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

Highly efficient Mukaiyama-Mannich reaction of *N*-Boc isatin ketimines and other active cyclic ketimines using difluoroenol silyl ethers catalyzed by $Ph_3PAuOTf$

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Contents

General: 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 refered to pure isolated substances. 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-400 or 300 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$, acetone-d_6 with the solvent resonance or $(CH_3)_4Si$ 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. Coupling constants (*J*) are reported in Hertz.

Anhydrous toluene was prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous CH_2Cl_2 and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2. Powdered MS 5Å was purchased from Aldrich and dried under vacuum at 150 ^{o}C for 12 hours, and then stored under nitrogen. The isatin derived ketimines **2**[1] and cyclic ketimines **7**[2] were prepared according to the corresponding literature report. The difluoroenoxysilanes **1** and mono-fluorinated analogue **9** were prepared according to literature reports.[3] The enol silyl ether **10** was prepared according to literature reports.[3c]

List of abbreviation:

Entry	Chemical name	Abbreviation
1	Petroleum ether	PE
2	Hexafluoroisopropyl alcohol	HFIP

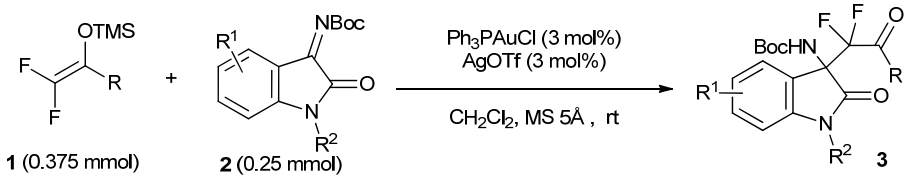
[1] (*a*) Y.-L. Liu and J. Zhou, *Chem. Commun.,* 2013, **49**, 4421; (*b*) W. Yan, D. Wang, J. Feng, P. Li, D. Zhao and R. Wang, *Org. Lett.,* 2012, **14**, 2512.

[2] (*a*) H. Wang, T. Jiang and M.-H. Xu, *J. Am. Chem. Soc.,* 2013, **135**, 971; (*b*) S. Zhang, L. Li, Y. Hu, Z. Zha, Z. Wang and T.-P. Loh, *Org. Lett.*, 2015, **17**, 1050; (*c*) T. Kano, S. Song, Y. Kubota and K. Maruoka, *Angew. Chem., Int. Ed.*, 2012, **51**, 1191.

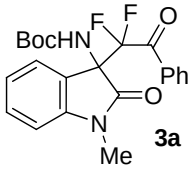
[3] (*a*) H. Amii, T. Kobayashi, Y. Hatamoto and K. Uneyama, *Chem. Commun.* 1999, 1323; (*b*) G. K. S. Prakash, J. Hu and G. A. Olah, *J. Fluorine Chem.* 2001, **112**, 357; (*c*) J. Eames, G. S. Coumbarides, M. J. Suggate and N. Weerasooriya, *Eur. J. Org. Chem.* 2003, 634.

Part I. General procedure for the Mukaiyama-Mannich reaction.

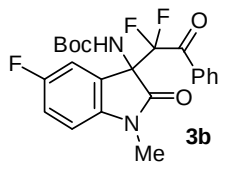
1) The Mukaiyama-Mannich reaction of *N*-Boc isatin ketimines 2.



Under an atmosphere of N_2, to a 25 mL dry Schleck tube were added Ph_3PAuCl (3.7 mg, 0.0075 mmol) and AgOTf (1.9 mg, 0.0075 mmol), followed by the addition of 2.5 mL of anhydrous CH_2Cl_2. The reaction mixture was stirred at room temperature for about 30 minutes, and then 200 mg activated MS 5Å was added, followed by the addition of *N*-Boc isatin ketimines **2** (0.25 mmol) and difluoroenoxysilanes **1** (0.375 mmol). The resulting mixture was stirred at room temperature till full conversion of **2** by TLC analysis and the reaction mixture was directly subjected to flash column chromatography to afford products **3**, using indicated eluent.

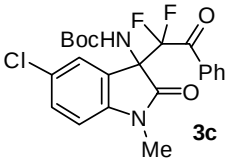


Column chromatography (CH_2Cl_2/EtOAc = 50:1 to 30:1) afforded product **3a** in 92% yield as white solid, Mp: 118-120 ^oC. IR (neat): 3261, 1750, 1701, 1369, 1154, 754, 712 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.60-7.56 (m, 1H), 7.42-7.33 (m, 4H), 7.03-7.00 (m, 1H), 6.84-6.82 (m, 1H), 6.18 (s, 1H), 3.21 (s, 3H), 1.27 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.17 (d, J = 275 Hz, 1F), -108.29 (d, J = 275 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.73 (t, J = 28 Hz), 170.73, 153.24, 144.85, 134.43, 132.70, 130.46, 129.94 (t, J = 3.6 Hz), 128.41, 125.08, 123.71, 122.75, 115.32 (t, J = 265 Hz), 108.36, 80.88, 65.17 (t, J = 23 Hz), 27.92, 26.59. MS (EI): 416 (M^+, 6), 316 (2), 205 (3), 161 (100), 105 (14), 77 (16), 57 (9), 44 (6). HRMS (EI): Exact mass calcd for $C_{22}H_{22}N_2O_4F_2$ $[M]^+$: 416.1548, Found: 416.1551.



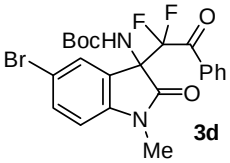
Column chromatography (CH_2Cl_2/EtOAc = 1:0 to 20:1) afforded product **3b** in 84% yield as white solid, Mp: 86-88 ^oC. IR (neat): 3348, 1718, 1494, 1272, 1160, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 2H), 7.63-7.59 (m, 1H), 7.45-7.42 (m, 2H), 7.17-7.14 (m, 1H), 7.08-7.03 (m, 1H), 6.79-6.76 (m, 1H), 6.21 (s, 1H),

3.22 (s, 3H), 1.31 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.52 (d, *J* = 279 Hz, 1F), -108.11 (d, *J* = 279 Hz, 1F), -119.81 (s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.36 (t, *J* = 28 Hz), 170.59, 159.10 (d, *J* = 240 Hz), 153.25, 140.95 (d, *J* = 2.1 Hz), 134.71, 132.44, 130.04 (t, *J* = 3.3 Hz), 128.57, 125.33 (d, *J* = 7.2 Hz), 116.71 (d, *J* = 23.4 Hz), 115.20 (t, *J* = 266 Hz), 113.47 (d, *J* = 25.6 Hz), 108.94 (d, *J* = 7.9 Hz), 81.22, 65.34 (t, *J* = 22.9 Hz), 28.00, 26.83. MS (EI): 434 (M^+, 6), 334 (3), 205 (3), 179 (100), 105 (15), 77 (15), 57 (10), 44 (5). HRMS (EI): Exact mass calcd for $C_{22}H_{21}N_2O_4F_3$ $[M]^+$: 434.1453, Found: 434.1450.



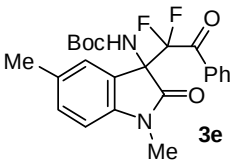
3c

Column chromatography (pure CH_2Cl_2) afforded product **3c** in 86% yield as pale yellow solid, Mp: 100-102 ^{o}C. IR (neat): 3252, 2924, 1717, 1367, 1125, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 2H), 7.63-7.59 (m, 1H), 7.46-7.42 (m, 2H), 7.36-7.31 (m, 2H), 6.79-6.76 (m, 1H), 6.19 (s, 1H), 3.22 (s, 3H), 1.31 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.38 (d, *J* = 280 Hz, 1F), -107.87 (d, *J* = 280 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.20 (t, *J* = 28 Hz), 170.44, 153.24, 143.57, 134.75, 132.36, 130.36, 130.06 (t, *J* = 4 Hz), 128.58, 128.15, 125.55, 125.48, 115.22 (t, *J* = 266 Hz), 109.35, 81.29, 65.09 (t, *J* = 23 Hz), 28.02, 26.83. MS (EI): 452 [M(^{37}Cl)$^+$, 2.6], 450[M(^{35}Cl)$^+$, 7.7], 350 (3), 221 (3), 195 (100), 197 (33), 105 (20), 77 (20), 57 (12), 44 (8). HRMS (EI): Exact mass calcd for $C_{22}H_{21}N_2O_4F_2{}^{35}Cl$ $[M]^+$: 450.1158, Found: 450.1160.



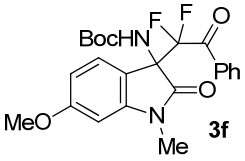
3d

Column chromatography (CH_2Cl_2/EtOAc = 1:0 to 20:1) afforded product **3d** in 85% yield as white foamy solid, Mp: 58-60 ^{o}C. IR (neat): 2979, 1718, 1488, 1365, 1159, 722 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.62-7.58 (m, 1H), 7.47-7.41 (m, 4H), 6.73-6.71 (m, 1H), 6.18 (s, 1H), 3.21 (s, 3H), 1.30 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.38 (d, *J* = 280 Hz, 1F), -107.83 (d, *J* = 280 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.18 (t, *J* = 28 Hz), 170.32, 153.23, 144.06, 134.75, 133.26, 132.36, 130.05 (t, *J* = 3.3 Hz), 128.58, 128.22, 125.82, 115.32, 115.23 (t, *J* = 266 Hz), 109.84, 81.30, 65.02 (t, *J* = 23 Hz), 28.02, 26.80. MS (EI): 496 [M(^{81}Cl)$^+$, 6], 494 [M(^{79}Cl)$^+$, 6], 394 (3), 267 (3), 265 (3), 241 (98), 239 (100), 9 (132), 105 (32), 77 (30), 57 (19), 44 (11). HRMS (EI): Exact mass calcd for $C_{22}H_{21}N_2O_4F_2{}^{79}Br$ $[M]^+$: 494.0653, Found: 494.0651.



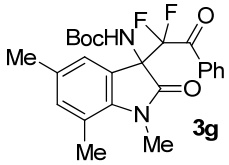
3e

Column chromatography (pure CH_2Cl_2) afforded product **3e** was obtained in 86% yield as white solid, Mp: 137-139 ^oC. IR (neat): 3258, 1747, 1699, 1368, 1154, 713 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81-7.80 (m, 2H), 7.60-7.56 (m, 1H), 7.42-7.38 (m, 2H), 7.14-7.12 (m, 2H), 6.71 (d, J = 7.6 Hz, 1H), 6.17 (s, 1H), 3.18 (s, 3H), 2.25 (s, 3H), 1.28 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.33 (d, J = 274 Hz, 1F), -108.52 (d, J = 274 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.80 (t, J = 28 Hz), 170.67, 153.31, 142.42, 134.43, 132.84, 132.40, 130.72, 130.03 (t, J = 3.7 Hz), 128.41, 125.92, 123.63, 115.38 (t, J = 266 Hz), 108.13, 80.91, 65.35 (t, J = 23 Hz), 28.00, 26.68, 21.00. MS (EI): 430 (M^+, 7), 330 (2), 201 (3), 175 (100), 132 (6), 105 (11), 77 (13), 57 (7), 44 (5). HRMS (EI): Exact mass calcd for $C_{23}H_{24}N_2O_4F_2$ $[M]^+$: 430.1704, Found: 430.1707.



3f

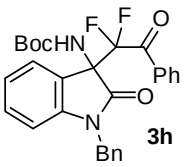
Column chromatography (CH_2Cl_2/EtOAc = 100:1 to 30:1) afforded product **3f** in 69% yield as white solid, Mp: 155-157 ^oC. IR (neat): 3376, 1728, 1710, 1512, 1160, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83-7.81 (m, 2H), 7.60-7.56 (m, 1H), 7.43-7.39 (m, 2H), 7.26-7.24 (m, 1H), 6.50-6.47 (m, 1H), 6.40-6.39 (m, 1H), 6.11 (s, 1H), 3.81 (s, 3H), 3.19 (s, 3H), 1.30 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.18 (d, J = 275 Hz, 1F), -108.23 (d, J = 275 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.83 (t, J = 28 Hz), 171.26, 161.87, 153.35, 146.26, 134.43, 132.79, 130.02 (t, J = 3.8 Hz), 128.46, 126.21, 115.46 (t, J = 265 Hz), 115.37, 106.52, 96.46, 80.84, 64.79 (t, J = 23 Hz), 55.44, 28.05, 26.67. MS (EI): 446 (M^+, 2), 346 (1), 291 (4), 191 (100), 148 (5), 105 (11), 77 (11), 57 (6), 44 (5). HRMS (EI): Exact mass calcd for $C_{23}H_{24}N_2O_5F_2$ $[M]^+$: 446.1653, Found: 446.1654.



3g

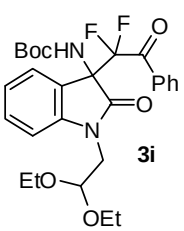
Column chromatography (CH_2Cl_2/EtOAc = 1:0 to 20:1) afforded product **3g** in 75% yield as white solid, Mp: 147-149 ^oC. IR (neat): 3401, 1708, 1497, 1161, 861, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79-7.71 (m, 2H), 7.59-7.56 (m, 1H), 7.42-7.38 (m, 2H), 6.98 (s, 1H), 6.86 (s, 1H), 6.19 (s, 1H), 3.42 (s, 3H), 2.49 (s, 3H), 2.19 (s, 3H), 1.29 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.70 (d, J = 269 Hz, 1F), -109.14 (d, J = 269 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.09 (t, J = 28 Hz), 171.41, 153.33, 140.01, 134.75, 134.29, 133.13, 132.21, 129.99 (t, J = 3.5 Hz), 128.34, 124.26, 123.69, 119.53, 115.31 (t, J = 265 Hz), 80.85, 65.06 (t, J = 23 Hz), 30.05, 28.03, 20.66, 18.88. MS (EI): 444 (M^+, 7), 344 (3), 215 (4),

190 (13), 189 (100), 146 (6), 105 (11), 77 (11), 57 (5), 44 (5). HRMS (EI): Exact mass calcd for $C_{24}H_{26}N_2O_4F_2$ $[M]^+$: 444.1861, Found: 444.1862.



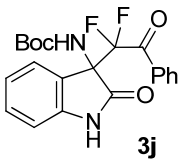
3h

Column chromatography (pure CH_2Cl_2) afforded product **3h** in 75% yield as pale yellow solid, Mp: 181-183 ^oC. IR (neat): 3390, 1714, 1686, 1511, 1276, 1118, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.59-7.55 (m, 1H), 7.39-7.21 (m, 9H), 6.99 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 8 Hz, 1H), 6.33 (s, 1H), 5.07, 4.80 (AB, J = 16 Hz, 2H), 1.30 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.54 (d, J = 275 Hz, 1F), -108.60 (d, J = 275 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.33 (t, J = 27 Hz), 171.13, 153.34, 144.26, 135.37, 134.48, 132.87, 130.37, 130.15 (t, J = 3.1 Hz), 128.70, 128.45, 127.57, 127.33, 125.24, 123.81, 122.88, 115.27 (t, J = 265 Hz), 80.99, 65.57 (t, J = 24 Hz), 44.50, 28.03. MS (EI): 492 (M^+, 7), 237 (26), 195 (8), 179 (24), 149 (8), 105 (51), 77 (38), 56 (17), 44 (100). HRMS (EI): Exact mass calcd for $C_{28}H_{26}N_2O_4F_2$ $[M]^+$: 492.1861, Found: 492.1863.



3i

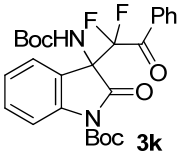
Column chromatography (PE/EtOAc = 10:1 to 6:1) afforded product **3i** in 78% yield as white solid, Mp: 128-130 ^oC. IR (neat): 3373, 2975, 1737, 1517, 1276, 1138, 772 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.42-7.38 (m, 2H), 7.32-7.28 (m, 2H), 7.08 (d, J = 8 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.18 (s, 1H), 4.71-4.68 (m, 1H), 4.03-3.98 (m, 1H), 3.79-3.49 (m, 5H), 1.27 (s, 9H), 1.17-1.10 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.06 (d, J = 274 Hz, 1F), -108.54 (d, J = 274 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.07 (t, J = 28 Hz), 171.13, 153.23, 144.79, 134.43, 132.84, 130.12, 130.03 (t, J = 3.4 Hz), 128.42, 124.85, 123.42, 122.54, 115.37 (t, J = 265 Hz), 110.23, 101.07, 80.90, 65.01 (t, J = 23 Hz), 63.92, 63.80, 44.30, 27.98, 15.24, 15.21. MS (EI): 518 (M^+, 6), 217 (8), 149 (5), 105 (46), 103 (100), 84 (17), 77 (22), 75 (23), 57 (9), 44 (33). HRMS (EI): Exact mass calcd for $C_{27}H_{32}N_2O_6F_2$ $[M]^+$: 518.2228, Found: 518.2224.



3j

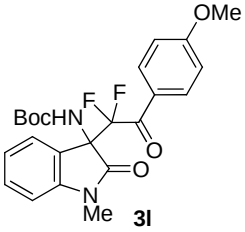
Column chromatography (CH_2Cl_2/EtOAc = 20:1 to 10:1) afforded product **3j** in 72% yield as white solid, Mp: 180-183 ^oC. IR (neat): 3277, 1749, 1682, 1280, 1158, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, br, 1H), 7.87-7.85 (m, 2H), 7.58-7.54 (m, 1H), 7.41-7.37 (m, 2H), 7.34-7.32 (m, 1H), 7.28-7.24 (m, 1H), 6.99 (t, J = 7.6 Hz, 1H),

6.81-6.79 (m, 1H), 6.33 (s, 1H), 1.31 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.71 (d, *J* = 276 Hz, 1F), -108.77 (d, *J* = 276 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.38 (t, *J* = 28 Hz), 172.72, 153.48, 142.20, 134.59, 132.82, 130.46, 130.16 (t, *J* = 3.6 Hz), 128.52, 125.37, 124.27, 122.83, 115.15 (t, *J* = 265 Hz), 110.52, 81.35, 65.87 (t, *J* = 25 Hz), 28.02. MS (EI): 402 (M^+, 4), 302 (1), 247 (4), 147 (100), 105 (23), 77 (20), 57 (15), 44 (13). HRMS (EI): Exact mass calcd for $C_{21}H_{20}N_2O_4F_2$ $[M]^+$: 402.1391, Found: 402.1395.



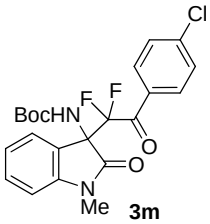
3k

Column chromatography (pure CH_2Cl_2) afforded product **3k** in 62% yield as white solid, Mp: 112-114 °C. IR (KBr): 3369, 2984, 1780, 1739, 1705, 1499, 1292, 1156, 759 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.91 (m, 1H), 7.83-7.81 (m, 2H), 7.61-7.57 (m, 1H), 7.42-7.35 (m, 4H), 7.13-7.09 (m, 1H), 6.20 (s, 1H), 1.63 (s, 9H), 1.25 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -106.53 (d, *J* = 280 Hz, 1F), -107.64 (d, *J* = 280 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.25 (t, *J* = 29 Hz), 168.98 (t, *J* = 3 Hz), 153.23, 148.81, 141.30, 134.69, 132.32, 130.61, 130.10 (t, *J* = 4 Hz), 128.51, 124.70, 124.48, 123.02, 115.37 (t, *J* = 267 Hz), 115.26, 84.50, 81.58, 65.25 (t, *J* = 23 Hz), 28.02, 27.83. MS (EI): 502 (M^+, 1), 402 (2), 346 (5), 191 (8), 147 (100), 119 (30), 105 (95), 77 (38), 57 (34), 43 (77). HRMS (EI): Exact mass calcd for $C_{26}H_{28}N_2O_6F_2$ $[M]^+$: 502.1915, Found: 502.1919.



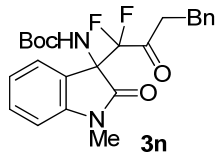
3l

Column chromatography (CH_2Cl_2/EtOAc = 80:1 to 20:1) afforded product **3l** in 99% yield as white solid, Mp: 140-142 °C. IR (neat): 3399, 2934, 1744, 1716, 1594, 1467, 1268, 1147, 759 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (m, 2H), 7.35-7.31 (m, 2H), 7.02-6.98 (m, 1H), 6.87-6.82 (m, 3H), 6.23 (s, 1H), 3.85 (s, 3H), 3.22 (s, 3H), 1.27 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.81 (d, *J* = 274 Hz, 1F), -107.69 (d, *J* = 274 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.66 (t, *J* = 28 Hz), 170.90, 164.68, 153.30, 144.93, 132.81 (t, *J* = 4 Hz), 130.35, 125.46, 125.11, 123.98, 122.68, 115.63 (t, *J* = 265 Hz), 113.82, 108.29, 80.83, 65.23 (t, *J* = 24 Hz), 55.52, 27.96, 26.65. MS (EI): 446 (M^+, 12), 346 (2), 285 (9), 225 (17), 187 (16), 161 (100), 135 (46),77 (14), 57 (21), 44 (32). HRMS (EI): Exact mass calcd for $C_{23}H_{24}N_2O_5F_2$ $[M]^+$: 446.1653, Found: 446.1657.



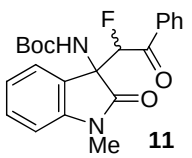
3m

Column chromatography (pure CH_2Cl_2) afforded product **3m** in 67% yield as white foamy solid, Mp: 55-58 ^oC. IR (neat): 3419, 2976, 1721, 1490, 1253, 1139, 869, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.75 (m, 2H), 7.40-7.34 (m, 4H), 7.05-7.01 (m, 1H), 6.84 (d, J = 8 Hz, 1H), 6.14 (s, 1H), 3.22 (s, 3H), 1.27 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.01 (d, J = 274 Hz, 1F), -108.68 (d, J = 274 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.78 (t, J = 30 Hz), 170.74, 153.24, 144.86, 141.32, 131.45 (t, J = 3.3 Hz), 131.11, 130.60, 128.90, 125.19, 123.64, 122.92, 115.35 (t, J = 265 Hz), 108.47, 81.07, 65.31 (t, J = 23 Hz), 27.99, 26.71. MS (EI): 450 (M^+, 4), 350 (1), 205 (3), 161 (100), 139 (10), 111 (9), 75 (4), 57 (9), 44 (6). HRMS (EI): Exact mass calcd for $C_{22}H_{21}N_2O_4F_2{}^{35}Cl$ $[M]^+$: 450.1158, Found: 450.1157.



3n

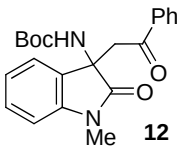
Column chromatography (PE/EtOAc = 6:1 to 5:1) afforded product **3n** in 88% yield as white solid, Mp: 121-123 ^oC. IR (neat): 3386, 2928, 1709, 1522, 1284, 1132, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.18 (m, 1H), 7.15-7.06 (m, 3H), 6.82 (d, J = 8 Hz, 1H), 6.16 (s, 1H), 3.23 (s, 3H), 2.91-2.84 (m, 4H), 1.26 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.29 (d, J = 261 Hz, 1F), -118.49 (d, J = 261 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.12 (dd, J = 33 Hz, J = 24 Hz), 170.94, 153.13, 144.68, 139.89, 130.60, 128.52, 128.34, 126.31, 124.80, 123.50, 123.10, 113.09 (dd, J = 264 Hz, J = 259 Hz), 108.56, 81.03, 65.31 (dd, J = 28 Hz, J = 23 Hz), 40.75, 28.38, 27.97, 26.72. MS (EI): 444 (M^+, 6), 344 (2), 196 (4), 161 (100), 131 (4), 105 (7), 91 (14), 77 (5), 57 (8), 44 (8). HRMS (EI): Exact mass calcd for $C_{24}H_{26}N_2O_4F_2$ $[M]^+$: 444.1861, Found: 444.1859.



11

Column chromatography (PE/EtOAc = 5:1 to 4:1) afforded product **11** in 99% yield as white solid, dr value was 9:1 determined by ^1H NMR analysis of crude mixture. Mp: 136-138^oC. IR (KBr): 3410, 2989, 1720, 1709, 1610, 1490, 1254, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 2H), 7.58-7.54 (m, 1H), 7.39-7.31 (m, 3H), 7.16-7.14 (m, 1H), 6.94-6.90 (m, 1H), 6.88-6.86 (m, 1H), 6.33 (s, 1H), 5.70 (d, J = 46 Hz, 1H), 3.27 (s, 3H), 1.28 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -193.27 (s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.61 (d, J = 22 Hz), 153.43, 144.65, 135.00 (d, J = 2.9 Hz), 134.29, 130.03, 129.63, 129.57,

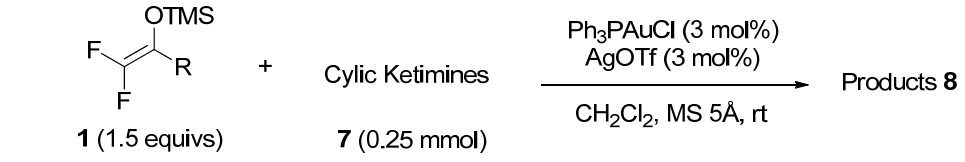
128.46, 125.70, 124.70, 122.61, 108.39, 92.50 (d, J = 195 Hz), 80.69, 63.49 (d, J = 26 Hz), 28.03, 26.70. HRMS (EI): Exact mass calcd for $C_{22}H_{23}N_2O_4F$ $[M]^+$: 398.1642, Found: 398.1639.

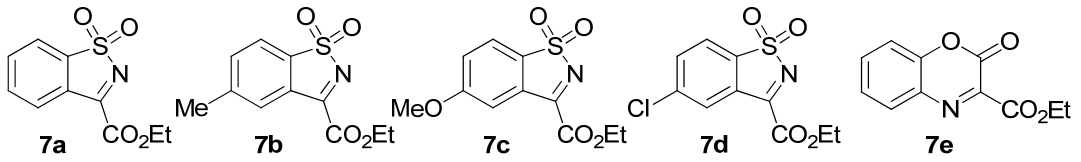


12

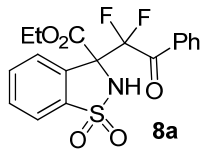
Column chromatography (PE/EtOAc = 5:1 to 4:1) afforded product **12** in 99% yield as pale yellow oil. IR (KBr): 3421, 2976, 2361, 1718, 1615, 1458, 1366, 1165, 751, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 2H), 7.55-7.51 (m, 1H), 7.41-7.37 (m, 3H), 7.28-7.24 (m, 1H), 6.96-6.92 (m, 1H), 6.87-6.85 (m, 1H), 6.51 (s, 1H), 3.63, 3.35 (AB, J = 16.8 Hz, 2H), 3.29 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.23, 175.87, 153.94, 143.28, 136.39, 133.66, 129.74, 128.92, 128.54, 128.06, 123.94, 122.54, 108.09, 80.06, 59.86, 43.64, 27.98, 26.52. HRMS (EI): Exact mass calcd for $C_{22}H_{24}N_2O_4$ $[M]^+$: 380.1736, Found: 380.1733.

2) The Mukaiyama-Mannich reaction of cyclic ketimines 7.



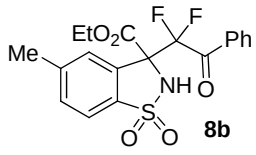


Under an atmosphere of N_2, to a 25 mL dry Schleck tube were added Ph_3PAuCl (3.7 mg, 0.0075 mmol) and AgOTf (1.9 mg, 0.0075 mmol), followed by the addition of 2.5 mL of anhydrous CH_2Cl_2. The reaction mixture was stirred at room temperature for about 30 minutes, and then 200 mg activated MS 5Å was added, followed by the addition of ketimines **7** (0.25 mmol) and difluoroenoxysilanes **1** (0.375 mmol). The resulting mixture was stirred at room temperature till full conversion of **7** by TLC analysis and the reaction mixture was directly subjected to flash column chromatography to afford products **8**, using the indicated eluent.



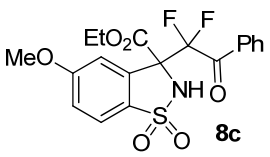
8a

Column chromatography (PE/EtOAc = 5:1 to 3:1) afforded product **8a** in 94% yield as white solid, Mp: 173-175 ^{o}C. IR (neat): 3266, 2923, 1753, 1698, 1319, 1249, 1091, 677 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 2H), 7.96-7.94 (m, 1H), 7.88-7.86 (m, 1H), 7.76-7.67 (m, 3H), 7.52-7.48 (m, 2H), 6.00 (s, 1H), 4.43-4.37 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.69 (d, *J* = 298 Hz, 1F), -105.73 (d, *J* = 298 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.75 (t, *J* = 32 Hz), 165.57 (d, *J* = 7.4 Hz), 136.53, 135.23, 133.58, 131.80, 131.10 (dd, *J* = 3.8 Hz, *J* = 2.9 Hz), 130.39 (dd, *J* = 3.8 Hz, *J* = 2.1 Hz), 130.29 (d, *J* = 2.1 Hz), 128.82, 127.01 (d, *J* = 5.6 Hz), 121.93, 115.38 (t, *J* = 268 Hz), 68.49 (dd, *J* = 26 Hz, *J* = 24 Hz), 64.39, 13.83. MS (EI): 395 (M^+, 0.2), 322 (15), 240 (22), 212 (7), 166 (6), 105 (100), 77 (31), 51 (6). HRMS (EI): Exact mass calcd for $C_{18}H_{15}NO_5F_2S$ $[M]^+$: 395.0639, Found: 395.0640.



8b

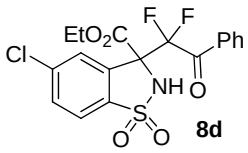
Column chromatography (PE/EtOAc = 4:1 to 2:1) afforded product **8b** in 88% yield as white solid, Mp: 189-191 ^{o}C. IR (neat): 3270, 1734, 1695, 1263, 1189, 1096, 817, 659 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 2H), 7.75-7.65 (m, 3H), 7.53-7.48 (m, 3H), 5.95 (s, 1H), 4.44-4.36 (m, 2H), 2.54 (s, 3H), 1.35 (t, *J* = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.71 (d, *J* = 298 Hz, 1F), -105.94 (d, *J* = 298 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.81 (t, *J* = 29 Hz), 165.63 (d, *J* = 7.4 Hz), 144.84, 135.19, 133.90, 132.71, 131.15 (t, *J* = 3.7 Hz), 130.59 (d, *J* = 1.7 Hz), 130.39 (dd, *J* = 3.7 Hz, *J* = 2.0 Hz), 128.81, 127.09 (d, *J* = 5.5 Hz), 121.63, 115.41 (t, *J* = 268 Hz), 68.30 (t, *J* = 25 Hz), 64.28, 21.91, 13.85. MS (EI): 409 (M^+, 0.2), 336 (16), 254 (23), 226 (6), 180 (5), 105 (100), 77 (28), 51 (4). HRMS (EI): Exact mass calcd for $C_{19}H_{17}NO_5F_2S$ $[M]^+$: 409.0796, Found: 409.0793.



8c

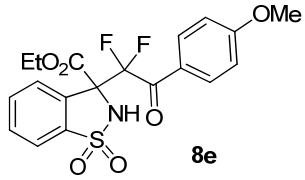
Column chromatography (PE/EtOAc = 4:1 to 2:1) afforded product **8c** in 99% yield as white solid, Mp: 158-160 ^{o}C. IR (neat): 3255, 2923, 1752, 1699, 1595, 1260, 1171, 717, 665 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 2H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.69-7.65 (m, 1H), 7.50 (t, *J* = 8 Hz, 2H), 7.37-7.36 (m, 1H), 7.22-7.20 (m, 1H), 5.96 (s, 1H), 4.48-4.34 (m, 2H), 3.93 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.83 (d, *J* = 297 Hz, 1F), -106.10 (d, *J* = 297 Hz, 1F); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 187.74 (dd, *J* = 32 Hz, *J* = 29 Hz), 165.50 (d, *J* = 7.4 Hz), 163.73, 135.20, 132.78 (d, *J* =1.8 Hz), 131.11 (t, *J* = 3.7 Hz), 130.39 (dd, *J* = 3.7 Hz, *J* = 1.9 Hz), 128.81, 128.49, 123.21, 118.25, 115.38 (t, *J* = 269 Hz), 111.30 (d, *J* = 5.8 Hz), 68.10 (t, *J* = 24 Hz), 64.33, 56.04, 13.88. MS (EI): 425 (M^+, 1), 352 (15), 270 (19), 242 (3), 196 (5), 105 (100), 77 (26), 51 (4). HRMS (EI): Exact mass calcd for $C_{19}H_{17}NO_6F_2S$ $[M]^+$: 425.0745, Found: 425.0749.



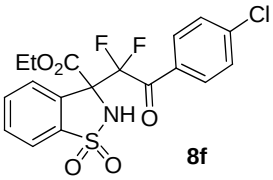
8d

Column chromatography (PE/EtOAc = 4:1 to 2:1) afforded product **8d** in 94% yield as white solid, Mp: 146-148 °C. IR (neat): 3259, 2923, 1737, 1696, 1254, 1180, 1094, 708, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09-8.08 (m, 2H), 7.92-7.91 (m, 1H), 7.81-7.79 (m, 1H), 7.72-7.67 (m, 2H), 7.53-7.49 (m, 2H), 6.05 (s, 1H), 4.46-4.40 (m, 2H), 1.37 (t, *J* = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.50 (d, *J* = 298 Hz, 1F), -105.42 (d, *J* = 298 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.44 (dd, *J* = 32 Hz, *J* = 29 Hz), 165.03 (d, *J* = 5.2 Hz), 140.19, 135.37, 135.10, 132.33, 132.26 (d, *J* = 1.8 Hz), 130.93 (t, *J* = 3.6 Hz), 130.40 (dd, *J* = 3.7 Hz, *J* = 2.1 Hz), 128.88, 127.18 (d, *J* = 6.0 Hz), 123.05, 115.27 (t, *J* = 269 Hz), 68.09 (dd, *J* = 26 Hz, *J* = 24 Hz), 64.73, 13.84. MS (EI): 429 (M^+, 0.3), 356 (7), 274 (13), 246 (4), 156 (5), 105 (100), 77 (31), 51 (5). HRMS (EI): Exact mass calcd for $C_{18}H_{14}NO_5F_2S^{35}Cl$ $[M]^+$: 429.0249, Found: 429.0247.



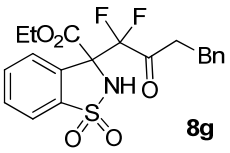
8e

Column chromatography (PE/EtOAc = 5:1 to 3:1) afforded product **8e** in 97% yield as white solid, Mp: 151-153 °C. IR (neat): 3308, 1750, 1674, 1594, 1245, 1090, 1020, 761 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (m, 2H), 7.96-7.93 (m, 1H), 7.88-7.86 (m, 1H), 7.76-7.72 (m, 2H), 6.98-6.94 (m, 2H), 5.98 (s, 1H), 4.43-4.35 (m, 2H), 3.89 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.3 (dd, *J* = 296 Hz, *J* = 4 Hz, 1F), -105.10 (dd, *J* = 298 Hz, *J* = 5 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.89 (t, *J* = 31 Hz), 165.69 (d, *J* = 7.4 Hz), 165.24, 136.59, 133.53, 133.09 (t, *J* = 20 Hz), 131.72, 130.46, 127.05 (d, *J* = 5.7 Hz), 123.96, 121.90, 115.75 (t, *J* = 268 Hz), 114.20, 68.55 (t, *J* = 24 Hz), 64.26, 55.66, 13.85. MS (EI): 425 (M^+, 2), 352 (4), 240 (2), 212 (2), 186 (12), 135 (100), 92 (6), 77 (9). HRMS (EI): Exact mass calcd for $C_{19}H_{17}NO_6F_2S$ $[M]^+$: 425.0745, Found: 425.0749.



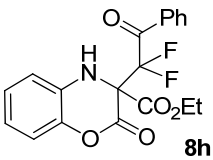
8f

Using 5 mol% of PPh_3AuOTf. Column chromatography (PE/EtOAc = 4:1 to 3:1) afforded product **8f** in 96% yield as white solid, Mp: 131-133 ^oC. IR (neat): 3258, 1739, 1699, 1590, 1091, 771, 709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H), 7.96-7.93 (m, 1H), 7.88-7.85 (m, 1H), 7.78-7.71 (m, 2H), 7.49-7.47 (m, 2H), 6.00 (s, 1H), 4.43-4.37 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.88 (d, *J* = 297 Hz, 1F), -105.87 (d, *J* = 297 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.76 (dd, *J* = 32 Hz, *J* = 29 Hz), 165.30 (d, *J* = 5.4 Hz), 142.04, 136.55, 133.62, 131.85, 131.75 (dd, *J* = 3.9 Hz, *J* = 2.1 Hz), 130.12 (d, *J* = 1.6 Hz), 129.49 (d, *J* = 3.5 Hz), 129.26, 126.97 (d, *J* = 5.3 Hz), 121.93, 115.27 (t, *J* = 268 Hz), 68.43 (dd, *J* = 26 Hz, *J* = 24 Hz), 64.48, 13.81. MS (EI): 429 (M^+, 0.2), 356 (15), 240 (24), 212 (8), 166 (7), 141 (33), 139 (100), 111 (24), 75 (9). HRMS (EI): Exact mass calcd for $C_{18}H_{14}NO_5F_2S^{35}Cl$ $[M]^+$: 429.0249, Found: 429.0236.



8g

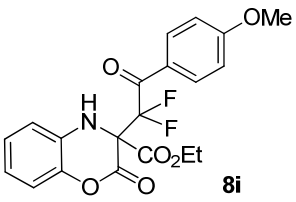
Using 5 mol% of PPh_3AuOTf. Column chromatography (PE/EtOAc = 4:1 to 3:1) afforded product **8g** in 96% yield as white solid, Mp: 85-87 ^oC. IR (neat): 3261, 1744, 1401, 1205, 1037, 774, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92-7.90 (m, 1H), 7.83-7.81 (m, 1H), 7.75-7.68 (m, 2H), 7.31-7.26 (m, 2H), 7.23-7.18 (m, 3H), 5.90 (s, 1H), 4.43-4.35 (m, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.89 (d, *J* = 278 Hz, 1F), -113.60 (d, *J* = 278 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.81 (t, *J* = 28 Hz), 165.12 (d, *J* = 5.7 Hz), 139.67, 136.25, 133.67, 131.80, 130.02, 128.57, 128.32, 127.00 (d, *J* = 3.3 Hz), 126.42, 121.83, 113.22 (t, *J* = 266 Hz), 68.21 (t, *J* = 26 Hz), 64.74, 39.25, 28.24, 13.81. MS (EI): 423 (M^+, 2), 403 (22), 350 (5), 330 (39), 240 (25), 133 (75), 105 (100), 91 (95), 77 (14). HRMS (EI): Exact mass calcd for $C_{20}H_{19}NO_5F_2S$ $[M]^+$: 423.0952, Found: 423.0953.



8h

Using 5 mol% of PPh_3AuOTf. Column chromatography (PE/EtOAc = 5:1 to 4:1) afforded product **8h** in 67% yield as yellow solid, Mp: 80-82 ^oC. IR (neat): 3347, 2924, 1780, 1716, 1258, 1028, 743, 663 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 2H), 7.68-7.64 (m, 1H), 7.52-7.49 (m, 2H), 7.08-7.02 (m, 2H), 6.93-6.86 (m, 2H), 5.05 (s, 1H), 4.32-4.27 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.84 (d,

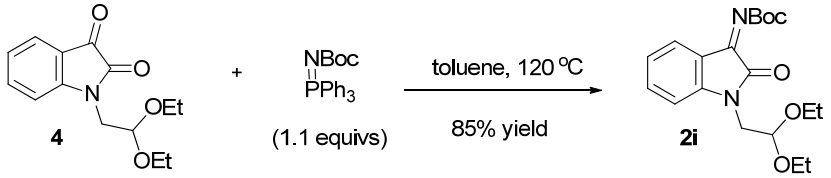
J = 301 Hz, 1F), -106.07 (d, *J* = 301 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.78 (dd, *J* = 31 Hz, *J* = 28 Hz), 164.92, 158.61, 139.98, 134.81, 131.53, 130.23 (dd, *J* = 3.6 Hz, *J* = 2.3 Hz), 128.74, 128.53, 125.57, 121.39, 116.86, 115.70, 115.10 (dd, *J* = 270 Hz, *J* = 265 Hz), 67.21 (t, *J* = 22 Hz), 63.72, 13.76. GC-MS: 375 (M^+, 11), 302 (4), 220 (46), 192 (15), 174 (30), 146 (10), 105 (100), 77 (36). HRMS (EI): Exact mass calcd for $C_{19}H_{15}NO_5F_2$ $[M]^+$: 375.0918, Found: 375.0919.



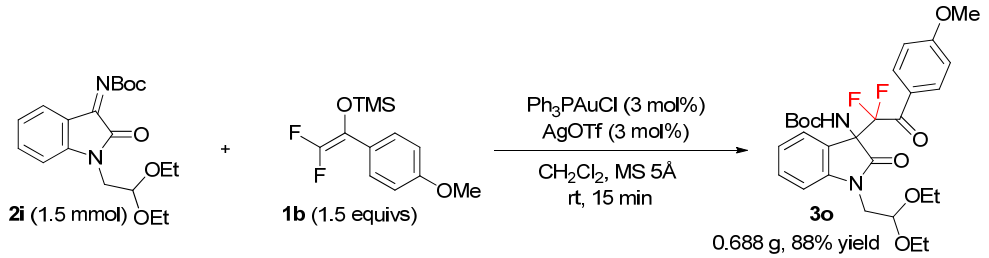
8i

Using 5 mol% of PPh_3AuOTf. Column chromatography (PE/EtOAc = 5:1 to 3:1) afforded product **8i** in 99% yield as yellow solid, Mp: 90-92 ^{o}C. IR (KBr): 3316, 2979, 2360, 1764, 1733, 1598, 1031, 881, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.08 (m, 2H), 7.08-7.01 (m, 2H), 6.99-6.95 (m, 2H), 6.91-6.84 (m, 2H), 5.06 (s, 1H), 4.32-4.27 (m, 2H), 3.89 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.92 (d, *J* = 301 Hz, 1F), -104.81 (d, *J* = 301 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.82 (t, *J* = 29 Hz), 165.00, 158.47, 139.94, 132.95 (t, *J* = 3 Hz), 128.59, 125.50, 124.14 (t, *J* = 3.4 Hz), 121.17, 116.80, 115.55 (t, *J* = 268 Hz), 115.54, 114.13, 67.11 (d, *J* = 22 Hz), 63.63, 55.61, 13.76. GC-MS: 405 (M^+, 18), 322 (4), 313 (5), 220 (13), 186 (84), 135 (100), 107 (18), 92 (15),77 (24). HRMS (EI): Exact mass calcd for $C_{20}H_{17}NO_6F_2$ $[M]^+$: 405.1024, Found: 405.1022.

Part II. Total synthesis of CF_2-AG-041R.



To a 100 mL seal tube were added *N*-Boc-triphenyliminophosphorane (943 mg, 2.5 mmol) and isatin **4** (580 mg, 2.2 mmol), followed by 10.0 mL of anhydrous toluene.[4] The reaction mixture was stirred vigorously at 120 °C until isatin **4** was completed (about 10 h), and cooled to room temperature. The resulting mixture was directly purified by column chromatography (PE/EtOAc = 10/1 to 7/1) to afford **2i** (680 mg) in 85% yield as yellow solid.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.47-7.43 (m, 1H), 7.09-7.05 (m, 2H), 4.68-4.66 (m, 1H), 3.81-3.71 (m, 4H), 3.56-3.47 (m, 1H), 1.63 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.46, 157.50, 153.05, 148.09, 135.01, 123.94, 123.23, 119.14, 111.09, 100.64, 83.33, 63.79, 43.55, 27.96, 15.17.



According to the general procedure of Mukaiyama-Mannich reaction described above, product **3o** was obtained in 88% yield (688.1 mg) as white foamy solid after column chromatography (using pure CH_2Cl_2 to CH_2Cl_2/EtOAc = 30/1 as the eluent). Mp = 103-105 °C. IR (neat): 3379, 2979, 1710, 1681, 1595, 1491, 1265, 1120, 747 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (m, 2H), 7.31-7.27 (m, 2H), 7.09-7.07 (m, 1H), 6.98-6.95 (m, 1H), 6.87-6.85 (m, 2H), 6.22 (s, 1H), 4.71-4.69 (m, 1H), 4.03-3.98 (m, 1H), 3.86 (s, 3H), 3.78-3.51 (m, 5H), 1.27 (s, 9H), 1.17-1.11 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.80 (d, *J* = 273 Hz, 1F), -107.90 (d, *J* = 273 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.92 (t, *J* = 28 Hz), 171.24, 164.67, 153.28, 144.84, 132.86 (t, *J* = 4.2 Hz), 129.99, 125.59, 124.85, 123.67, 122.44, 115.67 (t, *J* = 265 Hz), 113.78, 110.13, 101.09, 80.79, 65.06 (t, *J* = 24 Hz), 63.89, 63.76, 55.53, 44.33, 27.98, 15.24, 15.22. MS (EI): 548 (M^+, 6), 402 (8), 217 (44), 135 (72), 103 (100), 92 (7), 77 (15), 75 (25), 44 (18). HRMS (EI): Exact mass calcd for $C_{28}H_{34}N_2O_7F_2$ $[M]^+$: 548.2334, Found: 548.2336.

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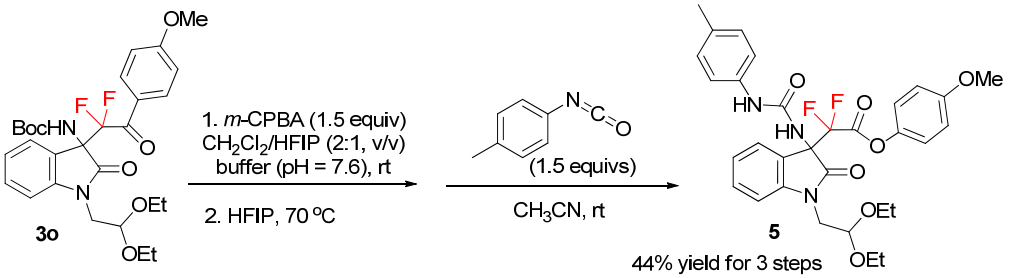
[4] W. Yan, D. Wang, J. Feng, P. Li, D. Zhao and R. Wang, *Org. Lett.*, 2012, **14**, 2512.

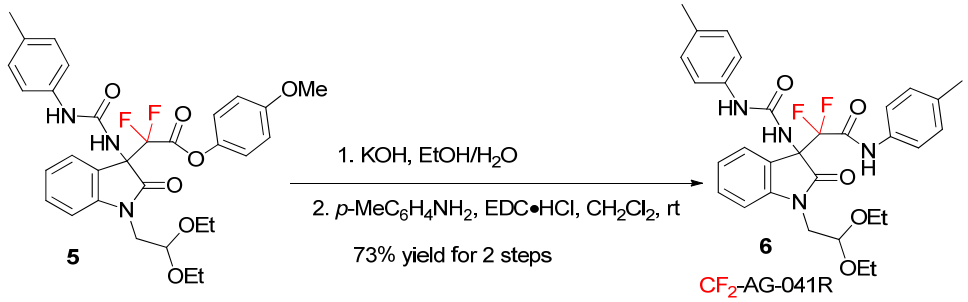
[5] N. Hara, S. Nakamura, M. Sano, R. Tamura, Y. Funahashi and N. Shibata, *Chem. Eur. J.*, 2012, **18**, 9276.



The product **3o** (129.6 mg, 0.25 mmol) was dissolved in CH_2Cl_2/HFIP (2:1, 3.0 mL), followed by the addition of *m*-chloroperoxybenzoic acid (*m*-CPBA) (78.7 mg, 0.375 mmol, 85%) and phosphate buffer (0.25 mL, pH = 7.6) at ambient temperature.[6] The mixture was stirred until full consumption of **3o** by TLC analysis (ca. 2 h), and then quenched by saturated $Na_2S_2O_3$ (aq), followed by extraction using CH_2Cl_2 (10.0 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ and brine (10.0 mL × 3), and then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was directly used for the next step.

Under N_2 atmosphere, 5.0 mL HFIP was added to the crude ester and the mixture was warmed to 70 °C and stirred at 70 °C until full consumption of crude ester by TLC analysis (about 72 h). Then the reaction mixture was concentrated under reduced pressure, and the residue was directly used for the next step.[5] To a solution of crude mixture in MeCN (1.0 mL) was added *p*-tolyl isocyanate (50.5 mg, 0.38 mmol) at room temperature. After the reaction was stirred overnight, the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (using PE/EtOAc = 5/1 to 4/1 as eluent) to afford **5** (66.0 mg, 44% yield for 3 steps) as a white foamy solid. Mp = 55-58 ºC. IR (KBr): 3369, 2976, 2828, 1779, 1733, 1613, 1548, 1502, 1315, 1180, 816, 754 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): 8.45 (s, 1H), δ 7.46-7.40 (m, 2H), 7.24-7.20 (m, 2H), 7.15-7.11 (m, 4H), 7.02-6.96 (m, 4H), 4.78-4.75 (m, 1H), 3.97-3.92 (m, 1H), 3.82 (s, 3H), 3.77-3.66 (m, 3H), 3.63-3.47 (m, 2H), 2.20 (s, 3H), 1.11-1.06 (m, 6H); ^{19}F NMR (376 MHz, acetone-d_6): δ 63.70 (d, J = 255 Hz, 1F), 61.90 (d, J = 255 Hz, 1F); ^{13}C NMR (100 MHz, acetone-d_6): δ 171.71 (d, J = 5 Hz), 161.43 (t, J = 31 Hz), 159.19, 153.84, 146.15, 144.16, 137.98, 132.18, 130.92, 129.96, 125.18, 125.10, 123.32, 122.94, 118.97, 118.88, 115.48, 114.37 (t, J = 265 Hz), 111.07, 101.47, 65.66 (dd, J = 27 Hz, J = 22 Hz), 63.76 (d, J = 5.9 Hz), 55.98, 45.09, 20.65, 15.64. MS (ESI): 620.03 [$(M+Na)^+$, 100]. HRMS (EI): Exact mass calcd for $C_{31}H_{33}N_3O_7F_2$ $[M]^+$: 597.2287, Found: 597.2285.

[6] S. Kobayashi, H. Tanaka, H. Amii and K. Uneyama, *Tetrahedron*, 2003, **59**, 1547.



