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

An efficient catalyst-free Mukaiyama-aldol reaction of fluorinated enol silyl ethers with tryptanthrin

Fu-Min Liao,† Yun-Lin Liu,† Jin-Sheng Yu,† Feng Zhou,† and Jian Zhou*†,‡

† Shanghai Key Laboratory of Green Chemistry and Chemical Process, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, P. R. China.

‡State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, P. R. China.

Contents **Page**

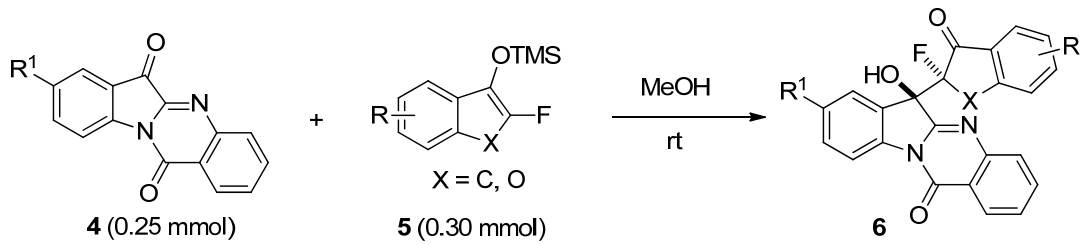
General information: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^{1}H, ^{19}F, ^{13}C NMR spectra were obtained using a Bruker DPX-300, Bruker DPX-400, Bruker DPX-500 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ or $(CD_3)_2SO$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

All reactions were carried out in air except noted. Absolute MeOH was treated by stirring commercial anhydrous methanol over magnesium chips, then distilled and stored under N_2 atmosphere. Anhydrous THF and toluene was prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous CH_2Cl_2 and CH_3CN was prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous acetone was prepared by first distillation over Ca_2SO_4, and stored over 4 Å MS. The tryptanthrins **4** were prepared according to the literature report.[1] The monofluoroenoxysilanes **5**[2] and difluoroenoxysilanes **1**[2b-c] were prepared according to the literature reports.

[1] V. M. Sharma, P. Prasanna, K. V. A. Seshu, B. Renuka, C. V. L. Rao, G. S. Kumar, C. P. Narasimhulu, P. A. Babu, R. C. Puranik, D. Subramanyam, A. Venkateswarlu, S. Rajagopal, K. B. S. Kumar, C. S. Rao, N. V. S. R. Mamidi, D. S. Deevi, R. Ajaykumar, R. Rajagopalan, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2303-2307.

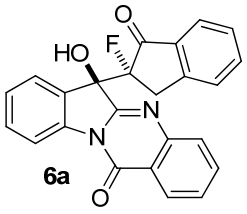
[2] a) É. Bélanger, K. Cantin, O. Messe, M. Tremblay, J.-F. Paquin, *J. Am. Chem. Soc.* **2007**, *129*, 1034-1035; b) H. Amii, T. Kobayashi, Y. Hatamoto, K. Uneyama, *Chem. Commun.* **1999**, 1323-1324; c) G. K. S. Prakash, J. Hu, G. A. Olah, *J. Fluorine Chem.* **2001**, *112*, 357-362.

1) The procedure for the Mukaiyama-aldol reaction of monofluoroenoxysilane 5



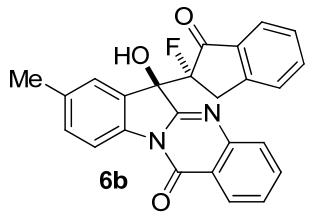
4 (0.25 mmol) **5** (0.30 mmol) **6**

To a 5.0 mL vial was added tryptanthrin **4** (0.25 mmol), followed by 2.5 mL of absolute MeOH and monofluoroenoxysilane **5** (0.30 mmol). The reaction mixture was stirred at room temperature till the full disappearance of **4** by TLC analysis (18-34 h), then the solvent was removed under reduced pressure, and the residue was directly subjected to the column chromatography by using dichloromethane/ethyl acetate (40:1) as the eluent to afford products **6**. The diastereoselectivity of **6** was determined by ^{19}F NMR analysis of the crude reaction mixture. It should be noted that the yield reported below represents the total yield of both diastereomers. Since we could isolate an analytic sample of the major diastereomer, we obtained the NMR spectra of the corresponding major diastereomer of each compound **6**.

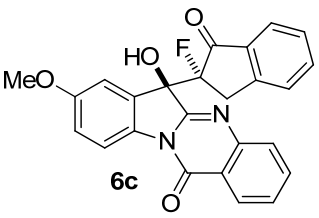


6a

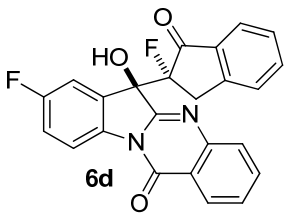
Column chromatography afforded product **6a** in 99% yield (m. p. 270-272 ^{o}C) as white solid, (dr = 3.5:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.43 (d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.79-7.67 (m, 4H), 7.61 (td, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.53 (m, 1H), 7.46 (td, *J* = 7.6, 0.8 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.33 (br, 1H), 7.26-7.22 (m, 1H), 4.79 (t, *J* = 18.0 Hz, 1H), 3.50 (dd, *J* = 26.4, 18.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.93 (d, *J* = 18 Hz, 1C), 158.35, 156.37 (d, *J* = 11 Hz, 1C), 152.29 (d, *J* = 3 Hz, 1C), 145.91, 139.00, 136.80, 134.89, 133.19, 130.53, 130.27, 128.16, 127.88, 127.45, 126.99 (d, *J* = 5 Hz, 1C), 126.64, 126.30, 124.00, 120.99, 115.65, 100.17 (d, *J* = 196 Hz, 1C), 77.23 (d, *J* = 24 Hz, 1C), 35.63 (d, *J* = 24 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.61; IR (ATR): 3332, 2922, 1716, 1654, 1636, 1595, 1461, 1008, 765, 736; MS (EI): 398 (M^+, 0.2), 248 (100), 150 (88), 130 (20), 122 (60), 102 (41), 90 (7), 76 (38); HRMS (EI): Exact mass calcd for $C_{24}H_{15}N_2O_3F$ $[M]^+$: 398.1067, Found: 398.1064.



Column chromatography afforded product **6b** in 96% yield (m. p. 299-301 ^{o}C) as white solid, (dr = 2.2:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.31 (d, *J* = 8.4 Hz, 1H), 8.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.74-7.66 (m, 3H), 7.59 (br, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.42-7.36 (m, 3H), 7.32 (s, 1H), 7.26-7.22 (m, 1H), 4.80 (t, *J* = 18.0 Hz, 1H), 3.50 (dd, *J* = 26.4, 18.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.00 (d, *J* = 18 Hz, 1C), 158.22, 156.57 (d, *J* = 12 Hz, 1C), 152.32 (d, *J* = 3 Hz, 1C), 145.98, 136.84, 136.00, 134.80, 133.27, 130.64, 128.12, 127.91, 127.47, 127.45 (d, *J* = 5 Hz, 1C), 126.68, 126.27, 124.03, 121.06, 115.47, 100.23 (d, *J* = 196 Hz, 1C), 77.31 (d, *J* = 24 Hz, 1C), 35.73 (d, *J* = 23 Hz, 1C), 21.05; ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.65; IR (ATR): 3350, 2921, 1719, 1657, 1639, 1467, 1123, 1078, 911, 774, 736; MS (EI): 412 (M^+, 0.6), 262 (100), 150 (67), 130 (15), 122 (43), 102 (30), 76 (26); HRMS (EI): Exact mass calcd for $C_{25}H_{17}N_2O_3F$ $[M]^+$: 412.1223, Found: 412.1225.

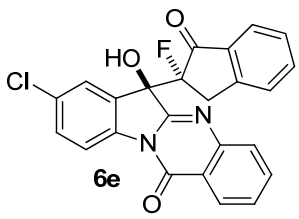


Column chromatography afforded product **6c** in 86% yield (m. p. 263-265 ^{o}C) as white solid, (dr = 2.2:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (d, *J* = 8.8 Hz, 1H), 8.17 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.74-7.66 (m, 3H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.41-7.36 (m, 3H), 7.30 (t, *J* = 2.6 Hz, 1H), 7.23 (td, *J* = 8.0, 2.0 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.80 (t, *J* = 17.8 Hz, 1H), 3.85 (s, 3H), 3.51 (dd, *J* = 26.4, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.92 (d, *J* = 18 Hz, 1C), 158.00, 157.88, 156.42 (d, *J* = 11 Hz, 1C), 152.33 (d, *J* = 3 Hz, 1C), 145.93, 136.85, 134.68, 133.23, 132.47, 132.18, 128.09, 127.92, 127.45, 126.68, 126.18, 124.04, 121.06, 116.65, 114.81, 113.10 (d, *J* = 5 Hz, 1C), 100.25 (d, *J* = 197 Hz, 1C), 77.32 (d, *J* = 24 Hz, 1C), 55.66, 35.68 (d, *J* = 23 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -161.11; IR (ATR): 3292, 2917, 1711, 1656, 1467, 1203, 1026, 908, 858, 777, 738; MS (EI): 428 (M^+, 1.9), 278 (86), 150 (100), 130 (27), 122 (69), 102 (45), 76 (34); HRMS (EI): Exact mass calcd for $C_{25}H_{17}N_2O_4F$ $[M]^+$: 428.1172, Found: 428.1168.



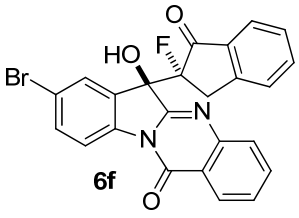
Column chromatography afforded product **6d** in 99% yield (m. p. 282-284 ^{o}C) as white solid, (dr = 3.1:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.44 (dd, *J* = 9.2, 4.8 Hz, 1H), 8.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.77-7.67 (m, 3H), 7.58-7.46 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 4.81 (t, *J* = 17.8 Hz, 1H), 3.52 (dd, *J* = 26.4, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.85 (d, *J* = 18 Hz, 1C), 161.54, 159.12, 158.17, 156.03 (d, *J* = 11 Hz, 1C),

152.38 (d, *J* = 3 Hz, 1C), 145.82, 136.99, 135.33, 135.01, 133.03, 132.93 (d, *J* = 9 Hz, 1C), 128.33, 127.97, 127.49, 126.68, 126.31, 124.10, 120.91, 117.10 (m, 1C), 114.32 (dd, *J* = 6, 6 Hz, 1C), 100.18 (d, *J* = 197 Hz, 1C), 77.08 (d, *J* = 22 Hz, 1C), 35.46 (d, *J* = 24 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.87, -114.82; IR (ATR): 3330, 1720, 1659, 1605, 1467, 1077, 911, 832, 777, 693; MS (EI): 416 (M^+, 1.1), 266 (100), 150 (82), 130 (18), 122 (53), 102 (32), 76 (34); HRMS (EI): Exact mass calcd for $C_{24}H_{14}N_2O_3F_2$ $[M]^+$: 416.0972, Found: 416.0967.



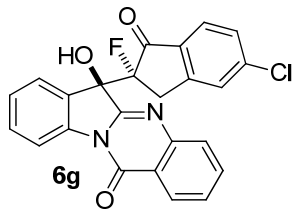
6e

Column chromatography afforded product **6e** in 92% yield (m. p. 332-334 ^{o}C) as white solid, (dr = 2.2:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.77-7.68 (m, 5H), 7.58-7.54 (m, 1H), 7.52 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 4.80 (t, *J* = 18.0 Hz, 1H), 3.53 (dd, *J* = 26.8, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.88 (d, *J* = 17 Hz, 1C), 158.23, 155.70 (d, *J* = 12 Hz, 1C), 152.39 (d, *J* = 3 Hz, 1C), 145.82, 137.79, 137.03, 135.12, 133.01, 132.70, 130.67, 130.34, 128.41, 128.00, 127.54, 126.79 (d, *J* = 6 Hz, 1C), 126.70, 126.38, 124.13, 120.86, 117.22, 100.16 (d, *J* = 197 Hz, 1C), 77.07 (d, *J* = 24 Hz, 1C), 35.43 (d, *J* = 24 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.64; IR (ATR): 3358, 2922, 1715, 1657, 1463, 1028, 903, 836, 780, 676; MS (EI): 434 ($[M+2]^+$, 0.26), 432 (M^+, 0.55), 282 (100), 150 (85), 130 (17), 122 (53), 102 (35), 76 (33); HRMS (EI): Exact mass calcd for $C_{24}H_{14}N_2O_3F^{35}Cl$ $[M]^+$: 432.0677, Found: 432.0681.

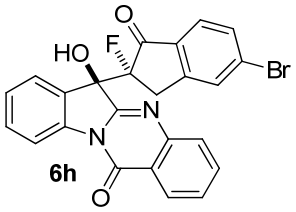


6f

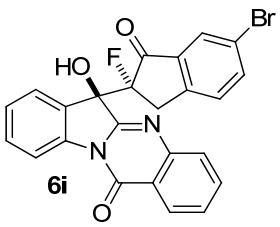
Column chromatography afforded **6f** in 88% yield (m. p. 295-297 ^{o}C) as white solid, (dr = 2.2:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.37 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.87-7.83 (m, 2H), 7.76-7.67 (m, 3H), 7.57-7.53 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 4.79 (t, *J* = 19.0 Hz, 1H), 3.53 (dd, *J* = 26.4, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.89 (d, *J* = 18 Hz, 1C), 158.26, 155.60 (d, *J* = 12 Hz, 1C), 152.40 (d, *J* = 3 Hz, 1C), 145.84, 138.21, 137.03, 135.12, 133.23, 133.02, 132.93, 129.59 (d, *J* = 6 Hz, 1C), 128.41, 128.00, 127.55, 126.71, 126.40, 124.14, 120.88, 118.80, 117.61, 100.18 (d, *J* = 197 Hz, 1C), 77.04 (d, *J* = 24 Hz, 1C), 35.45 (d, *J* = 23 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.55; IR (ATR): 3365, 2919, 1715, 1658, 1642, 1461, 1069, 901, 799, 736; MS (EI): 478 ($[M+2]^+$, 0.68), 476 (M^+, 0.62), 328 (65), 150 (100), 130 (21), 122 (63), 102 (39), 76 (35); HRMS (EI): Exact mass calcd for $C_{24}H_{14}N_2O_3F^{79}Br$ $[M]^+$:476.0172, Found: 476.0170.



Column chromatography afforded product **6g** in 88% yield (m. p. 261-263 °C) as white solid, (dr = 6.0:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.84 (br, 1H), 7.79-7.75 (m, 2H), 7.63-7.54 (m, 2H), 7.48-7.43 (m, 2H), 7.40 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 4.78 (t, *J* = 17.4 Hz, 1H), 3.52 (dd, *J* = 25.6, 18.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.75 (d, *J* = 18 Hz, 1C), 158.35, 156.20 (d, *J* = 12 Hz, 1C), 154.20 (d, *J* = 3 Hz, 1C), 145.89, 141.75, 138.99, 134.96, 131.91, 130.41, 130.26, 128.42, 128.27, 127.41, 127.03 (d, *J* = 5 Hz, 1C), 126.75, 126.71, 126.36, 125.69, 121.00, 115.71, 100.31 (d, *J* = 198 Hz, 1C), 77.20 (d, *J* = 24 Hz, 1C), 35.48 (d, *J* = 24 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.99; IR (ATR): 3307, 2938, 1720, 1657, 1598, 1461, 902, 779, 761, 692; MS (EI): 432 (M^+, 0.57), 248 (100), 184 (69), 164 (19), 156 (28), 138 (24), 110 (17), 75 (30); HRMS (EI): Exact mass calcd for $C_{24}H_{14}N_2O_3F^{35}Cl$ $[M]^+$: 432.0677, Found: 432.0691.

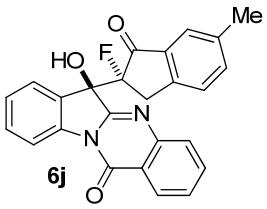


Column chromatography afforded product **6h** in 90% yield (m. p. 261-263 °C) as white solid, (dr = 4.5:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.00 (s, 1H), 7.79-7.75 (m, 2H), 7.63-7.55 (m, 2H), 7.48-7.38 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 17.4 Hz, 1H), 3.52 (dd, *J* = 25.8, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.95 (d, *J* = 18 Hz, 1C), 158.31, 156.17 (d, *J* = 12 Hz, 1C), 154.15 (d, *J* = 4 Hz, 1C), 145.85, 138.95, 134.89, 132.17, 131.20 (d, *J* = 2 Hz, 1C), 130.35, 130.22, 128.21, 127.38, 127.00, 126.94, 126.65, 126.32, 125.61, 120.96, 115.66, 100.22 (d, *J* = 198 Hz, 1C), 77.16 (d, *J* = 24 Hz, 1C), 35.37 (d, *J* = 24 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -161.06; IR (ATR): 3306, 2920, 1719, 1656, 1595, 1460, 899, 778, 760, 692; MS (ESI): 476 (^{79}Br), 478 (^{81}Br); HRMS (EI): Exact mass calcd for $C_{24}H_{14}N_2O_3F^{79}Br$ $[M]^+$: 476.0172, Found: 476.0169.

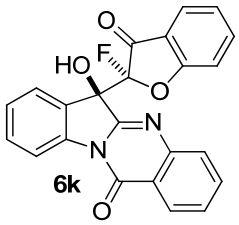


Column chromatography afforded product **6i** in 88% yield (m. p. 267-269 °C) as white solid, (dr = 1.8:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.43 (d, *J* = 8.0 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.79-7.75 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.64-7.54 (m, 3H), 7.48-7.41 (m, 2H), 7.39 (s, 1H), 4.74 (t, *J* = 17.8 Hz, 1H), 3.48 (dd, *J* = 26.0, 18.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.83 (d, *J* = 18 Hz, 1C), 158.37, 156.25 (d, *J* = 11 Hz, 1C), 151.42 (d, *J* = 3 Hz, 1C), 145.90, 139.27, 139.01, 135.10, 135.01, 130.45, 130.27, 128.92, 128.30,

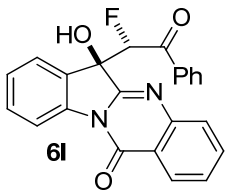
127.48, 127.04 (d, *J* = 5 Hz, 1C), 126.73, 126.46, 126.38, 121.06, 120.98, 115.74, 100.27 (d, *J* = 197 Hz, 1C), 77.17 (d, *J* = 24 Hz, 1C), 35.40 (d, *J* = 23 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -160.33; IR (ATR): 3335, 1719, 1660, 1640, 1597, 1462, 1188, 1077, 811, 759, 695; HRMS (ESI): Exact mass calcd for $C_{24}H_{15}{}^{79}BrFN_2O_3$ $[M+H]^+$: 477.0245, Found: 477.0242.



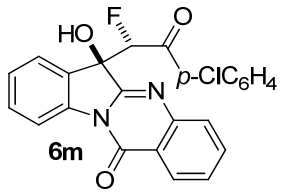
Column chromatography afforded product **6j** in 96% yield (m. p. 269-271 ^{o}C) as white solid, (dr = 4.0:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.74 (td, *J* = 8.4, 1.2 Hz, 1H), 7.63-7.43 (m, 6H), 7.33 (s, 1H), 7.18 (br, 1H), 4.76 (t, *J* = 18.8 Hz, 1H), 3.45 (dd, *J* = 26.4, 18.0 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.89 (d, *J* = 18 Hz, 1C), 158.42, 156.61 (d, *J* = 12 Hz, 1C), 149.70 (d, *J* = 2 Hz, 1C), 146.02, 139.09, 137.97, 137.58, 134.92, 133.40, 130.74, 130.28, 128.16, 127.57, 127.04 (d, *J* = 5 Hz, 1C), 126.65, 126.43, 126.36, 123.83, 121.11, 115.73, 100.39 (d, *J* = 196 Hz, 1C), 77.27 (d, *J* = 24 Hz, 1C), 35.41 (d, *J* = 23 Hz, 1C), 20.34; ^{19}F NMR (376 MHz, DMSO-d_6): δ -159.34; IR (ATR): 3370, 2917, 2348, 1713, 1660, 1598, 1461, 906, 759, 691, 671; MS (EI): 412 (M^+, 0.7), 248 (100), 164 (75), 144 (14), 135 (39), 115 (29), 90 (16), 76 (15); HRMS (EI): Exact mass calcd for $C_{25}H_{17}N_2O_3F$ $[M]^+$: 412.1223, Found: 412.1227.



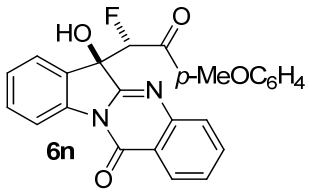
Column chromatography afforded **6k** in 81% yield (m. p. 261-263 ^{o}C) as white solid, (dr = 1.5:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.43 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 7.90 (t, *J* = 7.4 Hz, 1H), 7.78-7.72 (m, 2H), 7.68-7.64 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 190.64 (d, *J* = 19 Hz, 1C), 169.77, 158.62, 155.64, 146.31, 140.31, 139.53, 135.23, 131.36, 128.42, 127.96, 127.91, 126.73, 126.56, 126.16, 125.08, 124.32, 121.41, 118.46, 116.11, 113.20, 108.70 (d, *J* = 250 Hz, 1C), 77.78 (d, *J* = 28 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -129.95; IR (ATR): 3332, 1722, 1657, 1600, 1462, 1058, 911, 755, 686; MS (EI): 400 (M^+, 0.33), 248 (100), 152 (56), 124 (11), 104 (42), 76 (76); HRMS (EI): Exact mass calcd for $C_{23}H_{13}N_2O_4F$ $[M]^+$: 400.0859, Found: 400.0855.



Column chromatography afforded product **6l** in 95% yield (m. p. 280-282 °C) as white solid, (dr = 1.1:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.26 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.89 (td, *J* = 7.6, 1.6 Hz, 1H), 7.75-7.72 (m, 3H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.57 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40-7.33 (m, 3H), 7.26 (s, 1H), 6.63 (d, *J* = 45.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.79 (d, *J* = 22 Hz, 1C), 158.55, 157.80, 157.73, 146.54, 139.22, 134.95, 134.82, 133.73, 130.56, 130.41, 128.94 (d, *J* = 3 Hz, 1C), 128.30, 127.93, 127.63, 126.78, 126.45, 125.58, 121.31, 116.04, 95.62 (d, *J* = 192 Hz, 1C), 77.00 (d, *J* = 21 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -196.66; IR (ATR): 3340, 2927, 1687, 1597, 1464, 1322, 853, 760, 693, 663; MS (EI): 386 (M^+, 0.42), 248 (54), 138 (15), 117 (1.7), 105 (100), 77 (76); HRMS (EI): Exact mass calcd for $C_{23}H_{15}N_2O_3F$ $[M]^+$: 386.1067, Found: 386.1065.

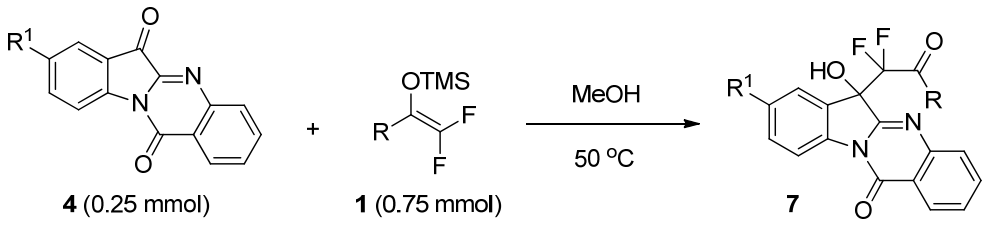


Column chromatography afforded product **6m** in 98% yield (m. p. 269-271 °C) as white solid, (dr = 1.9:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (d, *J* = 7.6 Hz, 1H), 8.27 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.91-7.87 (m, 1H), 7.77-7.71 (m, 4H), 7.65-7.61 (m, 1H), 7.59-7.55 (m, 1H), 7.43-7.38 (m, 3H), 7.27 (s, 1H), 6.63 (d, *J* = 45.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.82 (d, *J* = 21 Hz, 1C), 158.48, 157.50, 157.44, 146.41, 139.09, 138.64, 134.91, 133.76, 130.76, 130.73, 130.59, 130.27, 128.36, 127.94, 127.60, 126.77, 126.41, 125.52 (d, *J* = 2 Hz, 1C), 121.27, 116.02, 95.42 (d, *J* = 191 Hz, 1C), 77.11 (d, *J* = 22 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -196.95; IR (ATR): 3316, 1692, 1659, 1589, 1314, 1091, 822, 758, 692; HRMS (ESI): Exact mass calcd for $C_{23}H_{15}ClFN_2O_3$ $[M+H]^+$: 421.0750, Found: 421.0752.

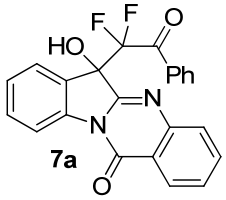


Column chromatography afforded product **6n** in 97% yield (m. p. 266-268 °C) as white solid, (dr = 1.1:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.27 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.90-7.86 (m, 1H), 7.76-7.73 (m, 3H), 7.68-7.66 (m, 1H), 7.64-7.60 (m, 1H), 7.55 (td, *J* = 8.0, 1.2 Hz, 1H), 7.37 (td, *J* = 7.6, 0.8 Hz, 1H), 7.23 (s, 1H), 6.88-6.85 (m, 2H), 6.55 (d, *J* = 45.6 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.41 (d, *J* = 20 Hz, 1C), 163.70, 158.60, 158.11, 158.03, 146.62, 139.30, 134.88, 131.55 (d, *J* = 4 Hz, 1C), 130.59, 130.39, 127.81, 127.61, 127.29, 126.69, 126.43, 125.55 (d, *J* = 3 Hz, 1C), 121.35, 116.02, 113.72, 95.75 (d, *J* = 192 Hz, 1C), 77.00 (d, *J* = 21 Hz, 1C), 55.55; ^{19}F NMR (376 MHz, DMSO-d_6): δ -195.56; IR (ATR): 3341, 1661, 1642, 1598, 1464, 1264, 1243, 1174, 778; HRMS (ESI): Exact mass calcd for $C_{24}H_{18}FN_2O_4$ $[M+H]^+$: 417.1245, Found: 417.1248.

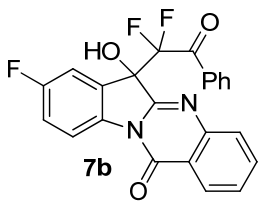
2) General procedure for the Mukaiyama-aldol reaction using difluoroenoxysilane 1



To a 5.0 mL vial was added tryptanthrins **4** (0.25 mmol), followed by 2.5 mL of absolute MeOH and difluoroenoxysilanes **1** (0.75 mmol). The reaction mixture was stirred at 50 ^{o}C. After the completion of tryptanthrins **4** by TLC analysis (3-12 h), the mixture was concentrated and directly subjected to column chromatography, to afford the desired product **7**, using dichloromethane/ethyl acetate (40:1) as the eluent.

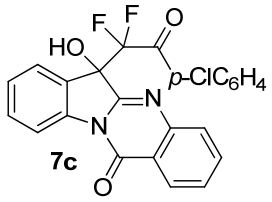


Column chromatography afforded product **7a** in 94% yield (m. p. 265-267 ^{o}C) as white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.06-8.04 (m, 2H), 7.91-7.88 (m, 2H), 7.76-7.62 (m, 5H), 7.57-7.53 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 187.66 (t, *J* = 29 Hz, 1C), 158.67, 155.90, 146.32, 139.64, 135.18, 135.10, 131.94, 131.45, 130.24, 128.95, 128.56, 128.35, 127.99, 126.91, 126.60, 125.93, 121.48, 116.90 (t, *J* = 263.5 Hz, 1C), 116.37, 77.64 (t, *J* = 24.5 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -108.17 (d, *J* = 282 Hz, 1F), -107.39 (d, *J* = 286 Hz, 1F); IR (ATR): 3307, 1696, 1659, 1597, 1464, 1182, 1103, 831, 765, 712; MS (EI): 404 (M^+, 1.7), 249 (100), 155 (11), 135 (86), 105 (38), 77 (57); HRMS (EI): Exact mass calcd for $C_{23}H_{14}N_2O_3F_2$ $[M]^+$: 404.0972, Found: 404.0970.



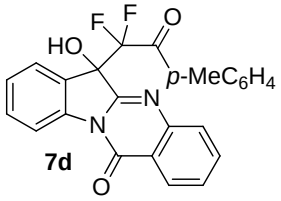
Column chromatography afforded product **7b** in 96% yield (m. p. 283-285 ^{o}C) as white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.53 (dd, *J* = 8.8, 4.8 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.06-8.04 (m, 3H), 7.89 (t, *J* = 8.4 Hz, 1H), 7.76-7.70 (m, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.57-7.47 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 187.48 (t, *J* = 29 Hz, 1C), 161.49, 159.06, 158.48, 155.72, 146.24, 135.98, 135.22, 131.74, 130.82 (d, *J* = 8 Hz, 1C), 130.25, 128.98, 128.44, 128.00, 126.57, 121.41, 118.11 (d, *J* = 6 Hz, 1C), 117.97, 116.69 (t, *J* = 264 Hz, 1C), 113.47 (d, *J* = 13 Hz, 1C), 77.48 (t, *J* = 24 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -114.01, -107.77, -107.75; IR (ATR): 3280, 1696,

1658, 1466, 1311, 1267, 1188, 923, 841, 773; MS (EI): 422 (M^+, 3), 267 (100), 156 (9), 105 (34), 77 (36); HRMS (EI): Exact mass calcd for $C_{23}H_{13}N_2O_3F_3$ $[M]^+$: 422.0878, Found: 422.0881.



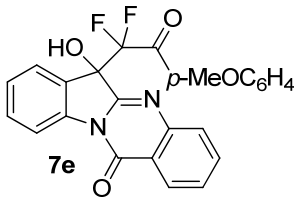
7c

Column chromatography afforded product **7c** in 99% yield (m. p. 267-269 ^oC) as white solid. ^1H NMR (400 MHz, DMSO-d_6): δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.09-8.07 (m, 2H), 7.92-7.88 (m, 2H), 7.74-7.72 (m, 2H), 7.69-7.62 (m, 4H), 7.44 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 186.57 (t, *J* = 29 Hz, 1C), 158.55, 155.53, 146.14, 140.03, 139.56, 135.13, 132.13, 131.48, 131.03, 129.01, 128.37, 128.26, 127.92, 126.88, 126.55, 125.97, 121.42, 116.74 (t, *J* = 262 Hz, 1C), 116.29, 77.74 (t, *J* = 25 Hz, 1C); ^{19}F NMR (376 MHz, DMSO-d_6): δ -108.69 (d, *J* = 278 Hz, 1F), -107.92 (d, *J* = 278 Hz, 1F); IR (ATR): 3275, 1702, 1662, 1587, 1465, 1181, 1087, 833, 757, 690; MS (EI): 440 ($[M+2]^+$, 0.44), 438 (M^+, 1.39), 249 (100), 139 (62), 111 (37), 75 (28); HRMS (EI): Exact mass calcd for $C_{23}H_{13}N_2O_3F_2{}^{35}Cl$ $[M]^+$: 438.0583, Found: 438.0588.



7d

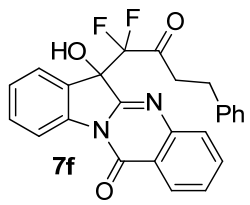
Column chromatography afforded product **7d** in 84% yield (m. p. 272-274 ^oC) as white solid. ^1H NMR (400 MHz, DMSO-d_6): δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.33 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.94-7.92 (m, 2H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.82 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70-7.61 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35-7.33 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 187.05 (t, *J* = 28.5 Hz, 1C), 158.65, 156.02, 146.34, 146.15, 139.61, 135.13, 131.34, 130.32, 129.51, 129.23, 128.65, 128.28, 127.95, 126.83, 126.55, 125.82, 121.44, 116.94 (t, *J* = 263.5 Hz, 1C), 116.32, 77.52 (t, *J* = 24 Hz, 1C), 21.34; ^{19}F NMR (376 MHz, DMSO-d_6): δ -108.01 (d, *J* = 286 Hz, 1F), -107.18 (d, *J* = 286 Hz, 1F); IR (ATR): 3327, 1695, 1661, 1604, 1465, 1182, 1096, 840, 774, 762, 750, 693; MS (EI): 418 (M^+, 2.49), 249 (100), 170 (11), 119 (59), 91 (48), 76 (11); HRMS (EI): Exact mass calcd for $C_{24}H_{16}N_2O_3F_2$ $[M]^+$: 418.1129, Found: 418.1125.



7e

Column chromatography afforded product **7e** in 95% yield (m. p. 269-271 ^oC) as white solid. ^1H NMR (400 MHz, DMSO-d_6): δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.33 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.03-8.01 (m, 2H), 7.90 (t, *J* = 8.0 Hz,1H), 7.77-7.75 (m, 2H), 7.68-7.60 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.08-7.05 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 185.60 (t, *J* =

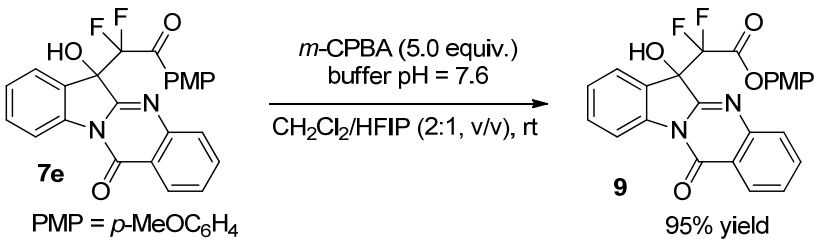
28.5 Hz, 1C), 164.69, 158.67, 156.19, 146.39, 139.61, 135.11, 132.90, 131.24, 128.82, 128.22, 127.94, 126.78, 126.53, 125.72, 124.24, 121.43, 117.13 (t, *J* = 262 Hz, 1C), 116.29, 114.38, 77.45 (t, *J* = 23.5 Hz, 1C), 55.81; ^{19}F NMR (376 MHz, DMSO-d_6): δ -107.42 (d, *J* = 286 Hz, 1F), -106.56 (d, *J* = 286 Hz, 1F); IR (ATR):3305, 1656, 1598, 1466, 1314, 1268, 1178, 844, 760, 689; MS (EI): 434 (M^+, 3), 249 (59), 186 (19), 135 (100), 107 (14), 77 (33); HRMS (EI): Exact mass calcd for $C_{24}H_{16}N_2O_4F_2$ $[M]^+$: 434.1078, Found: 434.1076.



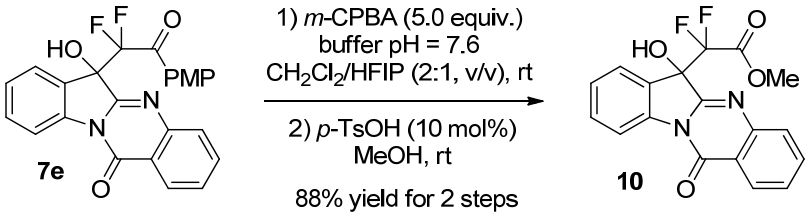
7f

Column chromatography afforded product **7f** in 53% yield (m. p. 264-266 ^{o}C) as white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (d, *J* = 7.6 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.95-7.91 (m, 1H), 7.86 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.71-7.63 (m, 3H), 7.46 (td, *J* = 7.6, 0.8 Hz, 1H), 7.29-7.17 (m, 5H), 3.43-3.35 (m, 1H), 3.22-3.14 (m, 1H), 2.96-2.82 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.20 (t, *J* = 27.5 Hz, 1C), 158.43, 155.32, 146.01, 140.37, 139.41, 135.21, 131.55, 128.48, 128.32, 128.24, 127.93, 127.81, 126.97, 126.60, 126.11, 126.03, 121.46, 116.23, 115.06 (t, *J* = 261 Hz, 1C), 77.93 (t, *J* = 27.5 Hz, 1C), 40.18, 28.17; ^{19}F NMR (376 MHz, DMSO-d_6): δ -116.63 (d, *J* = 259 Hz, 1F), -115.59 (d, *J* = 259 Hz, 1F); IR (ATR):3464, 1732, 1701, 1655, 1602, 1461, 1191, 1115, 986, 765, 701, 669; MS (EI): 432 (M^+, 20), 249 (100), 184 (18), 133 (27), 105 (52), 91 (90), 77 (24); HRMS (EI): Exact mass calcd for $C_{25}H_{18}N_2O_3F_2$ $[M]^+$: 432.1285, Found: 432.1288.

3) Product elaboration



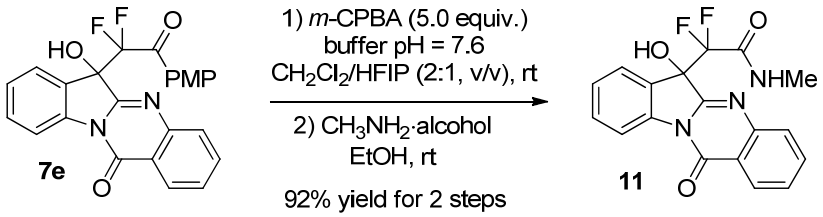
Compound **7e** (65.2 mg, 0.15 mmol) was dissolved in CH_2Cl_2/HFIP (2:1, 1.5 mL), followed by the addition of *m*-chloroperoxybenzoic acid (*m*-CPBA) (152 mg, 0.75 mmol, 85%) and phosphate buffer (0.15 mL, pH = 7.6) at room temperature.[3] The mixture was stirred until the complete consumption of **7e** as indicated by TLC analysis (about 1 h) before quenched by saturated aqueous $Na_2S_2O_3$. The mixture was extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic layer was washed with saturated $NaHCO_3$ (aq.) and brine (10.0 mL × 2), respectively. The solution was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (PE/ethyl acetate = 3/1) to afford ester **9** in 95% yield as white solid (m. p. 165-167 ^oC). ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.76 (td, *J* = 8.0, 1.2 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.56-7.49 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.07-7.05 (m, 2H), 6.91-6.89 (m, 2H), 5.06 (s, br, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.13 (t, *J* = 32 Hz, 1C), 159.06, 158.00, 155.01, 146.32, 142.90, 140.13, 134.75, 132.10, 128.31, 127.81, 127.17, 126.28, 125.16, 122.08, 121.58, 116.99, 114.58, 112.72 (t, *J* = 261 Hz, 1C), 78.56 (t, *J* = 26 Hz, 1C), 55.59; ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.31; IR (ATR): 3398, 2930, 1779, 1679, 1503, 1462, 1249, 1184, 901, 855, 773, 691; MS (EI): 450 (M^+, 4), 327 (100), 299 (72), 249 (63), 124 (35), 77 (10), 44 (39); HRMS (EI): Exact mass calcd for $C_{24}H_{16}N_2O_5F_2$ $[M]^+$: 450.1027, Found: 450.1031.



Starting from compound **7e** (65.2 mg, 0.15 mmol) by the same procedure for Baeyer-Villiger

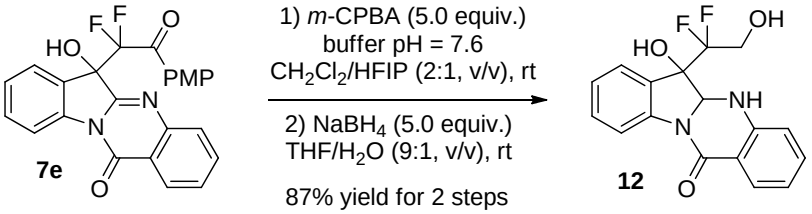
[3] S. Kobayashi, H. Tanaka, H. Amii, K. Uneyama, *Tetrahedron* **2003**, *59*, 1547-1552.

oxidation described above, the crude ester **9** was dissolved in 2.0 mL anhydrous MeOH, followed by the addition of *p*-TsOH (2.6 mg, 10 mol%) at room temperature. The resulting mixture was stirred until the completion of crude ester as indicated by TLC analysis (about 12 h). Then the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (PE/ethyl acetate = 1/1) to afford ester **10** in 88% yield as white solid (m. p. 192-194 ^{o}C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.47 (d, *J* = 8.0 Hz, 1H), 8.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.95 (td, *J* = 7.5, 1.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.74 (s, 1H), 7.72-7.68 (m, 2H), 7.66 (td, *J* = 8.0, 1.0 Hz, 1H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.57 (t, *J* = 31.25 Hz, 1C), 158.43, 155.00, 146.16, 139.39, 135.19, 131.64, 128.41, 128.00, 127.45, 126.91, 126.53, 126.06, 121.41, 116.17, 113.57 (t, *J* = 260 Hz, 1C), 77.83 (t, *J* = 25 Hz, 1C), 53.70; ^{19}F NMR (282 MHz, DMSO-d_6): δ -114.41; IR (ATR): 3341, 2929, 1756, 1663, 1600, 1435, 1326, 1187, 1099, 759, 692; MS (EI): 358 (M^+, 4), 249 (100), 59 (3), 44 (25); HRMS (EI): Exact mass calcd for $C_{18}H_{12}N_2O_4F_2$ $[M]^+$: 358.0765, Found: 358.0766.



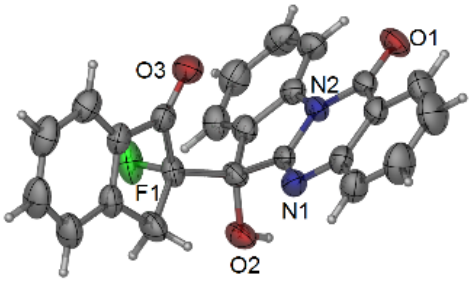
Starting from **7e** (65.2 mg, 0.15 mmol) by the same procedure for Baeyer-Villiger oxidation described above, the resulting crude ester 9 was dissolved in 1.0 mL anhydrous EtOH, followed by the addition of 0.5 mL ethanol solution of CH_3NH_2 (27-30% wt) at room temperature. The resulting mixture was stirred until the completion of crude ester as indicated by TLC analysis (about 0.5 h). Then the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (PE/ethyl acetate = 1/1) to afford amide **11** in 92% yield as white solid (m. p. 230-232 ^{o}C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.75 (d, *J* = 4.5 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.33 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.92 (td, *J* = 7.5, 1.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.68-7.64 (m, 2H), 7.61 (td, *J* = 7.5, 1.0 Hz, 1H), 7.56 (s, 1H), 7.42 (td, *J* = 7.5, 0.5 Hz, 1H), 2.40 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.62 (t, *J* = 27.5 Hz, 1C), 158.64, 156.07 (d, *J* = 6.25 Hz, 1C), 146.59, 139.58, 134.93, 131.19, 128.25 (d, *J* = 2.5 Hz, 1C), 127.96, 127.92, 126.57, 126.41, 125.77 (d, *J* = 1.25 Hz, 1C), 121.46, 116.10, 114.83 (t, *J* = 262.5

Hz. 1C), 77.37 (t, *J* = 23.75 Hz, 1C), 25.50; ^{19}F NMR (282 MHz, DMSO-d_6): δ -115.96 (d, *J* = 256.6 Hz, 1F), -112.33 (d, *J* = 259.4 Hz, 1F); IR (ATR): 3393, 3267, 2955, 1695, 1662, 1599, 1478, 1178, 1027, 935, 757, 692; MS (EI): 357 (M^+, 2), 296 (15), 249 (26), 109 (1), 89 (2), 58 (2); HRMS (EI): Exact mass calcd for $C_{18}H_{13}N_3O_3F_2$ $[M]^+$: 357.0925, Found: 357.0921.



Starting from **7e** (65.2 mg, 0.15 mmol) by the same procedure for Baeyer-Villiger oxidation described above, the resulting crude ester **9** was dissolved in 2.0 mL THF/H_2O (9:1, v/v), followed by the adddition of $NaBH_4$ (28.4 mg, 0.75 mmol) at room temperature. The resulting mixture was stirred until the completion of crude ester as indicated by TLC analysis (about 3 h). The reaction was quenched by the addition of 1.0 mL of saturated NH_4Cl (aq.), and the resulting mixture was stirred at room temperature until the generation of gas ceased. Then the mixture was extracted with ethyl acetate (5.0 mL × 4), the combined organic layer was washed with saturated brine (10.0 mL × 2) and dried over anhydrous Na_2SO_4, and concentrated under vacuum, and the residue was purified by column chromatography (PE/ethyl acetate = 1/1) to afford alcohol **12** in 87% yield as white solid (m. p. 231-233 ^oC), (dr = 4.0:1). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40-7.37 (m, 1H), 7.23-7.20 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.88-6.85 (m, 1H), 5.52 (s, 1H), 5.24 (t, *J* = 6.5 Hz, 1H), 4.08-3.97 (m, 1H), 3.48-3.38 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.00, 147.81, 140.42, 133.78, 130.37, 129.21, 127.44, 126.13, 124.05, 121.62 (t, *J* = 250 Hz, 1C), 118.83, 115.97, 115.23, 115.08, 81.35 (t, *J* = 22.5 Hz, 1C), 79.09, 59.54 (t, *J* = 22.5 Hz, 1C); ^{19}F NMR (282 MHz, DMSO-d_6): δ -118.99 (d, *J* = 248.2 Hz, 1F), -117.30 (d, *J* = 248.2 Hz, 1F); IR (ATR): 3373, 3305, 2920, 1628, 1507, 1429, 1161, 1054, 753, 649; MS (EI): 332 (M^+, 1), 296 (13), 281 (17), 251 (2), 81 (2), 64 (2), 44 (100), 43 (23); HRMS (EI): Exact mass calcd for $C_{17}H_{14}N_2O_3F_2$ $[M]^+$: 332.0972, Found: 332.0969.

