Supporting information

Trifluoromethylation of Propargylic Halides and Trifluoroacetates using $(Ph_3P)_3Cu(CF_3)$ Reagent

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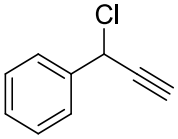
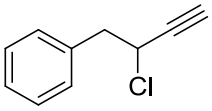
Experimental procedures and compound characterization

General information. Copper reagent **1a**[1] and starting materials **2f**[2], **2g**[3], **3a-d**[4] and **4**[5] were prepared according to literature procedures. All other chemicals were obtained from commercial suppliers and were used without further purification. All reactions were performed under air unless otherwise stated. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ on a 400 MHz instrument. All ^{1}H NMR spectra are measured relative to the signals for residual $CHCl_3$ (7.26 ppm) and all ^{13}C NMR spectral data are reported relative to $CDCl_3$ (77.16 ppm). For ^{19}F NMR, α,α,α-trifluorotoluene was used as an external standard (-63.73 ppm). All column chromatography was performed using silica gel (35-70 microns). GC analysis was performed using Varian 3800 instrument, equipped with a FID detector using a CP7503 column with a 1.8 mL/min N_2 flow. HRMS data were recorded on a micrOTOF instrument using ESI and APCI technique.

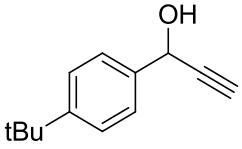
General method for trifluoromethylation of propargylic alcohol derivatives. Complex **1a** (912 mg, 0.100 mmol) and propargyl derivatives **2** or **3** (0.1 mmol) were dissolved in dry THF (0.4 ml) and the reaction mixture was stirred for 16 hours at the indicated temperatures (Table 1). Then, the reaction mixture was filtered and concentrated under reduced pressure followed by purification using column chromatography with pentane as eluent.



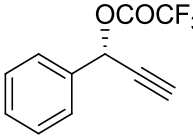
(1-Chloroprop-2-yn-1-yl)benzene (2a). To a stirred solution of triphenylphosphine (864 mg, 3.29 mmol) in THF (3 mL) was added 1-phenylprop-2-yn-1-ol (360 mg, 2.27 mmol) in THF (3 mL). Subsequently, N-chlorosuccinimide (455 mg, 3.41 mmol) in THF (3 mL) was added dropwise to the solution over 10 min at 0 °C and the resulted reaction mixture was refluxed for 16 hours. Then, pentane was added and the precipitate was filtered off. The resulted solution was concentrated and the crude product was purified by flash column chromatography (pentane : EtOAc 10:1) and isolated as a colorless oil (259 mg, 76% yield). The spectral data obtained for **2a** are in agreement with the literature values.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (1H, d, J = 2.4 Hz), 5.66 (1H, d, J = 2.4 Hz), 7.33-7.55 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.0, 76.8, 80.6, 127.5, 128.9, 129.2, 138.0.



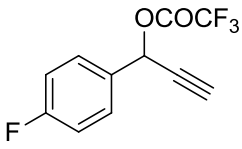
(2-Chlorobut-3-yn-1-yl)benzene (2e). This compound was synthesized according to the procedure described above for of **2a** using 1-phenylbut-3-yn-2-ol (0.3318 g, 2.27 mmol). The crude product was purified by flash column chromatography (pentane) and isolated as a yellow oil (359 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (1H, d, *J* = 2.3 Hz), 3.23 (1H, dd, *J* = 12.1, 7.1 Hz), 3.27 (1H, dd, *J* = 12.1, 7.1 Hz), 4.67 (1H, td, *J* = 7.2, 2.3 Hz), 7.27-7.74 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.1, 48.1, 75.2, 81.5, 127.4, 128.4, 129.6, 136.0. HRMS (ESI-): *m*/*z* calcd. for $[C_{10}H_8Cl]^-$ 163.0320/165.0292, found 163.0330/165.0305.



1-(4-(tert-Butyl)phenyl)prop-2-yn-1-ol. To a stirred solution of 4-(tert-butyl)benzaldehyde (1.62 mg, 10.0 mmol) in THF (10 ml) at 0 °C was added ethynyl magnesium bromide (0.5 M in THF, 25 ml, 12.5 mmol) dropwise over 5 min. After 4 hours the reaction was quenched with saturated aqueous NH_4Cl solution (20 ml), extracted with EtOAc (3x 15 ml) and washed with brine. The organic phase was dried over $MgSO_4$, filtered, evaporated and the crude alcohol was purified via column chromatography (pentane: EtOAc 10:1) and was isolated as a colorless oil (1.58 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (9H, s), 2.13 (1H, d, *J* = 6.1 Hz), 5.45 (1H, dd, *J* = 5.9, 1.9 Hz), 7.39 – 7.52 (4H, m).^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.6, 64.3, 74.6, 83.6, 125.7, 126.4, 137.1, 151.7. HRMS (ESI+): *m*/*z* calcd. for $[C_{13}H_{16}NaO]^+$ 211.1093, found 211.1097.

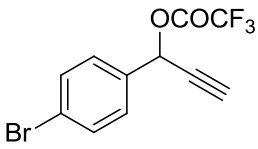


(R)-1-Phenylprop-2-yn-1-yl 2,2,2-trifluoroacetate (3a). This compound was prepared according to the literature procedure by Davies and co-workers[4] using commercially available (Aldrich) (*R*)-1-phenylprop-2-yn-1-ol (500 mg, 3.783 mmol). The crude product was purified by flash chromatography (pentane/EtOAc 10:1) and isolated as a colorless oil (845 mg, 98% yield, 90% ee). Spectral data is in agreement with the literature values reported by Davies and co-workers[4] for the racemic form. GC analysis: (*R*)-form R_f = 77.2 min and (*S*)-form 78.7 min using 0.1 °C/min heating gradient in the temperature range between 47 °C to 59 °C.

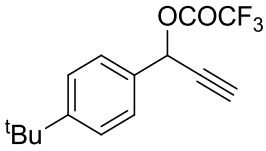


1-(4-Fluorophenyl)prop-2-yn-1-yl 2,2,2-trifluoroacetate (3b). This compound was synthesized according to the literature procedure by Davies and co-workers using 1-(4-fluorophenyl)prop-2-yn-1-ol (1.08 g, 7.20 mmol) as the alcohol component.[4] The crude product was purified by chromatography

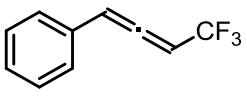
(pentane/EtOAc 10:1) and isolated as a colorless oil (1.45 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (1H, d, J = 2.2 Hz), 6.50 (1H, d, J = 2.2 Hz), 7.08-7.52 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8, 77.5, 78.2, 112.9, 114,3 (q, J_{CF} = 286.6 Hz), 116.1 (d, J_{CF} = 19.9 Hz), 130.2 (d, J_{CF} = 9.0 Hz), 156.3 (q, J_{CF} = 43.6 Hz), 163.6 (d, J_{CF} = 249.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -163.8 (tt, J_{FH} = 8.4, 5.2 Hz), -74.9 (s). HRMS (ESI-): *m*/*z* calcd. for $[C_{11}H_5F_4O_2]^-$ 245.0231, found 245.0219.



1-(4-Bromophenyl)prop-2-yn-1-yl 2,2,2-trifluoroacetate (3c). The compound was synthesized according to the literature procedure by Davies and co-workers[4] using 1-(4-bromophenyl)prop-2-yn-1-ol (1.05 g, 5.00 mmol) as the alcohol component. The crude product was purified by column chromatography (pentane/EtOAc 10:1) and isolated as a yellow oil (1.10 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (1H, d, J = 2.3 Hz), 6.48 (1H, d, J = 2.3 Hz), 7.60-7.41 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8, 77.2, 78.3, 114.3 (q, J_{CF} = 286.0 Hz), 124.5, 126.6, 132.3, 133.1, 156.3 (q, J_{CF} = 43.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.8 (s). HRMS (ESI-): *m*/*z* calcd. for $[C_{11}H_5BrF_3O_2]^-$ 304.9431/306.9411, found 304.9445/306.9425.



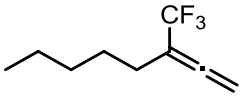
1-(4-(tert-Butyl)phenyl)prop-2-yn-1-yl 2,2,2-trifluoroacetate (3d). The compound was synthesized according to the literature procedure by Davies and co-workers using 1-(4-(tert-butyl)phenyl)prop-2-yn-1-ol (940 mg, 5.0 mmol) as the alcohol component.[4] The crude product was purified by flash column chromatography (pentane/EtOAc 10:1) and isolated as a colorless oil (739 mg, 52% yield). The product hydrolyses on silica and the alcohol was isolated as a byproduct. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (9H, s), 2.79 (1H, d, J = 2.4 Hz), 6.51 (1H, d, J = 2.2 Hz), 7.42-7.52 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 31.1, 68.0, 77.2, 83.3, 114.9 (q, J_{CF} = 279.5 Hz), 126.1, 127.8, 128.5, 153.3, 155.2, 185.6 (q, J_{CF} = 41.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.9 (s). HRMS (ESI-): *m*/*z* calcd. for $[C_{15}H_{14}F_3O_2]^-$ 283.0951, found 283.0956.



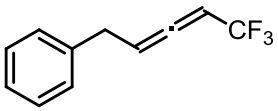
(4,4,4-Trifluorobuta-1,2-dien-1-yl)benzene (5a). This product was synthesized from **2a** and **3a** (entry 10, Table 1) using the above general method. Product **5a** was isolated as a colorless oil (12.8 mg, 68% from **2a**, 15.7 mg, 85% from **3a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (1H, app. quintett, J = 6.0 Hz), 6.67 (1H, dq, J = 3.9 Hz), 7.28-7.48 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.7 (q, J = 39.3 Hz), 101.3, 121.0, 127.5, 128.6, 129.0, 131.8, 207.0 (q, J_{CF} = 6.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$)

δ -60.2 (dd, *J* = 5.8, 3.8 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_{20}H_{15}F_6]^+$ 369.1072, found 369.1076, corresponding to $[2xM_{5a}+H]^+$.

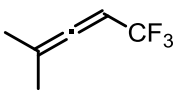
The enantiomerically enriched product was obtained using (*R*)-1-phenylprop-2-yn-1-yl 2,2,2-trifluoroacetate (90% ee) which was stirred at 4 ºC for 16 hours. The product could be isolated as a colorless oil (12.7 mg, 70% yield, 89% ee). The ee value was determined by GC analysis using a 0.1 °C/min heating gradient in the temperature range between 50 °C to 55 °C. Based on the analysis of the racemic mixture the R_f values for the two enantiomers are 67.4 min and 70.3 min.



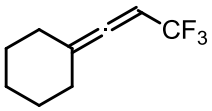
3-(Trifluoromethyl)octa-1,2-diene (5b). This product was synthesized from **2d** using the above general method. Product **5b** was isolated as colorless oil (12.1 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84-0.97 (4H, m), 1.30-1.38 (3H, m), 1.46-1.54 (2H, m), 2.11 (2H, app. septet, *J* = 3.7 Hz), 5.20 (2H, app. sextet, *J* = 3.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 25.7, 26.9, 31.1, 81.8, 98.7 (q, J_{CF} = 33 Hz), 123.9 (q, J_{CF} = 136 Hz), 206.5 (q, J_{CF} = 4.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.3 (app. t., J_{FH} = 3.7 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_9H_{14}F_3]^+$ 179.1042, found 179.1039.



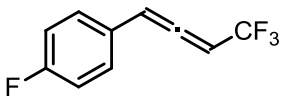
(5,5,5-Trifluoropenta-2,3-dien-1-yl)benzene (5c). The product was synthesized from **2e** using the general method. Product **5c** was isolated as a colorless oil (18.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (2H, dd, *J* = 7.4, 2.8 Hz), 5.47 (1H, dqt, *J* = 17.8, 6.0, 3.0 Hz), 5.86 (1H, dtq, *J* = 17.8, 7.5, 3.9 Hz), 7.22-7.42 (5H, m.). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3, 86.3 (q, J_{CF} = 39.7 Hz), 98.0, 126.8, 128.5, 128.6, 128.7, 133.6, 133.8, 138.2, 205.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.5 (dd, J_{FH} = 6.4, 4.1 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_{22}H_{19}F_6]^+$ 397.1385, found 397.1391 corresponding to $[2xM_{5c}+H]^+$.



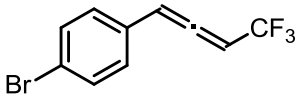
1,1,1-Trifluoro-4-methylpenta-2,3-diene (5d). The product was synthesized from **2f** using the above general method. Using ^{19}F NMR, an NMR yield of 86% was calculated using **5a** as internal standard. The product could not be isolated because of volatility. The ^{19}F NMR data is obtained by the analysis of the crude reaction mixture: ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.8.



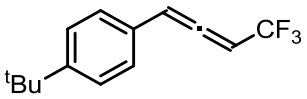
(3,3,3-Trifluoroprop-1-en-1-ylidene)cyclohexane (5e). This product was synthesized from **2g** using the general method. Product **5e** was isolated as a colorless oil (15.4 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 - 1.68 (6H, m), 2.12 - 2.28 (4H, m), 5.26 (1H, qp, J = 5.8, 5.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 26.9, 30.3, 30.3, 83.2 (q, J_{CF} = 38.3 Hz), 110.1, 121.7, 124.4, 199.0 (q, J_{CF} = 5.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.7 (d, J_{FH} = 5.8 Hz).



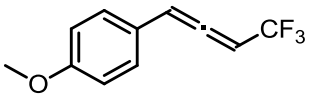
1-Fluoro-4-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene (5f). The product was obtained from **3b** using the general method as a colorless oil (17.5 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (1H, app. pentet, J = 5.9 Hz), 6.61 – 6.68 (1H, m), 7.04 – 7.30 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 90.8 (q, J_{CF} = 39.0 Hz), 101.3, 116.9 (d, J_{CF} = 21.0 Hz), 123.2 (q, J_{CF} = 270.9 Hz), 127.7 (q, J_{CF} = 1.4 Hz), 130.0 (d, J_{CF} = 8.3 Hz), 163.7 (d, J_{CF} = 246.9 Hz), 207.6 (qd, J_{CF} = 5.8, 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.5 (m), -60.3 (dd, J_{FH} = 5.5, 3.2 Hz). HRMS (ESI-): *m*/*z* calcd. for $[C_{10}H_5F_4]^-$ 201.0322, found 201.0322.



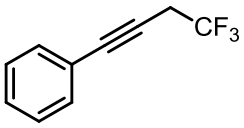
1-Bromo-4-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene (5g). This product was synthesized from **3c** using the above general method. Product **5g** was isolated as colorless oil (16.7 mg, 63% yield). The spectral data is in agreement with the literature values.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (1H, app. pentet, J = 5.9 Hz), 6.63 (1H, dq, J = 7.4, 3.4 Hz), 7.13 – 7.50 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.5 (q, J_{CF} = 40.0 Hz), 100.9, 114.5, 121.5 (q, J_{CF} = 270.0 Hz), 122.9, 128.8, 133.7, 206.7 (q, J_{CF} = 5.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.2 (dd, J_{FH} = 5.8, 3.8 Hz).



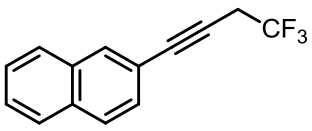
1-(tert-Butyl)-4-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene (5h). This product was synthesized from **3d** using the above general method. Product **5h** was isolated as a colorless oil (14.9 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (9H, s), 5.87 (1H, app. quintett, J = 5.9 Hz), 6.67 (1H, dq, J = 7.7, 3.5 Hz), 7.27 – 7.43 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 34.7, 89.5 (q, J_{CF} = 39.3 Hz), 101.0, 122.4 (q, J_{CF} = 271.6 Hz), 125.9, 127.3, 127.8 (q, J_{CF} = 1.2 Hz), 151.9, 207.0 (q, J_{CF} = 6.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.3 (app. t, J_{FH} = 4.9 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_{28}H_{31}F_6]^+$ 481.2324, found 481.2331 corresponding to $[2xM_{5h}+H]^+$.



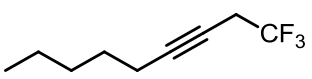
1-(tert-Butyl)-4-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene (5i). The trifluoroacetate of **4** decomposed under purification. Therefore **4** was reacted with trifluoroacetic anhydride prior to the trifluoromethylation reaction and the formed trifluoroacetate was used without purification. To a screw top vial were added **4** (0.1 mmol, 16.2 mg), dry THF (0.4 ml), DBU (0.12 mmol, 1.2 eq., 18.7 mg) and trifluoroacetic anhydride (0.14 mmol, 1.4 eq., 29.4 mg). The reaction mixture was stirred for 20 minutes, then **1a** (0.1 mmol) was added and stirring was continued for further 16 hours at ambient room temperature (22 °C). Subsequently, the reaction mixture was filtered, concentrated and purified by column chromatography using pentane as eluent. Product **5i** was obtained as colorless oil (11.1 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (3H, s), 5.85 (1H, app. quintett, J = 5.9 Hz), 6.63 (1H, dq, J = 7.7, 3.4 Hz), 6.84 – 7.28 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 89.5 (q, J_{CF} = 39.2 Hz), 100.9, 114.5, 122.4 (q, J_{CF} = 270.2 Hz), 128.8, 133.7 (q, J_{CF} = 20.0 Hz), 206.8 (q, J_{CF} = 5.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.3 (dd, J_{FH} = 6.0, 4.1 Hz). HRMS (ESI+): m/z calcd. for $[C_{11}H_{10}F_3O]^+$ 215.0678, found 215.0693.



(4,4,4-Trifluorobut-1-yn-1-yl)benzene (6a). This product was synthesized from **2a** (entry 2, Table 1), **2b** (entry 3, Table 1) and from **3a** (entry 10, Table 1) using the above general method. Product **6a** was isolated as a colorless oil (15.3 mg, 82% from **2a**, 13.7 mg, 74% from **2b**, 13.7 mg, 74% from **3a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (2H, q, J = 9.6 Hz), 7.28 – 7.51 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0 (app. d, J_{CF} = 34.6 Hz), 77.4, 100.5, 111.0, 119.3, 125.5, 129.3, 131.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.4 Hz).

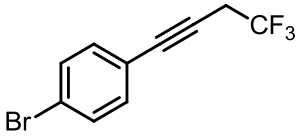


2-(4,4,4-Trifluorobut-1-yn-1-yl)naphthalene (6b). This product was synthesized from **2c** using the above general method. Product **6b** was isolated as yellow oil (20.3 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (2H, q, J = 9.6 Hz), 7.39 – 8.32 (7H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1 (q, J_{CF} = 34.5 Hz), 29.7, 77.2, 82.6, 119.8, 122.9, 125.1, 125.9, 126.5, 127.0, 128.3, 129.2, 130.8, 133.1, 133.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.8 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_{14}H_{10}F_3]^+$ 235.0729, found 235.0733.

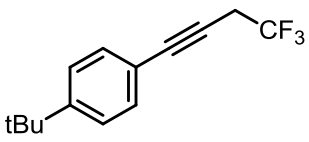


1,1,1-Trifluorononon-3-yne (6c). The product was synthesized from **2d** using the above general method. The product was isolated as colorless oil (11.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 - 0.95 (3H, m),

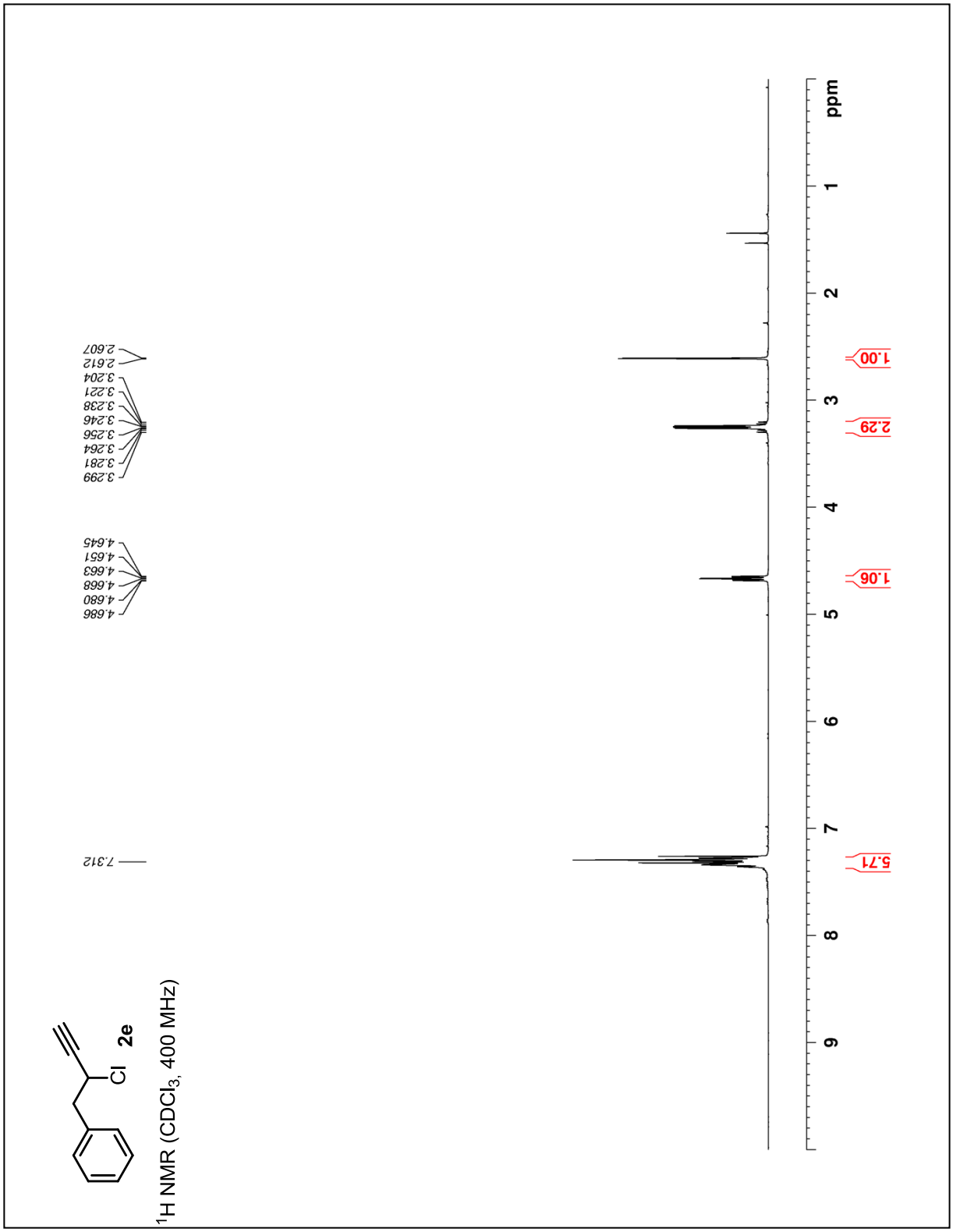
1.23 – 1.42 (4H, m), 1.44-1.46 (2H, m), 2.20 (2H, tt, J = 7.0, 2.3 Hz), 3.02 (2H, qt, J = 9.7, 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 18.8, 22.2, 28.1, 31.0, 31.3, 74.9, 87.8, 127.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.1 (t, J_{FH} = 9.8 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_9H_{14}F_3]^+$ 179.1042, found 179.1036.