KOH (7.5 mg, 0.13 mmol) was added to a solution of **5** (29.5 mg, 0.05 mmol) in EtOH/H2O (9:1, v/v, 5.0 mL) at 0 °C, and the mixture was warmed to room temperature and stirred until the complete conversion of **5** by TLC analysis (about 4 h). The reaction was poured onto H_2O (15 mL) and 1 *N* HCl (5.0 mL), extracted with EtOAc, washed with brine, dried over Na_2SO_4, concentrated in vacuo. To a solution of crude mixture in CH_2Cl_2 (3.0 mL) at 0 °C were added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC・HCl, 14.5 mg, 0.075 mmol) and *p*-toluidine (8.1 mg, 0.075 mmol) at 0 °C. The mixture was stirred for 2 h at 0 °C. The reaction was poured onto H_2O (15 mL) and 1 *N* HCl (5.0 mL), extracted with CH_2Cl_2. The combined organic layers were washed with brine (10.0 mL × 3), and then dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (using PE/EtOAc = 5/1 to 3/1 as eluent) to give CF_2-AG-041R (**6**) (21.1 mg, 73% yield for 2 steps) as white solid. Mp = 125-127 ºC. IR (neat): 3298, 2919, 1684, 1611, 1536, 1371, 1127, 1062, 812, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.38-7.31 (m, 4H), 7.14-7.03 (m, 8H), 6.97-6.95 (m, 2H), 4.76-4.73 (m, 1H), 4.04-3.99 (m, 1H), 3.79-3.65 (m, 3H), 3.59-3.48 (m, 2H), 2.32 (s, 3H), 2.23 (s, 3H), 1.12 (t, *J* = 6.8 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.33 (d, *J* = 262 Hz, 1F), -113.46 (d, *J* = 261 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.36, 160.29 (t, *J* = 28 Hz), 153.46, 144.41, 136.03, 135.48, 132.89, 132.82, 130.14, 129.67, 129.34, 124.86, 123.91, 122.98, 121.29, 120.16, 113.47 (t, *J* = 260 Hz), 110.40, 100.68, 65.23 (t, *J* = 25 Hz), 63.59, 44.37, 20.96, 20.72, 15.25, 15.22. MS (EI): 580 (M^+, 2), 427 (14), 370 (4), 133 (33), 106 (81), 103 (100), 75 (31), 44 (32); HRMS (EI): Exact mass calcd for $C_{31}H_{34}N_4O_5F_2$ $[M]^+$: 580.2497, Found: 580.2499.

Part III. Initial NMR experiments

To probe the mechanism of Mukaiyama-Mannich reaction of ketimine and difluoroenoxysilane **1a** catalyzed by $Ph_3PAuOTf$, NMR analysis was attempted. The ^{19}F, ^{31}P and ^{13}C NMR studies were recored using a Bruker Ascend 500 MHz spectrometer at room temperature in $CDCl_3$, which was used after distilled from CaH_2. The general procedure was as follows: To a 5 mm NMR tube was added imine **7a** (0.1 mmol) or difluoroenoxysilane **1a** (0.1 mmol), and then a solution of pre-prepared $Ph_3PAuOTf$ in $CDCl_3$ (0.025 mmol in 0.5 mL $CDCl_3$) was added. The resulting mixture was shaking vigorously and then for NMR analysis. The ^{31}P NMR studies was conducted using H_3PO_4 (δ = 0.00 ppm) as the external standard. The ^{19}F NMR studies was conducted using $CFCl_3$ (δ = 0.00 ppm) as the internal standard.

The NMR analysis suggested there might be some interaction between $Ph_3PAuOTf$ and imine **7a** at room temperature, as obvious difference between the characteristic peak of free $Ph_3PAuOTf$ and that of the mixture of ketimine **7a** and $Ph_3PAuOTf$ (25 mol%) were monitored by ^{19}F, ^{31}P and ^{13}C NMR analysis. On ^{19}F NMR spectra, the characteristic peak of CF_3 group of $Ph_3PAuOTf$ was at -77.258 ppm, which was shifted to -77.413 in the mixture of **7a** and $Ph_3PAuOTf$ (Figure S1). By ^{31}P NMR analysis, the peak corresponding to the bounded Ph_3P of $Ph_3PAuOTf$ at 28.374 ppm was shifted to 28.727 ppm in the mixture of **7a** and $Ph_3PAuOTf$ (Figure S2). In addition, the addition of $Ph_3PAuOTf$ to the solution of **7a** induced obvious shift of the characteristic peak of both CO_2Et and imine group on ^{13}C NMR spectra, although we could not assign them currently (Figure S3).

Figure S1. The ^{19}F NMR study of the mixture of imine **7a** (0.1 mmol) and $Ph_3PAuOTf$ (25 mol%).

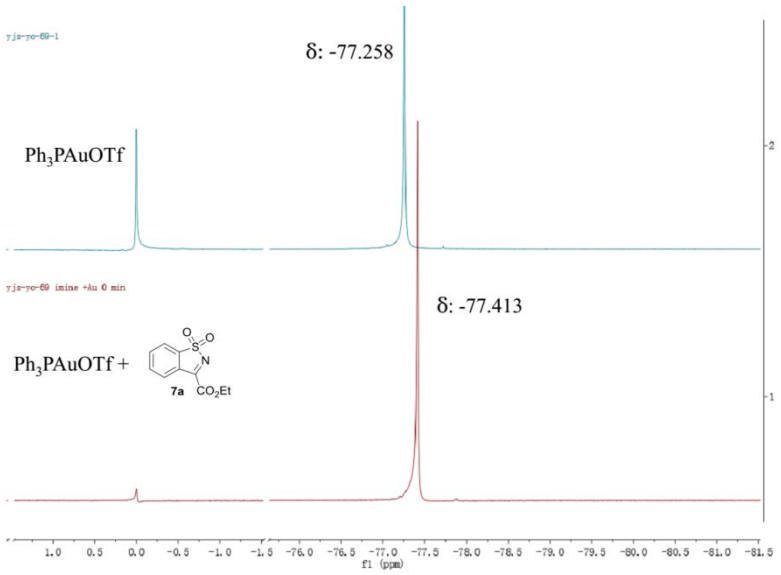


Figure S2. The ^{19}P NMR study of the mixture of imine **7a** (0.1 mmol) and $Ph_3PAuOTf$ (25 mol%).

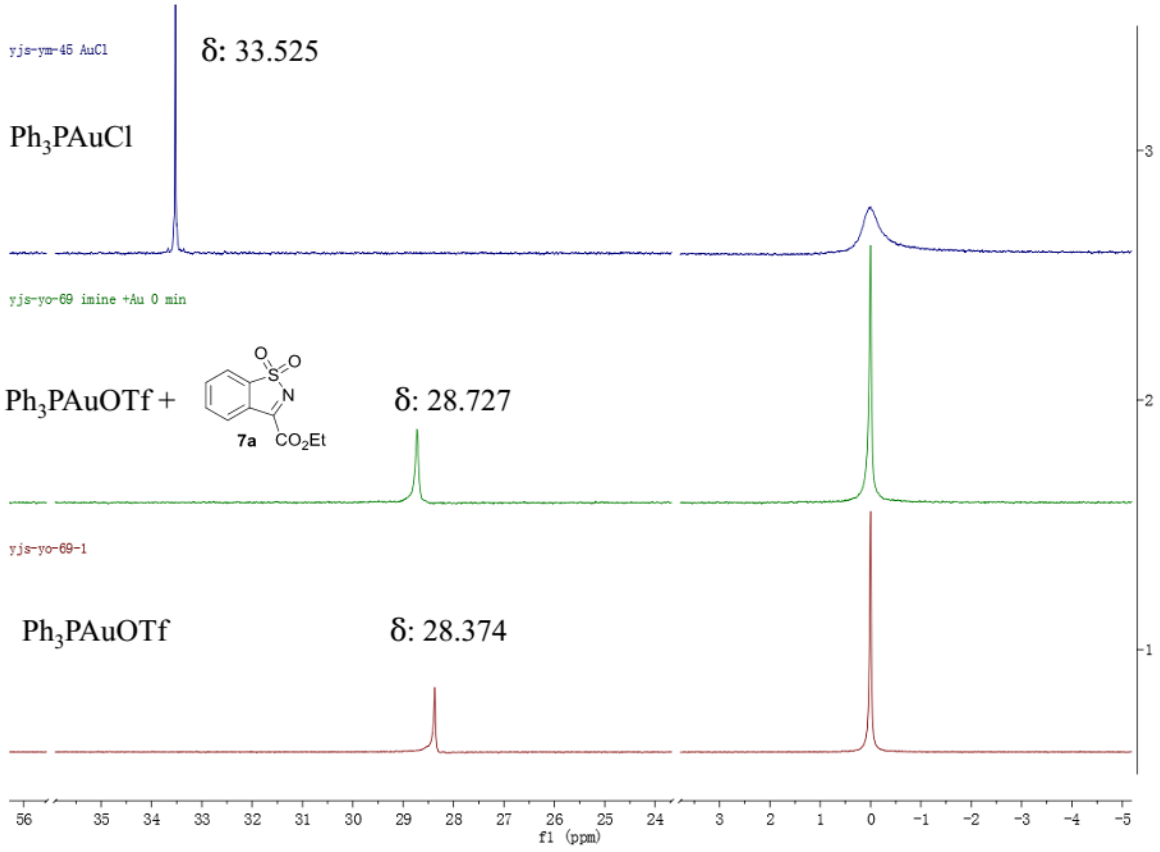
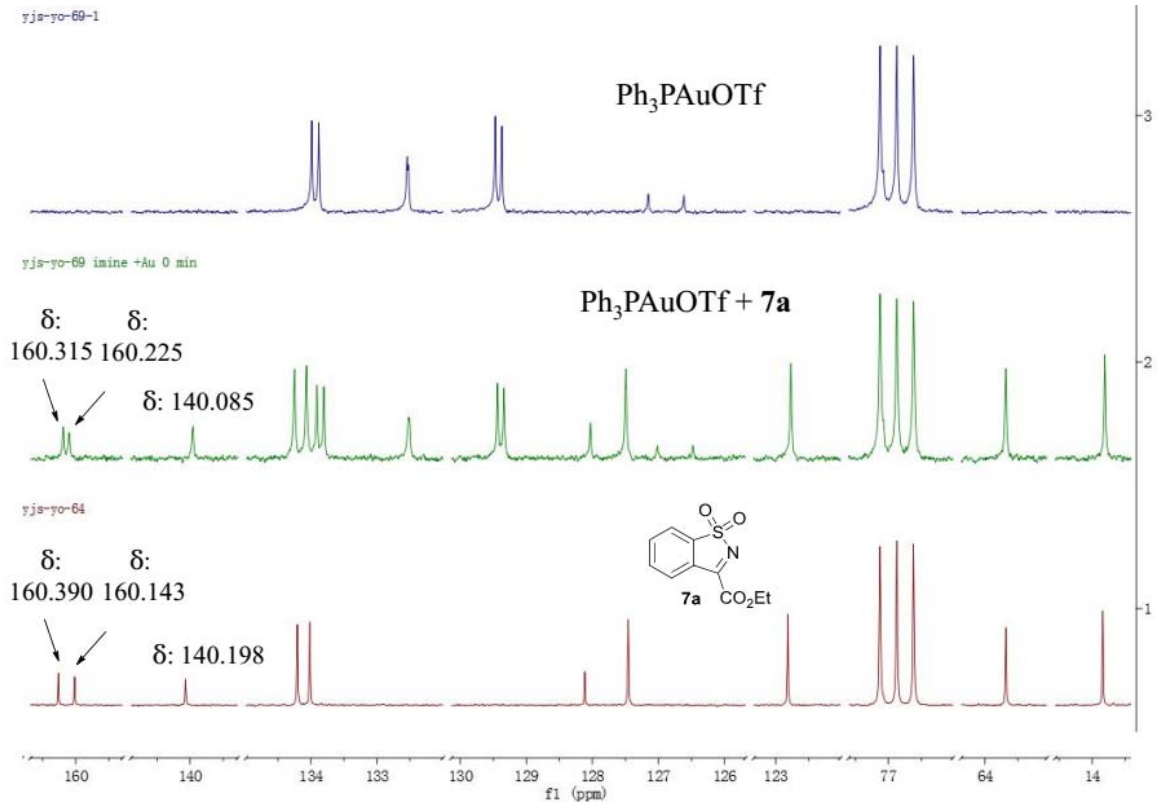


Figure S3. The ^{13}C NMR study of the mixture of imine **7a** (0.1 mmol) and $Ph_3PAuOTf$ (25 mol%).



Because difluoroenoxysilane **1a** contained a C=C double bond that might interact with Au(I), an excellent π acid capable of activating C=C bond, we then investigated whether there might be some interaction between difluoroenoxysilane **1a** and $Ph_3PAuOTf$ at room temperature. It was found that when mixing a solution of difluoroenoxysilane **1a** and $Ph_3PAuOTf$, a group of new peaks appeared at around -105 ppm and -115 ppm in ^{19}F NMR spectra (Figure S4). Meanwhile, the peak corresponding to $PhCOCF_2H$ generated from the hydrolysis of difluoroenoxysilane **1a** was also detected. On the other hand, on ^{31}P NMR spectra, a new signal at 45.636 ppm developed after mixing **1a** and $Ph_3PAuOTf$, whilst the corresponding peak of $Ph_3PAuOTf$ changed from 28.374 to 28.612 ppm (Figure S5). Currently, we cannot give a reasonable explanation for these observations.

Figure S4. The ^{19}P NMR study of the mixture of difluoroenoxysilane **1a** (0.1 mmol) and $Ph_3PAuOTf$ (25 mol%).

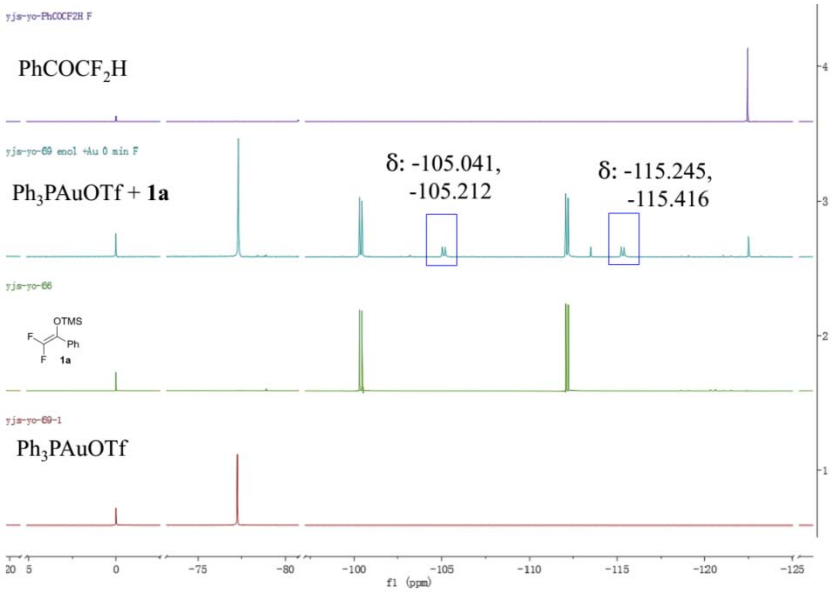
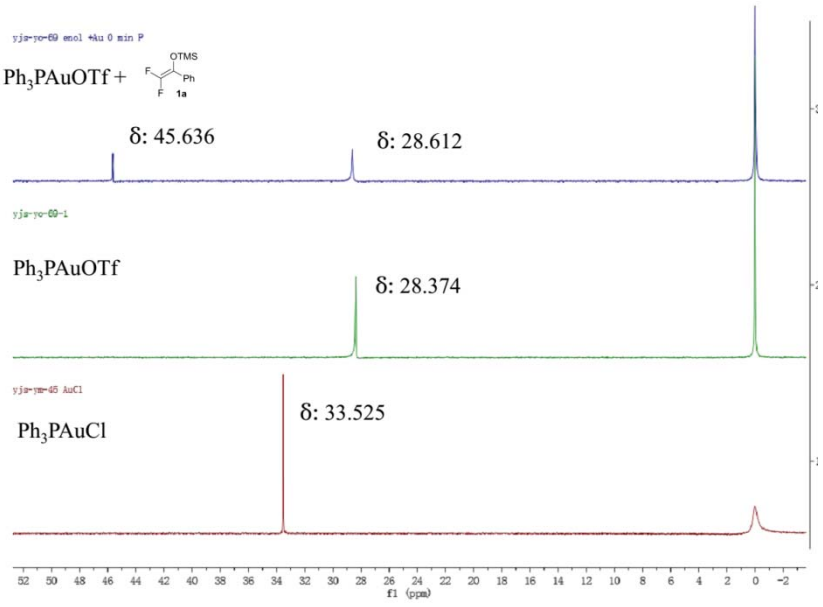
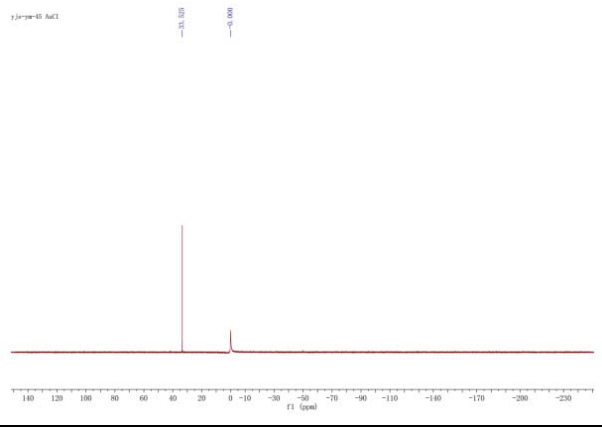


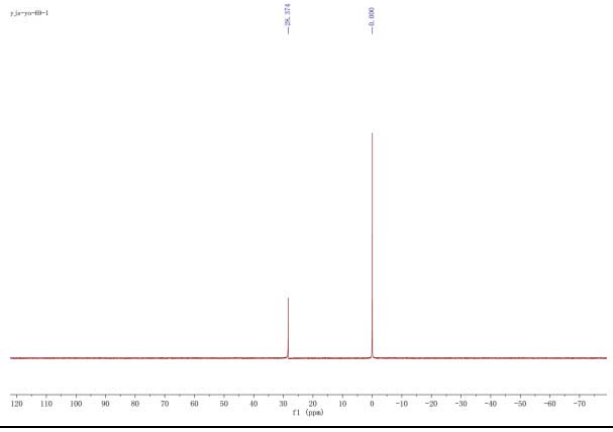
Figure S5. The ^{19}P NMR study of the mixture of difluoroenoxysilane **1a** (0.1 mmol) and $Ph_3PAuOTf$ (25 mol%).



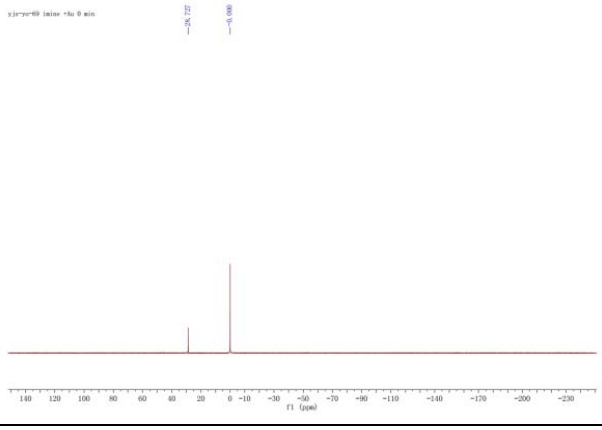
Full ^{31}P NMR spectrum in $CDCl_3$

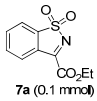


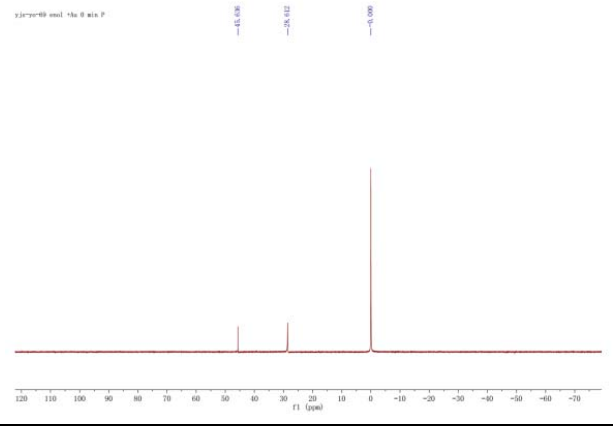
Ph_3PAuCl



$Ph_3PAuOTf$

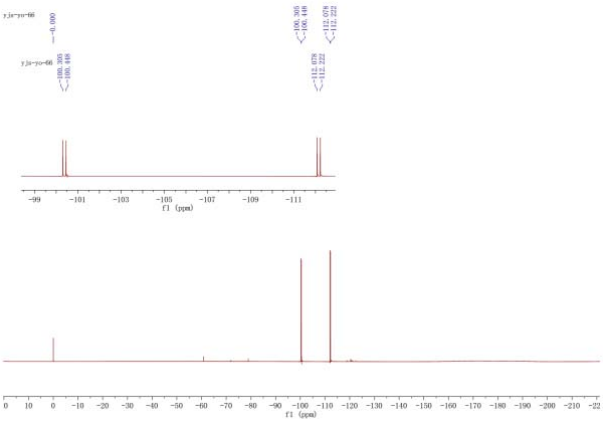


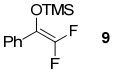
$Ph_3PAuOTf$ (25 mol%) +  **7a** (0.1 mmol)

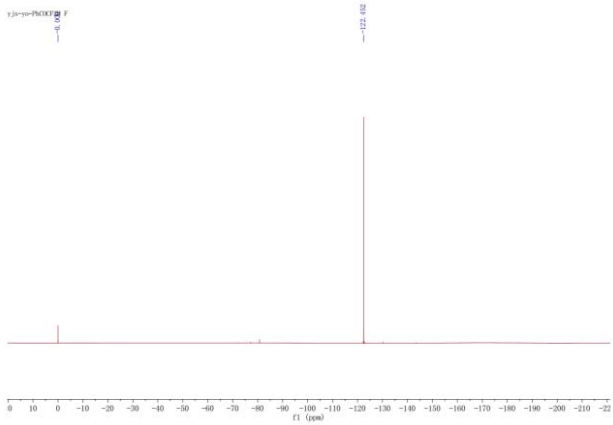


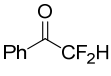
$Ph_3PAuOTf$ (25 mol%) +  **1a** (0.1 mmol)

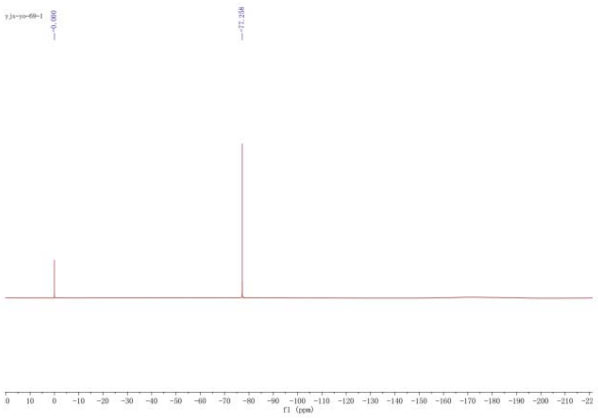
Full ^{19}F NMR spectrum in $CDCl_3$



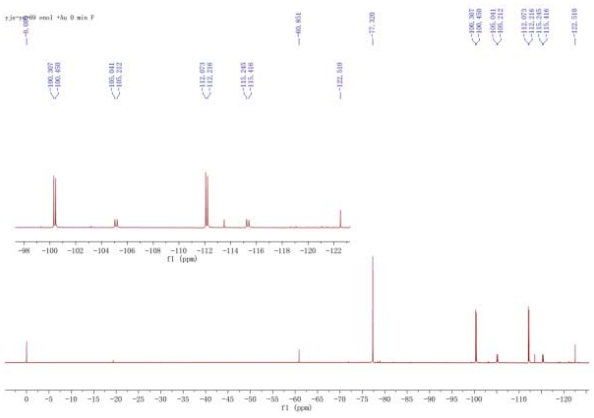
 **9**

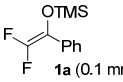


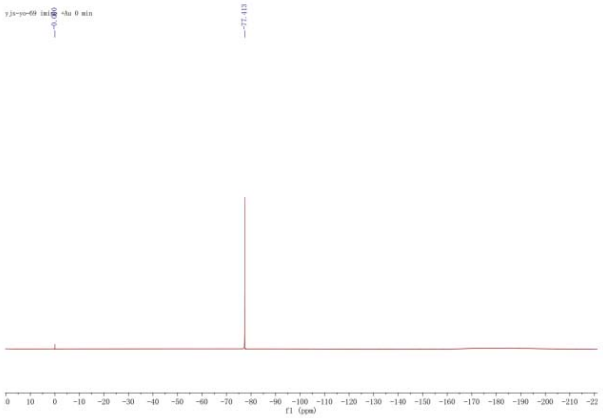


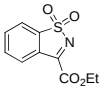


$Ph_3PAuOTf$

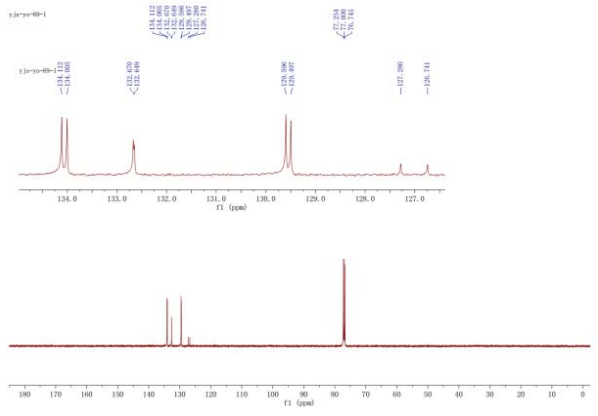


$Ph_3PAuOTf$ (25 mol%) +  **1a** (0.1 mmol)

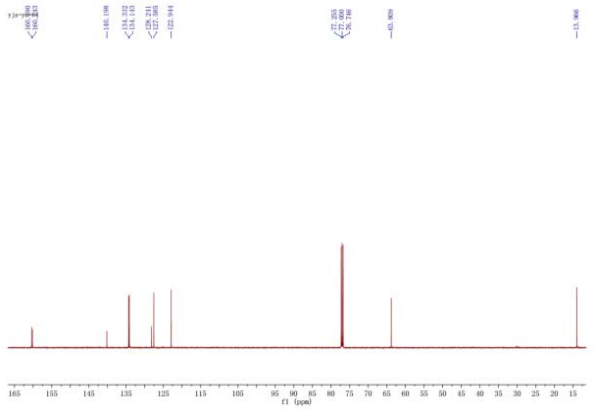


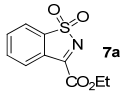
$Ph_3PAuOTf$ (25 mol%) +  **7a** (0.1 mmol)

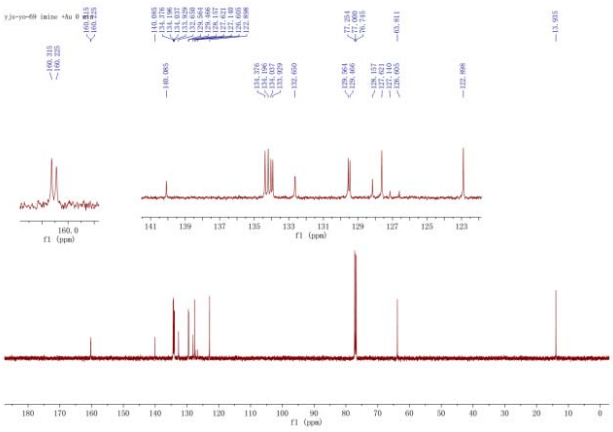
Full ^{19}C NMR spectrum in $CDCl_3$

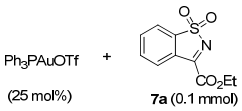


$Ph_3PAuOTf$

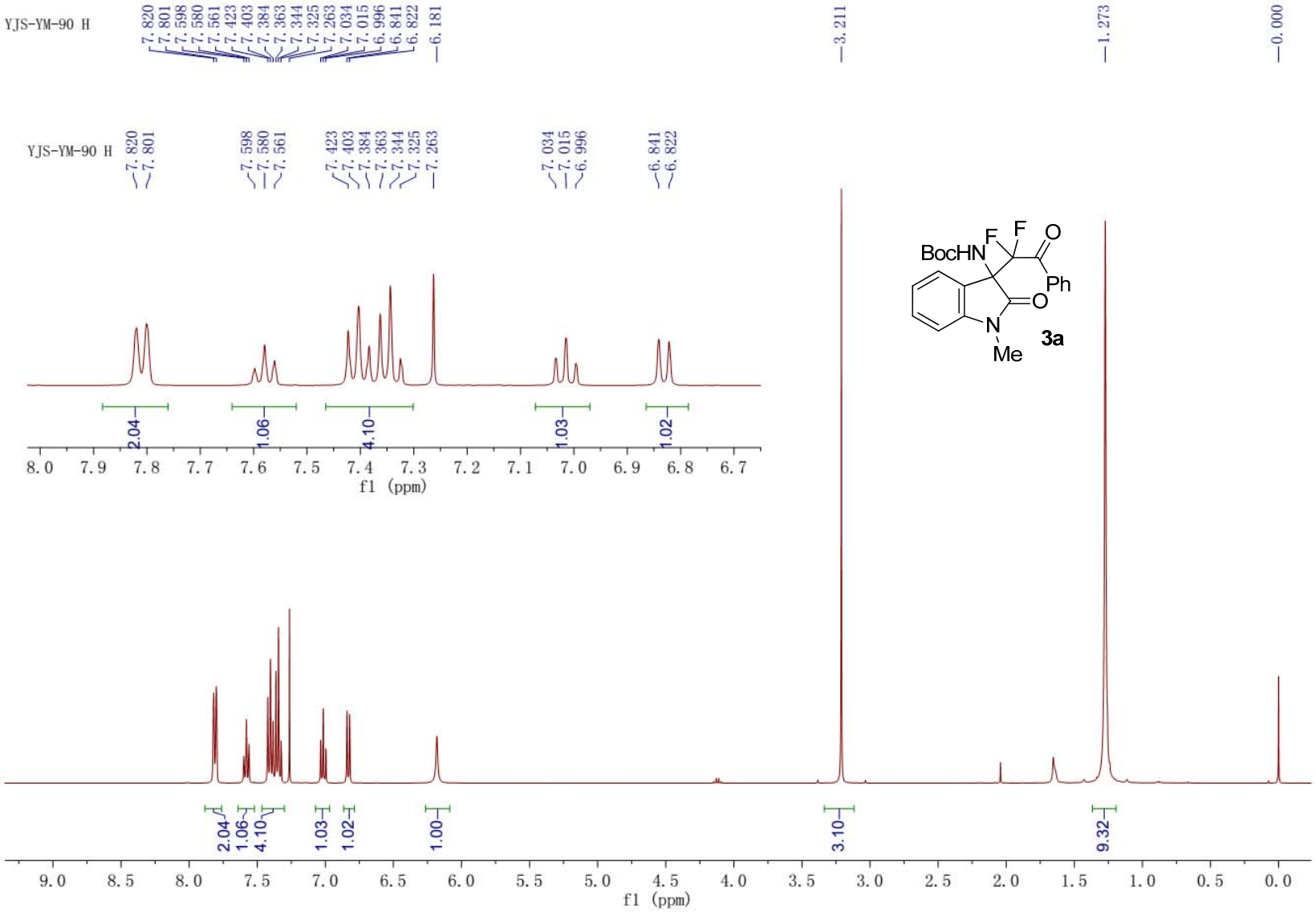


 **7a**

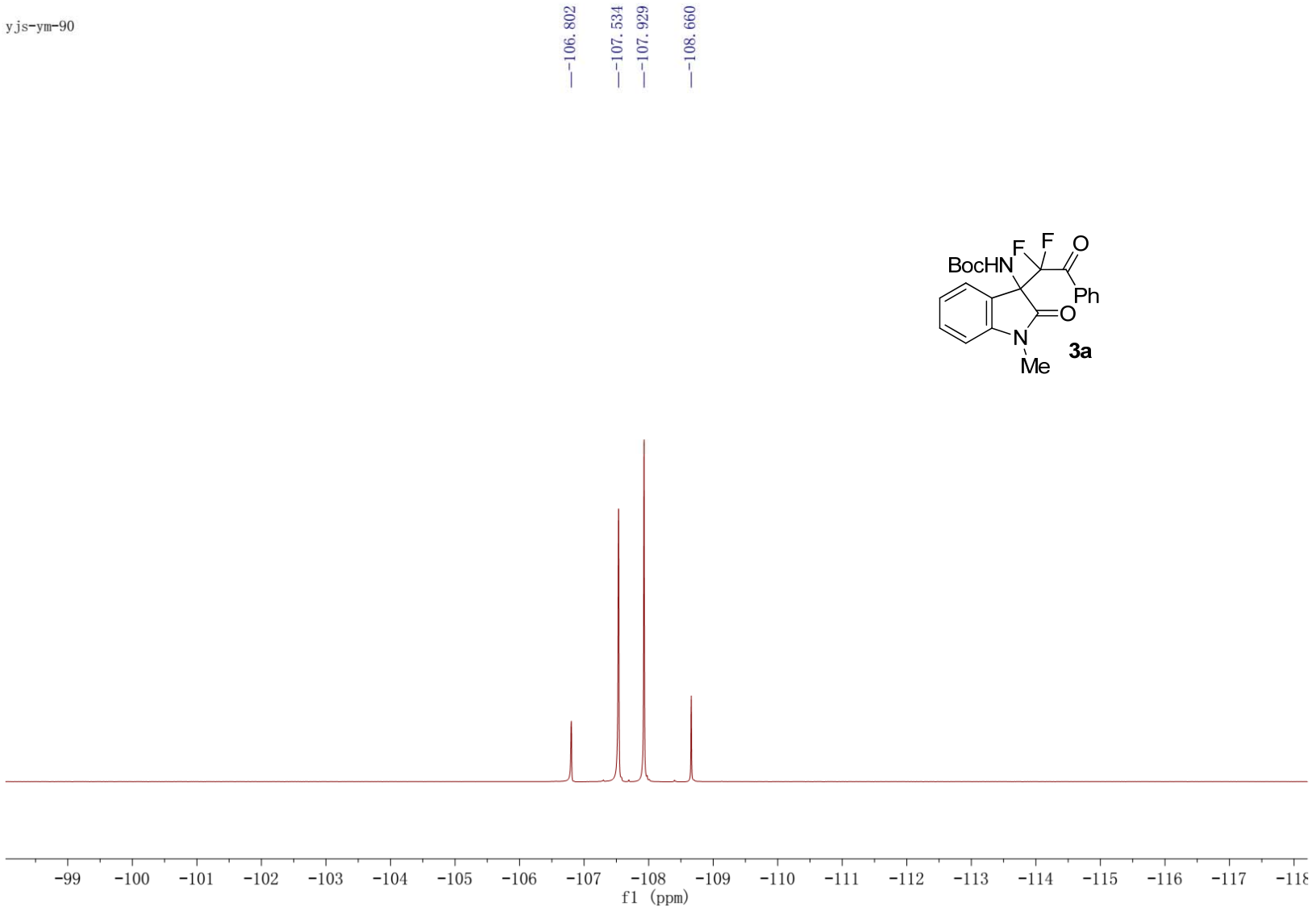


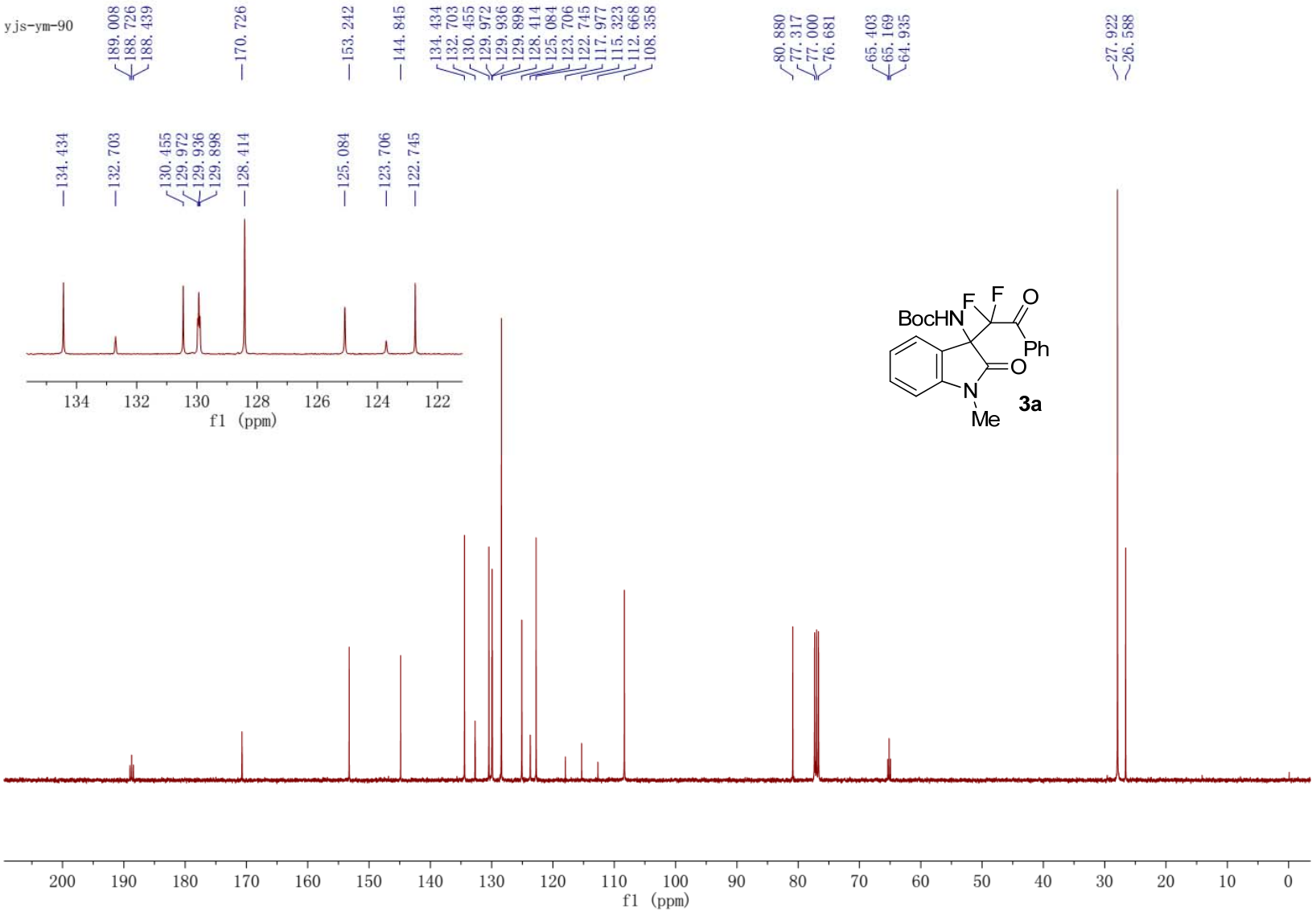


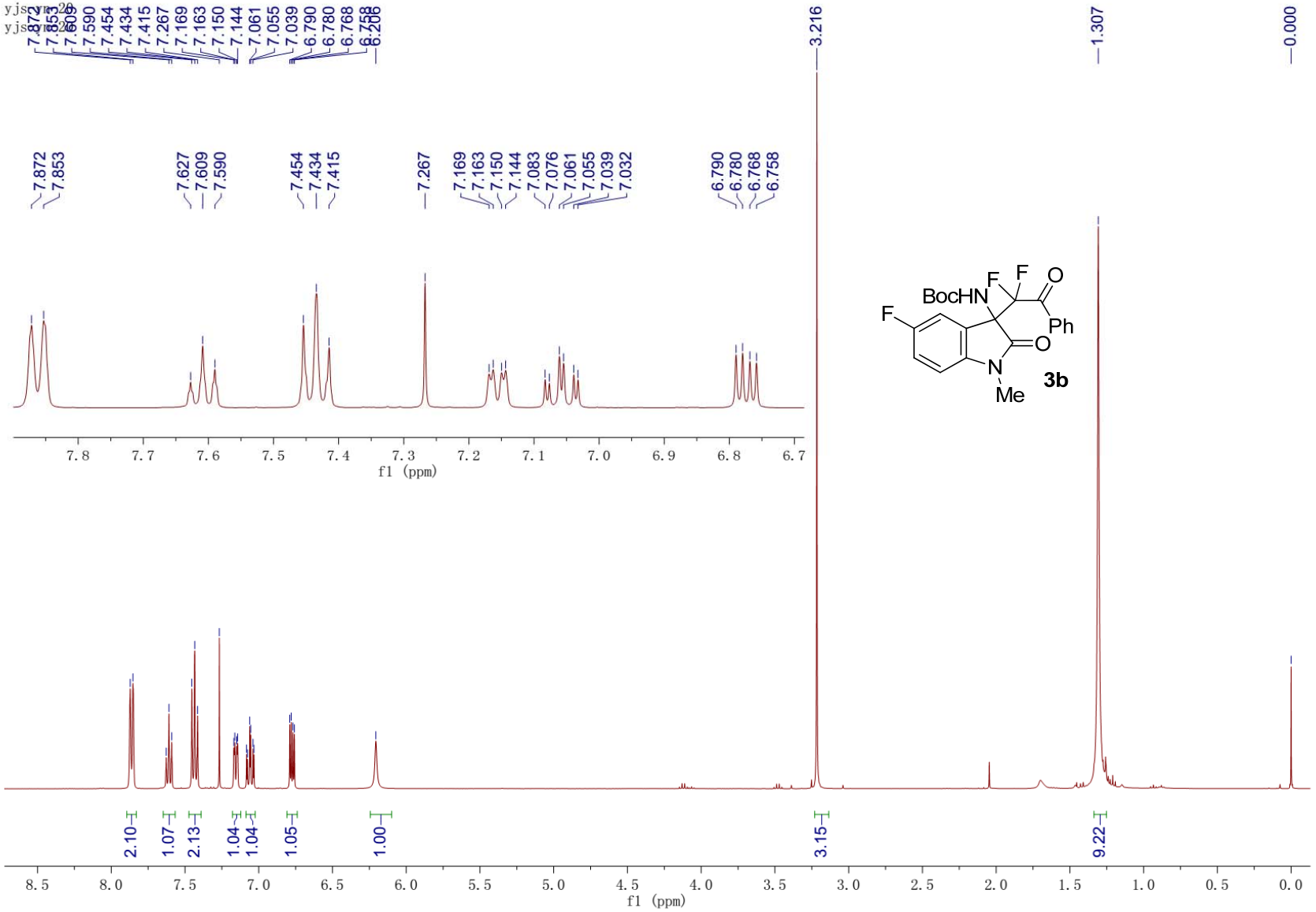
Part IV. ^{1}H, ^{19}F, ^{13}C NMR spectra

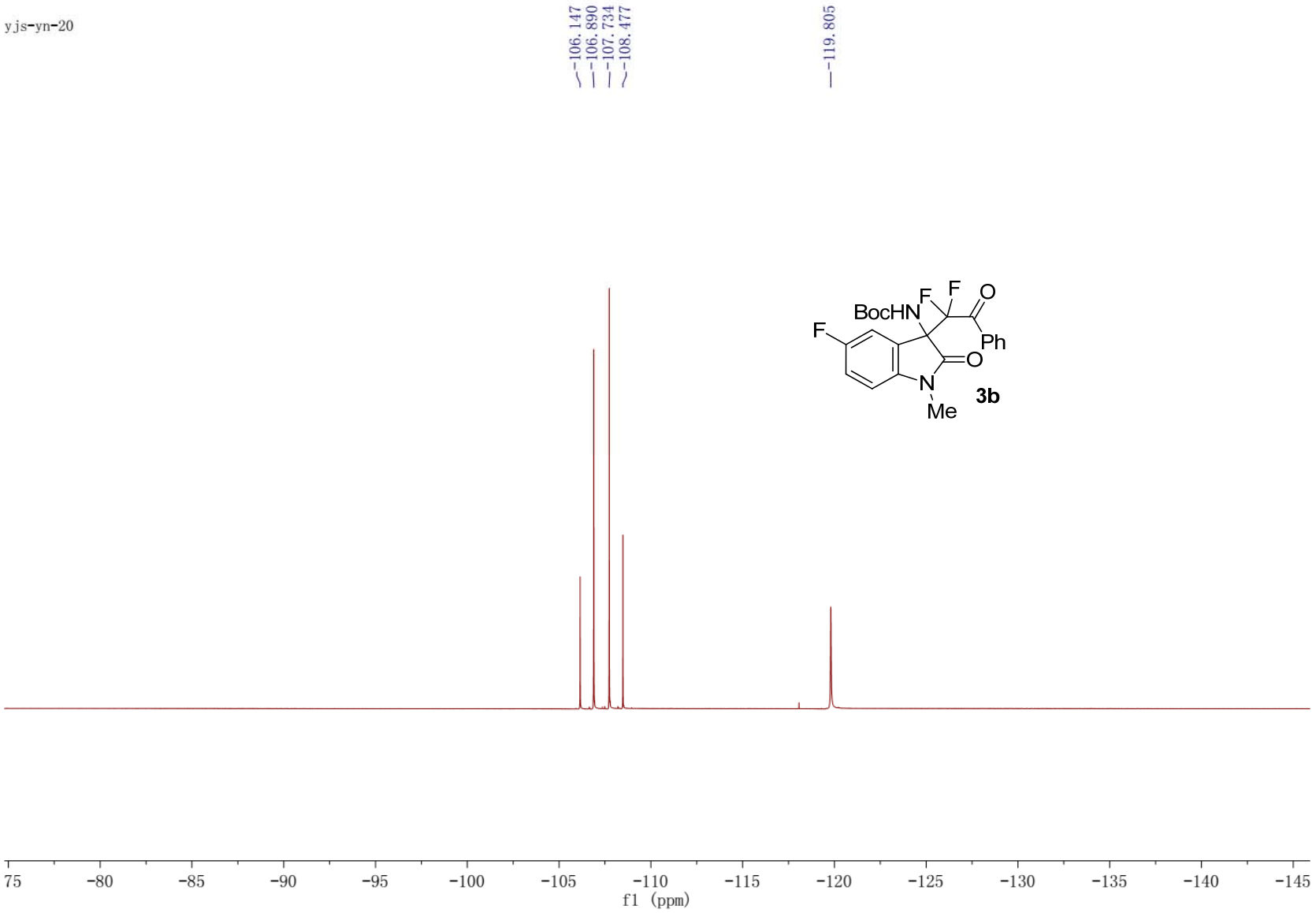

YJS-YM-90 H
7.820
7.801
7.598
7.580
7.561
7.423
7.403
7.384
7.363
7.344
7.325
7.263
7.034
7.015
6.996
6.841
6.822
6.181
3.211
1.273
0.000
BocHN
F
F
O
Ph
O
N
Me
3a
2.04
1.06
4.10
1.03
1.02
1.00
3.10
9.32
f1 (ppm)

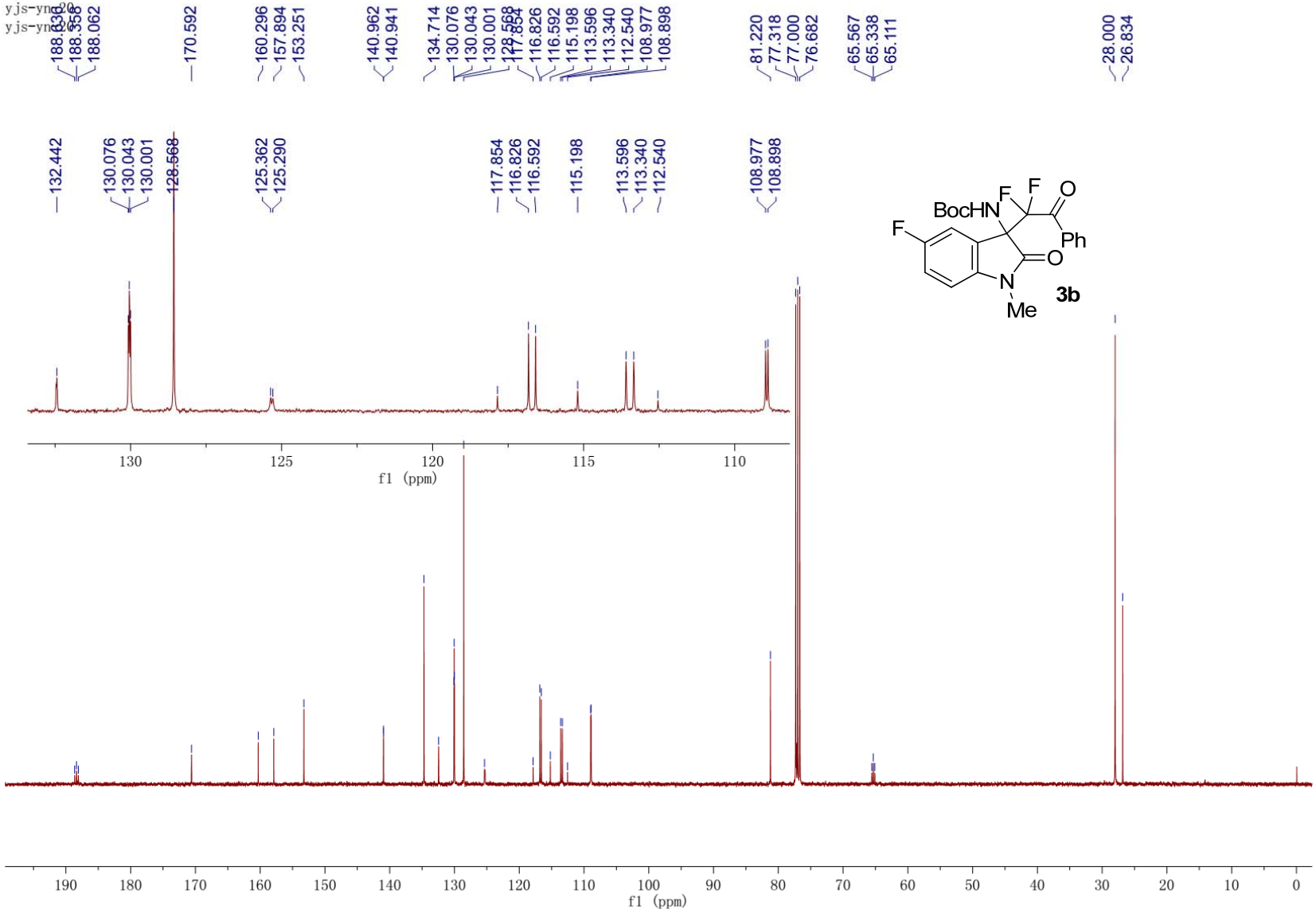
yjs-ym-90

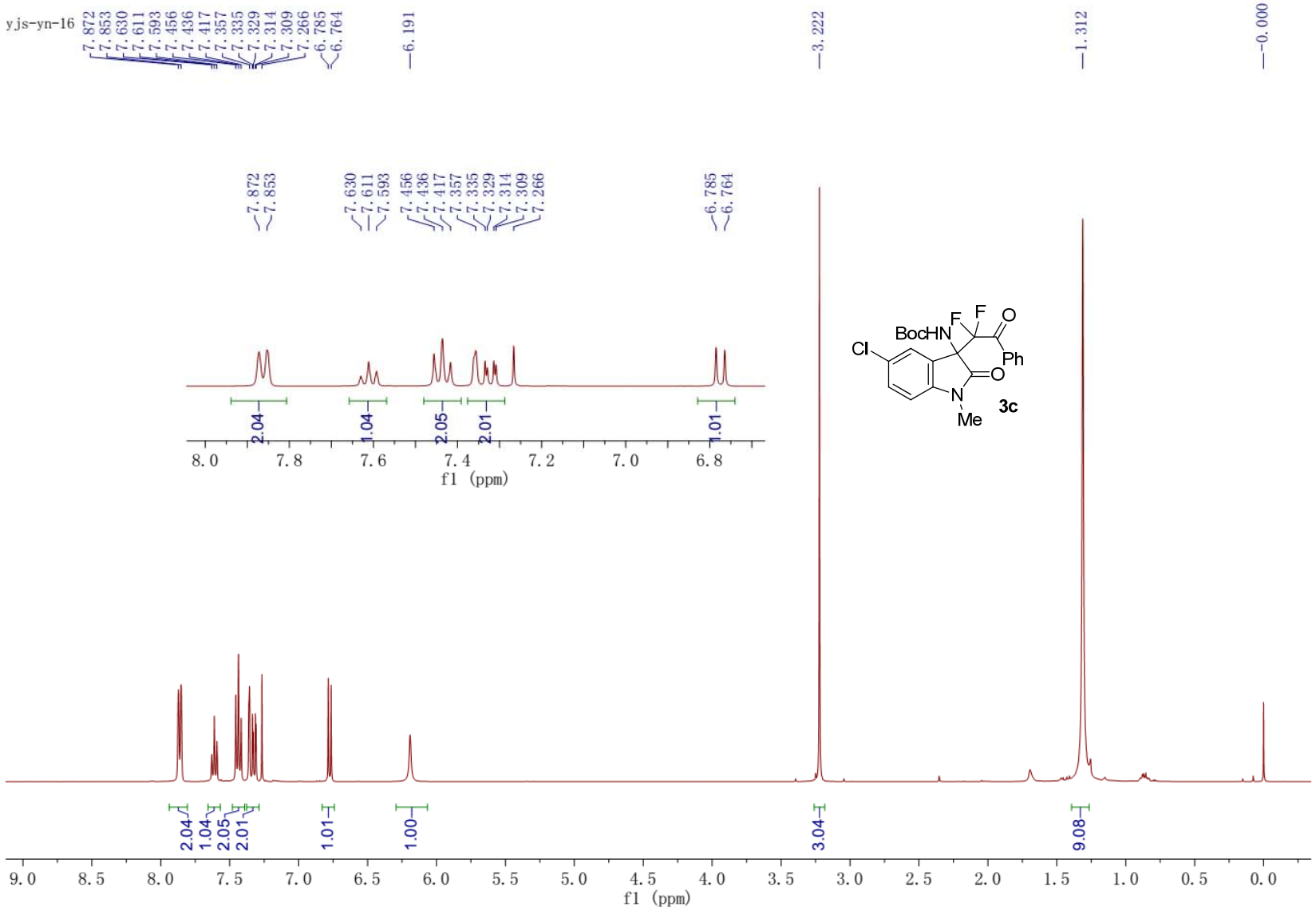

-106.802
-107.534
-107.929
-108.660
BocHN
F
F
O
Ph
O
N
Me
3a
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
f1 (ppm)


yjs-ym-90
189.008
188.726
188.439
170.726
153.242
144.845
134.434
132.703
130.455
129.972
129.936
129.898
128.414
125.084
123.706
122.745
117.977
115.323
112.668
108.358
80.880
77.317
77.000
76.681
65.403
65.169
64.935
27.922
26.588
f1 (ppm)
BocHN
F
F
O
Ph
O
N
Me
3a


