Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Palladium-catalyzed synthesis of nitriles from *N*-phthaloyl hydrazones

Yusuke Ano,*,† Masaya Higashino, Yuki Yamada, and Naoto Chatani

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

† *Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

ano@chem.eng.osaka-u.ac.jp

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1. General Information

^{1}H, ^{2}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL ECZ-400 spectrometer. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethylsilane (δ: 0.0). 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: 77.16). The chemical shifts in ^{19}F NMR spectra were recorded relative to $CFCl_3$ (δ: 0.0). Data are recorded as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, br = broad singlet, m = multiplet, c = complex), coupling constant (Hz), and integration. Infrared spectra (IR) were recorded on a JASCO FT/IR-4000 spectrometer using the ATR method. Absorption data are reported in reciprocal centimeters from 800 to 3500 cm^{-1} with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a SHIMDZU QP-2010 or QP-2020NX spectrometer with a quadrupole mass analyzer at 70 eV. Data were recorded as follows: mass/charge ratio (*m*/*z*) and relative intensity to the base peak at 100 %. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer with a time-of-flight mass analyzer. Melting points were determined on a Stanford Research Systems MPA100 apparatus equipped with a digital thermometer and are uncorrected. Preparative gel permeation chromatography (GPC) were carried out on a JAI LC-5060 equipped with two JAIGEL-2HR columns connected in series or two JAIGEL-2HR-40 columns connected in series. High-pressure liquid chromatography (HPLC) was performed with a SHIMADZU LC-20AR equipped with a SHIMADZU SPD-20A (UV Detector, λ = 254 nm) and Phenomenex Luna® Silica (5 μm, 210 × 21.2 mm).

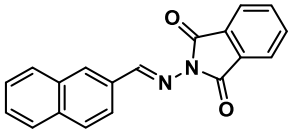
2. Materials

Toluene (dehydrated, –Super^{2} Plus–) [CAS RN: 108-88-3] was purchased from Kanto Chemical Co, Inc. and was purified by passage through activated alumina using a GlassContour Solvent Dispensing System. (IMes)Pd(allyl)Cl [CASRN: 478980-04-0] and (IPr)Pd(allyl)Cl [CAS RN: 478980-03-9] were purchased from Umicore and used as received. IMes·HCl [CAS RN: 141556-45-8], IPr·HCl [CAS RN: 250285-32-6], and *t*-BuOK [CAS RN: 865-47-4] were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Starting materials were prepared as described below.

General Procedure for the Preparation of *N*-Phthaloyl Hydrazones 1

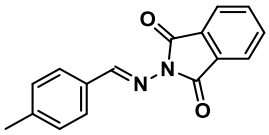
A two necked flask equipped with a Dean-Stark trap and a magnetic stirring bar was dried with a heat gun and purged with N_2. After allowing the flask to cool to room temperature, *N*-aminophthalimide (1 equiv), the aldehyde (1.05 equiv), $TsOH \cdot H_2O$ (5 mol%), and toluene (0.25 M) were added. The resulting mixture was then refluxed overnight. After allowing the mixture to cool to room temperature, the resulting precipitated *N*-phthaloyl hydrazone **2** was collected on a filter and the crude product was purified by recrystallization from toluene or EtOAc.

(*E*)-2-[(Naphthalen-2-ylmethylene)amino]isoindoline-1,3-dione (1a) [CAS RN: 82408-29-5].



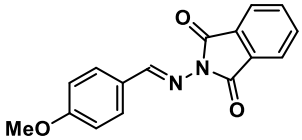
This compound was prepared on a 10 mmol scale. White solid (2.20 g, 73%). R_f = 0.27 (hexane/EtOAc = 3/1). Mp = 199.2–199.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.58 (s, 1H), 8.19–8.17 (c, 2H), 7.97–7.87 (c, 5H), 7.82–7.77 (m, 2H), 7.59–7.52 (c, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.3, 158.4, 135.2, 134.8, 133.1, 131.5, 131.3, 130.4, 128.9, 128.8, 128.1, 127.8, 126.8, 123.9, 123.3. IR (ATR): 3084 w, 3059 w, 1789 w, 1714 s, 1605 w, 1467 w, 1366 m, 1347 m, 1304 s, 1113 m, 1082 m. MS (EI, relative intensity, %) *m*/*z*: 300 (M^+, 31), 154 (14), 153 (100), 139 (14), 104 (20), 76 (18). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{13}N_2O_2$ 301.09715; Found 301.09665.

(*E*)-2-[(4-Methylbenzylidene)amino]isoindoline-1,3-dione (1b) [CAS RN: 32386-99-5].



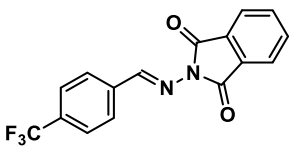
This compound was prepared on a 3 mmol scale. White solid (0.40 g, 50%). R_f =0.31 (hexane/EtOAc = 3/1). Mp = 161.3–161.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.33 (s, 1H), 7.95–7.90 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.80–7.76 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.3, 159.2, 142.5, 134.7, 131.0, 130.5, 129.7, 128.6, 123.9, 21.8. IR (ATR): 2920 w, 1771 w, 1720 s, 1609 w, 1465 w, 1364 m, 1304 s, 1117 m. MS (EI, relative intensity, %) *m*/*z*: 264 (M^+, 17), 148 (26), 130 (18), 118 (24), 117 (100), 105 (50), 104 (37), 77 (10), 76 (29). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_2$ 265.09715; Found 265.09611.

(*E*)-2-[(4-Methoxybenzylidene)amino]isoindoline-1,3-dione (1c) [CAS RN: 19279-70-0].



This compound was prepared on a 3 mmol scale. Light yellow solid (0.71 g, 85%). R_f = 0.24 (hexane/EtOAc = 2/1). Mp = 188.3–188.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.25 (s, 1H), 7.94–7.89 (m, 2H), 7.87–7.83 (m, 2H), 7.80–7.75 (m, 2H), 6.99–6.95 (m, 2H), 3.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.3, 162.7, 159.1, 134.6, 130.5, 130.4, 126.3, 123.8, 114.3, 55.6. IR (ATR): 3006 w, 2935 w, 2844 w, 1718 s, 1603 m, 1513 m, 1372 m, 1305 s, 1252 s, 1166 m, 1117 m, 1026 m. MS (EI, relative intensity, %) *m*/*z*: 280 (M^+, 28), 134 (14), 133 (100), 105 (13), 104 (20), 103 (13), 76 (17). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_3$ 281.09207; Found 281.09233.

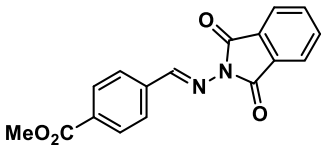
(*E*)-2-[(4-(Trifluoromethyl)benzylidene)amino]isoindoline-1,3-dione (1d) [CAS RN: 386275-75-8].



This compound was prepared on a 3.4 mmol scale. White solid (1.02 g, 95%). R_f = 0.28 (hexane/EtOAc = 3/1). Mp = 240.6–240.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.57 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.98–7.93 (m, 2H), 7.84–7.79 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.2, 155.7, 137.2, 135.0, 133.1 (q, *J* = 32.8 Hz), 130.3, 128.6, 125.9 (q, *J* = 3.5 Hz), 124.1, 123.9 (q, *J* = 272.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.8. IR

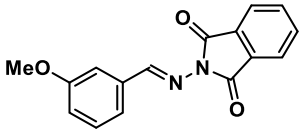
(ATR): 1773 w, 1721 s, 1613 w, 1468 w, 1374 w, 1299 s, 1158 m, 1116 s.. MS (EI, relative intensity, %) *m*/*z*: 318 (M^+, 5), 147 (55), 105 (100), 104 (51), 76 (36). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{10}N_2O_2F_3$ 319.06889; Found 319.06654.

Methyl (*E*)-4-{[(1,3-Dioxoisoindolin-2-yl)imino]methyl}benzoate (1e) [CAS RN: 159022-76-1].



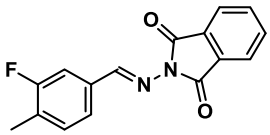
This compound was prepared on a 10 mmol scale. White solid (2.47 g, 80%). R_f = 0.21 (hexane/EtOAc = 3/1). Mp = 221.6–222.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.55 (s, 1H), 8.13 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.99–7.92 (c, 4H), 7.83–7.79 (m, 2H), 3.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.6, 165.1, 156.4, 137.9, 135.0, 132.7, 130.3, 130.1, 128.3, 124.1, 52.5. IR (ATR): 3071 w, 2953 w, 1773 w, 1712 s, 1608 w, 1433 w, 1350 m, 1279 s, 1098 m. MS (EI, relative intensity, %) *m*/*z*: 308 (M^+, 11), 162 (12), 161 (36), 160 (17), 147 (29), 130 (50), 105 (100), 104 (57), 76 (36). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_4$ 309.08698; Found 309.08504.

(*E*)-2-[(3-Methoxybenzylidene)amino]isoindoline-1,3-dione (1f) [CAS RN: 32387-03-4].



This compound was prepared on a 3 mmol scale. Light yellow solid (0.49 g, 58%). R_f = 0.20 (hexane/EtOAc = 3/1). Mp = 147.6–148.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.36 (s, 1H), 7.96–7.91 (m, 2H), 7.82–7.77 (m, 2H), 7.48 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.42 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.05 (ddd, *J* = 8.0, 2.6, 1.2 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.2, 160.0, 158.8, 135.0, 134.8, 130.4, 129.9, 123.9, 122.0, 118.7, 111.7, 55.6. IR (ATR): 3098 w, 3031 w, 2968 w, 2837 w, 1718 s, 1598 m, 1370 m, 1308 s. MS (EI, relative intensity, %) *m*/*z*: 280 (M^+, 19), 134 (12), 133 (100), 105 (24), 104 (27), 103 (15), 76 (22). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_3$ 281.09207; Found 281.09052.

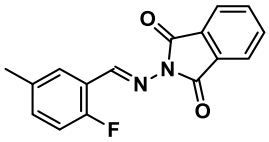
(*E*)-2-[(3-Fluoro-4-methylbenzylidene)amino]isoindoline-1,3-dione (1g).



This compound was prepared on a 10 mmol scale. White solid (2.10 g, 74%). R_f = 0.23 (hexane/$CHCl_3$ = 3/1). Mp = 177.7–178.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.37 (d, *J* = 0.7 Hz, 1H), 7.95–7.91 (m, 2H), 7.81–7.77 (m, 2H), 7.61 (dd, *J* = 10.2, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 2.34 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.1, 161.6 (d, *J* = 245.6 Hz), 157.1, 134.8, 133.5 (d, *J* = 7.7 Hz), 131.8 (d, *J* = 5.3 Hz), 130.4, 129.1 (d, *J* = 17.8 Hz), 124.5 (d, *J* = 2.9 Hz), 123.9, 114.0 (d, *J* = 23.6 Hz), 14.9 (d, *J* = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.1 (t, *J* = 8.7 Hz). IR (ATR): 3044 w, 2926 w, 2859 w, 1714 s, 1564 w, 1417 w, 1359 m,

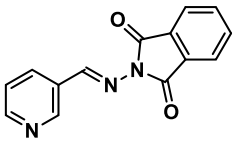
1338 m, 1306 s, 1127 s, 1083 m. MS (EI, relative intensity, %) *m*/*z*: 282 (M^+, 19), 262 (28), 148 (54), 136 (19), 135 (91), 130 (33), 105 (100), 104 (67). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{12}N_2O_2F$ 283.08773 Found 283.08819.

(*E*)-2-[(2-Fluoro-5-methylbenzylidene)amino]isoindoline-1,3-dione (1h).



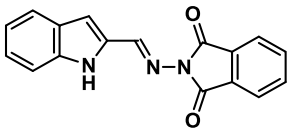
This compound was prepared on a 5 mmol scale. White solid (1.30 g, 92%). R_f = 0.29 (hexane/EtOAc = 3/1). Mp = 163.9–164.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.63 (s, 1H), 7.99 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.96–7.92 (m, 2H), 7.82–7.77 (m, 2H), 7.28–7.24 (m, 1H), 7.02 (dd, *J* = 10.1, 8.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.0, 160.6 (d, *J* = 251.4 Hz), 152.1 (d, *J* = 5.8 Hz), 134.8, 134.12 (d, *J* = 3.9 Hz), 134.11 (d, *J* = 7.7 Hz), 130.2, 127.0, 123.8, 121.0 (d, *J* = 9.6 Hz), 115.6 (d, *J* = 21.2 Hz), 20.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −124.7 (quint, *J* = 5.1 Hz). IR (ATR): 3057 w, 2931 w, 1727 s, 1491 m, 1303 s, 1249 m, 1212 m, 1110 m. MS (EI, relative intensity, %) *m*/*z*: 282 (M^+, 25), 148 (47), 136 (17), 135 (81), 130 (25), 105 (100), 104 (57), 76 (45). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{13}N_2O_2$ 283.08773; Found 283.08746.

(*E*)-2-[(Pyridin-3-ylmethylene)amino]isoindoline-1,3-dione (1i) [CAS: 321689-83-2].



This compound was prepared on a 9 mmol scale. White solid (1.83 g, 81%). R_f = 0.13 (hexane/EtOAc = 3/1). Mp = 174.8–175.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.56 (s, 1H), 8,98 (d, *J* = 1.6 Hz, 1H), 8.72 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.38 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.98–7.93 (m, 2H), 7.84–7.79 (m, 2H), 7.45 (dd, *J* = 8.0, 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.1, 154.7, 152.4, 150.5, 135.0, 134.4, 130.3, 130.0, 124.1, 124.0. IR (ATR): 2927 w, 1720 s, 1595 w, 1378 w, 1351 w, 1309 m, 1119 w. MS (EI, relative intensity, %) *m*/*z*: 251 (M^+, 4), 148 (16), 147 (18), 105 (100), 104 (50), 76 (37). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{10}N_3O_2$ 252.07675; Found 252.07652.

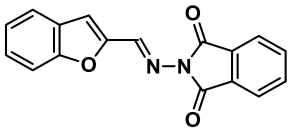
(*E*)-2-{[(1*H*-Indol-2-yl)methylene]amino}isoindoline-1,3-dione (1j).



This compound was prepared on a 1.4 mmol scale. White solid (0.33 g, 81%). R_f = 0.36 (hexane/EtOAc = 2/1). Mp = 249.5–249.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.50 (s, 1H), 9.21 (brs, 1H), 7.96–7.91 (m, 2H), 7.82–7.78 (m, 2H), 7.67 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.41 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.33–7.29 (m, 1H), 7.16–7.12 (m, 1H), 6.99 (dd, *J* = 2.1, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.4, 148.4, 137.6, 134.9, 132.4, 130.4, 128.2, 125.5, 123.9, 122.0, 120.7, 111.7, 111.2. IR (ATR): 3413 m, 3060 w, 1707 s, 1601 m, 1334 s, 1306 s, 1117 s. MS (EI, relative intensity, %) *m*/*z*: 290 (20), 289(M^+, 94), 143 (12), 142 (100), 115 (12), 104 (19), 102 (14). HRMS (DART) *m*/*z*: [M

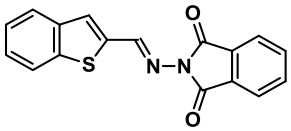
+ H]$^+$ Calcd for $C_{17}H_{12}N_3O_2$ 290.09240; Found 290.09342.

(*E*)-2-[(Benzofuran-2-ylmethylene)amino]isoindoline-1,3-dione (1k).



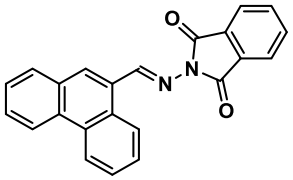
This compound was prepared on a 5 mmol scale. Pale yellow solid (1.1 g, 72%). R_f = 0.57 (hexane/EtOAc = 1/1). Mp = 217.8–218.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.55 (s, 1H), 7.97–7.93 (m, 2H), 7.83–7.78 (m, 2H), 7.66 (ddd, *J* = 7.8, 1.2, 0.8 Hz, 1H), 7.61 (ddd, *J* = 8.3, 1.7, 0.9 Hz, 1H), 7.44–7.40 (m, 1H), 7.31–7.26 (m, 1H), 7.29 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.0, 156.1, 150.4, 146.2, 134.9, 130.3, 127.8, 127.3, 124.0, 123.7, 122.2, 113.7, 112.3. IR (ATR): 3050 w, 1787 w, 1713 s, 1604 w, 1369 m, 1339 m, 1301 s, 1111 m, 1081 m. MS (EI, relative intensity, %) *m*/*z*: 290 (M$^+$, 42), 144 (11), 143 (100), 105 (14), 104 (26), 102 (11), 76 (27). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{17}H_{11}N_2O_3$ 291.07642; Found 291.07660.

(*E*)-2-[(Benzo[*b*]thiophen-2-ylmethylene)amino]isoindoline-1,3-dione (1l).



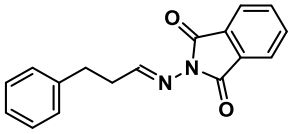
This compound was prepared on a 10 mmol scale. Yellow solid (2.4 g, 80%). R_f = 0.29 (hexane/EtOAc = 2/1). Mp = 282.1–282.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.73 (s, 1H), 7.96–7.92 (m, 2H), 7.88–7.78 (m, 4H), 7.73 (s, 1H), 7.36–7.45 (c, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.0, 152.3, 141.3, 139.4, 139.2, 134.9, 130.5, 130.4, 126.8, 124.9, 124.8, 124.0, 122.9. IR (ATR): 3051 w, 1787 w, 1714 s, 1577 w, 1519 w, 1367 s, 1296 s, 1230 m, 1111 s, 1081 m. MS (EI, relative intensity, %) *m*/*z*: 306 (M$^+$, 37), 159 (100), 104 (20), 102 (10), 76 (22). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{17}H_{11}N_2O_2S$ 307.05357; Found 307.05364.

(*E*)-2-[(phenanthren-9-ylmethylene)amino]isoindoline-1,3-dione (1m).



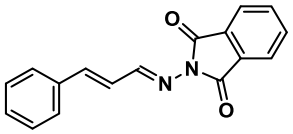
This compound was prepared on a 4.2 mmol scale. Pale yellow solid (1.24 g, 88%). R_f = 0.36 (hexane/EtOAc = 2/1). Mp = 238.3–238.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.13 (s, 1H), 8.81–8.76 (c, 2H), 8.71 (d, *J* = 8.2 Hz, 1H), 8.45 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.01–7.96 (m, 2H), 7.85–7.80 (m, 2H), 7.77–7.72 (c, 3H), 7.67–7.63 (m, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.4, 158.9, 134.8, 131.9, 131.0, 130.9, 130.8, 130.5, 130.1, 129.6, 128.6, 128.2, 127.7, 127.24, 127.17, 125.1, 124.0, 123.3, 122.8. IR (ATR): 3065 w, 1784 w, 1717 s, 1348 m, 1302 s, 1121 m. MS (EI, relative intensity, %) *m*/*z*: 350 (M$^+$, 31), 204 (26), 203 (100), 189 (14), 104 (11). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_{23}H_{15}N_2O_2$ 351.11280; Found 351.11304.

(*E*)-2-[(3-Phenylpropylidene)amino]isoindoline-1,3-dione (1n) [CAS RN: 121597-23-7].



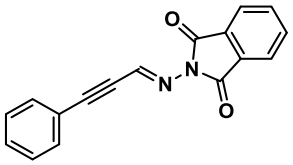
This compound was prepared on a 3 mmol scale. White solid (0.20 g, 24%). R_f = 0.31 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (t, *J* = 5.4 Hz, 1H), 7.93–7.87 (m, 2H), 7.79–7.74 (m, 5H), 7.34–7.21 (c, 5H), 3.01–2.96 (m, 2H), 2.88–2.82 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.2, 164.8, 140.5, 134.7, 130.3, 128.7, 128.6, 126.5, 123.9, 35.8, 32.5. IR (ATR): 3024 w, 2931 w, 1781 w, 1714 s, 1622 w, 1371 m, 1313 m, 1130 m. MS (EI, relative intensity, %) *m*/*z*: 278 (M^+, 3), 163 (23), 148 (10), 132 (36), 131 (18), 130 (100), 117 (79), 116 (76), 115 (20), 105 (29), 104 (74), 103 (10). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_2$ 279.11280; Found 279.11268.

2-{[(1*E*,2*E*)-3-Phenylallylidene]amino}isoindoline-1,3-dione (1o) [CAS RN: 32387-09-0].



This compound was prepared on a 3 mmol scale. Pale yellow solid (622 mg, 75%). R_f = 0.29 (hexane/EtOAc = 2/1). Mp = 191.2–191.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.33–9.24 (m, 1H), 7.94–7.90 (m, 2H), 7.81–7.76 (m, 2H), 7.54–7.51 (m, 2H), 7.41–7.36 (c, 3H), 7.19–7.10 (c, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.3, 159.7, 144.0, 135.6, 134.8, 130.4, 129.8, 129.1, 127.7, 125.8, 123.9. IR (ATR): 3030 w, 2985 w, 1717 s, 1624 w, 1341 w, 1299 s, 1110 m, 1079 m. MS (EI, relative intensity, %) *m*/*z*: 276 (M^+, 10), 275 (21), 199 (14), 130 (46), 129 (100), 115 (17), 105 (11), 104 (21), 76 (24). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2$ 277.09715; Found 277.09727.

(*E*)-2-[(3-Phenylprop-2-yn-1-ylidene)amino]isoindoline-1,3-dione (1p).



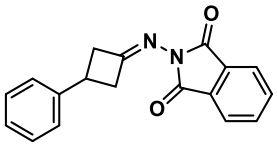
This compound was prepared on a 9.4 mmol scale. Pale yellow solid (818 mg, 32%). R_f = 0.34 (hexane/$CHCl_3$ = 1/3). Mp = 164.7–165.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.10 (s, 1H), 7.96–7.92 (m, 2H), 7.83–7.78 (m, 2H), 7.60–7.57 (m, 2H), 7.45–7.36 (c, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.9, 141.8, 135.1, 132.5, 130.2, 130.1, 128.7, 124.2, 121.4, 98.7, 84.7. IR (ATR): 3042 w, 2205 w, 1787 w, 1723 s, 1607 w, 1367 m, 1298 m, 1120 m. MS (EI, relative intensity, %) *m*/*z*: 274 (M^+, 21), 273 (47), 229 (11), 128 (19), 127 (100), 105 (62), 104 (37). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{11}N_2O_2$ 275.08150; Found 275.08260.

General Procedure for the Preparation of *N*-Phthaloyl Cyclobutanone Hydrazones 3

A two necked flask equipped with a Dean-Stark trap and magnetic stirring bar was dried with a heat gun and purged with N_2. After allowing the flask to cool to room temperature, *N*-aminophthalimide (1 equiv), cyclobutanone (1 equiv), CF_3CO_2H (30 mol%), and toluene (0.1 M) were added. The resulting mixture was subsequently refluxed overnight.

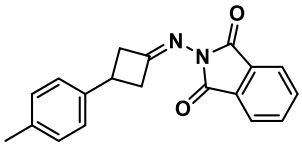
After the mixture was cooled to room temperature, the precipitated *N*-phthaloyl cyclobutanone hydrazone **3** was collected by filtration. The crude product was purified by recrystallization from toluene.

2-[(3-Phenylcyclobutylidene)amino]isoindoline-1,3-dione (3a).



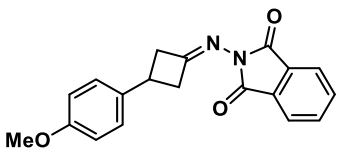
This compound was prepared on a 2.3 mmol scale. White solid (351 mg, 53%). R_f = 0.20 (hexane/EtOAc = 2/1). Mp = 137.8–138.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90–7.85 (m, 2H), 7.77–7.72 (m, 2H), 7.38–7.23 (c, 5H), 3.69–3.60 (m, 2H), 3.41–3.33 (m, 2H), 3.28–3.21 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 177.9, 164.1, 143.3, 134.4, 131.0, 128.8, 126.9, 126.6, 123.8, 45.0, 43.2, 31.8. IR (ATR): 3029 w, 2926 w, 1785 w, 1717 s, 1683 w, 1371 m, 1352 m, 1319 m. MS (EI, relative intensity, %) *m*/*z*: 290 (M^+, 88), 289 (21), 186 (23), 144 (57), 143 (59), 130 (44), 129 (32), 128 (46), 116 (34), 115 (22), 104 (100). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O_2$ 291.11280; Found 291.11370.

2-{[3-(*p*-Tolyl)cyclobutylidene]amino}isoindoline-1,3-dione (3b).



This compound was prepared on a 12 mmol scale. Colorless powder (1.35 g, 38%). R_f = 0.14 (hexane/EtOAc = 3/1). Mp = 160.1–160.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90–7.85 (m, 2H), 7.77–7.73 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.67–3.56 (m, 2H), 3.39–3.29 (m, 2H), 3.25–3.18 (m, 1H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 178.2, 164.1, 140.2, 136.5, 134.4, 131.0, 129.4, 126.5, 123.7, 45.0, 43.3, 31.4, 21.1. IR (ATR): 3025 w, 2974 w, 1785 w, 1716 s, 1682 w, 1370 m, 1351 m, 1320 m. MS (EI, relative intensity, %) *m*/*z*: 305 (22), 304 (M^+, 100), 158 (63), 157 (64), 143 (44), 130 (60), 128 (58), 118 (60), 117 (76), 115 (41), 104 (70). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2$ 305.12845; Found 305.12972.

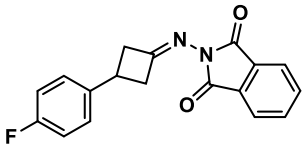
2-{[3-(4-Methoxyphenyl)cyclobutylidene]amino}isoindoline-1,3-dione (3c).



This compound was prepared on a 1 mmol scale. Colorless solid (101 mg, 31%). R_f = 0.34 (hexane/EtOAc = 2/1). Mp = 140.7–141.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90–7.85 (m, 2H), 7.77–7.72 (m, 2H), 7.25–7.22 (m, 2H), 6.91–6.87 (m, 2H), 3.81 (s, 3H), 3.66–3.54 (m, 2H), 3.38–3.27 (m, 2H), 3.24–3.15 (m, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 178.2, 164.1, 158.5, 135.4, 134.4, 131.0, 127.6, 123.7, 114.1, 55.4, 45.2, 43.4, 31.1. IR (ATR): 3035 w, 2963

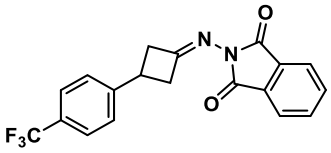
w, 1714 s, 1681 m, 1513 m, 1370 m, 1253 s, 1117 m. MS (EI, relative intensity, %) *m/z*: 321 (21), 320 (M^+, 74), 319 (32), 213 (12), 174 (100), 173 (86), 159 (69), 144 (35), 134 (82), 119 (52), 104 (48). HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_3$ 321.12337; Found 321.12397.

2-{[3-(4-fluorophenyl)cyclobutylidene]amino}isoindoline-1,3-dione (3d).



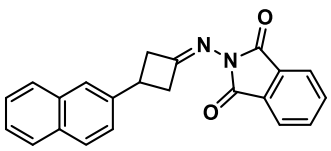
This compound was prepared on a 2 mmol scale. Colorless powder (213 mg, 35%). R_f = 0.25 (hexane/EtOAc = 2/1). Mp = 149.3–149.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90–7.85 (m, 2H), 7.77–7.73 (m, 2H), 7.29–7.25 (m, 2H), 7.07–7.01 (m, 2H), 3.69–3.58 (m, 2H), 3.42–3.27 (m, 2H), 3.25–3.17 (m, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 177.4, 164.1, 161.8 (d, *J* = 245.7 Hz), 139.0, 134.5, 131.0, 128.1 (d, *J* = 8.7 Hz), 123.8, 115.6 (d, *J* = 21.2 Hz), 45.2, 43.3, 31.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.9 (tt, *J* = 8.7, 5.8 Hz). IR (ATR): 3064 w, 2927 w, 1750 m, 1717 s, 1683 m, 1510 m. MS (EI, relative intensity, %) *m/z*: 309 (18), 308 (M^+, 85), 292 (29), 162 (39), 161 (49), 147 (26), 130 (41), 122 (33), 104 (100). HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}N_2O_2F$ 309.10338; Found 309.10327.

2-({3-[4-(trifluoromethyl)phenyl]cyclobutylidene}amino)isoindoline-1,3-dione (3e).



This compound was prepared on a 2 mmol scale. Pale yellow solid (352 mg, 49%). R_f = 0.34 (hexane/EtOAc = 2/1). Mp = 99.2–99.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91–7.85 (m, 2H), 7.77–7.72 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 3.75–3.65 (m, 2H), 3.47–3.32 (m, 2H), 3.30–3.22 (m, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 176.6, 164.1, 147.3, 134.5, 131.0, 129.3 (q, *J* = 32.4 Hz), 127.0, 125.8 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272.0 Hz), 123.8, 44.9, 43.1, 31.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.9. IR (ATR): 3071 w, 2976 w, 1725 s, 1685 m, 1321 s, 1158 m, 1111 m. MS (EI, relative intensity, %) *m/z*: 359 (20), 358 (M^+, 86), 212 (45), 211 (52), 186 (65), 130 (56), 128 (36), 104 (100). HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{14}N_2O_2F_3$ 359.10019; Found 359.10030.

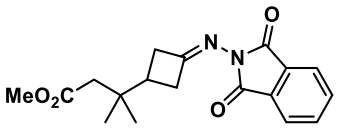
2-{[3-(naphthalen-2-yl)cyclobutylidene]amino}isoindoline-1,3-dione (3f).



This compound was prepared on a 1.5 mmol scale. Colorless powder (230 mg, 45%). R_f = 0.21 (hexane/EtOAc = 2/1). Mp = 149.1–149.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92–7.81 (c, 5H), 7.78–7.73 (c, 3H), 7.52–7.44 (c, 3H), 3.86–3.68 (c, 2H), 3.52–3.31 (c, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 177.8, 164.2, 140.6, 134.4, 133.5, 132.5, 131.1,

128.7, 127.8, 126.5, 125.0, 124.9, 123.8, 44.9, 43.1, 32.0 (three signals are obscured by overlap with other signals). IR (ATR): 3048 w, 1759 w, 1714 s, 1687 m, 1373 m, 1748 m, 1322 m, 1117 m. MS (EI, relative intensity, %) *m*/*z*: 340 (M^+, 11), 293 (19), 292 (100), 248 (25), 194 (10), 193 (13), 164 (10), 104 (78). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2O_2$ 341.12845; Found 341.12822.

Methyl 3-{3-[(1,3-Dioxoisoindolin-2-yl)imino]cyclobutyl}-3-methylbutanoate (3g).



This compound was prepared on a 1.1 mmol scale. White solid (173 mg, 48%). R_f = 0.20 (hexane/EtOAc = 2/1). Mp = 61.6–62.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87–7.85 (m, 2H), 7.75–7.73 (m, 2H), 3.66 (s, 3H), 3.13–2.97 (c, 2H), 2.91–2.78 (c, 2H), 2.47 (quint, *J* = 8.3 Hz, 1H), 2.22 (s, 2H), 1.06 (s, 3H), 1.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 178.1, 172.2, 164.1, 134.4, 131.0, 123.7, 51.6, 44.7, 38.4, 36.8, 36.3, 34.5, 23.40, 23.37. IR (ATR): 2959 w, 1783 w, 1716 s, 1684 m, 1467 w, 1352 m, 1319 m, 1114 m. MS (EI, relative intensity, %) *m*/*z*: 328 (M^+, 3), 255 (16), 214 (15), 213 (100), 186 (28), 130 (28), 122 (10), 108 (22), 107 (18), 104 (26), 103 (11). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{21}N_2O_4$ 329.14958; Found 329.15127.

3. General Procedure for the Pd-Catalyzed Transformation of *N*-Phthaloyl Hydrazones into Nitriles

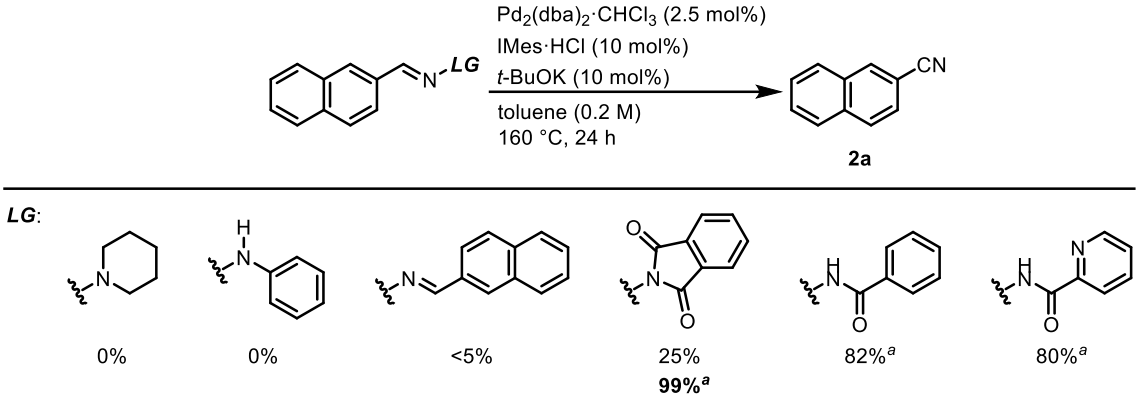
General Procedure for the Pd-Catalyzed Transformation of 1 into 2

A 25 mL of J. Young Schlenk flask was dried with a heat gun and purged with N_2. After allowing the flask to cool to room temperature, *t*-BuOK (3.4 mg, 0.03 mmol, 10 mol%), IMes·HCl (5.1 mg, 0.015 mmol, 5 mol%), (IMes)Pd(allyl)Cl (7.3 mg, 0.015 mmol, 5 mol%), and toluene (0.75 mL) were added. After the resulting mixture was then stirred at room temperature for 5 min, **1** (0.3 mmol) and toluene (0.75 mL) were successively added, and the Schlenk flask was sealed with a J. Young cap. After stirring the reaction mixture at 120 °C for 24 h, the resulting mixture was filtered through a pad of Celite and further eluted with EtOAc. The crude mixture was purified by flash column chromatography over silica gel.

General Procedure for the Pd-Catalyzed Transformation of 3 into 4

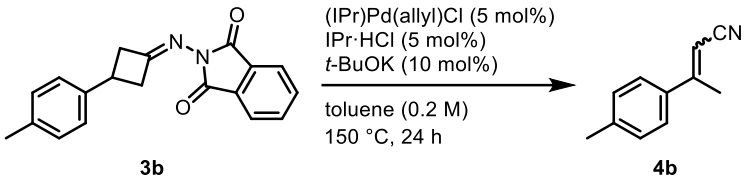
A 25 mL of J. Young Schlenk flask was dried with a heat gun and purged with N_2. After allowing the flask to cool to room temperature, *t*-BuOK (3.4 mg, 0.03 mmol, 10 mol%), IPr·HCl (6.4 mg, 0.015 mmol, 5 mol%), (IPr)Pd(allyl)Cl (8.6 mg, 0.015 mmol, 5 mol%), and toluene (0.75 mL) were added. After the resulting mixture was then stirred at room temperature for 5 min, **3** (0.3 mmol) and toluene (0.75 mL) were successively added, and the Schlenk flask was sealed with a J. Young cap. After stirring the reaction mixture at 150 °C for 24 h, the resulting mixture was filtered through a pad of Celite and further eluted with EtOAc. The crude mixture was purified by flash column chromatography over silica gel unless otherwise noted.

4. Optimization Studies



[a](IMes)Pd(allyl)Cl (5 mol%), IMes·HCl (5 mol%), *t*-BuOK (10 mol%) was used at 120 ºC.

Scheme S1 Screening of Leaving Groups for the Pd-Catalyzed Synthesis of Nitriles from *N*-Substituted Hydrazones. Yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethene as the internal standard.

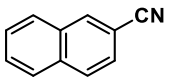


entry	deviation of reaction conditions	yield of **4b** [%]	*E*/*Z* ratio of **4b**
1	none	85	6.1:1
2	(IPr)Pd(allyl)Cl (5 mol%) and *t*-BuOK (5 mol%)	74	6.4:1
3	(IMes)Pd(allyl)Cl (5 mol%), IMes·HCl (5 mol%), and *t*-BuOK (10 mol%)	59	8.4:1
4	$Pd_2(dba)_3$·$CHCl_3$ (2.5 mol%) and IPr (10 mol%) in the absence of *t*-BuOK	22	4.5:1
5	K_2CO_3 instead of *t*-BuOK	81	6.4:1
6	1,4-dioxane instead of toluene	83	6.5:1
7	at 160 °C	84	6.6:1
8	at 140 °C	82	5.8:1
9	IPr (10 mol%) in the absence of Pd catalyst and base	0	—
10	*t*-BuOK (10 mol%) in the absence of Pd catalyst and NHC	0	—

Table S1 Screening of Reaction Conditions for the Pd-Catalyzed Synthesis of Nitriles from *N*-Substituted Cyclobutanone Hydrazones. Yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethene as the internal standard.

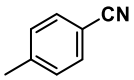
5. Characterization of Products

2-Naphthonitrile (2a) [CAS RN: 613-46-7].



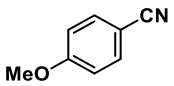
Colorless powder (44.7 mg, 97%). R_f = 0.46 (hexane/EtOAc = 4/1). Mp = 67.0–67.3 °C (lit.[1] mp = 68–70 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, 1H), 7.94–7.88 (c, 3H), 7.68–7.59 (c, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 134.8, 134.3, 132.4, 129.3, 129.2, 128.5, 128.2, 127.8, 126.5, 119.4, 109.5. MS (EI, relative intensity, %) *m*/*z*: 154 (12), 153 (M^+, 100), 126 (28). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_8N$ 154.06513; Found 154.06637.

4-Methylbenzonitrile (2b) [CAS RN: 104-85-8].



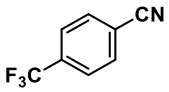
Colorless oil (30.2 mg, 86%, isolated by bulb-to-bulb distillation). R_f = 0.64 (hexane/EtOAc = 2/1). Bp = 90–91 °C (11 mmHg). Mp = 30.6–30.8 °C (lit.[1] mp = 26–28 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (dt, *J* = 8.2, 1.7 Hz, 2H), 7.28–7.25 (c, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.8, 132.2, 130.0, 119.3, 109.4, 22.0. MS (EI, relative intensity, %) *m*/*z*: 117 (M^+, 100), 116 (64), 90 (47), 89 (26). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_8H_8N 118.06513; Found 118.06457.

4-Methoxybenzonitrile (2c) [CAS RN: 874-90-8].



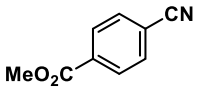
White solid (29.0 mg, 73%). R_f = 0.42 (hexane/EtOAc = 3/1). Mp = 58.9–59.2 °C (lit.[1] mp = 68–70 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (dt, *J* = 9.0, 2.4 Hz, 2H), 6.96 (dt, *J* = 9.4, 2.4 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.9, 134.1, 119.4, 114.8, 104.0, 55.7. MS (EI, relative intensity, %) *m*/*z*: 133 (M^+, 100), 118 (11), 104 (15), 103 (52), 90 (44), 76 (11). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_8H_8NO 134.06004; Found 134.06000.

4-(Trifluoromethyl)benzonitrile (2d) [CAS RN: 455-18-5].



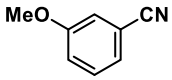
Colorless crystal (41.3 mg, 81%, isolated by bulb-to-bulb distillation). R_f = 0.70 (hexane/EtOAc = 2/1). Bp = 64–65 °C (23 mmHg). Mp = 37.7–38.4 °C (lit.[2] mp = 35 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 134.7 (q, *J* = 33.4 Hz), 132.8, 126.3 (q, *J* = 3.5 Hz), 123.2 (q, *J* = 272.9 Hz), 117.6, 116.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.0. MS (EI, relative intensity, %) *m*/*z*: 171 (M^+, 100), 170 (27), 152 (39), 121 (70). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{13}N_2O_2$ 172.03686; Found 172.03719.

Methyl 4-Cyanobenzoate (2e) [CAS RN: 1129-35-7].



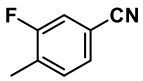
White solid (44.2 mg, 92%). R_f = 0.46 (hexane/EtOAc = 3/1). Mp = 67.9–68.2 °C (lit.[2] mp = 68–69 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (ddd, *J* = 8.2, 2.0, 1.4 Hz, 2H), 7.75 (ddd, *J* = 8.2, 2.0, 1.4 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.6, 134.1, 132.4, 130.2, 118.1, 116.5, 52.9. IR (ATR): 3003 w, 2956 w, 2851 w, 2231 w, 1712 s, 1437 m, 1361 m, 1278 s, 1108 m. MS (EI, relative intensity, %) *m*/*z*: 161 (M^+, 21), 160 (11), 130 (100), 102 (44). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_9H_8NO_2$ 162.05495; Found 162.05543.

3-Methoxybenzonitrile (2f) [CAS RN: 1527-89-5].



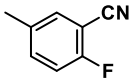
Pale yellow oil (31.7 mg, 79%). R_f = 0.51 (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.35 (m, 1H), 7.25 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.15–7.12 (c, 2H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.8, 130.5, 124.7, 119.5, 118.9, 117.0, 113.4, 55.7. MS (EI, relative intensity, %) *m*/*z*: 133 (M^+, 100), 104 (18), 103 (84), 102 (11), 90 (34), 76 (15). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_8H_8NO 134.06004; Found 134.06041.

3-Fluoro-4-methylbenzonitrile (2g) [CAS RN: 170572-49-3].



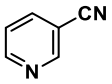
White solid (30.7 mg, 76%, isolated by bulb-to-bulb distillation). R_f = 0.67 (hexane/EtOAc = 3/1). Bp = 75–76 °C (0.5 mmHg). Mp = 51.5–52.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32–7.28 (c, 2H), 2.35 (d, *J* = 2.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.8 (d, *J* = 248.5 Hz), 132.6 (d, *J* = 4.8 Hz), 131.5 (d, *J* = 17.3 Hz), 128.1 (d, *J* = 3.9 Hz), 118.7 (d, *J* = 25.1 Hz), 118.0 (d, *J* = 2.9 Hz), 111.0 (d, *J* = 9.6 Hz), 15.1 (d, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.1. MS (EI, relative intensity, %) *m*/*z*: 135 (M^+, 100), 134 (86), 115 (12), 108 (57), 107 (38). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_8H_7NF 136.05570; Found 136.05557.

2-Fluoro-5-methylbenzonitrile (2h) [CAS RN: 64113-84-4].



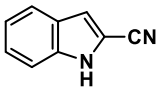
White solid (36.6 mg, 90%, isolated by bulb-to-bulb distillation). R_f = 0.68 (hexane/EtOAc = 3/1). Bp = 65–66 °C (1.5 mmHg). Mp = 49.9–50.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42–7.37 (c, 2H), 7.13–7.07 (m, 1H), 2.37 (d, *J* = 0.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.5 (d, *J* = 256.2 Hz), 135.8 (d, *J* = 8.7 Hz), 134.9 (d, *J* = 3.9 Hz), 133.5, 116.2 (d, *J* = 19.3 Hz), 114.3, 101.1 (d, *J* = 15.4 Hz), 20.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.9. MS (EI, relative intensity, %) *m*/*z*: 135 (M^+, 100), 134 (97), 115 (19), 108 (44), 107 (39). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_8H_7NF 136.05570; Found 136.05565.

Nicotinonitrile (2i) [CAS RN: 100-54-9].



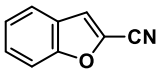
Colorless oil (25.6 mg, 82%). R_f = 0.06 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.91 (d, *J* = 1.4 Hz, 1H), 8.84 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.46 (ddd, *J* = 7.9, 5.0, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 153.1, 152.5, 139.4, 123.7, 116.6, 110.2. MS (EI, relative intensity, %) *m*/*z*: 104 (M^+, 100), 77 (63), 76 (19). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_6H_5N_2$ 105.04472; Found 105.04357.

1*H*-Indole-2-carbonitrile (2j) [CAS RN: 36193-65-3].



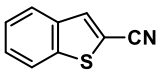
The reaction was performed in toluene (3 mL). Colorless solid (46.1 mg, 98%). R_f = 0.49 (hexane/EtOAc = 2/1) Mp = 101.8–102.0 °C (lit.[3] mp = 100–101 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (brs, 1H), 7.68 (ddd, *J* = 8.1, 1.7, 0.9 Hz, 1H), 7.45–7.37 (c, 2H), 7.25–7.20 (c, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 137.0, 126.4, 126.3, 122.2, 121.8, 114.6, 114.5, 111.9, 106.2. MS (EI, relative intensity, %) *m*/*z*: 143 (11), 142 (M^+, 100), 115 (42), 114 (15). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_9H_7N_2$ 143.06037; Found 143.06011.

Benzofuran-2-carbonitrile (2k) [CAS RN: 41717-32-2].



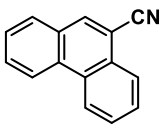
Pale yellow solid (37.2 mg, 87%). R_f = 0.54 (hexane/EtOAc = 3/1). Mp = 34.1–34.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.58–7.49 (c, 2H), 7.47 (d, *J* = 0.9 Hz, 1H), 7.37 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.8, 128.6, 127.4, 125.6, 124.7, 122.7, 118.6, 112.2, 112.0. MS (EI, relative intensity, %) *m*/*z*: 144 (M^+, 10), 143 (100), 115 (52), 114 (19), 88 (15). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_9H_6NO 144.04439; Found 144.04448.

Benzo[*b*]thiophene-2-carbonitrile (2l) [CAS RN: 55219-11-9].



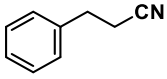
White solid (44.9 mg, 94%). R_f = 0.61 (hexane/EtOAc = 3/1). Mp = 27.2–27.9 °C (lit.[1] mp = 24–28 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92–7.86 (c, 3H), 7.57–7.46 (c, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.4, 137.5, 135.1, 128.0, 125.8, 125.4, 122.5, 114.6, 109.7. MS (EI, relative intensity, %) *m*/*z*: 159 (M^+, 100), 115 (10). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for C_9H_6NS 160.02155; Found 160.02205.

Phenanthrene-9-carbonitrile (2m) [CAS RN: 2510-55-6].



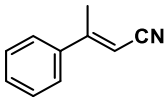
Colorless solid (57.5 mg, 94%). R_f = 0.66 (hexane/EtOAc = 2/1). Mp = 111.0–111.5 °C (lit.[4] mp = 108–109 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72–8.65 (c, 2H), 8.32–8.27 (m, 1H), 8.24 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.83–7.72 (c, 3H), 7.68 (td, *J* = 7.5, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 135.8, 131.9, 130.1, 130.0, 129.9, 129.6, 129.0, 128.3, 128.2, 127.7, 126.2, 123.2, 123.0, 118.1, 110.0. MS (EI, relative intensity, %) *m*/*z*: 204 (17), 203 (M^+, 100), 202 (11), 201 (10). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{10}N$ 204.08078; Found 204.08069.

3-Phenylpropanenitrile (2n) [CAS RN: 645-59-0].



Pale yellow oil (35.5 mg, 86%). R_f = 0.43 (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.31 (m, 2H), 7.30–7.21 (m, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.2, 129.0, 128.4, 127.4, 119.3, 31.7, 19.5. MS (EI, relative intensity, %) *m*/*z*: 131 (M^+, 29), 91 (100). HRMS (DART) *m*/*z*: [M + H]$^+$ Calcd for $C_9H_{10}N$ 132.08078; Found 132.08086.

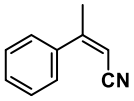
(*E*)-3-Phenylbut-2-enenitrile ((*E*)-4a) [CAS RN: 14368-40-2].



Colorless oil (31.9 mg, 74%, isolated by preparative HPLC). R_f = 0.67 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.44 (m, 2H), 7.43–7.38 (c, 3H), 5.63 (dd, *J* = 2.0, 0.9 Hz, 1H), 2.48 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.9, 138.3, 130.4, 129.0, 126.0, 117.8, 95.6, 20.4. MS (EI, relative intensity, %) *m*/*z*: 144 (12), 143 (M^+, 100), 142 (14), 128 (12), 117 (10), 116 (52), 115 (50), 103 (19), 78 (27). HRMS (D

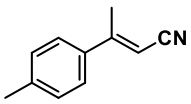
ART) *m*/*z*: $[M + H]^+$ Calcd for $C_{10}H_{10}N$ 144.08078; Found 144.08053.

(*Z*)-3-Phenylbut-2-enenitrile ((*Z*)-4a) [CAS RN: 14799-79-2].



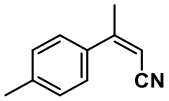
Colorless oil (5.0 mg, 12%, isolated by preparative HPLC). R_f = 0.60 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57–7.52 (m, 2H), 7.46–7.40 (c, 3H), 5.41 (dd, *J* = 2.9, 1.4 Hz, 1H), 2.29 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.2, 138.0, 130.0, 128.8, 127.2, 117.8, 95.6, 24.8. MS (EI, relative intensity, %) *m*/*z*: 144 (11), 143 (M^+, 100), 142 (14), 128 (12), 116 (52), 115 (50), 103 (17), 78 (23), 77 (14). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{10}H_{10}N$ 144.08078; Found 14408141.

(*E*)-3-(4-tolyl)but-2-enenitrile ((*E*)-4b) [CAS RN: 130240-32-3].



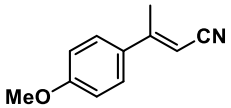
Colorless solid (32.0 mg, 68%, isolated by preparative HPLC). R_f = 0.63 (hexane/EtOAc = 3/1). Mp = 40.5–41.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (dt, *J* = 8.4, 1.9 Hz, 2H), 7.21 (dd, *J* = 8.6, 0.6 Hz, 2H), 5.60 (d, *J* = 0.9 Hz, 1H), 2.45 (d, *J* = 0.9 Hz, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.6, 140.8, 135.4, 129.6, 125.9, 118.0, 94.6, 21.4, 20.2. MS (EI, relative intensity, %) *m*/*z*: 158 (12), 157 (M^+, 100), 156 (56), 142 (31), 130 (14), 129 (28), 128 (11), 116 (10), 115 (38), 91 (19). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_{12}N$ 158.09643; Found 158.09701.

(*Z*)-3-(4-tolyl)but-2-enenitrile ((*Z*)-4b) [CAS RN: 1613466-43-5].



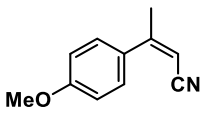
Colorless oil (7.3 mg, 15%, isolated by preparative HPLC). R_f = 0.57 (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (dt, *J* = 8.4, 1.9 Hz, 2H), 7.23 (dd, *J* = 8.5, 0.7 Hz, 2H), 5.35 (dd, *J* = 3.0, 1.4 Hz, 1H), 2.38 (s, 3H), 2.27 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.9, 140.3, 135.1, 129.4, 127.2, 118.0, 94.8, 24.7, 21.5. MS (EI, relative intensity, %) *m*/*z*: 158 (12), 157 (M^+, 100), 156 (56), 142 (32), 130 (15), 129 (32), 128 (13), 115 (44), 91 (22). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_{12}N$ 158.09643; Found 158.09725.

(*E*)-3-(4-Methoxyphenyl)but-2-enenitrile ((*E*)-4c) [CAS RN: 120695-60-5].



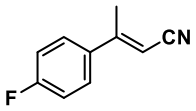
Colorless solid (34.6 mg, 67%, isolated by preparative HPLC). R_f = 0.42 (hexane/EtOAc = 3/1). Mp = 63.1–63.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46–7.42 (m, 2H), 6.93–6.90 (m, 2H), 5.55 (d, *J* = 0.9 Hz, 1H), 3.84 (s, 3H), 2.44 (d, *J* = 0.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.4, 158.9, 130.5, 127.5, 118.3, 114.2, 93.3, 55.6, 20.2. MS (EI, relative intensity, %) *m*/*z*: 174 (12), 173 (M^+, 100), 172 (15), 158 (33), 143 (16), 130 (20), 103 (36), 77 (19). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_{12}NO$ 174.09134; Found 174.09135.

(*Z*)-3-(4-Methoxyphenyl)but-2-enenitrile ((*Z*)-4c) [CAS RN: 120695-61-6].



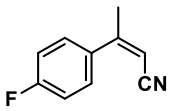
Colorless oil (5.8 mg, 11%, isolated by preparative HPLC). R_f = 0.40 (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59–7.54 (m, 2H), 6.96–6.92 (m, 2H), 5.30 (dd, *J* = 2.8, 1.5 Hz, 1H), 3.84 (s, 3H), 2.26 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.0, 160.1, 130.2, 128.9, 118.3, 114.0, 93.7, 55.5, 24.7. MS (EI, relative intensity, %) *m*/*z*: 174 (12), 173 (M^+, 100), 172 (14), 158 (30), 143 (14), 130 (16), 103 (30), 77 (13). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_{12}NO$ 174.09134; Found 174.09166.

(*E*)-3-(4-Fluorophenyl)but-2-enenitrile ((*E*)-4d) [CAS RN: 1613466-41-3].



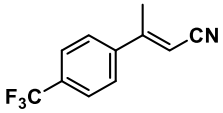
Pale yellow powder (31.0 mg, 64%). R_f = 0.60 (hexane/EtOAc = 3/1). Mp = 51.0–51.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.43 (m, 2H), 7.13–7.06 (m, 2H), 5.58–5.57 (m, 1H), 2.46 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.0 (d, *J* = 251.4 Hz), 158.6, 134.5, 128.0 (d, *J* = 8.7 Hz), 117.6, 116.0 (d, *J* = 22.2 Hz), 95.6, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.2. MS (EI, relative intensity, %) *m*/*z*: 162 (11), 161 (M^+, 100), 160 (12), 146 (14), 134 (38), 133 (38), 126 (14), 121 (13), 101 (10), 96 (29). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{10}H_9NF$ 162.07135; Found 162.07240.

(*Z*)-3-(4-Fluorophenyl)but-2-enenitrile ((*Z*)-4d) [CAS RN: 144477-79-2].



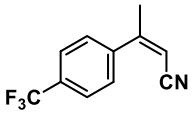
Pale yellow oil (6.8 mg, 14%). R_f = 0.48 (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58–7.52 (c, 2H), 7.15–7.09 (c, 2H), 5.40 (q, *J* = 1.5 Hz, 1H), 2.27 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 163.6 (d, *J* = 250.5 Hz), 159.8, 134.0, 129.3 (d, *J* = 8.7 Hz), 117.6, 115.9 (d, *J* = 21.2 Hz), 95.7, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.9. MS (EI, relative intensity, %) *m*/*z*: 162 (11), 161 (M^+, 100), 160 (11), 146 (14), 134 (33), 133 (35), 126 (12), 121 (13), 96 (26). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{10}H_9NF$ 162.07135; Found 162.07169.

(*E*)-3-[4-(Trifluoromethyl)phenyl]but-2-enenitrile ((*E*)-4e) [CAS RN: 1358804-70-2].



Pale yellow crystal (50.0 mg, 79%). R_f = 0.61 (hexane/EtOAc = 2/1). Mp = 40.3–41.0 °C.^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.57(d, *J* = 8.2 Hz, 2H), 5.67 (d, *J* = 1.2 Hz, 1H), 2.50 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.5, 141.8, 132.1 (q, *J* = 32.8 Hz), 126.4, 126.0 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 272.3 Hz), 117.0, 97.9, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.4. MS (EI, relative intensity, %) *m*/*z*: 212 (12), 211 (M^+, 100), 192 (11), 191 (25), 190 (15), 171 (14), 151 (11), 140 (12), 115 (26). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_9NF_3$ 212.06816; Found 212.06800.

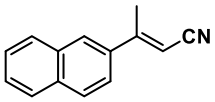
(*Z*)-3-(4-Trifluoromethylphenyl)but-2-enenitrile ((*Z*)-4e) [CAS RN: 2125749-93-9].



Pale yellow oil (5.0 mg, 8%). R_f = 0.48 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 5.50 (d, *J* = 1.5 Hz, 1H), 2.31 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.8, 141.5, 131.8 (q, *J* = 32.8 Hz), 127.6, 125.9 (q, *J* = 3.5 Hz), 123.8 (q, *J* = 272.3 Hz), 117.0, 97.5, 24.7. ^{19}F NMR

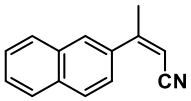
(376 MHz, $CDCl_3$): δ −63.4. MS (EI, relative intensity, %) *m*/*z*: 212 (12), 211 (M^+, 100), 192 (13), 191 (25), 190 (16), 151 (14), 141 (10), 140 (14), 115 (35). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{11}H_9NF_3$ 212.06816; Found 212.06905.

(*E*)-3-(Naphthalen-2-yl)but-2-enenitrile ((*E*)-4f) [CAS RN: 1622876-07-6].



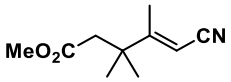
Pale yellow solid (41.9 mg, 72%, isolated by preparative HPLC). R_f = 0.66 (hexane/EtOAc = 2/1). Mp = 57.3–58.0 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 1.6 Hz, 1H), 7.90–7.83 (c, 3H), 7.57–7.51 (c, 3H), 5.77 (t, *J* = 0.9 Hz, 1H), 2.59 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.5, 135.4, 134.1, 133.0, 128.8, 128.7, 127.8, 127.5, 127.0, 126.2, 122.9, 117.9, 95.9, 20.3. MS (EI, relative intensity, %) *m*/*z*: 194 (15), 193 (M^+, 100), 192 (20), 165 (17), 128 (23). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{12}N$ 194.09643; Found 194.09582.

(*Z*)-3-(Naphthalen-2-yl)but-2-enenitrile ((*Z*)-4f) [CAS RN: 1622876-33-8].



Colorless oil (6.7 mg, 12%, isolated by preparative HPLC). R_f = 0.57 (hexane/EtOAc = 2/1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 1.4 Hz, 1H), 7.91–7.84 (c, 3H), 7.65 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.56–7.50 (c, 2H), 5.48 (dd, *J* = 3.0, 1.6 Hz, 1H), 2.38 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.0, 135.4, 133.9, 133.0, 128.7, 128.6, 127.8, 127.3, 127.1, 126.8, 124.4, 117.8, 95.8, 24.9. MS (EI, relative intensity, %) *m*/*z*: 194 (16), 193 (M^+, 100), 192 (19), 165 (17), 128 (22). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{12}N$ 194.09643; Found 194.09575.

Methyl (*E*)-5-cyano-3,3,4-trimethylpent-4-enoate ((*E*)-4g).



Colorless oil (27.3 mg, 50%). R_f = 0.32 (hexane/EtOAc = 3/1). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.20 (s, 1H), 3.64 (s, 3H), 2.46 (s, 2H), 2.11 (s, 3H), 1.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.1, 169.9, 117.6, 95.2, 51.7, 44.9, 39.9, 26.9, 18.1. MS (EI, relative intensity, %) *m*/*z*: 181 (M^+, 10), 150 (26), 149 (60), 139 (15), 134 (13), 122 (21), 121 (42), 108 (100), 107 (56), 106 (100), 95 (11), 94 (11), 93 (14), 81 (41), 80 (22), 79 (37), 74 (15) 73 (10). HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{10}H_{16}NO_2$ 182.11756; Found 182.11748.

