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Iodine(III)-Induced Regioselective Carbocyclization of Teminal Alkynes: A Facile Approach to Prepare 1,1-Diiodomethylene Substituted Cyclic Compounds

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Supporting Information

General experimental methods:

All reactions were performed in Schlenk tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm) or $KMnO_4$ solution Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

General Experimental procedure:

Procedure 1: the mixture of acetylenic malonate (0.2 mmol) with Bu_4NI (221 mg, 0.6 mmol) in CF_3CH_2OH (2 mL) was treated with PhIO (132 mg, 0.6 mmol) at 25 °C, and the reaction mixture was allowed to stir at 25 °C for 24 hr. Upon completion by TLC, the reaction was quenched with saturated $Na_2S_2O_3$, and extracted by ethyl acetate (50 mL x 3). The organic layer was dried over anhydrated Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15% ethyl acetate in hexanes) to give the corresponding product.

Procedure 2: the mixture of acetylenic malonate (0.2 mmol) with KI (99 mg, 0.6 mmol) and NaOAc (16 mg 0.2 mmol) in CF_3CH_2OH (2 mL) was treated with PhIO (132 mg, 0.6 mmol) at 50 °C, and the reaction mixture was allowed to stir at 25 °C for 24 hr. Upon completion by TLC, the reaction was quenched with saturated $Na_2S_2O_3$, and extracted by ethyl acetate (25 mL x 3). The organic layer was dried over anhydrated Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (10% ethyl acetate in hexanes) to give the corresponding product.

Diethyl (E)-1-(iodomethylene)-1,3-dihydro-2H-indene-2,2-dicarboxylate 2a: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 7.2 Hz,1 H), 7.26-7.36 (m, 3 H), 6.86 (s, 1 H), 4.22 (q, J = 7.2 Hz, 4 H), 3.66 (s, 2 H), 1.26 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 144.8, 144.6, 138.0, 130.1, 126.4, 124.9, 124.8, 73.6, 67.1, 62.3, 39.8, 14.1; IR (KBr) 2980, 2930, 1734, 1471, 1366, 1247 cm^{-1}; HRMS m/z calcd for $C_{16}H_{17}INaO_4$ ([M+Na]$^+$): 423.0069, found 423.0035.

Diethyl 1-(diiodomethylene)-1H-indene-2,2(3H)-dicarboxylate 3a: colorless solid; m.p. 143-145 ^{o}C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 7.6 Hz, 1 H), 7.21-7.33 (m, 3 H), 4.23-4.31 (m, 4 H), 3.64 (s, 2 H), 1.32 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 151.0, 144.7, 139.3, 130.2, 126.6, 126.4, 125.1, 71.8, 62.7, 42.3, 14.2, 2.4; IR (KBr) 2981, 2927, 1736, 1716, 1458, 1438 cm^{-1}; HRMS m/z calcd for $C_{16}H_{16}I_2NaO_4$ ([M+Na]$^+$): 548.9036, found 548.9025.

Dimethyl 1-(diiodomethylene)-1H-indene-2,2(3H)-dicarboxylate 3b: colorless solid; 155-157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 8.0 Hz, 1 H), 7.21-7.34 (m, 2 H), 7.22 (d, J = 7.2 Hz, 1 H), 3.80 (s, 6 H), 3.65 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 151.0, 144.6, 139.2, 130.4, 126.6, 126.5, 125.2, 71.8, 53.7, 42.4, 2.7; IR (KBr) 3054, 2987, 1735, 1601, 1433, 1265 cm^{-1}; HRMS m/z calcd for $C_{14}H_{12}I_2NaO_4$ ([M+Na]$^+$): 520.8723, found 520.8705.

Dibenzyl 1-(diiodomethylene)-1H-indene-2,2(3H)-dicarboxylate 3c: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 7.6 Hz, 1 H), 7.15-7.37 (m, 14 H), 5.22 (s. 4 H), 3.63 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 150.9, 144.5, 139.2, 135.1, 130.2, 128.6, 128.4, 128.3, 126.4, 125.0, 71.8, 68.1, 42.3, 2.6; IR (KBr) 3064, 3032, 2960, 2926, 1735, 1497, 1456 cm^{-1}; HRMS m/z calcd for $C_{26}H_{20}I_2NaO_4$ ([M+Na]$^+$): 672.9349, found 672.9349.

Diethyl 1-(diiodomethylene)-5-methyl-1H-indene-2,2(3H)-dicarboxylate 3d: colorless solid; m.p. 147-149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 8.4 Hz, 1 H), 7.08 (d, J = 8.4 Hz, 1 H), 7.03 (s, 1 H), 4.21-4.30 (m, 4 H), 3.59 (s, 2 H), 2.31 (s, 3 H), 1.31 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 150.9, 144.8, 140.6, 136.7, 127.2, 126.2, 125.4, 71.7, 62.5, 42.0, 21.6, 14.0, 0.7; IR (KBr) 2980, 2921, 1734, 1720, 1610, 1443 cm^{-1}; HRMS m/z calcd for $C_{17}H_{18}I_2NaO_4$ ([M+Na]$^+$): 562.9192, found 562.9154.

Diethyl 1-(diiodomethylene)-6-methoxy-1H-indene-2,2(3H)- dicarboxylate 3e: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.11 (d, J = 8.4 Hz, 1 H), 6.92 (d, J = 8.4 Hz, 1 H), 4.23-4.31 (m, 4 H), 3.82 (s, 3 H), 3.57 (s, 2 H), 1.32 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 158.4, 151.1, 140.4, 137.1, 125.7, 117.3, 111.3, 72.5, 62.8, 55.9, 41.8, 14.3, 2.4; IR (KBr) 2926, 2853, 1735, 1605, 1481, 1463 cm^{-1}; HRMS m/z calcd for $C_{17}H_{18}I_2NaO_5$ ([M+Na]$^+$): 578.9141, found 578.9101.

Diethyl 1-(diiodomethylene)-5,6-dimethoxy-1H-indene-2,2(3H)- dicarboxylate 3f: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1 H), 6.69 (s, 1 H), 4.22 - 4.32 (m, 4 H), 3.90 (s. 3 H), 3.89 (s. 3 H), 3.57 (s, 2 H), 1.33 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 151.1, 150.7, 147.4, 138.4, 131.5, 109.1, 106.7, 71.7, 62.6, 56.2, 56.1, 41.9, 14.0, -2.1; IR (KBr) 2930, 2854, 1735, 1604, 1502, 1465 cm^{-1}; HRMS m/z calcd for $C_{18}H_{20}I_2NaO_6$ ([M+Na]$^+$): 608.9247, found 608.9223.

Diethyl 5-chloro-1-(diiodomethylene)-1H-indene-2,2(3H)- dicarboxylate 3g: colorless solid; m.p. 122-124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 8.8 Hz, 1 H), 7.20-7.26 (m, 2 H), 4.22-4.32 (m, 4 H), 3.60 (s, 2 H), 1.32 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 150.0, 146.4, 137.9, 135.9, 127.6, 126.8, 125.2, 71.8, 62.9, 41.7, 14.2, 3.4; IR (KBr) 2979, 2925, 1718, 1593, 1463, 1366 cm^{-1}; HRMS m/z calcd for $C_{16}H_{15}ClI_2NaO_4$ ([M+Na]$^+$): 582.8646, found 582.8620.

Diethyl 1-(diiodomethylene)-5-fluoro-1H-indene-2,2(3H)-dicarboxylate 3h: colorless solid; m.p. 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (dd, J = 8.8, 5.2 Hz, 1 H), 6.98 (td, J = 8.8, 2.4 Hz, 1 H), 6.91 (d, J = 8.0 Hz, 1 H), 4.21-4.35 (m, 4 H), 3.61 (s, 2 H), 1.33 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 164.8, 162.3, 149.7, 147.3, 147.2, 135.3, 128.3, 128.2, 113.8, 113.6, 112.0, 111.7, 71.8, 62.7, 41.6, 14.0, 1.6; IR (KBr) 2981, 2925, 1736, 1605, 1479, 1439, 1366 cm^{-1}; HRMS m/z calcd for $C_{16}H_{15}FI_2NaO_4$ ([M+Na]$^+$): 566.8941, found 566.8901.

D**iethyl 1-(diiodomethylene)-6-fluoro-1H-indene-2,2(3H)-dicarboxylate 3i:** pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 11.2 Hz,1 H), 7.16 (t, J = 6.0 Hz, 1 H), 7.05 (t, J = 8.4 Hz, 1 H), 4.19-4.35 (m, 4 H), 3.59 (s, 2 H), 1.32 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 168.2, 162.4, 160.0, 150.0, 140.9, 140.8, 140.0, 125.9, 125.8, 117.3, 117.1, 113.5,

113.2, 72.2, 62.7, 41.5, 14.0, 4.4; IR (KBr) 2979, 2927, 2854, 1731, 1610, 1588, 1477, 1439 cm^{-1}; HRMS m/z calcd for $C_{16}H_{15}FI_2NaO_4$ ($[M+Na]^+$): 566.8941, found 566.8903.

Dimethyl 2-(diiodomethylene)cyclopentane-1,1-dicarboxylate 5a: pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 6 H), 2.63 (t, J = 6.8 Hz, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 1.77-1.85 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 155.8, 68.2, 53.2, 44.3, 41.3, 24.2, 8.7; IR (KBr) 2919, 2850, 1735, 1432, 1264 cm^{-1}; HRMS m/z calcd for $C_{10}H_{12}I_2NaO_4$ ($[M+Na]^+$): 472.8723, found 472.8767.

Diethyl 2-(diiodomethylene)cyclopentane-1,1-dicarboxylate 5b: pale yellow solid; 65-67 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 4.20-4.37 (m, 4 H), 2.62 (t, J = 7.2 Hz, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 1.78-1.84 (m, 2 H), 1.33 (t, J = 7.2 Hz, 6 H)**;** ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 155.9, 68.3, 62.2, 44.4, 41.2, 24.1, 14.1, 8.4**;** IR (KBr) 2978, 1728, 1444, 1366, 1261 cm^{-1}**;** HRMS m/z calcd for $C_{12}H_{16}I_2NaO_4$ ($[M+Na]^+$): 500.9036, found 500.9009.

Dibenzyl 2-(diiodomethylene)cyclopentane-1,1-dicarboxylate 5c: pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.40 (m, 10 H), 5.21 (s, 4 H), 2.63 (t, J = 6.4 Hz, 2 H), 2.51 (t, J = 7.2 Hz, 2 H), 1.70-1.80 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 155.9, 135.3, 128.6, 128.4, 128.1, 68.3, 67.9, 44.3, 41.5, 24.2, 8.8; IR (KBr) 2919, 2844, 1728, 1453, 1261 cm^{-1}; HRMS m/z calcd for $C_{22}H_{20}I_2NaO_4$ ($[M+Na]^+$): 624.9349, found 624.9377.

Di-*iso*-propyl 2-(4,5,5-triiodopent-4-en-1-yl)malonate 6d： yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 5.15 – 4.84 (m, 2H), 3.32 – 3.26 (m, 1H), 2.67 (t, J= 7.7 Hz, 1H), 2.42 (t, J = 7.0 Hz, 1H), 1.96 (m, 2H), 1.72 – 1.52 (m, 2H), 1.30 – 1.23 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.71, 93.56, 68.79, 51.86, 27.59, 26.13, 21.61, 21.54, 20.51, 18.11;HRMS (ESI) calcd for $C_{14}H_{21}I_3O_4$ $[M+H]^+$: m/z 634.8647, found: 634.8628

Di-*tert*-butyl 2-(4,5,5-triiodopent-4-en-1-yl)malonate 6e: yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 3.24 – 3.05 (m, 1H), 2.66 (t, J = 7.6 Hz, 1H), 2.41 (t, J = 7.0 Hz, 1H), 2.00 – 1.80 (m, 2H), 1.70 – 1.53 (m, 2H), 1.49 (s, 9H), 1.47 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.57, 93.72, 81.37, 53.45, 44.37, 27.88, 27.64, 26.12, 20.56, 18.16; HRMS (ESI) m/z calcd for $C_{16}H_{25}I_3O_4$ $[M+H]^+$ 662.8947, found: 662.8933

(E)-6-(Iodomethylene)spiro[4.4]nonane-1,4-dione 8: brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 1H), 4.02 (t, *J* = 6.1 Hz, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.70 – 2.58 (m, 2H), 2.58 – 2.35 (m, 2H), 2.16 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.95, 189.89, 105.02, 69.76, 47.12, 34.03, 28.56, 27.59. HRMS m/z calcd for $C_{10}H_{11}INaO_2$ ($[M+Na]^+$): 312.9696, found 312.9701

(E)-6-(Iodomethylene)spiro[4.5]decane-1,4-dione 10: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 1H), 4.01 (t, *J* = 6.2 Hz, 2H), 2.68 – 2.58 (m, 2H), 2.44 (m, 4H), 1.88 (m, 2H), 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.01, 190.15, 104.78, 93.60, 71.27, 33.98, 28.48, 27.61, 24.77, 20.41. HRMS m/z calcd for $C_{11}H_{14}IO_2$ ($[M+H]^+$): 305.0033, found 305.0030

Ethyl (E)-2-(iodomethylene)-1-nitrocyclopentane-1-carboxylate 12: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 2.6 Hz, 1H), δ 4.31 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.82 (m, 1H), 2.75 – 2.55 (m, 2H), 2.46 (m, 1H), 1.96 (m, 1H), 1.90 – 1.76 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.99, 147.03, 98.84, 85.24, 63.27, 39.05, 36.96, 21.85, 13.79. HRMS m/z calcd for $C_9H_{12}INNaO_4$ ($[M+Na]^+$): 347.9703 found 347.9695.

Methyl 1-cyano-2-(diiodomethylene)cyclopentane-1-carboxylate 14a: pale yellow solid; 65-66 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 2.96 – 2.76 (m, 1H), 2.71 – 2.61 (m, 1H), 2.61 – 2.48 (m, 2H), 2.19 – 1.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.18, 153.71, 116.15, 65.55, 53.94, 42.94, 24.60, 11.62, HRMS m/z calcd for $C_9H_{10}I_2NO_2$ ($[M+H]^+$): 417.8795, found: 417.8783.

Ethyl 1-cyano-2-(diiodomethylene)cyclopentane-1-carboxylate 14b: pale yellow solid; 86-87 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (q, *J* = 7.1, 2H), 2.90 – 2.74 (m, 1H), 2.72 – 2.37 (m, 3H), 2.19 – 1.85 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 153.75, 116.27, 63.38, 56.12, 43.02, 24.60, 13.99, 11.46, HRMS m/z calcd for $C_{10}H_{12}I_2NO_2$ ($[M+H]^+$) : 431.8956, found: 431.8952.

Isopropyl 1-cyano-2-(diiodomethylene)cyclopentane-1-carboxylate, 14c: colorless solid; 90-91 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 – 5.06 (m, 1H), 2.87 – 2.70 (m, 1H), 2.72 – 2.41 (m, 3H), 2.19 – 1.88 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.96, 153.76, 116.35, 71.51, 56.22, 43.08, 43.05, 24.56, 21.57, 21.52, 11.24. HRMS m/z calcd for $C_{11}H_{14}I_2NO_2$ ($[M+H]^+$) : 445.9108, found: 431.8952.

***tert*-Butyl 1-cyano-2-(diiodomethylene)cyclopentane-1-carboxylate, 14d:** yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (m, 1H), 2.69 – 2.49 (m, 3H), 2.17 – 1.93 (m, 2H), 1.55 (s, 9H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 118.90, 117.52, 84.48, 49.77, 35.60, 27.97, 24.49, 19.65. HRMS m/z calcd for $C_{12}H_{16}I_2NO_2$ ($[M+H]^+$) : 459.9265, found: 459.9258.

Dimethyl 2-(diiodomethylene)cyclohexane-1,1-dicarboxylate, 16a: pale yellow solid; 75-76 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 6H), 2.66 – 2.55 (m, 2H), 2.25 – 2.18 (m, 2H), 1.70 – 1.59 (m, 2H), 1.52 – 1.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66, 118.62, 54.02, 50.15, 39.86, 28.05, 26.57, 0.99. HRMS m/z calcd for $C_{11}H_{25}I_2O_4$ ($[M+H]^+$) : 464.9054, found: 464.9068.

Diethyl 2-(diiodomethylene)cyclohexane-1,1-dicarboxylate, 16b: pale yellow solid; 87-89 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (q, J = 7.1, 4H), 2.39 (t, J = 6.9 Hz, 2H), 2.23 – 2,06 (m, 2H), 1.62 – 1.52 (m, 2H), 1.52 – 1.37 (m, 2H), 1.28 (t, J = 7.1, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.08, 93.86, 63.04, 50.19, 39.34, 27.81, 26.66, 20.48, 13.83, -6.53.HRMS (ESI) m/z calcd for $C_{13}H_{18}I_2O_4$ ($[M+H]^+$): 492.9367, found: 492.9381.

Methyl 1-cyano-2-(diiodomethylene)cyclohexane-1-carboxylate, **16c:** colorless solid; 68-69 ^{o}C. 1H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 2.85 – 2.52 (m, 1H), 2.48 – 2.36 (m, 1H), 2.36 – 2.27 (m, 1H), 2.27 – 2.12 (m, 1H), 1.91 – 1.64 (m, 4H). ^{113}C NMR (101 MHz, $CDCl_3$) δ 167.43, 145.48, 116.21, 53.99, 53.19, 35.85, 33.98, 19.19, 19.08, 16.91. HRMS (ESI) m/z calcd for $C_{10}H_{12}I_2NO_2$ ($[M+H]^+$) : 431.8957, found: 431.8953

Isopropyl 1-cyano-2-(diiodomethylene)cyclohexane-1-carboxylate 16d: pale yellow solid; 112-113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (m, 1H), 2.75 – 2.55 (m, 1H), 2.47 – 2.26 (m, 2H), 2.25 – 2.12 (m, 1H), 1.90 – 1.67 (m, 4H), 1.35 (d, J = 6.0 Hz, 3H), 1.34 (d, J = 6.0 Hz, 3H).. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.10, 145.64, 116.36, 71.42, 53.32, 35.82, 34.02, 21.52, 21.45, 19.09, 18.68, 16.82. HRMS (ESI) m/z calcd for $C_{12}H_{16}I_2NO_2$ $[M+H]^+$: 459.9265, found: 459.9278.

Diethyl 4-(diiodomethylene)-2-methyldihydrofuran-3,3(2H)-dicarboxylate, 18: light yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (d, J = 16.3 Hz, 1H), 4.37 (d, J = 16.3 Hz, 1H), 4.24 (m, 4H), 3.72 (q, J = 6.0 Hz, 1H), 1.45 (d, J = 6.0 Hz, 2H), 1.31 (t, J = 5.1 Hz, 3H), 1.27 (t, J = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.07, 166.18, 90.09, 63.37, 62.82, 57.96, 53.27,

19.40, 13.93, 13.67, 3.13. HRMS m/z calcd for $C_{12}H_{16}I_2NaO_5$ ([M+Na]$^+$) : 516.8985, found: 516.8991

Diethyl 4-(diiodomethylene)-2-methyldihydro-2H-pyran-3,3(4H)-dicarboxylate, 20: light yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 – 4.13 (m, 4H), 3.79 (dd, *J* = 15.9, 7.1 Hz, 1H), 3.63 (dd, *J* = 15.7, 7.3 Hz, 1H), 3.56 (q, *J* = 5.9 Hz, 1H), 2.90 (td, *J* = 7.2, 2.2 Hz, 2H), 1.45 (d, *J* = 6.0 Hz, 3H), 1.33 (t, *J* = 6.1 Hz, 3H), 1.29 (t, *J* = 6.1 Hz, 3H)..^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 166.37, 113.71, 78.53, 66.76, 63.24, 62.79, 52.77, 50.53, 19.24, 13.97, 13.71, 0.96. HRMS m/z calcd for $C_{13}H_{18}I_2NaO_5$ ([M+Na]$^+$) : 530.9136, found: 530.9140

Ethyl 4-(diiodomethyl)-2-phenylquinoline-3-carboxylate, 22a: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 7.9 Hz, 1H), 8.25 (t, *J* = 8.6 Hz, 1H), 7.91 – 7.76 (m, 2H), 7.68 – 7.58 (m, 2H), 7.50 – 7.42 (m, 3H), 7.05 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.93, 154.56, 147.36, 142.34, 139.93, 135.57, 133.61, 130.19, 128.78, 128.36, 128.26, 124.84, 123.80, 117.41, 62.23, 13.42. HRMS m/z calcd for $C_{19}H_{16}I_2NO_2$ ([M+H]$^+$) : 543.9270, found: 543.9274

3-Ethyl 4-(2,2,2-trifluoroethyl) 2-phenylquinoline-3,4-dicarboxylate 23a: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.69 (m, 3H), 7.50 (m, 3H), 4.82 (q, *J* = 8.3 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 164.80, 155.94, 146.93, 139.98, 138.98, 136.76, 134.04, 129.77, 128.85, 128.38, 124.61, 123.59, 123.49, 121.86, 62.33, 62.08, 61.96, 61.59, 61.22, 13.28. HRMS m/z calcd for $C_{21}H_{17}F_3NO_4$ ([M+H]$^+$) :404.1110, found: 404.1111

Ethyl 4-(diiodomethyl)-6-methyl-2-phenylquinoline-3-carboxylate, 22b: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.88 – 7.55 (m, 3H), 7.55 – 7.45 (m, 3H), 7.07 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.98, 154.62, 147.41, 142.40, 139.98, 135.63, 133.66, 130.24, 128.84, 128.41, 128.31, 124.89, 123.85, 117.46, 62.28, 22.57, 13.48. HRMS m/z calcd for $C_{20}H_{18}I_2NO_2$ ([M+H]$^+$) : 557.9427, found: 557.9428

3-Ethyl 4-(2,2,2-trifluoroethyl) 6-methyl-2-phenylquinoline-3,4-dicarboxylate, 23b: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H)., 7.78 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.49 (m, 3H), 4.82 (q, *J* = 8.3 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.60 (s,

3H), 0.96 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 164.80, 155.94, 146.93, 139.98, 138.98, 134.04, 129.77, 128.85, 128.38, 128.21, 123.59, 123.49, 121.86, 62.33, 62.08, 61.96, 61.59, 61.22, 21.92, 13.28. HRMS m/z calcd for $C_{22}H_{19}F_3NO_4$ ($[M+H]^+$) :418.1266, found: 418.1279

Ethyl 6-bromo-4-(diiodomethyl)-2-phenylquinoline-3-carboxylate, 22c: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.9, 1H)., 7.67 – 7.62 (m, 2H), 7.50 – 7.47 (m, 3H). 7.04 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.47, 155.97, 147.44, 142.44, 139.53, 134.88, 132.05, 129.20, 128.50, 128.32, 128.24, 125.19, 119.50, 62.50, 13.46. HRMS m/z calcd for $C_{19}H_{14}I_2BrNO_2$ ($[M+H]^+$) : 621.8370, found: 621.8376

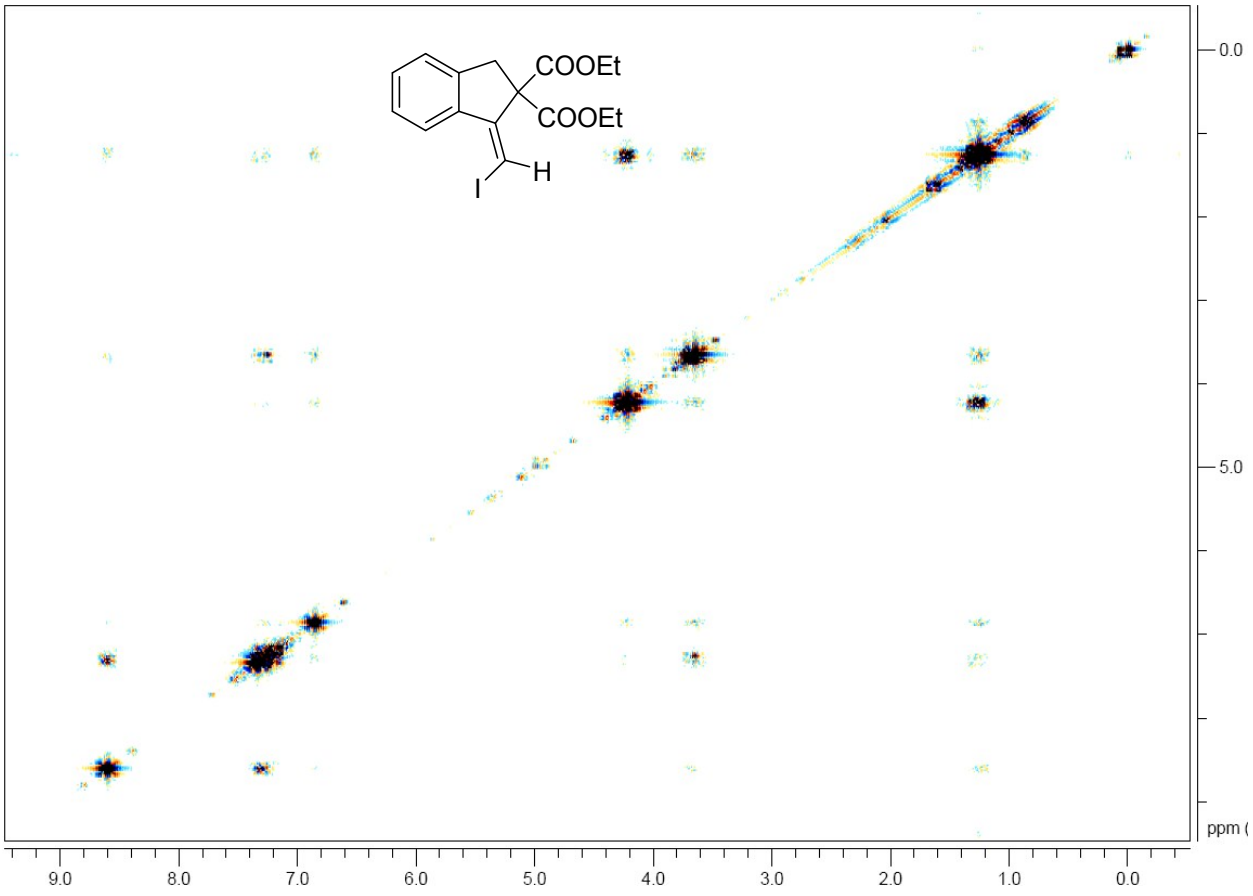
3-Ethyl 4-(2,2,2-trifluoroethyl) 6-bromo-2-phenylquinoline-3,4-dicarboxylate, 23c: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 2.0 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.94 (dd, J = 9.0, 2.0 Hz, 1H), 7.72 - 7.62 (m, 2H), 7.59 – 7.44 (m, 3H), 4.81 (q, J = 8.3 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 0.97 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.47, 164.86, 155.99, 146.99, 140.03, 139.03, 136.82, 134.10, 126.07, 124.67, 123.86, 123.55, 121.92, 121.66, 119.46. HRMS m/z calcd for $C_{21}H_{16}BrF_3NO_4$ ($[M+H]^+$) : 482.0215, found:482.0210

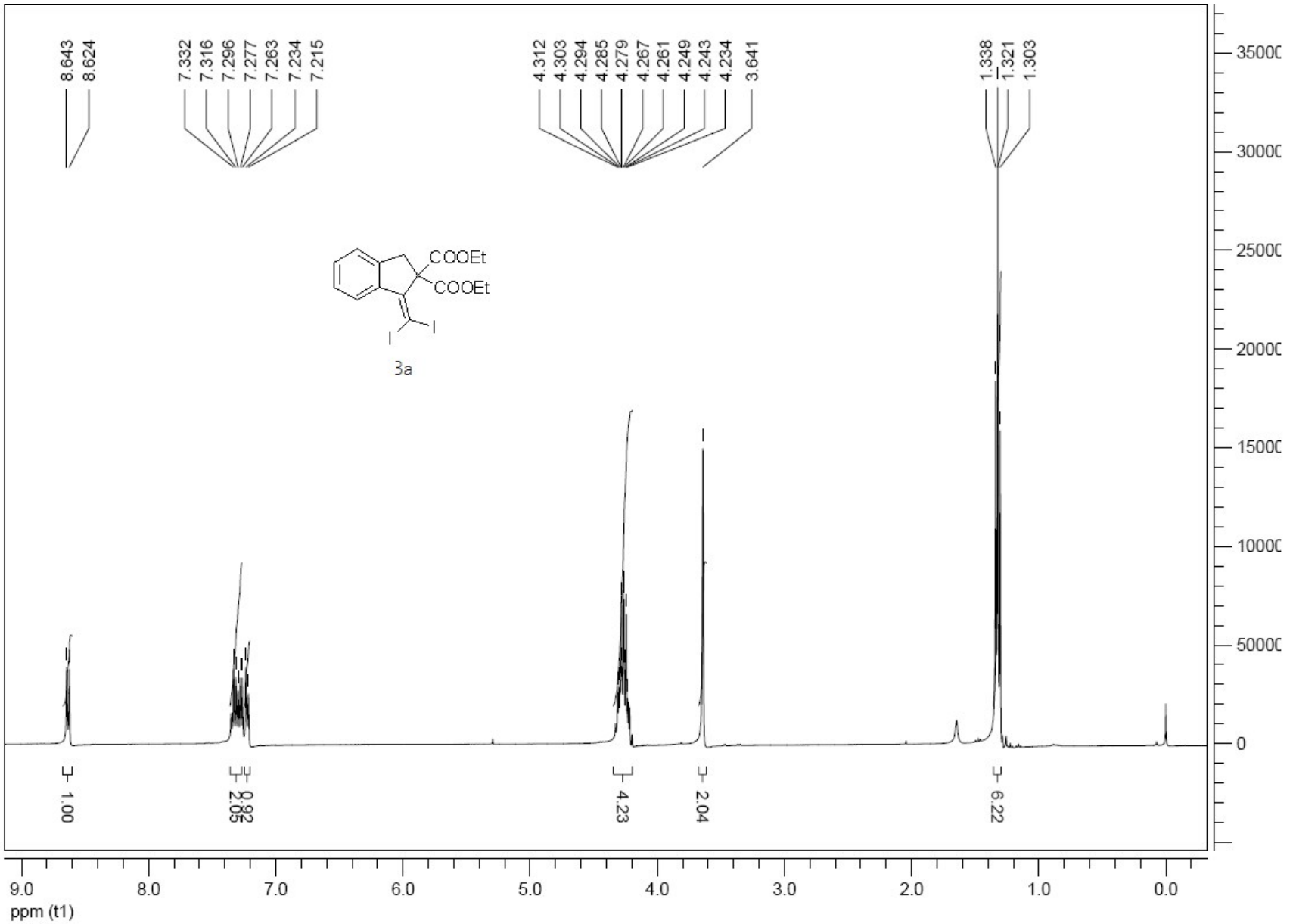
Diethyl 2-(2-(iodoethynyl)phenyl)malonate 25: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.47 (m, 2 H), 7.35 (t, J = 7.6 Hz, 1 H), 7.25-7.29 (m, 1 H), 5.22 (s, 1 H), 4.22 (q, J = 7.2 Hz, 4 H), 1.28 (t, J = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 135.9, 133.0, 129.2, 128.7, 127.9, 123.9, 91.9, 62.0, 55.8, 14.2, 11.8; IR (KBr) 2979, 2926, 1735, 1488, 1467, 1445, 1367 cm^{-1}; HRMS m/z calcd for $C_{15}H_{15}INaO_4$ ($[M+Na]^+$): 408.9913, found 408.9877.

Diethyl 1-(1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ylidene)-1H-indene- 2,2(3H)-dicarboxylate 26: pale yellow oil; ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 11.2 Hz, 1 H), 7.20-7.32 (m, 3 H), 4.20 (q, J = 6.8 Hz, 4 H), 3.65 (s, 2 H), 1.27 (t, J = 6.8 Hz, 6 H), 0.30 (s, 9 H), 0.22 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 153.9, 144.6, 138.1, 130.4, 126.9, 125.9, 124.6, 102.5, 101.8, 101.2, 100.4, 66.0, 62.0, 41.8, 14.1, -0.2; HRMS m/z calcd for $C_{26}H_{34}NaO_4Si_2$ ($[M+Na]^+$): 489.1893, found 489.1915.

Diethyl 2-(1,5-diphenylpenta-1,4-diyn-3-ylidene)cyclopentane-1,1-dicarboxylate 27: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ7.54 – 7.50 (m, 4H), 7.36 – 7.31 (m, 6H)., 4.32 – 4.13 (m, 4H),

2.89 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.95 – 1.81 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.18, 217.91, 169.67, 158.85, 131.52, 131.38, 129.87, 128.39, 128.26, 128.21, 128.17, 123.22, 123.01, 103.45, 65.80, 61.80, 38.70, 34.71, 23.89, 13.94. HRMS m/z calcd for $C_{28}H_{27}O_4$ ([M+H]$^+$) : 427.1904, found:427.1902