7.872
7.853
7.627
7.609
7.590
7.454
7.434
7.415
7.267
7.169
7.163
7.150
7.144
7.083
7.076
7.061
7.055
7.039
7.032
6.790
6.780
6.768
6.758
3.216
1.307
0.000
BocHN
F
F
O
Ph
O
N
Me
3b
f1 (ppm)
2.10
1.07
2.13
1.04
1.04
1.05
1.00
3.15
9.22

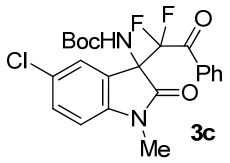

yjs-yn-20
-106.147
-106.890
-107.734
-108.477
-119.805
BocHN
F
F
O
Ph
O
N
Me
3b
75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)


yjs-ynmr-20
yjs-ynmr-20
188.336
188.358
188.062
170.592
160.296
157.894
153.251
140.962
140.941
134.714
130.076
130.043
130.001
128.568
117.854
116.826
116.592
115.198
113.596
113.340
112.540
108.977
108.898
81.220
77.318
77.000
76.682
65.567
65.338
65.111
28.000
26.834
132.442
130.076
130.043
130.001
128.568
125.362
125.290
117.854
116.826
116.592
115.198
113.596
113.340
112.540
108.977
108.898
130
125
120
115
110
f1 (ppm)
BocHN
F
F
O
Ph
O
N
Me
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

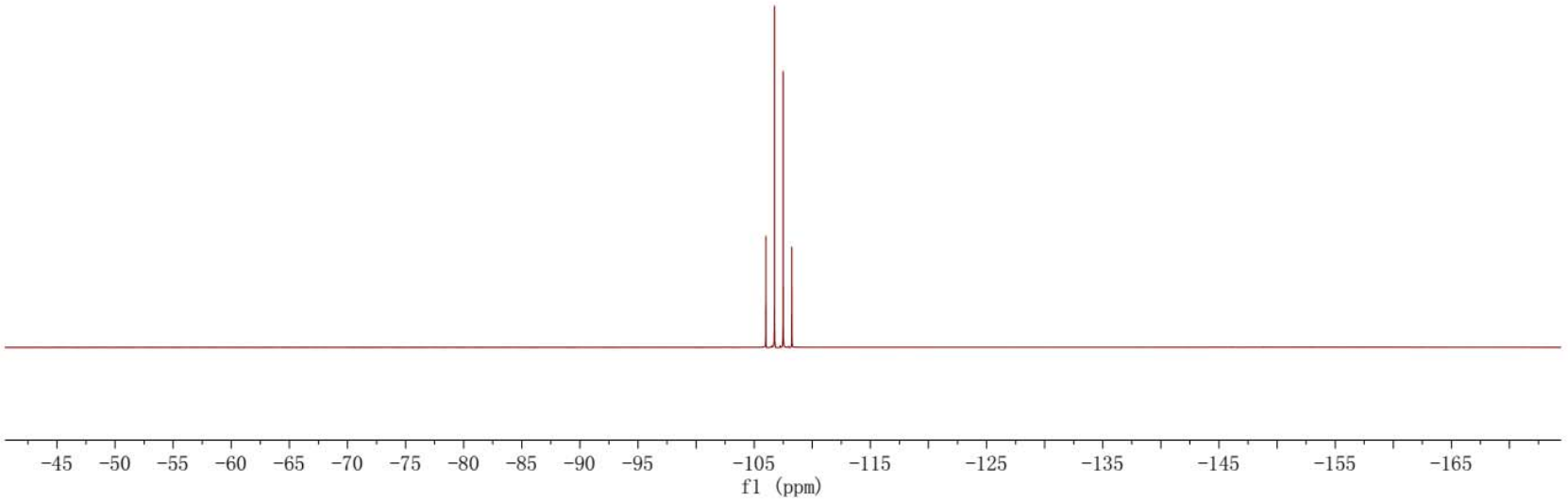

yjs-yn-16
7.872
7.853
7.630
7.611
7.593
7.456
7.436
7.417
7.357
7.335
7.329
7.314
7.309
7.266
6.785
6.764
6.191
3.222
1.312
0.000
2.04
1.04
2.05
2.01
1.01
1.00
3.04
9.08
f1 (ppm)
BocHN
F
F
O
Cl
Ph
O
N
Me
3c

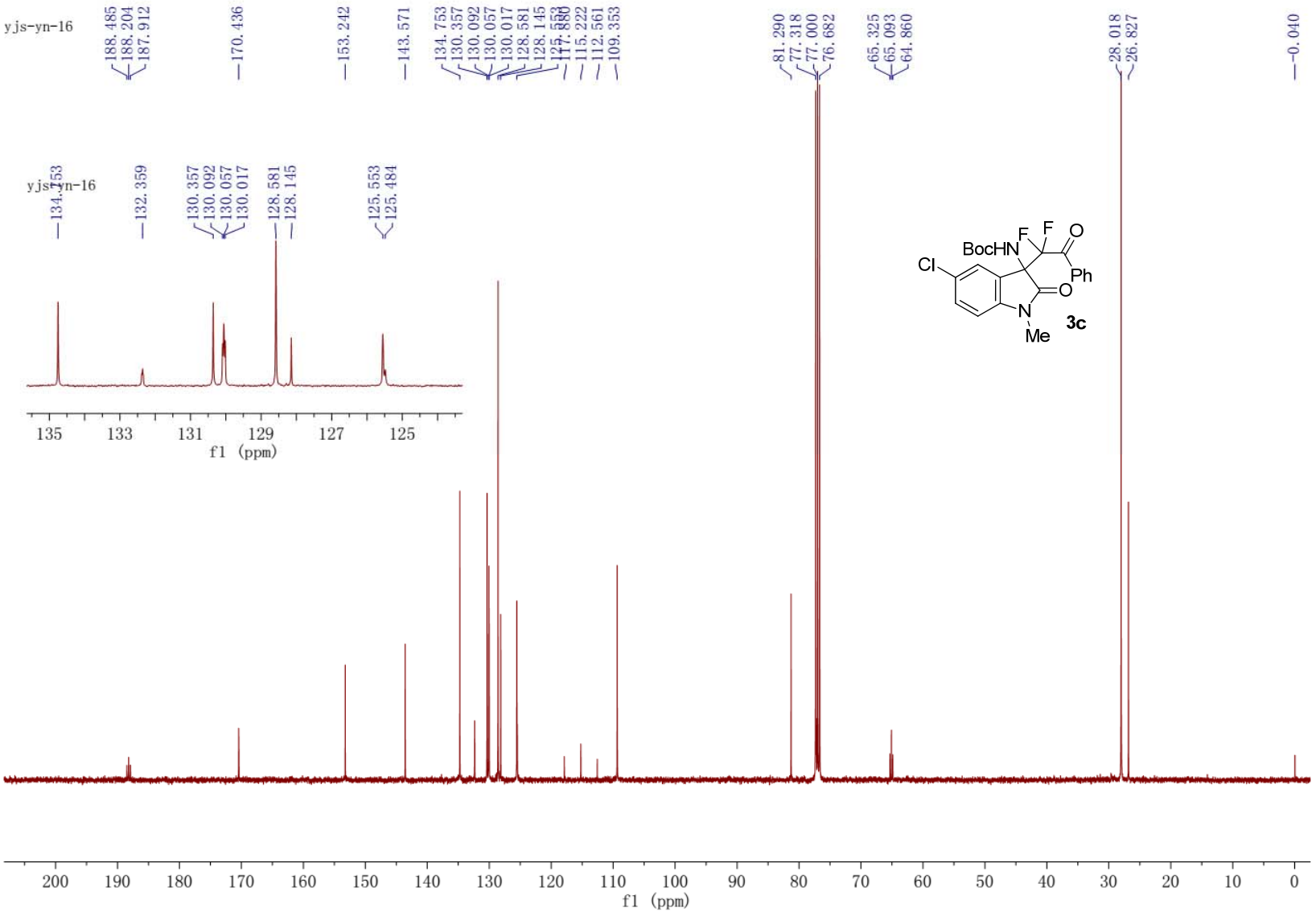
yjs-yn-16

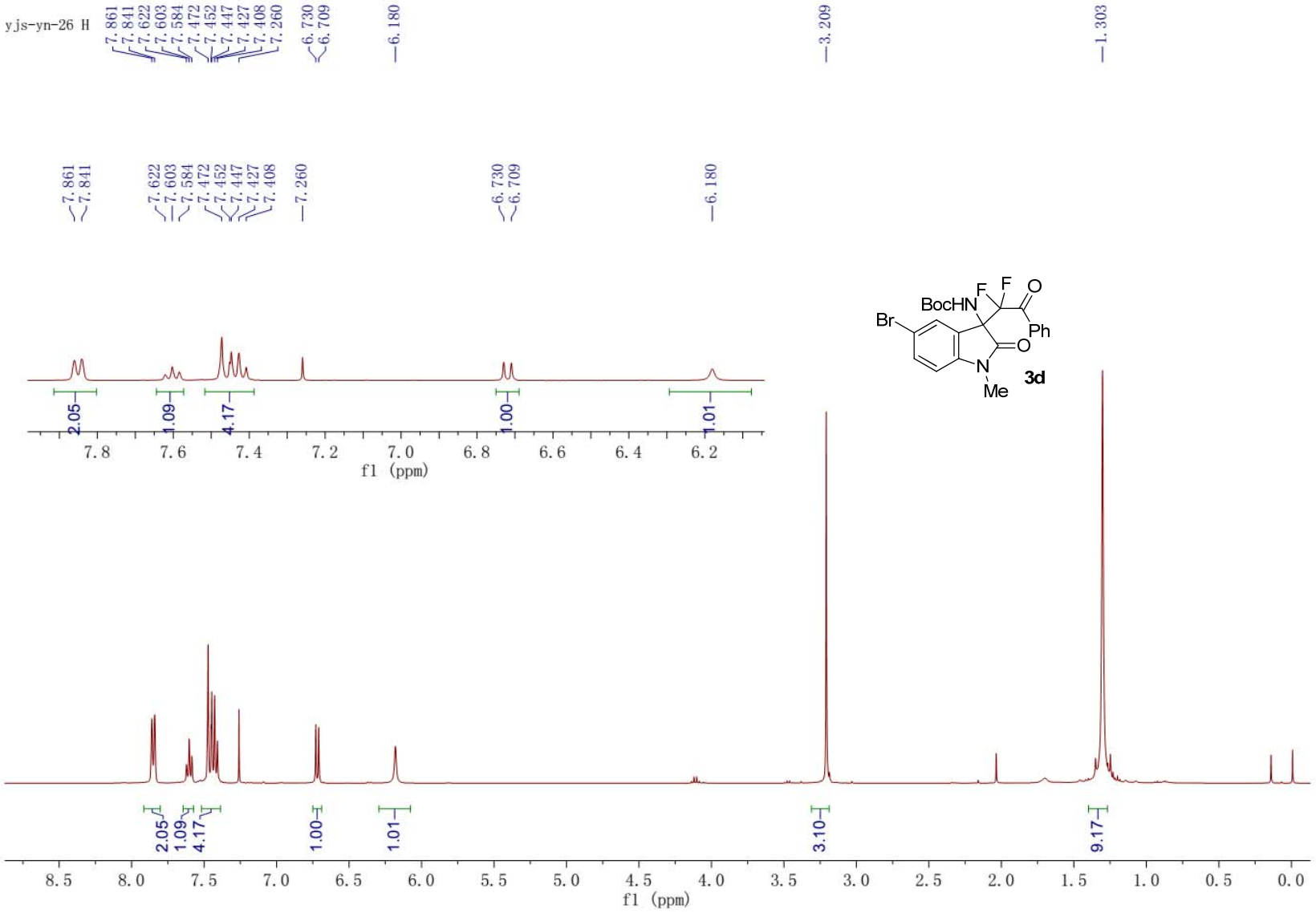
-106.002
-106.748
-107.494
-108.240



3c

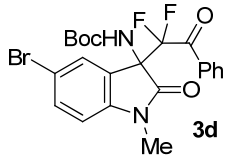



yjs-yn-16
188.485
188.204
187.912
170.436
153.242
143.571
134.753
130.357
130.092
130.057
130.017
128.581
128.145
125.553
117.880
115.222
112.561
109.353
81.290
77.318
77.000
76.682
65.325
65.093
64.860
28.018
26.827
0.040
yjs-yn-16
134.753
132.359
130.357
130.092
130.057
130.017
128.581
128.145
125.553
125.484
135
133
131
129
127
125
f1 (ppm)
BocHN
F
F
O
Cl
Ph
O
N
Me
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

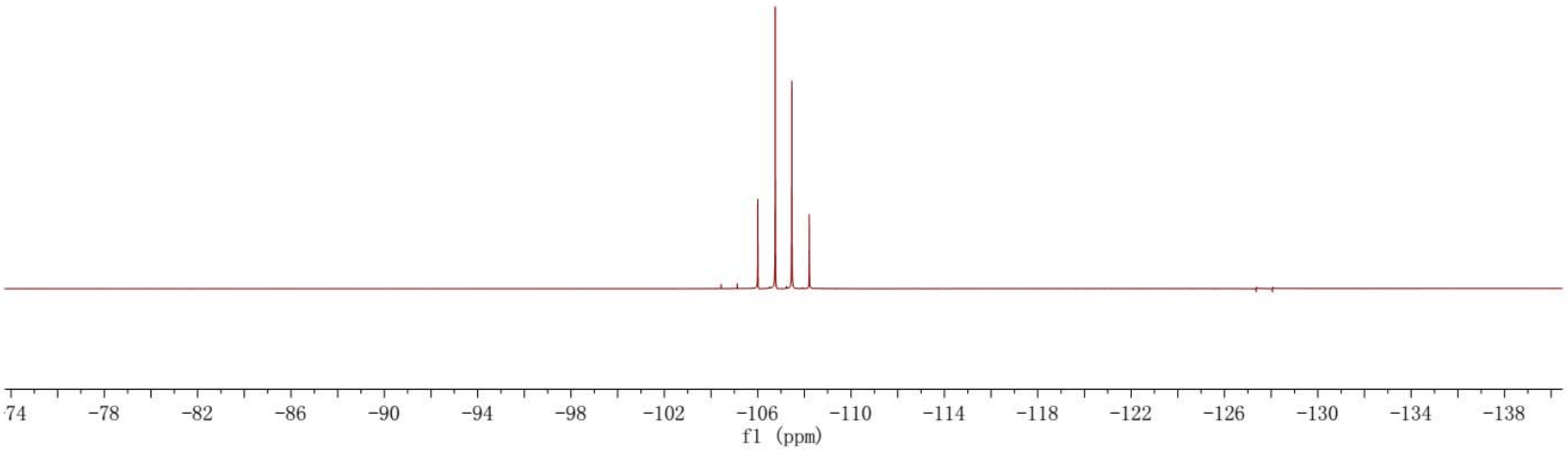

yjs-yn-26 H
7.861
7.841
7.622
7.603
7.584
7.472
7.452
7.447
7.427
7.408
7.260
6.730
6.709
6.180
3.209
1.303
2.05
1.09
4.17
1.00
1.01
3.10
9.17
f1 (ppm)
BocHN
F
F
O
Br
Ph
O
N
Me
3d

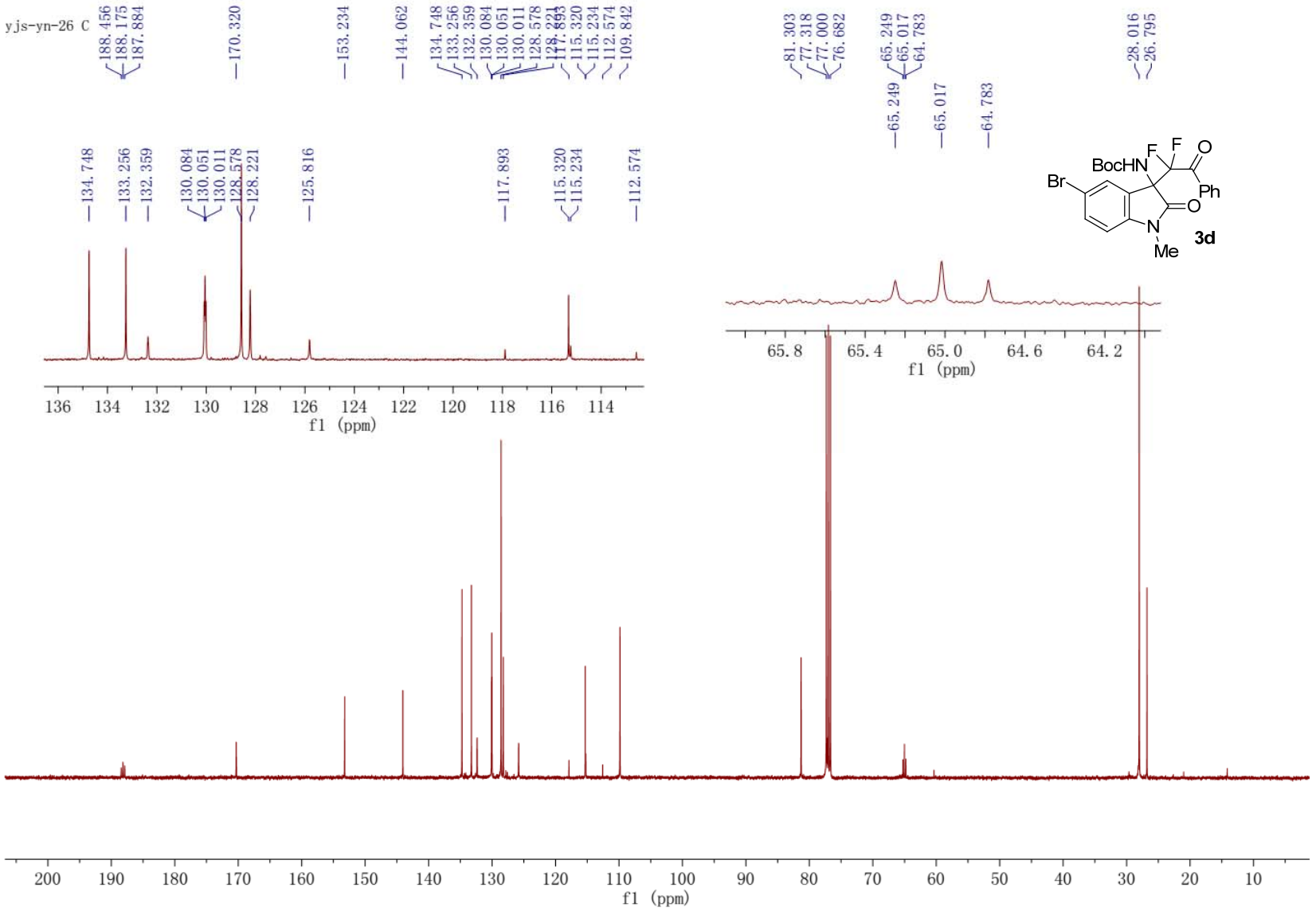
yjs-yn-26 F

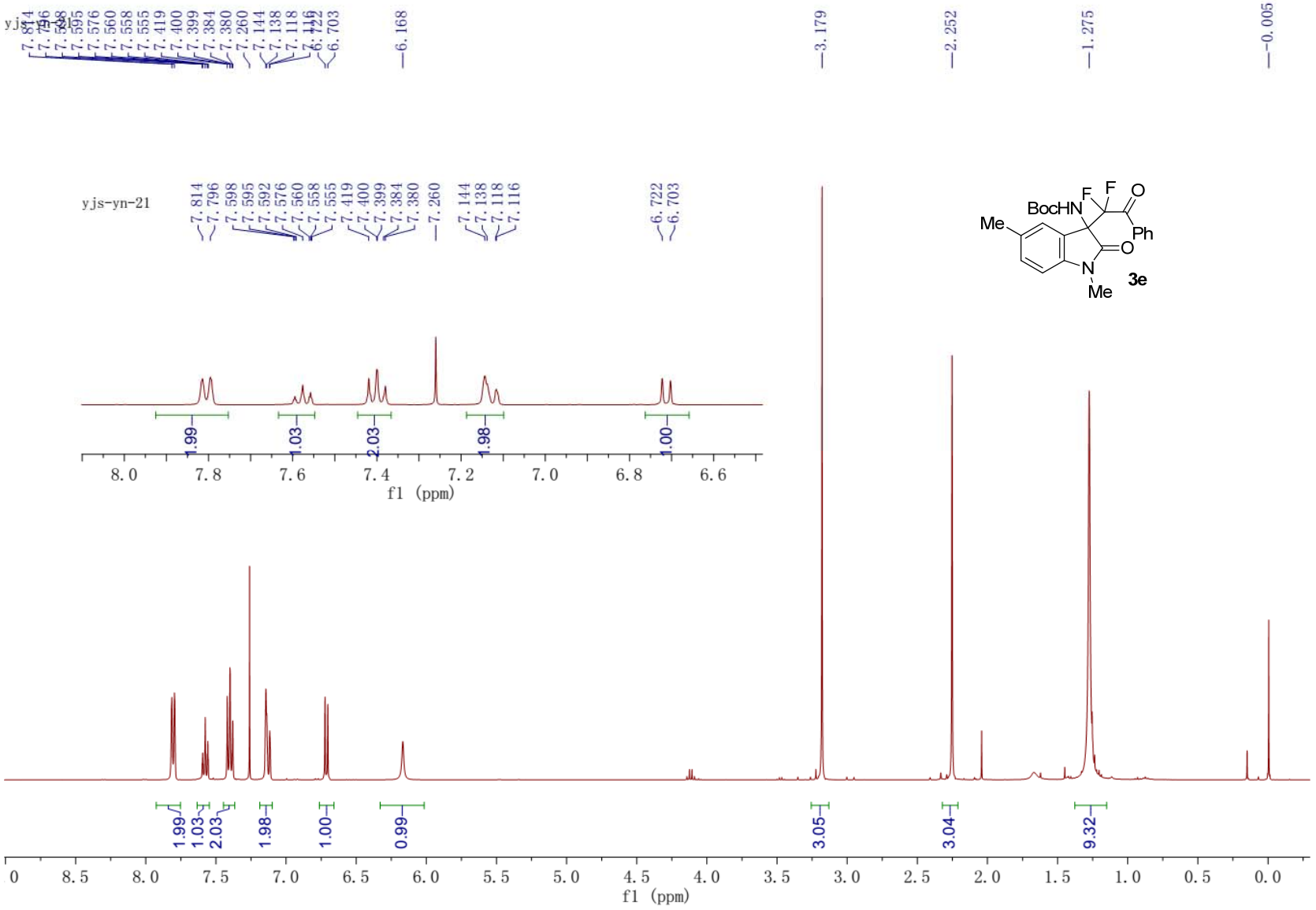
-106.006
-106.752
-107.461
-108.208



3d

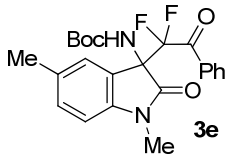



yjs-yn-26 C
188.456
188.175
187.884
170.320
153.234
144.062
134.748
133.256
132.359
130.084
130.051
130.011
128.578
128.221
117.893
115.320
115.234
112.574
109.842
81.303
77.318
77.000
76.682
65.249
65.017
64.783
28.016
26.795
BocHN
F
F
O
Ph
Br
O
N
Me
3d
f1 (ppm)

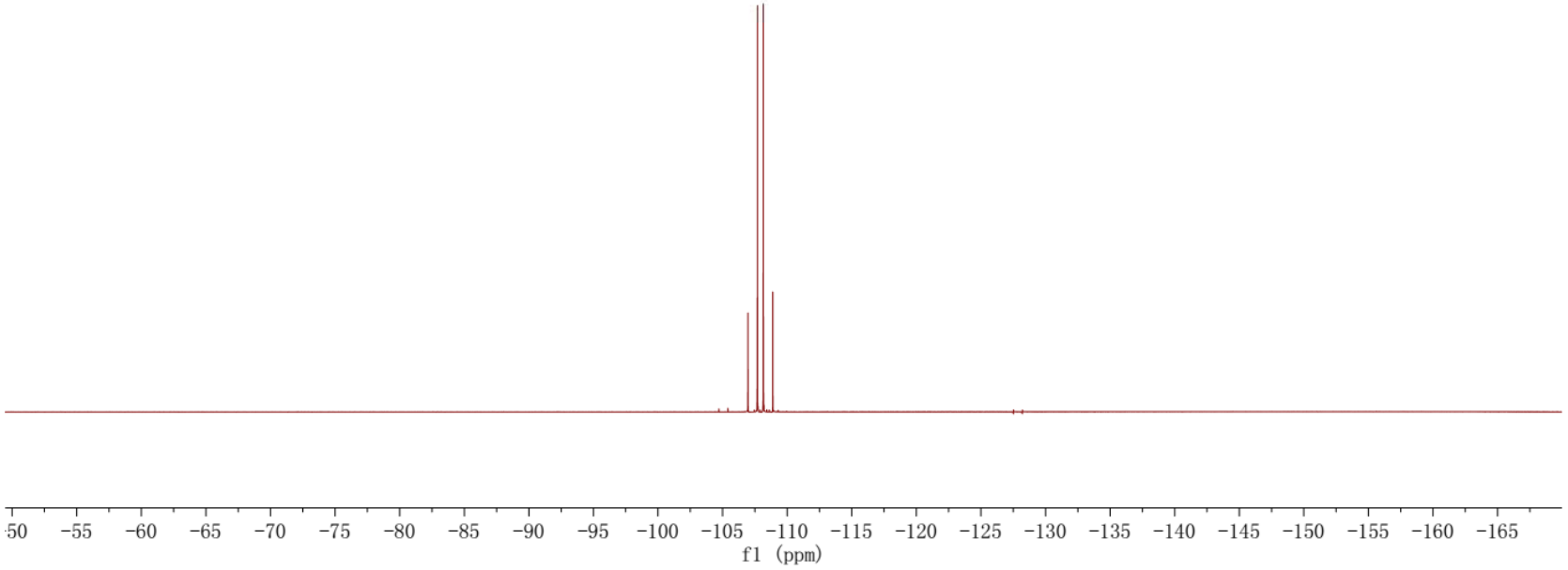

yjs-yn-21
7.814
7.796
7.598
7.595
7.592
7.576
7.560
7.558
7.555
7.419
7.400
7.399
7.384
7.380
7.260
7.144
7.138
7.118
7.116
6.722
6.703
6.168
3.179
2.252
1.275
-0.005
1.99
1.03
2.03
1.98
1.00
0.99
3.05
3.04
9.32
f1 (ppm)
BocHN
F
F
O
Me
Ph
O
N
Me
3e

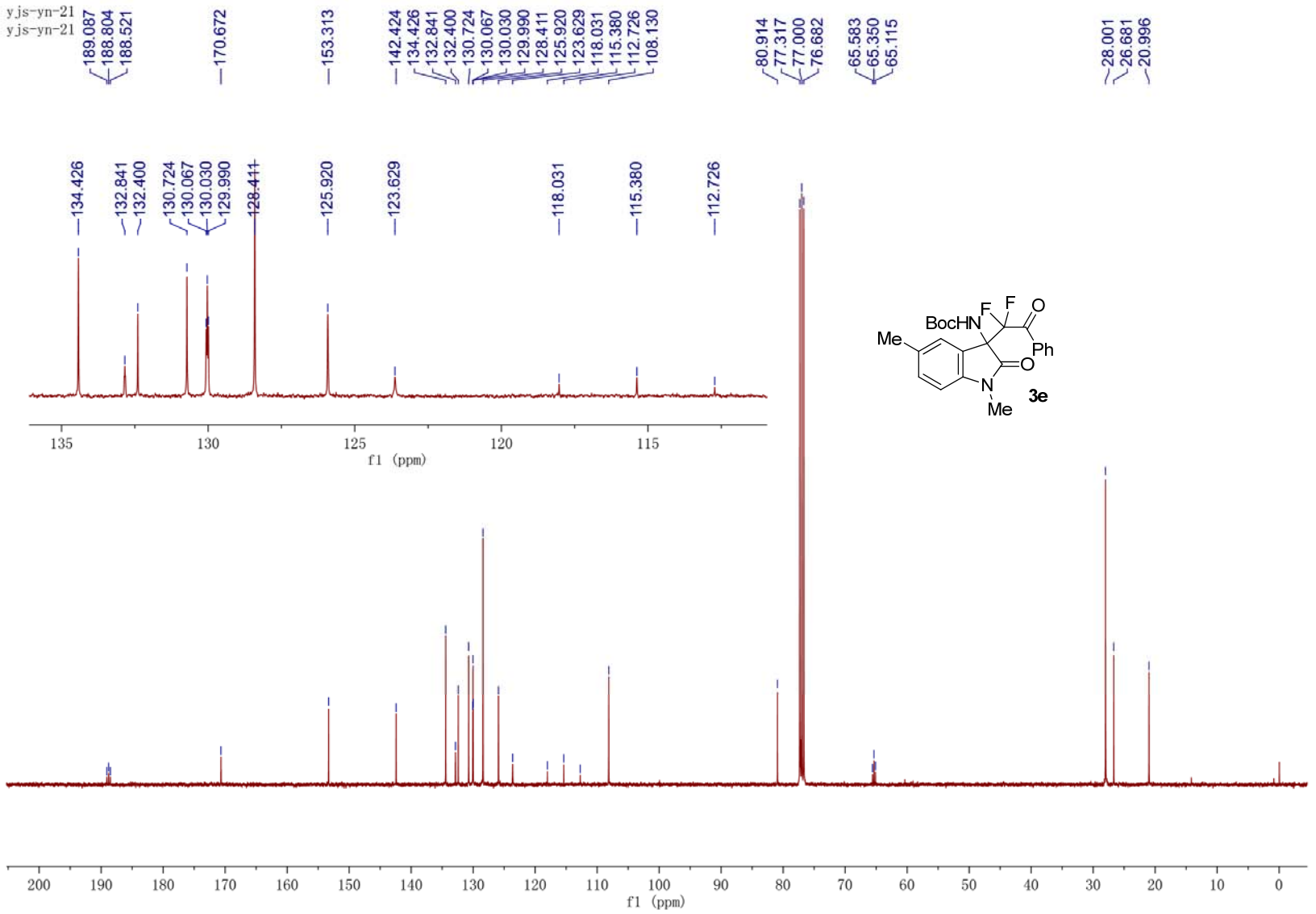
yjs-yn-21

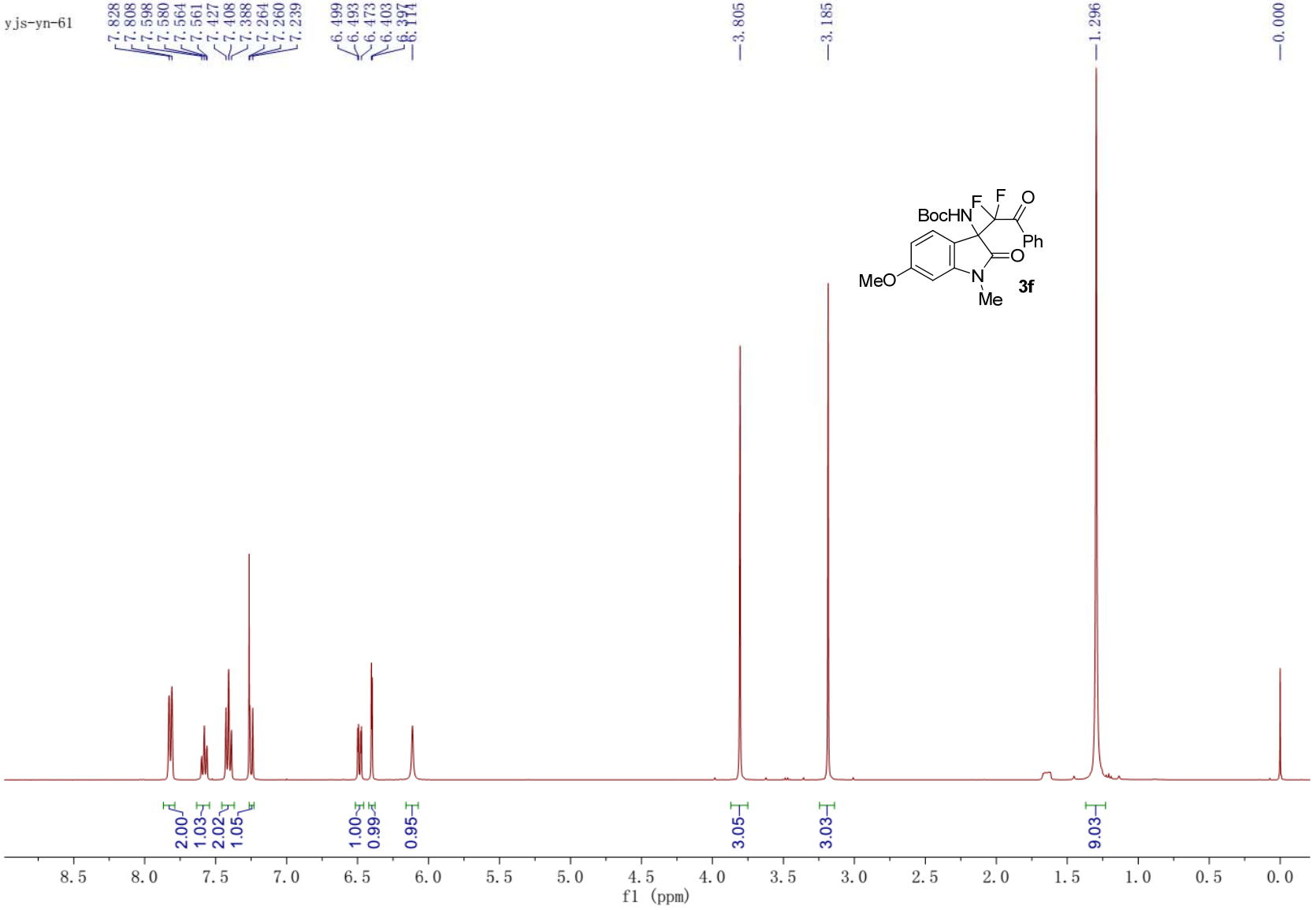
-106.965
-107.693
-108.151
-108.879



3e

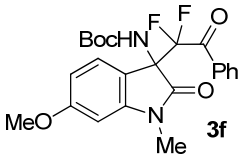



yjs-yn-21
yjs-yn-21
189.087
188.804
188.521
170.672
153.313
142.424
134.426
132.841
132.400
130.724
130.067
130.030
129.990
128.411
125.920
123.629
118.031
115.380
112.726
108.130
80.914
77.317
77.000
76.682
65.583
65.350
65.115
28.001
26.681
20.996
f1 (ppm)
BocHN
F
F
O
Me
Ph
O
N
Me
3e

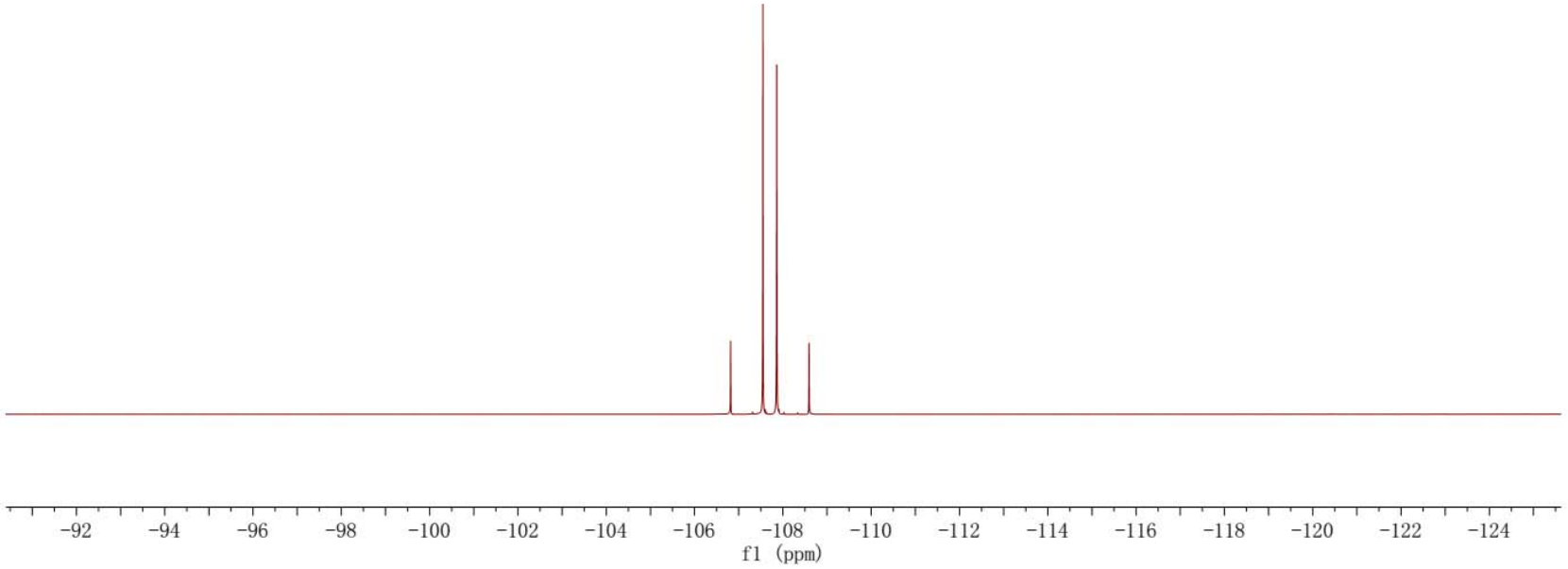

yjs-yn-61
7.828
7.808
7.598
7.580
7.564
7.561
7.427
7.408
7.388
7.264
7.260
7.239
6.499
6.493
6.473
6.403
6.397
6.114
3.805
3.185
1.296
0.000
BocHN
F
F
O
Ph
O
MeO
N
Me
3f
2.00
1.03
2.02
1.05
1.00
0.99
0.95
3.05
3.03
9.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

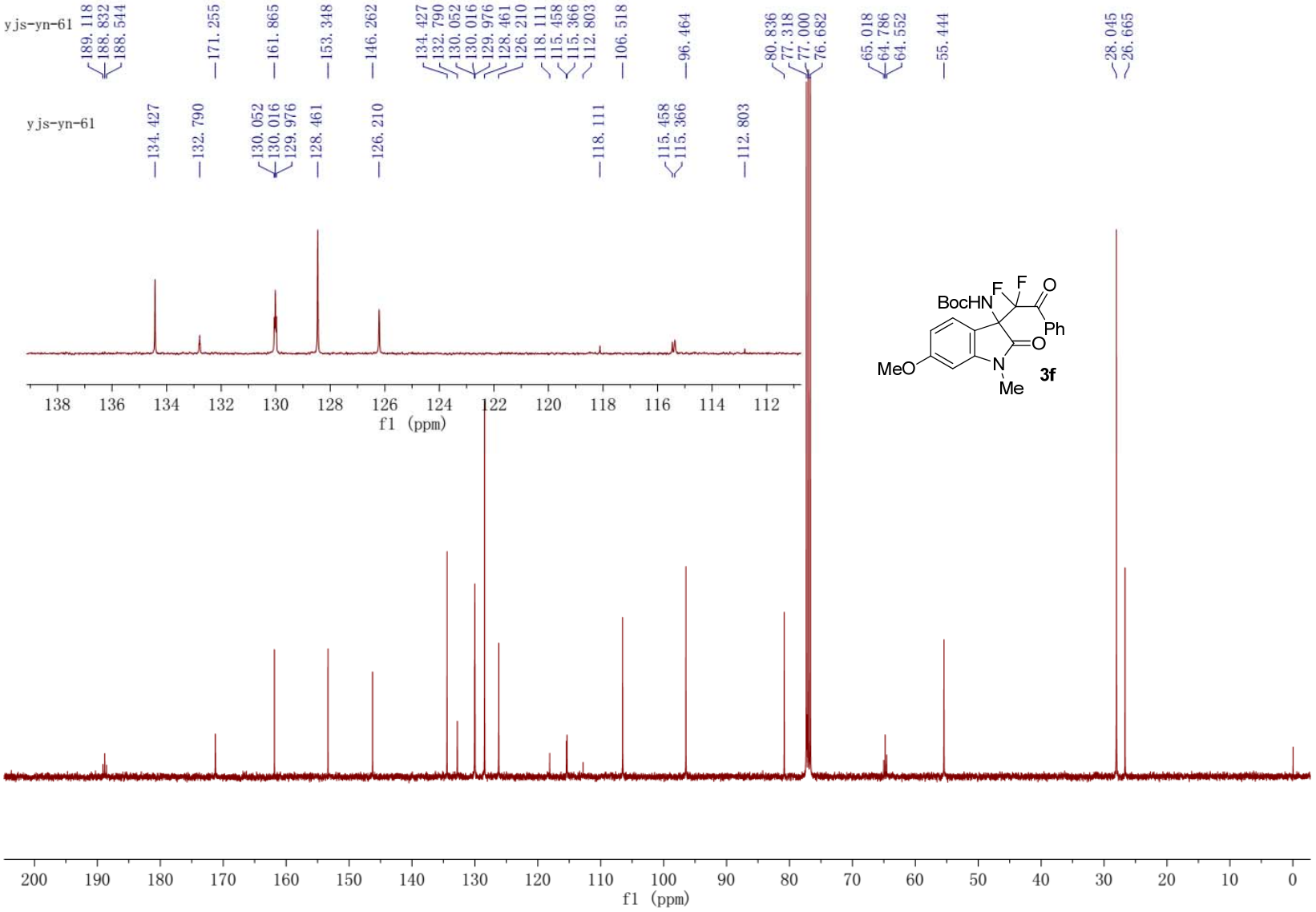
yjs-yn-61

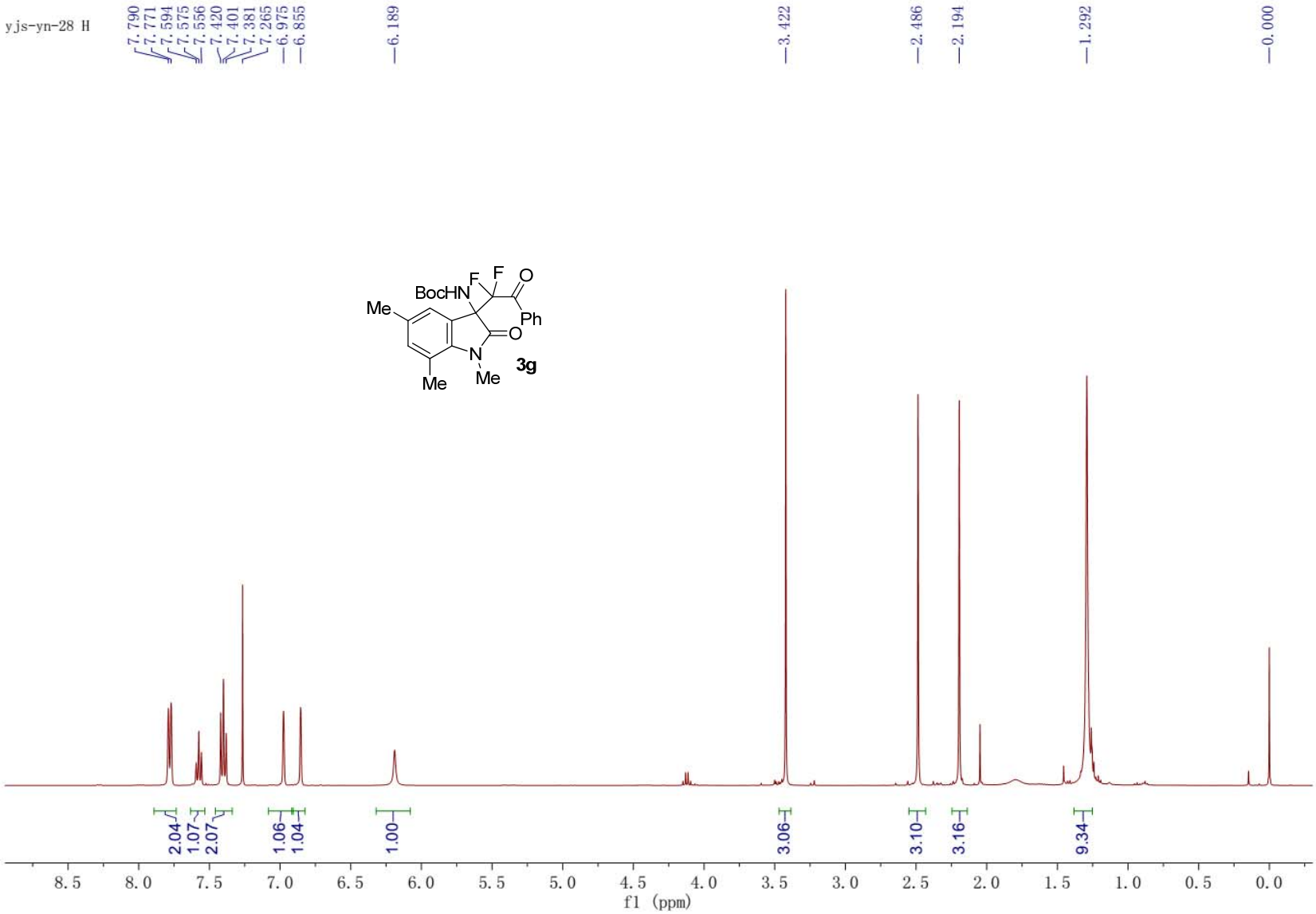
-106.817
-107.548
-107.861
-108.593



3f

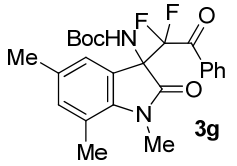



yjs-yn-61
189.118
188.832
188.544
171.255
161.865
153.348
146.262
134.427
132.790
130.052
130.016
129.976
128.461
126.210
118.111
115.458
115.366
112.803
106.518
96.464
80.836
77.318
77.000
76.682
65.018
64.786
64.552
55.444
28.045
26.665
yjs-yn-61
134.427
132.790
130.052
130.016
129.976
128.461
126.210
118.111
115.458
115.366
112.803
138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)
BocHN
F
F
O
Ph
O
N
Me
MeO
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

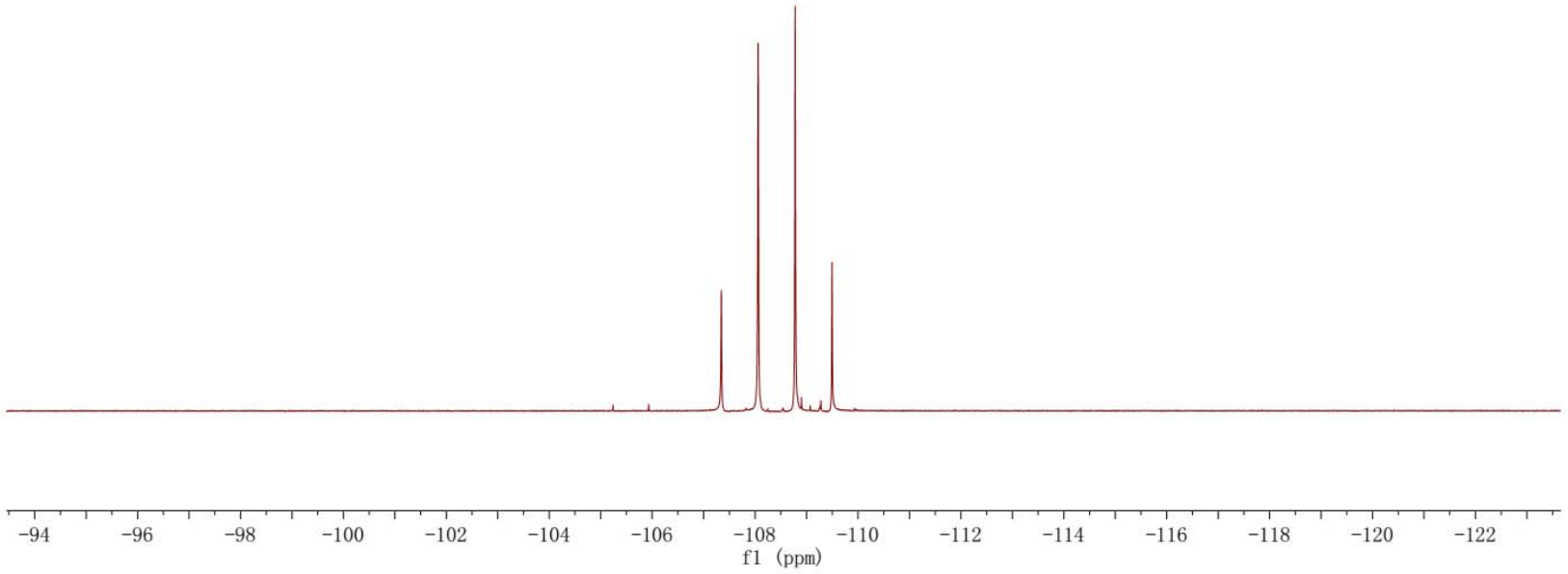

yjs-yn-28 H
7.790
7.771
7.594
7.575
7.556
7.420
7.401
7.381
7.265
6.975
6.855
6.189
3.422
2.486
2.194
1.292
0.000
BocHN
F
F
O
Ph
Me
O
N
Me
Me
3g
2.04
1.07
2.07
1.06
1.04
1.00
3.06
3.10
3.16
9.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

