

Supporting Information

Copper-Catalyzed Stereodefined Synthesis of Halogenated Spirohydrofurans

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1. General Information

EtOAc refers to ethyl acetate, PE refers to Petroleum Ethers (60–90 °C), DCM refers to dichloromethane, THF refers to tetrahydrofuran, DMF refers to *N,N*-dimethylformamide. Unless otherwise stated, all other starting materials and solvents were commercially available and used without further purification. Dried THF was delivered from an Innovation Technology solvent system. ¹HNMR (¹³C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl₃ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, m = multiplet), coupling constant (Hz)]. HRMS (APCI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. **3o** was confirmed by X-ray diffraction analysis (Figure S1).

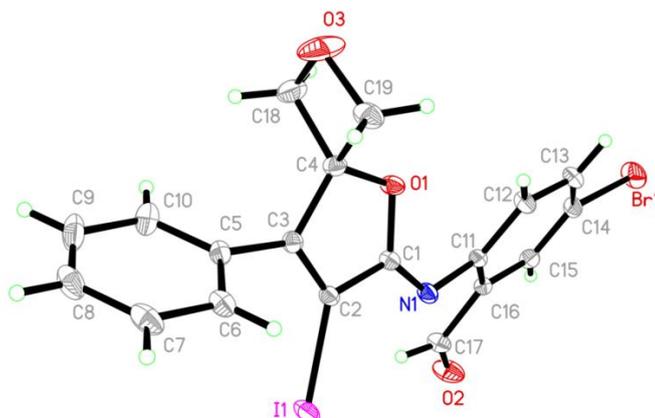
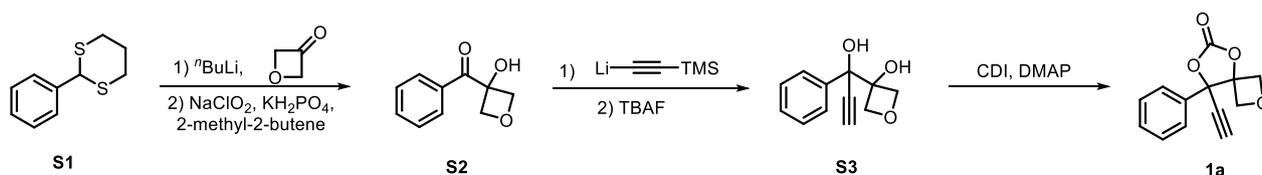


Figure S1. X-Ray Structure of **3o**

2. General procedure for the preparation of compounds **1**

Example for the synthesis of **1a**



To a dry flask were added THF (30 mL) and **S1** (1.96 g, 10 mmol) and the flask was cooled to $-30\text{ }^{\circ}\text{C}$. *n*-BuLi (6.0 mL, 2.5 M in Hexane, 15 mmol) was added to the mixture, which was left stirring at $-30\text{ }^{\circ}\text{C}$ for 1 h, then oxetan-3-one (0.87 mL, 15 mmol) was added to the reaction mixture and the reaction mixture was warmed to $-10\text{ }^{\circ}\text{C}$. After 2.5 h, the reaction was quenched with saturated NH₄Cl solution (20 mL). The product was extracted with ethyl acetate (30 mL \times 3), and dried over anhydrous Na₂SO₄. After filtration and evaporation in vacuo, to a solution of the residue (3.5 g, 9.2 mmol) in 50 mL of EtOH was successively added 2-methyl-2-butene (10.0 mL, 92 mmol), KH₂PO₄ (2.63 g, 19.3 mmol, dissolved in 10 mL of water) and NaClO₂ (6.24 g, 69 mmol) at $0\text{ }^{\circ}\text{C}$. After stirring for 30 min, the reaction was quenched with saturated Na₂S₂O₃ solution (80 mL). The product was extracted with ethyl acetate (50 mL \times 3), and dried over anhydrous Na₂SO₄. After filtration and evaporation in vacuo, the residue was

purified with flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 2:1) to afford **S2** (1.13 g, 52% yield).

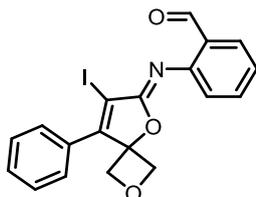
To a dry flask were added THF (5 mL) and ethynyltrimethylsilane (1.8 mL, 12.5 mmol) and the flask was cooled to $-78\text{ }^{\circ}\text{C}$. $n\text{-BuLi}$ (5.0 mL, 2.5 M in Hexane, 12.5 mmol) was added to the mixture, which was left stirring at $-78\text{ }^{\circ}\text{C}$ for 5 min, then allowed to warm to room temperature. In addition, a solution of **S2** (0.89 g, 5 mmol) in THF (15 mL) was cooled to $-78\text{ }^{\circ}\text{C}$. To this mixture was slowly added the solution of ((trimethylsilyl)ethynyl) lithium. After the addition, the reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was then allowed to warm to room temperature, and it was stirred for 2 h. the reaction was quenched with saturated NH_4Cl (20 mL) solution. The product was extracted with ethyl acetate (15 mL \times 3), and dried over anhydrous Na_2SO_4 . After filtration and evaporation in vacuo, to a solution of the residue (1.12 g, 4.2 mmol) in 10 mL of THF was added TBAF (4.42 g, 17 mmol) at room temperature. After stirring for 30 min, the reaction was quenched with saturated NH_4Cl solution. The product was extracted with ethyl acetate (30 mL \times 3), and dried over anhydrous Na_2SO_4 . After filtration and evaporation in vacuo, the residue (**S3**) was directly used to the next step without purification. To the resulting crude mixture was added CH_2Cl_2 (15 mL), DMAP (207.2 mg, 1.7 mmol), Et_3N (1.2 mL, 8.4 mmol), and 1,1'-carbonyldiimidazole (1.4 g, 8.4 mmol). The mixture was stirred at room temperature overnight. After removing the solvent under vacuum, the crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford product **1a** (552 mg, 48% yield) as a yellow oil.

3. General procedure for the synthesis of compounds 3

To a 25 mL sealed tube equipped with a stir bar was added CuOTf (8.5 mg, 0.04 mmol, 20 mol%), 1,10-phen (9.0 mg, 0.05 mmol, 25 mol%) and DCE (1.0 mL) under air atmosphere. The mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 30 min. Subsequently, propargylic cyclic carbonate **1** (0.2 mmol, 1.0 equiv), benzo[*c*]isoxazole **2** (0.3 mmol, 1.5 equiv), NaI (60 mg, 0.4 mmol, 2.0 equiv), 18-crown-6 (63.4 mg, 0.24 mmol, 1.2 equiv) and DCE (2.0 mL) were added. The resulting mixture was then stirred at $110\text{ }^{\circ}\text{C}$ for 5 h. Upon completion, the mixture was filtered and the clear filtrate was collected. After removing the solvents *in vacuo*, the crude product obtained was purified by flash column chromatography on silica gel to give the desired product **3**.

4. Characterization data of compounds 3

(Z)-2-((7-iodo-8-phenyl-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (**3a**)

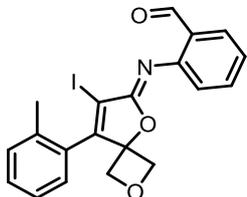


White solid (64.7 mg, 75% yield); *Z/E* = 14:1.

m.p. $124\text{--}126\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 10.51 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.66 - 7.57 (m, 6H), 7.33 (d, J = 8.0 Hz, 1H), 7.28-7.26 (m, 2H), 4.98 (d, J = 8.0 Hz, 2H), 4.92 (d, J = 7.6 Hz, 2H); $^{13}\text{C NMR}$ (100

MHz, Chloroform-*d*) δ 191.9, 159.5, 158.1, 148.8, 134.7, 130.5, 129.4, 128.2, 127.8, 127.5, 124.9, 123.1, 92.4, 78.9; **IR** (KBr, ν , cm^{-1}) 3011, 1741, 1682, 1590, 1488, 1382, 1187, 1001, 975, 810. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{15}\text{INO}_3$ 432.0097; Found 432.0091.

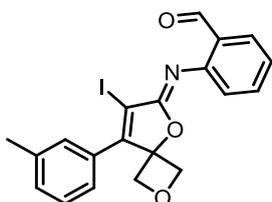
(Z)-2-((7-iodo-8-(*o*-tolyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3b)



White solid (50.7 mg, 57% yield); $Z/E = 17:1$.

m.p. 114-115 °C; **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*): δ 10.52 (s, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.47 - 7.36 (m, 4H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 5.09 (d, $J = 7.6$ Hz, 1H), 4.91 - 4.87 (m, 2H), 4.72 (d, $J = 7.6$ Hz, 1H), 2.28 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, Chloroform-*d*) δ 191.9, 161.0, 157.8, 148.5, 135.5, 134.7, 131.3, 131.1, 130.1, 128.6, 128.3, 127.5, 126.7, 124.9, 123.3, 93.9, 92.9, 78.2, 77.8, 19.8; **IR** (KBr, ν , cm^{-1}) 2911, 2855, 1760, 1662, 1548, 1443, 1387, 1193, 1013, 982, 805. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}_3$ 446.0253; Found 446.0247.

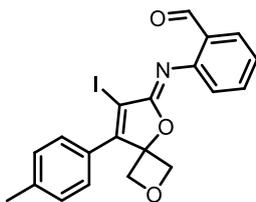
(Z)-2-((7-iodo-8-(*m*-tolyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3c)



White solid (56.9 mg, 64% yield); $Z/E = 20:1$.

m.p. 104-105 °C; **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*): δ 10.50 (s, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.47 - 7.44 (m, 1H), 7.41 - 7.31 (m, 4H), 7.24 (t, $J = 7.2$ Hz, 1H), 4.95 (d, $J = 7.6$ Hz, 2H), 4.92 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, Chloroform-*d*) δ 191.9, 159.9, 158.2, 148.9, 139.2, 134.7, 131.6, 131.3, 129.4, 129.3, 128.5, 128.3, 128.1, 124.9, 124.8, 123.2, 92.5, 90.1, 78.8, 21.7; **IR** (KBr, ν , cm^{-1}) 3032, 1766, 1642, 1554, 1466, 1392, 1177, 995, 966, 815. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}_3$ 446.0253; Found 446.0252.

(Z)-2-((7-iodo-8-(*p*-tolyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3d)

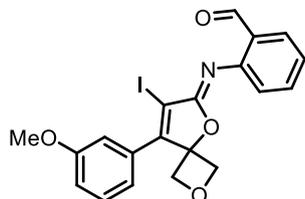


White solid (63.2 mg, 71% yield); $Z/E = 10:1$.

m.p. 119-120 °C; **$^1\text{H NMR}$** (400 MHz, Chloroform-*d*): δ 10.50 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.62 - 7.56 (m,

3H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 4.97 (d, $J = 7.6$ Hz, 2H), 4.91 (d, $J = 7.6$ Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 191.9, 159.3, 158.3, 148.9, 141.0, 134.7, 130.1, 128.5, 128.1, 127.7, 124.8, 123.2, 92.4, 89.3, 79.1, 21.6; IR (KBr, ν , cm^{-1}) 3044, 1768, 1646, 1561, 1492, 1402, 1200, 1023, 985, 801. HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}_3$ 446.0253; Found 446.0253.

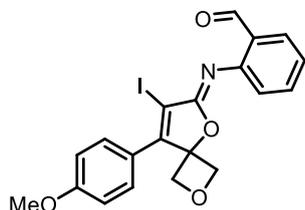
(Z)-2-((7-iodo-8-(3-methoxyphenyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3e)



White solid (60.8 mg, 66% yield); $Z/E > 20:1$.

m.p. 103-105 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Chloroform- d): δ 10.53 (s, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.62 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.30 - 7.28 (m, 1H), 7.24 - 7.20 (m, 2H), 7.11 (d, $J = 8.4$ Hz, 1H), 4.99 (d, $J = 7.6$ Hz, 2H), 4.96 (d, $J = 7.6$ Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 191.8, 160.0, 159.3, 158.0, 148.7, 134.6, 132.6, 130.6, 128.4, 128.1, 124.8, 123.1, 119.8, 115.9, 113.6, 92.4, 90.2, 78.8, 55.5; IR (KBr, ν , cm^{-1}) 3042, 1738, 1650, 1582, 1477, 1380, 1177, 1030, 980. HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}_4$ 462.0202; Found 462.0204.

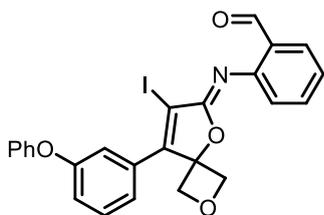
(Z)-2-((7-iodo-8-(4-methoxyphenyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3f)



White solid (67.3 mg, 73% yield); $Z/E = 10:1$.

m.p. 114-116 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Chloroform- d): δ 10.50 (s, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.58 (t, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 5.00 (d, $J = 7.6$ Hz, 2H), 4.93 (d, $J = 7.6$ Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 192.0, 161.4, 158.4, 158.2, 149.0, 134.7, 129.6, 128.5, 128.1, 124.7, 123.2, 114.8, 114.8, 92.2, 87.7, 79.4, 78.7, 55.6; IR (KBr, ν , cm^{-1}) 2950, 1743, 1685, 1593, 1488, 1392, 1201, 1011, 967, 818. HRMS (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}_4$ 462.0202; Found 462.0202.

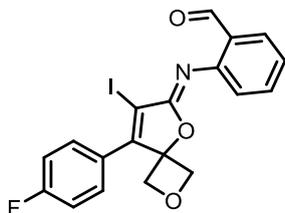
(Z)-2-((7-iodo-8-(4-methoxyphenyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3g)



White solid (64.8 mg, 62% yield); $Z/E = 10:1$.

m.p. 121-123 °C; $^1\text{H NMR}$ (400 MHz, Chloroform- d): δ 10.49 (s, 1H), 7.91 (d, $J = 7.6$ Hz, 1H), 7.61 - 7.52 (m, 2H), 7.43 - 7.39 (m, 2H), 7.35 - 7.30 (m, 2H), 7.26 - 7.17 (m, 4H), 7.13 (d, $J = 7.6$ Hz, 2H), 4.97 (d, $J = 8.0$ Hz, 2H), 4.89 (d, $J = 8.0$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, Chloroform- d) δ 191.8, 158.9, 158.3, 157.9, 156.2, 148.6, 134.6, 133.0, 130.9, 130.1, 130.1, 128.4, 128.2, 124.9, 124.3, 123.0, 122.0, 120.2, 119.7, 119.7, 117.6, 92.3, 90.6, 78.8; **IR** (KBr, ν , cm^{-1}) 3033, 1757, 1666, 1591, 1454, 1377, 1195, 1001, 976, 821. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{19}\text{INO}_4$ 524.0359; Found 524.0357.

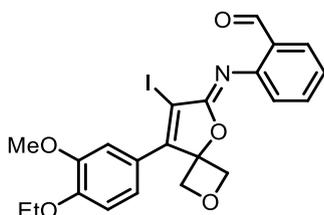
(Z)-2-((8-(4-fluorophenyl)-7-iodo-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3h)



White solid (65.4 mg, 73% yield); $Z/E = 8:1$.

m.p. 111-113 °C; $^1\text{H NMR}$ (400 MHz, Chloroform- d): δ 10.49 (s, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.74 - 7.70 (m, 2H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.34 - 7.27 (m, 3H), 7.26 - 7.24 (m, 1H), 4.99 (d, $J = 8.0$ Hz, 2H), 4.88 (d, $J = 7.6$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, Chloroform- d) δ 191.9, 163.9 (d, $J_{CF} = 251.1$ Hz), 158.2, 157.9, 148.6, 134.7, 130.1 ($^4J_{CF} = 8.5$ Hz), 128.5, 128.3, 127.4 ($J_{CF} = 3.4$ Hz), 124.9, 123.1, 116.7 ($J_{CF} = 21.7$ Hz), 92.2, 90.4, 78.9; **IR** (KBr, ν , cm^{-1}) 3012, 1749, 1652, 1591, 1472, 1384, 1183, 1009, 966, 833. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{14}\text{FINO}_4$ 450.0002; Found 450.0007.

(Z)-2-((8-(4-ethoxy-3-methoxyphenyl)-7-iodo-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3i)

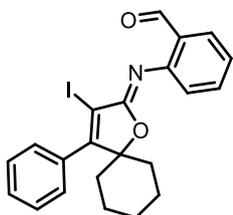


White solid (73.7 mg, 73% yield); $Z/E > 20:1$.

m.p. 124-126 °C; $^1\text{H NMR}$ (400 MHz, Chloroform- d): δ 10.45 (s, 1H), 8.01 (s, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.61 - 7.53 (m, 2H), 7.26 - 7.24 (m, 1H), 7.04 (d, $J = 8.8$ Hz, 1H), 5.03 (d, $J = 8.0$ Hz, 2H), 4.98 (d, $J = 7.6$ Hz, 2H), 4.21 (q, $J = 7.2$ Hz, 2H), 3.97 (s, 3H), 1.53 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, Chloroform- d) δ 190.6, 158.9,

157.8, 150.7, 149.3, 147.7, 137.3, 130.7, 130.0, 125.1, 122.7, 121.0, 118.1, 112.4, 111.3, 92.4, 86.4, 79.7, 64.5, 56.2, 14.7; **IR** (KBr, ν , cm^{-1}) 2933, 1762, 1659, 1577, 1482, 1372, 1184, 1005, 979, 816. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{INO}_5$ 506.0464; Found 506.0464.

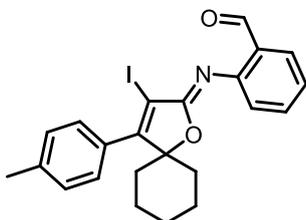
(Z)-2-((3-iodo-4-phenyl-1-oxaspiro[4.5]dec-3-en-2-ylidene)amino)benzaldehyde (3j)



White solid (48.5 mg, 53% yield); $Z/E > 20:1$.

m.p. 108-110 °C; **^1H NMR** (400 MHz, Chloroform- d): δ 10.59 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.45 - 7.52 (m, 3H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.26 - 7.16 (m, 3H), 1.78 (d, $J = 13.2$ Hz, 2H), 1.72 - 1.64 (m, 5H), 1.61 - 1.51 (m, 2H), 1.11 - 1.01 (m, 1H); **^{13}C NMR** (100 MHz, Chloroform- d) δ 192.3, 170.2, 159.7, 149.7, 134.5, 133.8, 129.4, 128.9, 128.8, 127.6, 127.5, 124.2, 123.5, 95.8, 89.3, 34.0, 24.3, 22.1; **IR** (KBr, ν , cm^{-1}) 3031, 1758, 1660, 1588, 1475, 1380, 1191, 1007, 976, 811. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{INO}_2$ 458.0617; Found 458.0617.

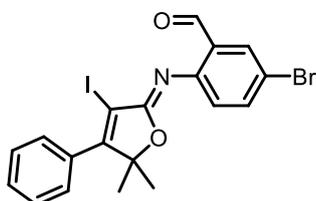
(Z)-2-((3-iodo-4-(p-tolyl)-1-oxaspiro[4.5]dec-3-en-2-ylidene)amino)benzaldehyde (3k)



White solid (46.2 mg, 49% yield); $Z/E > 20:1$.

m.p. 104-106 °C; **^1H NMR** (400 MHz, Chloroform- d): δ 10.58 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 1.78 - 1.72 (m, 3H), 1.68 - 1.61 (m, 5H), 1.57 - 1.54 (m, 1H), 1.11 - 1.01 (m, 1H); **^{13}C NMR** (100 MHz, Chloroform- d) δ 192.3, 170.3, 159.8, 149.8, 139.5, 134.5, 130.7, 129.6, 128.7, 127.5, 127.4, 124.2, 123.5, 95.8, 89.1, 34.1, 24.3, 22.1, 21.5; **IR** (KBr, ν , cm^{-1}) 3013, 1766, 1661, 1584, 1476, 1388, 1190, 1001, 966, 845. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{23}\text{INO}_2$ 472.0773; Found 472.0773.

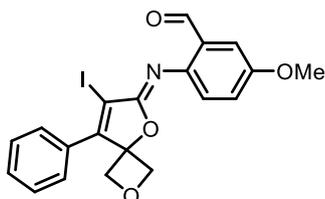
(Z)-5-bromo-2-((3-iodo-5,5-dimethyl-4-phenylfuran-2(5H)-ylidene)amino)benzaldehyde (3l)



White solid (67.2 mg, 68% yield); *Z/E* = 10:1.

m.p. 94-96 °C; ¹H NMR (400 MHz, Chloroform-*d*): δ 10.33 (s, 1H), 7.97 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.54 - 7.46 (m, 6H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 1.67 (s, 6H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.6, 165.2, 162.7, 149.6, 137.2, 130.3, 129.4, 129.1, 127.3, 125.7, 118.0, 117.0, 92.1, 26.6; IR (KBr, ν, cm⁻¹) 3032, 1734, 1648, 1565, 1461, 1362, 1175, 986, 802. HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₁₉H₁₆BrINO₂ 495.9409; Found 495.9411.

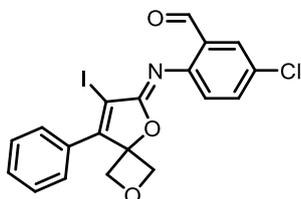
(*Z*)-2-((7-iodo-8-phenyl-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)-5-methoxybenzaldehyde (3m)



White solid (56.4 mg, 61% yield); *Z/E* > 20:1.

m.p. 104-106 °C; ¹H NMR (400 MHz, Chloroform-*d*): δ 10.65 (s, 1H), 7.66 - 7.63 (m, 2H), 7.60 - 7.57 (m, 3H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.40 (s, 1H), 7.22 - 7.14 (m, 1H), 5.02 (d, *J* = 7.6 Hz, 2H), 4.94 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.1, 158.7, 157.0, 142.0, 131.7, 130.5, 130.2, 129.4, 127.8, 124.8, 122.6, 109.5, 92.4, 91.0, 79.1, 55.7; IR (KBr, ν, cm⁻¹) 3024, 1753, 1661, 1548, 1455, 1381, 1195, 1008, 973, 821. HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₂₀H₁₇INO₄ 462.0202; Found 462.0200.

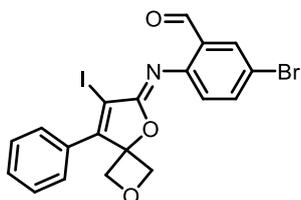
(*Z*)-5-chloro-2-((7-iodo-8-phenyl-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3n)



White solid (54.9 mg, 59% yield); *Z/E* = 8:1.

m.p. 116-117 °C; ¹H NMR (400 MHz, Chloroform-*d*): δ 10.48 (s, 1H), 7.86 (s, 1H), 7.66 - 7.63 (m, 2H), 7.59 - 7.57 (m, 3H), 7.55 - 7.52 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 4.99 (d, *J* = 8.0 Hz, 2H), 4.93 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.7, 159.8, 158.5, 147.0, 134.5, 131.4, 131.2, 130.8, 130.7, 129.9, 129.5, 129.5, 127.8, 127.7, 127.5, 124.8, 92.7, 90.0; IR (KBr, ν, cm⁻¹) 3011, 1759, 1666, 1581, 1445, 1359, 1184, 1016, 956, 825. HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₁₉H₁₄ClINO₄ 465.9707; Found 465.9708.

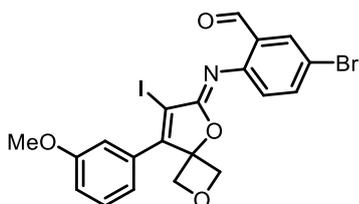
(*Z*)-5-bromo-2-((7-iodo-8-phenyl-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3o)



White solid (57.9 mg, 57% yield); *Z/E* = 8:1.

m.p. 104-106 °C; ¹H NMR (400 MHz, Chloroform-*d*): δ 10.46 (s, 1H), 8.00 (s, 1H), 7.68 - 7.63 (m, 3H), 7.59 - 7.56 (m, 3H), 7.28 - 7.26 (m, 1H), 4.98 (d, *J* = 8.0 Hz, 2H), 4.93 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.5, 159.9, 158.5, 147.5, 137.3, 131.4, 130.8, 130.7, 130.1, 129.5, 127.8, 125.1, 118.3, 92.7, 90.0, 78.7; IR (KBr, ν, cm⁻¹) 3021, 1759, 1662, 1582, 1471, 1388, 1192, 1027, 972, 831. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₉H₁₄BrINO₄ 509.9202; Found 509.9202.

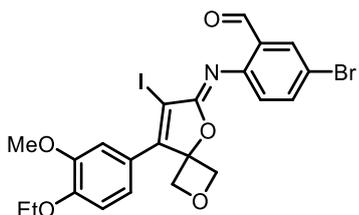
(*Z*)-5-bromo-2-((7-iodo-8-(3-methoxyphenyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3p)



White solid (70.1 mg, 65% yield); *Z/E* > 20:1.

m.p. 124-126 °C; ¹H NMR (400 MHz, Chloroform-*d*): δ 10.46 (s, 1H), 8.01 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.98 (d, *J* = 7.6 Hz, 2H), 4.94 (d, *J* = 7.6 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.5, 160.1, 159.6, 158.5, 147.4, 137.3, 132.5, 130.7, 130.6, 130.0, 125.1, 119.8, 118.3, 115.9, 113.6, 92.7, 89.9, 78.7, 55.5; IR (KBr, ν, cm⁻¹) 3010, 1759, 1652, 1585, 1492, 1376, 1181, 1014, 973, 799. HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₂₀H₁₆BrINO₄ 539.9307; Found 539.9307.

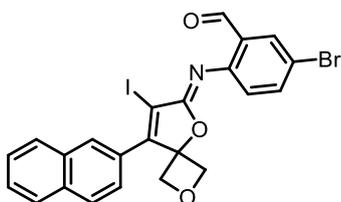
(*Z*)-5-bromo-2-((8-(4-ethoxy-3-methoxyphenyl)-7-iodo-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3q)



White solid (61.8 mg, 53% yield); *Z/E* = 8:1.

m.p. 116-117 °C; ¹H NMR (400 MHz, Chloroform-*d*): δ 10.45 (s, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.57-7.56 (m, 2H), 7.25 - 7.23 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.03 (d, *J* = 8.0 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 1.53 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.6, 158.9, 157.8, 150.7, 149.3, 147.7, 137.3, 130.7, 130.0, 125.1, 122.7, 121.0, 118.1, 112.4, 111.3, 92.4, 86.4, 79.7, 64.5, 56.2, 14.7; IR (KBr, ν, cm⁻¹) 3021, 1752, 1682, 1600, 1473, 1373, 1195, 1014, 973, 820. HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₂₂H₂₀BrINO₅ 583.9570; Found 583.9570.

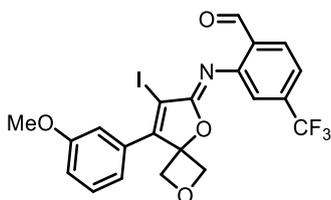
(*Z*)-5-bromo-2-((7-iodo-8-(naphthalen-2-yl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3r)



White solid (58.1 mg, 52% yield); $Z/E = 14:1$.

m.p. 111-113 °C; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 10.53 (s, 1H), 8.07 - 8.05 (m, 2H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.62 - 7.54 (m, 3H), 7.43 - 7.38 (m, 2H), 5.12 (d, $J = 7.6$ Hz, 1H), 4.97 (d, $J = 8.0$ Hz, 1H), 4.90 (d, $J = 7.6$ Hz, 1H), 4.68 (d, $J = 8.0$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 190.6, 160.6, 158.2, 147.2, 137.4, 133.9, 131., 130.8, 130.6, 130.2, 129.7, 129.3, 129.3, 129.0, 127.8, 127.6, 126.9, 125.8, 125.5, 125.4, 125.2, 124.1, 118.5, 94.2, 78.3, 77.6; **IR** (KBr, ν , cm^{-1}) 3016, 1771, 1656, 1582, 1478, 1390, 1187, 1009, 975, 850. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{16}\text{BrINO}_3$ 559.9358; Found 559.9357.