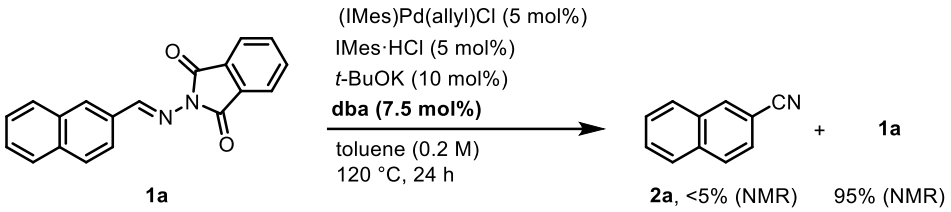
6. Large-Scale Preparation of 2a

A 50 mL of two-necked flask was dried with a heat gun and purged with N_2. After allowing the flask to cool to room temperature, **1a** (1.0 g, 3.3 mmol), *t*-BuOK (37.5 mg, 0.33 mmol, 10 mol%), IMes·HCl (57.0 mg, 0.17 mmol, 5 mol%), (IMes)Pd(allyl)Cl (81.2 mg, 0.17 mmol, 5 mol%), and toluene (17 mL) were added. After the reaction mixture

was then stirred at 120 °C for 24 h, the resulting mixture was filtered through a pad of Celite and the filtrate further eluted with EtOAc. The crude mixture was concentrated under reduced pressure and purified by flash column chromatography over silica gel to afford **2a** as a white solid (504.7 mg, 99% yield).

7. Mechanistic Studies

Control Experiment.



Scheme S2 A control experiment in the presence of dba. Yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethene as the internal standard.

KIE experiment.

Six oven-dried 25 mL of J. Young Schlenk flasks were allowed to cool to room temperature and filled with nitrogen. To each of these Schlenk flasks, *t*-BuOK (1.1 mg, 0.01 mmol, 10 mol%), IMes·HCl (1.7 mg, 0.005 mmol, 5 mol%), (IMes)Pd(allyl)Cl (2.4 mg, 0.005 mmol, 5 mol%), and toluene (0.25 mL) were added. The mixtures were then stirred at room temperature for 5 min, after which, **1a** (30.0 mg, 0.1 mmol) and toluene (0.25 mL) were added to each Schlenk flask. The Schlenk flasks were sealed with a J. Young cap and the reaction mixtures were stirred at 120 °C. At set intervals, the reaction mixtures were quickly placed in an ice bath. The resulting mixture was filtered through a pad of Celite and the filtrate further eluted with EtOAc. The concentrated crude mixture was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The same monitoring experiments were executed three times. The reaction of **1a**-[D_1] (30.1 mg, 0.1 mmol) was also monitored following the same procedure.

1a			**2a**		
time [h]	recovery [%]	*c* [mol/L]	time [h]	yield [%]	*c* [mol/L]
0	100	0.2	0	0	0
0.25	86.8	0.174	0.25	9.3	0.019
0.50	73.9	0.148	0.50	24.3	0.049
0.75	59.7	0.119	0.75	39.1	0.078
1	49.8	0.100	1	48.9	0.098
2	27.0	0.054	2	71.2	0.142
3	12.8	0.026	3	86.7	0.173

Table S2 Tabular data for the reaction with **1**.

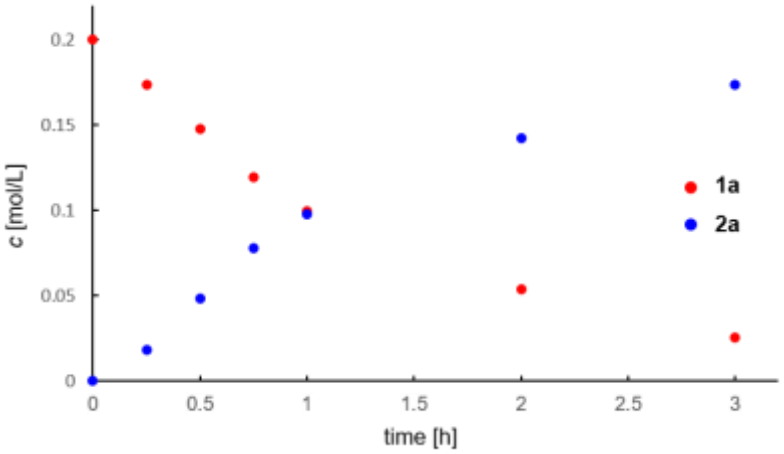


Figure S1 Reaction profiles for the reaction with **1**.

1a-[D1]			**2a**		
time [h]	recovery [%]	*c* [mol/L]	time [h]	yield [%]	*c* [mol/L]
0	100	0.2	0	0	0
0.25	95.5	0.191	0.25	3.0	0.006
0.50	89.6	0.180	0.50	7.1	0.014
0.75	80.2	0.160	0.75	16.5	0.033
1	70.9	0.142	1	24.2	0.048
2	44.7	0.0892	2	53.3	0.107
3	34.0	0.0682	3	58.1	0.116

Table S3 Tabular data for the reaction with **1a**-[D1].

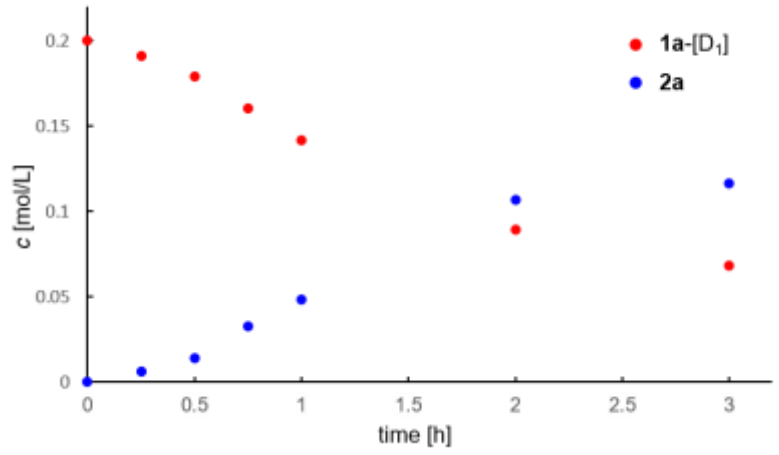


Figure S2 Reaction profiles for the reaction with **1a**-[D1].

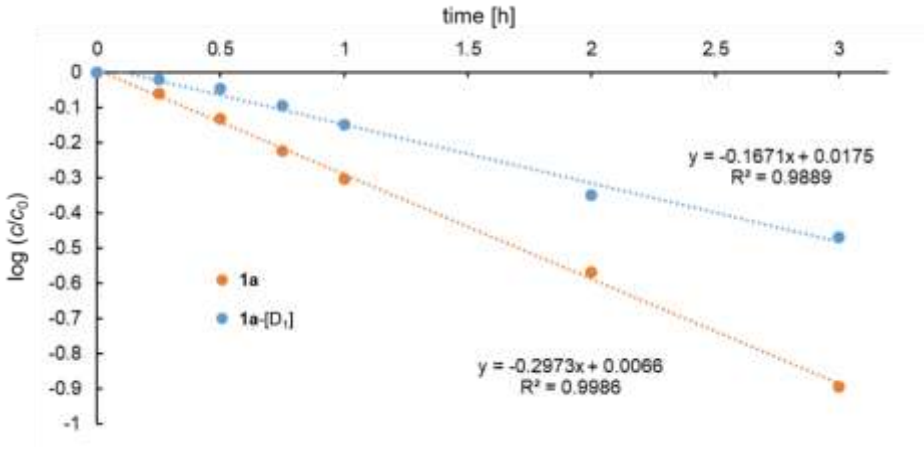


Figure S3 H/D kinetic isotope effect for the reaction of **1a** and **1a**-[D_1].

8. References

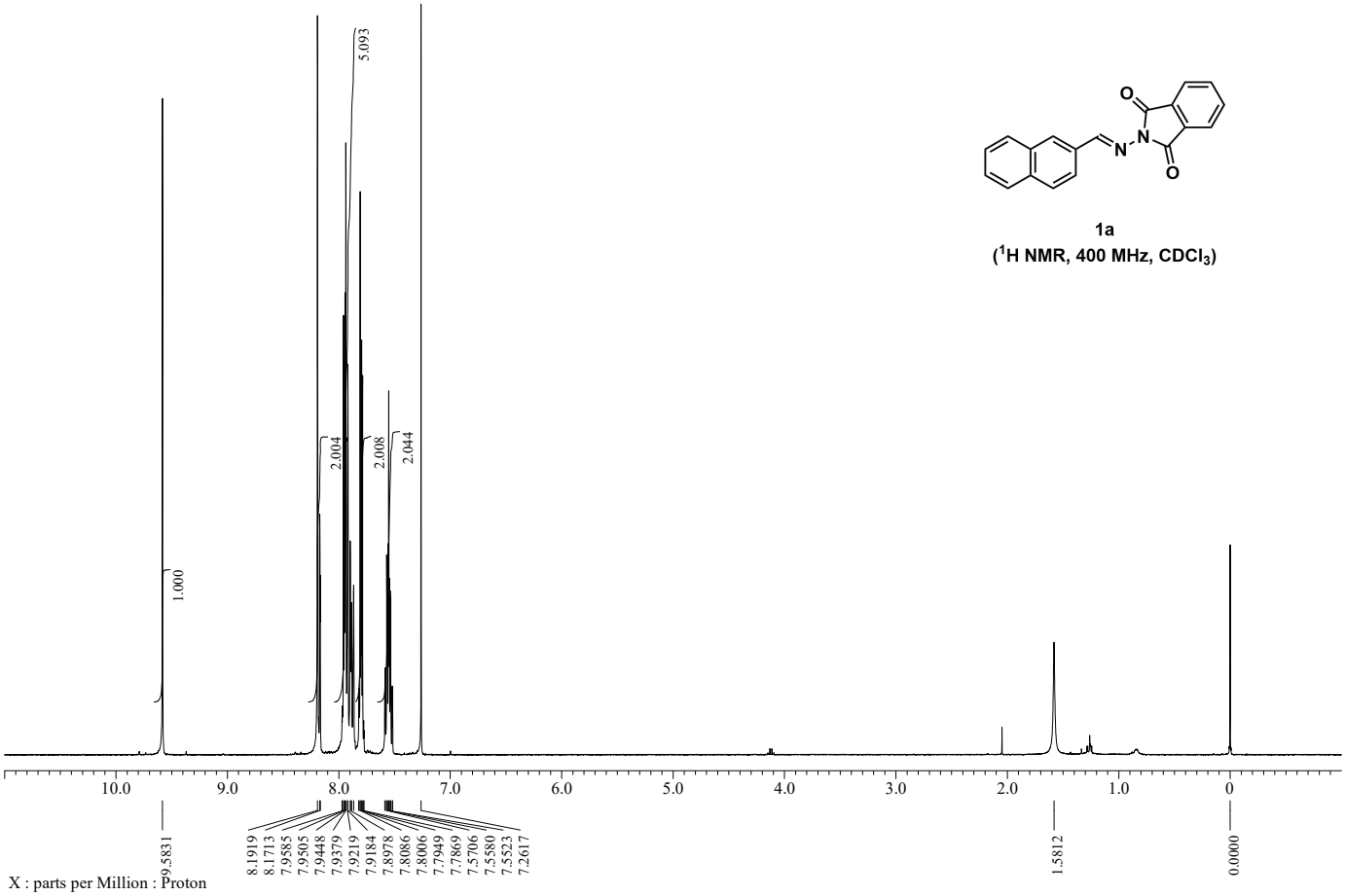
1. S. Ushijima and H. Togo, *Synlett*, **2010**, 1562–1566.

2. M. Hatsuda and M. Seki, *Tetrahedron*, **2005**, *61*, 9908–9917.

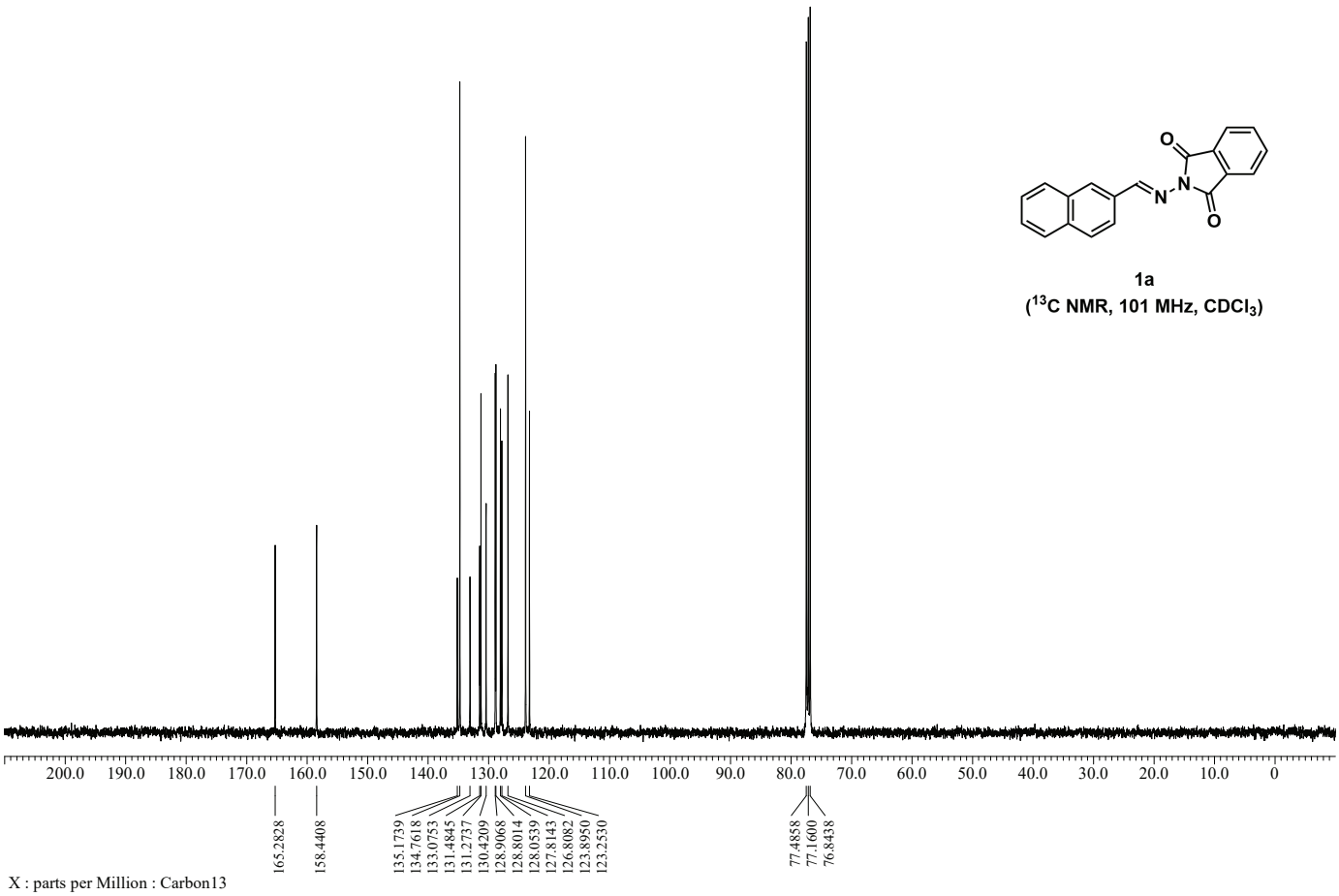
3. R. A. Abramovitch and B. W. Cue, *J. Org. Chem.*, **1980**, *45*, 5316–5319.

4. T. Itou, Y. Yoshimi, T. Morita, Y. Tokunaga and M. Hatanaka, *Tetrahedron*, **2009**, *65*, 263–269.

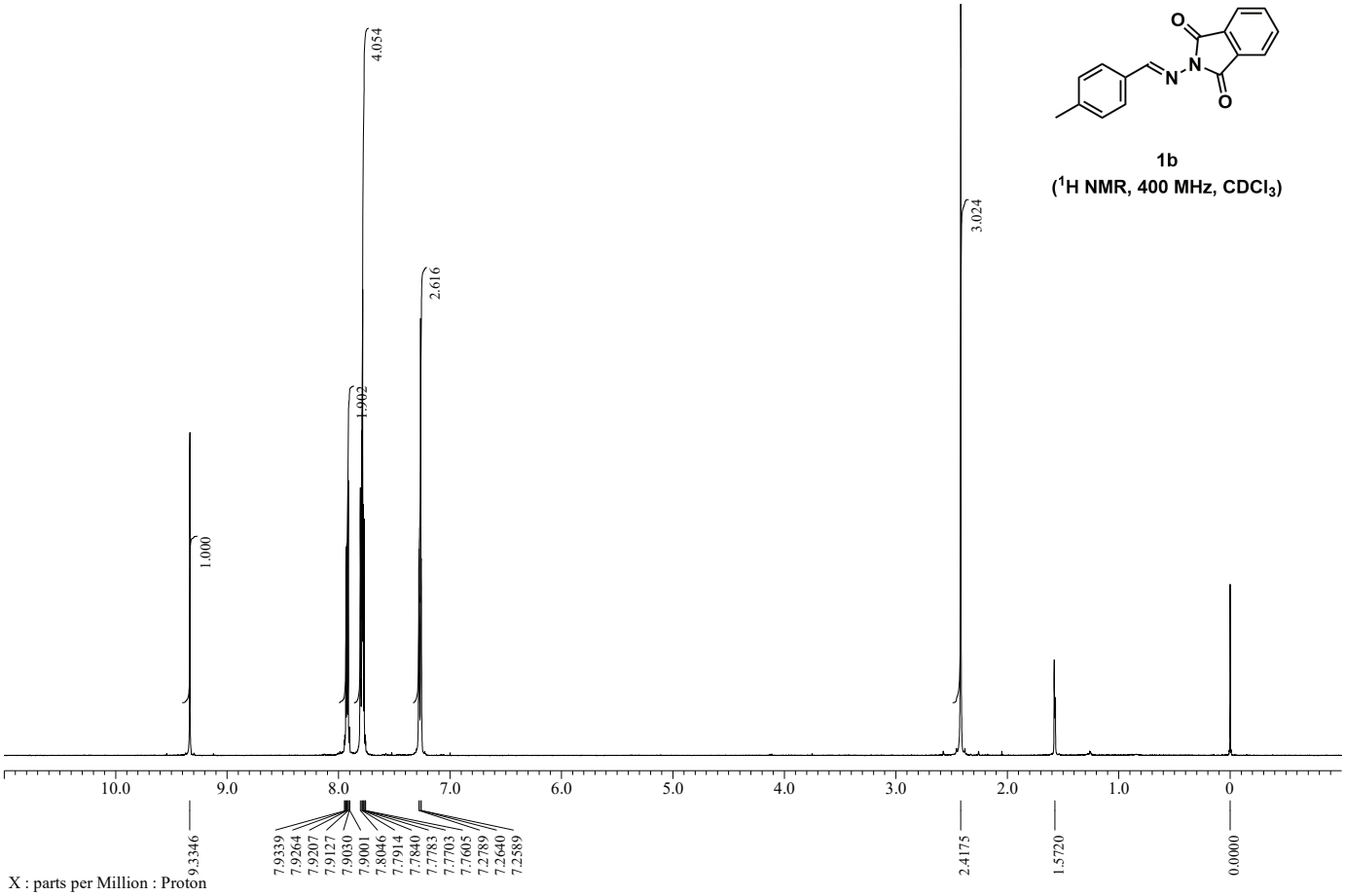
9. Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra



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

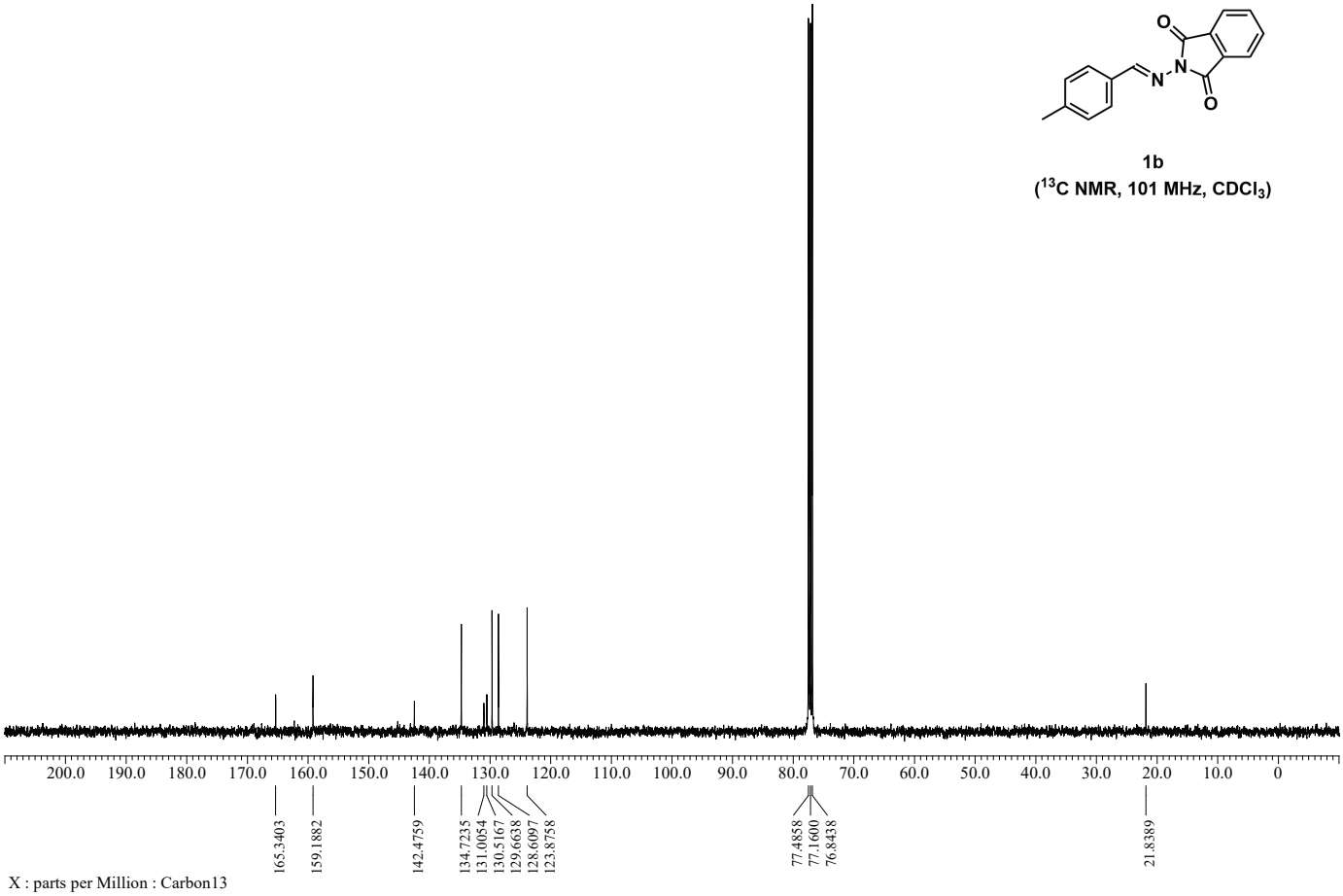


1a
(^{13}C NMR, 101 MHz, $CDCl_3$)



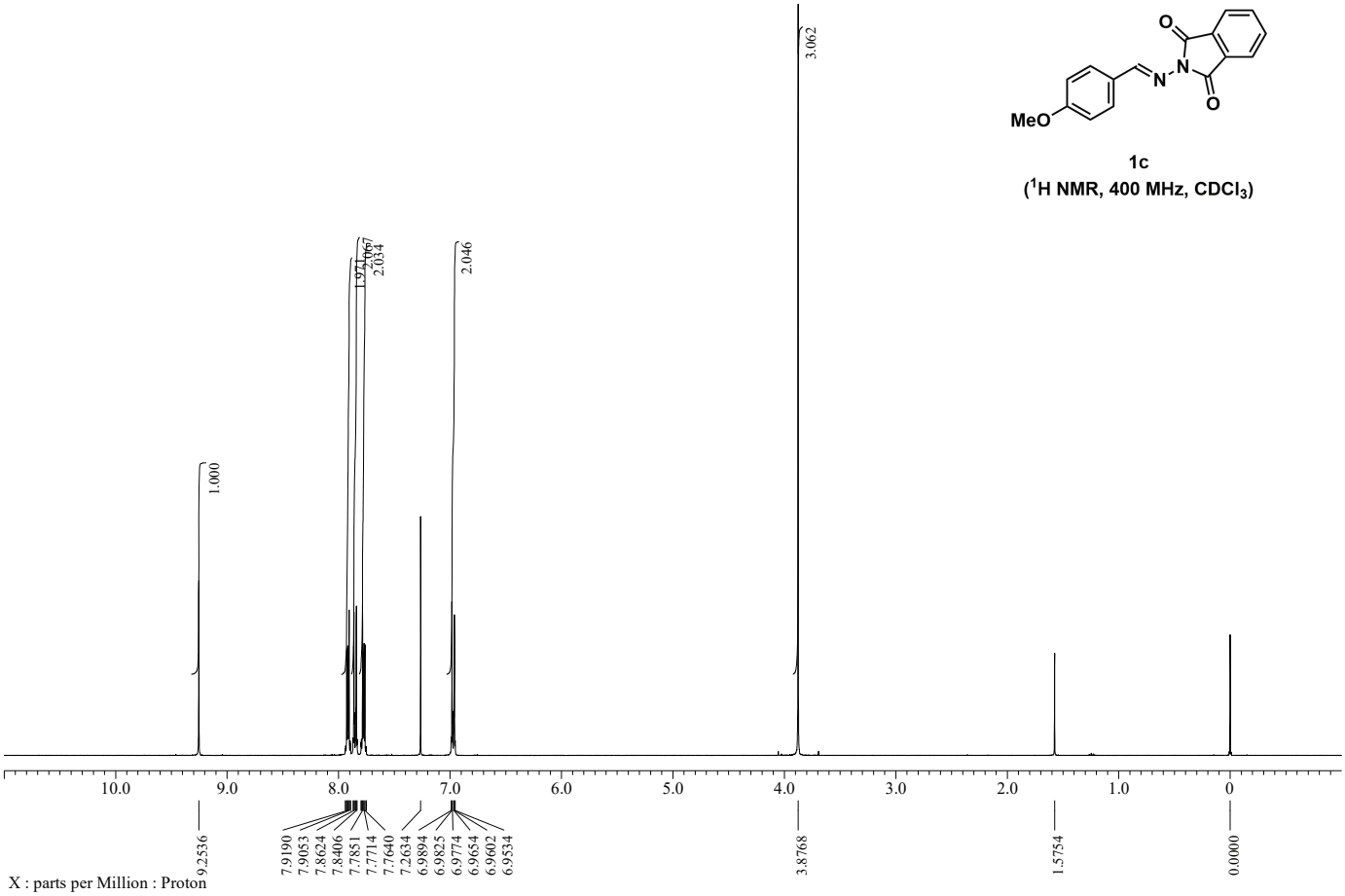
1b

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

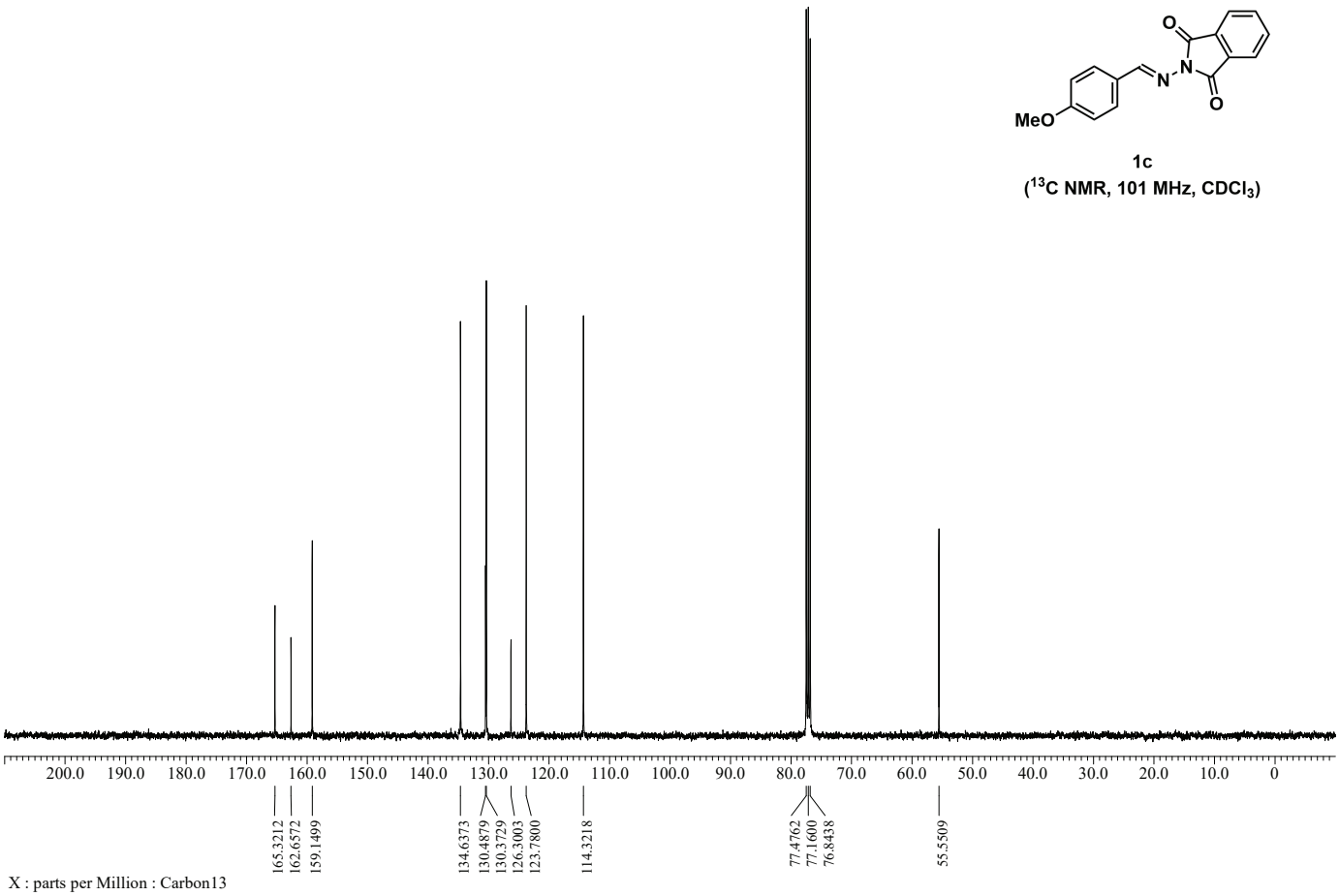


1b

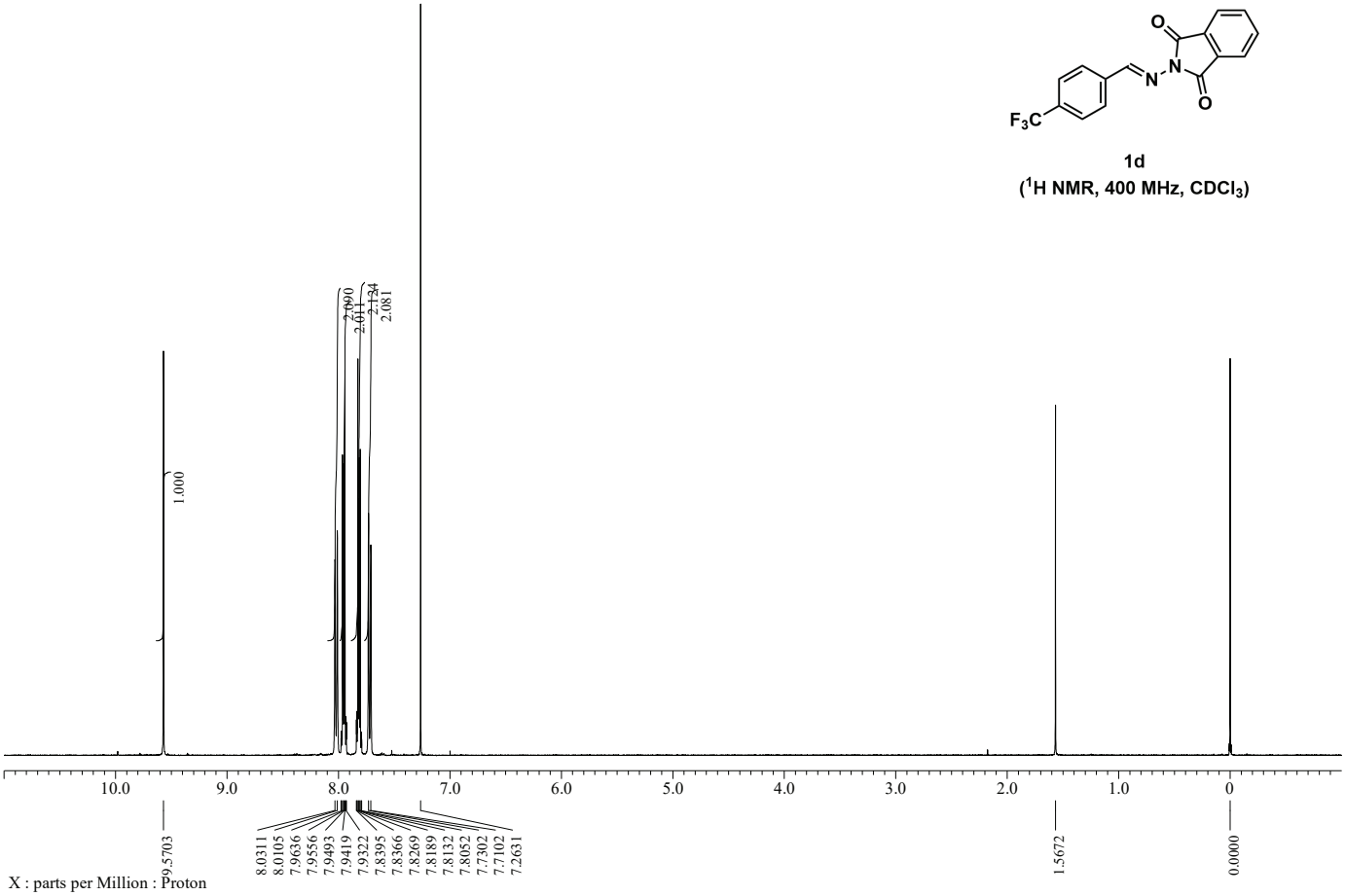
(^{13}C NMR, 101 MHz, $CDCl_3$)



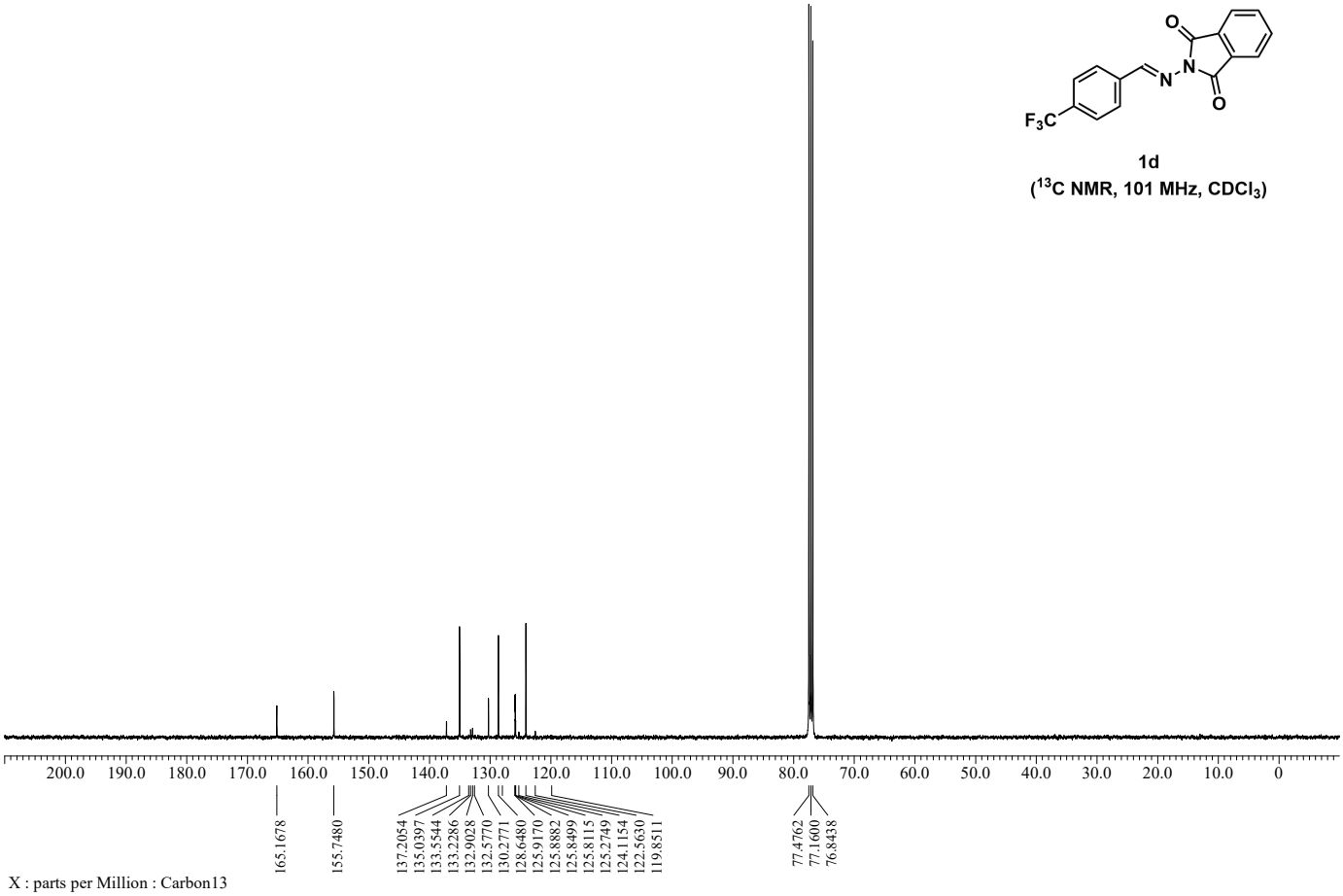
1c
(^{1}H NMR, 400 MHz, $CDCl_3$)



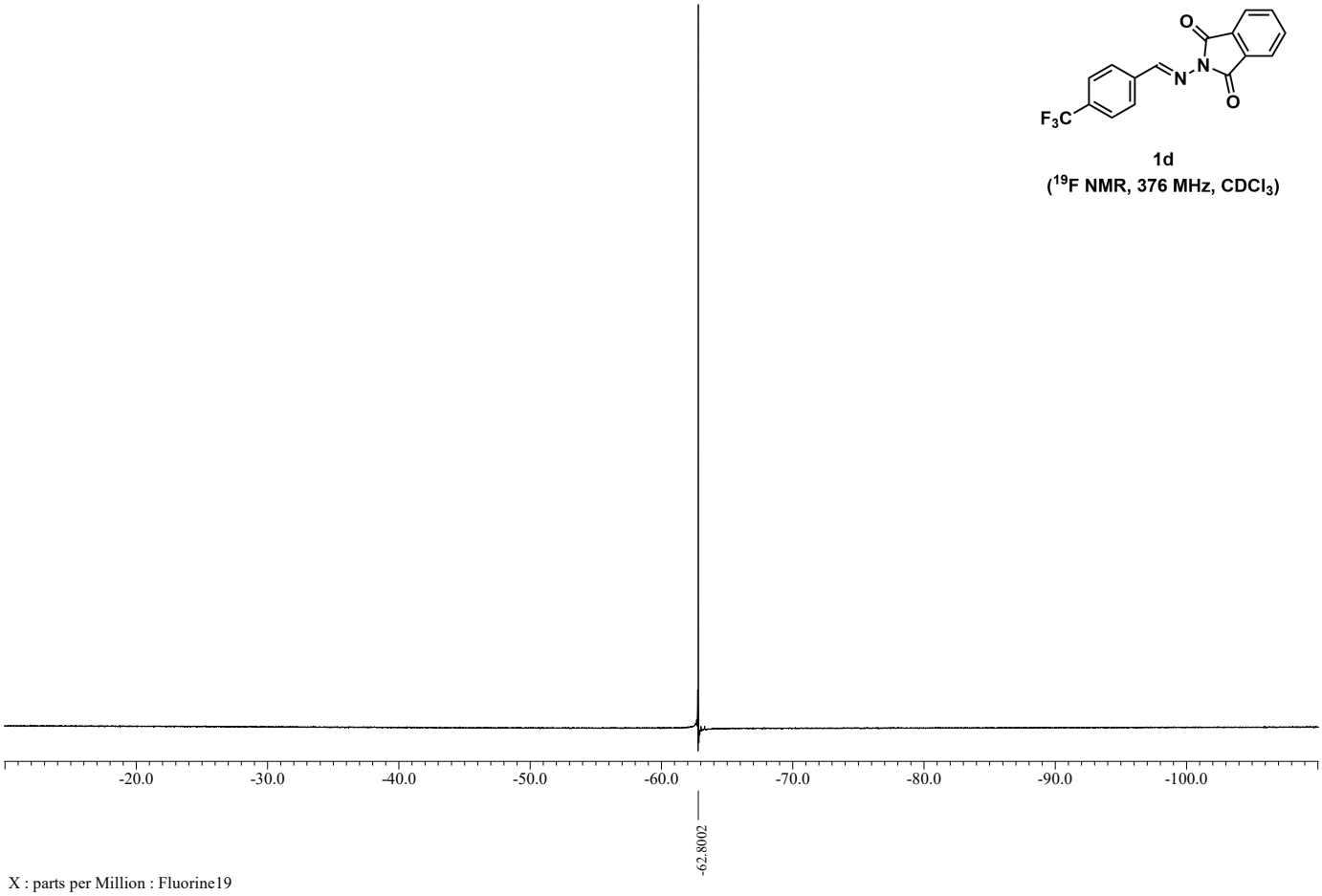
1c
(^{13}C NMR, 101 MHz, $CDCl_3$)



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

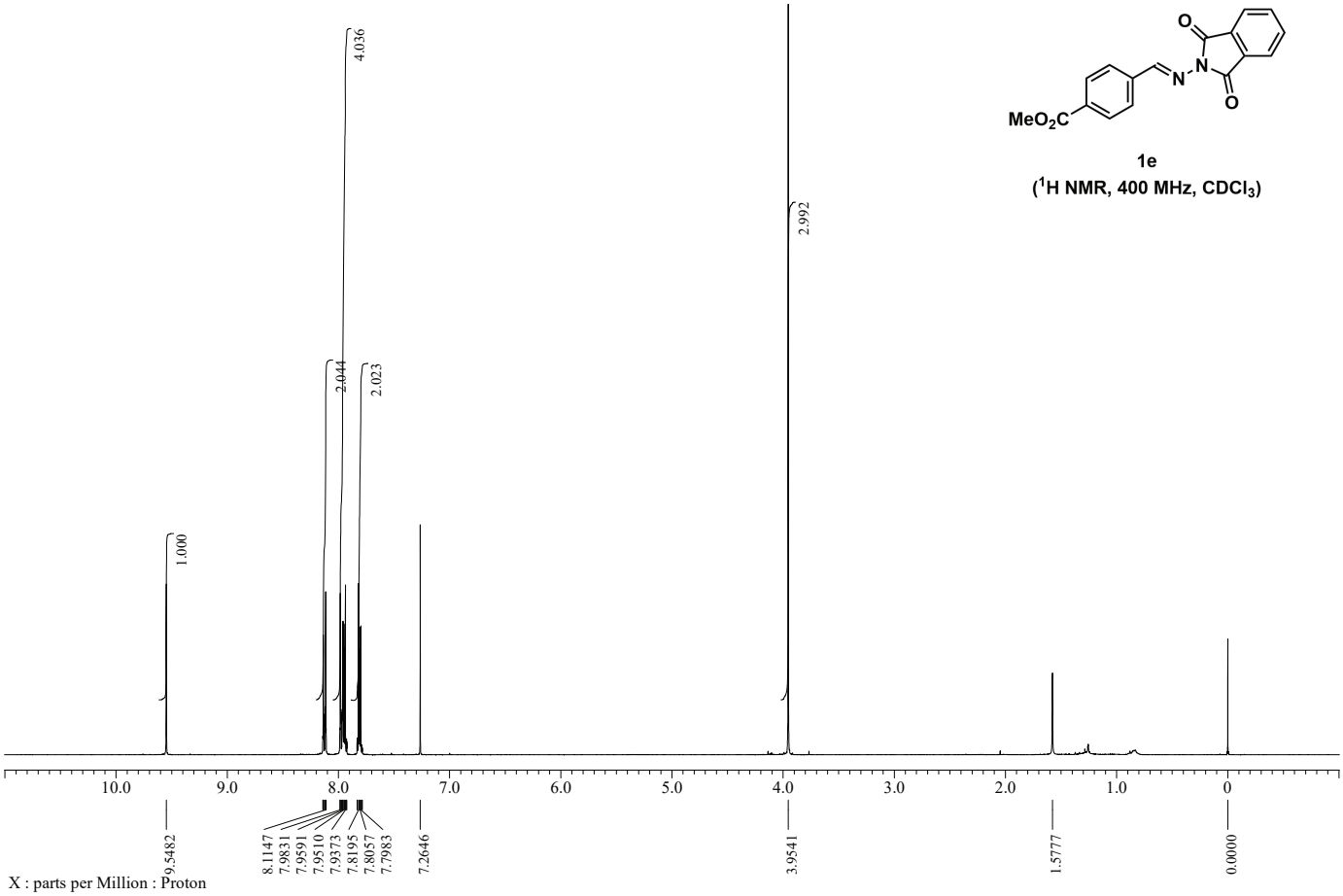


1d
(^{13}C NMR, 101 MHz, $CDCl_3$)



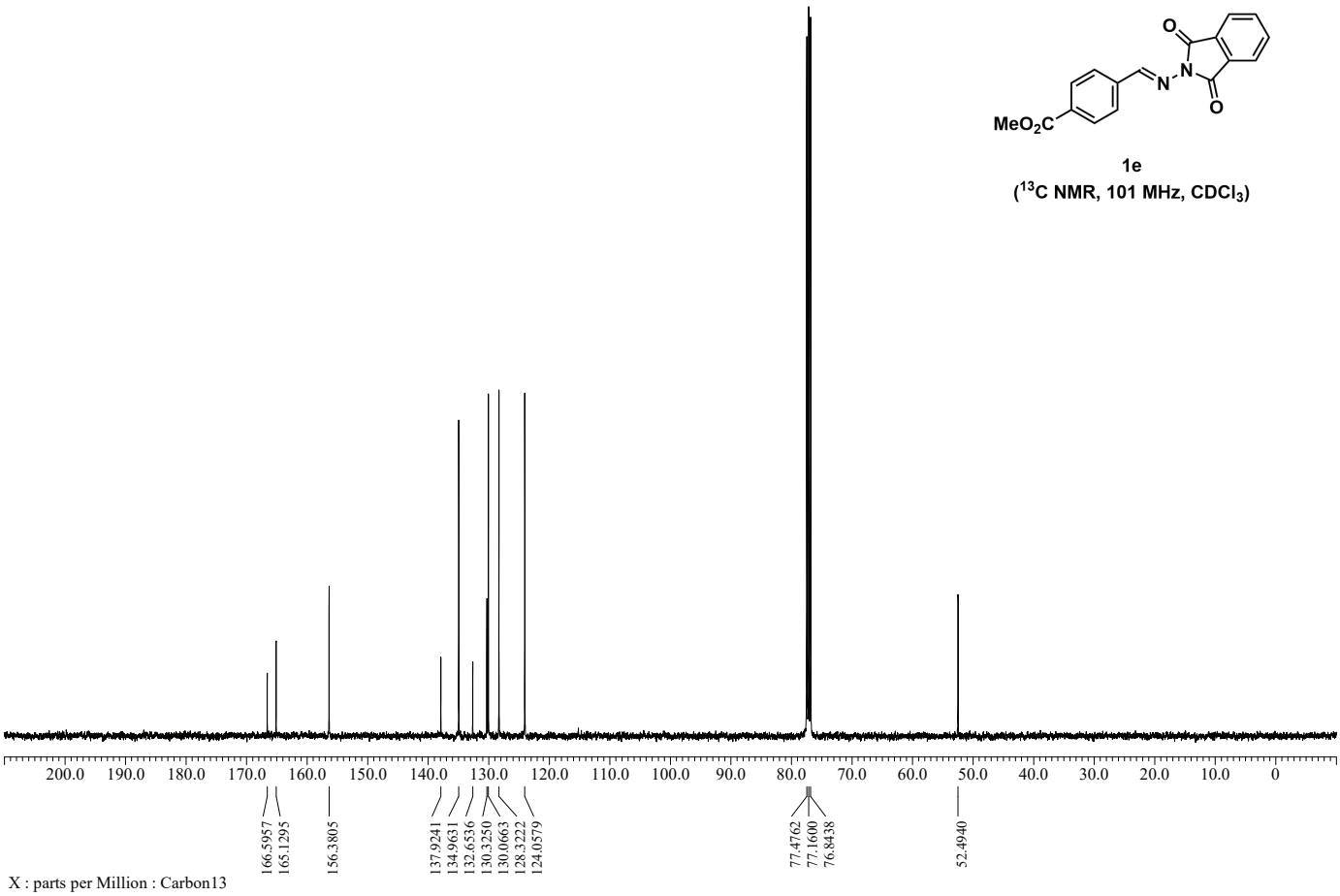
1d
(^{19}F NMR, 376 MHz, $CDCl_3$)

X : parts per Million : Fluorine19

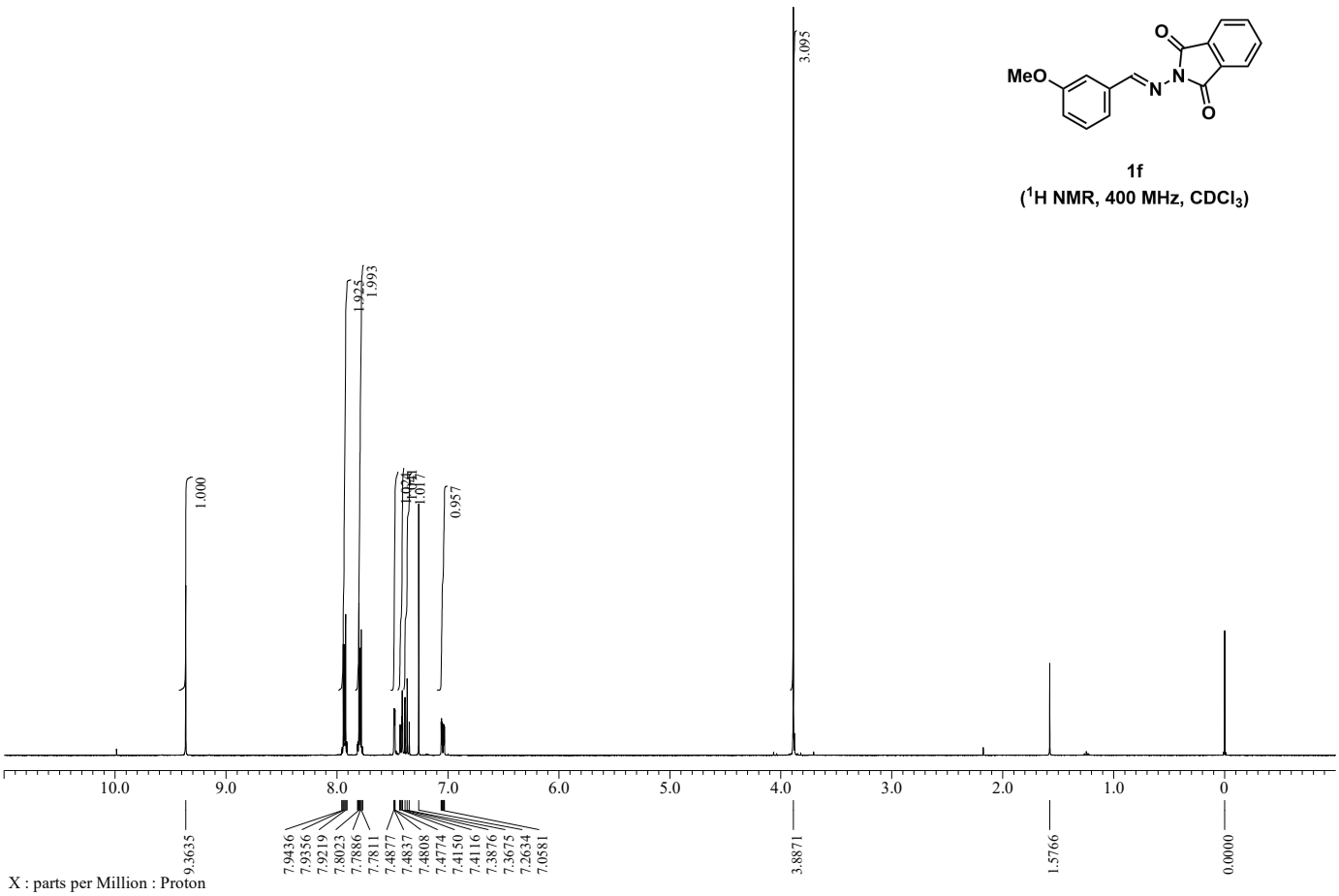


1e
(^{1}H NMR, 400 MHz, $CDCl_3$)

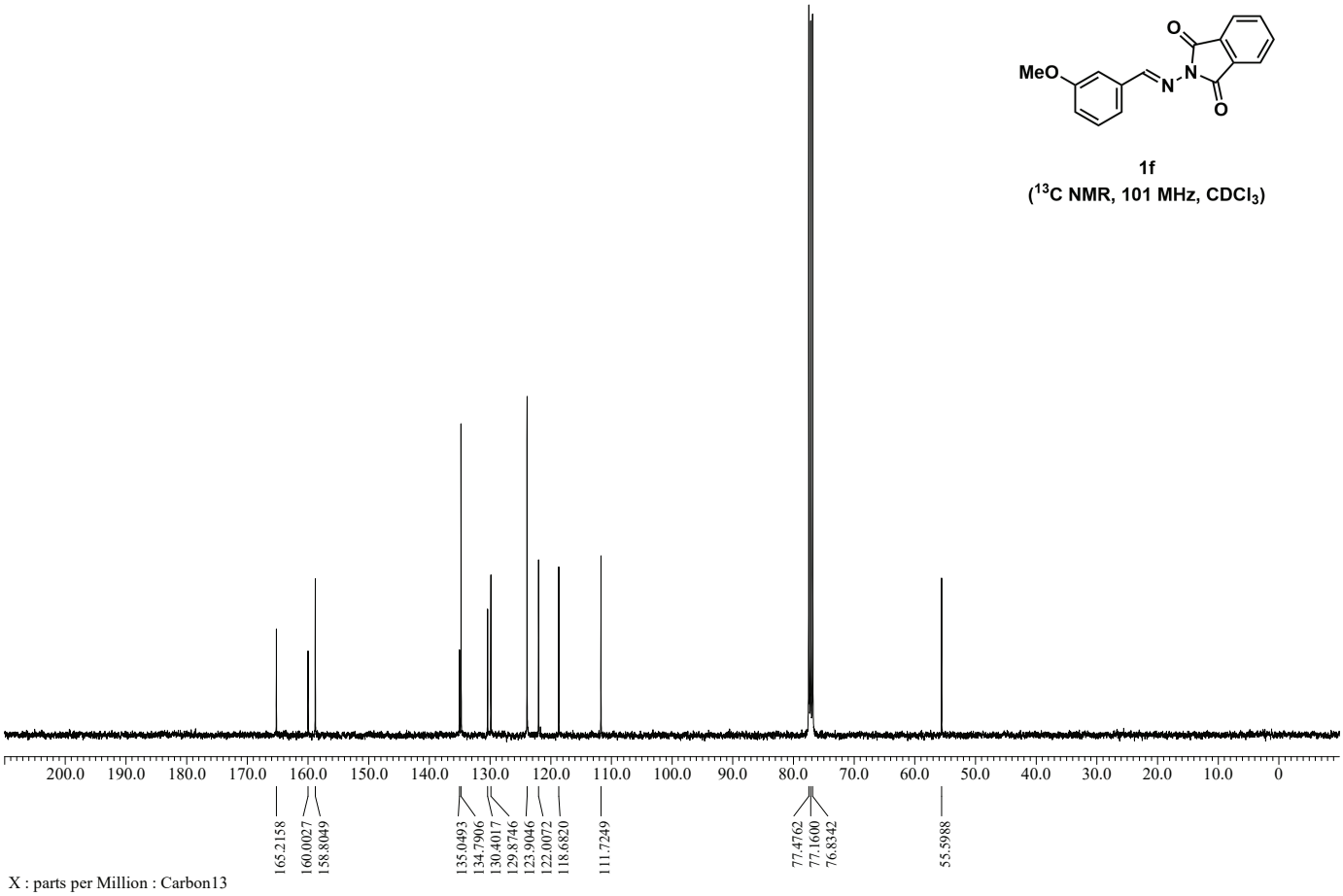
X : parts per Million : Proton



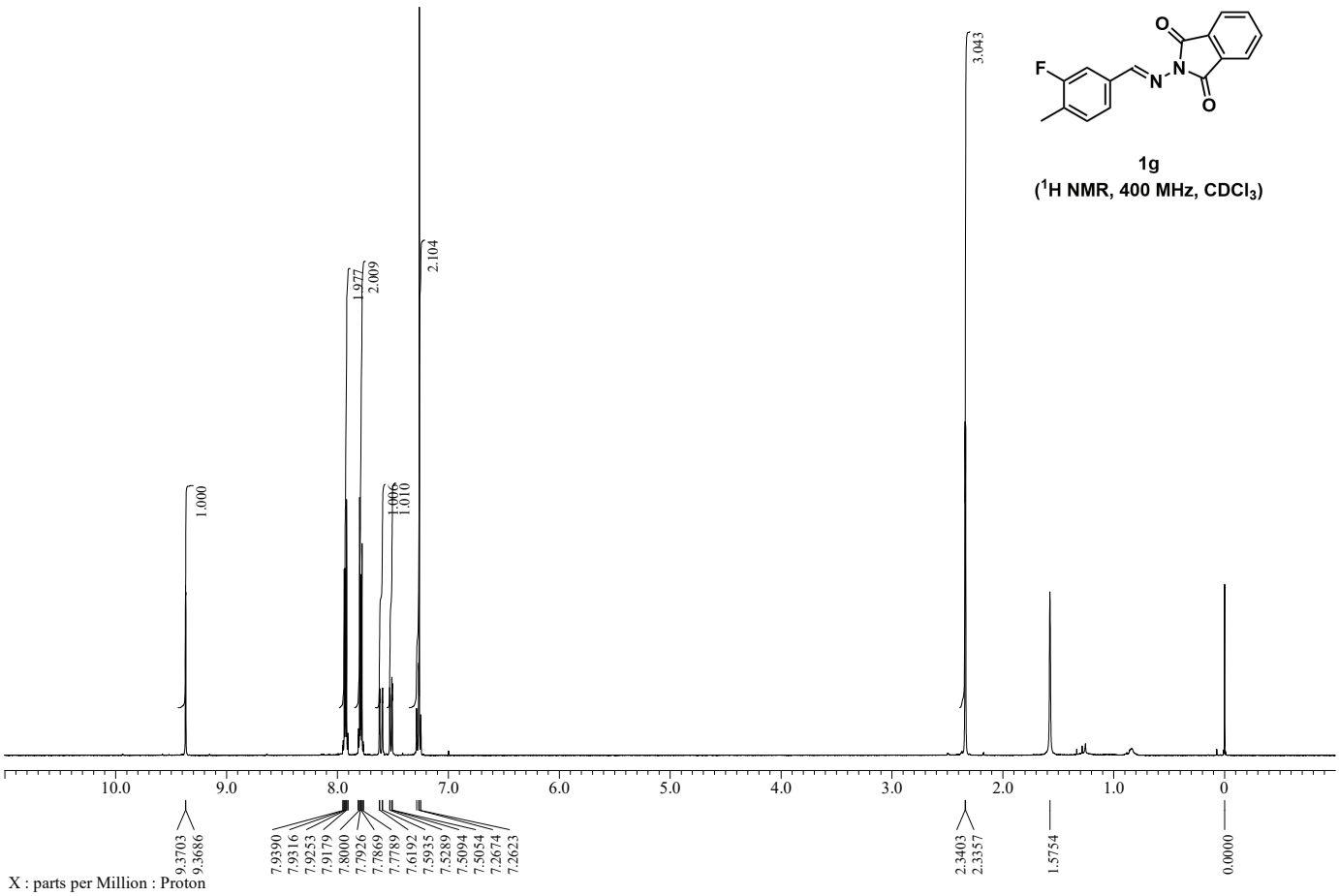
1e
(^{13}C NMR, 101 MHz, $CDCl_3$)