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4.261
4.249
4.243
4.234
3.641
1.338
1.321
1.303
COOEt
COOEt
I
I
3a
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0.82
4.23
2.04
6.22
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8.0
7.0
6.0
5.0
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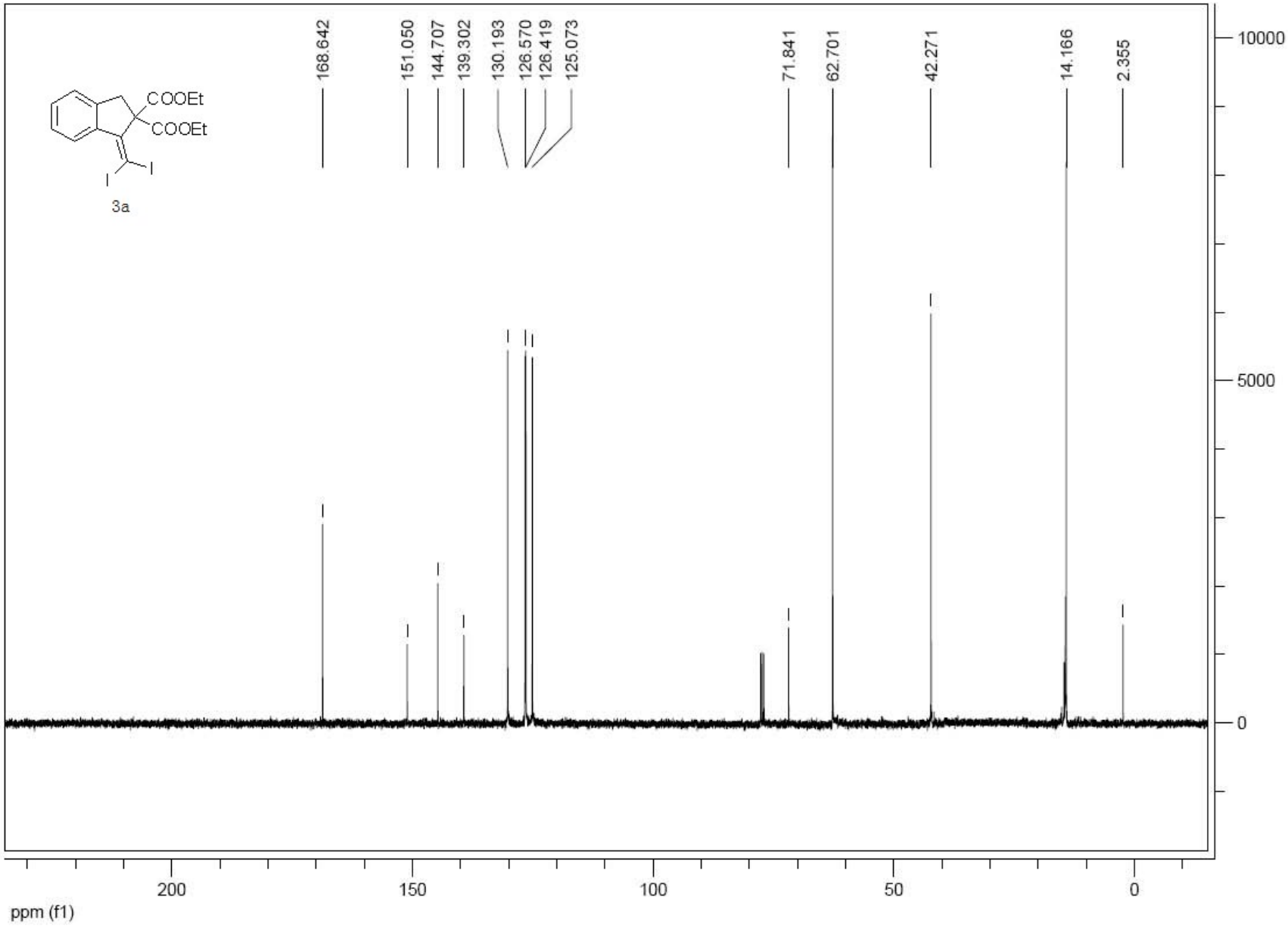
20000
15000
10000
5000
0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50
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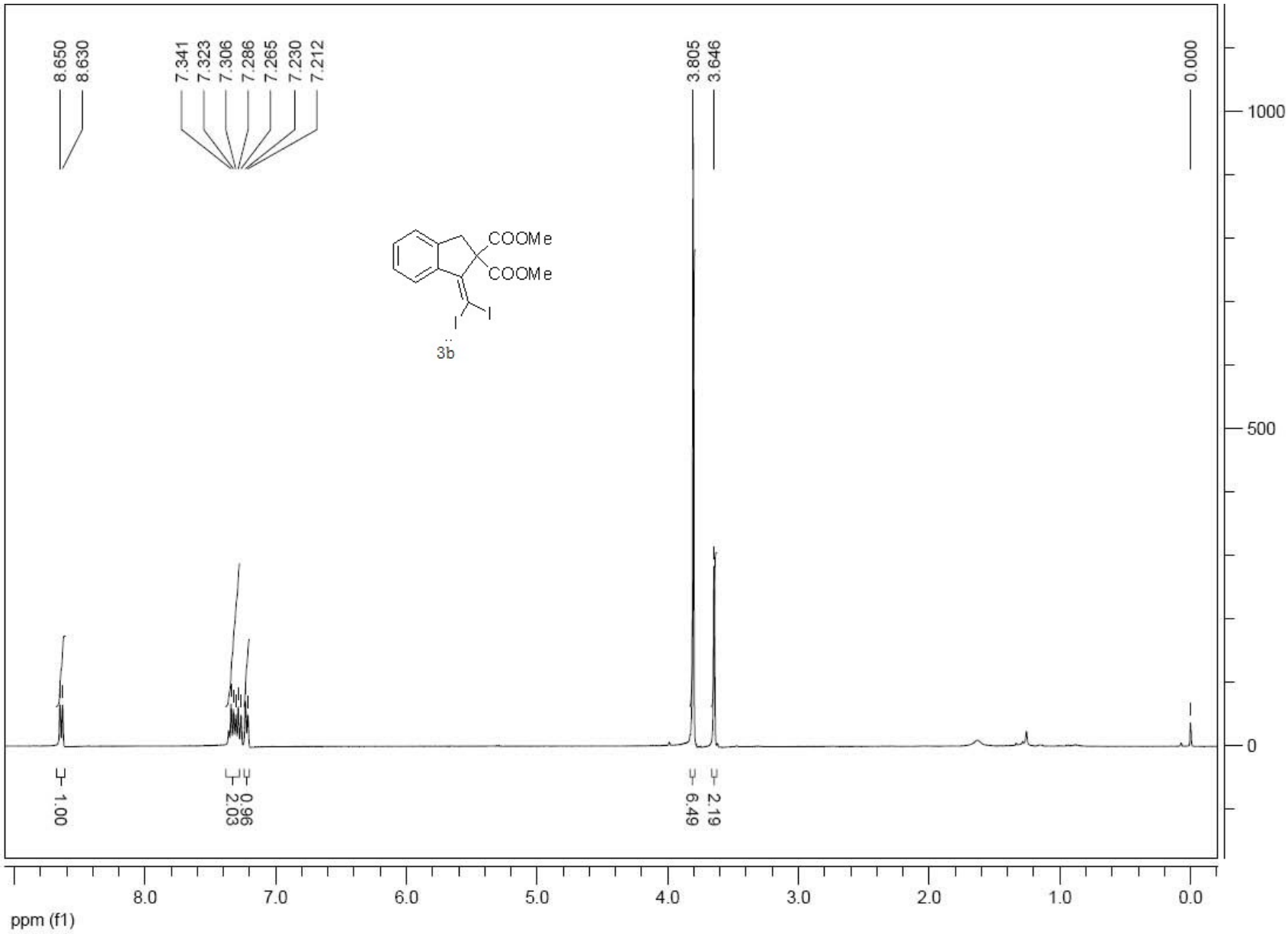
ppm (f1)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COOMe
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I
I
3b
1000
500
0
1.00
2.03
0.96
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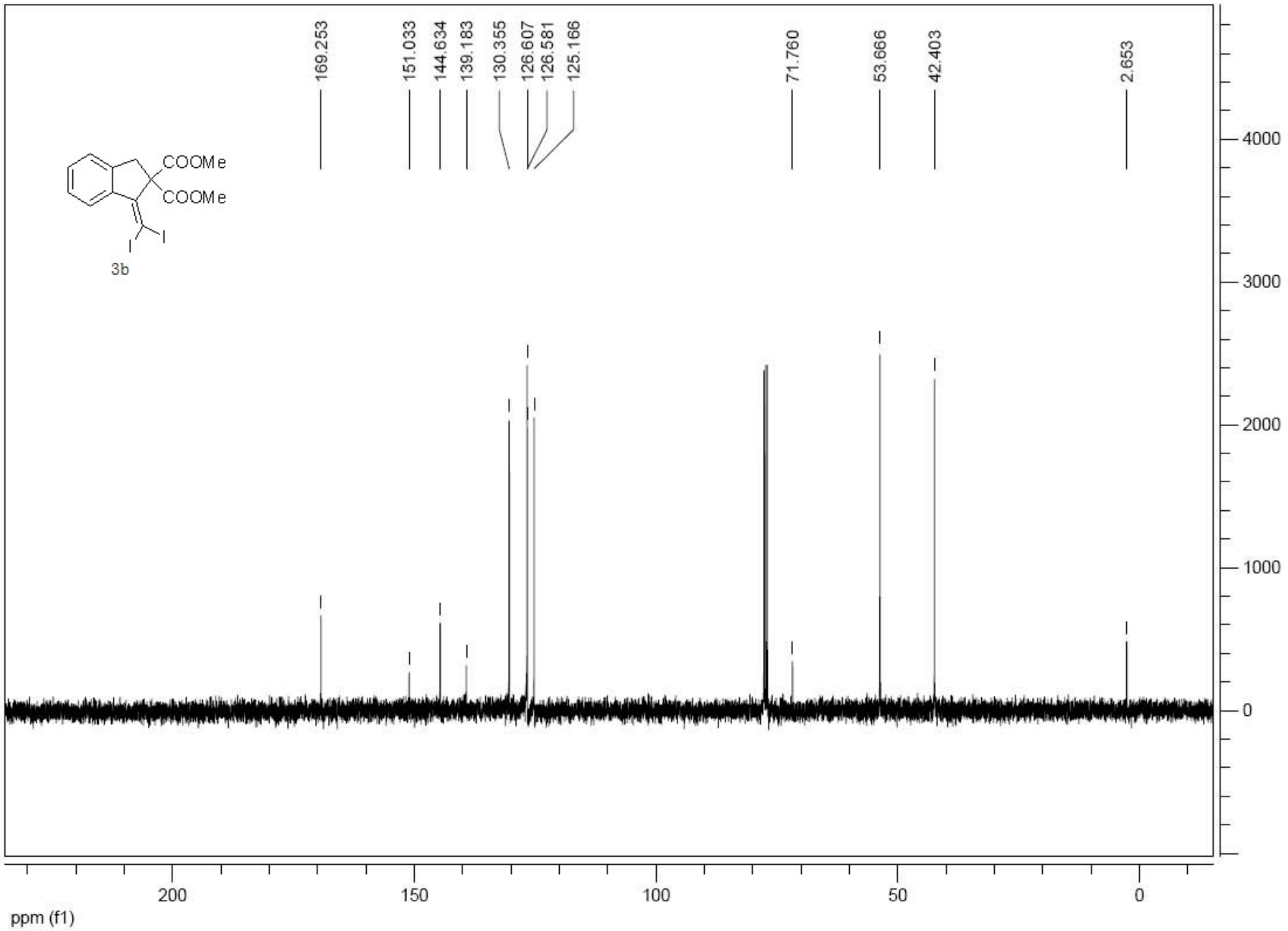
ppm (f1)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COOMe
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I
3b
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2000
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0
200
150
100
50
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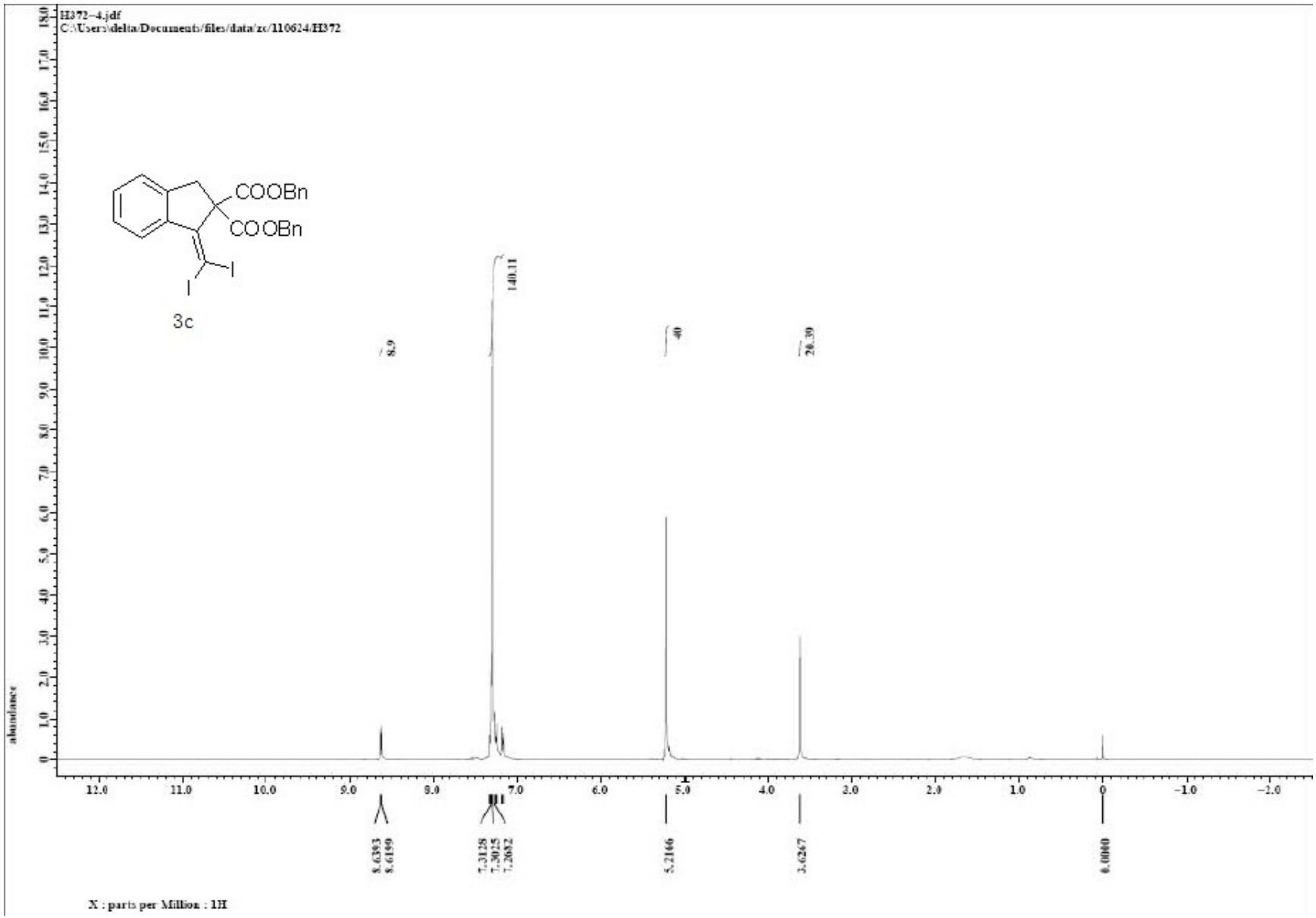
ppm (f1)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I
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40
26.39
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7.3128
7.3025
7.2652
5.2146
3.6267
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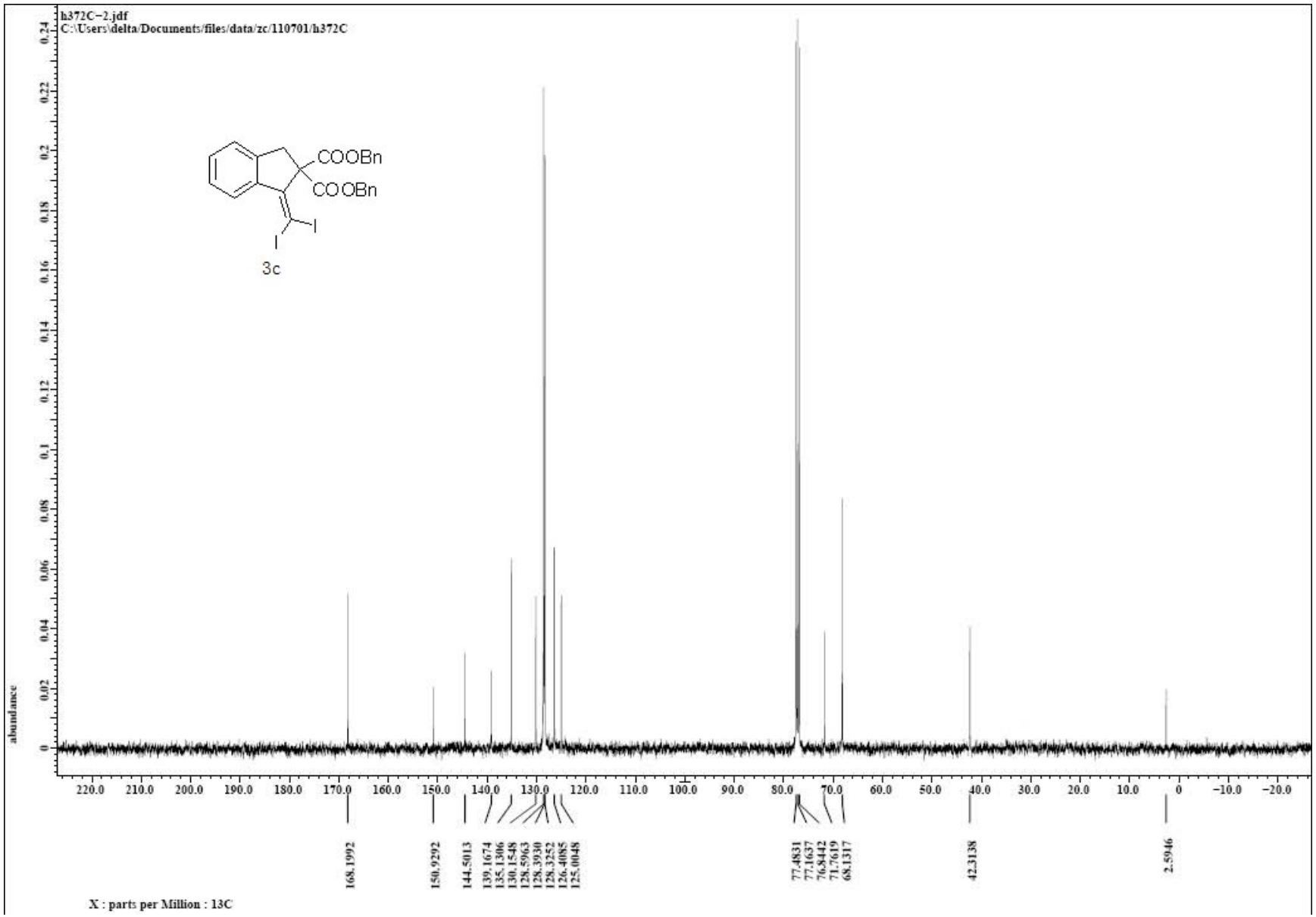
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COOBn
I
I
3c
abundance
X : parts per Million : 13C
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144.5013
139.1674
135.1306
130.1548
128.5963
128.3930
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125.0048
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77.1637
76.8442
71.7619
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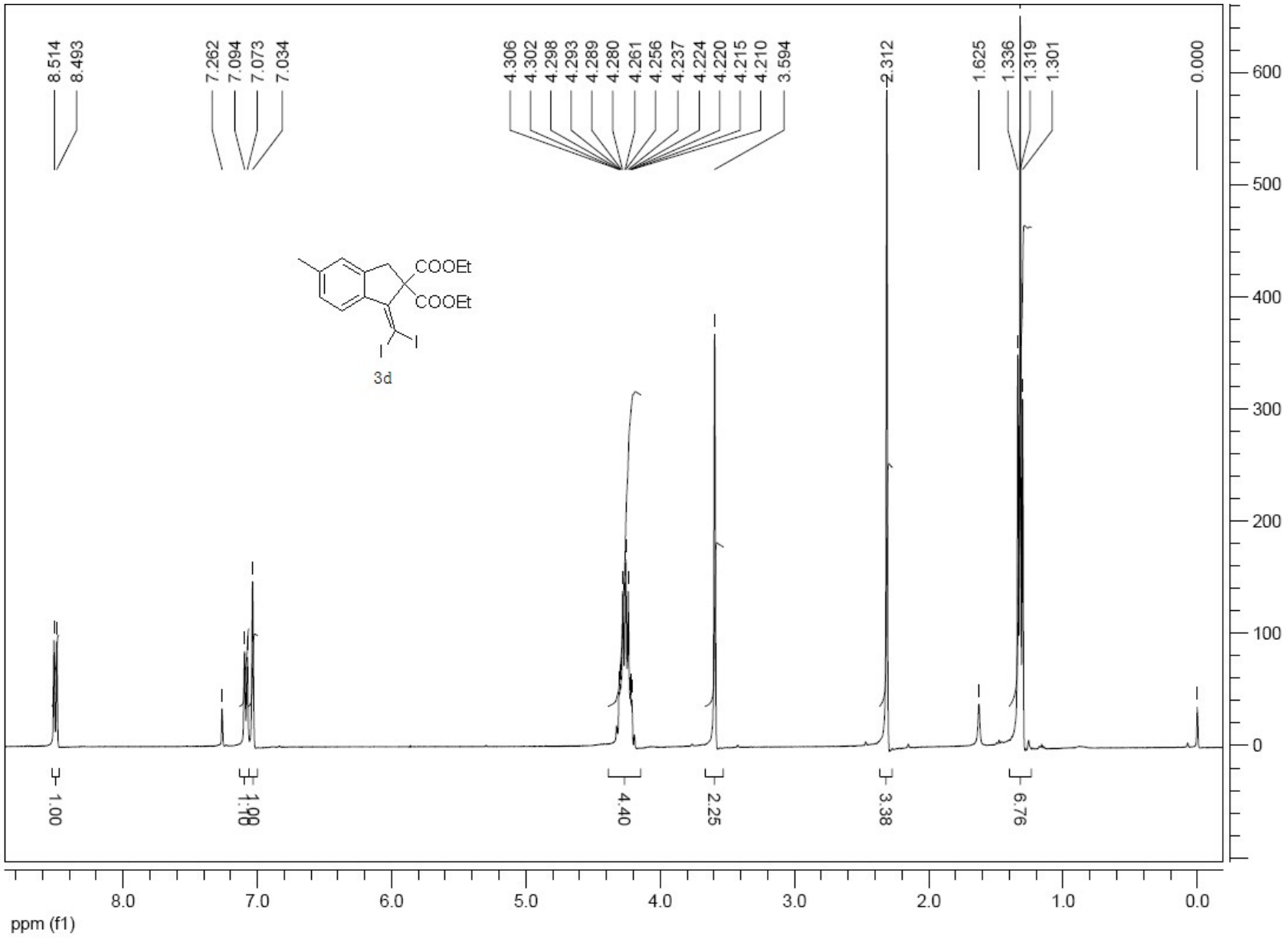
42.3138
2.5946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4.256
4.237
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4.220
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4.210
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1.336
1.319
1.301
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COOEt
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I
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400
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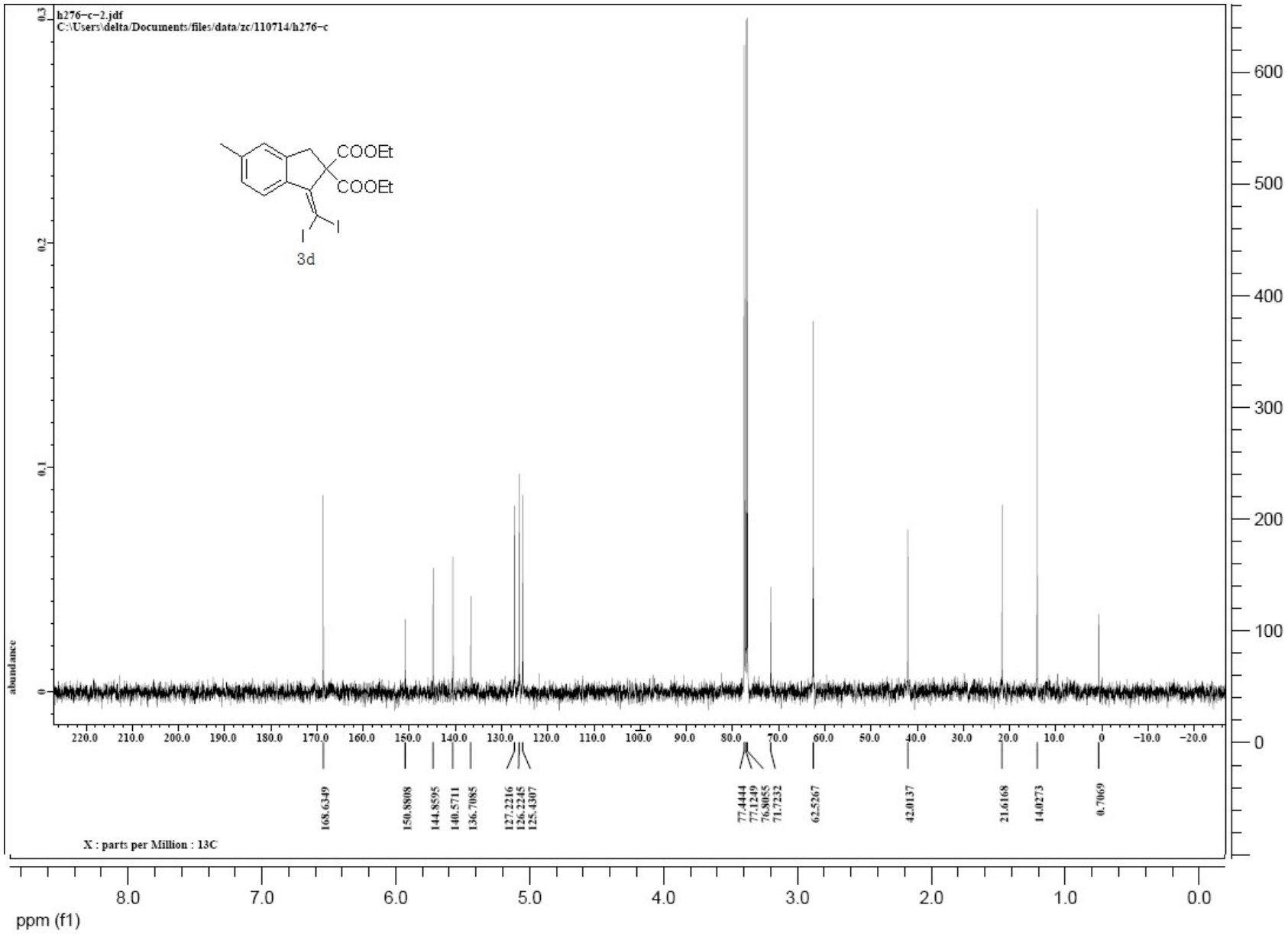
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I
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500
400
300
200
100
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
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144.8595
140.5711
136.7085
127.2216
126.2245
125.4307
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77.1249
76.8055
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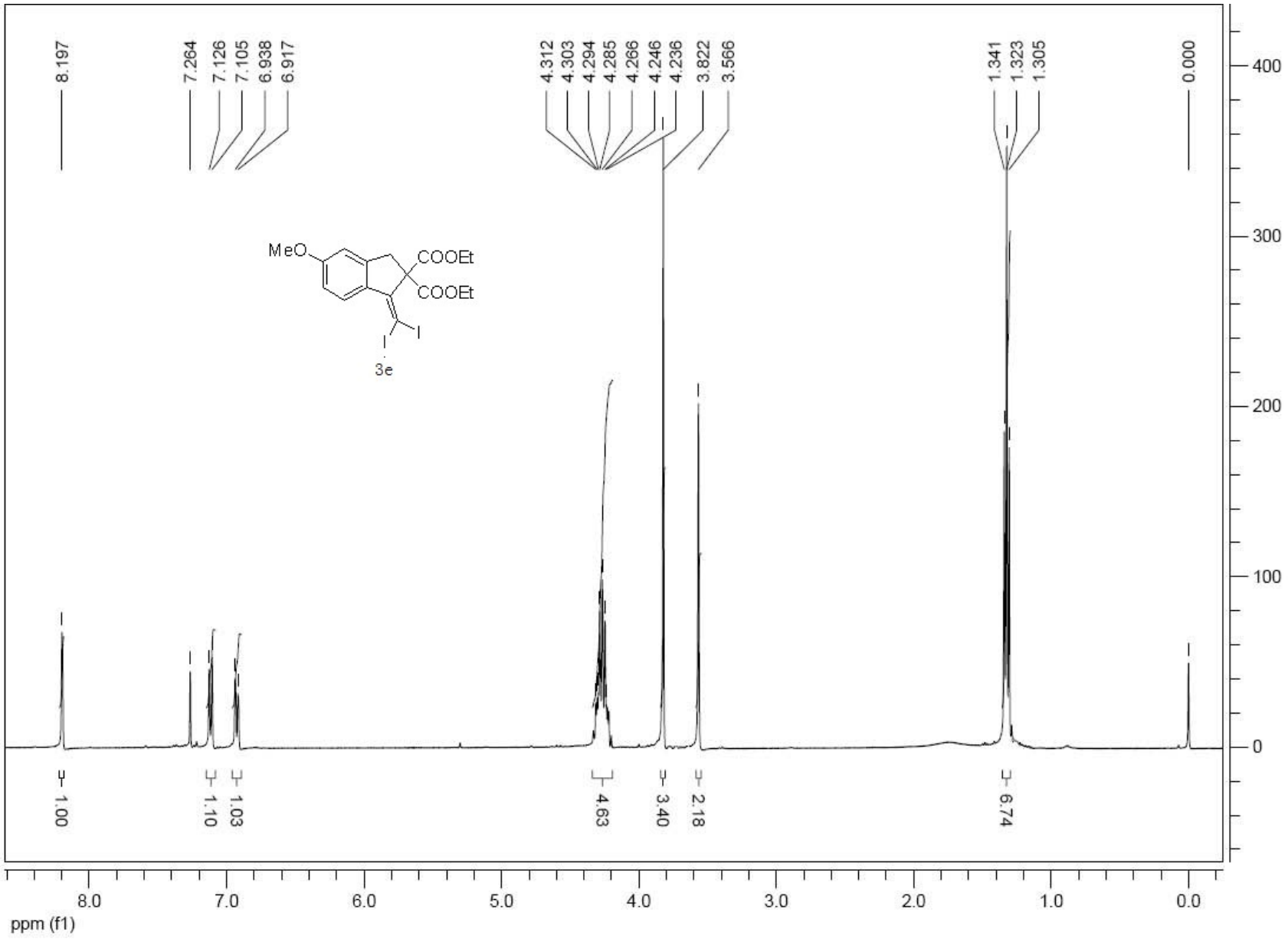
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4.236
3.822
3.566
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1.323
1.305
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COOEt
I
I
3e
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1.10
1.03
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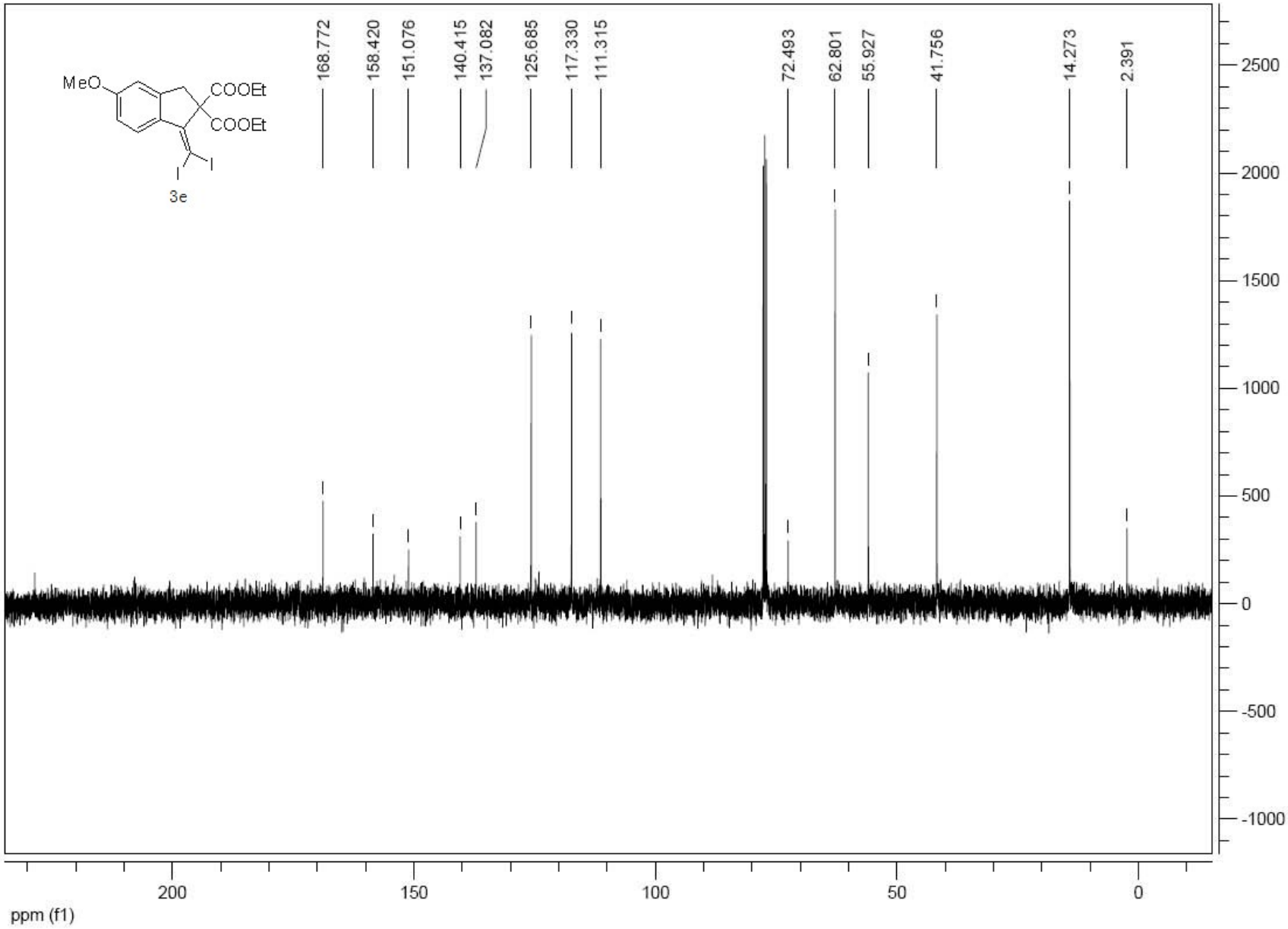
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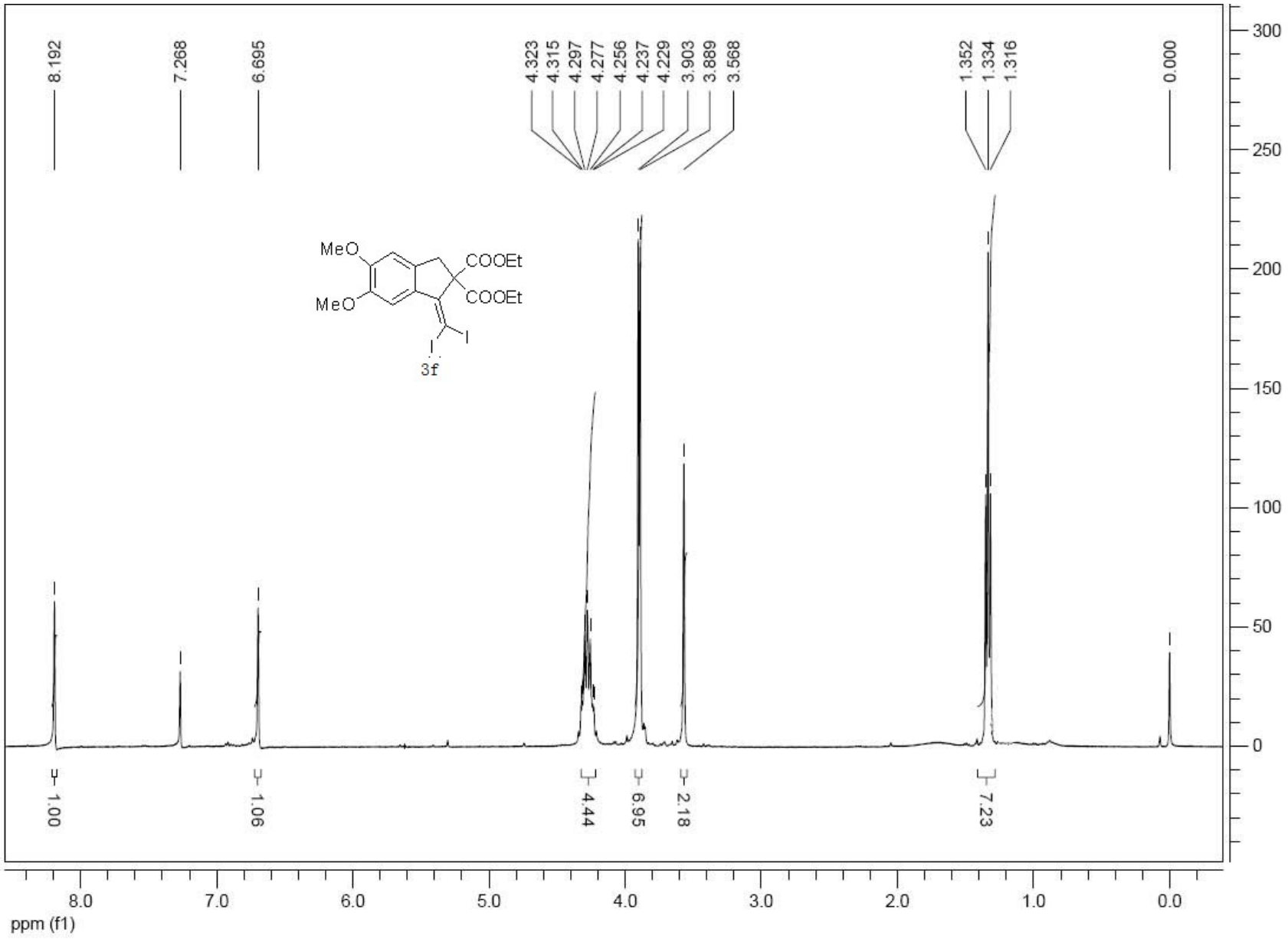
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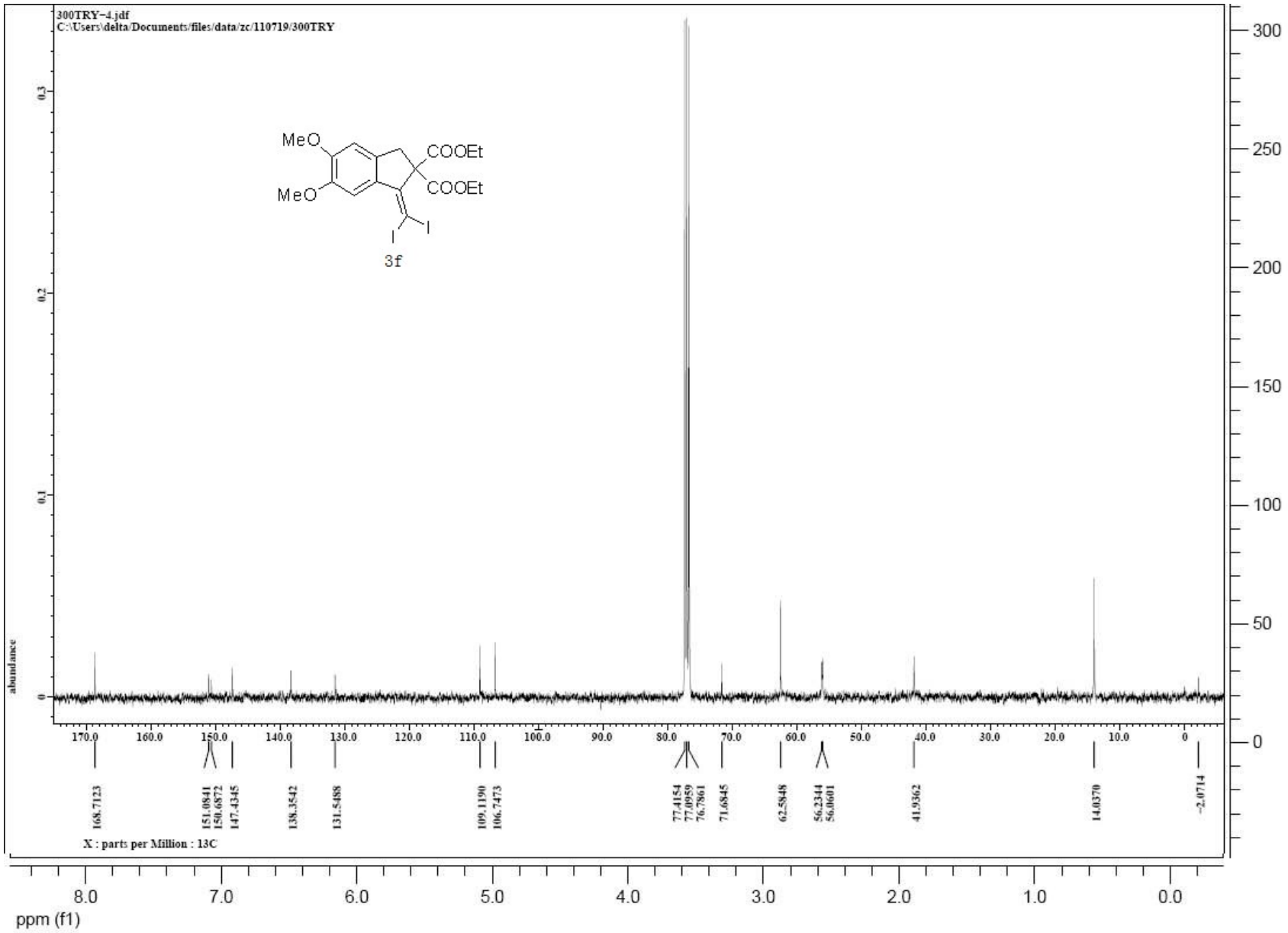
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I
I
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200
150
100
50
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147.4345
138.3542
131.5488
109.1190
106.7473
77.4154
77.0959
76.7861
71.6845
62.5848
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56.0601
41.9362
14.0370
-2.0714
X : parts per Million : 13C
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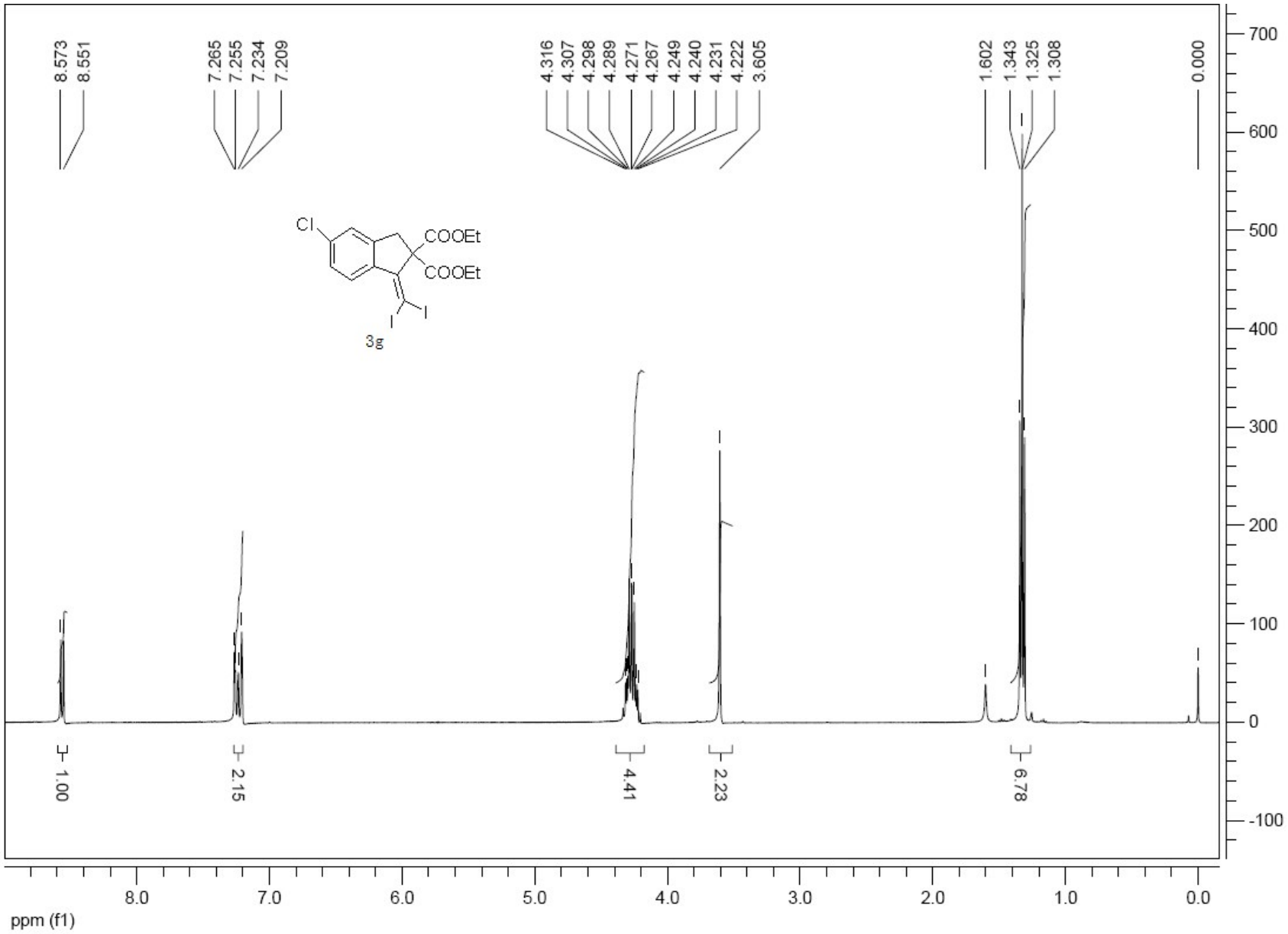
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4.240
4.231
4.222
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1.602
1.343
1.325
1.308
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Cl
COOEt
COOEt
I
I
3g
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9.78
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200
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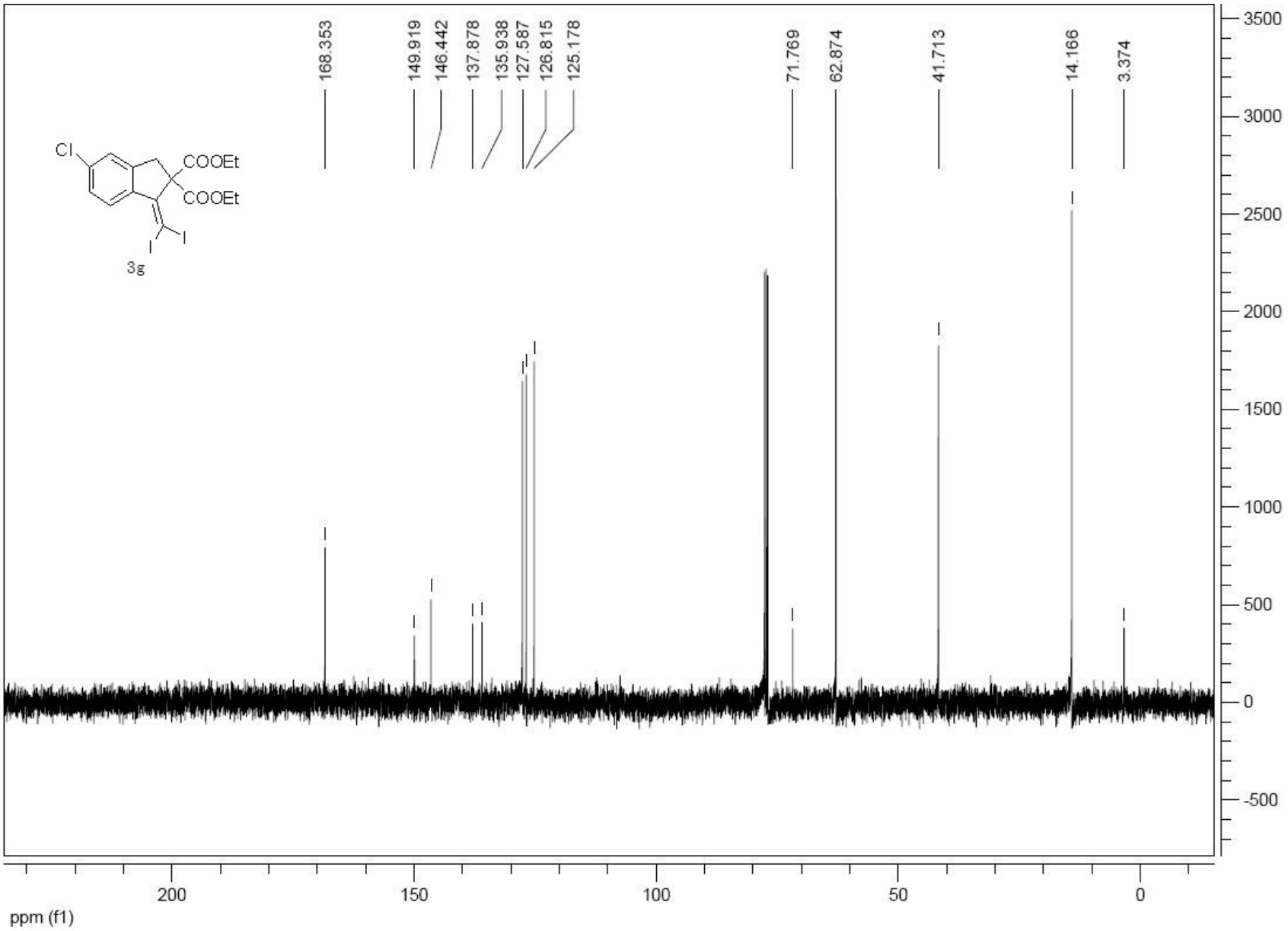
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Cl
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COOEt
I
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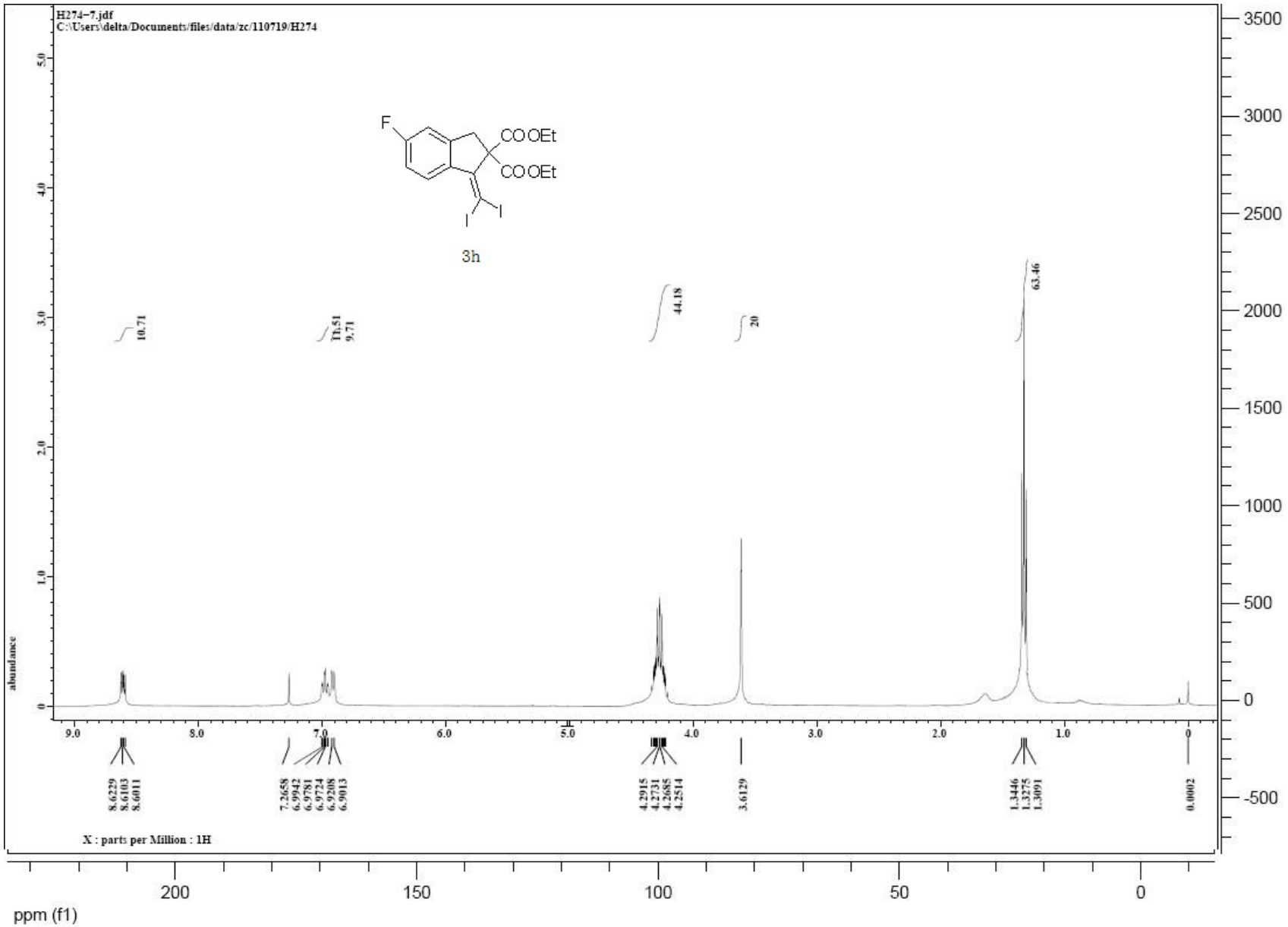
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COOEt
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I
3h
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9.71
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20
63.46
abundance
X : parts per Million : 1H
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8.6103
8.6011
7.2658
6.9942
6.9781
6.9724
6.9208
6.9013
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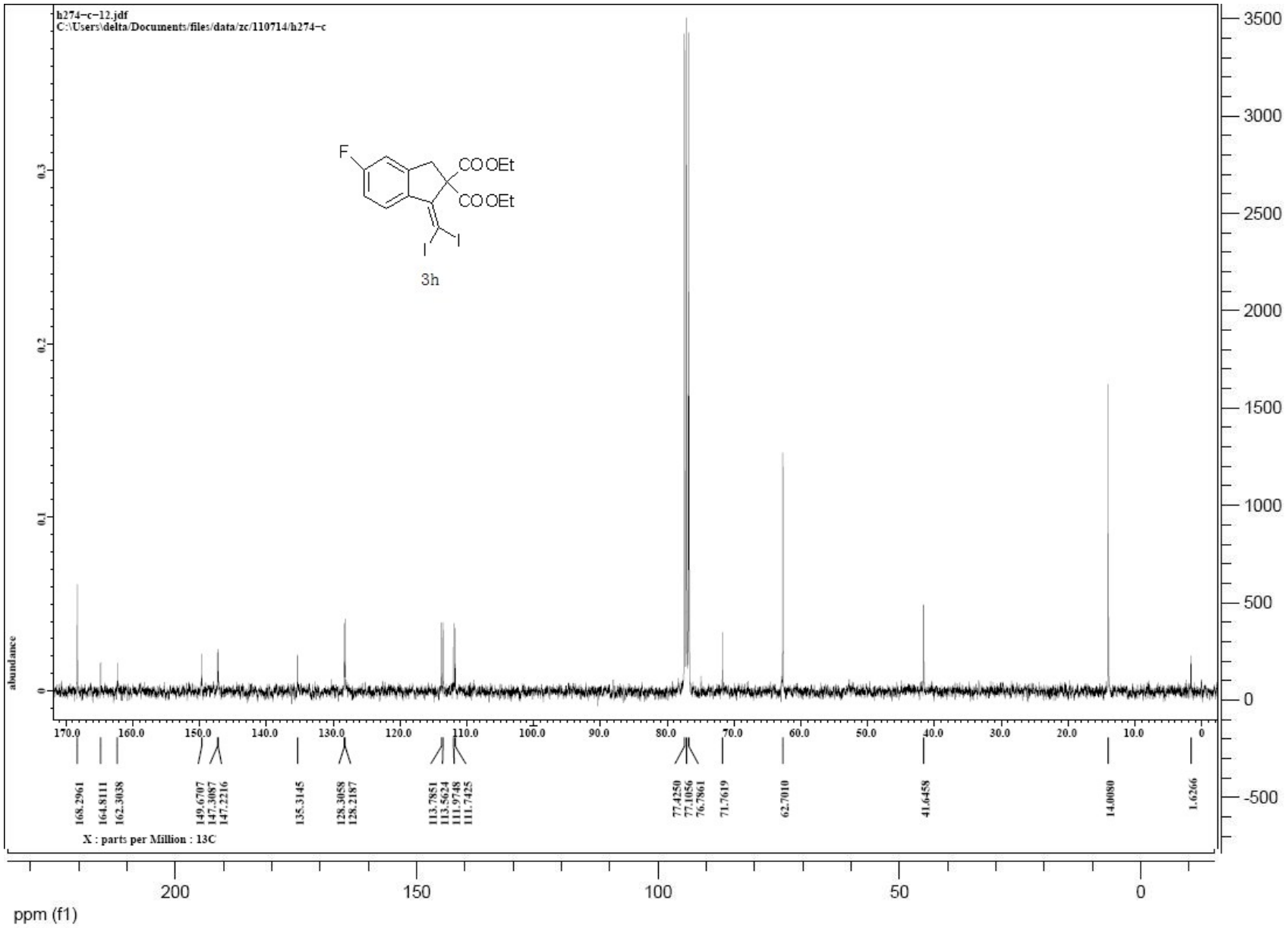
ppm (f1)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COOEt
I
I
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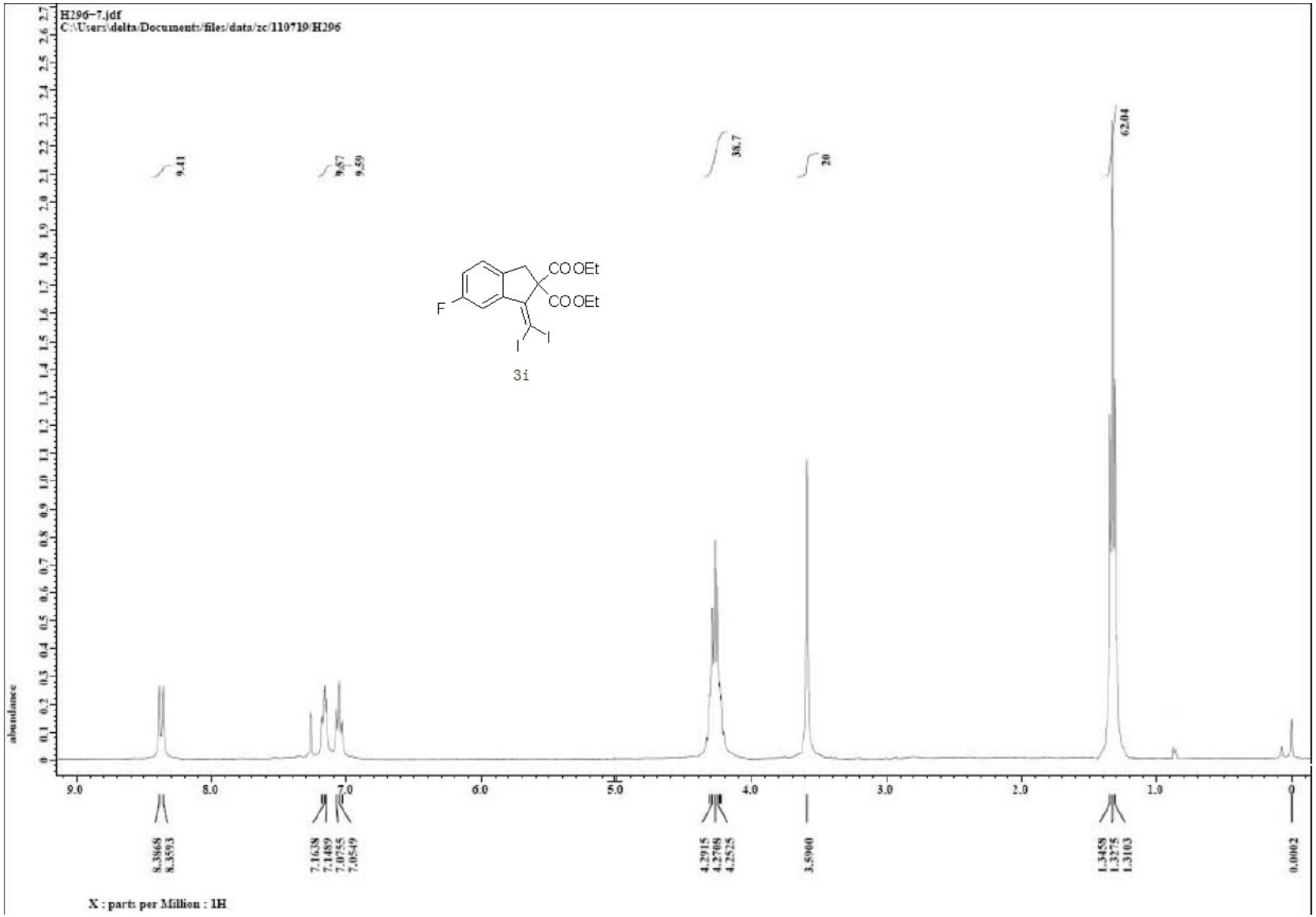
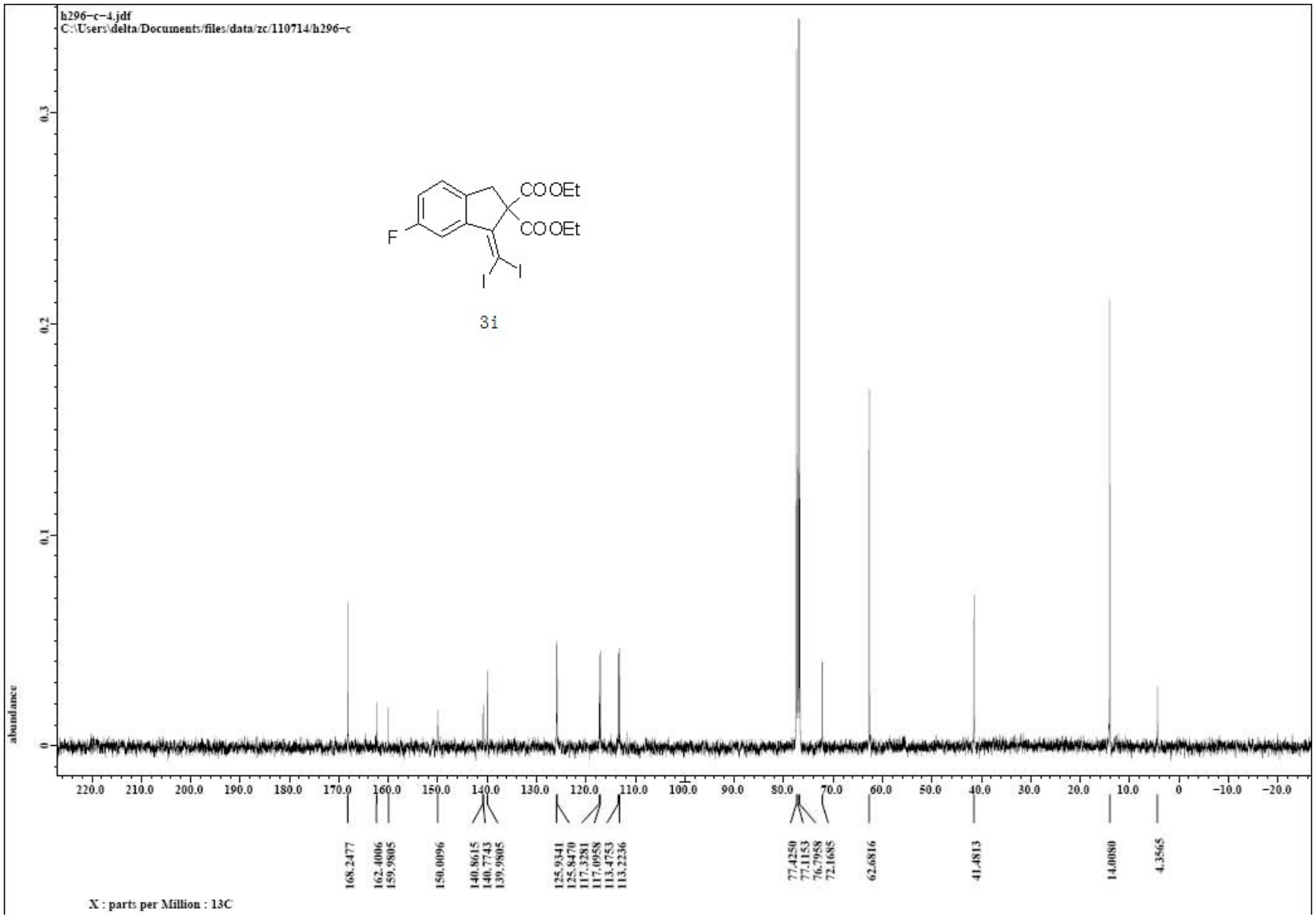
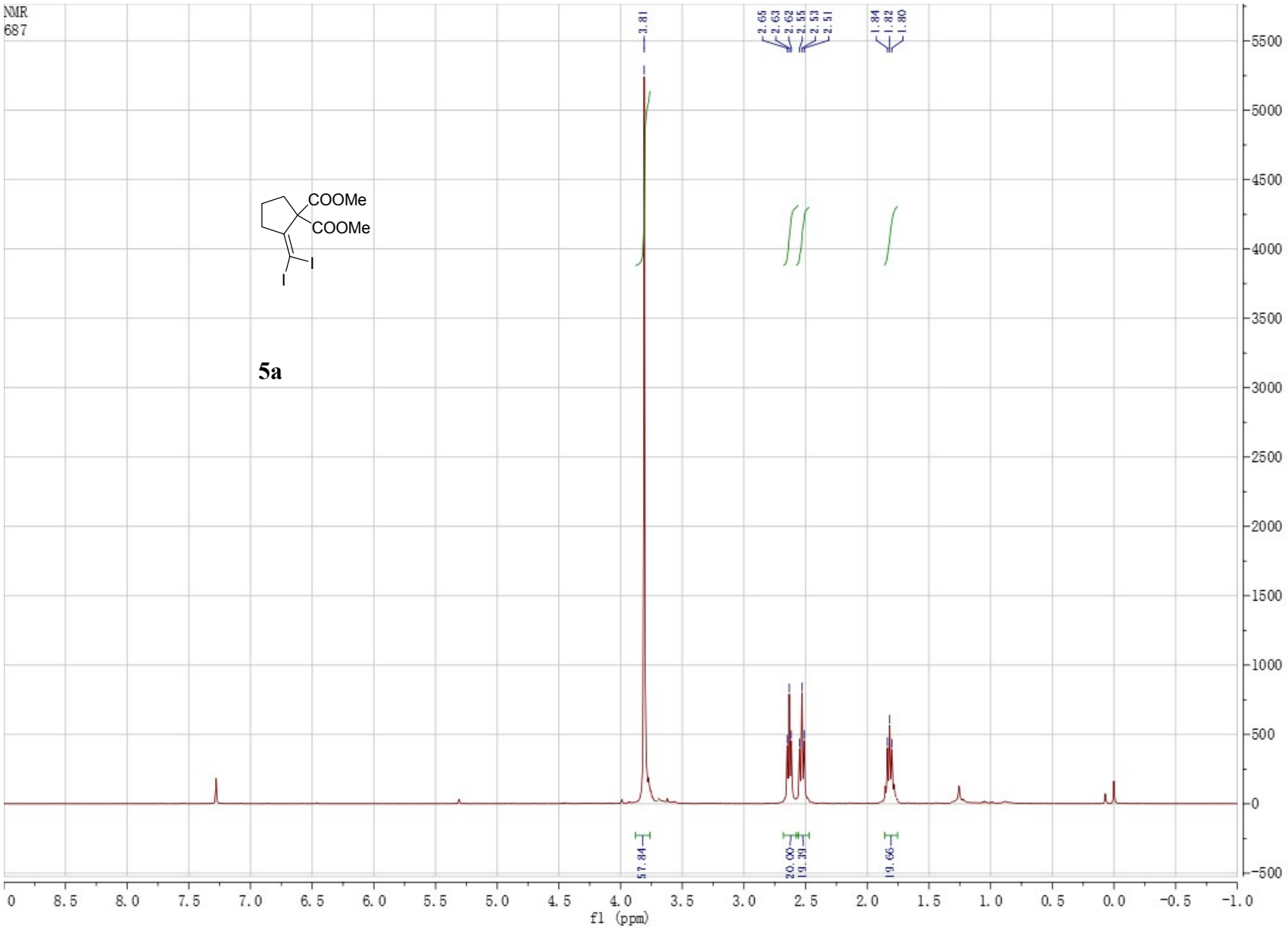
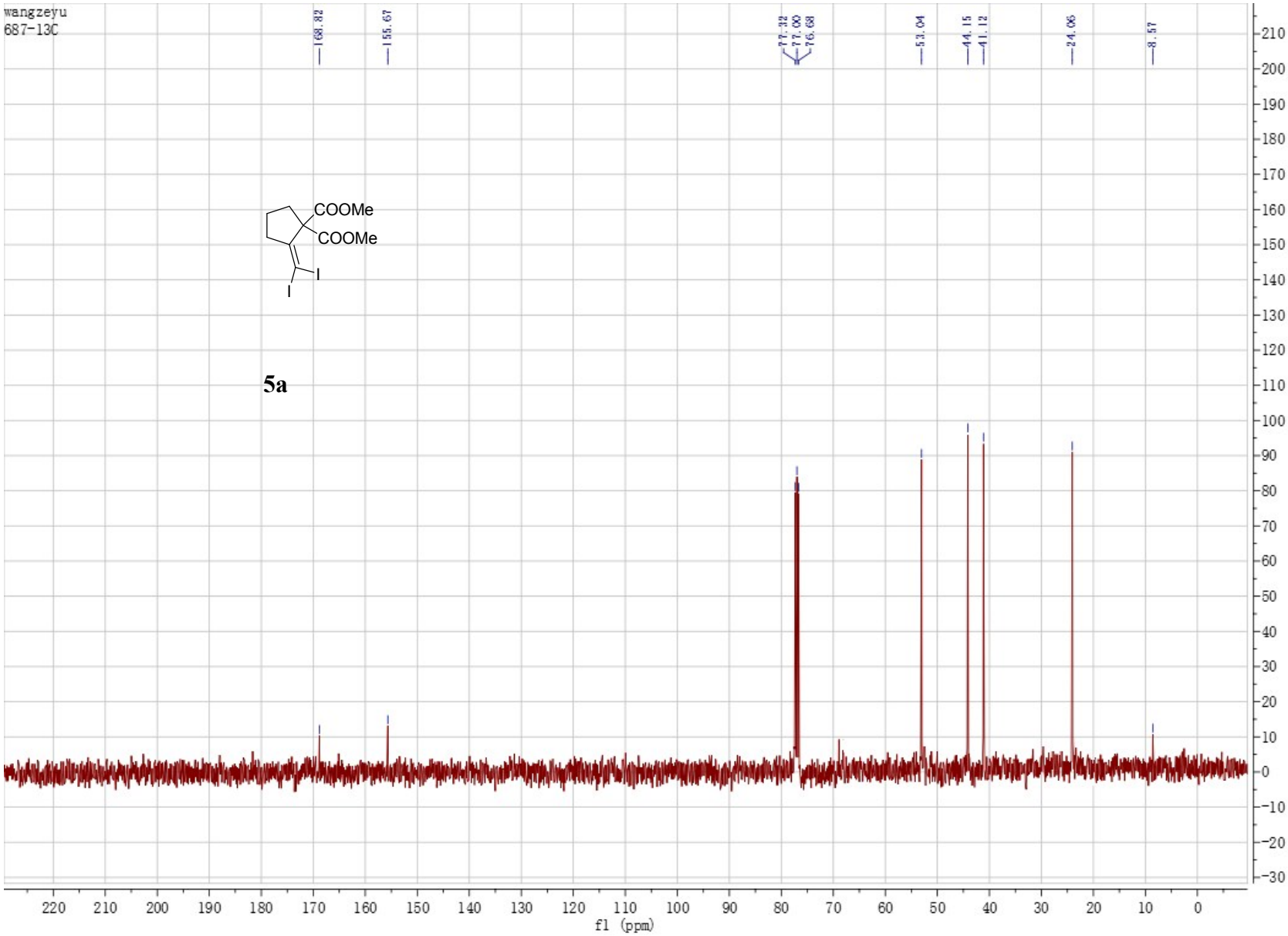
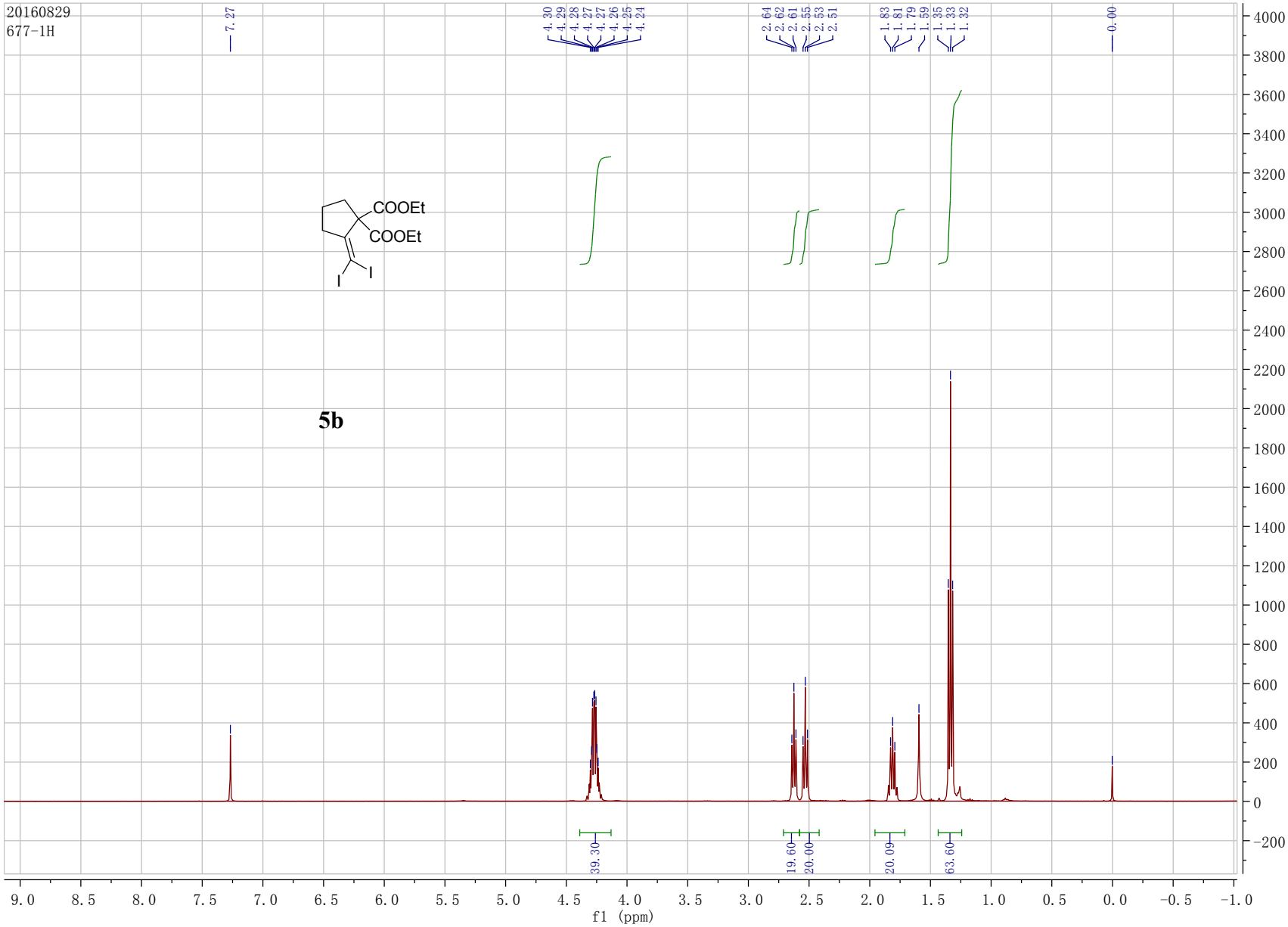
abundance
0.3
0.2
0.1
0
3500
3000
2500
2000
1500
1000
500
0
-500
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.2961
164.8111
162.3038
149.6707
147.3087
147.2216
135.3145
128.3058
128.2187
113.7851
113.5624
111.9748
111.7425
77.4250
77.1056
76.7861
71.7619
62.7010
41.6458
14.0080
1.6266
X : parts per Million : 13C
200
150
100
50
0
ppm (f1)