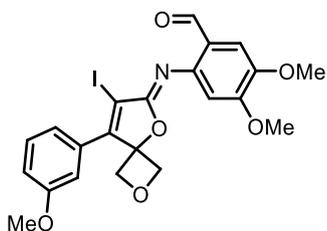
***(Z)*-2-((7-iodo-8-(3-methoxyphenyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)-4-(trifluoromethyl)benzaldehyde (3s)**



White solid (64.7 mg, 61% yield); $Z/E > 20:1$.

m.p. 109-111 °C; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 10.50 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.59 (s, 1H), 7.53 - 7.48 (m, 2H), 7.23 (d, $J = 8.0$ Hz, 1H), 7.19 (s, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 4.99 (d, $J = 8.0$ Hz, 2H), 4.94 (d, $J = 8.0$ Hz, 2H), 3.90 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 190.8, 160.14, 160.08, 159.2, 149.0, 135.7 (q, $J_{\text{CF}} = 32.3$ Hz), 132.4, 130.7, 130.4, 128.8, 123.5 (q, $J_{\text{CF}} = 271.3$ Hz), 121.3 (q, $J_{\text{CF}} = 3.7$ Hz), 120.5 (q, $J_{\text{CF}} = 3.7$ Hz), 119.8, 116.0, 113.6, 92.8, 89.3, 78.6, 55.5; **IR** (KBr, ν , cm^{-1}) 2955, 1755, 1667, 1601, 1469, 1373, 1183, 1015, 960, 827. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{16}\text{F}_3\text{INO}_4$ 530.0076; Found 530.0077.

***(Z)*-2-((7-iodo-8-(3-methoxyphenyl)-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)-4-(trifluoromethyl)benzaldehyde (3t)**

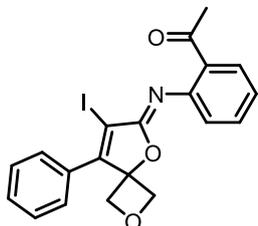


White solid (63.6 mg, 61% yield); $Z/E > 20:1$.

m.p. 101-103 °C; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 10.38 (s, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.38 (s, 1H), 7.22 - 7.17 (m, 2H), 7.09 (d, $J = 8.4$ Hz, 1H), 6.88 (s, 1H), 4.98 (d, $J = 8.0$ Hz, 2H), 4.95 (d, $J = 7.6$ Hz, 2H), 3.97 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 190.3, 160.0, 158.9, 157.6, 154.3, 146.7,

144.4, 132.6, 130.6, 121.9, 119.8, 115.8, 113.7, 108.2, 105.5, 92.4, 90.3, 79.0, 56.2, 56.1, 55.5; **IR** (KBr, ν , cm^{-1}) 3012, 1778, 1668, 1582, 1477, 1349, 1169, 1018, 978, 819. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{INO}_6$ 522.0414; Found 522.0411.

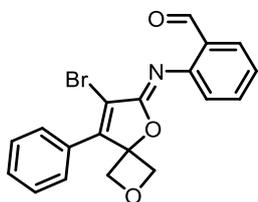
(Z)-1-(2-((7-iodo-8-phenyl-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)phenyl)ethan-1-one (3u)



White solid (54.4 mg, 61% yield); $Z/E > 20:1$.

m.p. 109-111 °C; **^1H NMR** (400 MHz, Chloroform- d): δ 7.72 (d, $J = 7.6$ Hz, 1H), 7.65 - 7.61 (m, 2H), 7.58 - 7.56 (m, 2H), 7.51 - 7.48 (m, 1H), 7.42 - 7.35 (m, 1H), 7.23 - 7.18 (m, 2H), 4.96 (d, $J = 7.6$ Hz, 2H), 4.90 (d, $J = 7.6$ Hz, 2H), 2.67 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform- d) δ 201.6, 159.1, 157.3, 145.1, 132.9, 132.1, 131.6, 130.4, 129.3, 129.2, 128.9, 128.7, 127.8, 125.2, 124.4, 123.0, 92.1, 78.9, 78.0, 69.8, 31.0; **IR** (KBr, ν , cm^{-1}) 3037, 1763, 1654, 1590, 1480, 1380, 1186, 1010, 966, 808. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}_3$ 446.0253; Found 446.0255.

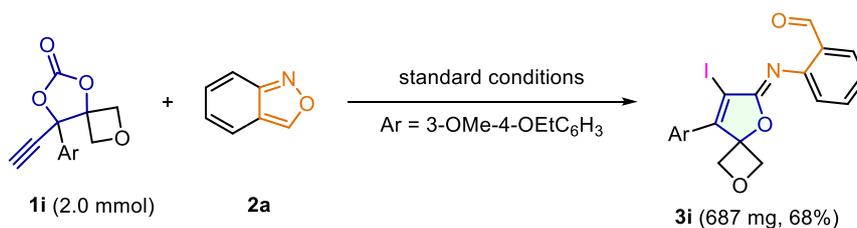
(Z)-2-((7-bromo-8-phenyl-2,5-dioxaspiro[3.4]oct-7-en-6-ylidene)amino)benzaldehyde (3v)



White solid (42.2 mg, 55% yield); $Z/E = 4:1$.

m.p. 90-82 °C; **^1H NMR** (400 MHz, Chloroform- d): δ 10.56 (s, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.71 - 7.69 (m, 2H), 7.67 - 7.57 (m, 3H), 7.38 (d, $J = 8.4$ Hz, 1H), 5.04 (d, $J = 8.0$ Hz, 2H), 4.98 (d, $J = 7.6$ Hz, 2H); **^{13}C NMR** (100 MHz, Chloroform- d) δ 190.5, 159.9, 158.5, 147.5, 137.3, 131.4, 130.8, 130.7, 130.1, 129.5, 127.8, 125.1, 118.3, 92.7, 90.0, 78.7; **IR** (KBr, ν , cm^{-1}) 3033, 1767, 1649, 1573, 1471, 1369, 1188, 1011, 980, 812. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_3$ 384.0235; Found 384.0236.

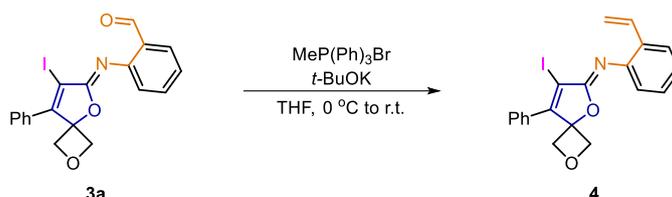
5. Gram-scale synthesis



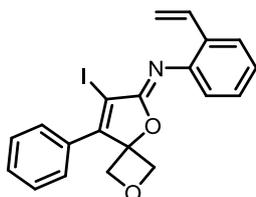
To a 100 mL sealed tube equipped with a stir bar was added CuOTf (85.4 mg, 0.4 mmol, 20 mol%), 1,10-phen

(90 mg, 0.5 mmol, 25 mol%) and DCE (10 mL) under air atmosphere. The mixture was stirred at 50 °C for 30 min. Subsequently, **1i** (608 mg, 2.0 mmol, 1.0 equiv), **2a** (357 mg, 3.0 mmol, 1.5 equiv), NaI (600 mg, 4.0 mmol, 2.0 equiv), 18-crown-6 (634 mg, 2.4 mmol, 1.2 equiv) and DCE (20 mL) were added. The resulting mixture was then stirred at 110 °C for 5 h. Upon completion, the mixture was filtered and the clear filtrate was collected. After removing the solvents *in vacuo*, the crude product obtained was purified by flash column chromatography on silica gel to give the desired product **3i** (687 mg, 68% yield).

6. Transformation of the compounds

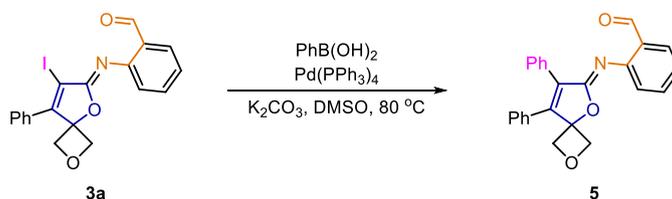


MePPh₃Br (107.2 mg, 0.3 mmol), *t*-BuOK (33.7 mg, 0.3 mmol) were dissolved in dry THF (2 mL) under N₂, the mixture was stirred at room temperature for 30 min. Then, **3a** (86.2 mg, 0.2 mmol) was added at 0 °C. The reaction mixture was allowed to stir at room temperature for 3h. After completion, THF was evaporated *in vacuo* and the residue was purified by flash silica gel column chromatography (PE/EtOAc = PE to 30/1) to give products **4**.

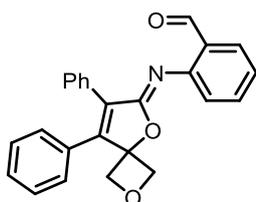


White solid (79.1 mg, 92% yield); *Z/E* > 20:1.

m.p. 78-79 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.51 (m, 6H), 7.30 – 7.25 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.17 – 7.04 (m, 2H), 5.76 (d, *J* = 17.7 Hz, 1H), 5.25 (d, *J* = 11.1 Hz, 1H), 4.97 (d, *J* = 7.7 Hz, 2H), 4.88 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) 158.3, 156.3, 143.4, 133.5, 131.7, 130.8, 130.2, 129.2, 127.9, 127.7, 125.5, 124.6, 122.1, 114.0, 91.7, 90.9, 79.0; IR (KBr, ν, cm⁻¹) 3021, 1646, 1455, 1361, 1178, 1026, 961, 828. HRMS (ESI -TOF) *m/z*: [M+H]⁺ Calcd for C₂₀H₁₇INO₂ 430.0298; Found 430.0283



To an oven-dried 10 mL Schlenk tube equipped with a stirrer bar were added **3a** (86.2 mg, 0.2 mmol), PhB(OH)₂ (36.6 mg, 0.3mmol), Pd(PPh₃)₄ (11.6 mg, 0.01 mmol), K₂CO₃ (55.3 mg, 0.4 mmol) and DMSO (3 mL). The reaction mixture was stirred at 80 °C for 5 h. After complete consumption of starting material, the mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with water, brine and dried over Na₂SO₄. After evaporation of solvent, residual material was purified by silica gel column chromatography (PE/EA = 20:1) to afford product **5**.

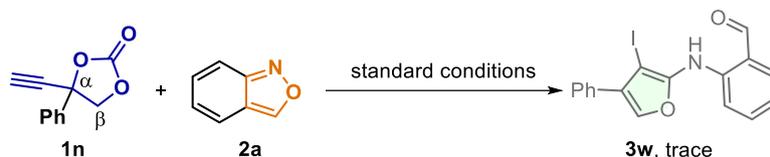


White solid (49.7 mg, 65% yield); $Z/E = 3:1$.

m.p. 115-116 °C; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 10.56 (s, 1H), 7.97 – 7.92 (m, 1H), 7.71 – 7.69 (m, 2H), 7.65 – 7.63 (m, 3H), 7.52 – 7.50 (m, 3H), 7.48 – 7.44 (m, 2H), 7.39 – 7.34 (m, 3H), 5.04 (d, $J = 7.6$ Hz, 2H), 4.98 (d, $J = 8.0$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 191.9, 148.7, 134.6, 131.5, 131.1, 130.5, 129.9, 129.5, 129.43, 129.38, 129.3, 129.2, 128.6, 128.6, 128.5, 128.2, 128.1, 127.8, 127.4, 124.8, 123.1, 92.4, 78.8. **IR** (KBr, ν , cm^{-1}) 3032, 1752, 1664, 1576, 1452, 1367, 1175, 1026, 966, 818. **HRMS** (ESI -TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{15}\text{BrNO}_3$ 382.1438; Found 382.1444.

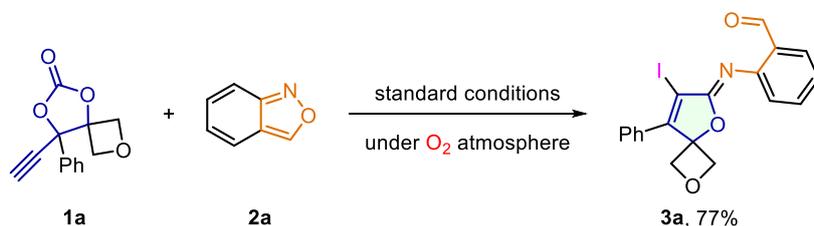
7. Mechanism Studies

(a)



To a 25 mL Schlenk tube equipped with a stir bar was added CuOTf (8.5 mg, 0.04 mmol, 20 mol%), 1,10-phen (9.0 mg, 0.05 mmol, 25 mol%) and DCE (1.0 mL) under air atmosphere. The mixture was stirred at 50 °C for 30 min. Subsequently, **1n** (37.6 mg, 0.2 mmol, 1.0 equiv), **2a** (35.7 mg, 0.3 mmol, 1.5 equiv), NaI (60.0 mg, 0.4 mmol, 2.0 equiv), 18-crown-6 (63.4 mg, 0.24 mmol, 1.2 equiv) and DCE (2.0 mL) were added. The resulting mixture was then stirred at 110 °C for 5 h. Only a trace amount of product **3w** was detected by TLC and $^1\text{H NMR}$ analysis of the crude reaction mixture.

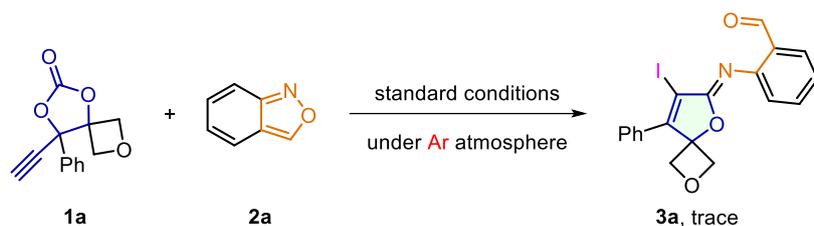
(b)



To a 25 mL Schlenk tube equipped with a stir bar was added CuOTf (8.5 mg, 0.04 mmol, 20 mol%), 1,10-phen (9.0 mg, 0.05 mmol, 25 mol%) and DCE (1.0 mL) under O_2 atmosphere. The mixture was stirred at 50 °C for 30 min. Subsequently, **1a** (46.0 mg, 0.2 mmol, 1.0 equiv), **2a** (35.7 mg, 0.3 mmol, 1.5 equiv), NaI (60.0 mg, 0.4 mmol, 2.0 equiv), 18-crown-6 (63.4 mg, 0.24 mmol, 1.2 equiv) and DCE (2.0 mL) were added. The resulting mixture was then stirred at 110 °C for 5 h. Upon completion, the mixture was filtered and the clear filtrate was collected. After removing the solvents *in vacuo*, the crude product obtained was purified by flash column chromatography on silica

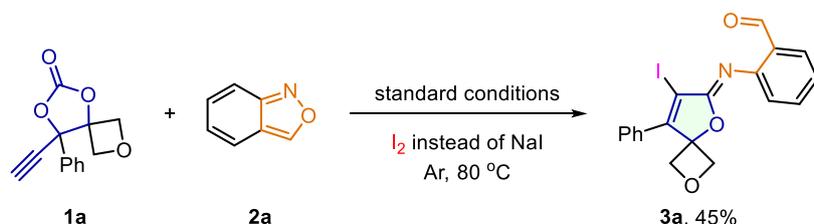
gel to give the desired product **3a** (66.5 mg, 77% yield).

(c)



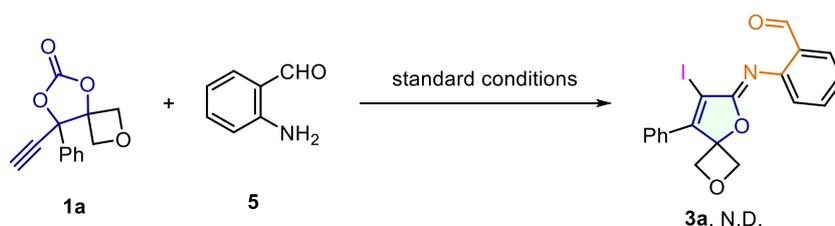
To a 25 mL Schlenk tube equipped with a stir bar was added CuOTf (8.5 mg, 0.04 mmol, 20 mol%), 1,10-phen (9.0 mg, 0.05 mmol, 25 mol%) and DCE (1.0 mL) under Ar atmosphere. The mixture was stirred at 50 °C for 30 min. Subsequently, **1a** (46.0 mg, 0.2 mmol, 1.0 equiv), **2a** (35.7 mg, 0.3 mmol, 1.5 equiv), NaI (60.0 mg, 0.4 mmol, 2.0 equiv), 18-crown-6 (63.4 mg, 0.24 mmol, 1.2 equiv) and DCE (2.0 mL) were added. The resulting mixture was then stirred at 110 °C for 5 h. Only a trace amount of product **3a** was detected by TLC and ¹H NMR analysis of the crude reaction mixture.

(d)



To a 25 mL Schlenk tube equipped with a stir bar was added CuOTf (4.3 mg, 0.02 mmol, 20 mol%), 1,10-phen (4.5 mg, 0.025 mmol, 25 mol%) and DCE (0.5 mL) under Ar atmosphere. The mixture was stirred at 50 °C for 30 min. Subsequently, **1a** (23.0 mg, 0.1 mmol, 1.0 equiv), **2a** (17.9 mg, 0.15 mmol, 1.5 equiv) and DCE (2.0 mL) were added. I₂ (25.4 mg, 0.1 mmol, 1.0 equiv) was dissolved in DCE (1.0 mL), and the resulting solution was added dropwise to the mixture over 12 h. The reaction mixture was then stirred at 80 °C for 5 h. Upon completion, the mixture was filtered and the clear filtrate was collected. After removing the solvents *in vacuo*, the crude product obtained was purified by flash column chromatography on silica gel to give the desired product **3a** (19.5 mg, 45% yield).

(e)



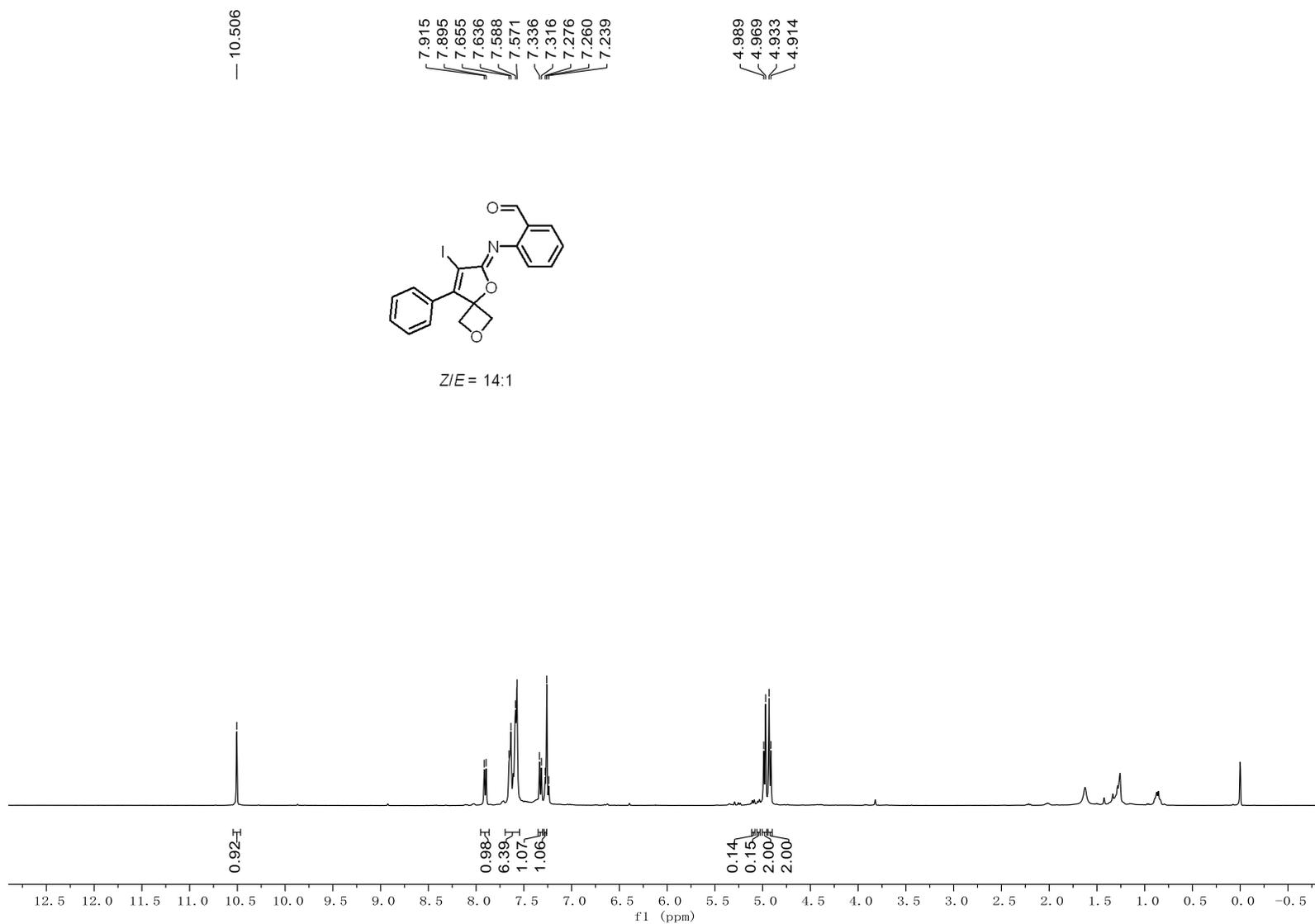
To a 25 mL Schlenk tube equipped with a stir bar was added CuOTf (8.5 mg, 0.04 mmol, 20 mol%), 1,10-phen (9.0 mg, 0.05 mmol, 25 mol%) and DCE (1.0 mL) under air atmosphere. The mixture was stirred at 50 °C for 30 min. Subsequently, **1a** (46.0 mg, 0.2 mmol, 1.0 equiv), **5** (36.3 mg, 0.3 mmol, 1.5 equiv), NaI (60.0 mg, 0.4 mmol,

2.0 equiv), 18-crown-6 (63.4 mg, 0.24 mmol, 1.2 equiv) and DCE (2.0 mL) were added. The resulting mixture was then stirred at 110 °C for 5 h. The desired product **3a** was not detected by TLC and ¹H NMR analysis of the crude reaction mixture.

