Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

Cooperative Photoredox/Gold Catalysed Cyclization of 2-Alkynylbenzoates with Arenediazonium Salts: Synthesis of 3,4-disubstituted Isocoumarins

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General Remarks

All the reactions, that involve the use of reagents sensitive to oxygen or hydrolysis, were carried out under a nitrogen atmosphere. The glassware was previously dried with a heating gun and set with cycles of vacuum and nitrogen. Syringes, used to transfer reagents and solvents, were previously set under nitrogen atmosphere. All chemicals and solvents are commercially available and were used without further purification. The chromatographic column separations were performed by flash technique, using silica gel (pore size 60, particle size 230–400 mesh, Merck Grade 9385). For thin-layer chromatography (TLC), Silica on TLC Alu foils with fluorescent indicator (254 nm) was employed and the detection was performed by irradiation with UV light (λ = 254 nm and/or 366 nm).

^{1}H NMR analyses were performed with 300 and 400 MHz spectrometer at room temperature. The coupling constants (J) are expressed in Hertz (Hz), the chemical shifts (δ) in ppm. The multiplicity of the proton spectra were described by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), dt (double triplet), dd (double doublet), m (multiplet), br (broad). ^{13}C NMR analyses were performed with the same instruments at 74.45 MHz MHz; APT sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. All ^{13}C NMR spectra were recorded with complete proton decoupling. Low-resolution MS spectra were recorded with electron impact source and electrospray/ion trap instruments, using a syringe pump device to directly inject sample solutions. The values are expressed as mass-charge ratio and the relative intensities of the most significant peaks are shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano.

2-alkynylbenzoates **1a-f**, **1h-m**[1] and aryldiazonium salts **2a-h**[2] are known compounds and were prepared according to literature procedures.

PPh_3PAuCl, $Au(PPh_3)NTf_2$, $Ru(bpy)_3(PF_6)_2$, $Ru(bpy)_3Cl_2$, and Eosin Y were purchased from commercial suppliers and used as received, while Au(JohnPhos)NTf_2 Au(P(*p*-CF_3Ph)$_3$)NTf_2 were prepared following literature procedures.[3]

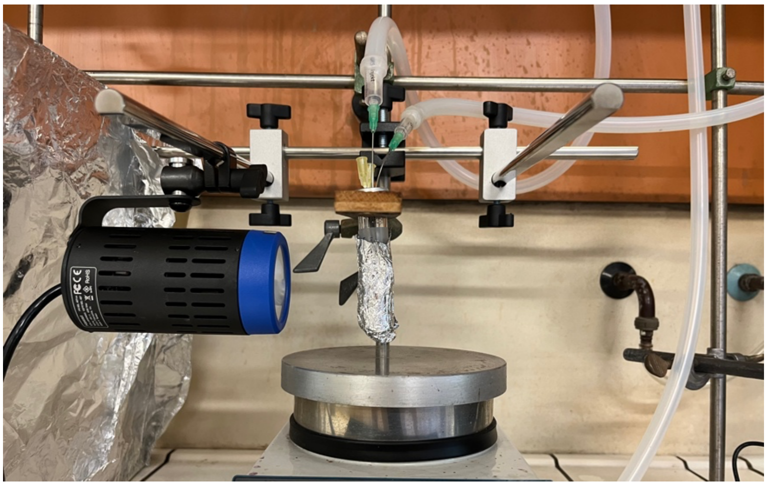
[1] a) F. Curti, M. Tiecco, V. Pirovano, R. Germani, A. Caselli, E. Rossi and G. Abbiati, *Eur. J. Org. Chem.*, 2019, 1904-1914; b) J. Gianni, V. Pirovano and G. Abbiati, *Org. Biomol. Chem.*, 2018, **16**, 3213-3219; c) X. Lin, Z. Fang, C. Zeng, C. Zhu, X. Pang, C. Liu, W. He, J. Duan, N. Qin and K. Guo, *Chem. Eur. J.*, 2020, **26**, 13738-13742.

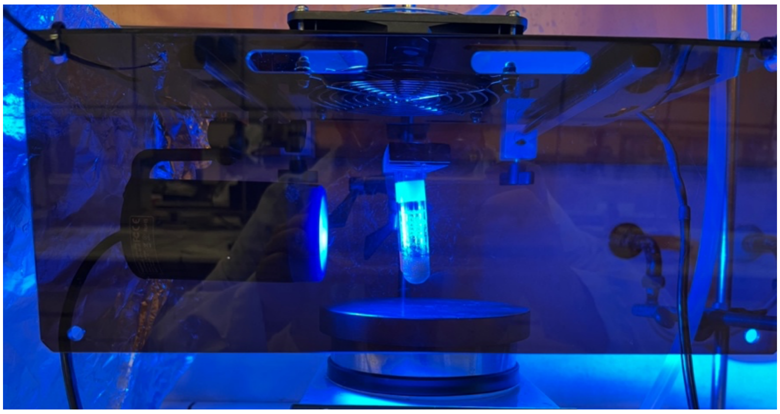
[2] J. Liu, E. Xu, J. Jiang, Z. Huang, L. Zheng and Z.-Q. Liu, *Chem. Commun*., 2020, **56**, 2202-2205.

[3] S. Nonaka, K. Sugimoto, H. Ueda and H. Tokuyamaa, *Adv. Synth. Catal.*, 2016, **358**, 380-385.

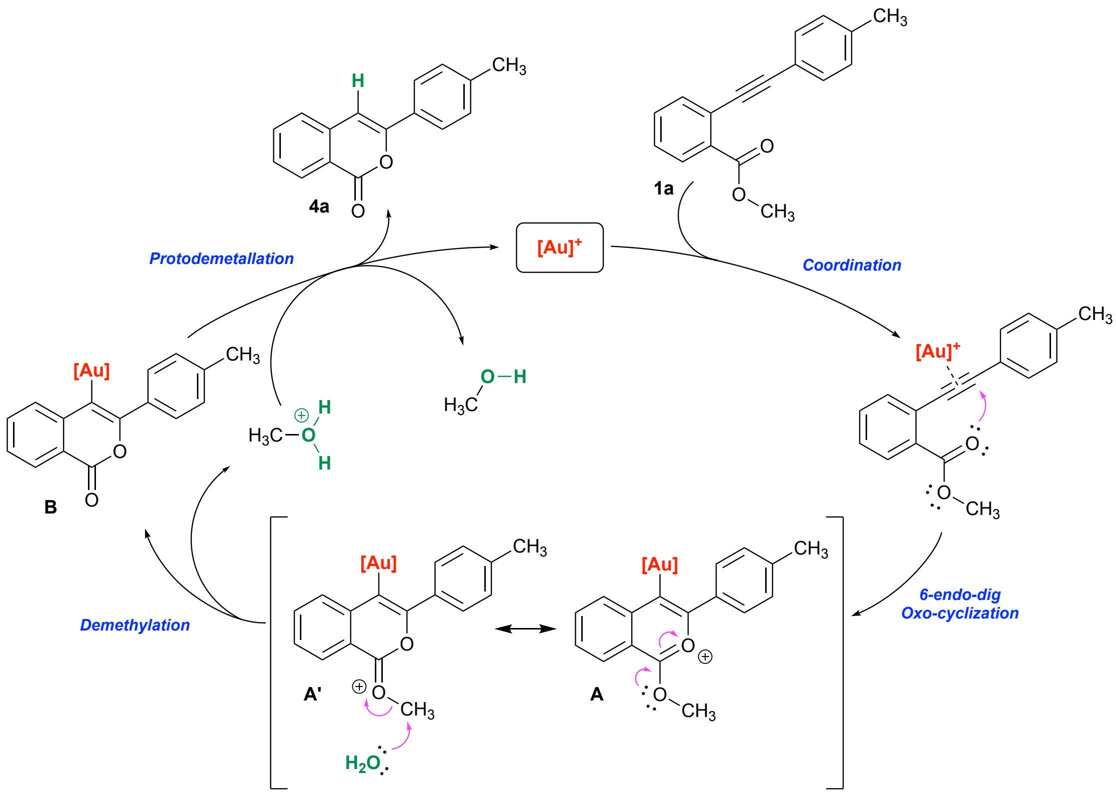
Set-up of catalytic reactions

Blue led and green led irradiation were performed using a Kessil PR160L 467 and a Kessil PR160L 525 lamp, respectively. CFL bulb was instead a Leuci Gemini Saving (21 W) purchased in a local shop.
Catalytic reactions were performed into vials capped with aluminum crimp seals with septa, mounted into a Kessil PR160 RIG with Fan Kit (4 cm from light).



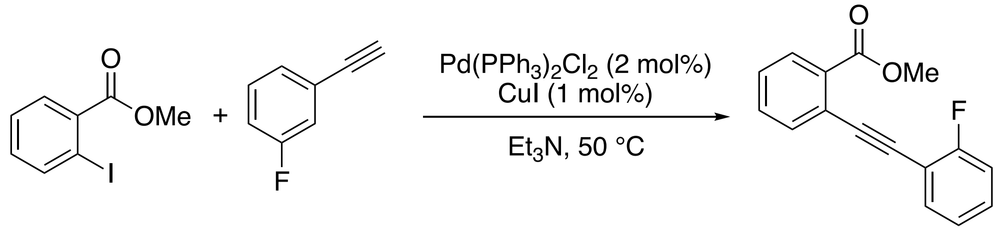


Proposed reaction mechanism for the formation of 4a



Scheme SI 1: Proposed mechanism for gold-catalysed cyclization when the reaction is performed in the dark (Table 1, entry 17).

Synthesis of methyl 2-((2-fluorophenyl)ethynyl)benzoate (1g)



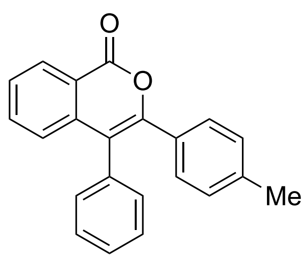
To a stirred and N_2-flushed solution of methyl 2-iodobenzoate (300 mg, 1.14mmol) in anhydrous triethylamine (5 mL), 1-ethynyl-3-fluorobenzene (165 mg, 1.37 mmol, 1.2 equiv) and trans-dichlorobis-(triphenylphosphine)palladium(II) (16 mg, 2 mol%) were added. The reaction was stirred at rt for 10 min, then CuI (3 mg, 1 mol%) was added. The reaction mixture was stirred at 60 °C until no more starting product was detected by TLC analysis (3 h), then it was filtered on Celite and the solvent was removed at reduced pressure. The crude material was purified by flash chromatography over silica gel (Hex/EtOAc 98:2) to yield methyl 2-((2-fluorophenyl)ethynyl)benzoate (**1g**) (268 mg, 93%) as a white wax.

^{1}H NMR (300 MHz, $CDCl_3$): 7.99 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.68 (ddd, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.57 (m, 1H), 7.50 (td, *J* = 7.6, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.33 (m, 1H), 7.15 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.11 (m, 1H), 3.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.8 (C), 162.7 (d, J^1_{C-F} = 252 Hz, C), 134.2 (CH), 133.7 (d, J^4_{C-F} = 1.4 Hz, CH), 131.9 (C), 131.7 (CH), 130.5 (CH), 130.3 (d, J^3_{C-F} = 8.0 Hz, CH), 128.3 (CH), 124.0 (d, J^3_{C-F} = 3.7 Hz, CH), 123.2 (C), 115.6 (d, J^2_{C-F} = 20.9 Hz, CH), 112.0 (d, J^2_{C-F} = 15.7 Hz, C), 93.2 (d, J^3_{C-F} = 3.2 Hz, C), 87.5 (C), 52.2 (CH_3). MS ESI(+): m/z (%) = 255 (100) $[M+H]^+$. Elemental analysis calcd for $C_{16}H_{11}FO_2$: C, 75.58; H, 4.36; found C, 75.32; H, 4.34.

General procedure for the synthesis of 3,4-hetero-substituted Isocoumarins

Eosin Y (2.5 mol%), [Au(PPh_3)NTf_2] (10 mol%), 2-alkynylbenzoate **1a-l** (0. 15 mmol) and aryldiazonium salt **2a-h** (0.6 mmol) were charged into a dry vial equipped with a stirring bar. The vial was capped with an aluminum crimp seal with septum and was evacuated and refilled with N_2 (3x). In the absence of light CH_3CN (1.5 ml, 0.1 M) and H_2O (27 µl, 10 equiv.) were added and the mixture was degassed with N_2 for 5 minutes. Then, the blue LEDs (465 nm, 40 W) were switched on and the reaction mixture was stirred for 1 h at room temperature (fan cooling). After that time, the solvent was evaporated under vacuum and the residue was taken up with EtOAc (5 ml). $NaHCO_3$ ss (5 ml) was added and the crude was extract with EtOAc (3x). Combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. Purification by column chromatography on silica gel yield the corresponding 3,4-disubstituted isocumarin **3a-t**.

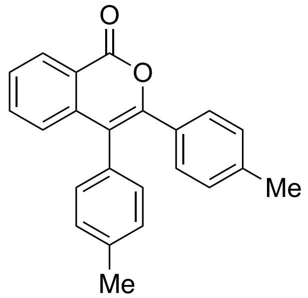
4-phenyl-3-(*p*-tolyl)-1*H*-isochromen-1-one (3a)



General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3a** (45 mg, 96%) as a yellow solid.

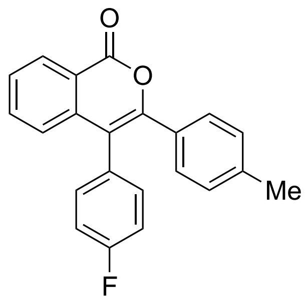
^{1}H NMR (300 MHz, $CDCl_3$): 8.40 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.63 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H), 7.51 (ddd, *J* = 7.9, 7.3, 1.2 Hz, 1H)., 7.44 – 7.38 (m, 3H), 7.30 – 7.21 (m, 4H), 7.18 (d, *J* = 8.1, Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (C), 151.1 (C), 139.1 (C), 139.0 (C), 134.6 (CH), 134.6 (C), 131.2 (CH), 130.0 (C), 129.5 (CH), 129.1 (CH), 128.6 (CH), 128.0 (CH), 127.9 (CH), 125.2 (CH), 120.3 (C), 116.4 (C), 21.3 (CH_3). MS ESI(+): m/z (%) = 335 (100) $[M+Na]^+$. Elemental analysis calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16; found C, 84.71; H, 5.17.

3,4-di-p-tolyl-1H-isochromen-1-one (3b)



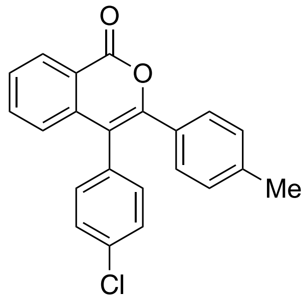
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 4-methylbenzenediazonium tetrafluoroborate (**2b**) (124 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3b** (32 mg, 65%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.39 (ddd, *J* = 7.9, 1.5, 0.6 Hz, 1H), 7.62 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H), 7.49 (ddd, *J* = 7.9, 7.3, 1.2 Hz, 1H), 7.25 – 7.22 (m, 4H), 7.19 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.01 (m, 2H), 2.42 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (C), 150.9 (C), 139.2 (C), 139.0 (C), 137.8 (C), 134.5 (CH), 131.4 (C), 131.0 (CH), 130.1 (C), 129.8 (CH), 129.5 (CH), 129.1 (CH), 128.6 (CH), 127.8 (CH), 125.3 (CH), 120.3 (C), 116.3 (C), 21.4 (CH_3), 21.3 (CH_3). MS ESI(+): m/z (%) = 349 (100) $[M+Na]^+$. Elemental analysis calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56; found C, 84.44; H 5.55.

4-(4-fluorophenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3c)



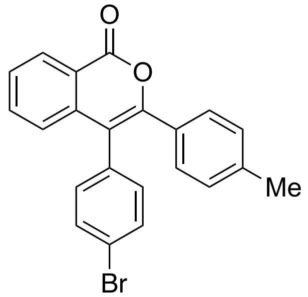
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 4-fluorobenzenediazonium tetrafluoroborate (**2c**) (126 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3c** (43 mg, 87%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.40 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 1H), 7.52 (td, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.18 – 7.07 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.5 (d, J^1_{C-F} = 247 Hz, C), 162.2 (C), 139.3 (C), 138.8 (C), 134.7 (CH), 133.0 (d, J^3_{C-F} = 8.2 Hz, CH) 130.4 (d, J^4_{C-F} = 3.5 Hz, C), 129.9 (C), 129.6 (CH), 129.1 (CH), 128.7 (CH), 128.0 (CH), 125.0 (CH), 120.3 (C), 116.2 (d, J^2_{C-F} = 22 Hz, CH), 115.4 (C), 21.3 (CH_3). One quaternary carbon is missing, probably overlapped. MS ESI(+): m/z (%) = 331 (75) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{15}FO_2$: C, 79.99; H, 4.58; found C, 80.12; H, 4.60.

4-(4-chlorophenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3d)



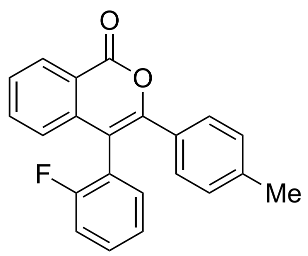
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 4-chlorobenzenediazonium tetrafluoroborate (**2d**) (136 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3d** (36 mg, 68%) as a yellowish solid.
1H NMR (300 MHz, CDCl3): 8.40 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.64 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.52 (ddd, *J* = 7.9, 7.3, 1.2 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.24 – 7.18 (m, 4H), 7.15 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.28 (C), 150.9 (C) 139.5 (C), 138.7 (C), 134.8 (CH), 134.3 (C), 133.2 (C), 132.8 (CH), 129.9 (C), 129.8 (CH), 129.5 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 125.0 (CH), 120.5 (C), 115.4 (C), 21.4 (CH_3). MS ESI(+): m/z (%) = 347 (100) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{15}ClO_2$: C, 76.19; H, 4.36; found C, 75.99; H, 4.37.

4-(4-bromophenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3e)



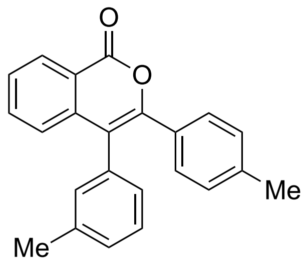
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 4-bromobenzenediazonium tetrafluoroborate (**2e**) (163 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3e** (43 mg, 73%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (ddd, *J* = 7.9, 1.5, 0.6 Hz, 1H), 7.64 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.59 – 7.45 (m, 3H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.1 (C), 151.4 (C), 139.4 (C), 138.5 (C), 134.7 (CH), 133.6 (C), 133.0 (CH), 132.3 (CH), 129.7 (C), 129.7 (CH), 129.1 (CH), 128.8 (CH), 128.1 (CH), 124.9 (CH), 122.3 (C), 120.3 (C), 115.2 (C), 21.3 (CH_3). MS ESI(+): m/z (%) = 392 (75) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{15}BrO_2$: C, 67.54; H, 3.86; found C, 67.61; H, 3.83.

4-(2-fluorophenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3f)



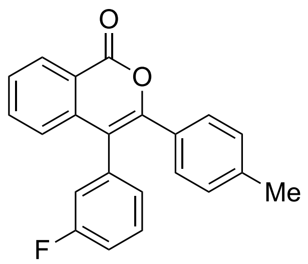
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 2-fluorobenzenediazonium tetrafluoroborate (**2f**) (126 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3f** (42 mg, 84%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.40 (m, 1H), 7.65 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.42 (m, 1H), 7.28 – 7.24 (m, 3H), 7.21 – 7.13 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.2 (C), 161.0 (d, J^1_{C-F} = 246 Hz, C), 152.4 (C), 139.5 (C), 138.2 (C), 134.8 (CH), 133.1 (d, J^4_{C-F} = 3 Hz, CH), 130.5 (d, J^3_{C-F} = 8 Hz, CH), 129.6 (C), 128.8 (CH), 128.6 (CH), 128.1 (CH), 124.9 (CH), 124.7 (d, J^3_{C-F} = 10 Hz, CH), 124.7 (CH), 122.1 (d, J^2_{C-F} = 17 Hz, C), 120.2 (C), 116.1 (d, J^2_{C-F} = 21.6 Hz, CH), 110.4 (C), 21.3 (CH_3). MS ESI(+): m/z (%) = 331 (100) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{15}FO_2$: C, 79.99; H, 4.58; found C, 79.88, H, 4.59.

4-(*m*-tolyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3g)



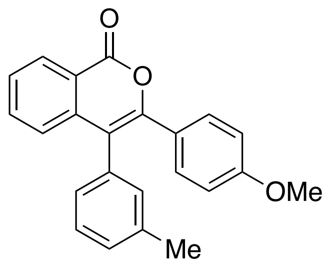
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 3-methylbenzenediazonium tetrafluoroborate (**2g**) (126 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3g** (36 mg, 73%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.39 (m, 1H), 7.62 (m, 1H), 7.50 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.36 – 7.25 (m, 2H), 7.25 – 7.12 (m, 3H), 7.12 – 6.97 (m, 4H), 2.36 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.4 (C), 150.8 (C), 139.2 (C), 139.0 (C), 138.7 (C), 134.5 (CH), 134.4 (C), 131.7 (CH), 130.1 (C), 129.4 (CH), 129.0 (CH), 129.0 (CH), 128.8 (CH), 128.6 (CH), 128.2 (CH), 127.8 (CH), 125.4 (CH), 120.3 (C), 116.4 (C), 21.5 (CH_3), 21.3 (CH_3). MS ESI(+): m/z (%) = 349 (100) $[M+Na]^+$. Elemental analysis calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56; found C 84.77, H, 5.55.

4-(3-fluorophenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3h)



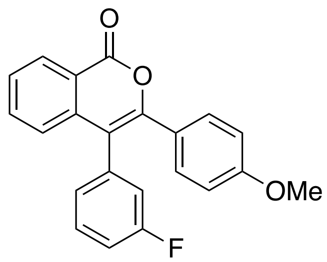
General procedure was followed using methyl 2-(*p*-tolylethynyl)benzoate (**1a**) (37.5 mg, 0.15 mmol) and 3-fluorobenzenediazonium tetrafluoroborate (**2h**) (126 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3h** (42 mg, 85%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.40 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.65 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.40 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.06 (m, 3H), 7.06 – 6.96 (m, 3H), 2.30 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$): 163.1 (d, J^1_{C-F} = 245 Hz, C), 161.4 (C), 151.4 (C), 139.4 (C), 138.5 (C), 136.8 (d, J^3_{C-F} = 8.0 Hz, C) 134.7 (CH), 130.7 (d, J^3_{C-F} = 8.4 Hz, CH), 129.7 (CH), 129.0 (CH), 128.7 (CH), 128.1 (CH), 127.1 (d, J^4_{C-F} = 3.0 Hz, CH), 124.9 (CH), 120.3 (C), 118.3 (d, J^2_{C-F} = 21.7 Hz, CH), 115.7 (C) 115.2 (d, J^2_{C-F} = 21 Hz, CH), 21.3 (CH_3). One quaternary carbon is missing, probably overlapped. MS ESI(+): m/z (%) = 331 (100) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{15}FO_2$: C, 79.99; H, 4.58; found C, 80.06, H, 4.60.

3-(4-methoxyphenyl)-4-(*m*-tolyl)-1*H*-isochromen-1-one (3i)



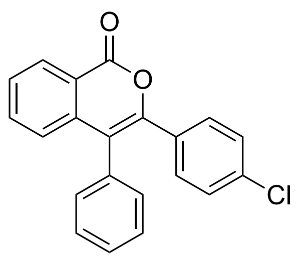
General procedure was followed using methyl 2-((4-methoxyphenyl)ethynyl)benzoate (**1b**) (40 mg, 0.15 mmol) and 3-methylbenzenediazonium tetrafluoroborate (**2g**) (124 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3i** (33 mg, 64%) as a yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.41 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.3, 7.2, 1.5 Hz, 1H), 7.51 (m, 1H), 7.39 – 7.29 (m, 3H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.19 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.74 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.4 (C), 160.0 (C), 150.6 (C), 139.3 (C), 138.9 (C), 134.6 (CH), 134.5 (C), 131.6 (CH), 130.6 (CH), 129.5 (CH), 129.0 (CH), 128.8 (CH), 128.3 (CH), 127.7 (CH), 125.4 (C), 125.2 (CH), 120.1 (C), 115.8 (C), 113.3 (CH), 55.3 (CH_3), 21.5 (CH_3). ESI(+): m/z (%) = 343 (100) $[M+H]^+$. Elemental analysis calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30; found C, 80.91; H, 5.33.

4-(3-fluorophenyl)-3-(4-methoxyphenyl)-1*H*-isochromen-1-one (3j)



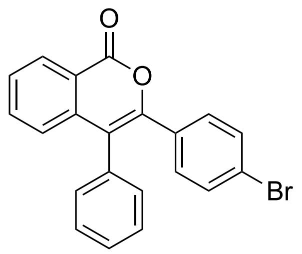
General procedure was followed using methyl 2-((4-methoxyphenyl)ethynyl)benzoate (**1b**) (40 mg, 0.15 mmol) and 3-fluorobenzenediazonium tetrafluoroborate (**2h**) (126 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3j** (32 mg, 62%) as a brown solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.42 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.66 (ddd, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.53 (td, *J* = 7.6, 1.1 Hz, 1H), 7.43 (td, *J* = 8.0, 6.0 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.11 (m, 2H), 7.09 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.02 (ddd, *J* = 9.4, 2.6, 1.5 Hz, 1H), 6.76 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 163.2 (d, $J^1_{C\text{-}F}$ = 248 Hz, C), 162.1 (C), 160.2 (C), 151.2 (C), 138.6 (C), 137.0 (d, $J^3_{C\text{-}F}$ = 8.0 Hz, C) , 134.7 (CH), 130.8 (d, $J^3_{C\text{-}F}$ = 8.3 Hz, CH), 130.6 (CH), 129.7 (CH), 127.9 (CH), 127.2 (d, $J^4_{C\text{-}F}$ = 3.0 Hz, CH), 125.0 (C), 124.8 (CH), 120.2 (C), 118.3 (d, $J^2_{C\text{-}F}$ = 21.4 Hz, CH), 115.2 (d, $J^2_{C\text{-}F}$ = 20.8 Hz, CH), 114.7 (C), 113.5 (CH), 55.3 (CH_3). ESI(+): m/z (%) = 369 (100) $[M+Na]^+$. Elemental analysis calcd for $C_{22}H_{15}FO_3$: C, 76.29; H, 4.37 found C, 76.51; H, 4.40.

3-(4-chlorophenyl)-4-phenyl-1*H*-isochromen-1-one (3k)



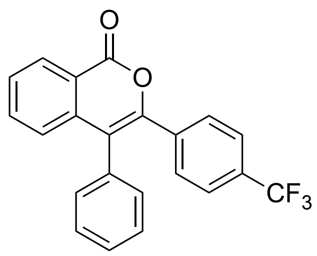
General procedure was followed using methyl 2-((4-chlorophenyl)ethynyl)benzoate (**1c**) (41 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3k** (38 mg, 76%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.41 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.65 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.54 (ddd, *J* = 7.8, 7.3, 1.2 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.29 – 7.23 (m, 4H), 7.21 – 7.14 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.0 (C), 149.7 (C), 138.7 (C), 135.0 (C), 134.7 (CH), 134.1 (C), 131.4 (C), 131.1 (CH), 130.5 (CH), 129.6 (CH), 129.3 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 125.4 (CH), 120.5 (C), 117.3 (C). MS ESI(+): m/z (%) = 333 (100) $[M+H]^+$. Elemental analysis calcd for $C_{21}H_{13}ClO_2$: C, 75.79; H, 3.94; found C, 76.01; H, 3.95.

3-(4-bromophenyl)-4-phenyl-1*H*-isochromen-1-one (3l)



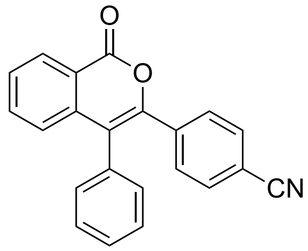
General procedure was followed using methyl 2-((4-bromophenyl)ethynyl)benzoate (**1d**) (37.2 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3l** (34 mg, 60%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.43 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67 (td, *J* = 7.7, 1.5 Hz, 1H), 7.56 (m, 1H), 7.49 – 7.43 (m, 3H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.0 (C), 149.7 (C), 138.7 (C), 134.8 (CH), 134.0 (C), 131.8 (C), 131.2 (CH), 131.1 (CH), 130.7 (CH), 129.6 (CH), 129.3 (CH), 128.4 (CH), 128.4 (CH), 125.5 (CH), 123.4 (C), 120.5 (C), 117.3 (C). MS ESI(+): m/z (%) = 378 (80) $[M+H]^+$. Elemental analysis calcd for $C_{21}H_{13}BrO_2$: C, 66.86; H, 3.47; found C, 66.99; H, 3.49.

4-phenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-isochromen-1-one (3m)



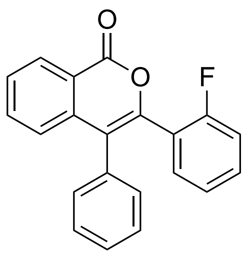
General procedure was followed using methyl 2-((4-(trifluoromethyl)phenyl)ethynyl)benzoate (**1e**) (46 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3m** (39 mg, 71%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.42 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.67 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.56 (ddd, *J* = 7.8, 7.3, 1.2 Hz, 1H), 7.49 – 7.39 (m, 7H), 7.29 – 7.24 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): 161.8 (C), 149.1 (C), 138.4 (C), 136.6 (C), 135.0 (CH), 133.7 (C), 131.0 (CH), 130.6 (q, J^2_{C-F} = 32.8 Hz, C), 129.7 (CH), 129.4 (CH), 129.3 (CH), 129.7 (CH), 128.6 (CH), 125.6 (CH), 124.8 (q, J^3_{C-F} = 3.8 Hz, CH), 123.8 (q, J^1_{C-F} = 272 Hz, C), 120.6 (C), 118.2 (C). MS ESI(+): m/z (%) = 389 (100) $[M+Na]^+$. Elemental analysis calcd for $C_{22}H_{13}F_3O_2$: C, 72.13; H, 3.58; found C, 71.94; H, 3.56.