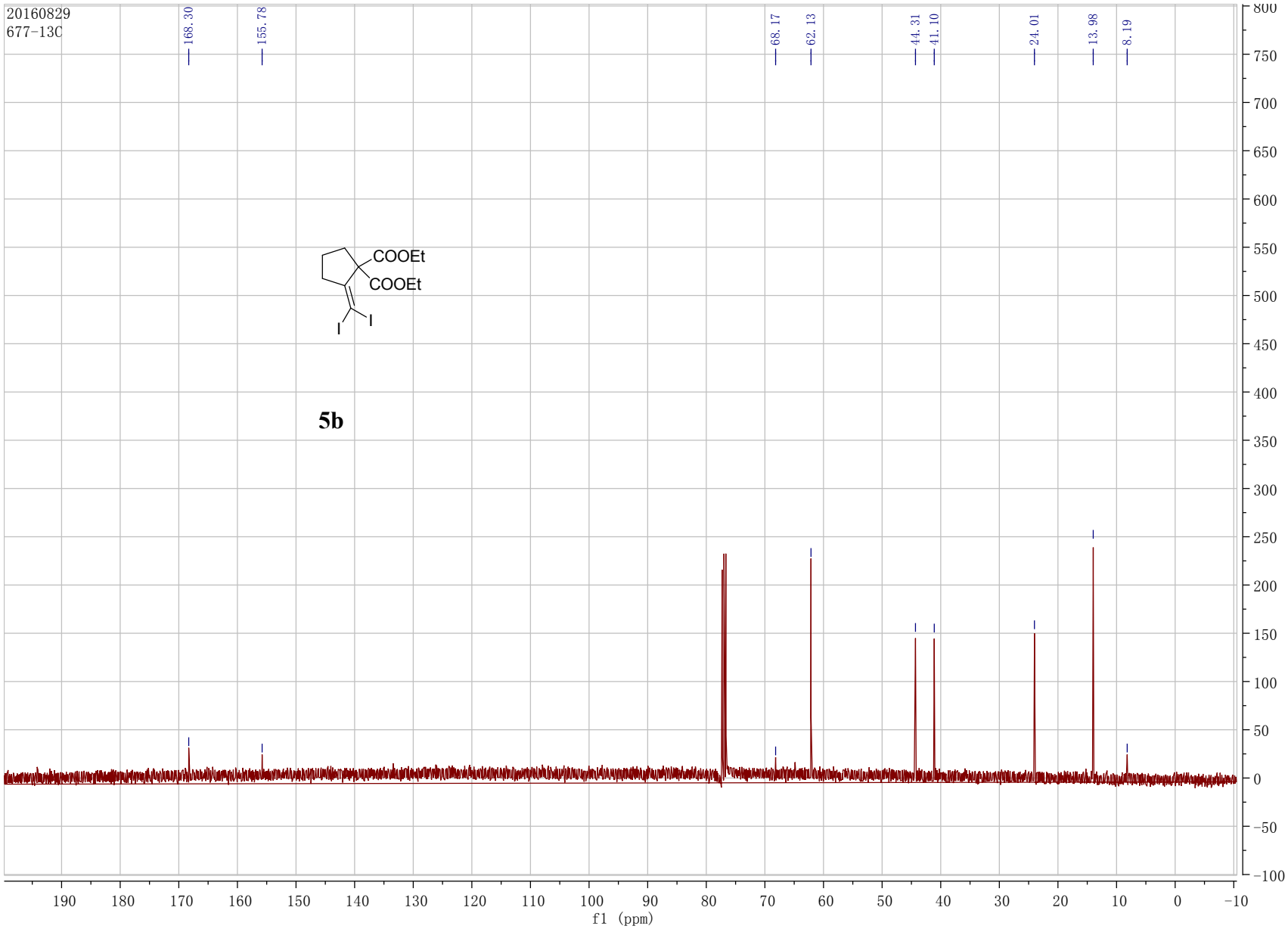

H296-7.jdf
C:\Users\delta\Documents\files\data\zc\110719\H296
abundance
9.41
9.57
9.59
38.7
20
62.04
CO OEt
CO OEt
F
I
I
3i
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.3868
8.3593
7.1638
7.1489
7.0755
7.0549
4.2915
4.2708
4.2525
3.5900
1.3458
1.3275
1.3103
0.0002
X : parts per Million : 1H

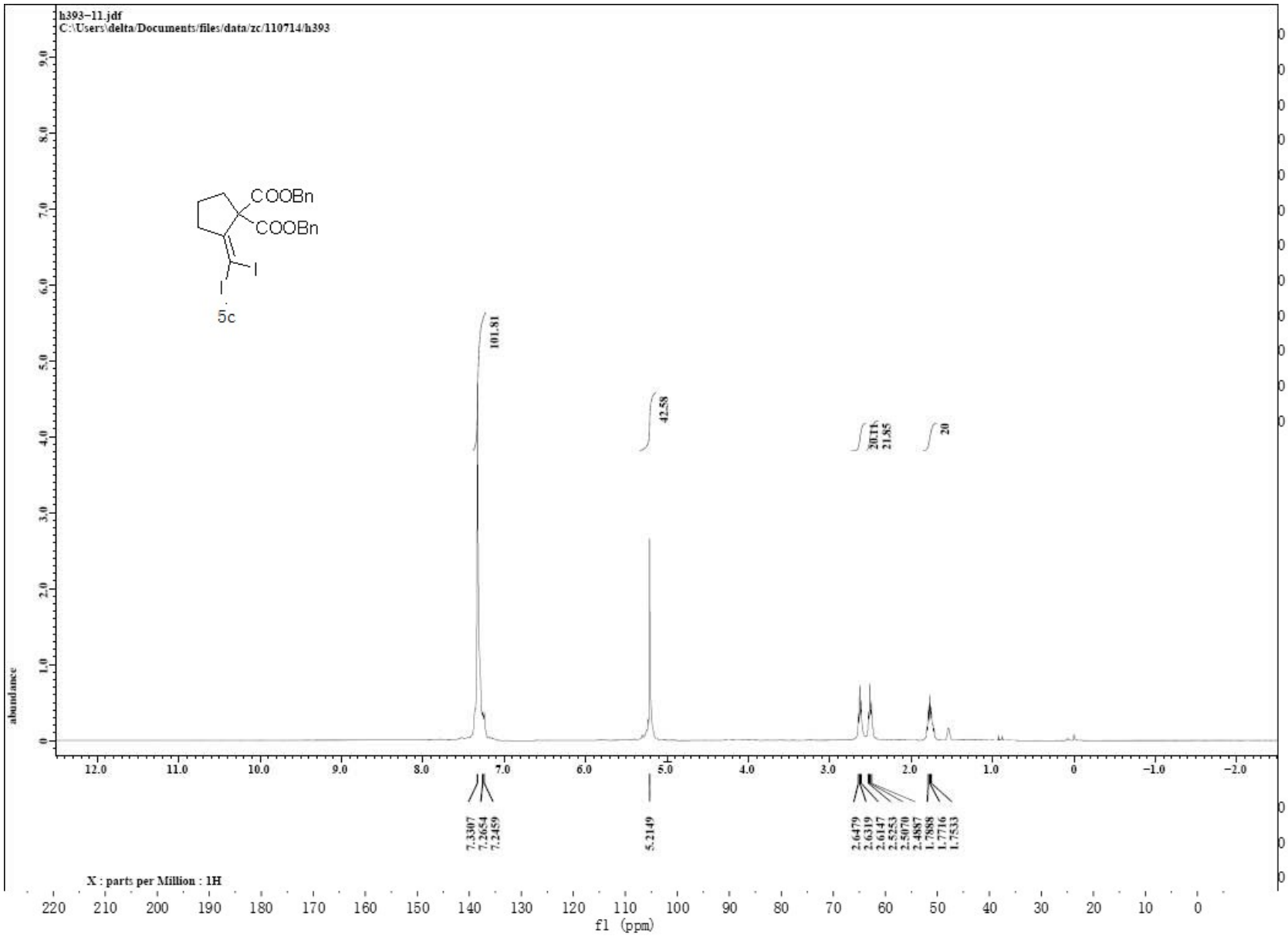

h296-c-4.jdf
C:\Users\delta/Documents/files/data/zc/110714/h296-c
COOEt
COOEt
F
I
I
3i
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
168.2477
162.4006
159.9805
150.0096
140.8615
140.7743
139.9805
125.9341
125.8470
117.3281
117.0958
113.4753
113.2236
77.4250
77.1153
76.7958
72.1685
62.6816
41.4813
14.0080
4.3565
X : parts per Million : 13C

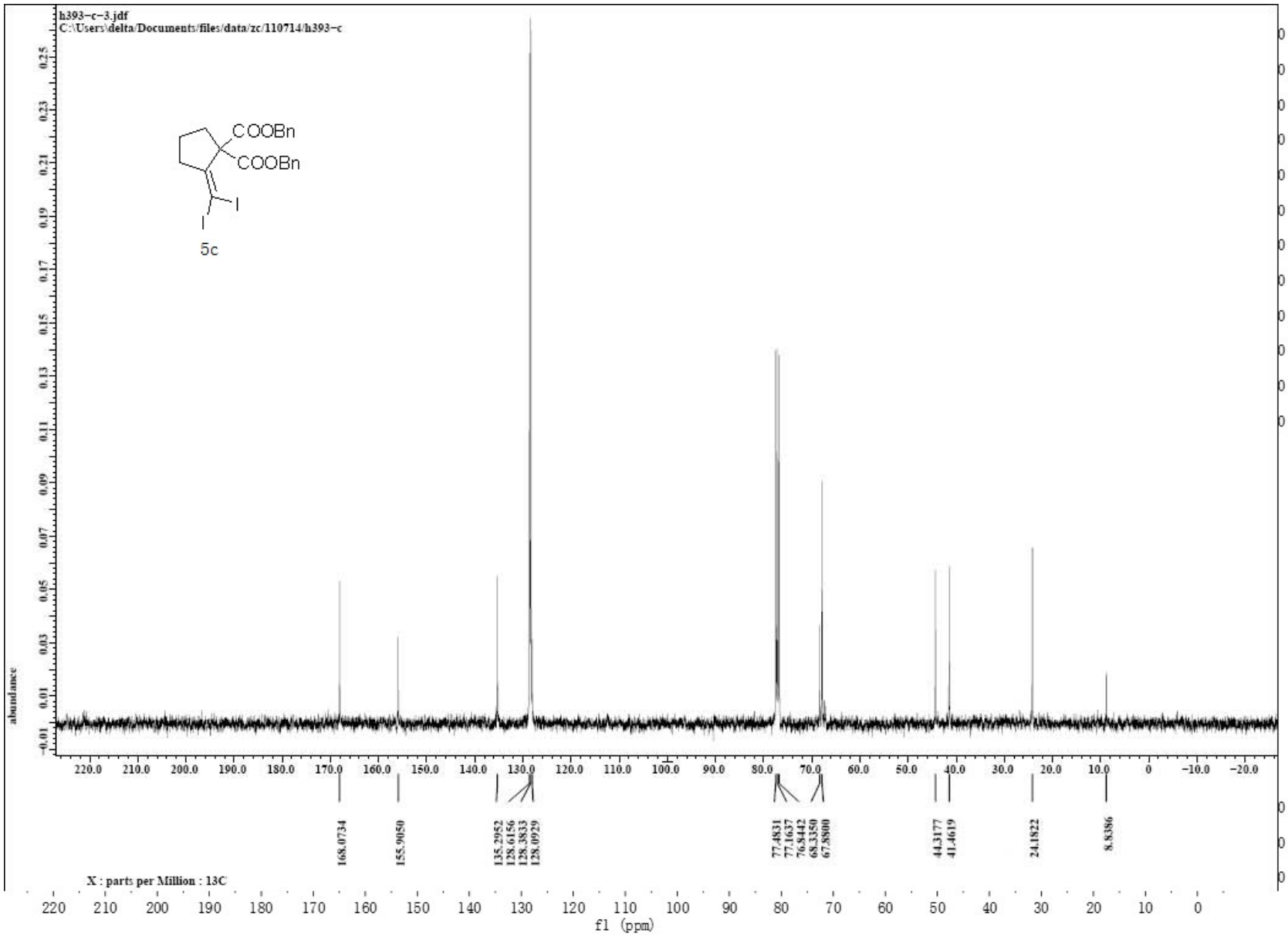

NMR
687
COOMe
COOMe
I
I
5a
3.81
2.65
2.63
2.62
2.55
2.53
2.51
1.84
1.82
1.80
57.84
20.00
19.39
19.66
f1 (ppm)