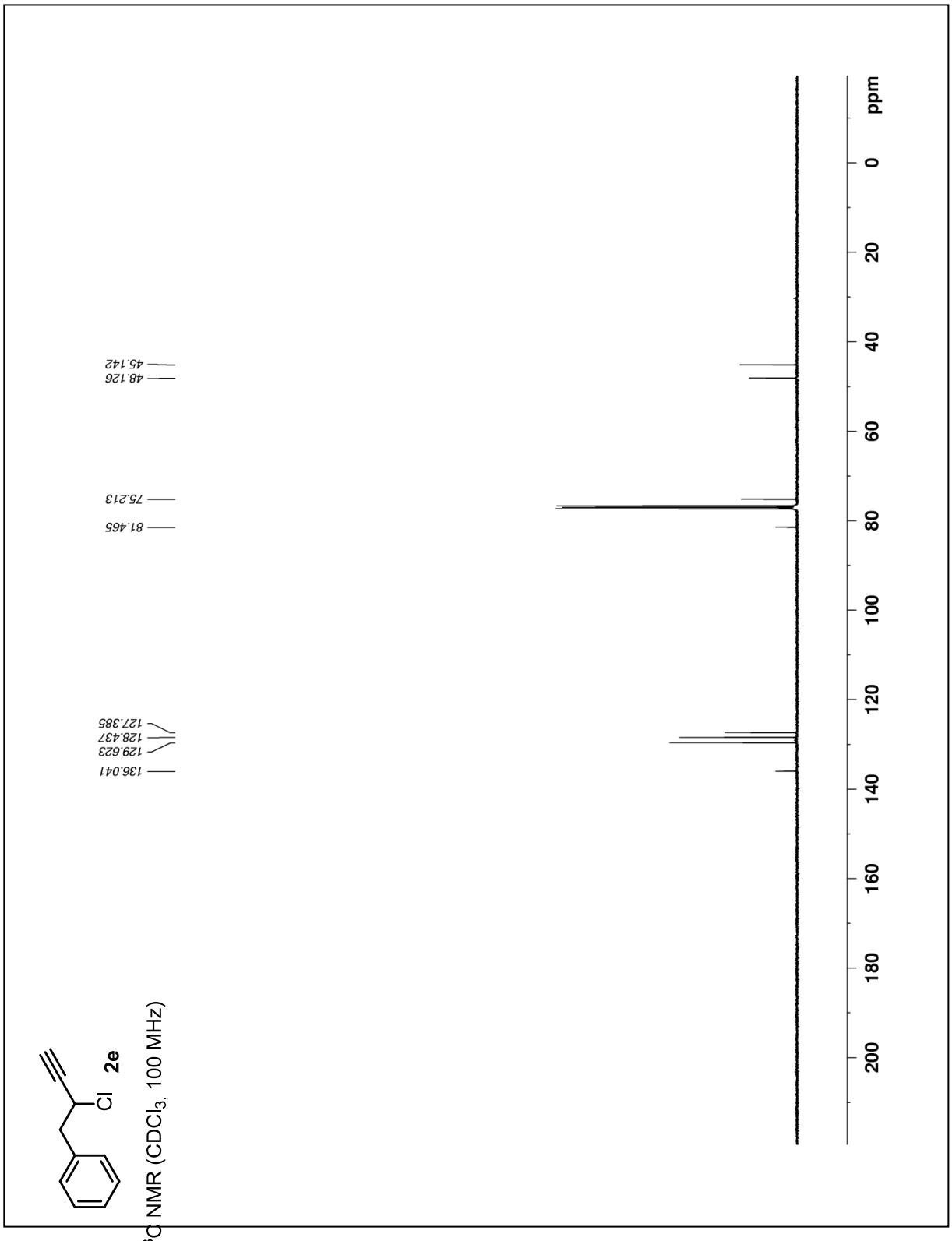


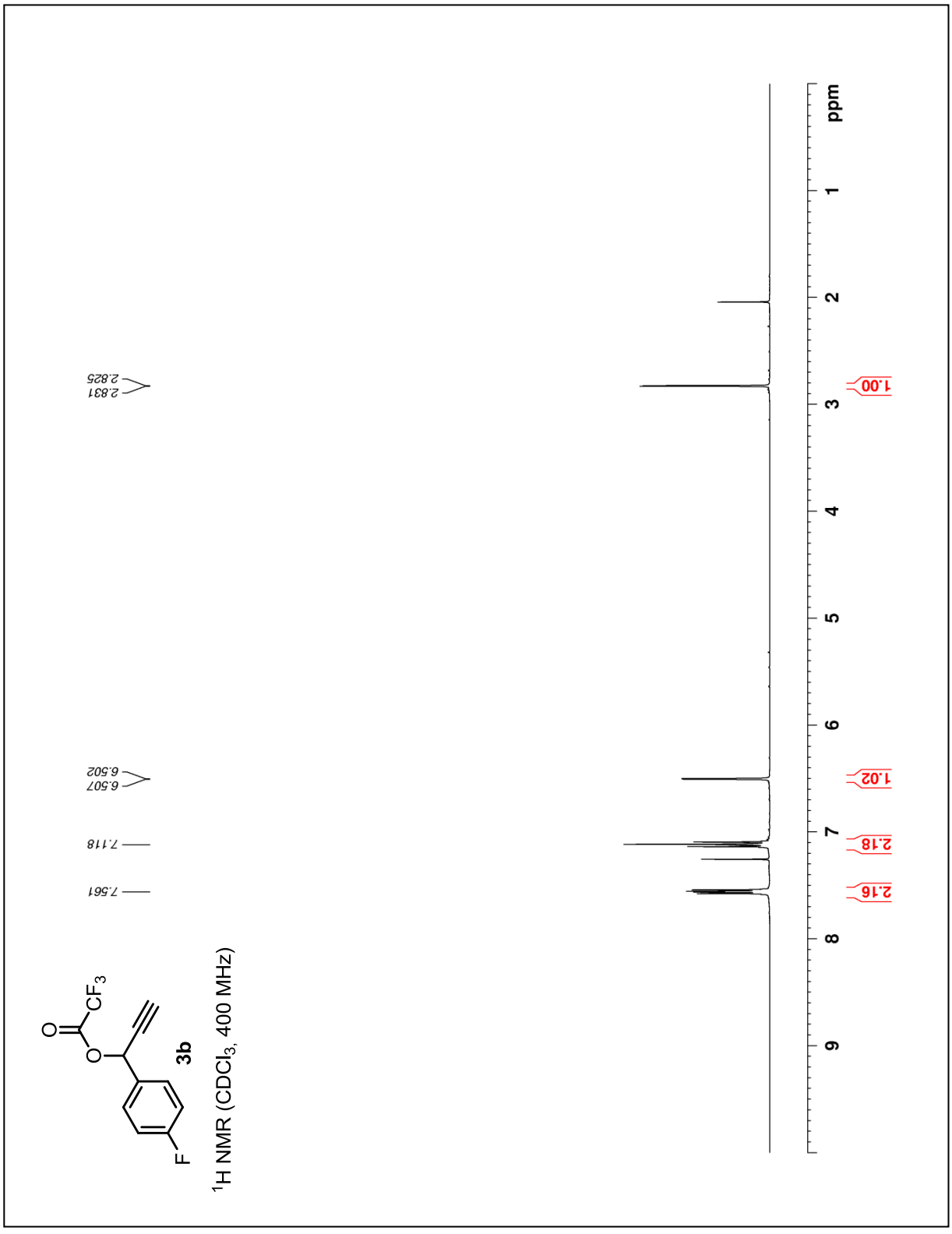
1-Bromo-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (6d). The product was synthesized from **3c** using the general method. The product was isolated as a yellow oil (16.6 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (2H, q, J = 9.6 Hz), 7.28 – 7.50 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8 (q, J_{CF} = 34.6 Hz), 77.2, 83.4, 121.1, 123.0, 125.4, 131.6, 133.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, J_{FH} = 9.4 Hz). HRMS (APCI-): *m*/*z* calcd. for $[C_{10}H_5BrF_3]^-$ 260.9532/260.9555, found 260.9540/261.9498.

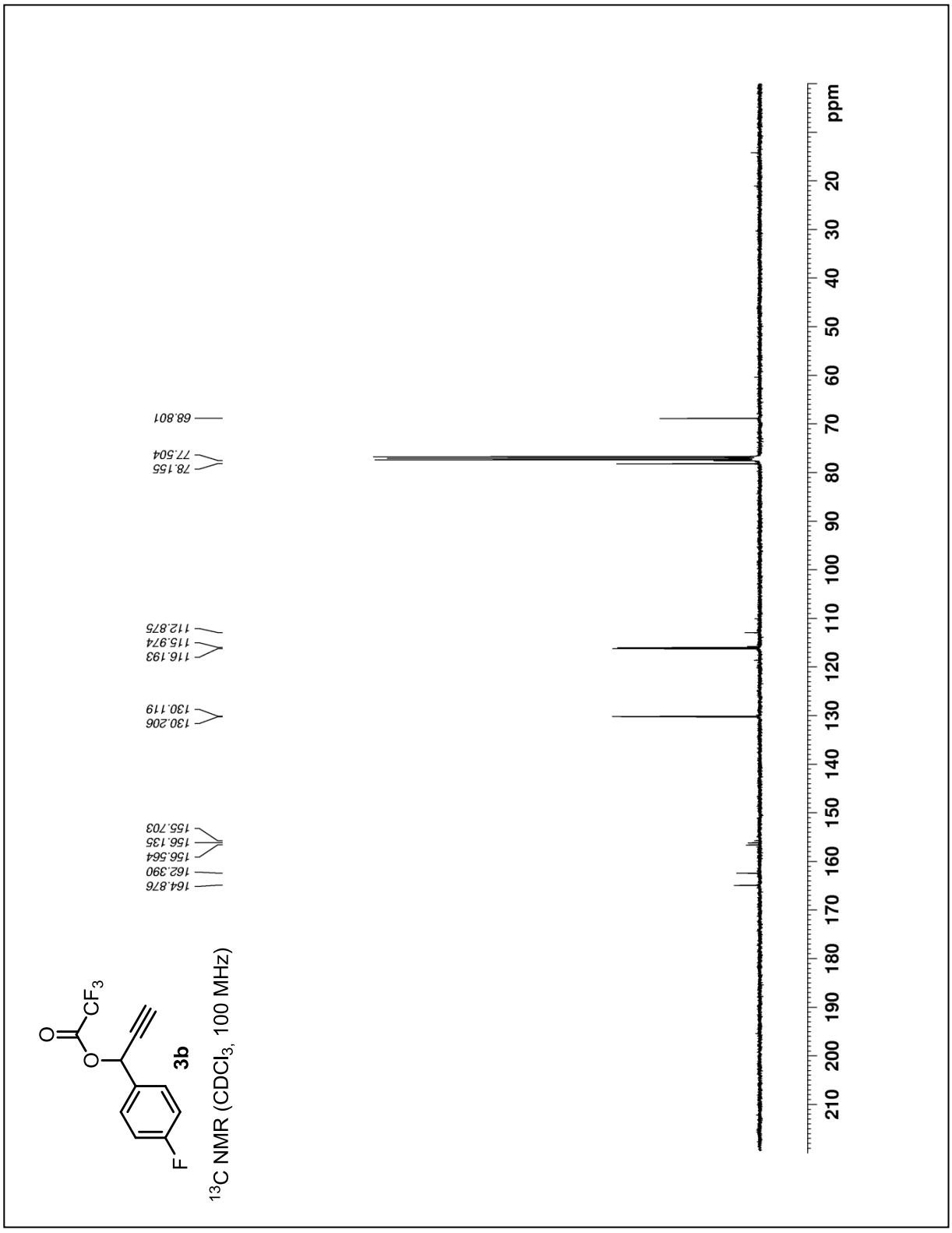


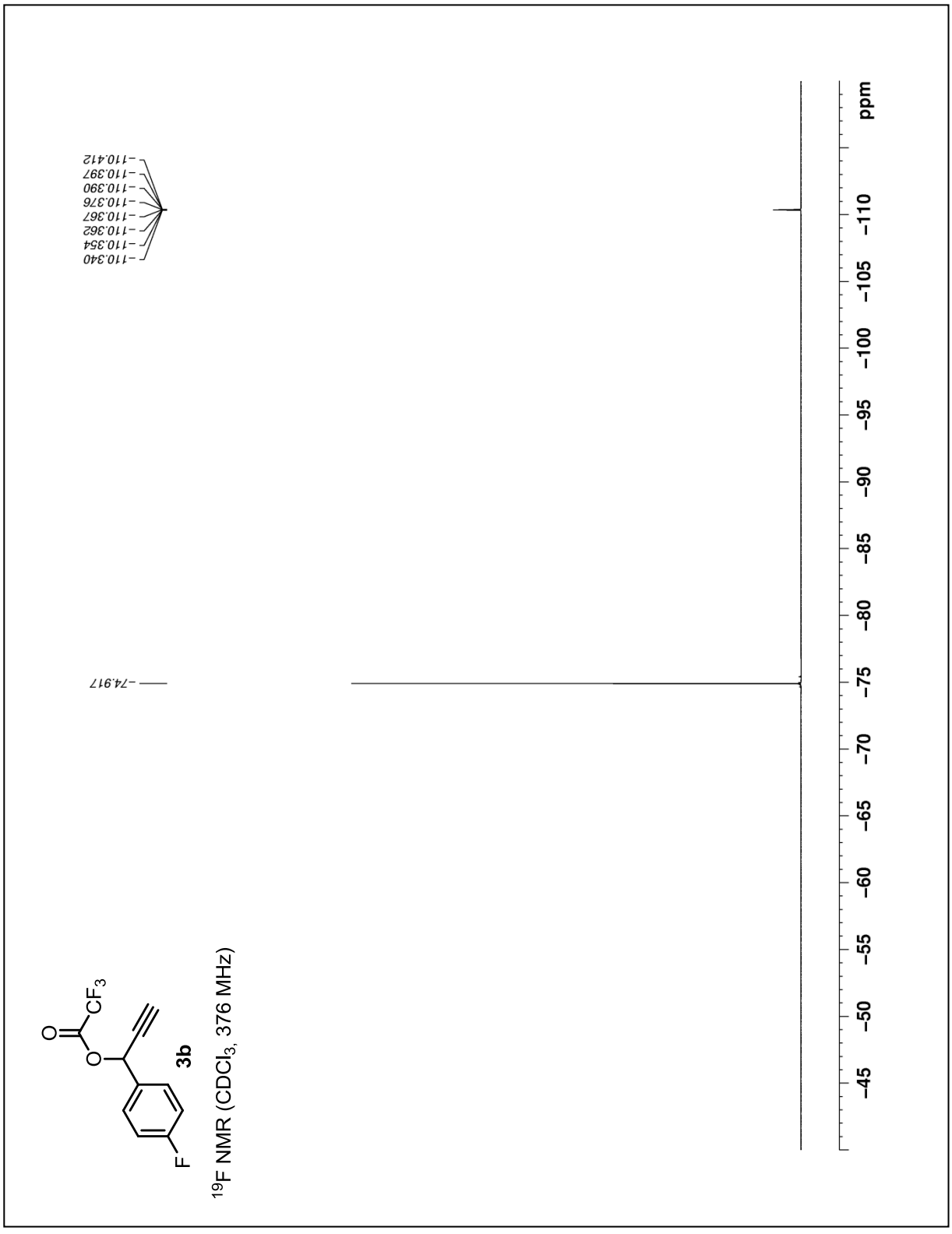
1-(tert-Butyl)-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (6e). The product was synthesized from **3d** using the general method. The reaction was stirred at 50 °C. The product was isolated as a yellow oil (17.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (9H, s), 3.26 (2H, q, J = 9.6 Hz), 7.30 – 7.44 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 31.1, 34.8, 85.5, 100.5, 111.0, 119.2, 125.3, 131.6, 152.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.8 Hz). HRMS (ESI+): *m*/*z* calcd. for $[C_{14}H_{16}F_3]^+$ 241.1199, found 241.1205.

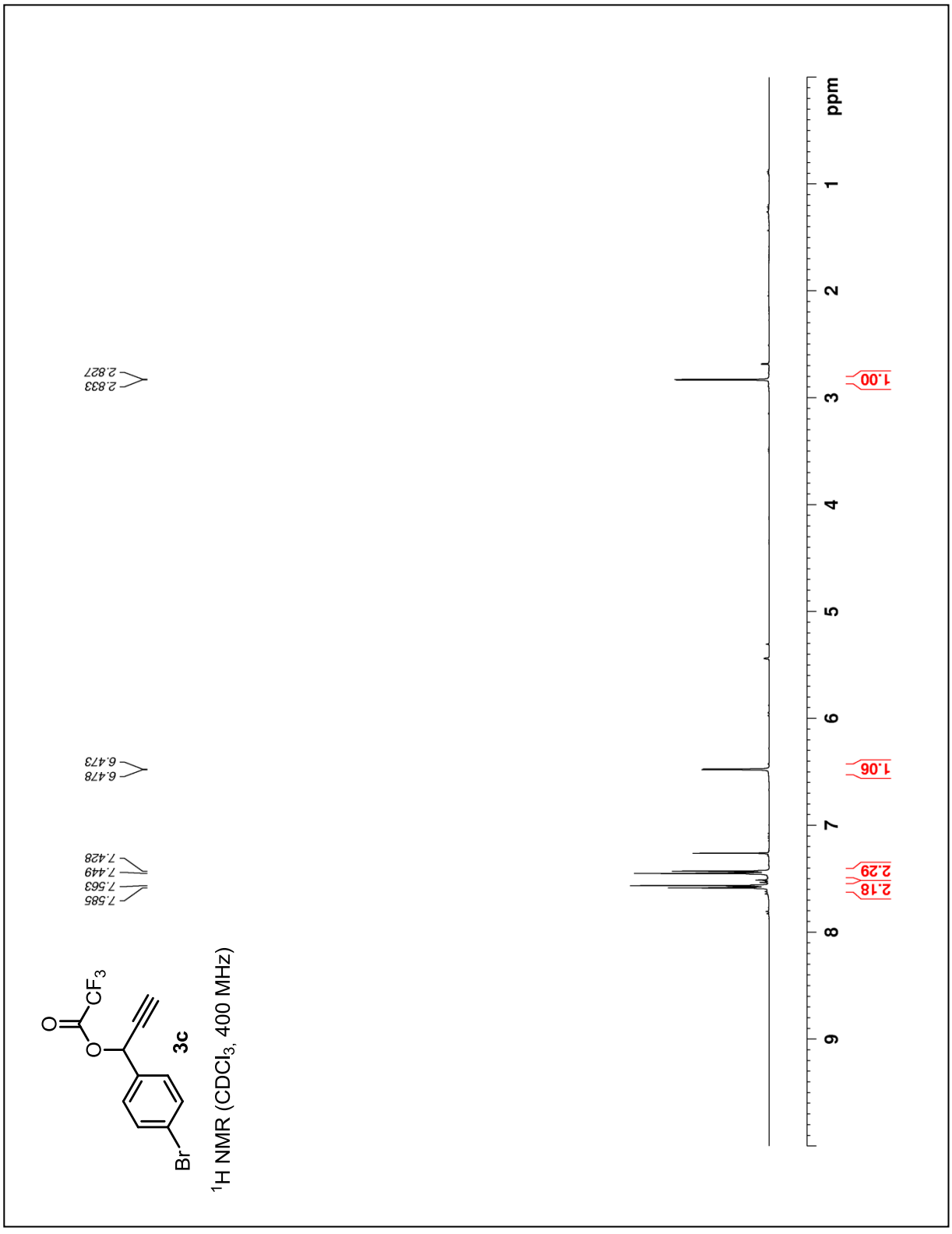

2e
Cl
^{1}H NMR ($CDCl_3$, 400 MHz)
7.312
4.686
4.680
4.668
4.663
4.651
4.645
3.299
3.281
3.264
3.256
3.246
3.238
3.221
3.204
2.612
2.607
ppm
1
2
3
4
5
6
7
8
9
5.71
1.06
2.29
1.00

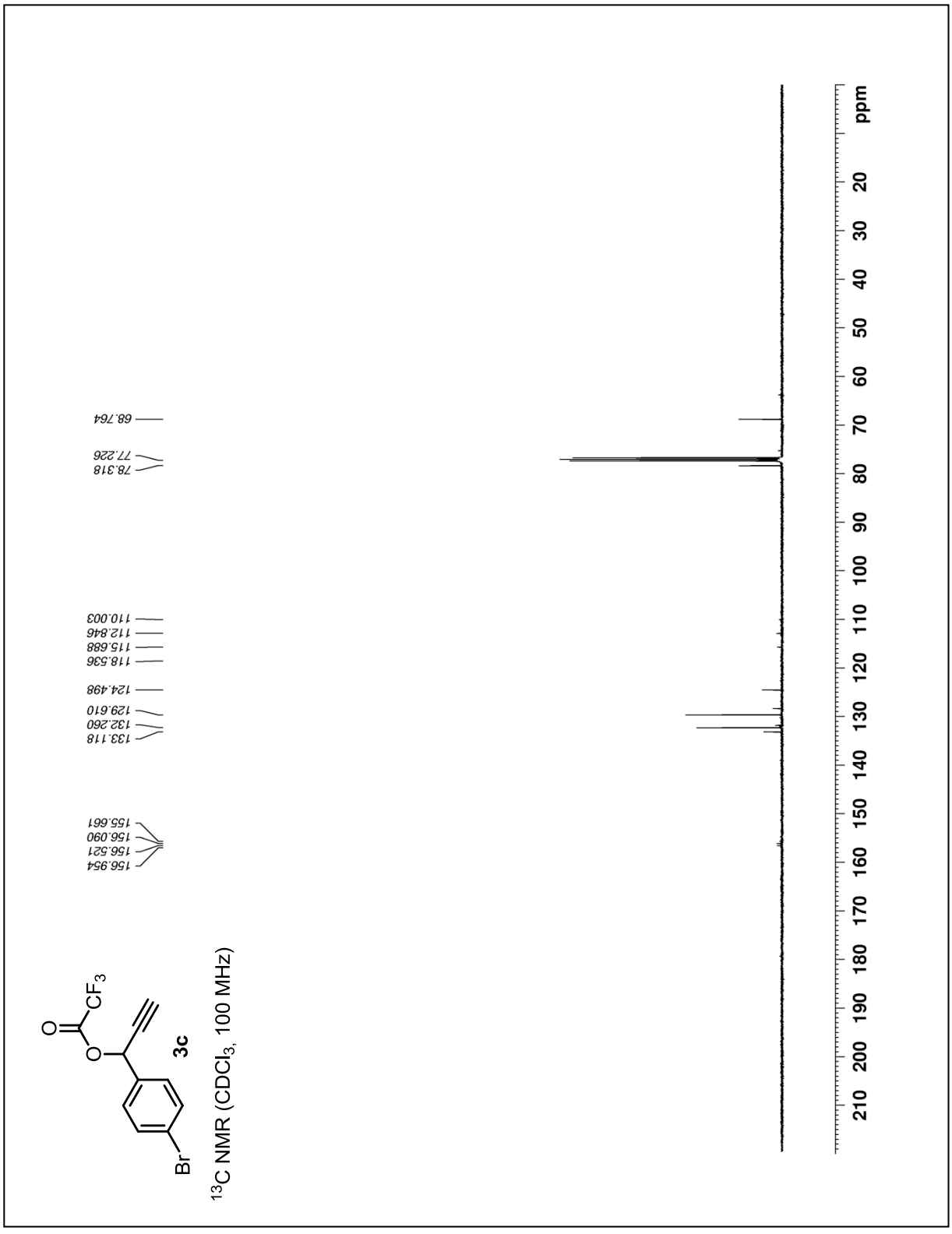

Cl
2e
^{13}C NMR ($CDCl_3$, 100 MHz)
45.142
48.126
75.213
81.465
127.385
128.437
129.623
136.041
ppm
0
20
40
60
80
100
120
140
160
180
200

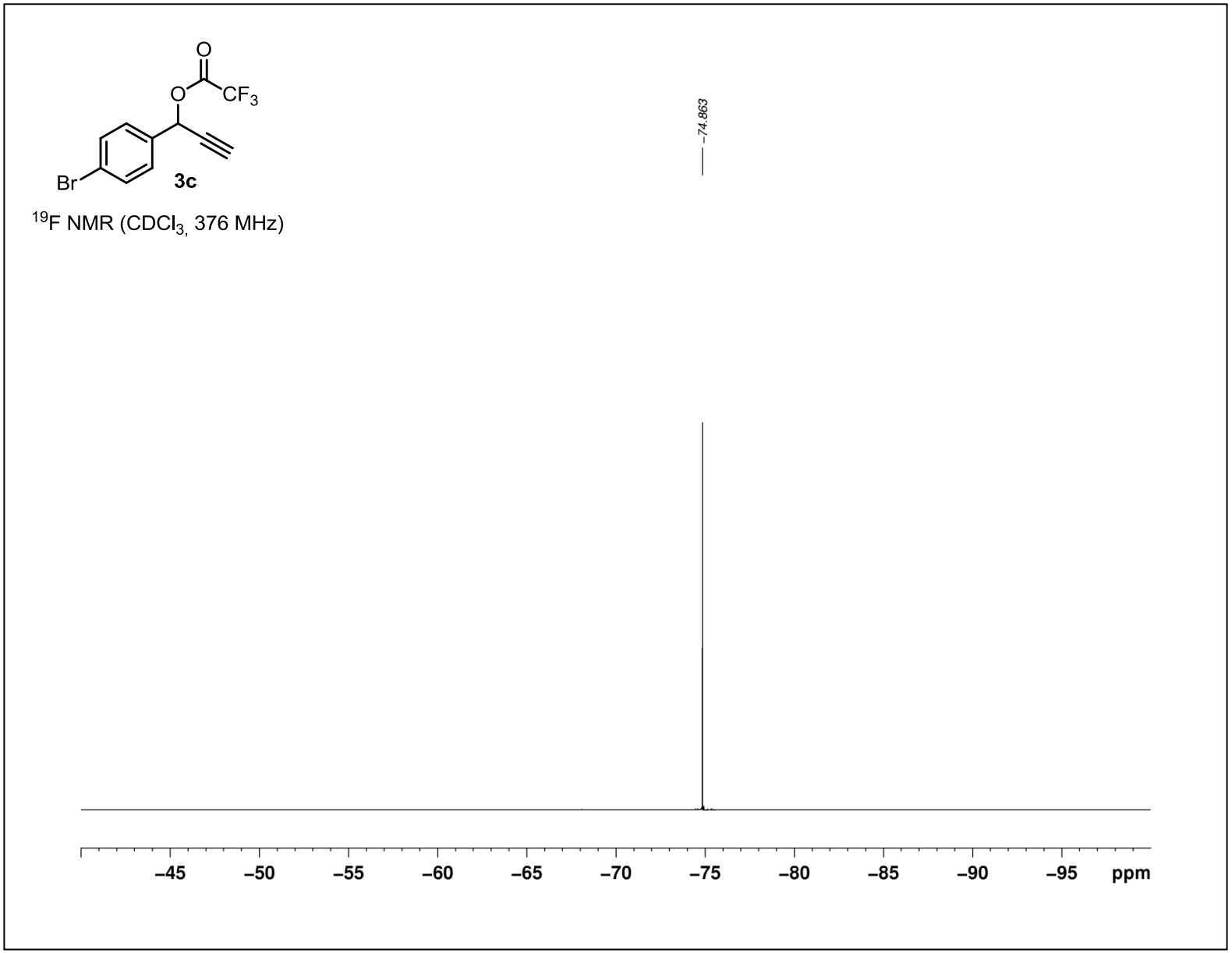

2.831
2.825
6.507
6.502
7.118
7.561
3b
^{1}H NMR ($CDCl_3$, 400 MHz)
1.00
1.02
2.18
2.16
ppm

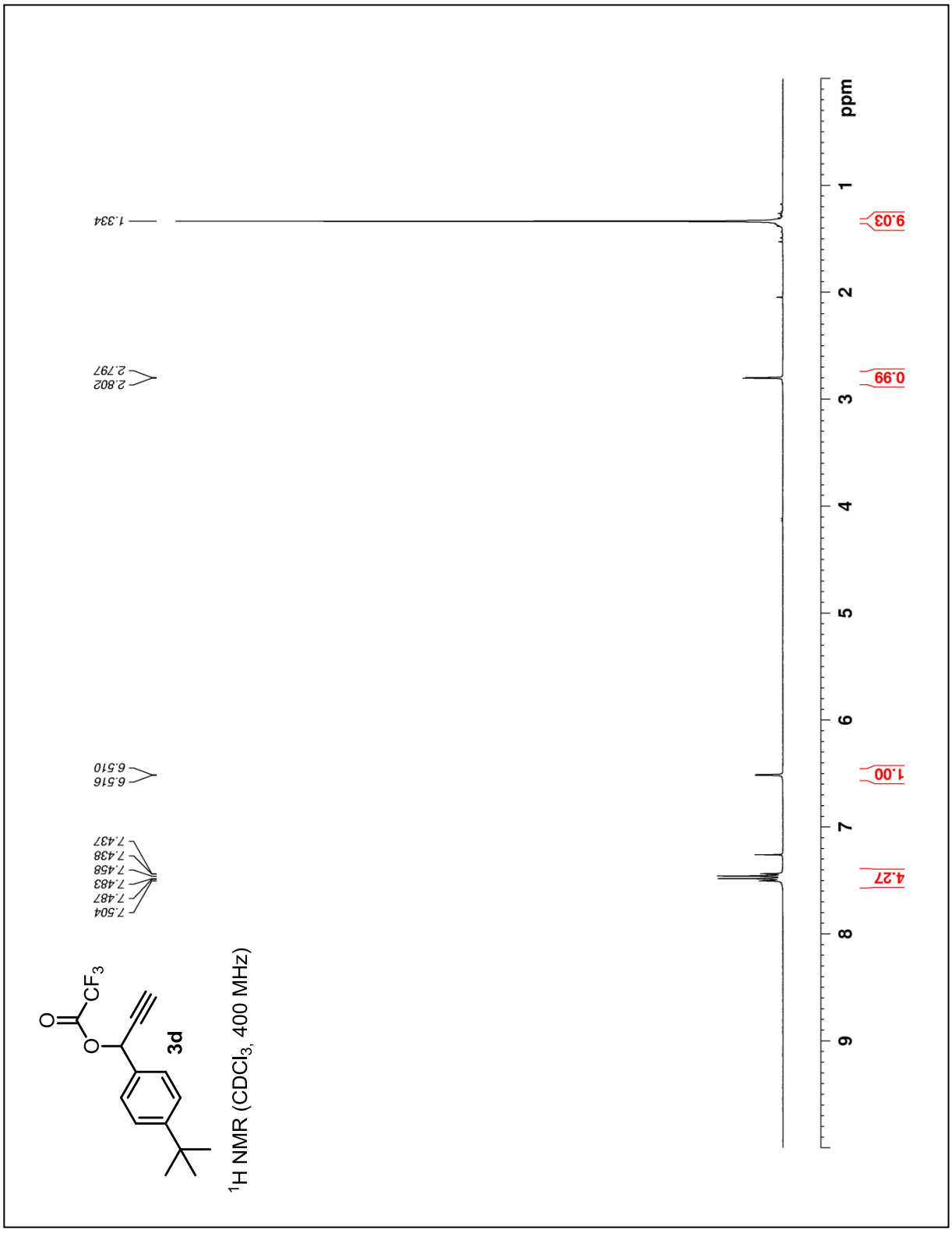

O
O
CF3
F
3b
13C NMR (CDCl3, 100 MHz)
164.876
162.390
156.564
156.135
155.703
130.206
130.119
116.193
115.974
112.875
78.155
77.504
68.801
ppm