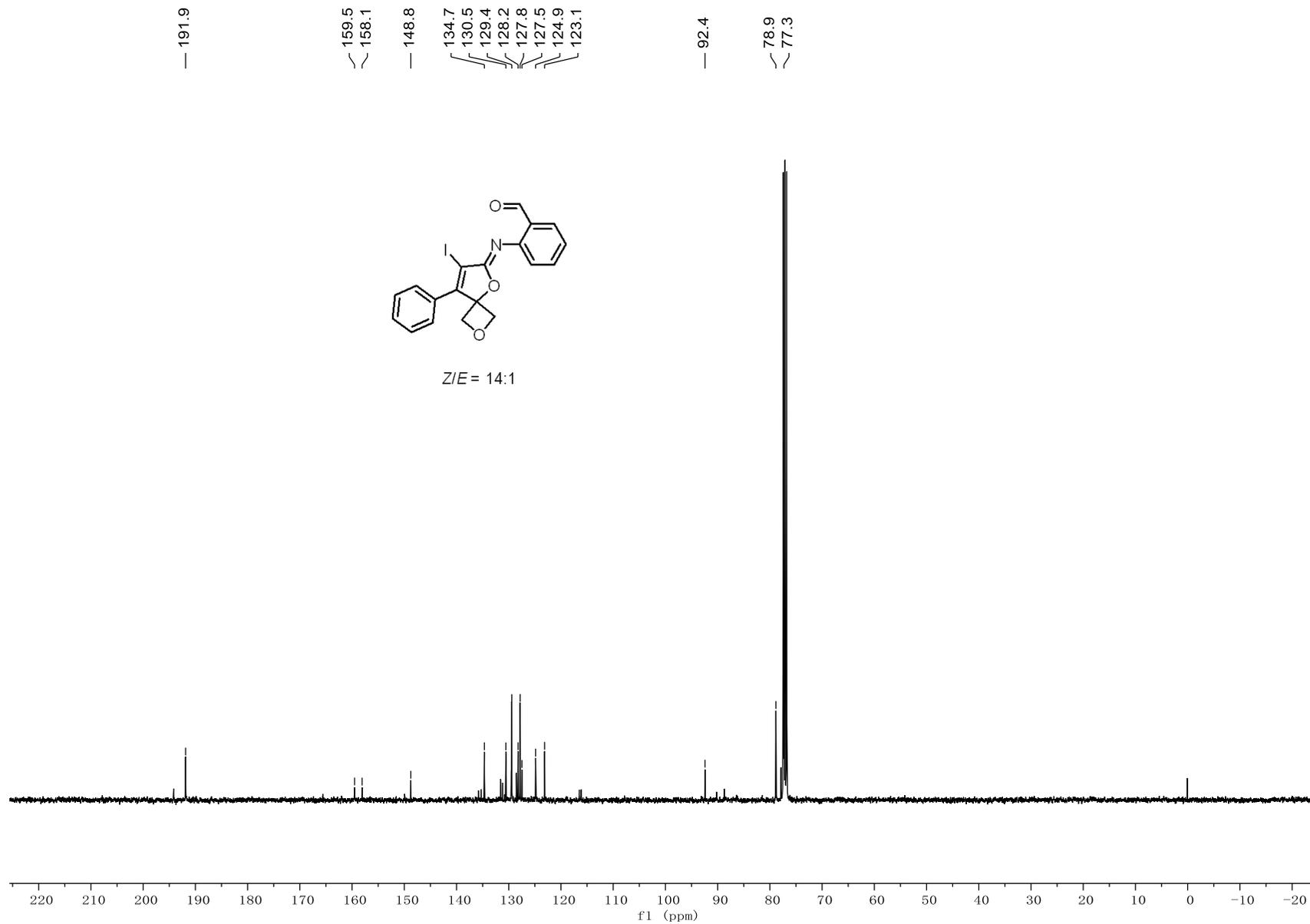
8. Reference

1. F. Gong, X.-J. Meng, S.-A. Lan, J.-G. Liu, S. Yang, X.-Q. Fang, *ACS Catal.* **2022**, *12*, 12036–12044.

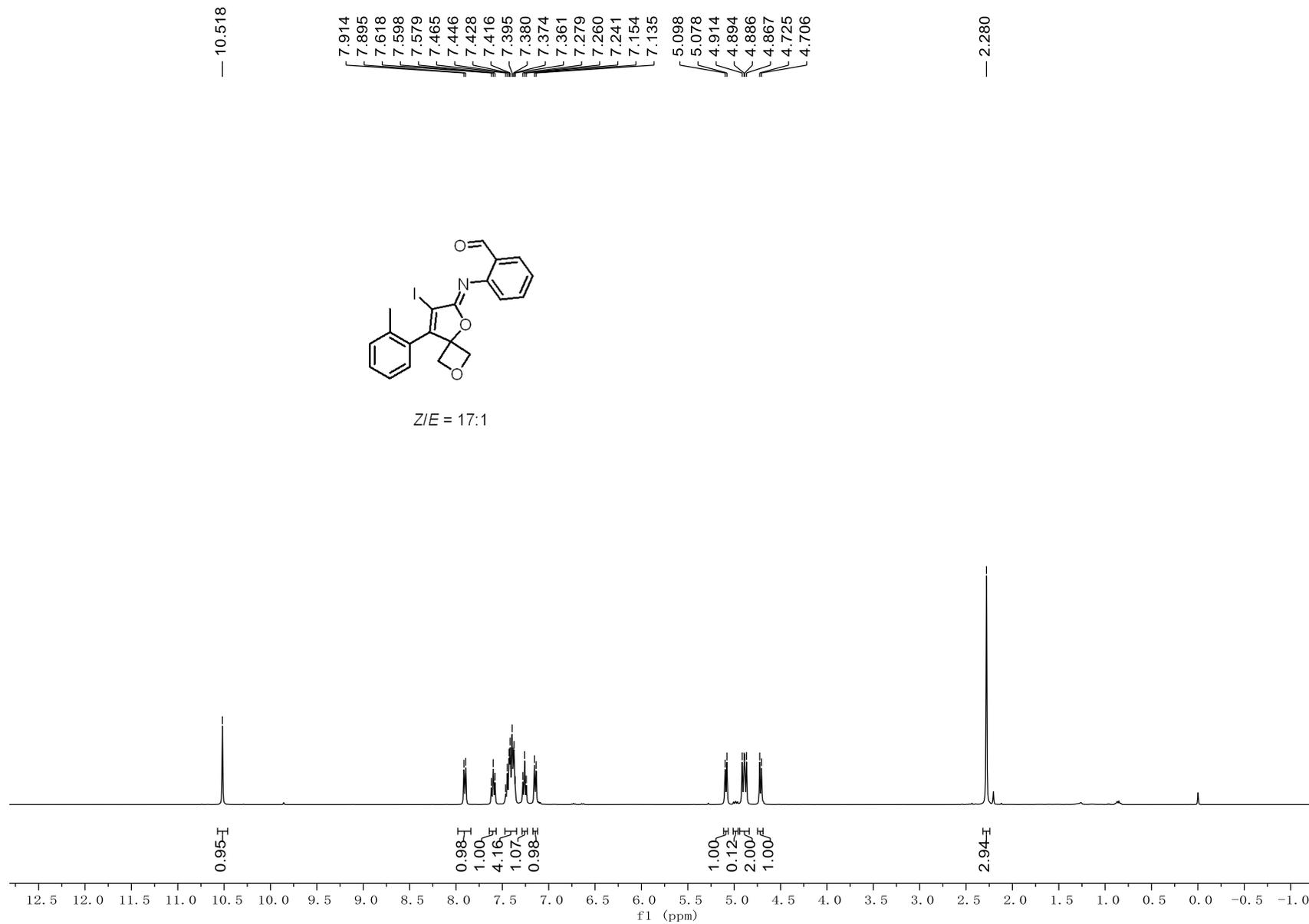
9. NMR Spectra

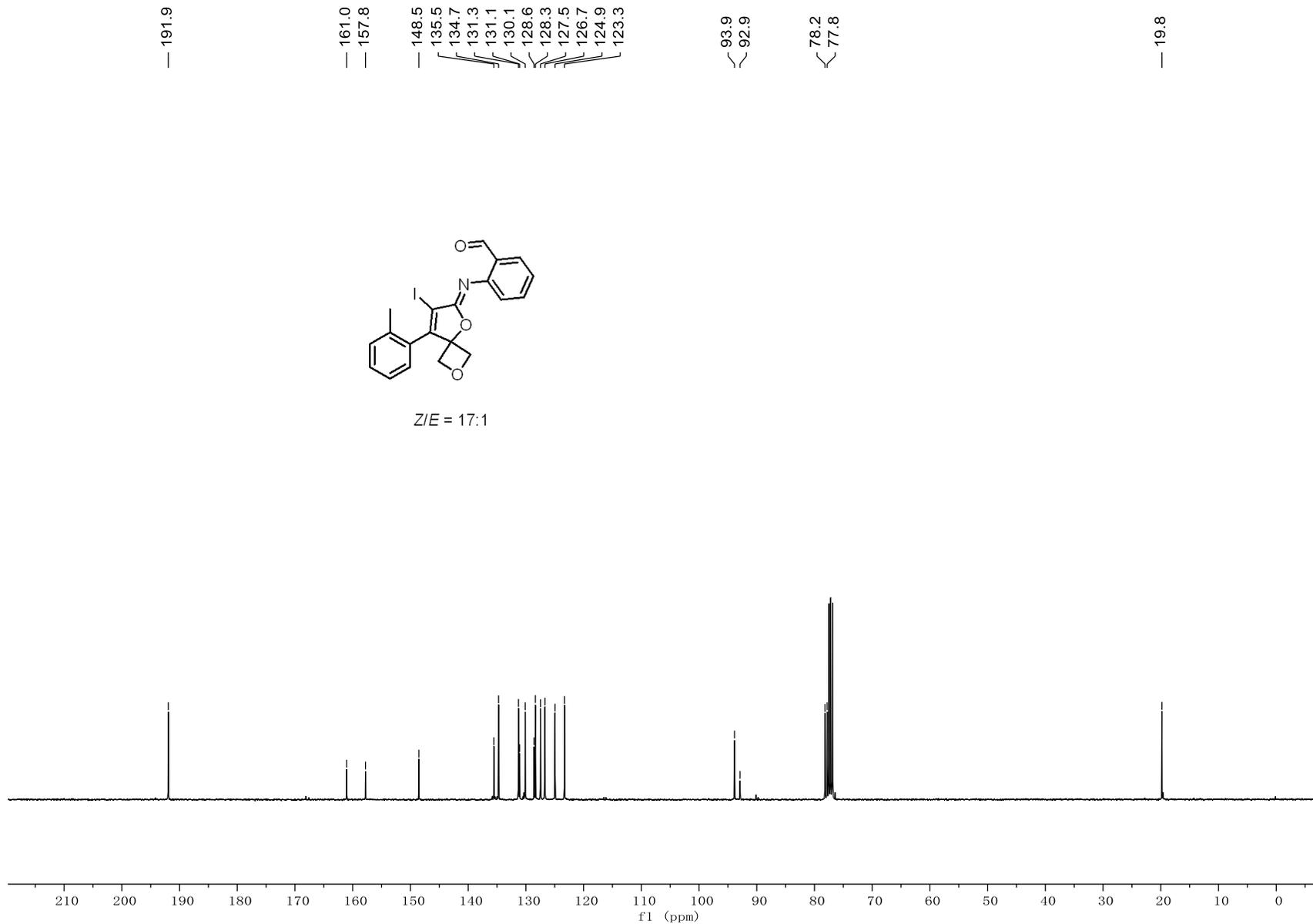


^1H NMR Spectrum (400 MHz, CDCl_3) of 3a

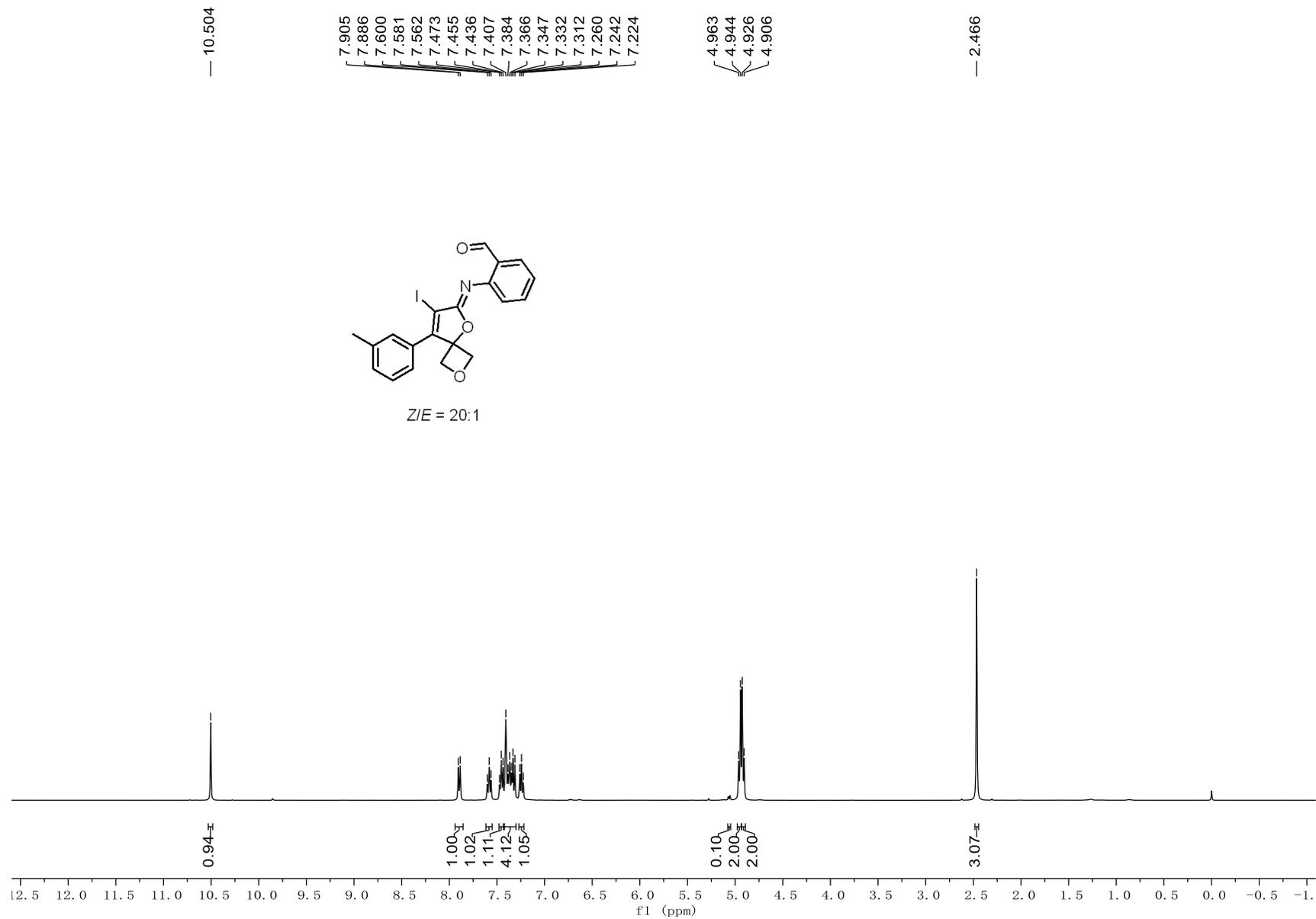


¹³C NMR Spectrum (100 MHz, CDCl₃) of 3a

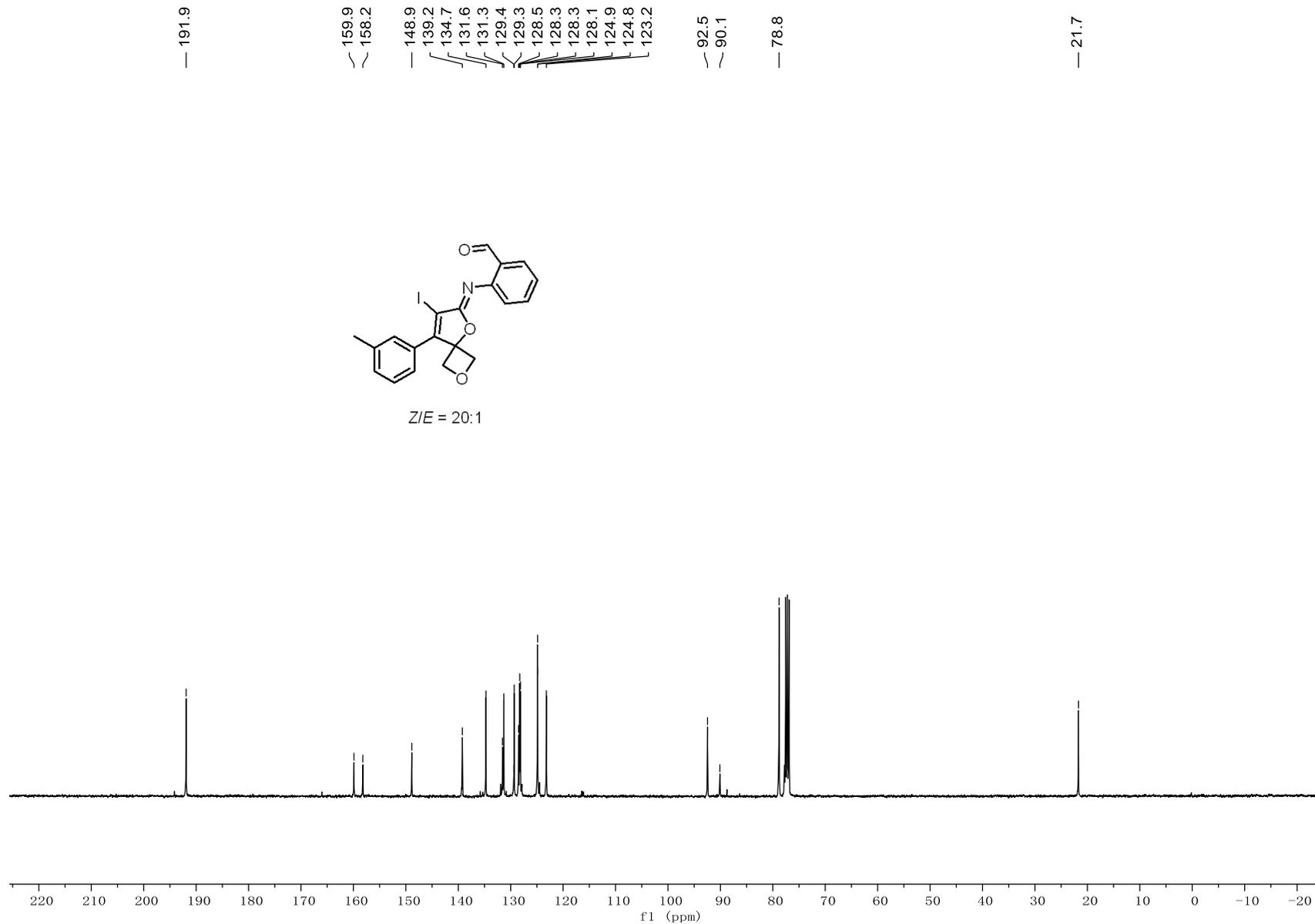




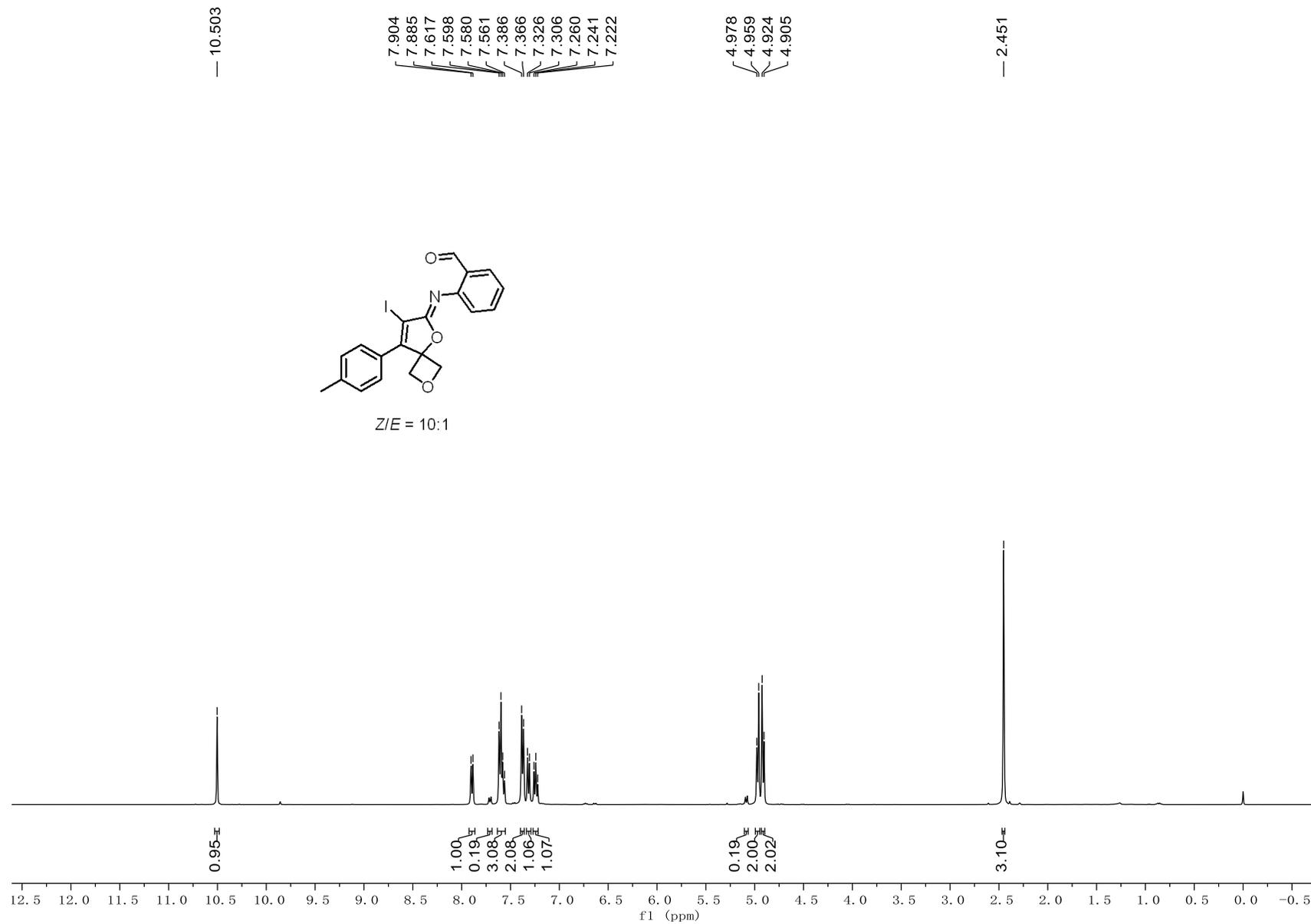
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3b



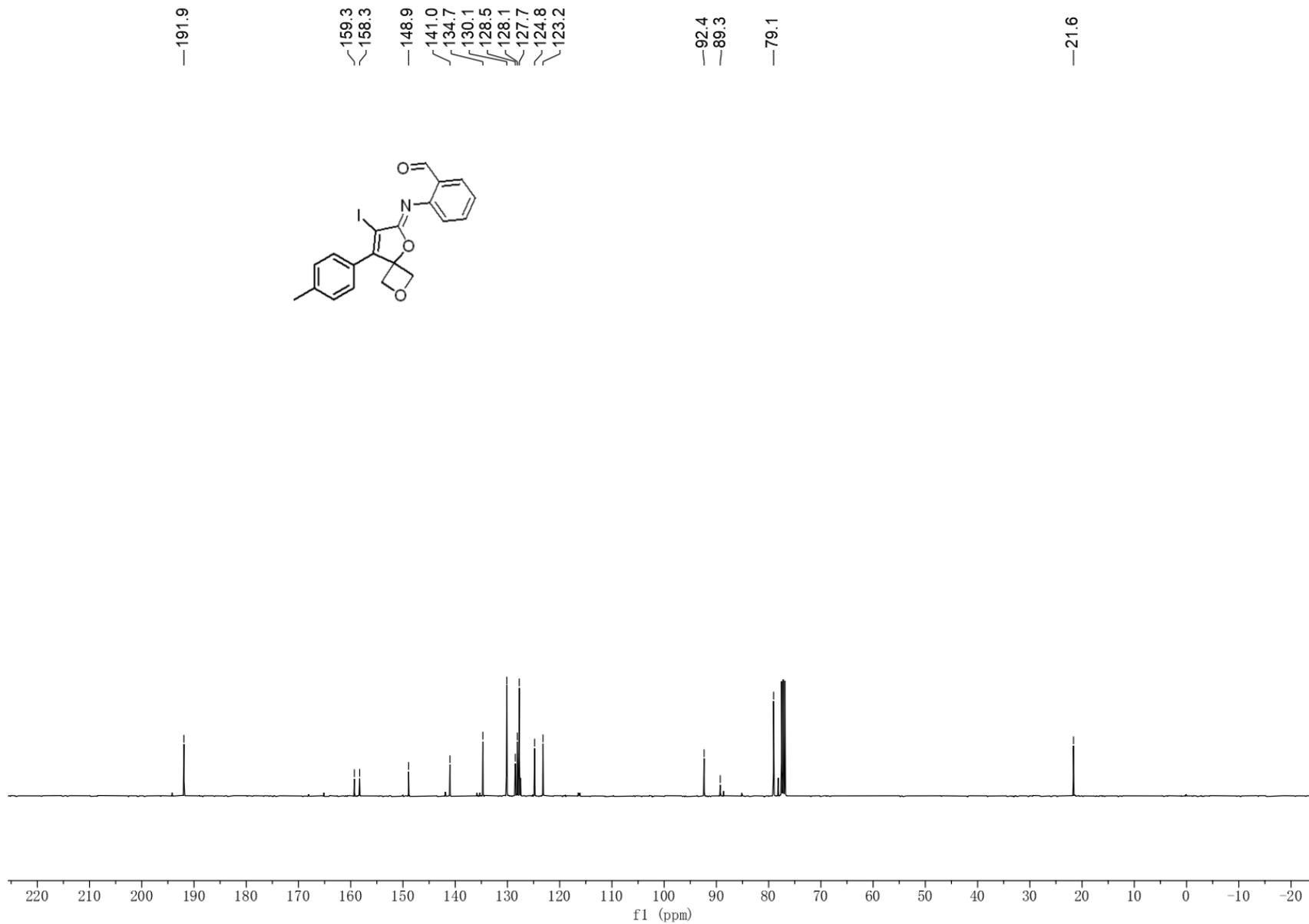
¹H NMR Spectrum (400 MHz, CDCl₃) of 3c



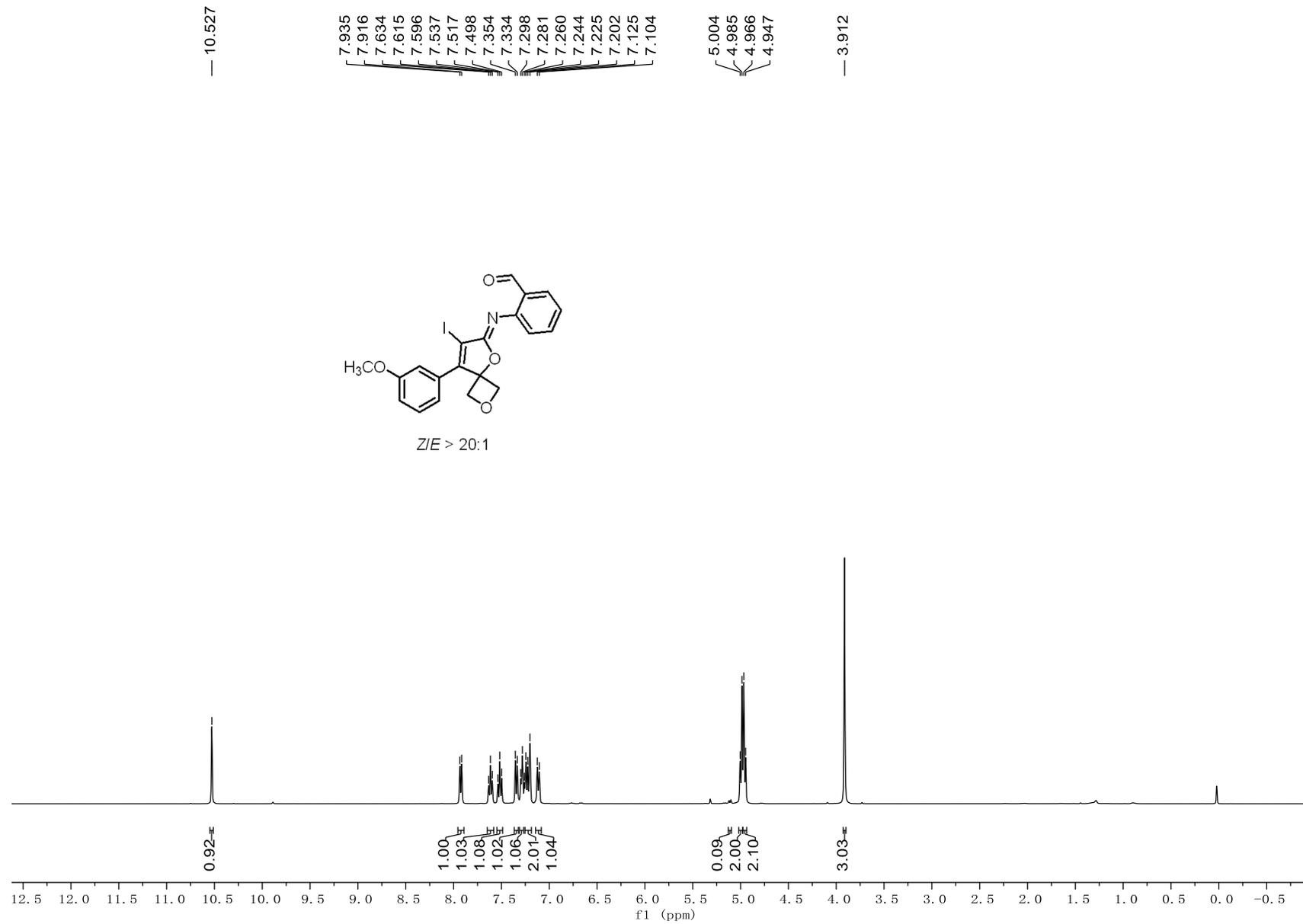
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3c