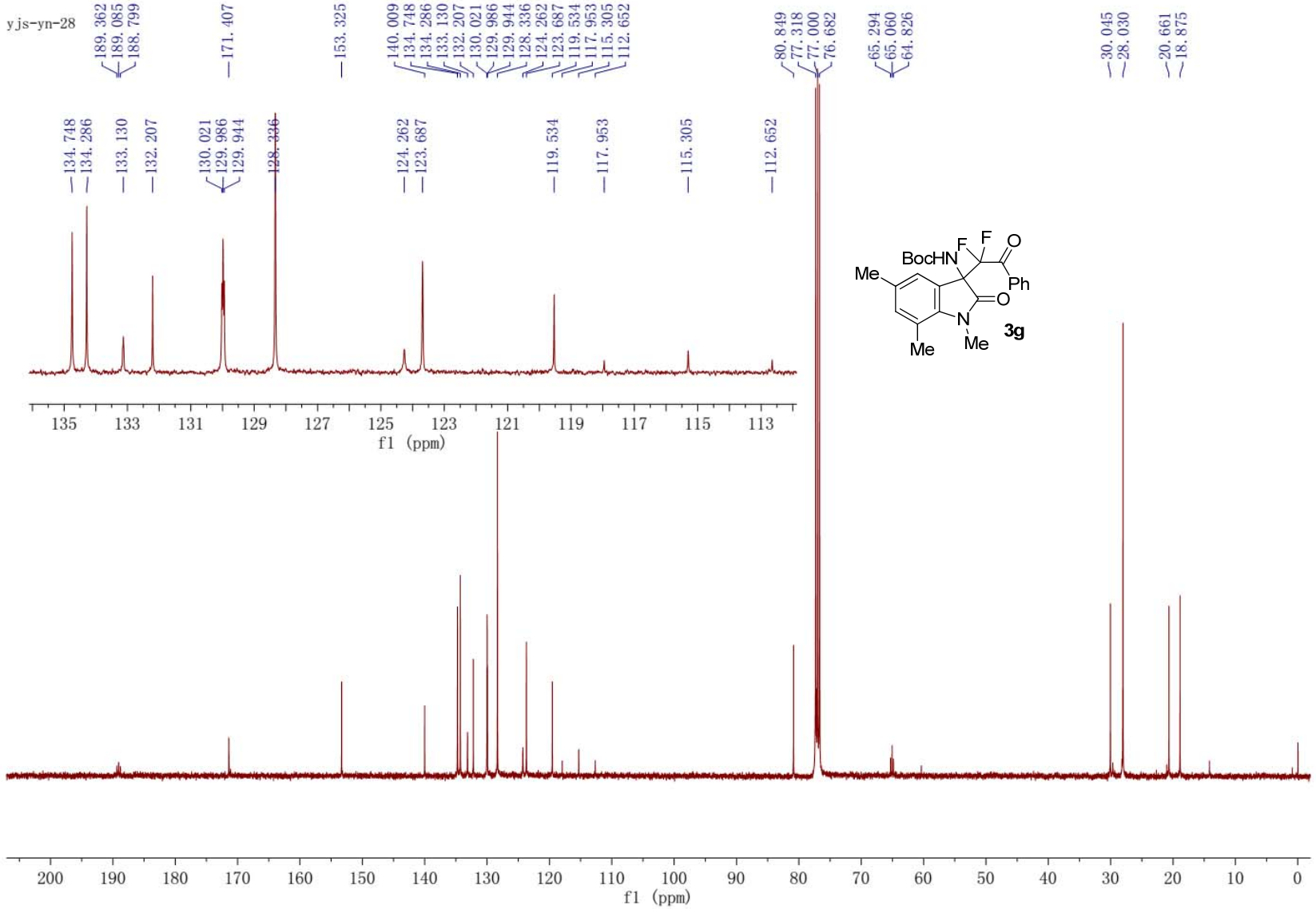
yjs-yn-28 F

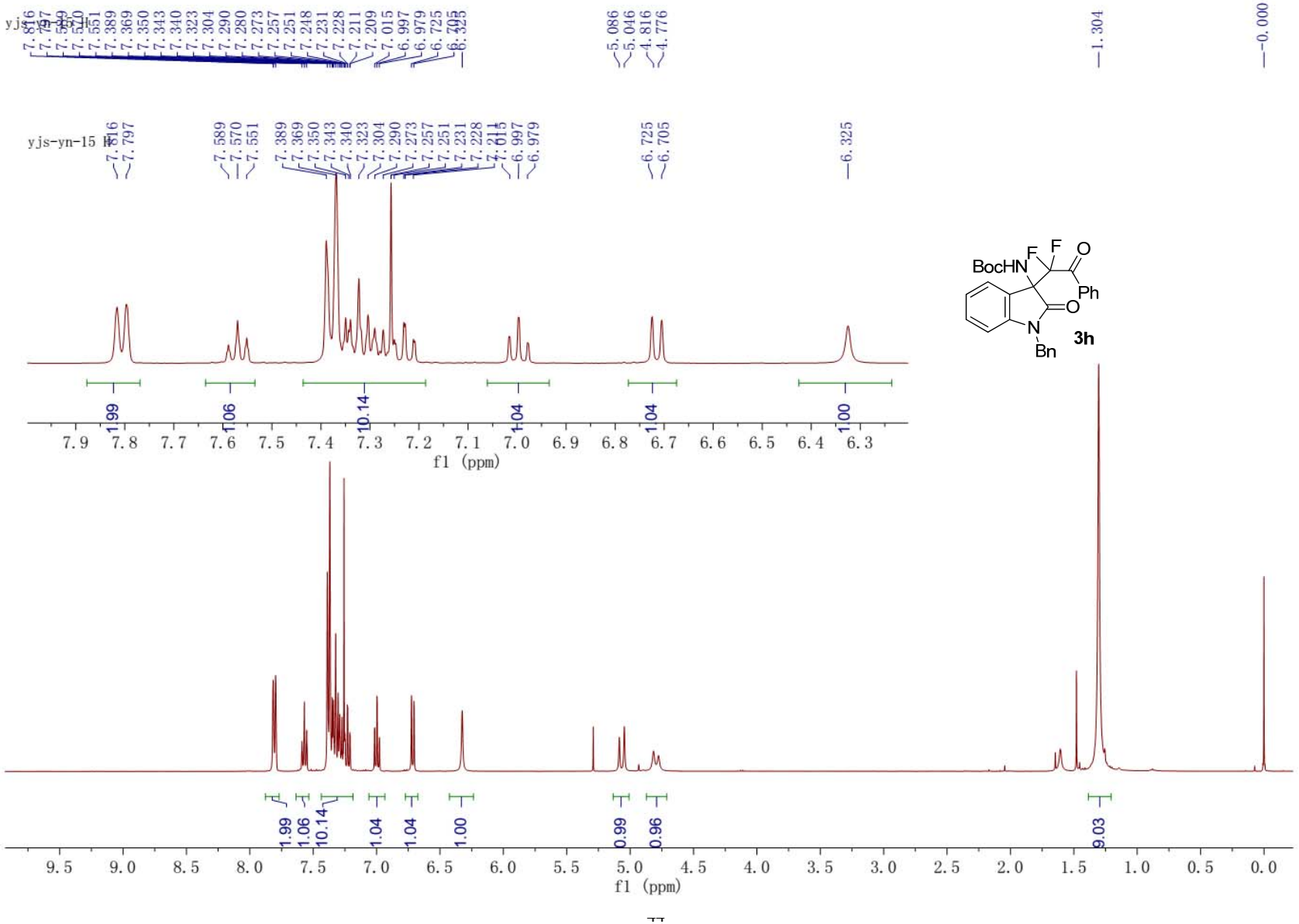
-107.343
-108.059
-108.778
-109.494



3g

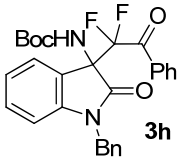



yjs-yn-28
189.362
189.085
188.799
171.407
153.325
140.009
134.748
134.286
133.130
132.207
130.021
129.986
129.944
128.336
124.262
123.687
119.534
117.953
115.305
112.652
80.849
77.318
77.000
76.682
65.294
65.060
64.826
30.045
28.030
20.661
18.875
BocHN
F
F
O
Ph
Me
O
N
Me
Me
3g
f1 (ppm)
f1 (ppm)

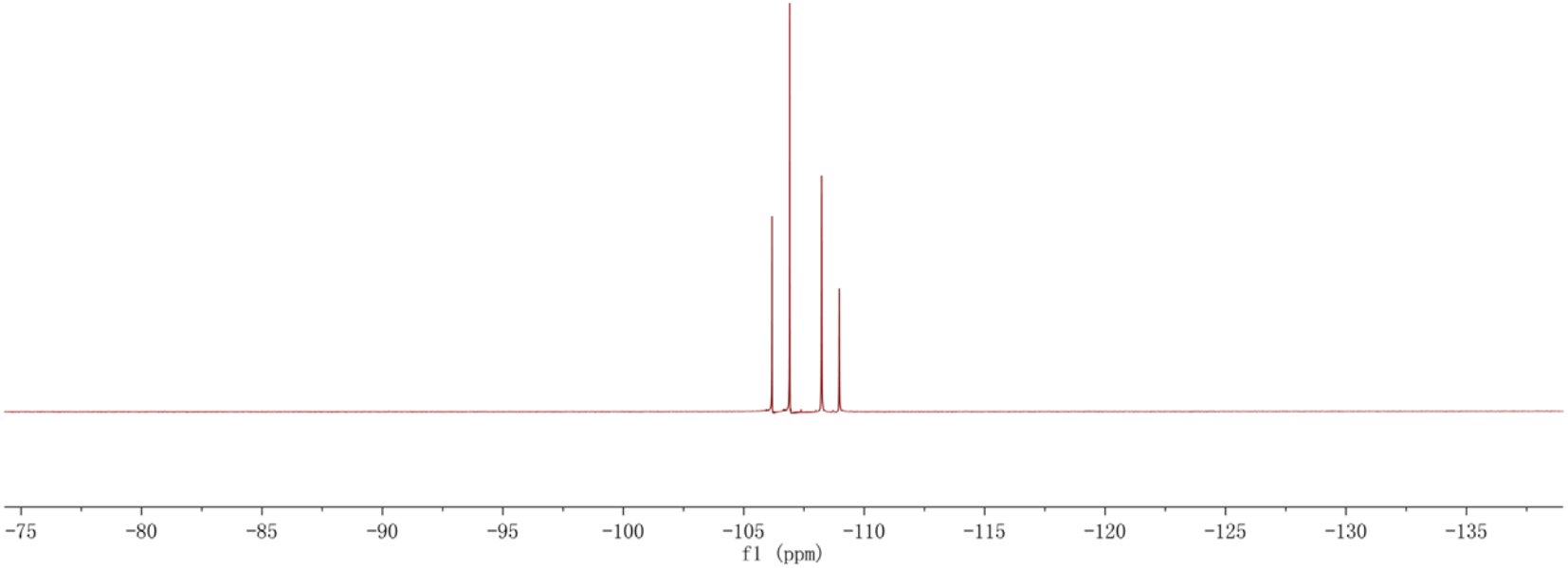

yjs-yn-15 H
7.816
7.797
7.589
7.570
7.551
7.389
7.369
7.350
7.343
7.340
7.323
7.304
7.290
7.273
7.257
7.251
7.231
7.228
7.211
7.015
6.997
6.979
6.725
6.705
6.325
5.086
5.046
4.816
4.776
1.304
0.000
1.99
1.06
10.14
1.04
1.04
1.00
0.99
0.96
9.03
f1 (ppm)
BocHN
F
F
O
Ph
O
N
Bn
3h

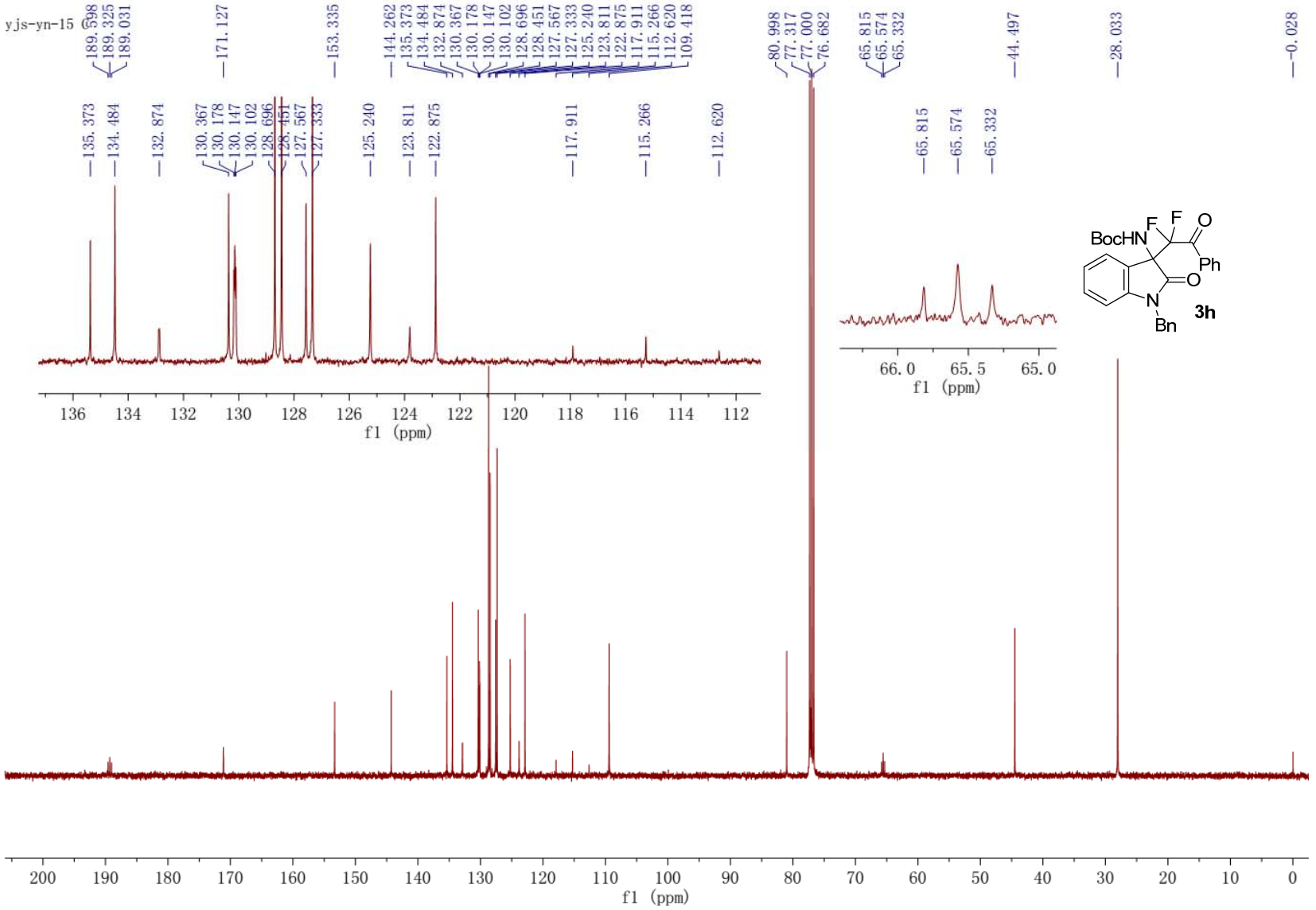
yjs-yn-15 F

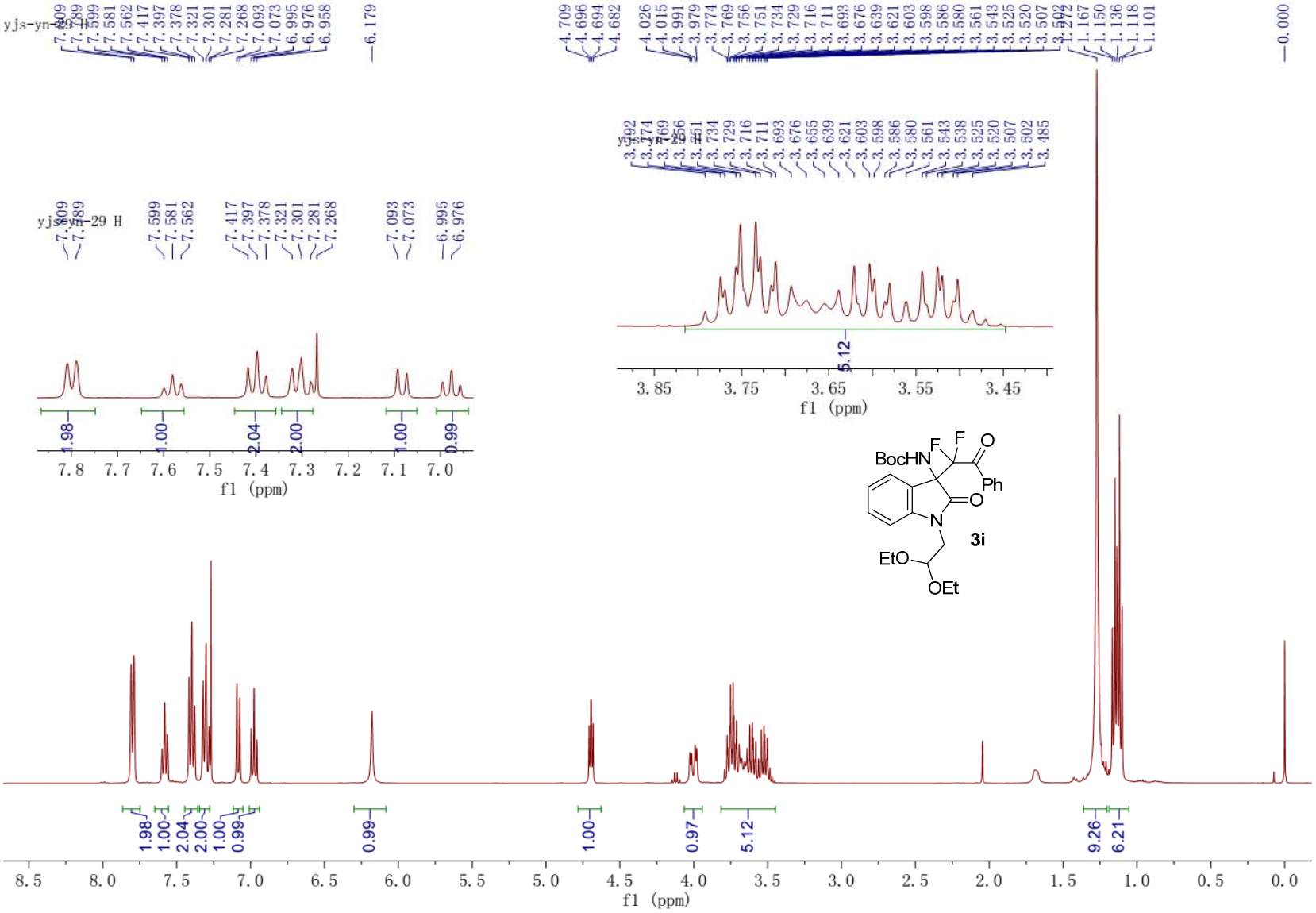
-106.173
-106.905
-108.230
-108.963



3h

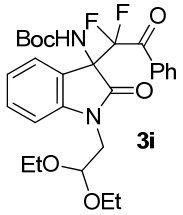



yjs-yn-15
189.598
189.325
189.031
171.127
153.335
144.262
135.373
134.484
132.874
130.367
130.178
130.147
130.102
128.696
128.451
127.567
127.333
125.240
123.811
122.875
117.911
115.266
112.620
109.418
80.998
77.317
77.000
76.682
65.815
65.574
65.332
44.497
28.033
-0.028
f1 (ppm)
BocHN
F
F
O
Ph
O
N
Bn
3h

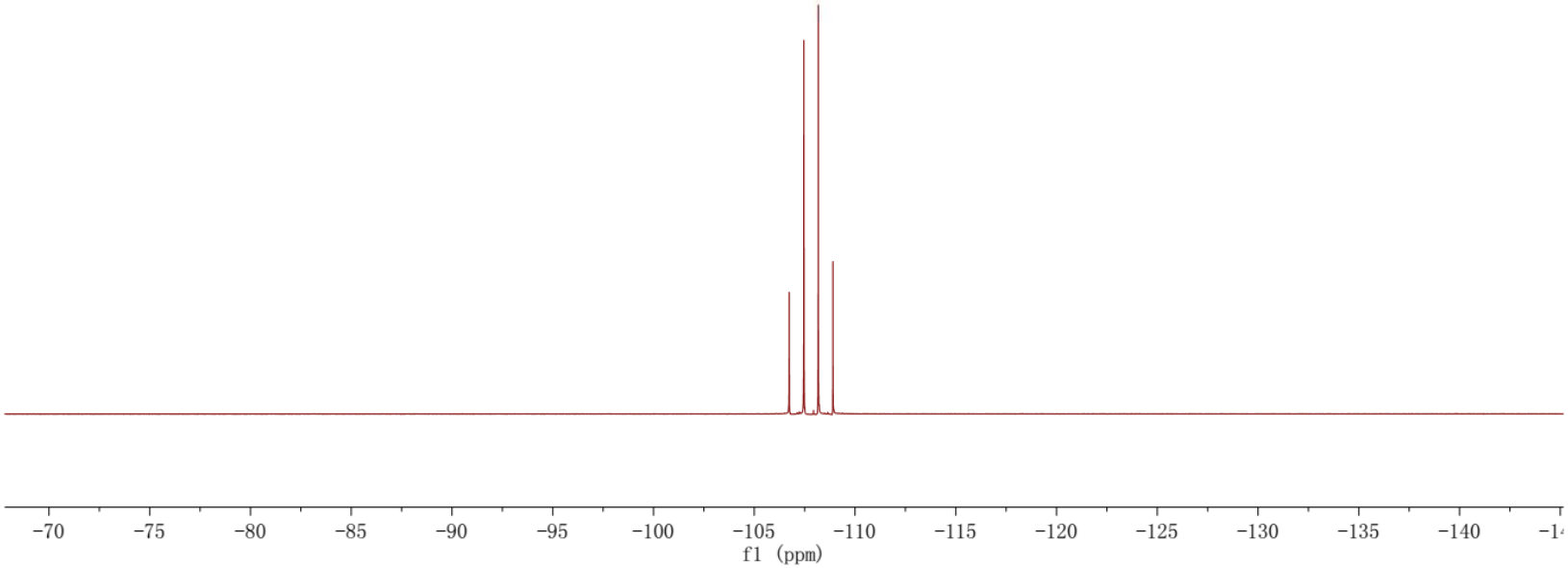

yjs-yn-29 H
7.709
7.696
7.694
7.682
4.026
4.015
3.991
3.979
3.774
3.769
3.756
3.751
3.734
3.729
3.716
3.711
3.693
3.676
3.639
3.621
3.603
3.598
3.586
3.580
3.561
3.543
3.525
3.520
3.507
1.167
1.150
1.136
1.118
1.101
6.179
0.000
7.599
7.581
7.562
7.417
7.397
7.378
7.321
7.301
7.281
7.268
7.093
7.073
6.995
6.976
1.98
1.00
2.04
2.00
1.00
0.99
5.12
0.97
9.26
6.21
f1 (ppm)
BocHN
F
F
O
Ph
O
N
EtO
OEt
3i

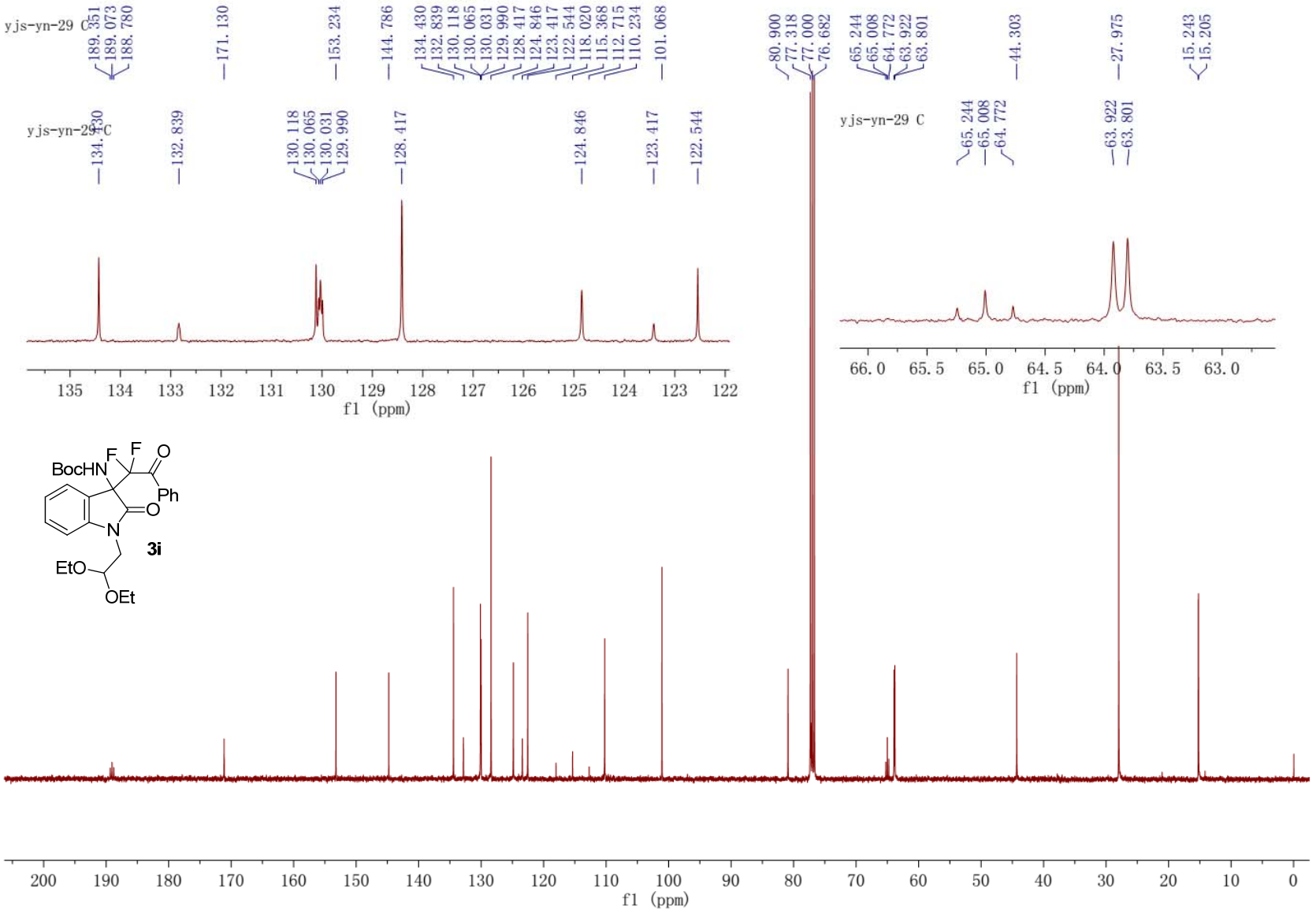
yjs-yn-29 F

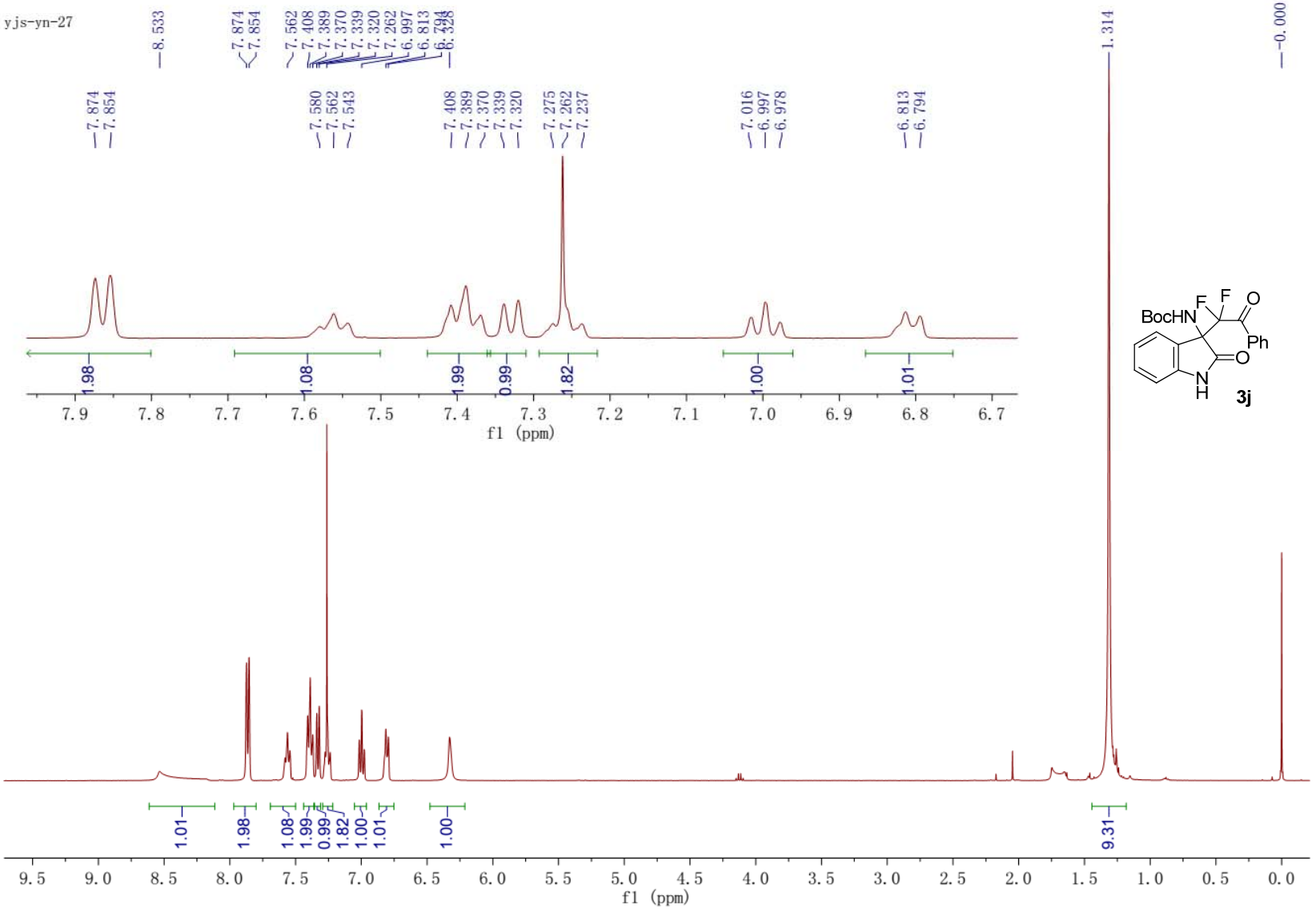
-106.734
-107.463
-108.177
-108.906



3i

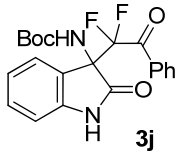



yjs-yn-29 C
189.351
189.073
188.780
171.130
153.234
144.786
134.430
132.839
130.118
130.065
130.031
129.990
128.417
124.846
123.417
122.544
118.020
115.368
112.715
110.234
101.068
80.900
77.318
77.000
76.682
65.244
65.008
64.772
63.922
63.801
44.303
27.975
15.243
15.205
yjs-yn-29 C
134.430
132.839
130.118
130.065
130.031
129.990
128.417
124.846
123.417
122.544
f1 (ppm)
yjs-yn-29 C
65.244
65.008
64.772
63.922
63.801
f1 (ppm)
BocHN
F
F
O
Ph
O
N
EtO
OEt
3i
f1 (ppm)

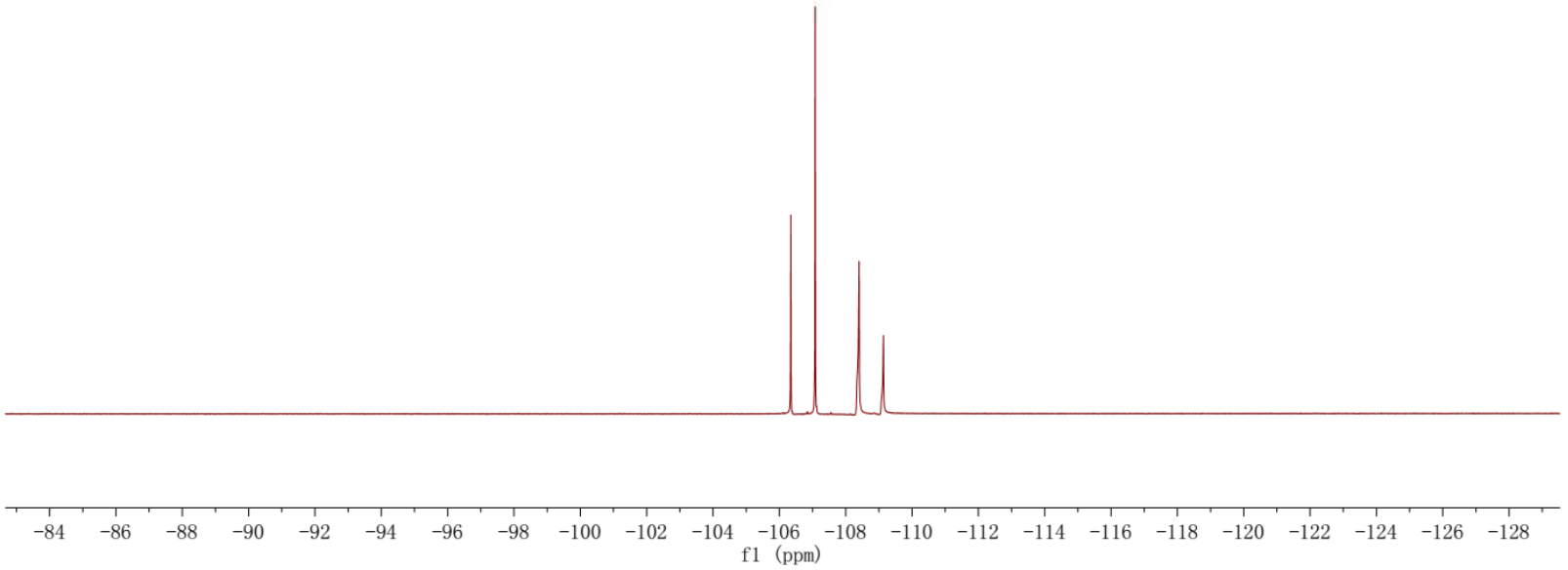

yjs-yn-27
8.533
7.874
7.854
7.562
7.408
7.389
7.370
7.339
7.320
7.262
6.997
6.813
6.794
6.328
1.314
0.000
7.580
7.543
7.275
7.237
7.016
6.978
1.98
1.08
1.99
0.99
1.82
1.00
1.01
9.31
f1 (ppm)
BocHN
F
O
Ph
N
H
3j

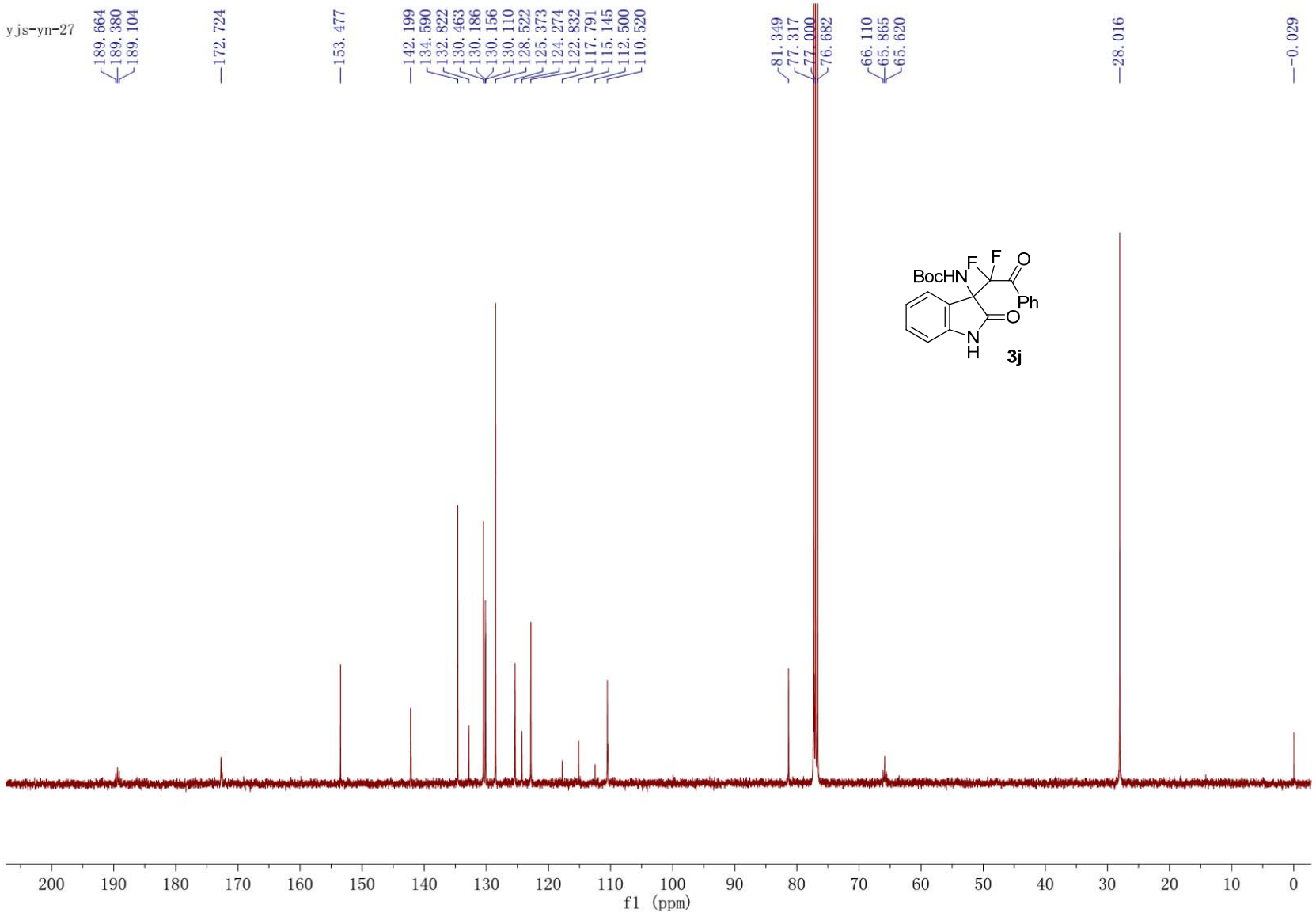
yjs-yn-27

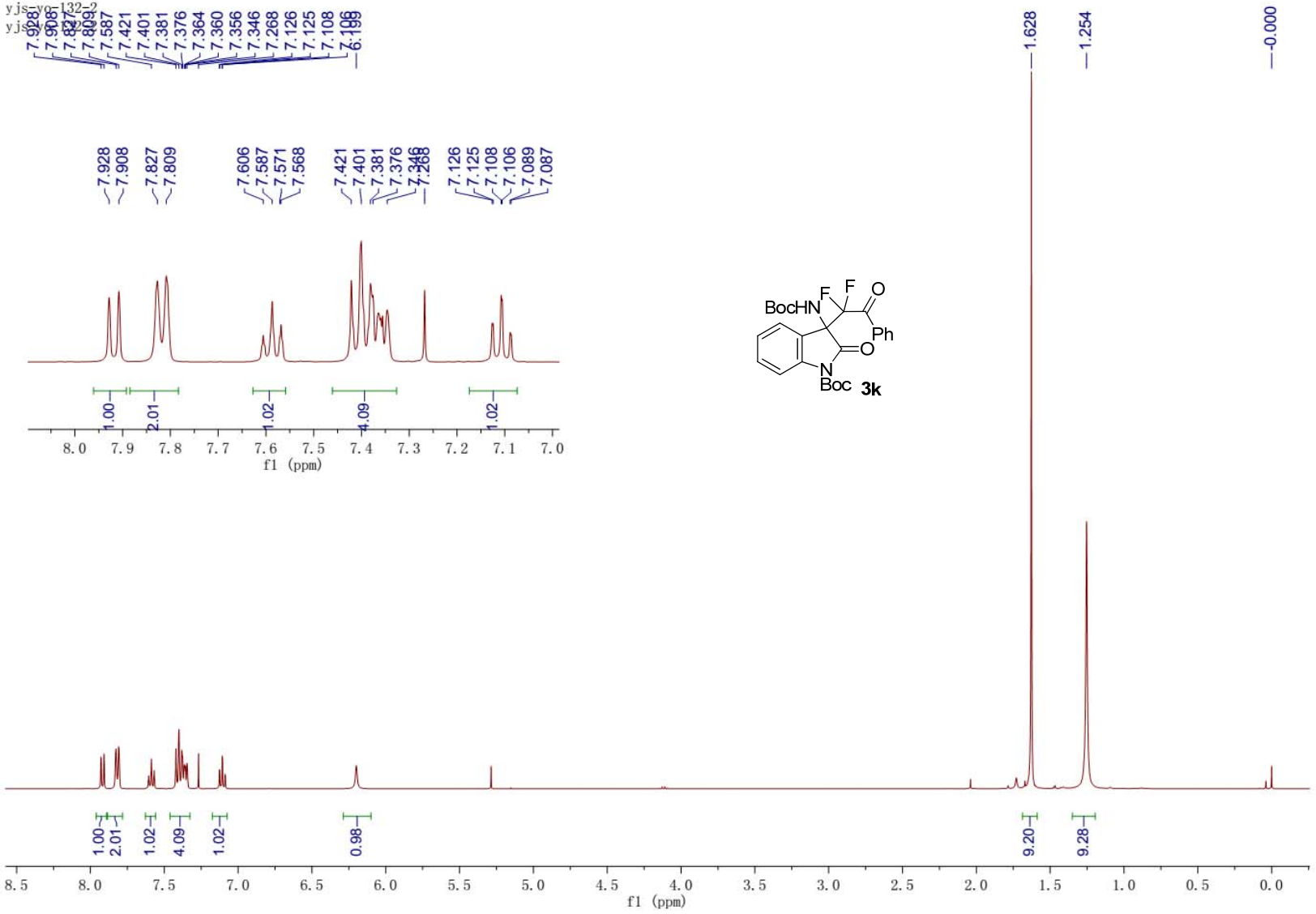
−106.344
−107.079
−108.403
−109.138

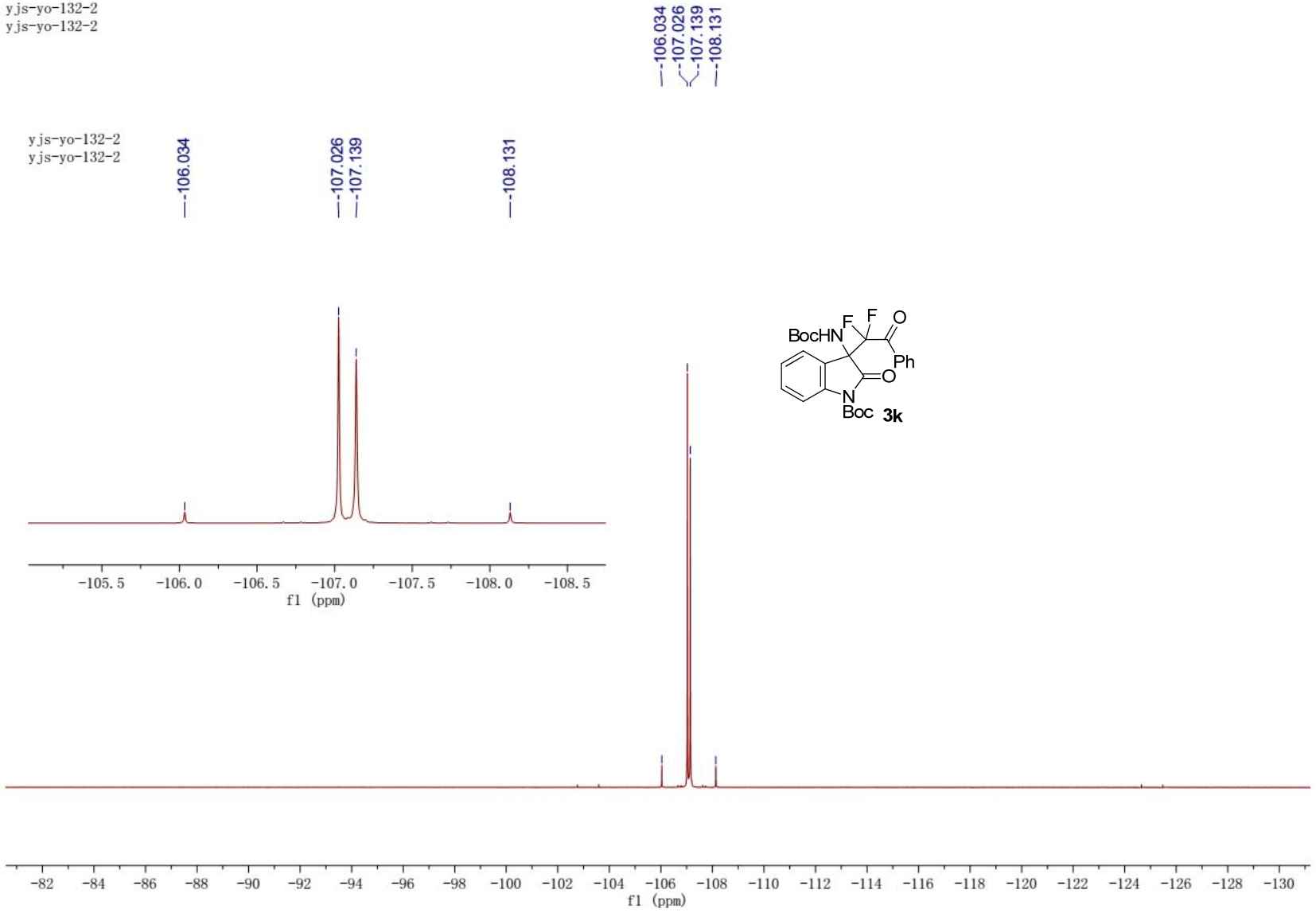


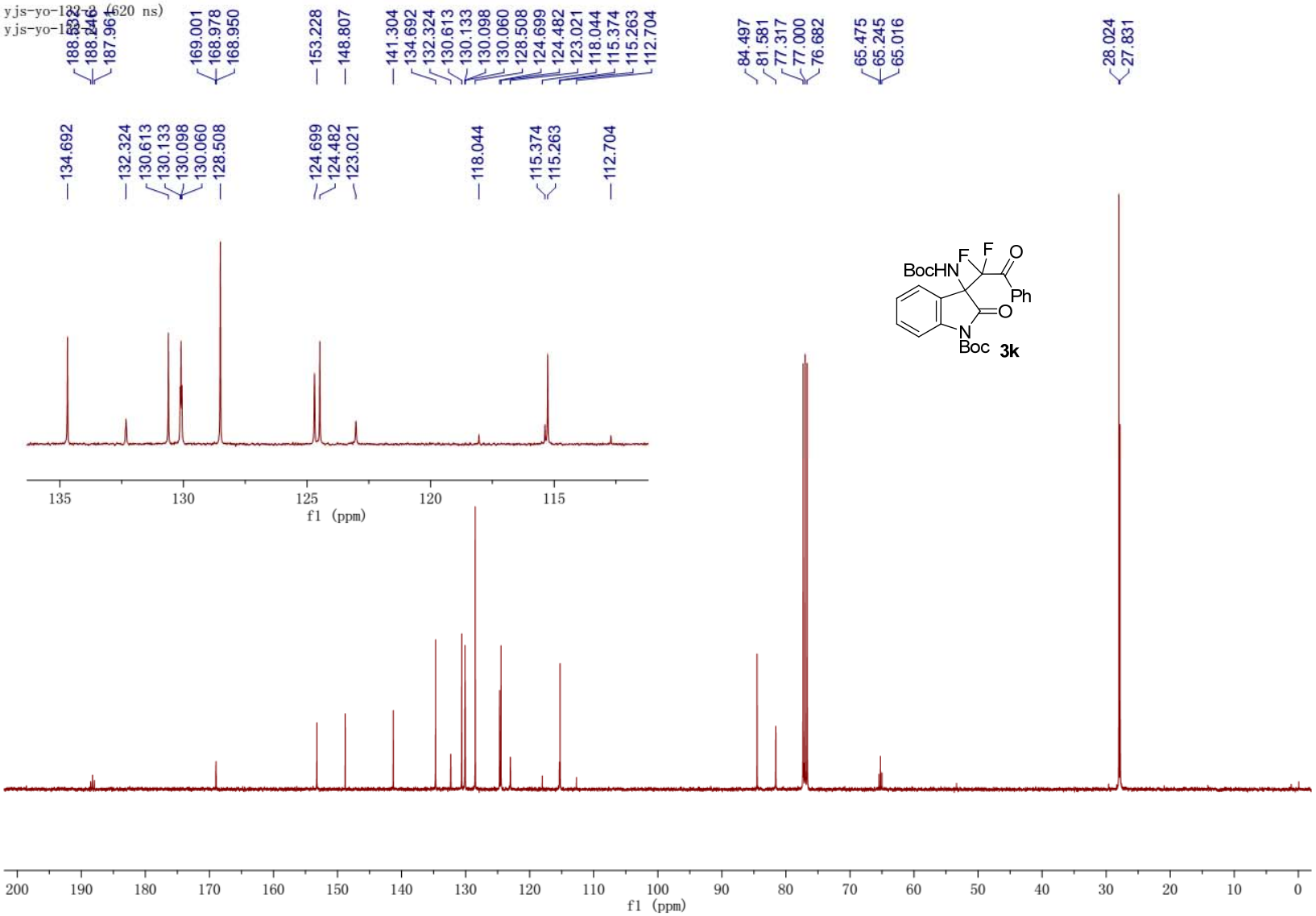
3j

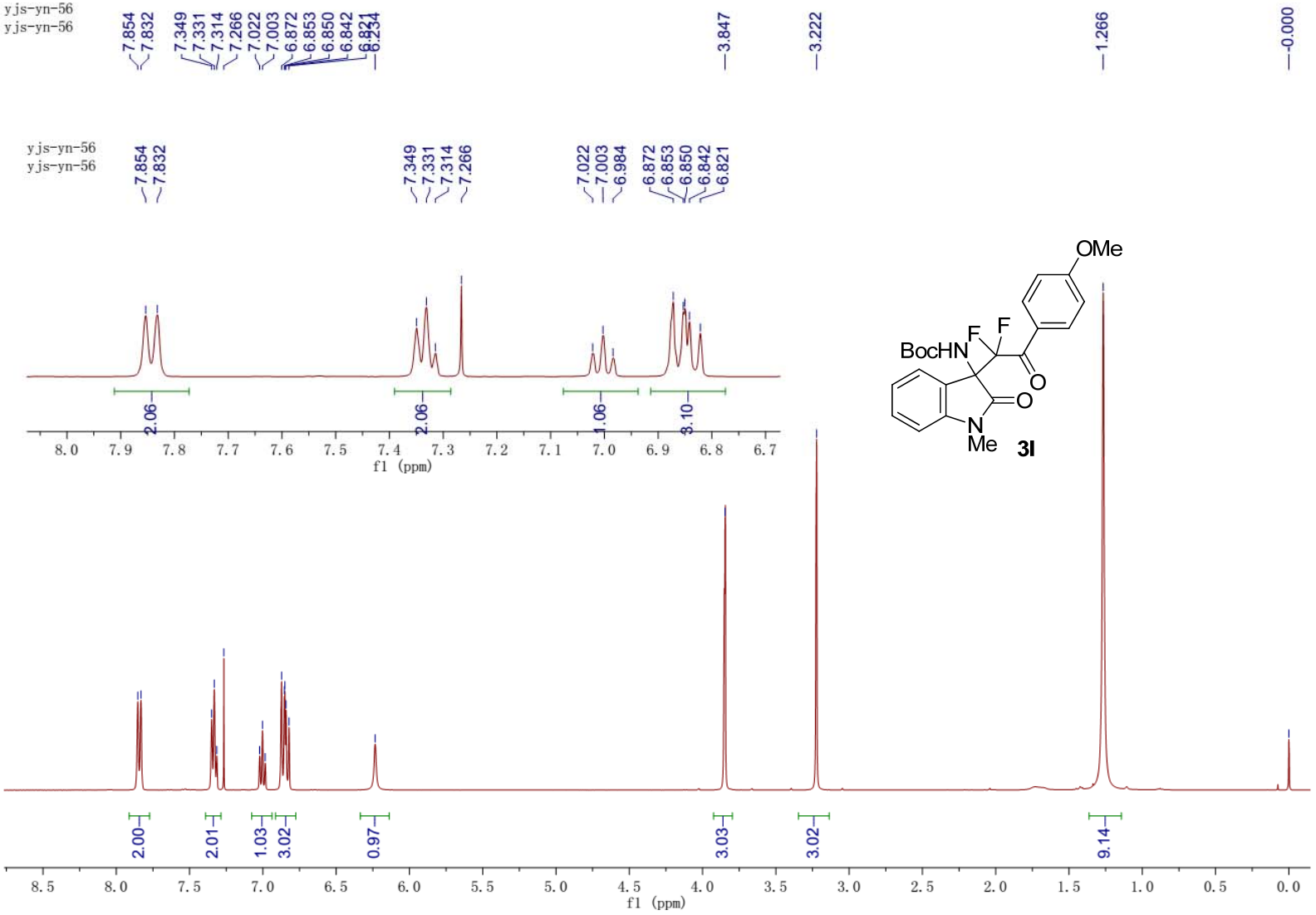



yjs-yn-27
189.664
189.380
189.104
172.724
153.477
142.199
134.590
132.822
130.463
130.186
130.156
130.110
128.522
125.373
124.274
122.832
117.791
115.145
112.500
110.520
81.349
77.317
77.000
76.682
66.110
65.865
65.620
28.016
-0.029
BocHN
F
F
O
Ph
O
N
H
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