4) X-Ray crystal data of 6a[4]



Data intensity of **6a** was collected using a Bruker SMART APEX II (Mo radiation) at 296 K in a nitrogen stream. The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **6a**: $C_{24}H_{15}FN_2O_3$, T = 296(2) K, monoclinic, space group P2(1)/c, a = 11.1245(10) Å, b = 11.5825(11) Å, c = 14.9885(14) Å, α = 90 deg, β = 107.083 deg, γ = 90 deg, V = 1846.1(3) Å^3. Z = 4, d_{calc} = 1.433 mg/m^3. Total number of reflections 21149 (R_{int} = 0.0684), R_1 = 0.0844, wR_2 = 0.1011 (all data), GOF = 1.008, and 271 parameters.

Table 1. Crystal data and structure refinement for z.

Identification code	z
Empirical formula	$C_{24}H_{15}FN_2O_3$
Formula weight	398.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.1245(10) Å alpha = 90 deg.
	b = 11.5825(11) Å beta = 107.083(3) deg.
	c = 14.9885(14) Å gamma = 90 deg.
Volume	1846.1(3) Å^3
Z, Calculated density	4, 1.433 Mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	824
Crystal size	0.25 x 0.16 x 0.12 mm

[4] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 1054454)

Theta range for data collection	1.92 to 25.01 deg.
Limiting indices	-13<=h<=13, -13<=k<=13, -17<=l<=17
Reflections collected / unique	21149 / 3247 [R(int) = 0.0684]
Completeness to theta = 25.01	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9878 and 0.9748
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3247 / 0 / 271
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.0819
R indices (all data)	R1 = 0.0844, wR2 = 0.1011
Largest diff. peak and hole	0.149 and -0.168 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for z.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	4871(1)	-95(1)	1465(1)	64(1)
O(1)	-872(1)	-1996(1)	669(1)	52(1)
O(2)	2689(1)	1486(1)	965(1)	52(1)
O(3)	3458(2)	-1877(2)	2298(1)	57(1)
N(1)	1434(2)	427(2)	2326(1)	41(1)
N(2)	872(2)	-851(2)	1028(1)	37(1)
C(1)	395(2)	7(2)	2571(2)	42(1)
C(2)	144(2)	459(2)	3362(2)	53(1)
C(3)	-855(3)	55(3)	3632(2)	69(1)
C(4)	-1619(3)	-815(3)	3129(2)	73(1)
C(5)	-1406(2)	-1256(2)	2346(2)	59(1)
C(6)	-399(2)	-846(2)	2052(2)	43(1)
C(7)	-189(2)	-1295(2)	1205(2)	41(1)
C(8)	1618(2)	-10(2)	1595(1)	36(1)
C(9)	2692(2)	299(2)	1196(1)	39(1)
C(10)	2439(2)	-489(2)	358(1)	40(1)
C(11)	3053(2)	-583(2)	-315(2)	53(1)
C(12)	2614(3)	-1356(2)	-1040(2)	60(1)
C(13)	1567(3)	-2024(2)	-1093(2)	59(1)
C(14)	913(2)	-1929(2)	-437(2)	51(1)
C(15)	1368(2)	-1147(2)	277(1)	39(1)
C(16)	3961(2)	91(2)	1939(1)	41(1)

C(17)	4445(2)	1063(2)	2628(2)	52(1)
C(18)	5254(2)	446(2)	3478(2)	44(1)
C(19)	6147(2)	901(2)	4245(2)	56(1)
C(20)	6735(2)	164(3)	4962(2)	63(1)
C(21)	6459(2)	-1002(3)	4929(2)	61(1)
C(22)	5567(2)	-1462(2)	4171(2)	52(1)
C(23)	4979(2)	-727(2)	3443(1)	41(1)
C(24)	4047(2)	-996(2)	2548(2)	42(1)

Table 3. Bond lengths [Å] and angles [deg] for z.

F(1)-C(16)	1.414(2)
O(1)-C(7)	1.235(2)
O(2)-C(9)	1.418(2)
O(2)-H(2B)	0.8200
O(3)-C(24)	1.211(3)
N(1)-C(8)	1.277(3)
N(1)-C(1)	1.399(3)
N(2)-C(7)	1.382(3)
N(2)-C(8)	1.395(3)
N(2)-C(15)	1.434(3)
C(1)-C(2)	1.397(3)
C(1)-C(6)	1.399(3)
C(2)-C(3)	1.373(3)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.389(4)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.362(4)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.401(3)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.454(3)
C(8)-C(9)	1.527(3)
C(9)-C(10)	1.510(3)
C(9)-C(16)	1.539(3)
C(10)-C(11)	1.378(3)
C(10)-C(15)	1.389(3)
C(11)-C(12)	1.382(3)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.381(4)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.388(3)
C(13)-H(13A)	0.9300

C(14)-C(15)	1.380(3)
C(14)-H(14A)	0.9300
C(16)-C(17)	1.516(3)
C(16)-C(24)	1.541(3)
C(17)-C(18)	1.507(3)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-C(19)	1.383(3)
C(18)-C(23)	1.391(3)
C(19)-C(20)	1.378(3)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.382(4)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.378(3)
C(21)-H(21A)	0.9300
C(22)-C(23)	1.387(3)
C(22)-H(22A)	0.9300
C(23)-C(24)	1.468(3)
C(9)-O(2)-H(2B)	109.5
C(8)-N(1)-C(1)	116.18(19)
C(7)-N(2)-C(8)	122.17(19)
C(7)-N(2)-C(15)	127.54(18)
C(8)-N(2)-C(15)	110.29(17)
C(2)-C(1)-N(1)	118.6(2)
C(2)-C(1)-C(6)	119.1(2)
N(1)-C(1)-C(6)	122.4(2)
C(3)-C(2)-C(1)	120.2(2)
C(3)-C(2)-H(2A)	119.9
C(1)-C(2)-H(2A)	119.9
C(2)-C(3)-C(4)	120.5(3)
C(2)-C(3)-H(3A)	119.8
C(4)-C(3)-H(3A)	119.8
C(5)-C(4)-C(3)	120.3(3)
C(5)-C(4)-H(4A)	119.8
C(3)-C(4)-H(4A)	119.8
C(4)-C(5)-C(6)	120.1(3)
C(4)-C(5)-H(5A)	120.0
C(6)-C(5)-H(5A)	120.0
C(1)-C(6)-C(5)	119.8(2)
C(1)-C(6)-C(7)	120.0(2)
C(5)-C(6)-C(7)	120.2(2)
O(1)-C(7)-N(2)	121.1(2)
O(1)-C(7)-C(6)	125.3(2)
N(2)-C(7)-C(6)	113.6(2)

N(1)-C(8)-N(2)	125.6(2)
N(1)-C(8)-C(9)	125.81(19)
N(2)-C(8)-C(9)	108.63(18)
O(2)-C(9)-C(10)	113.41(17)
O(2)-C(9)-C(8)	112.11(18)
C(10)-C(9)-C(8)	102.02(17)
O(2)-C(9)-C(16)	105.29(17)
C(10)-C(9)-C(16)	114.52(19)
C(8)-C(9)-C(16)	109.64(17)
C(11)-C(10)-C(15)	119.3(2)
C(11)-C(10)-C(9)	130.1(2)
C(15)-C(10)-C(9)	110.44(19)
C(10)-C(11)-C(12)	119.3(2)
C(10)-C(11)-H(11A)	120.3
C(12)-C(11)-H(11A)	120.3
C(13)-C(12)-C(11)	120.3(2)
C(13)-C(12)-H(12A)	119.8
C(11)-C(12)-H(12A)	119.8
C(12)-C(13)-C(14)	121.6(2)
C(12)-C(13)-H(13A)	119.2
C(14)-C(13)-H(13A)	119.2
C(15)-C(14)-C(13)	116.9(2)
C(15)-C(14)-H(14A)	121.6
C(13)-C(14)-H(14A)	121.6
C(14)-C(15)-C(10)	122.5(2)
C(14)-C(15)-N(2)	128.9(2)
C(10)-C(15)-N(2)	108.61(18)
F(1)-C(16)-C(17)	107.03(18)
F(1)-C(16)-C(9)	107.43(16)
C(17)-C(16)-C(9)	116.37(19)
F(1)-C(16)-C(24)	104.08(17)
C(17)-C(16)-C(24)	104.81(17)
C(9)-C(16)-C(24)	116.14(18)
C(18)-C(17)-C(16)	103.17(19)
C(18)-C(17)-H(17A)	111.1
C(16)-C(17)-H(17A)	111.1
C(18)-C(17)-H(17B)	111.1
C(16)-C(17)-H(17B)	111.1
H(17A)-C(17)-H(17B)	109.1
C(19)-C(18)-C(23)	120.0(2)
C(19)-C(18)-C(17)	128.8(2)
C(23)-C(18)-C(17)	111.19(19)
C(20)-C(19)-C(18)	118.2(3)
C(20)-C(19)-H(19A)	120.9

C(18)-C(19)-H(19A)	120.9
C(19)-C(20)-C(21)	121.8(2)
C(19)-C(20)-H(20A)	119.1
C(21)-C(20)-H(20A)	119.1
C(22)-C(21)-C(20)	120.4(2)
C(22)-C(21)-H(21A)	119.8
C(20)-C(21)-H(21A)	119.8
C(21)-C(22)-C(23)	118.1(2)
C(21)-C(22)-H(22A)	121.0
C(23)-C(22)-H(22A)	121.0
C(22)-C(23)-C(18)	121.5(2)
C(22)-C(23)-C(24)	129.2(2)
C(18)-C(23)-C(24)	109.3(2)
O(3)-C(24)-C(23)	129.3(2)
O(3)-C(24)-C(16)	124.9(2)
C(23)-C(24)-C(16)	105.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for z.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
F(1)	38(1)	108(1)	48(1)	3(1)	12(1)	-6(1)
O(1)	47(1)	47(1)	52(1)	0(1)	-2(1)	-15(1)
O(2)	52(1)	42(1)	50(1)	8(1)	-5(1)	-11(1)
O(3)	54(1)	45(1)	62(1)	2(1)	-1(1)	0(1)
N(1)	36(1)	40(1)	42(1)	-4(1)	4(1)	1(1)
N(2)	32(1)	35(1)	38(1)	-3(1)	1(1)	-3(1)
C(1)	32(1)	44(1)	44(1)	2(1)	4(1)	6(1)
C(2)	44(2)	60(2)	52(2)	-7(1)	10(1)	5(1)
C(3)	56(2)	95(2)	60(2)	-6(2)	22(2)	8(2)
C(4)	53(2)	99(2)	72(2)	4(2)	26(2)	-5(2)
C(5)	43(2)	69(2)	62(2)	6(1)	11(1)	-8(1)
C(6)	33(1)	44(2)	47(1)	8(1)	4(1)	2(1)
C(7)	34(1)	36(1)	44(1)	6(1)	-1(1)	0(1)
C(8)	28(1)	32(1)	39(1)	1(1)	-3(1)	1(1)
C(9)	37(1)	36(1)	40(1)	1(1)	3(1)	-6(1)
C(10)	37(1)	44(2)	35(1)	2(1)	3(1)	0(1)
C(11)	43(1)	68(2)	44(1)	2(1)	7(1)	2(1)
C(12)	58(2)	74(2)	46(2)	-2(1)	12(1)	11(2)
C(13)	69(2)	57(2)	42(1)	-12(1)	3(1)	13(2)

C(14)	51(2)	44(2)	49(1)	-7(1)	0(1)	-1(1)
C(15)	38(1)	37(1)	36(1)	0(1)	1(1)	3(1)
C(16)	29(1)	54(2)	37(1)	1(1)	8(1)	-4(1)
C(17)	44(1)	51(2)	51(1)	2(1)	-3(1)	-11(1)
C(18)	32(1)	60(2)	38(1)	-5(1)	6(1)	1(1)
C(19)	39(1)	71(2)	50(2)	-12(1)	2(1)	0(1)
C(20)	44(2)	94(2)	42(2)	-14(2)	-2(1)	9(2)
C(21)	50(2)	88(2)	39(1)	6(2)	4(1)	19(2)
C(22)	51(2)	60(2)	44(1)	5(1)	11(1)	14(1)
C(23)	32(1)	54(2)	37(1)	0(1)	9(1)	8(1)
C(24)	35(1)	44(2)	46(1)	-2(1)	10(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for z.

	x	y	z	U(eq)
H(2B)	2138	1608	474	78
H(2A)	657	1036	3706	64
H(3A)	-1023	367	4155	83
H(4A)	-2280	-1098	3328	87
H(5A)	-1929	-1829	2007	71
H(11A)	3756	-131	-281	63
H(12A)	3026	-1428	-1495	72
H(13A)	1293	-2549	-1579	71
H(14A)	202	-2372	-477	62
H(17A)	4934	1611	2390	63
H(17B)	3757	1467	2768	63
H(19A)	6344	1683	4275	67
H(20A)	7333	460	5483	76
H(21A)	6880	-1478	5421	73
H(22A)	5364	-2243	4149	63

Table 6. Torsion angles [deg] for z.

C(8)-N(1)-C(1)-C(2)	-179.6(2)
C(8)-N(1)-C(1)-C(6)	0.2(3)
N(1)-C(1)-C(2)-C(3)	-179.0(2)
C(6)-C(1)-C(2)-C(3)	1.1(3)
C(1)-C(2)-C(3)-C(4)	0.7(4)
C(2)-C(3)-C(4)-C(5)	-1.8(4)
C(3)-C(4)-C(5)-C(6)	1.1(4)

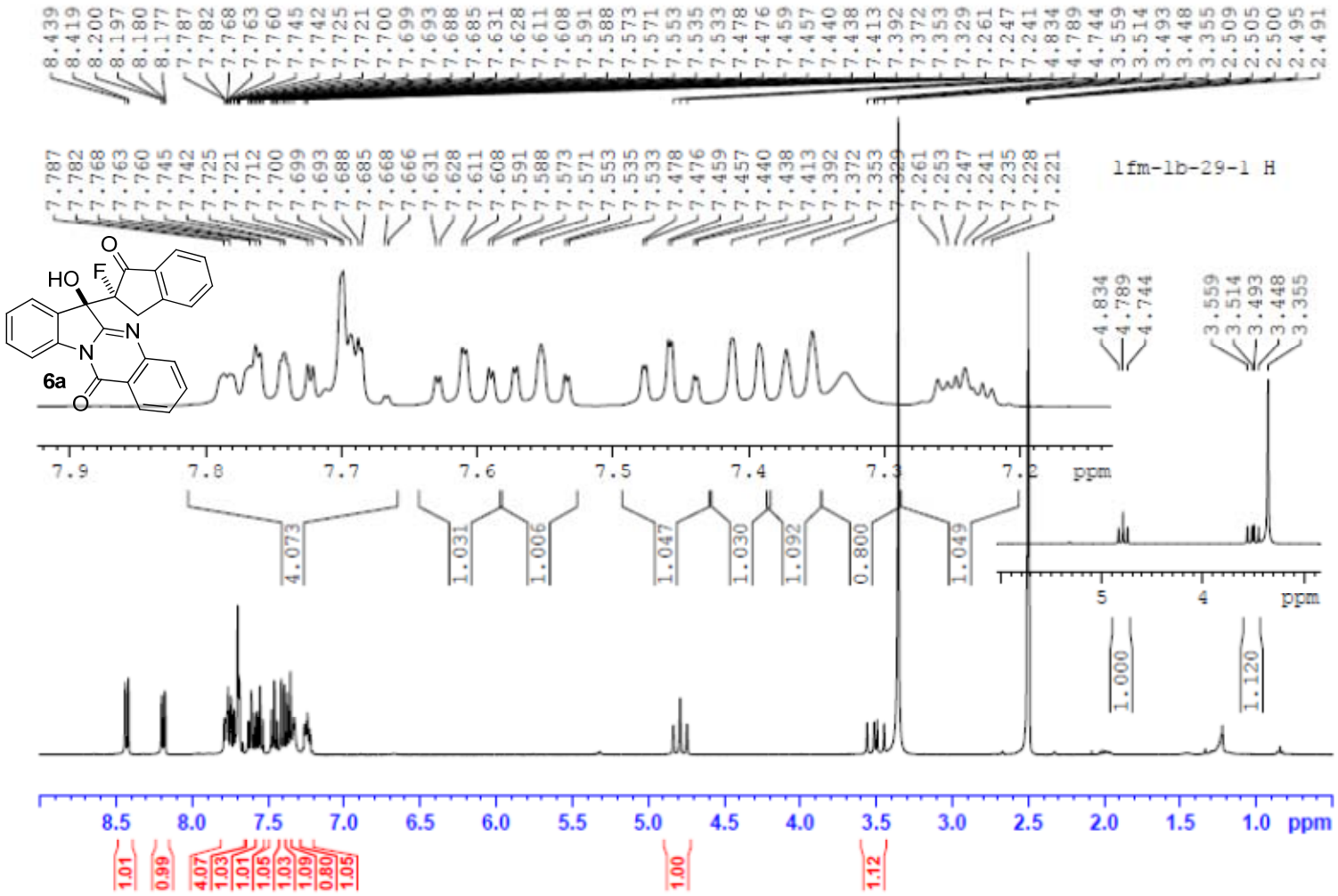
C(2)-C(1)-C(6)-C(5)	-1.9(3)
N(1)-C(1)-C(6)-C(5)	178.3(2)
C(2)-C(1)-C(6)-C(7)	177.4(2)
N(1)-C(1)-C(6)-C(7)	-2.4(3)
C(4)-C(5)-C(6)-C(1)	0.8(4)
C(4)-C(5)-C(6)-C(7)	-178.5(2)
C(8)-N(2)-C(7)-O(1)	176.28(19)
C(15)-N(2)-C(7)-O(1)	-3.4(3)
C(8)-N(2)-C(7)-C(6)	-3.0(3)
C(15)-N(2)-C(7)-C(6)	177.33(19)
C(1)-C(6)-C(7)-O(1)	-175.6(2)
C(5)-C(6)-C(7)-O(1)	3.7(3)
C(1)-C(6)-C(7)-N(2)	3.7(3)
C(5)-C(6)-C(7)-N(2)	-177.0(2)
C(1)-N(1)-C(8)-N(2)	0.5(3)
C(1)-N(1)-C(8)-C(9)	-179.33(18)
C(7)-N(2)-C(8)-N(1)	1.0(3)
C(15)-N(2)-C(8)-N(1)	-179.3(2)
C(7)-N(2)-C(8)-C(9)	-179.08(18)
C(15)-N(2)-C(8)-C(9)	0.6(2)
N(1)-C(8)-C(9)-O(2)	-59.2(3)
N(2)-C(8)-C(9)-O(2)	120.92(18)
N(1)-C(8)-C(9)-C(10)	179.1(2)
N(2)-C(8)-C(9)-C(10)	-0.7(2)
N(1)-C(8)-C(9)-C(16)	57.4(3)
N(2)-C(8)-C(9)-C(16)	-122.51(18)
O(2)-C(9)-C(10)-C(11)	56.1(3)
C(8)-C(9)-C(10)-C(11)	176.8(2)
C(16)-C(9)-C(10)-C(11)	-64.8(3)
O(2)-C(9)-C(10)-C(15)	-120.1(2)
C(8)-C(9)-C(10)-C(15)	0.6(2)
C(16)-C(9)-C(10)-C(15)	119.0(2)
C(15)-C(10)-C(11)-C(12)	-2.0(3)
C(9)-C(10)-C(11)-C(12)	-177.9(2)
C(10)-C(11)-C(12)-C(13)	0.3(4)
C(11)-C(12)-C(13)-C(14)	1.1(4)
C(12)-C(13)-C(14)-C(15)	-0.8(4)
C(13)-C(14)-C(15)-C(10)	-0.9(3)
C(13)-C(14)-C(15)-N(2)	178.3(2)
C(11)-C(10)-C(15)-C(14)	2.4(3)
C(9)-C(10)-C(15)-C(14)	179.0(2)
C(11)-C(10)-C(15)-N(2)	-176.99(19)
C(9)-C(10)-C(15)-N(2)	-0.3(2)
C(7)-N(2)-C(15)-C(14)	0.2(3)

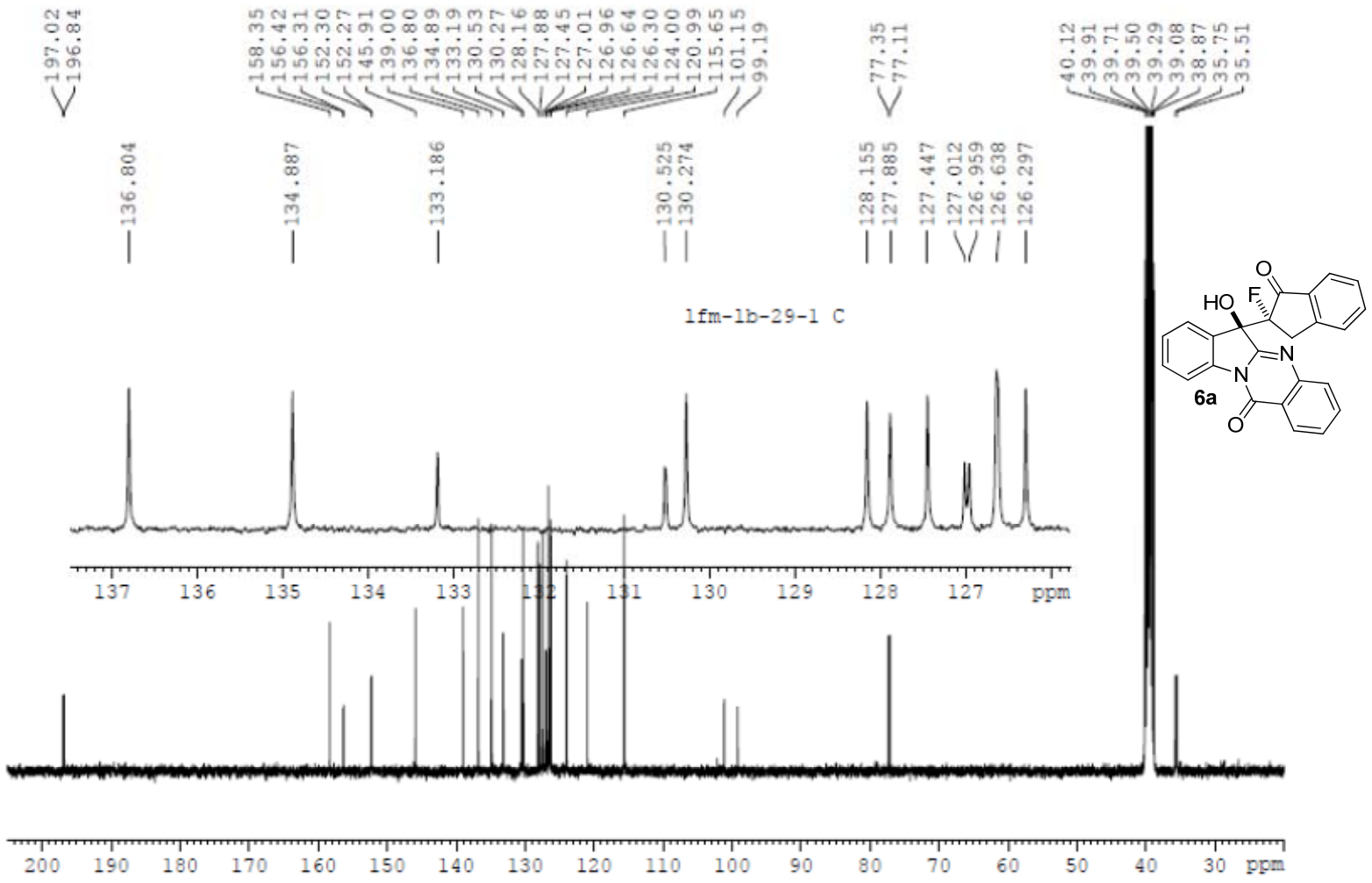
C(8)-N(2)-C(15)-C(14)	-179.5(2)
C(7)-N(2)-C(15)-C(10)	179.47(19)
C(8)-N(2)-C(15)-C(10)	-0.2(2)
O(2)-C(9)-C(16)-F(1)	-83.6(2)
C(10)-C(9)-C(16)-F(1)	41.7(2)
C(8)-C(9)-C(16)-F(1)	155.60(17)
O(2)-C(9)-C(16)-C(17)	36.3(2)
C(10)-C(9)-C(16)-C(17)	161.54(19)
C(8)-C(9)-C(16)-C(17)	-84.5(2)
O(2)-C(9)-C(16)-C(24)	160.40(17)
C(10)-C(9)-C(16)-C(24)	-74.3(2)
C(8)-C(9)-C(16)-C(24)	39.6(3)
F(1)-C(16)-C(17)-C(18)	-86.7(2)
C(9)-C(16)-C(17)-C(18)	153.17(18)
C(24)-C(16)-C(17)-C(18)	23.4(2)
C(16)-C(17)-C(18)-C(19)	164.3(2)
C(16)-C(17)-C(18)-C(23)	-17.8(3)
C(23)-C(18)-C(19)-C(20)	-0.5(3)
C(17)-C(18)-C(19)-C(20)	177.2(2)
C(18)-C(19)-C(20)-C(21)	0.3(4)
C(19)-C(20)-C(21)-C(22)	-0.7(4)
C(20)-C(21)-C(22)-C(23)	1.2(4)
C(21)-C(22)-C(23)-C(18)	-1.4(3)
C(21)-C(22)-C(23)-C(24)	177.1(2)
C(19)-C(18)-C(23)-C(22)	1.1(3)
C(17)-C(18)-C(23)-C(22)	-177.0(2)
C(19)-C(18)-C(23)-C(24)	-177.7(2)
C(17)-C(18)-C(23)-C(24)	4.2(3)
C(22)-C(23)-C(24)-O(3)	11.3(4)
C(18)-C(23)-C(24)-O(3)	-170.0(2)
C(22)-C(23)-C(24)-C(16)	-167.5(2)
C(18)-C(23)-C(24)-C(16)	11.1(2)
F(1)-C(16)-C(24)-O(3)	-88.5(2)
C(17)-C(16)-C(24)-O(3)	159.3(2)
C(9)-C(16)-C(24)-O(3)	29.4(3)
F(1)-C(16)-C(24)-C(23)	90.47(18)
C(17)-C(16)-C(24)-C(23)	-21.8(2)
C(9)-C(16)-C(24)-C(23)	-151.68(18)

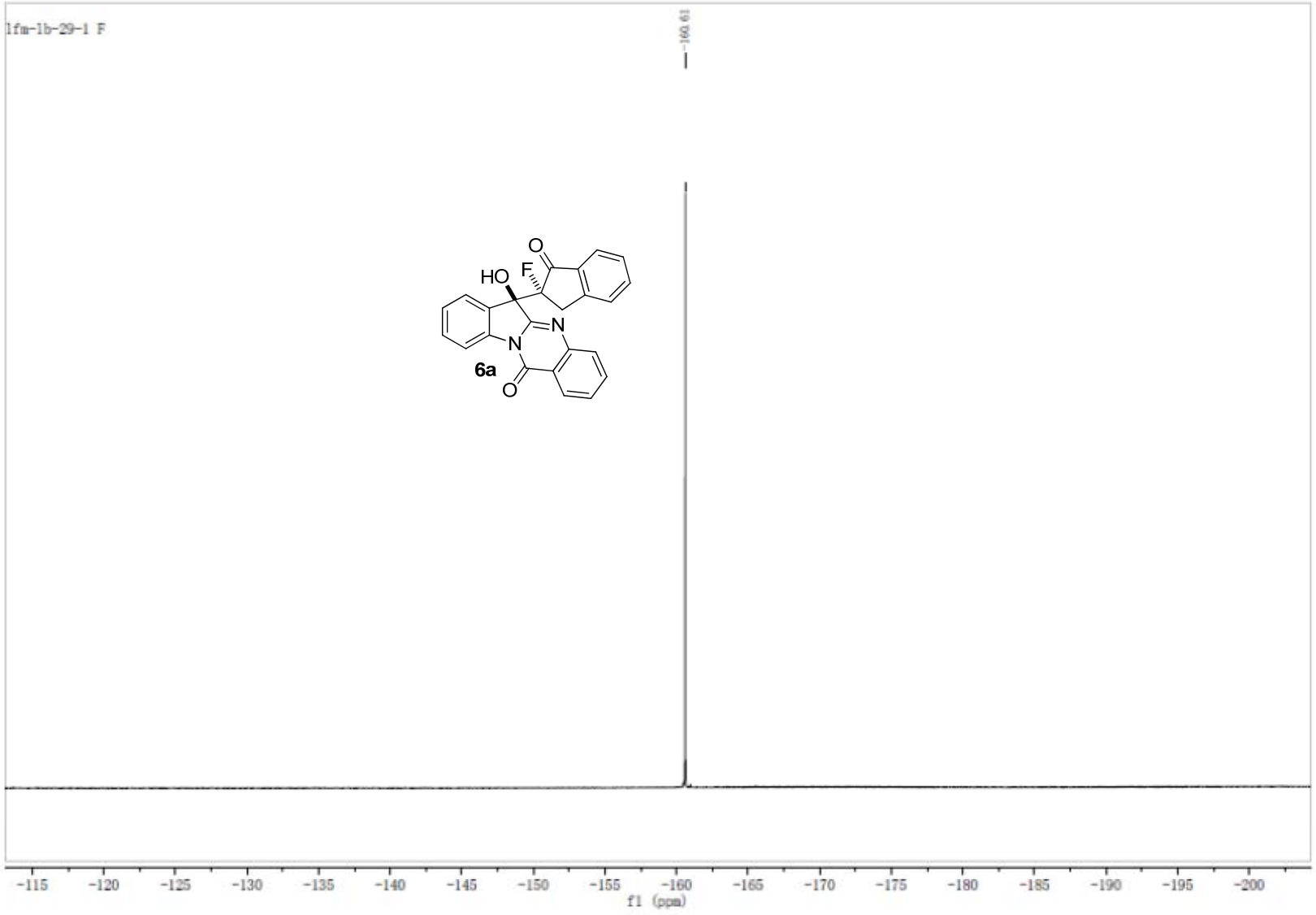
Symmetry transformations used to generate equivalent atoms:

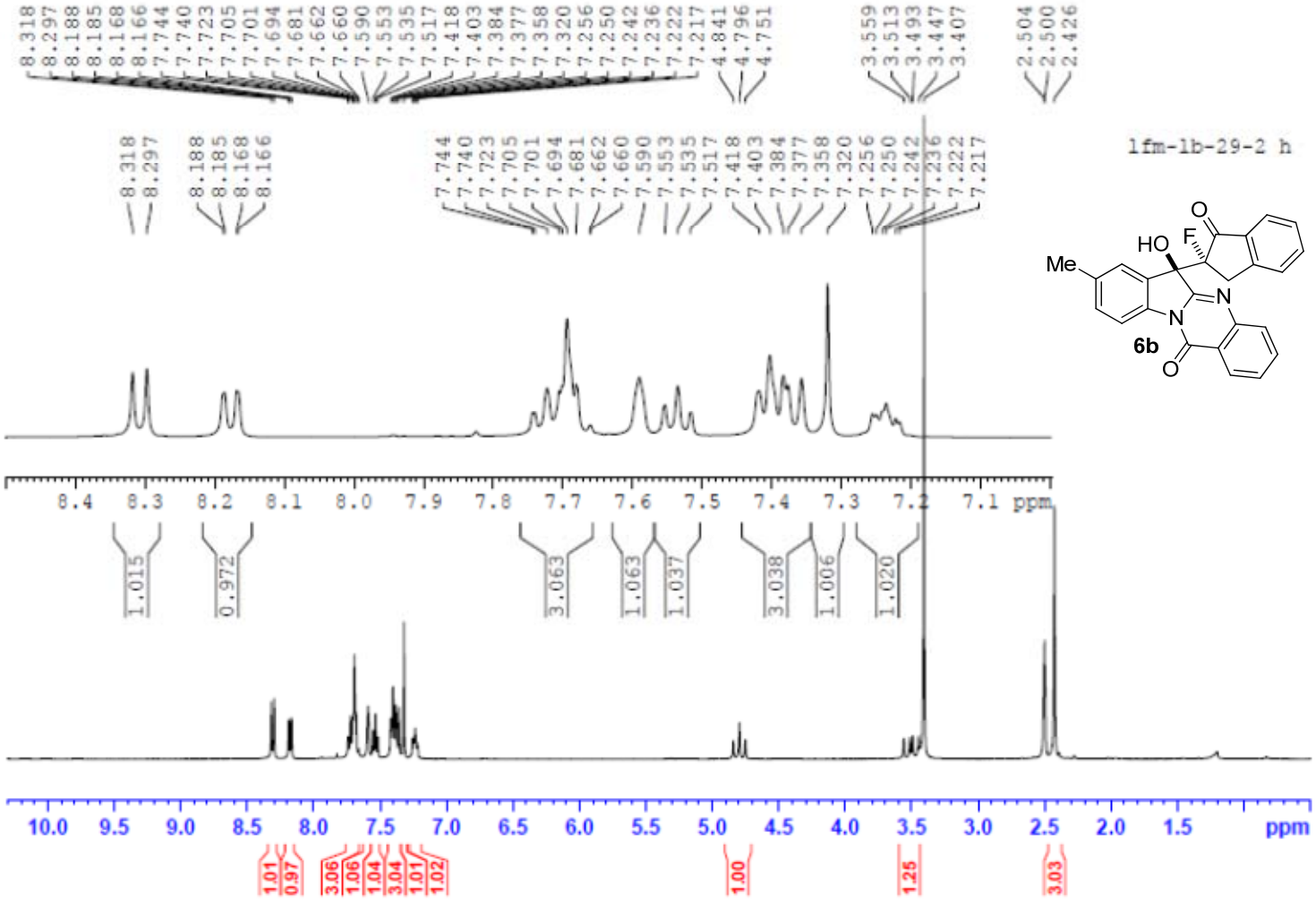
Table 7. Hydrogen bonds for z [A and deg.].

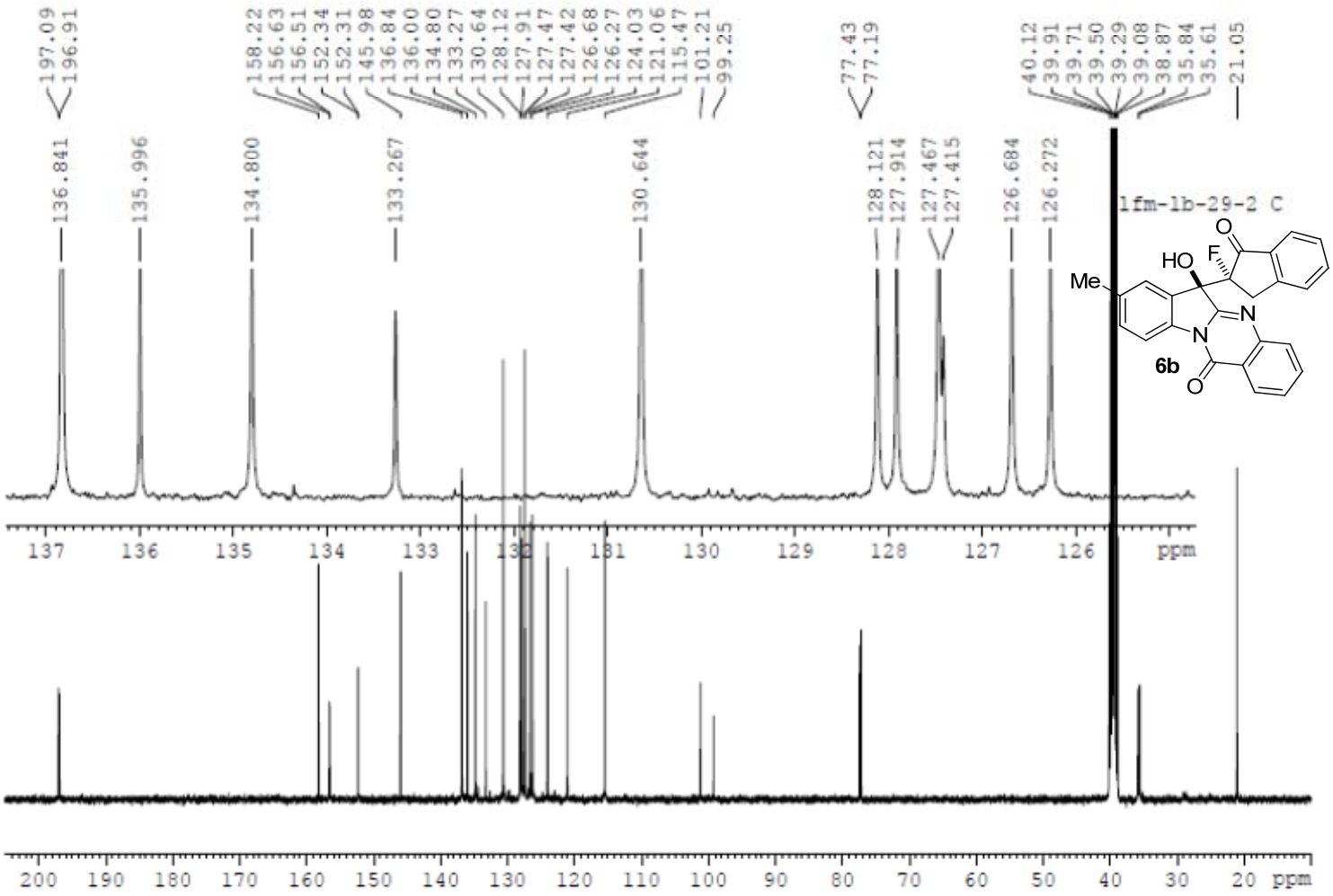
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

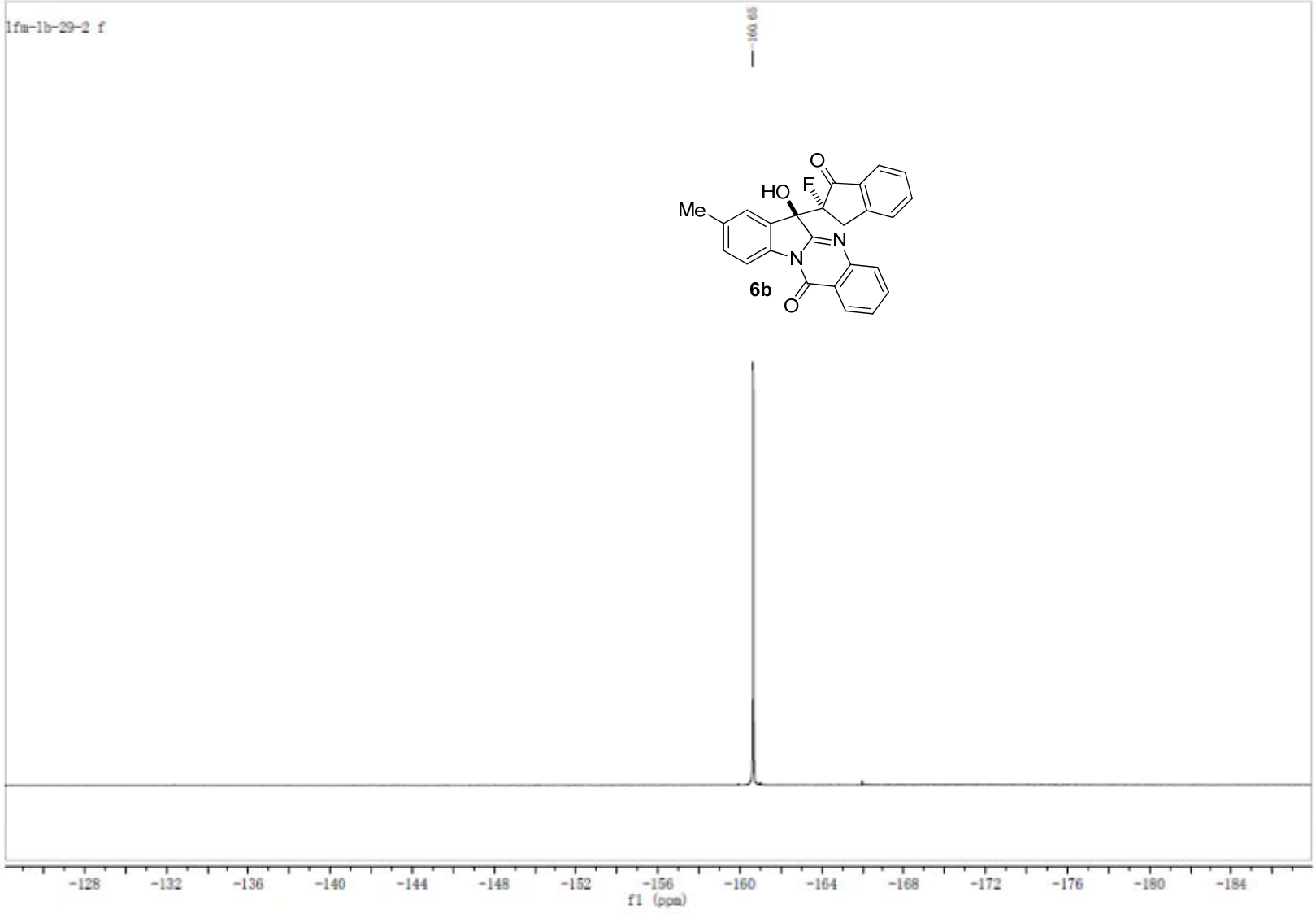

1fm-1b-29-1 H
HO
F
O
N
N
O
6a
ppm

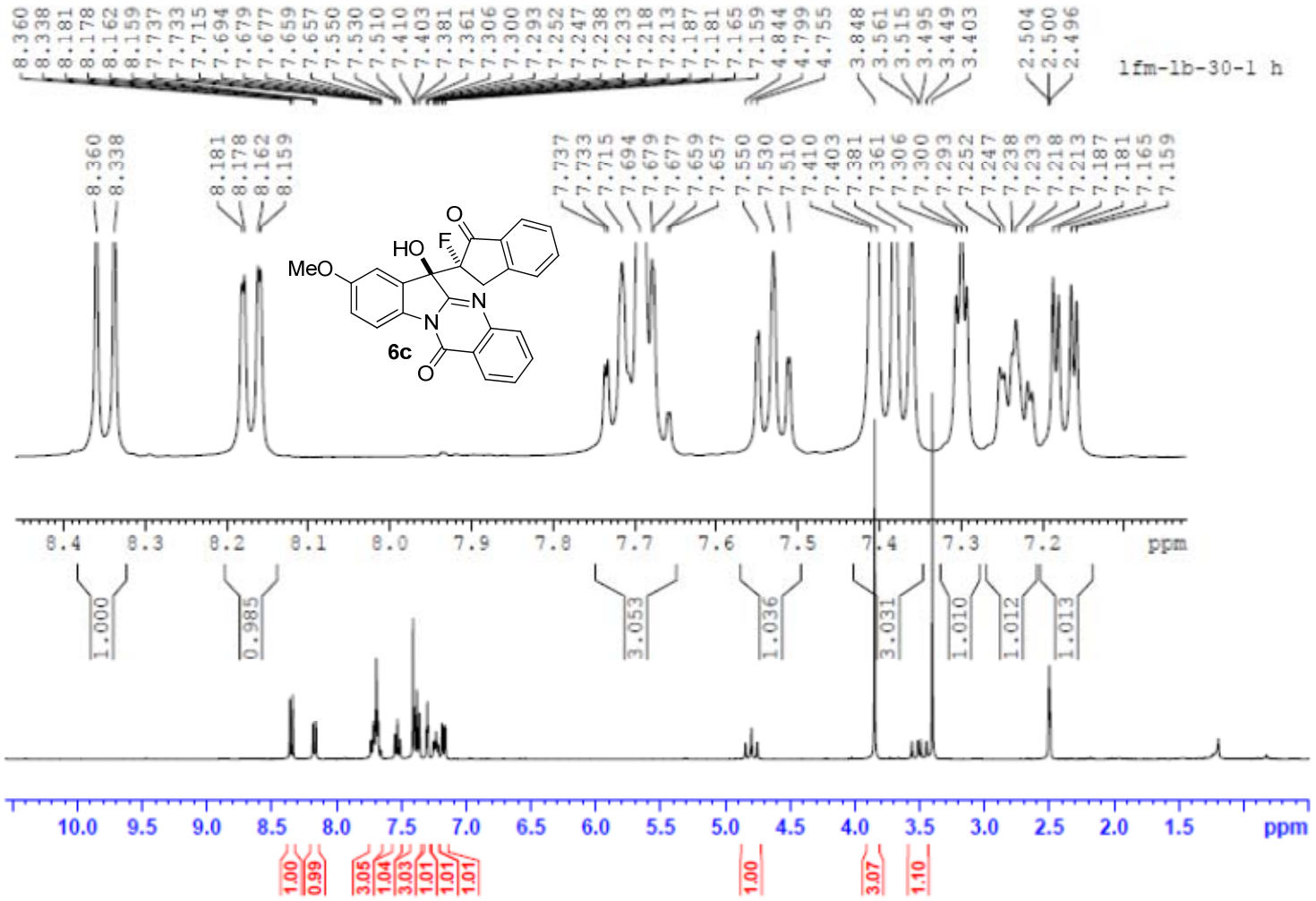

197.02
196.84
158.35
156.42
156.31
152.30
152.27
145.91
139.00
136.80
134.89
133.19
130.53
130.27
128.16
127.88
127.45
127.01
126.96
126.64
126.30
124.00
120.99
115.65
101.15
99.19
77.35
77.11
40.12
39.91
39.71
39.50
39.29
39.08
38.87
35.75
35.51
136.804
134.887
133.186
130.525
130.274
128.155
127.885
127.447
127.012
126.959
126.638
126.297
lfm-1b-29-1 C
137
136
135
134
133
132
131
130
129
128
127
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm
HO
F
O
N
N
O
6a

