Supporting Information

Metal-Free Radical Cascade Cyclization/Haloazidation of enynones for the synthesis of functionalized 1-indanone

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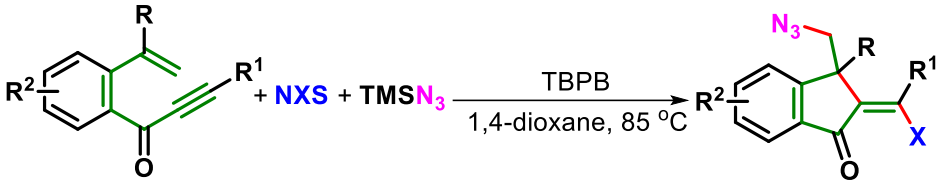
Contents

General Information

PE refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, as well as DCE refers to dichloroethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated. All reactions were heated by metal sand bath (WATTCAS, LAB-500, http://www.wattcas.com). ^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ 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. The melting points were measured with digital melting point detector. Enynones **1** and **5** was prepared by the report[1].

General procedure for the synthesis of compounds 4 and 6



To a Schlenk tube (10 ml) were added enynones **1** or **5** (0.20 mmol, 1.0 equiv), halogen source (NIS, NCS, NBS) **2** (0.6 mmol, 3.0 equiv), azidotrimethylsilane **3** (0.40 mmol, 2.0 equiv), *tert*-butyl peroxybenzoate (TBPB, 0.40 mmol, 2.0 equiv) and anhydrous 1,4-dioxane (2.0 mL) under air condition. The resulting mixture was stirring at 85 °C in metal sand bath about 12 hours. After the reaction was complete (by TLC), the reaction mixture was cooled to room temperature and diluted with DCM (10 ml) and H_2O (20 ml). The organic layer was separated, and the aqueous layer was extracted with DCM (2 ×10 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purified product **4** or **6** was obtained after column chromatography on silica gel (PE/EA= 60/1 v/v).

Crystallographic Data of Compound 4a

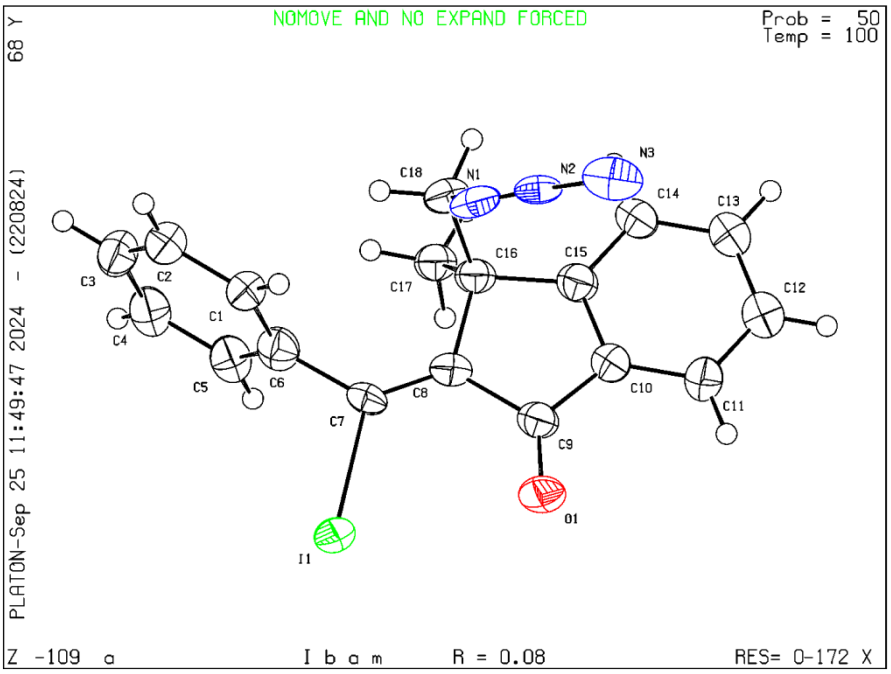


Fig. S1 ORTEP view of X-crystal structure of **4a** (CCDC number 2390559).

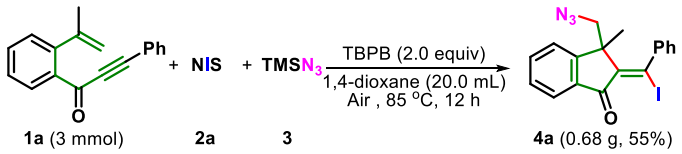
Procedure for recrystallization of compounds **4a**: the hexane was slowly added into the solution of **4a** in chloroform

(with different concentration), then the chloroform was evaporated from the mixed solvent system at room temperature under dark and the crystals were obtained after a few days.

Table S1 Crystal data and structure refinement for 4a.

Identification code	**4a**
CCDC	2390559
Empirical formula	$C_{18}H_{14}IN_3O$
Formula weight	415.22
Temperature/K	100.1(7)
Crystal system	orthorhombic
Space group	Ibam
a/Å	10.5176(3)
b/Å	42.1854(13)
c/Å	7.4578(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3308.95(16)
Z	8
ρ_{calc}g/cm^3	1.667
μ/mm^{-1}	15.268
F(000)	1632.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	8.384 to 152.154
Index ranges	$-12 \le h \le 12$, $-51 \le k \le 49$, $-8 \le l \le 9$
Reflections collected	5878
Independent reflections	1752 [R_{int} = 0.0594, R_{sigma} = 0.0435]
Data/restraints/parameters	1752/150/183
Goodness-of-fit on F^2	1.174
Final R indexes [I>=2σ (I)]	R_1 = 0.0787, wR_2 = 0.2101
Final R indexes [all data]	R_1 = 0.0812, wR_2 = 0.2113
Largest diff. peak/hole / e Å^{-3}	1.94/-0.85

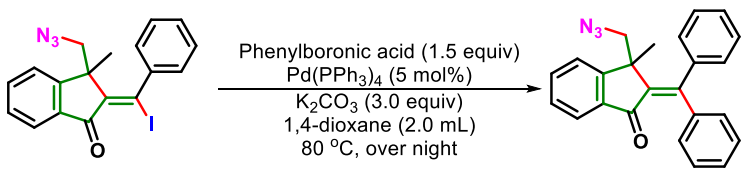
Scale-up transformation of 4a



1a (3 mmol) **2a** **3** **4a** (0.68 g, 55%)

To a Schlenk tube (50 ml) were added enynone **1a** (0.738 g, 3.0 mmol, 1.0 equiv), NIS **2a** (2.025 g, 9.0 mmol, 3.0 equiv), azidotrimethylsilane **3** (0.691 g, 6.0 mmol, 2.0 equiv), TBPB (1.165 g, 6.0 mmol, 2.0 equiv) and anhydrous 1,4-dioxane (20.0 mL) under air condition. The resulting mixture was stirring at 85 °C in metal sand bath about 12 hours. After the reaction was complete (by TLC), the reaction mixture was cooled to room temperature and diluted with DCM (50 ml) and H_2O (100 ml). The organic layer was separated, and the aqueous layer was extracted with DCM (2 ×50 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purified product **4a** (0.68 g, 55%) was obtained after column chromatography on silica gel (PE/EA= 60/1 v/v).

The synthesis of 7

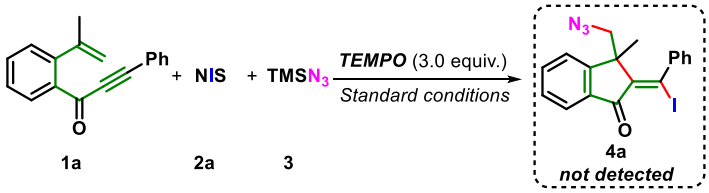


4a **7**, 68%

Under a nitrogen atmosphere, the following components were introduced into a 10 mL Schlenk tube: **4a** (0.20 mmol, 1.0 equiv), phenylboronic acid (0.3 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (0.60 mmol, 3.0 equiv), and 1,4-dioxane (2.0 mL). The resultant mixture was agitated in a metal sand bath at 80°C for an entire night. Upon completion of the reaction, confirmed by TLC analysis, the mixture was allowed to cool to ambient temperature. Subsequently, the solution was filtered and concentrated under reduced pressure. Then, the crude product was purified through flash

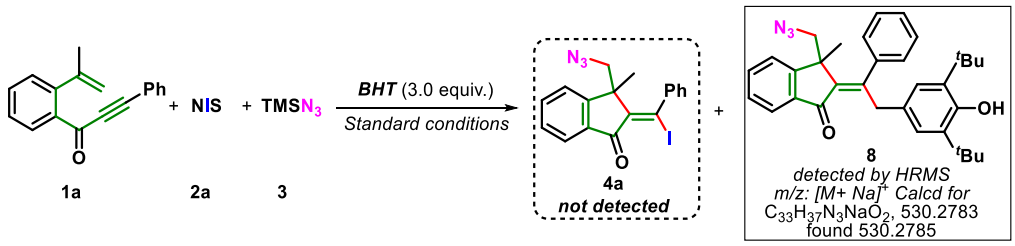
chromatography on silica gel using a PE/EA mixture (60/1 v/v) as the eluent, yielding the target product **7** (49 mg, 68% yield), as a pale yellow solid, mp: 120-121°C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.76 (d, J = 7.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.48 – 7.40 (m, 5H), 7.37 – 7.32 (m, 4H), 7.28 (d, J = 6.8 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 3.57 (d, J = 12.4 Hz, 1H), 3.36 (d, J = 12.4 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 192.8, 154.9, 153.6, 142.0, 140.6, 138.4, 137.9, 135.0, 128.6, 128.5, 128.2, 128.2, 127.9, 127.8, 127.8, 124.1, 123.1, 59.4, 48.0, 26.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}N_3NaO$ 388.1421; Found 388.1429.

Radical inhibition experiments with TEMPO



To a Schlenk tube (10 ml) were added enynones **1a** (0.20 mmol, 1.0 equiv), NIS **2a** (0.60 mmol, 3.0 equiv), azidotrimethylsilane **3** (0.40 mmol, 2.0 equiv), TBPB (0.40 mmol, 2.0 equiv), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 0.60 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (2.0 mL) under air condition. The resulting mixture was stirring at 85 °C in metal sand bath about 12 hours. The desired product **4a** was not detected by TLC.

Radical inhibition experiments with BHT



To a Schlenk tube (10 ml) were added enynones **1a** (0.20 mmol, 1.0 equiv), NIS **2a** (0.60 mmol, 3.0 equiv), azidotrimethylsilane **3** (0.40 mmol, 2.0 equiv), TBPB (0.40 mmol, 2.0 equiv), 2,6-Di-tert-butylphenol (BHT, 0.60 mmol, 3.0 equiv.) and anhydrous 1,4-dioxane (2.0 mL) under air condition. The resulting mixture was stirring at 85 °C in metal sand bath about 12 hours. The desired product **4a** was not detected by TLC, but HRMS analysis of the solution revealed signal peaks at m/z 530.2785 corresponding to the BHT adduct **8**.

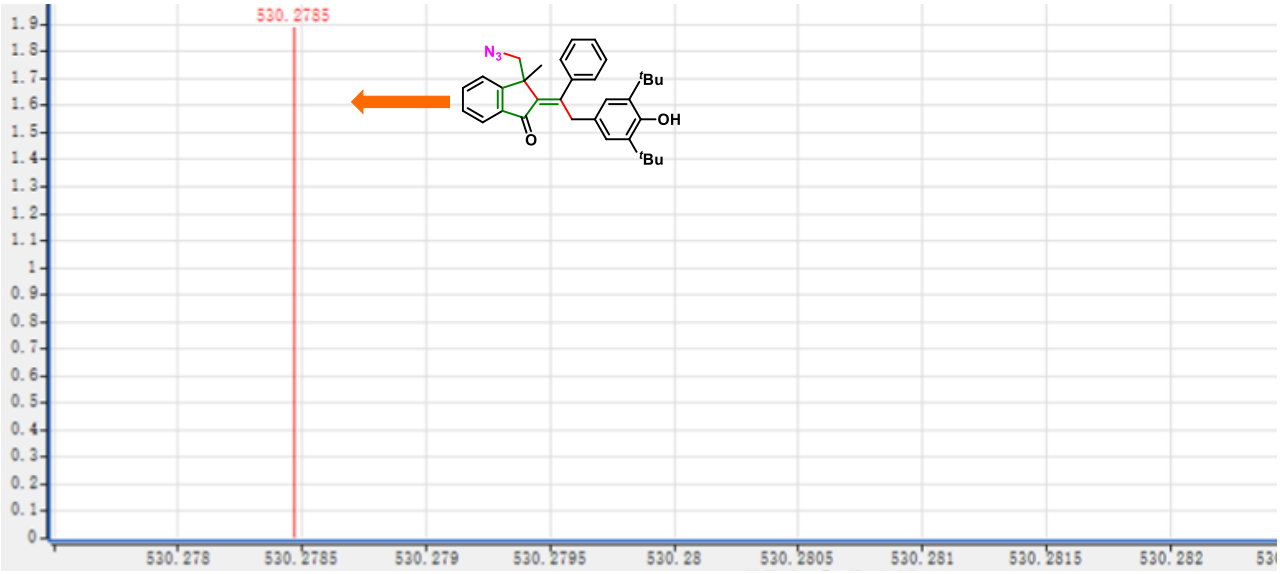
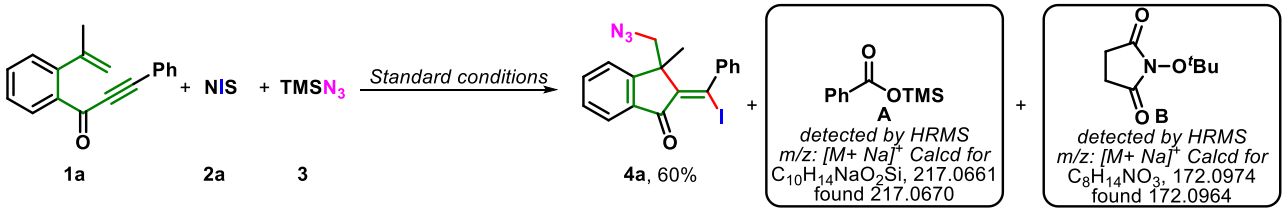


Fig. S2 HRMS analysis for the adduct BHT adduct **8**.

HRMS analysis of reaction solution



To a Schlenk tube (10 ml) were added enynones **1a** (0.20 mmol, 1.0 equiv), NIS **2a** (0.60 mmol, 3.0 equiv), azidotrimethylsilane **3** (0.40 mmol, 2.0 equiv), TBPB (0.40 mmol, 2.0 equiv) and anhydrous 1,4-dioxane (2.0 mL) under air condition. The resulting mixture was stirring at 85 °C in metal sand bath about 12 hours. HRMS analysis of the solution revealed signal peaks at m/z 217.0670 and 172.0964 corresponding to trimethylsilyl 2-iodobenzoate **A** and1-(*tert*-butoxy)pyrrolidine-2,5-dione **B**, respectively .

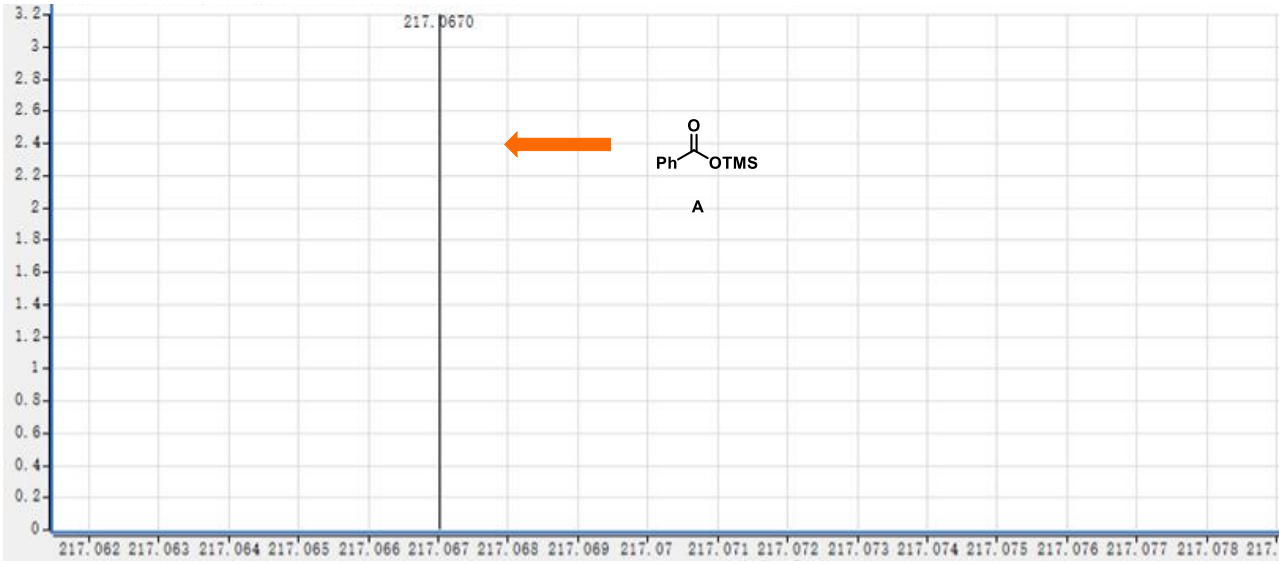


Fig. S3 HRMS analysis for the detection of trimethylsilyl 2-iodobenzoate **A**

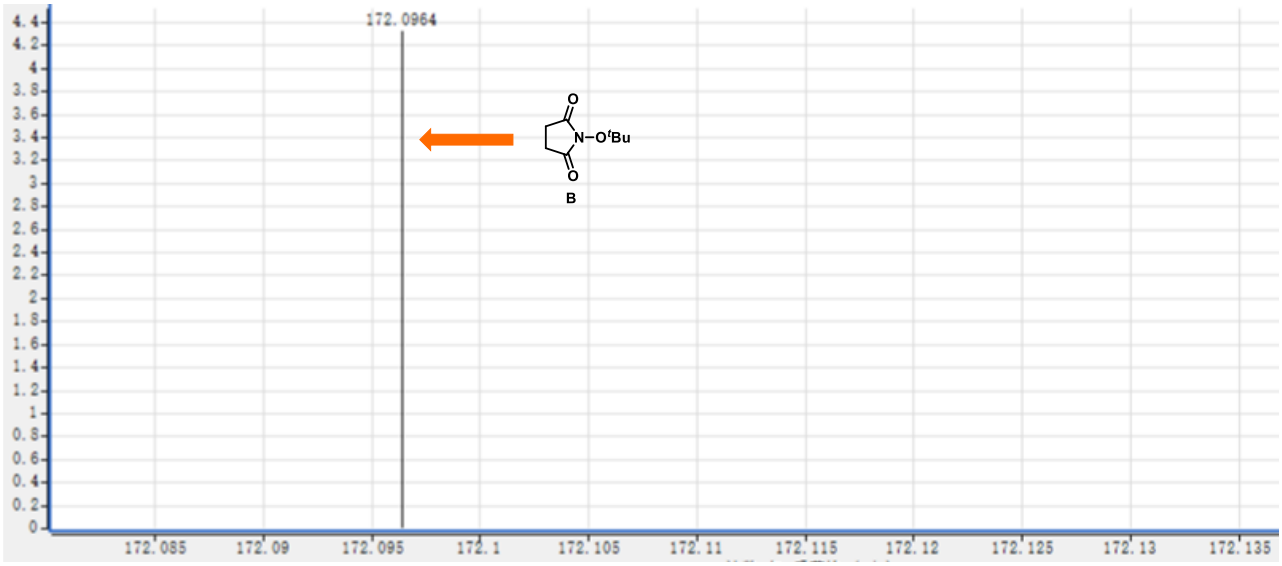


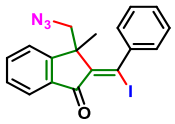
Fig. S4 HRMS analysis for the detection of1-(*tert*-butoxy)pyrrolidine-2,5-dione **B**

Reference

1. F. Wu and S. Zhu, *Org. Lett.* 2019, **21**, 1488-1492.

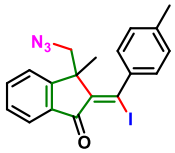
Characterization data

(Z)-3-(azidomethyl)-2-(iodo(phenyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4a)



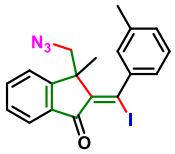
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 50 mg, 60% yield, *Z/E* = 4: 1; mp: 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.14 (d, *J* = 7.6 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.69 – 7.66 (m, 3H), 7.59 – 7.53 (m, 2H), 7.47 – 7.40 (m, 2H), 3.73 (d, *J* = 12.4 Hz, 1H), 3.46 (d, *J* = 12.4 Hz, 1H), 1.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 190.3, 152.8, 144.9, 142.3, 137.2, 135.7, 130.2, 128.8, 128.6, 124.7, 122.6, 105.8, 59.1, 51.3, 25.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}IN_3NaO$ 438.0074; Found 438.0082.

(Z)-3-(azidomethyl)-2-(iodo(p-tolyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (syn isomer, 4b)



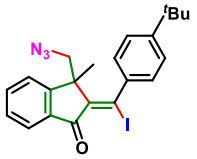
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 41 mg, 48% yield, *Z/E* = 1.5: 1; mp: 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.68 (m, 6H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.40 (m, 9H), 7.38 – 7.29 (m, 7H), 7.16 – 7.12 (m, 5H), 7.09– 7.04 (m, 9H), 4.65 (d, *J* = 12.4 Hz, 2H), 3.67 (d, *J* = 12.8 Hz, 2H), 3.55 – 3.48 (m, 3H), 3.30 – 3.24 (m, 3H), 2.39 (s, 9H), 2.37 (s, 6H), 1.78 (s, 6H), 1.26 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) δ 190.4, 187.5, 155.6, 152.8, 144.8, 143.5, 142.3, 138.9, 138.7, 137.3, 136.3, 135.7, 135.4, 129.1, 128.9, 128.8(2), 128.8(0), 126.6, 124.8, 124.6, 123.6, 122.6, 117.5, 106.5, 59.1, 56.5, 51.3, 49.9, 25.3, 22.6, 21.5, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}IN_3NaO$ 452.0231; Found 452.0236.

(Z)-3-(azidomethyl)-2-(iodo(m-tolyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4c, major)



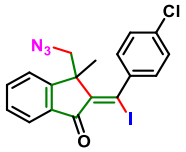
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 39 mg, 45% yield, *Z/E* = 4: 1; mp: 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.50 – 7.45 (m, 2H), 7.20 – 7.15 (m, 3H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.28 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.4, 155.6, 146.2, 144.8, 137.9, 136.3, 135.7, 135.4, 129.5, 128.8, 128.0, 127.0, 124.6, 123.6, 117.2, 56.5, 49.8, 22.6, 21.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}IN_3NaO$ 452.0231; Found 452.0235.

(Z)-3-(azidomethyl)-2-((4-(tert-butyl)phenyl)iodomethylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4d, major)



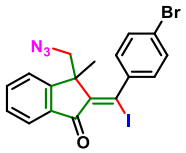
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 58 mg, 62% yield, *Z/E* = 5: 1; mp: 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 (d, *J* = 7.6 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.48 – 7.45 (m, 4H), 7.23 – 7.17 (m, 2H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 1.36 (s, 9H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 190.4, 152.8, 152.1, 142.3, 142.1, 137.3, 135.7, 128.8, 126.5, 125.3, 124.8, 122.6, 106.7, 59.2, 51.3, 34.8, 31.4, 25.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}IN_3NaO$ 494.0700; Found 494.0707.

(Z)-3-(azidomethyl)-2-((4-chlorophenyl)iodomethylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4e, major)



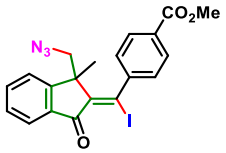
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 52 mg, 58% yield, *Z/E* = 5: 1; mp: 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.94 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.52 – 7.44 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.55 (d, *J* = 12.4 Hz, 1H), 3.24 (d, *J* = 12.4 Hz, 1H), 1.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.5, 155.6, 145.6, 144.5, 136.1, 135.7, 134.5, 129.0, 128.5, 128.1, 124.7, 123.6, 114.6, 56.4, 49.9, 22.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{13}ClIN_3NaO$ 471.9685; Found 471.9691.

(Z)-3-(azidomethyl)-2-((4-bromophenyl)iodomethylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4f, major)



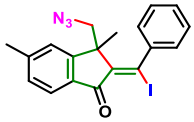
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 59 mg, 60% yield, *Z/E* = 10: 1; mp: 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.94 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.60 (s, 2H), 7.50 – 7.46 (m, 2H), 7.20 – 7.08 (m, 2H), 3.55 (d, *J* = 12.4 Hz, 1H), 3.24 (d, *J* = 12.4 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 190.1, 152.6, 143.8, 135.9, 135.6, 131.7, 131.4, 129.0, 128.3, 124.9, 124.6, 123.6, 122.6, 114.5, 59.2, 51.4, 22.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{13}BrIN_3NaO$ 515.9179; Found 515.9186.

methyl (Z)-4-((1-(azidomethyl)-1-methyl-3-oxo-1,3-dihydro-2H-inden-2-ylidene)iodomethyl)benzoate (syn isomer, 4g)



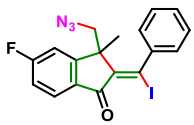
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 67 mg, 71% yield, *Z/E* = 1: 1; mp: 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.13 – 8.08 (m, 4H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.32 (m, 4H), 4.64 (d, *J* = 12.4 Hz, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 3.68 (d, *J* = 12.4 Hz, 1H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.21 (d, *J* = 12.4 Hz, 1H), 1.79 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.5, 166.5, 155.6, 152.7, 150.5, 149.0, 145.7, 142.6, 136.0(1), 136.0(8), 135.7, 130.4, 129.9, 129.6, 129.0, 126.5, 124.9, 124.7, 123.6, 122.6, 114.1, 103.8, 59.2, 56.5, 52.5, 52.2, 51.4, 49.9, 25.2, 22.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}IN_3NaO_3$ 496.0129; Found 496.0135.

(Z)-3-(azidomethyl)-2-(iodo(phenyl)methylene)-3,5-dimethyl-2,3-dihydro-1H-inden-1-one (4h, major)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 49 mg, 57% yield, *Z/E* = 4: 1; mp: 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.86 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.39 – 7.36 (m, 1H), 7.34 – 7.28 (m, 3H), 3.54 (d, *J* = 12.0 Hz, 1H), 3.28 (d, *J* = 12.4 Hz, 1H), 2.51 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.1, 156.1, 146.9, 145.3, 142.6, 134.1, 130.2, 128.6, 128.2, 126.5, 124.5, 123.8, 116.0, 56.4, 49.7, 22.6, 22.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}IN_3NaO$ 452.0231; Found 452.0233.

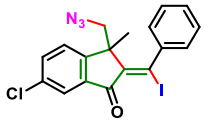
(Z)-3-(azidomethyl)-5-fluoro-2-(iodo(phenyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4i, major)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 61 mg, 71% yield, *Z/E* = 5: 1; mp: 152-153°C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.97 – 7.93 (m, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.33 (m, 1H), 7.20 – 7.16 (m, 2H),

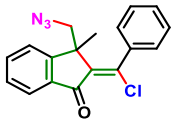
7.12 (d, J = 8.4 Hz, 1H), 3.48 (d, J = 12.4 Hz, 1H), 3.27 (d, J = 12.0 Hz, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 188.7, 167.6 ($^1J_{CF}$ = 255.9 Hz), 155.8 ($^3J_{CF}$ = 9.2 Hz), 144.8, 142.0, 133.7, 129.0, 127.4, 127.3, 117.3 ($^2J_{CF}$ = 23.5 Hz), 109.8, 109.6, 106.3, 58.9, 51.2, 25.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ ppm: -100.55. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{13}FIN_3NaO$ 455.9980; Found 455.9986.

(Z)-3-(azidomethyl)-6-chloro-2-(iodo(phenyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4j, major)



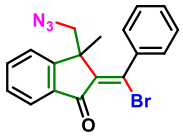
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 42 mg, 47% yield, Z/E = 10: 1; mp: 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.87 (d, J = 1.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.25 (m, 2H), 3.49 (d, J = 12.4 Hz, 1H), 3.27 (d, J = 12.0 Hz, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 189.1, 150.9, 144.8, 142.1, 138.6, 135.8, 135.2, 129.0, 128.3, 126.4, 124.5, 124.1, 107.2, 58.9, 51.1, 25.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{13}ClIN_3NaO$ 471.9685; Found 471.9694.

