Supporting Information

Stereoselective Intermolecular Allylic C-H Trifluoroacetoxylation of Functionalized Alkenes.

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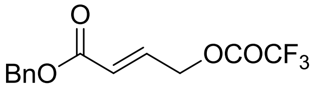
General Information

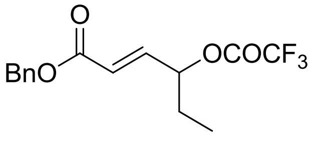
Alkenes **2a**, **2b** and **2d** and **2i-l** were prepared according to literature procedures literature procedures.[1-4] Compound **2m**[5] was synthesized from commercially available 3-cyclohexene-1-carboxaldehyde. All other chemicals were obtained from commercial sources and used as received. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C), using 400 MHz and 500 MHz spectrometers. High resolution mass data (HRMS) were obtained using ESI technique. For column chromatography, silica gel (35-70 microns) was used.

Experimental Procedures and Spectral Data

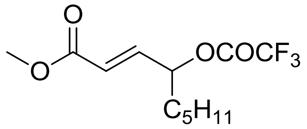
General Procedure: Allylic C-H Trifluoroacetoxylation (Table 1). The corresponding compound **2** (0.3 mmol) was dissolved in dimethyl carbonate (for the reactions conducted at 0 °C, a mixture of DMC:DCM=10:1 was used as solvent to prevent the freezing of DMC at that temperature), followed by the addition of PIFA **1a** (0.45 mmol) and palladium acetate (0.015 mmol, 5 mol %). Then, the reaction mixture was stirred for the indicated times and temperatures given in Table 1. The crude products were purified by silica gel chromatography.



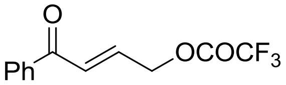
(*E*)-benzyl 4-(2,2,2-trifluoroacetoxy)but-2-enoate (3a). The compound was prepared according to above general procedure, except that 0.6 mmol of LiTFA was also added. Product **3a** was isolated in 52% yield (45.0 mg) using ether:pentane (1:10) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.34 (m, 5H), 6.97 (dt, J = 15.8, 4.8 Hz, 1H), 6.14 (dt, J = 15.8, 1.9 Hz, 1H), 5.21 (s, 2H), 4.99 (dd, J = 4.8, 1.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1, 157.0 (q, $^2J_{\mathbf{C\text{-}F}}$ =43.0 Hz), 138.4, 135.7, 128.8, 128.6, 128.5, 124.0, 114.5 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.3 Hz), 66.9, 65.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.8; HRMS (pos. ESI) m/z: Calcd for $C_{13}H_{11}F_3O_4Na$ $[M+Na]^+$ 311.0502. Found, 311.0502.



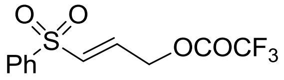
(*E*)-benzyl 4-(2,2,2-trifluoroacetoxy)hex-2-enoate (3b). The compound was prepared according to above general procedure, except that 0.6 mmol of LiTFA was also added. Product **3b** was isolated in 66% yield (63.0 mg) using pentane:dichloromethane (2:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 5H), 6.88 (dt, J = 15.7, 5.7 Hz, 1H), 6.07 (dt, J = 15.7, 1.5 Hz, 1H), 5.53-5.48 (m, 1H), 5.24-5.17 (m, 2H), 1.88-1.80 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 156.8 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.5 Hz), 142.7, 135.7, 128.8, 128.6, 128.5, 123.3, 114.6 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.8 Hz), 78.1, 66.9, 26.8, 9.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.0; HRMS (pos. ESI) m/z: Calcd for $C_{15}H_{15}F_3O_4Na$ $[M+Na]^+$ 339.0815. Found, 339.0814.



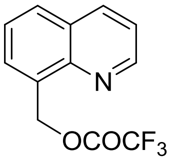
(*E*)-methyl 4-(2,2,2-trifluoroacetoxy)non-2-enoate (3c). The compound was prepared according to above general procedure, except that 0.6 mmol of LiTFA was also added. Product **3c** was isolated in 88% yield (74.8 mg) using pentane:dichloromethane (1:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (dd, J = 15.8, 5.8 Hz, 1H), 6.01 (dd, J = 15.8, 1.4 Hz, 1H), 5.5 (q, J = 5.9 Hz, 1H), 3.77 (s, 3H), 1.86-1.72 (m, 2H), 1.39-1.25 (m, 6H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 156.8 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.5 Hz), 142.7, 123.0, 114.5 (q, $^1J_{C\text{-}F}$ =283.4 Hz), 52.1, 33.6, 31.4, 24.4, 22.5, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.0; HRMS (pos. ESI) m/z: Calcd for $C_{12}H_{17}F_3O_4Na$ $[M+Na]^+$ 305.0971. Found, 305.0978.



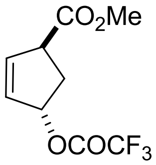
(*E*)-4-(trifluorocetoxy)-1-phenyl-2-buten-1-one (3d). The compound was prepared according to above mentioned general procedure, except that 0.6 mmol of LiTFA was also added. Product **3d** was isolated in 70% yield (54.2 mg) using pentane:ether (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.93 (m, 2H), 7.63-7.58 (m, 1H), 7.53-7.48 (m, 2H), 7.17 (dt, J = 15.5, 1.8 Hz, 1H), 7.00 (dt, J = 15.5, 4.8 Hz, 1H), 5.11 (dd, J = 4.7, 1.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.3, 157.1 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.8 Hz), 137.6, 137.1, 133.6, 128.9, 128.8, 127.4, 114.5 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.4 Hz), 66.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.7; HRMS (pos. ESI) m/z: Calcd for $C_{12}H_9F_3O_3Na$ $[M+Na]^+$ 281.0396. Found, 281.0405.



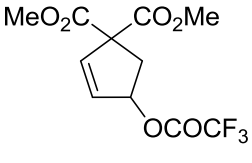
(*E*)-3-(phenylsulfonyl)allyl 2,2,2-trifluoroacetate (3e). The compound was prepared according to above general procedure, except that 0.6 mmol of LiTFA was also added. Product **3e** was isolated in 94% yield (83.4 mg) using ether:pentane (1:3) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.93-7.90 (m, 2H), 7.70-7.65 (m, 1H), 7.61-7.56 (m, 2H), 7.00 (dt, *J* = 15.2, 4.2 Hz, 1H), 6.62 (dt, *J* = 15.2, 2.0 Hz, 1H), 5.03 (dd, *J* = 4.2, 2.0 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 156.7 (q, $^{2}J_{\mathbf{C\text{-}F}}$ =43.3 Hz), 139.4, 136.2, 134.1, 133.1, 129.7, 128.0, 114.3 (q, $^{1}J_{\mathbf{C\text{-}F}}$ =285.3 Hz), 64.4; ^{19}F NMR (282 MHz, CDCl$_3$) δ -75.2; HRMS (pos. ESI) m/z: Calcd for $C_{11}H_9F_3O_4SNa$ [M+Na]$^+$ 317.0066. Found, 317.0076.



quinolin-8-ylmethyl 2,2,2-trifluoroacetate (3f). The compound was prepared according to above general procedure, except that 0.6 mmol of LiTFA and 3.0 mmol of $(CF_3CO)_2O$ were also added. Compound **3f** rapidly hydrolyzed on silica, and therefore it was not isolated. The NMR yield was determined using phenyl iodide as an internal standard from ^{1}H NMR of the crude reaction mixture. Spectral information is based on data determined for the crude reaction mixture. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 9.41 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.65 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.10 (d, *J* = 8.3, 1H), 8.01(d, *J* = 7.0, 1H) 7.85-7.78 (m, 2H), 6.02 (s, 2H); ^{19}F NMR (282 MHz, CDCl$_3$) δ -74.8.

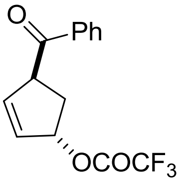


(1R,4R)-methyl 4-(2,2,2-trifluoroacetoxy)cyclopent-2 encarboxylate (3g). The compound was prepared according to above mentioned general procedure. Product **3g** was isolated in 75% yield (54 mg) using ether:pentane (1:20) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 6.25-6.23 (m, 1H), 6.02-5.99 (m, 1H), 5.97-5.94 (m, 1H), 3.88-3.83 (m, 1H), 3.71 (s, 3H), 2.68 (ddd, *J* = 15.0, 7.4, 5.2 Hz, 1H), 2.22 (ddd, *J* = 15.0, 8.1, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 173.1, 157.4 (q, $^{2}J_{\mathbf{C\text{-}F}}$ =42.1 Hz), 138.2, 130.0, 114.5 (q, $^{1}J_{\mathbf{C\text{-}F}}$ =286.1 Hz), 84.3, 52.5, 49.7, 33.1; ^{19}F NMR (282 MHz, CDCl$_3$) δ -75.2; HRMS (pos. ESI) m/z: Calcd for $C_9H_{10}F_3O_4$ [M+H]$^+$ 239.0526. Found, 239.0537.

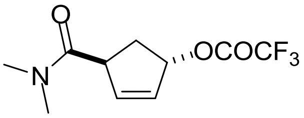


dimethyl 4-(2,2,2-trifluoroacetoxy)cyclopent-2-ene-1,1-dicarboxylate (3h). The compound was prepared according to above mentioned general procedure. Product **3h** was isolated in 86% yield (76.0 mg) using ether:pentane (1:3) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 6.30 (dd, *J* = 5.6, 1.0 Hz, 1H), 6.07

(dd, *J* = 5.6, 2.1 Hz, 1H), 5.93-5.90 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.05 (dd, *J* = 14.9, 7.4 Hz, 1H), 2.48 (dd, *J* = 14.9, 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 170.1, 169.9, 157.2 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.5 Hz), 136.8, 131.7, 114.5 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.8 Hz), 82.6, 65.6, 53.5, 53.3, 37.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.1; HRMS (pos. ESI) m/z: Calcd for $C_{11}H_{11}F_3O_6Na_2$[M+2Na]$^+$ 342.0298. Found, 342.0285

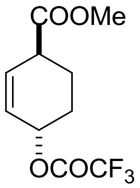


(1R,4R)-4-benzoylcyclopent-2-en-1-yl 2,2,2-trifluoroacetate (3i). The compound was prepared according to above mentioned general procedure. Product **3i** was isolated in 49% yield (42.0 mg) using ether:pentane (1:25) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.01-7.99 (m, 2H), 7.64-7.60 (m, 1H), 7.53-7.50 (m, 2H), 6.31-6.30 (m, 1H), 6.06-6.02 (m, 2H), 4.85-4.81 (m, 1H), 2.83 (ddd, *J* = 14.8, 7.3, 5.1 Hz, 1H), 2.28 (ddd, *J* = 14.7, 8.0, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 198.4, 157.1 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.0 Hz), 138.8, 136.0, 133.8, 130.0, 129.1, 128.7, 114.6 (q, $^1J_{\mathbf{C\text{-}F}}$ =286.1 Hz), 84.7, 52.8, 33.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.1; HRMS (pos. ESI) m/z: Calcd for $C_{14}H_{11}F_3O_3Na$ [M+Na]$^+$ 307.0552. Found, 307.0565.

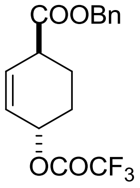


(1S,4S)-4-(dimethylcarbamoyl)cyclopent-2-en-1-yl 2,2,2-trifluoroacetate (3j). The compound was prepared according to above mentioned general procedure. Product **3j** was obtained as a 3:1 mixture of two regio-isomer (see table 1) and isolated in total 59 % yield (44.0 mg) using pentane:EtOAc (1:1) as eluent for silica gel chromatography. *Major regioisomer*, ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.17 (dd, *J* = 5.1, 2.1, 1H), 6.04-6.00 (m, 2H), 4.12-4.07 (m, 1H), 3.13 (s, 3H), 2.97 (s, 3H), 2.70 (ddd, *J* = 14.5, 7.2, 5.2 Hz, 1H), 2.18 (ddd, *J* = 14.5, 7.8, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 172.3, 157.4 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.0 Hz), 138.7, 129.9, 114.6 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.8 Hz), 85.0, 47.4, 37.5, 36.1, 34.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.2; HRMS (pos. ESI) m/z: Calcd for $C_{10}H_{13}F_3NO_3$ [M+H]$^+$ 252.0842. Found, 252.0831.

Minor regioisomer, ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.26 (br s, 1H), 6.14-6.11 (m, 1H), 5.88-5.85 (m, 1H), 3.41 (ddd, *J* = 9.0, 5.1, 3.8 Hz, 1H), 3.08 (s, 3H), 3.01 (s, 3H), 2.96-2.88 (m, 1H), 2.58-2.52(m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 172.8, 157.2 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.0 Hz), 137.4, 127.3, 114.6 (q, $^1J_{\mathbf{C\text{-}F}}$ =286.1 Hz), 88.5, 45.6, 37.7, 36.6, 36.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.1; HRMS (pos. ESI) m/z: Calcd for $C_{10}H_{13}F_3NO_3$ $[M+H]^+$ 252.0842. Found, 252.0845.



(1S,4S)-methyl 4-(2,2,2-trifluoroacetoxy)cyclohex-2-enecarboxylate (3k). The compound was prepared according to above mentioned general procedure. Product **3k** was isolated in 53% yield (51.0 mg) using ether:pentane (1:20) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.15 (ddd, *J* = 10.1, 3.7, 1.2 Hz, 1H), 5.88 (dd, *J* = 10.1, 3.0 Hz, 1H), 5.47-5.43 (m, 1H), 3.72 (s, 3H), 3.24-3.19 (m, 1H), 2.23-2.15 (m, 1H), 2.13-2.05 (m, 1H), 2.02-1.94 (m, 1H), 1.87-1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 173.1, 157.3 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.3 Hz), 131.6, 125.7, 114.6 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.8 Hz), 72.4, 52.3, 40.5, 26.2, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.1; HRMS (pos. ESI) m/z: Calcd for $C_{10}H_{12}F_3O_4$ $[M+H]^+$ 253.0682. Found, 253.0695.



(1S,4S)-benzyl 4-(2,2,2-trifluoroacetoxy)cyclohex-2-enecarboxylate (3l). Prepared according to above general procedure. Product **3l** was isolated in 51% yield (51.0 mg) using ether:pentane (1:10) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.40-7.32 (m, 5H), 6.17 (ddd, *J* = 10.1, 3.7, 1.2 Hz, 1H), 5.88 (dd, *J* = 10.1, 3.0 Hz, 1H), 5.47-5.43 (m, 1H), 5.19-5.12 (m, 2H), 3.29-6.23 (m, 1H), 2.23-2.16 (m, 1H), 2.14-2.07 (m, 1H), 2.04-1.96 (m, 1H), 1.87-1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 172.4, 157.3 (q, $^2J_{\mathbf{C\text{-}F}}$ =42.0 Hz), 135.8, 131.5, 128.8, 128.5, 128.3, 125.8, 114.6 (q, $^1J_{\mathbf{C\text{-}F}}$ =285.8 Hz), 72.4, 66.9, 40.6, 26.2, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.2; HRMS (pos. ESI) m/z: Calcd for $C_{16}H_{15}F_3O_4Na$$[M+Na]^+$ 351.0815. Found, 351.0815.

Determination of Stereochemistry of 3l: The connectivity of carbons and hydrogens were determined by COSY and HSQC techniques. Subsequently, we performed a series of dNOE experiments varying mixing times (**τ**) from 0.5s to 3s. Irradiating the proton at the trifluoroacetate group ($H_{\mathbf{1a}}$) we observed NOE for the neighboring double bond proton H_2 , and for two other neighboring protons $H_{\mathbf{6a}}$ and $H_{\mathbf{6e}}$. In addition, we get 1.7% dNOE for another proton via through space interaction. This proton was identified as $H_{\mathbf{5a}}$ as shown in Figure 1.

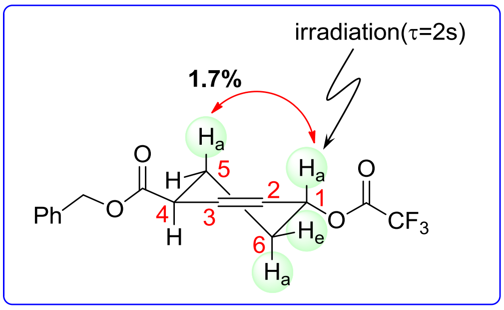


Figure 1. Observed NOE irradiating H_{1a}.

Similarly, when proton H_{4a} (attached to the ester group) was irradiated, we observed a through space dNOE interaction with a proton of 2.5%. We identified this proton as H_{6a} as shown in Figure 2.

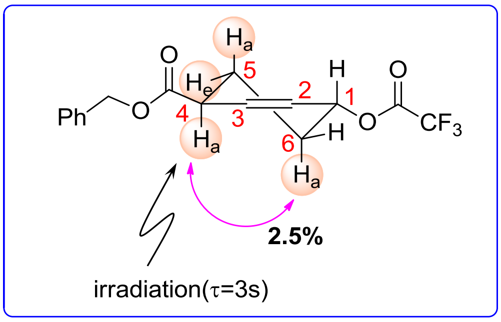
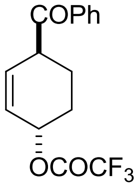


Figure 2. Observed NOE irradiating H_{4a}.

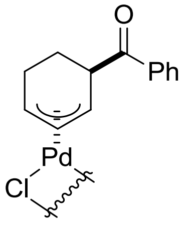
Accordingly, based on COSY, HSQC and the above dNOE experiments, we identify compond **3l** as an *anti*-isomer. Considering the similarities of the chemical shifts and coupling patterns we conclude that the structure of the main isomer arising from the trifluoroacetoxylation of monosubstituted alkenes are also anti-diastereomers.



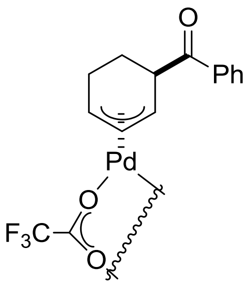
(1S,4S)-4-benzoylcyclohex-2-en-1-yl 2,2,2-trifluoroacetate (3m). The compound was prepared according to above mentioned general procedure. Product **3m** was obtained as a 15:1 mixture of two regio-isomer and isolated in total 50% (45 mg) using dichloromethane:toluene (1:1) as eluent for silica gel chromatography. *Major regioisomer*, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.94 (m, 2H), 7.62-7.58 (m, 1H), 7.52-7.48 (m, 2H), 6.14-6.10 (m, 1H), 5.99-5.95 (m, 1H), 5.53-5.49 (m, 1H), 4.23-

4.18 (m, 1H), 2.30-2.22 (m, 1H), 2.20-2.12 (m, 1H), 2.07-2.19 (m, 1H), 1.95-1.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.6, 157.3 (q, $^{2}J_{\mathbf{C\text{-}F}}$ =42.1 Hz), 135.8, 133.6, 132.1, 129.1, 128.7, 126.3, 114.7 (q, $^{1}J_{\mathbf{C\text{-}F}}$ =287.6 Hz), 72.6, 43.2, 26.1, 22.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.1; HRMS (pos. ESI) m/z: Calcd for $C_{15}H_{14}F_3O_3$ $[M+H]^+$ 299.0890. Found, 299.0898.

Minor regioisomer, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (m, 2H), 7.63-7.58 (m, 1H), 7.52-7.48 (m, 2H), 6.08-6.03 (m, 1H), 5.81-5.77 (m, 1H), 3.84 (ddd, J = 11.2, 8.0, 3.3 Hz, 1H), 2.35-2.24 (m, 1H), 2.21-2.08 (m, 2H), 1.91-1.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.7, 157.0 (q, $^{2}J_{\mathbf{C\text{-}F}}$ =42.3 Hz), 135.8, 133.7, 132.6, 129.0, 128.5, 124.1, 114.6 (q, $^{1}J_{\mathbf{C\text{-}F}}$ =286.1 Hz), 74.6, 45.9, 25.1, 24.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -75.2; HRMS (pos. ESI) m/z: Calcd for $C_{15}H_{13}F_3O_3Na$ $[M+Na]^+$ 321.0709. Found, 321.0696.



Complex 4a. Compound **3m** (0.087 mmol) was dissolved in C_6D_6 (1.2 mL) followed by addition of $Pd_2(dba)_3$ (0.058 mmol) and this mixture was stirred at room temperature for overnight. Subsequently, LiCl (0.26 mmol) was added and stirring was continues for an additional 12h. Product **4a** was isolated in 63% yield (18 mg) by silica gel chromatography using Et_2O: DCM (1:20) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.62-7.58 (m, 1H), 7.53-7.49 (m, 2H), 5.60 (t, J= 6.4 Hz, 1H), 5.39-5.35 (m, 1H), 5.17 (d, J= 6.4 Hz, 1H), 3.92-3.88 (m, 2H), 2.03-1.97 (m, 3H), 1.35-1.26 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.2, 135.1, 133.8, 129.1, 102.0, 80.7, 75.2, 47.7, 27.6, 22.5; HRMS (pos. ESI) m/z: Calcd for $C_{26}H_{26}Cl_2NaO_2Pd_2[M+Na]^+$ 674.9249. Found, 674.9272.



Complex 4b. Complex **4a** (0.018 mmol) was dissolved in $CDCl_3$ followed by addition of AgTFA (0.022 mmol) and this suspension was stirred for 2 hours at room temperature. Then the crude reaction mixture was filtered through a silica plug and washed by DCM. After evaporation product **4b** was isolated in 78% yield (4.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J= 7.5 Hz, 2H), 7.62-7.59 (m, 1H), 7.49 (t, J= 7.5 Hz, 2H), 5.54 (br s, 1H),

5.31 (m, t, *J*= 5.9 Hz, 1H), 5.08 (d, *J*= 5.9 Hz, 1H), 3.9 (dd, *J*= 10.9, 5.1 Hz, 1H), 2.14-2.08 (m, 1H), 2.01-1.94 (m, 1H), 1.88-1.85 (m, 1H), 1.34-1.27 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.5

References:

(1) Pilarski, L. T.; Janson, P. G.; Szabó, K. J. *J. Org. Chem.* **2011**, *76*, 1503.

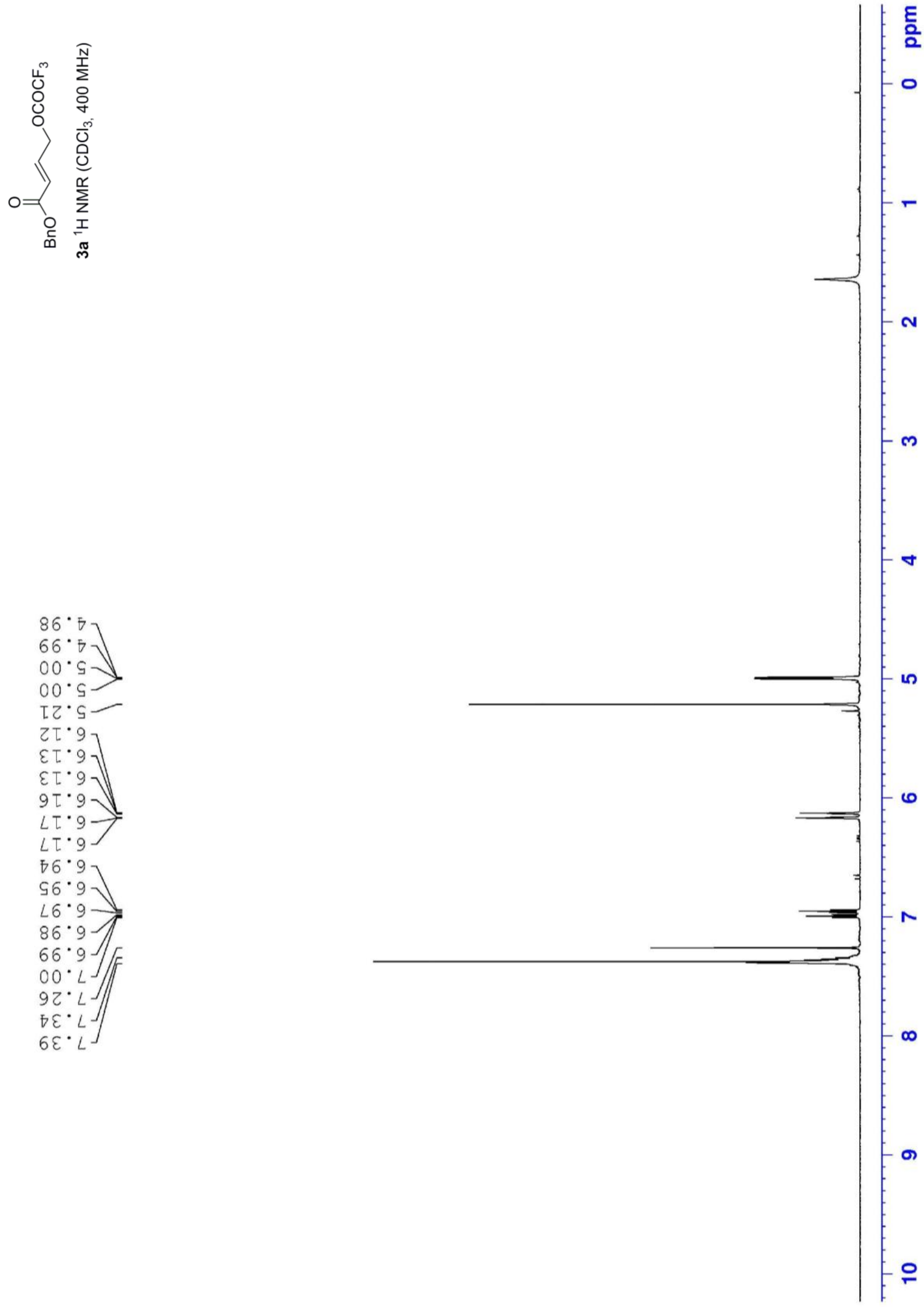
(2) Nahm, S.; Weinreb, S. M. *Tetrahedron Letters* **1981**, *22*, 3815.