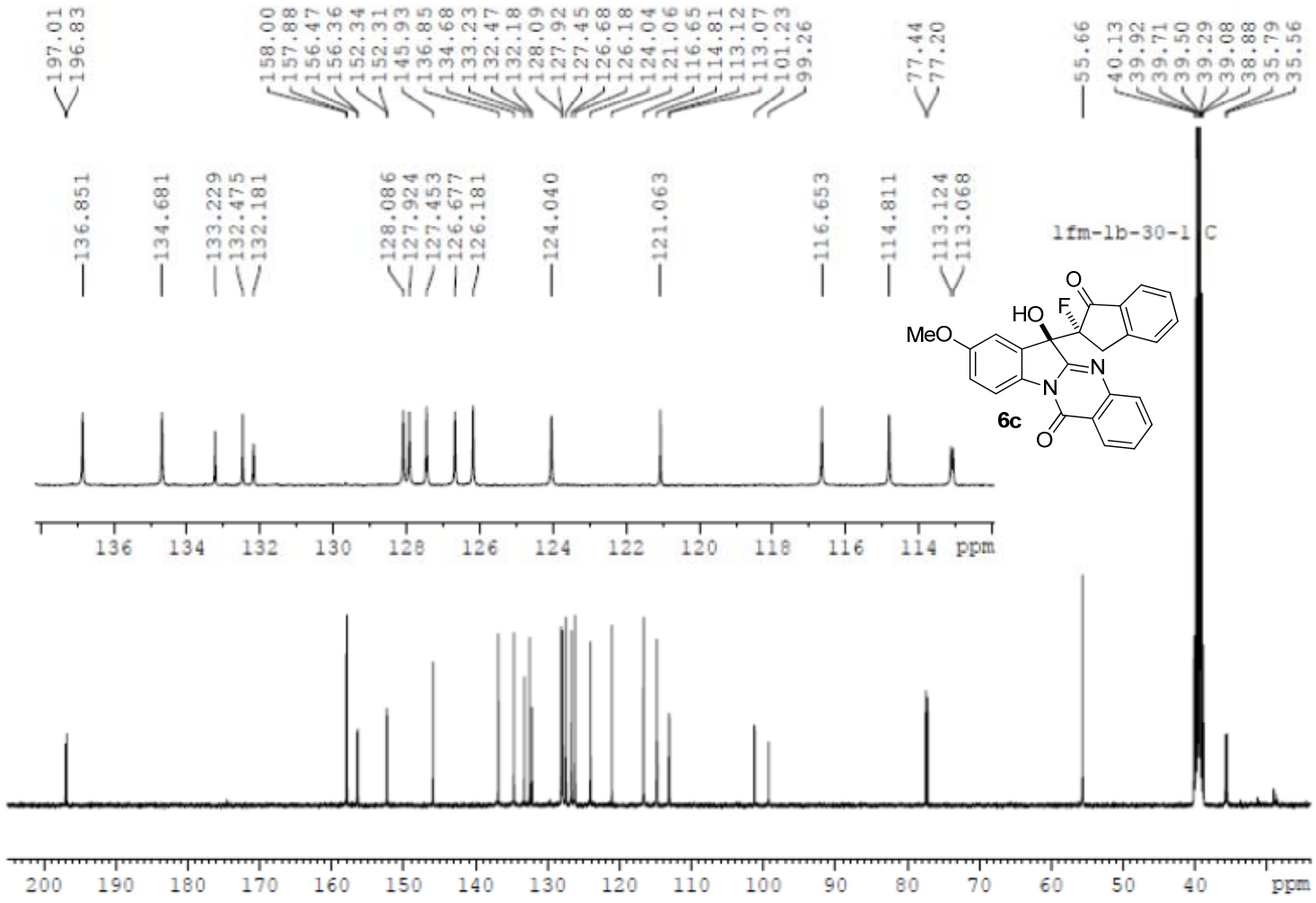

lfm-1b-29-1 F
-160.61
O
F
HO
N
N
O
6a
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
f1 (ppm)

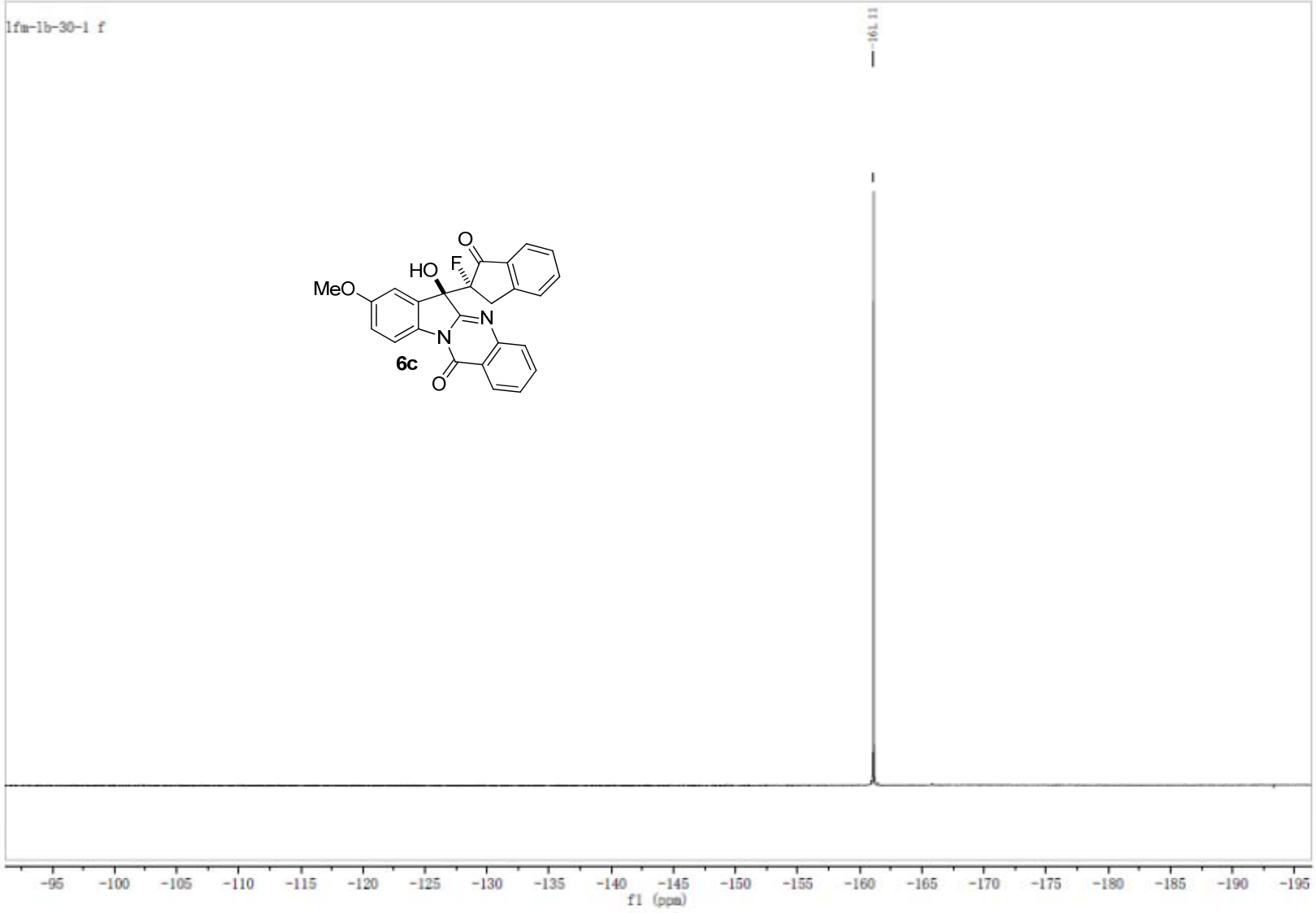

lfm-1b-29-2 h
HO
F
O
Me
N
N
O
6b
ppm

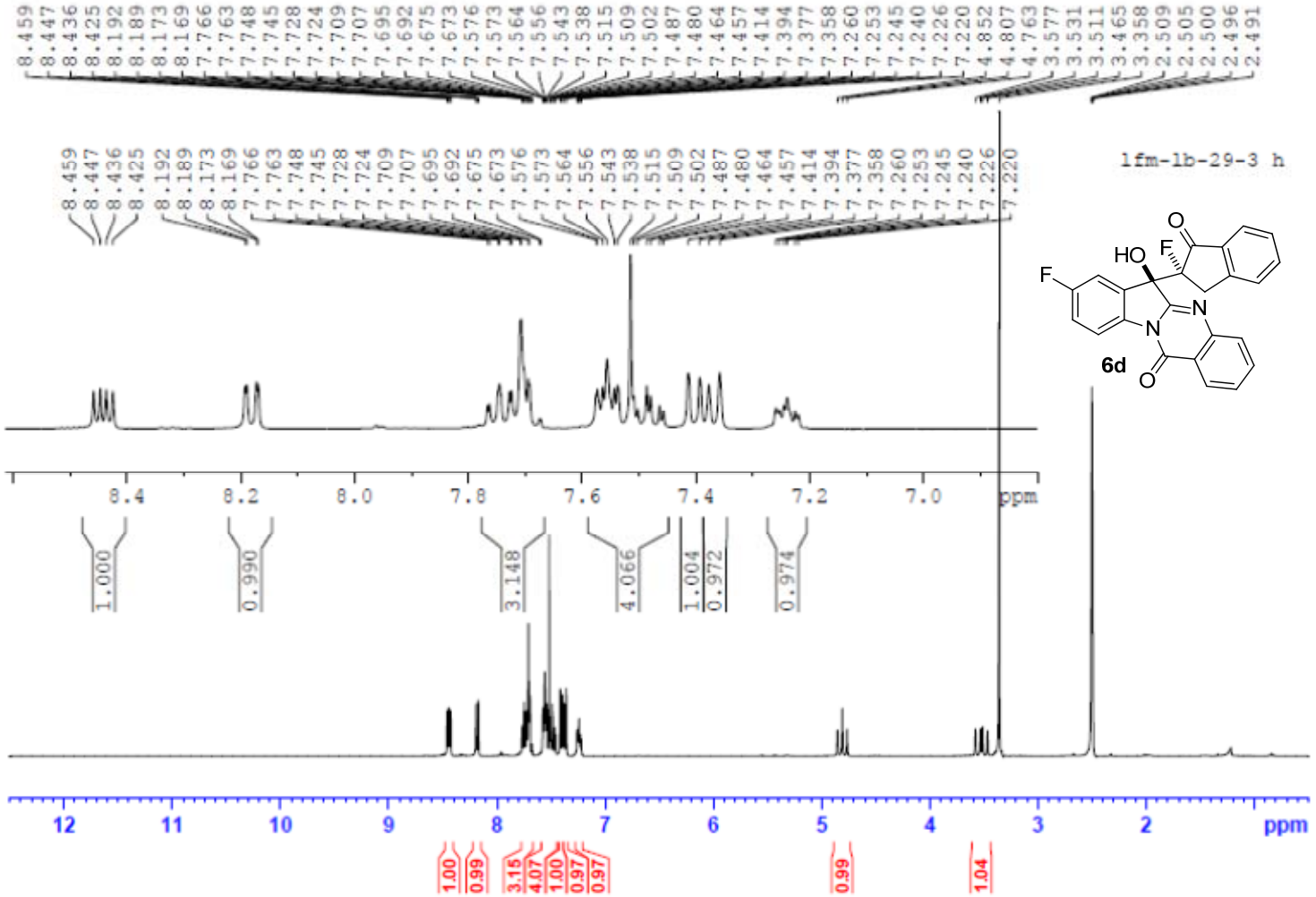

197.09
196.91
158.22
156.63
156.51
152.34
152.31
145.98
136.84
136.00
134.80
133.27
130.64
128.12
127.91
127.47
127.42
126.68
126.27
124.03
121.06
115.47
101.21
99.25
77.43
77.19
40.12
39.91
39.71
39.50
39.29
39.08
38.87
35.84
35.61
21.05
136.841
135.996
134.800
133.267
130.644
128.121
127.914
127.467
127.415
126.684
126.272
lfm-1b-29-2 C
O
F
HO
Me
N
N
6b
O
137
136
135
134
133
132
131
130
129
128
127
126
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

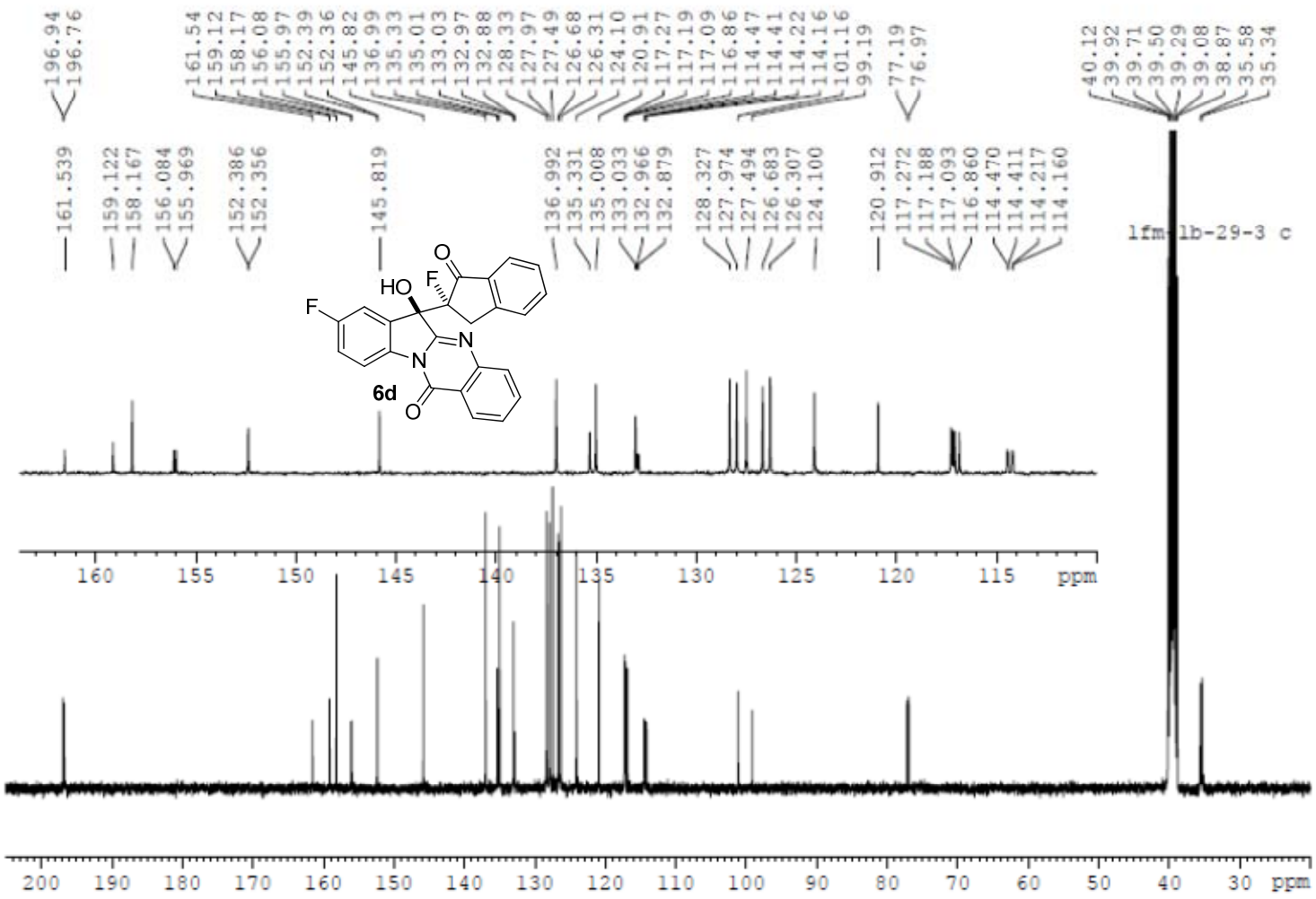

lfm-1b-29-2 f
-160.65
O
F
HO
Me
N
N
O
6b
-128
-132
-136
-140
-144
-148
-152
-156
-160
-164
-168
-172
-176
-180
-184
f1 (ppm)

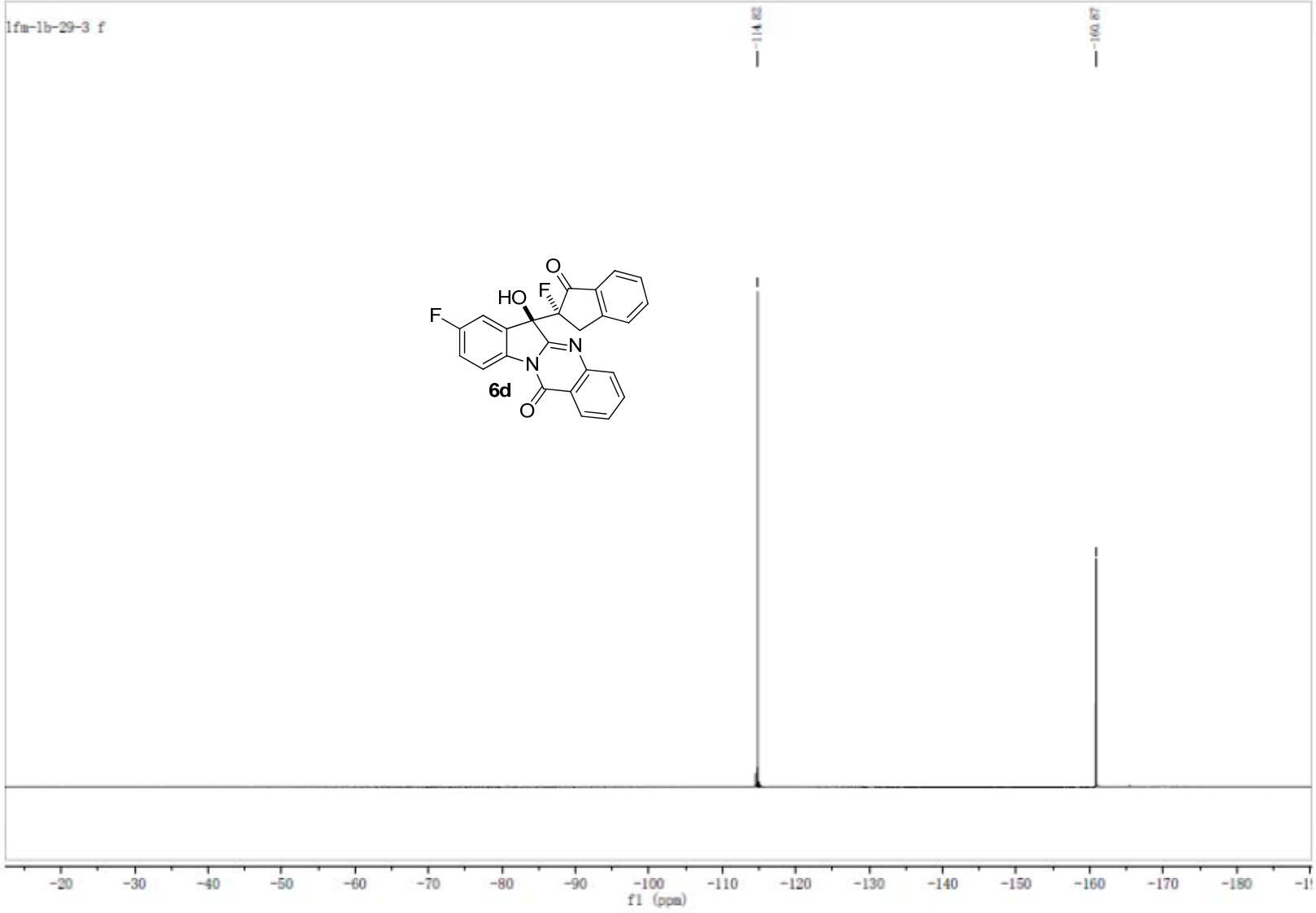

lfm-lb-30-1 h
HO
F
O
MeO
N
N
O
6c
ppm

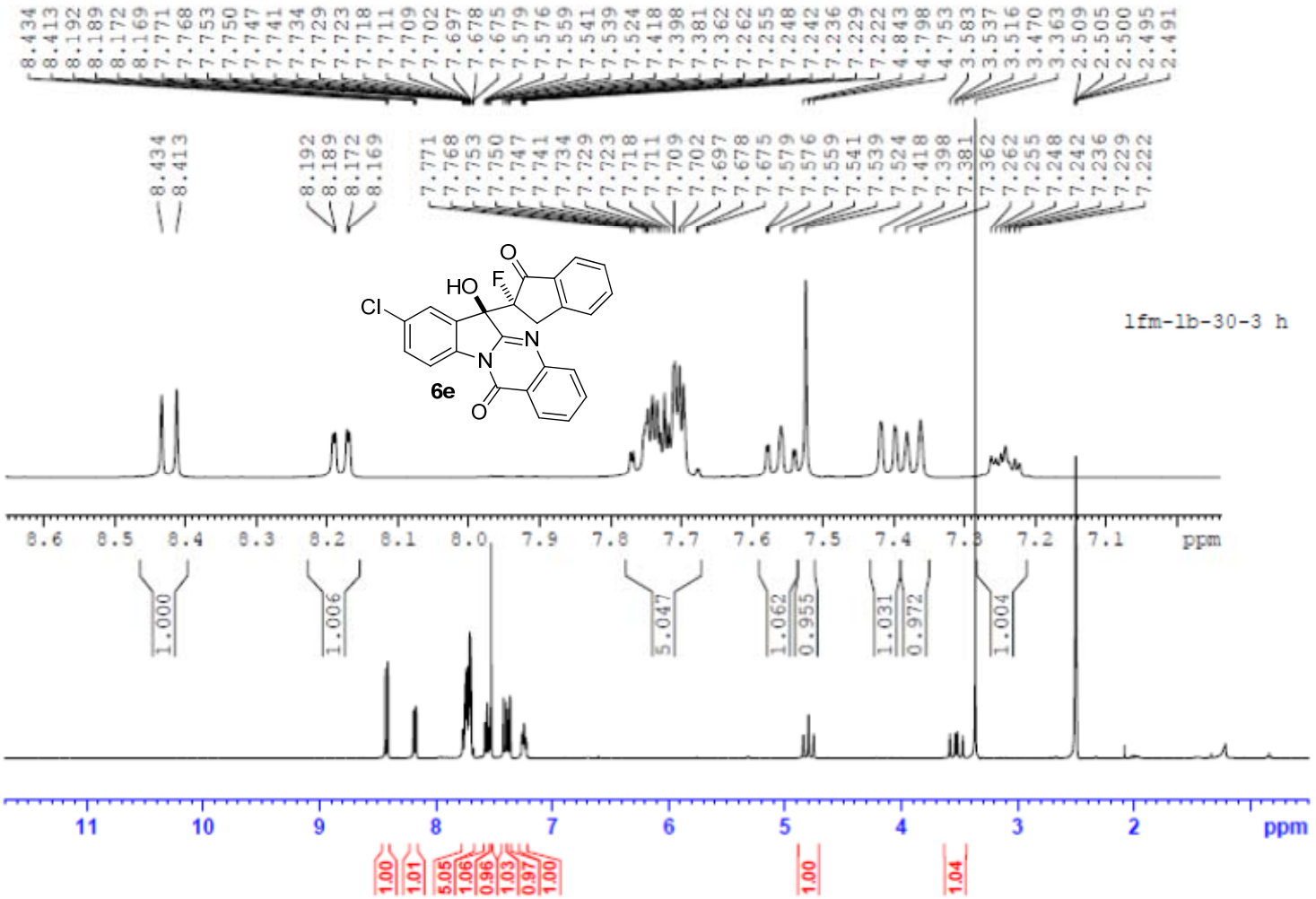

197.01
196.83
158.00
157.88
156.47
156.36
152.34
152.31
145.93
136.85
134.68
133.23
132.47
132.18
128.09
127.92
127.45
126.68
126.18
124.04
121.06
116.65
114.81
113.12
113.07
101.23
99.26
77.44
77.20
55.66
40.13
39.92
39.71
39.50
39.29
39.08
38.88
35.79
35.56
136.851
134.681
133.229
132.475
132.181
128.086
127.924
127.453
126.677
126.181
124.040
121.063
116.653
114.811
113.124
113.068
lfm-lb-30-1 C
MeO
HO
F
O
N
N
O
6c
136
134
132
130
128
126
124
122
120
118
116
114
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

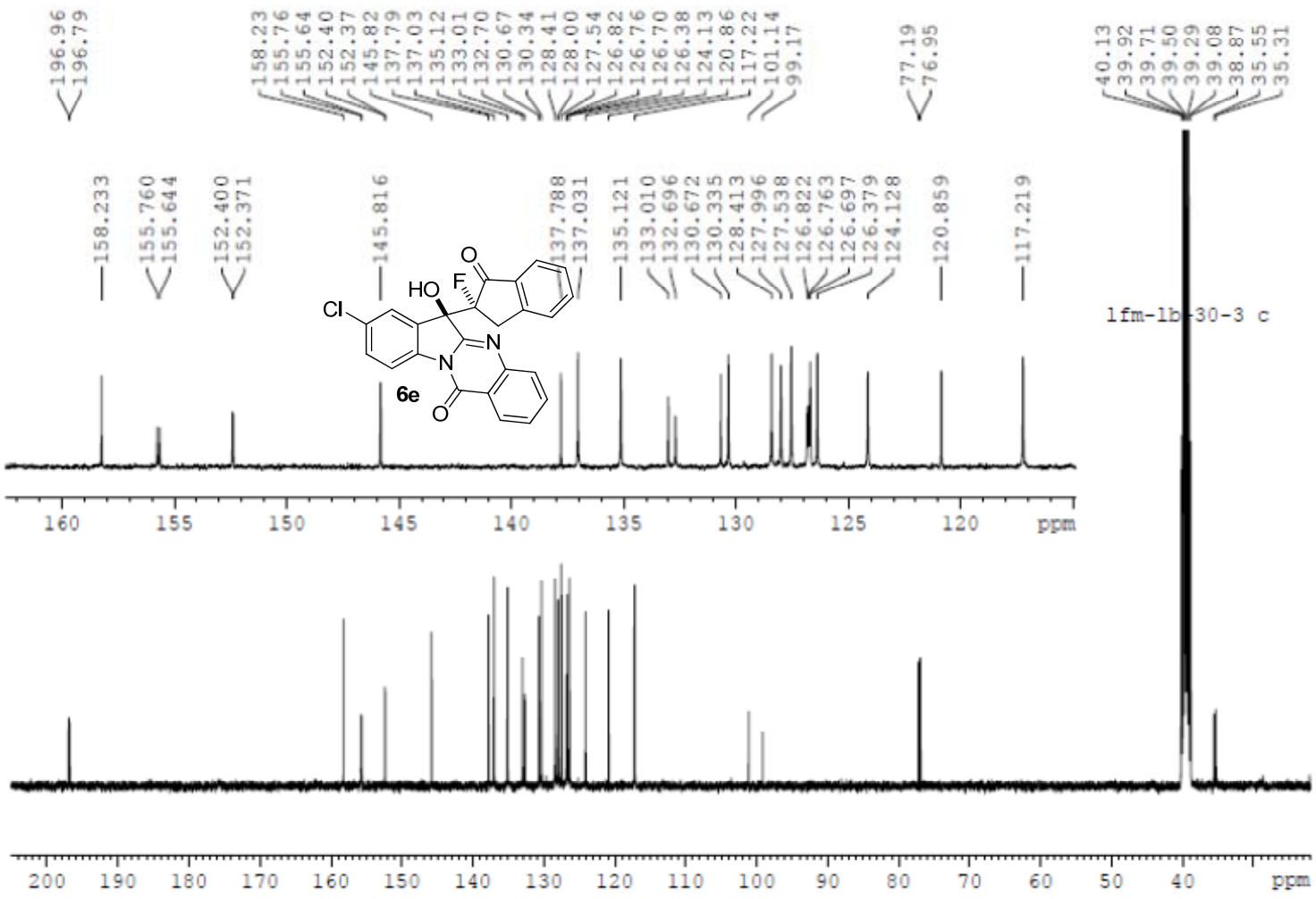

lfm-1b-30-1 f
-161.11
O
F
HO
MeO
N
N
O
6c
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
f1 (ppm)

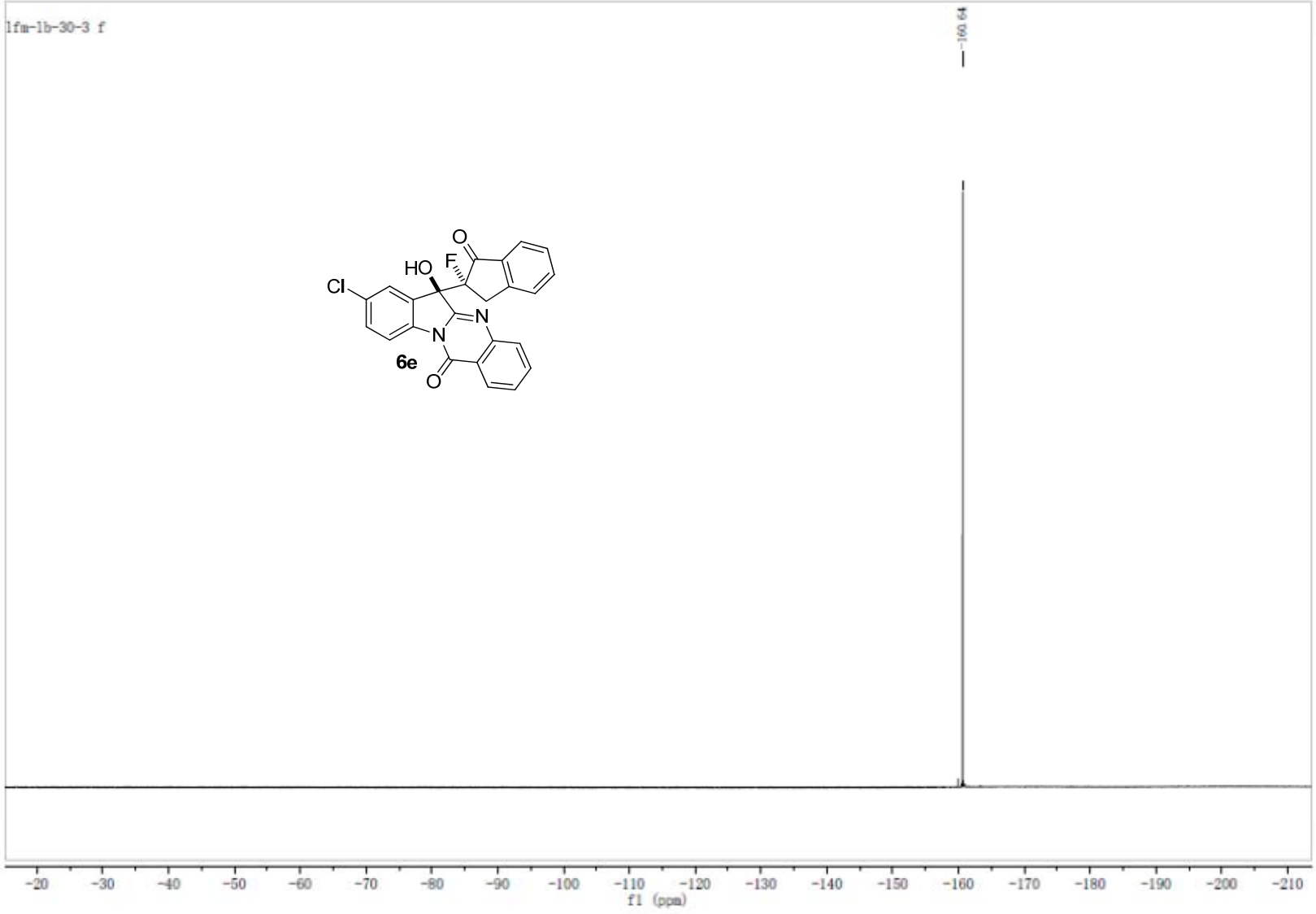

8.459
8.447
8.436
8.425
8.192
8.189
8.173
8.169
7.766
7.763
7.748
7.745
7.728
7.724
7.709
7.707
7.695
7.692
7.675
7.673
7.576
7.573
7.564
7.556
7.543
7.538
7.515
7.509
7.502
7.487
7.480
7.464
7.457
7.414
7.394
7.377
7.358
7.260
7.253
7.245
7.240
7.226
7.220
4.852
4.807
4.763
3.577
3.531
3.511
3.465
3.358
2.509
2.505
2.500
2.496
2.491
lfm-lb-29-3 h
HO
F
F
O
O
N
N
6d
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.000
0.990
3.148
4.066
1.004
0.972
0.974
12
11
10
9
8
7
6
5
4
3
2
ppm
1.00
0.99
3.15
4.07
1.00
0.97
0.97
0.99
1.04

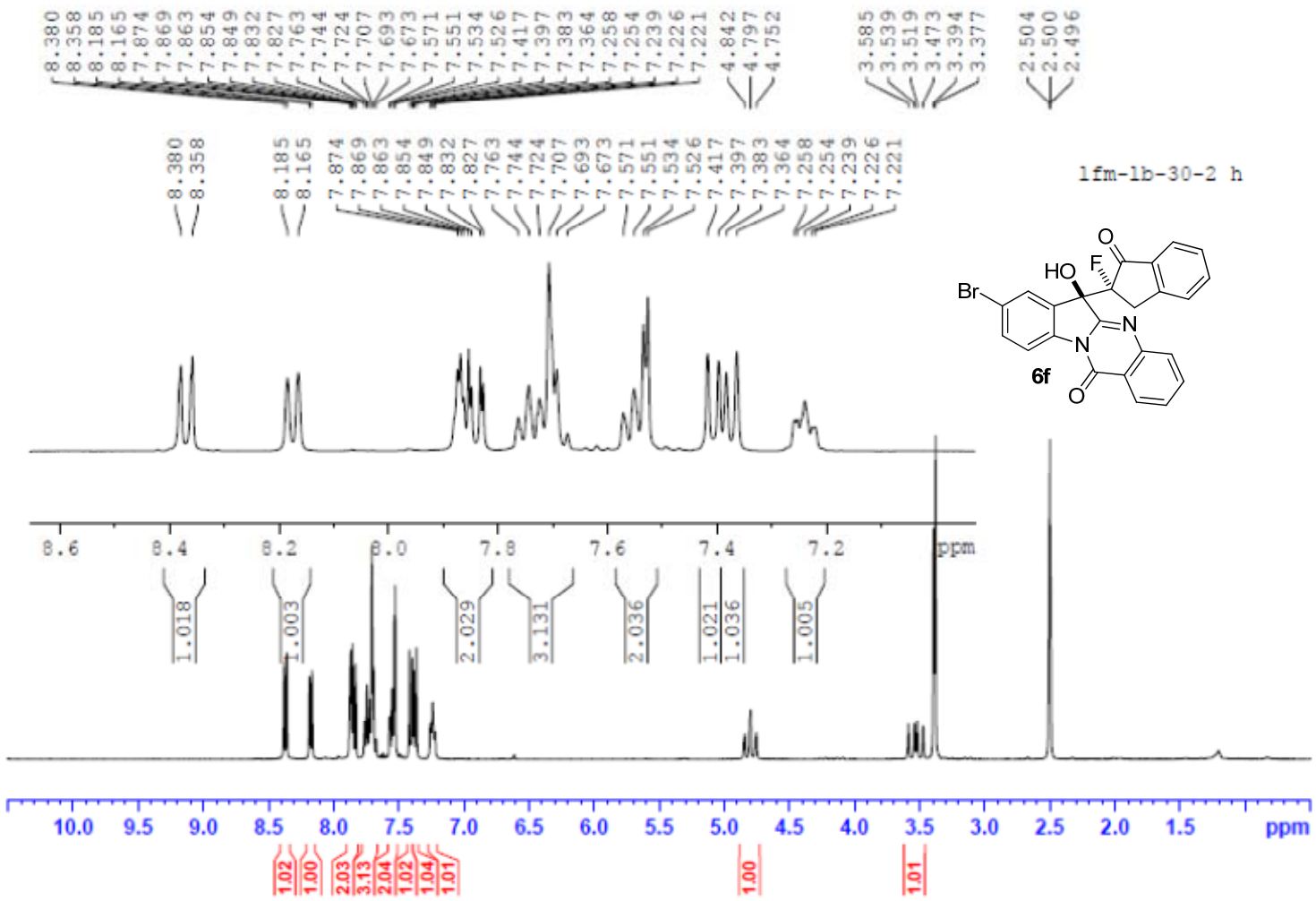

196.94
196.76
161.54
159.12
158.17
156.08
155.97
152.39
152.36
145.82
136.99
135.33
135.01
133.03
132.97
132.88
128.33
127.97
127.49
126.68
126.31
124.10
120.91
117.27
117.19
117.09
116.86
114.47
114.41
114.22
114.16
101.16
99.19
77.19
76.97
40.12
39.92
39.71
39.50
39.29
39.08
38.87
35.58
35.34
161.539
159.122
158.167
156.084
155.969
152.386
152.356
145.819
136.992
135.331
135.008
133.033
132.966
132.879
128.327
127.974
127.494
126.683
126.307
124.100
120.912
117.272
117.188
117.093
116.860
114.470
114.411
114.217
114.160
lfm-1b-29-3 c
HO
F
F
O
O
N
N
6d
160
155
150
145
140
135
130
125
120
115
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

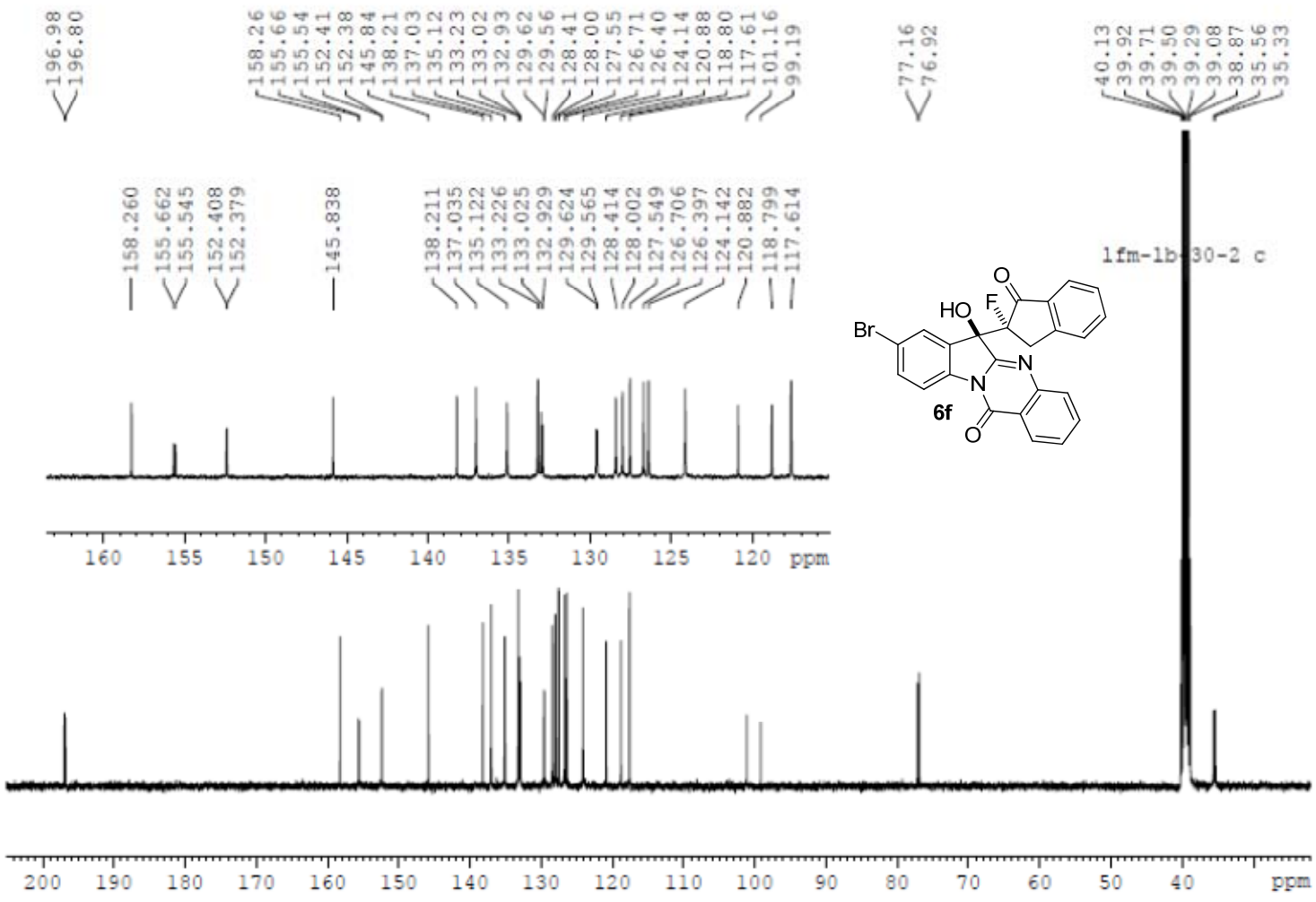

lfm-lb-29-3 f
-114.82
-160.87
HO
F
F
O
N
N
O
6d
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