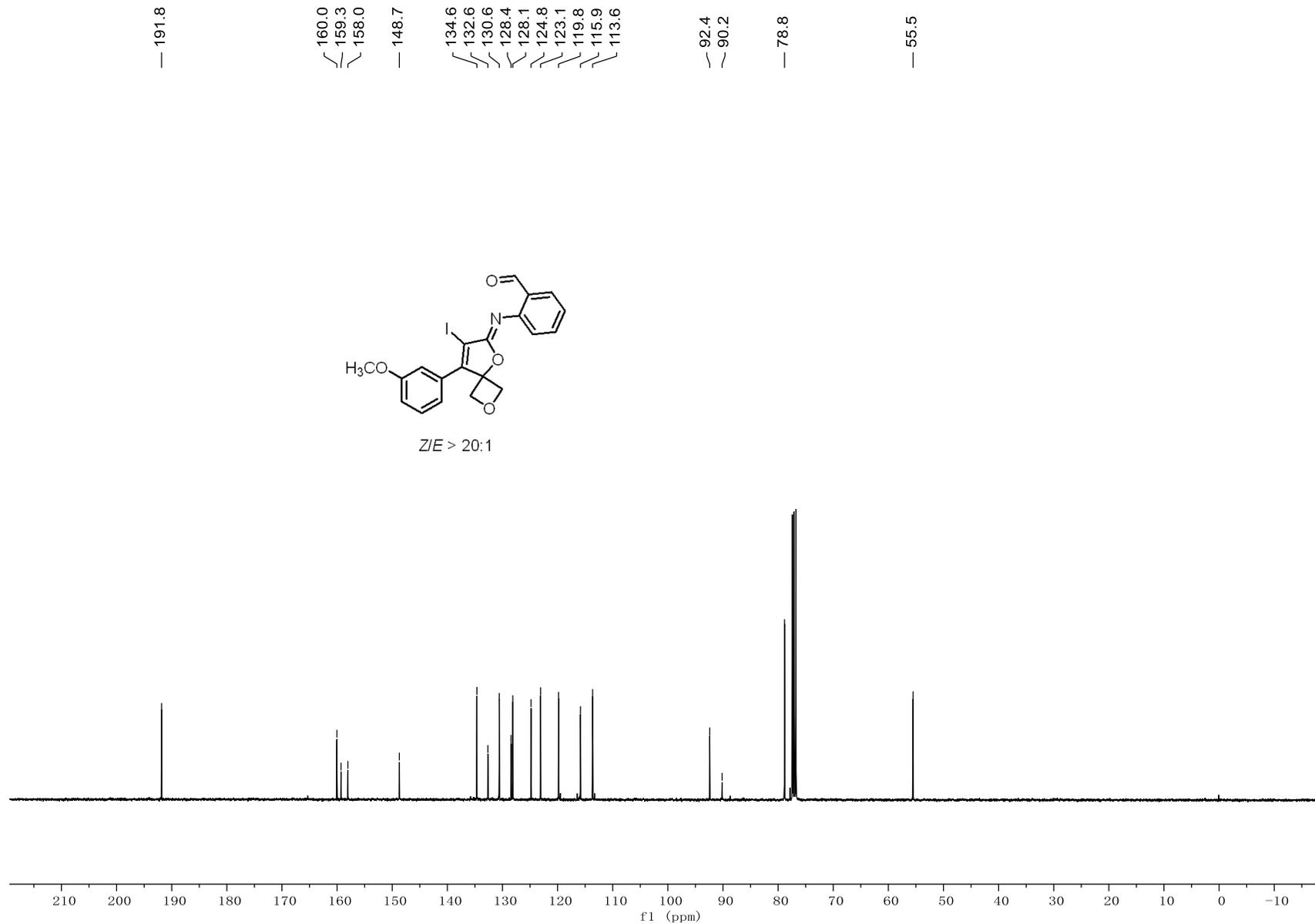
¹H NMR Spectrum (400 MHz, CDCl₃) of 3d



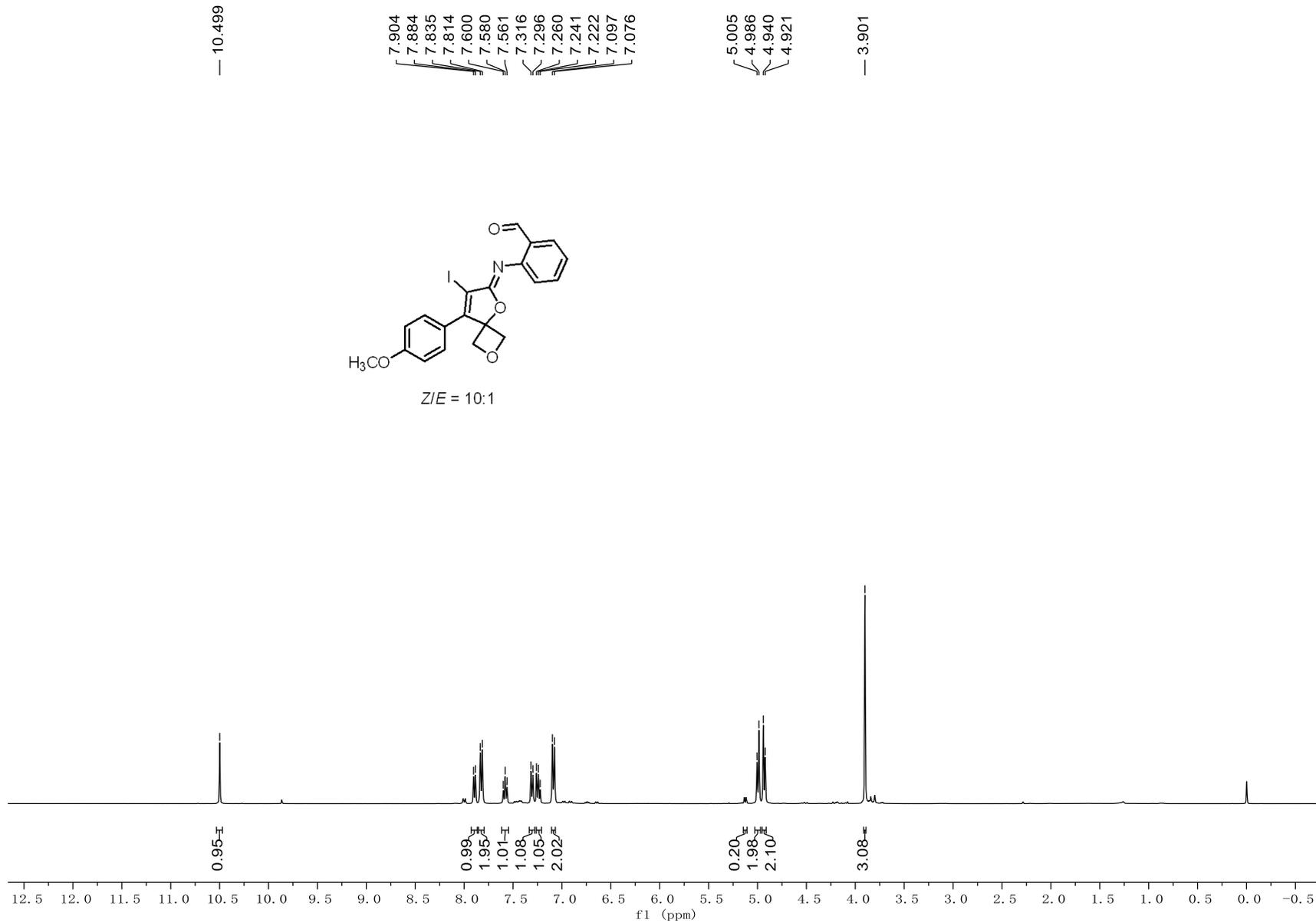
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3d



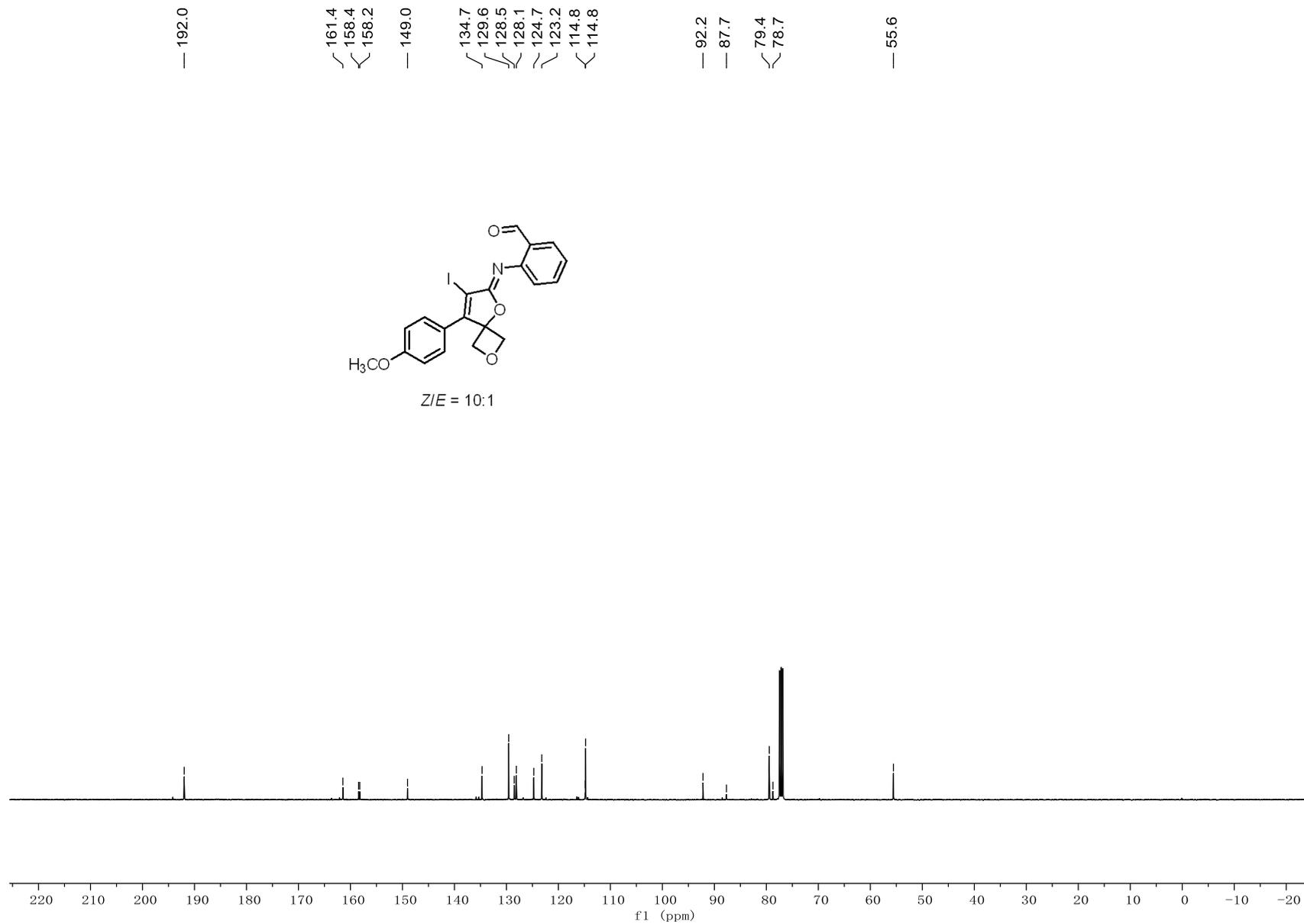
¹H NMR Spectrum (400 MHz, CDCl₃) of 3e



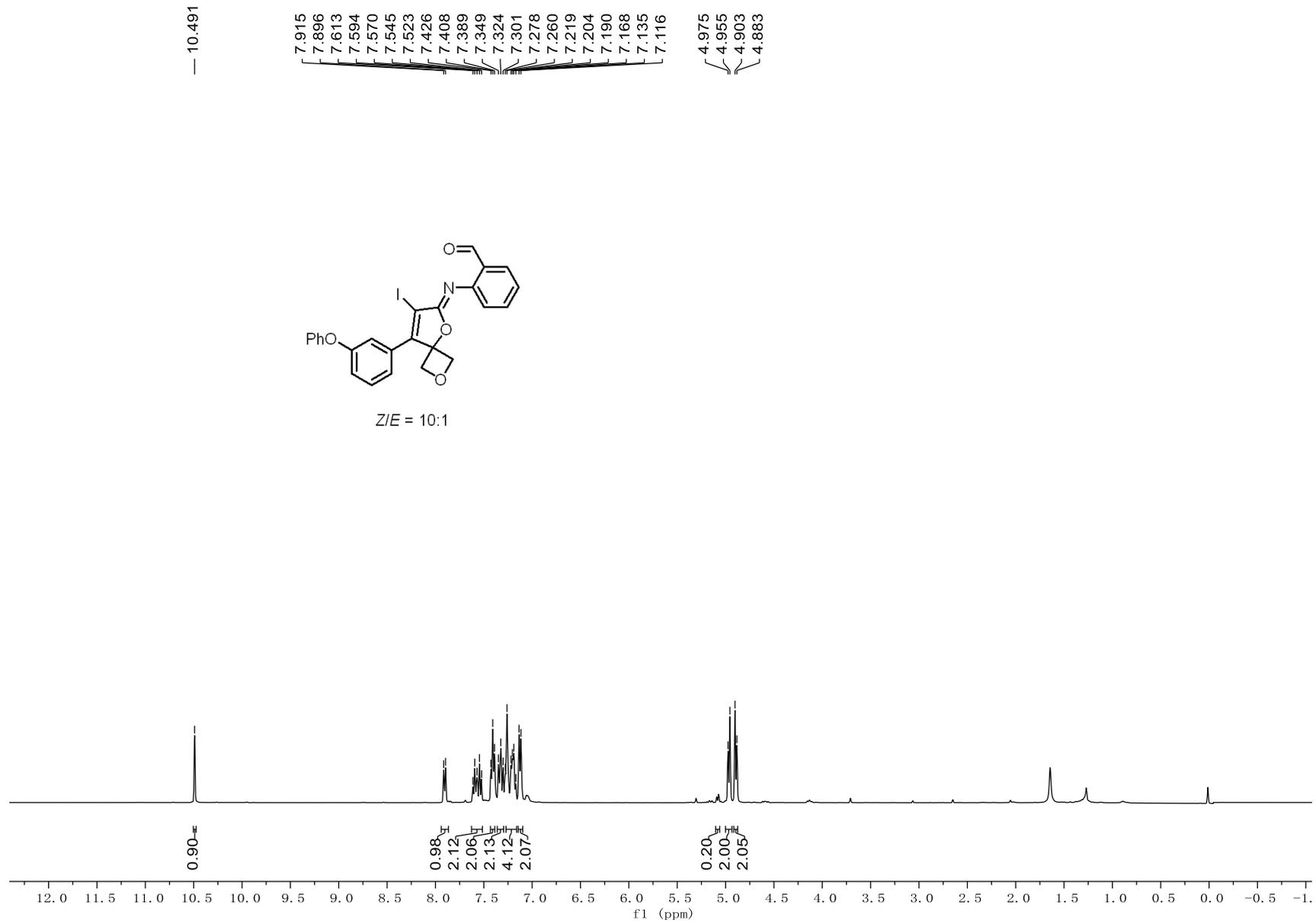
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3e



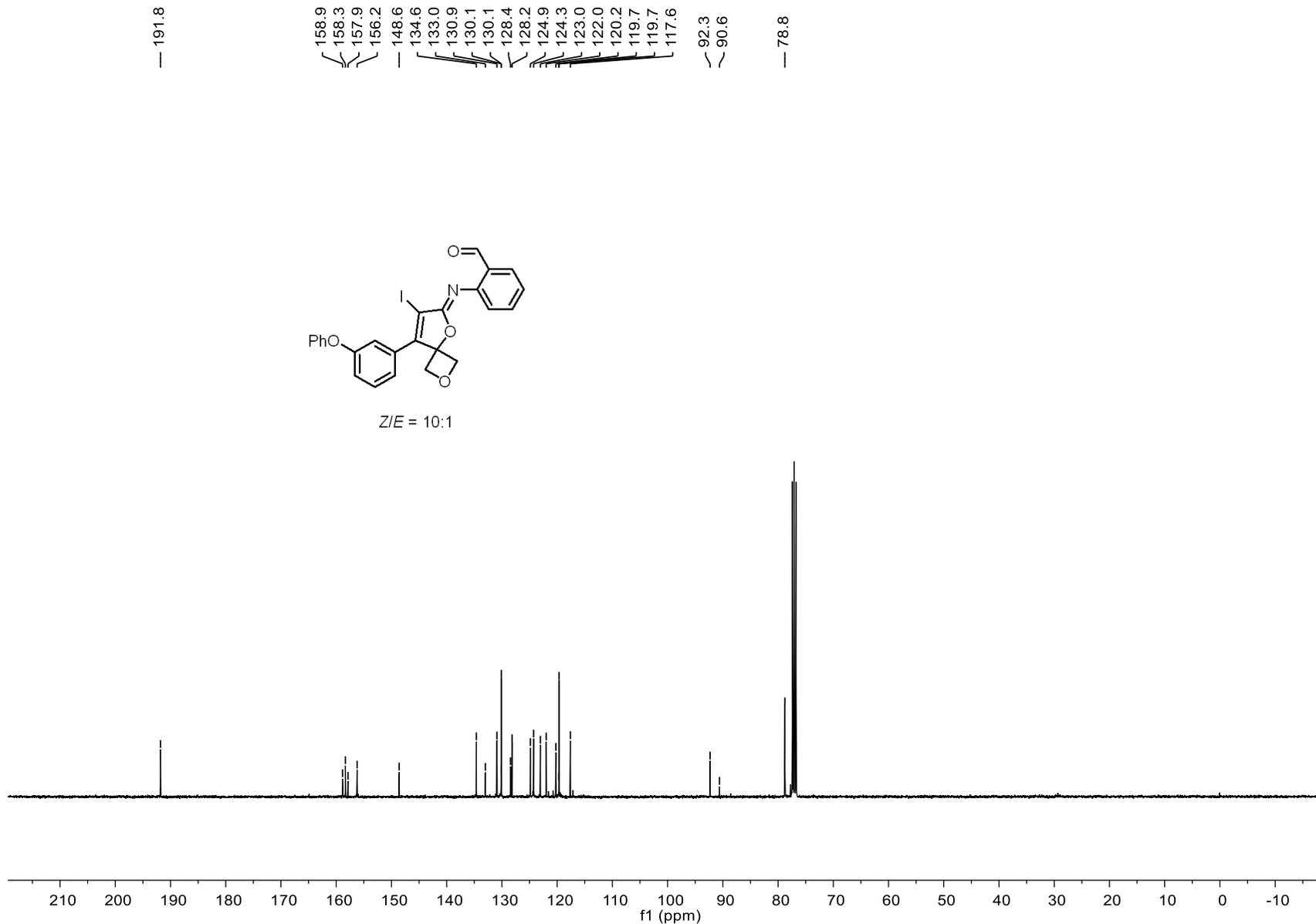
^1H NMR Spectrum (400 MHz, CDCl_3) of **3f**



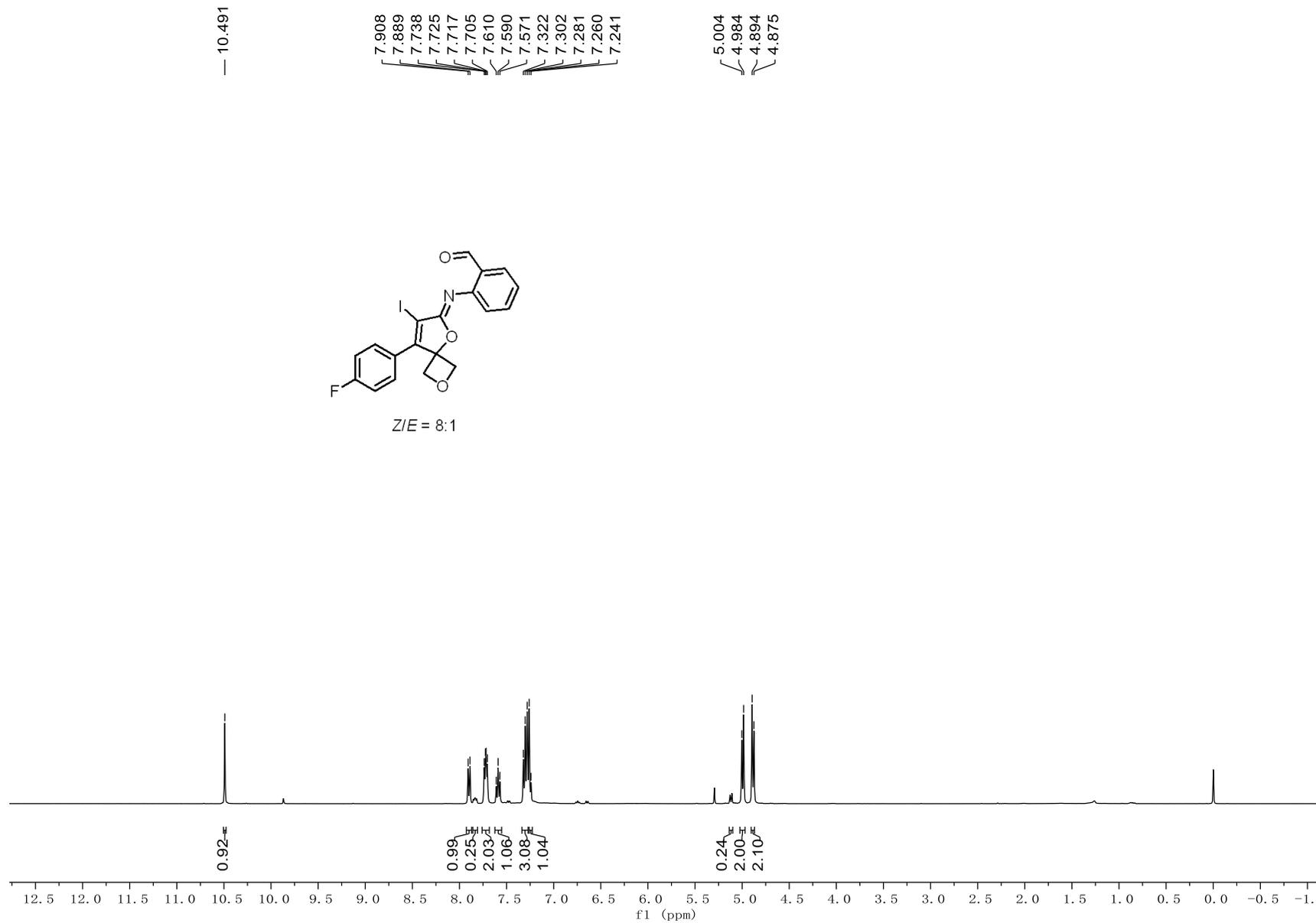
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3f

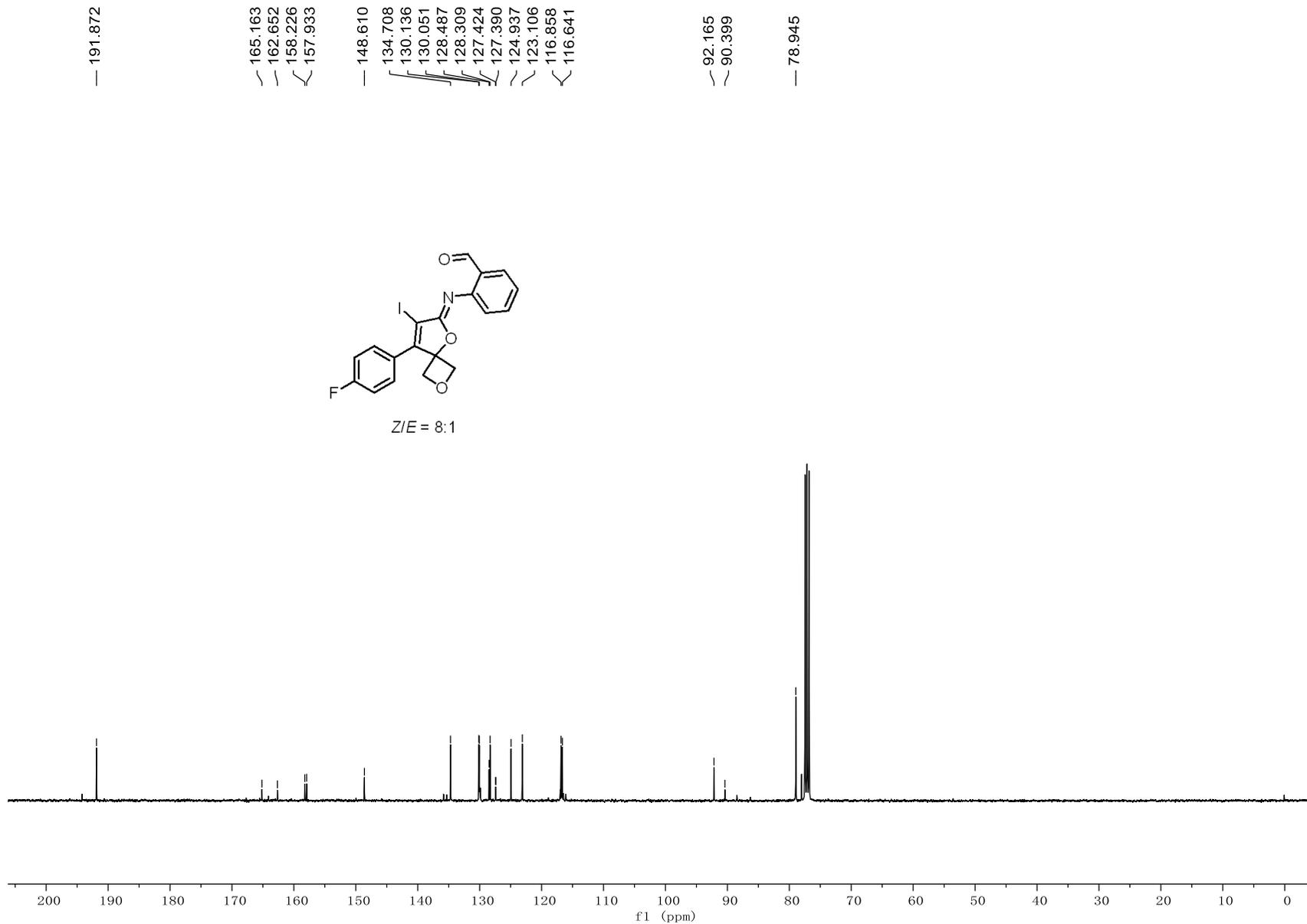


¹H NMR Spectrum (400 MHz, CDCl₃) of 3g



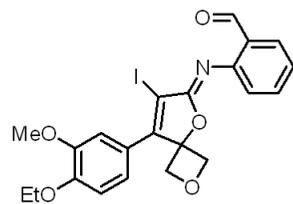
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3g





