

Supporting Information

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

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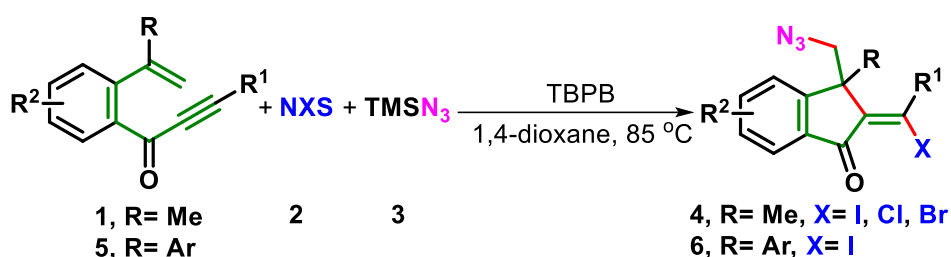
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General Information

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>). ¹H NMR (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. The melting points were measured with digital melting point detector. Enynones **1** and **5** was prepared by the report¹.

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 H₂O (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 MgSO₄, 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**

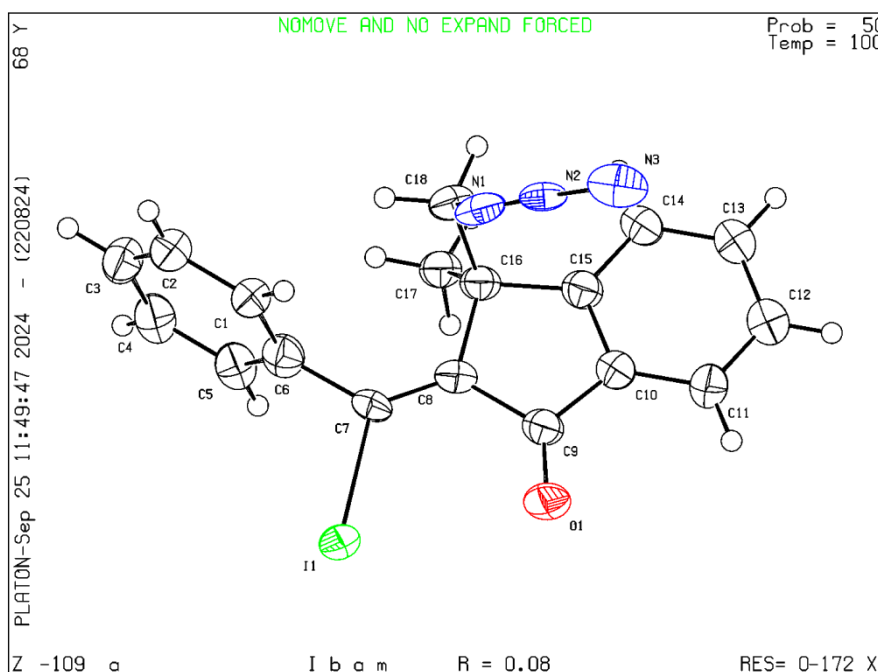


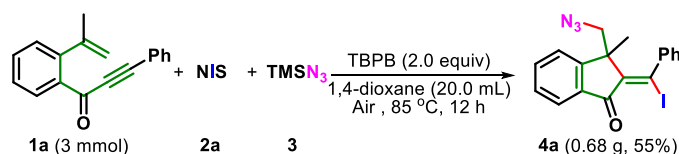
Fig. S1 ORTEP view of X-crystal structure of **4a** (CCDC number 2390559).

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.

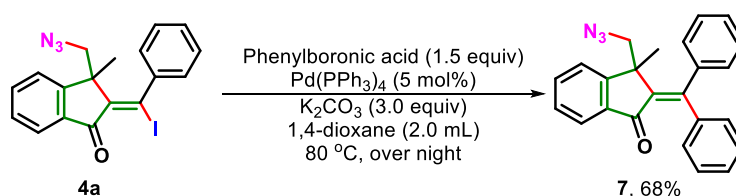
Table S1 Crystal data and structure refinement for 4a.	
Identification code	4a
CCDC	2390559
Empirical formula	C ₁₈ H ₁₄ IN ₃ O
Formula weight	415.22
Temperature/K	100.1(7)
Crystal system	orthorhombic
Space group	Ibam
a/Å	10.5176(3)
b/Å	42.1854(13)
c/Å	7.4578(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3308.95(16)
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 ≤ h ≤ 12, -51 ≤ k ≤ 49, -8 ≤ l ≤ 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



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 H₂O (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 MgSO₄, 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).

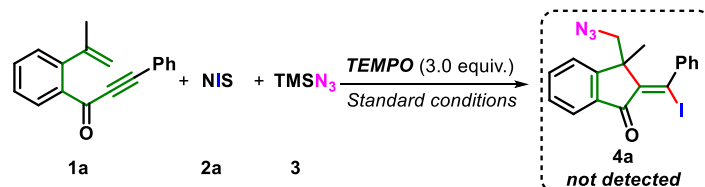
The synthesis of 7



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(PPh₃)₄ (5 mol%), K₂CO₃ (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

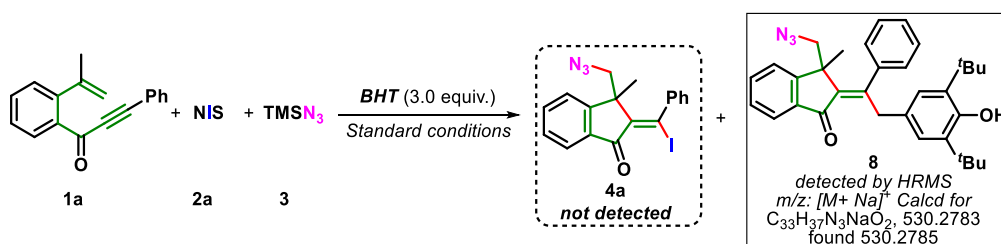
chromatography on silica gel using a PE/EA mixture (60/1 v/v) as the eluent, yielding the target product **7** (49 mg, 68% yield), as a pale yellow solid, mp: 120-121°C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.76 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.48 – 7.40 (m, 5H), 7.37 – 7.32 (m, 4H), 7.28 (d, *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). ¹³C NMR (100 MHz, CDCl₃) (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 C₂₄H₁₉N₃NaO 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**.

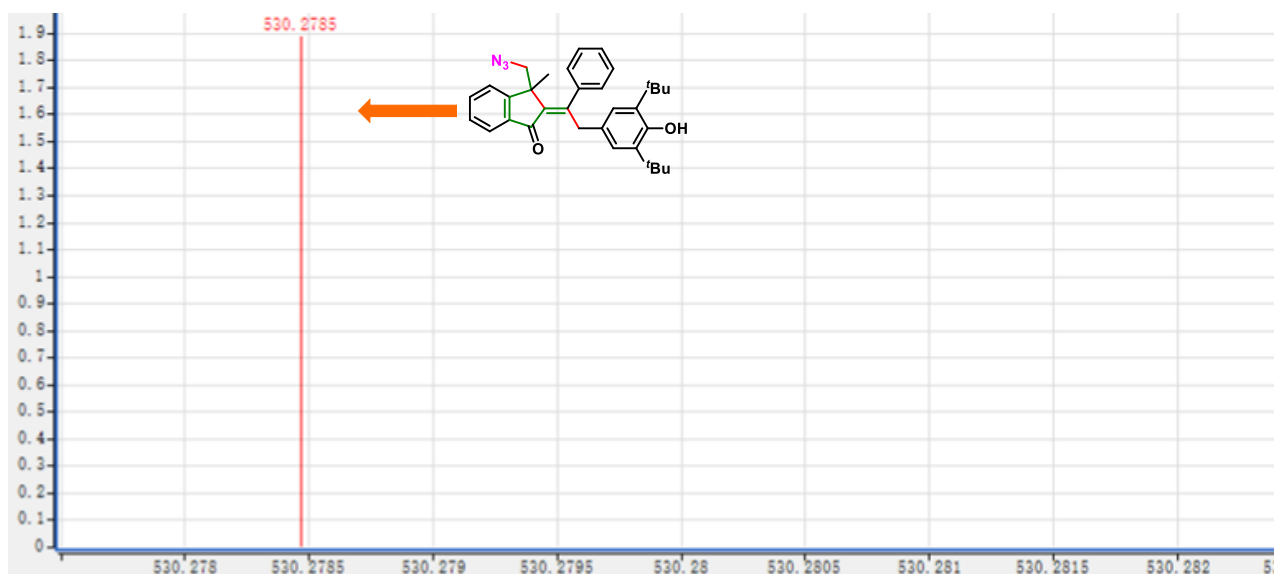
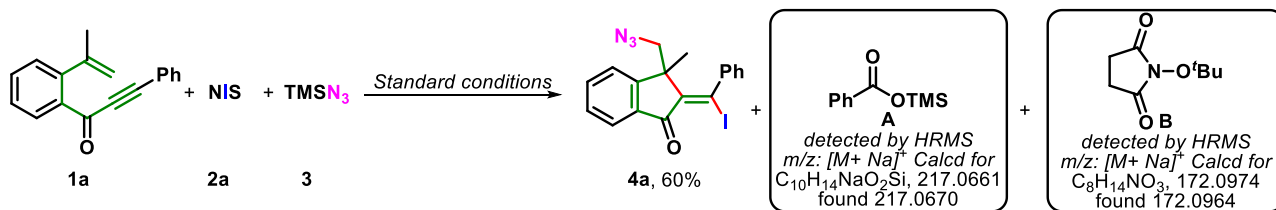


Fig. S2 HRMS analysis for the adduct BHT adduct **8**.

HRMS analysis of reaction solution



To a Schlenk tube (10 ml) were added enynes **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** and 1-(*tert*-butoxy)pyrrolidine-2,5-dione **B**, respectively.

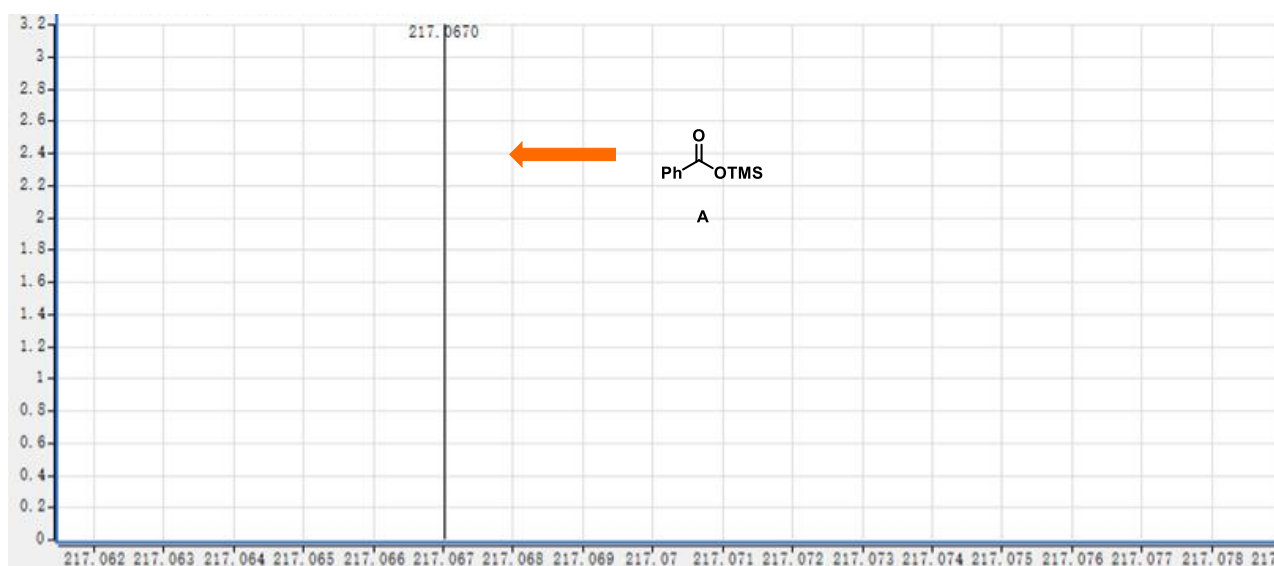


Fig. S3 HRMS analysis for the detection of trimethylsilyl 2-iodobenzoate **A**

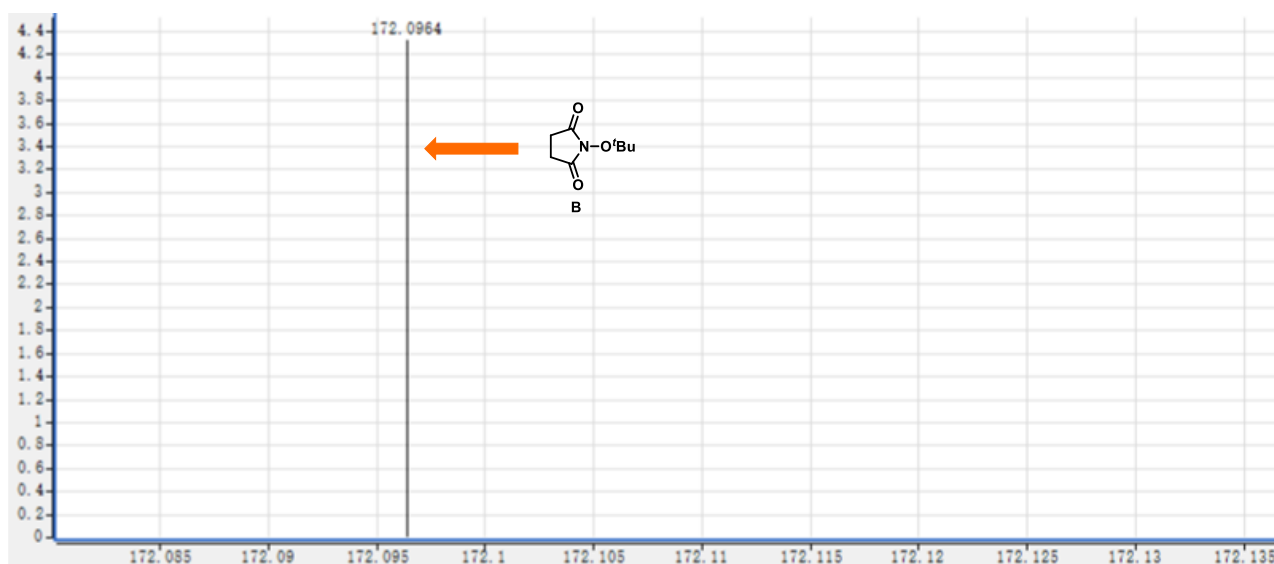


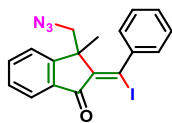
Fig. S4 HRMS analysis for the detection of 1-(*tert*-butoxy)pyrrolidine-2,5-dione **B**

Reference

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

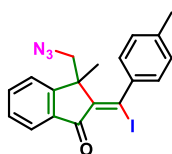
Characterization data

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



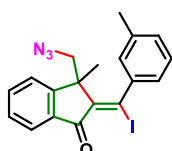
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 50 mg, 60% yield, *Z/E* = 4: 1; mp: 143-144 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 8.14 (d, *J* = 7.6 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.69 – 7.66 (m, 3H), 7.59 – 7.53 (m, 2H), 7.47 – 7.40 (m, 2H), 3.73 (d, *J* = 12.4 Hz, 1H), 3.46 (d, *J* = 12.4 Hz, 1H), 1.46 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) (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 C₁₈H₁₄IN₃NaO 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)



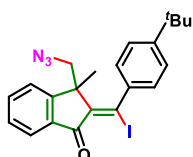
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 41 mg, 48% yield, *Z/E* = 1.5: 1; mp: 169-170 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.93 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.68 (m, 6H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.40 (m, 9H), 7.38 – 7.29 (m, 7H), 7.16 – 7.12 (m, 5H), 7.09– 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). ¹³C NMR (75 MHz, CDCl₃) (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 C₁₉H₁₆IN₃NaO 452.0231; Found 452.0236.

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



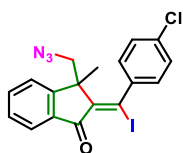
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 39 mg, 45% yield, *Z/E* = 4: 1; mp: 111-112 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.93 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.50 – 7.45 (m, 2H), 7.20 – 7.15 (m, 3H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.28 (d, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 1.26 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) (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 C₁₉H₁₆IN₃NaO 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)



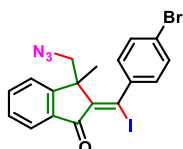
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 58 mg, 62% yield, *Z/E* = 5: 1; mp: 151-152 °C; ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.93 (d, *J* = 7.6 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.48 – 7.45 (m, 4H), 7.23 – 7.17 (m, 2H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 1.36 (s, 9H), 1.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (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 C₂₂H₂₂IN₃NaO 494.0700; Found 494.0707.

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



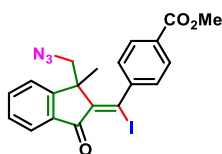
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 52 mg, 58% yield, $Z/E = 5:1$; mp: 155-156 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.94 (d, $J = 7.6$ Hz, 1H), 7.73 – 7.70 (m, 1H), 7.52 – 7.44 (m, 4H), 7.21 (d, $J = 8.4$ Hz, 2H), 3.55 (d, $J = 12.4$ Hz, 1H), 3.24 (d, $J = 12.4$ Hz, 1H), 1.26 (s, 3H). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{13}\text{ClIN}_3\text{NaO}$ 471.9685; Found 471.9691.

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



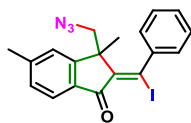
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 59 mg, 60% yield, $Z/E = 10:1$; mp: 164-165 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.94 (d, $J = 7.6$ Hz, 1H), 7.73 – 7.70 (m, 1H), 7.60 (s, 2H), 7.50 – 7.46 (m, 2H), 7.20 – 7.08 (m, 2H), 3.55 (d, $J = 12.4$ Hz, 1H), 3.24 (d, $J = 12.4$ Hz, 1H), 1.27 (s, 3H). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{13}\text{BrIN}_3\text{NaO}$ 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)



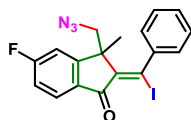
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 67 mg, 71% yield, $Z/E = 1:1$; mp: 134-135 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 8.13 – 8.08 (m, 4H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.73 – 7.70 (m, 3H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 8.0$ 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). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{16}\text{IN}_3\text{NaO}_3$ 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; $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{16}\text{IN}_3\text{NaO}$ 452.0231; Found 452.0233.

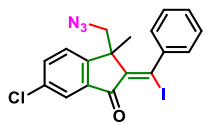
(Z)-3-(azidomethyl)-5-fluoro-2-(iodo(phenyl)methylene)-3-methyl-2,3-dihydro-1H-inden-1-one (4i, major)



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; $^1\text{H NMR}$ (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),

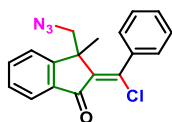
7.12 (d, $J = 8.4$ Hz, 1H), 3.48 (d, $J = 12.4$ Hz, 1H), 3.27 (d, $J = 12.0$ Hz, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 188.7, 167.6 ($^1J_{\text{CF}} = 255.9$ Hz), 155.8 ($^3J_{\text{CF}} = 9.2$ Hz), 144.8, 142.0, 133.7, 129.0, 127.4, 127.3, 117.3 ($^2J_{\text{CF}} = 23.5$ Hz), 109.8, 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{13}\text{FIN}_3\text{NaO}$ 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)



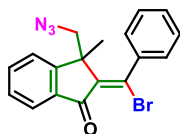
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 42 mg, 47% yield, $Z/E = 10:1$; mp: 151-152 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.87 (d, $J = 1.2$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.25 (m, 2H), 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{13}\text{ClIN}_3\text{NaO}$ 471.9685; Found 471.9694.

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



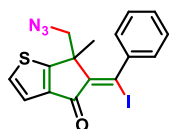
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 19 mg, 30% yield, $Z/E > 19:1$; mp: 148-149 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.12 – 8.10 (m, 2H), 7.70 – 7.64 (m, 2H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.46 (s, 3H), 7.40 – 7.37 (m, 1H), 4.26 (d, $J = 15.2$ Hz, 2H), 1.70 (s, 3H). ^{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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{14}\text{ClN}_3\text{NaO}$ 346.0718; Found 346.0727.

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



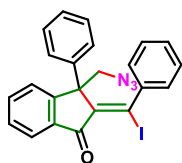
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 26 mg, 36% yield, $Z/E = 10:1$; mp: 134-136 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.72 – 7.69 (m, 2H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.47 – 7.42 (m, 4H), 7.38 (d, $J = 7.6$ Hz, 2H), 4.70 (d, $J = 10.4$ Hz, 1H), 3.83 (d, $J = 10.4$ 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{14}\text{BrN}_3\text{NaO}$ 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)



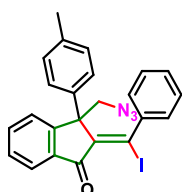
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 27 mg, 32% yield, $Z/E = 1:1$; mp: 134-136 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.91 – 7.88 (m, 2H), 7.49 – 7.44 (m, 2H), 7.41 – 7.30 (m, 4H), 7.27 (s, 1H), 7.26 – 7.19 (m, 3H), 7.15 (d, $J = 4.8$ Hz, 1H), 7.06 (d, $J = 4.8$ Hz, 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{12}\text{IN}_3\text{NaOS}$ 443.9638; Found 443.9640.

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



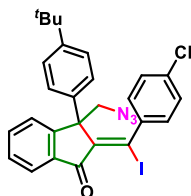
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 48 mg, 50% yield, $Z/E = 5:1$; mp: 130-131 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.77 (d, $J = 7.6$ Hz, 1H), 7.59 – 7.54 (m, 2H), 7.41 (d, $J = 7.6$ Hz, 3H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.33 – 7.31 (m, 3H), 7.18 (d, $J = 8.0$ 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). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{16}\text{IN}_3\text{NaO}$ 500.0231; Found 500.0239.

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



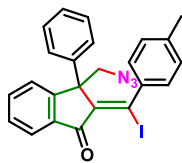
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 46 mg, 47% yield, $Z/E = 5:1$; mp: 183-184 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.75 (d, $J = 7.2$ Hz, 1H), 7.58 – 7.56 (m, 1H), 7.42 – 7.39 (m, 4H), 7.34 – 7.33 (m, 1H), 7.30 (d, $J = 7.6$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 4H), 5.02 (d, $J = 11.6$ Hz, 1H), 4.27 (d, $J = 11.6$ Hz, 1H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{18}\text{IN}_3\text{NaO}$ 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; $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{23}\text{ClIN}_3\text{NaO}$ 590.0467; Found 590.0476.

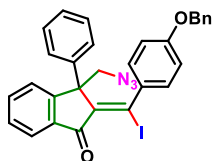
(Z)-3-(azidomethyl)-2-(iodo(p-tolyl)methylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (syn isomer, 6d)



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; $^1\text{H NMR}$ (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, $J = 11.6$

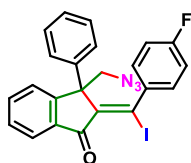
Hz, 1H), 3.81 (d, $J = 12.0$ Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 191.0, 187.6, 155.1, 153.0, 146.3, 144.0, 143.2, 142.6, 141.7, 141.6, 138.9, 138.1, 137.8, 136.9, 136.0, 135.5, 129.0, 128.8(4), 128.8(1), 128.8(9), 128.5, 128.4, 127.5, 127.2, 126.9, 126.8, 126.7, 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{18}\text{IN}_3\text{NaO}$ 514.0387; Found 514.0396.

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



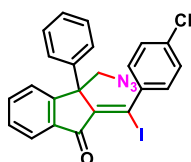
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 78 mg, 67% yield, $Z/E = 2.5$: 1; mp: 144-145 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.02 (d, $J = 7.6$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.43 (m, 6H), 7.42 – 7.36 (m, 4H), 7.13 – 7.10 (m, 3H), 7.03 (d, $J = 8.8$ Hz, 1H), 6.69 (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{22}\text{IN}_3\text{NaO}_2$ 606.0649; Found 606.0651.

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



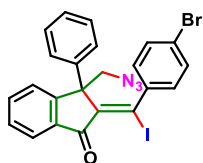
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 62 mg, 63% yield, $Z/E = 10$: 1; mp: 133-134 °C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.77 (d, $J = 7.6$ Hz, 1H), 7.59 – 7.55 (m, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 7.2$ Hz, 2H), 7.31 (d, $J = 7.2$ Hz, 3H), 7.24 (d, $J = 8.0$ 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 ($^1J_{\text{CF}} = 247.7$ Hz), 155.1, 147.0, 141.5, 141.3 ($^3J_{\text{CF}} = 3.6$ 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 ($^2J_{\text{CF}} = 21.9$ Hz), 57.8, 55.8. ^{19}F NMR (282 MHz, CDCl_3) δ ppm: -111.99. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{FIN}_3\text{NaO}$ 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; ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{ClIN}_3\text{NaO}$ 533.9841; Found 533.9845.

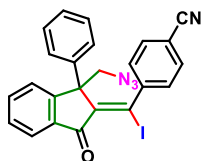
(Z)-3-(azidomethyl)-2-((4-bromophenyl)iodomethylene)-3-phenyl-2,3-dihydro-1H-inden-1-one (6h, major)



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; ^1H 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

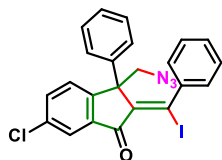
– 7.41 (m, 1H), 7.39 – 7.35 (m, 2H), 7.31 (d, $J = 6.8$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 3H), 5.01 (d, $J = 11.6$ Hz, 1H), 4.29 (d, $J = 11.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 187.7, 155.2, 147.1, 144.2, 141.3, 136.7, 135.9, 131.3, 129.0(4), 129.0(0), 128.5, 127.4, 127.4, 125.1, 124.6, 123.0, 117.5, 57.7, 55.8. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{BrIN}_3\text{NaO}$ 577.9336; Found 577.9340.