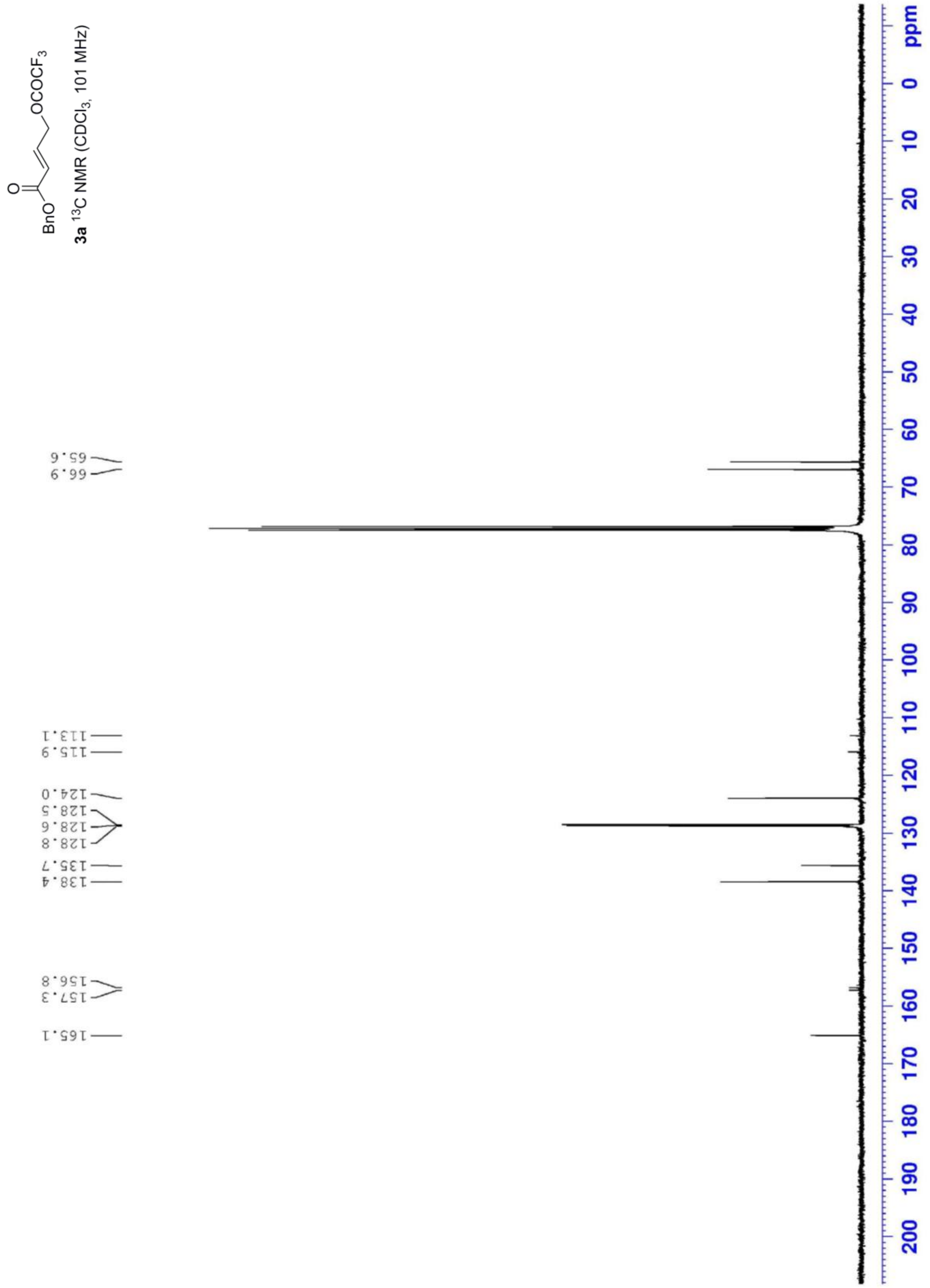
(3) Organic Syntheses, **1981**; Vol. 59, p 49.

(4) O'Connor, B.; Just, G. *Tetrahedron Letters* **1987**, *28*, 3235.

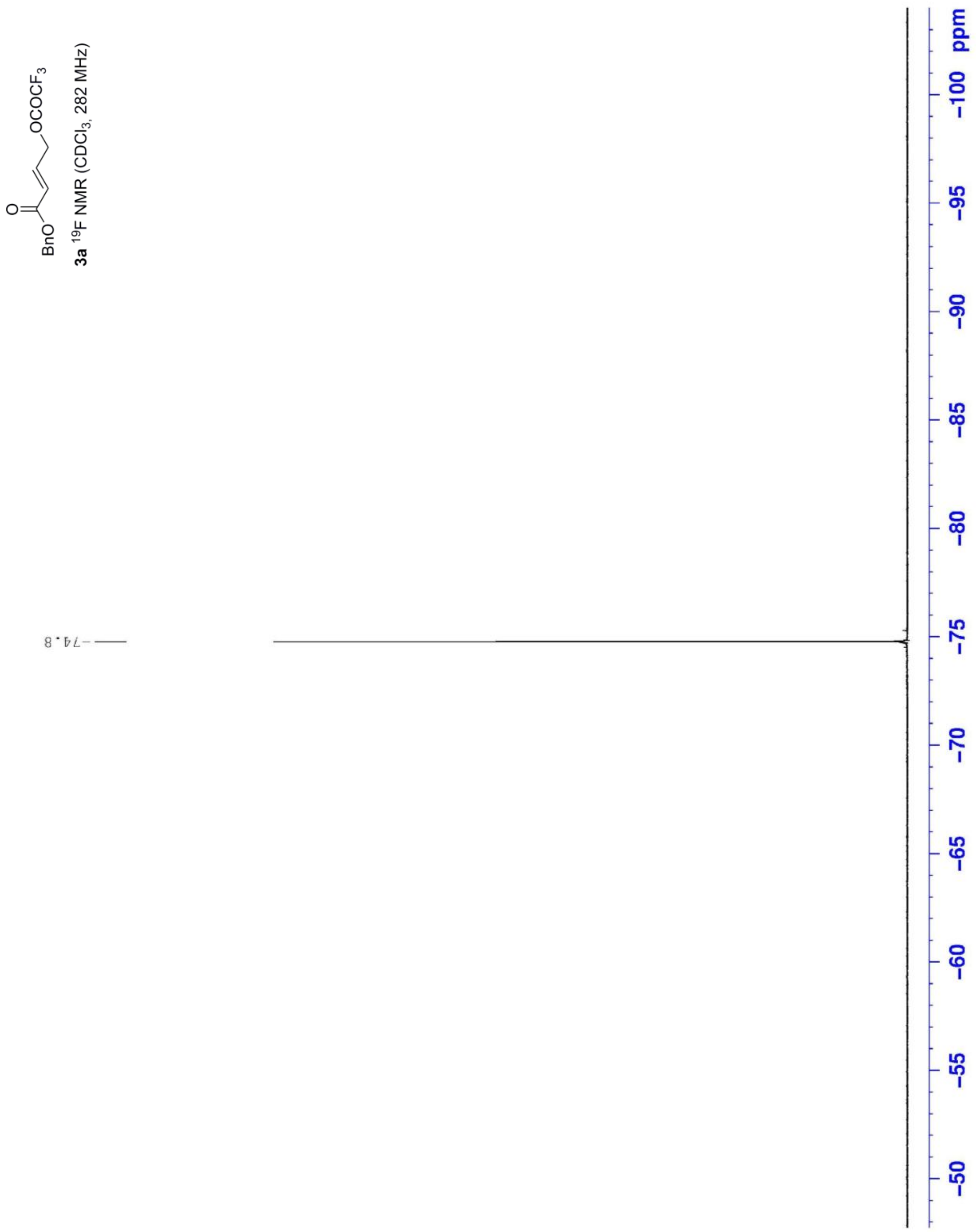
(5) Bower, J. F.; Patman, R. L.; Krische, M. J. *Org. Lett.* **2008**, *10*, 1033.

4. NMR spectra

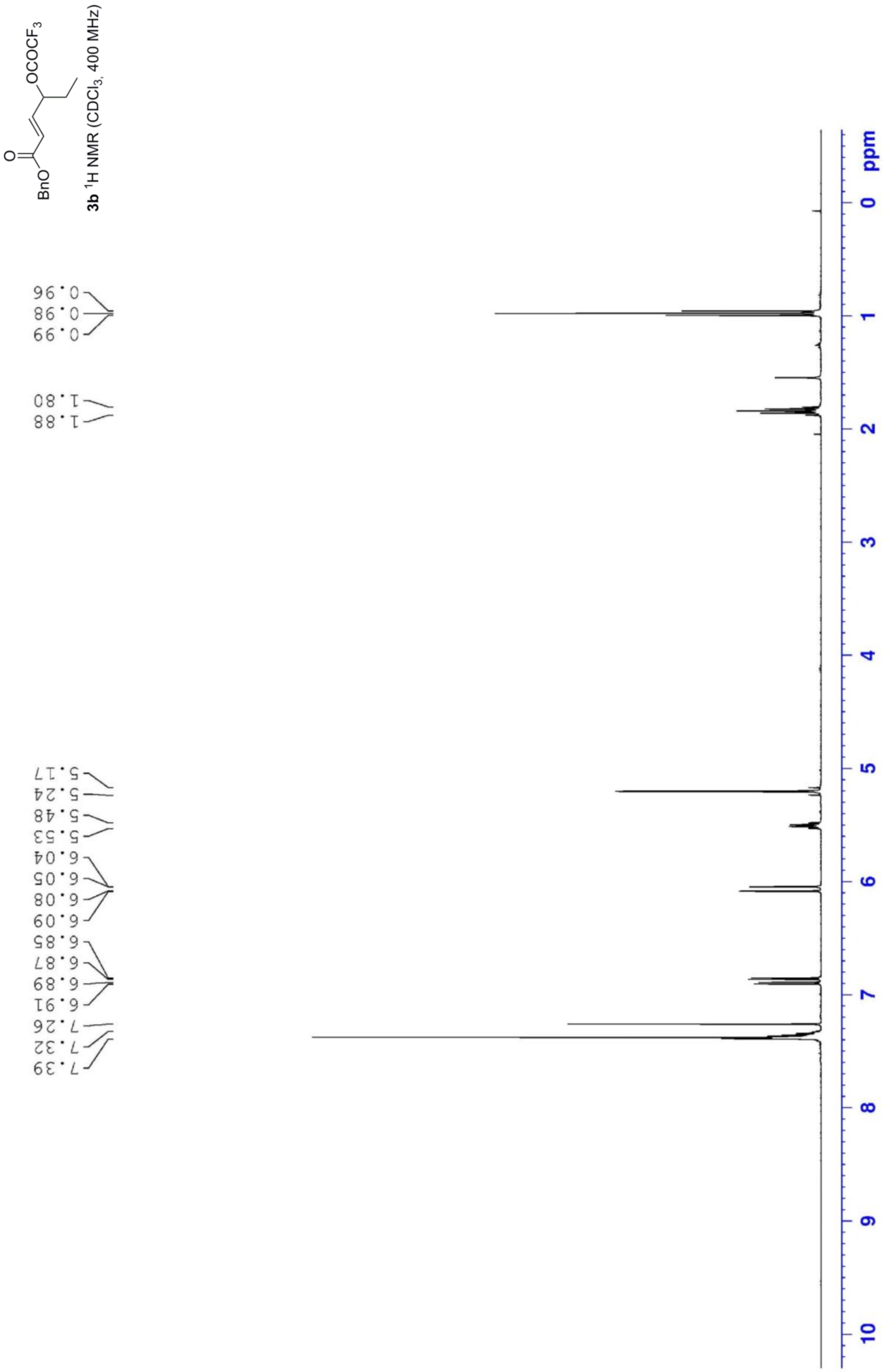

3a ^{1}H NMR ($CDCl_3$, 400 MHz)



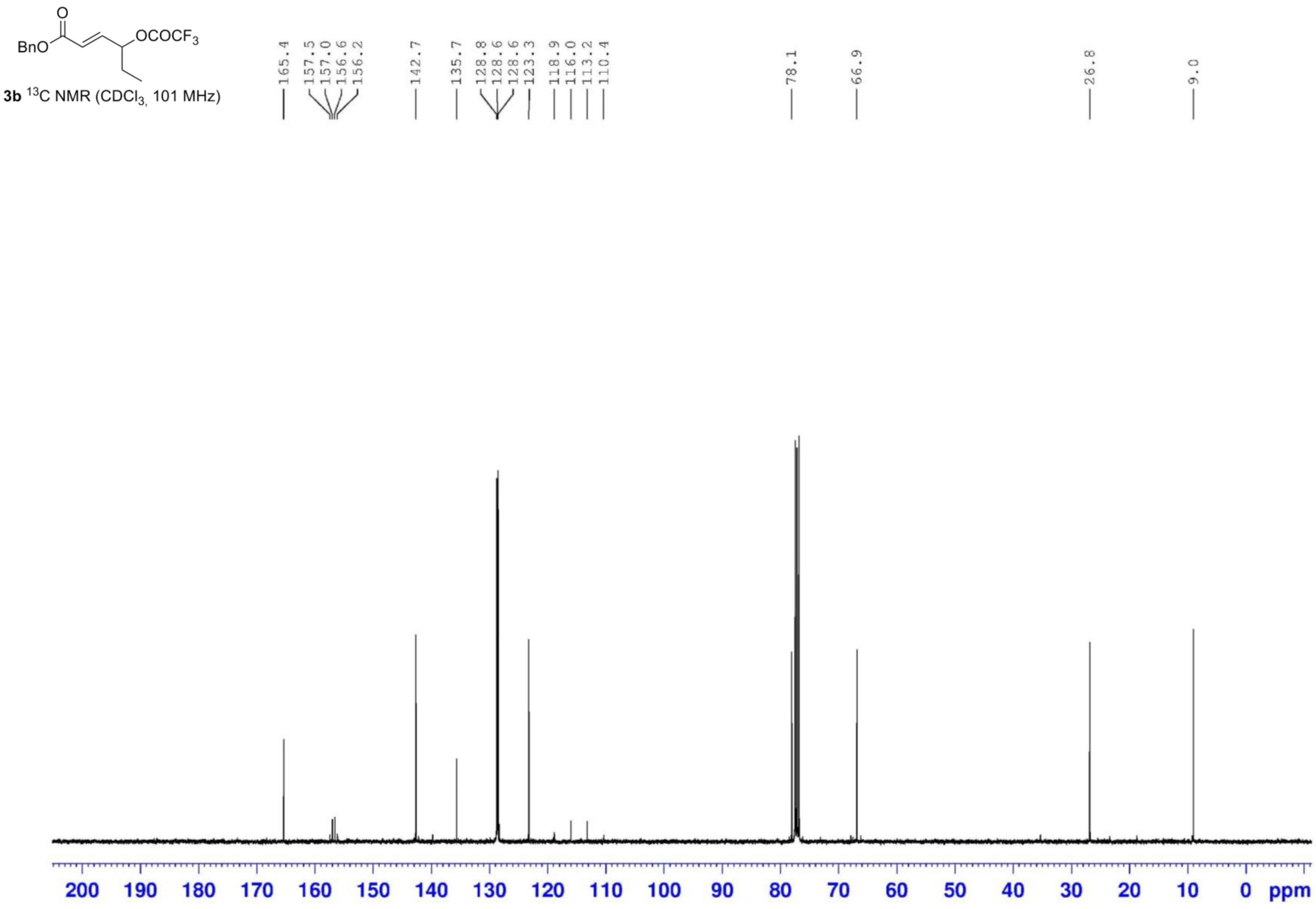
3a ^{13}C NMR (CDCl$_3$, 101 MHz)



3a ^{19}F NMR ($CDCl_3$, 282 MHz)



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



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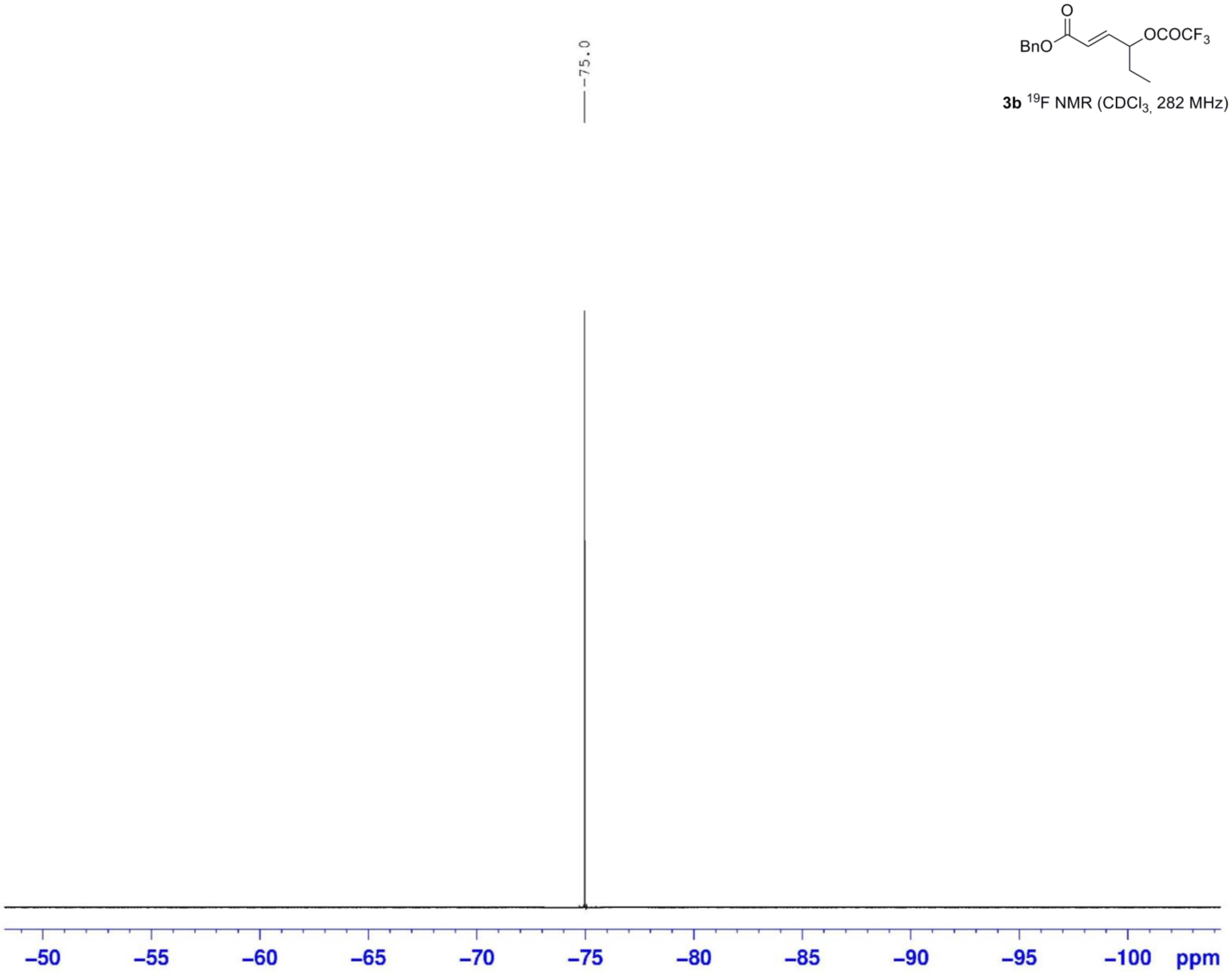

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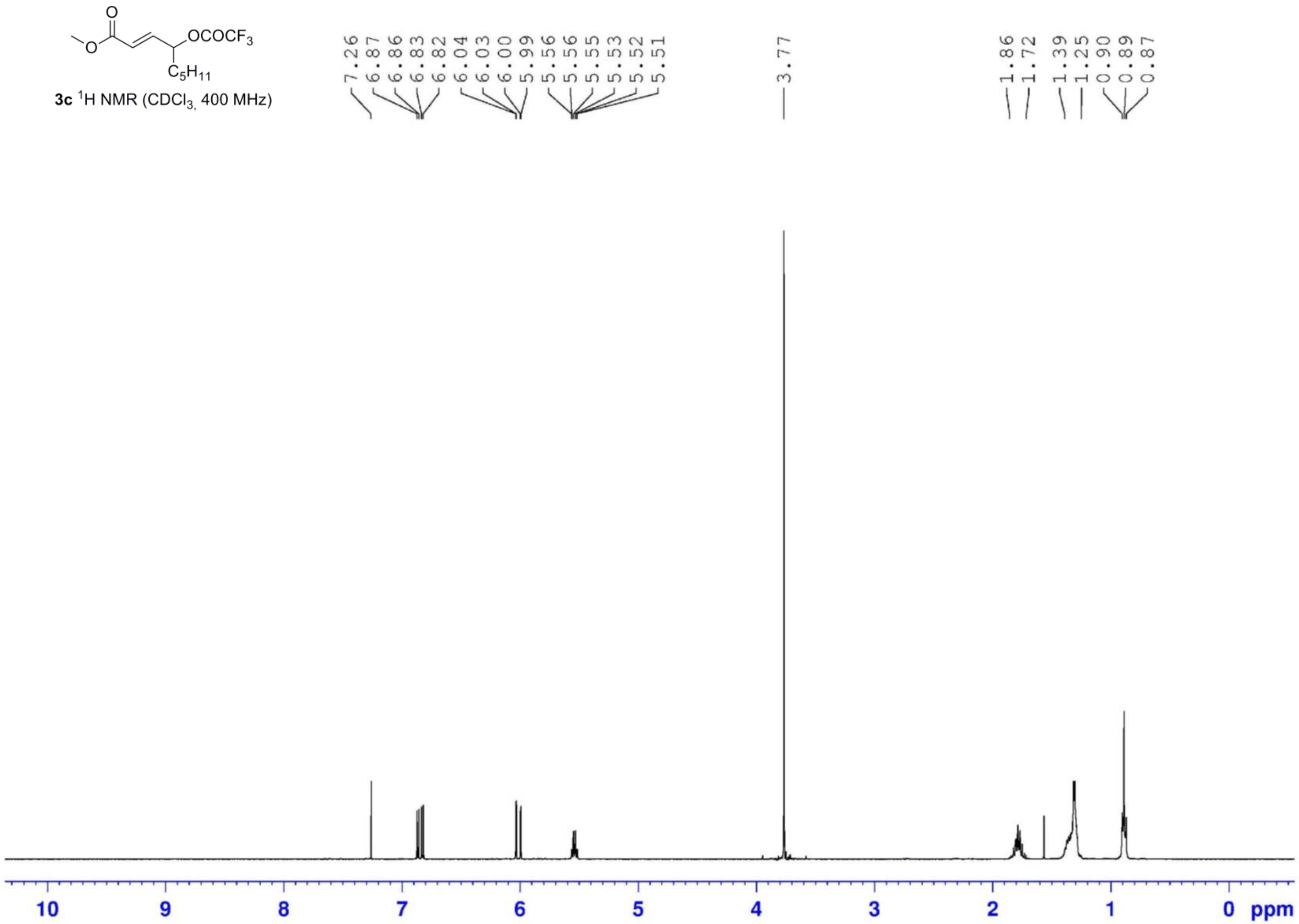

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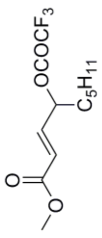