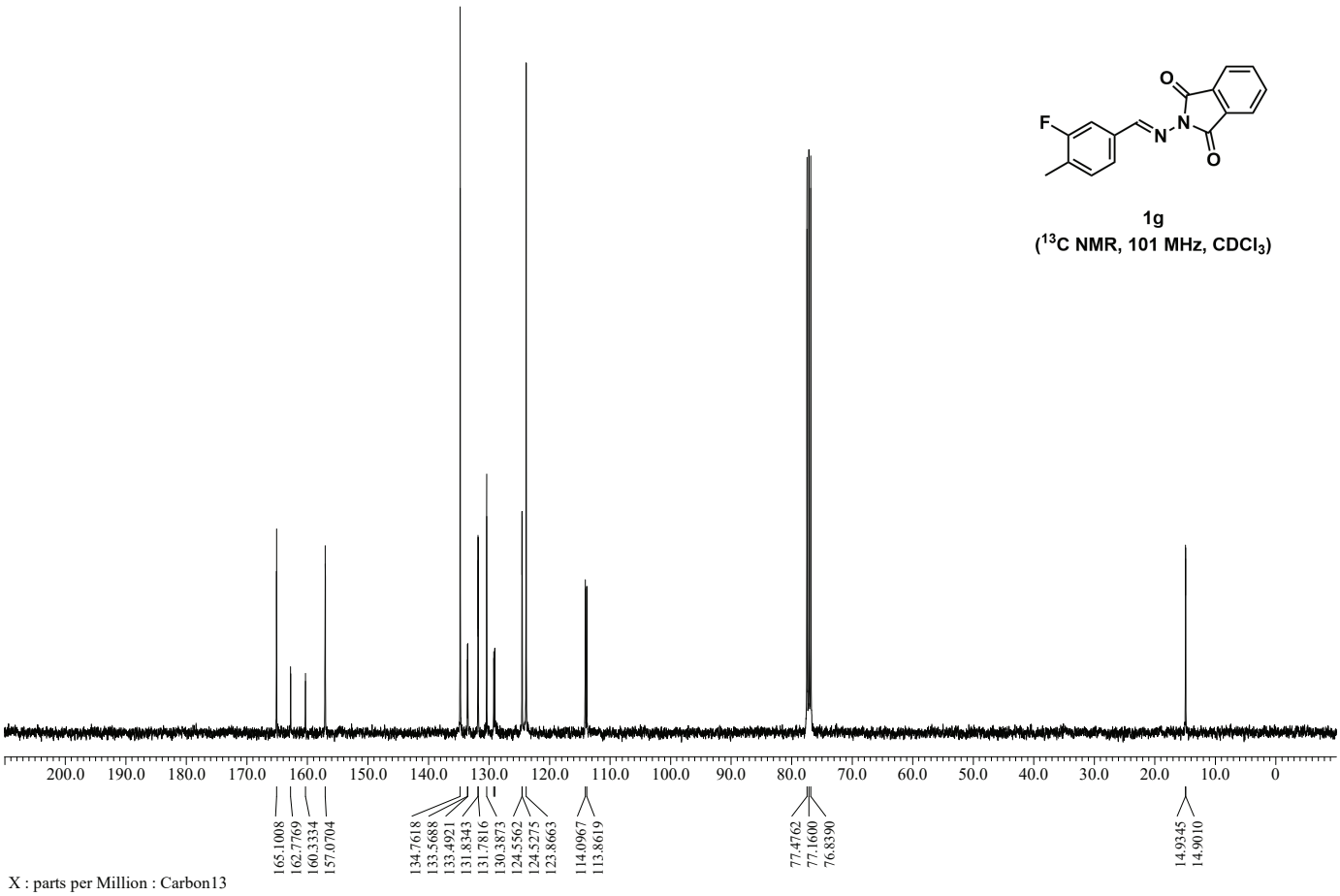
1f
(^{1}H NMR, 400 MHz, $CDCl_3$)



1f
(^{13}C NMR, 101 MHz, $CDCl_3$)

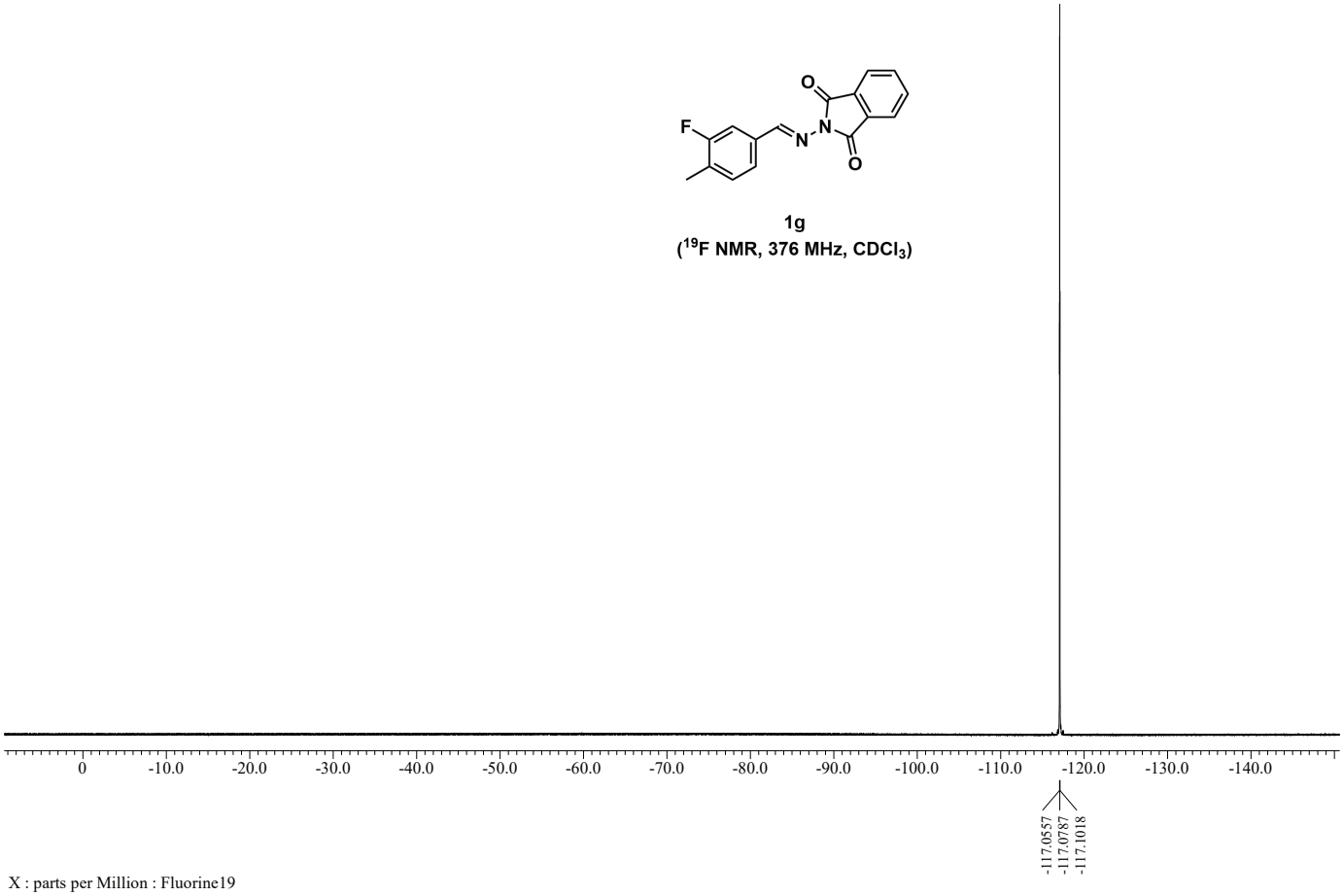


1g
(^{1}H NMR, 400 MHz, $CDCl_3$)



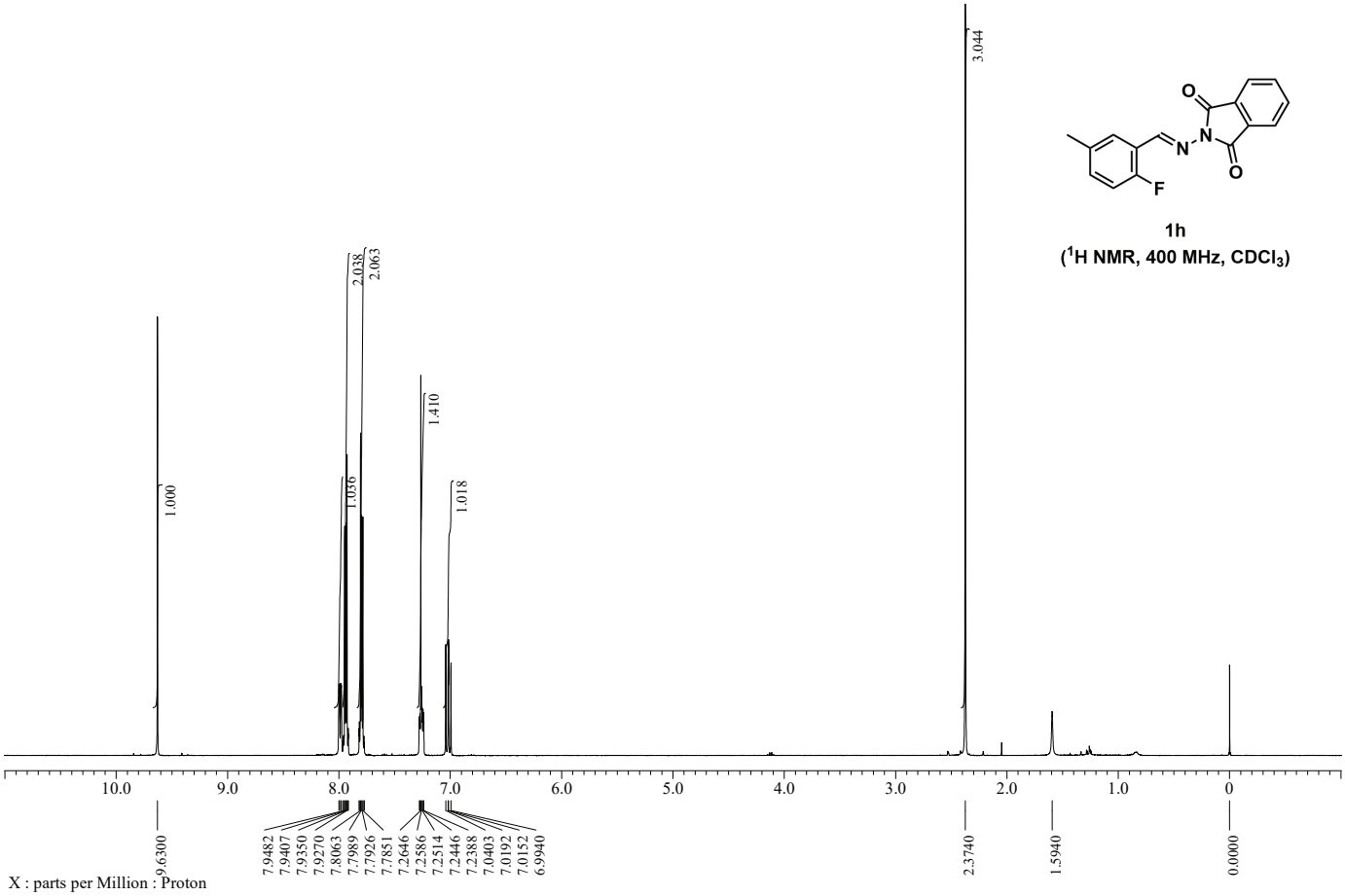
1g
(^{13}C NMR, 101 MHz, $CDCl_3$)

X : parts per Million : Carbon13

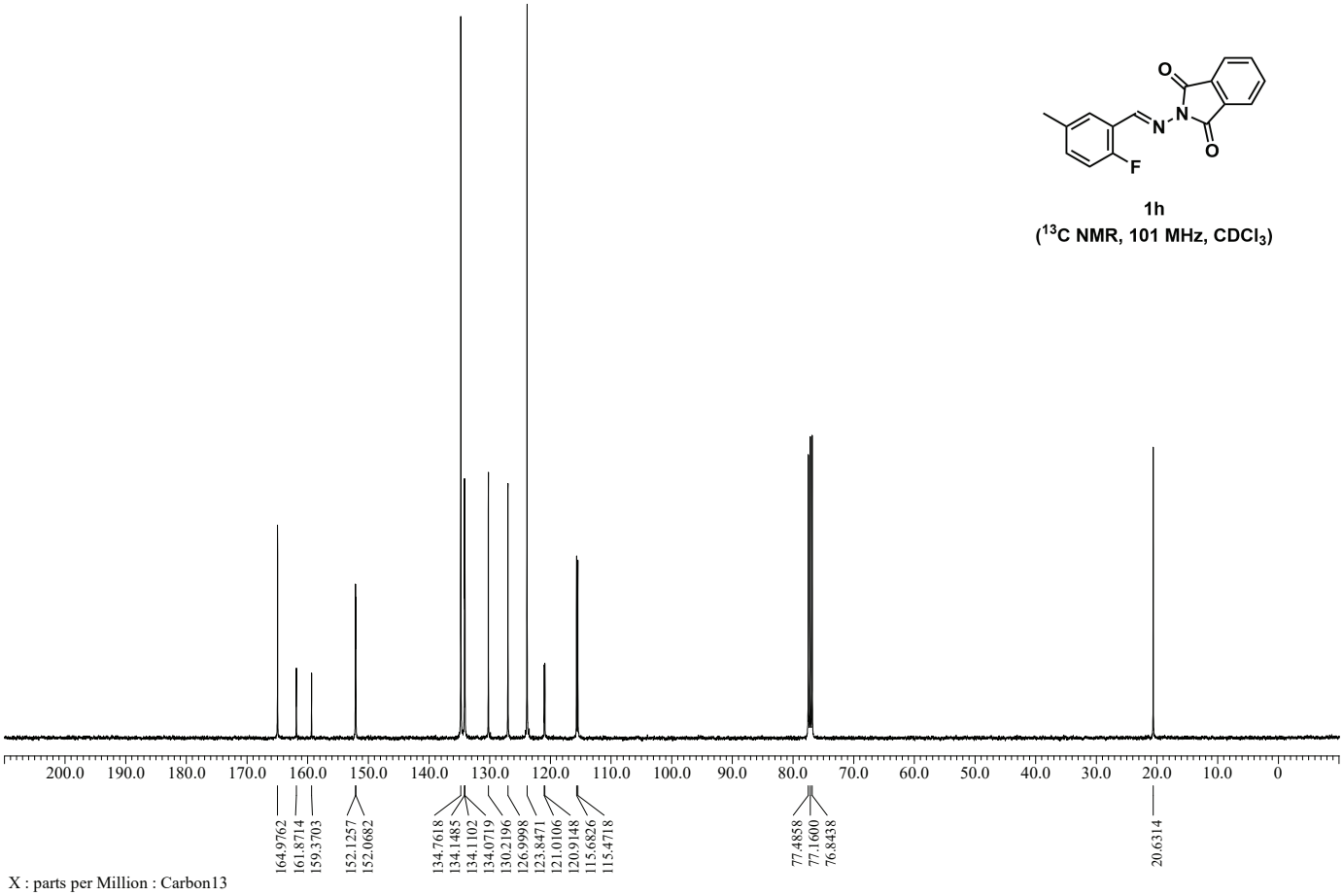


1g
(^{19}F NMR, 376 MHz, $CDCl_3$)

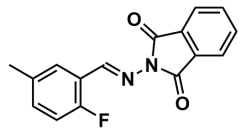
X : parts per Million : Fluorine19



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

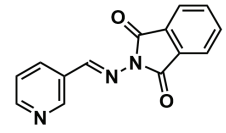


1h
(^{13}C NMR, 101 MHz, $CDCl_3$)



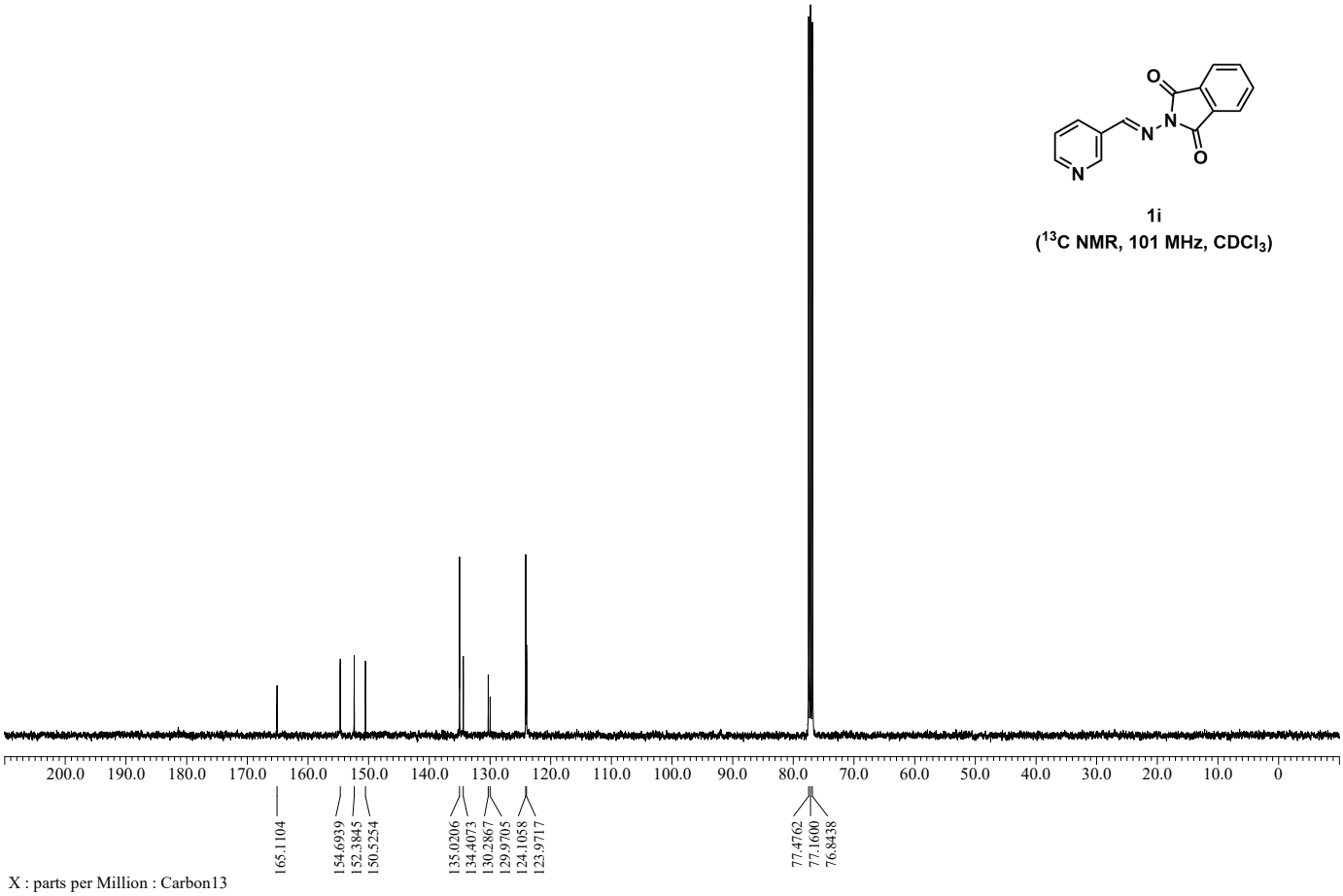
1h
(^{19}F NMR, 376 MHz, $CDCl_3$)

X : parts per Million : Fluorine19

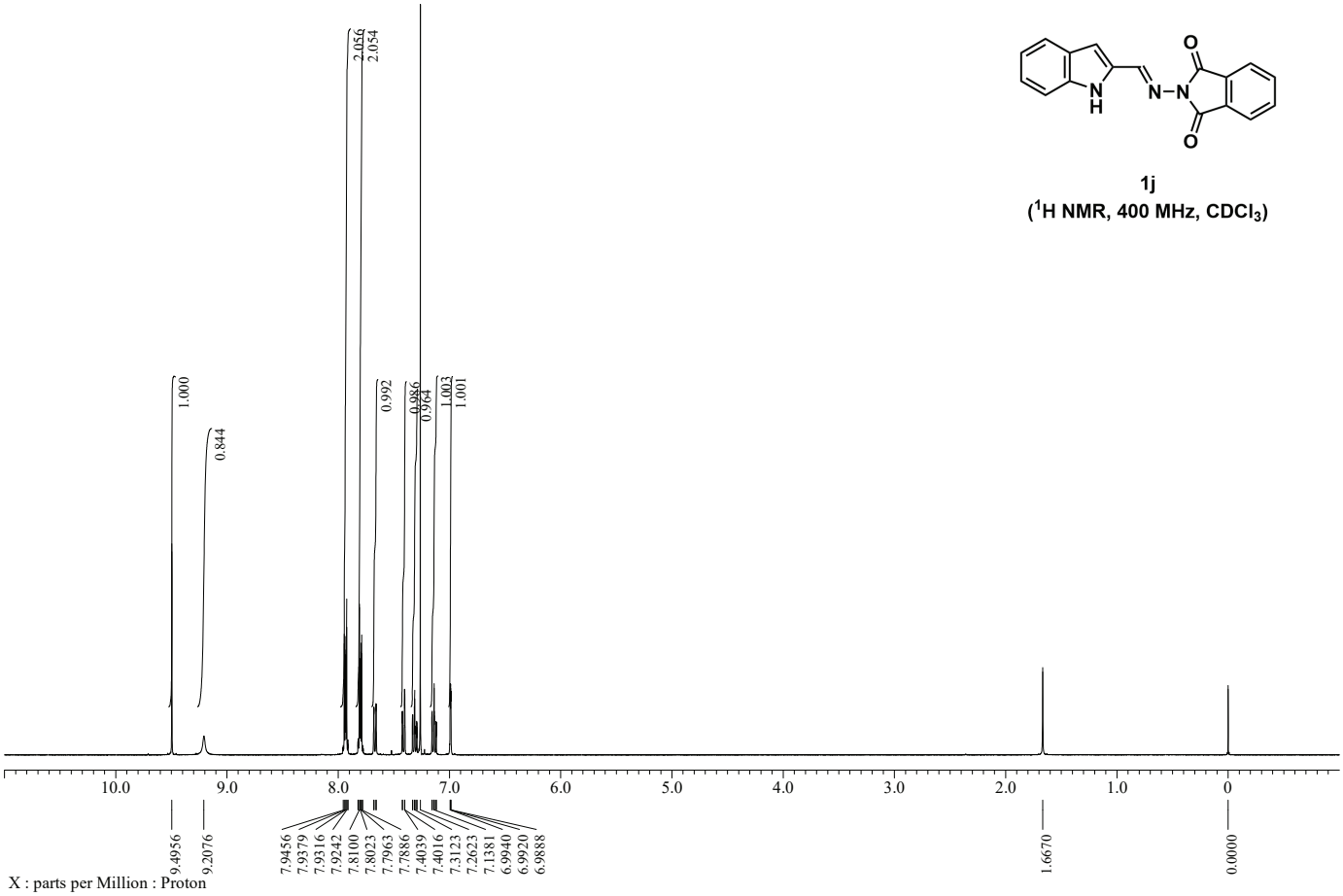


1i
(^{1}H NMR, 400 MHz, $CDCl_3$)

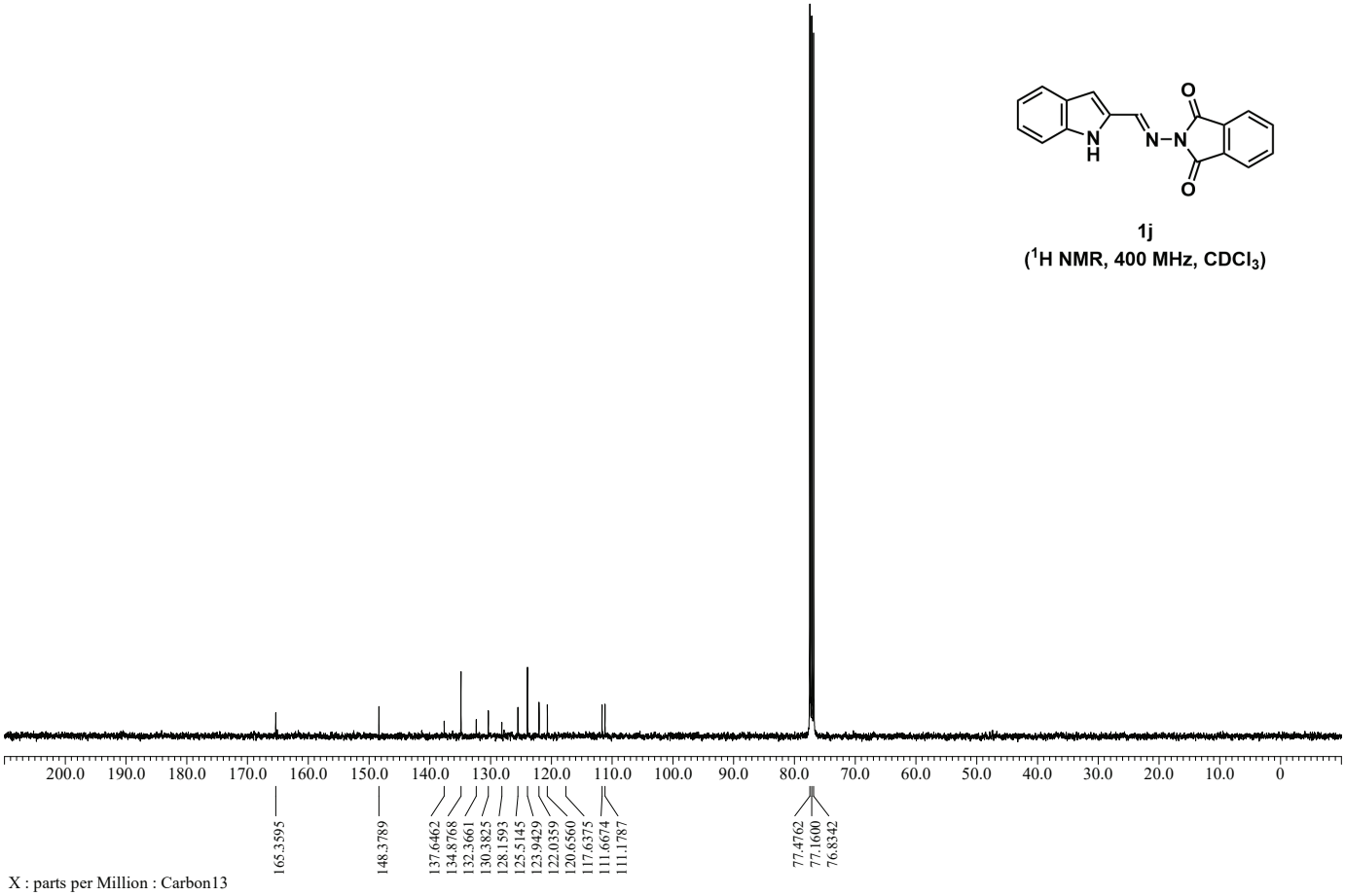
X : parts per Million : Proton



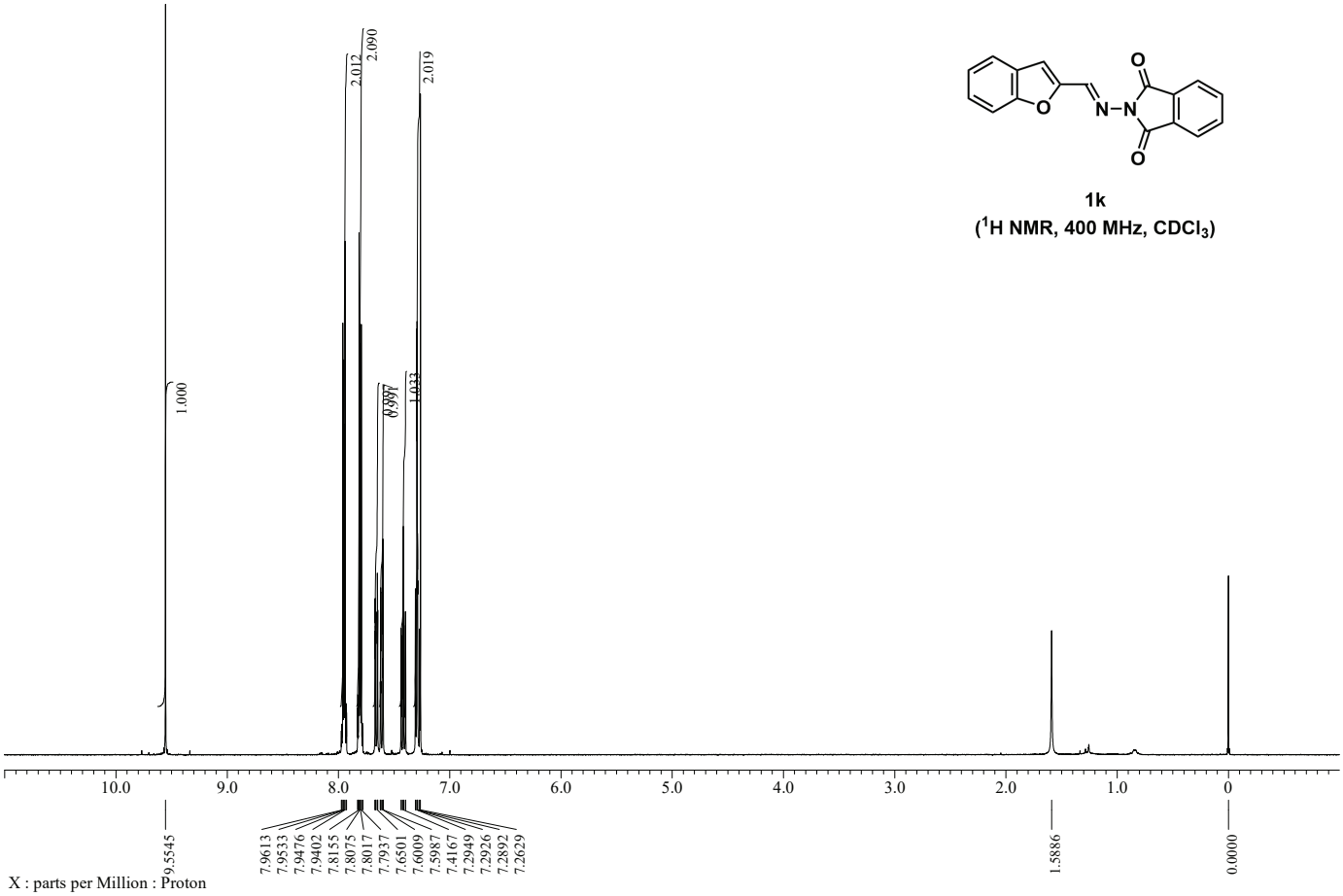
1i
(^{13}C NMR, 101 MHz, $CDCl_3$)



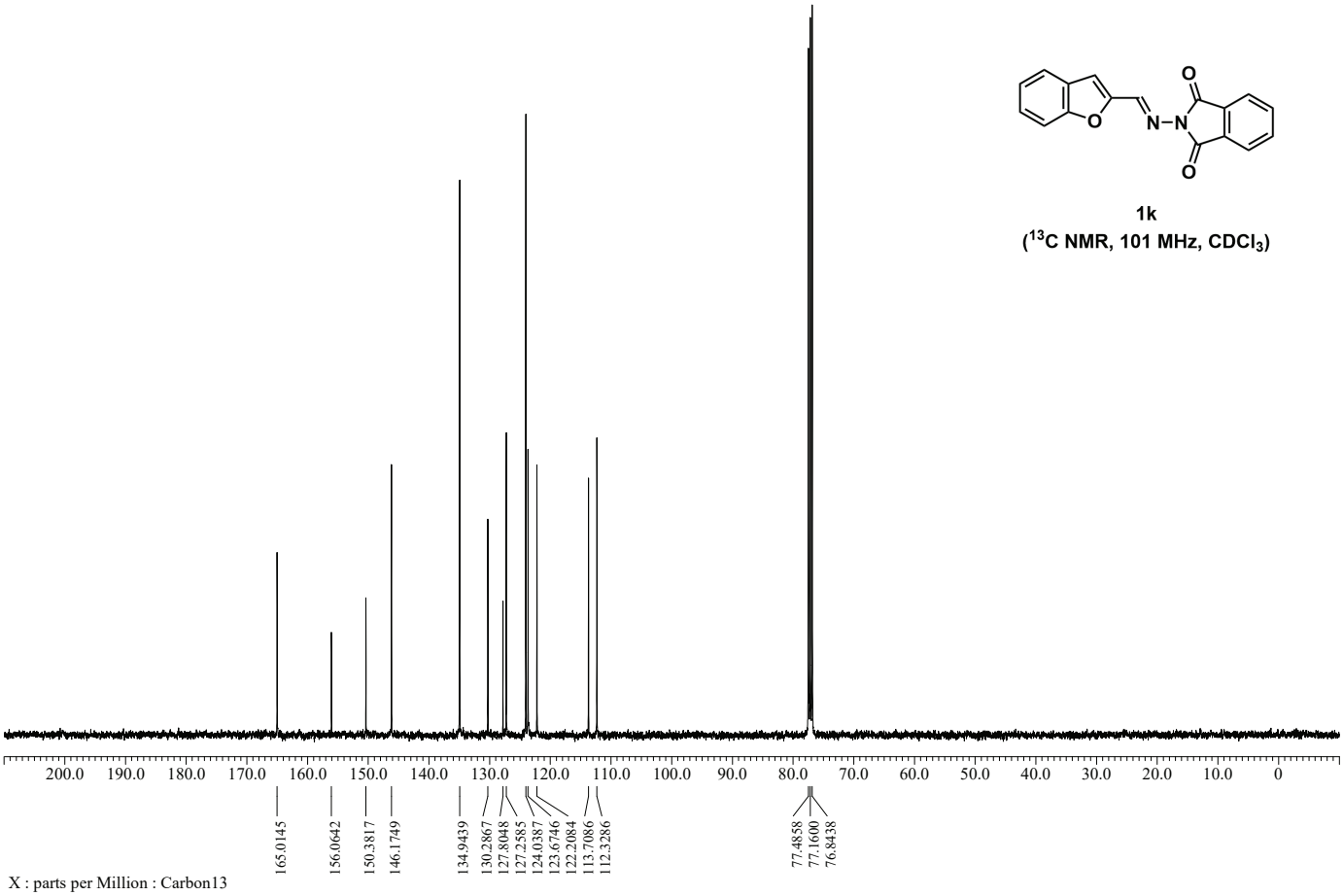
1j
(^{1}H NMR, 400 MHz, $CDCl_3$)



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

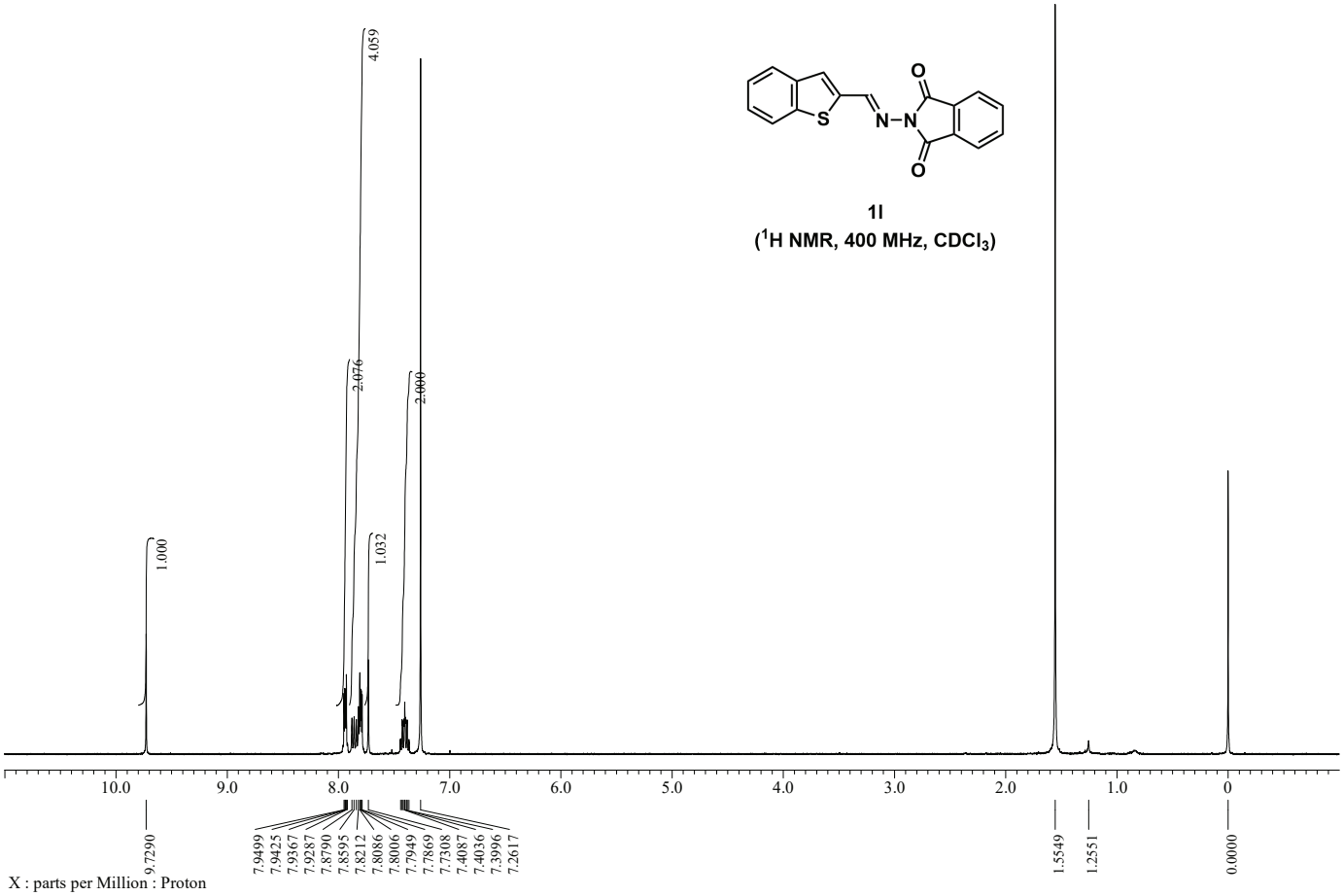


1k
(^{1}H NMR, 400 MHz, $CDCl_3$)



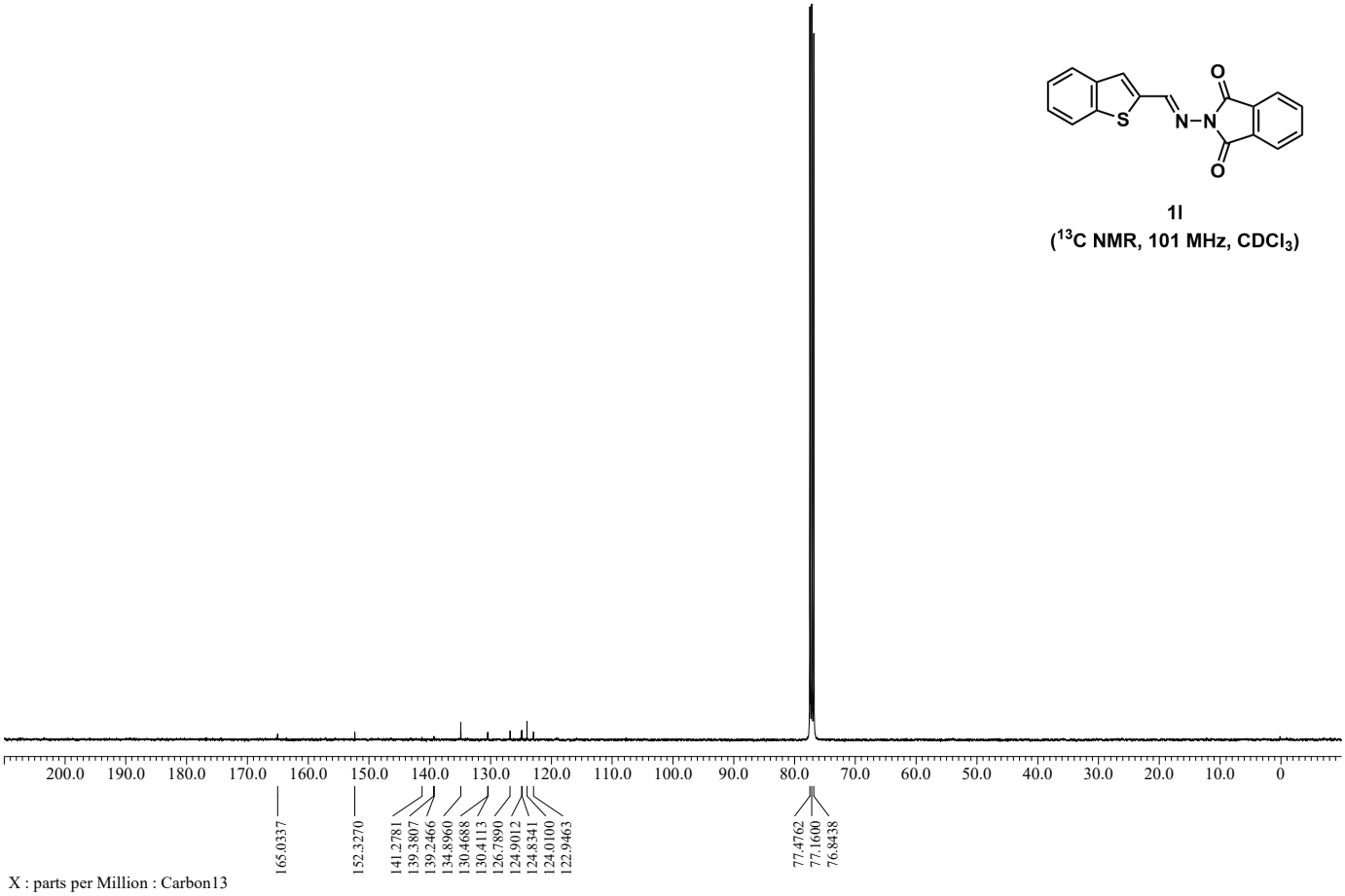
1k

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



1l

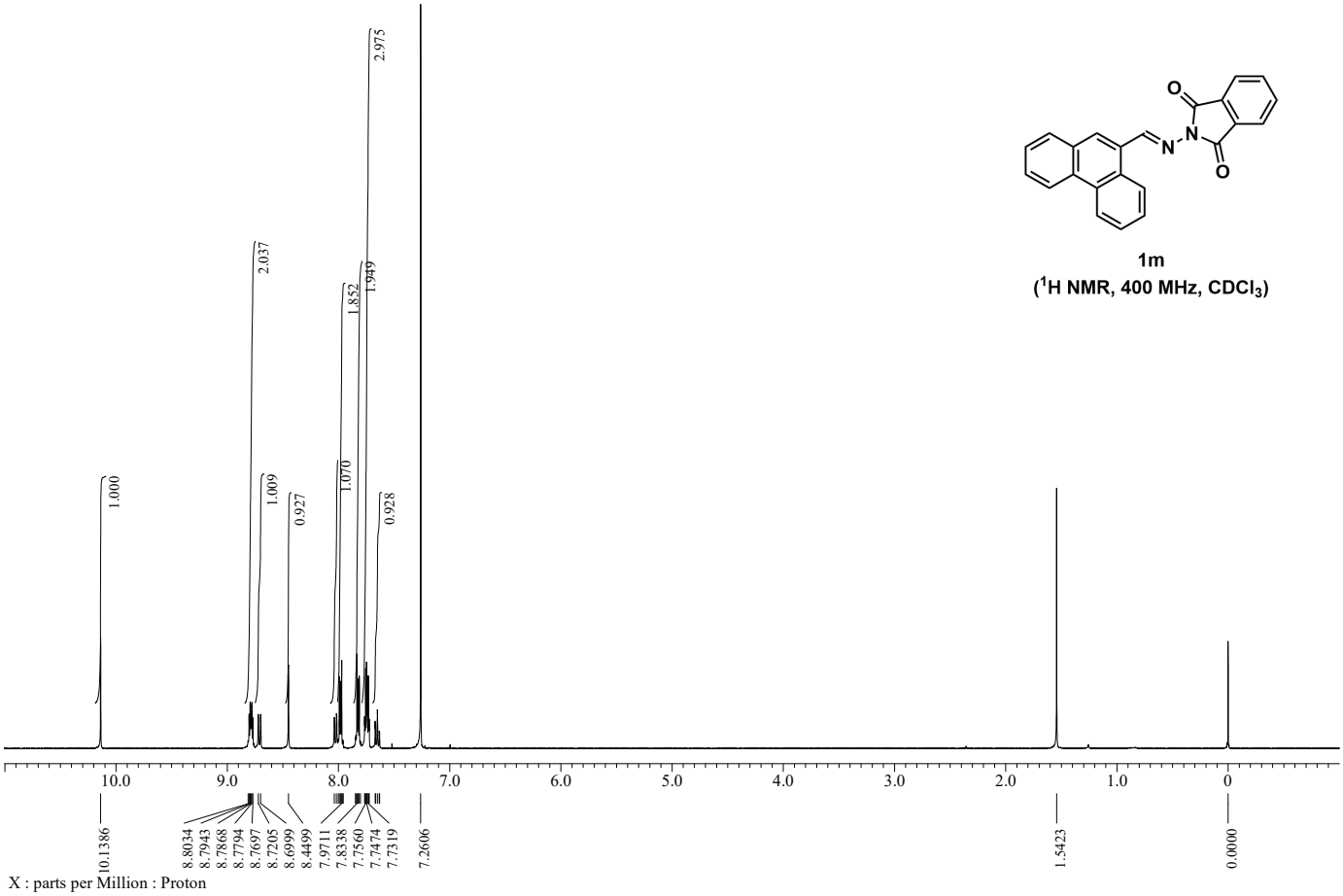
(^{1}H NMR, 400 MHz, $CDCl_3$)



X : parts per Million : Carbon13

1l

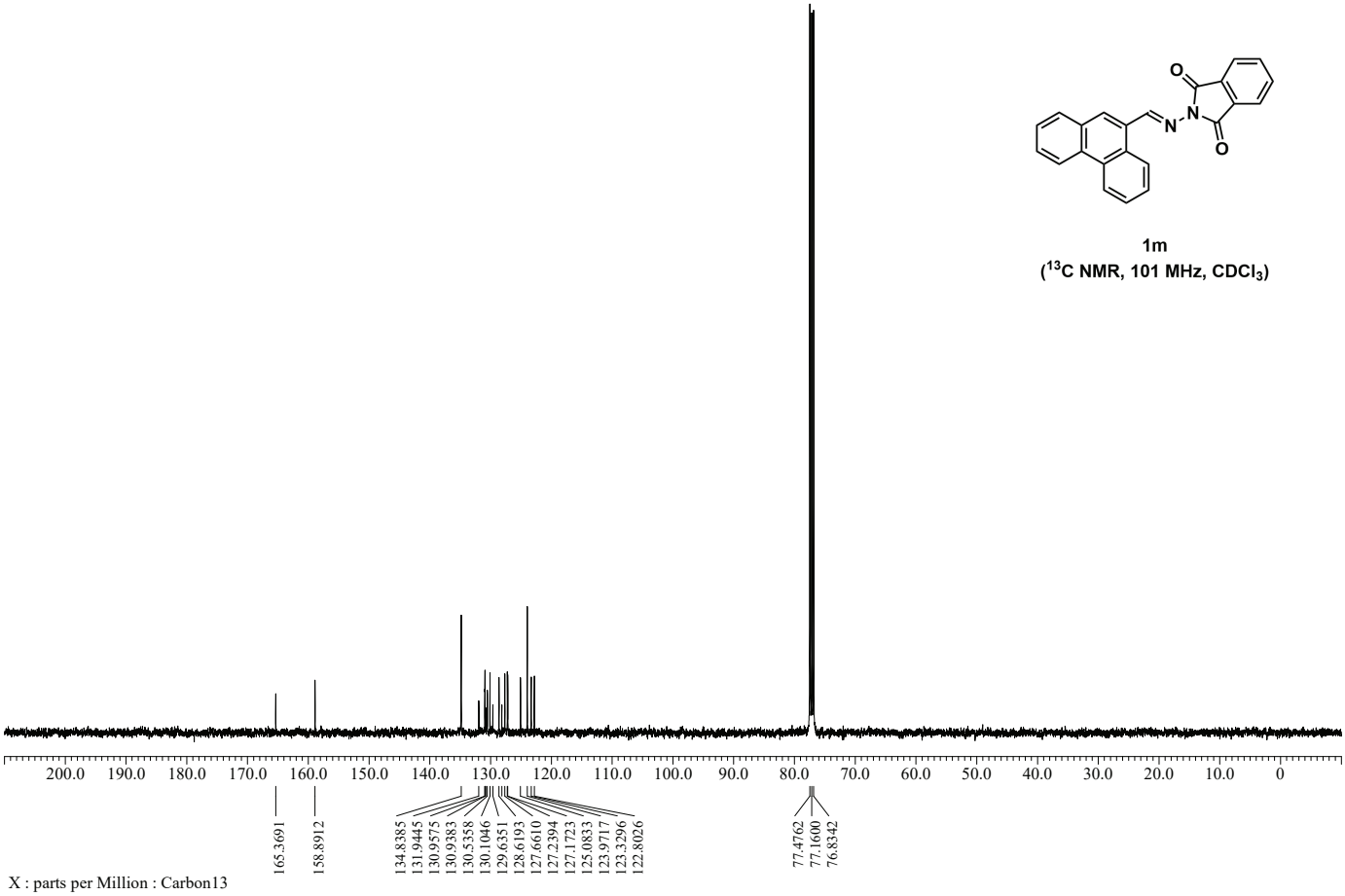
(^{13}C NMR, 101 MHz, $CDCl_3$)



X : parts per Million : Proton

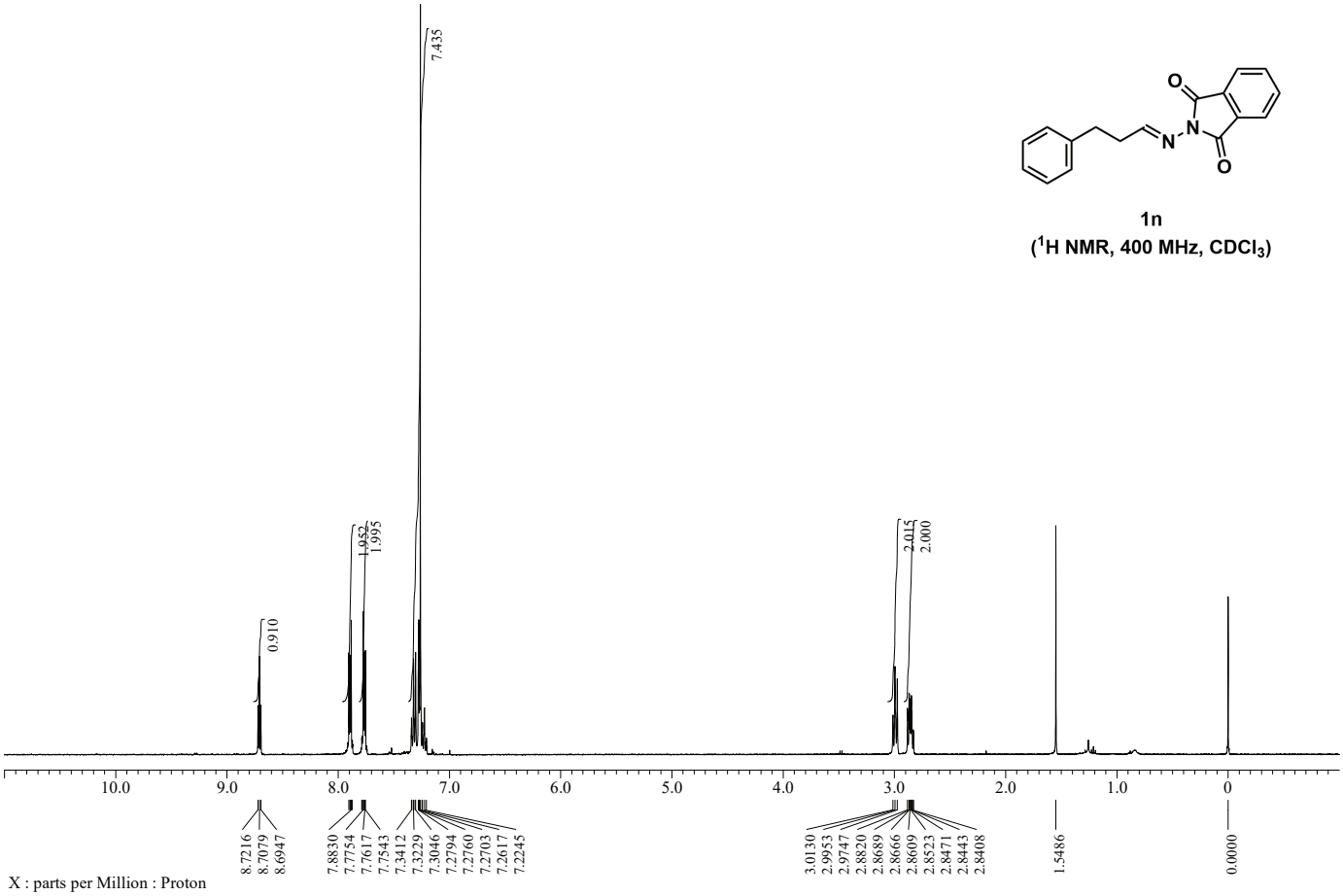
1m

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



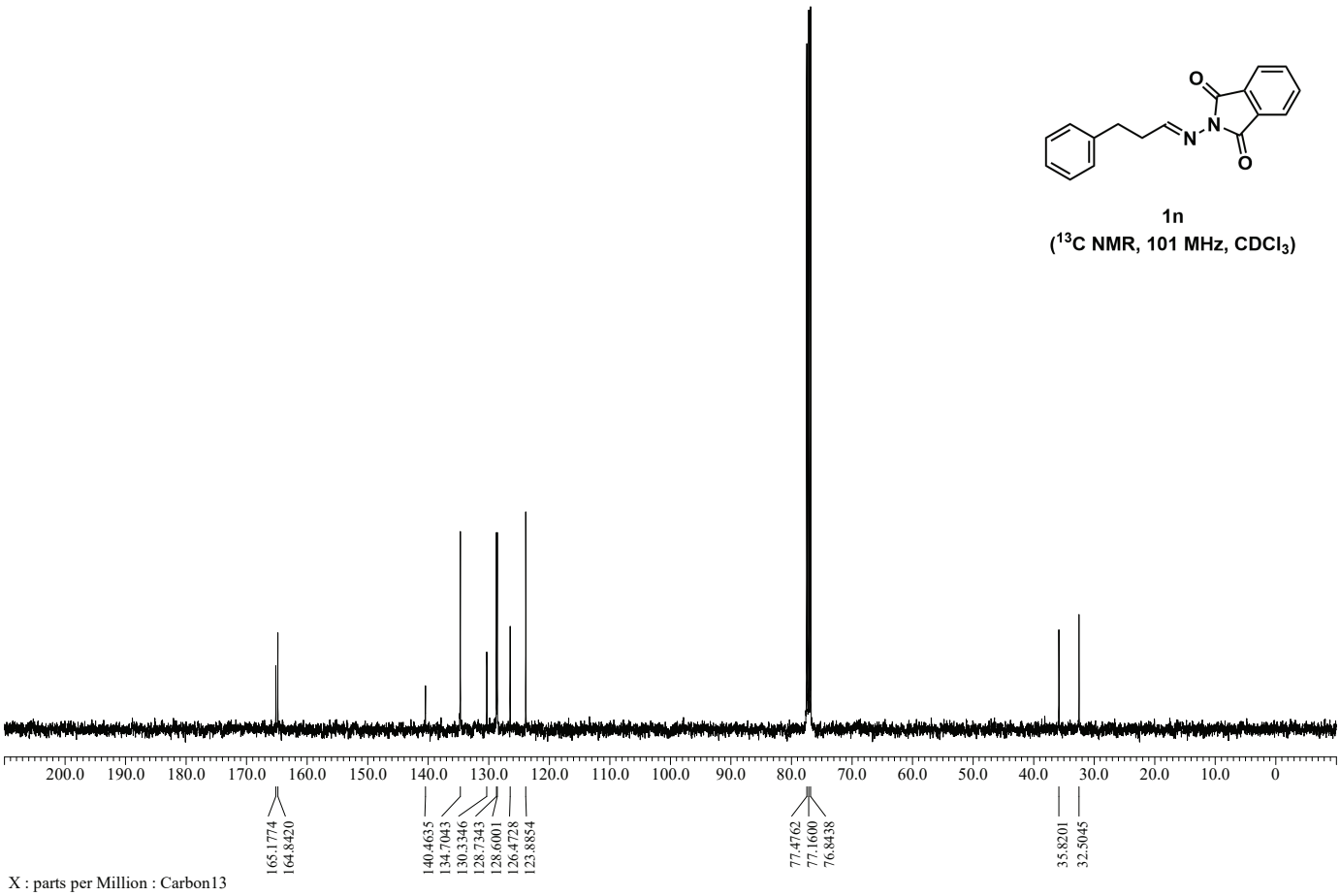
X : parts per Million : Carbon13

1m
(^{13}C NMR, 101 MHz, $CDCl_3$)