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



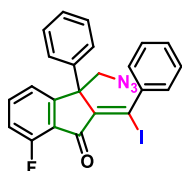
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 72 mg, 72% yield, $Z/E = 4:1$; mp: 145-146°C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.80 – 7.76 (m, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.62 – 7.58 (m, 1H), 7.46 – 7.43 (m, 1H), 7.40 – 7.35 (m, 4H), 7.23 (d, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 8.0$ 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{15}\text{IN}_4\text{NaO}$ 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; ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{ClIN}_3\text{NaO}$ 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)



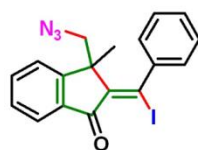
Isolation by column chromatography (PE/EA= 60/1 v/v) Pale yellow solid; 51 mg, 52% yield, $Z/E = 10:1$; mp: 165-166°C; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.55 – 7.50 (m, 1H), 7.40 – 7.38 (m, 5H), 7.34 – 7.28 (m, 5H), 7.04 – 7.00 (m, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 5.05 (d, $J = 11.6$ Hz, 1H), 4.28 (d, $J = 11.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 184.2, 159.5 ($^1J_{\text{CF}} = 247.7$ Hz), 157.2, 145.9, 145.1, 141.2, 137.1 ($^3J_{\text{CF}} = 8.3$ Hz), 129.1, 128.9, 128.6, 128.2, 127.9, 127.5, 127.4, 126.6, 120.9 ($^4J_{\text{CF}} = 4.1$ Hz), 120.3, 115.6 ($^2J_{\text{CF}} = 18.9$ Hz), 57.7, 55.9. ^{19}F NMR (282 MHz, CDCl_3) δ ppm: -114.54. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{15}\text{FIN}_3\text{NaO}$ 518.0137; Found 518.0143.

maxiaoming16
yhf-1

8.147
8.128
7.919
7.901
7.882
7.688
7.677
7.659
7.589
7.560
7.543
7.525
7.469
7.445
7.400

3.741
3.710
3.476
3.445

1.459



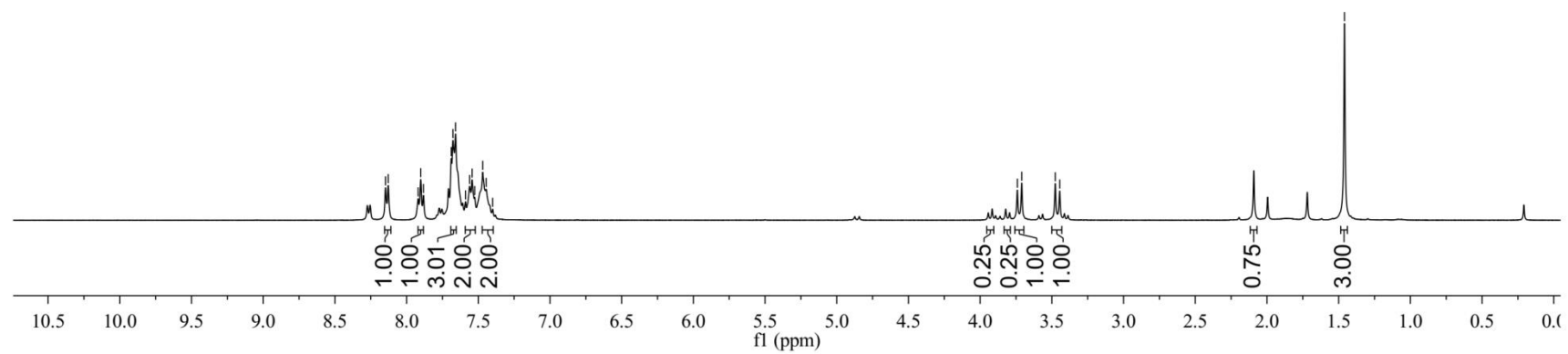
Z configuration



E configuration

Z/E= 4: 1

¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4a

YHF-1

—190.29

—152.75
—144.93
—142.27
—137.24
—135.73
—130.23
—128.79
—128.56
—124.72
—122.58

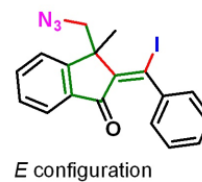
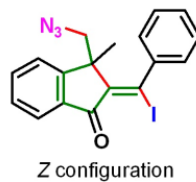
—105.84

{ 77.25
—77.04
76.83 }

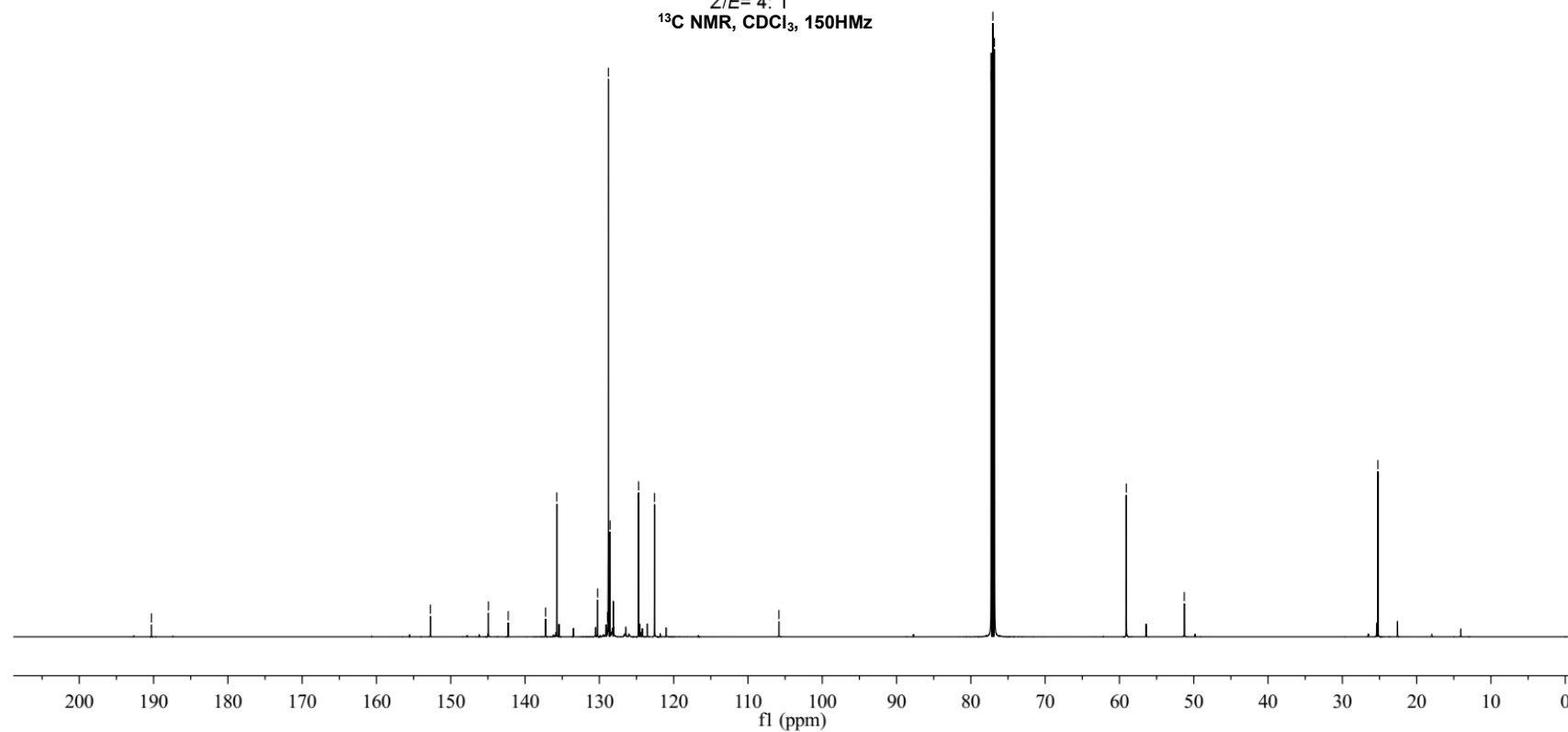
—59.08

—51.28

—25.21

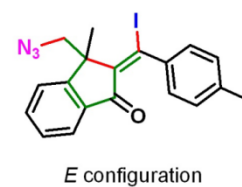
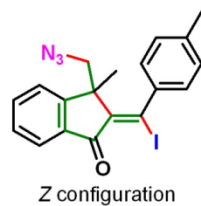
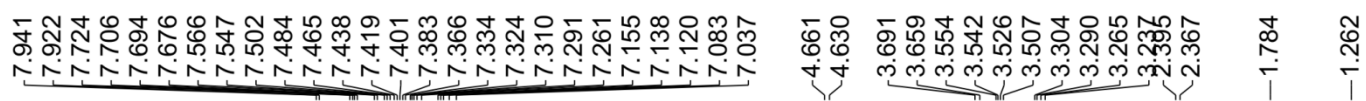


Z/E= 4: 1
¹³C NMR, CDCl₃, 150MHz

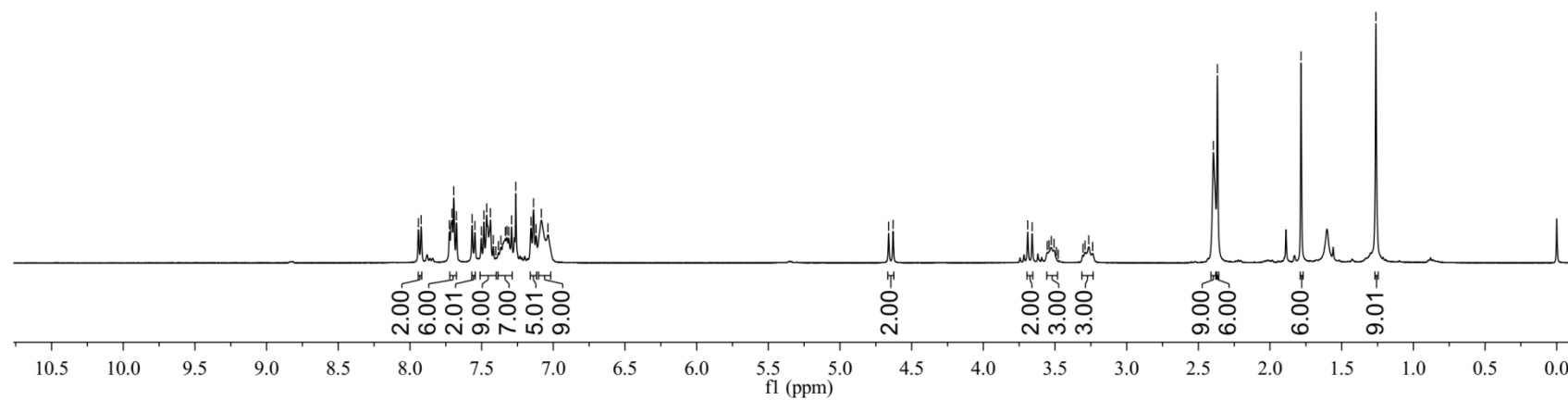


¹³C NMR Spectrum of Compound 4a

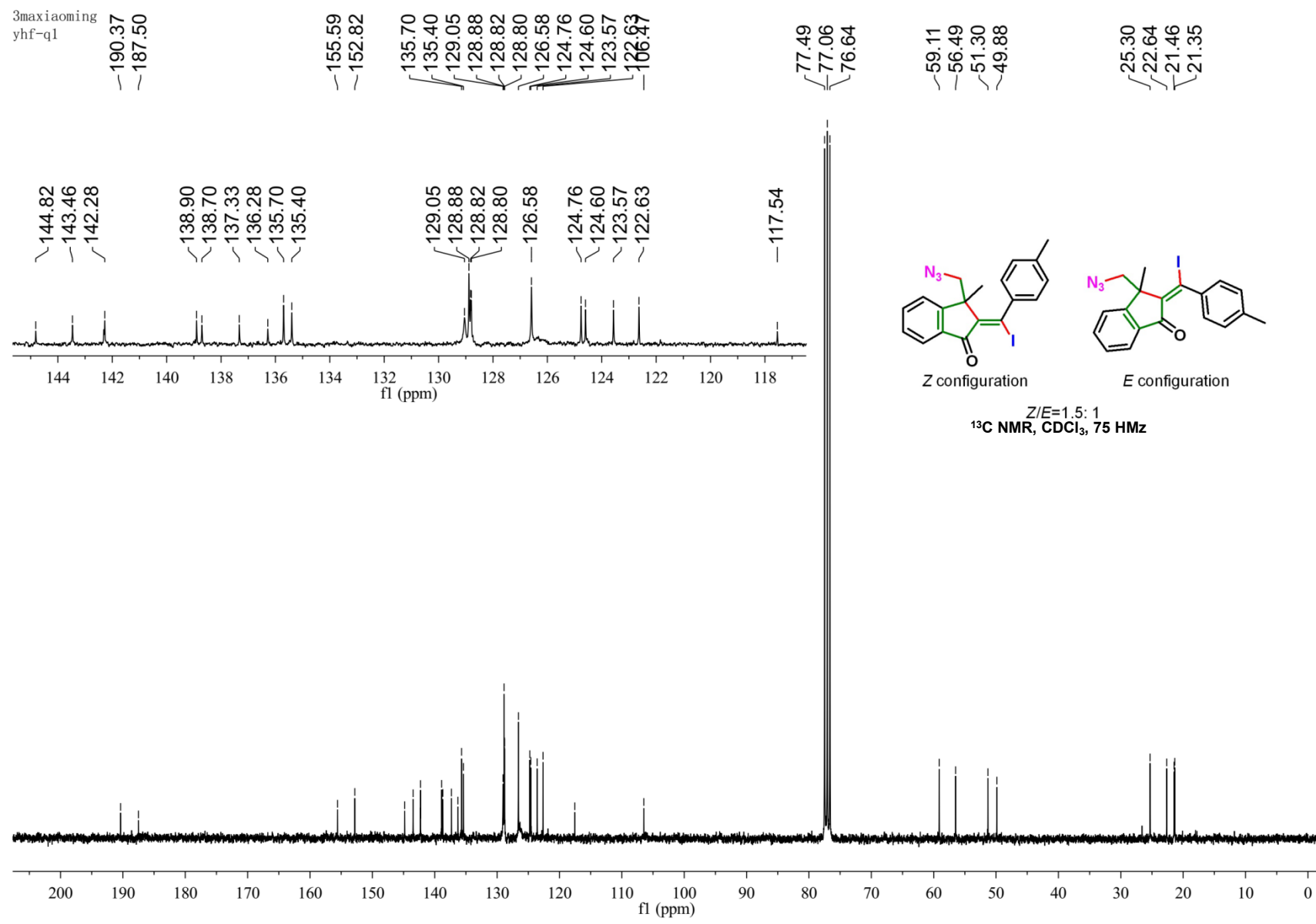
maxiaoming12
yhf-q2



Z/E=1.5:1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4b



¹³C NMR Spectrum of Compound 4b

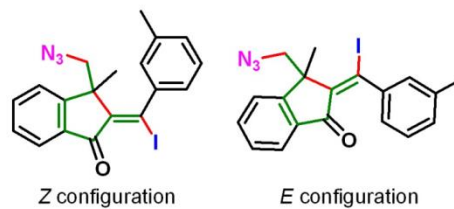
maxiaoming11.104.61
yhf

7.939
7.920
7.725
7.709
7.693
7.674
7.501
7.482
7.469
7.450
7.262
7.203
7.186
7.165
7.152

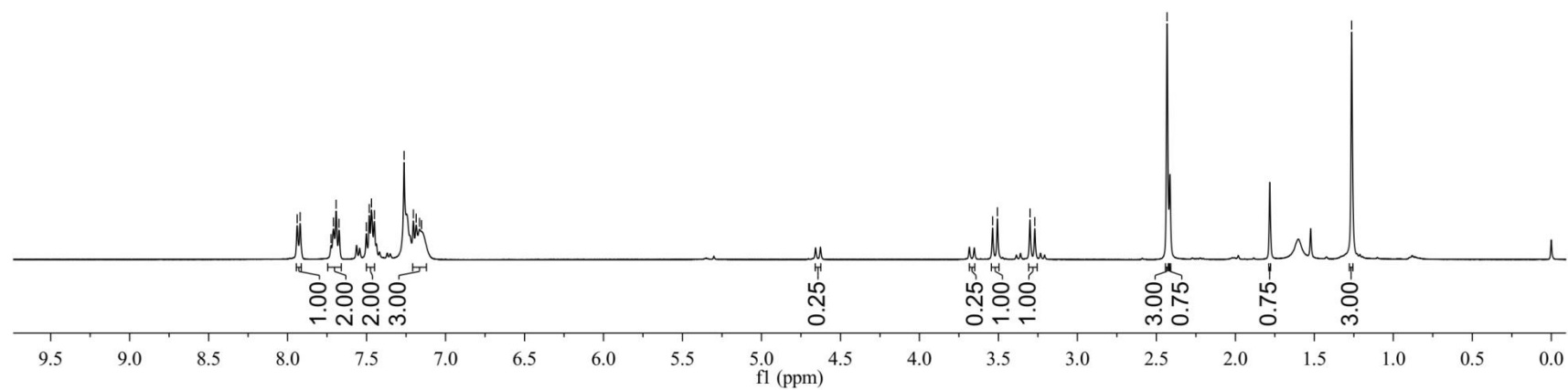
3.537
3.506
3.300
3.270

-2.432

-1.264

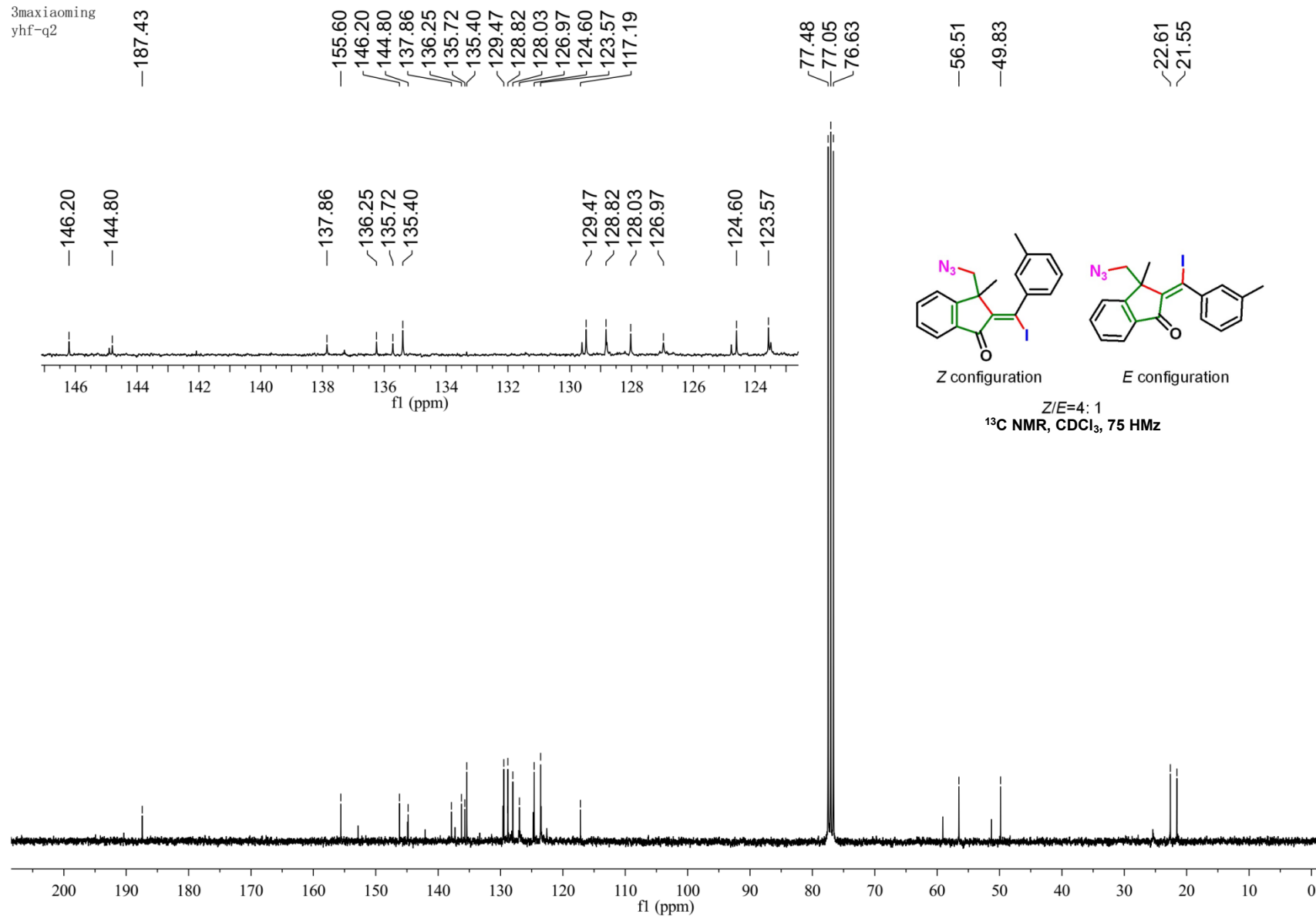


Z/E=4:1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4c

3maxiaoming
yhf-q2



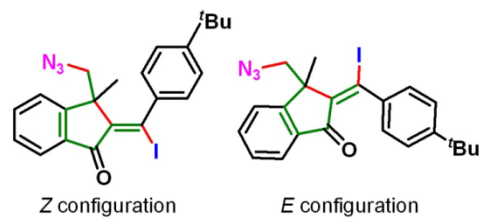
¹³C NMR Spectrum of Compound 4c

maxiaoming
yhf-9-13

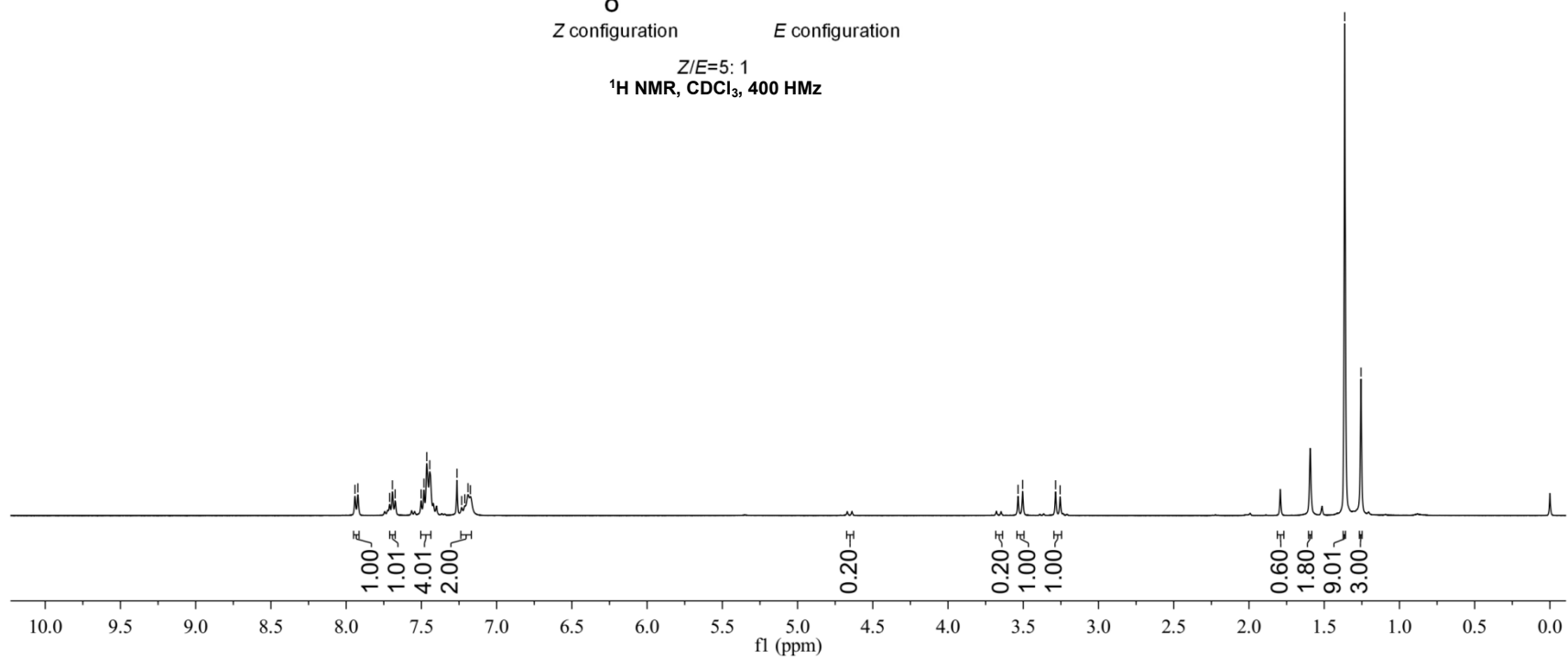
7.941
7.922
7.711
7.693
7.674
7.502
7.483
7.464
7.445
7.264
7.232
7.212
7.190
7.174