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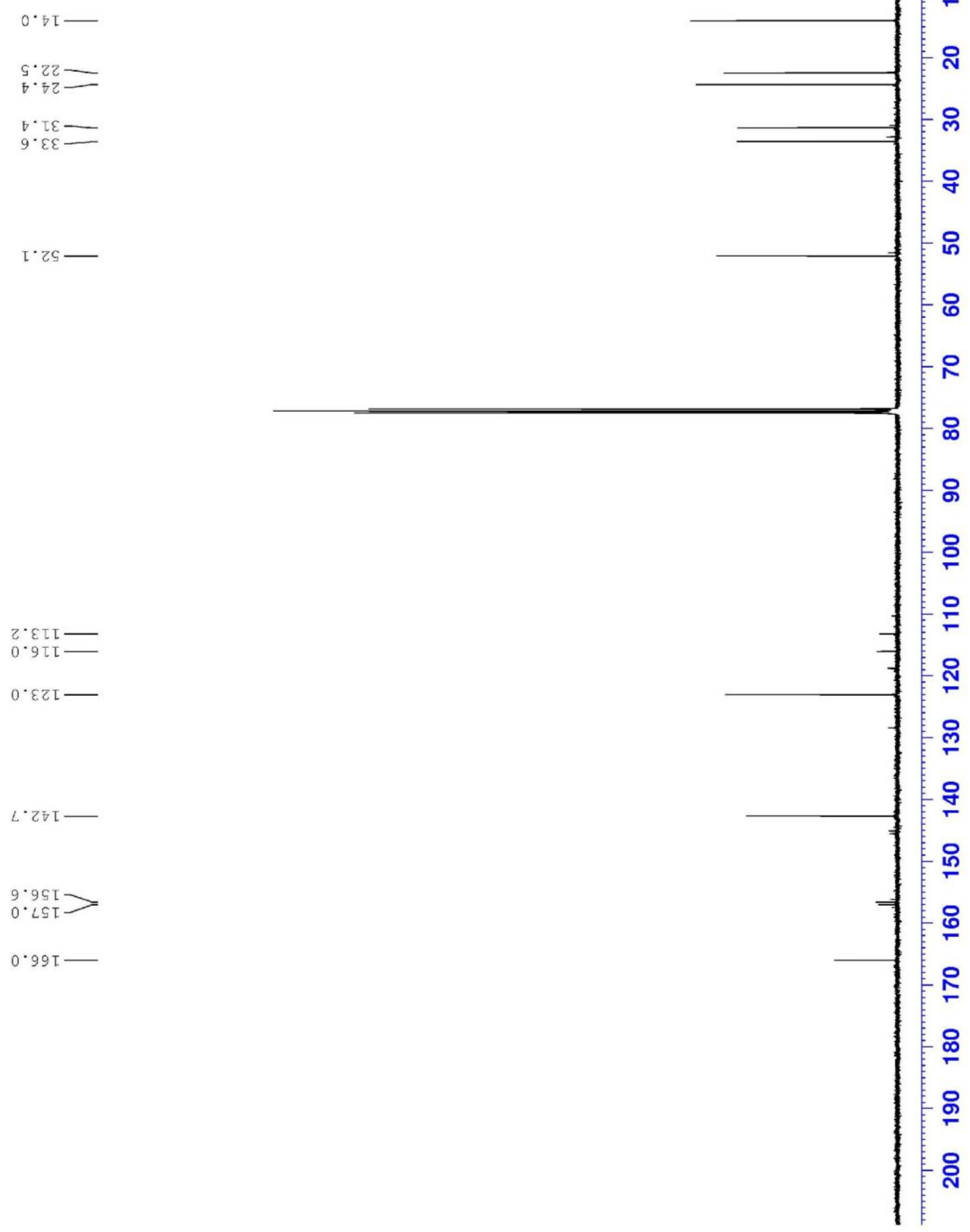
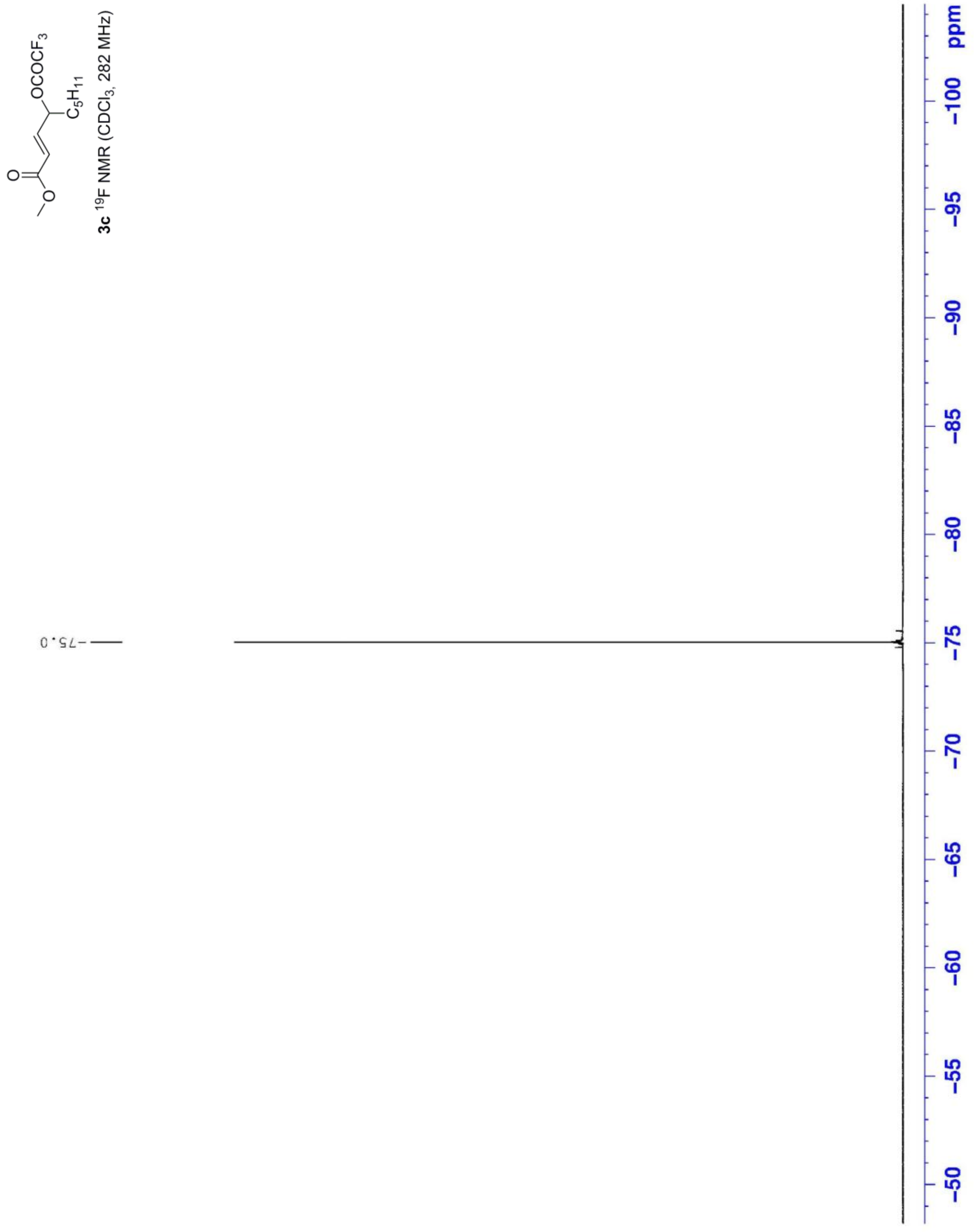
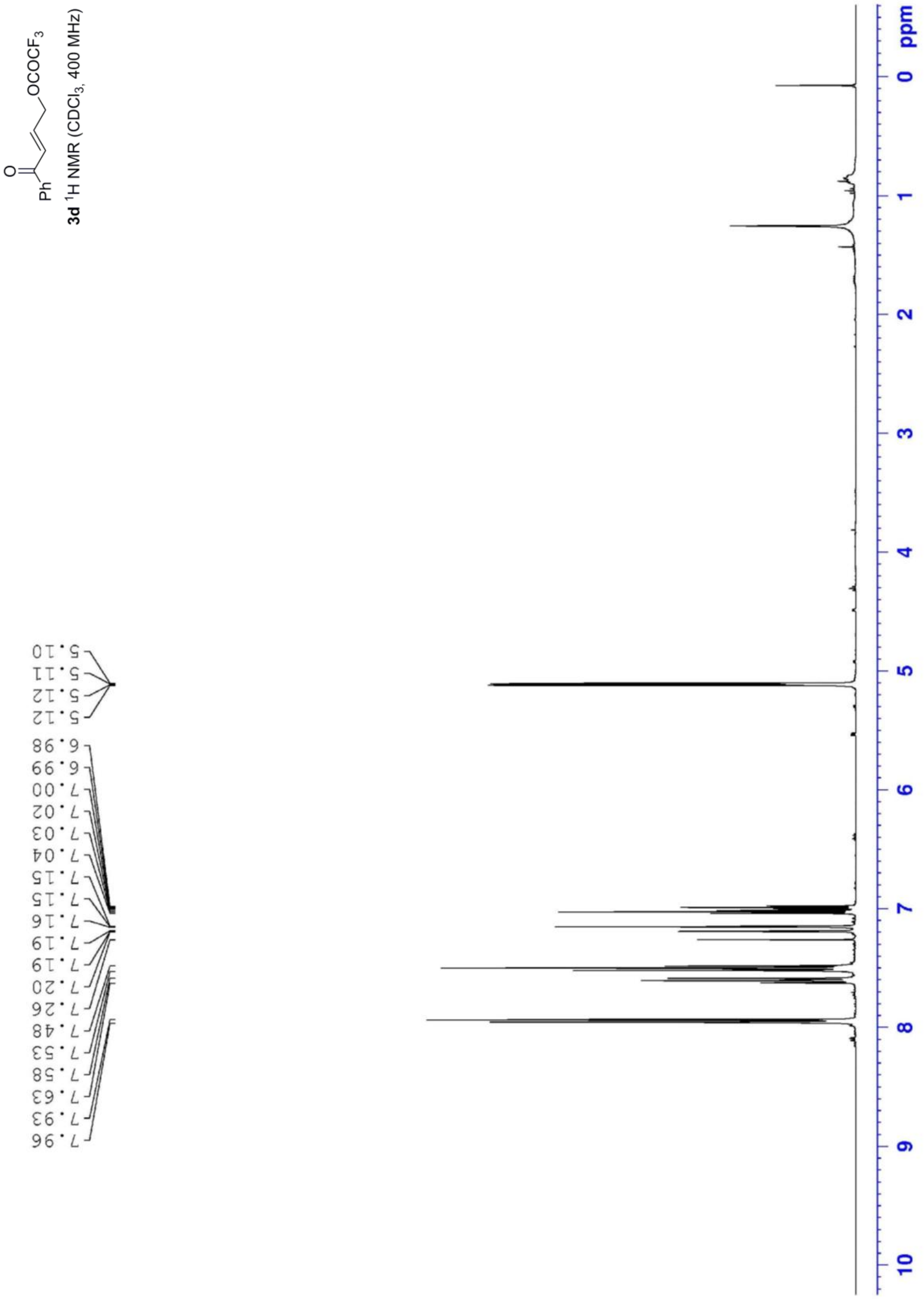




3c ^{19}F NMR ($CDCl_3$, 282 MHz)



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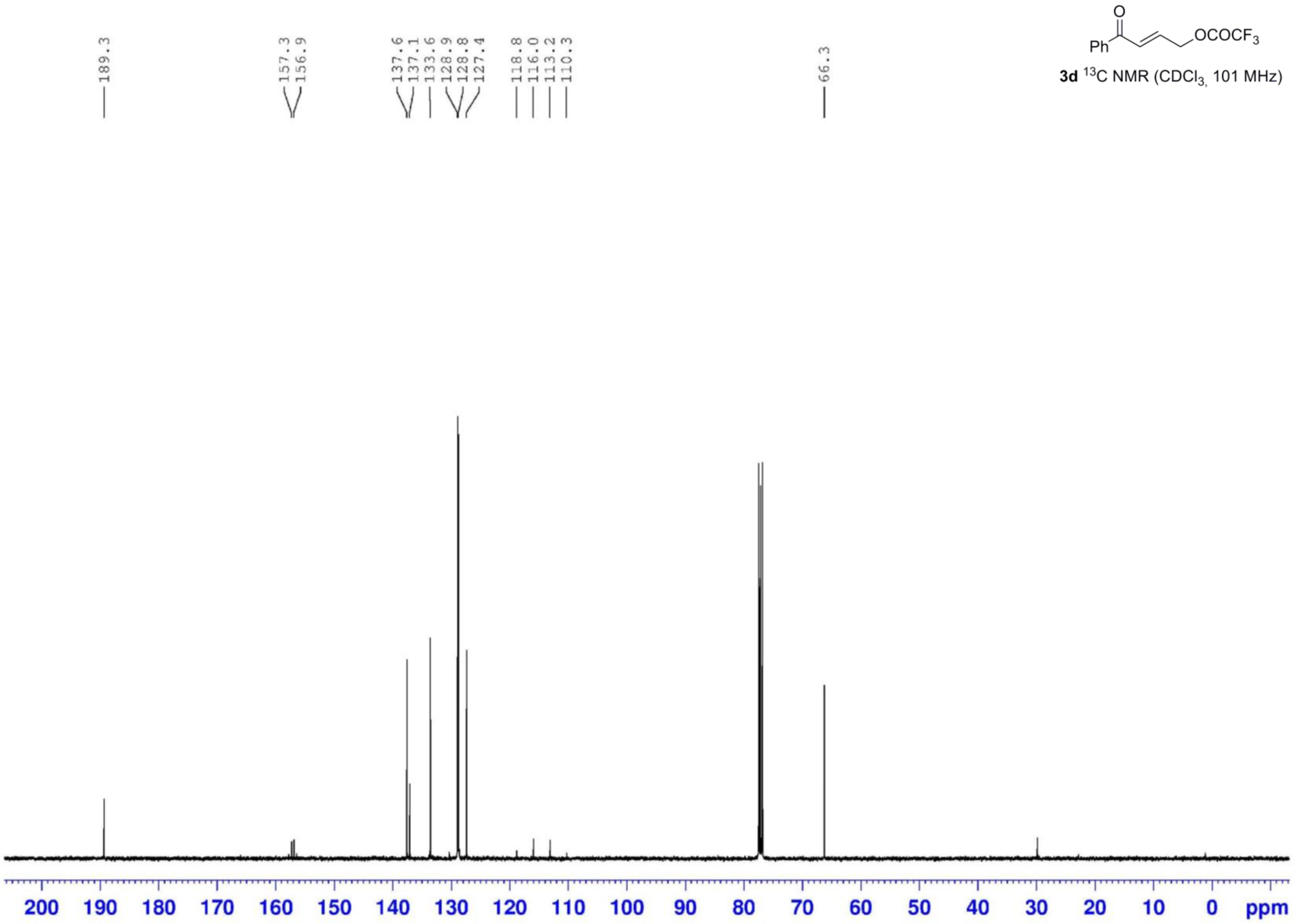

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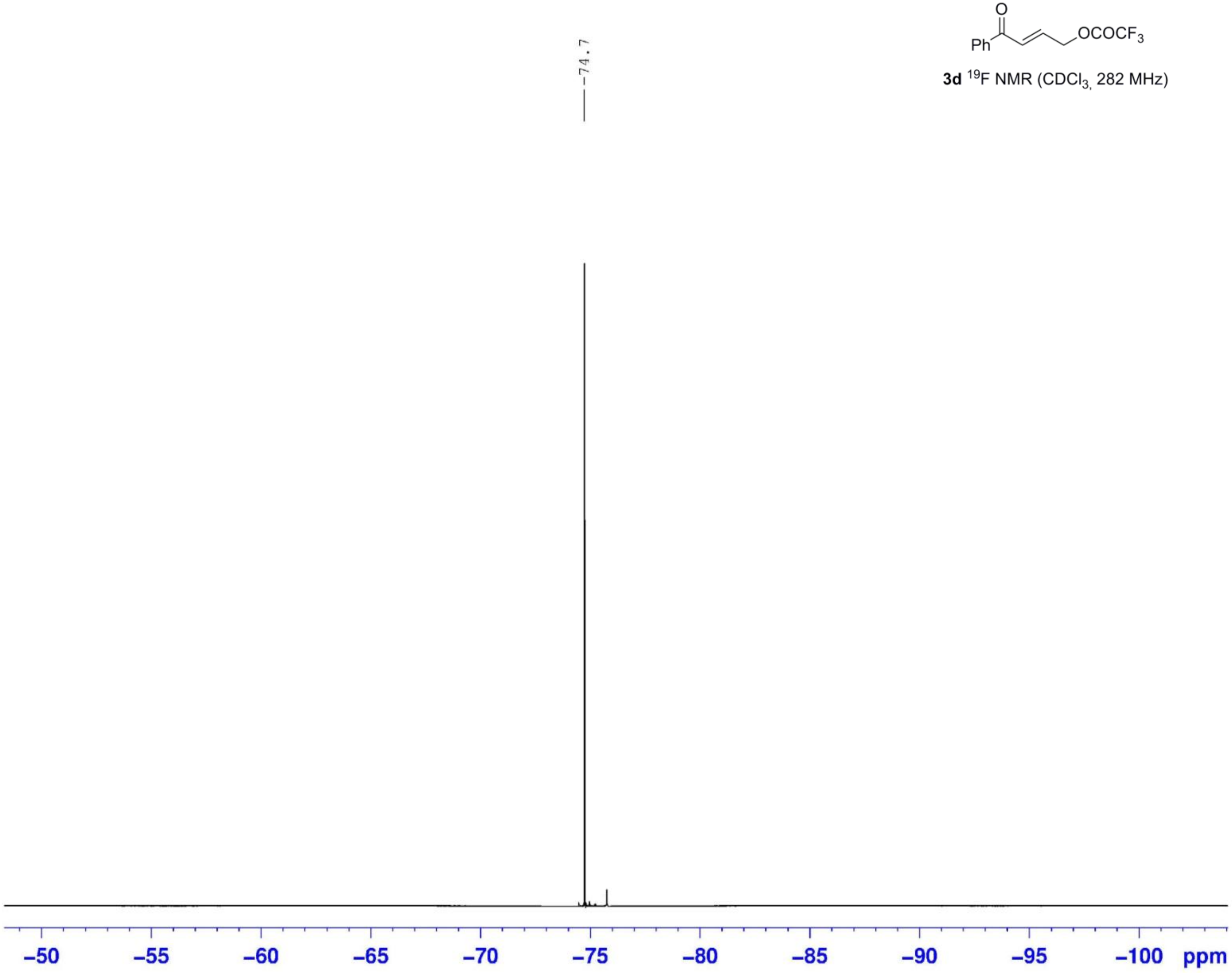

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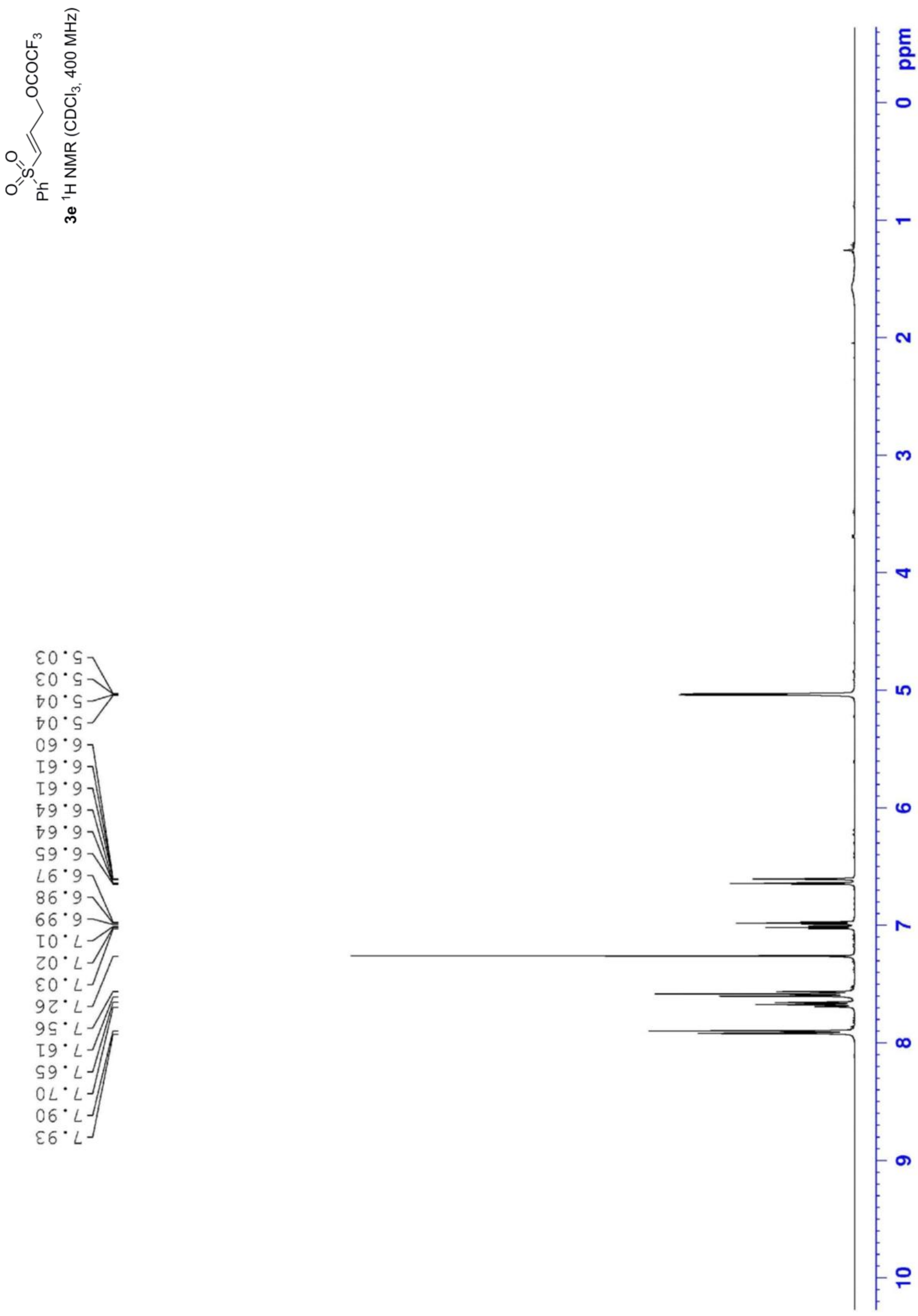

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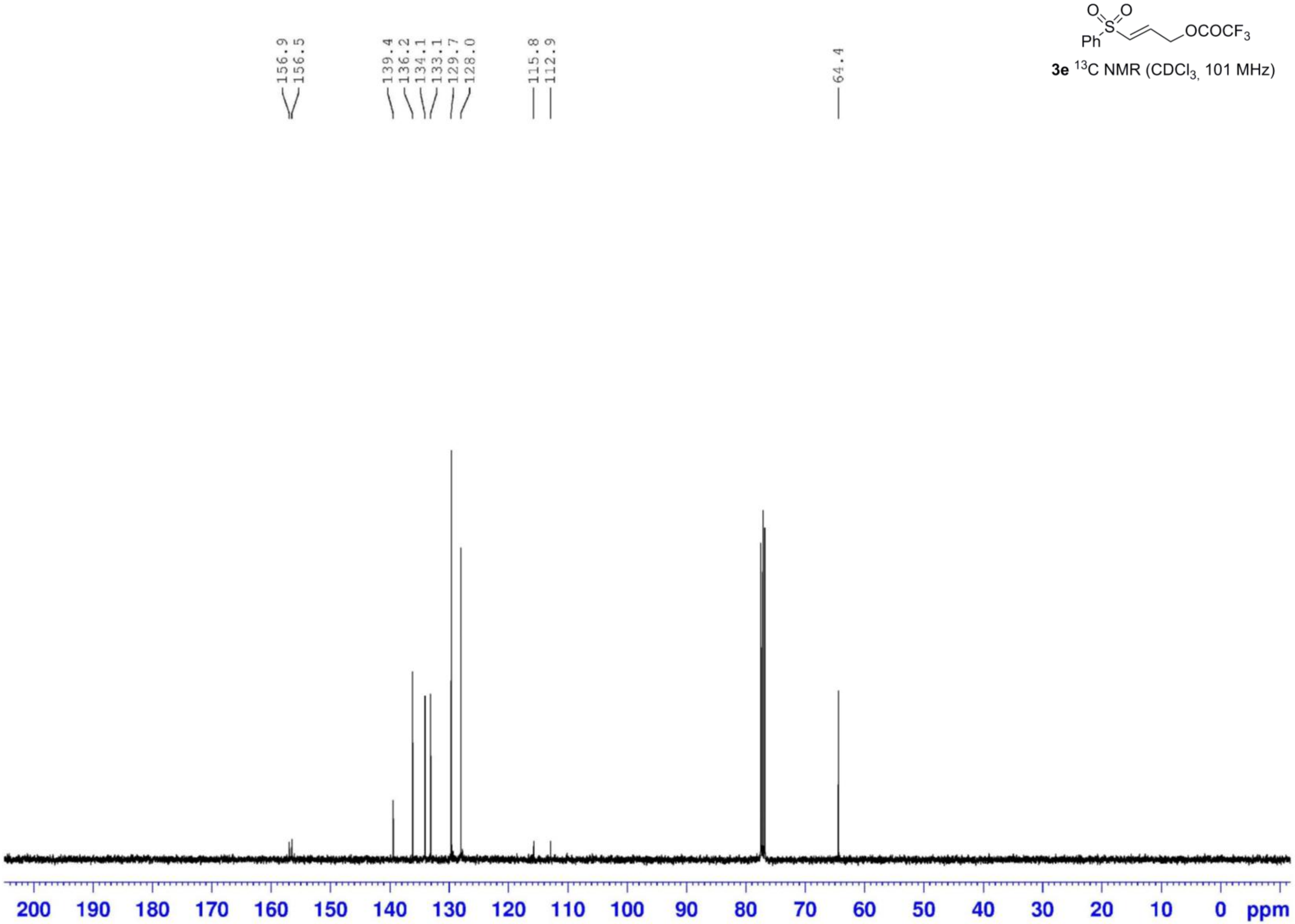