4-(1-oxo-4-phenyl-1*H*-isochromen-3-yl)benzonitrile (3n)



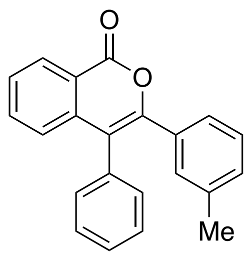
General procedure was followed using methyl 2-((4-cyanophenyl)ethynyl)benzoate (**1f**) (39.2 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3n** (33 mg, 68%) as a yellowish thick oil.
^{1}H NMR (300 MHz, $CDCl_3$): 8.42 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.68 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 7.58 (ddd, *J* = 7.8, 7.3, 1.2 Hz, 1H), 7.49 (m, 1H), 7.48 – 7.40 (m, 6H), 7.28 – 7.20 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.6 (C), 148.5 (C), 138.2 (C), 137.2 (C), 134.9 (CH), 133.4 (C), 131.6 (CH), 130.9 (CH), 129.7 (CH), 129.6 (CH), 129.4 (CH), 129.0 (CH), 128.8 (CH), 125.8 (CH), 120.7 (C), 118.9 (C), 118.3 (C), 112.4 (C).
MS ESI(+): m/z (%) = 324 (100) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{13}NO_2$: C, 81.72; H, 4.05; N, 4.33; found C, 81.96; H, 4.04; N, 4.31.

3-(2-fluorophenyl)-4-phenyl-1*H*-isochromen-1-one (3o)



General procedure was followed using methyl 2-((2-fluorophenyl)ethynyl)benzoate (**1g**) (38.1 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3o** (31 mg, 65%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.45 (d, *J* = 7.9 Hz, 1H), 7.69 (td, *J* = 7.7, 1.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.15 (m, 5H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 9.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.1 (C), 159.8 (d, $J^1_{C\text{-}F}$ = 252 Hz, C), 147.1 (C), 138.1 (C), 134.7 (CH), 133.4 (C), 131.7 (d, $J^4_{C\text{-}F}$ = 2.5 Hz, CH), 131.3 (d, $J^3_{C\text{-}F}$ = 8.3 Hz, CH), 130.8 (CH), 129.8 (CH), 128.5 (CH), 128.5 (CH), 128.0 (CH), 125.3 (CH), 123.7 (d, $J^3_{C\text{-}F}$ = 3.7 Hz, CH), 121.5 (d, $J^2_{C\text{-}F}$ = 15 Hz, C), 120.9 (C), 119.6 (C), 115.8 (q, $J^2_{C\text{-}F}$ = 21.6 Hz, CH). MS ESI(+): m/z (%) = 339 (30) $[M+H]^+$. Elemental analysis calcd for $C_{21}H_{13}FO_2$: C, 79.74; H, 4.14; found C, 79.66; H, 4.15.

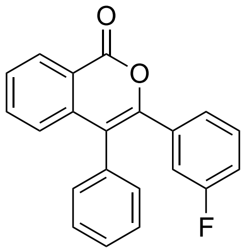
4-phenyl-3-(*m*-tolyl)-1*H*-isochromen-1-one (3p)



General procedure was followed using methyl 2-(*m*-tolylethynyl)benzoate (**1h**) (37.6 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3p** (40 mg, 87%) as a grey solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.41 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.3, 7.2, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.2 Hz, 1H), 7.42 – 7.40 (m, 3H), 7.31 – 7.19 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.3 (C), 151.1 (C), 138.9 (C), 137.6 (C), 134.6 (CH), 134.5 (C), 132.8 (C), 131.3 (CH), 129.8

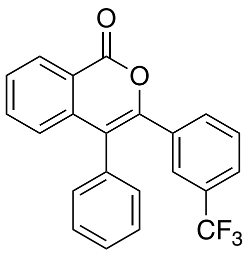
(CH), 129.7 (CH), 129.6 (CH), 129.0 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 126.4 (CH), 125.3 (CH), 120.4 (C), 116.8 (C), 21.3 (CH_3). MS ESI(+): m/z (%) = 313 (100) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16; found C, 84.43; H, 5.18.

3-(3-fluorophenyl)-4-phenyl-1*H*-isochromen-1-one (3q)



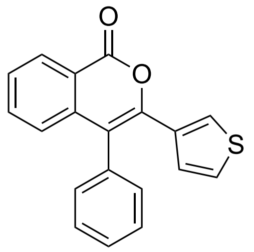
General procedure was followed using methyl 2-((3-fluorophenyl)ethynyl)benzoate (**1i**) (38.1 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3q** (20 mg, 42%) as a white thick solid.
^{1}H NMR (400 MHz, CDCl3): 8.44 (dd, J = 7.9, 1.5 Hz, 1H), 7.68 (ddd, J = 8.3, 7.3, 1.5 Hz, 1H), 7.57 (td, J = 7.6, 1.2 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.39 – 7.25 (m, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.07 (m, 1H), 6.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.2 (d, J^1_{C-F} = 244 Hz, C), 161.9 (C), 149.4 (d, J^4_{C-F} = 2.8 Hz, C), 138.6 (C), 135.0 (d, J^3_{C-F} = 8.1 Hz, C), 134.8 (CH), 133.9 (C), 131.1 (CH), 129.6 (CH), 129.4 (d, J^3_{C-F} = 8.2 Hz, CH), 129.3 (CH), 128.5 (CH), 128.4 (CH), 125.6 (CH), 124.9 (d, J^4_{C-F} = 3.0 Hz, CH), 120.6 (C), 117.6 (C), 116.2 (d, J^2_{C-F} = 21.6 Hz, CH), 116.0 (d, J^2_{C-F} = 18.8 Hz, CH).MS ESI(+): m/z (%) = (338) $[M+Na]^+$. Elemental analysis calcd for $C_{21}H_{13}FO_2$: C, 79.74; H, 4.14; found C, 79.91, H, 4.13.

4-phenyl-3-(3-(trifluoromethyl)phenyl)-1*H*-isochromen-1-one (3r)



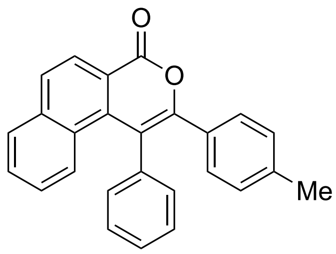
General procedure was followed using methyl 2-((3-(trifluoromethyl)phenyl)ethynyl)benzoate (**1j**) (45.6 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3r** (23 mg, 42%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 8.43 (ddd, J = 7.8, 1.5, 0.6 Hz, 1H), 7.67 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.61 – 7.53 (m, 3H), 7.51 – 7.41 (m, 4H), 7.37 – 7.29 (m, 1H), 7.29 – 7.21 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.8 (C), 149.1 (C), 138.4 (C), 134.8 (CH), 133.6 (C), 132.2 (q, J^4_{C-F} = 1.4 Hz, CH), 131.0 (CH), 130.4 (q, J^2_{C-F} = 31.7 Hz, C), 129.7 (CH), 129.3 (CH), 128.6 (CH), 128.6 (CH), 128.4 (CH), 127.3 (q, J^1_{C-F} = 272 Hz, C), 126.1 (q, J^3_{C-F} = 4 Hz, CH), 125.6 (CH), 126.4 (q, J^3_{C-F} = 3.7 Hz, CH), 121.8 (C), 120.6 (C), 118.0 (C). MS ESI(+): m/z (%) = 367 (30) $[M+H]^+$. Elemental analysis calcd for $C_{22}H_{13}F_3O_2$: C, 72.13; H, 3.58; found C, 72.09; H, 3.61.

4-phenyl-3-(thiophen-3-yl)-1*H*-isochromen-1-one (3s)



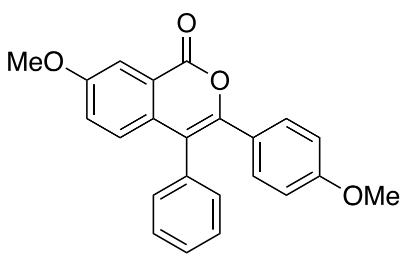
General procedure was followed using methyl 2-(thiophen-3-ylethynyl)benzoate (**1k**) (36.4 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3s** (26 mg, 56%) as a yellow wax.
^{1}H NMR (400 MHz, $CDCl_3$): 8.40 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1H), 7.62 (m, 1H), 7.58 – 7.45 (m, 4H), 7.41 – 7.32 (m, 3H), 7.12 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.74 (dd, *J* = 5.2, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.0 (C), 146.9 (C), 139.3 (C), 134.6 (CH), 134.1 (C), 130.9 (CH), 129.6 (CH), 129.5 (CH), 128.7 (CH), 127.9 (CH), 127.2 (CH), 126.9 (CH), 125.4 (CH), 125.0 (CH), 120.3 (C), 115.5 (C). One quaternary carbon is missing, probably overlapped. MS ESI(+): m/z (%) = 305 (33) $[M+H]^+$. Elemental analysis calcd for $C_{19}H_{12}O_2S$: C, 74.98; H, 3.97; found C, 75.11; H, 4.00.

1-phenyl-2-(*p*-tolyl)-4*H*-benzo[*f*]isochromen-4-one (3t)



General procedure was followed using methyl 1-(*p*-tolylethynyl)-2-naphthoate (**1l**) (45 mg, 0.15 mmol) and benzenediazonium tetrafluoroborate (**2a**) (115 mg, 0.6 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3t** (28 mg, 52%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.41 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.33 – 7.22 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.05 (m, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 162.8 (C), 153.3 (C), 138.7 (C), 137.8 (C), 137.5 (C), 137.0 (C), 131.6 (CH), 130.8 (C), 129.9 (CH), 129.5 (CH), 129.2 (CH), 129.0 (CH), 128.8 (C), 128.4 (CH), 128.4 (CH), 128.1 (CH), 128.1 (CH), 125.6 (CH), 124.4 (CH), 119.0 (C), 117.3 (C), 21.3 (CH_3). MS ESI(+): m/z (%) = 384 (20) $[M+Na]^+$. Elemental analysis calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01; found C, 86.28; H, 5.03.

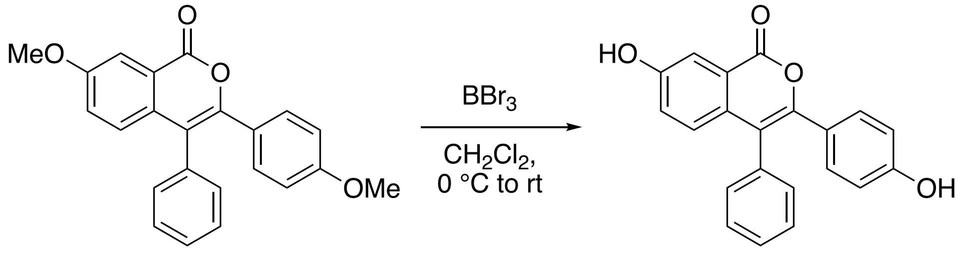
7-methoxy-3-(4-methoxyphenyl)-4-phenyl-1*H*-isochromen-1-one (3u)



General procedure was followed using methyl 5-methoxy-2-((4-methoxyphenyl)ethynyl)benzoate (**1m**) (74.1 mg, 0.25 mmol) and benzenediazonium tetrafluoroborate (**2a**) (192 mg, 1 mmol). Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3u** (49 mg, 55%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): 7.80 (d, *J* = 2.7 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.29 – 7.23 (m, 4H), 7.20 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.10 (dd, *J* = 8.9, 0.5 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 2H), 3.93 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (75 MHz,

$CDCl_3$): 162.5 (C), 159.7 (C), 159.2 (C), 148.9 (C), 134.8 (C), 132.8 (C), 131.2 (CH), 130.5 (CH), 129.1 (CH), 128.0 (CH), 126.9 (CH), 125.4 (C), 124.2 (CH), 121.3 (C), 115.7 (C), 113.3 (CH), 109.8 (CH), 55.8 (CH_3), 55.2 (CH_3). MS ESI(+): m/z (%) = 381 (70) $[M+Na]^+$. Elemental analysis calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06; found C, 77.34; H, 5.08.

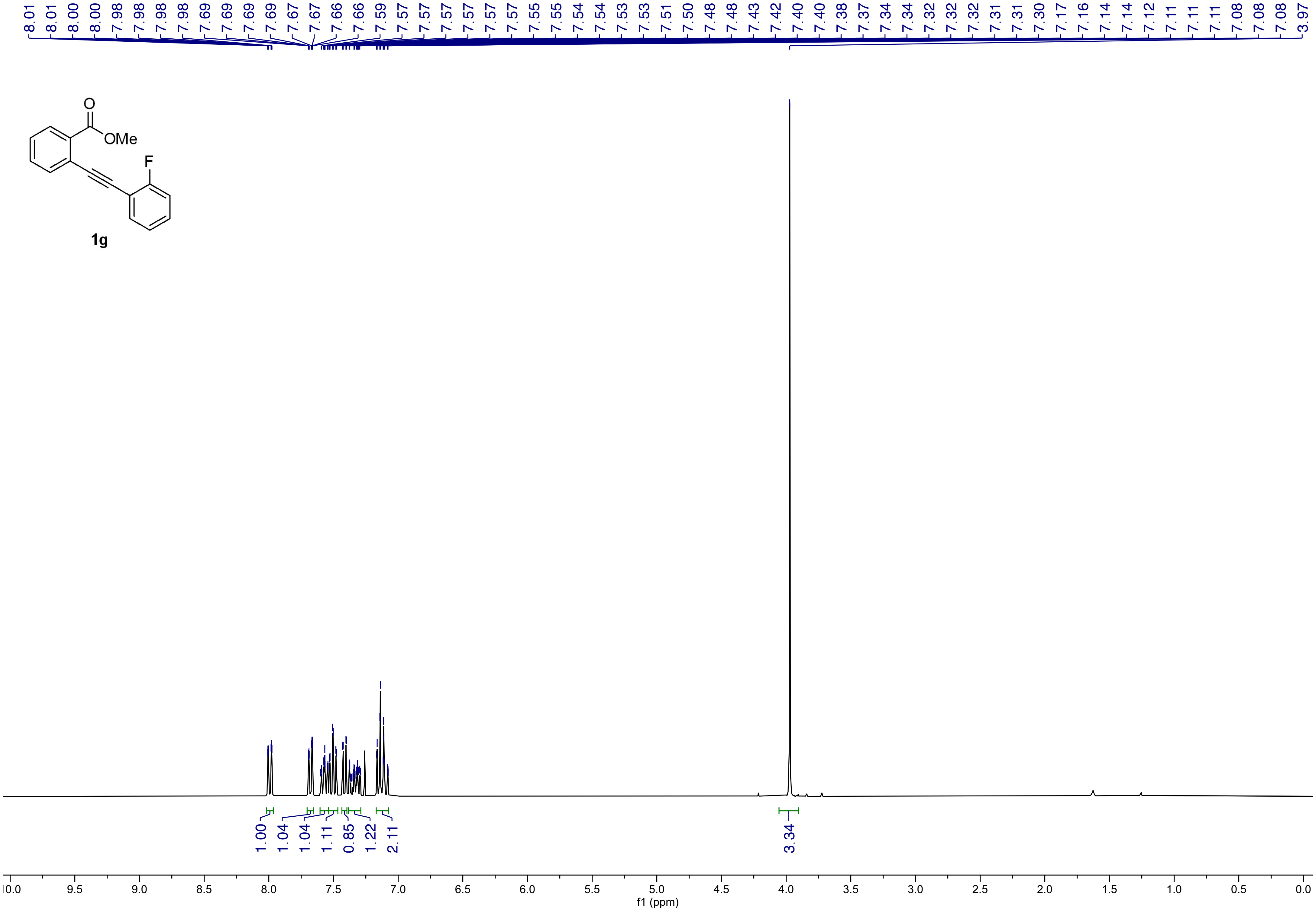
Synthesis of 7-hydroxy-3-(4-hydroxyphenyl)-4-phenyl-1*H*-isochromen-1-one (3v)



3u **3v**

Product **3v** was synthetized following the method described by Katzenellenbogen and coworkers.[4] A solution of **3u** (20 mg, 0.05 mmol) in CH_2Cl_2 (1.0 ml) was cooled at 0 °C and BBr_3 (26 µl, 3 equiv.) was added dropwise. The reaction was warmed up to rt and stirred for 24 h. After that time the reaction was quenched with H_2O (1 ml) and extracted with EtOAc (3x5ml). The combined organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified with column chromatography (SiO_2, Hex/EtOAc 3:1 to 1:1) to yield **3v** (15 mg, 90%) as a yellow solid.
^{1}H NMR (300 MHz, acetone-d_6): 9.18 (s, 1H), 8.65 (s, 1H), 7.72 (dd, *J* = 2.7, 0.5 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.31 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.26 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.03 (dd, *J* = 8.8, 0.5 Hz, 1H), 6.73 – 6.65 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6): 161.3 (C), 157.8 (C), 157.2 (C), 148.8 (C), 135.2 (C), 131.5 (C), 131.2 (CH), 130.5 (CH), 128.9 (CH), 127.8 (CH), 127.0 (CH), 124.7 (C), 123.5 (CH), 121.5 (C), 115.3 (C), 114.7 (CH), 113.0 (CH). MS ESI(+): m/z (%) = 353 (100) $[M+Na]^+$. Elemental analysis calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.27; found C, 76.28; H, 4.30.

[4] M. De Angelis, F. Stossi, M. Waibel, B. S. Katzenellenbogen and J. A. Katzenellenbogen, *Bioorg. Med. Chem.*, 2005, **13**, 6529-6542.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O
OMe
F
1g
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1.04
1.11
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1.22
2.11
3.34
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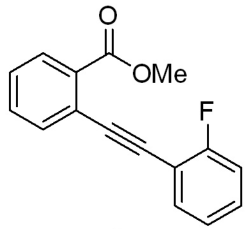
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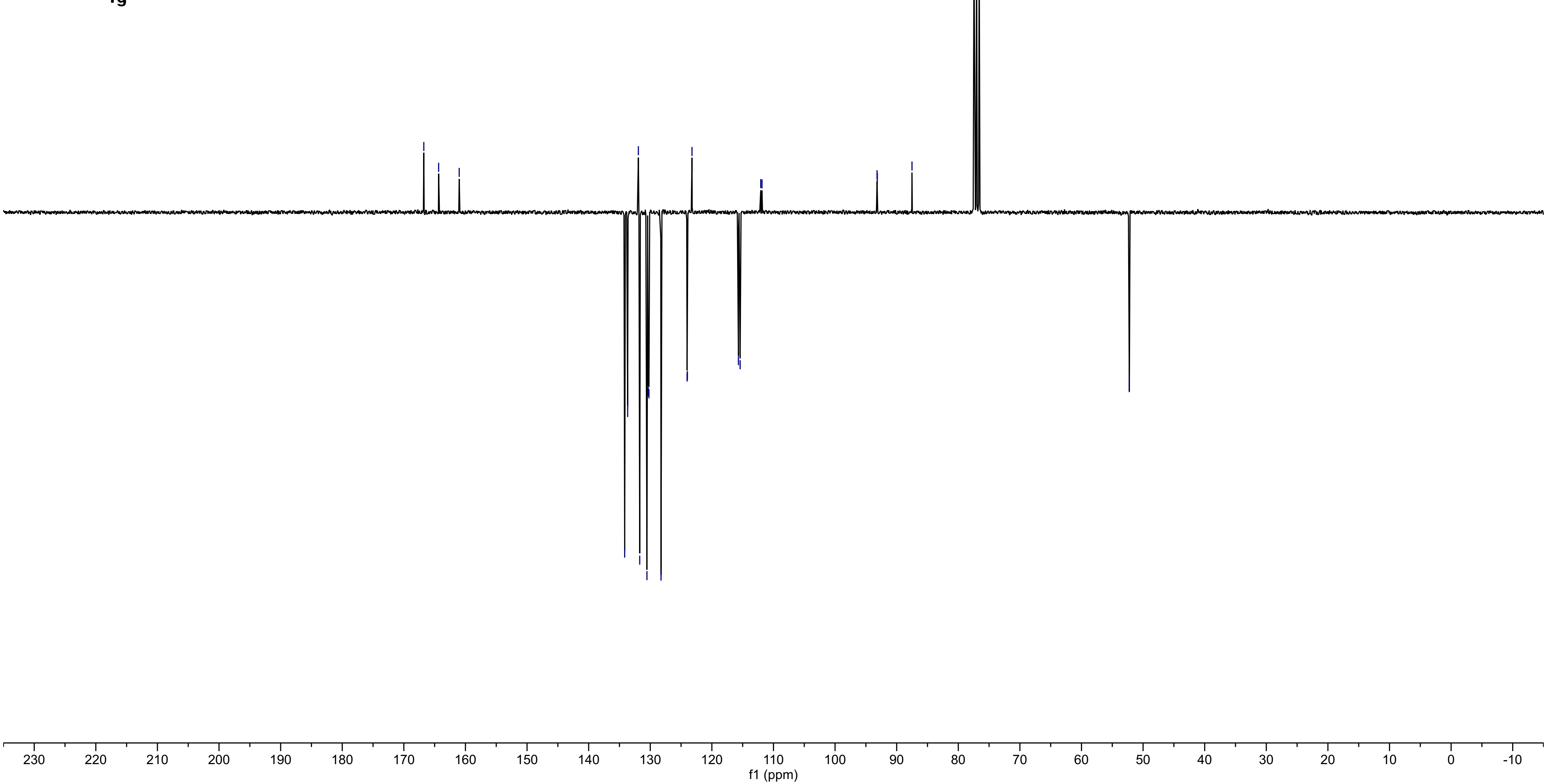
1g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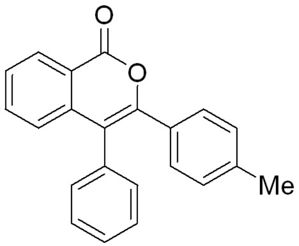
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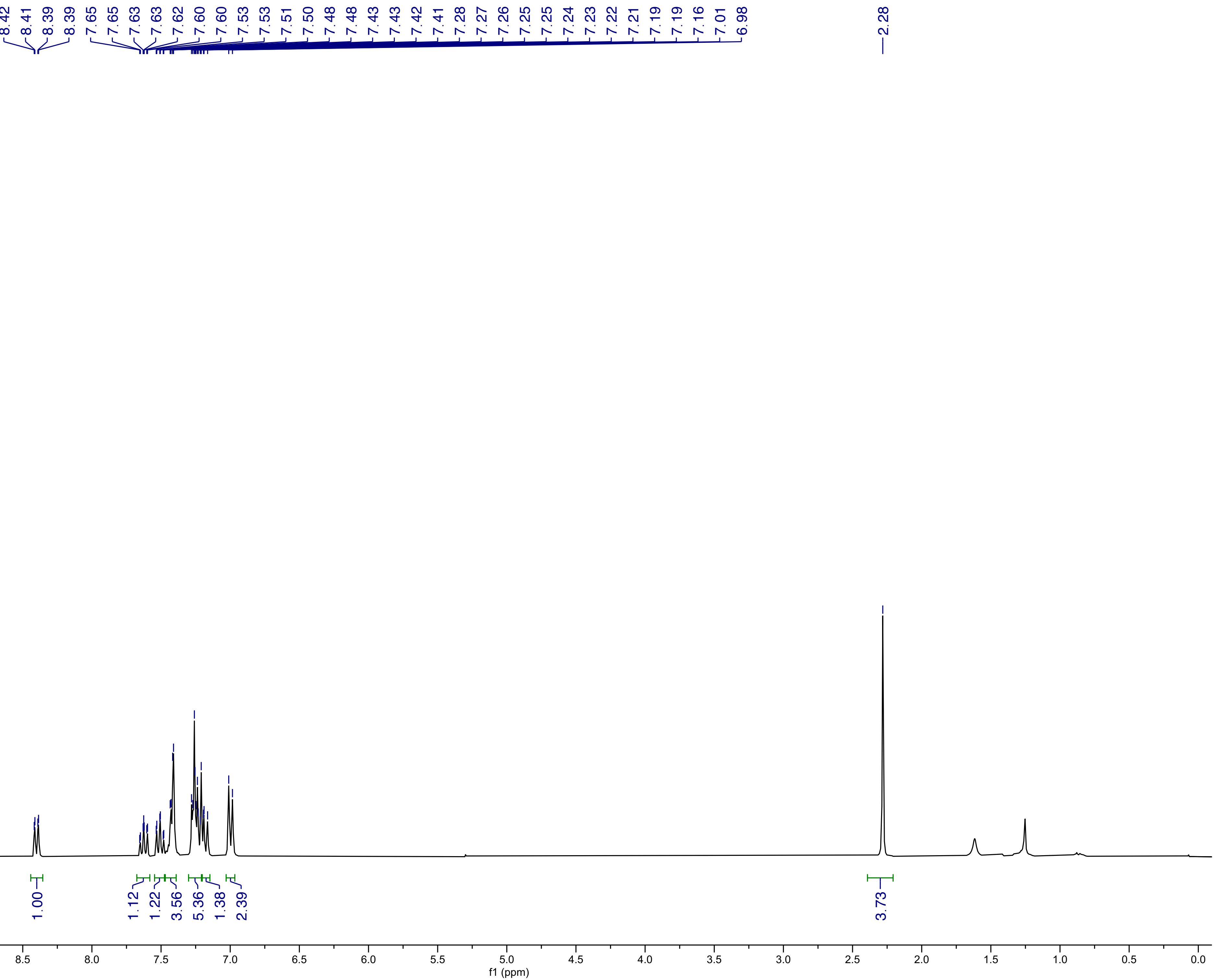
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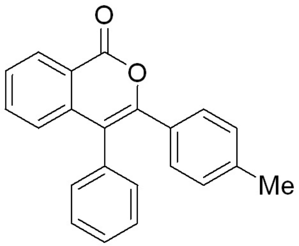
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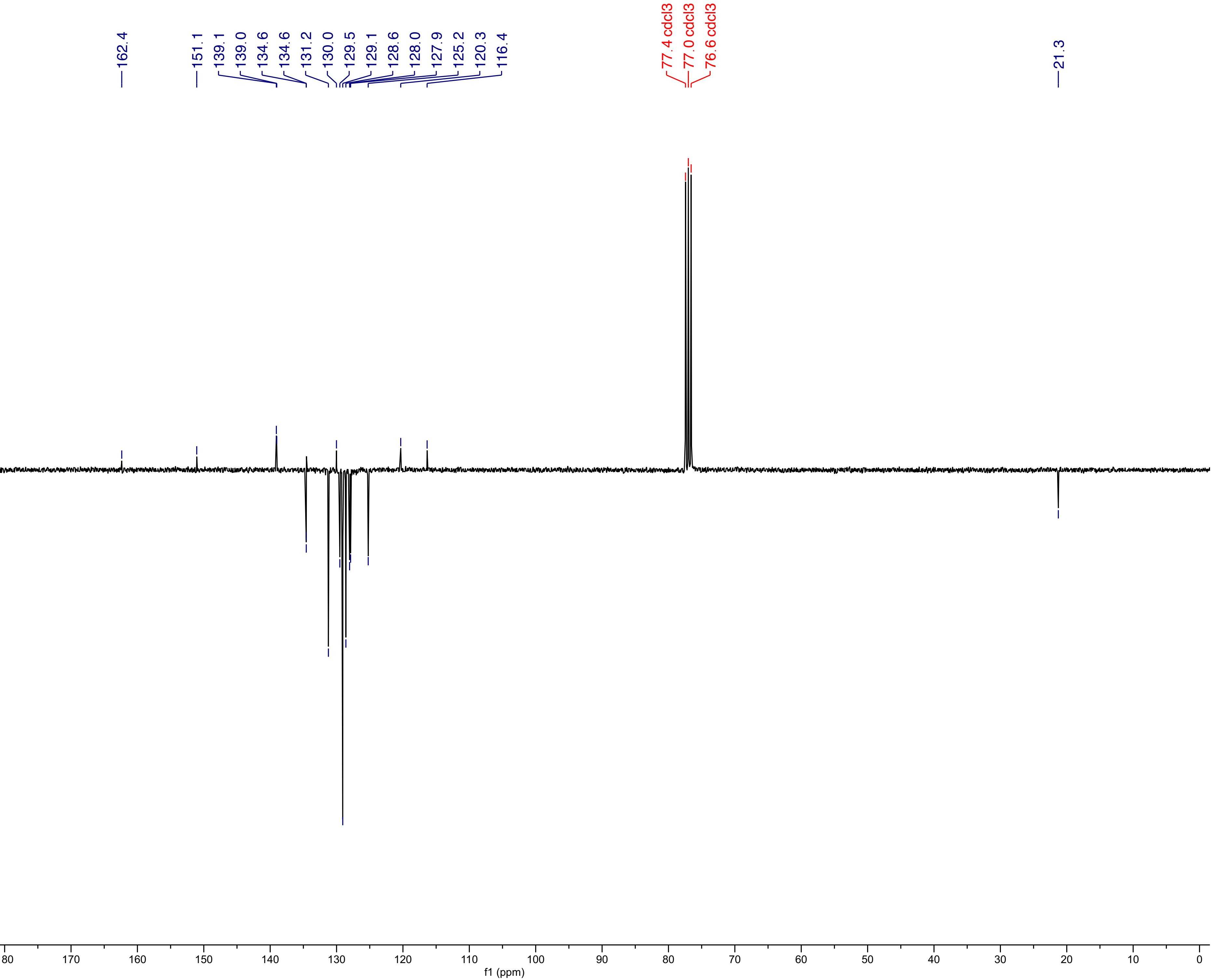
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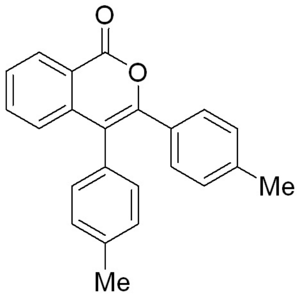
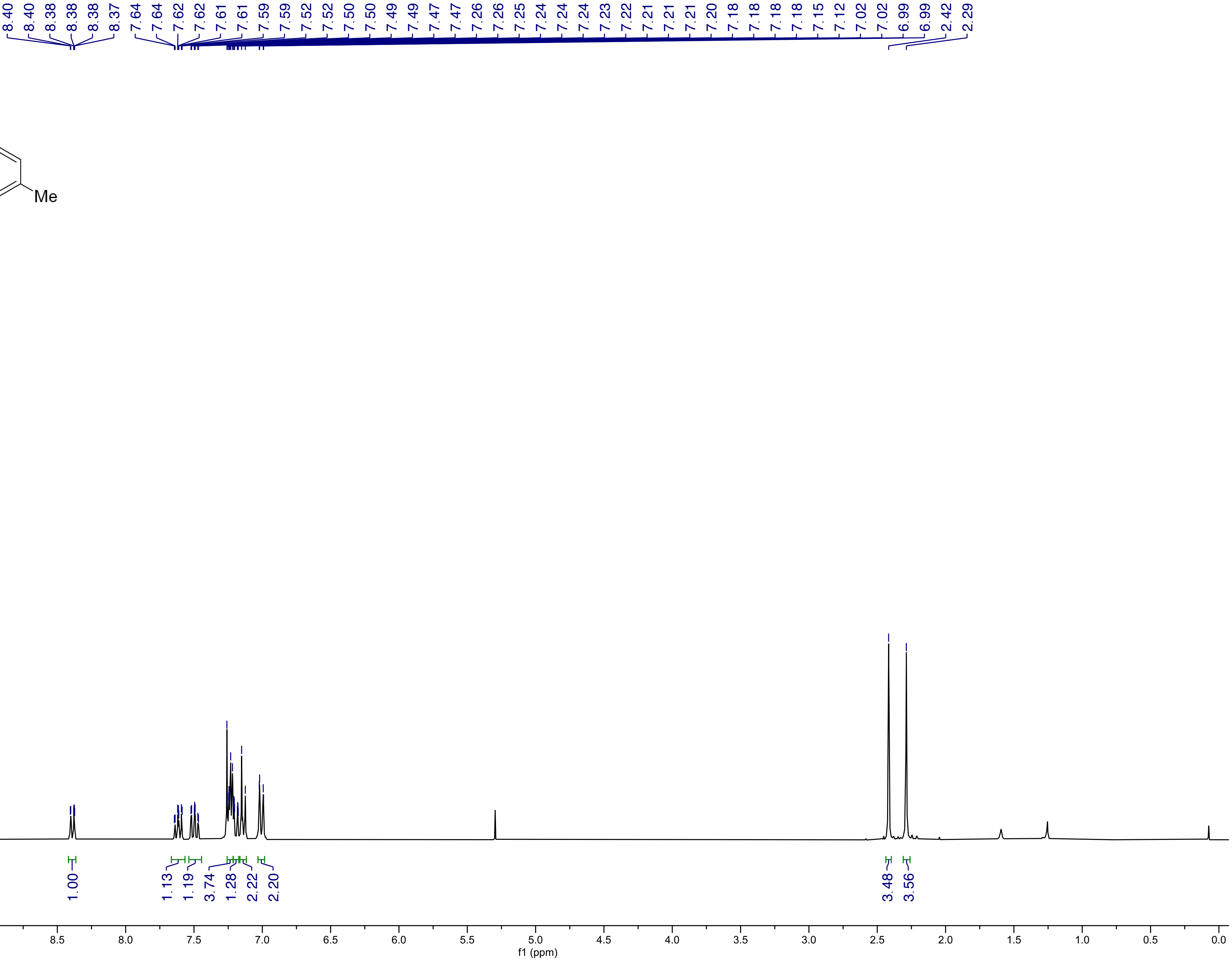
f1 (ppm)



