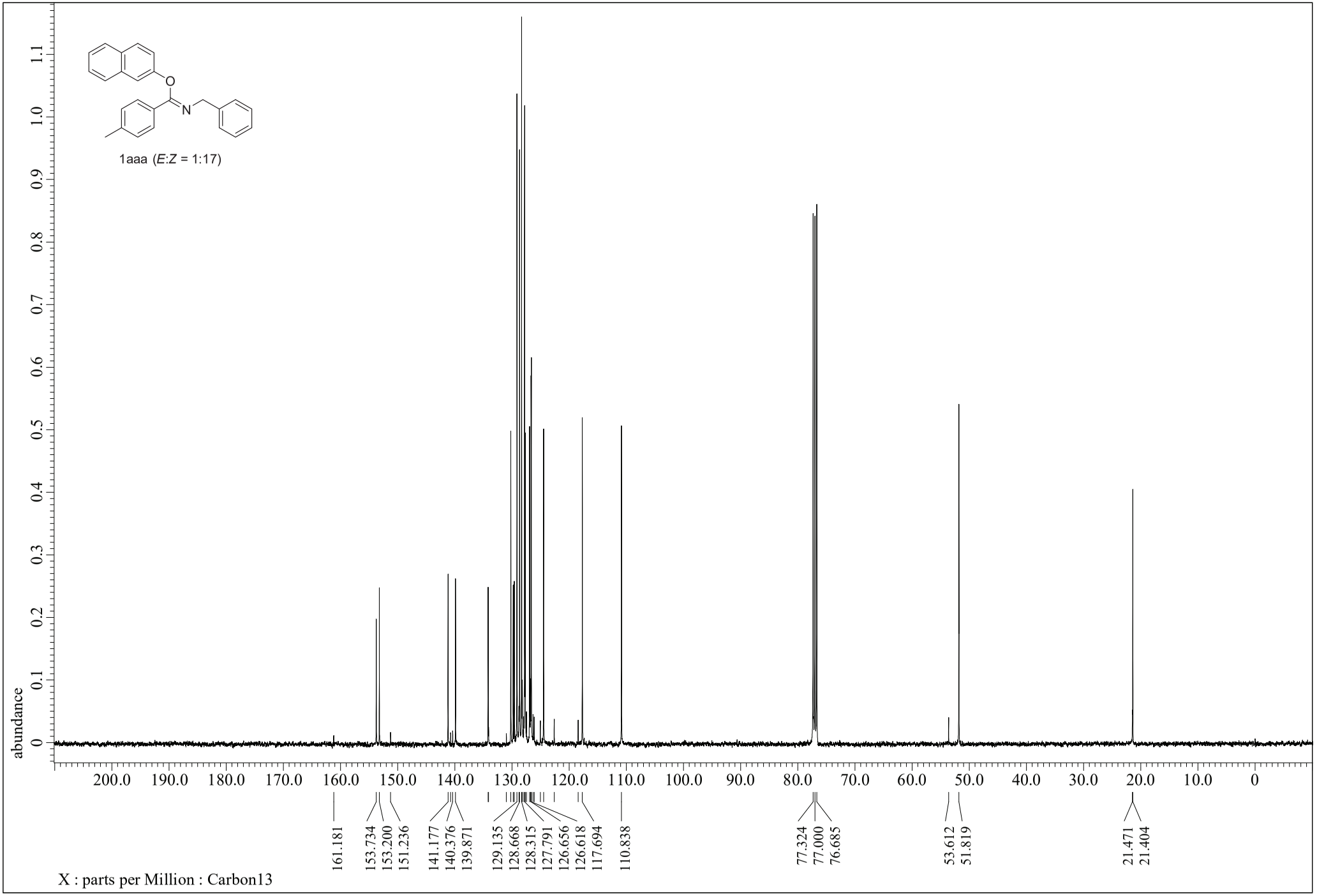
[3] S. J. Barraza, S. E. Denmark. *Synlett*, 2017, **28**, 2891.

XV. Copies of NMR spectra

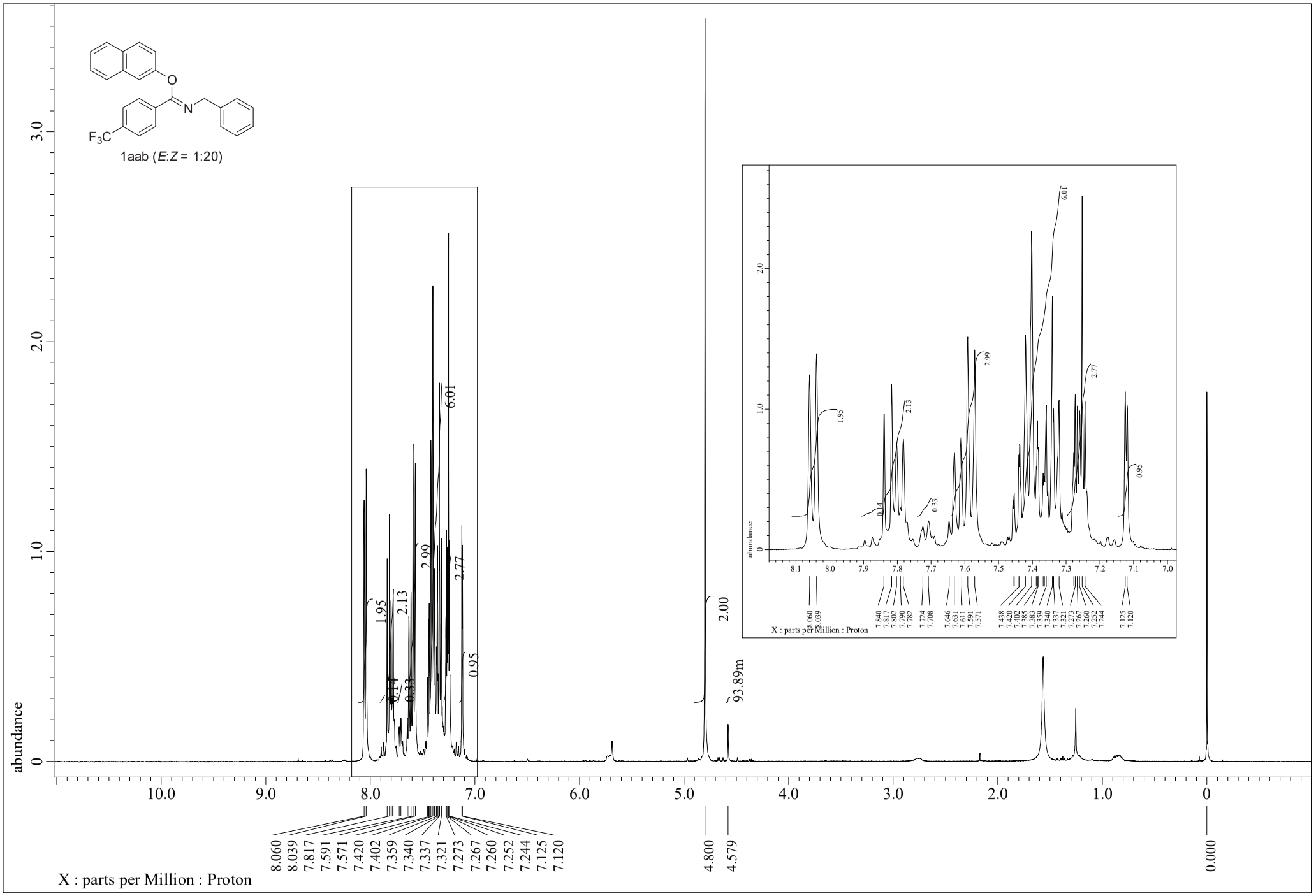
^{1}H NMR (400 MHz, $CDCl_3$)



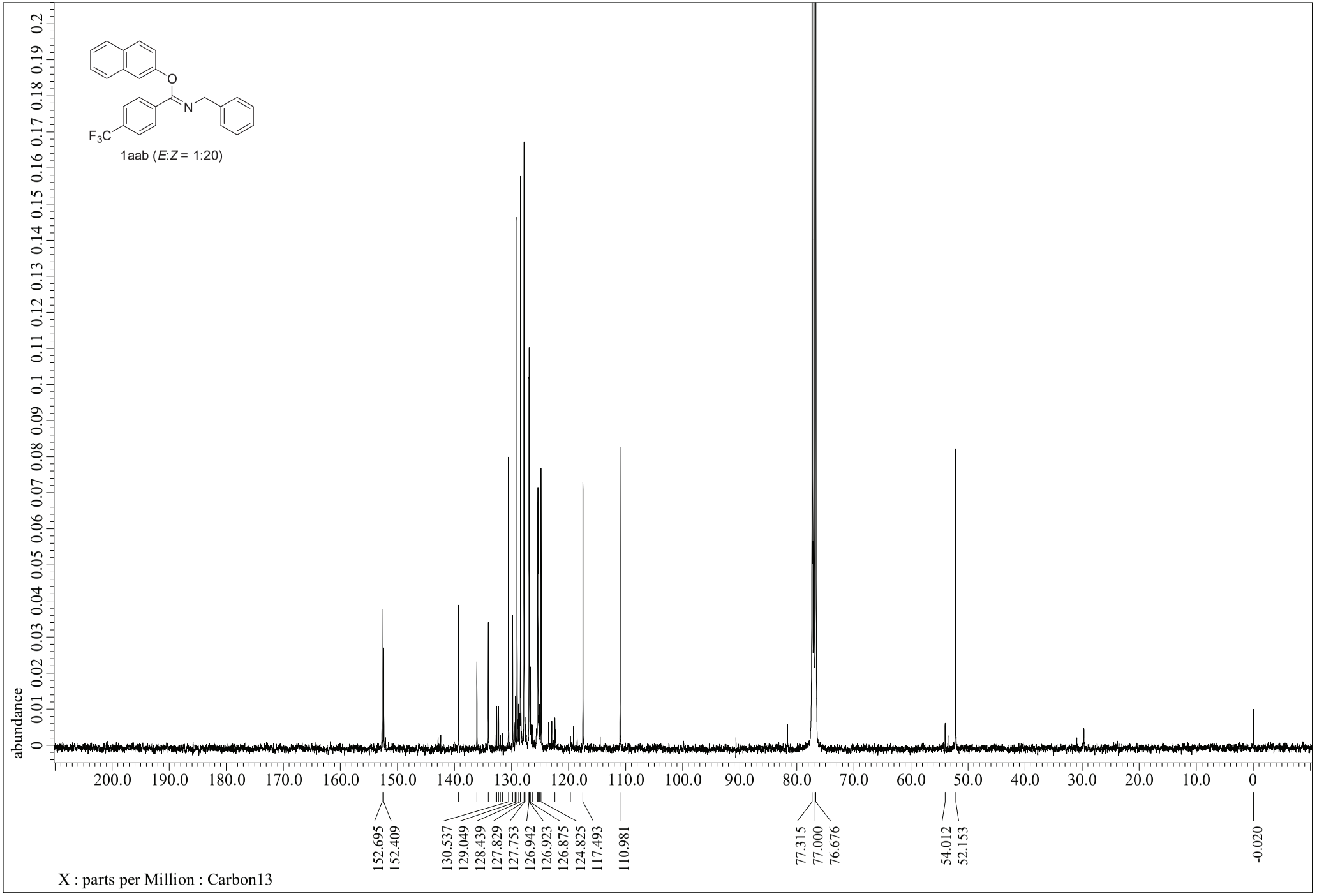
^{13}C NMR (101 MHz, $CDCl_3$)



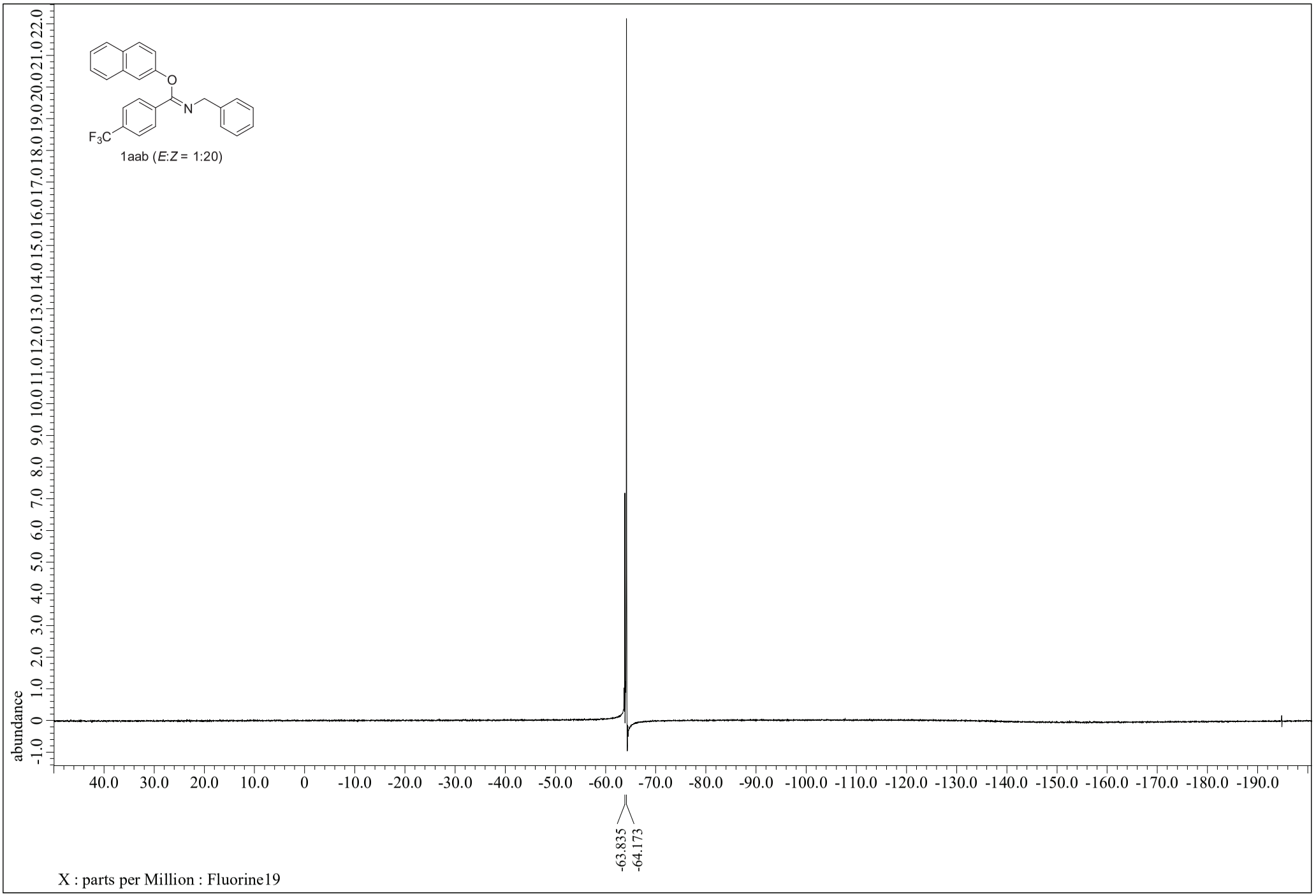
^{1}H NMR (400 MHz, $CDCl_3$)



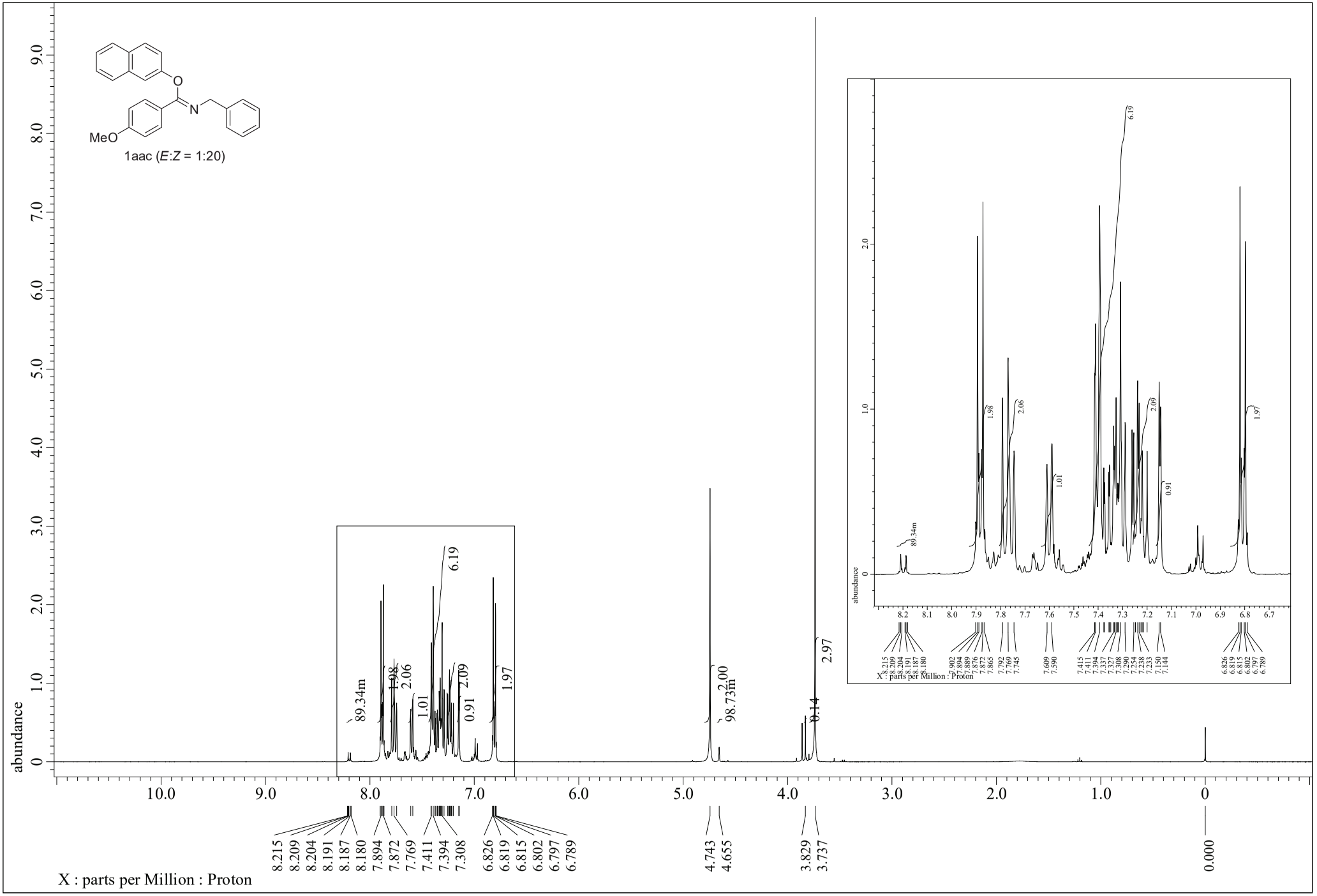
^{13}C NMR (101 MHz, $CDCl_3$)



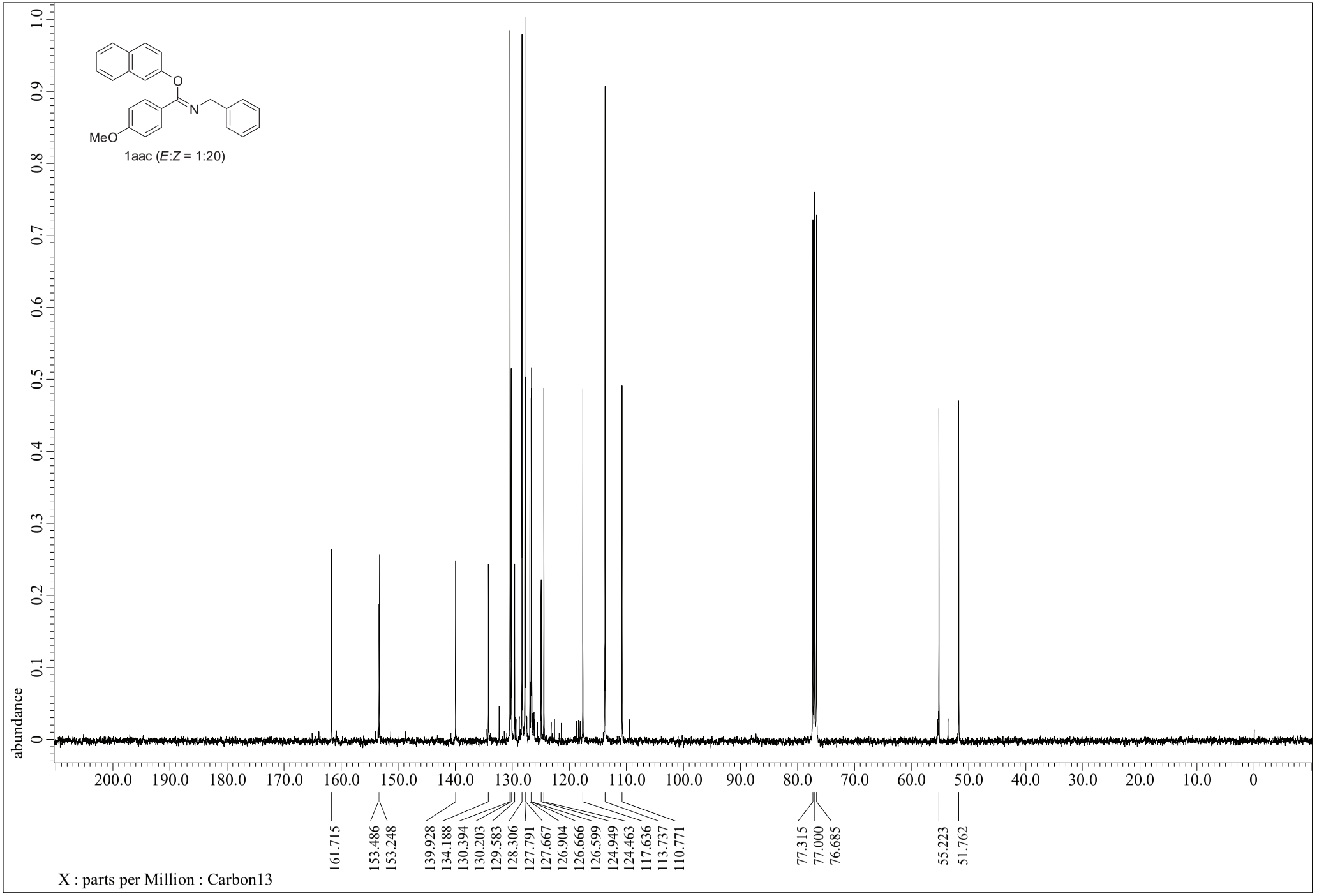
^{19}F NMR (376 MHz, $CDCl_3$)



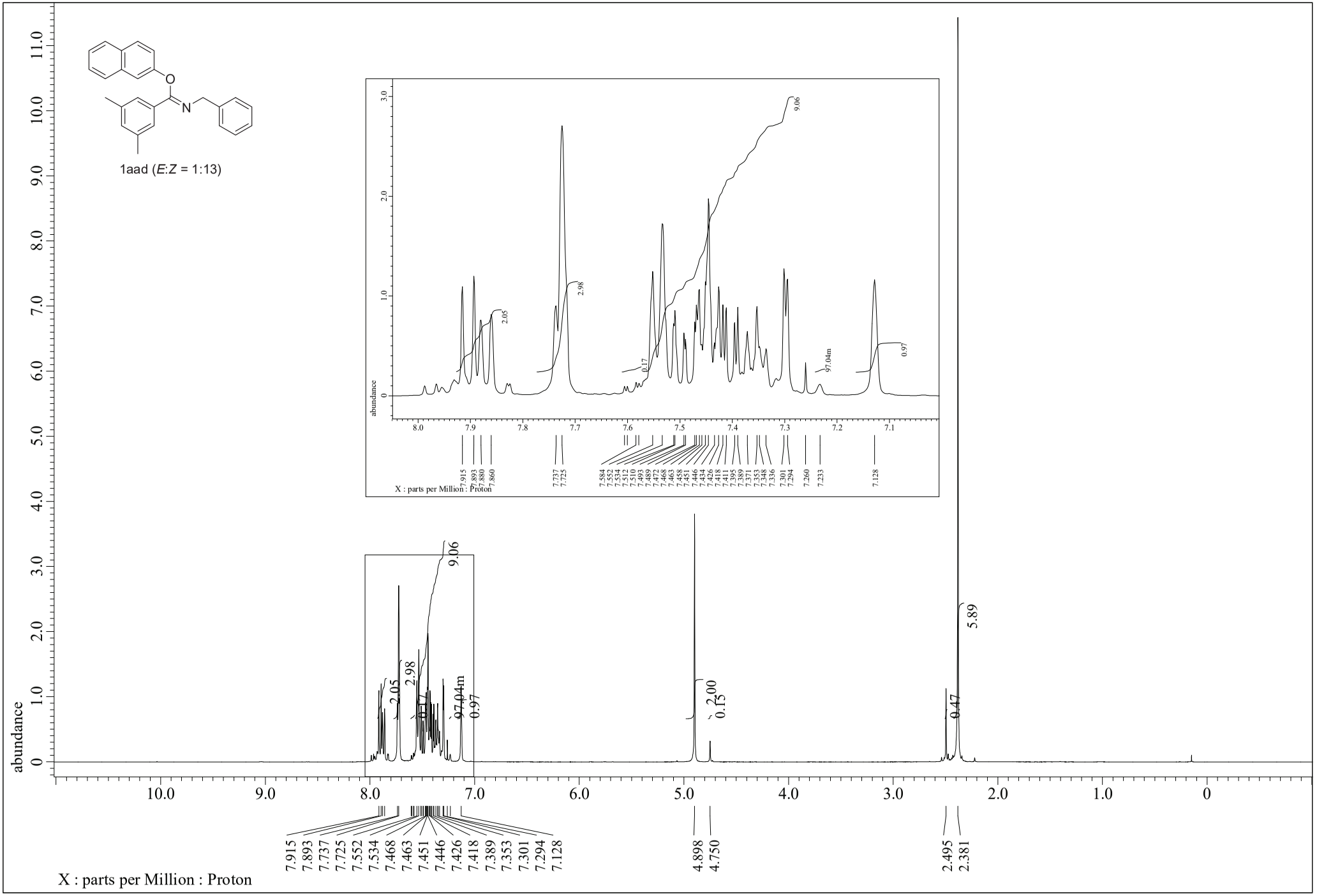
^{1}H NMR (400 MHz, $CDCl_3$)



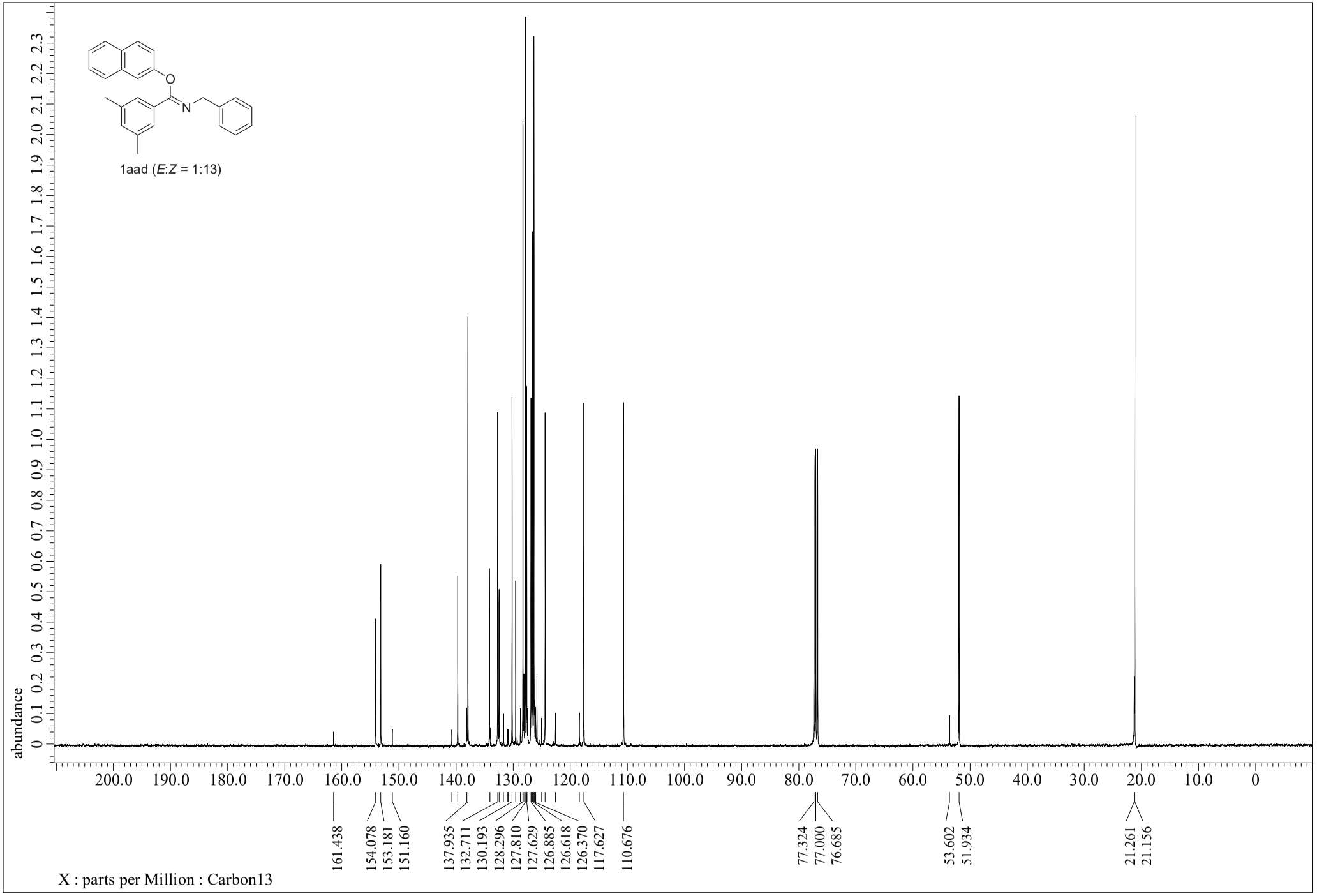
^{13}C NMR (101 MHz, $CDCl_3$)



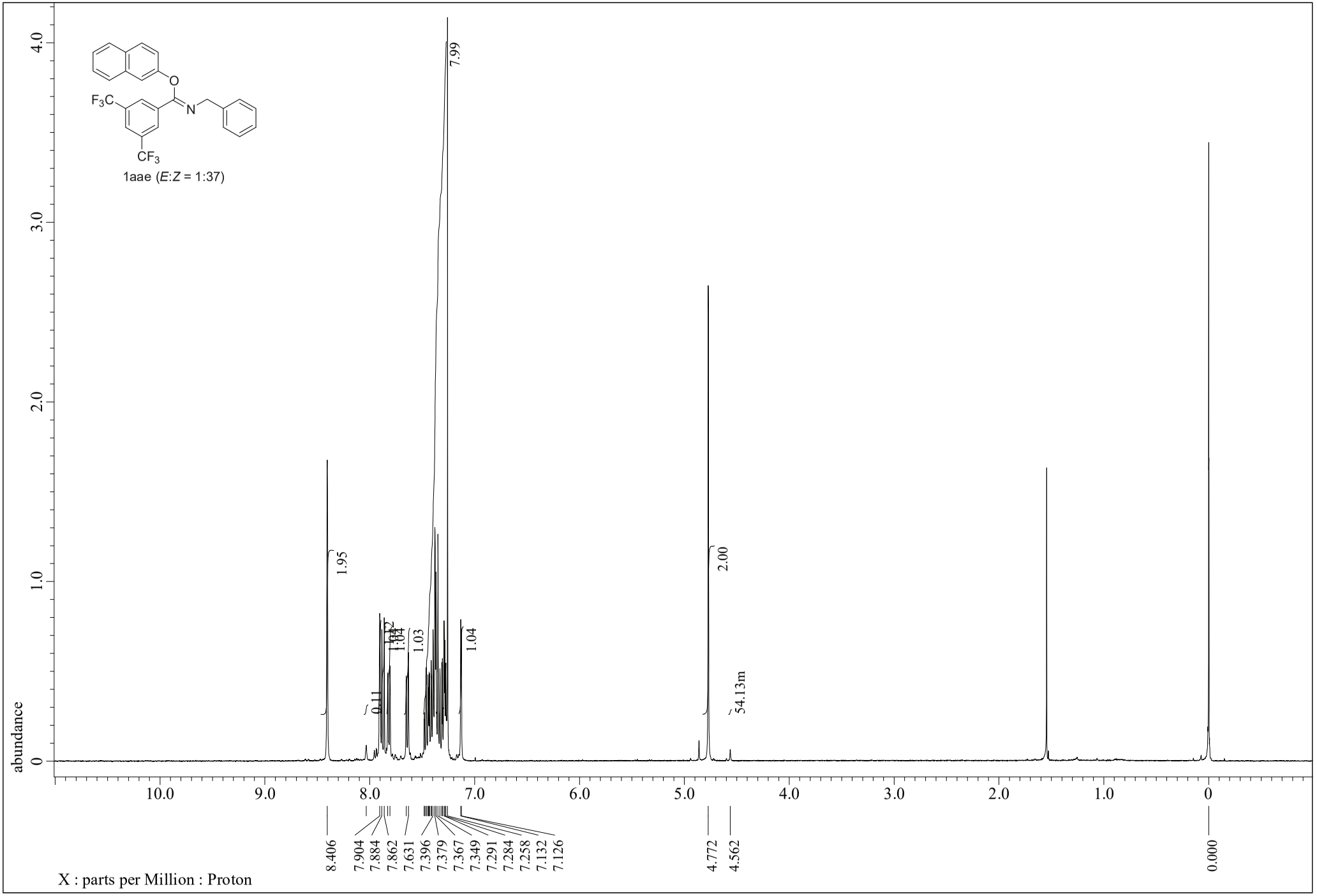
^{1}H NMR (400 MHz, $CDCl_3$)



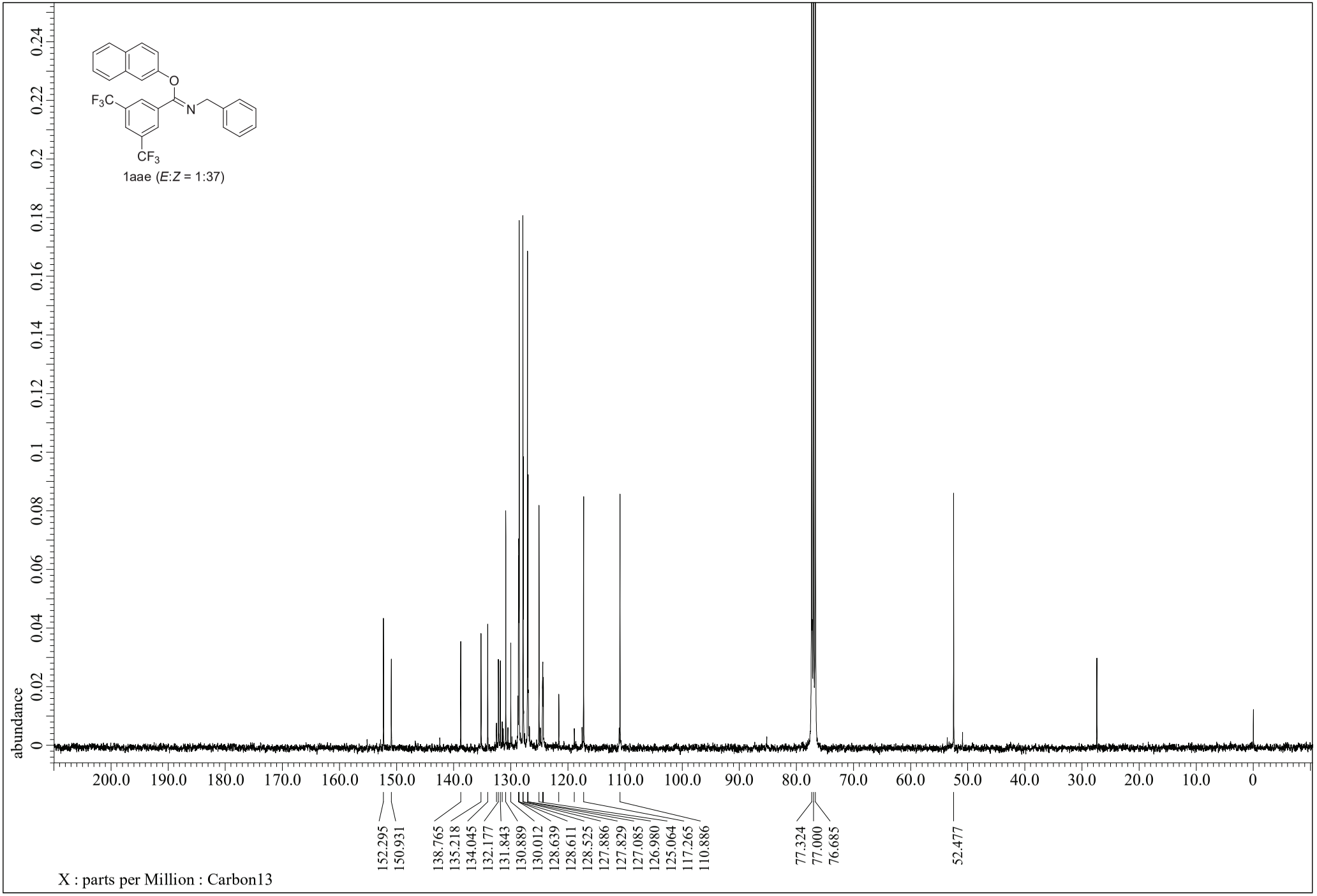
^{13}C NMR (101 MHz, $CDCl_3$)



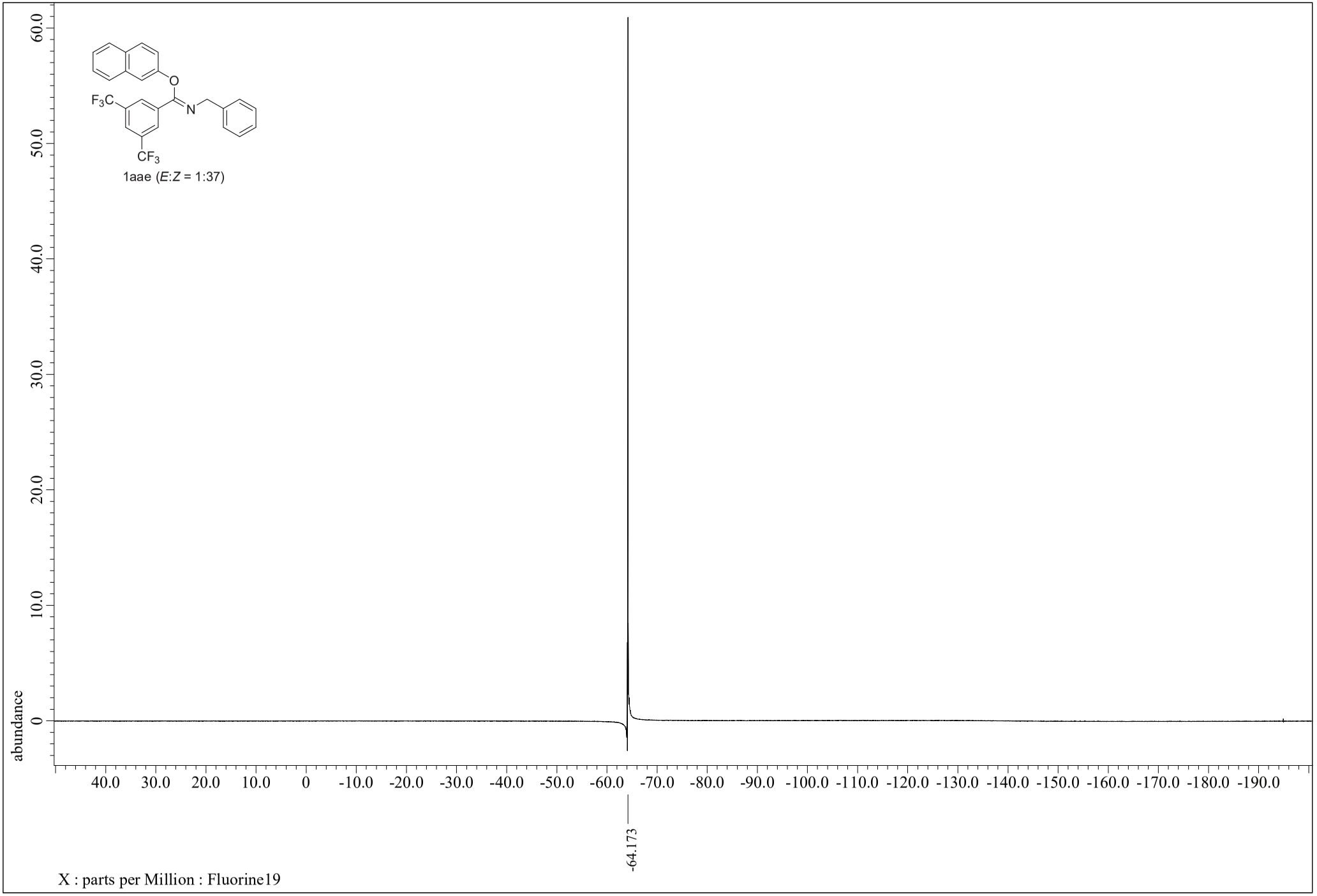
^{1}H NMR (400 MHz, $CDCl_3$)



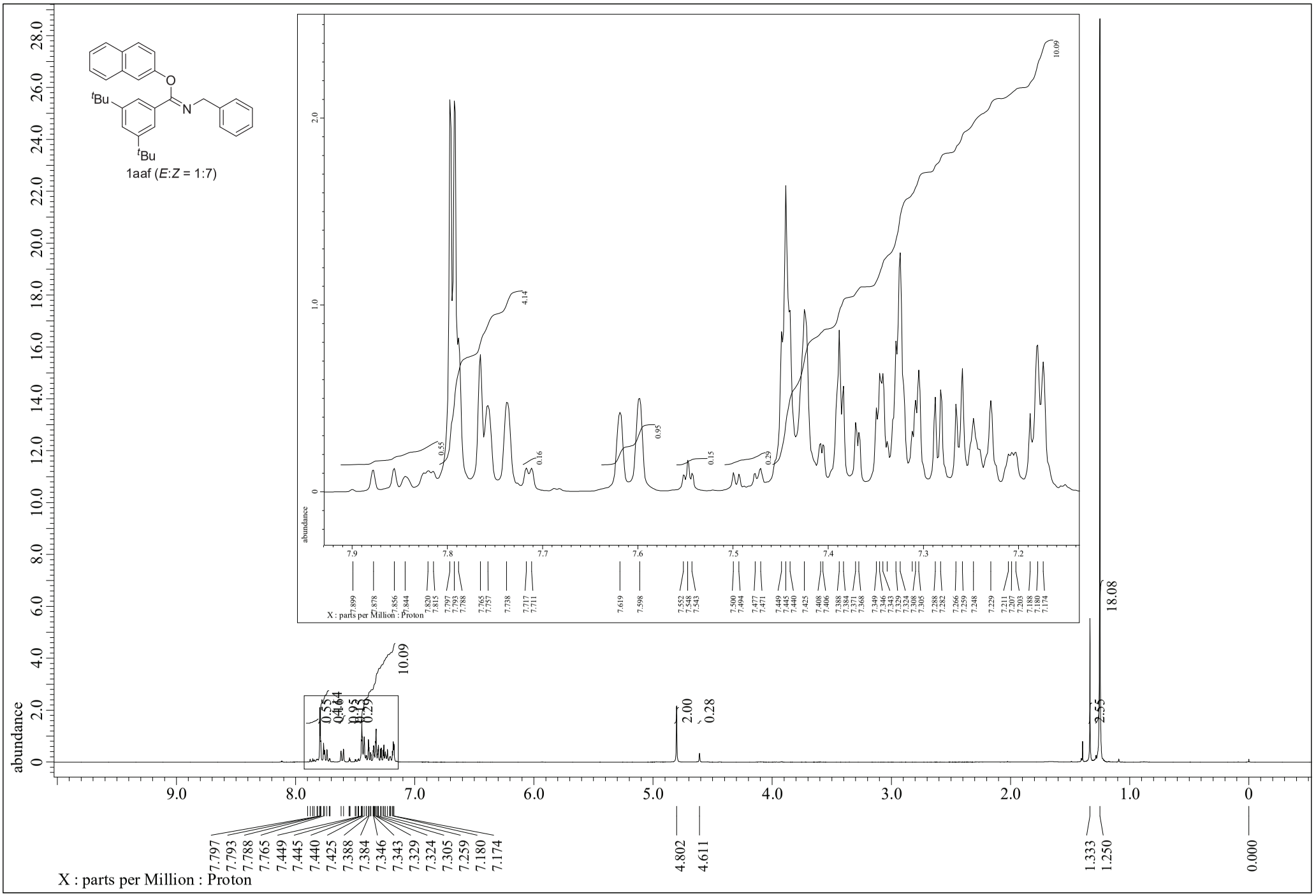
^{13}C NMR (101 MHz, $CDCl_3$)



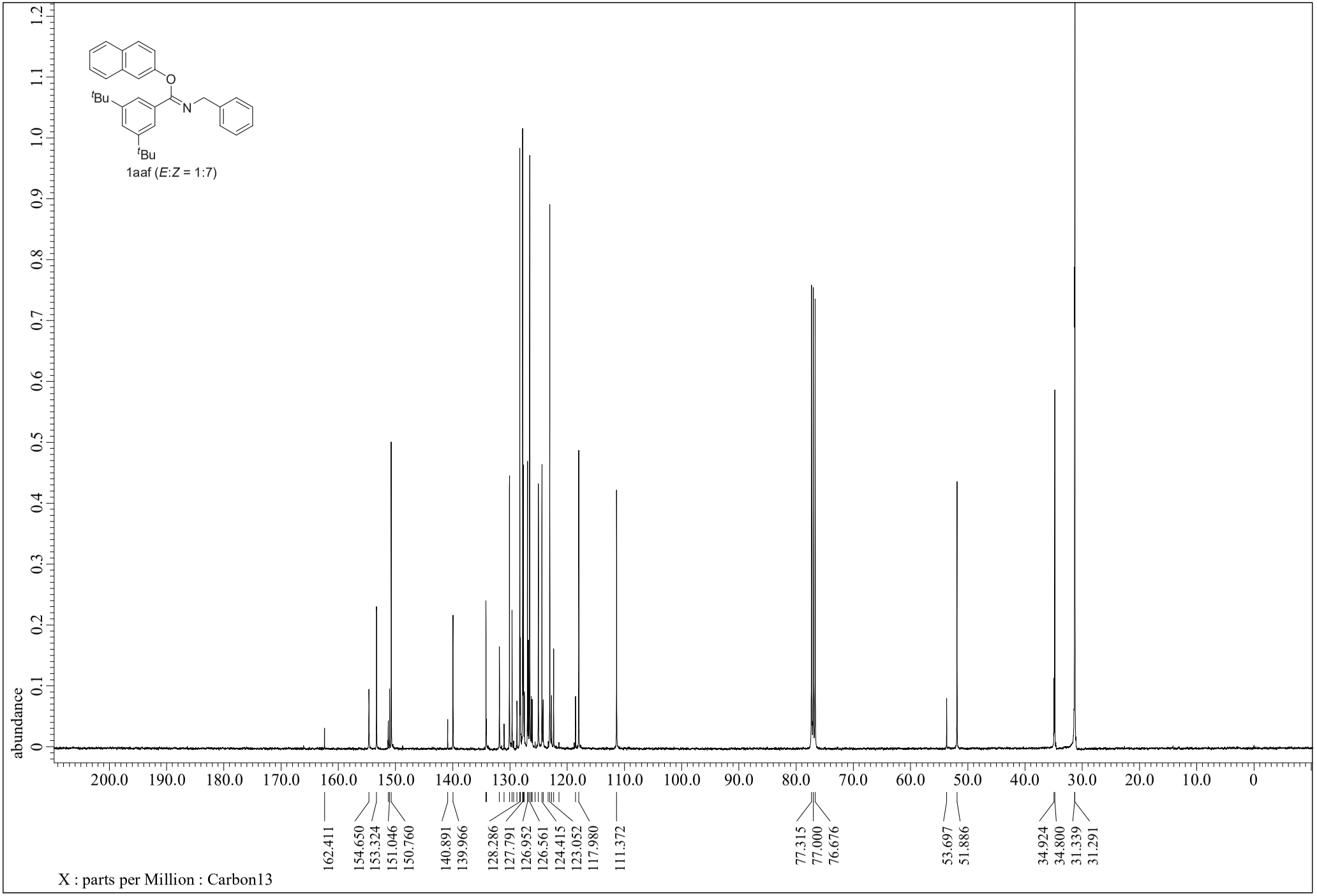
^{19}F NMR (376 MHz, $CDCl_3$)



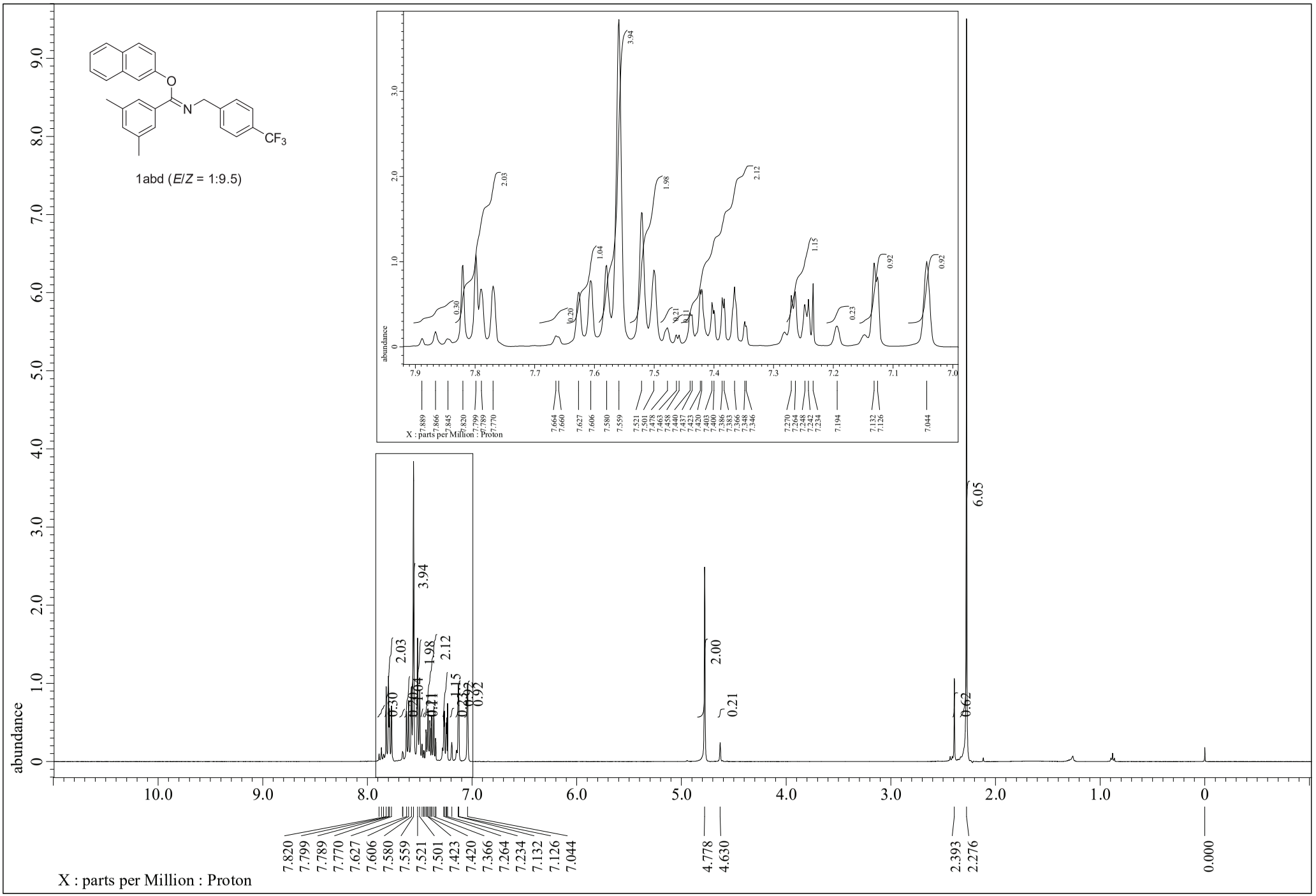
^{1}H NMR (400 MHz, $CDCl_3$)



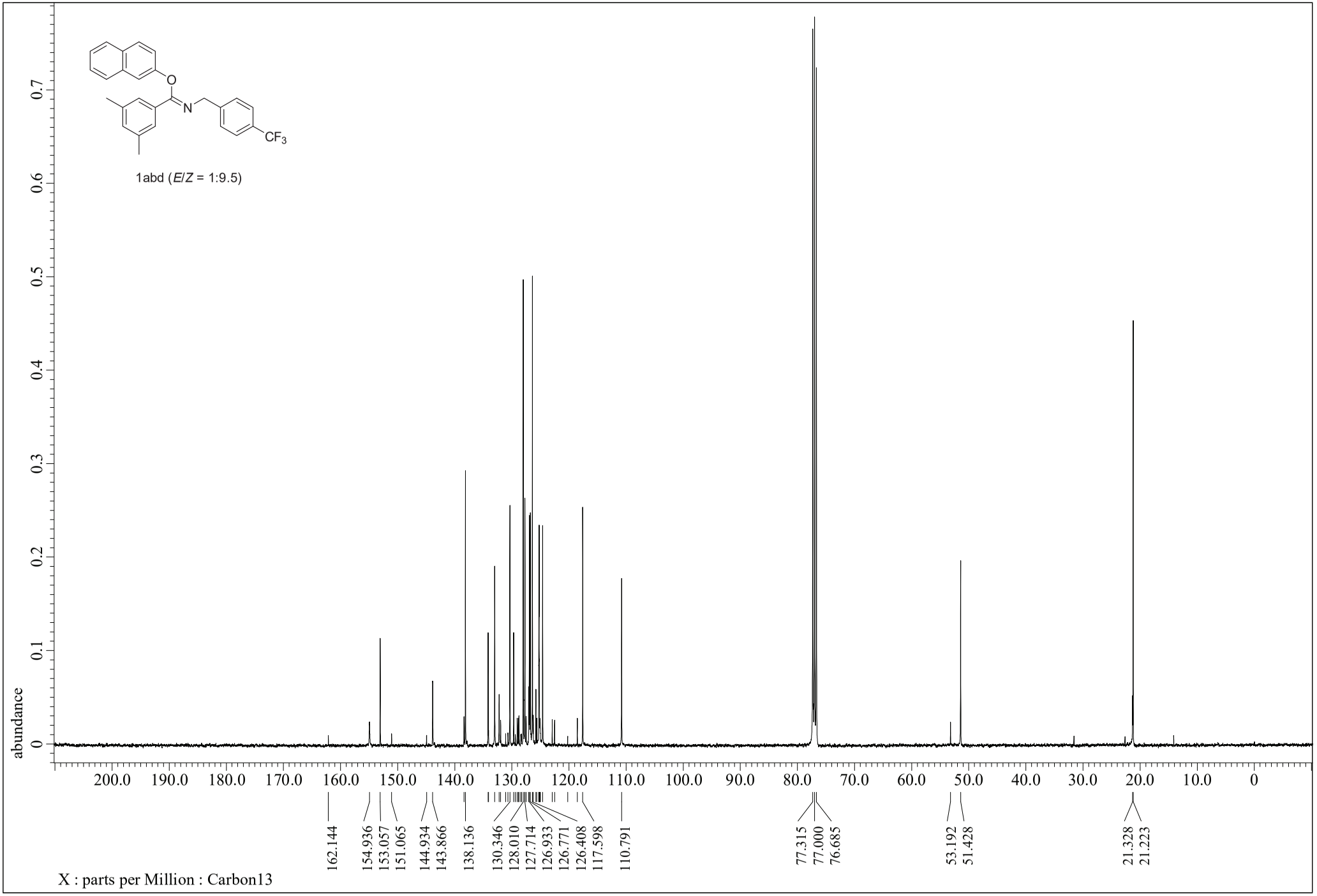
^{13}C NMR (101 MHz, $CDCl_3$)



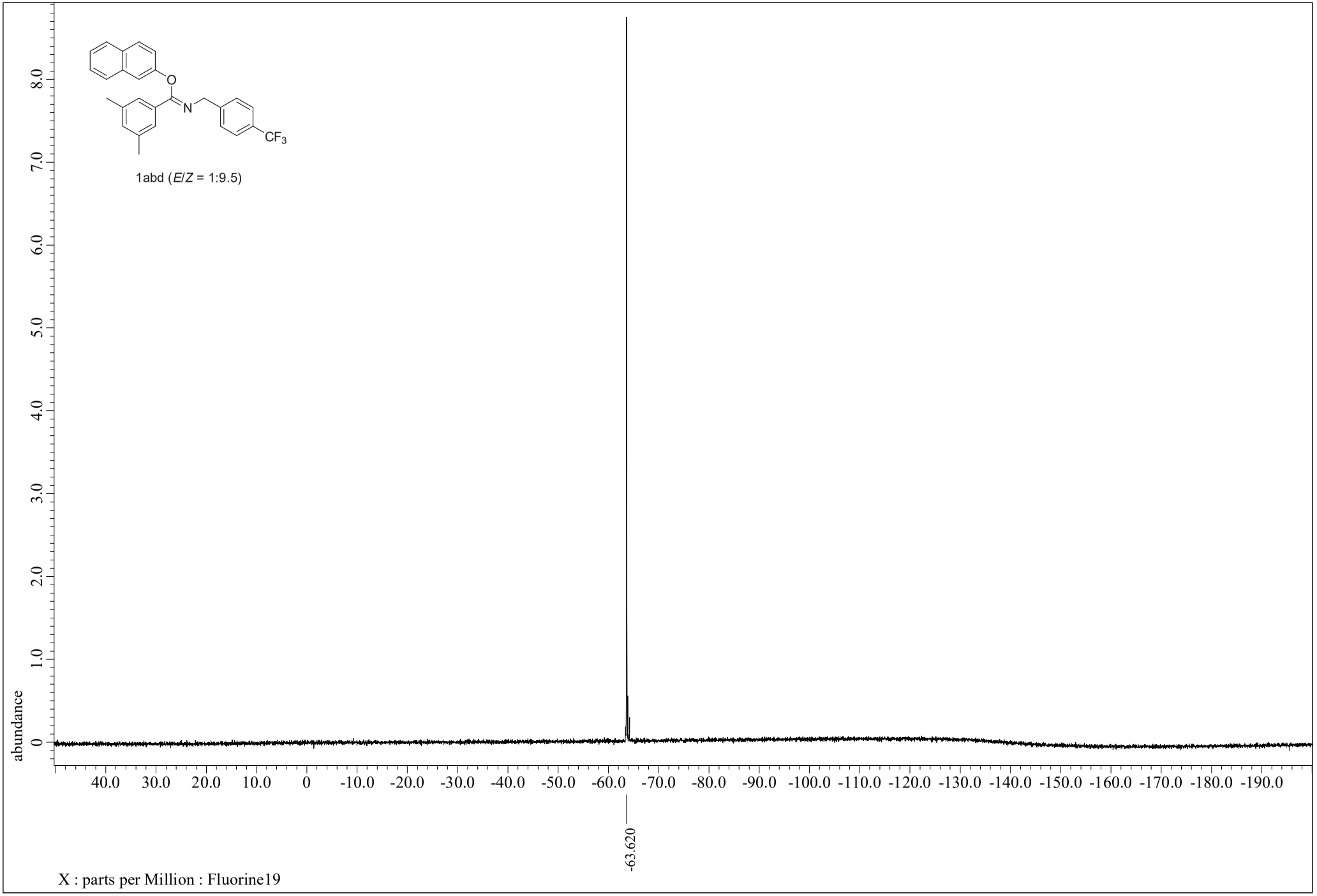
^{1}H NMR (400 MHz, $CDCl_3$)



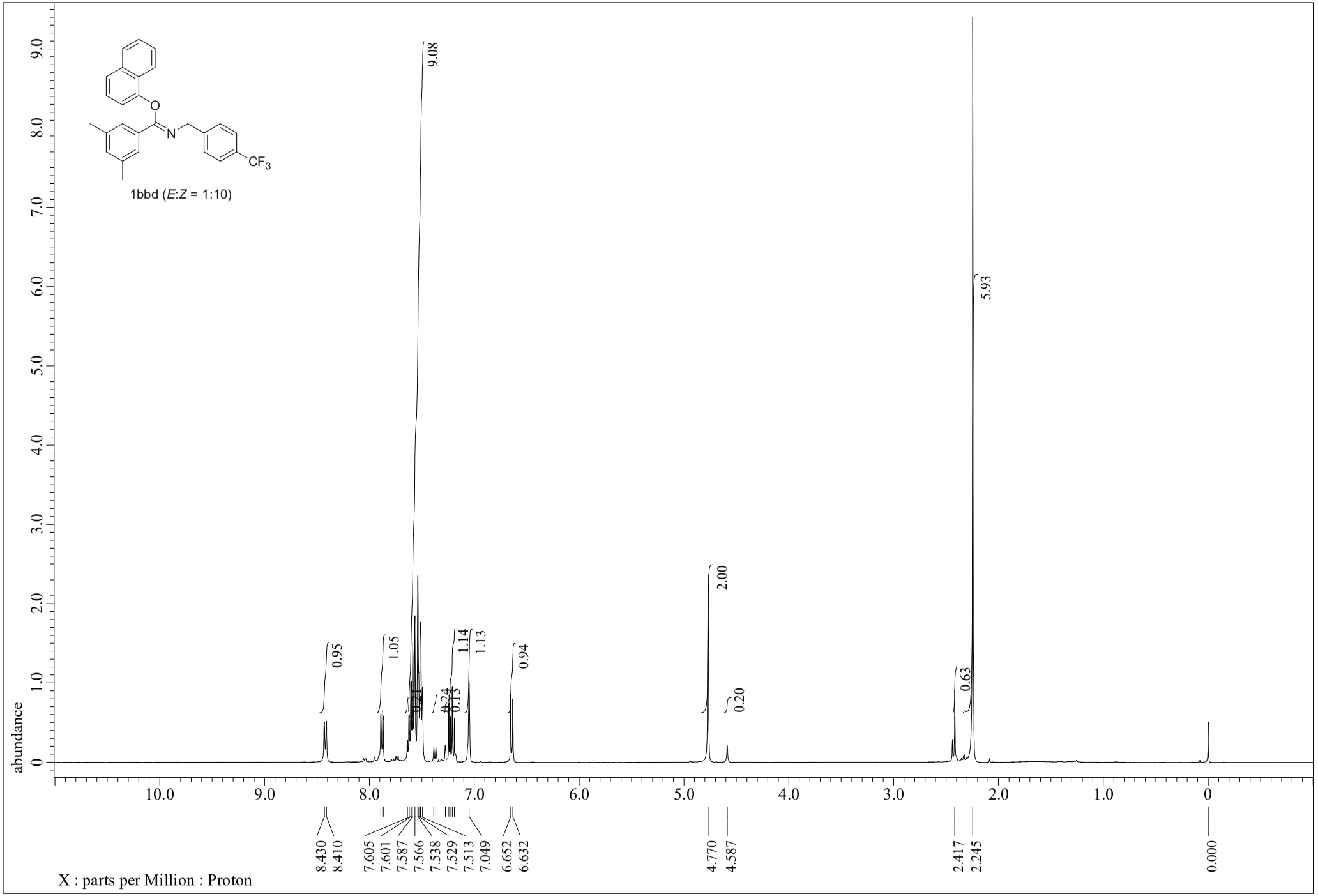
^{13}C NMR (101 MHz, $CDCl_3$)



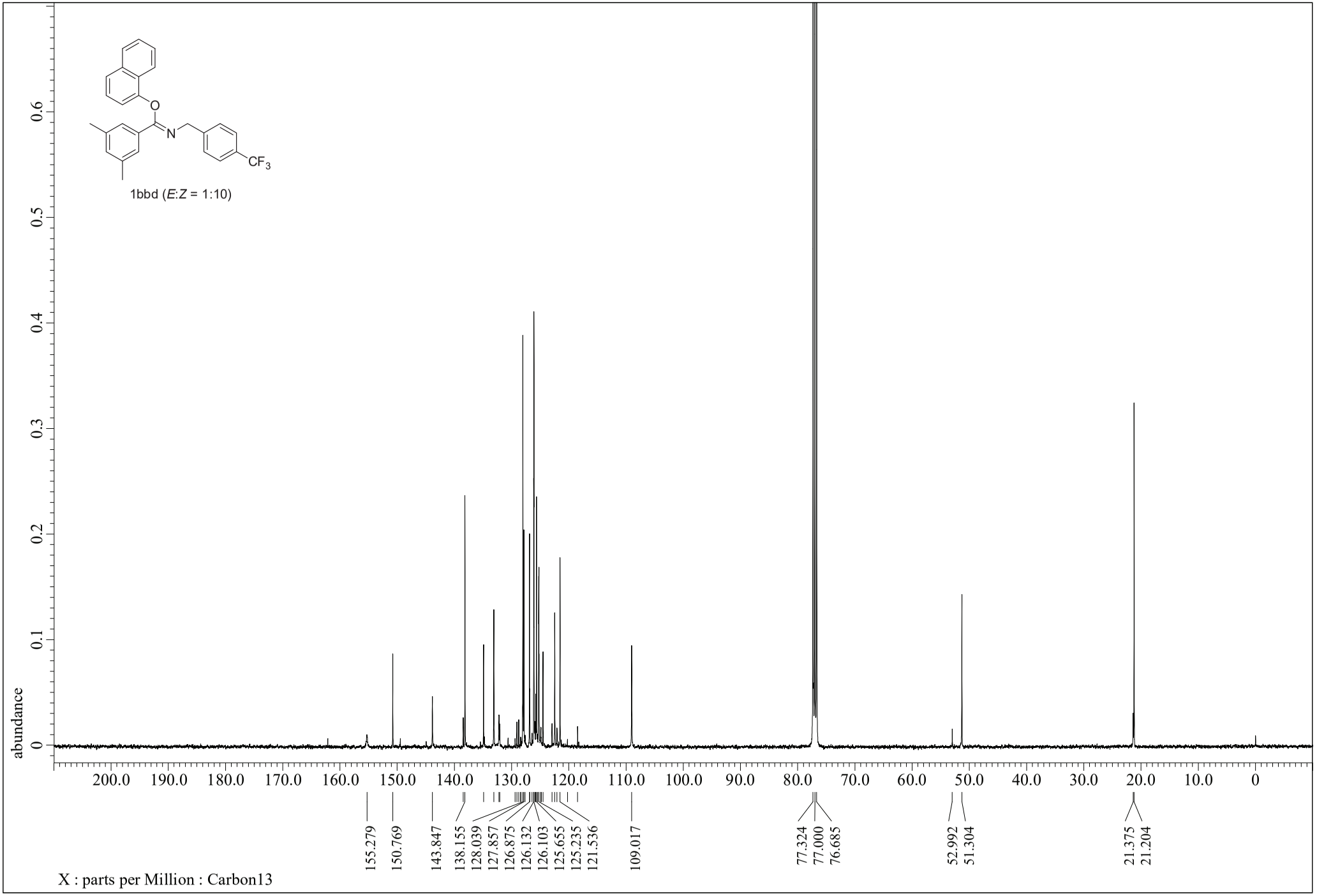
^{19}F NMR (376 MHz, $CDCl_3$)



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



^{13}C NMR (101 MHz, $CDCl_3$)