(Z)-3-(azidomethyl)-2-(chloro(phenyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4k, major)



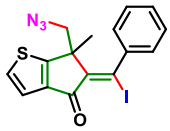
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 19 mg, 30% yield, Z/E > 19: 1; mp: 148-149°C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.12 – 8.10 (m, 2H), 7.70 – 7.64 (m, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.46 (s, 3H), 7.40 – 7.37 (m, 1H), 4.26 (d, J = 15.2 Hz, 2H), 1.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 188.8, 155.1, 146.4, 137.4, 135.5, 131.0, 129.7, 128.8, 128.4, 128.2, 128.1, 124.4, 123.3, 57.2, 49.5, 22.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}ClN_3NaO$ 346.0718; Found 346.0727.

(Z)-3-(azidomethyl)-2-(bromo(phenyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4l, major)



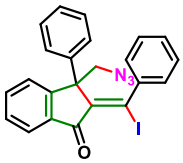
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 26 mg, 36% yield, Z/E = 10: 1; mp: 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.72 – 7.69 (m, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.38 (d, J = 7.6 Hz, 2H), 4.70 (d, J = 10.4 Hz, 1H), 3.83 (d, J = 10.4 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 188.1, 155.4, 141.2, 140.3, 138.5, 137.1, 135.5, 129.3, 128.8, 128.2, 127.9, 124.4, 122.8, 49.8, 38.6, 23.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}BrN_3NaO$ 390.0213; Found 390.0220.

(Z)-6-(azidomethyl)-5-(iodo(phenyl)methylene)-6-methyl-5,6-dihydro-4H-cyclopenta[b]thiophen-4-one (syn isomer, 4l)



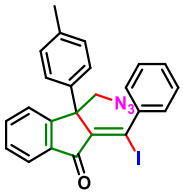
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 27 mg, 32% yield, Z/E = 1: 1; mp: 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.91 – 7.88 (m, 2H), 7.49 – 7.44 (m, 2H), 7.41 – 7.30 (m, 4H), 7.27 (s, 1H), 7.26 – 7.19 (m, 3H), 7.15 (d, J = 4.8 Hz, 1H), 7.06 (d, J = 4.8 Hz, 1H), 4.39 (d, J = 12.4 Hz, 1H), 3.78 (d, J = 12.4 Hz, 1H), 3.43 (d, J = 12.4 Hz, 1H), 3.19 (d, J = 12.0 Hz, 1H), 1.78 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) δ 181.8, 179.2, 168.5, 165.6, 147.7, 145.6, 145.2, 144.7, 142.6, 141.2, 140.5, 140.4, 128.8, 128.6, 128.1, 126.6, 121.9, 120.9, 113.8, 103.9, 58.6, 56.0, 50.2, 49.1, 24.3, 21.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{12}IN_3NaOS$ 443.9638; Found 443.9640.

(Z)-3-(azidomethyl)-2-(iodo(phenyl)methylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6a, major)



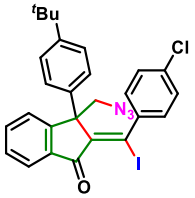
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 48 mg, 50% yield, *Z/E* = 5: 1; mp: 130-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.31 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 4.31 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.6, 155.2, 145.4, 141.6, 136.9, 135.6, 129.0, 128.8, 128.5, 128.1, 127.5, 127.3, 126.8, 125.1, 124.6, 119.7, 107.3, 57.8, 55.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{16}IN_3NaO$ 500.0231; Found 500.0239.

(Z)-3-(azidomethyl)-2-(iodo(phenyl)methylene)-3-(p-tolyl)-2,3-dihydro-1H-inden-1-one (6b, major)



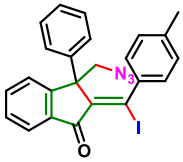
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 46 mg, 47% yield, *Z/E* = 5: 1; mp: 183-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.75 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.42 – 7.39 (m, 4H), 7.34 – 7.33 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 5.02 (d, *J* = 11.6 Hz, 1H), 4.27 (d, *J* = 11.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.7, 155.4, 146.6, 145.5, 138.5, 137.0, 136.8, 135.6, 129.7, 128.8(9), 128.8(6), 128.1, 127.3, 126.7, 125.0, 124.5, 119.6, 57.5, 55.9, 21.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}IN_3NaO$ 514.0387; Found 514.0391.

(Z)-3-(azidomethyl)-3-(4-(tert-butyl)phenyl)-2-((4-chlorophenyl)iodomethylene)-2,3-dihydro-1H-inden-1-one (syn isomer, 6c)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 59 mg, 52% yield, *Z/E* = 2: 1; mp: 208-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.99 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.60 – 7.56 (m, 3H), 7.51 – 7.47 (m, 2H), 7.44 – 7.40 (m, 3H), 7.38 – 7.34 (m, 8H), 7.26 – 7.19 (m, 8H), 7.14 – 7.10 (m, 7H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.01 (d, *J* = 11.6 Hz, 2H), 4.26 (d, *J* = 11.6 Hz, 2H), 4.09 (d, *J* = 11.6 Hz, 1H), 3.83 (d, *J* = 12.0 Hz, 1H), 1.31 (s, 18H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 190.9, 187.9, 155.3, 152.9, 150.4, 150.3, 147.1, 143.8, 142.7, 138.1, 137.7, 136.7, 136.2, 135.8, 134.6, 129.0, 128.9, 128.4, 128.3, 127.9, 127.4, 127.0, 126.4, 125.9, 125.4, 125.1, 124.5, 117.5, 57.5, 57.4, 57.2, 55.8, 34.5, 31.3, 31.3, 29.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{23}ClIN_3NaO$ 590.0467; Found 590.0476.

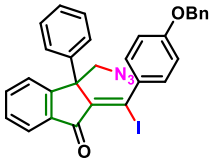
(Z)-3-(azidomethyl)-2-(iodo(p-tolyl)methylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (syn isomer, 6d)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 47 mg, 48% yield, *Z/E* = 1: 1; mp: 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.99 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.49 – 7.45 (m, 1H), 7.43 – 7.39 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.18 (m, 6H), 7.14 – 7.08 (m, 6H), 6.97 – 6.80 (m, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 5.03 (d, *J* = 11.6 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.10 (d, *J* = 11.6

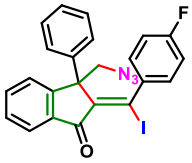
Hz, 1H), 3.81 (d, J = 12.0 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 191.0, 187.6, 155.1, 153.0, 146.3, 144.0, 143.2, 142.6, 141.7, 141.6, 138.9, 138.1, 137.8, 136.9, 136.0, 135.5, 129.0, 128.8(4), 128.8(1), 128.8(9), 128.5, 128.4, 127.5, 127.2, 126.9, 126.8, 126.7, 125.9, 125.1, 124.6, 124.5, 124.3, 120.5, 107.9, 57.8, 57.3, 56.7, 55.9, 21.5, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}IN_3NaO$ 514.0387; Found 514.0396.

(Z)-3-(azidomethyl)-2-((4-(benzyloxy)phenyl)iodomethylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6e, major)



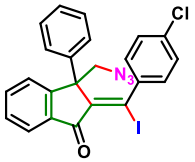
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 78 mg, 67% yield, Z/E = 2.5: 1; mp: 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.02 (d, J = 7.6 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.43 (m, 6H), 7.42 – 7.36 (m, 4H), 7.13 – 7.10 (m, 3H), 7.03 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 6.8 Hz, 1H), 5.13 (s, 1H), 5.06 (d, J = 4.8 Hz, 1H), 4.21 – 4.10 (m, 1H), 3.93 – 3.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 191.0, 158.3, 152.9, 144.3, 143.3, 137.8, 137.2, 136.6, 136.0, 128.9, 128.7, 128.5, 128.2, 128.1, 127.7, 127.5, 126.9, 126.7, 124.5, 124.3, 114.2, 70.0, 57.3, 56.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{22}IN_3NaO_2$ 606.0649; Found 606.0651.

(Z)-3-(azidomethyl)-2-((4-fluorophenyl)iodomethylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6f, major)



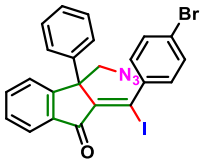
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 62 mg, 63% yield, Z/E = 10: 1; mp: 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 (d, J = 7.6 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 3H), 7.24 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.11 – 7.07 (m, 2H), 5.03 (d, J = 12.0 Hz, 1H), 4.29 (d, J = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.7, 162.8 ($^1J_{CF}$ = 247.7 Hz), 155.1, 147.0, 141.5, 141.3 ($^3J_{CF}$ = 3.6 Hz), 136.8, 135.8, 129.0(4), 129.0(6), 127.4, 127.3, 126.7, 125.1, 124.6, 118.2, 115.2 ($^2J_{CF}$ = 21.9 Hz), 57.8, 55.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ ppm: -111.99. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{15}FIN_3NaO$ 518.0137; Found 518.0144.

(Z)-3-(azidomethyl)-2-((4-chlorophenyl)iodomethylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (syn isomer, 6g)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 57 mg, 56% yield, Z/E = 2: 1; mp: 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 (d, J = 7.6 Hz, 3H), 7.60 – 7.56 (m, 3H), 7.45 – 7.41 (m, 4H), 7.38 (d, J = 7.2 Hz, 7H), 7.35 (d, J = 4.8 Hz, 6H), 7.32 – 7.29 (m, 4H), 7.24 (d, J = 8.4 Hz, 8H), 7.18 – 7.14 (m, 4H), 5.08 (d, J = 9.6 Hz, 1H), 5.02 (d, J = 11.6 Hz, 2H), 4.29 (d, J = 12.0 Hz, 2H), 4.14 (d, J = 9.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.6, 155.1, 147.1, 144.8, 143.7, 142.9, 142.7, 141.4, 137.7, 136.7, 136.2, 135.8, 134.7, 134.1, 129.0(2), 129.0(6), 128.6, 128.4, 128.3, 128.1, 127.8, 127.4, 127.3, 127.2, 126.7, 125.1, 124.6, 124.3, 117.5, 105.1, 57.7, 57.4, 57.0, 55.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{15}ClIN_3NaO$ 533.9841; Found 533.9845.

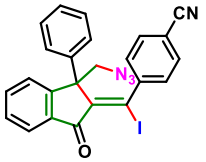
(Z)-3-(azidomethyl)-2-((4-bromophenyl)iodomethylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6h, major)



Isolation by column chromatography (PE/EA=60/1 v/v) Pale yellow solid; 44 mg, 40% yield, Z/E = 10: 1; mp: 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 (d, J = 7.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.45

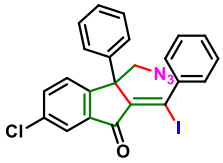
– 7.41 (m, 1H), 7.39 – 7.35 (m, 2H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 3H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.29 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.7, 155.2, 147.1, 144.2, 141.3, 136.7, 135.9, 131.3, 129.0(4), 129.0(0), 128.5, 127.4, 127.4, 125.1, 124.6, 123.0, 117.5, 57.7, 55.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{15}BrIN_3NaO$ 577.9336; Found 577.9340.

(Z)-4-((1-(azidomethyl)-3-oxo-1-phenyl-1,3-dihydro-2H-inden-2-ylidene)iodomethyl)benzonitrile (6i, major)



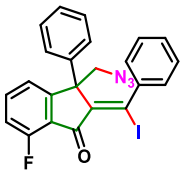
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 72 mg, 72% yield, *Z/E* = 4: 1; mp: 145-146°C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.80 – 7.76 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.46 – 7.43 (m, 1H), 7.40 – 7.35 (m, 4H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.29 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.7, 155.3, 149.6, 147.9, 141.0, 136.4, 136.1, 132.8, 132.0, 129.1, 127.6, 127.5, 127.4, 125.1, 124.6, 118.5, 114.8, 112.3, 57.6, 55.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{15}IN_4NaO$ 525.0183; Found 525.0188.

(Z)-3-(azidomethyl)-6-chloro-2-(iodo(phenyl)methylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6j, major)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 82 mg, 80% yield, *Z/E* = 5: 1; mp: 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.70 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.35 (d, *J* = 5.6 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 1H), 5.03 (d, *J* = 11.8 Hz, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.06 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 186.3, 153.3, 146.3, 145.1, 141.0, 138.2, 135.7, 135.2, 129.1, 129.0, 128.2, 127.5, 127.4, 126.7, 126.6, 124.2, 120.8, 57.5, 55.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{15}ClIN_3NaO$ 533.9841; Found 533.9848.

(Z)-3-(azidomethyl)-7-fluoro-2-(iodo(phenyl)methylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6k, major)



Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 51 mg, 52% yield, *Z/E* = 10: 1; mp: 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.55 – 7.50 (m, 1H), 7.40 – 7.38 (m, 5H), 7.34 – 7.28 (m, 5H), 7.04 – 7.00 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 184.2, 159.5 ($^1J_{CF}$ = 247.7 Hz), 157.2, 145.9, 145.1, 141.2, 137.1 ($^3J_{CF}$ = 8.3 Hz), 129.1, 128.9, 128.6, 128.2, 127.9, 127.5, 127.4, 126.6, 120.9 ($^4J_{CF}$ = 4.1 Hz), 120.3, 115.6 ($^2J_{CF}$ = 18.9 Hz), 57.7, 55.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ ppm: -114.54. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{15}FIN_3NaO$ 518.0137; Found 518.0143.

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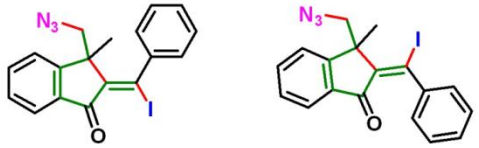
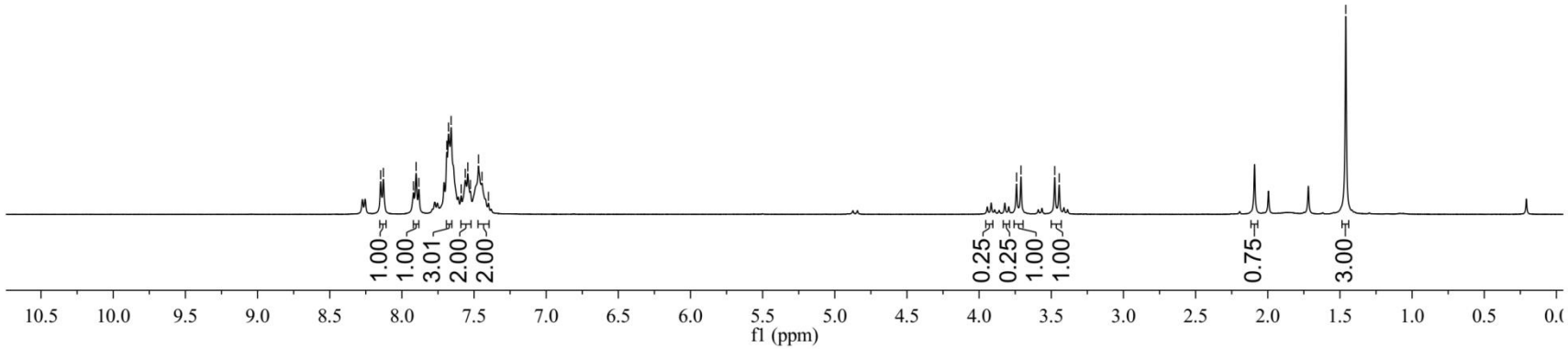