¹³C NMR Spectrum (100 MHz, CDCl₃) of 3h

— 10.454

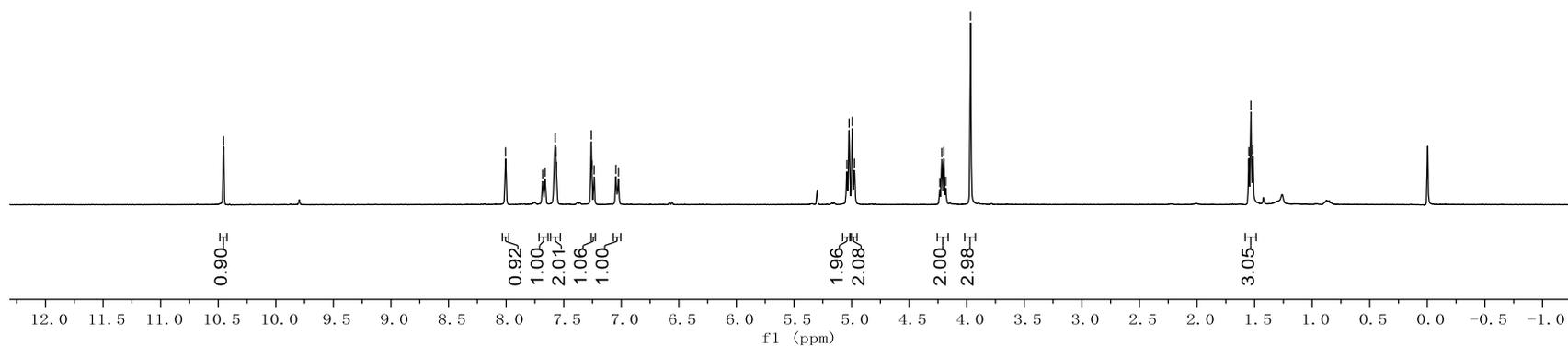


Z/E > 20:1

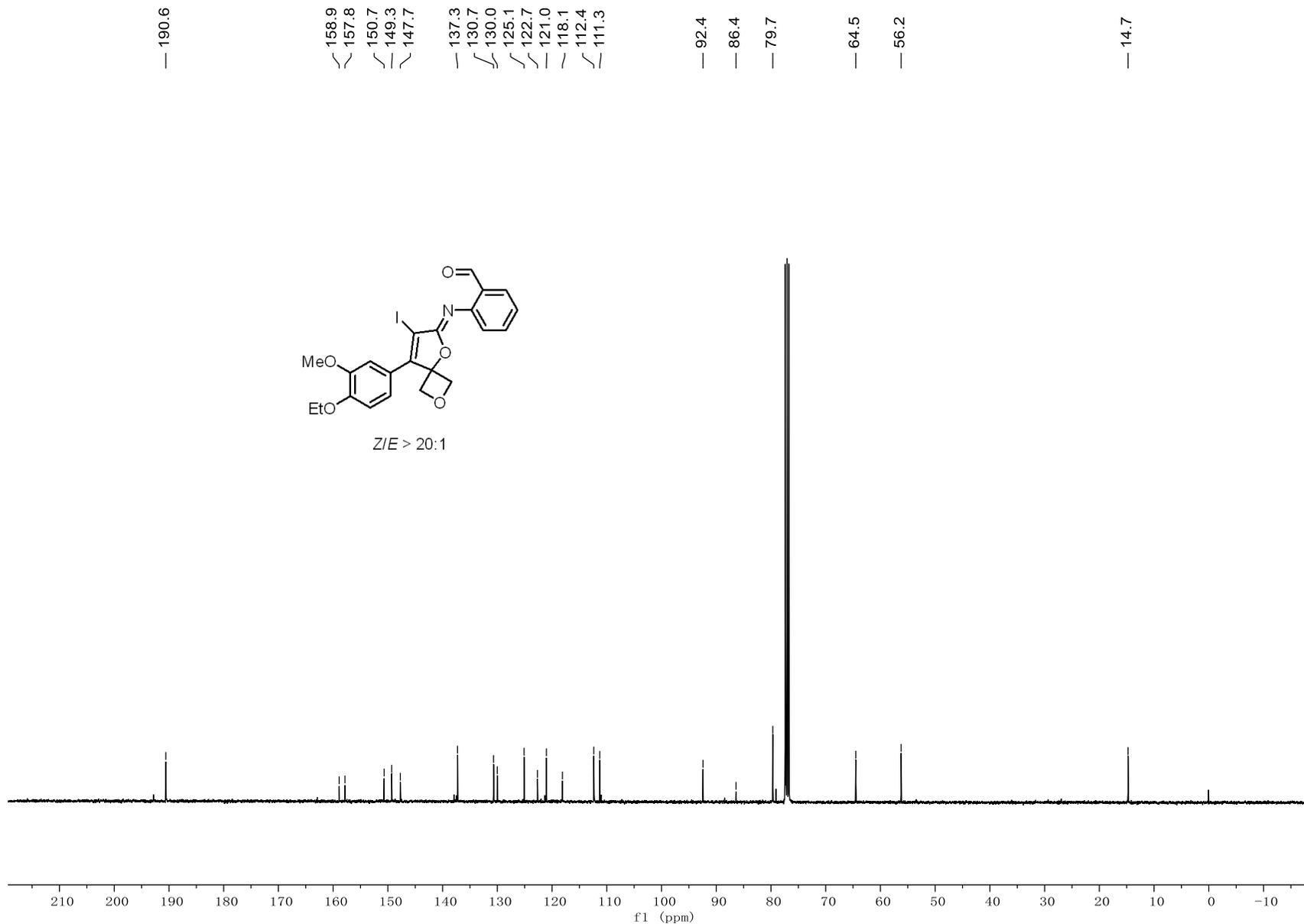
8.005
7.663
7.662
7.574
7.567
7.562
7.260
7.255
7.236
7.046
7.024

5.041
5.021
4.994
4.975
4.234
4.217
4.199
4.181
3.966

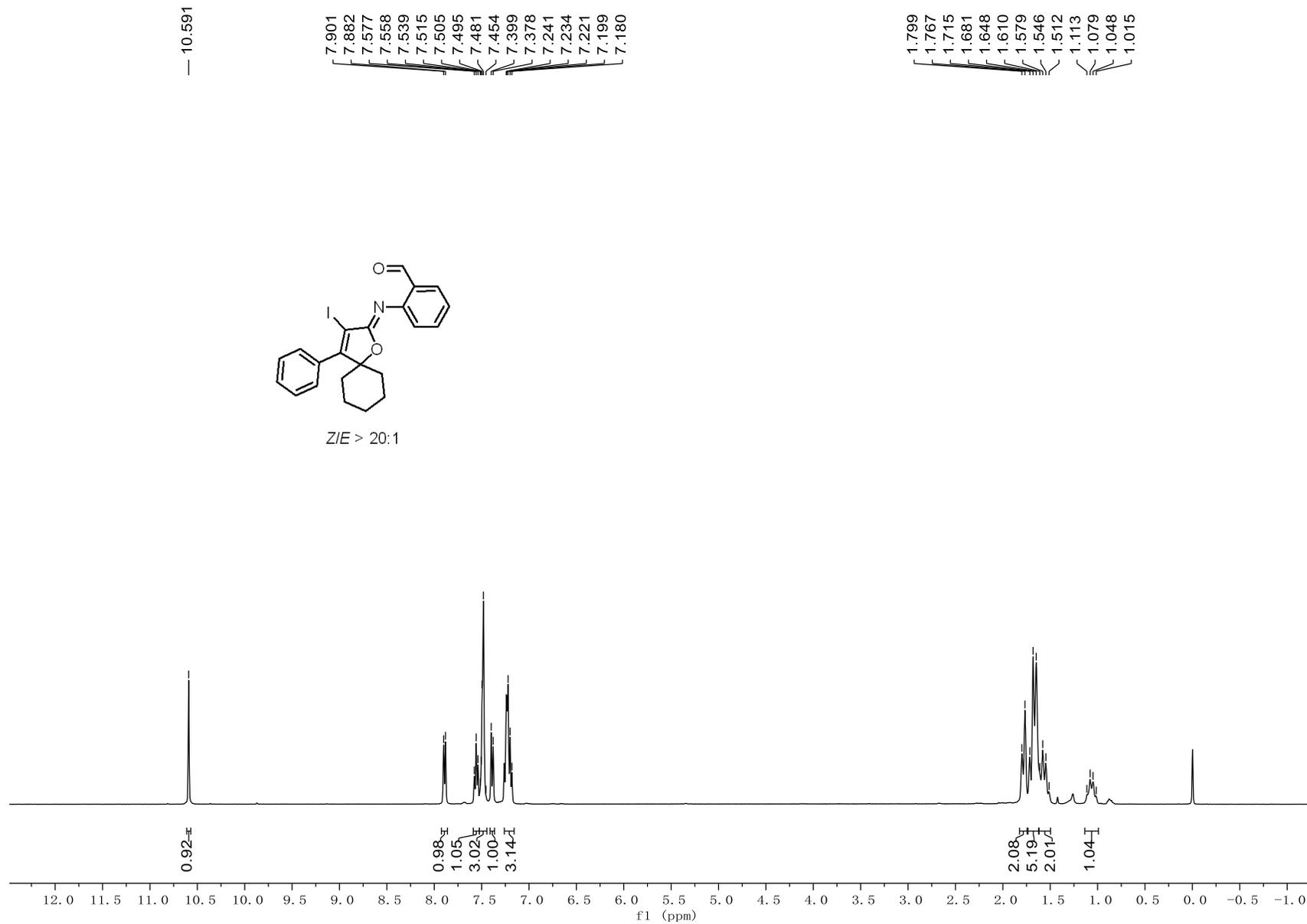
1.550
1.533
1.515

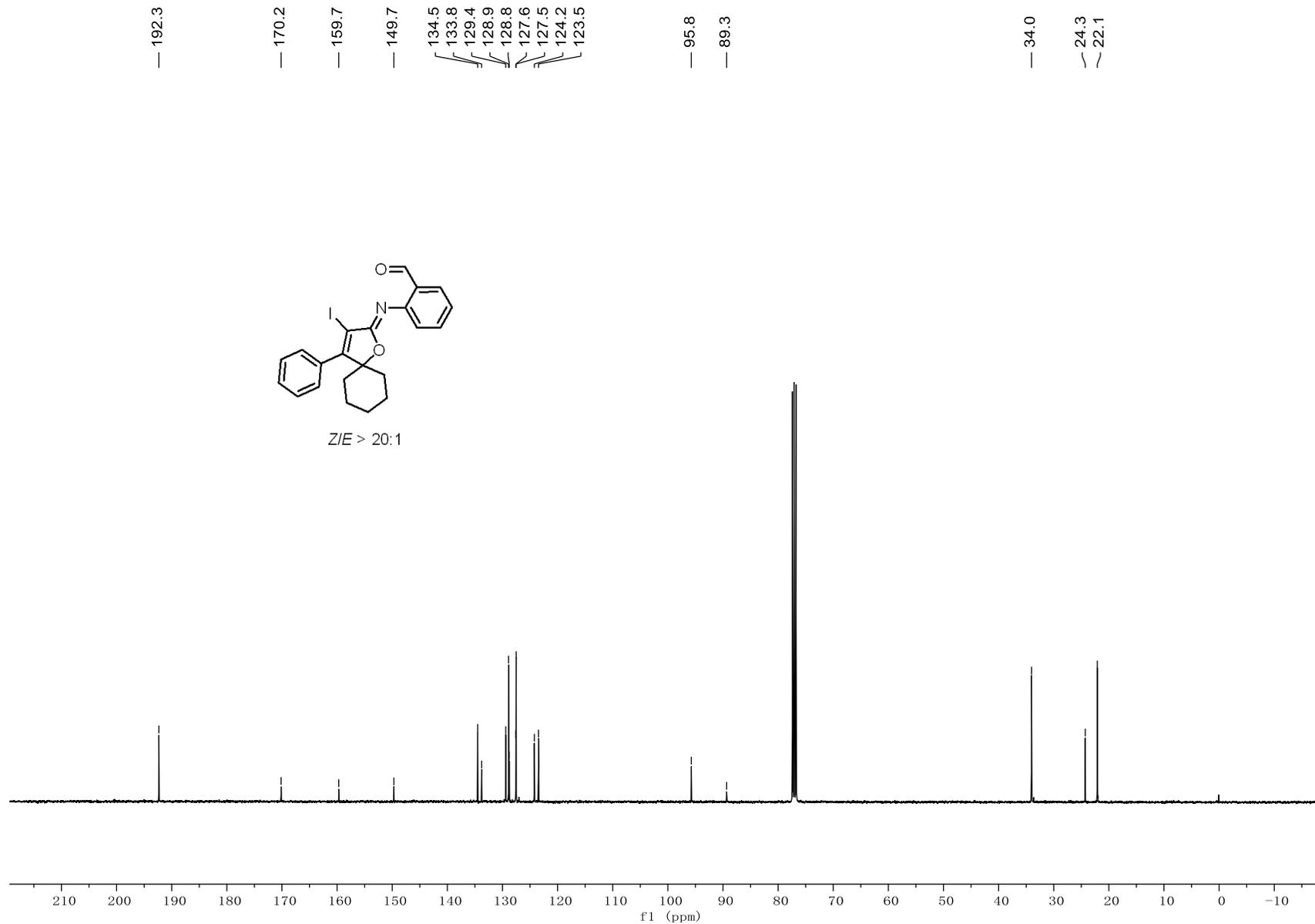


¹H NMR Spectrum (400 MHz, CDCl₃) of 3i

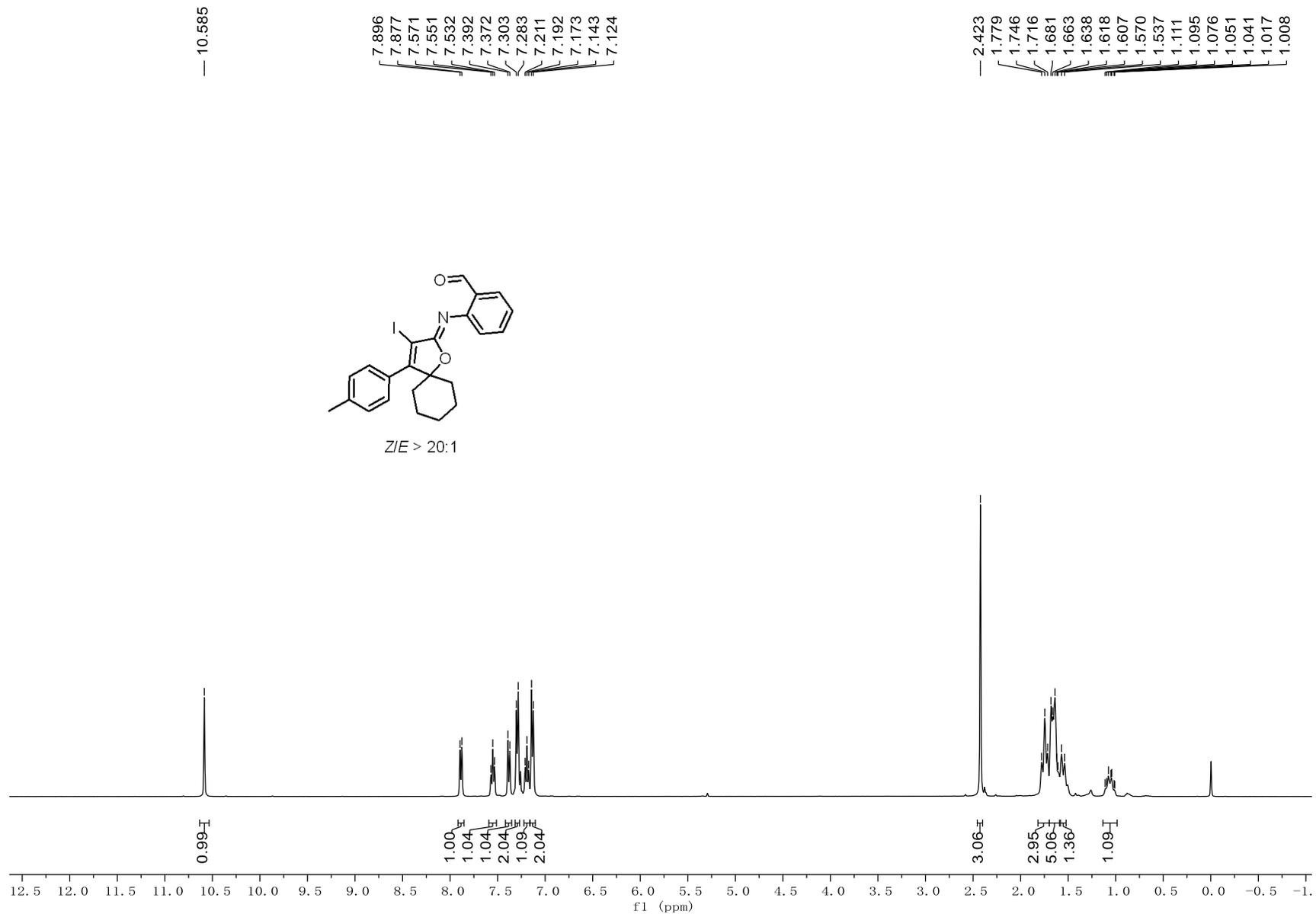


¹³C NMR Spectrum (100 MHz, CDCl₃) of 3i

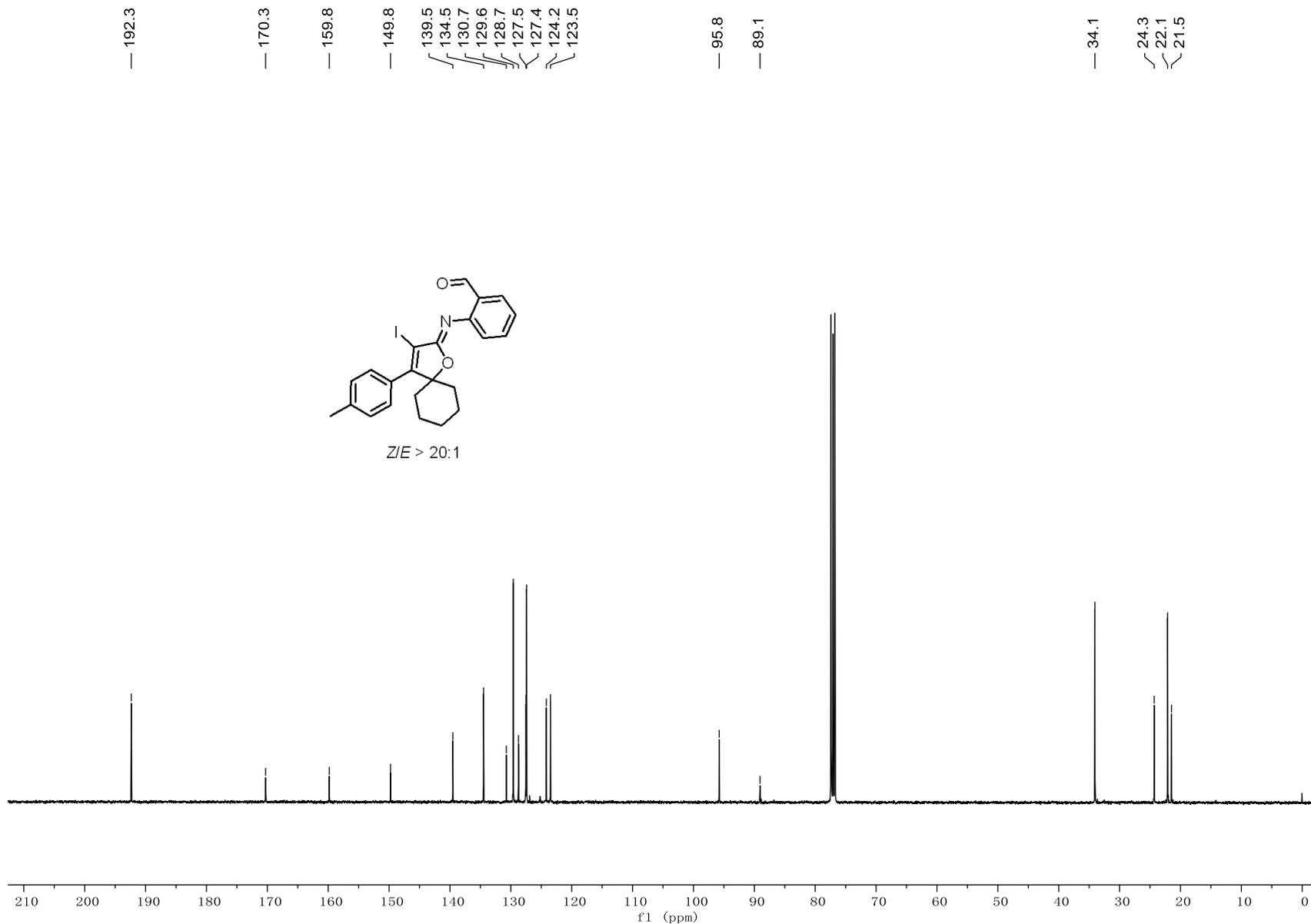




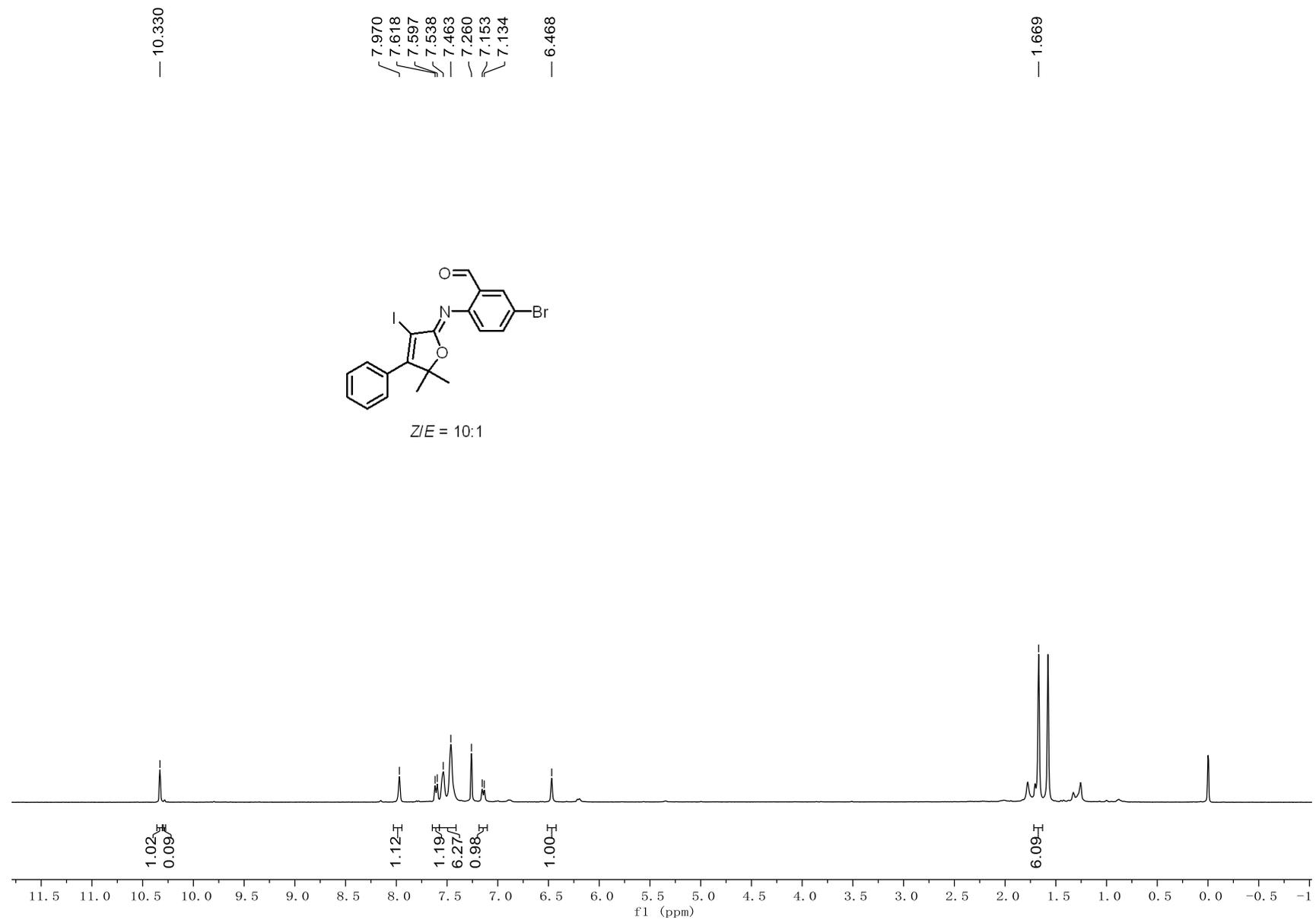
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3j



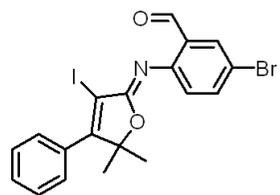
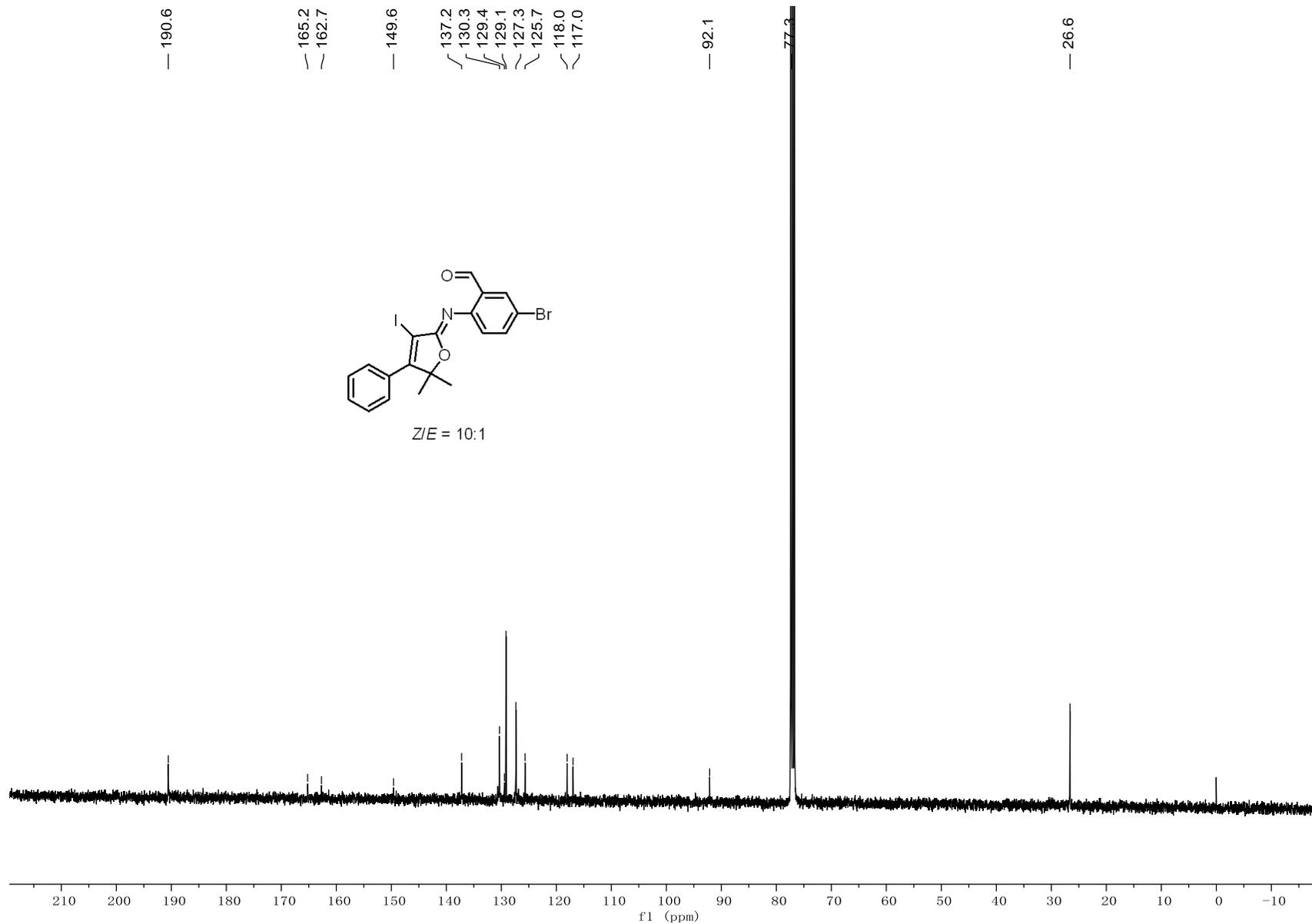
¹H NMR Spectrum (400 MHz, CDCl₃) of 3k