3.535
3.504
3.285
3.255

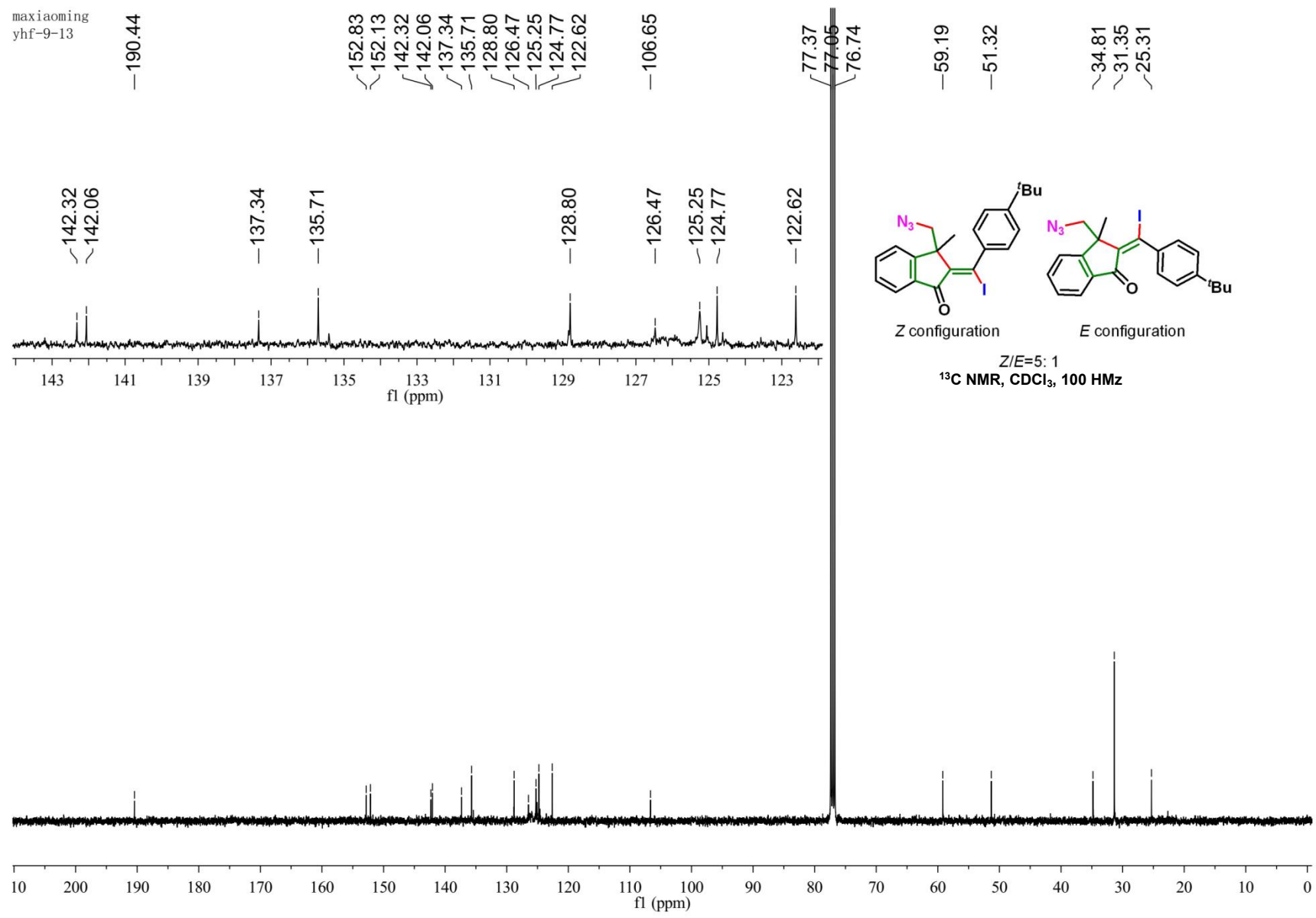
1.364
1.256



Z/E=5:1
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 4d



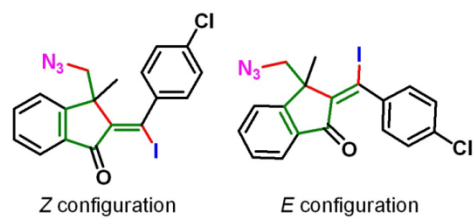
¹³C NMR Spectrum of Compound 4d

maxiaoming12
yhf

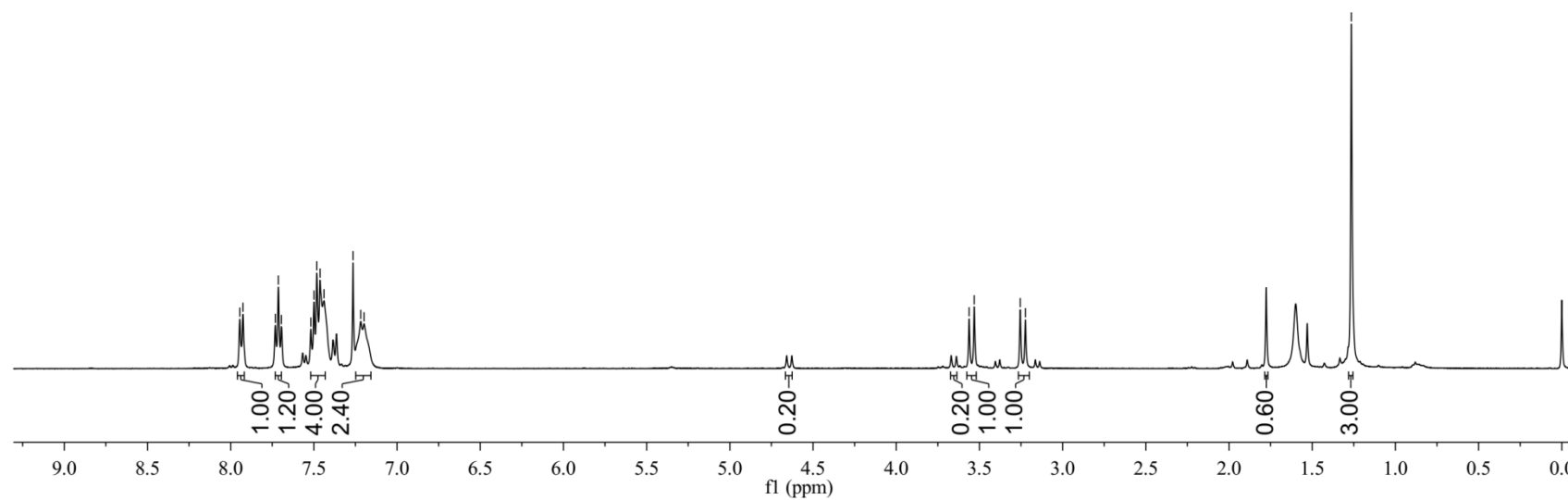
7.945
7.926
7.732
7.713
7.695
7.518
7.499
7.482
7.463
7.439
7.264
7.219
7.198

3.562
3.531
3.255
3.224

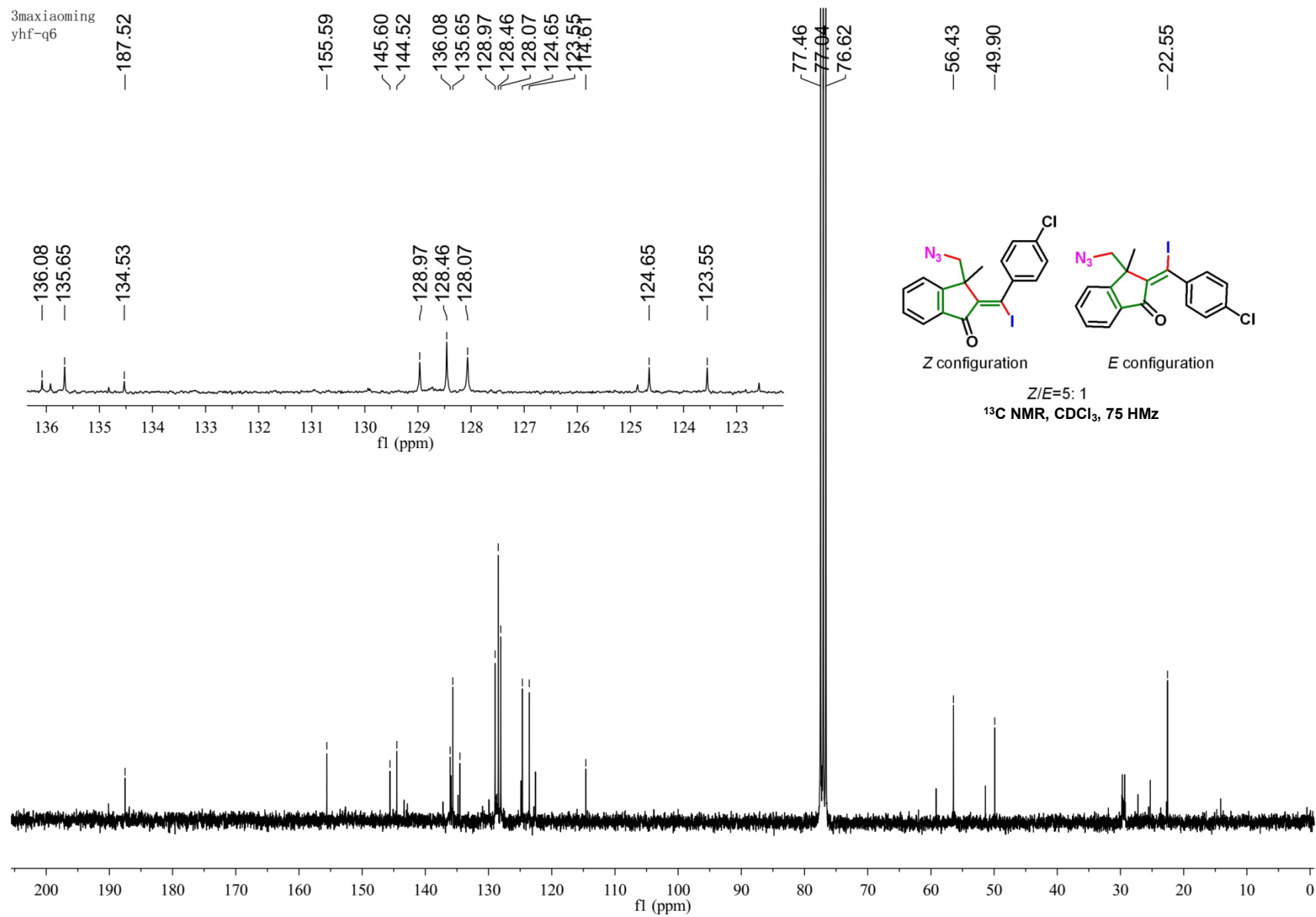
1.265



Z/E=5:1
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 4e



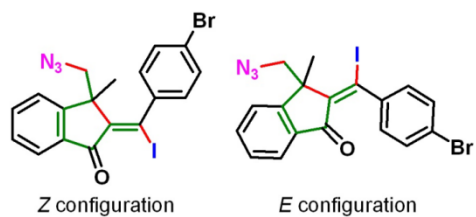
¹³C NMR Spectrum of Compound 4e

maxiaoming12
yhfq-8

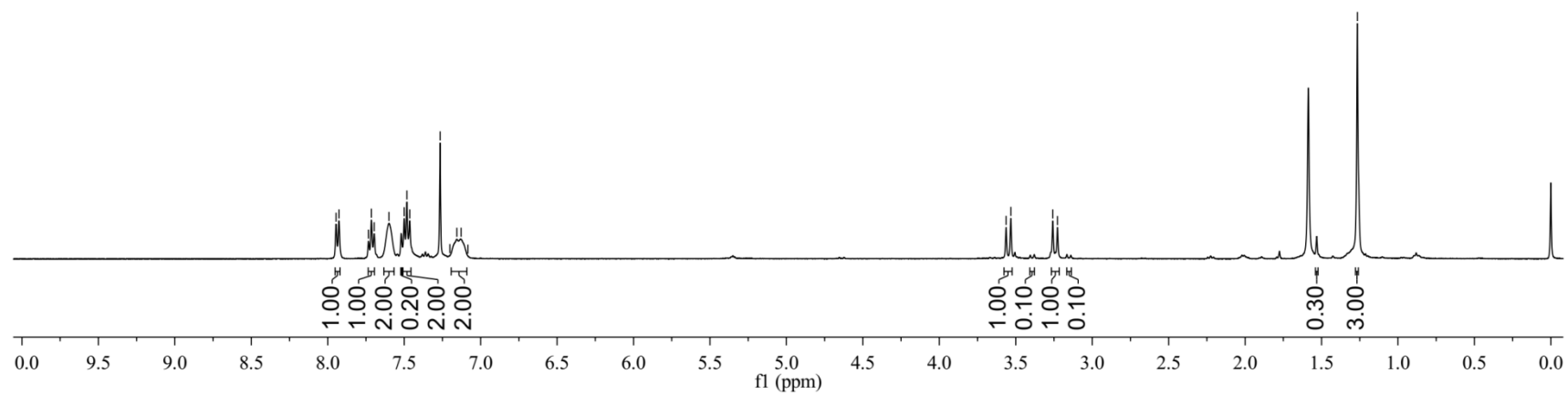
7.945
7.926
7.733
7.715
7.696
7.599
7.500
7.482
7.463
7.265
7.201
7.155
7.128
7.084

3.563
3.532
3.258
3.227

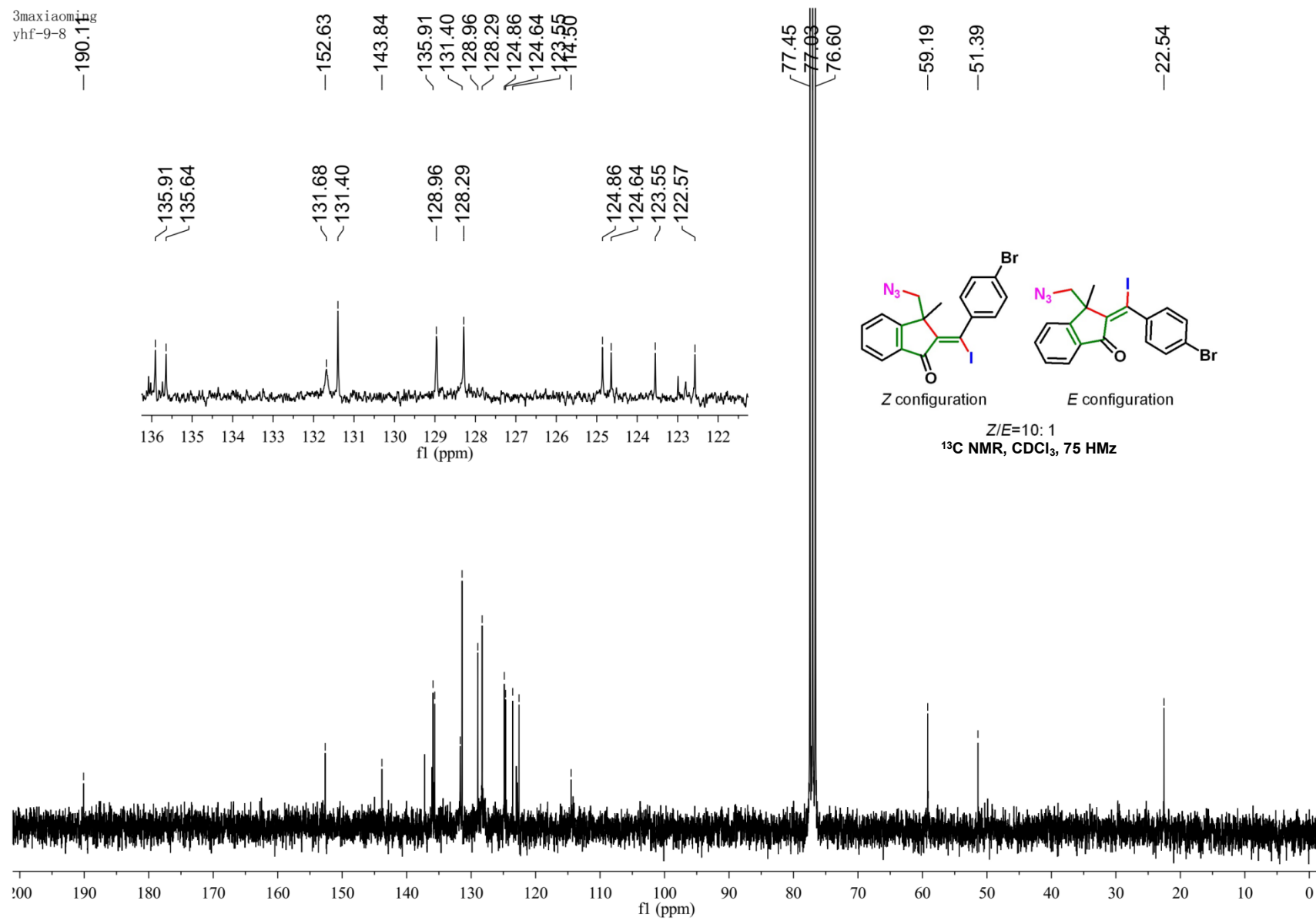
—1.266



Z/E=10: 1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4f



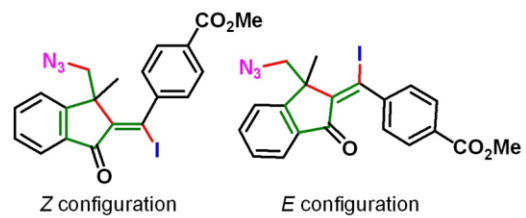
¹³C NMR Spectrum of Compound 4f

8.134
 8.098
 8.077
 7.951
 7.932
 7.731
 7.714
 7.696
 7.576
 7.556
 7.521
 7.502
 7.474
 7.454
 7.373
 7.353
 7.320
 7.266

4.657
 4.626
 3.968
 3.935
 3.691
 3.660
 3.537
 3.506
 3.227
 3.196

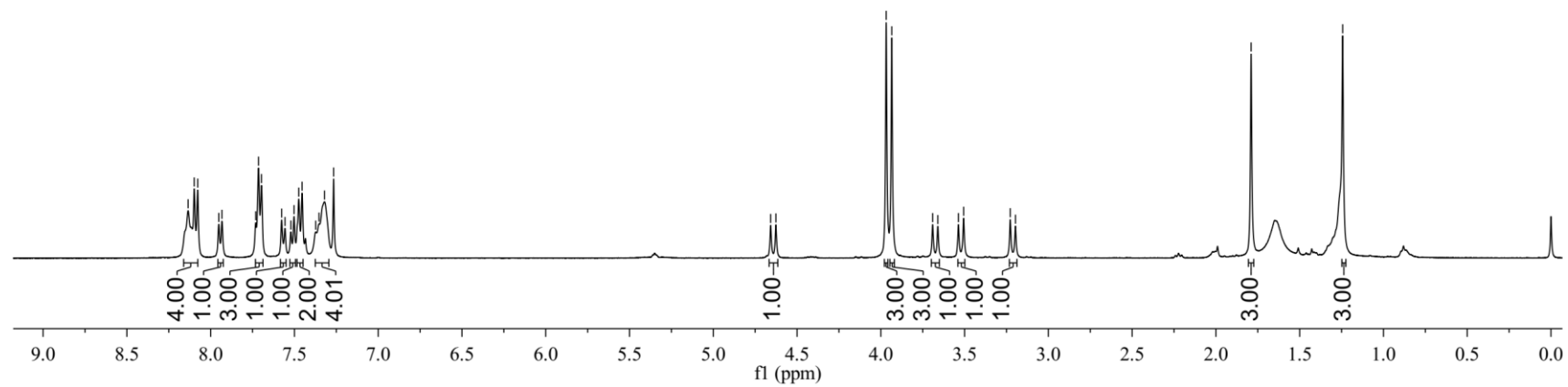
— 1.790

— 1.243

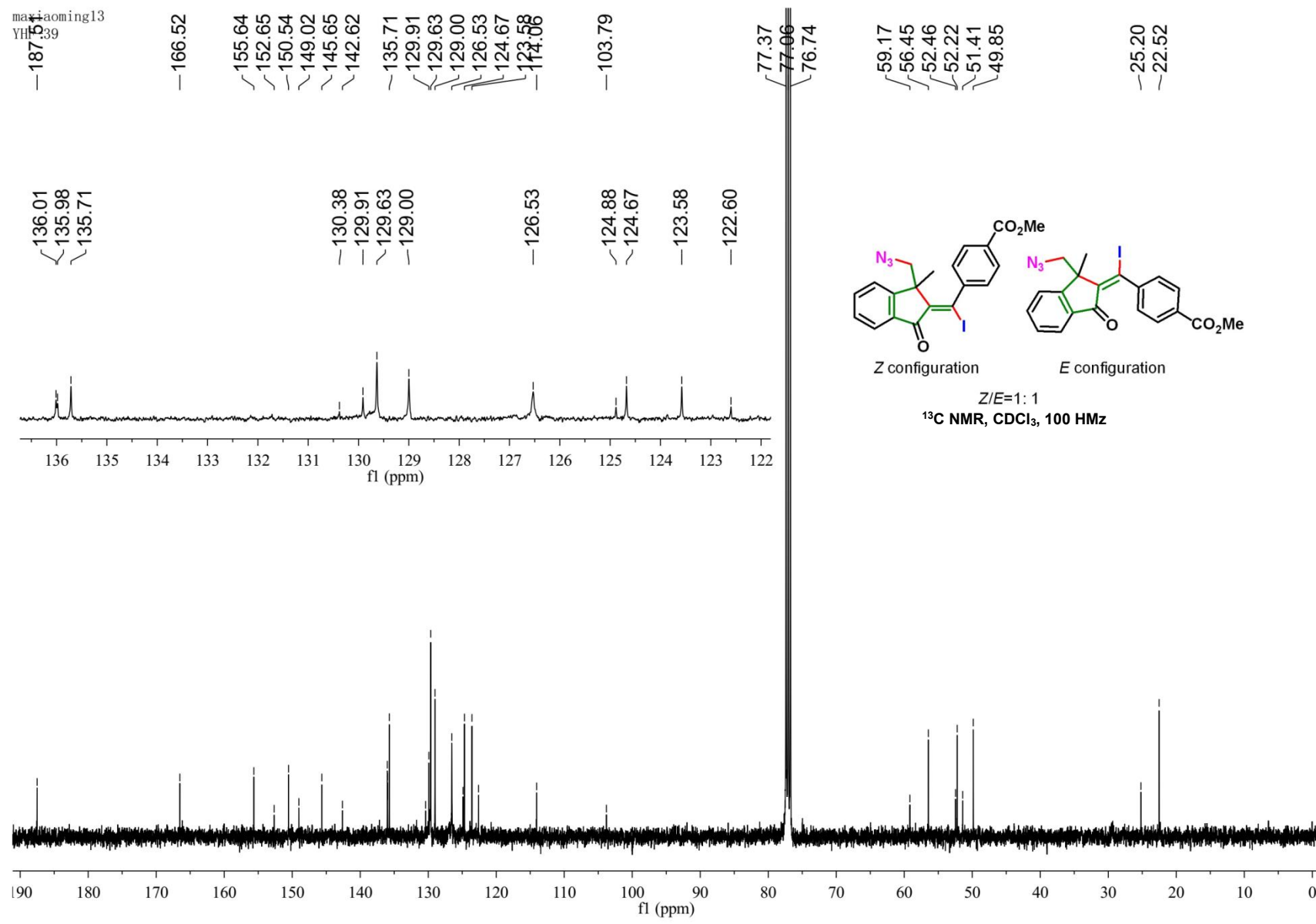


Z/E=1:1

¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4g



¹³C NMR Spectrum of Compound 4g

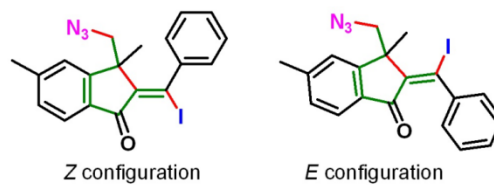
maxiaoming12
yhf45

7.870
7.851
7.555
7.503
7.486
7.427
7.392
7.374
7.355
7.335
7.315
7.304
7.277
7.260