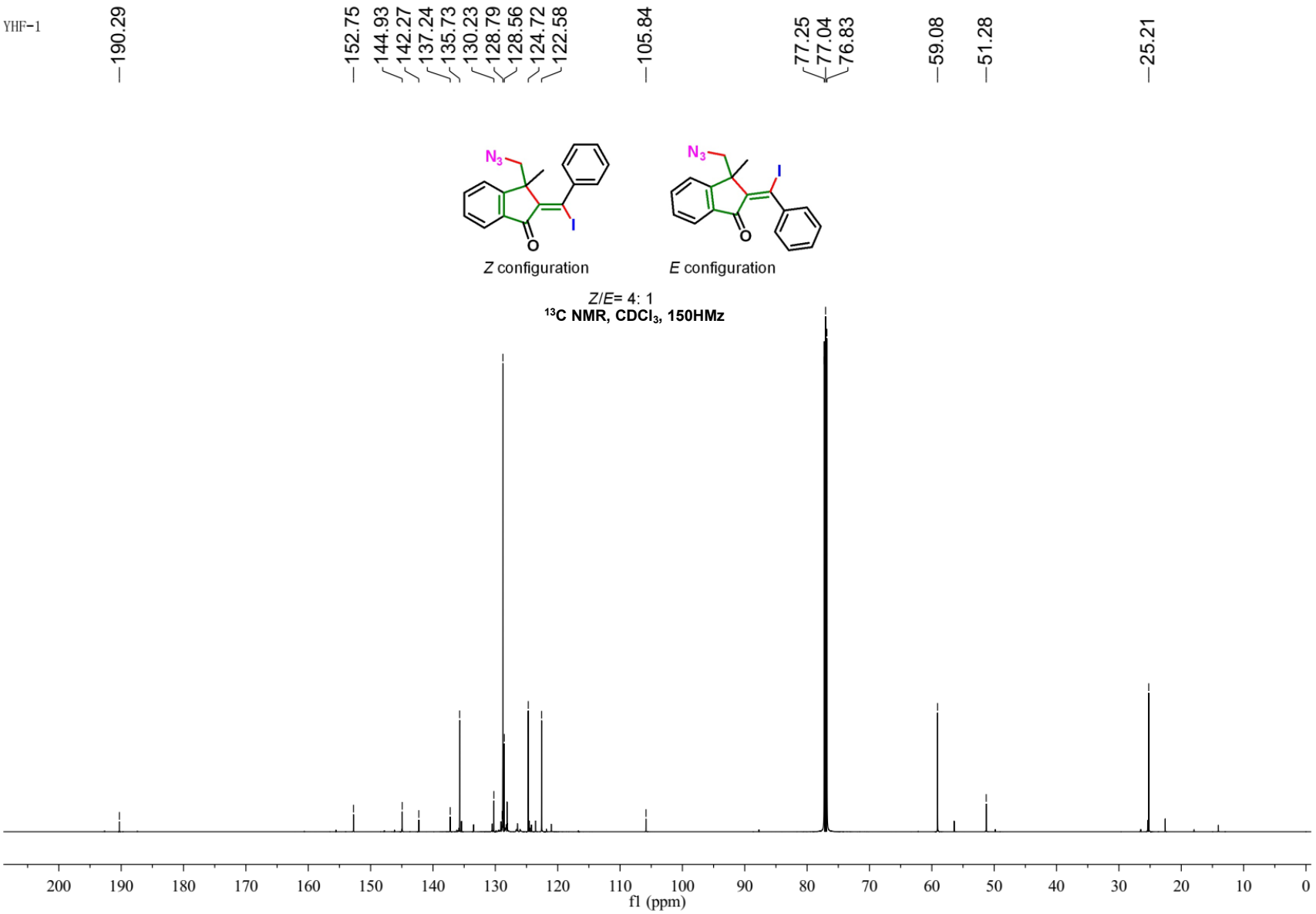
Z configuration *E* configuration

Z/*E*= 4: 1

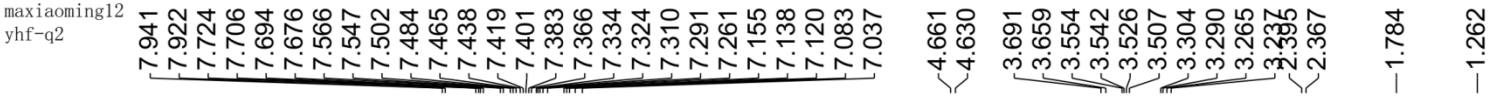
^{1}H NMR, $CDCl_3$, 400 HMz

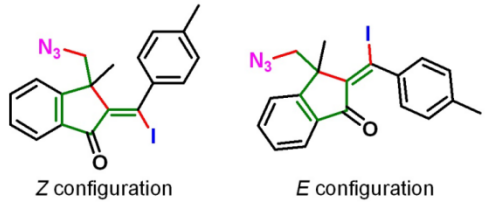


^{1}H NMR Spectrum of Compound 4a



^{13}C NMR Spectrum of Compound 4a

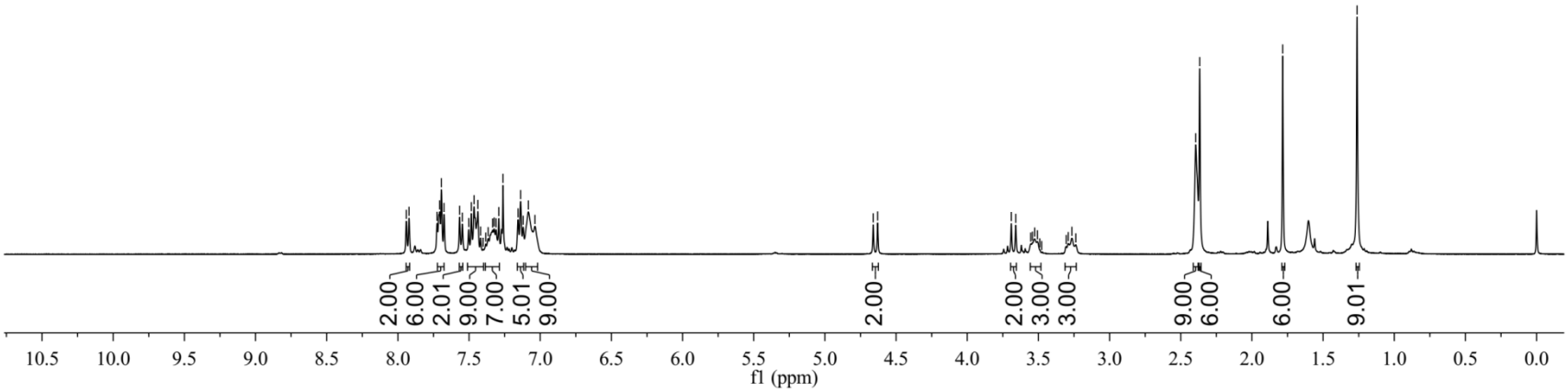




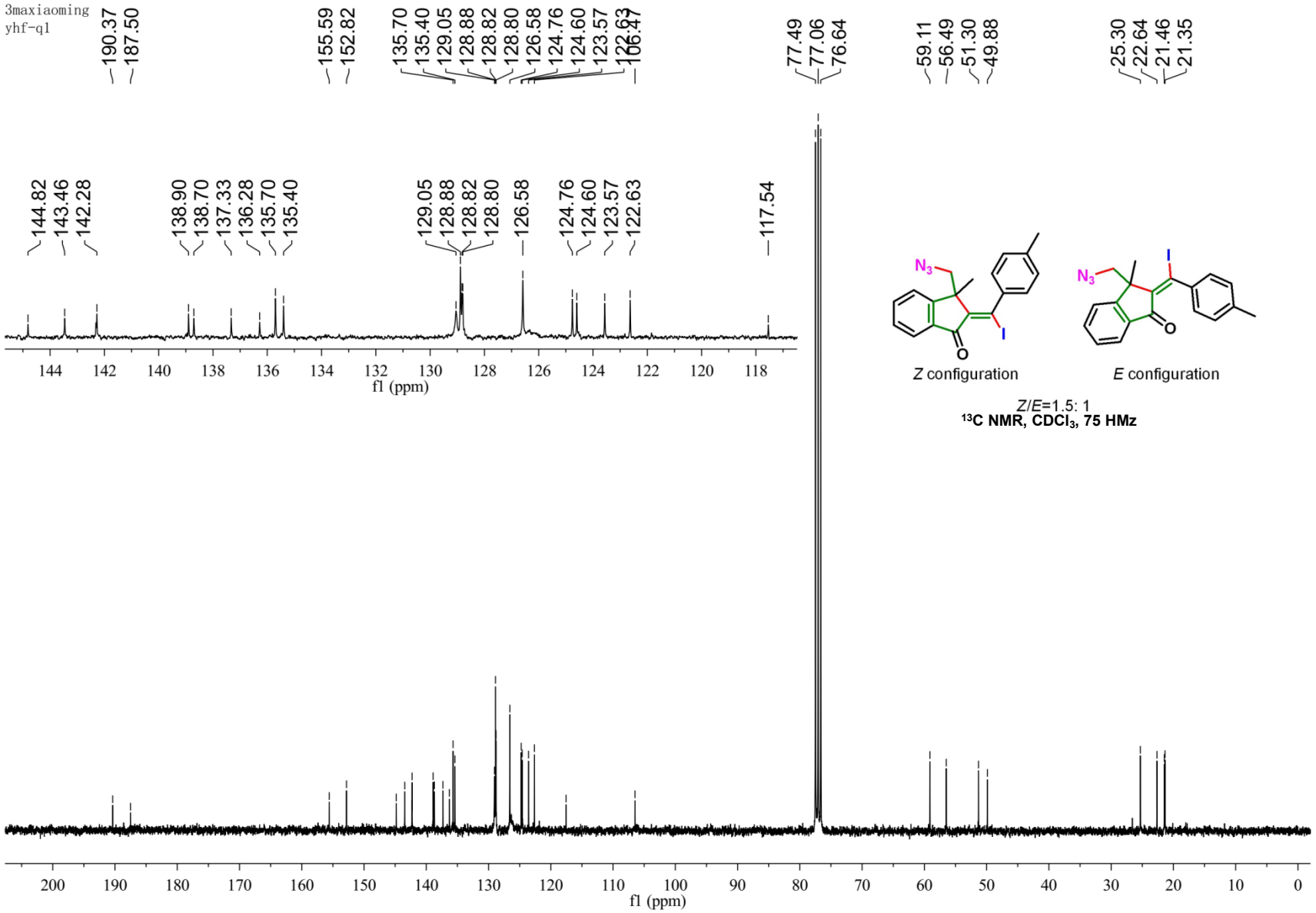
Z configuration *E* configuration

Z/*E*=1.5: 1

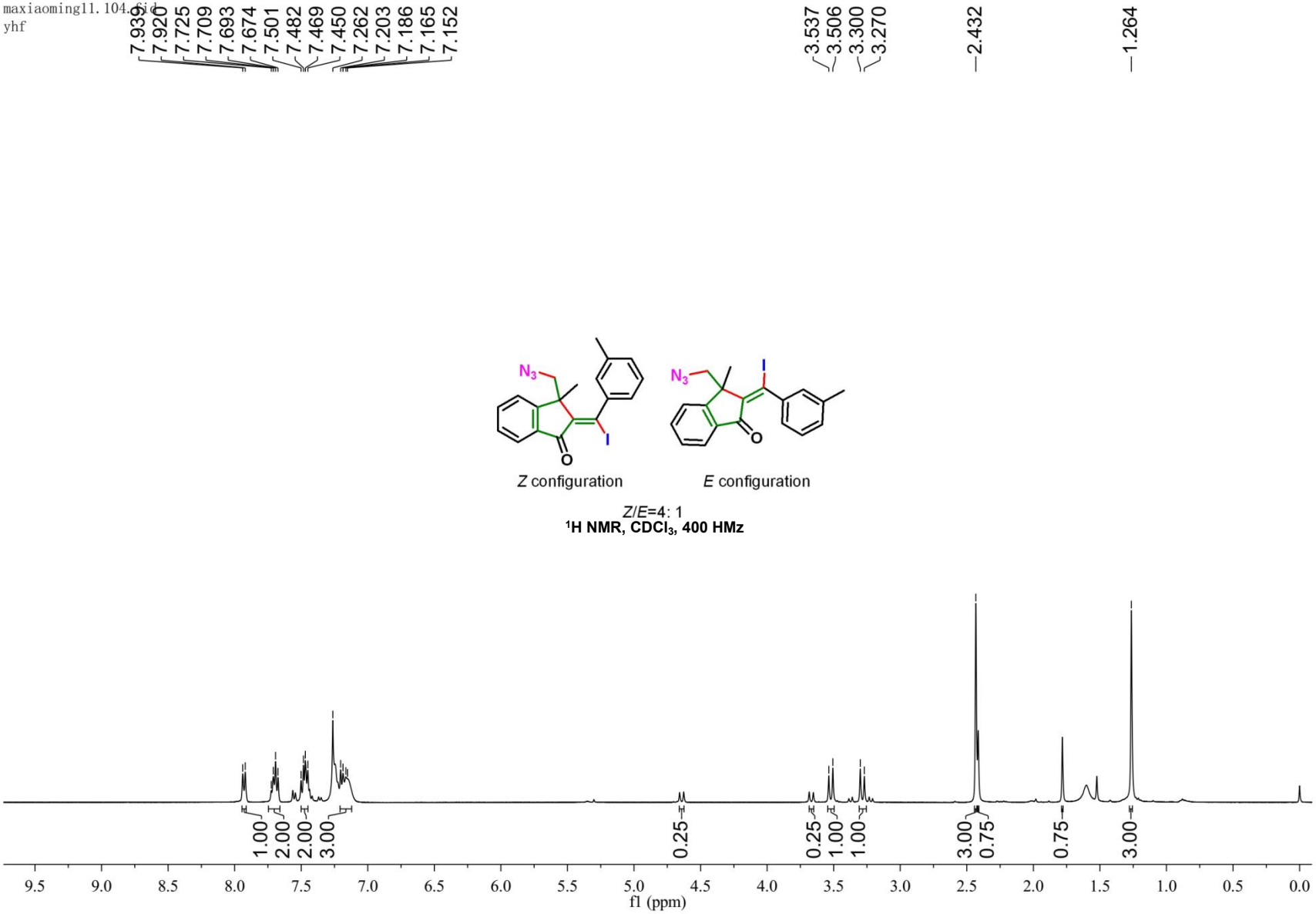
^{1}H NMR, $CDCl_3$, 400 HMz



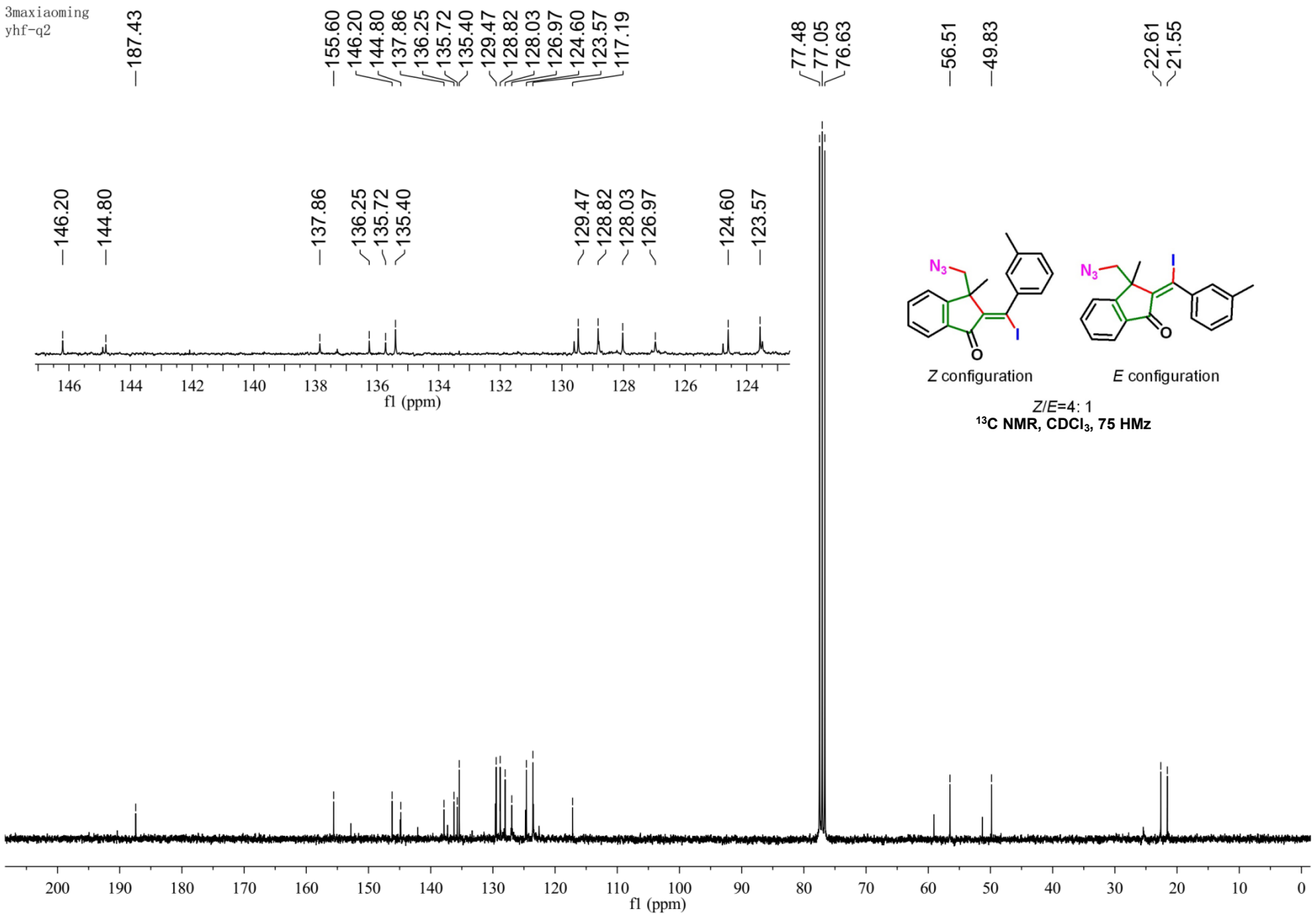
^{1}H NMR Spectrum of Compound 4b



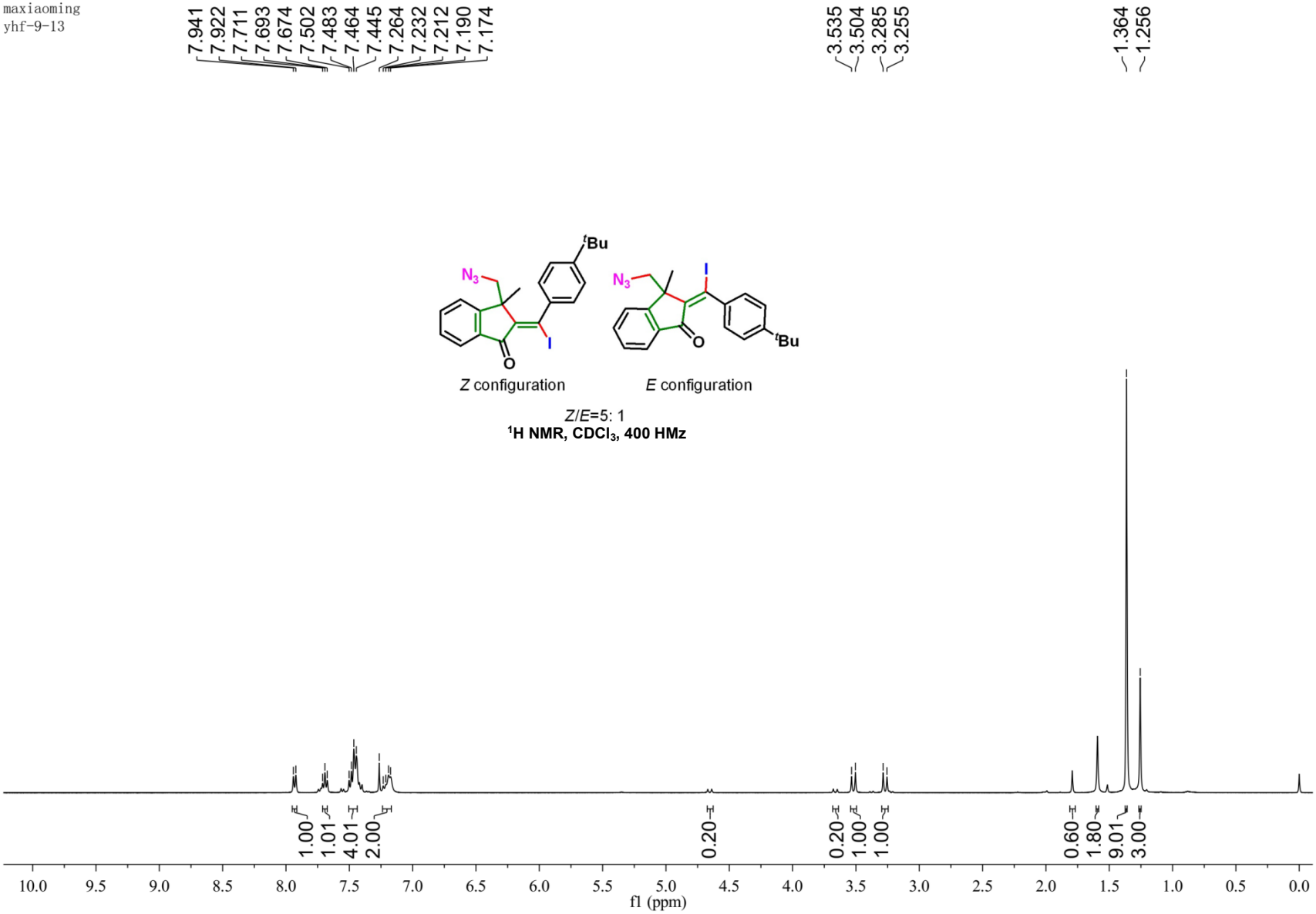
^{13}C NMR Spectrum of Compound 4b



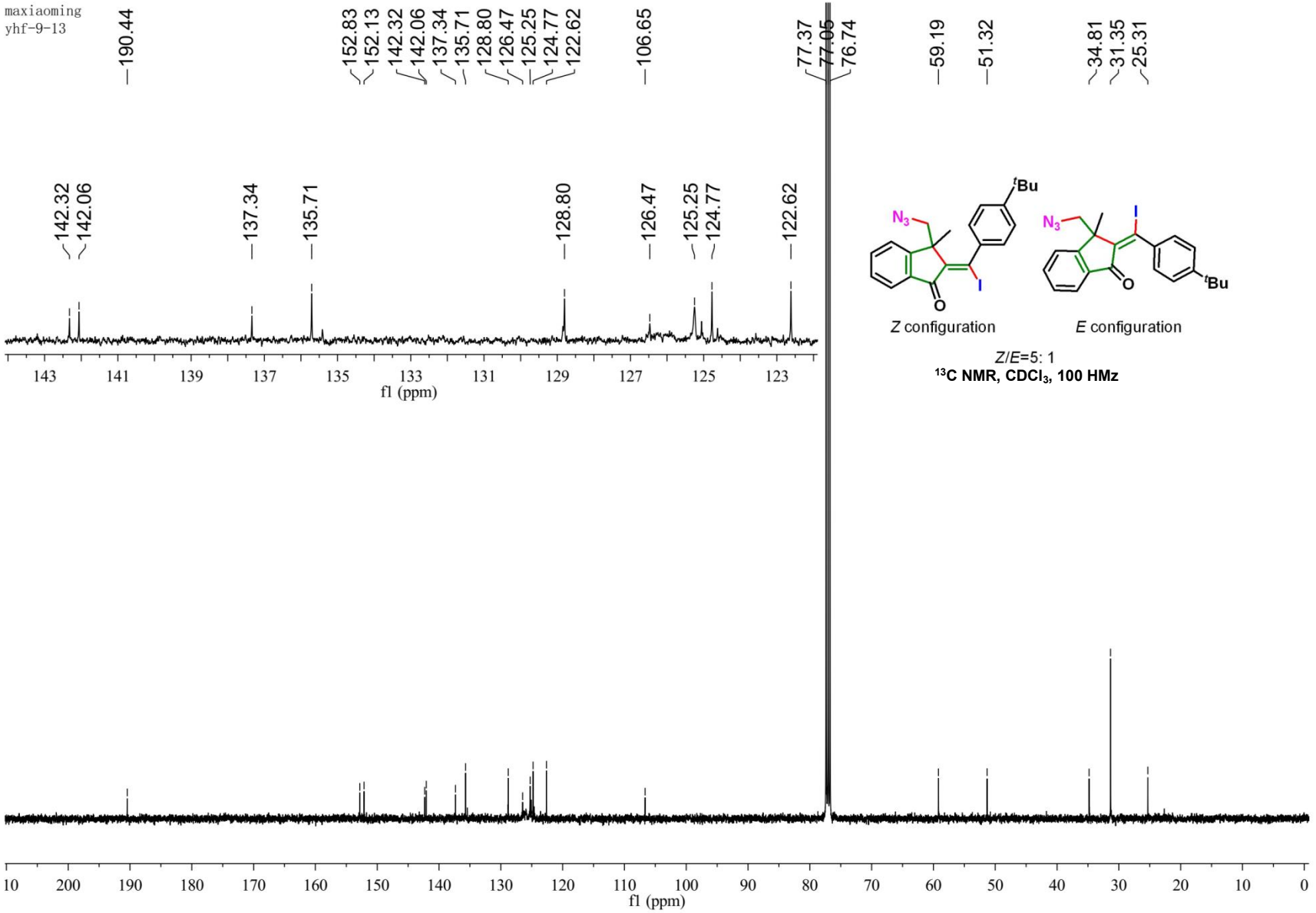
^{1}H NMR Spectrum of Compound 4c



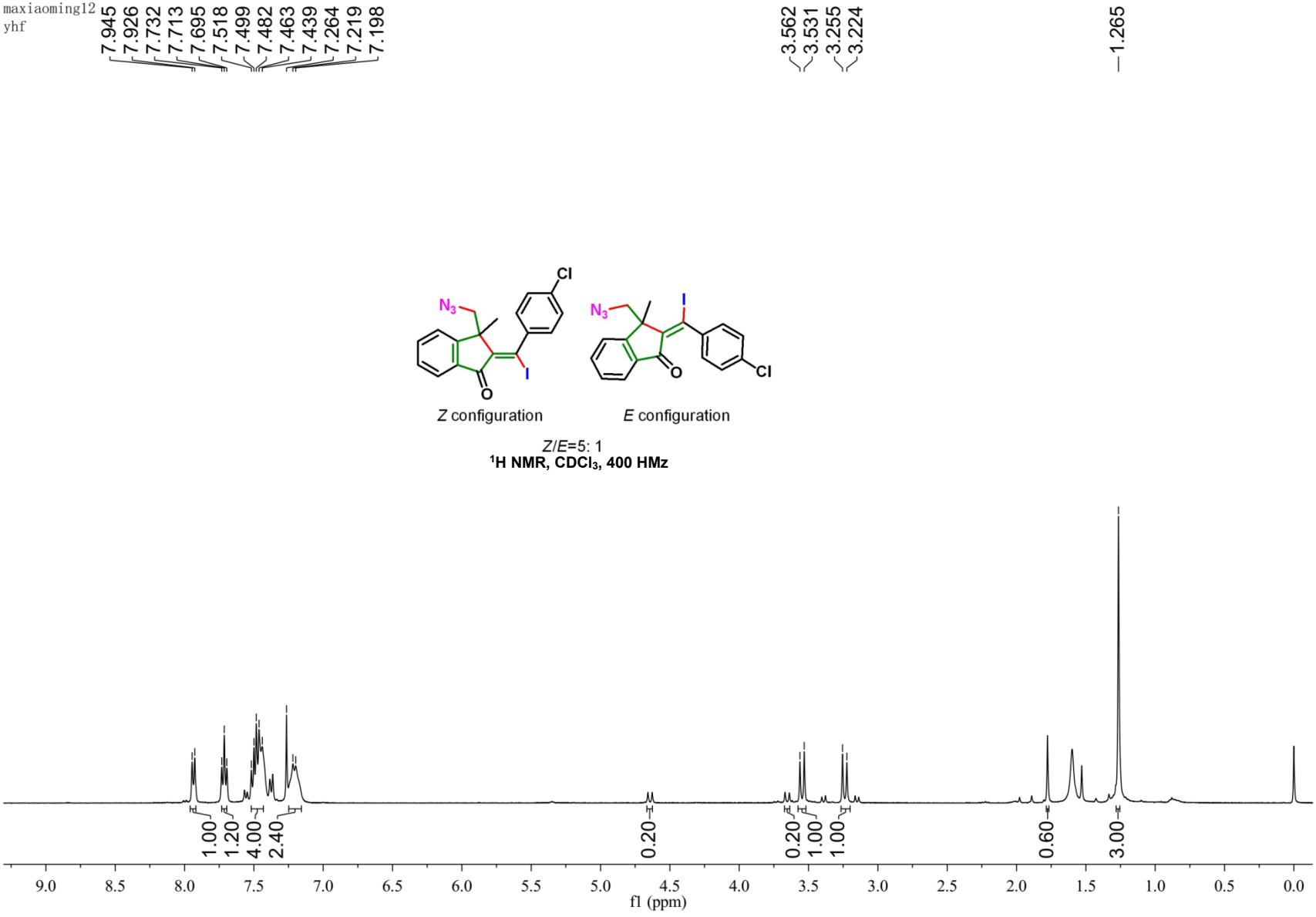
^{13}C NMR Spectrum of Compound 4c



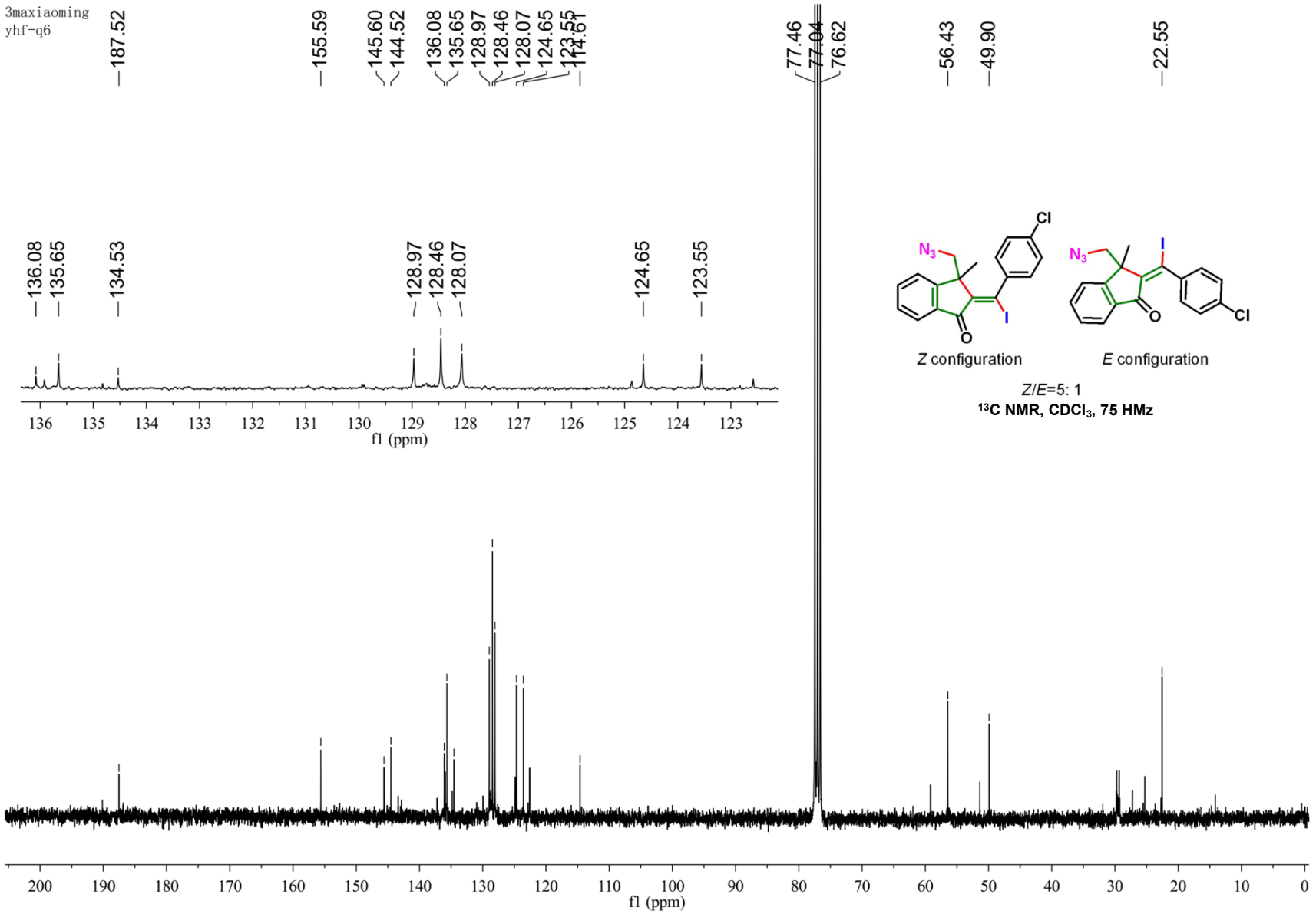