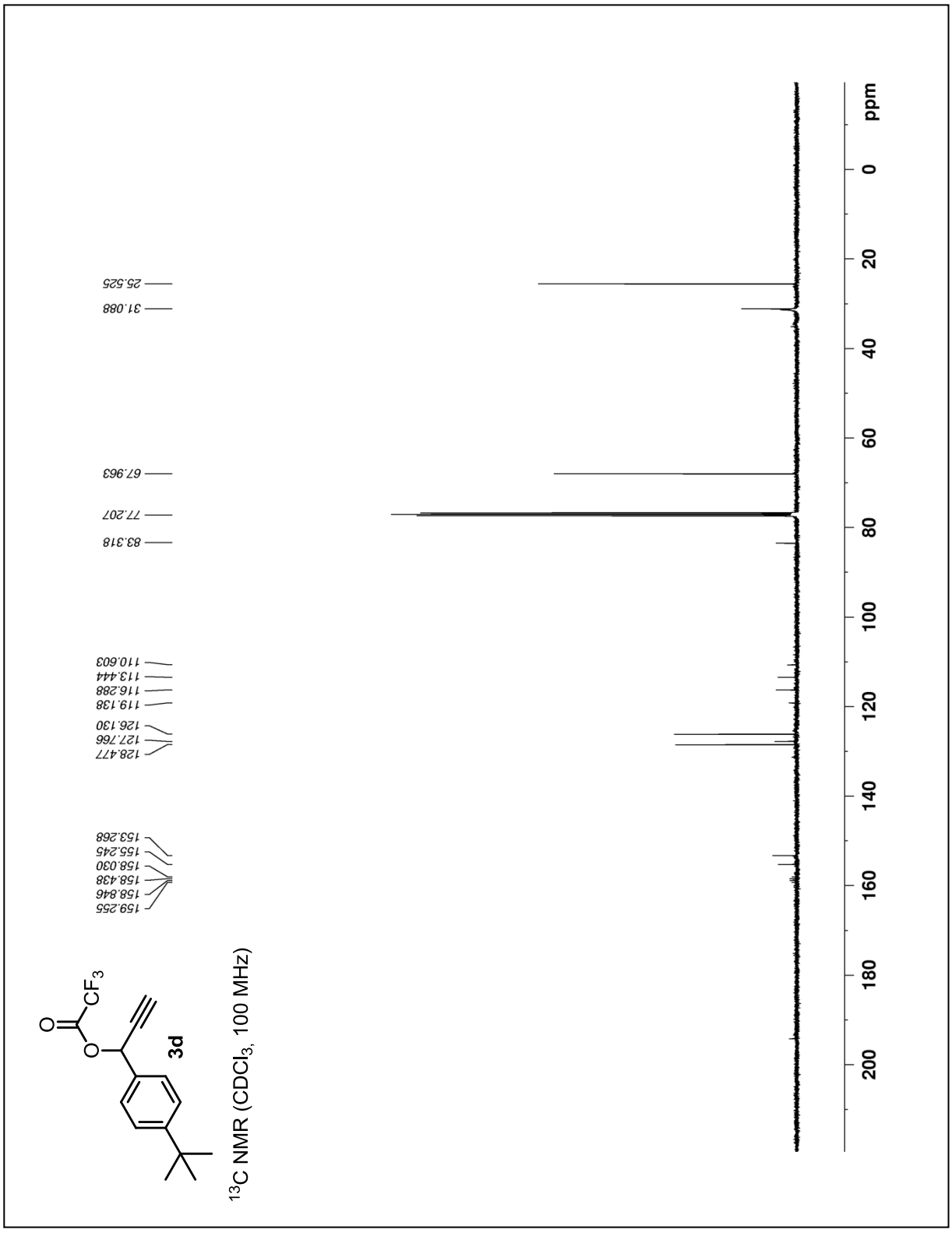

O
O
CF3
F
3b
19F NMR (CDCl3, 376 MHz)
-74.917
-110.340
-110.354
-110.362
-110.367
-110.376
-110.390
-110.397
-110.412
ppm
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110

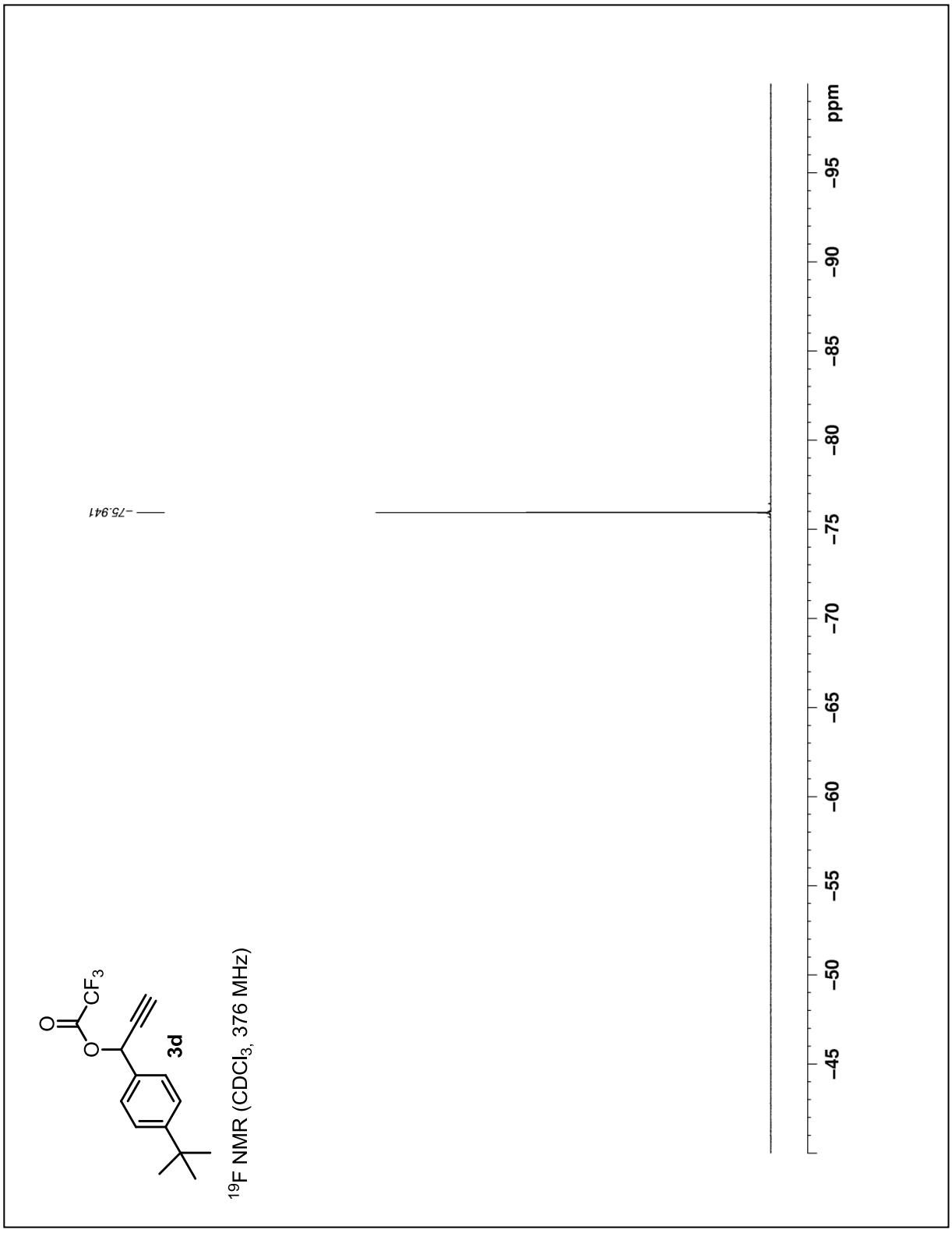

2.833
2.827
6.478
6.473
7.585
7.563
7.449
7.428
O
O
CF3
Br
3c
1H NMR (CDCl3, 400 MHz)
1.00
1.06
2.29
2.18
ppm
1
2
3
4
5
6
7
8
9

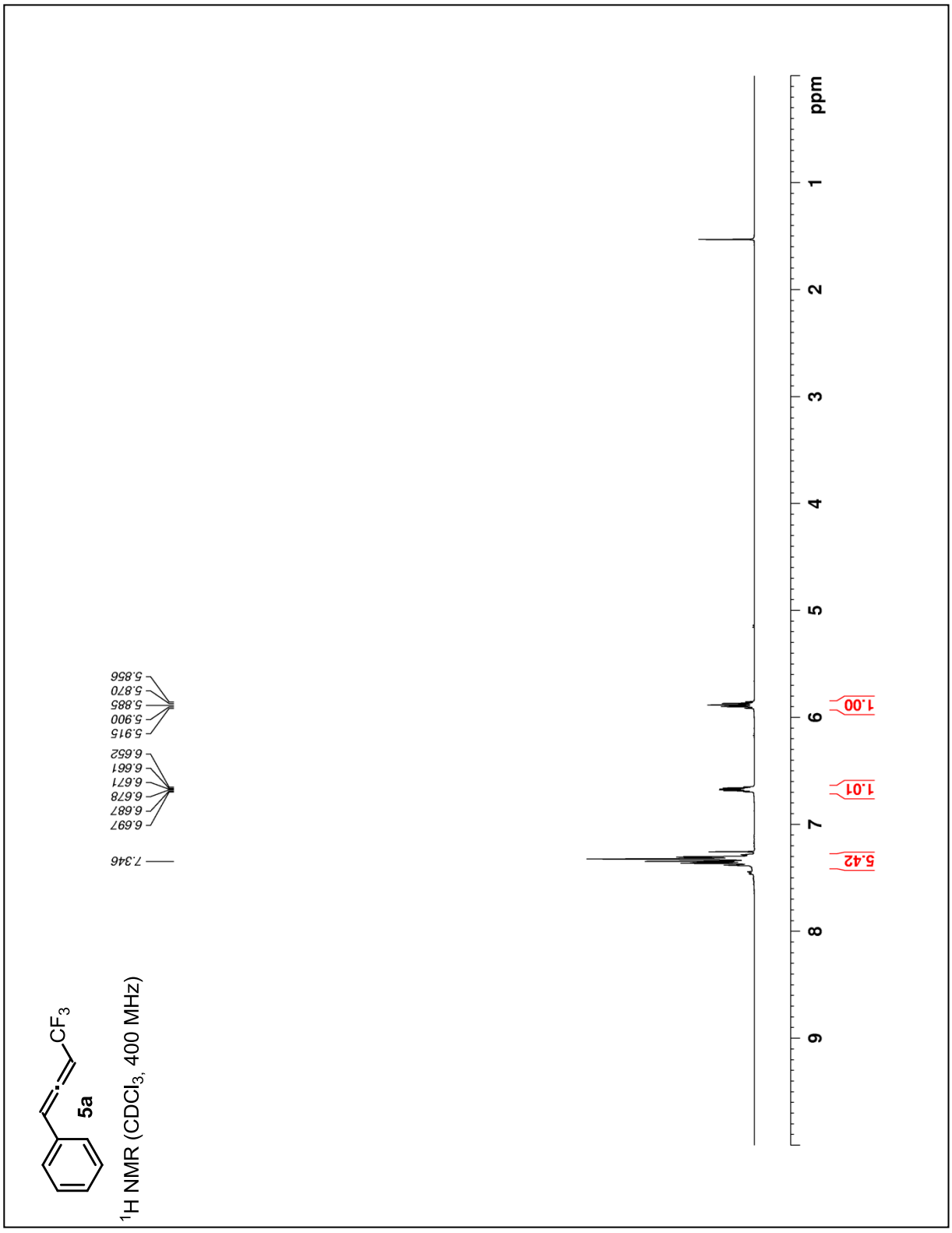

3c
^{13}C NMR ($CDCl_3$, 100 MHz)
156.954
156.521
156.090
155.661
133.118
132.260
129.610
124.498
118.536
115.688
112.846
110.003
78.318
77.226
68.764
ppm

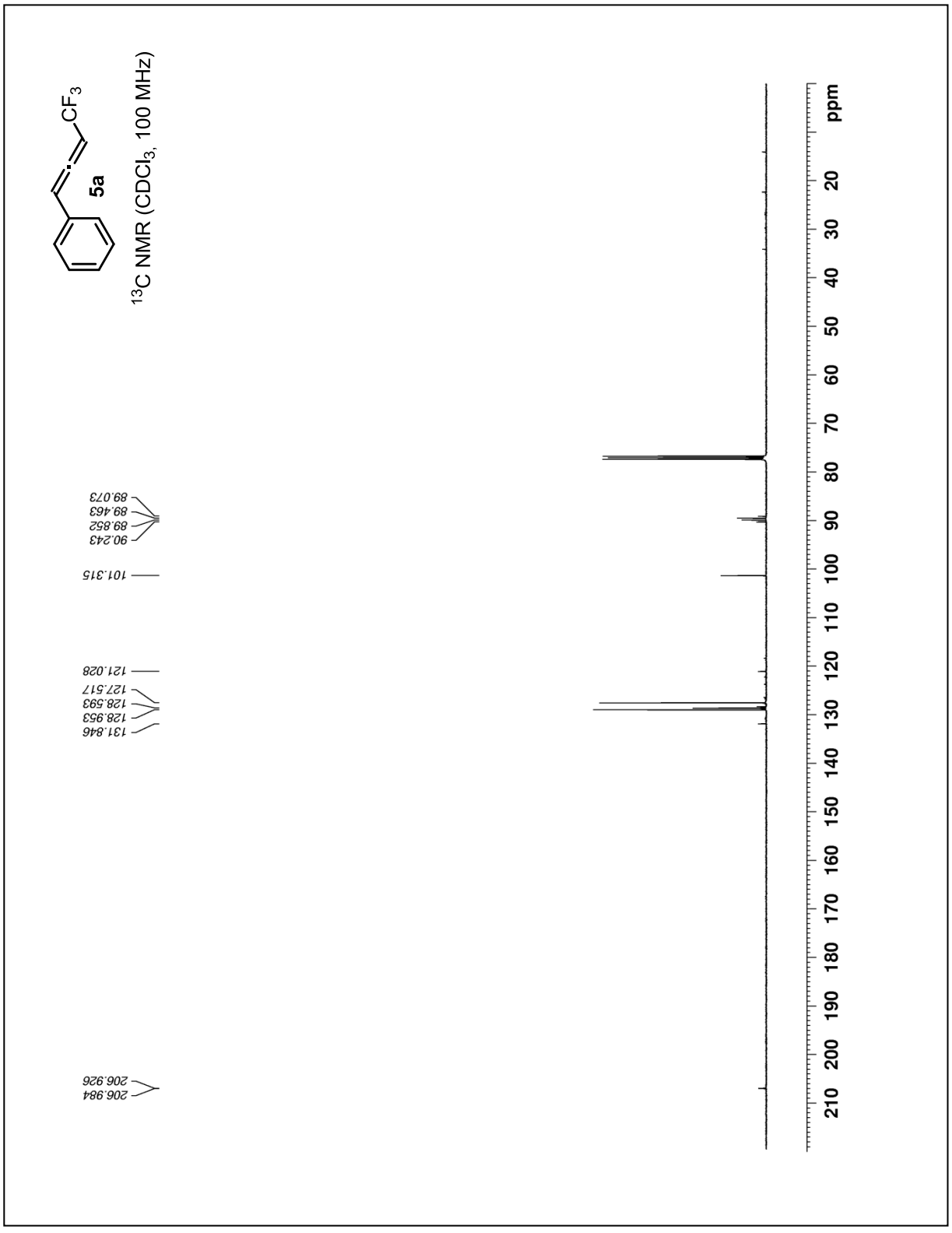

O
O
CF3
Br
3c
19F NMR (CDCl3, 376 MHz)
-74.863
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

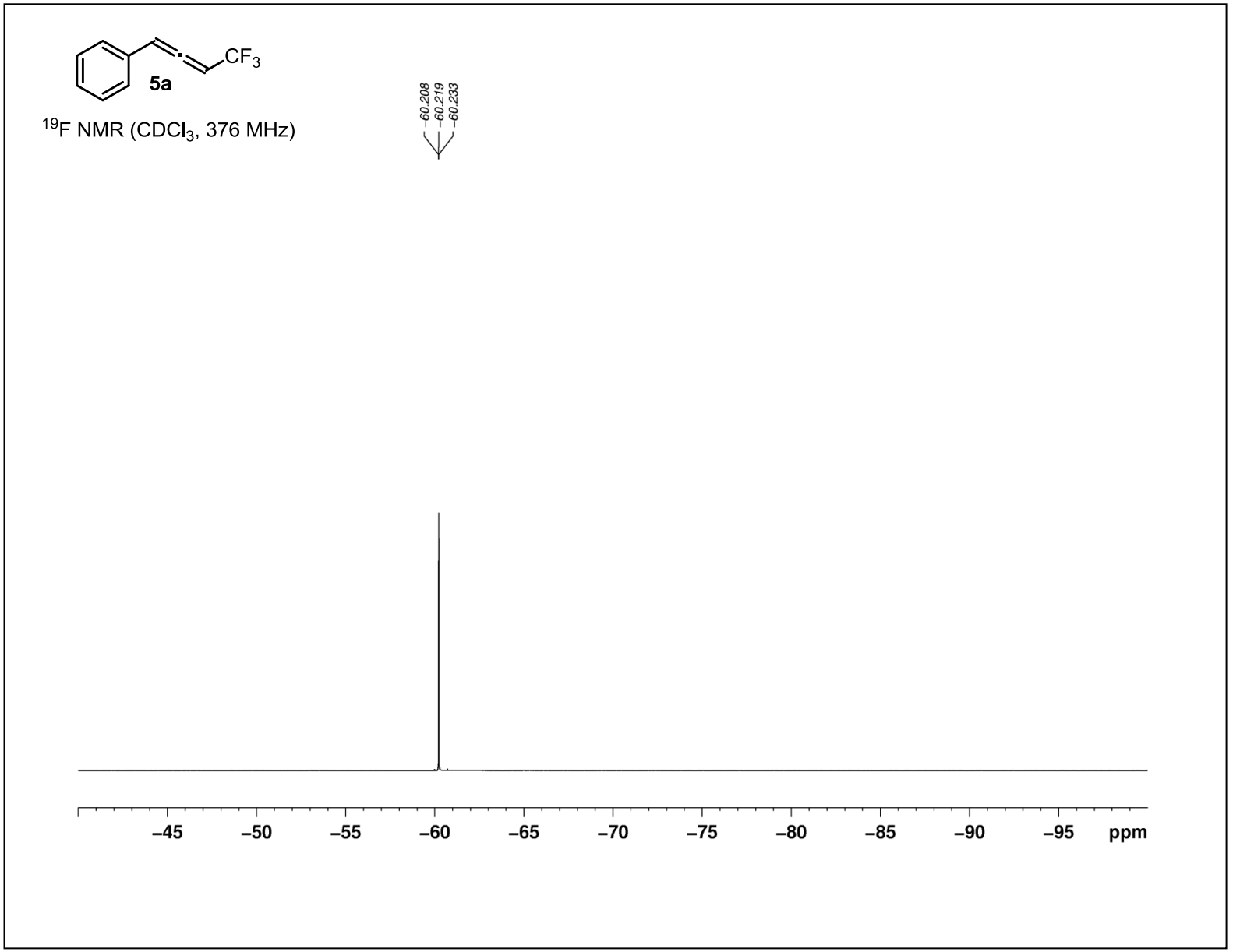

3d
^{1}H NMR ($CDCl_3$, 400 MHz)
1.334
2.802
2.797
6.516
6.510
7.504
7.487
7.483
7.458
7.438
7.437
9.03
0.99
1.00
4.27
ppm

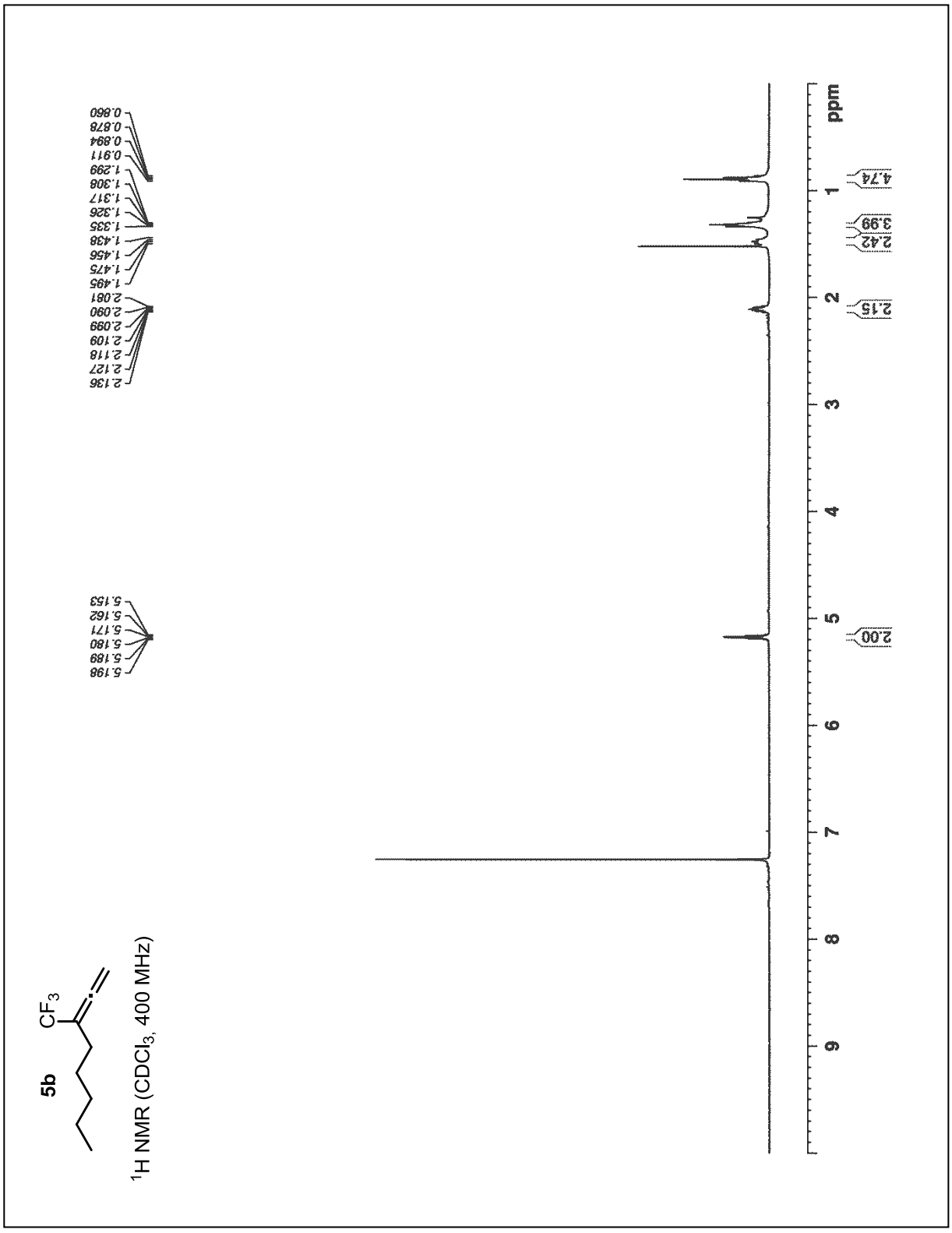

3d
^{13}C NMR ($CDCl_3$, 100 MHz)
159.255
158.846
158.438
158.030
155.245
153.268
128.477
127.766
126.130
119.138
116.288
113.444
110.603
83.318
77.207
67.963
31.088
25.525
ppm

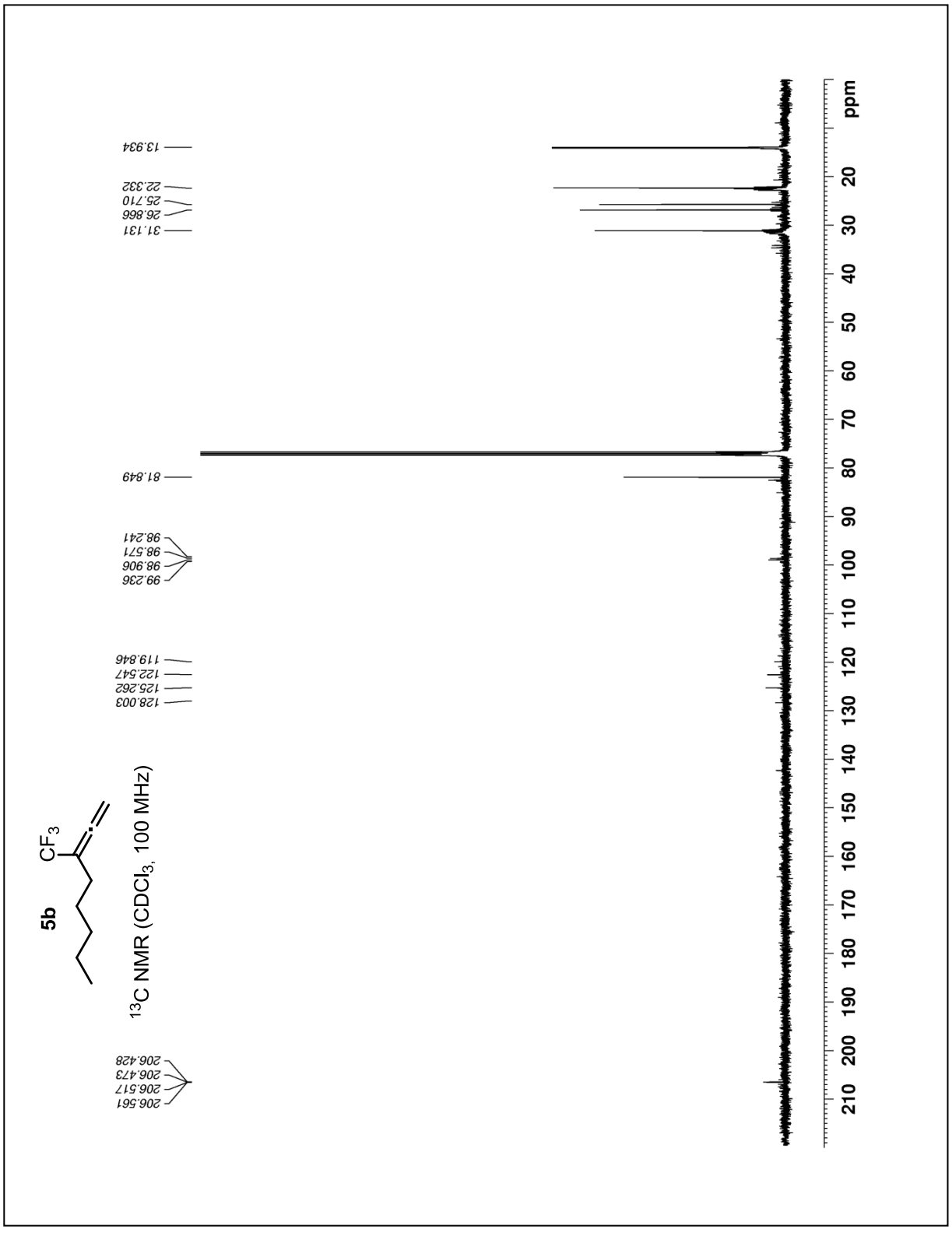

O
O
CF3
3d
19F NMR (CDCl3, 376 MHz)
−75.941
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
ppm