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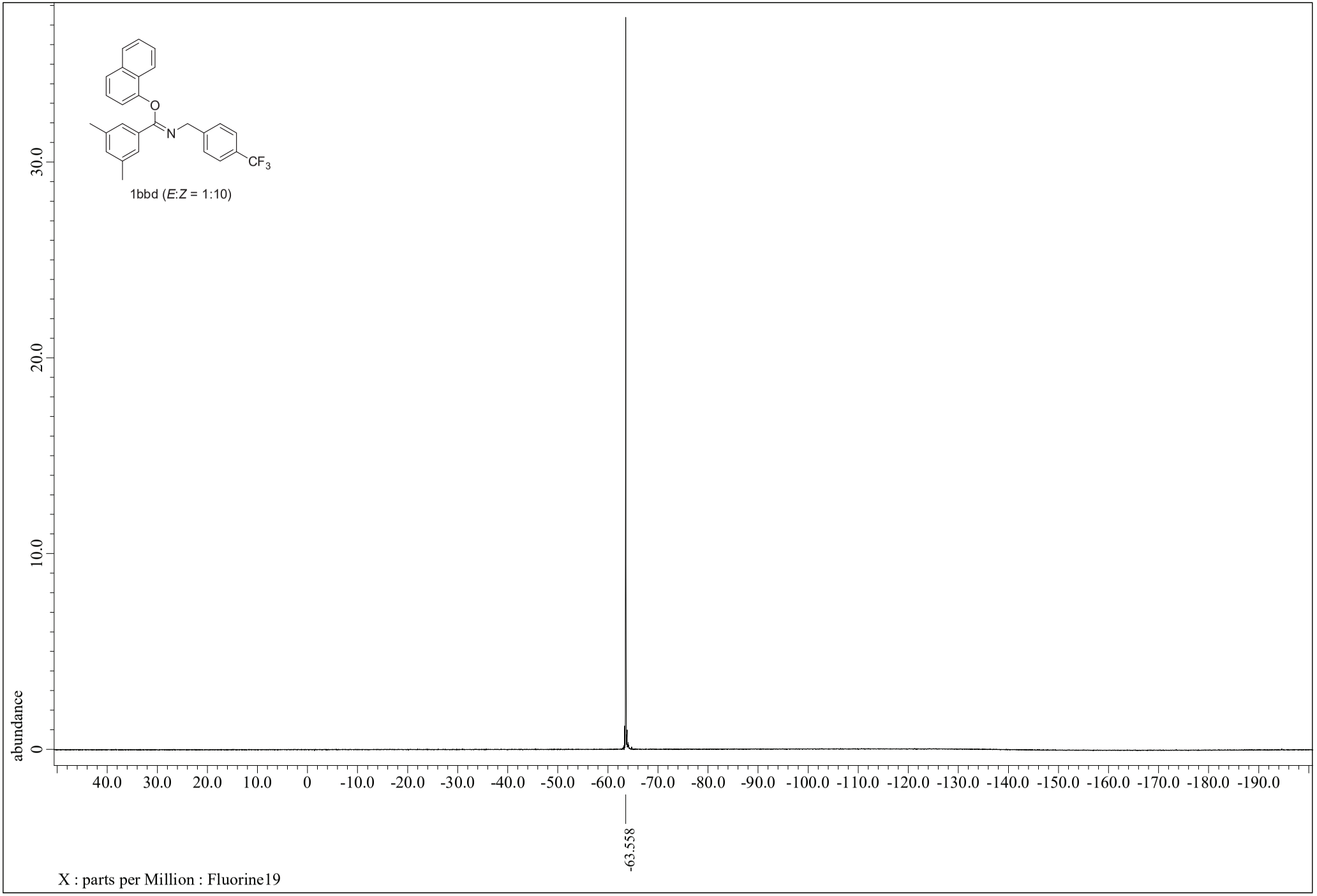

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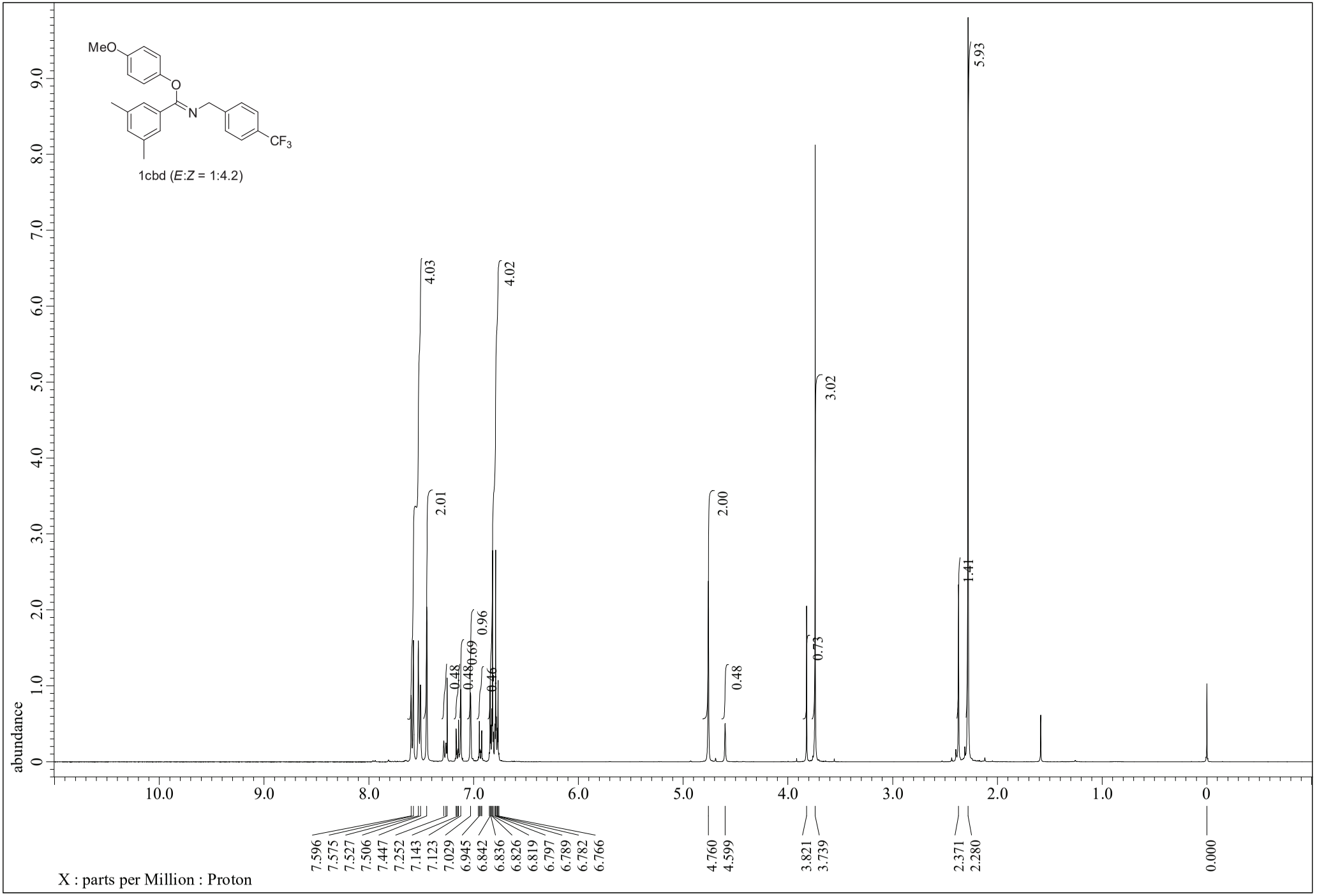
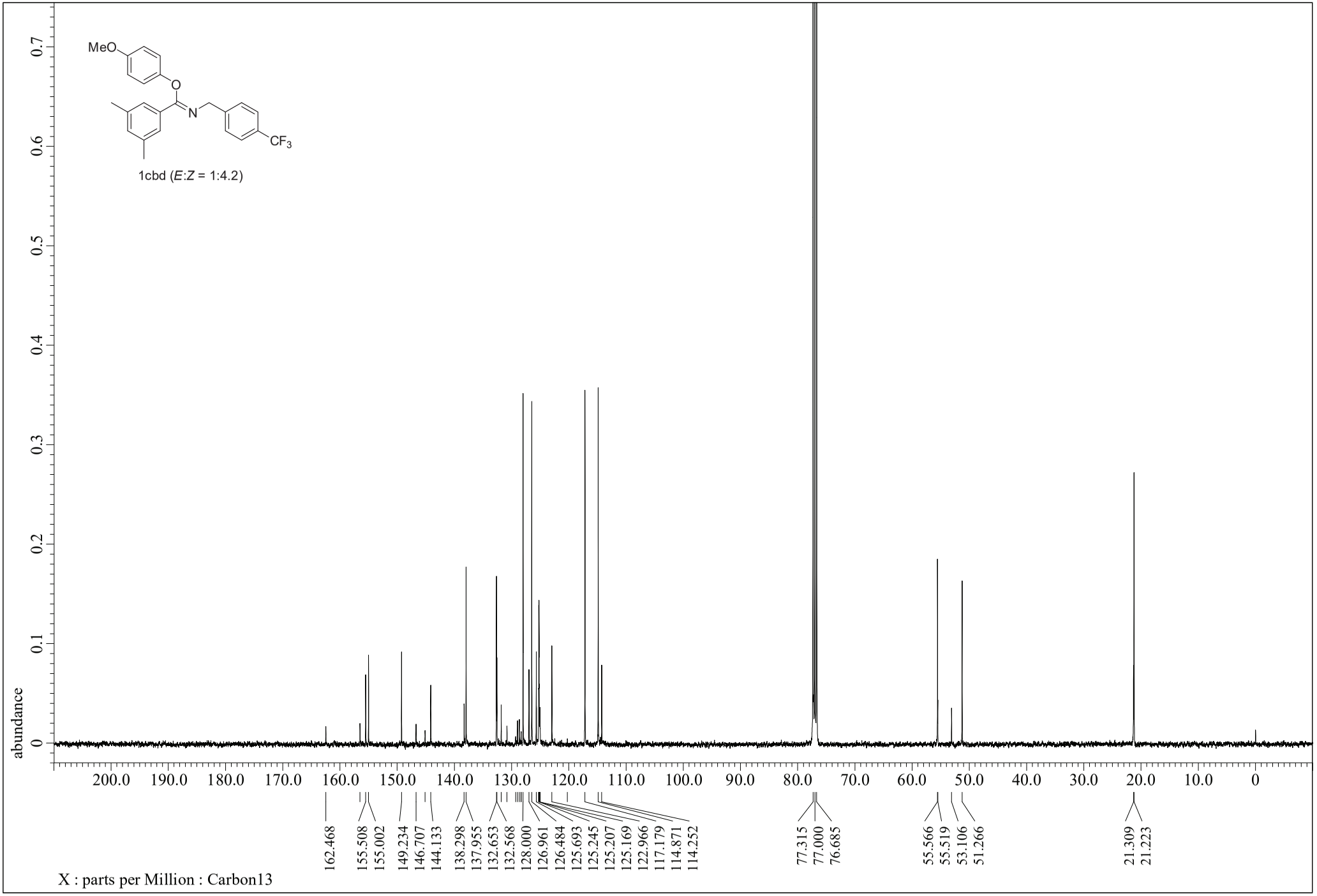
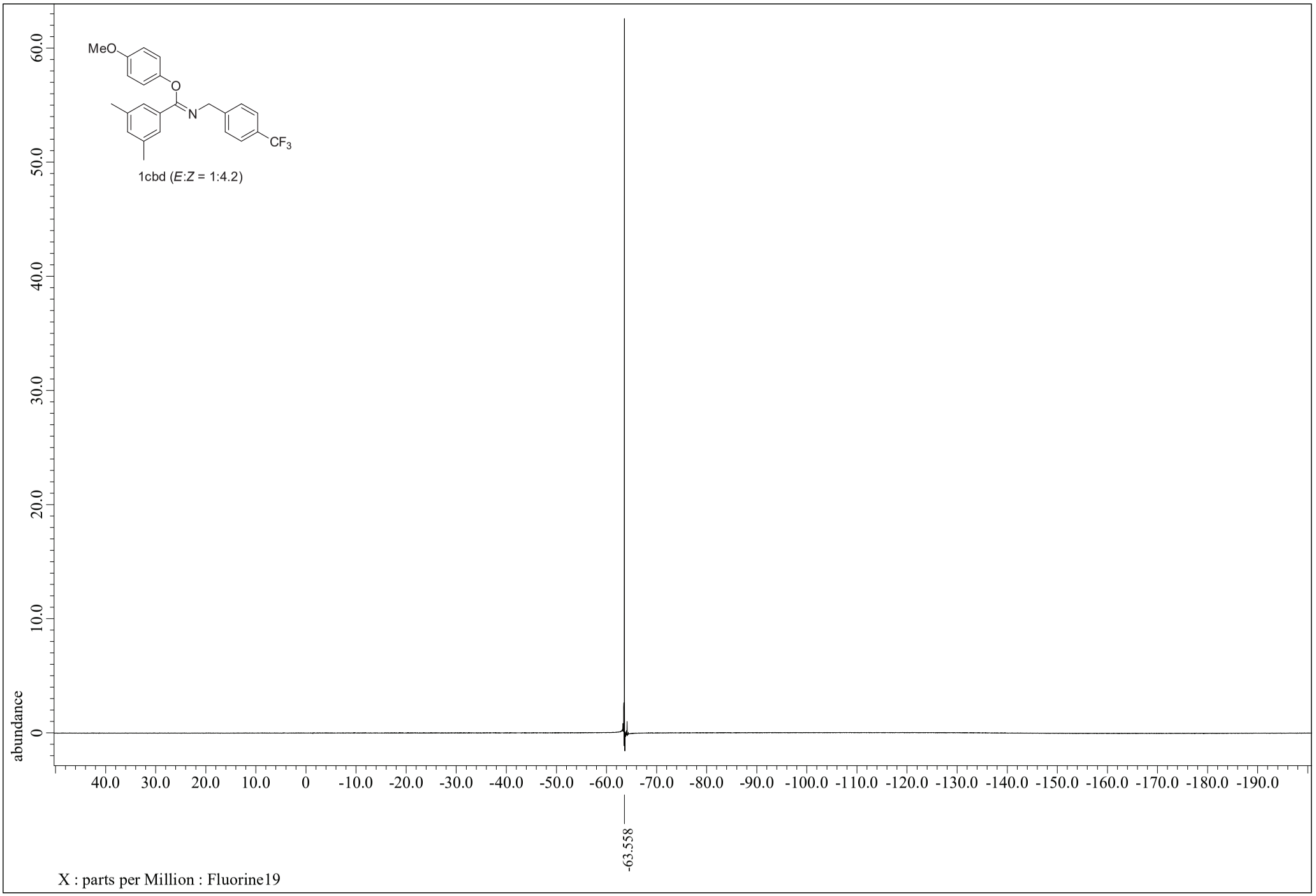


^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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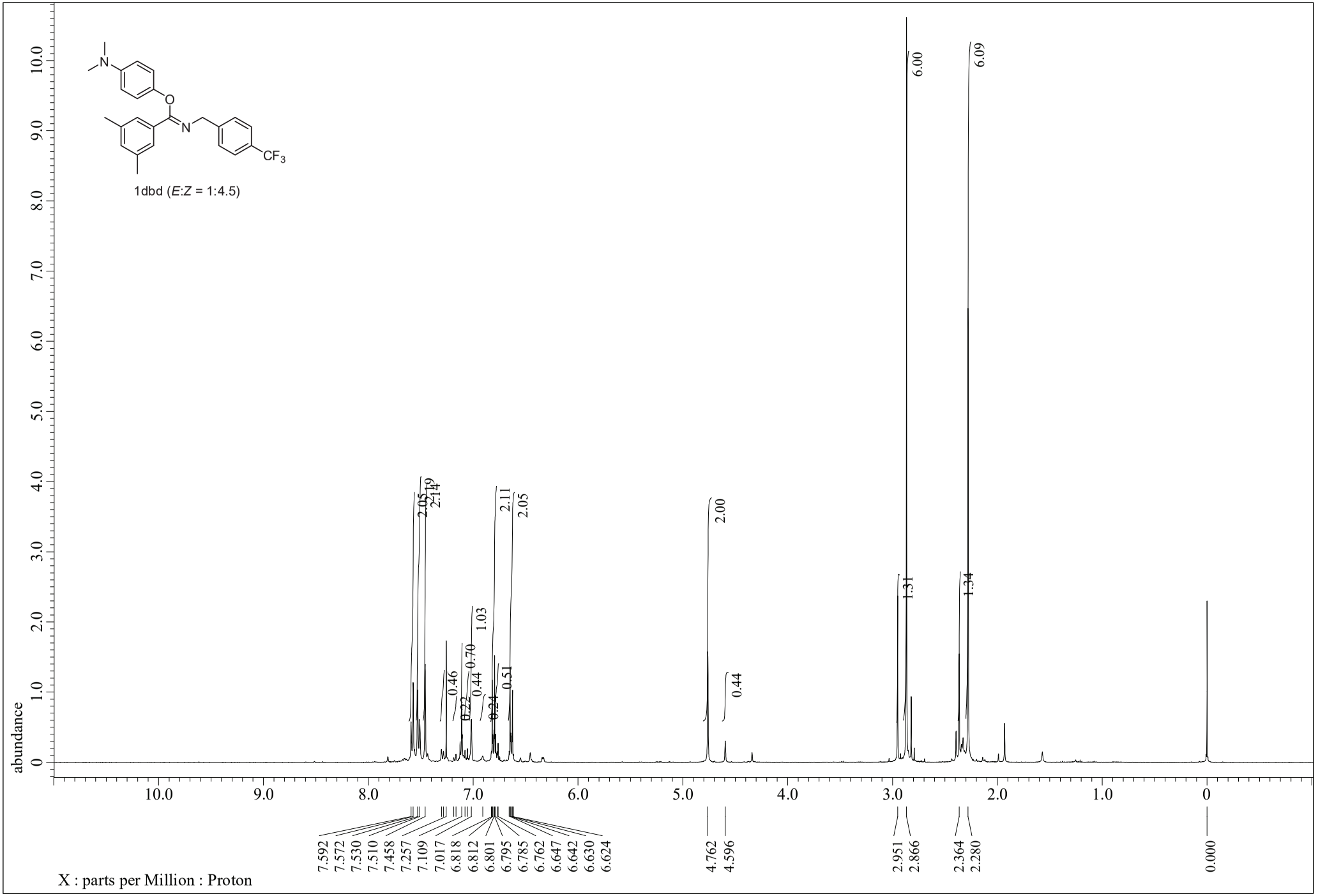

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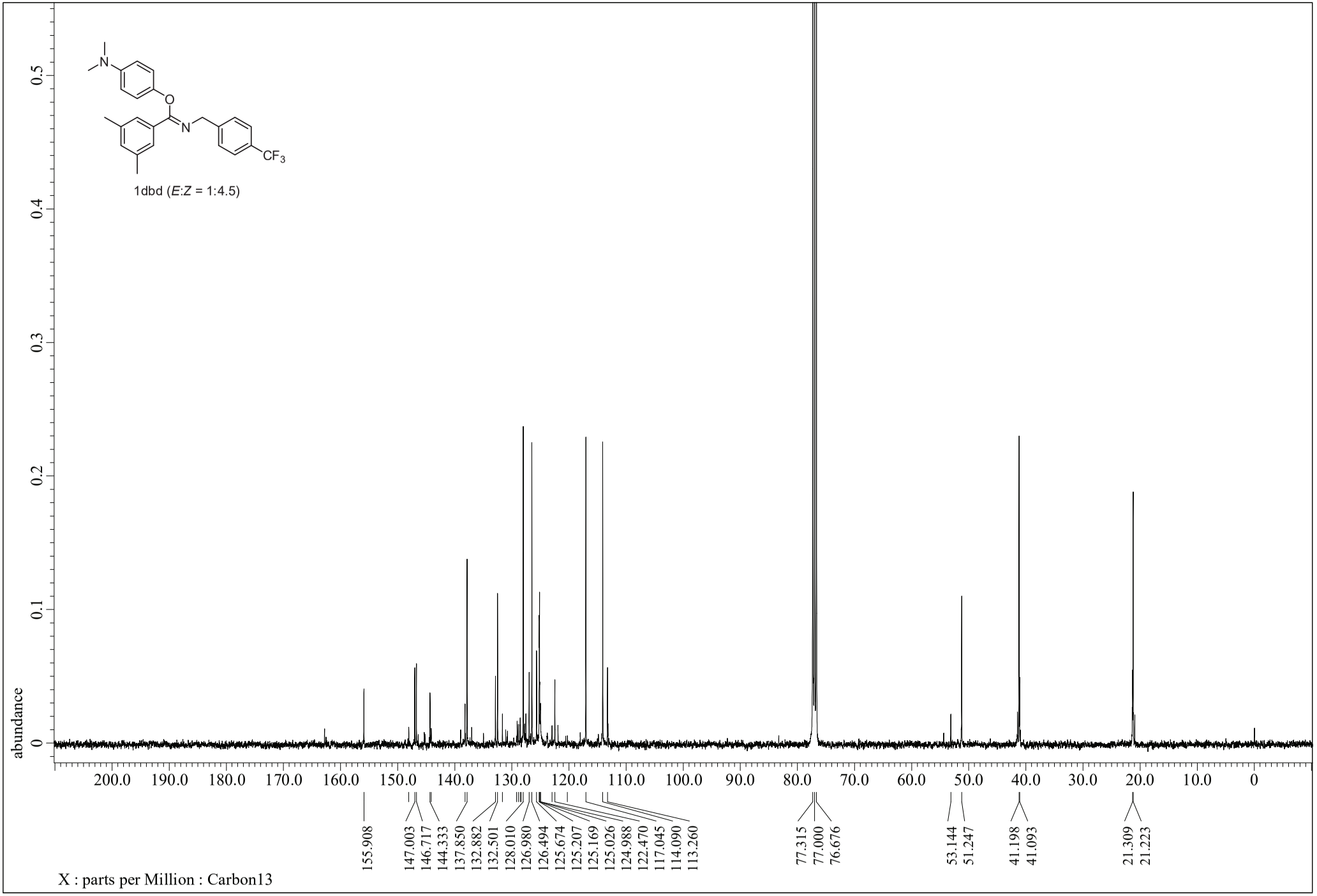

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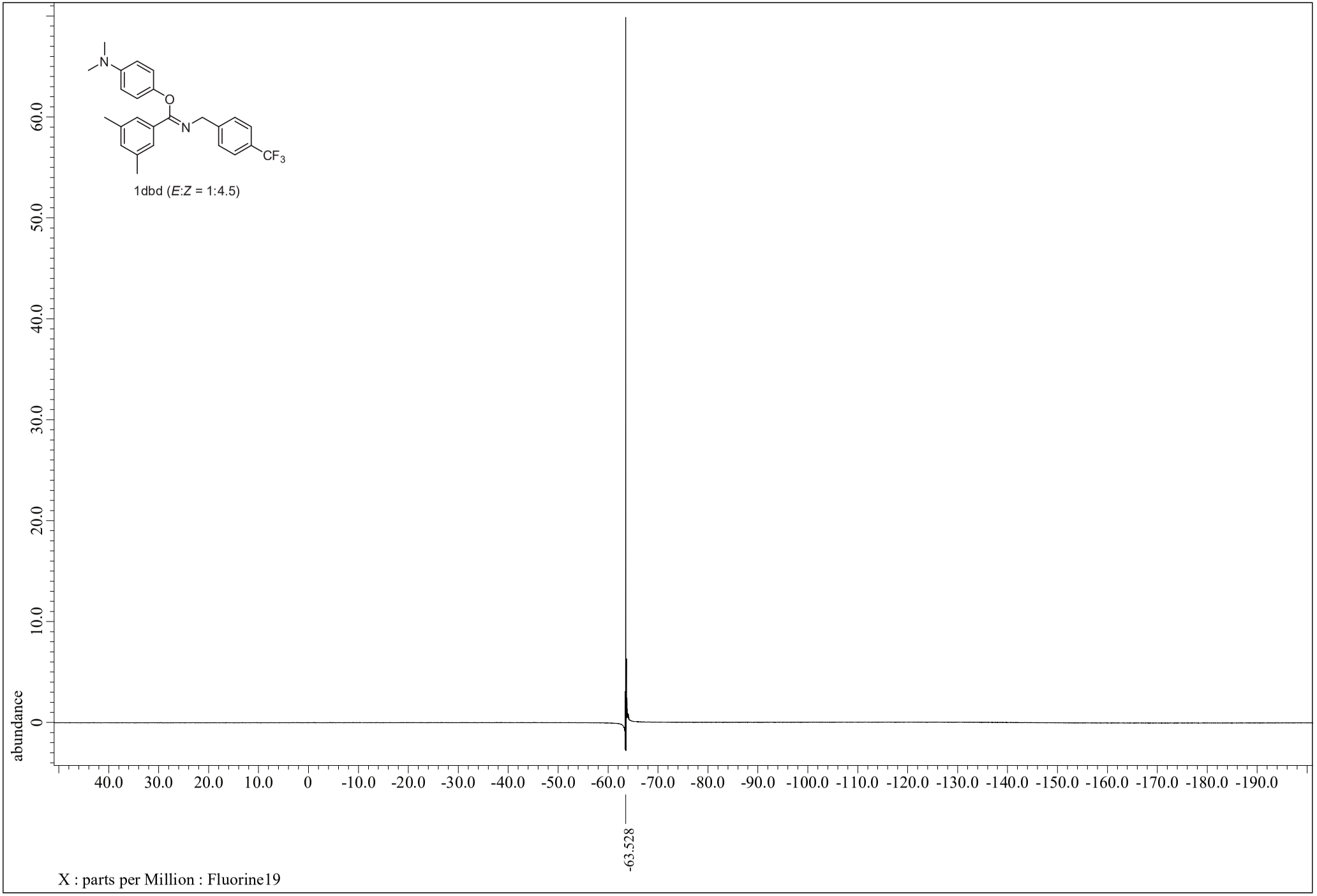
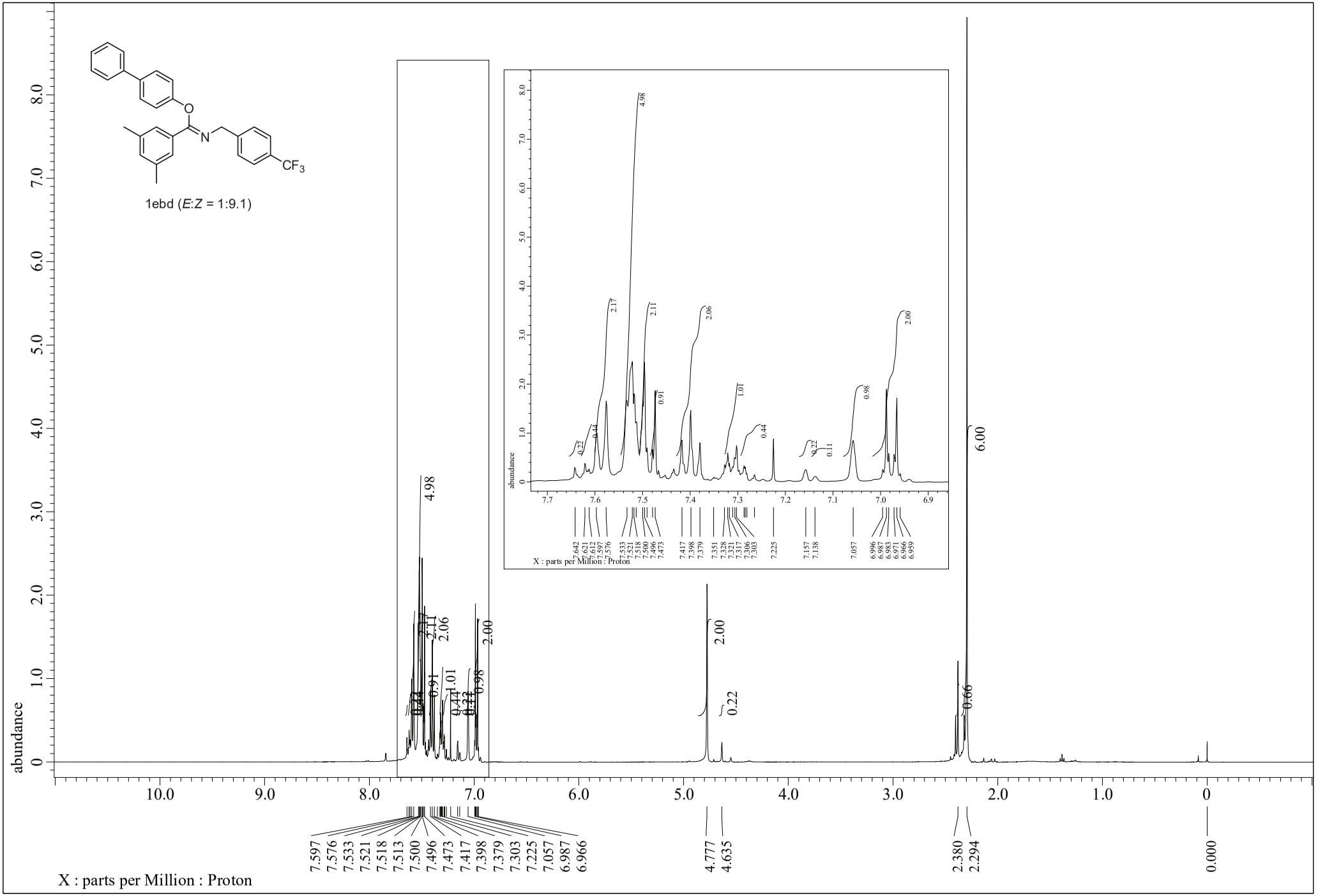


^{1}H NMR (400 MHz, $CDCl_3$)



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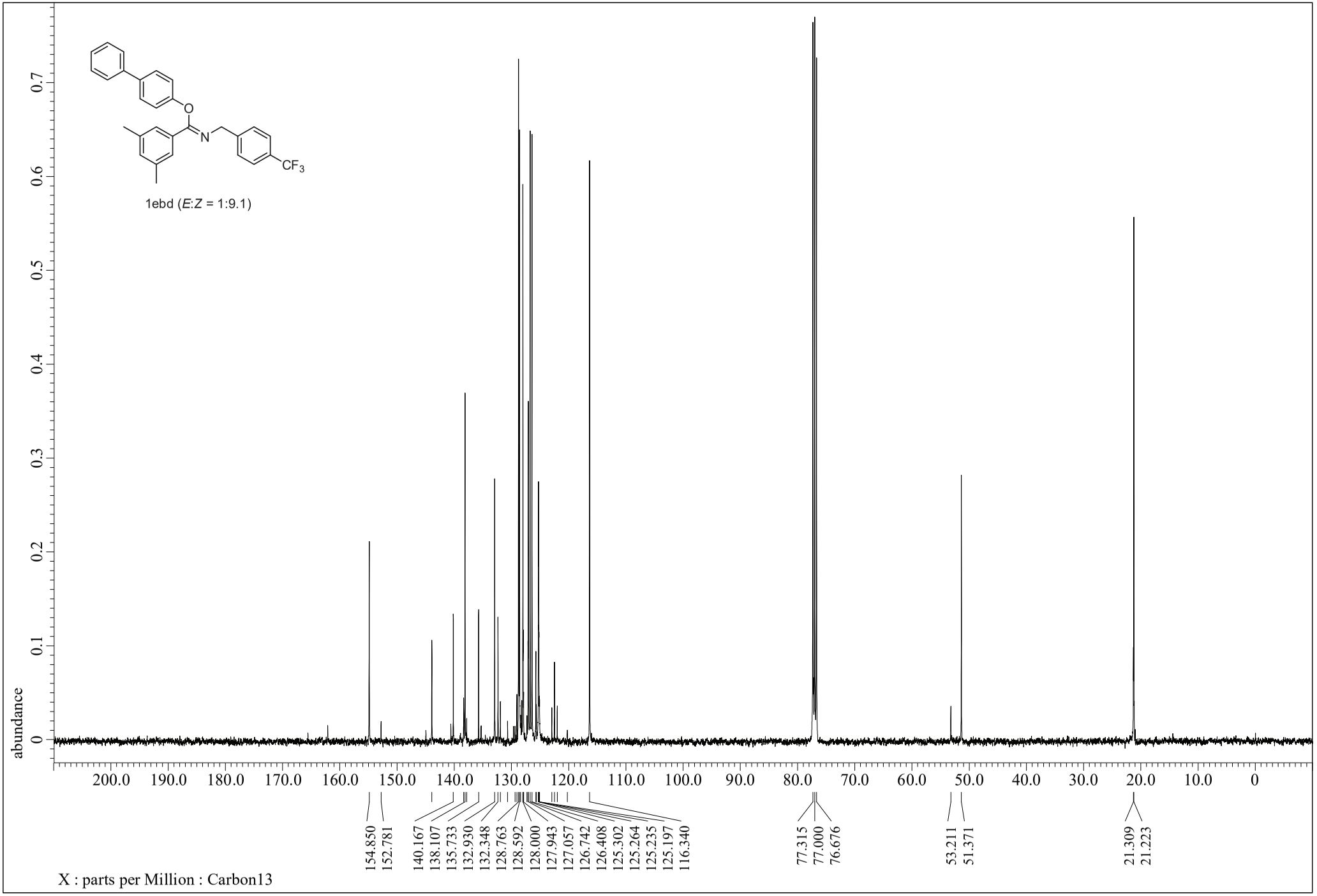

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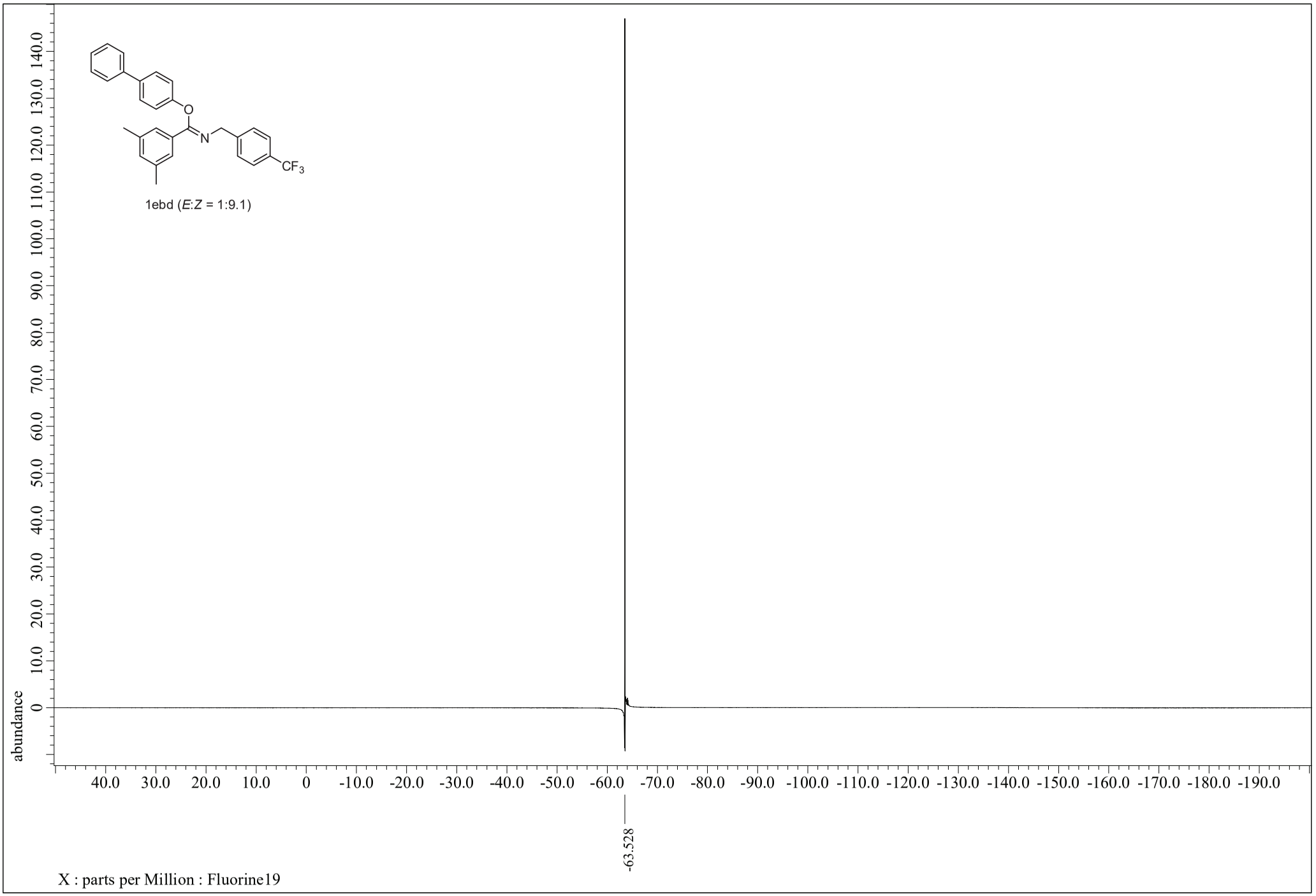

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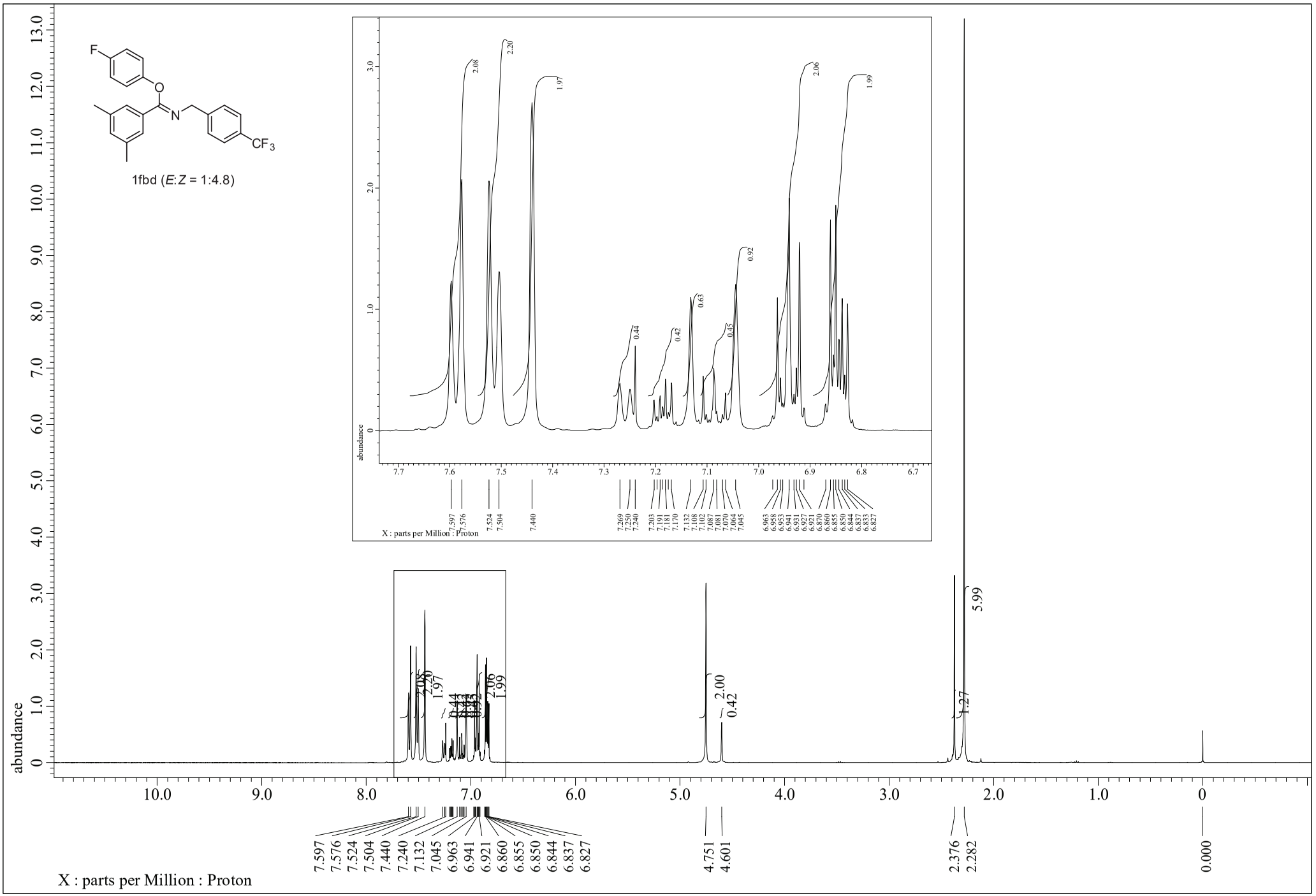
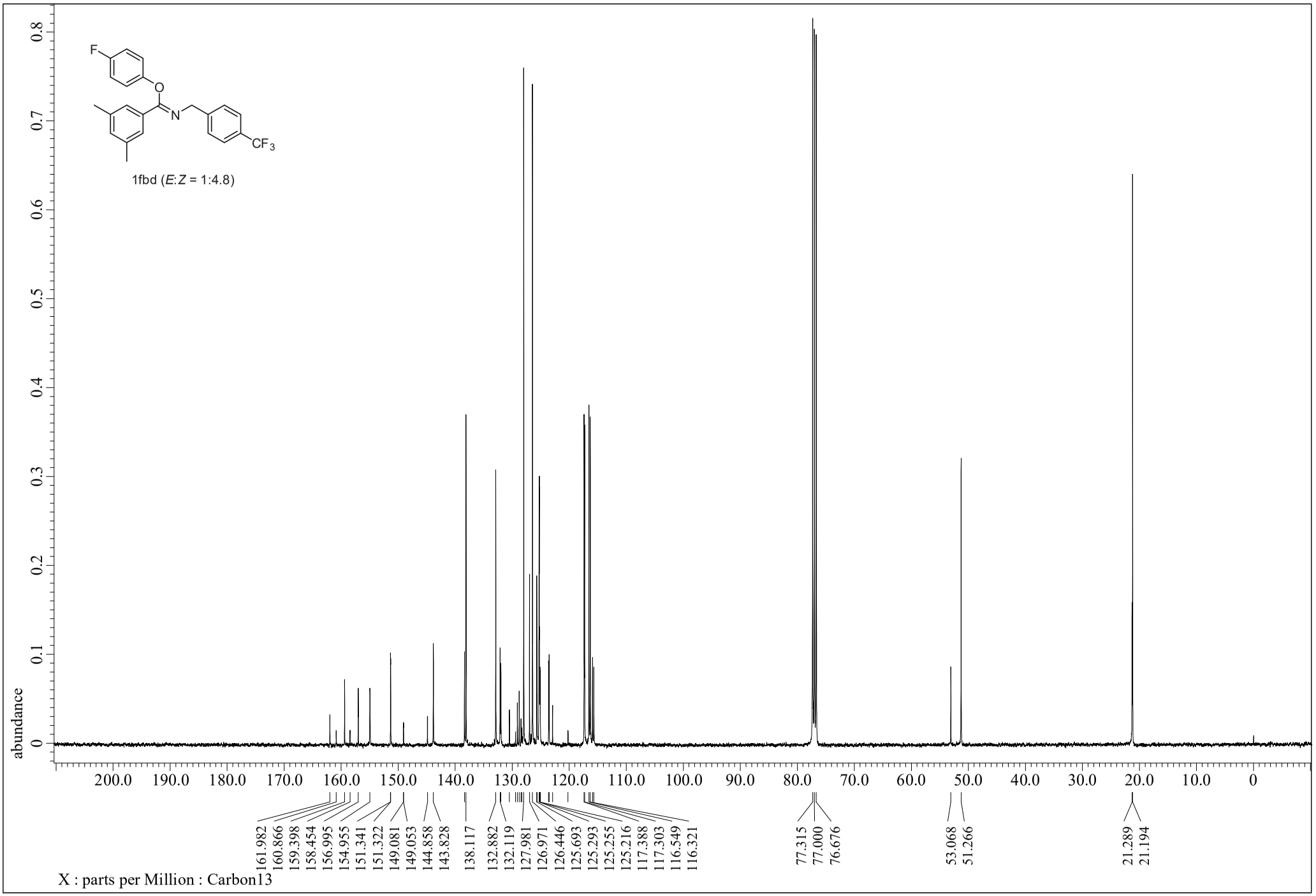
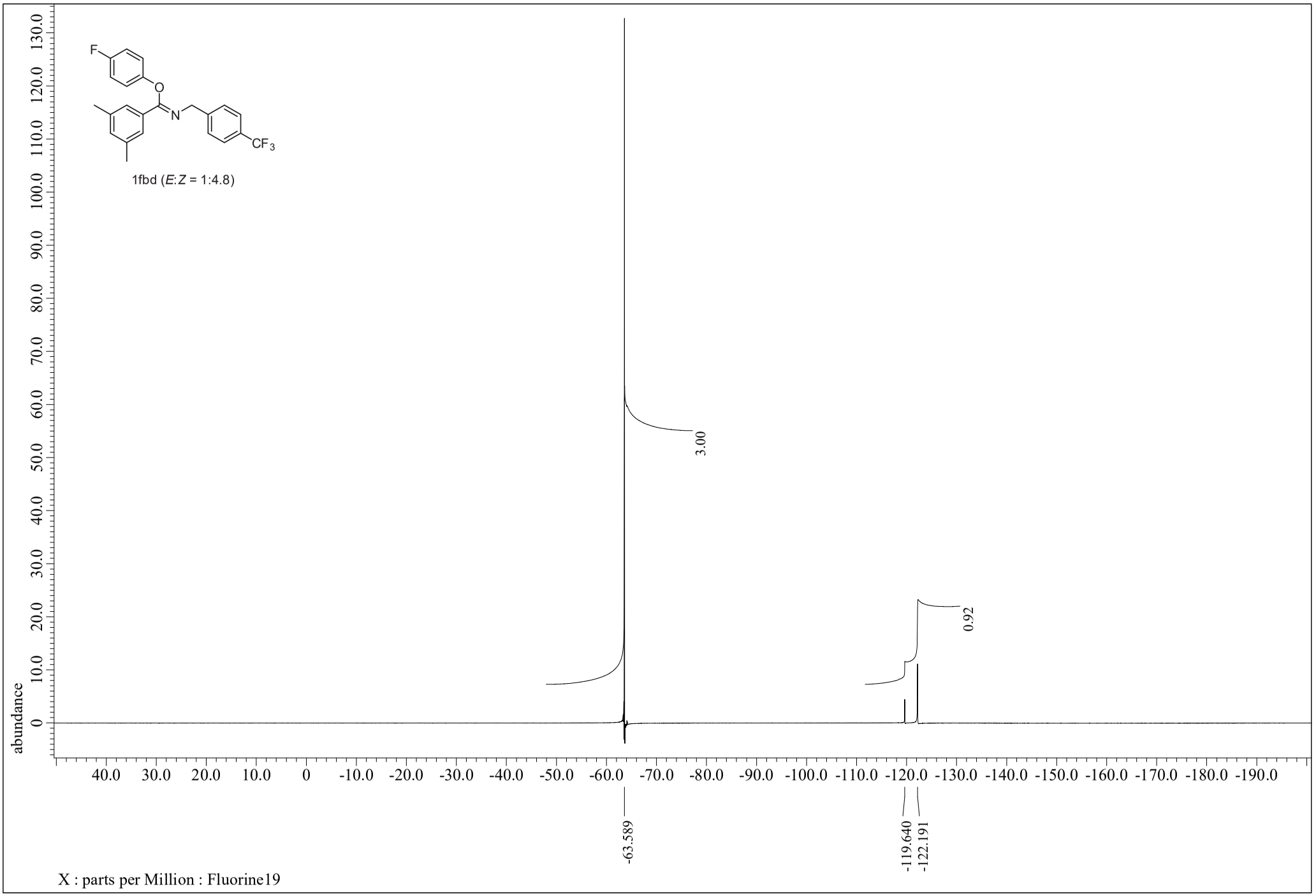


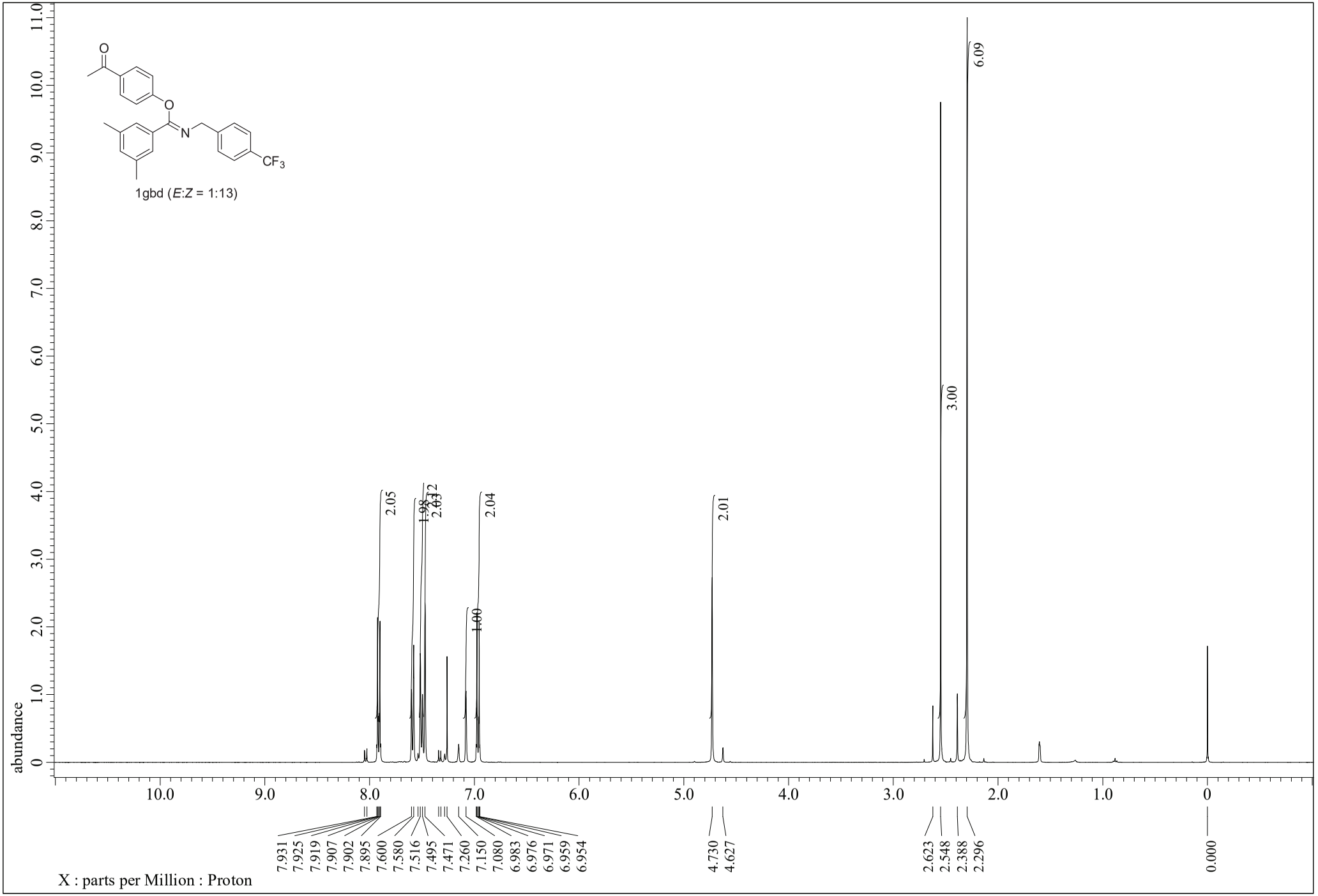
^{13}C NMR (101 MHz, $CDCl_3$)



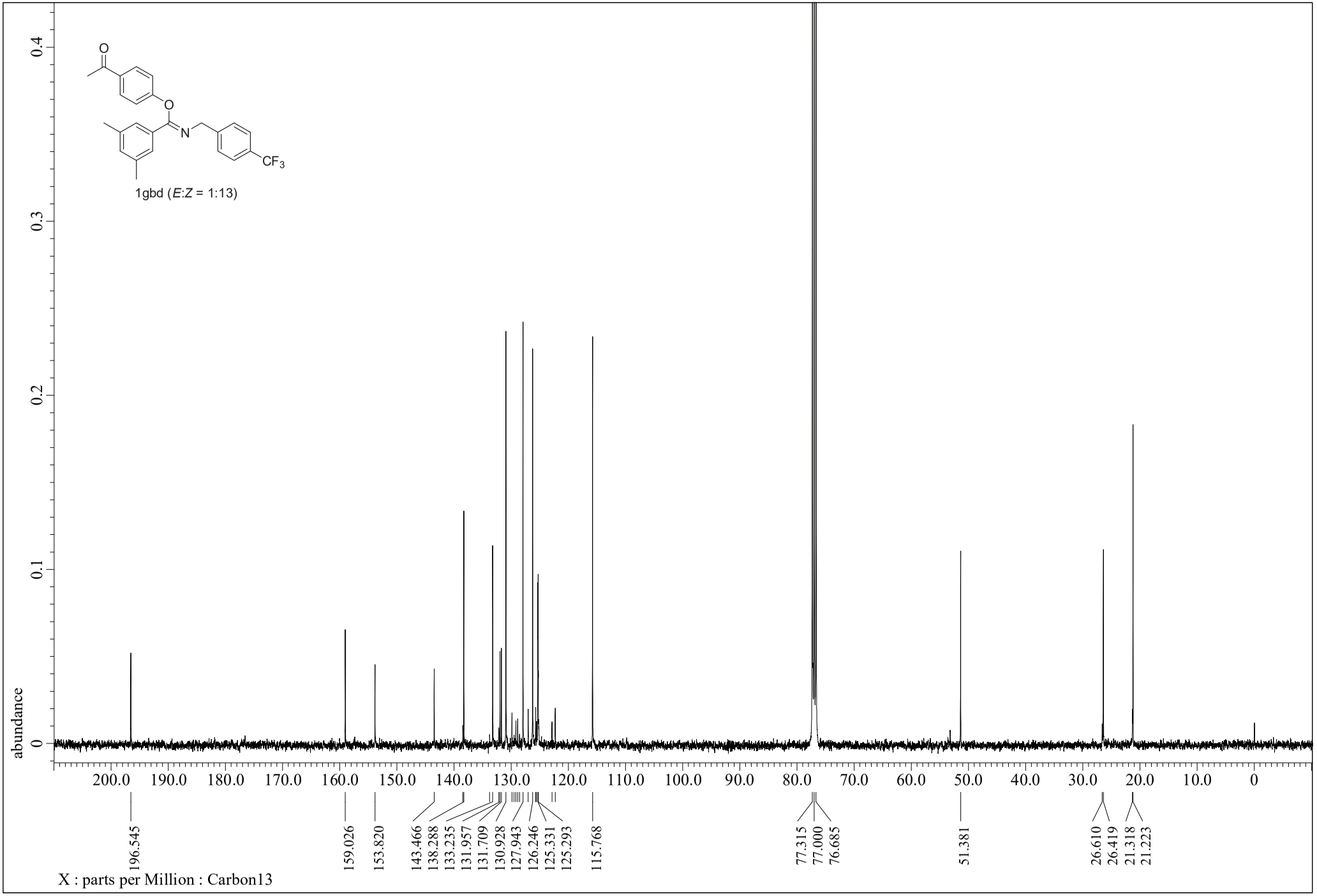
^{19}F NMR (376 MHz, $CDCl_3$)



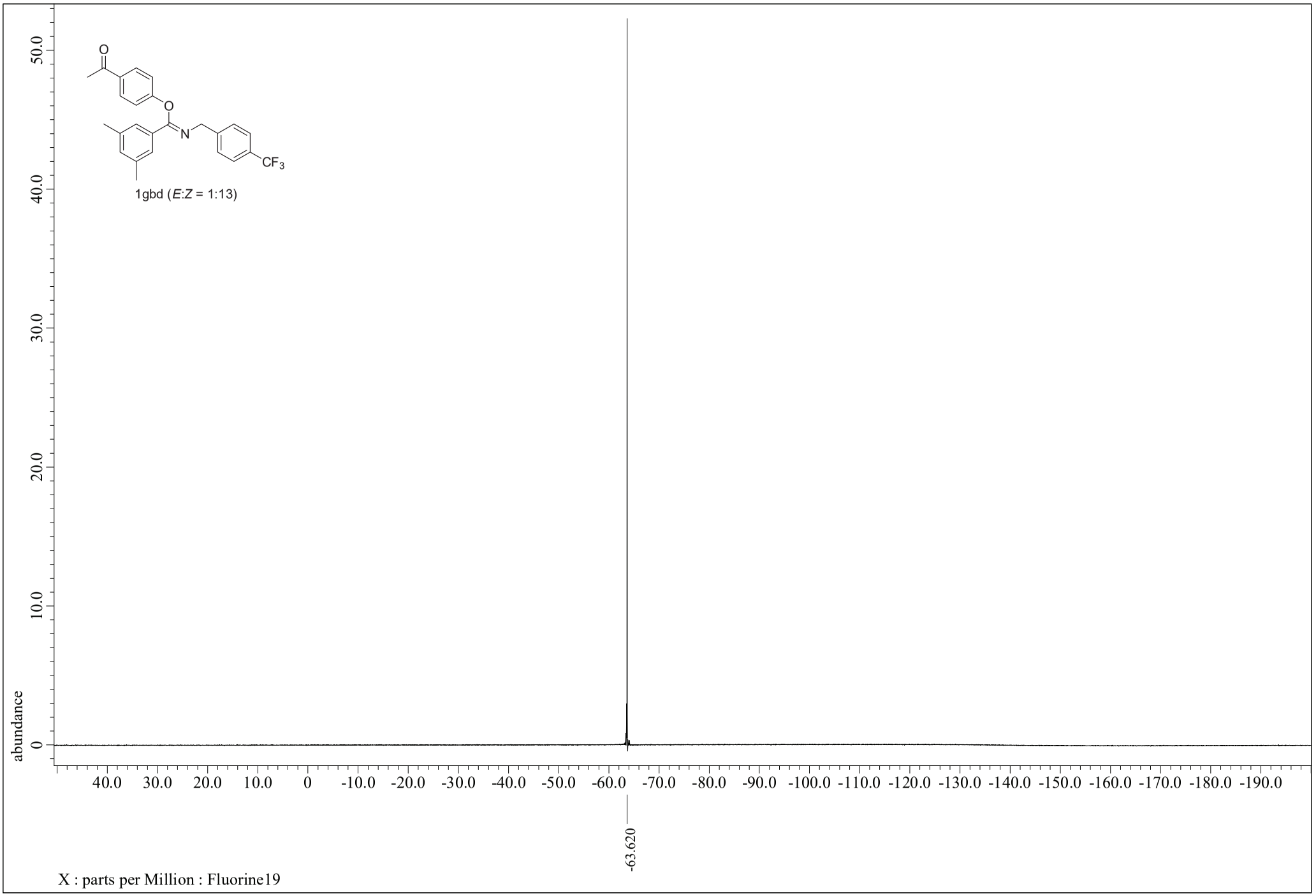
^{1}H NMR (400 MHz, $CDCl_3$)



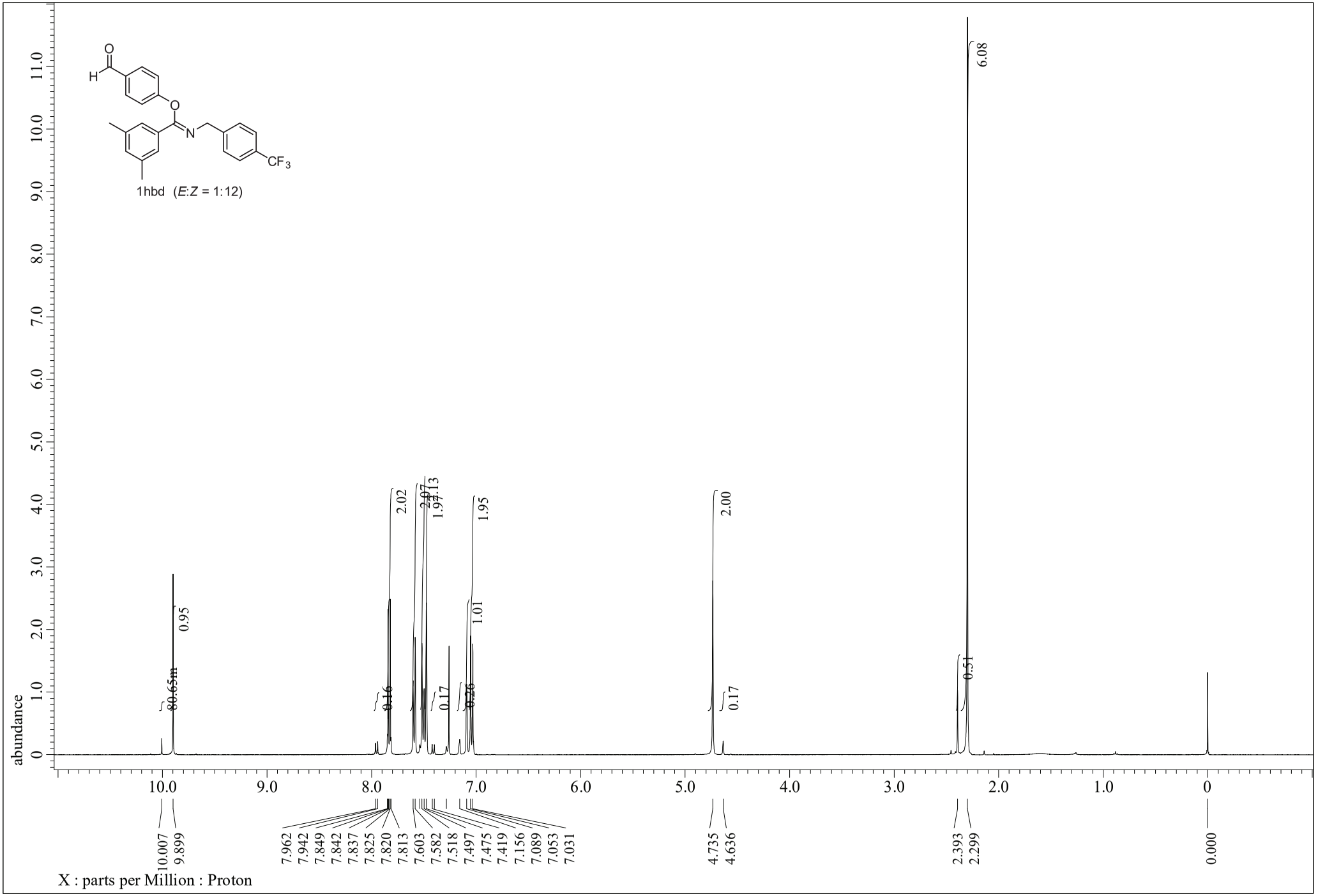
^{13}C NMR (101 MHz, $CDCl_3$)



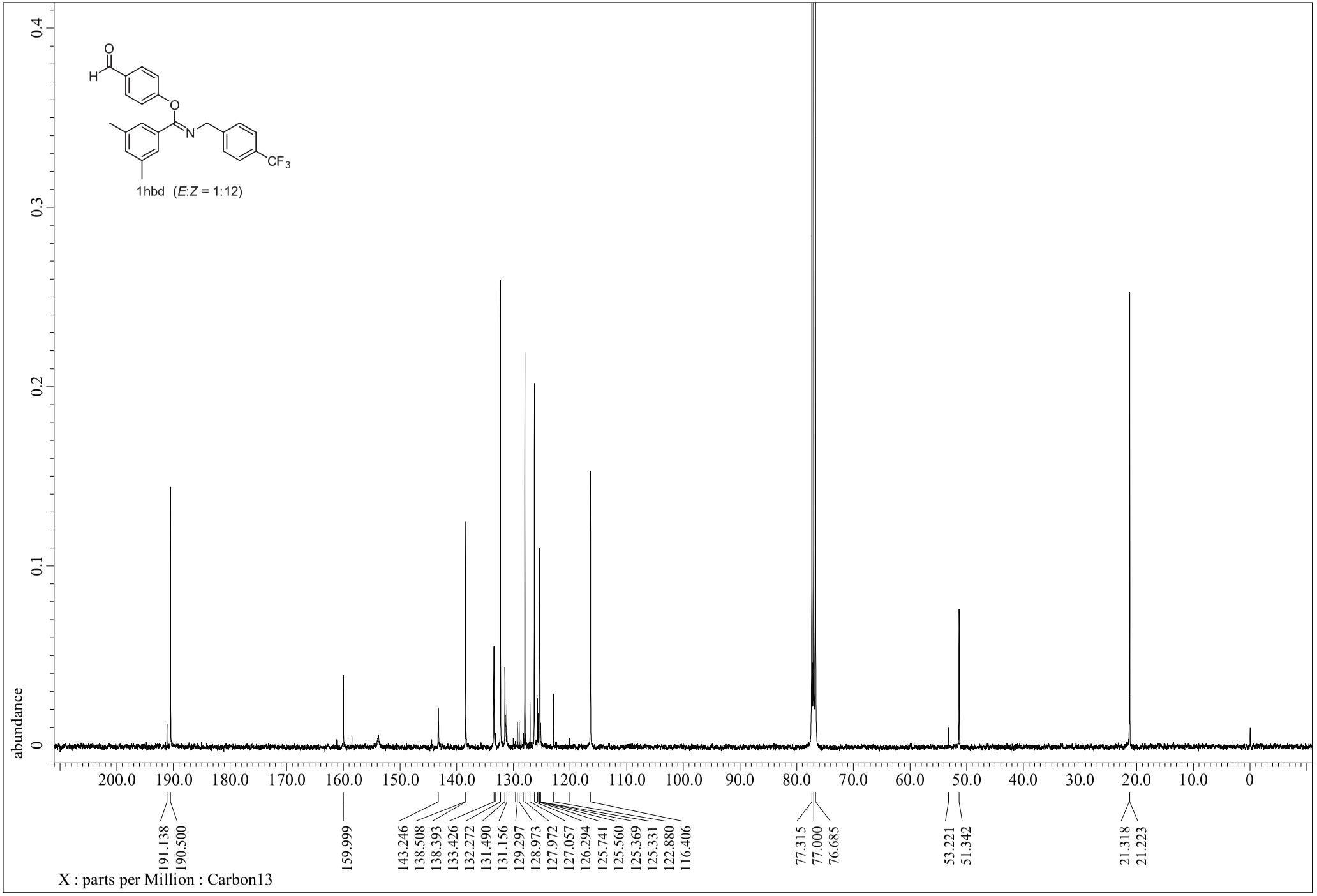
^{19}F NMR (376 MHz, $CDCl_3$)



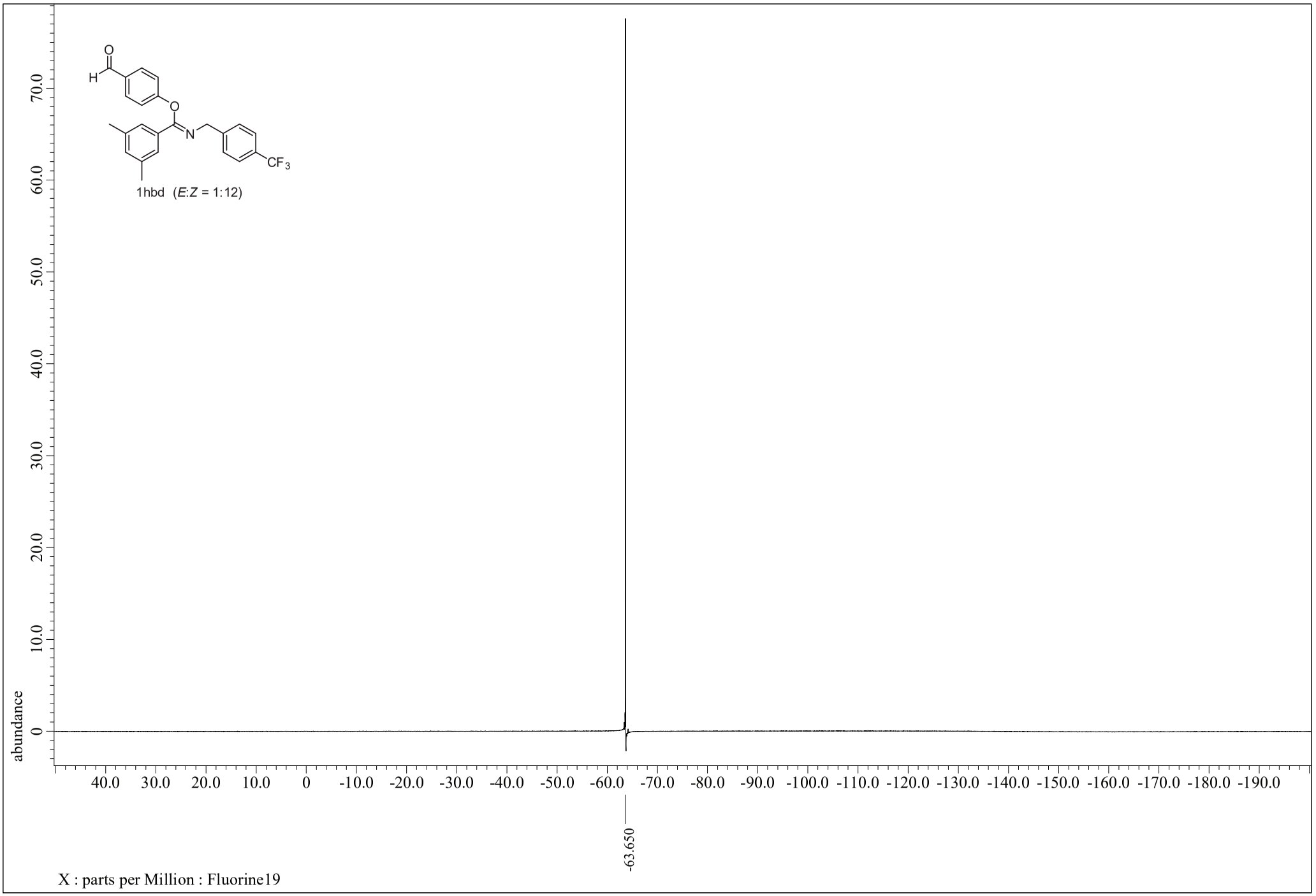
^{1}H NMR (400 MHz, $CDCl_3$)