^{1}H NMR Spectrum of Compound 4d



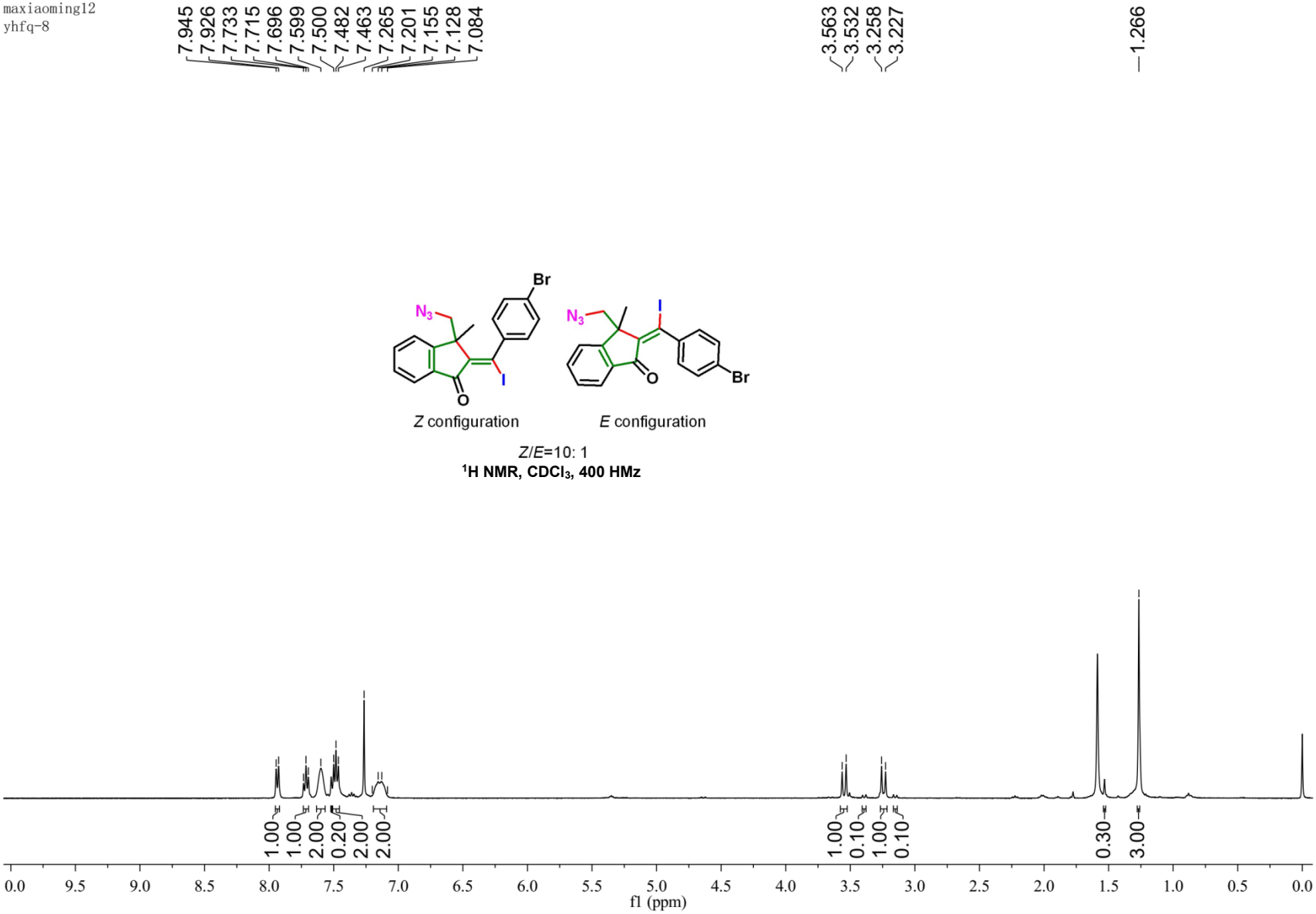
^{13}C NMR Spectrum of Compound 4d



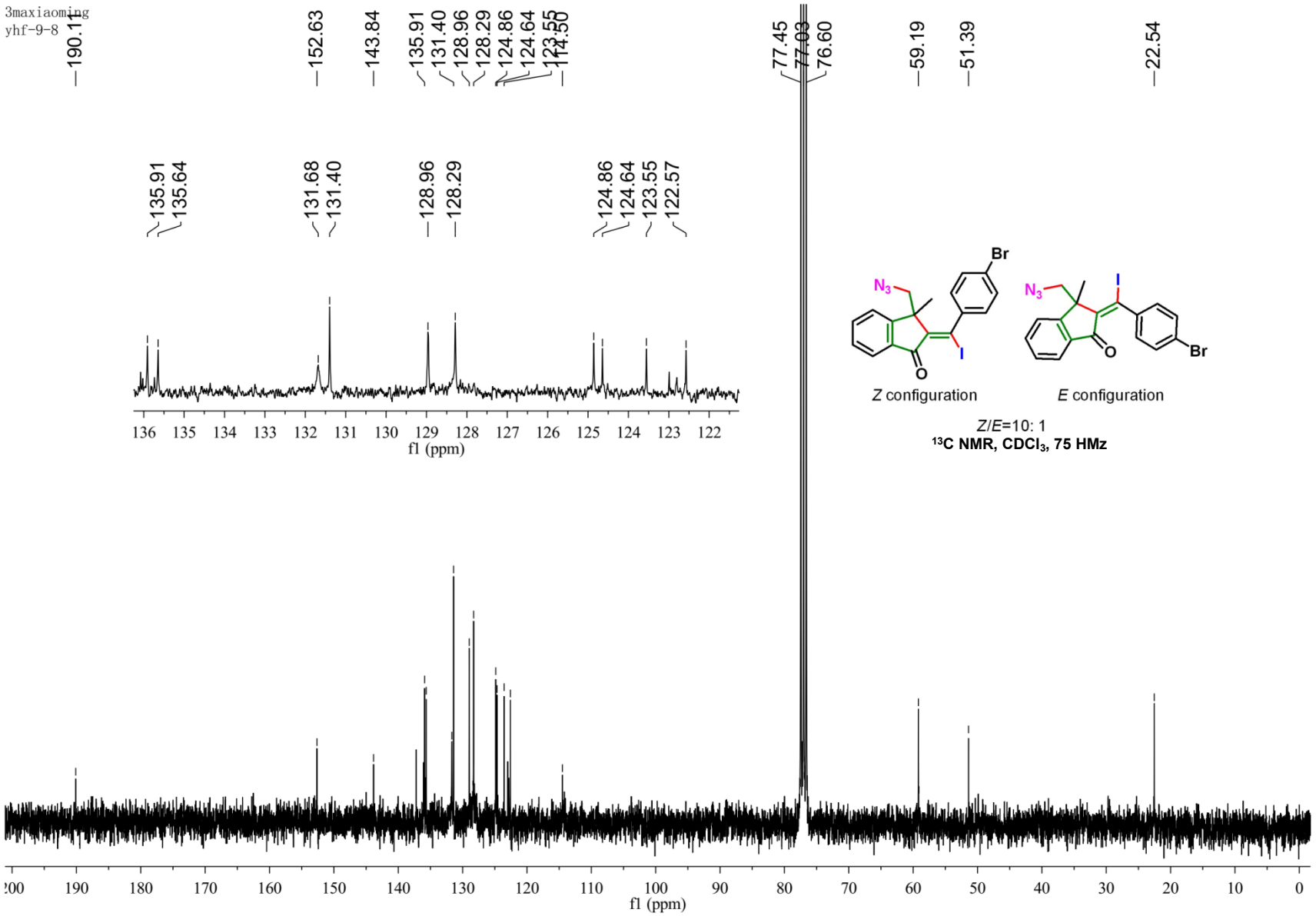
^{1}H NMR Spectrum of Compound 4e



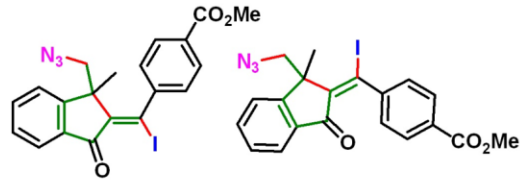
^{13}C NMR Spectrum of Compound 4e



^{1}H NMR Spectrum of Compound 4f



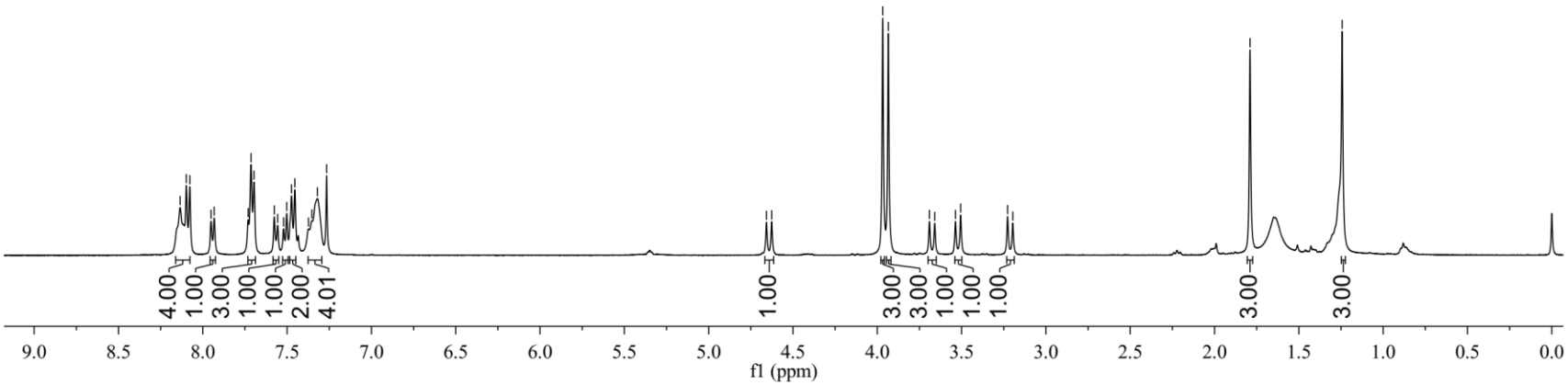
^{13}C NMR Spectrum of Compound 4f



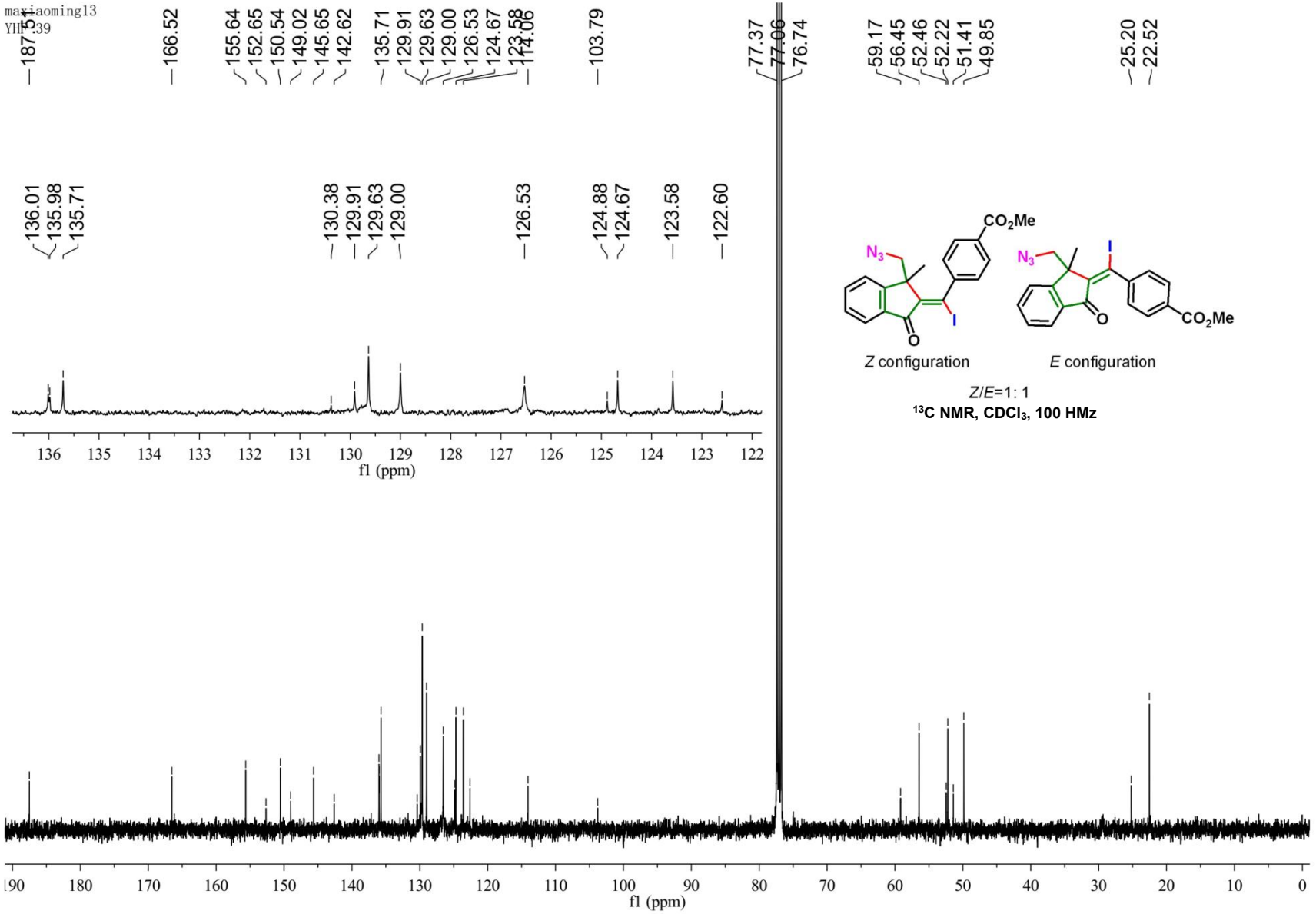
Z configuration *E* configuration

Z/*E*=1: 1

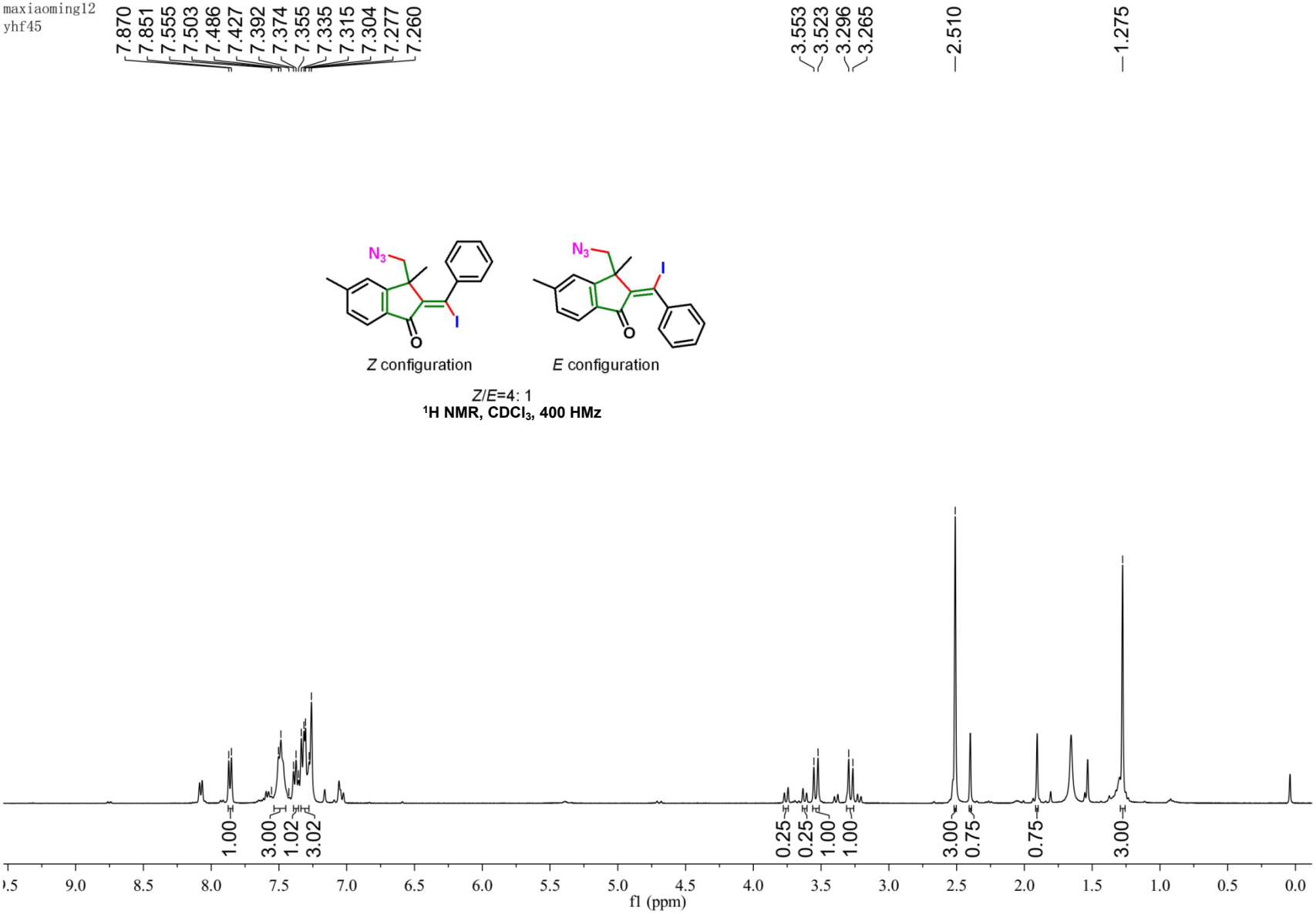
^{1}H NMR, $CDCl_3$, 400 HMz



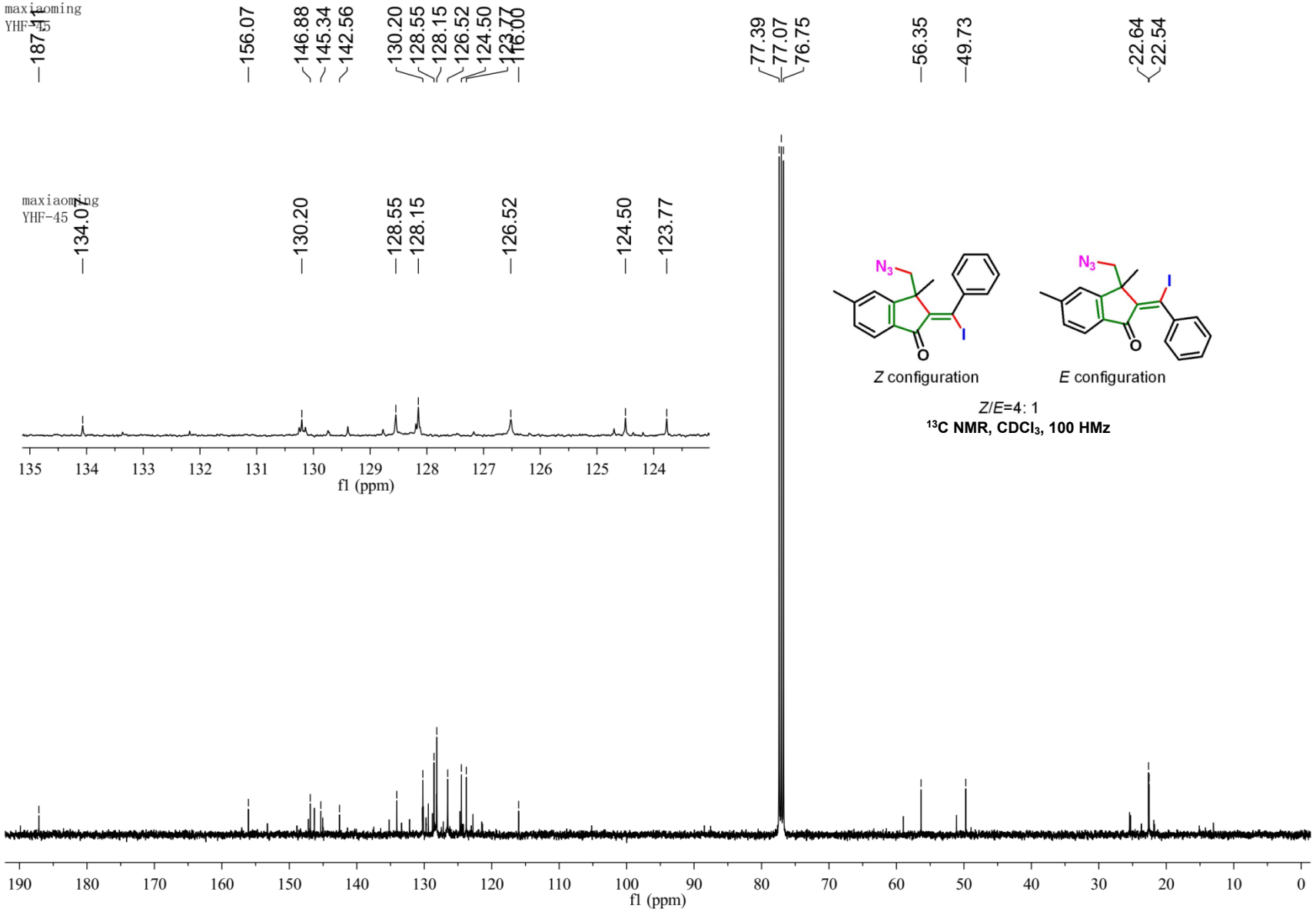
^{1}H NMR Spectrum of Compound 4g



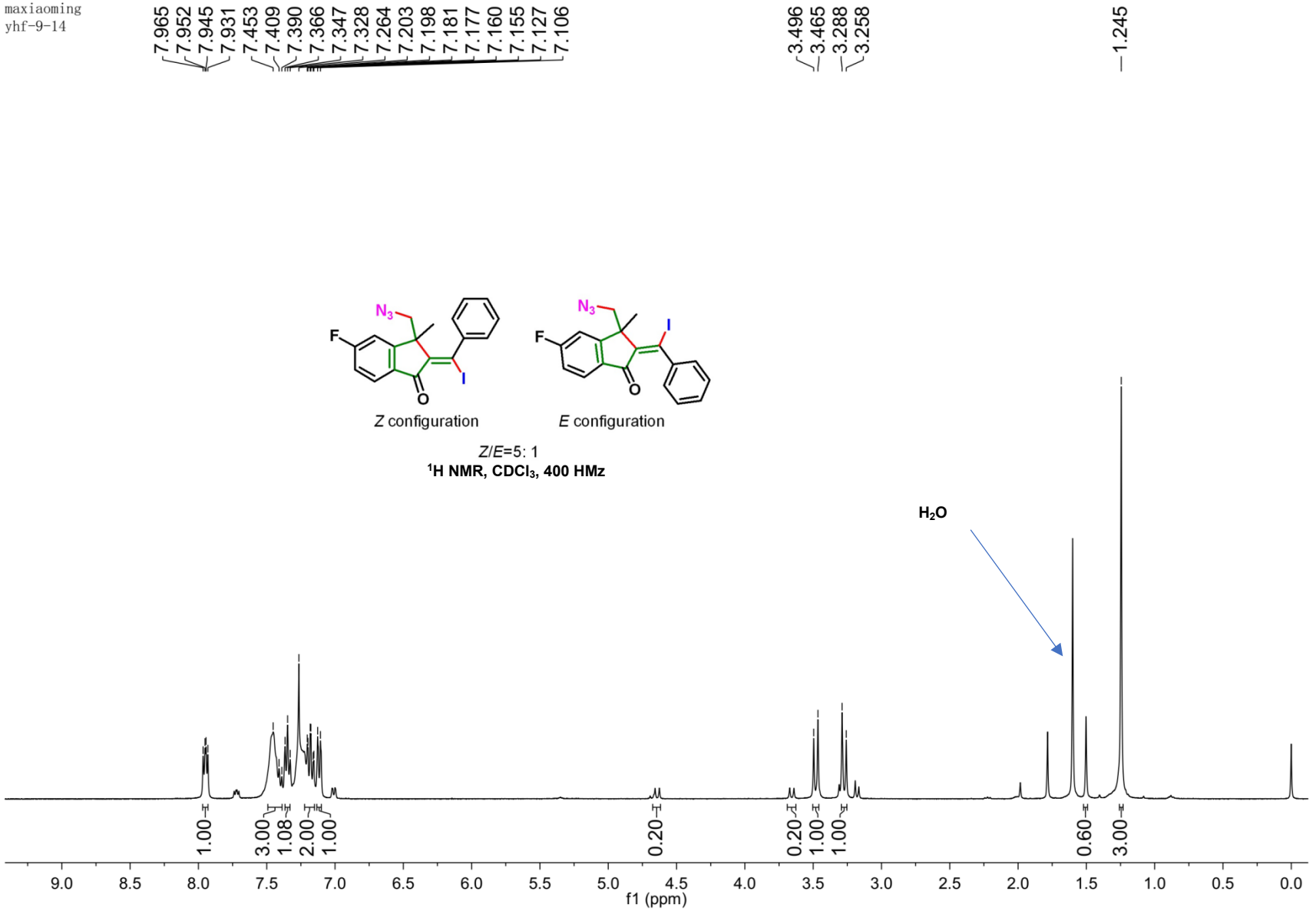
^{13}C NMR Spectrum of Compound 4g



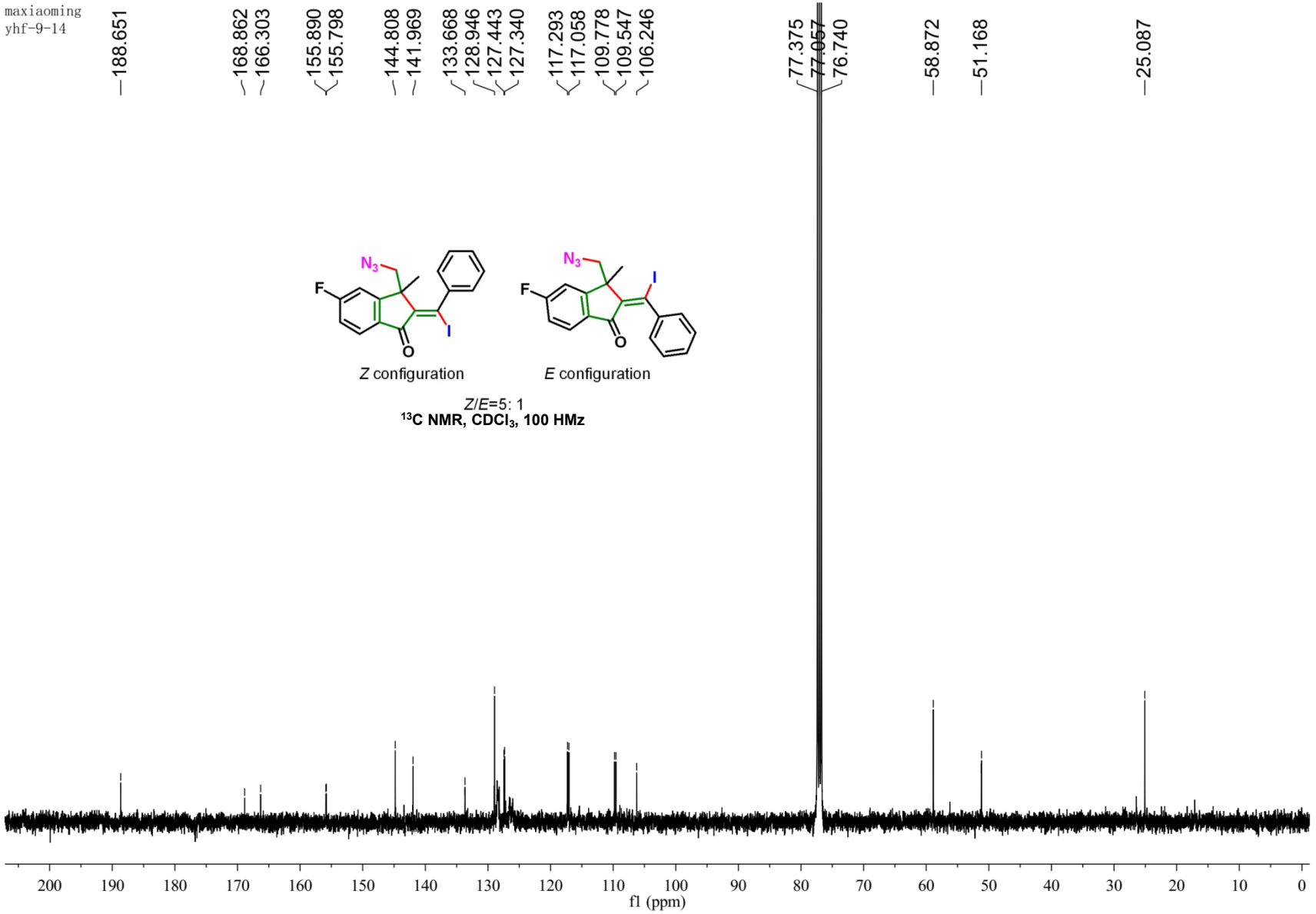
^{1}H NMR Spectrum of Compound 4h



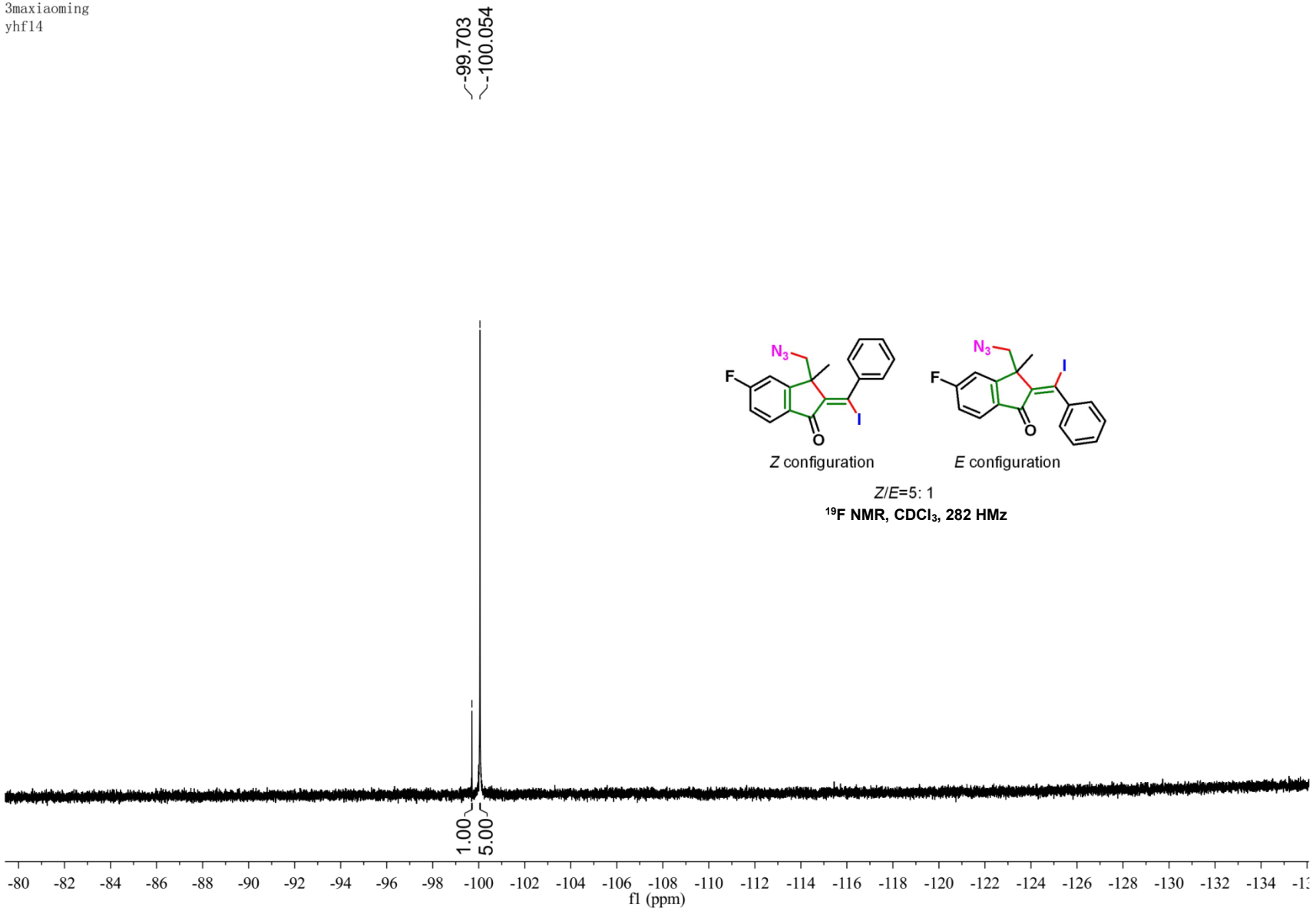