¹³C NMR Spectrum (100 MHz, CDCl₃) of 3k

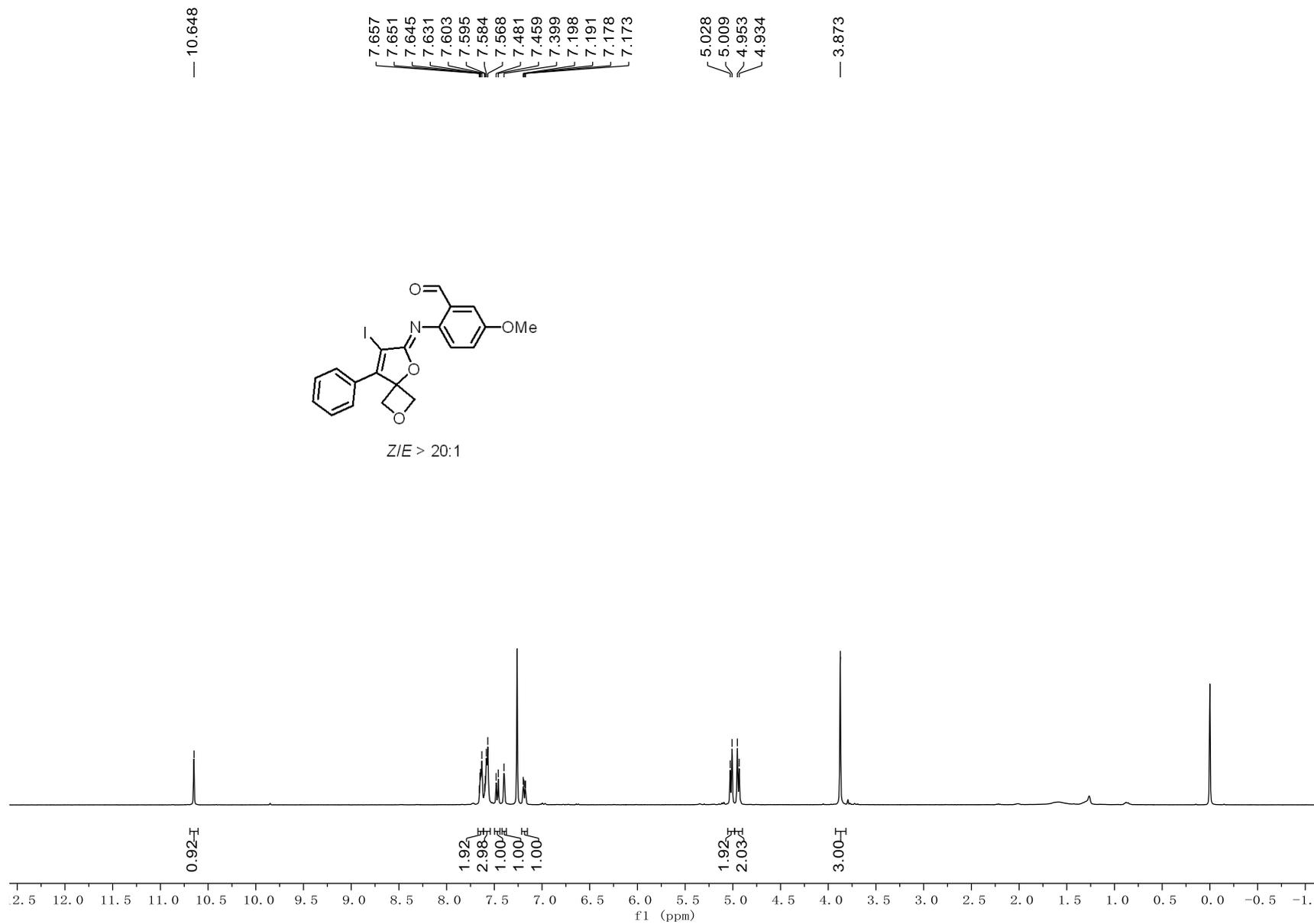


¹H NMR Spectrum (400 MHz, CDCl₃) of 31

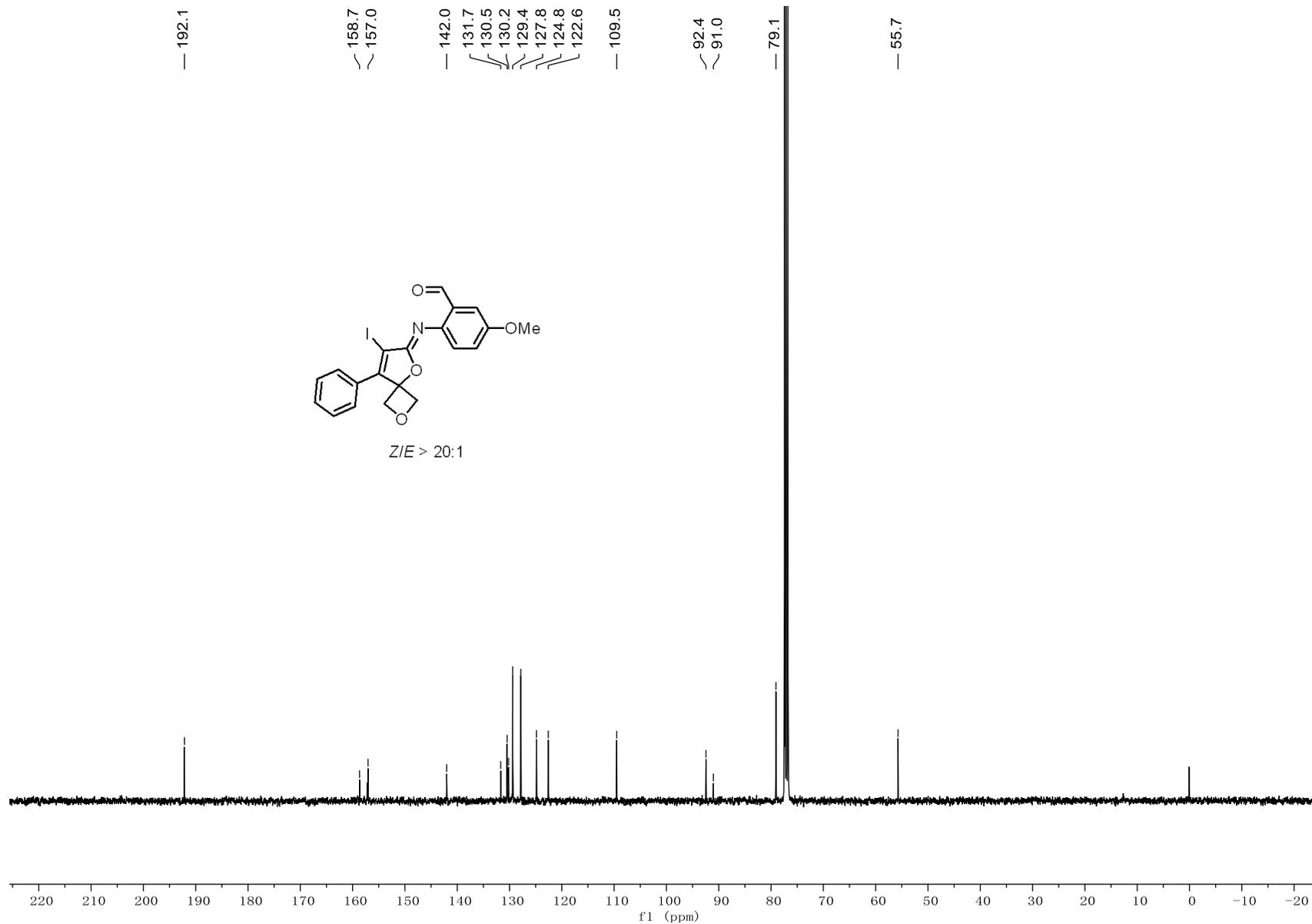


Z/E = 10:1

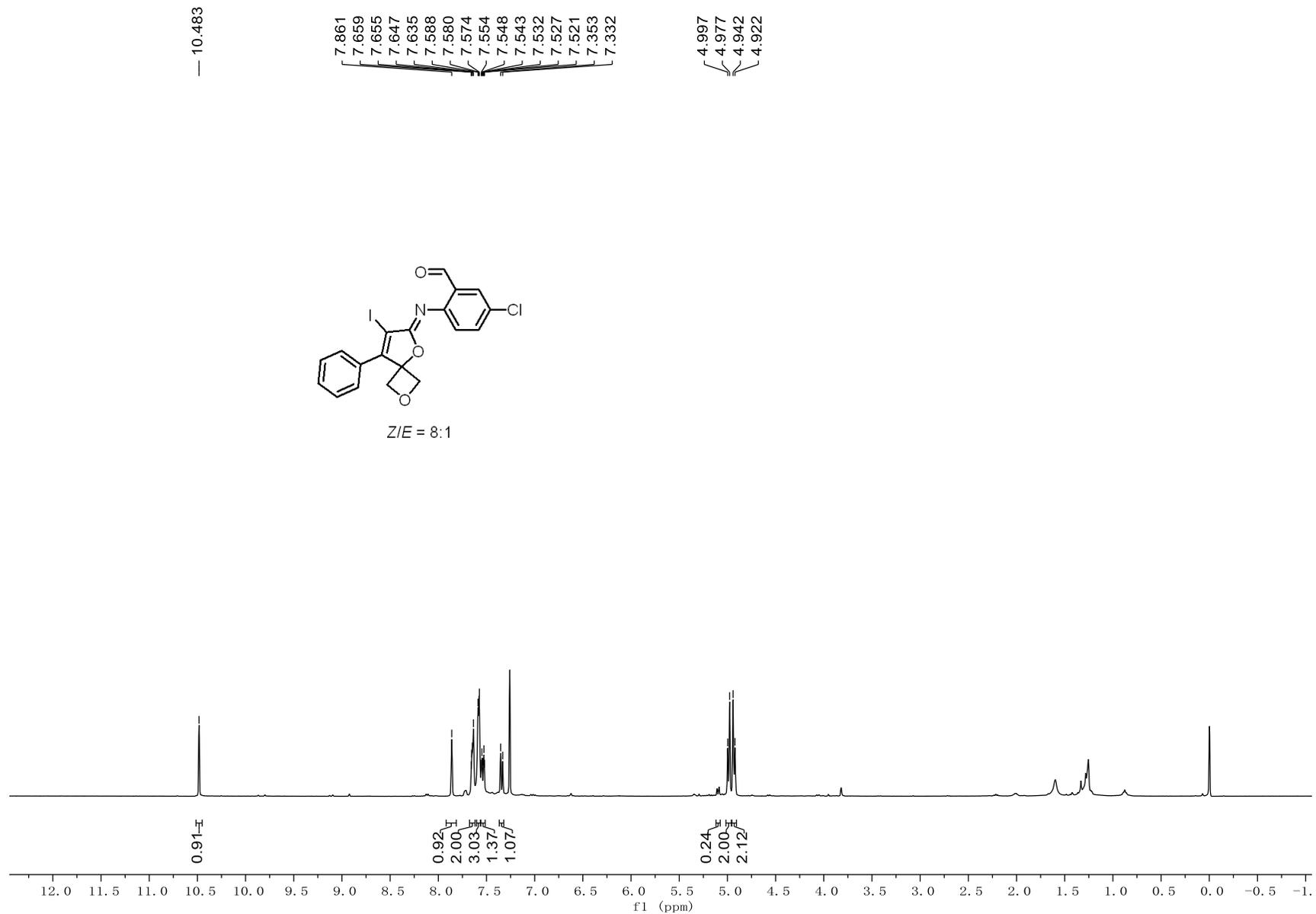
¹³C NMR Spectrum (100 MHz, CDCl₃) of 31



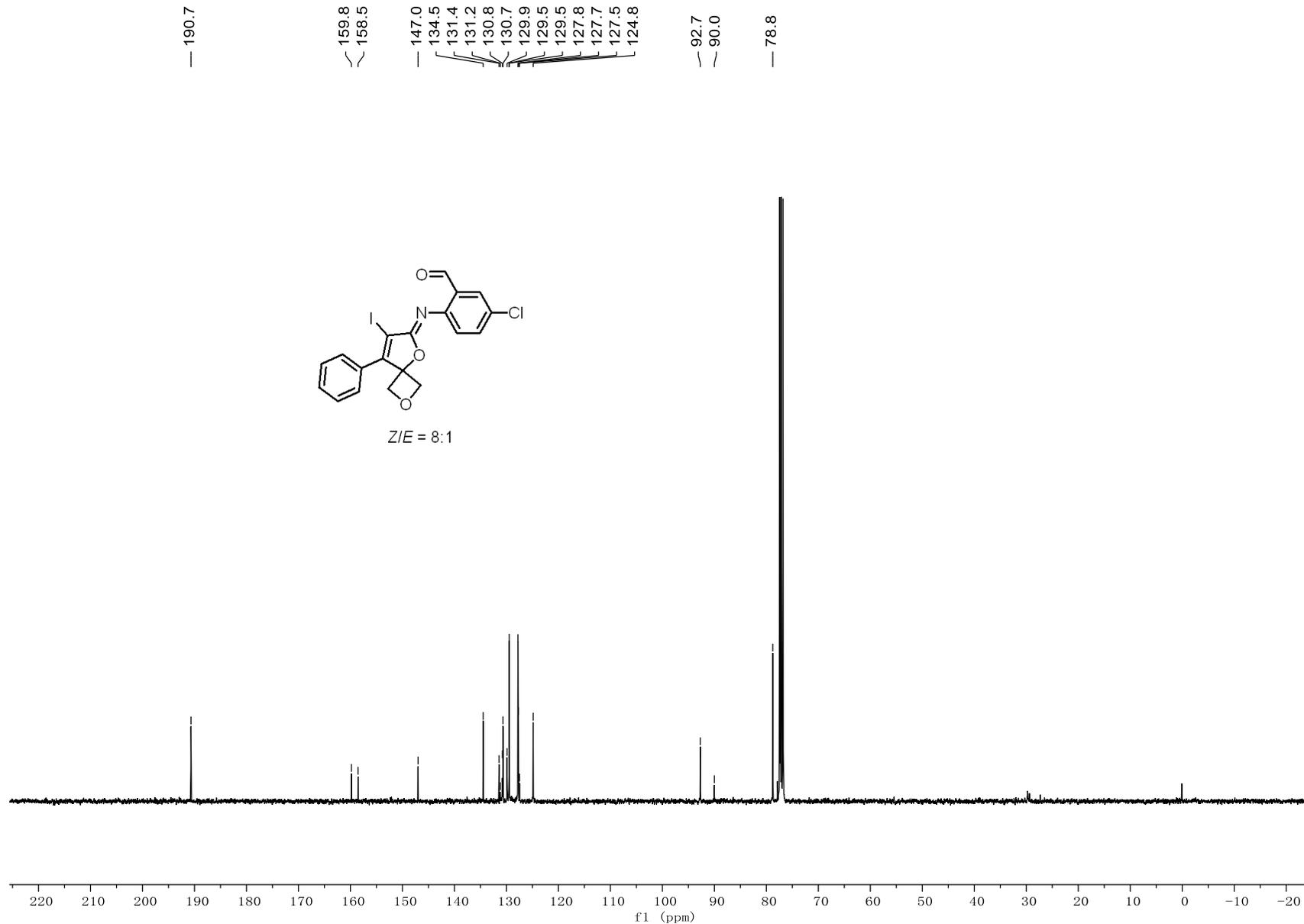
¹H NMR Spectrum (400 MHz, CDCl₃) of 3m



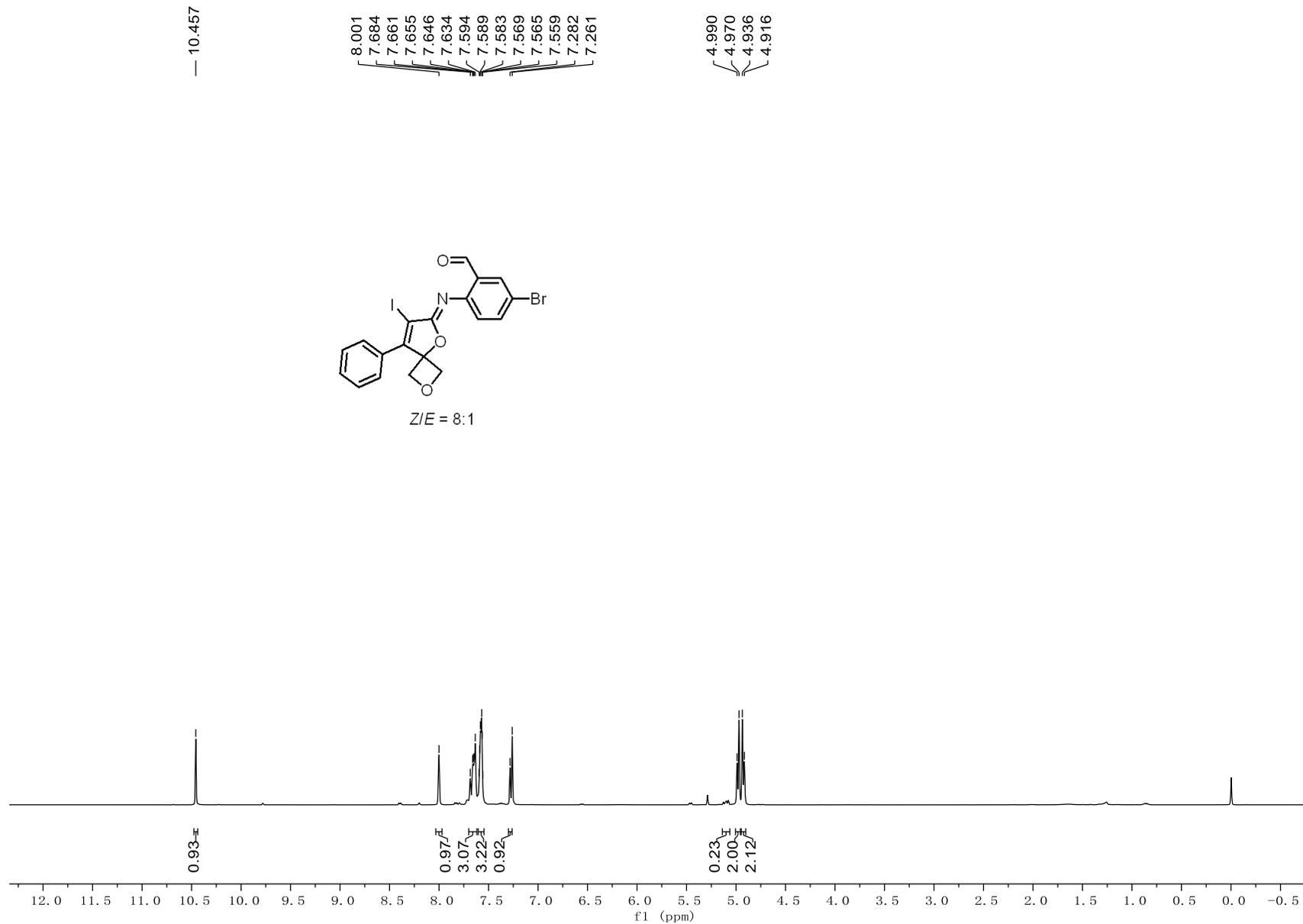
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3m



¹H NMR Spectrum (400 MHz, CDCl₃) of 3n



¹³C NMR Spectrum (100 MHz, CDCl₃) of 3n



— 190.5

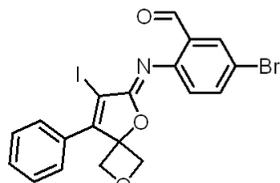
— 159.9
— 158.5

— 147.5

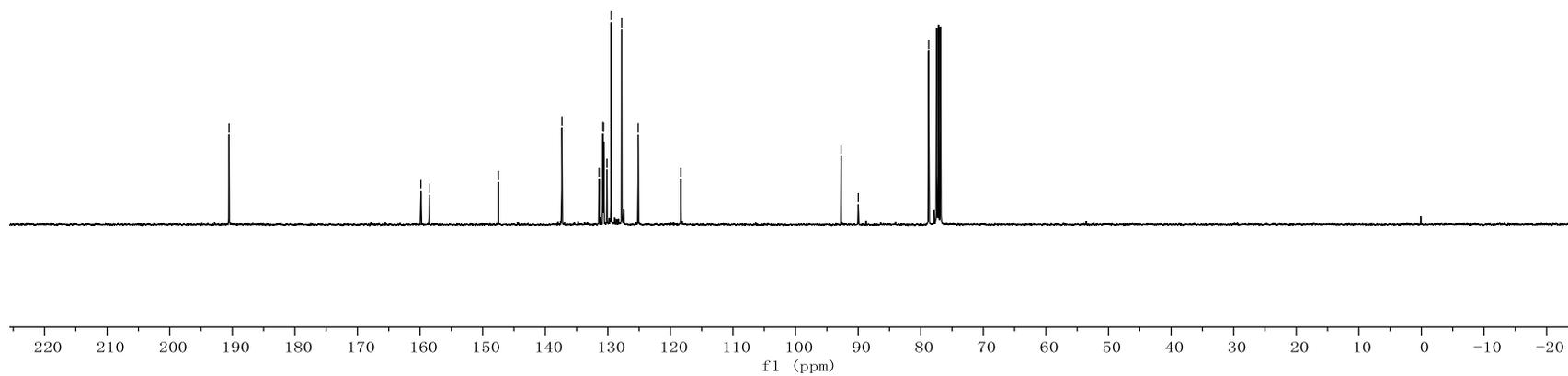
— 137.3
— 131.4
— 130.8
— 130.7
— 130.1
— 129.5
— 127.8
— 125.1
— 118.3