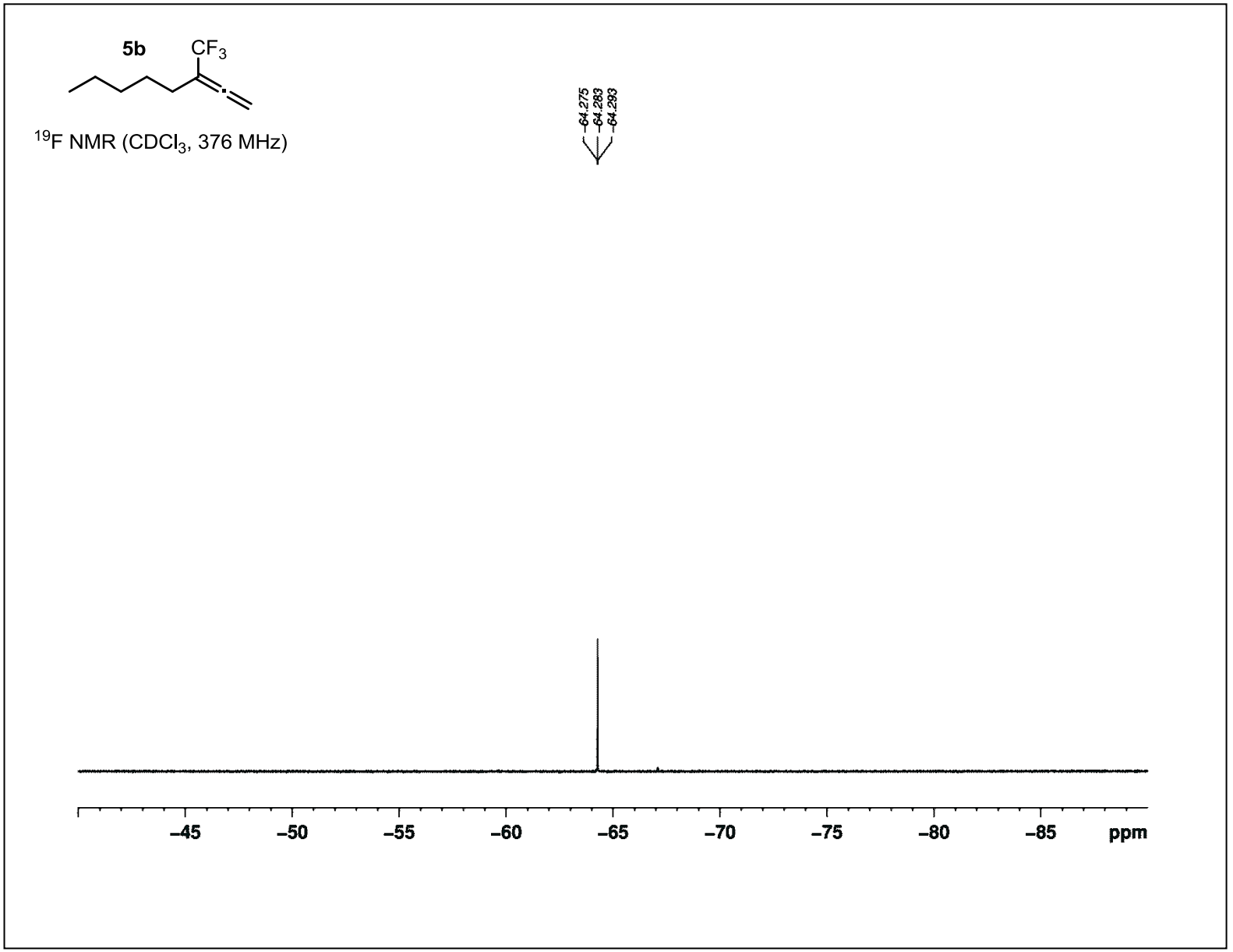

CF3
5a
1H NMR (CDCl3, 400 MHz)
7.346
6.697
6.687
6.678
6.671
6.661
6.652
5.915
5.900
5.885
5.870
5.856
5.42
1.01
1.00
ppm

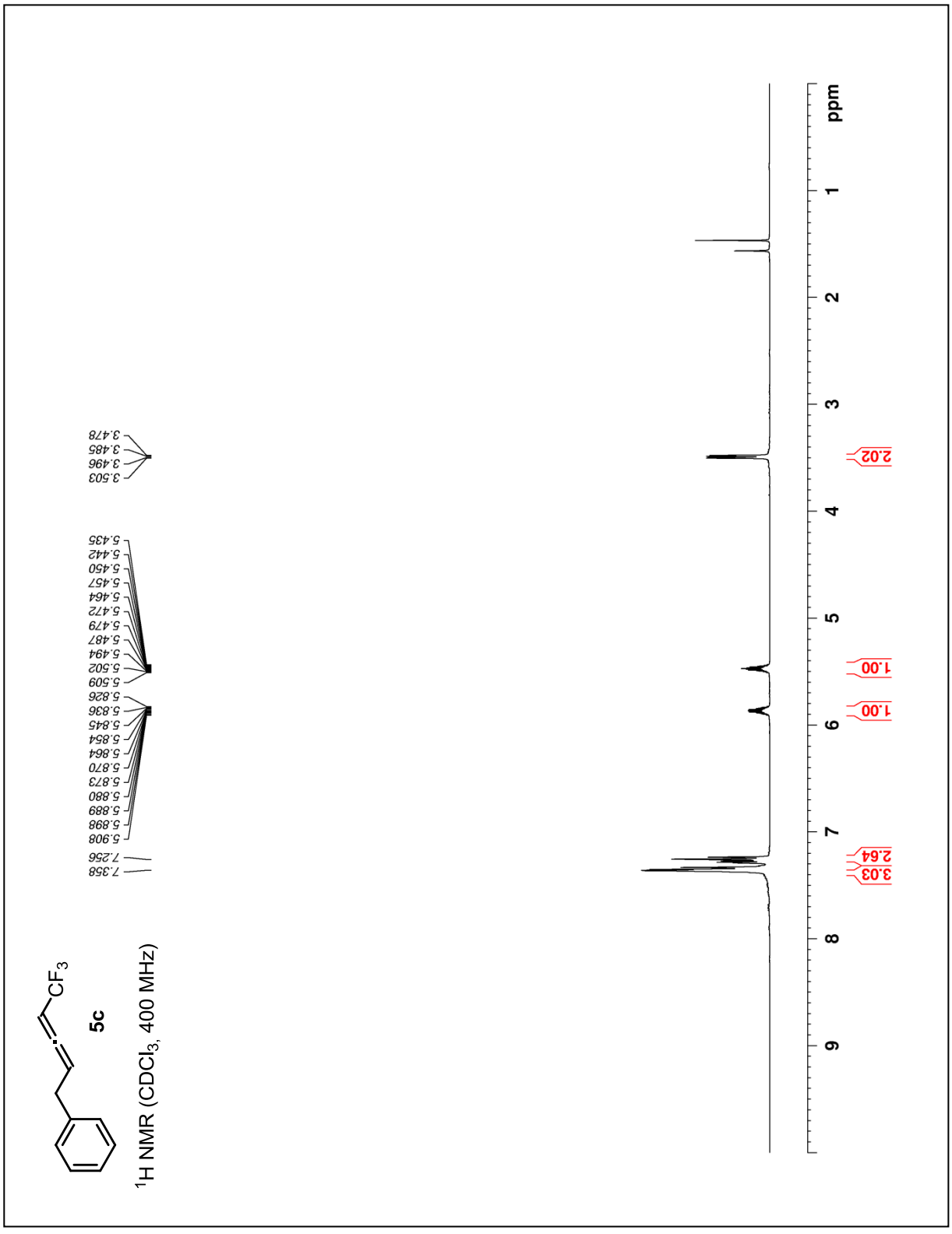

5a
^{13}C NMR ($CDCl_3$, 100 MHz)
206.984
206.926
131.846
128.953
128.593
127.517
121.028
101.315
90.243
89.852
89.463
89.073
ppm

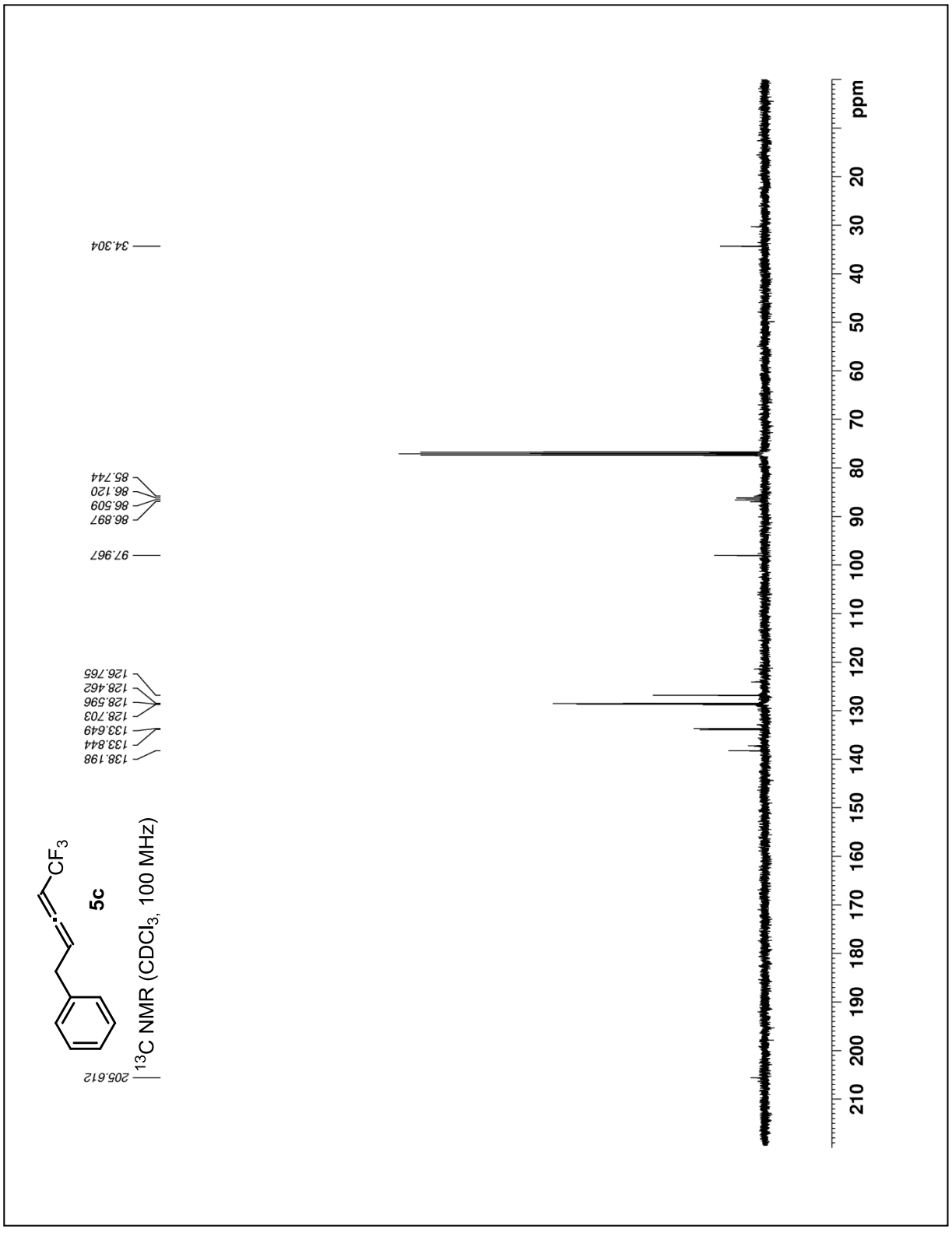

CF3
5a
19F NMR (CDCl3, 376 MHz)
-60.208
-60.219
-60.233
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

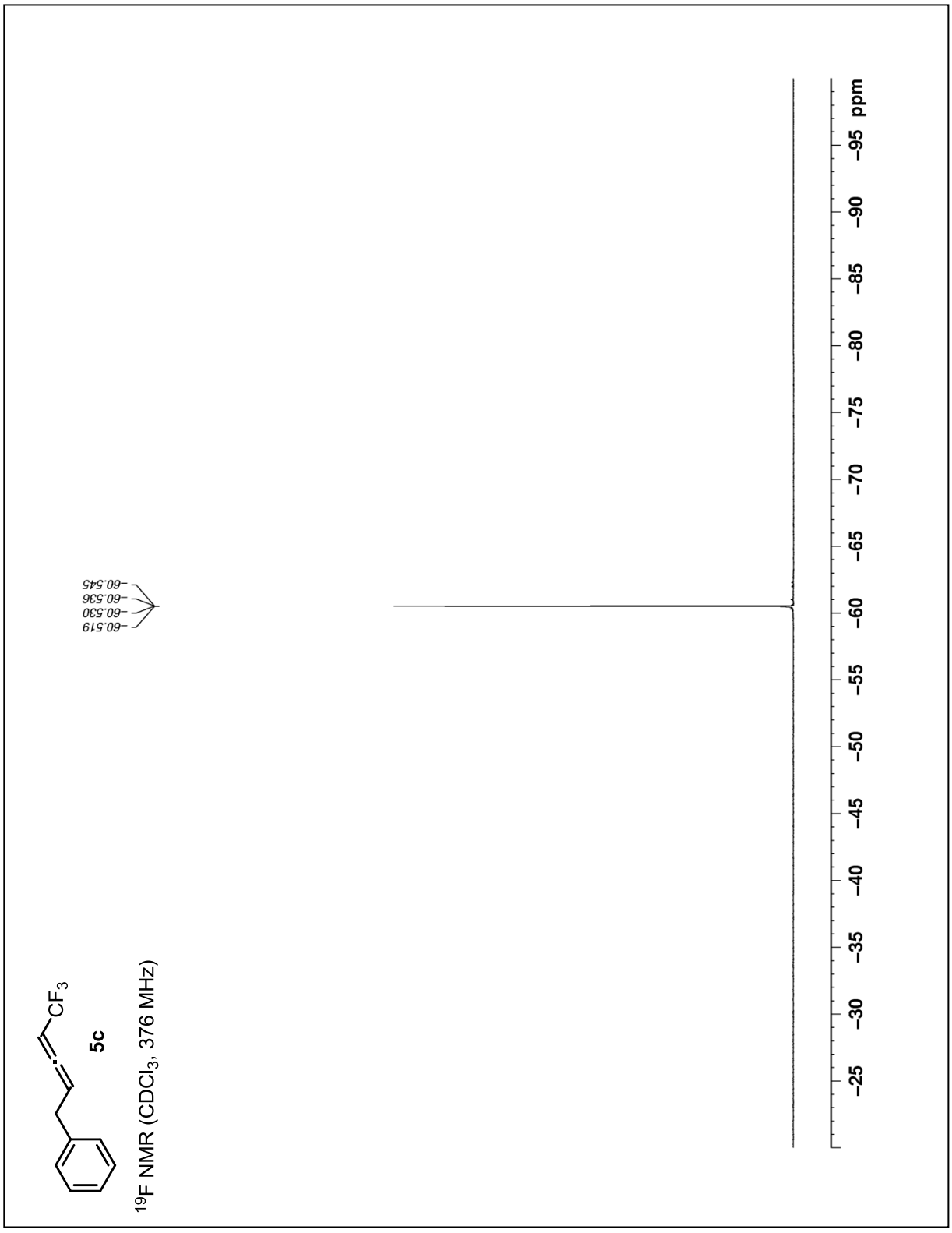

5b
CF3
1H NMR (CDCl3, 400 MHz)
0.860
0.878
0.894
0.911
1.299
1.308
1.317
1.326
1.335
1.438
1.456
1.475
1.495
2.081
2.090
2.099
2.109
2.118
2.127
2.136
5.153
5.162
5.171
5.180
5.189
5.198
ppm
1
2
3
4
5
6
7
8
9
4.74
3.99
2.42
2.15
2.00

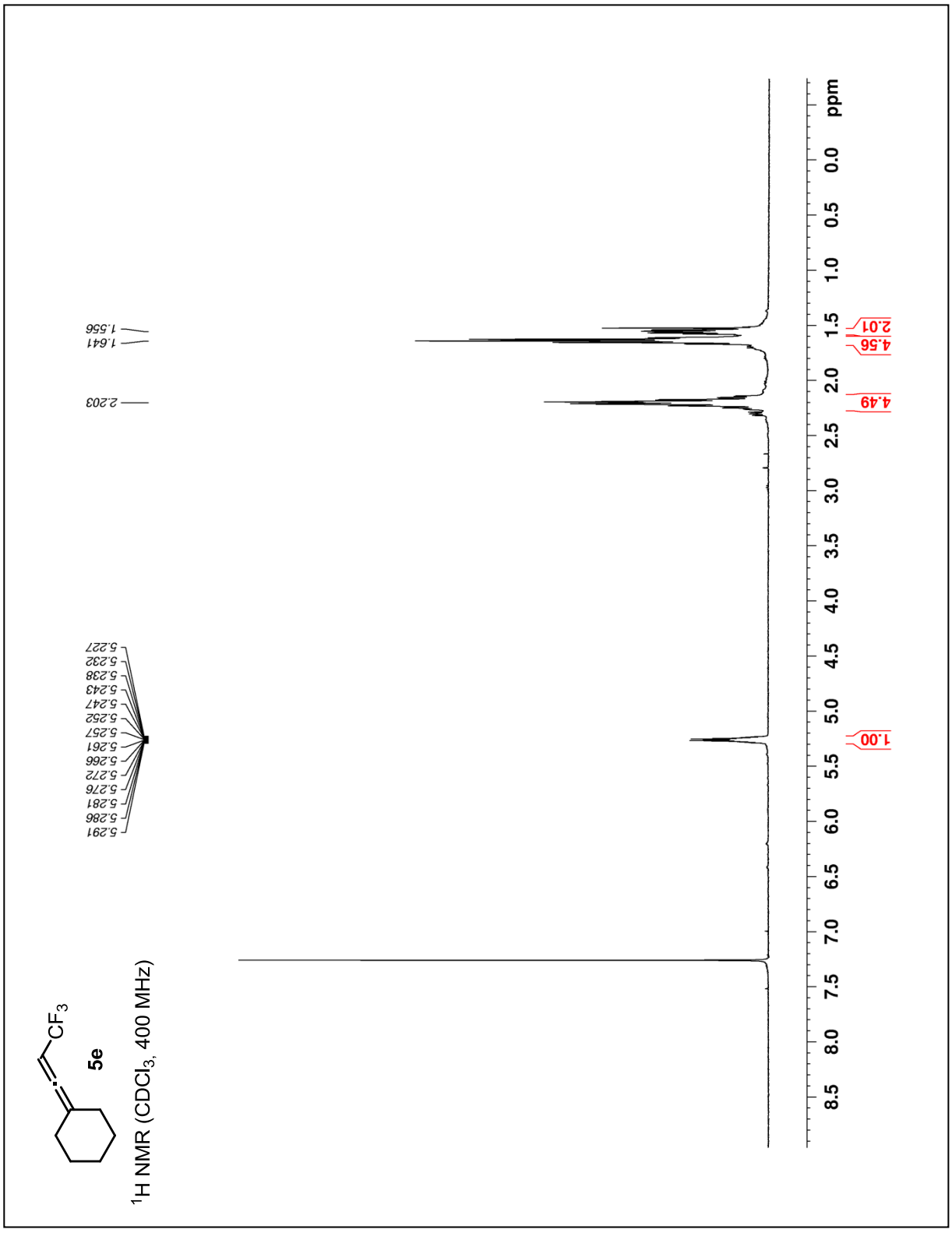

5b
CF3
13C NMR (CDCl3, 100 MHz)
13.934
22.332
25.710
26.866
31.131
81.849
98.241
98.571
98.906
99.236
119.846
122.547
125.262
128.003
206.428
206.473
206.517
206.561
ppm

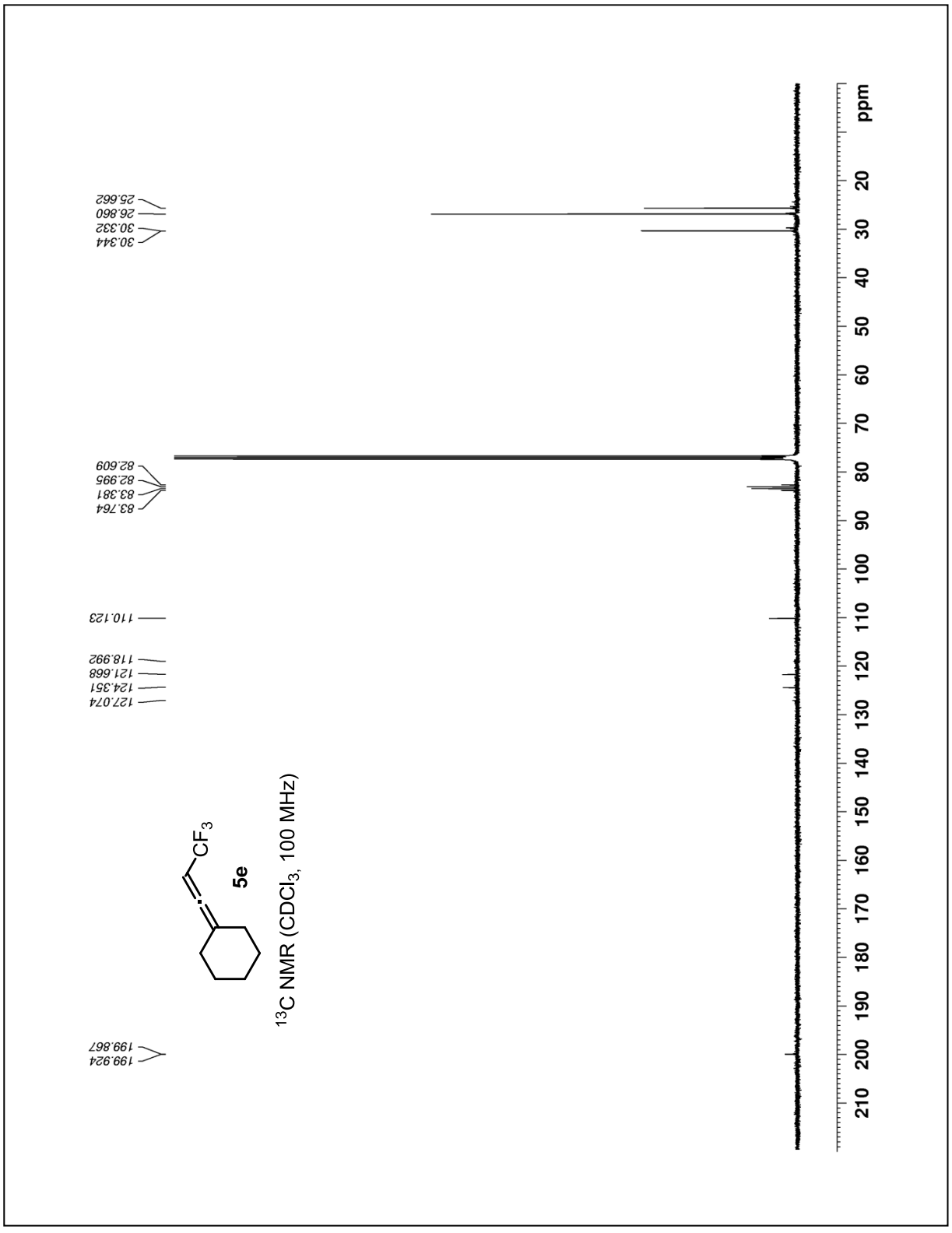

5b
CF3
19F NMR (CDCl3, 376 MHz)
-64.275
-64.283
-64.293
-45
-50
-55
-60
-65
-70
-75
-80
-85
ppm

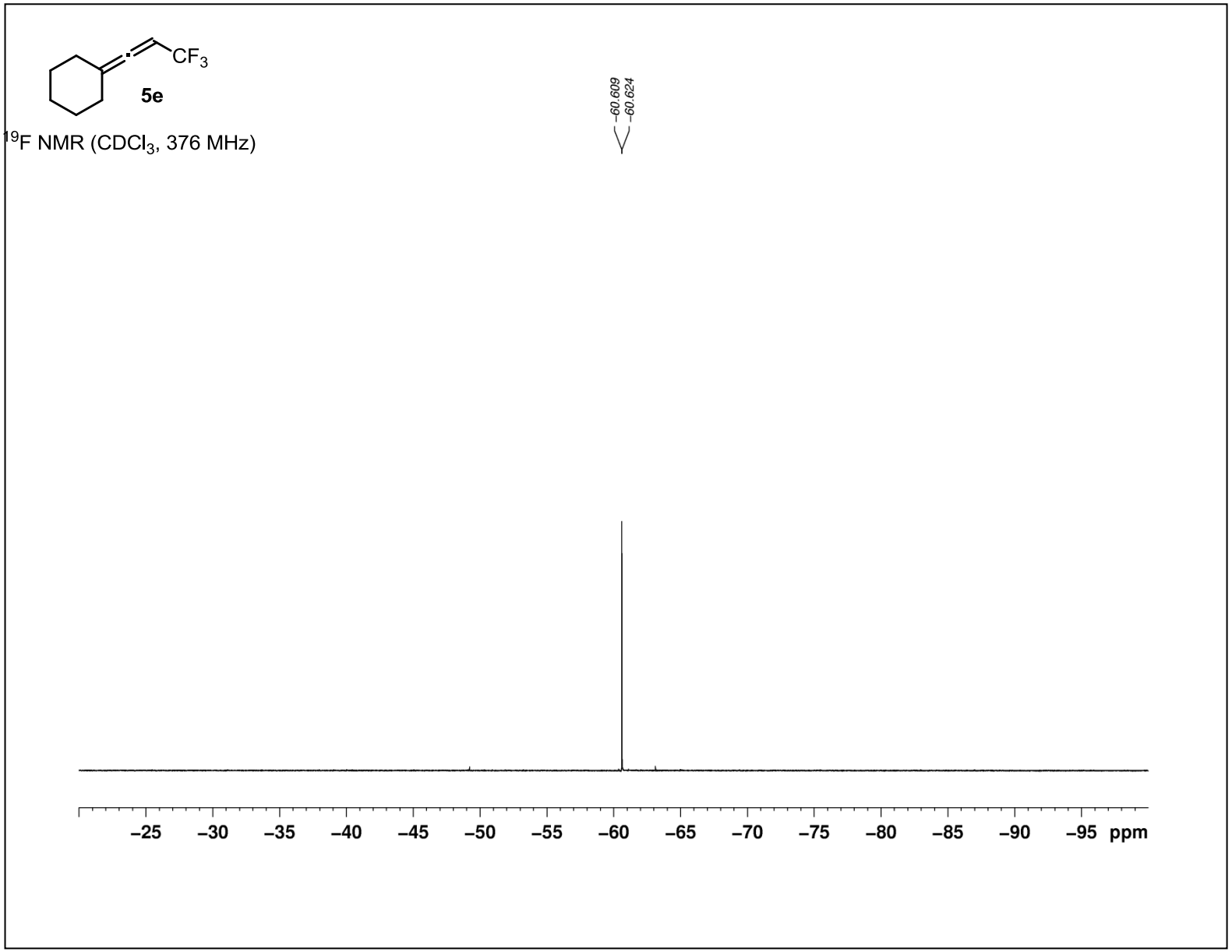

CF3
5c
1H NMR (CDCl3, 400 MHz)
7.358
7.256
5.908
5.898
5.889
5.880
5.873
5.870
5.864
5.854
5.845
5.836
5.826
5.509
5.502
5.494
5.487
5.479
5.472
5.464
5.457
5.450
5.442
5.435
3.503
3.496
3.485
3.478
ppm
1
2
3
4
5
6
7
8
9
2.02
1.00
1.00
3.03
2.64