^{13}C NMR Spectrum of Compound 4h



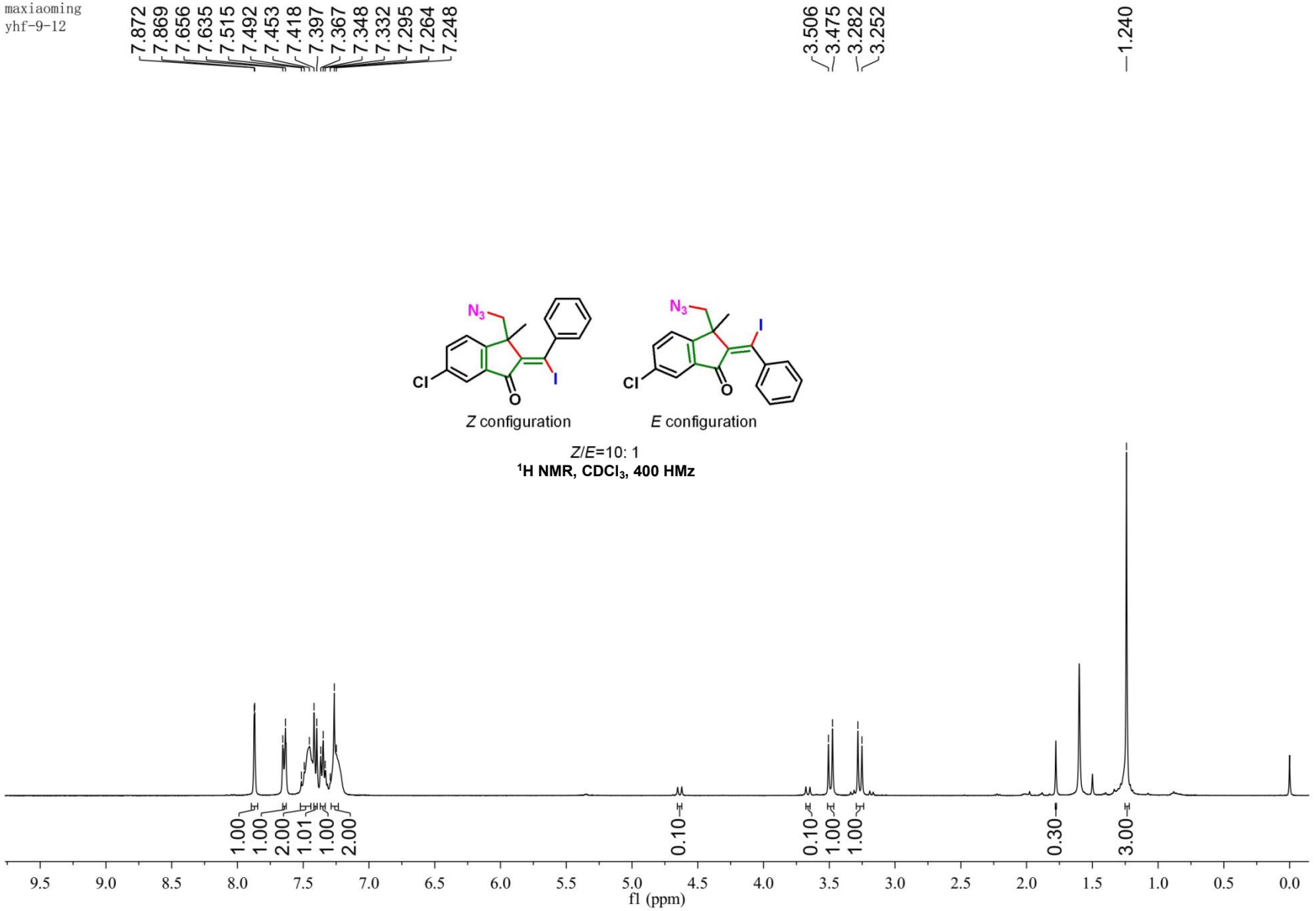
^{1}H NMR Spectrum of Compound 4i



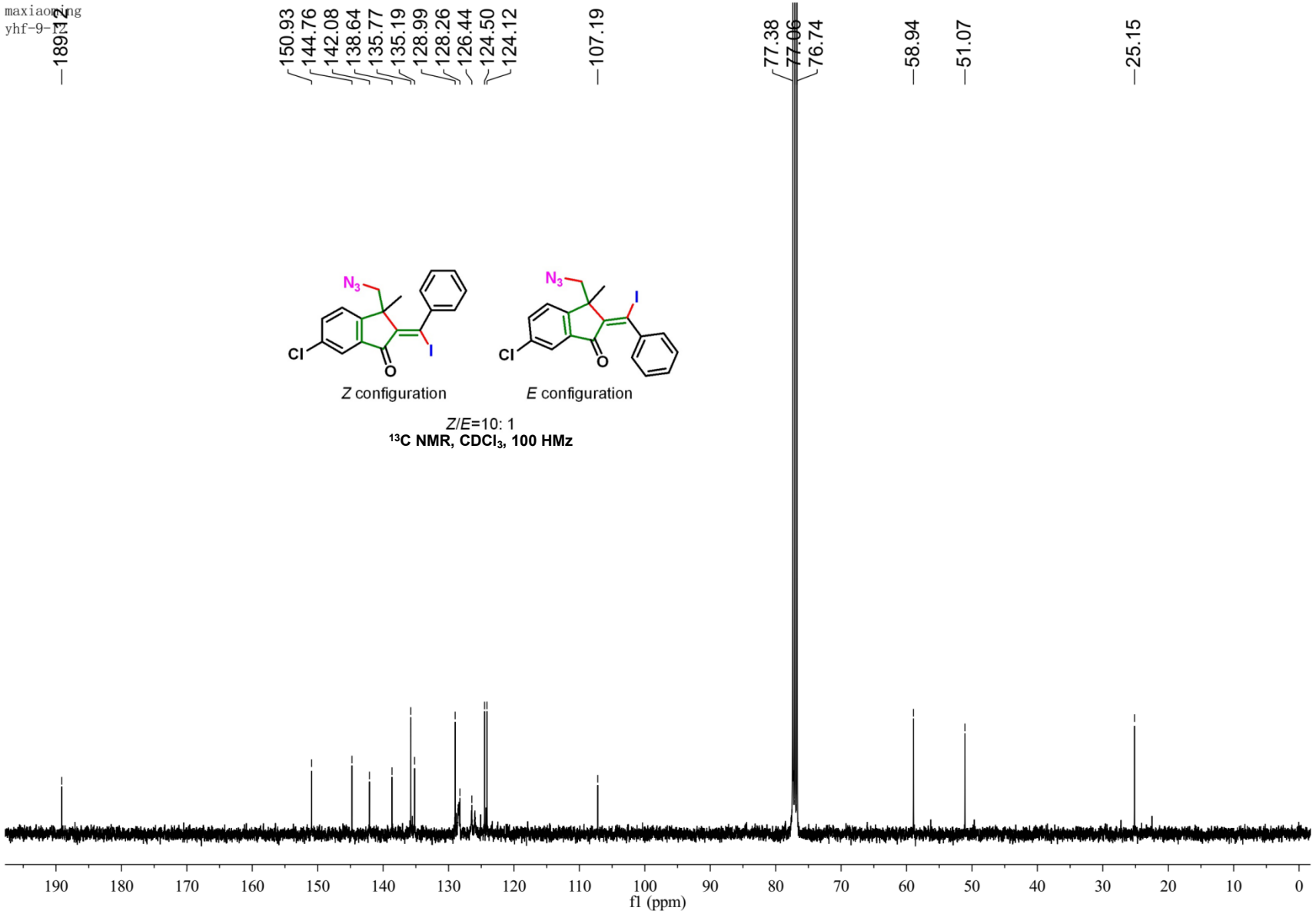
^{13}C NMR Spectrum of Compound 4i



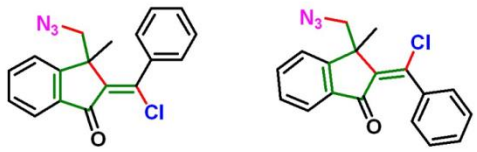
^{19}F NMR Spectrum of Compound 4i



^{1}H NMR Spectrum of Compound 4j



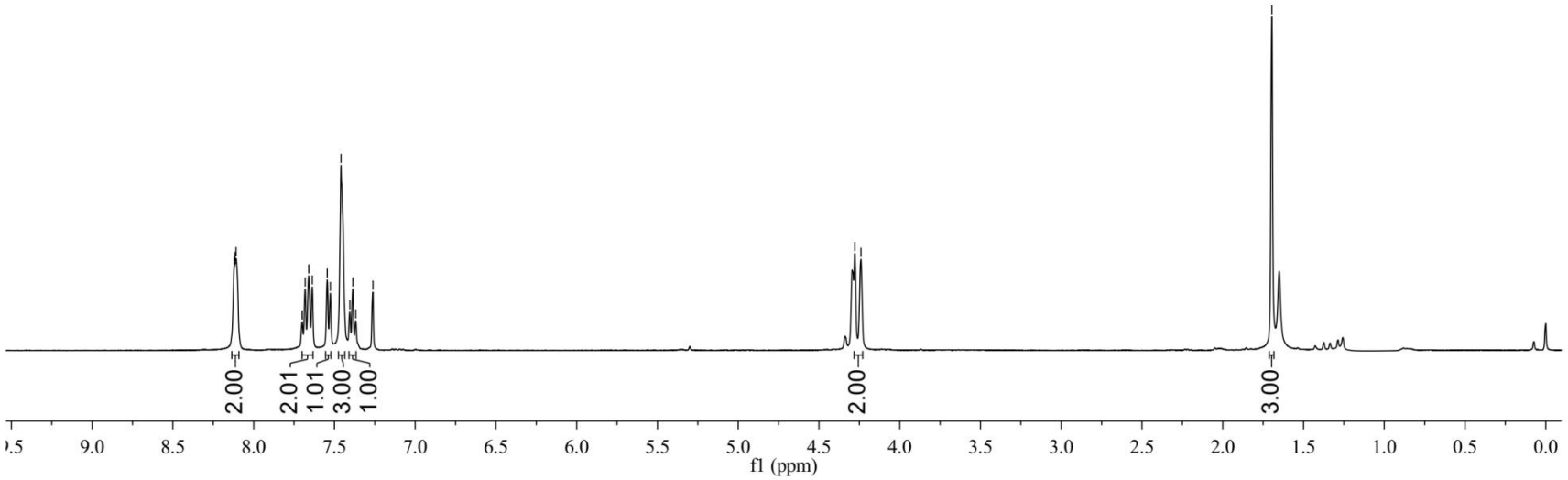
^{13}C NMR Spectrum of Compound 4j



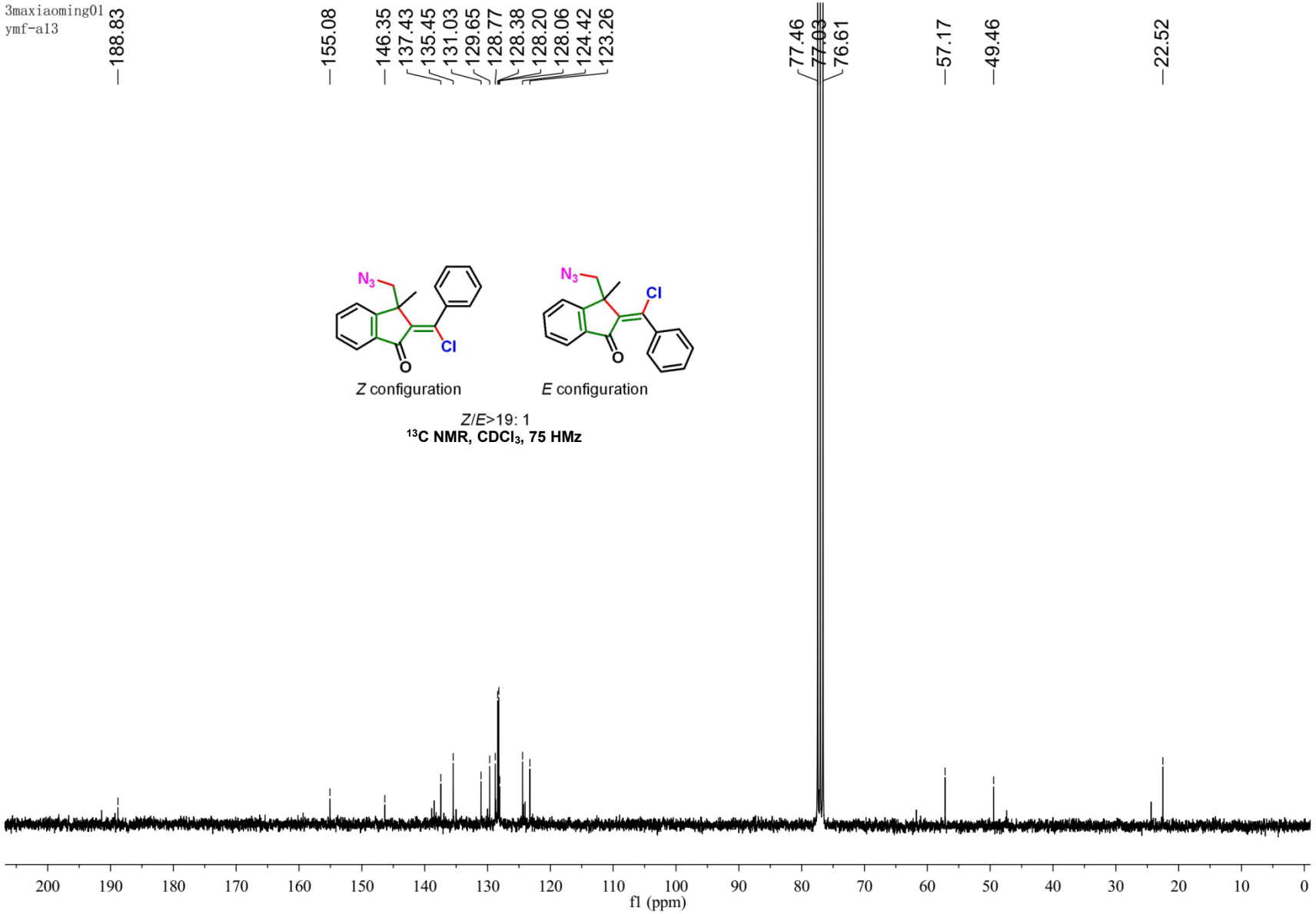
Z configuration *E* configuration

Z/*E*>19: 1

^{1}H NMR, $CDCl_3$, 400 HMz



^{1}H NMR Spectrum of Compound 4k



^{13}C NMR Spectrum of Compound 4k

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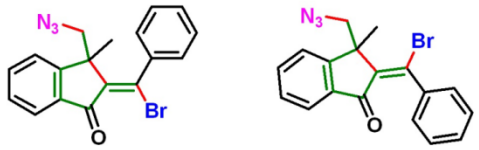
yhf-nbs

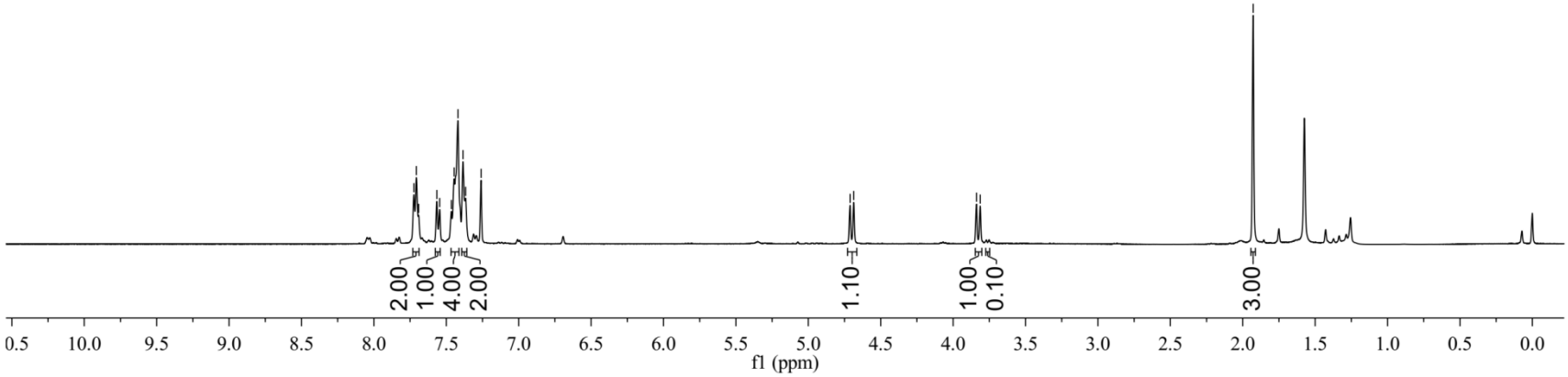
7.724
7.707
7.691
7.565
7.546
7.465
7.446
7.420
7.385
7.366
7.260
4.712
4.686
3.839
3.813
1.928