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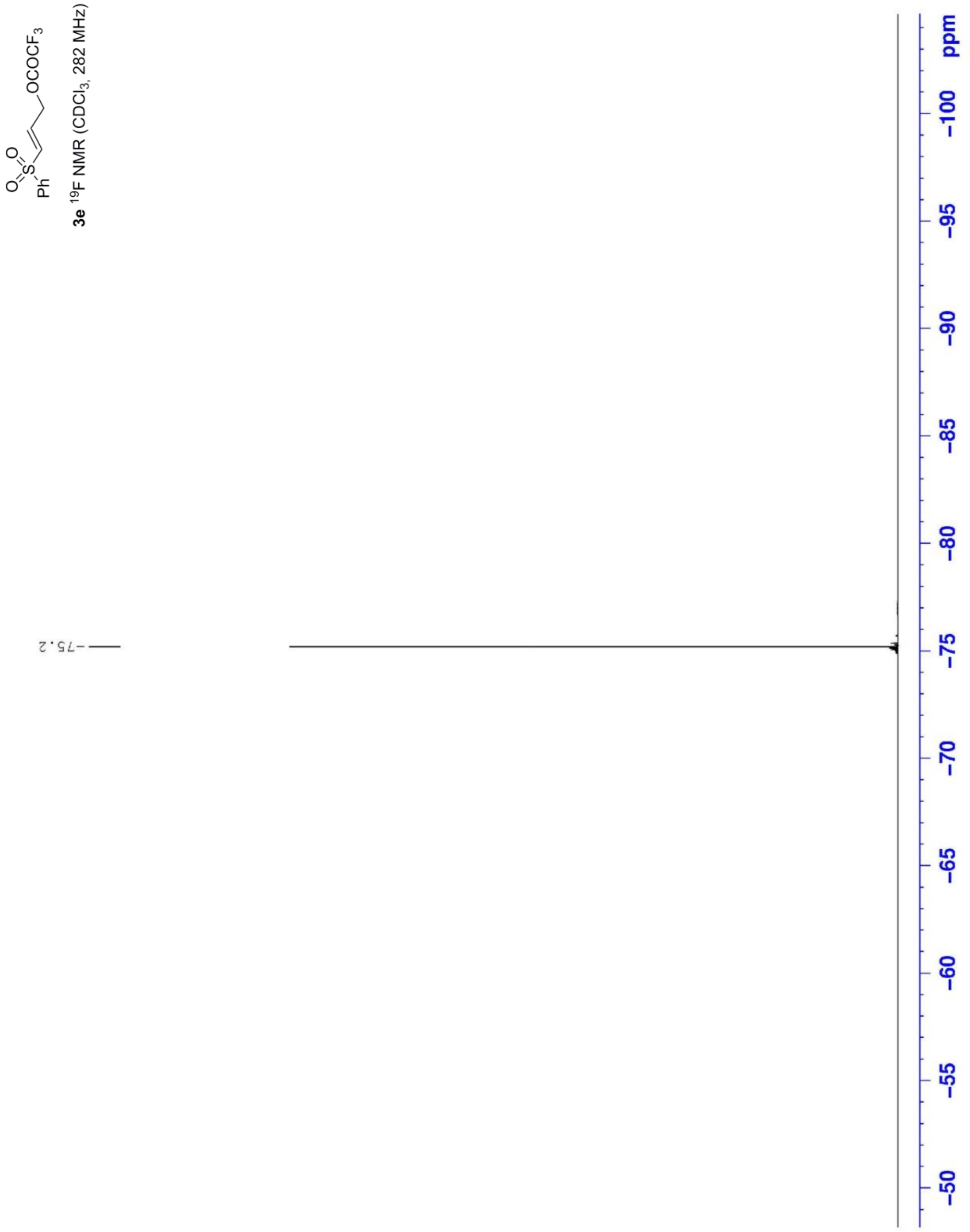

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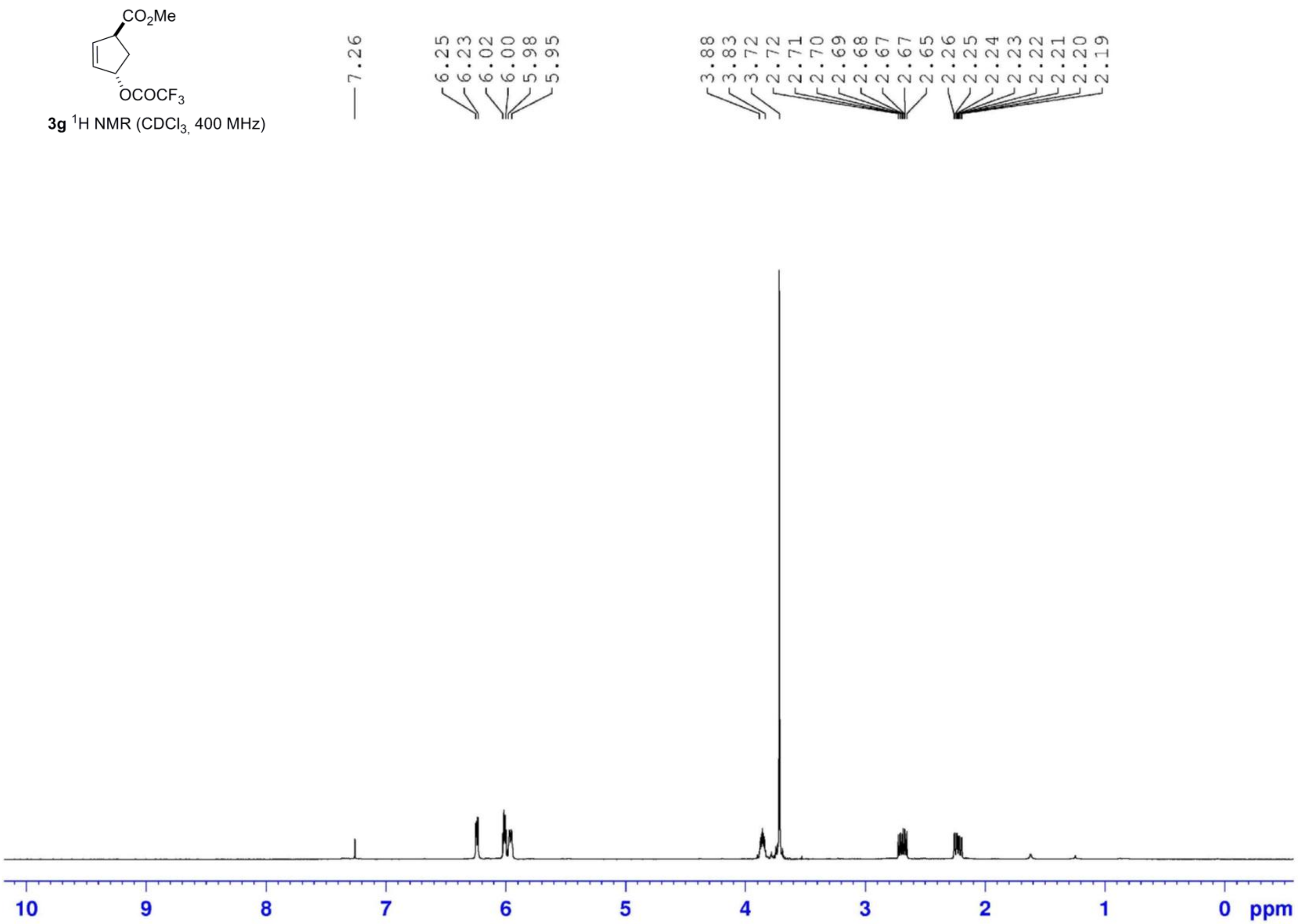

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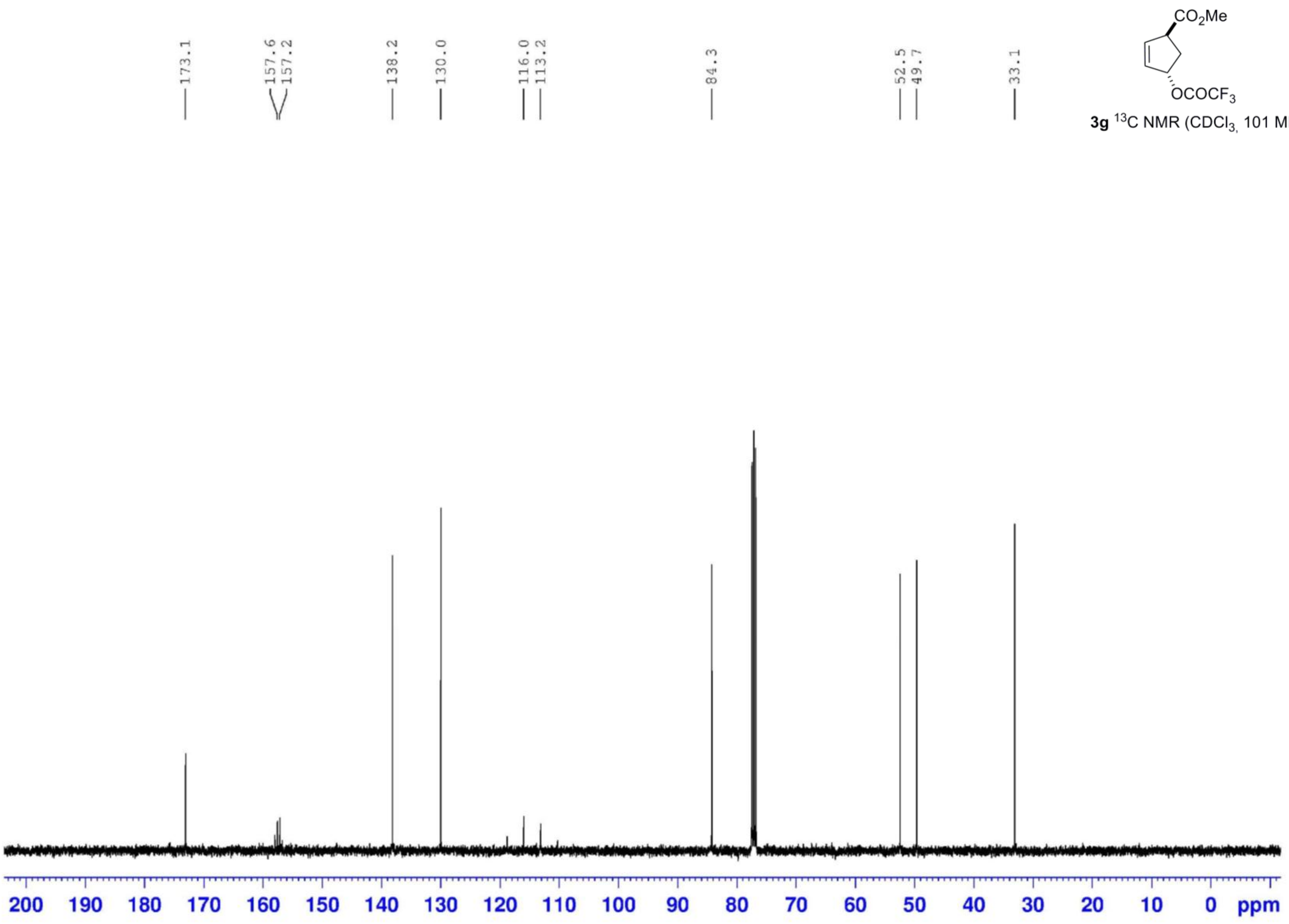
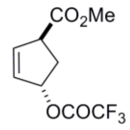
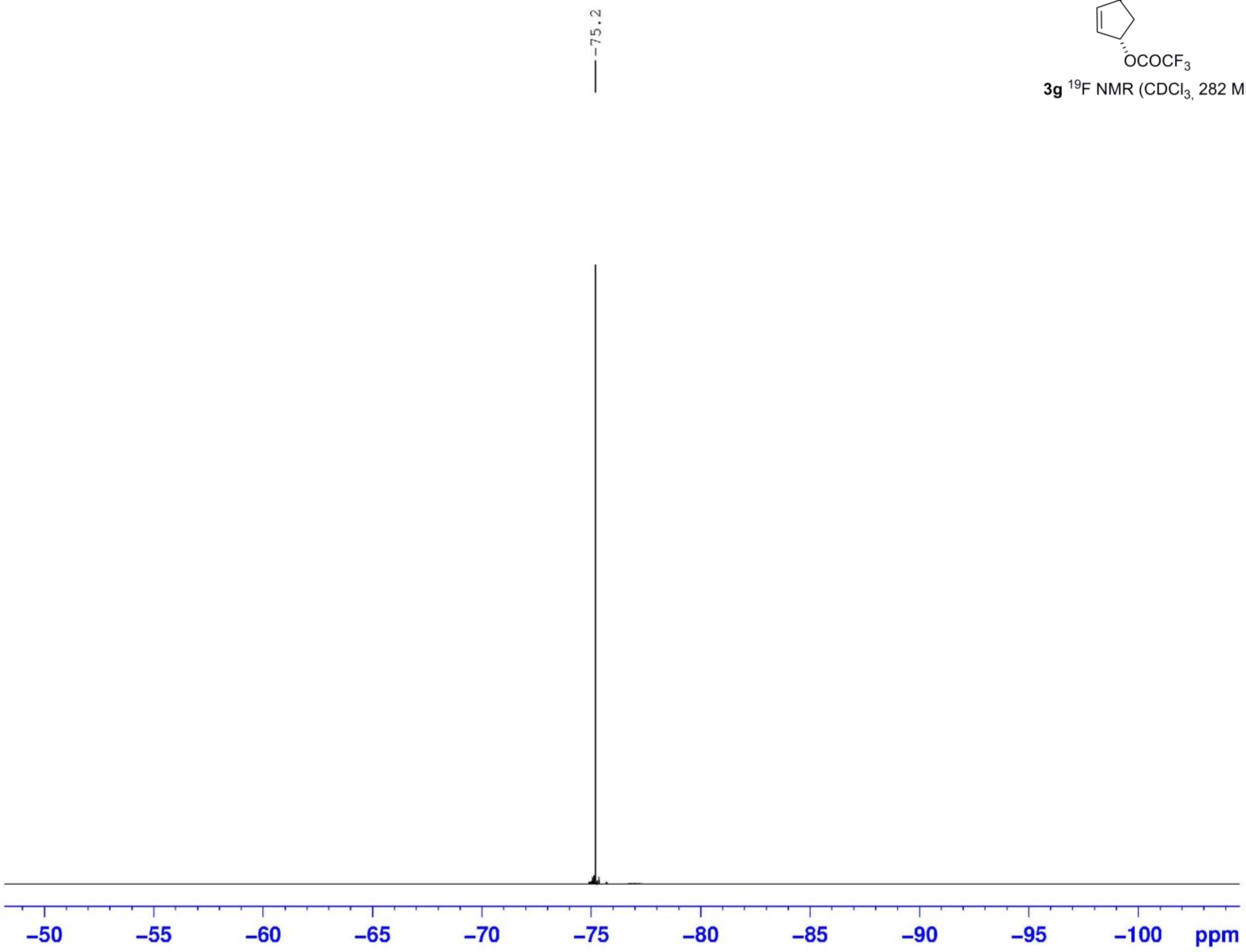
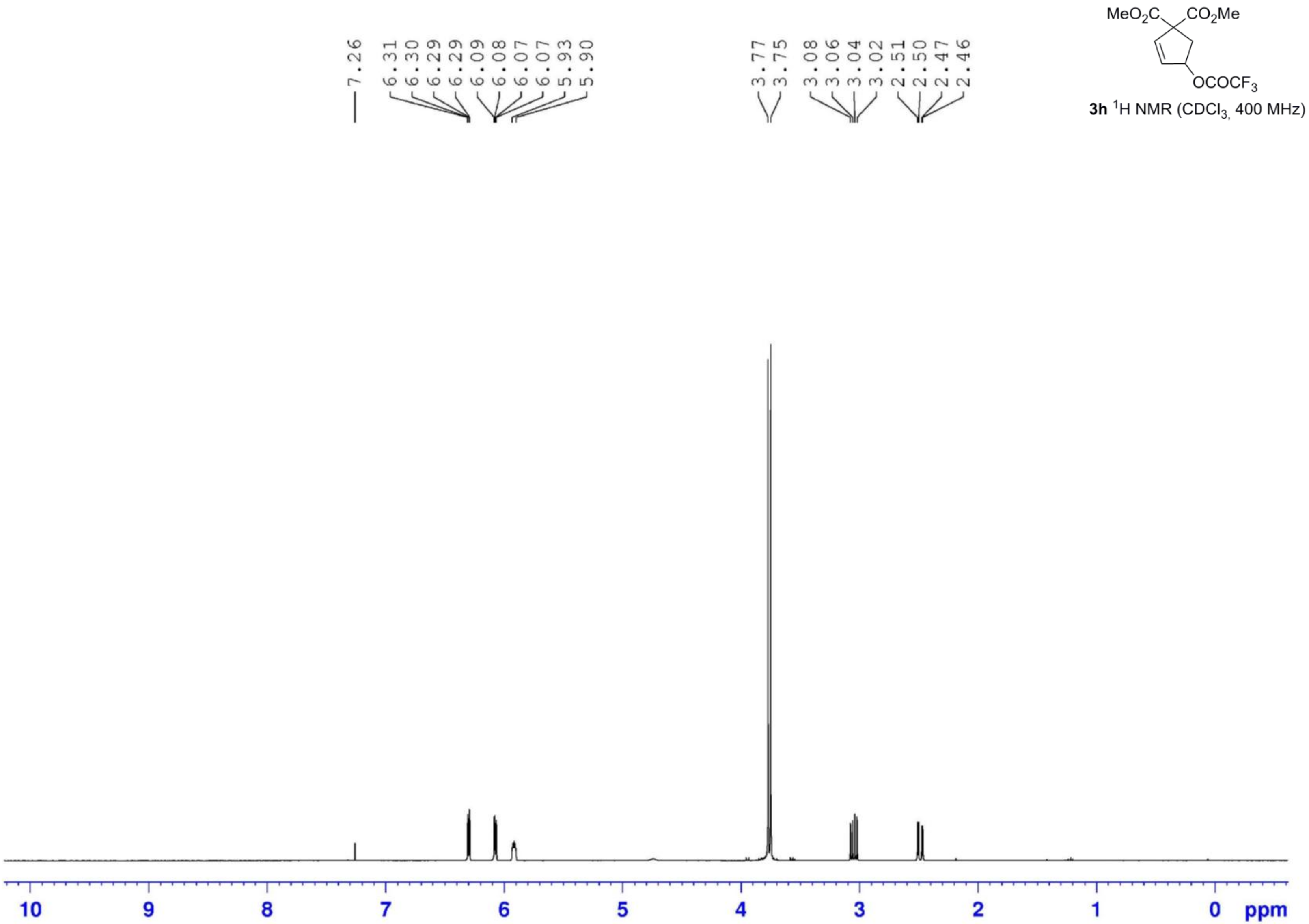


3g ^{13}C NMR (CDCl$_3$, 101 MHz)



3g ^{19}F NMR (CDCl$_3$, 282 MHz)