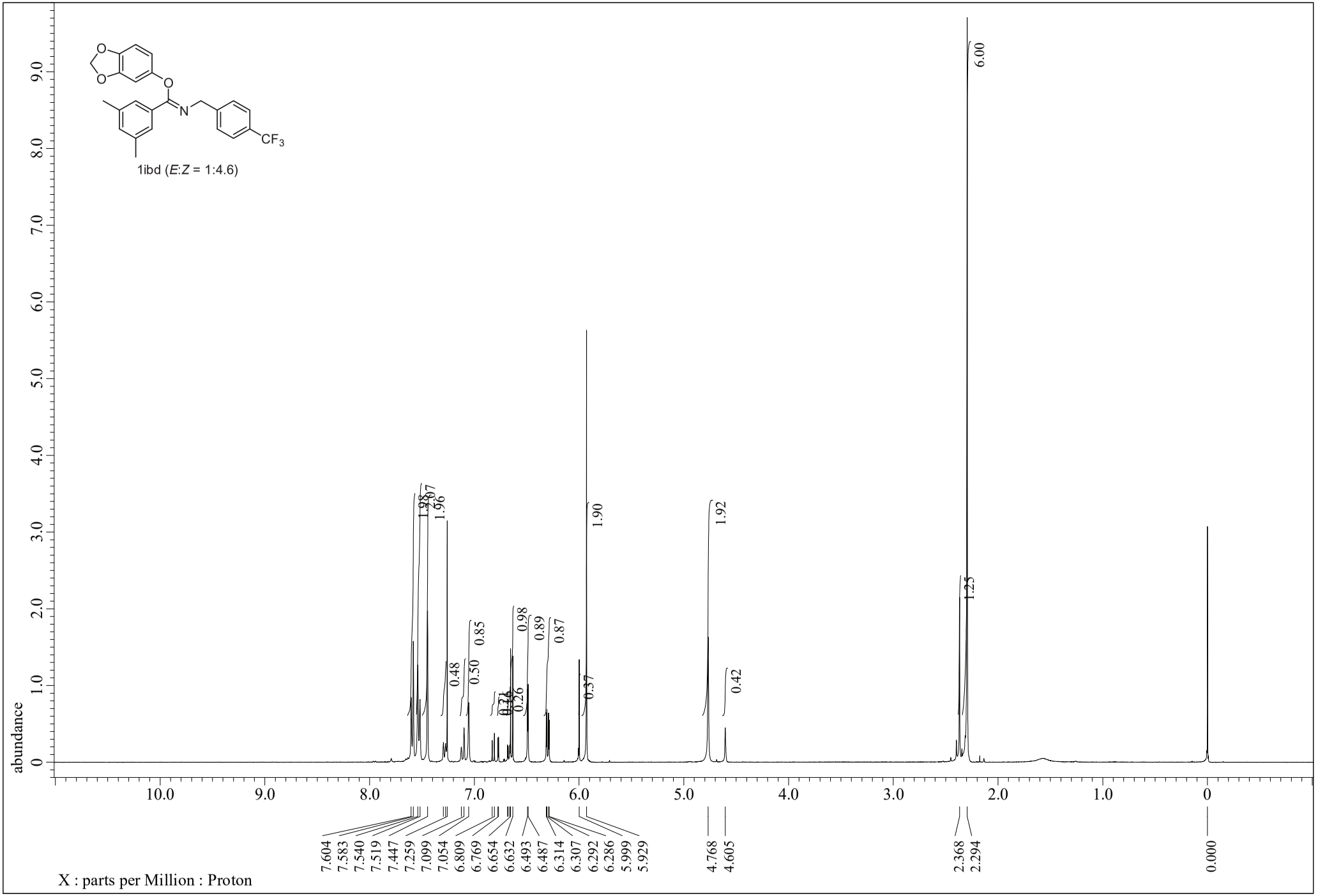
^{13}C NMR (101 MHz, $CDCl_3$)



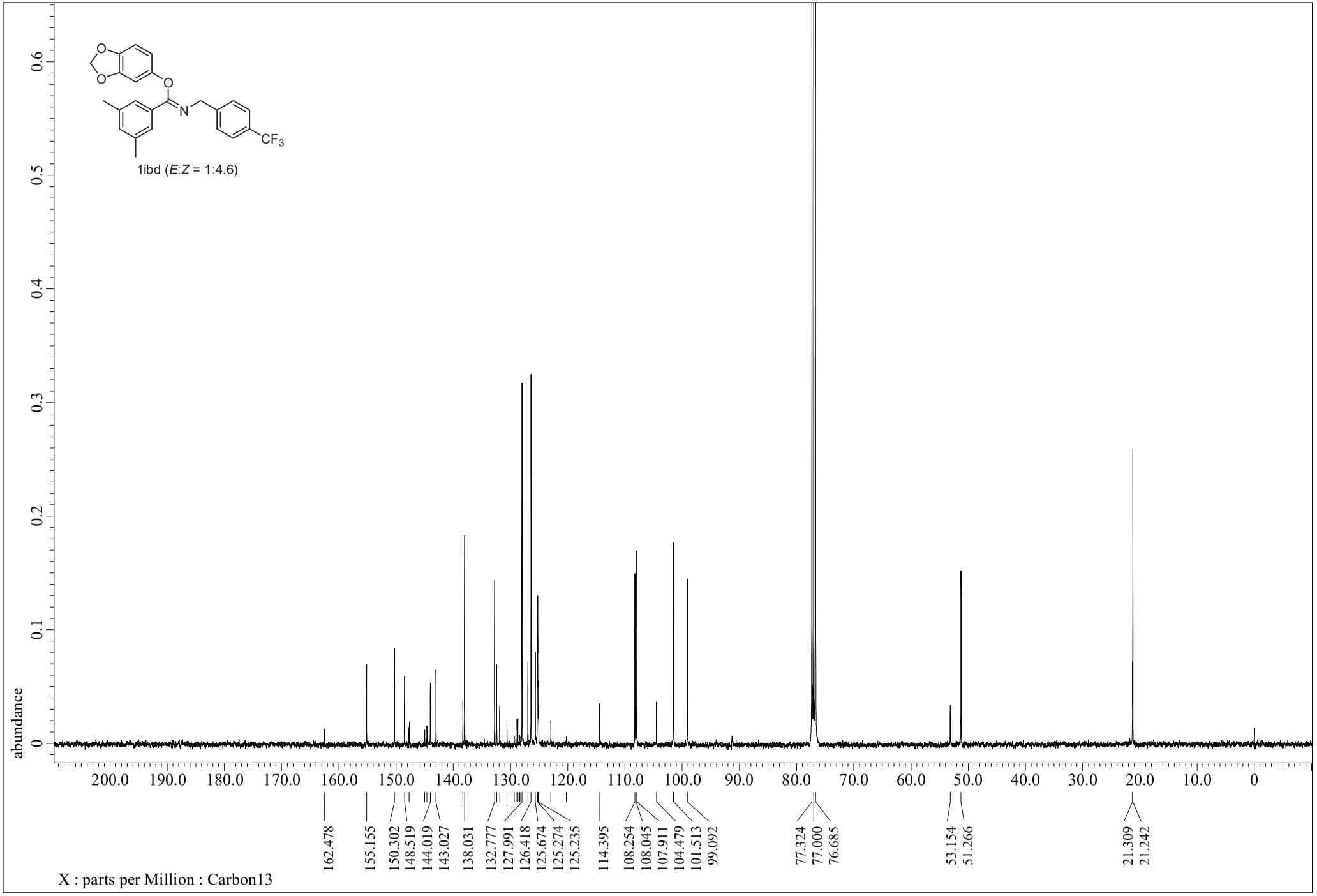
^{19}F NMR (376 MHz, $CDCl_3$)



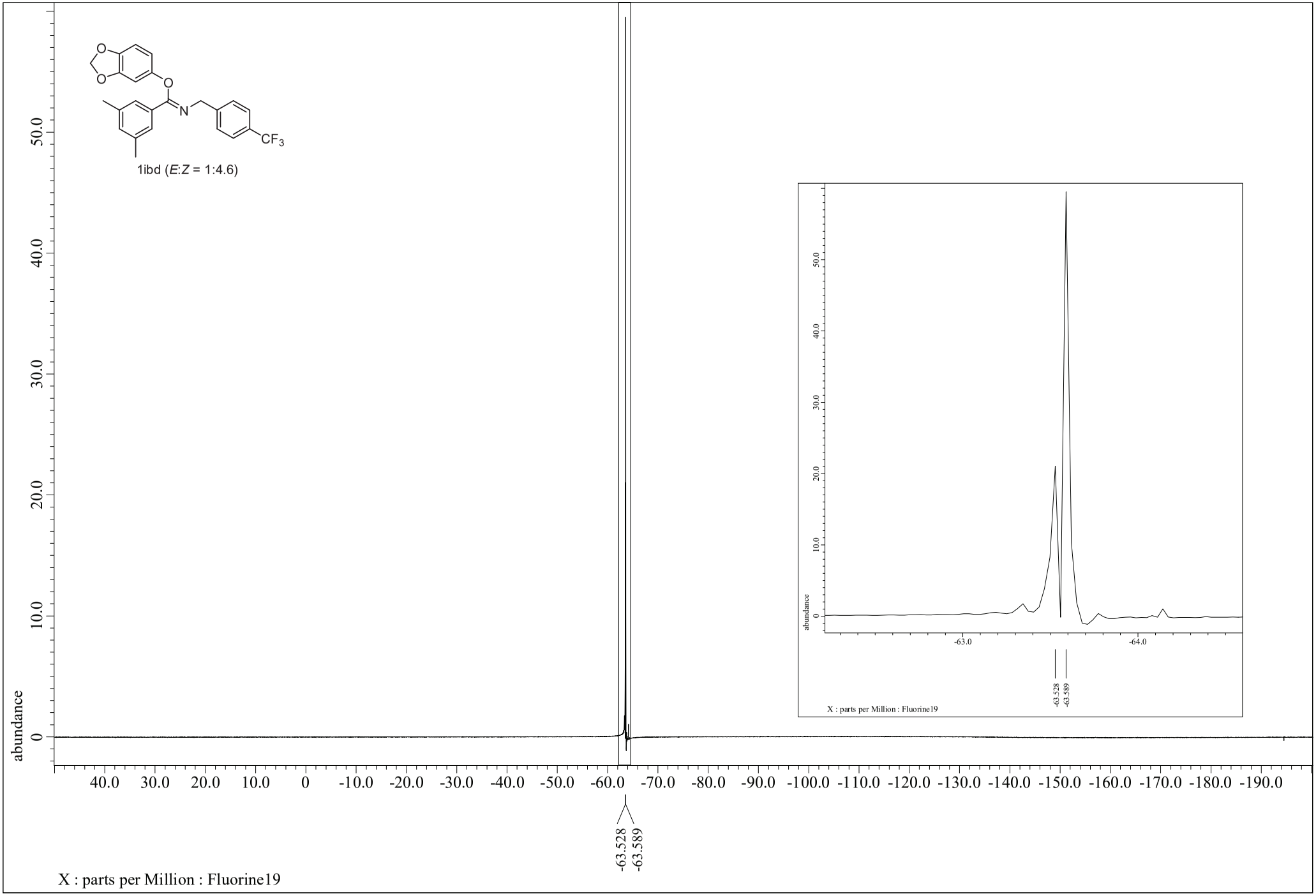
^{1}H NMR (400 MHz, $CDCl_3$)



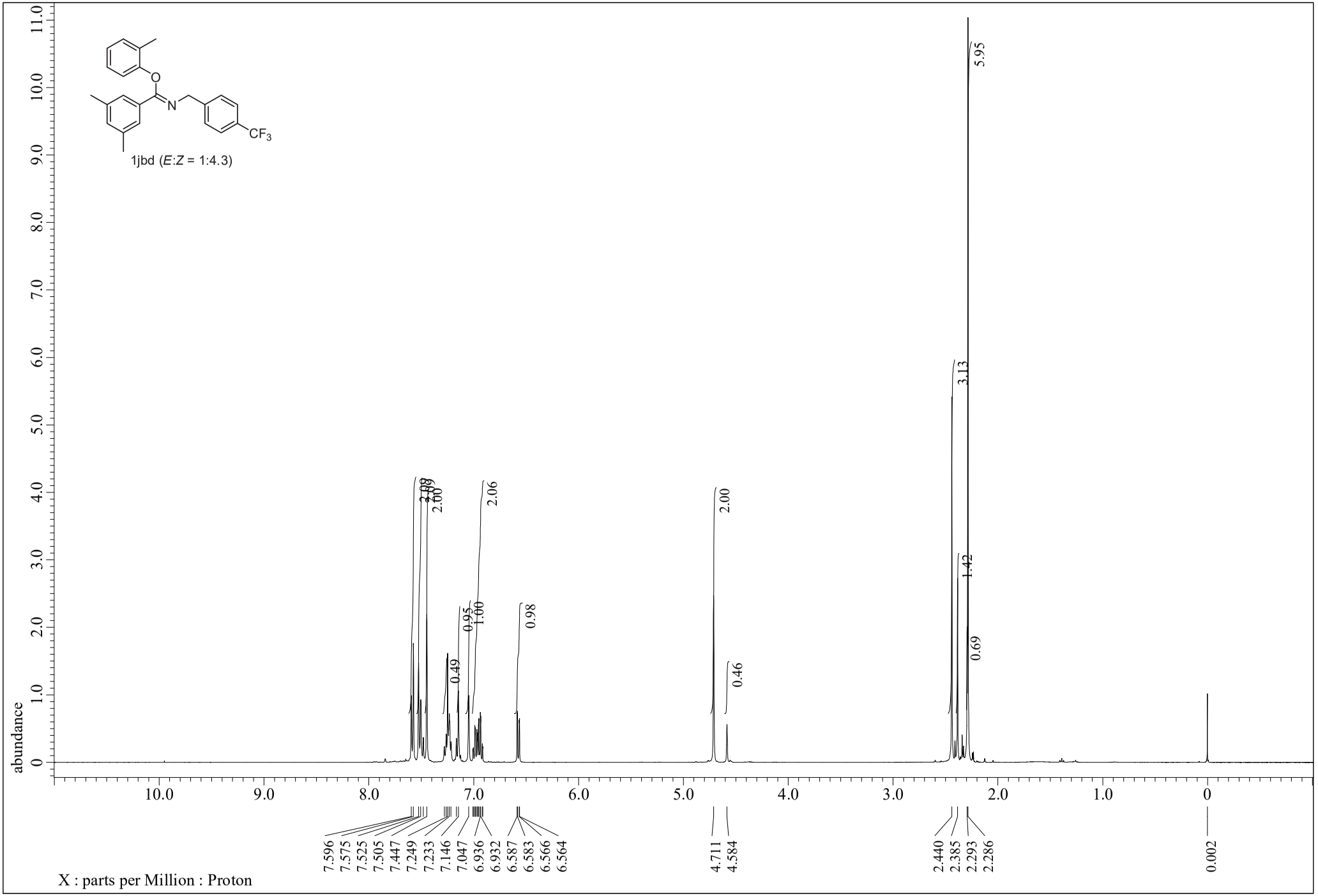
^{13}C NMR (101 MHz, $CDCl_3$)



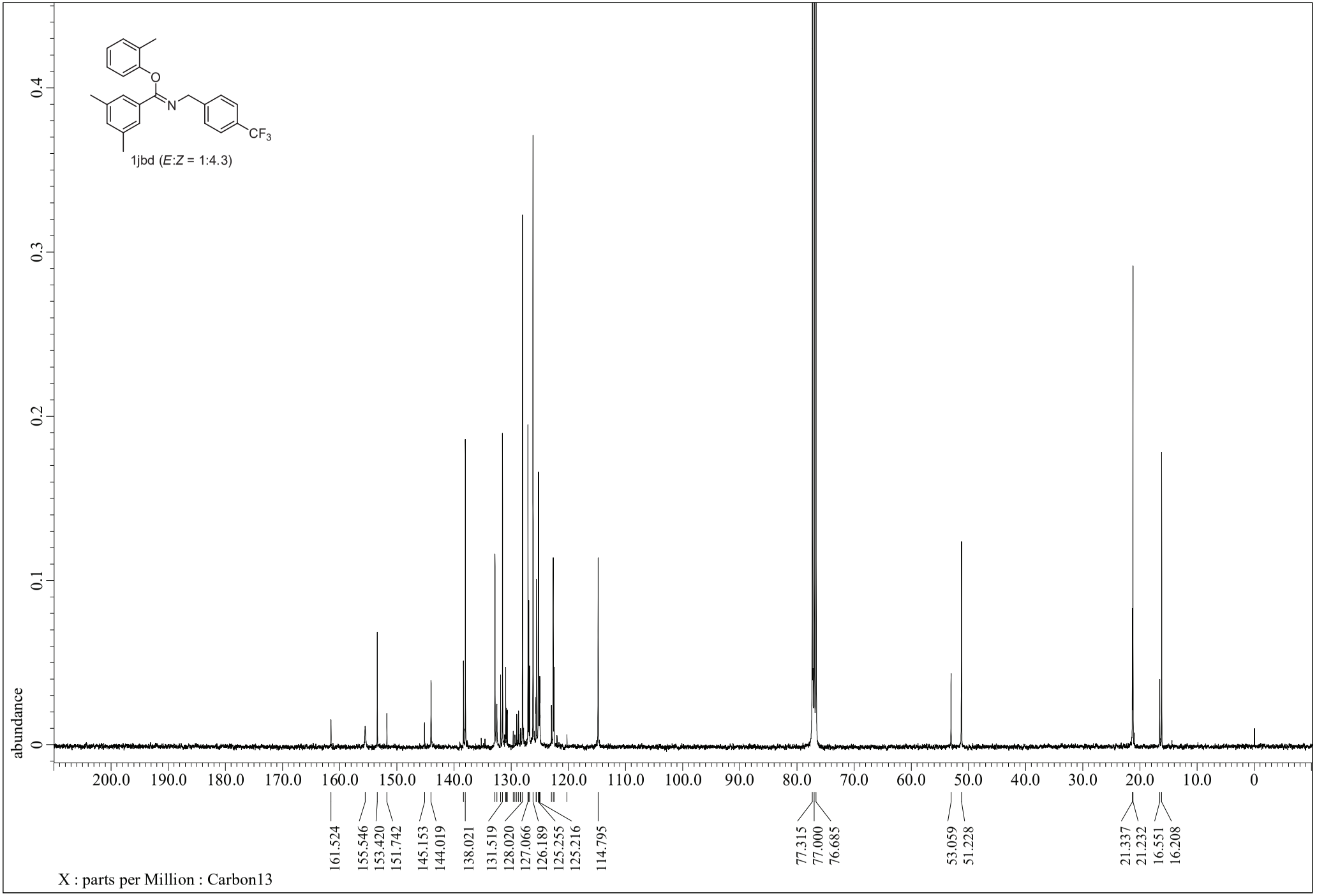
^{19}F NMR (376 MHz, $CDCl_3$)



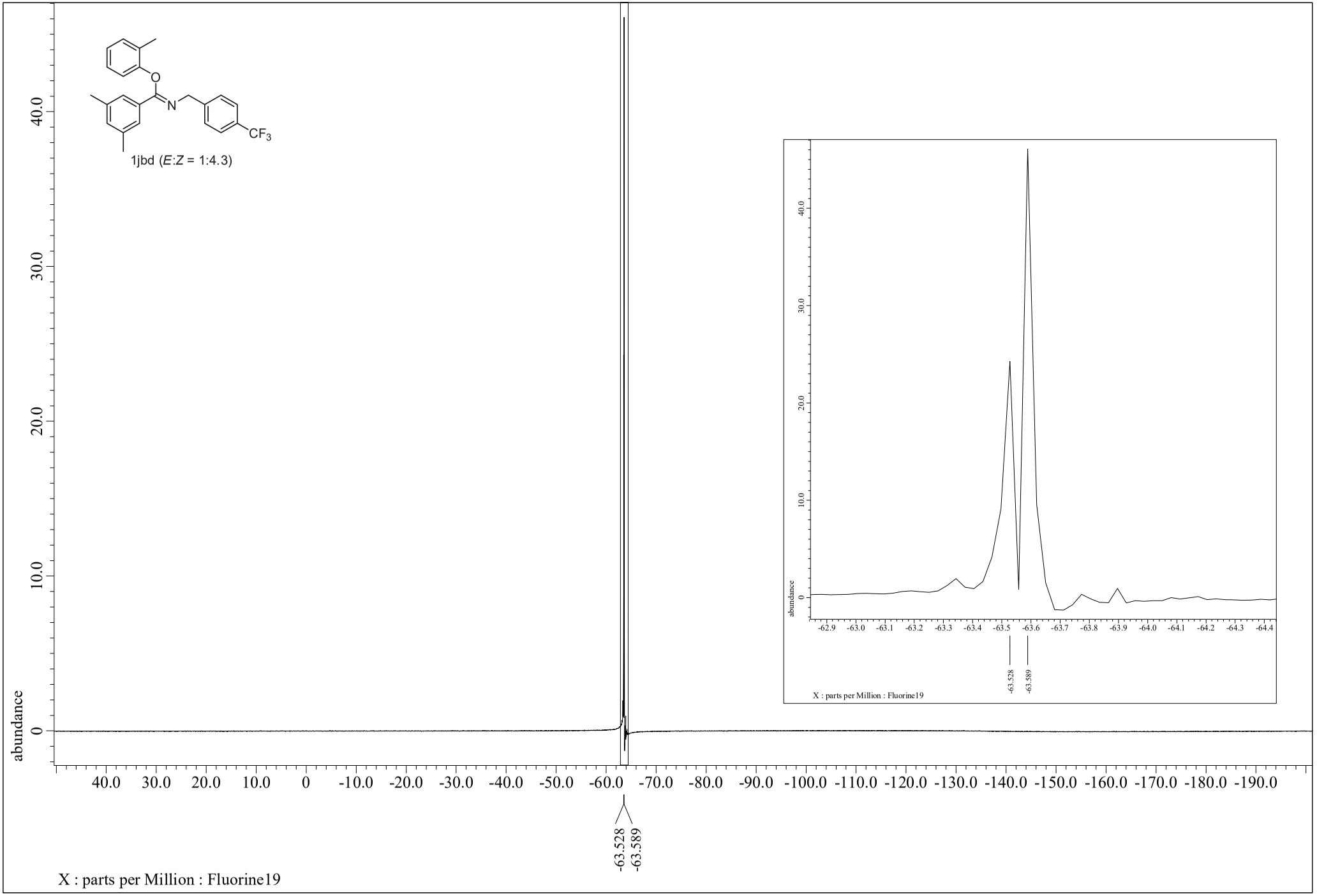
^{1}H NMR (400 MHz, $CDCl_3$)



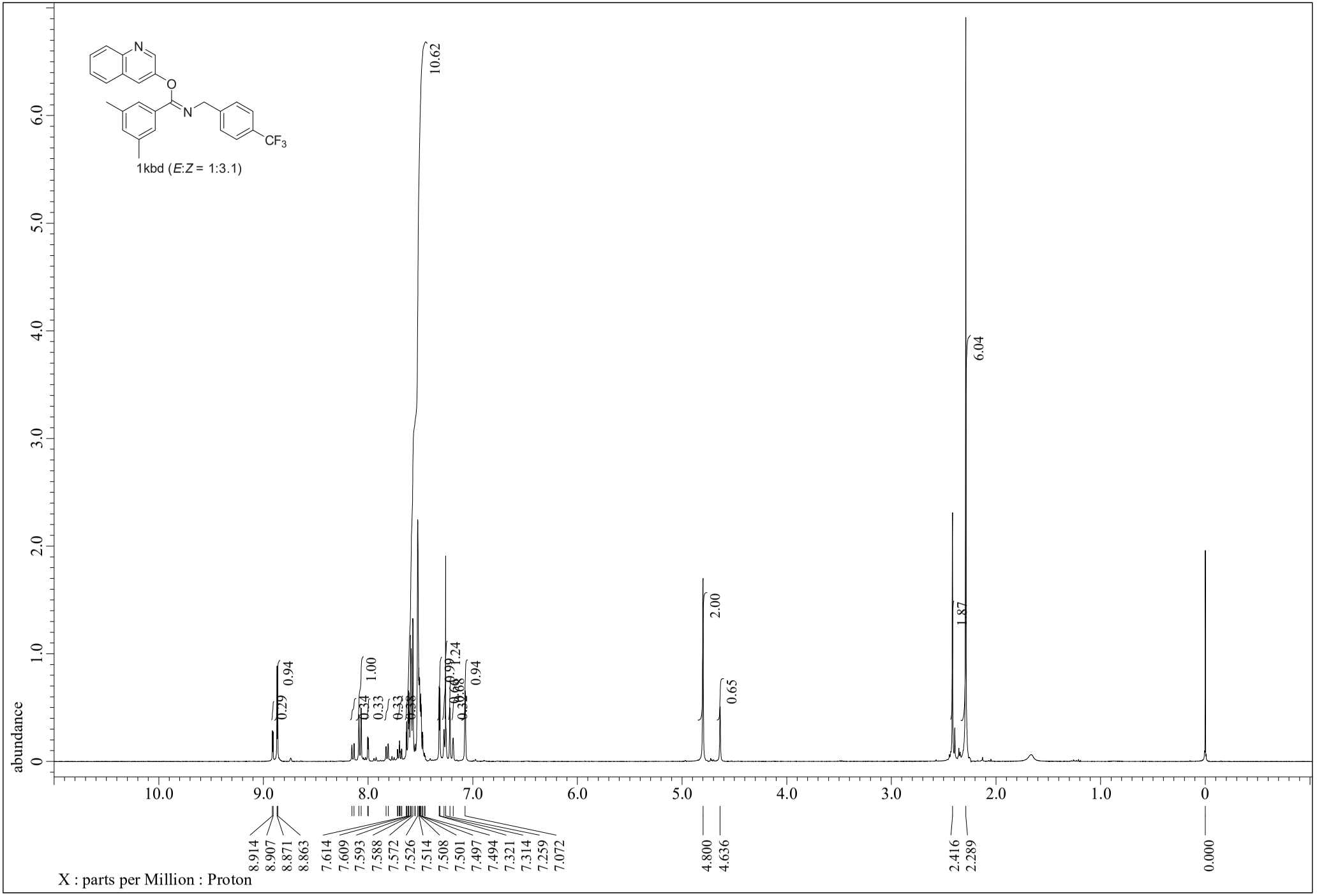
^{13}C NMR (101 MHz, $CDCl_3$)



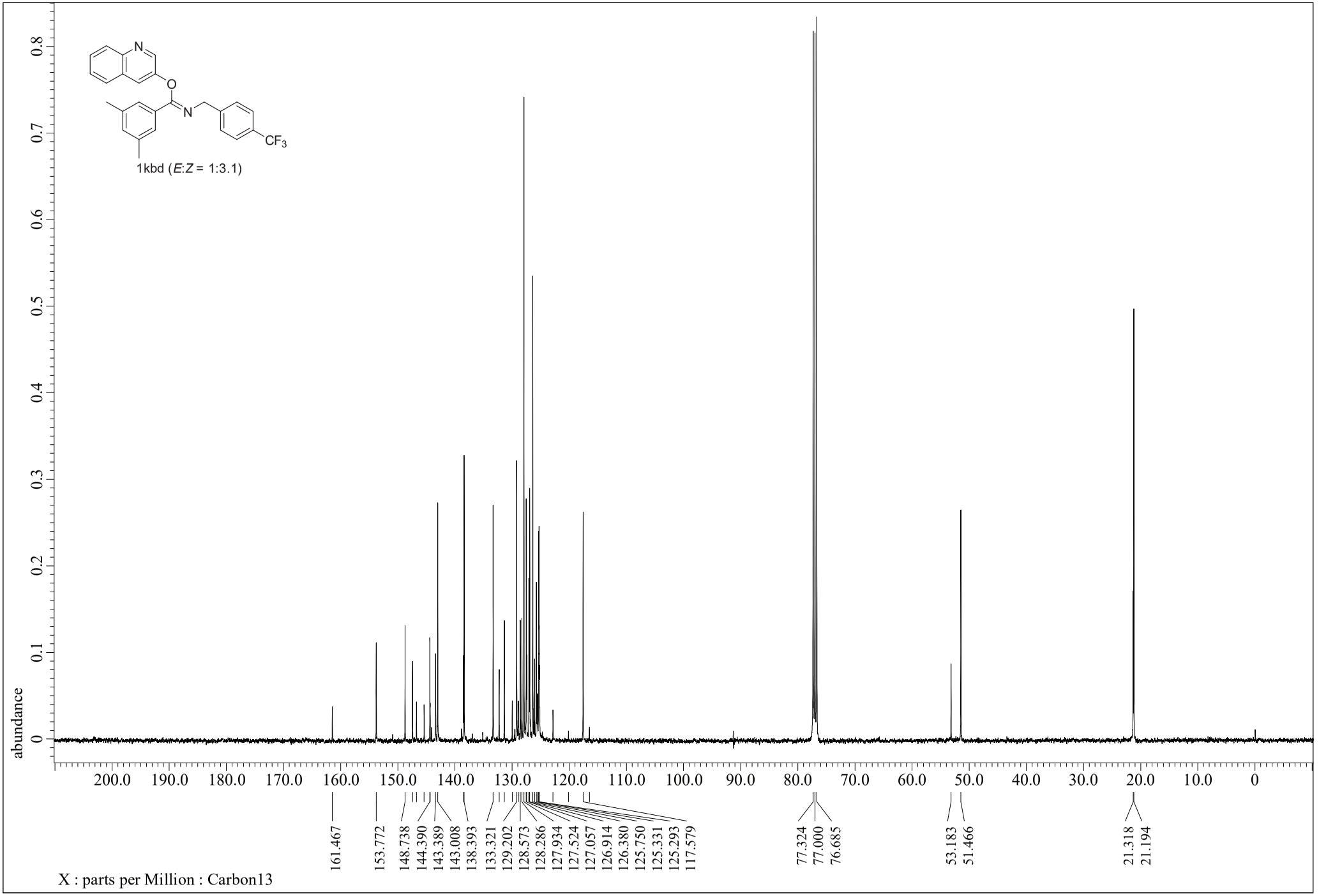
^{19}F NMR (376 MHz, $CDCl_3$)



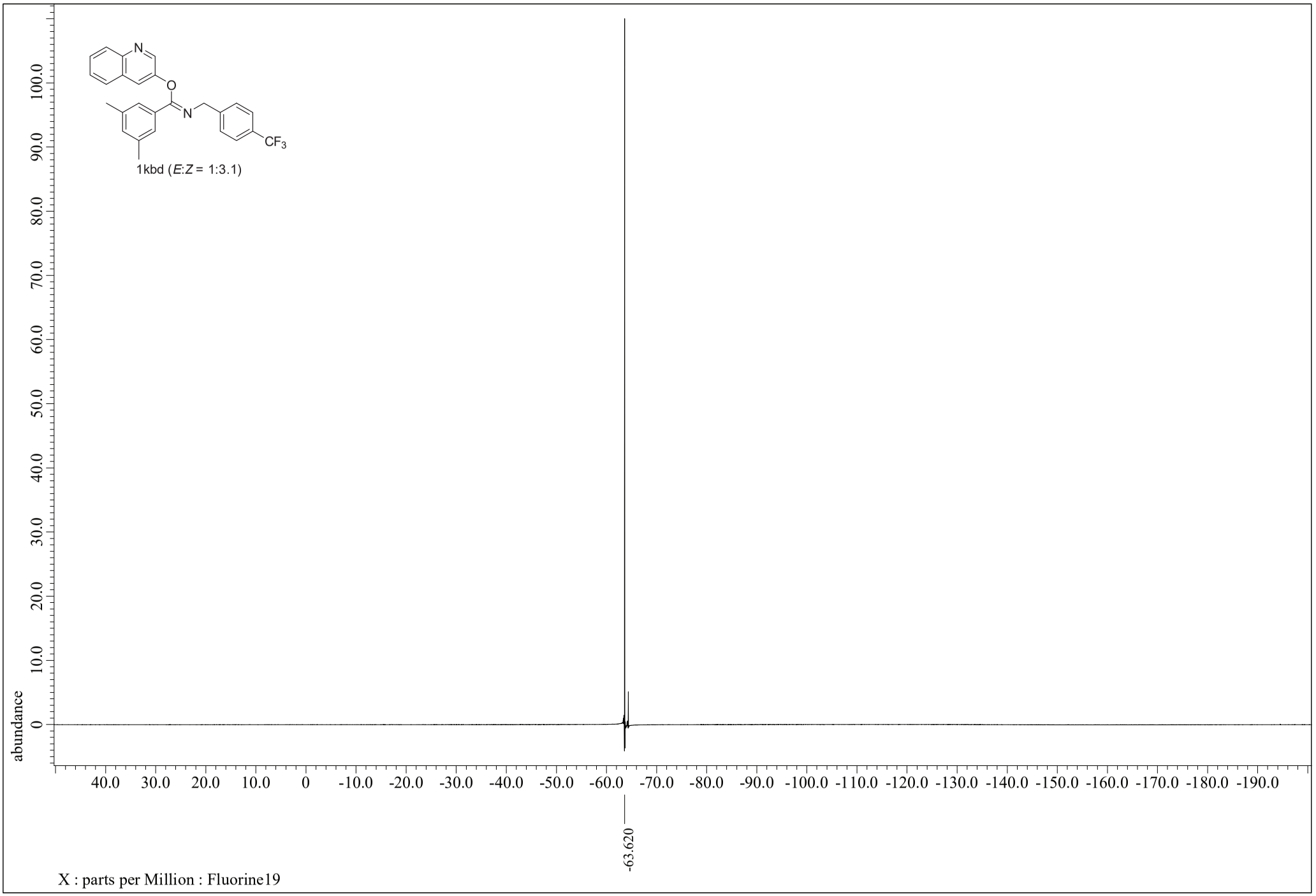
^{1}H NMR (400 MHz, $CDCl_3$)



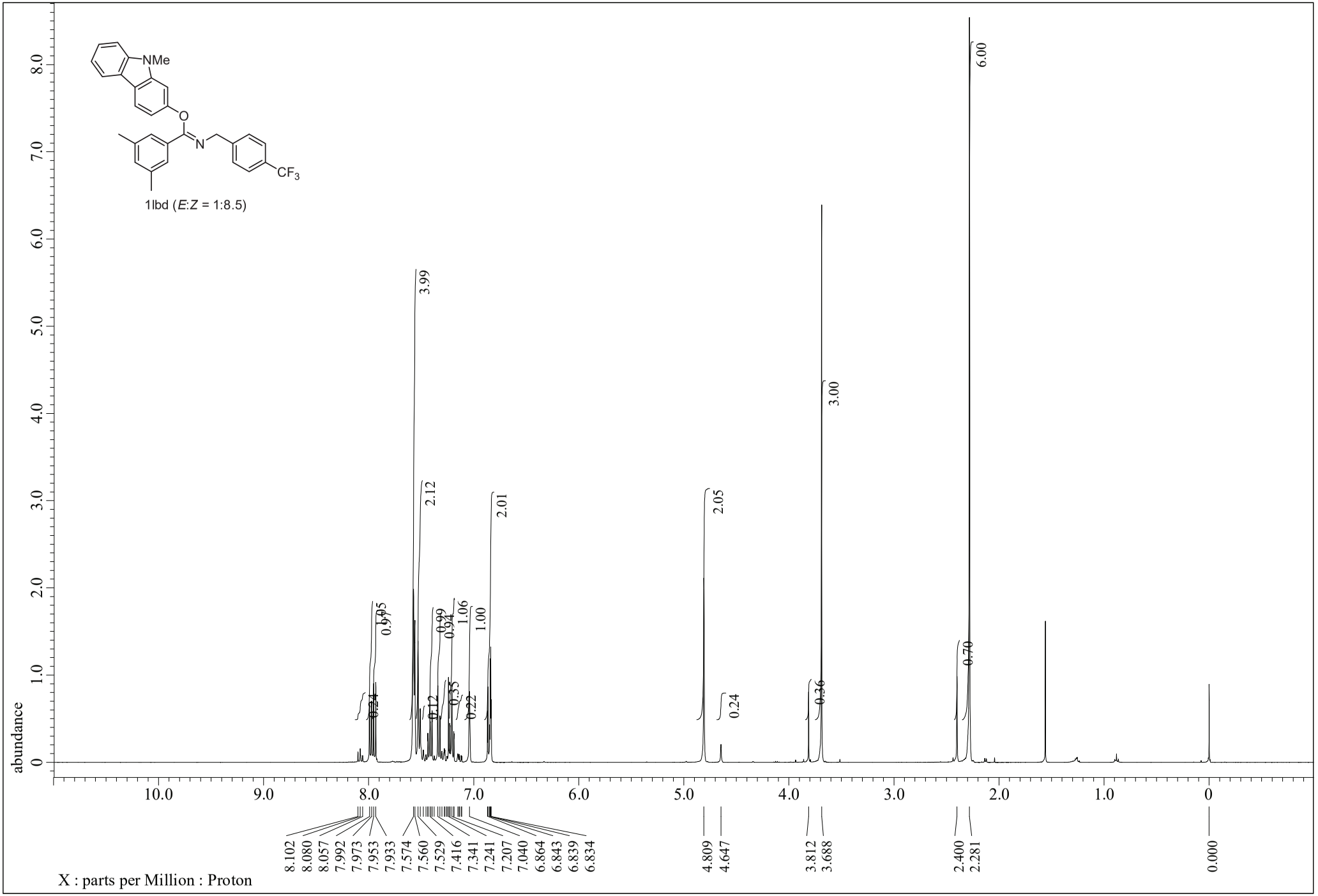
^{13}C NMR (101 MHz, $CDCl_3$)



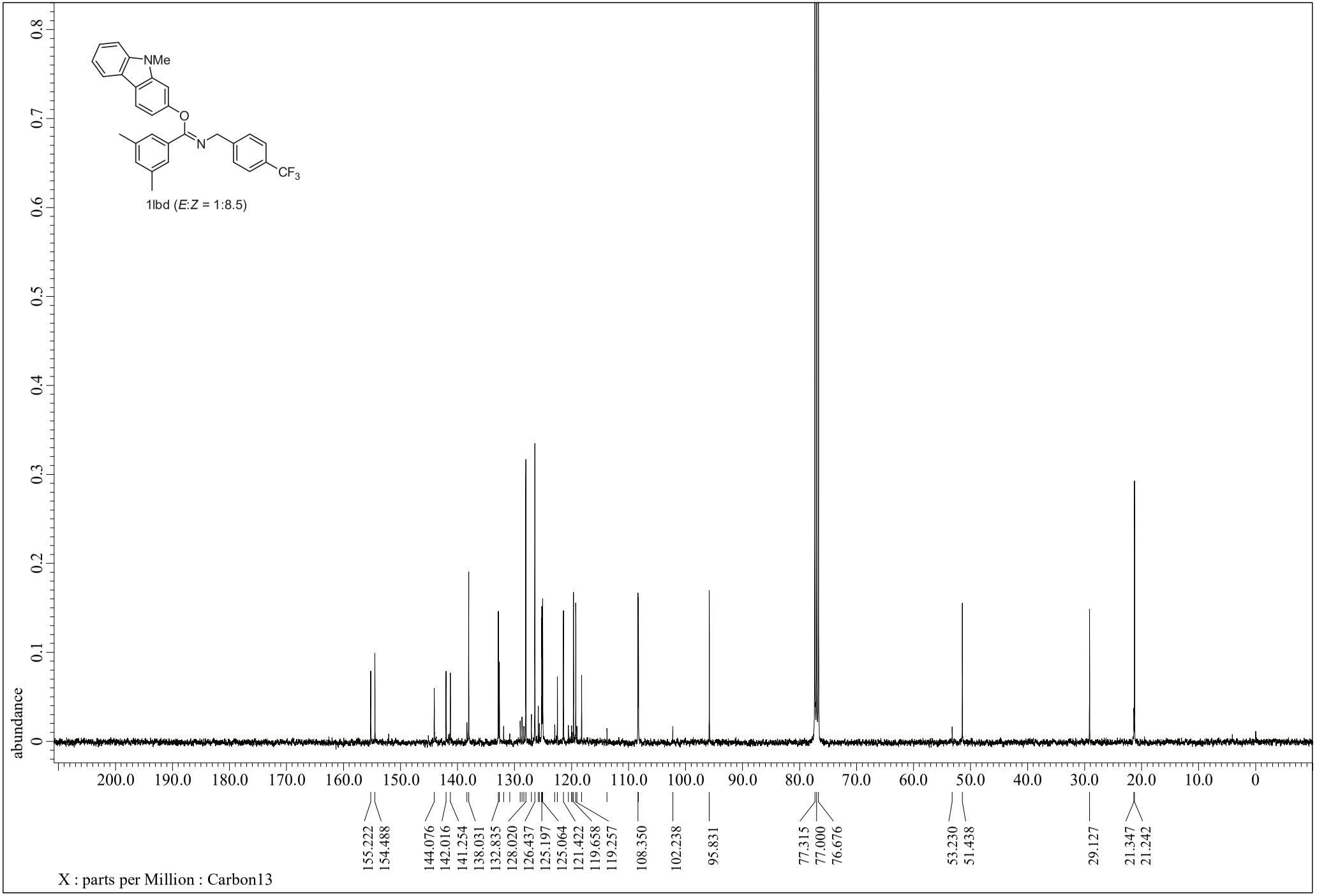
^{19}F NMR (376 MHz, $CDCl_3$)



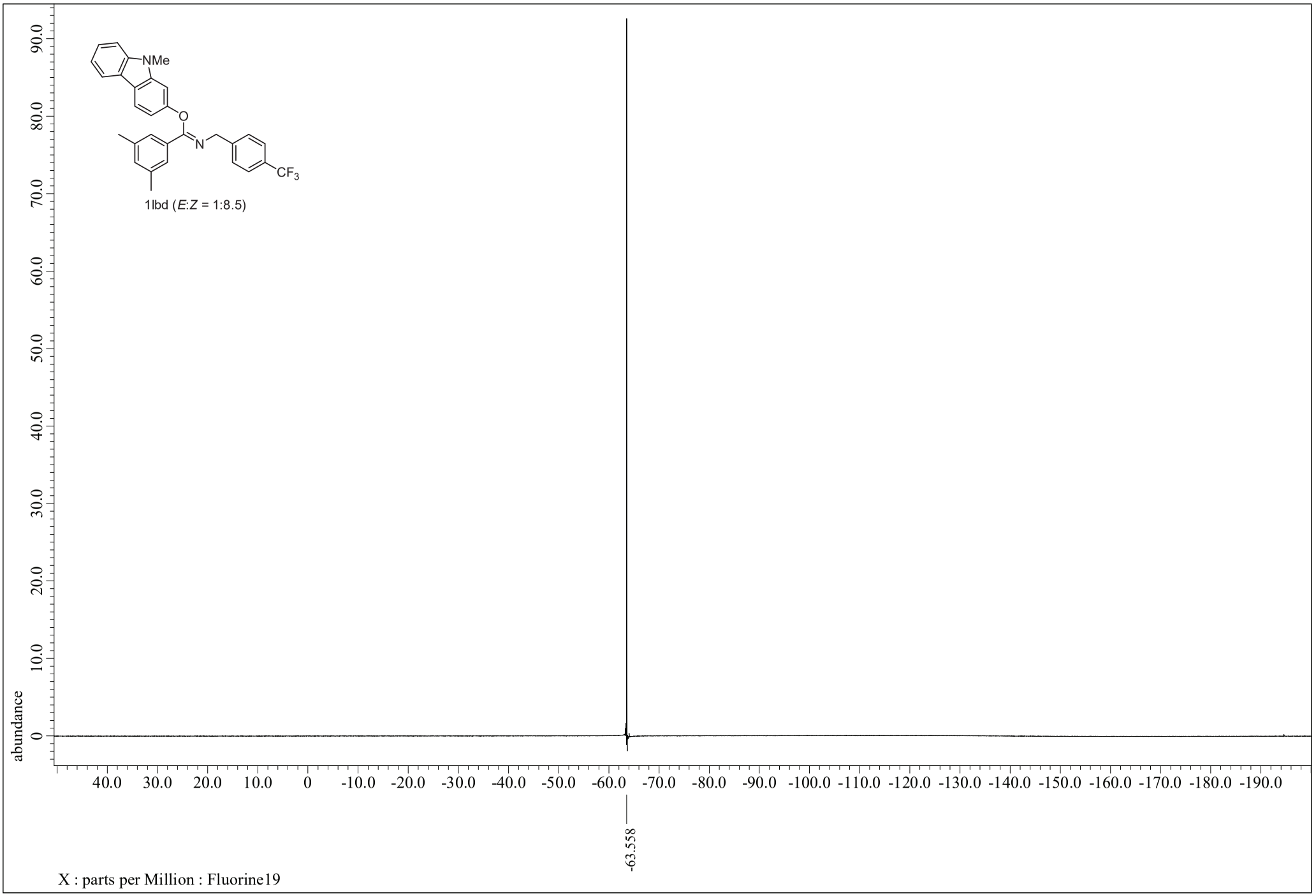
^{1}H NMR (400 MHz, $CDCl_3$)



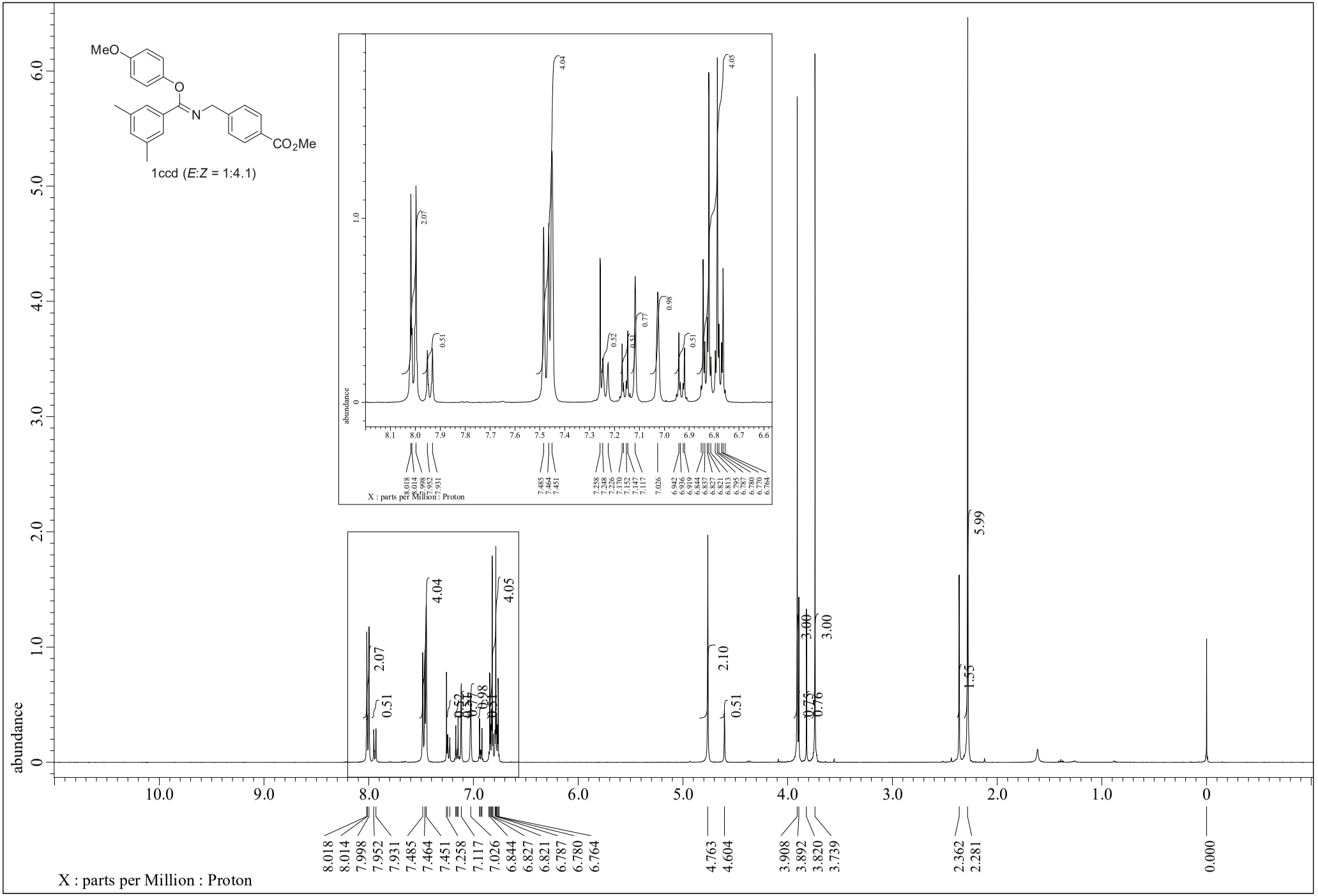
^{13}C NMR (101 MHz, $CDCl_3$)



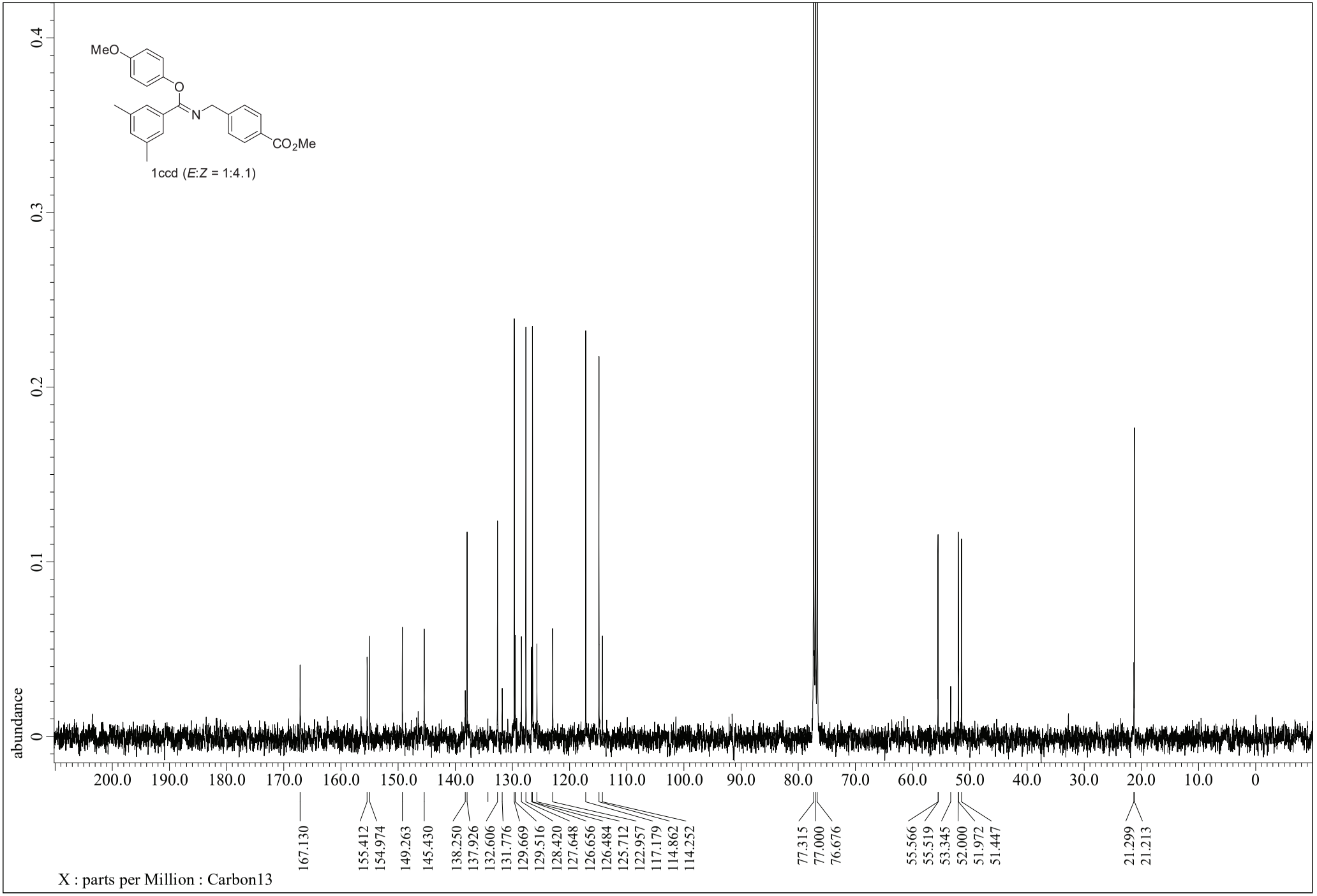
^{19}F NMR (376 MHz, $CDCl_3$)



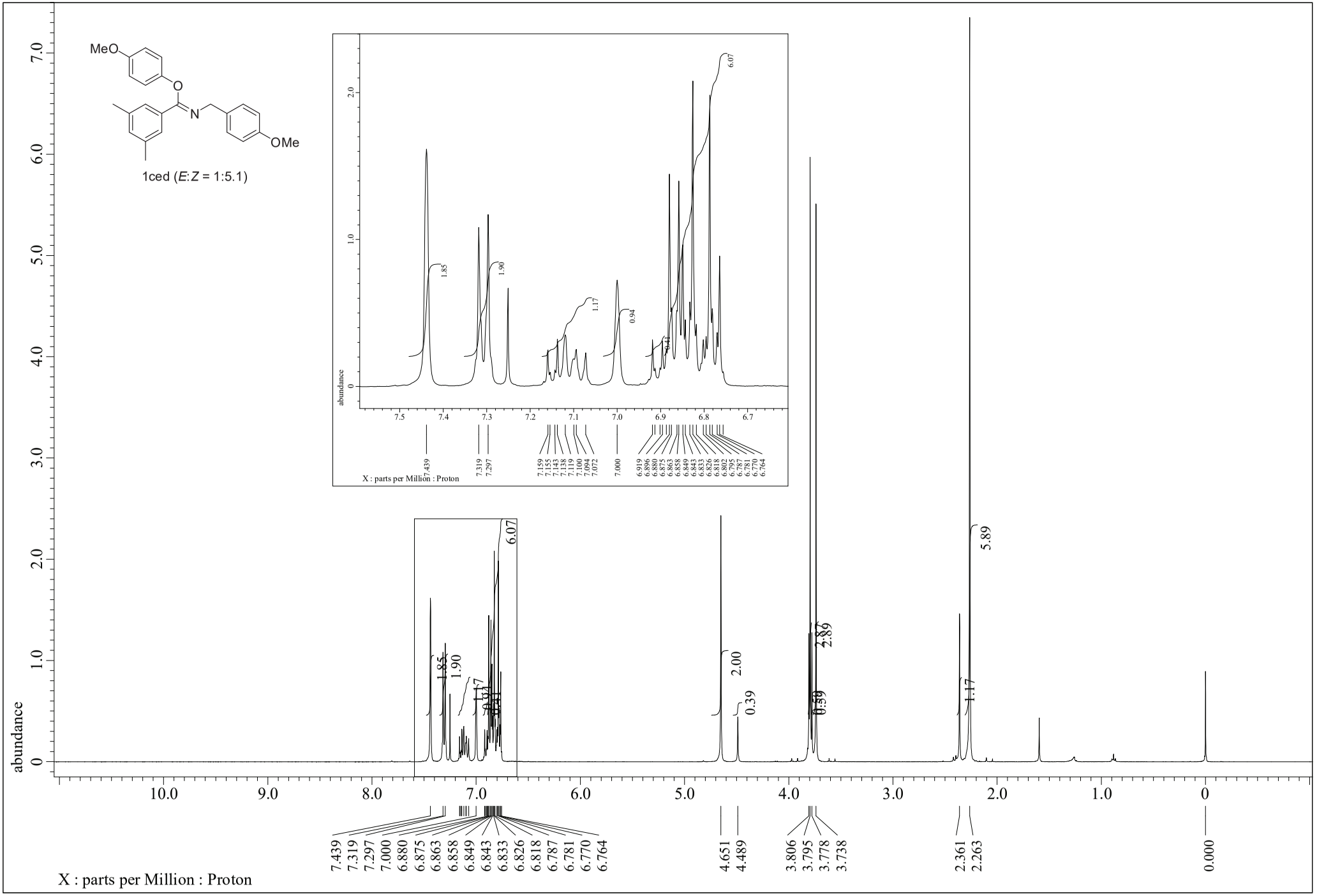
^{1}H NMR (400 MHz, $CDCl_3$)



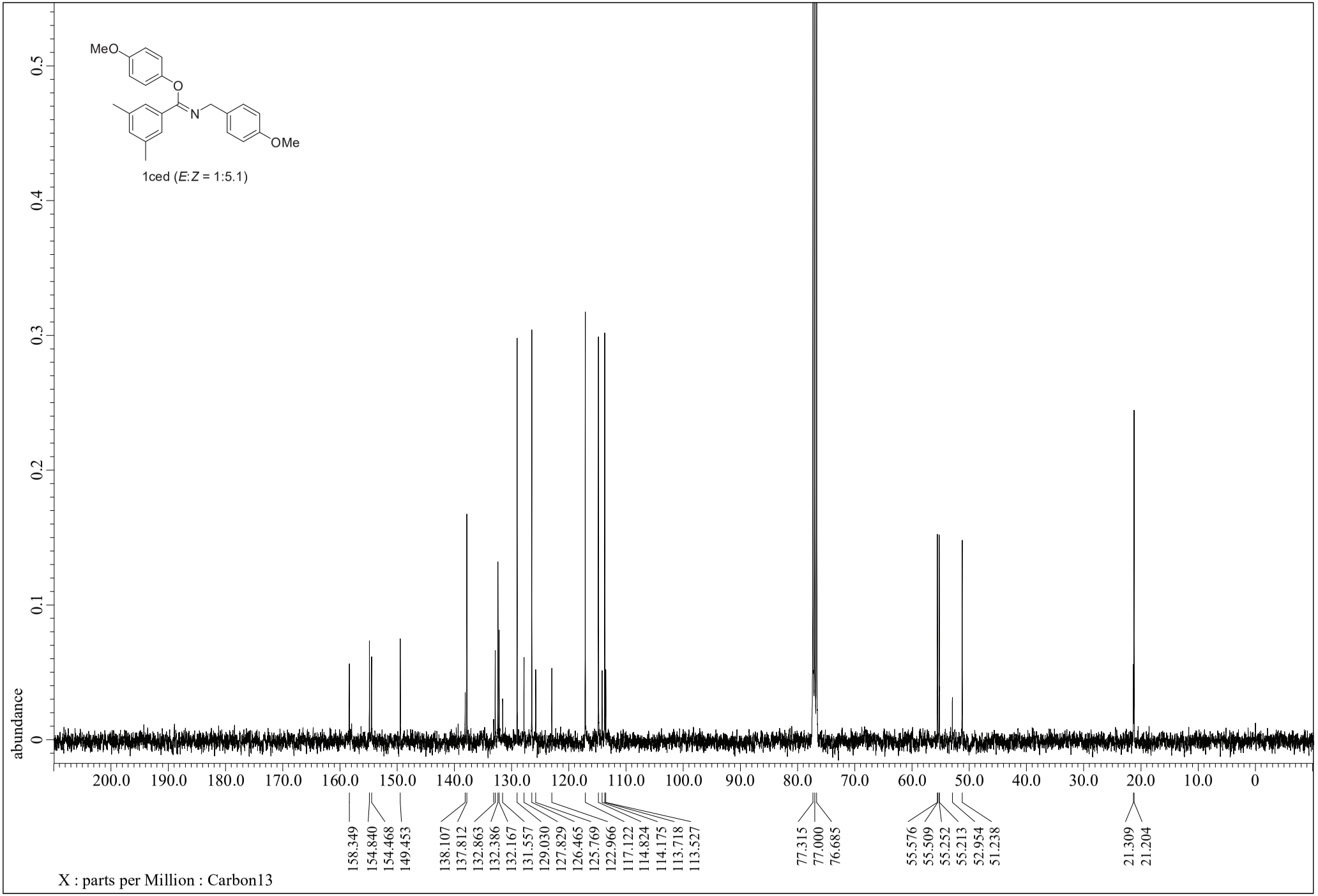
^{13}C NMR (101 MHz, $CDCl_3$)



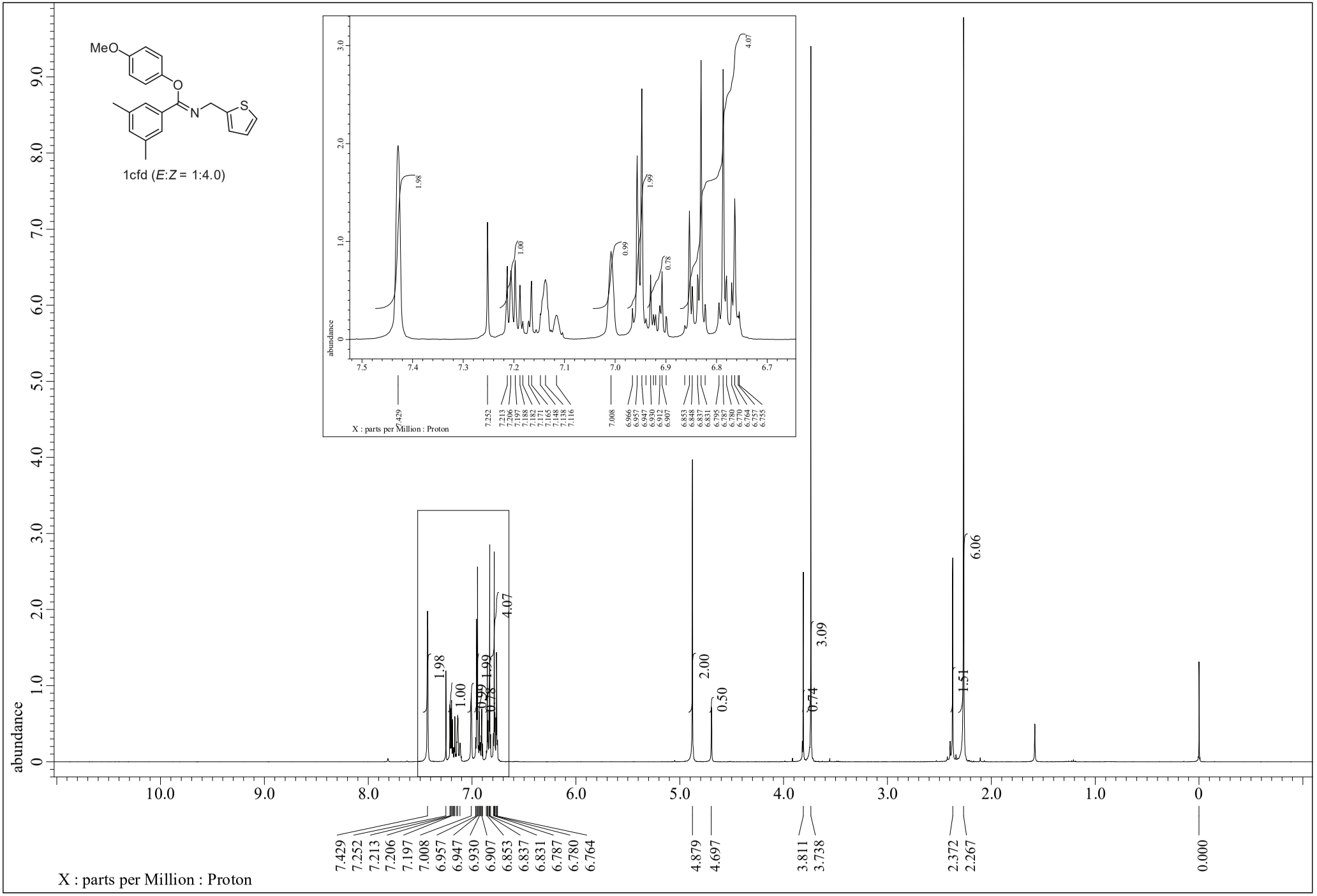
^{1}H NMR (400 MHz, $CDCl_3$)



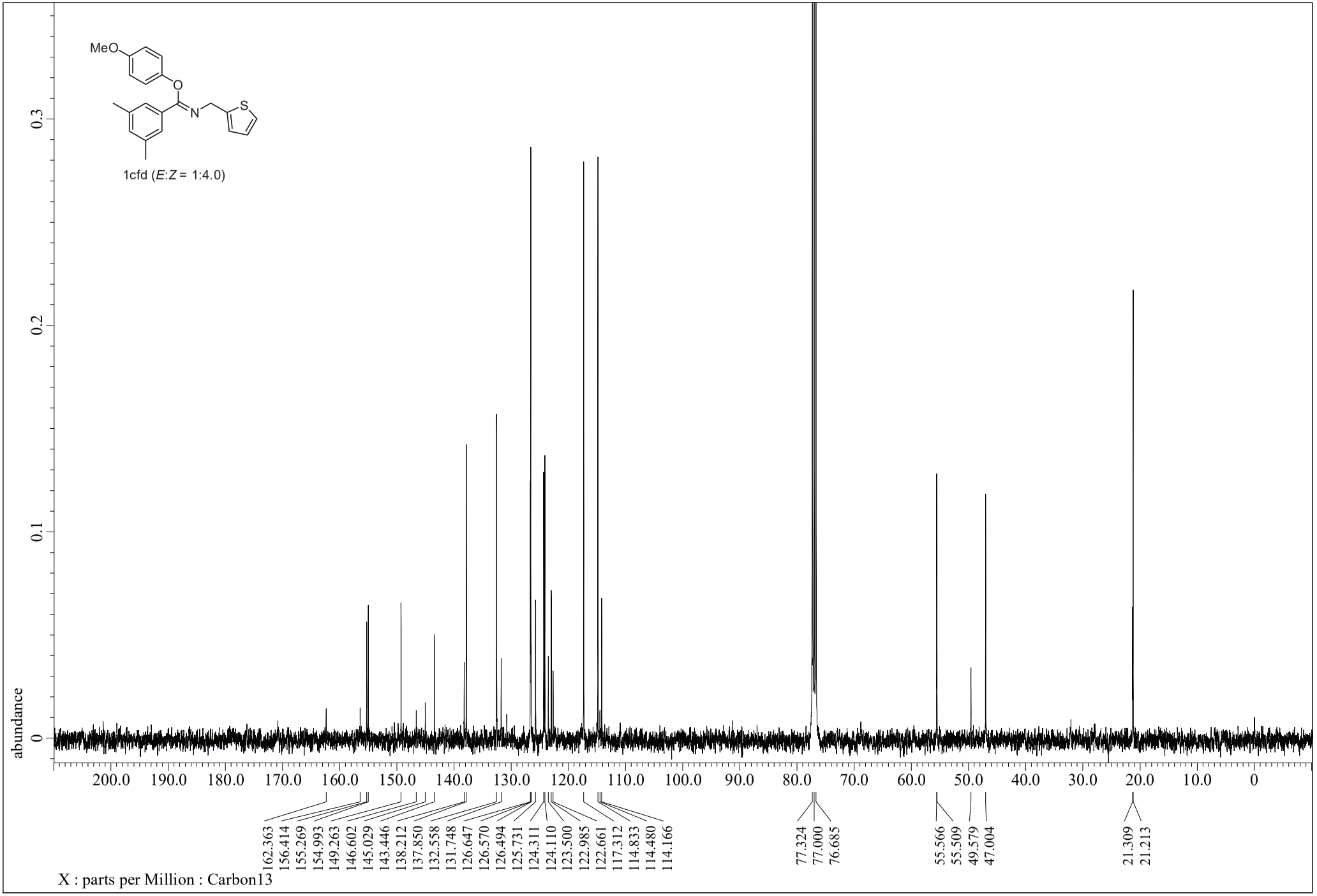
^{13}C NMR (101 MHz, $CDCl_3$)