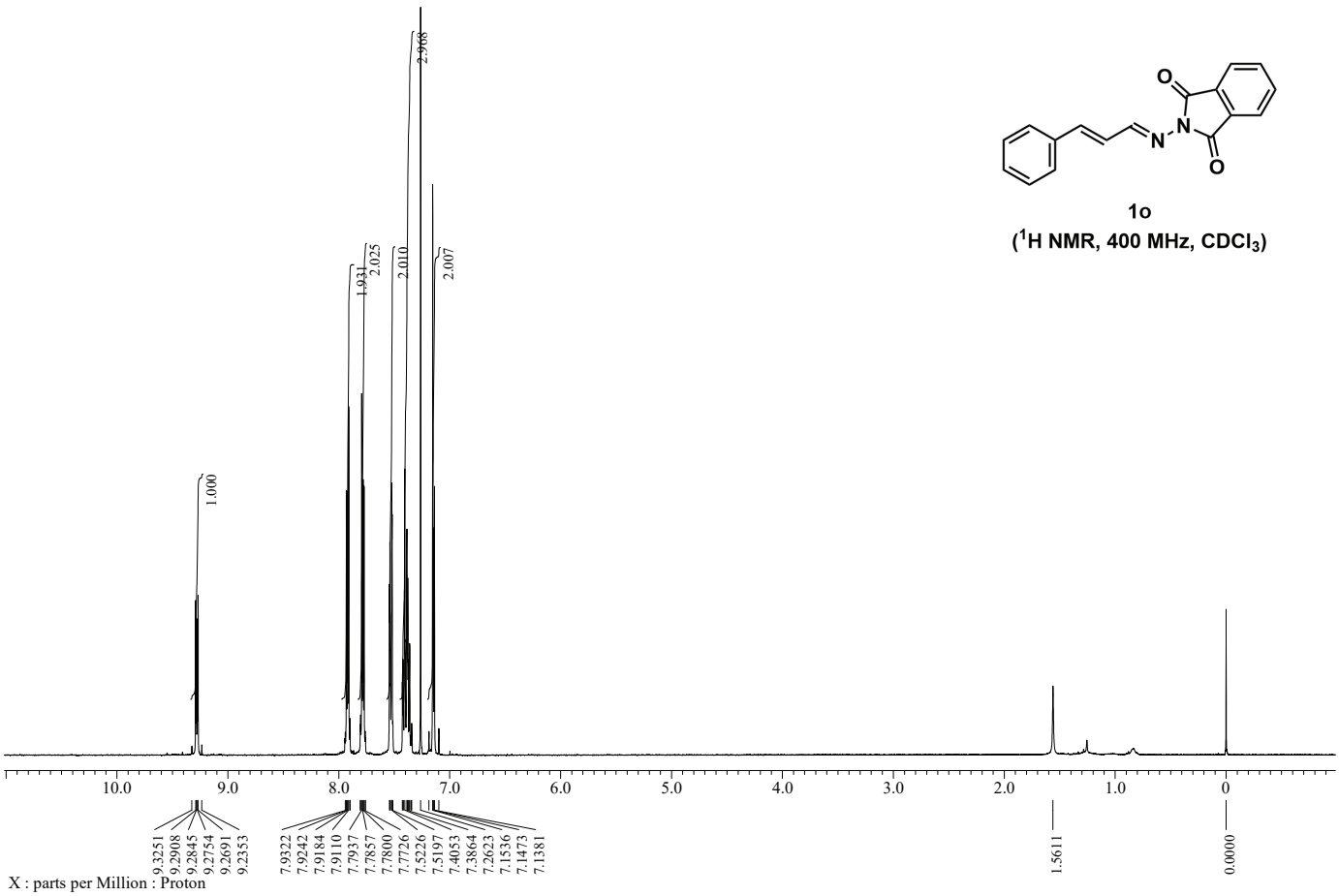
X : parts per Million : Proton

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



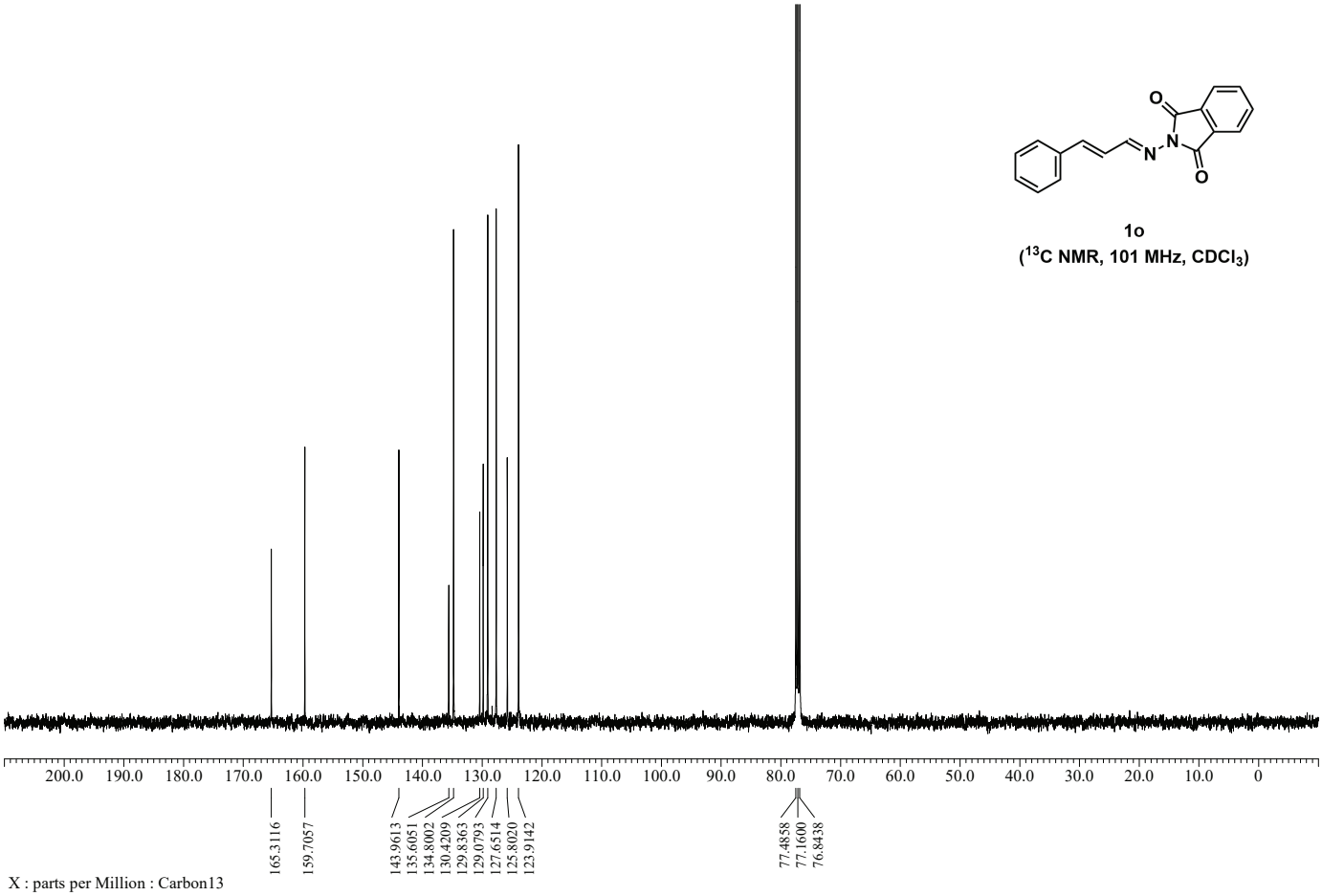
1n

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

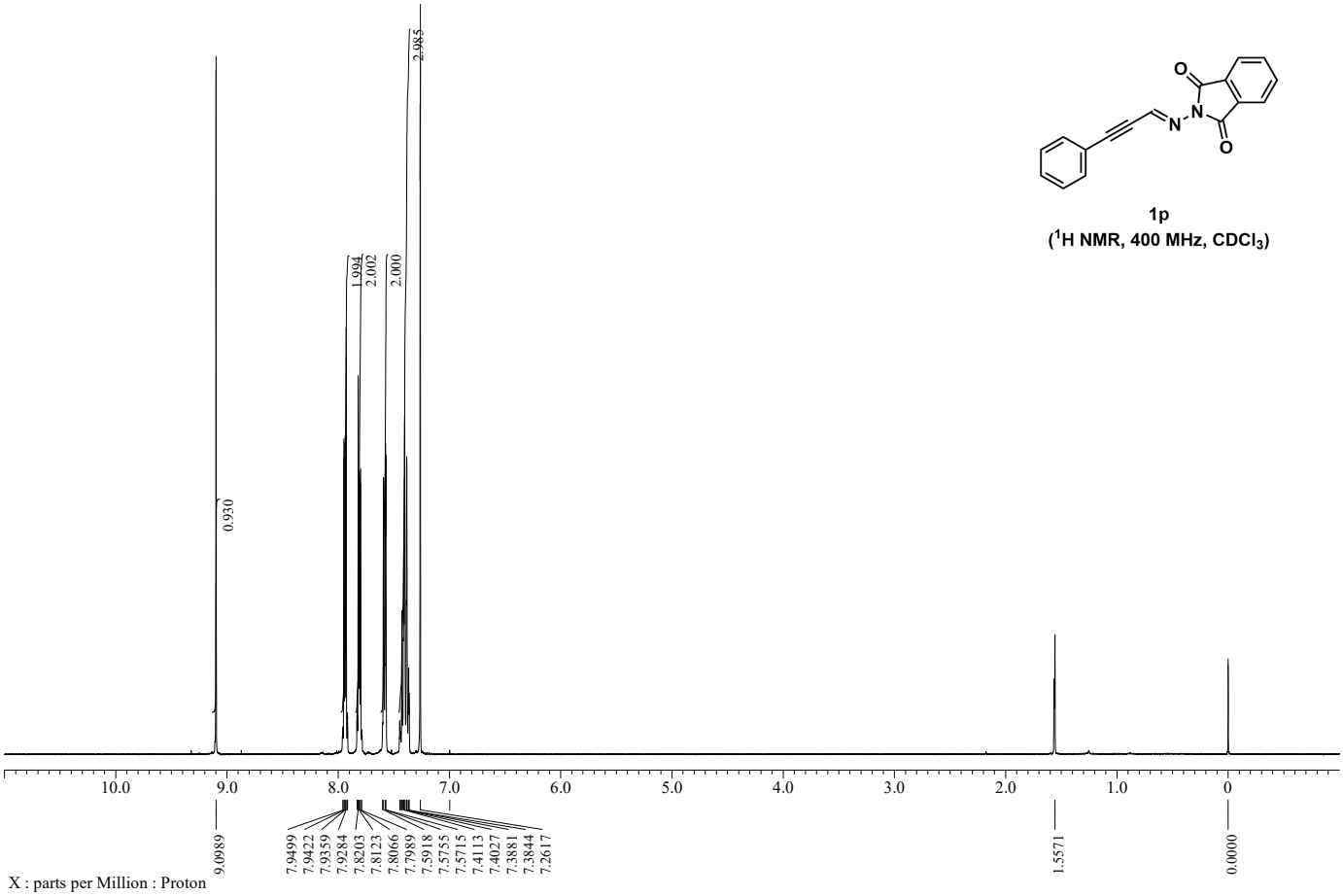


1o

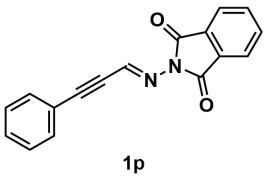
(^{1}H NMR, 400 MHz, $CDCl_3$)



1o
(^{13}C NMR, 101 MHz, $CDCl_3$)



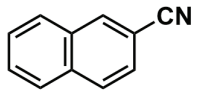
1p
(^{1}H NMR, 400 MHz, $CDCl_3$)



1p

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

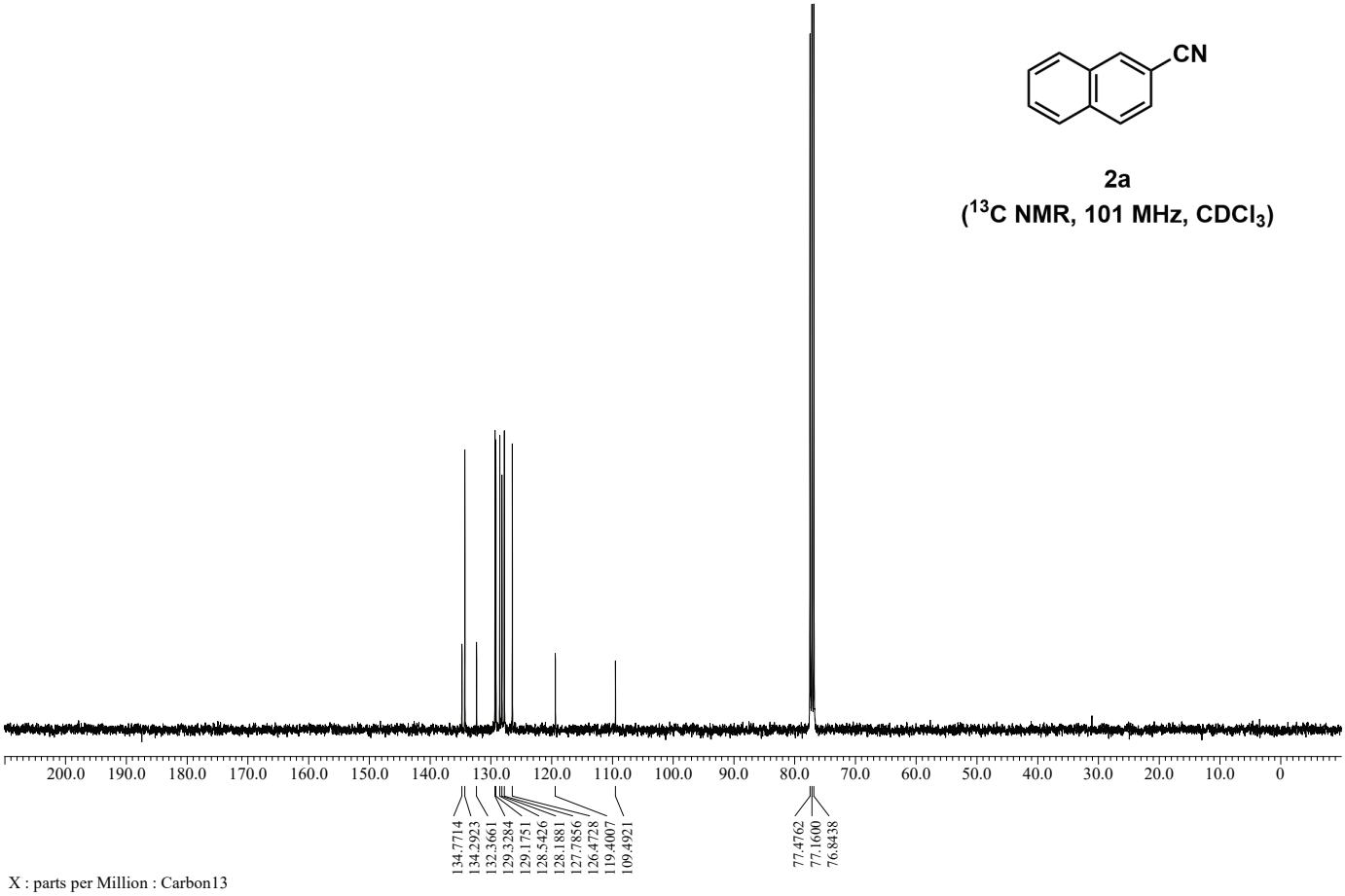
X : parts per Million : Carbon13



2a

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

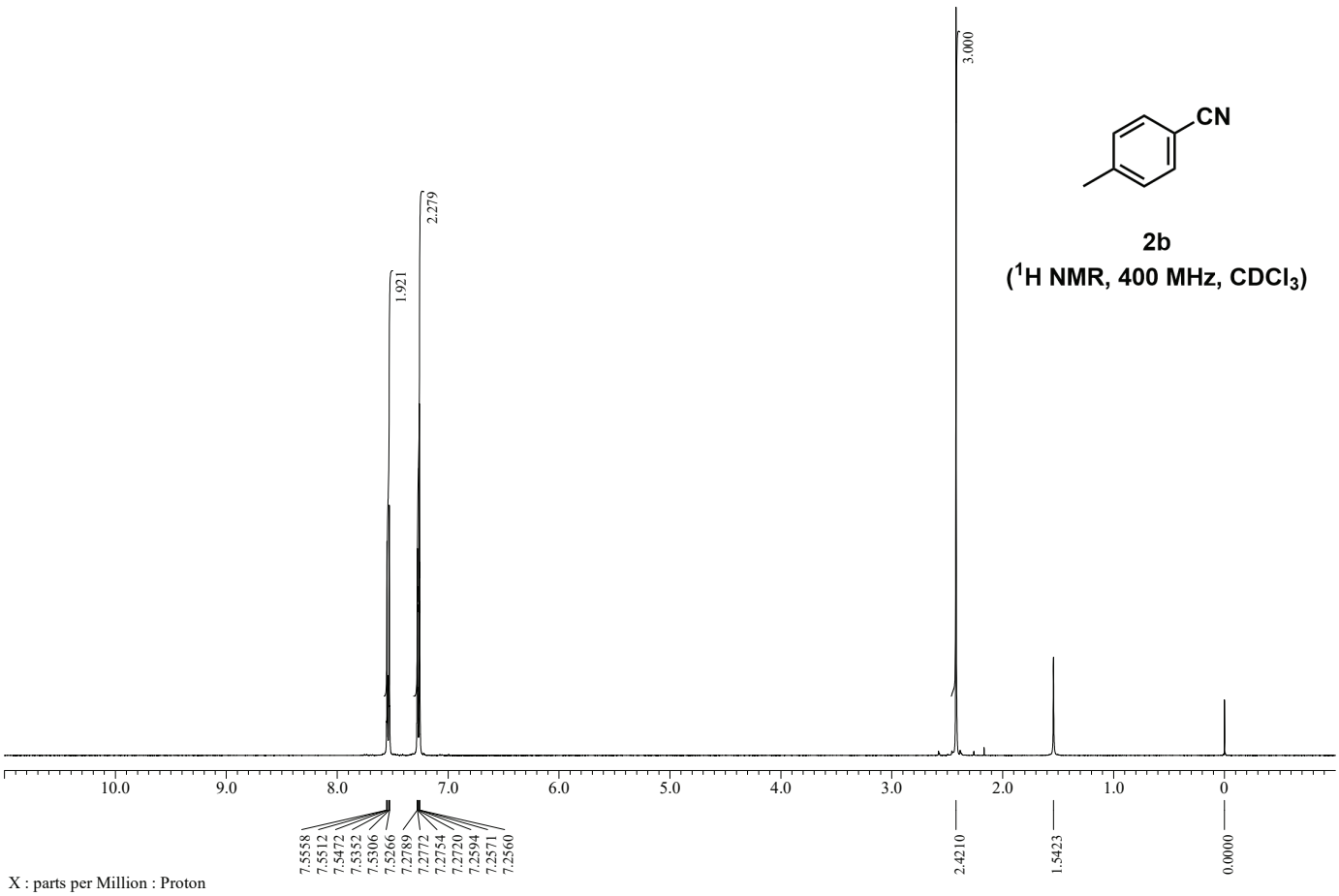
X : parts per Million : Proton



2a

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

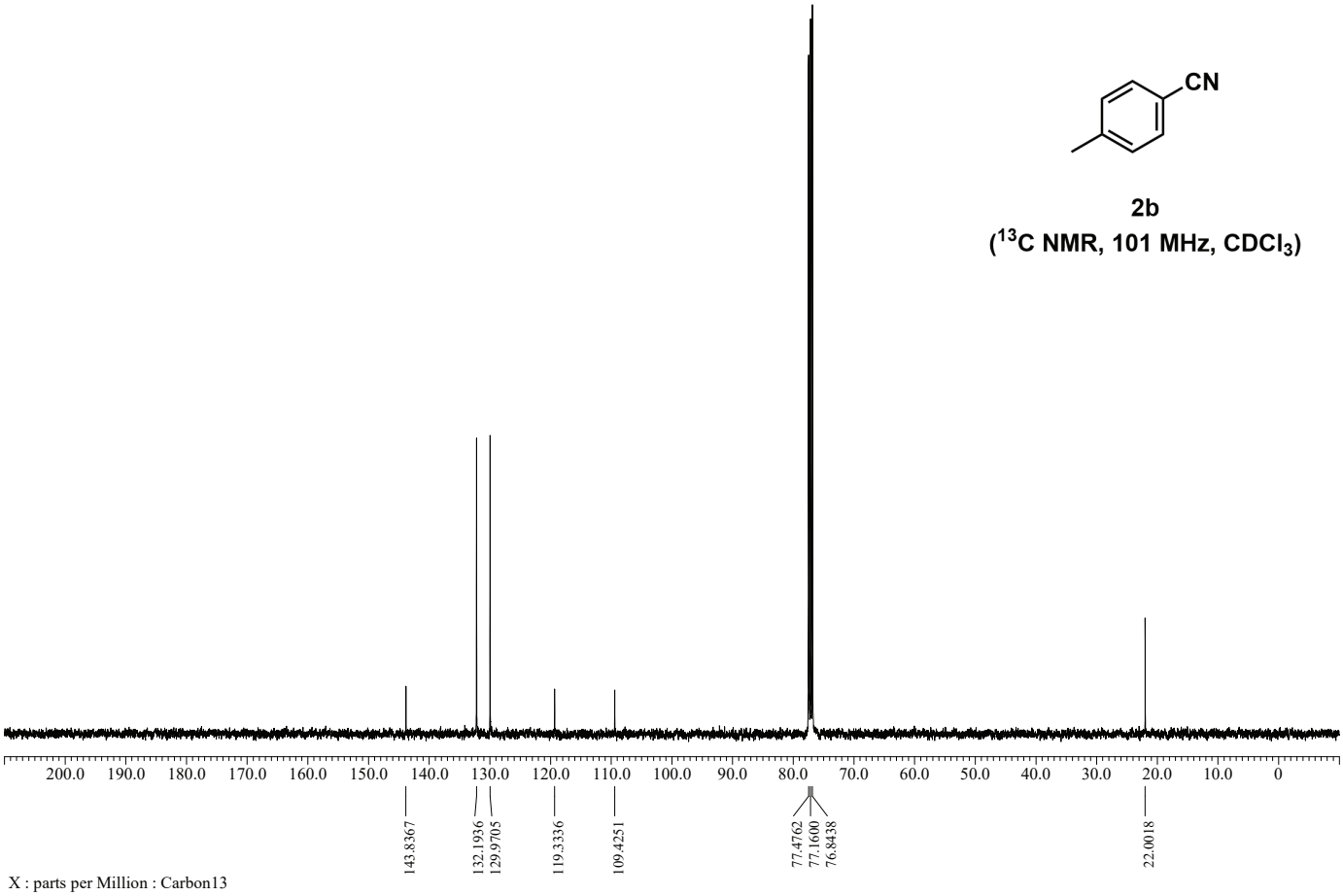
X : parts per Million : Carbon13



2b

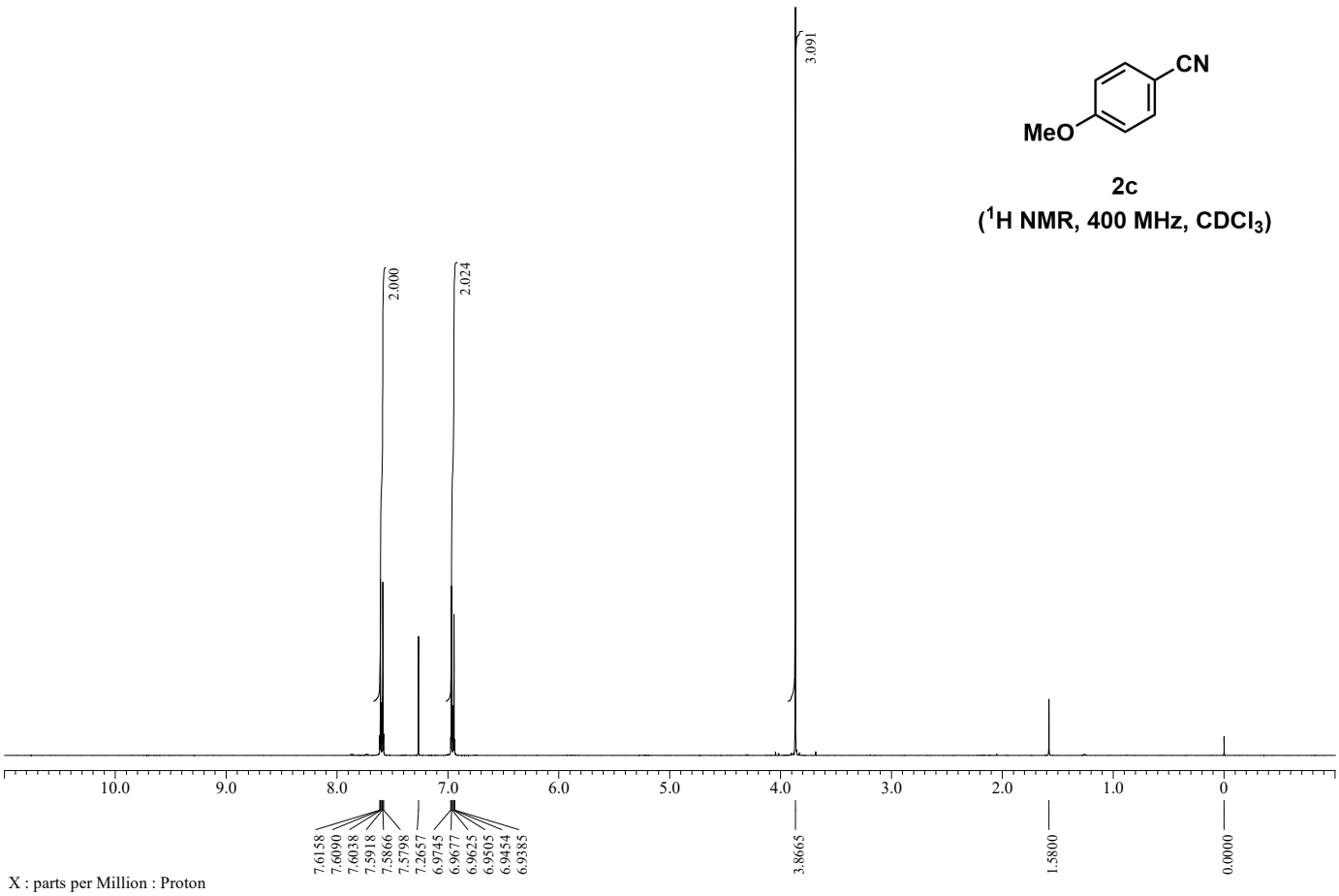
(^{1}H NMR, 400 MHz, $CDCl_3$)

X : parts per Million : Proton



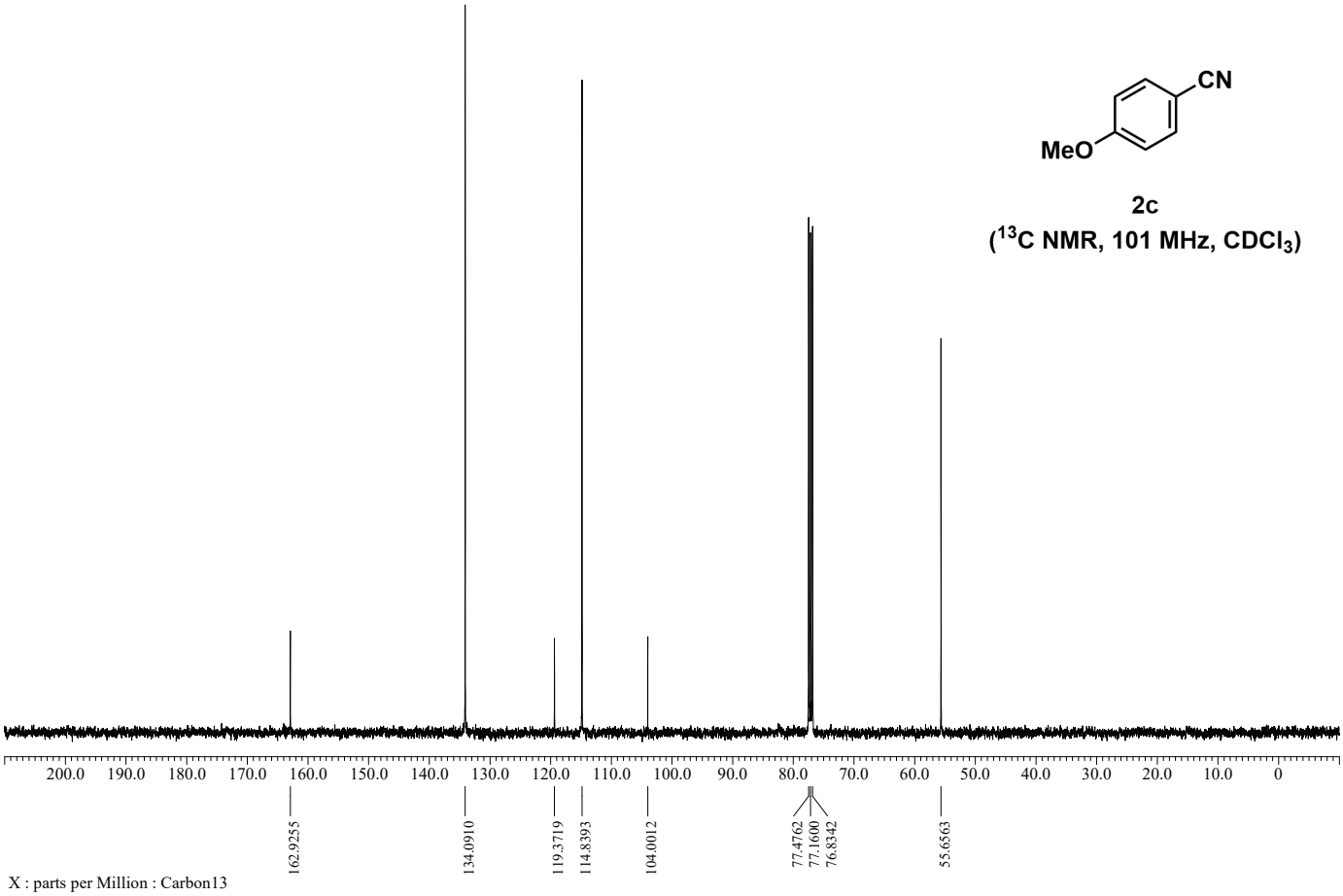
2b

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



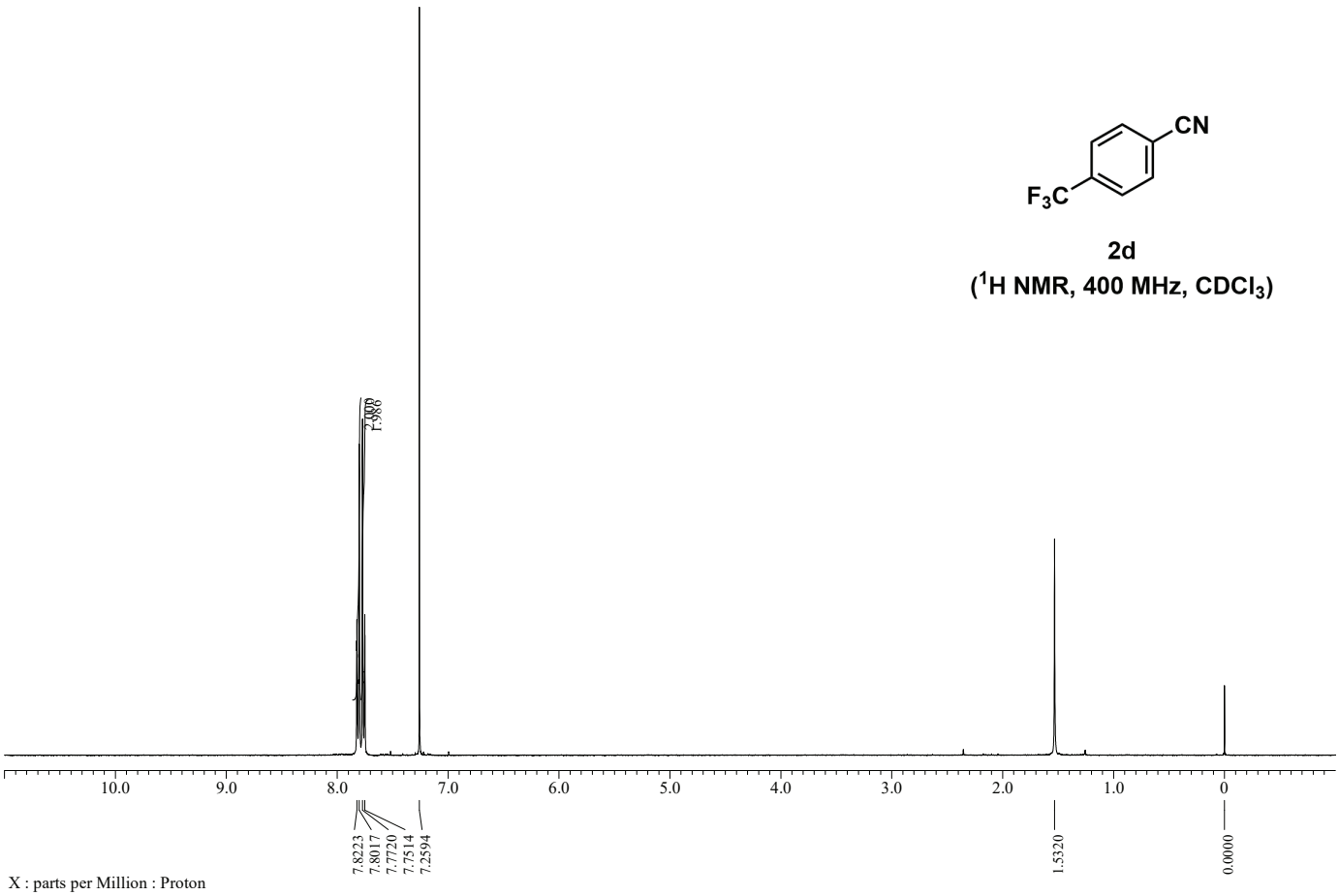
2c

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



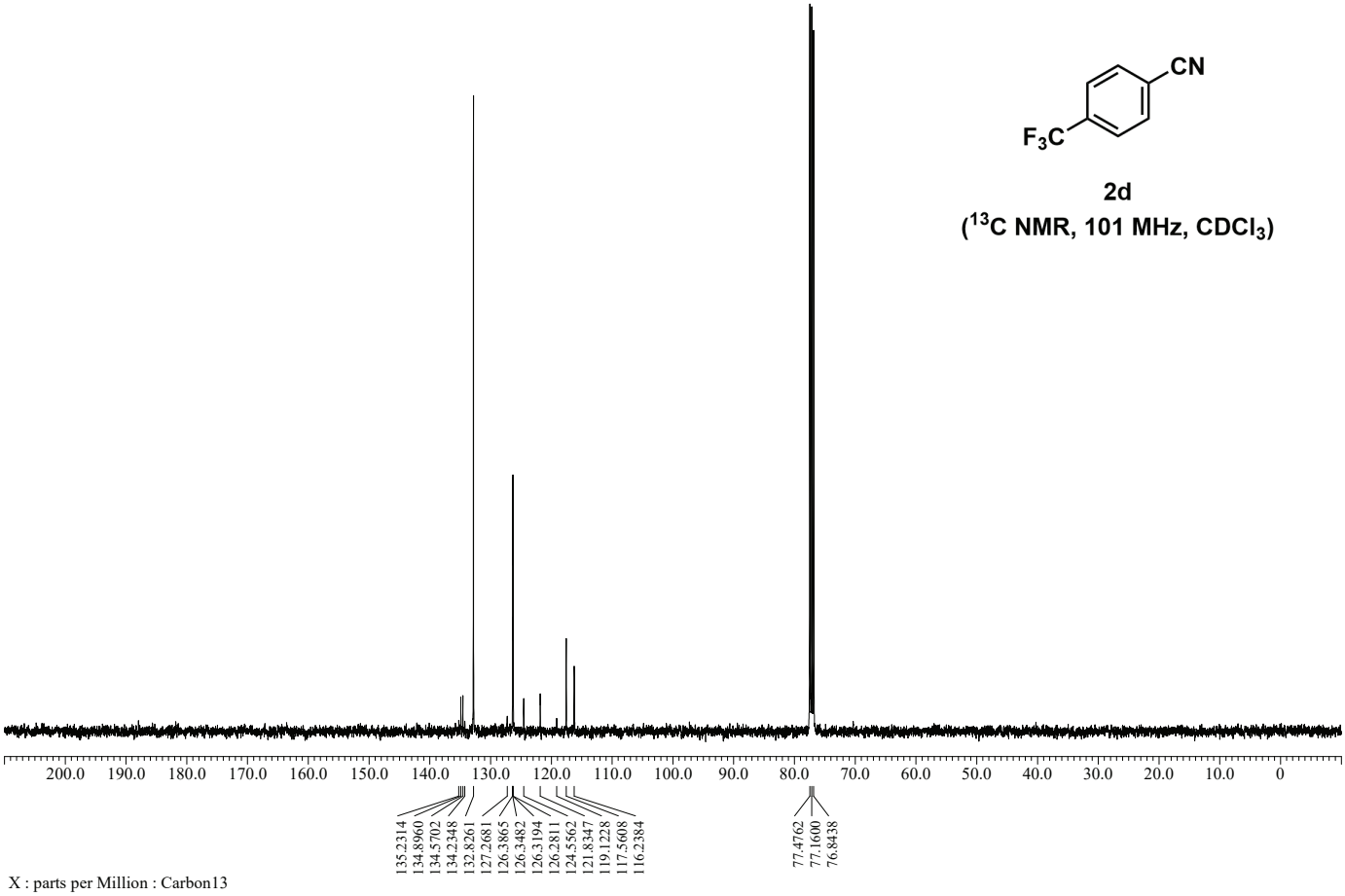
2c

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



2d

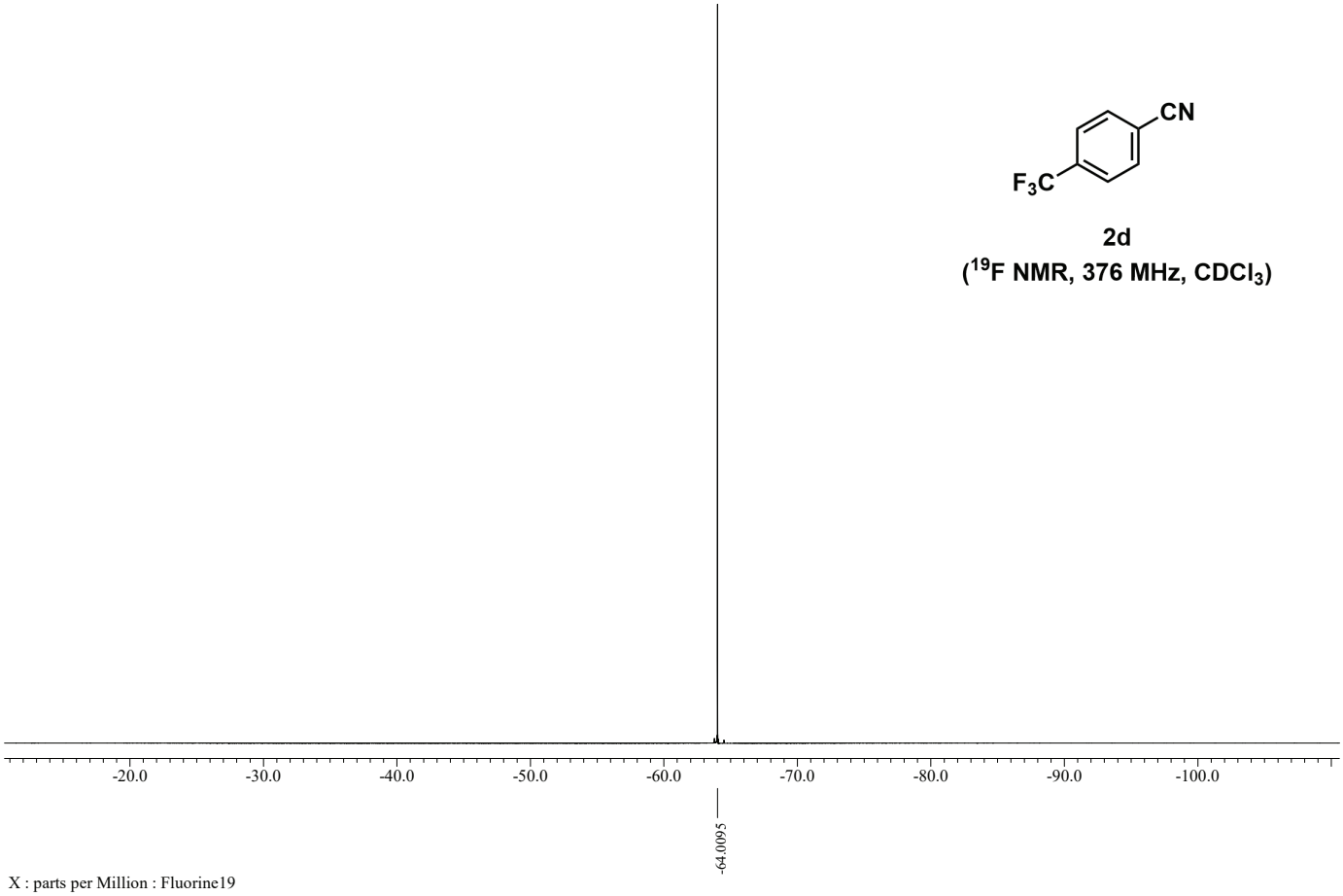
(^{1}H NMR, 400 MHz, $CDCl_3$)



2d

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

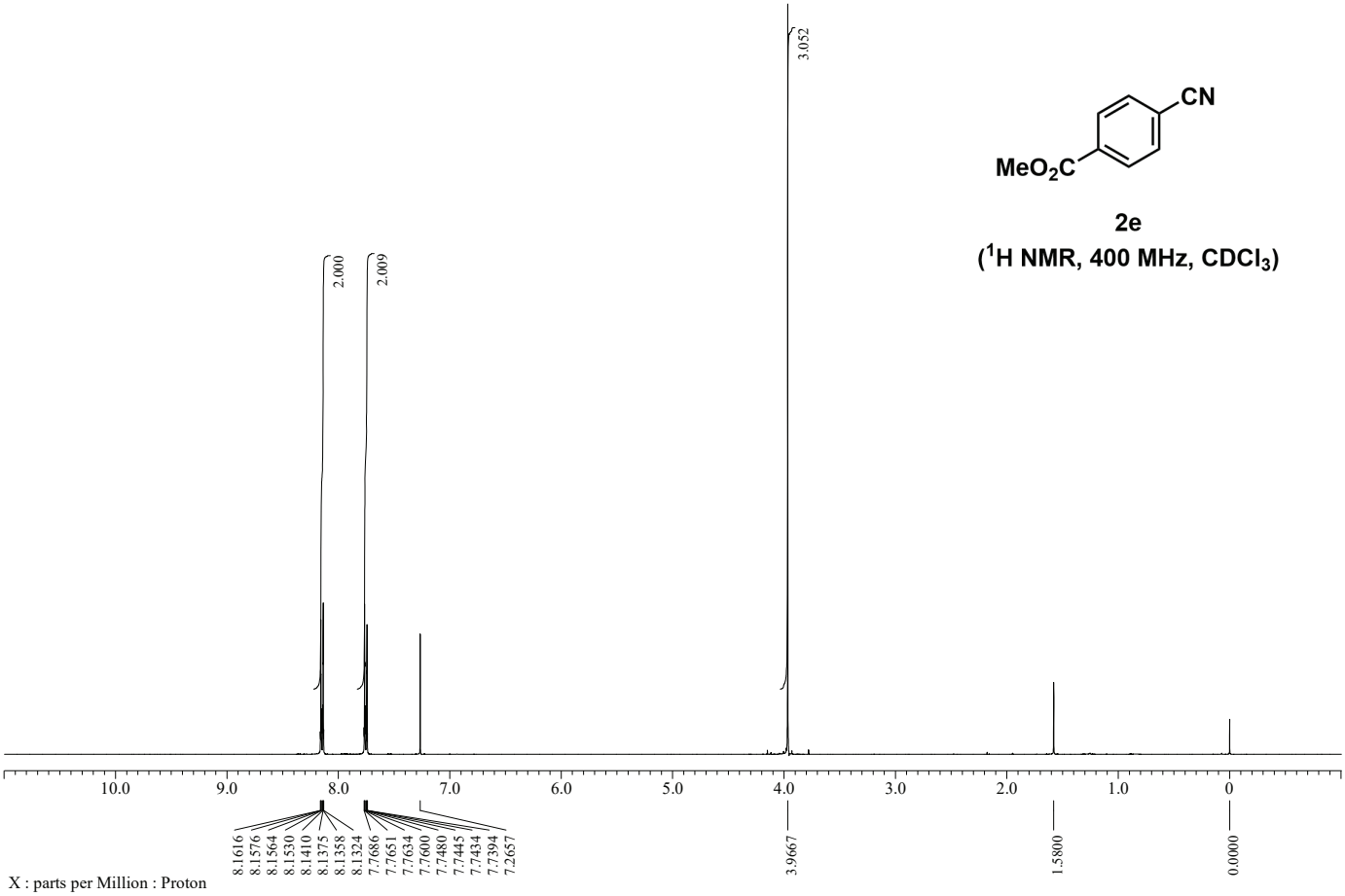
X : parts per Million : Carbon13



2d

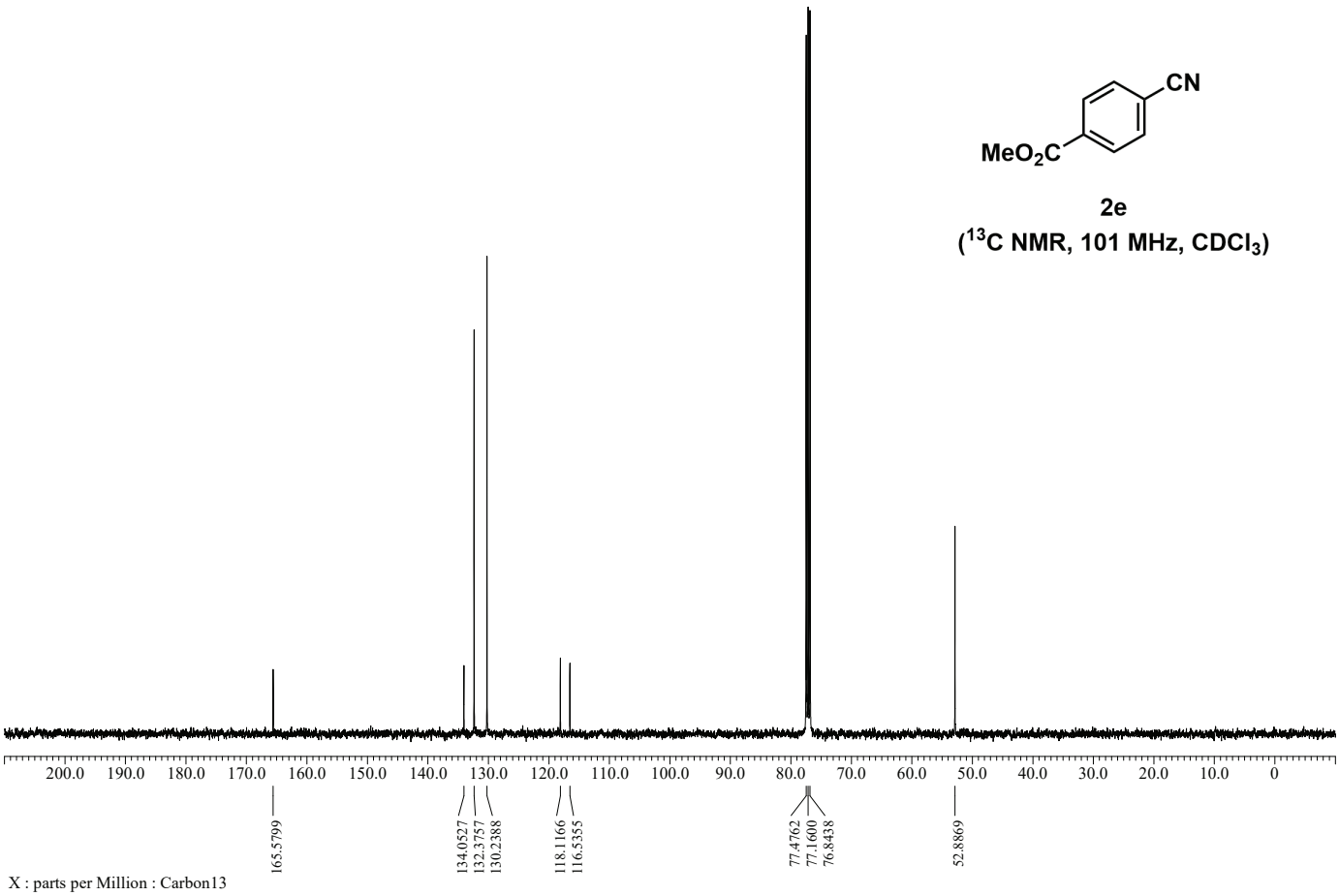
(^{19}F NMR, 376 MHz, $CDCl_3$)

X : parts per Million : Fluorine19



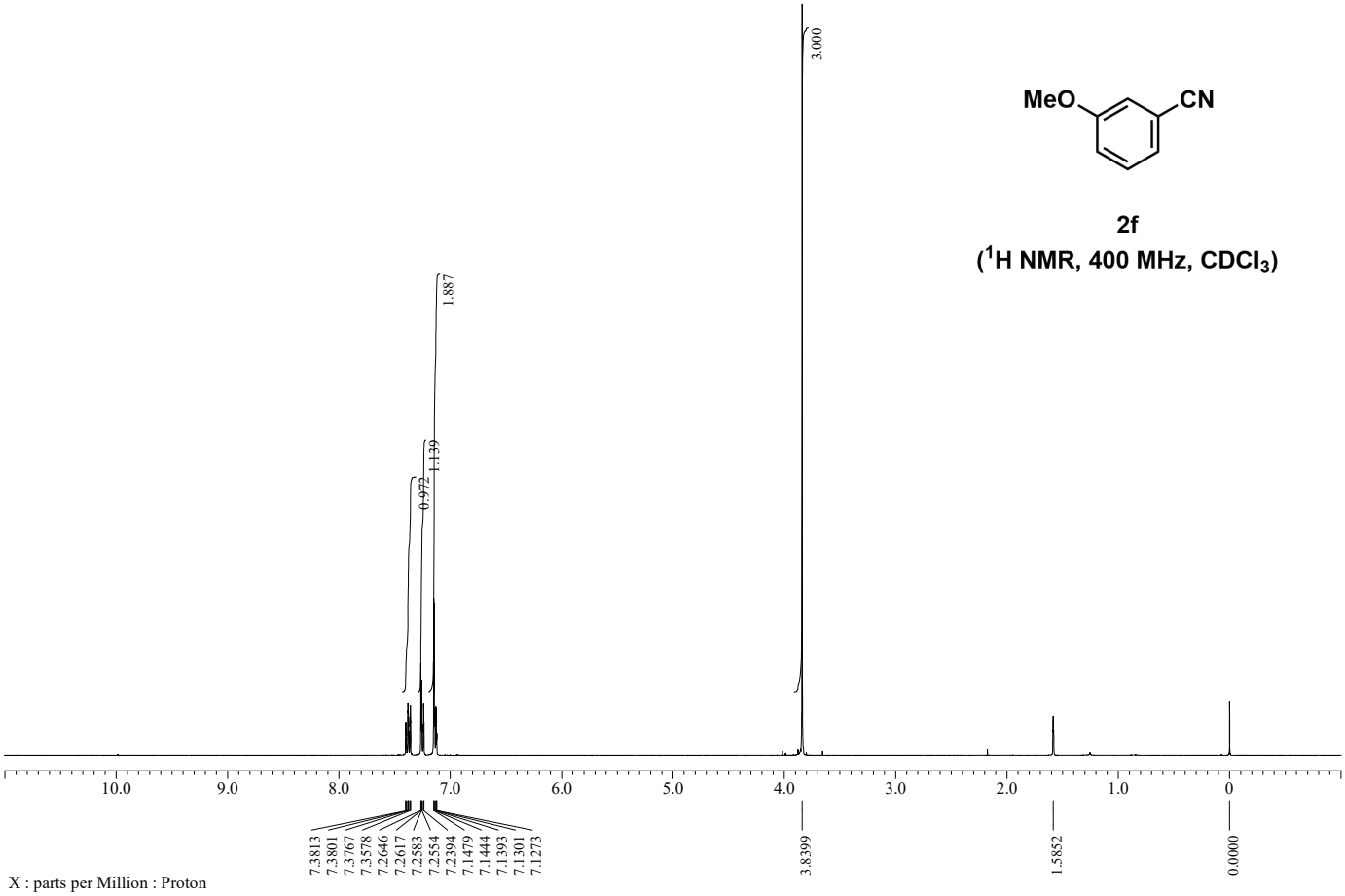
2e

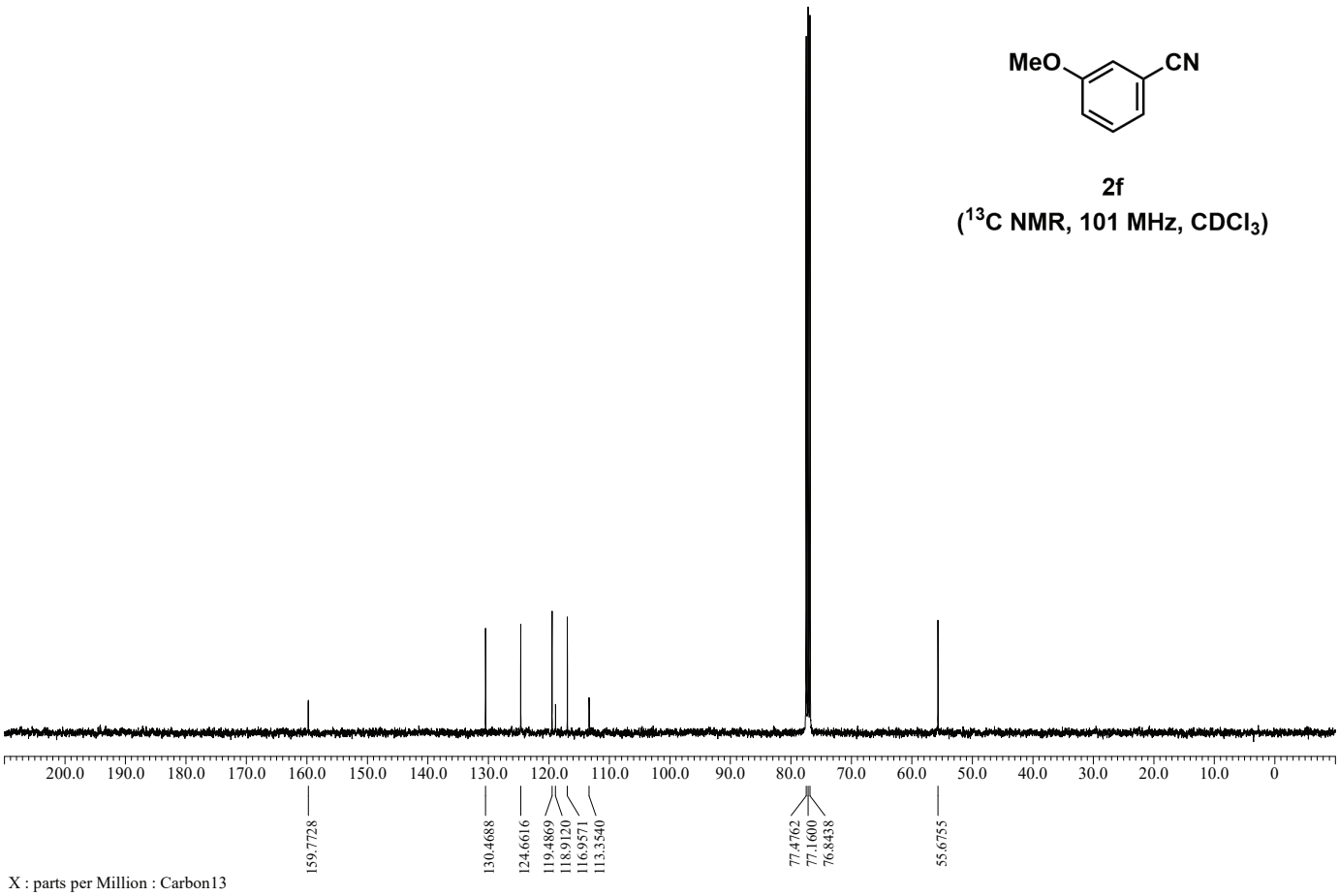
(^{1}H NMR, 400 MHz, $CDCl_3$)

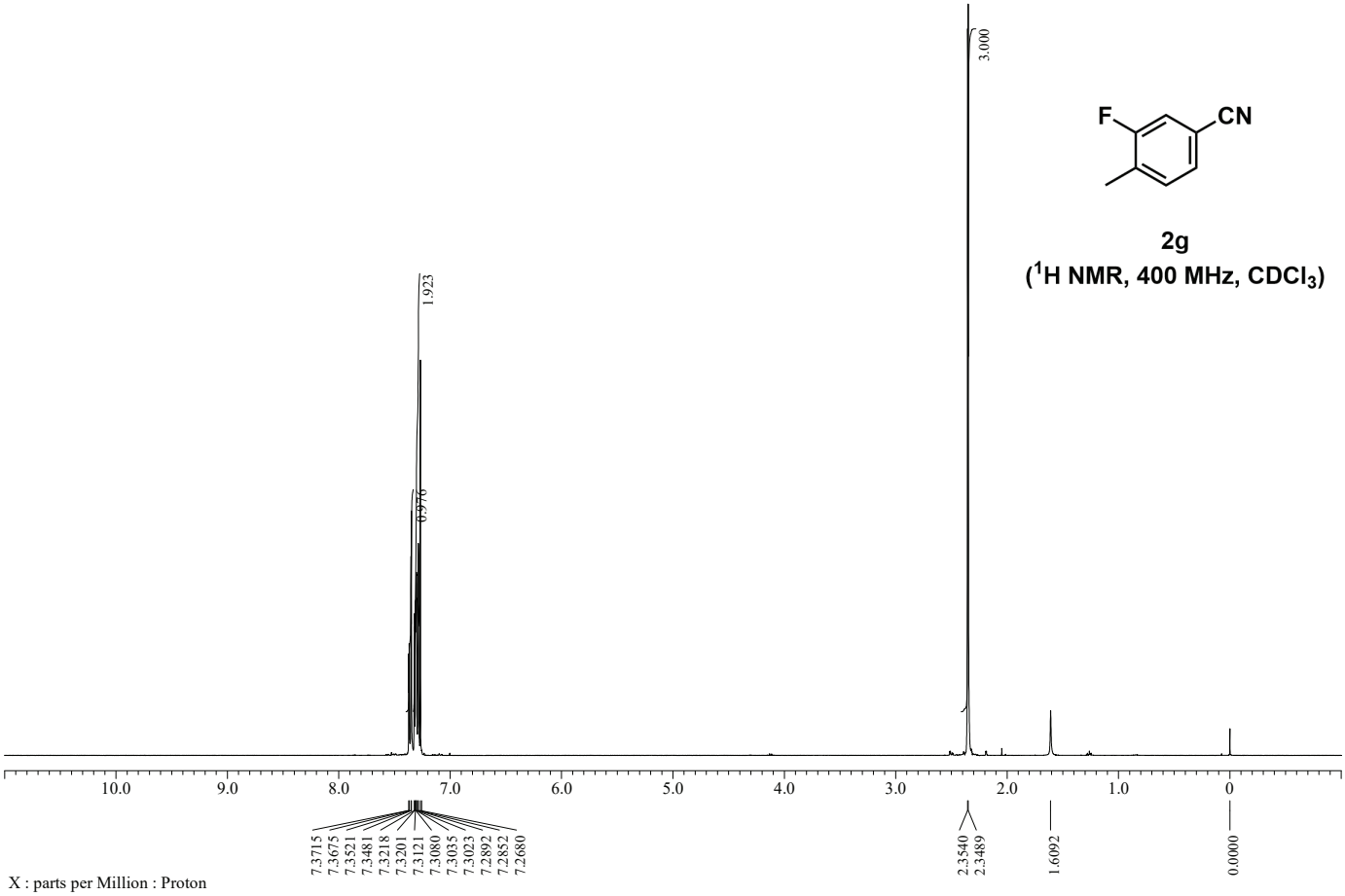


2e

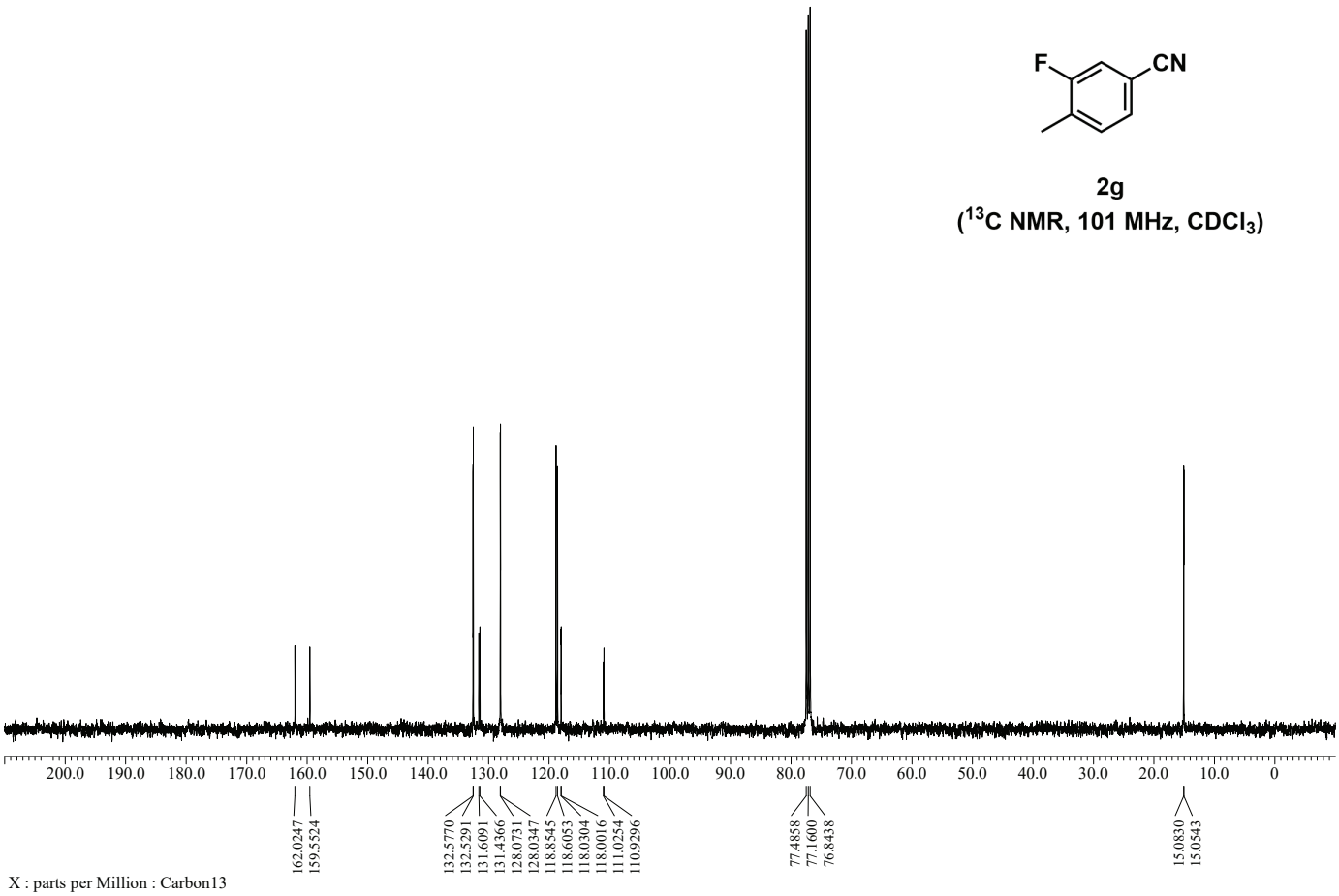
(^{13}C NMR, 101 MHz, $CDCl_3$)