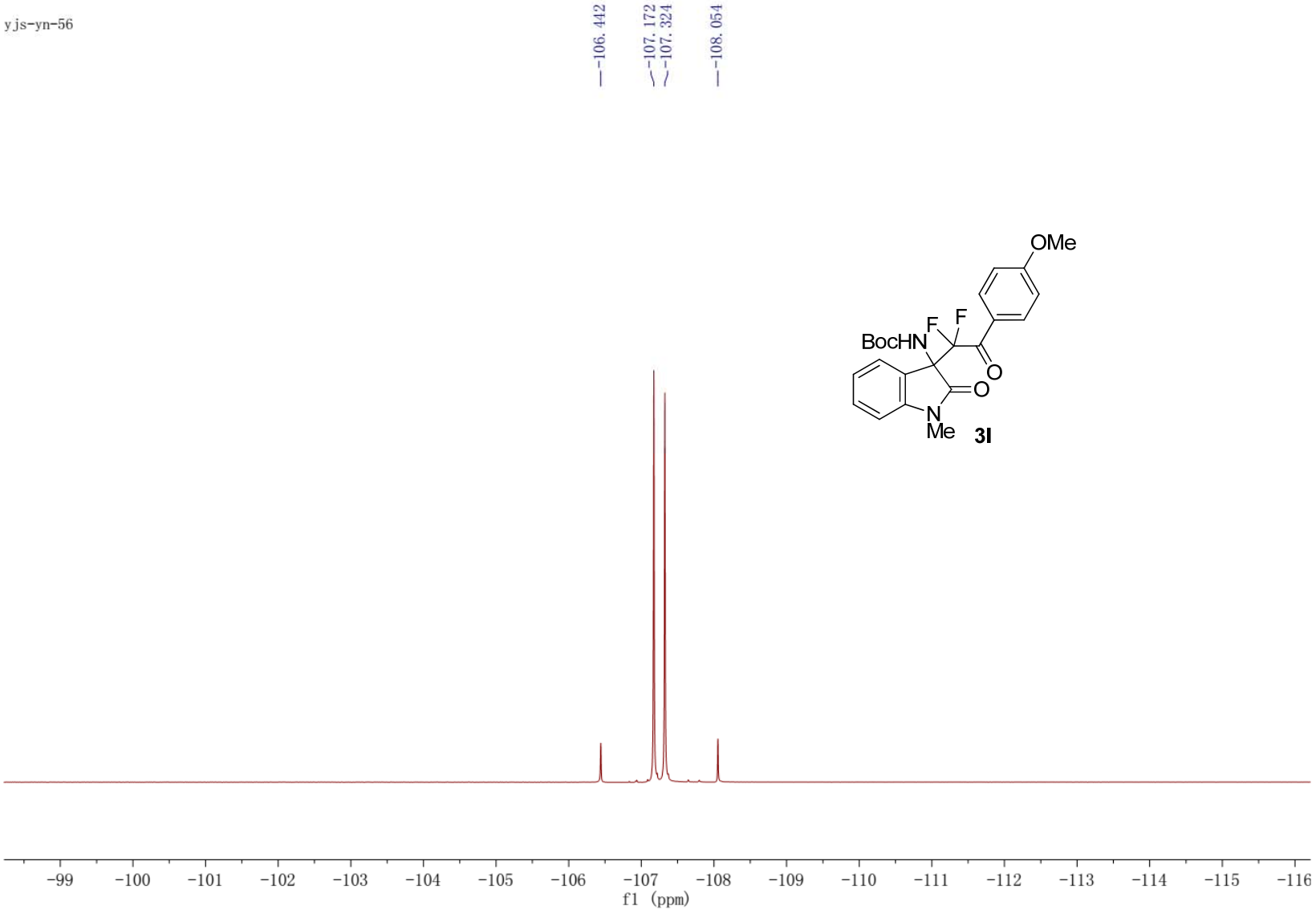

yjs-yc-132-2
7.928
7.908
7.827
7.809
7.606
7.587
7.571
7.568
7.421
7.401
7.381
7.376
7.126
7.125
7.108
7.106
7.089
7.087
1.628
1.254
-0.000
BocHN
F
F
O
Ph
O
N
Boc
3k
1.00
2.01
1.02
4.09
1.02
0.98
9.20
9.28
f1 (ppm)

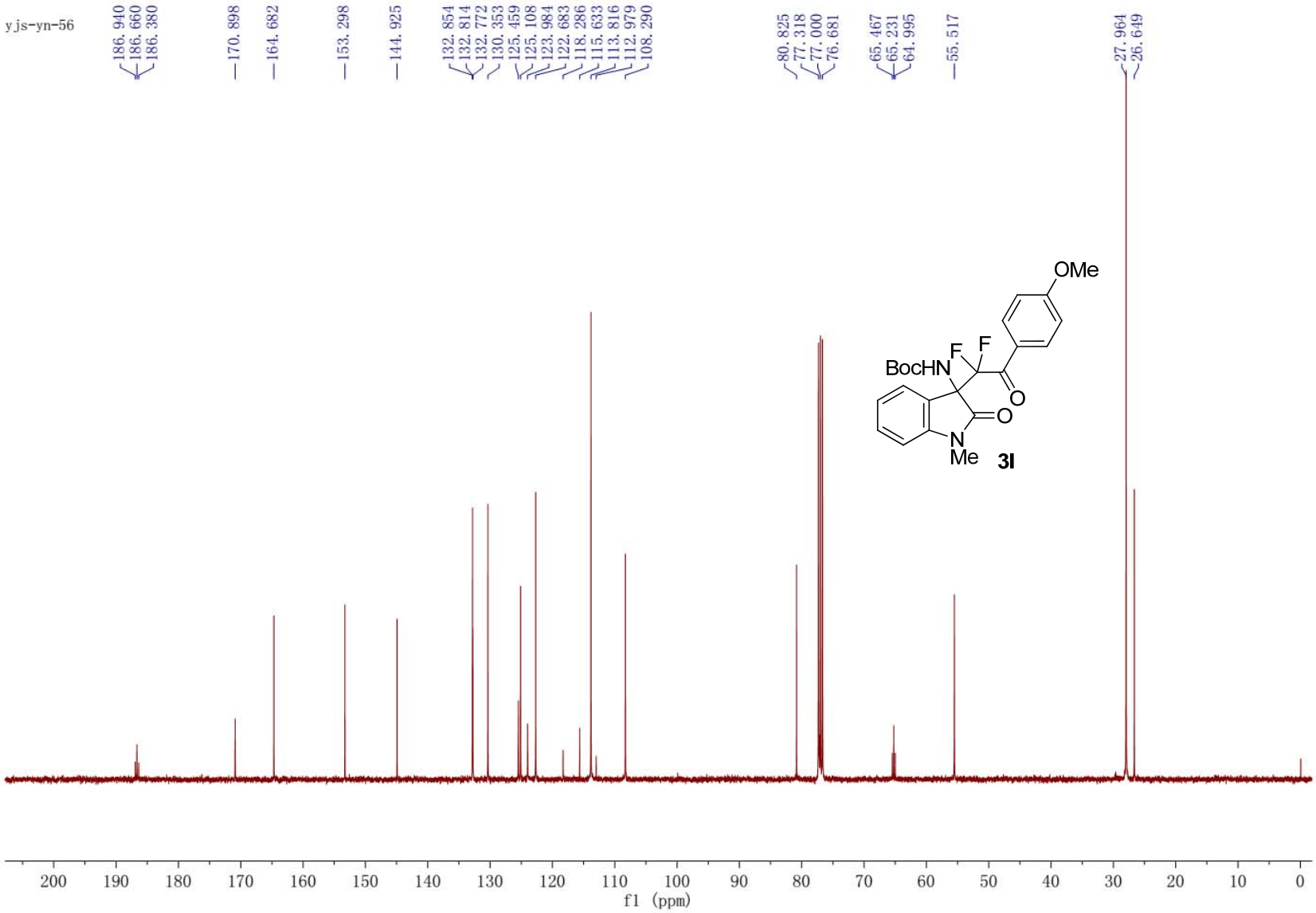

yjs-yo-132-2
yjs-yo-132-2
-106.034
-107.026
-107.139
-108.131
yjs-yo-132-2
yjs-yo-132-2
-106.034
-107.026
-107.139
-108.131
BocHN
F
F
O
Ph
O
N
Boc
3k
-105.5
-106.0
-106.5
-107.0
-107.5
-108.0
-108.5
f1 (ppm)
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
f1 (ppm)

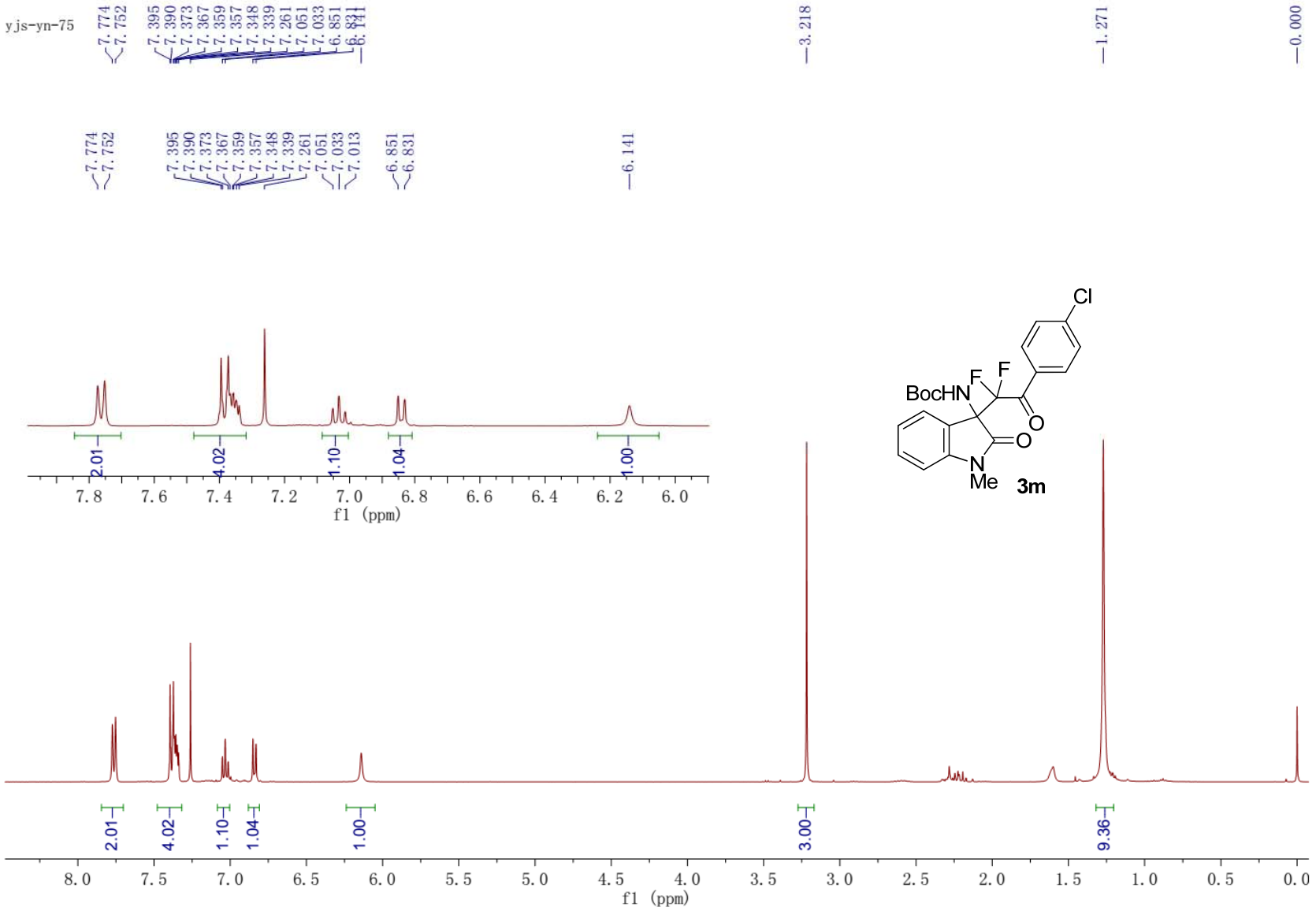

yjs-yo-132-3 (620 ns)
yjs-yo-132-3
188.532
188.246
187.961
169.001
168.978
168.950
153.228
148.807
141.304
134.692
132.324
130.613
130.133
130.098
130.060
128.508
124.699
124.482
123.021
118.044
115.374
115.263
112.704
84.497
81.581
77.317
77.000
76.682
65.475
65.245
65.016
28.024
27.831
BocHN
F
F
O
Ph
O
N
Boc
3k
f1 (ppm)


yjs-yn-56
yjs-yn-56
7.854
7.832
7.349
7.331
7.314
7.266
7.022
7.003
6.872
6.853
6.850
6.842
6.821
6.234
3.847
3.222
1.266
0.000
yjs-yn-56
yjs-yn-56
7.854
7.832
7.349
7.331
7.314
7.266
7.022
7.003
6.984
6.872
6.853
6.850
6.842
6.821
2.06
2.06
1.06
3.10
f1 (ppm)
OMe
BocHN
F
F
O
O
N
Me
3l
2.00
2.01
1.03
3.02
0.97
3.03
3.02
9.14
f1 (ppm)

yjs-yn-56

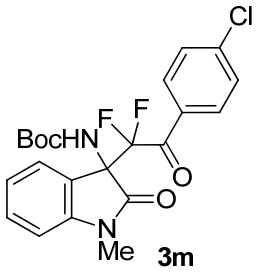

-106.442
-107.172
-107.324
-108.054
OMe
F
F
BocHN
O
O
N
Me
3l
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
f1 (ppm)


yjs-yn-56
186.940
186.660
186.380
170.898
164.682
153.298
144.925
132.854
132.814
132.772
130.353
125.459
125.108
123.984
122.683
118.286
115.633
113.816
112.979
108.290
80.825
77.318
77.000
76.681
65.467
65.231
64.995
55.517
27.964
26.649
OMe
F
F
BocHN
O
O
N
Me
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

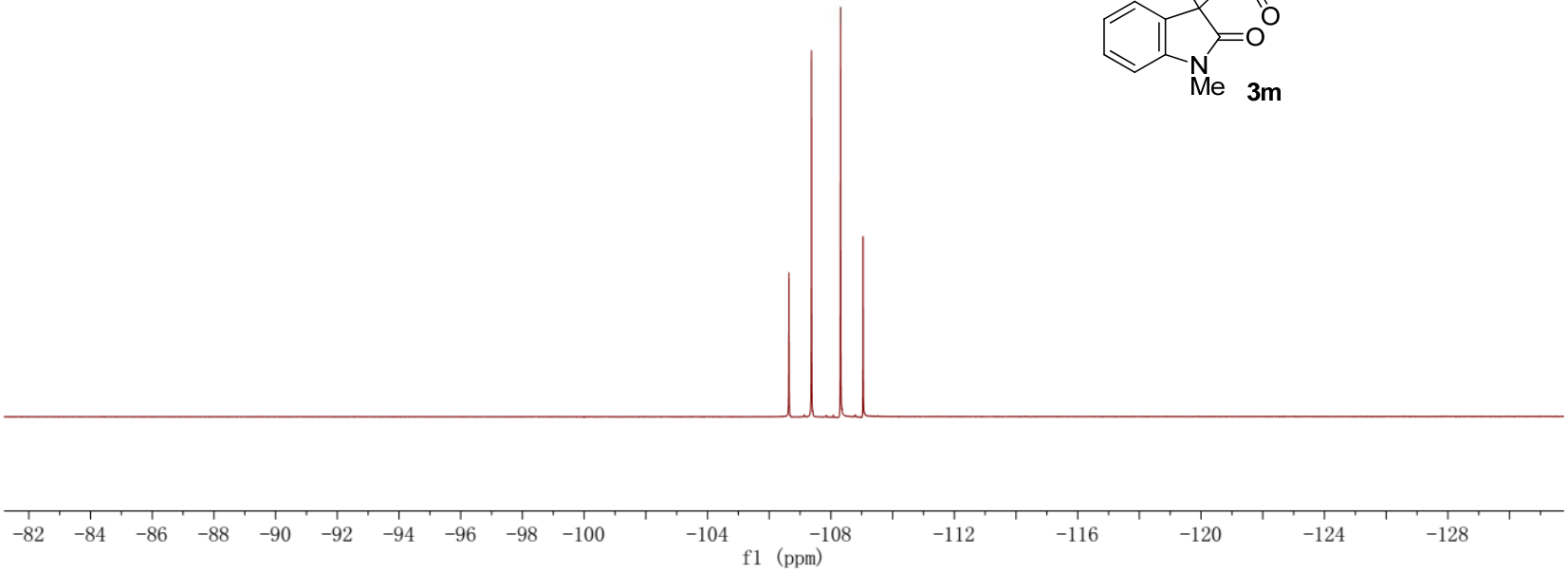

yjs-yn-75
7.774
7.752
7.395
7.390
7.373
7.367
7.359
7.357
7.348
7.339
7.261
7.051
7.033
6.851
6.831
6.141
3.218
1.271
0.000
7.013
2.01
4.02
1.10
1.04
1.00
3.00
9.36
f1 (ppm)
Cl
F
F
BocHN
O
O
N
Me
3m

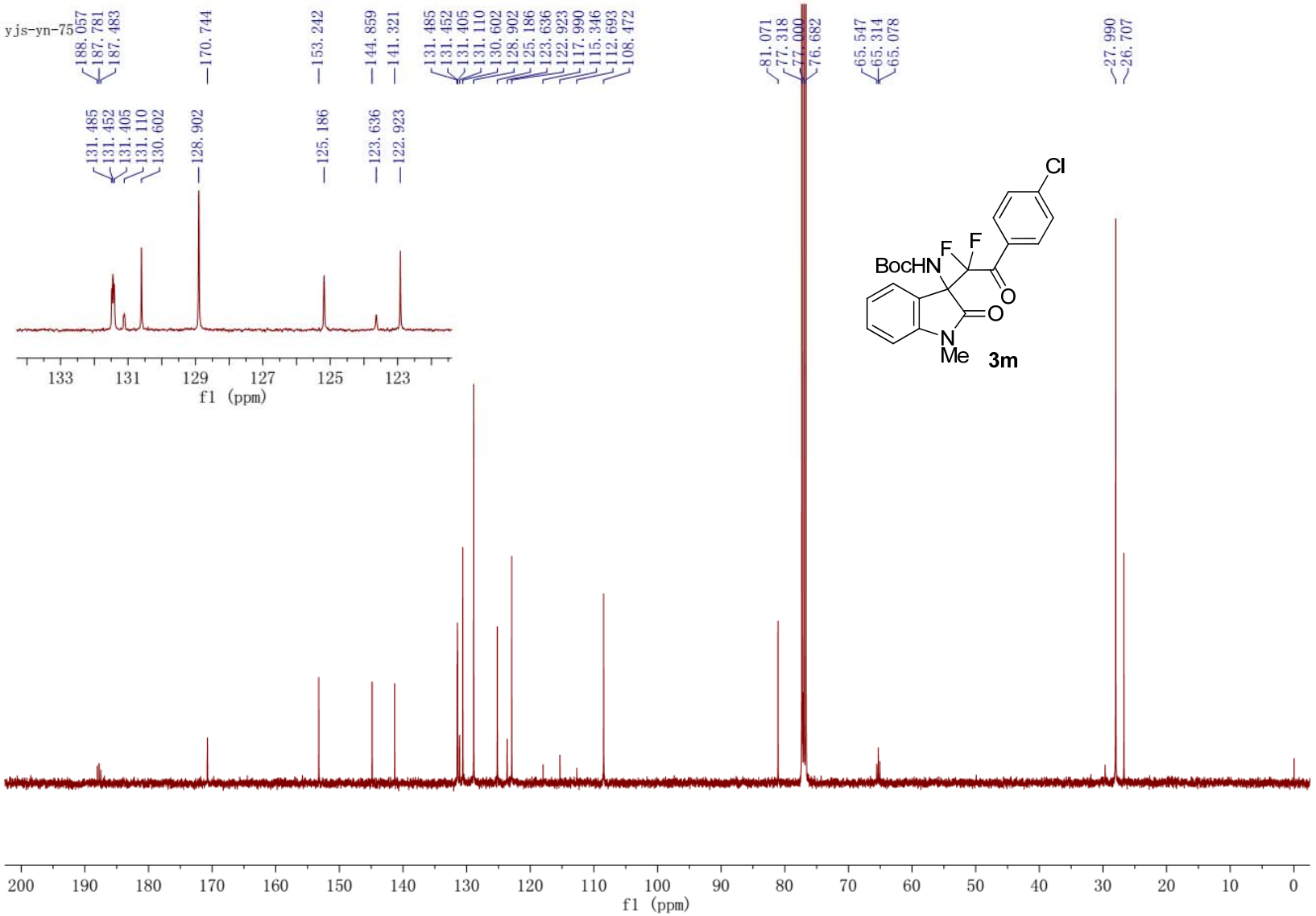
yjs-yn-75

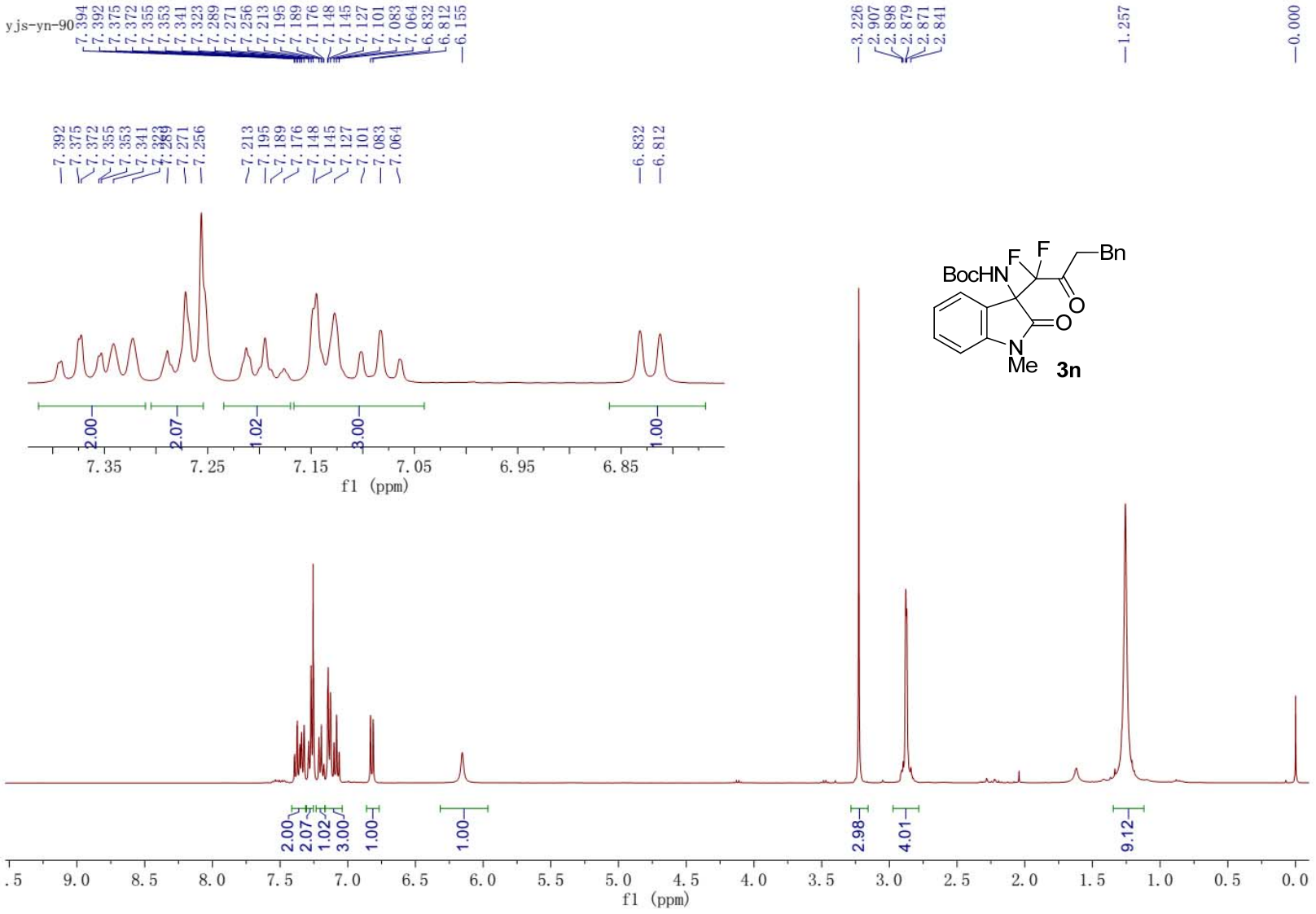
-106.640
-107.370
-108.313
-109.043



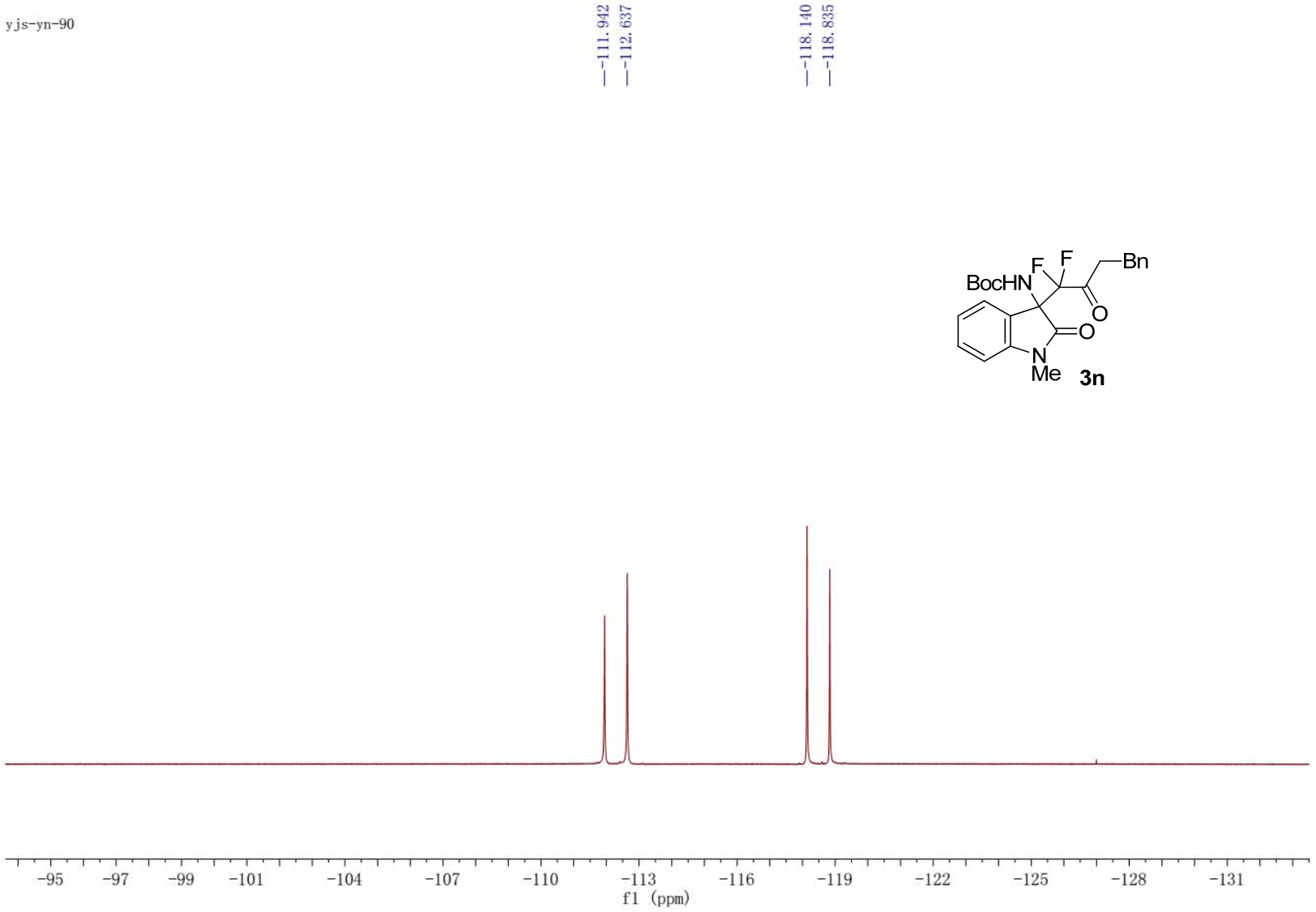
3m

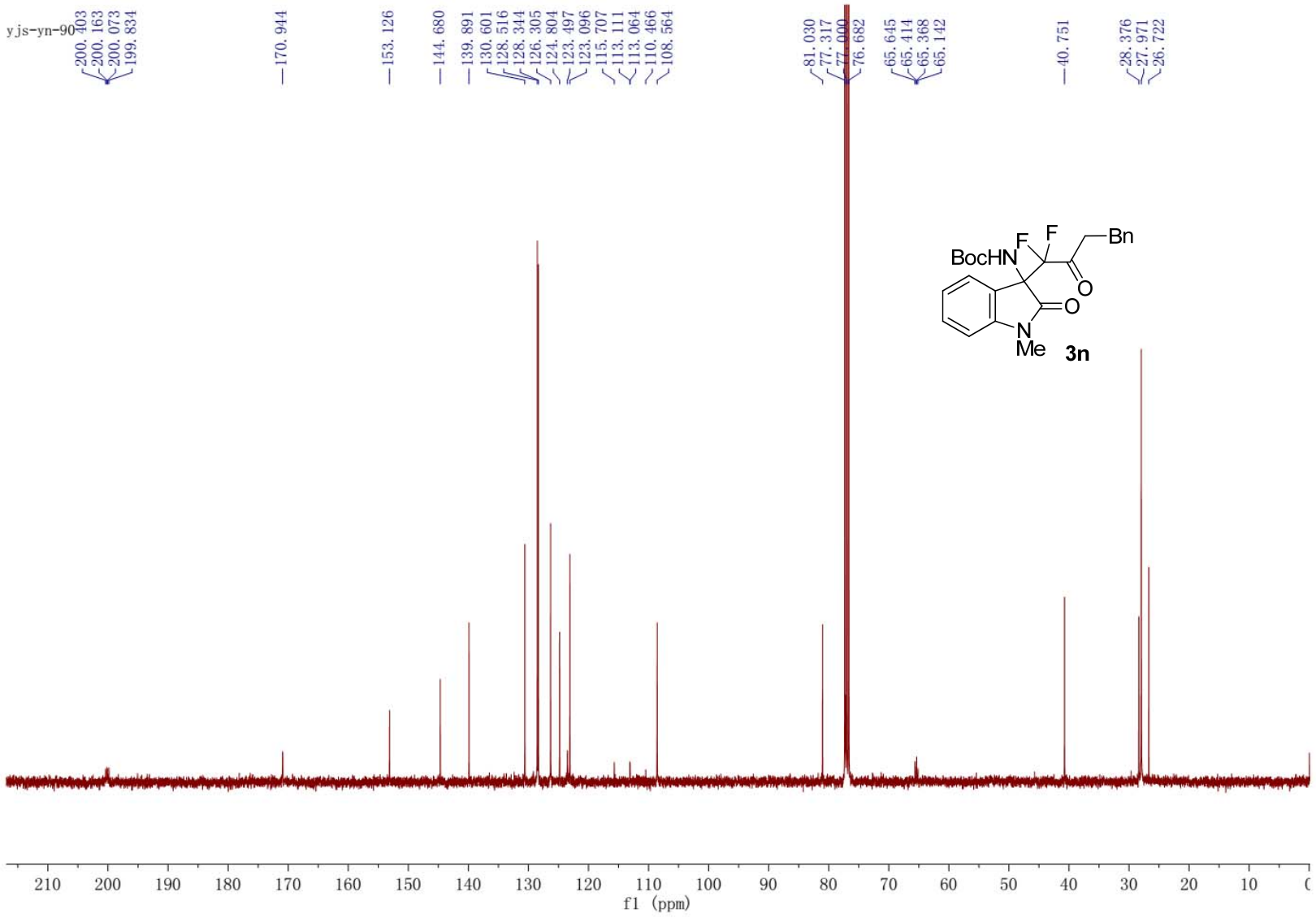


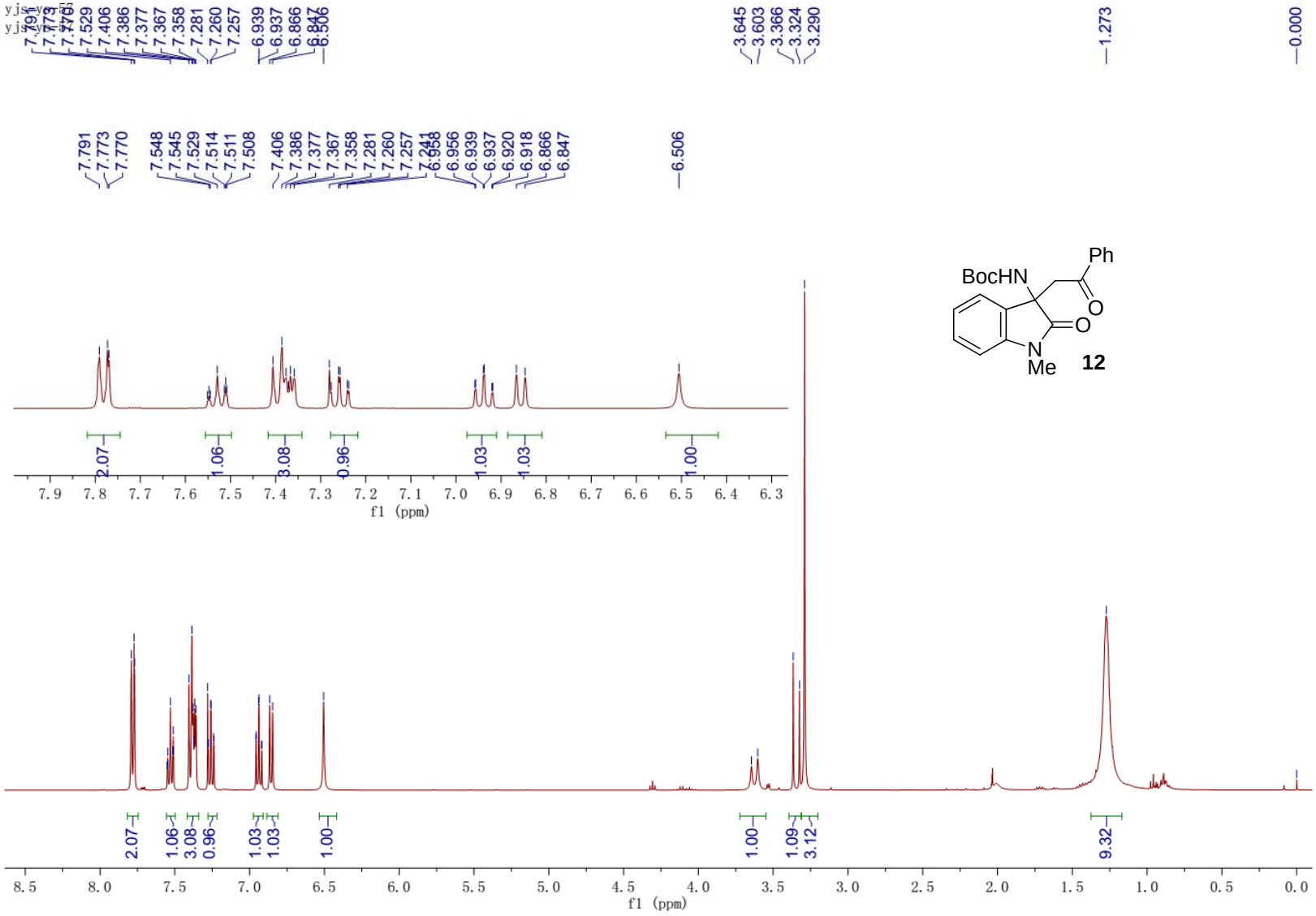

yjs-yn-75
188.057
187.781
187.483
170.744
153.242
144.859
141.321
131.485
131.452
131.405
131.110
130.602
128.902
125.186
123.636
122.923
117.990
115.346
112.693
108.472
81.071
77.318
77.000
76.682
65.547
65.314
65.078
27.990
26.707
f1 (ppm)
Cl
F
F
BocHN
O
O
N
Me
3m

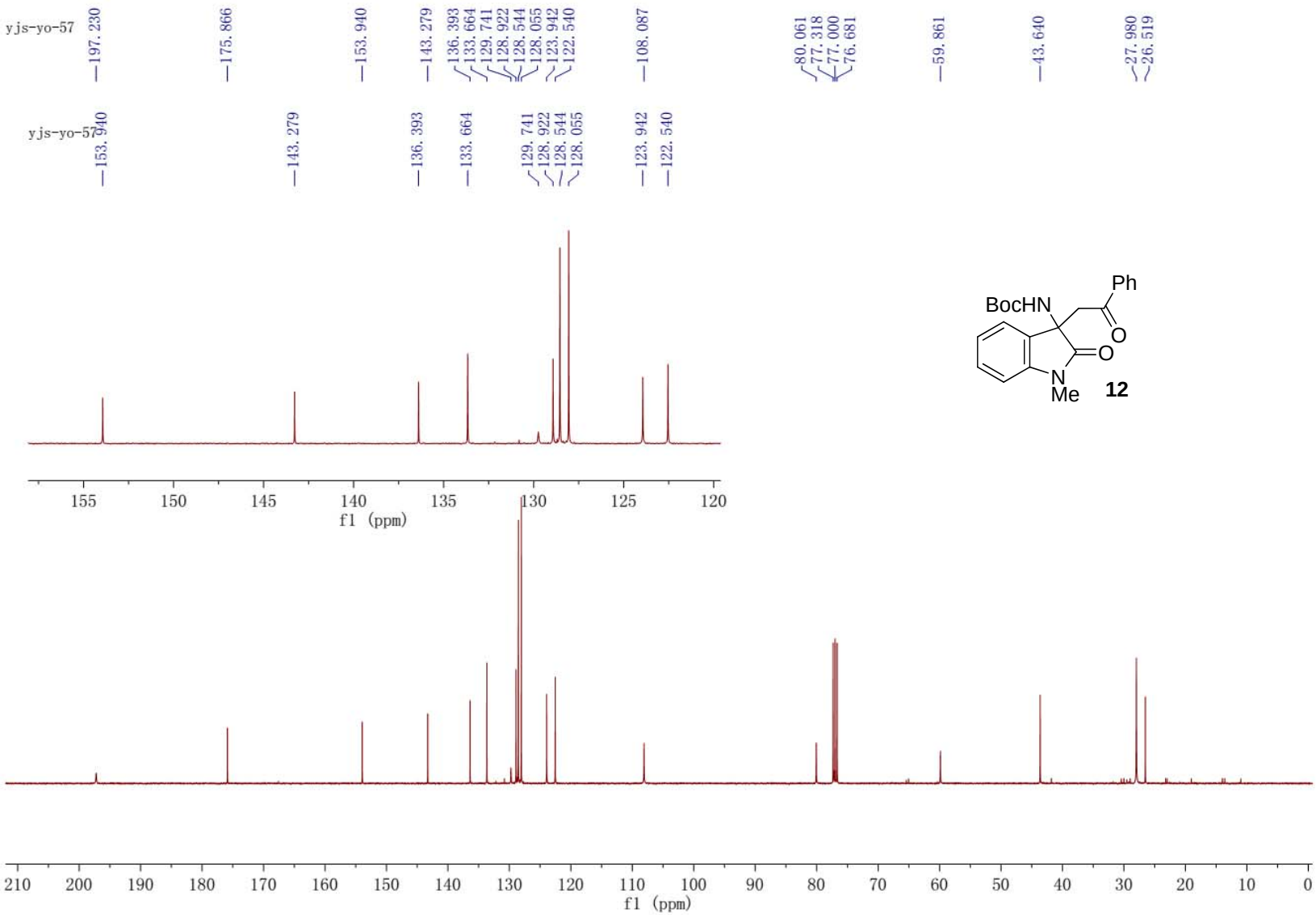

yjs-yn-90
7.394
7.392
7.375
7.372
7.355
7.353
7.341
7.323
7.289
7.271
7.256
7.213
7.195
7.189
7.176
7.148
7.145
7.127
7.101
7.083
7.064
6.832
6.812
6.155
3.226
2.907
2.898
2.879
2.871
2.841
1.257
0.000
BocHN
F
F
Bn
O
O
N
Me
3n
2.00
2.07
1.02
3.00
1.00
1.00
2.98
4.01
9.12
f1 (ppm)

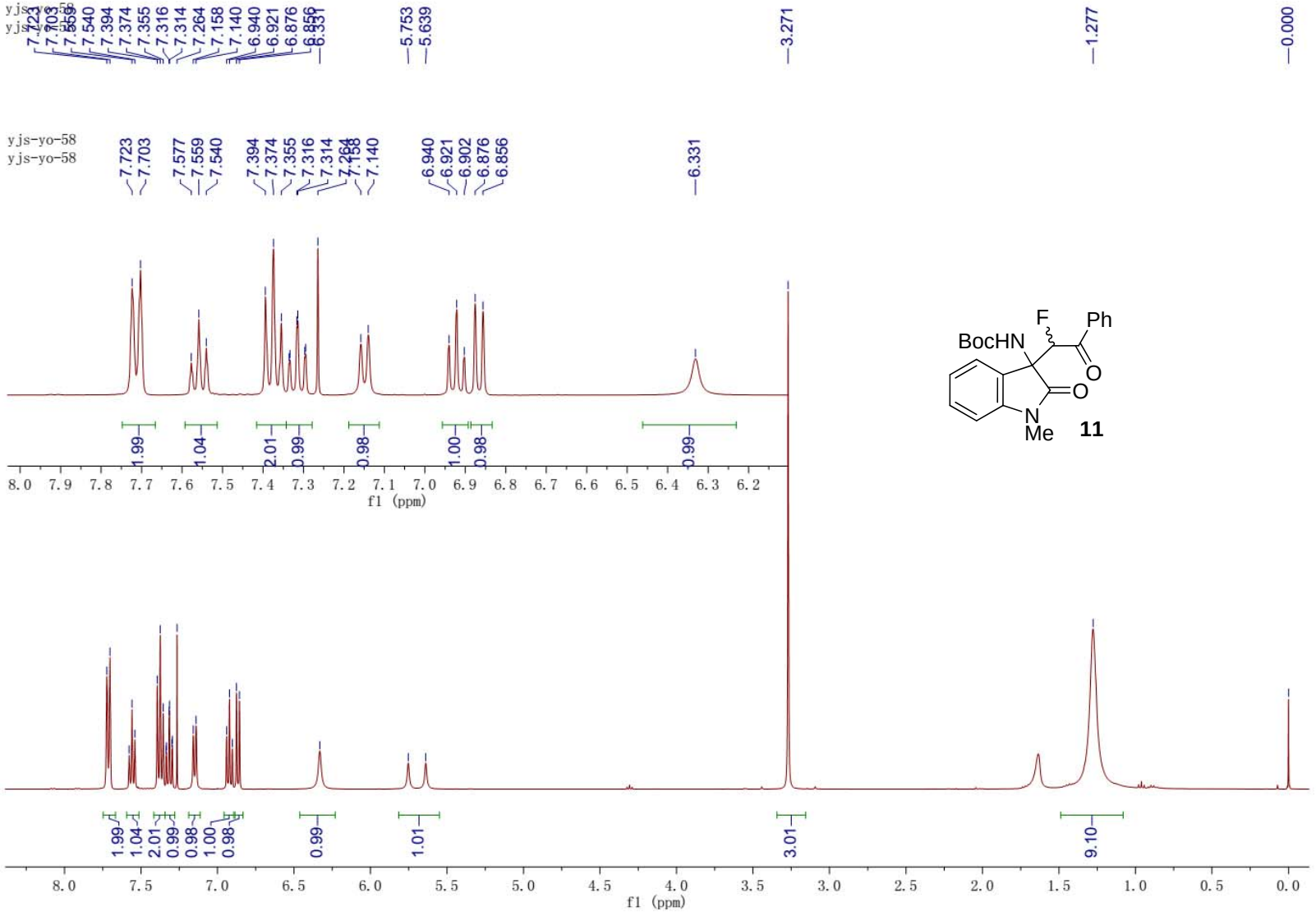
yjs-yn-90


-111.942
-112.637
-118.140
-118.835
BocHN
F
F
Bn
O
O
N
Me
3n
-95
-97
-99
-101
-104
-107
-110
-113
-116
-119
-122
-125
-128
-131
f1 (ppm)

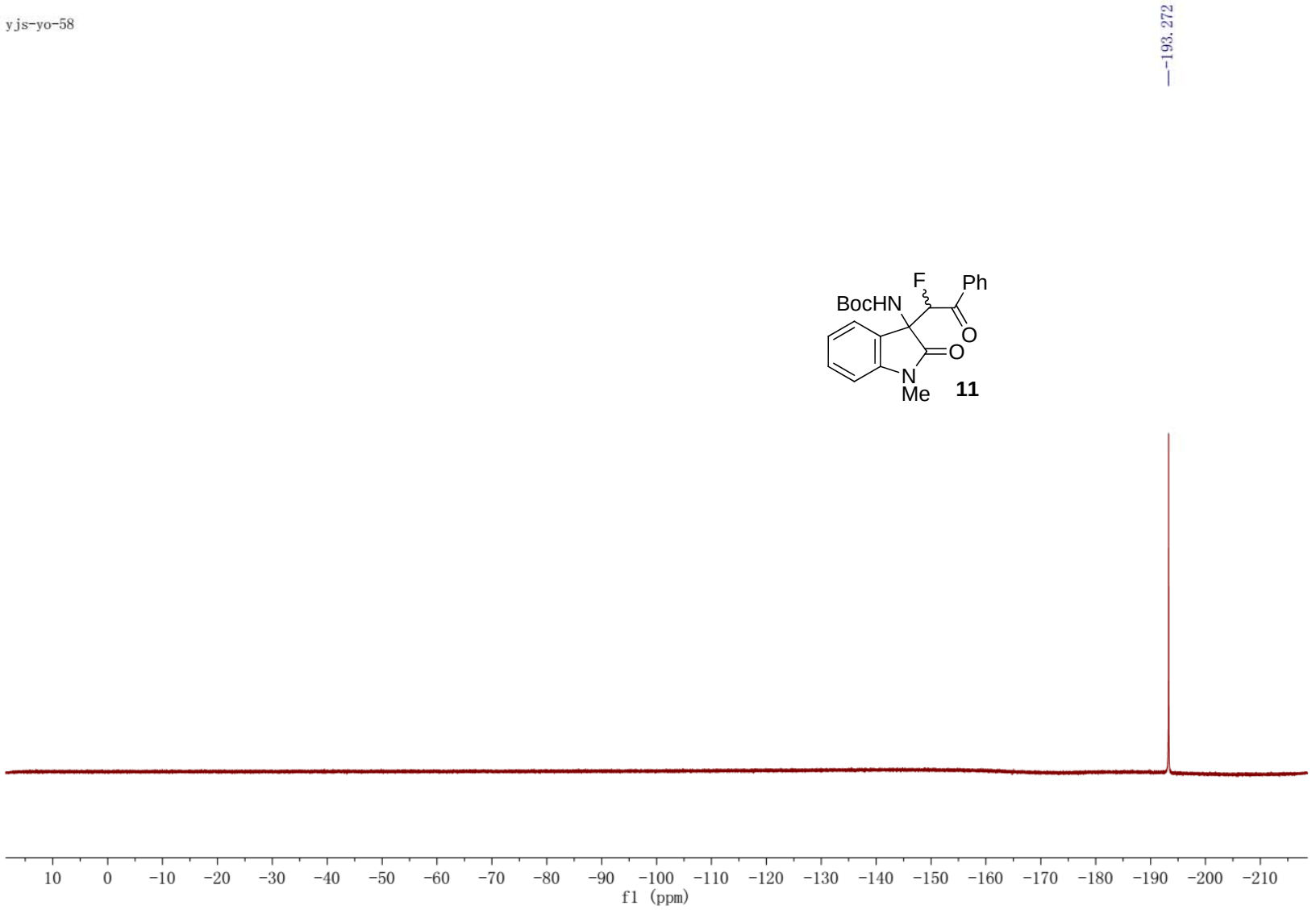

yjs-yn-90
200.403
200.163
200.073
199.834
170.944
153.126
144.680
139.891
130.601
128.516
128.344
126.305
124.804
123.497
123.096
115.707
113.111
113.064
110.466
108.564
81.030
77.317
77.000
76.682
65.645
65.414
65.368
65.142
40.751
28.376
27.971
26.722
BocHN
F
F
Bn
O
O
N
Me
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