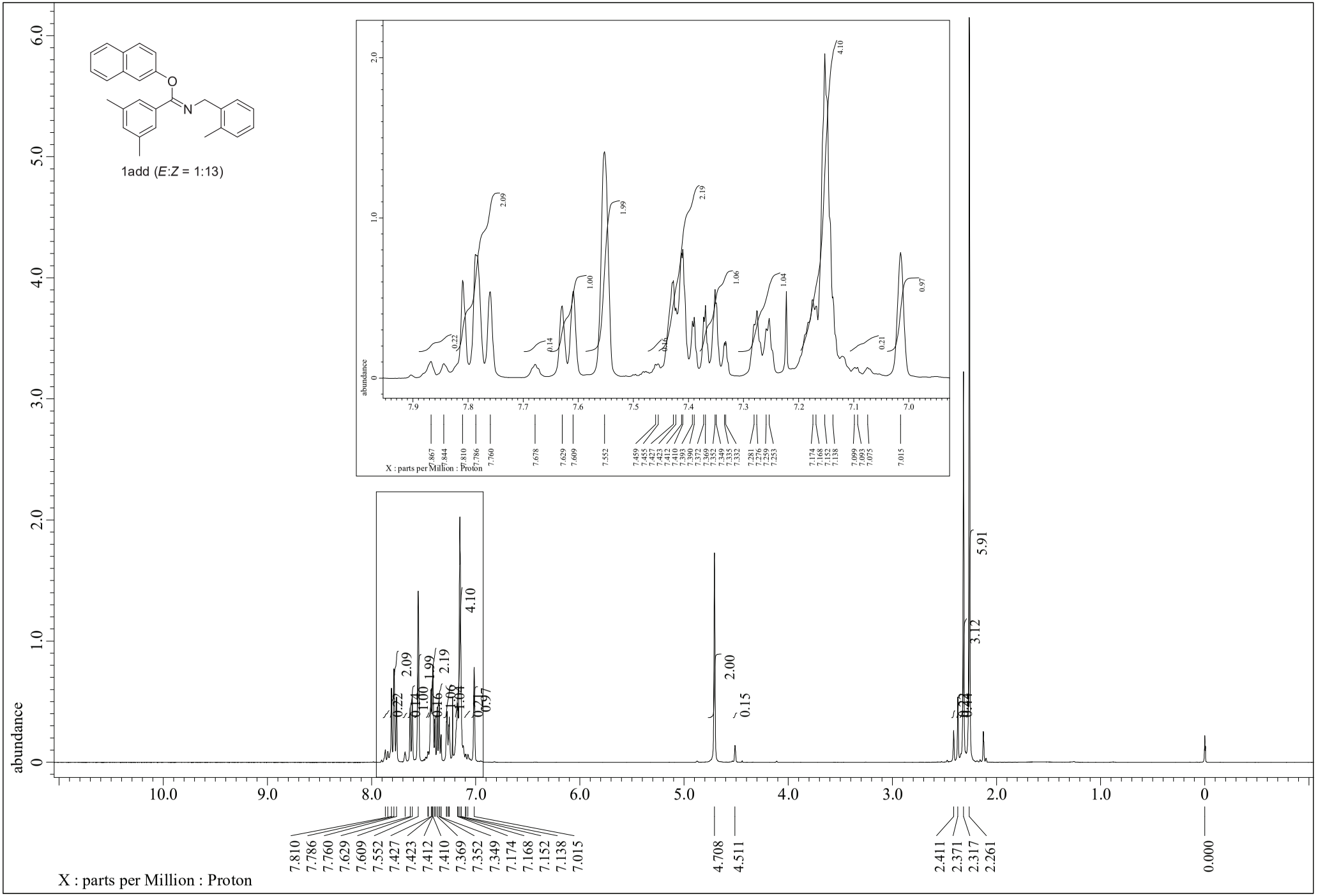
^{1}H NMR (400 MHz, $CDCl_3$)



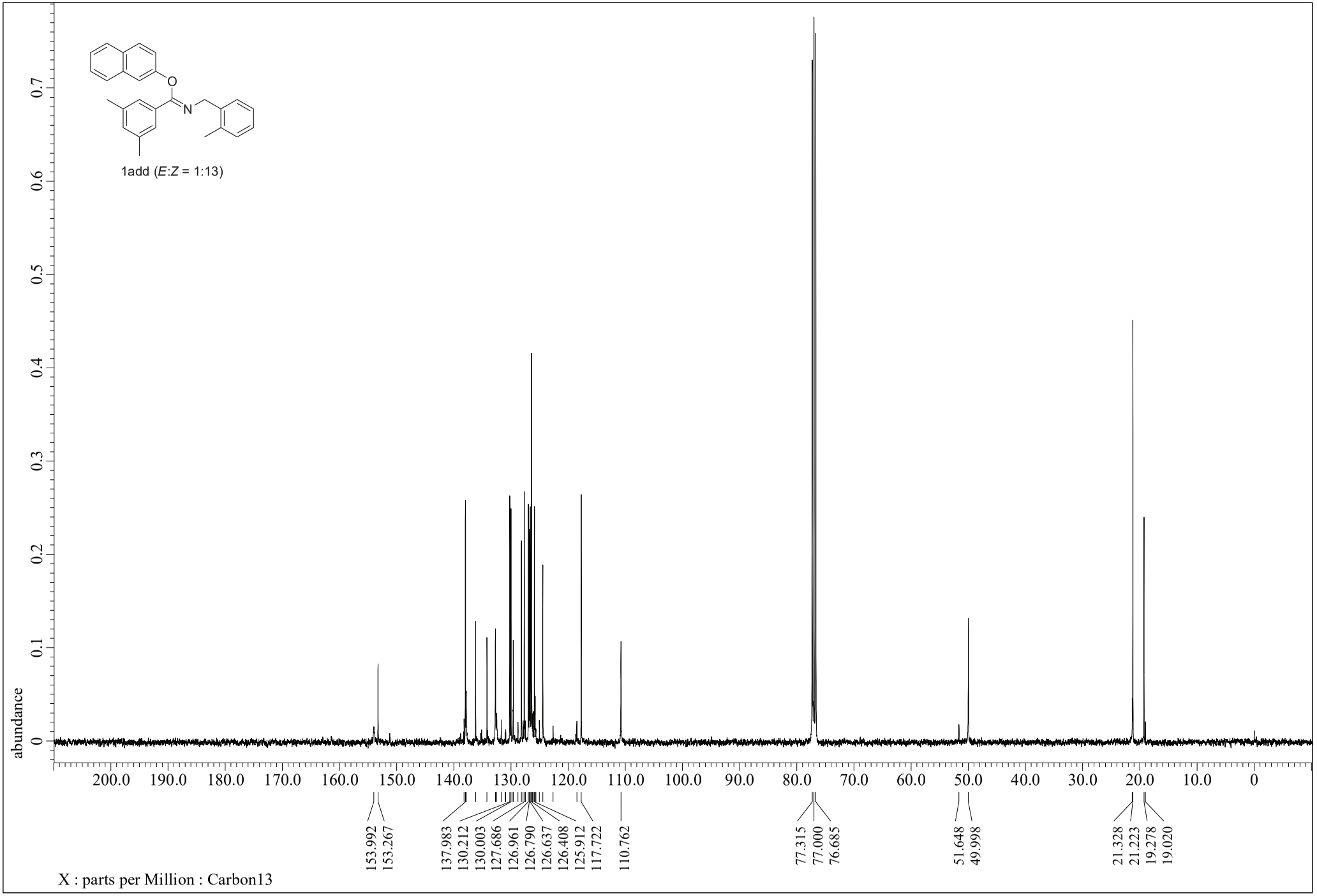
^{13}C NMR (101 MHz, $CDCl_3$)



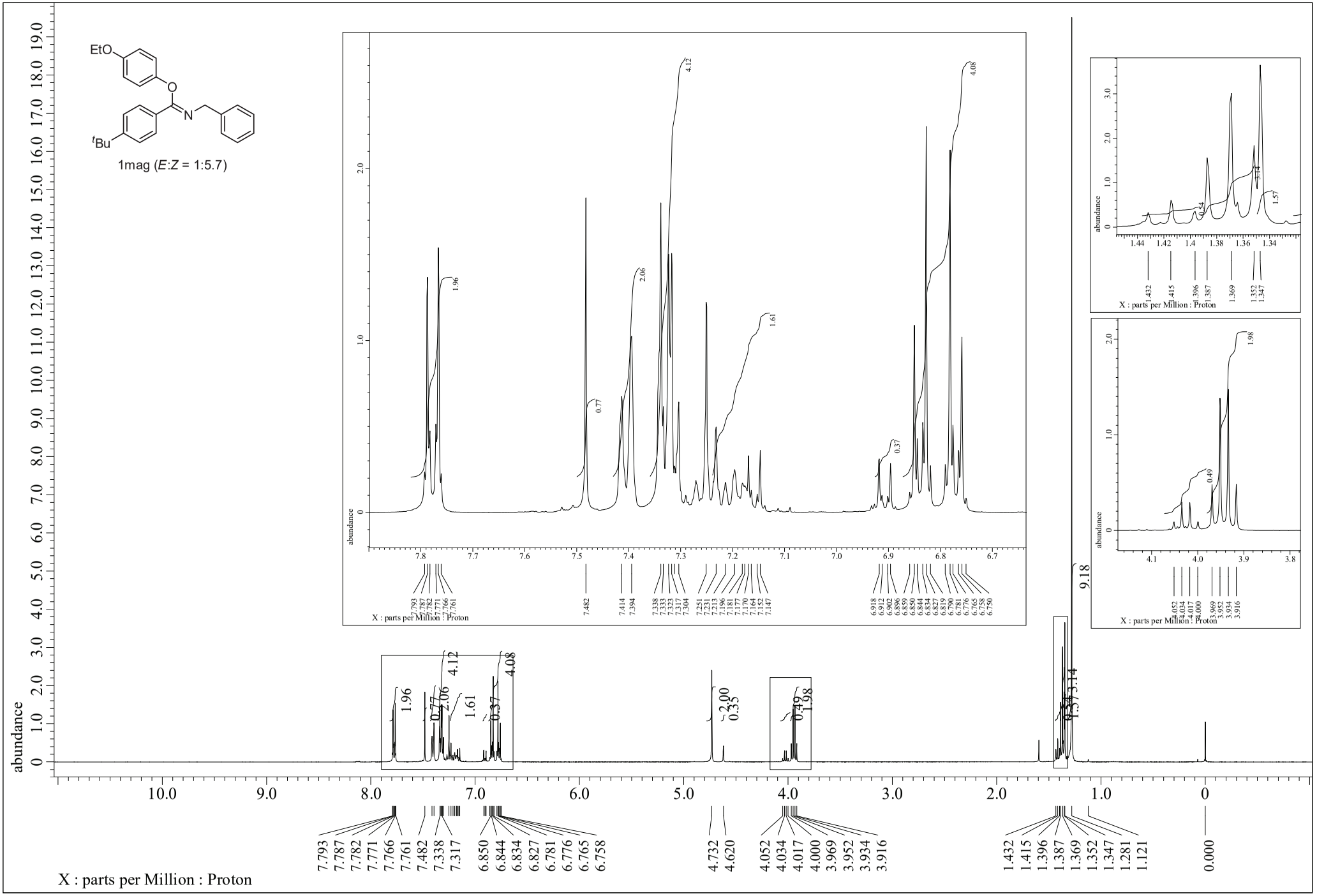
^{1}H NMR (400 MHz, $CDCl_3$)



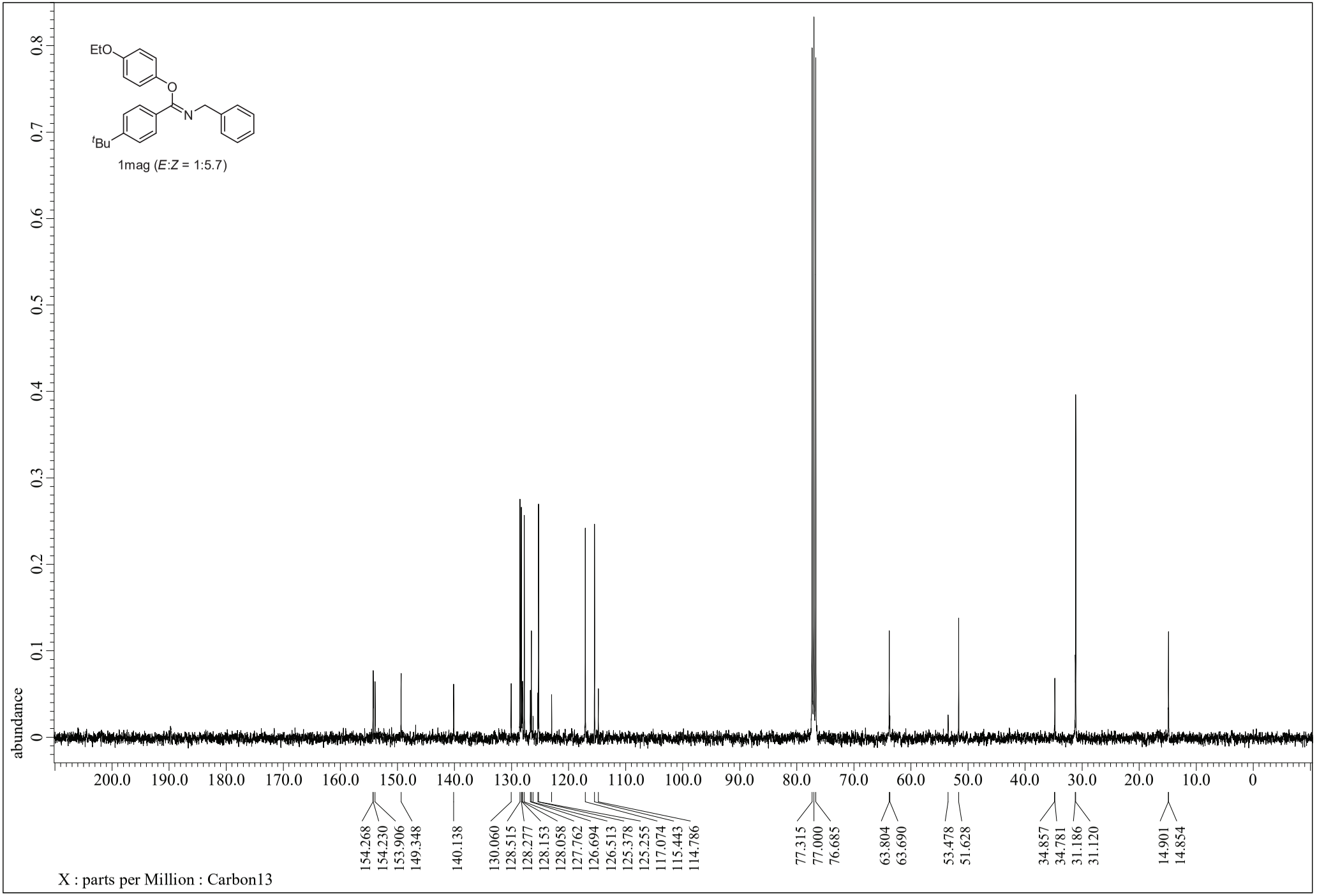
^{13}C NMR (101 MHz, $CDCl_3$)



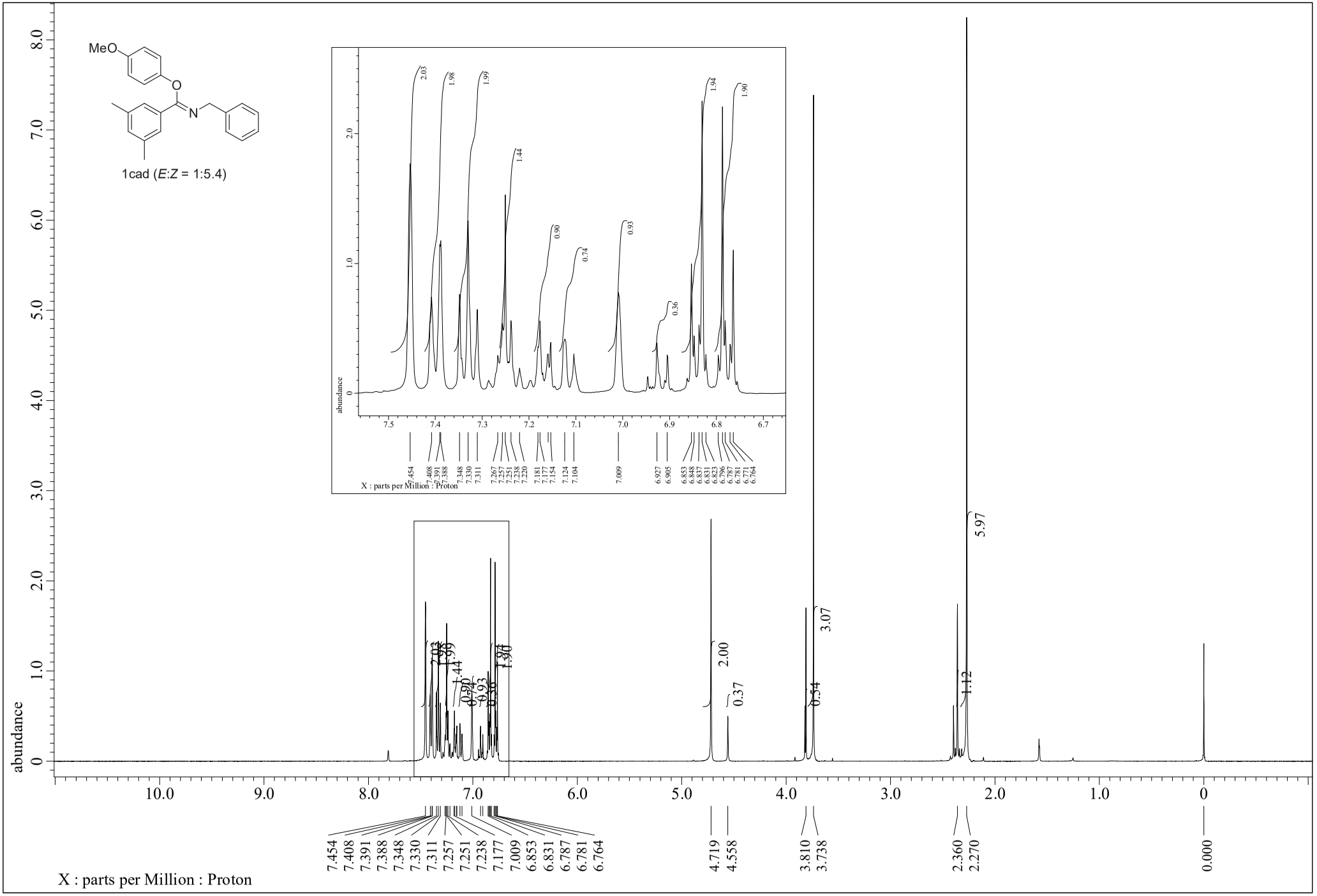
^{1}H NMR (400 MHz, $CDCl_3$)



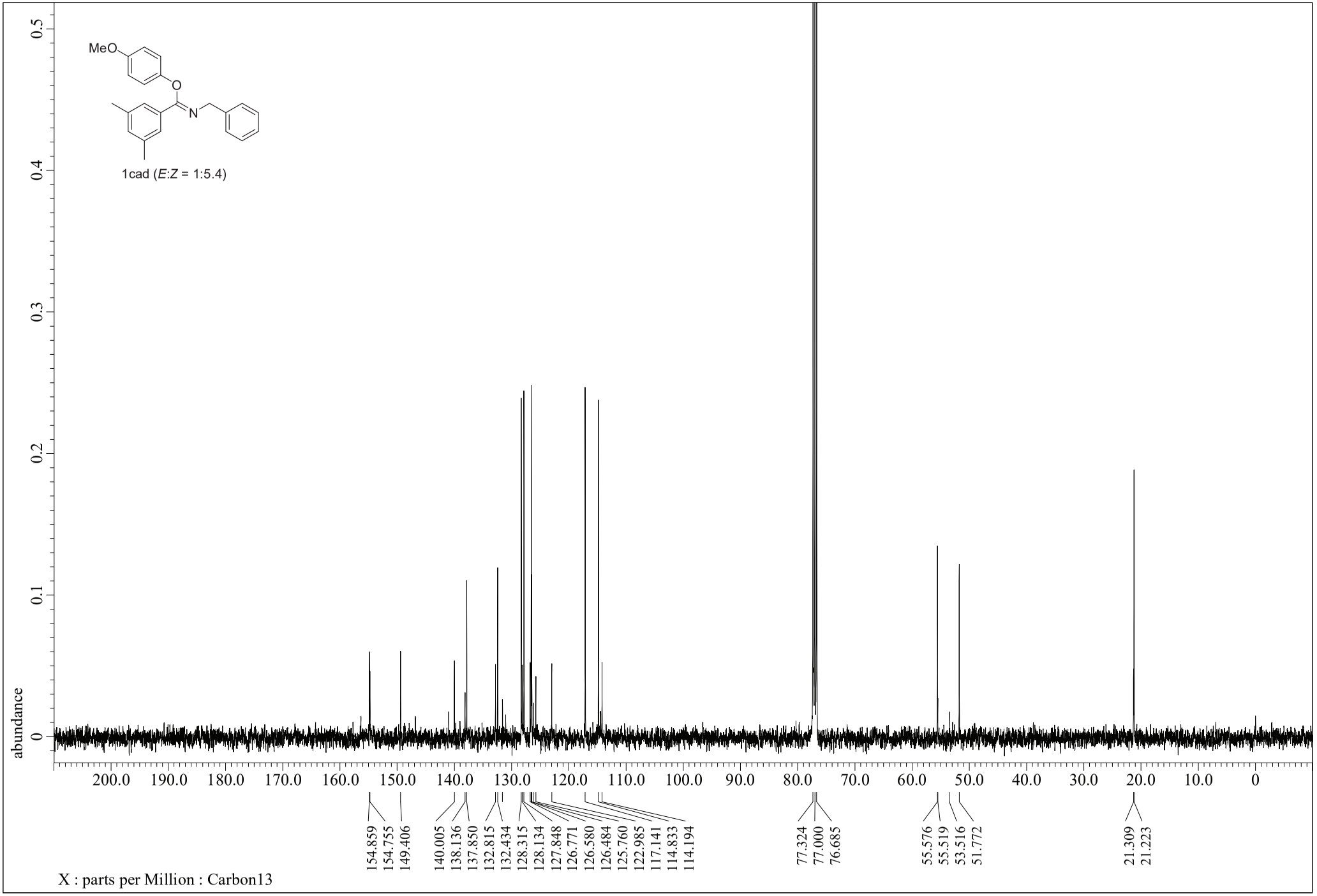
^{13}C NMR (101 MHz, $CDCl_3$)



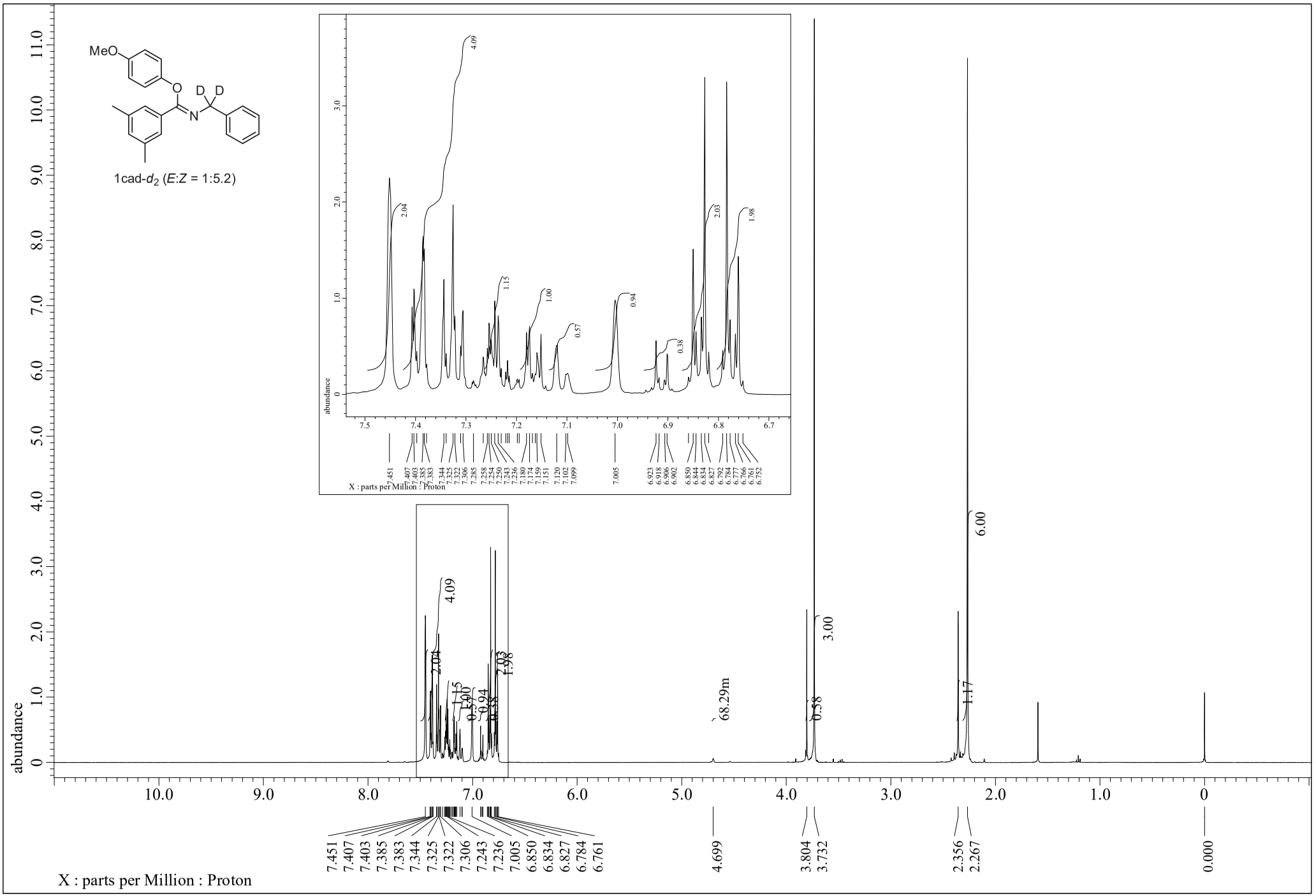
^{1}H NMR (400 MHz, $CDCl_3$)



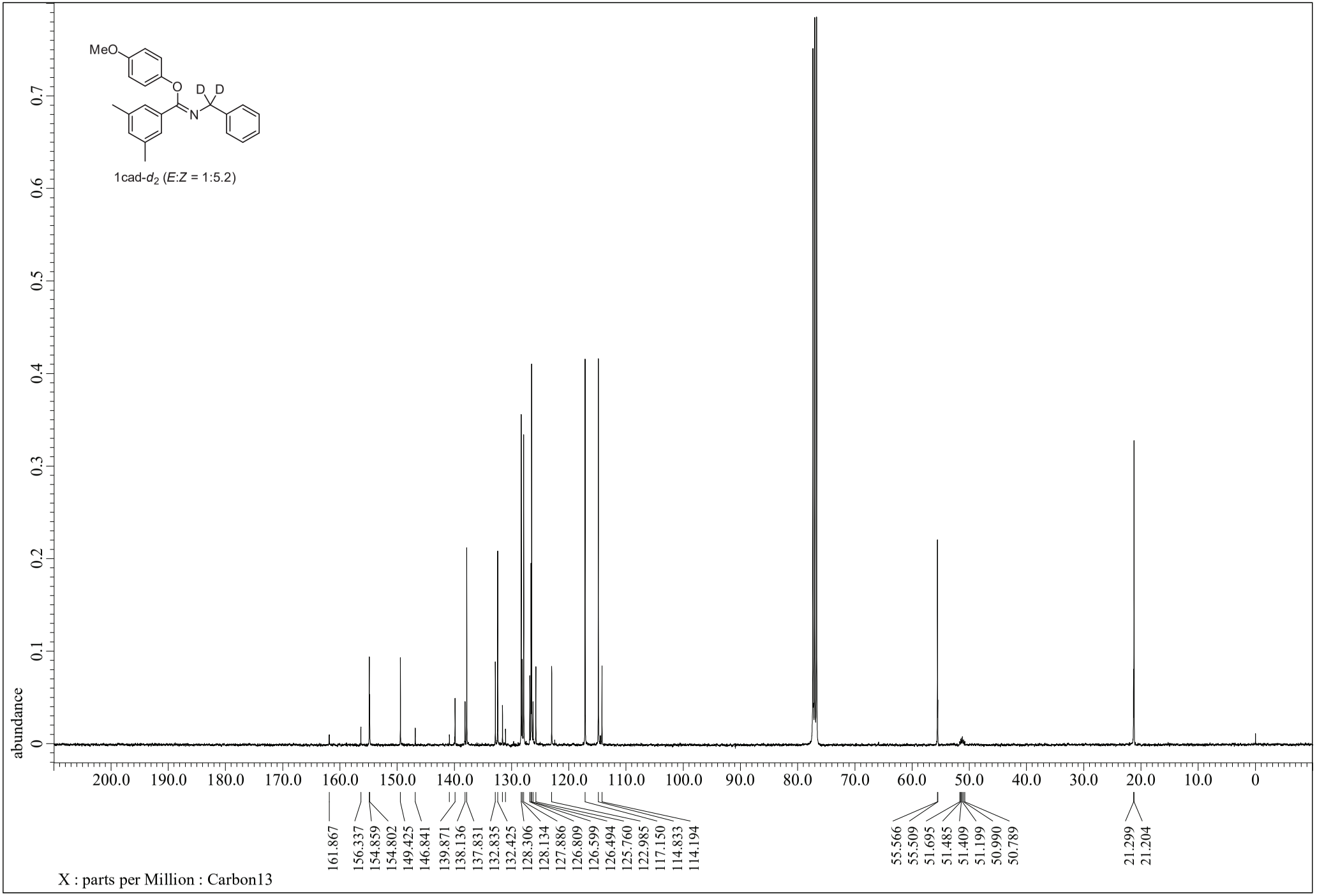
^{13}C NMR (101 MHz, $CDCl_3$)



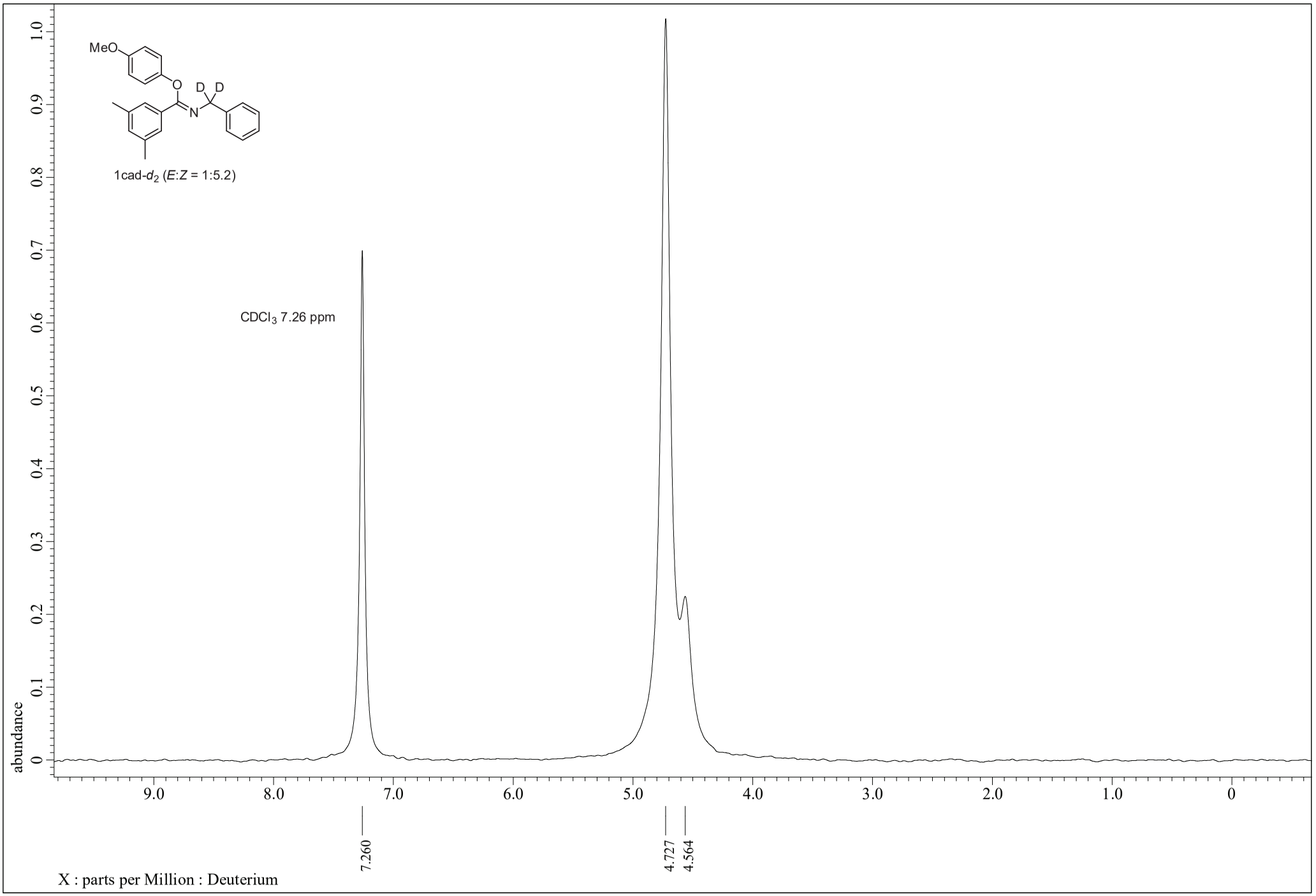
^{1}H NMR (400 MHz, $CDCl_3$)

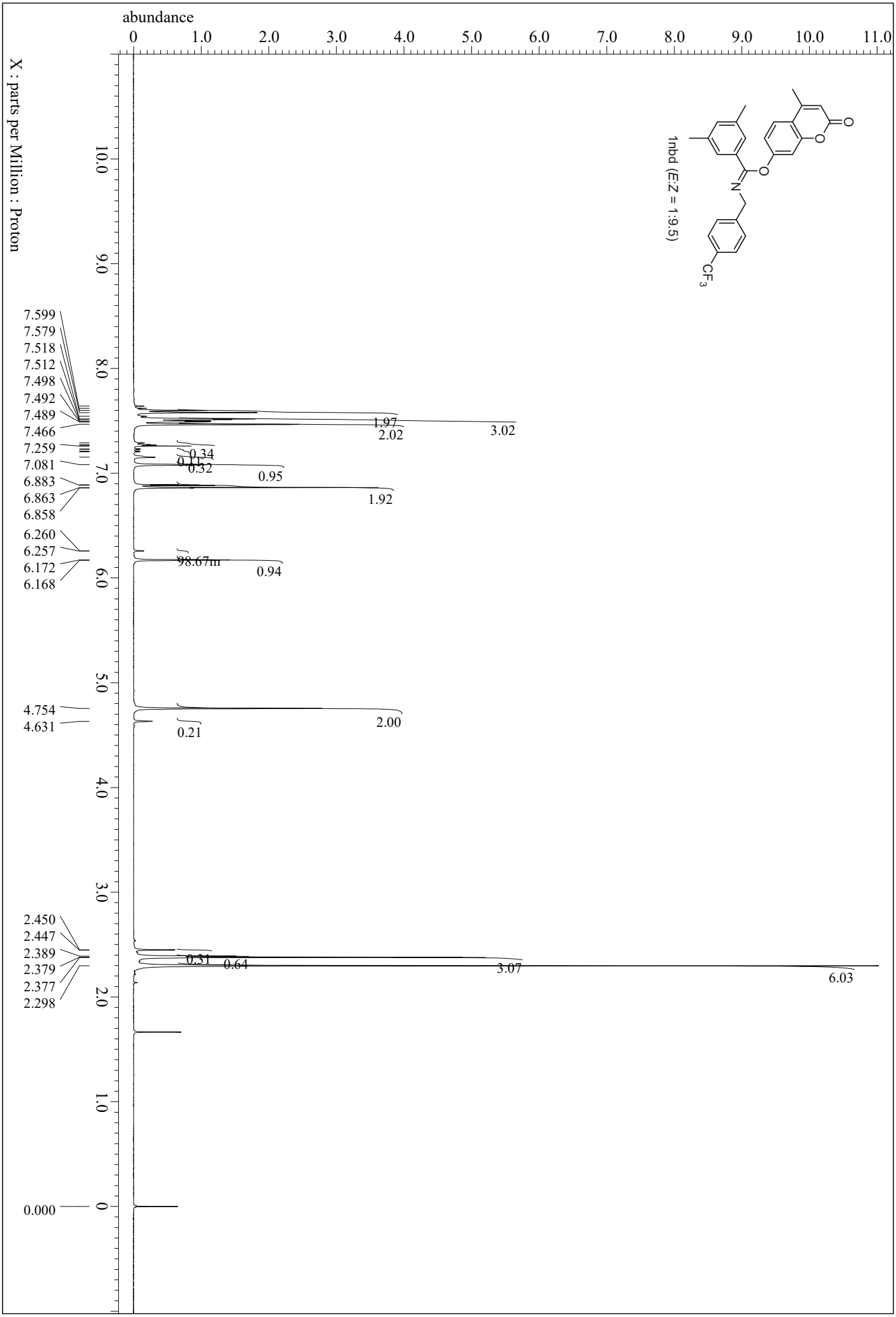


^{13}C NMR (101 MHz, $CDCl_3$)

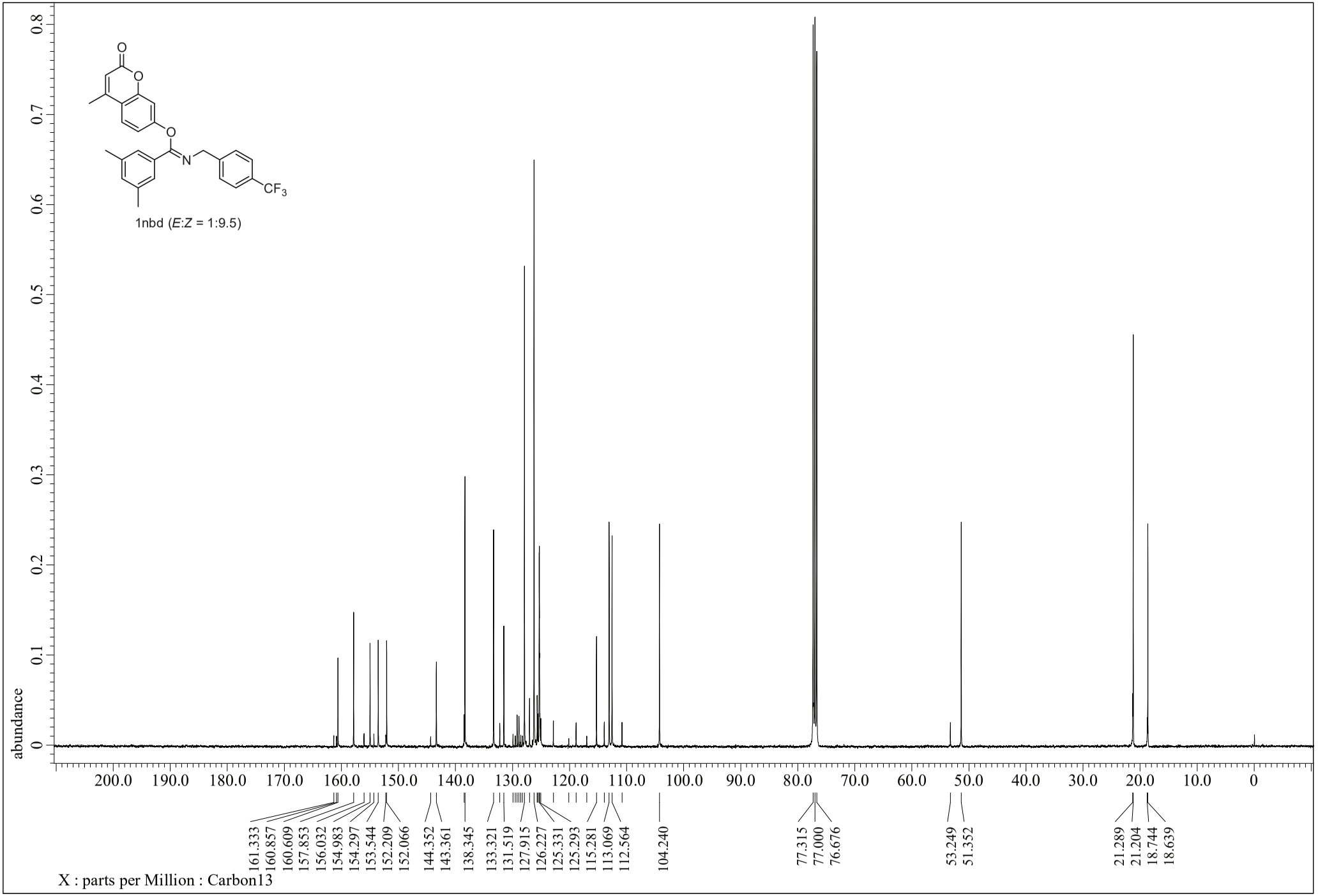


^{2}H NMR (61.37 MHz, $CHCl_3$)

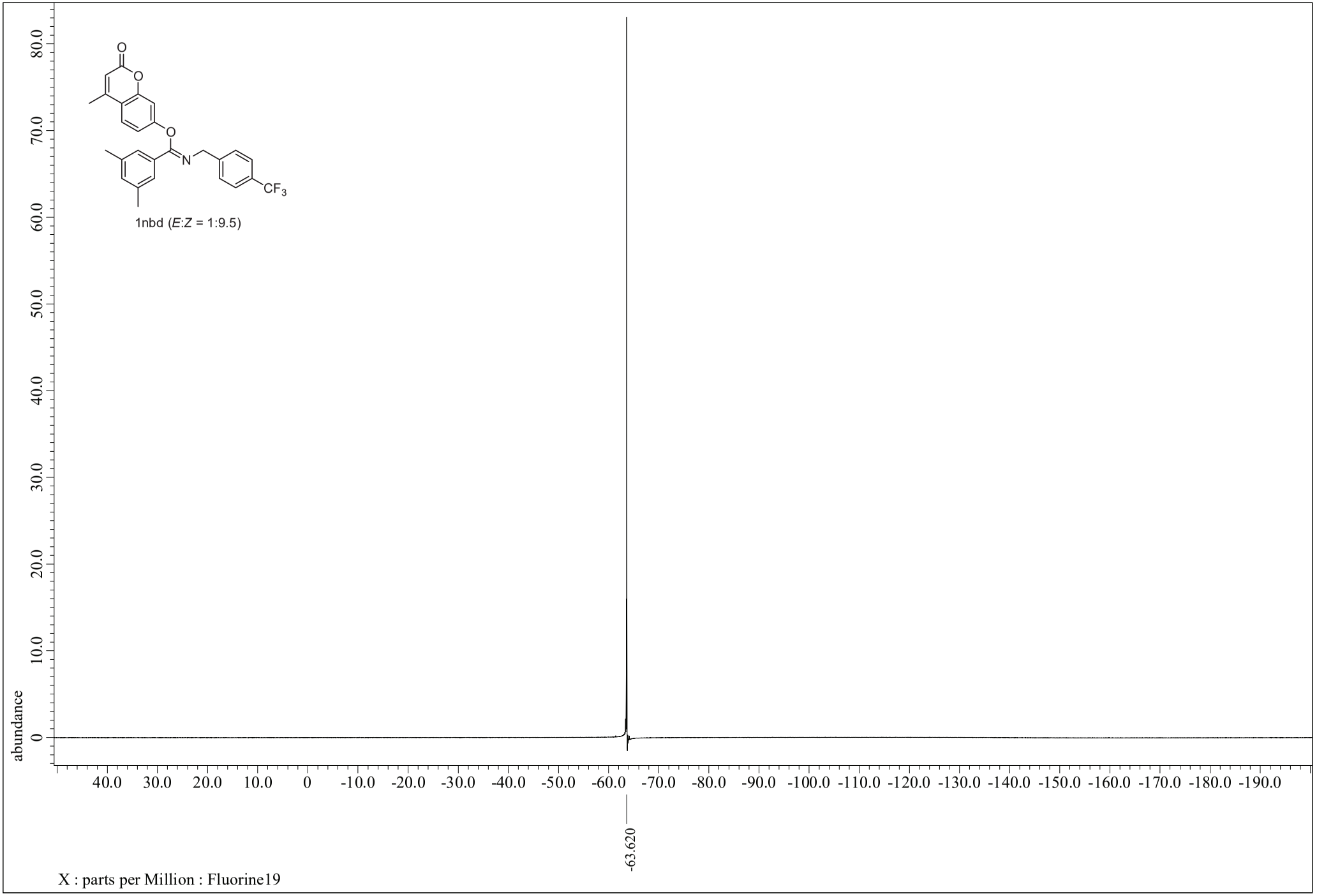



^{1}H NMR (400 MHz, $CDCl_3$)
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0
X : parts per Million : Proton
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
1nbd (E:Z = 1:9.5)
O
O
O
N
CF3
7.599
7.579
7.518
7.512
7.498
7.492
7.489
7.466
7.259
7.081
6.883
6.863
6.858
6.260
6.257
6.172
6.168
4.754
4.631
2.450
2.447
2.389
2.379
2.377
2.298
0.000
1.97
2.02
3.02
0.34
0.32
0.95
1.92
98.67m
0.94
2.00
0.21
0.31
0.64
3.07
6.03

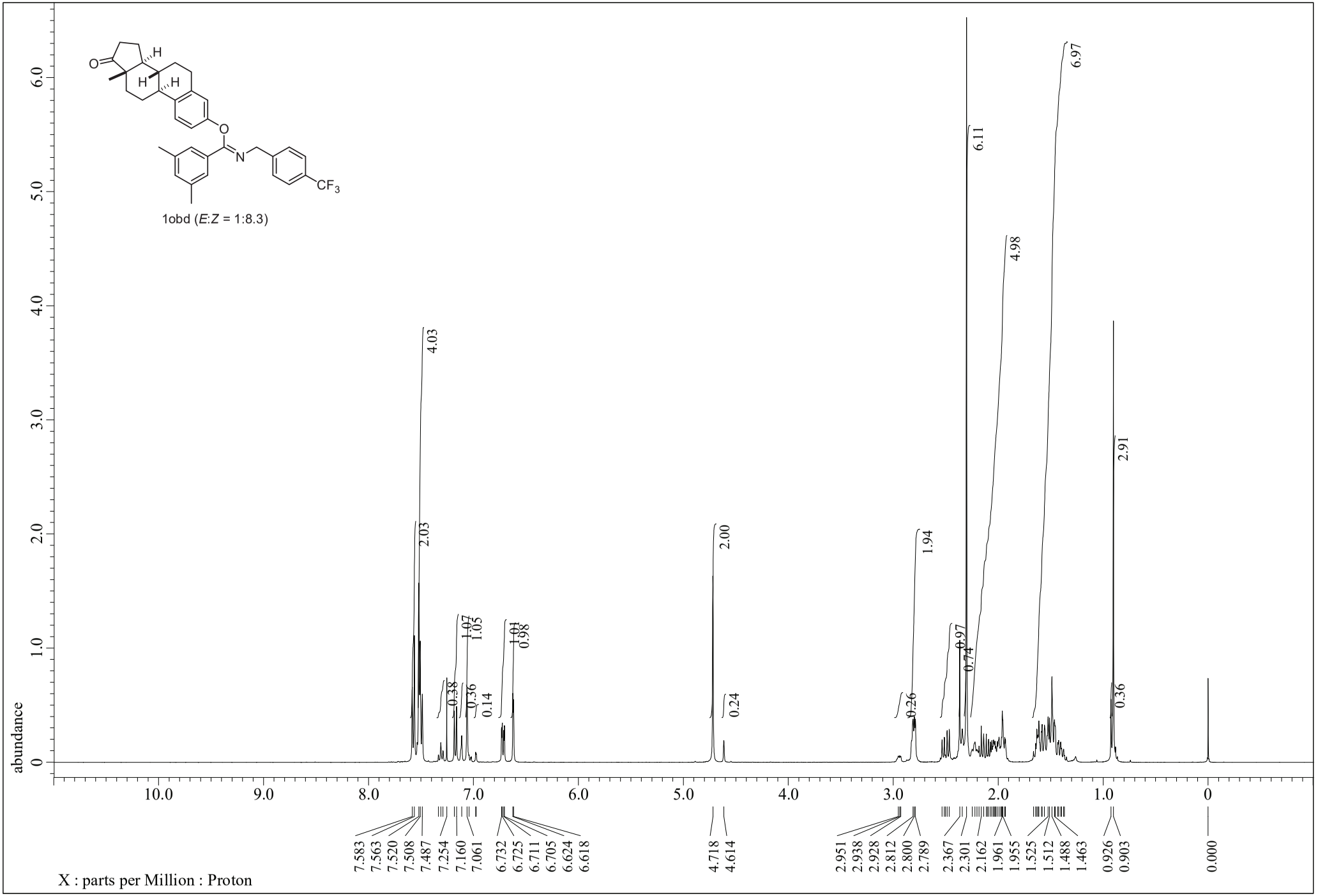
^{13}C NMR (101 MHz, $CDCl_3$)



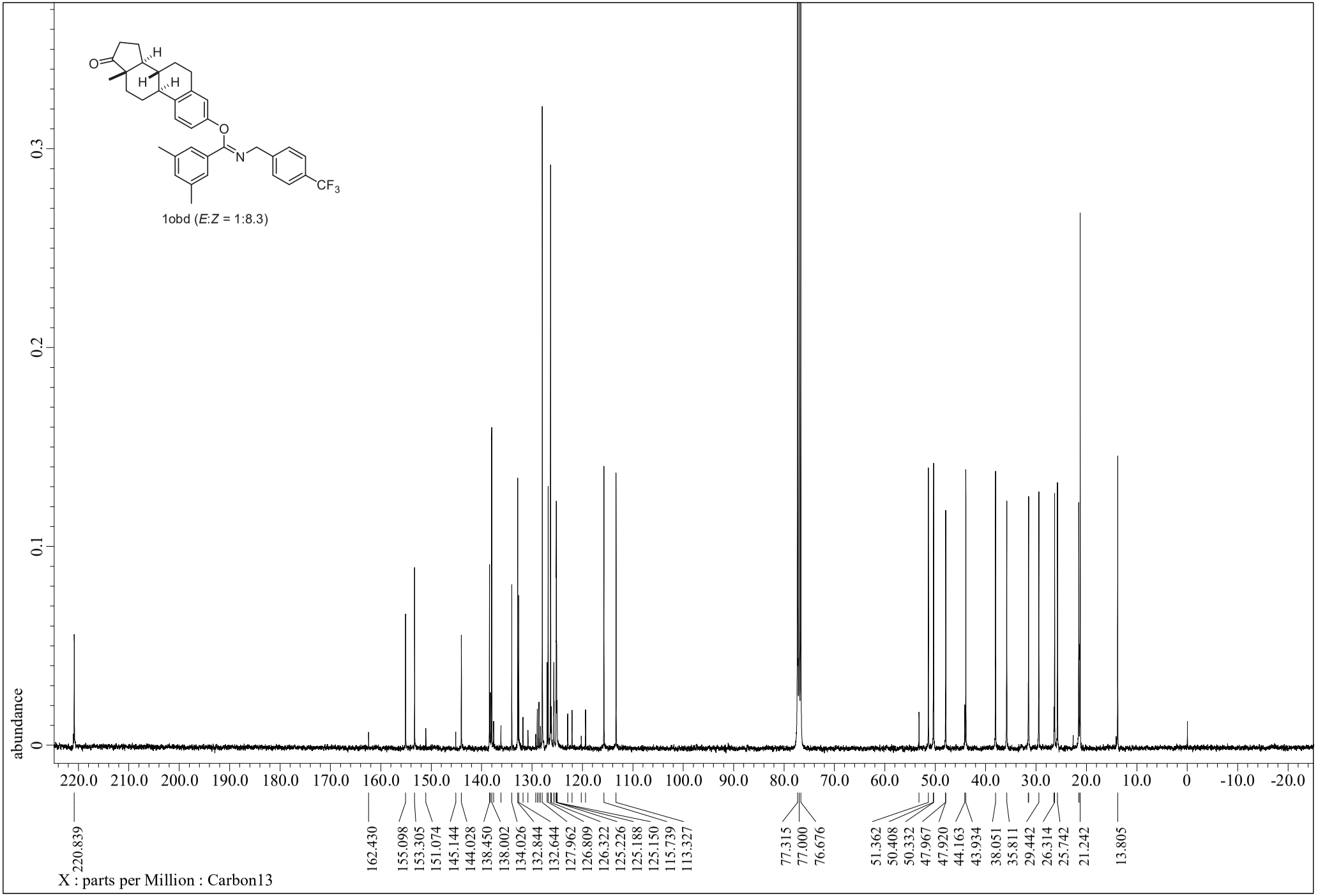
^{19}F NMR (376 MHz, $CDCl_3$)



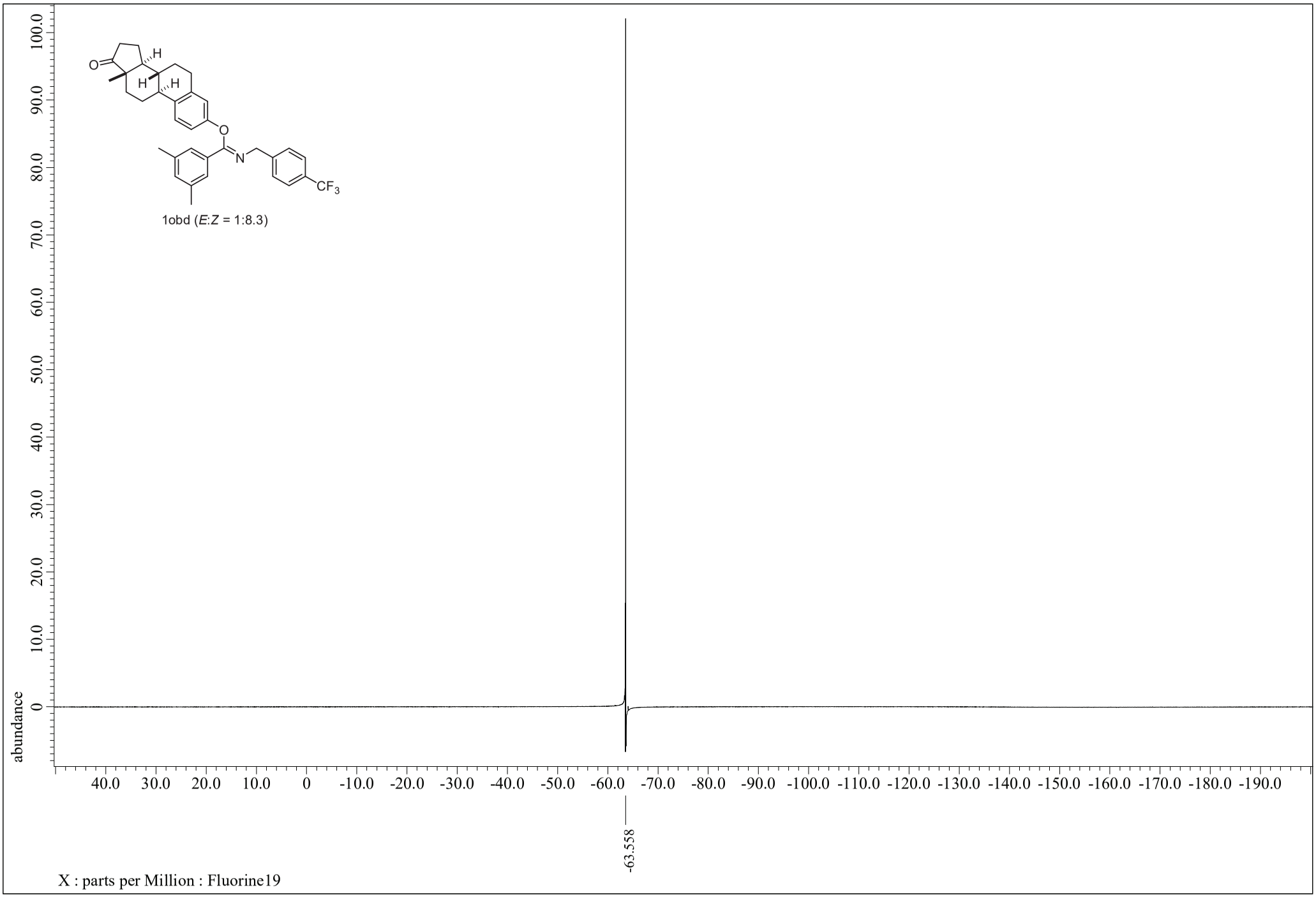
^{1}H NMR (400 MHz, $CDCl_3$)



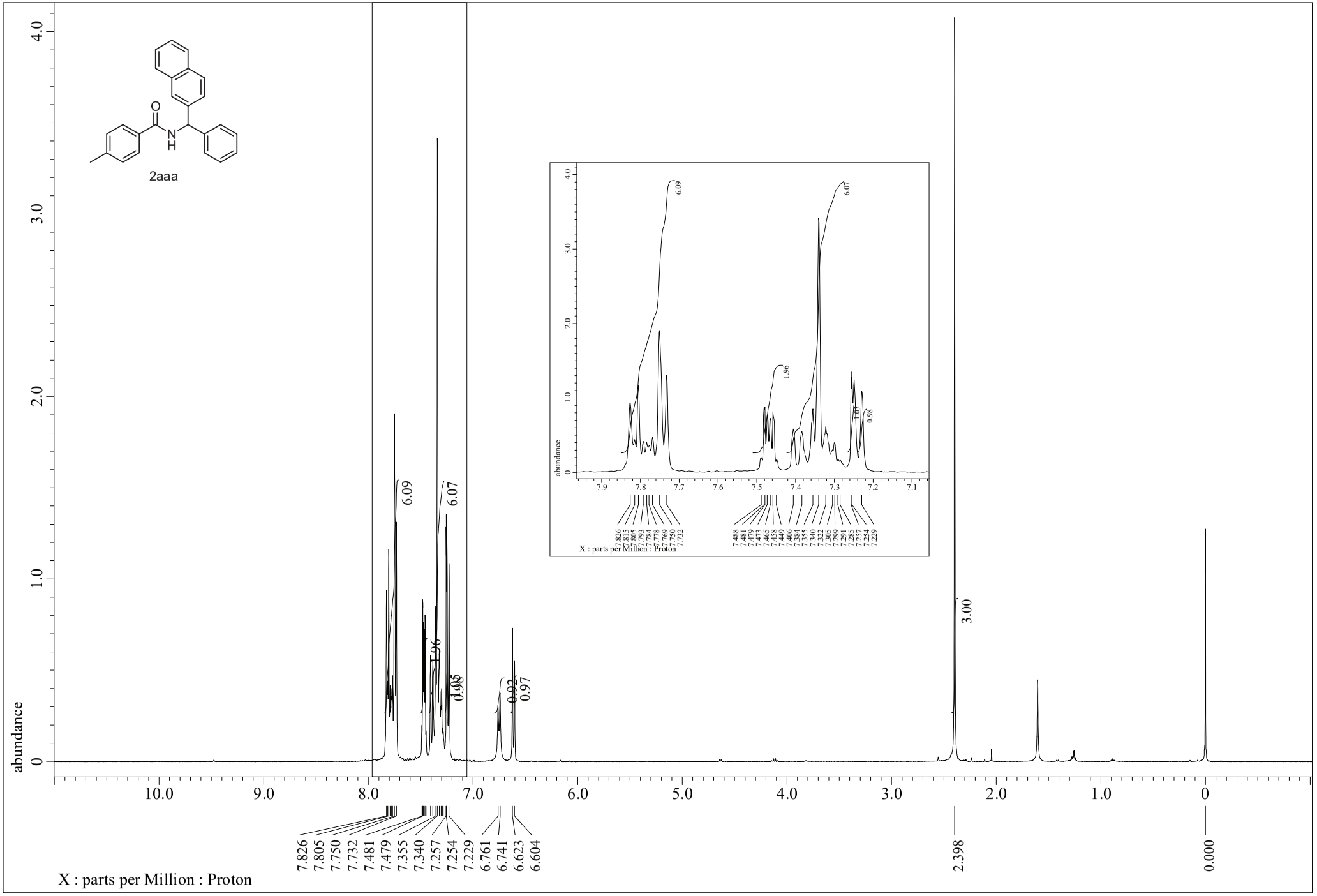
^{13}C NMR (101 MHz, $CDCl_3$)



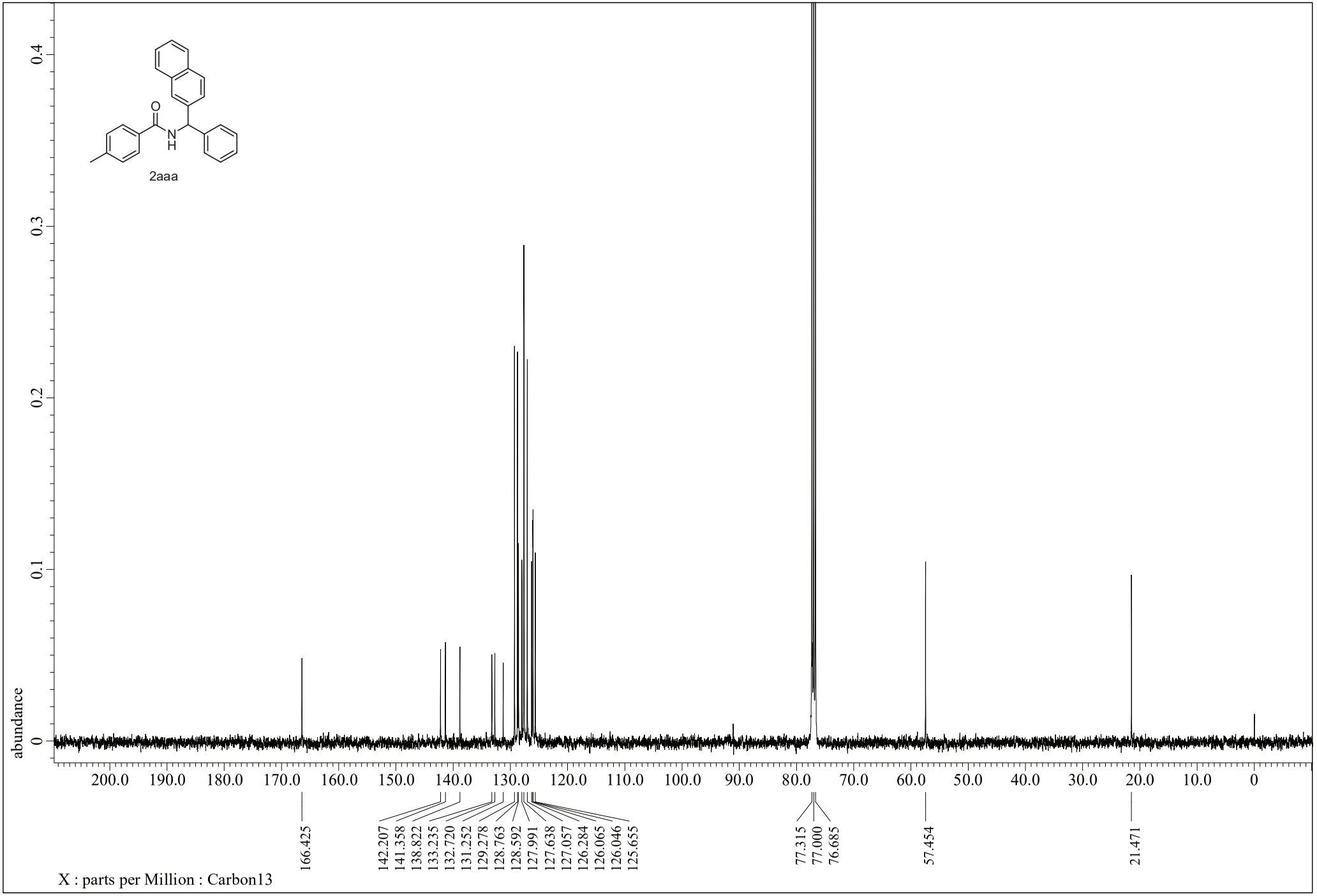
^{19}F NMR (376 MHz, $CDCl_3$)



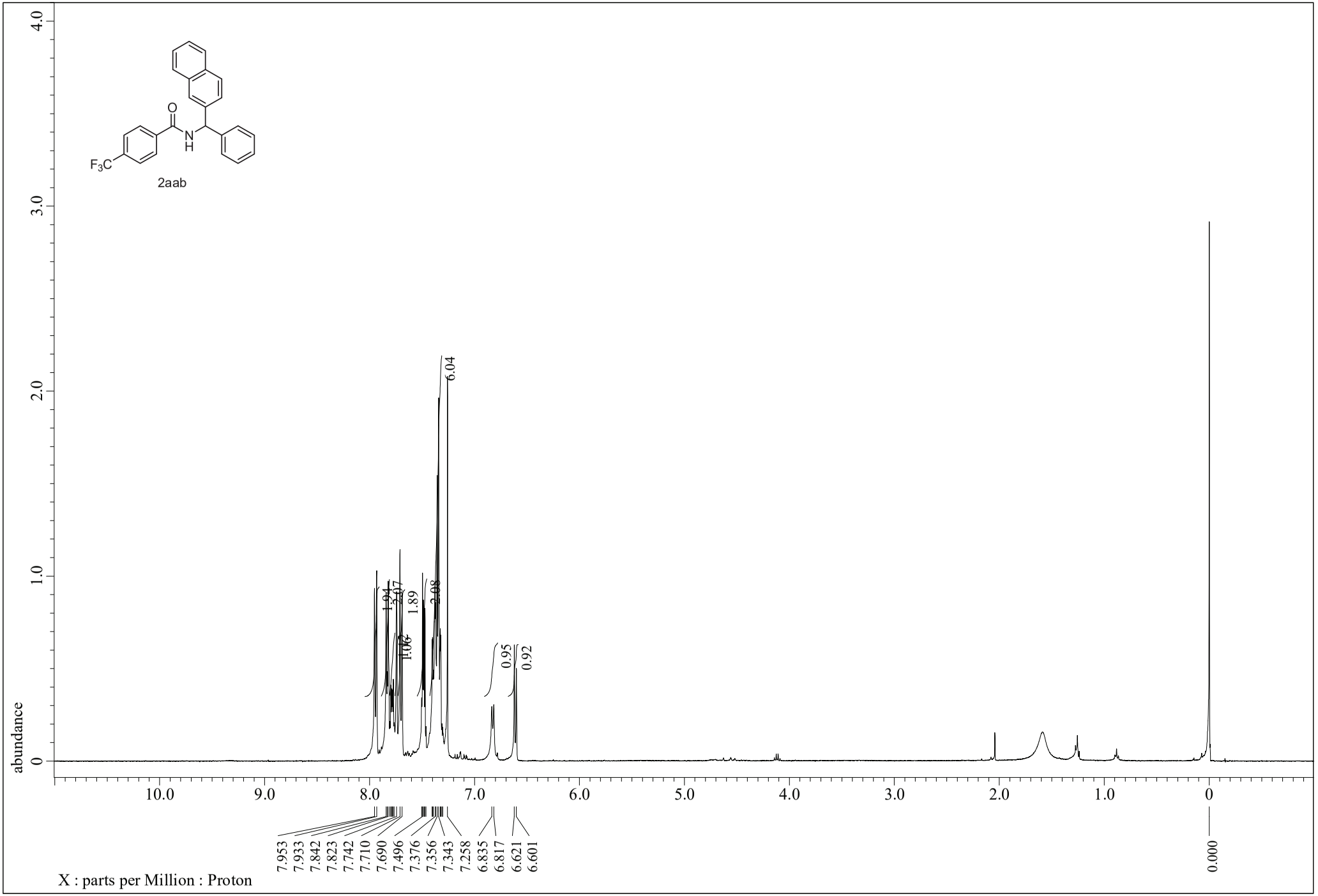
^{1}H NMR (400 MHz, $CDCl_3$)



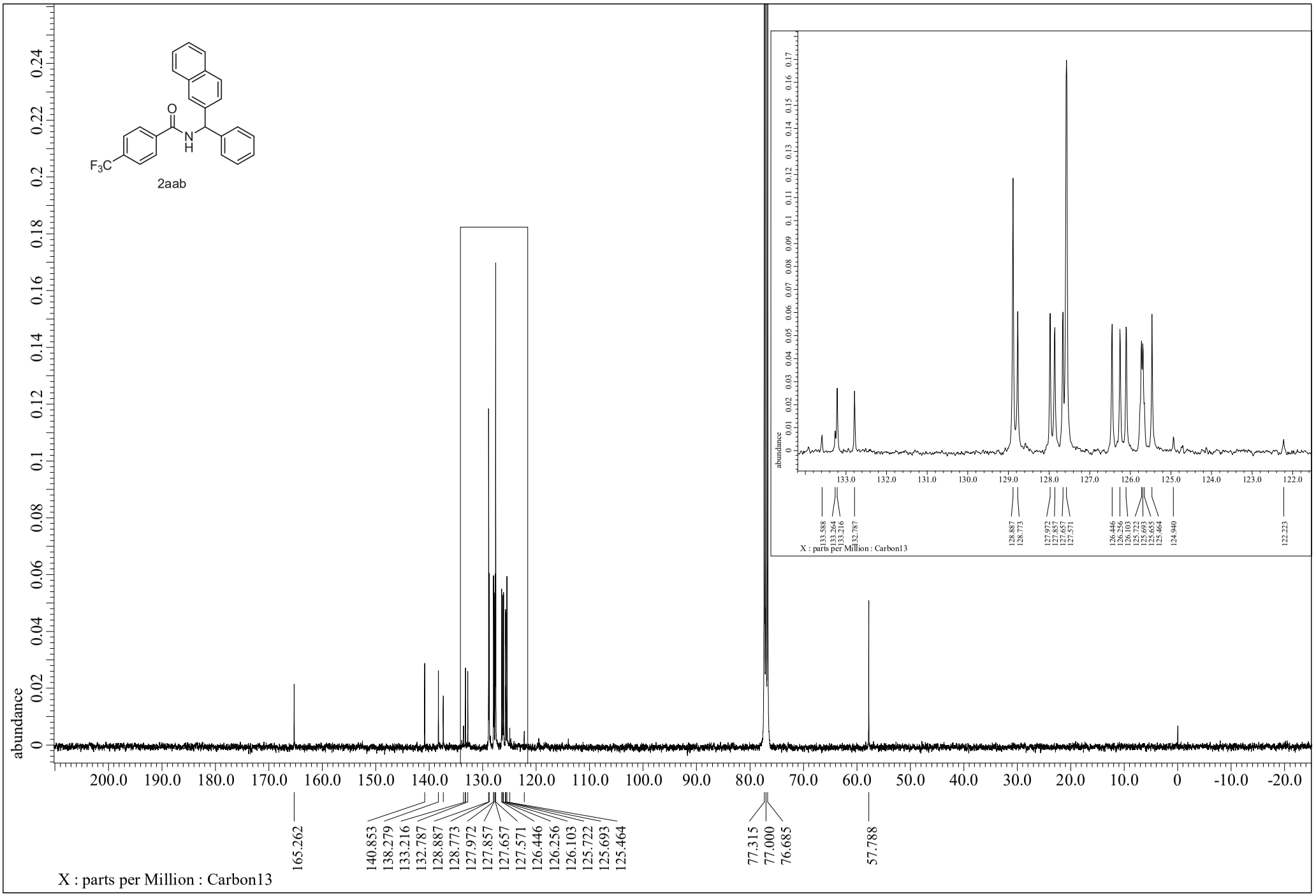
^{13}C NMR (101 MHz, $CDCl_3$)