MeO
CN
2f
(1H NMR, 400 MHz, CDCl3)
3.000
1.887
1.139
0.972
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3813
7.3801
7.3767
7.3578
7.2646
7.2617
7.2583
7.2554
7.2394
7.1479
7.1444
7.1393
7.1301
7.1273
3.8399
1.5852
0.0000
X : parts per Million : Proton

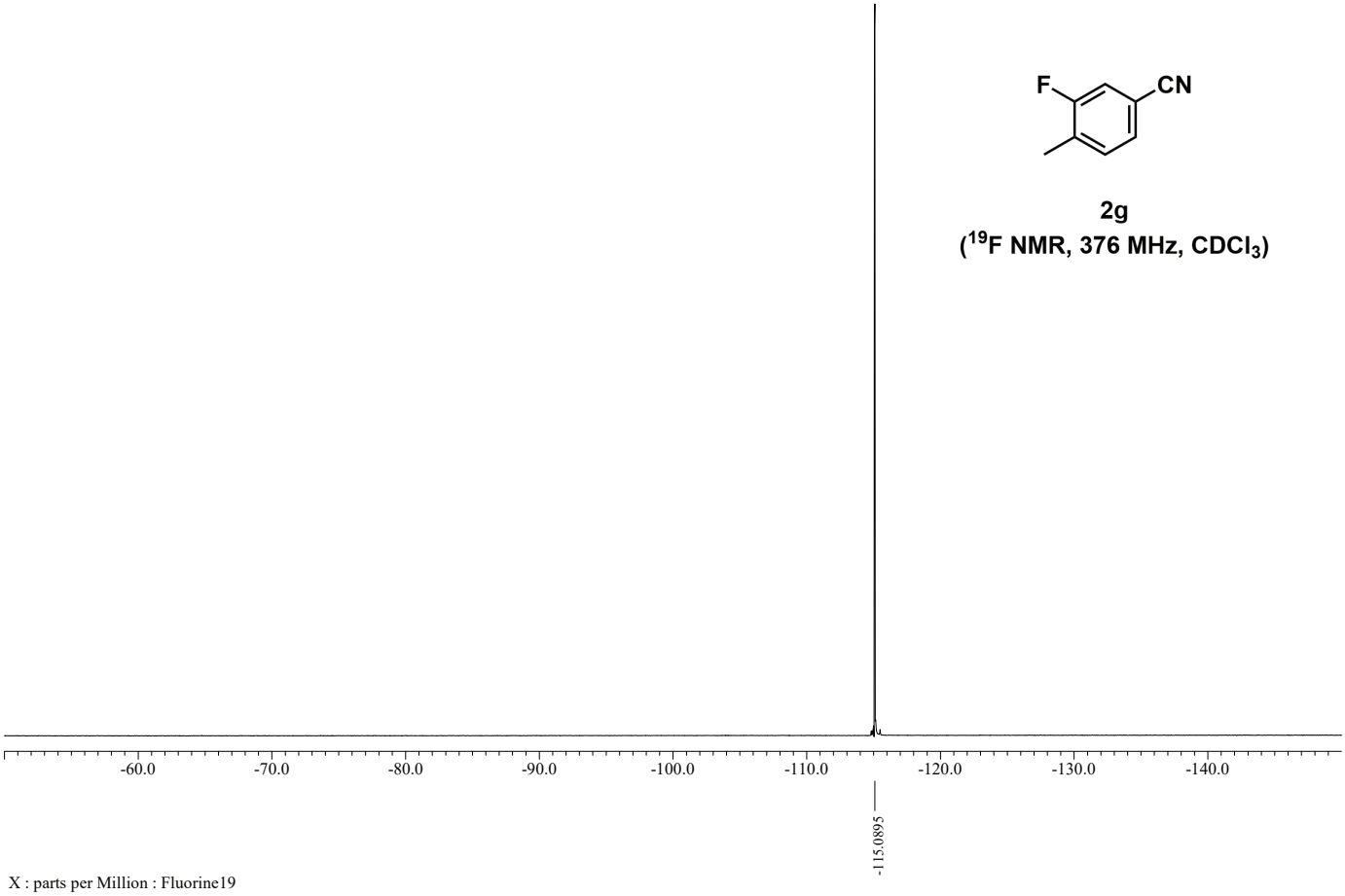

MeO
CN
2f
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.7728
130.4688
124.6616
119.4869
118.9120
116.9571
113.3540
77.4762
77.1600
76.8438
55.6755
X : parts per Million : Carbon13



2g
(^{1}H NMR, 400 MHz, $CDCl_3$)

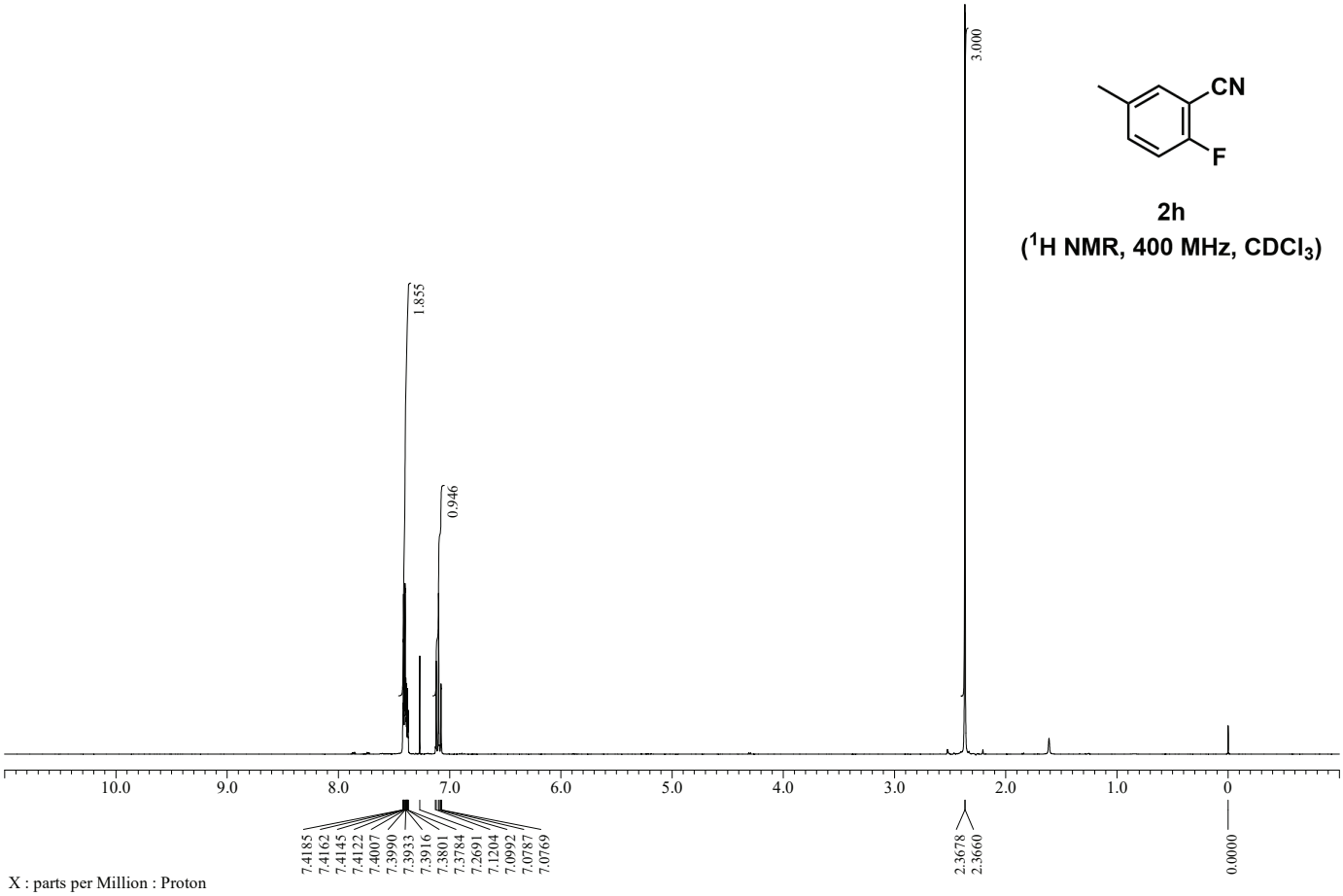


2g
(^{13}C NMR, 101 MHz, $CDCl_3$)



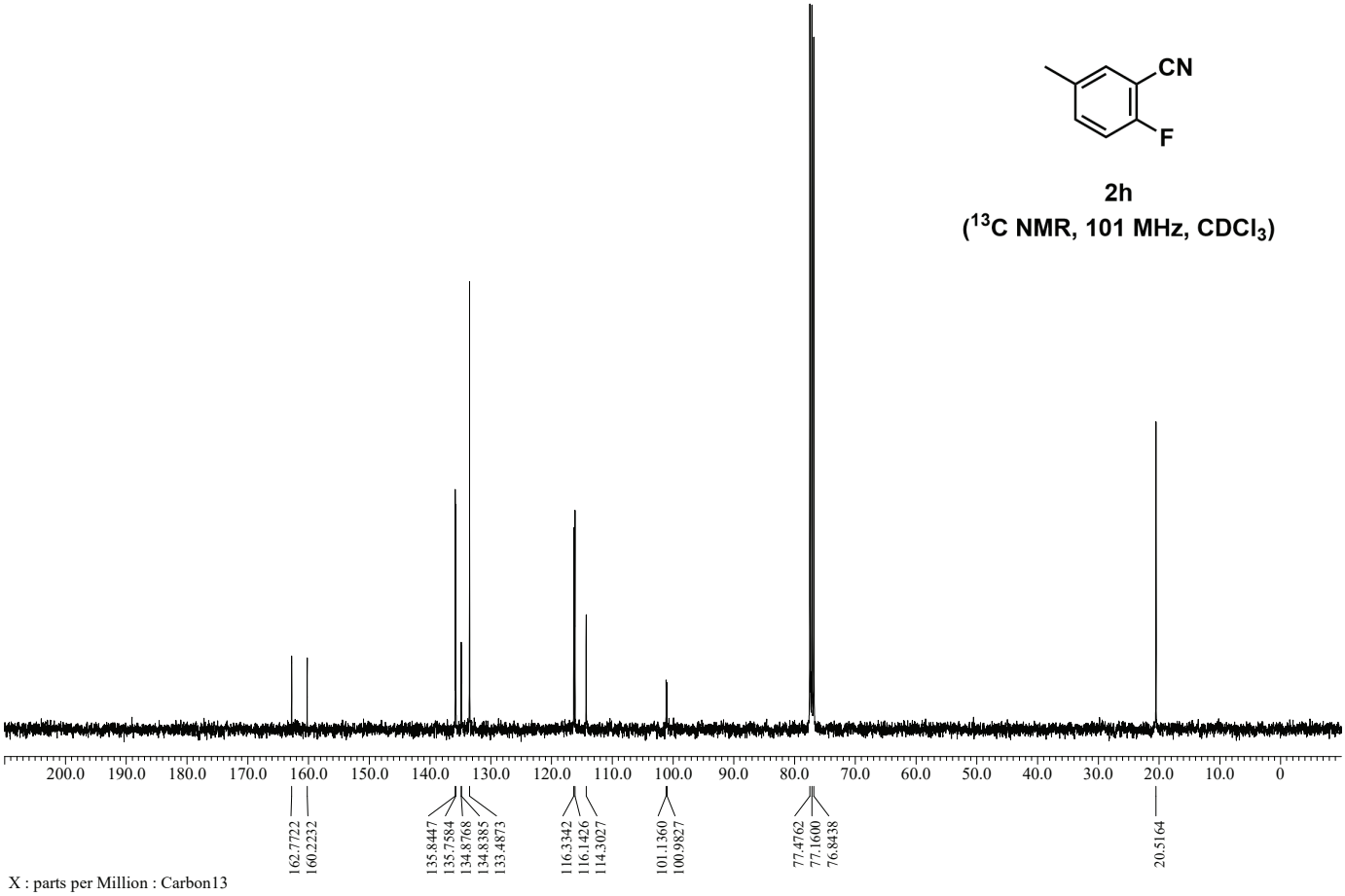
2g
(^{19}F NMR, 376 MHz, $CDCl_3$)

X : parts per Million : Fluorine19



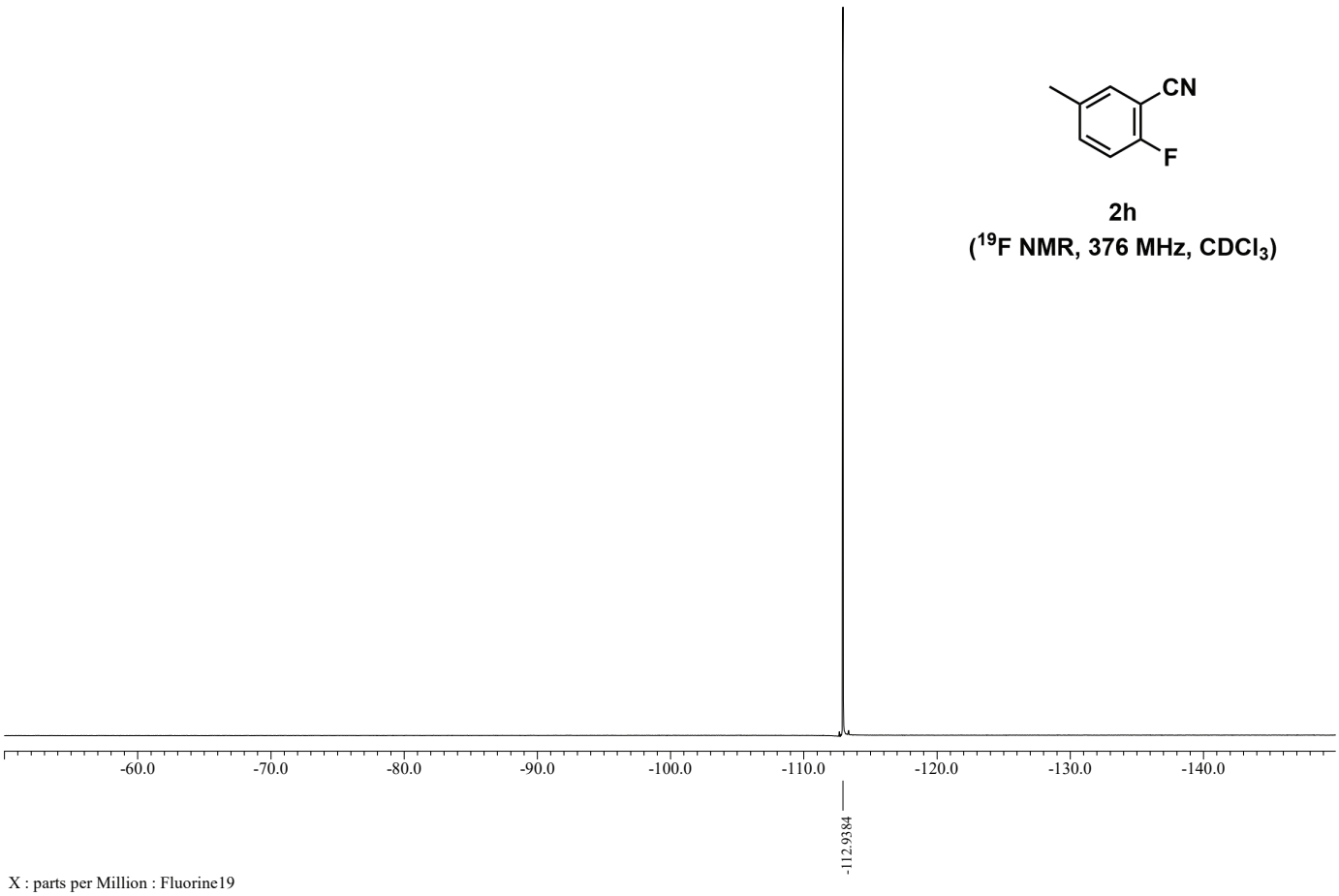
2h
(^{1}H NMR, 400 MHz, $CDCl_3$)

X : parts per Million : Proton



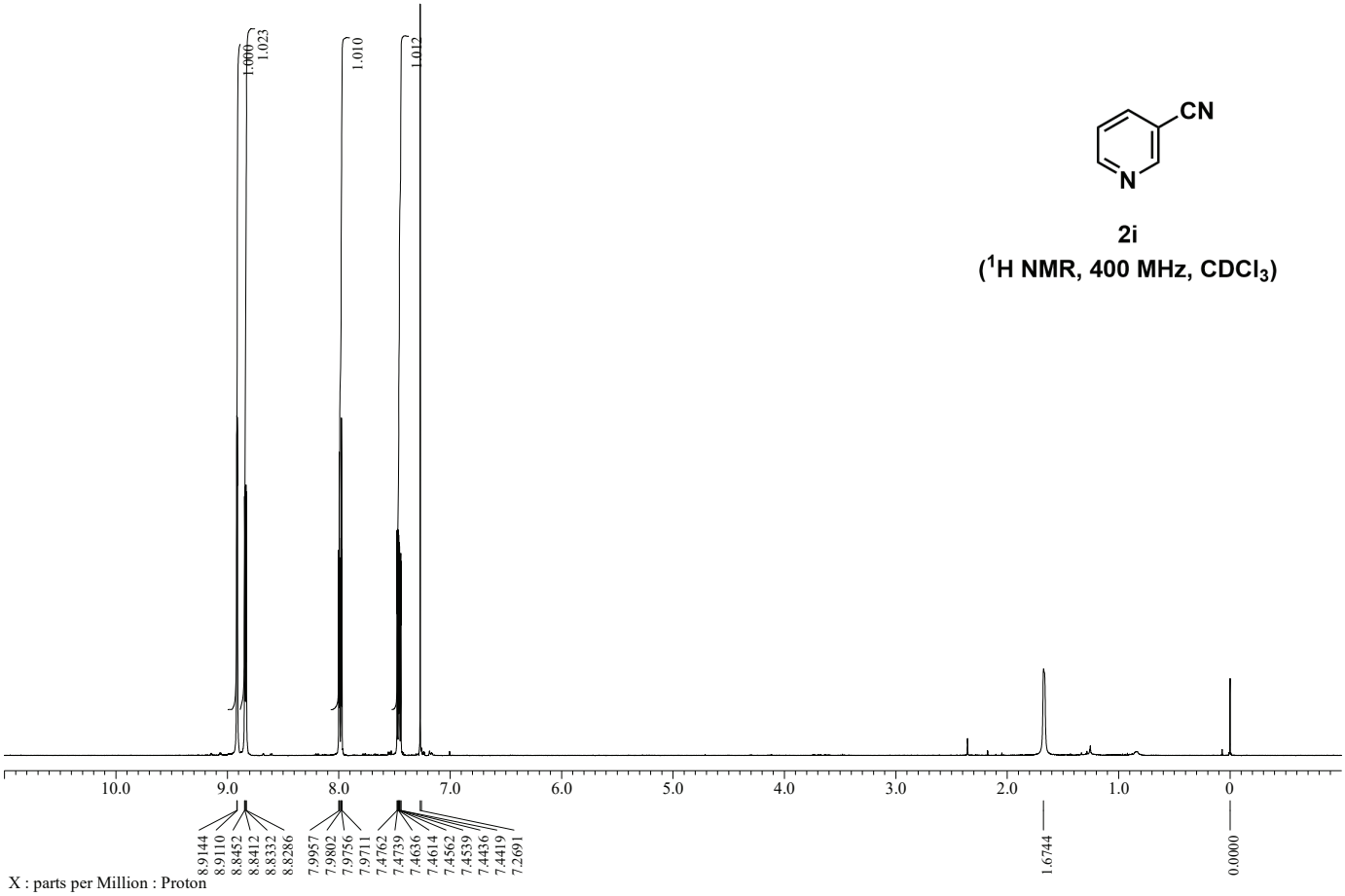
2h
(^{13}C NMR, 101 MHz, $CDCl_3$)

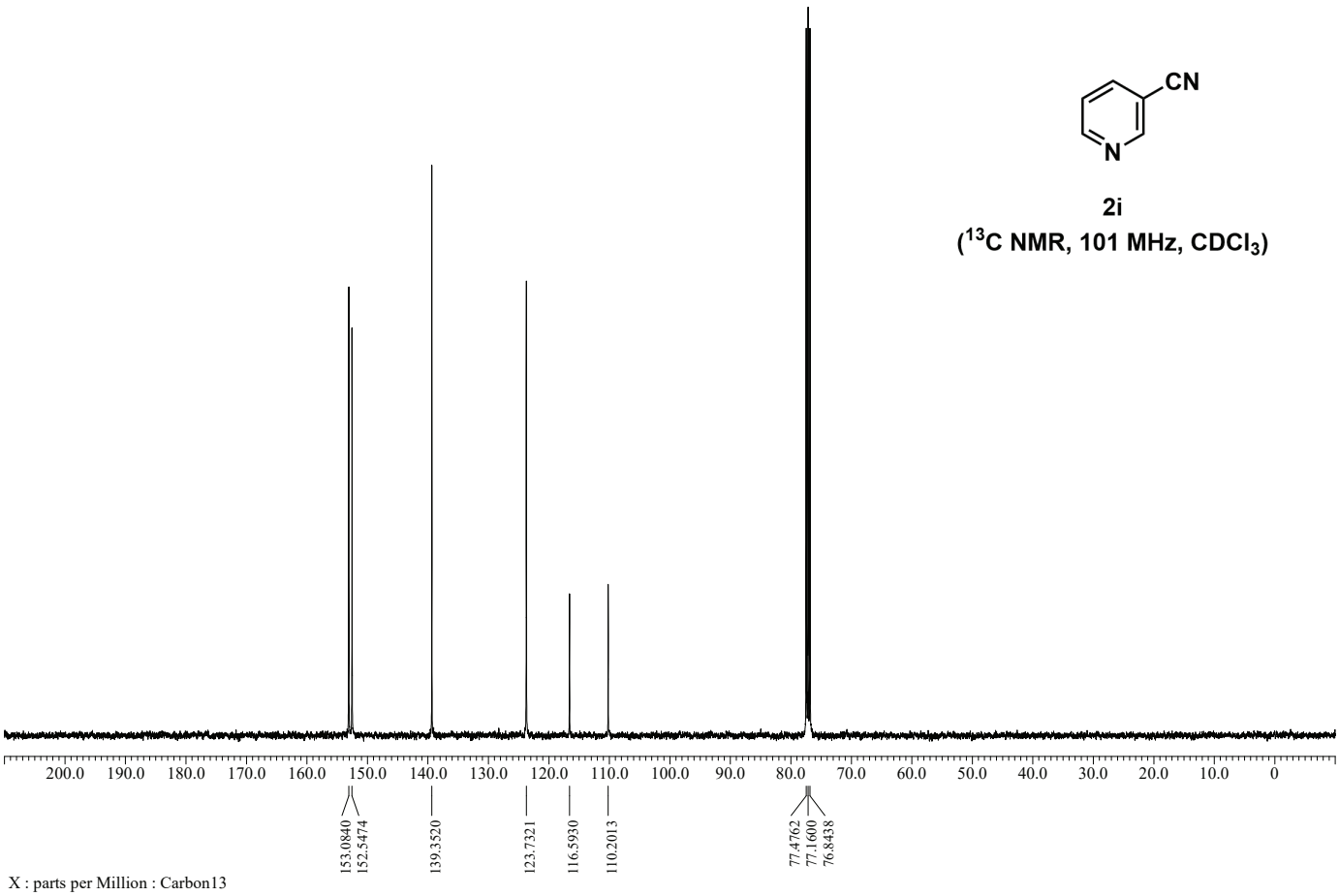
X : parts per Million : Carbon13

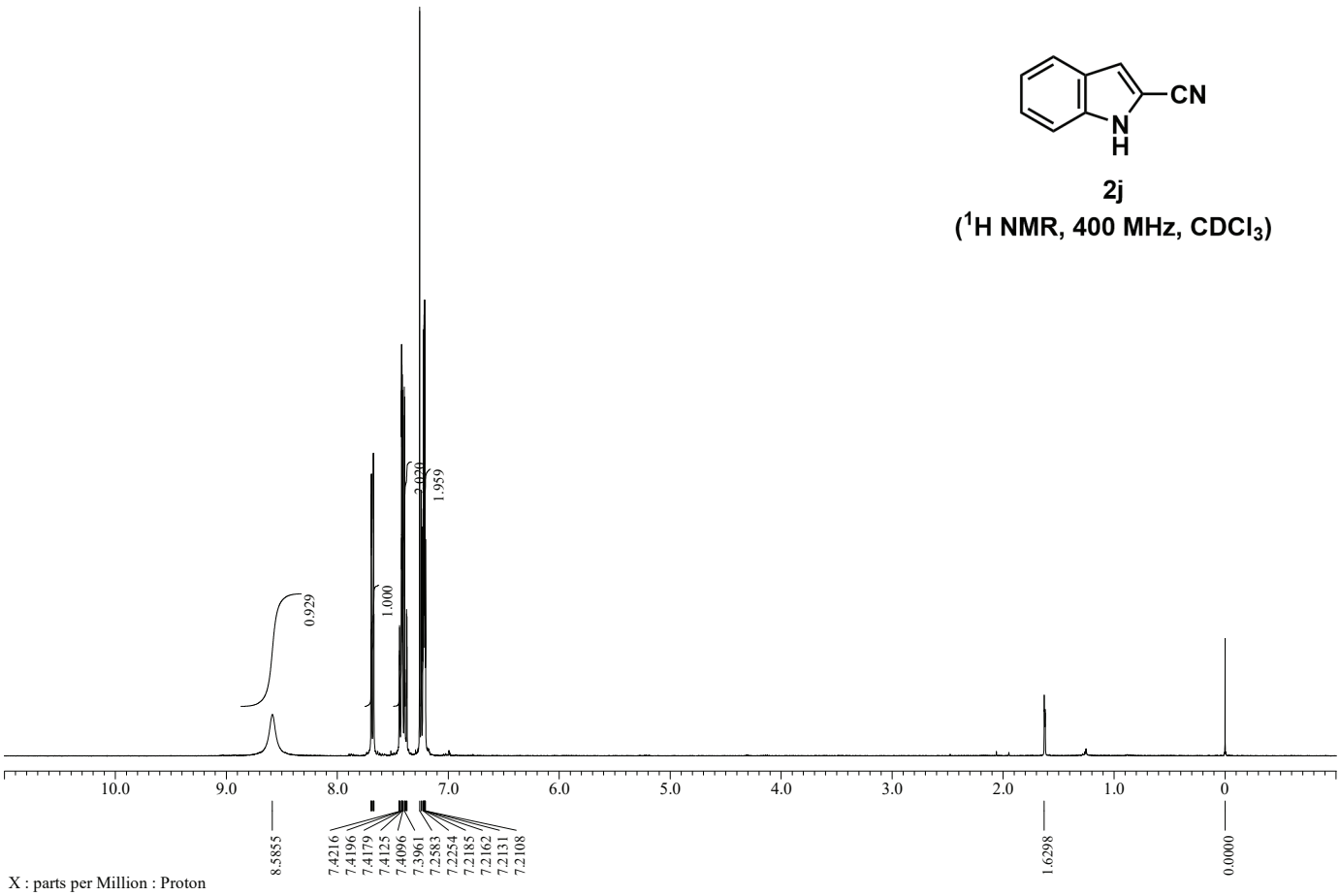


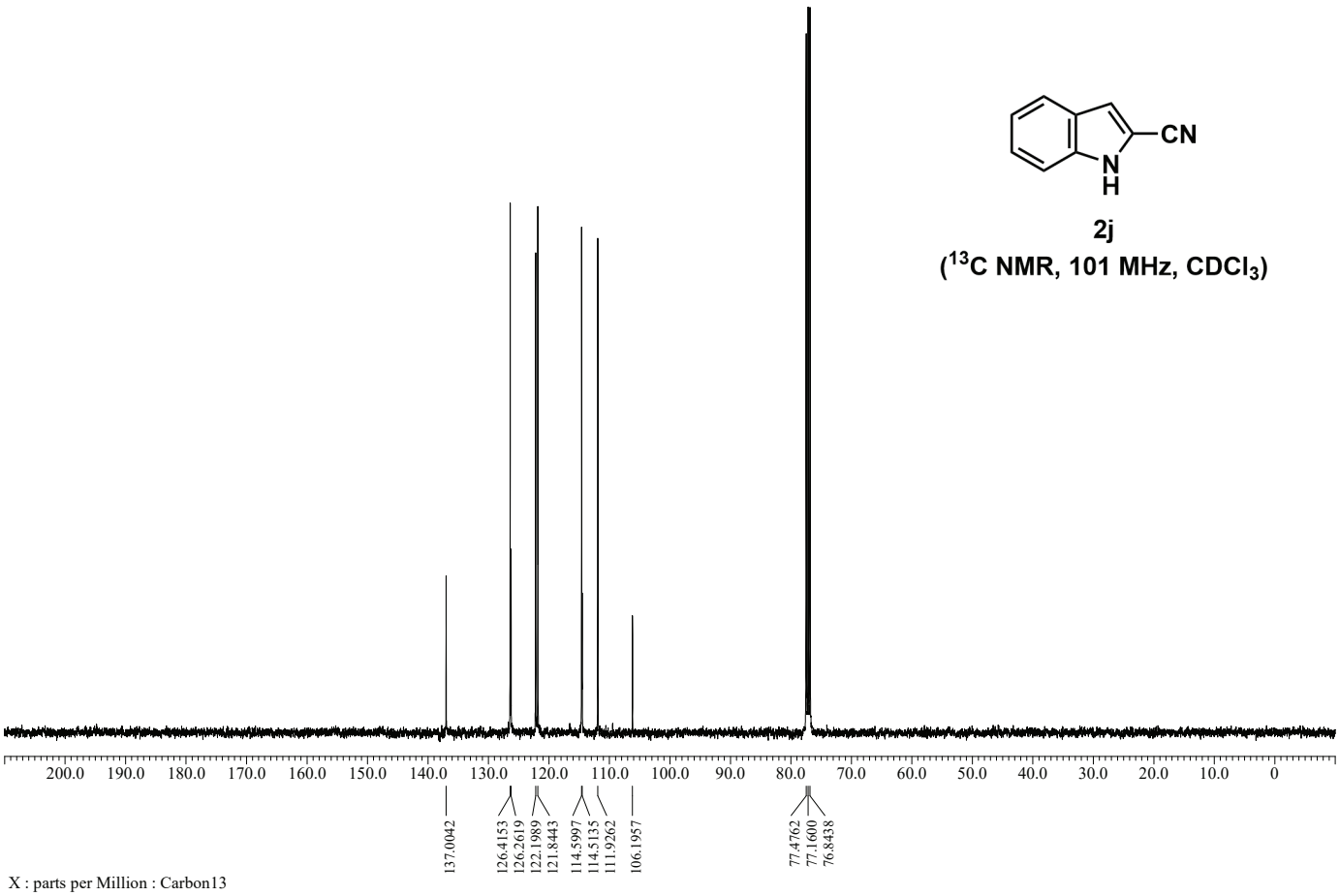
2h
(^{19}F NMR, 376 MHz, $CDCl_3$)

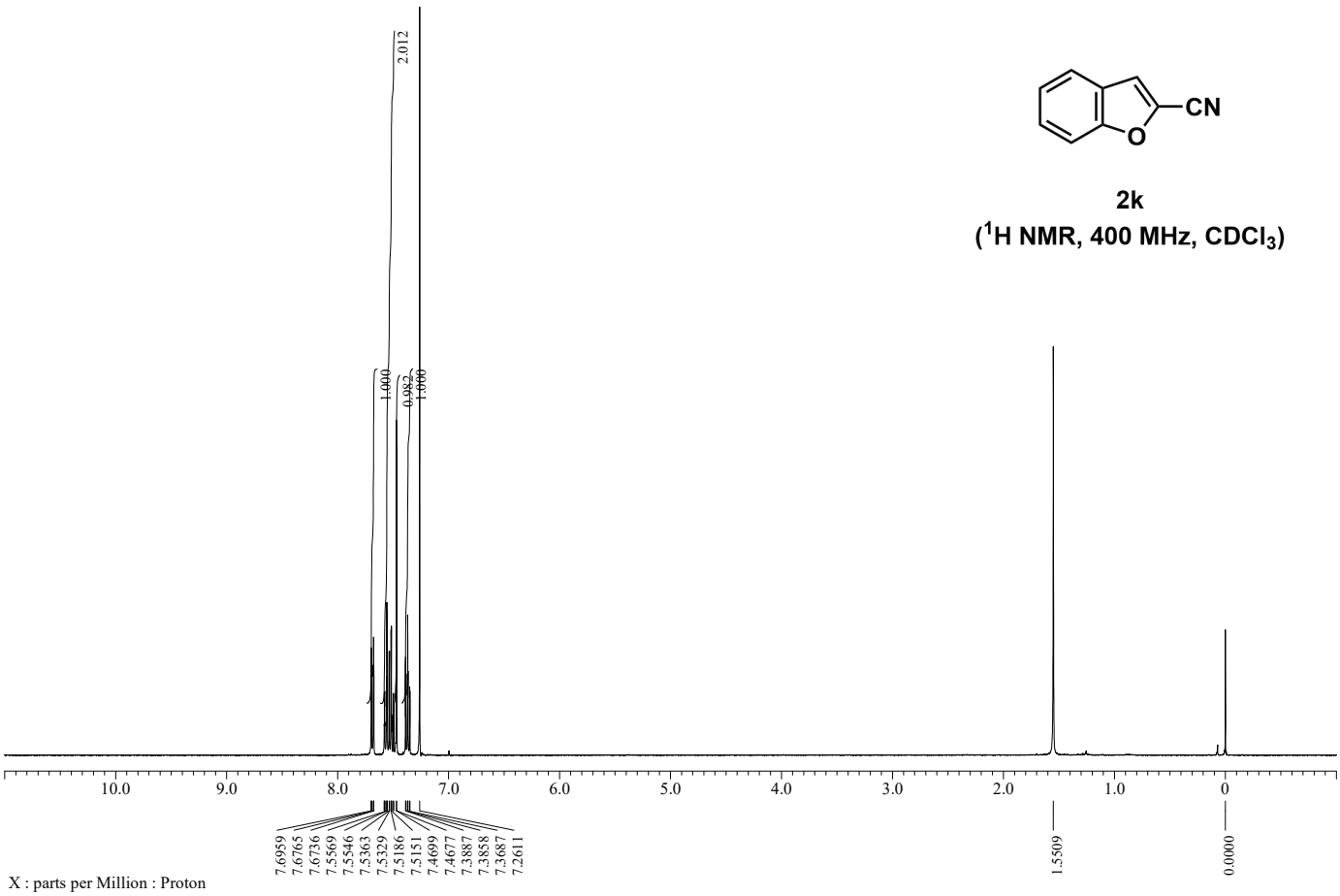
X : parts per Million : Fluorine19


1.000
1.023
1.010
1.012
CN
N
2i
(1H NMR, 400 MHz, CDCl3)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.9144
8.9110
8.8452
8.8412
8.8332
8.8286
7.9957
7.9802
7.9756
7.9711
7.4762
7.4739
7.4636
7.4614
7.4562
7.4539
7.4436
7.4419
7.2691
1.6744
0.0000
X : parts per Million : Proton


CN
N
2i
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.0840
152.5474
139.3520
123.7321
116.5930
110.2013
77.4762
77.1600
76.8438
X : parts per Million : Carbon13

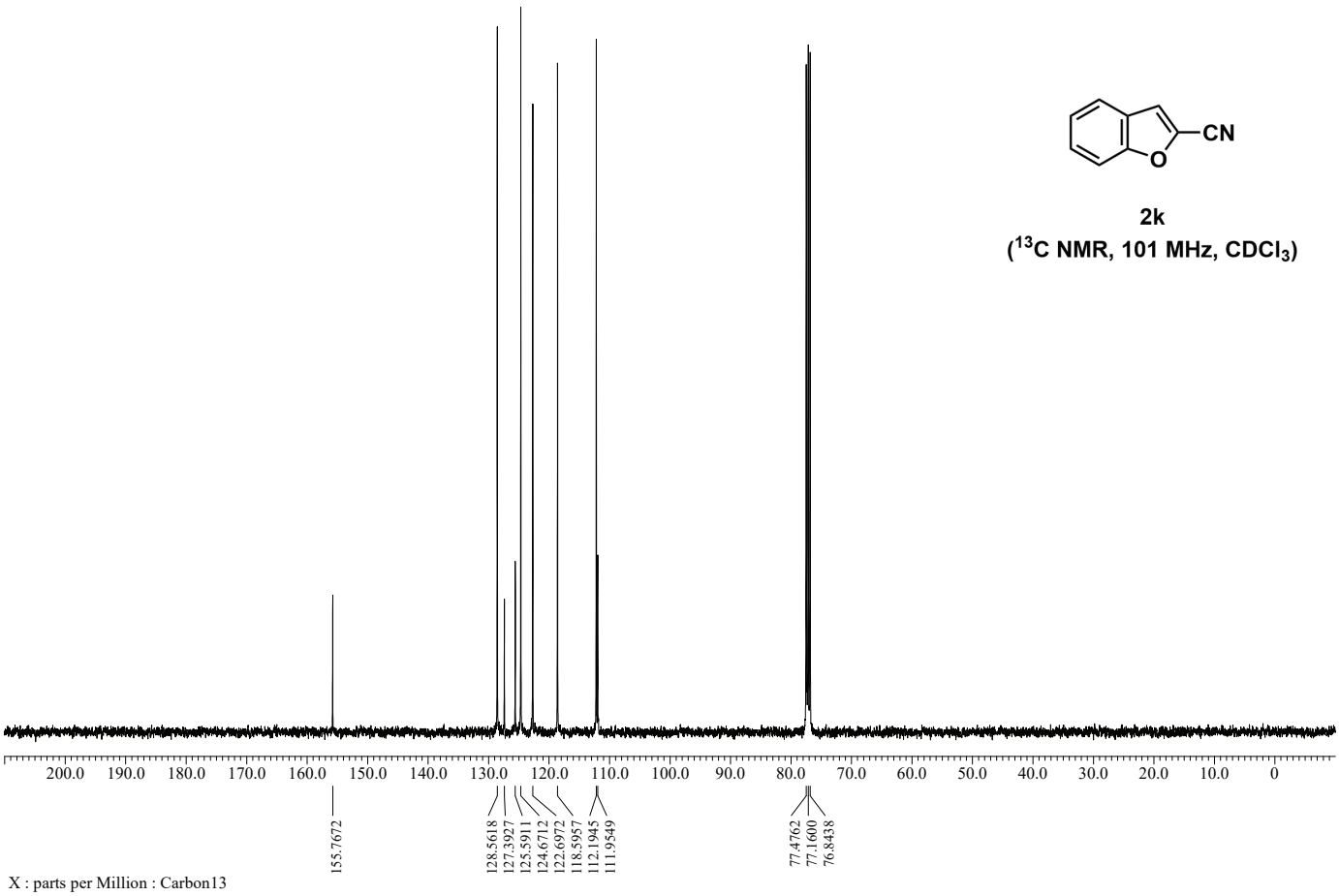

CN
N
H
2j
(1H NMR, 400 MHz, CDCl3)
0.929
1.000
3.030
1.959
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.5855
7.4216
7.4196
7.4179
7.4125
7.4096
7.3961
7.2583
7.2254
7.2185
7.2162
7.2131
7.2108
1.6298
0.0000
X : parts per Million : Proton


CN
N
H
2j
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
137.0042
126.4153
126.2619
122.1989
121.8443
114.5997
114.5135
111.9262
106.1957
77.4762
77.1600
76.8438
X : parts per Million : Carbon13



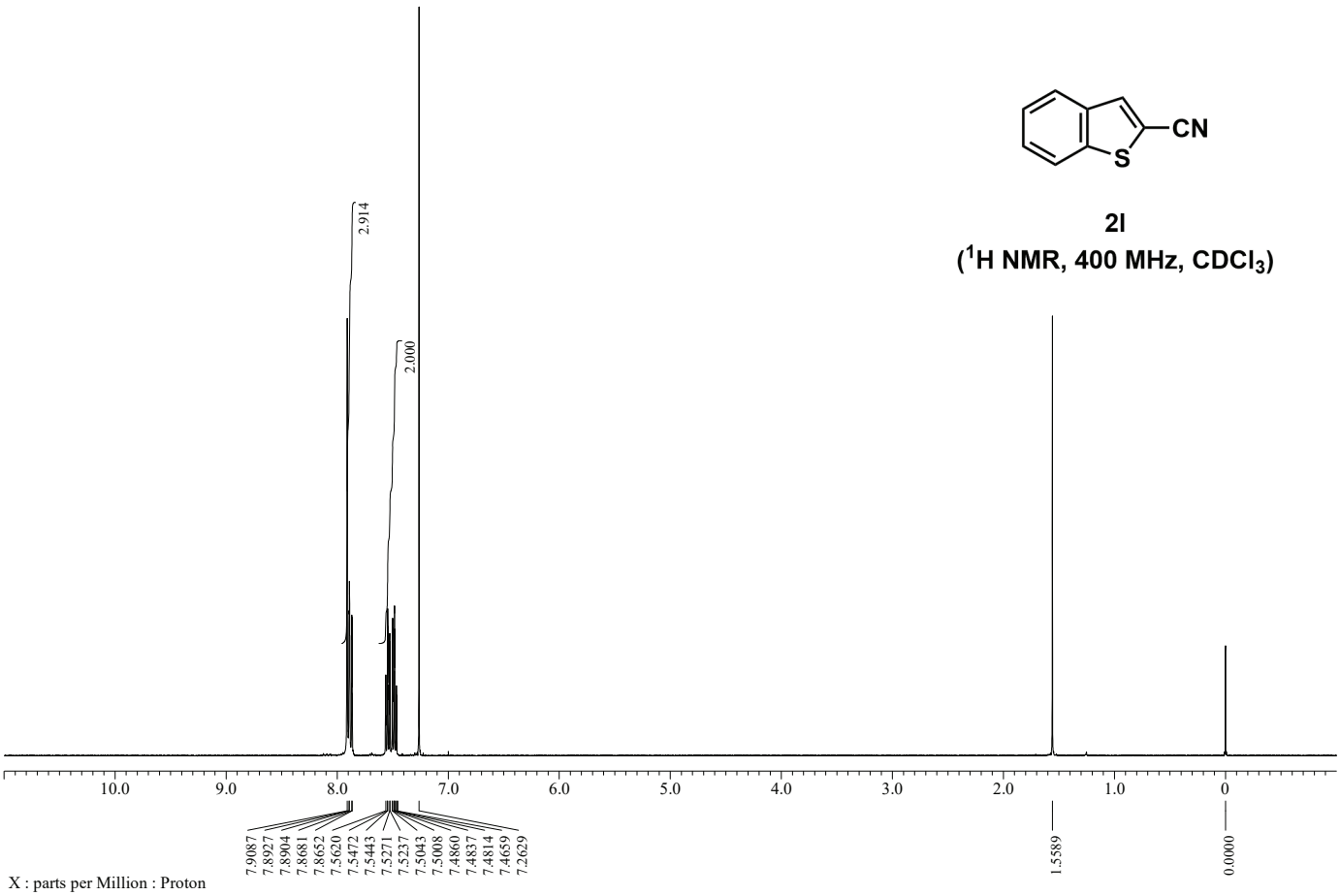
2k

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



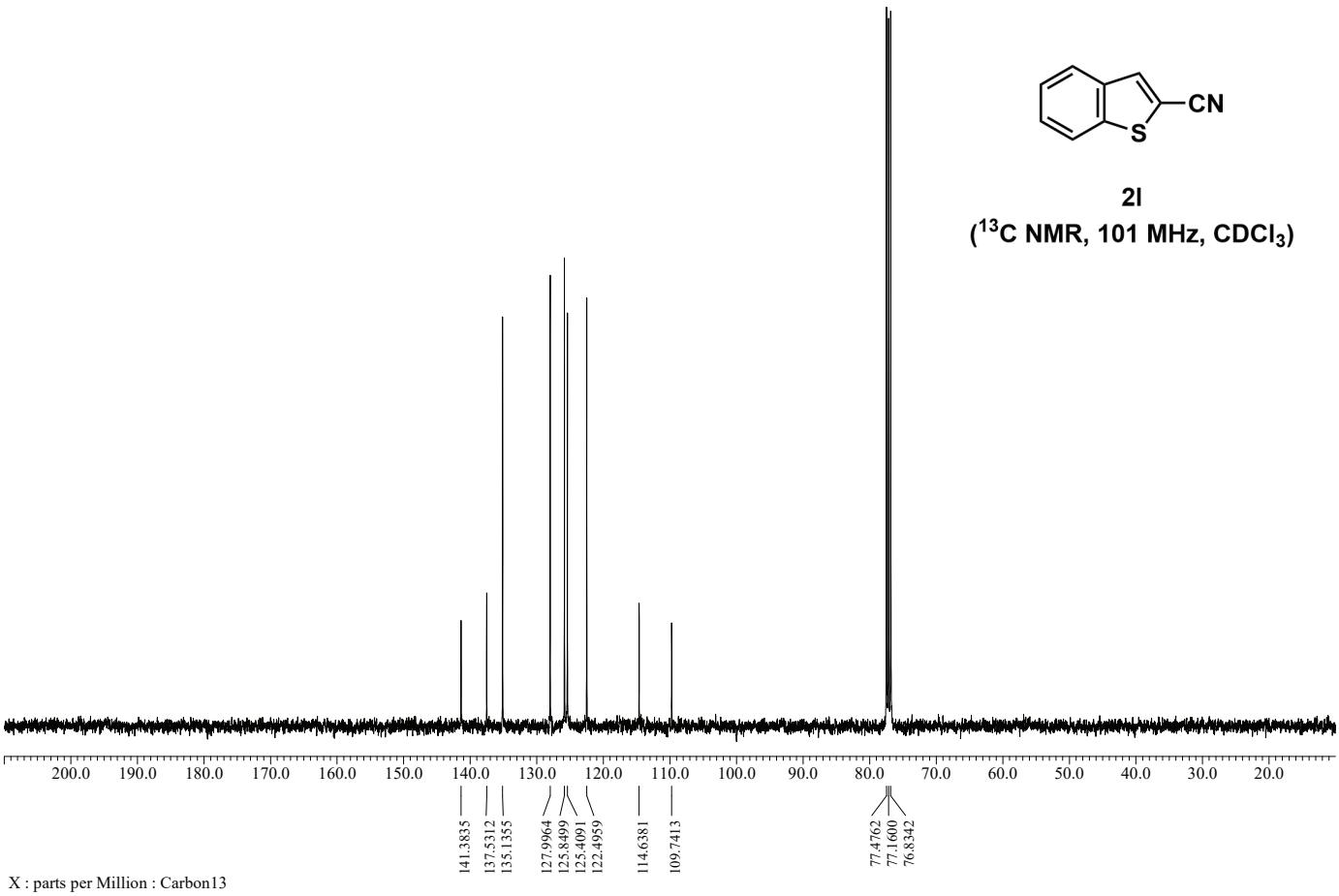
2k

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



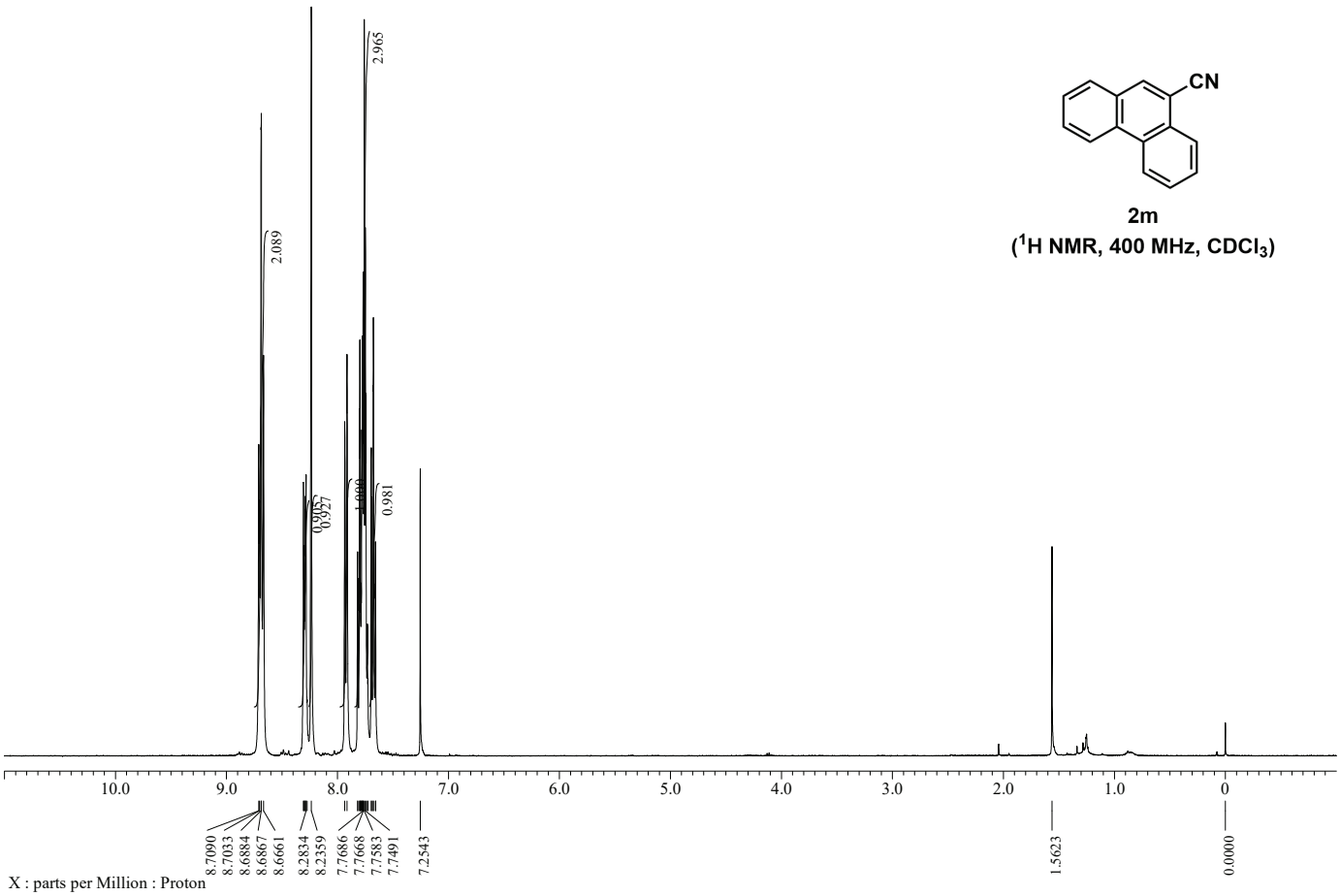
2l

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

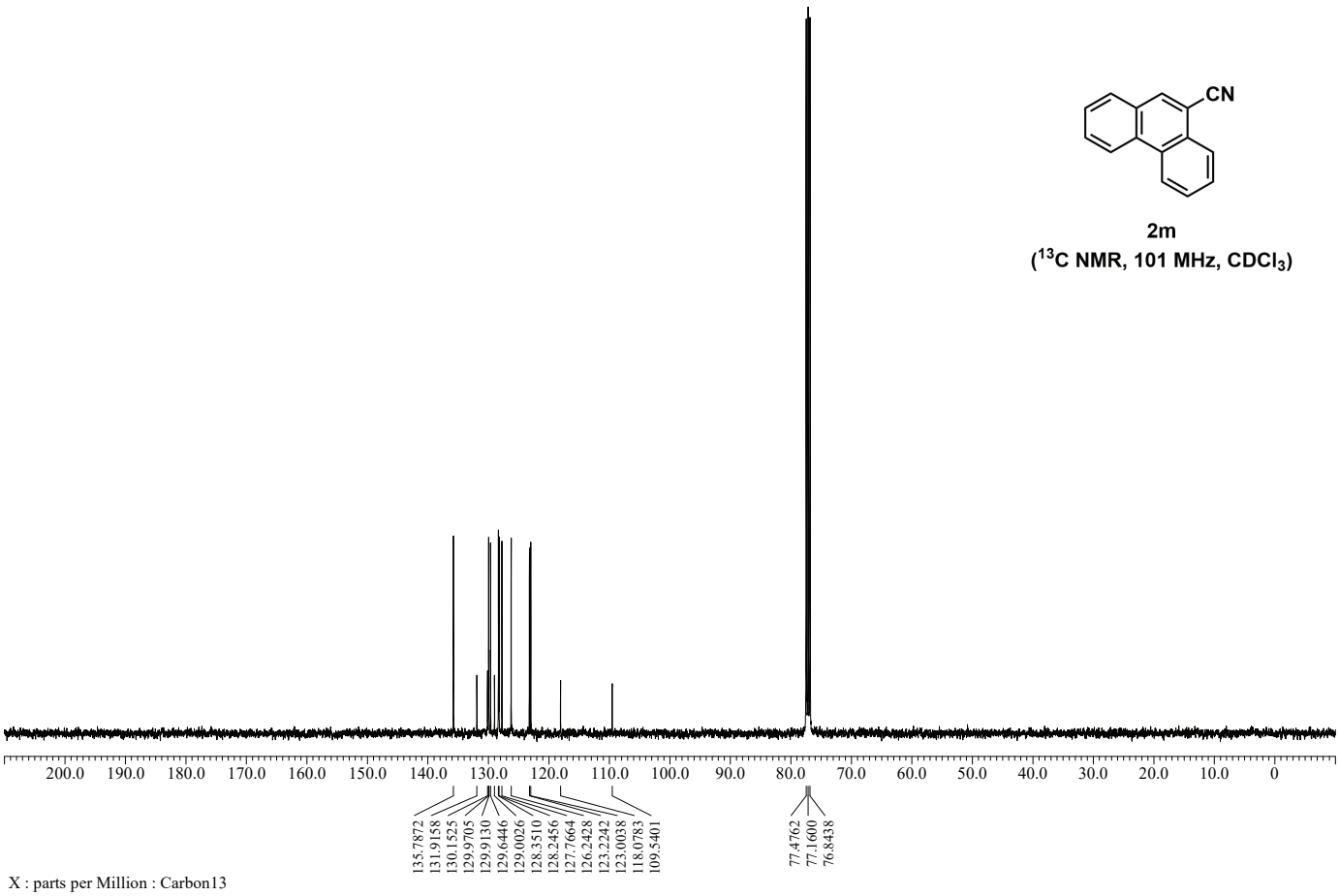


2l

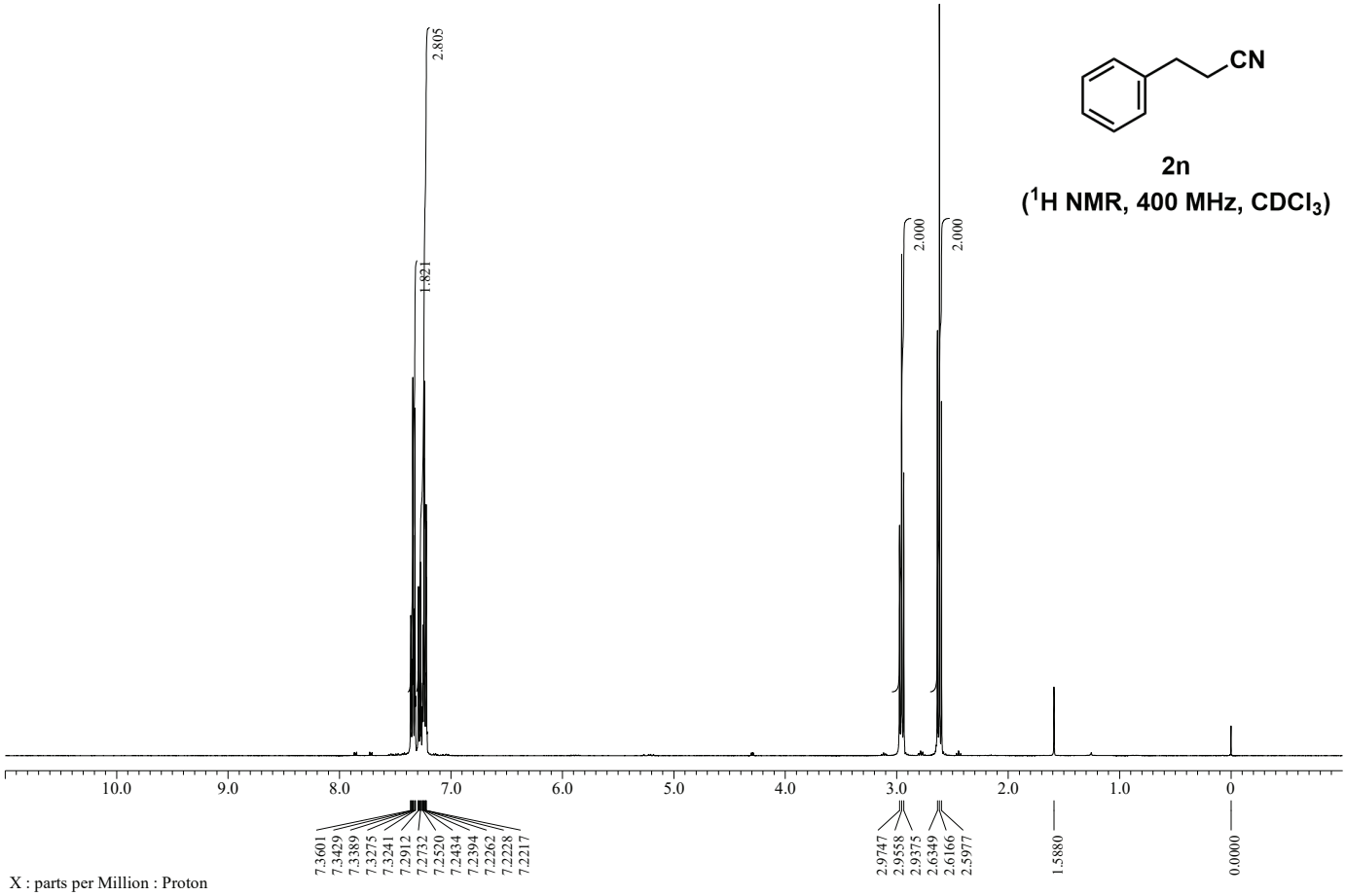
(^{13}C NMR, 101 MHz, $CDCl_3$)