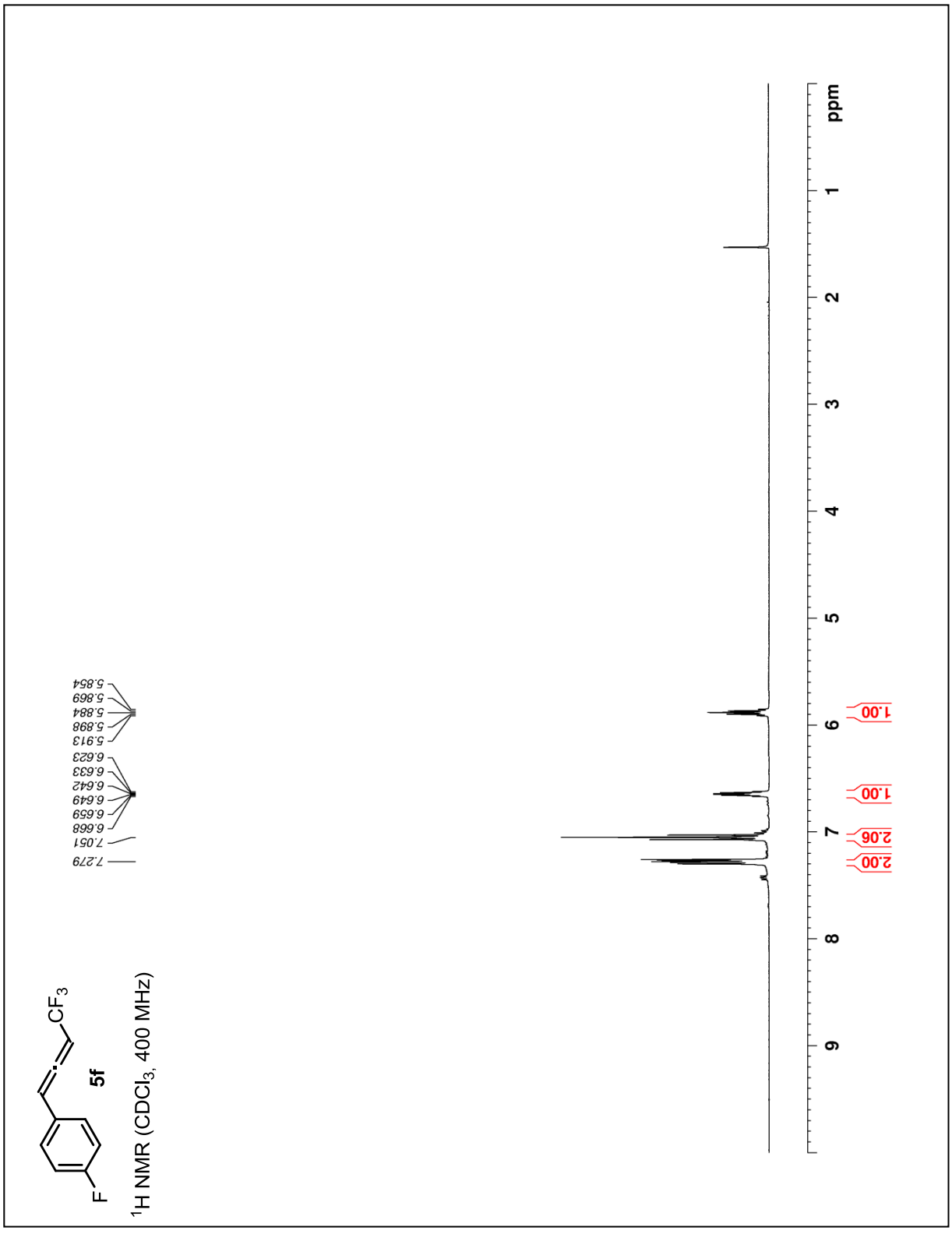

205.612
138.198
133.844
133.649
128.703
128.596
128.462
126.765
97.967
86.897
86.509
86.120
85.744
34.304
5c
^{13}C NMR ($CDCl_3$, 100 MHz)
CF_3
ppm

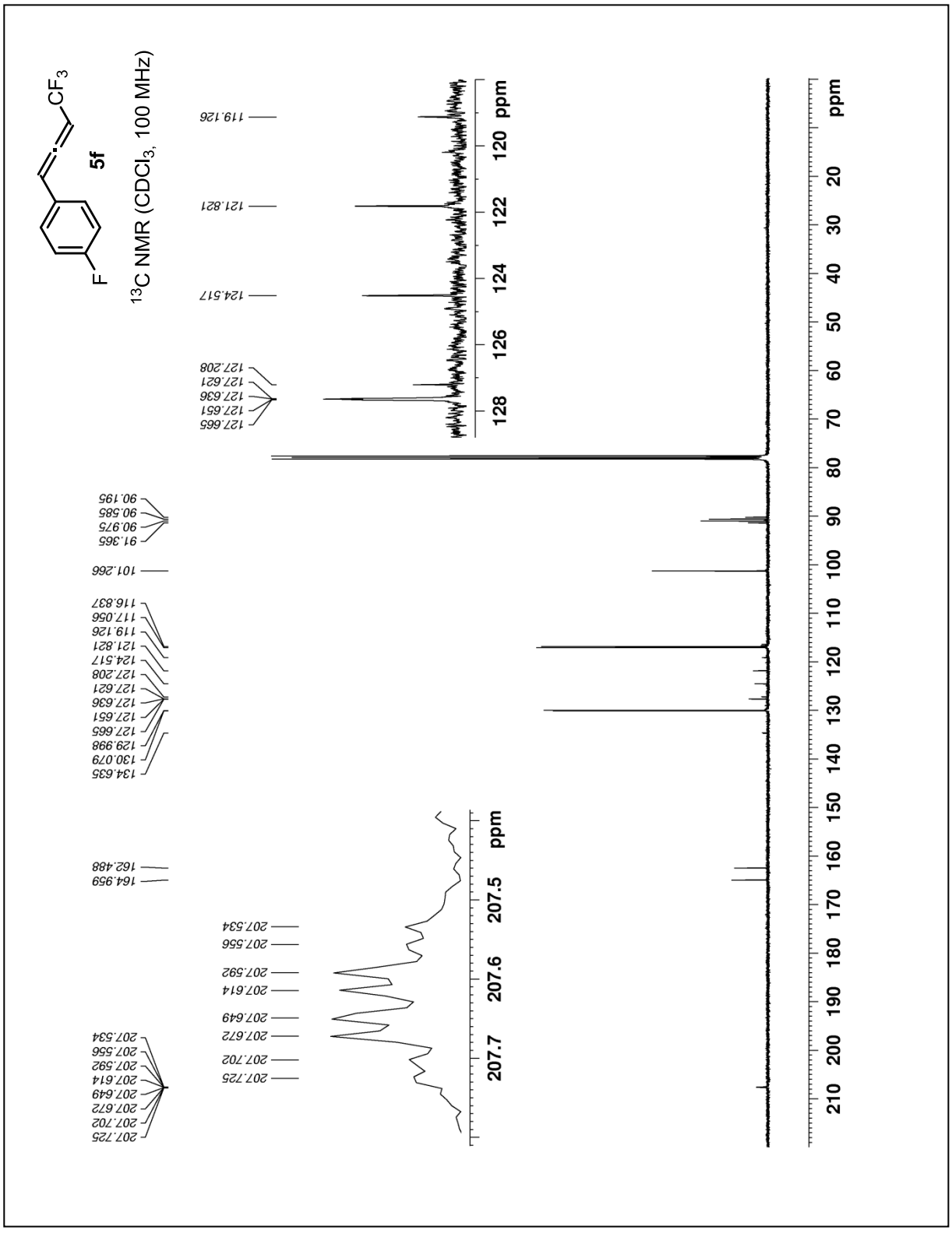

CF3
5c
19F NMR (CDCl3, 376 MHz)
−60.519
−60.530
−60.536
−60.545
−25 −30 −35 −40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 ppm

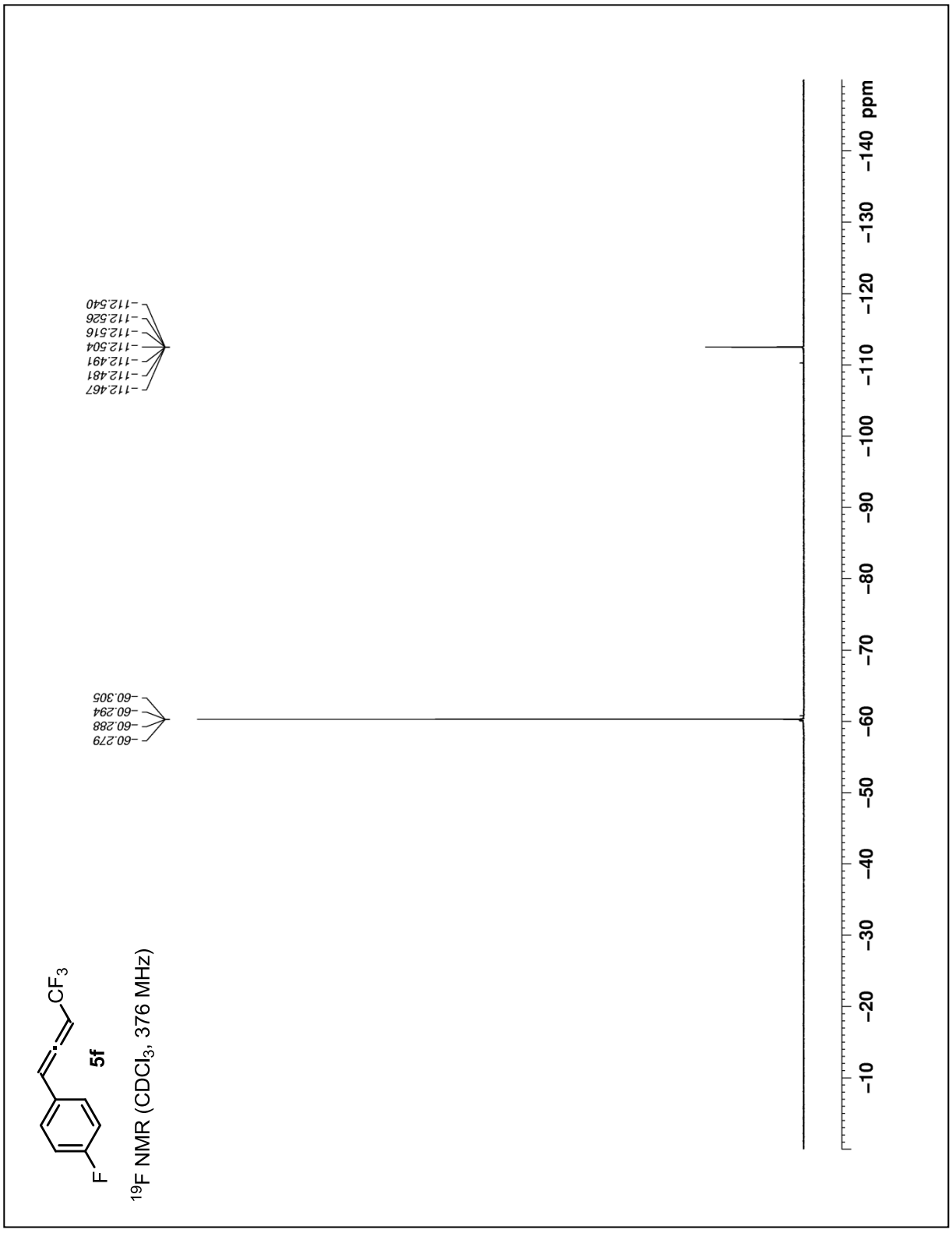

5e
^{1}H NMR ($CDCl_3$, 400 MHz)
1.556
1.641
2.203
5.227
5.232
5.238
5.243
5.247
5.252
5.257
5.261
5.266
5.272
5.276
5.281
5.286
5.291
1.00
4.49
4.56
2.01
ppm

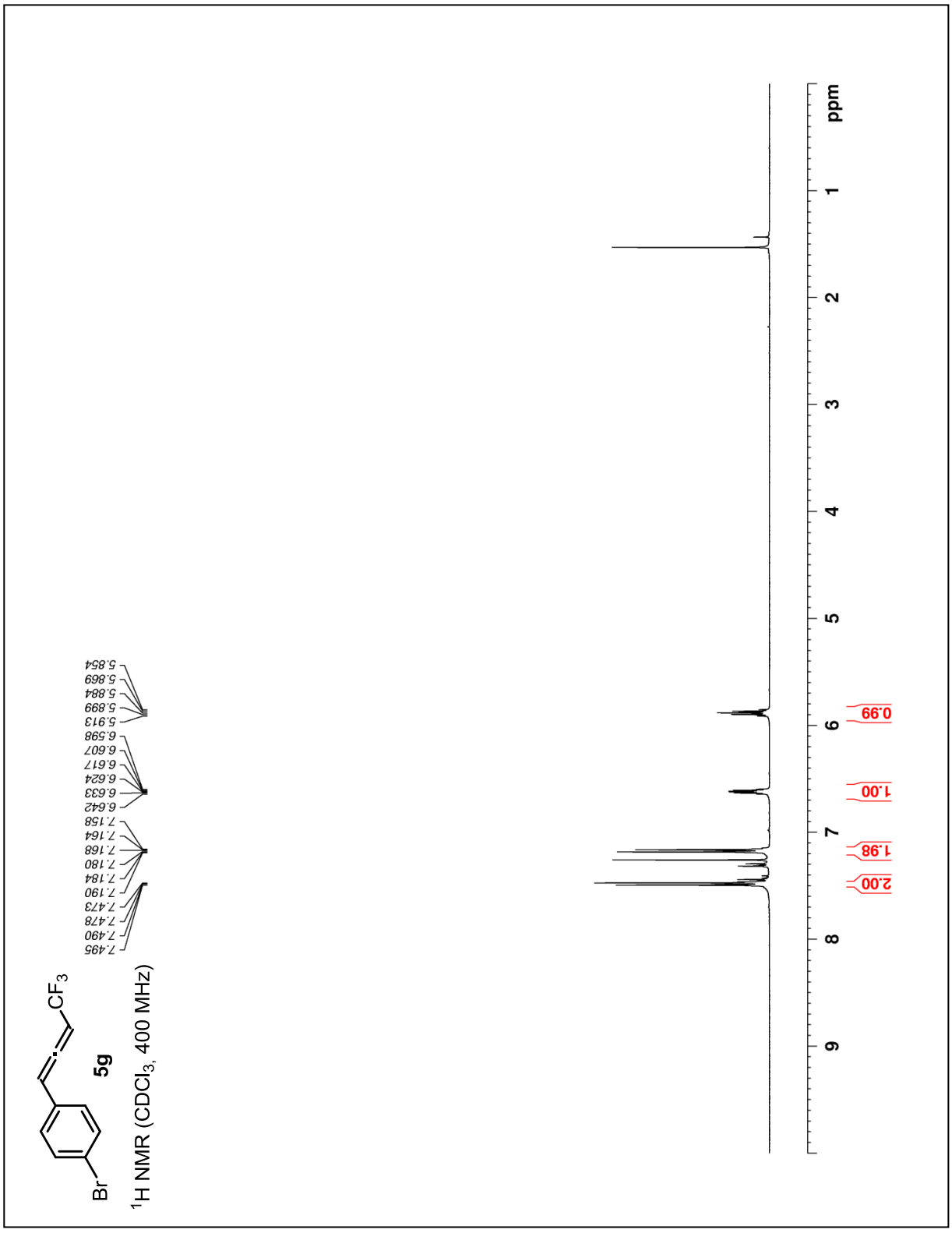

199.924
199.867
127.074
124.351
121.668
118.992
110.123
83.764
83.381
82.995
82.609
30.344
30.332
26.860
25.662
^{13}C NMR ($CDCl_3$, 100 MHz)
CF_3
5e
ppm

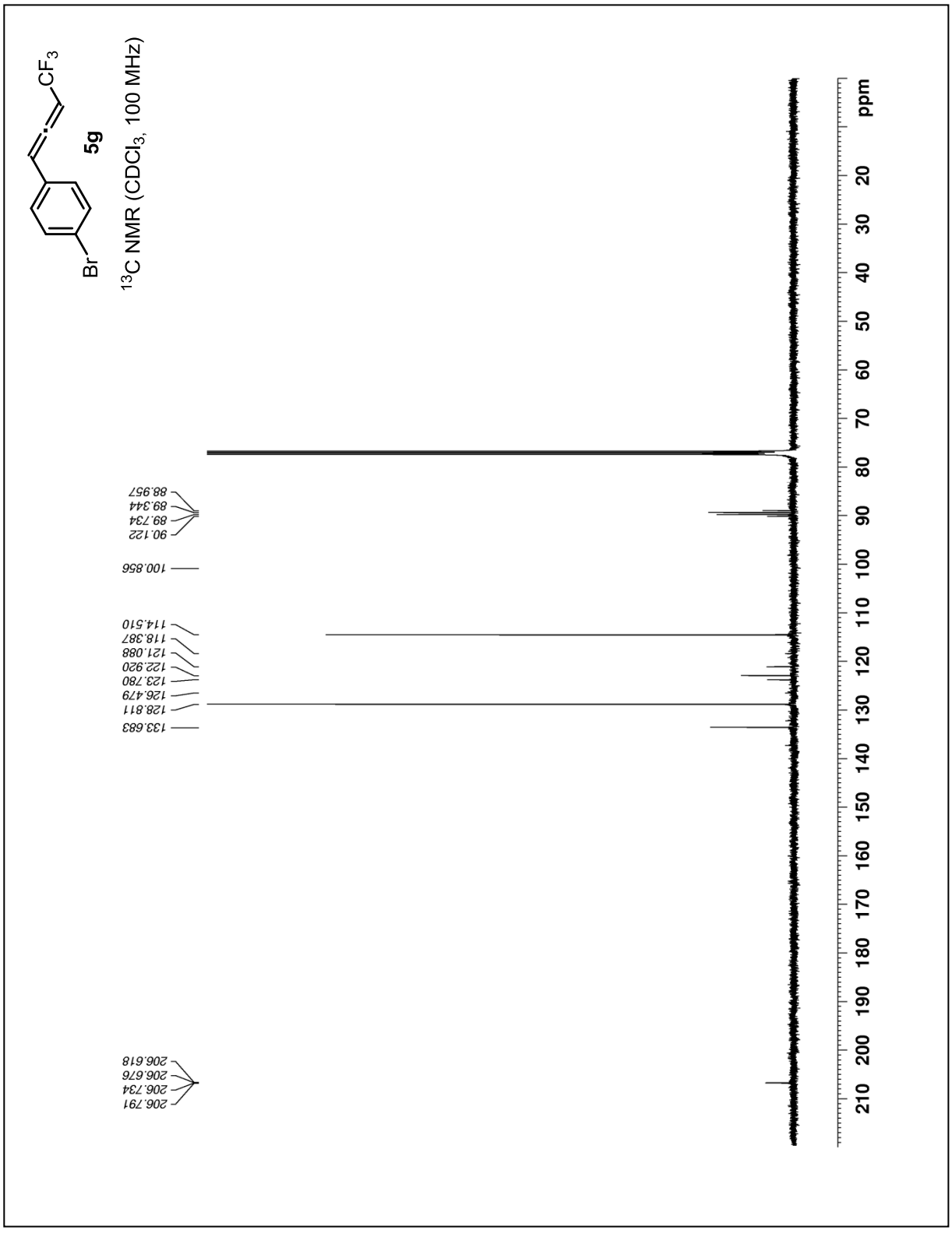

CF3
5e
19F NMR (CDCl3, 376 MHz)
-60.609
-60.624
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

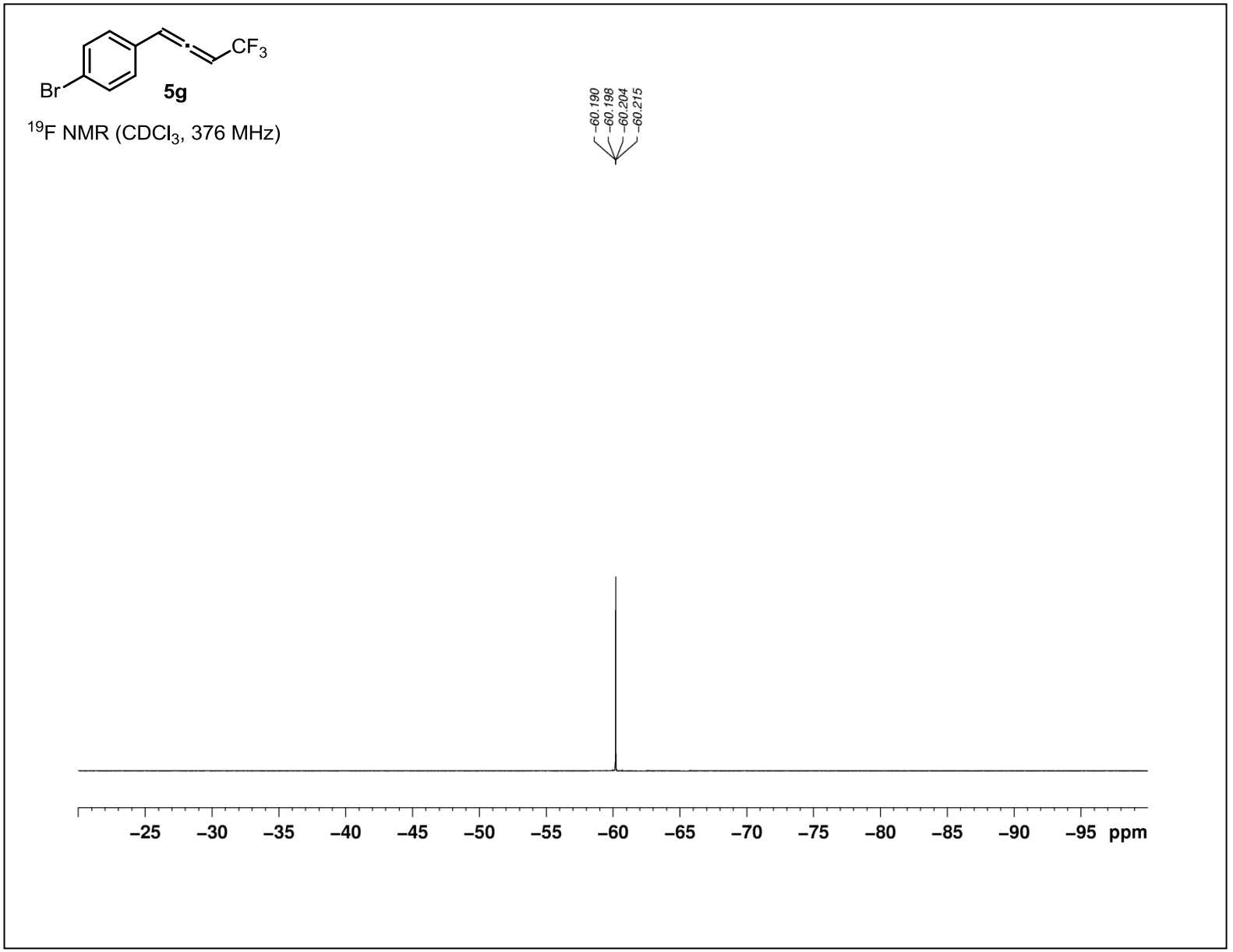

5f
^{1}H NMR ($CDCl_3$, 400 MHz)
7.279
7.051
6.668
6.659
6.649
6.642
6.633
6.623
5.913
5.898
5.884
5.869
5.854
ppm
1.00
1.00
2.06
2.00

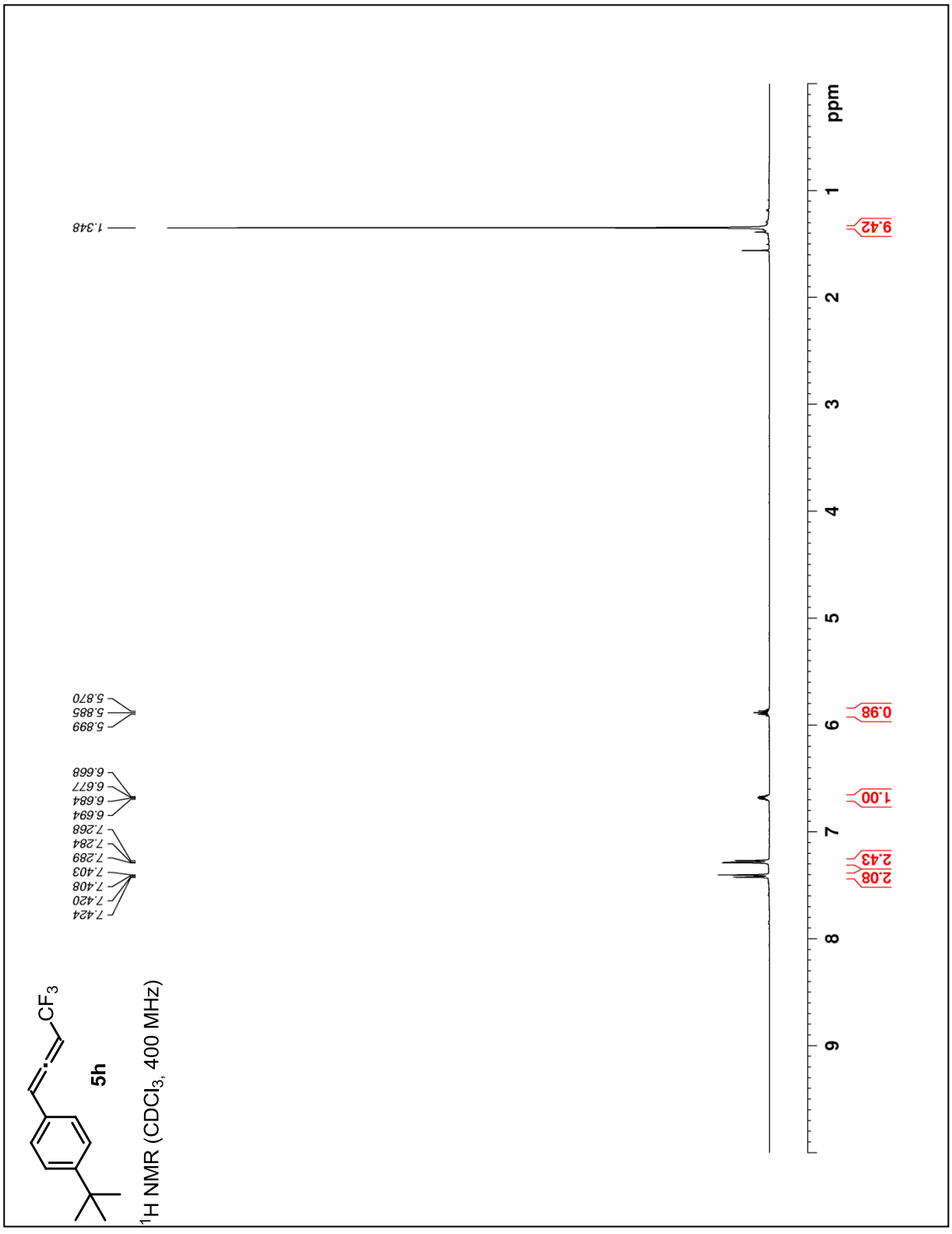

CF3
F
5f
13C NMR (CDCl3, 100 MHz)
119.126
121.821
124.517
127.208
127.621
127.636
127.651
127.665
91.365
90.975
90.585
90.195
101.266
116.837
117.056
119.126
121.821
124.517
127.208
127.621
127.636
127.651
127.665
129.998
130.079
134.635
162.488
164.959
207.534
207.556
207.592
207.614
207.649
207.672
207.702
207.725
ppm