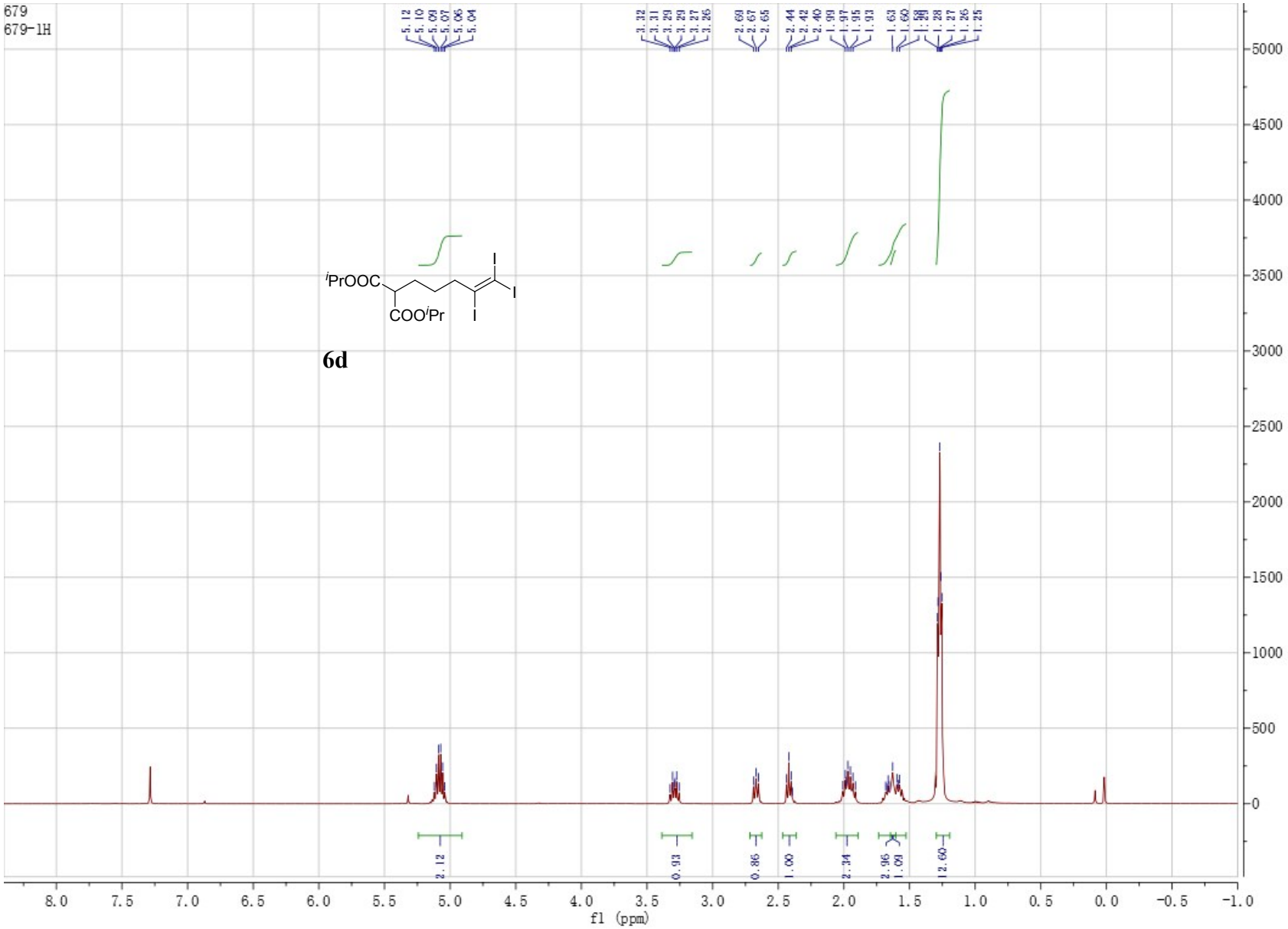

wangzeyu
687-13C
168.82
155.67
77.32
77.00
76.68
53.04
44.15
41.12
24.06
8.57
COOMe
COOMe
I
I
5a
f1 (ppm)

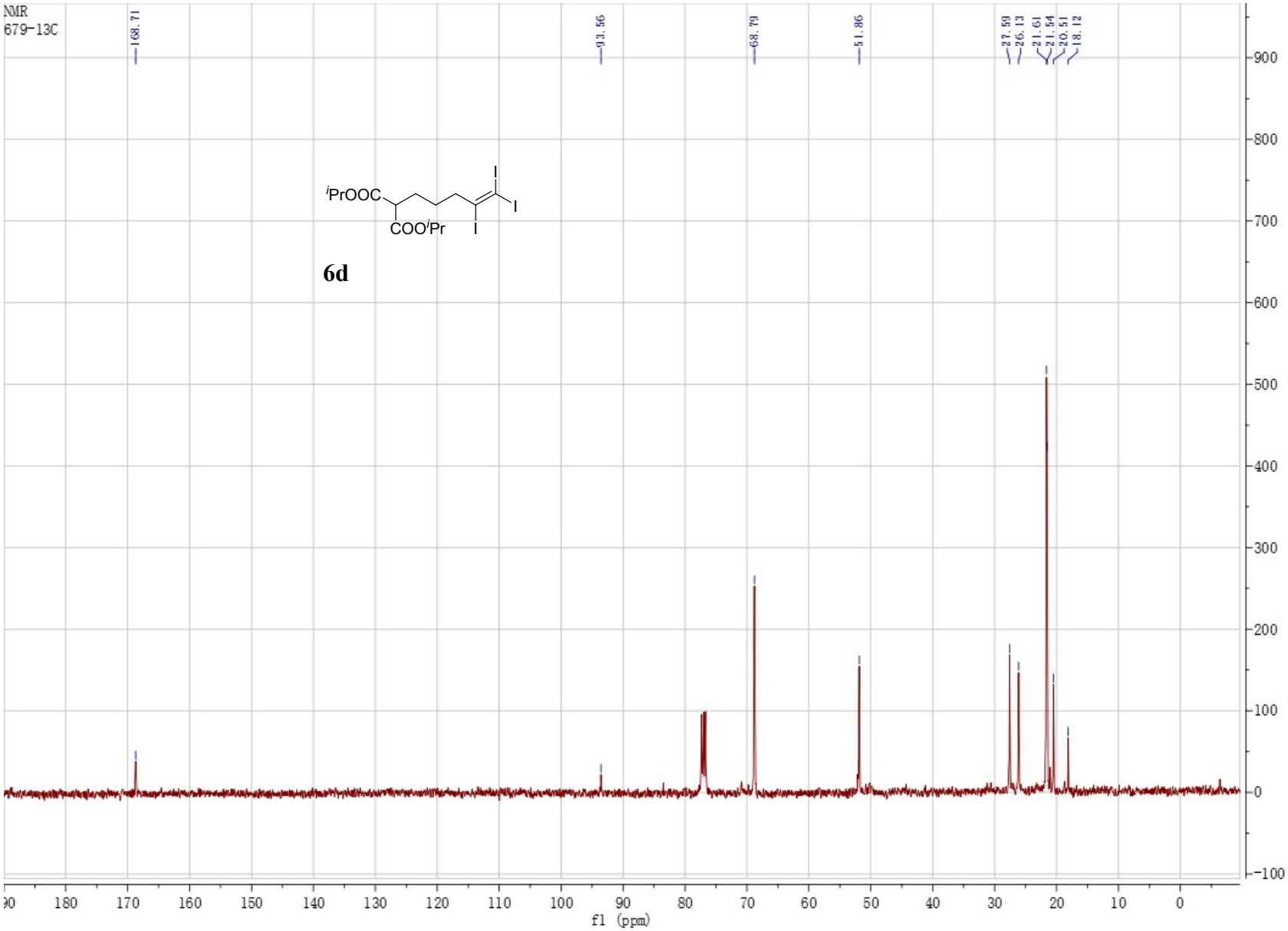

20160829
677-1H
7.27
4.30
4.29
4.28
4.27
4.27
4.26
4.25
4.24
2.64
2.62
2.61
2.55
2.53
2.51
1.83
1.81
1.79
1.59
1.35
1.33
1.32
0.00
COOEt
COOEt
I
I
5b
39.30
19.60
20.00
20.09
63.60
f1 (ppm)

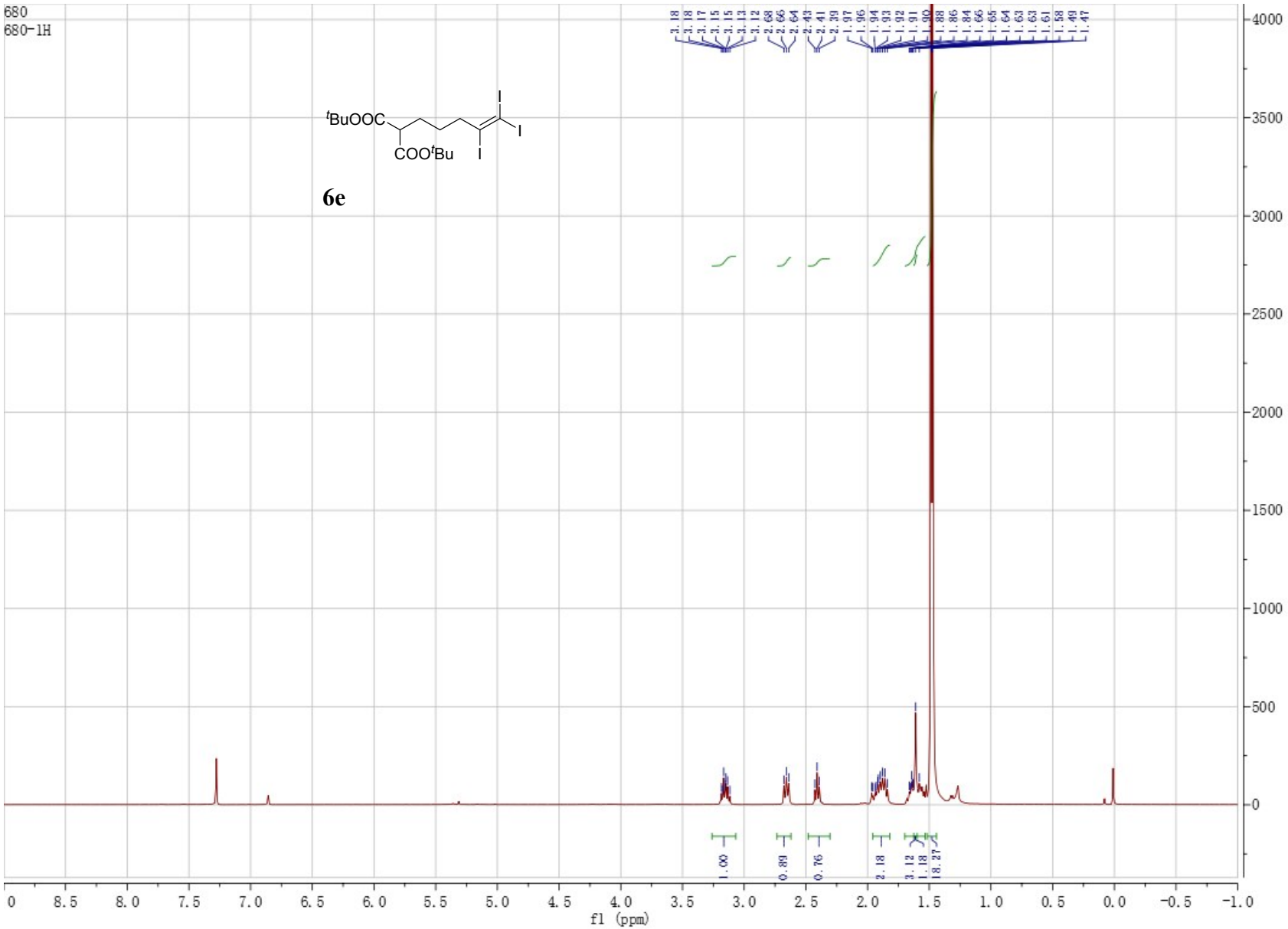

20160829
677-13C
168.30
155.78
68.17
62.13
44.31
41.10
24.01
13.98
8.19
COOEt
COOEt
I
I
5b
f1 (ppm)

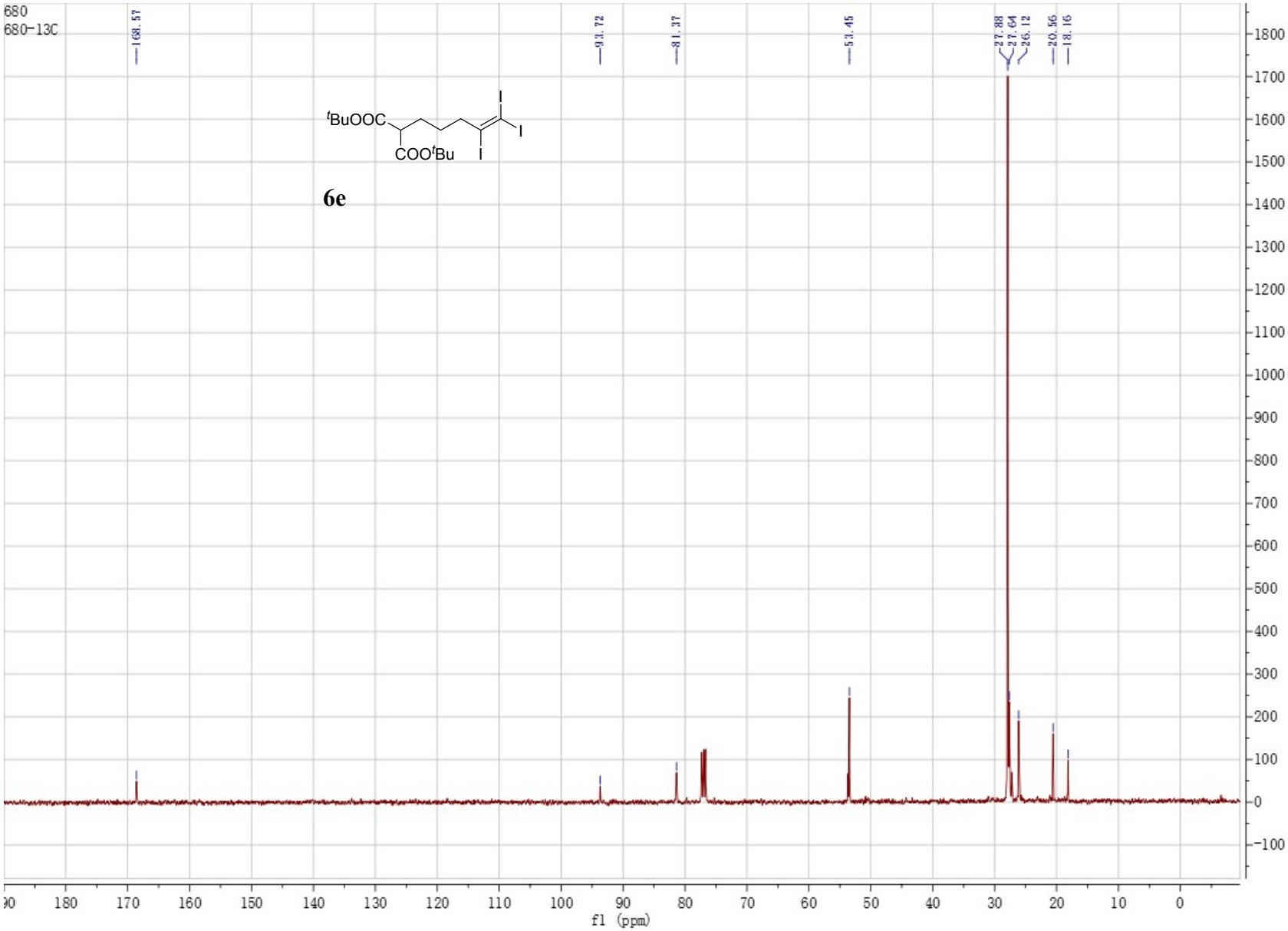

h393-11.jdf
C:\Users\delta\Documents\files\data\zc\110714\h393
COOBn
COOBn
I
I
5c
101.81
42.58
20.11
21.85
20
7.3307
7.2654
7.2459
5.2149
2.6479
2.6319
2.6147
2.5253
2.5070
2.4887
1.7888
1.7716
1.7533
abundance
X : parts per Million : 1H
f1 (ppm)

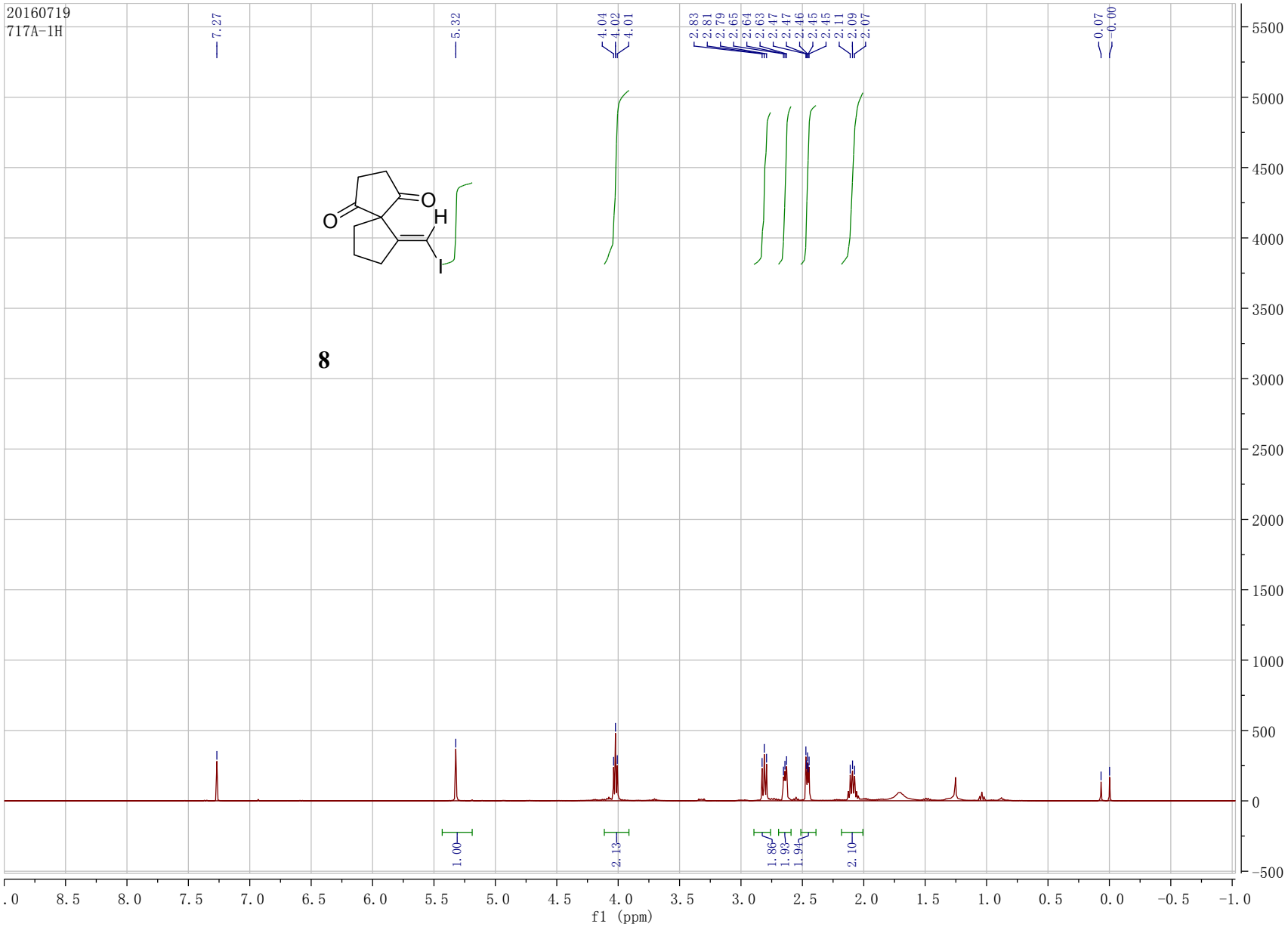

h393-c-3.jdf
C:\Users\delta\Documents\files\data\zc\110714\h393-c
COOBn
COOBn
I
I
5c
abundance
168.0734
155.9050
135.2952
128.6156
128.3833
128.0929
77.4831
77.1637
76.8442
68.3350
67.8800
44.3177
41.4619
24.1822
8.8386
X : parts per Million : 13C
f1 (ppm)

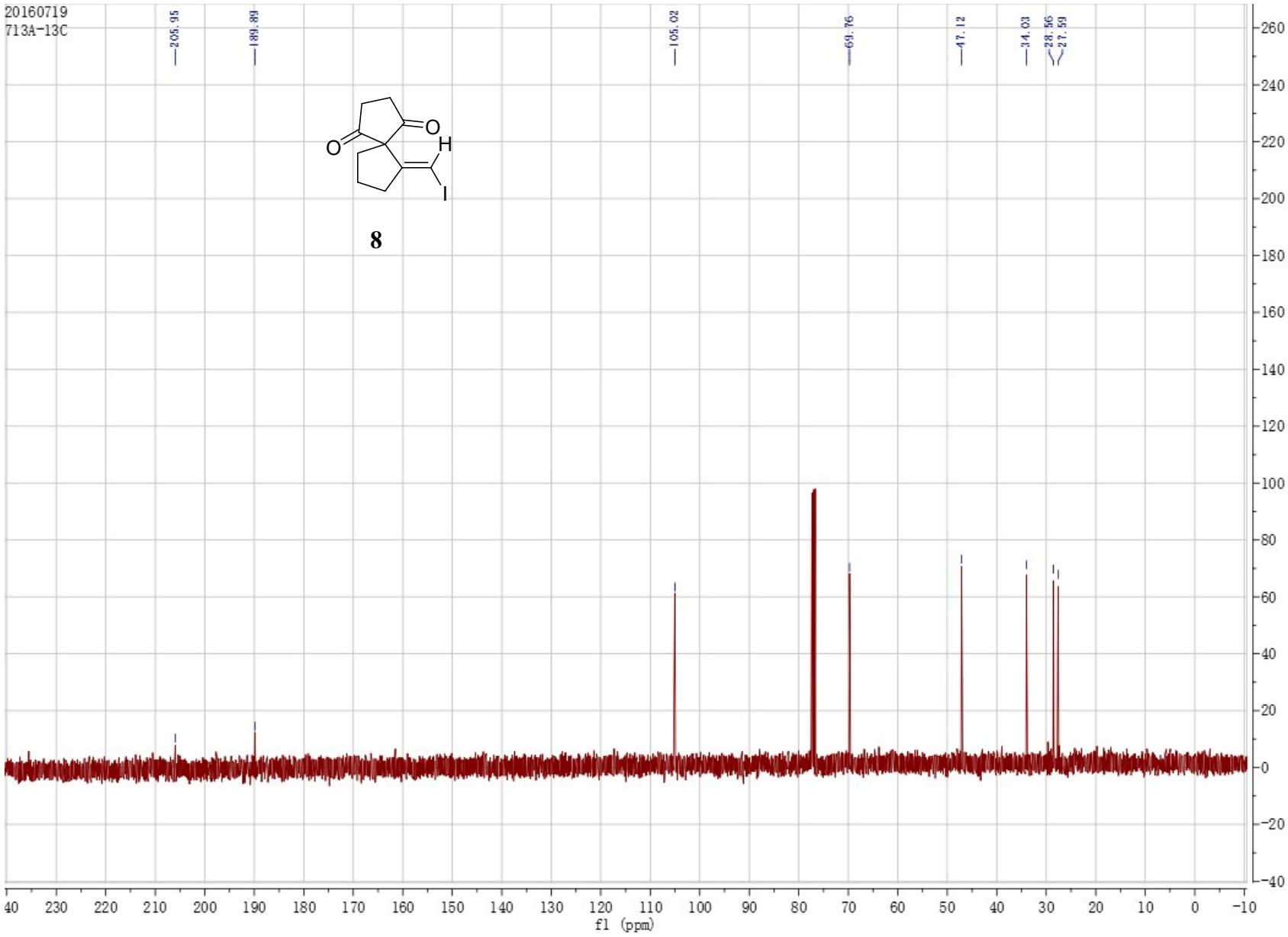

679
679-1H
5.12
5.10
5.09
5.07
5.06
5.04
3.32
3.31
3.29
3.29
3.27
3.26
2.69
2.67
2.65
2.44
2.42
2.40
1.99
1.97
1.95
1.93
1.63
1.60
1.28
1.27
1.26
1.25
iPrOOC
COOiPr
I
I
I
6d
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2.12
0.93
0.86
1.00
2.34
2.96
1.09
12.60
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

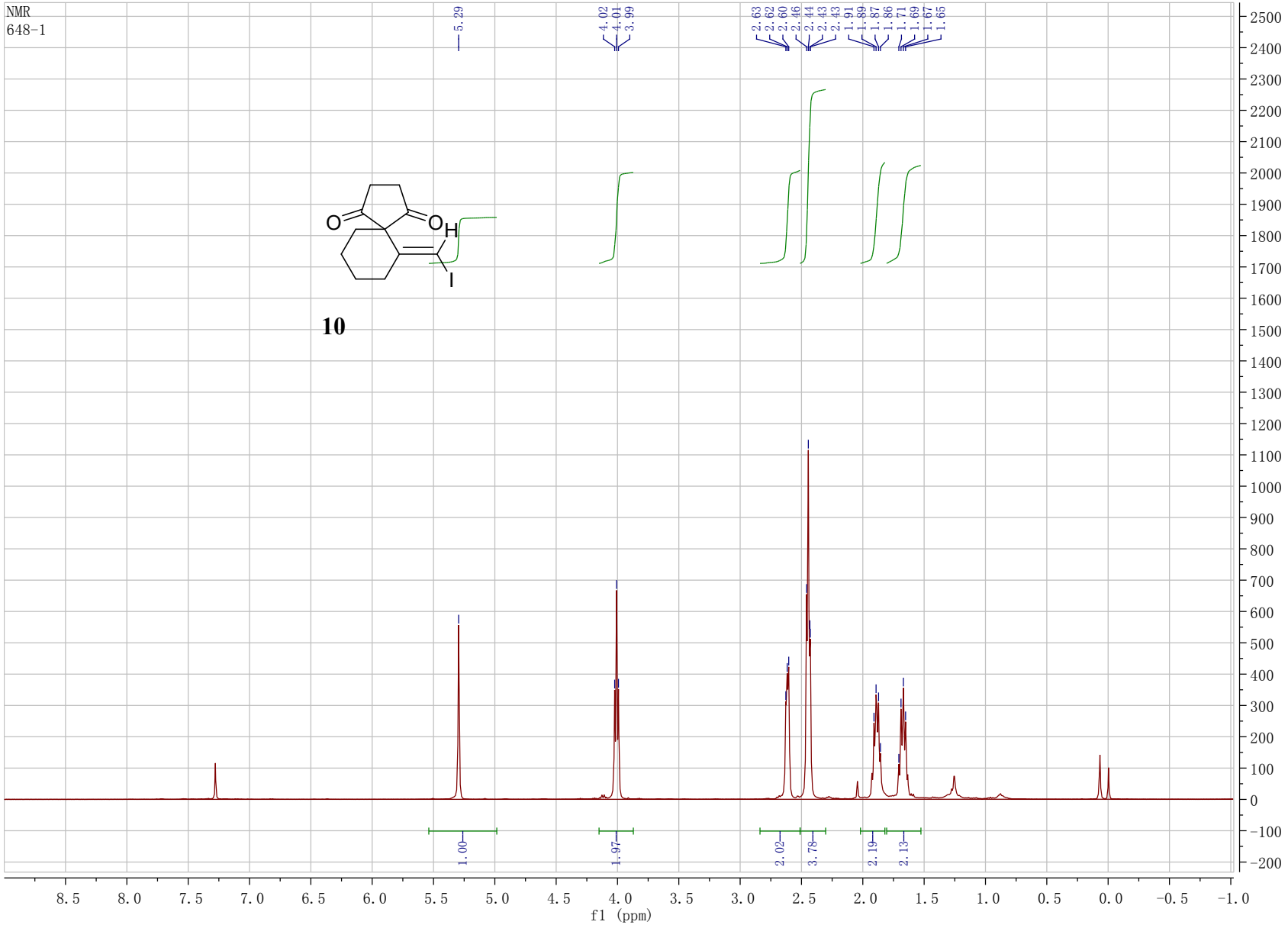

NMR
679-13C
168.71
93.56
68.79
51.86
27.59
26.13
21.61
21.54
20.51
18.12
iPrOOC
COOiPr
I
I
I
6d
900
800
700
600
500
400
300
200
100
0
-100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

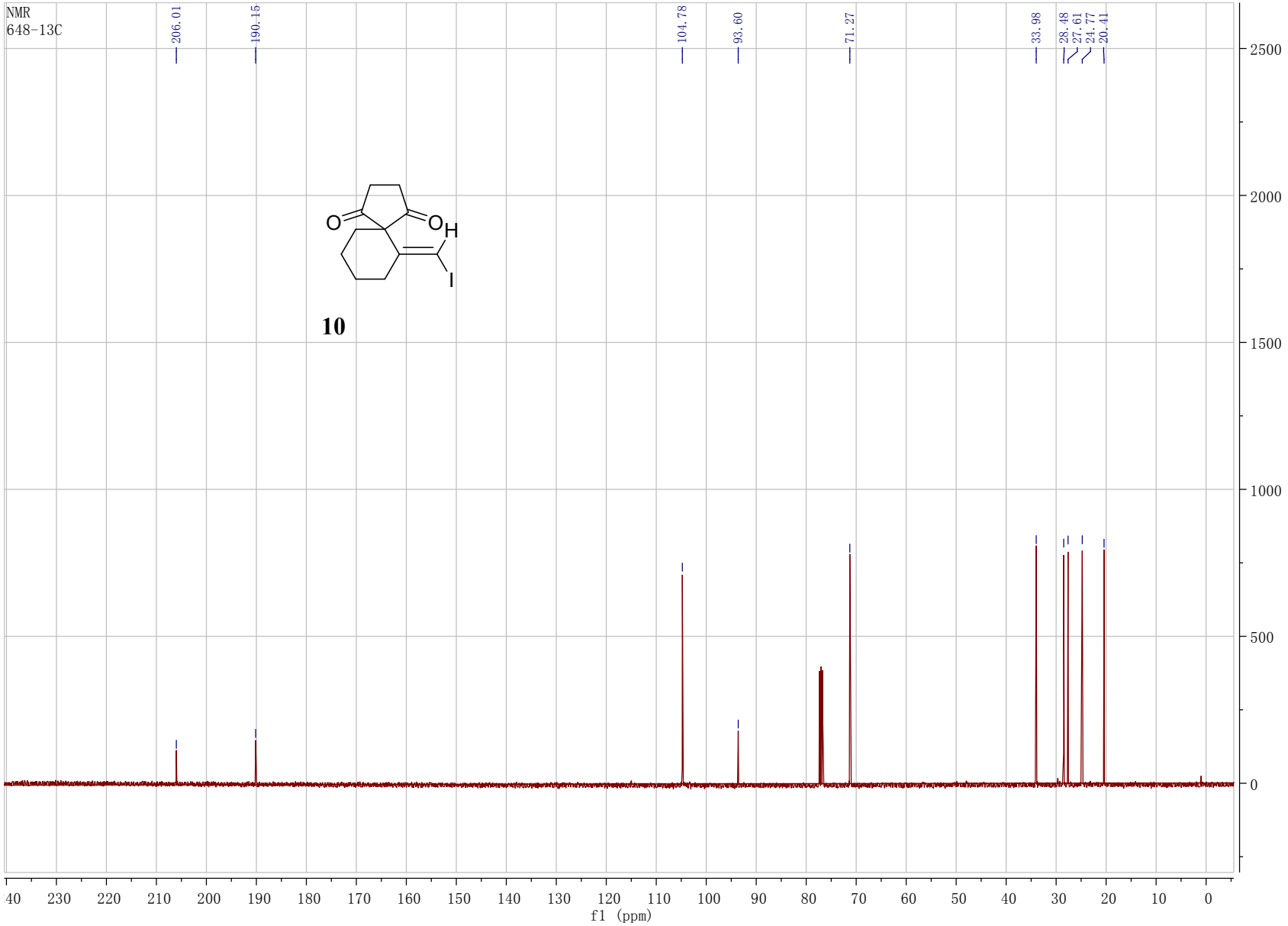

680
680-1H
tBuOOC
COOtBu
I
I
I
6e
fl (ppm)

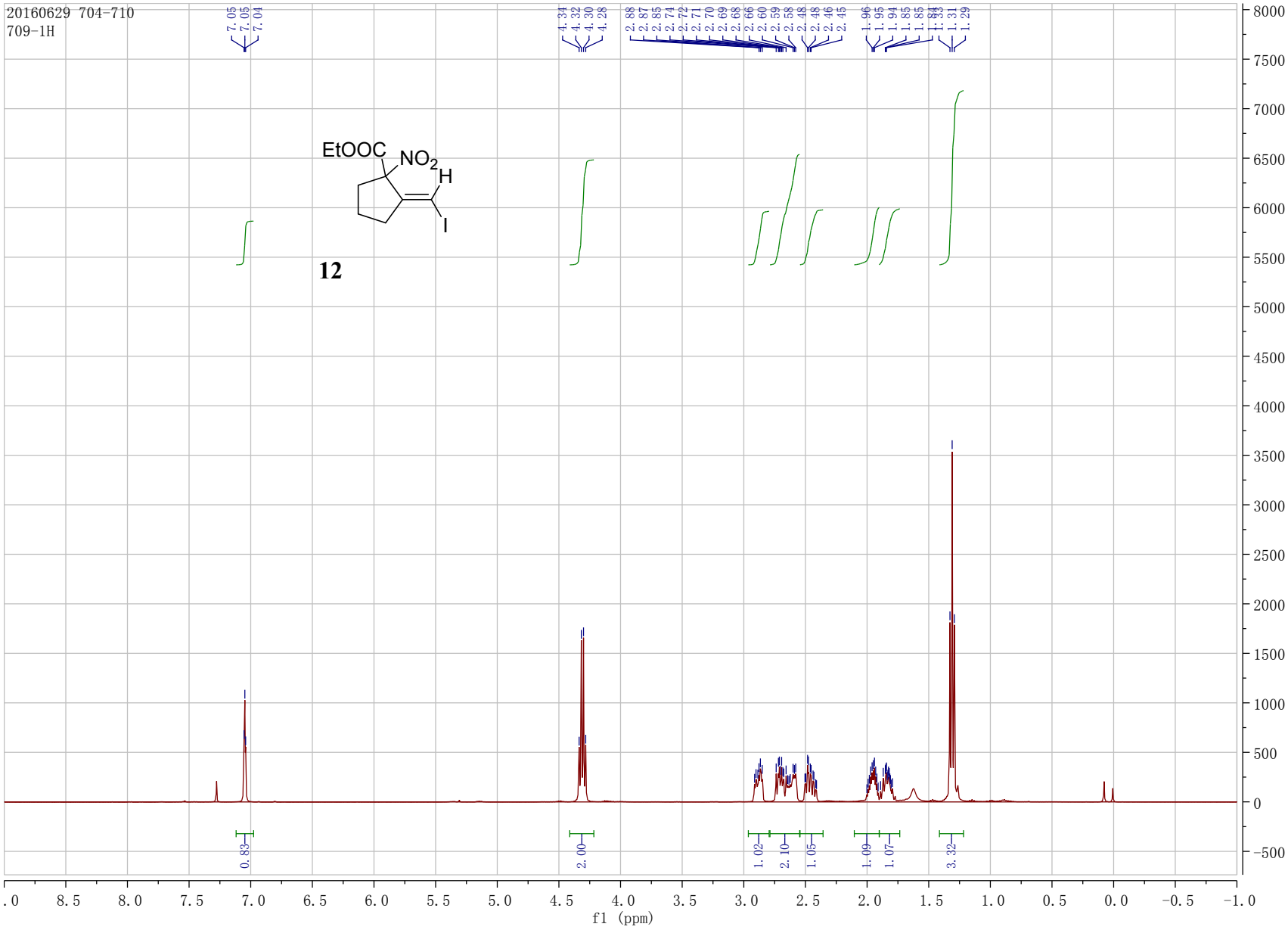

680
680-13C
168.57
93.72
81.37
53.45
27.88
27.64
26.12
20.56
18.16
tBuOOC
COOtBu
I
I
I
6e
f1 (ppm)

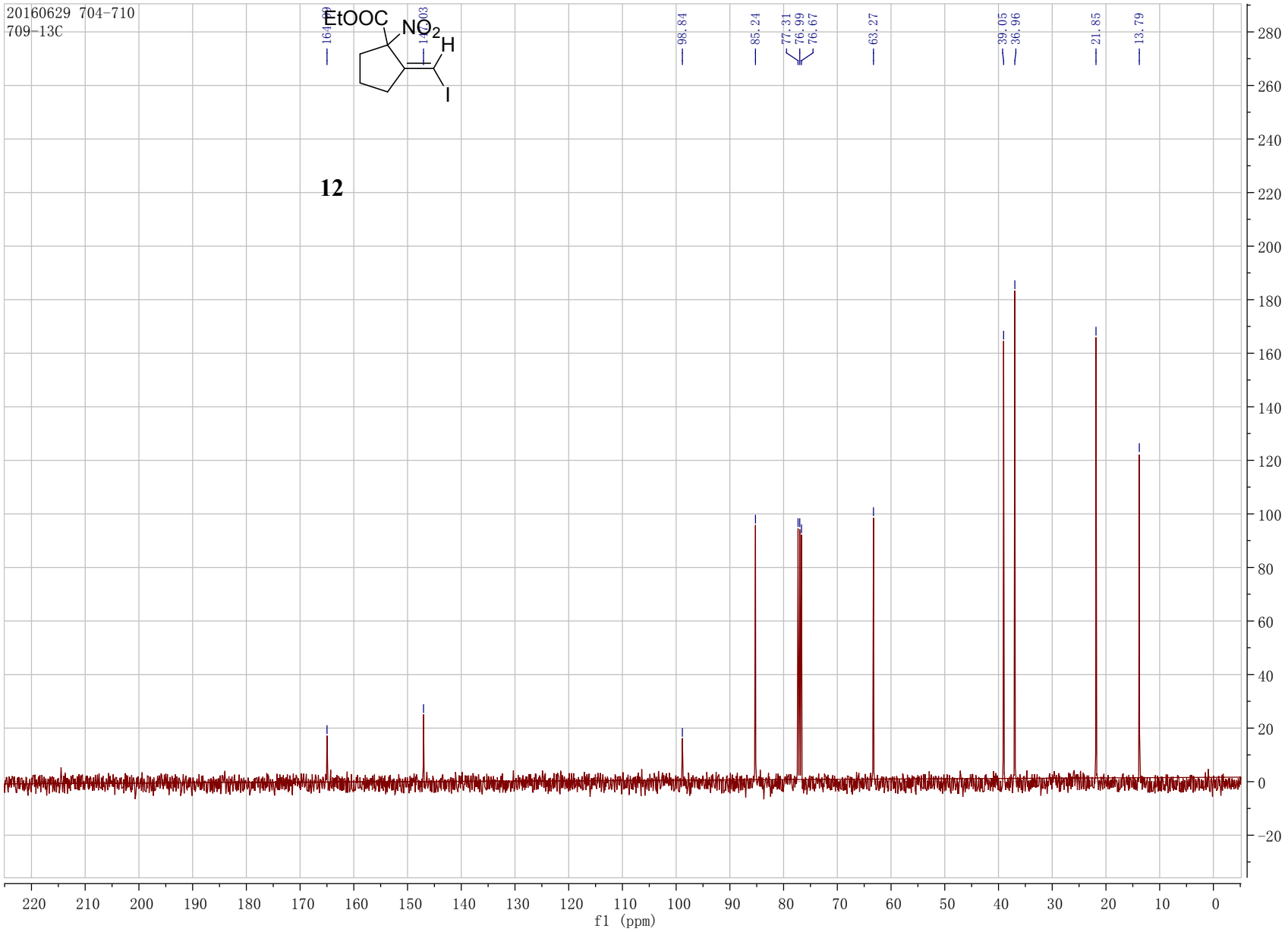

20160719
717A-1H
7.27
5.32
4.04
4.02
4.01
2.83
2.81
2.79
2.65
2.64
2.63
2.47
2.47
2.46
2.45
2.45
2.11
2.09
2.07
0.07
0.00
O
O
H
I
8
1.00
2.13
1.86
1.93
1.94
2.10
f1 (ppm)