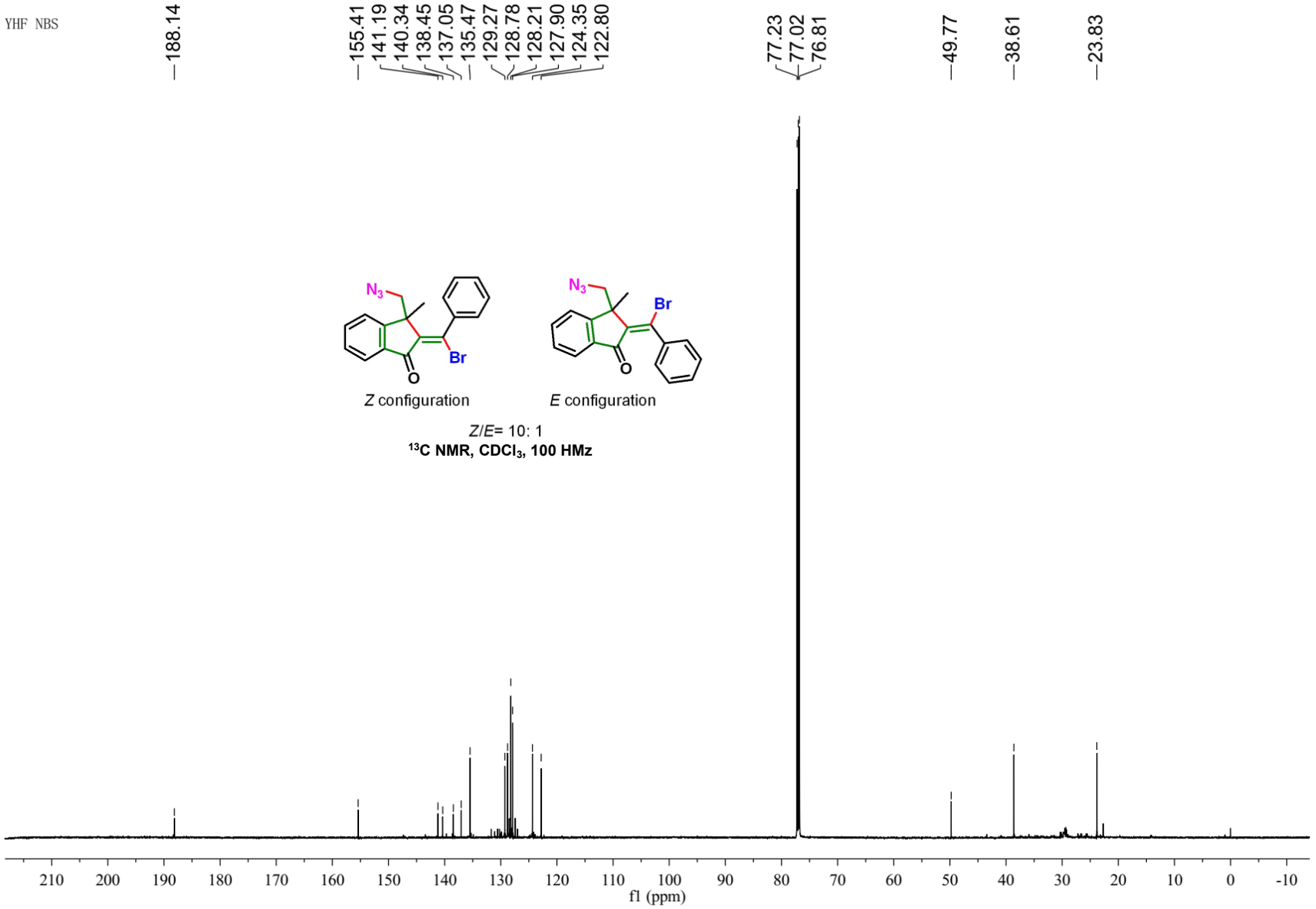
Z configuration *E* configuration

Z/*E*= 10: 1

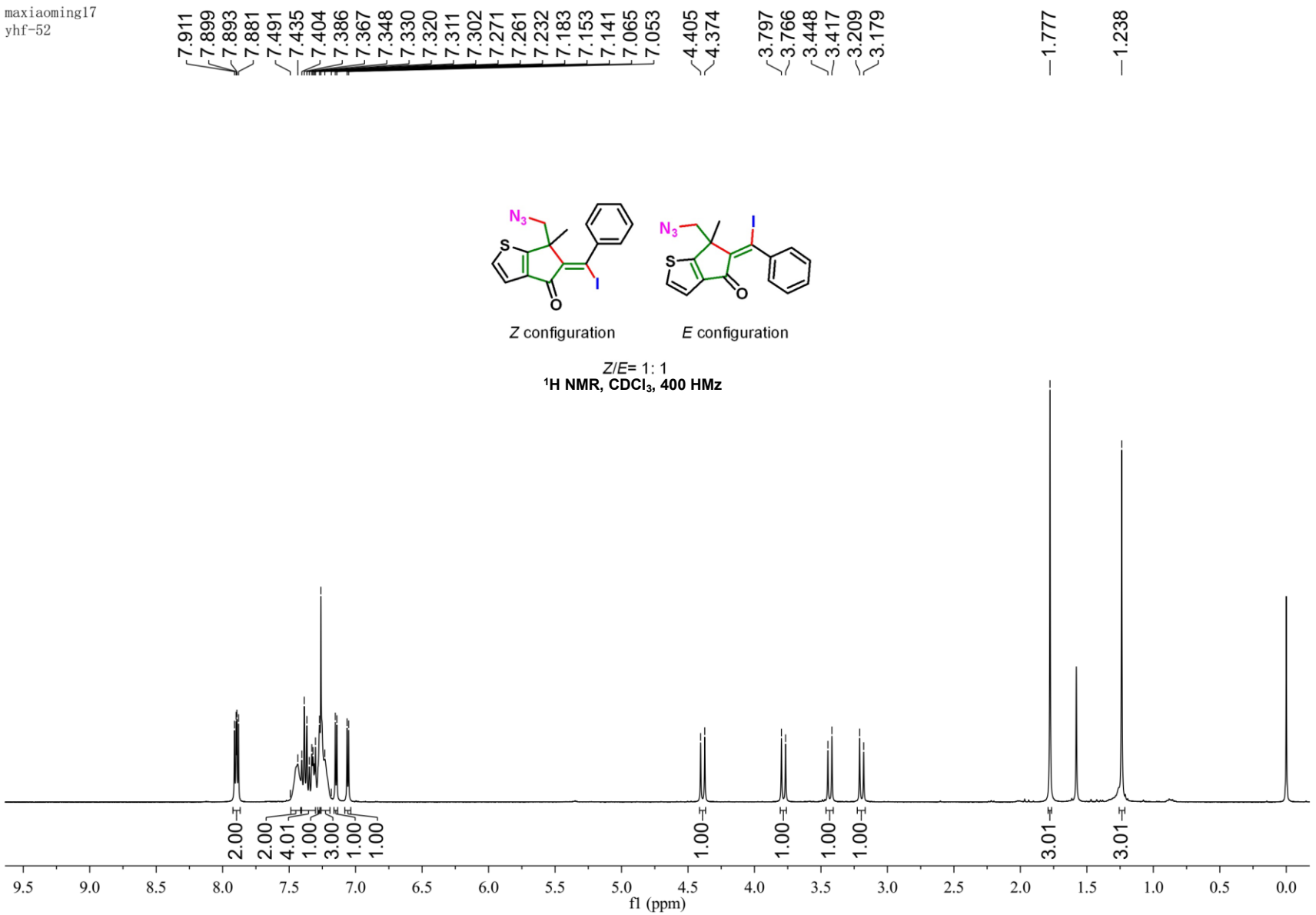
^{1}H NMR, $CDCl_3$, 400 HMz



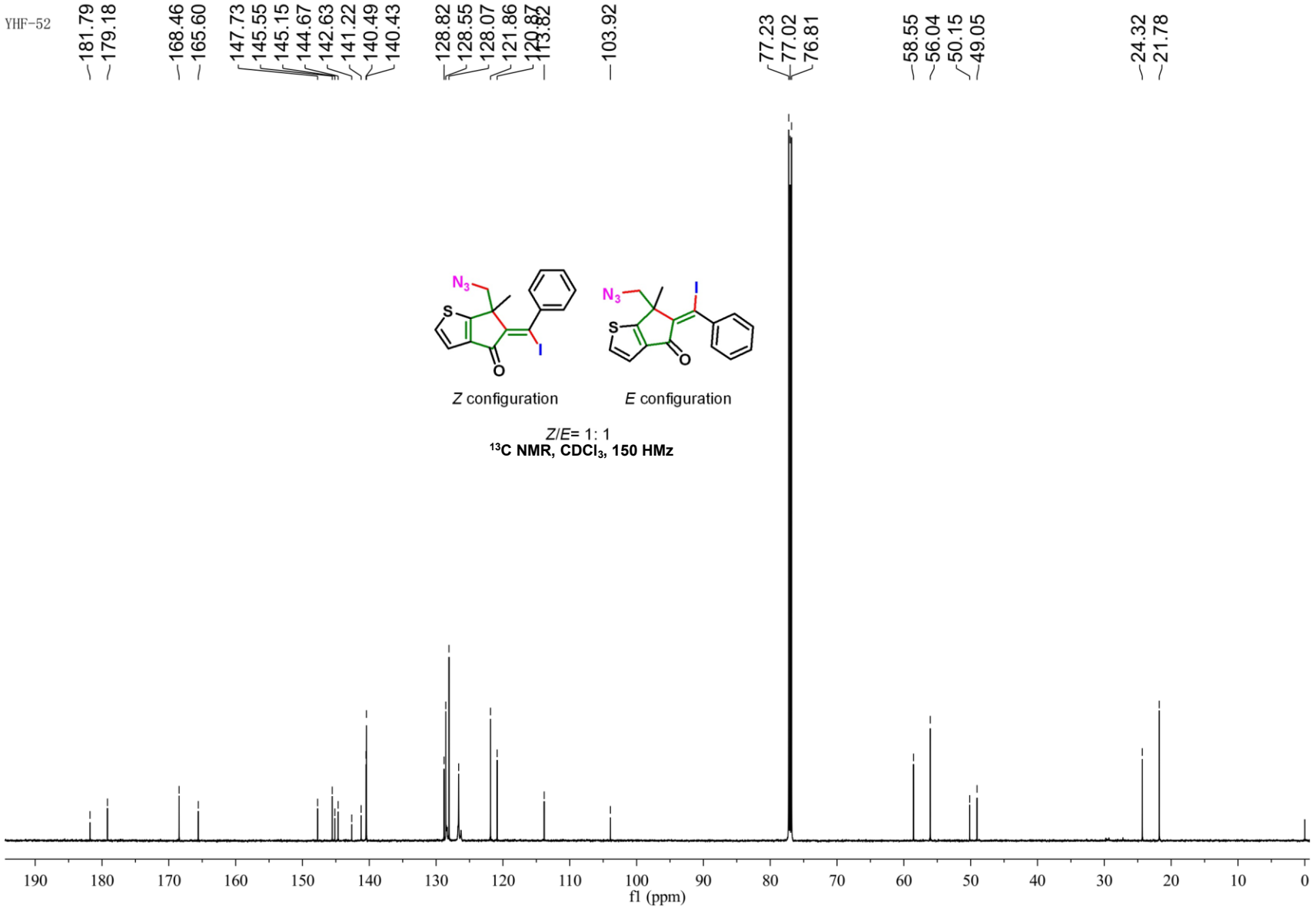
^{1}H NMR Spectrum of Compound 4l



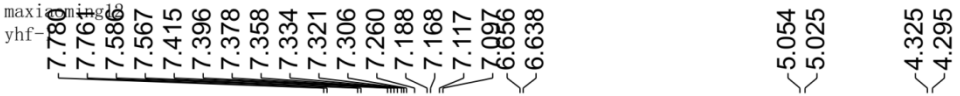
^{13}C NMR Spectrum of Compound 4l

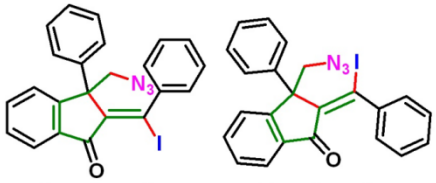


^{1}H NMR Spectrum of Compound 4m



^{13}C NMR Spectrum of Compound 4m

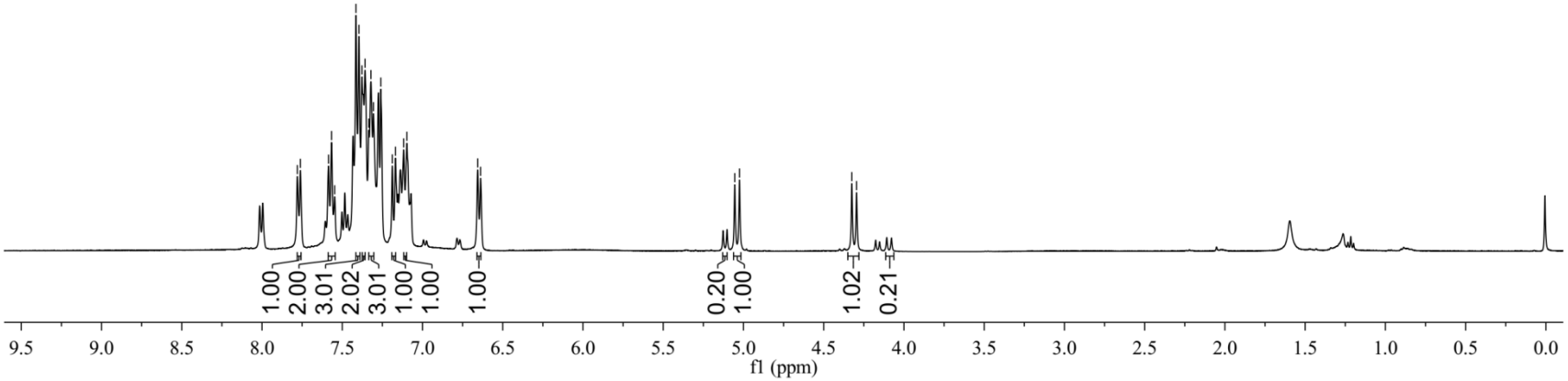




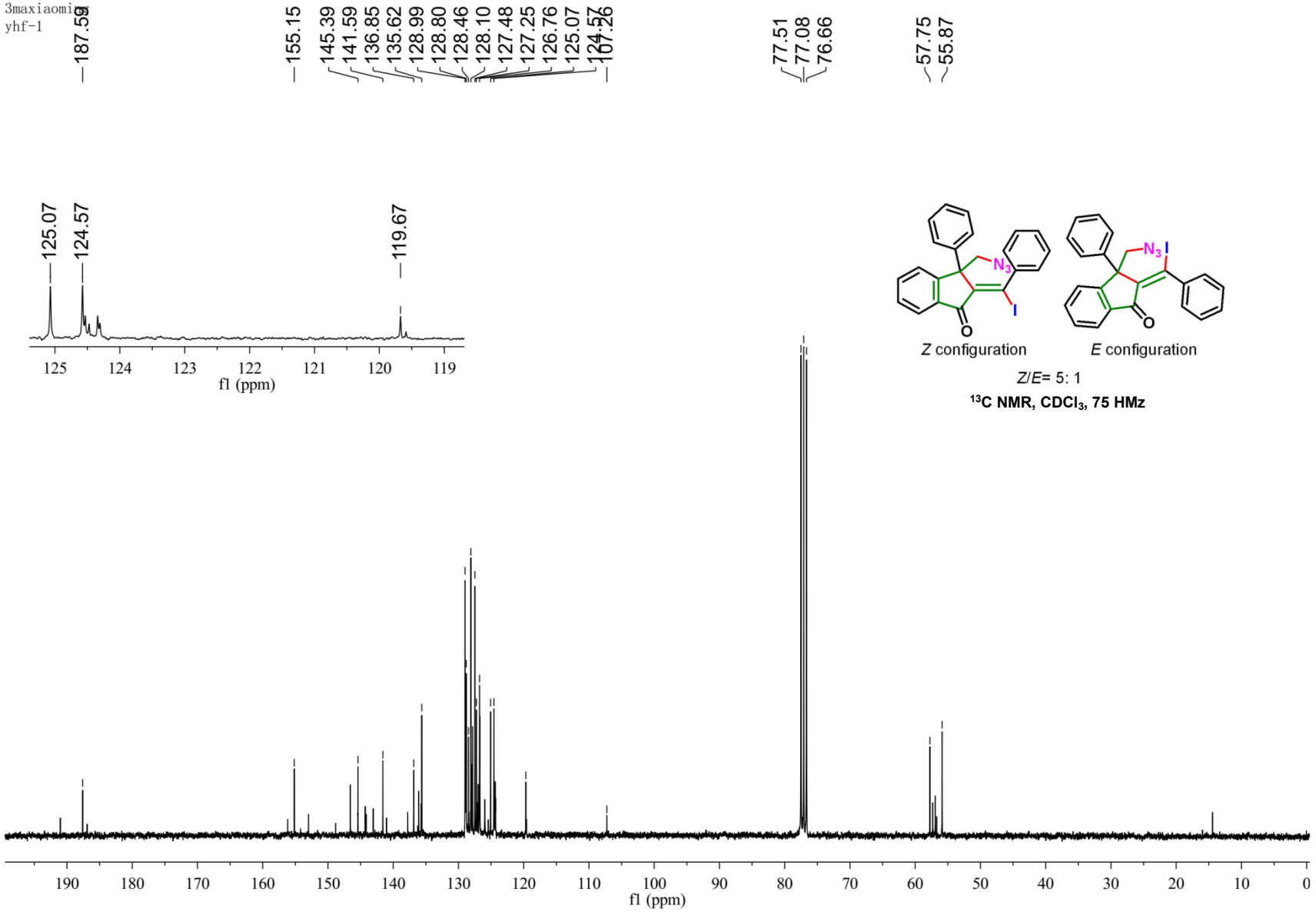
Z configuration *E* configuration

Z/*E*= 5: 1

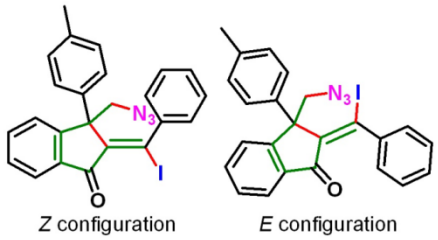
^{1}H NMR, $CDCl_3$, 400 HMz



^{1}H NMR Spectrum of Compound 6a



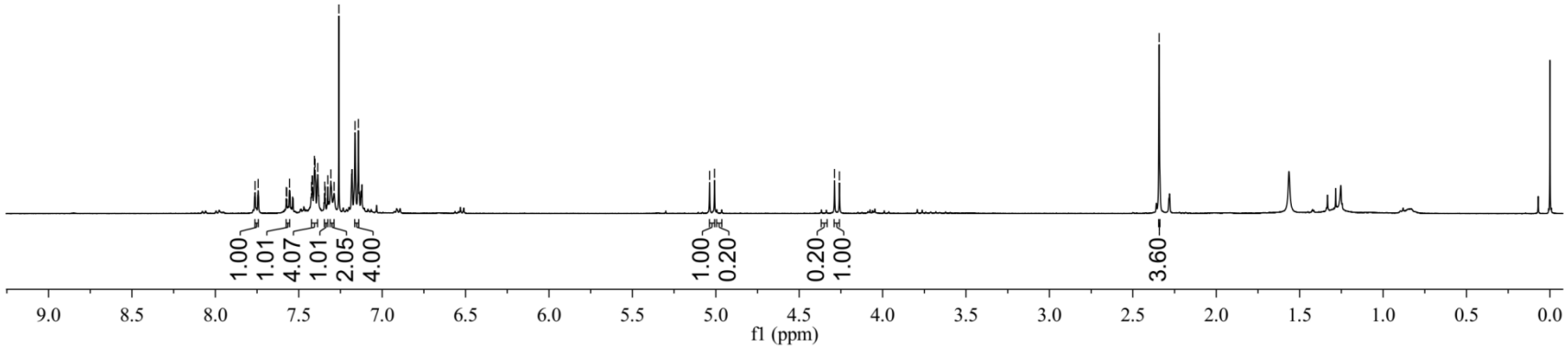
^{13}C NMR Spectrum of Compound 6a



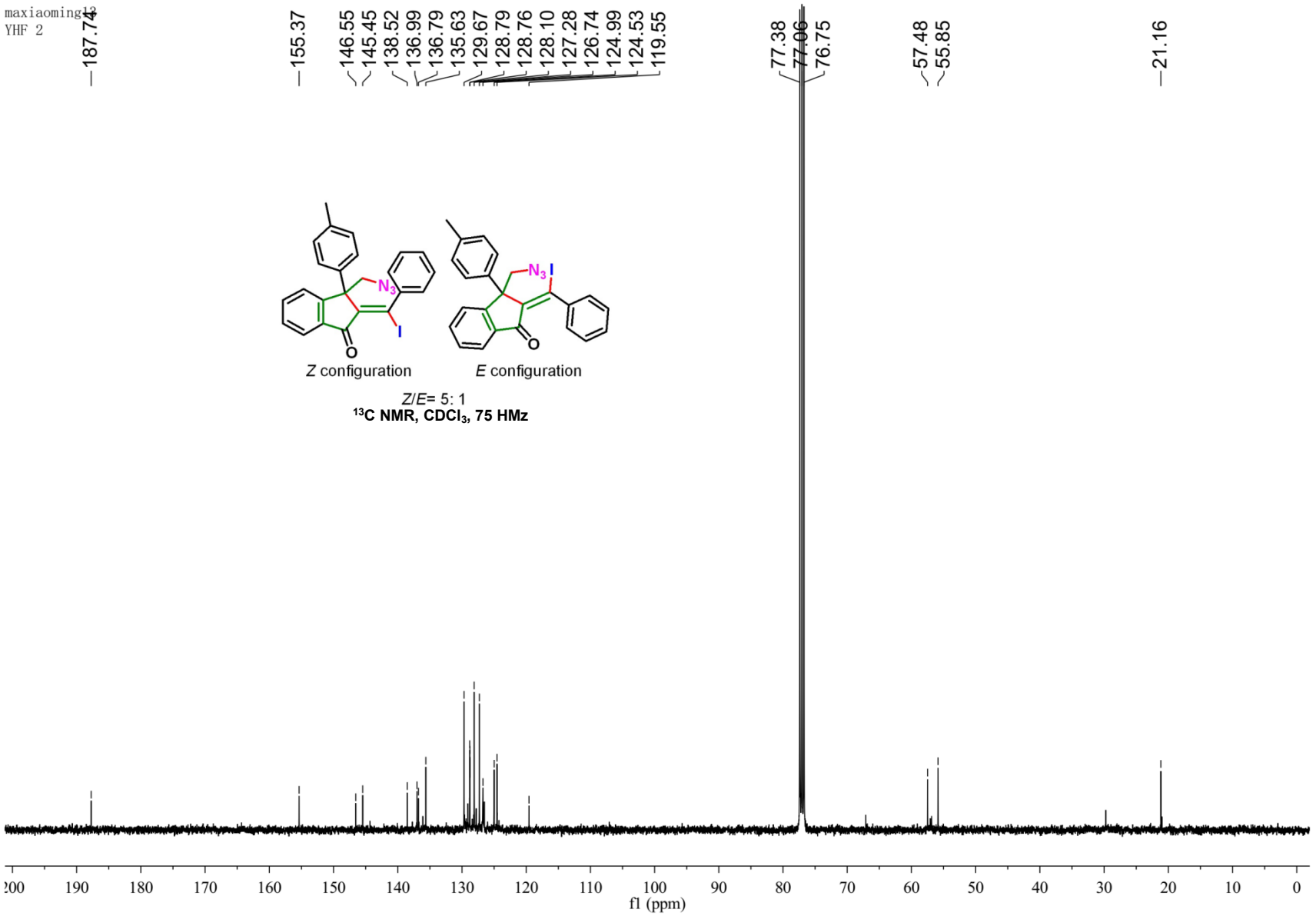
Z configuration *E* configuration

Z/*E*= 5: 1

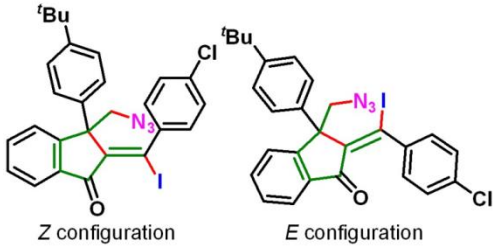
^{1}H NMR, $CDCl_3$, 400 HMz



^{1}H NMR Spectrum of Compound 6b



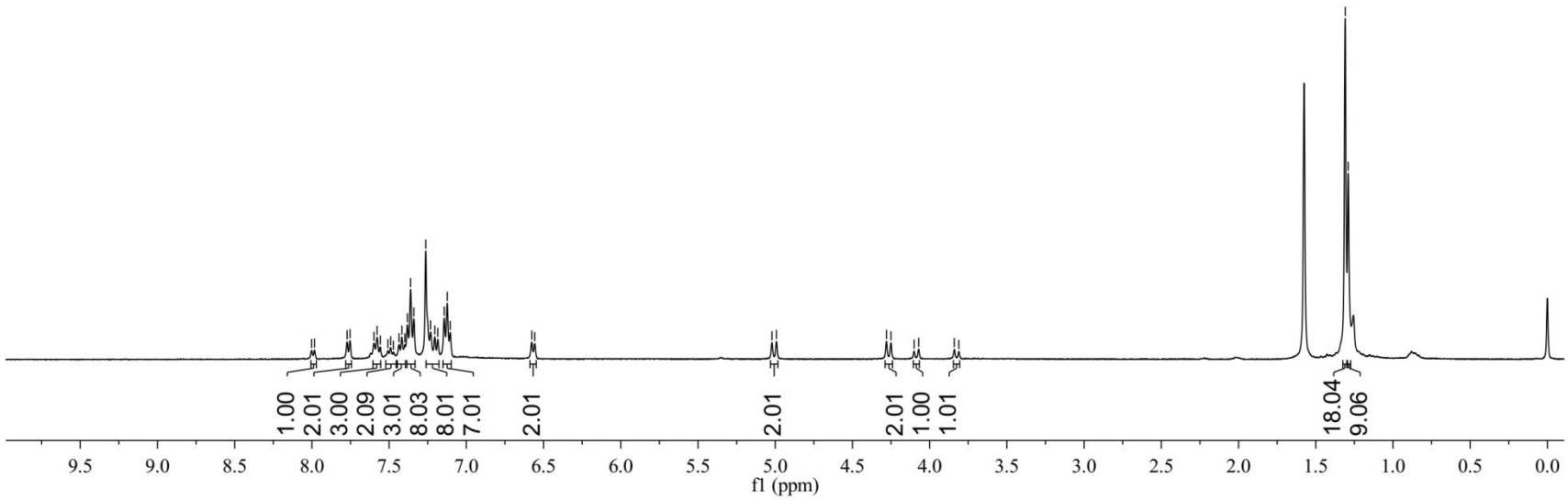
^{13}C NMR Spectrum of Compound 6b



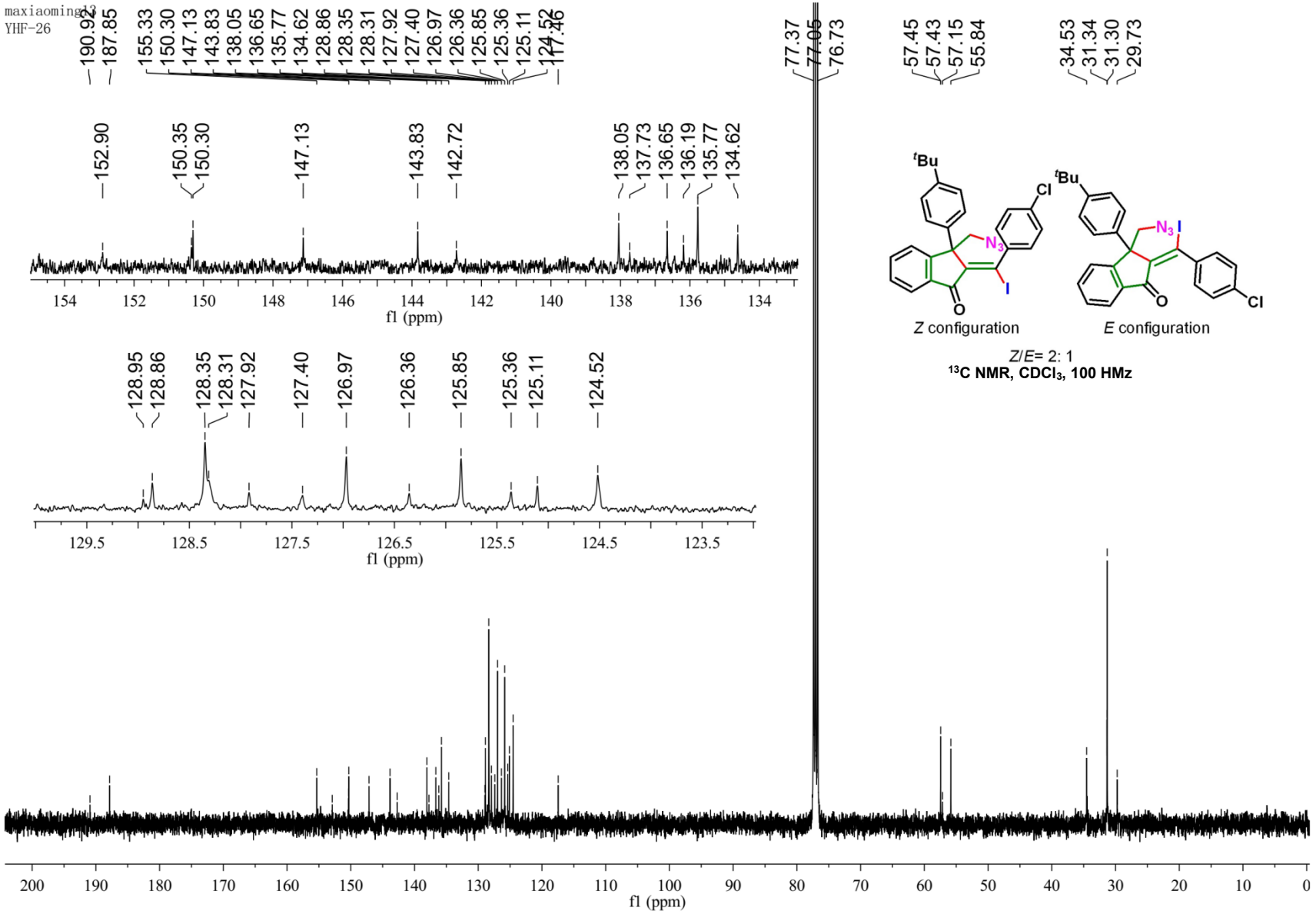
Z configuration *E* configuration

Z/*E*= 2: 1

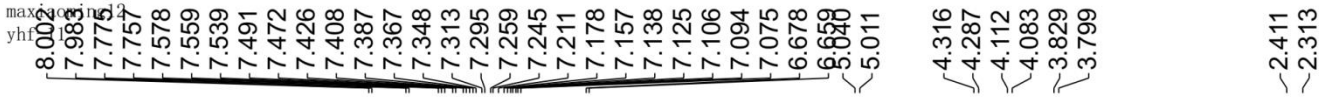
^{1}H NMR, $CDCl_3$, 400 HMz

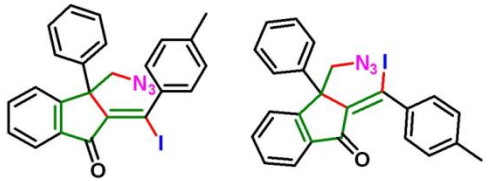