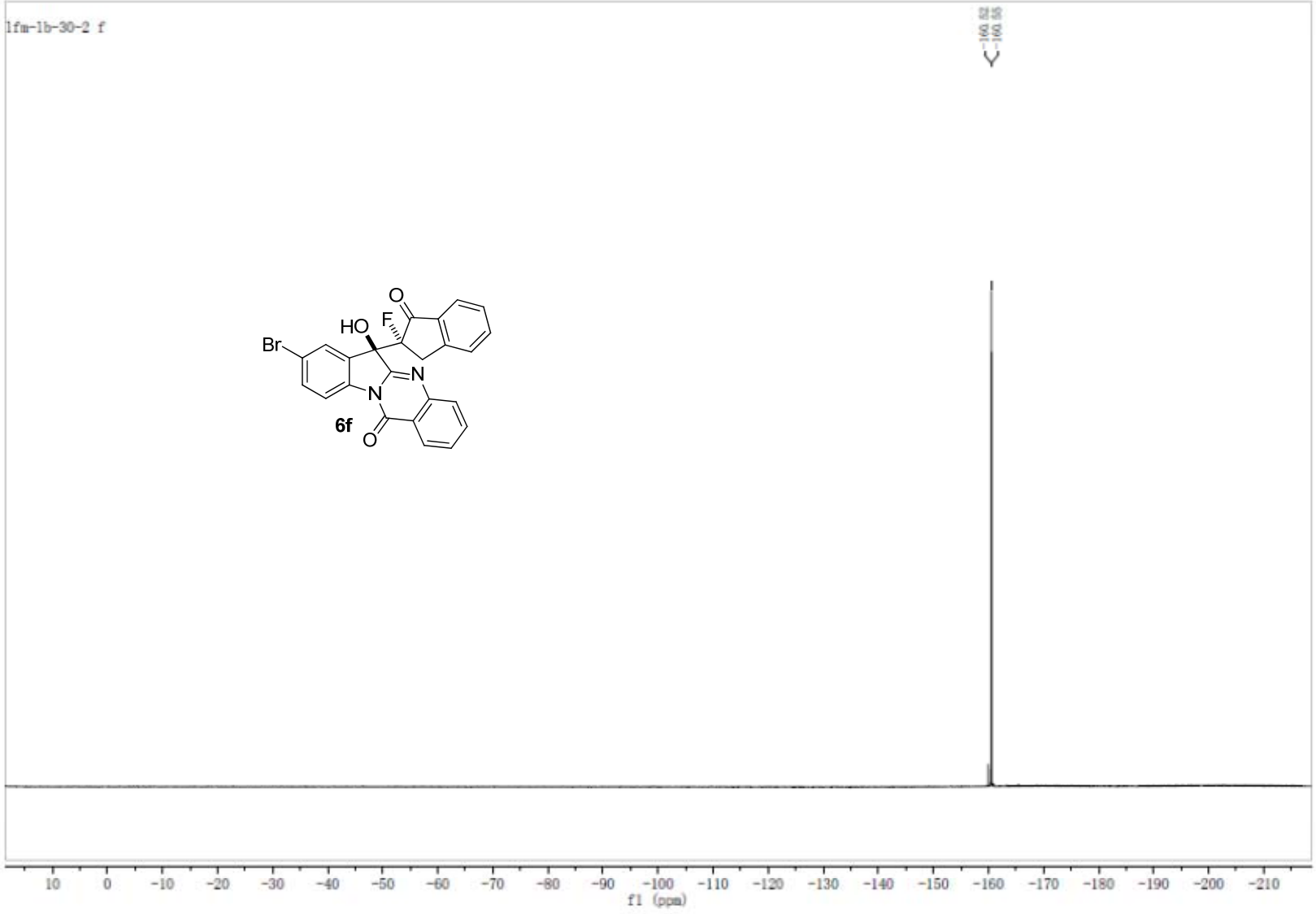

lfm-lb-30-3 h
HO
F
O
Cl
N
N
O
6e
ppm
ppm

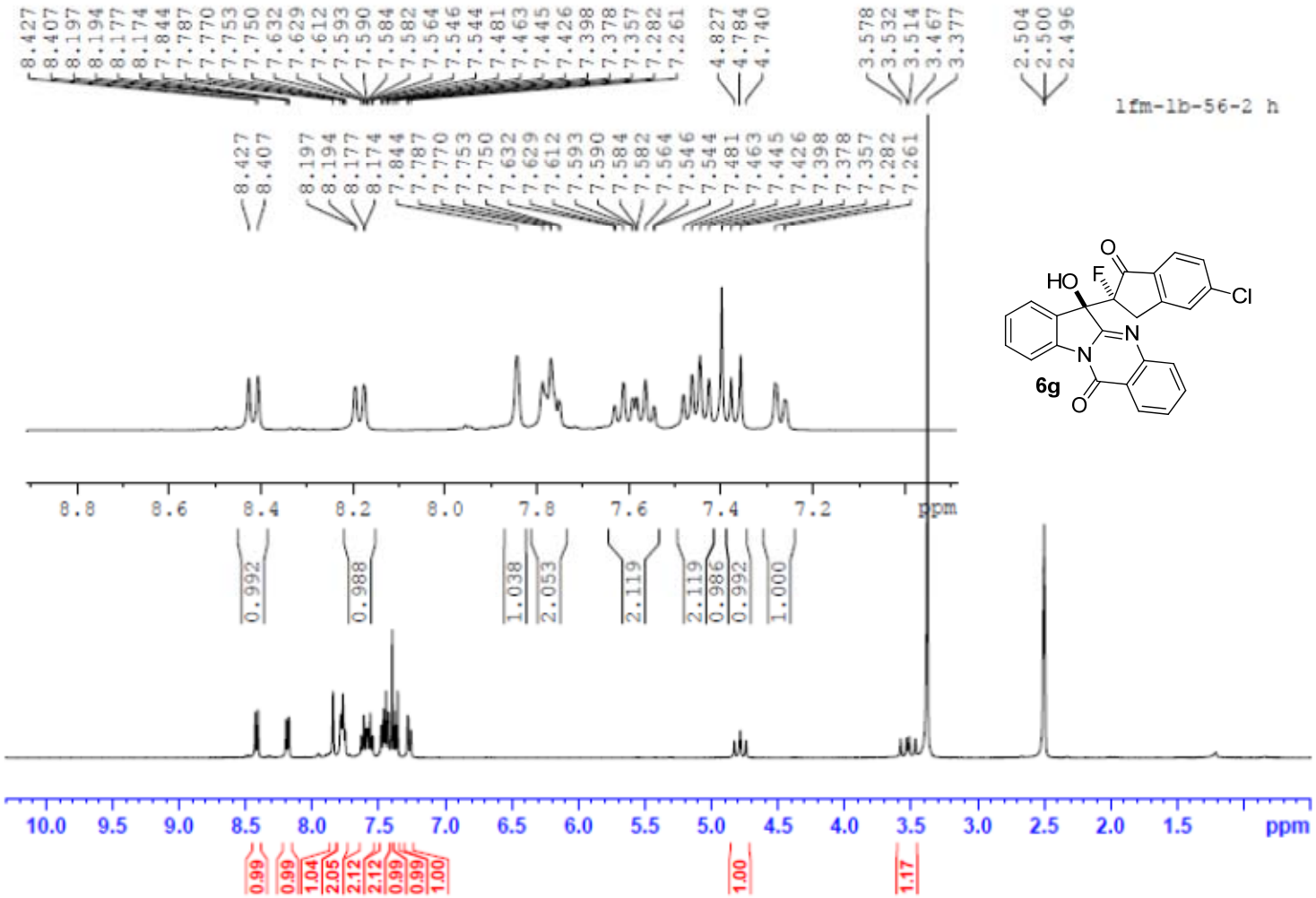

196.96
196.79
158.23
155.76
155.64
152.40
152.37
145.82
137.79
137.03
135.12
133.01
132.70
130.67
130.34
128.41
128.00
127.54
126.82
126.76
126.70
126.38
124.13
120.86
117.22
101.14
99.17
77.19
76.95
40.13
39.92
39.71
39.50
39.29
39.08
38.87
35.55
35.31
158.233
155.760
155.644
152.400
152.371
145.816
137.788
137.031
135.121
133.010
132.696
130.672
130.335
128.413
127.996
127.538
126.822
126.763
126.697
126.379
124.128
120.859
117.219
lfm-lb-30-3 c
HO
F
O
Cl
N
N
O
6e
160
155
150
145
140
135
130
125
120
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

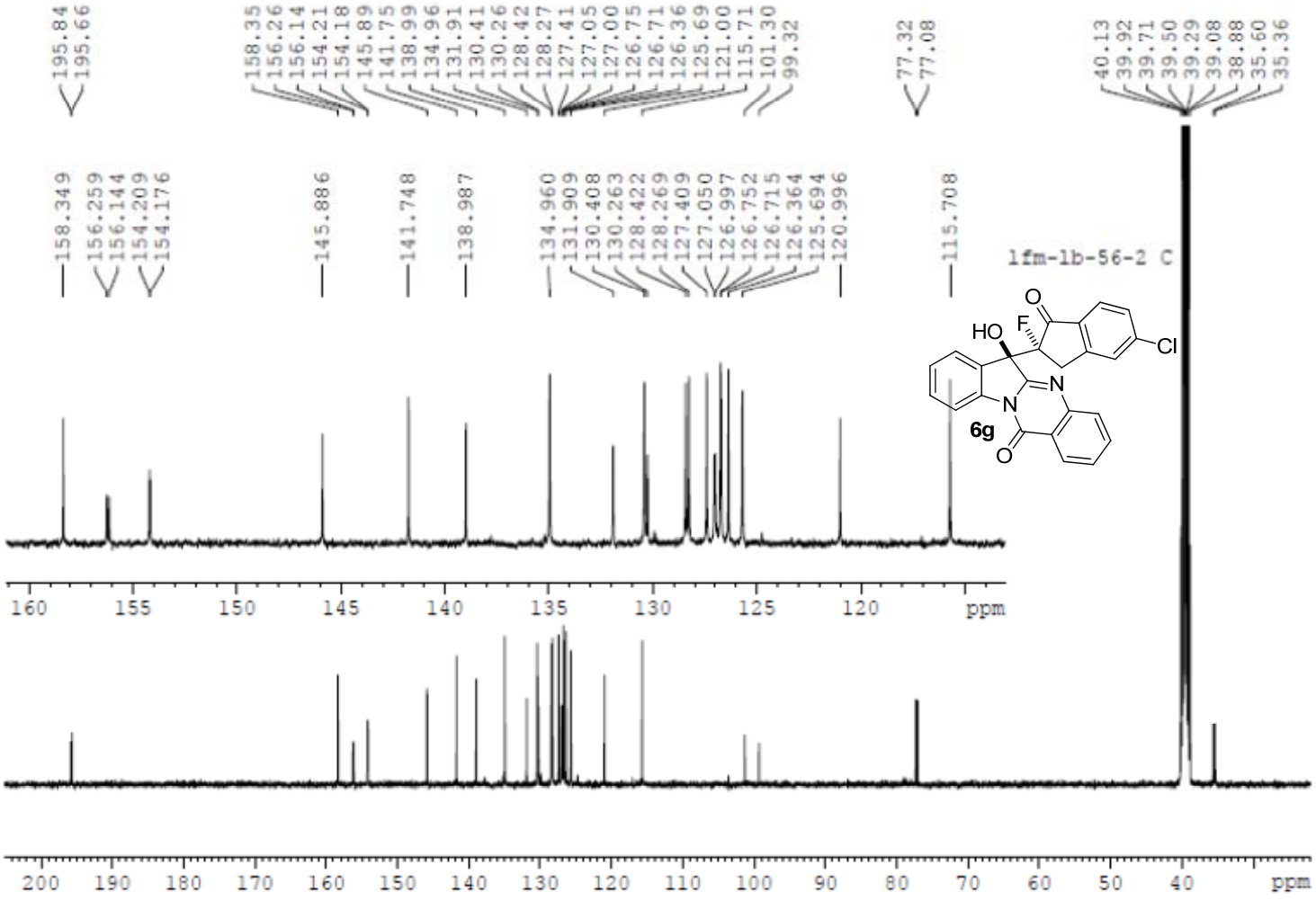

lfm-1b-30-3 f
-160.64
O
HO
F
Cl
N
N
O
6e
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

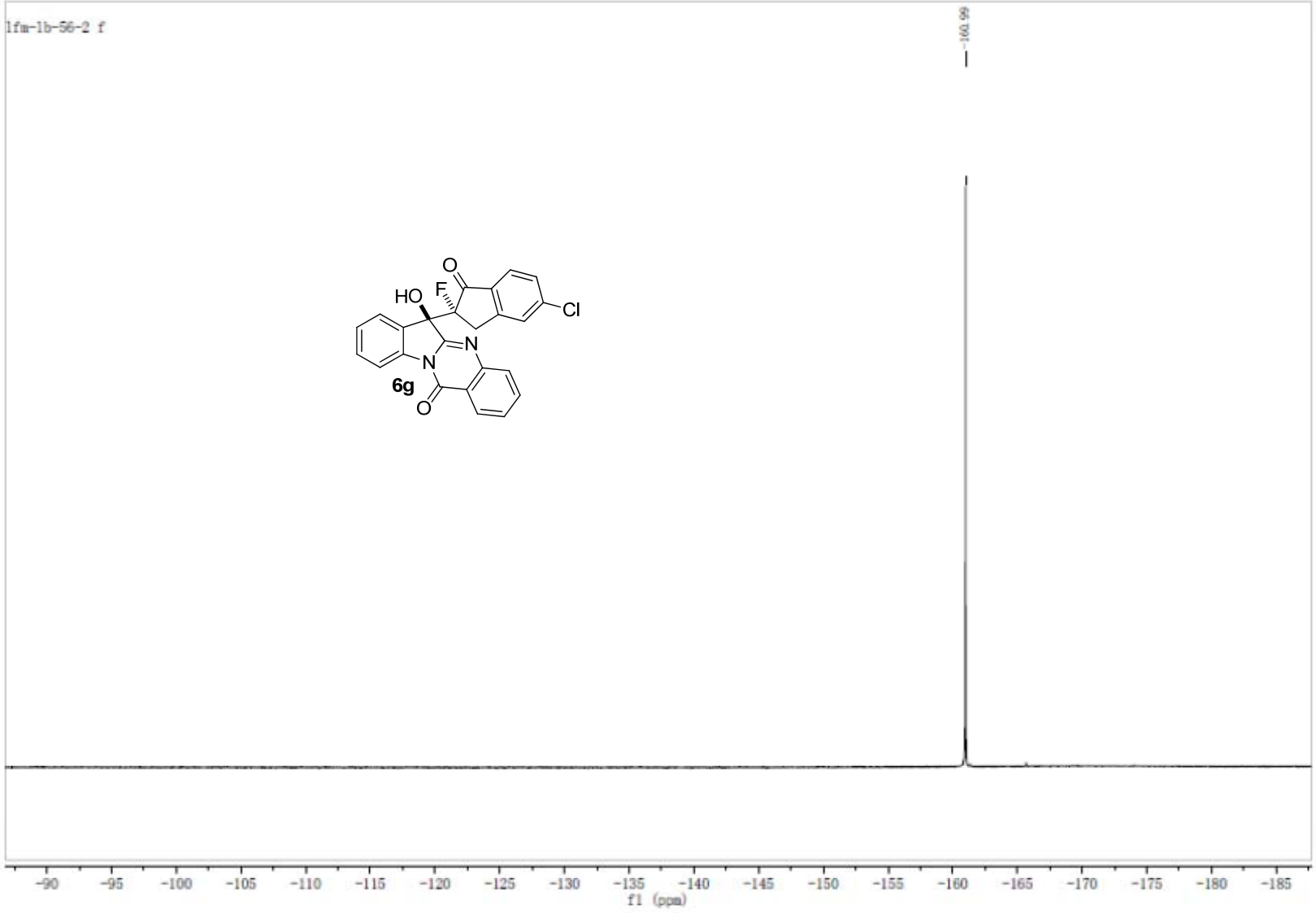

8.380
8.358
8.185
8.165
7.874
7.869
7.863
7.854
7.849
7.832
7.827
7.763
7.744
7.724
7.707
7.693
7.673
7.571
7.551
7.534
7.526
7.417
7.397
7.383
7.364
7.258
7.254
7.239
7.226
7.221
4.842
4.797
4.752
3.585
3.539
3.519
3.473
3.394
3.377
2.504
2.500
2.496
lfm-lb-30-2 h
HO
F
O
Br
N
N
O
6f
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.018
1.003
2.029
3.131
2.036
1.021
1.036
1.005
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
ppm
1.02
1.00
2.03
3.13
2.04
1.02
1.04
1.01
1.00
1.01

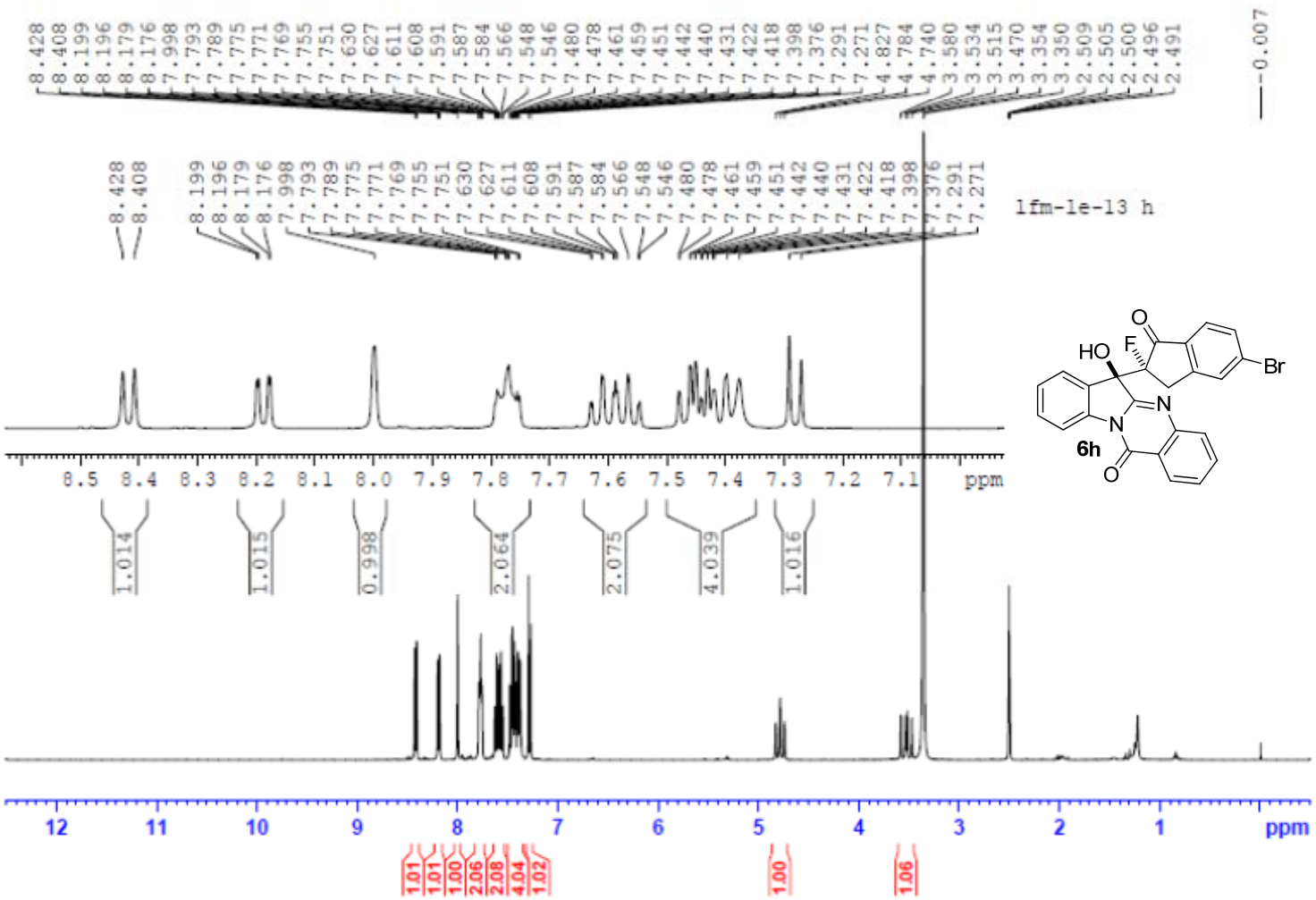

196.98
196.80
158.26
155.66
155.54
152.41
152.38
145.84
138.21
137.03
135.12
133.23
133.02
132.93
129.62
129.56
128.41
128.00
127.55
126.71
126.40
124.14
120.88
118.80
117.61
101.16
99.19
77.16
76.92
40.13
39.92
39.71
39.50
39.29
39.08
38.87
35.56
35.33
158.260
155.662
155.545
152.408
152.379
145.838
138.211
137.035
135.122
133.226
133.025
132.929
129.624
129.565
128.414
128.002
127.549
126.706
126.397
124.142
120.882
118.799
117.614
160
155
150
145
140
135
130
125
120
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm
O
HO
F
Br
N
N
O
6f

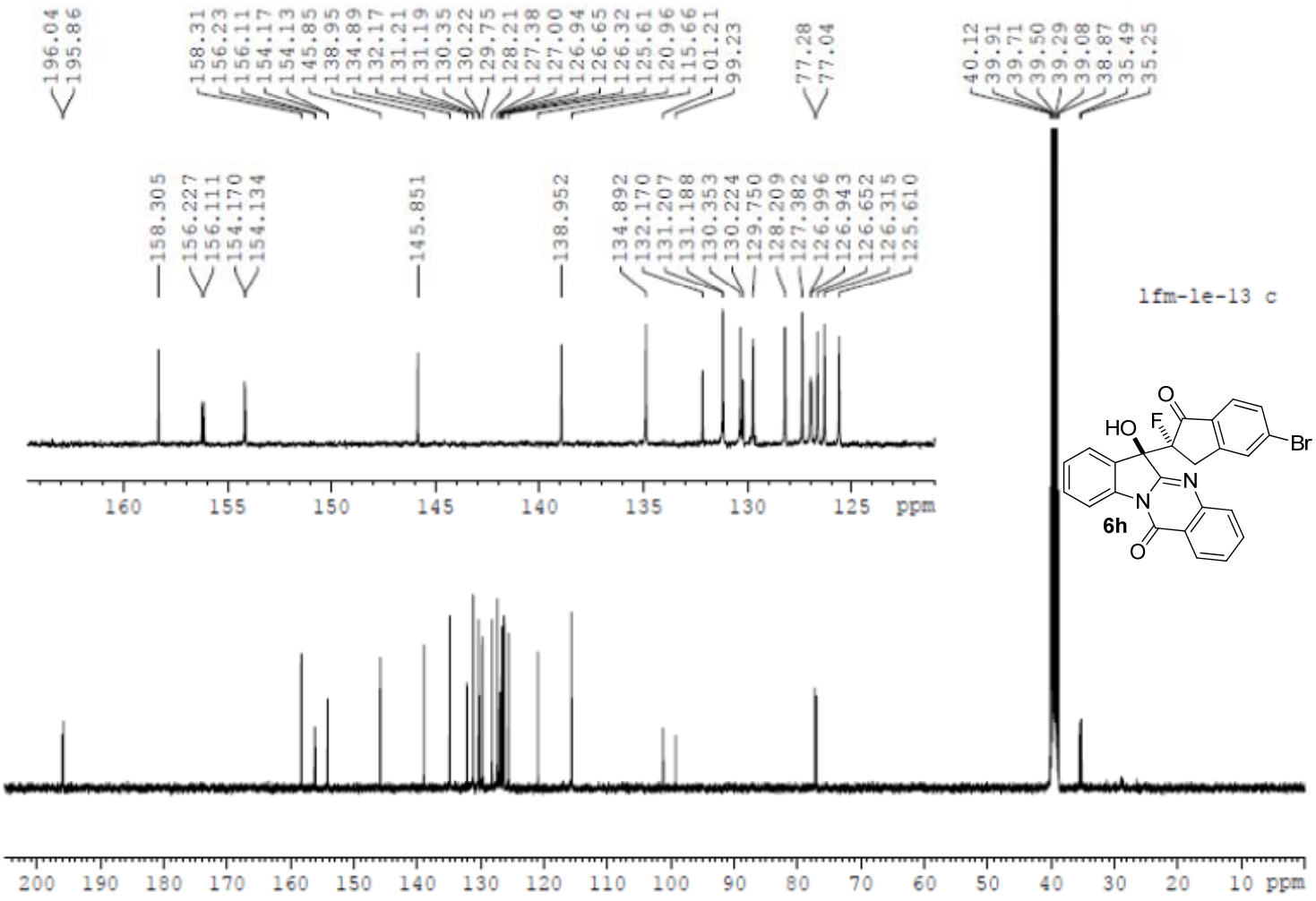

lfm-1b-30-2 f
160.52
160.55
O
HO
F
Br
N
N
6f
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

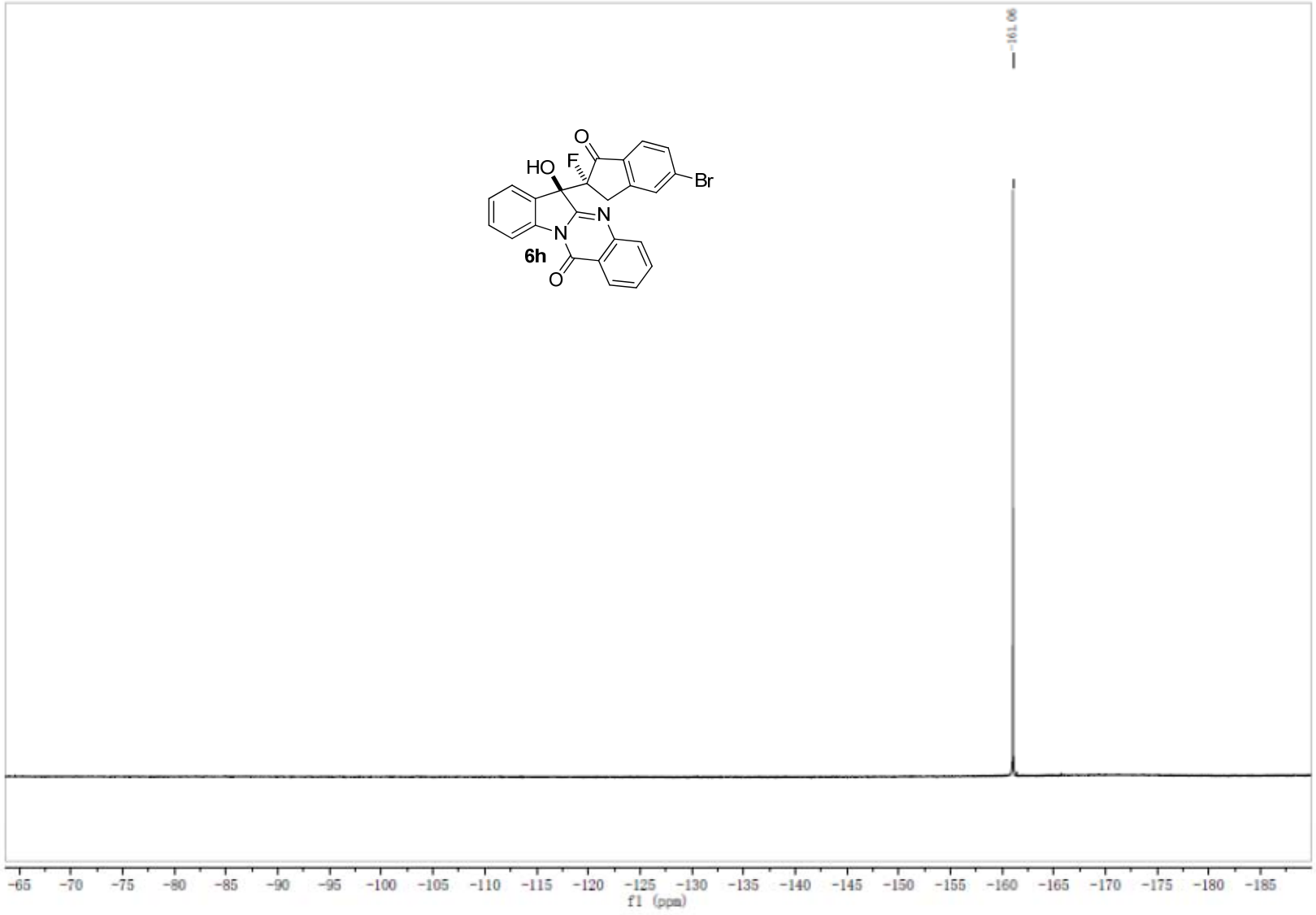

lfm-lb-56-2 h
8.427
8.407
8.197
8.194
8.177
8.174
7.844
7.787
7.770
7.753
7.750
7.632
7.629
7.612
7.593
7.590
7.584
7.582
7.564
7.546
7.544
7.481
7.463
7.445
7.426
7.398
7.378
7.357
7.282
7.261
4.827
4.784
4.740
3.578
3.532
3.514
3.467
3.377
2.504
2.500
2.496
HO
F
O
Cl
N
N
O
6g
ppm
0.992
0.988
1.038
2.053
2.119
2.119
0.986
0.992
1.000
0.99
0.99
1.04
2.05
2.12
2.12
0.99
0.99
1.00
1.00
1.17

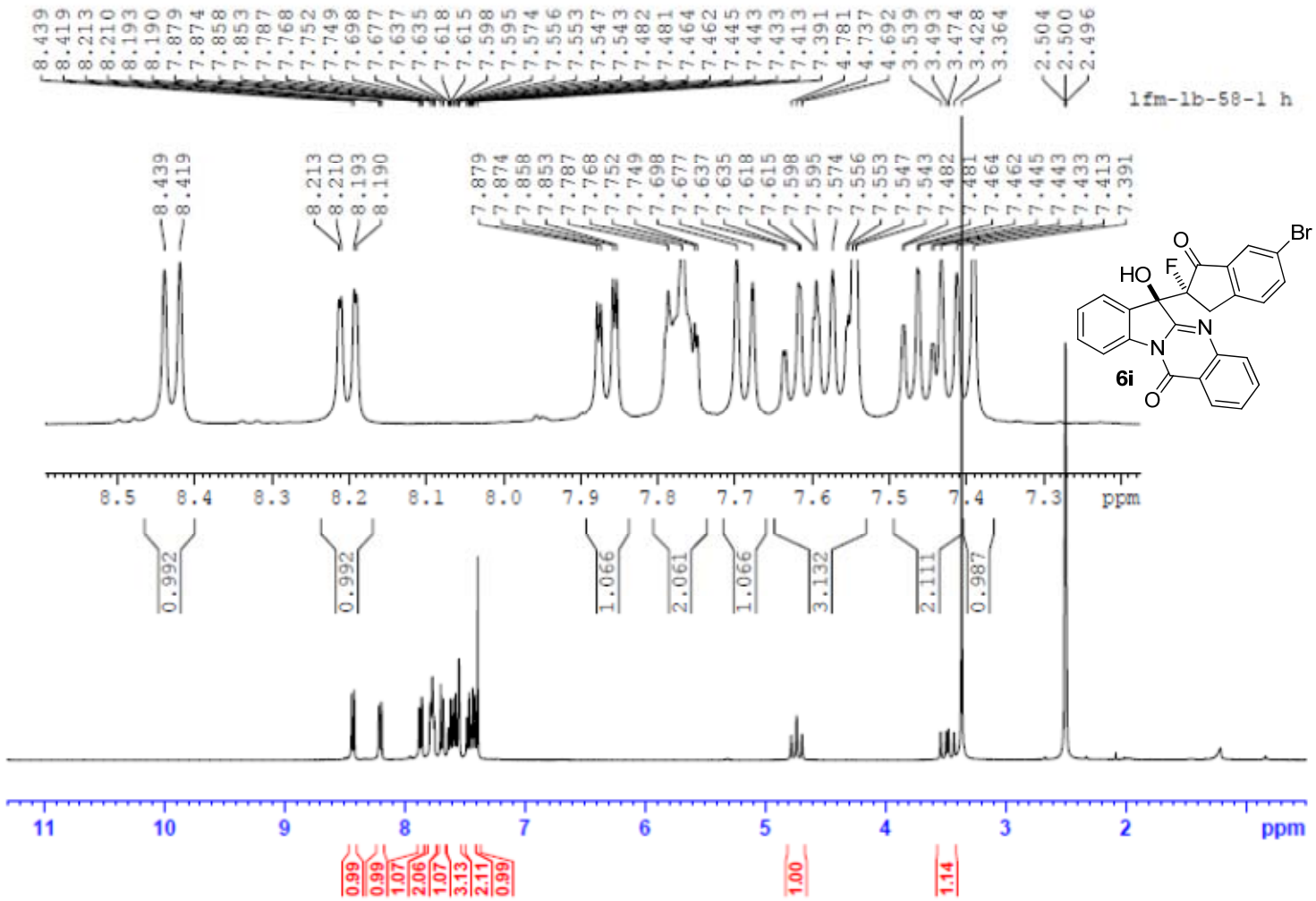

195.84
195.66
158.35
156.26
156.14
154.21
154.18
145.89
141.75
138.99
134.96
131.91
130.41
130.26
128.42
128.27
127.41
127.05
127.00
126.75
126.71
126.36
125.69
121.00
115.71
101.30
99.32
77.32
77.08
40.13
39.92
39.71
39.50
39.29
39.08
38.88
35.60
35.36
158.349
156.259
156.144
154.209
154.176
145.886
141.748
138.987
134.960
131.909
130.408
130.263
128.422
128.269
127.409
127.050
126.997
126.752
126.715
126.364
125.694
120.996
115.708
lfm-lb-56-2 C
HO
F
O
Cl
N
N
O
6g
160
155
150
145
140
135
130
125
120
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

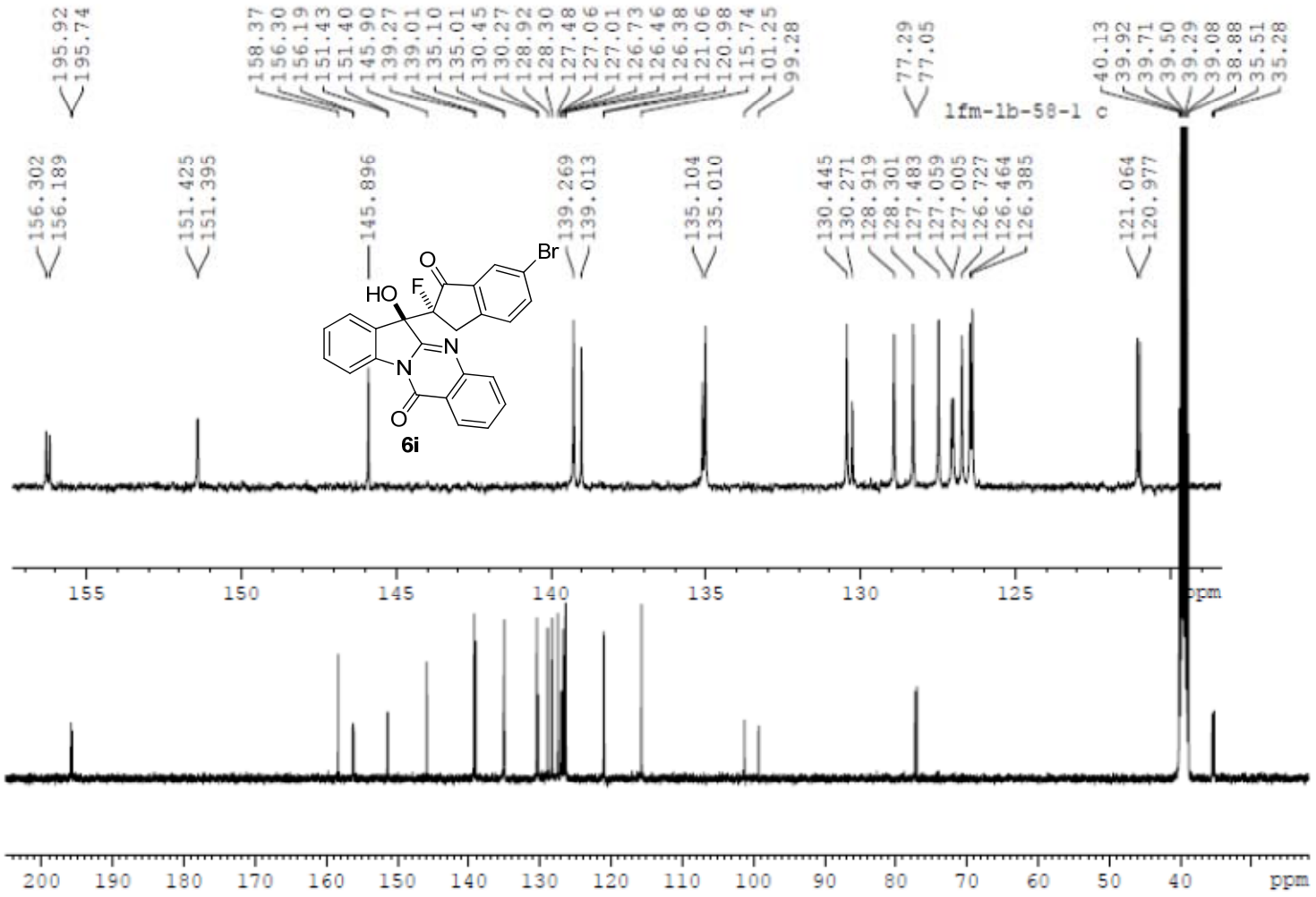

lfm-1b-56-2 f
-160.99
HO
F
O
Cl
N
N
O
6g
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
f1 (ppm)

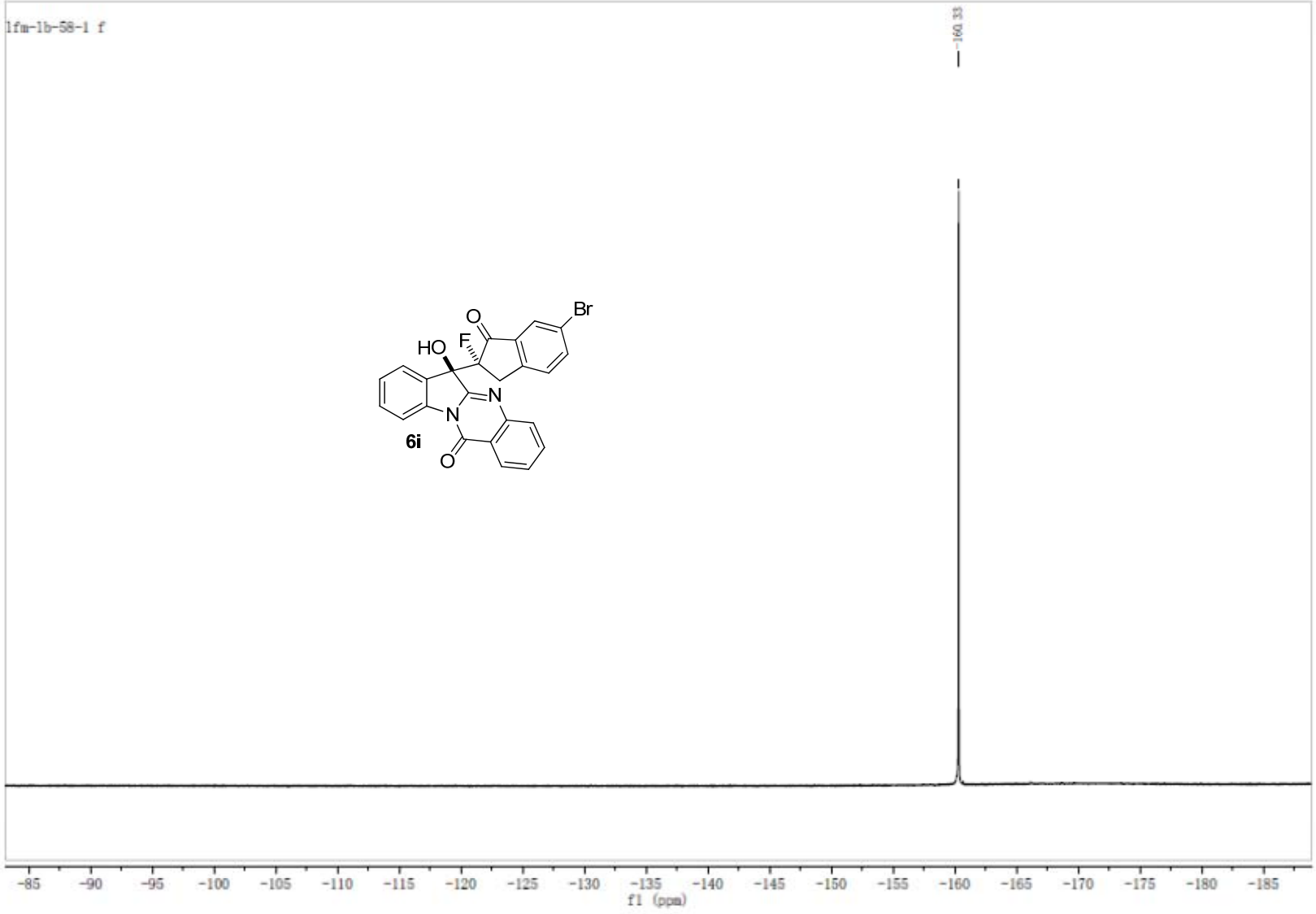

8.428 8.408 8.199 8.196 8.179 8.176 7.998 7.793 7.789 7.775 7.771 7.769 7.755 7.751 7.630 7.627 7.611 7.608 7.591 7.587 7.584 7.566 7.548 7.546 7.480 7.478 7.461 7.459 7.451 7.442 7.440 7.431 7.422 7.418 7.398 7.376 7.291 7.271 4.827 4.784 4.740 3.580 3.534 3.515 3.470 3.354 3.350 2.509 2.505 2.500 2.496 2.491 -0.007
lfm-1e-13 h
HO
F
O
Br
N
N
O
6h
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
1.014 1.015 0.998 2.064 2.075 4.039 1.016
12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.01 1.01 1.00 2.06 2.08 4.04 1.02 1.00 1.06

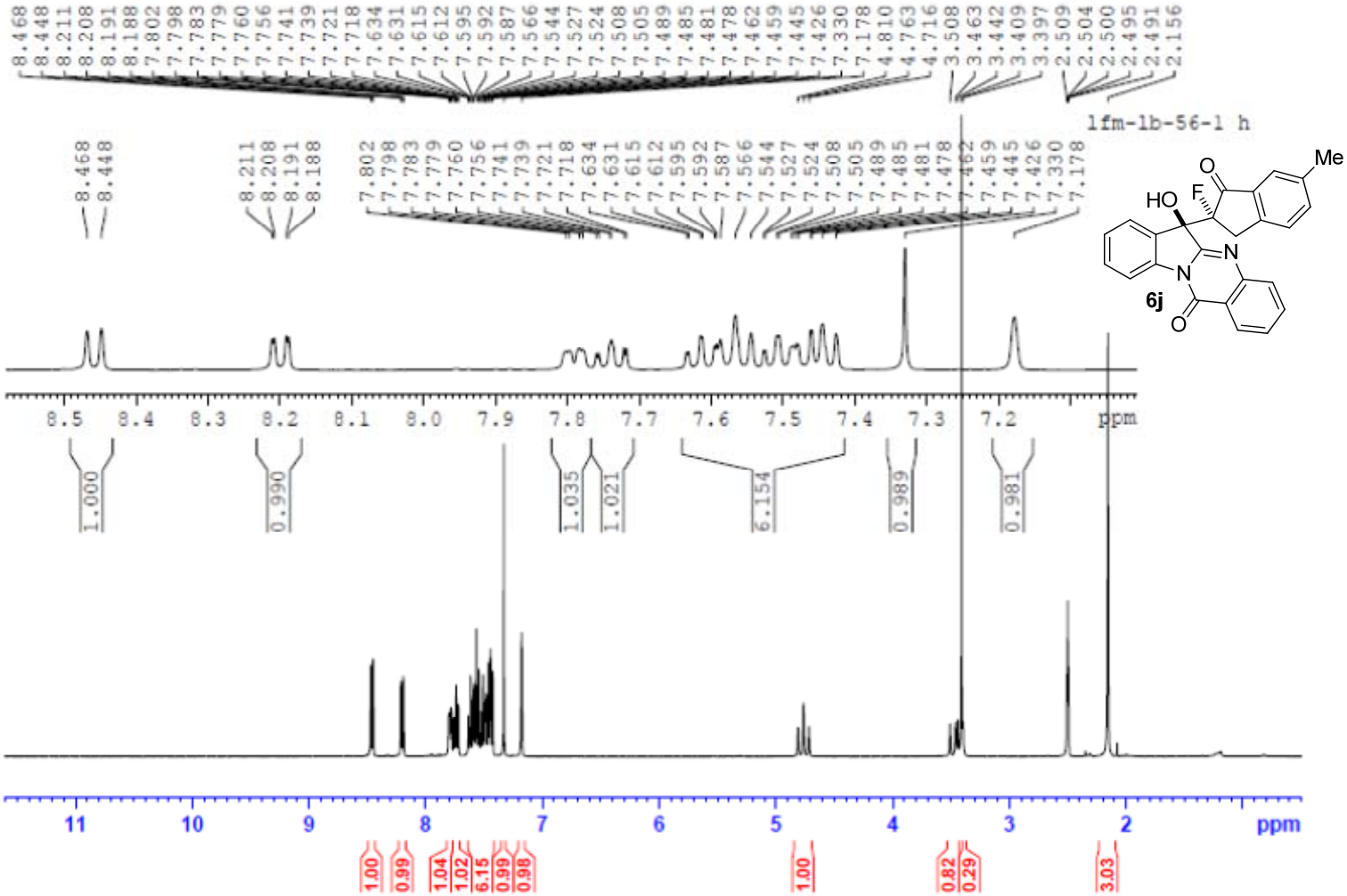

196.04
195.86
158.31
156.23
156.11
154.17
154.13
145.85
138.95
134.89
132.17
131.21
131.19
130.35
130.22
129.75
128.21
127.38
127.00
126.94
126.65
126.32
125.61
120.96
115.66
101.21
99.23
77.28
77.04
40.12
39.91
39.71
39.50
39.29
39.08
38.87
35.49
35.25
158.305
156.227
156.111
154.170
154.134
145.851
138.952
134.892
132.170
131.207
131.188
130.353
130.224
129.750
128.209
127.382
126.996
126.943
126.652
126.315
125.610
160
155
150
145
140
135
130
125
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
lfm-le-13 c
HO
F
O
Br
N
N
O
6h