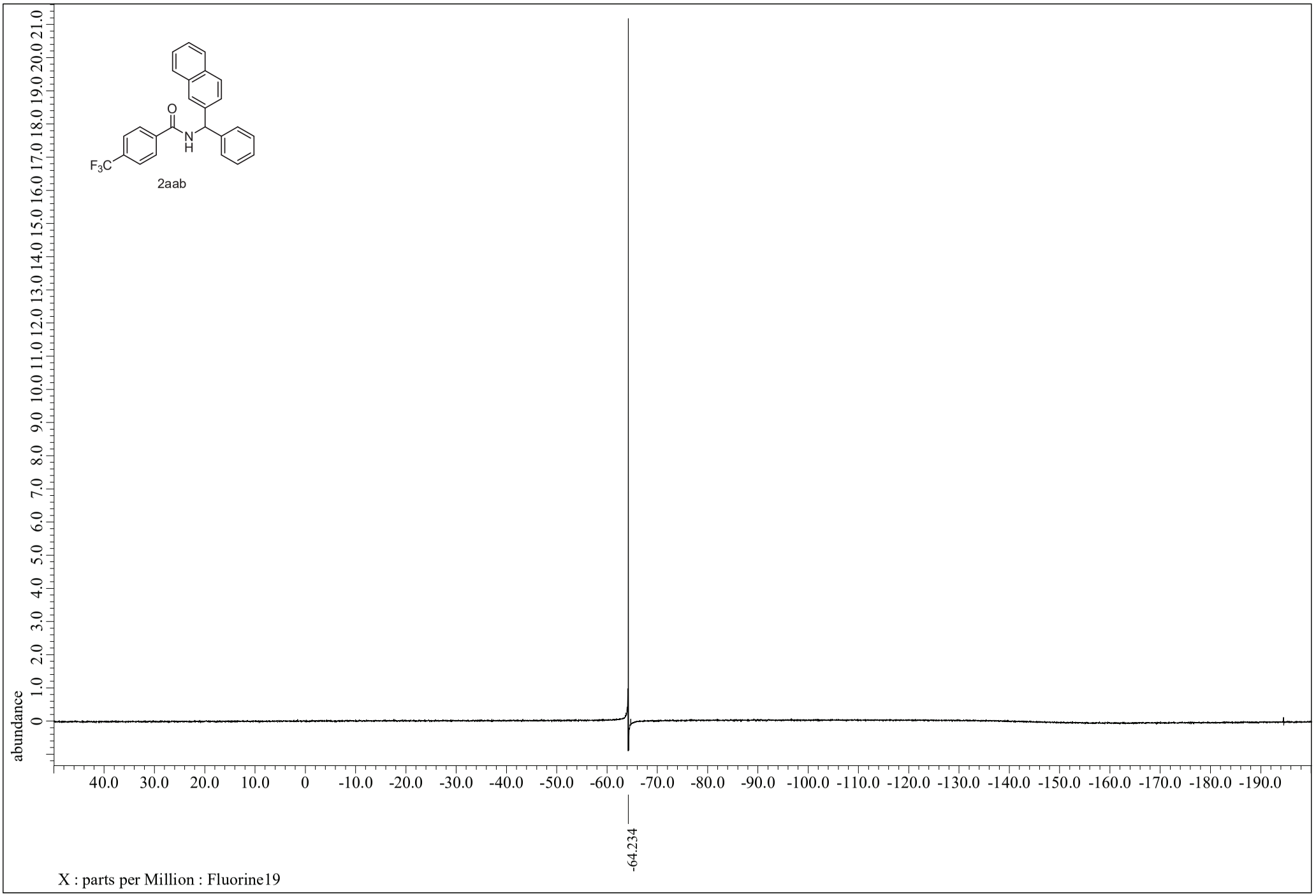
^{1}H NMR (400 MHz, $CDCl_3$)



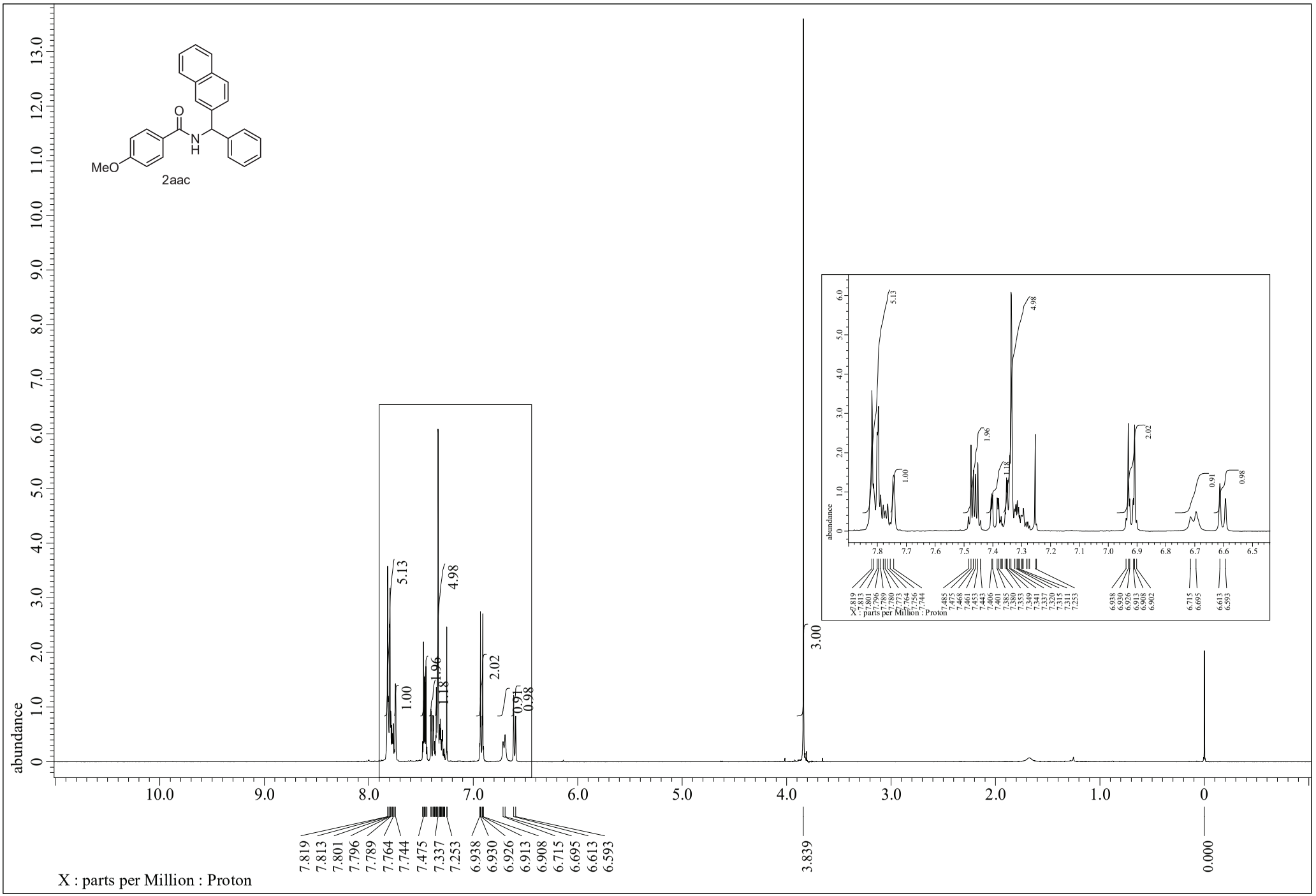
^{13}C NMR (101 MHz, $CDCl_3$)



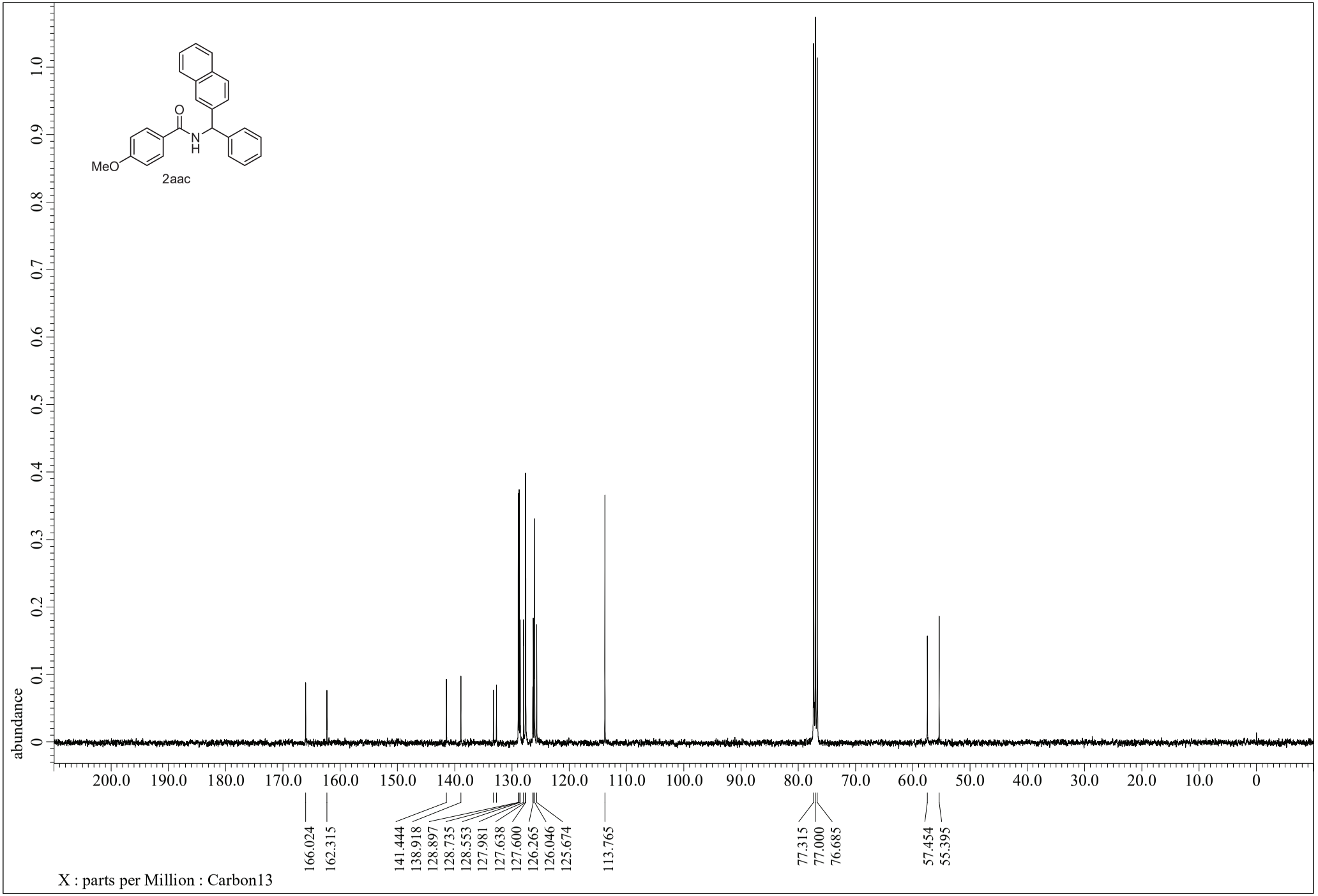
^{19}F NMR (376 MHz, $CDCl_3$)



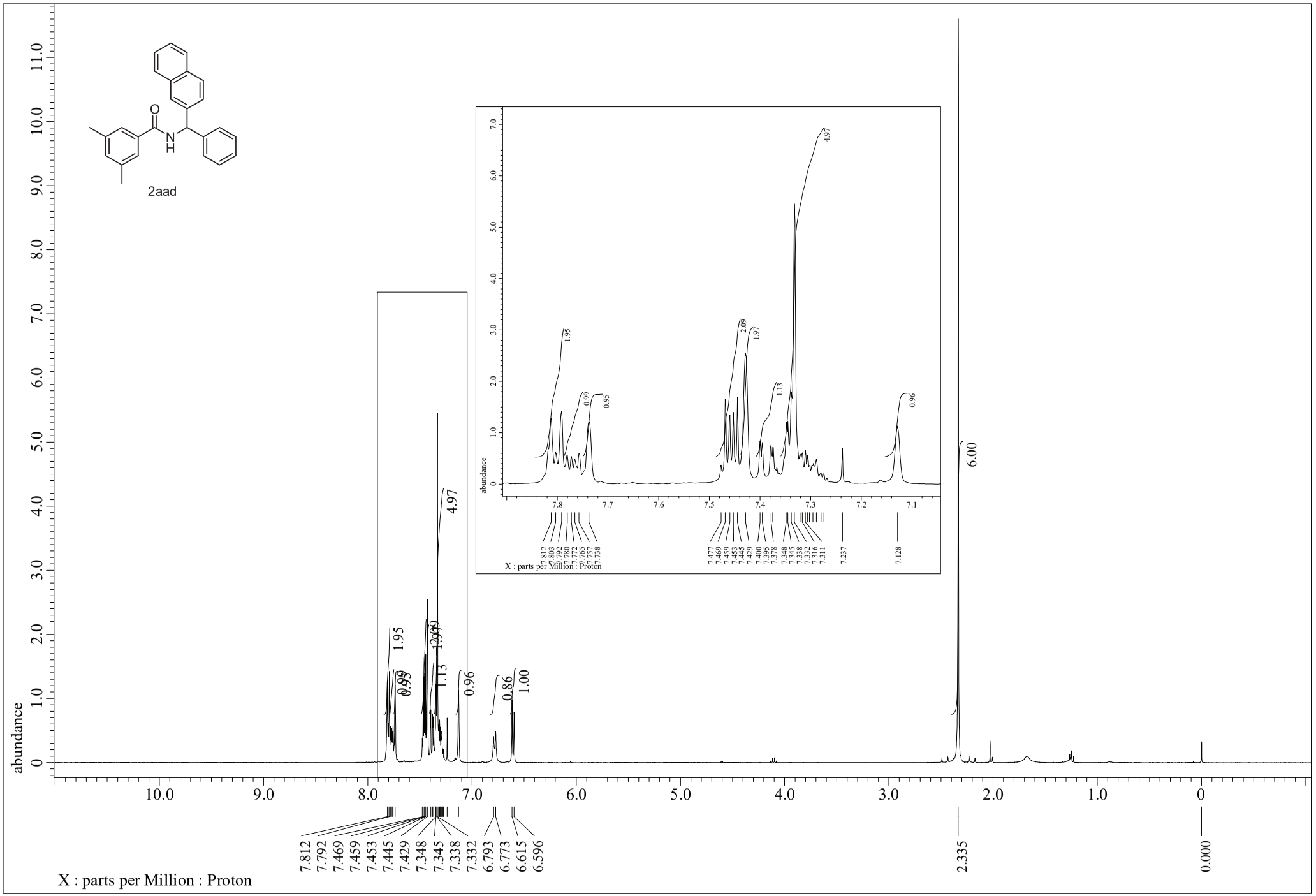
^{1}H NMR (400 MHz, $CDCl_3$)



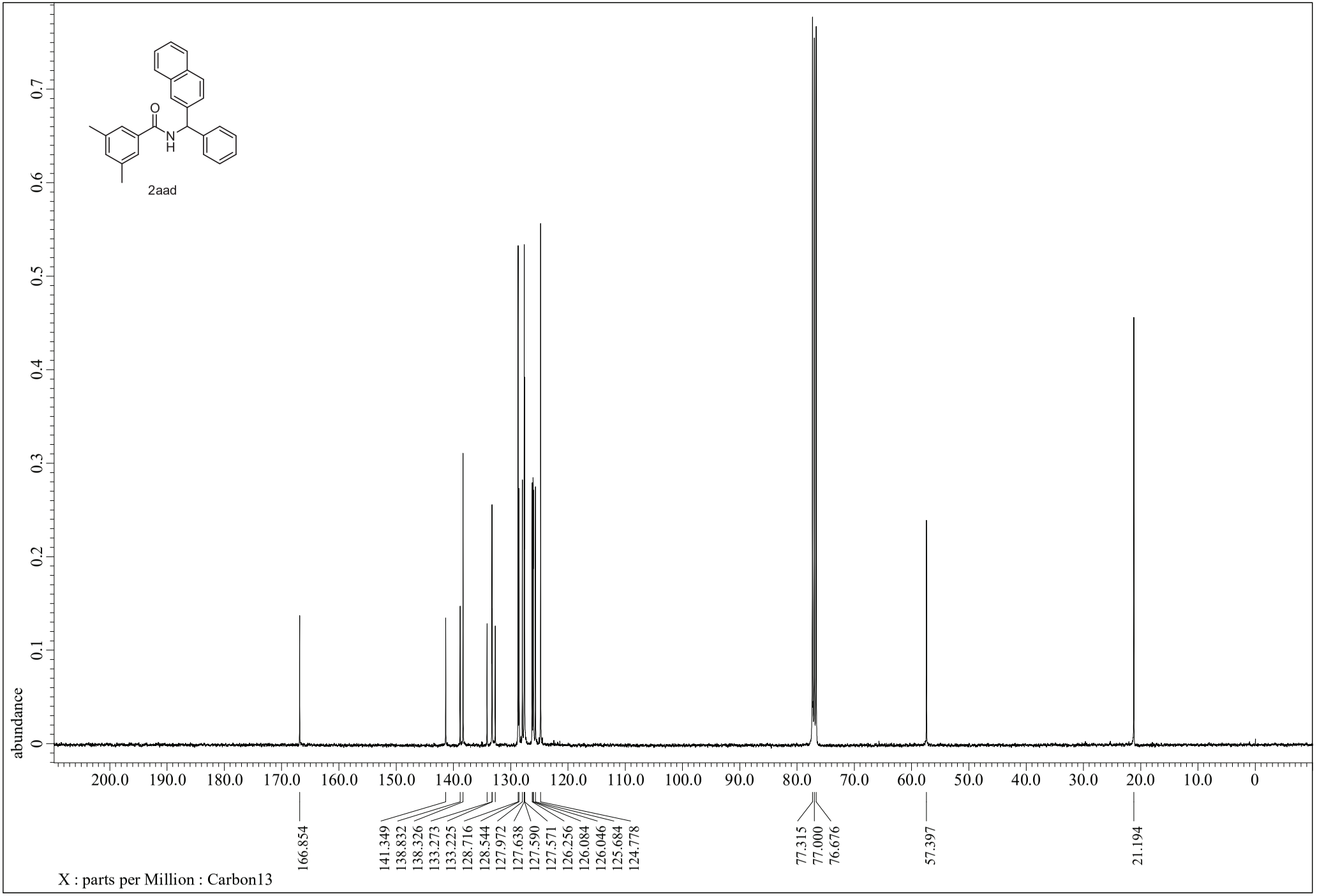
^{13}C NMR (101 MHz, $CDCl_3$)



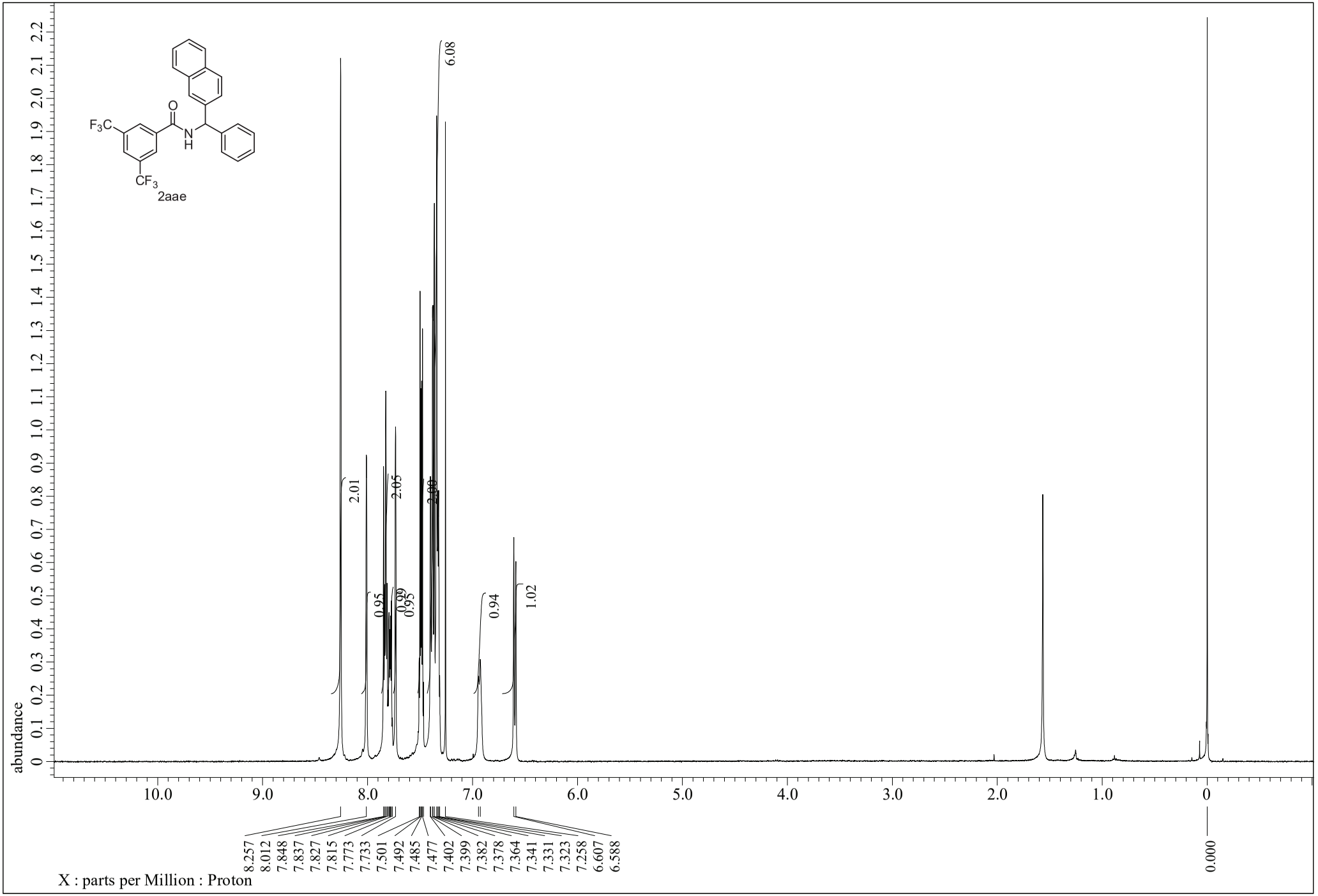
^{1}H NMR (400 MHz, $CDCl_3$)



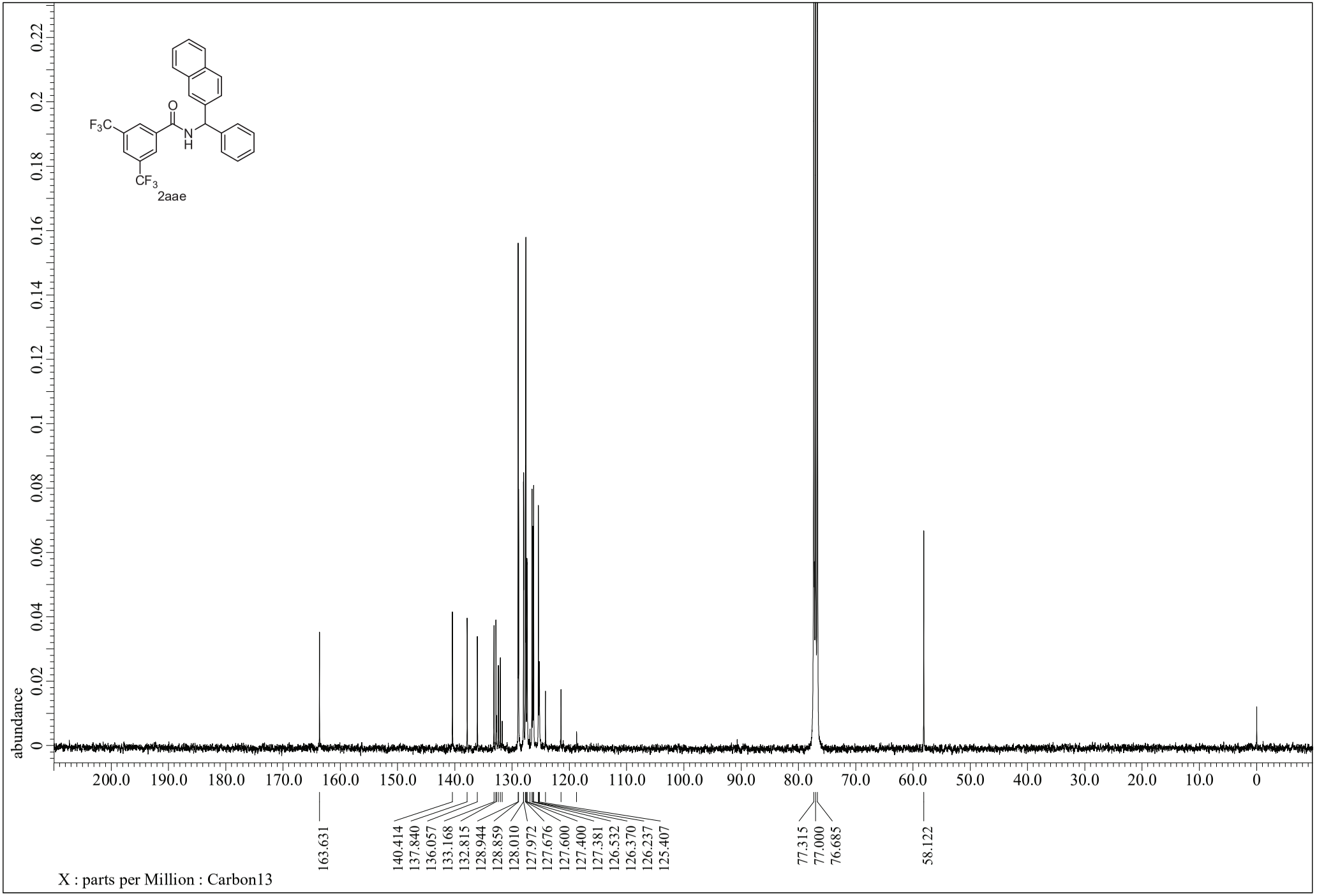
^{13}C NMR (101 MHz, $CDCl_3$)



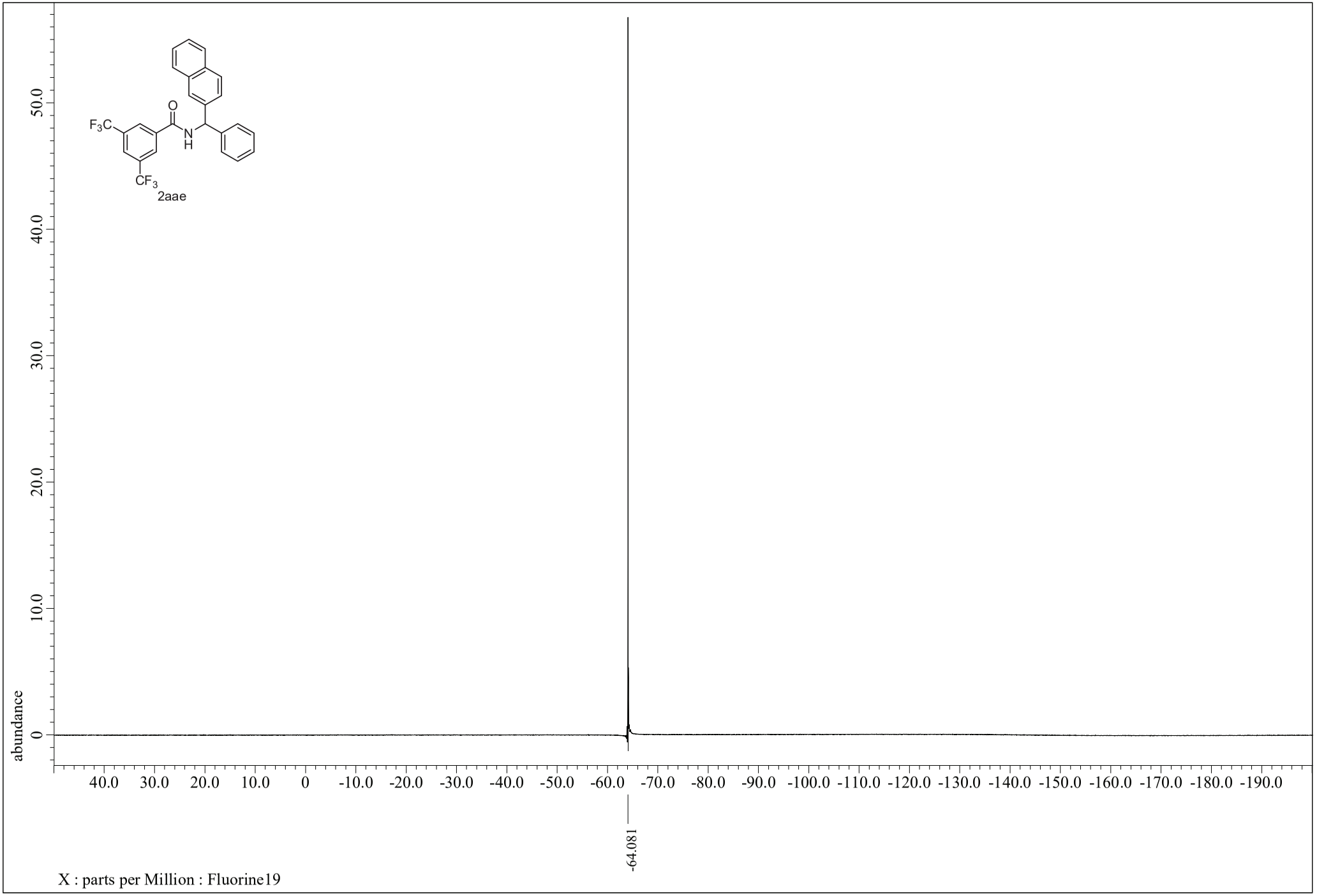
^{1}H NMR (400 MHz, $CDCl_3$)



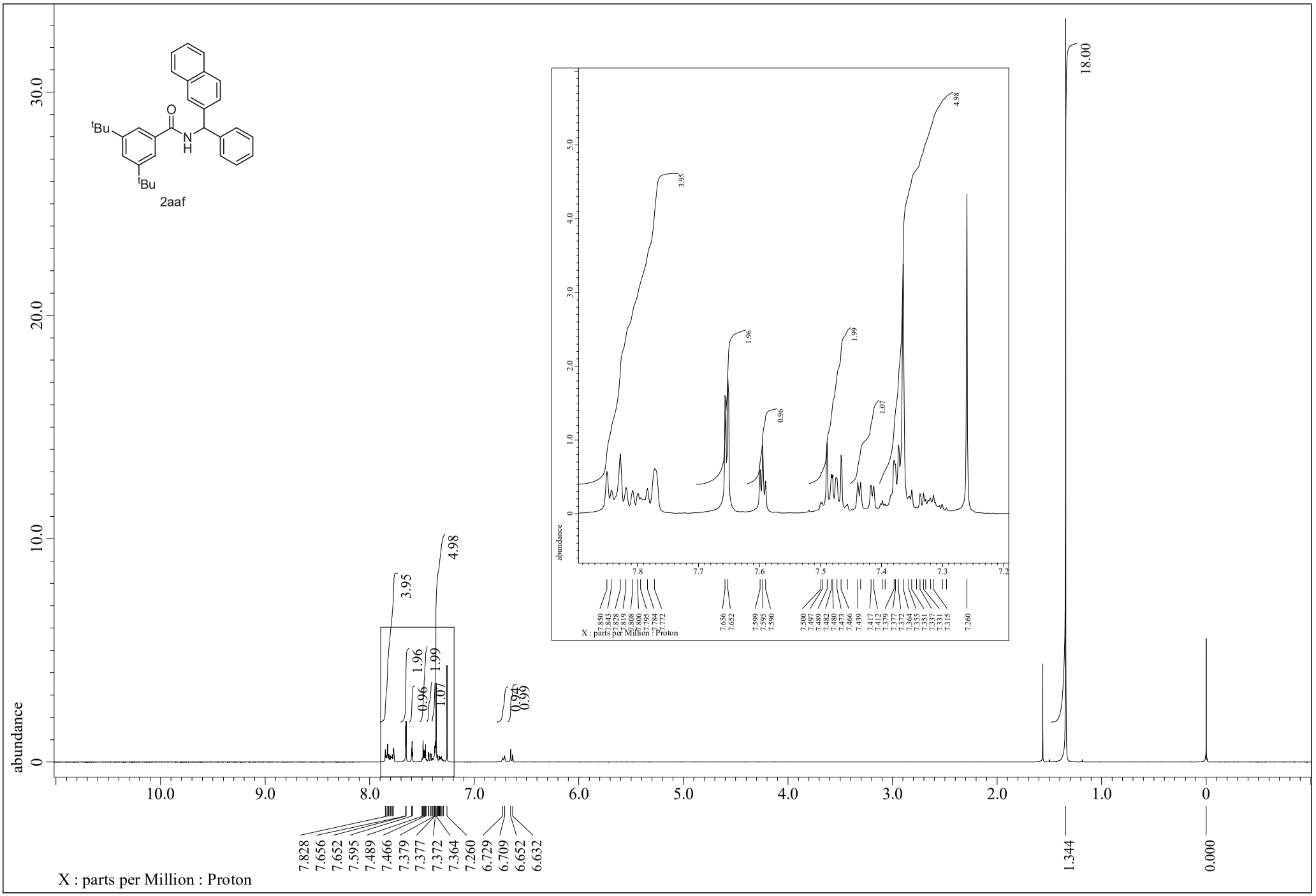
^{13}C NMR (101 MHz, $CDCl_3$)



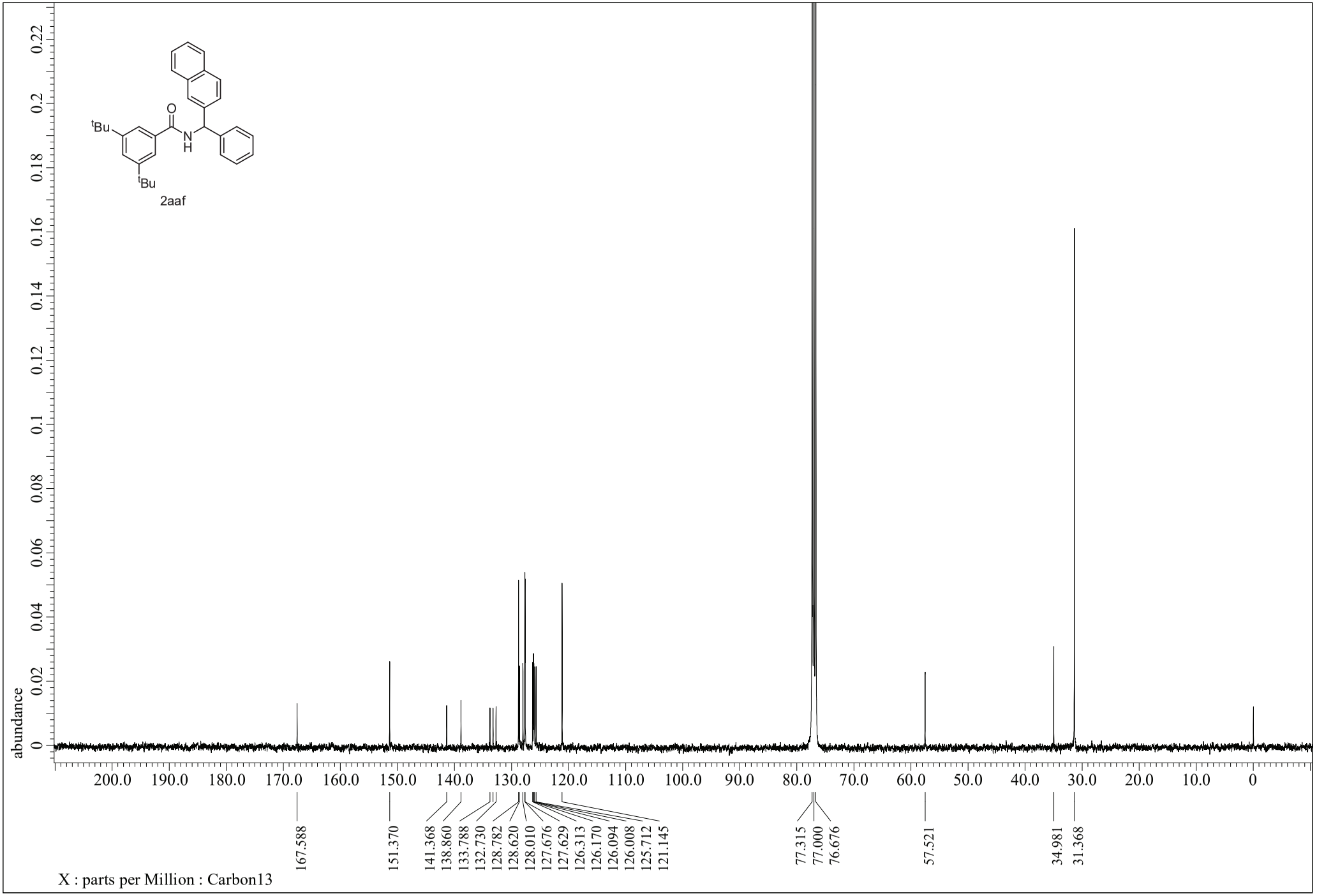
^{19}F NMR (376 MHz, $CDCl_3$)



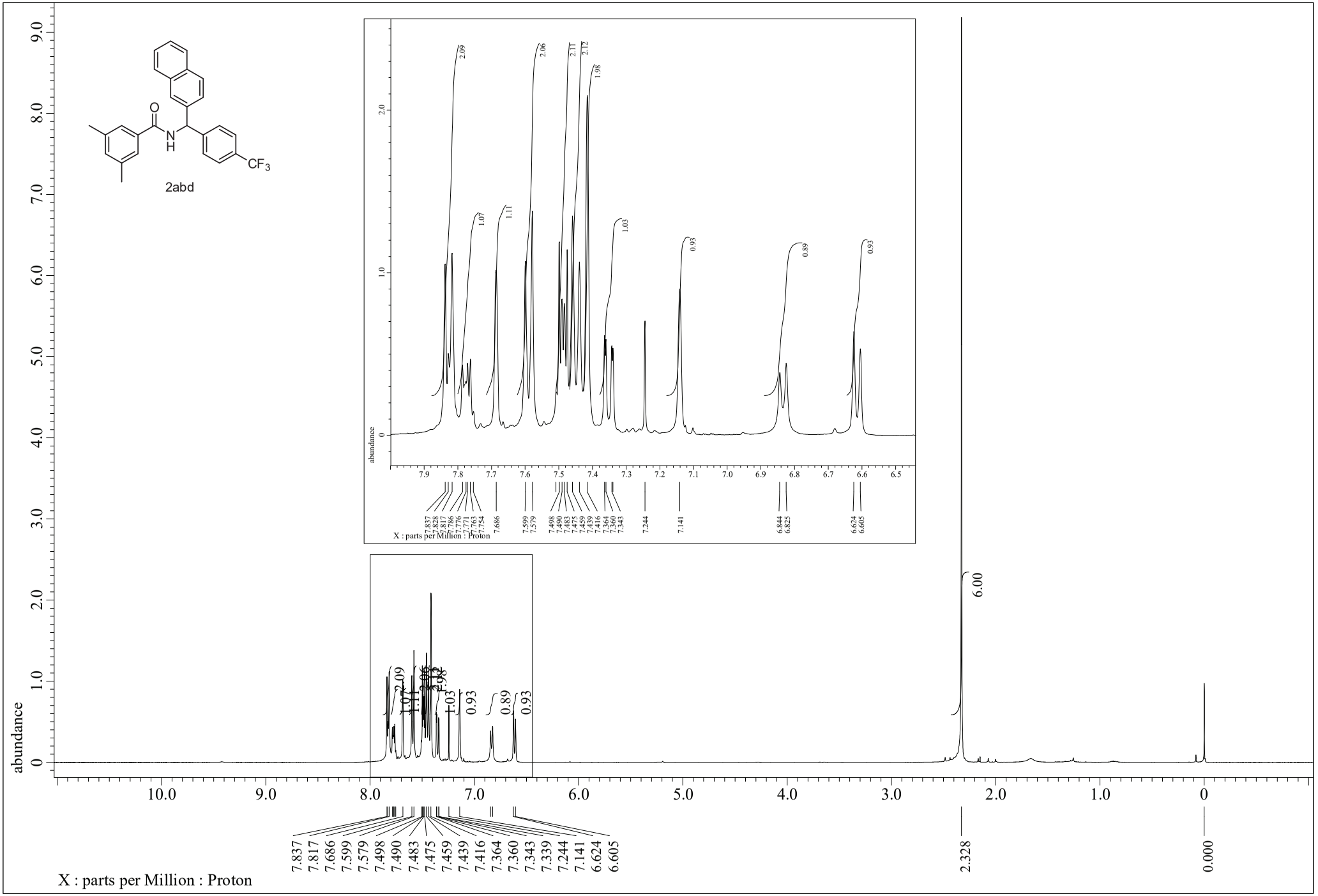
^{1}H NMR (400 MHz, $CDCl_3$)



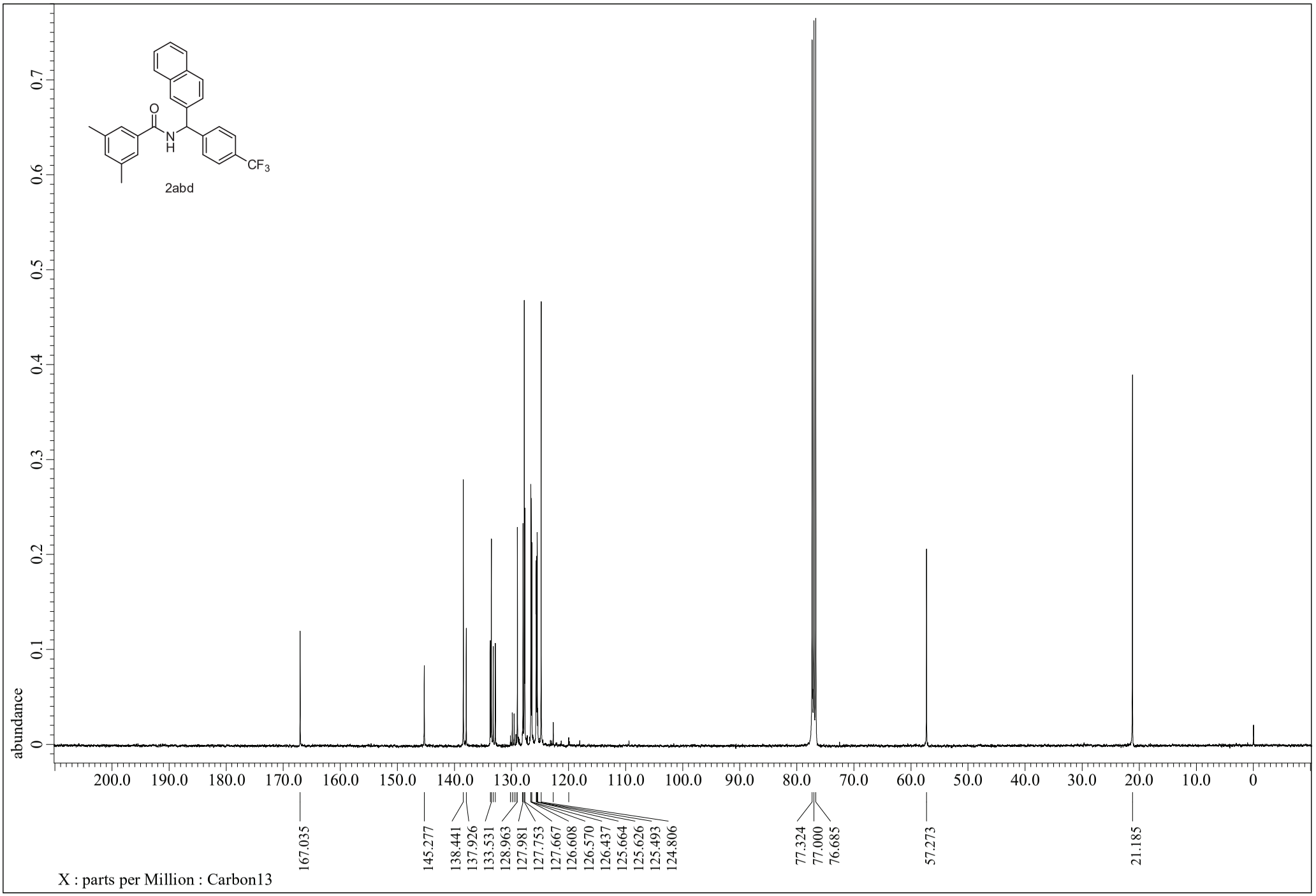
^{13}C NMR (101 MHz, $CDCl_3$)



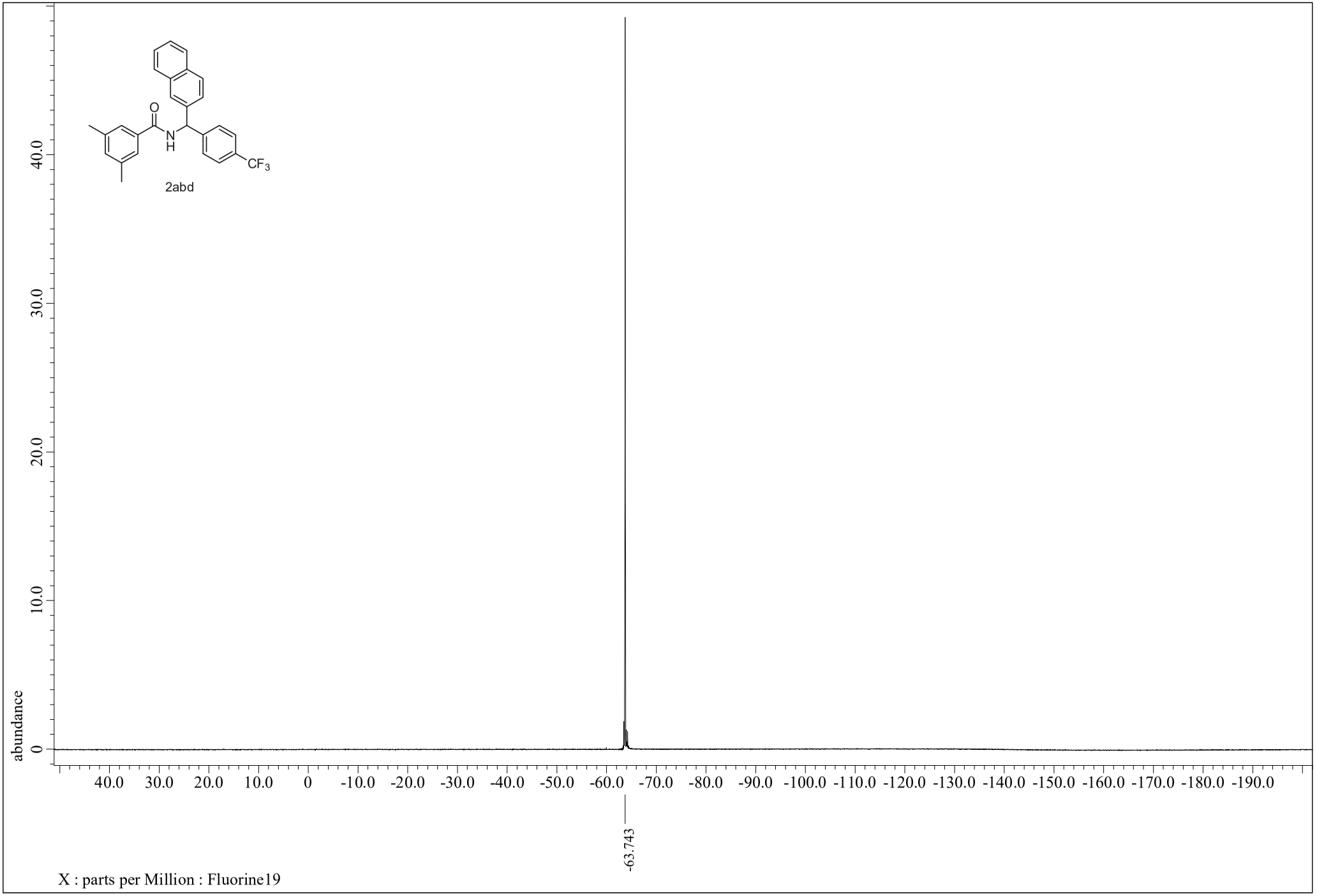
^{1}H NMR (400 MHz, $CDCl_3$)



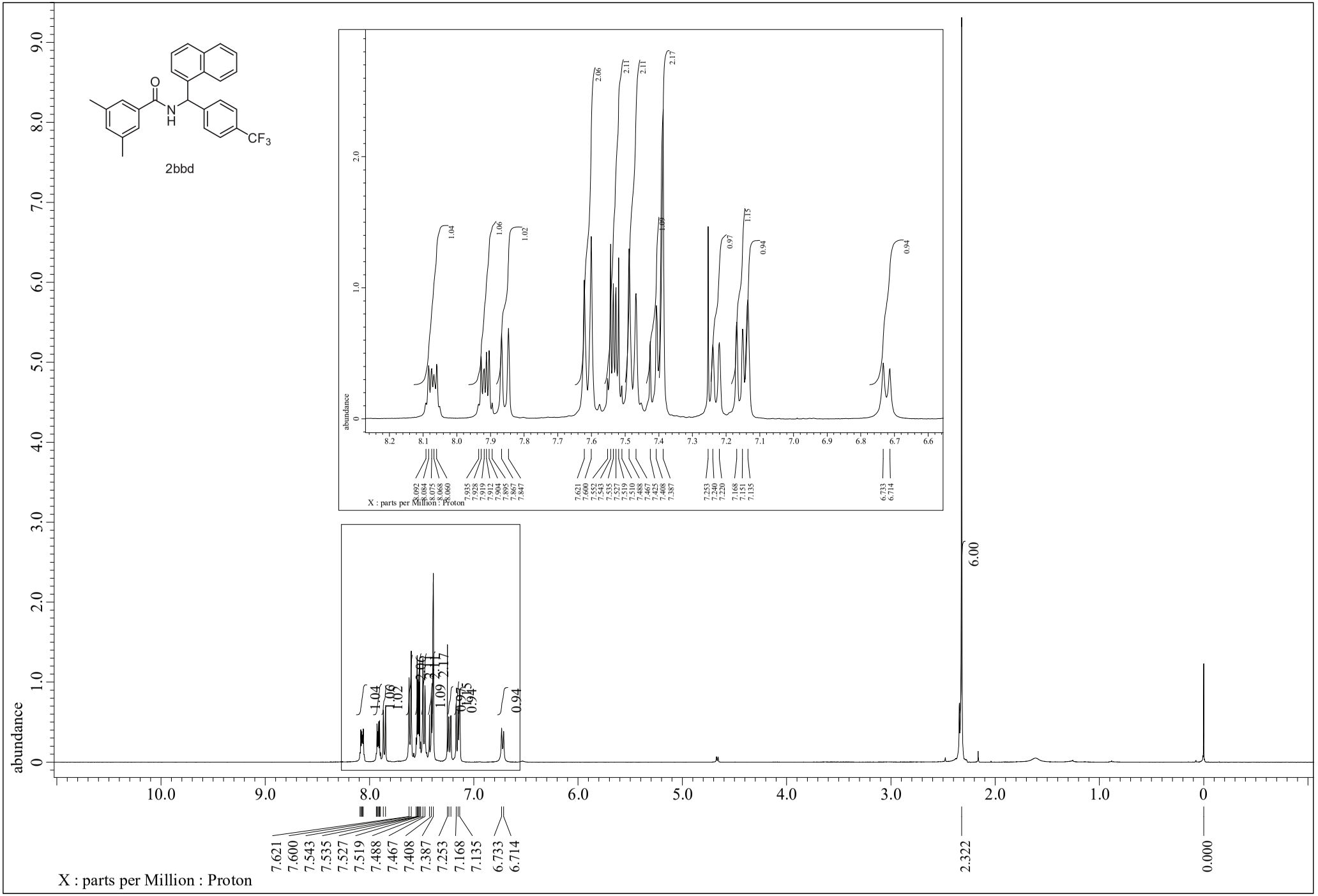
^{13}C NMR (101 MHz, $CDCl_3$)



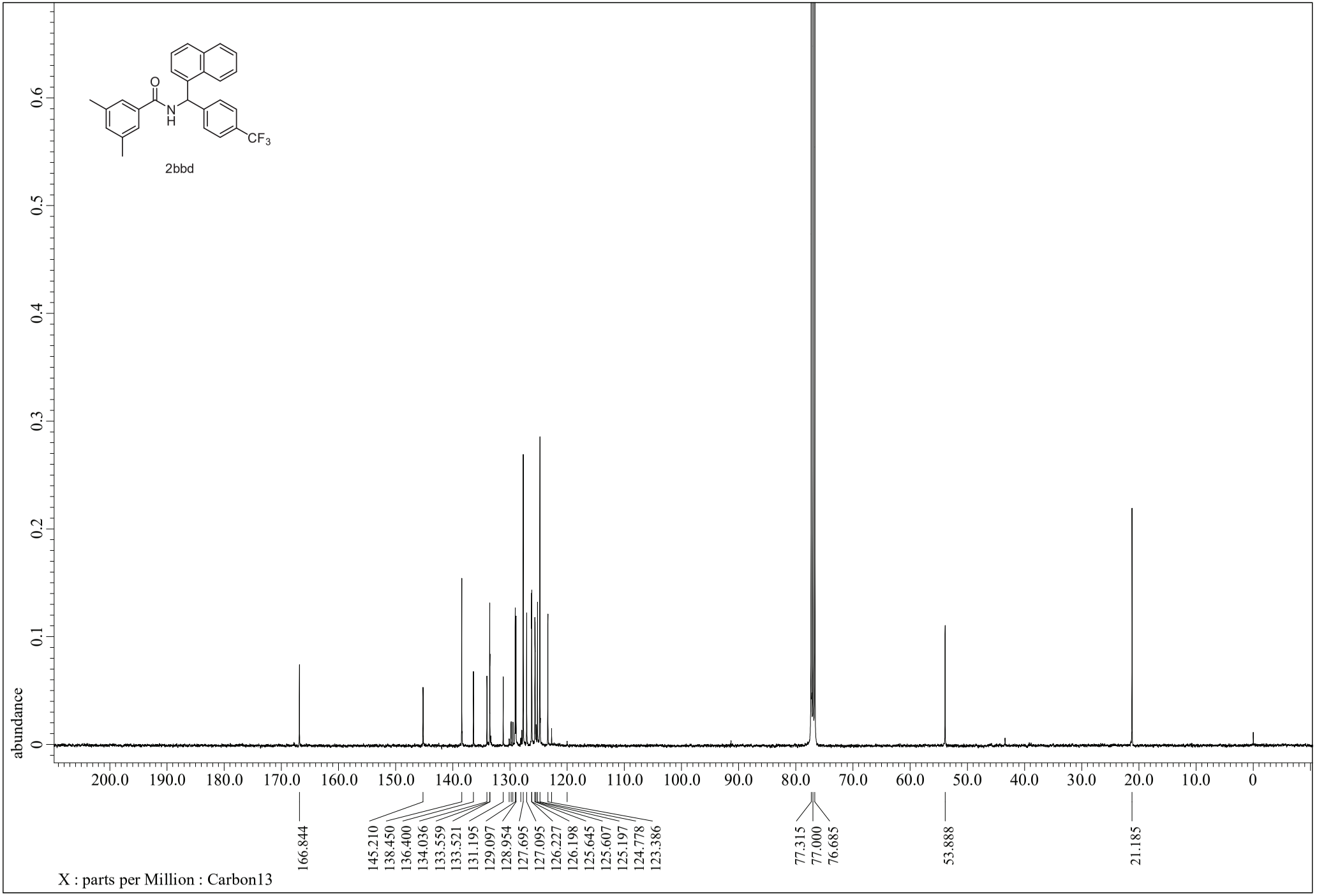
^{19}F NMR (376 MHz, $CDCl_3$)



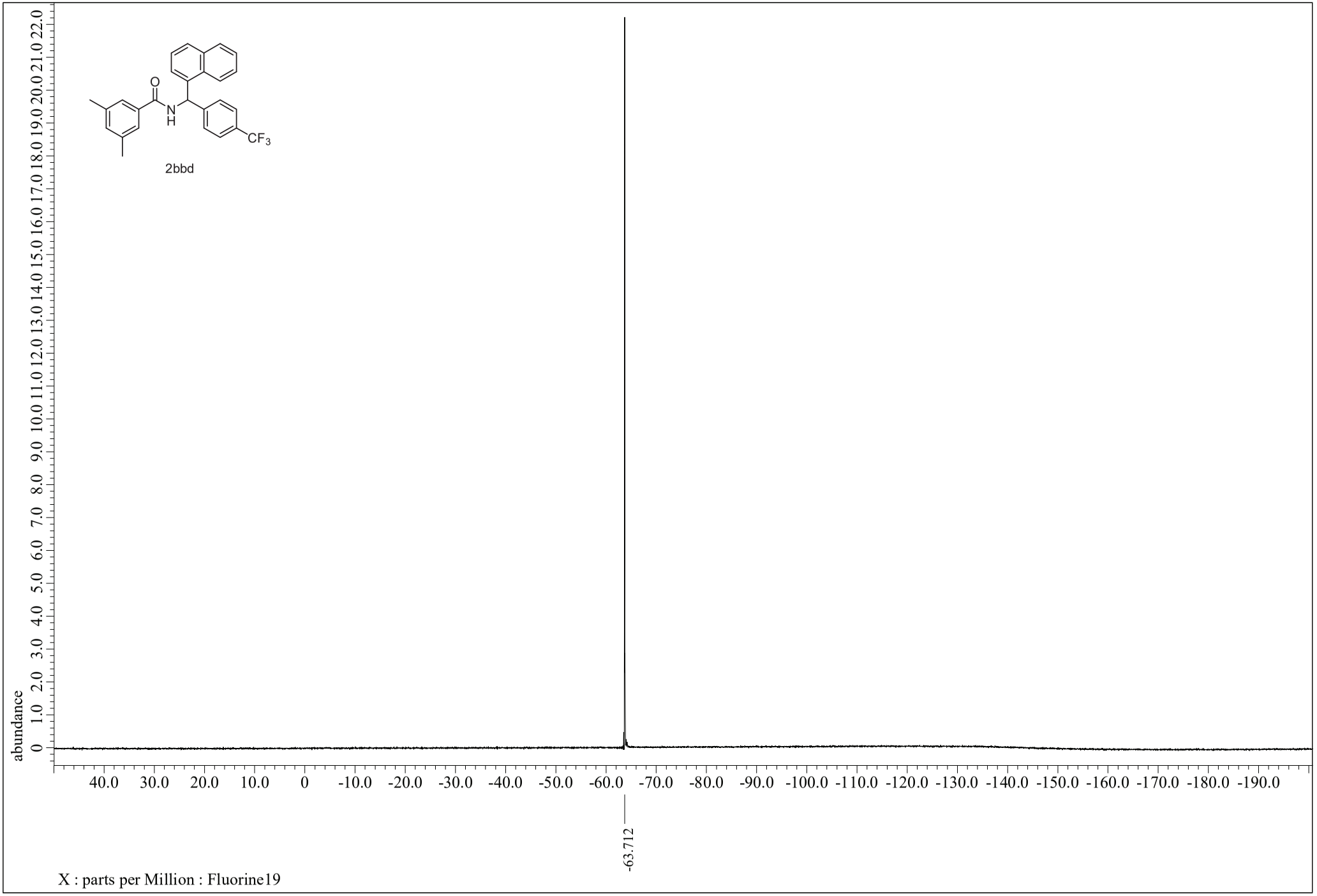
^{1}H NMR (400 MHz, $CDCl_3$)



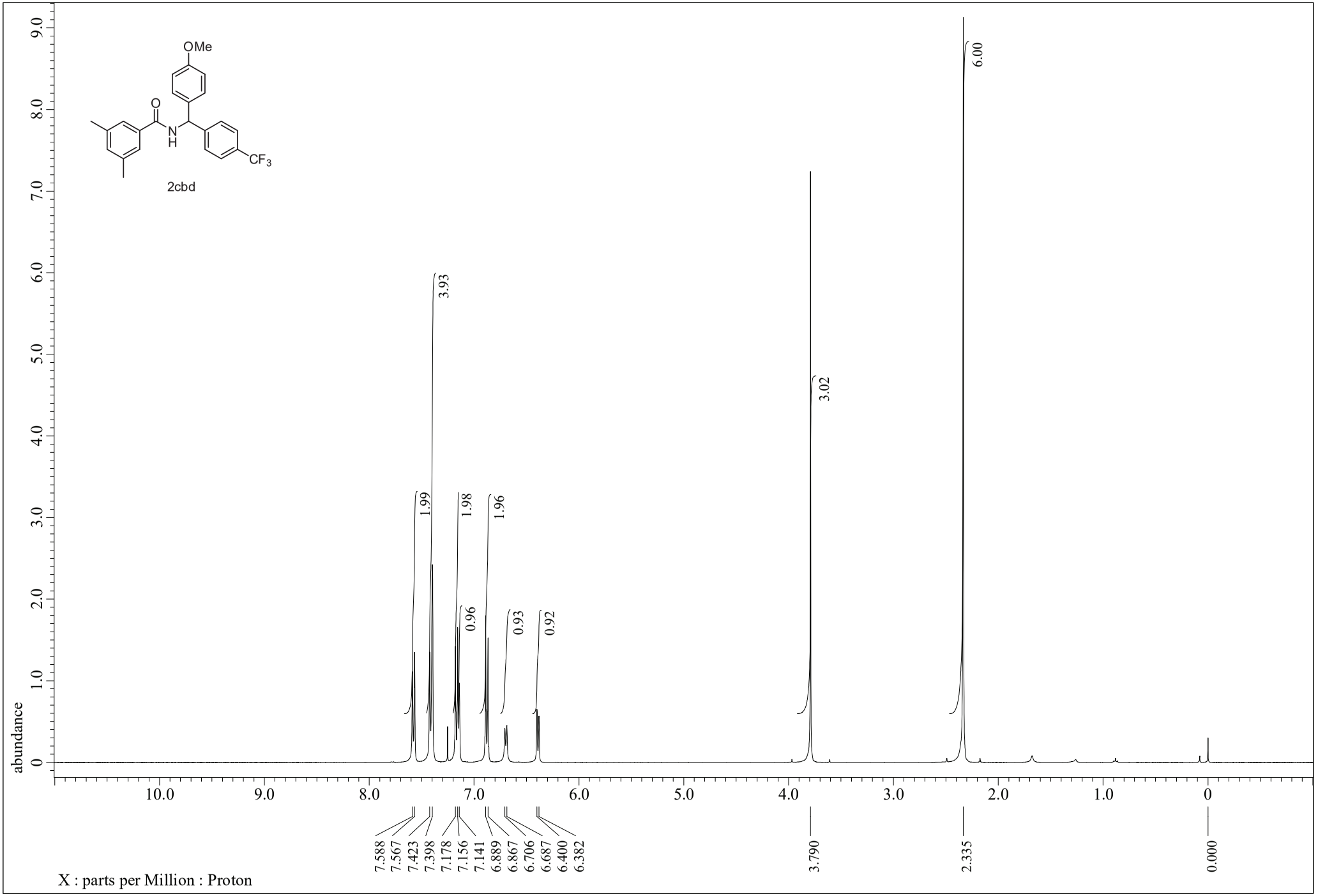
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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



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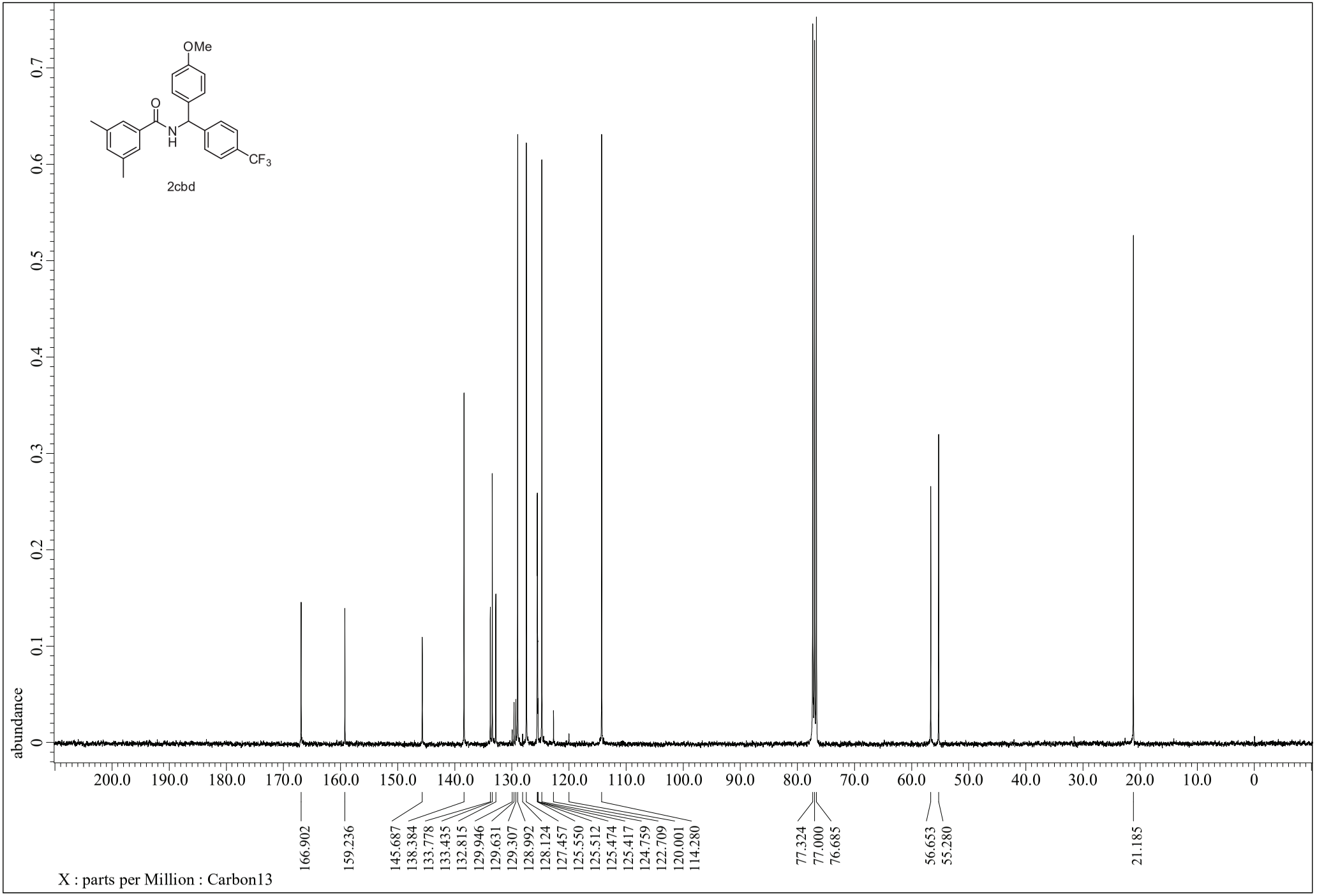