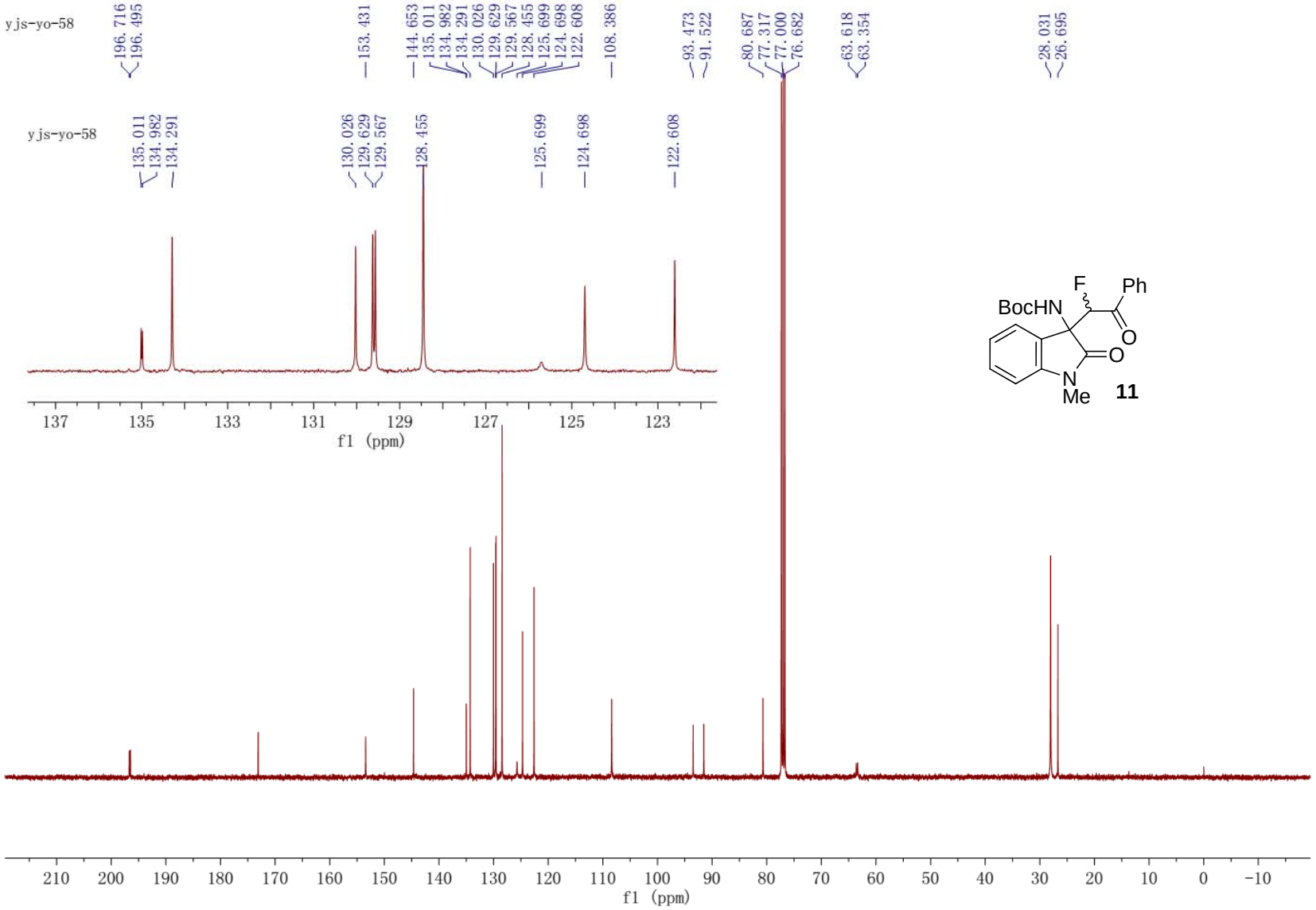

7.791
7.773
7.770
7.548
7.545
7.529
7.514
7.511
7.508
7.406
7.386
7.377
7.367
7.358
7.281
7.260
7.257
6.939
6.937
6.866
6.847
6.506
3.645
3.603
3.366
3.324
3.290
1.273
0.000
BocHN
Ph
O
O
N
Me
12
f1 (ppm)

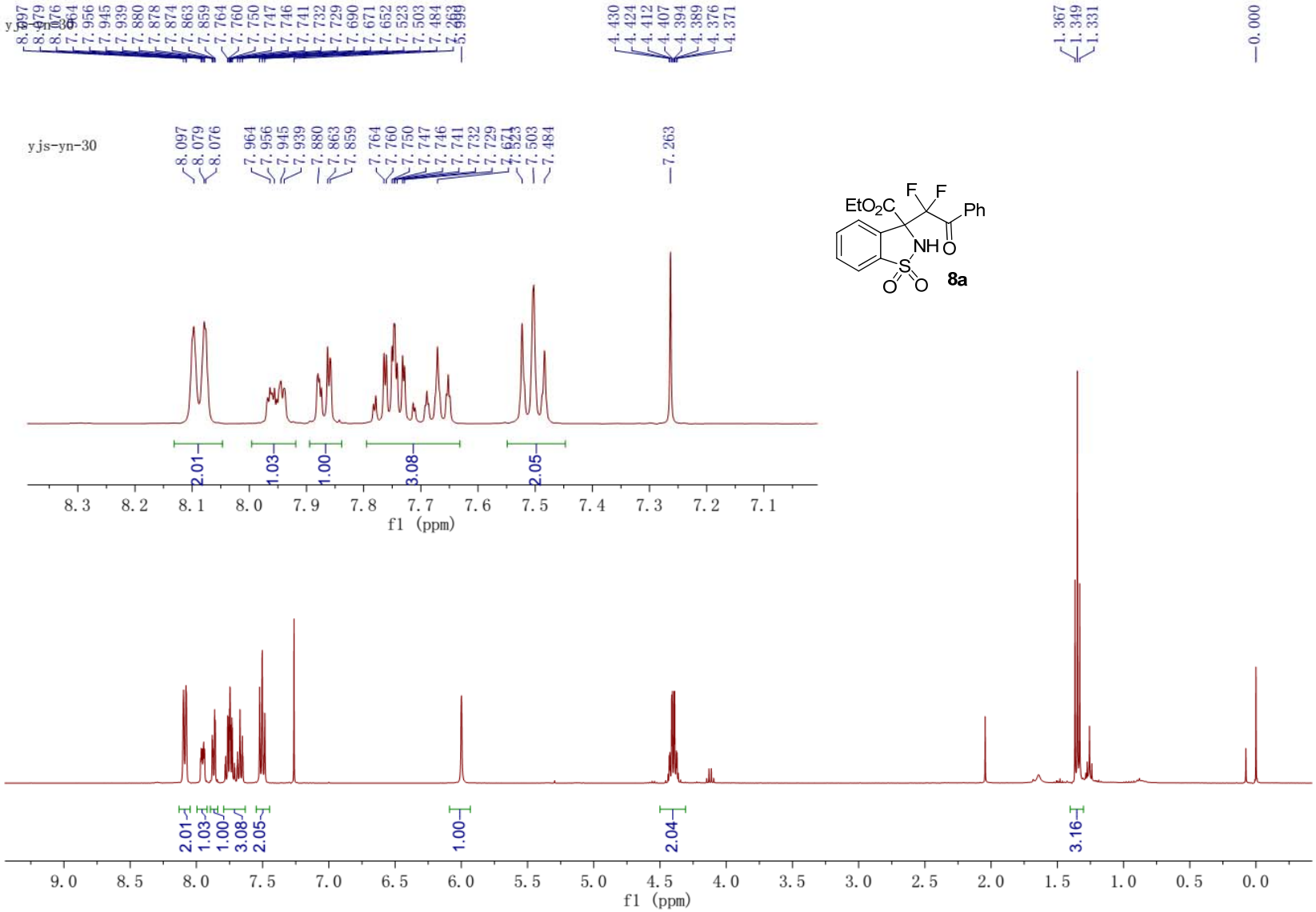

yjs-yo-57
197.230
175.866
153.940
143.279
136.393
133.664
129.741
128.922
128.544
128.055
123.942
122.540
108.087
80.061
77.318
77.000
76.681
59.861
43.640
27.980
26.519
yjs-yo-57
153.940
143.279
136.393
133.664
129.741
128.922
128.544
128.055
123.942
122.540
155
150
145
140
135
130
125
120
f1 (ppm)
BocHN
Ph
O
O
N
Me
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


yjs-yo-58
yjs-yo-58
7.723
7.703
7.577
7.559
7.540
7.394
7.374
7.355
7.316
7.314
7.264
7.158
7.140
6.940
6.921
6.902
6.876
6.856
6.331
5.753
5.639
3.271
1.277
0.000
1.99
1.04
2.01
0.99
0.98
1.00
0.98
0.99
f1 (ppm)
F
Ph
BocHN
O
O
N
Me
11

yjs-yo-58

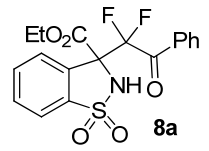

-193.272
F
Ph
BocHN
O
O
N
Me
11
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


yjs-yo-58
196.716
196.495
153.431
144.653
135.011
134.982
134.291
130.026
129.629
129.567
128.455
125.699
124.698
122.608
108.386
93.473
91.522
80.687
77.317
77.000
76.682
63.618
63.354
28.031
26.695
yjs-yo-58
135.011
134.982
134.291
130.026
129.629
129.567
128.455
125.699
124.698
122.608
137
135
133
131
129
127
125
123
f1 (ppm)
F
Ph
BocHN
O
O
N
Me
11
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)

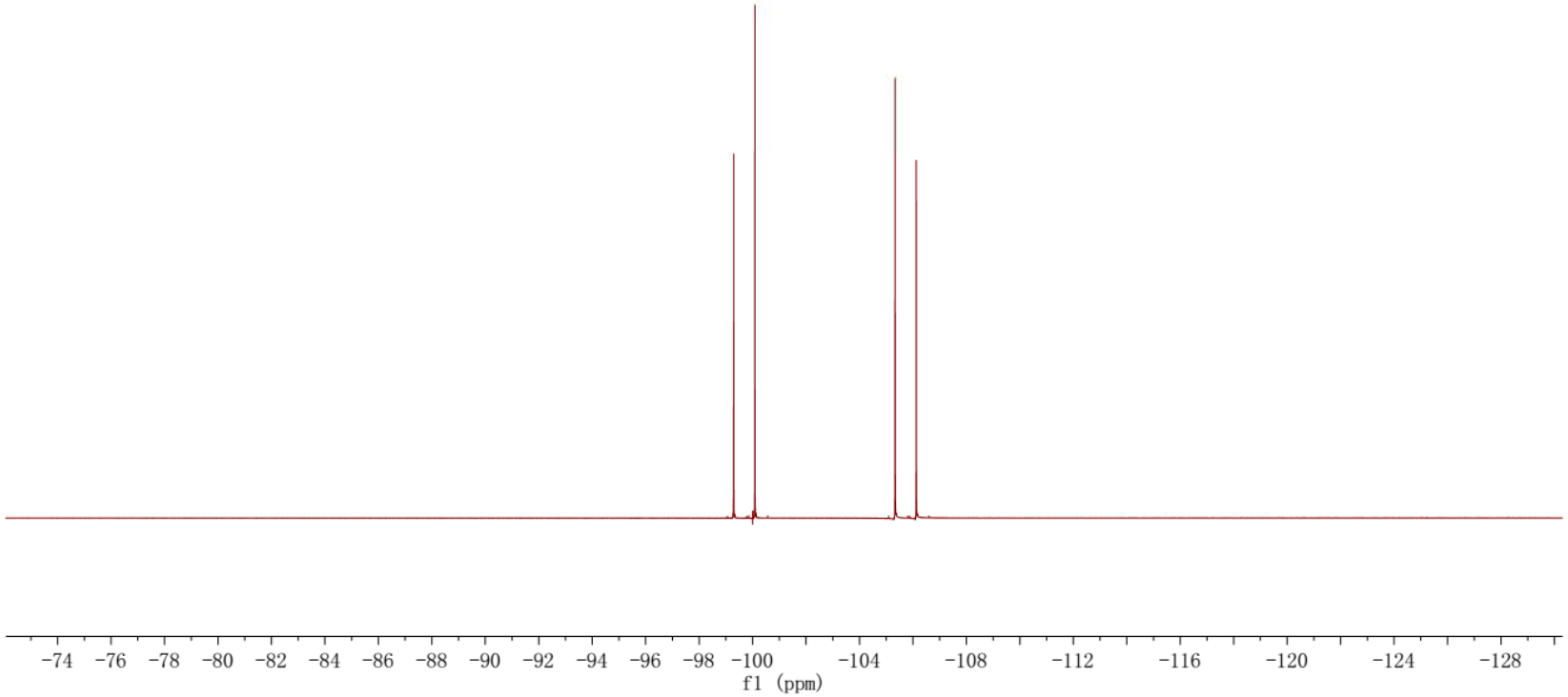

yjs-yn-30
8.097
8.079
8.076
7.964
7.956
7.945
7.939
7.880
7.863
7.859
7.764
7.760
7.750
7.747
7.746
7.741
7.732
7.729
7.503
7.484
7.263
4.430
4.424
4.412
4.407
4.394
4.389
4.376
4.371
1.367
1.349
1.331
0.000
EtO2C
F
F
Ph
NH
O
S
O
O
8a
2.01
1.03
1.00
3.08
2.05
1.00
2.04
3.16
f1 (ppm)

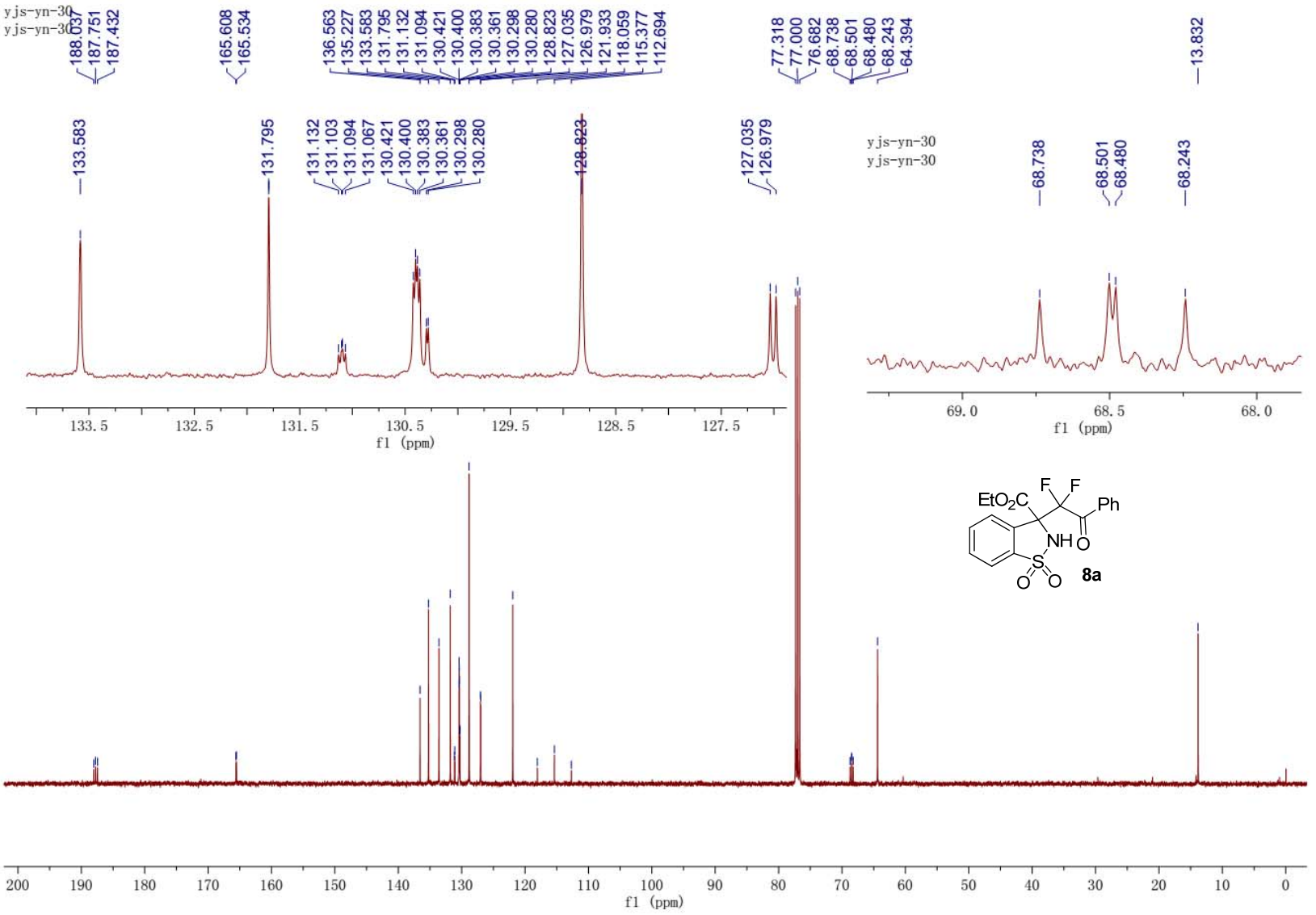
yjs-yn-30

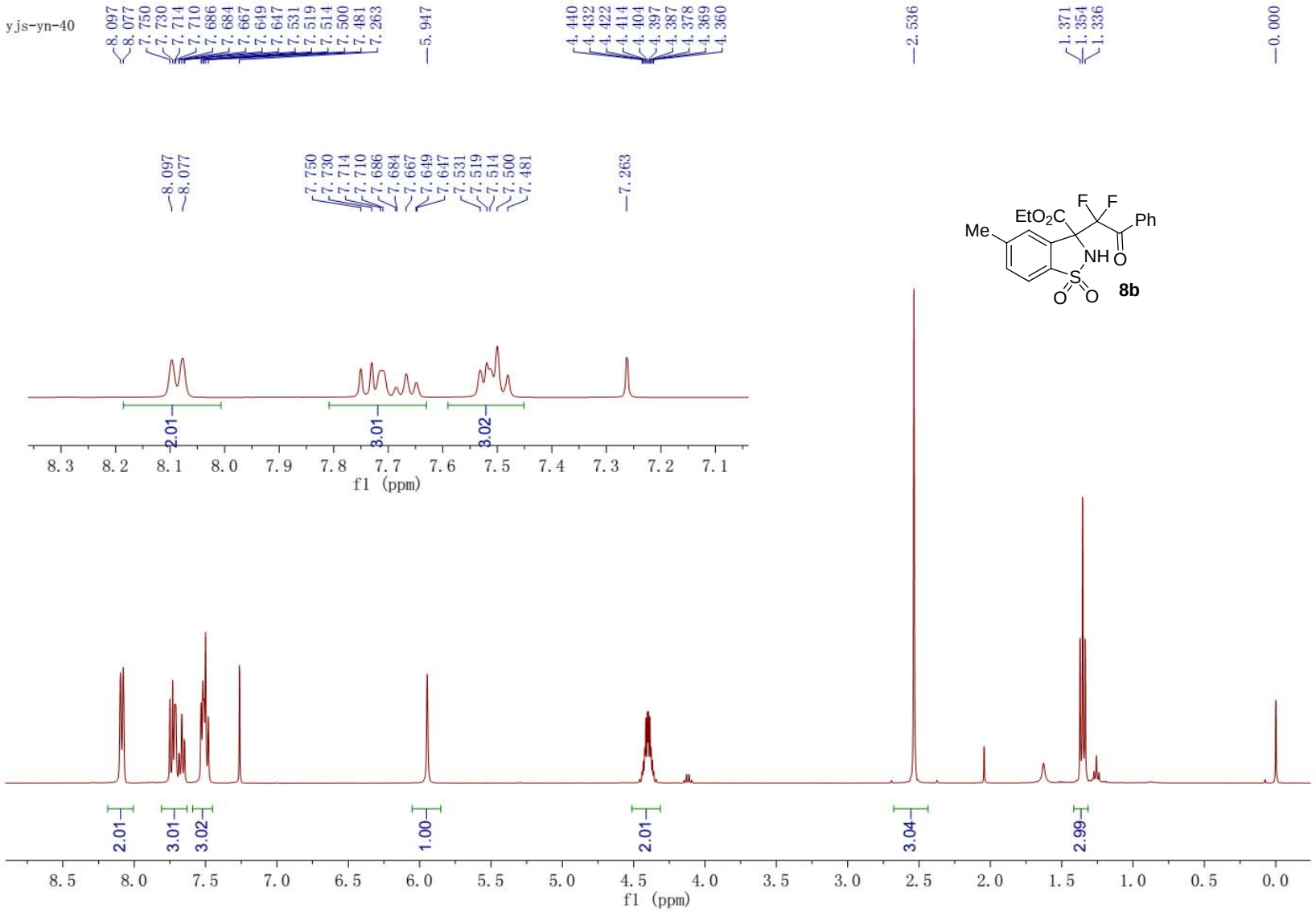
−99.293
−100.086
−105.330
−106.123



8a

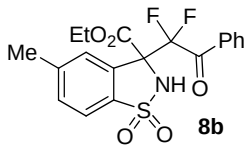



yjs-yn-30
yjs-yn-30
188.037
187.751
187.432
165.608
165.534
136.563
135.227
133.583
131.795
131.132
131.103
131.094
131.067
130.421
130.400
130.383
130.361
130.298
130.280
128.823
127.035
126.979
121.933
118.059
115.377
112.694
77.318
77.000
76.682
68.738
68.501
68.480
68.243
64.394
13.832
133.583
131.795
131.132
131.103
131.094
131.067
130.421
130.400
130.383
130.361
130.298
130.280
128.823
127.035
126.979
133.5
132.5
131.5
130.5
129.5
128.5
127.5
f1 (ppm)
yjs-yn-30
yjs-yn-30
68.738
68.501
68.480
68.243
69.0
68.5
68.0
f1 (ppm)
EtO2C
F
F
Ph
NH
O
S
O
O
8a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

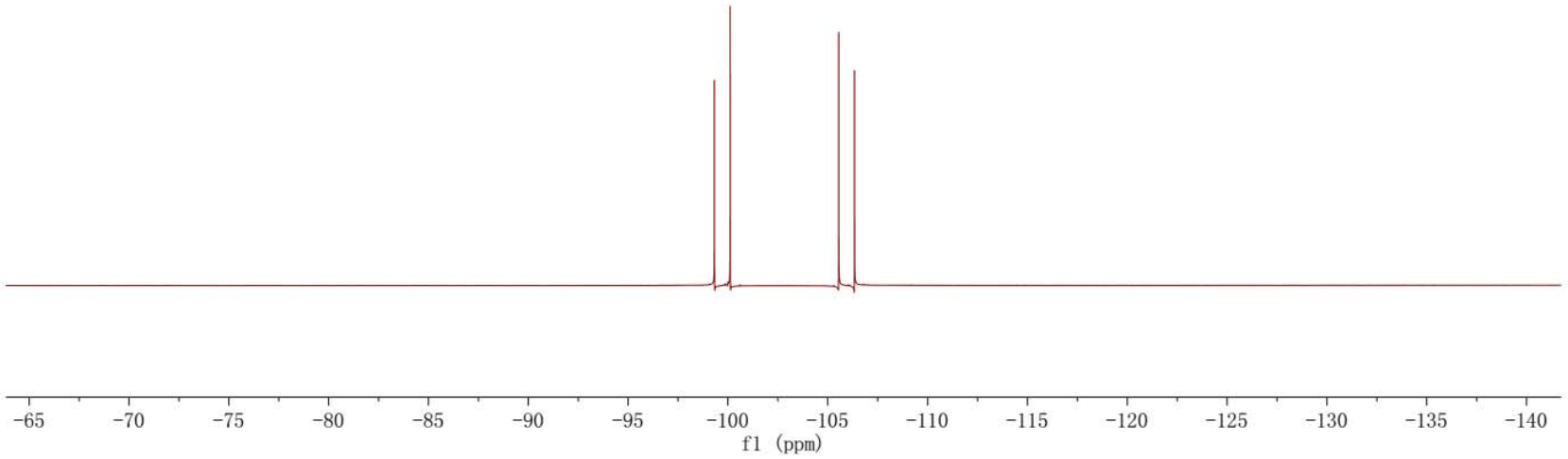

yjs-yn-40
8.097
8.077
7.750
7.730
7.714
7.710
7.686
7.684
7.667
7.649
7.647
7.531
7.519
7.514
7.500
7.481
7.263
5.947
4.440
4.432
4.422
4.414
4.404
4.397
4.387
4.378
4.369
4.360
2.536
1.371
1.354
1.336
0.000
EtO2C
F
F
Ph
Me
NH
O
S
O
O
8b
2.01
3.01
3.02
1.00
2.01
3.04
2.99
f1 (ppm)

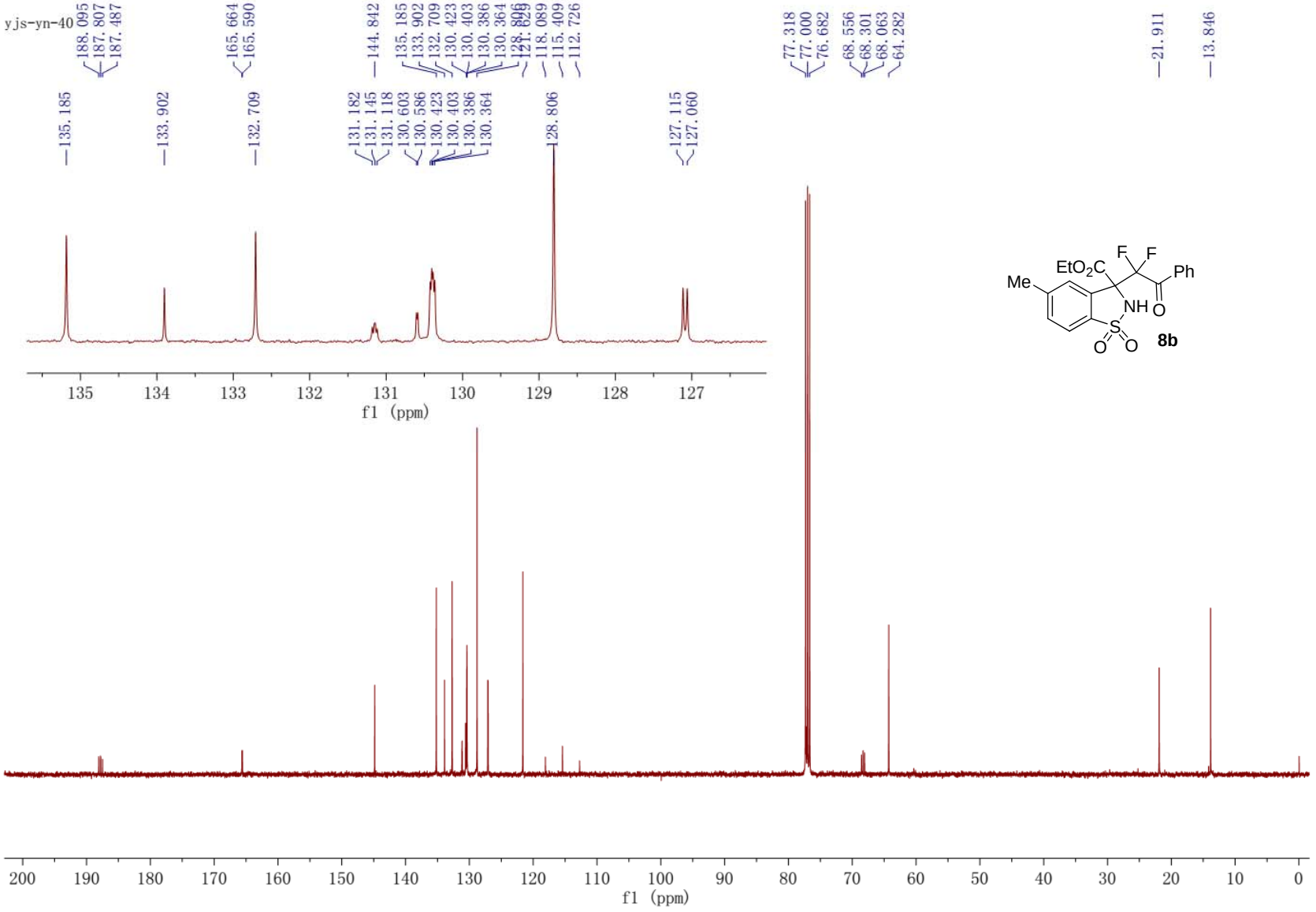
yjs-yn-40

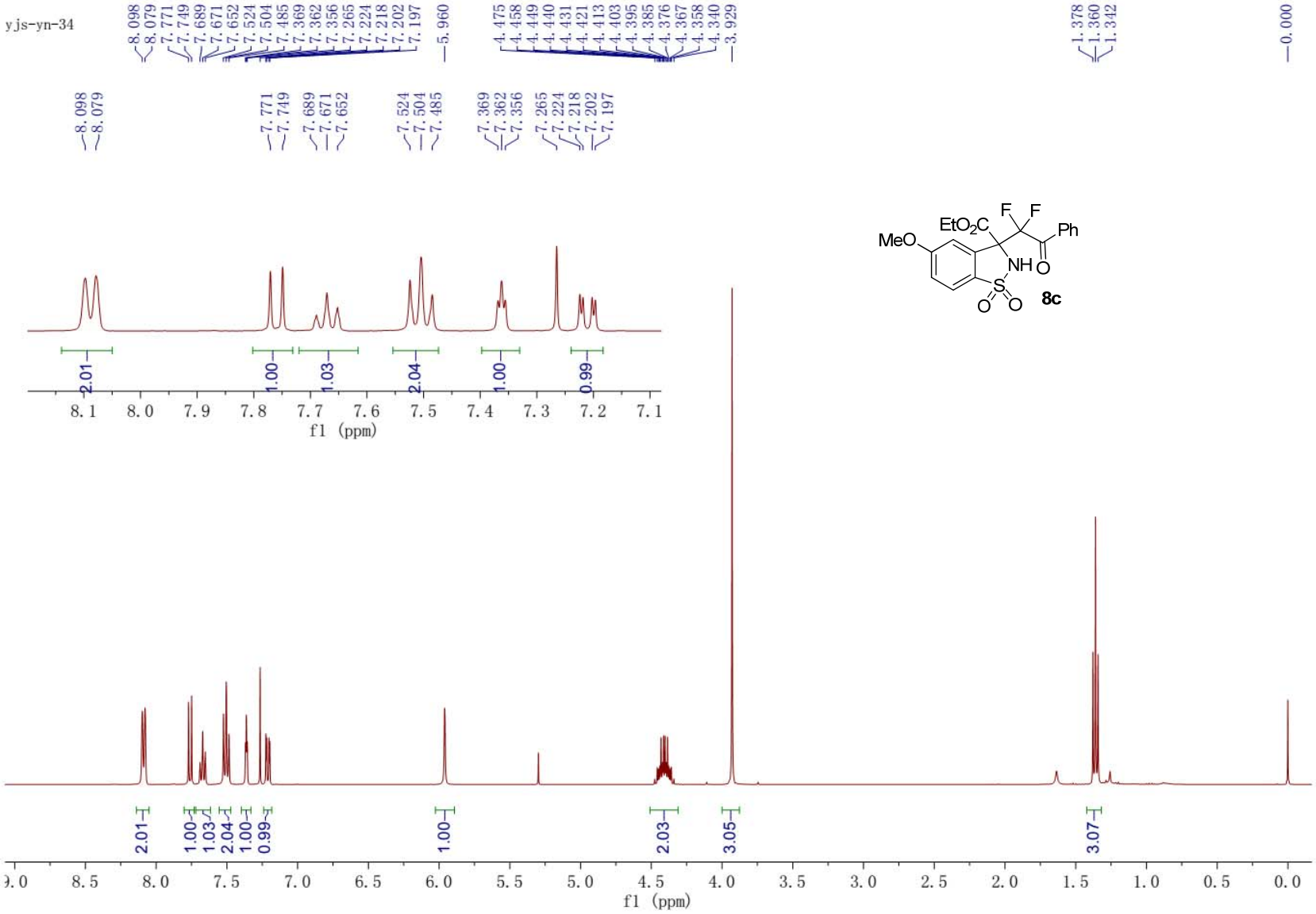
-99.318
-100.110
-105.544
-106.336



8b

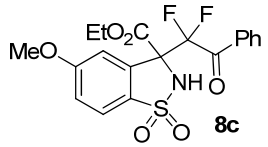



yjs-yn-40
188.095
187.807
187.487
165.664
165.590
144.842
135.185
133.902
132.709
130.423
130.403
130.386
130.364
128.806
118.089
115.409
112.726
77.318
77.000
76.682
68.556
68.301
68.063
64.282
21.911
13.846
135.185
133.902
132.709
131.182
131.145
131.118
130.603
130.586
130.423
130.403
130.386
130.364
128.806
127.115
127.060
f1 (ppm)
f1 (ppm)
EtO2C
F
F
Ph
Me
NH
O
S
O
O
8b

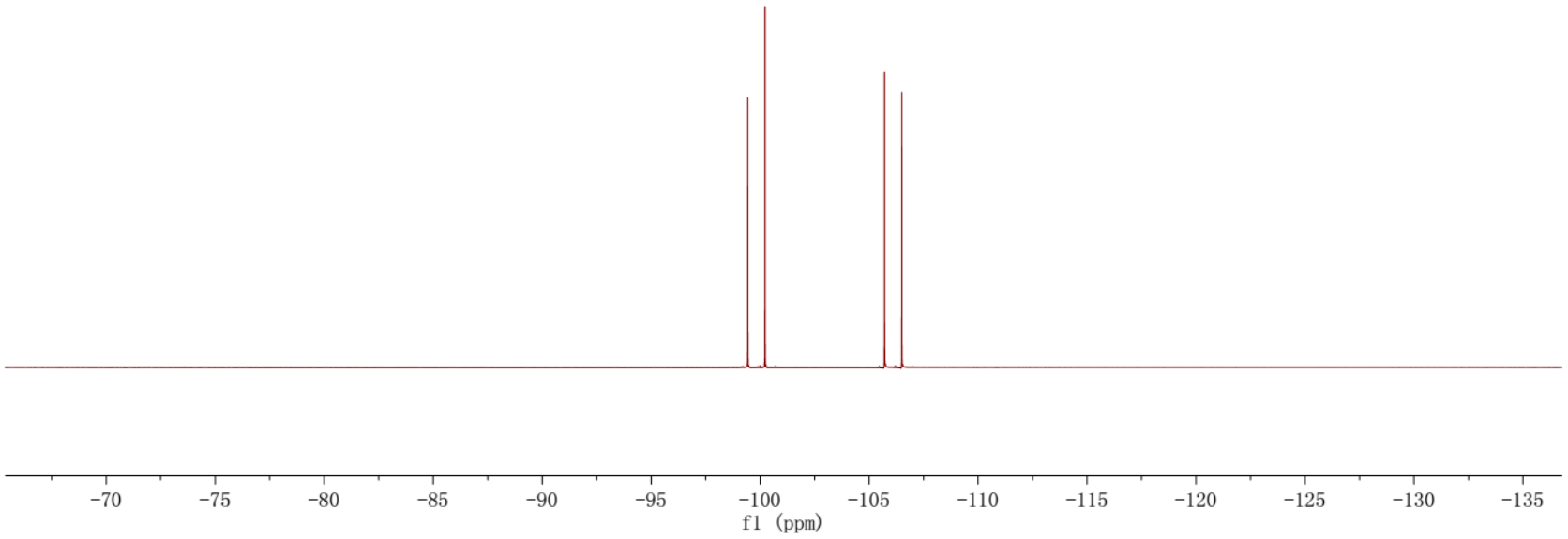

yjs-yn-34
8.098
8.079
7.771
7.749
7.689
7.671
7.652
7.524
7.504
7.485
7.369
7.362
7.356
7.265
7.224
7.218
7.202
7.197
5.960
4.475
4.458
4.449
4.440
4.431
4.421
4.413
4.403
4.395
4.385
4.376
4.367
4.358
4.340
3.929
1.378
1.360
1.342
0.000
2.01
1.00
1.03
2.04
1.00
0.99
1.00
2.03
3.05
3.07
f1 (ppm)
MeO
EtO2C
F
F
Ph
NH
O
S
O
O
8c

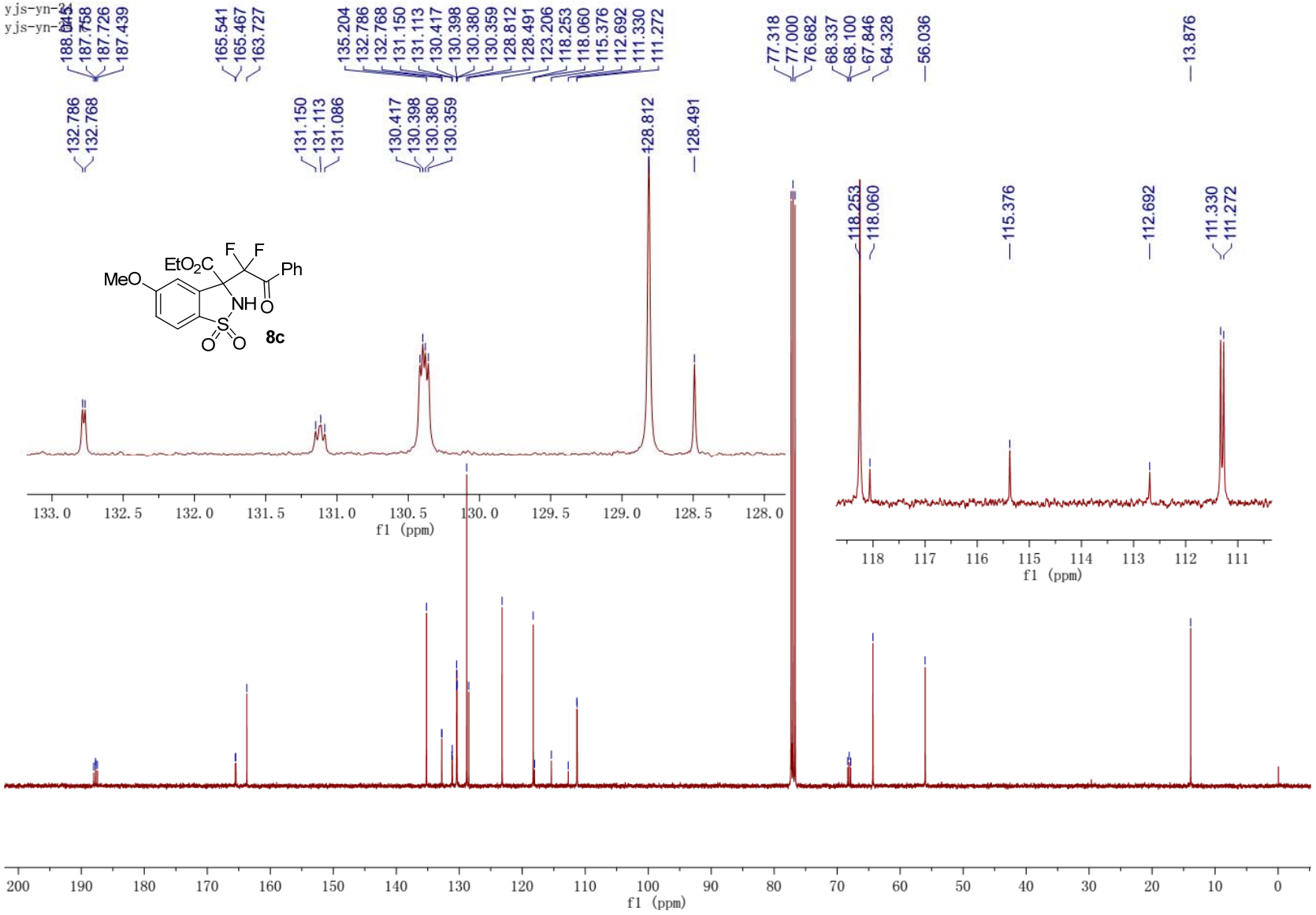
yjs-yn-34 F

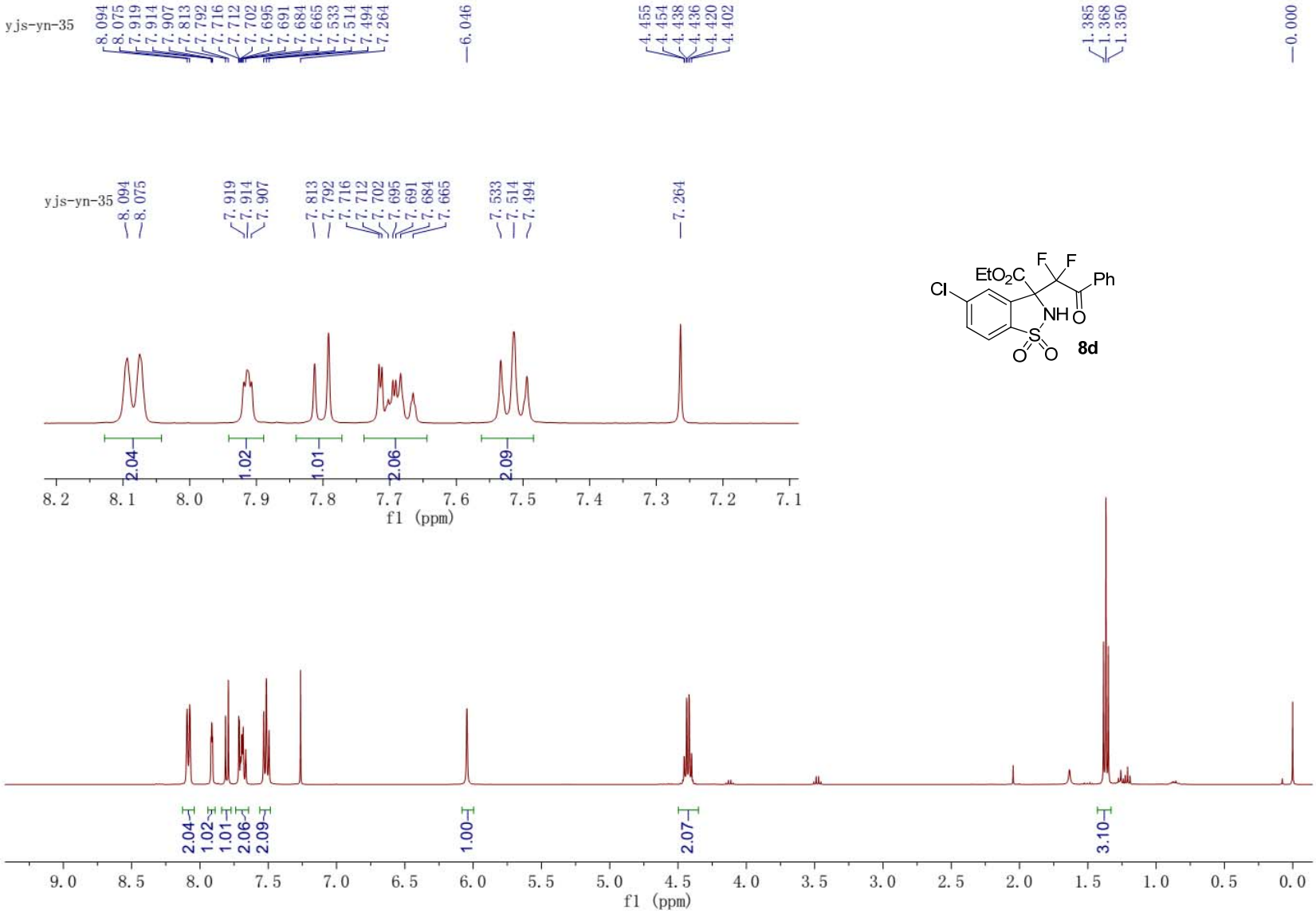
-99.434
-100.225
-105.709
-106.499



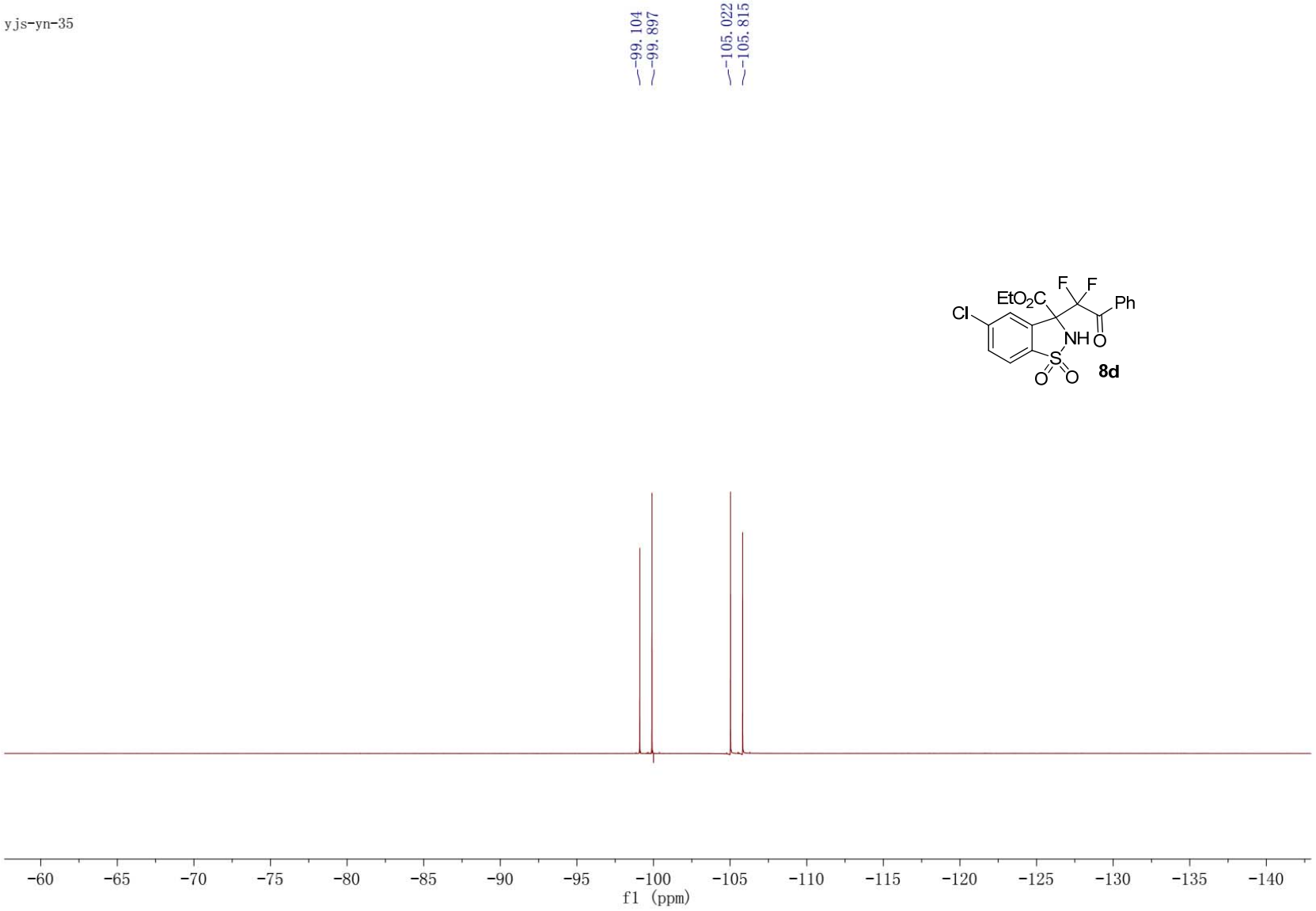
8c

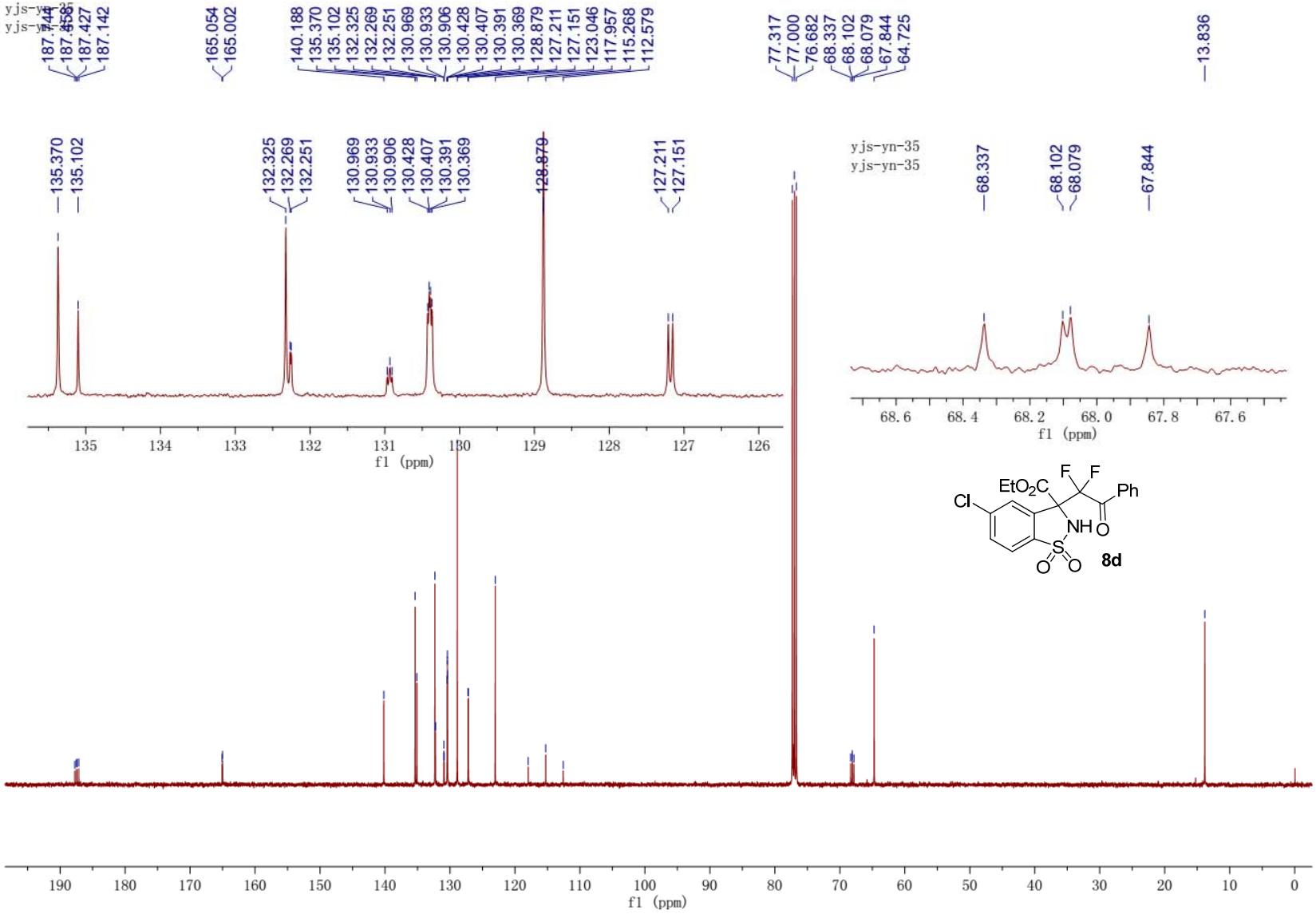


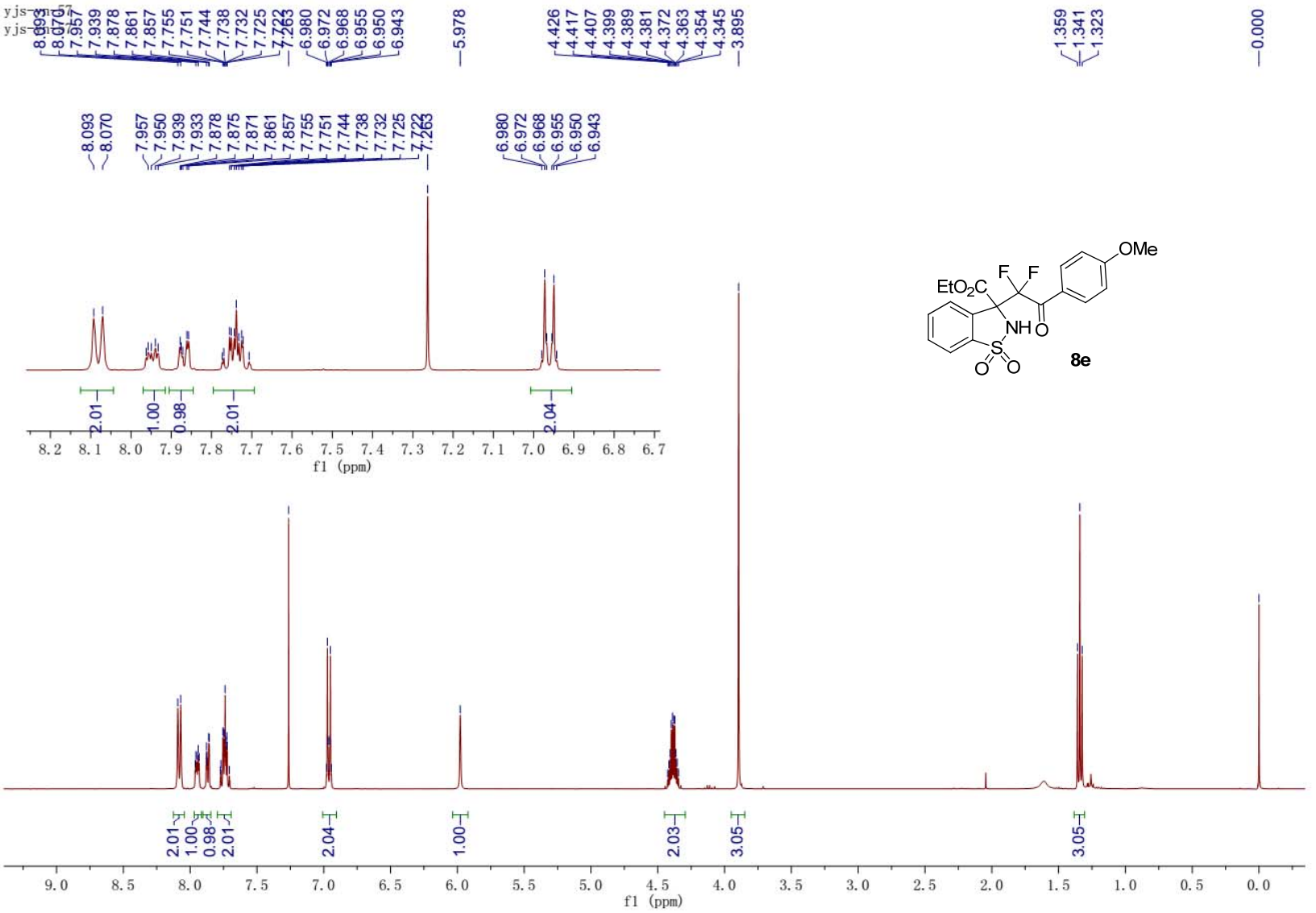

yjs-yn-2
yjs-yn-2
188.045
187.758
187.726
187.439
165.541
165.467
163.727
135.204
132.786
132.768
131.150
131.113
131.086
130.417
130.398
130.380
130.359
128.812
128.491
123.206
118.253
118.060
115.376
112.692
111.330
111.272
77.318
77.000
76.682
68.337
68.100
67.846
64.328
56.036
13.876
MeO
EtO2C
F
F
Ph
NH
O
S
O
O
8c
f1 (ppm)


yjs-yn-35
8.094
8.075
7.919
7.914
7.907
7.813
7.792
7.716
7.712
7.702
7.695
7.691
7.684
7.665
7.533
7.514
7.494
7.264
6.046
4.455
4.454
4.438
4.436
4.420
4.402
1.385
1.368
1.350
0.000
yjs-yn-35
8.094
8.075
7.919
7.914
7.907
7.813
7.792
7.716
7.712
7.702
7.695
7.691
7.684
7.665
7.533
7.514
7.494
7.264
2.04
1.02
1.01
2.06
2.09
f1 (ppm)
Cl
EtO2C
F
F
Ph
NH
O
S
O
O
8d
2.04
1.02
1.01
2.06
2.09
1.00
2.07
3.10
f1 (ppm)

yjs-yn-35

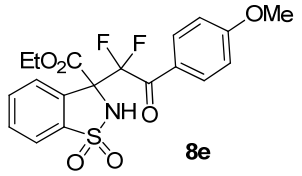

-99.104
-99.897
-105.022
-105.815
F
F
EtO2C
Ph
Cl
NH
O
S
O
O
8d
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
f1 (ppm)


yjs-yn-35
yjs-yn-35
187.444
187.427
187.142
165.054
165.002
140.188
135.370
135.102
132.325
132.269
132.251
130.969
130.933
130.906
130.428
130.407
130.391
130.369
128.879
127.211
127.151
123.046
117.957
115.268
112.579
77.317
77.000
76.682
68.337
68.102
68.079
67.844
64.725
13.836
f1 (ppm)
68.6
68.4
68.2
68.0
67.8
67.6
Cl
EtO2C
F
F
Ph
NH
O
S
O
O
8d