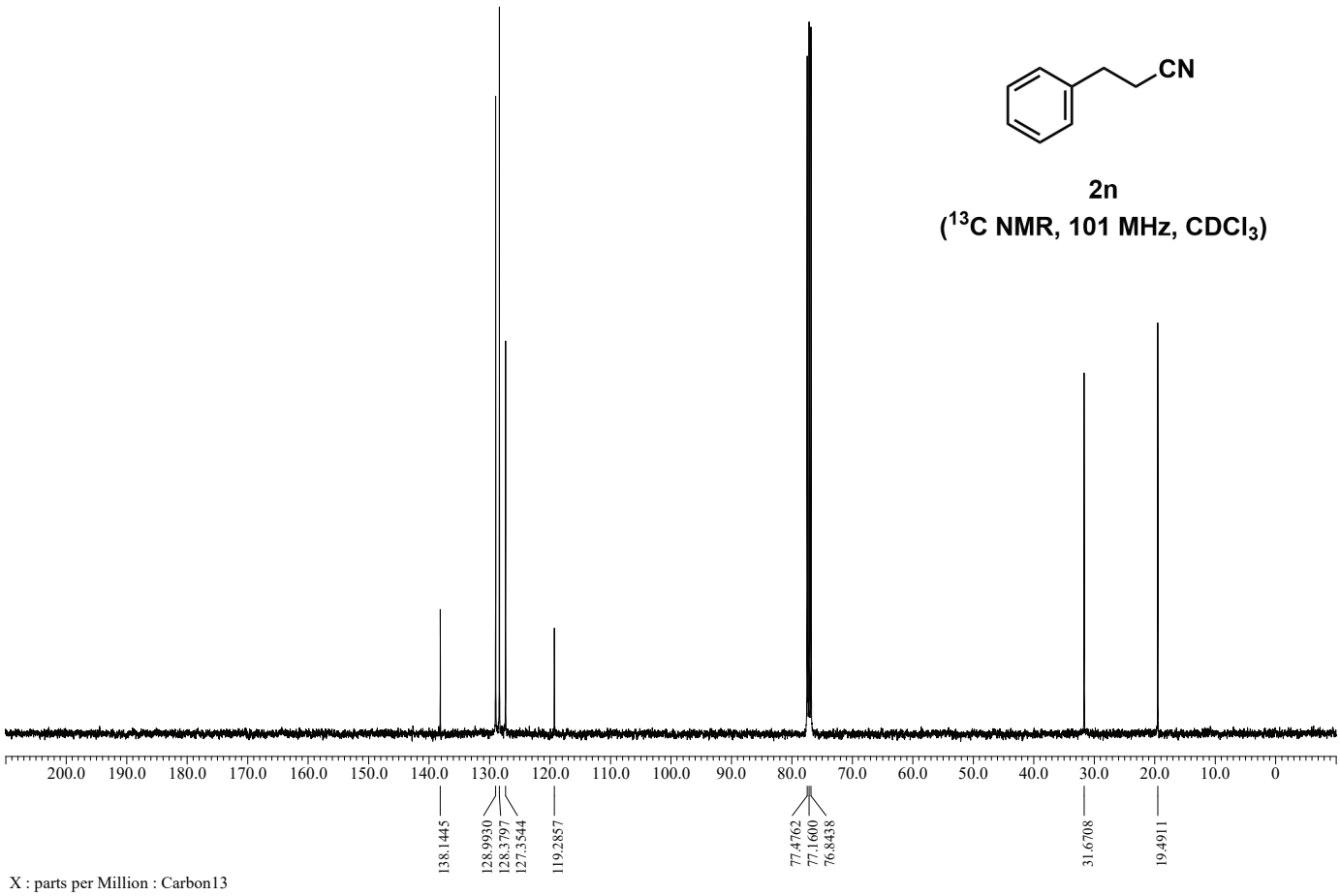


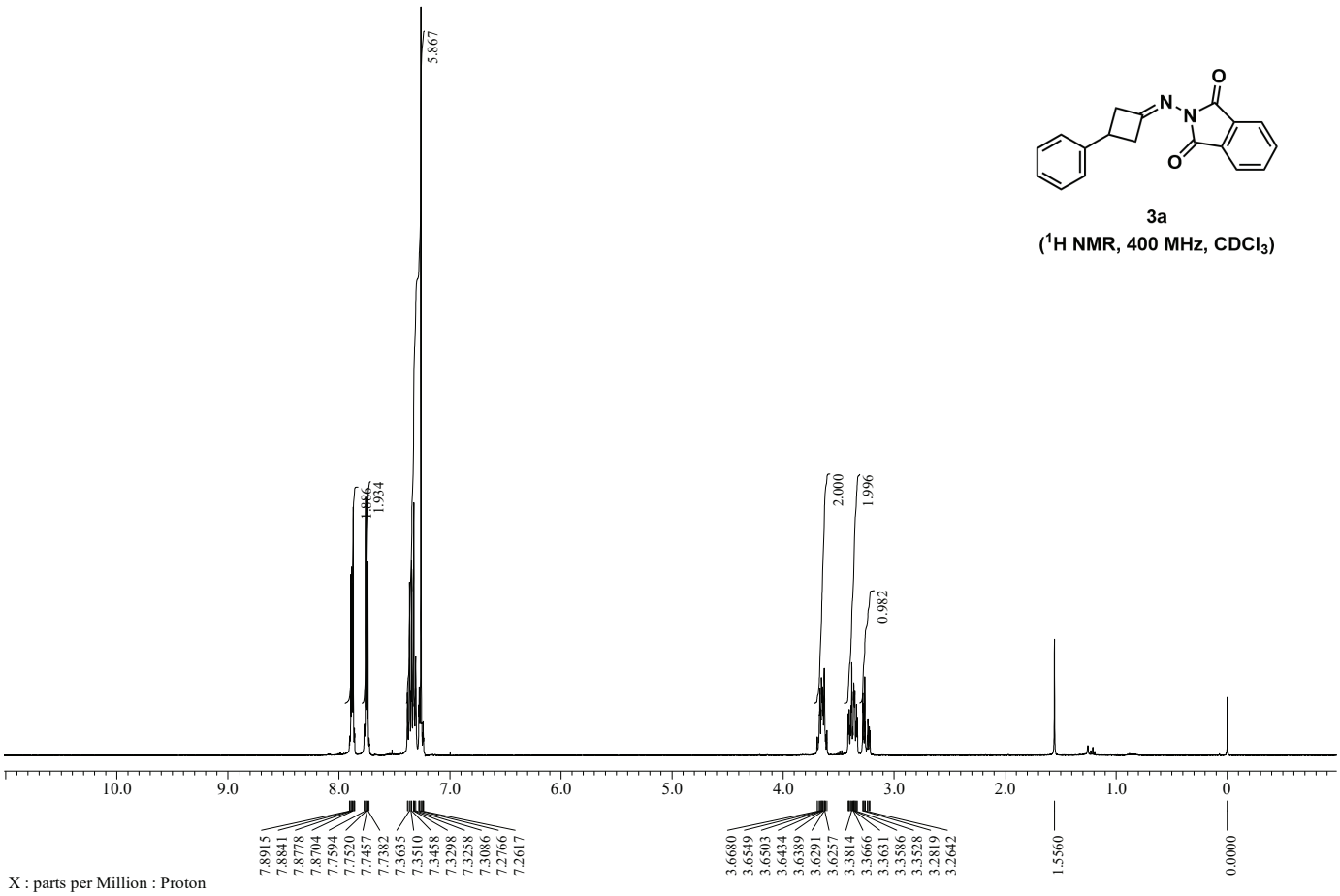
2m
(^{1}H NMR, 400 MHz, $CDCl_3$)



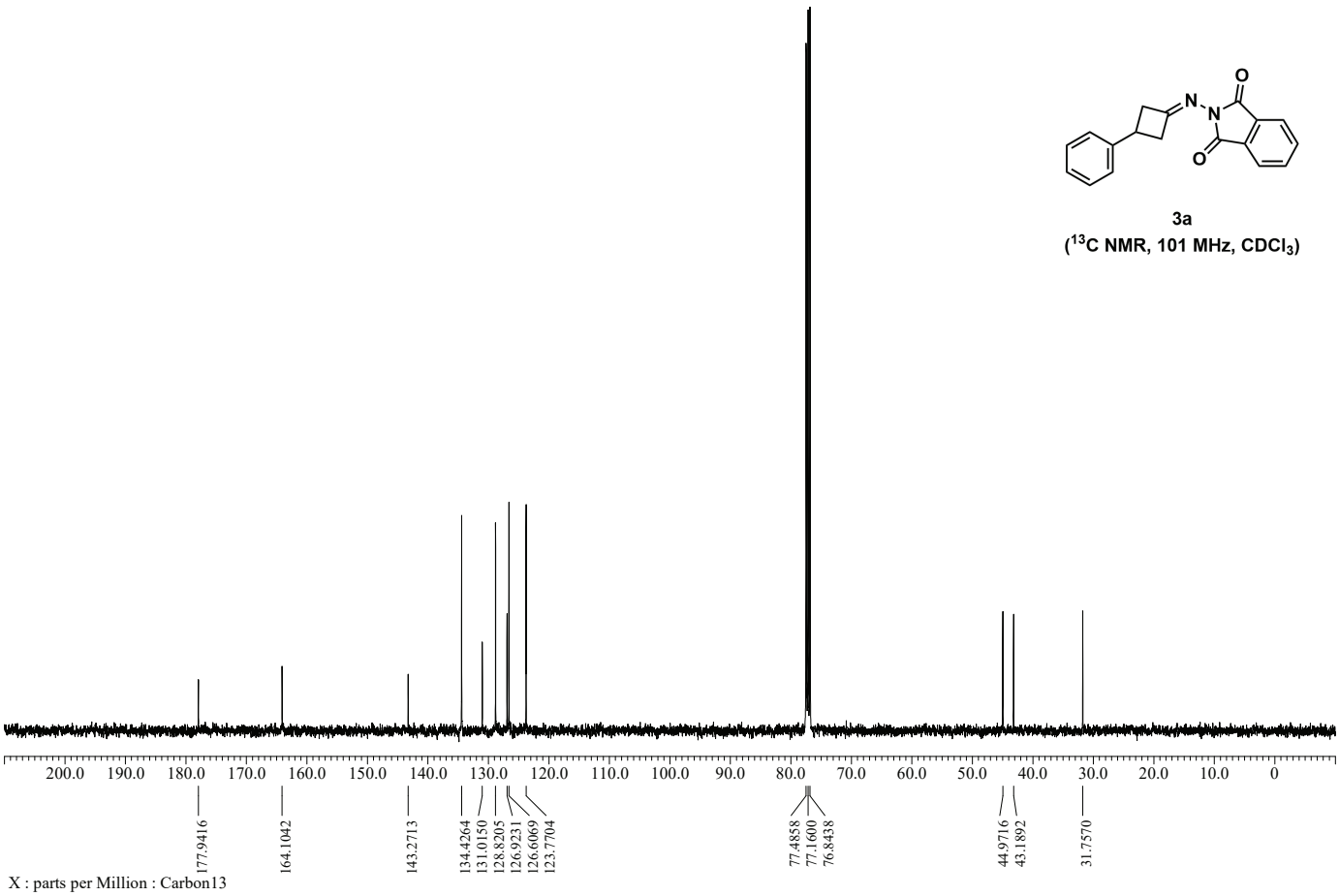
2m
(^{13}C NMR, 101 MHz, $CDCl_3$)


2.805
1.821
2.000
2.000
CN
2n
(1H NMR, 400 MHz, CDCl3)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3601
7.3429
7.3389
7.3275
7.3241
7.2912
7.2732
7.2520
7.2434
7.2394
7.2262
7.2228
7.2217
2.9747
2.9558
2.9375
2.6349
2.6166
2.5977
1.5880
0.0000
X : parts per Million : Proton

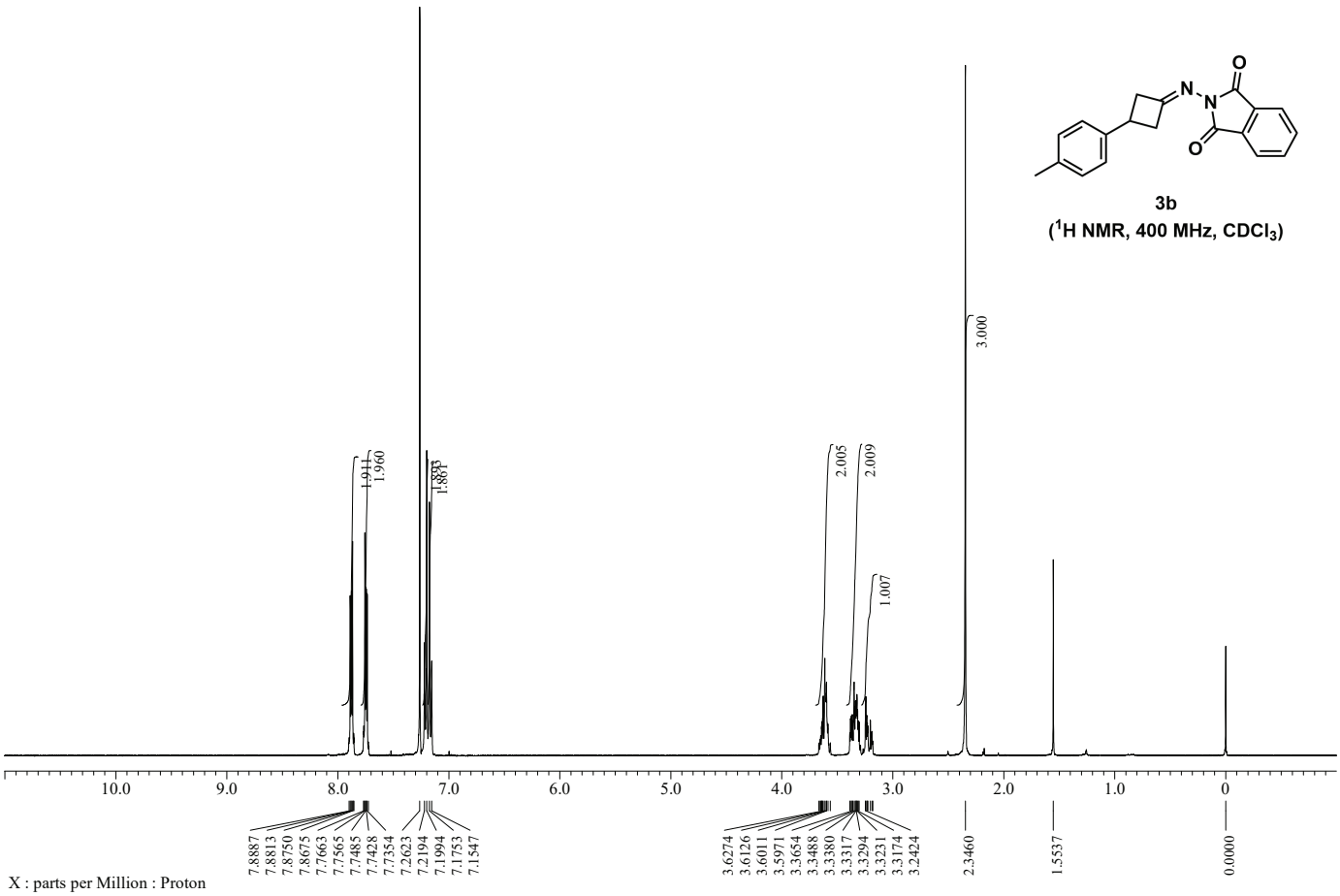

CN
2n
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.1445
128.9930
128.3797
127.3544
119.2857
77.4762
77.1600
76.8438
31.6708
19.4911
X : parts per Million : Carbon13

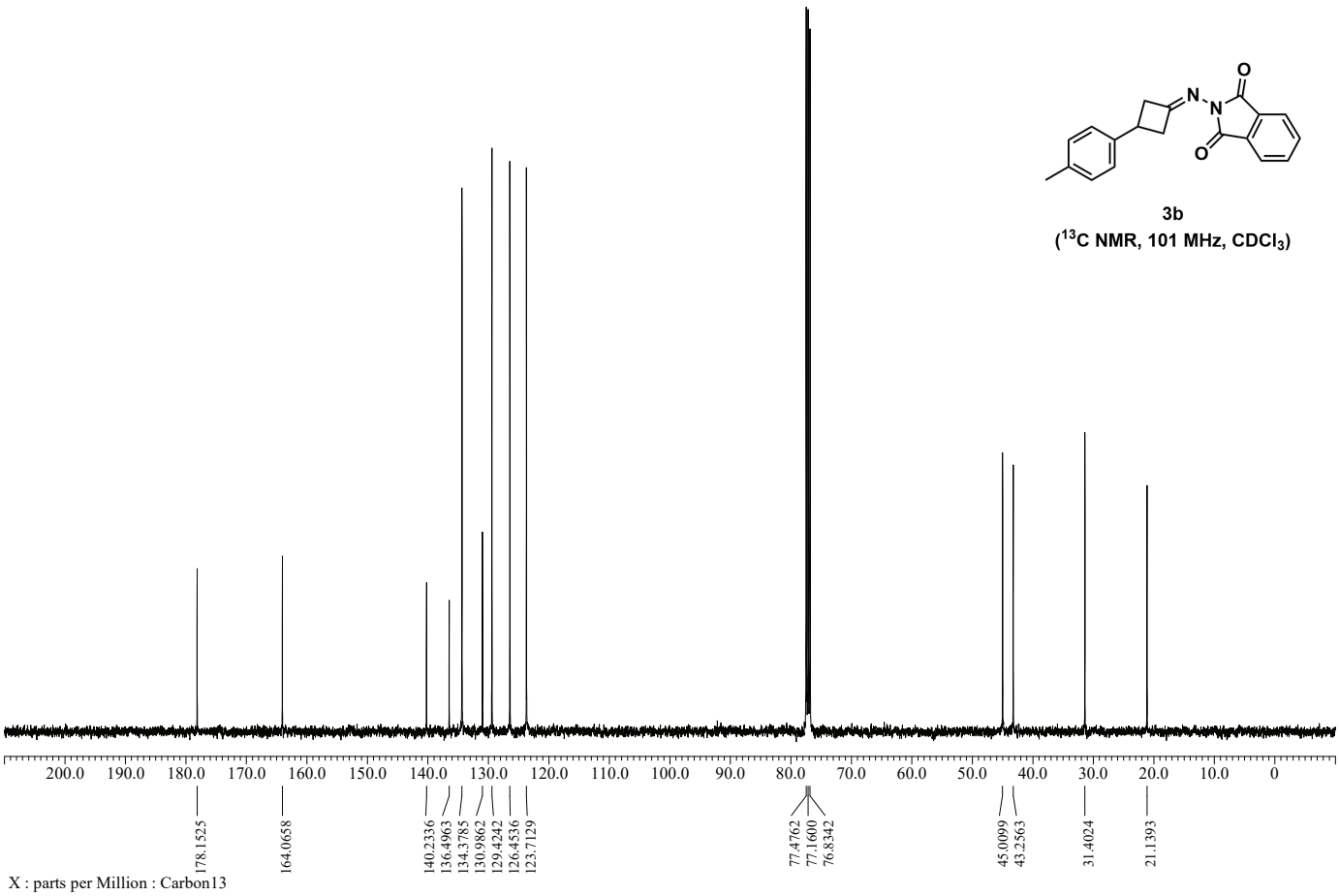


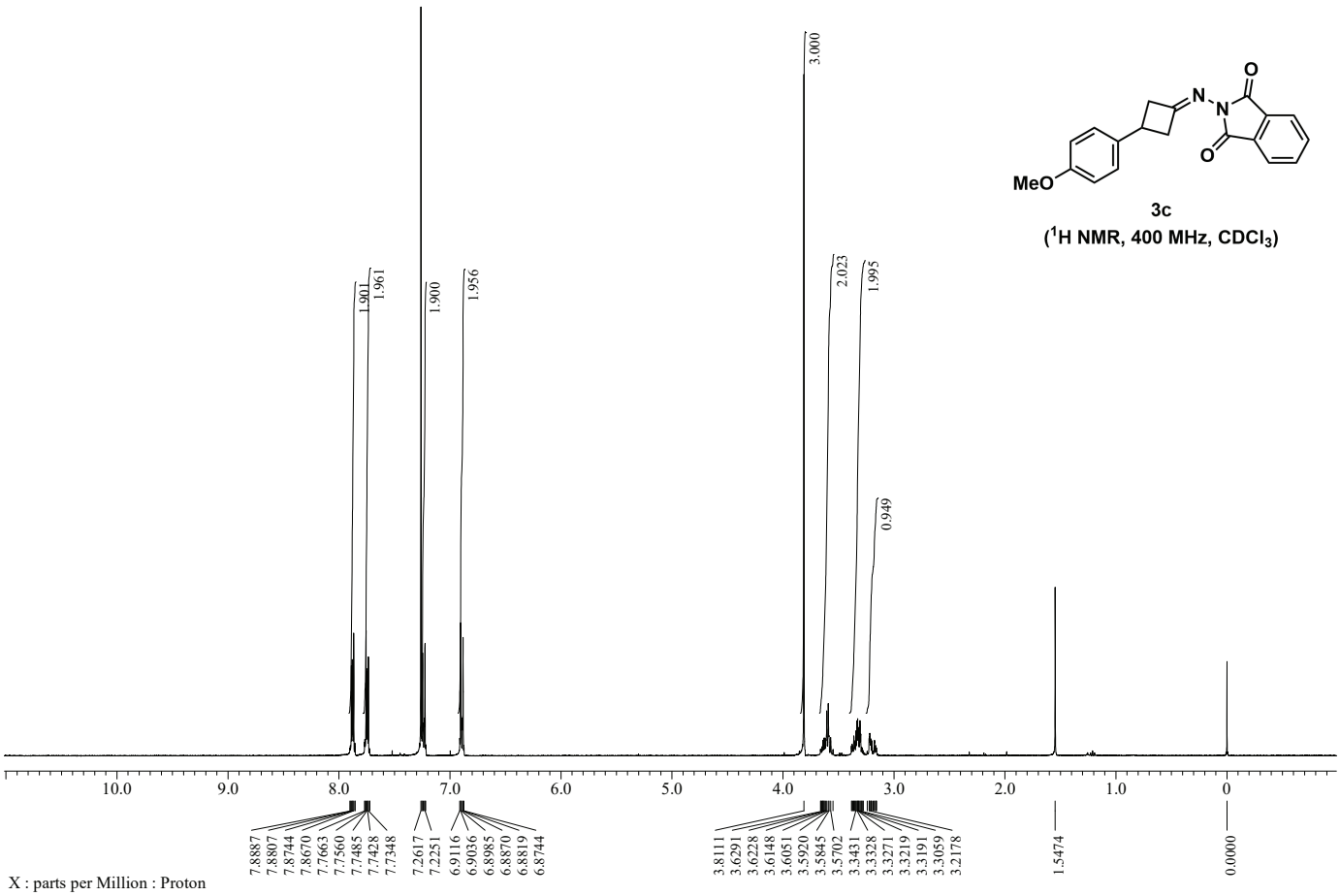
3a
(^{1}H NMR, 400 MHz, $CDCl_3$)



3a
(^{13}C NMR, 101 MHz, $CDCl_3$)


3b
(^{1}H NMR, 400 MHz, $CDCl_3$)
3.000
2.005
2.009
1.007
1.911
1.960
1.867
X : parts per Million : Proton

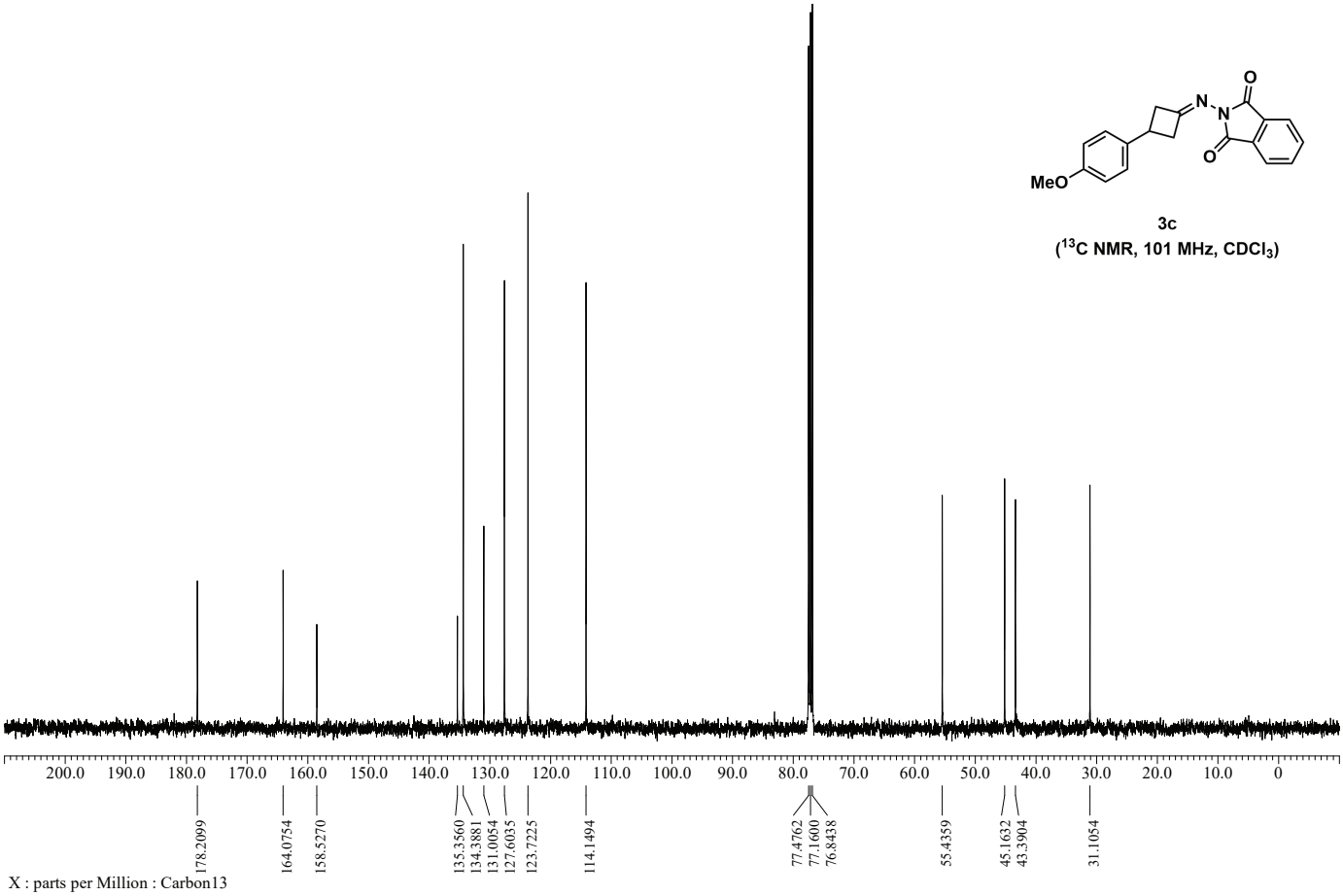

3b
(^{13}C NMR, 101 MHz, $CDCl_3$)
178.1525
164.0658
140.2336
136.4963
134.3785
130.9862
129.4242
126.4536
123.7129
77.4762
77.1600
76.8342
45.0099
43.2563
31.4024
21.1393
X : parts per Million : Carbon13



X : parts per Million : Proton

3c

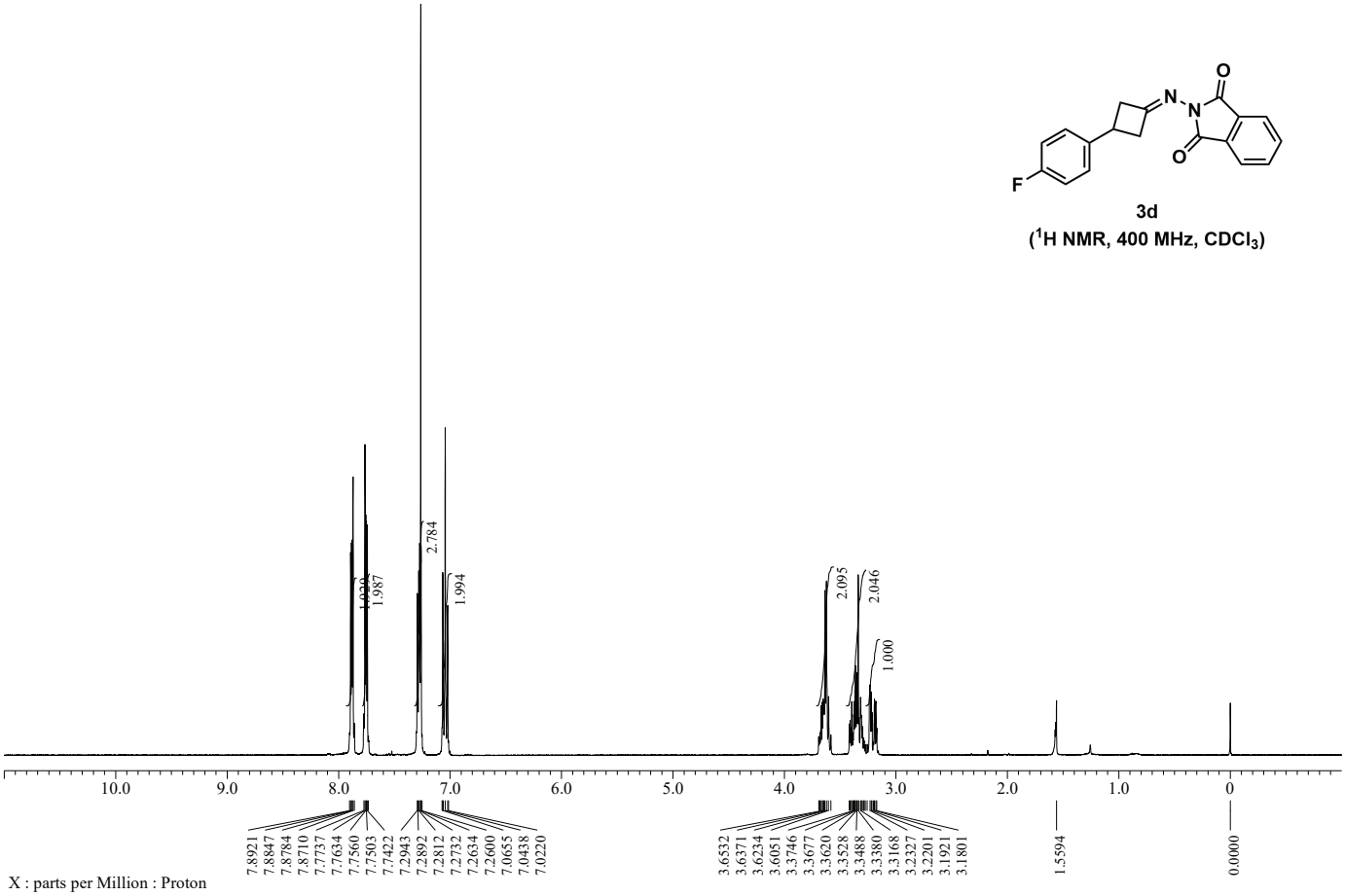
(^{1}H NMR, 400 MHz, $CDCl_3$)

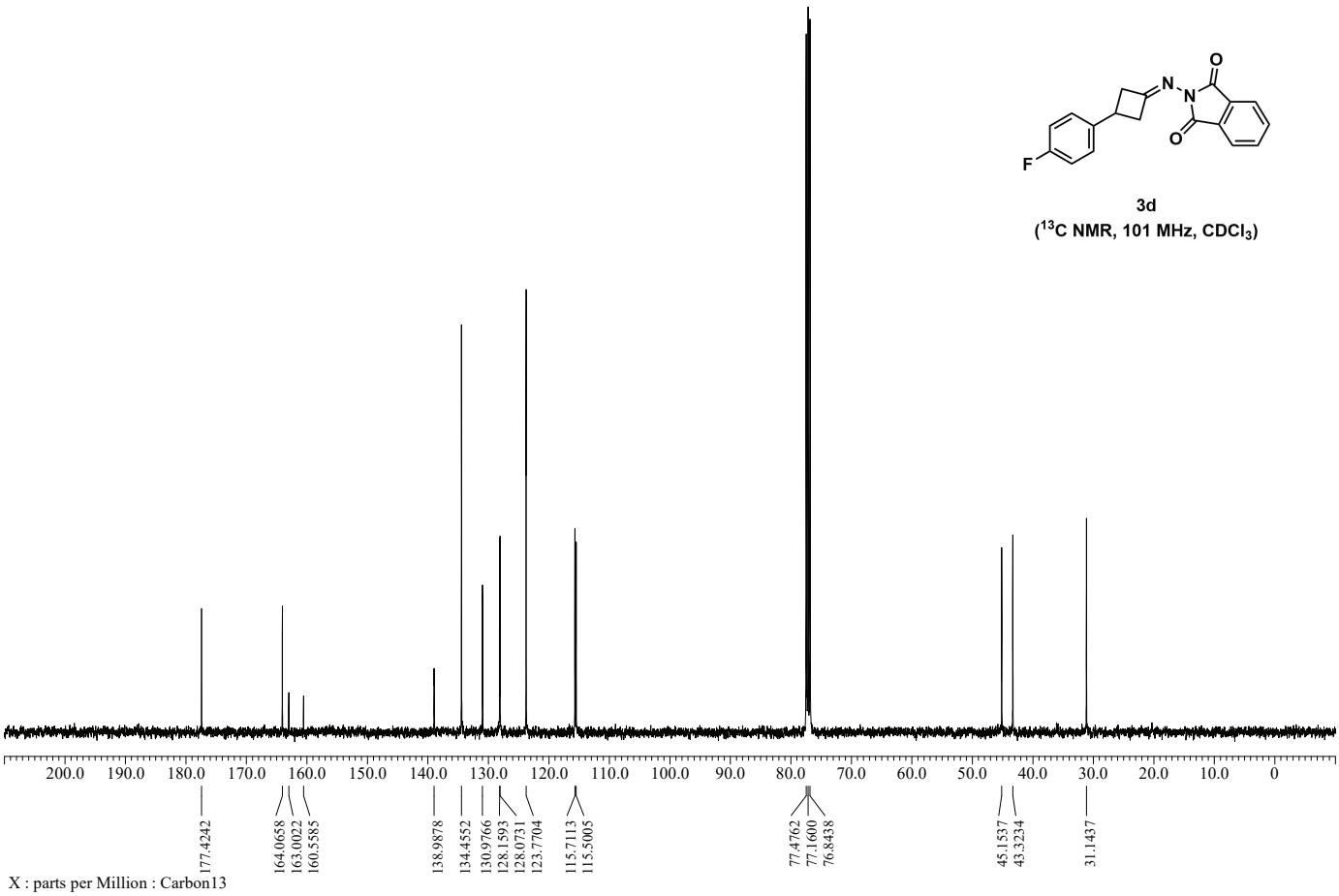


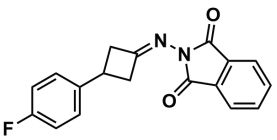
X : parts per Million : Carbon13

3c

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


3d
(1H NMR, 400 MHz, CDCl3)
2.784
1.994
1.987
2.095
2.046
1.000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.8921
7.8847
7.8784
7.8710
7.7737
7.7634
7.7560
7.7503
7.7422
7.2943
7.2892
7.2812
7.2732
7.2634
7.2600
7.0655
7.0438
7.0220
3.6532
3.6371
3.6234
3.6051
3.3746
3.3677
3.3620
3.3528
3.3488
3.3380
3.3168
3.2327
3.2201
3.1921
3.1801
1.5594
0.0000
X : parts per Million : Proton

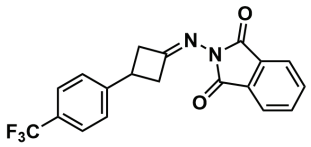

3d
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
177.4242
164.0658
163.0022
160.5585
138.9878
134.4552
130.9766
128.1593
128.0731
123.7704
115.7113
115.5005
77.4762
77.1600
76.8438
45.1537
43.3234
31.1437
X : parts per Million : Carbon13



3d

(^{19}F NMR, 373 MHz, $CDCl_3$)

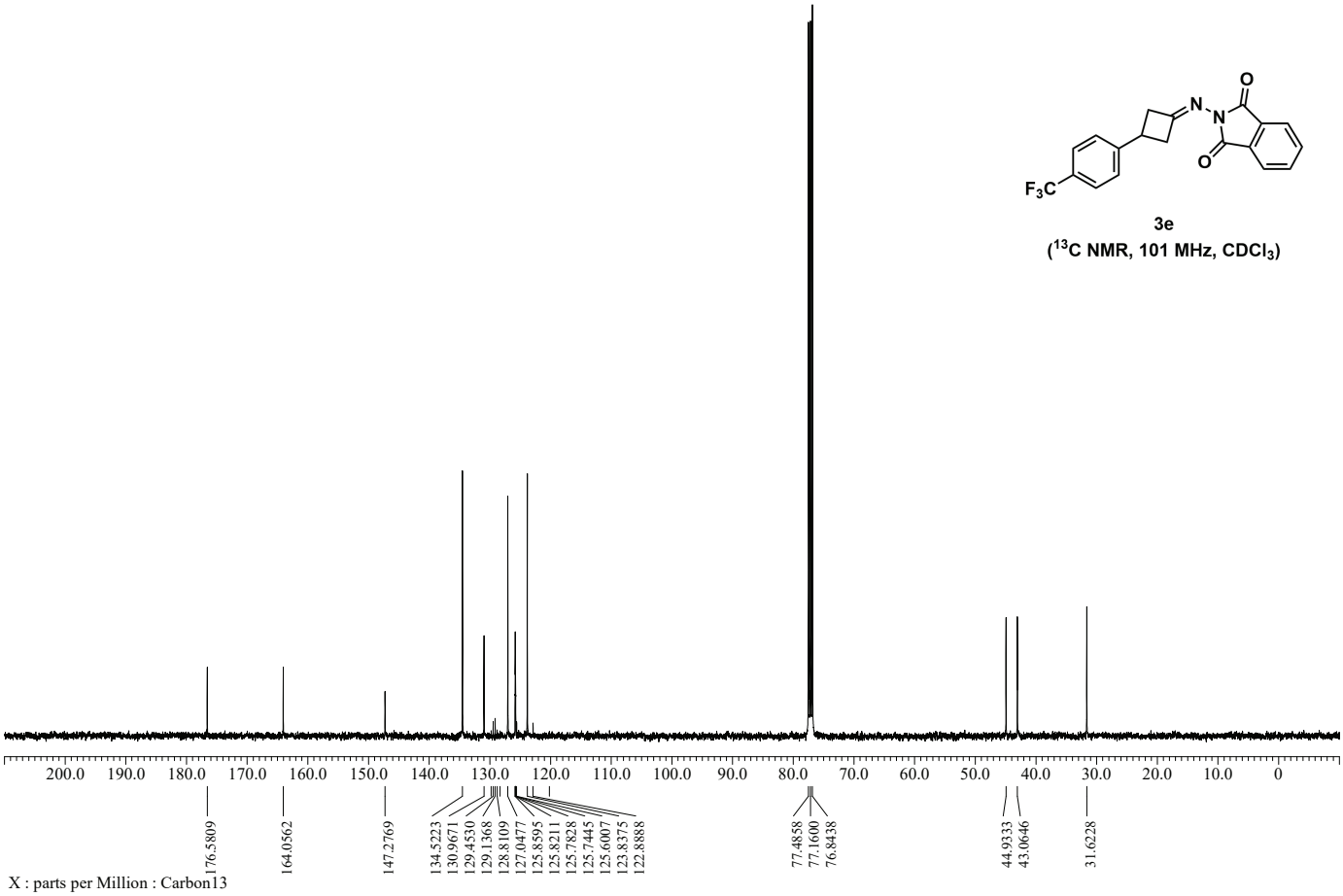
X : parts per Million : Fluorine19



3e

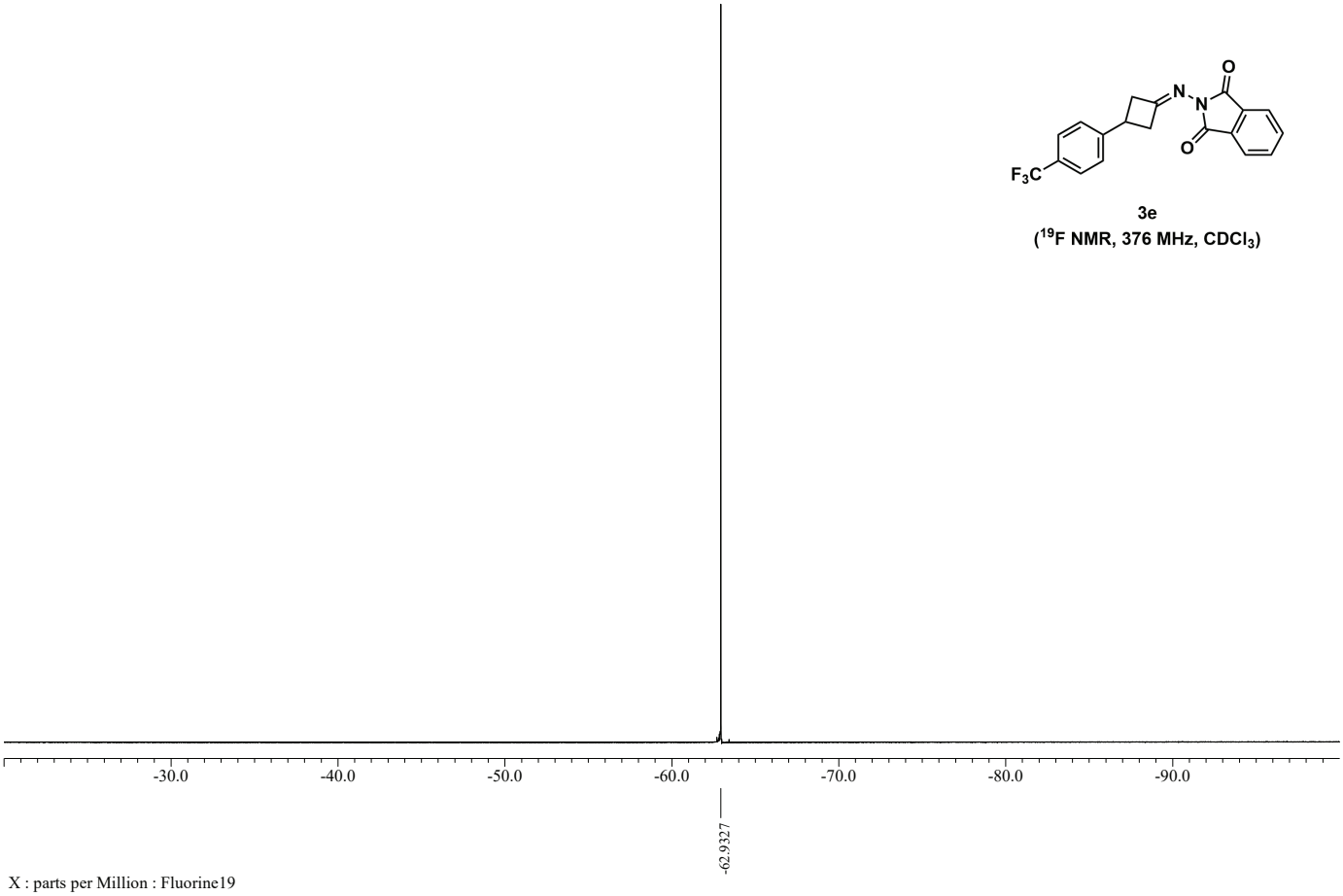
(^{1}H NMR, 400 MHz, $CDCl_3$)

X : parts per Million : Proton



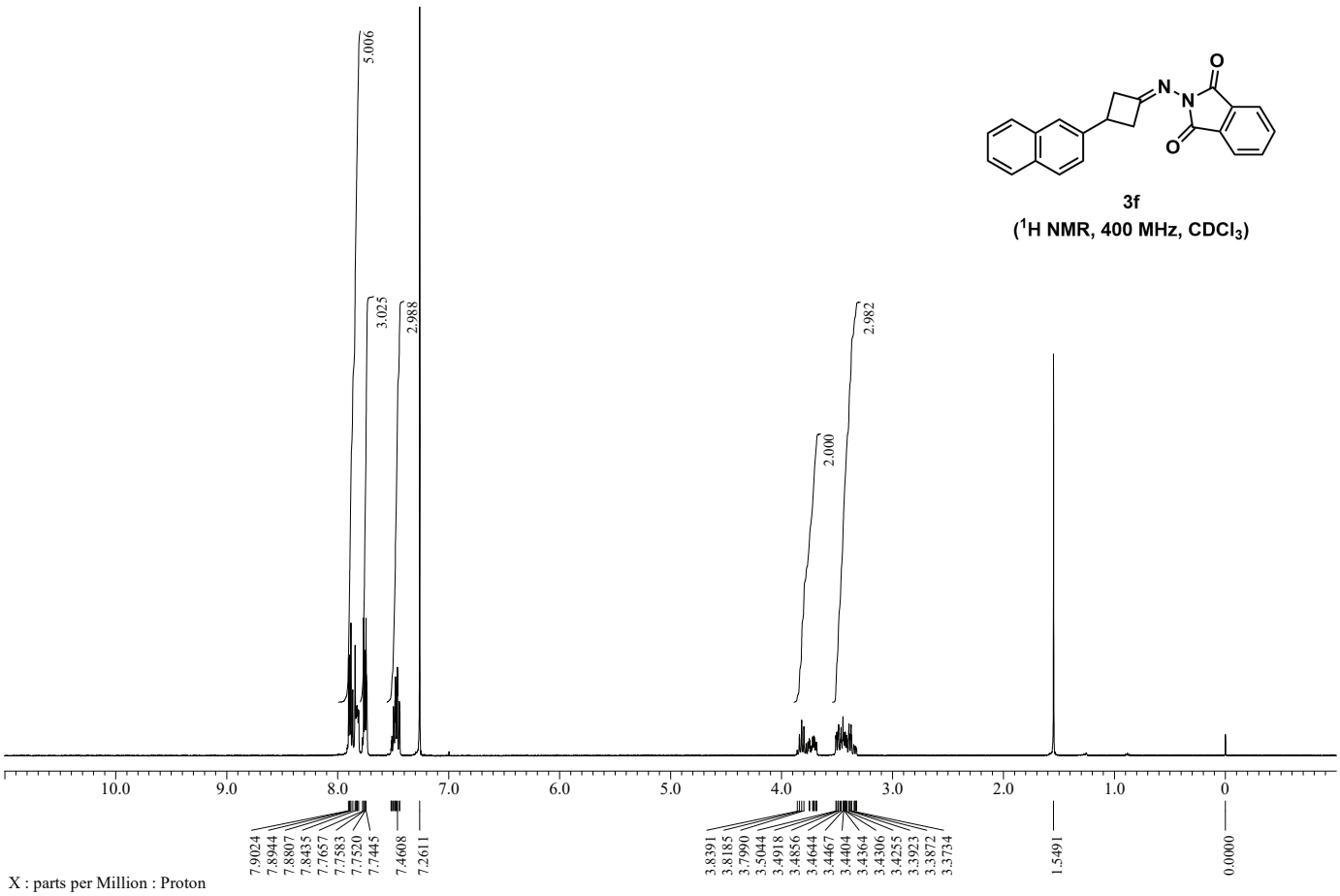
3e

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

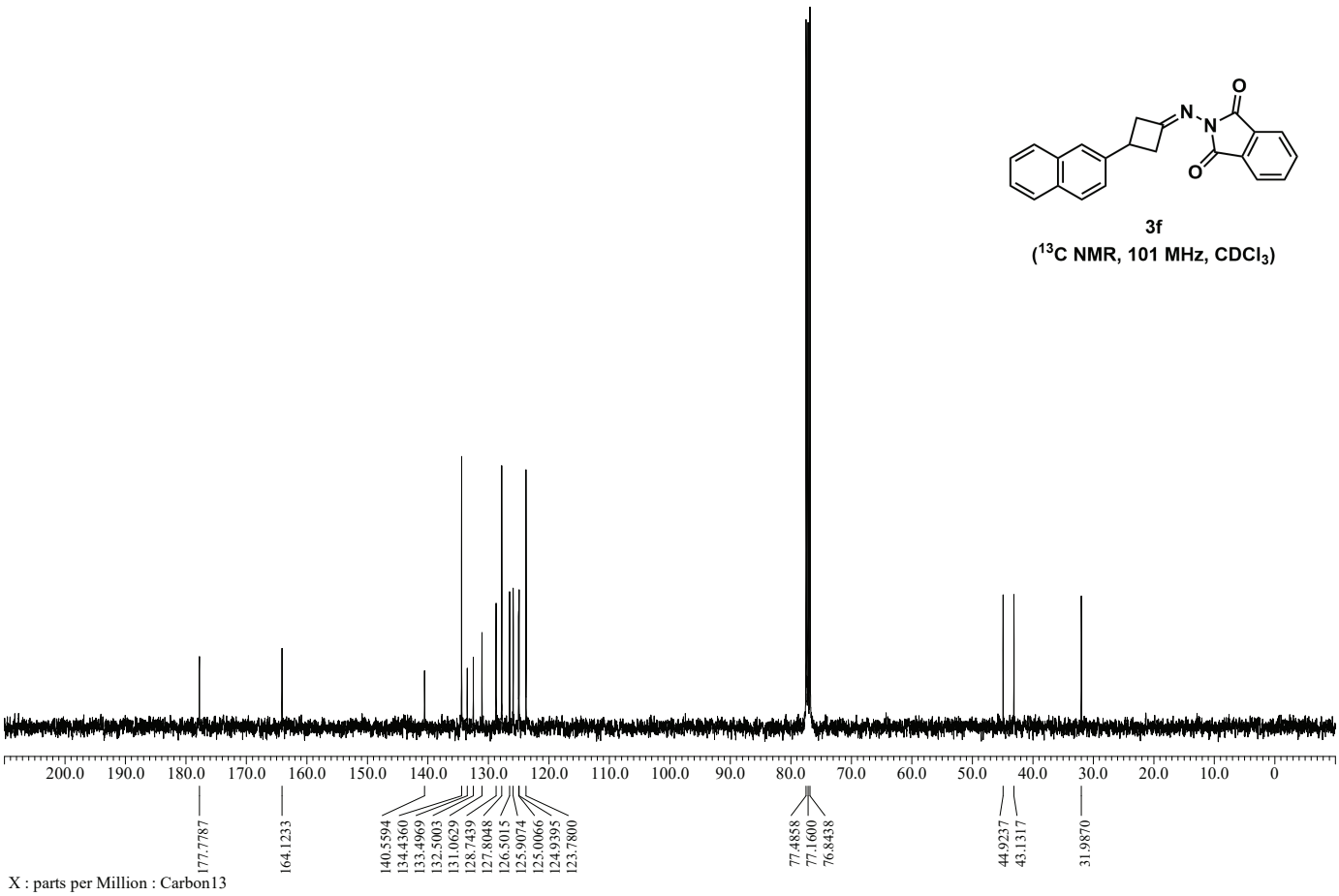


3e

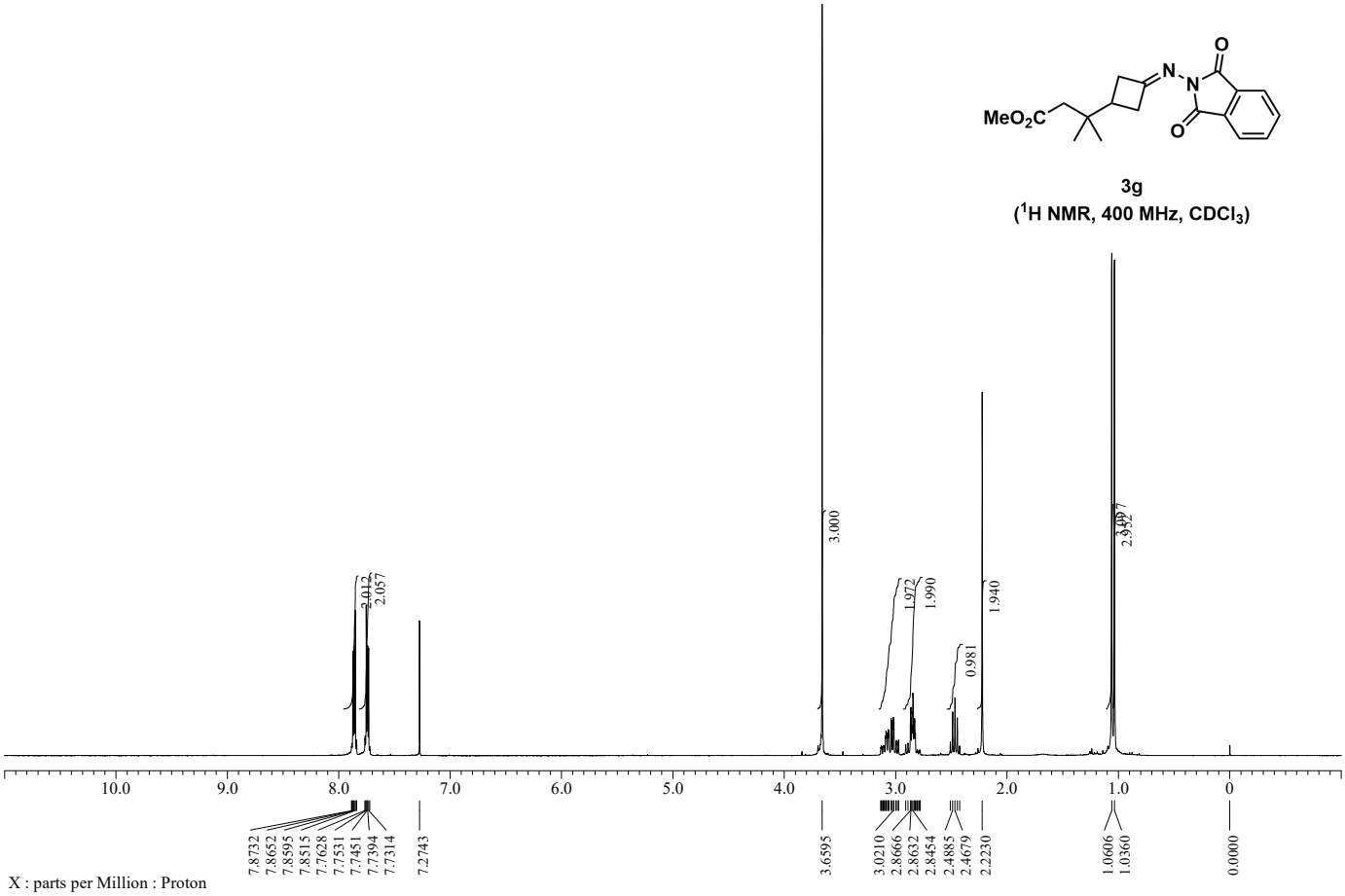
(^{19}F NMR, 376 MHz, $CDCl_3$)