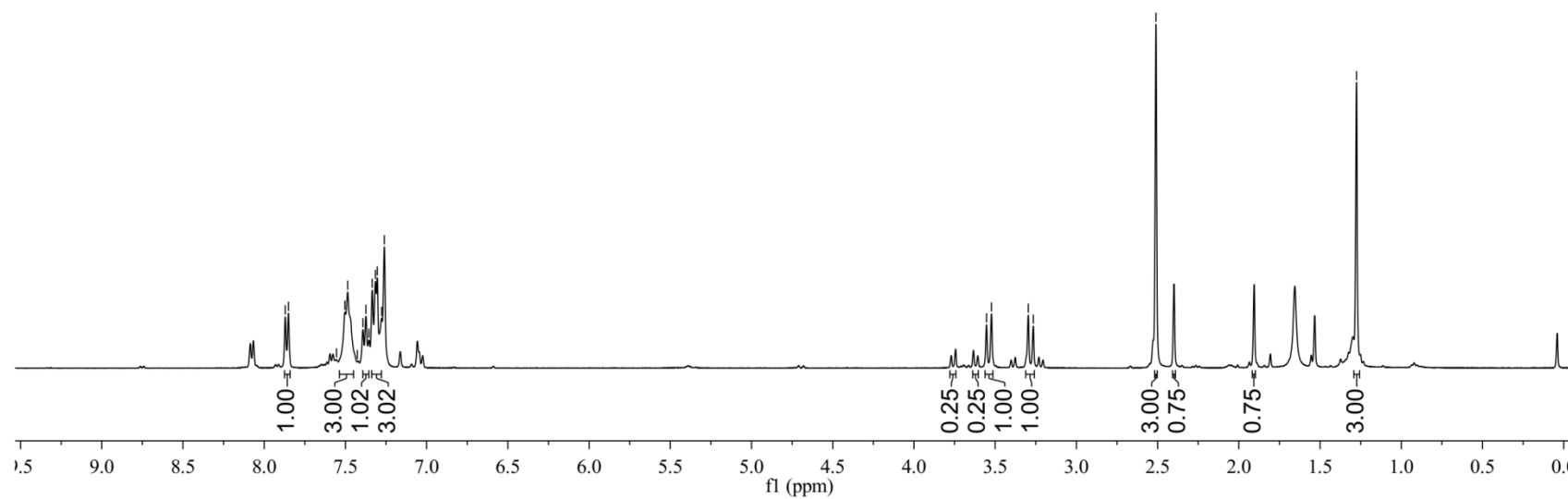
3.553
3.523
3.296
3.265

—2.510

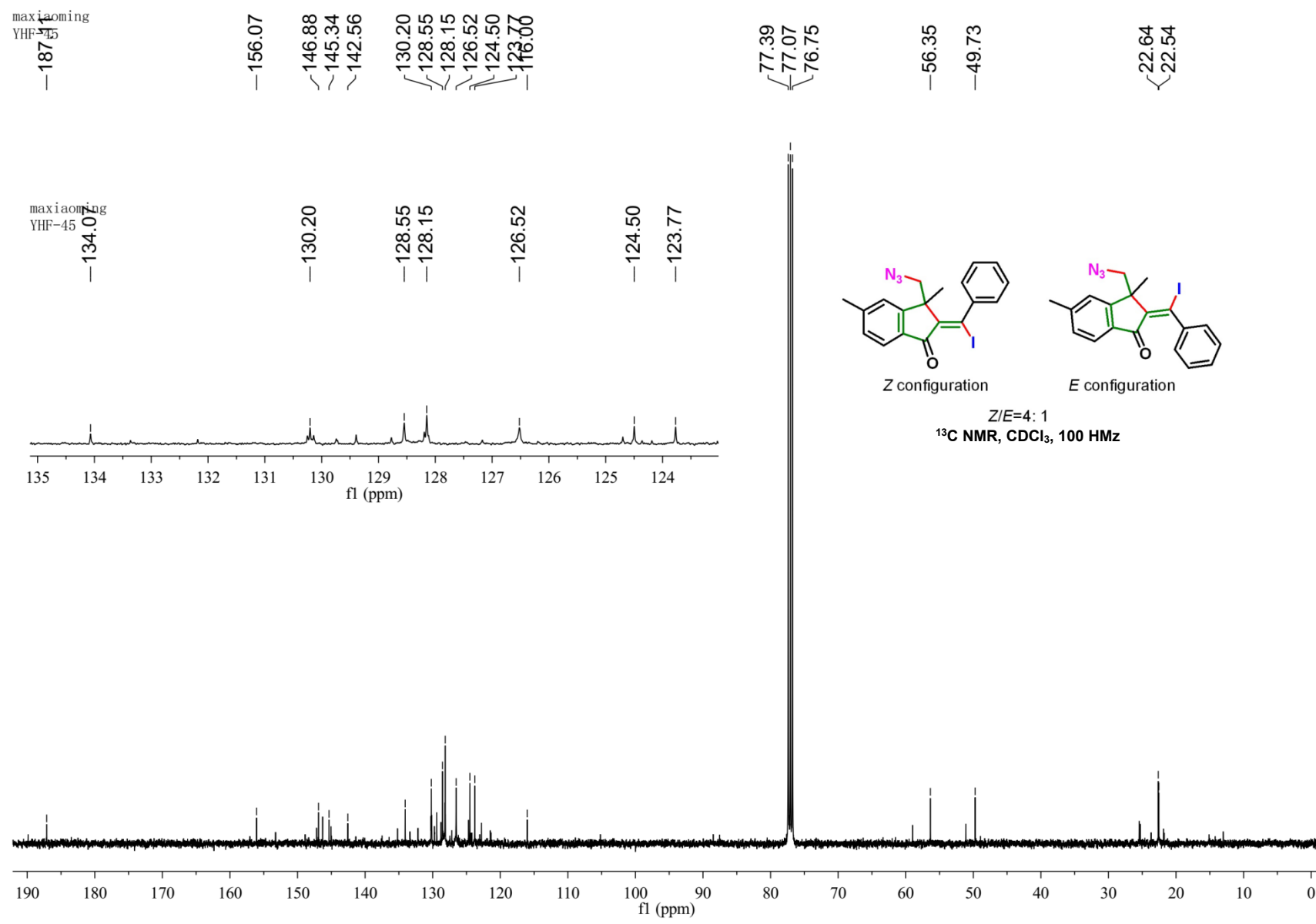
—1.275



Z/E=4:1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4h



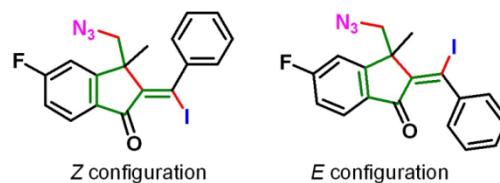
¹³C NMR Spectrum of Compound 4h

maxiaoming
yhf-9-14

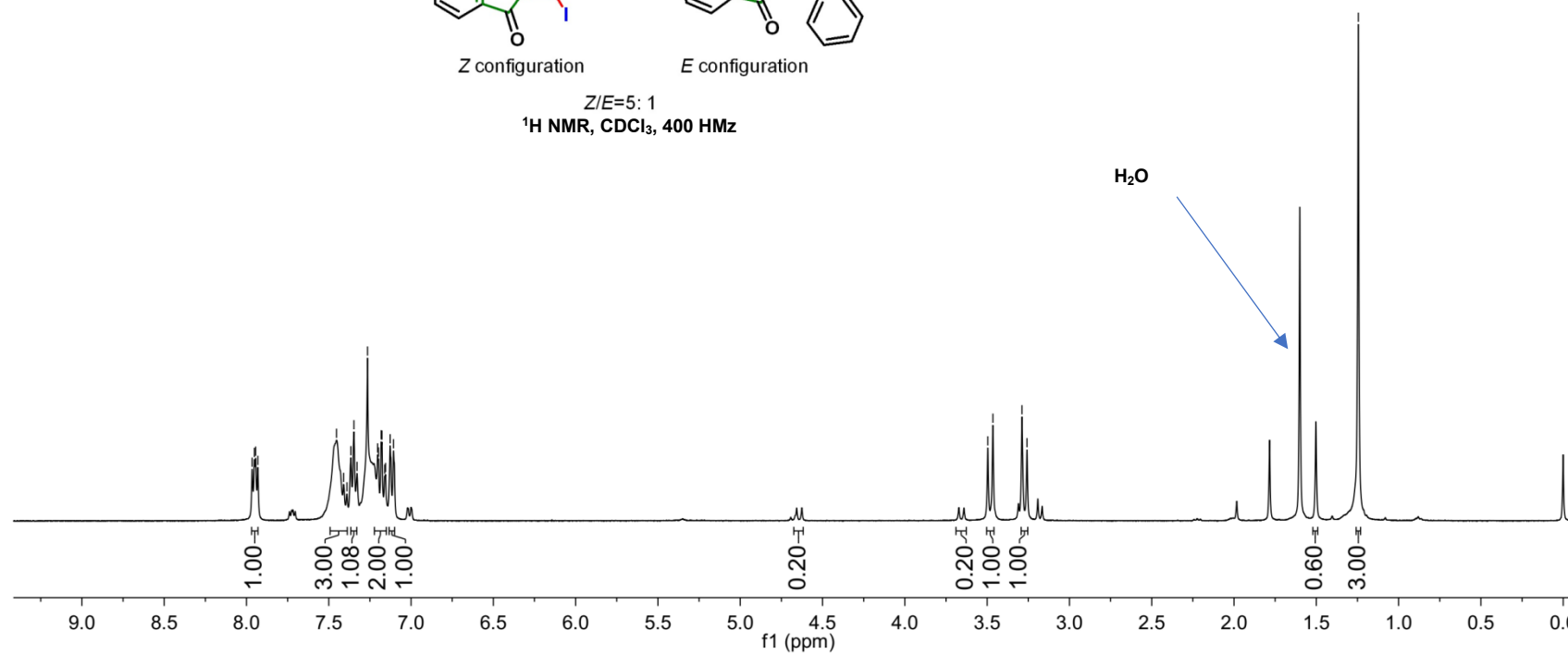
7.965
7.952
7.945
7.931
7.453
7.409
7.390
7.366
7.347
7.328
7.264
7.203
7.198
7.181
7.177
7.160
7.155
7.127
7.106

3.496
3.465
3.288
3.258

1.245

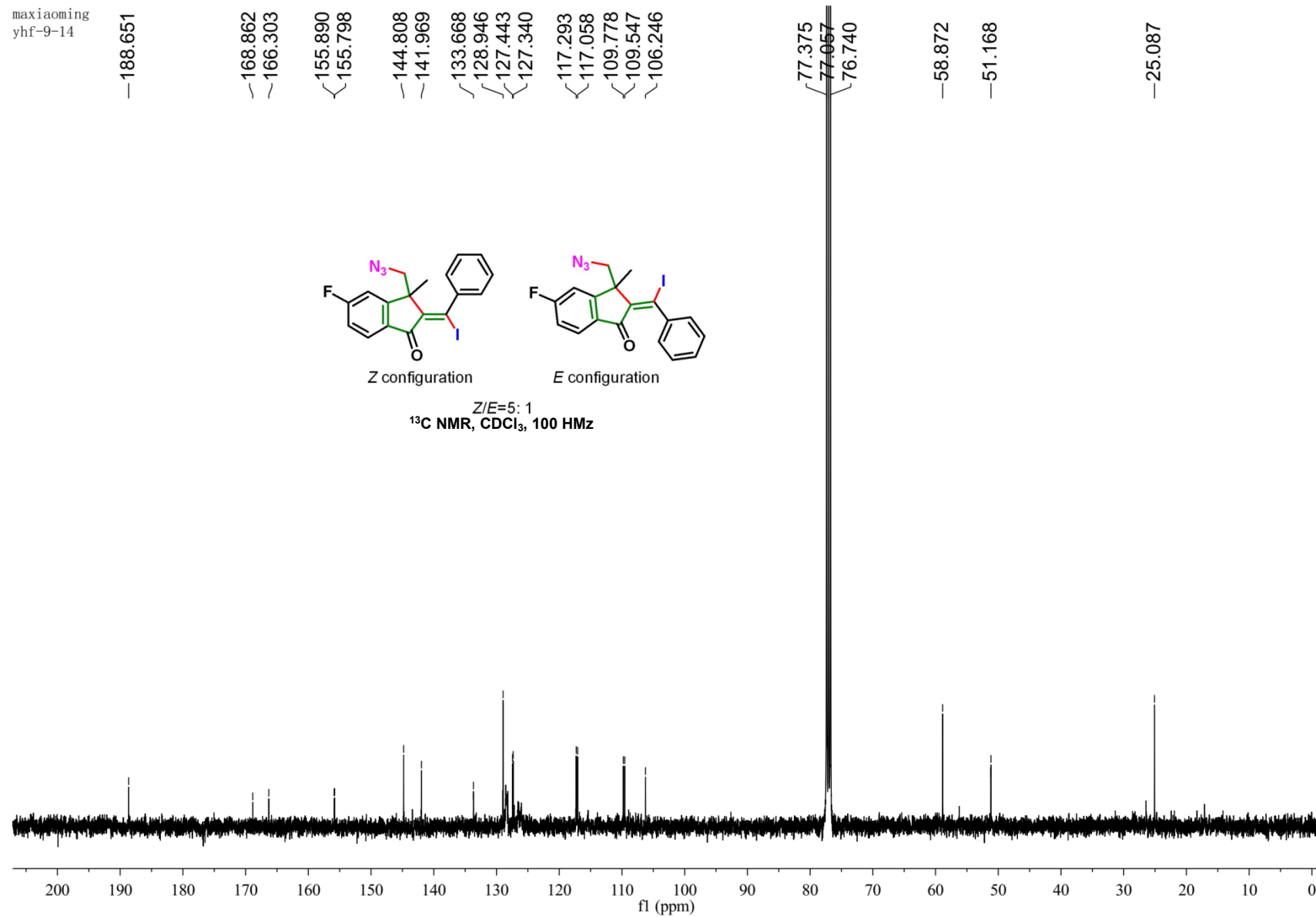


Z/E=5:1
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 4i

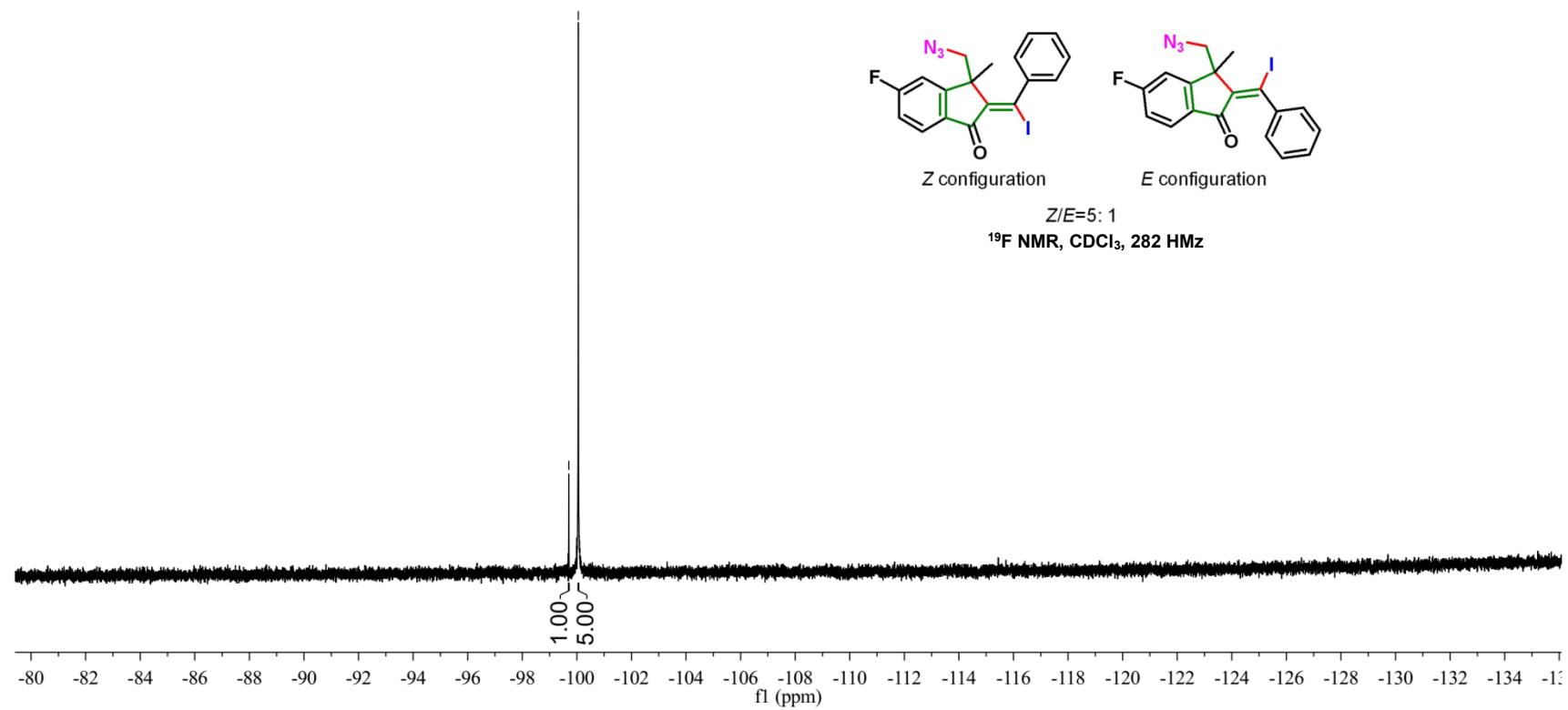
maxiaoming
yhf-9-14



¹³C NMR Spectrum of Compound 4i

3maxiaoming
yhf14

~99.703
~100.054



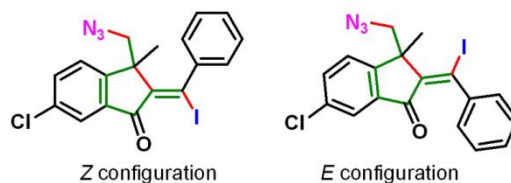
^{19}F NMR Spectrum of Compound 4i

maxiaoming
yhf-9-12

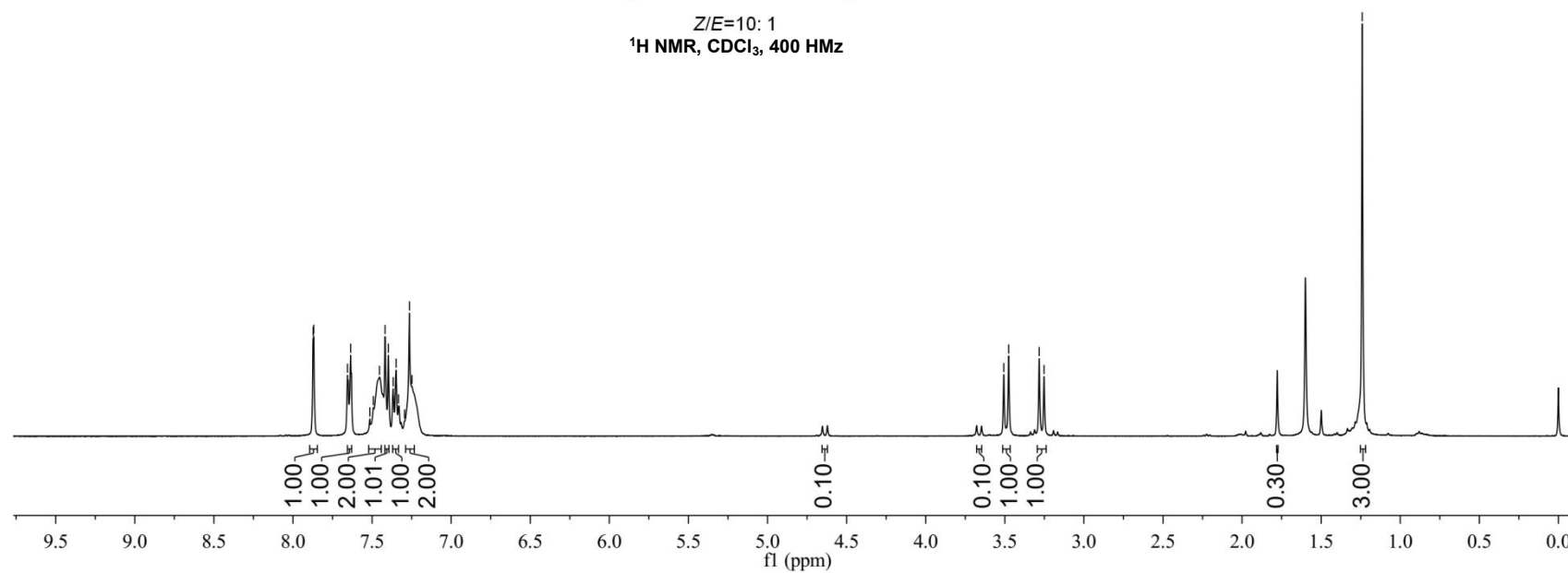
7.872
7.869
7.656
7.635
7.515
7.492
7.453
7.418
7.397
7.367
7.348
7.332
7.295
7.264
7.248

3.506
3.475
3.282
3.252

—1.240

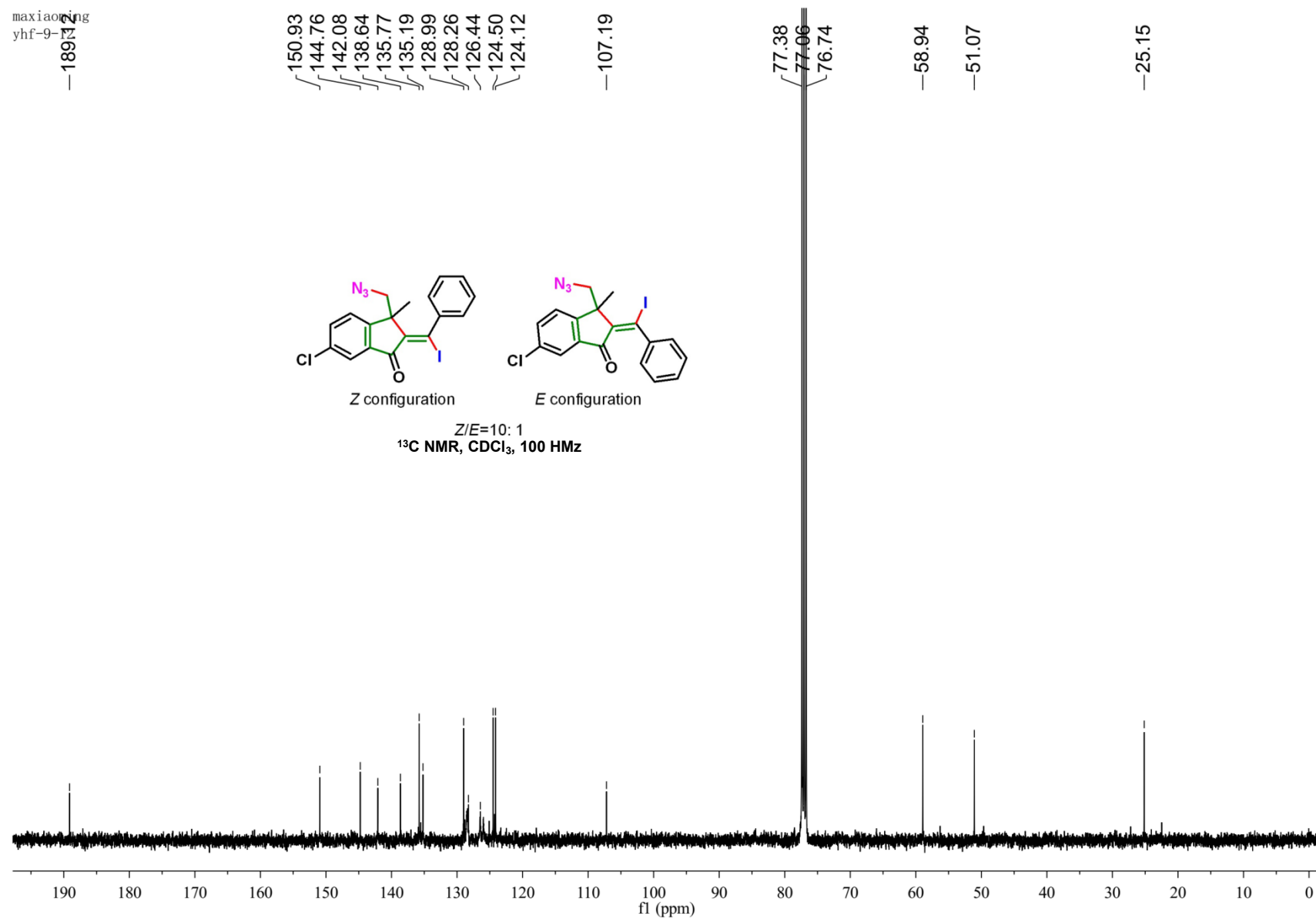


Z/E=10: 1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4j

maxiaoqing
yhf-9-12



Z/E=10:1
¹³C NMR, CDCl₃, 100 MHz

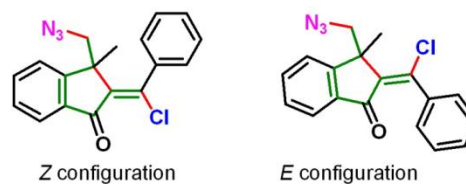
¹³C NMR Spectrum of Compound 4j

maxiaoming13
yhf-n

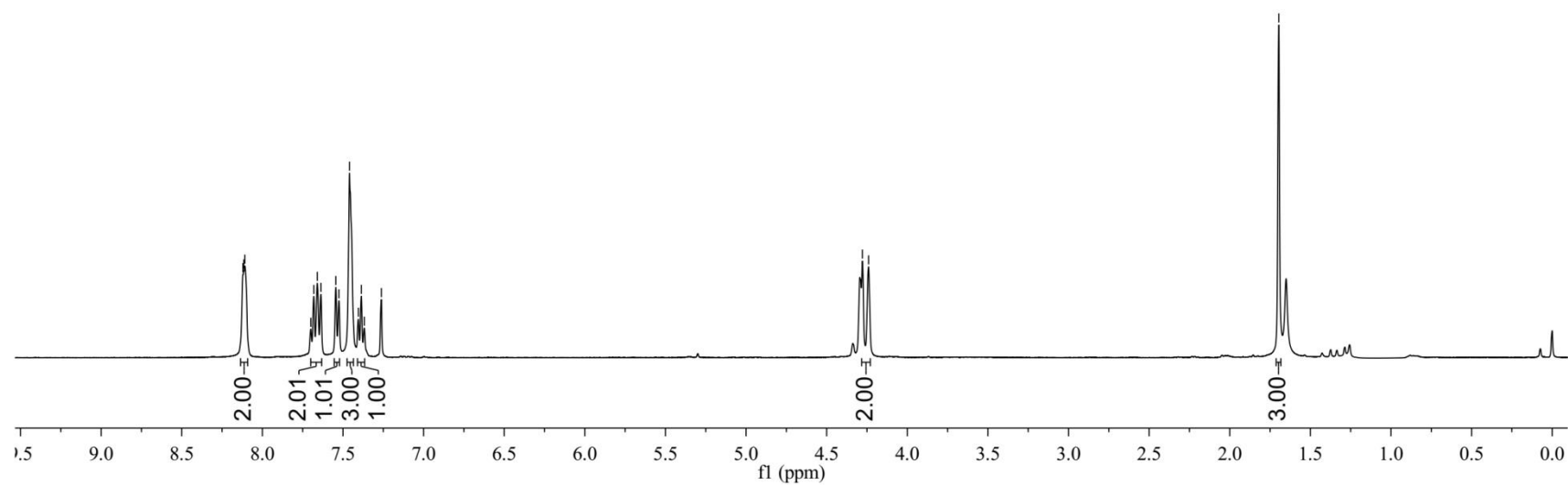
8.120
8.115
8.108
7.700
7.681
7.659
7.637
7.544
7.525
7.459
7.404
7.386
7.368
7.262