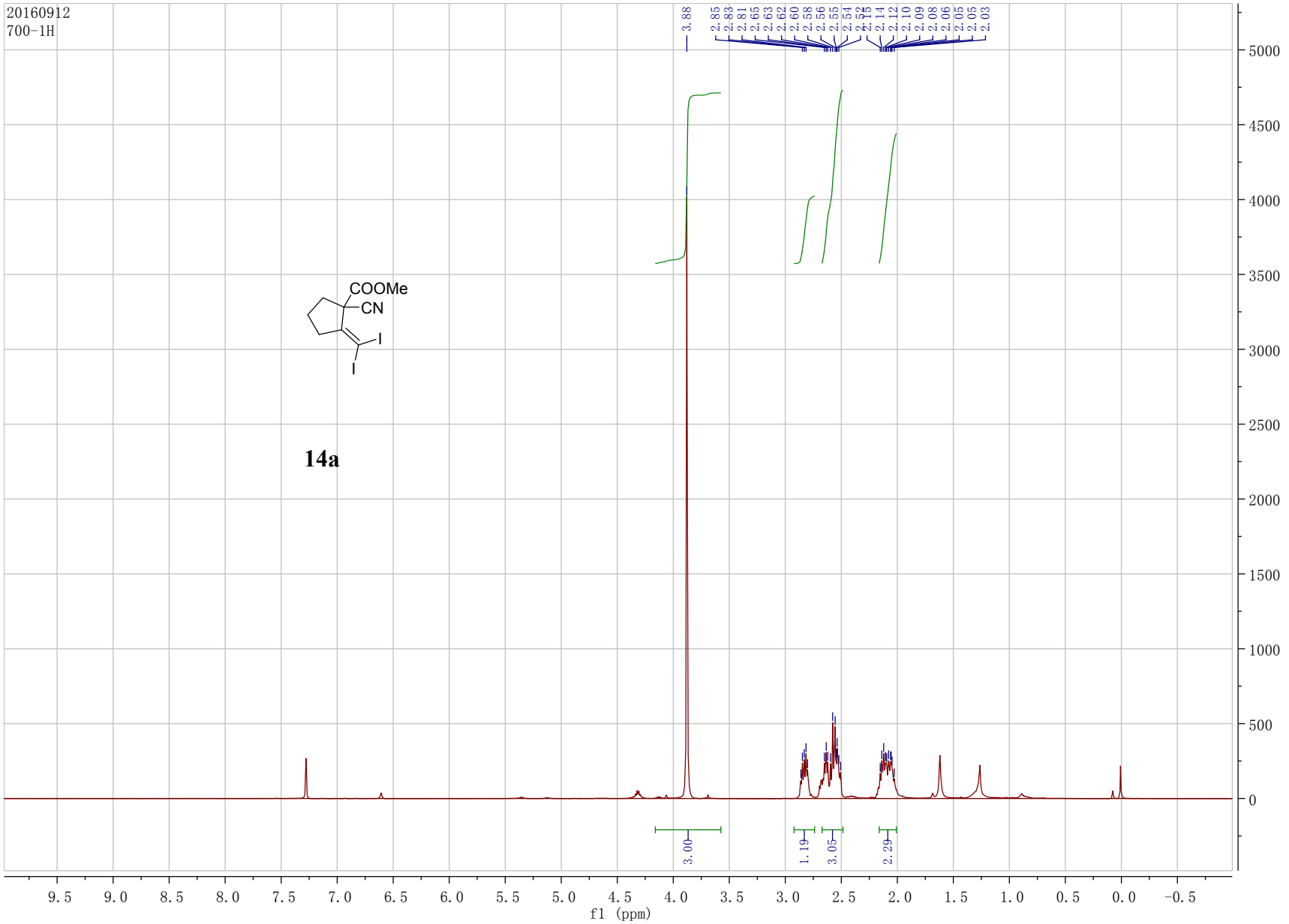

20160719
713A-13C
205.95
189.89
105.02
69.76
47.12
34.03
28.56
27.59
O
O
H
I
8
fl (ppm)

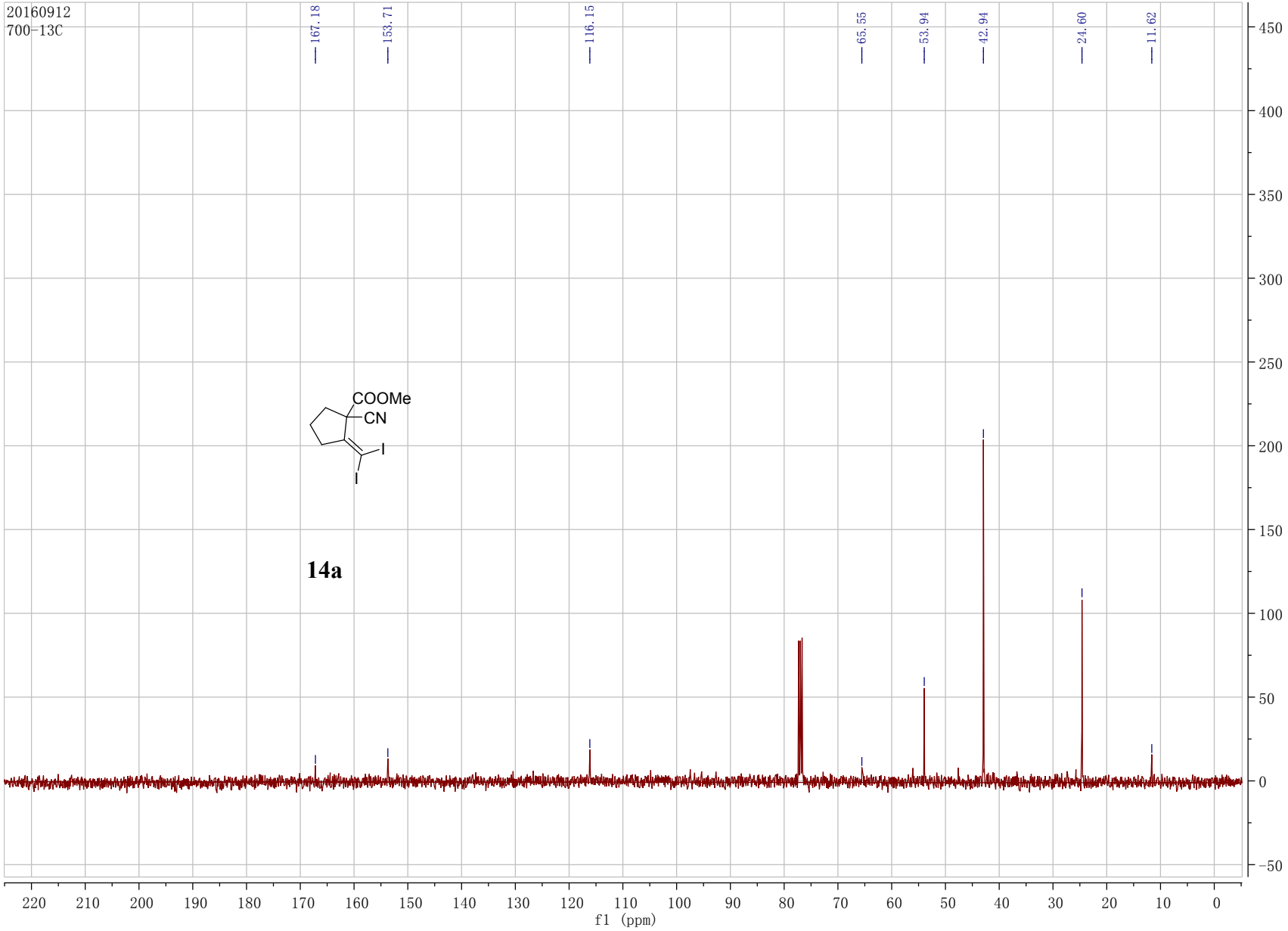

NMR
648-1
5.29
4.02
4.01
3.99
2.63
2.62
2.60
2.46
2.44
2.43
1.91
1.89
1.87
1.86
1.71
1.69
1.67
1.65
O
O
H
I
10
1.00
1.97
2.02
3.78
2.19
2.13
f1 (ppm)

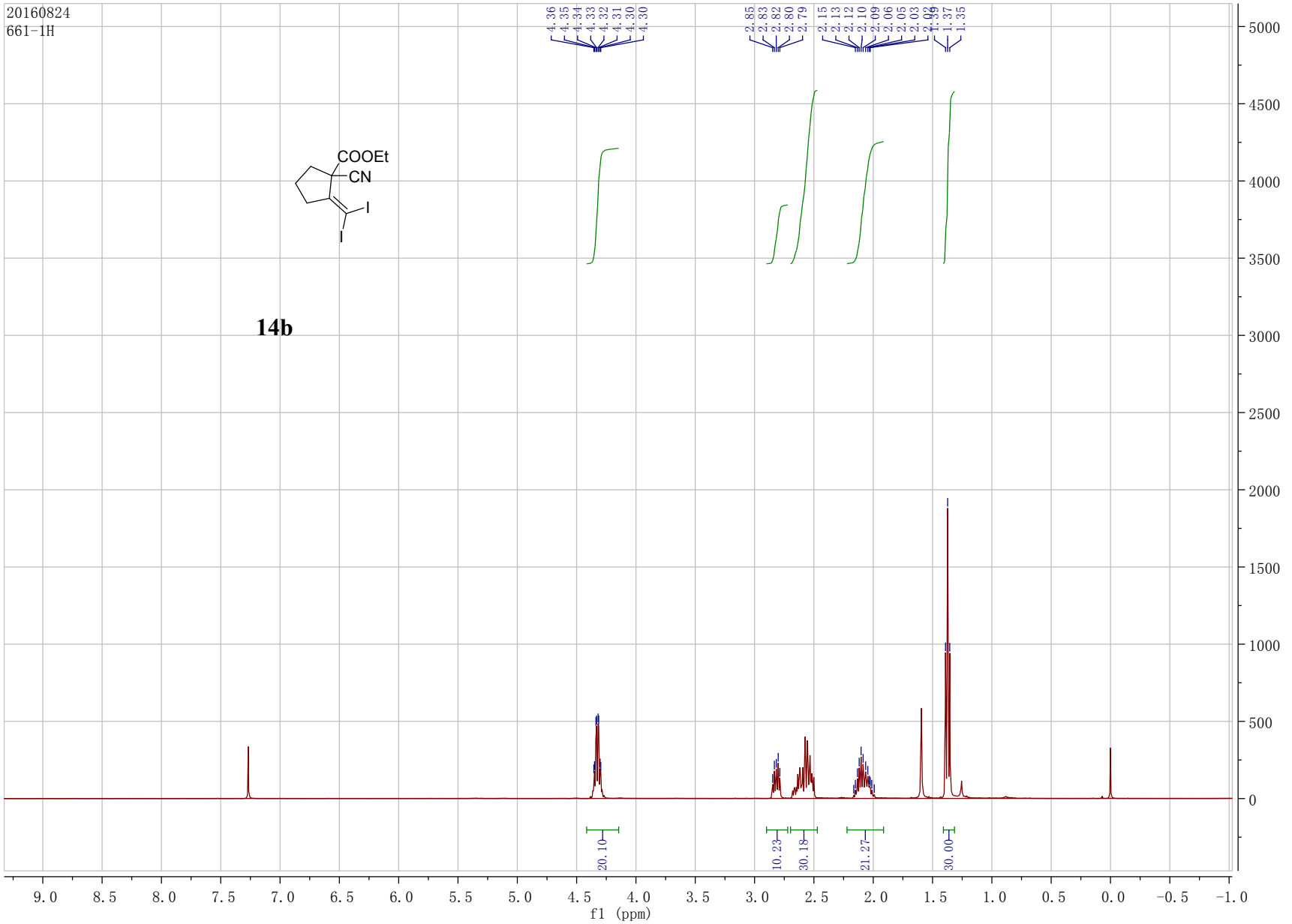

NMR
648-13C
206.01
190.16
104.78
93.60
71.27
33.98
28.48
27.61
24.77
20.41
O
OH
I
10
2500
2000
1500
1000
500
0
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

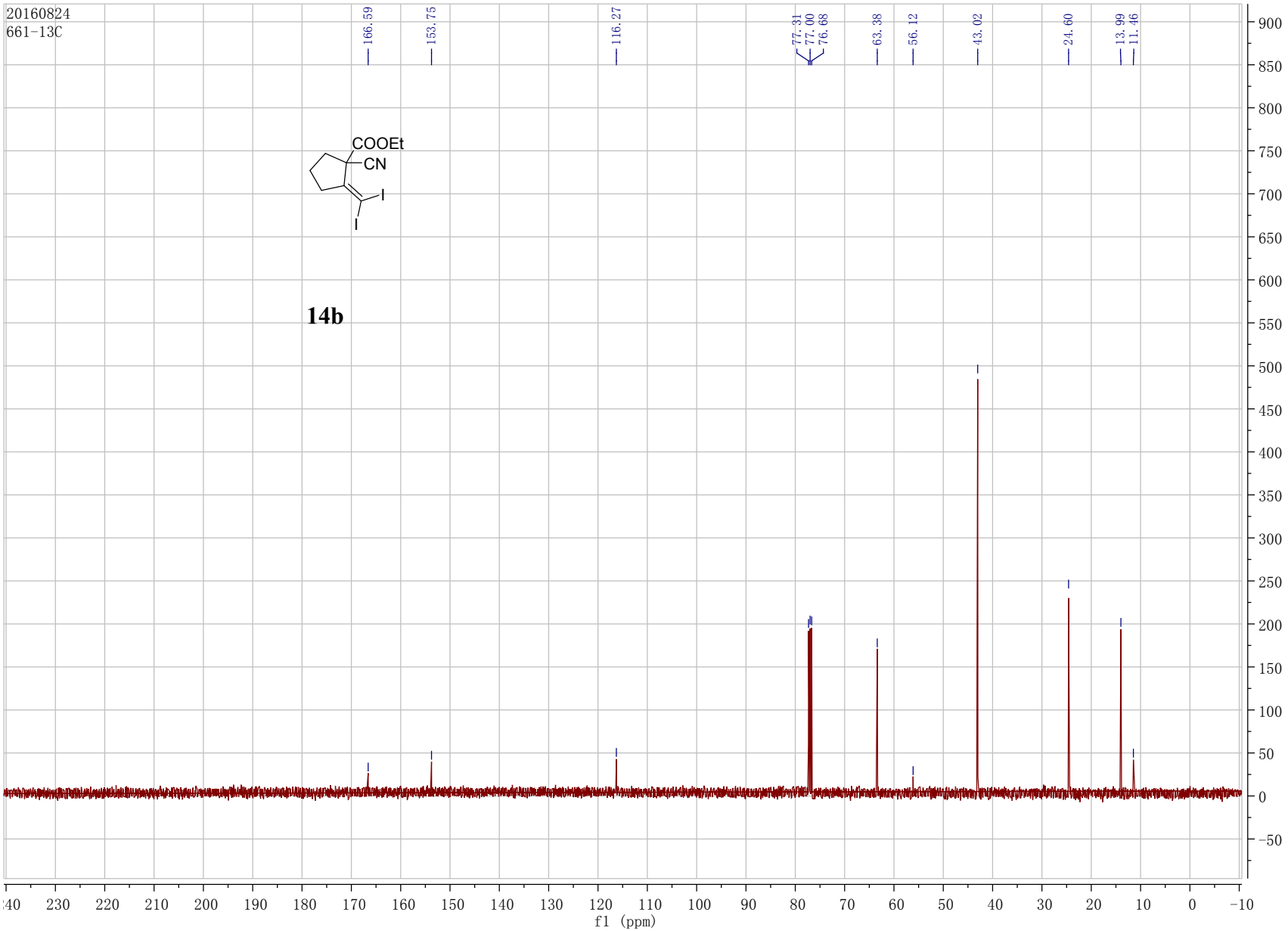

20160629 704-710
709-1H
EtOOC
NO2
H
I
12
f1 (ppm)

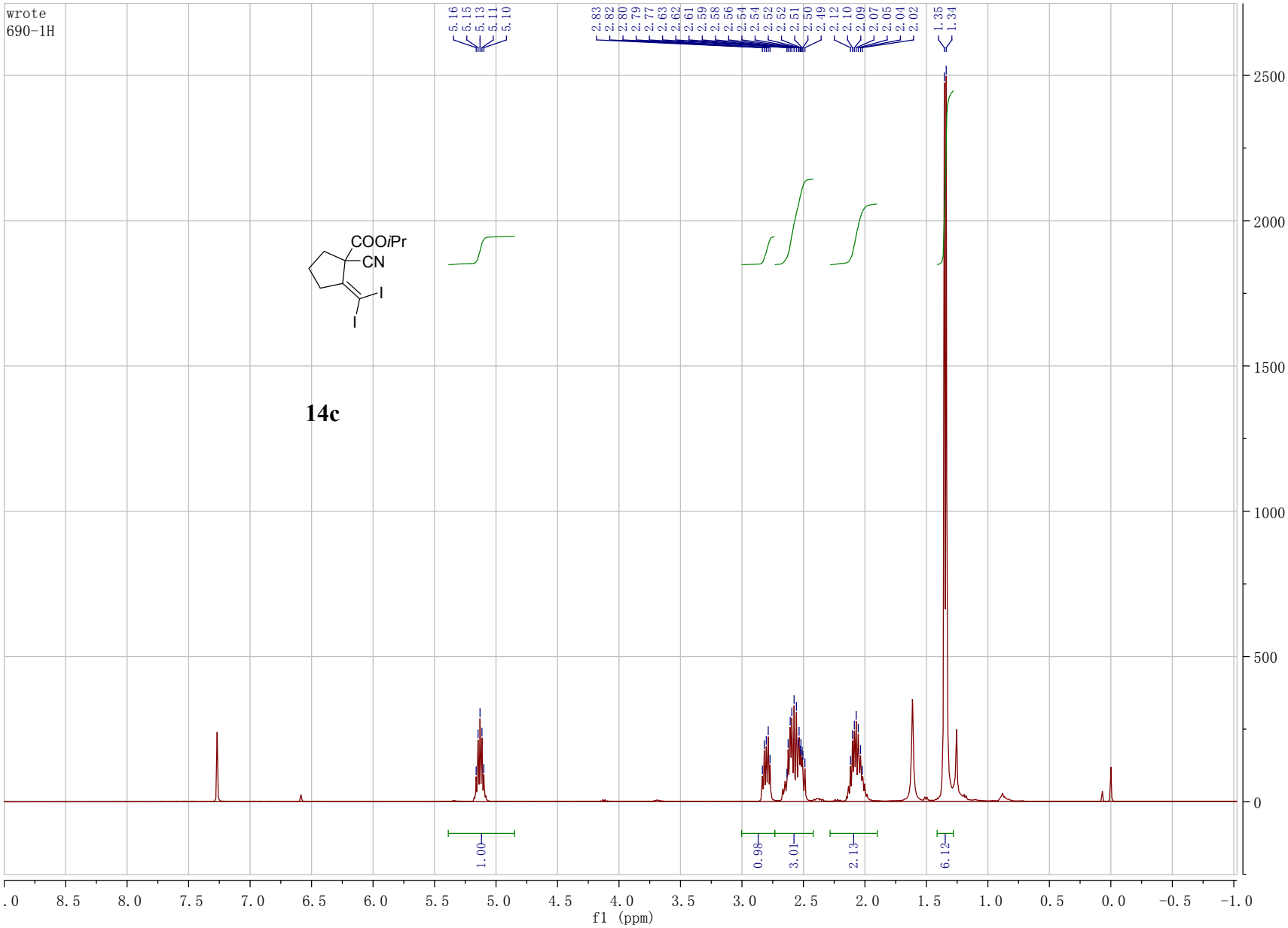

20160629 704-710
709-13C
EtOOC
NO2
H
I
12
98.84
85.24
77.31
76.99
76.67
63.27
39.05
36.96
21.85
13.79
f1 (ppm)

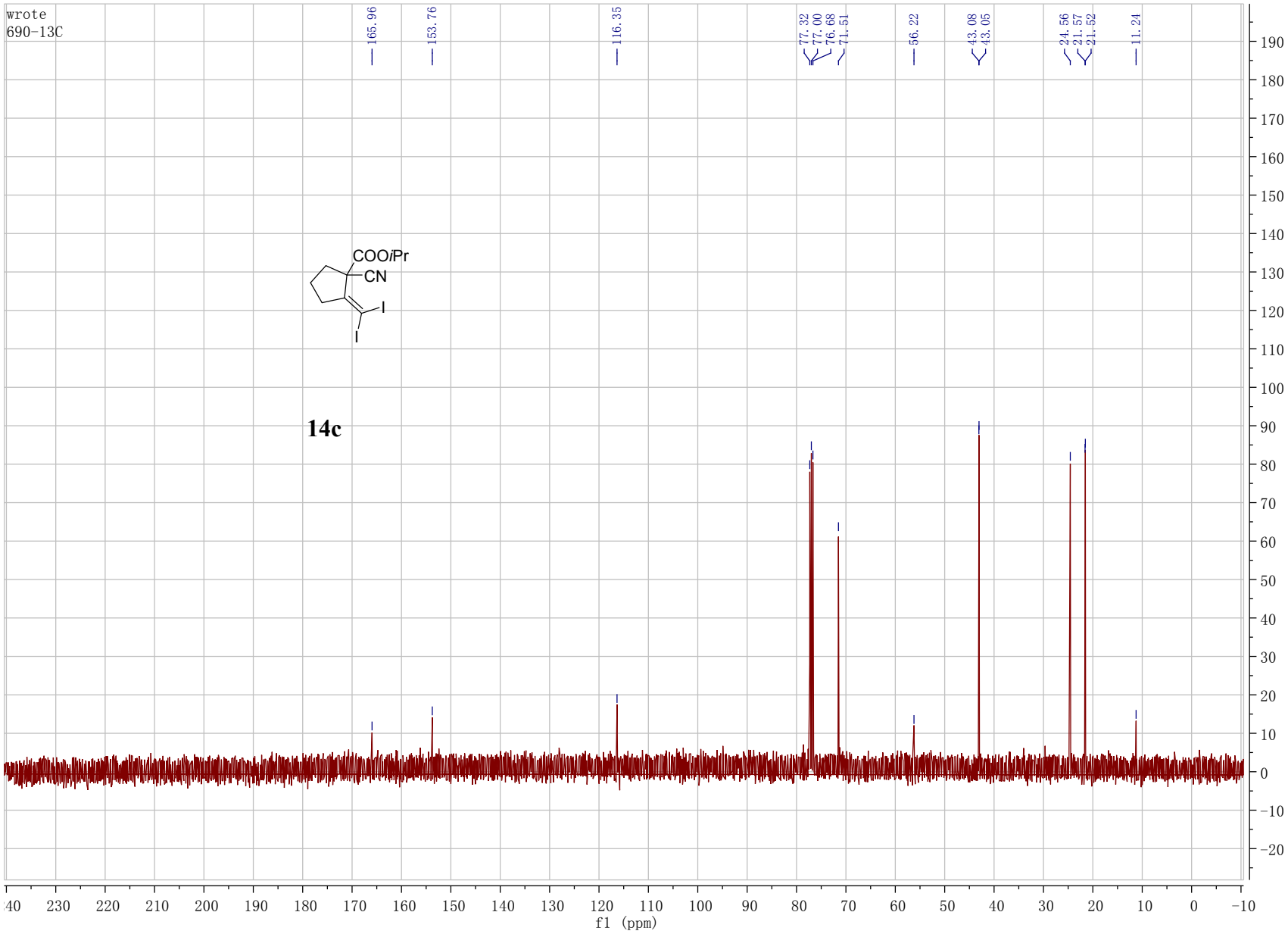

20160912
700-1H
3.88
2.85
2.83
2.81
2.65
2.63
2.62
2.60
2.58
2.56
2.55
2.54
2.14
2.12
2.10
2.09
2.08
2.06
2.05
2.03
COOMe
CN
I
I
14a
3.00
1.19
3.05
2.29
f1 (ppm)

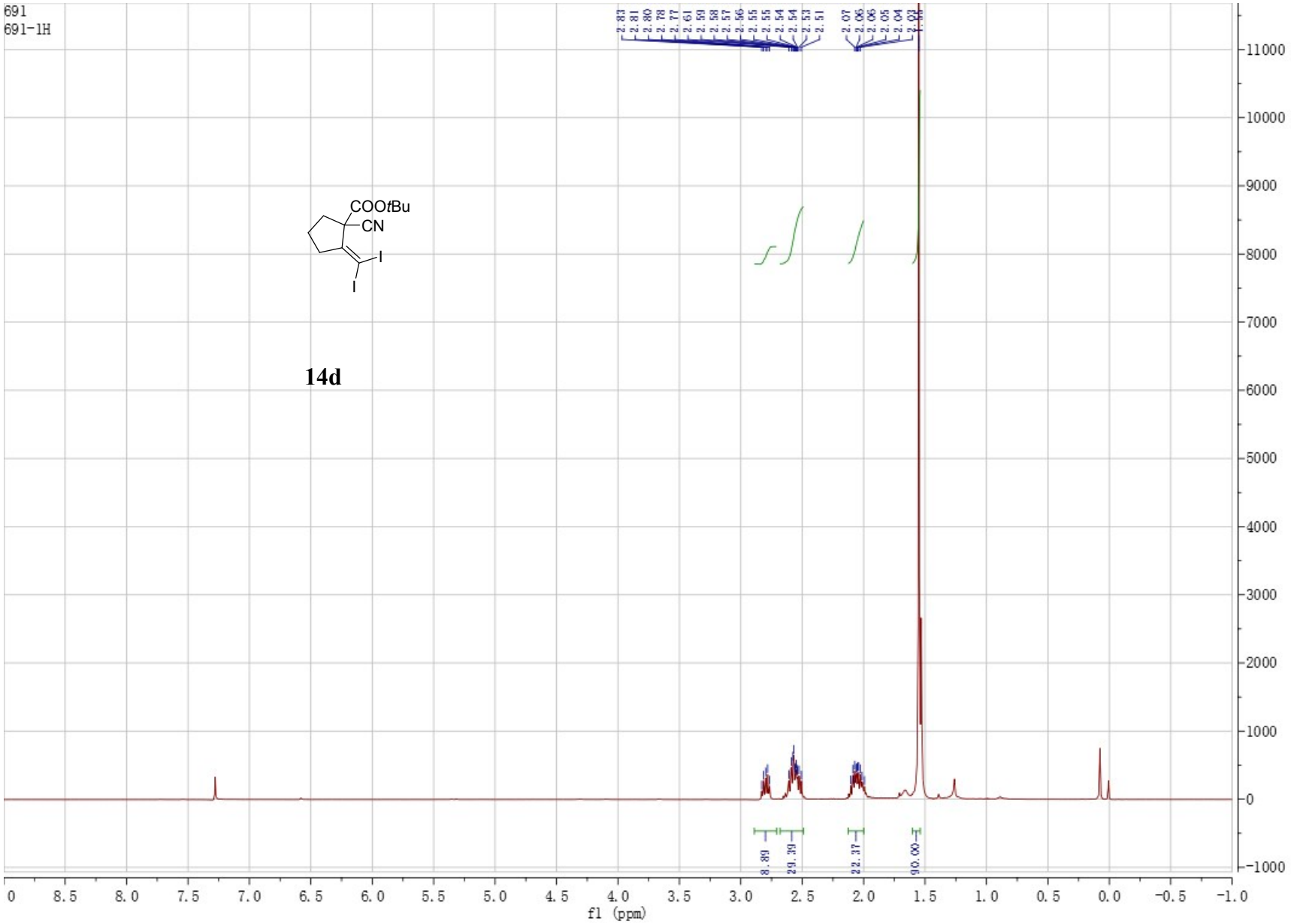

20160912
700-13C
167.18
153.71
116.15
65.55
53.94
42.94
24.60
11.62
COOMe
CN
I
I
14a
f1 (ppm)

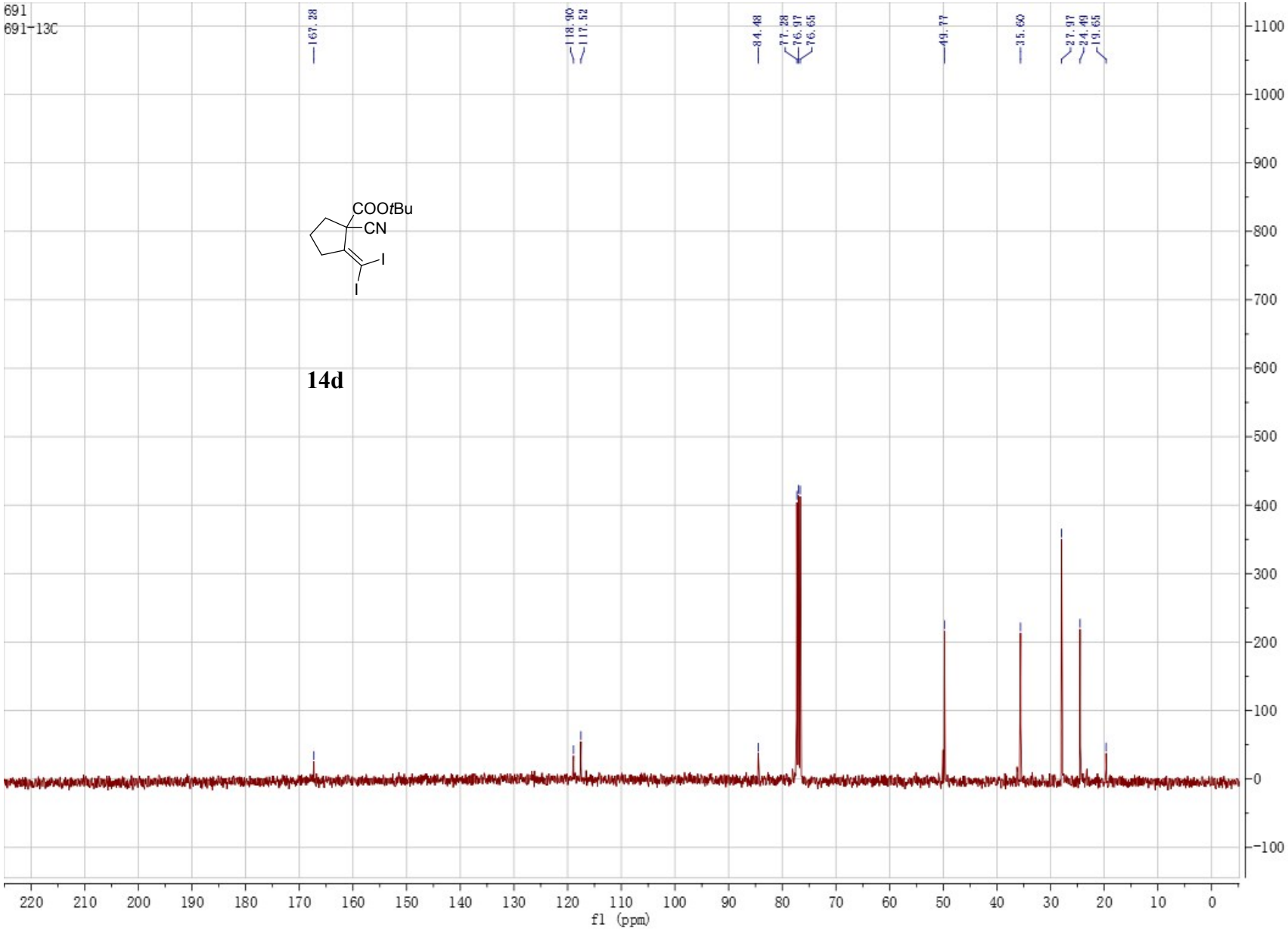

20160824
661-1H
COOEt
CN
I
I
14b
4.36
4.35
4.34
4.33
4.32
4.31
4.30
4.30
2.85
2.83
2.82
2.80
2.79
2.15
2.13
2.12
2.10
2.09
2.06
2.05
2.03
2.02
1.39
1.37
1.35
20.10
10.23
30.18
21.27
30.00
f1 (ppm)

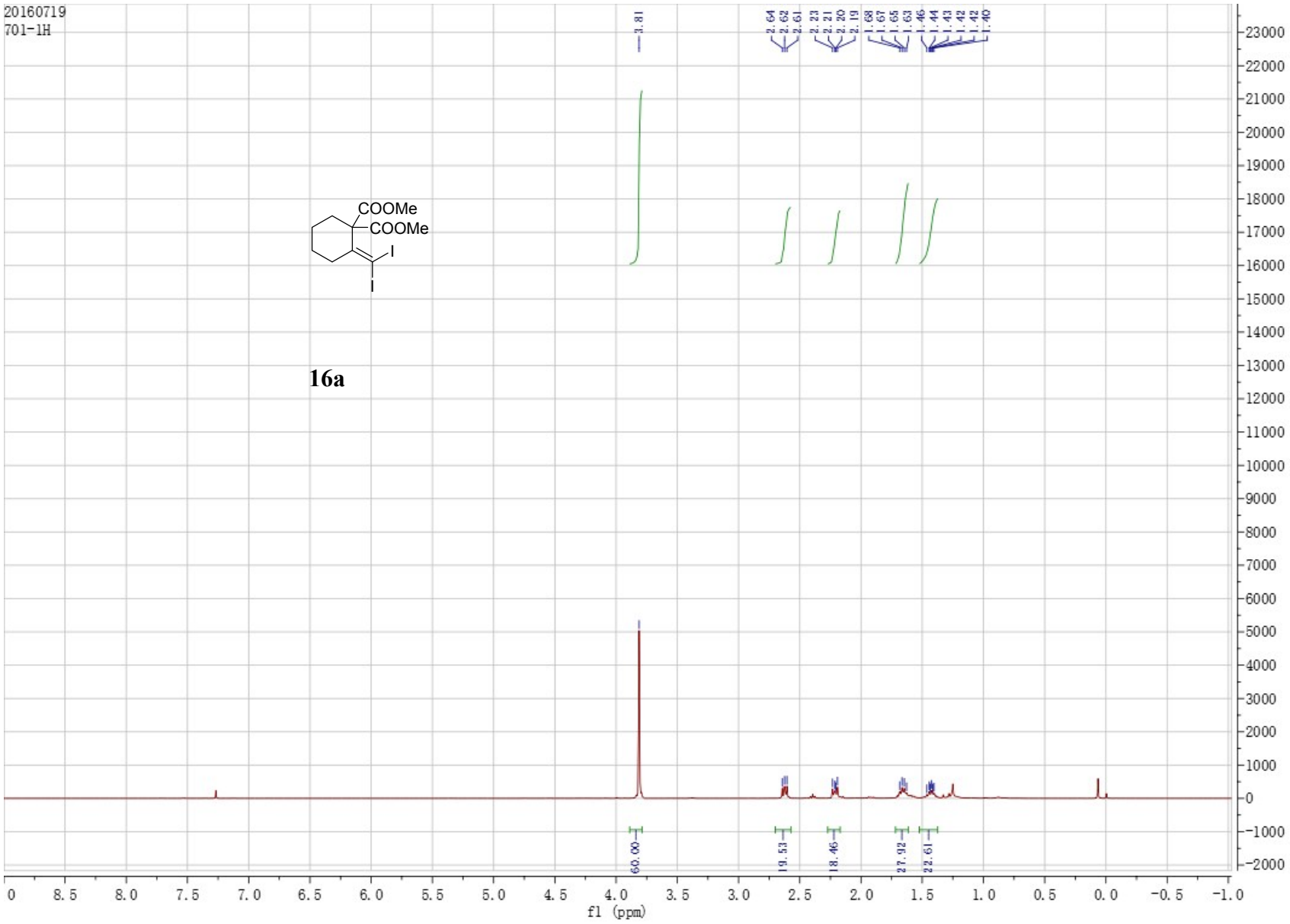

20160824
661-13C
166.59
153.75
116.27
77.31
77.00
76.68
63.38
56.12
43.02
24.60
13.99
11.46
COOEt
CN
I
I
14b
f1 (ppm)


wrote
690-1H
5.16
5.15
5.13
5.11
5.10
2.83
2.82
2.80
2.79
2.77
2.63
2.62
2.61
2.59
2.58
2.56
2.54
2.54
2.52
2.52
2.51
2.50
2.49
2.12
2.10
2.09
2.07
2.05
2.04
2.02
1.35
1.34
COOiPr
CN
I
I
14c
2500
2000
1500
1000
500
0
1.00
0.98
3.01
2.13
6.12
f1 (ppm)

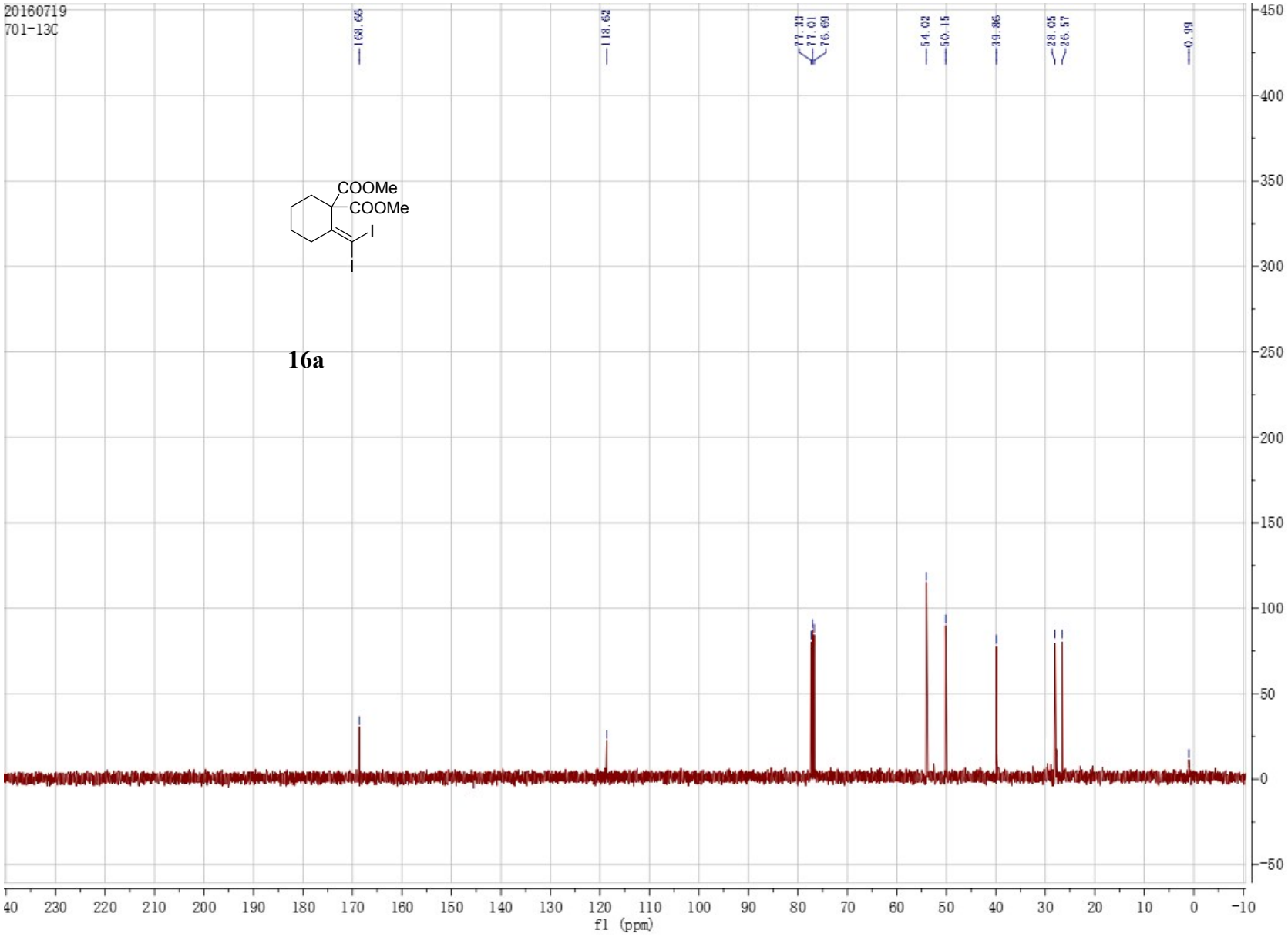

wrote
690-13C
165.96
153.76
116.35
77.32
77.00
76.68
71.51
56.22
43.08
43.05
24.56
21.57
21.52
11.24
COOiPr
CN
I
I
14c
f1 (ppm)