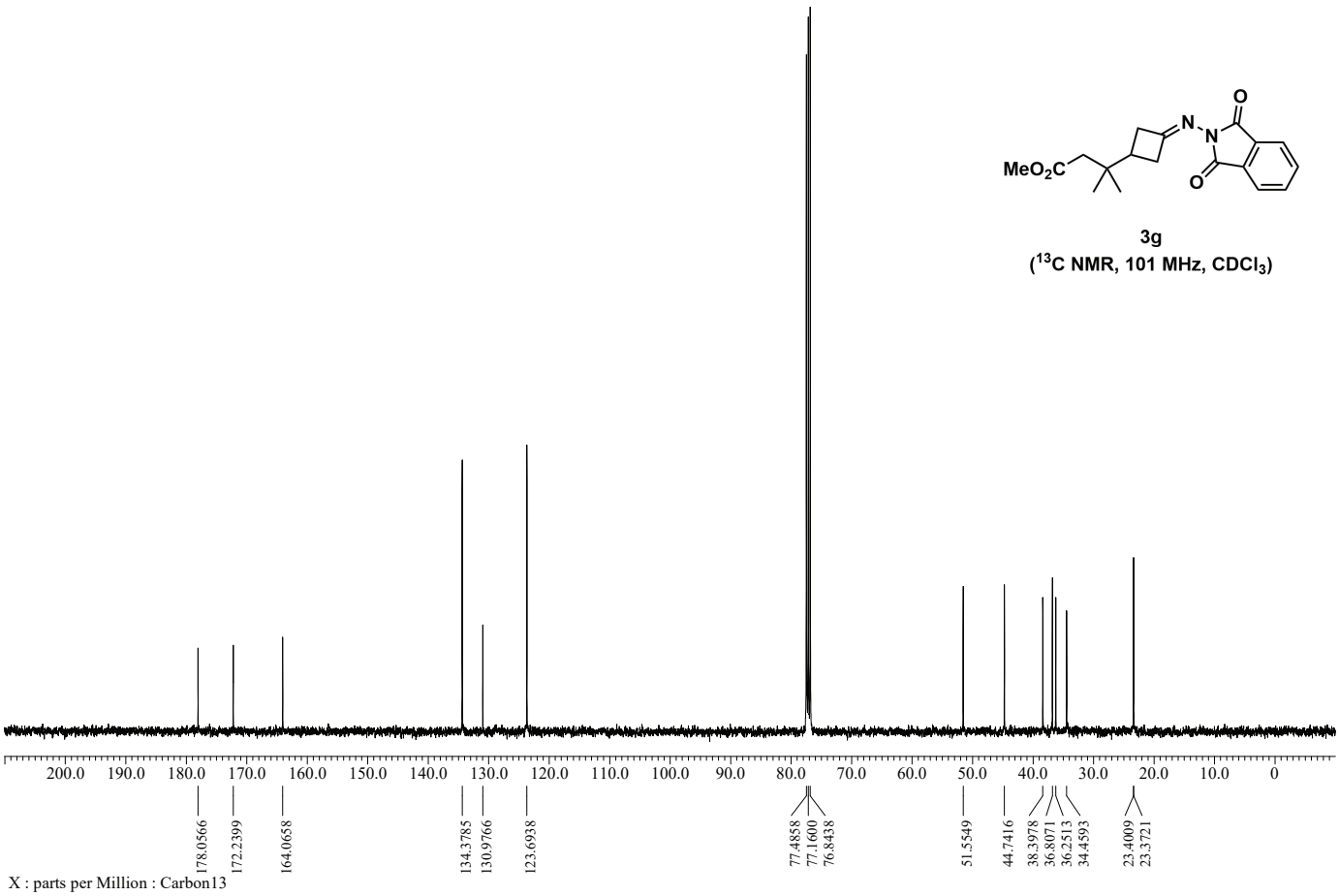


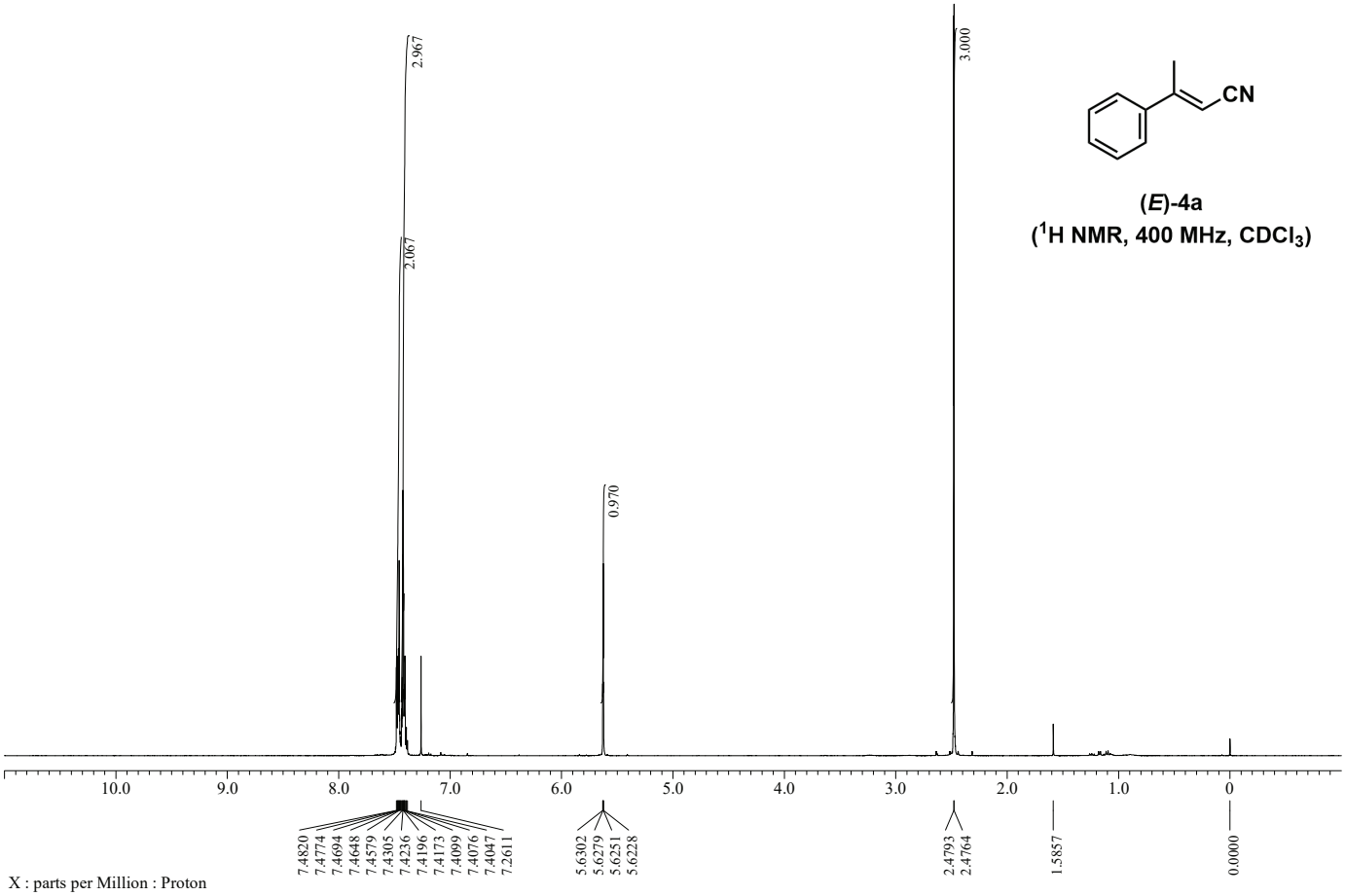
3f
(^{1}H NMR, 400 MHz, $CDCl_3$)



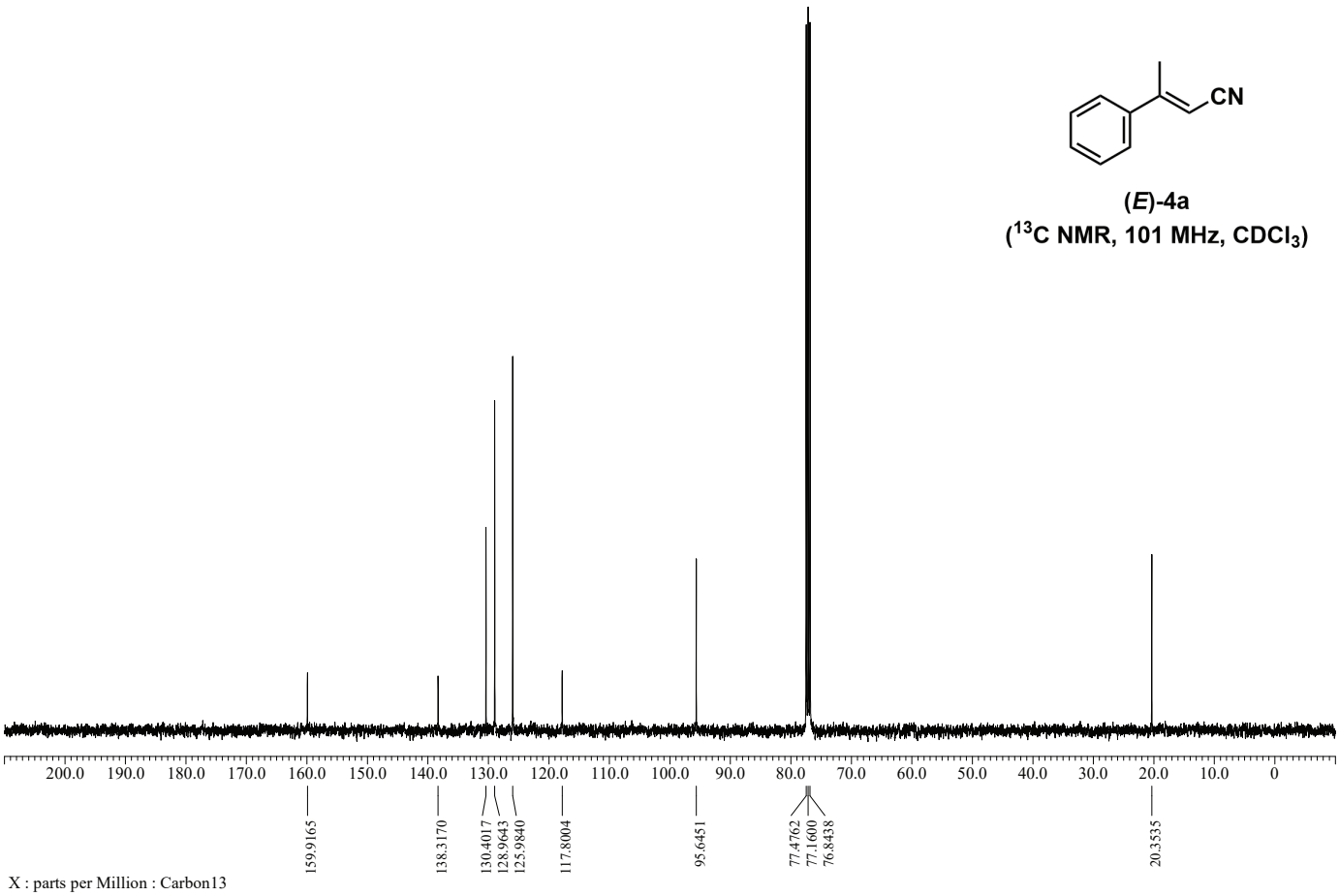
3f
(^{13}C NMR, 101 MHz, $CDCl_3$)


MeO2C
N
N
O
O
3g
(1H NMR, 400 MHz, CDCl3)
3.000
2.057
2.012
1.990
1.972
1.940
0.981
2.932
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.8732
7.8652
7.8595
7.8515
7.7628
7.7531
7.7451
7.7394
7.7314
7.2743
3.6595
3.0210
2.8666
2.8632
2.8454
2.4885
2.4679
2.2230
1.0606
1.0360
0.0000
X : parts per Million : Proton

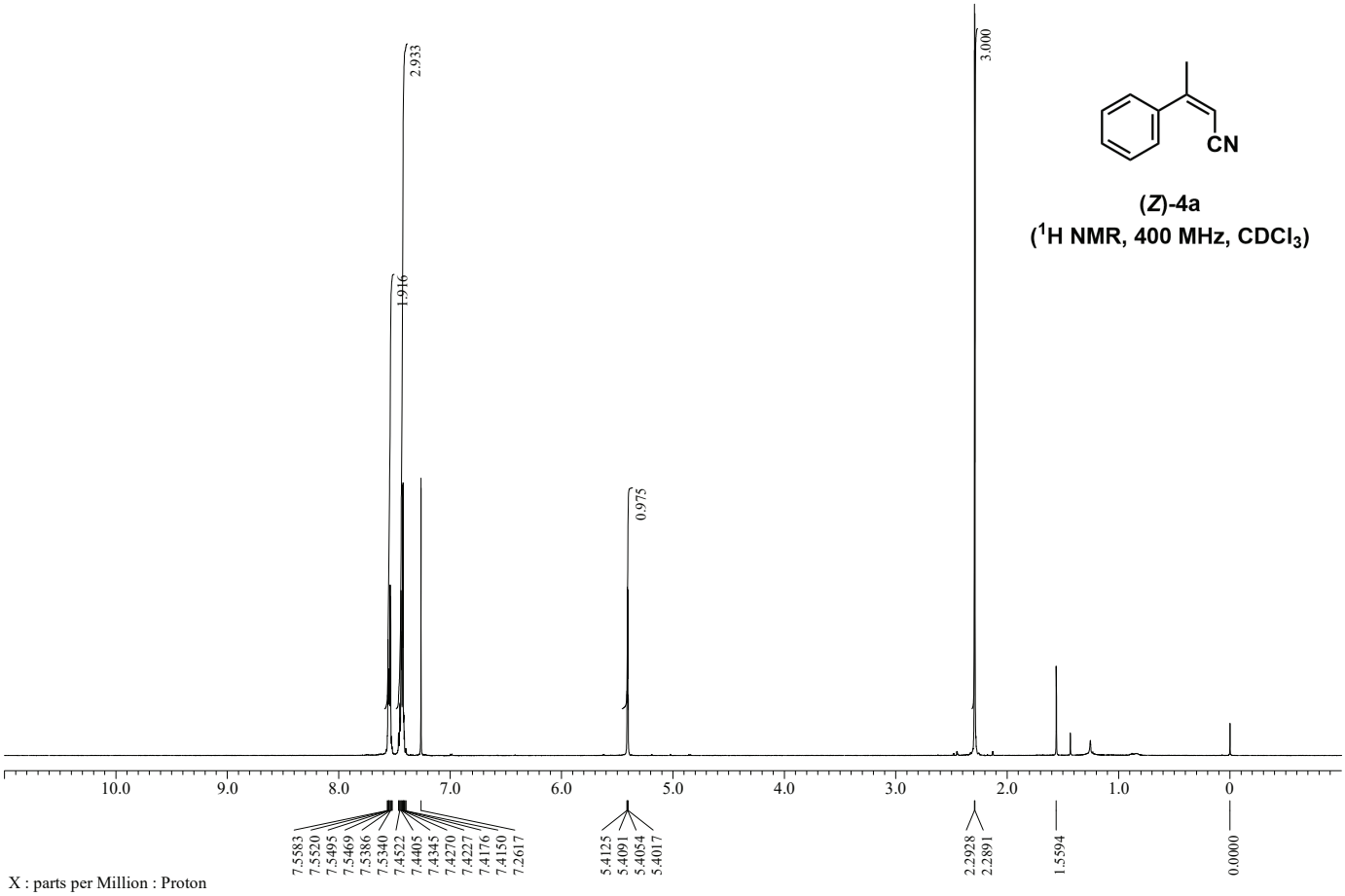

MeO2C
N
N
O
O
3g
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
178.0566
172.2399
164.0658
134.3785
130.9766
123.6938
77.4858
77.1600
76.8438
51.5549
44.7416
38.3978
36.8071
36.2513
34.4593
23.4009
23.3721
X : parts per Million : Carbon13



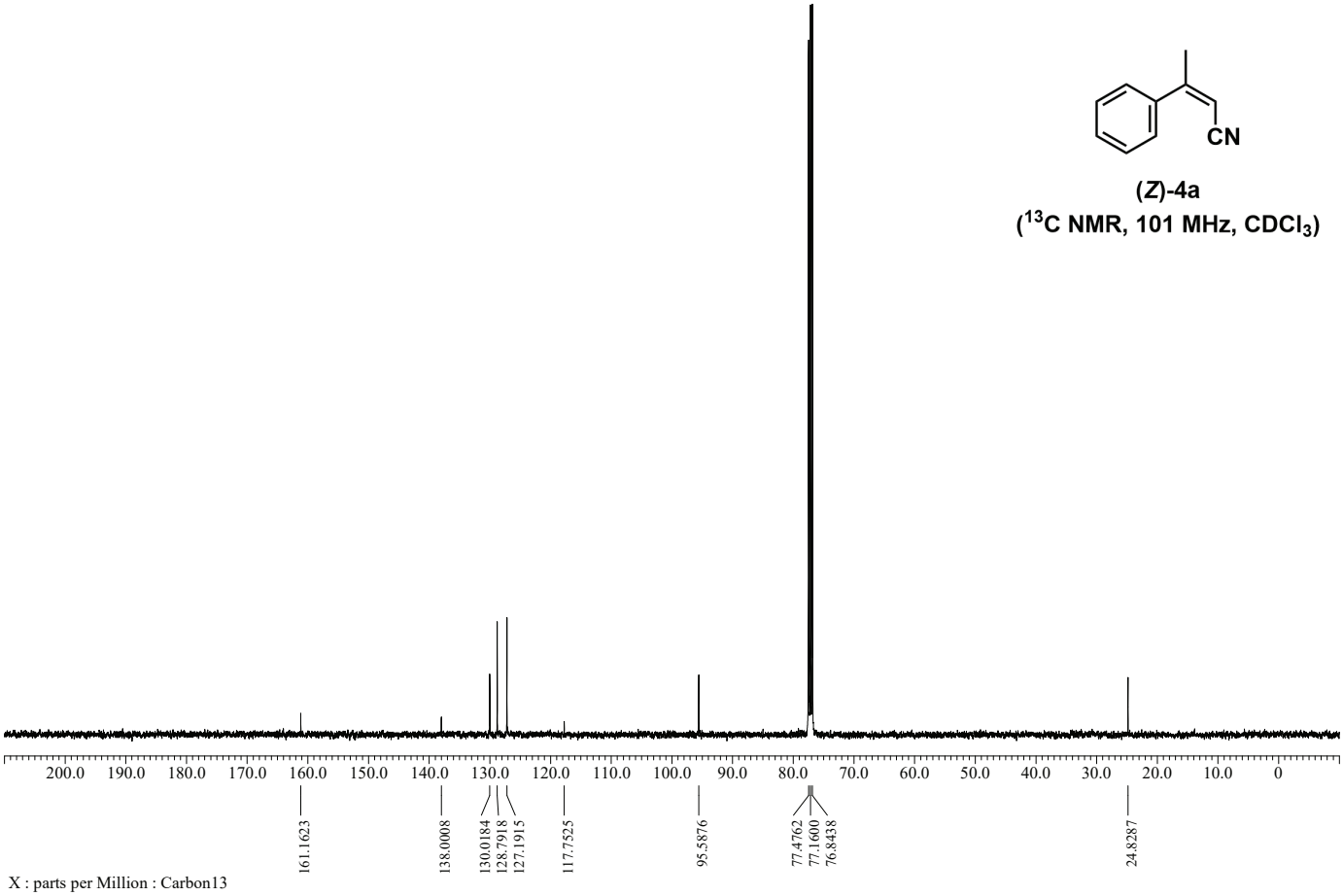
(*E*)-4a
(^{1}H NMR, 400 MHz, $CDCl_3$)



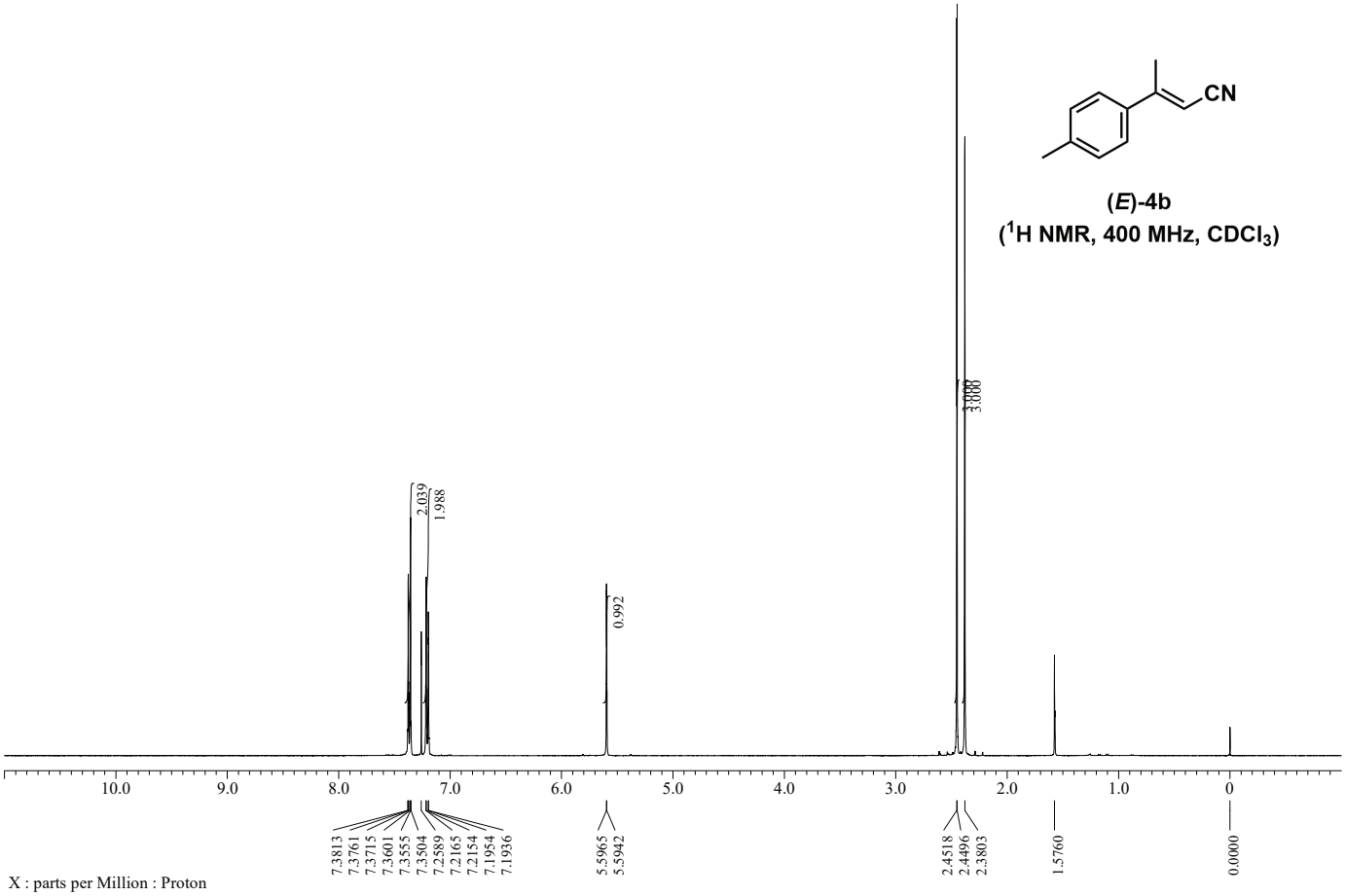
(*E*)-4a
(^{13}C NMR, 101 MHz, $CDCl_3$)

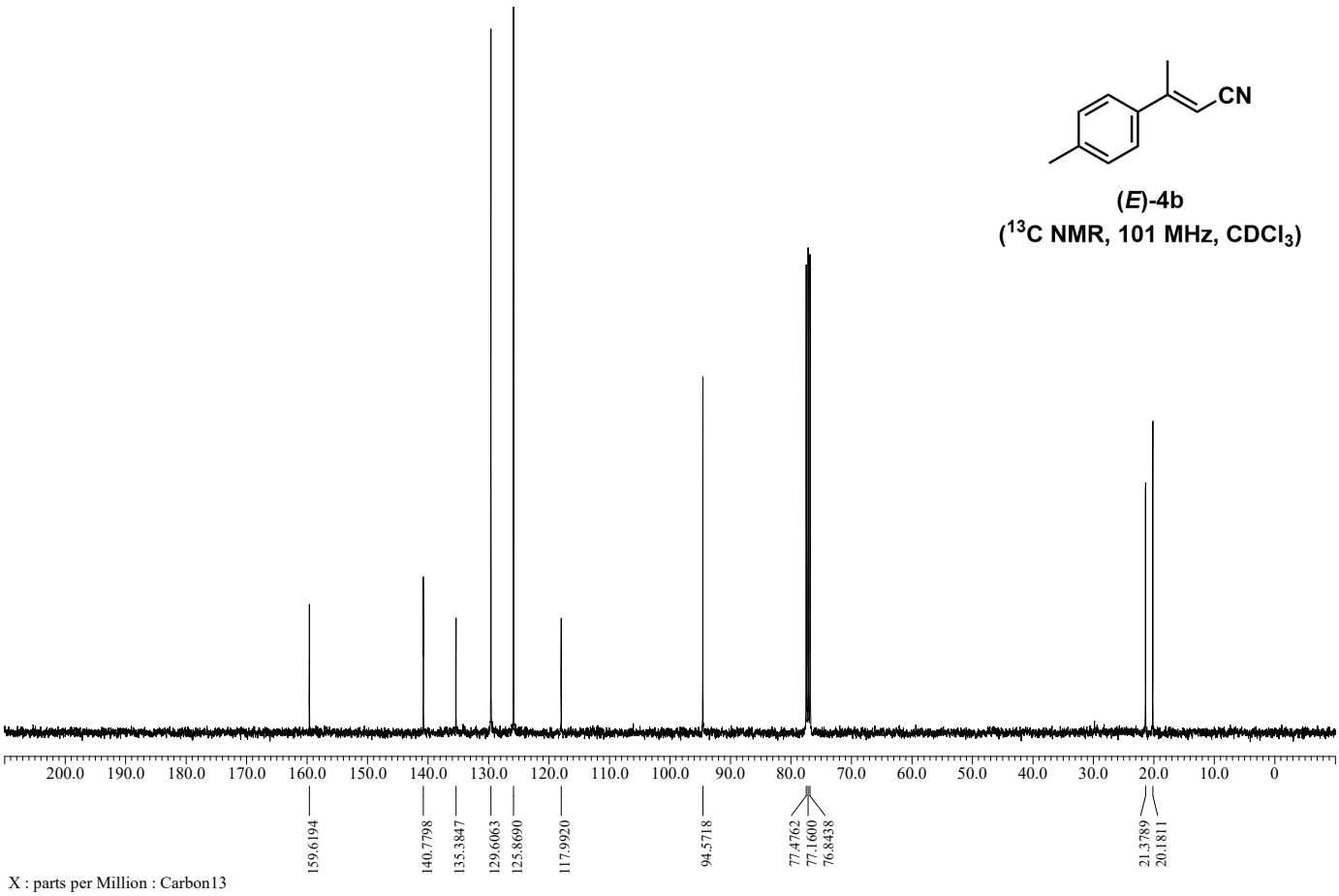


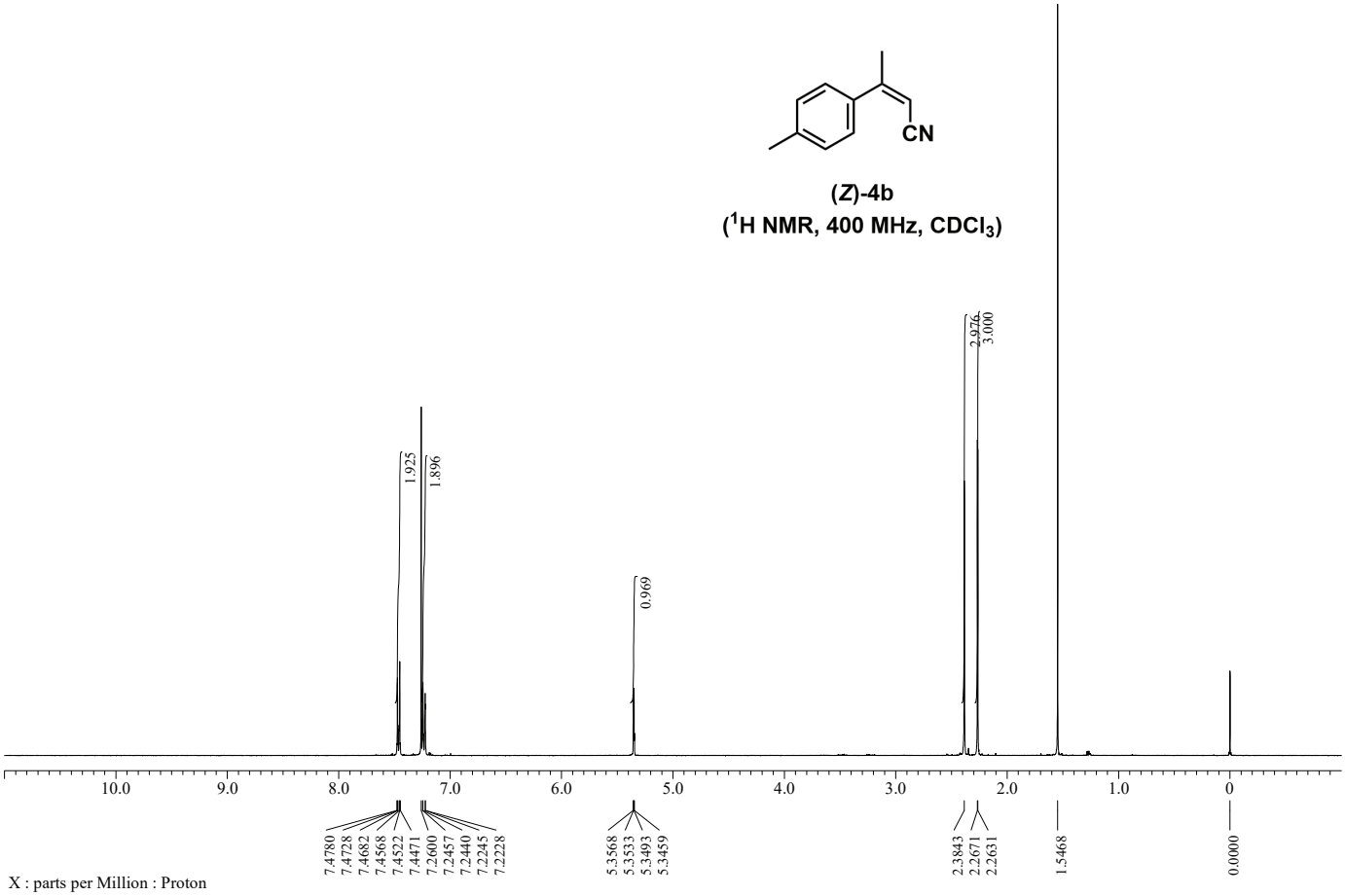
(*Z*)-4a
(^{1}H NMR, 400 MHz, $CDCl_3$)



(*Z*)-4a
(^{13}C NMR, 101 MHz, $CDCl_3$)

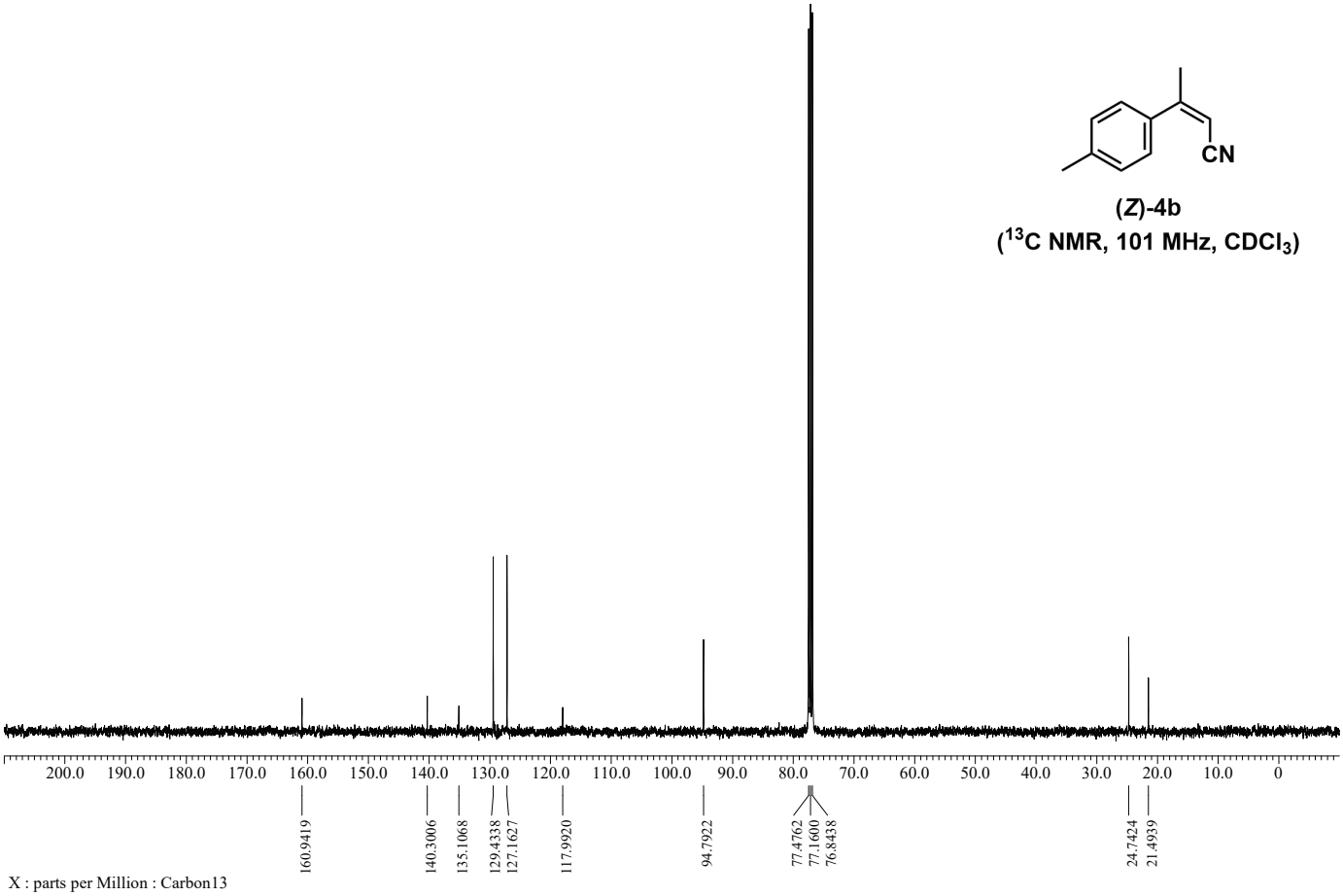

CN
(E)-4b
(1H NMR, 400 MHz, CDCl3)
2.039
1.988
0.992
3.000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3813
7.3761
7.3715
7.3601
7.3555
7.3504
7.2589
7.2165
7.2154
7.1954
7.1936
5.5965
5.5942
2.4518
2.4496
2.3803
1.5760
0.0000
X : parts per Million : Proton


CN
(E)-4b
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.6194
140.7798
135.3847
129.6063
125.8690
117.9920
94.5718
77.4762
77.1600
76.8438
21.3789
20.1811
X : parts per Million : Carbon13



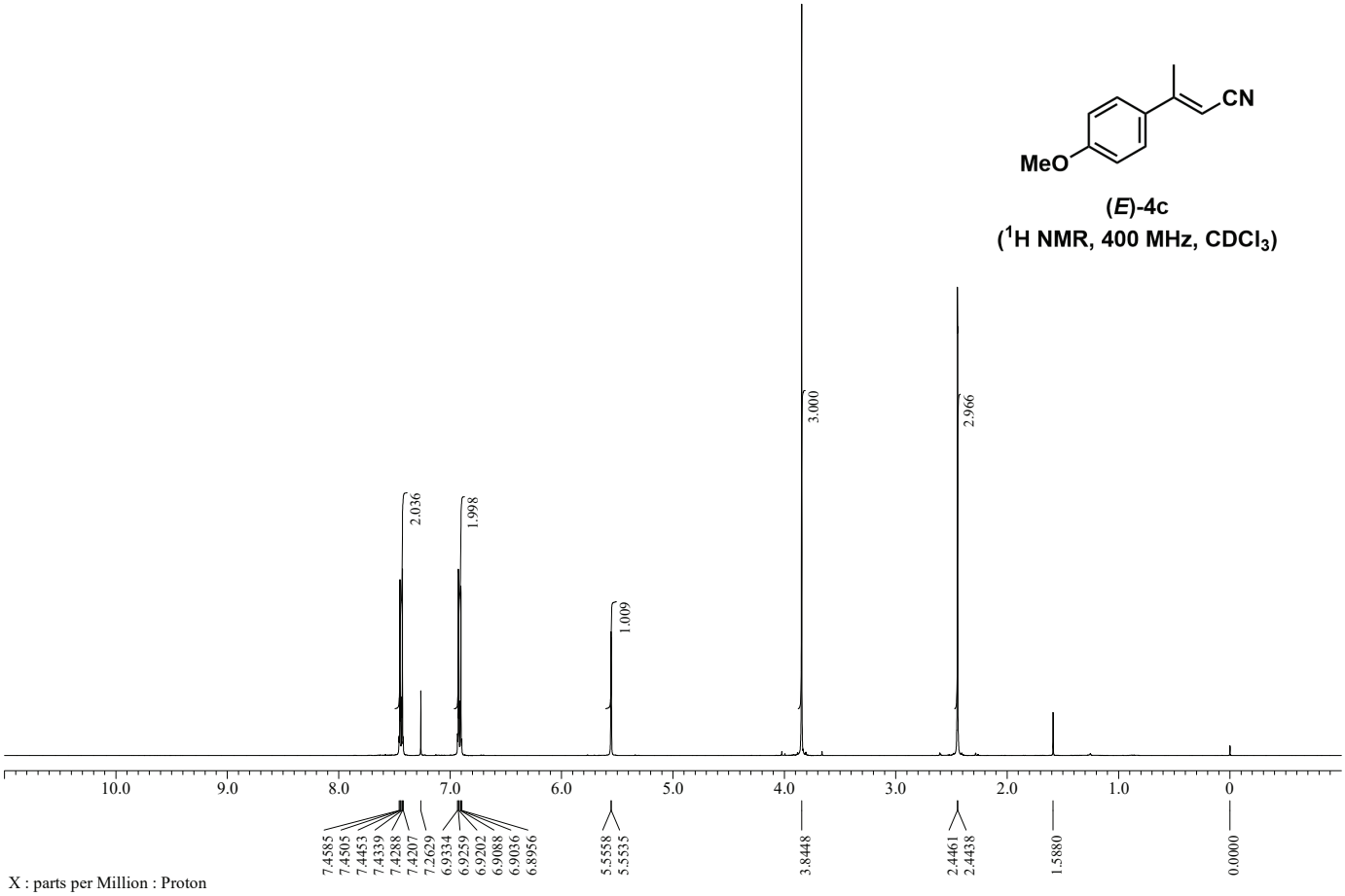
(*Z*)-4b
(^{1}H NMR, 400 MHz, $CDCl_3$)

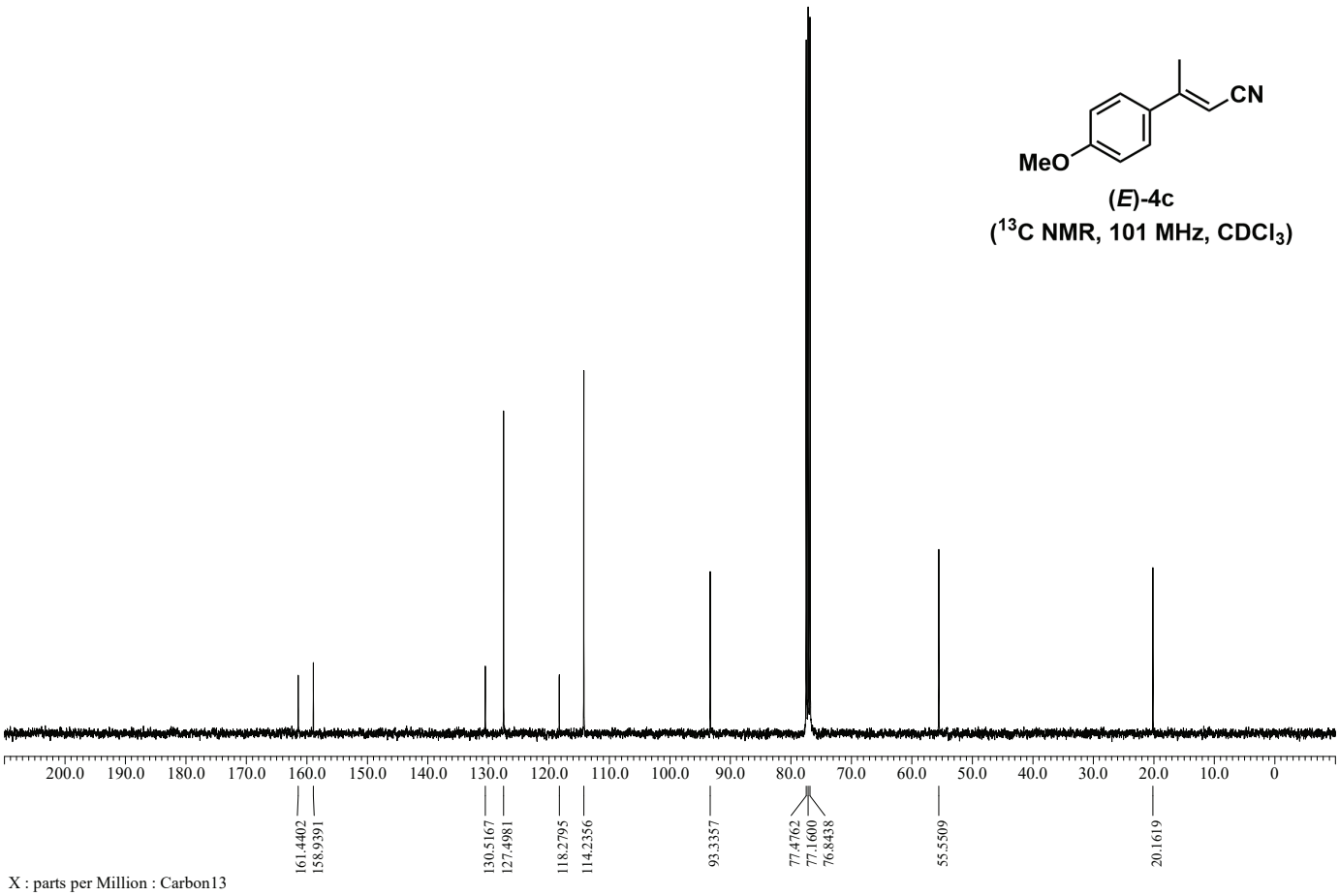
X : parts per Million : Proton

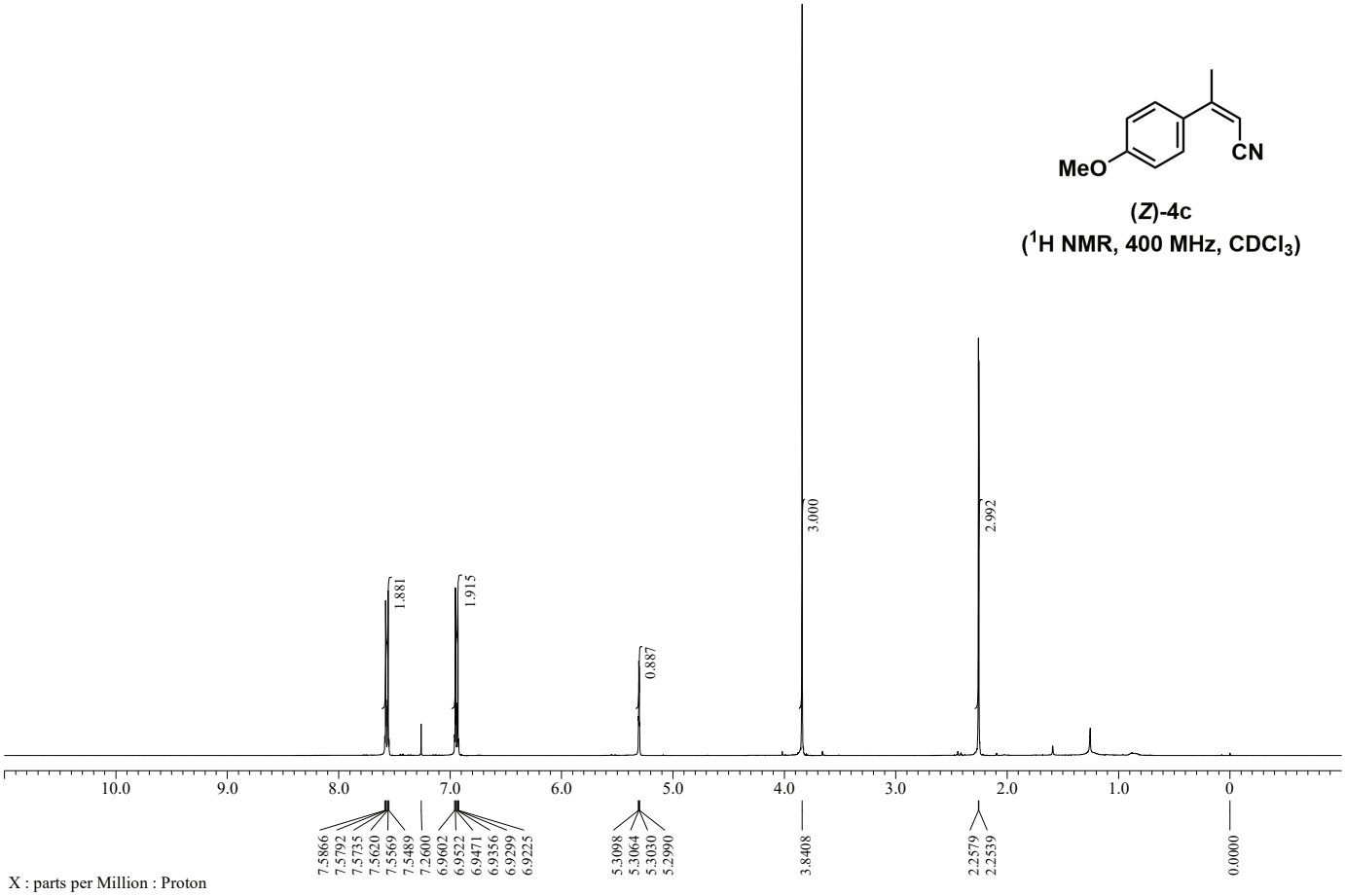


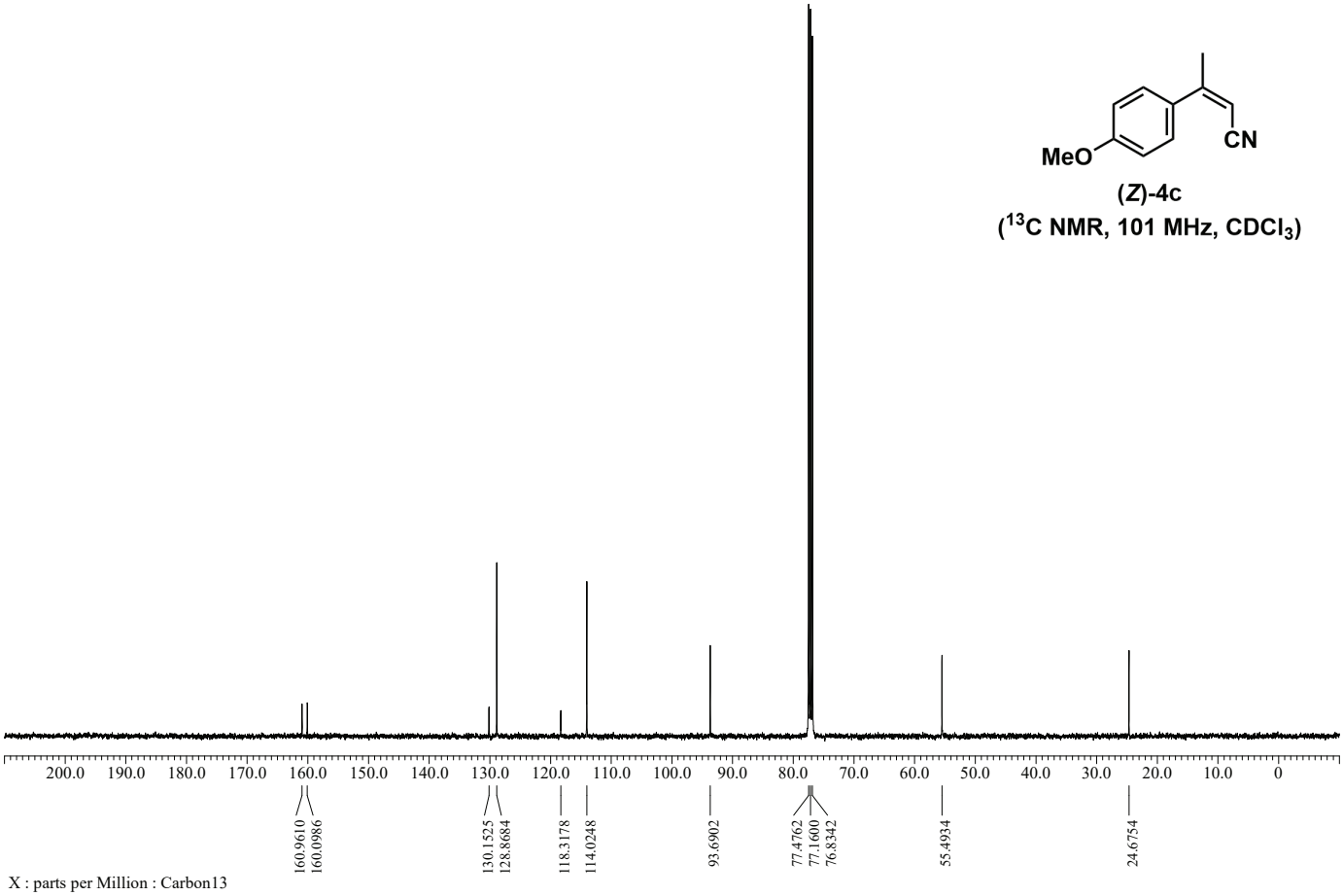
(*Z*)-4b
(^{13}C NMR, 101 MHz, $CDCl_3$)

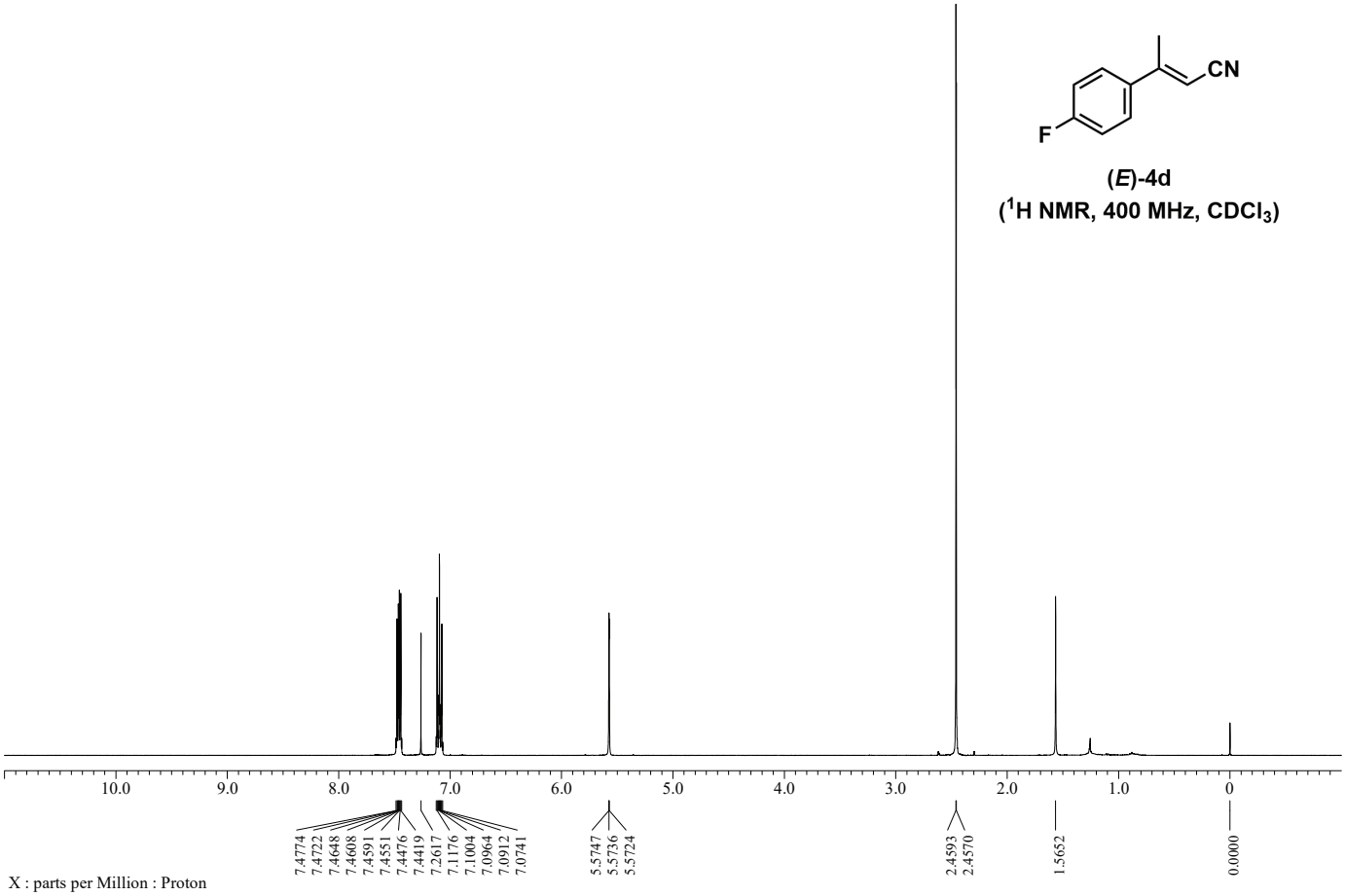
X : parts per Million : Carbon13


CN
MeO
(E)-4c
(1H NMR, 400 MHz, CDCl3)
3.000
2.966
2.036
1.998
1.009
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.4585
7.4505
7.4453
7.4339
7.4288
7.4207
7.2629
6.9334
6.9259
6.9202
6.9088
6.9036
6.8956
5.5558
5.5535
3.8448
2.4461
2.4438
1.5880
0.0000
X : parts per Million : Proton

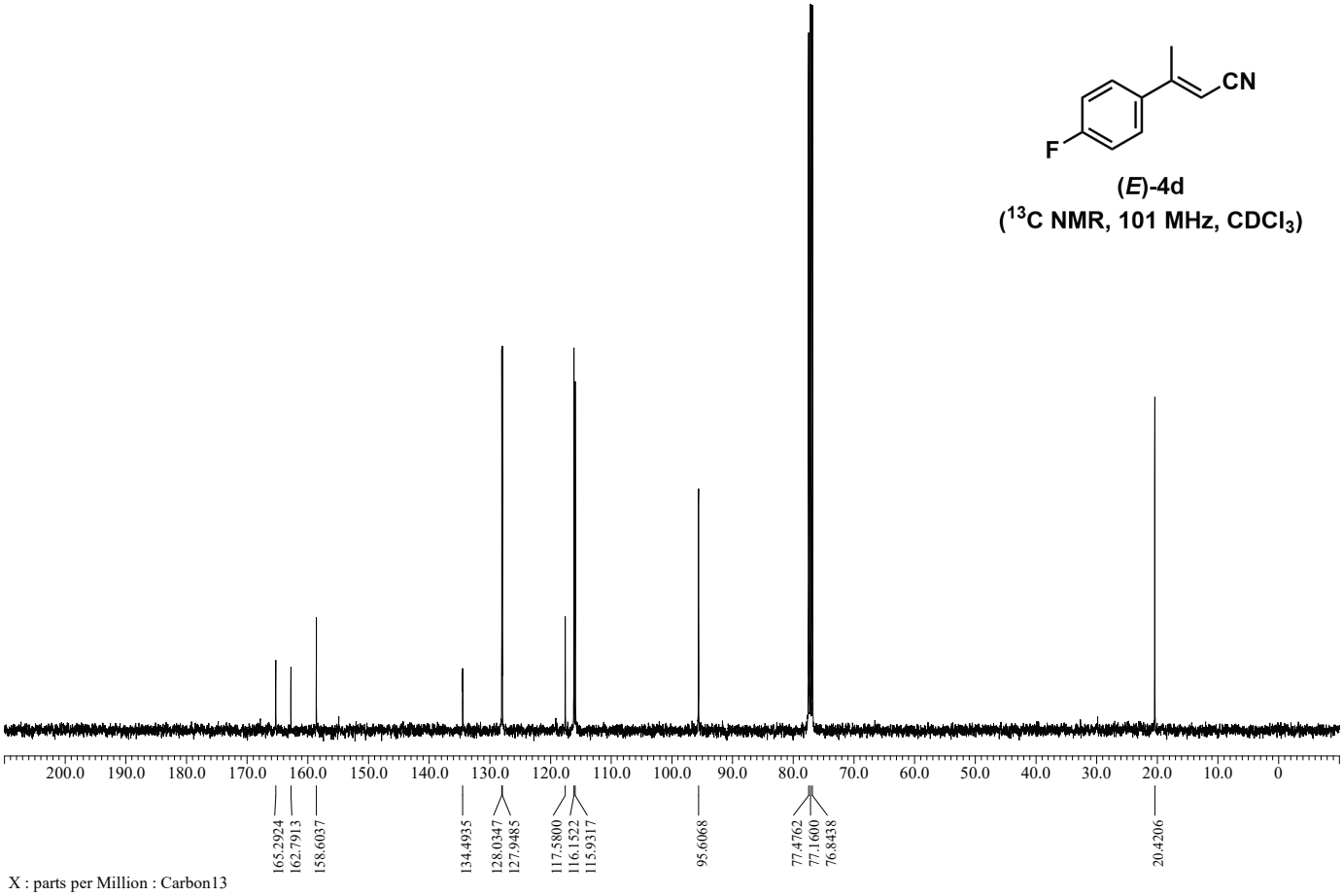

CN
MeO
(E)-4c
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.4402
158.9391
130.5167
127.4981
118.2795
114.2356
93.3357
77.4762
77.1600
76.8438
55.5509
20.1619
X : parts per Million : Carbon13


MeO
CN
(Z)-4c
(1H NMR, 400 MHz, CDCl3)
1.881
1.915
0.887
3.000
2.992
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5866
7.5792
7.5735
7.5620
7.5569
7.5489
7.2600
6.9602
6.9522
6.9471
6.9356
6.9299
6.9225
5.3098
5.3064
5.3030
5.2990
3.8408
2.2579
2.2539
0.0000
X : parts per Million : Proton

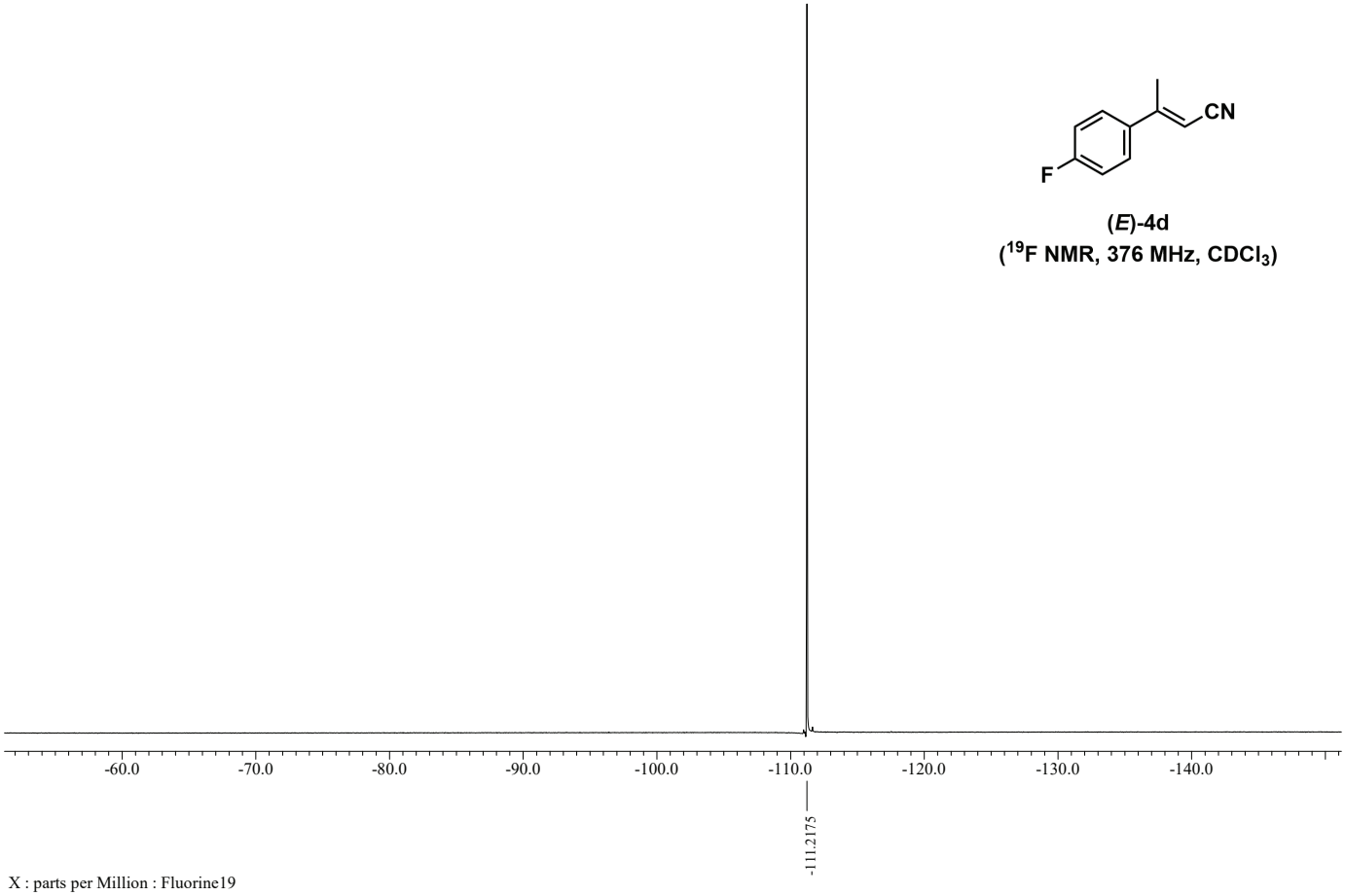

MeO
CN
(Z)-4c
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.9610
160.0986
130.1525
128.8684
118.3178
114.0248
93.6902
77.4762
77.1600
76.8342
55.4934
24.6754
X : parts per Million : Carbon13