O
O
Me
Me

3b



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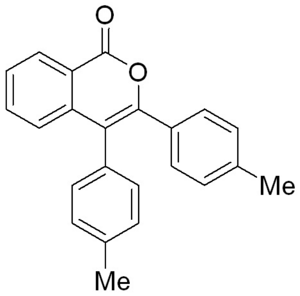
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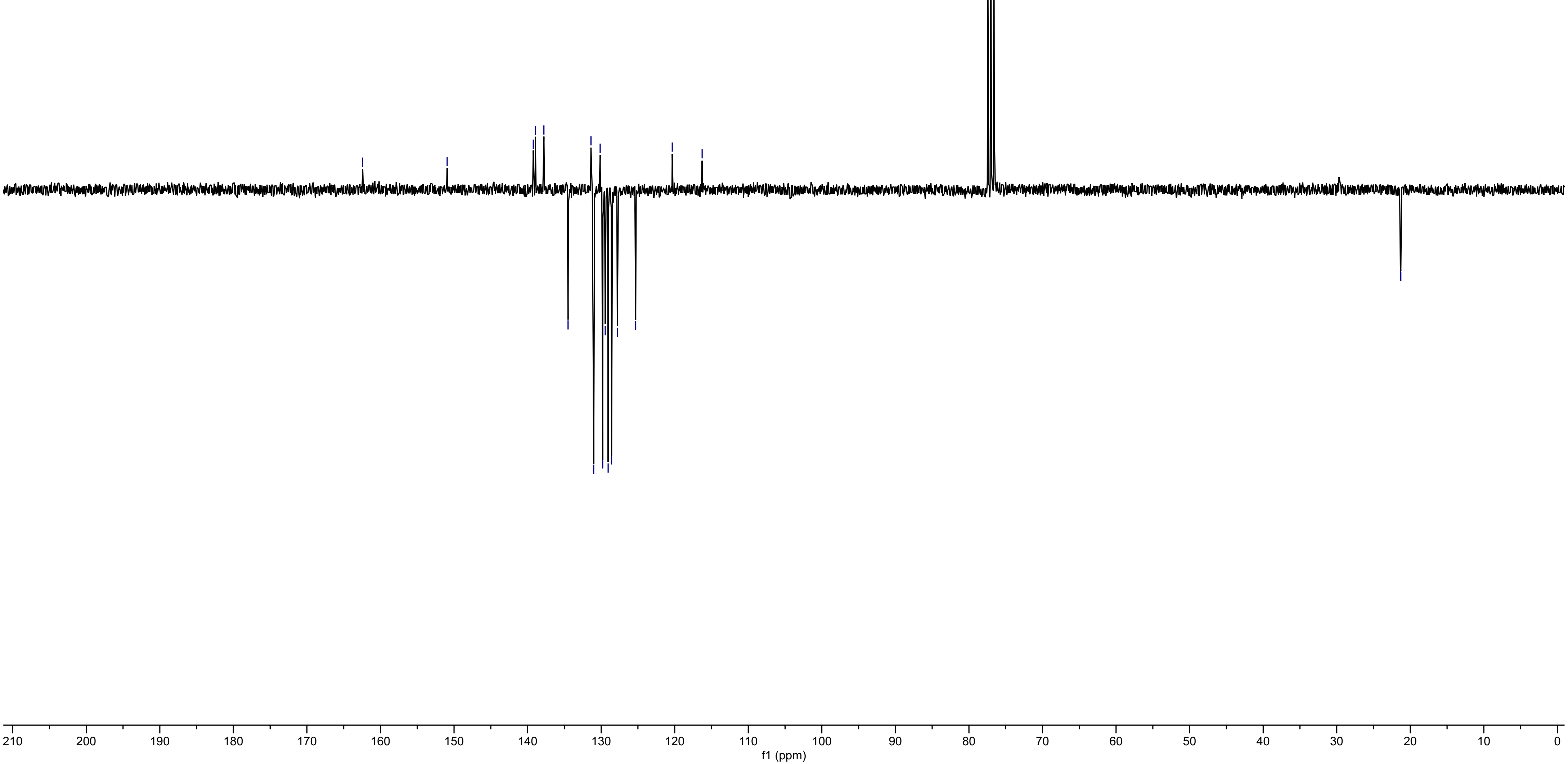
O
Me
Me

3b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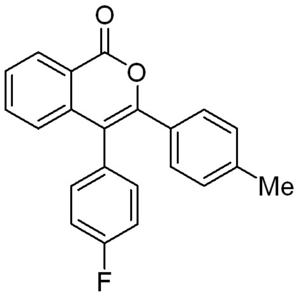
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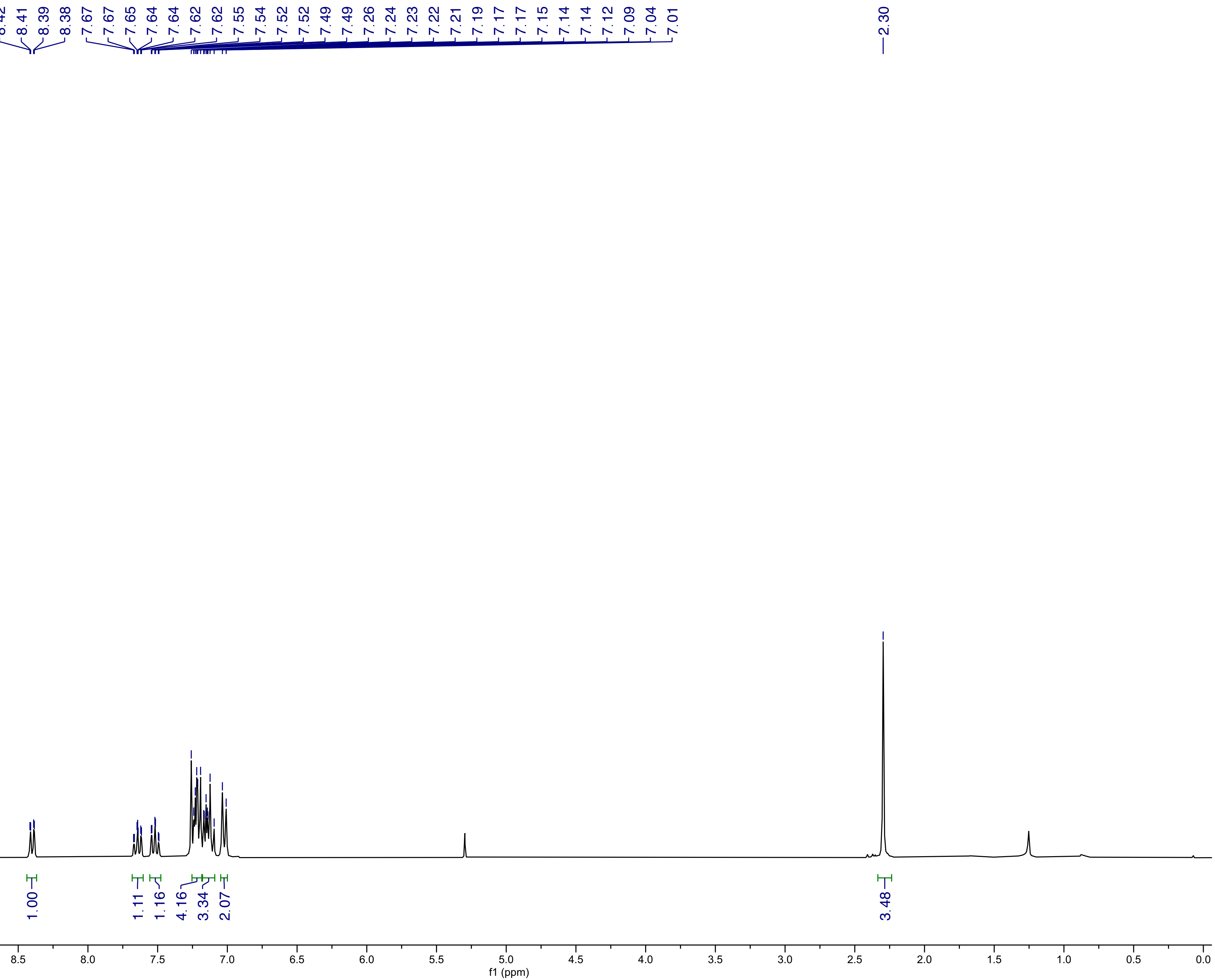
3c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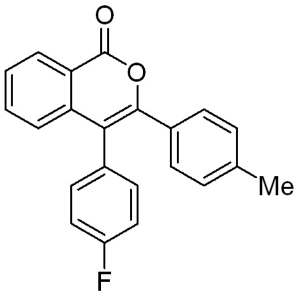
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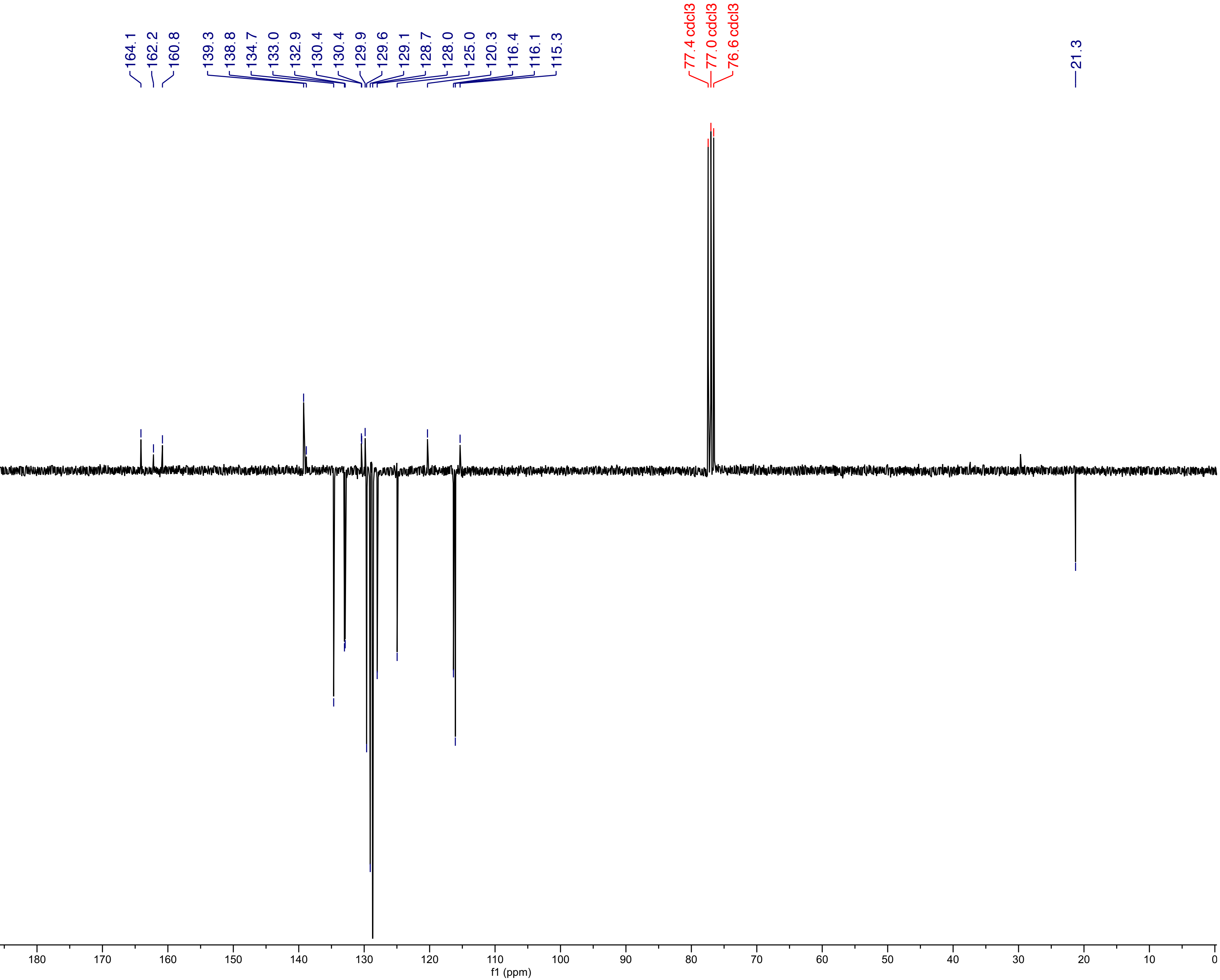
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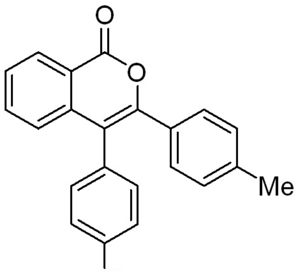
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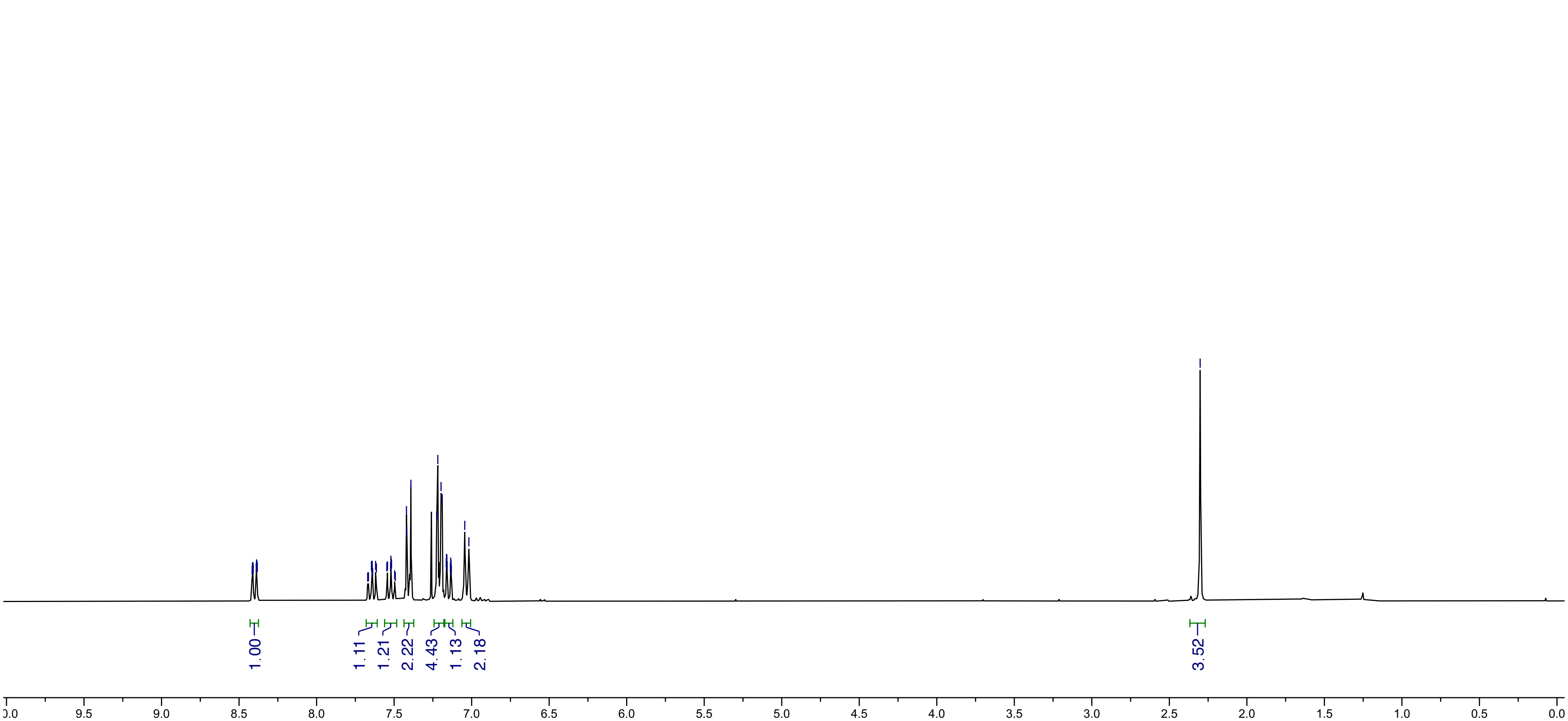
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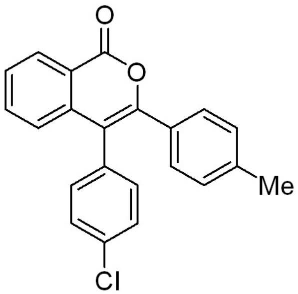
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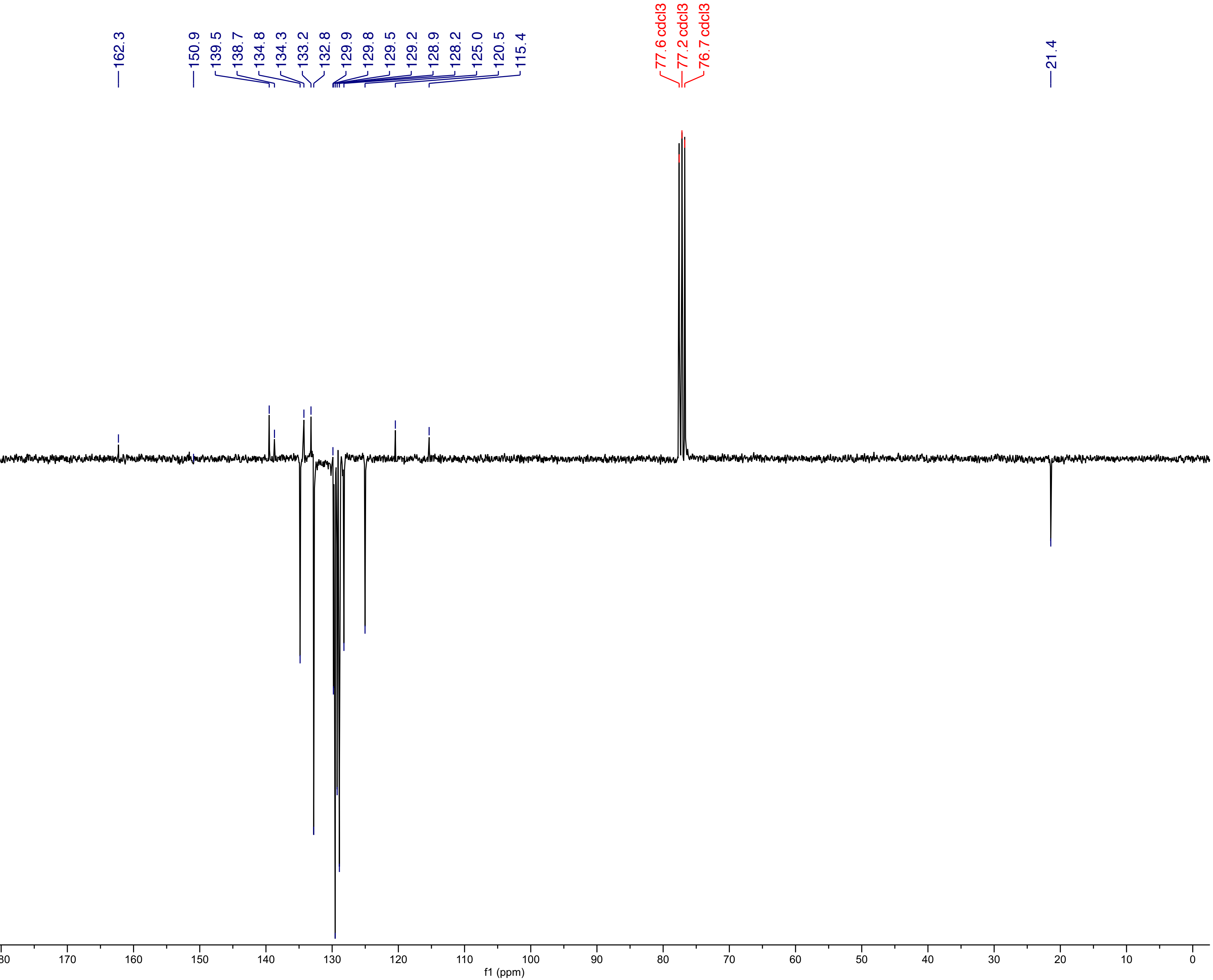
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77.2 cdcl3
76.7 cdcl3
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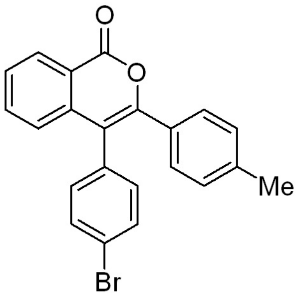
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Me
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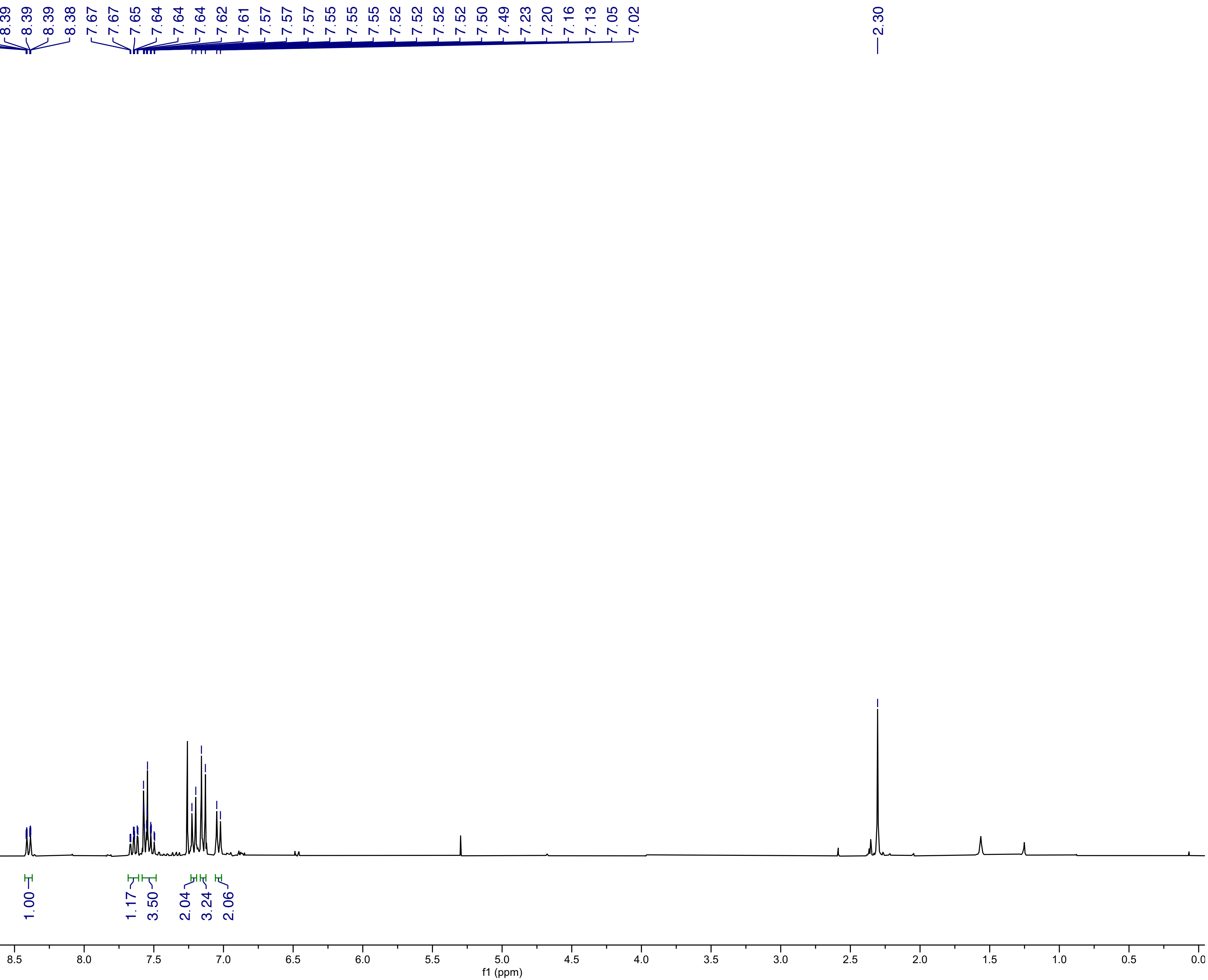
3e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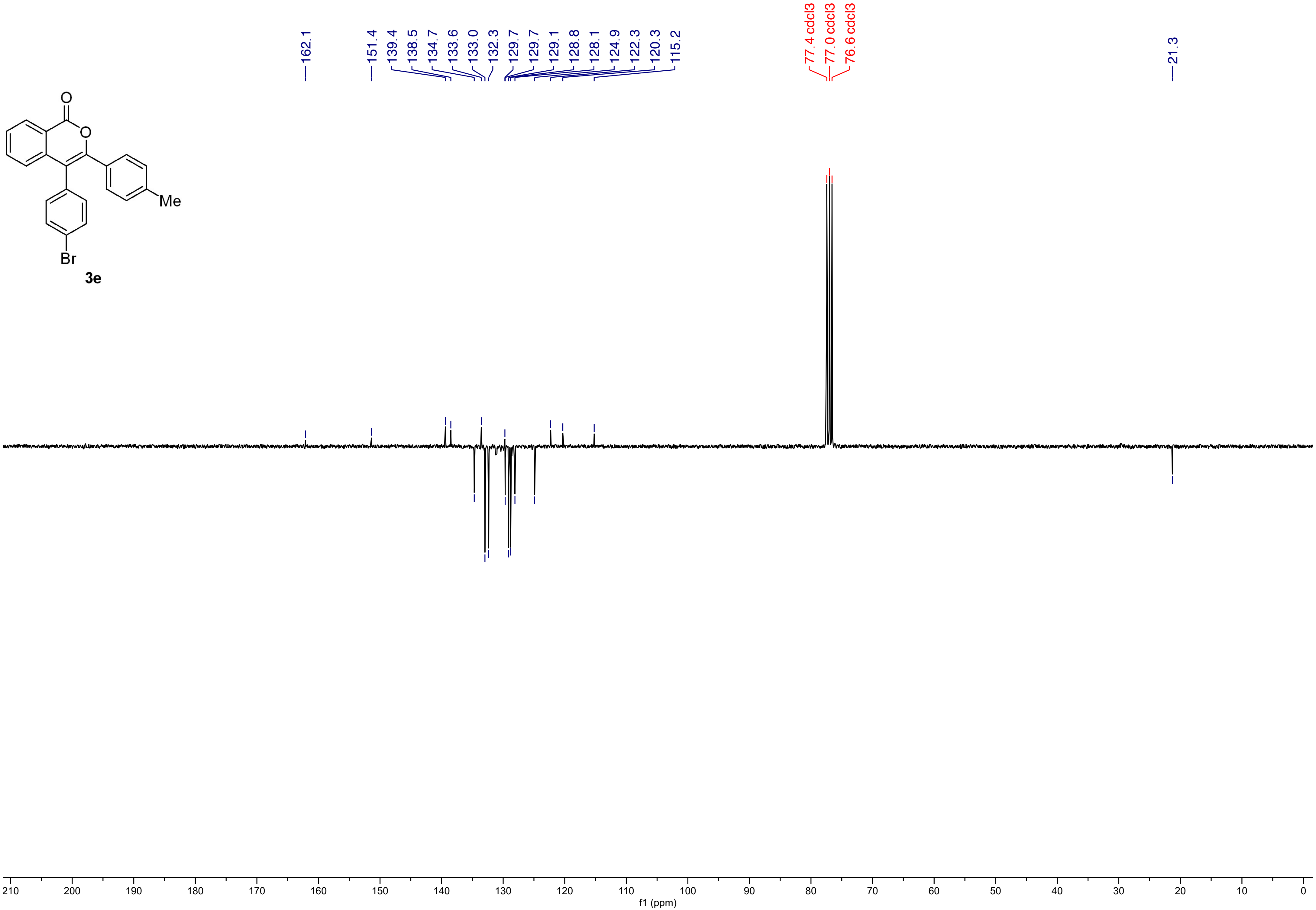
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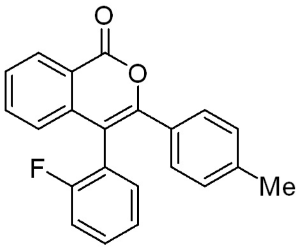
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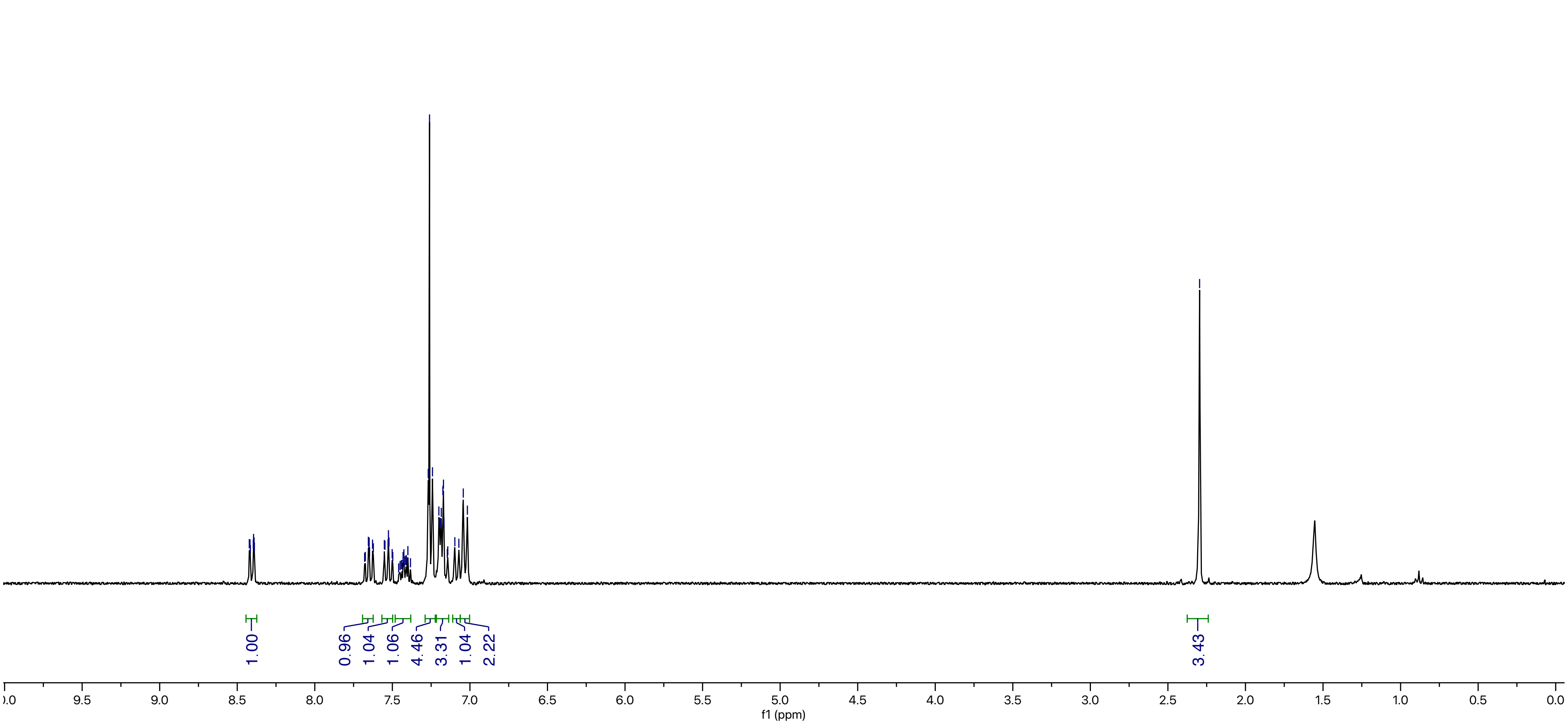
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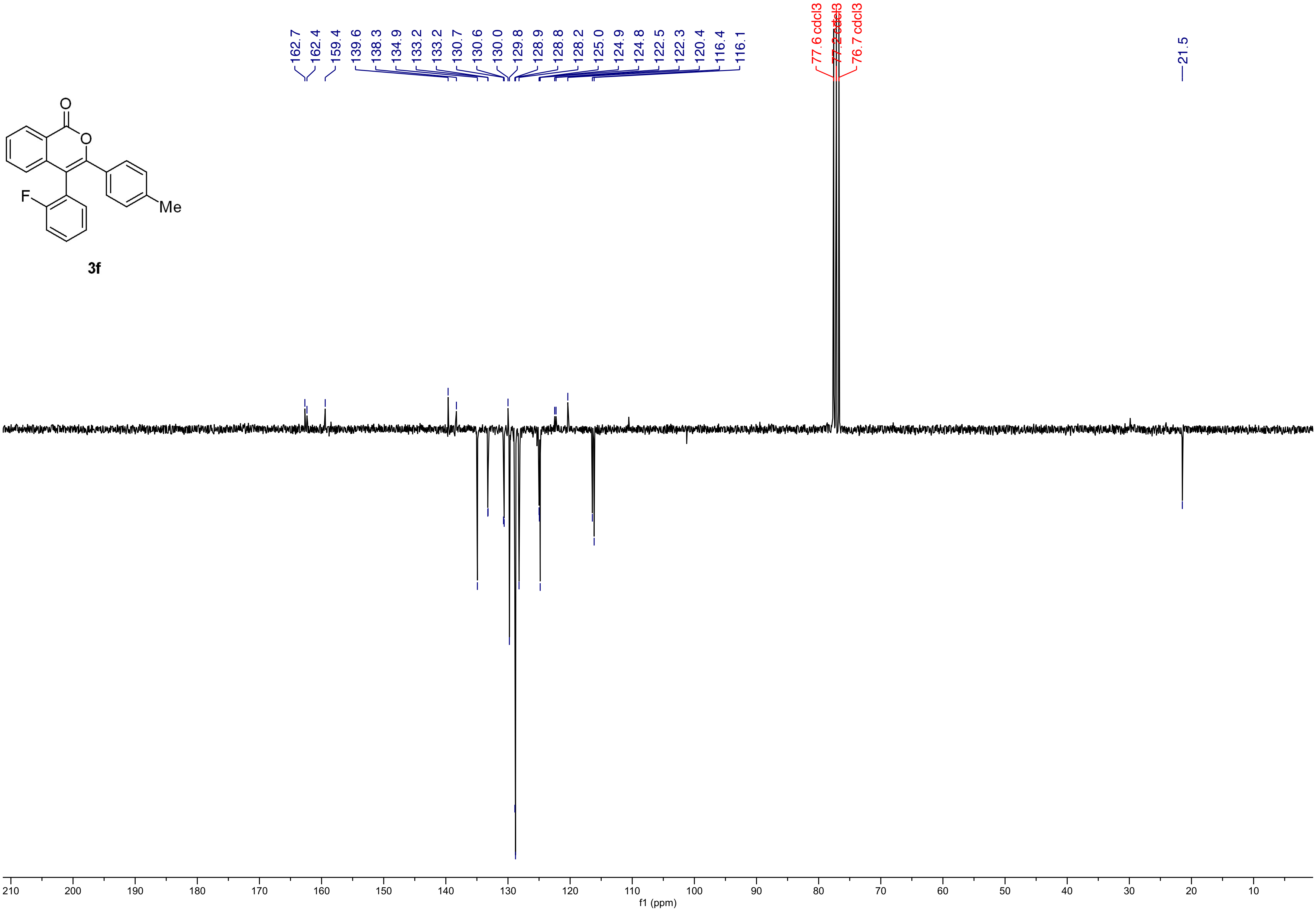
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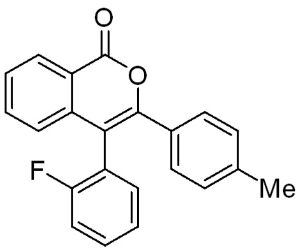
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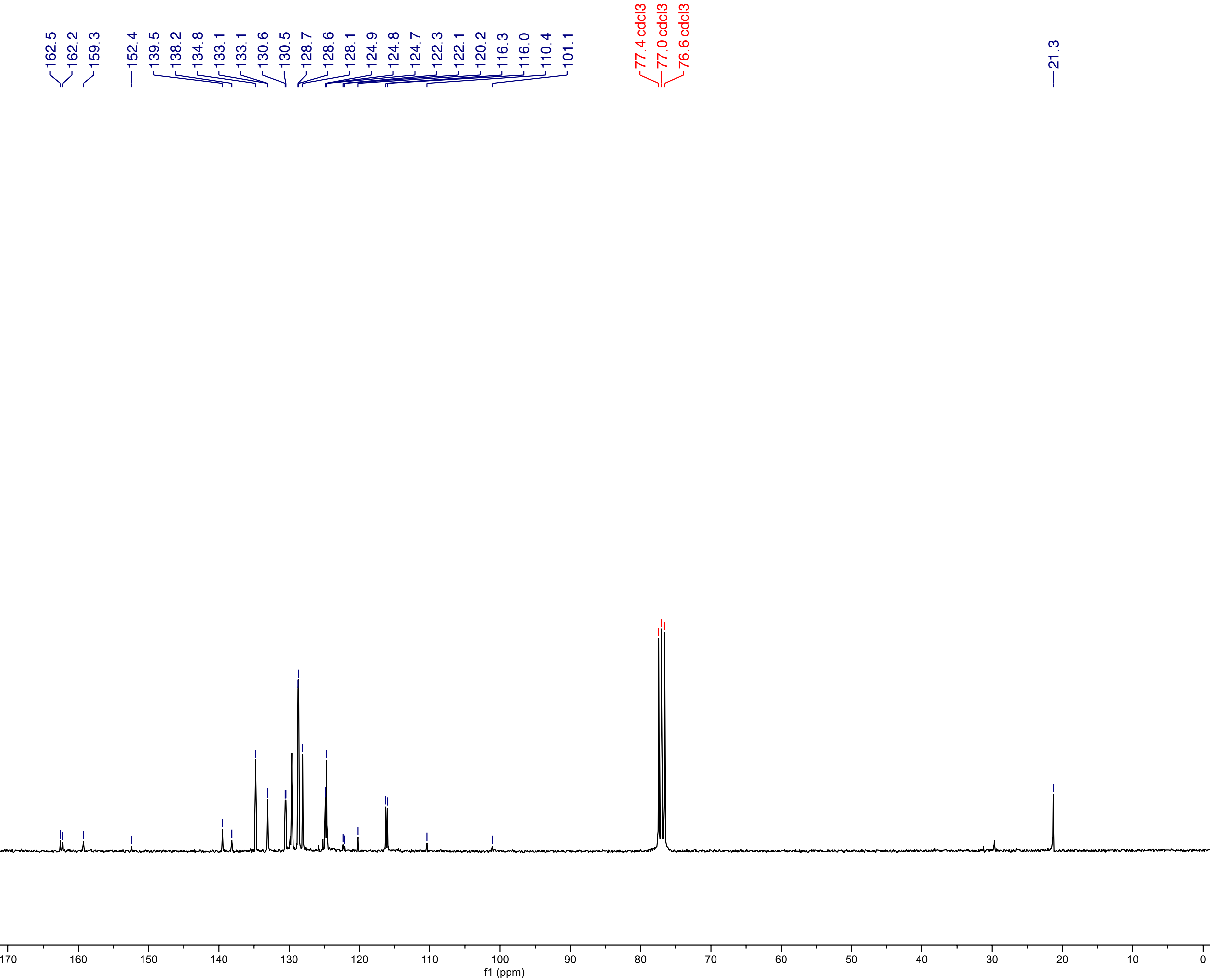
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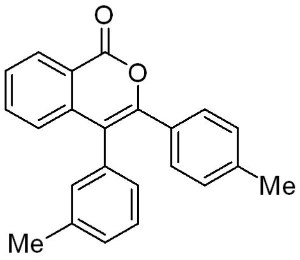
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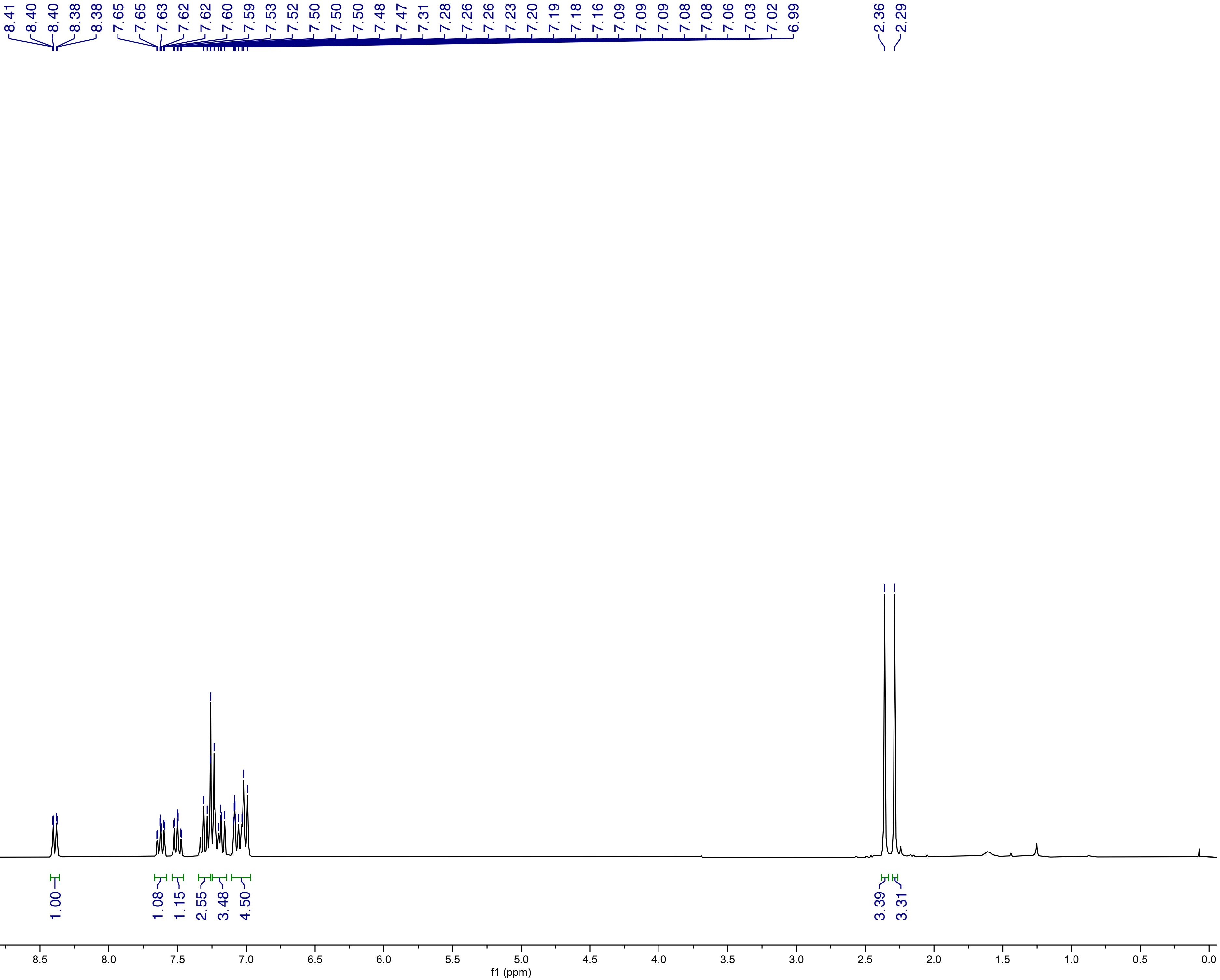
Me
Me