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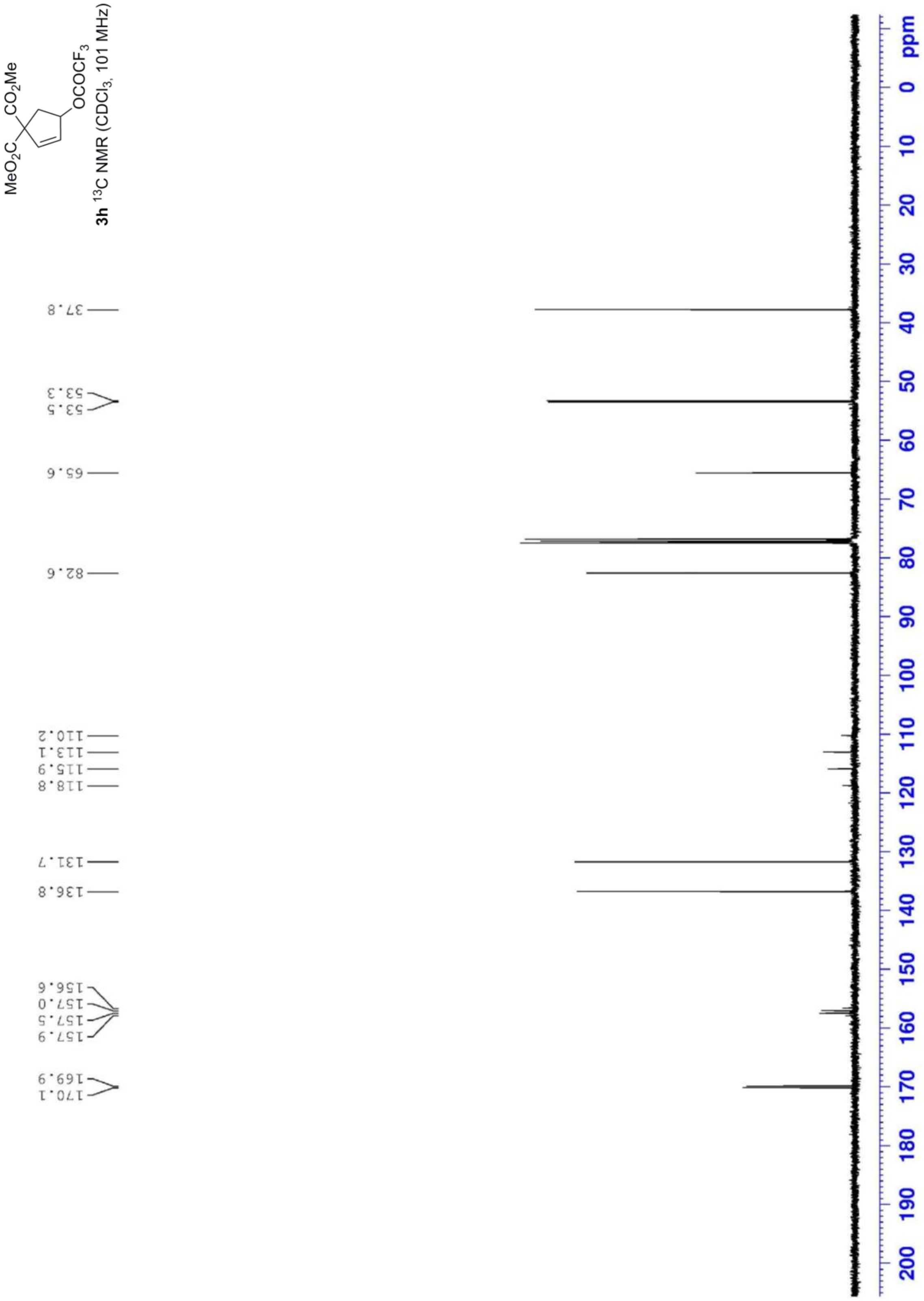
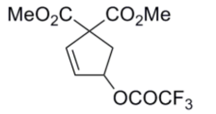
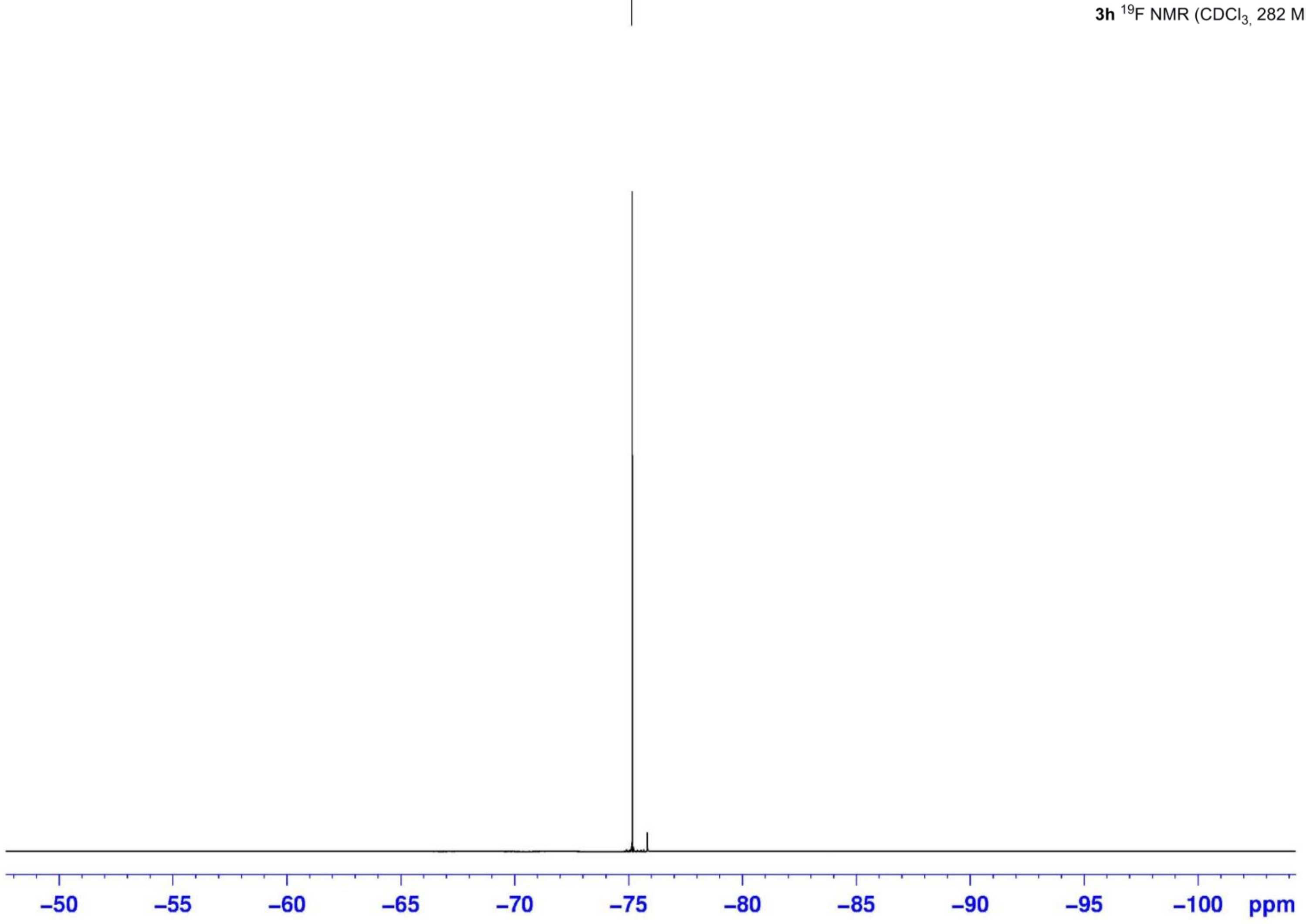
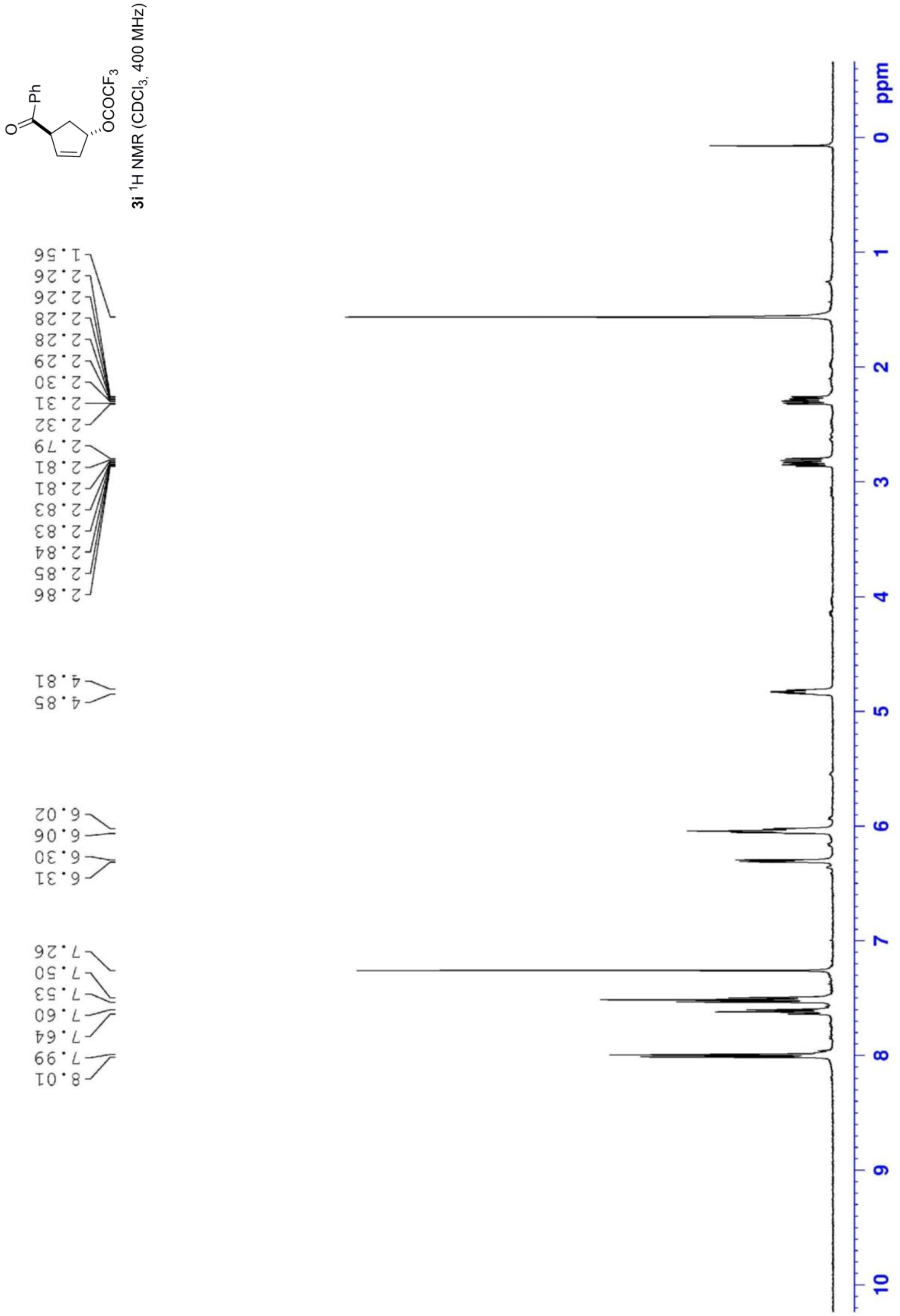


3h ^{13}C NMR ($CDCl_3$, 101 MHz)



3h ^{19}F NMR ($CDCl_3$, 282 MHz)

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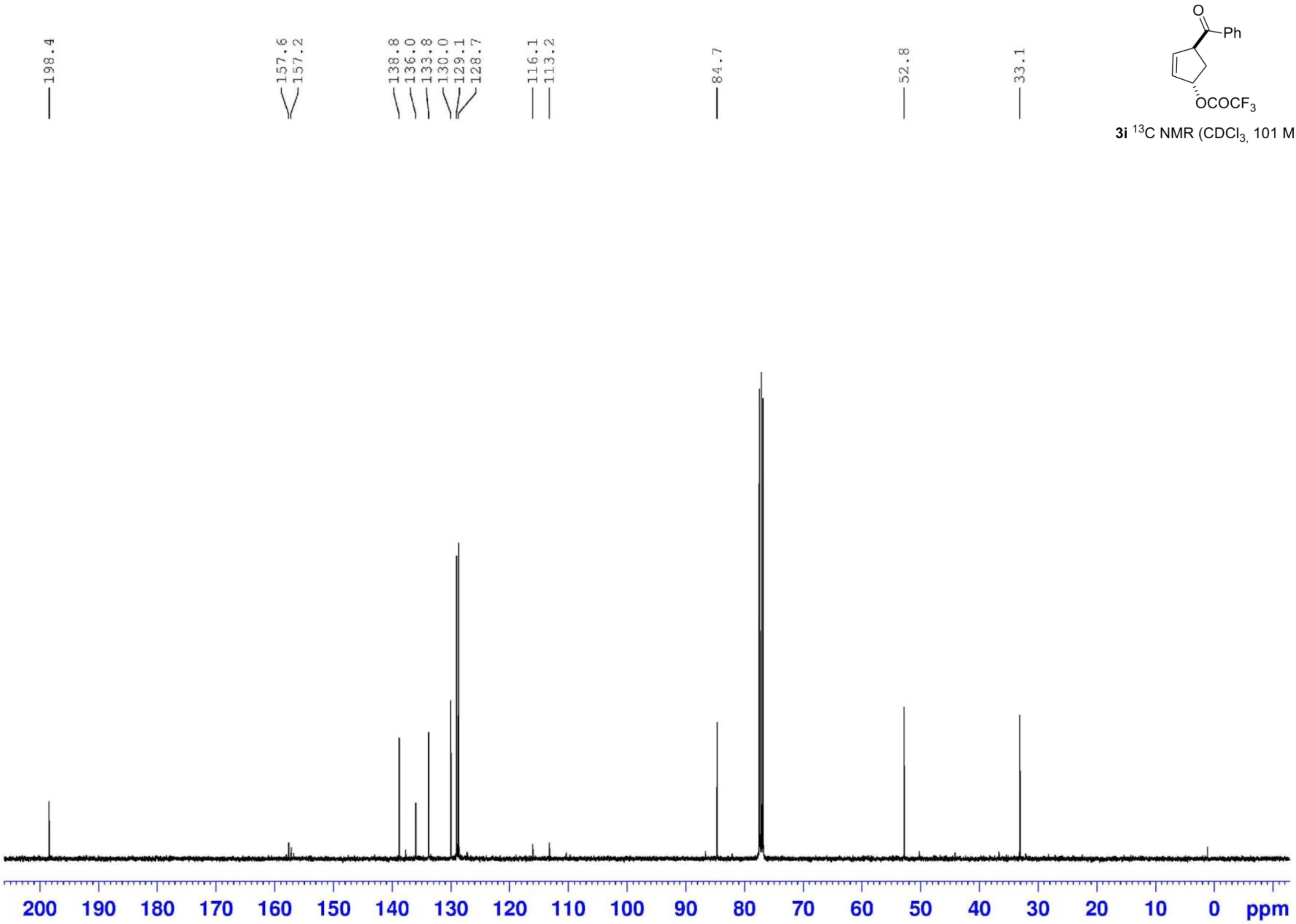
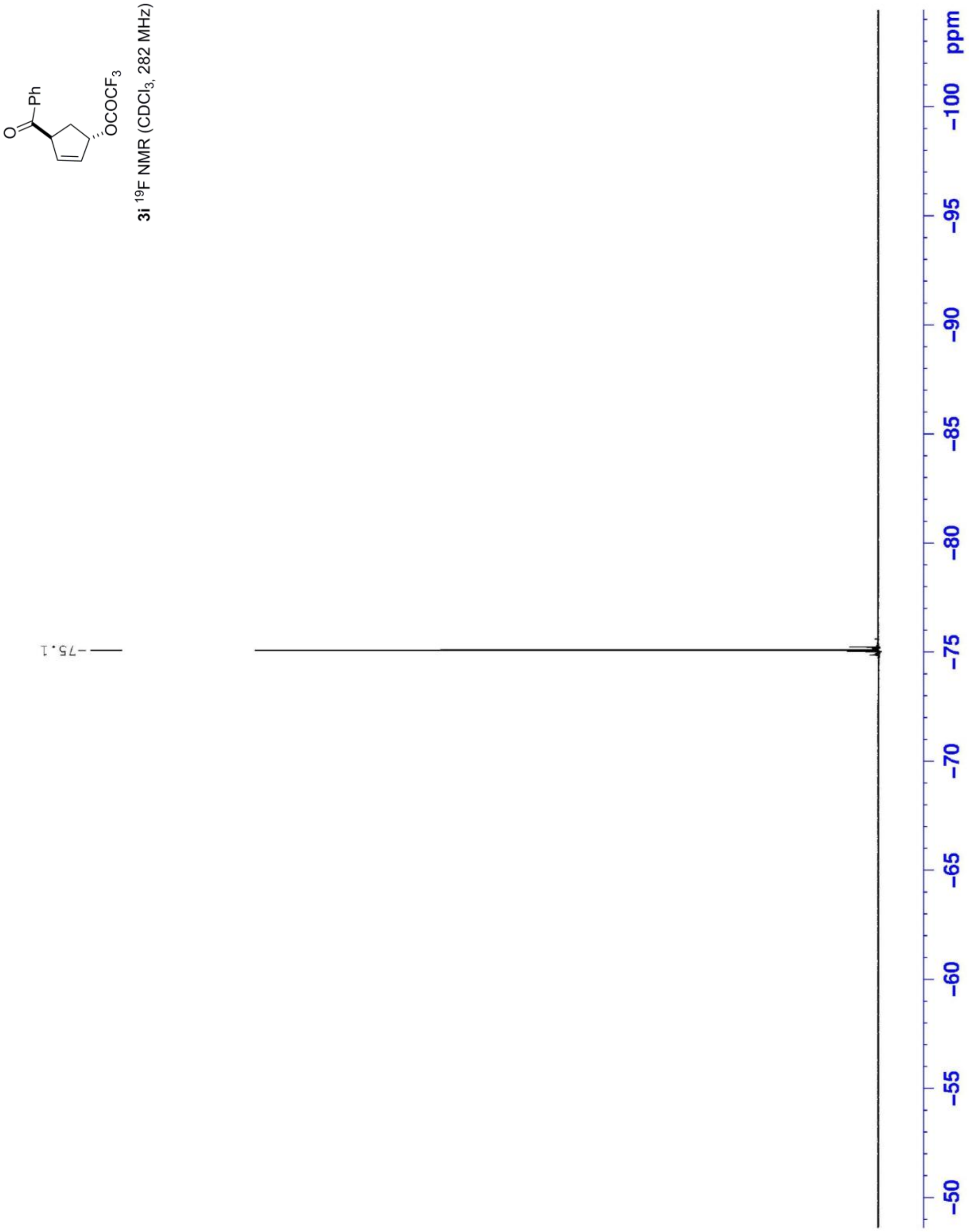


3i ^{13}C NMR (CDCl$_3$, 101 MHz)



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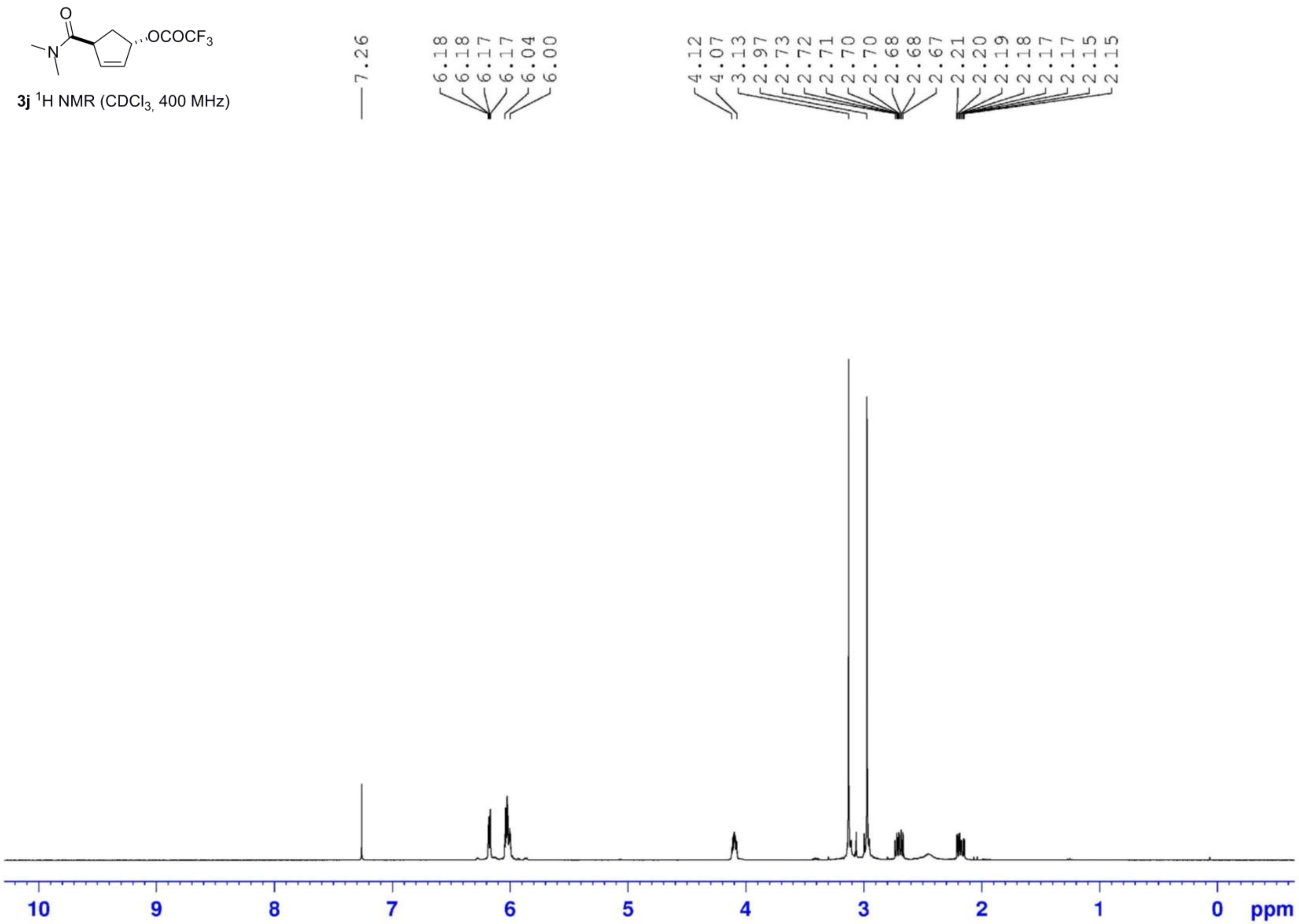

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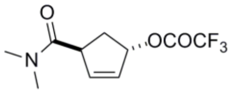

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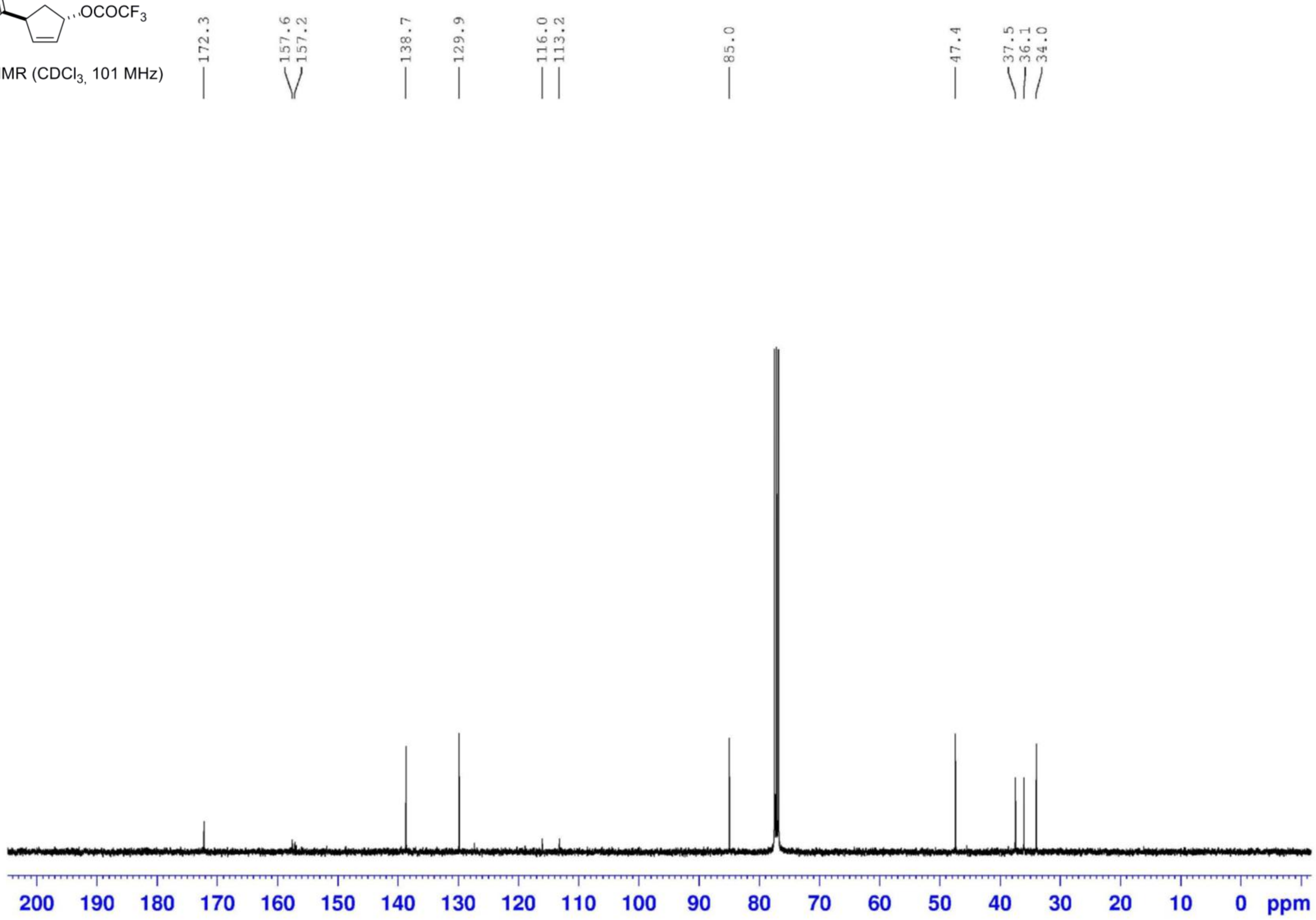
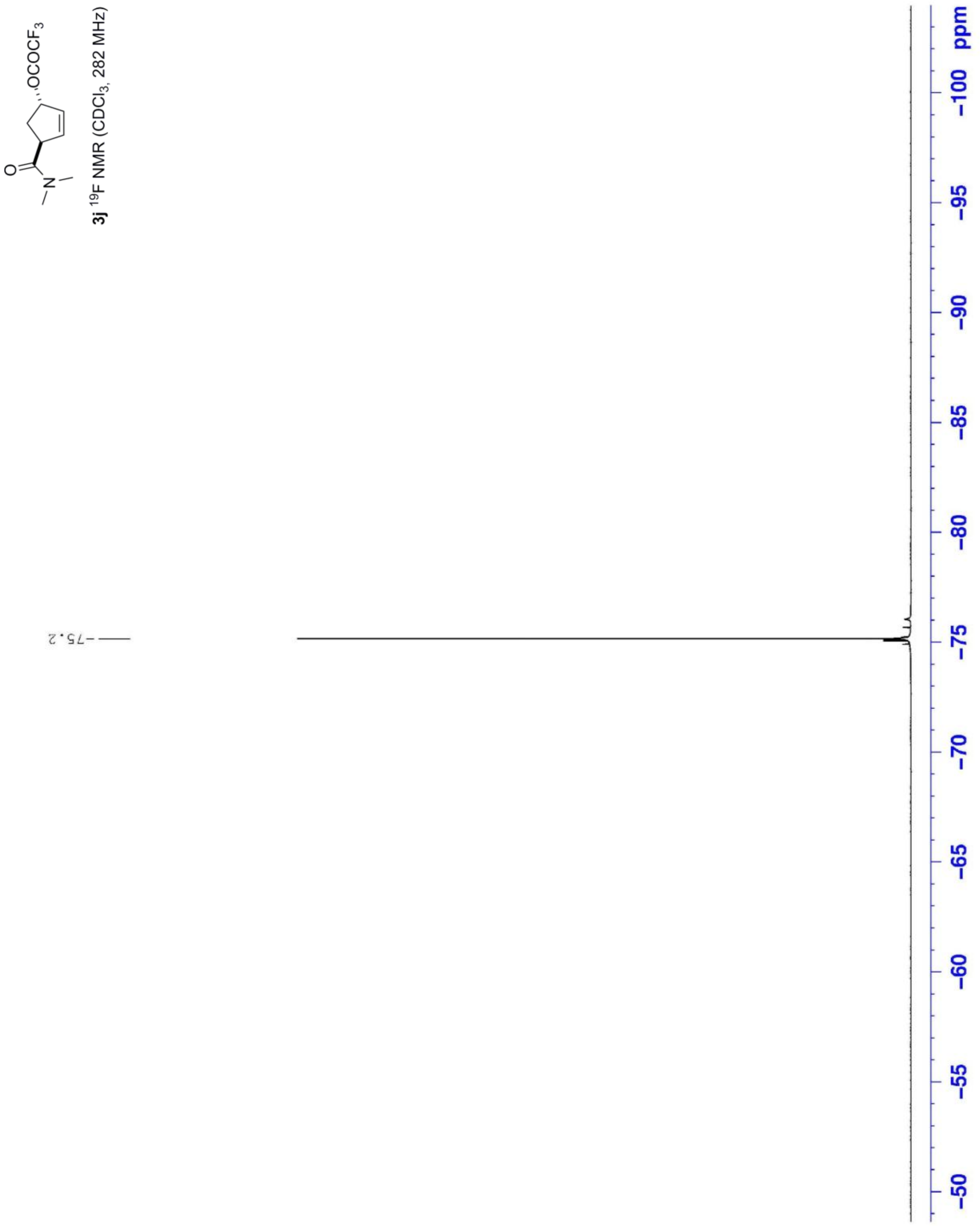
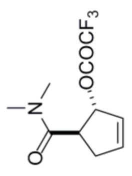