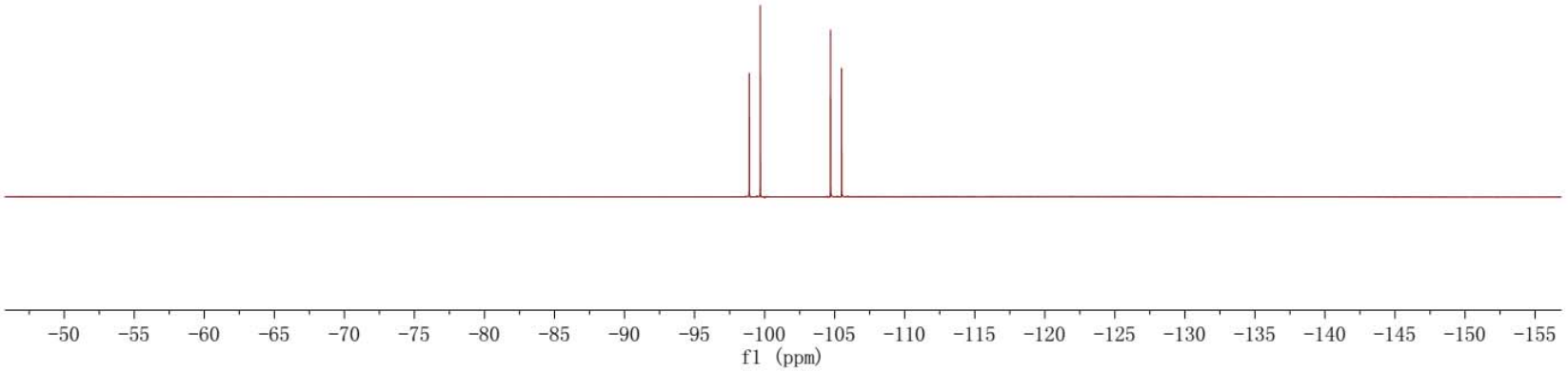

8.093
8.070
7.957
7.950
7.939
7.933
7.878
7.875
7.871
7.861
7.857
7.755
7.751
7.744
7.738
7.732
7.725
7.722
7.263
6.980
6.972
6.968
6.955
6.950
6.943
5.978
4.426
4.417
4.407
4.399
4.389
4.381
4.372
4.363
4.354
4.345
3.895
1.359
1.341
1.323
0.000
2.01
1.00
0.98
2.01
2.04
f1 (ppm)
2.01
1.00
0.98
2.01
2.04
1.00
2.03
3.05
3.05
f1 (ppm)
OMe
F
F
EtO2C
NH
O
S
O
O
8e

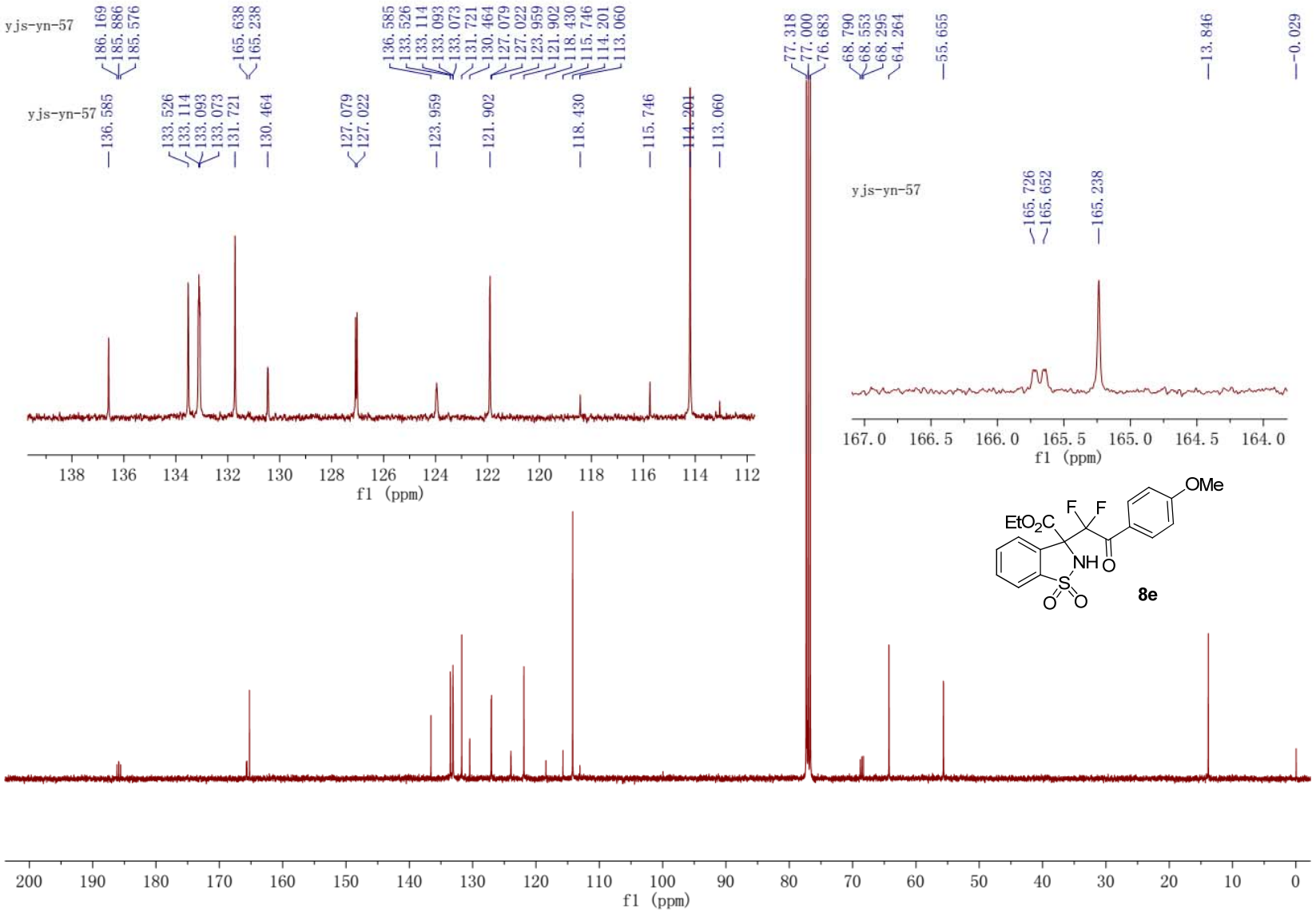
yjs-yn-57

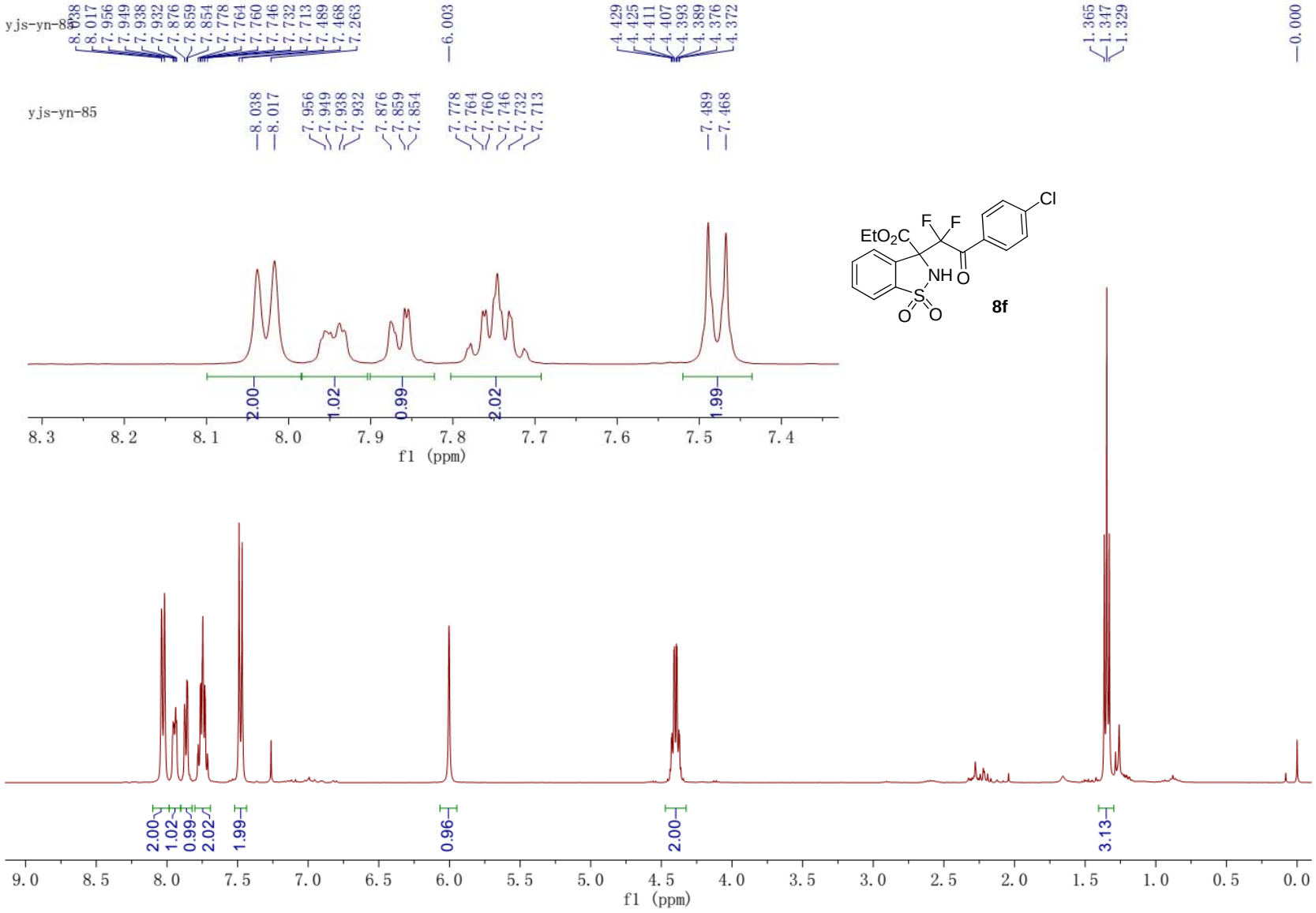
-98.906
-98.910
-99.692
-99.696
-104.702
-104.707
-105.488
-105.493



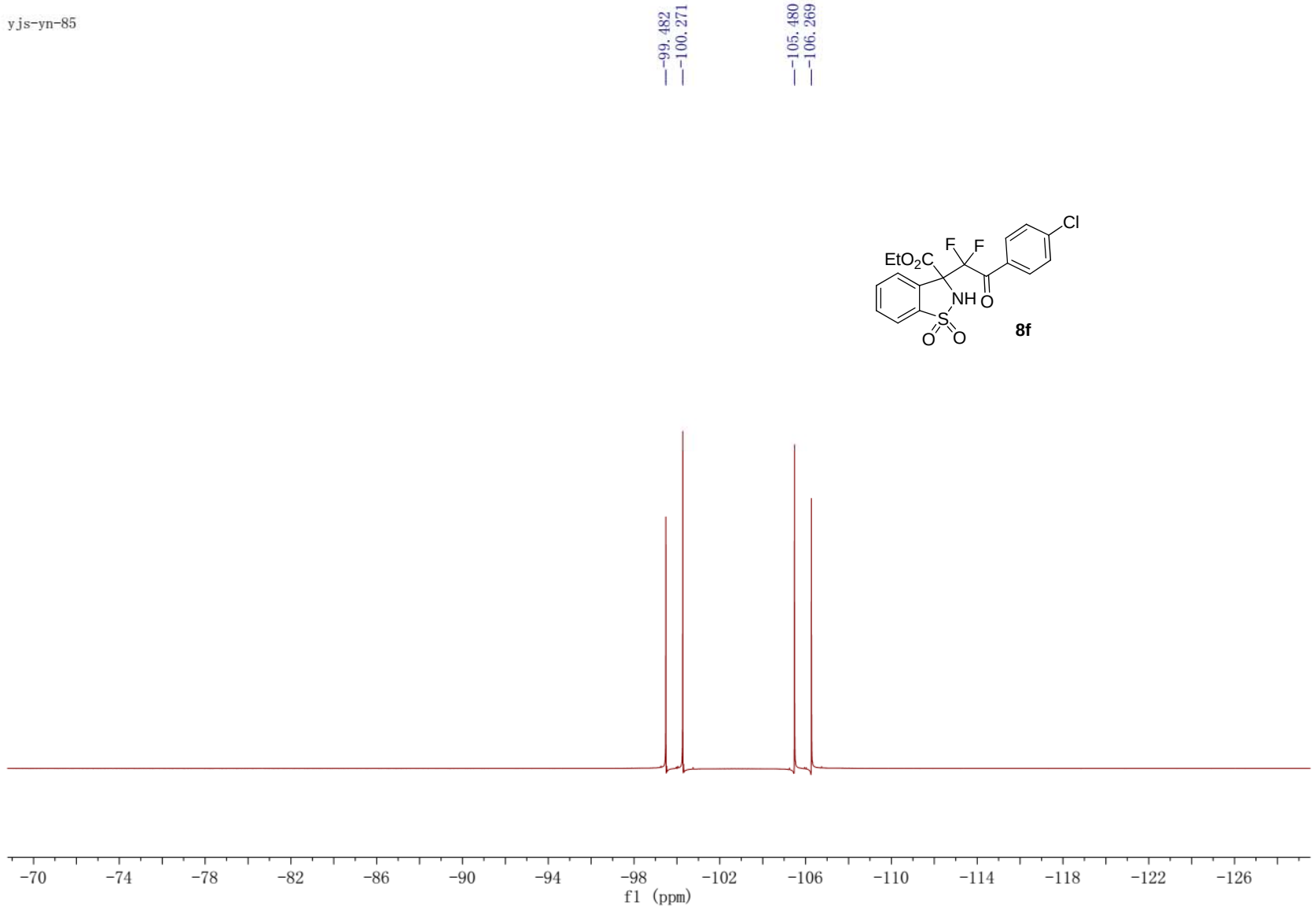
8e

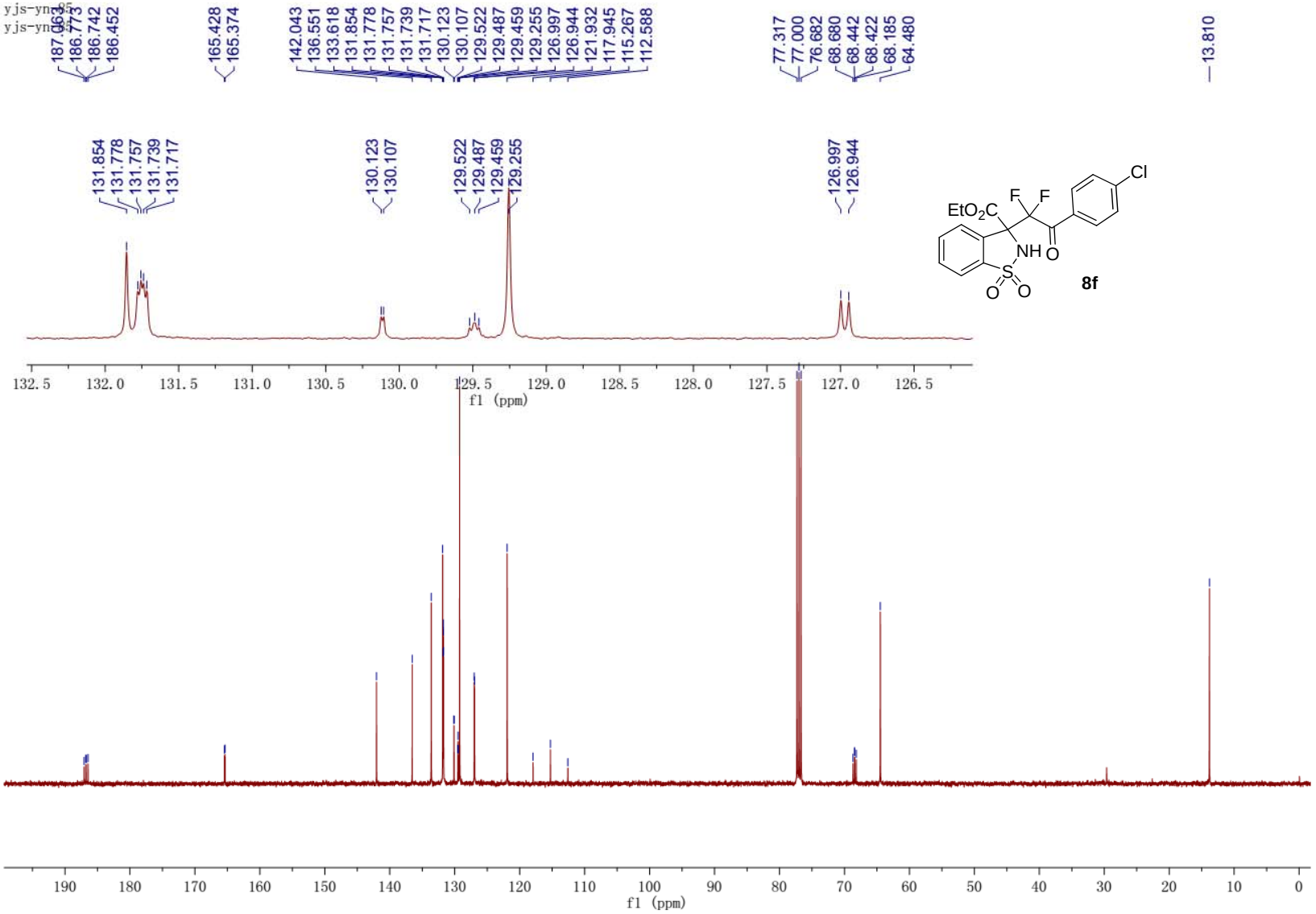


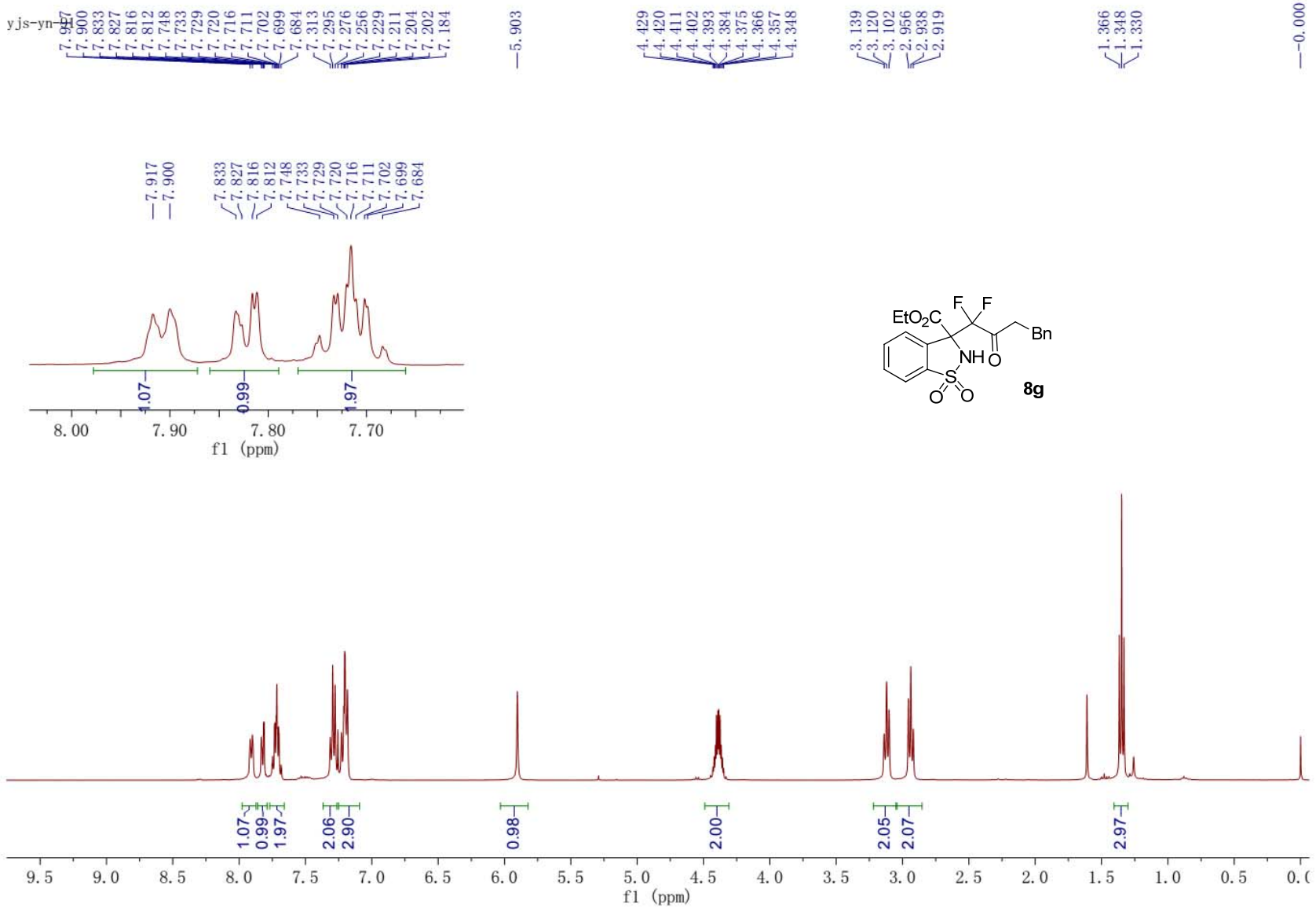

yjs-yn-57
186.169
185.886
185.576
165.638
165.238
136.585
133.526
133.114
133.093
133.073
131.721
130.464
127.079
127.022
123.959
121.902
118.430
115.746
114.201
113.060
77.318
77.000
76.683
68.790
68.553
68.295
64.264
55.655
13.846
-0.029
yjs-yn-57
136.585
133.526
133.114
133.093
133.073
131.721
130.464
127.079
127.022
123.959
121.902
118.430
115.746
114.201
113.060
138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)
yjs-yn-57
165.726
165.652
165.238
167.0 166.5 166.0 165.5 165.0 164.5 164.0
f1 (ppm)
OMe
F
F
EtO2C
NH
O
S
O
O
8e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


yjs-yn-85
8.038
8.017
7.956
7.949
7.938
7.932
7.876
7.859
7.854
7.778
7.764
7.760
7.746
7.732
7.713
7.489
7.468
7.263
6.003
4.429
4.425
4.411
4.407
4.393
4.389
4.376
4.372
1.365
1.347
1.329
0.000
EtO2C
F
F
Cl
NH
O
S
O
O
8f
2.00
1.02
0.99
2.02
1.99
0.96
2.00
3.13
f1 (ppm)

yjs-yn-85

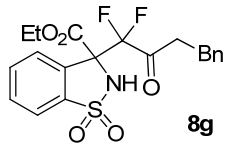

-99.482
-100.271
-105.480
-106.269
Cl
F
F
EtO2C
NH
O
S
O
O
8f
-70
-74
-78
-82
-86
-90
-94
-98
-102
-106
-110
-114
-118
-122
-126
f1 (ppm)


yjs-ynmr-05
yjs-ynmr-05
187.063
186.773
186.742
186.452
165.428
165.374
142.043
136.551
133.618
131.854
131.778
131.757
131.739
131.717
130.123
130.107
129.522
129.487
129.459
129.255
126.997
126.944
121.932
117.945
115.267
112.588
77.317
77.000
76.682
68.680
68.442
68.422
68.185
64.480
13.810
Cl
F
F
EtO2C
NH
O
S
O
O
8f
f1 (ppm)
f1 (ppm)

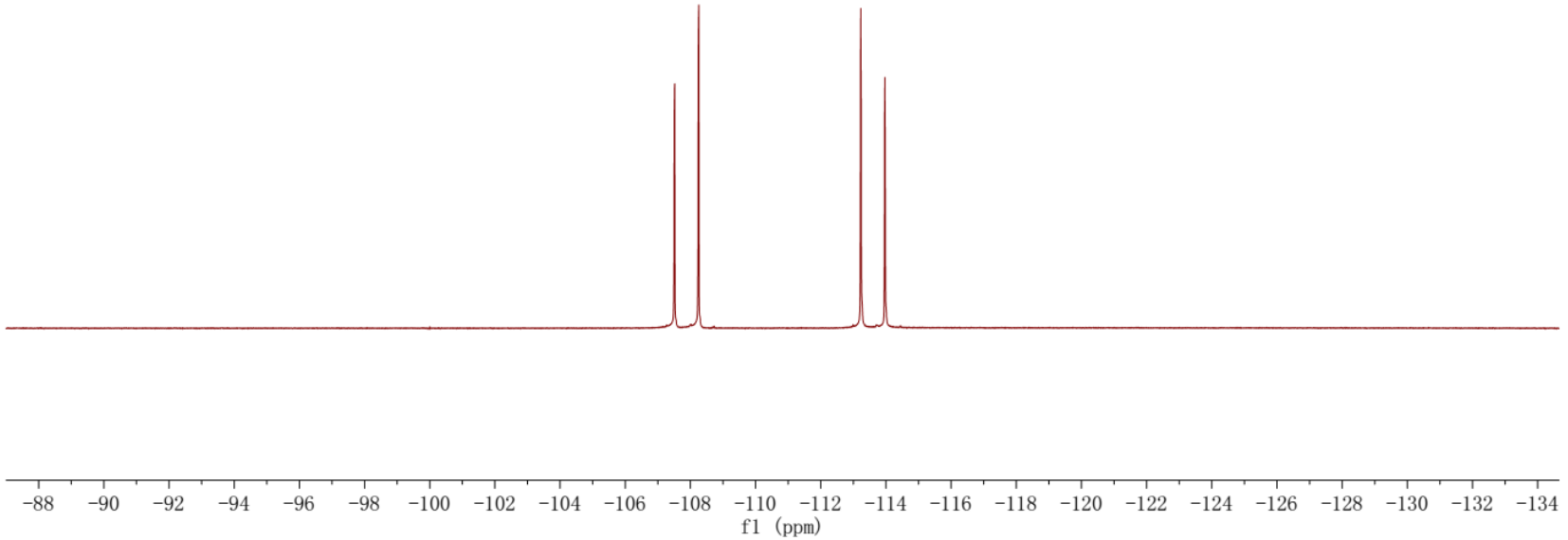

yjs-yn-1H
7.917
7.900
7.833
7.827
7.816
7.812
7.748
7.733
7.729
7.720
7.716
7.711
7.702
7.699
7.684
7.313
7.295
7.276
7.256
7.229
7.211
7.204
7.202
7.184
5.903
4.429
4.420
4.411
4.402
4.393
4.384
4.375
4.366
4.357
4.348
3.139
3.120
3.102
2.956
2.938
2.919
1.366
1.348
1.330
0.000
1.07
0.99
1.97
8.00
7.90
7.80
7.70
f1 (ppm)
EtO2C
F
F
Bn
NH
O
S
O
O
8g
1.07
0.99
1.97
2.06
2.90
0.98
2.00
2.05
2.07
2.97
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)

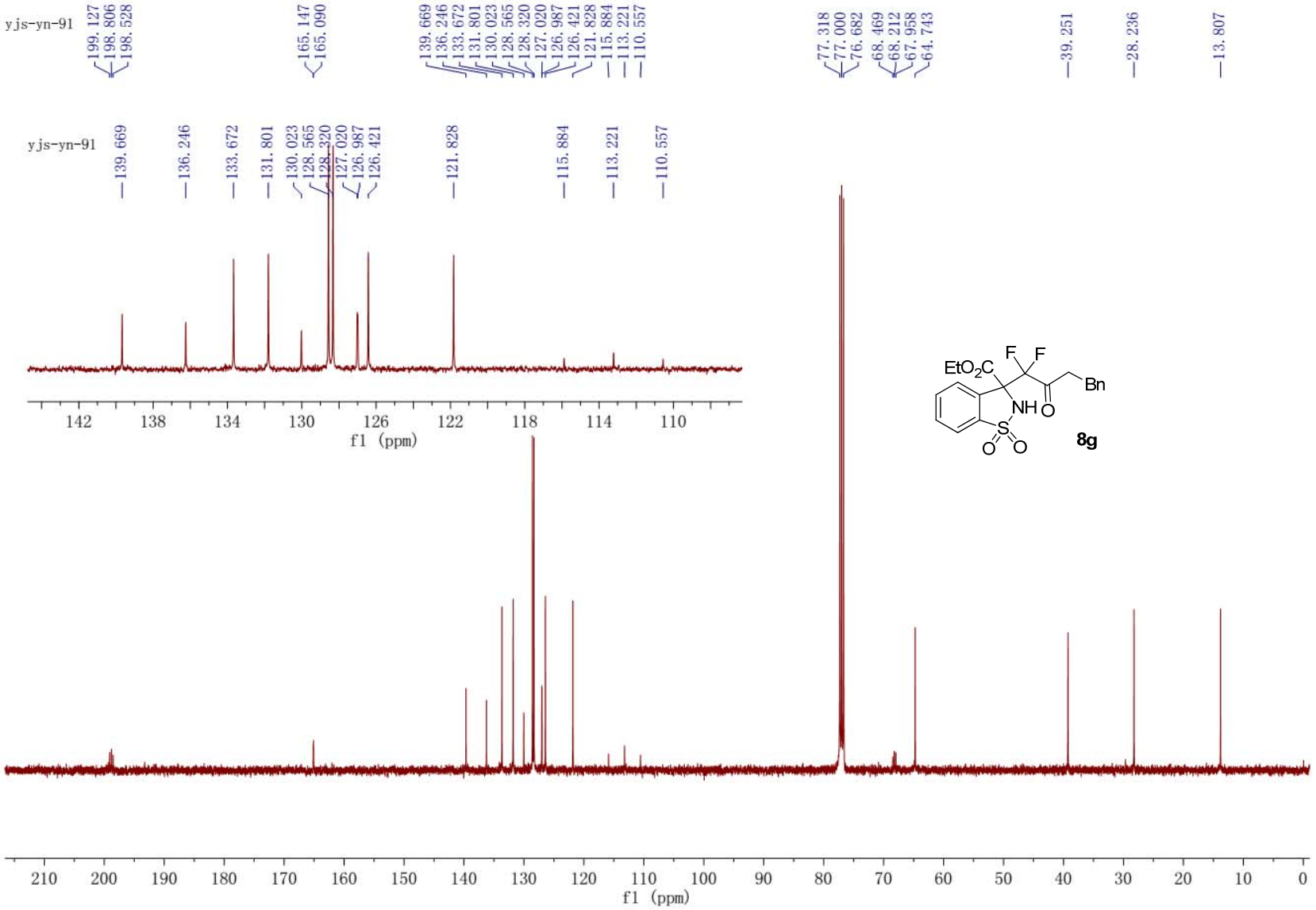
yjs-yn-91

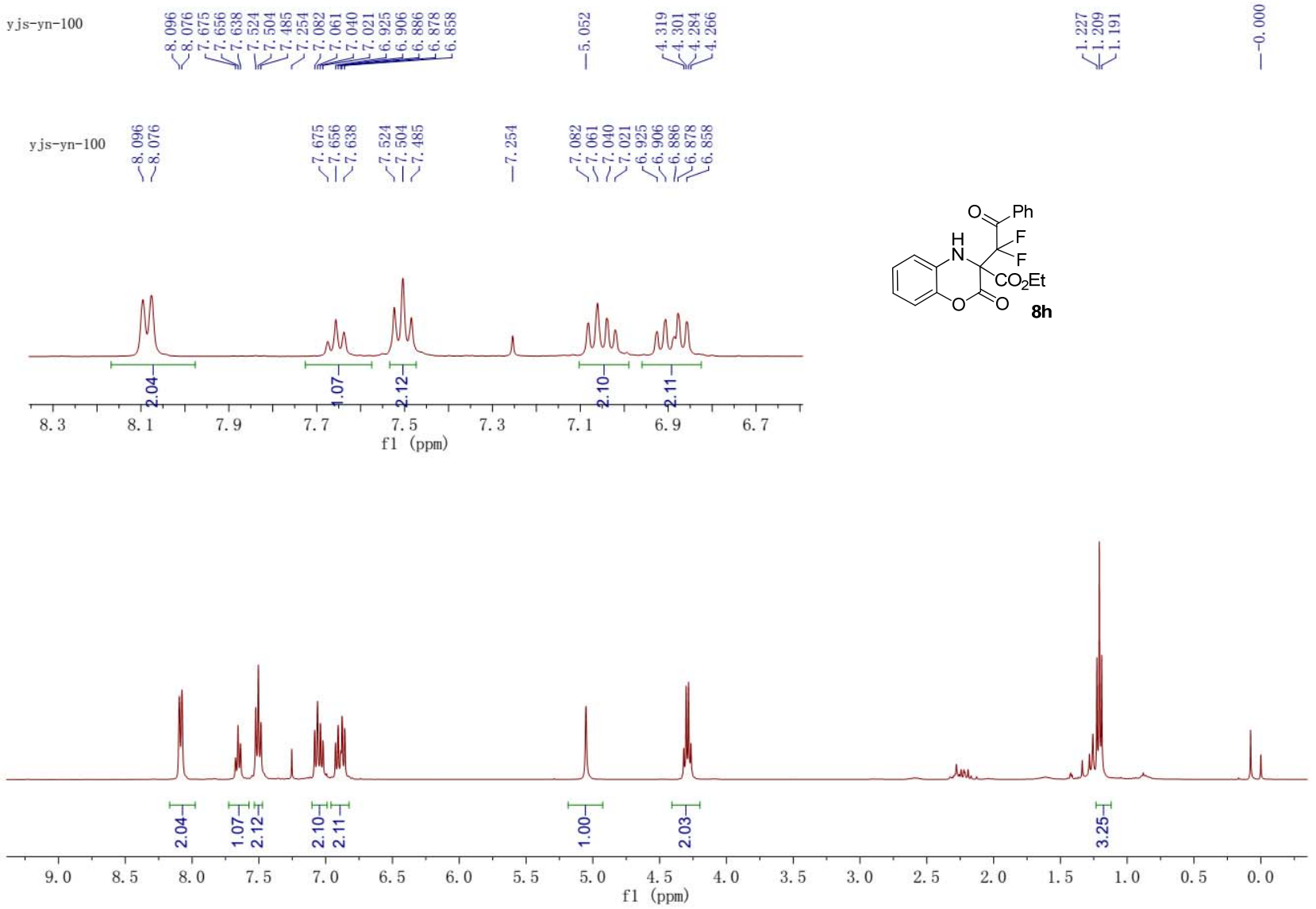
−107.516
−108.255
−113.227
−113.966

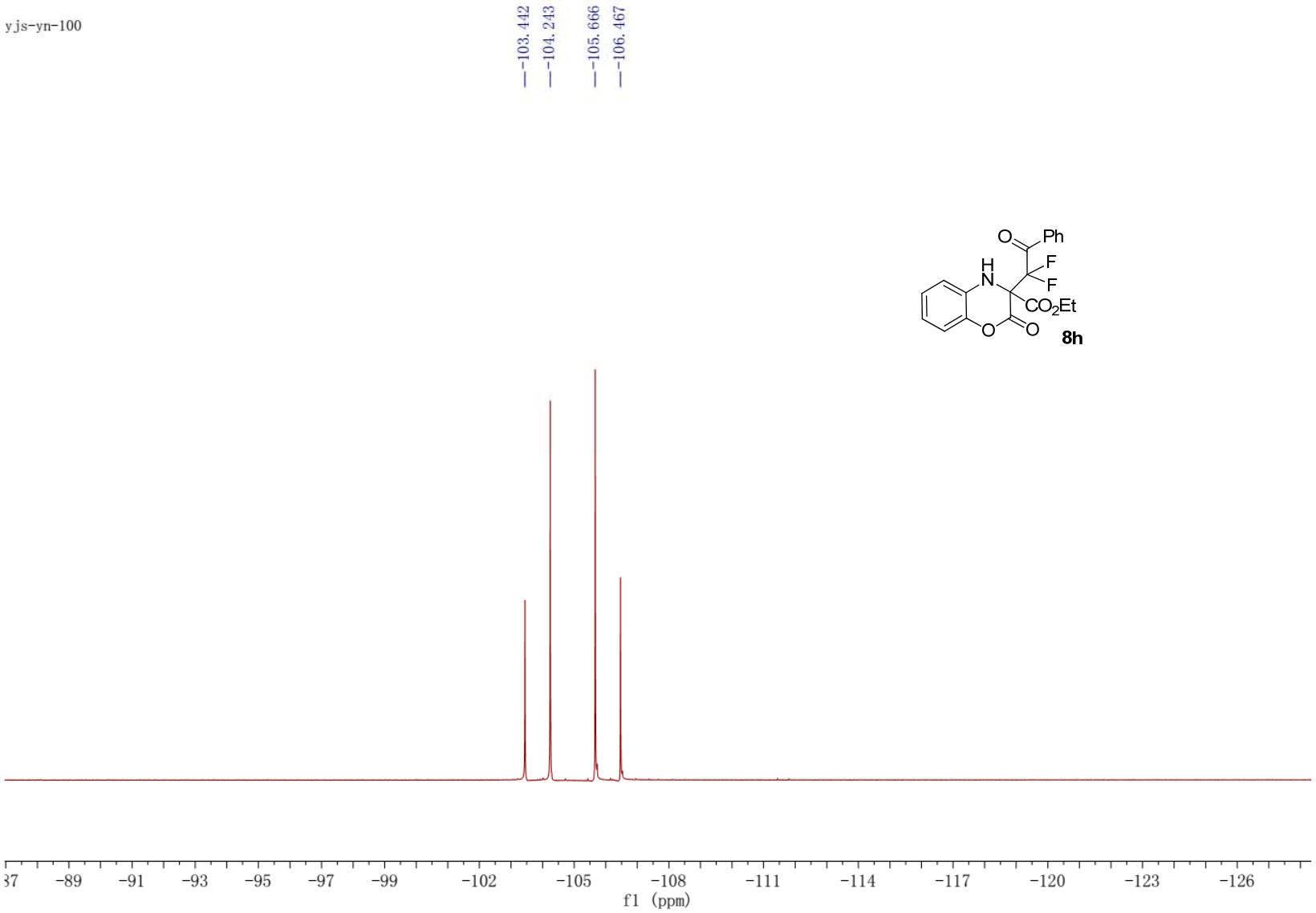


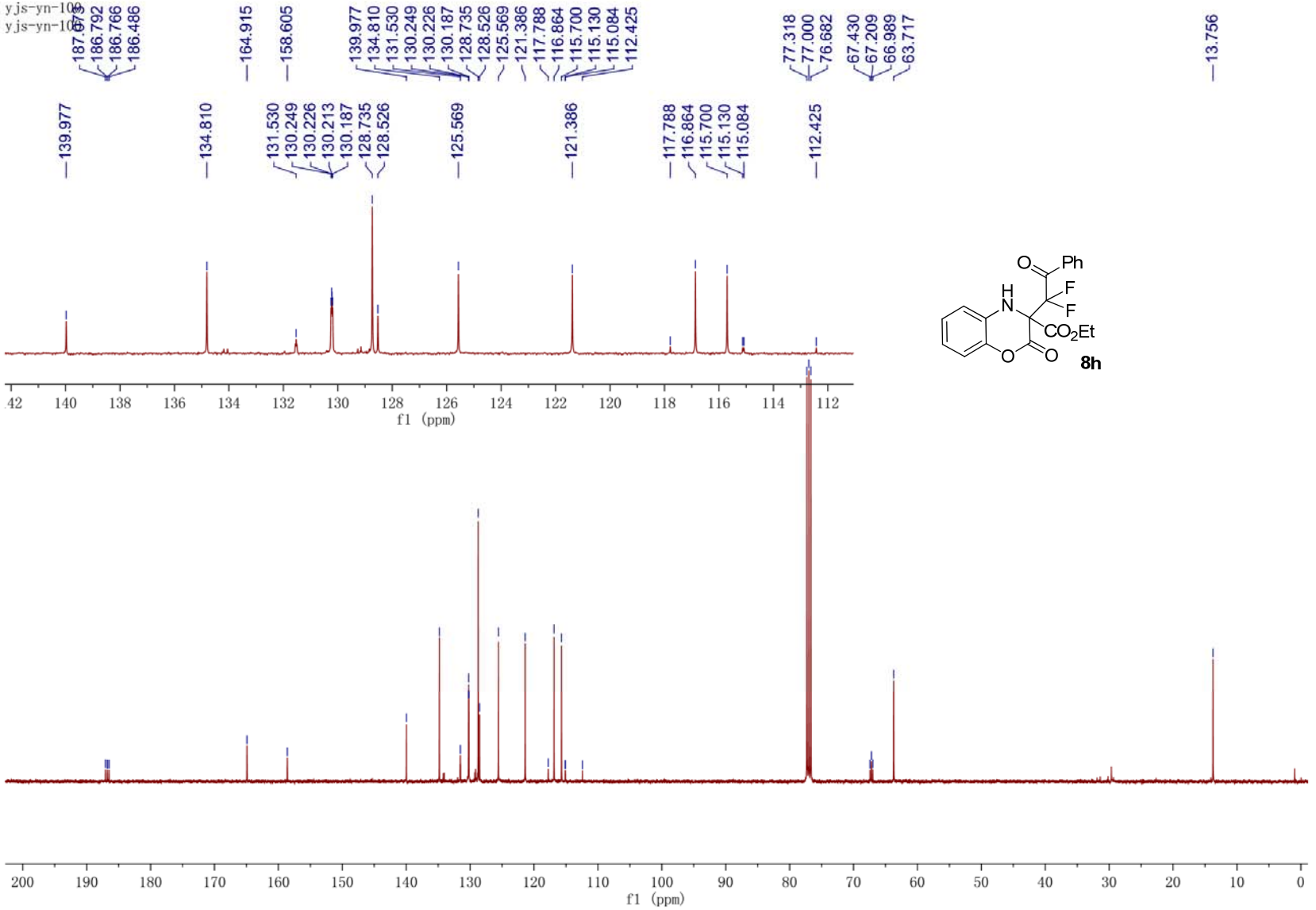
8g

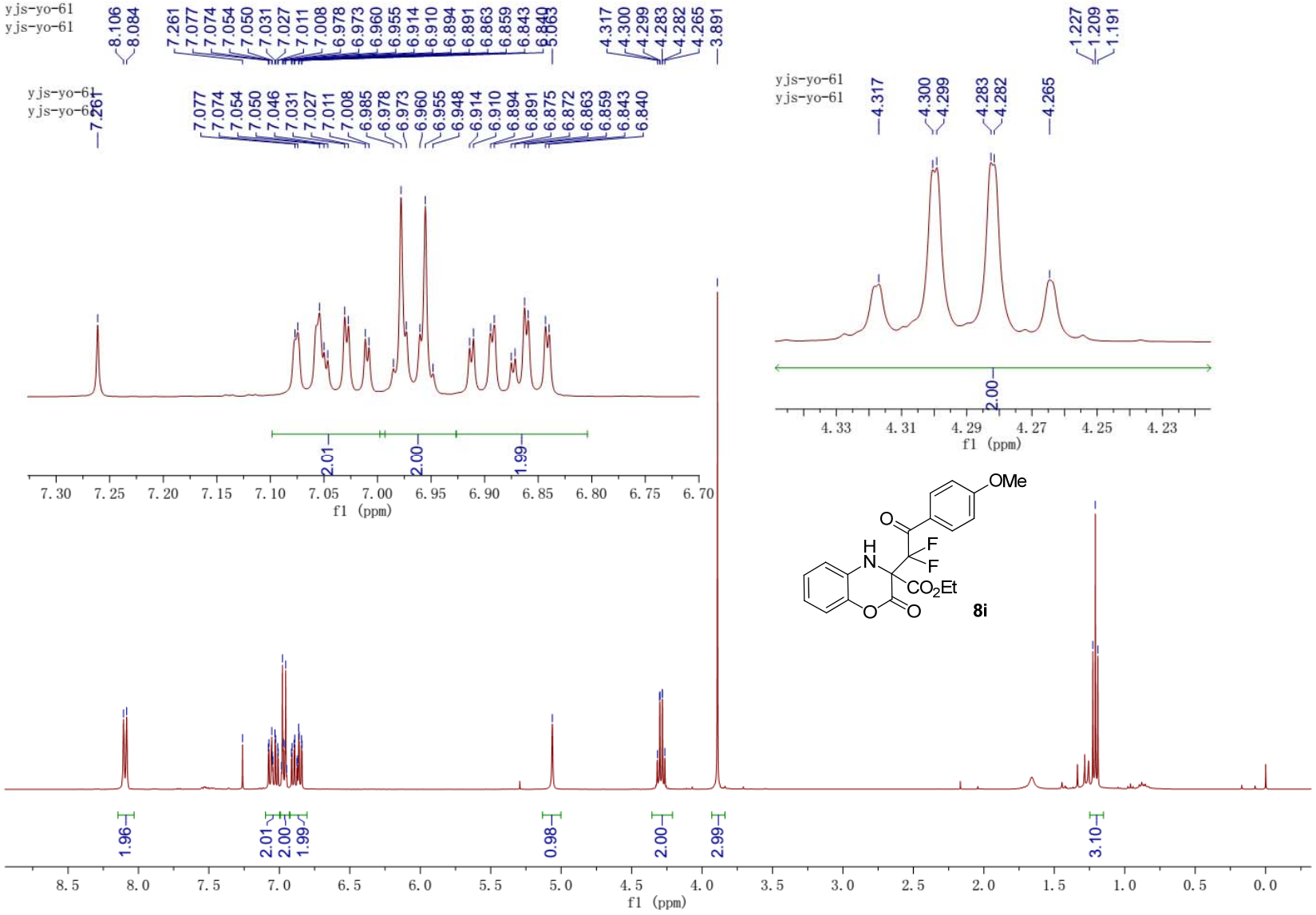



yjs-yn-91
199.127
198.806
198.528
165.147
165.090
139.669
136.246
133.672
131.801
130.023
128.565
128.320
127.020
126.987
126.421
121.828
115.884
113.221
110.557
77.318
77.000
76.682
68.469
68.212
67.958
64.743
39.251
28.236
13.807
f1 (ppm)
EtO2C
F
F
Bn
NH
O
S
O
O
8g


yjs-yn-100
8.096
8.076
7.675
7.656
7.638
7.524
7.504
7.485
7.254
7.082
7.061
7.040
7.021
6.925
6.906
6.886
6.878
6.858
5.052
4.319
4.301
4.284
4.266
1.227
1.209
1.191
0.000
yjs-yn-100
Ph
O
H
N
F
F
CO2Et
O
O
8h
2.04
1.07
2.12
2.10
2.11
f1 (ppm)
2.04
1.07
2.12
2.10
2.11
1.00
2.03
3.25
f1 (ppm)