3g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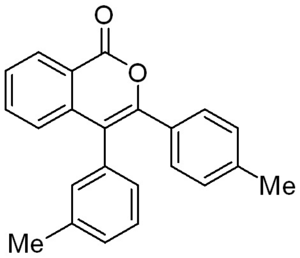
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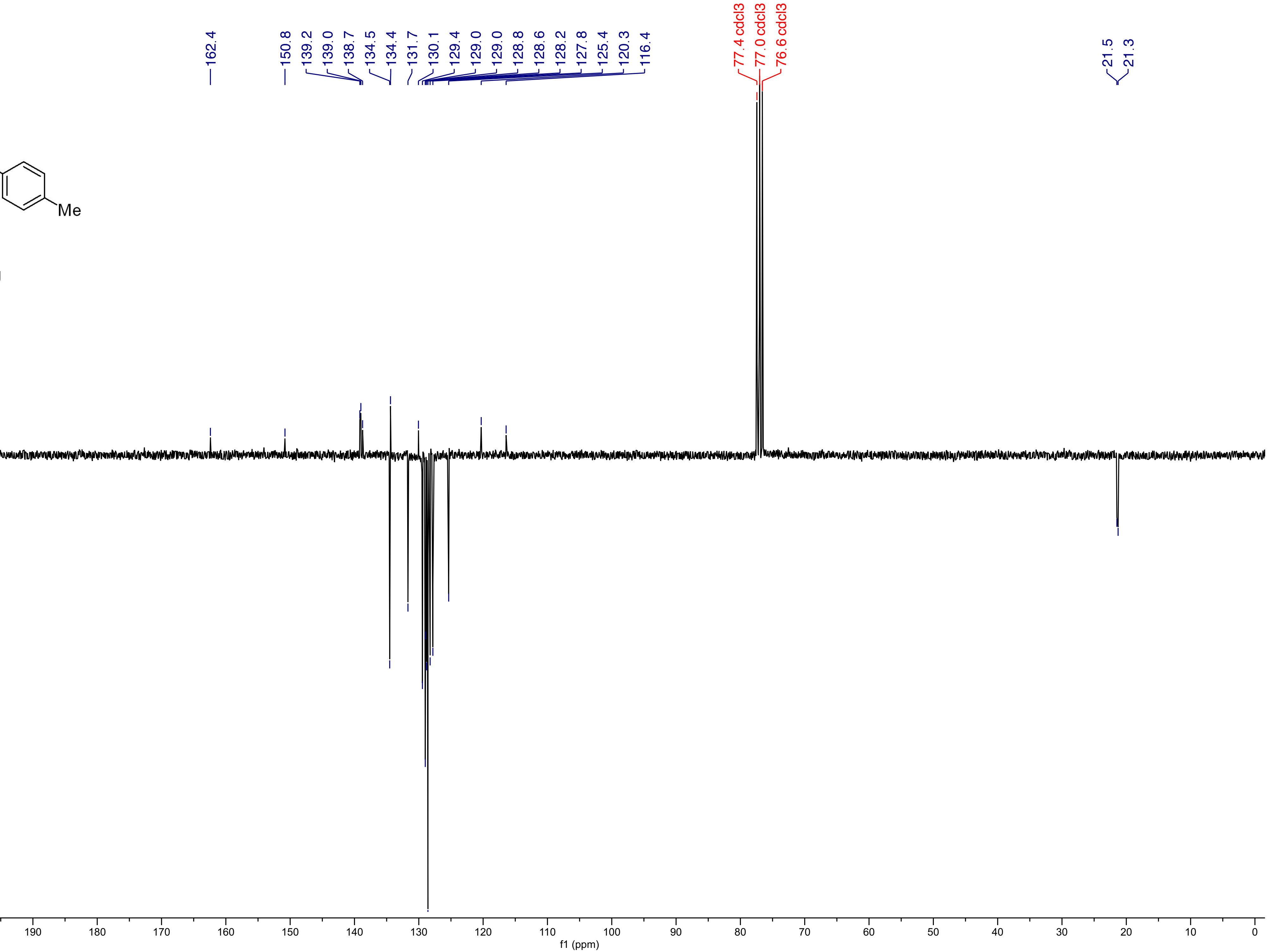
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21.3
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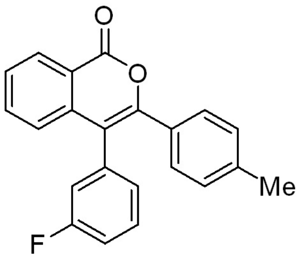
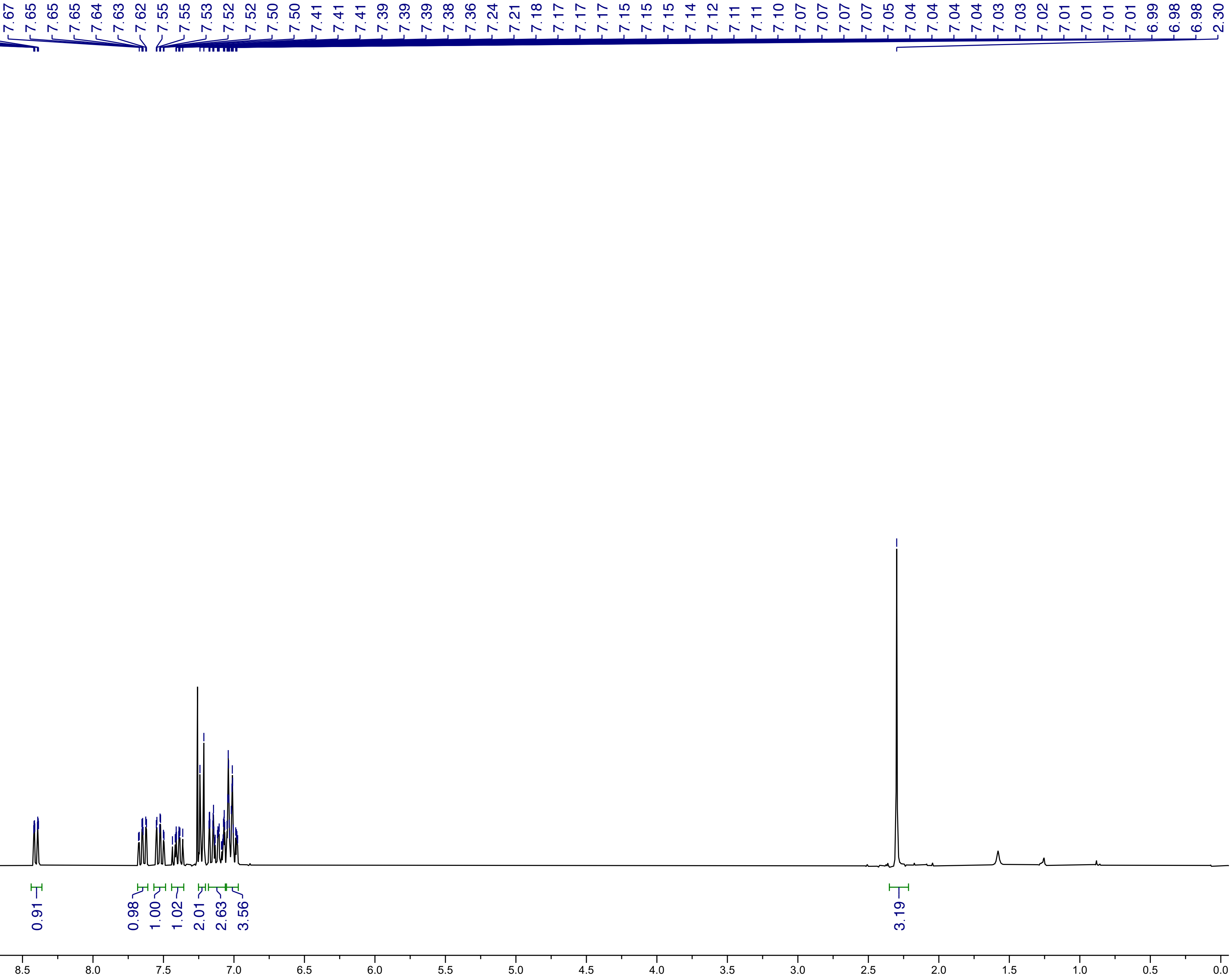
f1 (ppm)


O
O
Me
F

3h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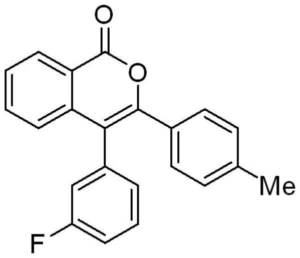
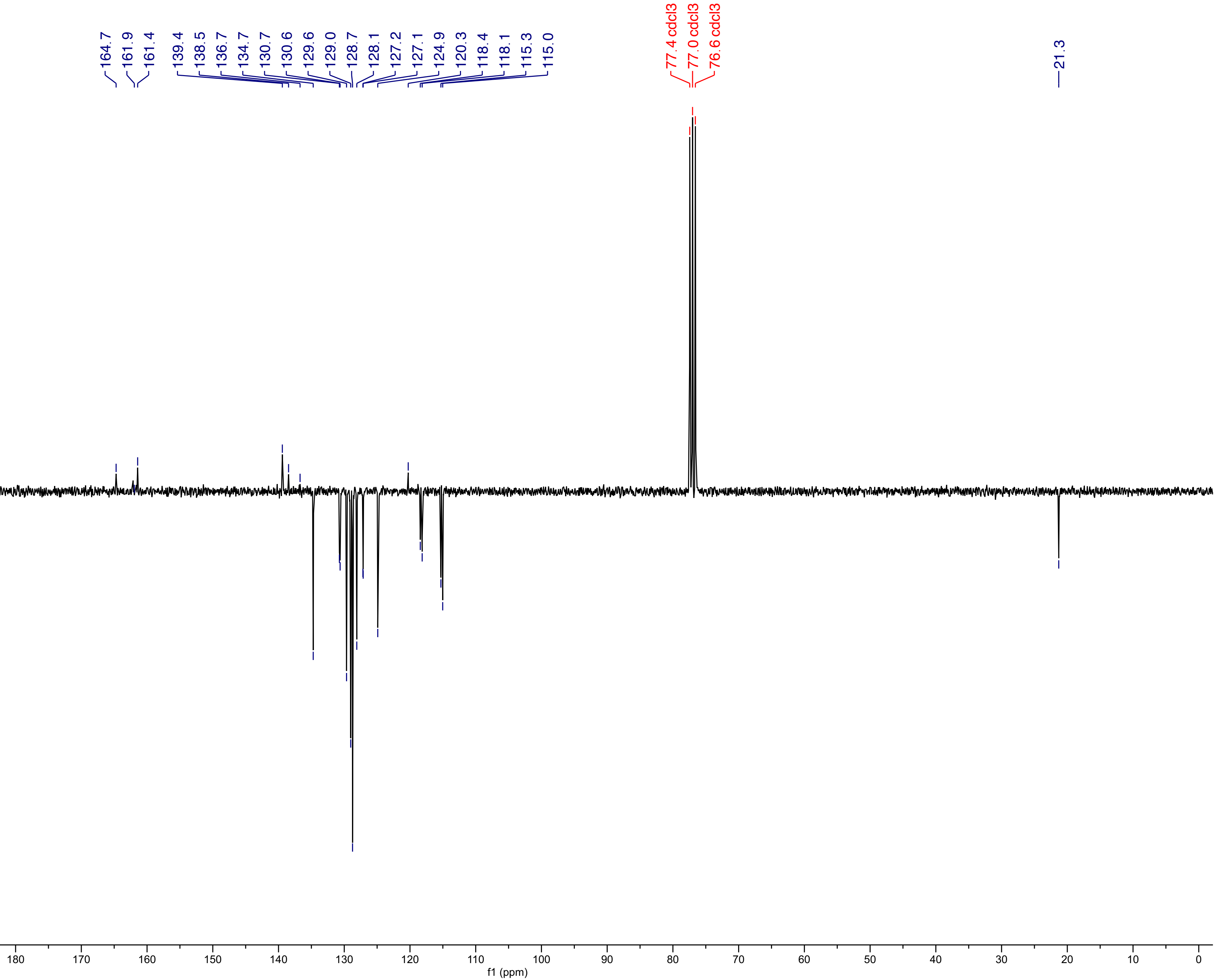
0.91
0.98
1.00
1.02
2.01
2.63
3.56
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
O
Me
F