3j ^{19}F NMR (CDCl$_3$, 282 MHz)



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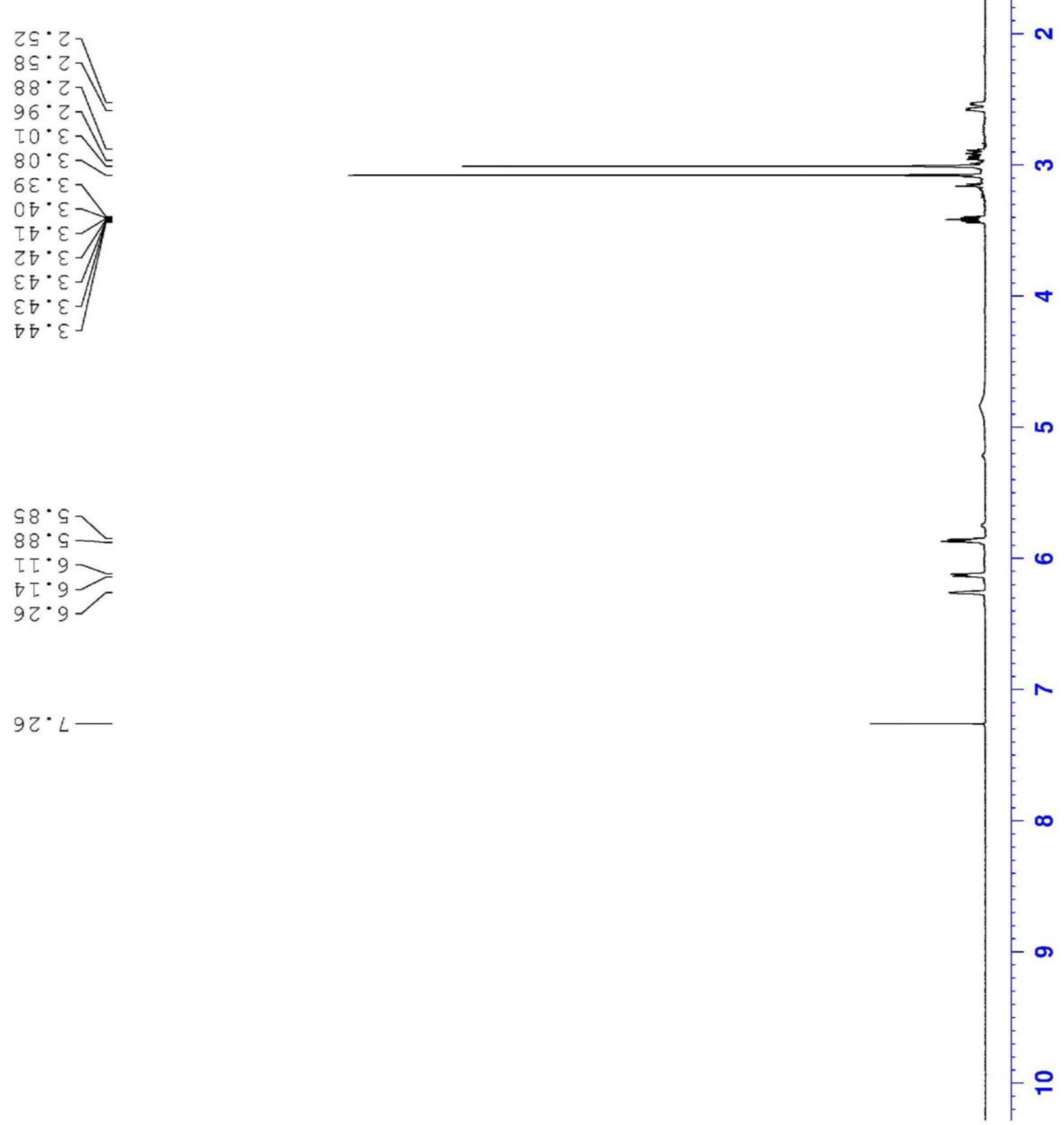

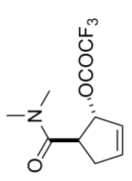

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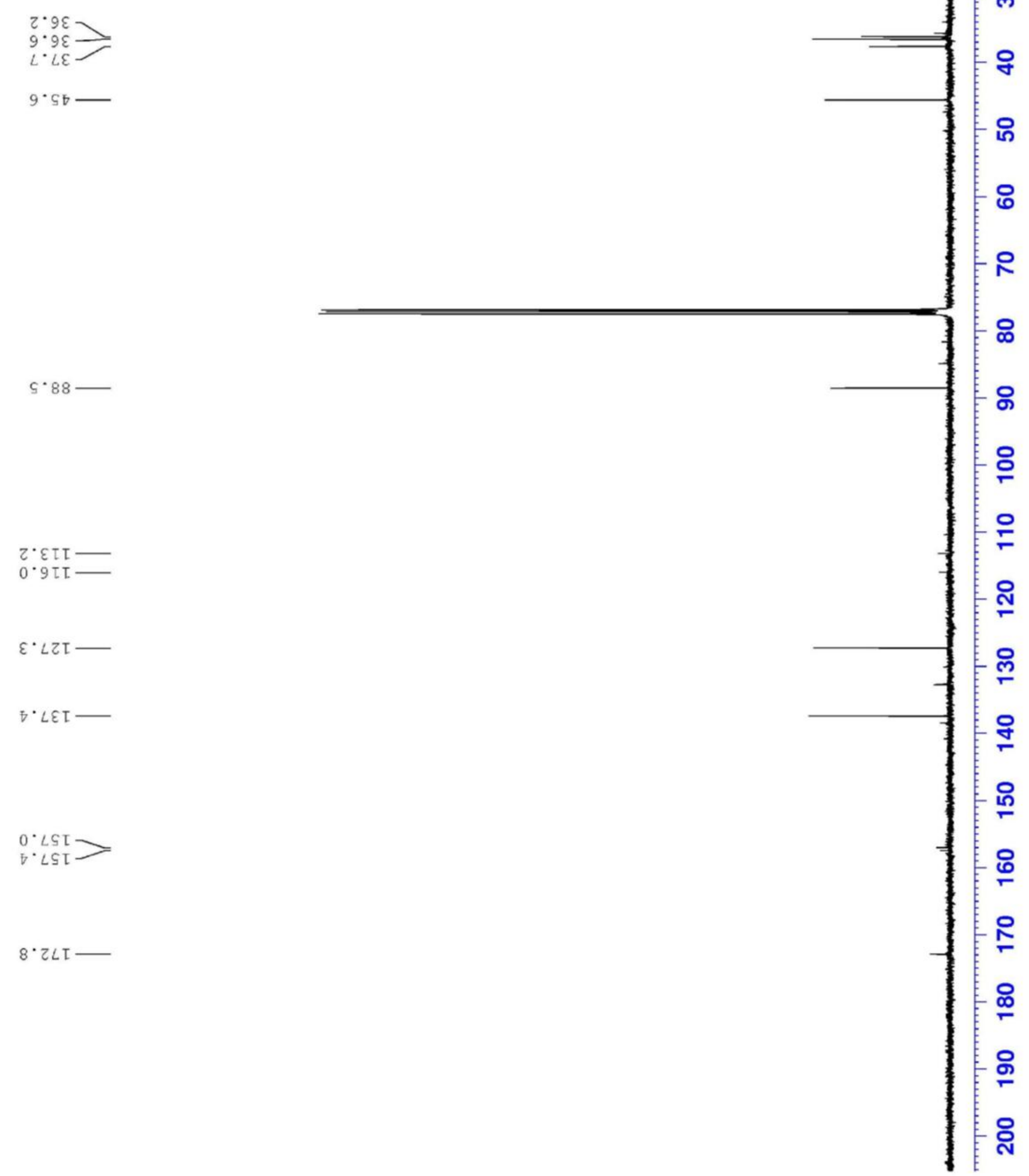

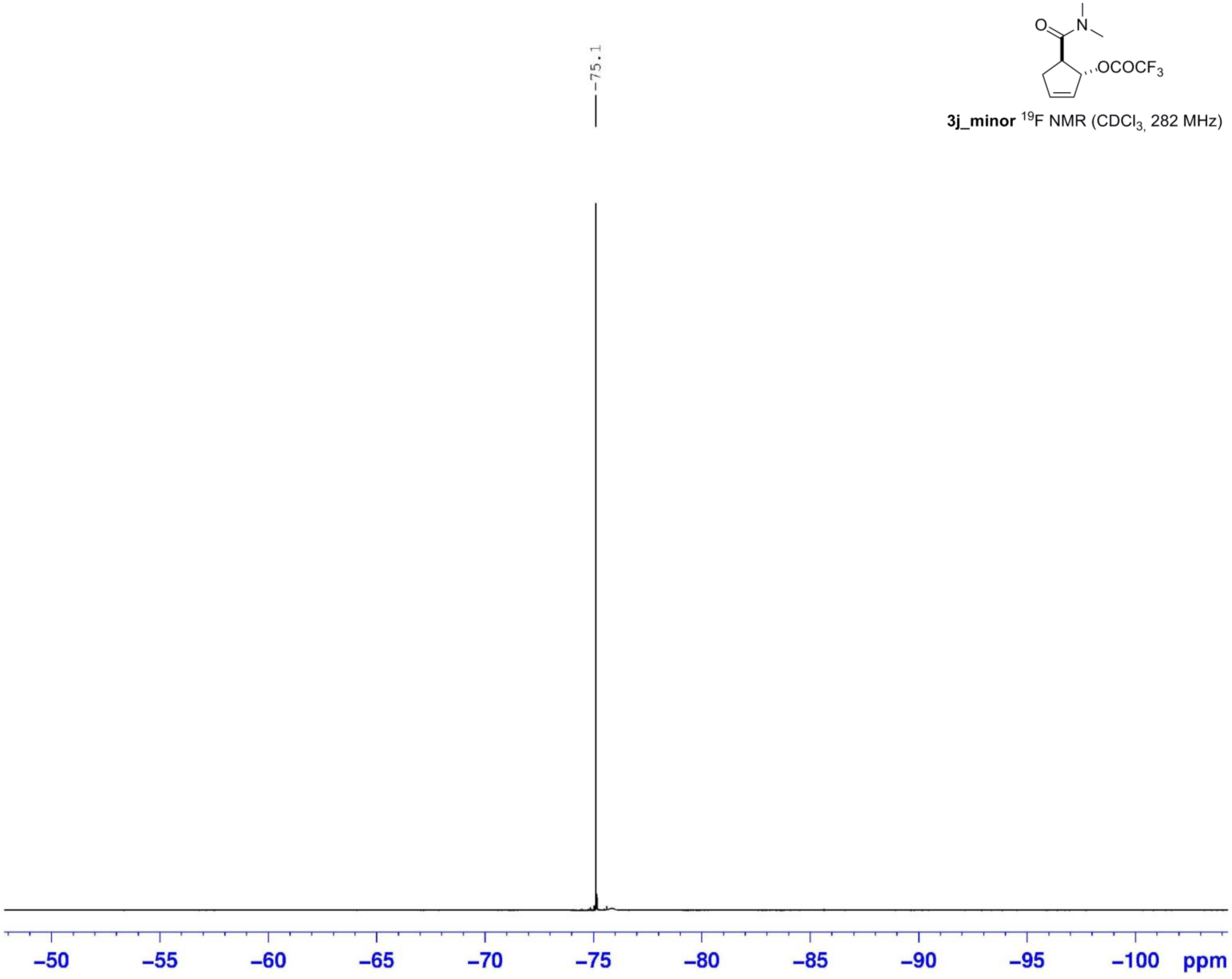

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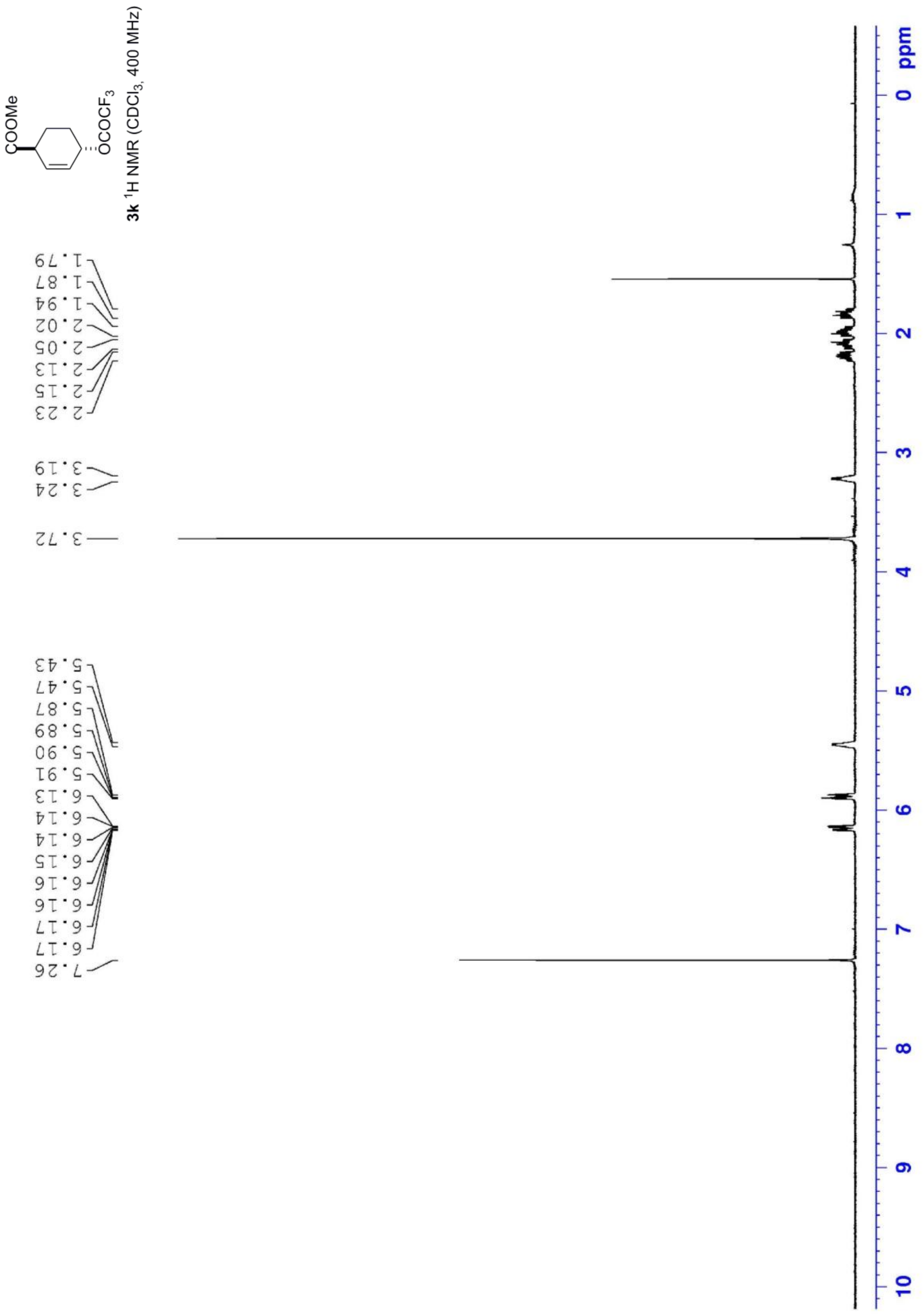

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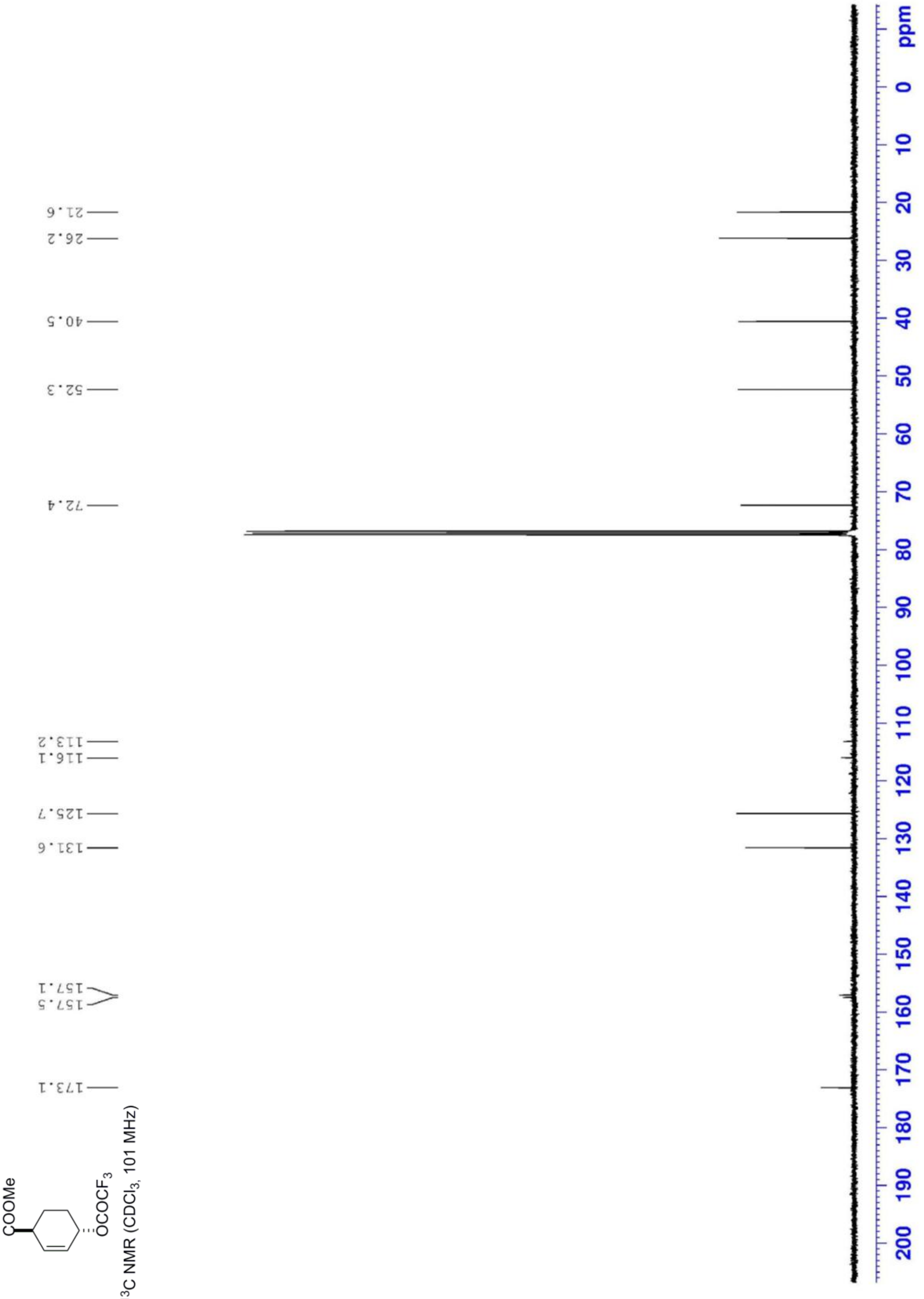
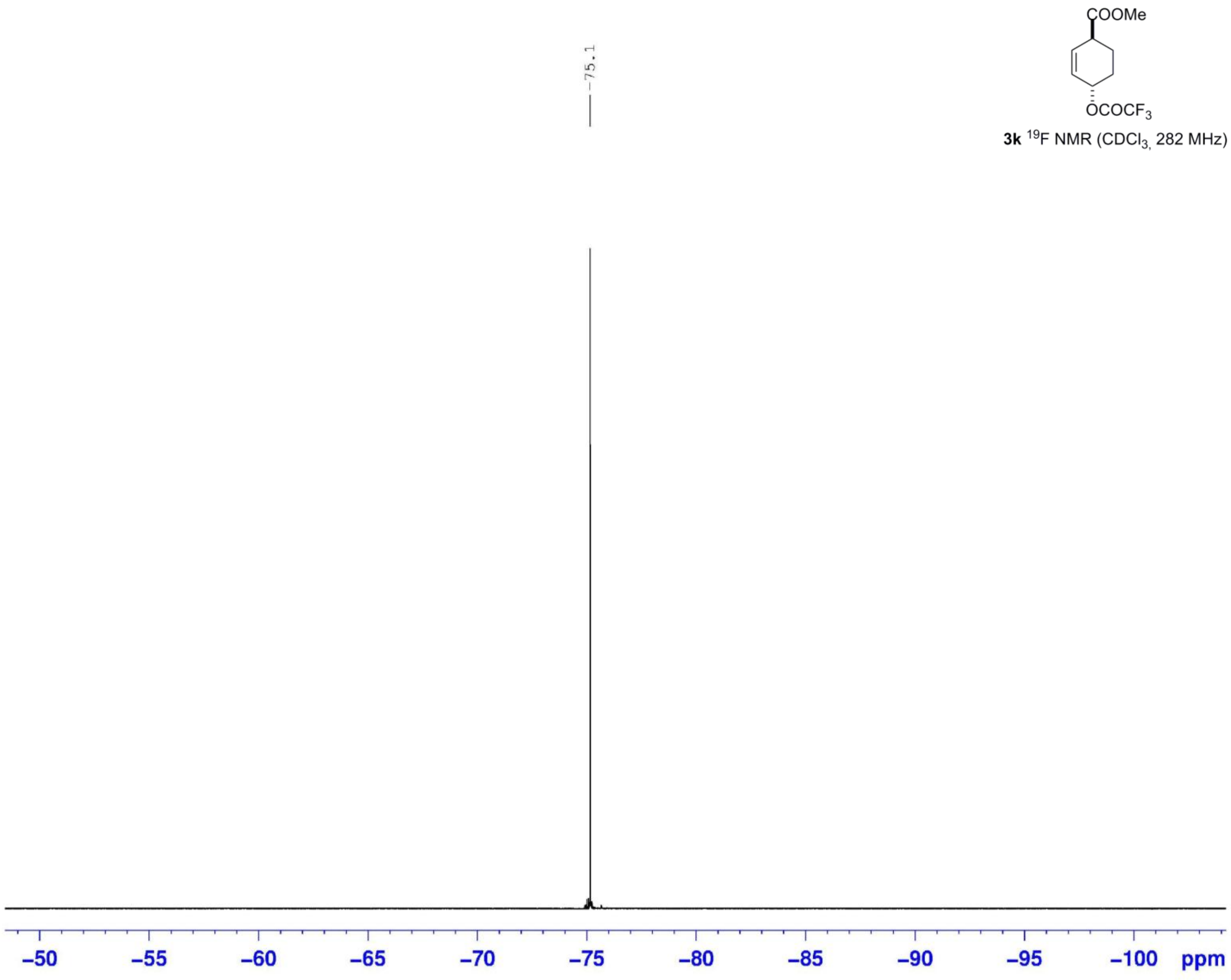