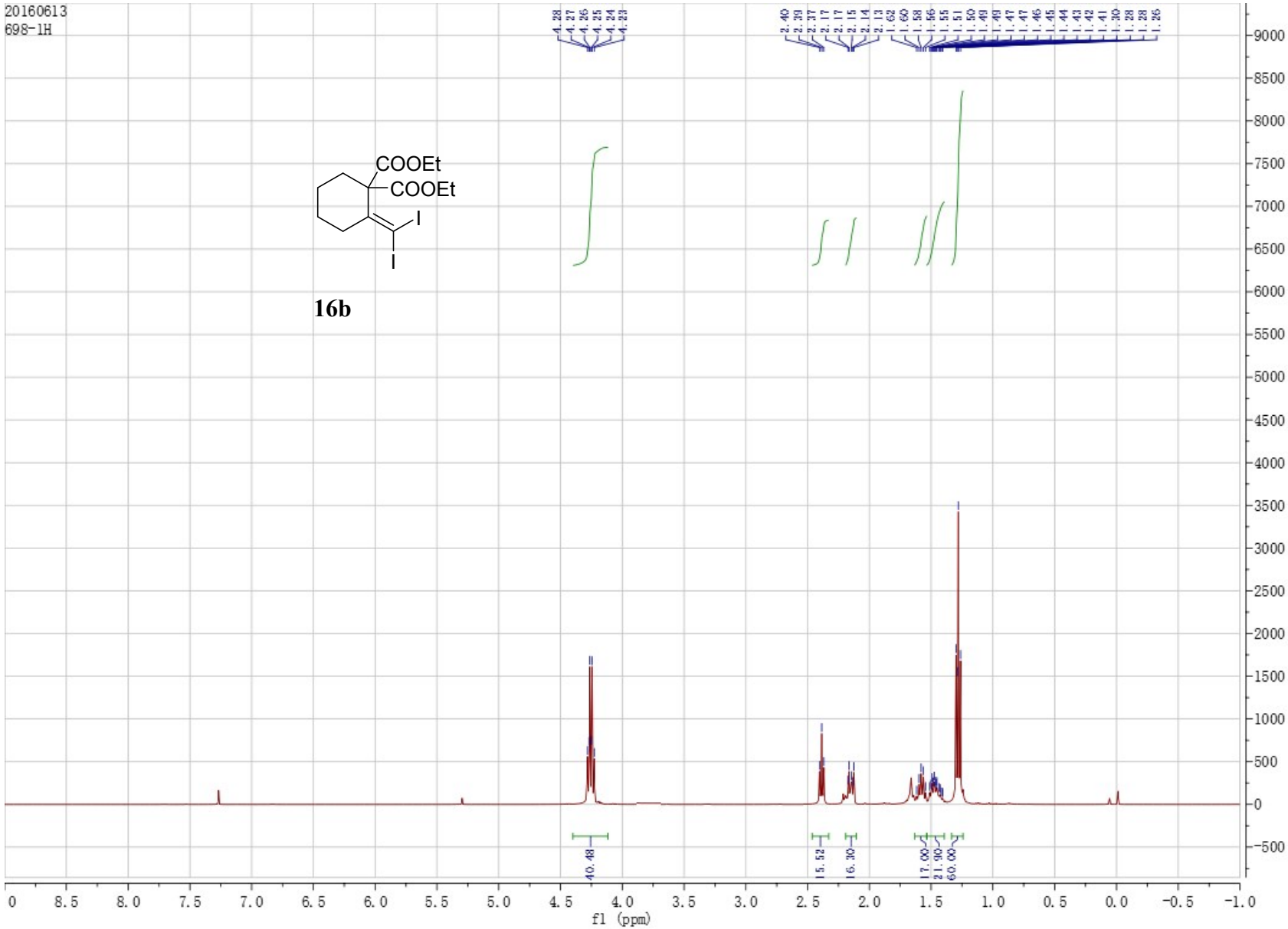

691
691-1H
COOtBu
CN
I
I
14d
f1 (ppm)

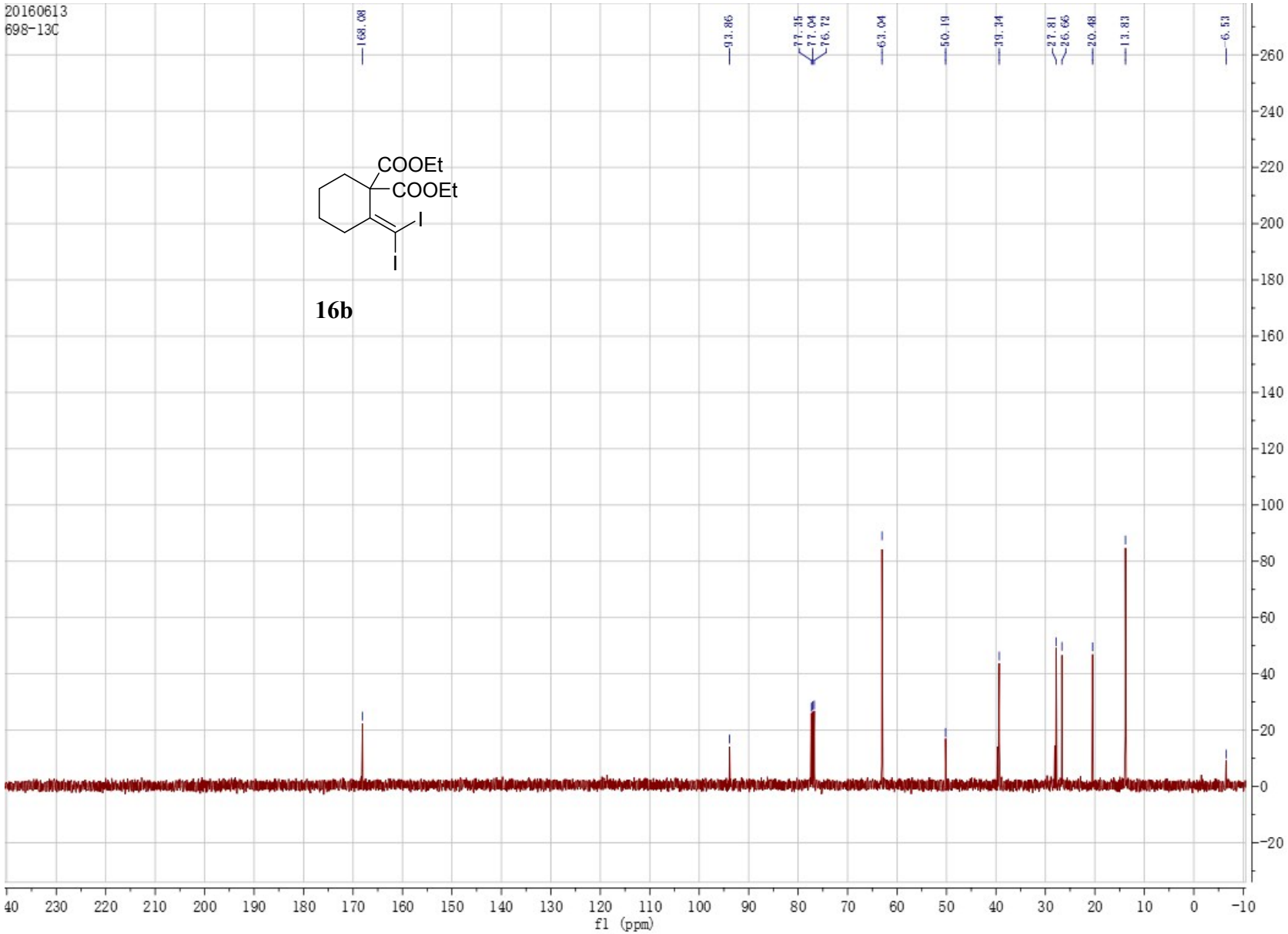

691
691-13C
167.28
118.90
117.52
84.48
77.28
76.97
76.65
49.77
35.60
27.97
24.49
19.65
COOtBu
CN
I
I
14d
f1 (ppm)

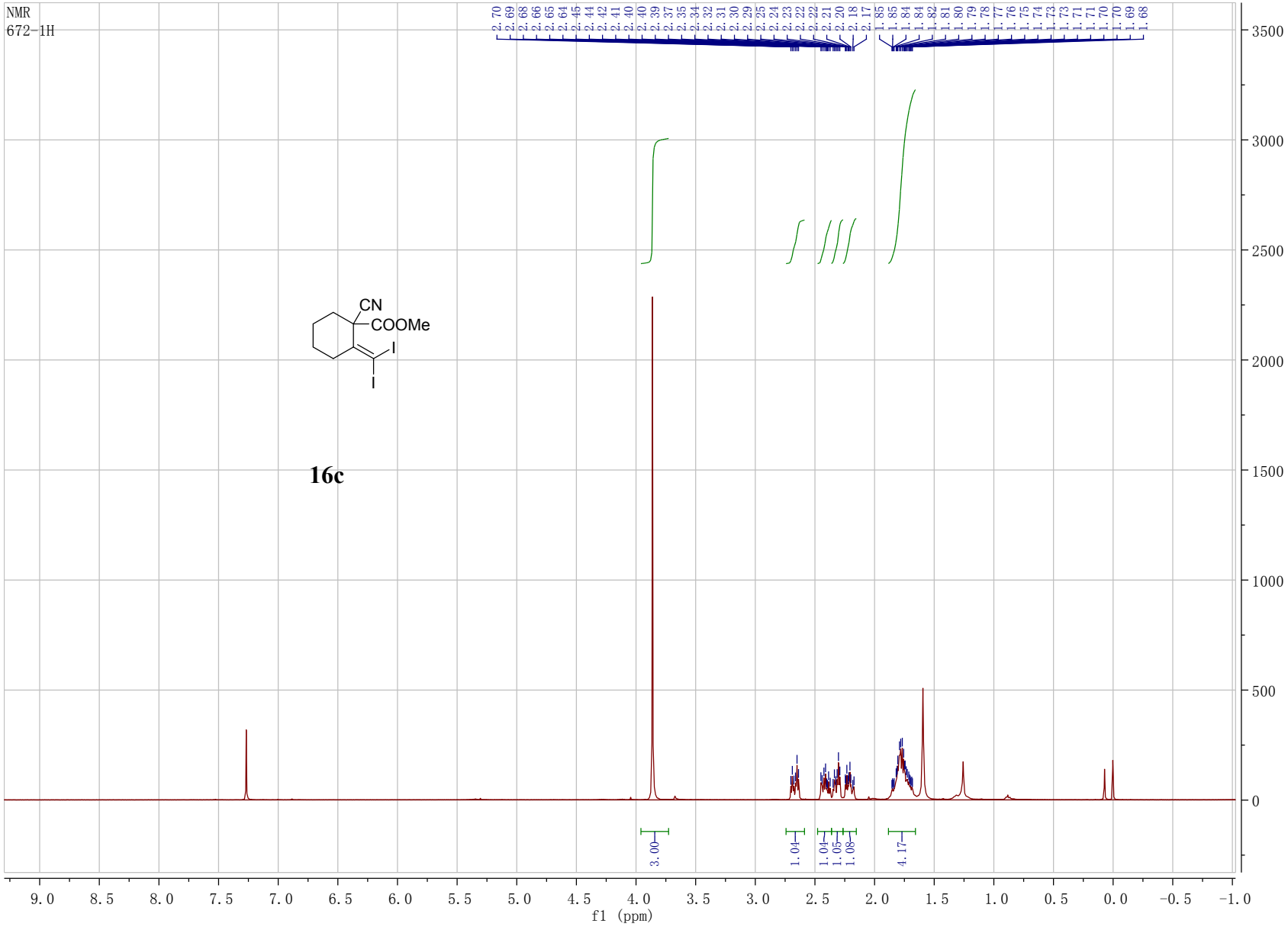

20160719
701-1H
COOMe
COOMe
I
I
3.81
2.64
2.62
2.61
2.23
2.21
2.20
2.19
1.68
1.67
1.65
1.63
1.46
1.44
1.43
1.42
1.42
1.40
60.00
19.53
18.46
27.92
22.61
f1 (ppm)

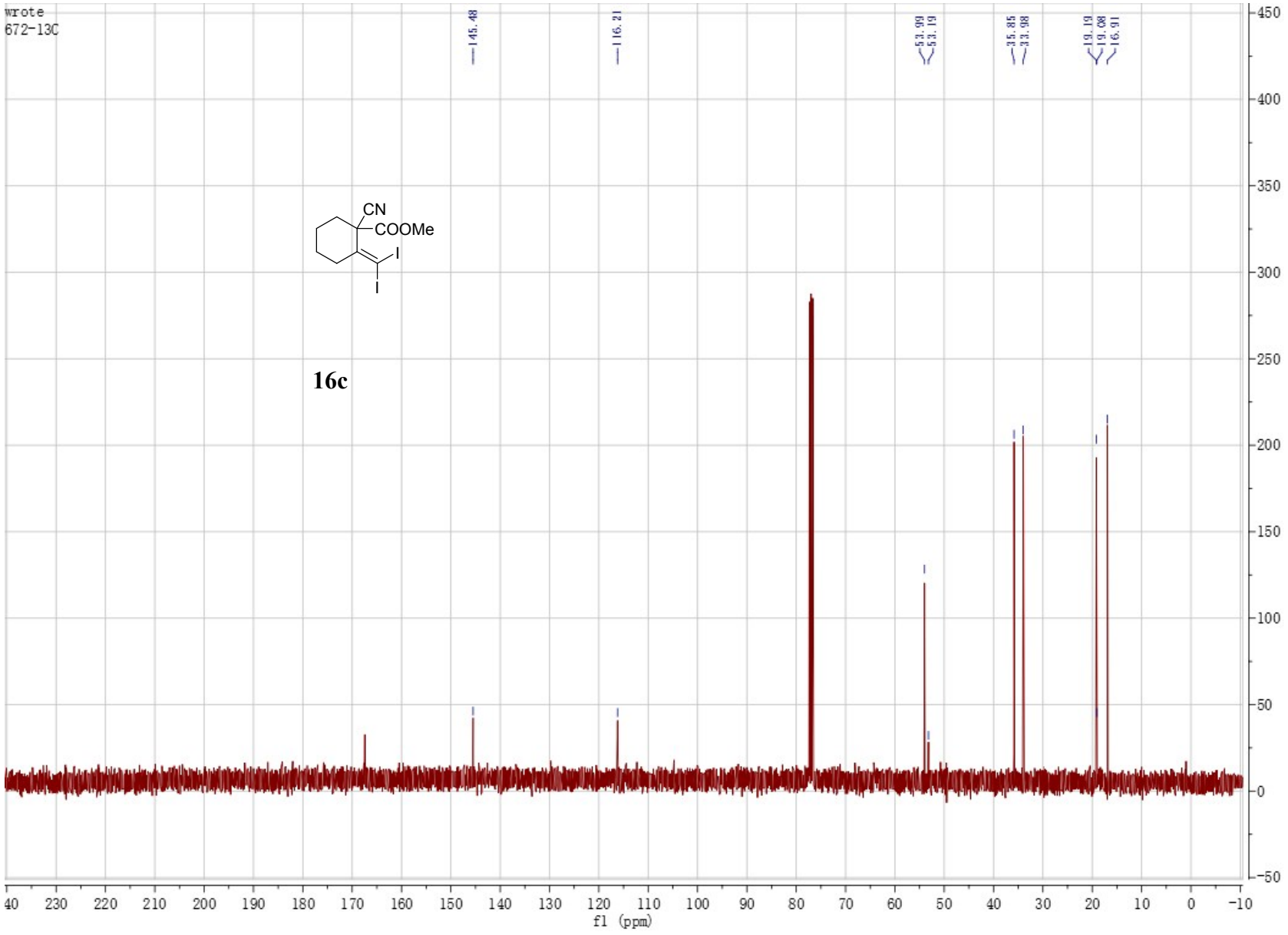
16a

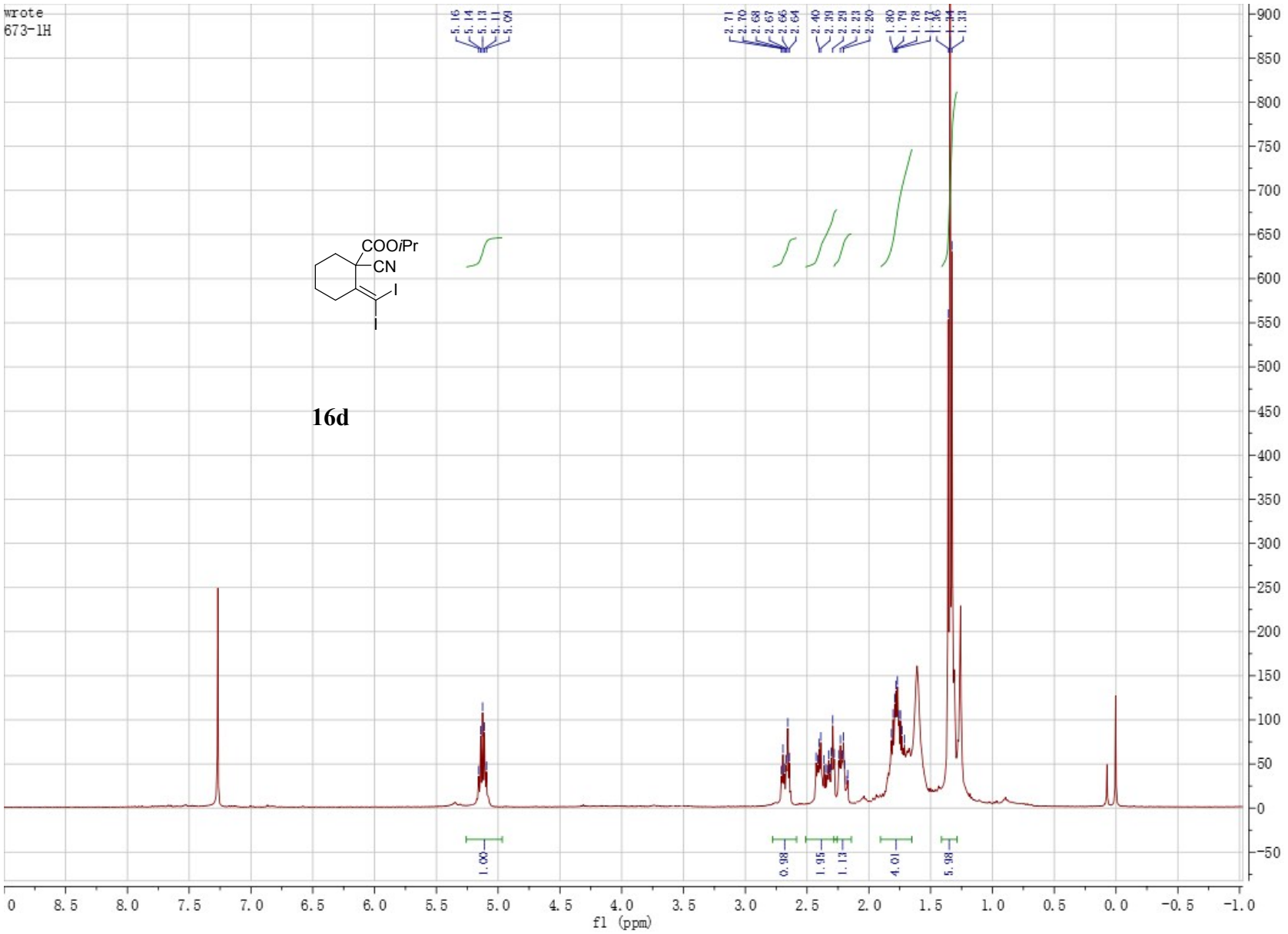

20160719
701-13C
168.66
118.62
77.33
77.01
76.69
54.02
50.15
39.86
28.05
26.57
0.99
COOMe
COOMe
I
I
16a
f1 (ppm)

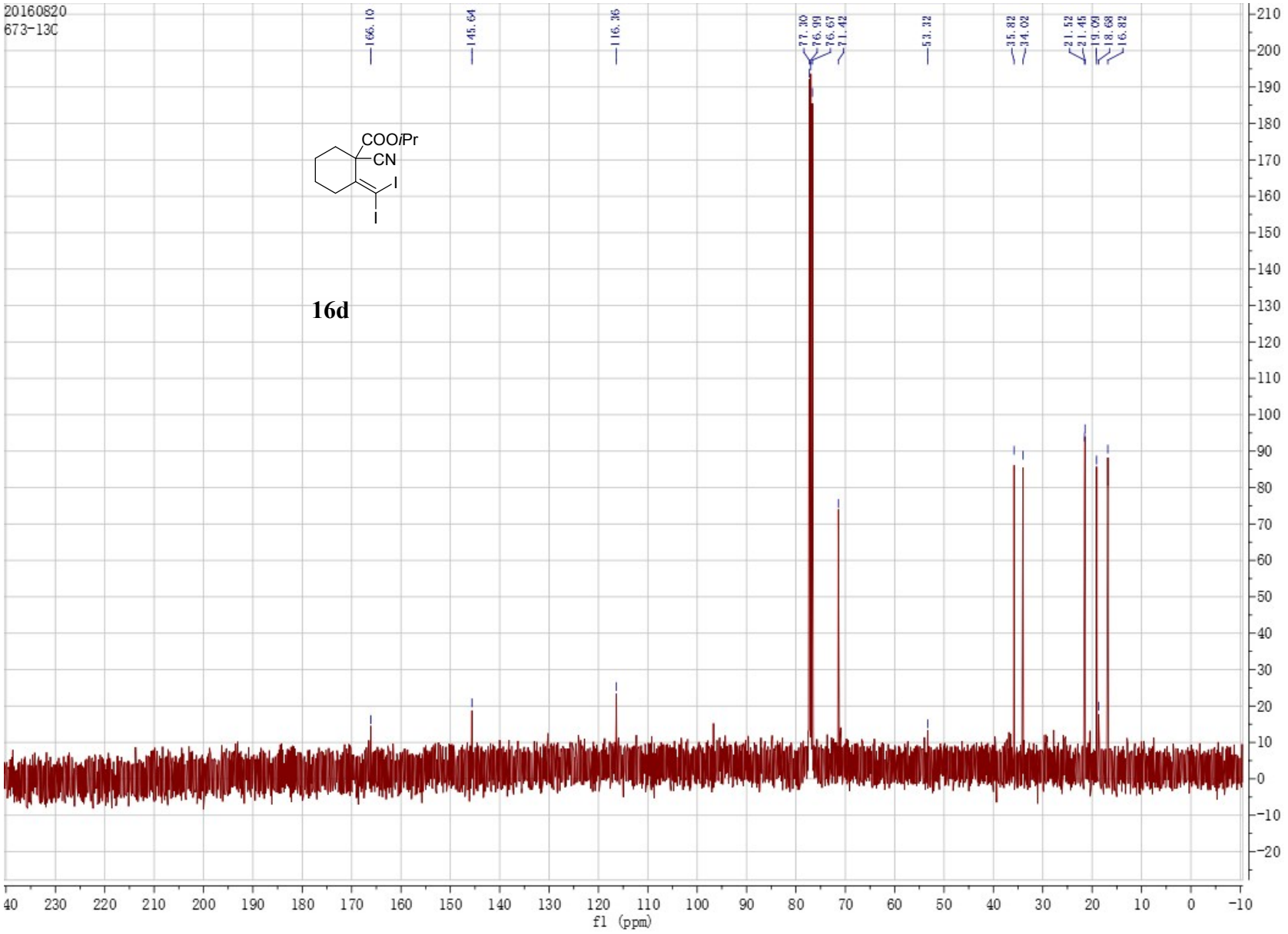

20160613
698-1H
COOEt
COOEt
I
I
16b
f1 (ppm)

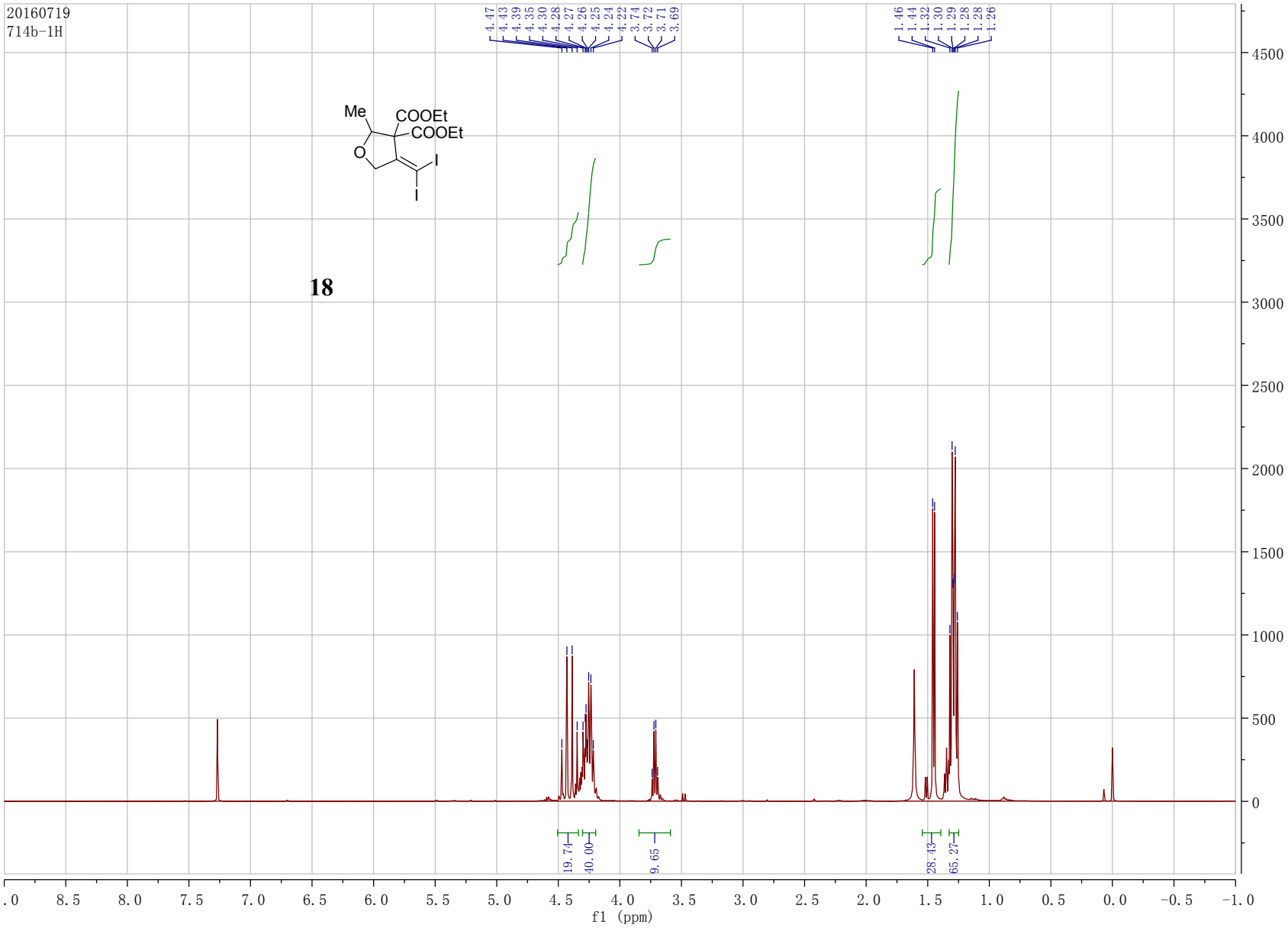

20160613
698-13C
168.08
93.86
77.35
77.04
76.72
63.04
50.19
39.34
27.81
26.66
20.48
13.83
6.53
COOEt
COOEt
I
I
16b
f1 (ppm)

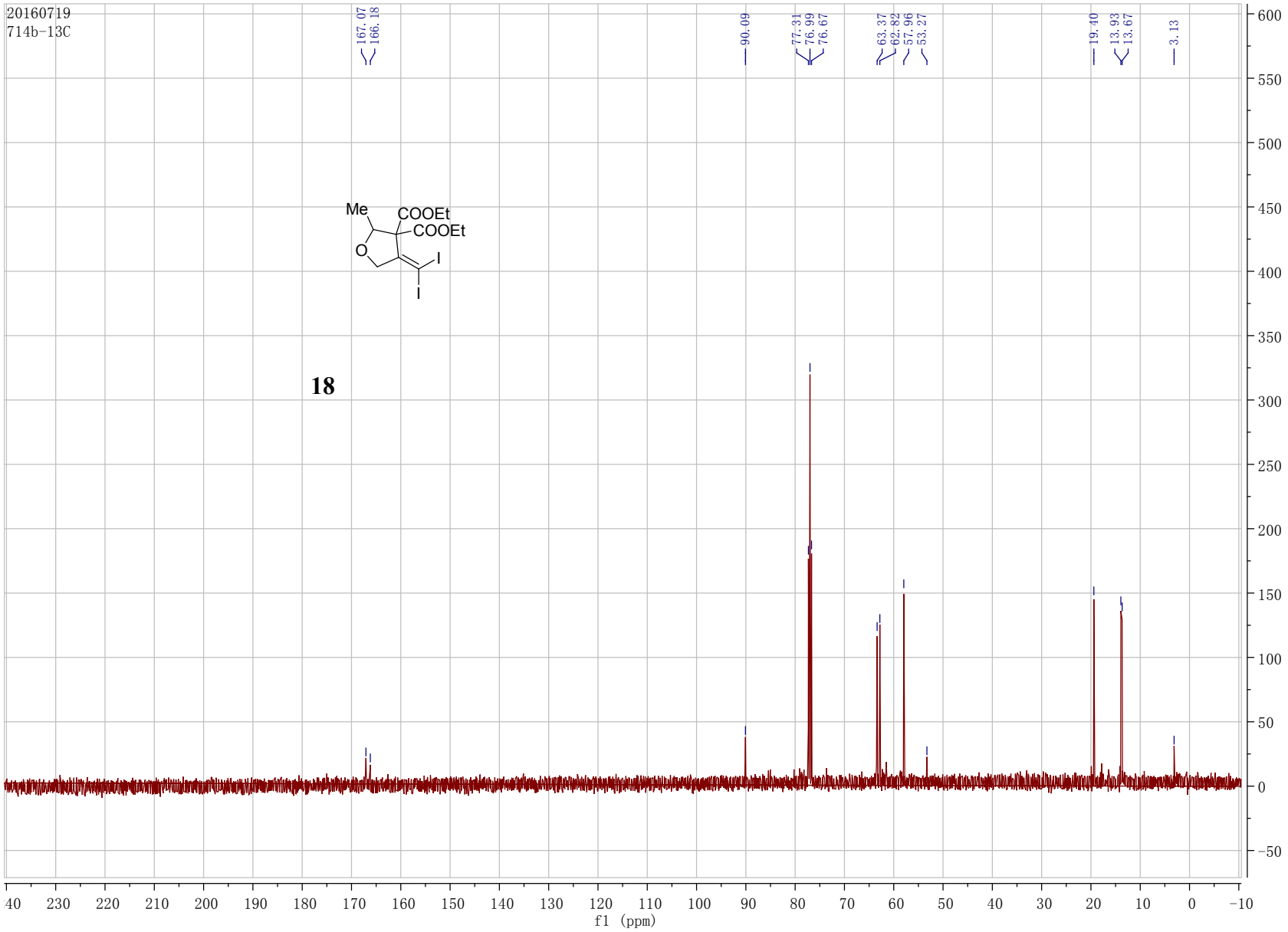

NMR
672-1H
CN
COOMe
I
I
16c
f1 (ppm)

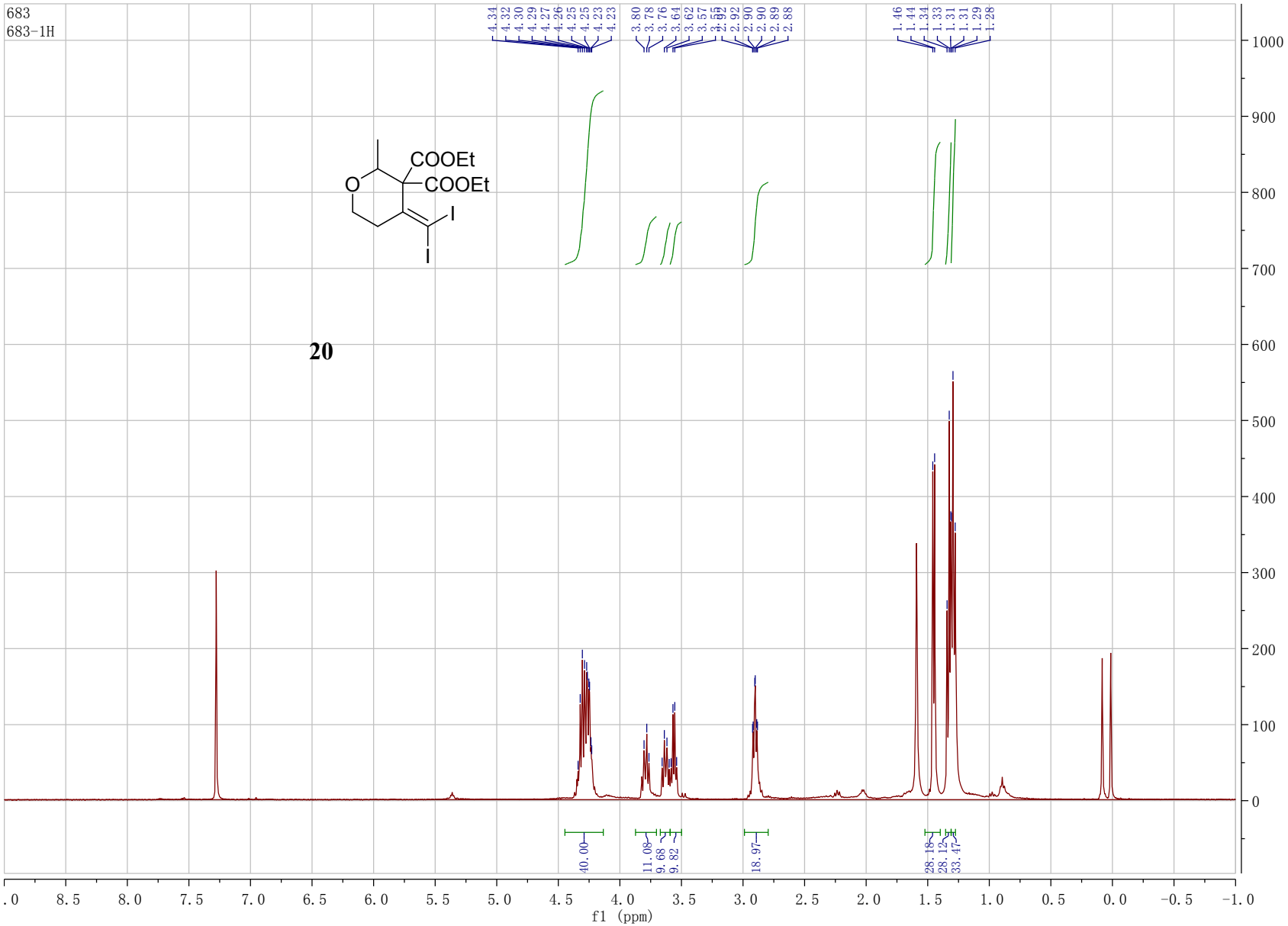

wrote
672-13C
145.48
116.21
53.99
53.19
35.85
33.98
19.19
19.08
16.91
CN
COOMe
I
I
16c
f1 (ppm)

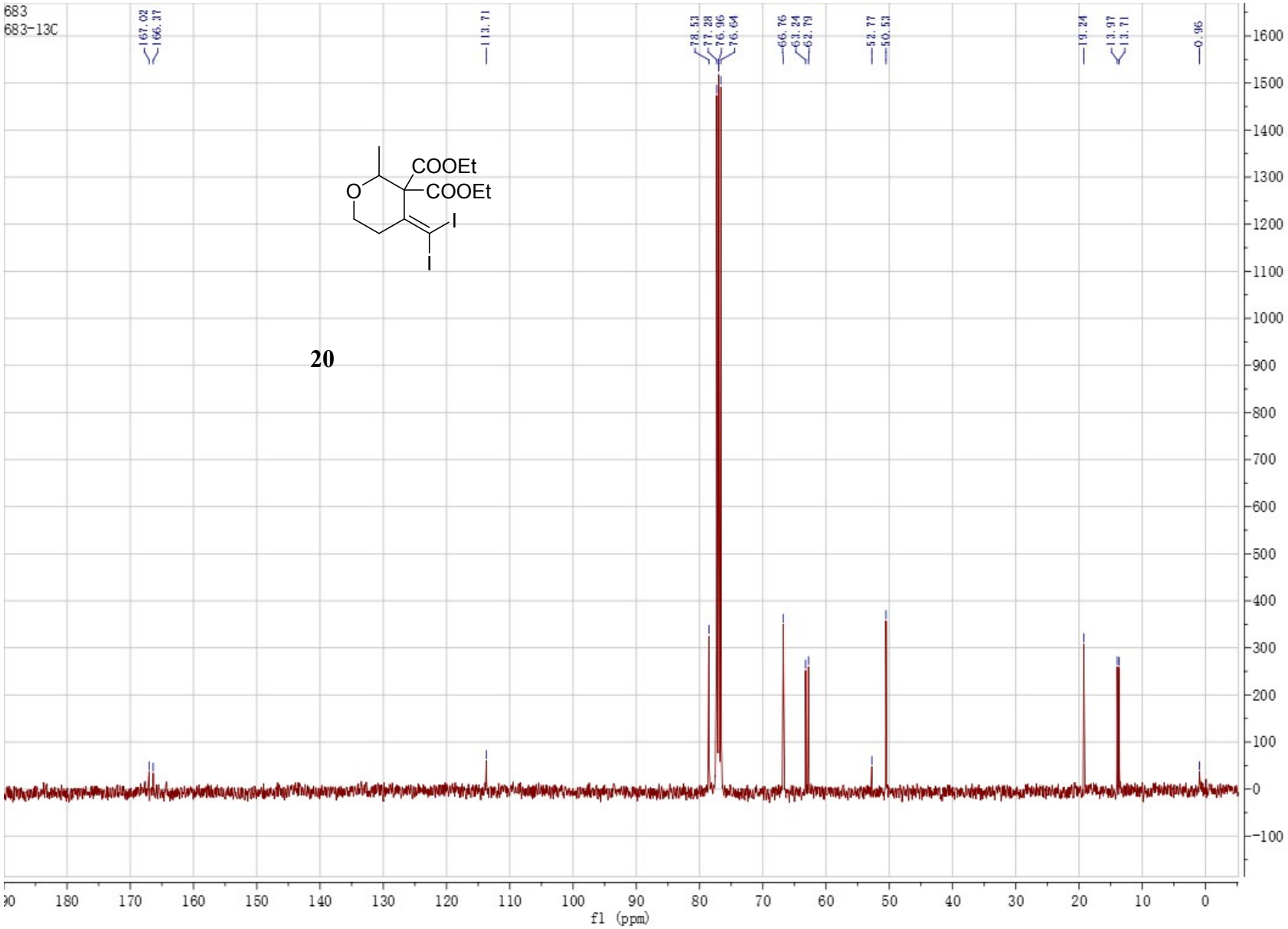

wrote
673-1H
COO*i*Pr
CN
I
I
16d
f1 (ppm)


20160820
673-13C
166.10
145.64
116.36
77.30
76.99
76.67
71.42
53.32
35.82
34.02
21.52
21.45
19.09
18.68
16.82
COOiPr
CN
I
I
16d
f1 (ppm)