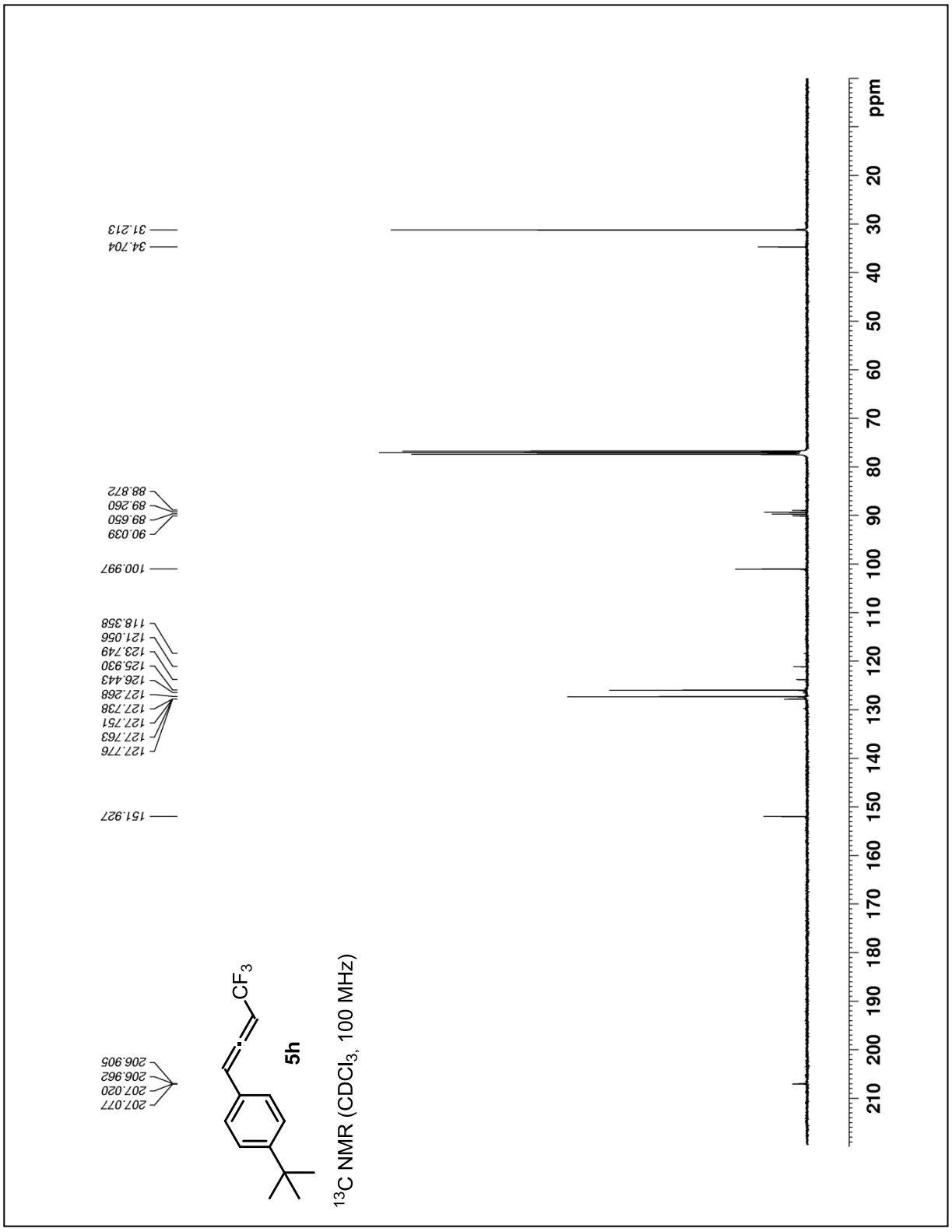

CF3
F
5f
19F NMR (CDCl3, 376 MHz)
-60.279
-60.288
-60.294
-60.305
-112.467
-112.481
-112.491
-112.504
-112.516
-112.526
-112.540
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

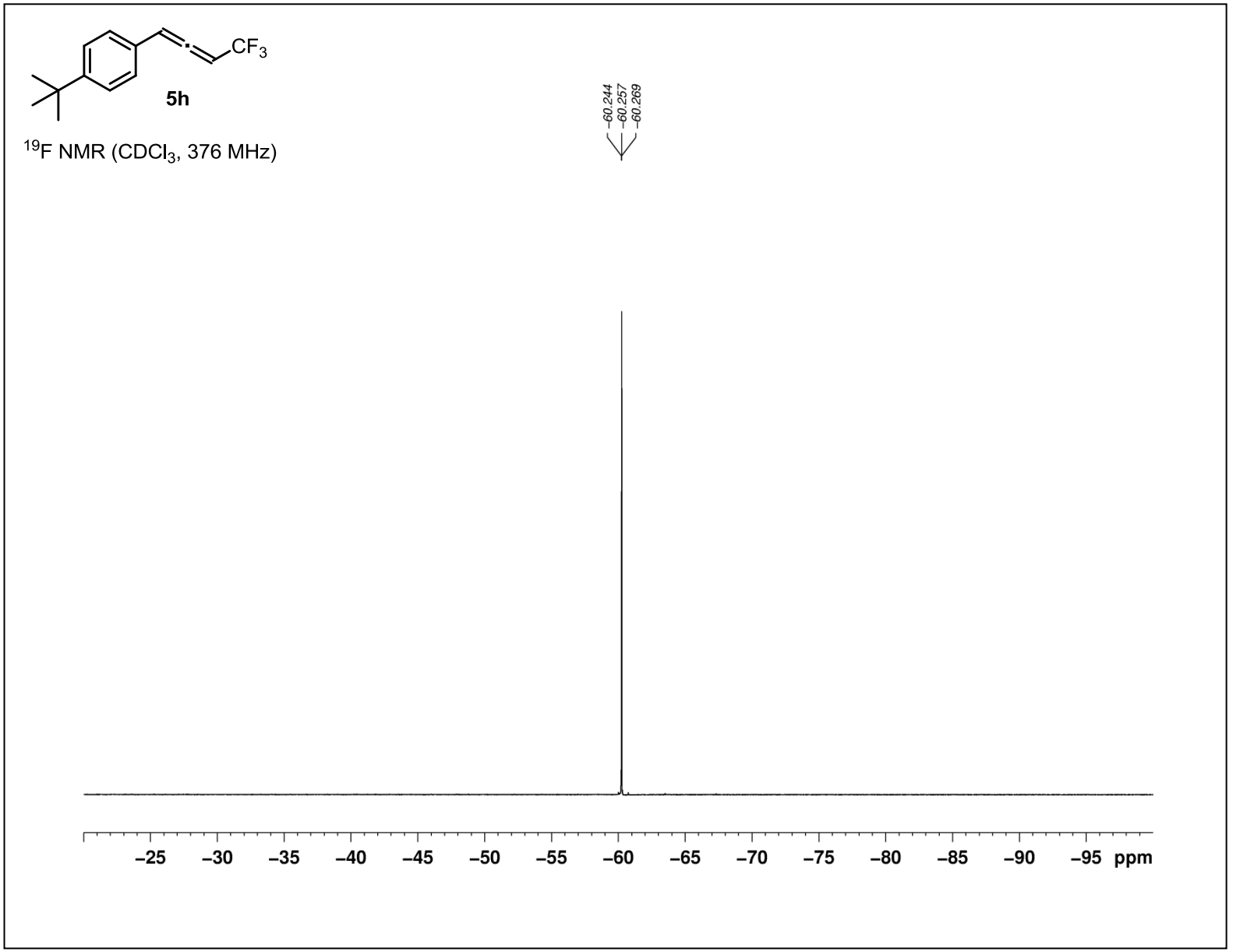

CF3
Br
5g
1H NMR (CDCl3, 400 MHz)
7.495
7.490
7.478
7.473
7.190
7.184
7.180
7.168
7.164
7.158
6.642
6.633
6.624
6.617
6.607
6.598
5.913
5.899
5.884
5.869
5.854
ppm
0.99
1.00
1.98
2.00

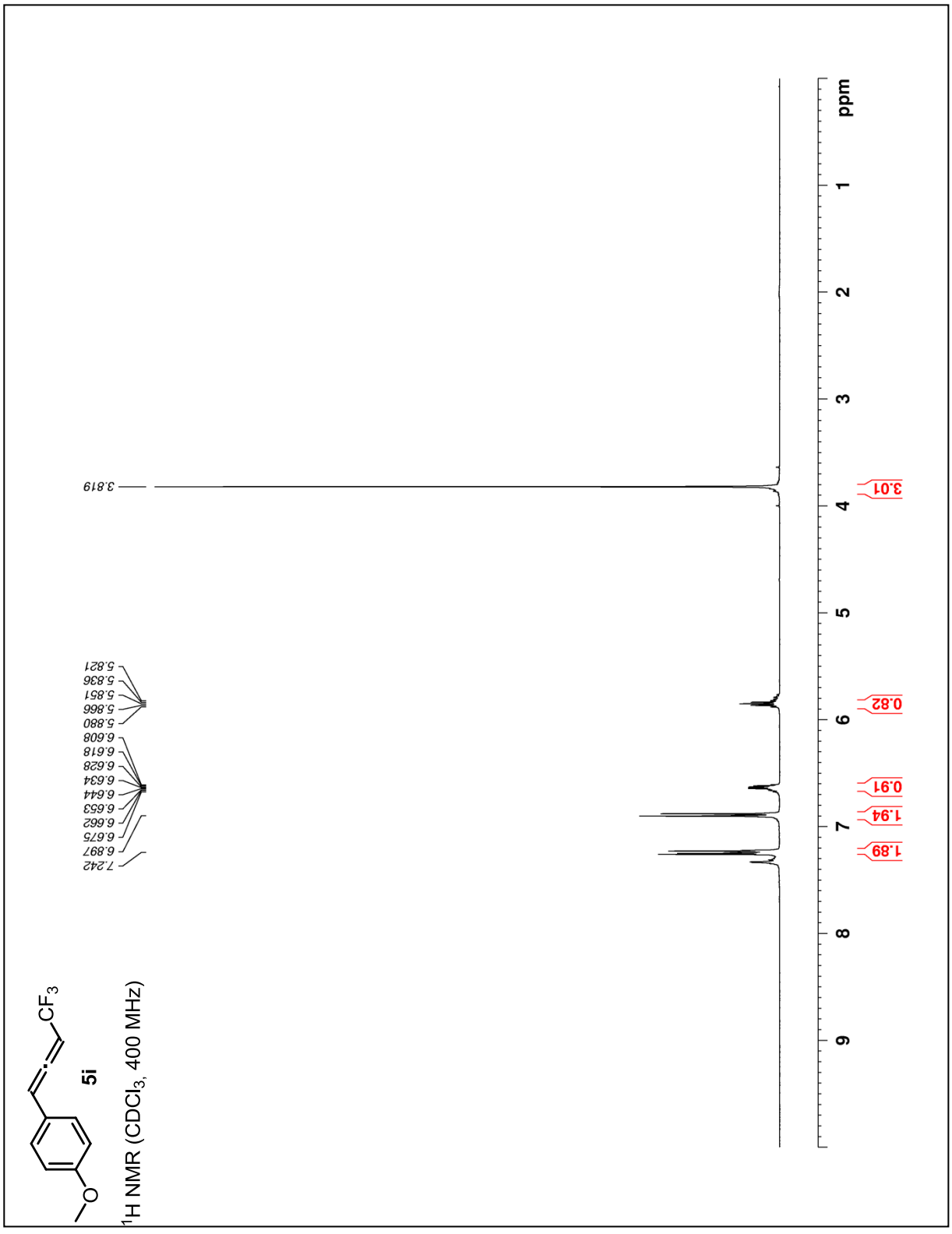

CF3
Br
5g
13C NMR (CDCl3, 100 MHz)
206.791
206.734
206.676
206.618
133.683
128.811
126.479
123.780
122.920
121.088
118.387
114.510
100.856
90.122
89.734
89.344
88.957
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

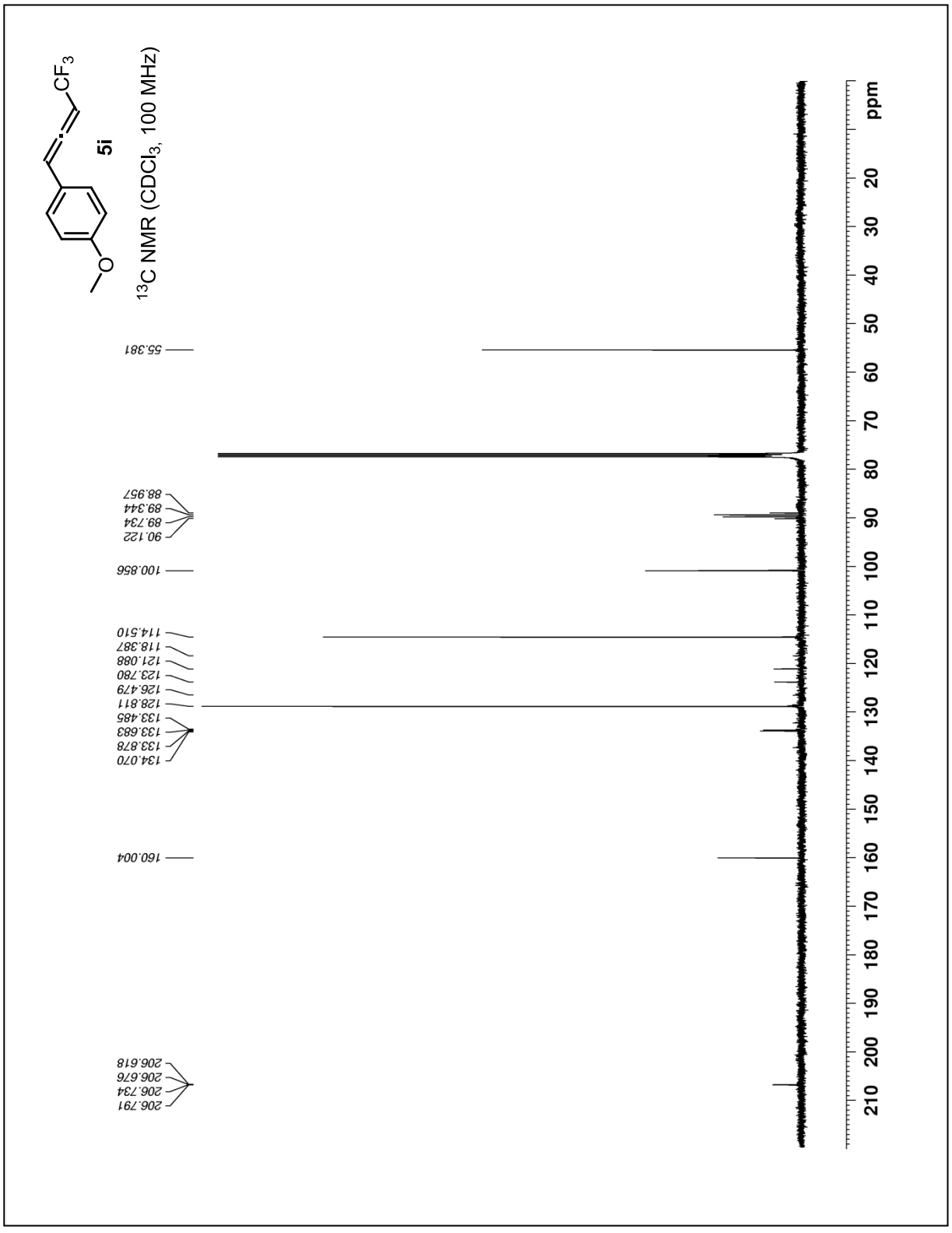

Br
CF3
5g
19F NMR (CDCl3, 376 MHz)
-60.190
-60.198
-60.204
-60.215
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

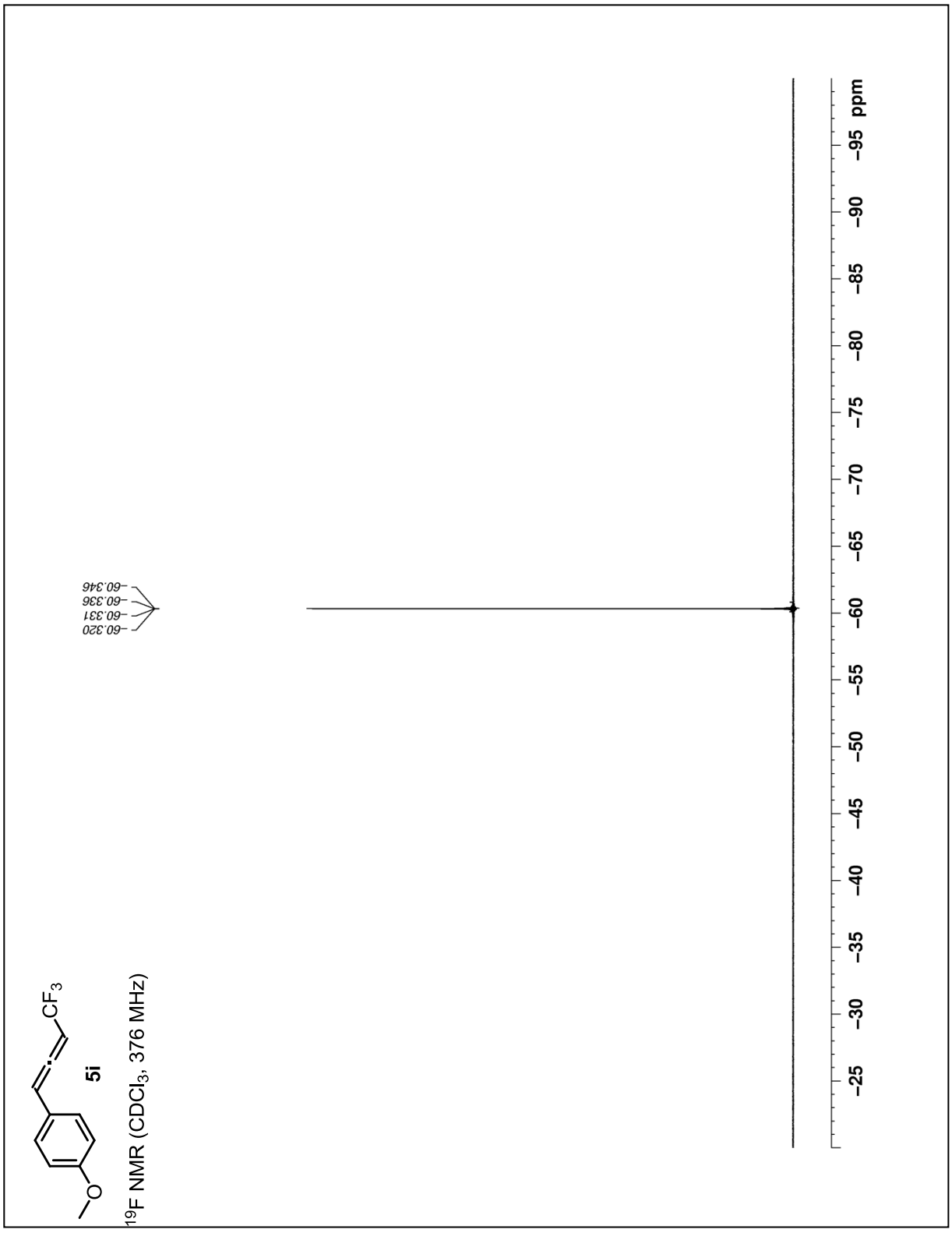

5h
^{1}H NMR ($CDCl_3$, 400 MHz)
CF3
1.348
5.870
5.885
5.899
6.668
6.677
6.684
6.694
7.268
7.284
7.289
7.403
7.408
7.420
7.424
9.42
0.98
1.00
2.43
2.08
ppm

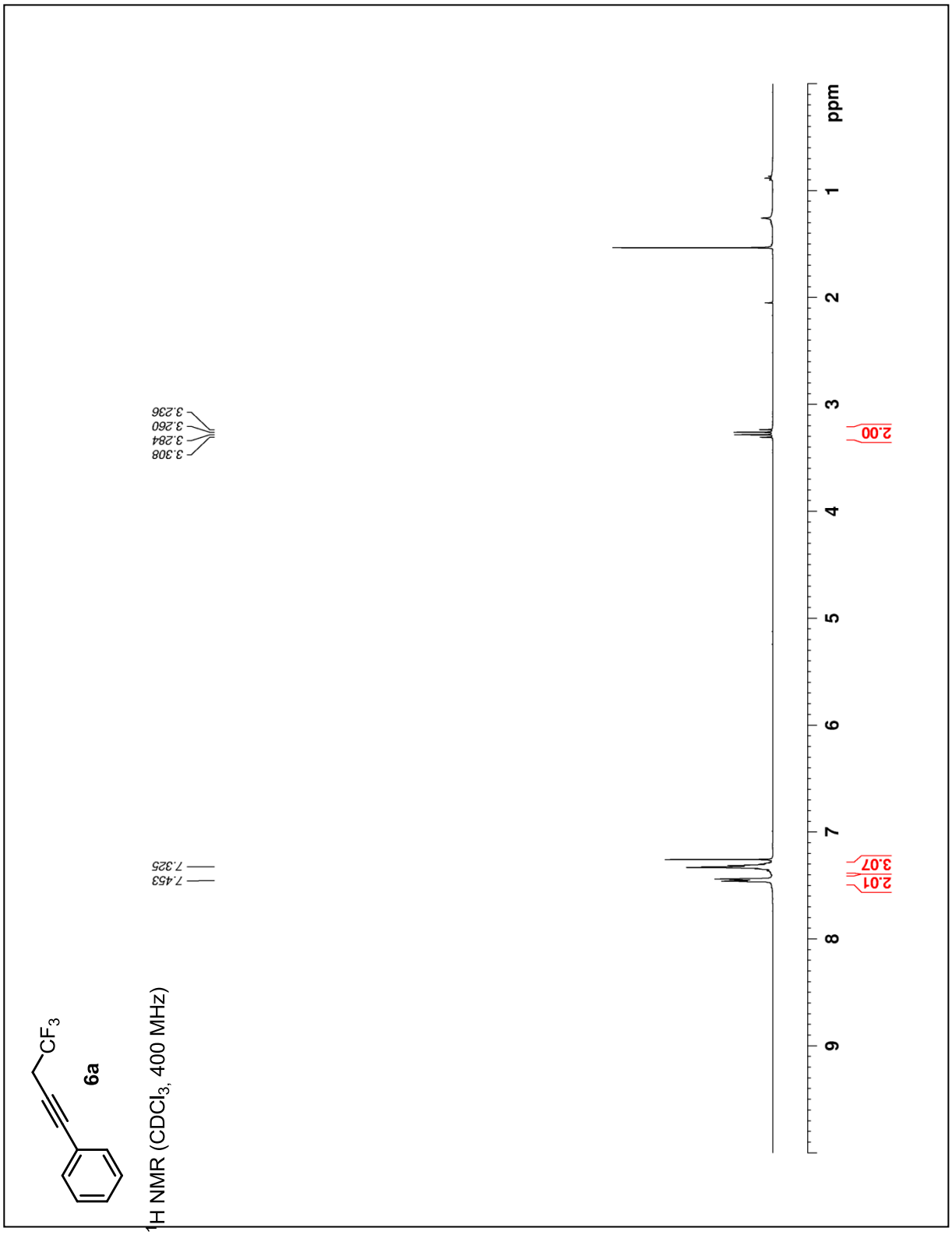

31.213
34.704
88.872
89.260
89.650
90.039
100.997
118.358
121.056
123.749
125.930
126.443
127.268
127.738
127.751
127.763
127.776
151.927
207.077
207.020
206.962
206.905
CF3
5h
13C NMR (CDCl3, 100 MHz)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