4.278
4.240

1.696

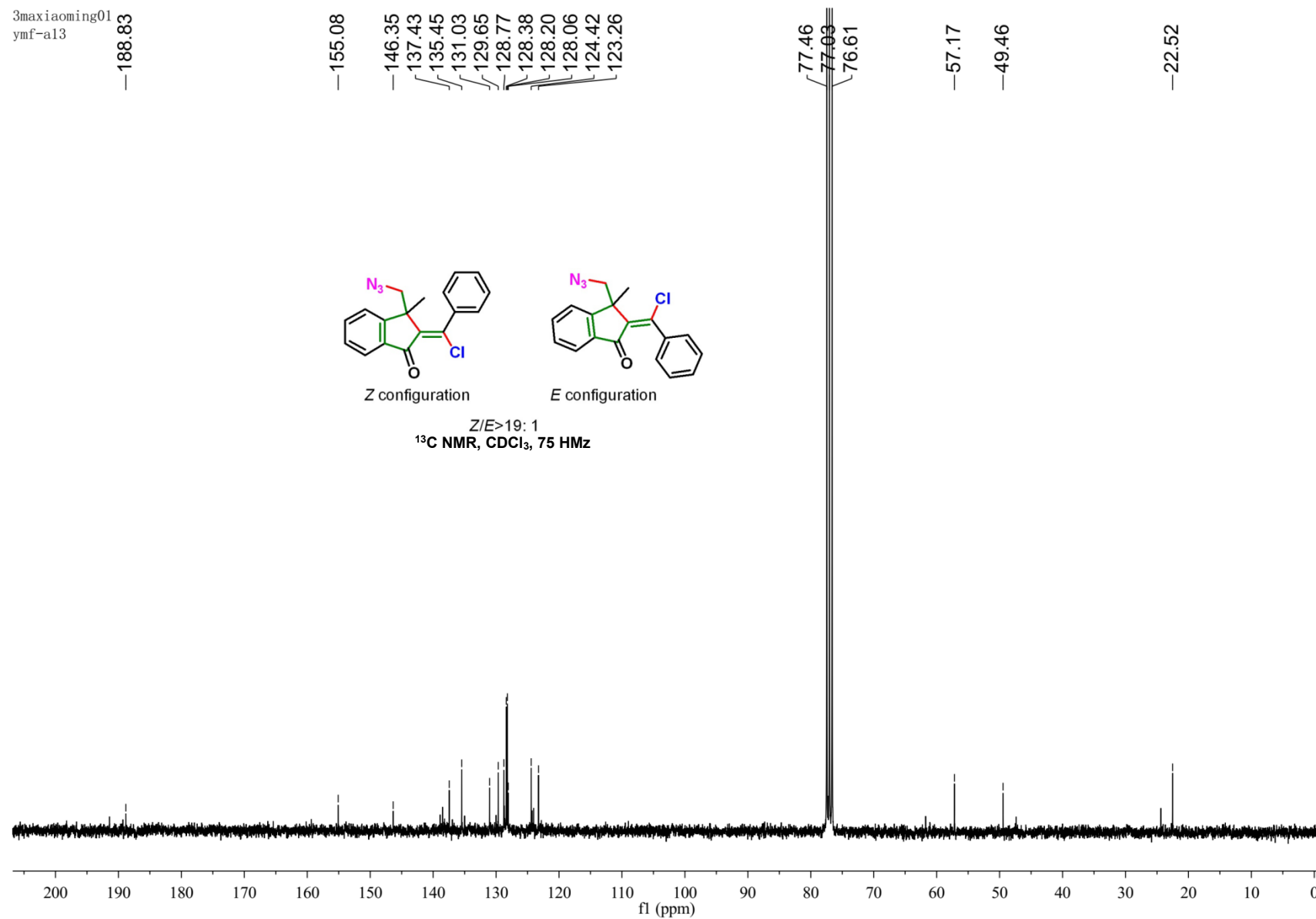


Z/E>19:1
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 4k

3maxiaoming01
ymf-a13



¹³C NMR Spectrum of Compound 4k

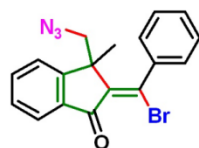
maxiaoming13
yhf-nbs

7.724
7.707
7.691
7.565
7.546
7.465
7.446
7.420
7.385
7.366
7.260

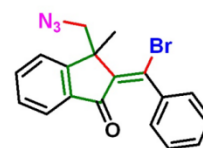
4.712
4.686

3.839
3.813

— 1.928



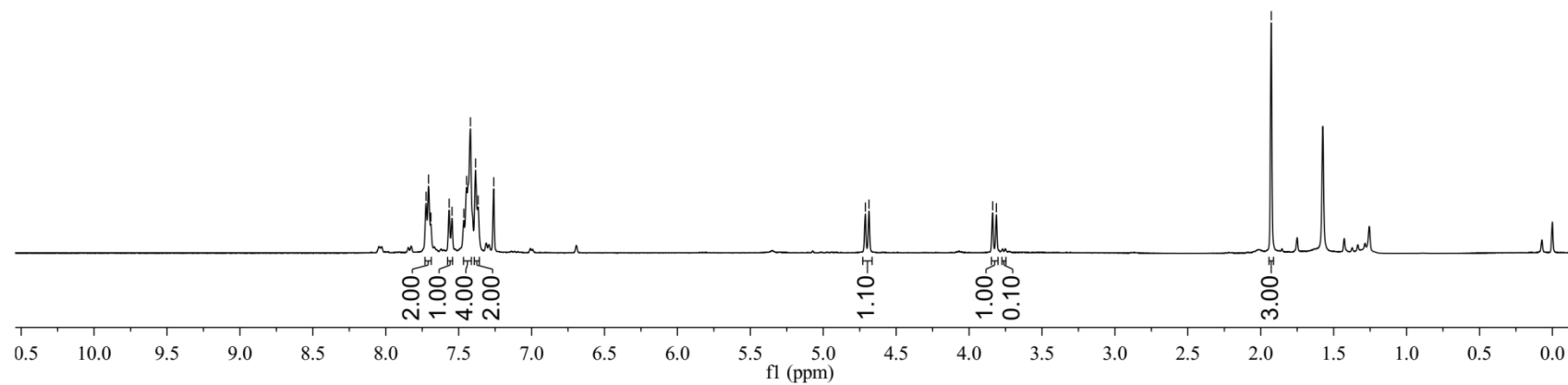
Z configuration



E configuration

Z/E= 10: 1

¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 4l

YHF NBS

—188.14

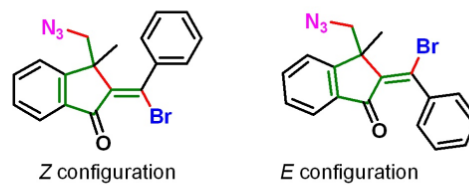
—155.41
—141.19
—140.34
—138.45
—137.05
—135.47
—129.27
—128.78
—128.21
—127.90
—124.35
—122.80

{ 77.23
77.02
76.81

—49.77

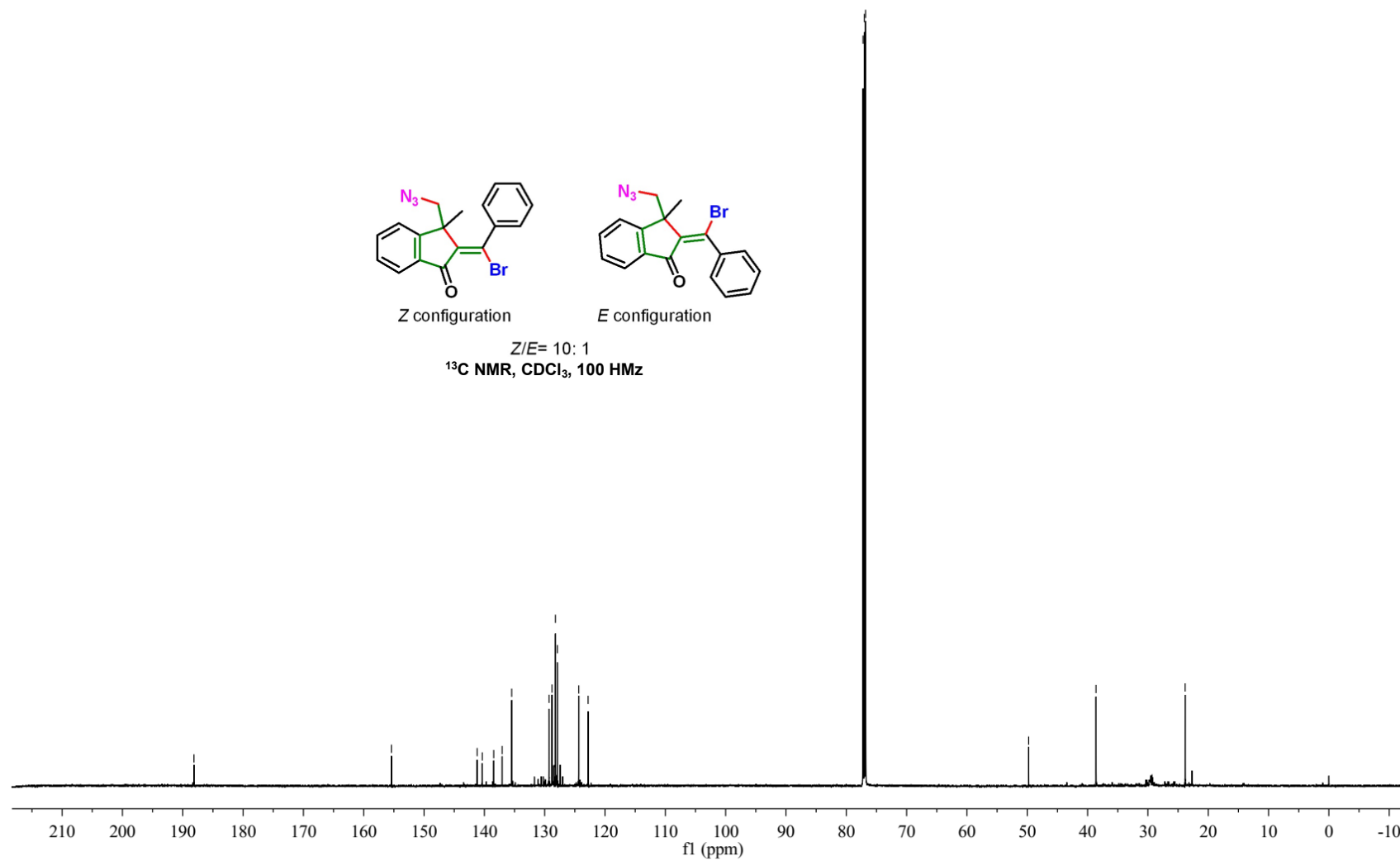
—38.61

—23.83



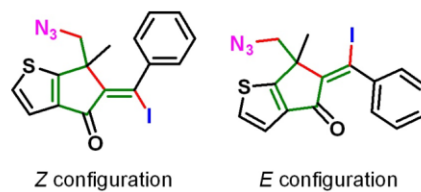
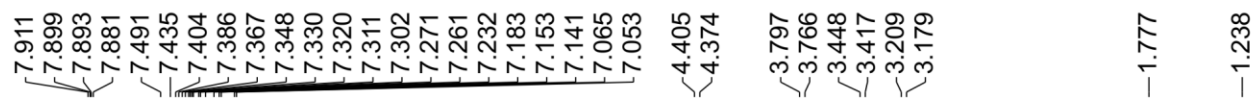
Z/E= 10: 1

¹³C NMR, CDCl₃, 100 HMz

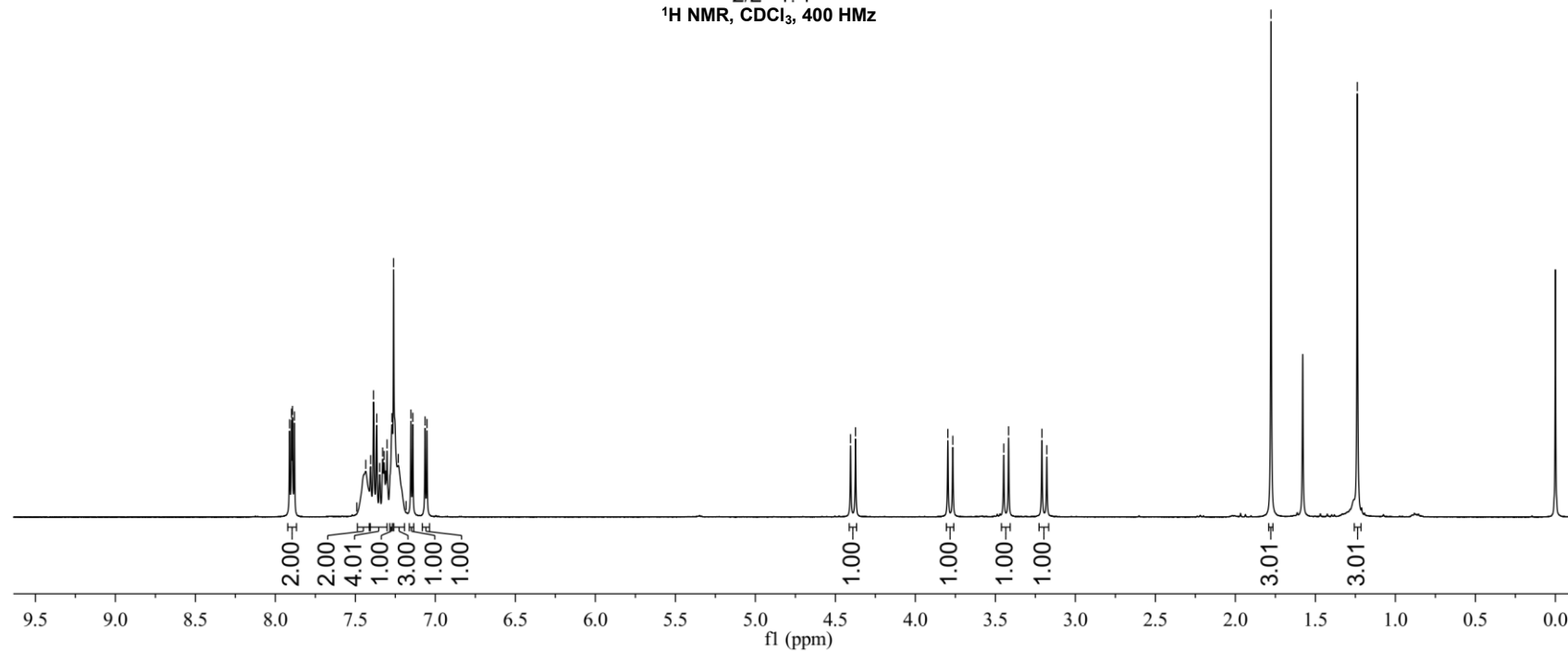


¹³C NMR Spectrum of Compound 41

maxiaoming17
yhf-52

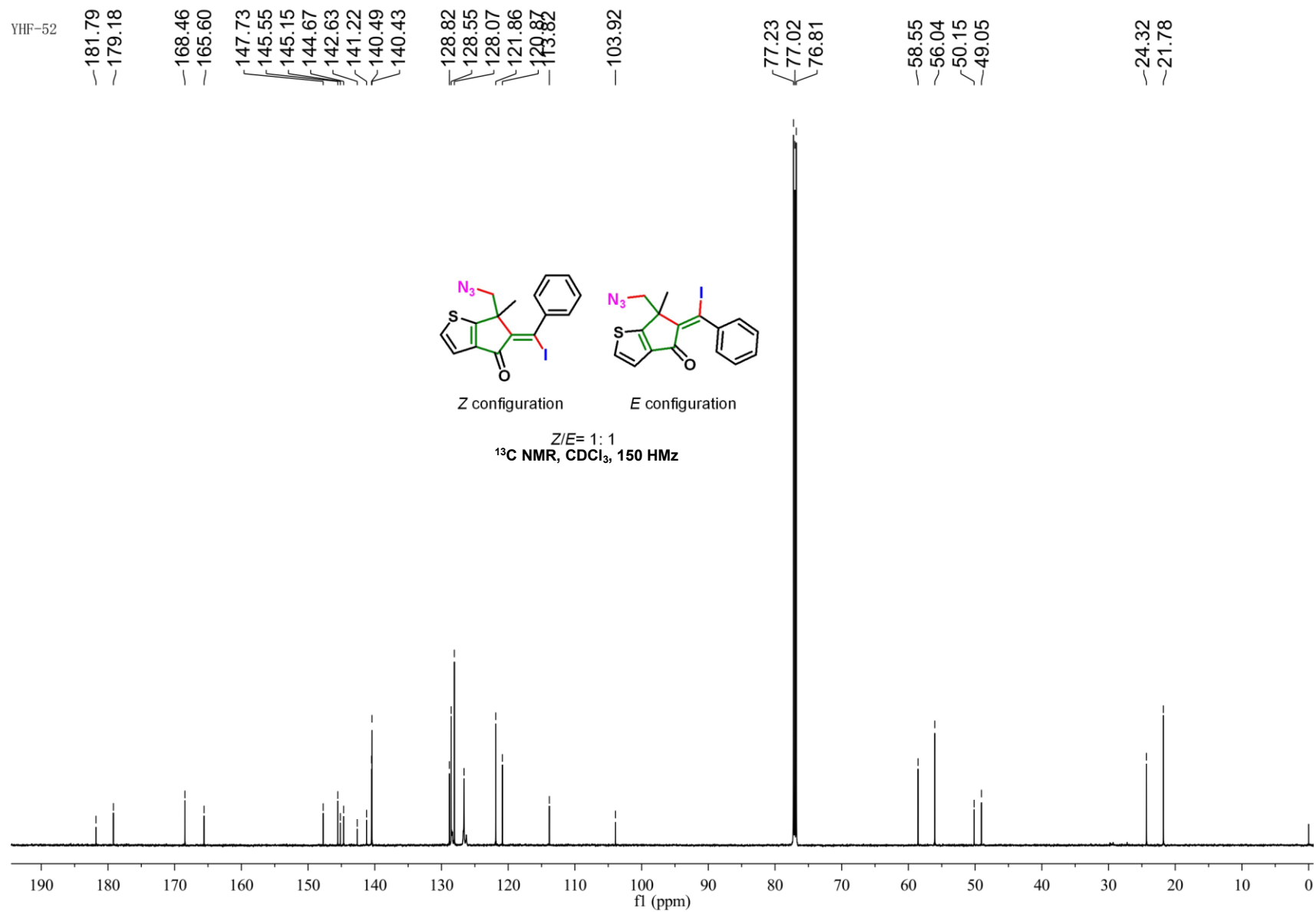


Z/E= 1:1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 4m

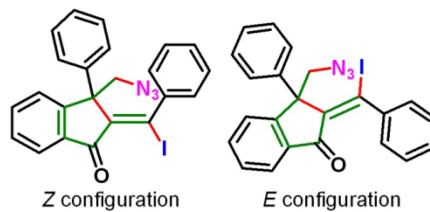
YHF-52



¹³C NMR Spectrum of Compound 4m

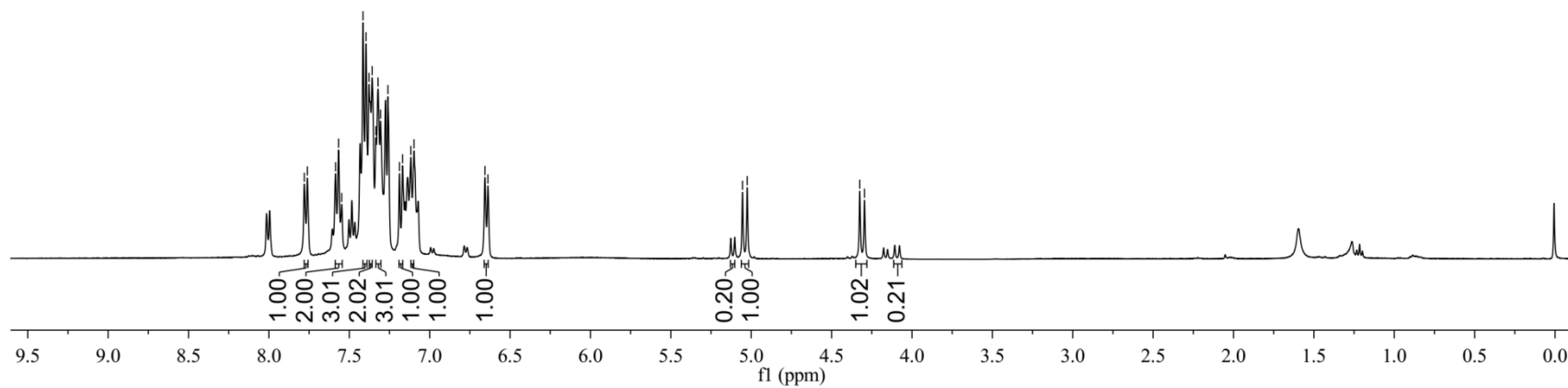
maximum
 yhf
 7.780
 7.766
 7.586
 7.567
 7.415
 7.396
 7.378
 7.358
 7.334
 7.321
 7.306
 7.260
 7.188
 7.168
 7.117
 7.097
 6.656
 6.638