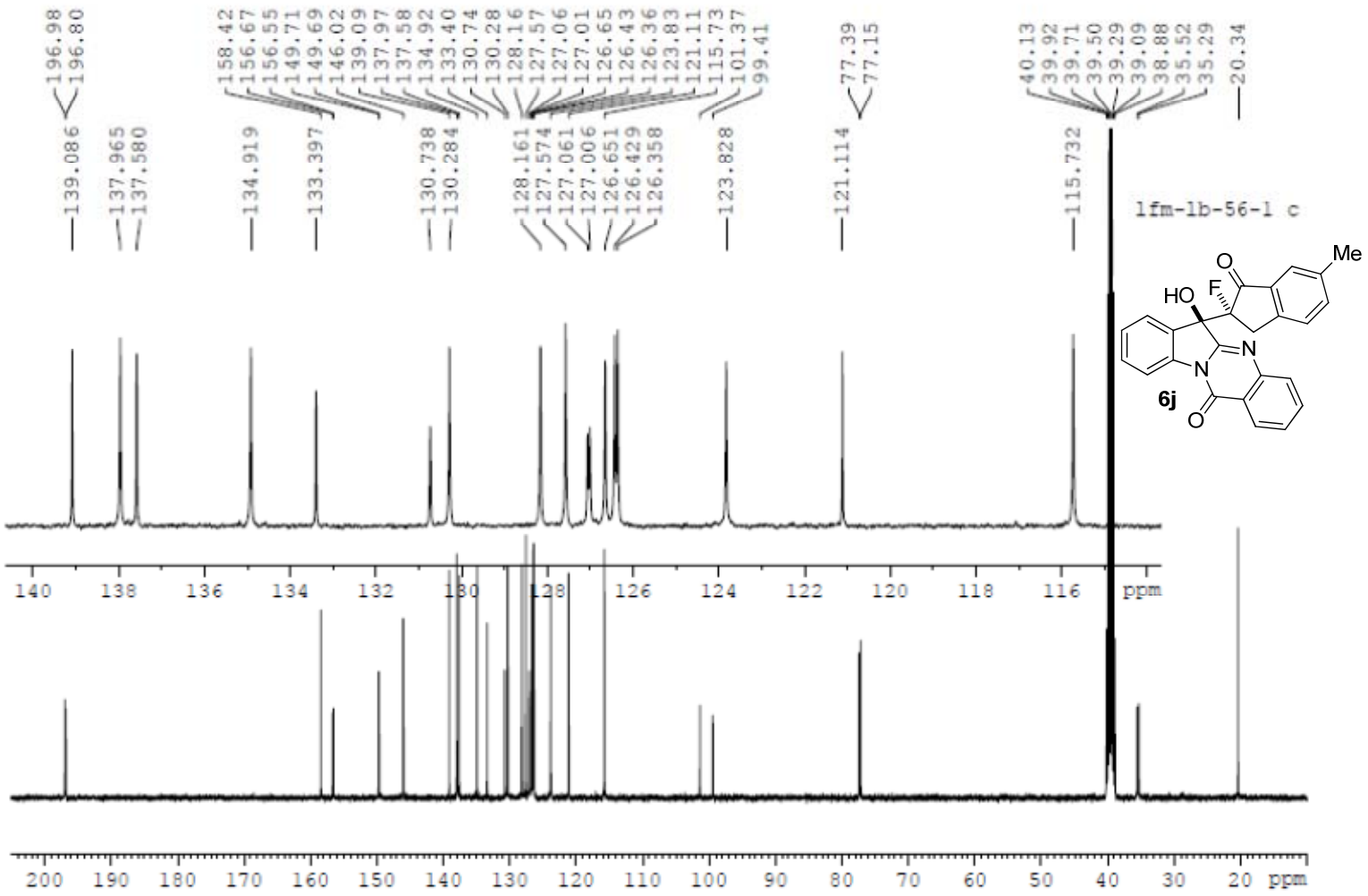

-161.06
HO
F
O
Br
N
N
O
6h
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)

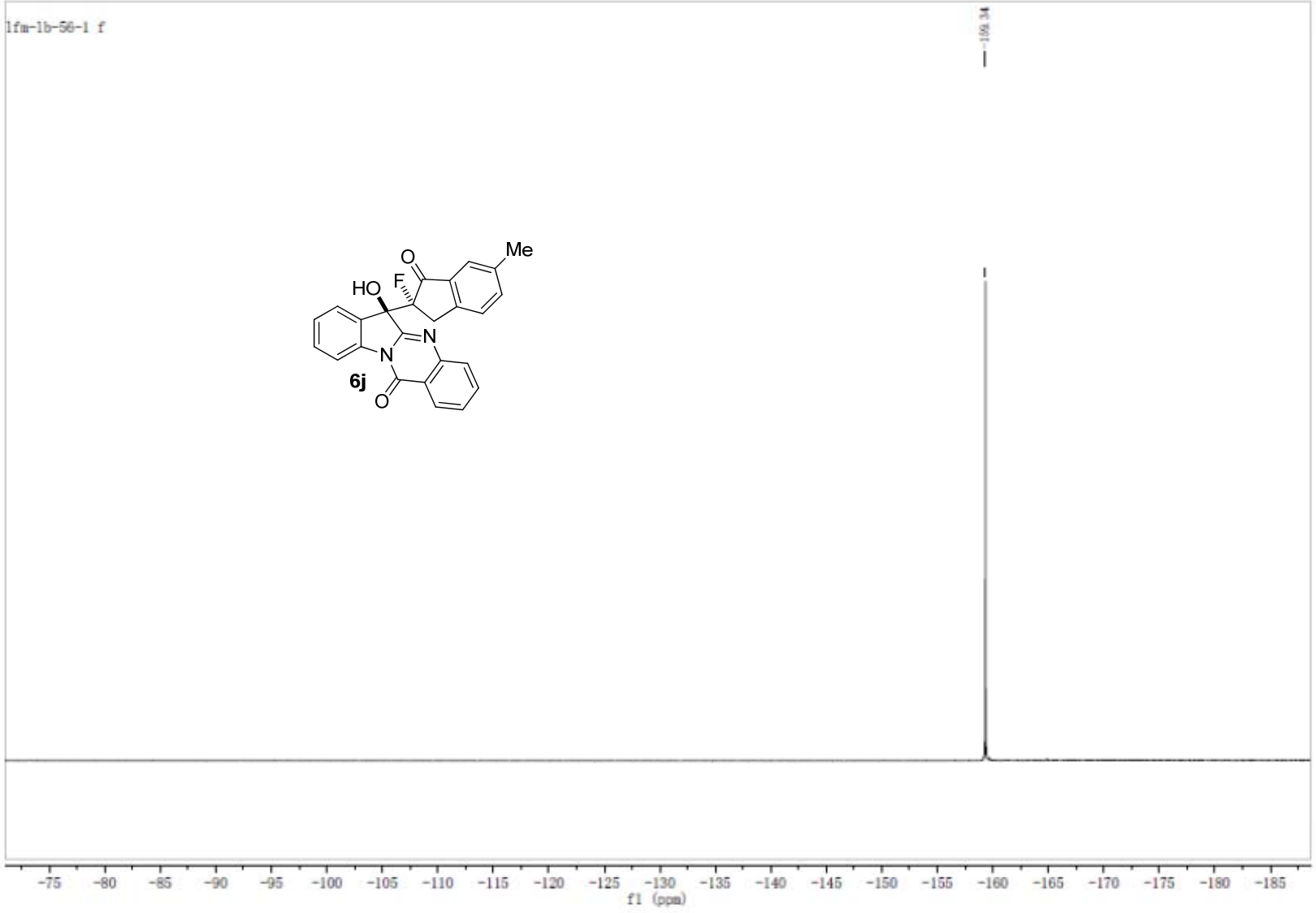

lfm-1b-58-1 h
HO
F
O
Br
N
N
O
6i
ppm

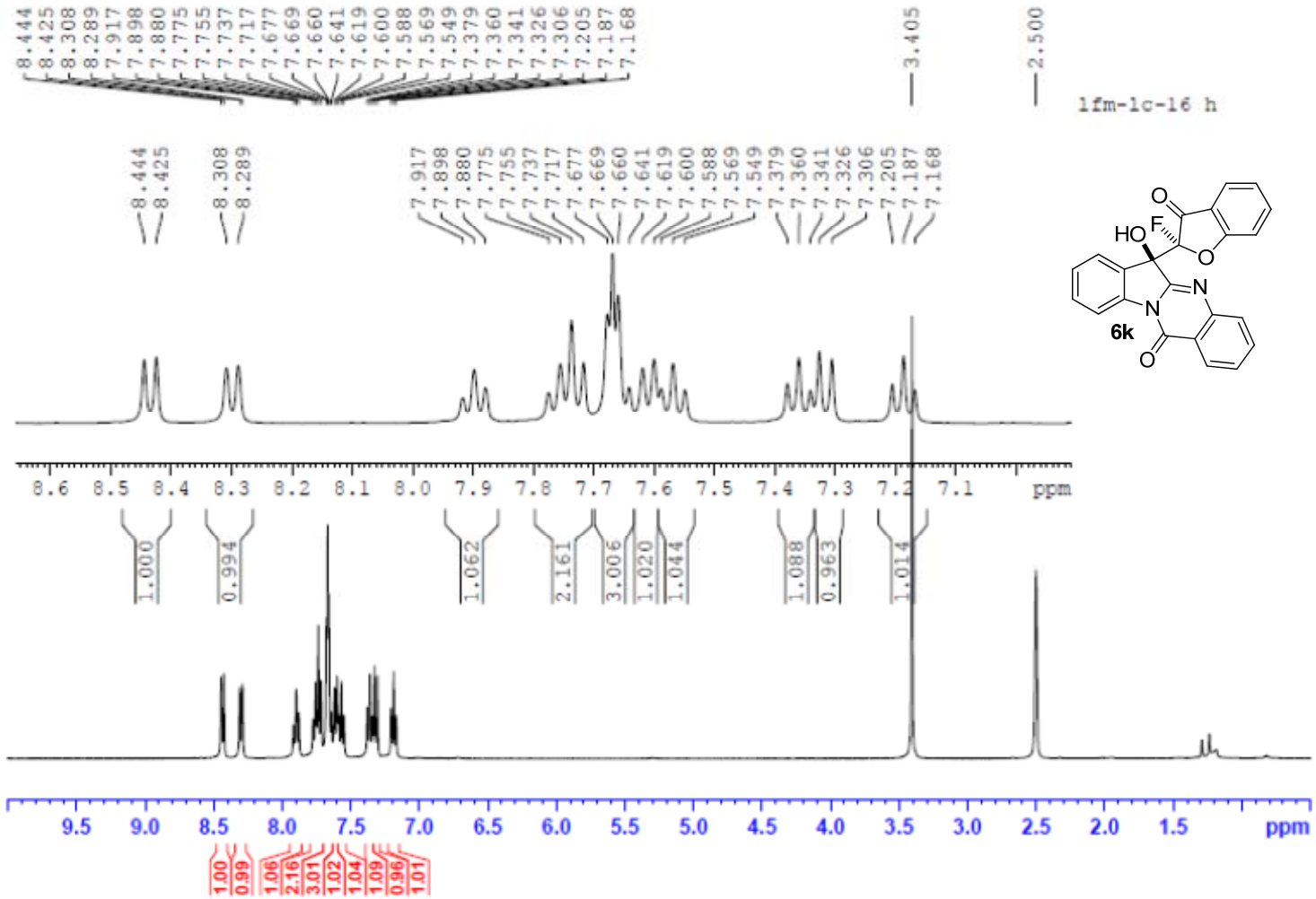

195.92
195.74
158.37
156.30
156.19
151.43
151.40
145.90
139.27
139.01
135.10
135.01
130.45
130.27
128.92
128.30
127.48
127.06
127.01
126.73
126.46
126.38
121.06
120.98
115.74
101.25
99.28
77.29
77.05
40.13
39.92
39.71
39.50
39.29
39.08
38.88
35.51
35.28
lfm-1b-58-1 c
156.302
156.189
151.425
151.395
145.896
139.269
139.013
135.104
135.010
130.445
130.271
128.919
128.301
127.483
127.059
127.005
126.727
126.464
126.385
121.064
120.977
Br
O
F
HO
N
N
O
6i
155
150
145
140
135
130
125
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

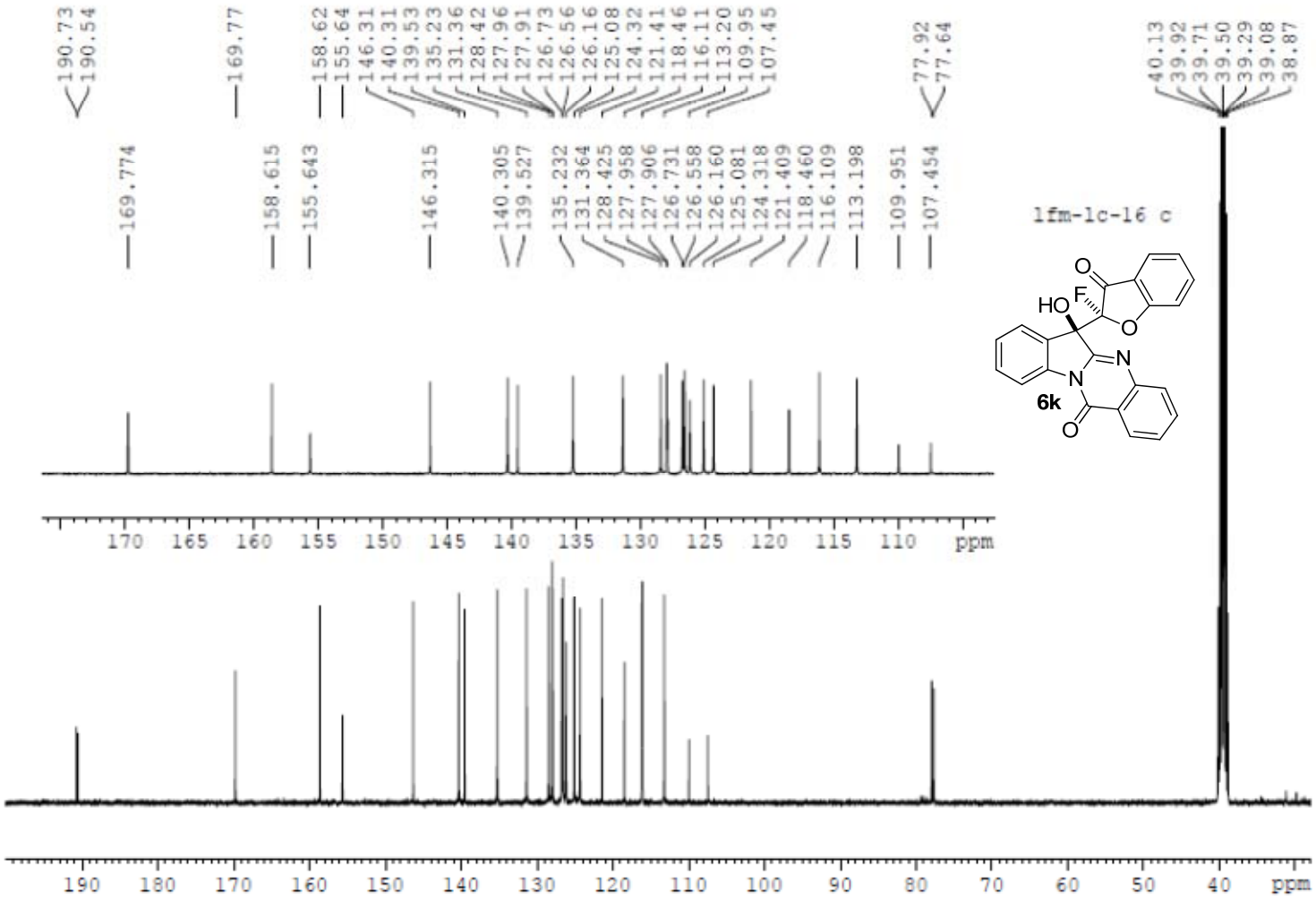

lfm-lb-58-1 f
-160.33
Br
O
F
HO
N
N
O
6i
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
f1 (ppm)

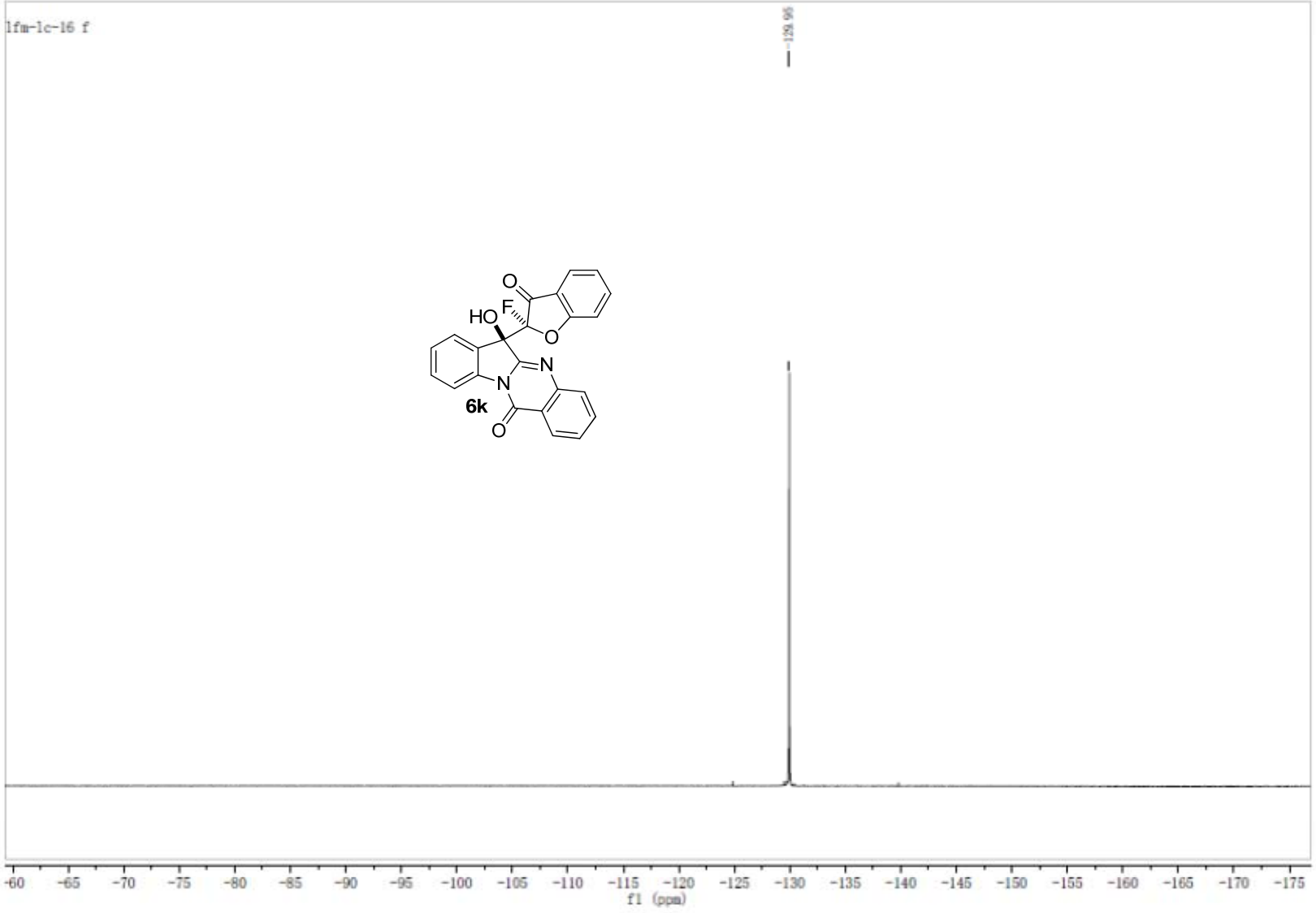

lfm-1b-56-1 h
HO
F
O
Me
N
N
O
6j
ppm
ppm

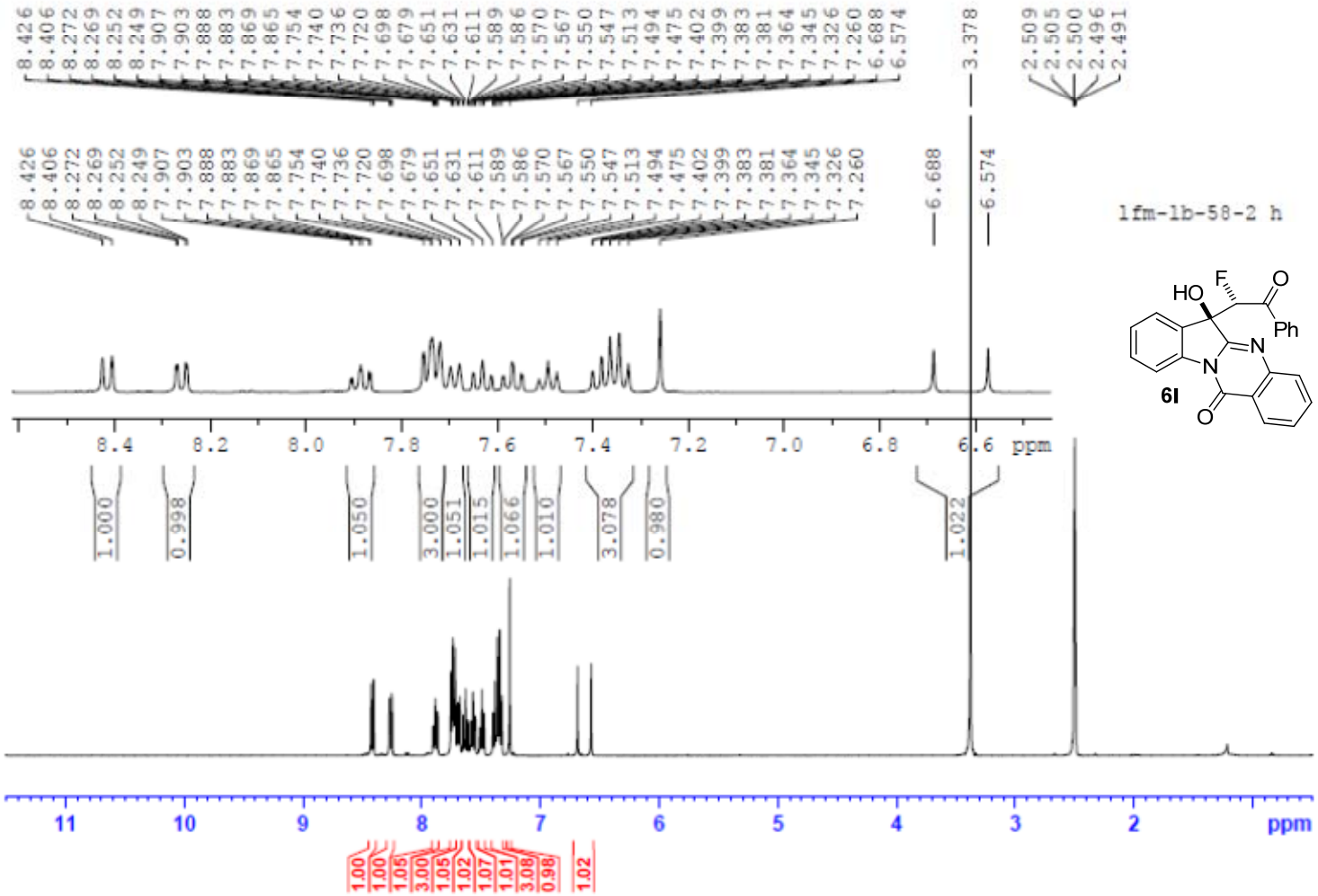

196.98
196.80
158.42
156.67
156.55
149.71
149.69
146.02
139.09
137.97
137.58
134.92
133.40
130.74
130.28
128.16
127.57
127.06
127.01
126.65
126.43
126.36
123.83
121.11
115.73
101.37
99.41
77.39
77.15
40.13
39.92
39.71
39.50
39.29
39.09
38.88
35.52
35.29
20.34
139.086
137.965
137.580
134.919
133.397
130.738
130.284
128.161
127.574
127.061
127.006
126.651
126.429
126.358
123.828
121.114
115.732
lfm-lb-56-1 c
Me
O
F
HO
N
N
O
6j
140
138
136
134
132
130
128
126
124
122
120
118
116
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

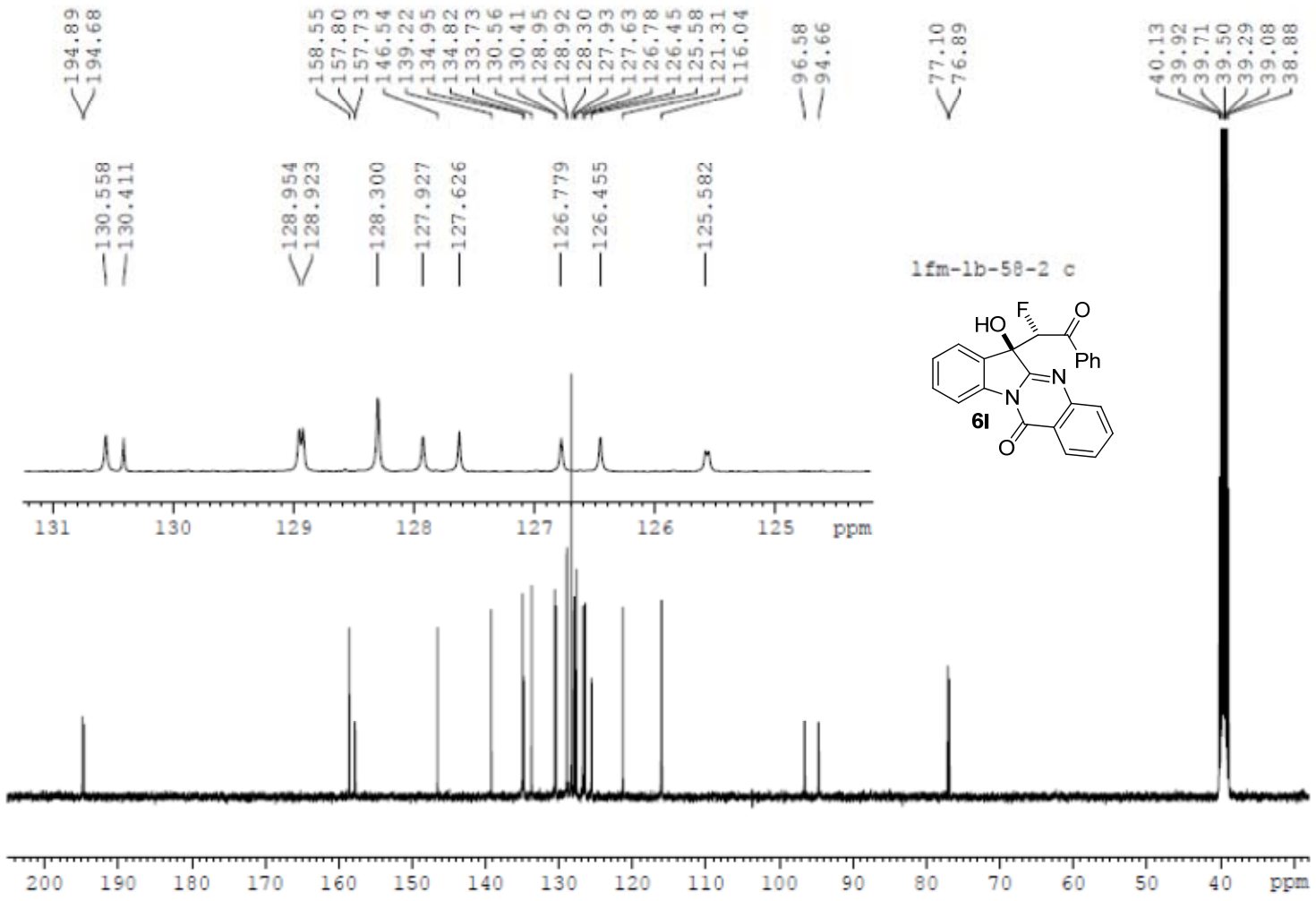

lfm-1b-56-1 f
-159.34
Me
O
F
HO
N
N
O
6j
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)

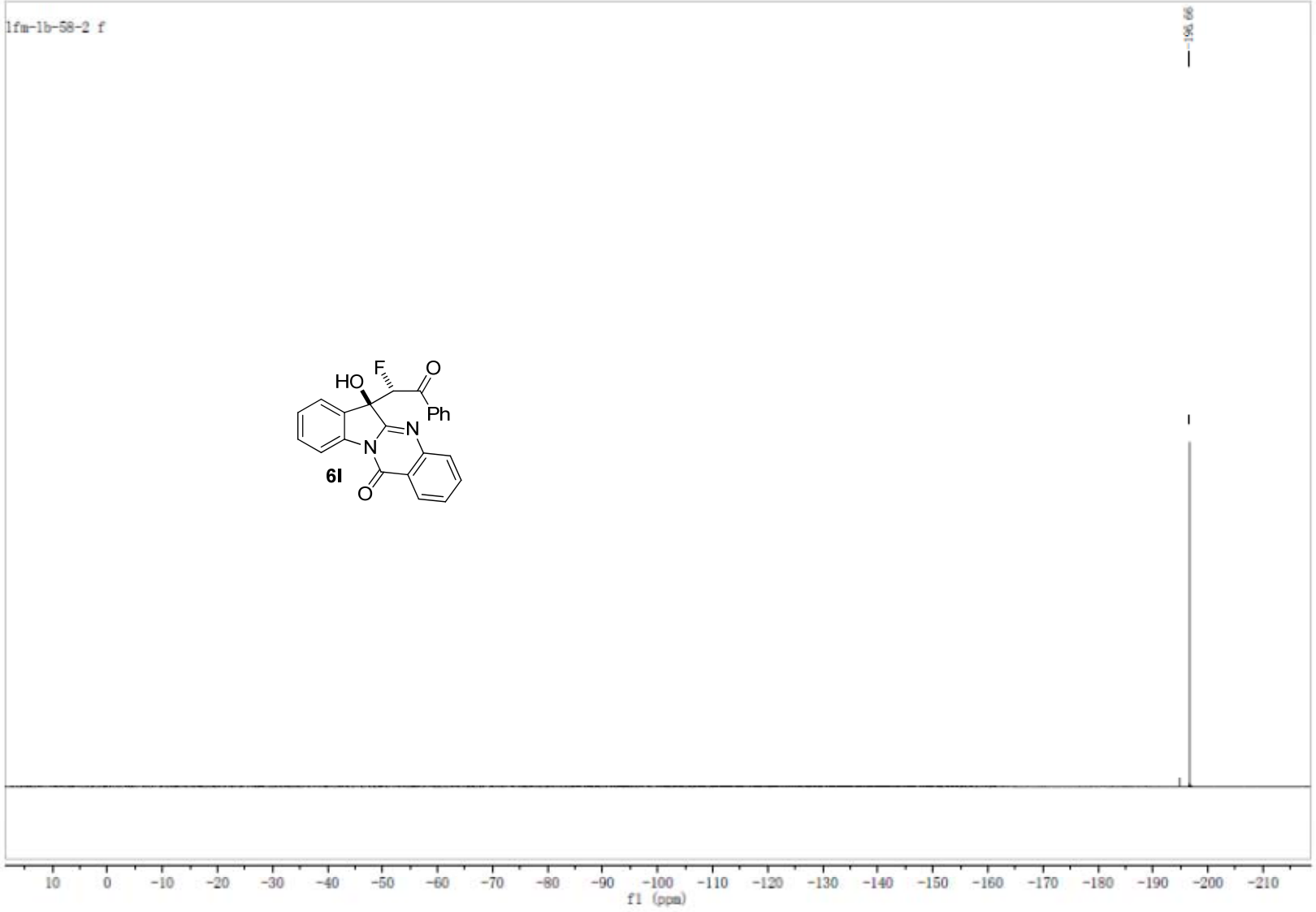

8.444
8.425
8.308
8.289
7.917
7.898
7.880
7.775
7.755
7.737
7.717
7.677
7.669
7.660
7.641
7.619
7.600
7.588
7.569
7.549
7.379
7.360
7.341
7.326
7.306
7.205
7.187
7.168
3.405
2.500
lfm-lc-16 h
HO
F
O
N
6k
ppm
1.000
0.994
1.062
2.161
3.006
1.020
1.044
1.088
0.963
1.014
1.00
0.99
1.06
2.16
3.01
1.02
1.04
1.09
0.96
1.01

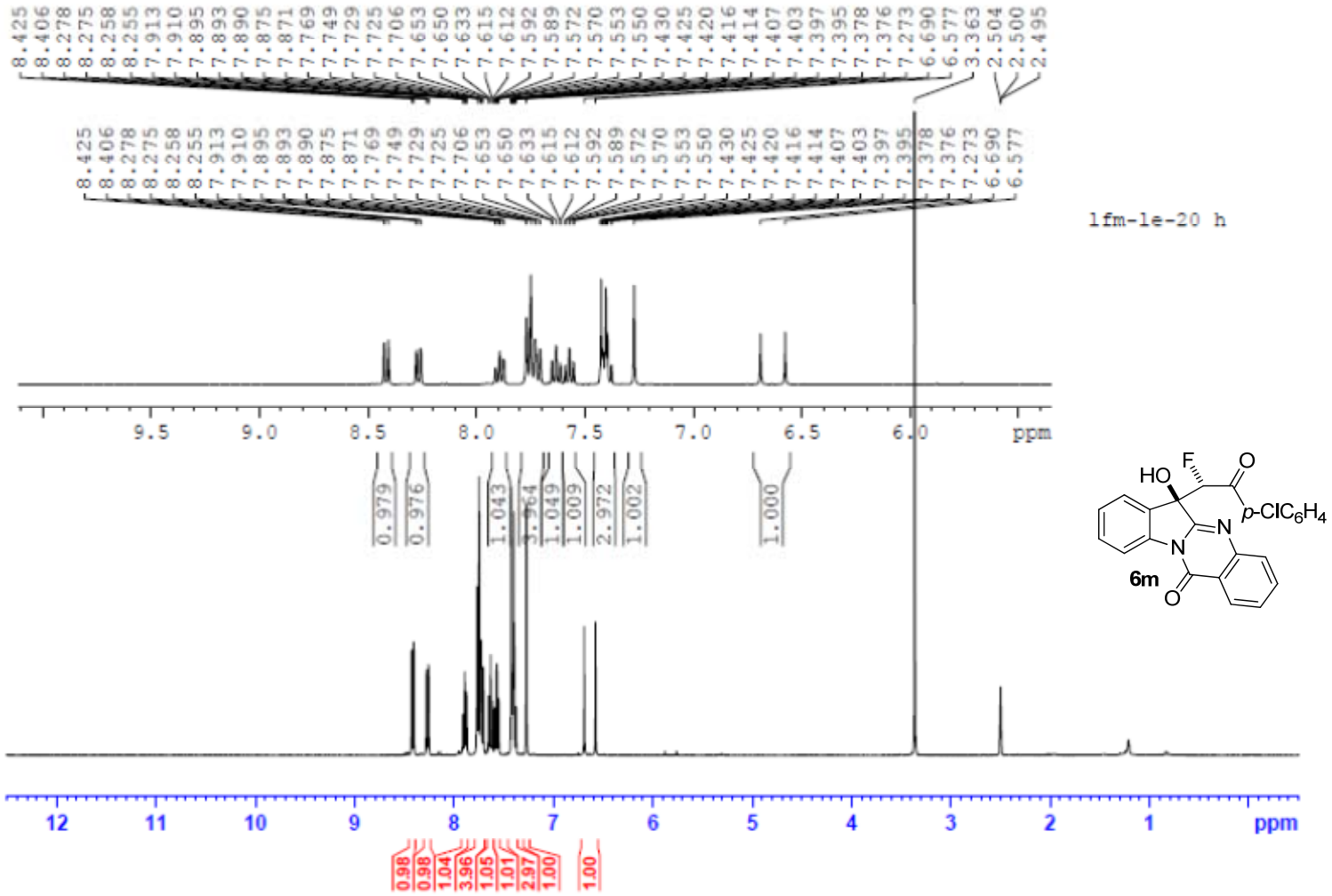

190.73
190.54
169.77
158.62
155.64
146.31
140.31
139.53
135.23
131.36
128.42
127.96
127.91
126.73
126.56
126.16
125.08
124.32
121.41
118.46
116.11
113.20
109.95
107.45
77.92
77.64
40.13
39.92
39.71
39.50
39.29
39.08
38.87
169.774
158.615
155.643
146.315
140.305
139.527
135.232
131.364
128.425
127.958
127.906
126.731
126.558
126.160
125.081
124.318
121.409
118.460
116.109
113.198
109.951
107.454
lfm-1c-16 c
HO
F
O
O
N
N
O
6k
170 165 160 155 150 145 140 135 130 125 120 115 110 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

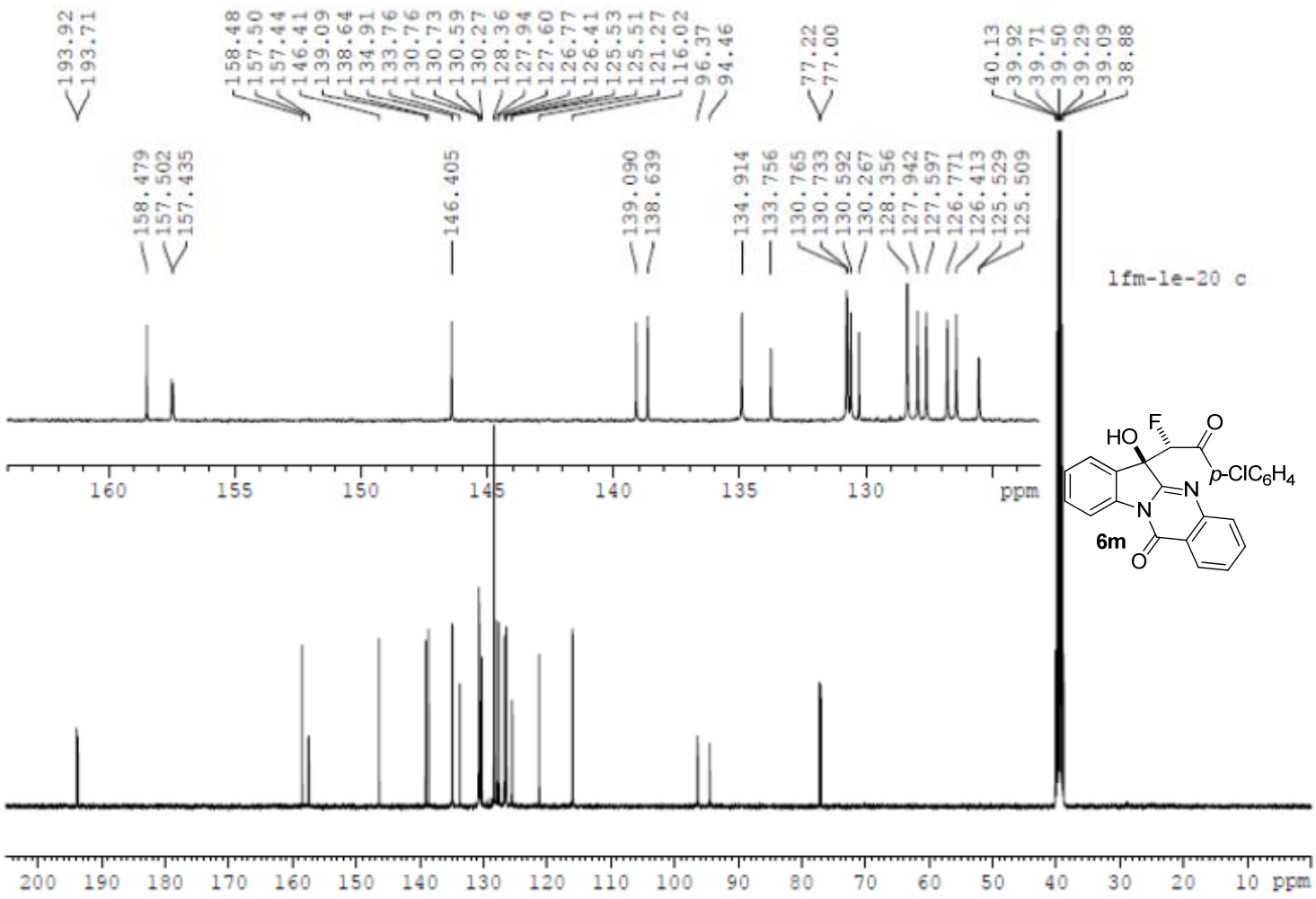

lfm-lc-16 f
-129.95
O
F
HO
O
N
N
O
6k
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175
f1 (ppm)

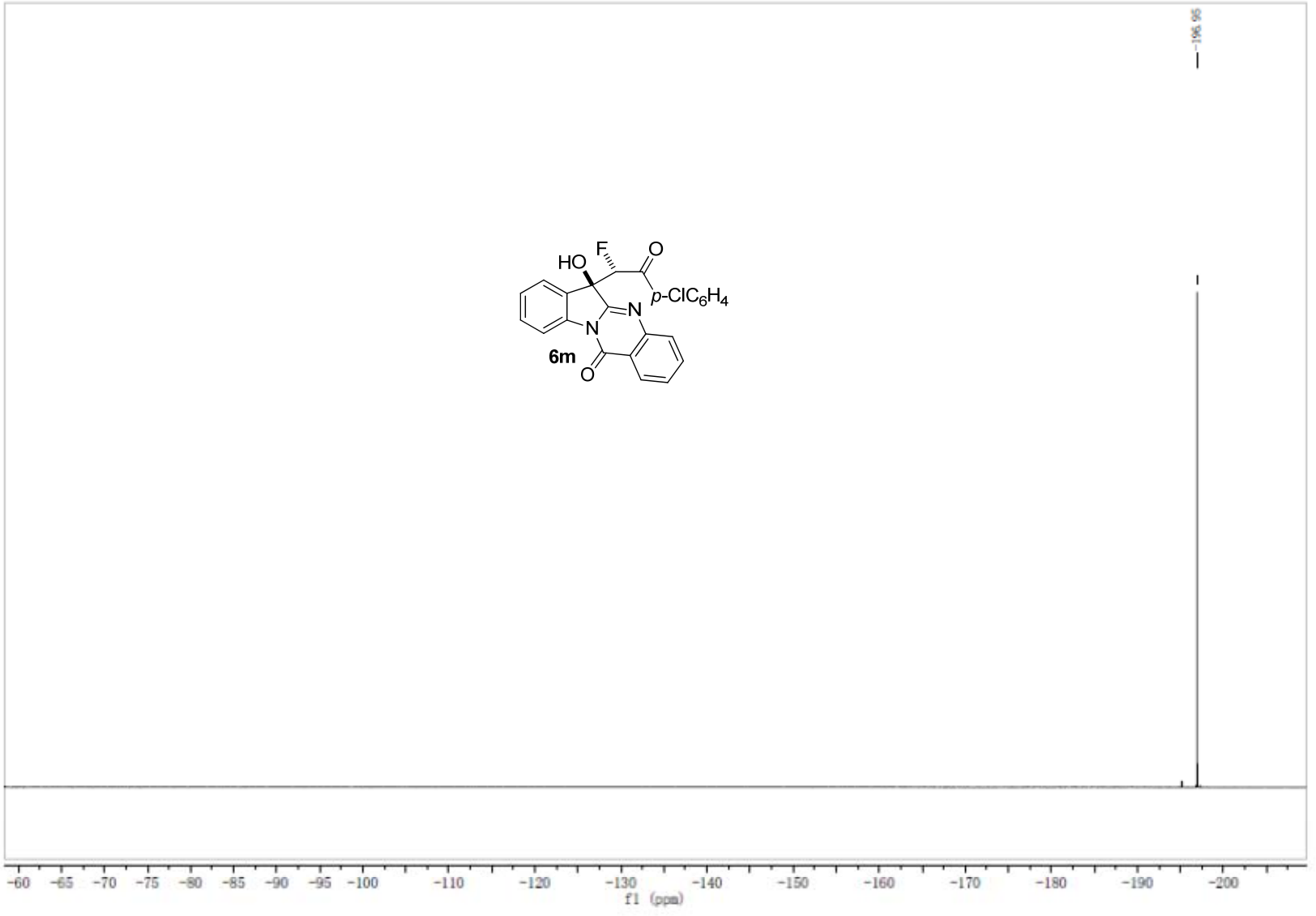

8.426
8.406
8.272
8.269
8.252
8.249
7.907
7.903
7.888
7.883
7.869
7.865
7.754
7.740
7.736
7.720
7.698
7.679
7.651
7.631
7.611
7.589
7.586
7.570
7.567
7.550
7.547
7.513
7.494
7.475
7.402
7.399
7.383
7.381
7.364
7.345
7.326
7.260
6.688
6.574
3.378
2.509
2.505
2.500
2.496
2.491
lfm-lb-58-2 h
HO
F
O
Ph
N
N
O
6l
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm
1.000
0.998
1.050
3.000
1.051
1.015
1.066
1.010
3.078
0.980
1.022
11
10
9
8
7
6
5
4
3
2
ppm
1.00
1.00
1.05
3.00
1.05
1.02
1.07
1.01
3.08
0.98
1.02