3k ^{13}C NMR (CDCl$_3$, 101 MHz)



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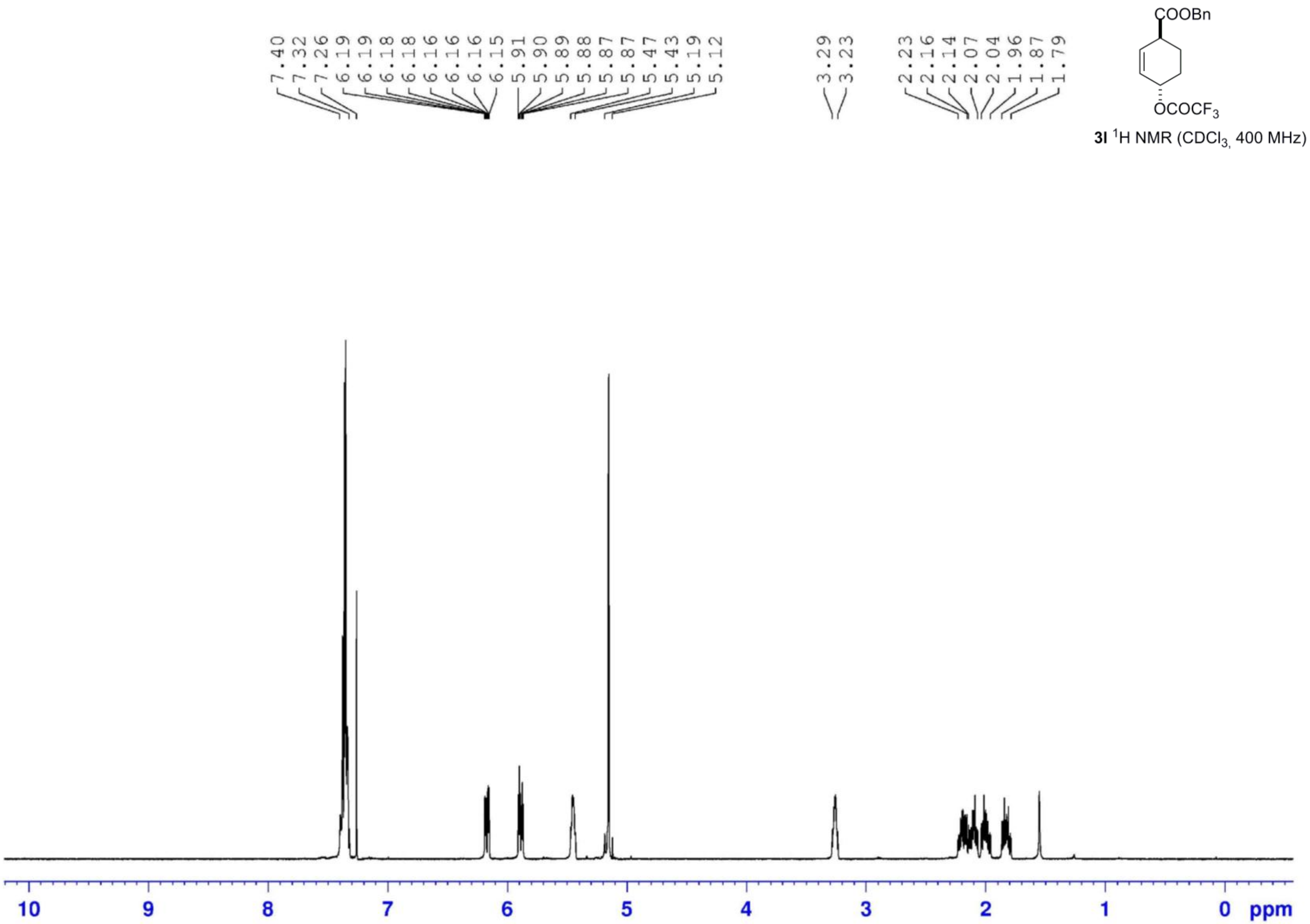

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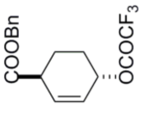

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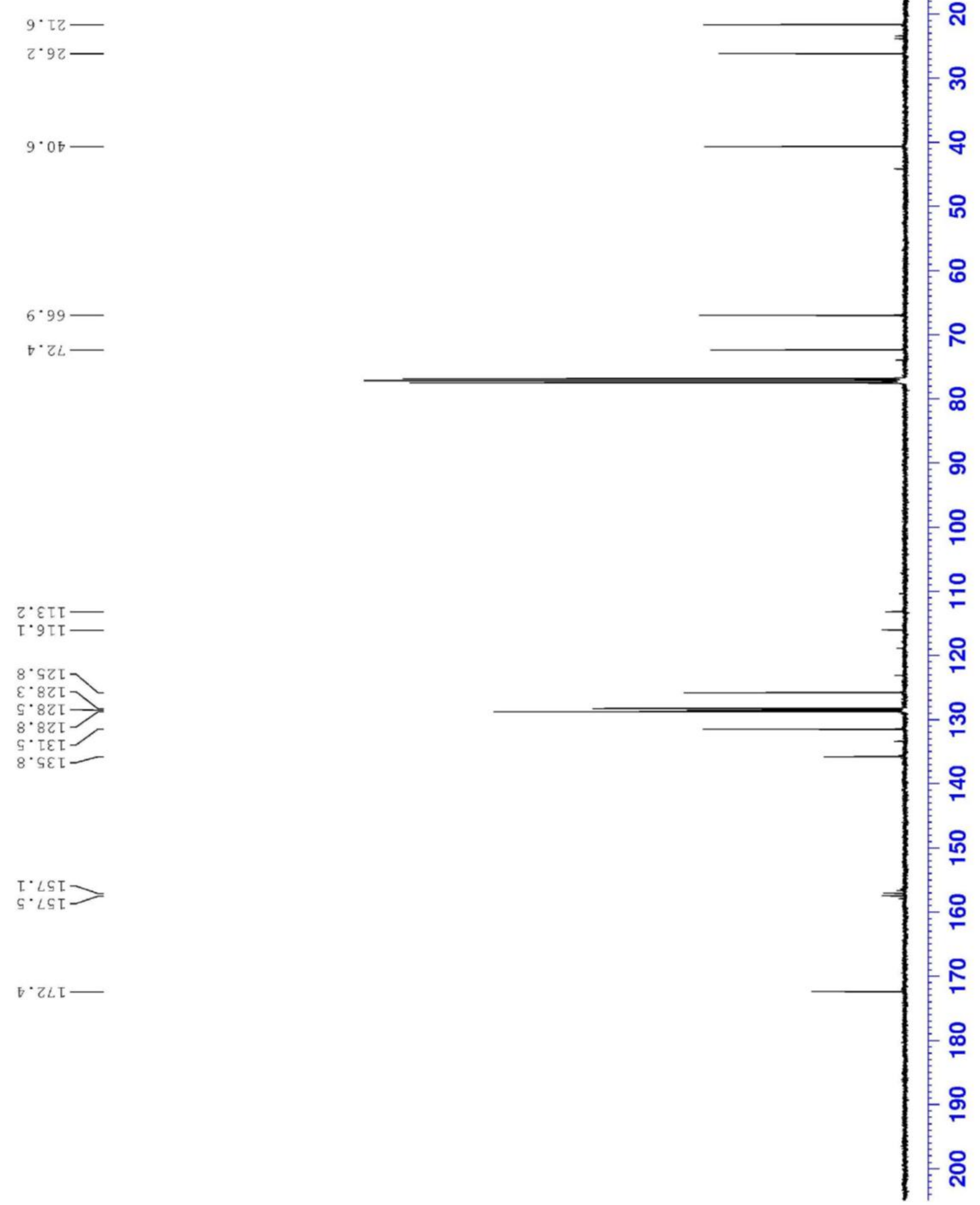

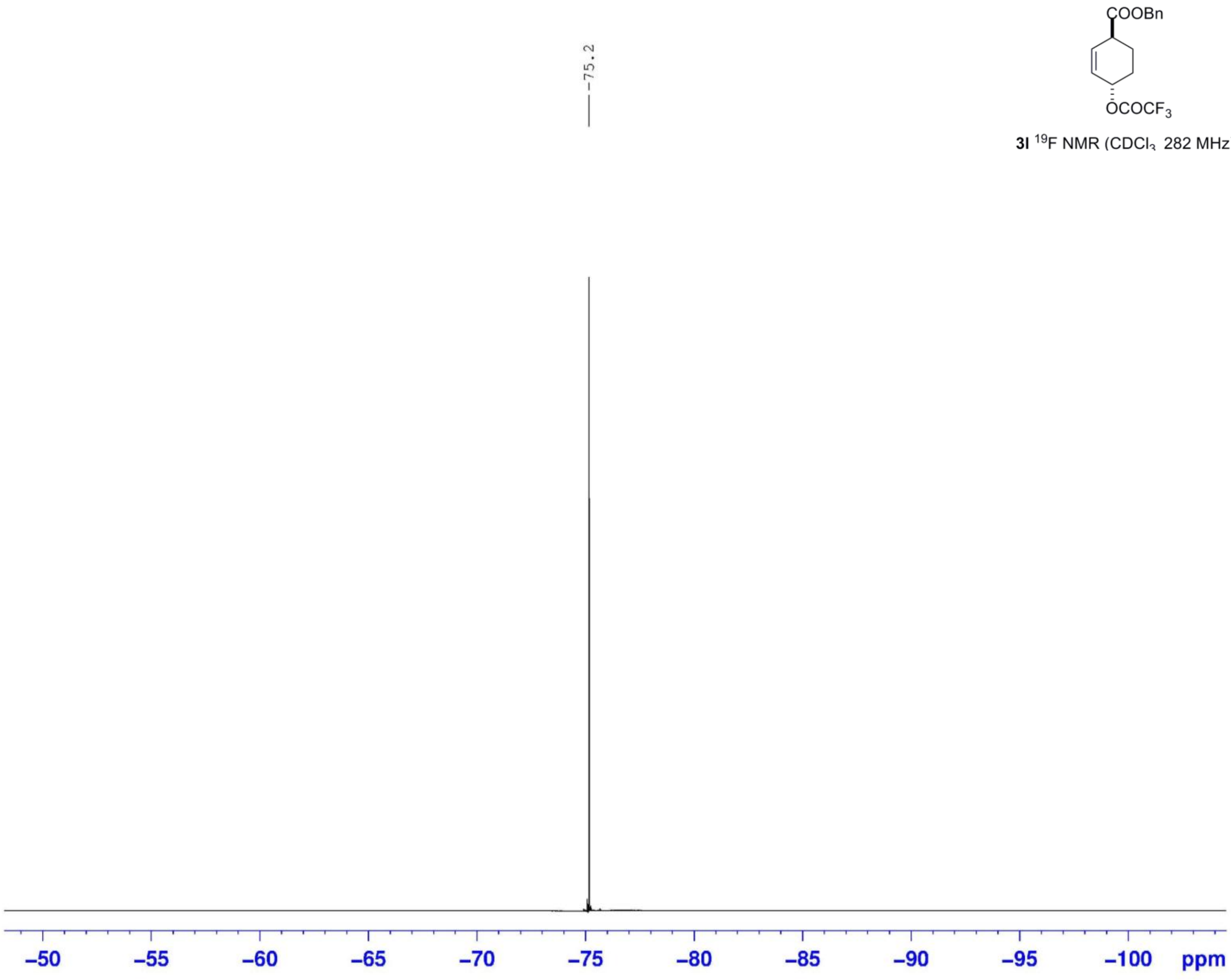

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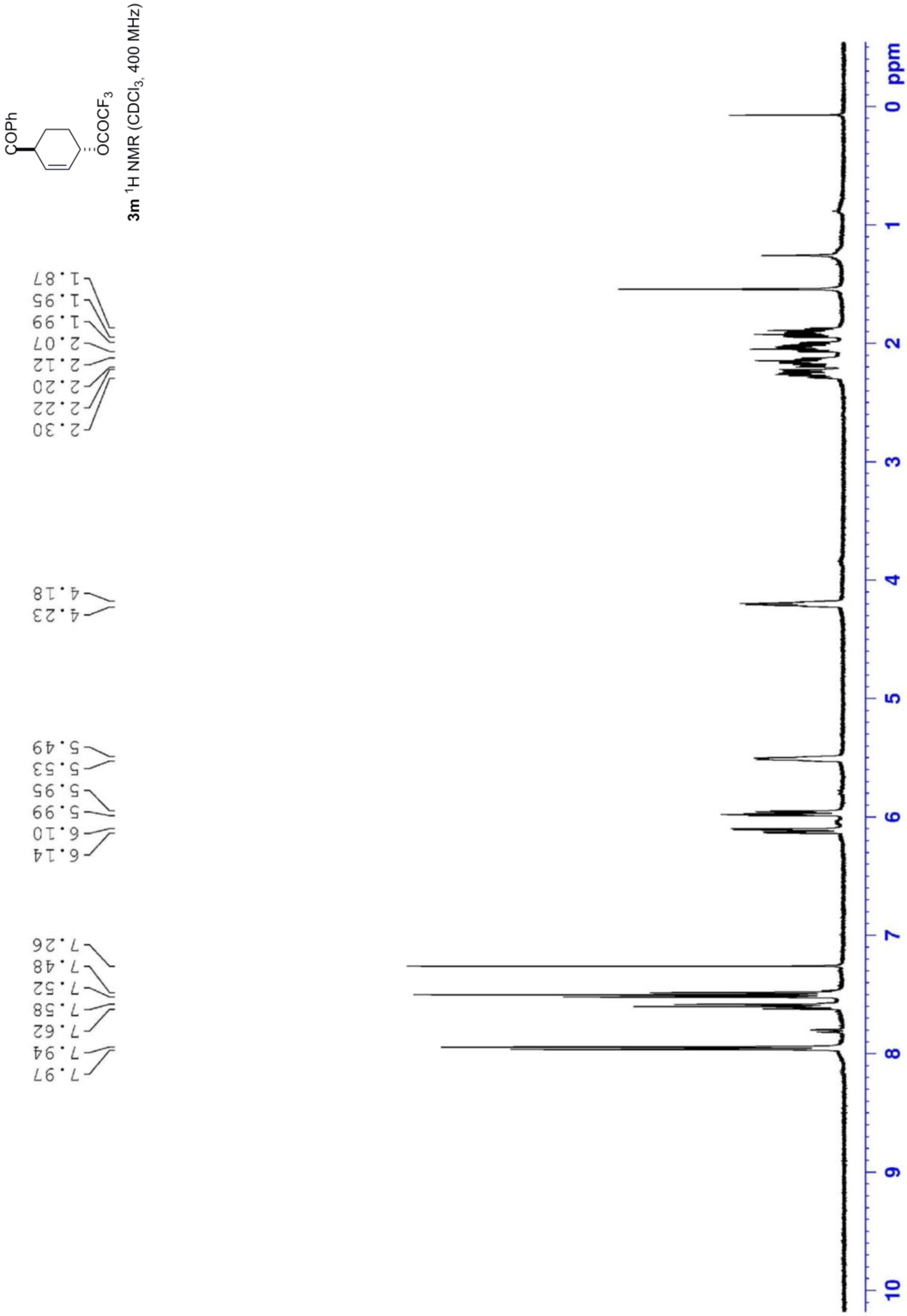

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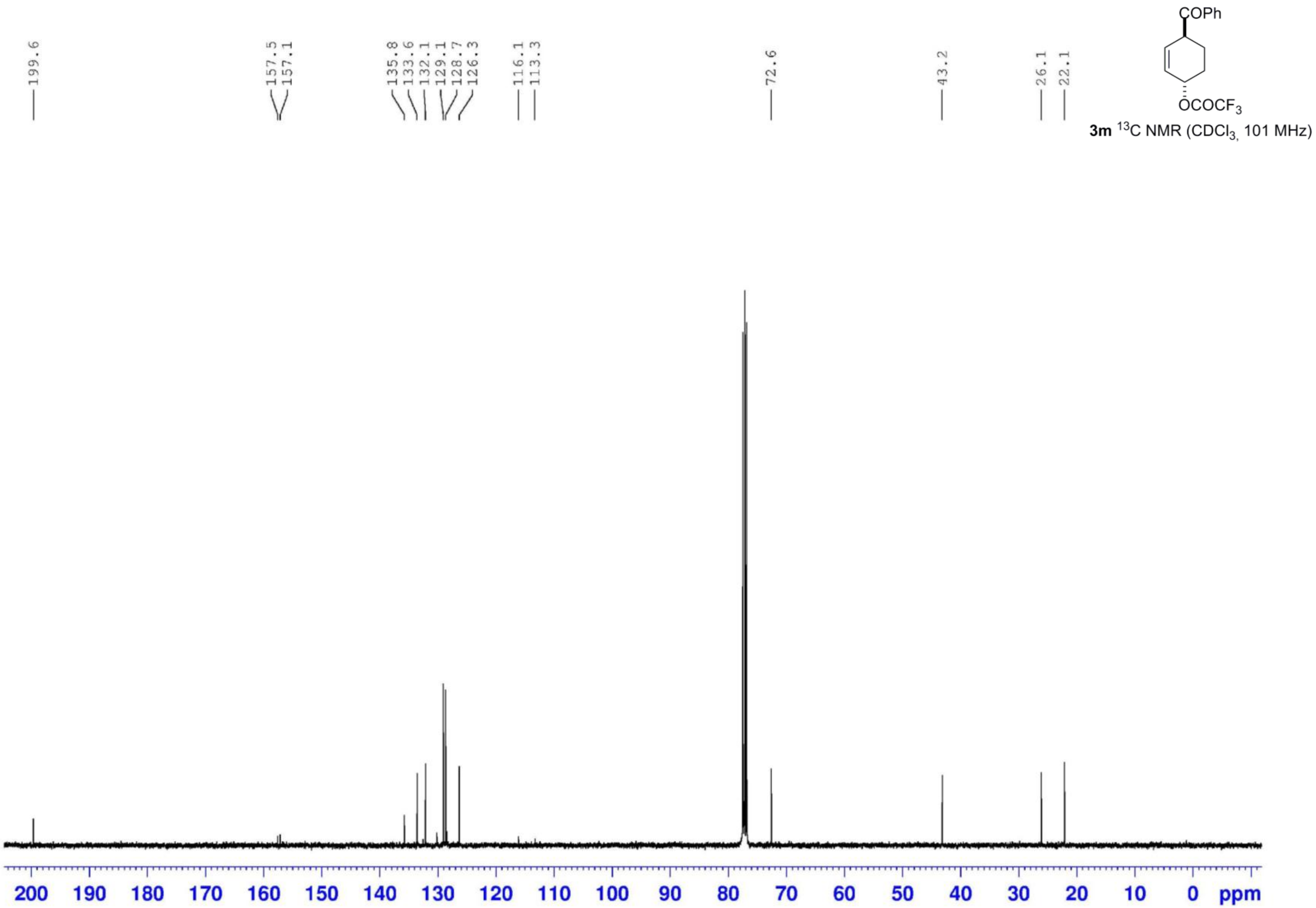

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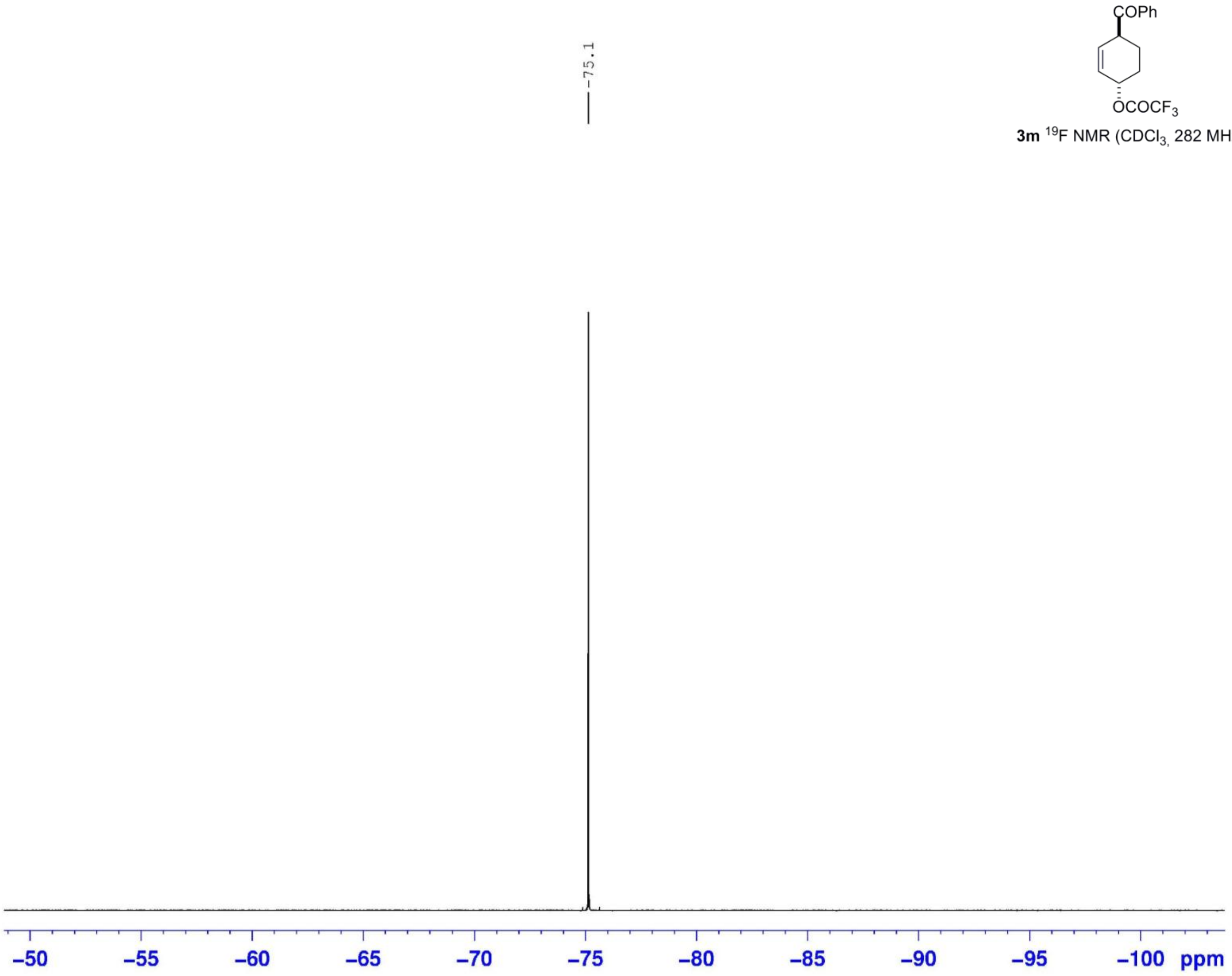
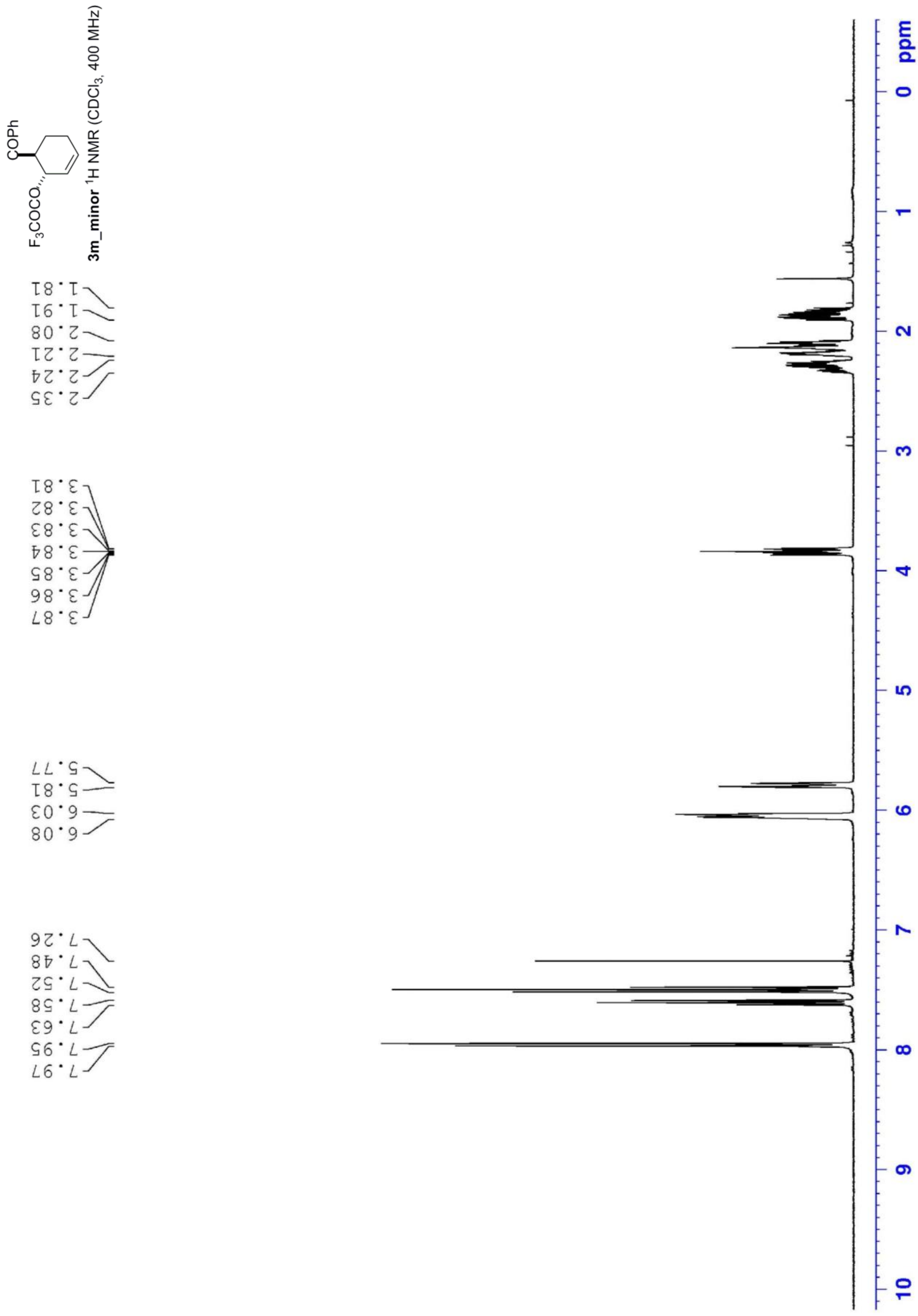