5.054
 5.025
 4.325
 4.295



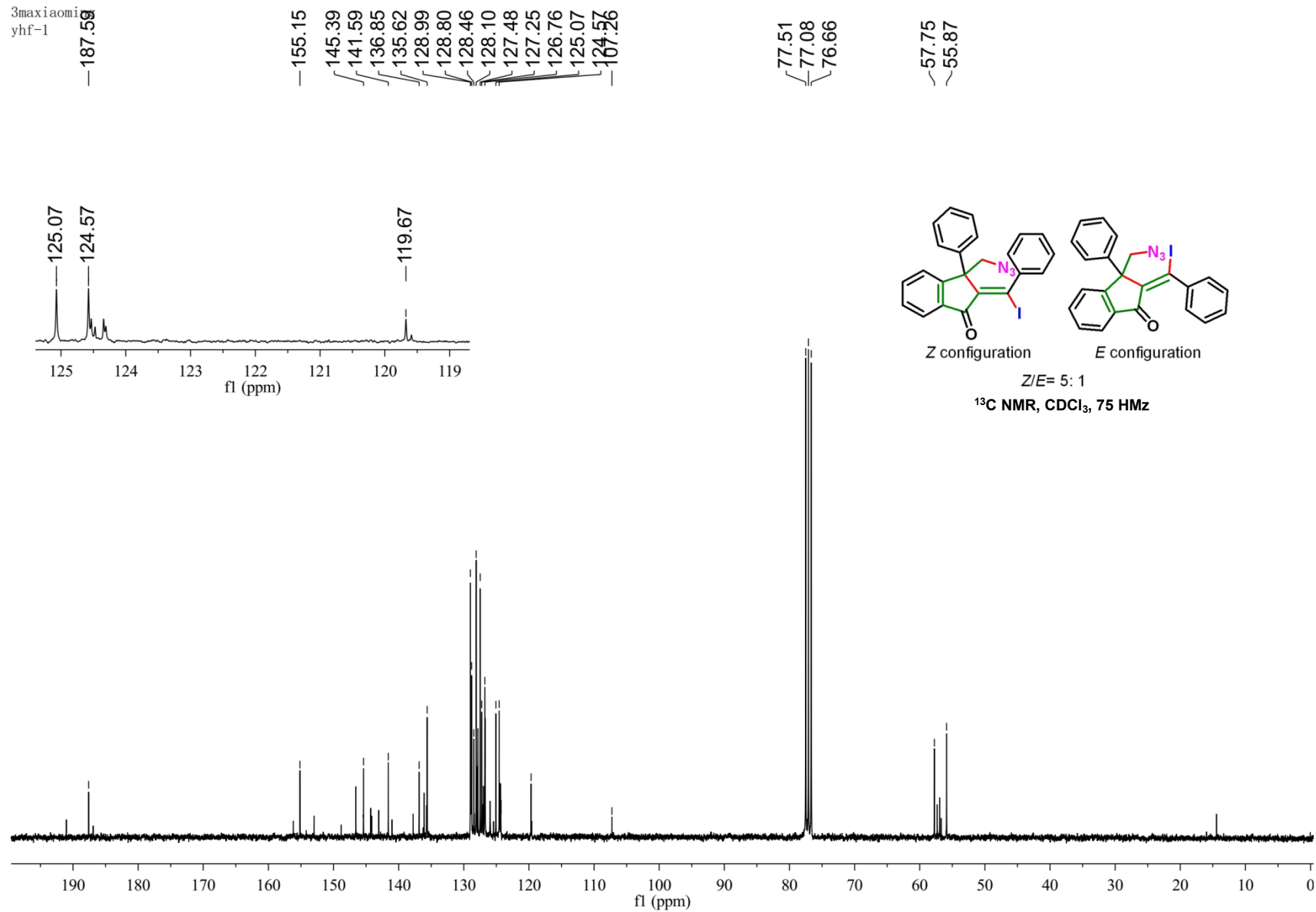
Z/E= 5: 1

¹H NMR, CDCl₃, 400 HMz

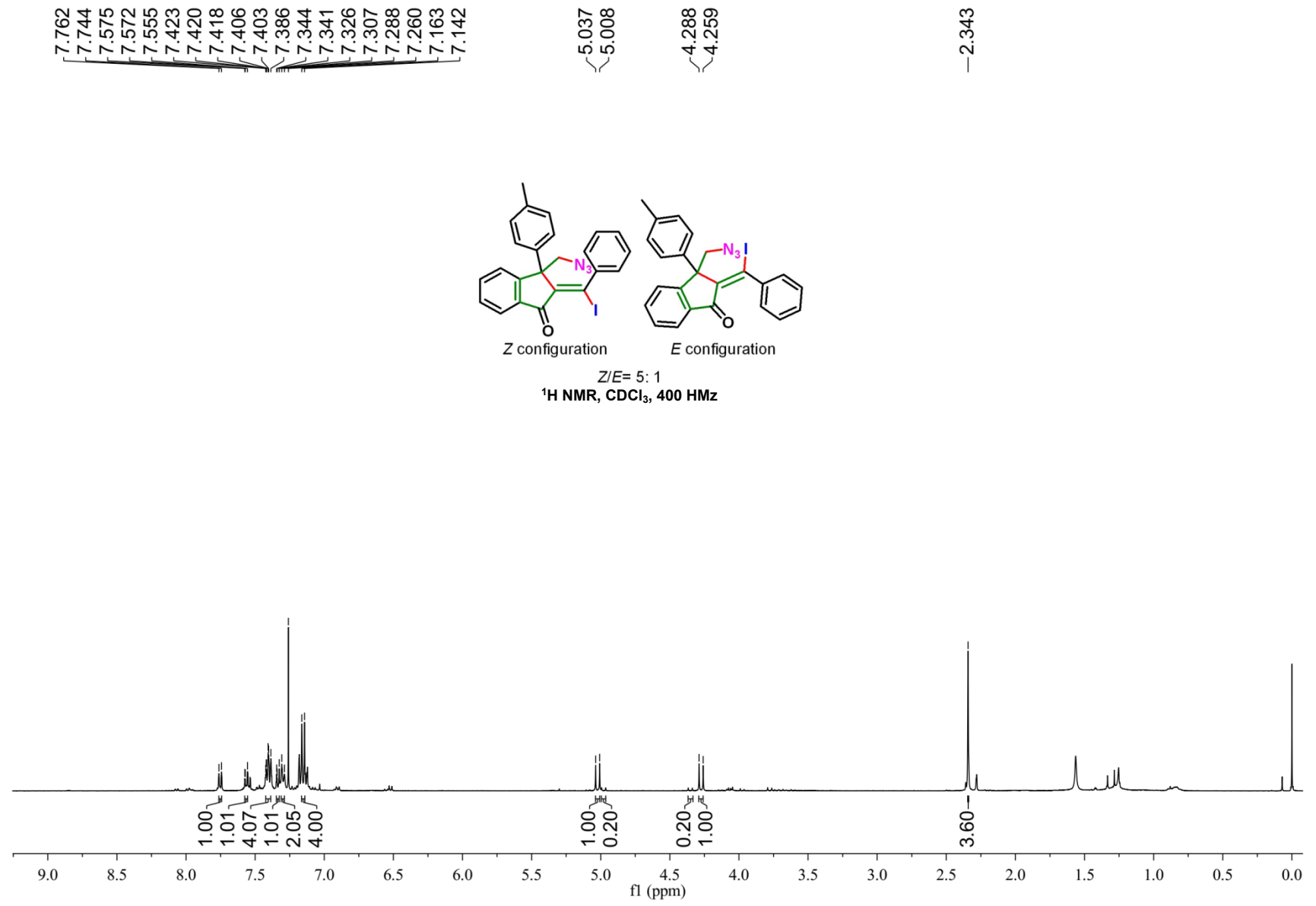


¹H NMR Spectrum of Compound 6a

3maxiaomi
yhf-1

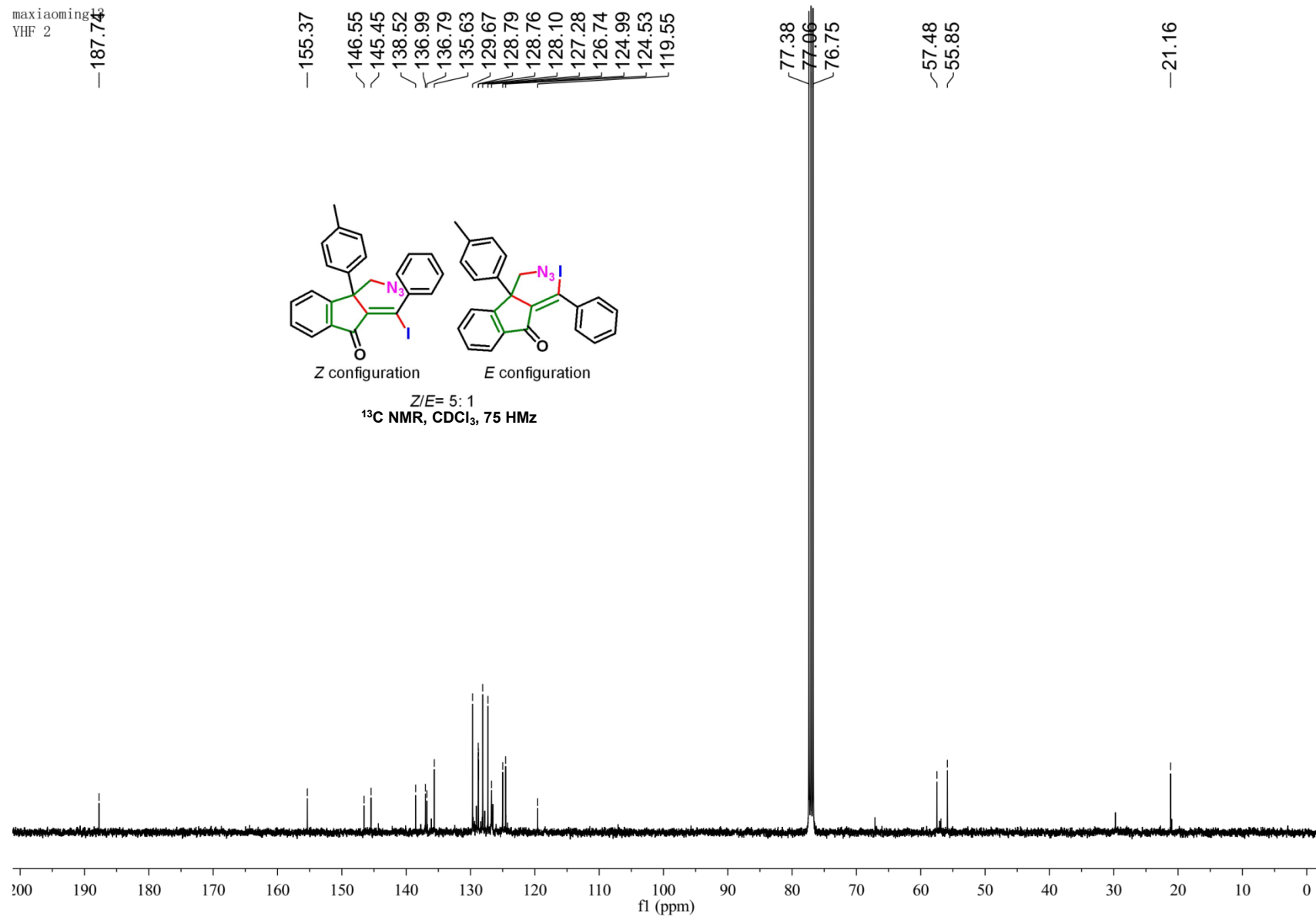


^{13}C NMR Spectrum of Compound 6a



¹H NMR Spectrum of Compound 6b

maxiaoming18
YHF 2



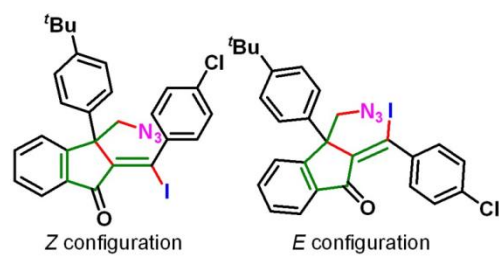
¹³C NMR Spectrum of Compound 6b

7.772
 7.759
 7.596
 7.578
 7.557
 7.436
 7.417
 7.398
 7.382
 7.361
 7.340
 7.262
 7.231
 7.204
 7.185
 7.143
 7.123
 7.104
 6.577
 6.557

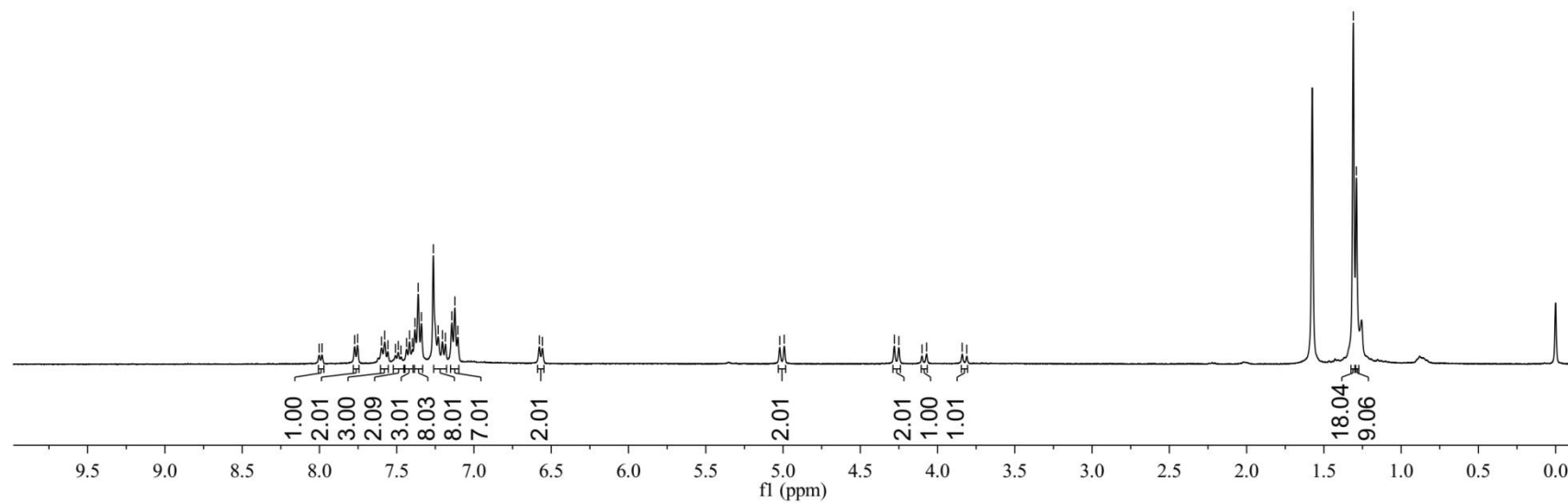
 5.021
 4.992

 4.279
 4.250
 4.100
 4.071
 3.841
 3.811

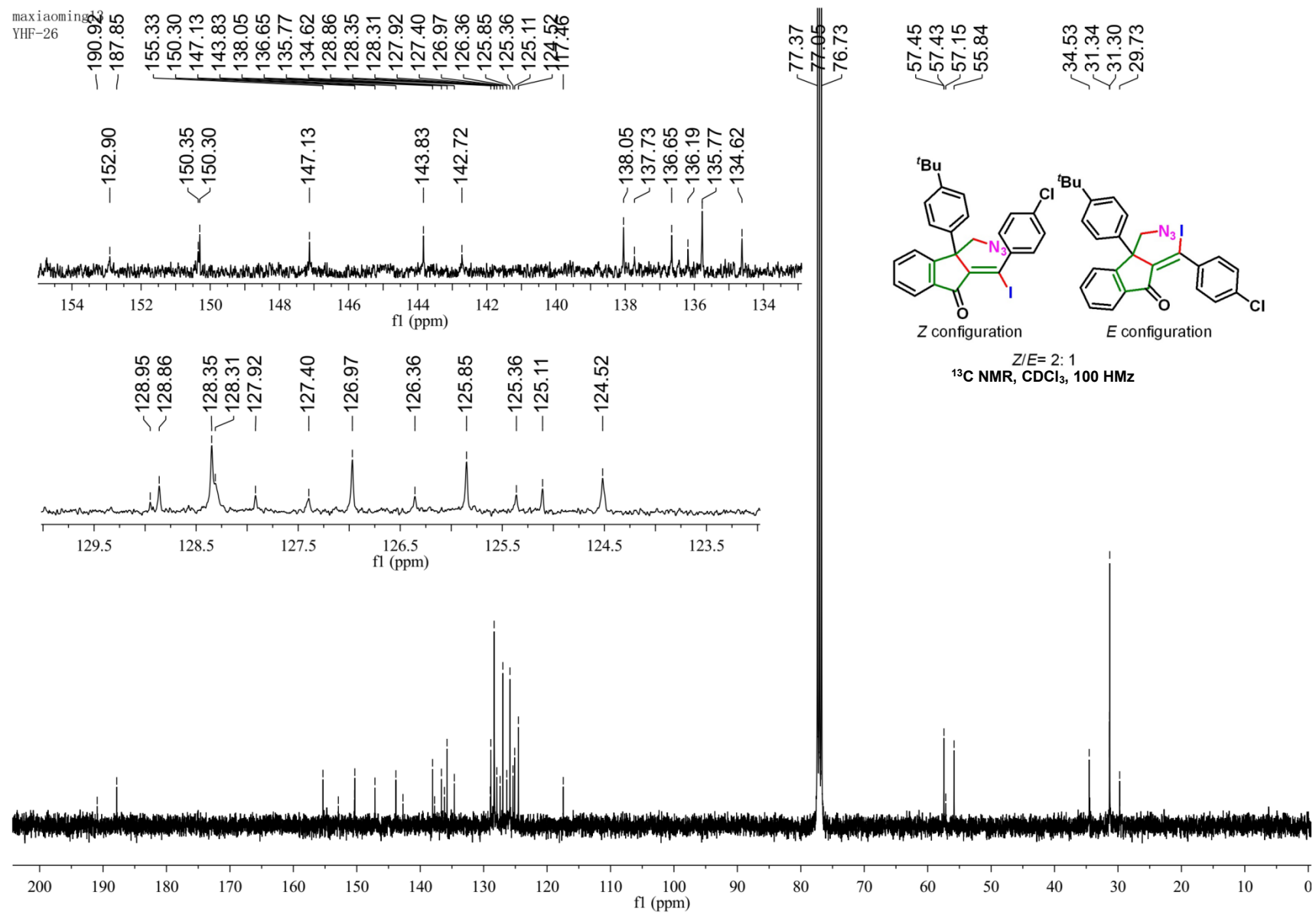
 1.309
 1.289



$Z/E = 2:1$
 $^1\text{H NMR, CDCl}_3, 400 \text{ MHz}$



$^1\text{H NMR}$ Spectrum of Compound 6c



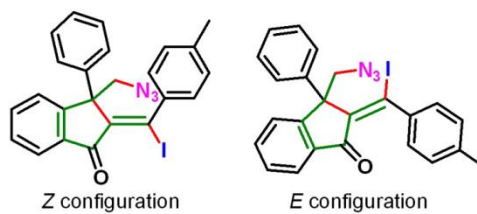
$^{13}\text{C NMR Spectrum of Compound 6c}$

max: 0.00
 yhf

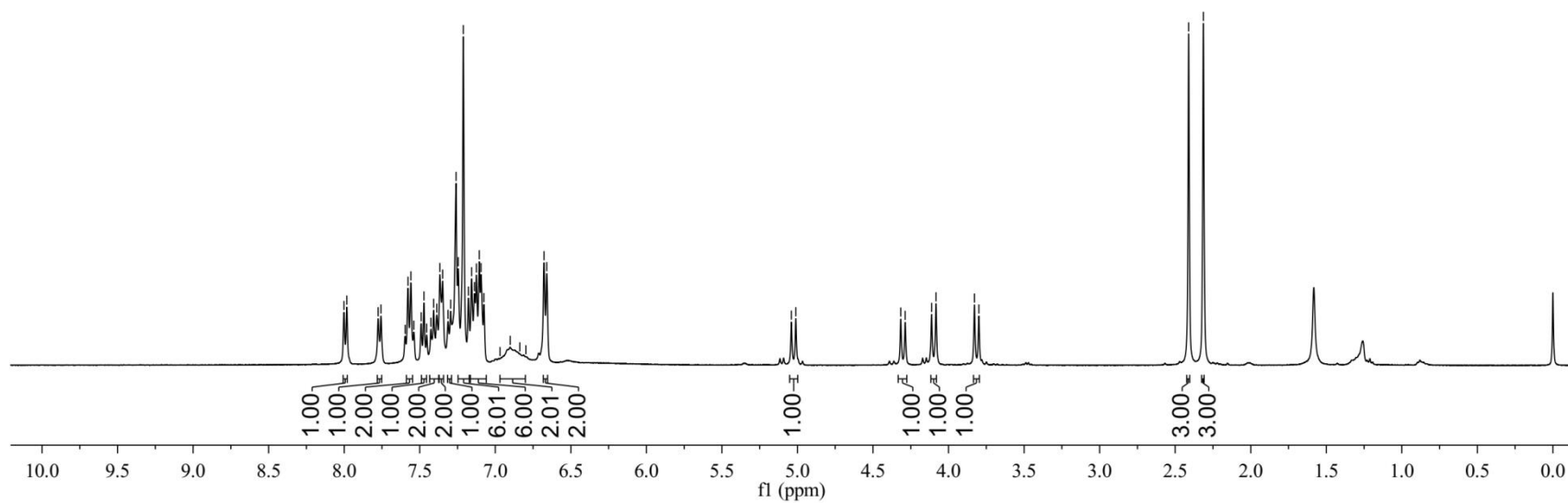
8.002
 7.983
 7.775
 7.757
 7.578
 7.559
 7.539
 7.491
 7.472
 7.426
 7.408
 7.387
 7.367
 7.348
 7.313
 7.295
 7.259
 7.245
 7.211
 7.178
 7.157
 7.138
 7.125
 7.106
 7.094
 7.075
 6.678
 6.659
 6.640
 5.011

4.316
 4.287
 4.112
 4.083
 3.829
 3.799

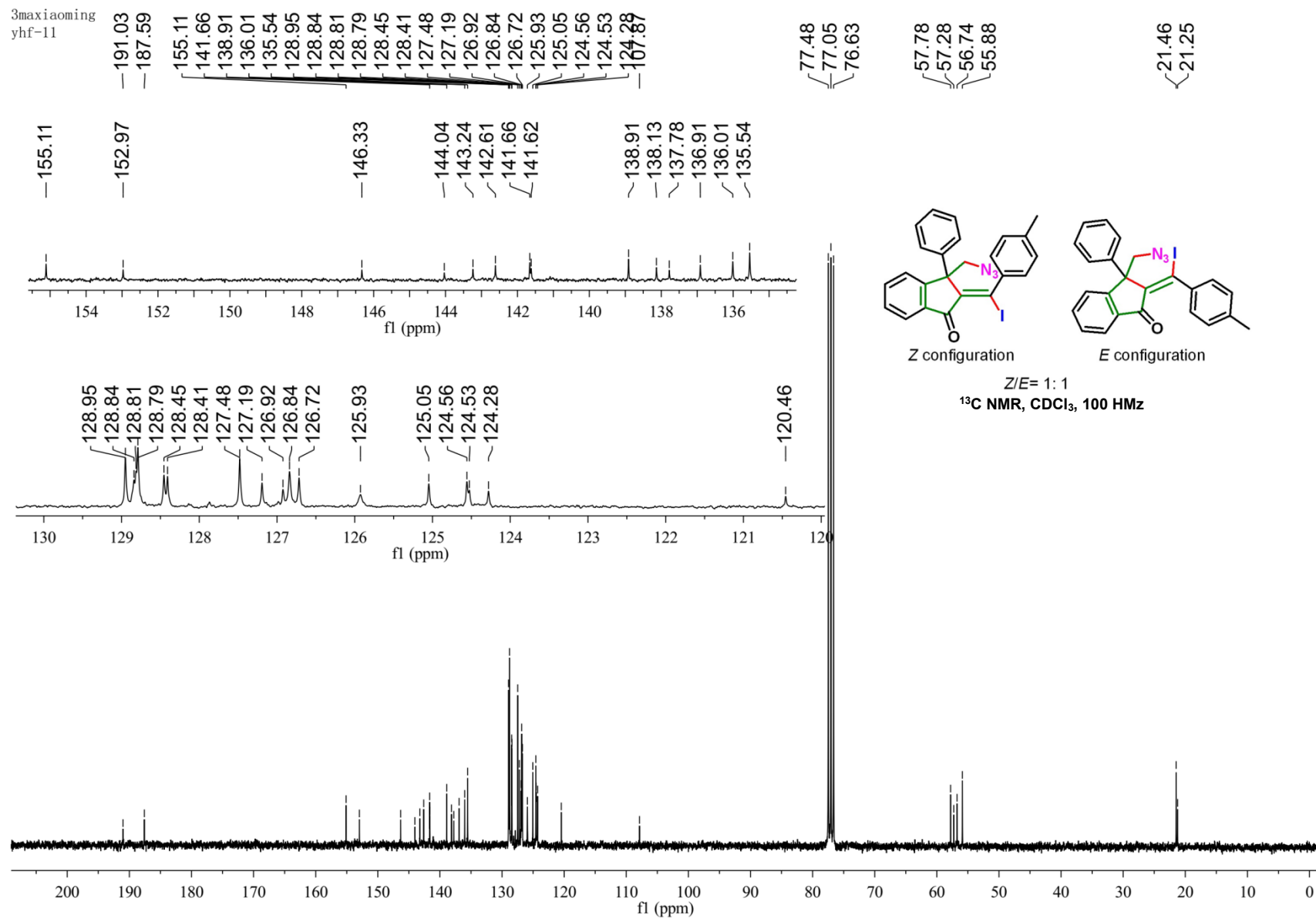
2.411
 2.313



Z/E = 1:1
¹H NMR, CDCl₃, 400 MHz



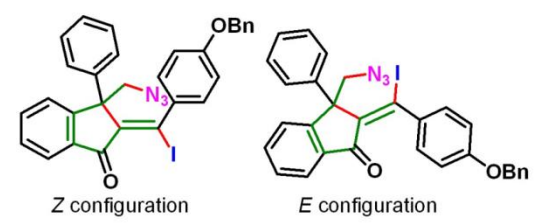
¹H NMR Spectrum of Compound 6d



$^{13}\text{C NMR Spectrum of Compound 6d}$

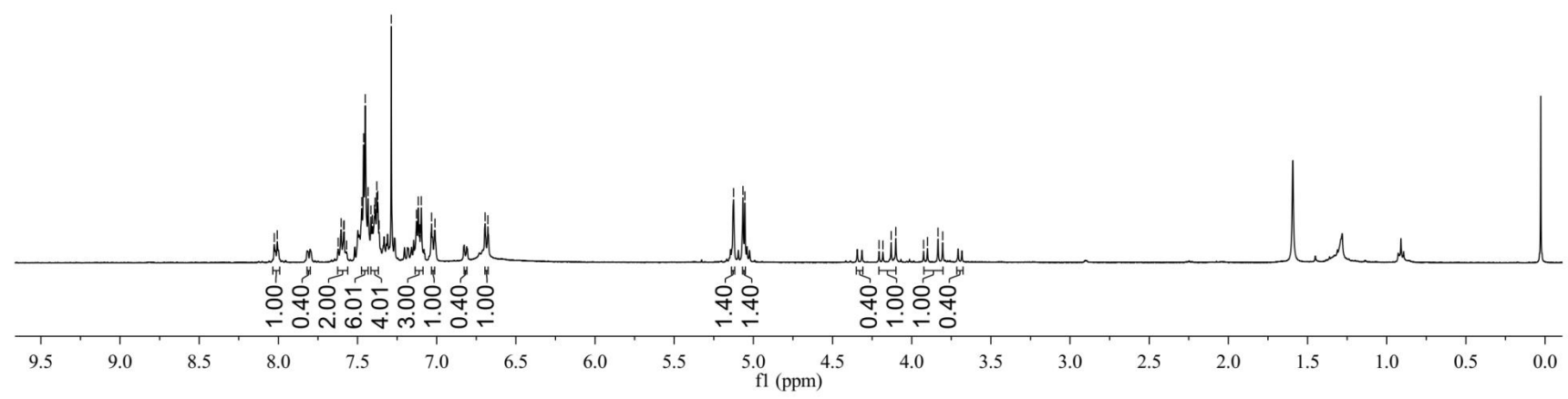
YHF-2.27-16.7.fid

8.026
8.007
7.473
7.461
7.451
7.434
7.415
7.393
7.389
7.378
7.372
7.287
7.127
7.116
7.097
7.033
6.994
5.925
5.066
5.054
4.206
4.182
4.130
4.101
3.925
3.901
3.834
3.804