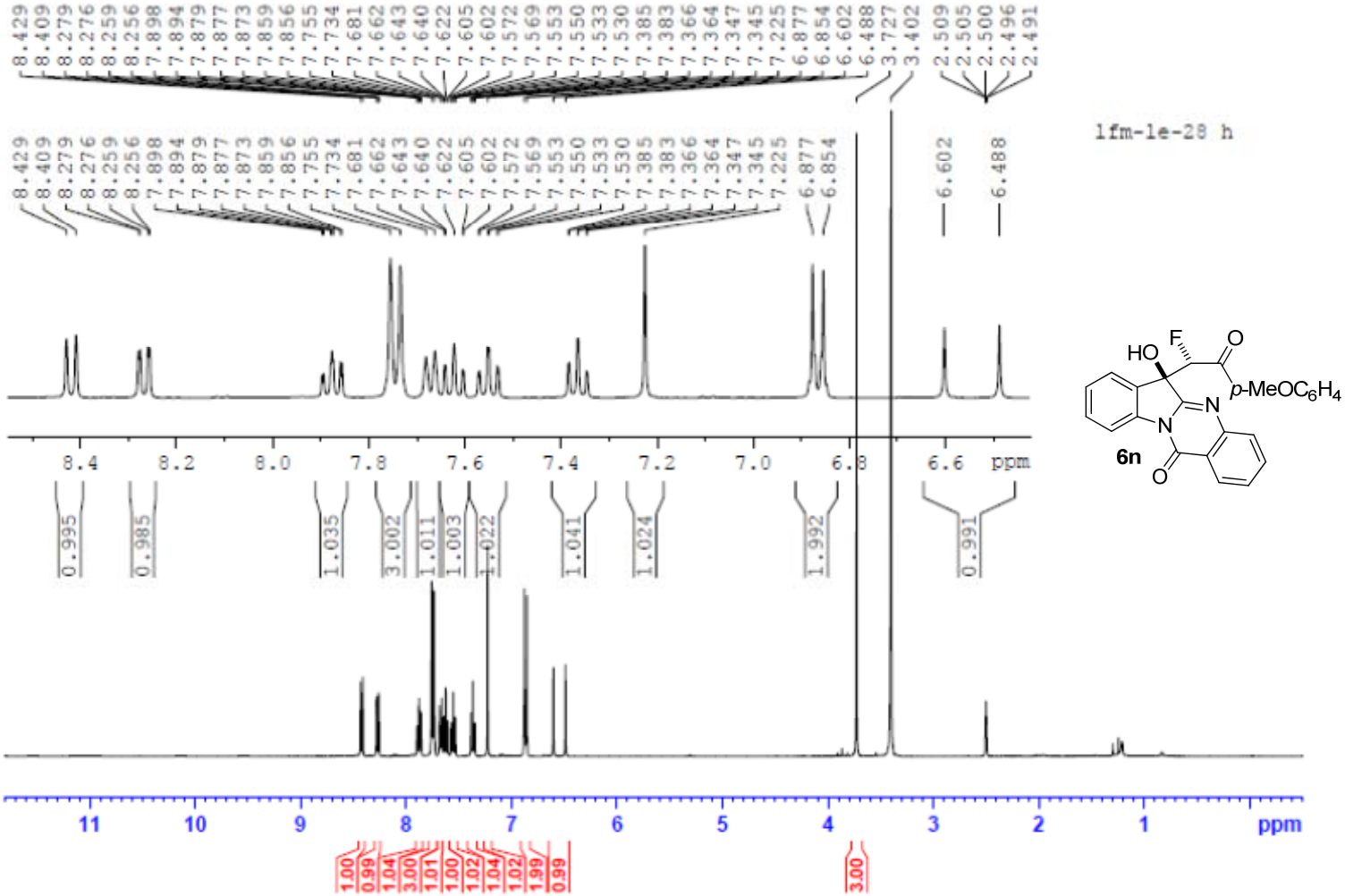

194.89
194.68
158.55
157.80
157.73
146.54
139.22
134.95
134.82
133.73
130.56
130.41
128.95
128.92
128.30
127.93
127.63
126.78
126.45
125.58
121.31
116.04
96.58
94.66
77.10
76.89
40.13
39.92
39.71
39.50
39.29
39.08
38.88
130.558
130.411
128.954
128.923
128.300
127.927
127.626
126.779
126.455
125.582
lfm-lb-58-2 c
HO
F
O
Ph
N
N
O
6l
131
130
129
128
127
126
125
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

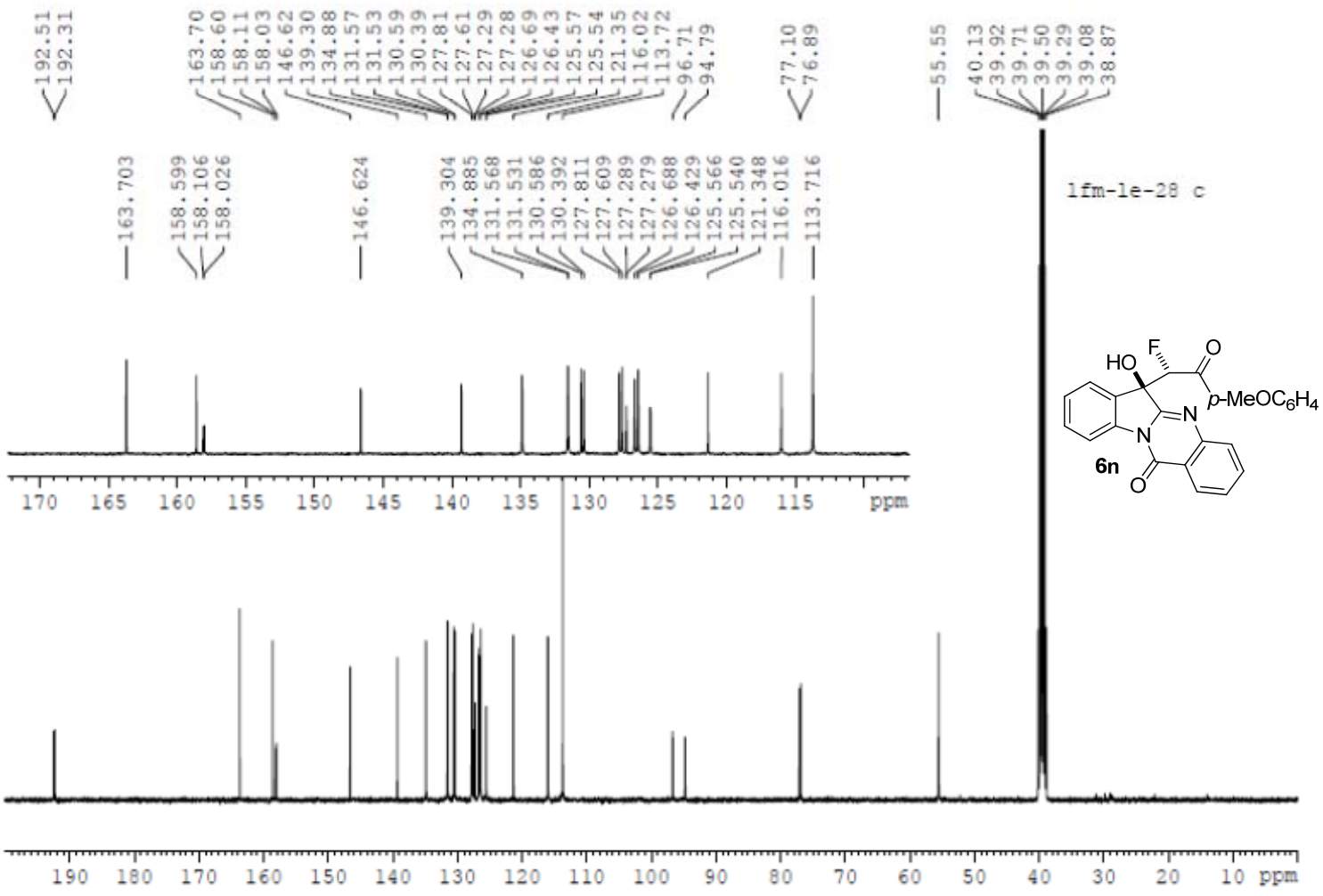

lfm-1b-58-2 f
-196.66
HO
F
O
Ph
N
N
O
6l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

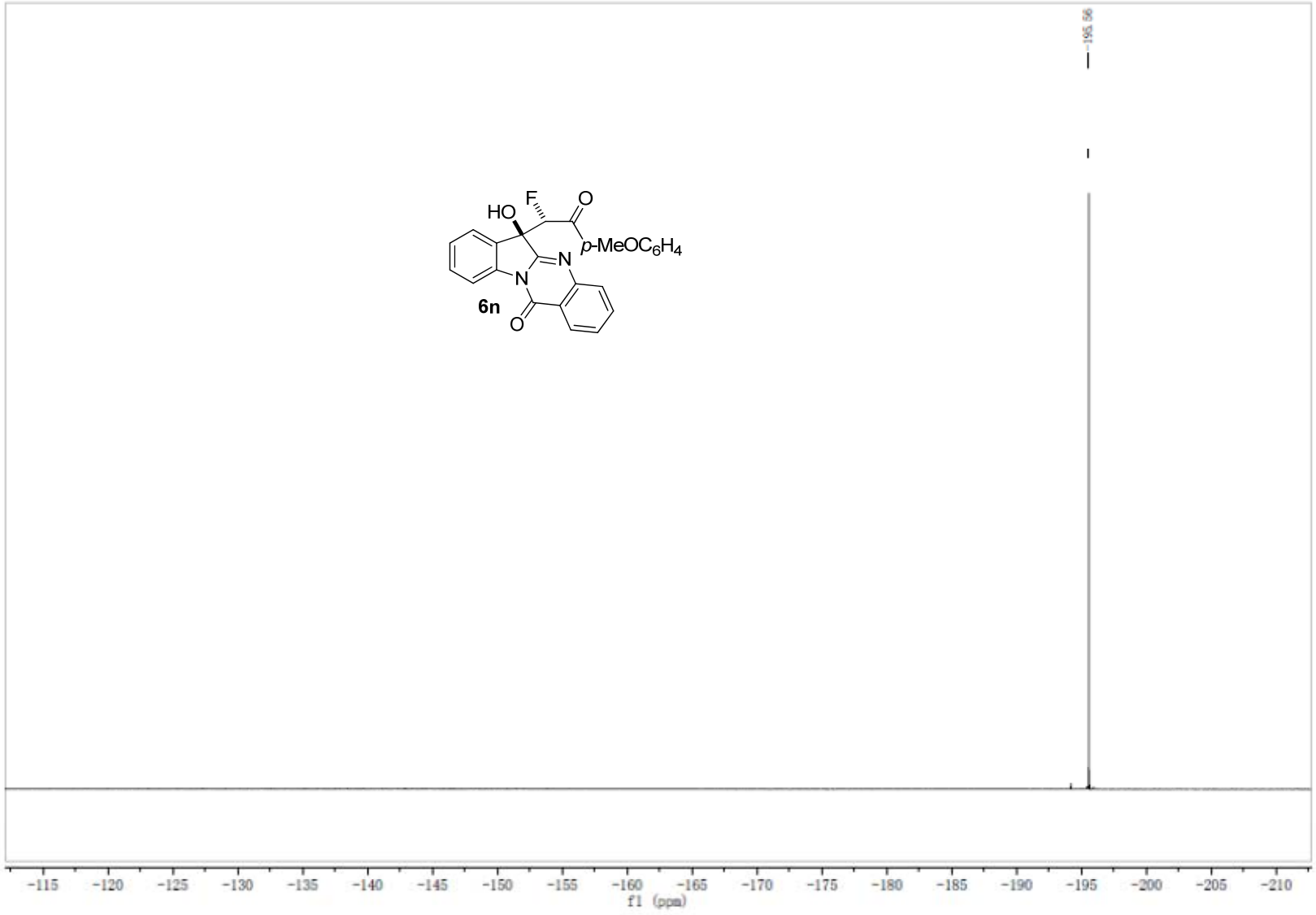

lfm-le-20 h
HO
F
O
p-ClC6H4
N
N
O
6m
ppm

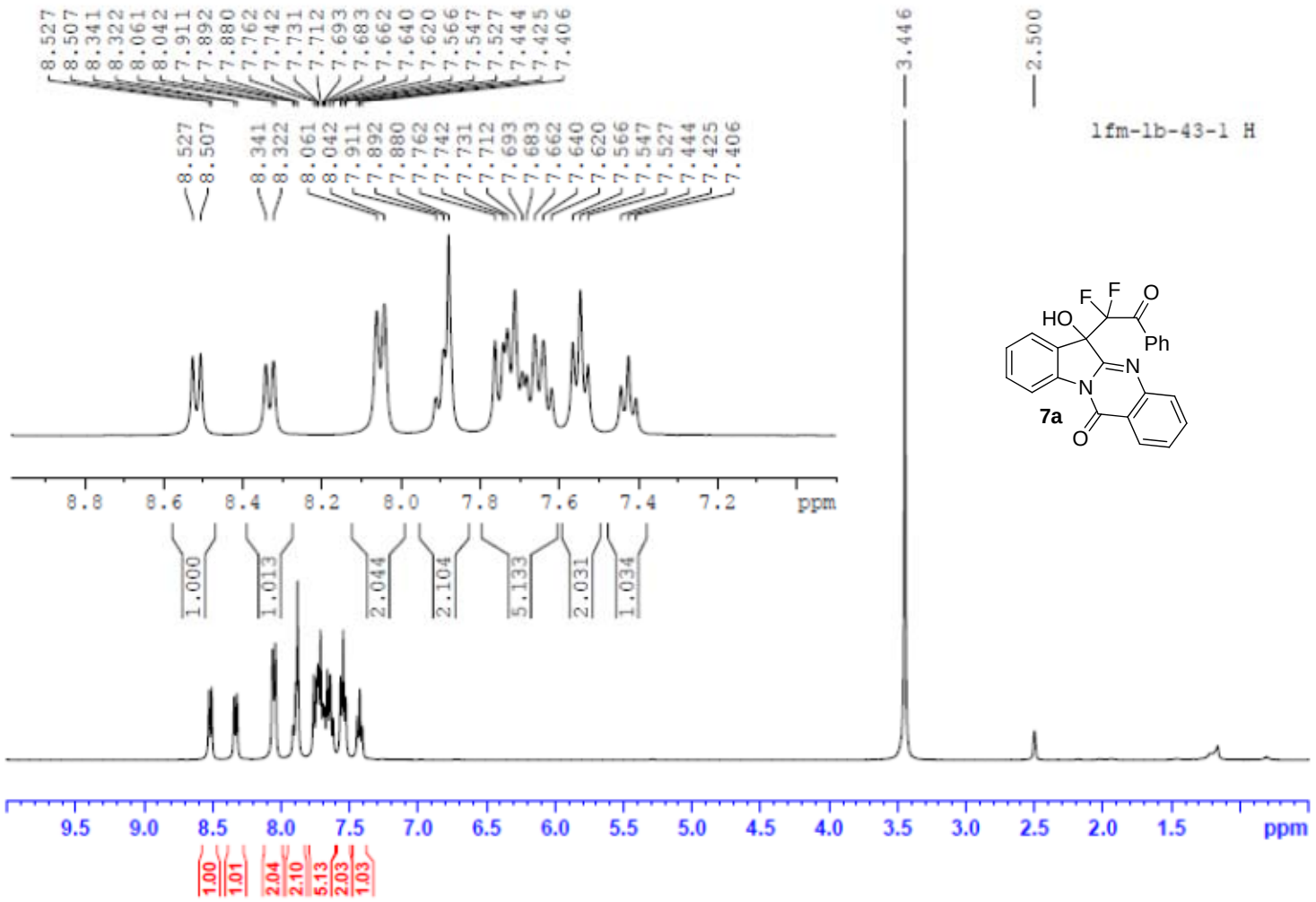

193.92
193.71
158.48
157.50
157.44
146.41
139.09
138.64
134.91
133.76
130.76
130.73
130.59
130.27
128.36
127.94
127.60
126.77
126.41
125.53
125.51
121.27
116.02
96.37
94.46
77.22
77.00
40.13
39.92
39.71
39.50
39.29
39.09
38.88
158.479
157.502
157.435
146.405
139.090
138.639
134.914
133.756
130.765
130.733
130.592
130.267
128.356
127.942
127.597
126.771
126.413
125.529
125.509
lfm-le-20 c
160
155
150
145
140
135
130
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm
HO
F
O
p-ClC6H4
N
N
O
6m

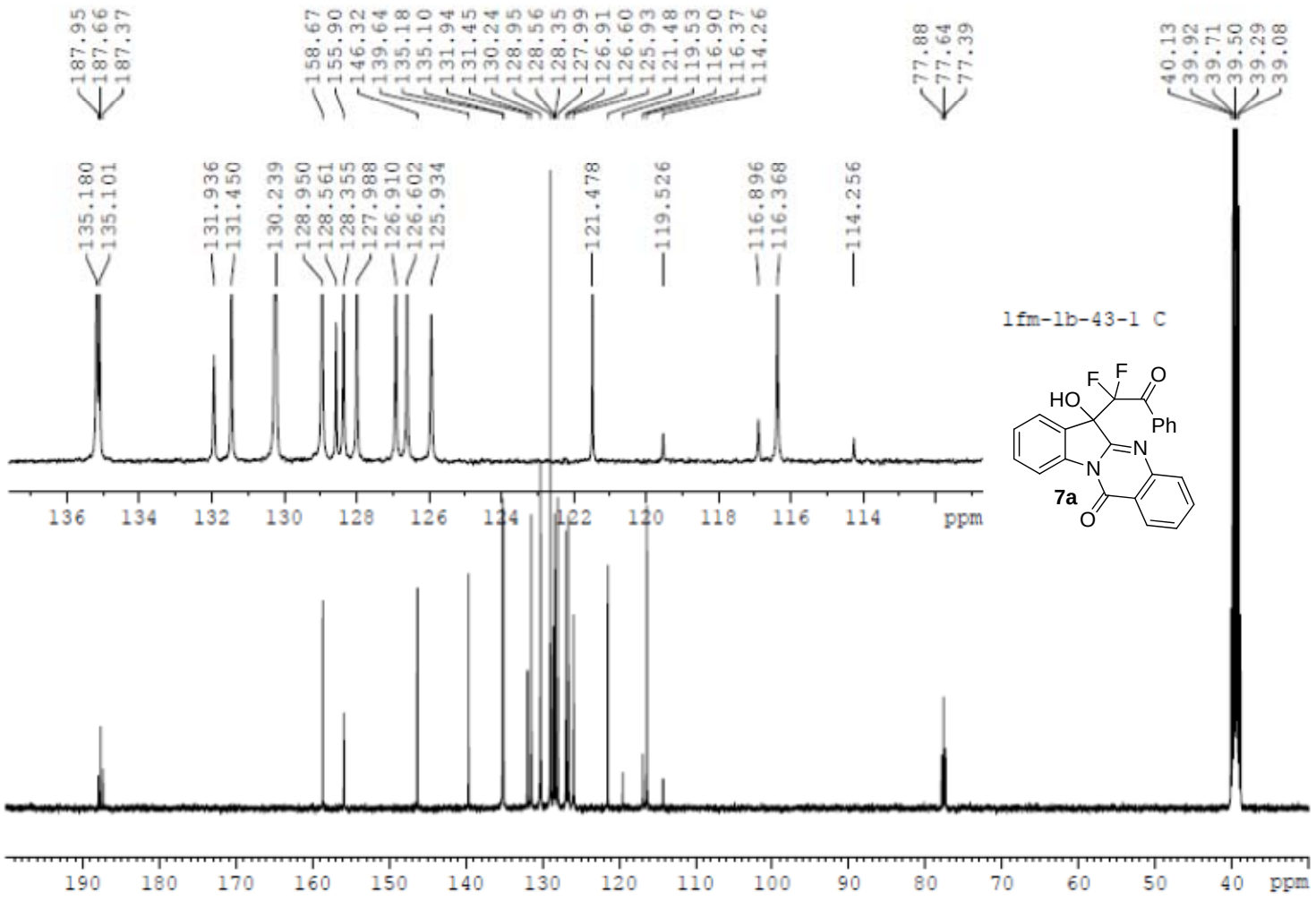

-196.95
HO
F
O
p-ClC6H4
N
N
O
6m
-60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

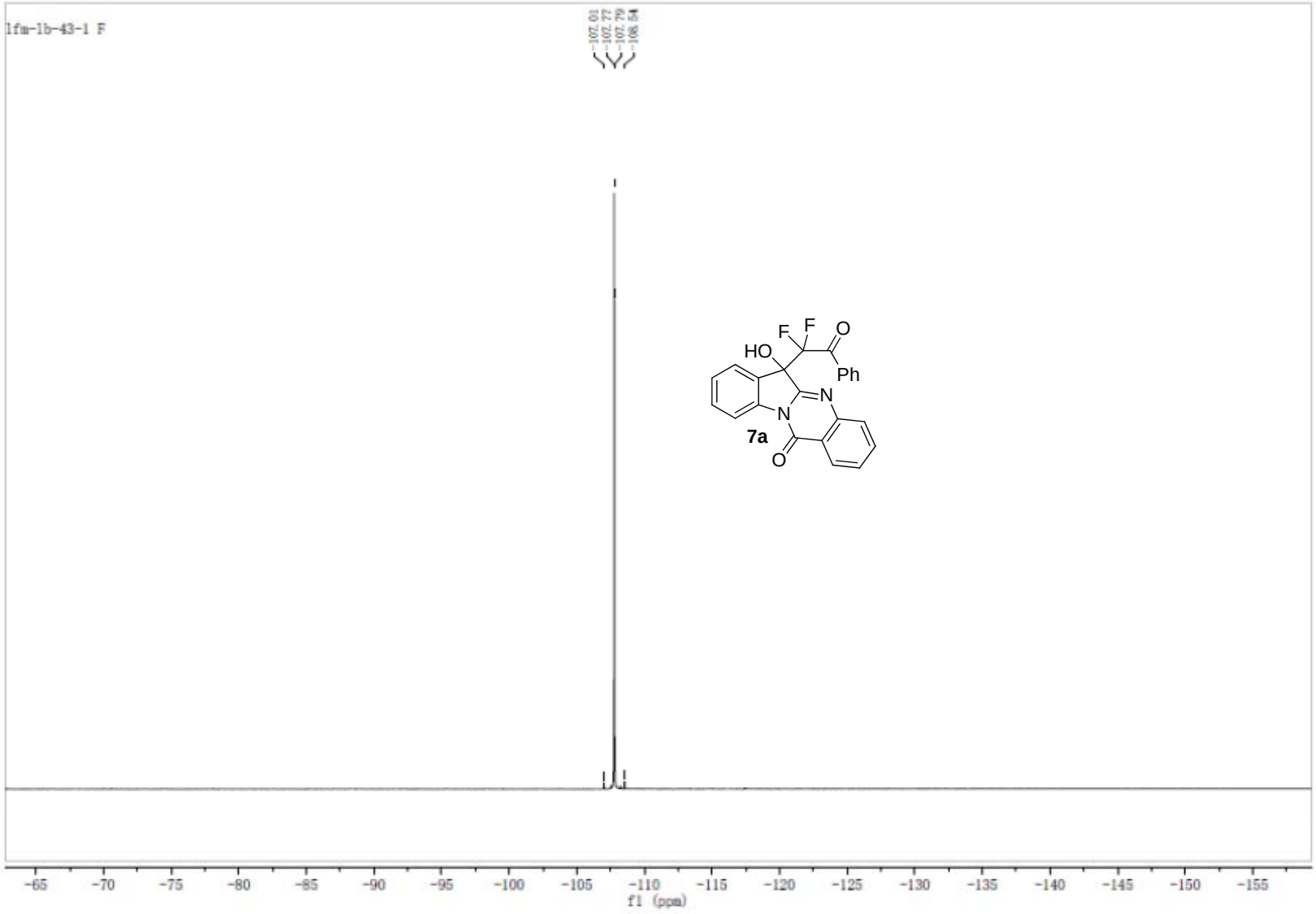

8.429 8.409 8.279 8.276 8.259 8.256 7.898 7.894 7.879 7.877 7.873 7.859 7.856 7.755 7.734 7.681 7.662 7.643 7.640 7.622 7.605 7.602 7.572 7.569 7.553 7.550 7.533 7.530 7.385 7.383 7.366 7.364 7.347 7.345 7.225 6.877 6.854 6.602 6.488 3.727 3.402 2.509 2.505 2.500 2.496 2.491
1fm-1e-28 h
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 ppm
0.995 0.985 1.035 3.002 1.011 1.003 1.022 1.041 1.024 1.992 0.991
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 0.99 1.04 3.00 1.01 1.00 1.02 1.04 1.02 1.99 0.99 3.00
HO F O p-MeOC6H4 N N O
6n

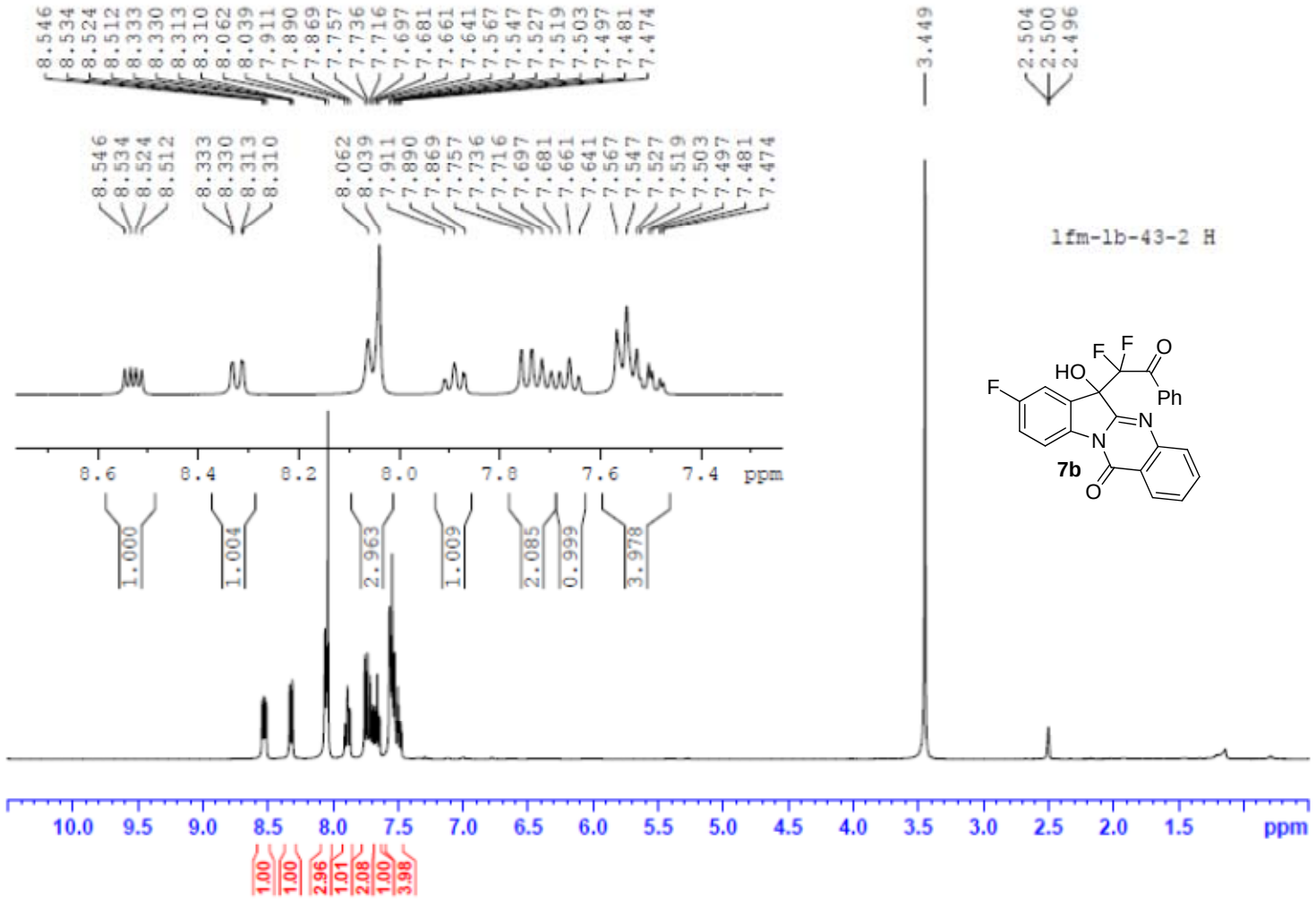

192.51
192.31
163.70
158.60
158.11
158.03
146.62
139.30
134.88
131.57
131.53
130.59
130.39
127.81
127.61
127.29
127.28
126.69
126.43
125.57
125.54
121.35
116.02
113.72
96.71
94.79
77.10
76.89
55.55
40.13
39.92
39.71
39.50
39.29
39.08
38.87
163.703
158.599
158.106
158.026
146.624
139.304
134.885
131.568
131.531
130.586
130.392
127.811
127.609
127.289
127.279
126.688
126.429
125.566
125.540
121.348
116.016
113.716
lfm-le-28 c
170 165 160 155 150 145 140 135 130 125 120 115 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
HO
F
O
N
N
O
p-MeOC6H4
6n

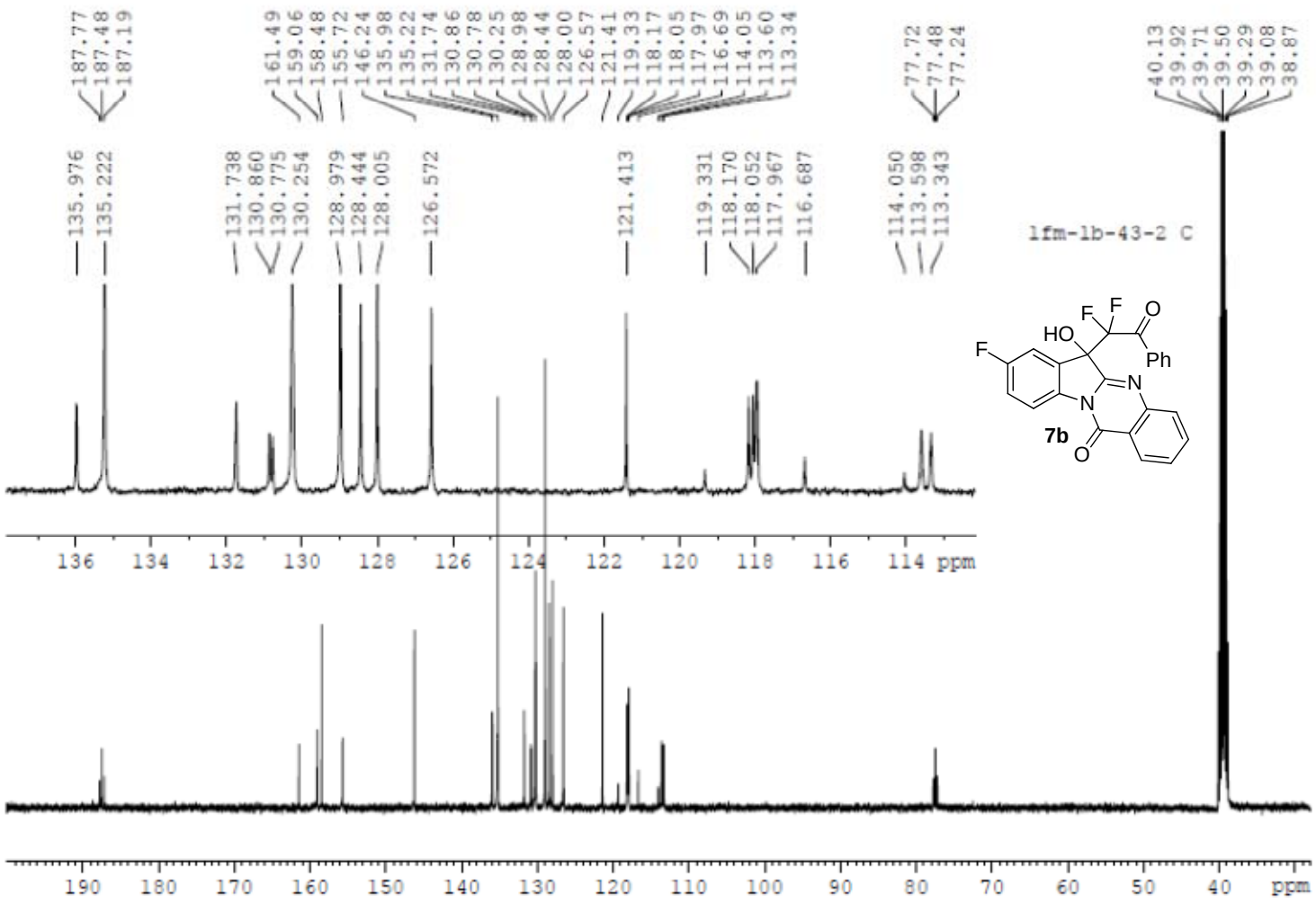

HO
F
O
p-MeOC6H4
N
N
O
6n
-193.56
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
-205
-210
f1 (ppm)

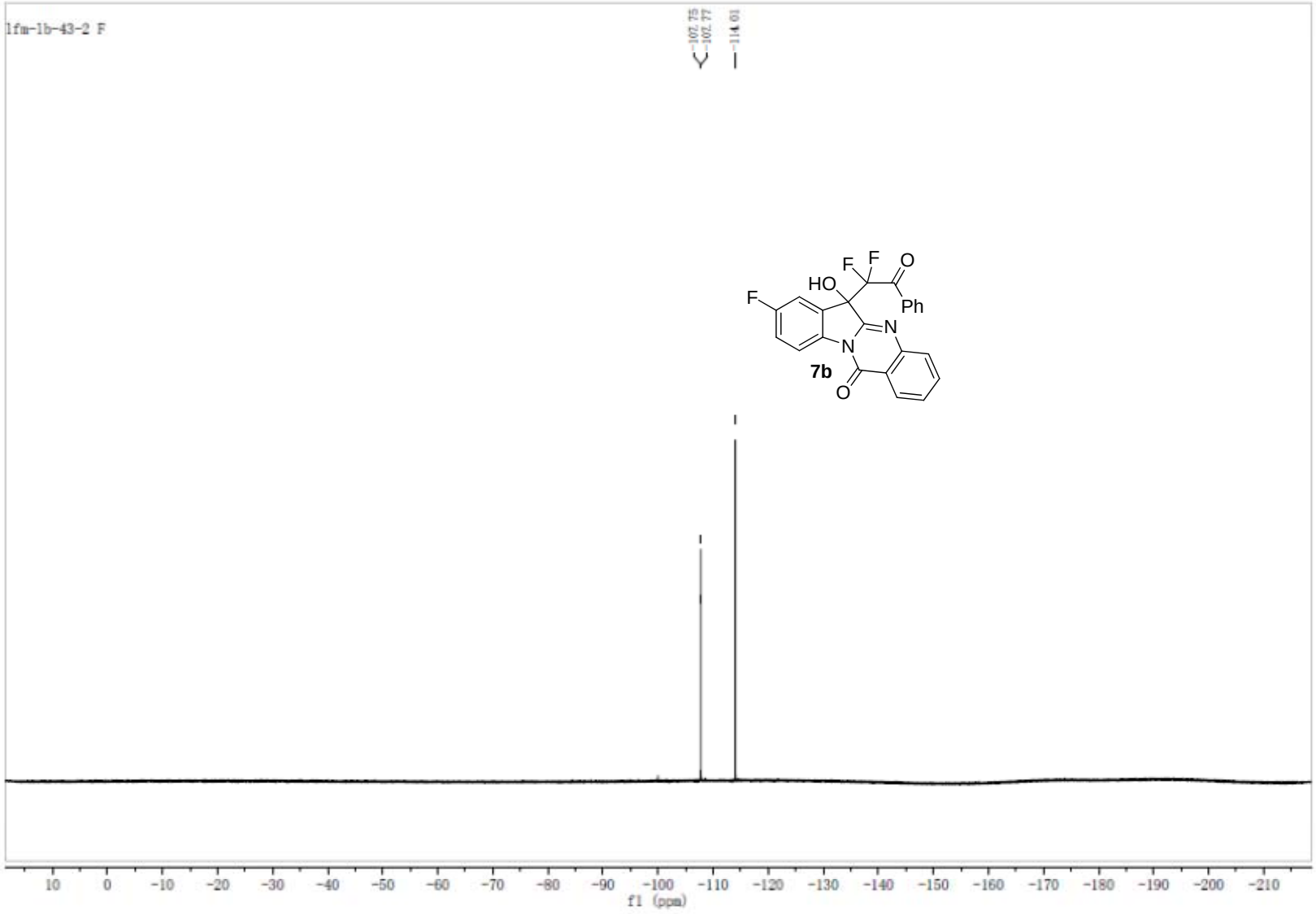

8.527
8.507
8.341
8.322
8.061
8.042
7.911
7.892
7.880
7.762
7.742
7.731
7.712
7.693
7.683
7.662
7.640
7.620
7.566
7.547
7.527
7.444
7.425
7.406
3.446
2.500
lfm-lb-43-1 H
F
F
O
HO
Ph
N
N
O
7a
ppm
1.000
1.013
2.044
2.104
5.133
2.031
1.034
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.01
2.04
2.10
5.13
2.03
1.03

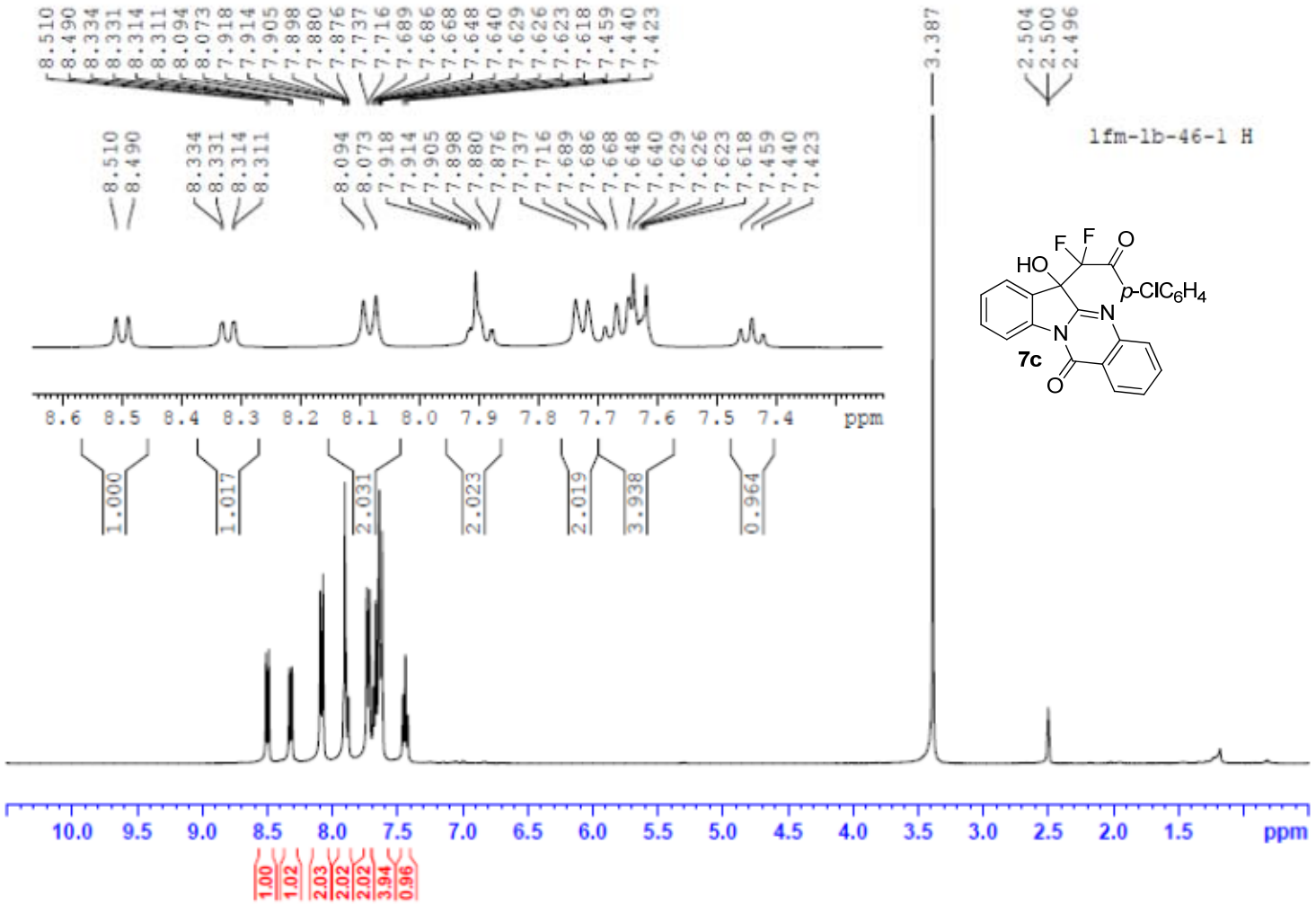

187.95
187.66
187.37
158.67
155.90
146.32
139.64
135.18
135.10
131.94
131.45
130.24
128.95
128.56
128.35
127.99
126.91
126.60
125.93
121.48
119.53
116.90
116.37
114.26
77.88
77.64
77.39
40.13
39.92
39.71
39.50
39.29
39.08
135.180
135.101
131.936
131.450
130.239
128.950
128.561
128.355
127.988
126.910
126.602
125.934
121.478
119.526
116.896
116.368
114.256
lfm-1b-43-1 C
F
F
O
HO
Ph
N
N
O
7a
136
134
132
130
128
126
124
122
120
118
116
114
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

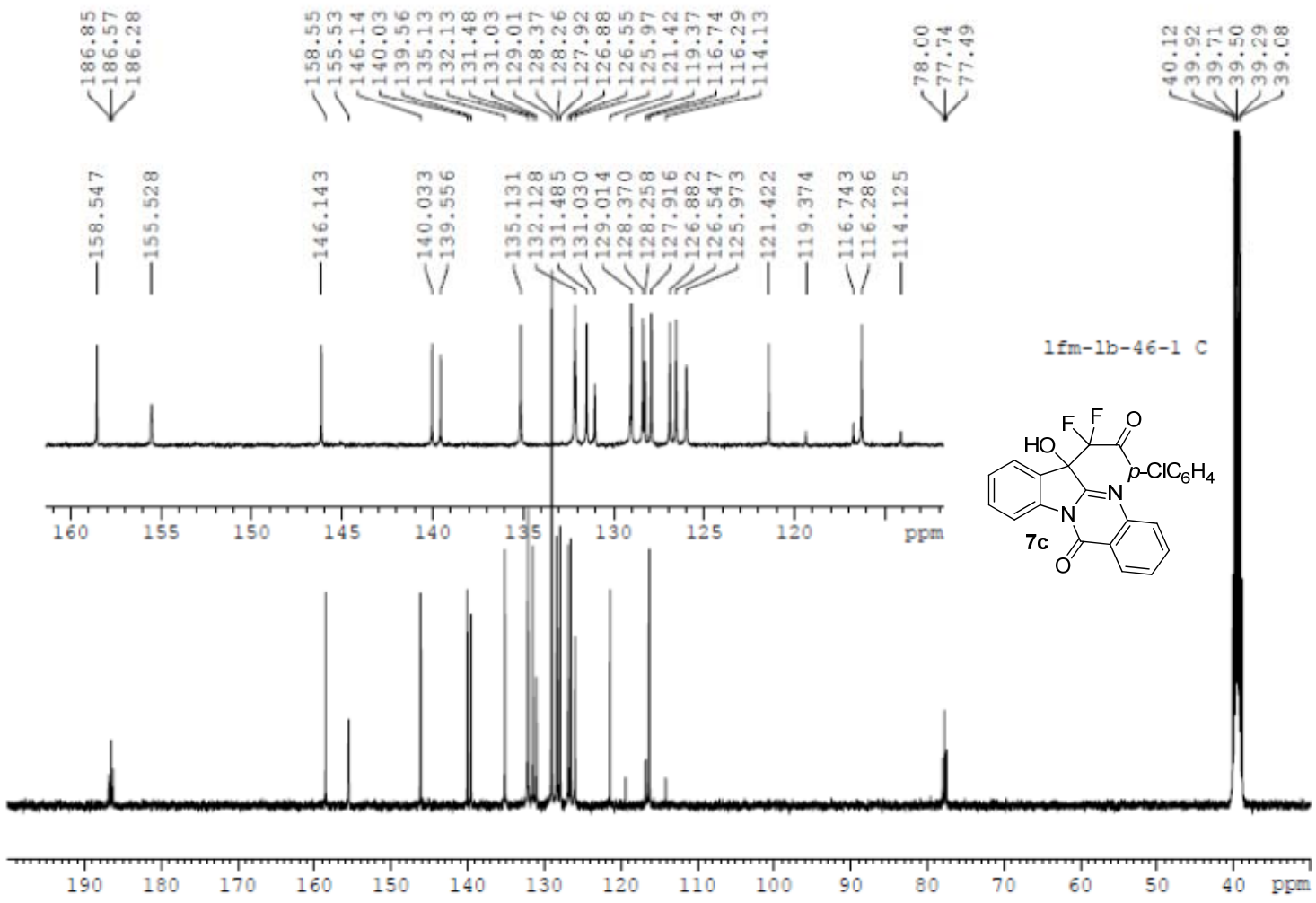

lfm-lb-43-1 F
-107.01
-107.72
-107.79
-108.54
F
F
O
HO
Ph
N
N
7a
O
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