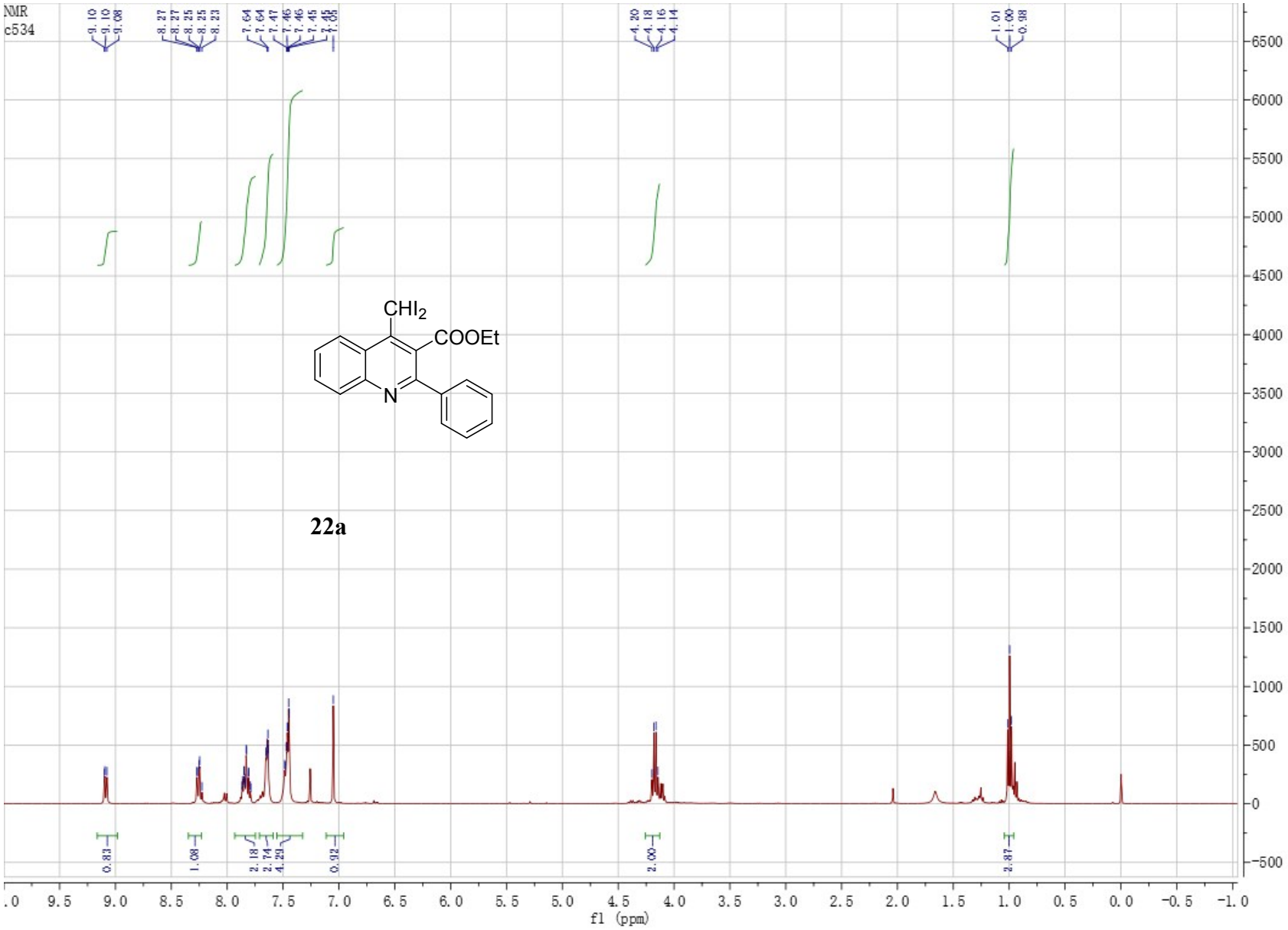

20160719
714b-1H
Me
COOEt
COOEt
O
I
I
18
4.47
4.43
4.39
4.35
4.30
4.28
4.27
4.26
4.25
4.24
4.22
3.74
3.72
3.71
3.69
1.46
1.44
1.32
1.30
1.29
1.28
1.28
1.26
19.74
40.00
9.65
28.43
65.27
f1 (ppm)

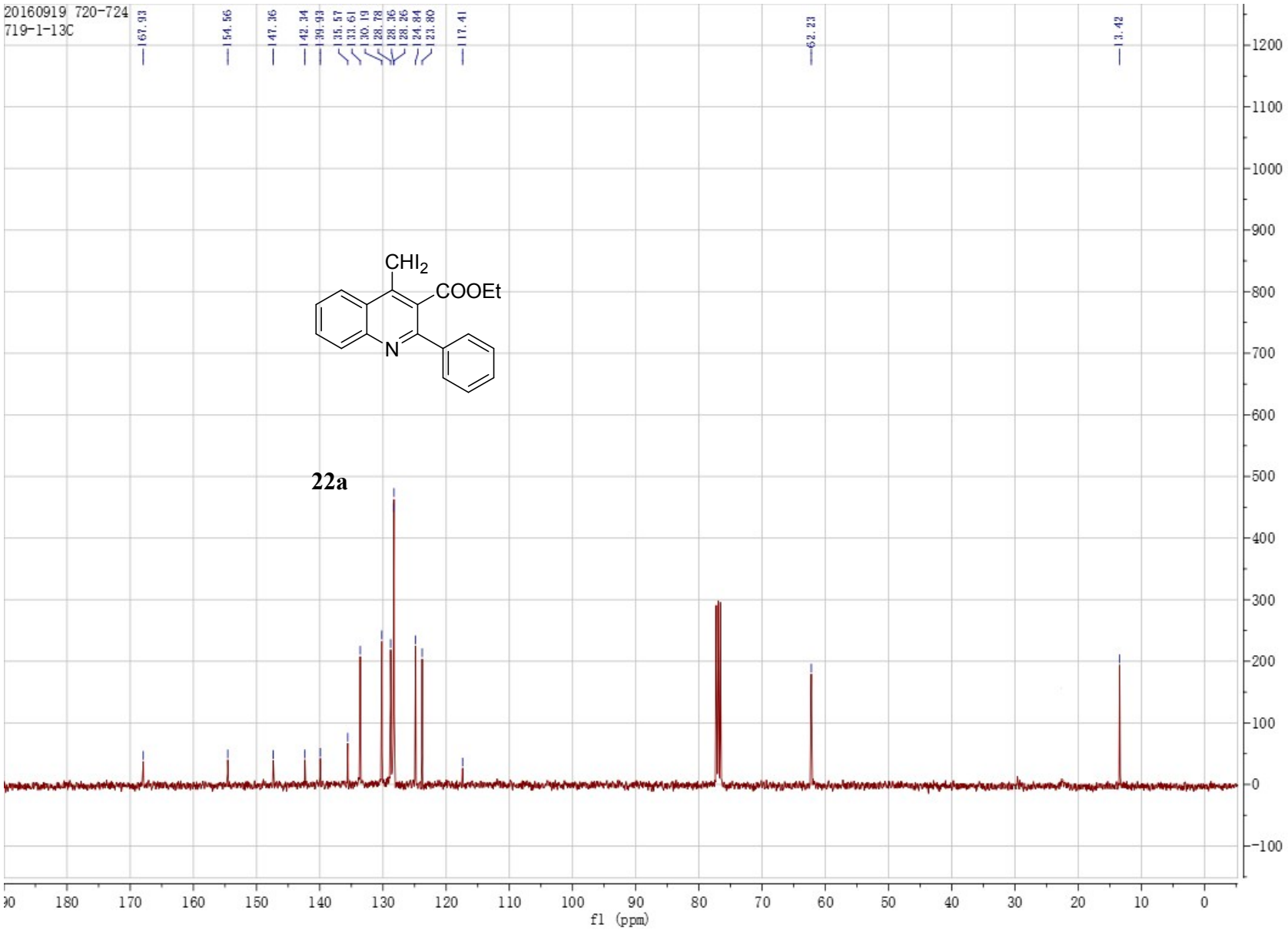

20160719
714b-13C
167.07
166.18
90.09
77.31
76.99
76.67
63.37
62.82
57.96
53.27
19.40
13.93
13.67
3.13
Me
COOEt
COOEt
O
I
I
18
f1 (ppm)

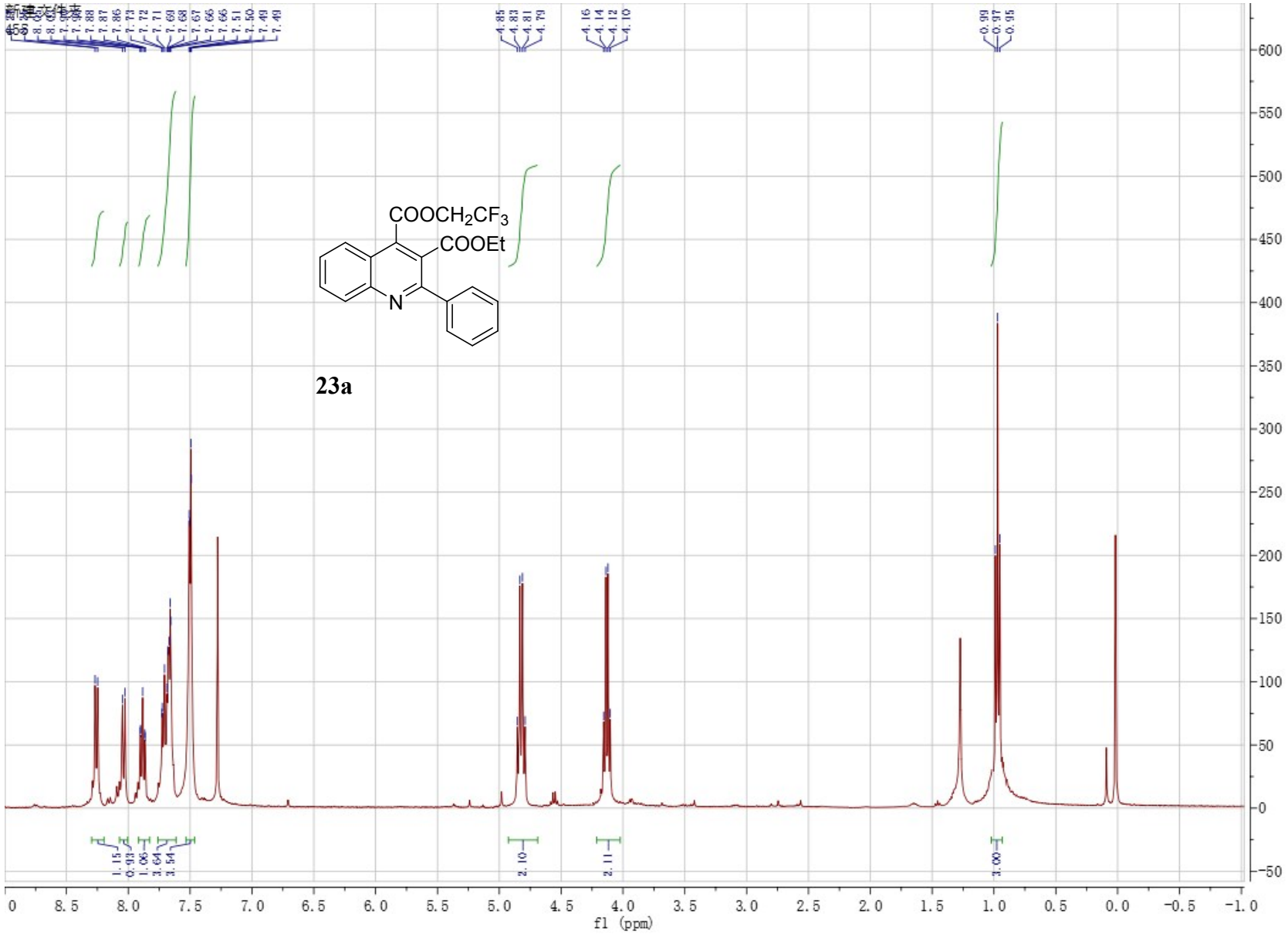

683
683-1H
COOEt
COOEt
O
I
I
20
4.34
4.32
4.30
4.29
4.27
4.26
4.25
4.23
3.80
3.78
3.76
3.64
3.62
3.57
2.92
2.90
2.89
2.88
1.46
1.44
1.34
1.33
1.31
1.29
1.28
40.00
11.08
9.68
9.82
18.97
28.18
28.12
33.47
f1 (ppm)

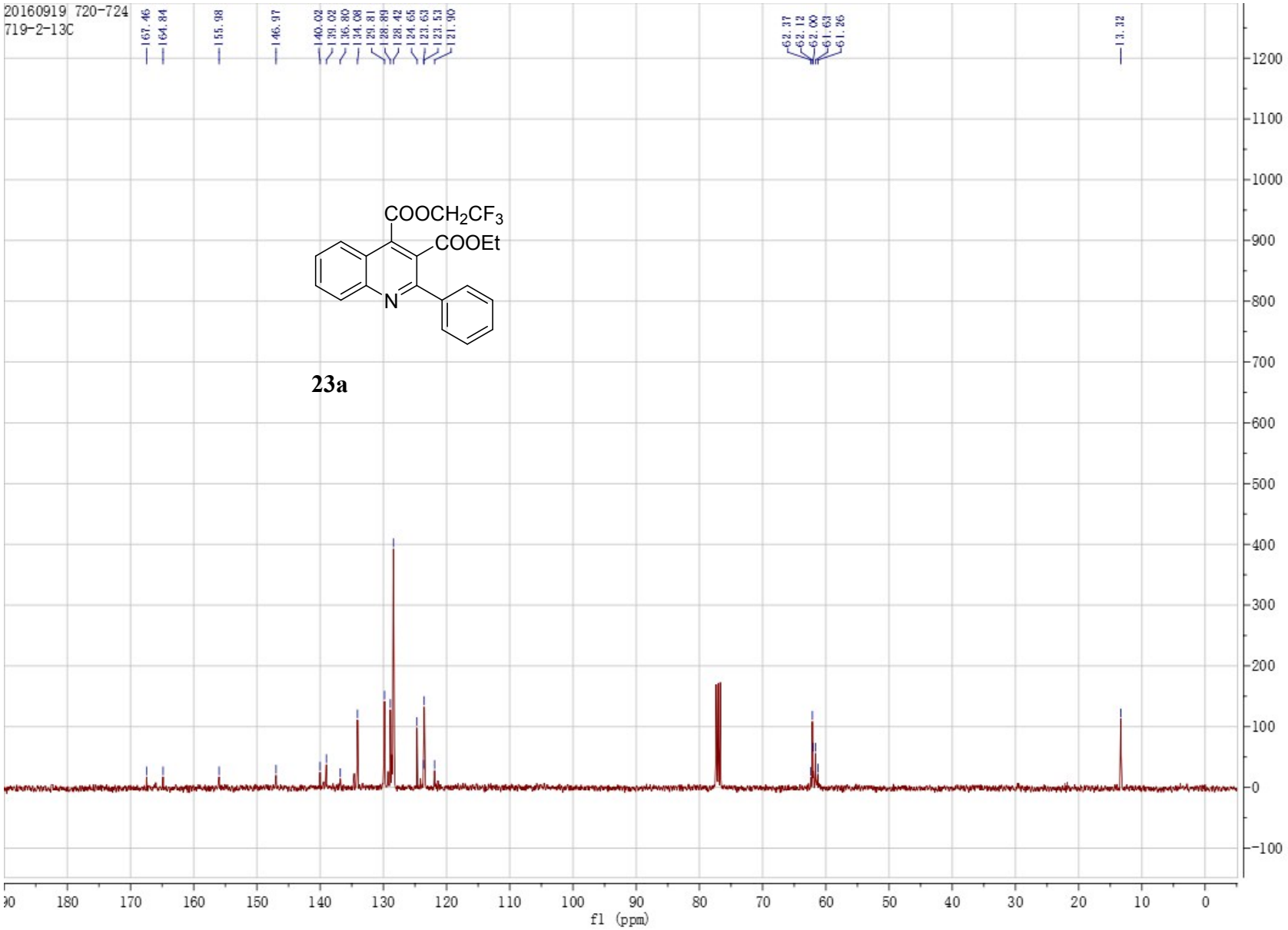

683
683-13C
167.02
166.37
113.71
78.53
77.28
76.96
76.64
66.76
63.24
62.79
52.77
50.53
19.24
13.97
13.71
0.96
COOEt
COOEt
O
I
I
f1 (ppm)

20

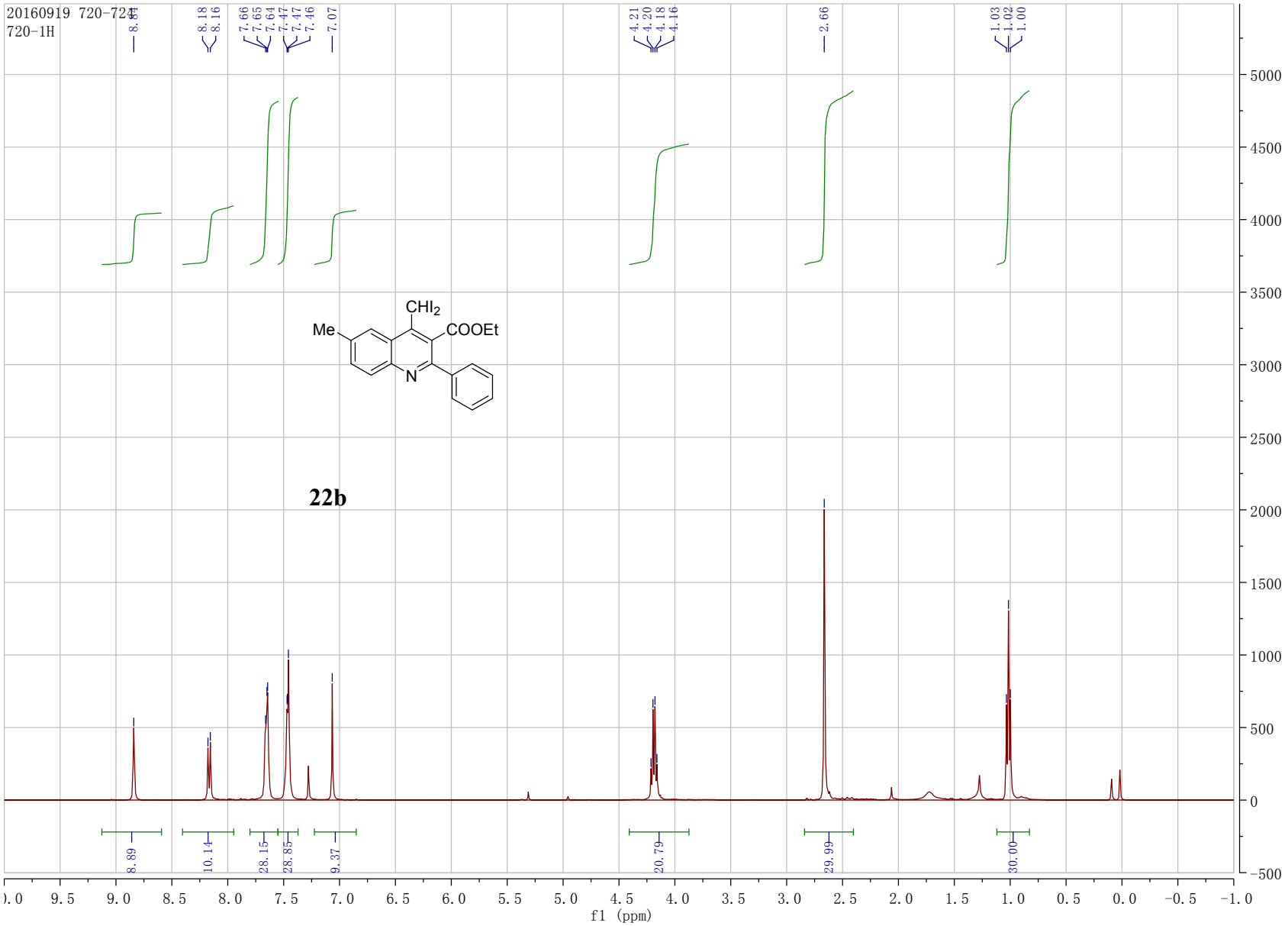

NMR
c534
CHI2
COOEt
N
22a
f1 (ppm)

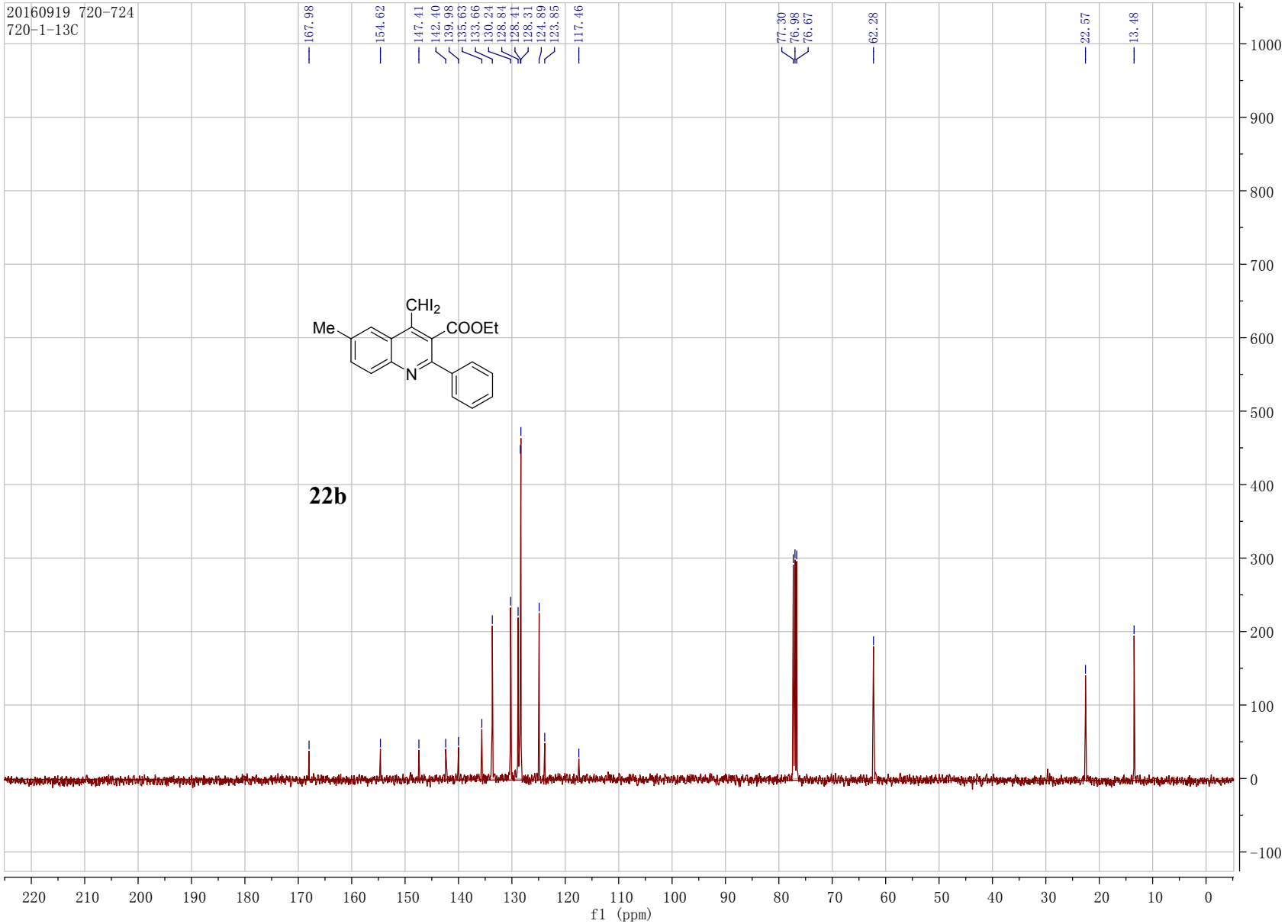

20160919 720-724
719-1-13C
167.93
154.56
147.36
142.34
139.93
135.57
133.61
130.19
128.78
128.36
128.26
124.84
123.86
117.41
62.23
13.42
CHI2
COOEt
N
22a
f1 (ppm)

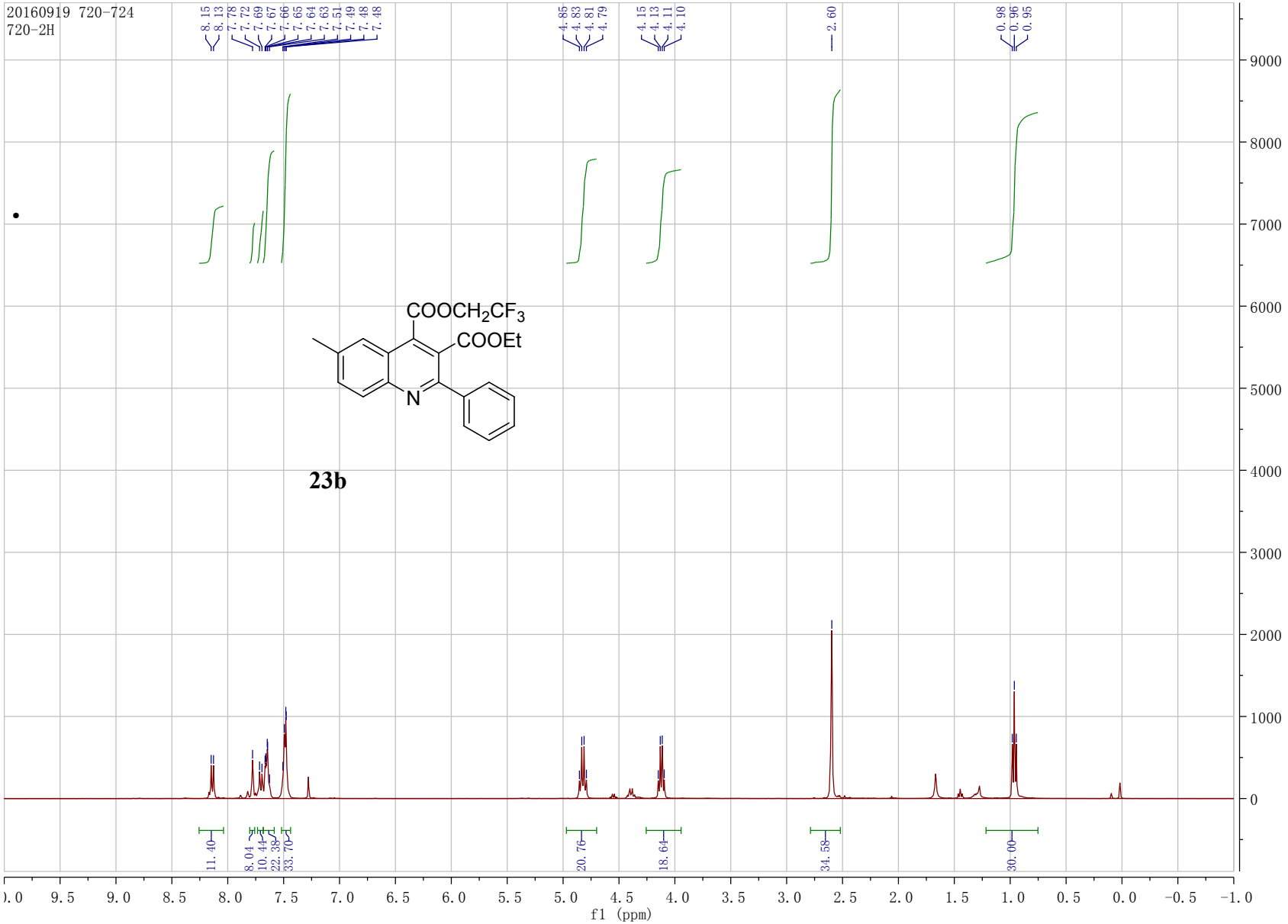

COOCH2CF3
COOEt
N
23a
f1 (ppm)

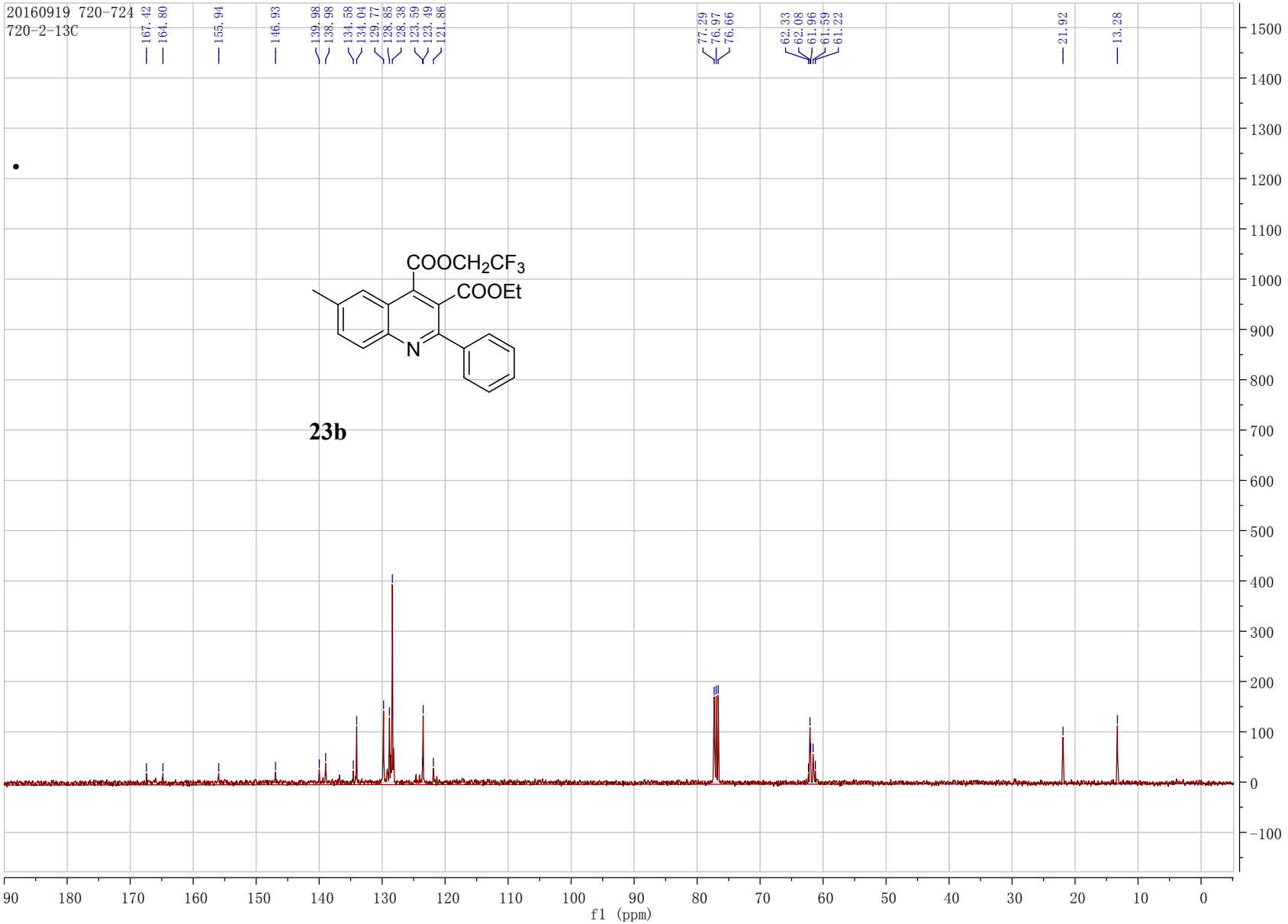

20160919 720-724
719-2-13C
167.46
164.84
155.98
146.97
140.02
139.02
135.80
134.08
129.81
128.89
128.42
124.65
123.63
123.53
121.90
62.37
62.12
62.00
61.63
61.26
13.32
COOCH2CF3
COOEt
N
f1 (ppm)

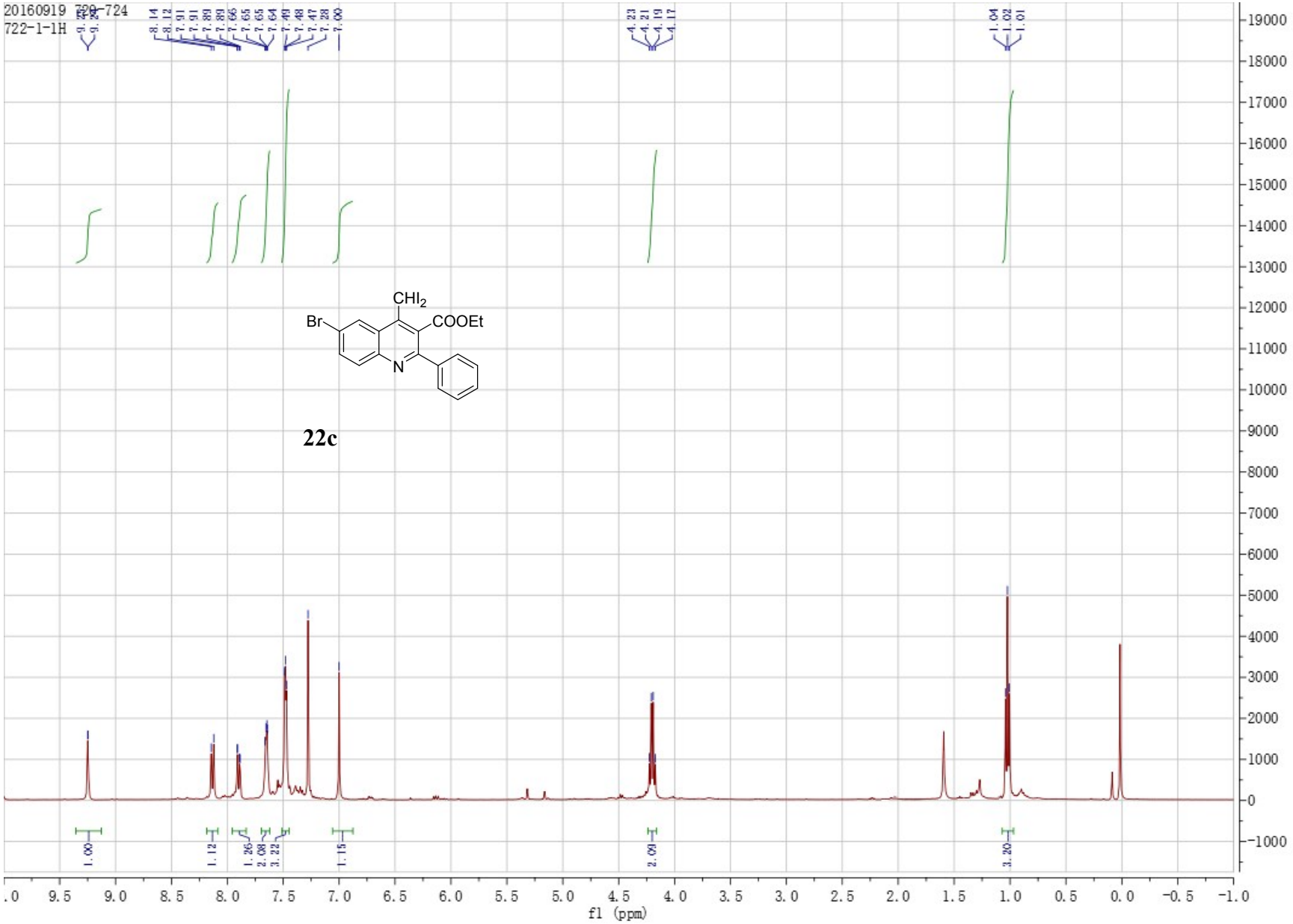
23a

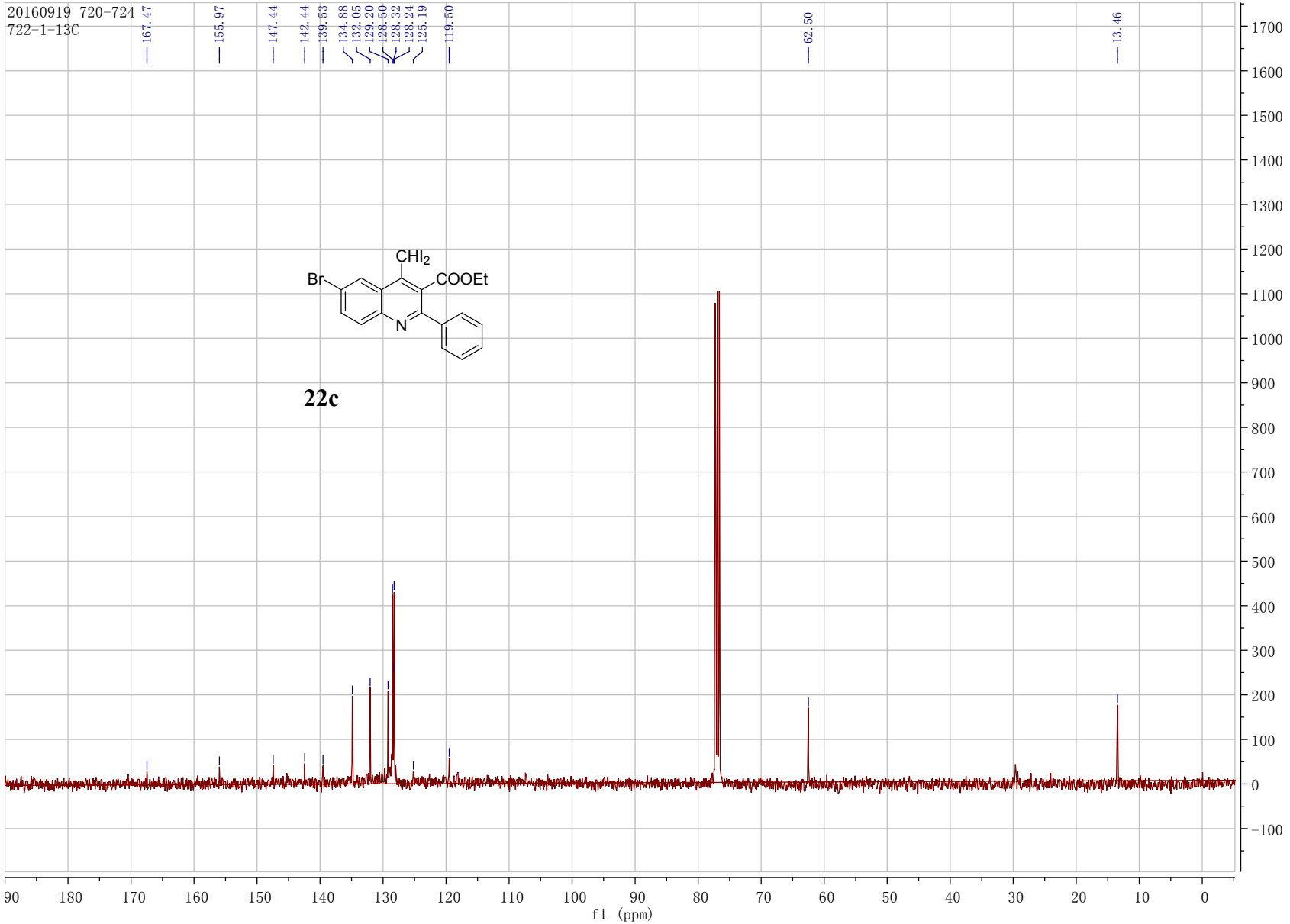

20160919 720-724
720-1H
8.89
8.18
8.16
7.66
7.65
7.64
7.47
7.47
7.46
7.07
4.21
4.20
4.18
4.16
2.66
1.03
1.02
1.00
CHI2
Me
COOEt
N
22b
8.89
10.14
28.15
28.85
9.37
20.79
29.99
30.00
f1 (ppm)