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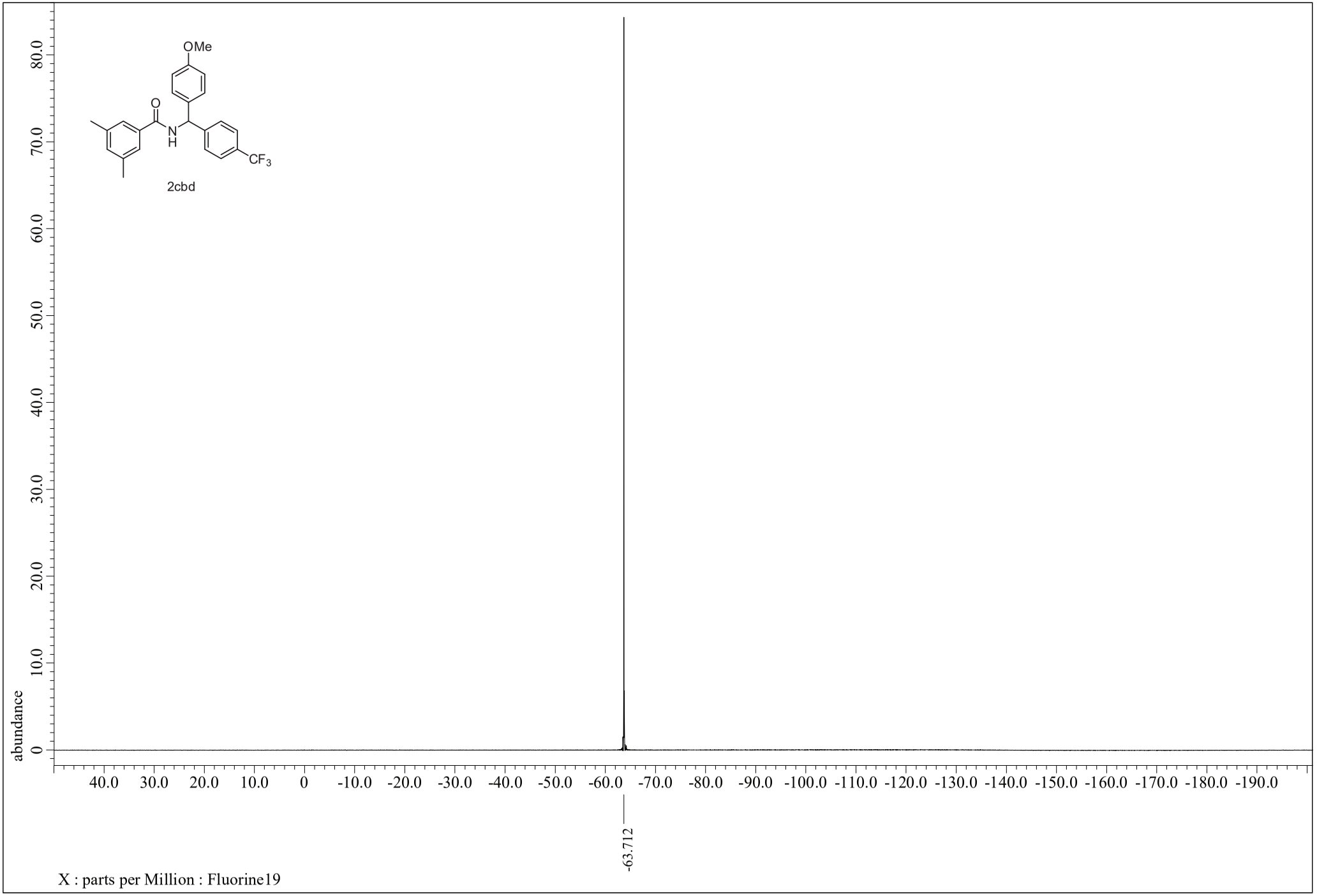

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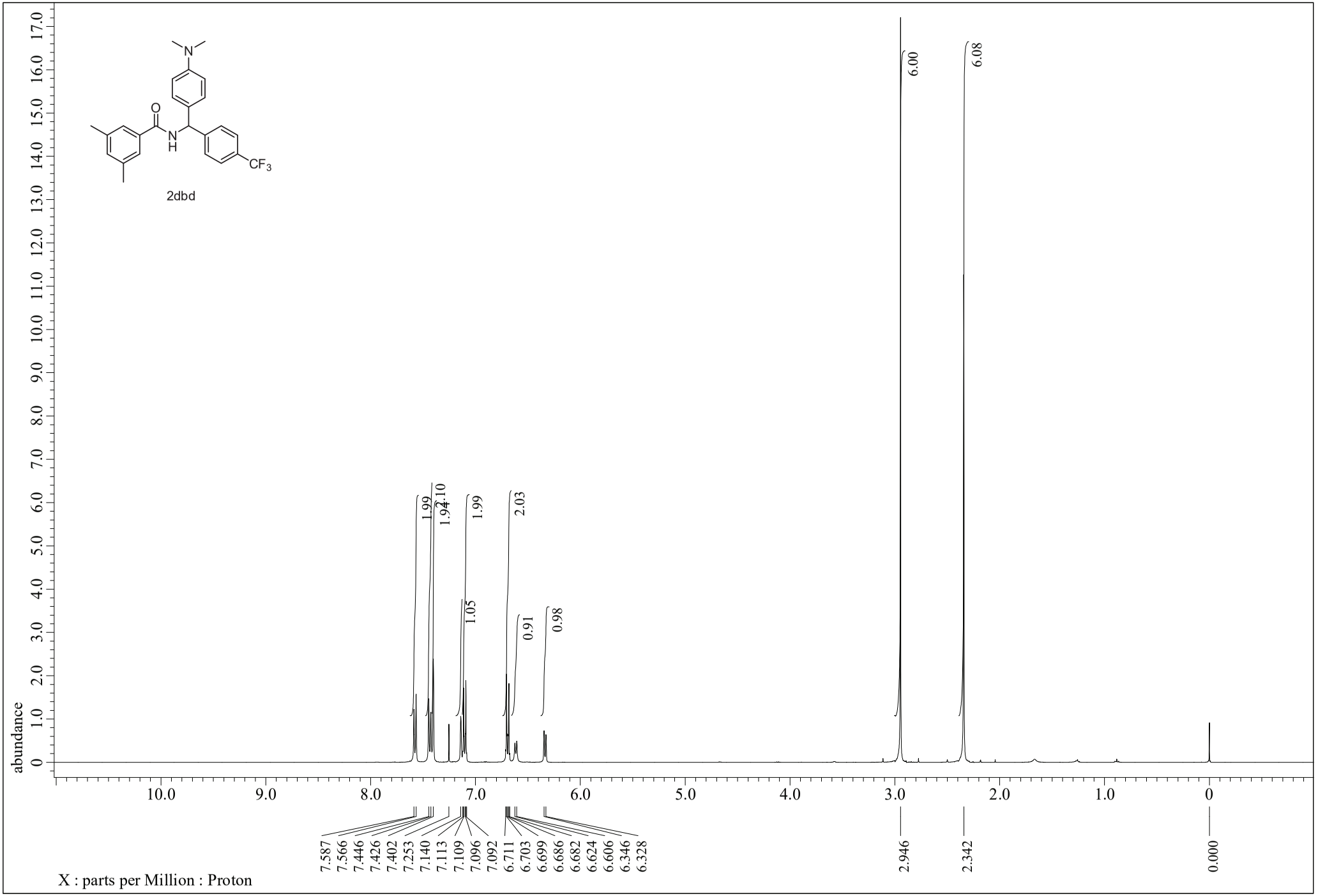
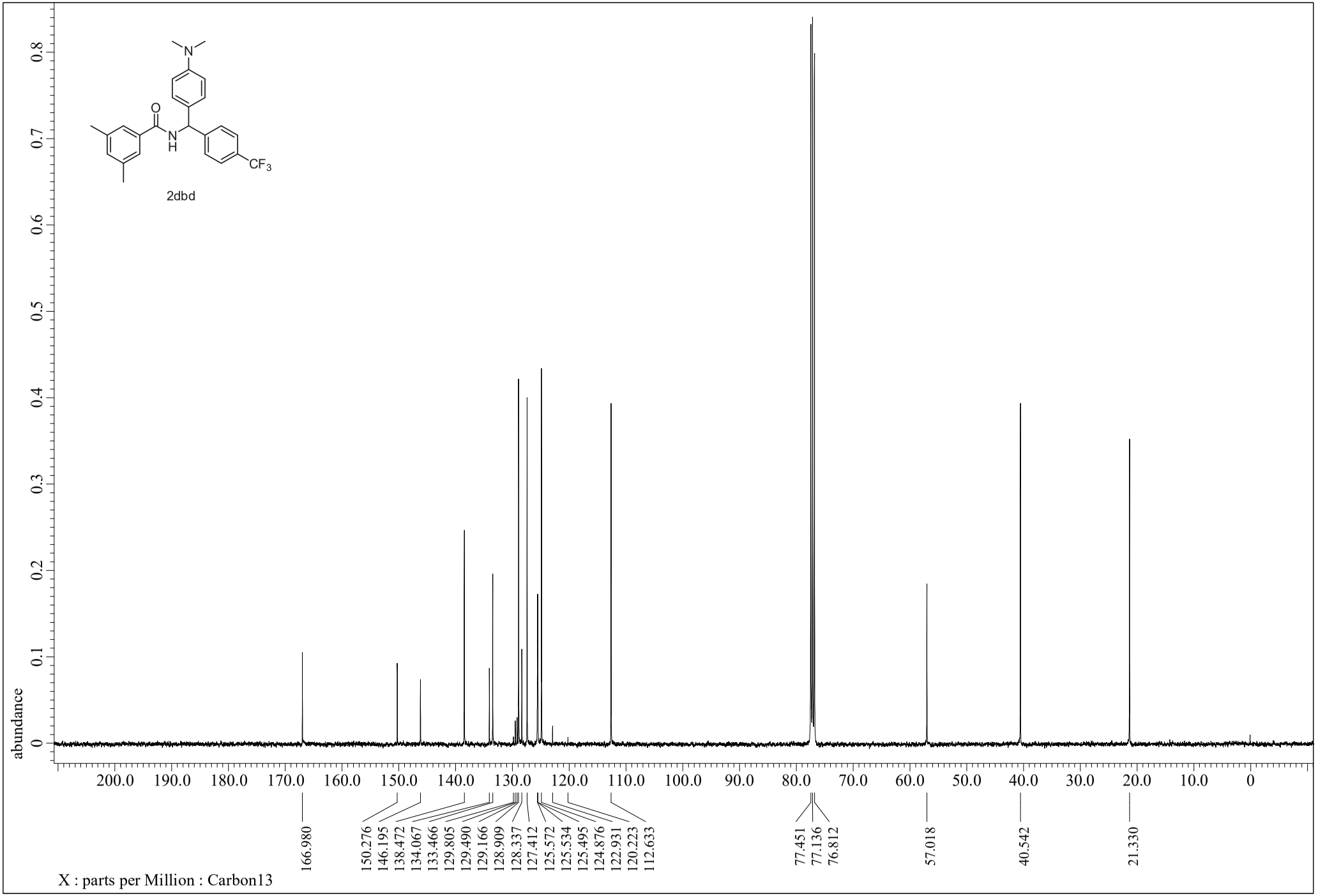


^{13}C NMR (101 MHz, $CDCl_3$)



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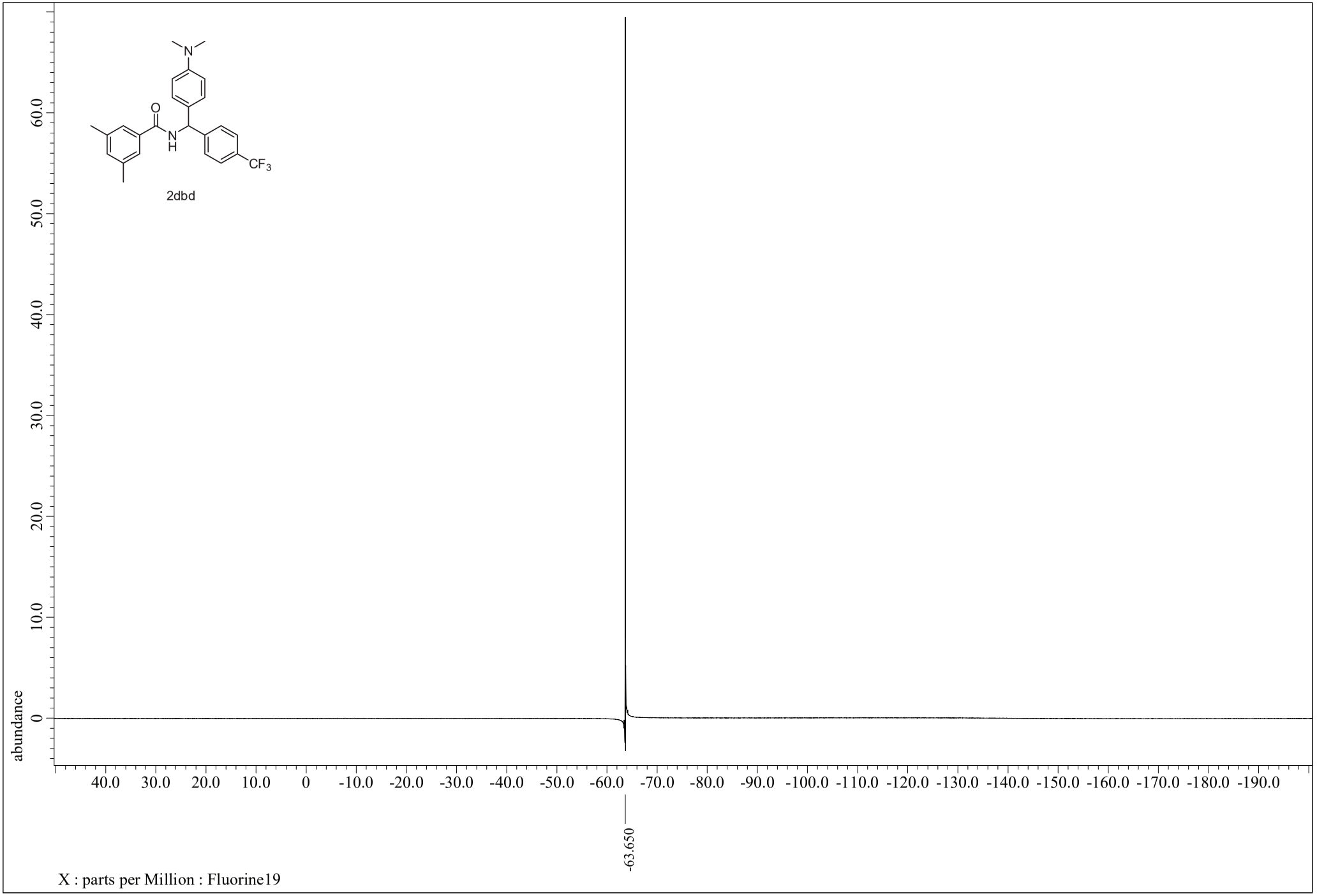

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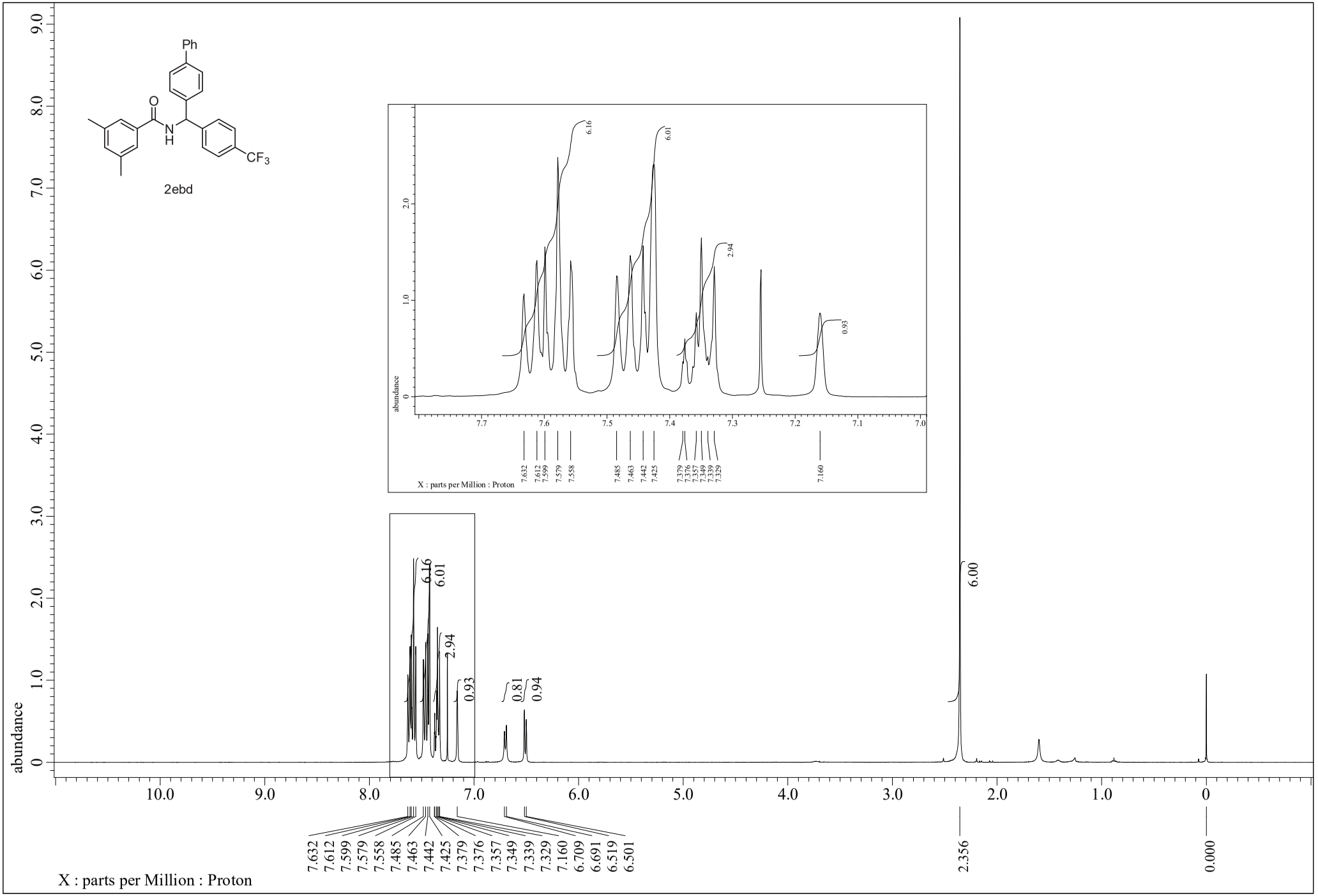
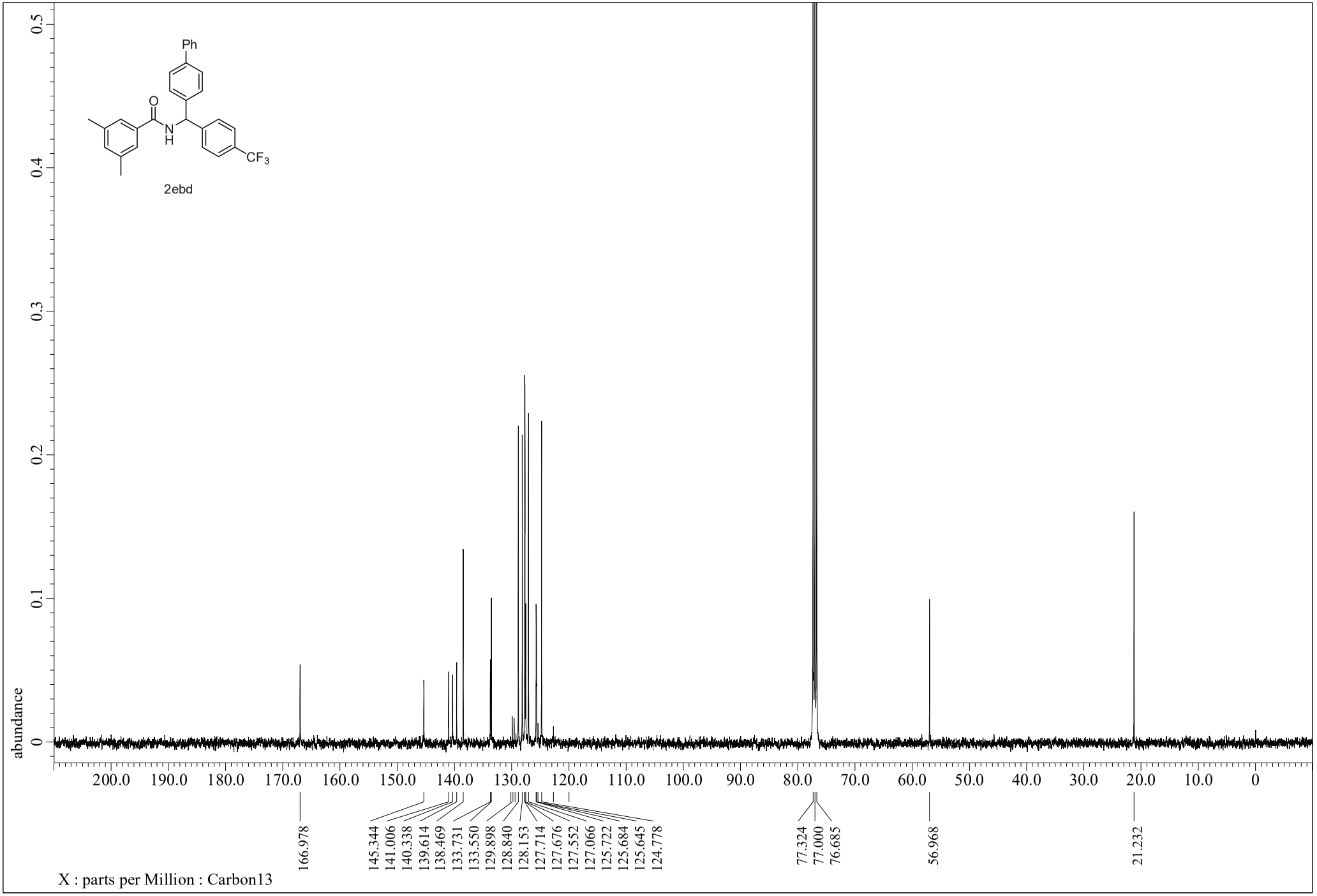
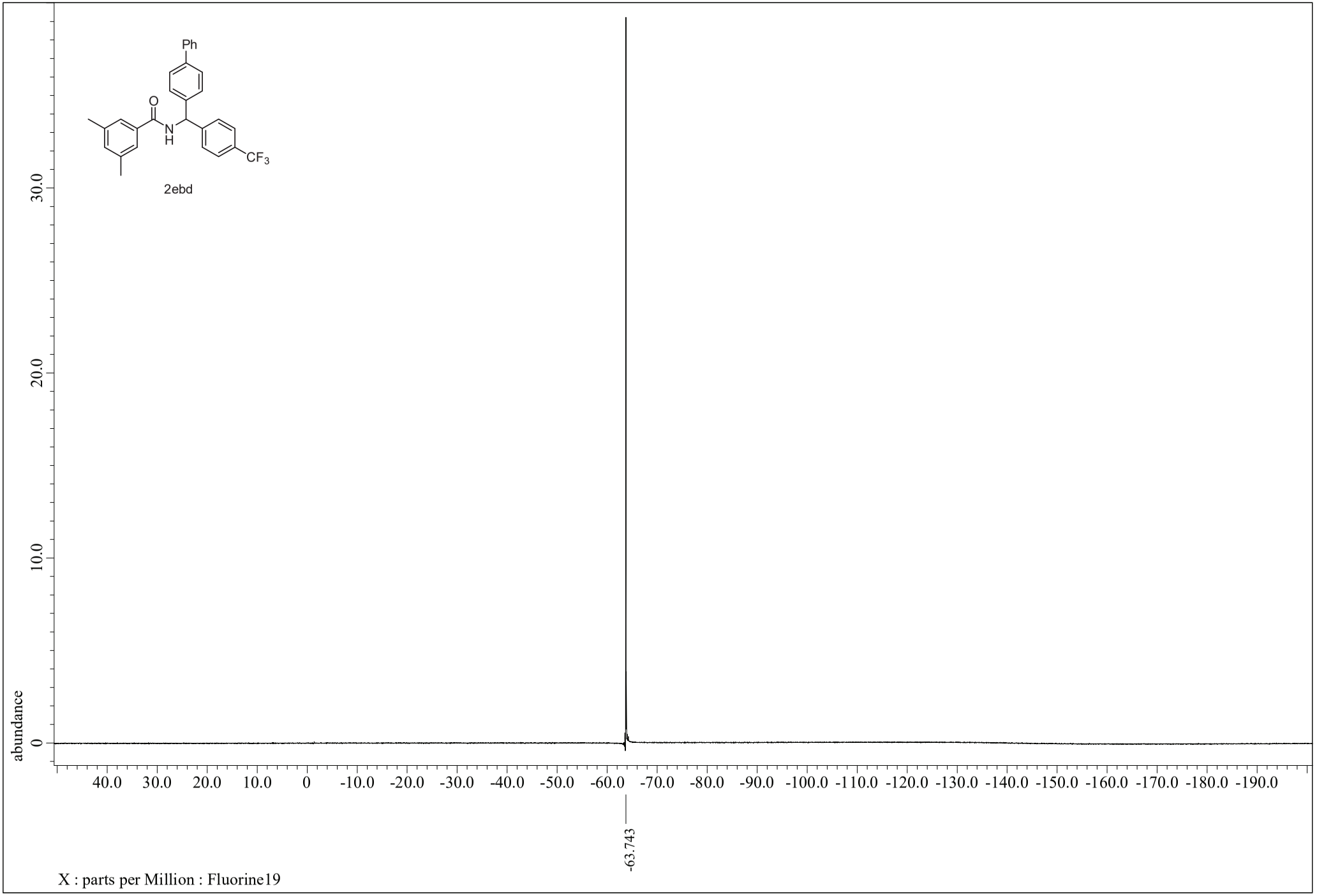


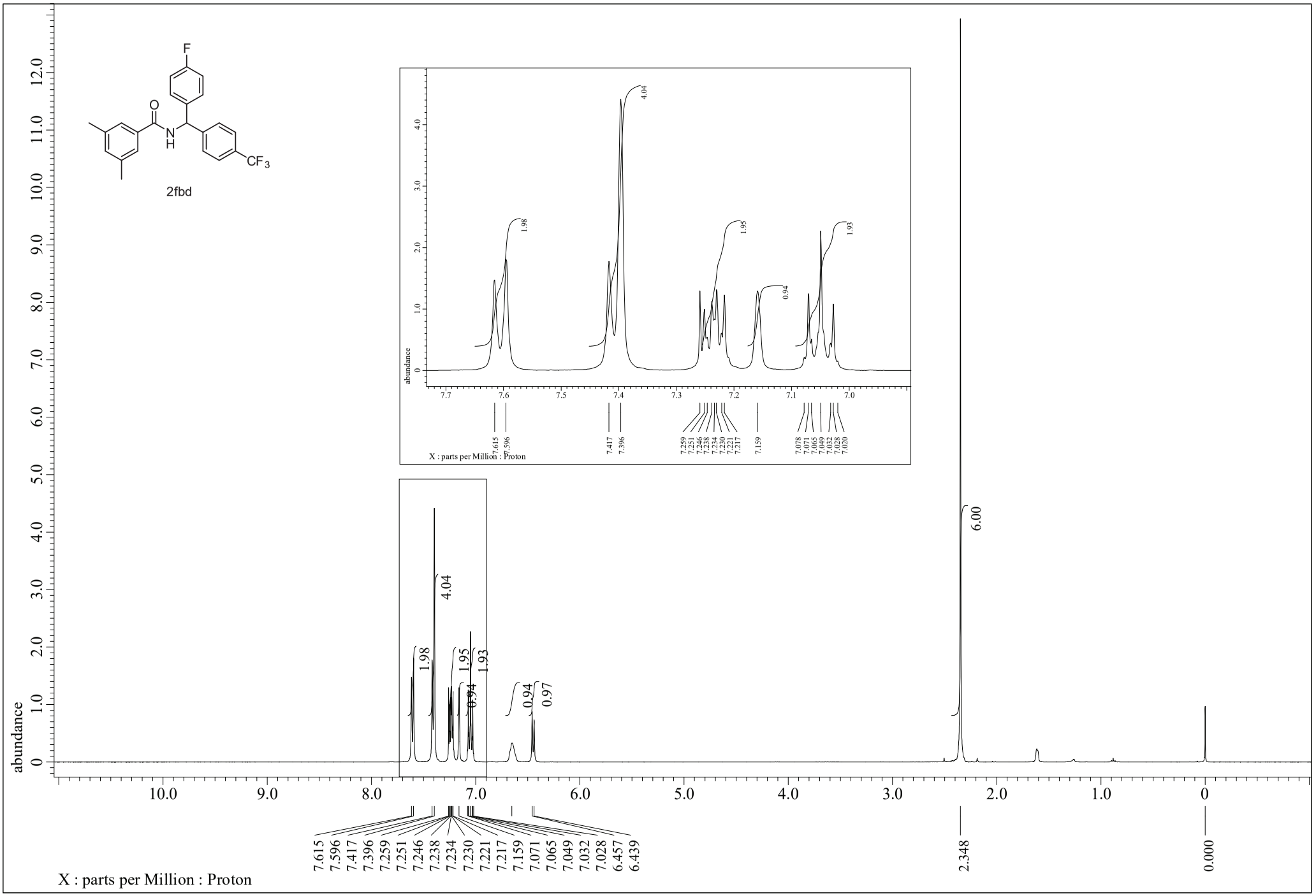
^{13}C NMR (101 MHz, $CDCl_3$)



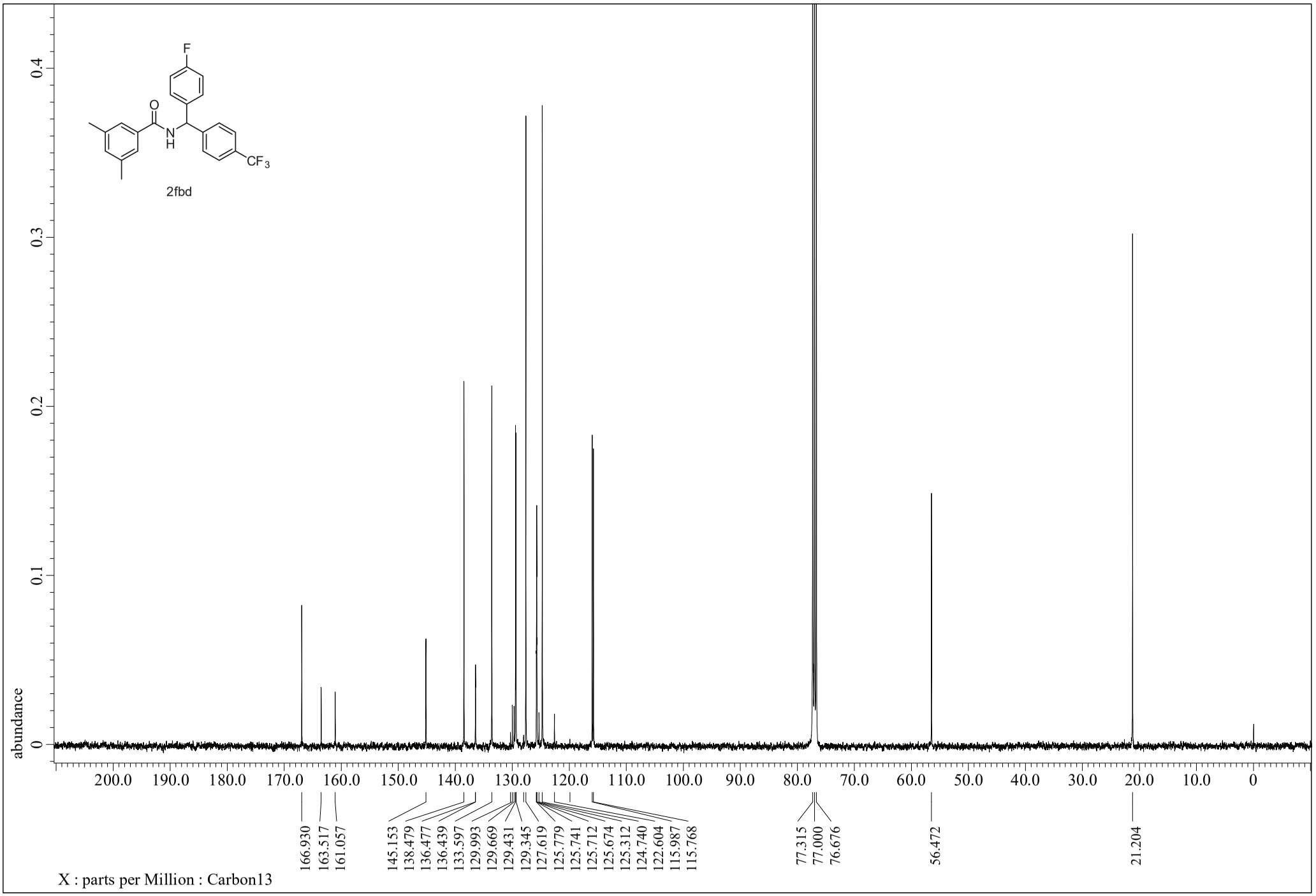
^{19}F NMR (376 MHz, $CDCl_3$)



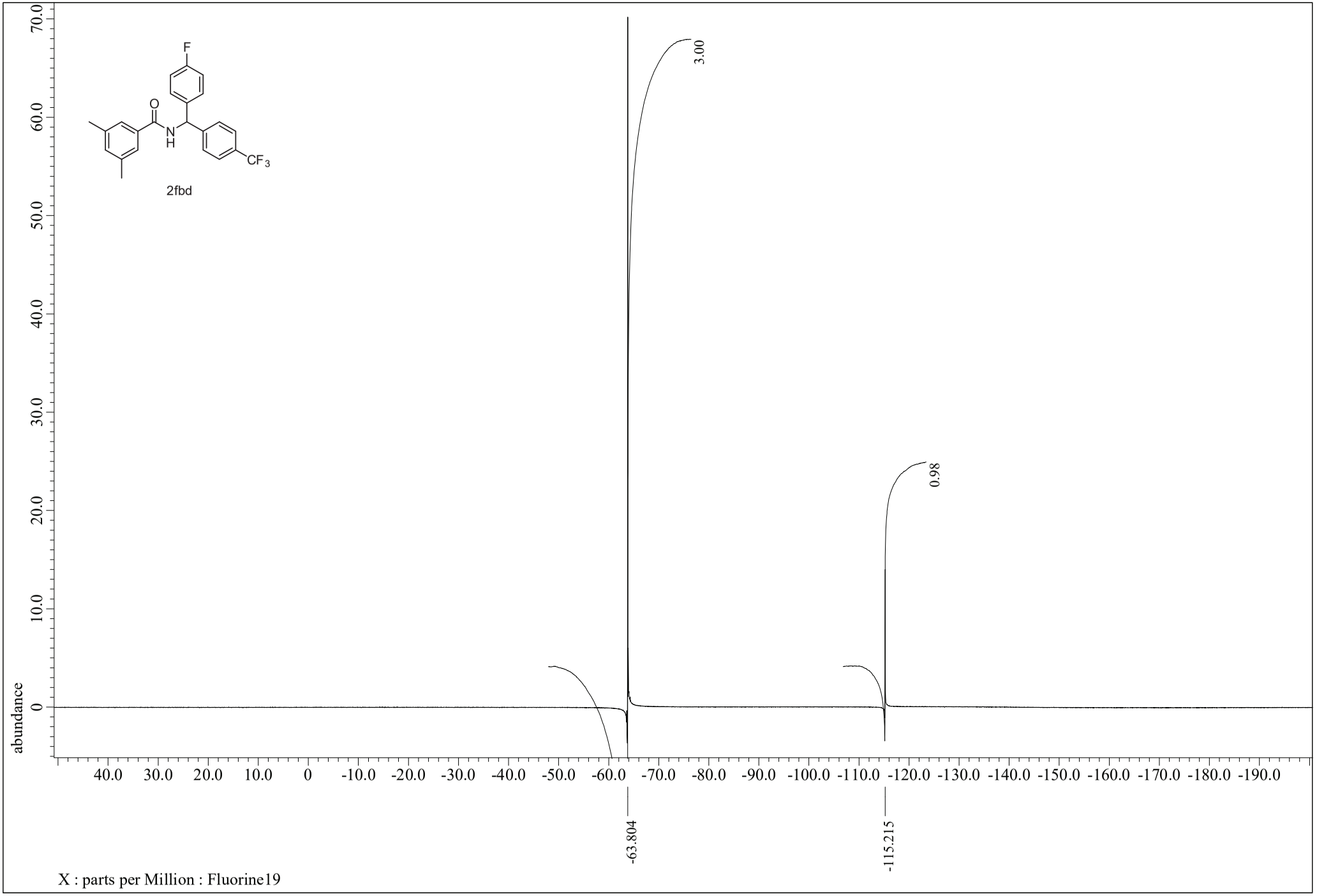
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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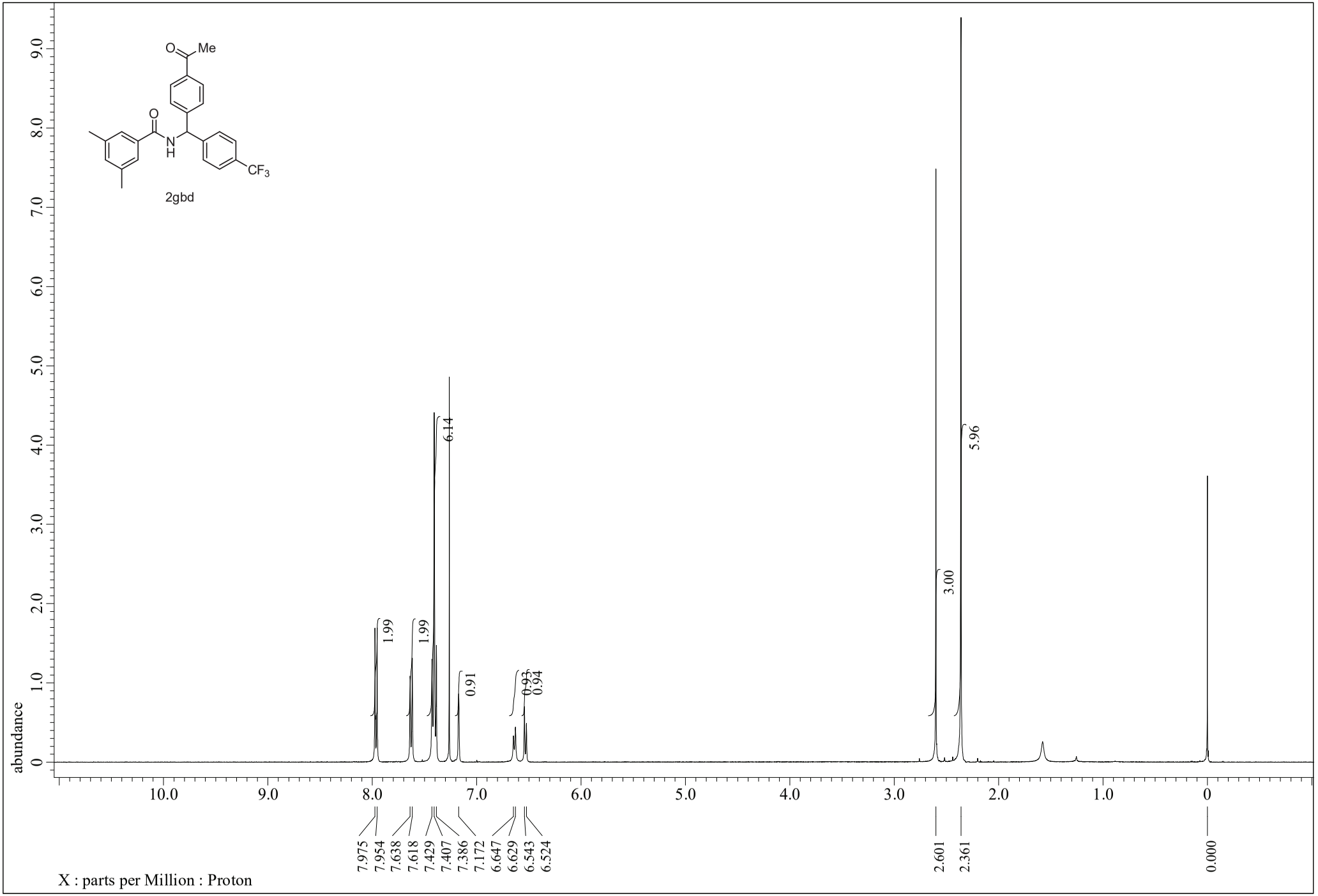

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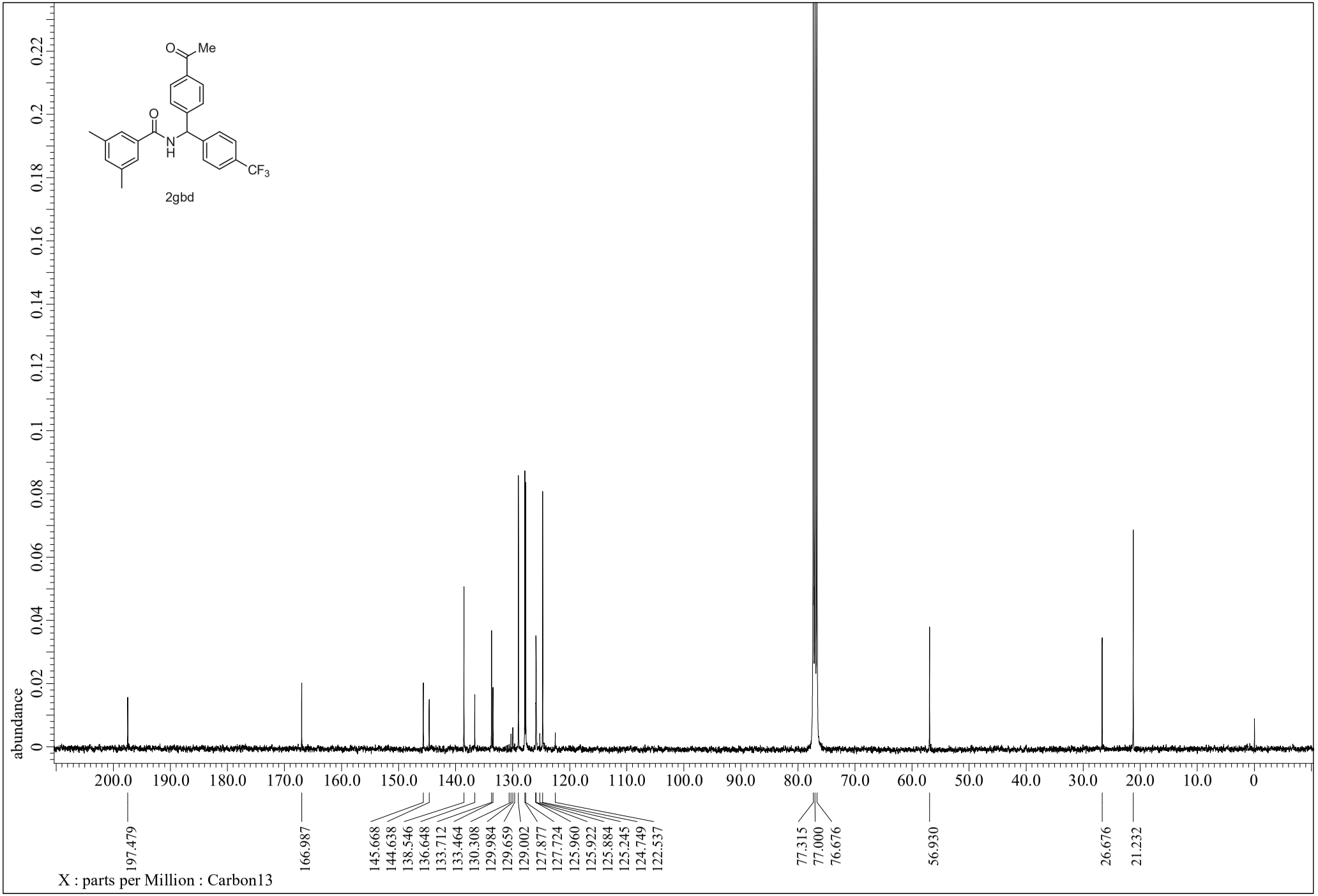
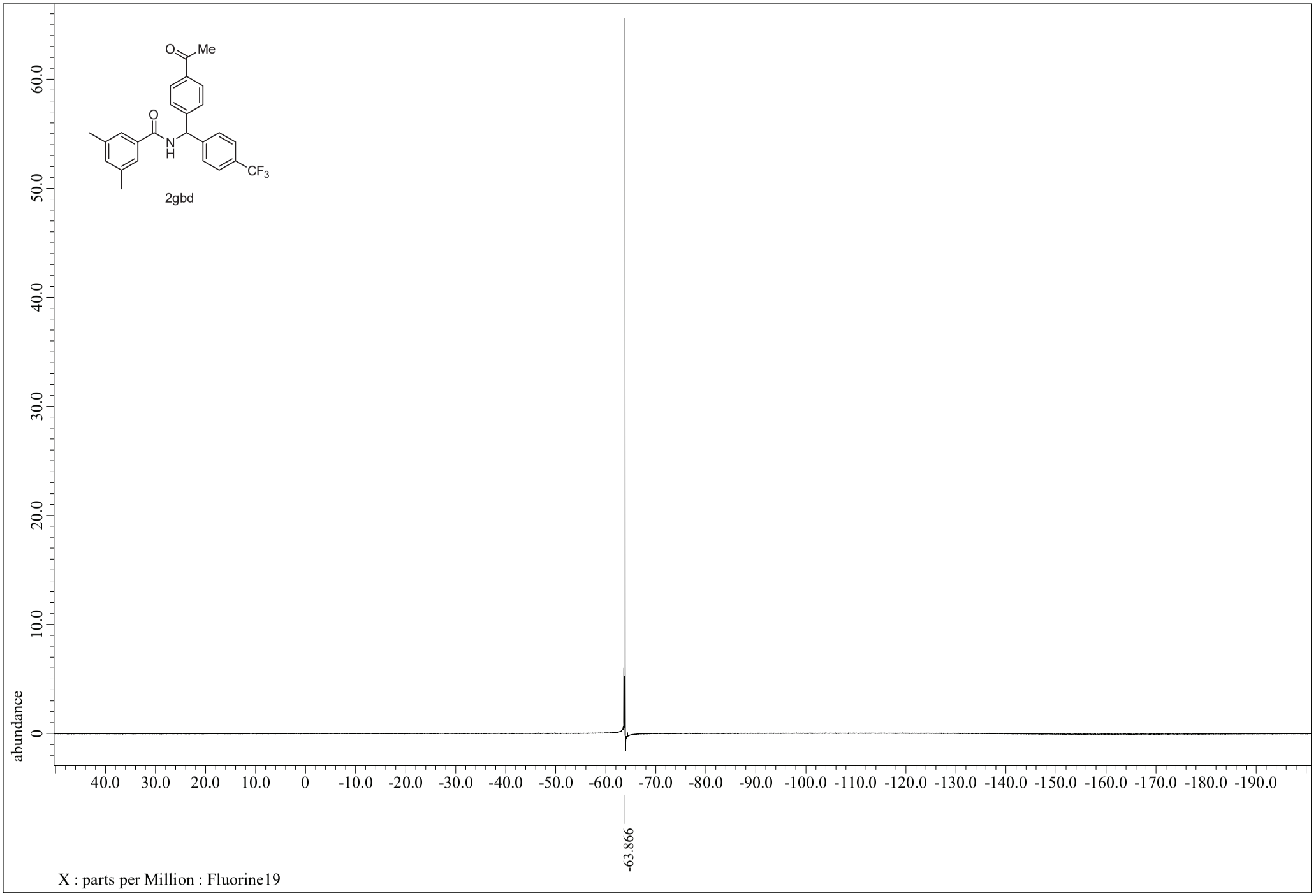


^{19}F NMR (376 MHz, $CDCl_3$)



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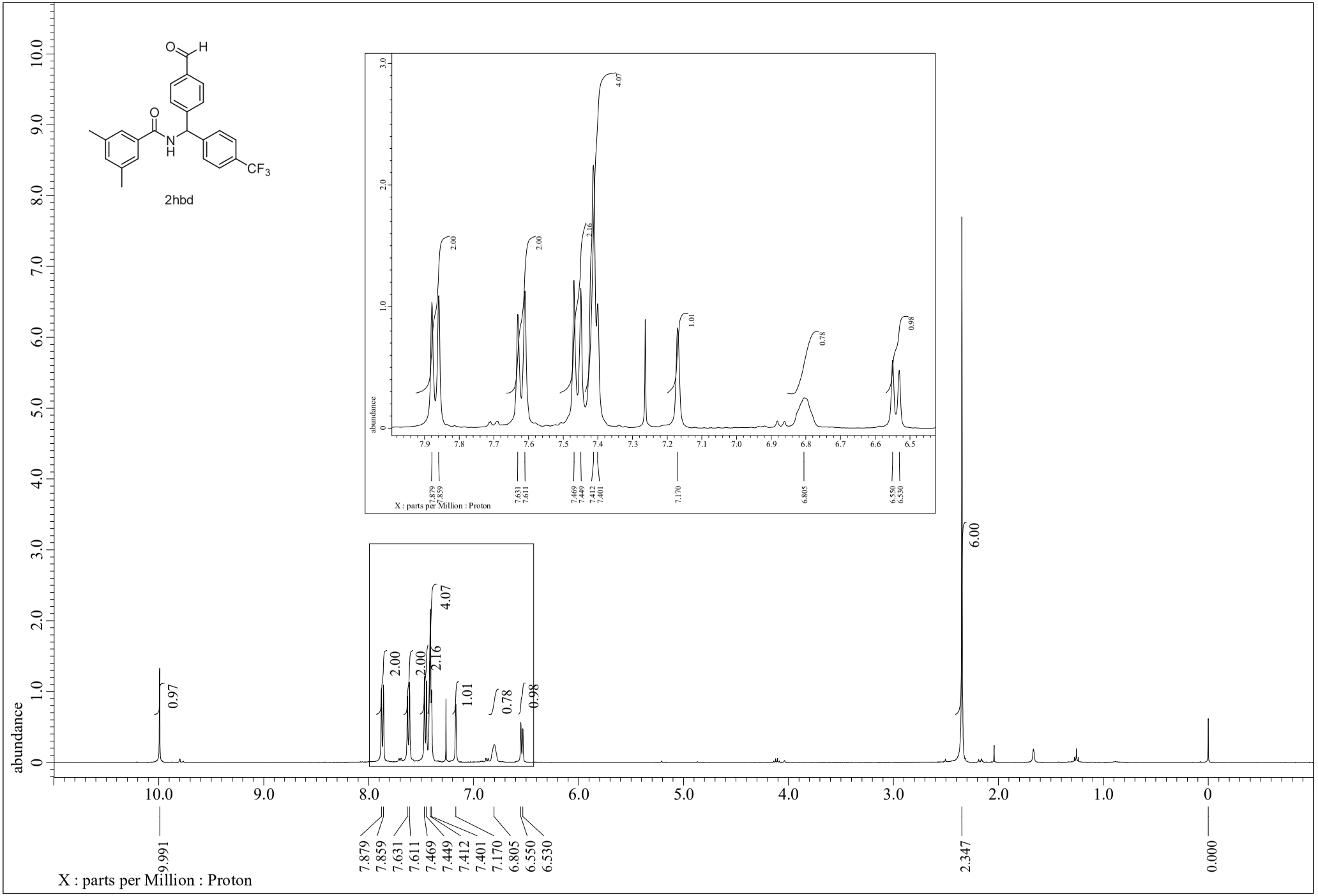

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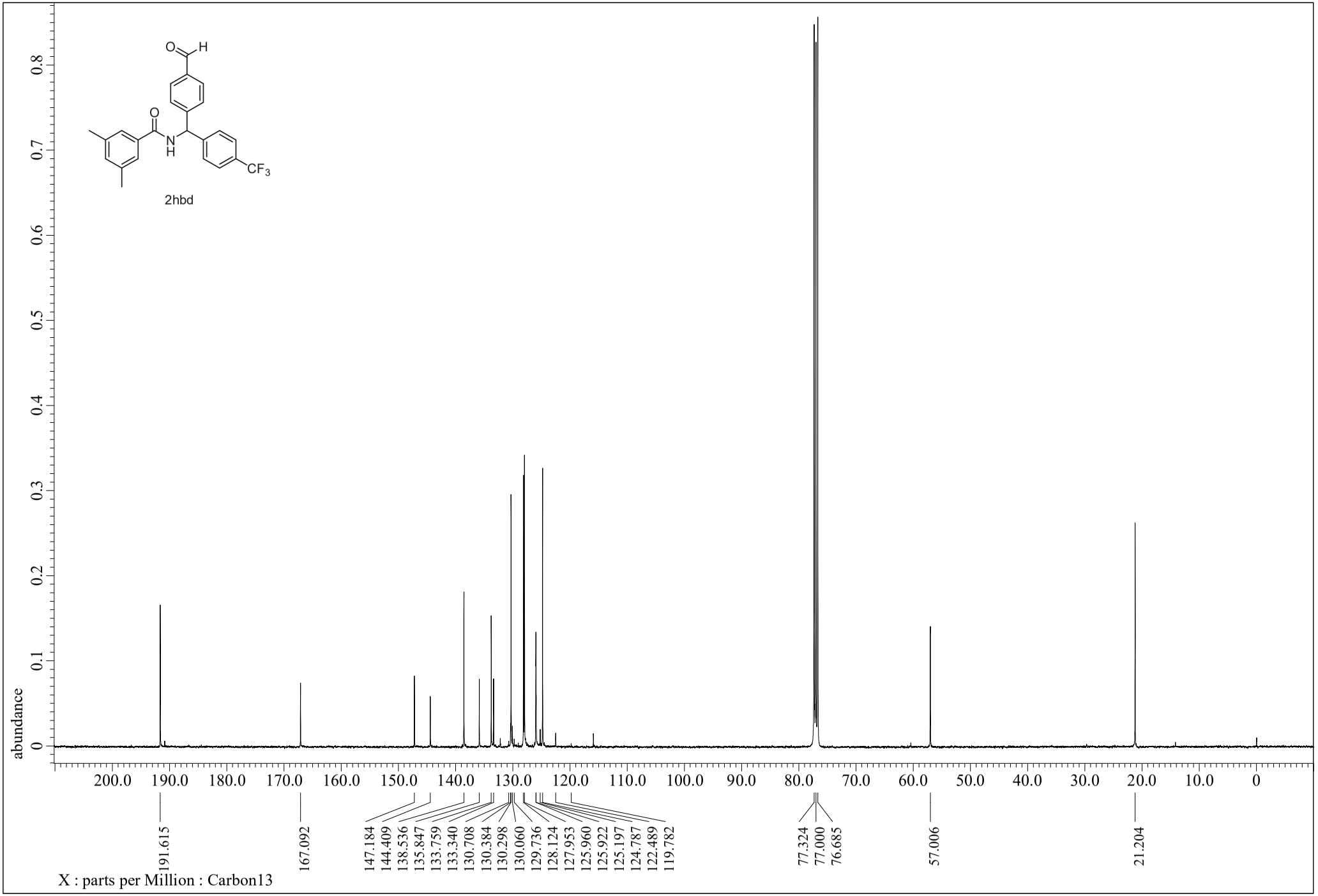

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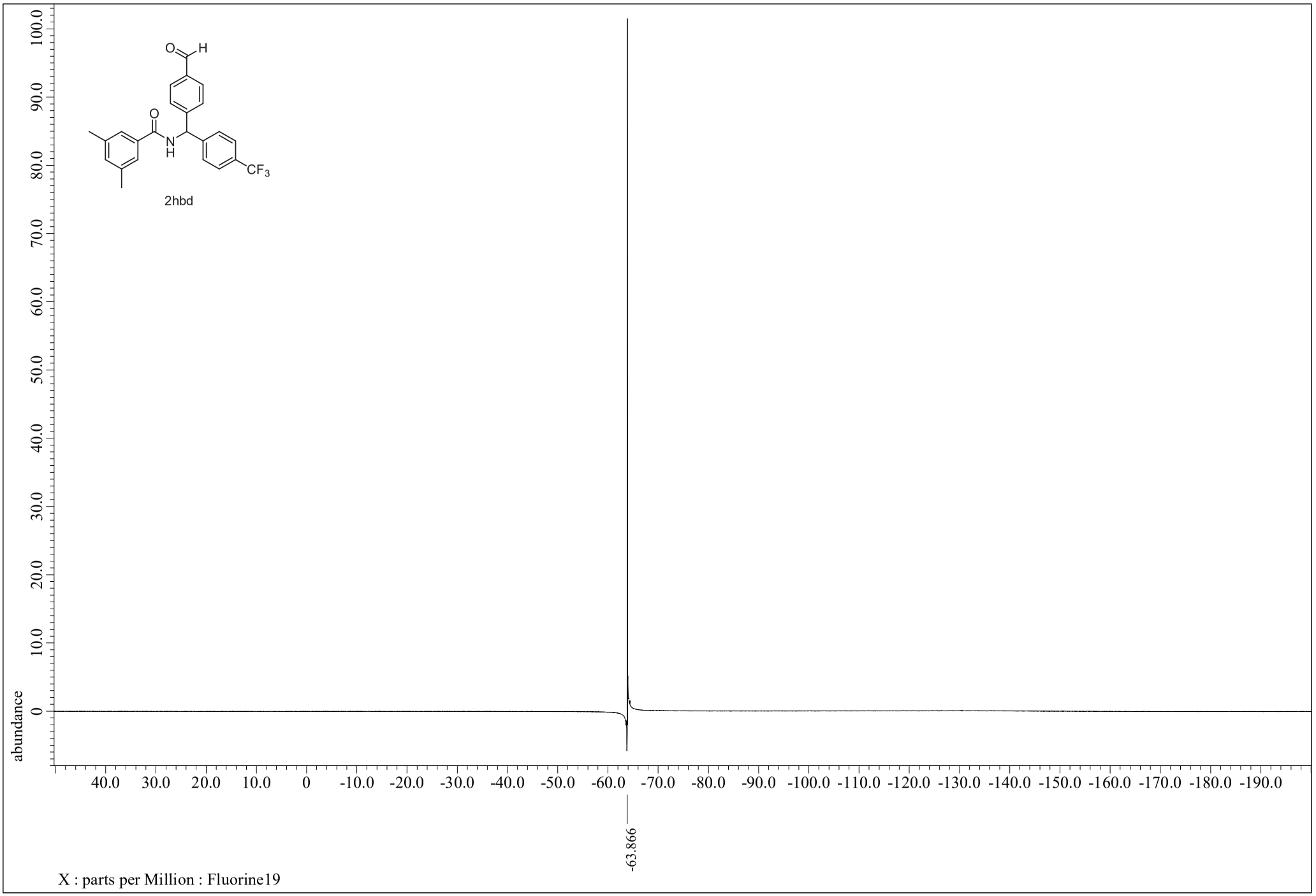
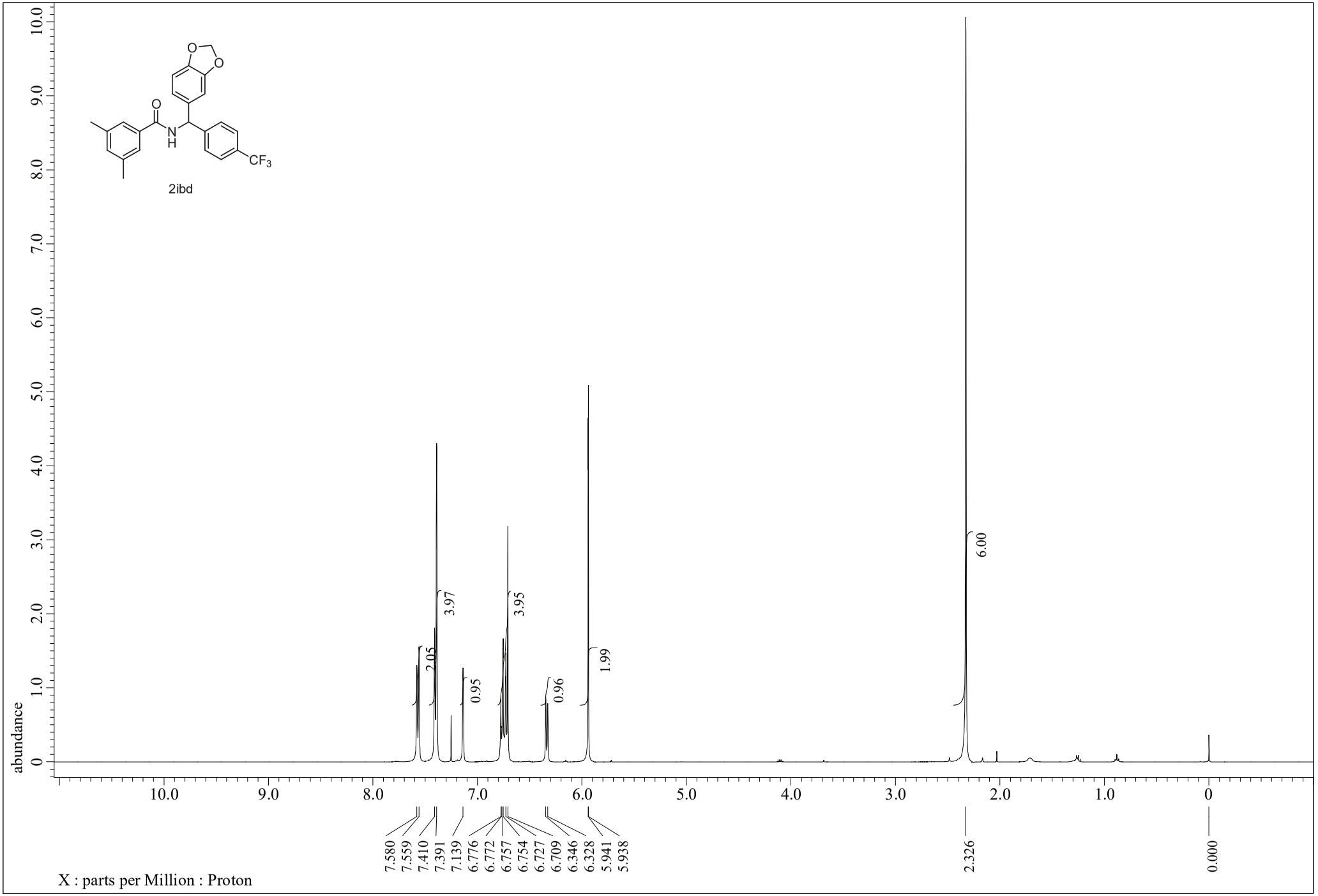


^{1}H NMR (400 MHz, $CDCl_3$)



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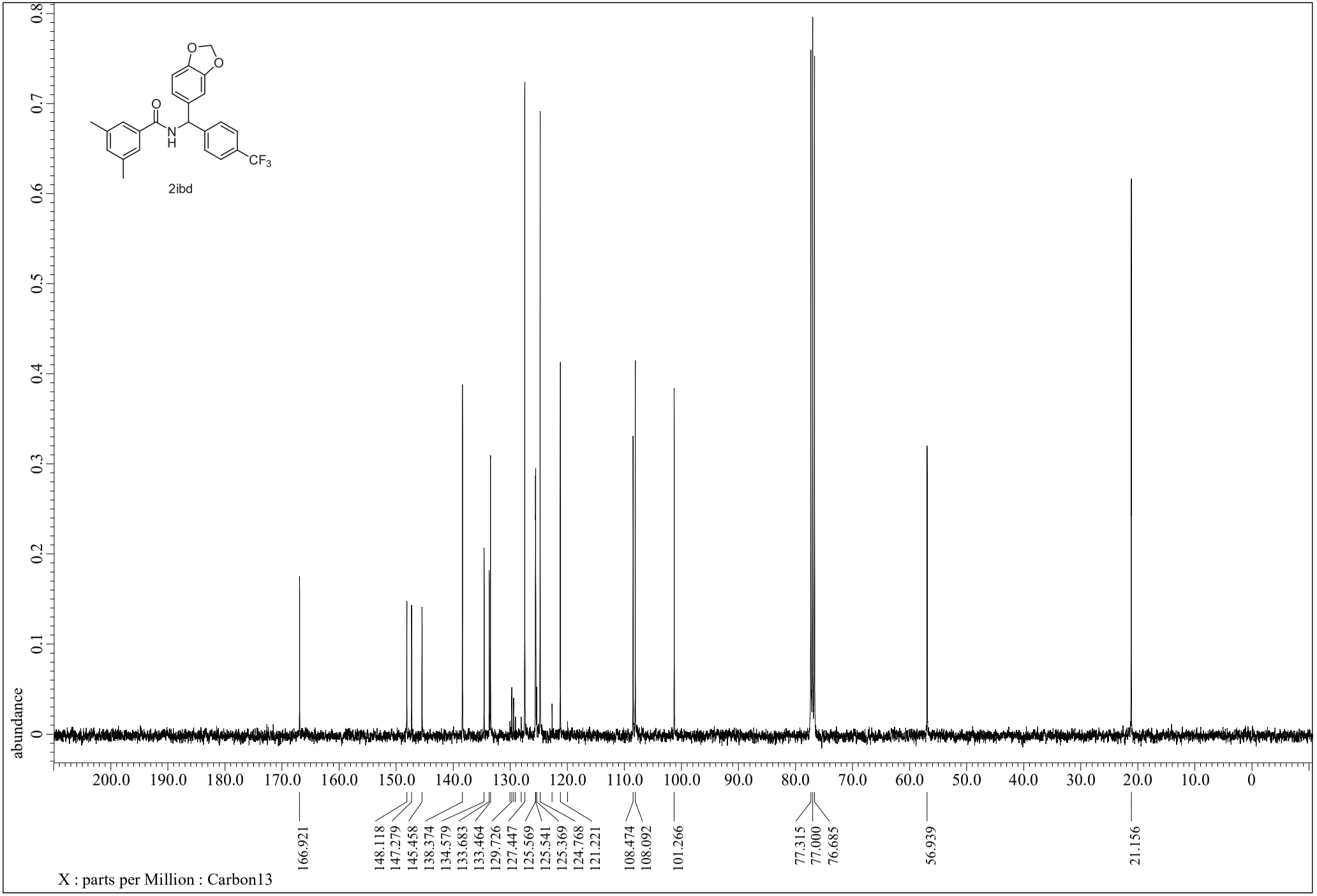
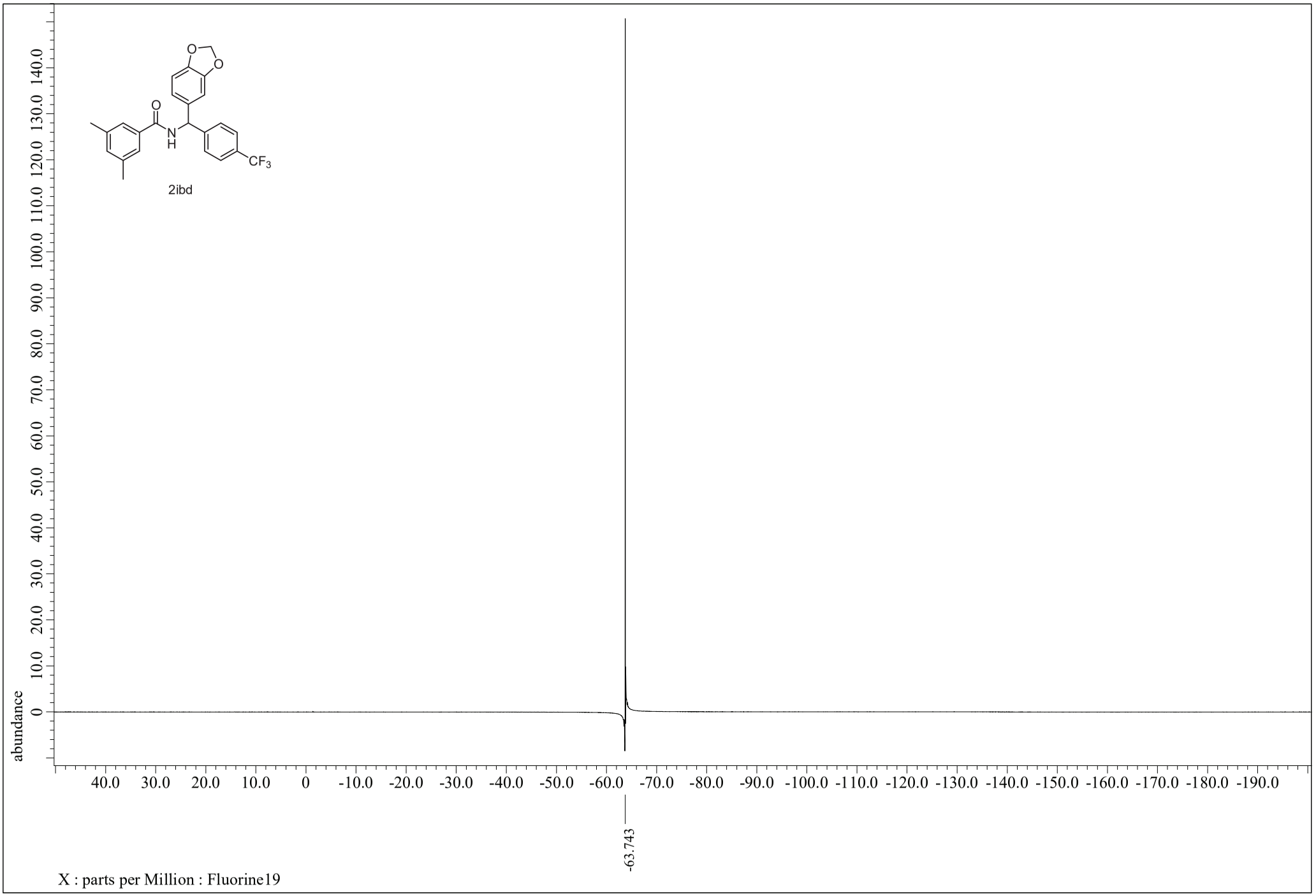