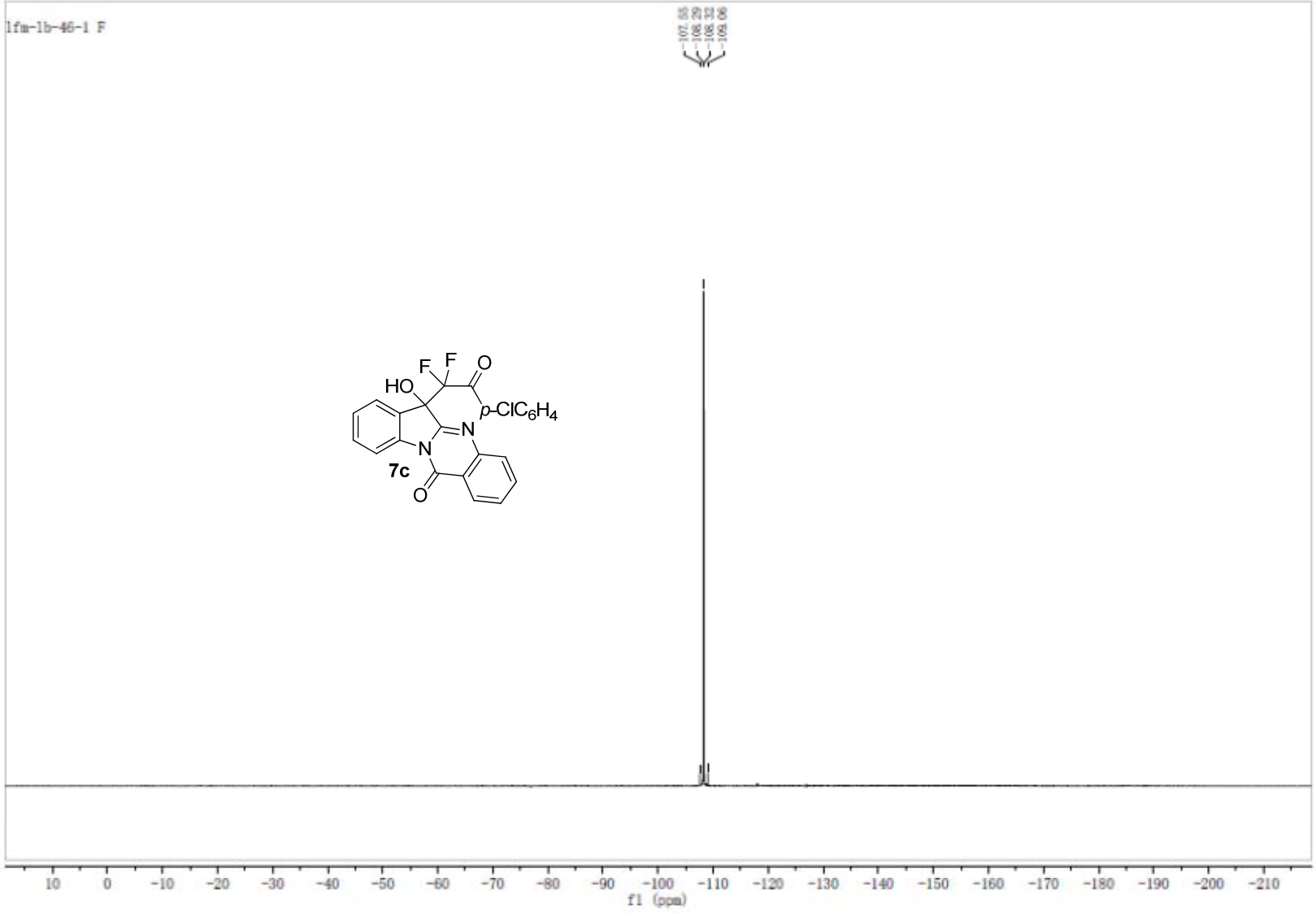

8.546
8.534
8.524
8.512
8.333
8.330
8.313
8.310
8.062
8.039
7.911
7.890
7.869
7.757
7.736
7.716
7.697
7.681
7.661
7.641
7.567
7.547
7.527
7.519
7.503
7.497
7.481
7.474
3.449
2.504
2.500
2.496
lfm-lb-43-2 H
HO
F
F
O
Ph
F
N
N
O
7b
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
1.000
1.004
2.963
1.009
2.085
0.999
3.978
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
ppm
1.00
1.00
2.96
1.01
2.08
1.00
3.98

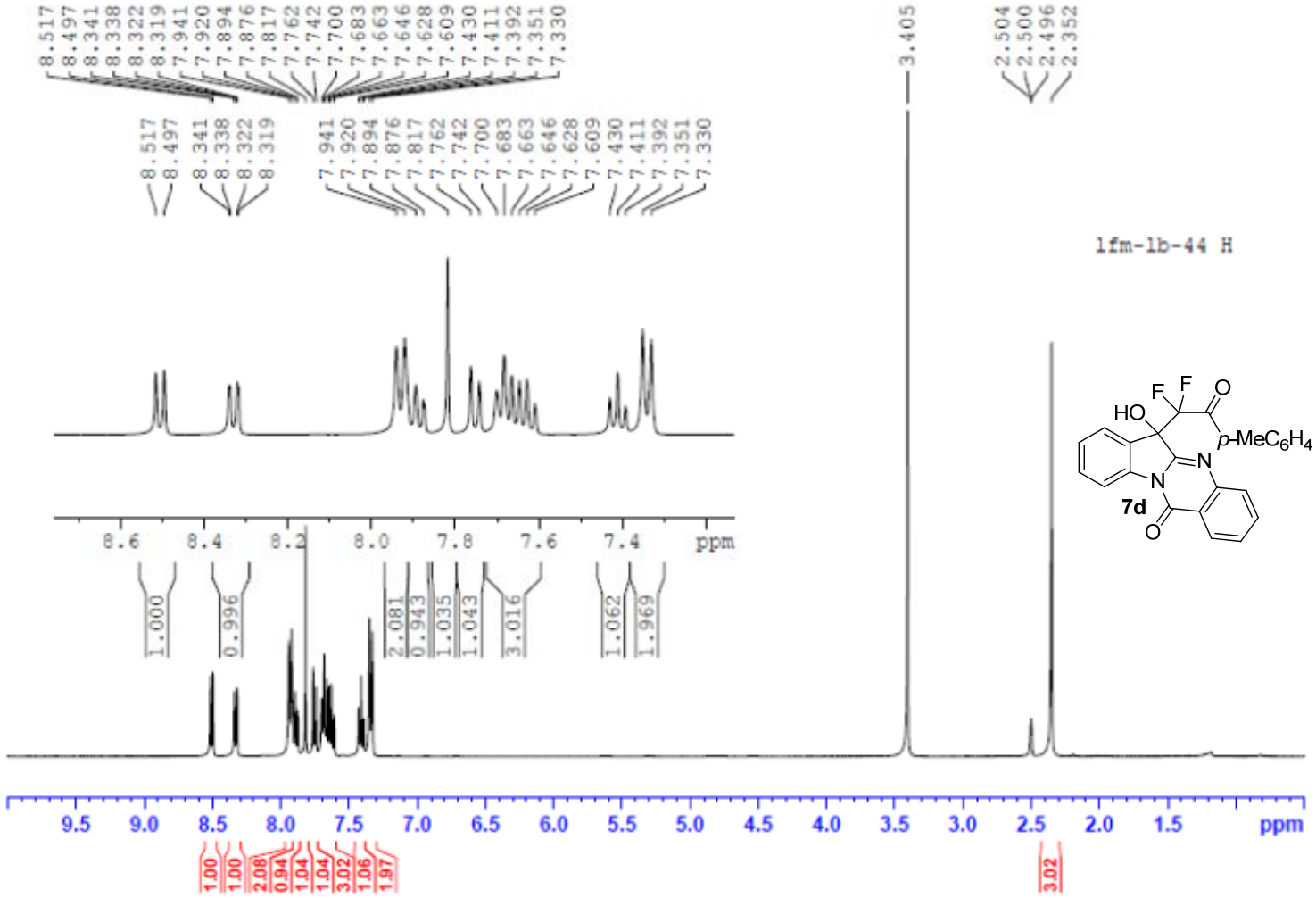

187.77
187.48
187.19
161.49
159.06
158.48
155.72
146.24
135.98
135.22
131.74
130.86
130.78
130.25
128.98
128.44
128.00
126.57
121.41
119.33
118.17
118.05
117.97
116.69
114.05
113.60
113.34
77.72
77.48
77.24
40.13
39.92
39.71
39.50
39.29
39.08
38.87
135.976
135.222
131.738
130.860
130.775
130.254
128.979
128.444
128.005
126.572
121.413
119.331
118.170
118.052
117.967
116.687
114.050
113.598
113.343
lfm-lb-43-2 C
F
F
O
HO
Ph
F
N
N
O
7b
136
134
132
130
128
126
124
122
120
118
116
114 ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

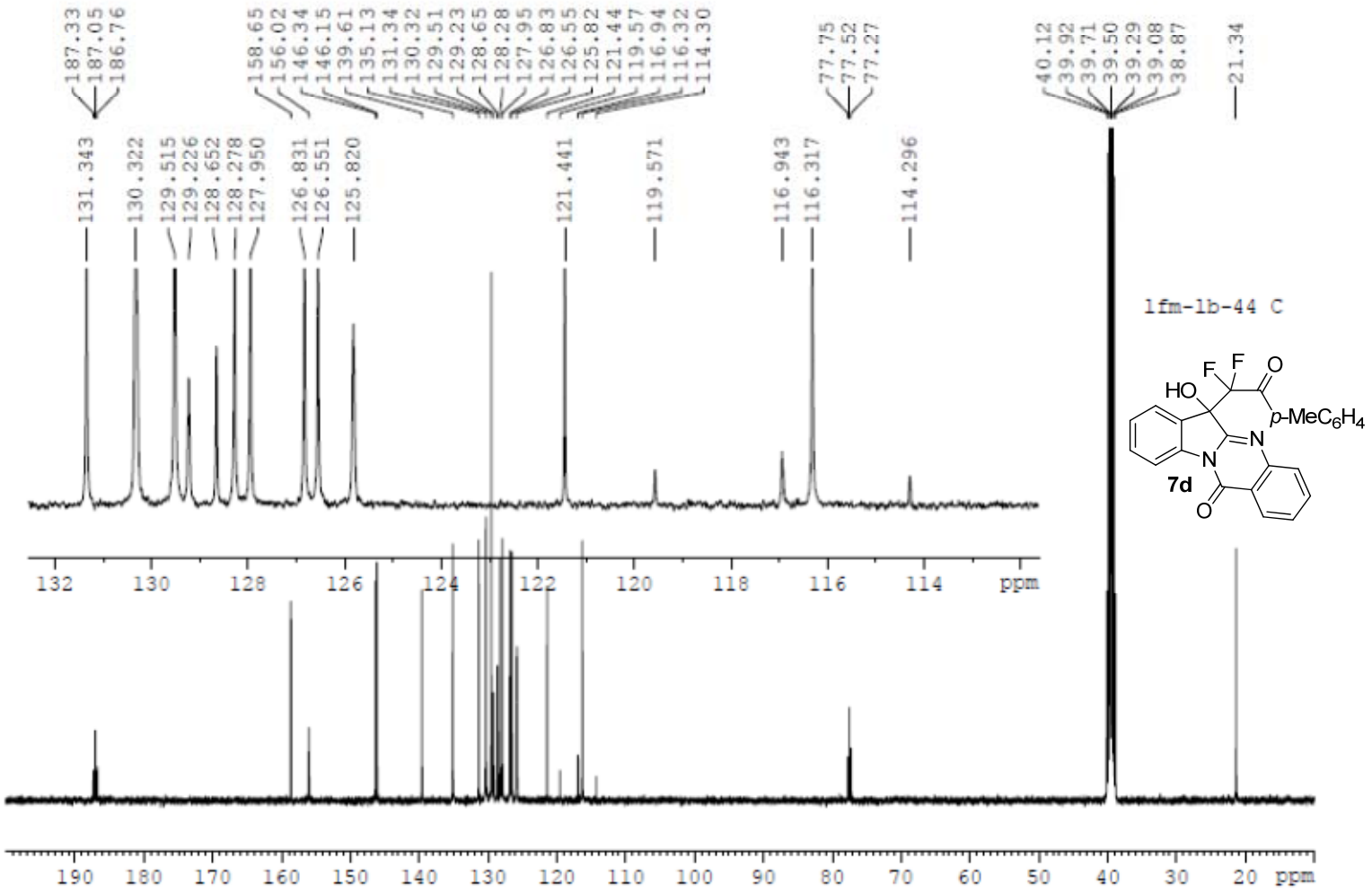

lfm-lb-43-2 F
-107.75
-107.77
-114.61
F
F
O
HO
Ph
F
N
N
O
7b
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

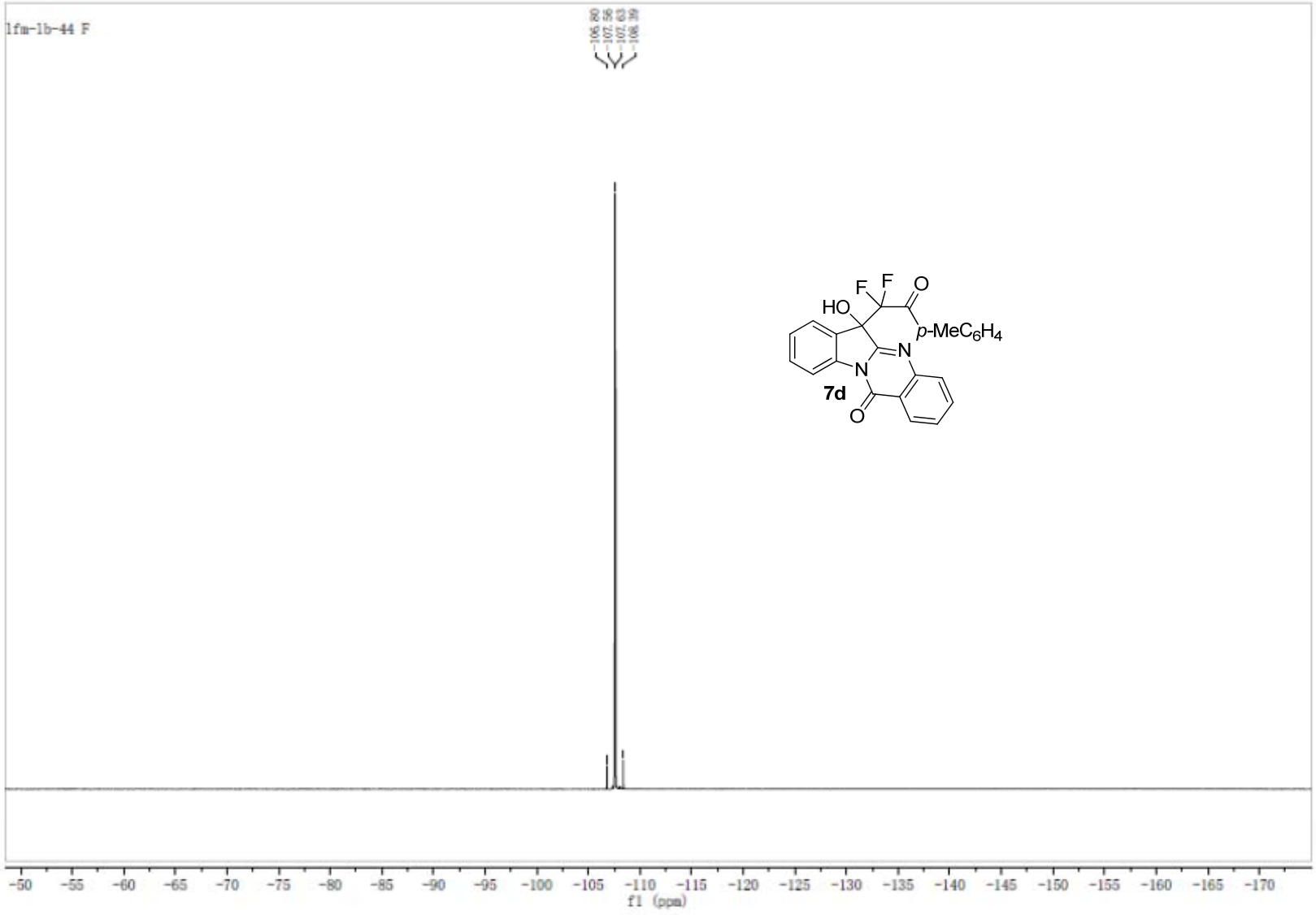

8.510
8.490
8.334
8.331
8.314
8.311
8.094
8.073
7.918
7.914
7.905
7.898
7.880
7.876
7.737
7.716
7.689
7.686
7.668
7.648
7.640
7.629
7.626
7.623
7.618
7.459
7.440
7.423
3.387
2.504
2.500
2.496
lfm-lb-46-1 H
F
F
O
HO
p-ClC6H4
N
N
O
7c
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
1.000
1.017
2.031
2.023
2.019
3.938
0.964
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 ppm
1.00
1.02
2.03
2.02
2.02
3.94
0.96

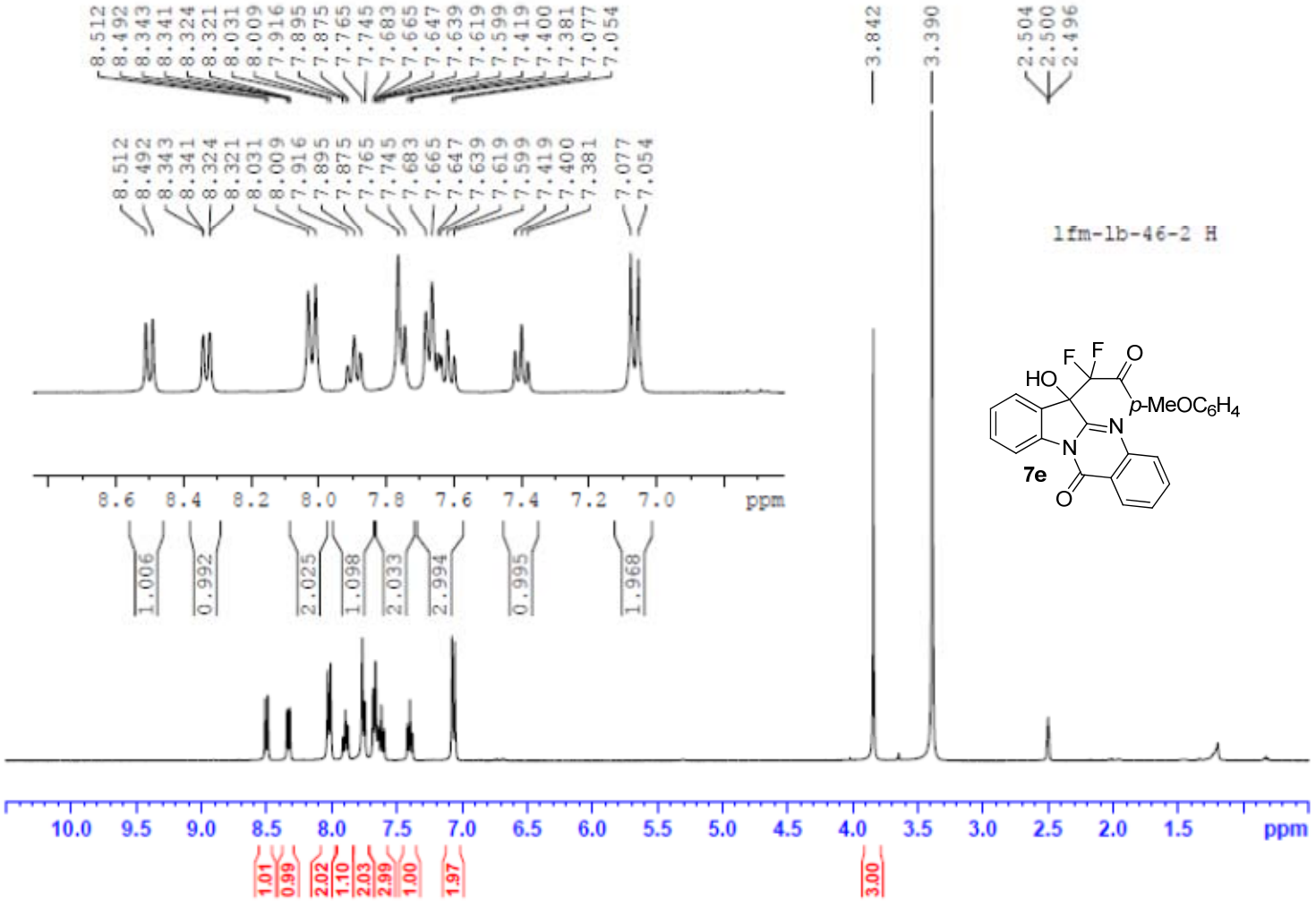

186.85
186.57
186.28
158.55
155.53
146.14
140.03
139.56
135.13
132.13
131.48
131.03
129.01
128.37
128.26
127.92
126.88
126.55
125.97
121.42
119.37
116.74
116.29
114.13
78.00
77.74
77.49
40.12
39.92
39.71
39.50
39.29
39.08
158.547
155.528
146.143
140.033
139.556
135.131
132.128
131.485
131.030
129.014
128.370
128.258
127.916
126.882
126.547
125.973
121.422
119.374
116.743
116.286
114.125
160
155
150
145
140
135
130
125
120
ppm
lfm-1b-46-1 C
F
F
O
HO
p-ClC6H4
N
N
O
7c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

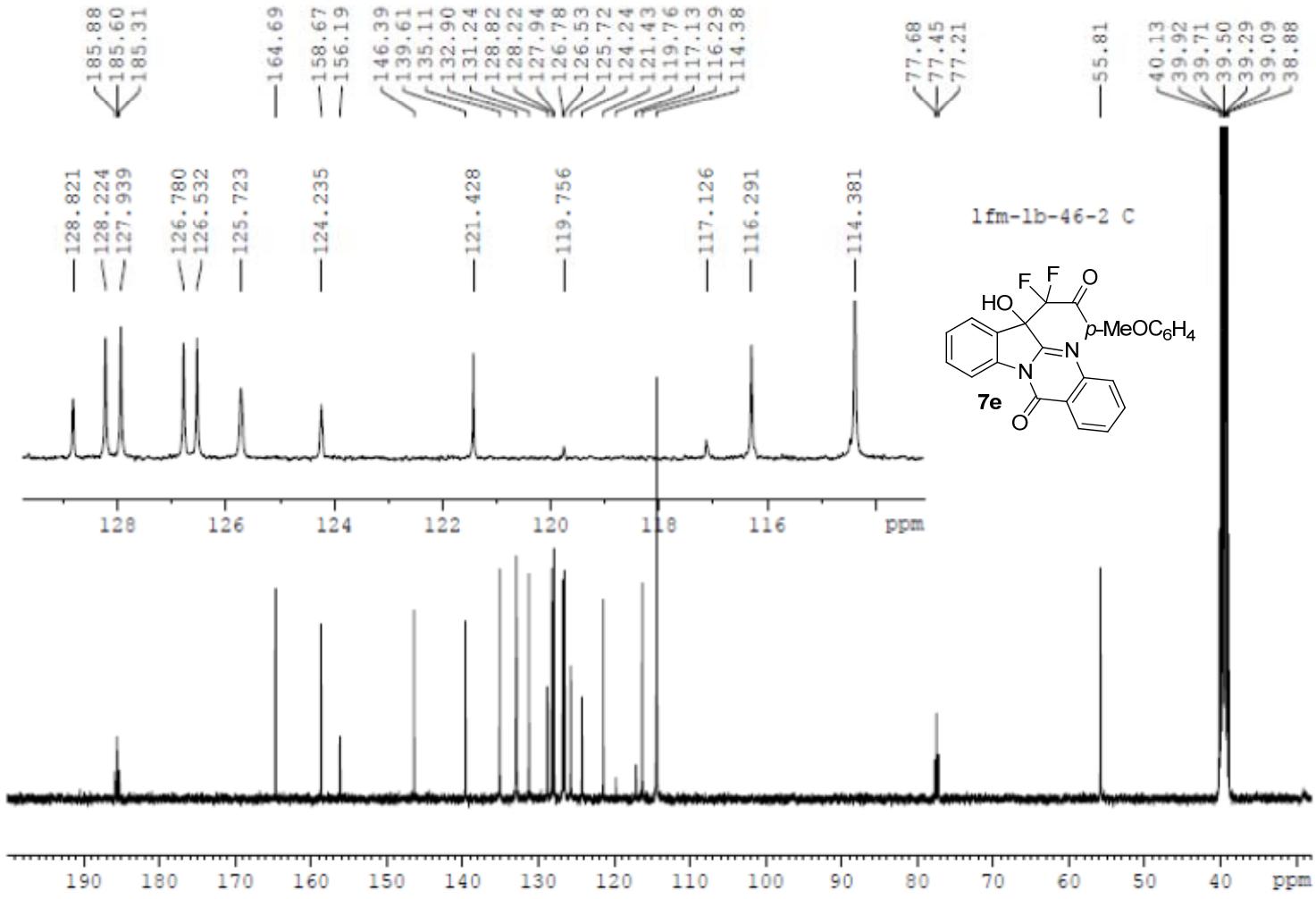

lfm-lb-46-1 F
-107.55
-108.29
-108.32
-109.06
F
F
O
HO
p-ClC6H4
N
N
O
7c
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

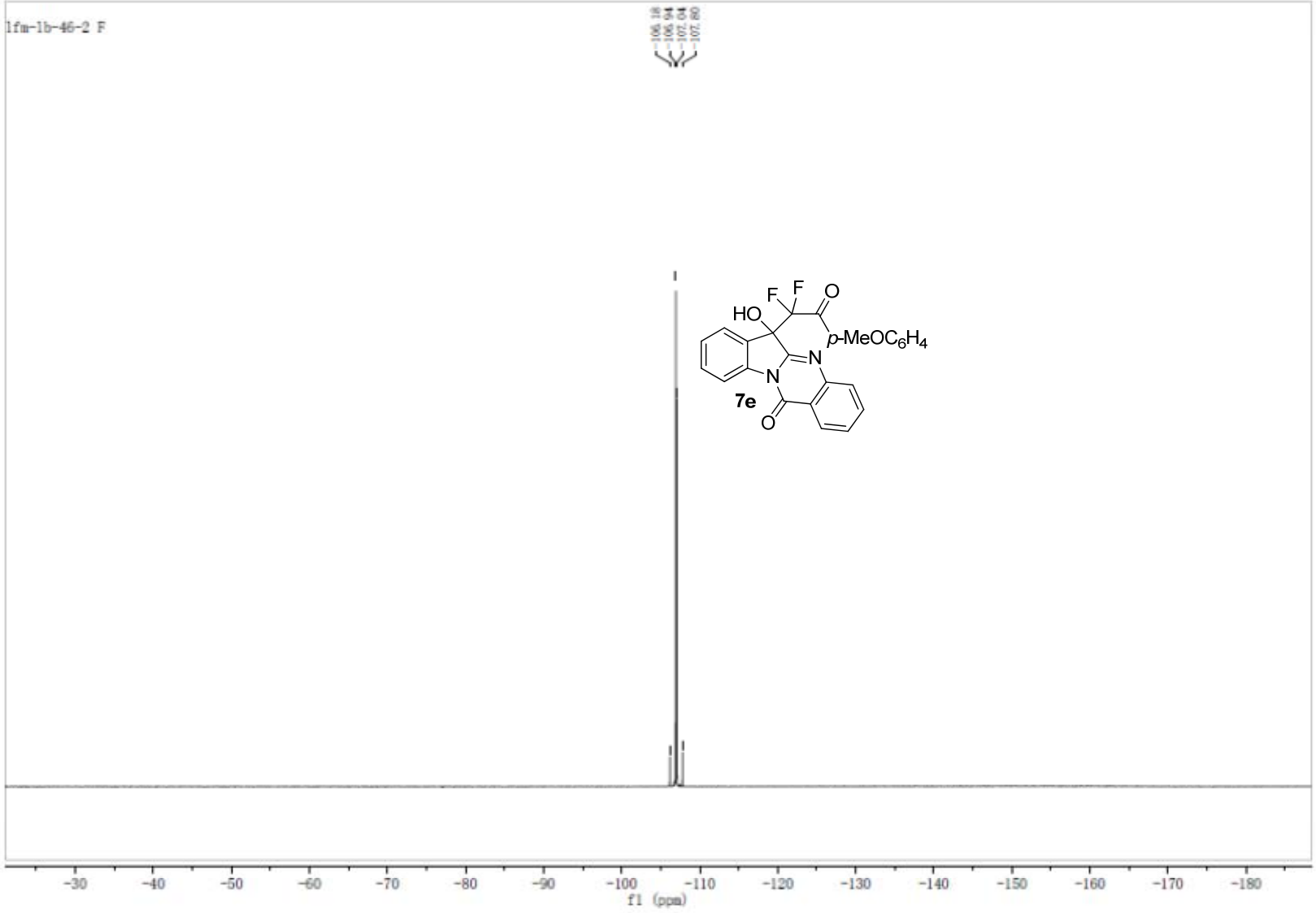

8.517
8.497
8.341
8.338
8.322
8.319
7.941
7.920
7.894
7.876
7.817
7.762
7.742
7.700
7.683
7.663
7.646
7.628
7.609
7.430
7.411
7.392
7.351
7.330
3.405
2.504
2.500
2.496
2.352
lfm-1b-44 H
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
1.000
0.996
2.081
0.943
1.035
1.043
3.016
1.062
1.969
F
F
O
HO
p-MeC6H4
N
N
O
7d
9.5
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
ppm
1.00
1.00
2.08
0.94
1.04
1.04
3.02
1.06
1.97
3.02

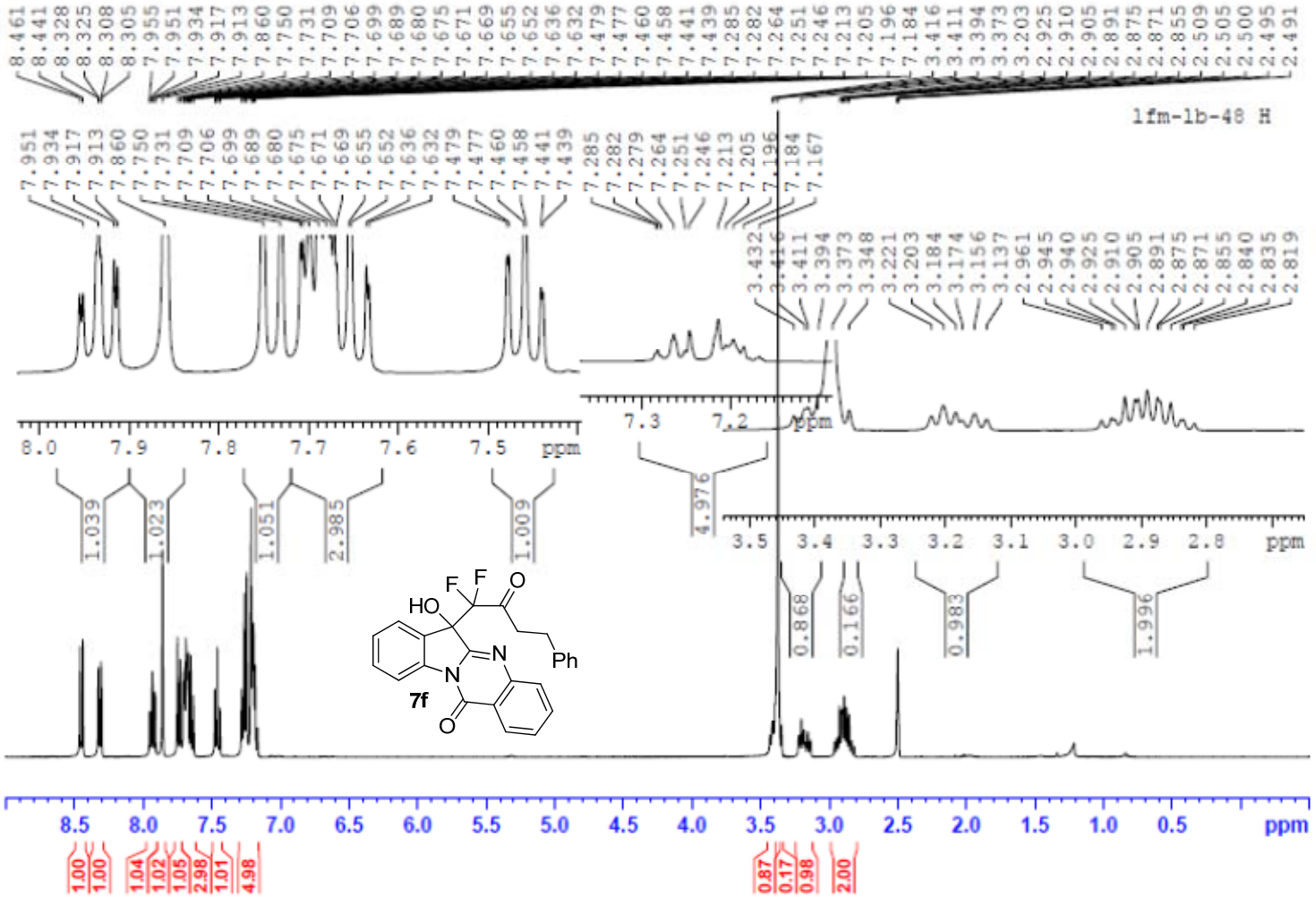

187.33
187.05
186.76
158.65
156.02
146.34
146.15
139.61
135.13
131.34
130.32
129.51
129.23
128.65
128.28
127.95
126.83
126.55
125.82
121.44
119.57
116.94
116.32
114.30
77.75
77.52
77.27
40.12
39.92
39.71
39.50
39.29
39.08
38.87
21.34
131.343
130.322
129.515
129.226
128.652
128.278
127.950
126.831
126.551
125.820
121.441
119.571
116.943
116.317
114.296
132
130
128
126
124
122
120
118
116
114
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
lfm-1b-44 C
F
F
O
HO
p-MeC6H4
N
N
7d
O

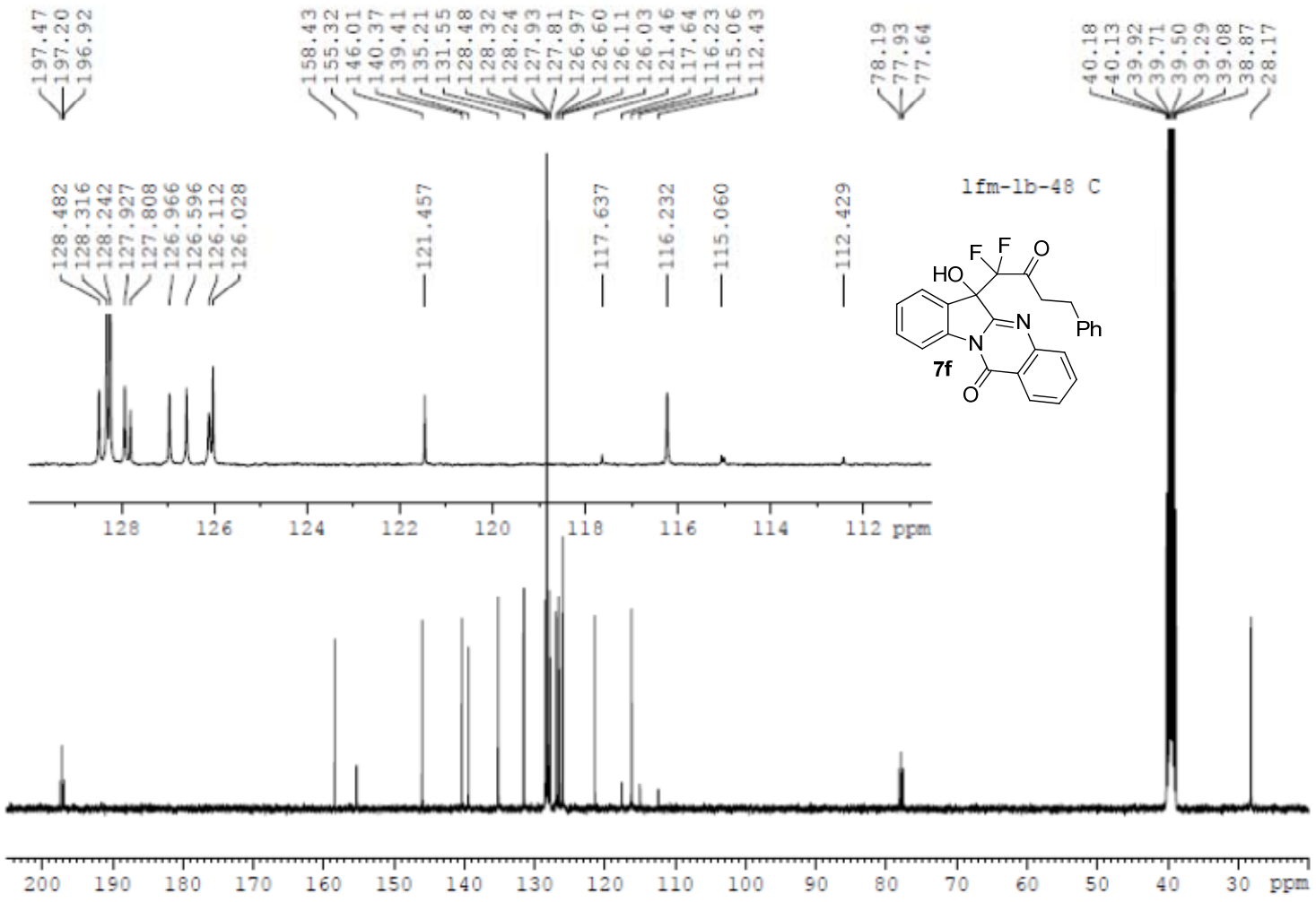

lfm-lb-44 F
F
F
O
HO
p-MeC6H4
N
N
O
7d
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

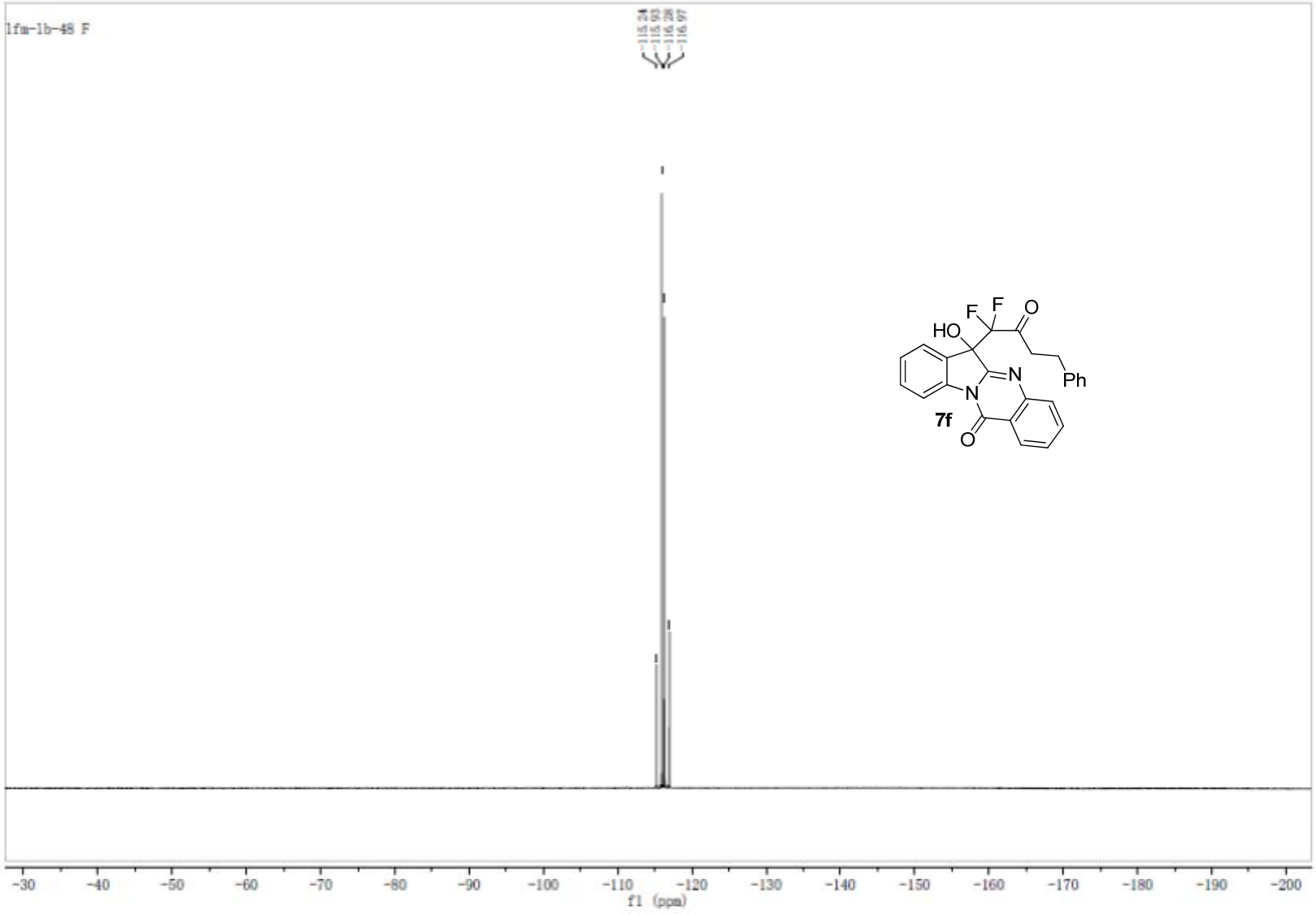

8.512
8.492
8.343
8.341
8.324
8.321
8.031
8.009
7.916
7.895
7.875
7.765
7.745
7.683
7.665
7.647
7.639
7.619
7.599
7.419
7.400
7.381
7.077
7.054
3.842
3.390
2.504
2.500
2.496
lfm-1b-46-2 H
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.006
0.992
2.025
1.098
2.033
2.994
0.995
1.968
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.01
0.99
2.02
1.10
2.03
2.99
1.00
1.97
3.00
F
F
O
HO
p-MeOC6H4
N
N
7e
O

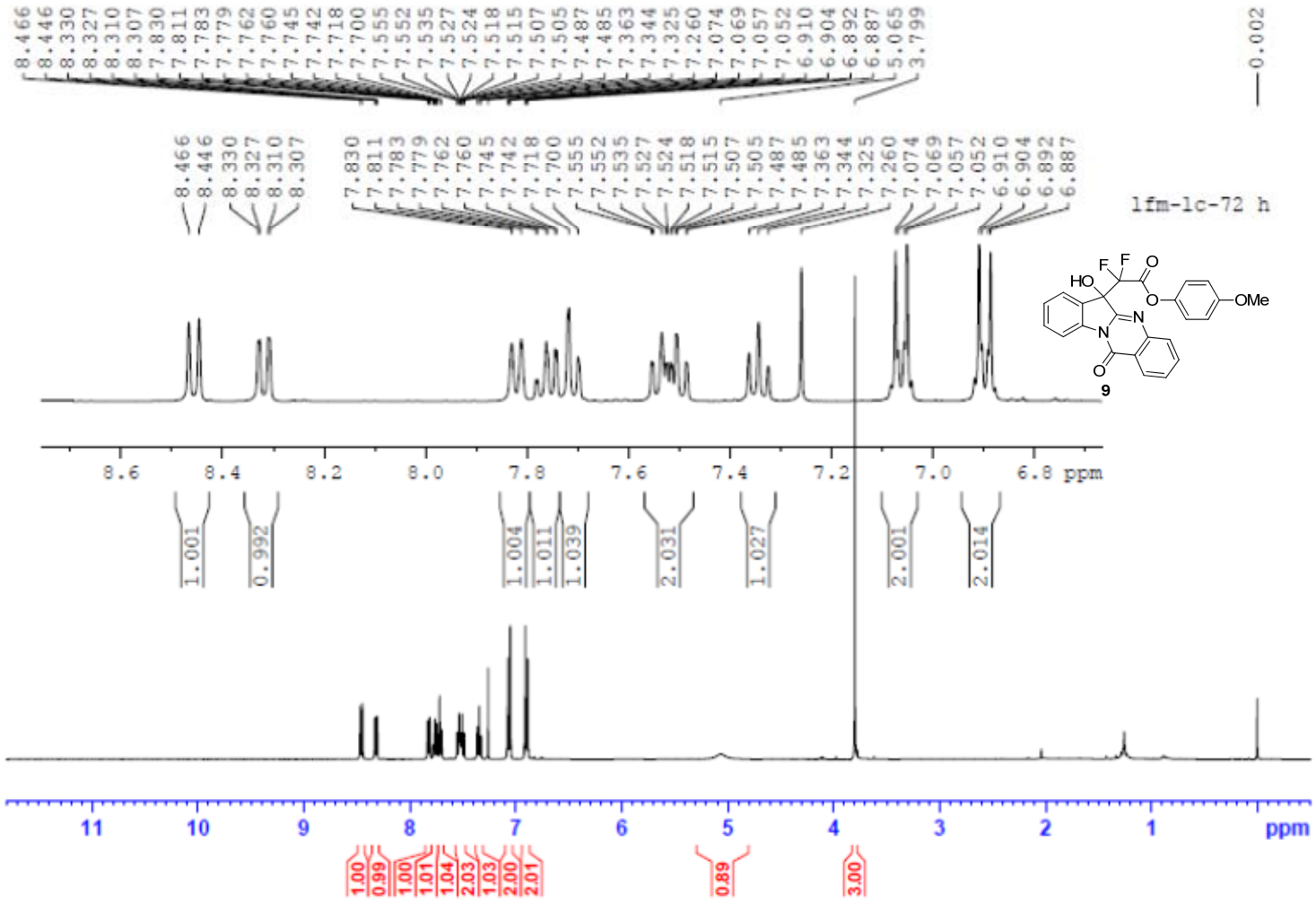

185.88
185.60
185.31
164.69
158.67
156.19
146.39
139.61
135.11
132.90
131.24
128.82
128.22
127.94
126.78
126.53
125.72
124.24
121.43
119.76
117.13
116.29
114.38
77.68
77.45
77.21
55.81
40.13
39.92
39.71
39.50
39.29
39.09
38.88
128.821
128.224
127.939
126.780
126.532
125.723
124.235
121.428
119.756
117.126
116.291
114.381
lfm-lb-46-2 C
F
F
O
HO
p-MeOC6H4
N
N
O
7e
128
126
124
122
120
118
116
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