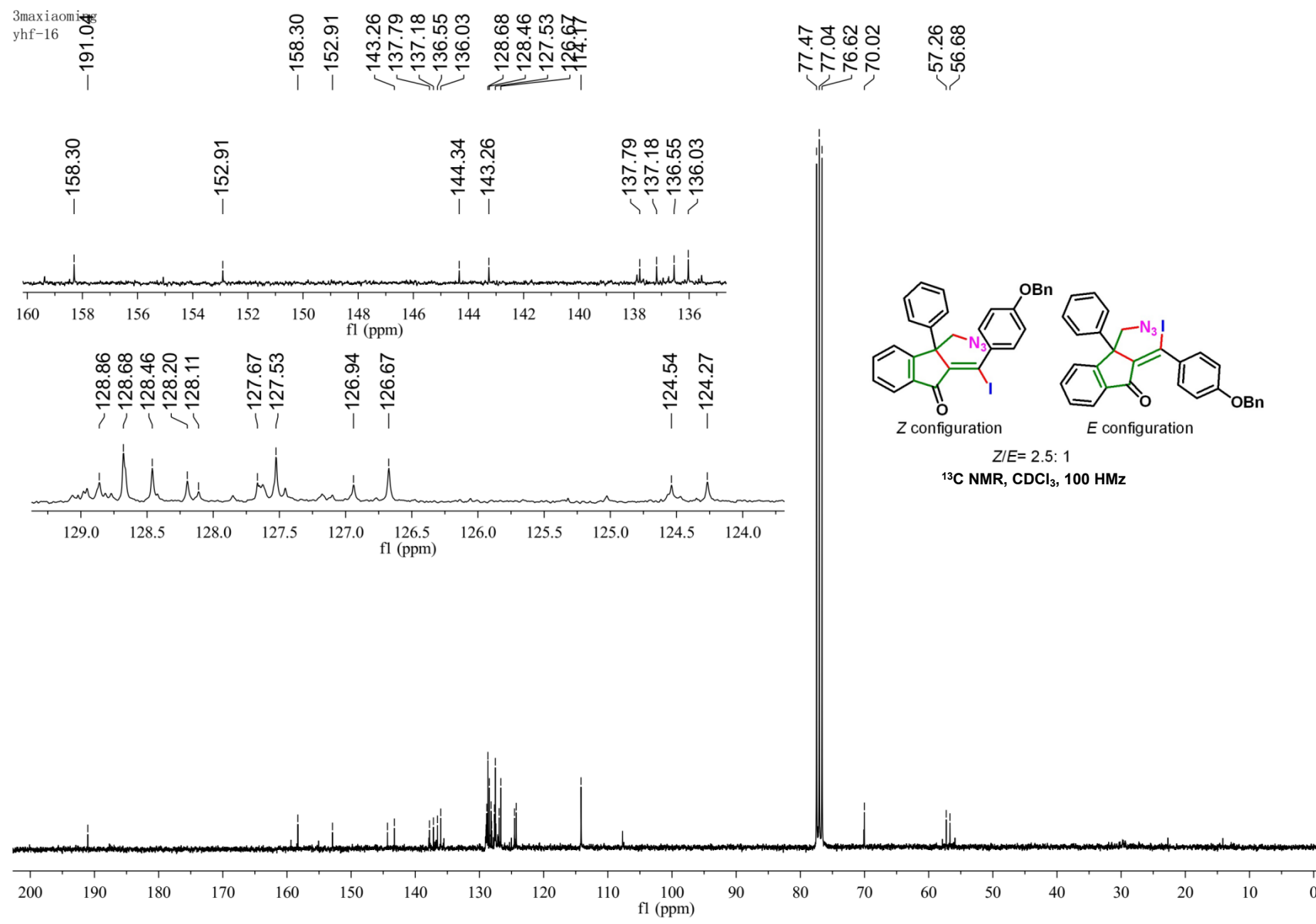


Z/E= 2.5: 1

¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 6c



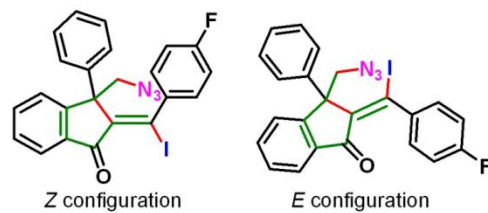
¹³C NMR Spectrum of Compound 6e

maxiaomings
yhf-17

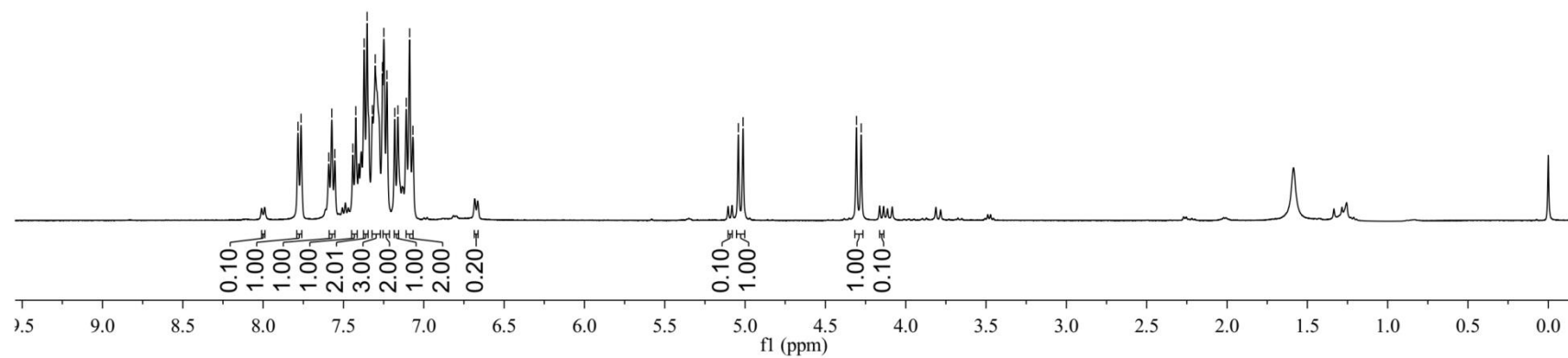
7.783
7.764
7.591
7.573
7.554
7.442
7.423
7.371
7.353
7.320
7.302
7.257
7.249
7.229
7.181
7.161
7.109
7.088

5.042
5.012

4.307
4.277



Z/E = 10:1
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 6f

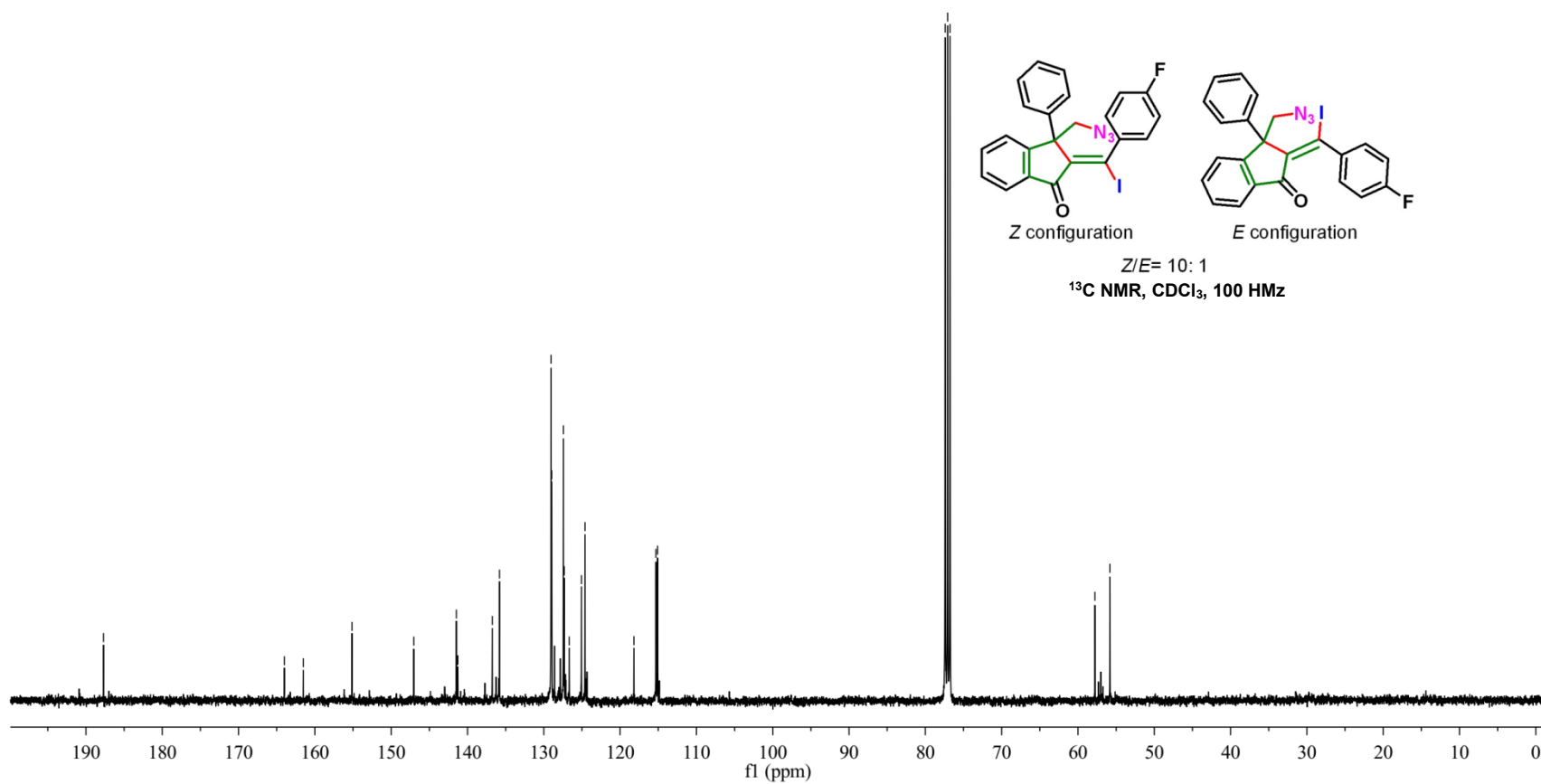
maxiaomin
YHF-17

— 187.696

~ 163.998
~ 161.521
~ 155.134
~ 147.036
~ 141.457
~ 141.300
~ 141.264
~ 136.756
~ 135.807
~ 129.041
~ 128.961
~ 127.436
~ 127.322
~ 126.659
~ 125.066
~ 124.601
~ 118.188
~ 115.309
~ 115.090

~ 77.396
~ 77.079
~ 76.761

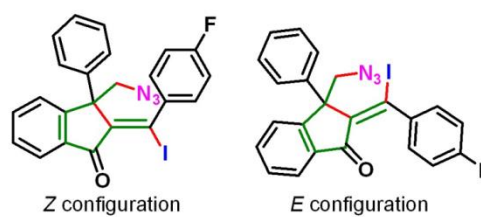
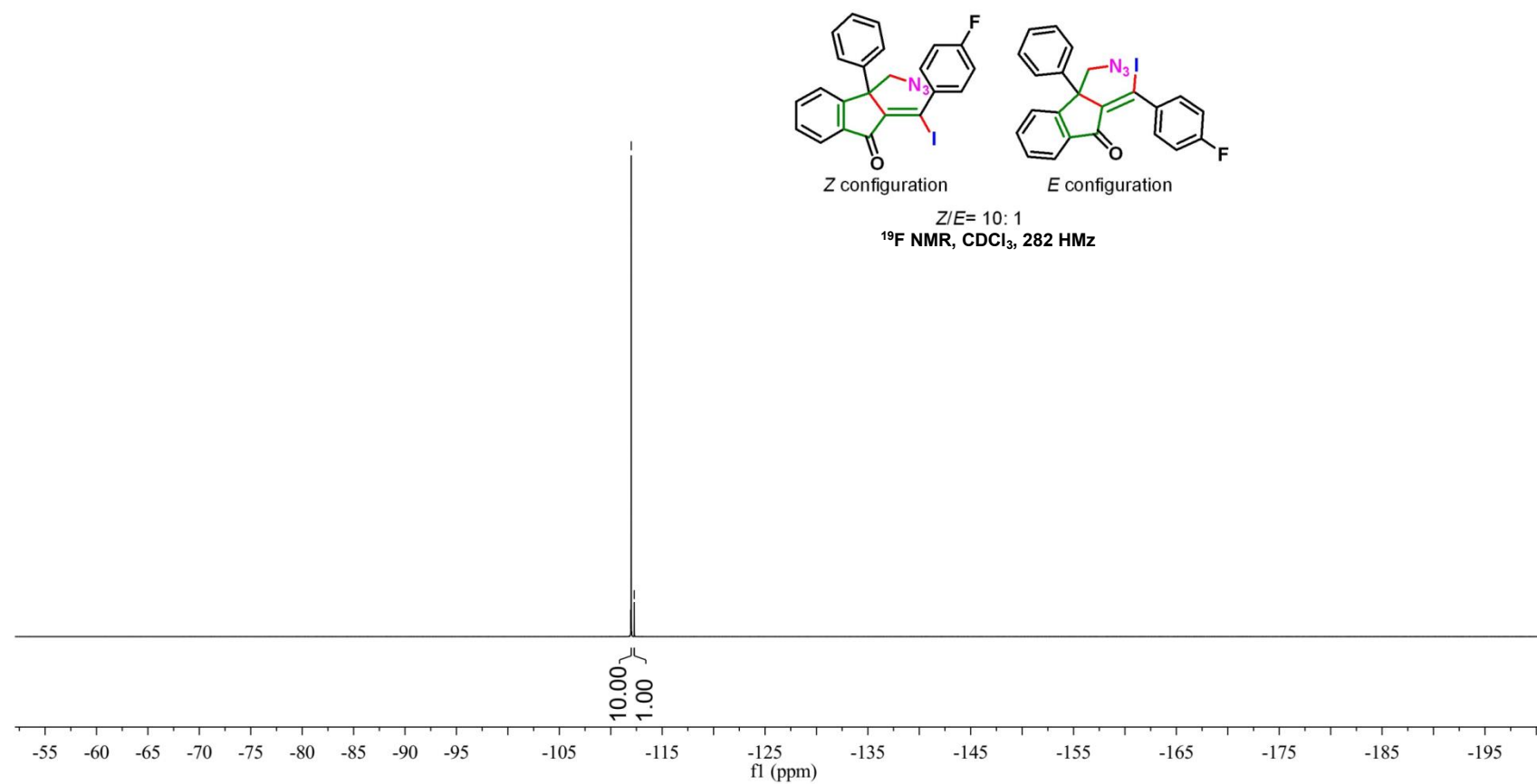
~ 57.771
~ 55.814



¹³C NMR Spectrum of Compound 6f

3maxiaoming
yhf17

-111.991
-112.285

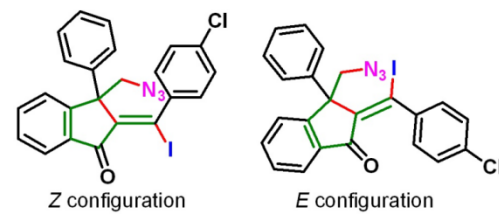


Z/E= 10: 1
 ^{19}F NMR, CDCl_3 , 282 MHz

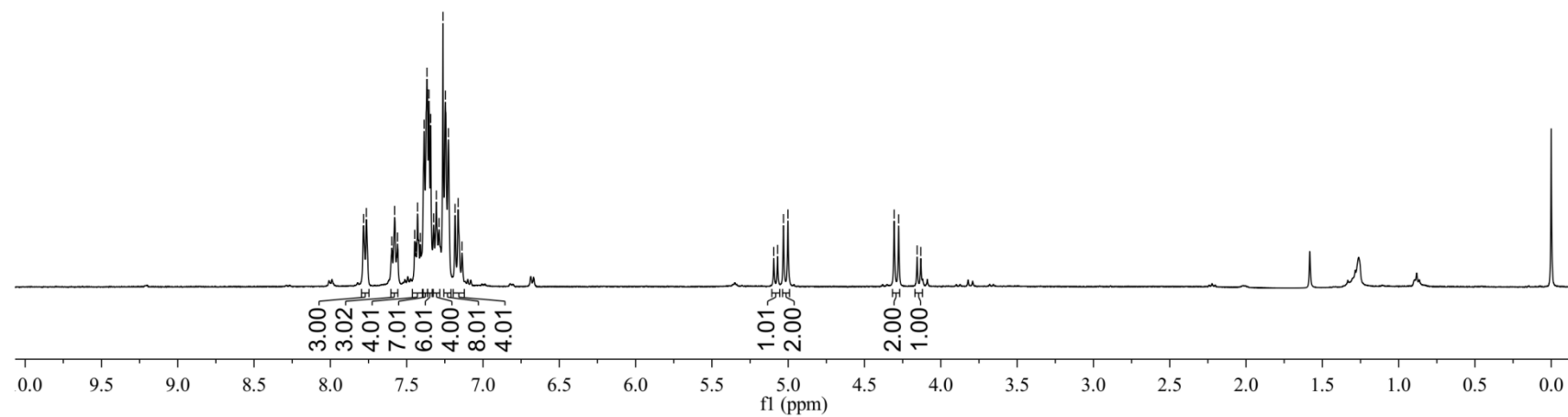
^{19}F NMR Spectrum of Compound 6f

maxiaoming12
yhf-18

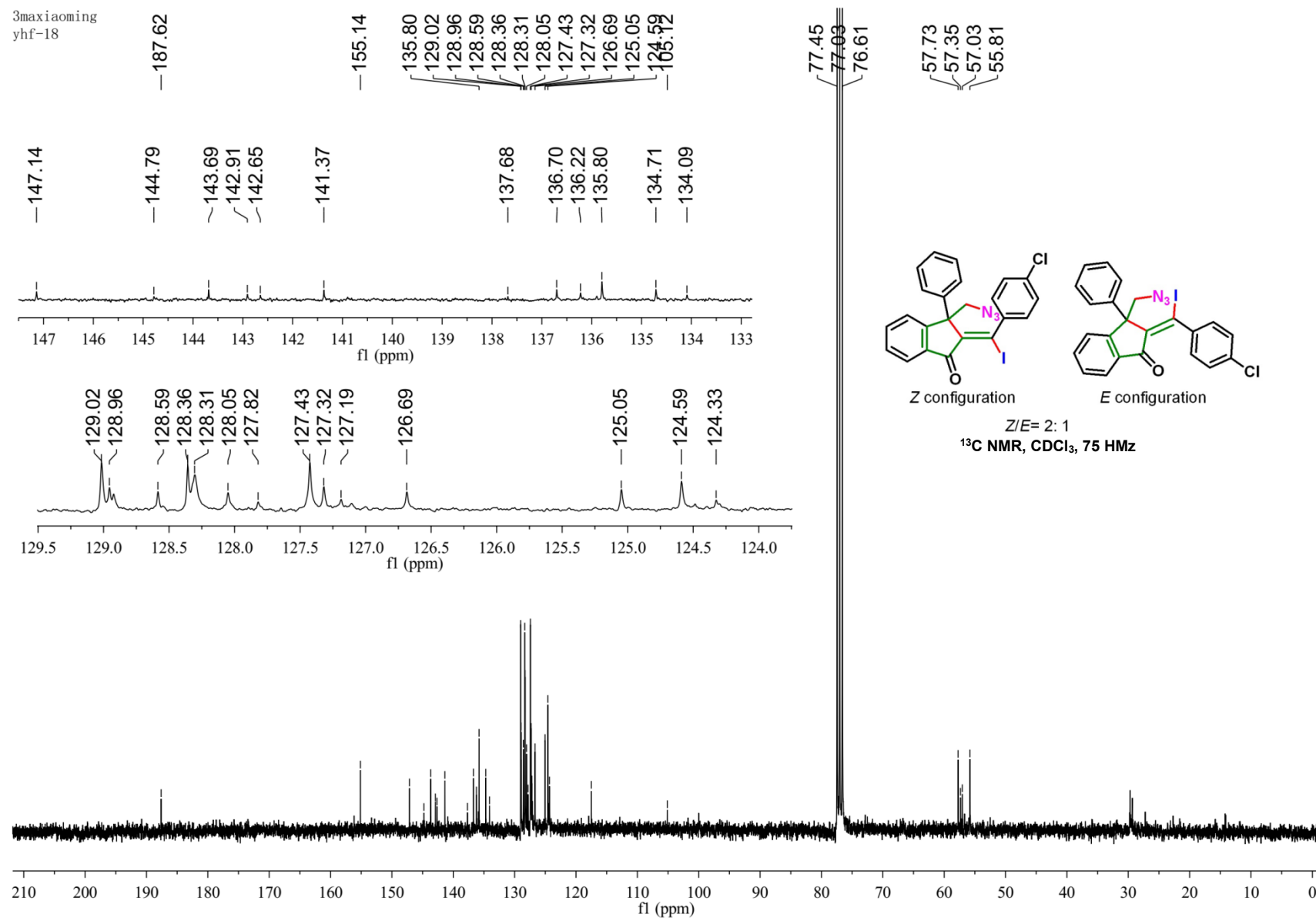
7.783
7.764
7.598
7.579
7.560
7.448
7.438
7.429
7.410
7.386
7.368
7.354
7.342
7.323
7.306
7.288
7.262
7.247
7.226
7.183
7.163
7.137
5.094
5.070
5.031
5.002
4.306
4.276
4.155
4.131



Z/E= 2: 1
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 6g



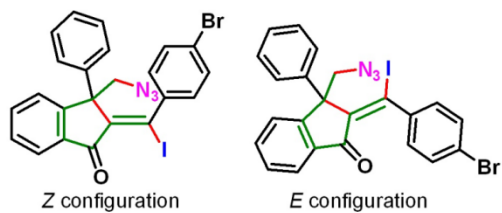
^{13}C NMR Spectrum of Compound 6g

maxiaomi
yhf-20

7.785
7.764
7.597
7.578
7.559
7.541
7.520
7.447
7.428
7.410
7.389
7.372
7.353
7.322
7.305
7.261
7.241
7.223
7.183
7.163

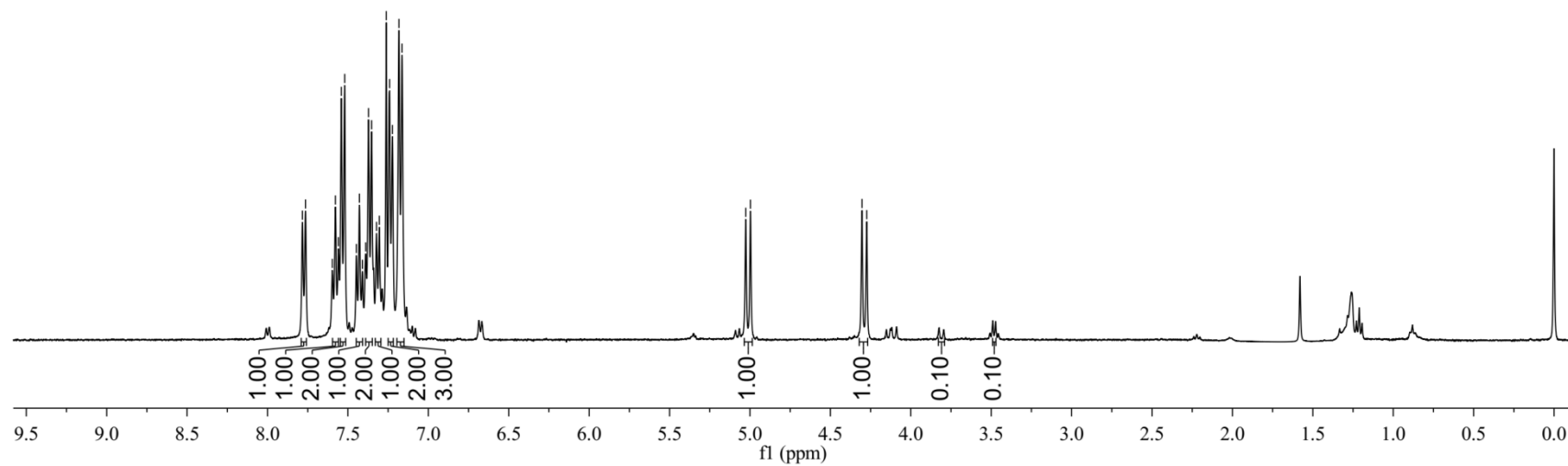
5.026
4.997

4.303
4.274



Z/E= 10:1

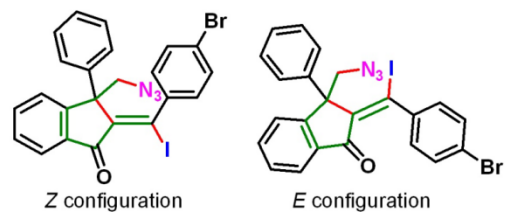
¹H NMR, CDCl₃, 400 MHz



¹H NMR Spectrum of Compound 6h

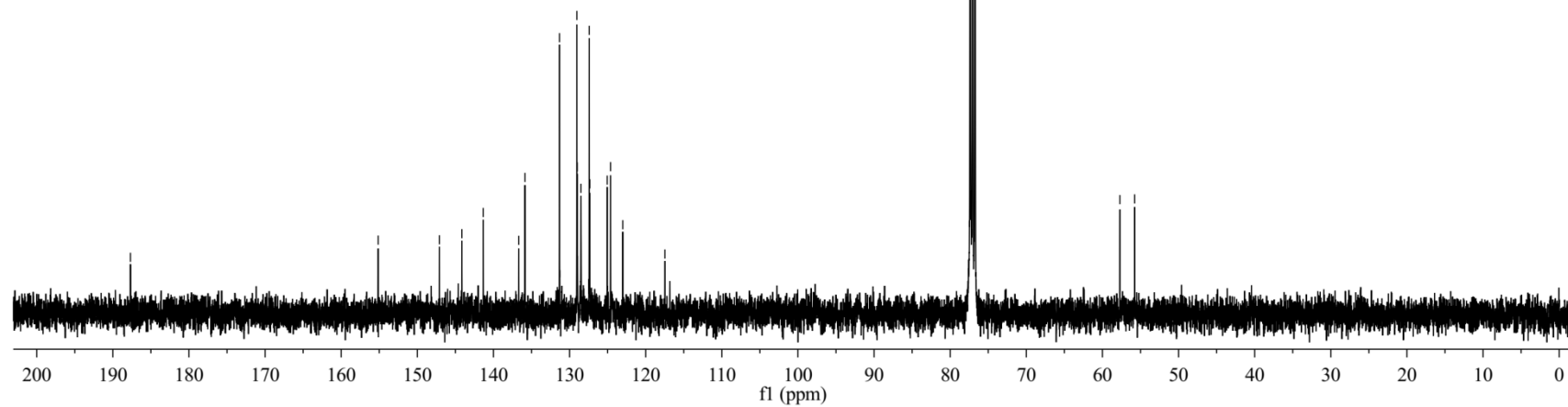
maxiaoming
yhf-20
—187.68

155.15
147.11
144.15
141.34
136.68
135.86
131.33
129.04
129.00
128.51
127.42
127.35
125.05
124.62
123.02
117.48
77.37
77.05
76.74
57.71
55.77