^{19}F NMR (376 MHz, $CDCl_3$)



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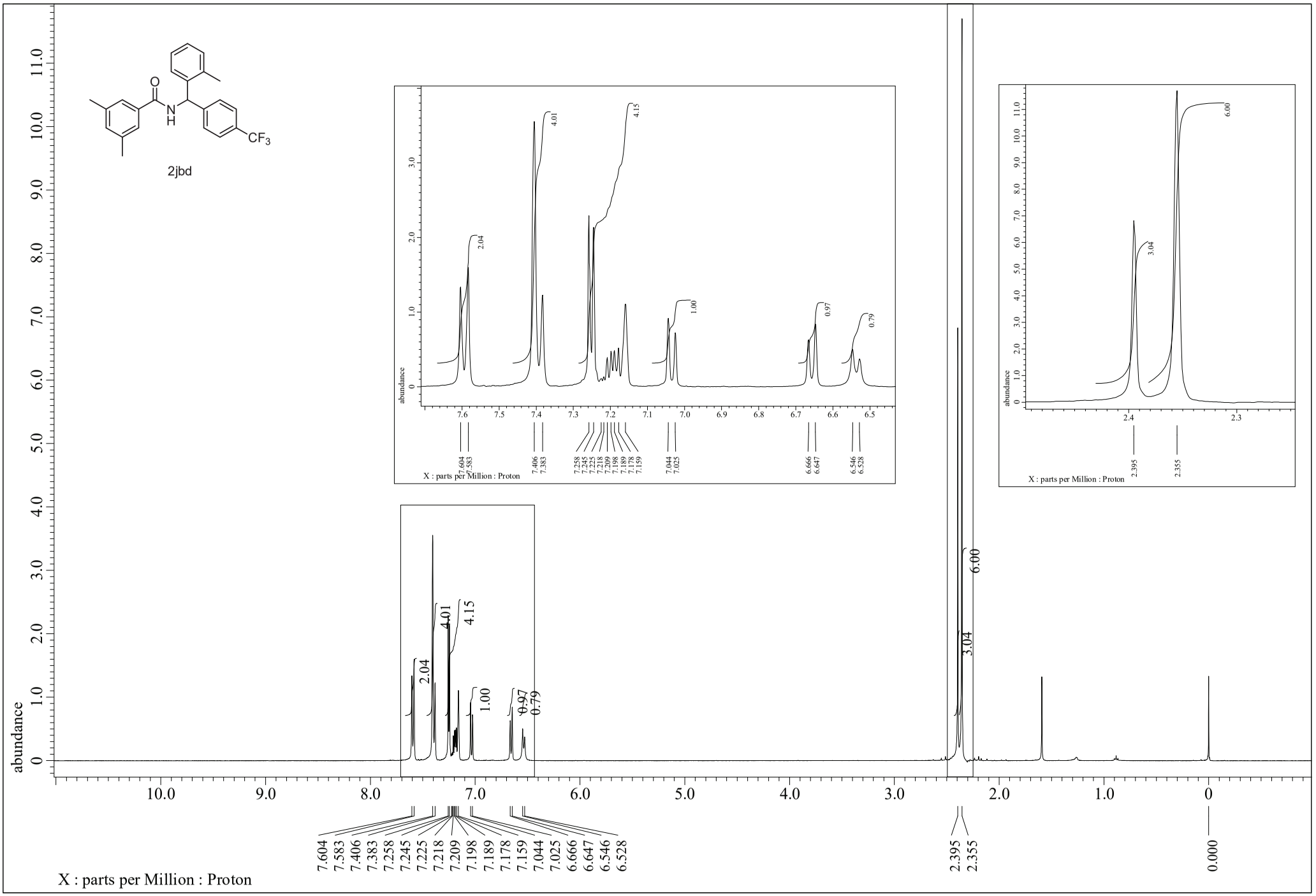

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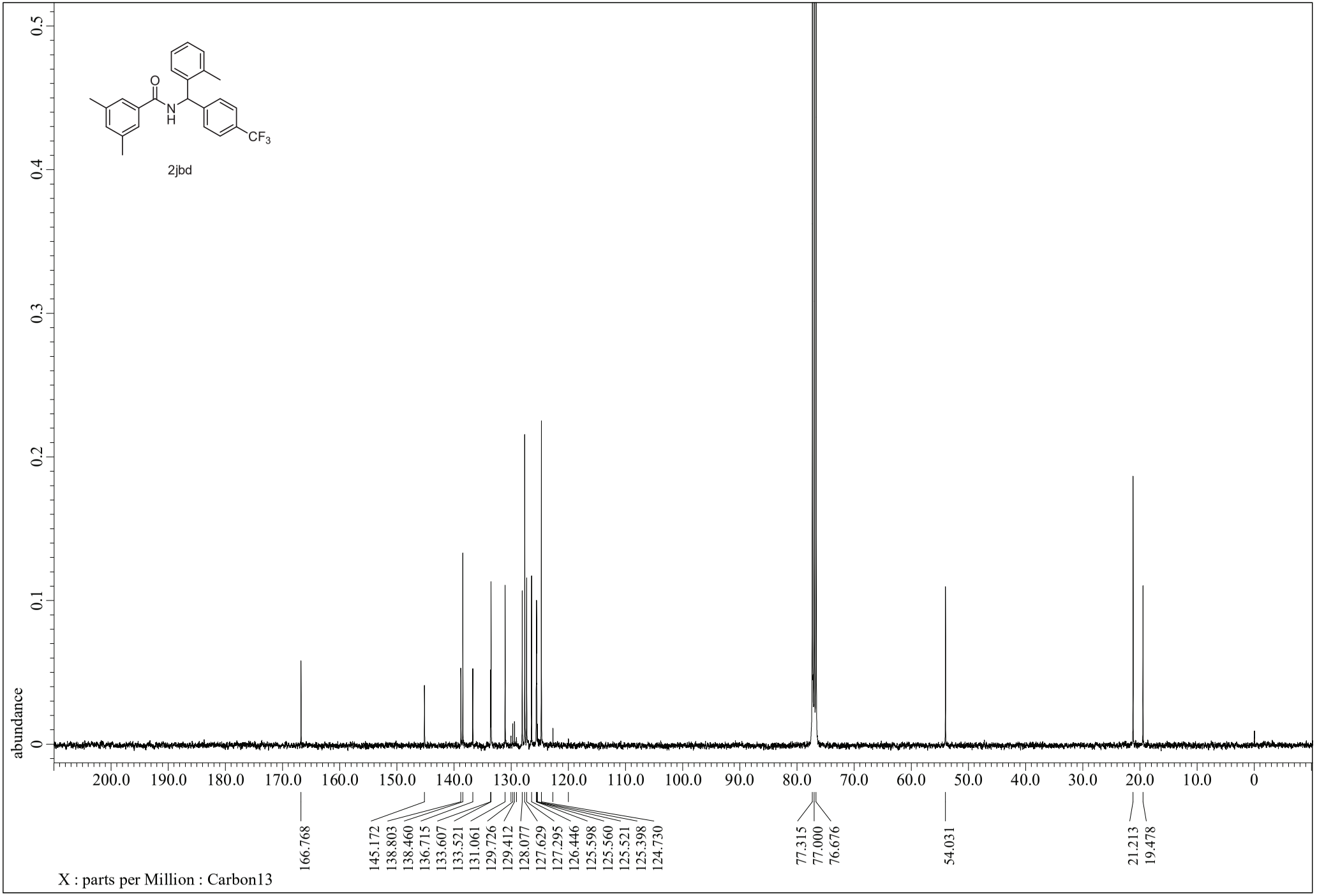

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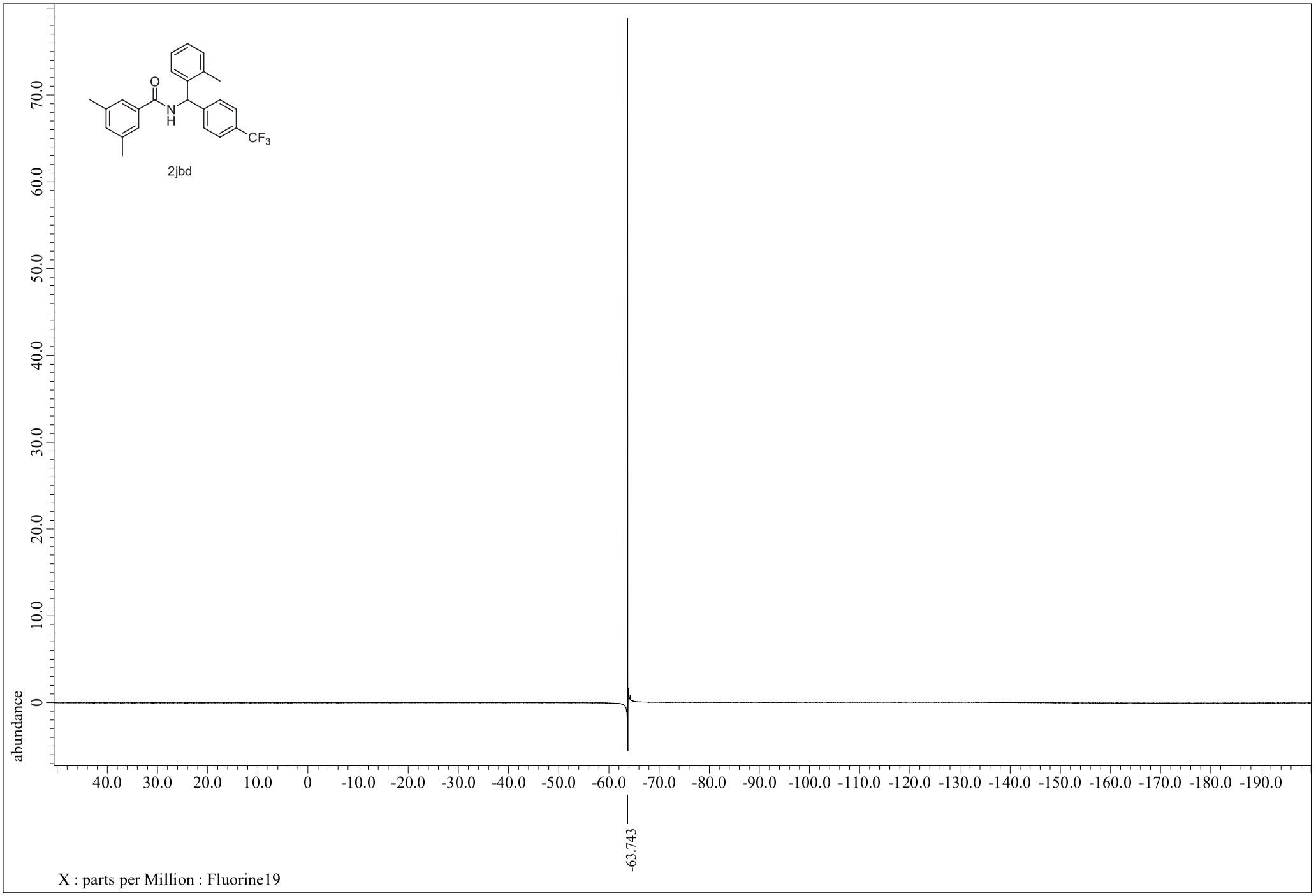

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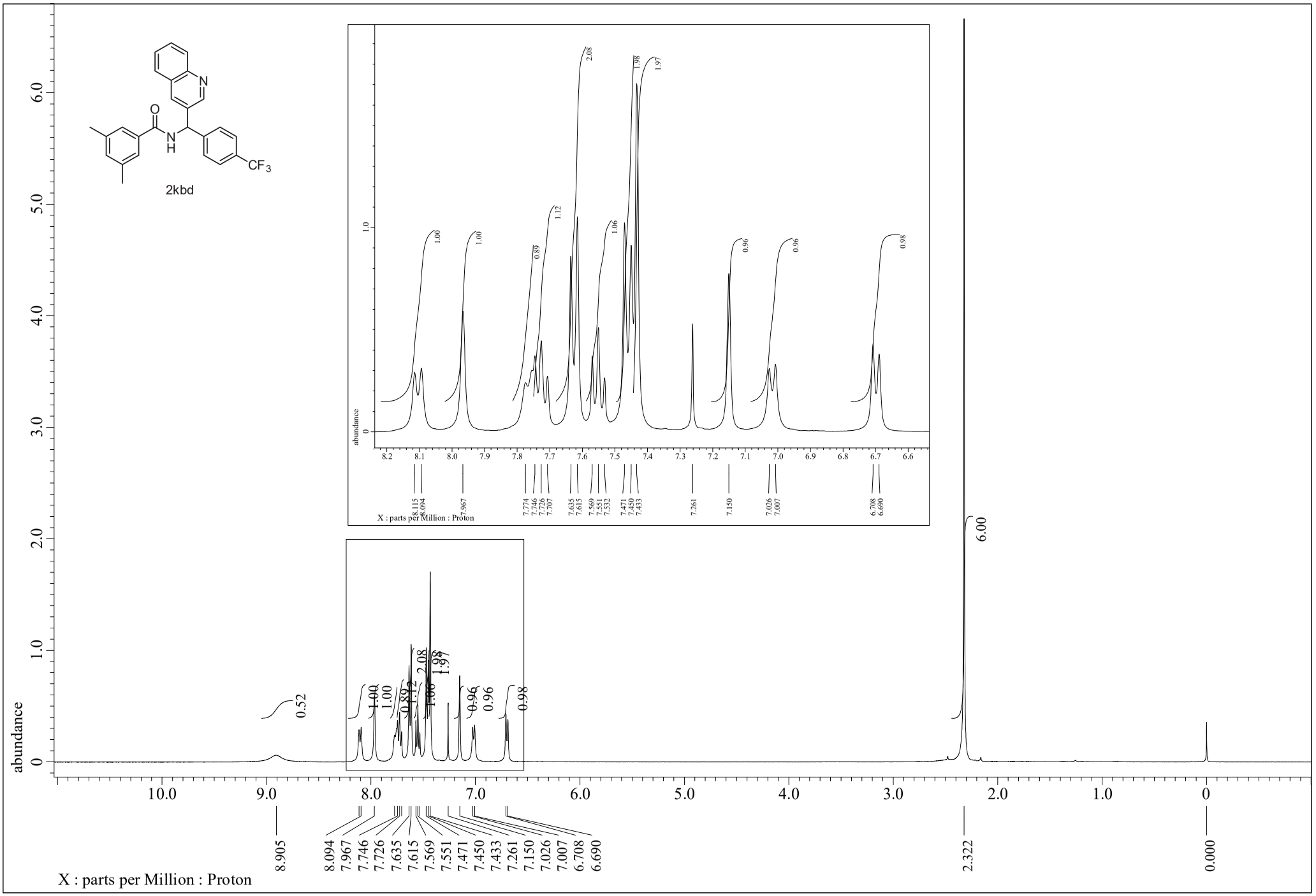

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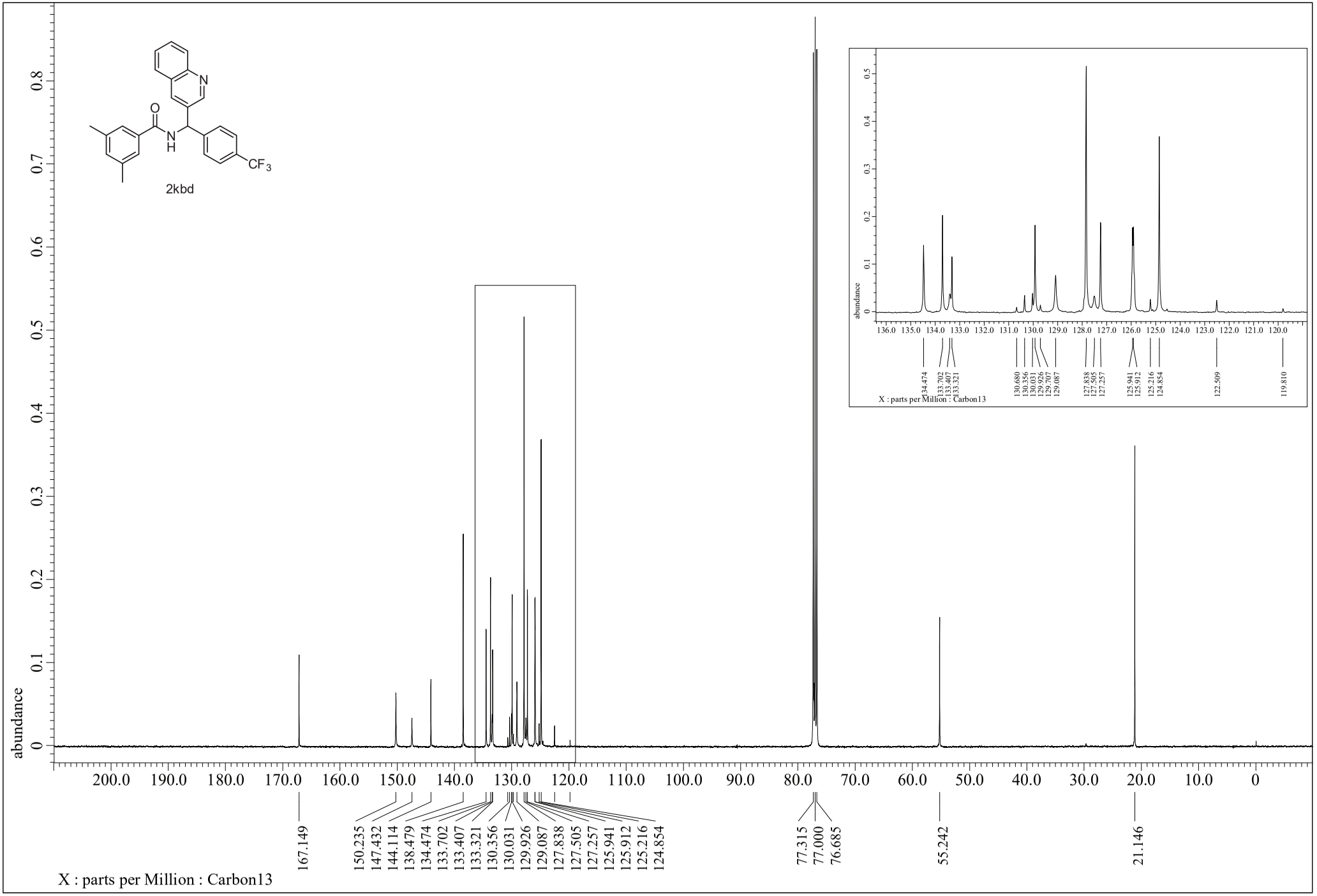

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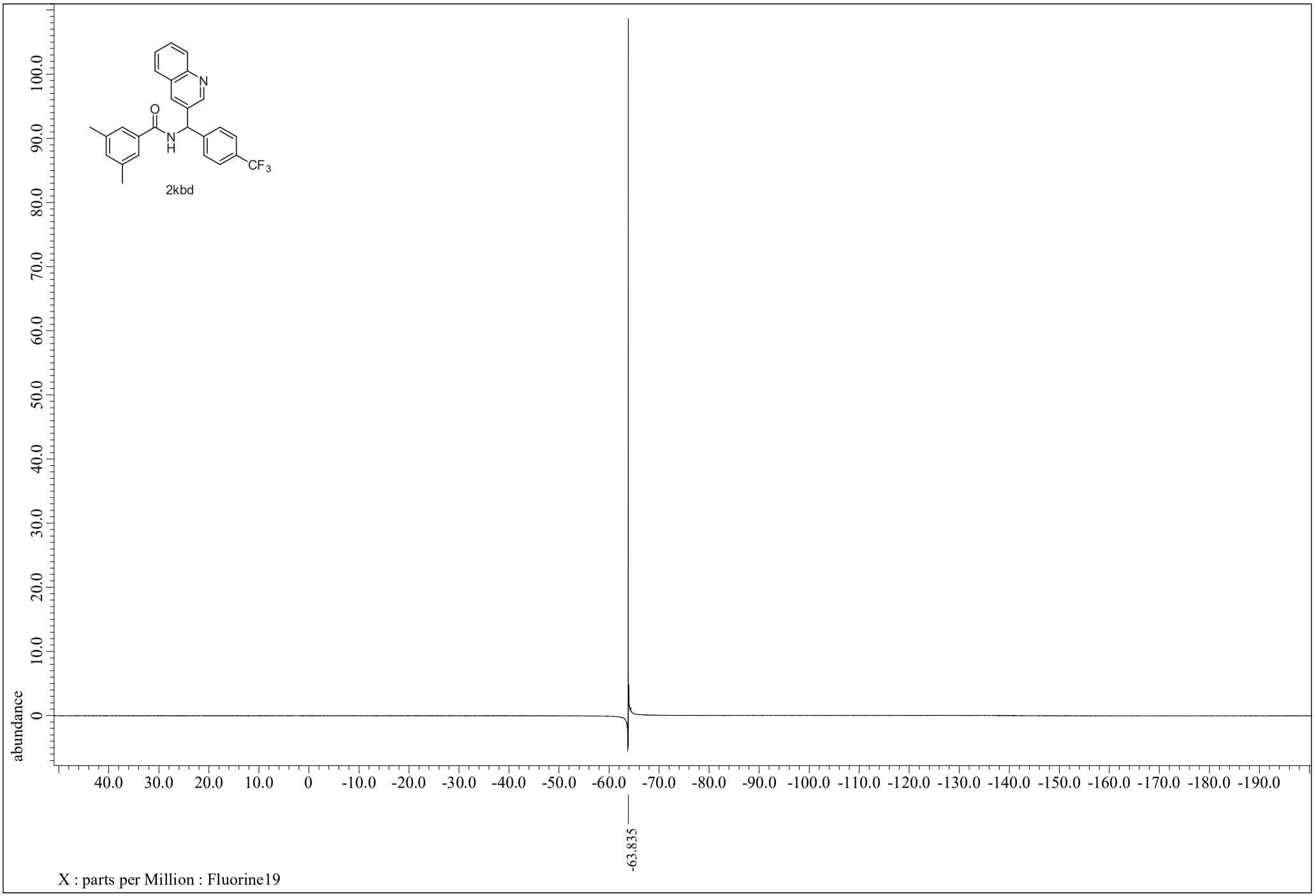

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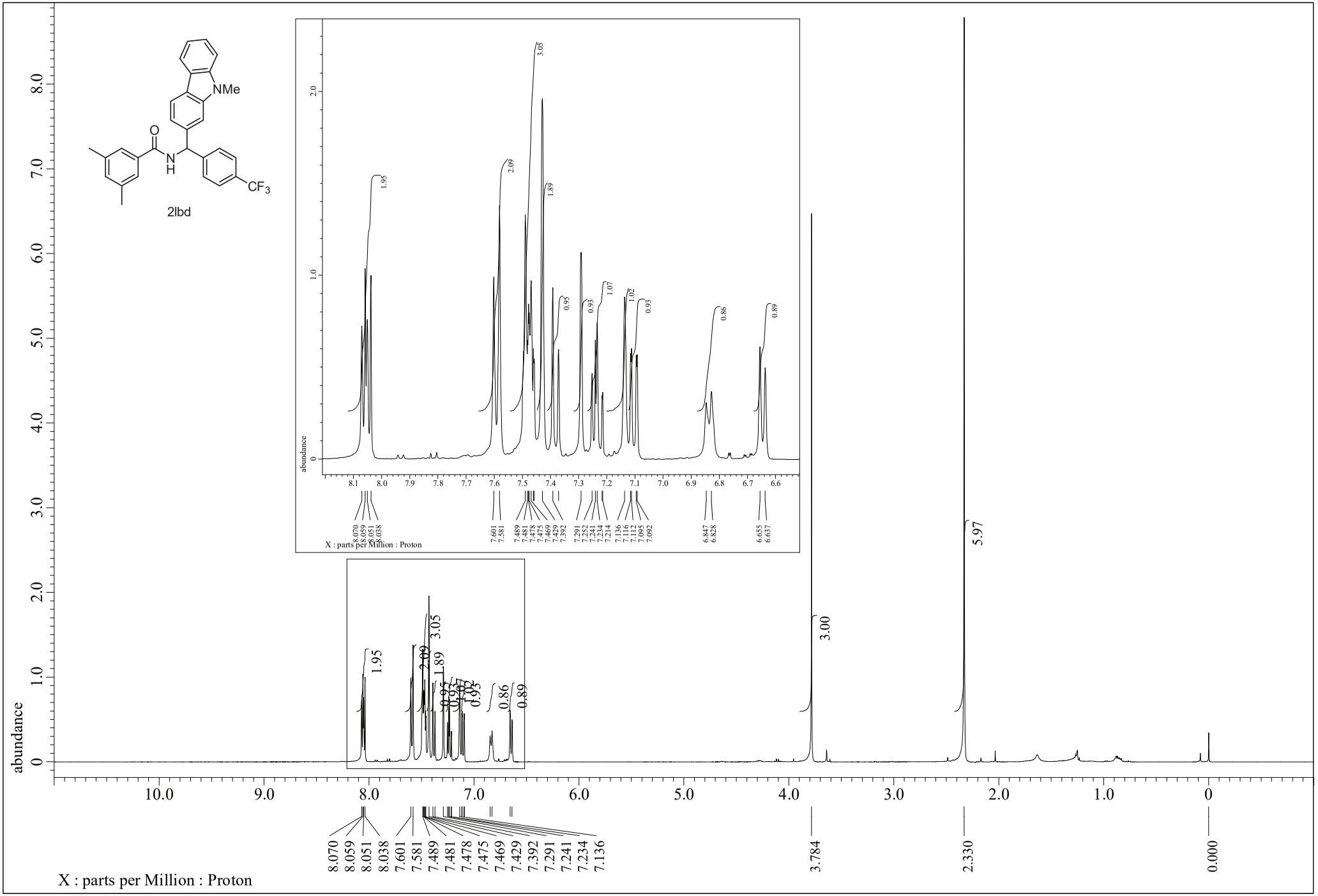
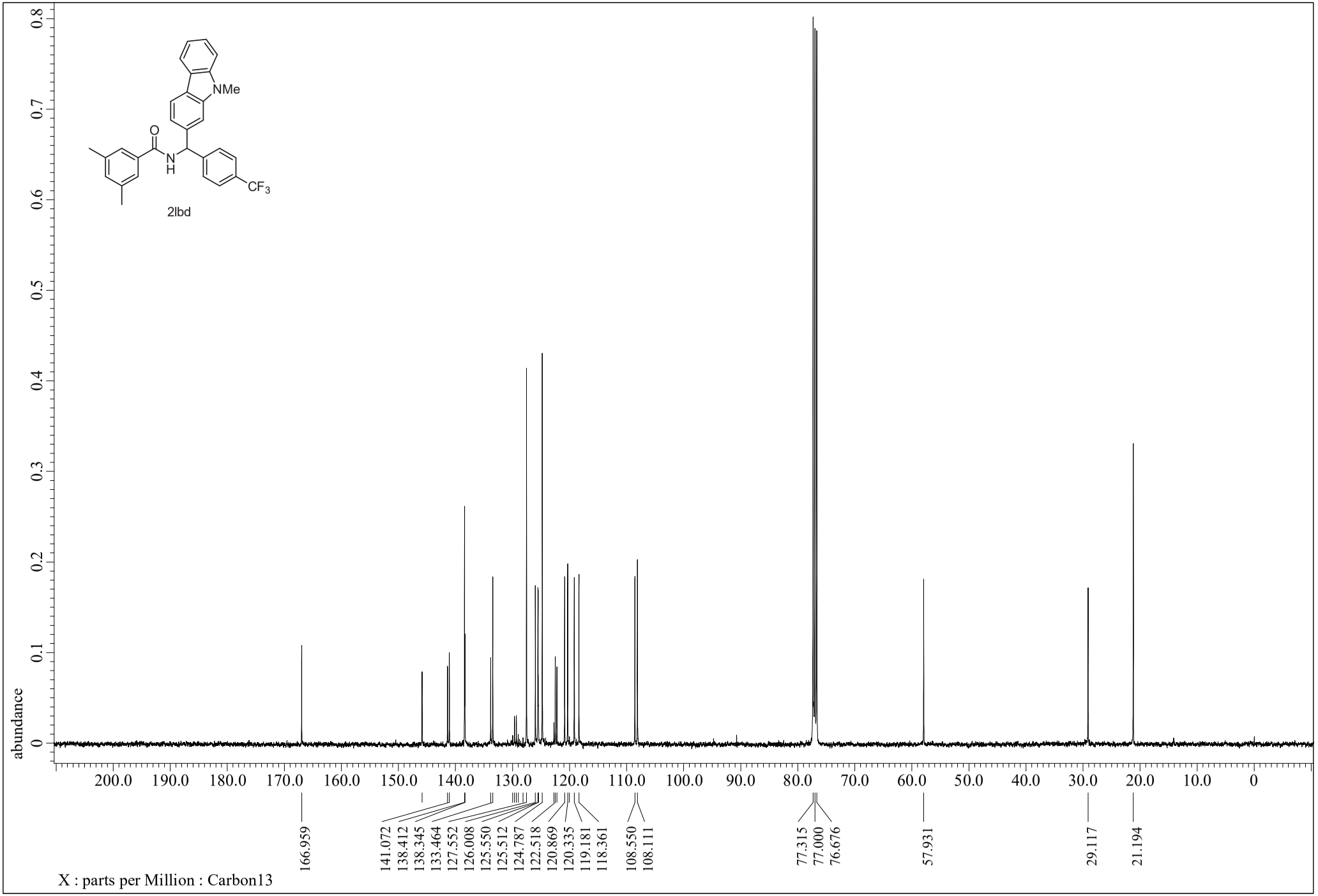
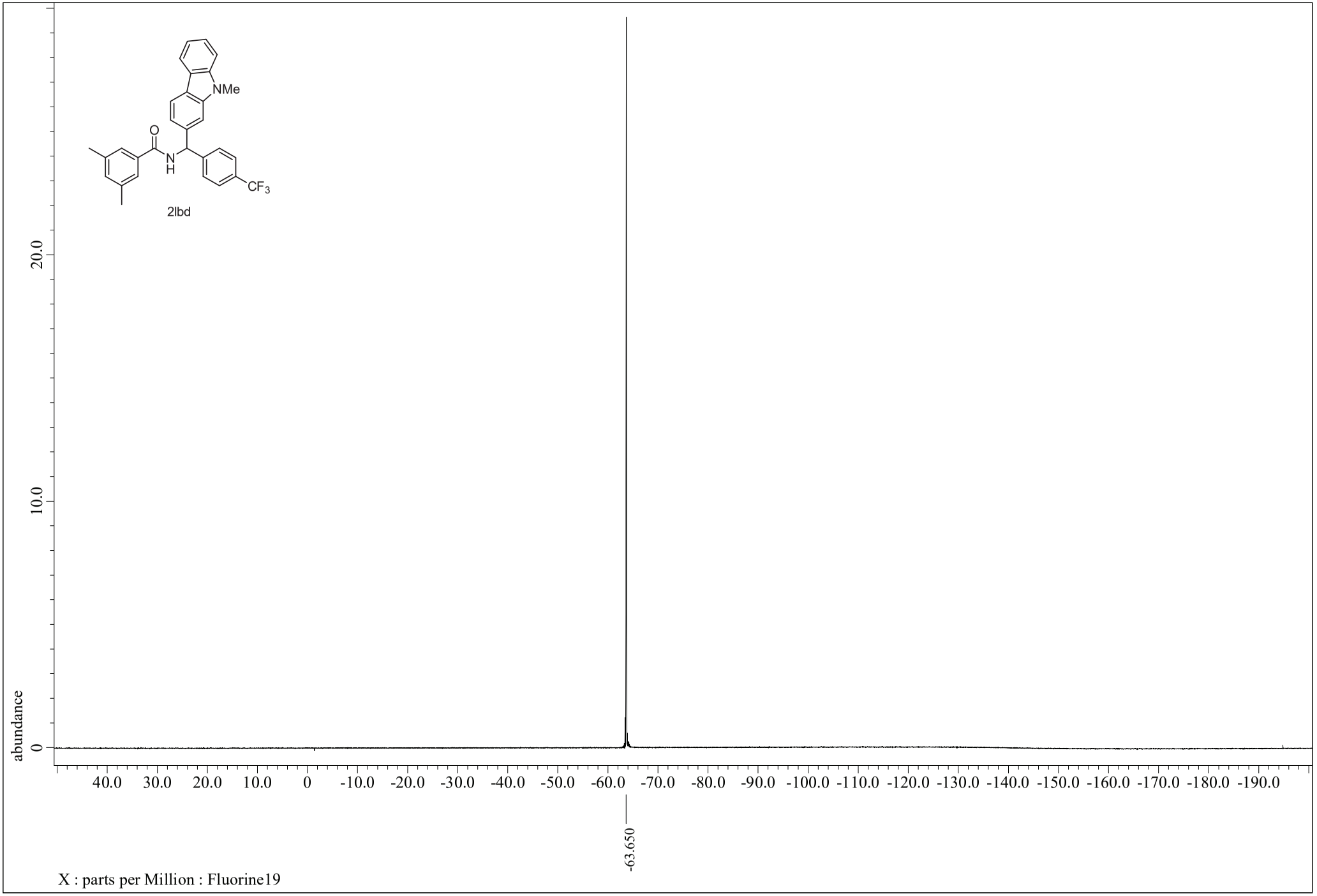


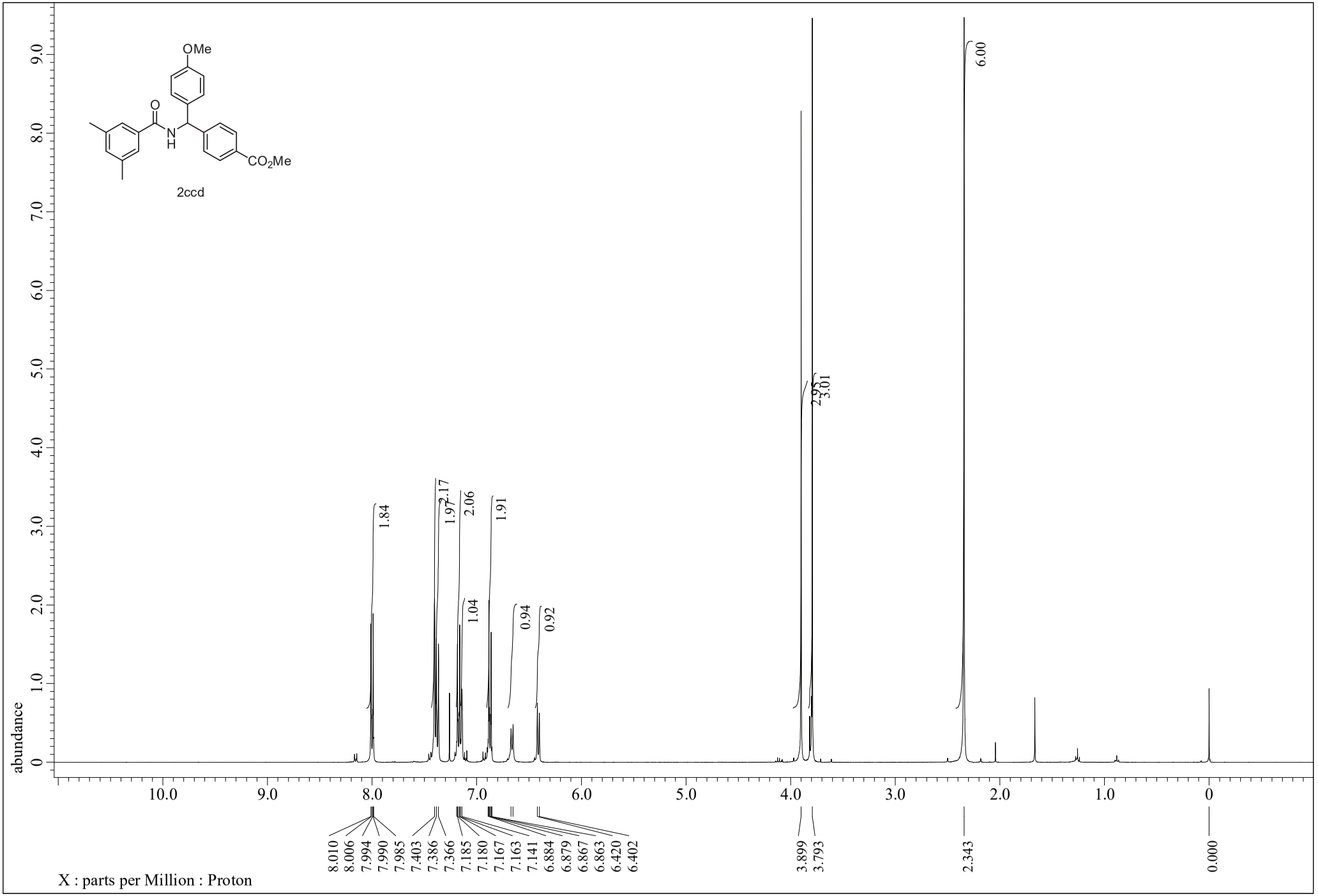
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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



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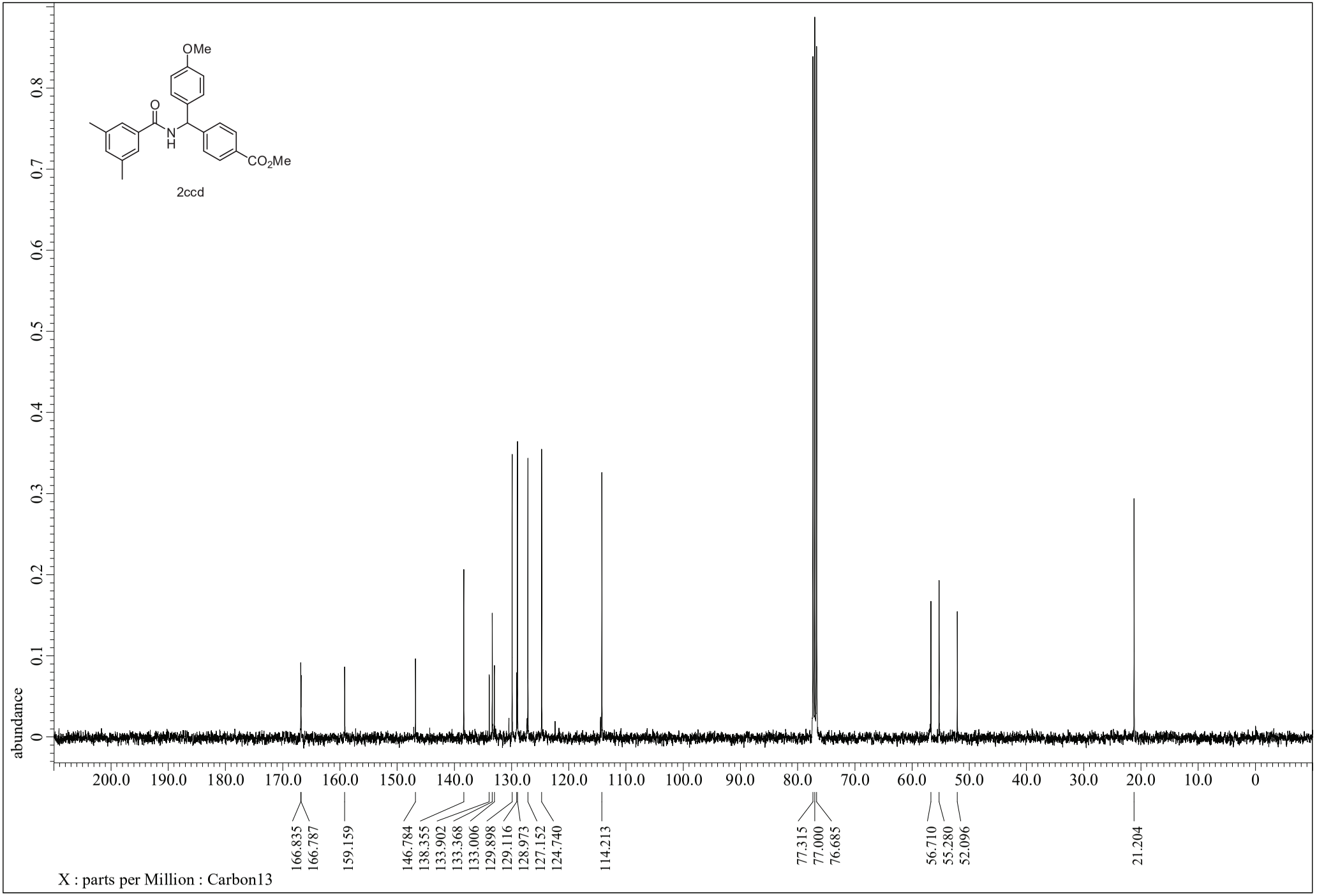
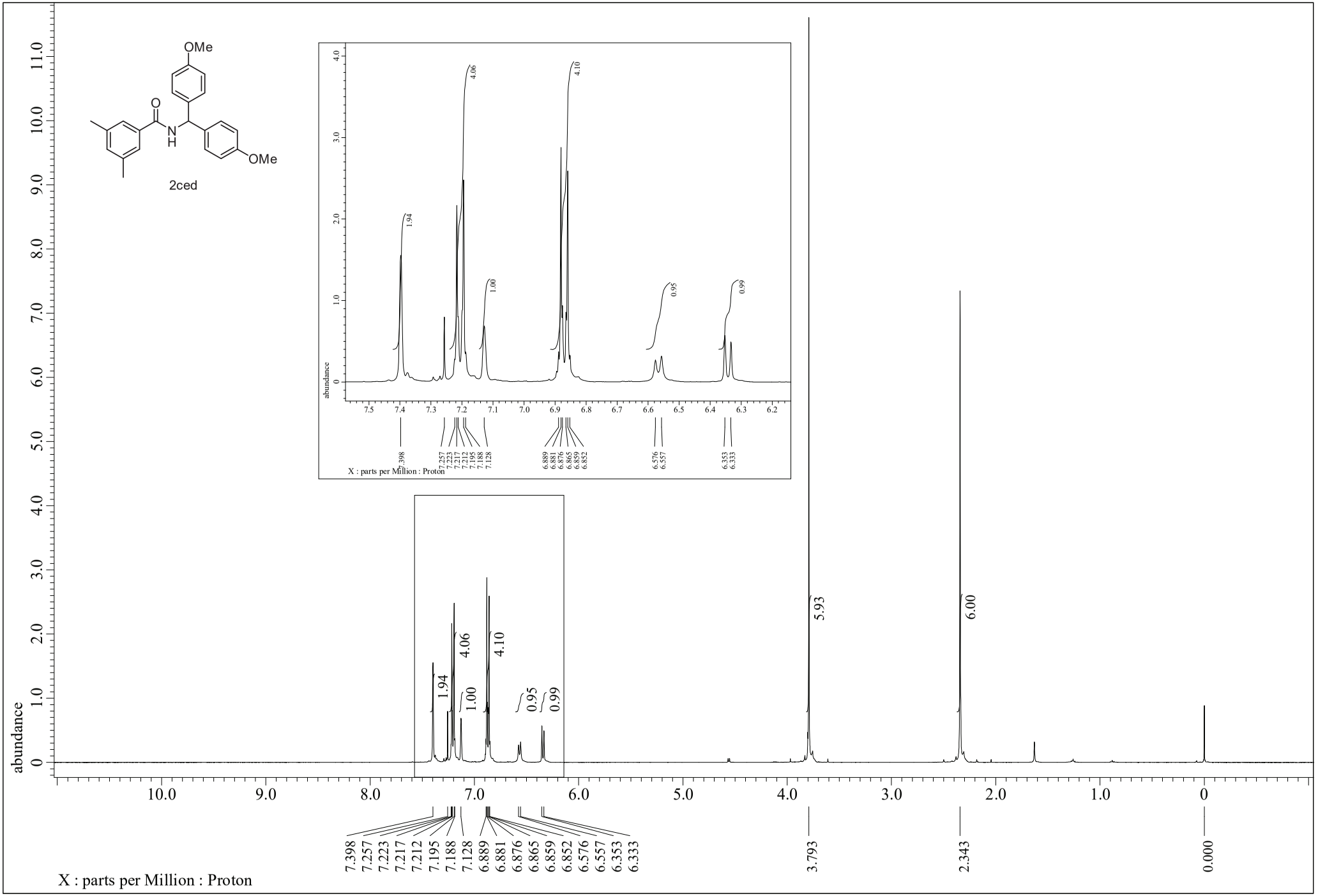


^{1}H NMR (400 MHz, $CDCl_3$)



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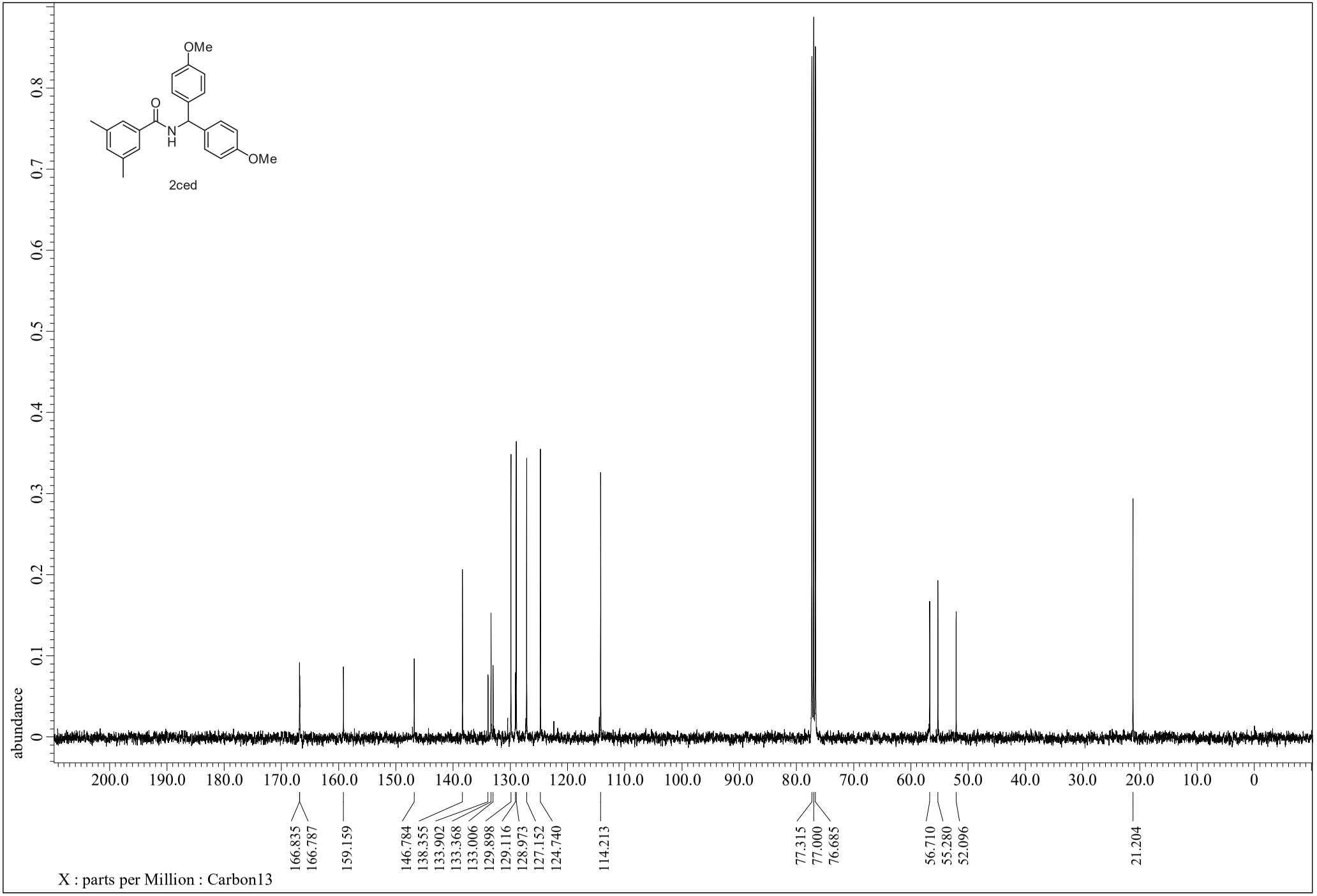

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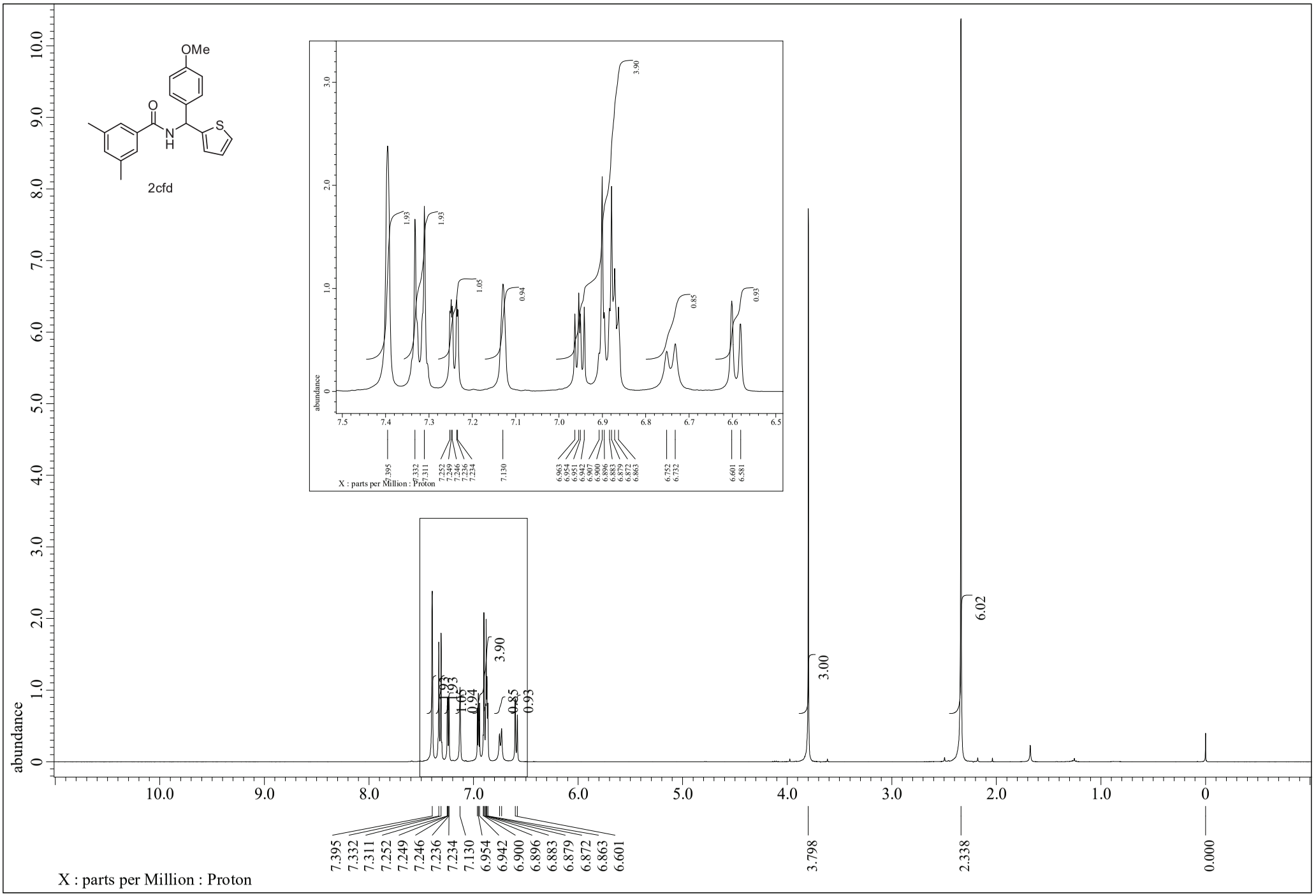
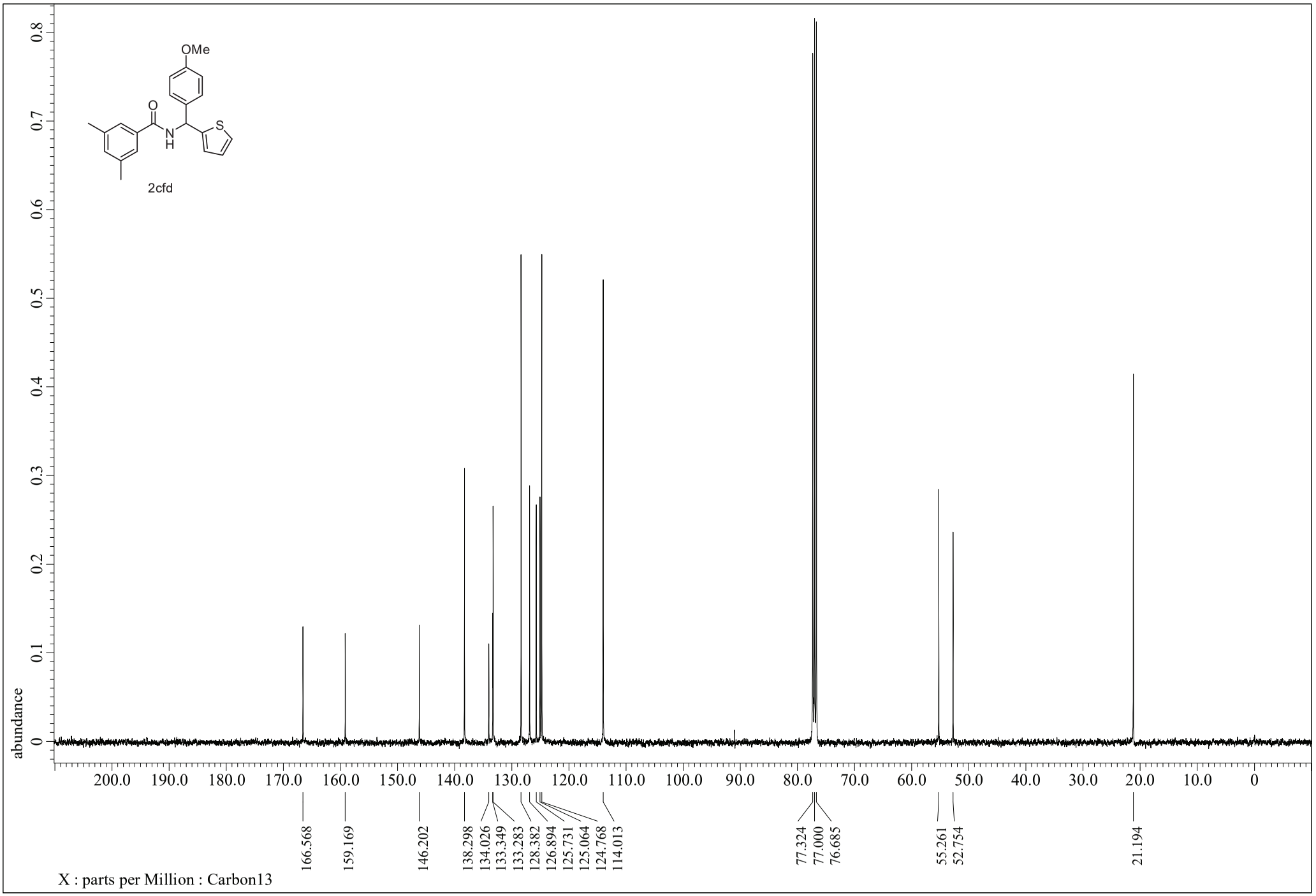


^{13}C NMR (101 MHz, $CDCl_3$)



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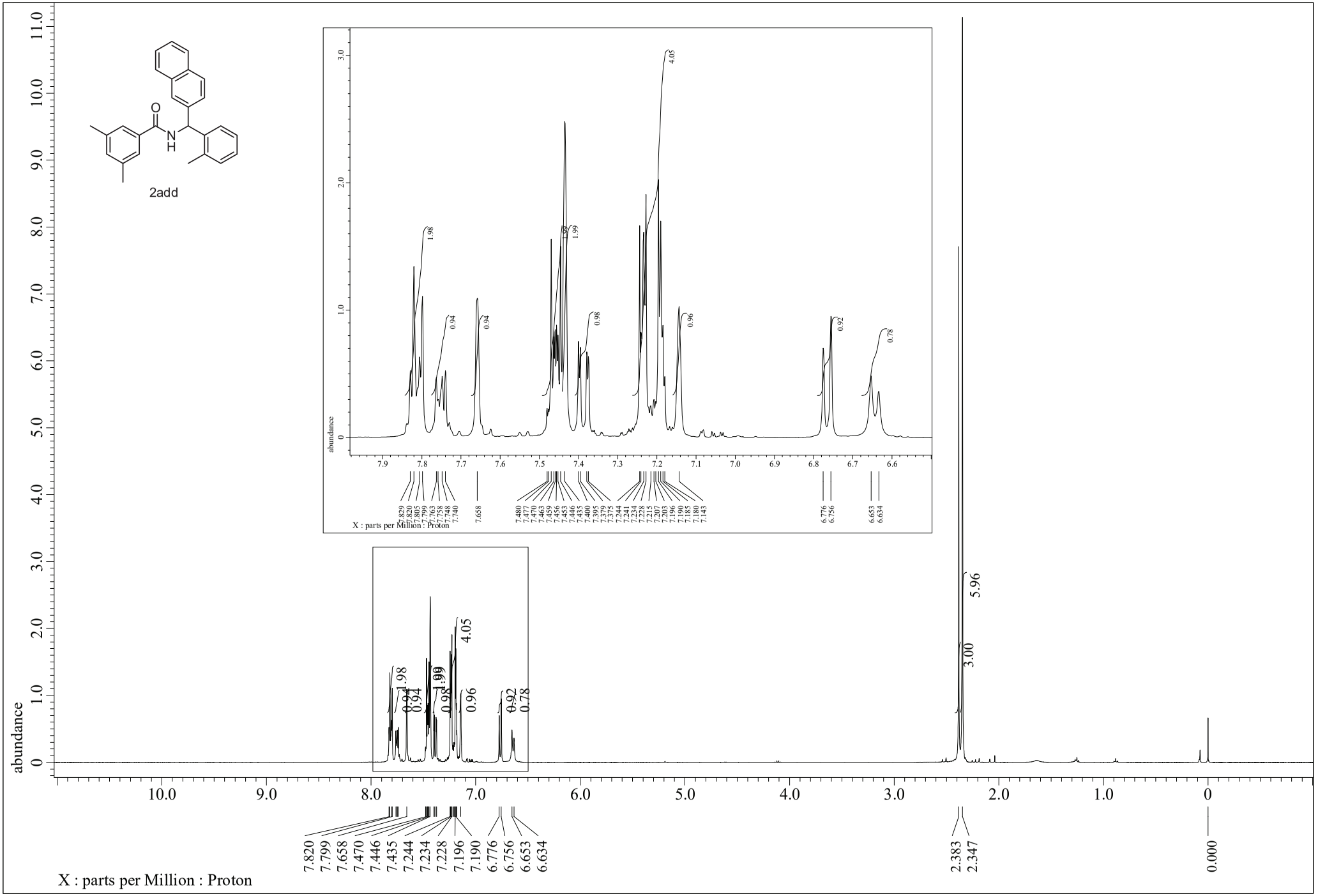

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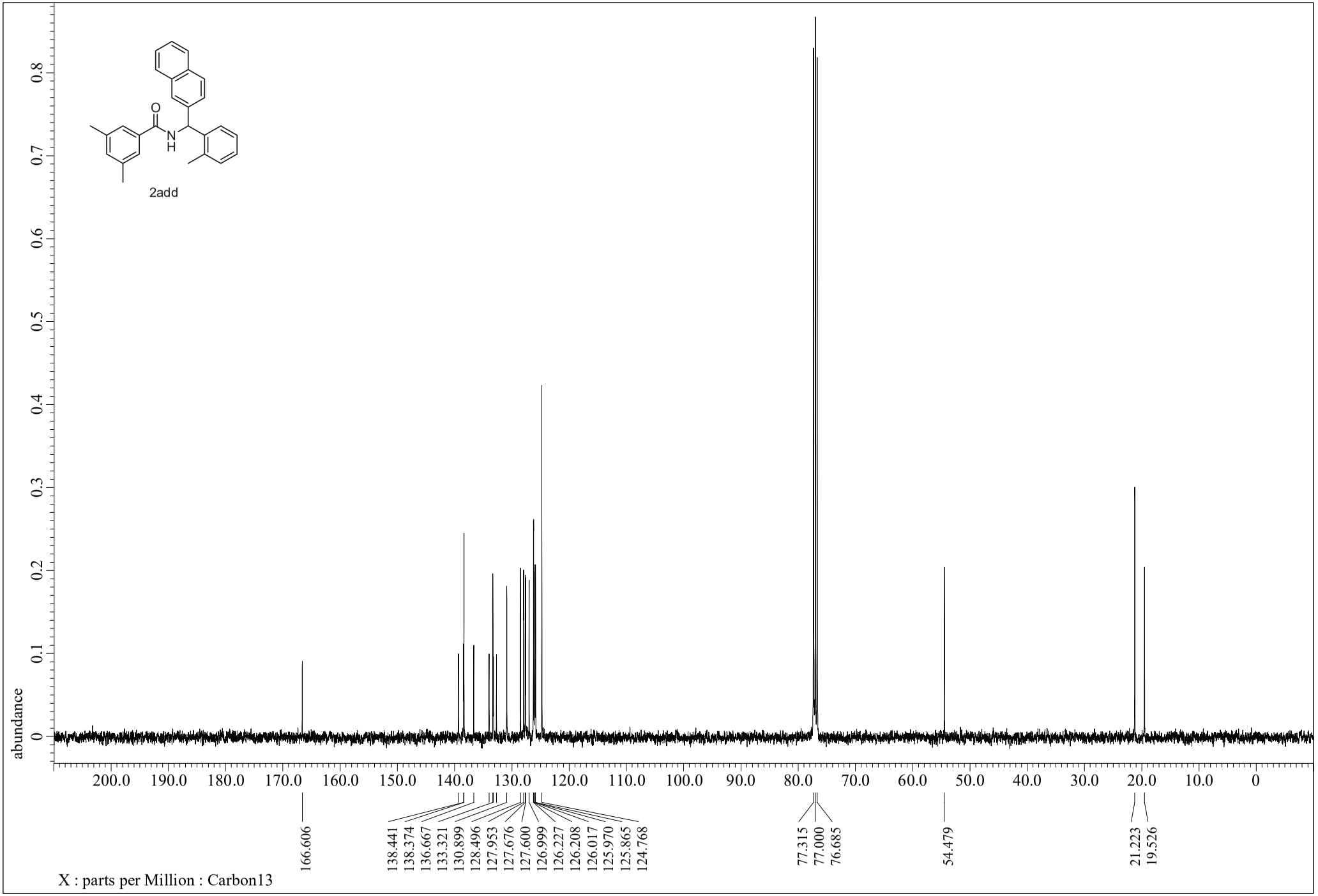

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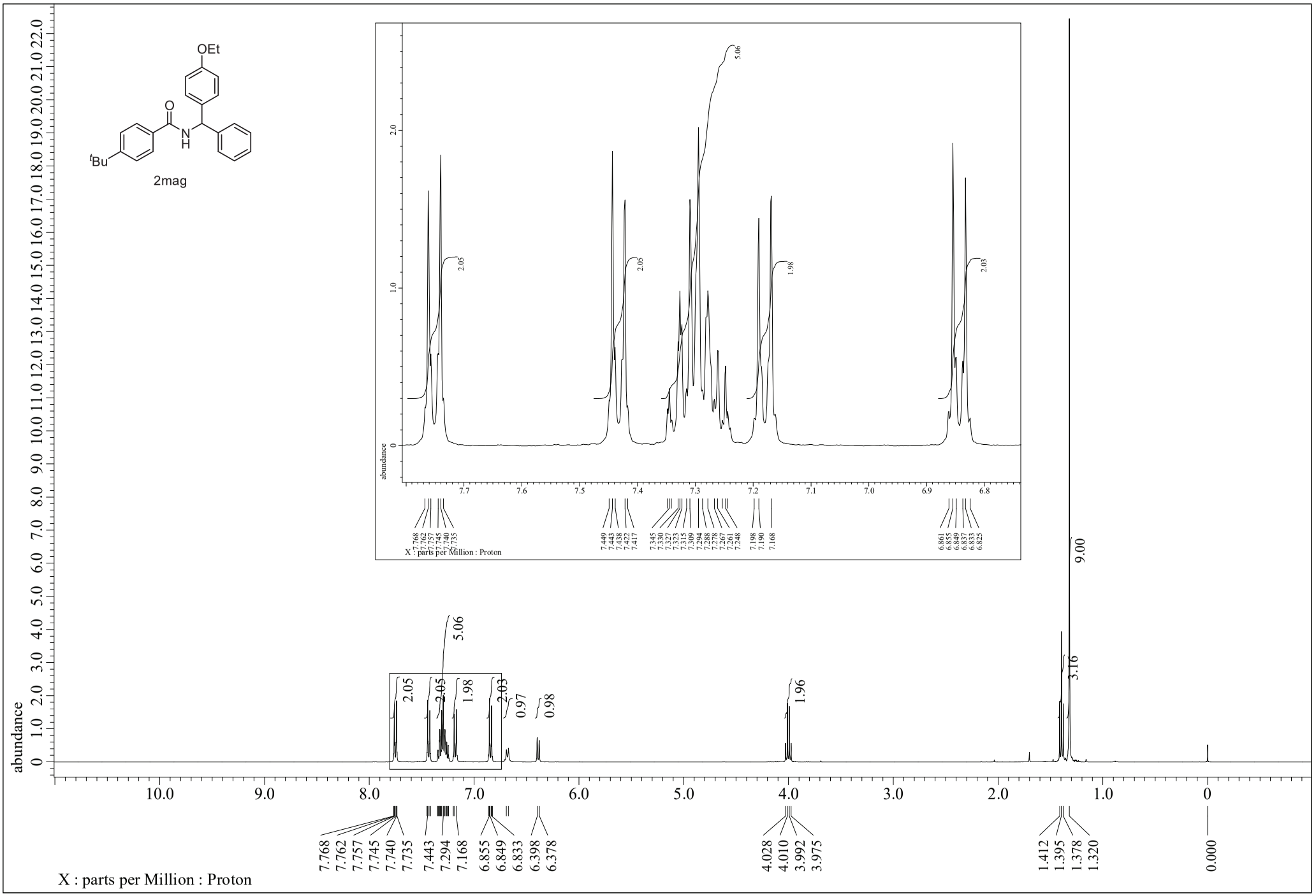

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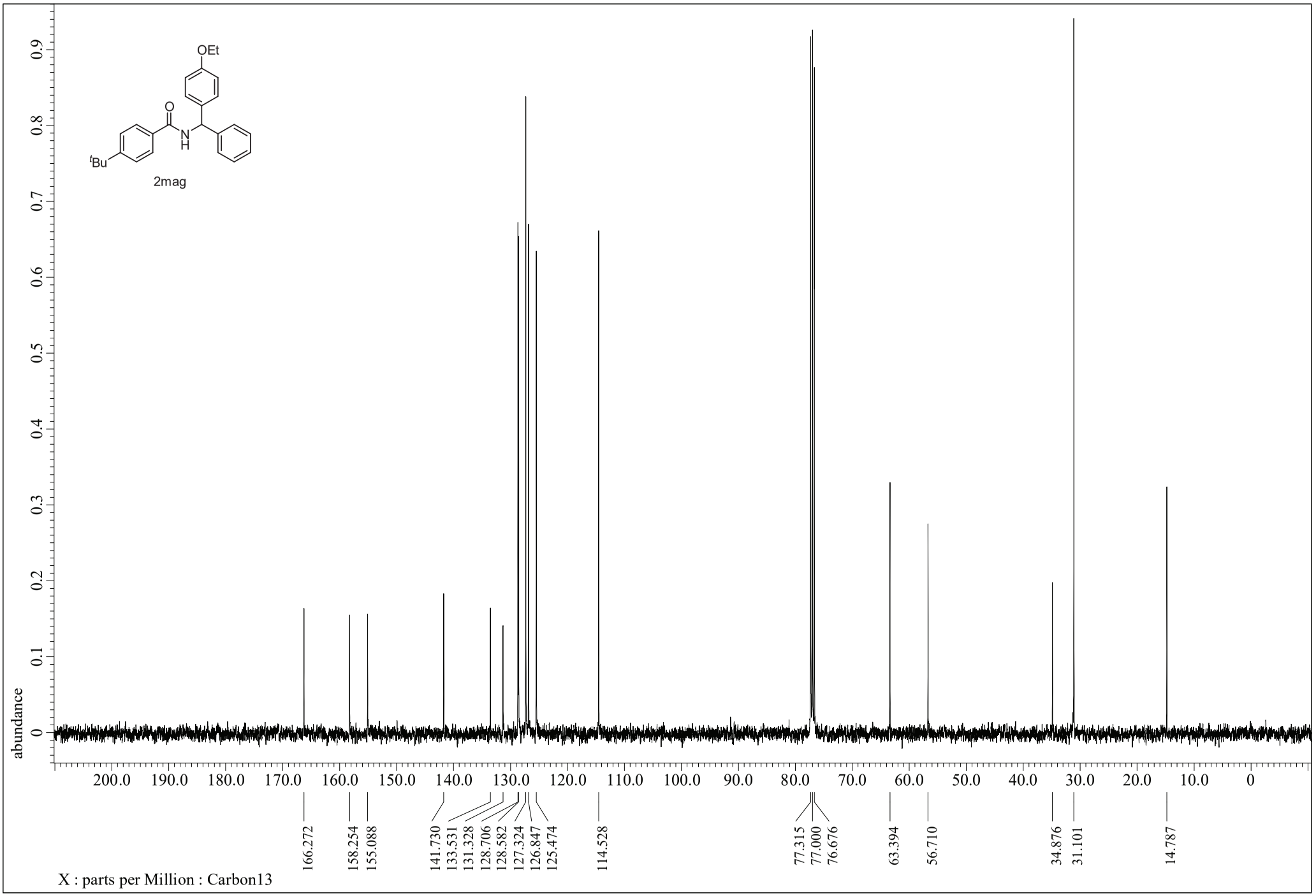