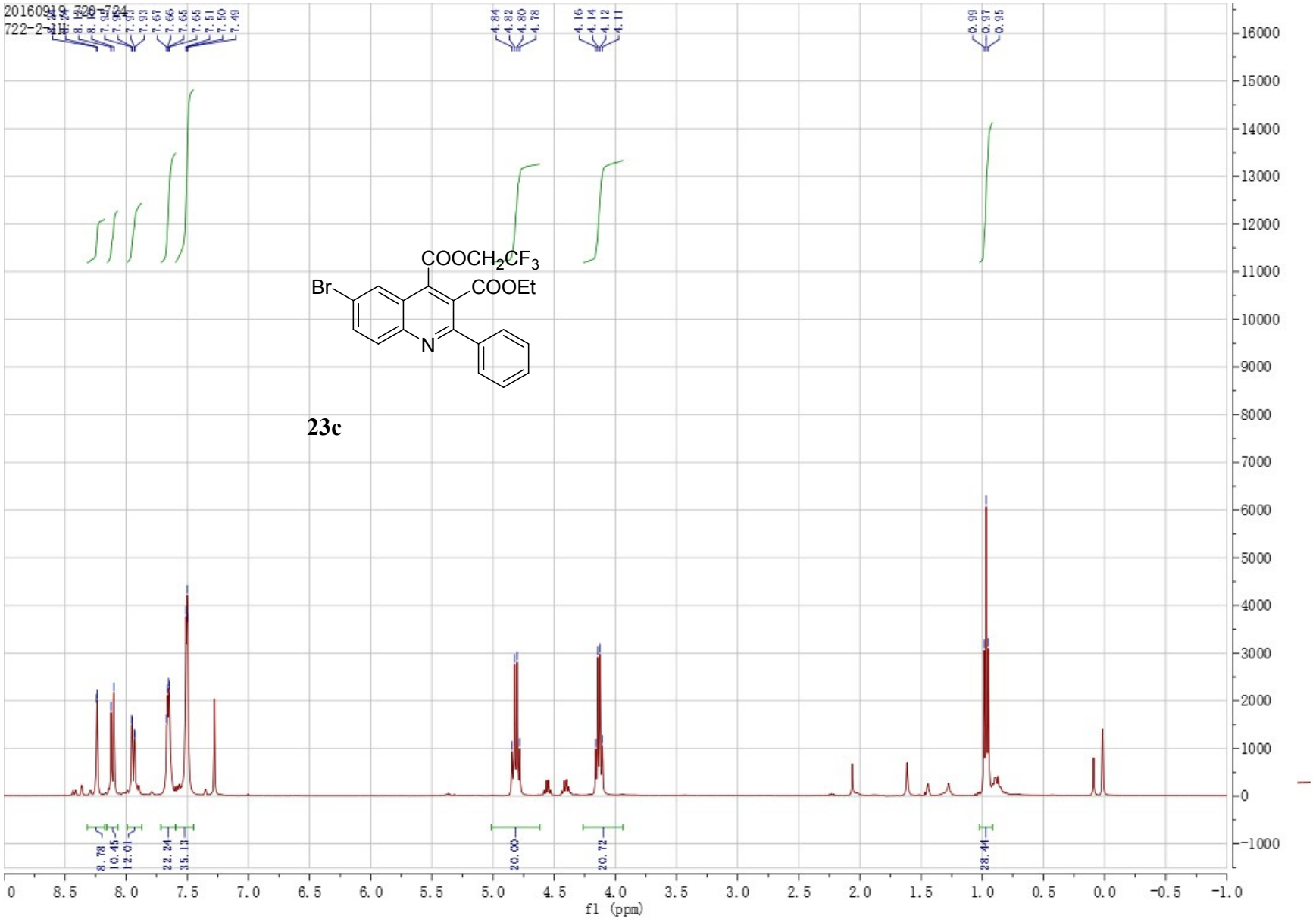

20160919 720-724
720-1-13C
167.98
154.62
147.41
142.40
139.98
135.63
133.66
130.24
128.84
128.41
128.31
124.89
123.85
117.46
77.30
76.98
76.67
62.28
22.57
13.48
CHI2
Me
COOEt
N
22b
f1 (ppm)

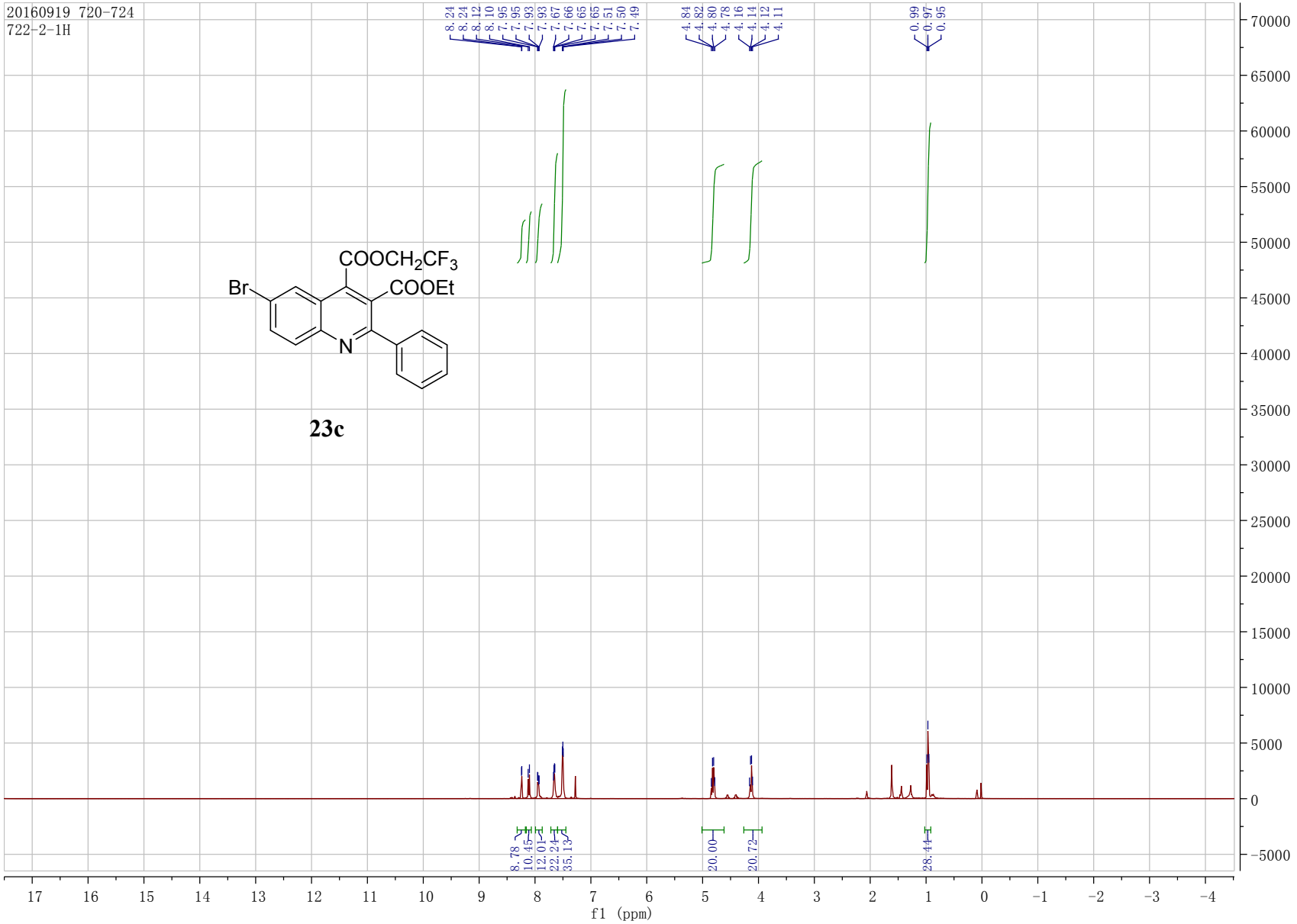

20160919 720-724
720-2H
8.15
8.13
7.78
7.72
7.69
7.67
7.66
7.65
7.64
7.63
7.51
7.49
7.48
7.48
4.85
4.83
4.81
4.79
4.15
4.13
4.11
4.10
2.60
0.98
0.96
0.95
COOCH2CF3
COOEt
N
23b
11.40
8.04
10.44
22.38
33.70
20.76
18.64
34.58
30.00
f1 (ppm)

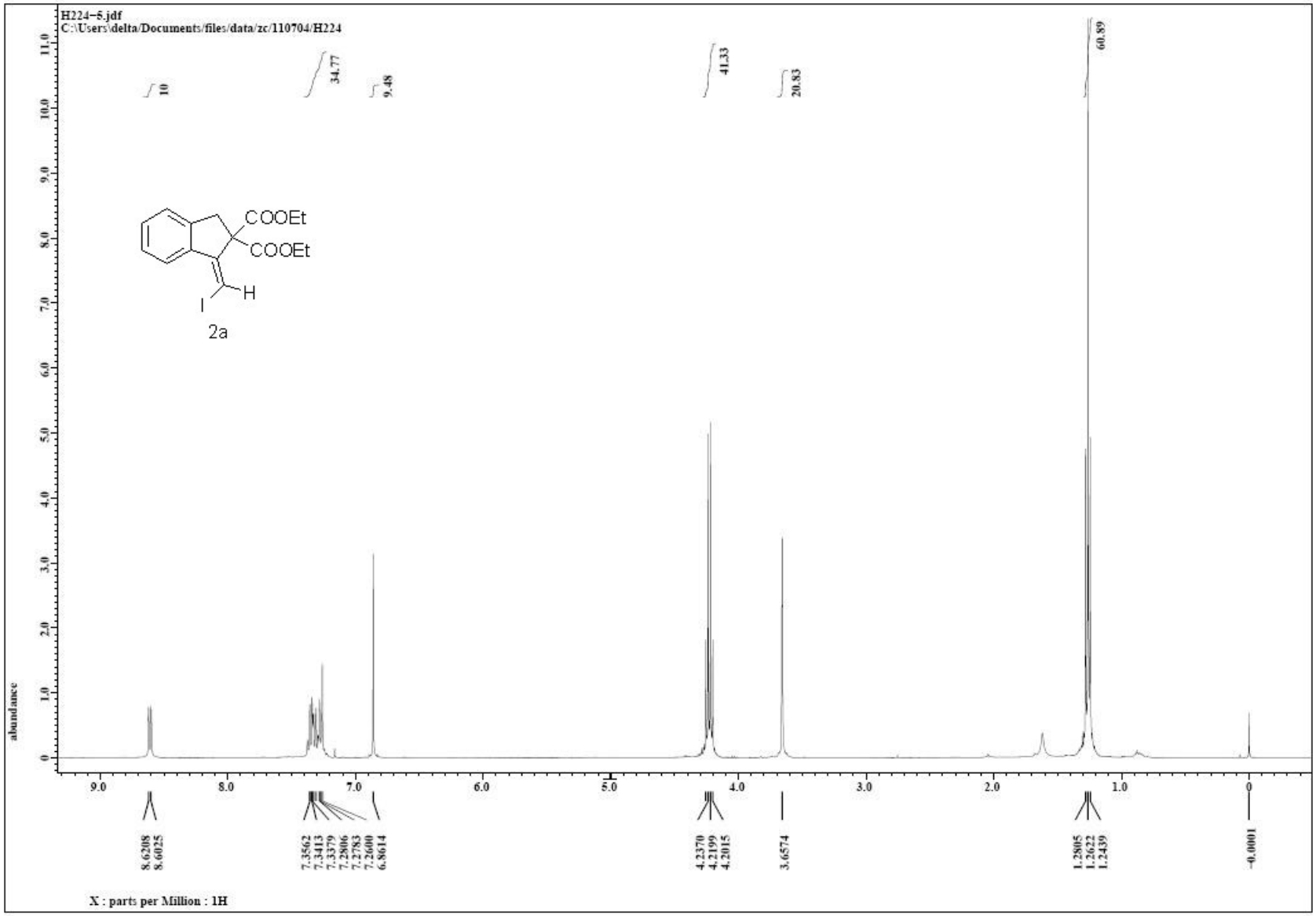

20160919 720-724
720-2-13C
167.42
164.80
155.94
146.93
139.98
138.98
134.58
134.04
129.77
128.85
128.38
123.59
123.49
121.86
77.29
76.97
76.66
62.33
62.08
61.96
61.59
61.22
21.92
13.28
COOCH2CF3
COOEt
N
23b
f1 (ppm)

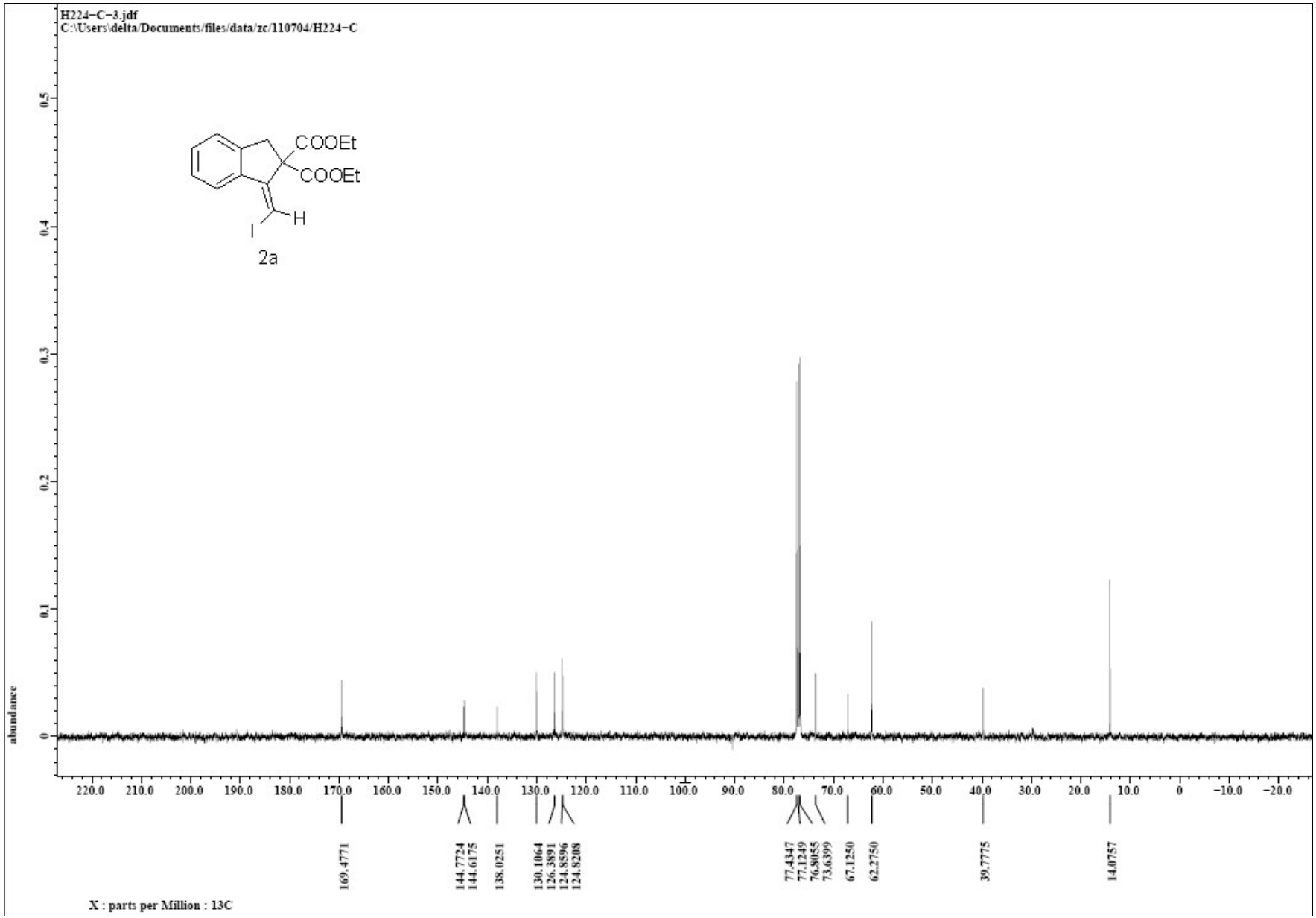

20160919 720-724
722-1-1H
CHI2
Br
COOEt
N
22c
f1 (ppm)

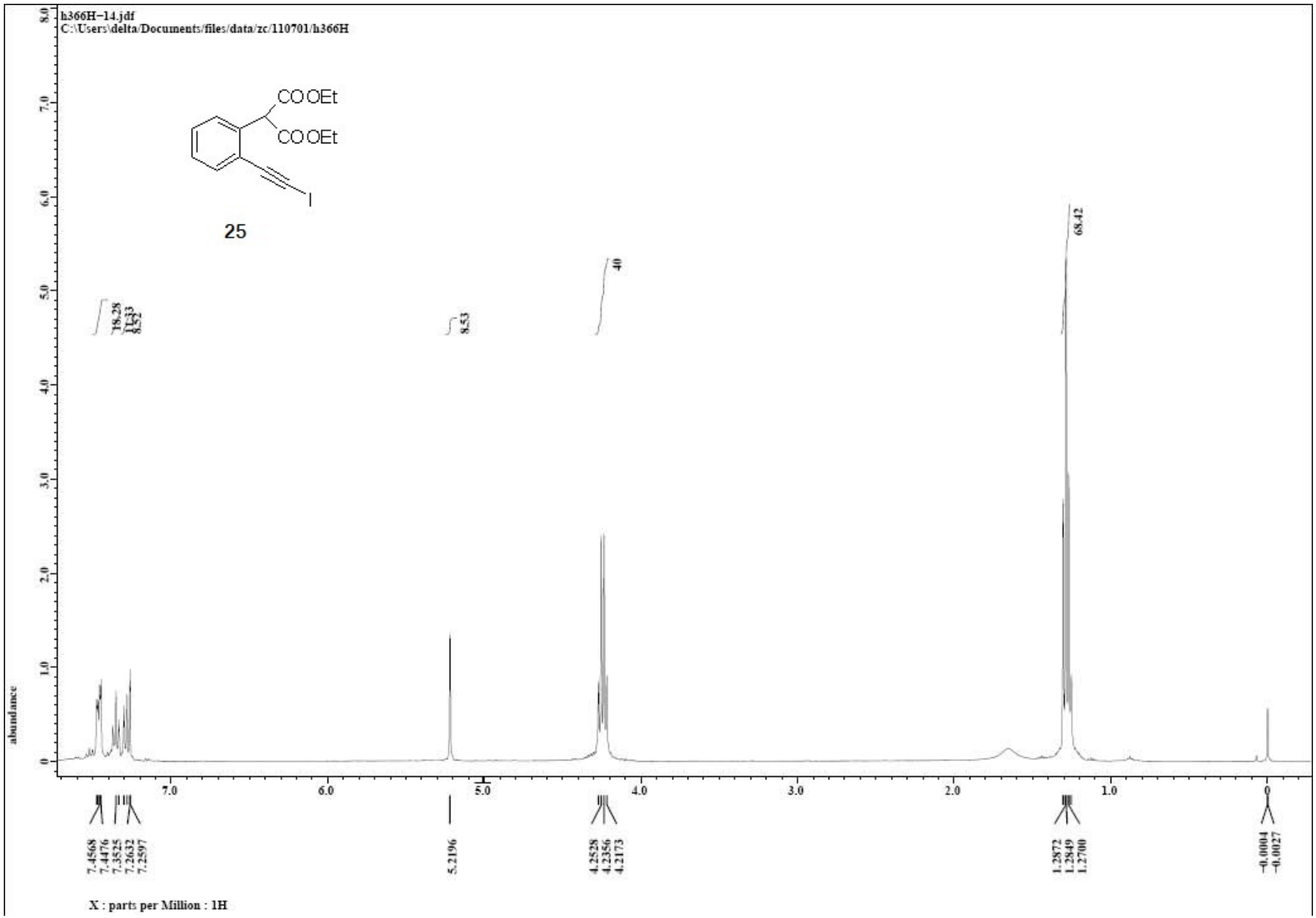

20160919 720-724
722-1-13C
167.47
155.97
147.44
142.44
139.53
134.88
132.05
129.20
128.50
128.32
128.24
125.19
119.50
62.50
13.46
CHI2
Br
COOEt
N
22c
f1 (ppm)

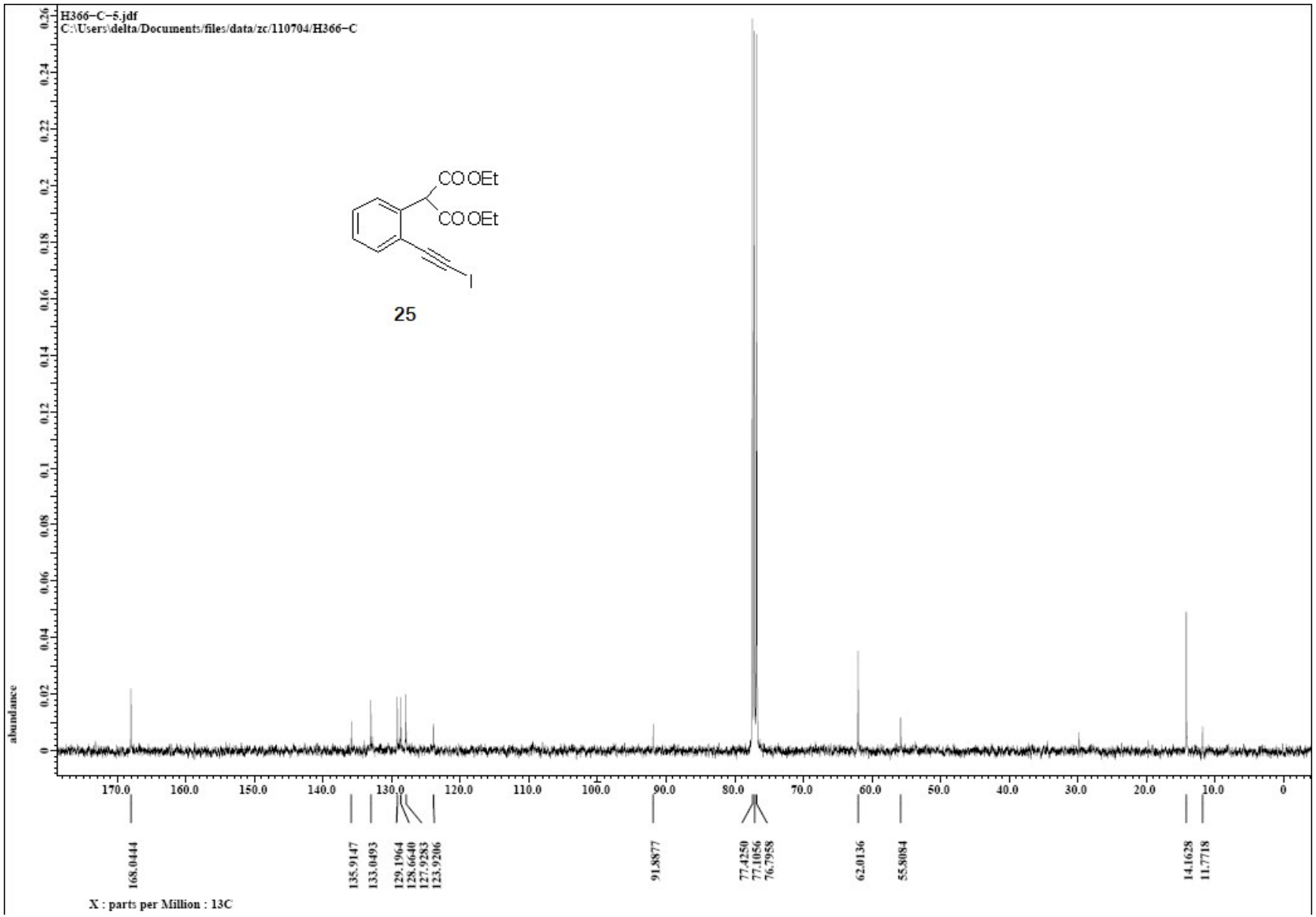

COOCH2CF3
COOEt
Br
N
23c
f1 (ppm)

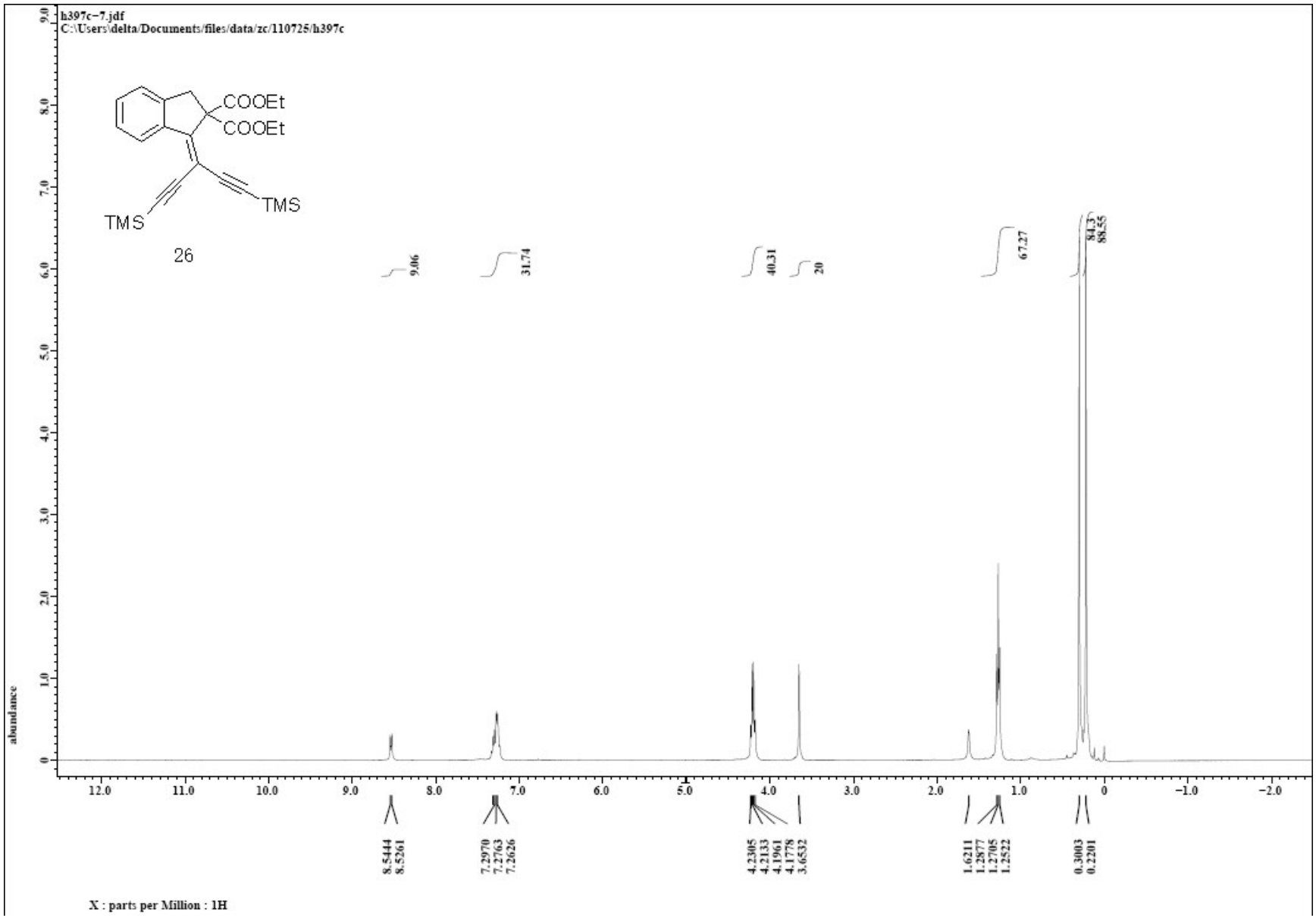

20160919 720-724
722-2-1H
8.24
8.24
8.12
8.10
7.95
7.95
7.93
7.93
7.67
7.66
7.65
7.65
7.51
7.50
7.49
4.84
4.82
4.80
4.78
4.16
4.14
4.12
4.11
0.99
0.97
0.95
COOCH2CF3
COOEt
Br
N
23c
8.78
10.45
12.01
22.24
35.13
20.00
20.72
28.44
f1 (ppm)

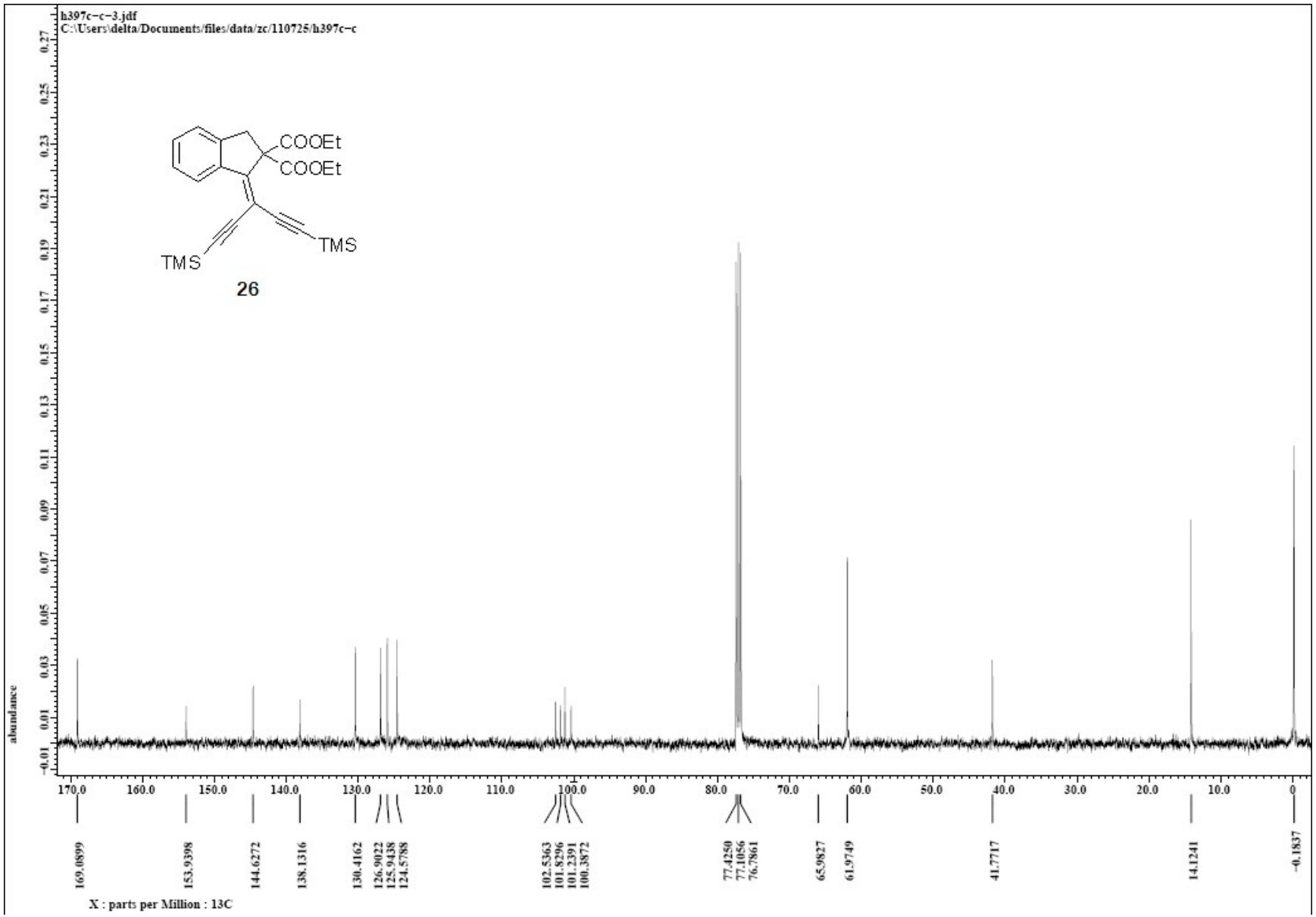

H224-5.jdf
C:\Users\delta/Documents/files/data/zc/110704/H224
10
34.77
9.48
41.33
20.83
60.89
COOEt
COOEt
H
I
2a
abundance
8.6208
8.6025
7.3562
7.3413
7.3379
7.2806
7.2783
7.2600
6.8614
4.2370
4.2199
4.2015
3.6574
1.2805
1.2622
1.2439
-0.0001
X : parts per Million : 1H

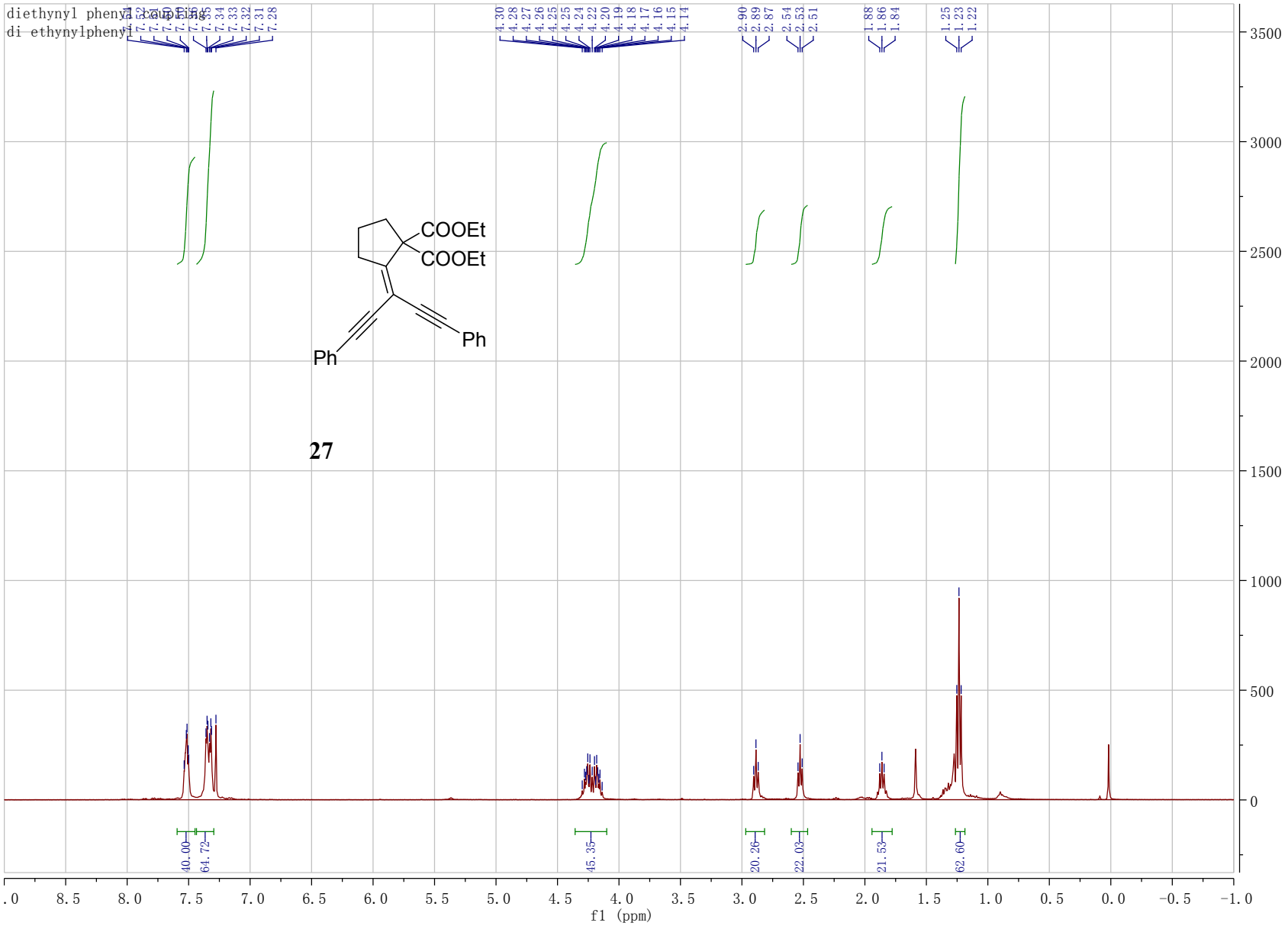

H224-C-3.jdf
C:\Users\delta/Documents/files/data/zc/110704/H224-C
COOEt
COOEt
H
I
2a
abundance
169.4771
144.7724
144.6175
138.0251
130.1064
126.3891
124.8596
124.8208
77.4347
77.1249
76.8055
73.6399
67.1250
62.2750
39.7775
14.0757
X : parts per Million : 13C

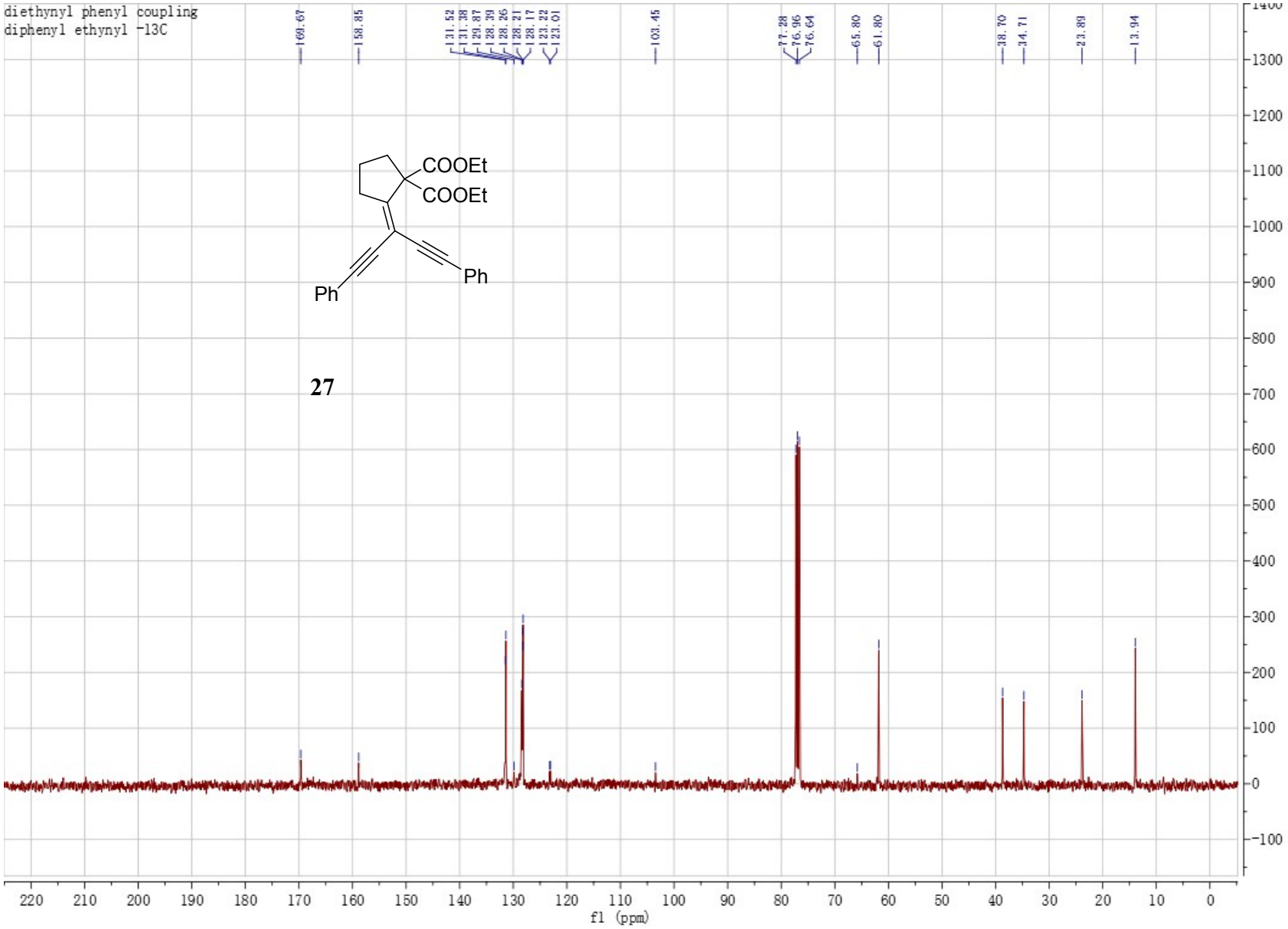

h366H-14.jdf
C:\Users\delta/Documents/files/data/zc/110701/h366H
COOEt
COOEt
I
25
18.28
11.33
8.52
8.53
40
68.42
abundance
7.4568
7.4476
7.3525
7.2632
7.2597
5.2196
4.2528
4.2356
4.2173
1.2872
1.2849
1.2700
-0.0004
-0.0027
X : parts per Million : 1H


H366-C-5.jdf
C:\Users\delta/Documents/files/data/zc/110704/H366-C
CO OEt
CO OEt
I
25
abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
0.26
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.0444
135.9147
133.0493
129.1964
128.6640
127.9283
123.9206
91.8877
77.4250
77.1056
76.7958
62.0136
55.5084
14.1628
11.7718
X : parts per Million : 13C


h397c-7.jdf
C:\Users\delta/Documents/files/data/zc/110725/h397c
COOEt
COOEt
TMS
TMS
26
9.06
31.74
40.31
20
67.27
84.3
88.55
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.5444
8.5261
7.2970
7.2763
7.2626
4.2305
4.2133
4.1961
4.1778
3.6532
1.6211
1.2877
1.2705
1.2522
0.3003
0.2201
X : parts per Million : 1H


h397c-c-3.jdf
C:\Users\delta\Documents/files/data/zc/110725/h397c-c
COOEt
COOEt
TMS
TMS
26
abundance
169.0899
153.9398
144.6272
138.1316
130.4162
126.9022
125.9438
124.5788
102.5363
101.8296
101.2391
100.3872
77.4250
77.1056
76.7861
65.9827
61.9749
41.7717
14.1241
-0.1837
X : parts per Million : 13C


diethynyl phenyl malonate
di ethynylphenyl
COOEt
COOEt
Ph
Ph
27
f1 (ppm)


diethynyl phenyl coupling
diphenyl ethynyl -13C
169.67
158.85
131.52
131.38
129.87
128.39
128.26
128.21
128.17
123.22
123.01
103.45
77.28
76.96
76.64
65.80
61.80
38.70
34.71
23.89
13.94
COOEt
COOEt
Ph
Ph
27
f1 (ppm)