^{1}H NMR Spectrum of Compound 6c



^{13}C NMR Spectrum of Compound 6c

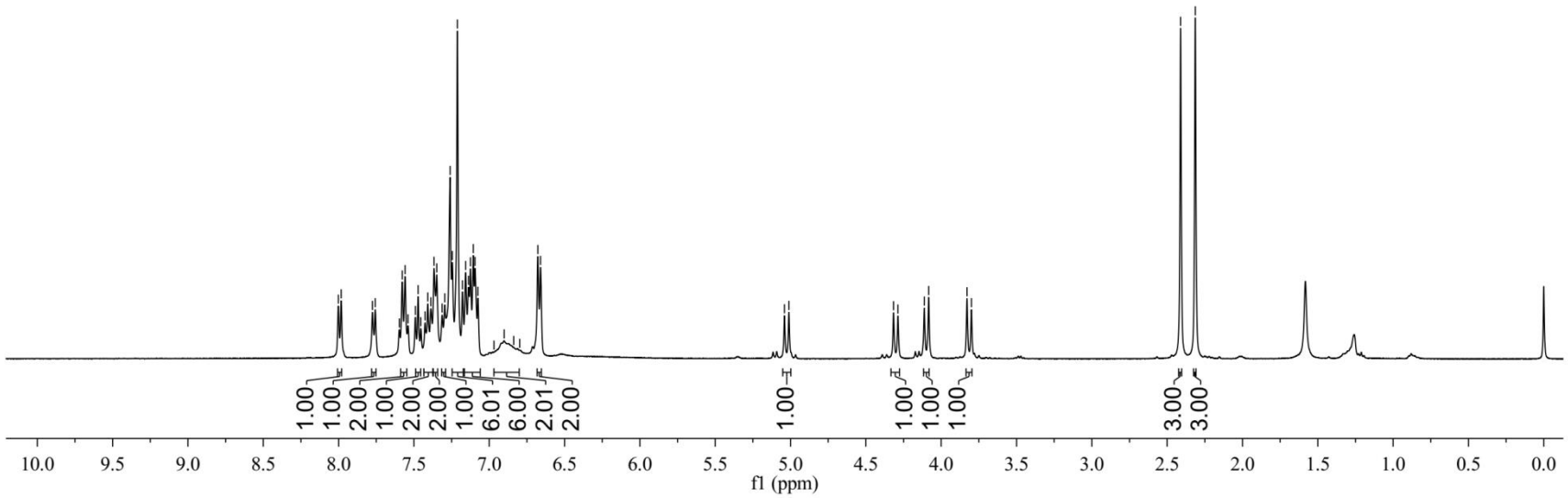




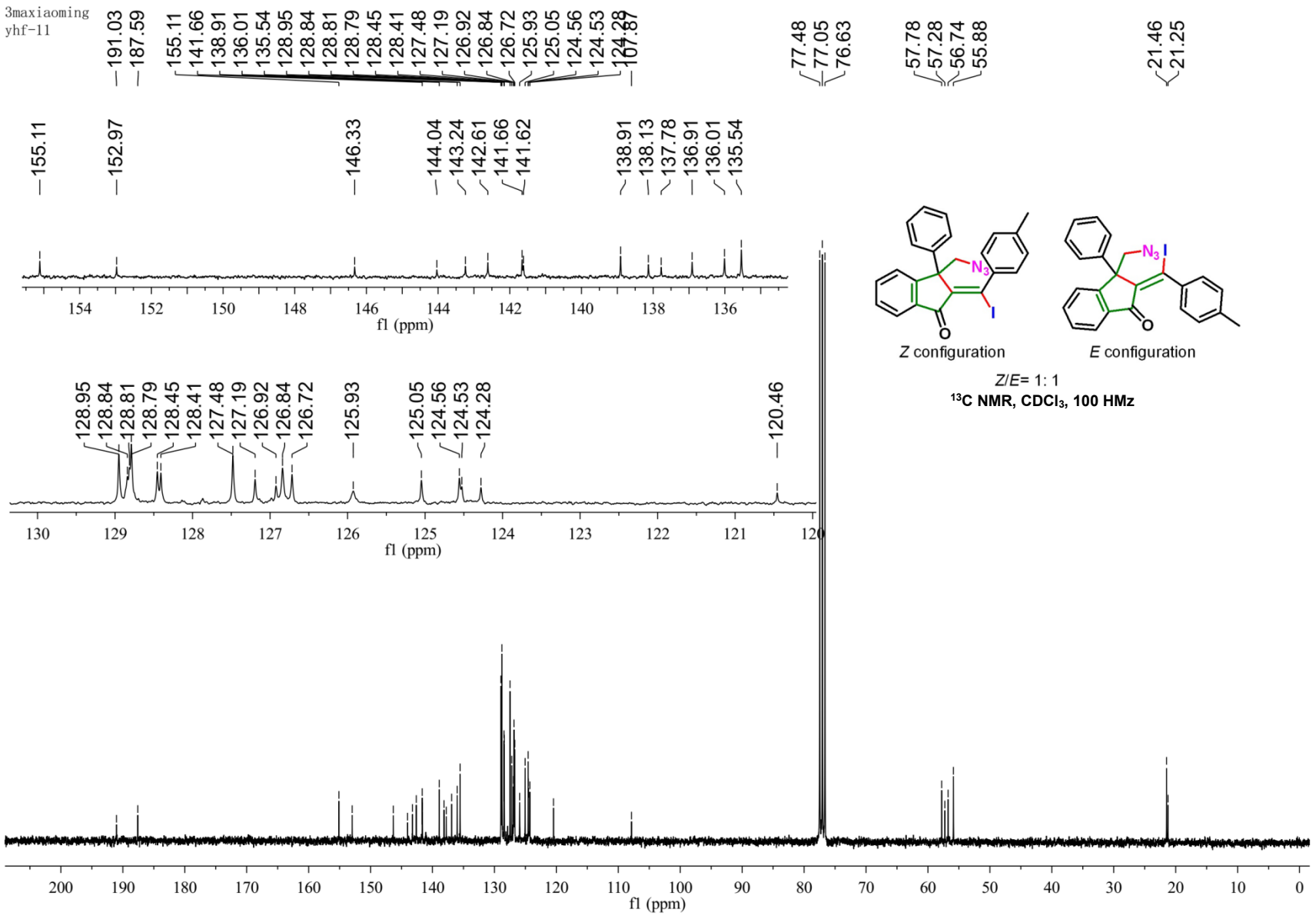
Z configuration *E* configuration

Z/*E*= 1: 1

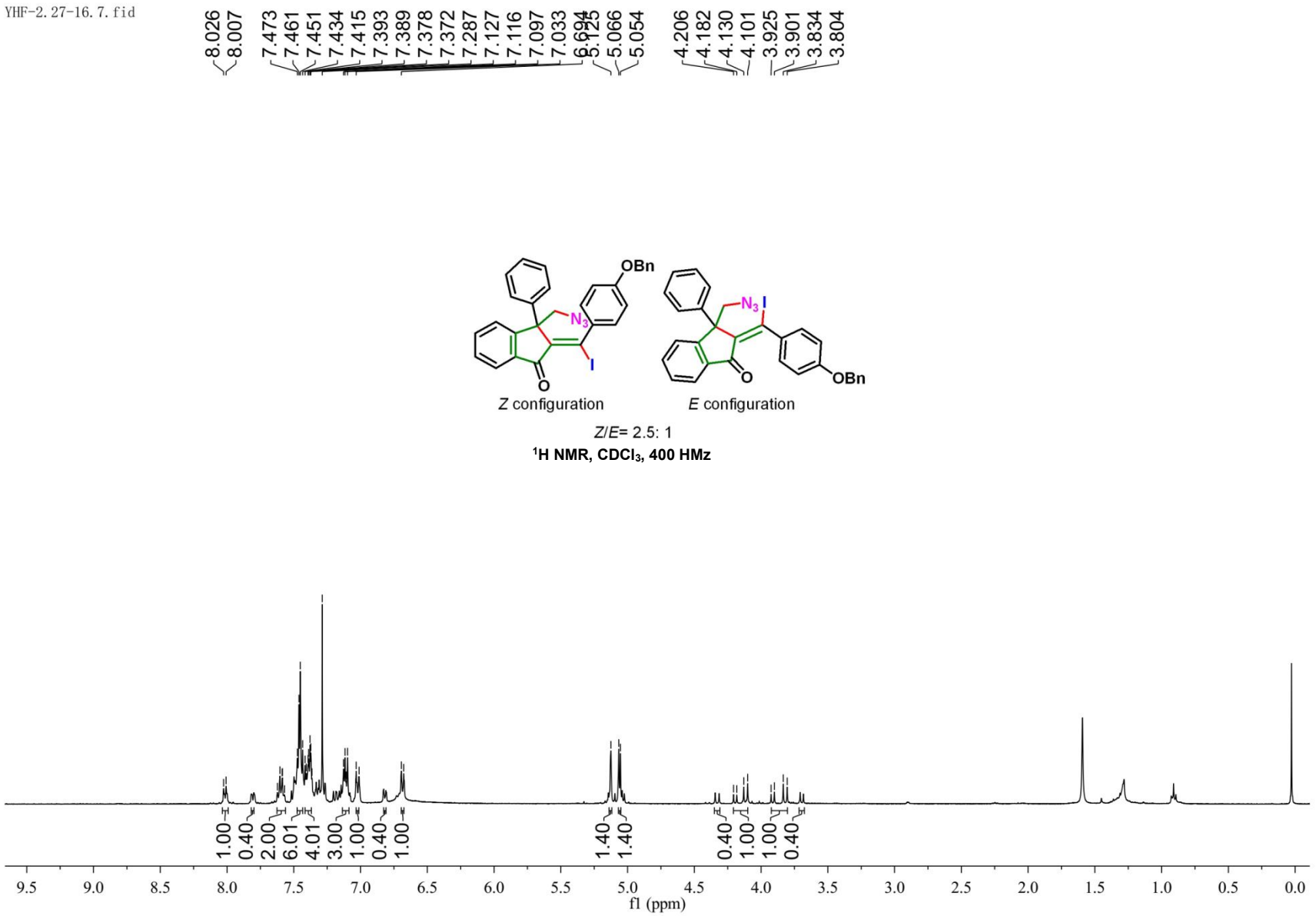
^{1}H NMR, $CDCl_3$, 400 HMz



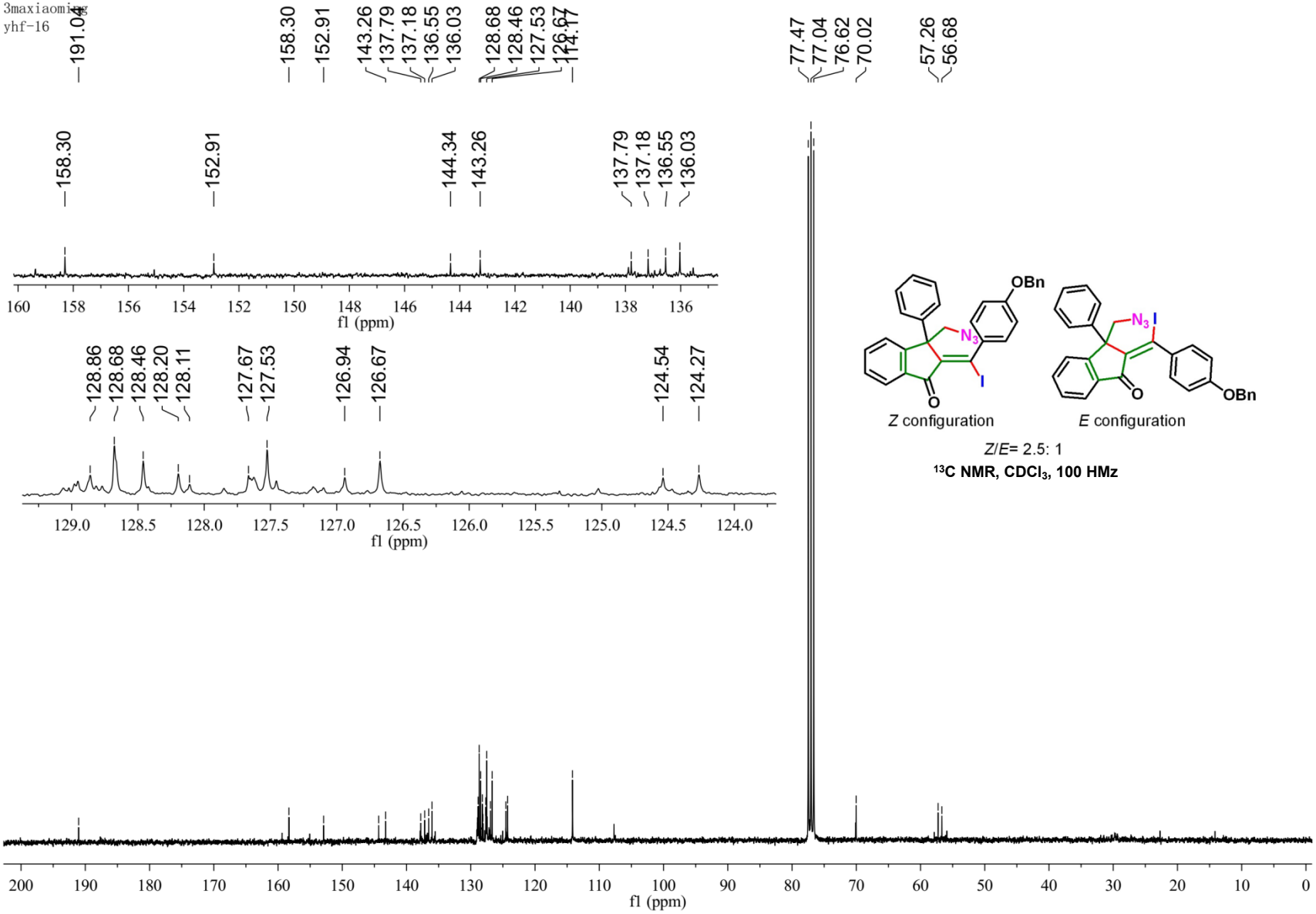
^{1}H NMR Spectrum of Compound 6d



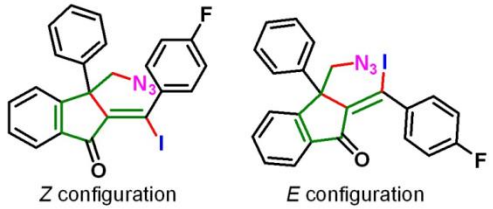
^{13}C NMR Spectrum of Compound 6d



^{1}H NMR Spectrum of Compound 6e



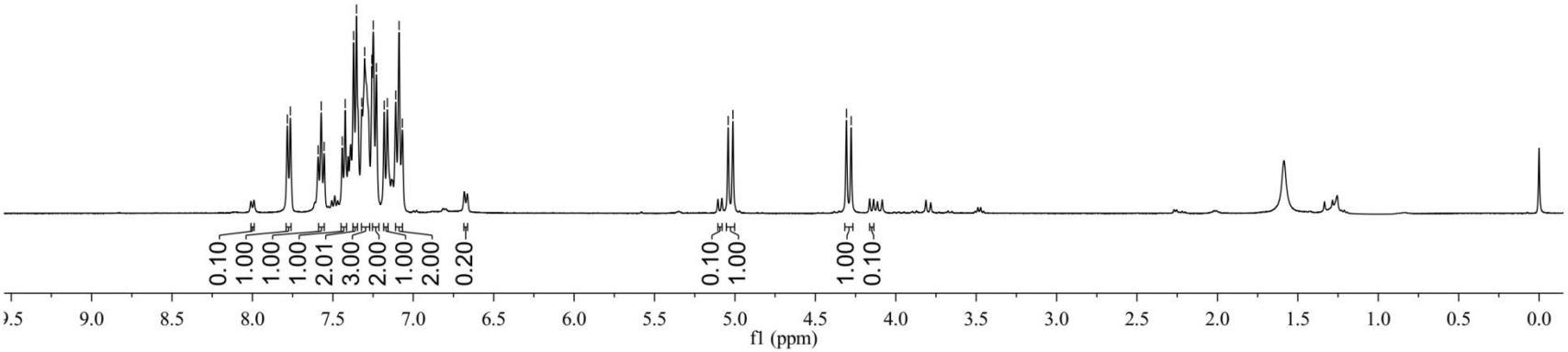
^{13}C NMR Spectrum of Compound 6e



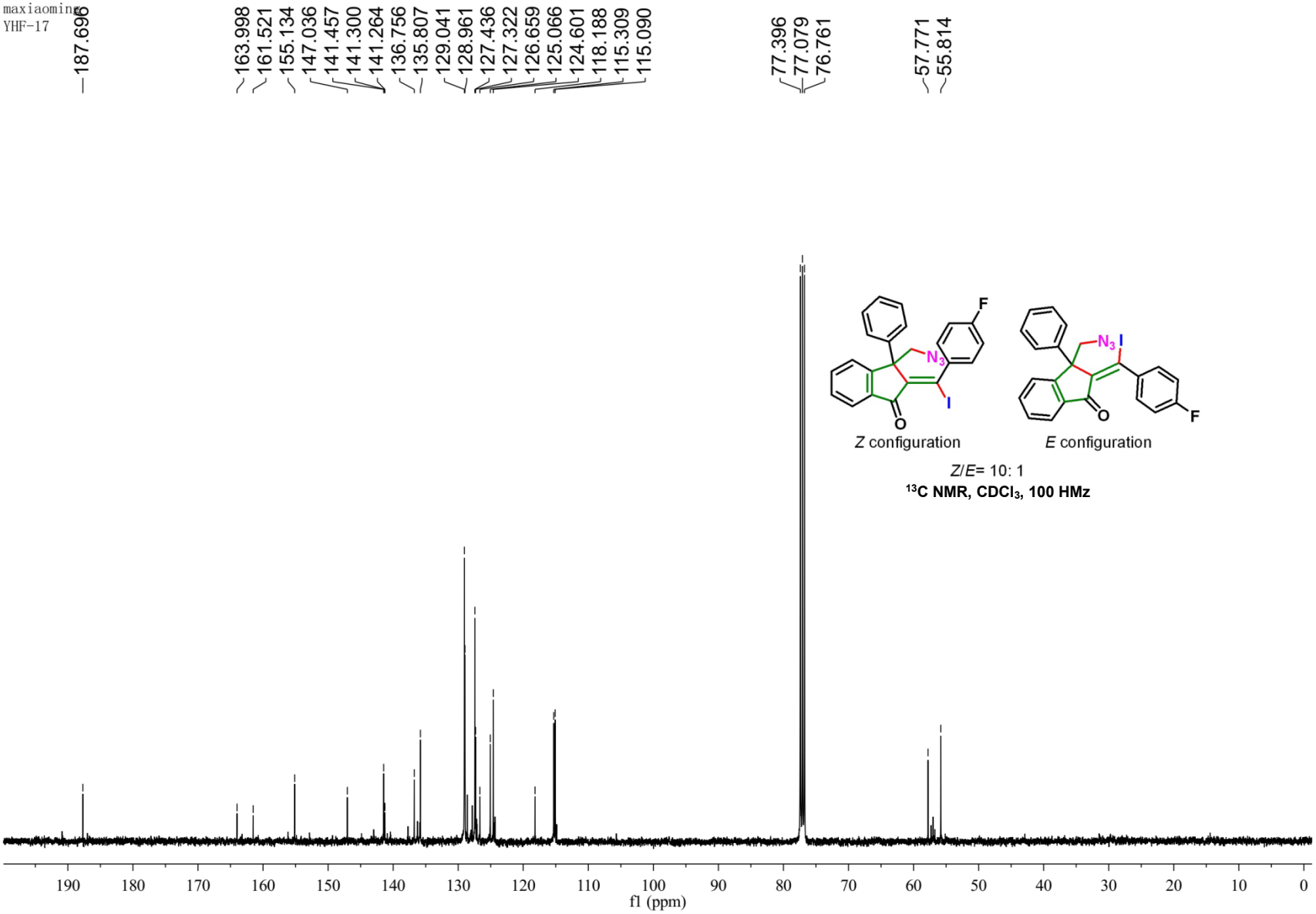
Z configuration *E* configuration

Z/*E*= 10: 1

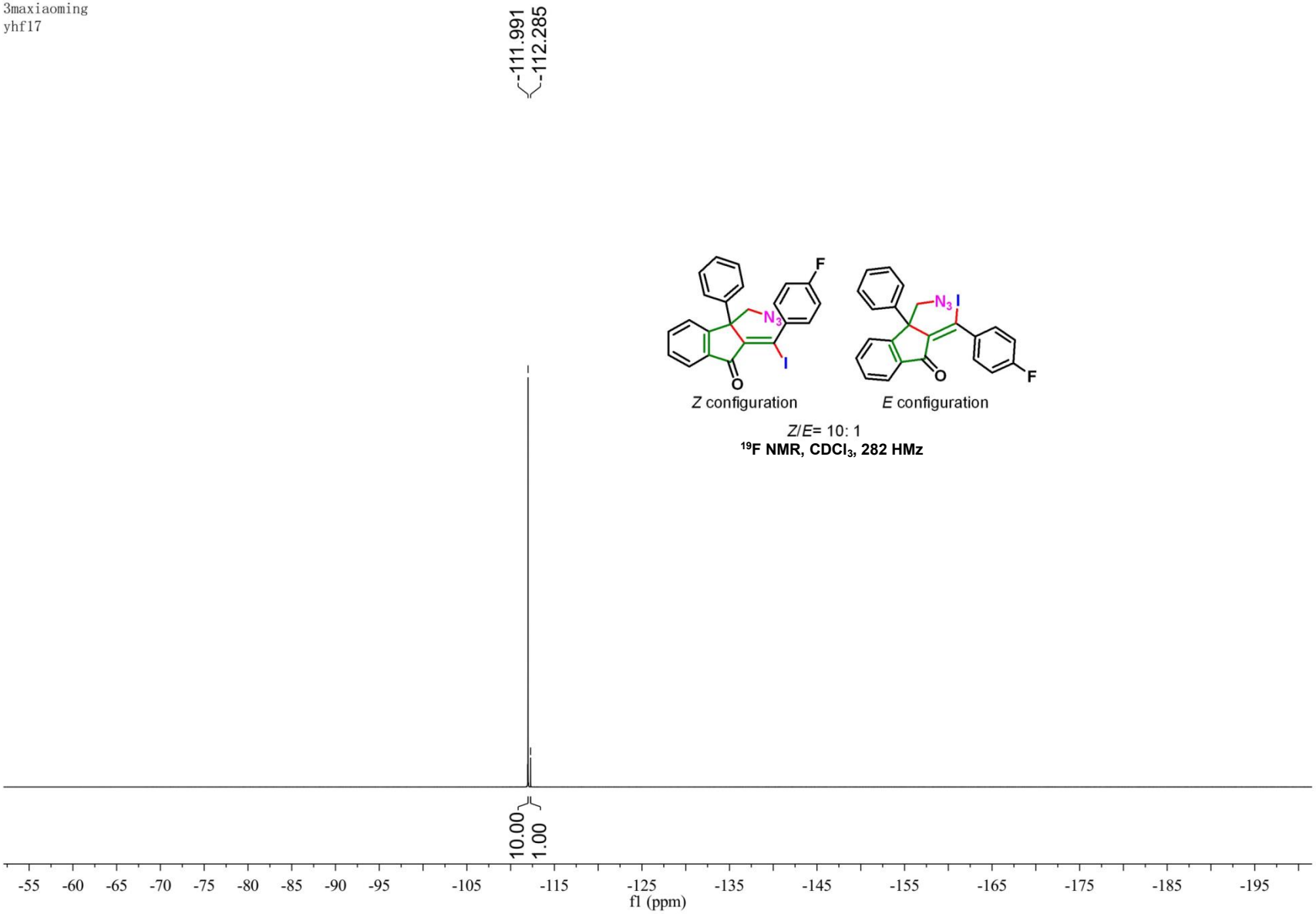
^{1}H NMR, $CDCl_3$, 400 HMz



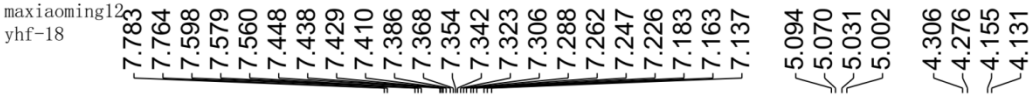
^{1}H NMR Spectrum of Compound 6f

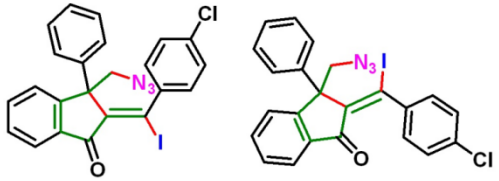


^{13}C NMR Spectrum of Compound 6f



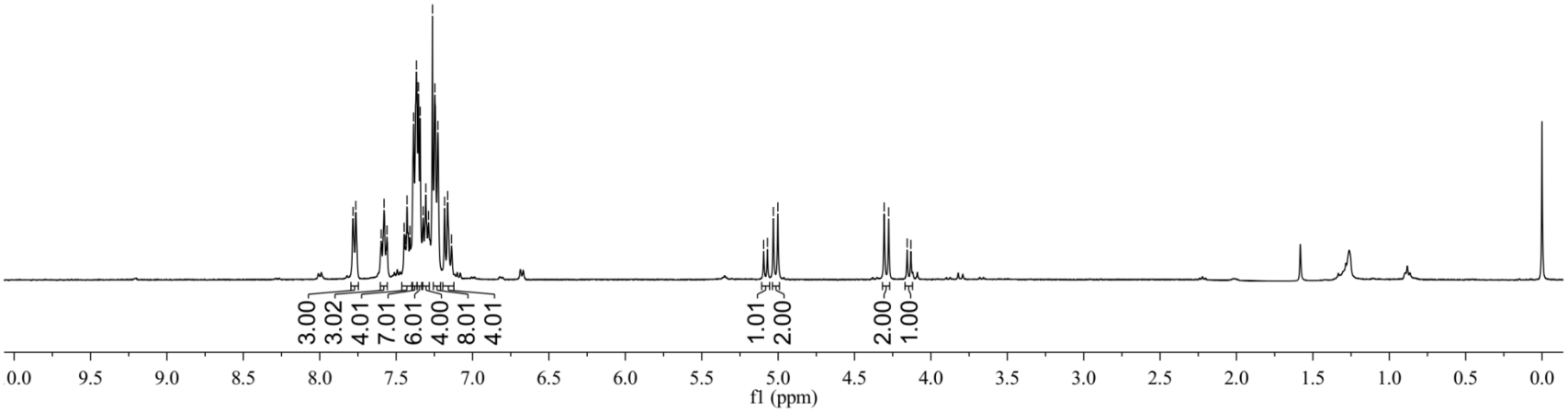
^{19}F NMR Spectrum of Compound 6f



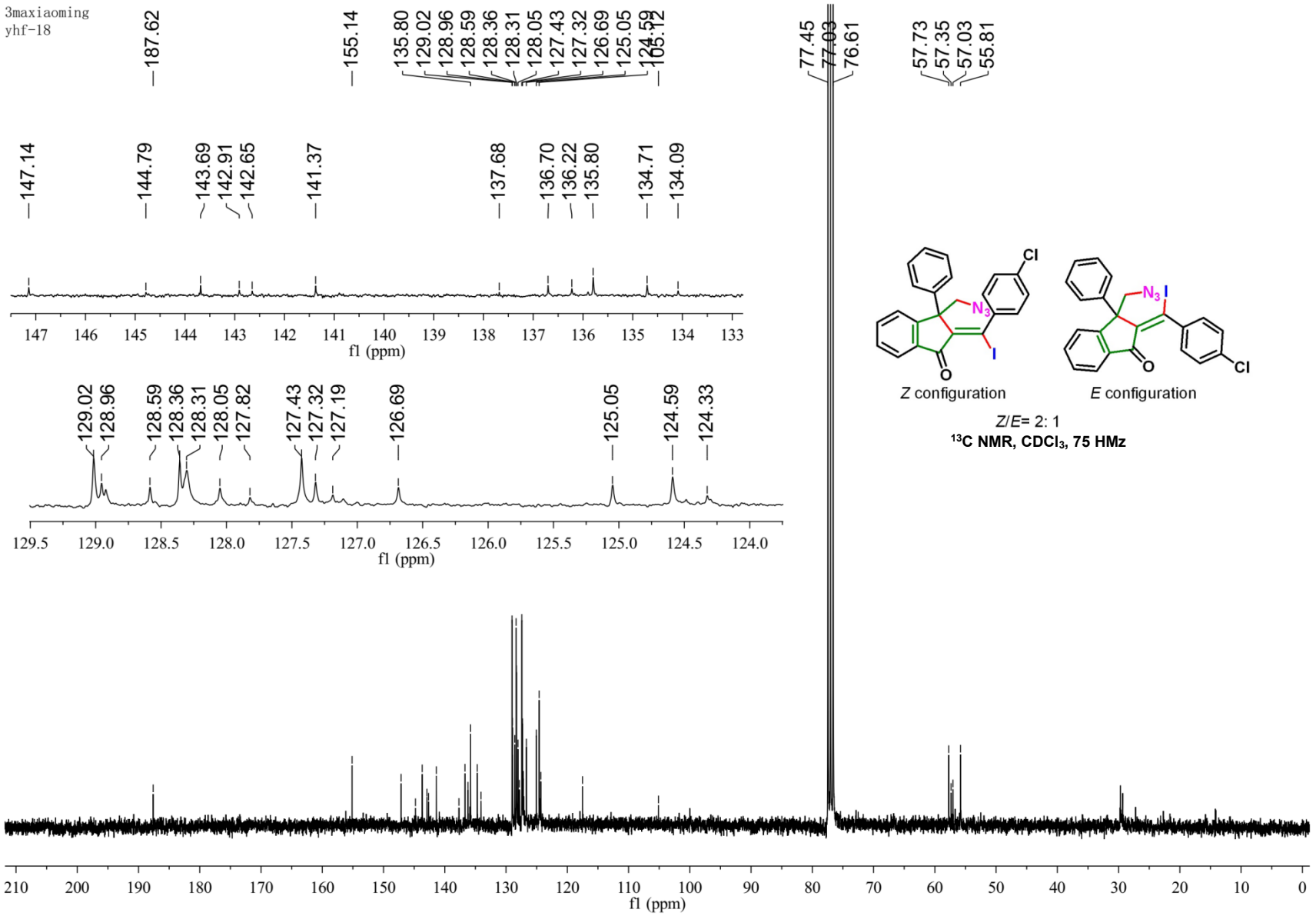


Z/*E*= 2: 1

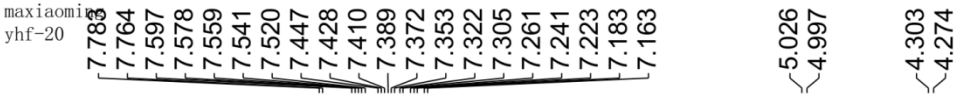
^{1}H NMR, $CDCl_3$, 400 HMz

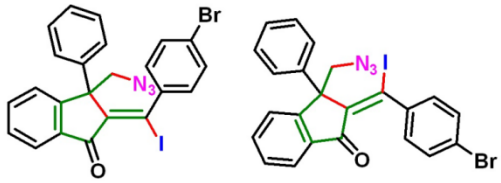


^{1}H NMR Spectrum of Compound 6g



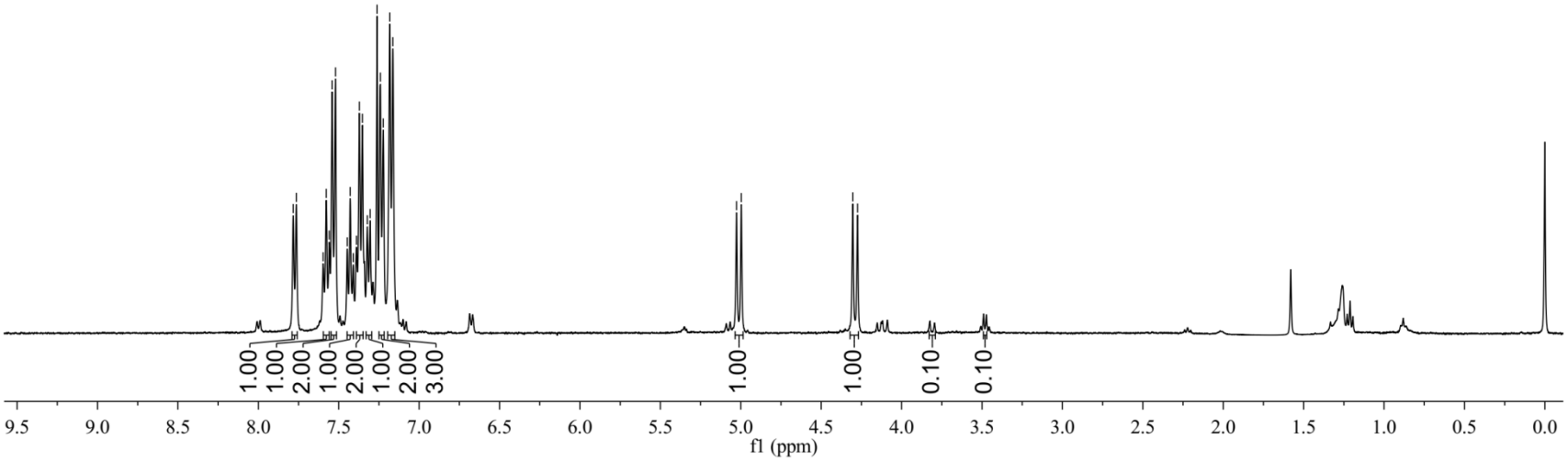