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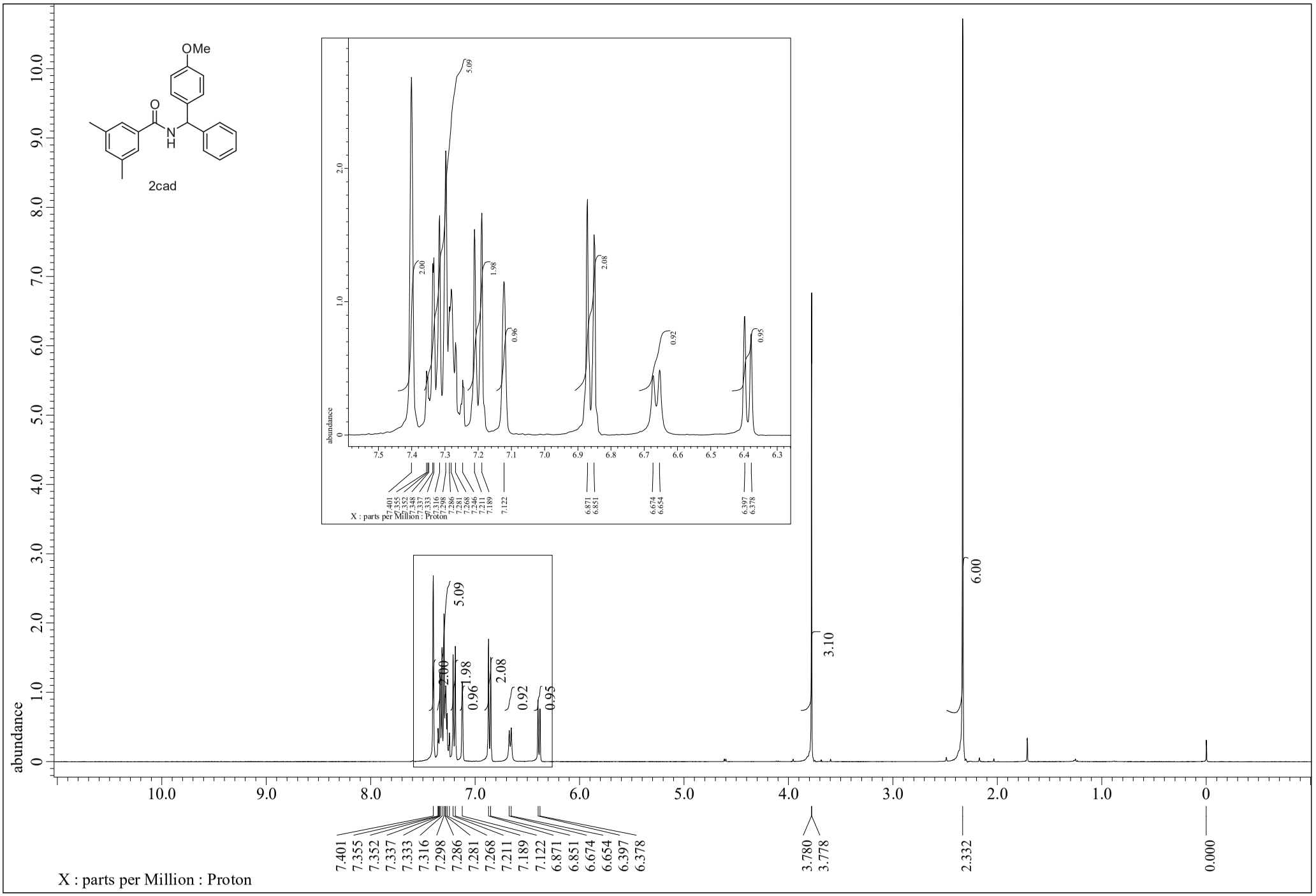
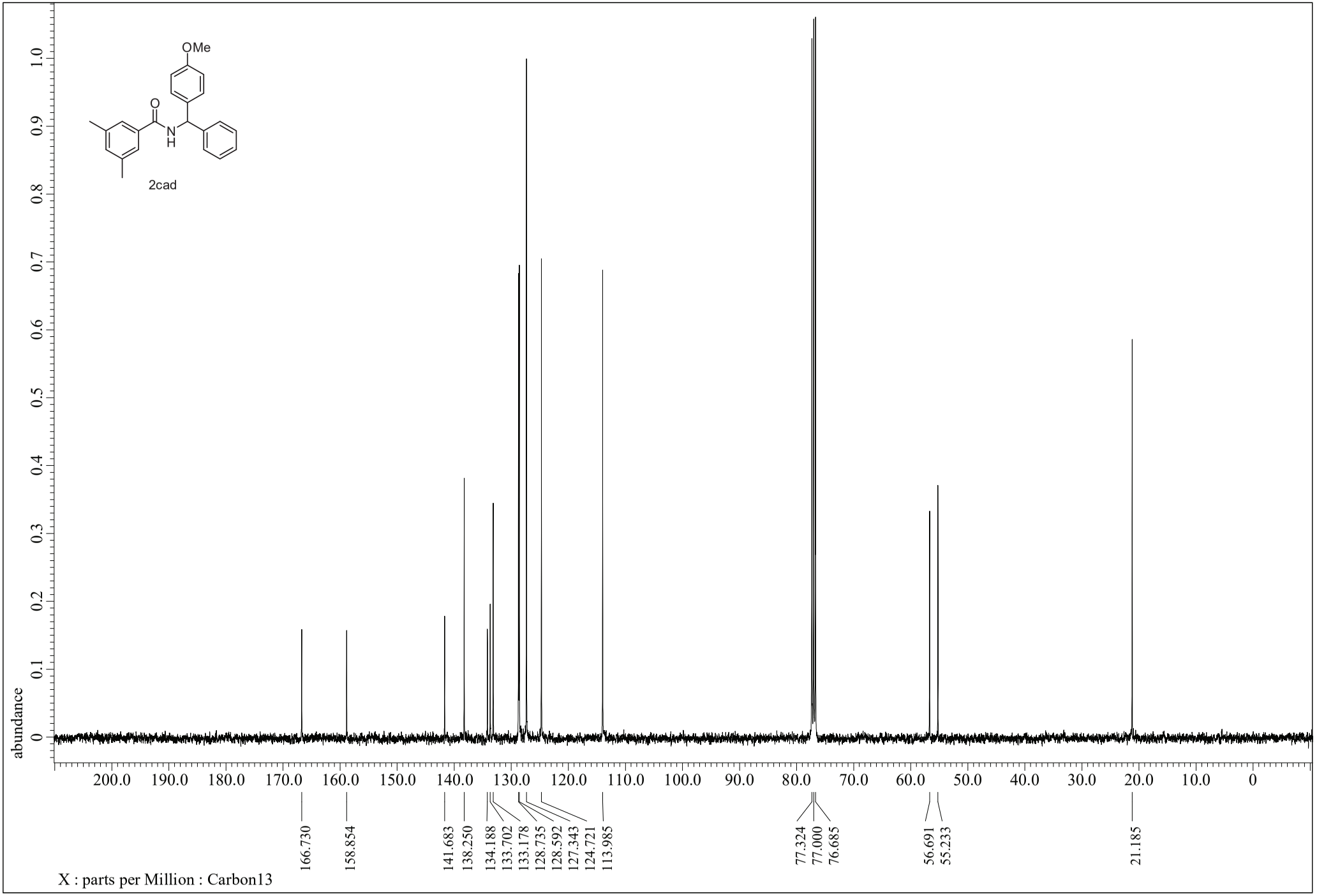
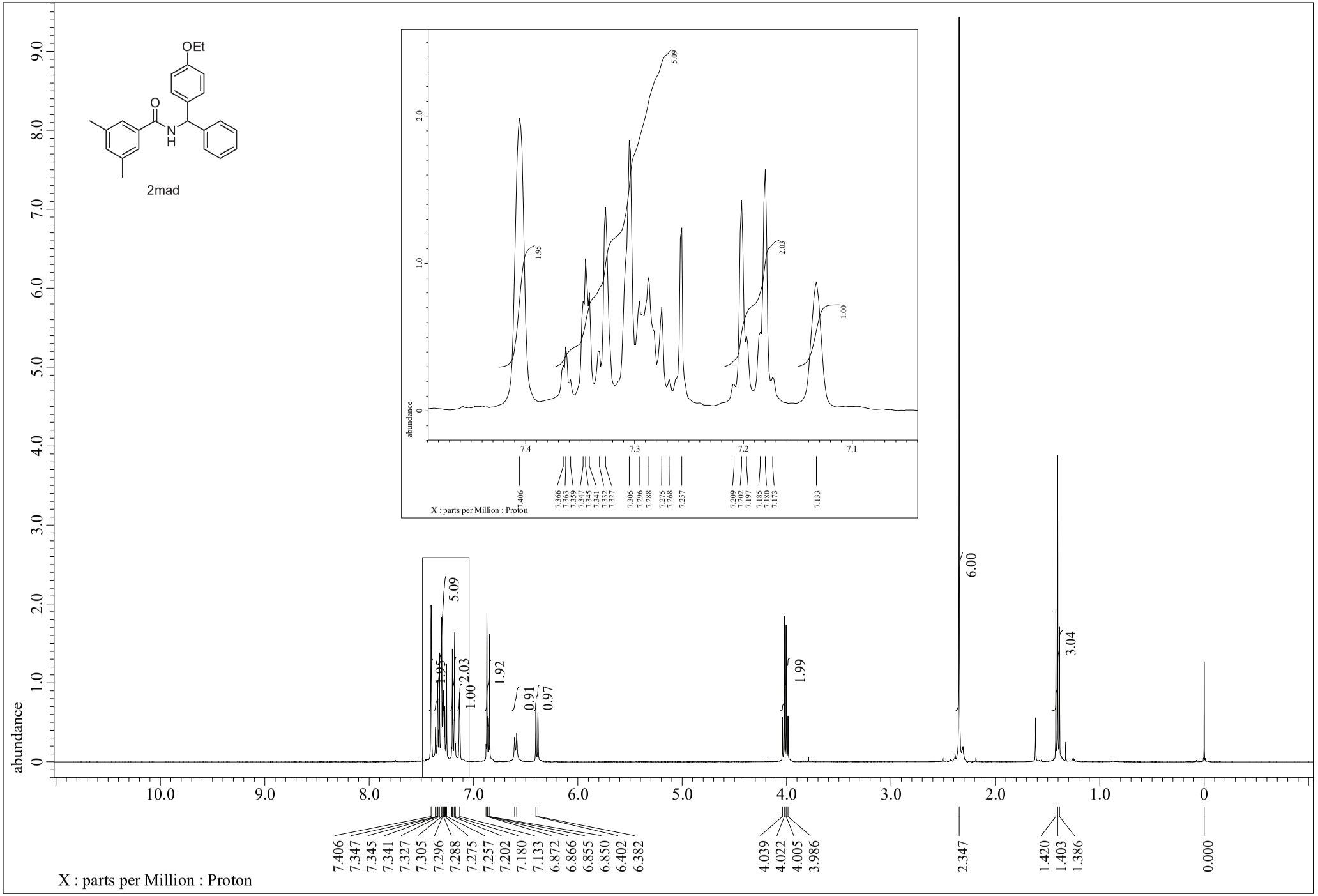


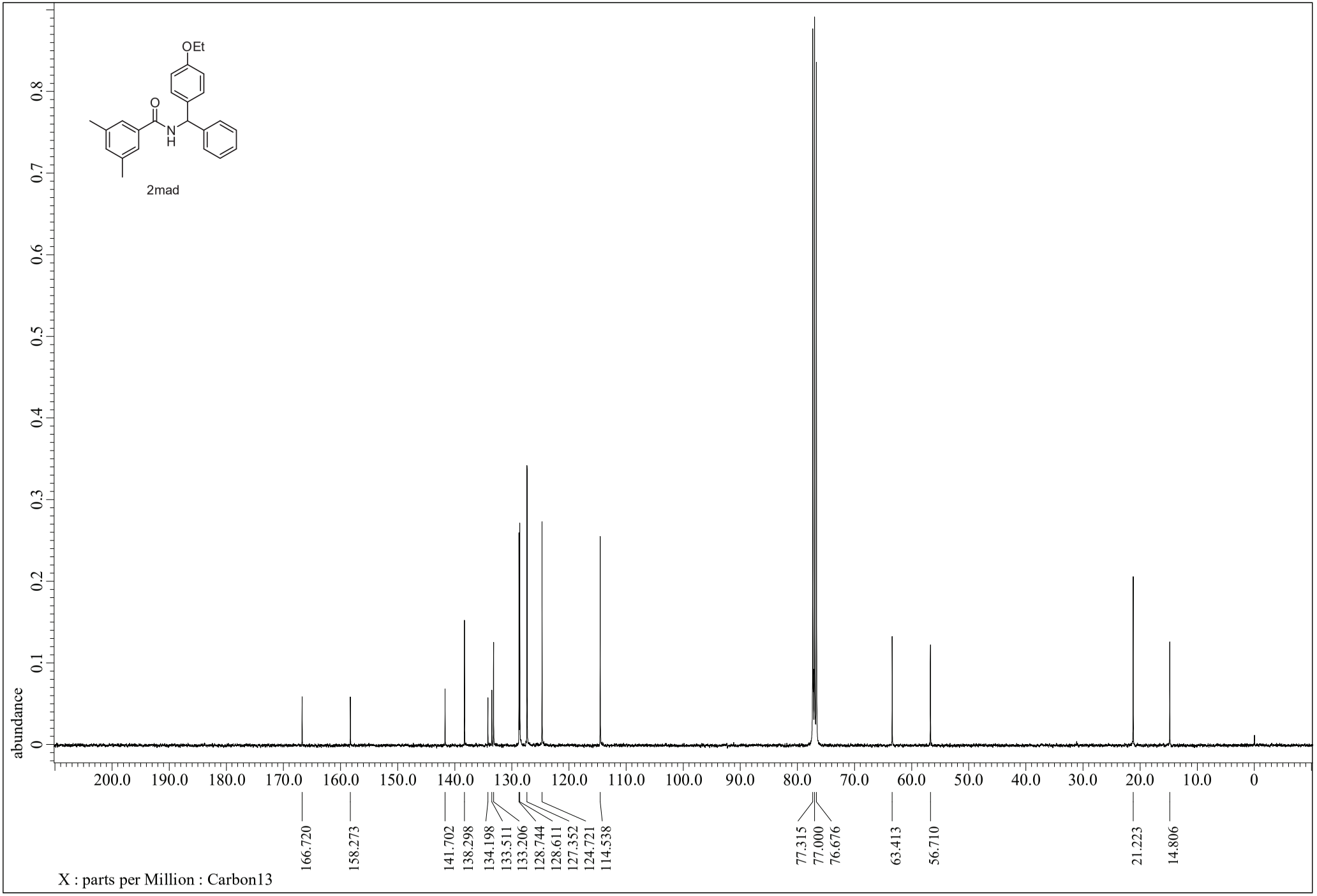
^{13}C NMR (101 MHz, $CDCl_3$)



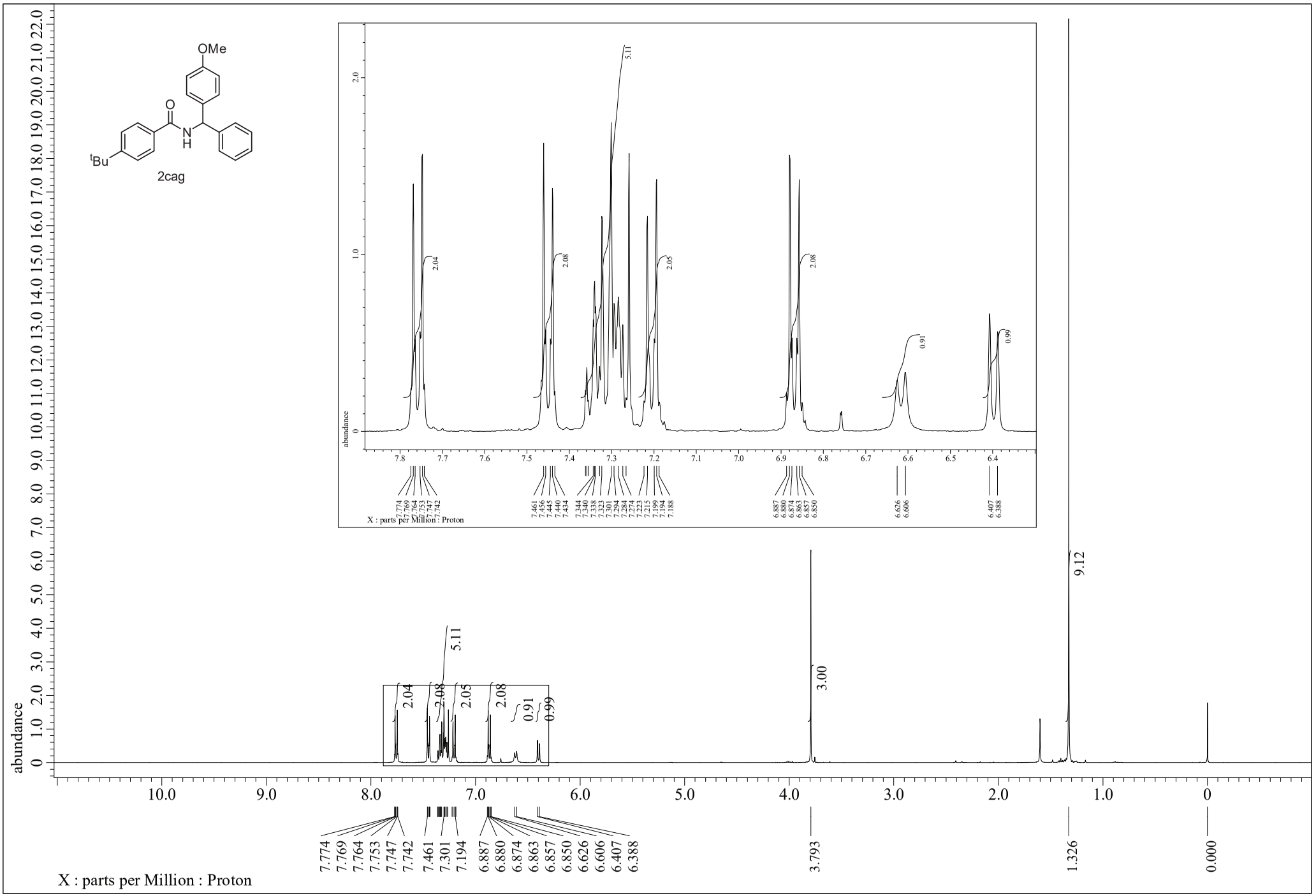
^{1}H NMR (400 MHz, $CDCl_3$)



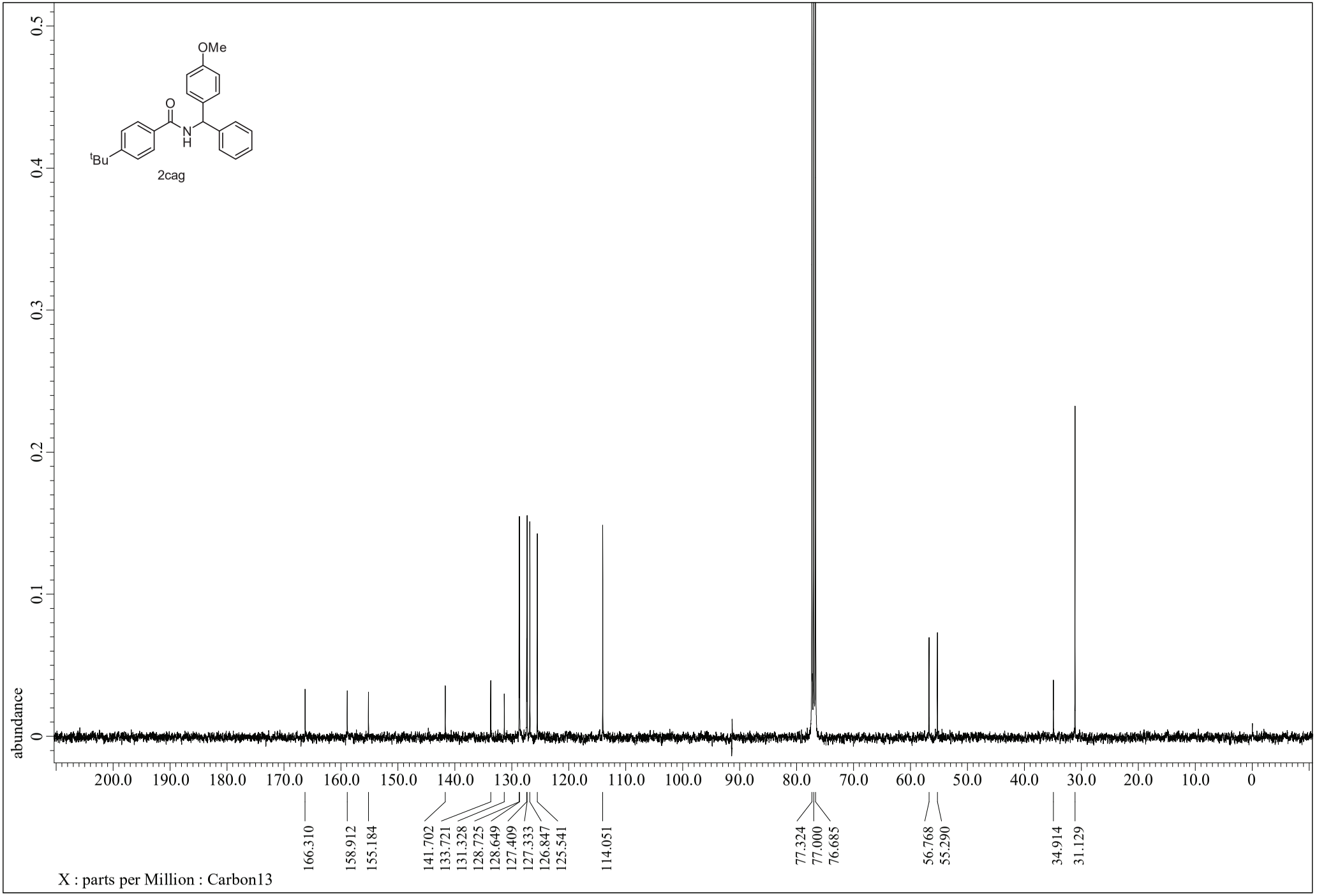
^{13}C NMR (101 MHz, $CDCl_3$)



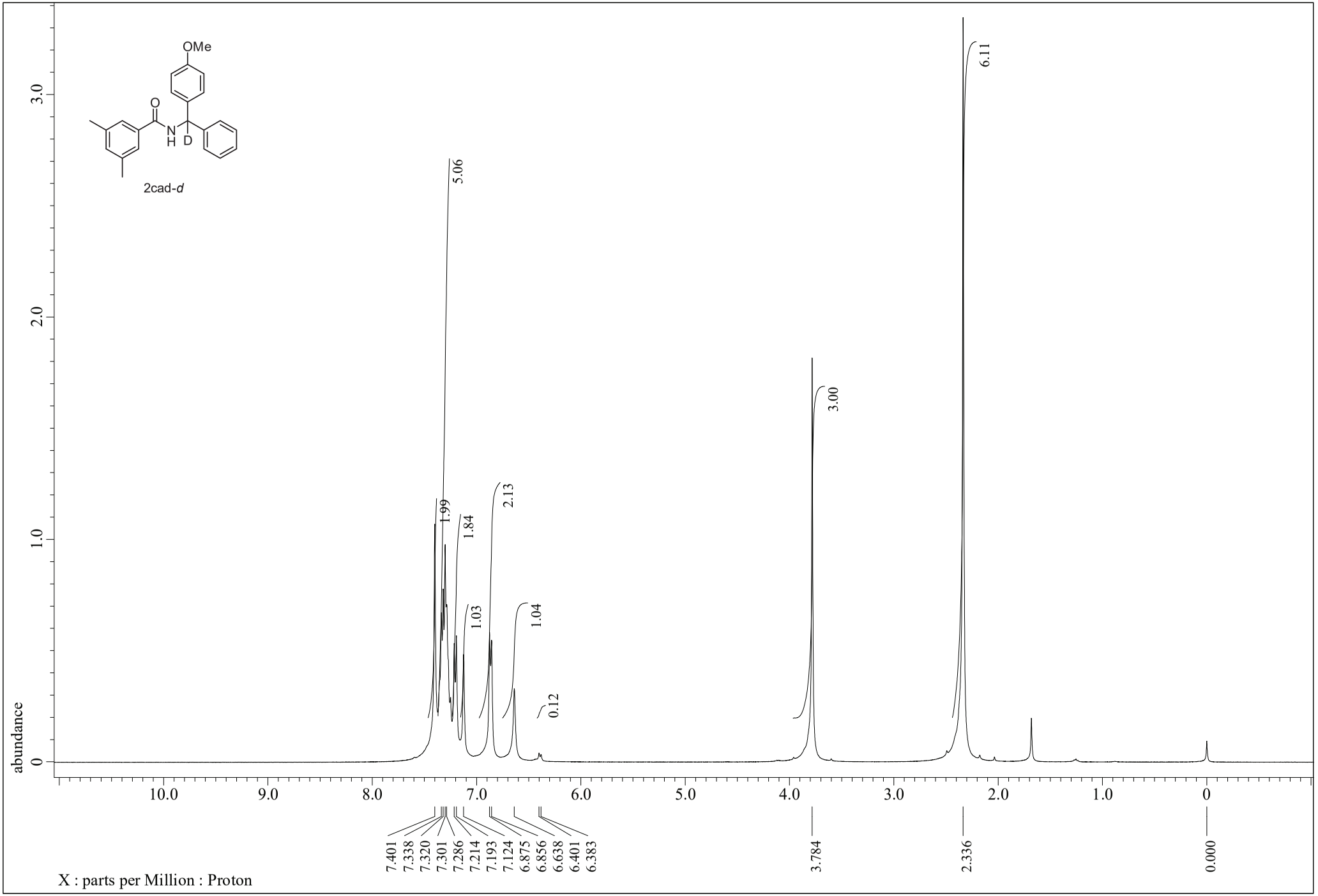
^{1}H NMR (400 MHz, $CDCl_3$)



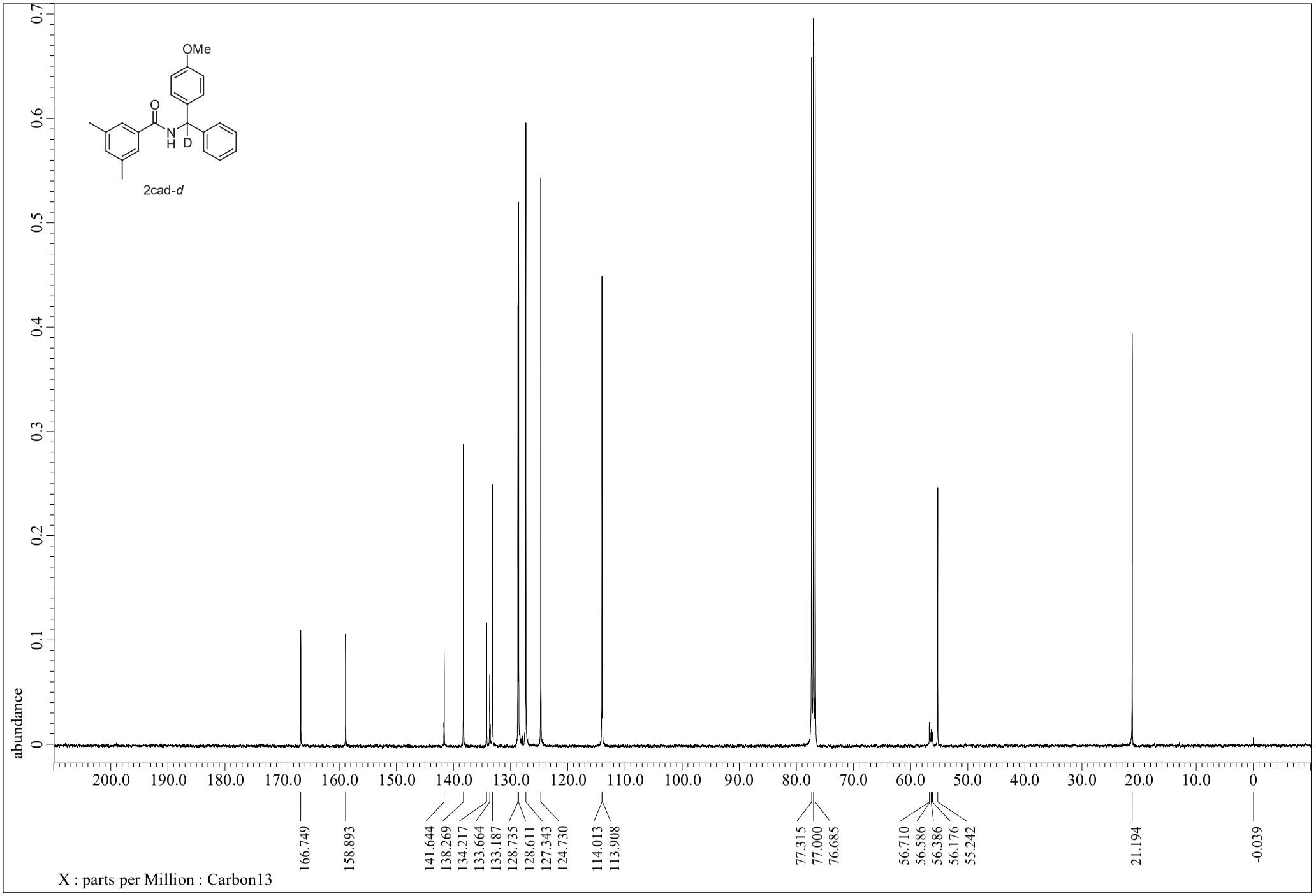
^{13}C NMR (101 MHz, $CDCl_3$)



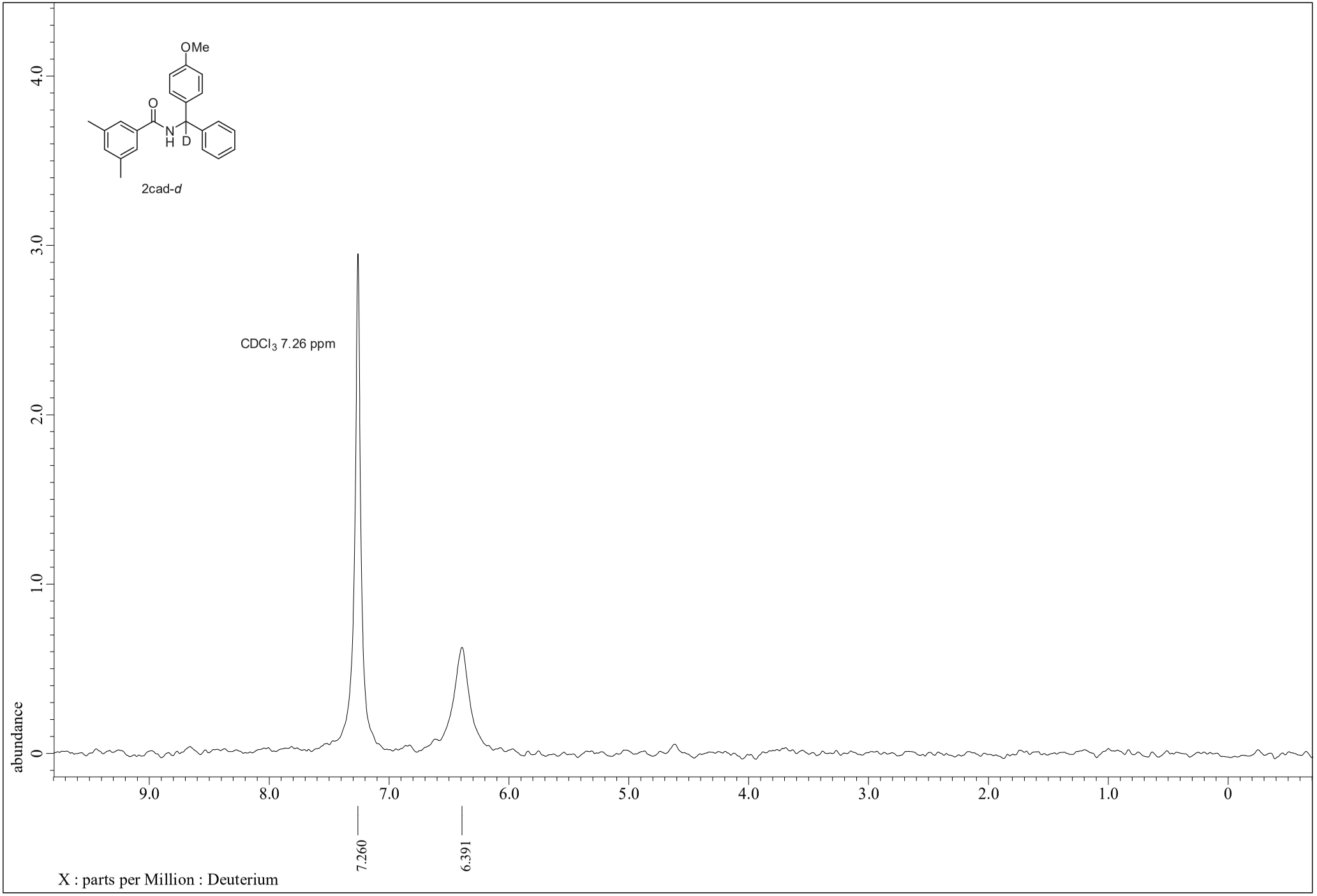
^{1}H NMR (400 MHz, $CDCl_3$)



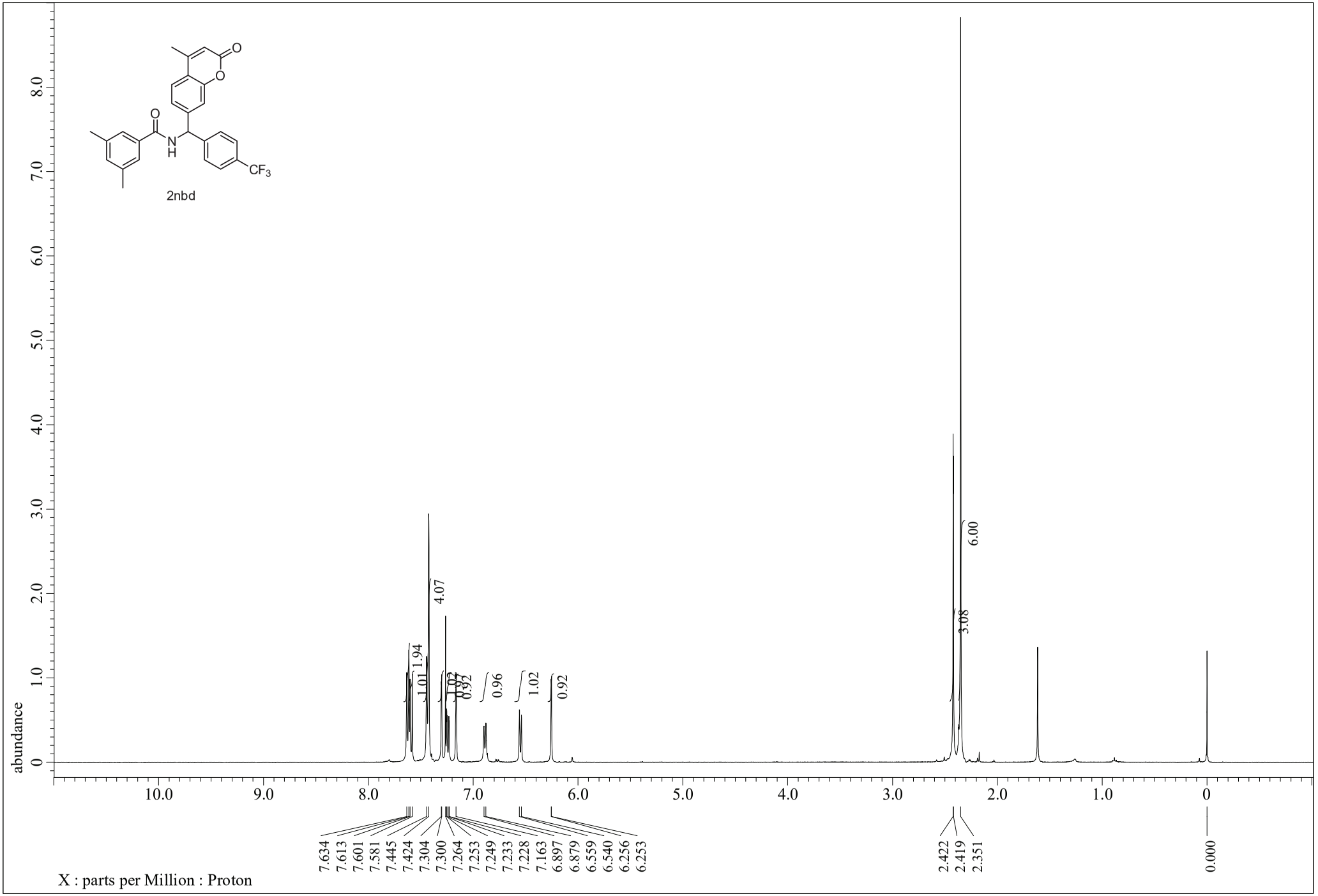
^{13}C NMR (101 MHz, $CDCl_3$)



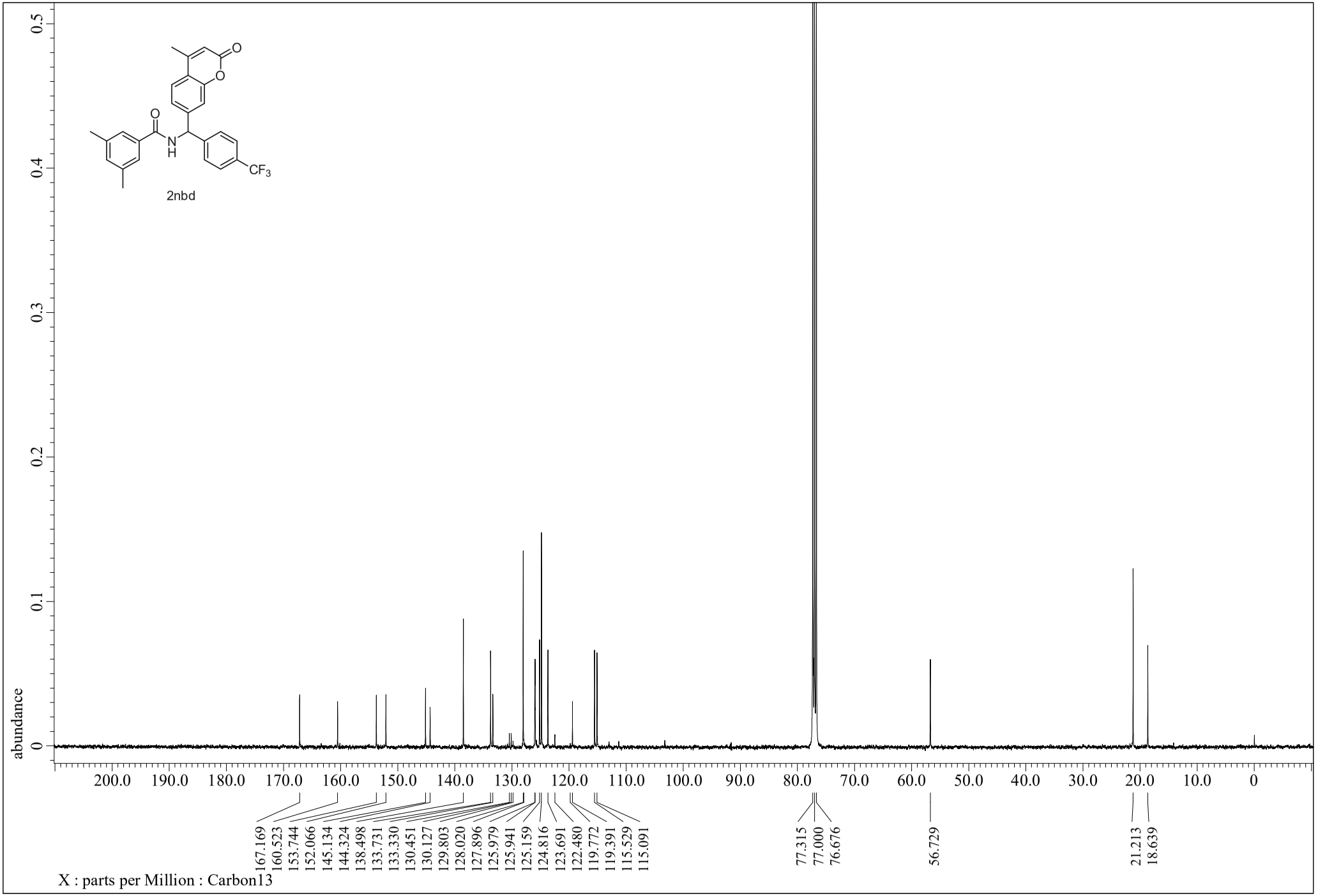
^{2}H NMR (61.37 MHz, $CHCl_3$)



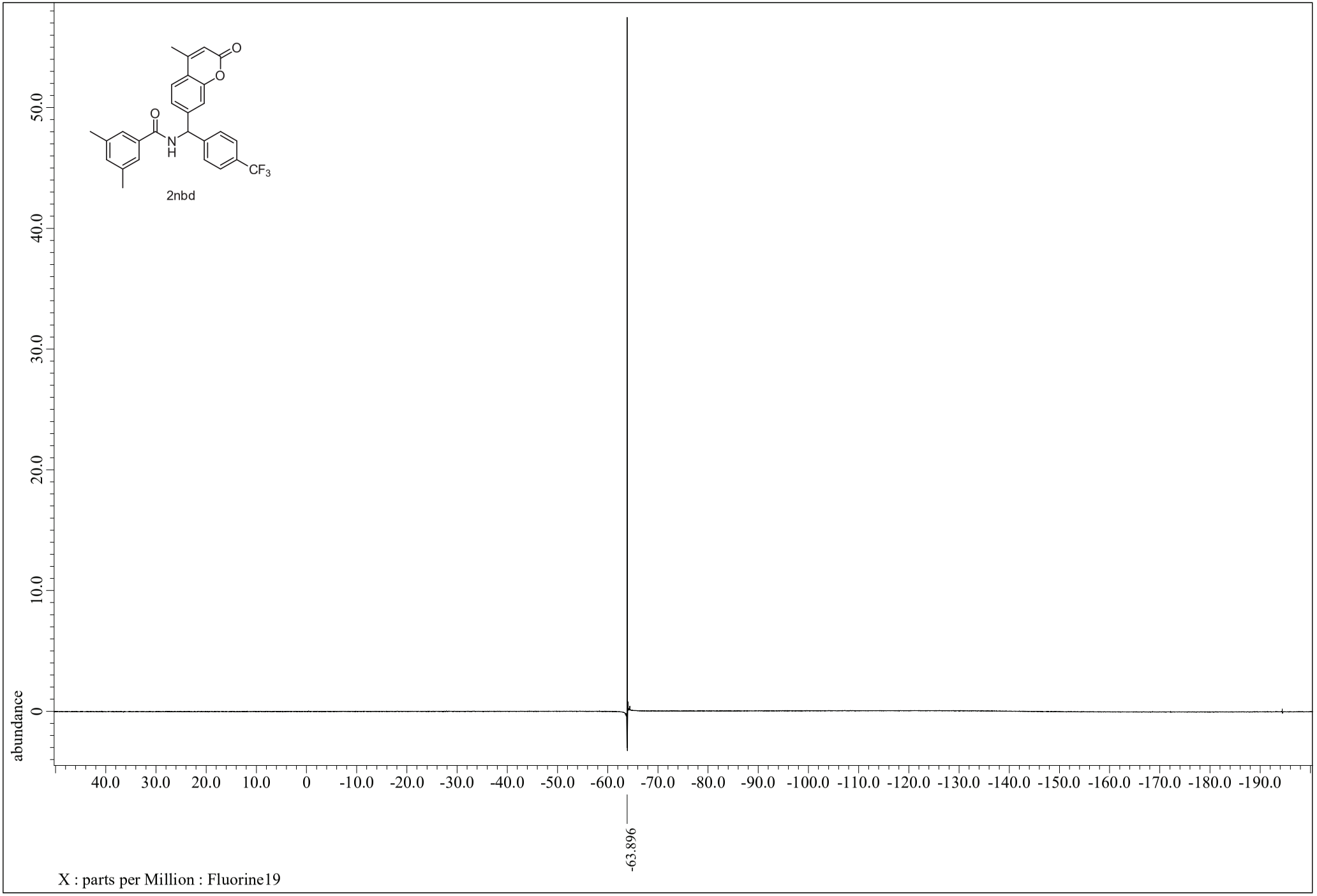
^{1}H NMR (400 MHz, $CDCl_3$)



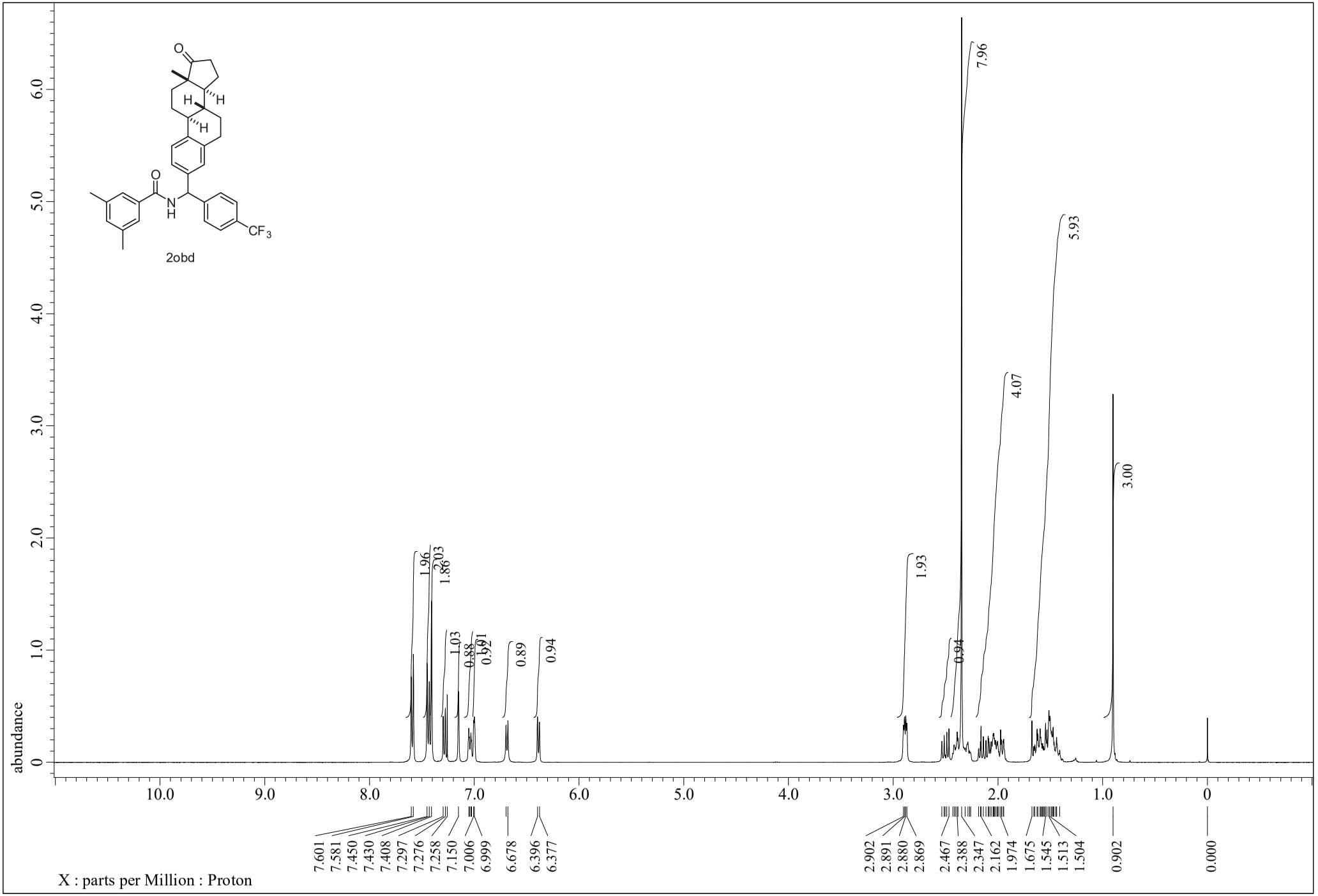
^{13}C NMR (101 MHz, $CDCl_3$)



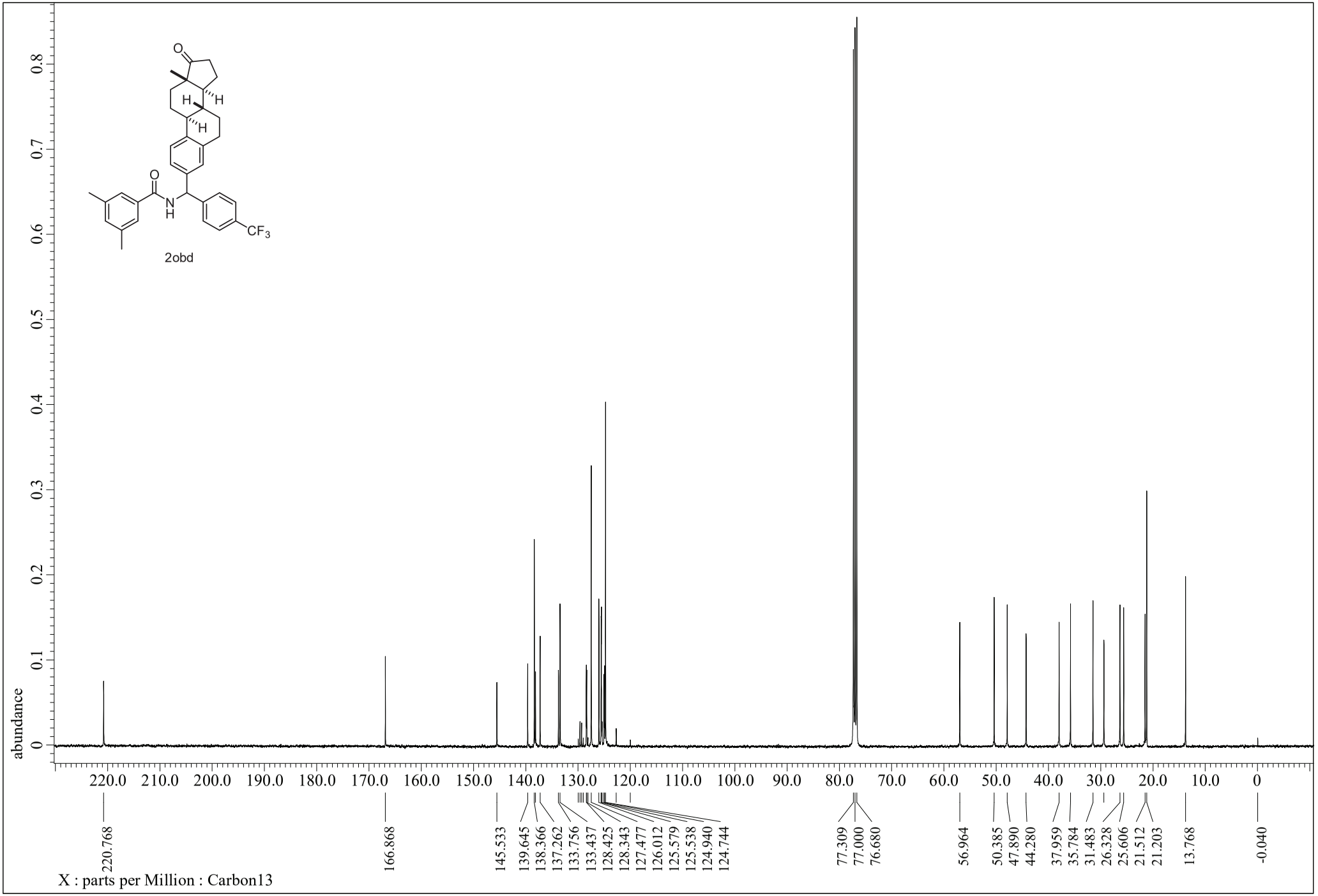
^{19}F NMR (376 MHz, $CDCl_3$)



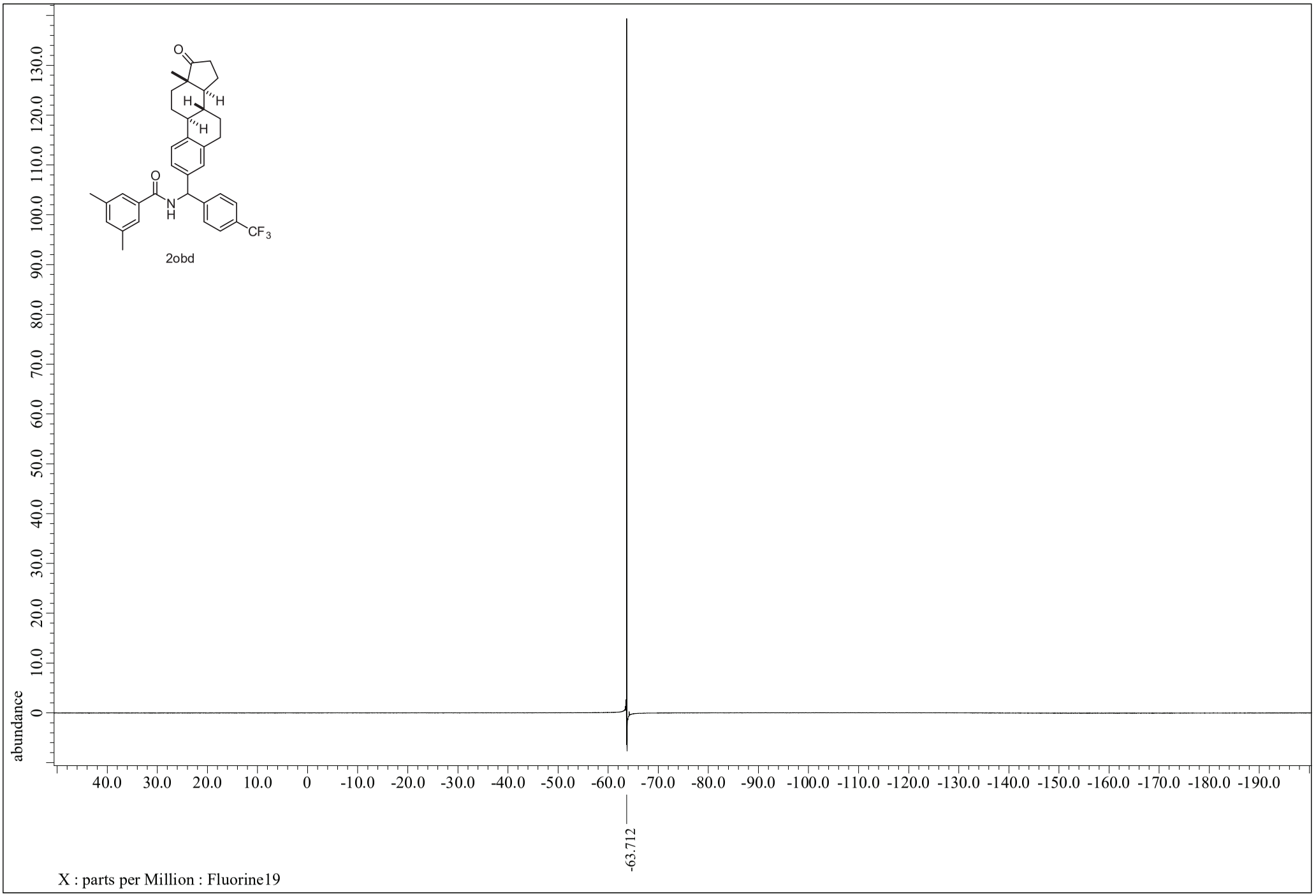
^{1}H NMR (400 MHz, $CDCl_3$)



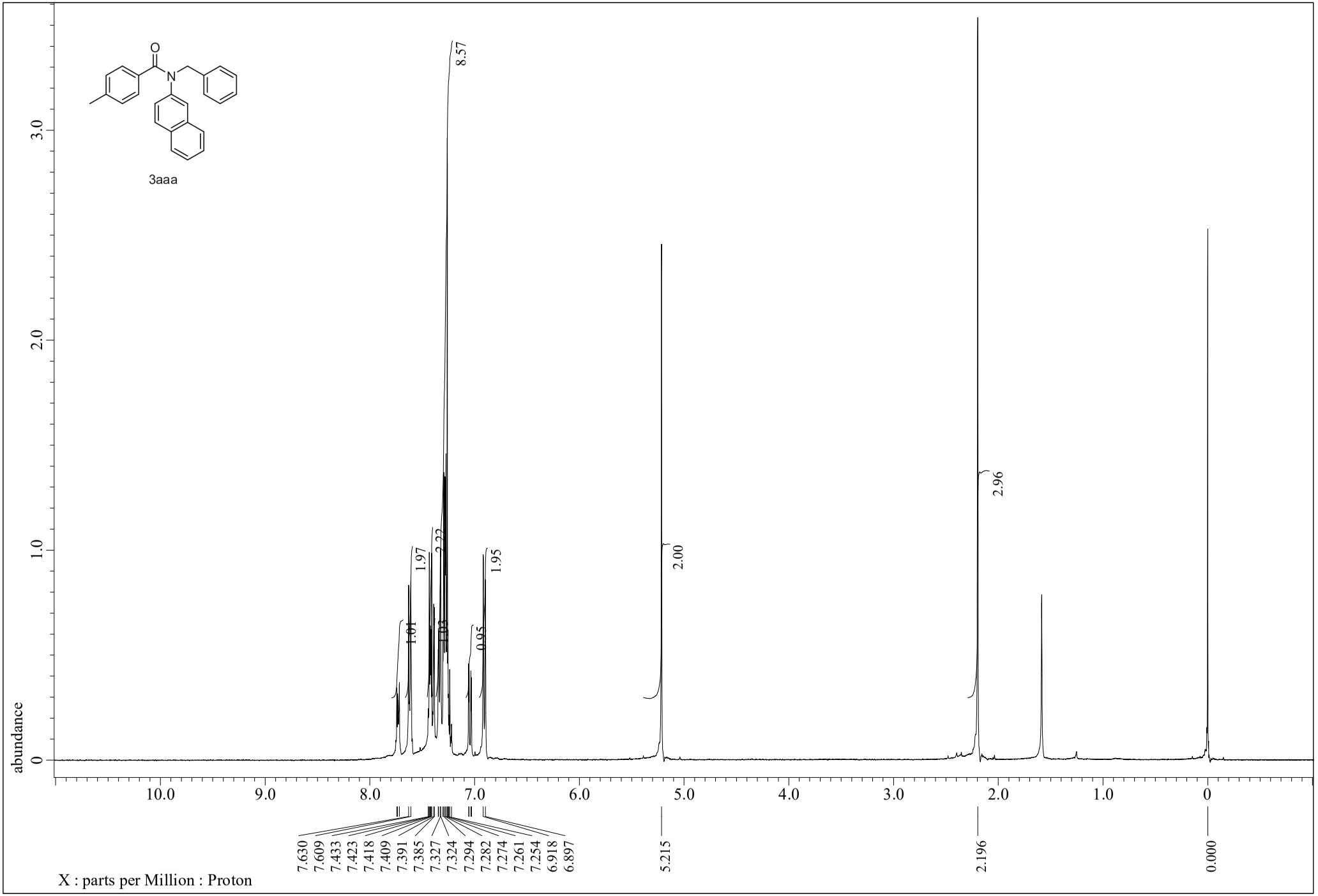
^{13}C NMR (101 MHz, $CDCl_3$)



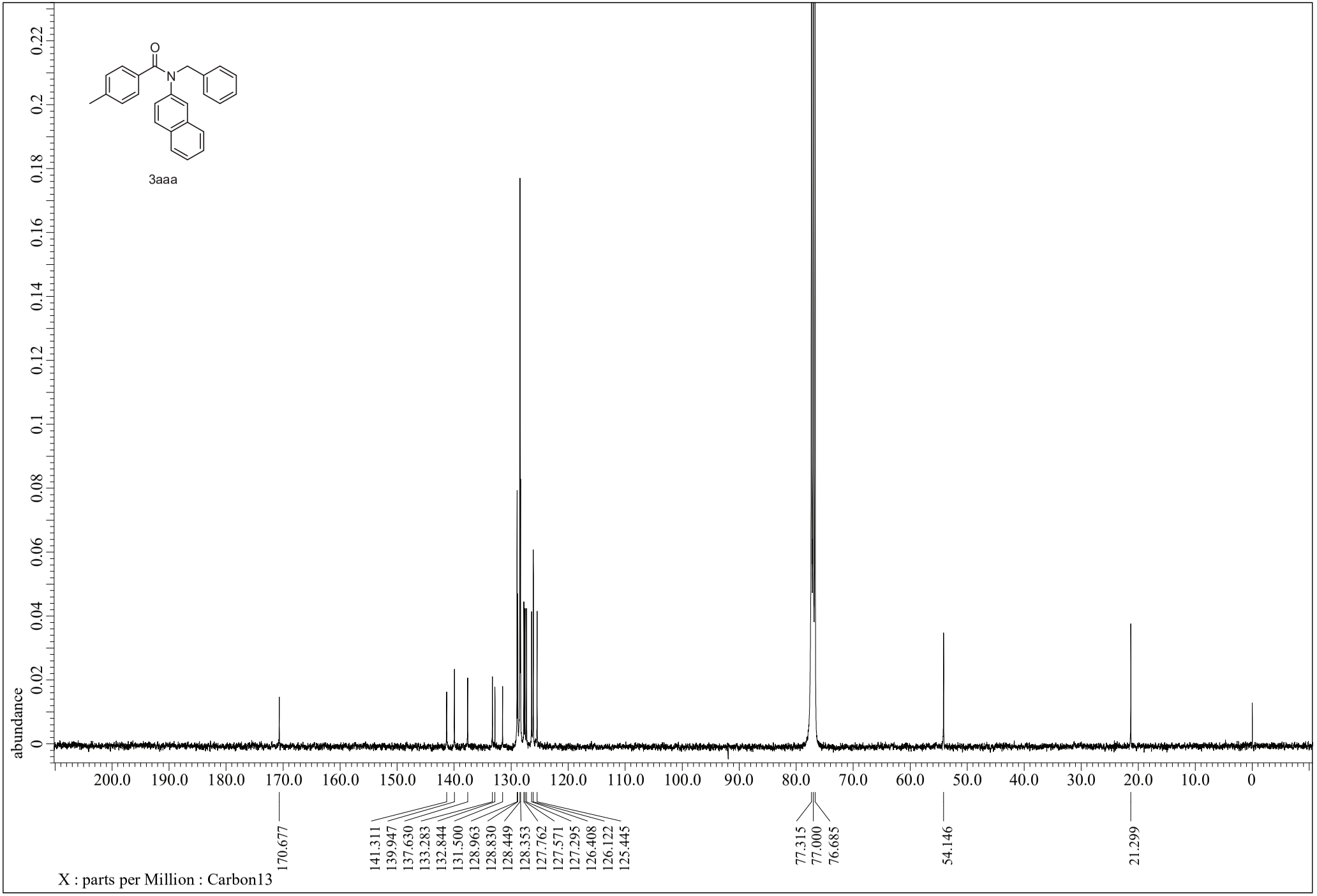
^{19}F NMR (376 MHz, $CDCl_3$)



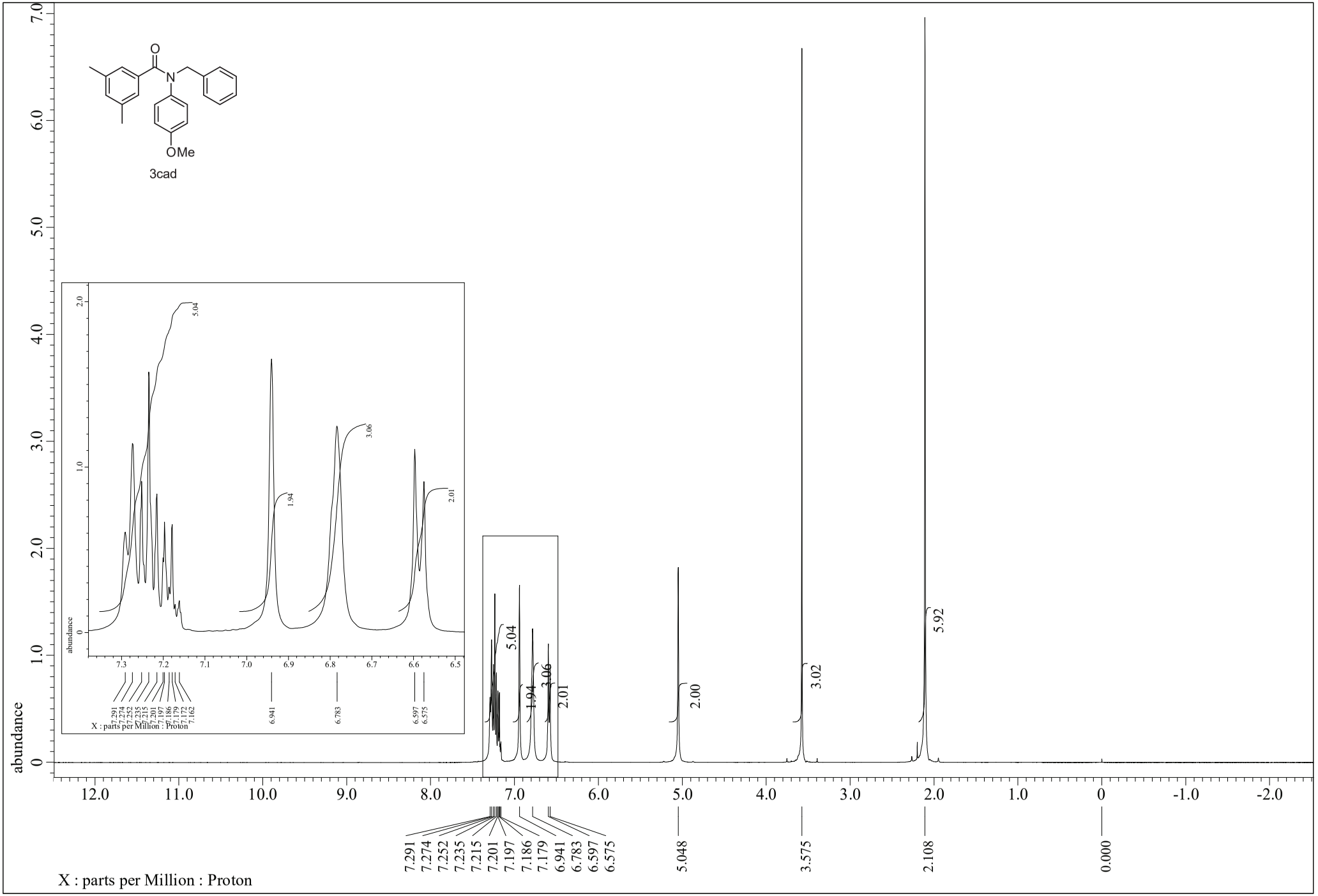
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



^{13}C NMR (101 MHz, $CDCl_3$)