3h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128.1
127.2
127.1
124.9
120.3
118.4
118.1
115.3
115.0
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
21.3
210
200
190
180
170
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130
120
110
100
90
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70
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50
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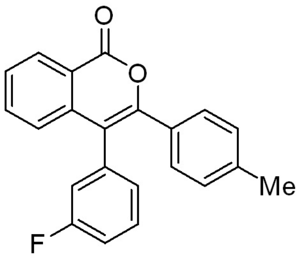
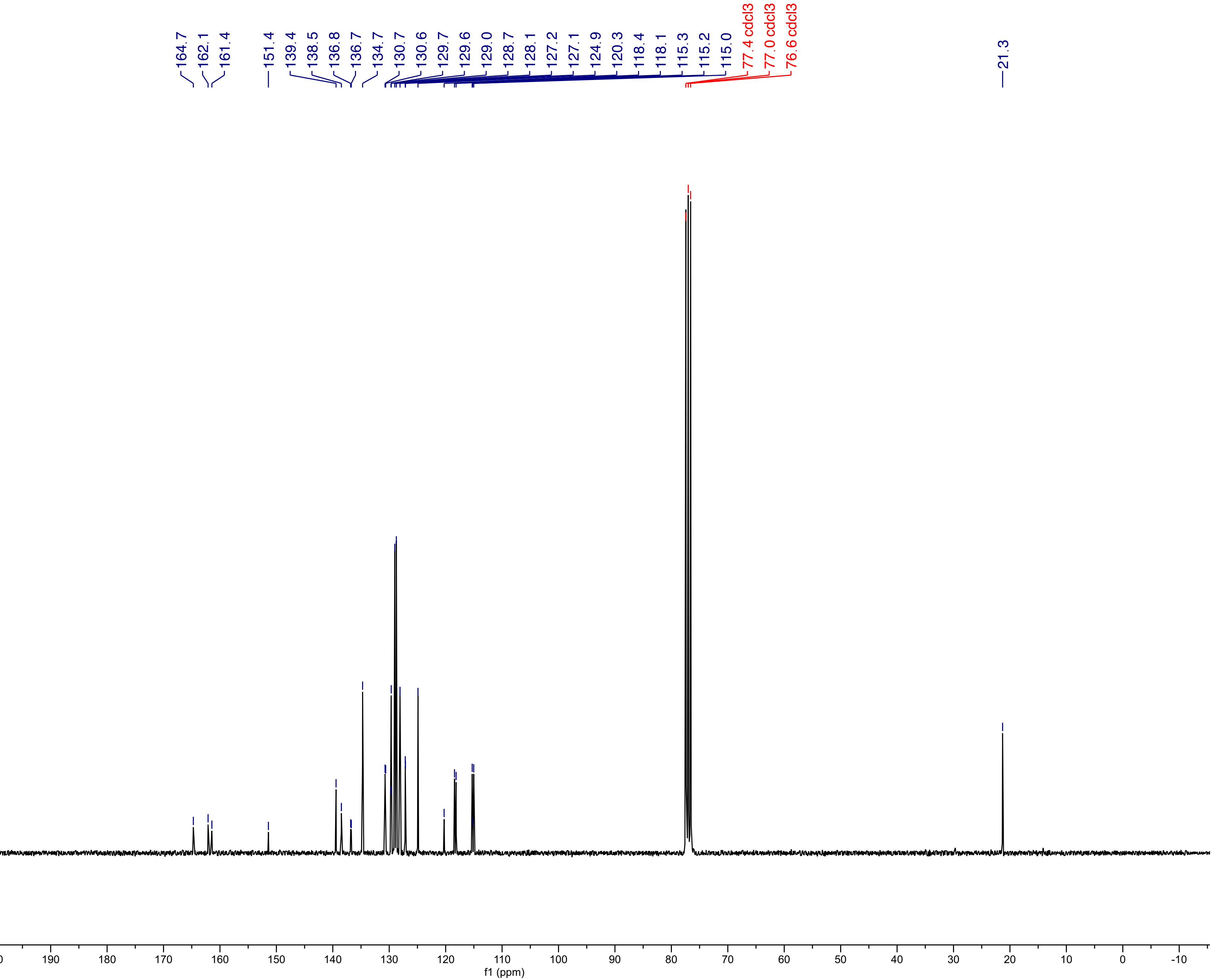
0
f1 (ppm)


O
O
Me
F

3h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129.6
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128.7
128.1
127.2
127.1
124.9
120.3
118.4
118.1
115.3
115.2
115.0
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
21.3
230
220
210
200
190
180
170
160
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140
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100
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80
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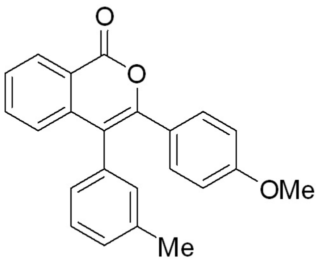
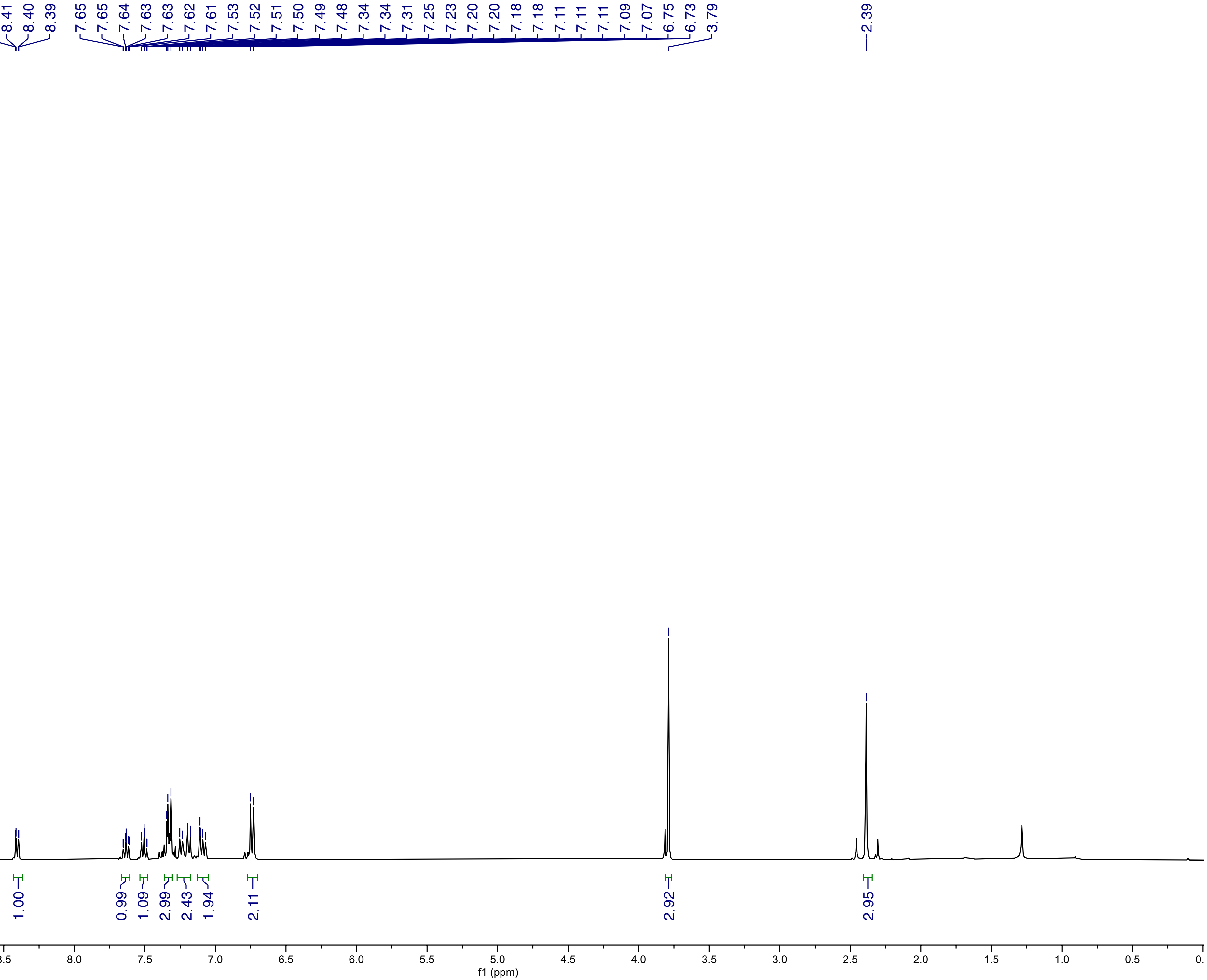
50
40
30
20
10
0
-10
f1 (ppm)


O
O
OMe
Me

3i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8.40
8.39
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7.64
7.63
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7.62
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7.53
7.52
7.51
7.50
7.49
7.48
7.34
7.34
7.31
7.25
7.23
7.20
7.20
7.18
7.18
7.11
7.11
7.11
7.09
7.07
6.75
6.73
3.79
2.39
1.00
0.99
1.09
2.99
2.43
1.94
2.11
2.92
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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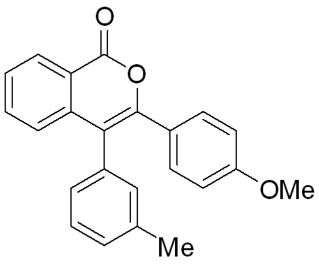
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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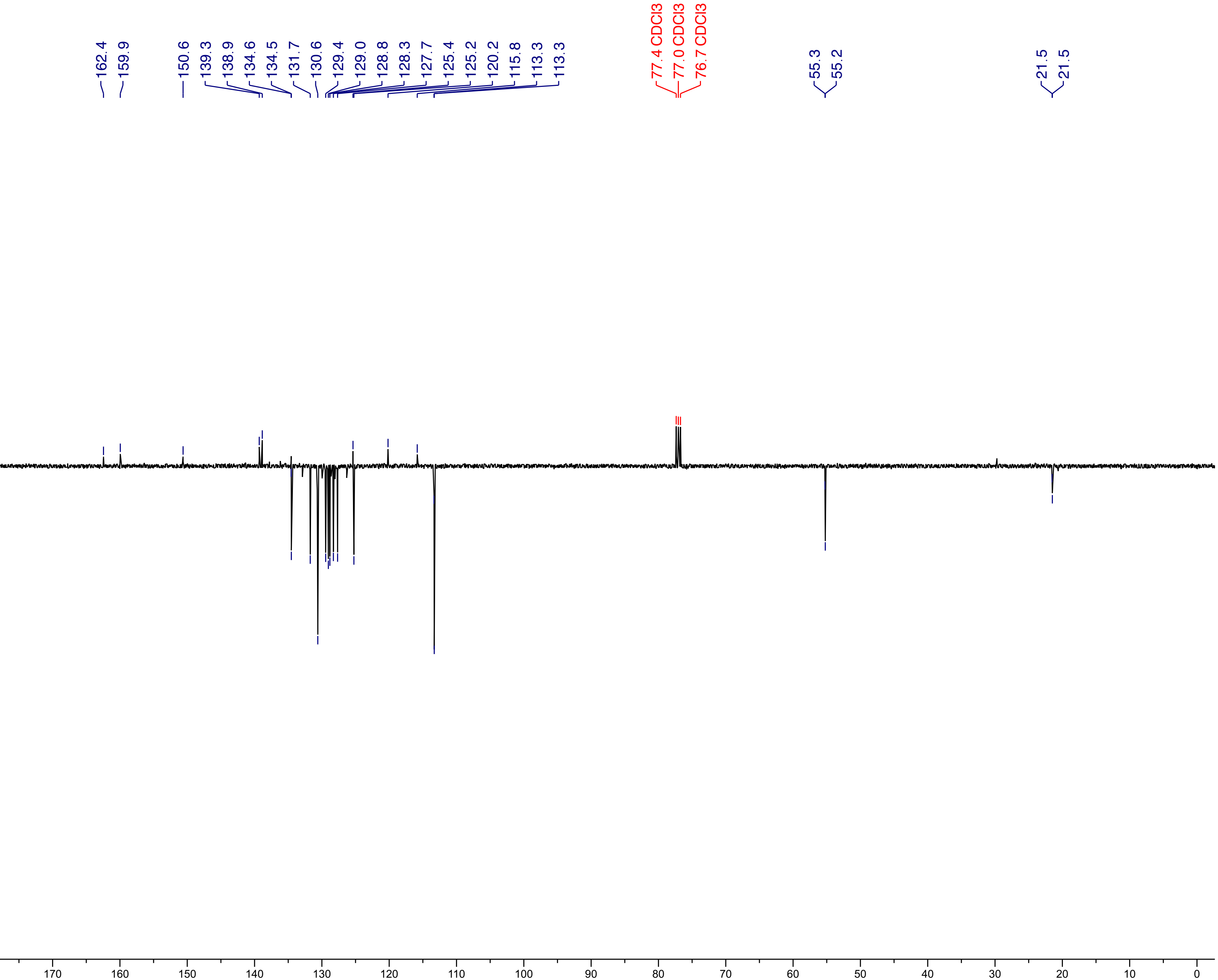
O
OMe
Me

3i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131.7
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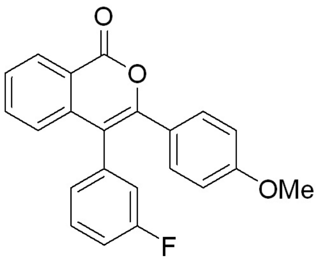
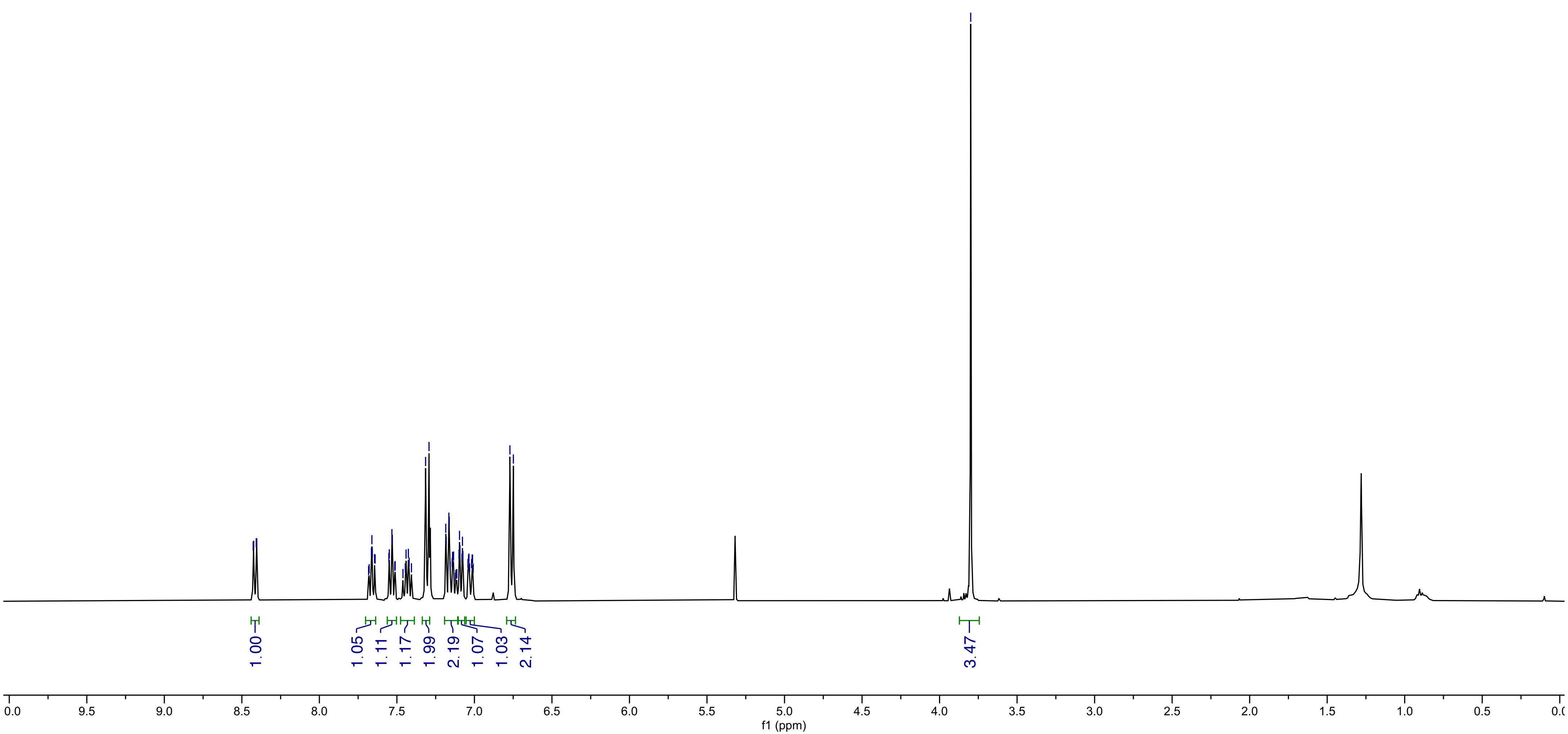
129.4
129.0
128.8
128.3
127.7
125.4
125.2
120.2
115.8
113.3
113.3
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
55.3
55.2
21.5
21.5
f1 (ppm)



O
O
OMe
F

3j



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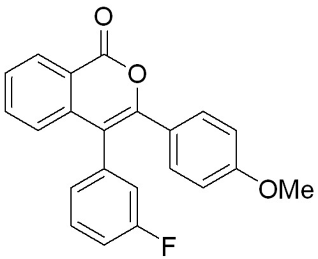
1.00
1.05 1.11 1.17 1.99 2.19 1.07 1.03 2.14
3.47
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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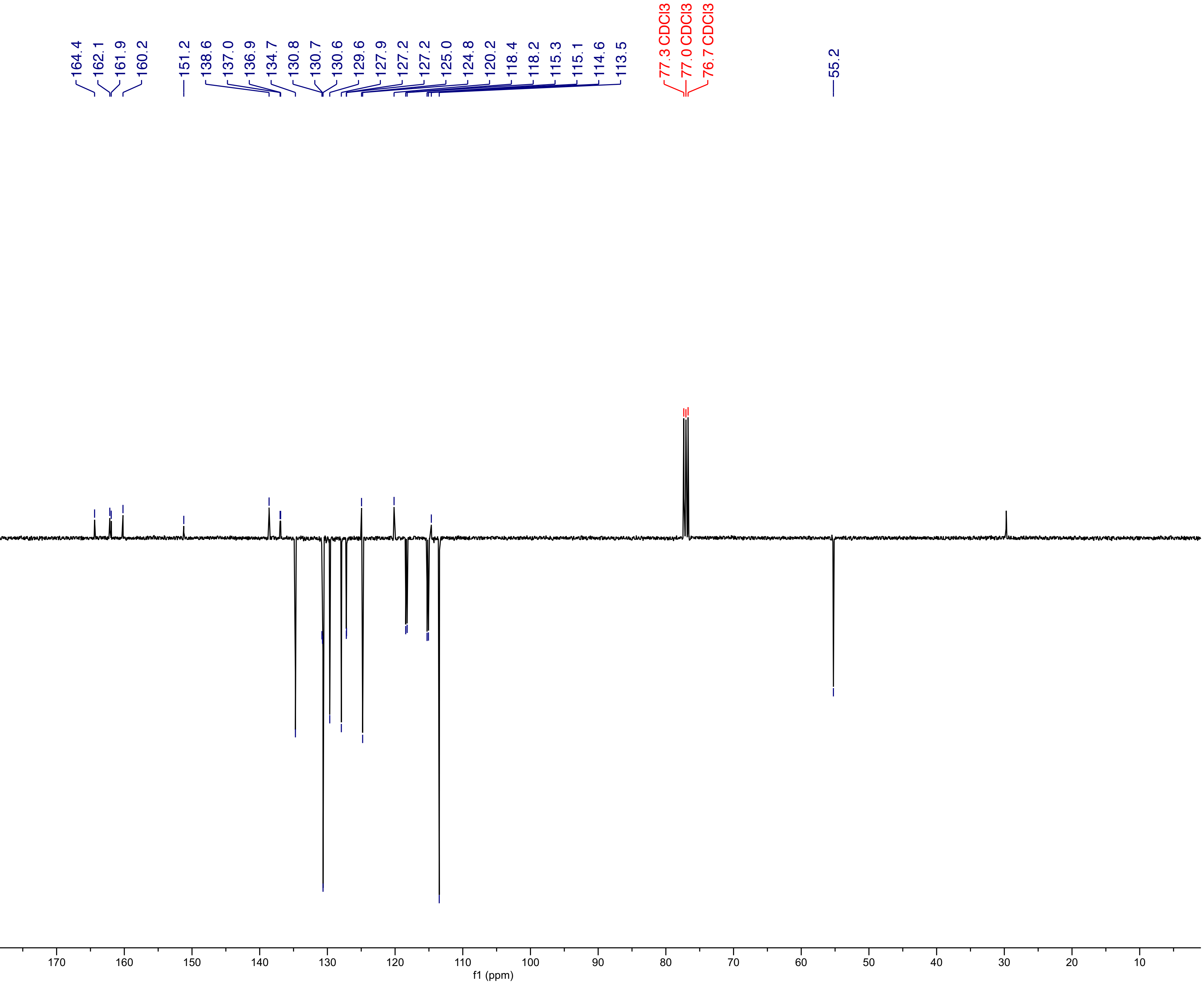
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161.9
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138.6
137.0
136.9
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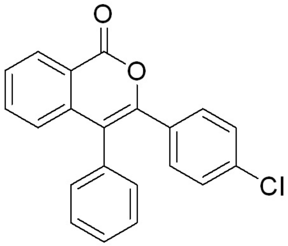
130.8
130.7
130.6
129.6
127.9
127.2
127.2
125.0
124.8
120.2
118.4
118.2
115.3
115.1
114.6
113.5
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
55.2
f1 (ppm)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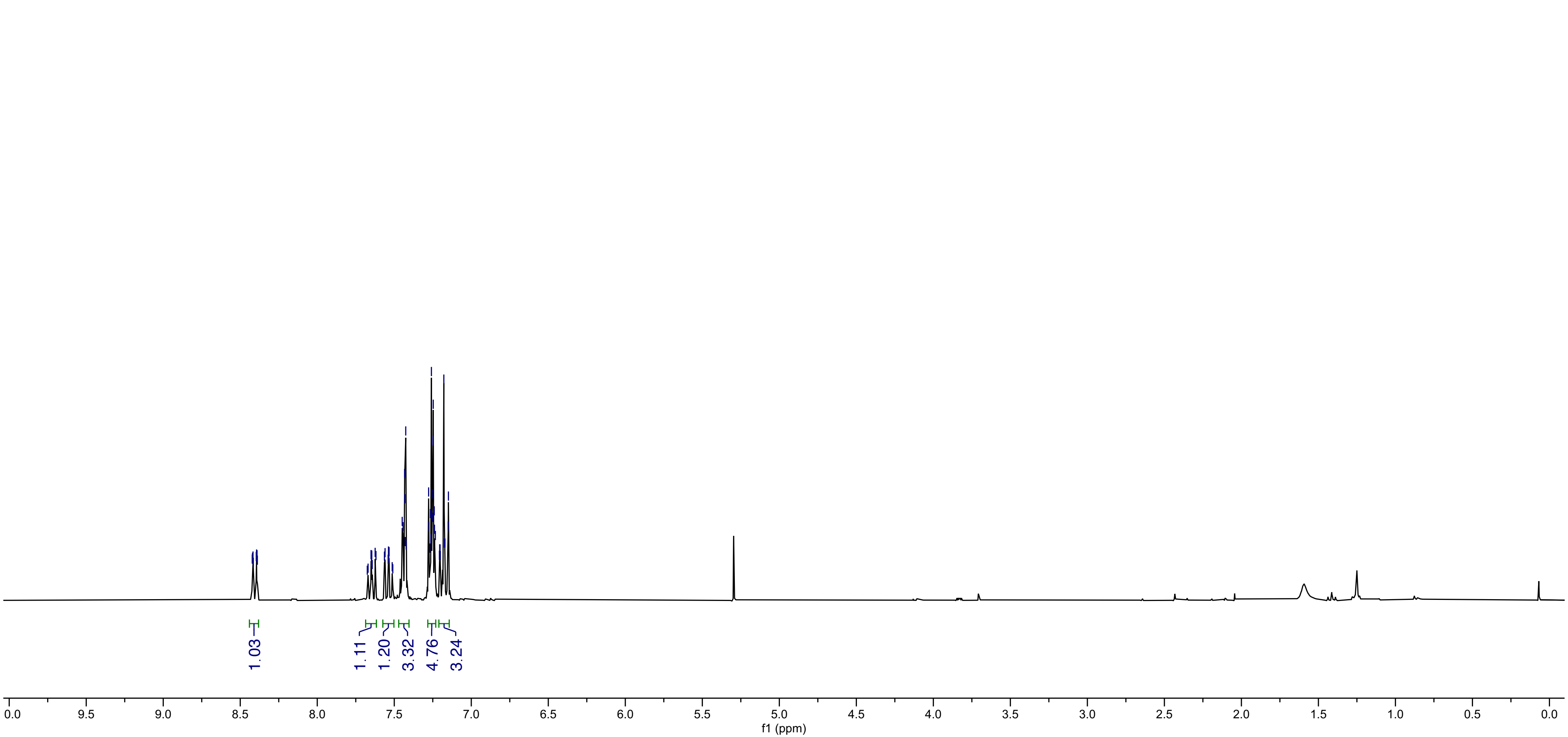
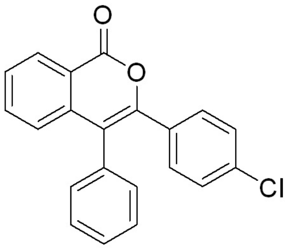
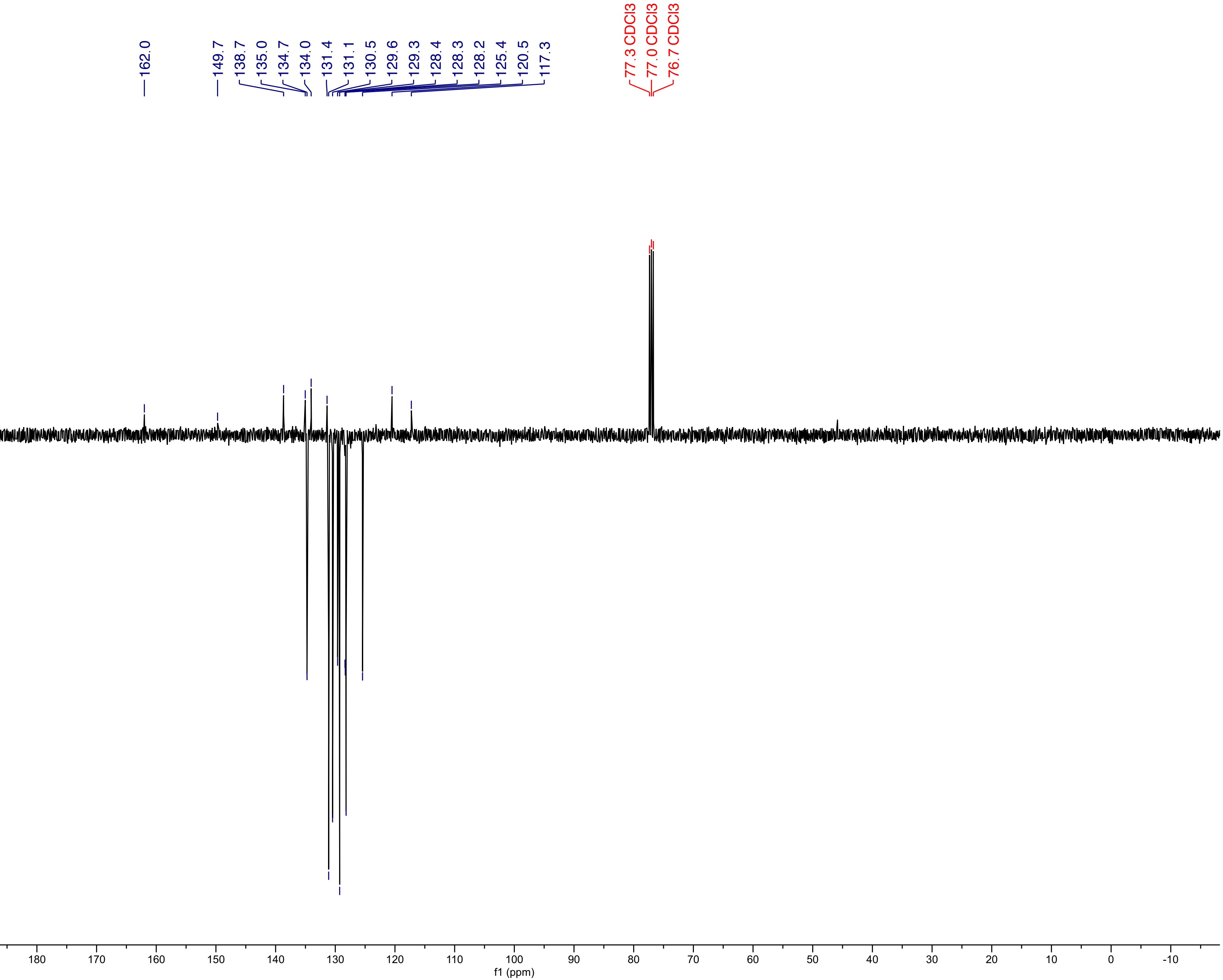
O
Cl

3k


8.42 8.42 8.42 8.41 8.40 8.39 8.39 8.39 7.68 7.67 7.65 7.65 7.65 7.64 7.62 7.62 7.56 7.56 7.54 7.54 7.54 7.53 7.51 7.51 7.45 7.44 7.43 7.43 7.43 7.43 7.42 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.23 7.21 7.20 7.20 7.20 7.18 7.17 7.17 7.15 7.15
1.03
1.11
1.20
3.32
4.76
3.24
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