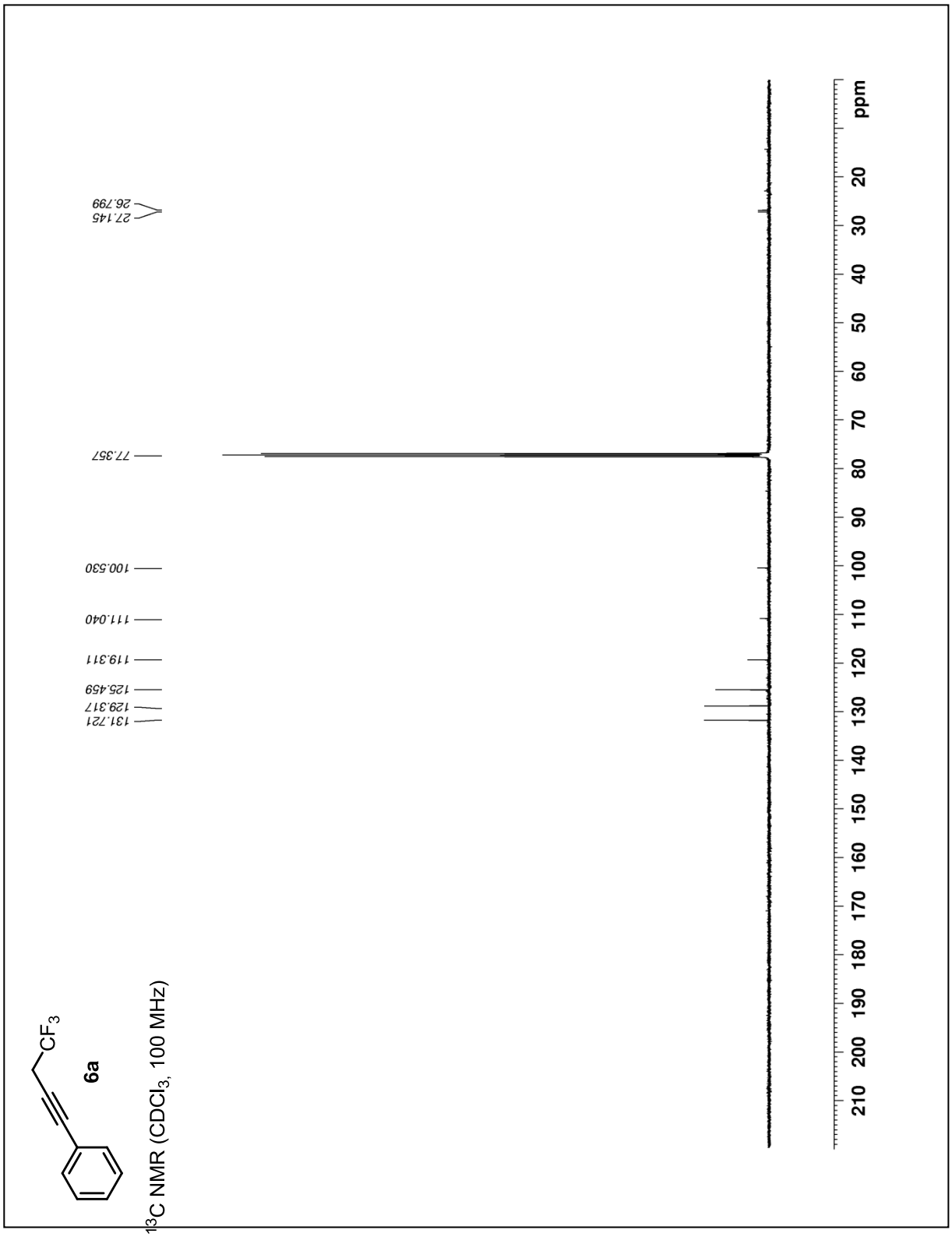

CF3
5h
19F NMR (CDCl3, 376 MHz)
-60.244
-60.257
-60.269
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

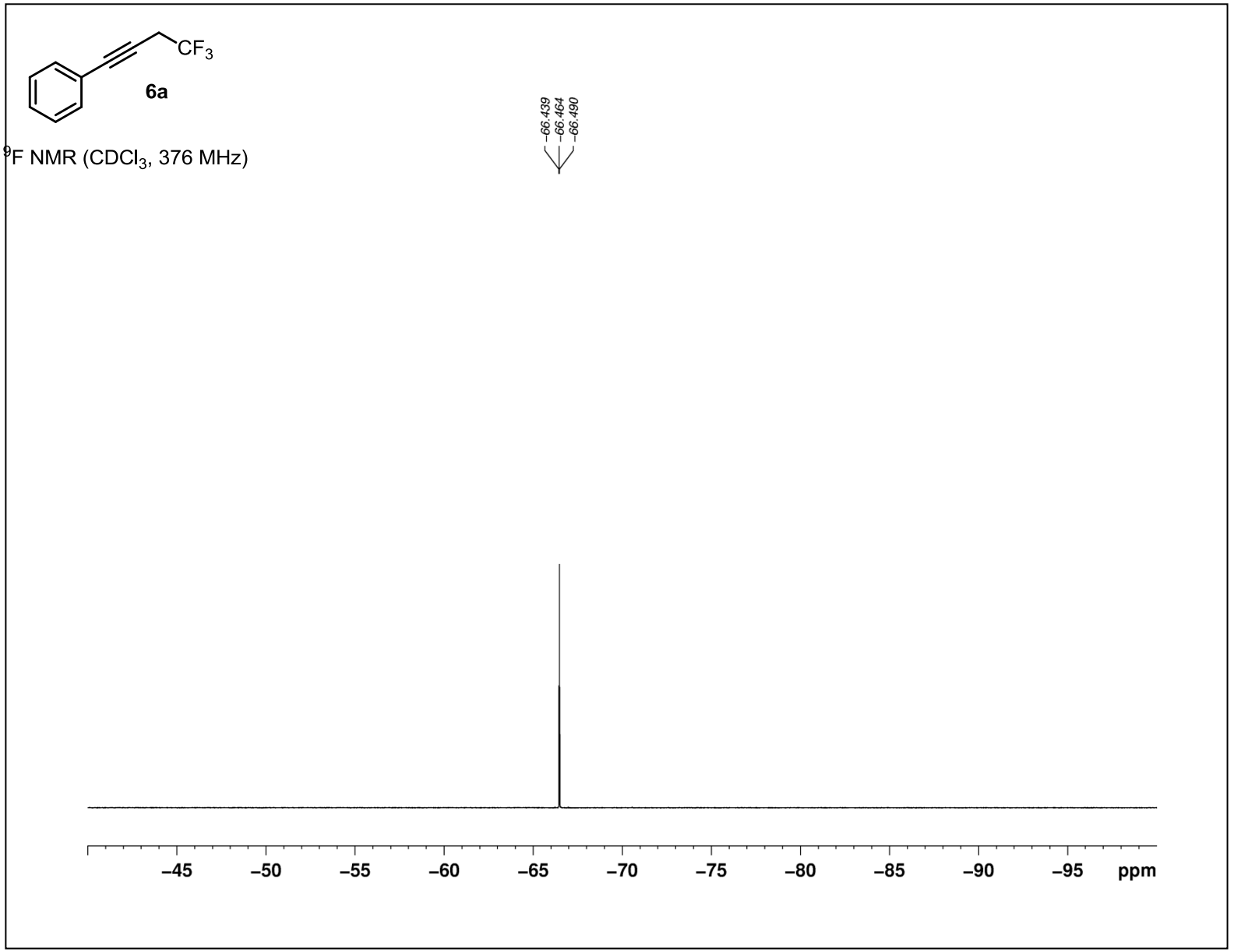

5i
^{1}H NMR ($CDCl_3$, 400 MHz)
3.819
7.242
6.897
6.675
6.662
6.653
6.644
6.634
6.628
6.618
6.608
5.880
5.866
5.851
5.836
5.821
3.01
0.82
0.91
1.94
1.89
ppm

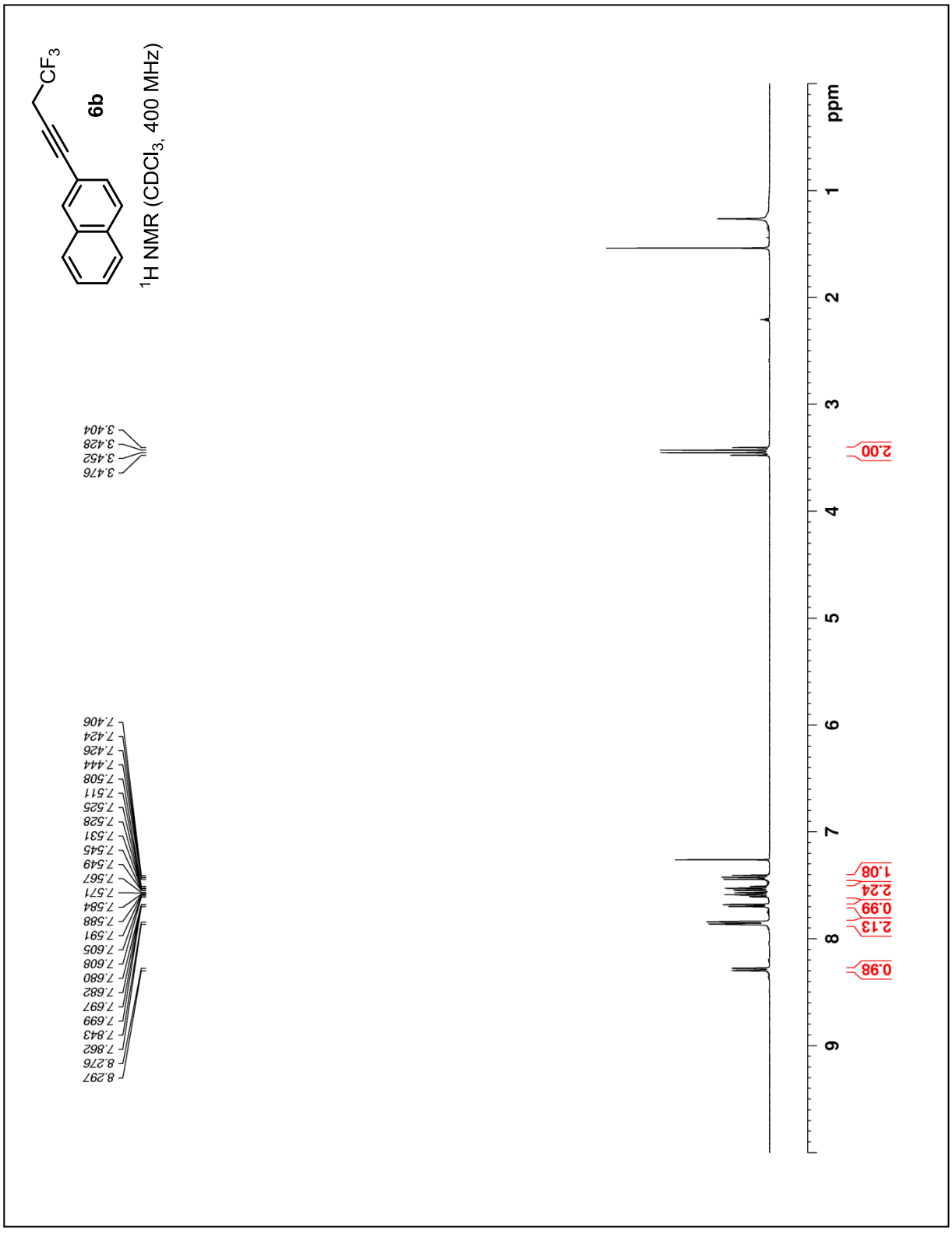

5i
^{13}C NMR ($CDCl_3$, 100 MHz)
55.381
88.957
89.344
89.734
90.122
100.856
114.510
118.387
121.088
123.780
126.479
128.811
133.485
133.683
133.878
134.070
160.004
206.618
206.676
206.734
206.791
ppm

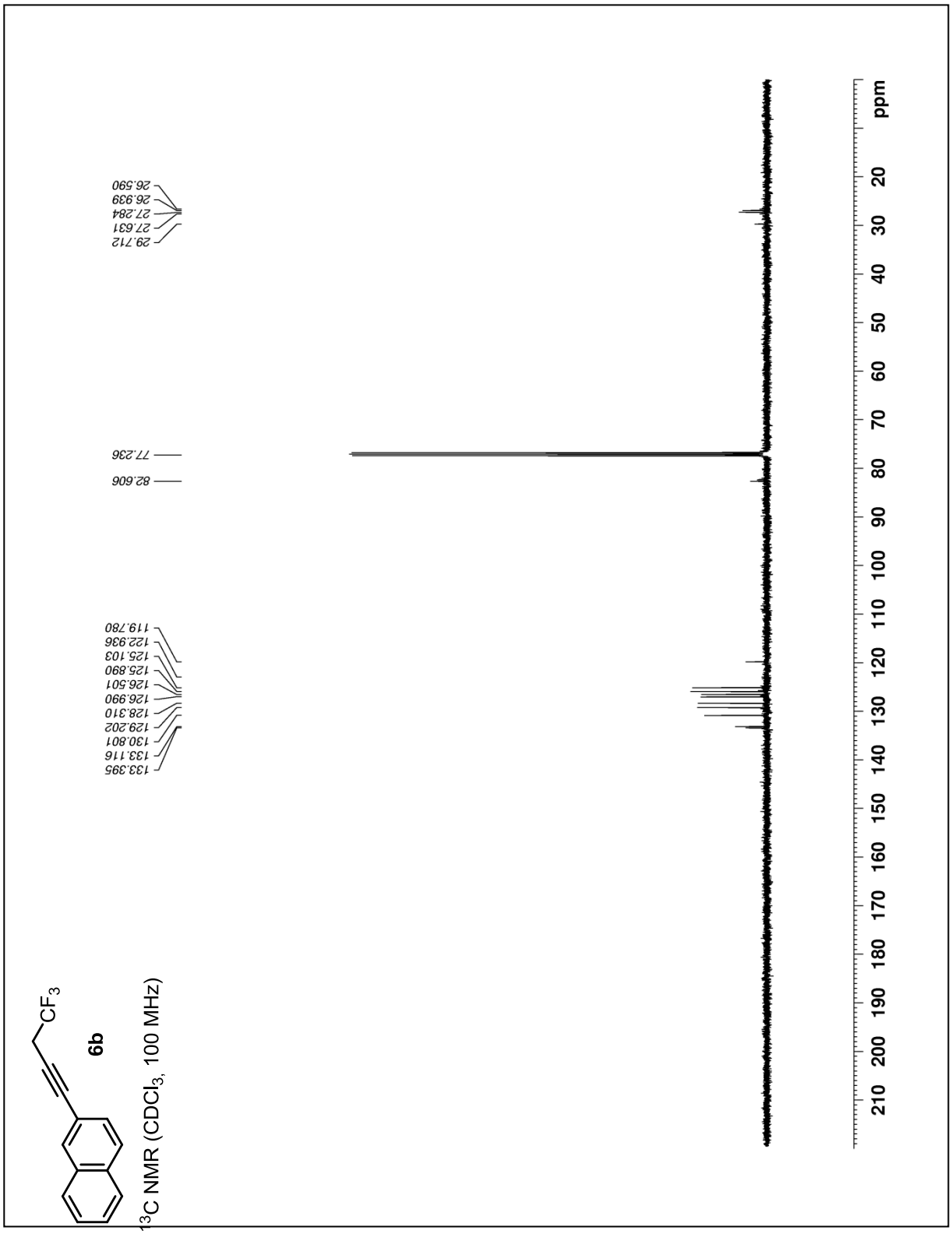

5i
^{19}F NMR ($CDCl_3$, 376 MHz)
−60.320
−60.331
−60.336
−60.346
−25 −30 −35 −40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 ppm

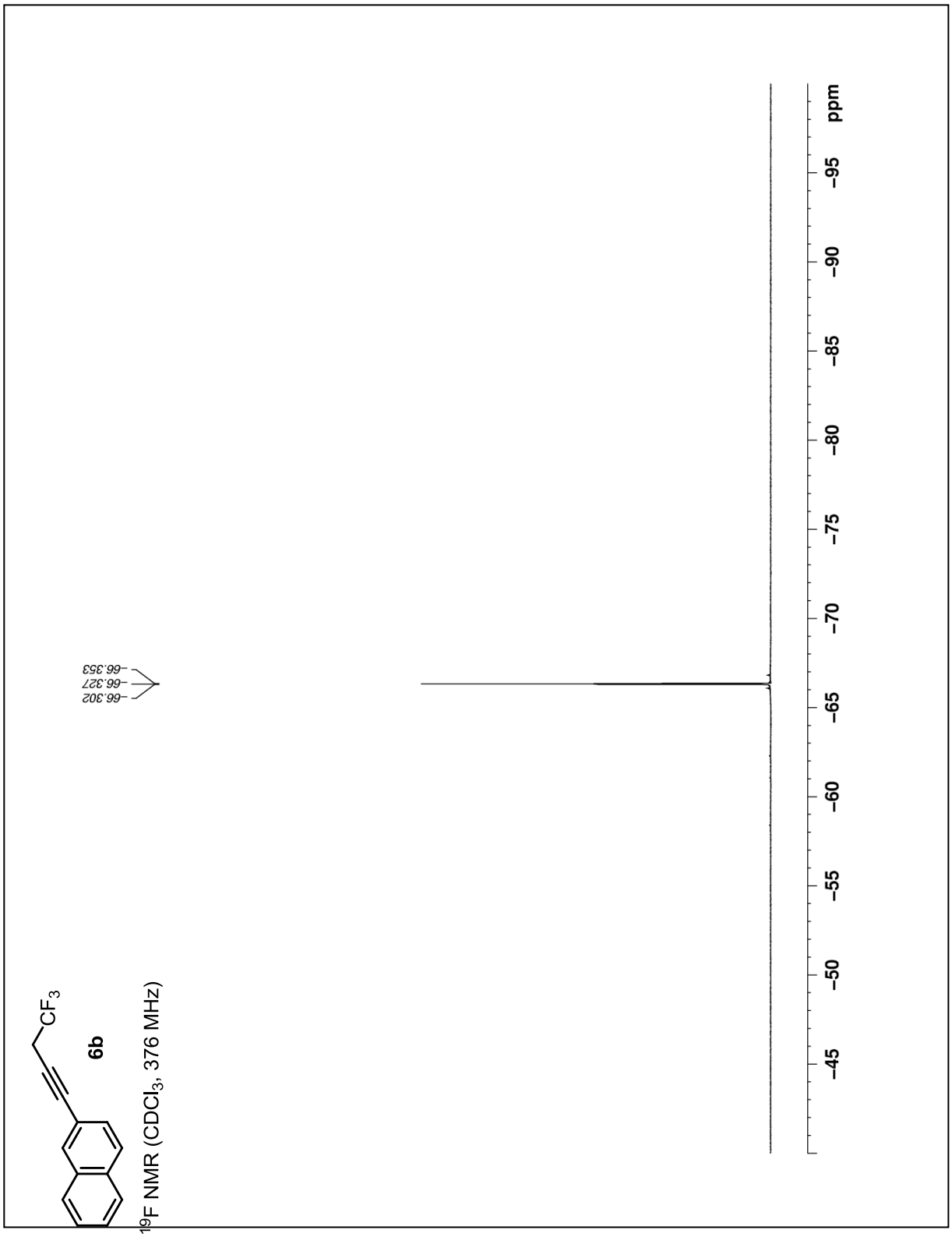

CF3
6a
1H NMR (CDCl3, 400 MHz)
7.453
7.325
3.308
3.284
3.260
3.236
2.00
2.01
3.07
ppm
1
2
3
4
5
6
7
8
9

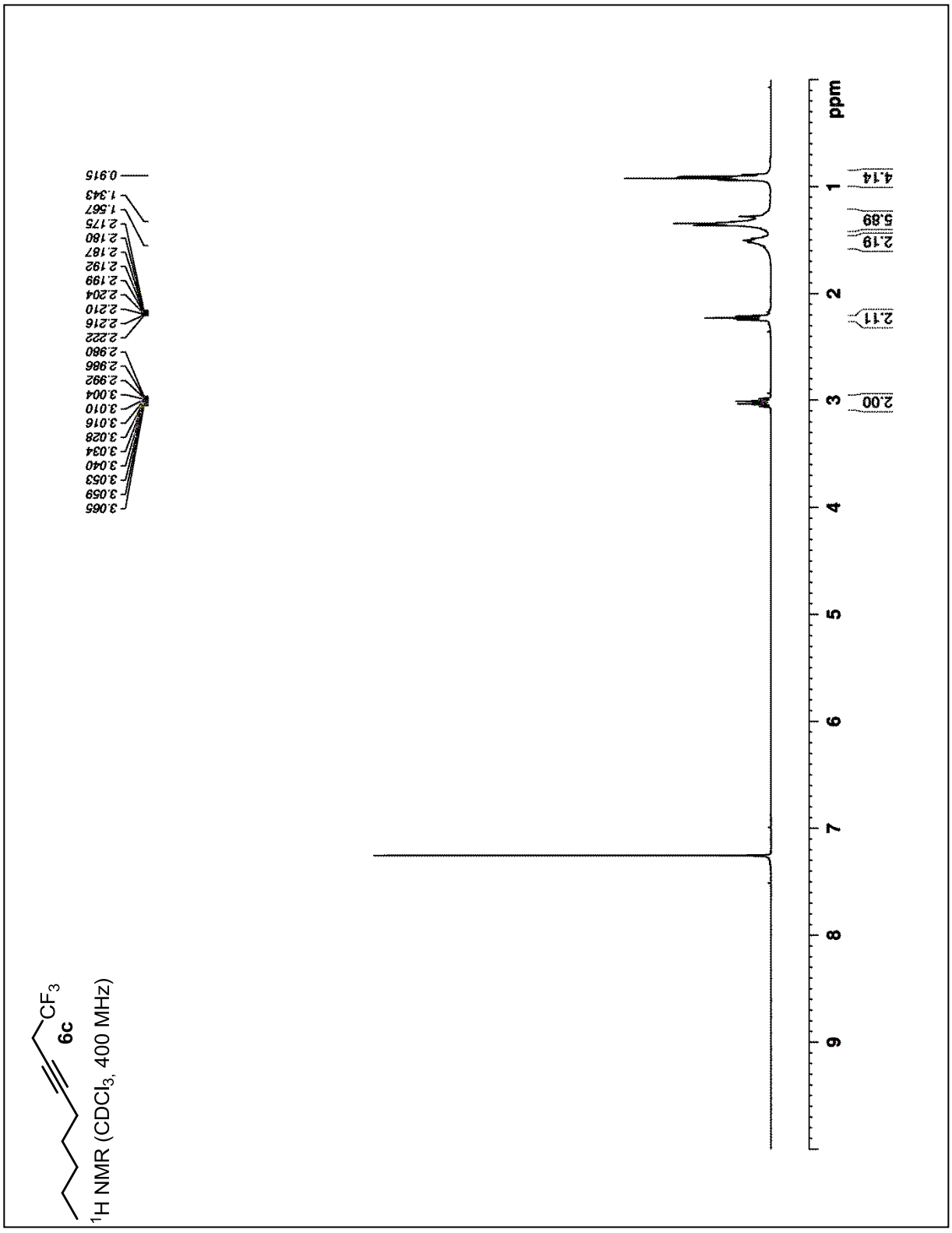

CF3
6a
13C NMR (CDCl3, 100 MHz)
131.721
129.317
125.459
119.311
111.040
100.530
77.357
27.145
26.799
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

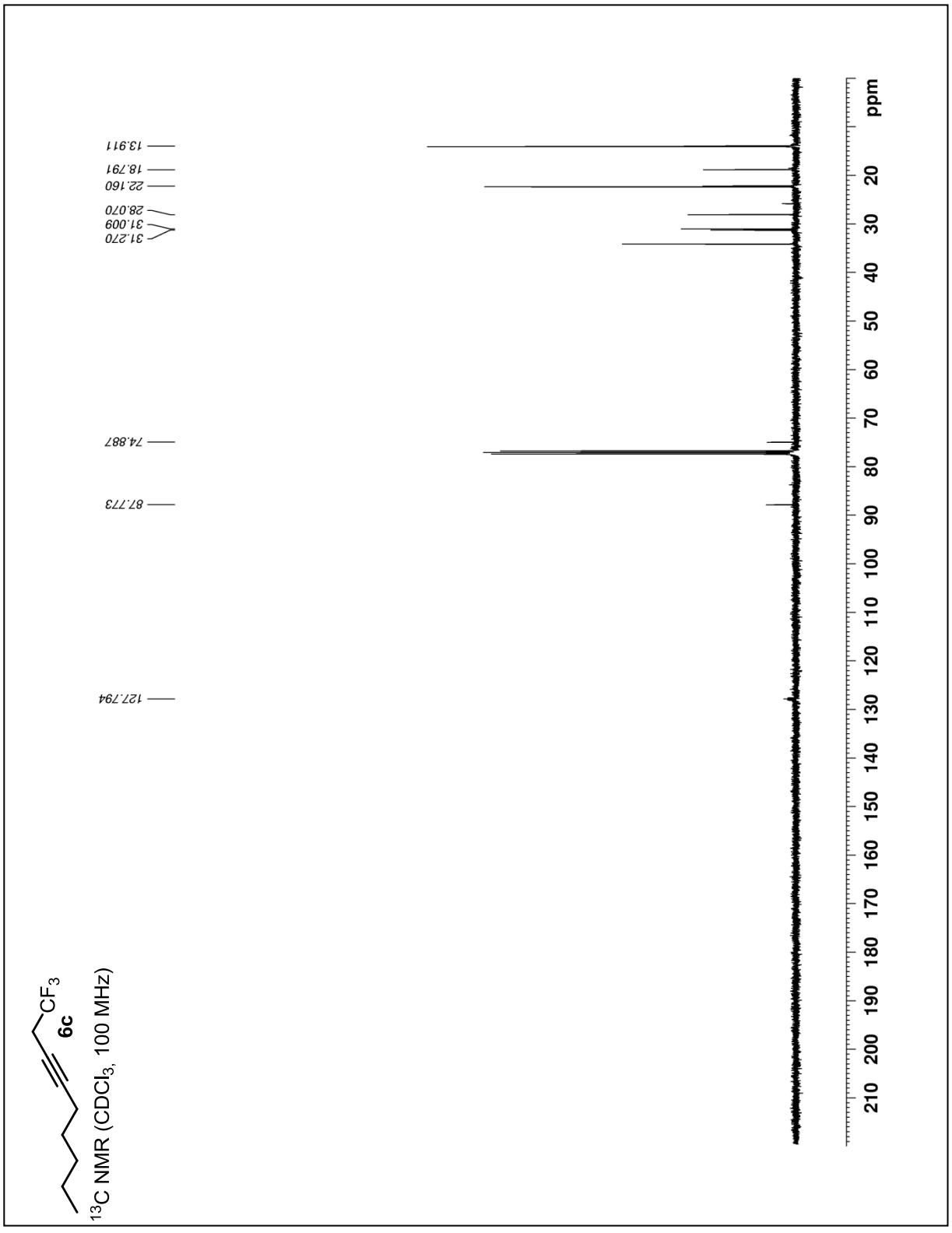

CF3
6a
19F NMR (CDCl3, 376 MHz)
-66.439
-66.464
-66.490
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