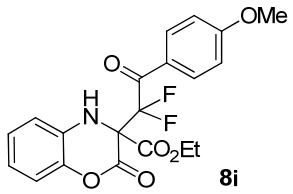

yjs-yn-100
-103.442
-104.243
-105.666
-106.467
O
Ph
F
F
H
N
CO2Et
O
O
8h
37
-89
-91
-93
-95
-97
-99
-102
-105
-108
-111
-114
-117
-120
-123
-126
f1 (ppm)


yjs-yn-109
yjs-yn-109
187.673
186.792
186.766
186.486
164.915
158.605
139.977
134.810
131.530
130.249
130.226
130.187
128.735
128.526
125.569
121.386
117.788
116.864
115.700
115.130
115.084
112.425
77.318
77.000
76.682
67.430
67.209
66.989
63.717
13.756
f1 (ppm)
O
Ph
F
F
H
N
CO2Et
O
O
8h

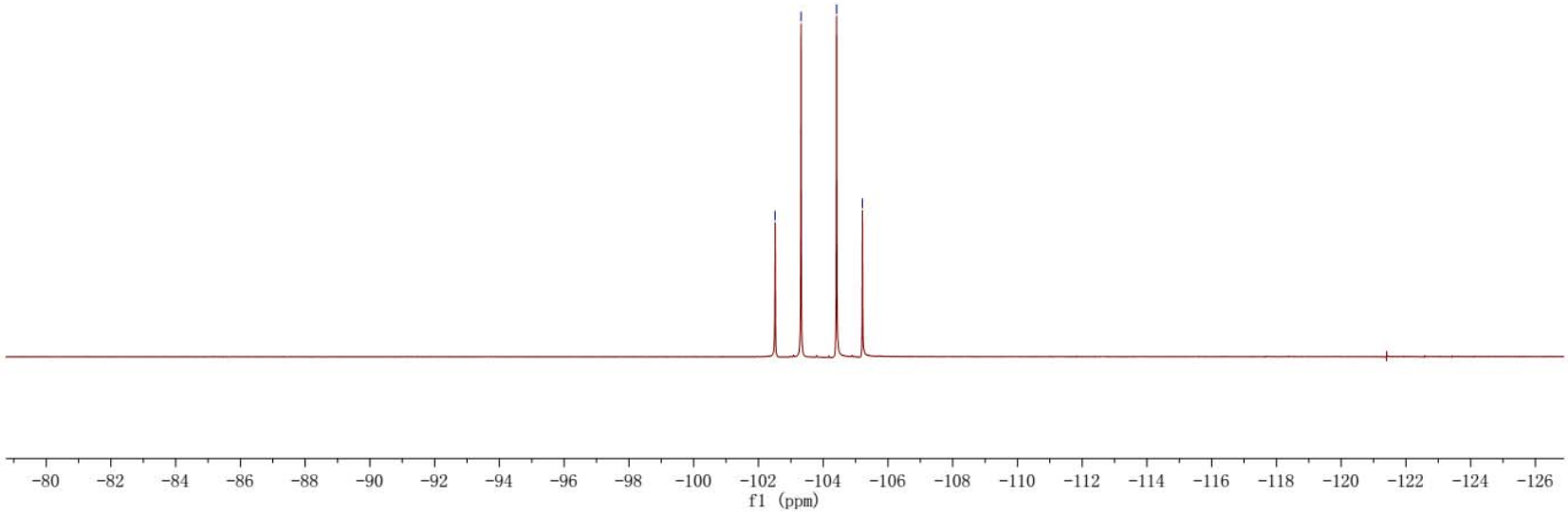

yjs-yo-61
yjs-yo-61
8.106
8.084
7.261
7.077
7.074
7.054
7.050
7.031
7.027
7.011
7.008
6.978
6.973
6.960
6.955
6.914
6.910
6.894
6.891
6.863
6.859
6.843
6.840
5.063
4.317
4.300
4.299
4.283
4.282
4.265
3.891
1.227
1.209
1.191
2.01
2.00
1.99
f1 (ppm)
4.33
4.31
4.29
4.27
4.25
4.23
OMe
O
H
N
F
F
CO2Et
O
O
8i
1.96
2.01
2.00
1.99
0.98
2.00
2.99
3.10
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

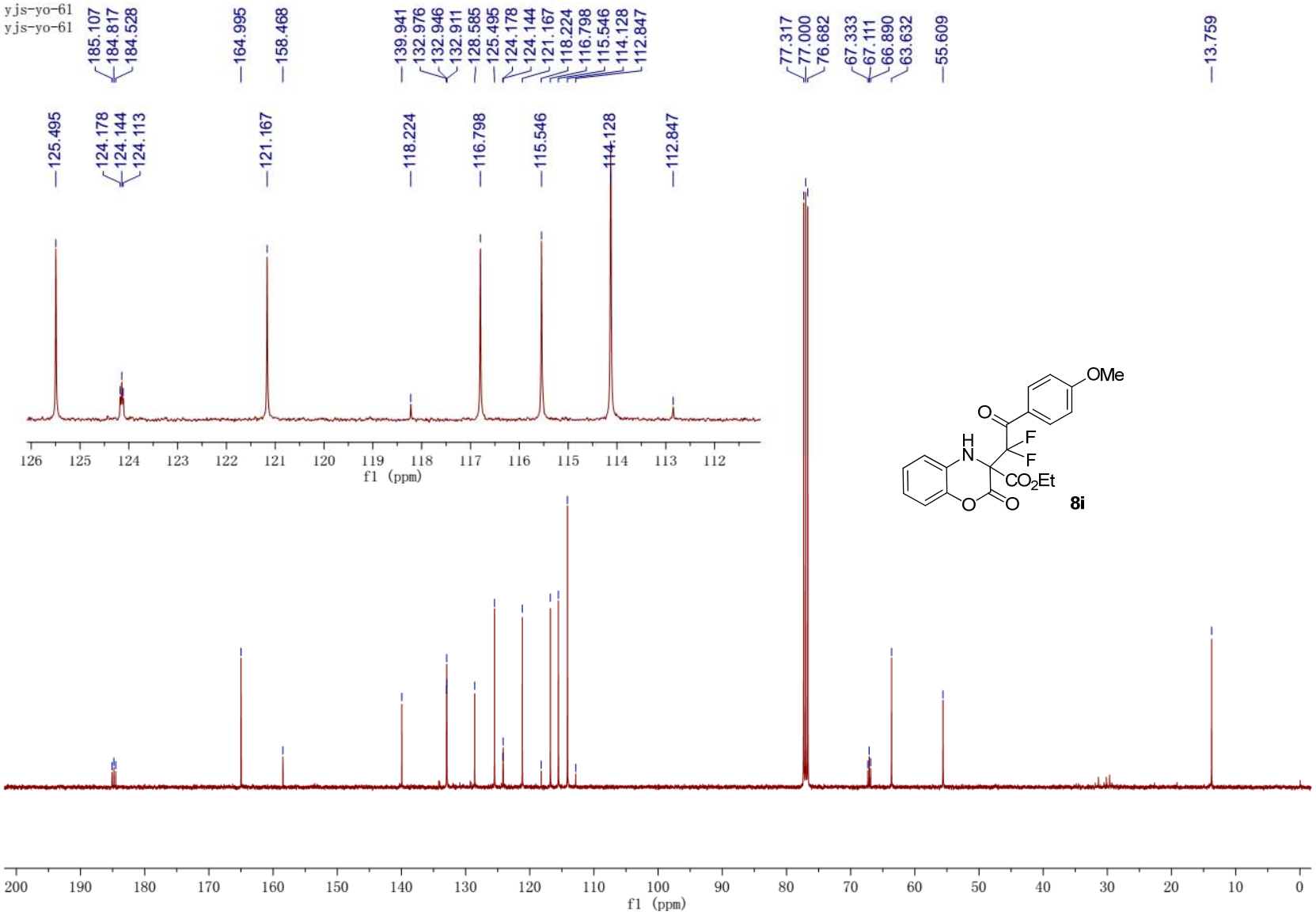
yjs-yo-61
yjs-yo-61

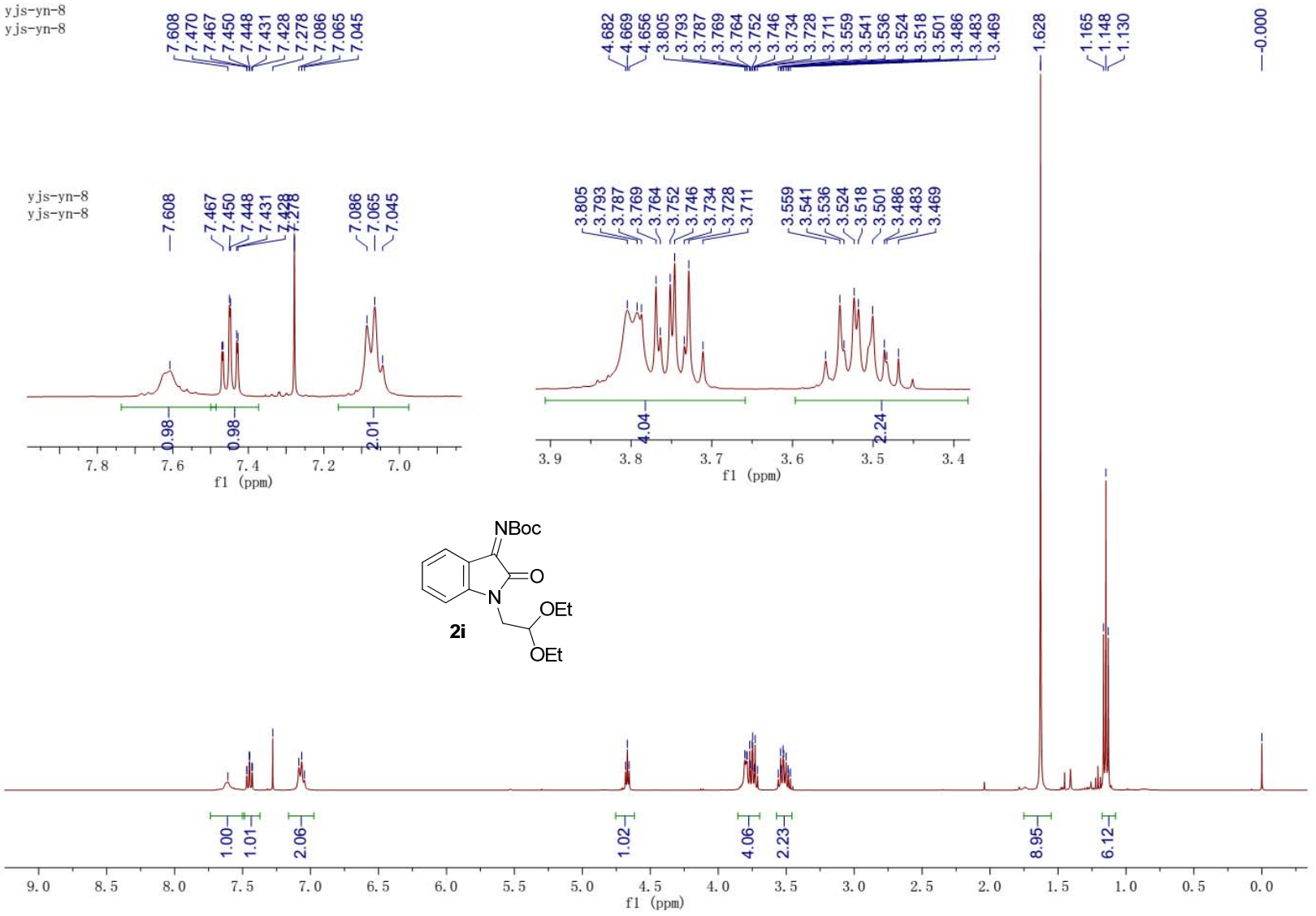
-102.516
-103.316
-104.412
-105.212

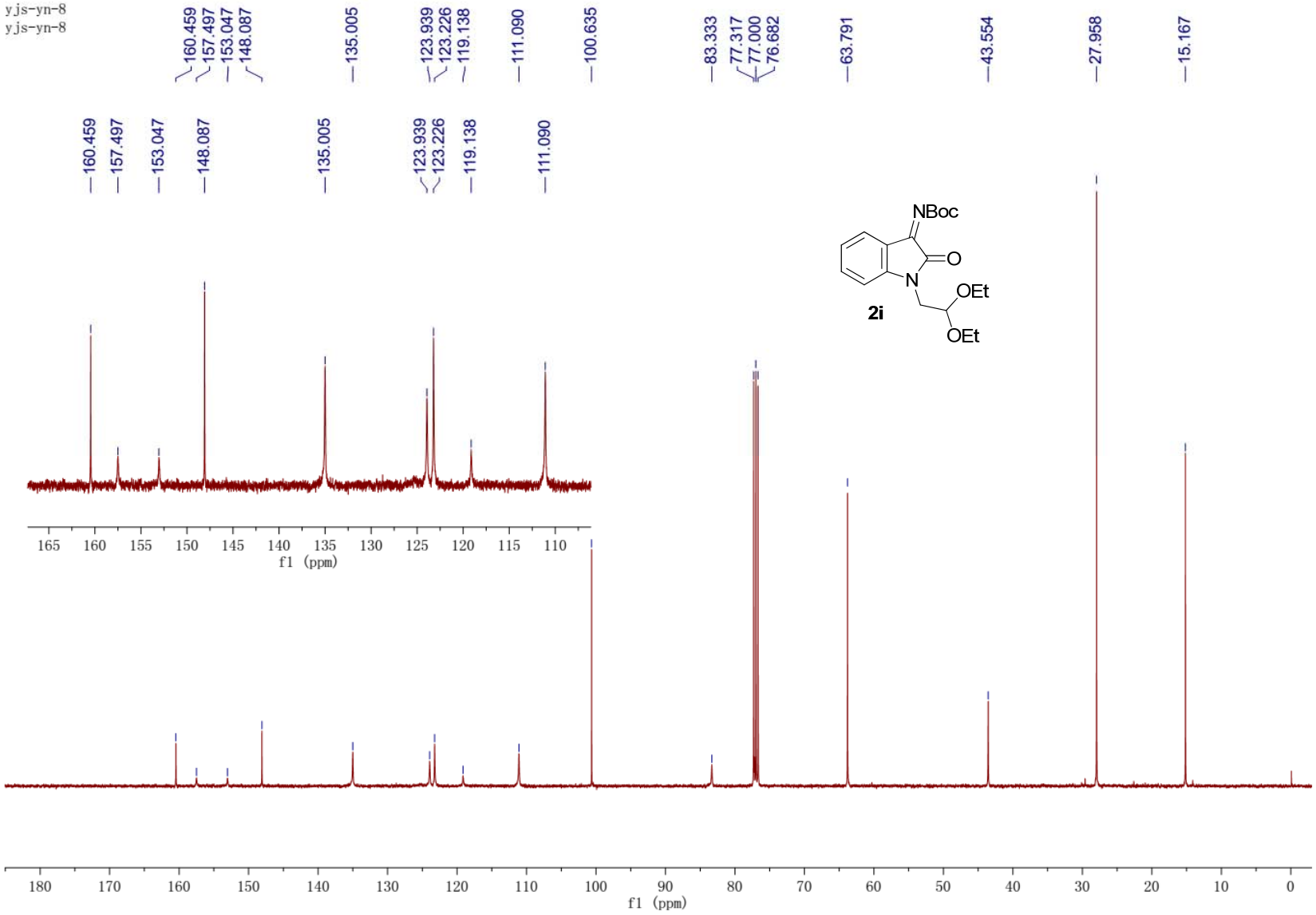


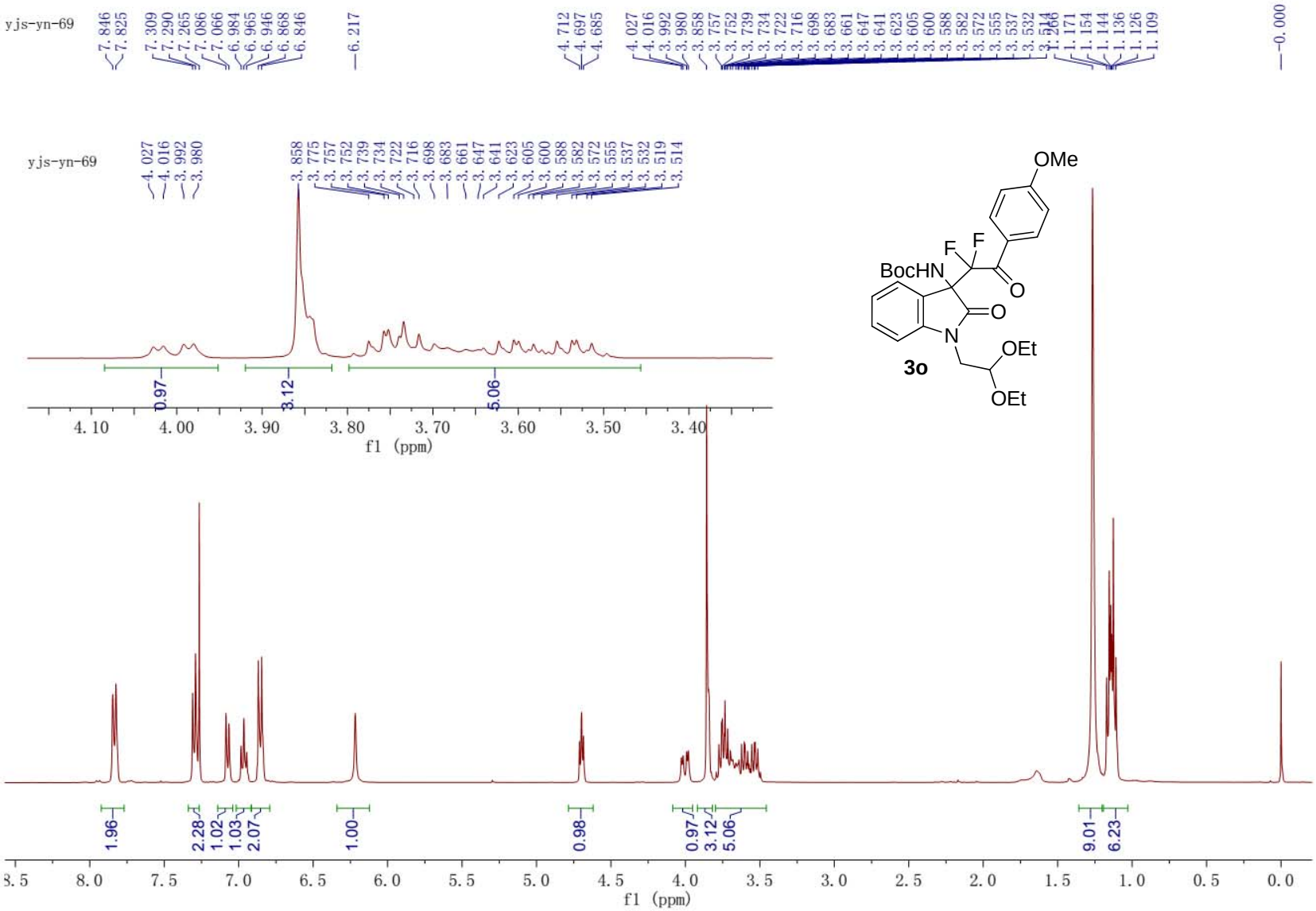
8i




yjs-yo-61
yjs-yo-61
185.107
184.817
184.528
164.995
158.468
139.941
132.976
132.946
132.911
128.585
125.495
124.178
124.144
124.113
121.167
118.224
116.798
115.546
114.128
112.847
77.317
77.000
76.682
67.333
67.111
66.890
63.632
55.609
13.759
f1 (ppm)
OMe
O
H
N
F
F
CO2Et
O
O
8i

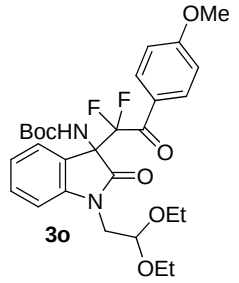

yjs-yn-8
yjs-yn-8
7.608
7.470
7.467
7.450
7.448
7.431
7.428
7.278
7.086
7.065
7.045
4.682
4.669
4.656
3.805
3.793
3.787
3.769
3.764
3.752
3.746
3.734
3.728
3.711
3.559
3.541
3.536
3.524
3.518
3.501
3.486
3.483
3.469
1.628
1.165
1.148
1.130
-0.000
0.98
0.98
2.01
4.04
2.24
f1 (ppm)
NBoc
O
N
OEt
OEt
2i
1.00
1.01
2.06
1.02
4.06
2.23
8.95
6.12


yjs-yn-8
yjs-yn-8
160.459
157.497
153.047
148.087
135.005
123.939
123.226
119.138
111.090
100.635
83.333
77.317
77.000
76.682
63.791
43.554
27.958
15.167
NBoc
O
N
OEt
OEt
2i
f1 (ppm)
f1 (ppm)

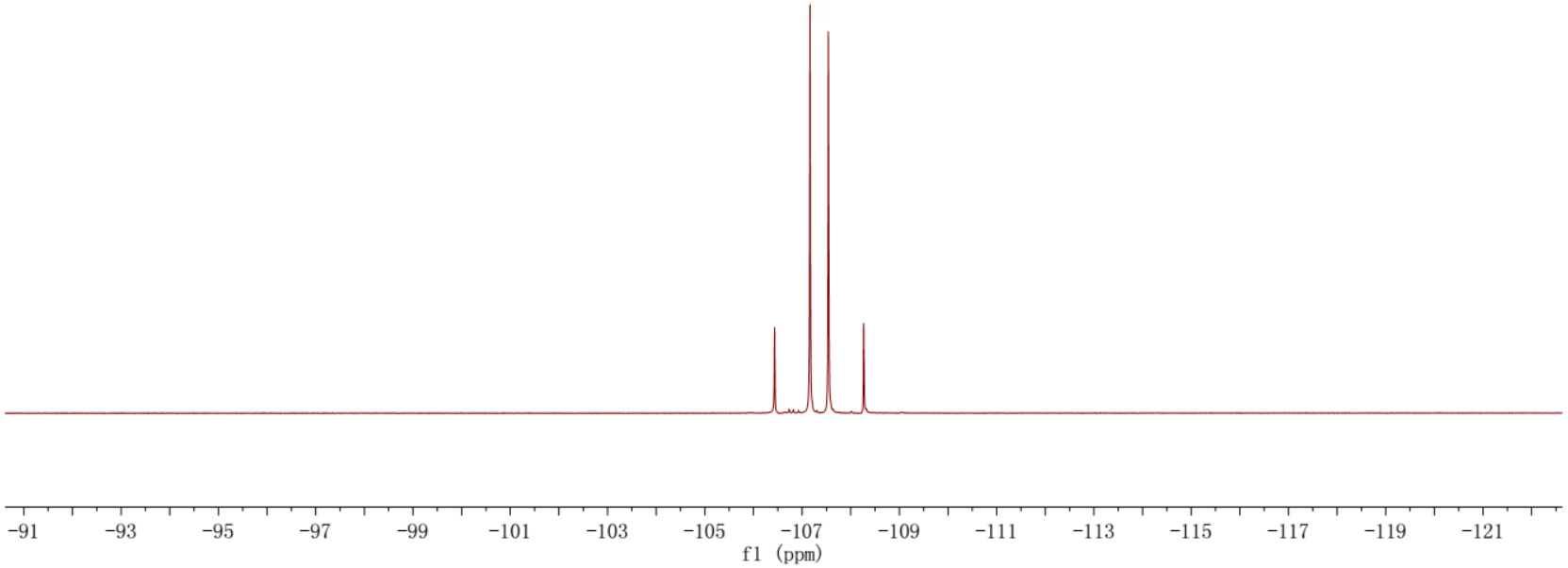

yjs-yn-69
7.846
7.825
7.309
7.290
7.265
7.086
7.066
6.984
6.965
6.946
6.868
6.846
6.217
4.712
4.697
4.685
4.027
4.016
3.992
3.980
3.858
3.757
3.752
3.739
3.734
3.722
3.716
3.698
3.683
3.661
3.647
3.641
3.623
3.605
3.600
3.588
3.582
3.572
3.555
3.537
3.532
3.519
3.514
1.266
1.171
1.154
1.144
1.136
1.126
1.109
0.000
yjs-yn-69
4.027
4.016
3.992
3.980
3.858
3.775
3.757
3.752
3.739
3.734
3.722
3.716
3.698
3.683
3.661
3.647
3.641
3.623
3.605
3.600
3.588
3.582
3.572
3.555
3.537
3.532
3.519
3.514
0.97
3.12
5.06
4.10
4.00
3.90
3.80
3.70
3.60
3.50
3.40
f1 (ppm)
OMe
F
F
BocHN
O
O
N
OEt
OEt
3o
1.96
2.28
1.02
1.03
2.07
1.00
0.98
0.97
3.12
5.06
9.01
6.23
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)

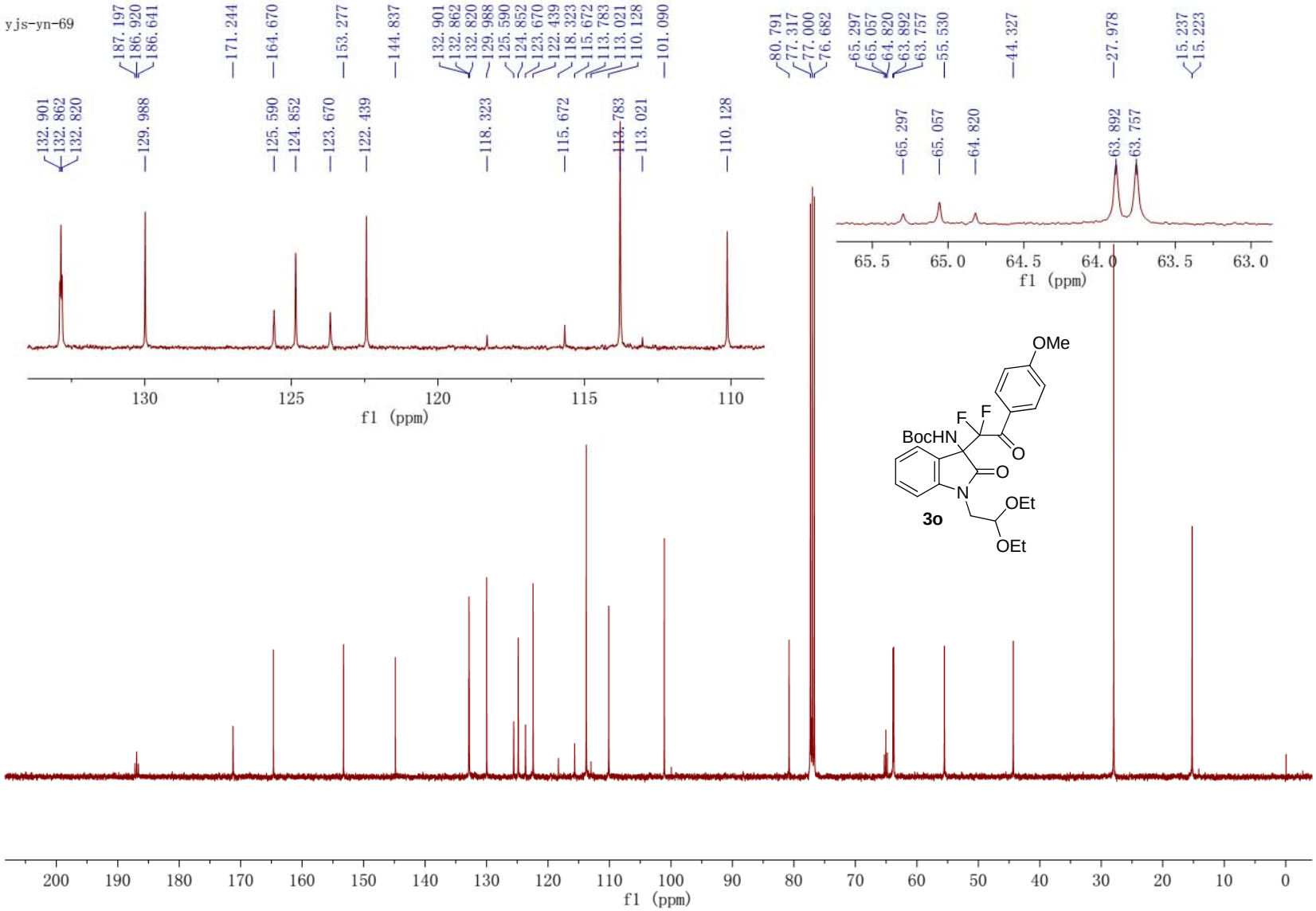
yjs-yn-69

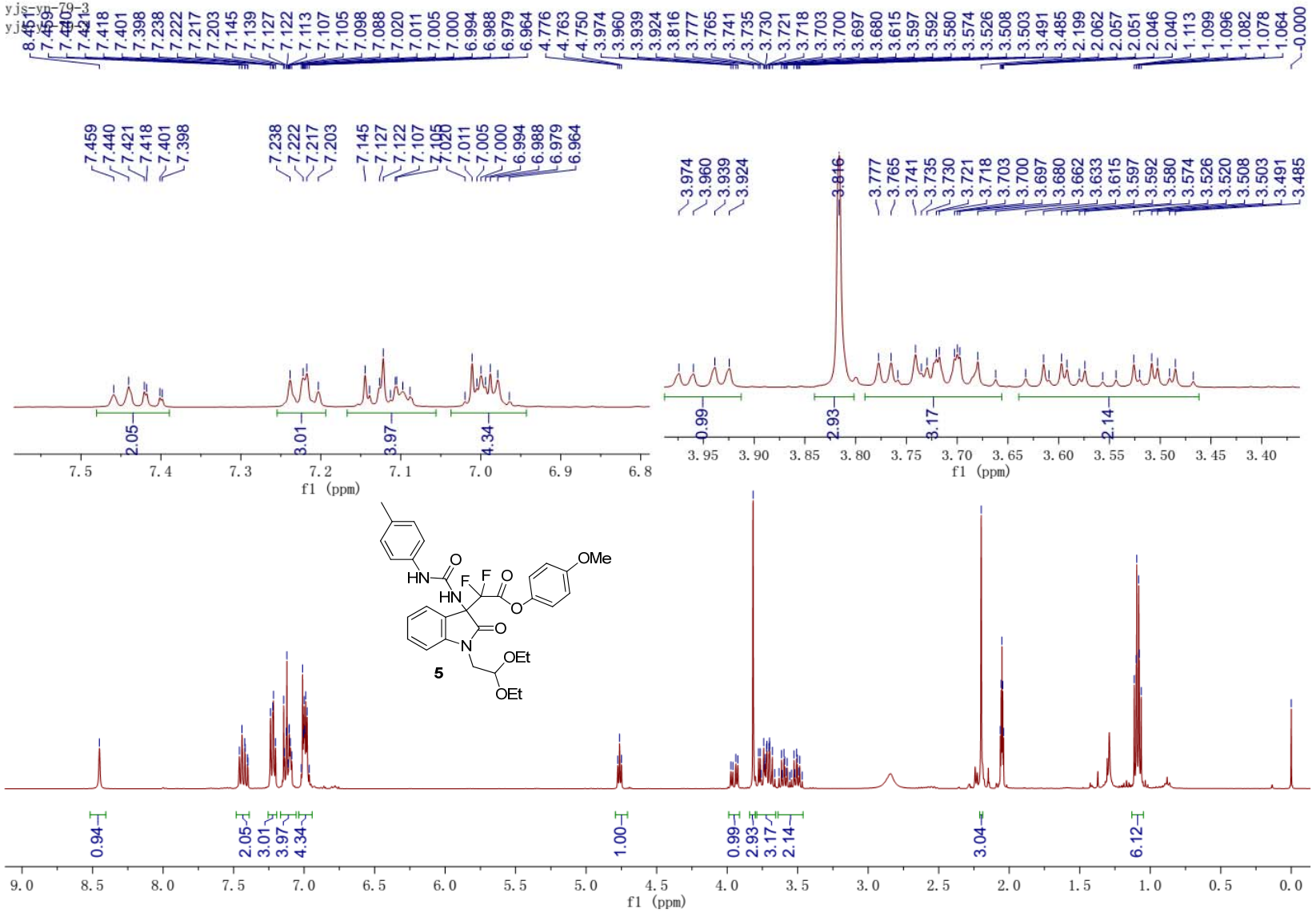
-106.435
-107.162
-107.538
-108.264



3o

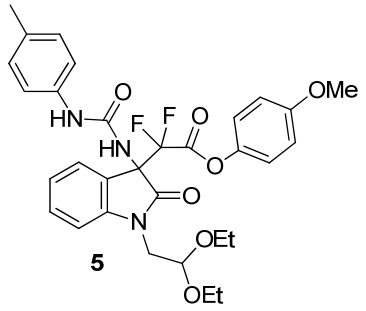



yjs-yn-69
187.197
186.920
186.641
171.244
164.670
153.277
144.837
132.901
132.862
132.820
129.988
125.590
124.852
123.670
122.439
118.323
115.672
113.783
113.021
110.128
101.090
80.791
77.317
77.000
76.682
65.297
65.057
64.820
63.892
63.757
55.530
44.327
27.978
15.237
15.223
f1 (ppm)
OMe
F
F
BocHN
O
O
N
OEt
OEt
3o

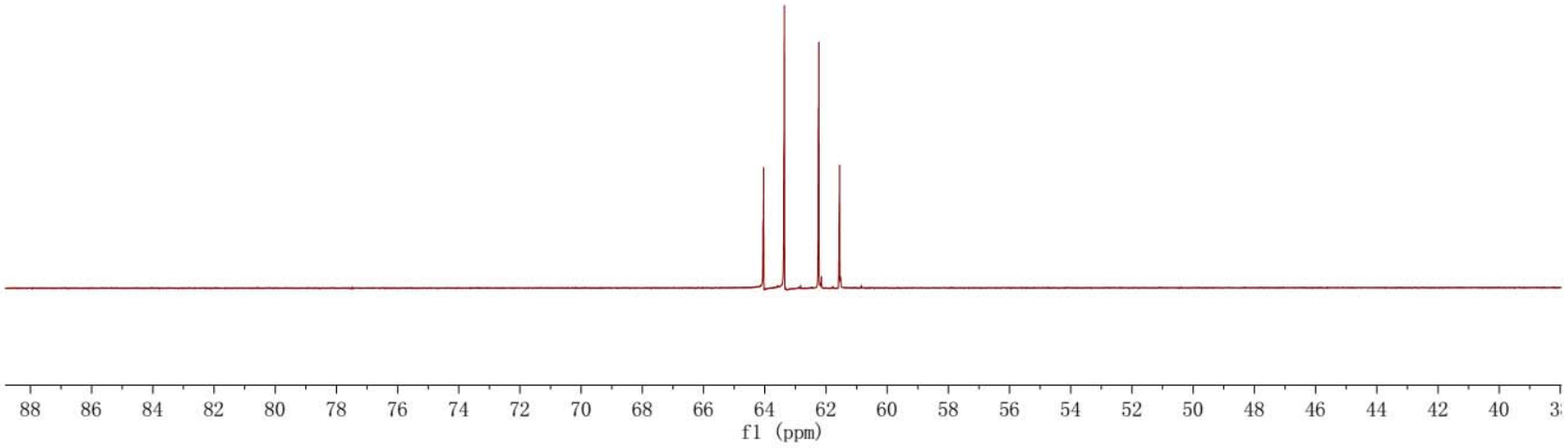

yjs-yp-79-3
f1 (ppm)
HN
O
F
F
O
HN
OMe
O
O
N
OEt
OEt
5

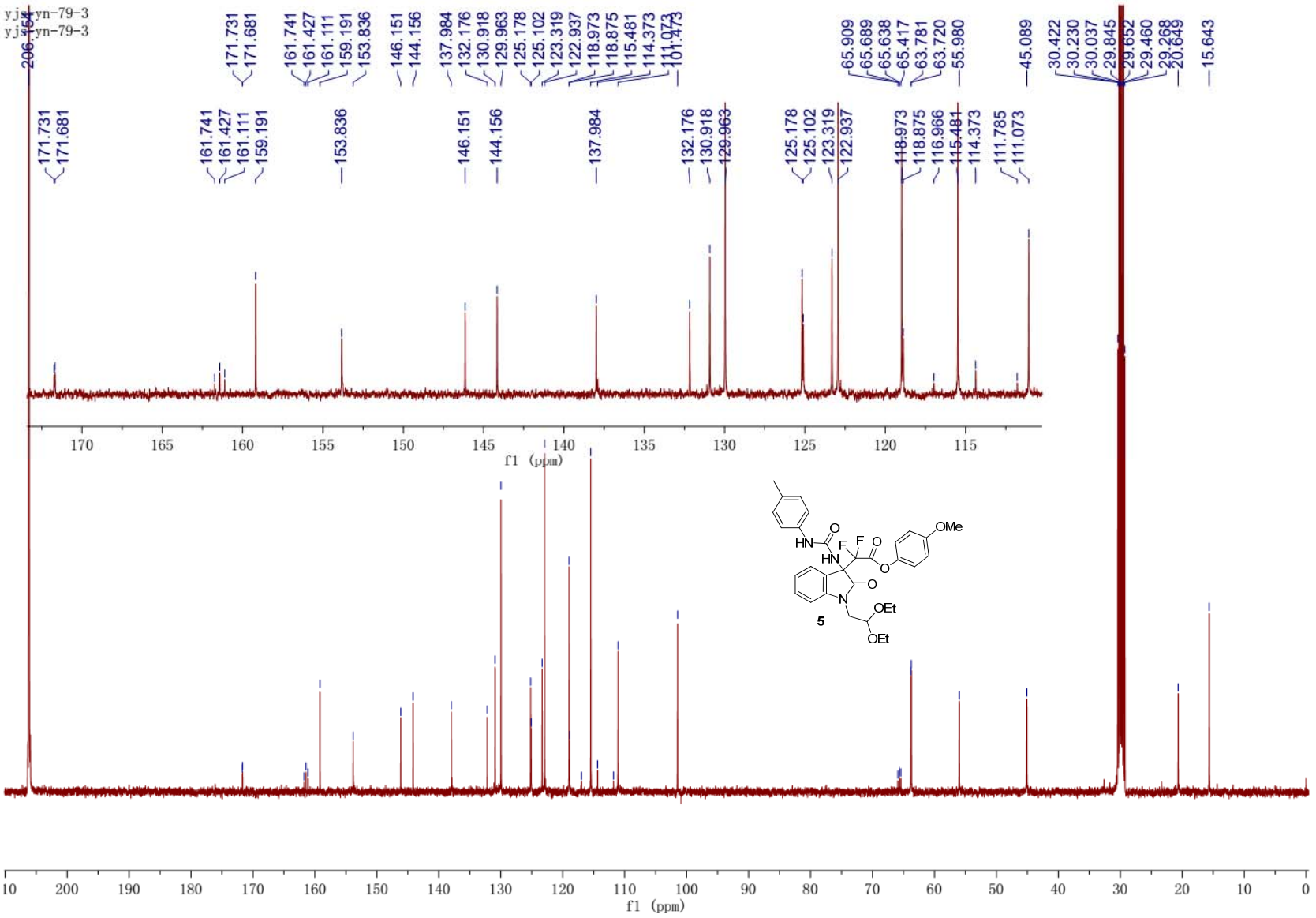
yjs-yn-79-3

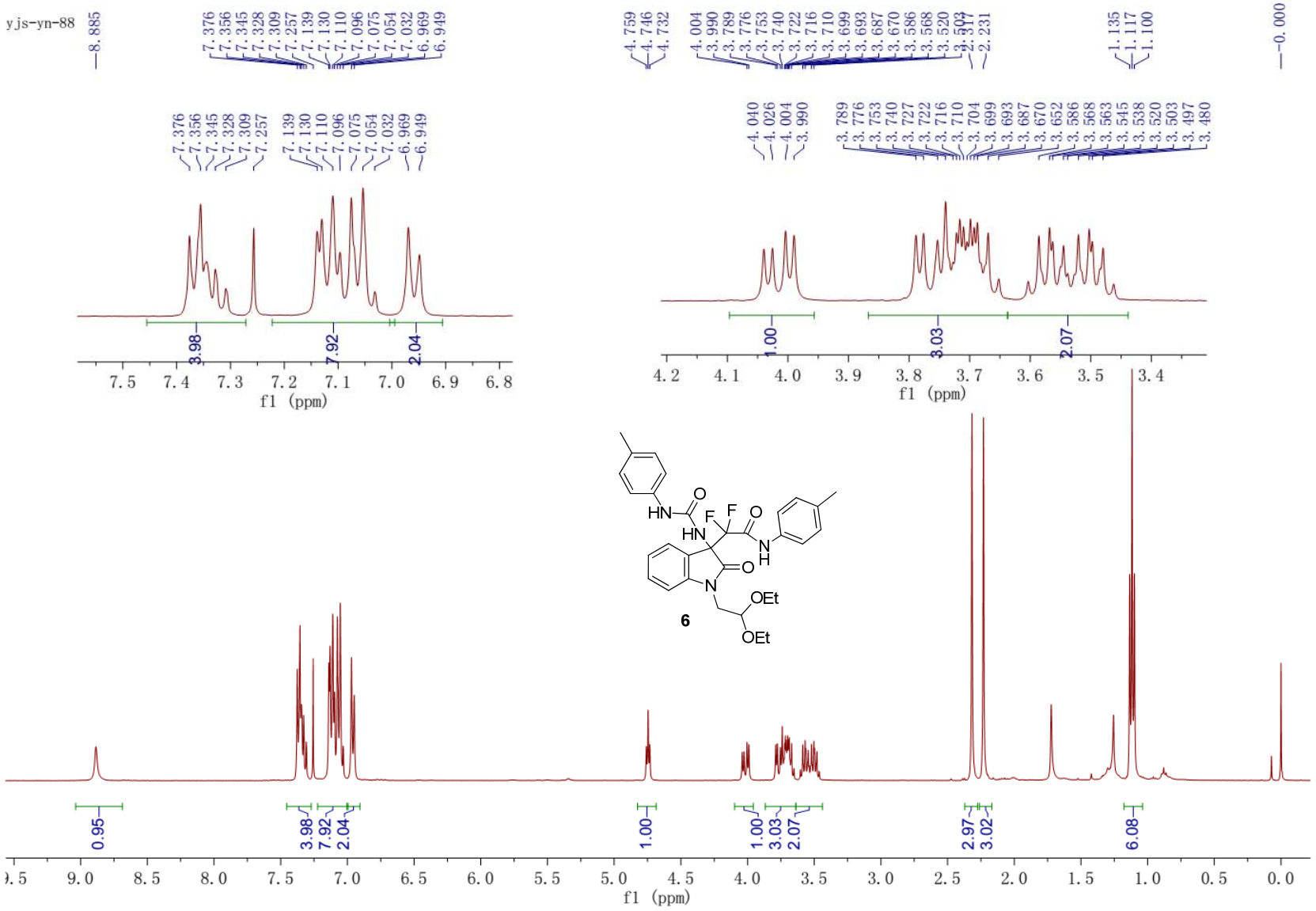
64.038
63.361
62.235
61.557



5

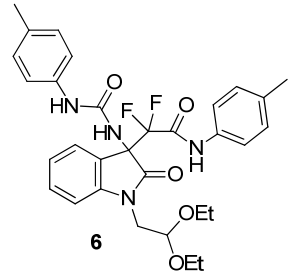



yjl-yn-79-3
yjl-yn-79-3
206.164
171.731
171.681
161.741
161.427
161.111
159.191
153.836
146.151
144.156
137.984
132.176
130.918
129.963
125.178
125.102
123.319
122.937
118.973
118.875
115.481
114.373
111.073
101.473
65.909
65.689
65.638
65.417
63.781
63.720
55.980
45.089
30.422
30.230
30.037
29.845
29.652
29.460
29.268
20.649
15.643
f1 (ppm)
HN
O
F
F
O
HN
O
N
OMe
OEt
OEt
5

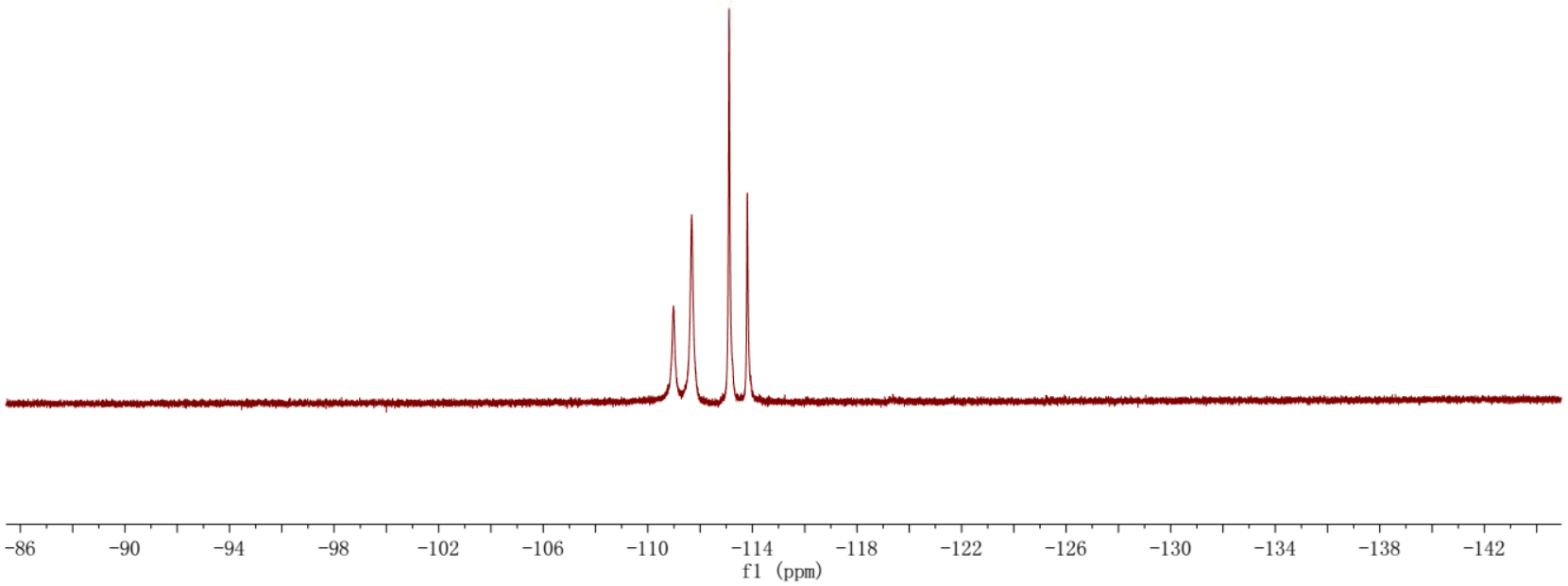

yjs-yn-88
8.885
7.376
7.356
7.345
7.328
7.309
7.257
7.139
7.130
7.110
7.096
7.075
7.054
7.032
6.969
6.949
4.759
4.746
4.732
4.004
3.990
3.789
3.776
3.753
3.740
3.722
3.716
3.710
3.699
3.693
3.687
3.670
3.586
3.568
3.520
3.503
2.317
2.231
1.135
1.117
1.100
0.000
4.040
4.026
4.004
3.990
3.789
3.776
3.753
3.740
3.727
3.722
3.716
3.710
3.704
3.699
3.693
3.687
3.670
3.652
3.586
3.568
3.563
3.545
3.538
3.520
3.503
3.497
3.480
3.98
7.92
2.04
1.00
3.03
2.07
f1 (ppm)
HN
O
F
F
O
HN
N
H
O
N
OEt
OEt
6
0.95
3.98
7.92
2.04
1.00
1.00
3.03
2.07
2.97
3.02
6.08
f1 (ppm)

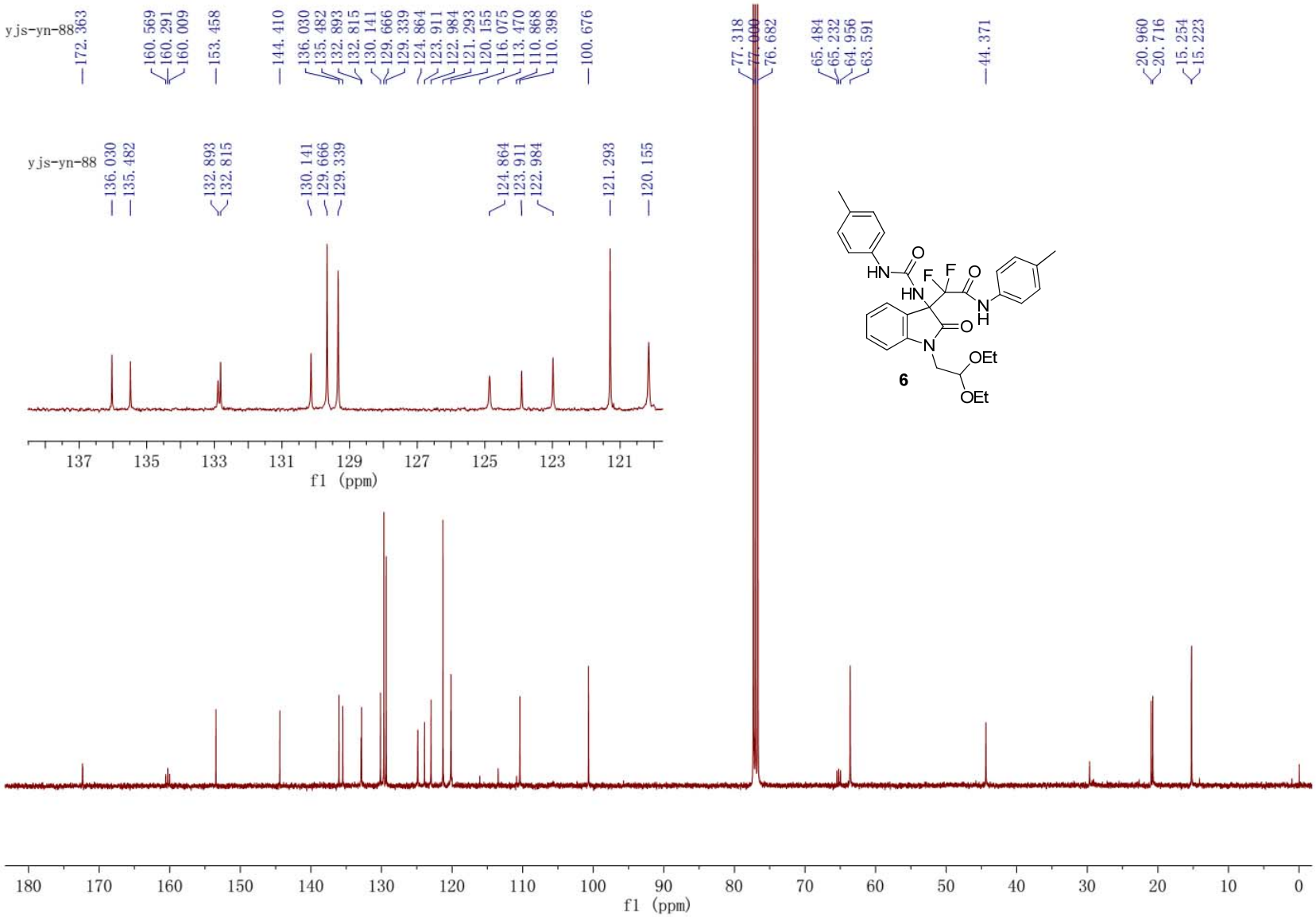
yjs-yn-88

-110.983
-111.680
-113.110
-113.805



6




yjs-yn-88
172.363
160.569
160.291
160.009
153.458
144.410
136.030
135.482
132.893
132.815
130.141
129.666
129.339
124.864
123.911
122.984
121.293
120.155
116.075
113.470
110.868
110.398
100.676
77.318
77.000
76.682
65.484
65.232
64.956
63.591
44.371
20.960
20.716
15.254
15.223
f1 (ppm)
HN
O
F
F
O
HN
N
H
O
N
OEt
OEt
6