(*E*)-4d
(^{1}H NMR, 400 MHz, $CDCl_3$)

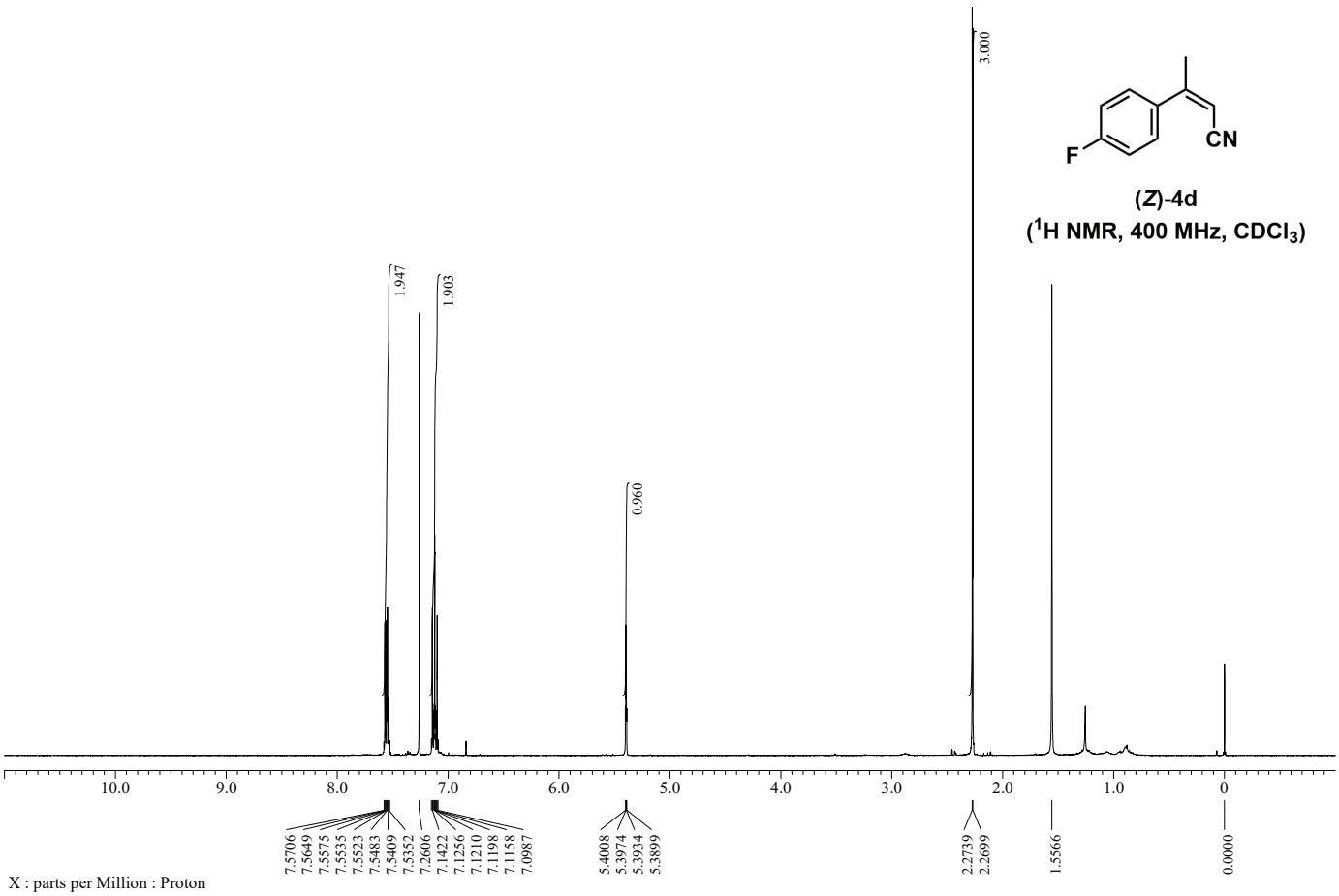


(*E*)-4d
(^{13}C NMR, 101 MHz, $CDCl_3$)



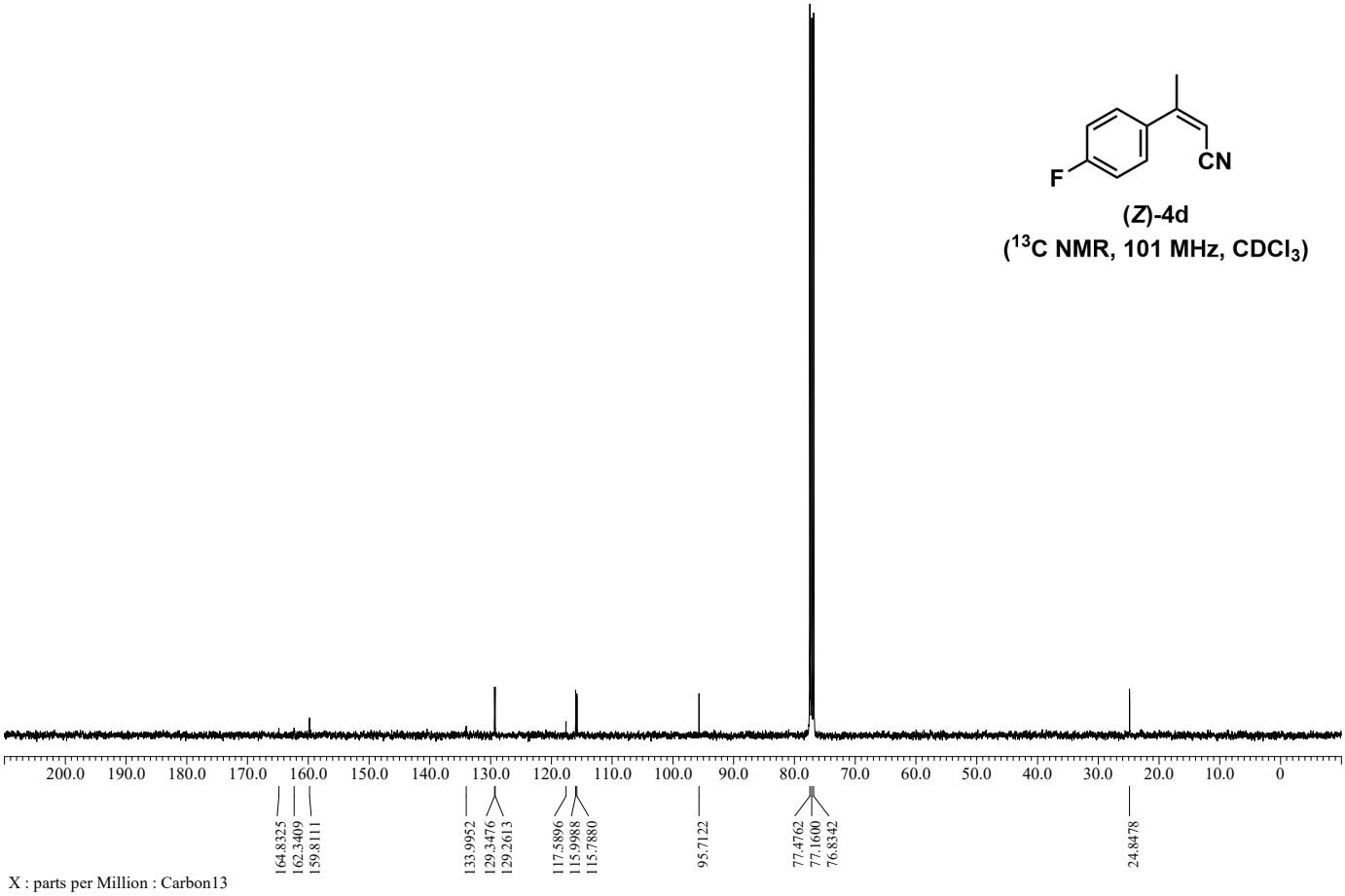
(*E*)-4d
(^{19}F NMR, 376 MHz, $CDCl_3$)

X : parts per Million : Fluorine19

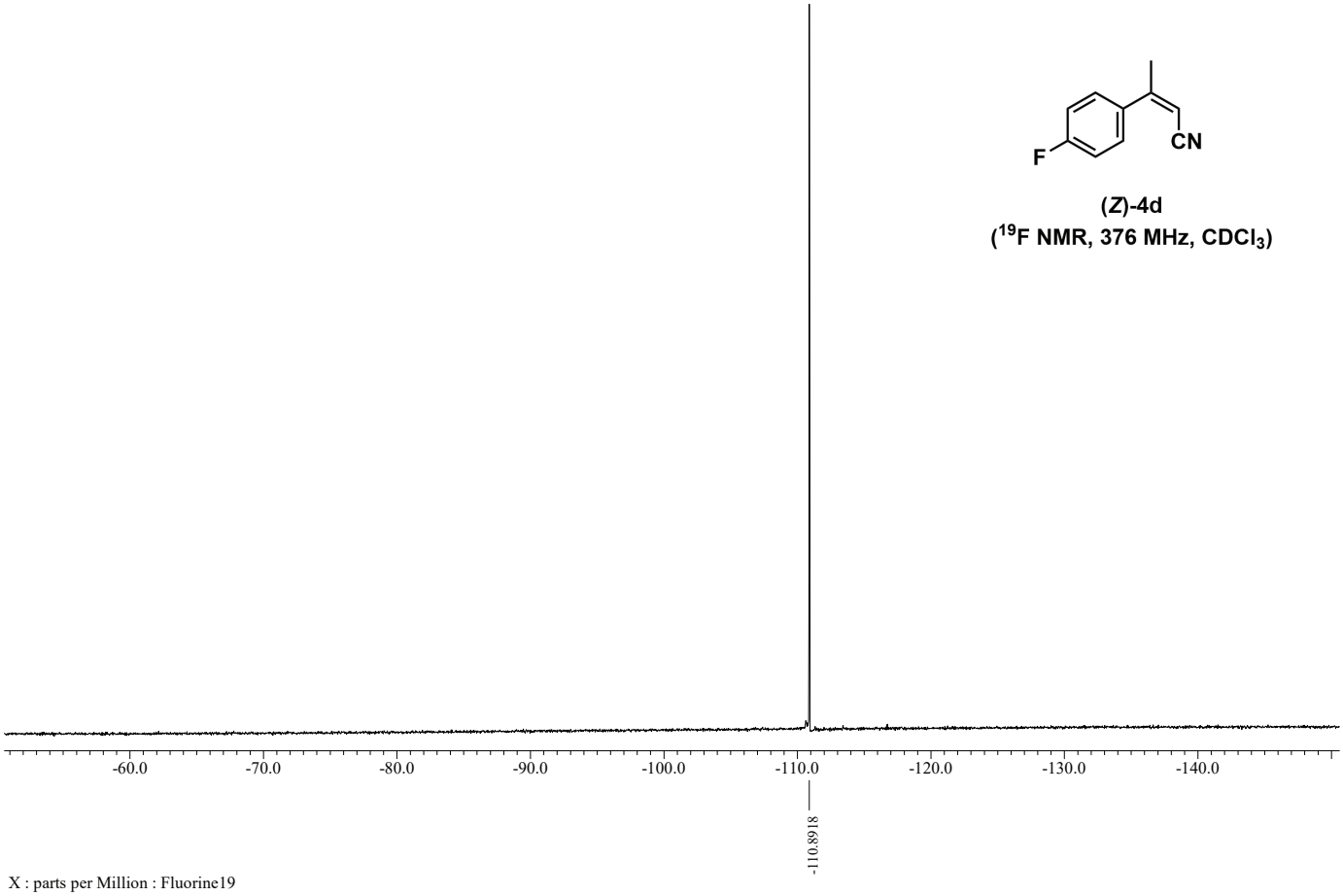


(*Z*)-4d
(^{1}H NMR, 400 MHz, $CDCl_3$)

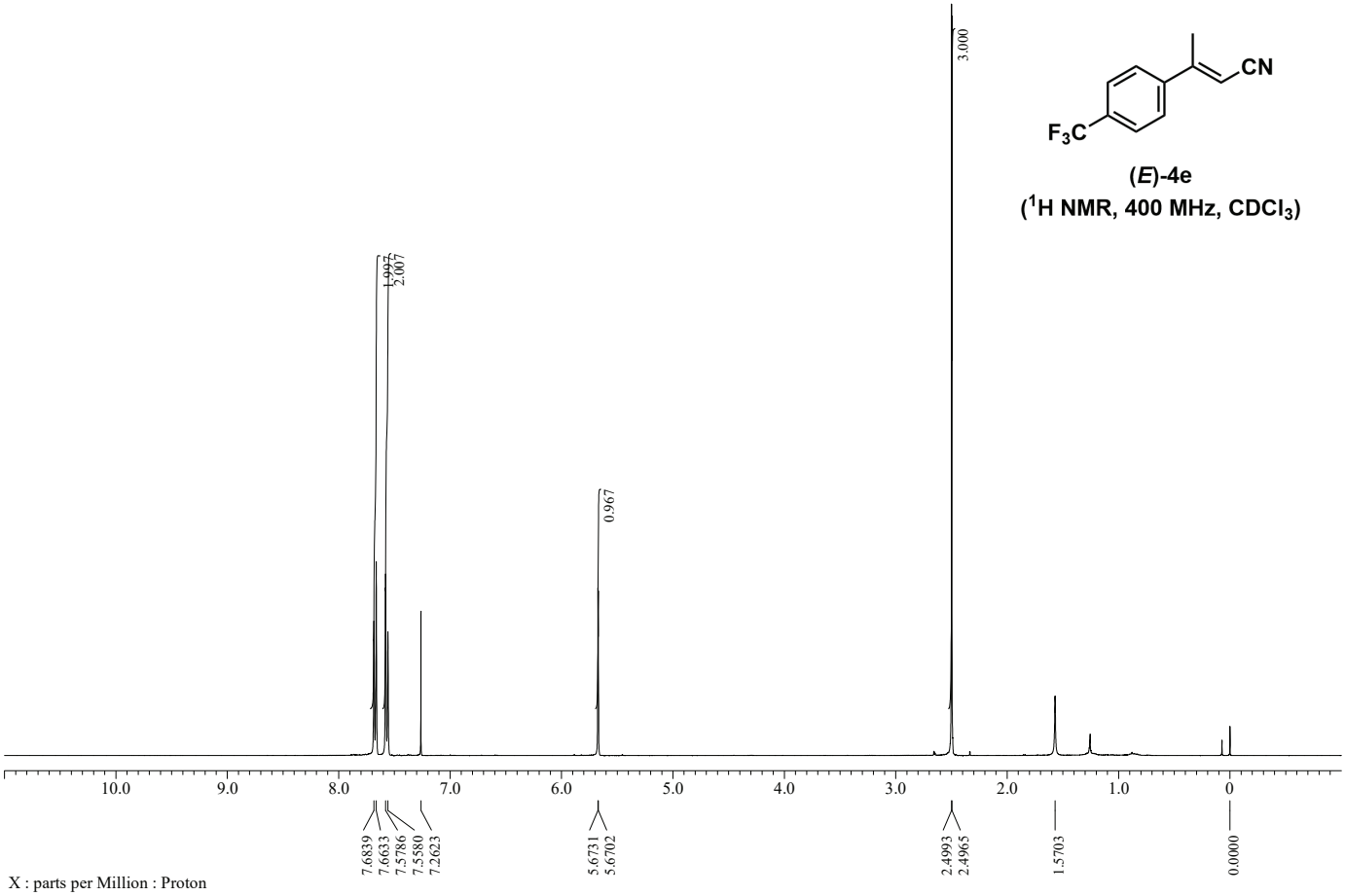
X : parts per Million : Proton



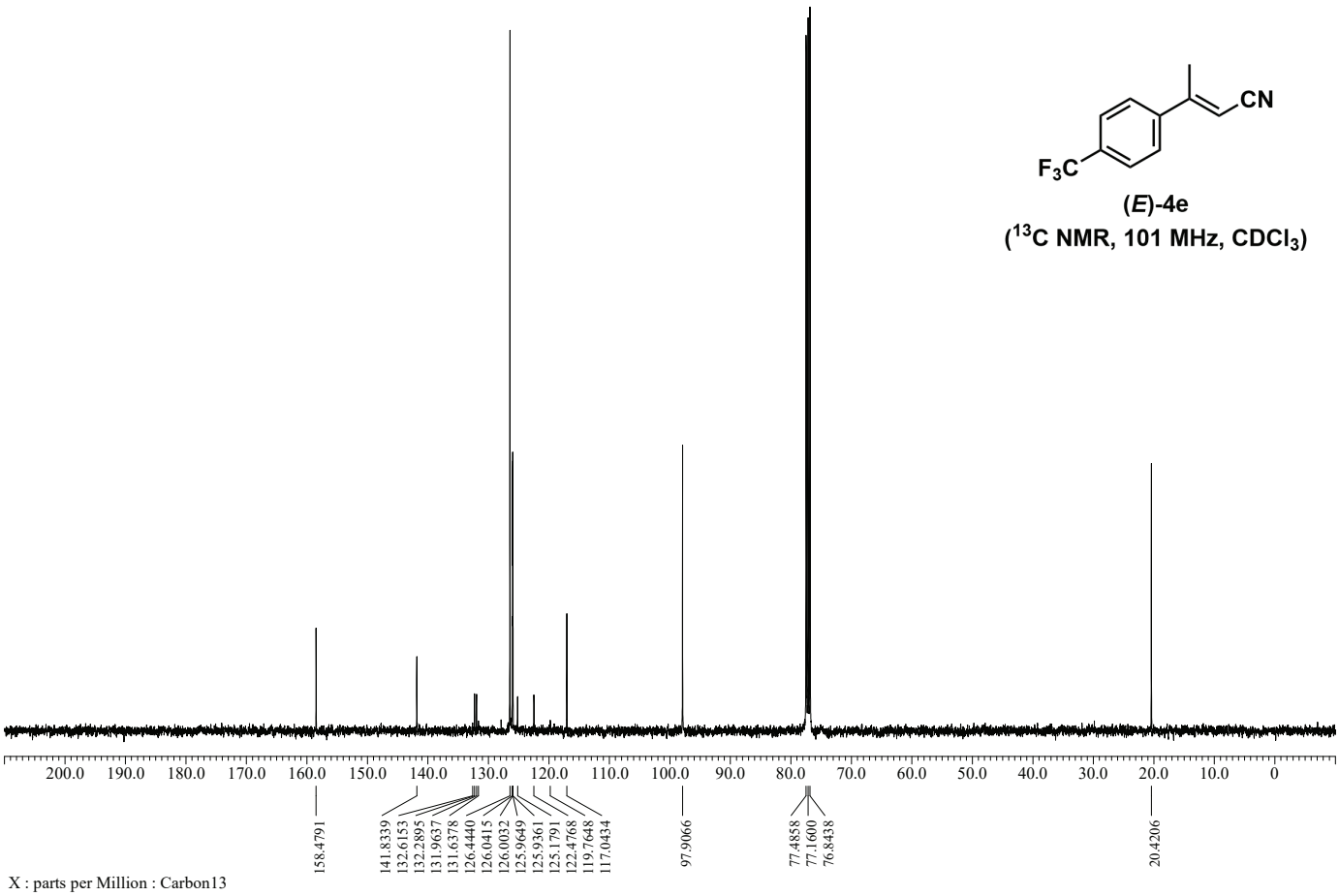
(*Z*)-4d
(^{13}C NMR, 101 MHz, $CDCl_3$)



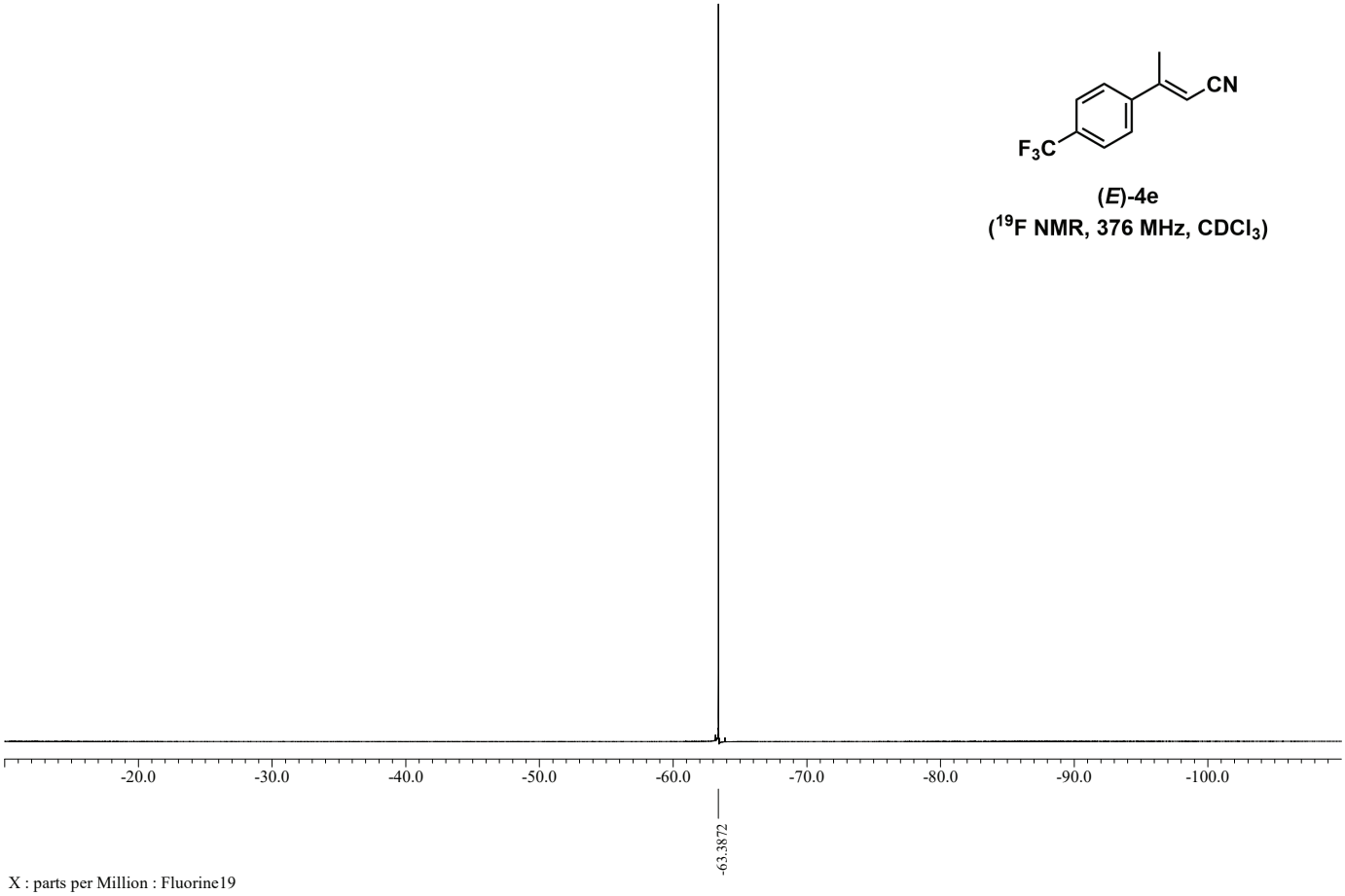
(*Z*)-4d
(^{19}F NMR, 376 MHz, $CDCl_3$)



(*E*)-4e
(^{1}H NMR, 400 MHz, $CDCl_3$)

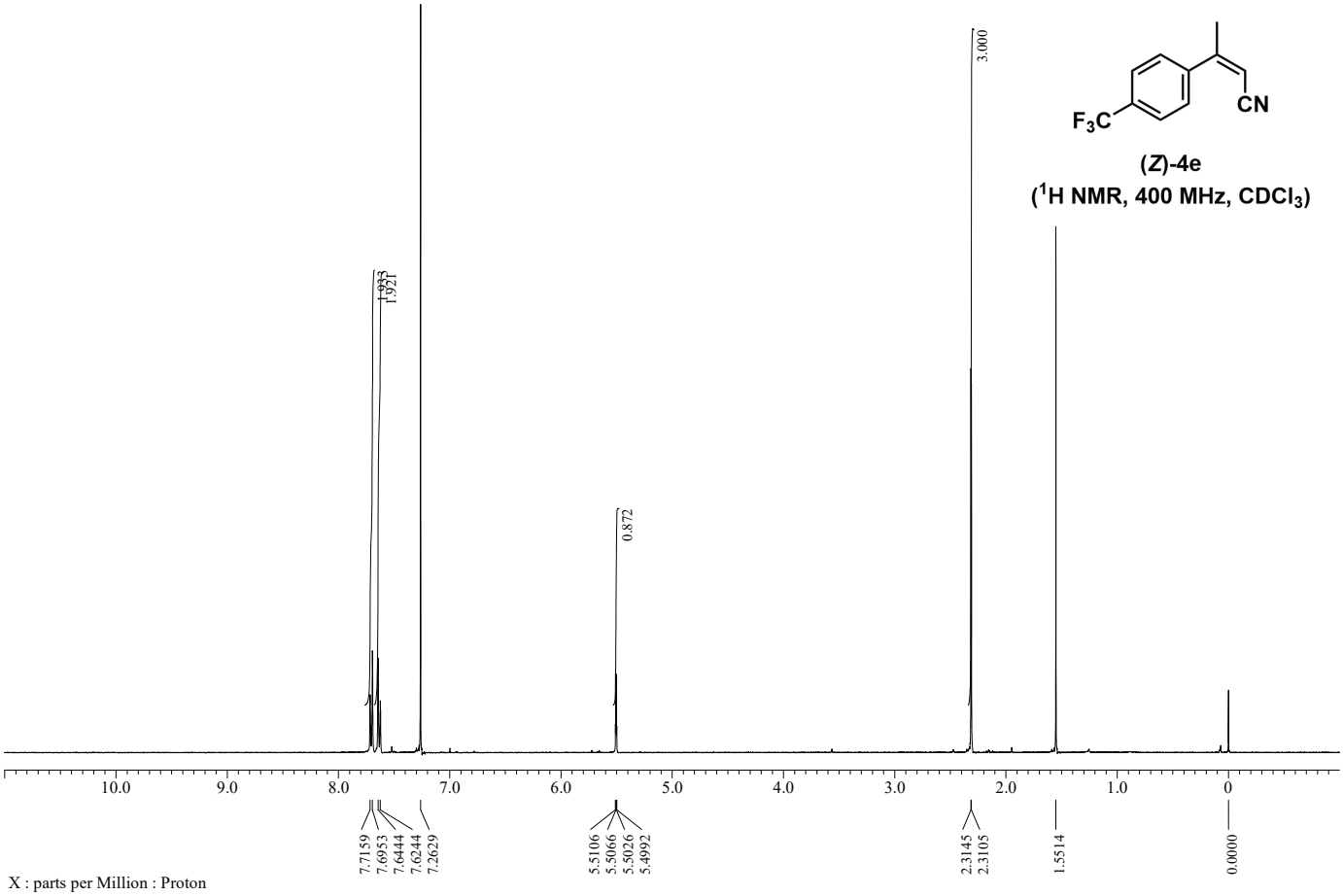


(*E*)-4e
(^{13}C NMR, 101 MHz, $CDCl_3$)



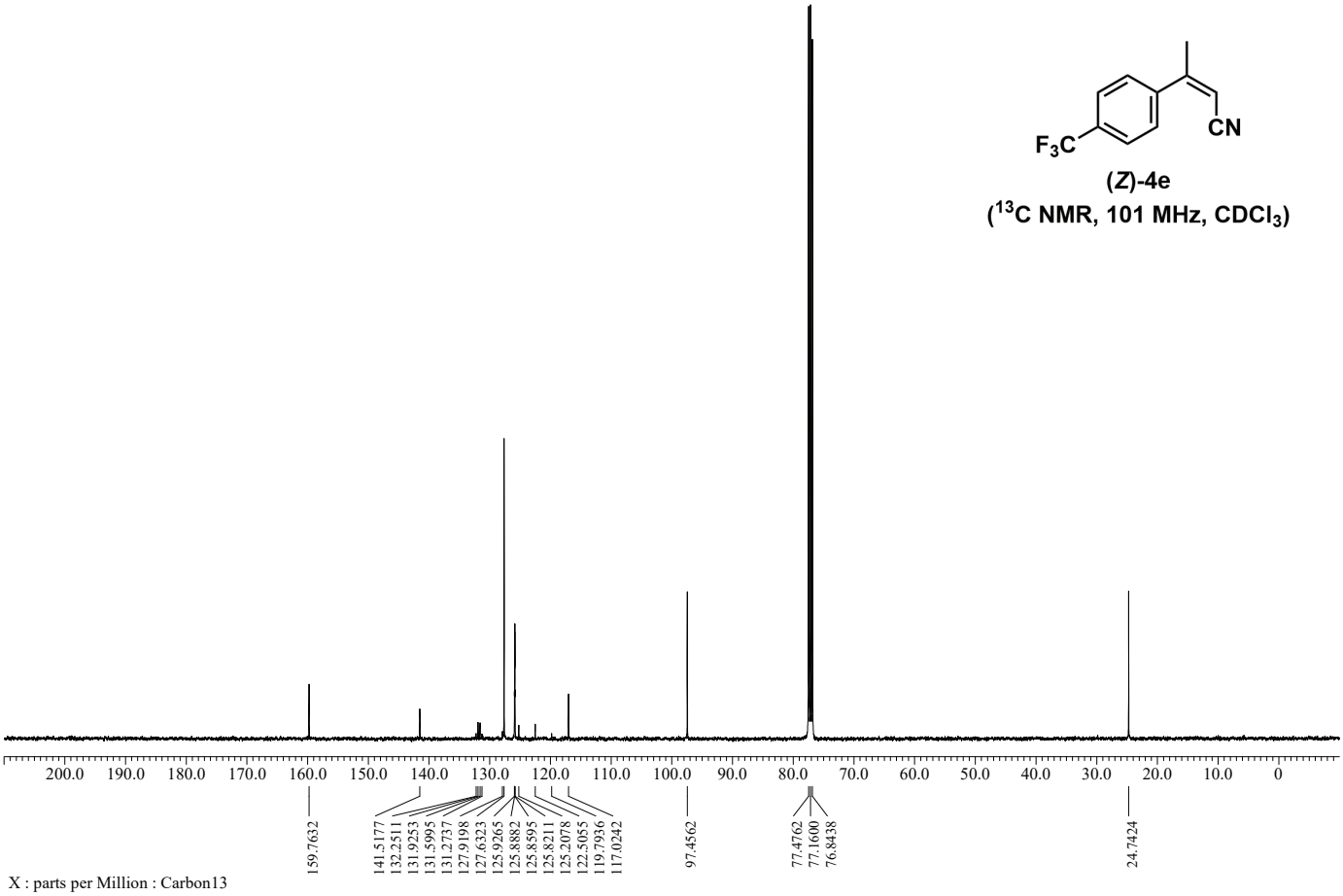
(*E*)-4e
(^{19}F NMR, 376 MHz, $CDCl_3$)

X : parts per Million : Fluorine19



(*Z*)-4e
(^{1}H NMR, 400 MHz, $CDCl_3$)

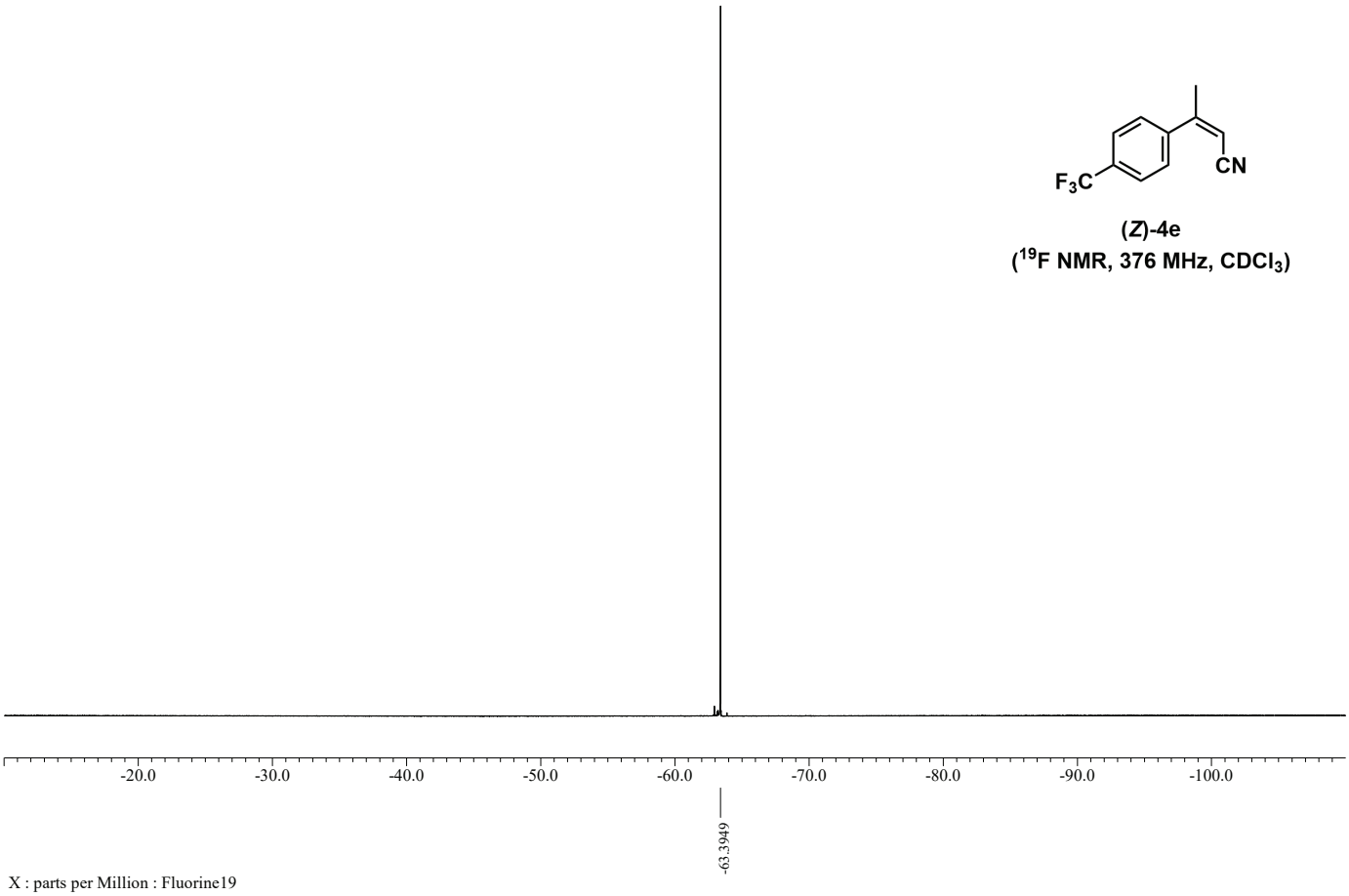
X : parts per Million : Proton



(*Z*)-4e

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

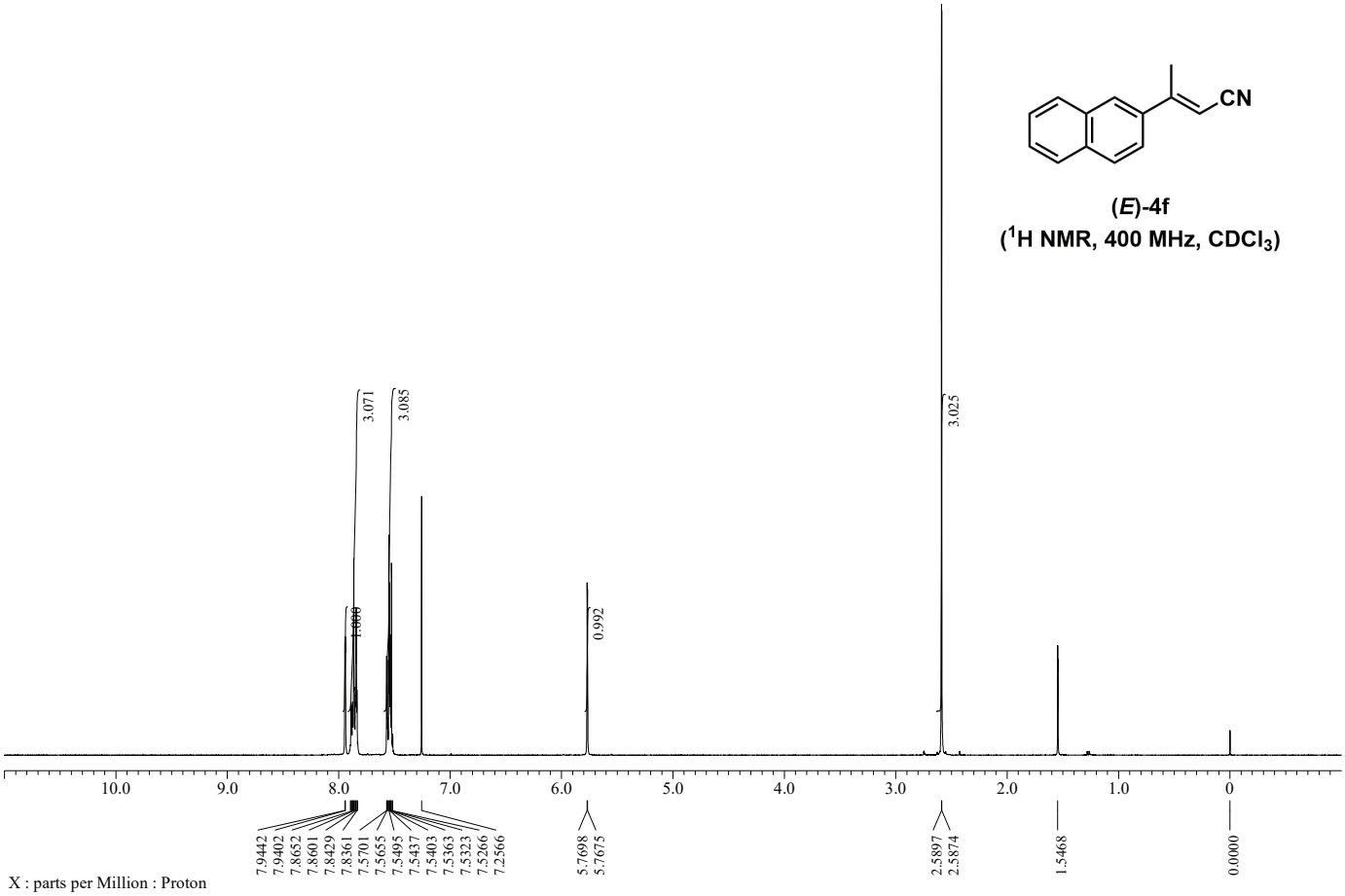
X : parts per Million : Carbon13

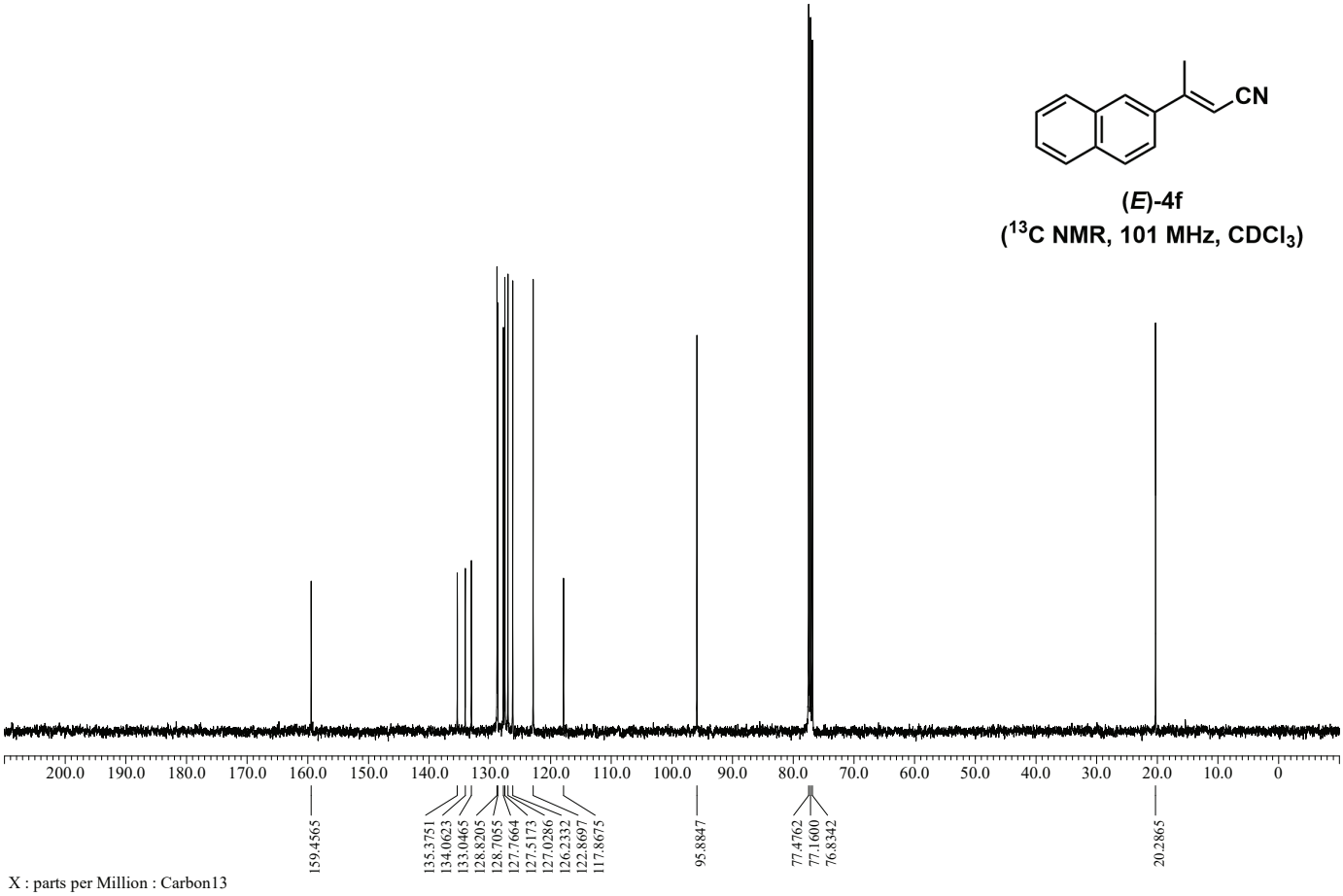


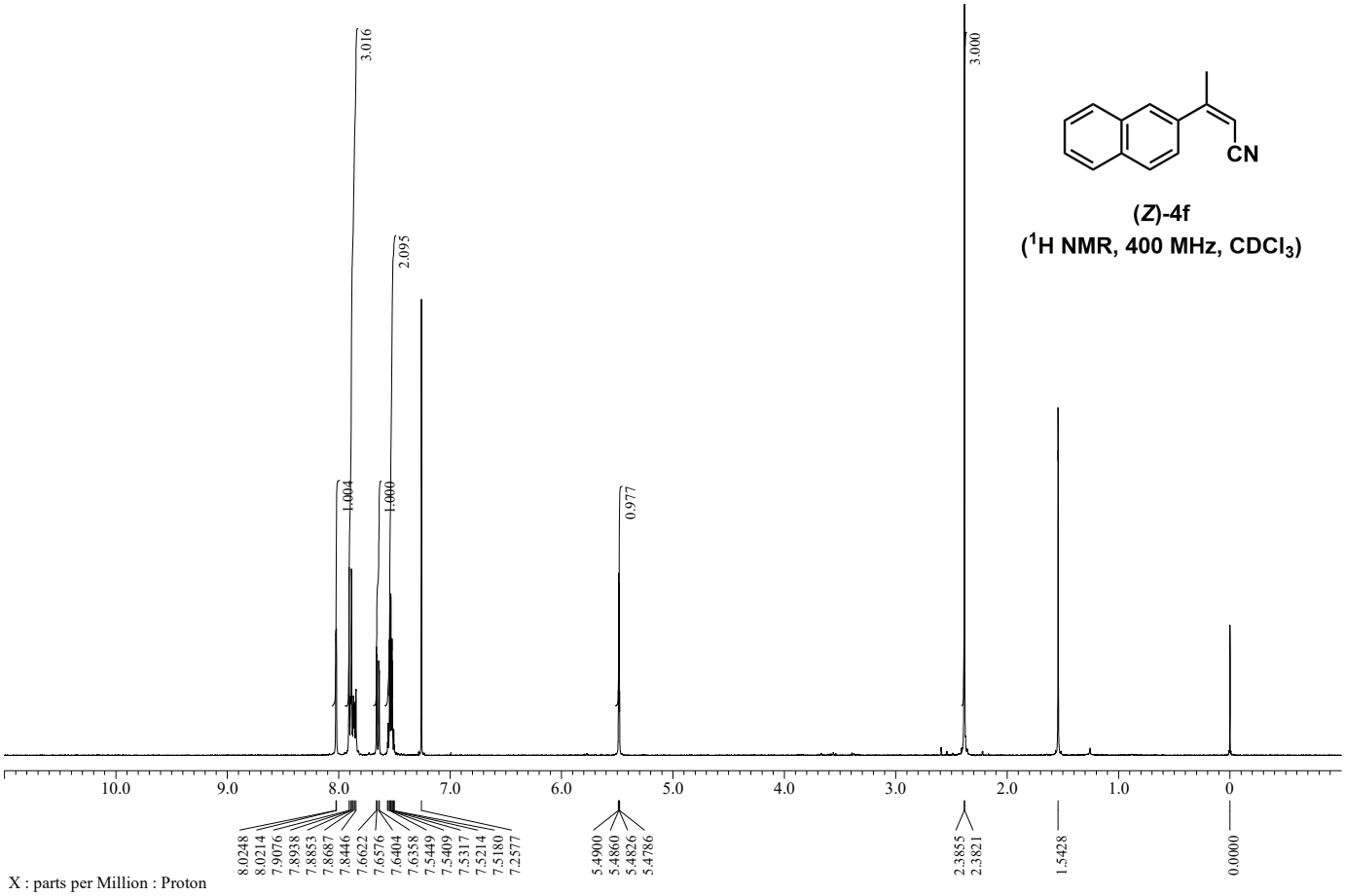
(*Z*)-4e

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

X : parts per Million : Fluorine19

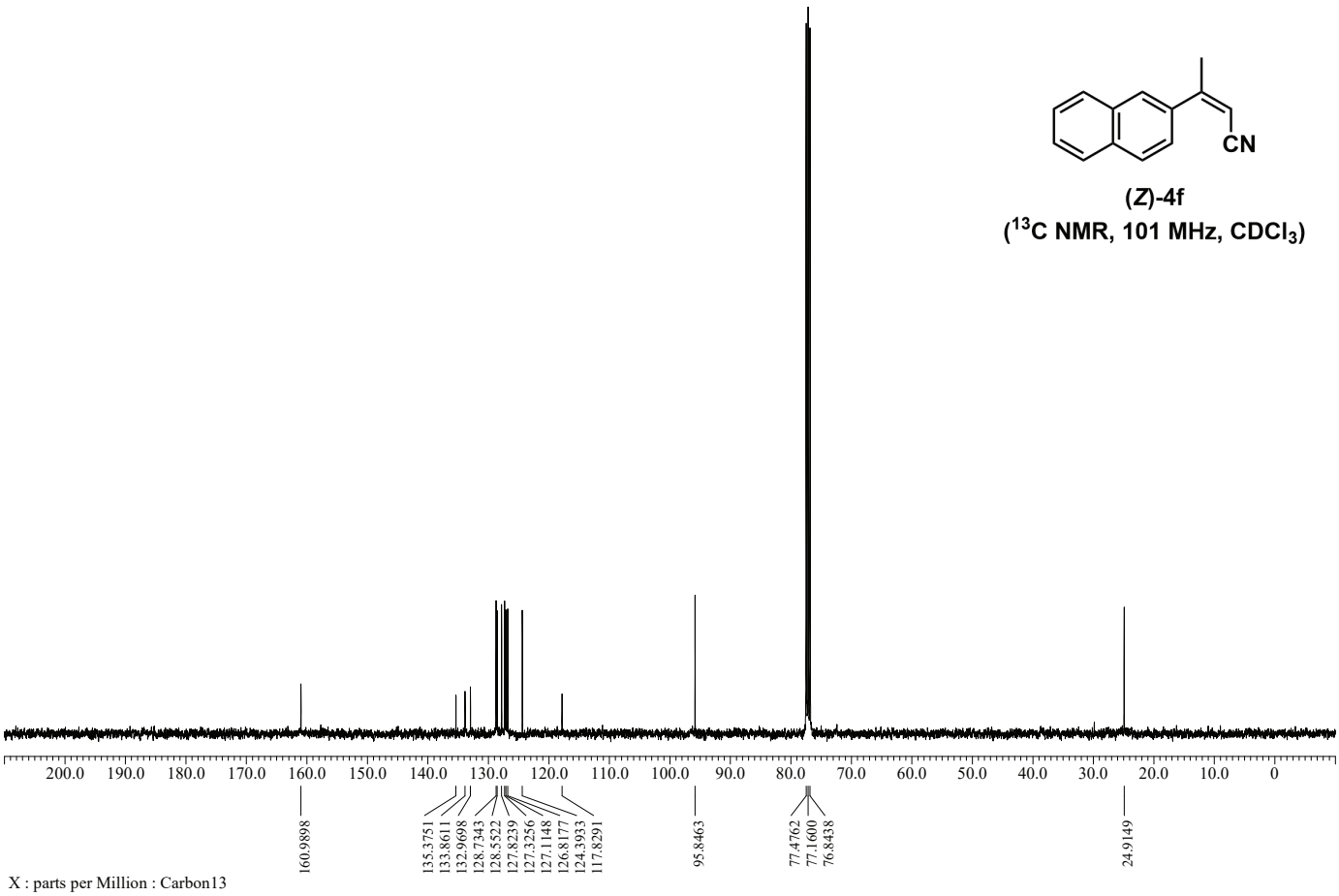

CN
(E)-4f
(1H NMR, 400 MHz, CDCl3)
3.071
3.085
3.025
1.000
0.992
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.9442
7.9402
7.8652
7.8601
7.8429
7.8361
7.5701
7.5655
7.5495
7.5437
7.5403
7.5363
7.5323
7.5266
7.2566
5.7698
5.7675
2.5897
2.5874
1.5468
0.0000
X : parts per Million : Proton


CN
(E)-4f
(13C NMR, 101 MHz, CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.4565
135.3751
134.0623
133.0465
128.8205
128.7055
127.7664
127.5173
127.0286
126.2332
122.8697
117.8675
95.8847
77.4762
77.1600
76.8342
20.2865
X : parts per Million : Carbon13



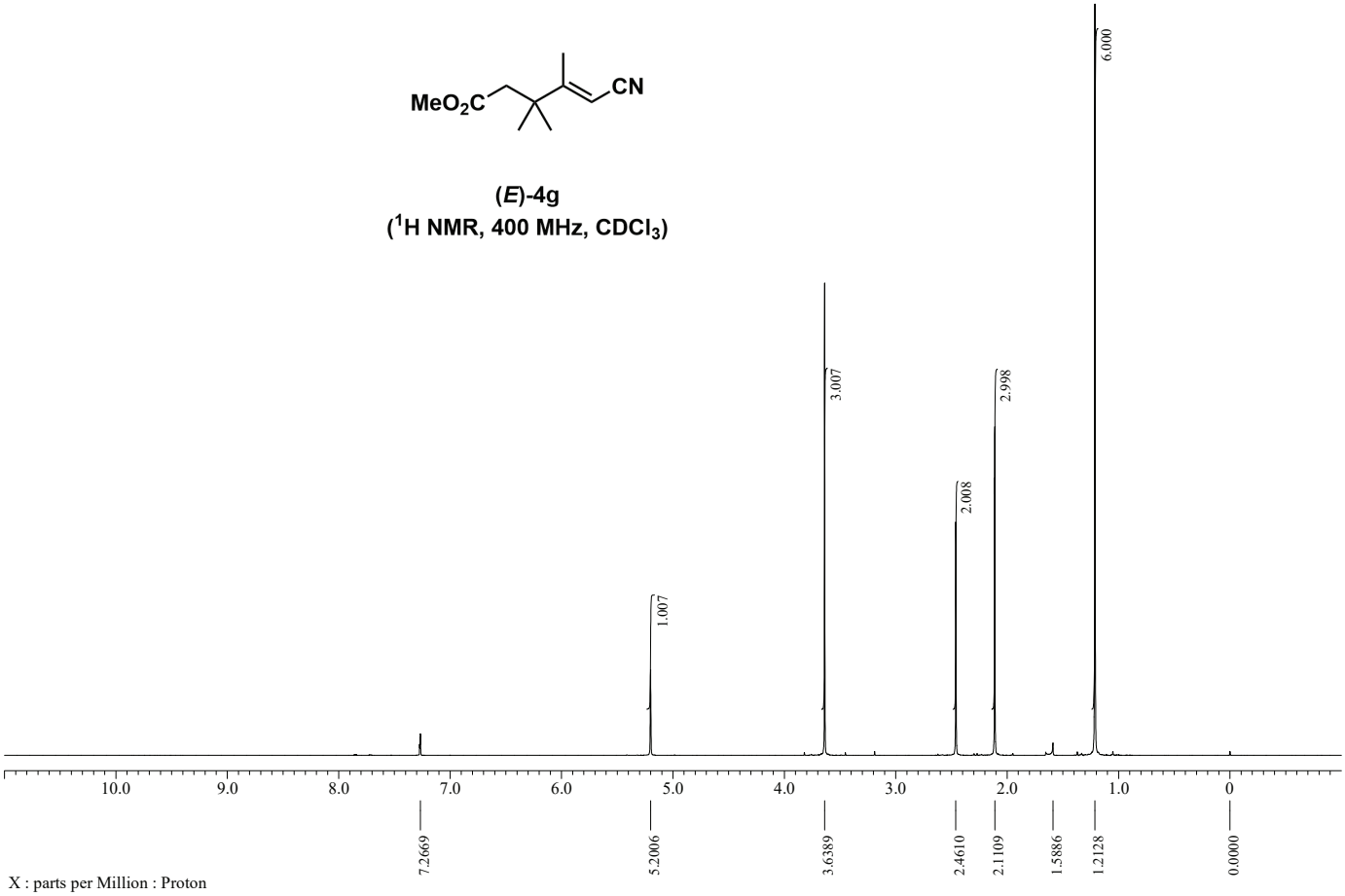
(*Z*)-4f
(^{1}H NMR, 400 MHz, $CDCl_3$)

X : parts per Million : Proton

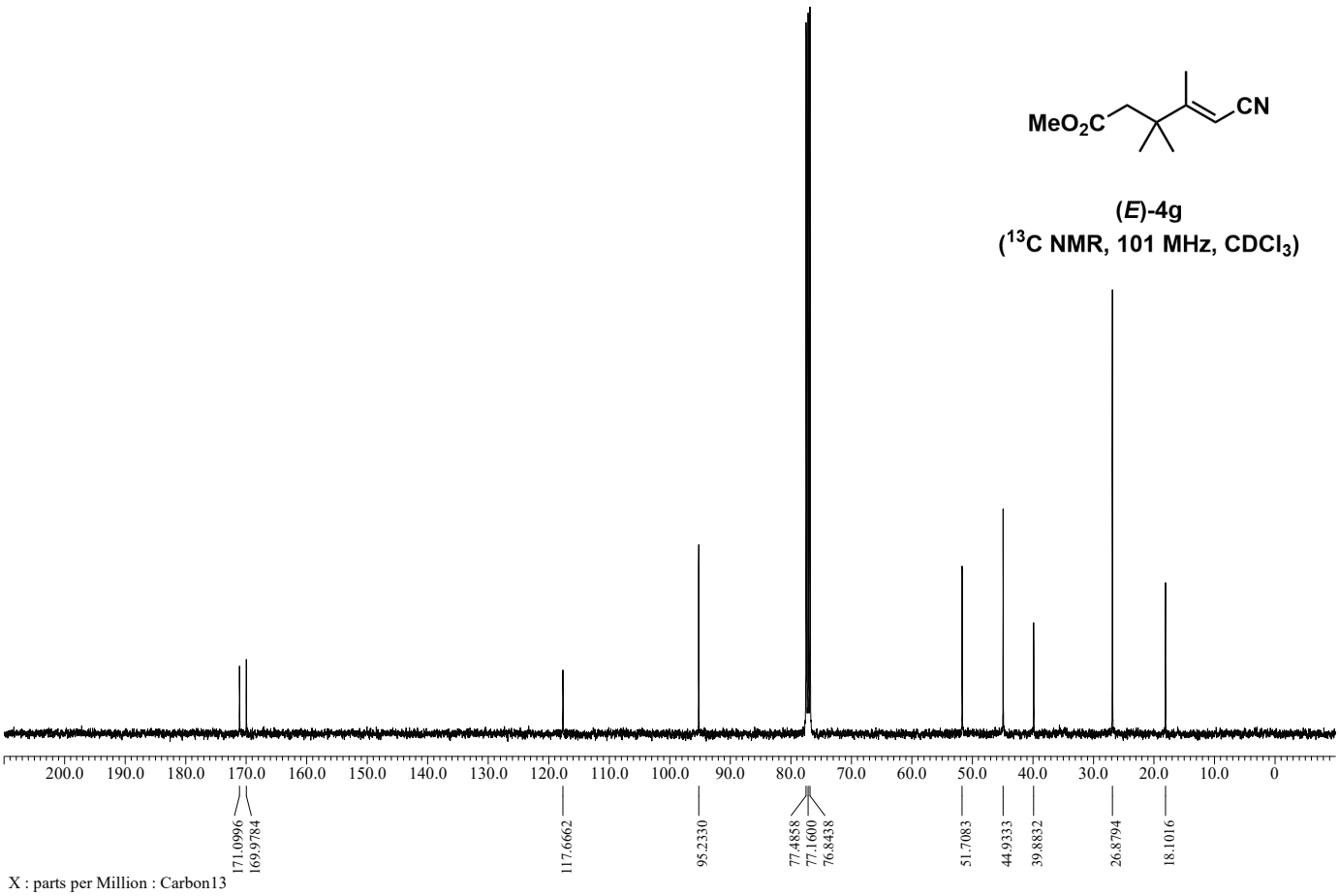


(*Z*)-4f
(^{13}C NMR, 101 MHz, $CDCl_3$)

X : parts per Million : Carbon13



(*E*)-4g
(^{1}H NMR, 400 MHz, $CDCl_3$)



(*E*)-4g
(^{13}C NMR, 101 MHz, $CDCl_3$)