— 92.7
— 90.0

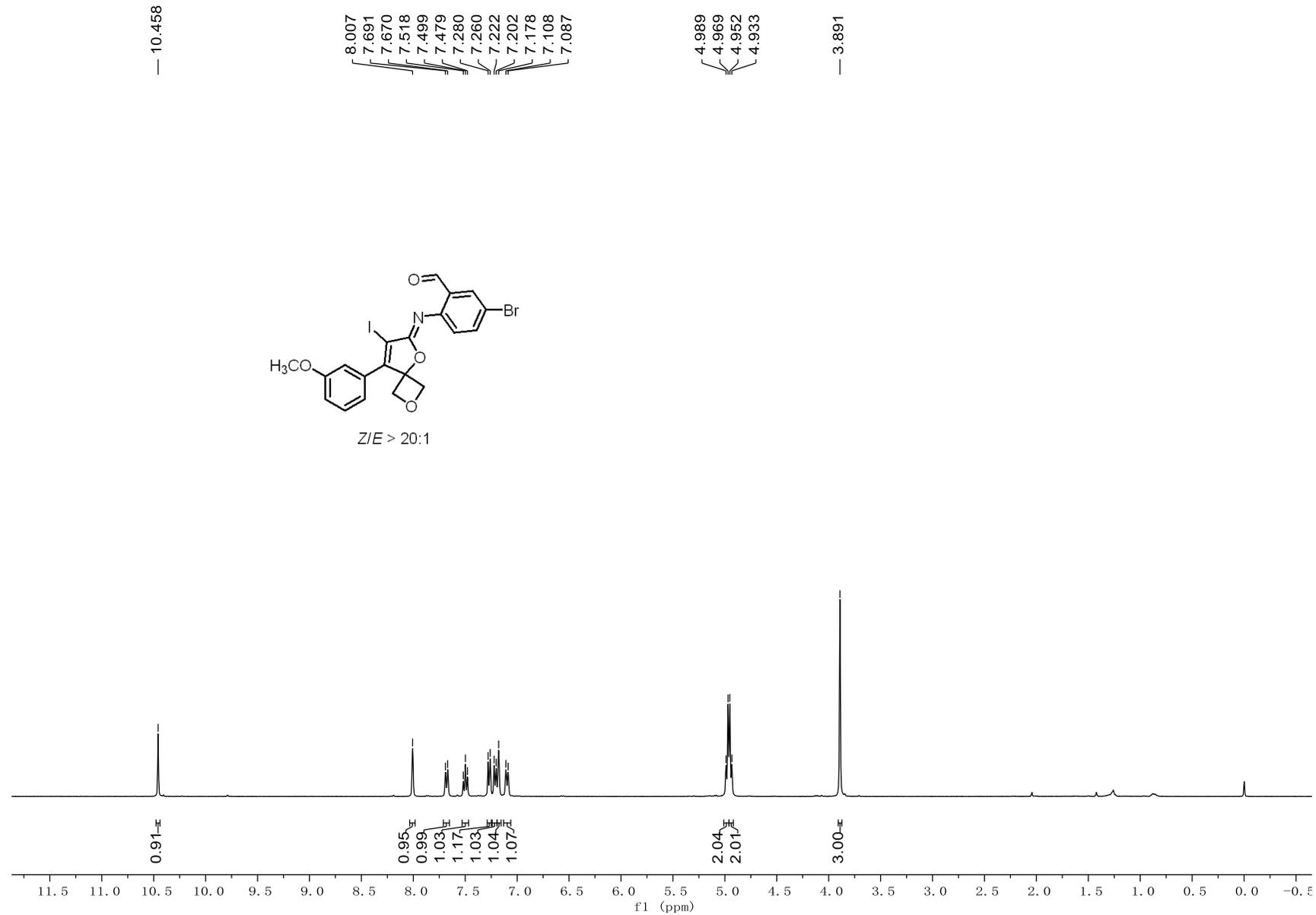
— 78.7



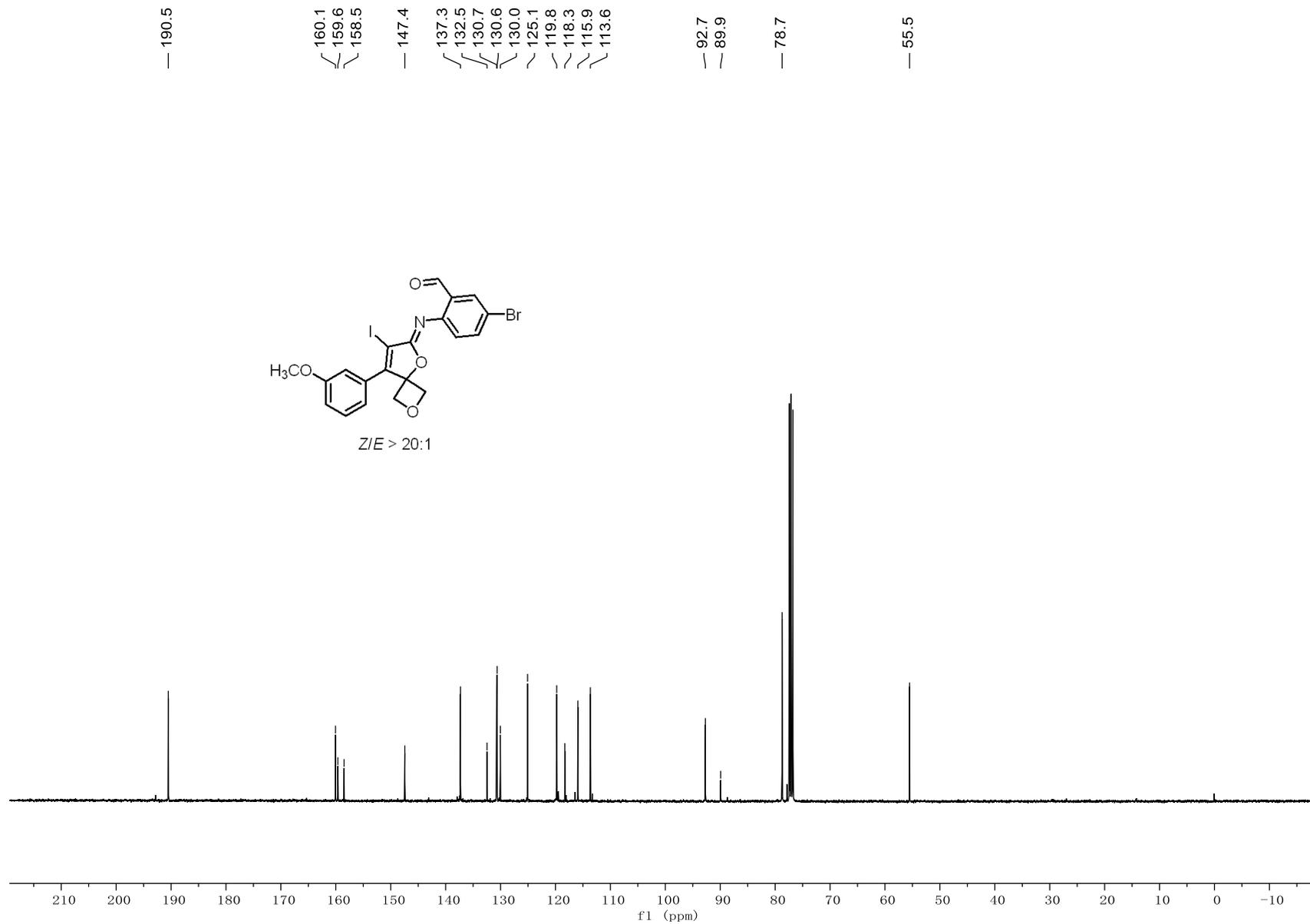
Z/E = 8:1



¹³C NMR Spectrum (100 MHz, CDCl₃) of 3o

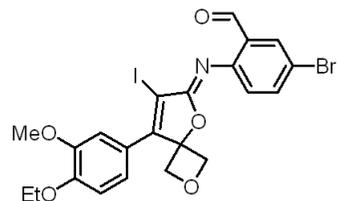


¹H NMR Spectrum (400 MHz, CDCl₃) of 3p



^{13}C NMR Spectrum (100 MHz, CDCl_3) of 3p

— 10.451

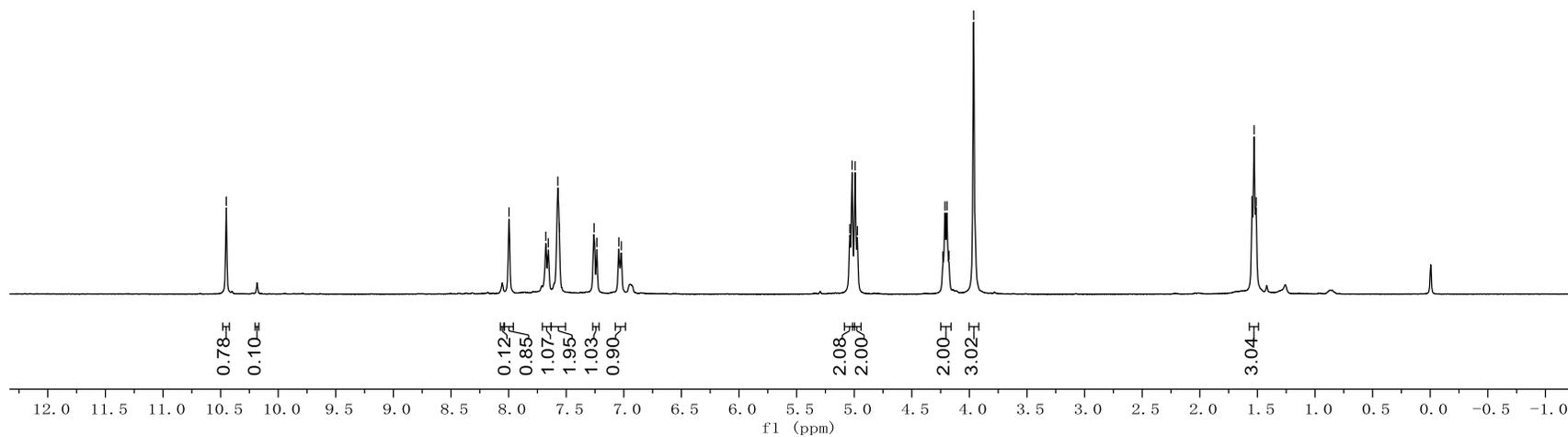


Z/E = 8:1

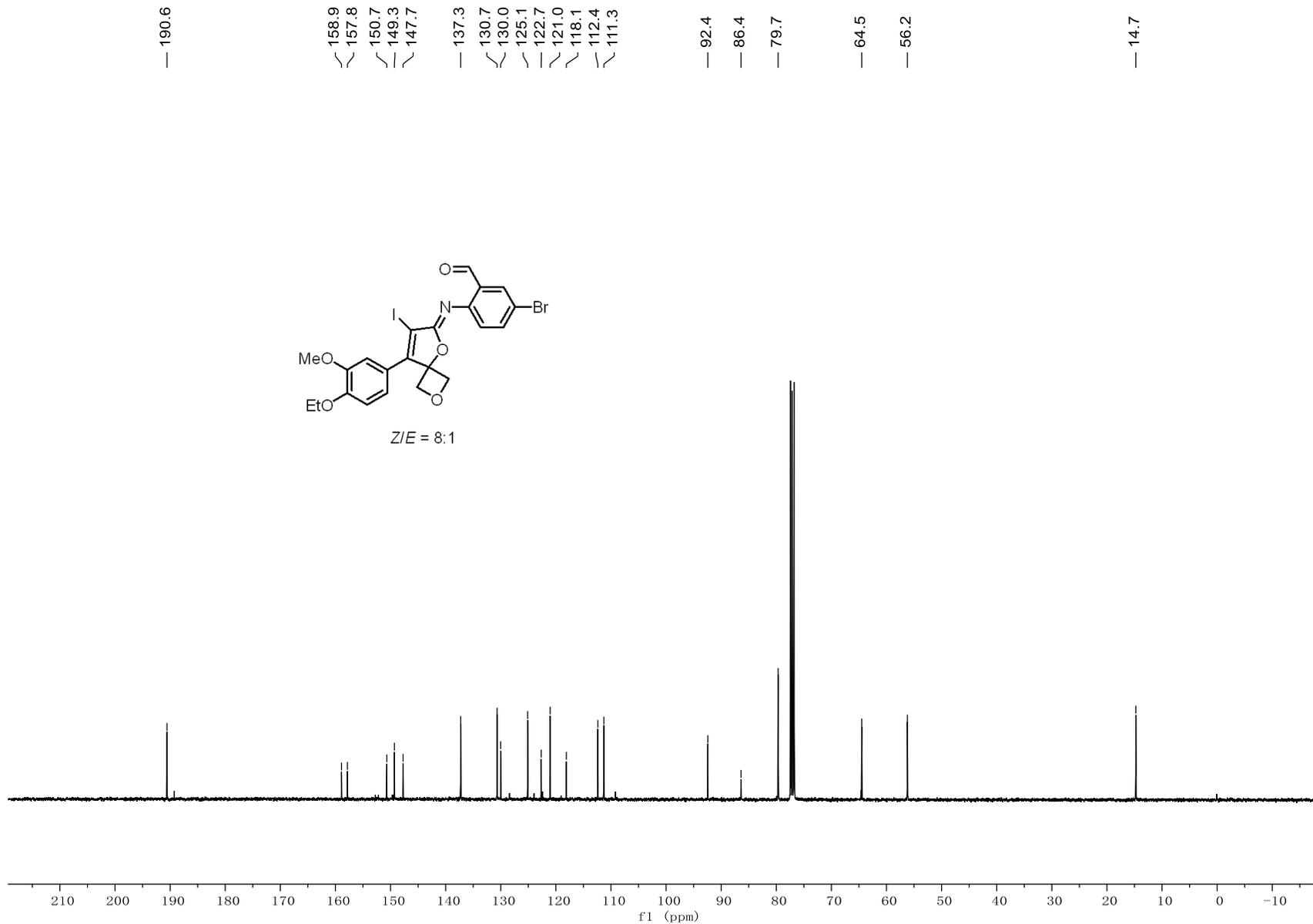
7.997
7.677
7.656
7.573
7.559
7.258
7.234
7.043
7.022

5.039
5.019
4.992
4.972
4.230
4.212
4.195
4.177
3.963

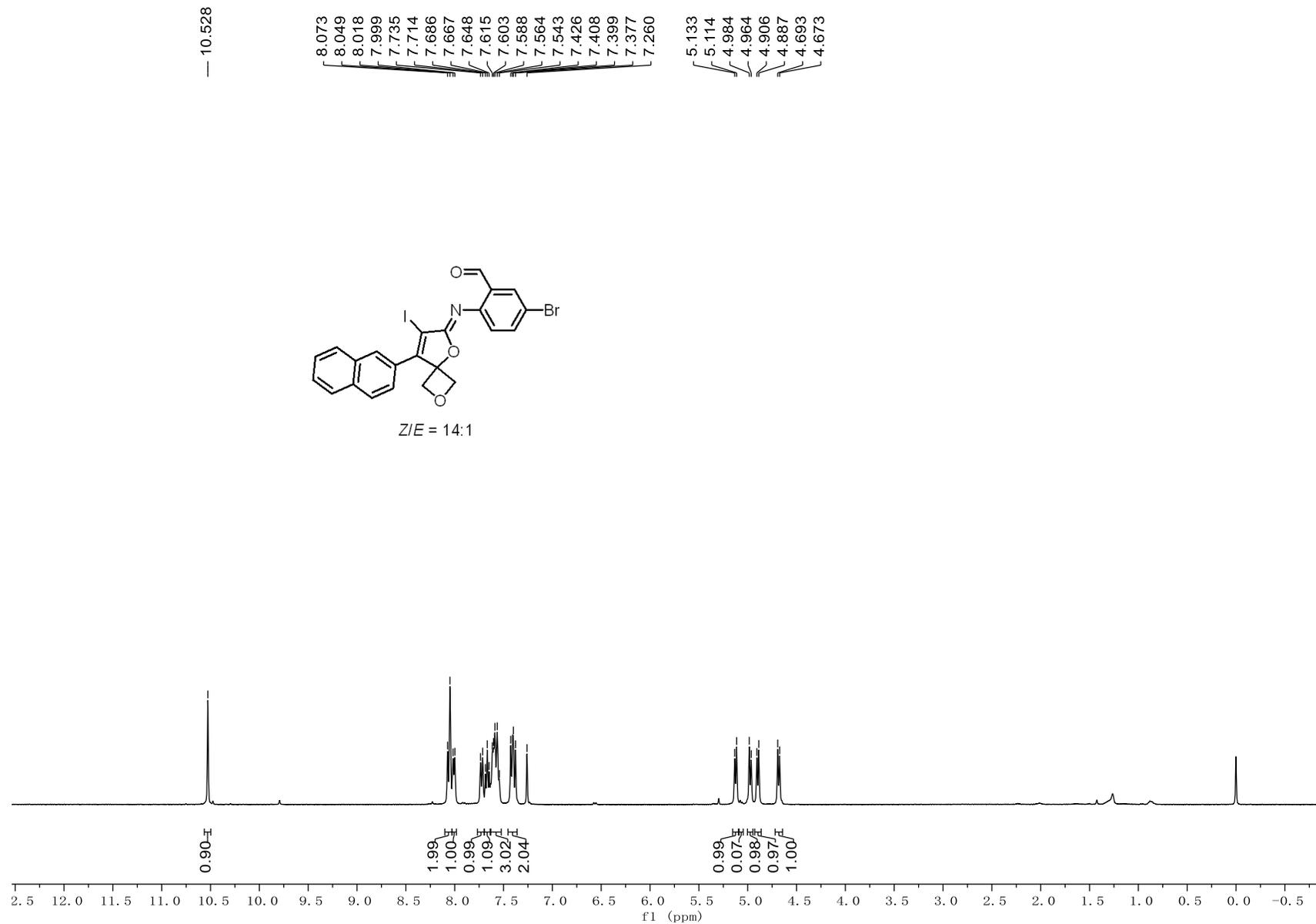
1.547
1.529
1.511



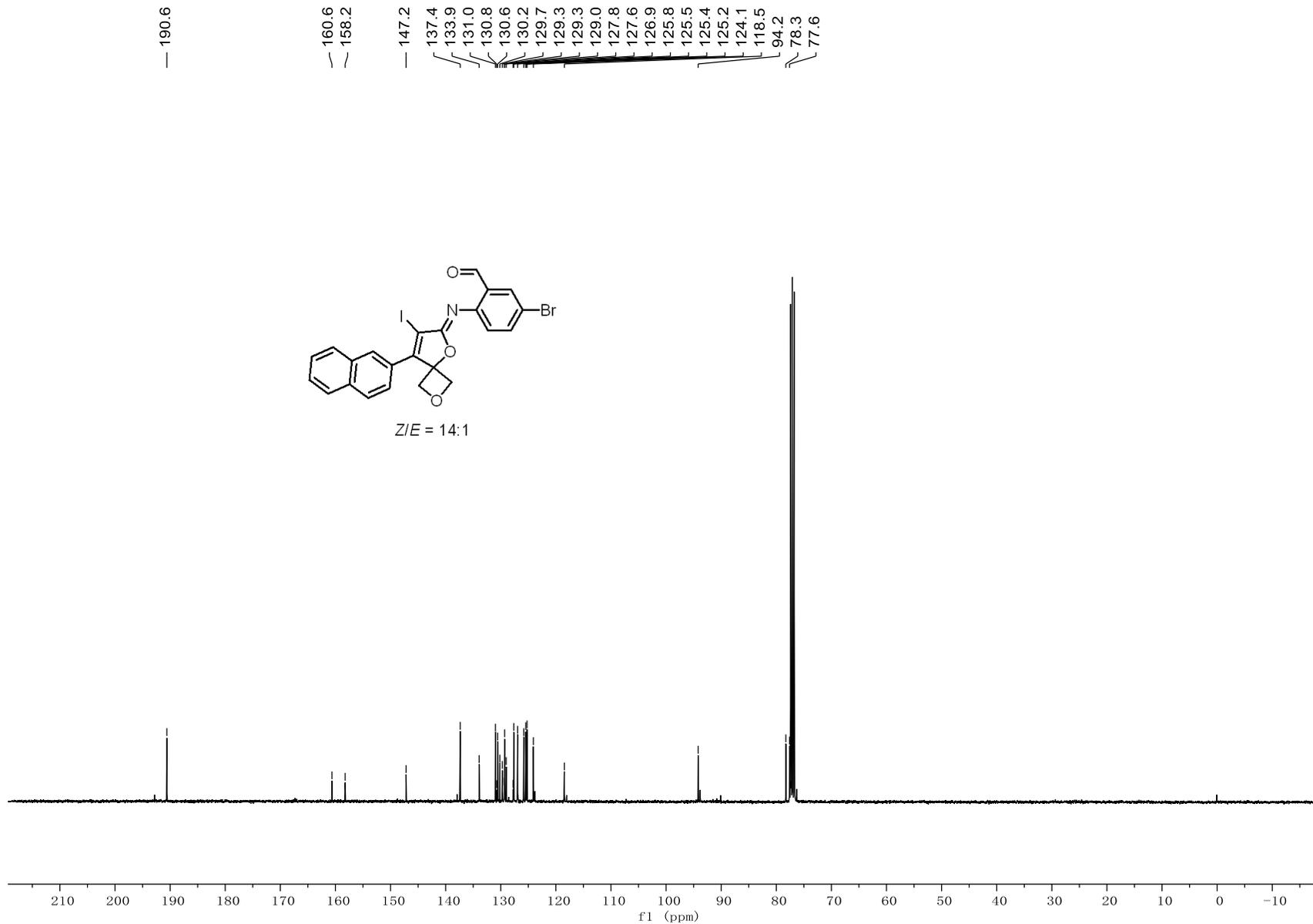
^1H NMR Spectrum (400 MHz, CDCl_3) of 3q



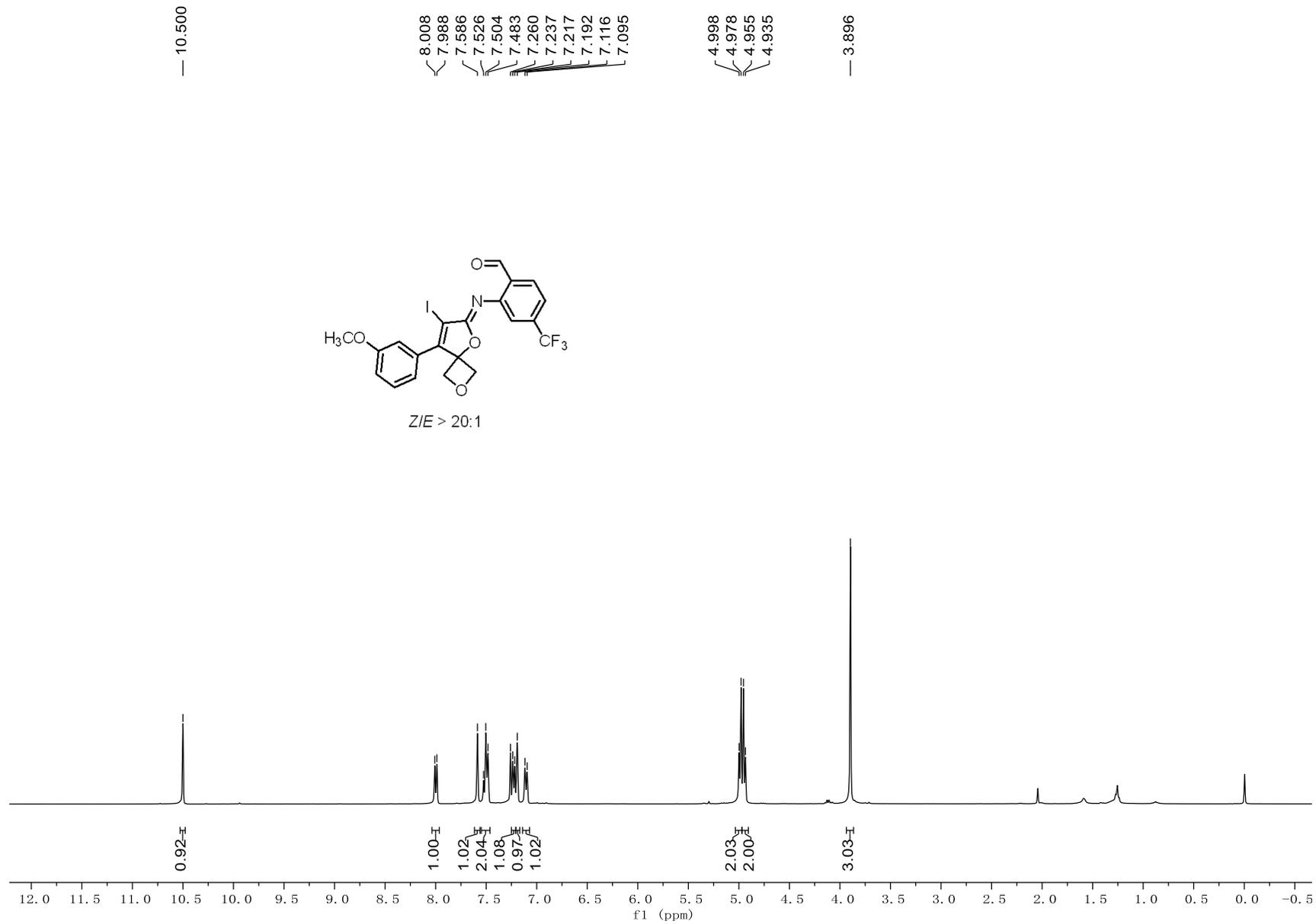
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3q

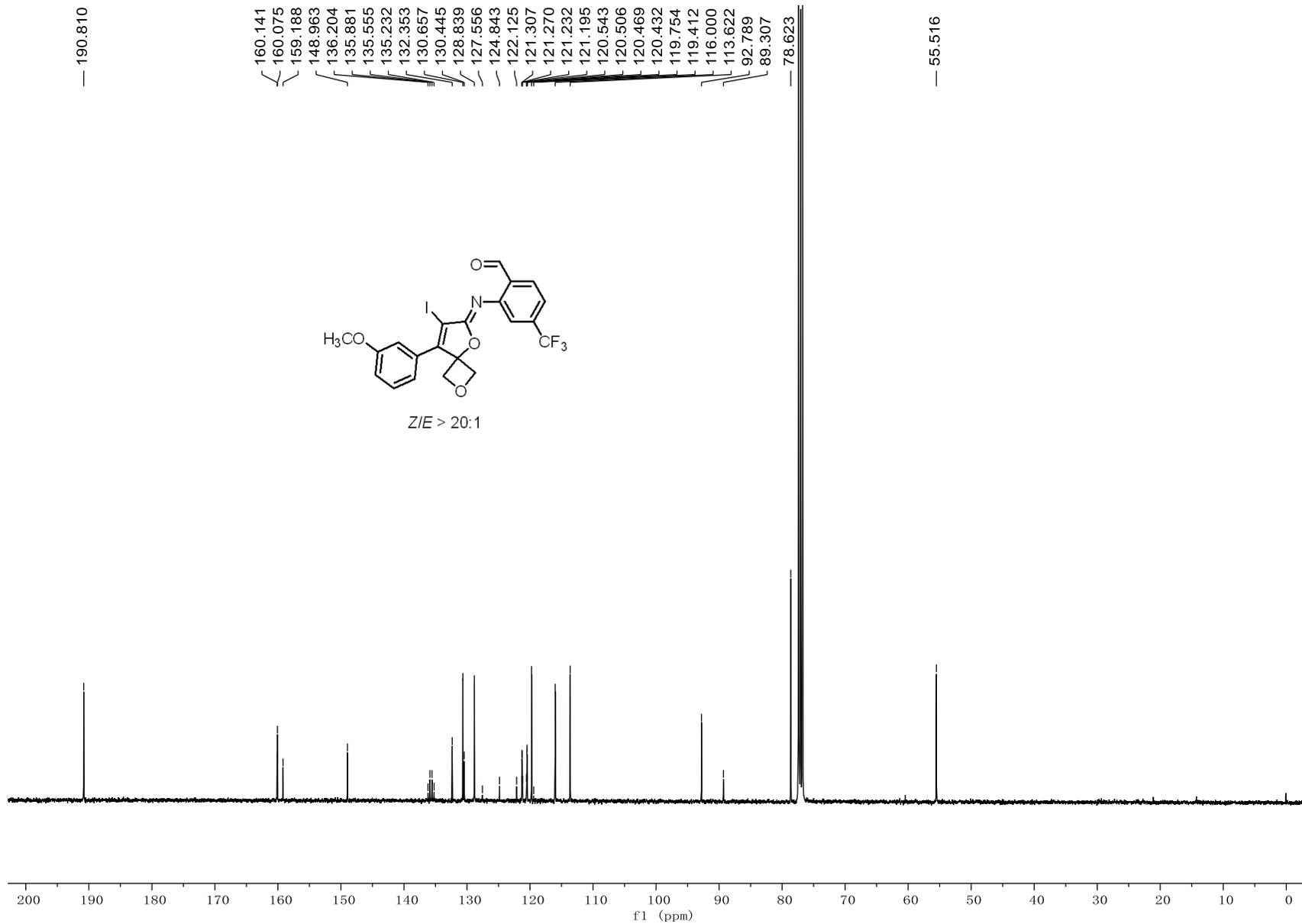


¹H NMR Spectrum (400 MHz, CDCl₃) of 3r

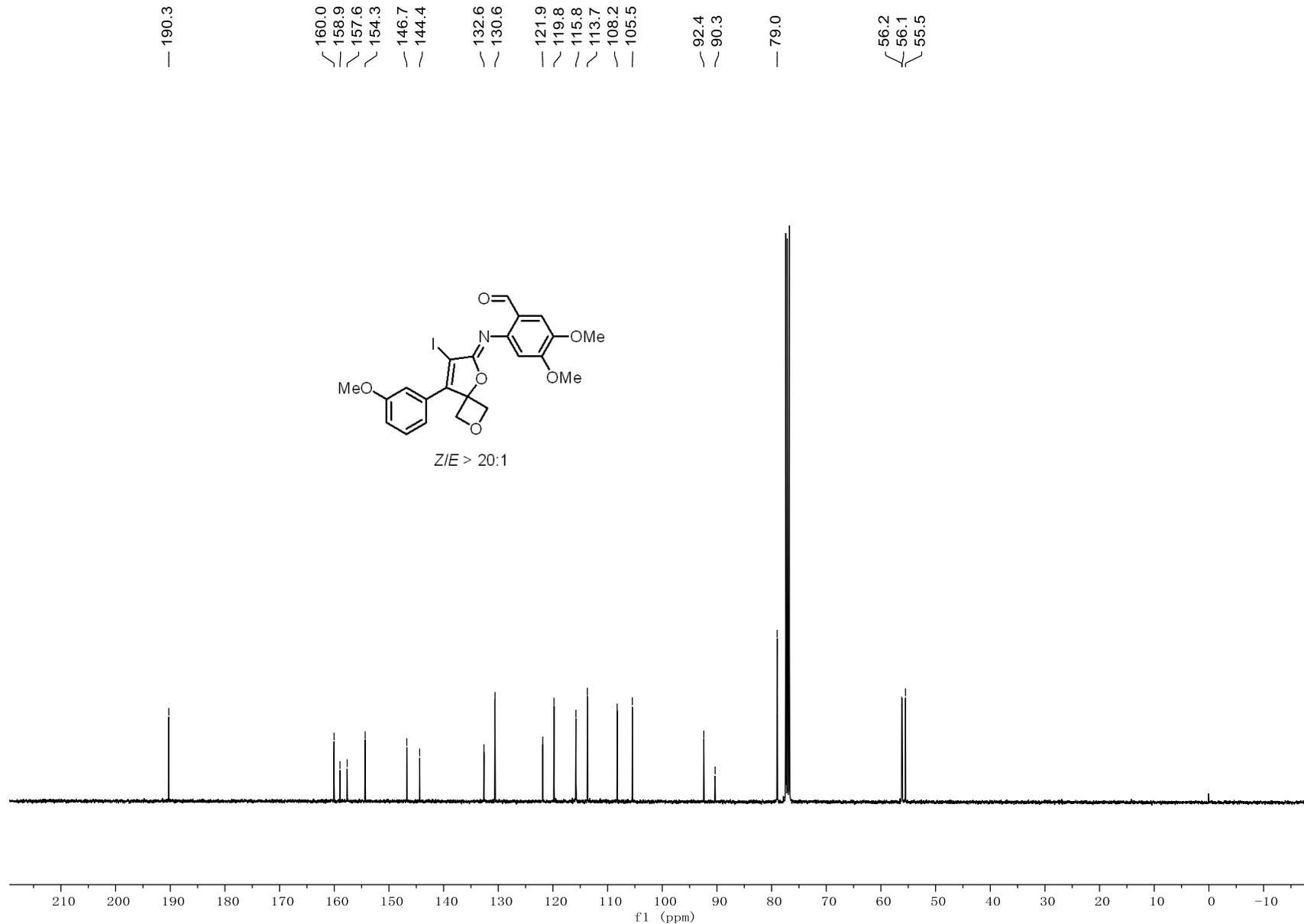


¹³C NMR Spectrum (100 MHz, CDCl₃) of 3r

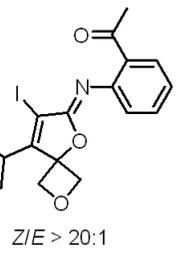
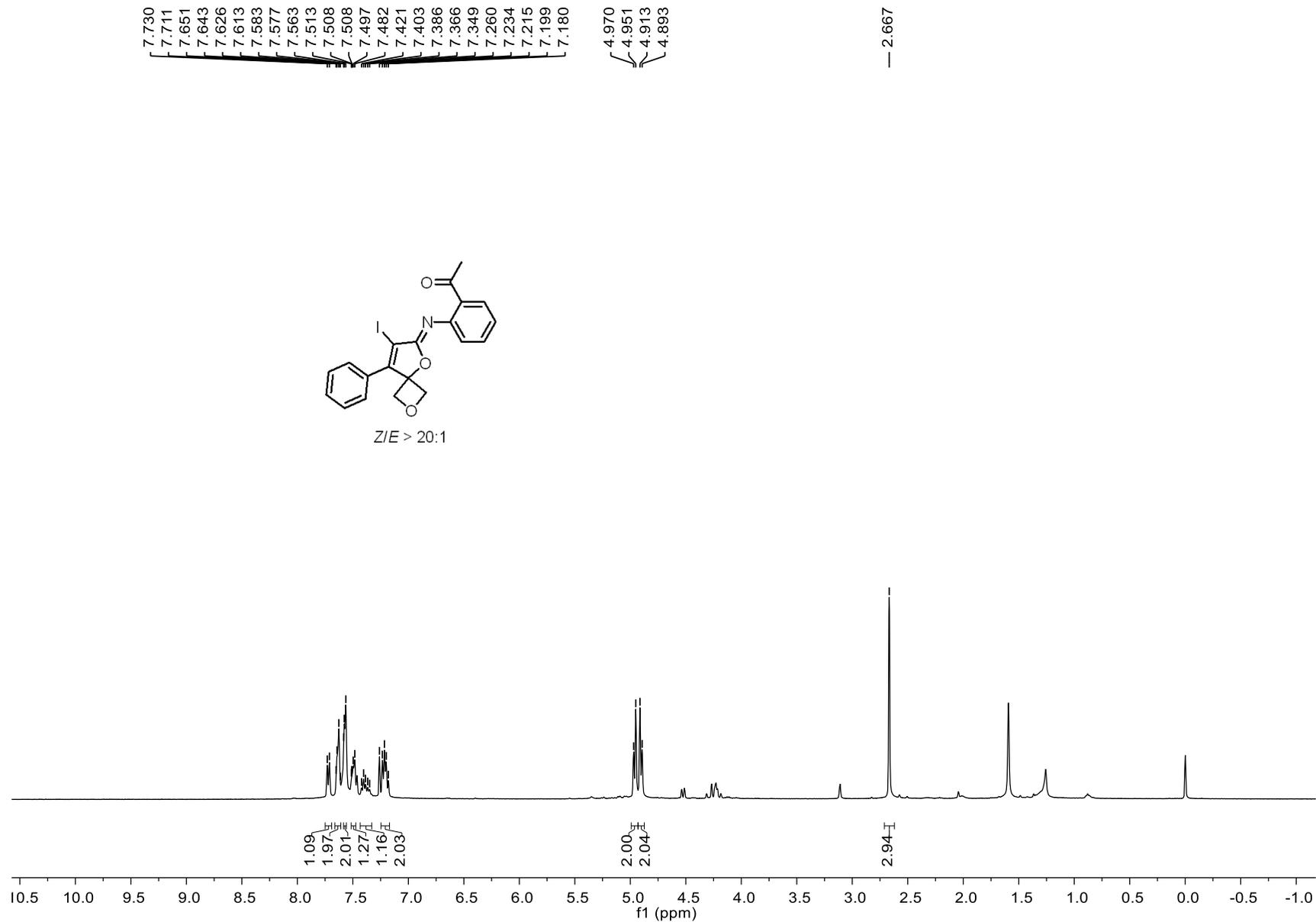