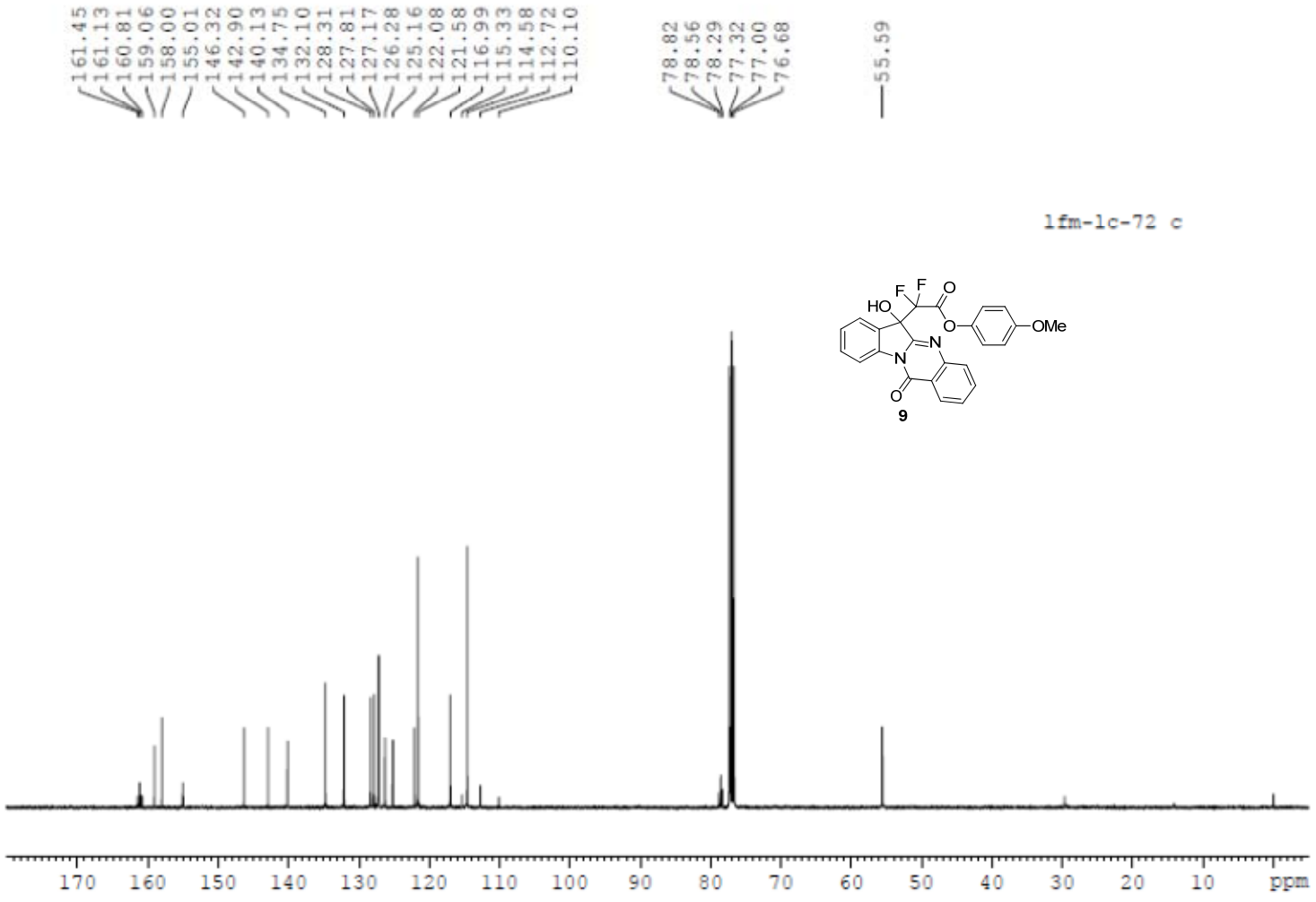

lfm-1b-46-2 F
F
F
O
HO
p-MeOC6H4
N
N
O
7e
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

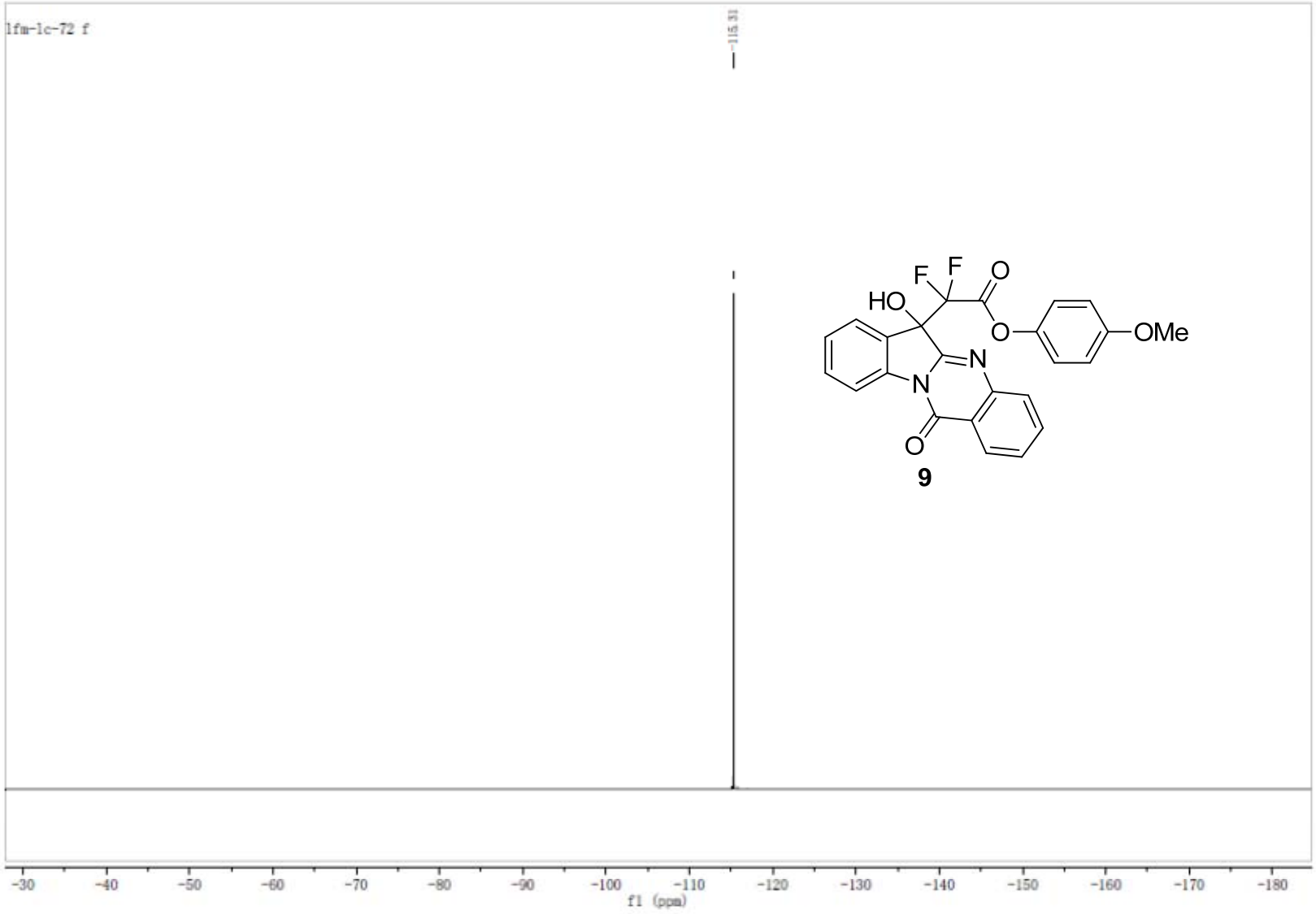

lfm-lb-48 H
7f
HO
F
F
O
N
N
Ph
O
ppm


197.47
197.20
196.92
158.43
155.32
146.01
140.37
139.41
135.21
131.55
128.48
128.32
128.24
127.93
127.81
126.97
126.60
126.11
126.03
121.46
117.64
116.23
115.06
112.43
78.19
77.93
77.64
40.18
40.13
39.92
39.71
39.50
39.29
39.08
38.87
28.17
128.482
128.316
128.242
127.927
127.808
126.966
126.596
126.112
126.028
121.457
117.637
116.232
115.060
112.429
lfm-1b-48 C
F
F
O
HO
N
N
Ph
O
7f
128
126
124
122
120
118
116
114
112 ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

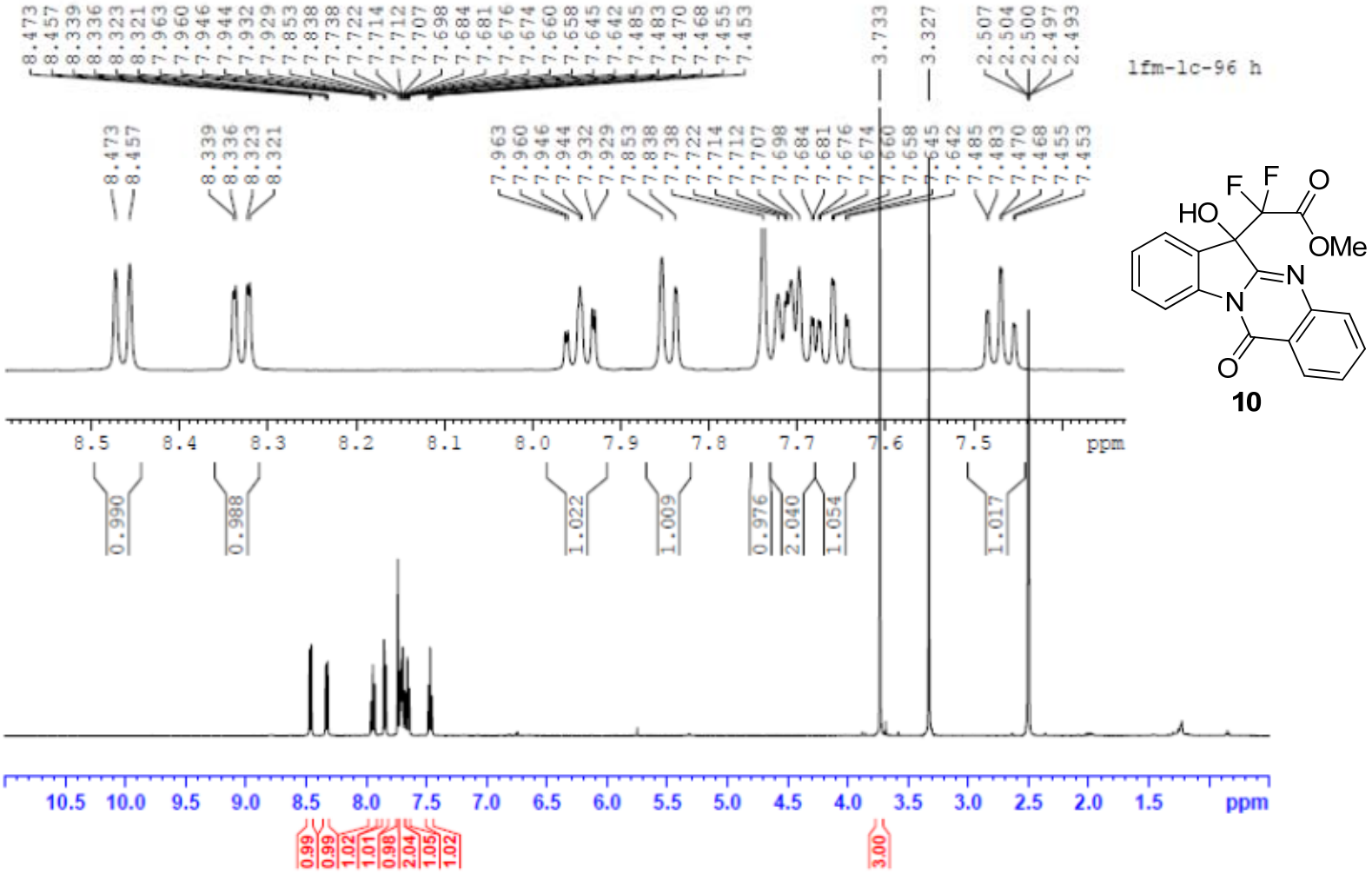

lfm-lb-48 F
F
F
O
HO
N
N
Ph
O
7f
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

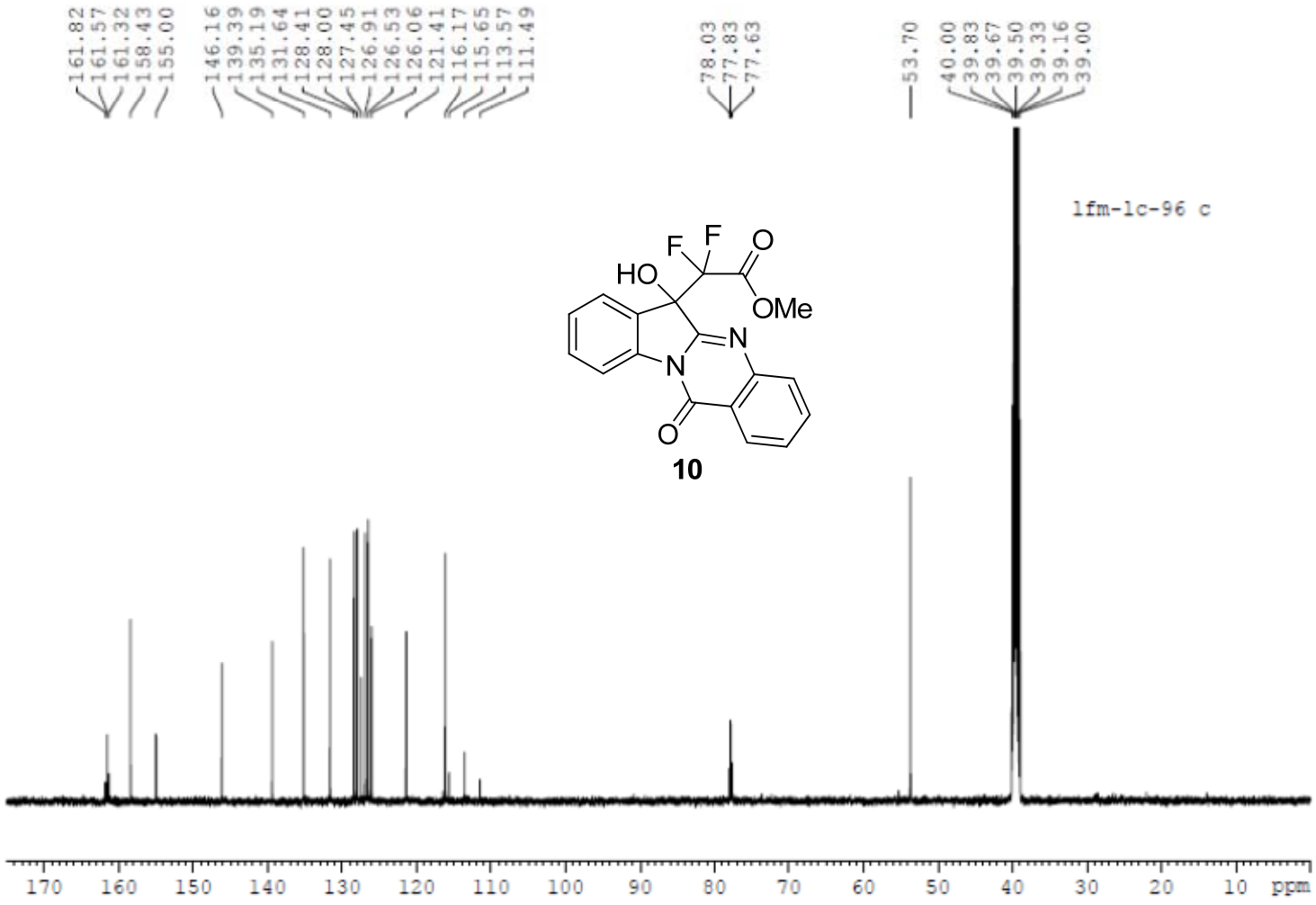

lfm-lc-72 h
9

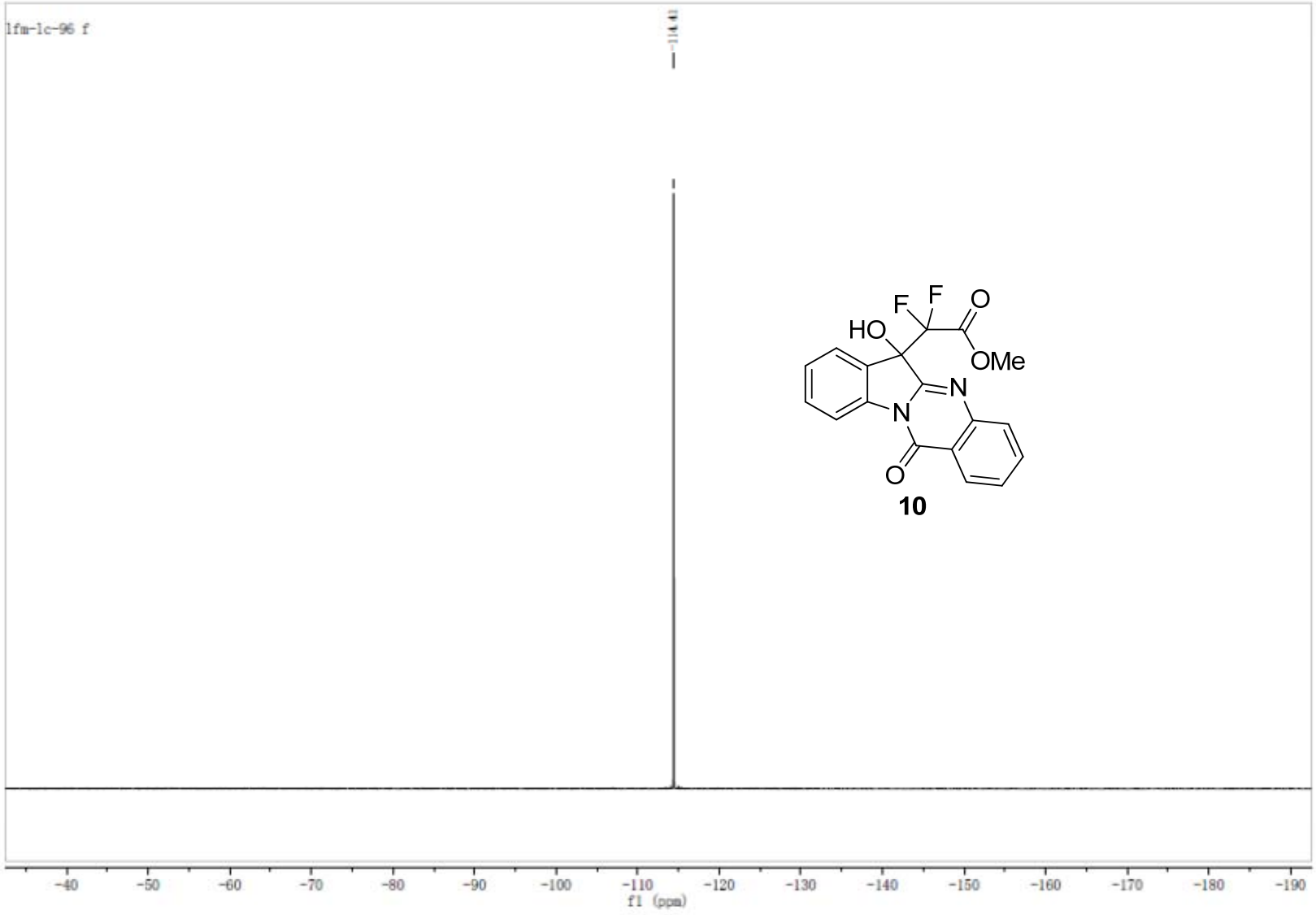

161.45
161.13
160.81
159.06
158.00
155.01
146.32
142.90
140.13
134.75
132.10
128.31
127.81
127.17
126.28
125.16
122.08
121.58
116.99
115.33
114.58
112.72
110.10
78.82
78.56
78.29
77.32
77.00
76.68
55.59
lfm-lc-72 c
F
F
O
HO
O
OMe
N
N
O
9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


lfm-lc-72 f
-115.31
F
F
O
HO
O
OMe
N
N
O
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

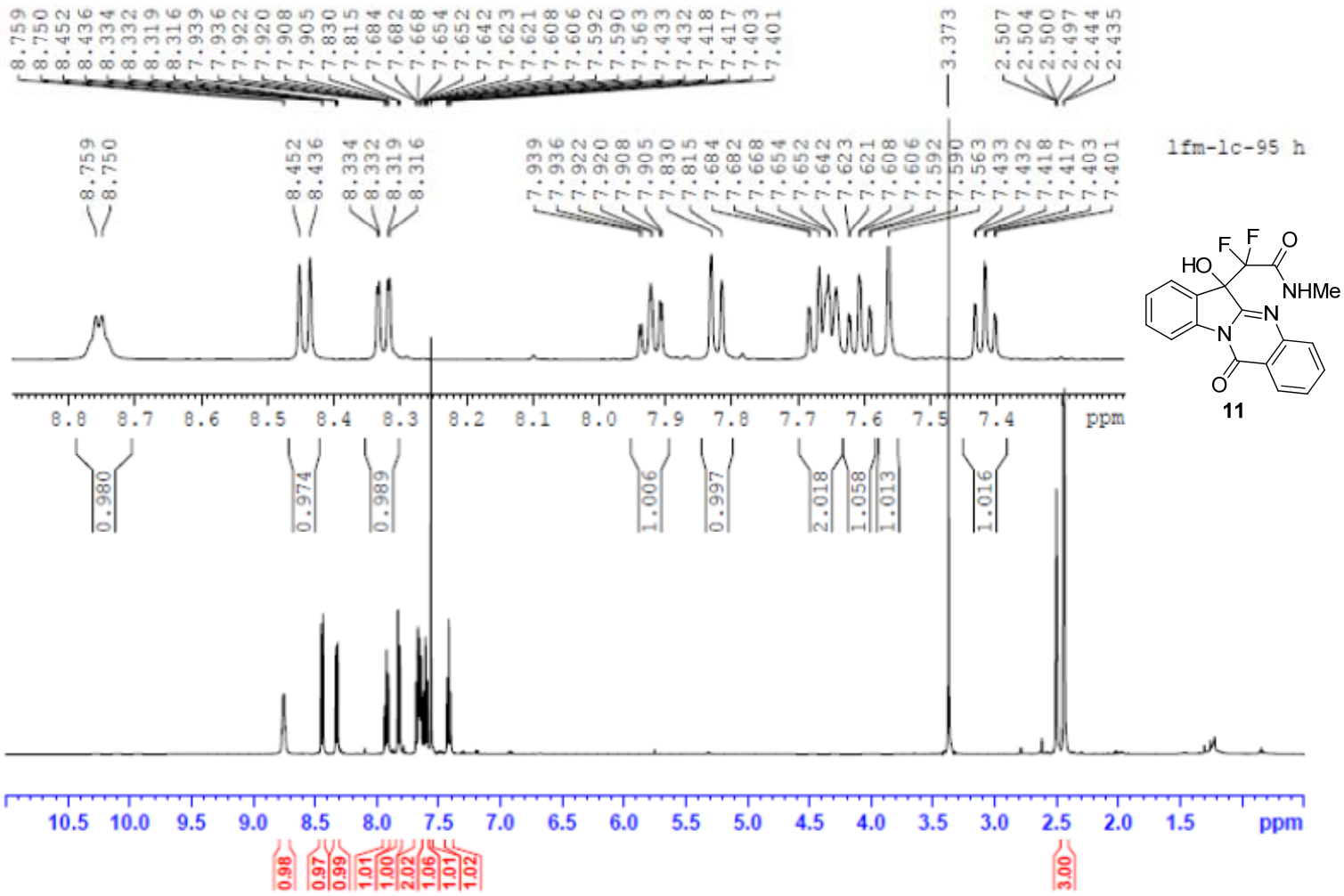
9

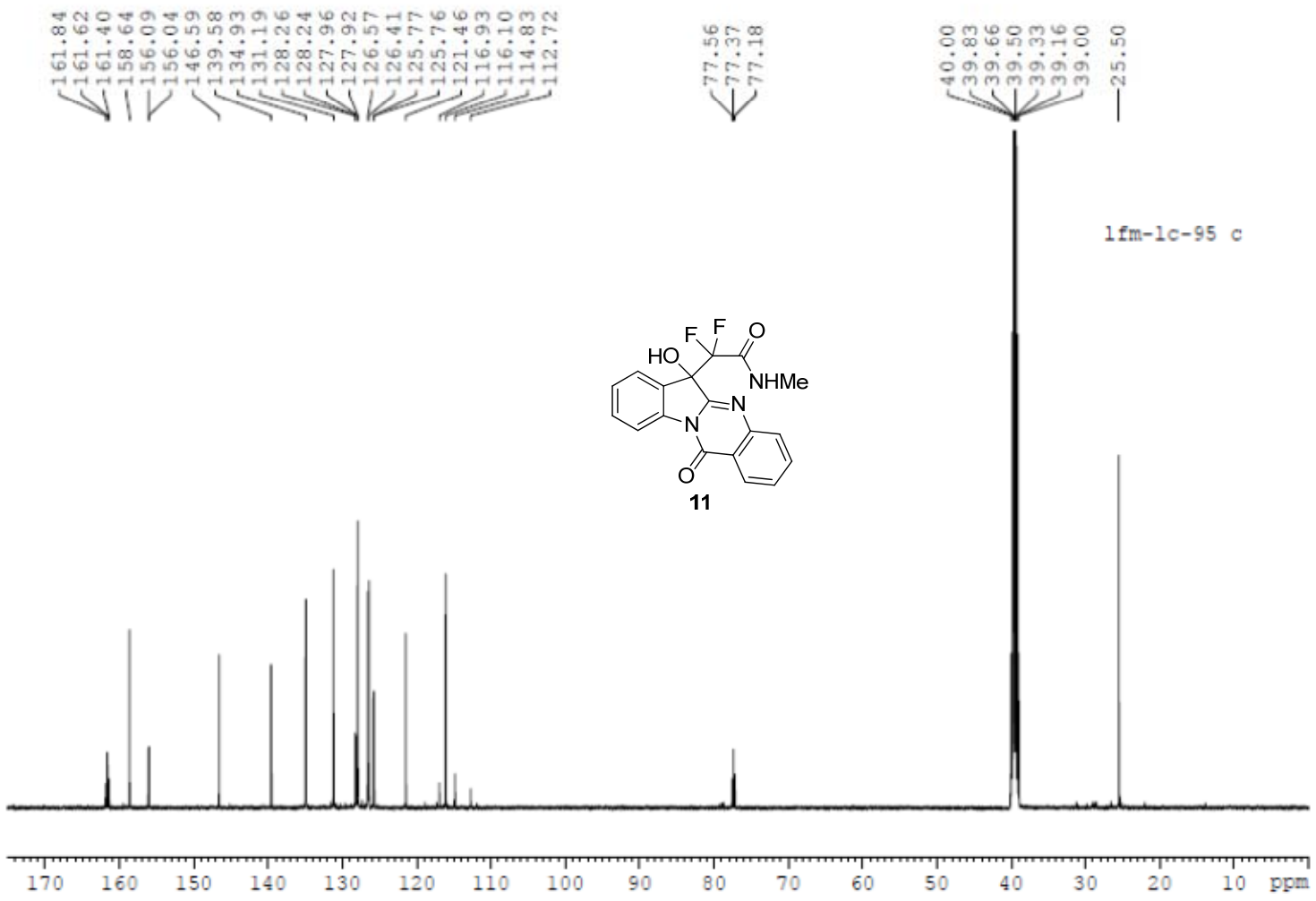

lfm-1c-96 h
10

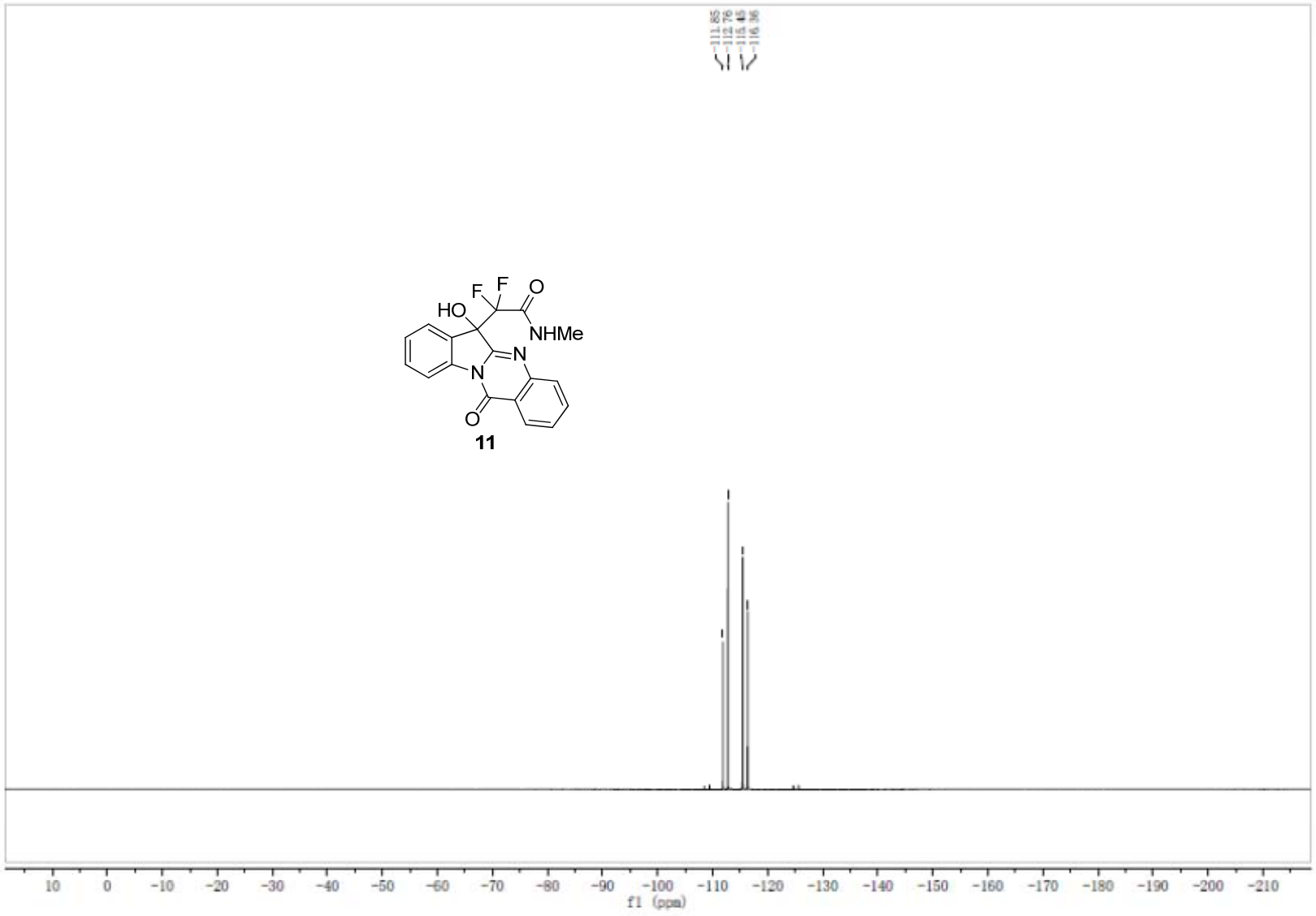

161.82
161.57
161.32
158.43
155.00
146.16
139.39
135.19
131.64
128.41
128.00
127.45
126.91
126.53
126.06
121.41
116.17
115.65
113.57
111.49
78.03
77.83
77.63
53.70
40.00
39.83
39.67
39.50
39.33
39.16
39.00
lfm-lc-96 c
F
F
O
HO
OMe
N
N
O
10
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

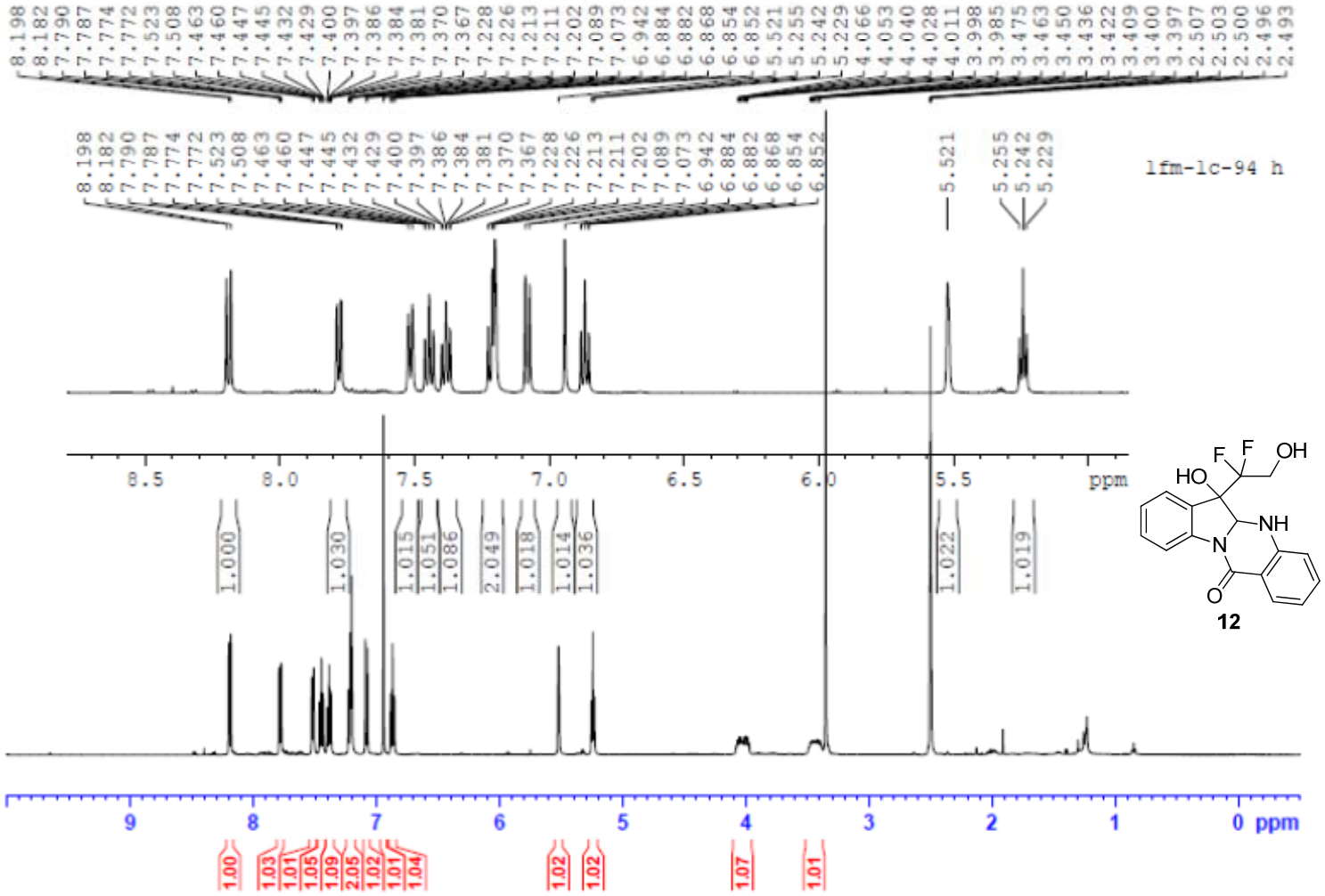

lfm-lc-96 f
-114.41
F
F
O
HO
OMe
N
N
O
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

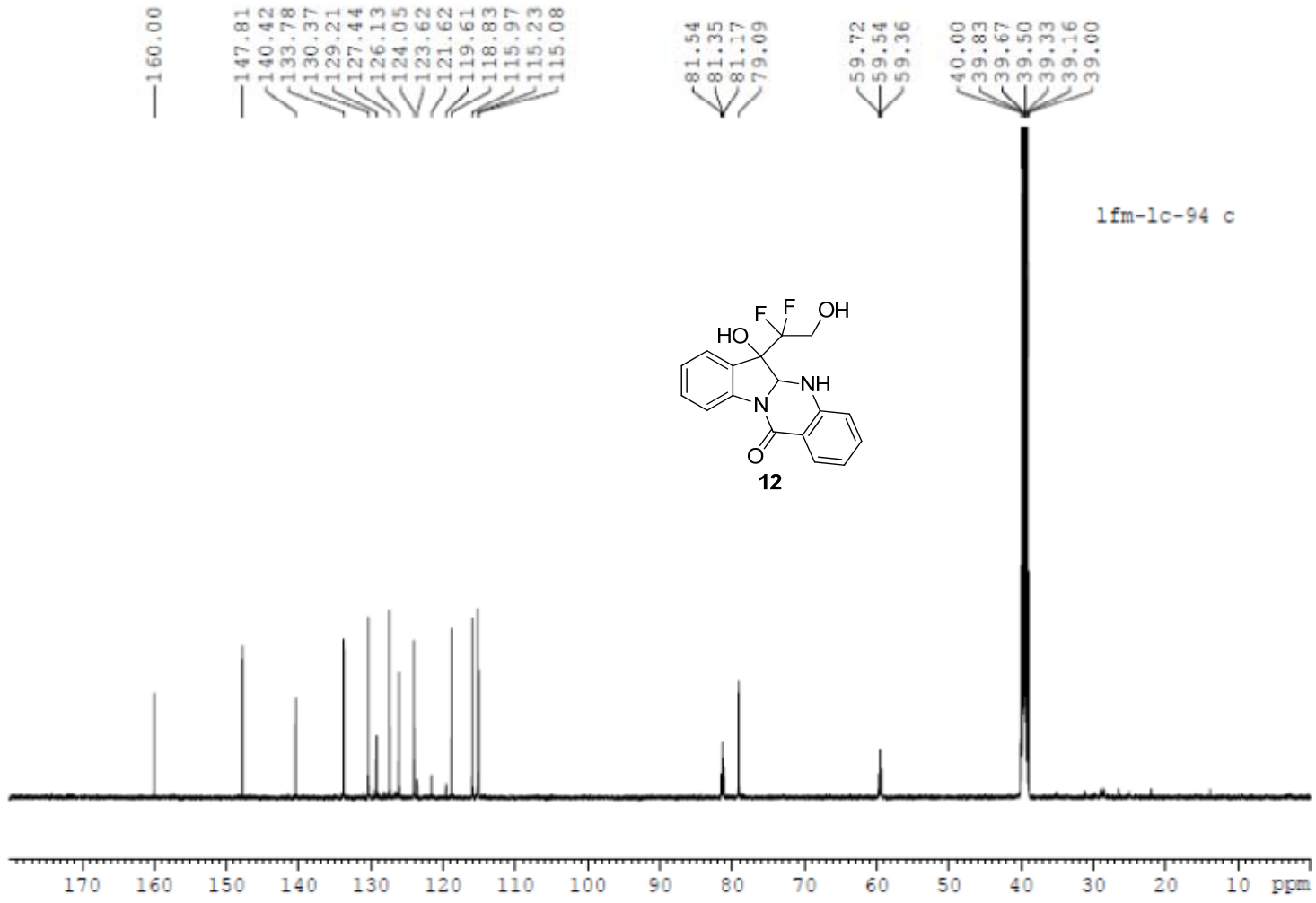
10

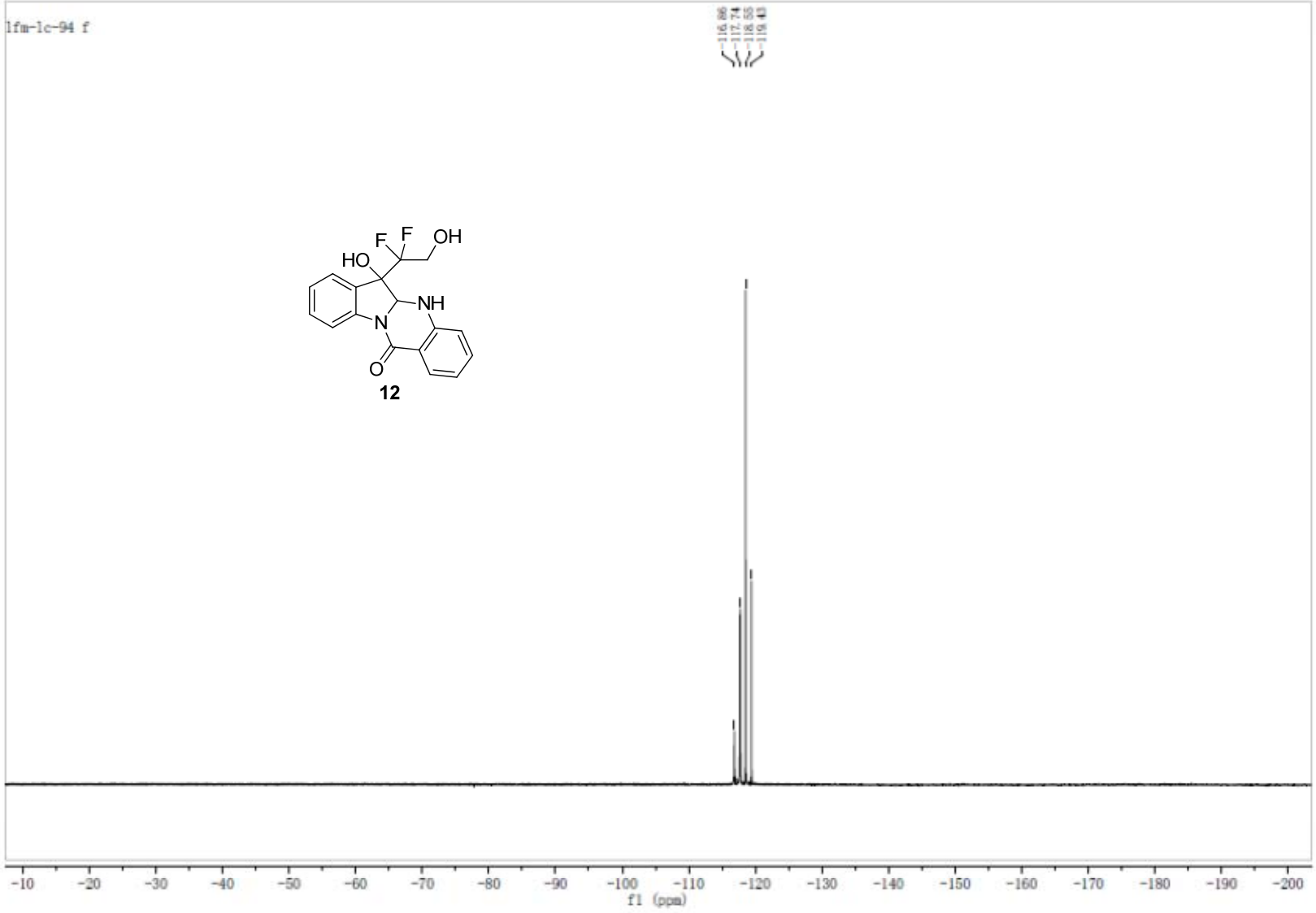

lfm-lc-95 h
11


161.84
161.62
161.40
158.64
156.09
156.04
146.59
139.58
134.93
131.19
128.26
128.24
127.96
127.92
126.57
126.41
125.77
125.76
121.46
116.93
116.10
114.83
112.72
77.56
77.37
77.18
40.00
39.83
39.66
39.50
39.33
39.16
39.00
25.50
lfm-1c-95 c
F
F
O
HO
NHMe
N
N
O
11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-111.85
-112.76
-115.43
-116.36
F
F
O
HO
NHMe
N
N
O
11
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


lfm-lc-94 h
ppm
12


160.00
147.81
140.42
133.78
130.37
129.21
127.44
126.13
124.05
123.62
121.62
119.61
118.83
115.97
115.23
115.08
81.54
81.35
81.17
79.09
59.72
59.54
59.36
40.00
39.83
39.67
39.50
39.33
39.16
39.00
lfm-lc-94 c
F
F
OH
HO
NH
N
O
12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


lfm-lc-94 f
-116.86
-117.74
-118.55
-119.43
F
F
OH
HO
NH
N
O
12
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)