3k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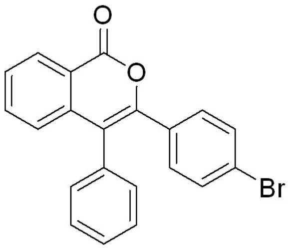
138.7
135.0
134.7
134.0
131.4
131.1
130.5
129.6
129.3
128.4
128.3
128.2
125.4
120.5
117.3
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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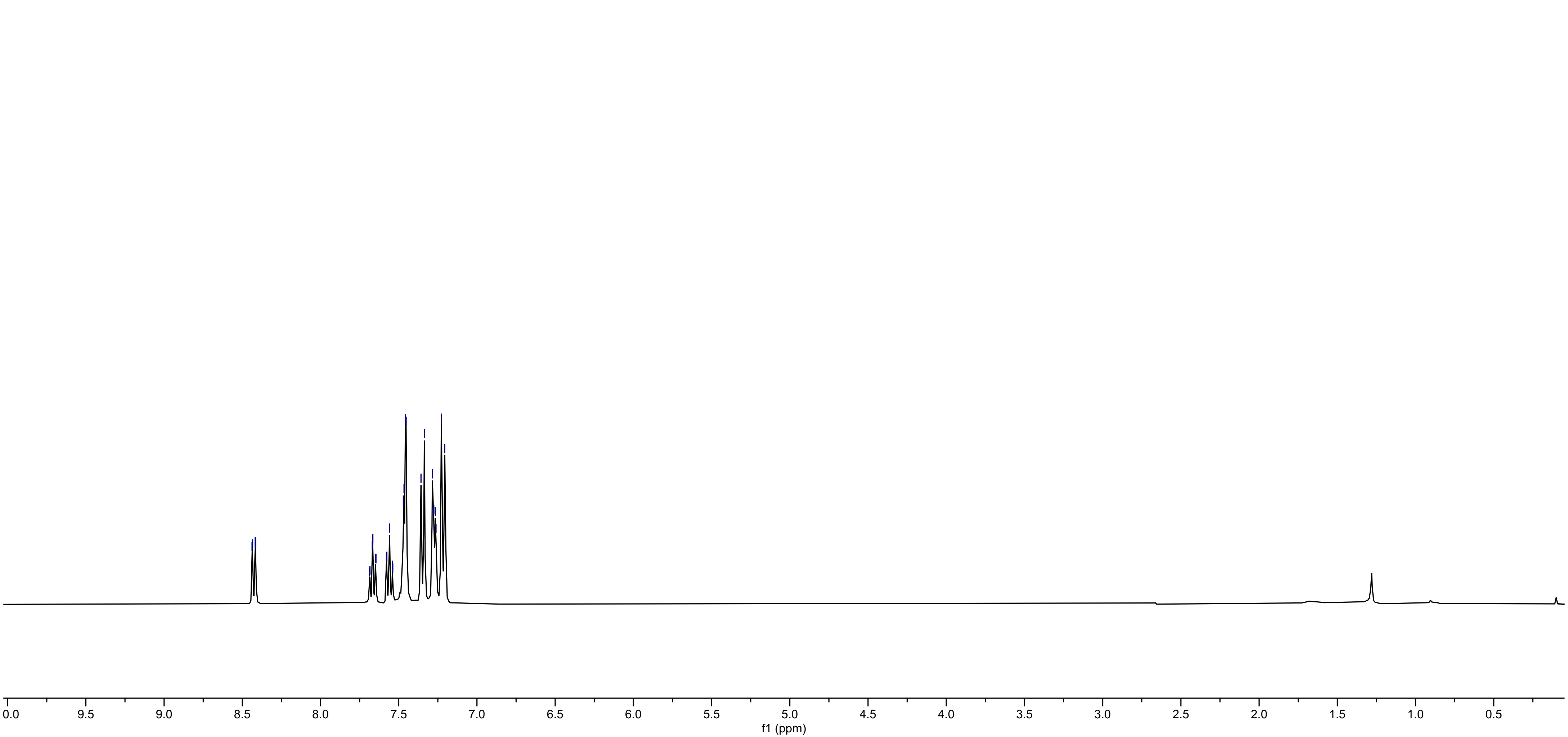
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8.43
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7.67
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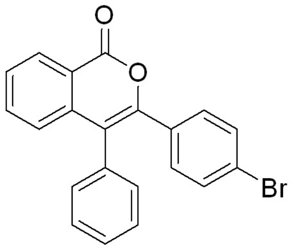
7.65
7.58
7.58
7.56
7.54
7.54
7.47
7.47
7.46
7.45
7.36
7.34
7.28
7.28
7.27
7.26
7.23
7.21
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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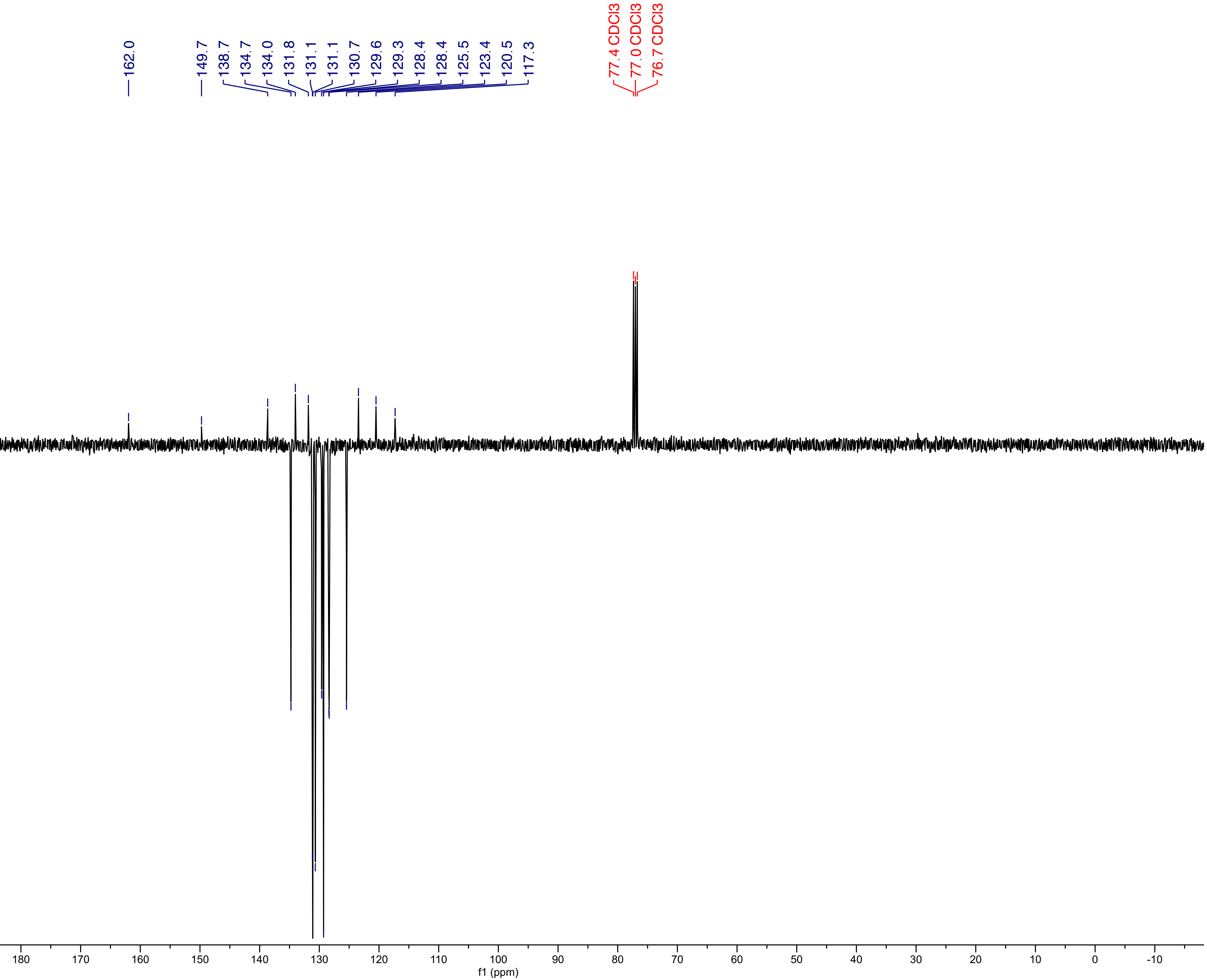

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138.7
134.7
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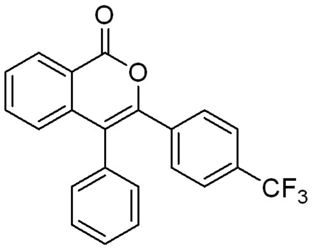
131.1
130.7
129.6
129.3
128.4
128.4
125.5
123.4
120.5
117.3
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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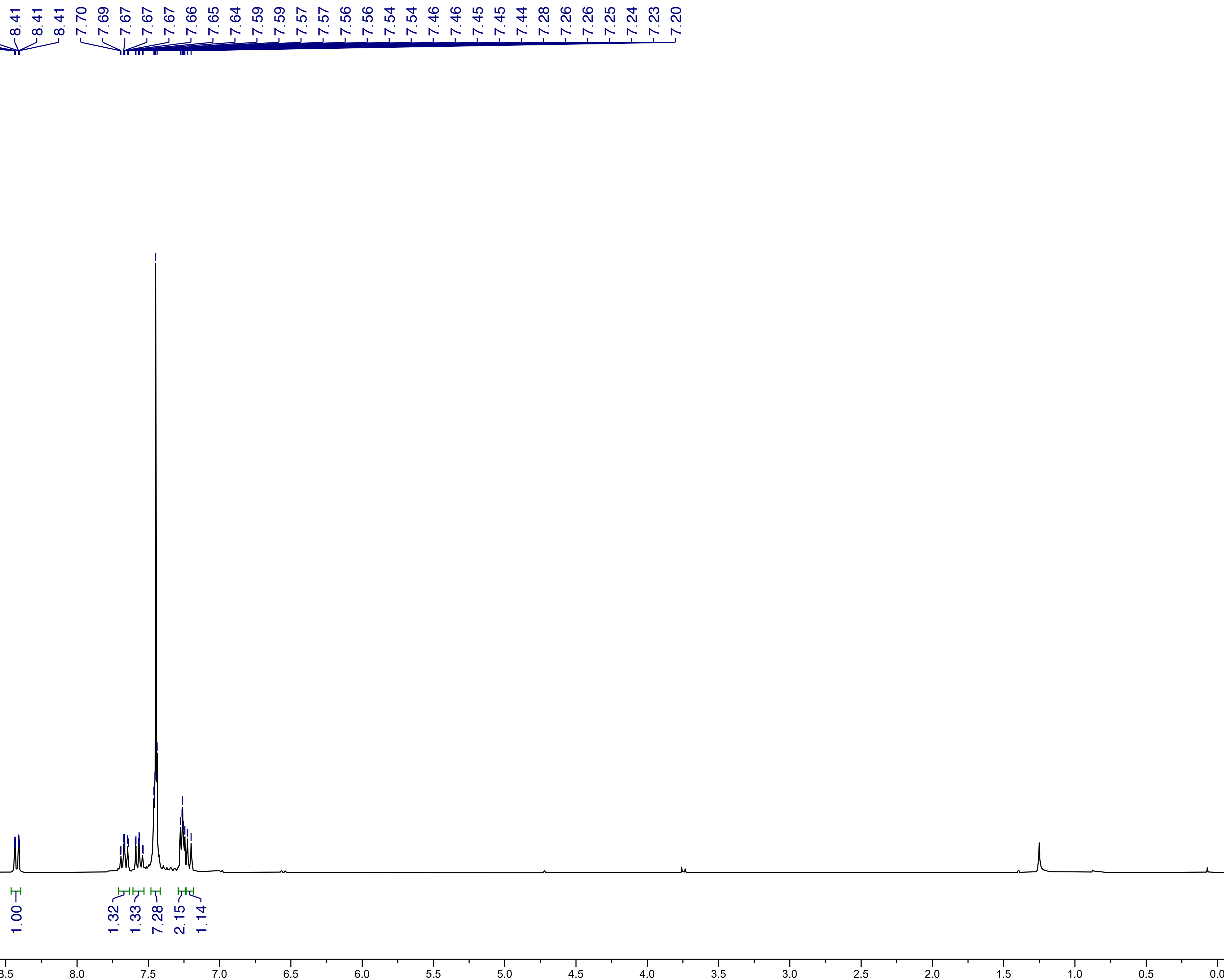
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1.00
1.32
1.33
7.28
2.15
1.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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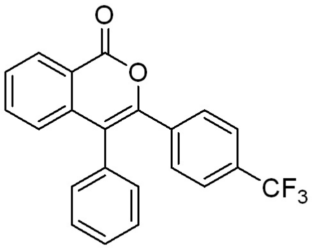
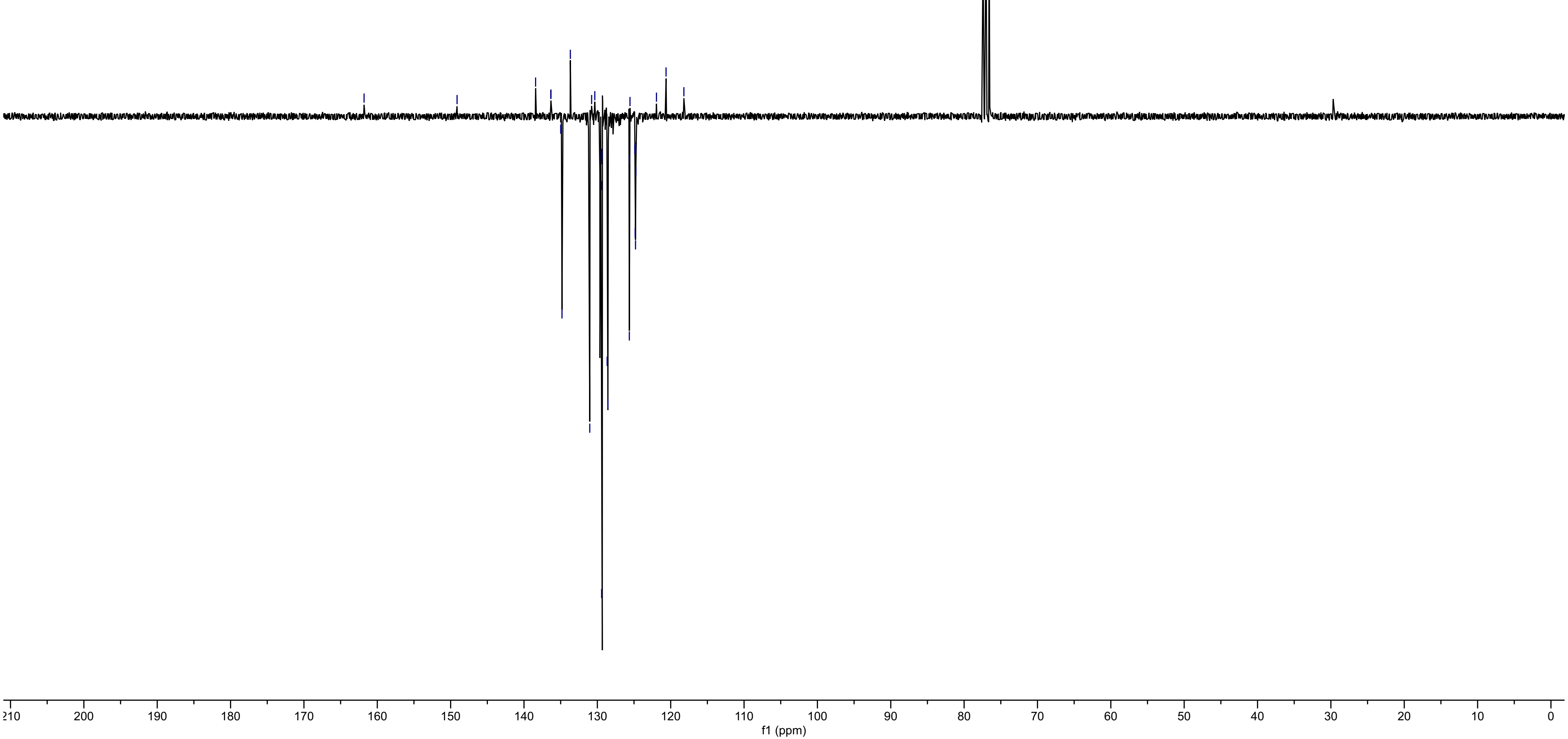

O
O
CF3

3m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129.5
129.4
129.4
129.4
128.7
128.6
125.6
125.6
125.6
124.9
124.8
124.8
124.8
124.8
124.7
121.9
120.6
118.2
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
210
200
190
180
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150
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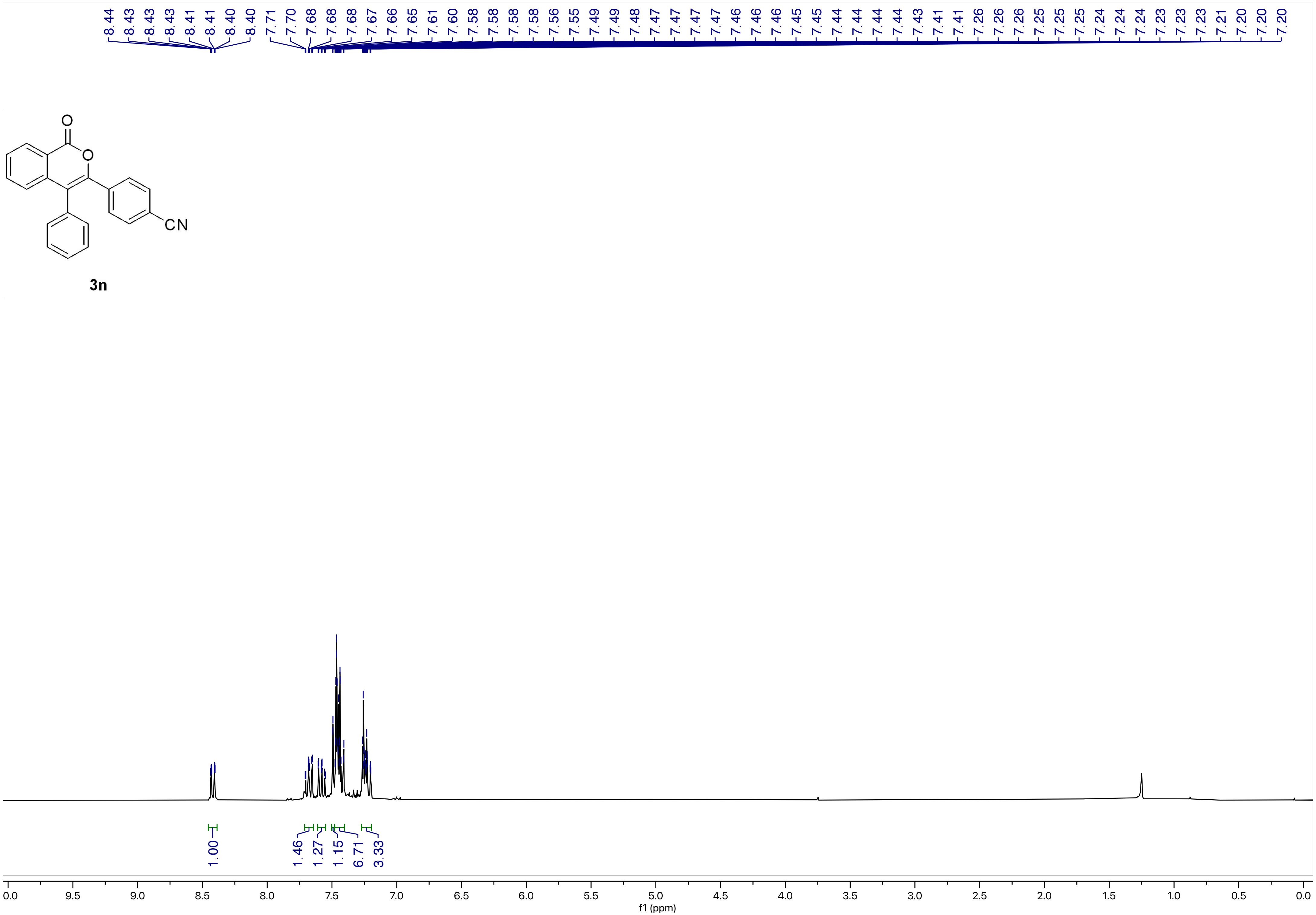
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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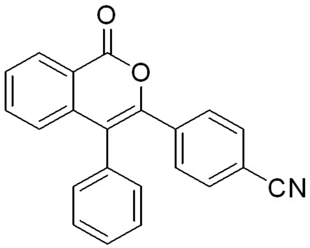
1.00
1.46
1.27
1.15
6.71
3.33
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
O
CN

3n



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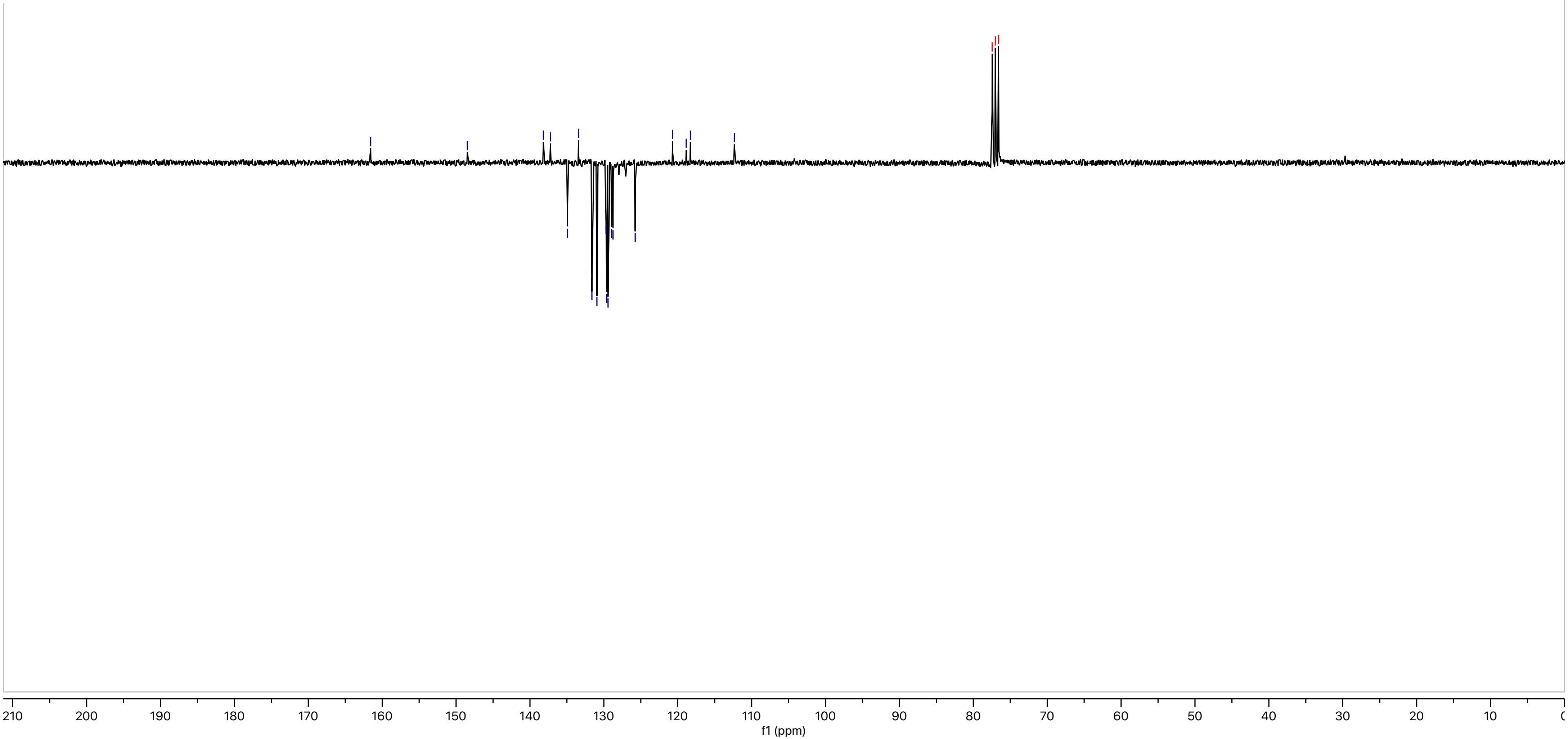

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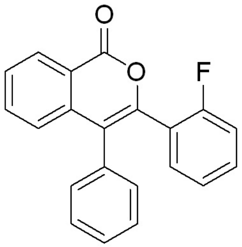
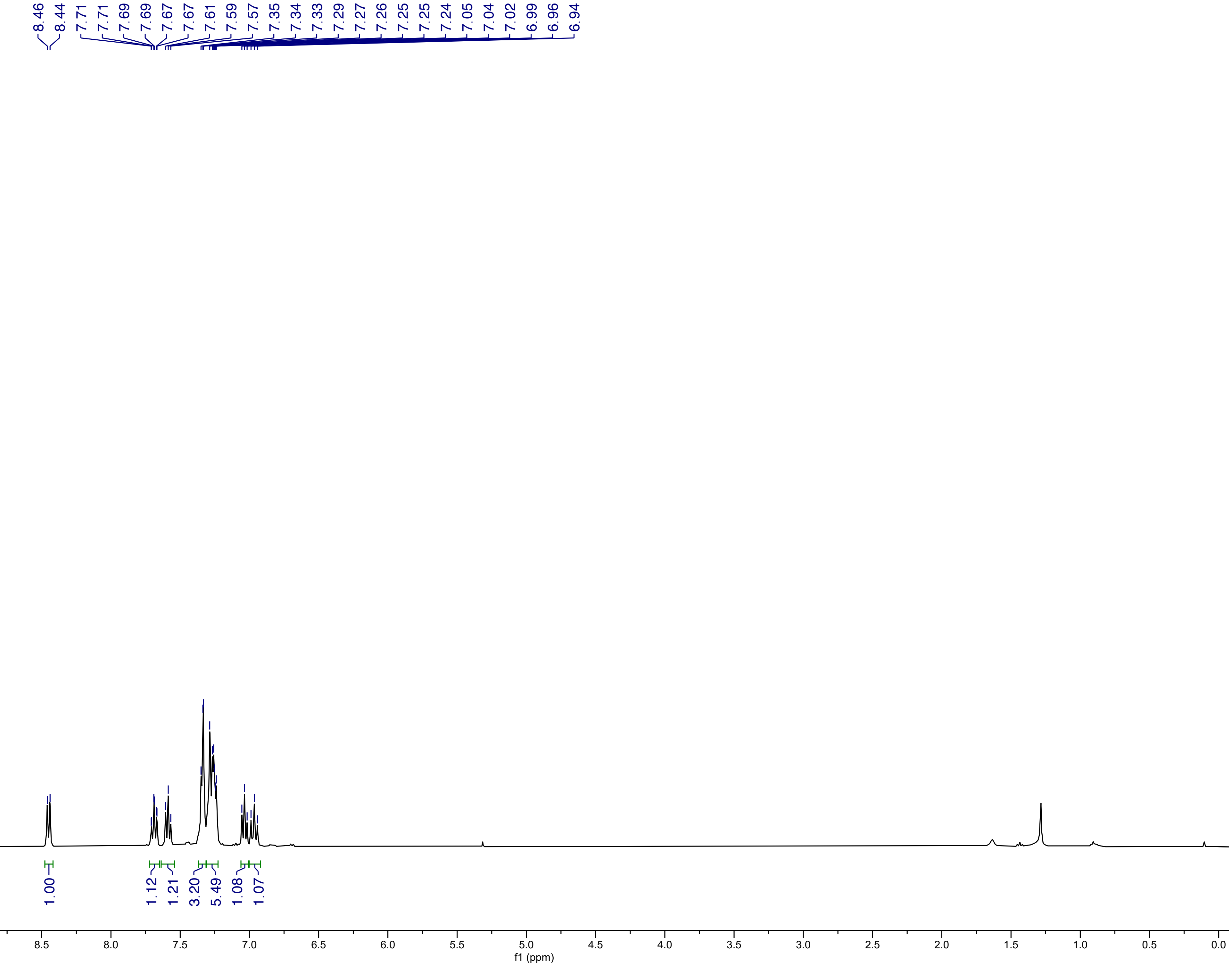
129.6
129.4
129.0
128.8
125.8
120.7
118.9
118.3
112.3
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
F