^{13}C NMR Spectrum of Compound 6g



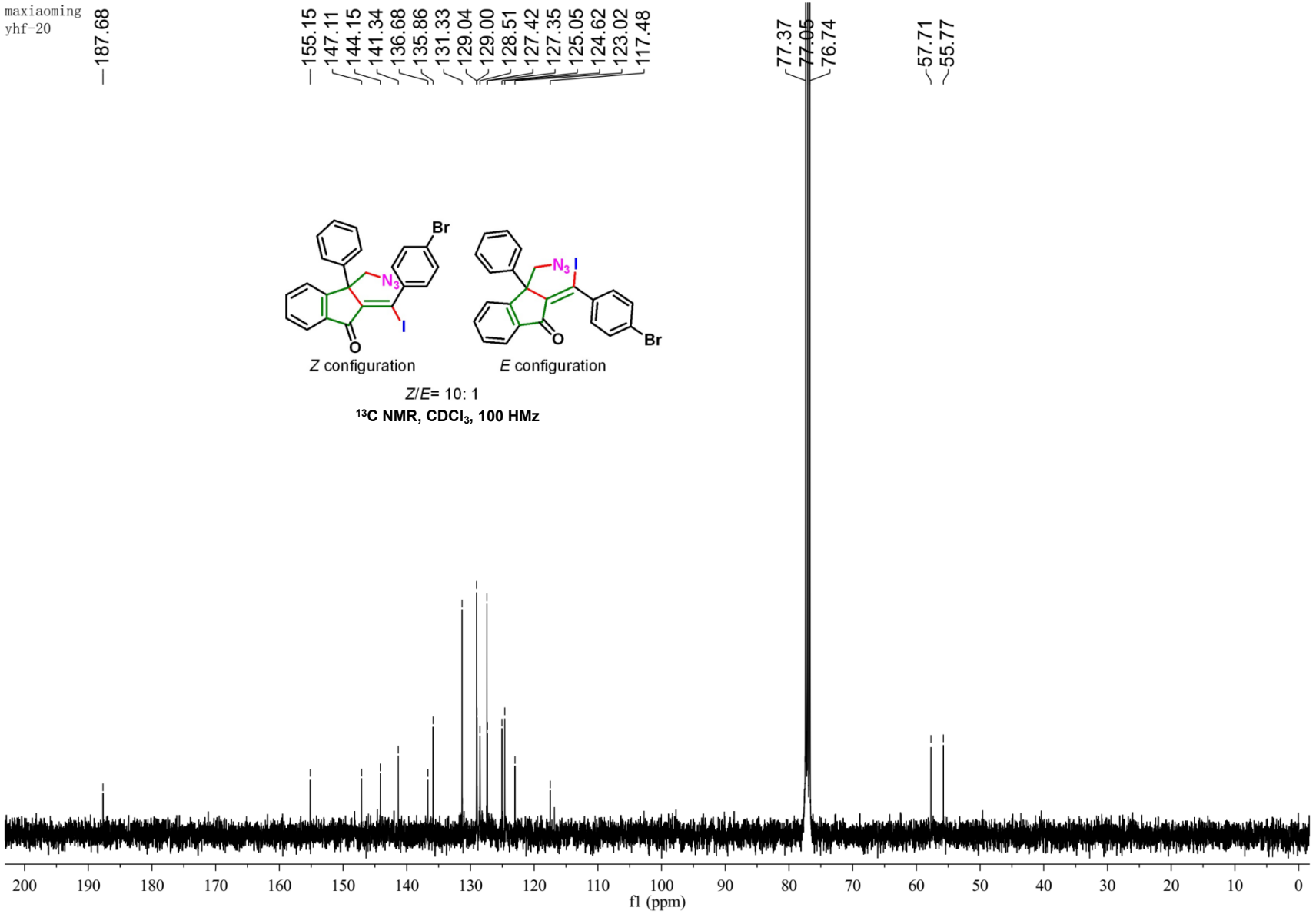


Z/*E*= 10: 1

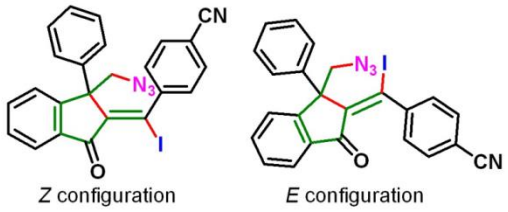
^{1}H NMR, $CDCl_3$, 400 HMz



^{1}H NMR Spectrum of Compound 6h

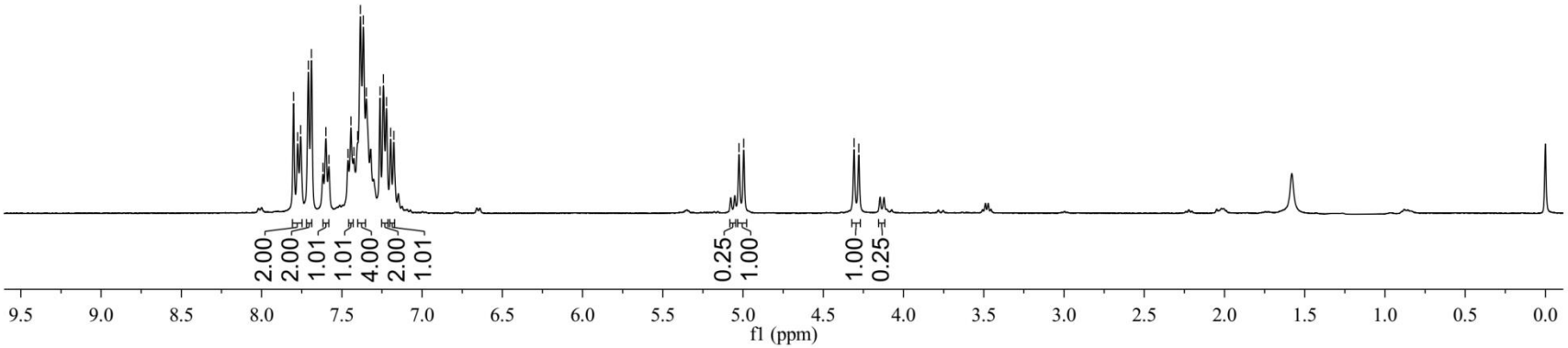


^{13}C NMR Spectrum of Compound 6h

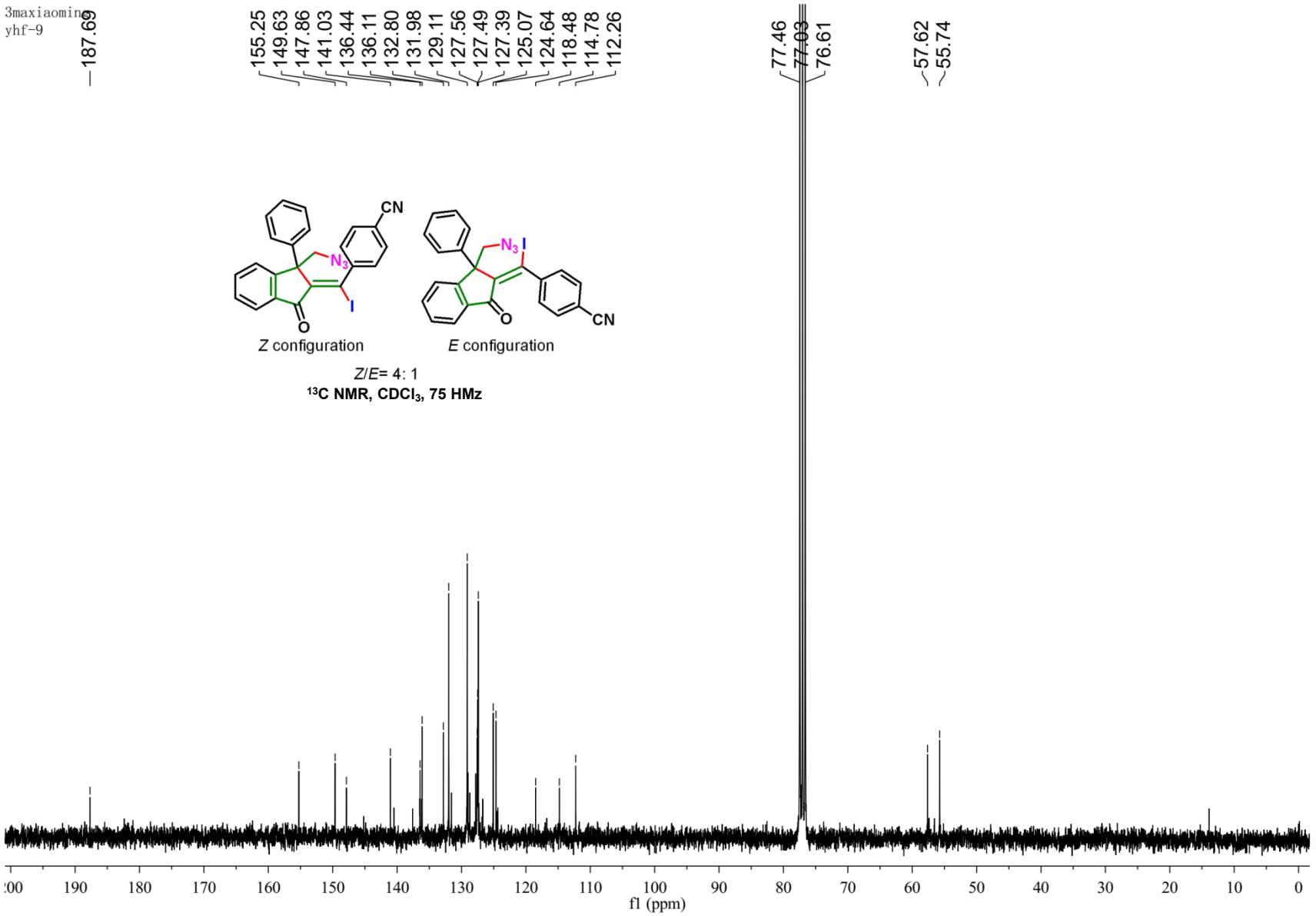


Z/*E*= 4: 1

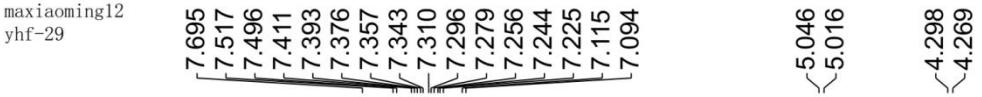
^{1}H NMR, $CDCl_3$, 400 HMz

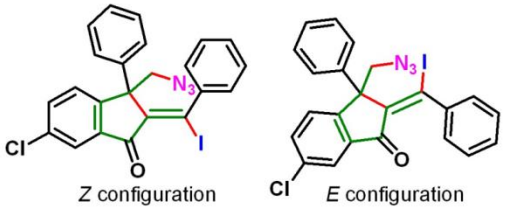


^{1}H NMR Spectrum of Compound 6i



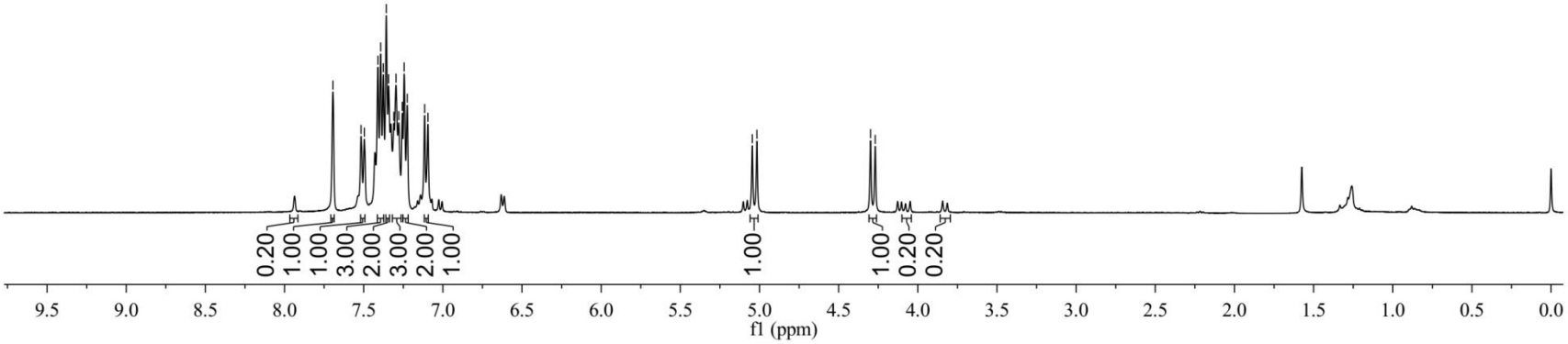
^{13}C NMR Spectrum of Compound 6i



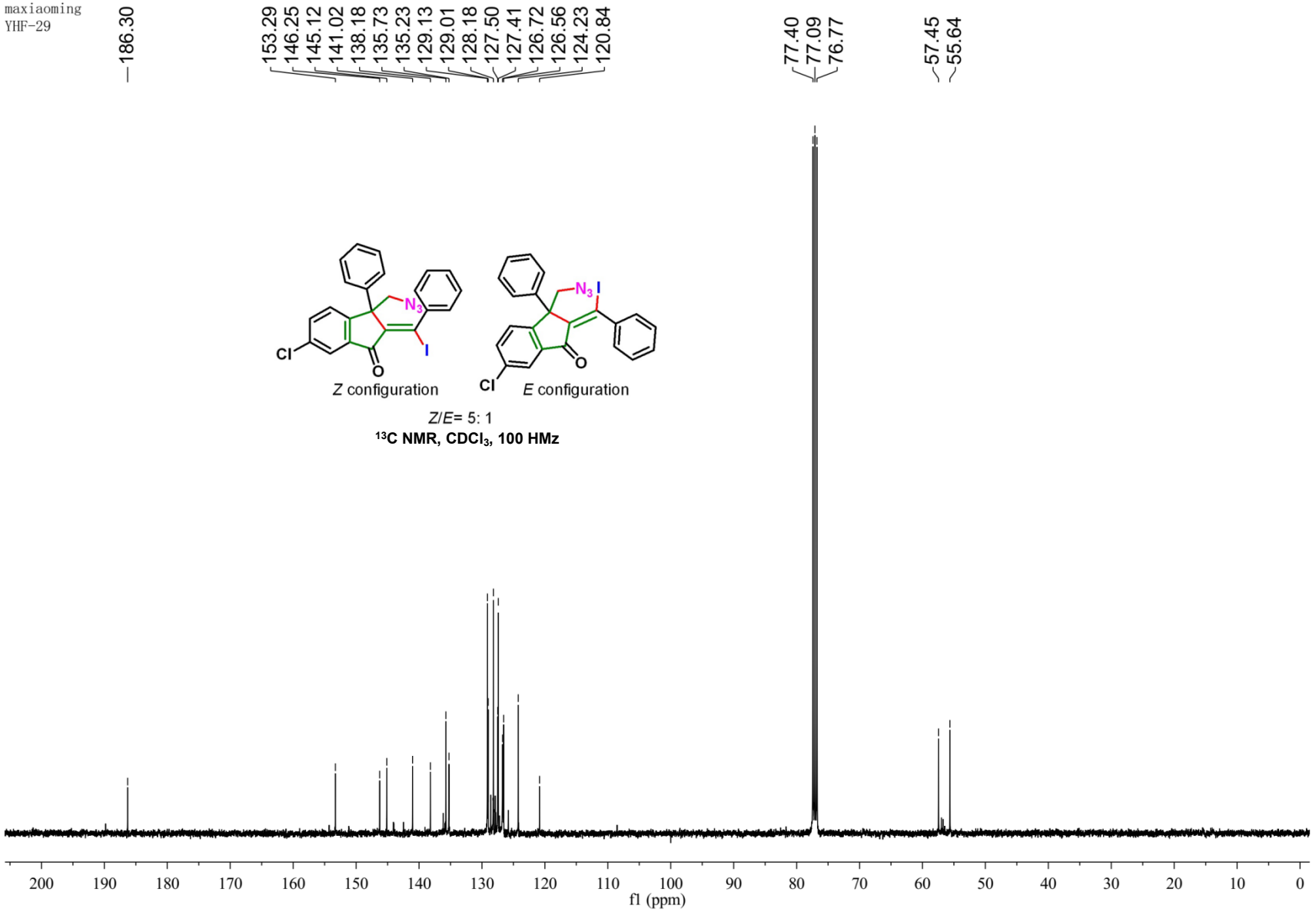


Z/*E*= 5: 1

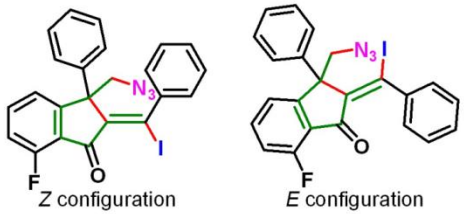
^{1}H NMR, $CDCl_3$, 400 HMz



^{1}H NMR Spectrum of Compound 6j

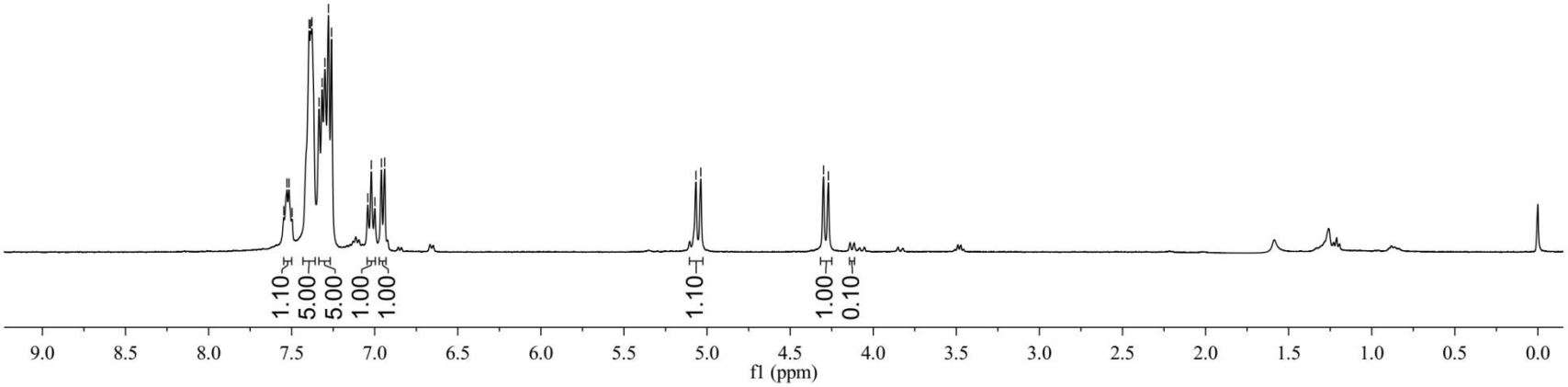


^{13}C NMR Spectrum of Compound 6j

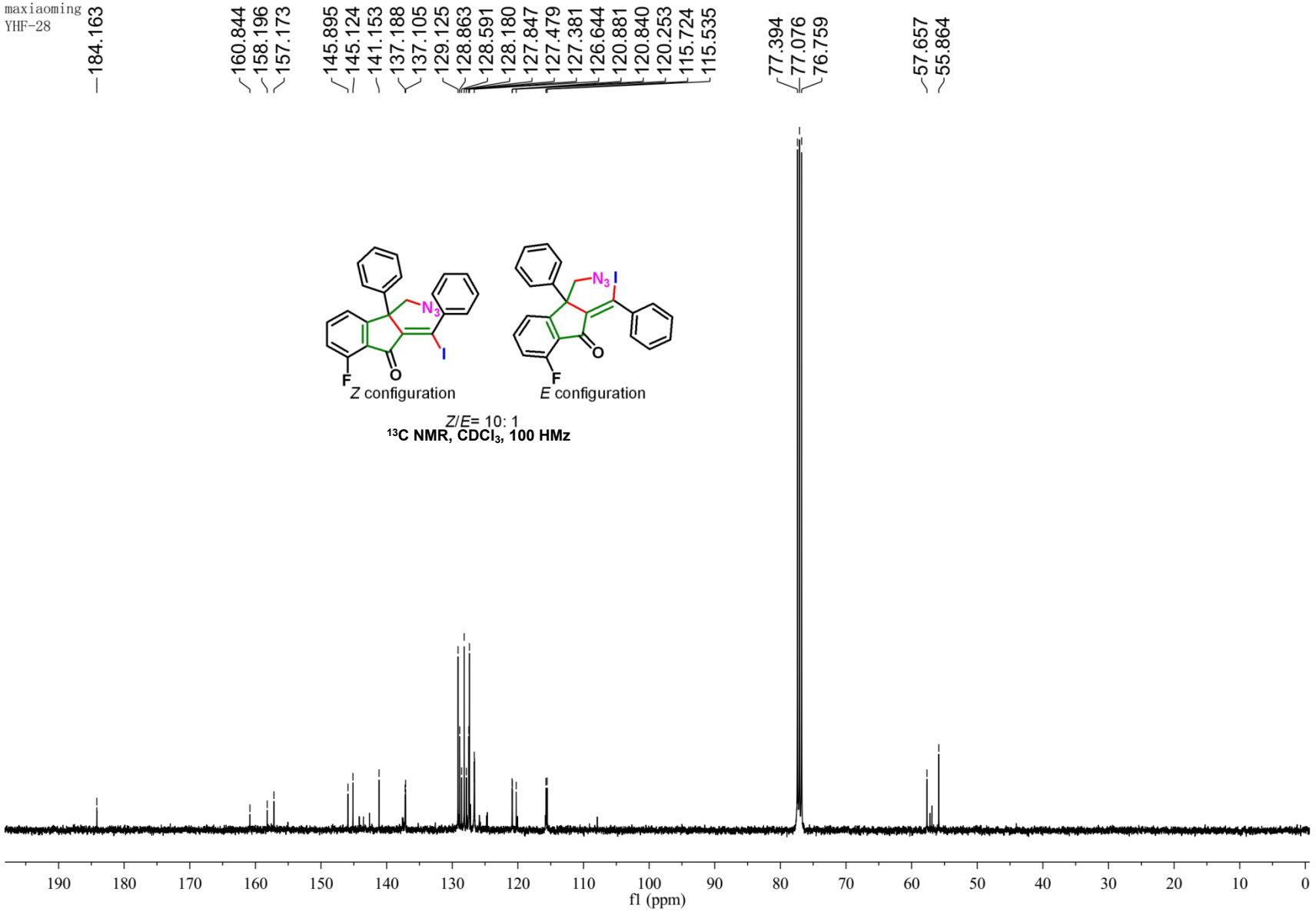


Z/*E*= 10: 1

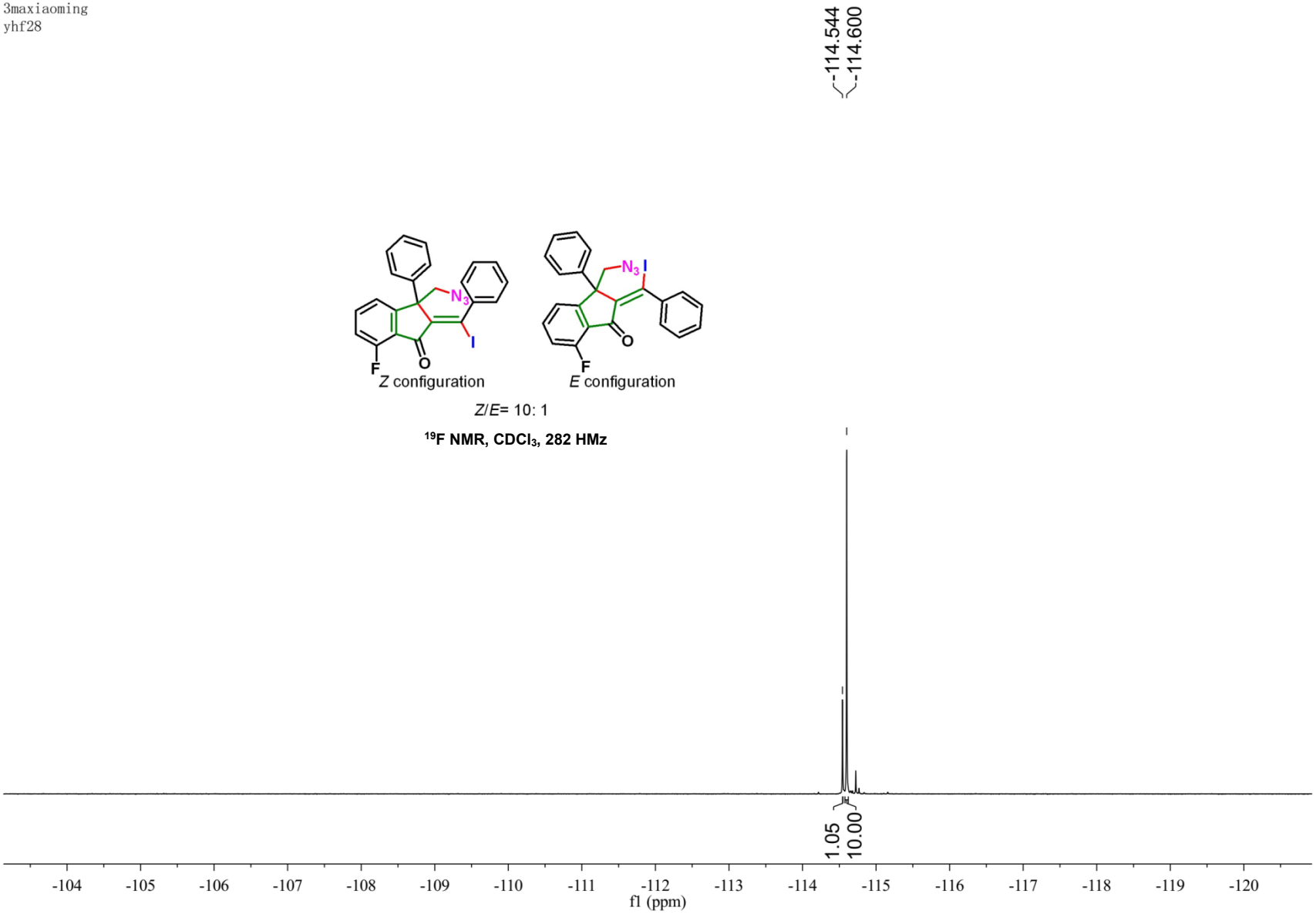
^{1}H NMR, $CDCl_3$, 400 HMz



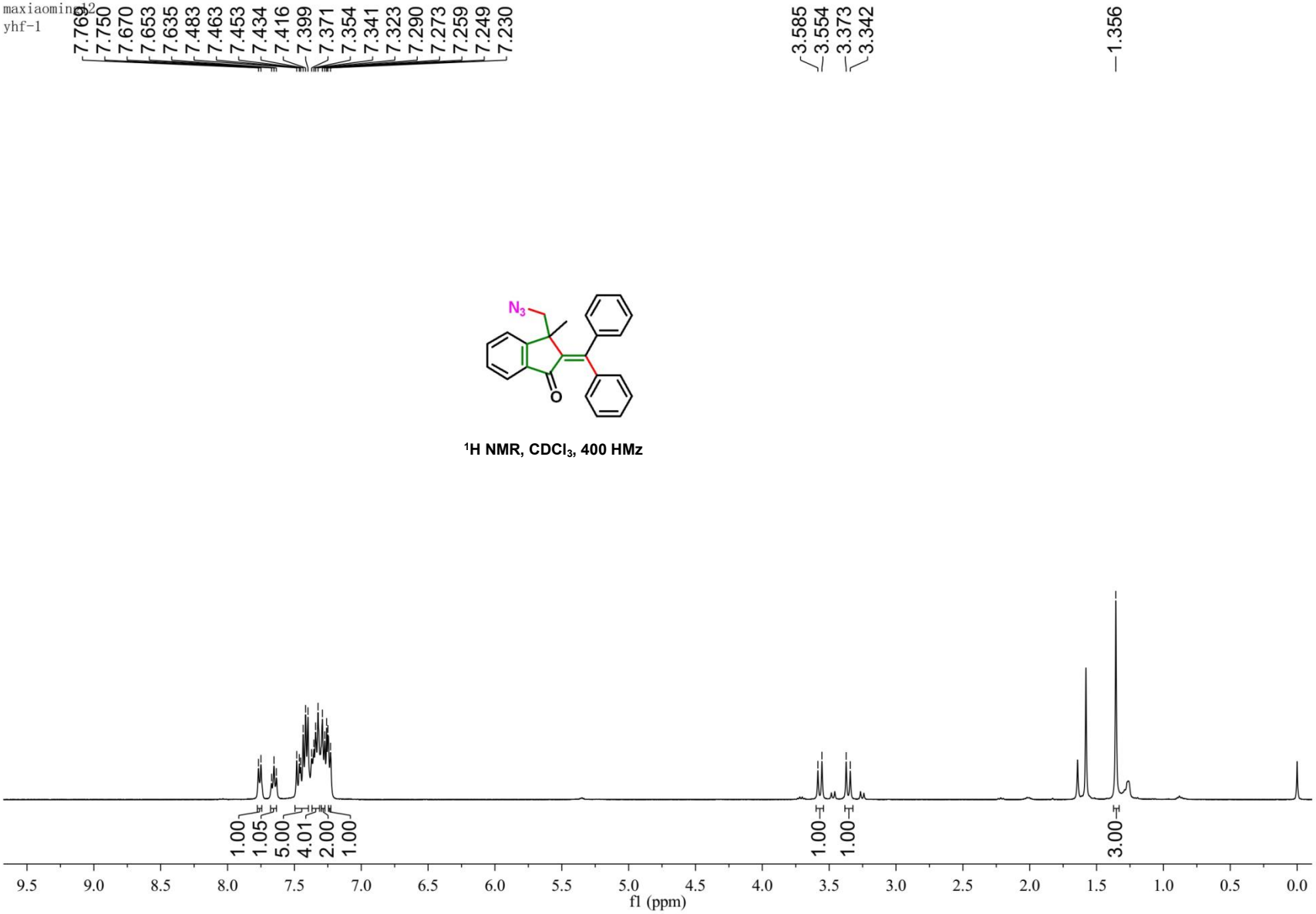
^{1}H NMR Spectrum of Compound 6k



^{13}C NMR Spectrum of Compound 6k

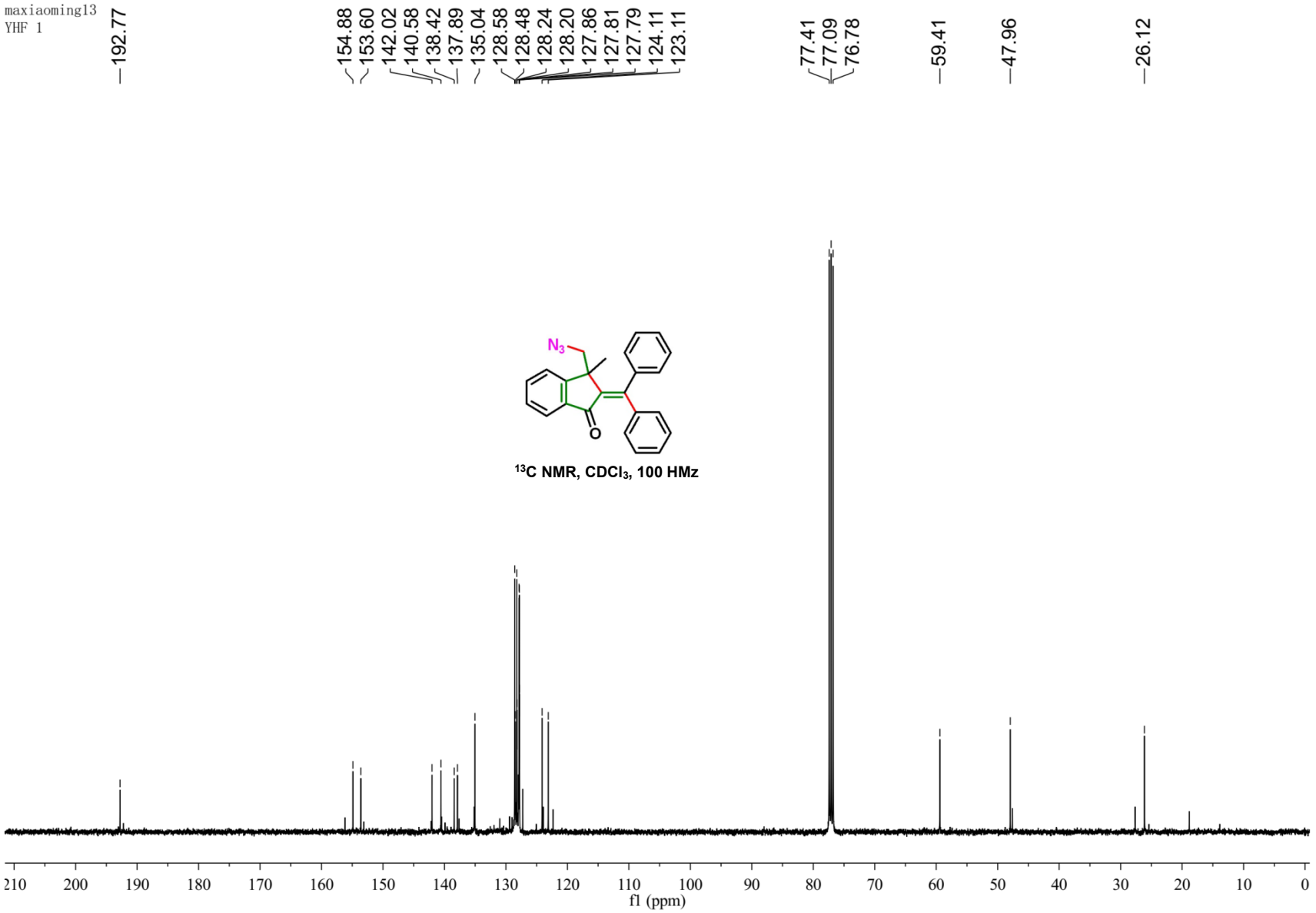


^{19}F NMR Spectrum of Compound 6k



^{1}H NMR, $CDCl_3$, 400 HMz

^{1}H NMR Spectrum of Compound 7



^{13}C NMR Spectrum of Compound 7