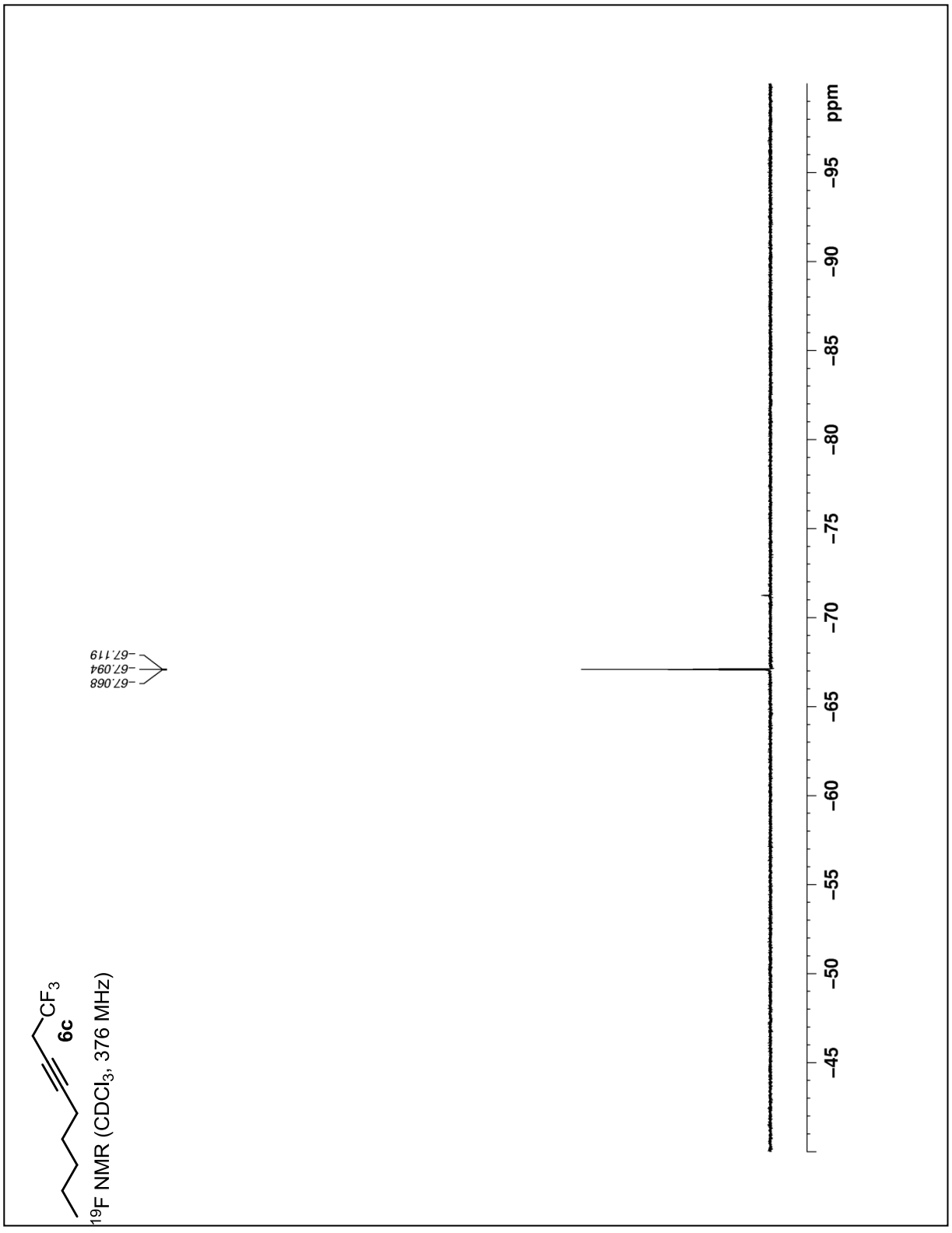

CF3
6b
1H NMR (CDCl3, 400 MHz)
3.404
3.428
3.452
3.476
7.406
7.424
7.426
7.444
7.508
7.511
7.525
7.528
7.531
7.545
7.549
7.567
7.571
7.584
7.588
7.591
7.605
7.608
7.680
7.682
7.697
7.699
7.843
7.862
8.276
8.297
ppm
1
2
3
4
5
6
7
8
9
2.00
1.08
2.24
0.99
2.13
0.98

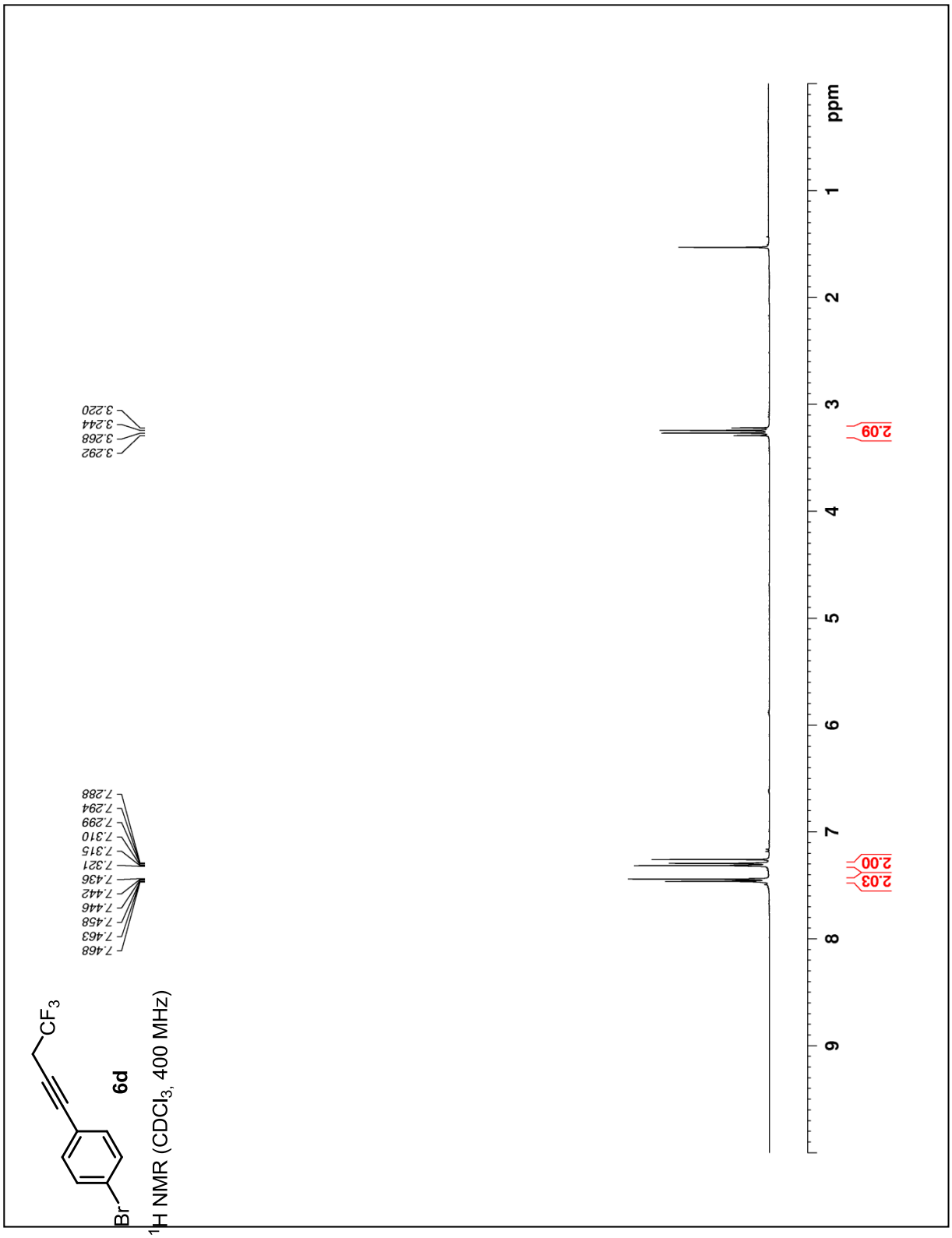

CF3
6b
13C NMR (CDCl3, 100 MHz)
133.395
133.116
130.801
129.202
128.310
126.990
126.501
125.890
125.103
122.936
119.780
82.606
77.236
29.712
27.631
27.284
26.939
26.590
ppm

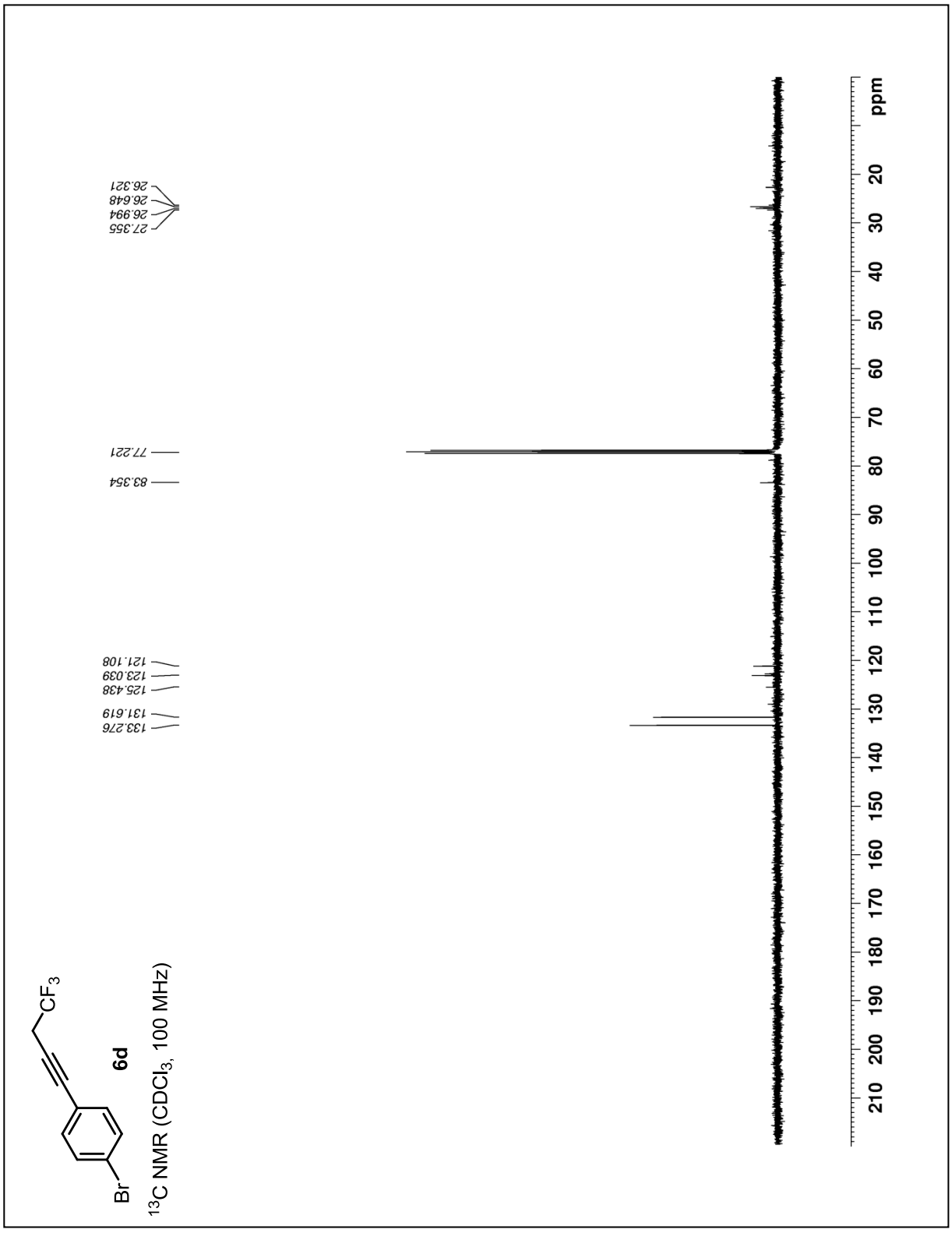

CF3
6b
19F NMR (CDCl3, 376 MHz)
−66.302
−66.327
−66.353
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
ppm

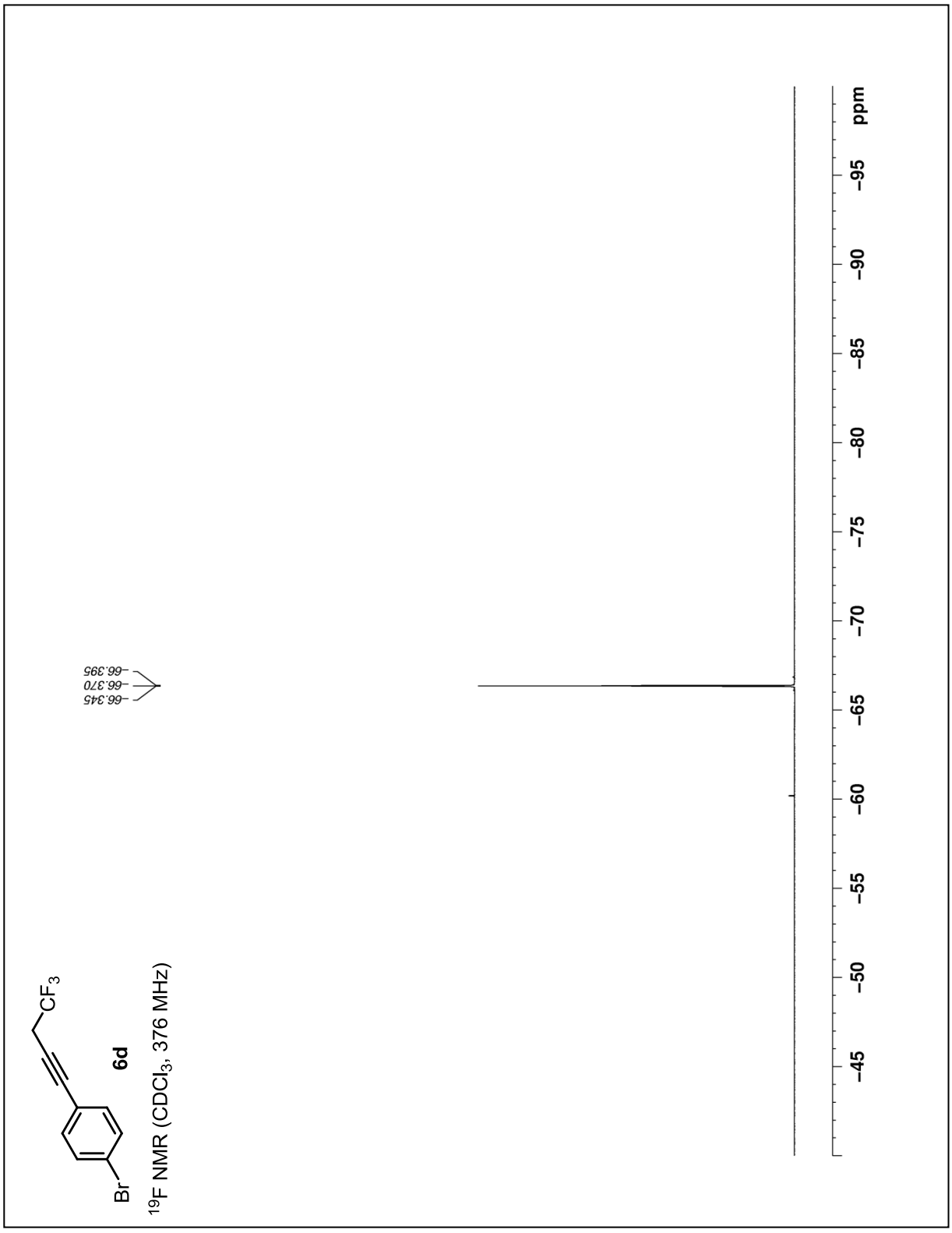

CF3
6c
1H NMR (CDCl3, 400 MHz)
0.915
1.343
1.567
2.175
2.180
2.187
2.192
2.199
2.204
2.210
2.216
2.222
2.980
2.986
2.992
3.004
3.010
3.016
3.028
3.034
3.040
3.053
3.059
3.065
4.14
5.89
2.19
2.11
2.00
ppm

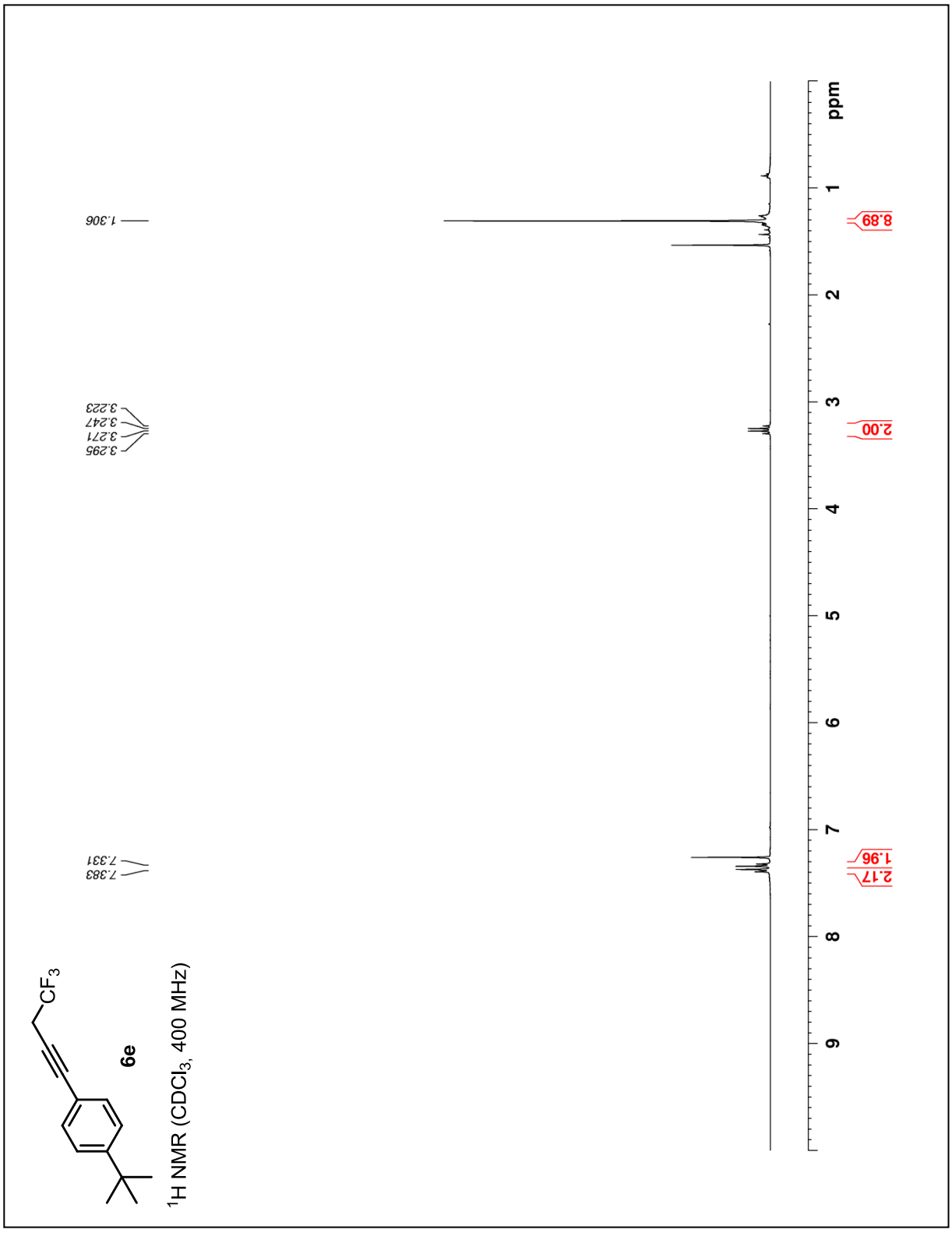

CF3
6c
13C NMR (CDCl3, 100 MHz)
13.911
18.791
22.160
28.070
31.009
31.270
74.887
87.773
127.794
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

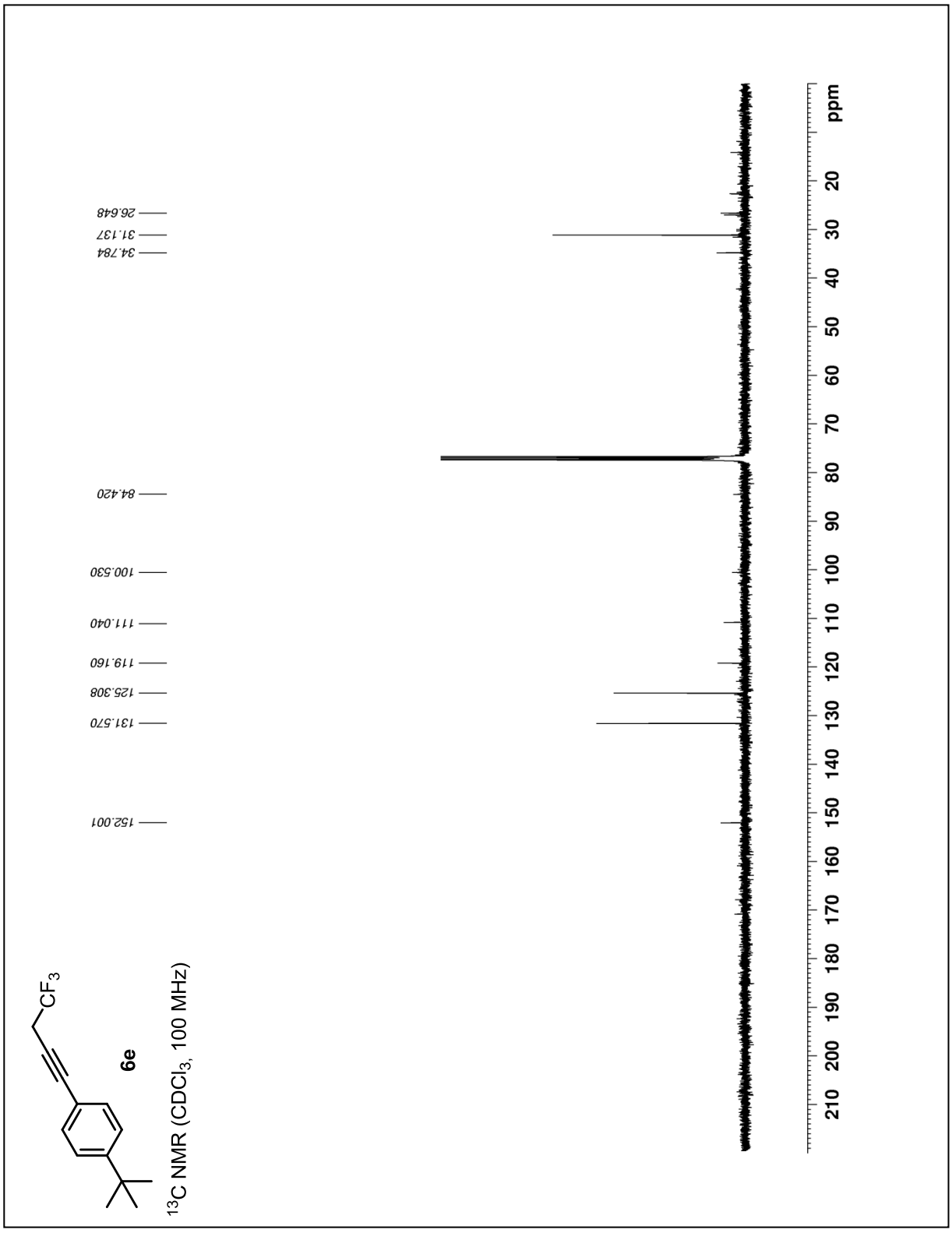

CF3
6c
19F NMR (CDCl3, 376 MHz)
−67.068
−67.094
−67.119
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
ppm

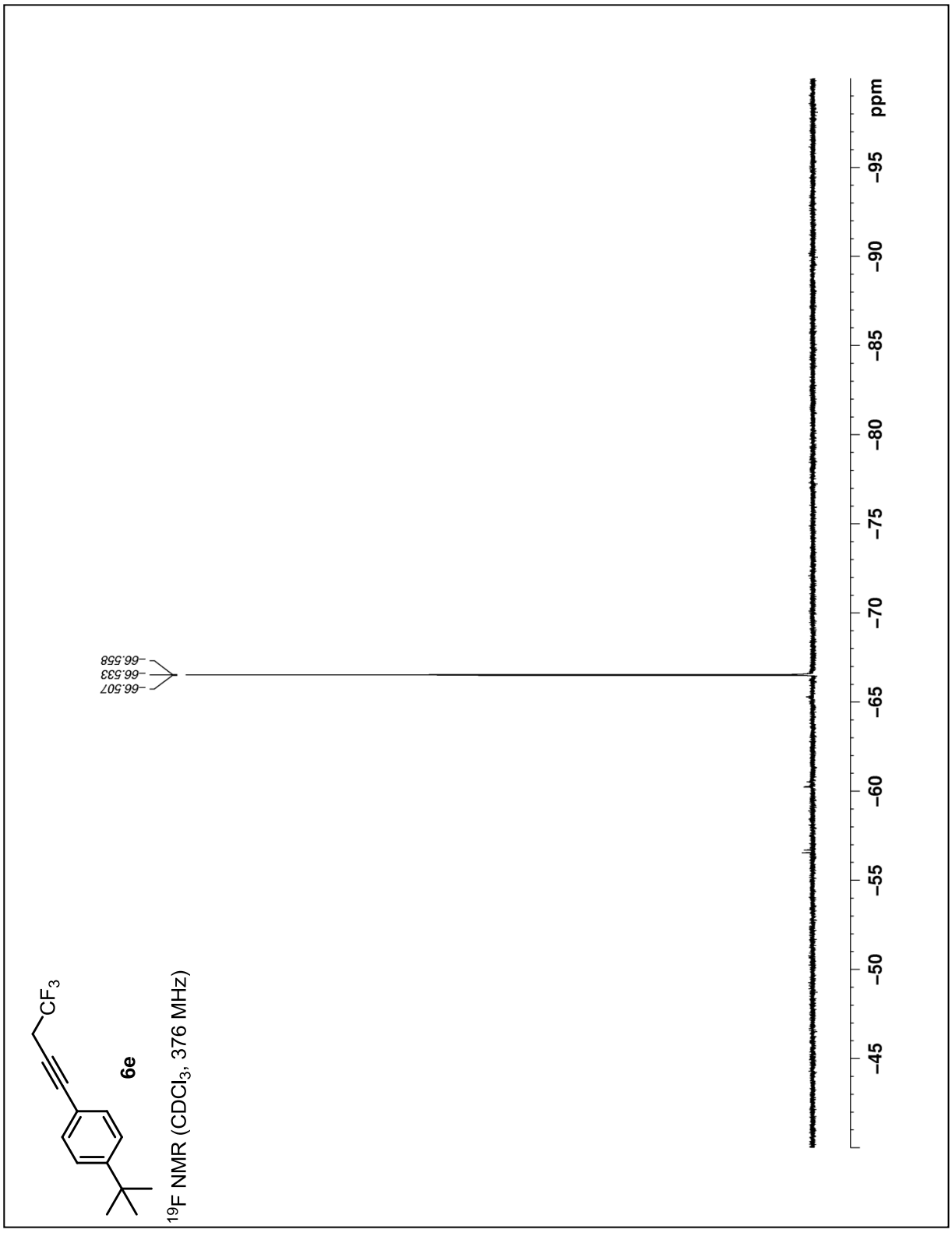

6d
^{1}H NMR ($CDCl_3$, 400 MHz)
CF_3
Br
7.468
7.463
7.458
7.446
7.442
7.436
7.321
7.315
7.310
7.299
7.294
7.288
3.292
3.268
3.244
3.220
2.09
2.03
2.00
ppm


CF3
Br
6d
13C NMR (CDCl3, 100 MHz)
133.276
131.619
125.438
123.039
121.108
83.354
77.221
27.355
26.994
26.648
26.321
ppm


CF3
Br
6d
19F NMR (CDCl3, 376 MHz)
−66.345
−66.370
−66.395
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
ppm


CF3
6e
1H NMR (CDCl3, 400 MHz)
7.383
7.331
3.295
3.271
3.247
3.223
1.306
ppm
1
2
3
4
5
6
7
8
9
8.89
2.00
2.17
1.96


CF3
6e
13C NMR (CDCl3, 100 MHz)
26.648
31.137
34.784
84.420
100.530
111.040
119.160
125.308
131.570
152.001
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20


CF3
6e
19F NMR (CDCl3, 376 MHz)
−66.507
−66.533
−66.558
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
ppm

References

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2. Stulgies, B.; Prinz, P.; Magull, J.; Rauch, K.; Meindl, K.; Rühl, S.; Meijere, A.; *Chem. Eur. J.*, **2005**, *11*, 308
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