3o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7.59
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7.33
7.29
7.27
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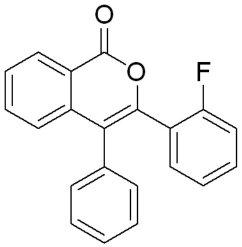
7.25
7.25
7.24
7.05
7.04
7.02
6.99
6.96
6.94
1.00
1.12
1.21
3.20
5.49
1.08
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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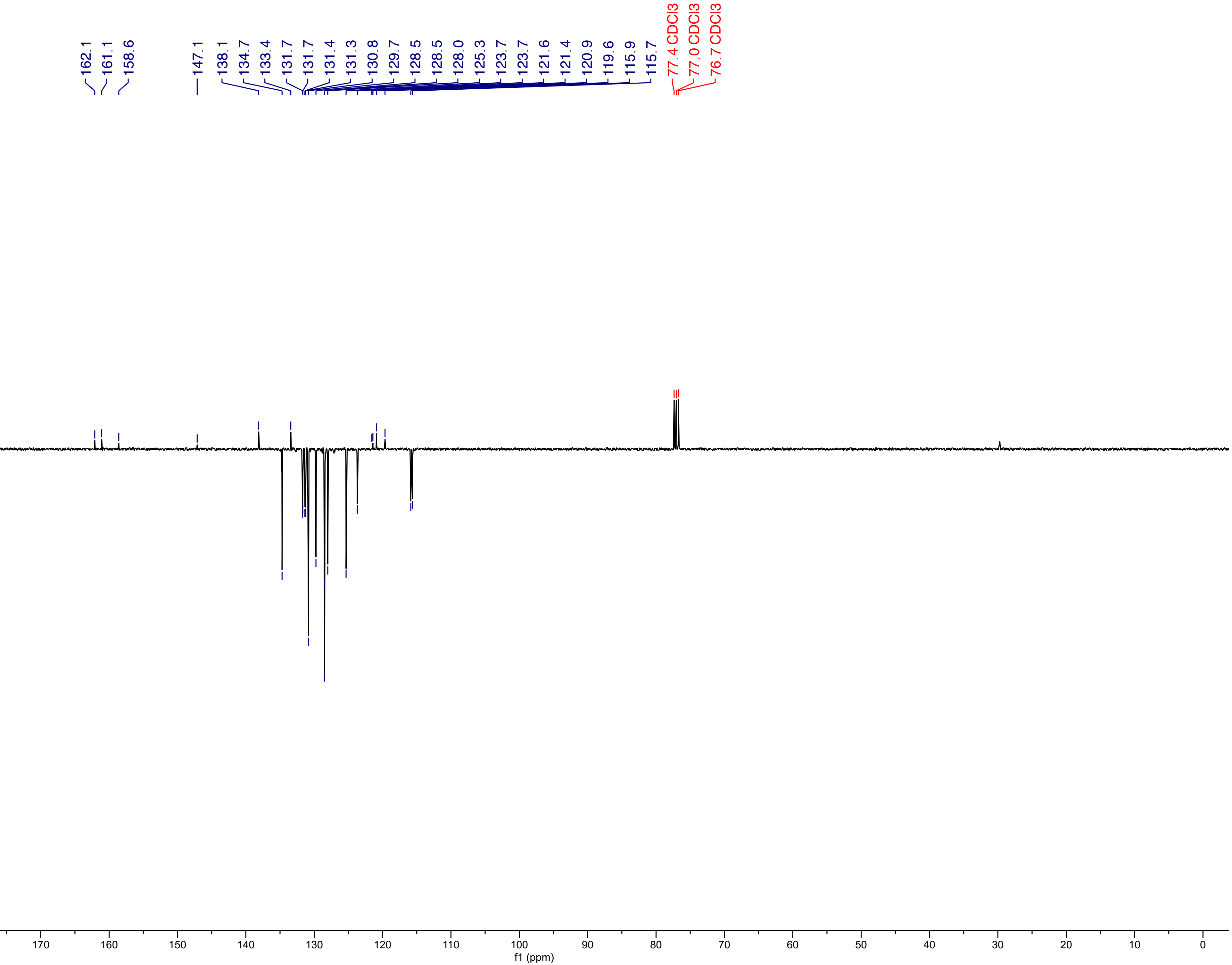
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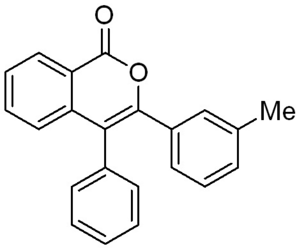
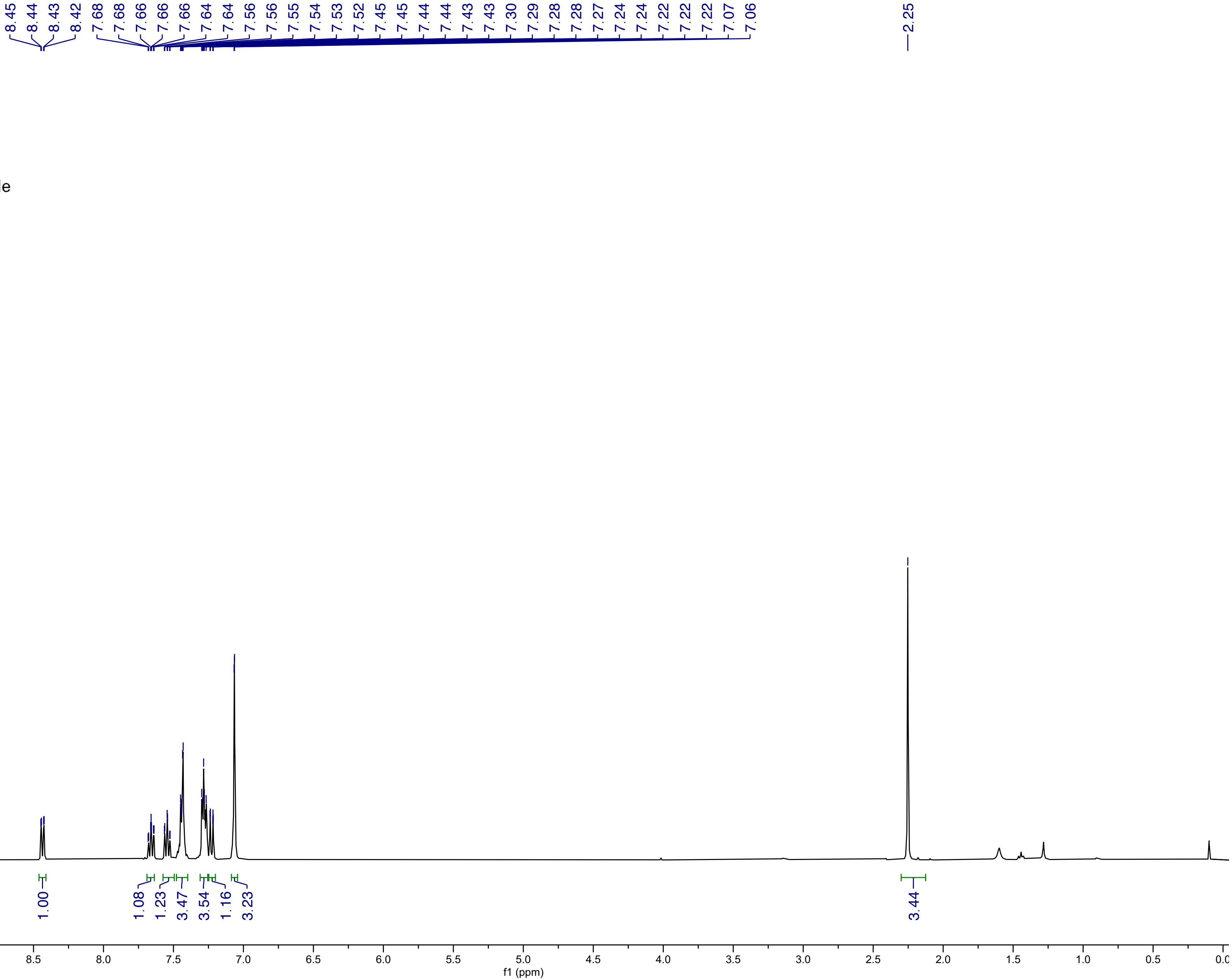
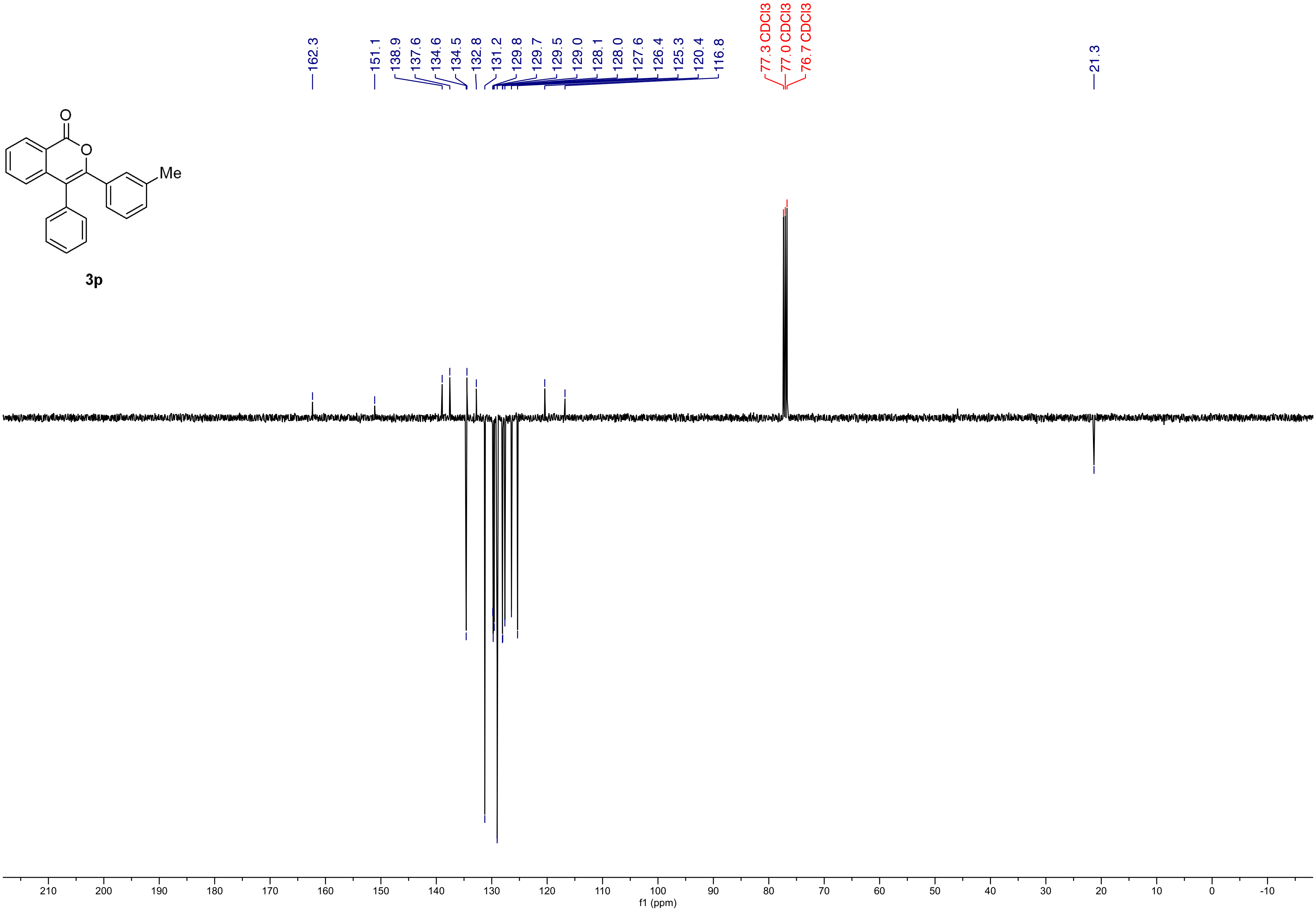
129.7
128.5
128.5
128.0
125.3
123.7
123.7
121.6
121.4
120.9
119.6
115.9
115.7
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
Me

3p


8.45 8.44 8.43 8.42 7.68 7.68 7.66 7.66 7.66 7.64 7.64 7.56 7.56 7.55 7.54 7.53 7.52 7.45 7.45 7.44 7.44 7.43 7.43 7.30 7.29 7.28 7.28 7.27 7.24 7.24 7.22 7.22 7.22 7.07 7.06
2.25
1.00
1.08
1.23
3.47
3.54
1.16
3.23
3.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.2
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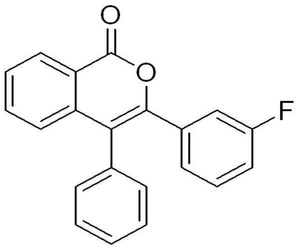
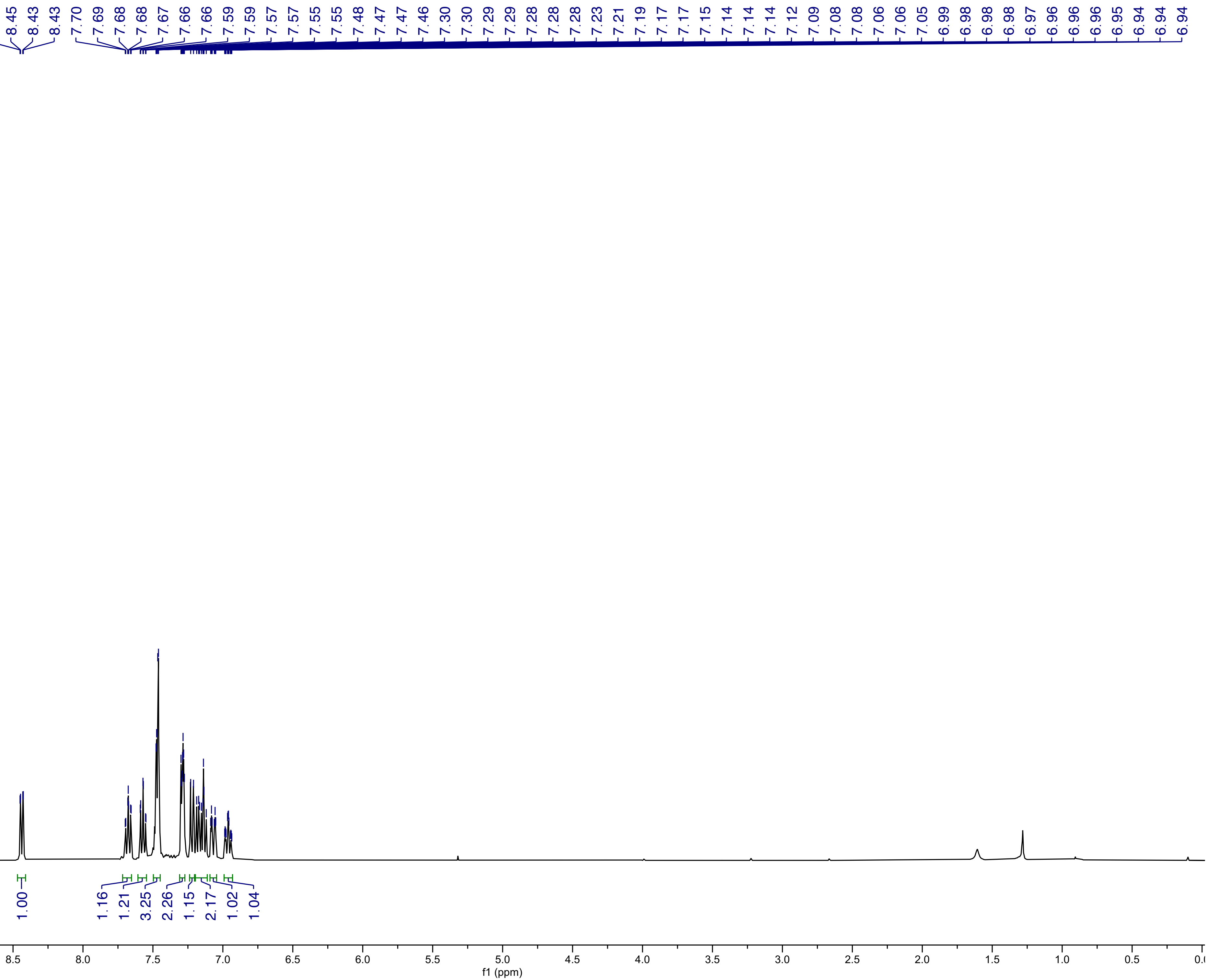
129.7
129.5
129.0
128.1
128.0
127.6
126.4
125.3
120.4
116.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
21.3
O
O
Me
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3q



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7.57
7.55
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7.21
7.19
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7.15
7.14
7.14
7.12
7.09
7.08
7.08
7.06
7.06
7.05
6.99
6.98
6.98
6.98
6.97
6.96
6.96
6.96
6.95
6.94
6.94
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2.17
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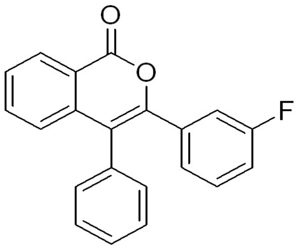
1.04
f1 (ppm)



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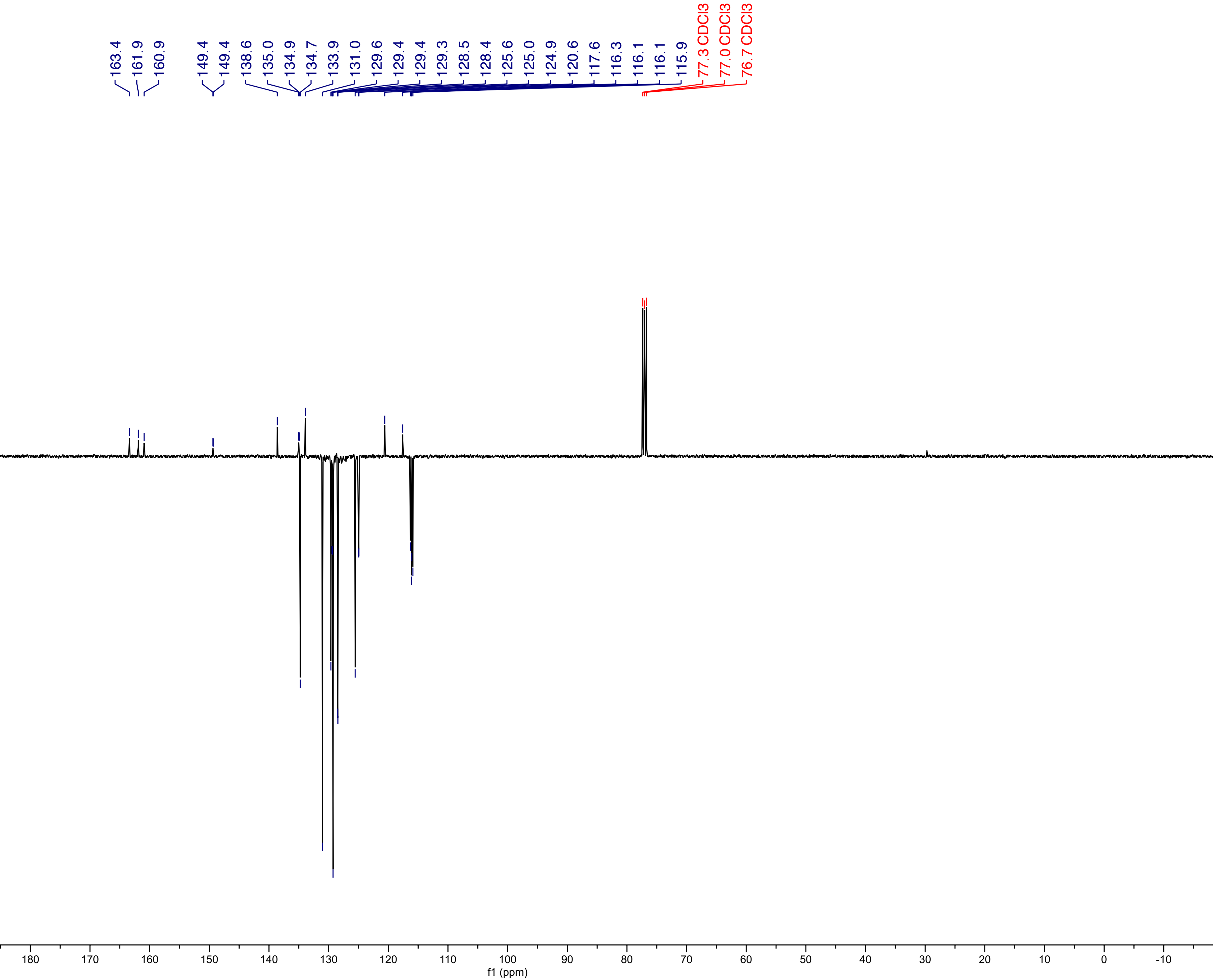

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161.9
160.9
149.4
149.4
138.6
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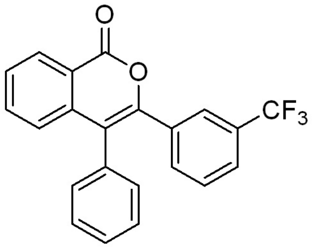
134.9
134.7
133.9
131.0
129.6
129.4
129.4
129.3
128.5
128.4
125.6
125.0
124.9
120.6
117.6
116.3
116.1
116.1
115.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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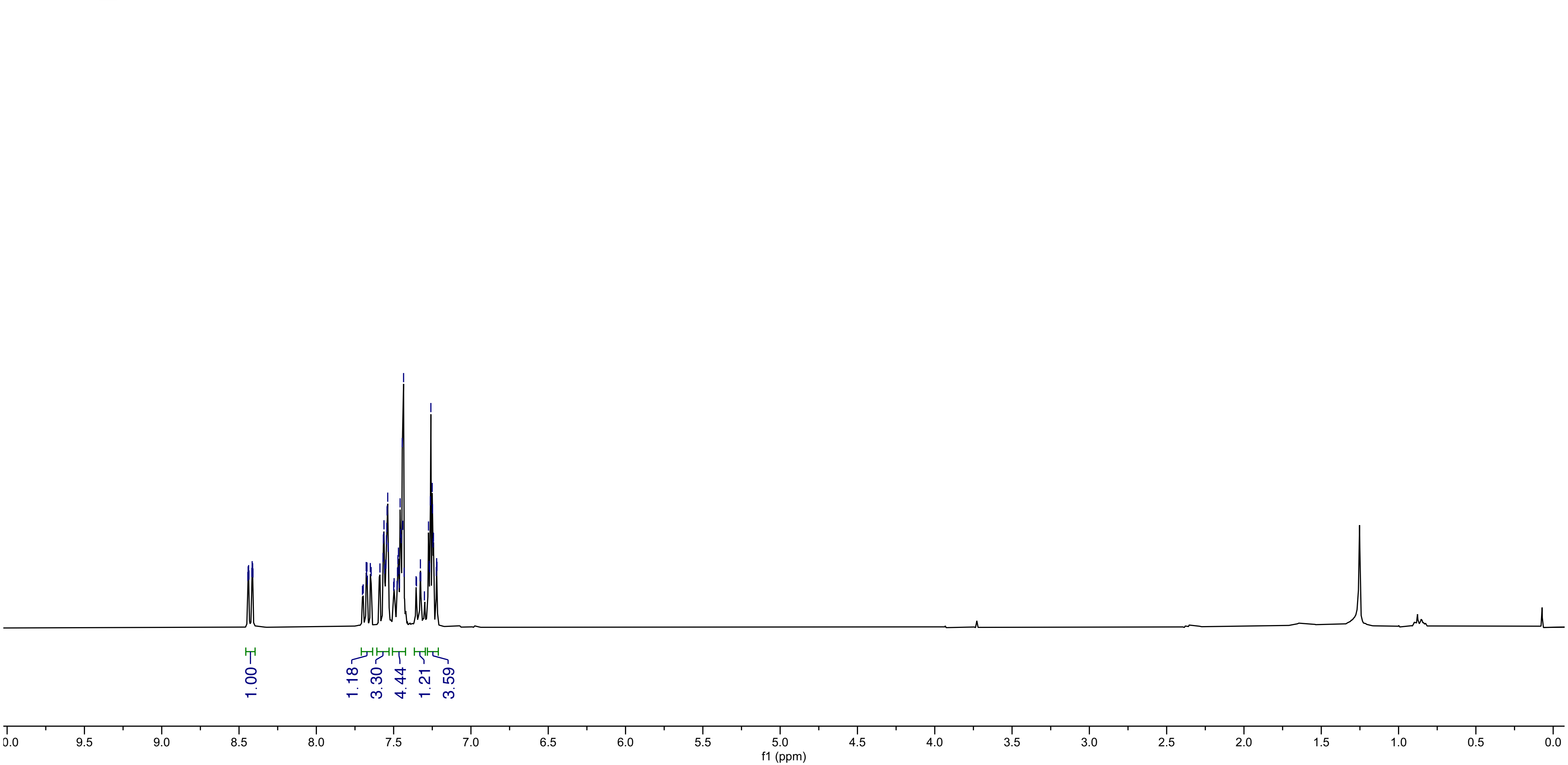
O
CF3

3r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7.65
7.65
7.59
7.57
7.57
7.56
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7.56
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7.54
7.54
7.54
7.54
7.54
7.50
7.50
7.48
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7.47
7.47
7.47
7.46
7.46
7.45
7.45
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7.44
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7.26
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7.25
7.25
7.24
7.24
7.22
7.22
1.00
1.18
3.30
4.44
1.21
3.59
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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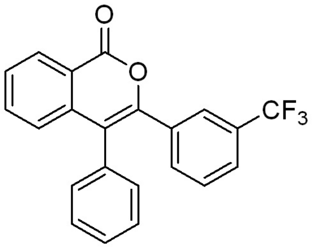
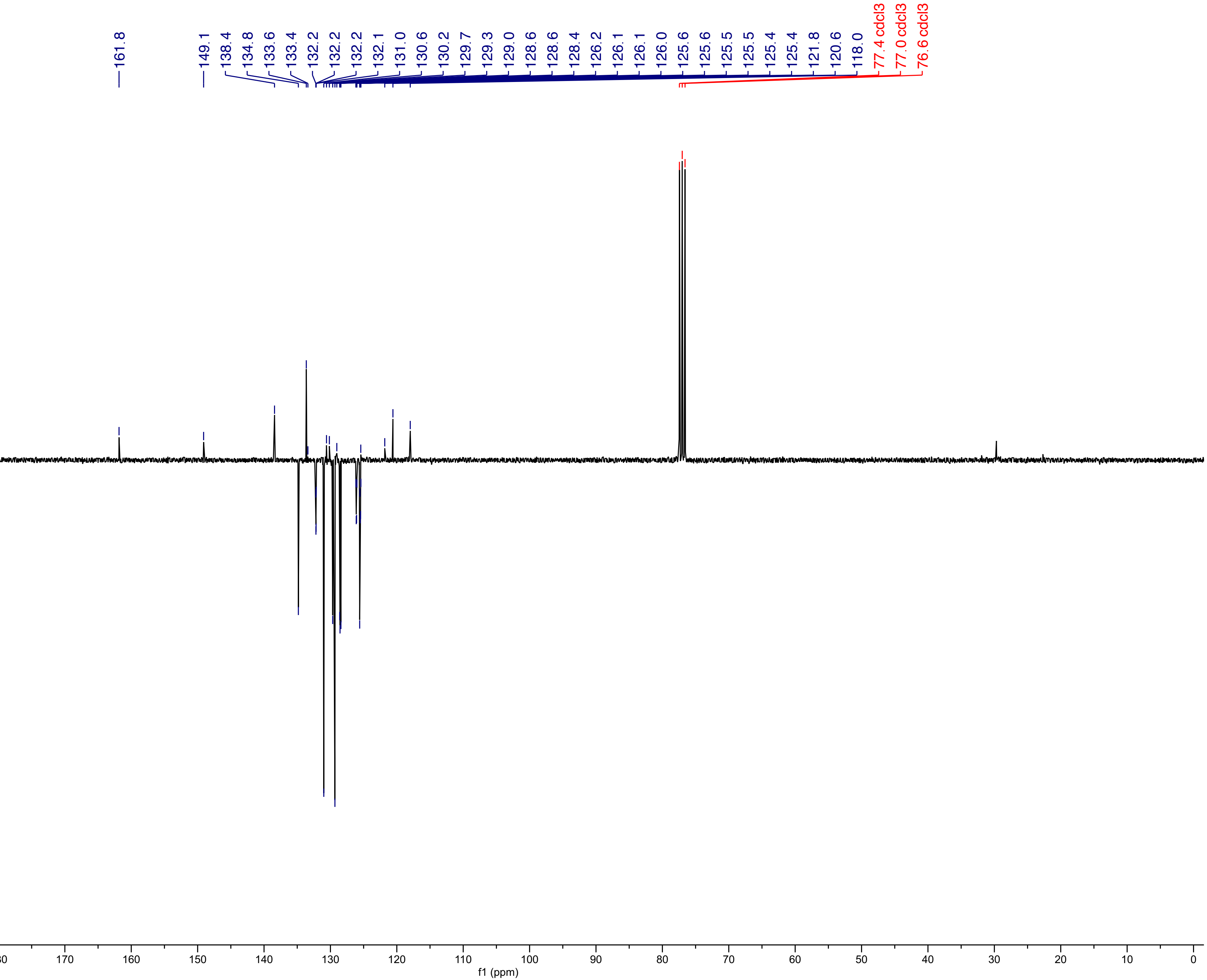
0.0
f1 (ppm)


O
O
CF3

3r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133.4
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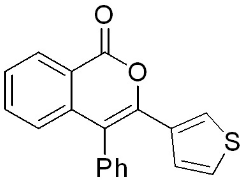
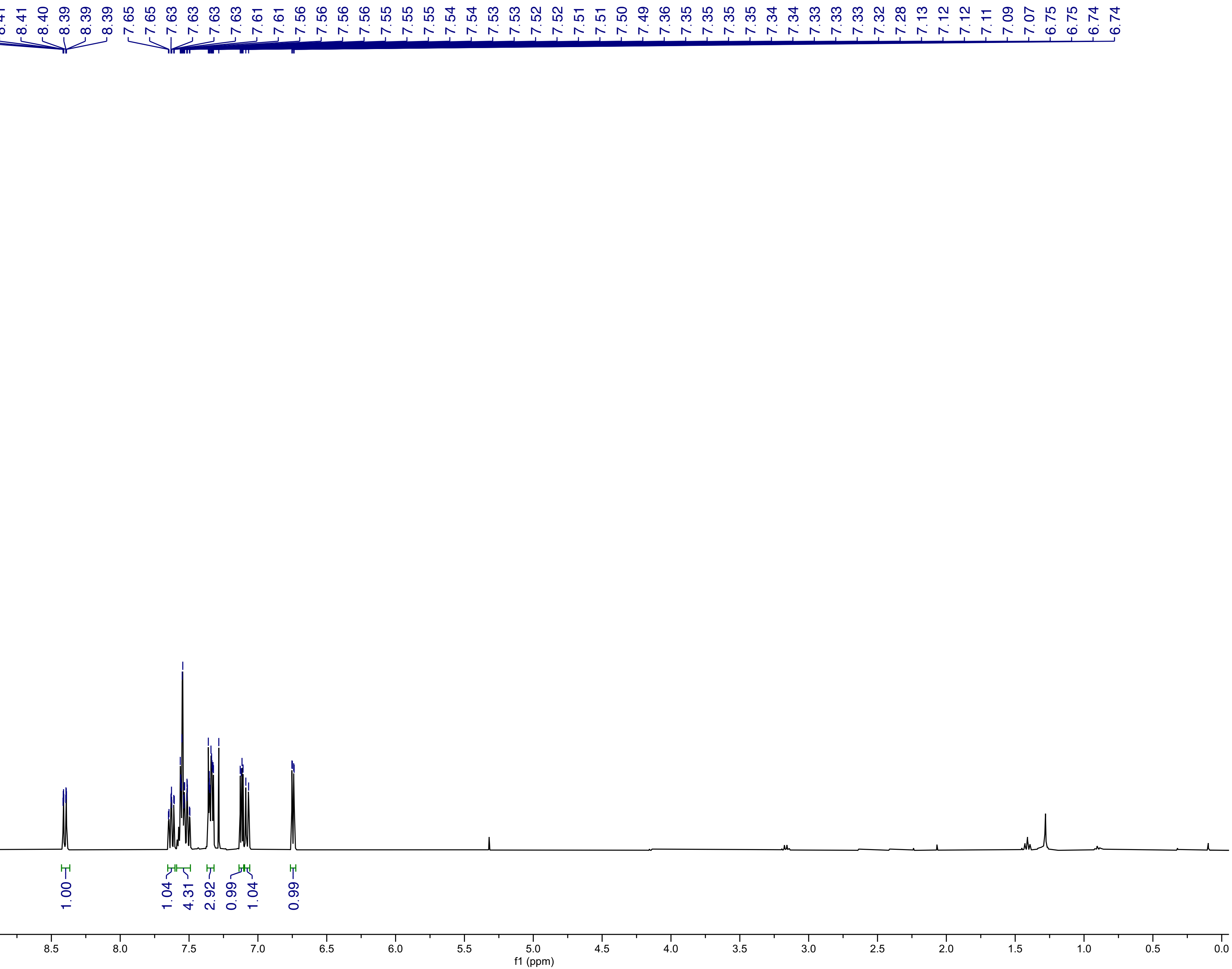
132.1
131.0
130.6
130.2
129.7
129.3
129.0
128.6
128.6
128.4
126.2
126.1
126.1
126.0
125.6
125.6
125.5
125.5
125.4
125.4
121.8
120.6
118.0
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
Ph