3m ^{19}F NMR (CDCl$_3$, 282 MHz)



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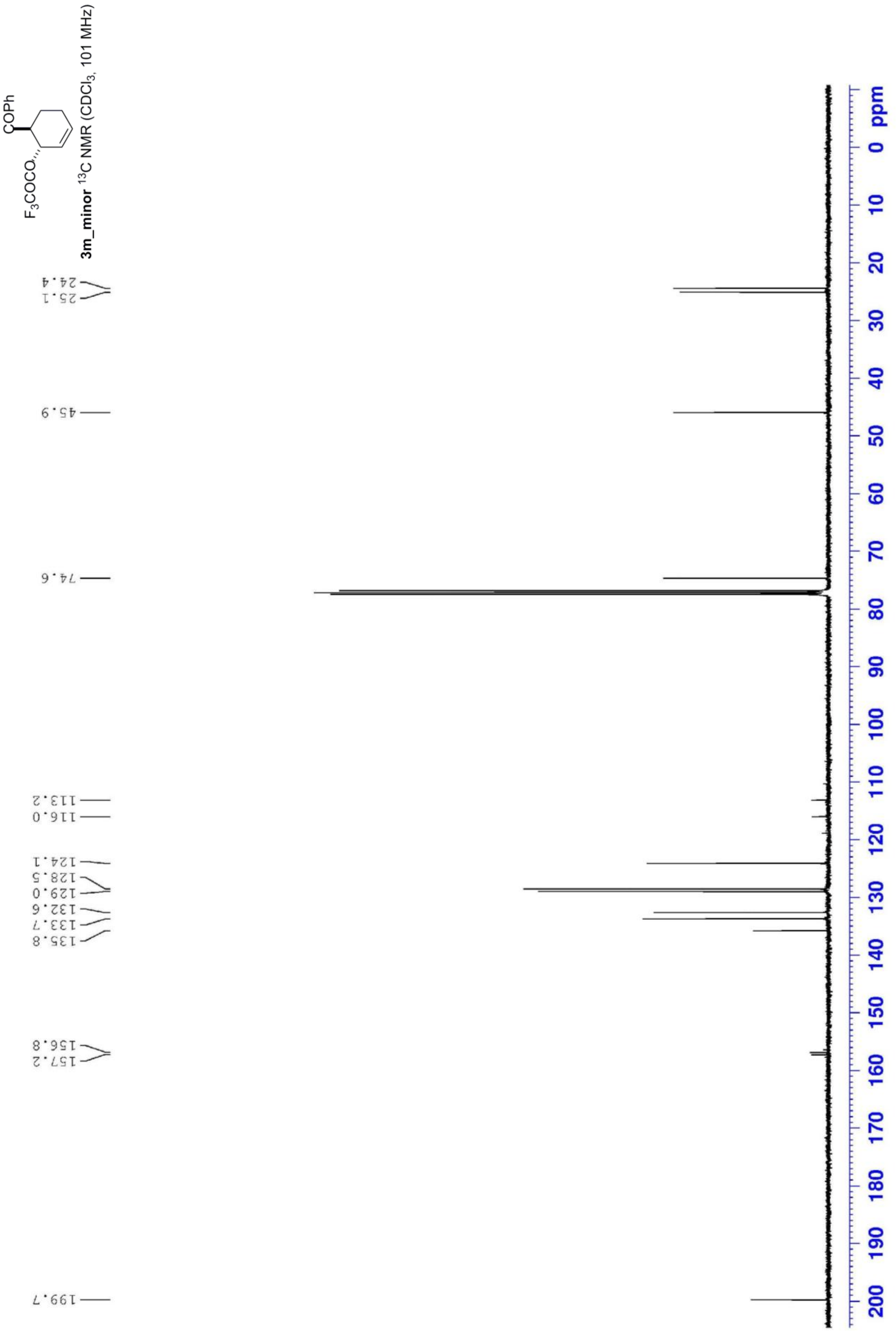

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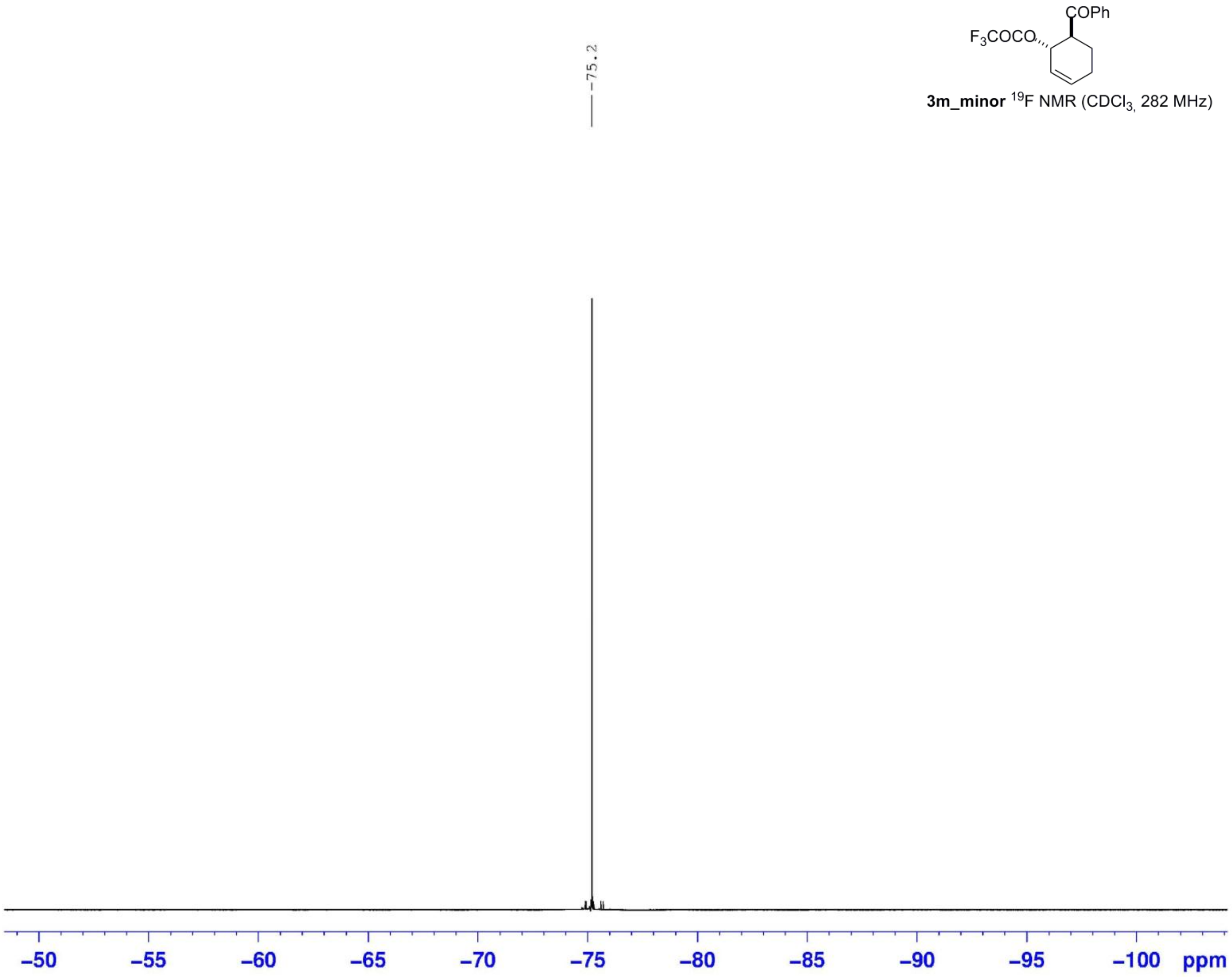

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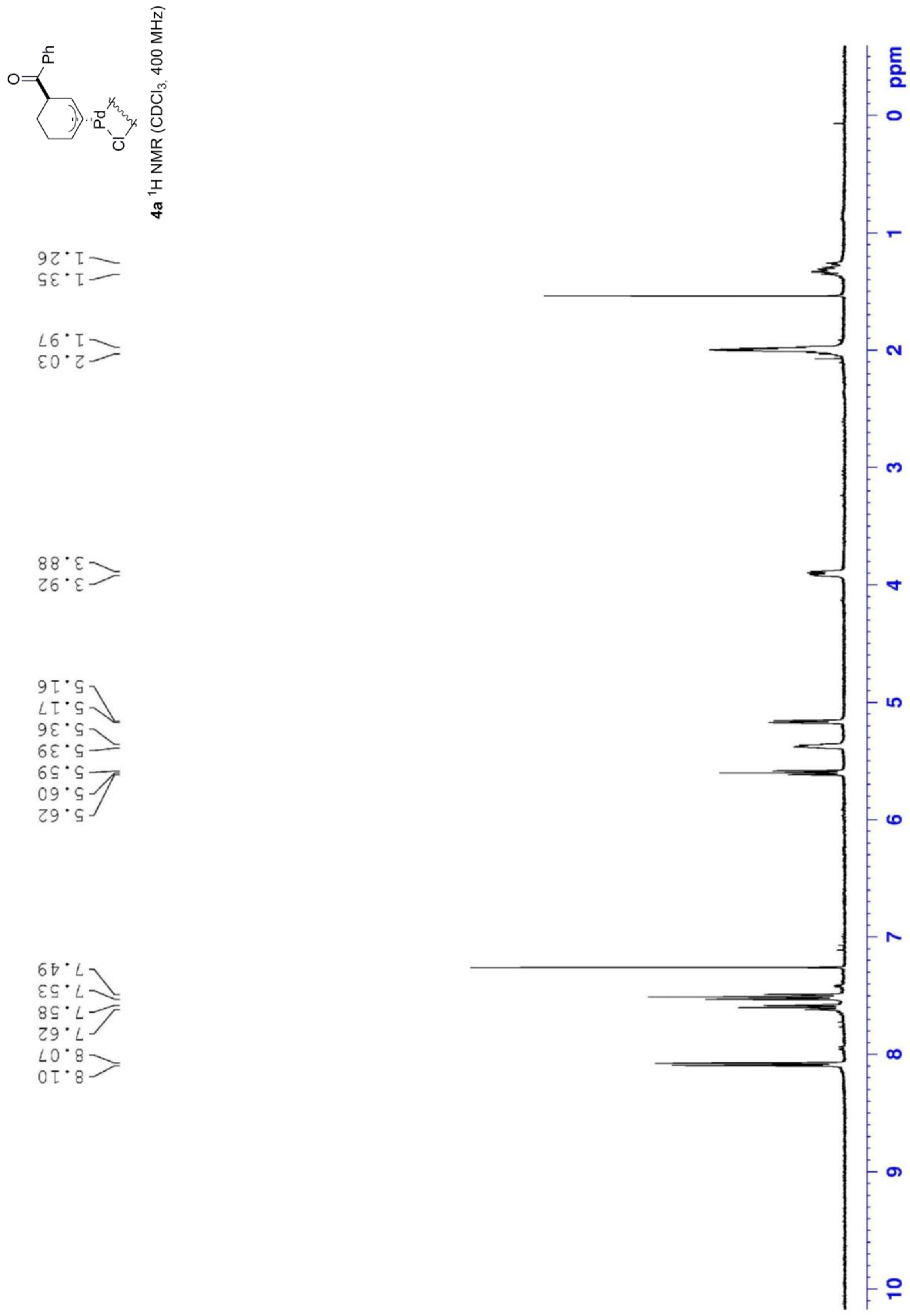

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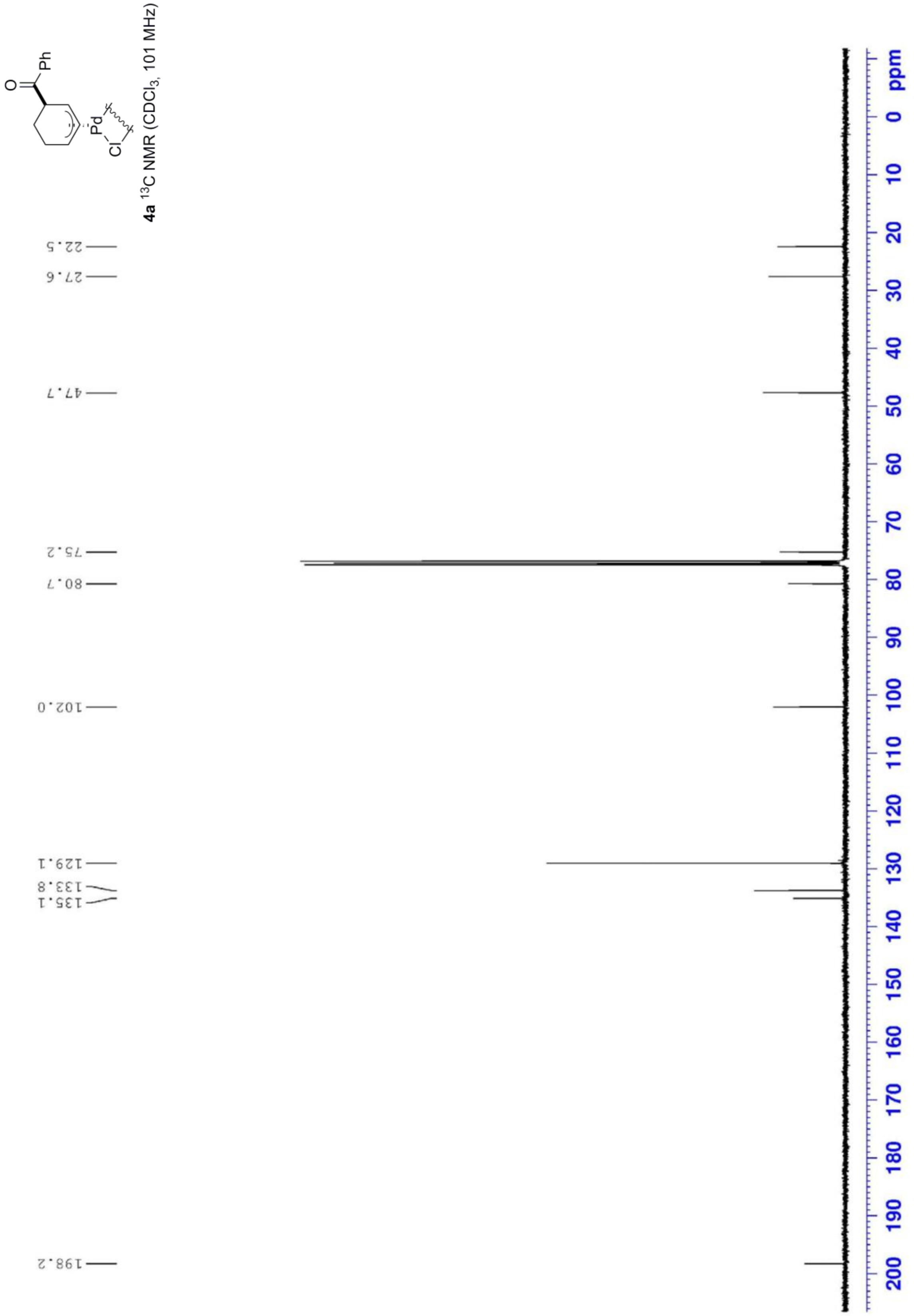
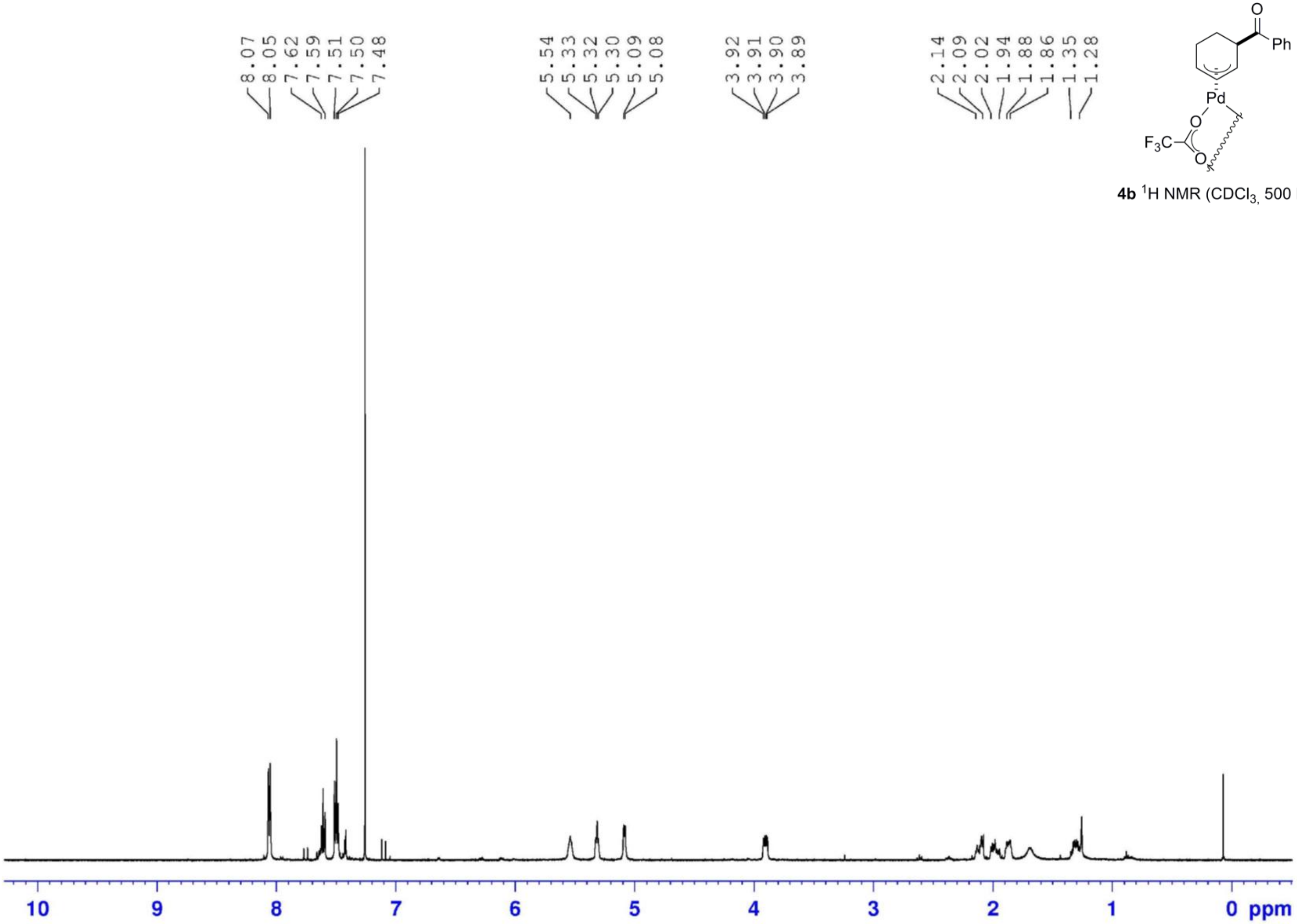


4a ^{13}C NMR ($CDCl_3$, 101 MHz)



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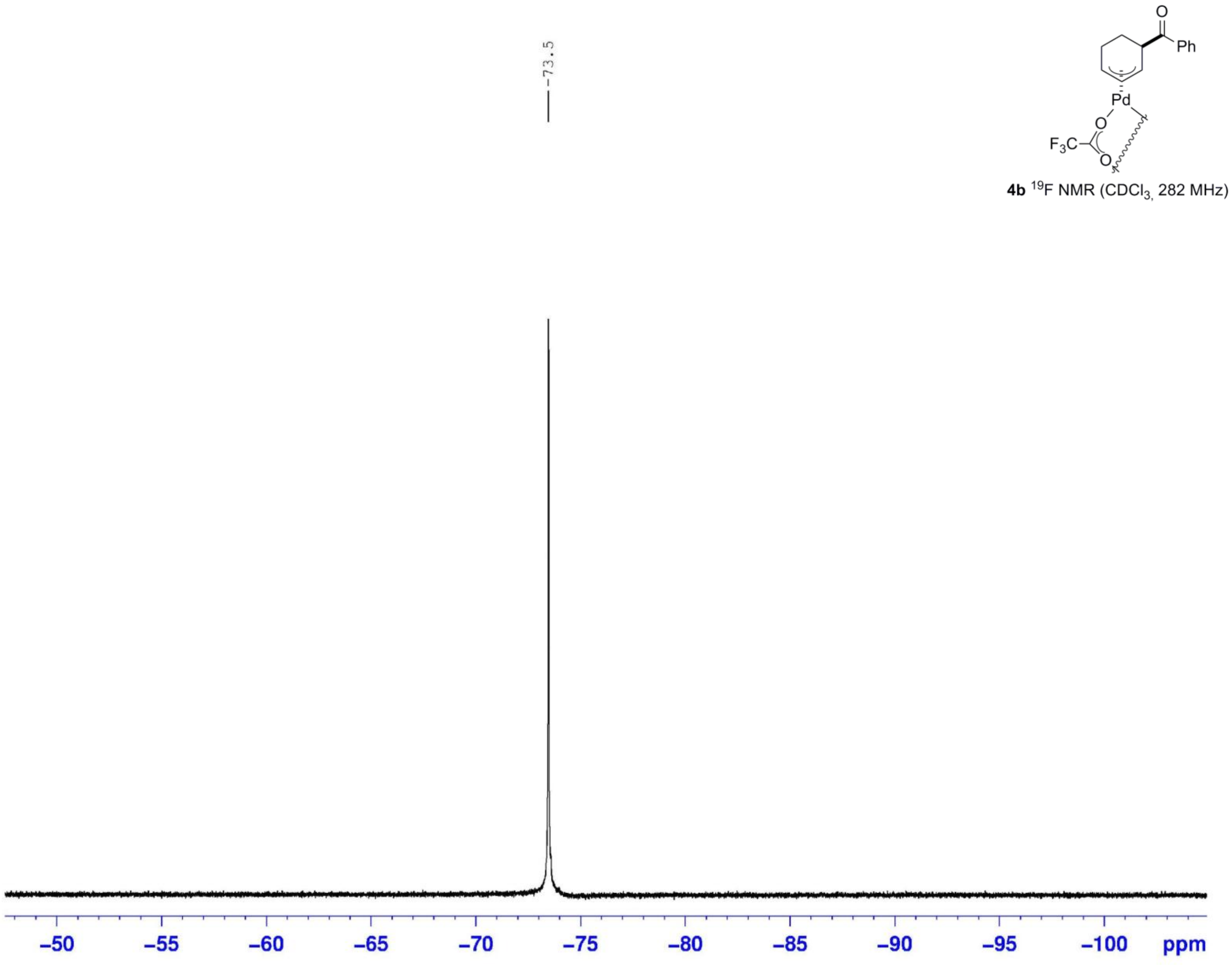

4b ^{19}F NMR (CDCl$_3$, 282 MHz)