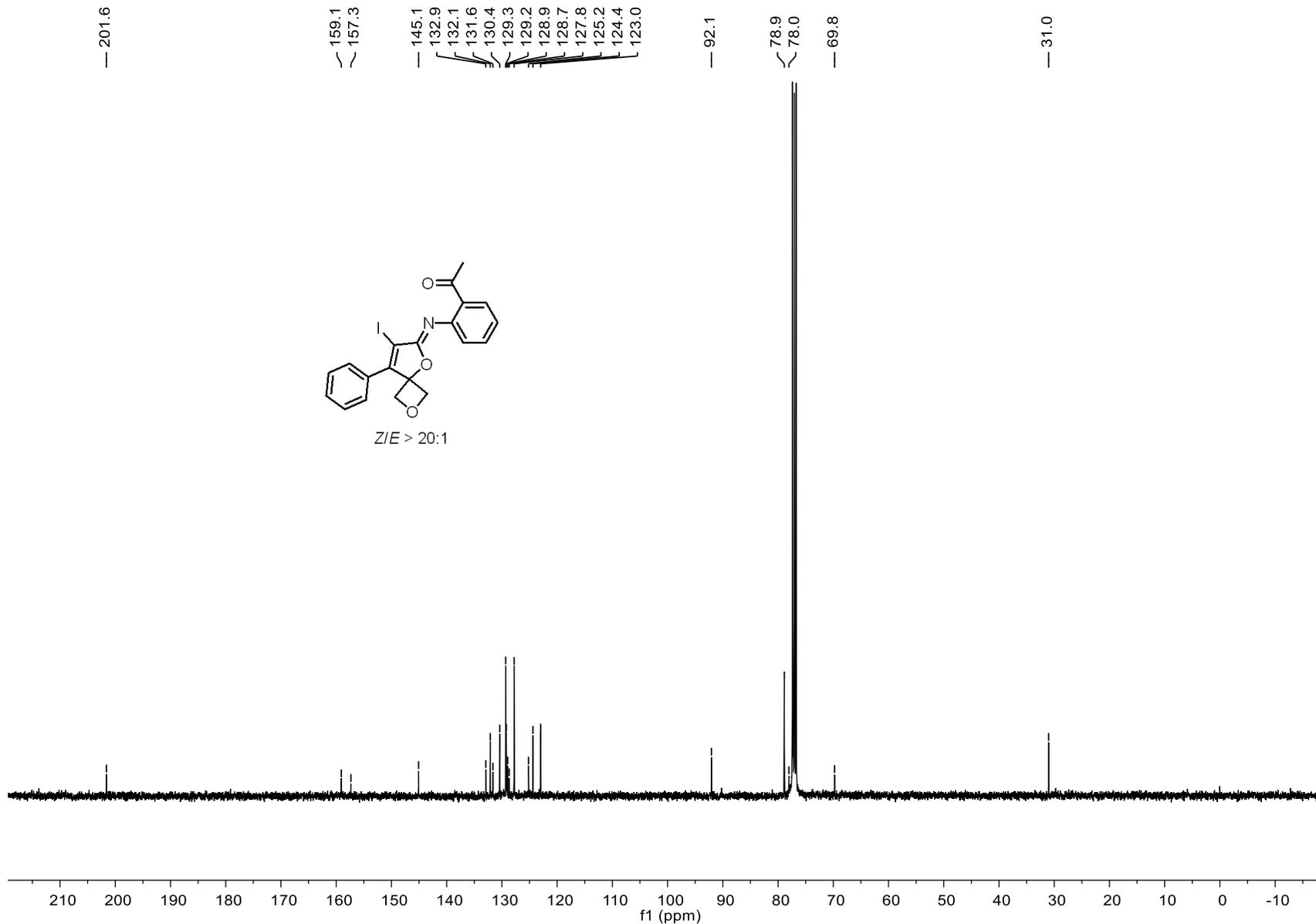
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3s



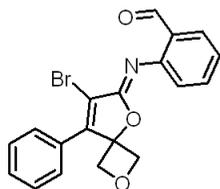
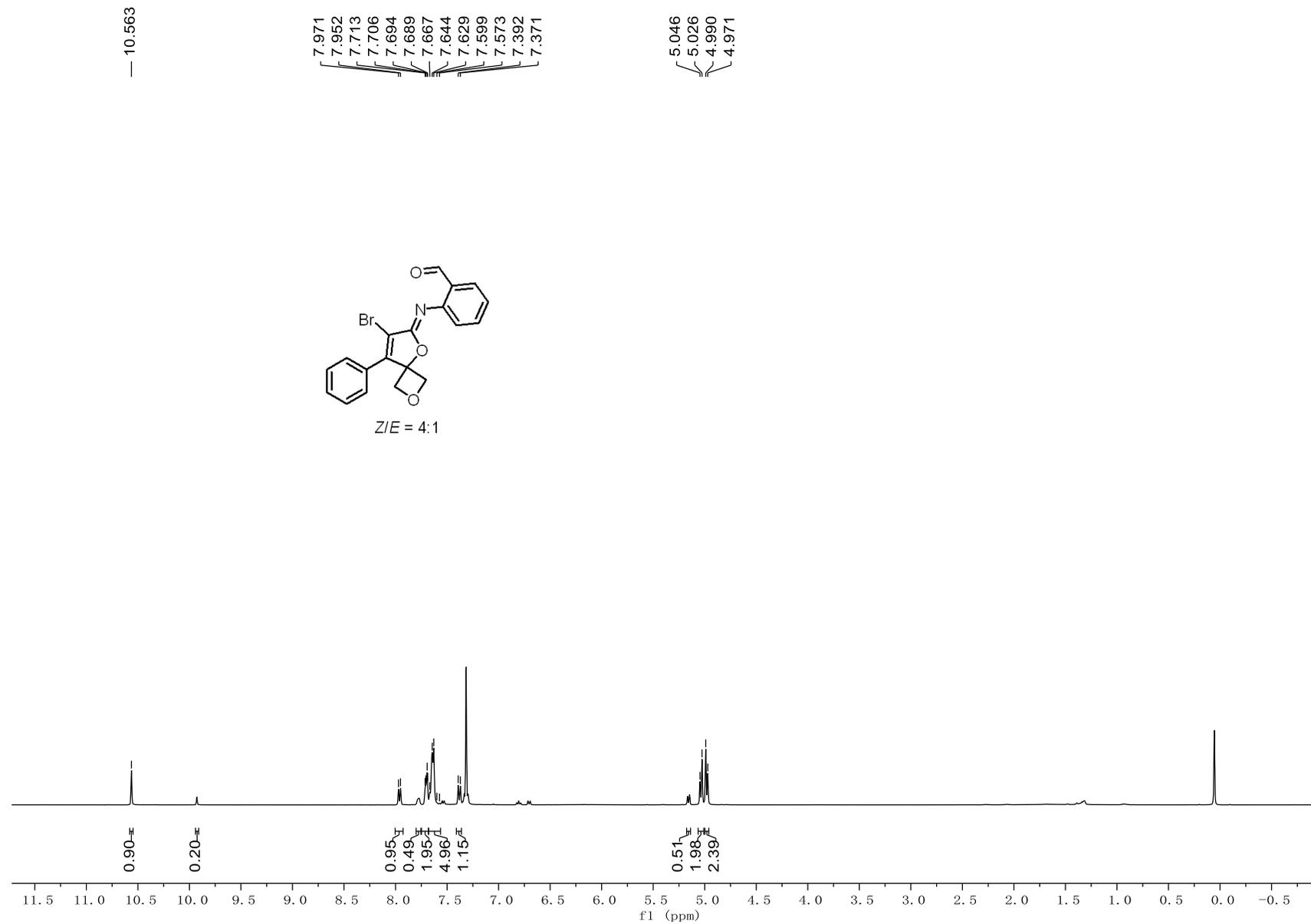
¹³C NMR Spectrum (100 MHz, CDCl₃) of 3t



¹H NMR Spectrum (400 MHz, CDCl₃) of 3u



¹³C NMR Spectrum (100 MHz, CDCl₃) of 3u



Z/E = 4:1

¹H NMR Spectrum (400 MHz, CDCl₃) of 3v

— 190.5

— 159.9

— 158.5

— 147.5

— 137.3

— 131.4

— 130.8

— 130.7

— 130.1

— 129.5

— 127.8

— 125.1

— 118.3

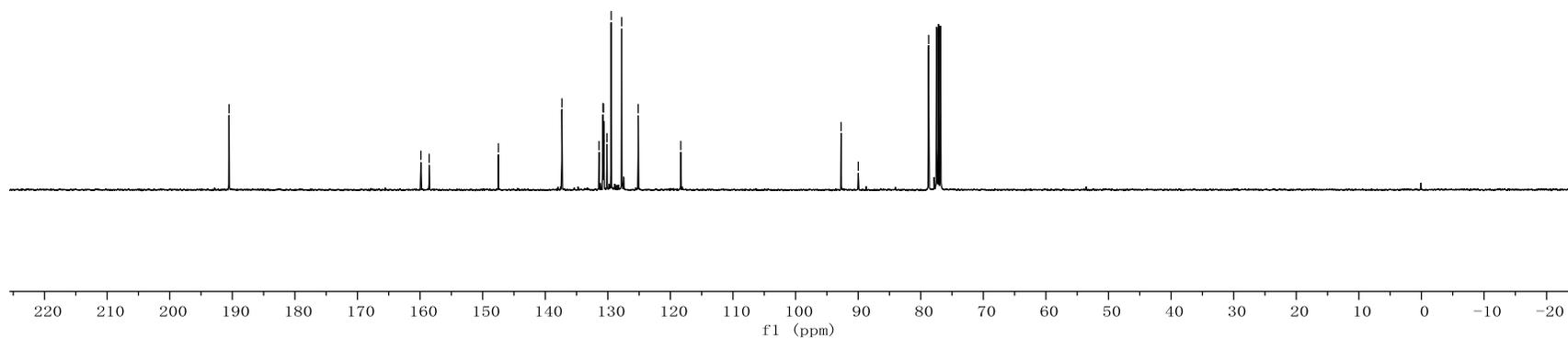
— 92.7

— 90.0

— 78.7

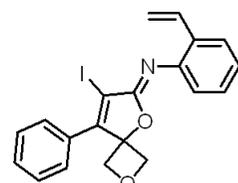


Z/E = 4:1

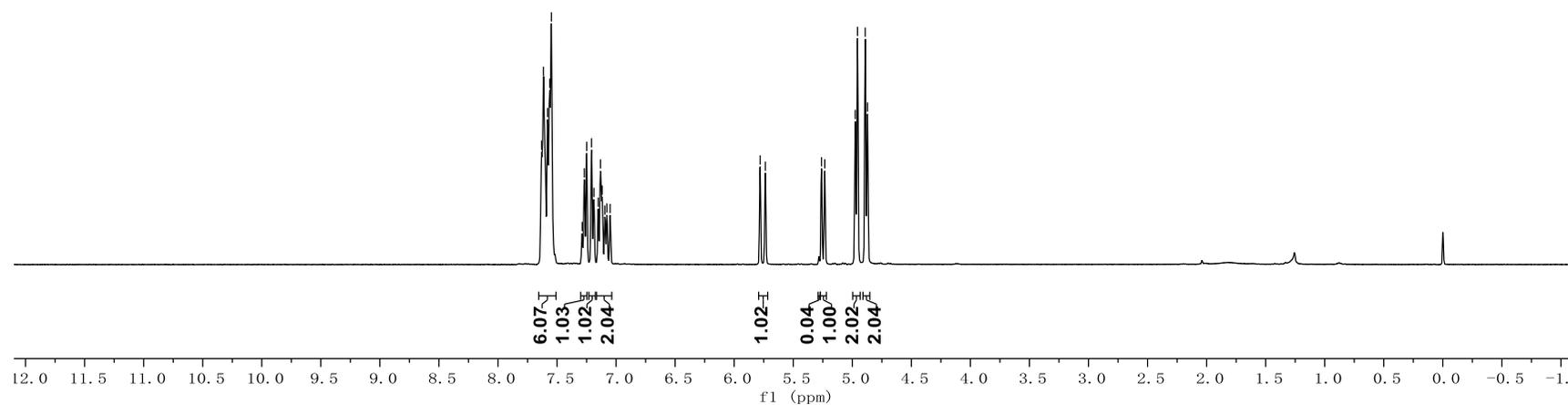


¹³C NMR Spectrum (100 MHz, CDCl₃) of 3v

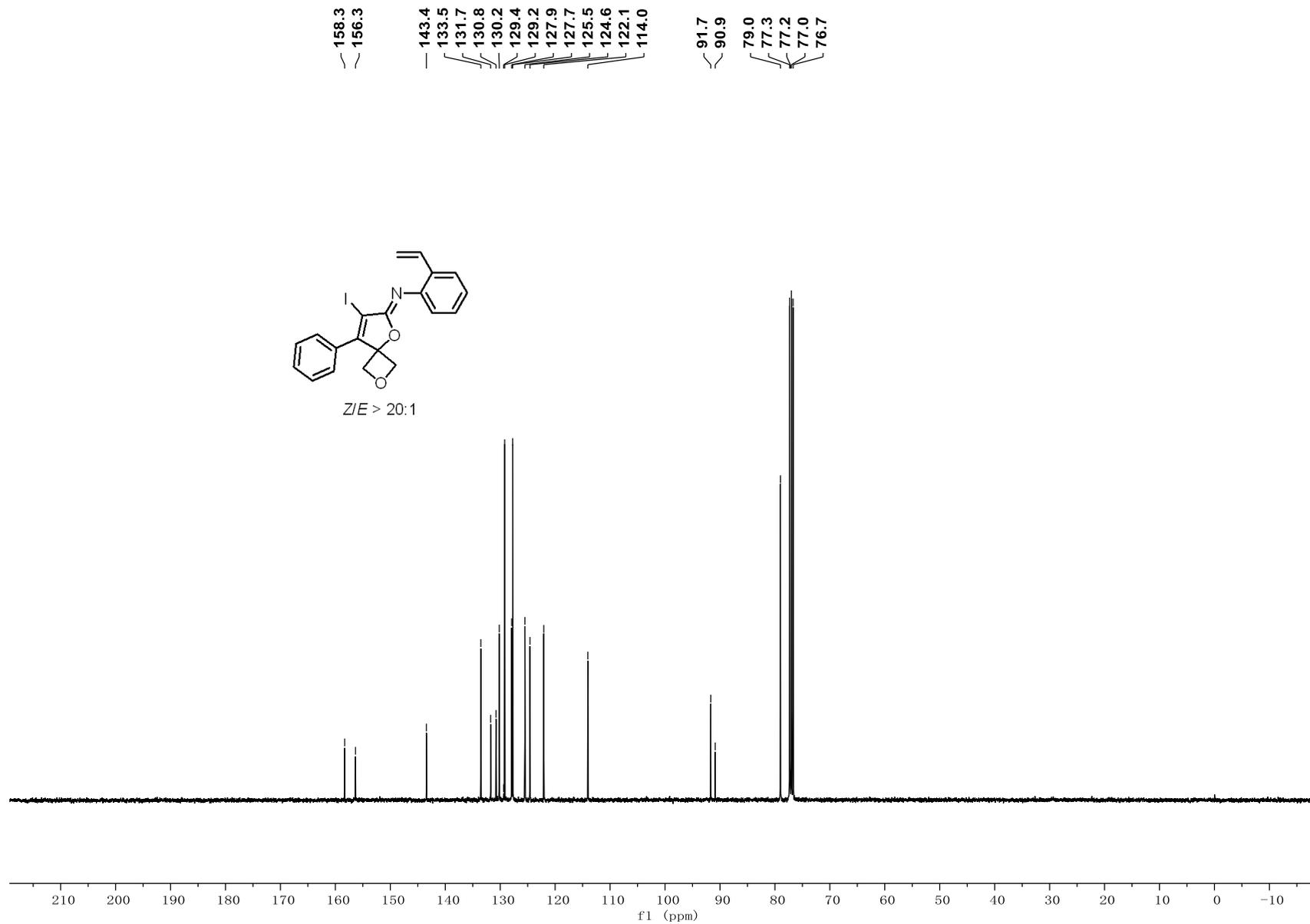
7.63
7.62
7.58
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7.55
7.29
7.27
7.25
7.21
7.19
7.15
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5.74
5.26
5.23
4.98
4.96
4.89
4.87



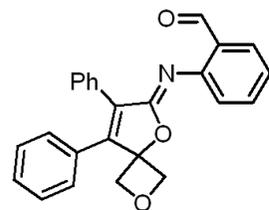
Z/E > 20:1



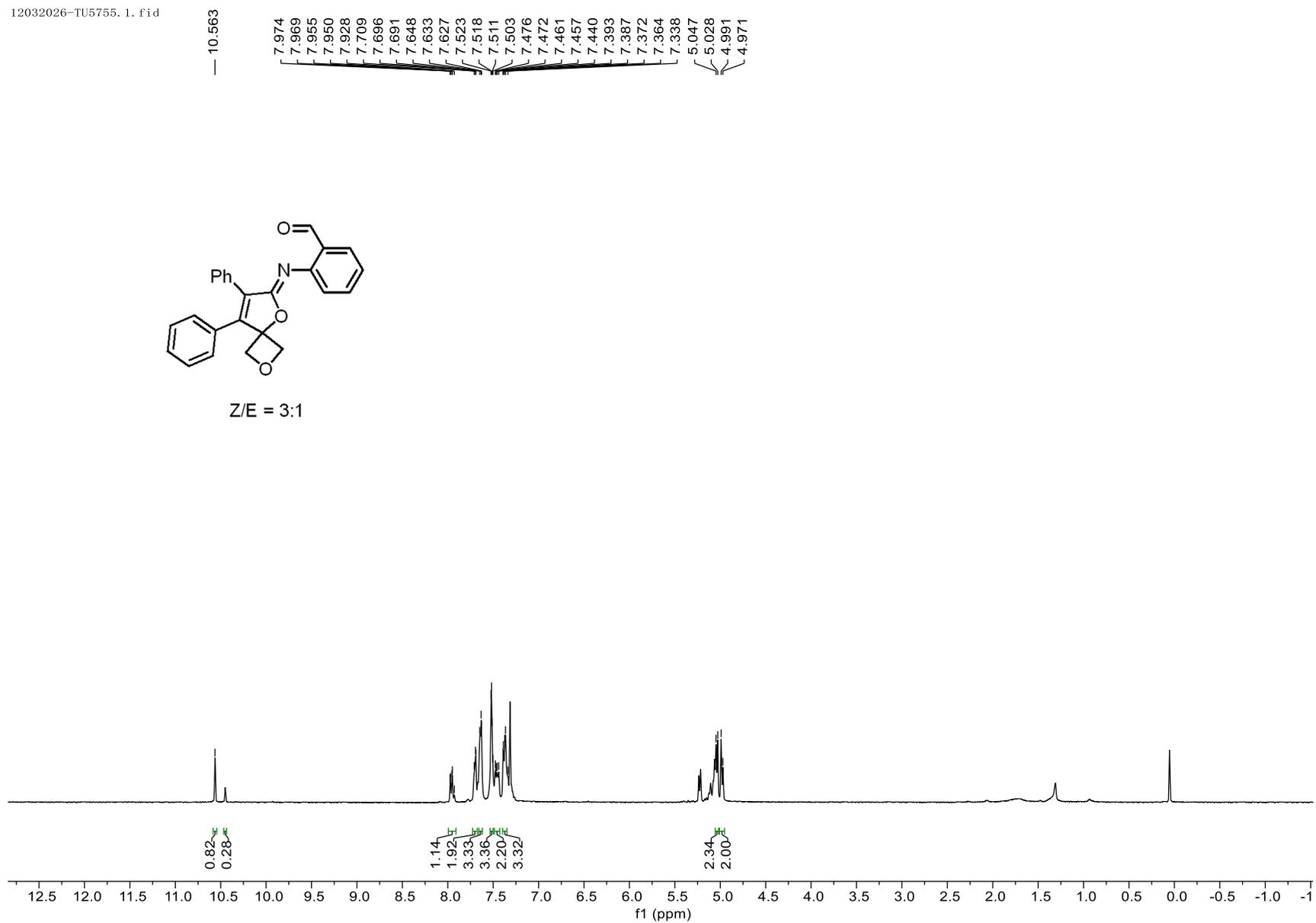
¹H NMR Spectrum (400 MHz, CDCl₃) of 4



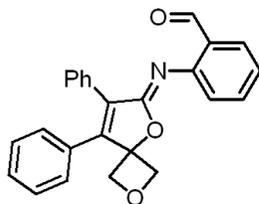
¹³C NMR Spectrum (100 MHz, CDCl₃) of 4



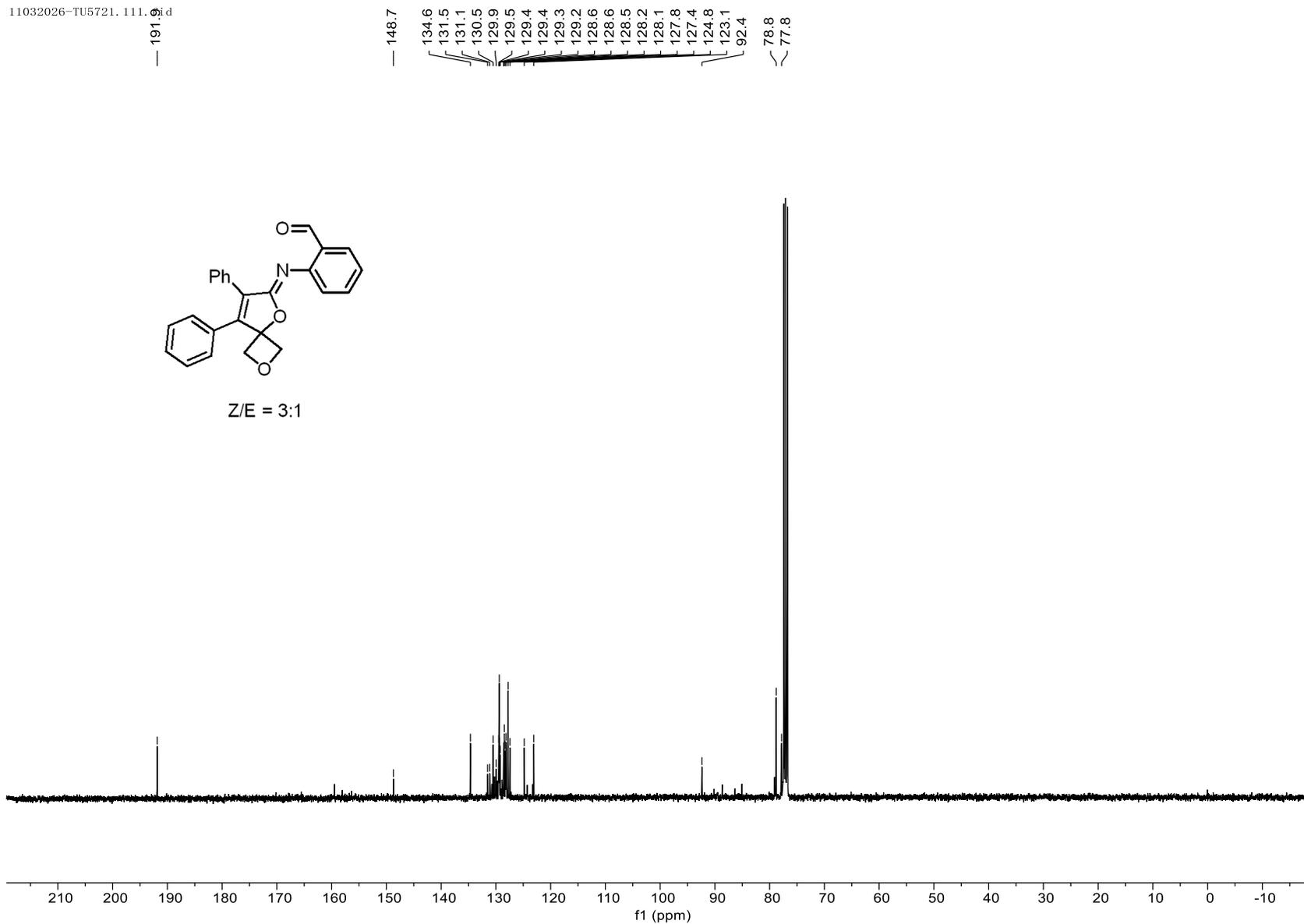
Z/E = 3:1

**¹H NMR Spectrum (400 MHz, CDCl₃) of 5**

191.9



Z/E = 3:1



¹³C NMR Spectrum (100 MHz, CDCl₃) of 5