3s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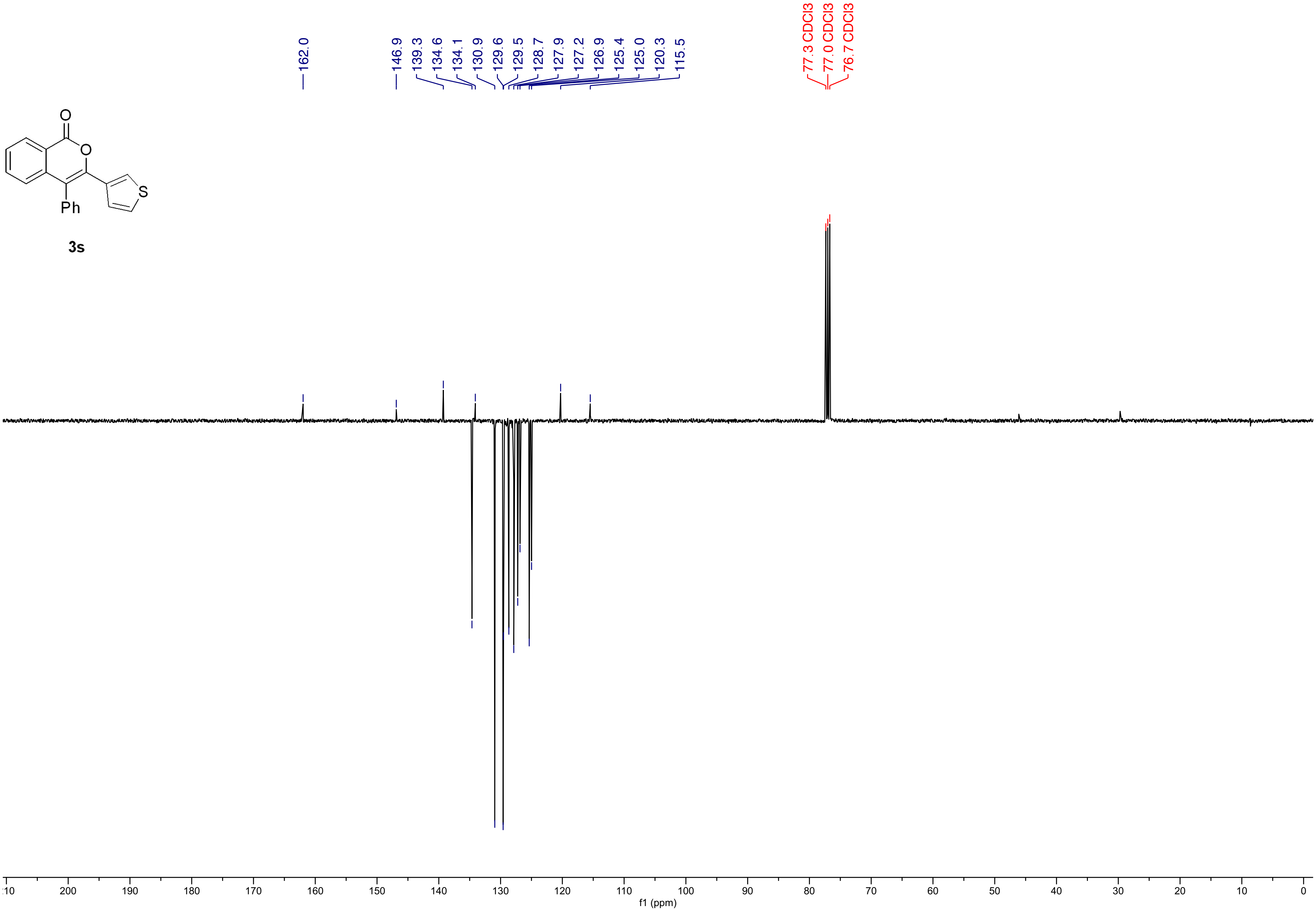
1.00
1.04
4.31
2.92
0.99
1.04
0.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


3s
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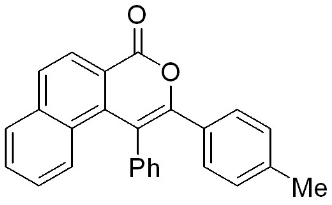
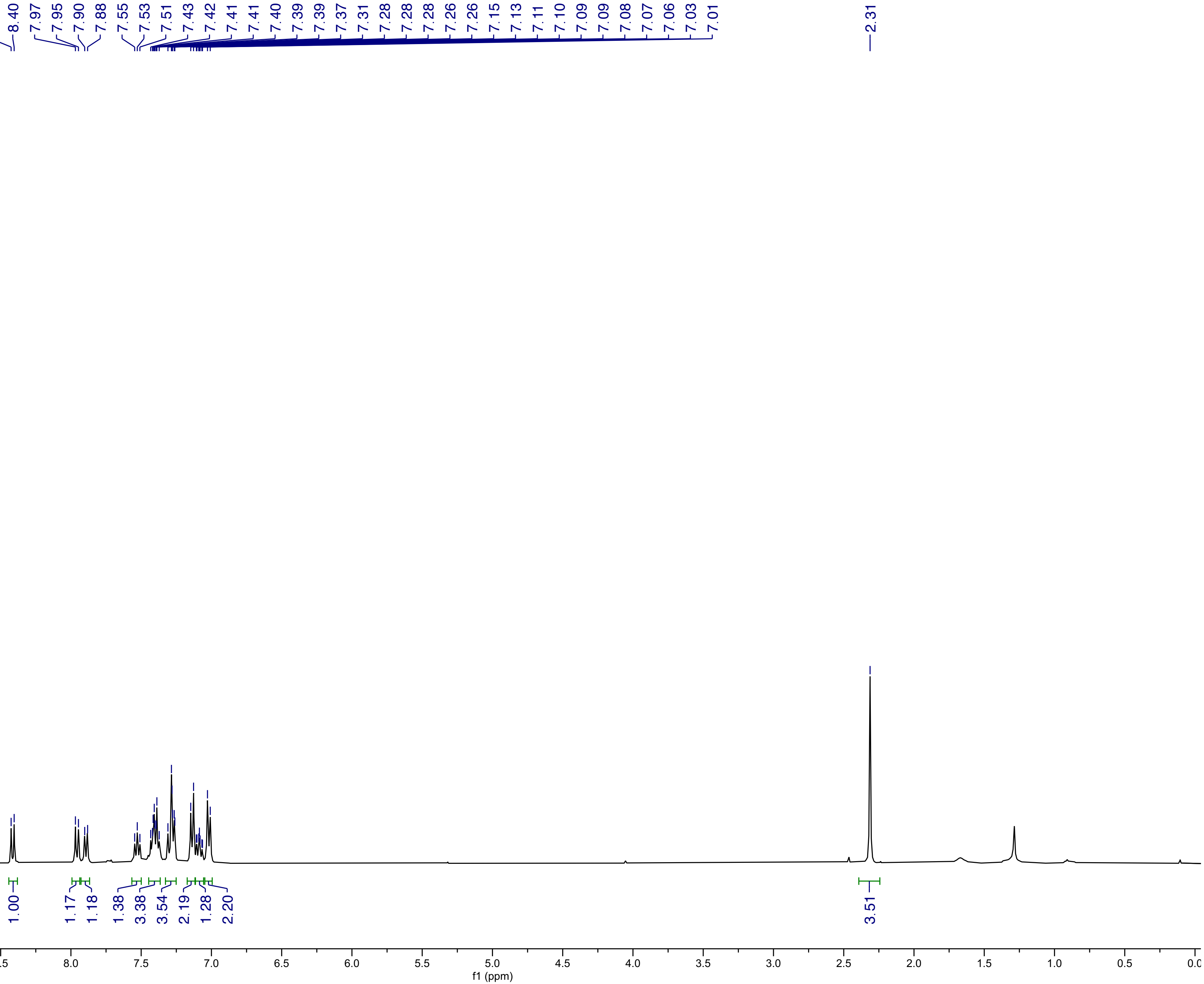
134.1
130.9
129.6
129.5
128.7
127.9
127.2
126.9
125.4
125.0
120.3
115.5
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



O
O
Ph
Me

3t



8.43
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7.53
7.51
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.37
7.31
7.28
7.28
7.28
7.26
7.26
7.15
7.13
7.11
7.10
7.09
7.09
7.08
7.07
7.06
7.03
7.01
2.31
1.00
1.17
1.18
1.38
3.38
3.54
2.19
1.28
2.20
3.51
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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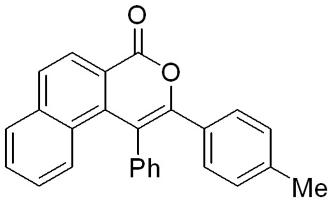
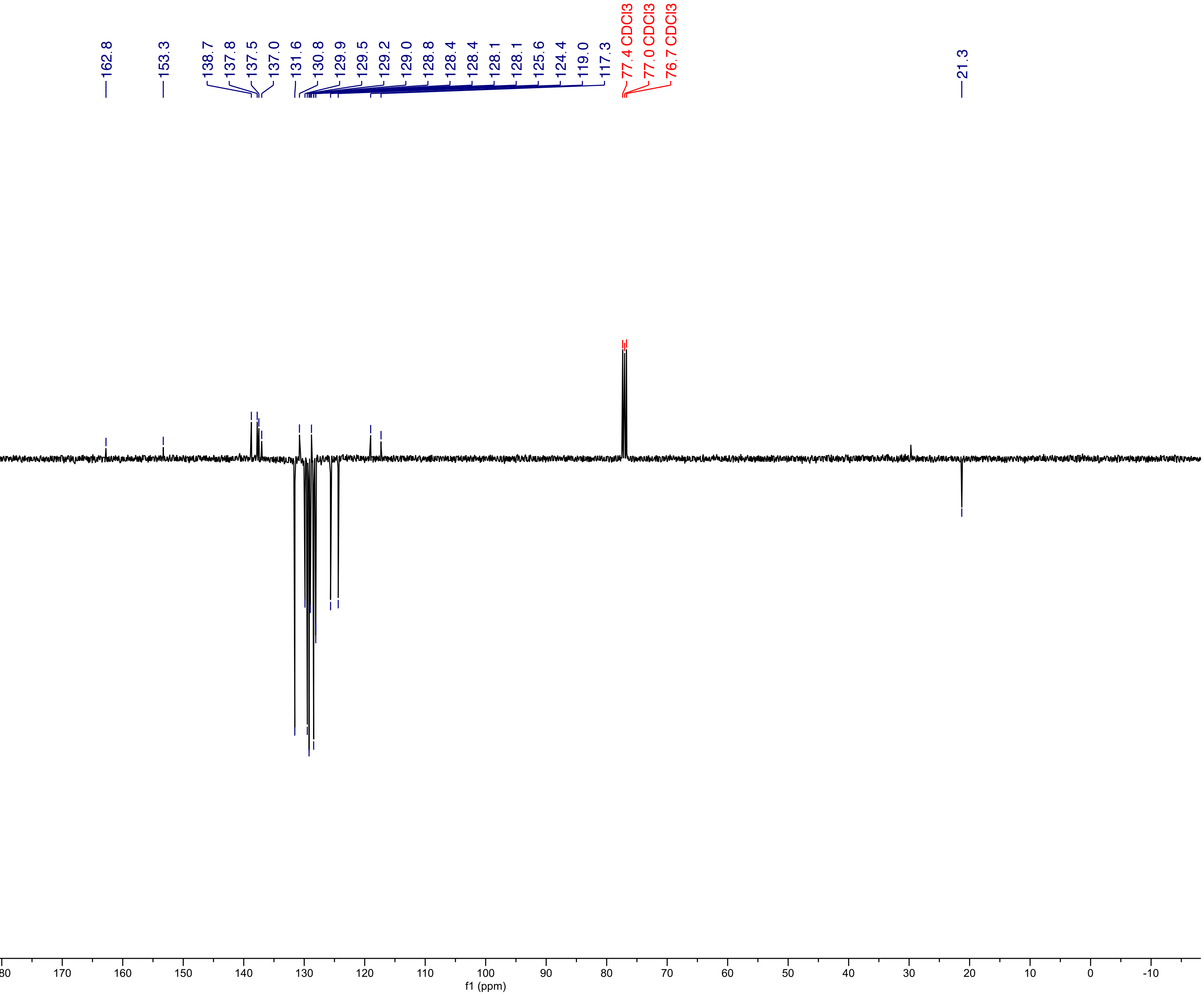
0.0
f1 (ppm)


O
O
Ph
Me

3t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137.0
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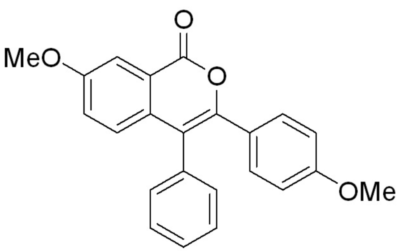
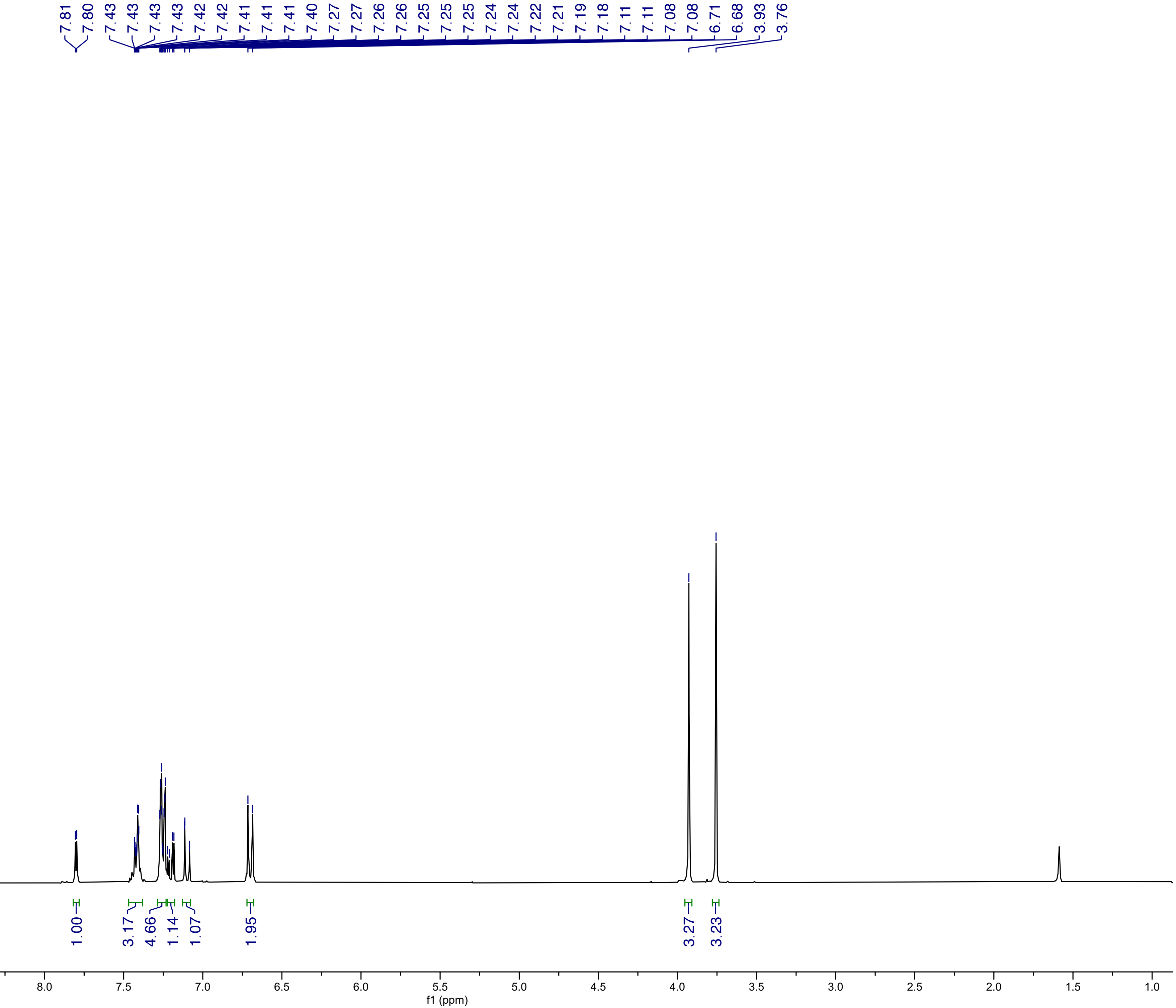
130.8
129.9
129.5
129.2
129.0
128.8
128.4
128.4
128.1
128.1
125.6
124.4
119.0
117.3
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
21.3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
O
O
OMe

3u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7.41
7.40
7.27
7.27
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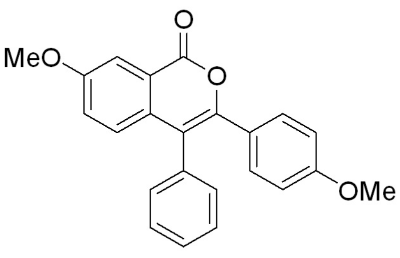
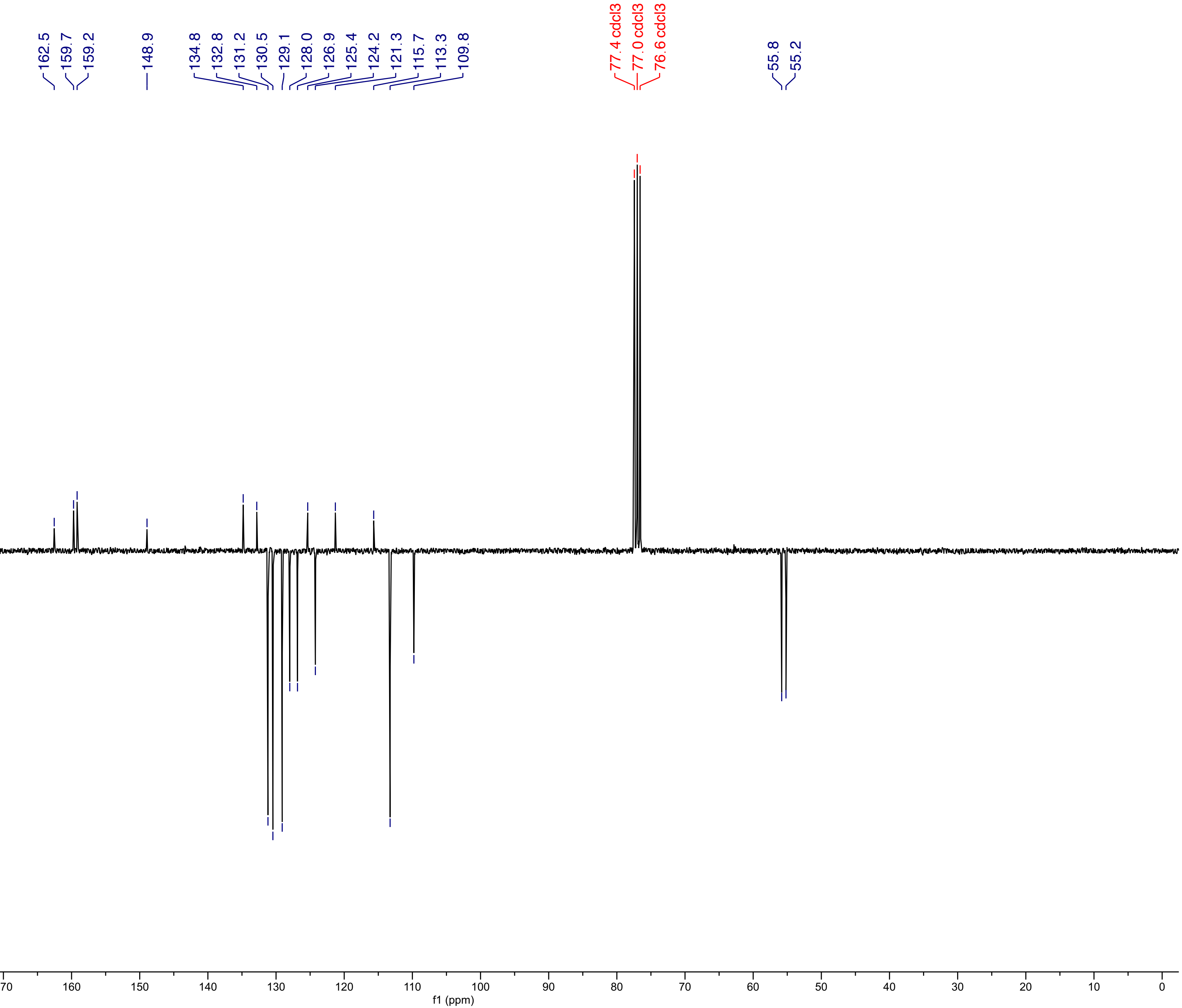
7.26
7.25
7.25
7.25
7.24
7.24
7.22
7.21
7.19
7.18
7.11
7.11
7.08
7.08
6.71
6.68
3.93
3.76
1.00
3.17
4.66
1.14
1.07
1.95
3.27
3.23
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


MeO
O
O
OMe
3u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159.2
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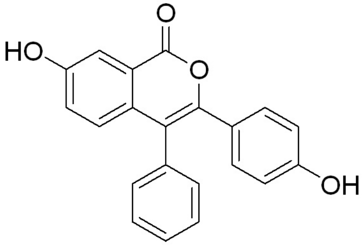
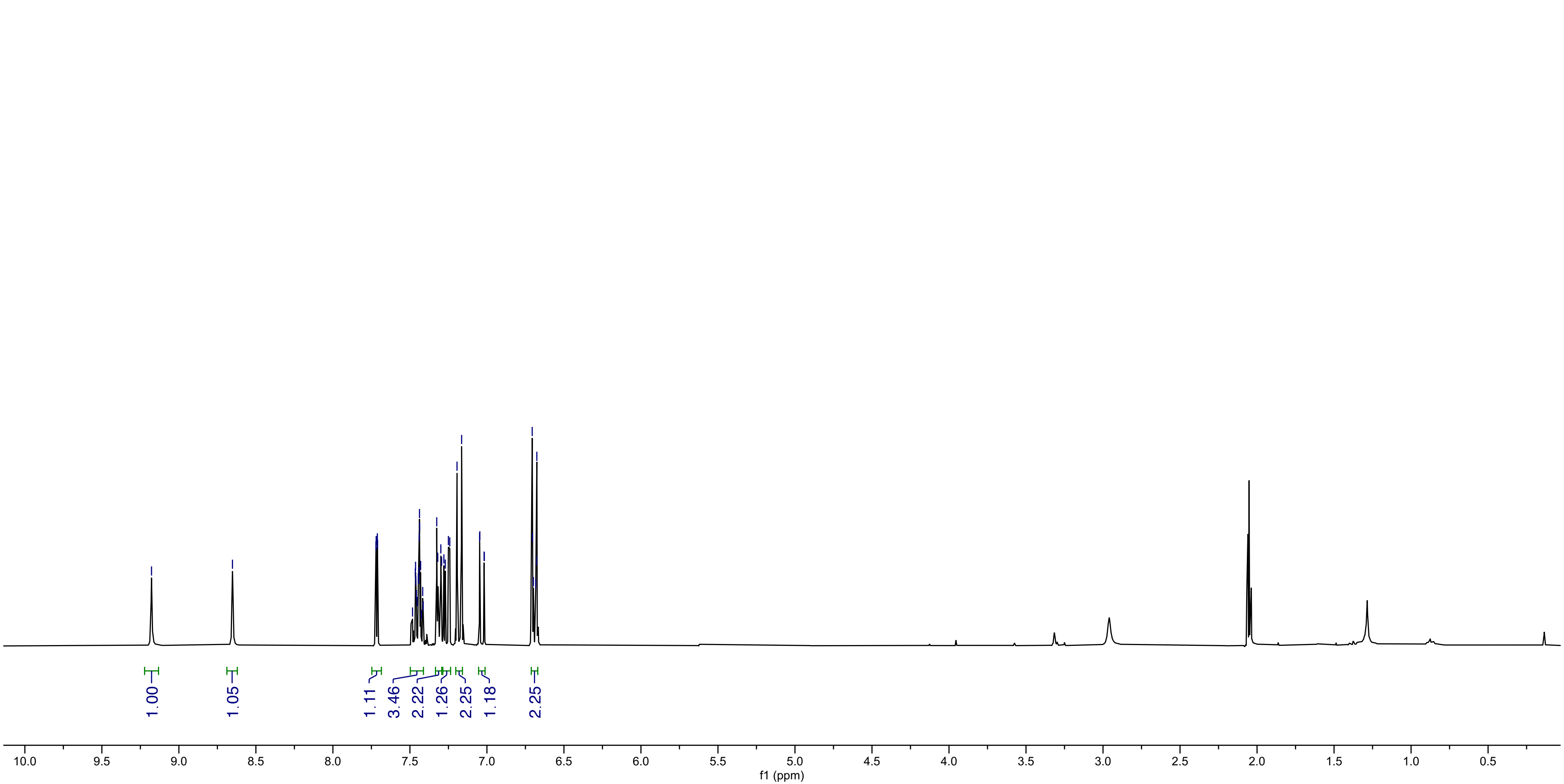
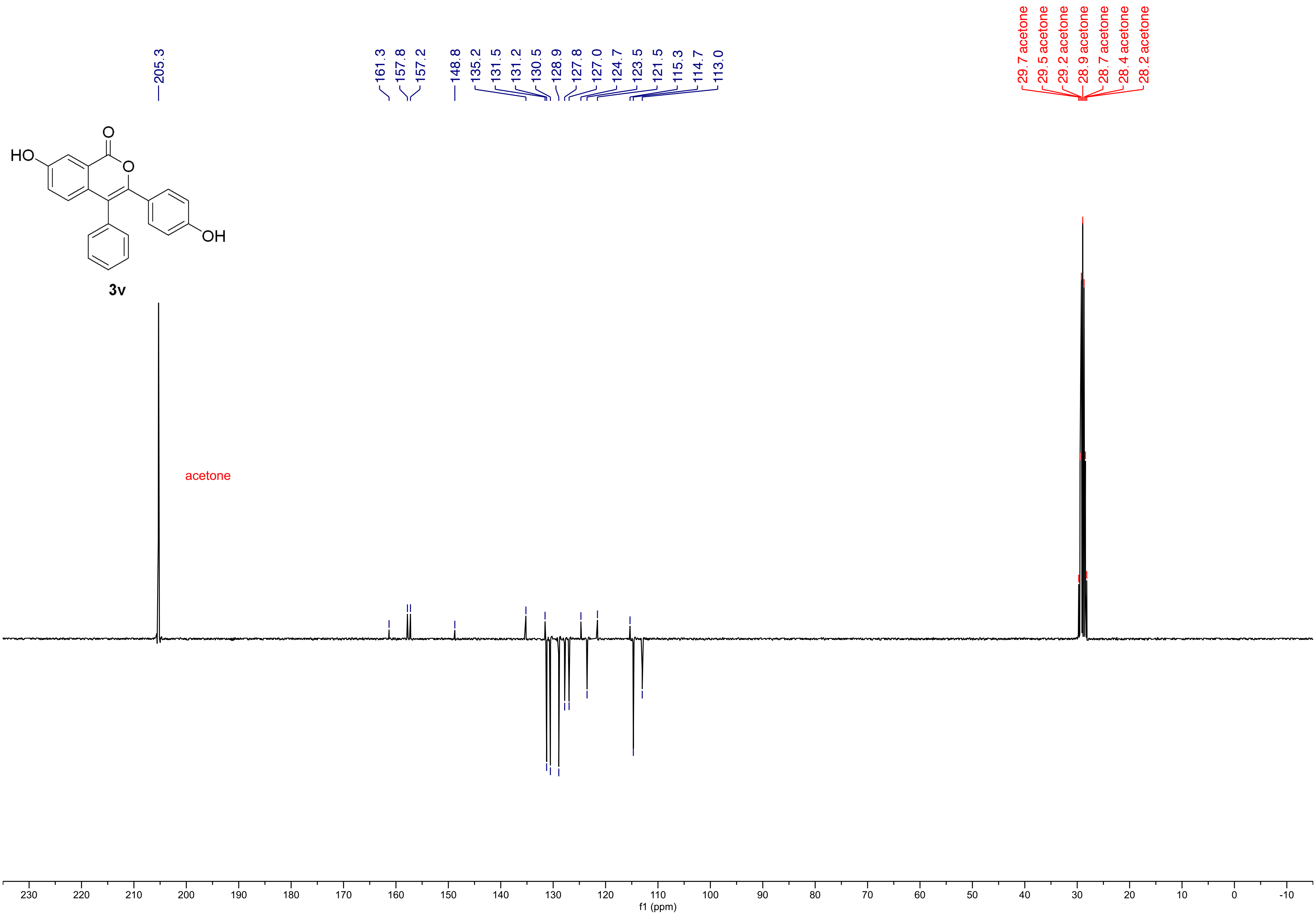
132.8
131.2
130.5
129.1
128.0
126.9
125.4
124.2
121.3
115.7
113.3
109.8
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
55.8
55.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O
O
OH

3v


9.18
8.65
7.72 7.72 7.71 7.71 7.48 7.47 7.46 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.44 7.44 7.44 7.43 7.43 7.42 7.41 7.33 7.32 7.30 7.29 7.28 7.27 7.25 7.24 7.19 7.16 7.05 7.05 7.02 7.02 6.71 6.70 6.70 6.68 6.68 6.68
1.00
1.05
1.11
3.46
2.22
1.26
2.25
1.18
2.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


205.3
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157.8
157.2
148.8
135.2
131.5
131.2
130.5
128.9
127.8
127.0
124.7
123.5
121.5
115.3
114.7
113.0
29.7 acetone
29.5 acetone
29.2 acetone
28.9 acetone
28.7 acetone
28.4 acetone
28.2 acetone
HO
O
O
OH
3v
acetone
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)