Z/E= 10: 1

¹³C NMR, CDCl₃, 100 HMz



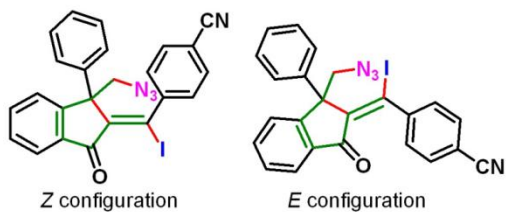
¹³C NMR Spectrum of Compound 6h

maxiaomilp
yhf-9

7.806
7.775
7.757
7.709
7.689
7.617
7.599
7.581
7.461
7.443
7.425
7.401
7.384
7.366
7.347
7.262
7.241
7.222
7.196
7.176

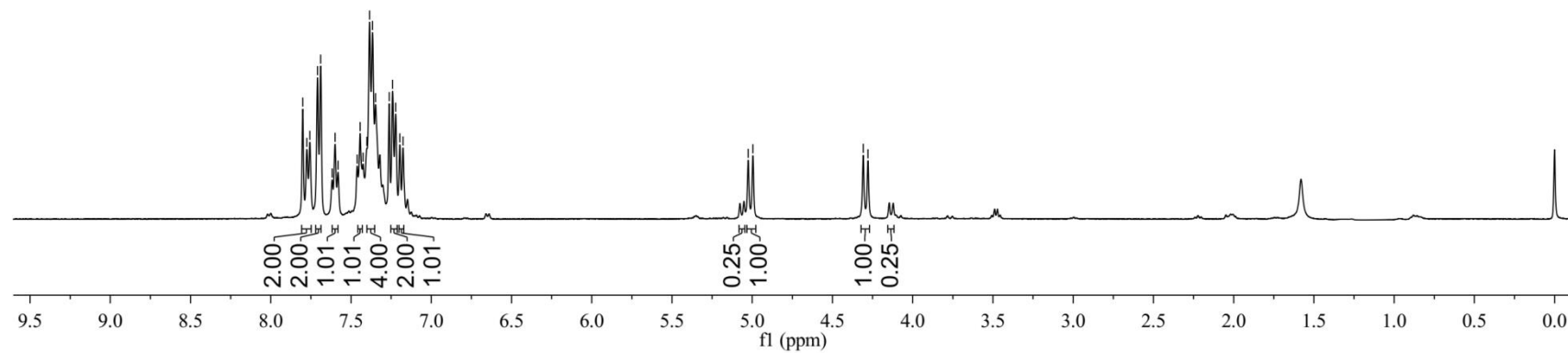
5.025
4.996

4.308
4.279



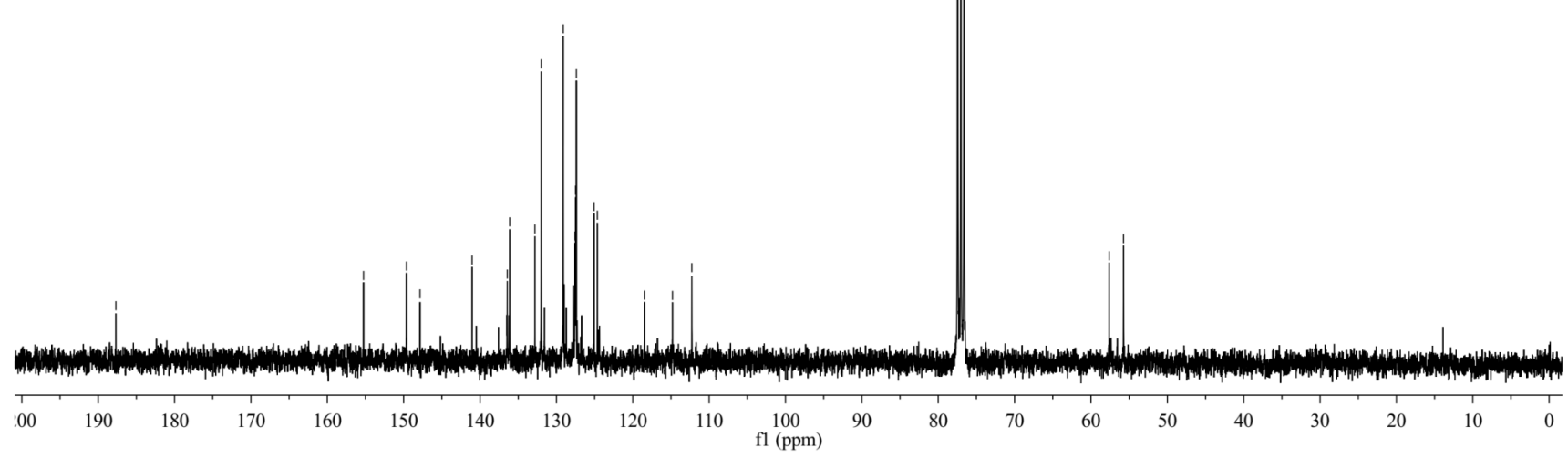
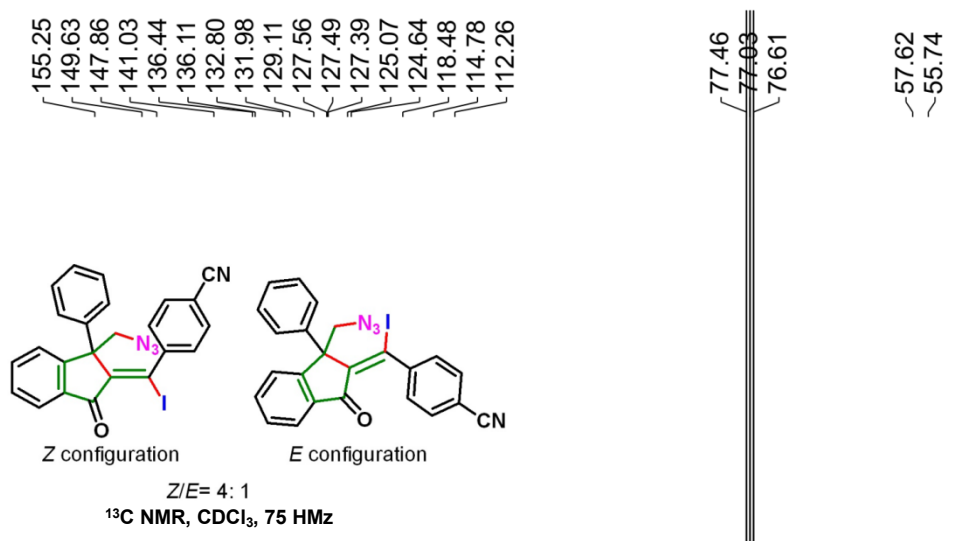
Z/E= 4: 1

¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 6i

3maxiaomin
yhf-9
—187.69



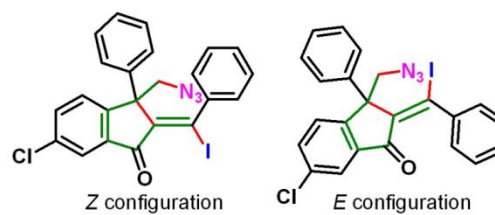
¹³C NMR Spectrum of Compound 6i

maxiaoming12
yhf-29

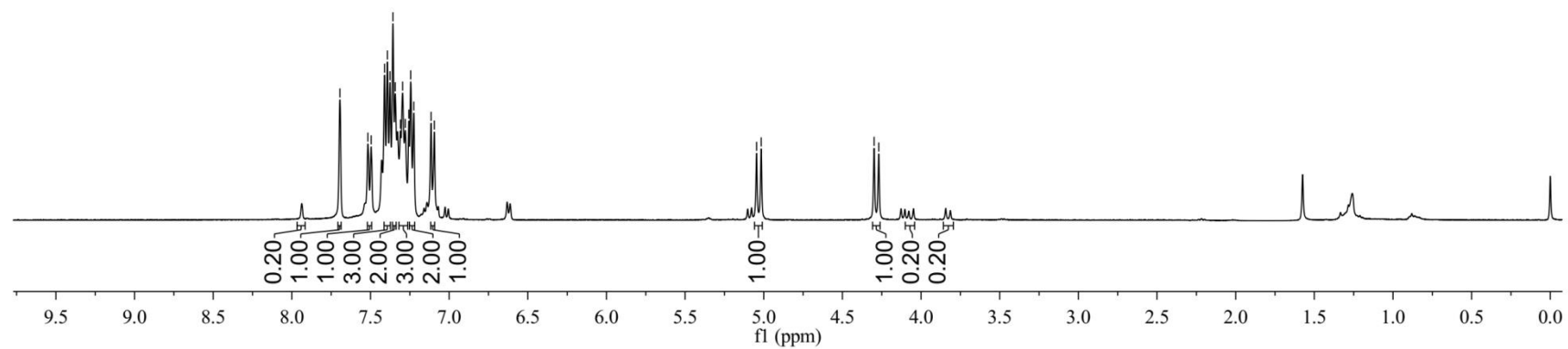
7.695
7.517
7.496
7.411
7.393
7.376
7.357
7.343
7.310
7.296
7.279
7.256
7.244
7.225
7.115
7.094

5.046
5.016

4.298
4.269

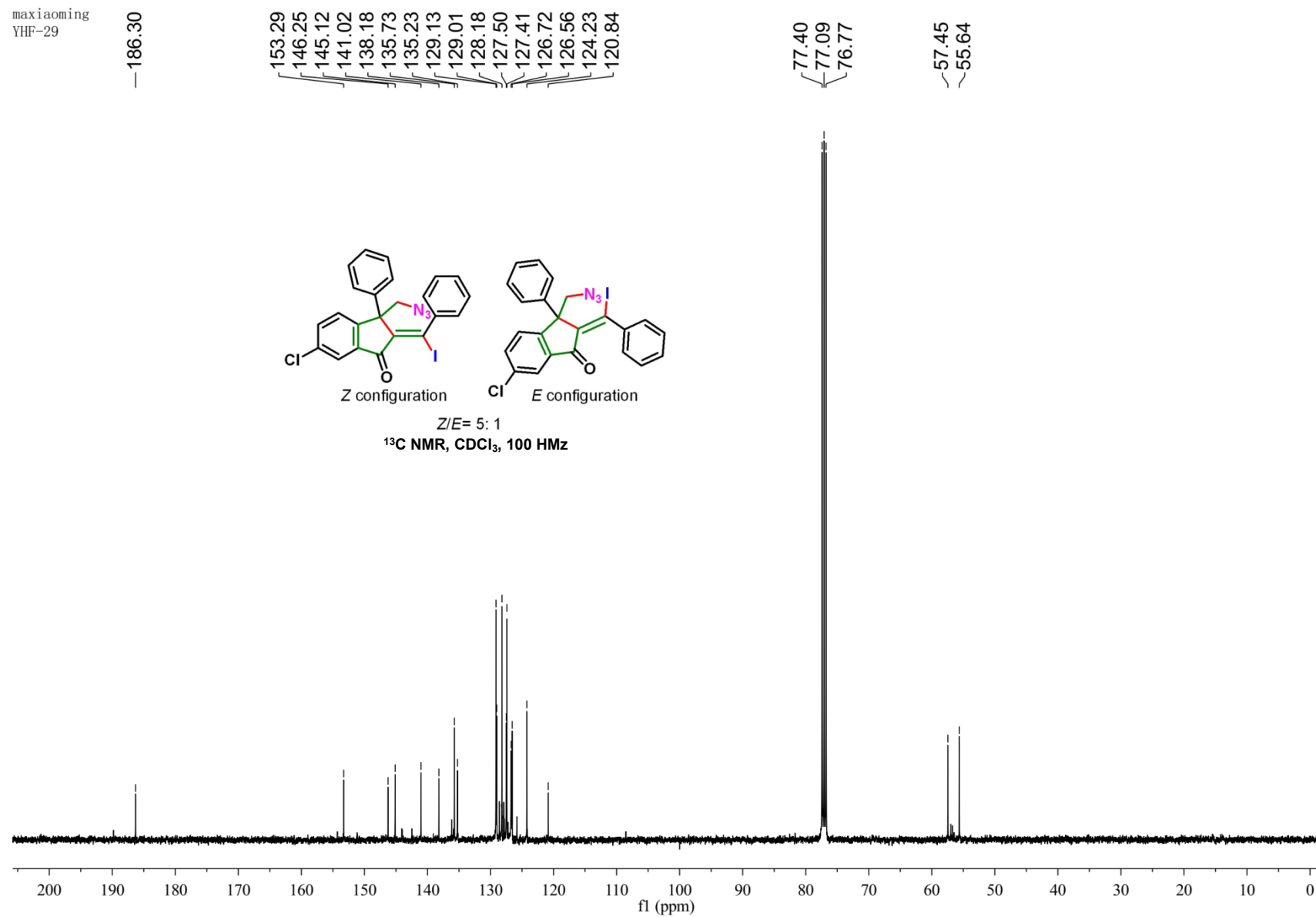


Z/E= 5:1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 6j

maxiaoming
YHF-29



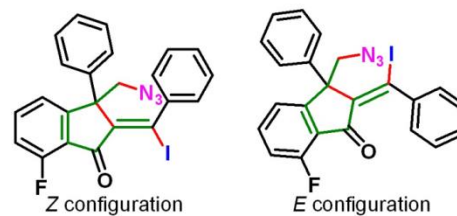
¹³C NMR Spectrum of Compound 6j

maxiaoming12
YHF

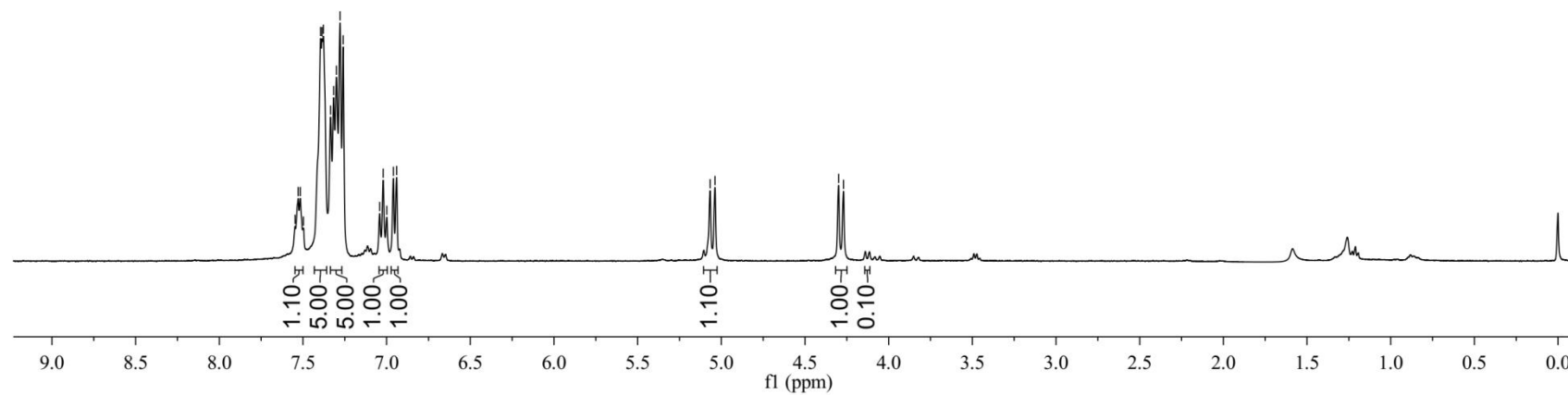
7.547
7.528
7.516
7.497
7.395
7.386
7.378
7.335
7.317
7.299
7.279
7.259
7.041
7.021
6.999
6.959
6.940

5.067
5.038

4.299
4.270



Z/E= 10: 1
¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 6k

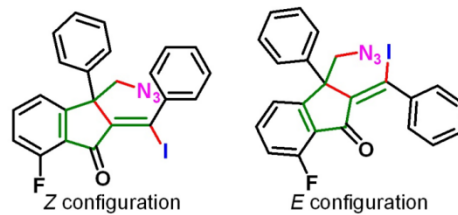
maxiaoming
YHF-28
— 184.163

160.844
158.196
157.173

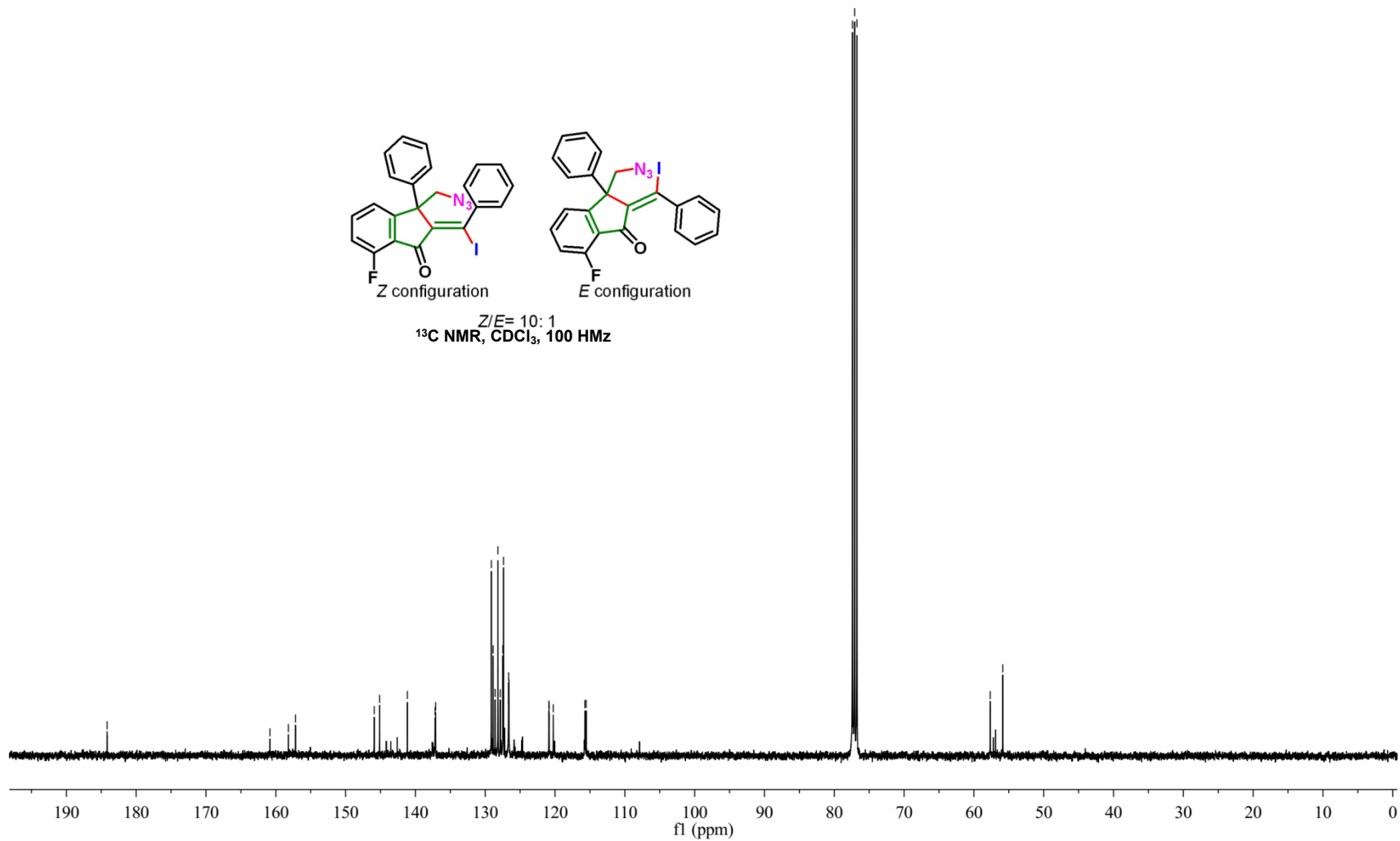
145.895
145.124
141.153
137.188
137.105
129.125
128.863
128.591
128.180
127.847
127.479
127.381
126.644
120.881
120.840
120.253
115.724
115.535

77.394
77.076
76.759

57.657
55.864



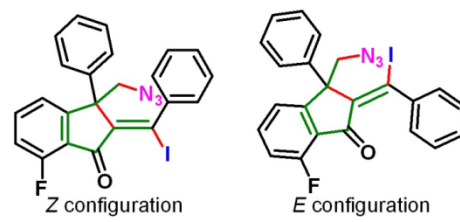
Z/E= 10:1
¹³C NMR, CDCl₃, 100 MHz



¹³C NMR Spectrum of Compound 6k

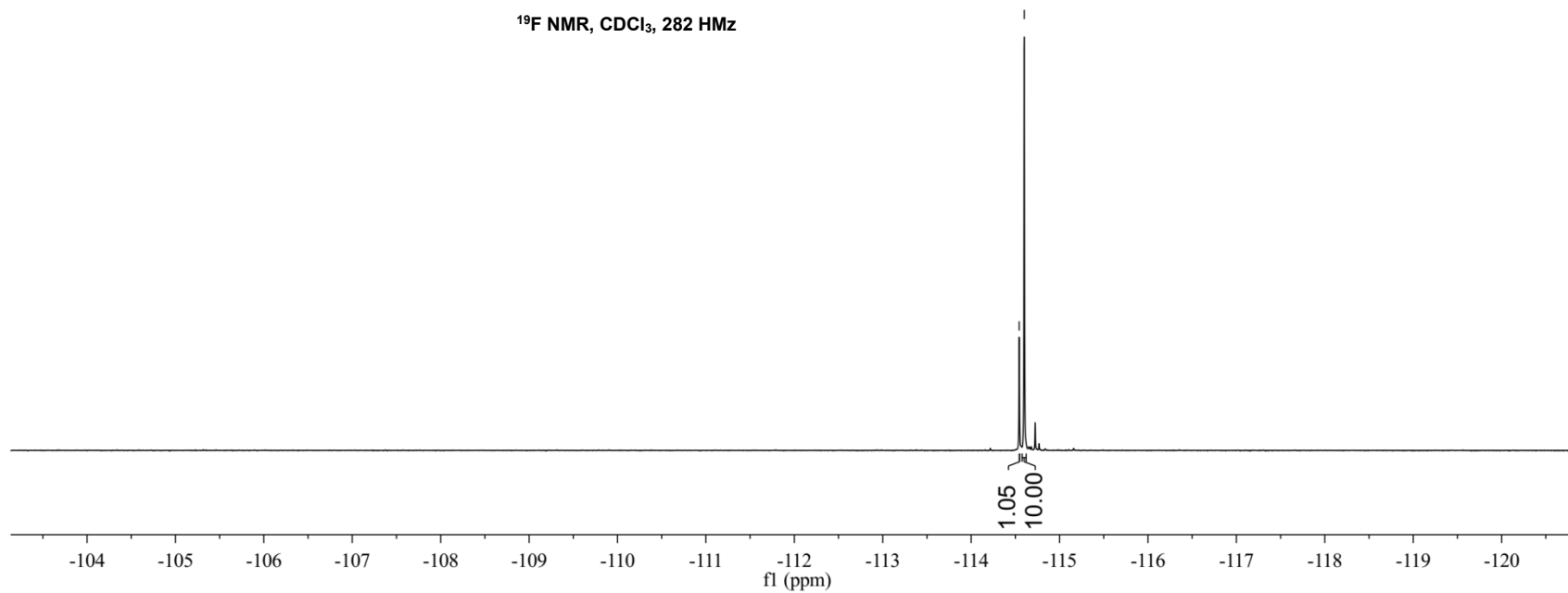
3maxiaoming
yhf28

-114.544
-114.600



Z/E= 10: 1

¹⁹F NMR, CDCl₃, 282 HMz



¹⁹F NMR Spectrum of Compound 6k

maxiaomin12
yhf-1

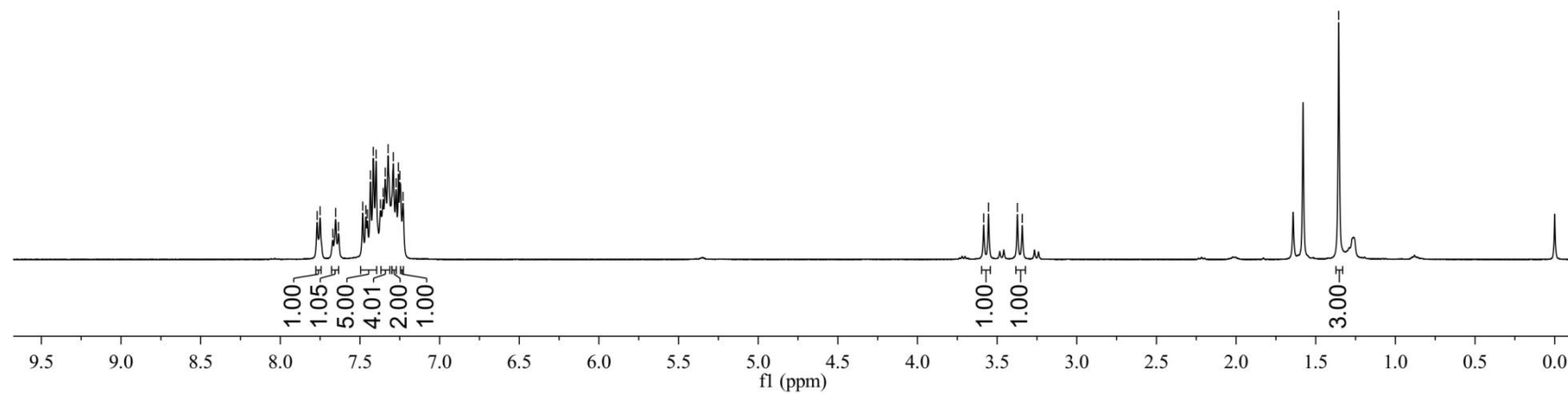
7.769
7.750
7.670
7.653
7.635
7.483
7.463
7.453
7.434
7.416
7.399
7.371
7.354
7.341
7.323
7.290
7.273
7.259
7.249
7.230

3.585
3.554
3.373
3.342

1.356

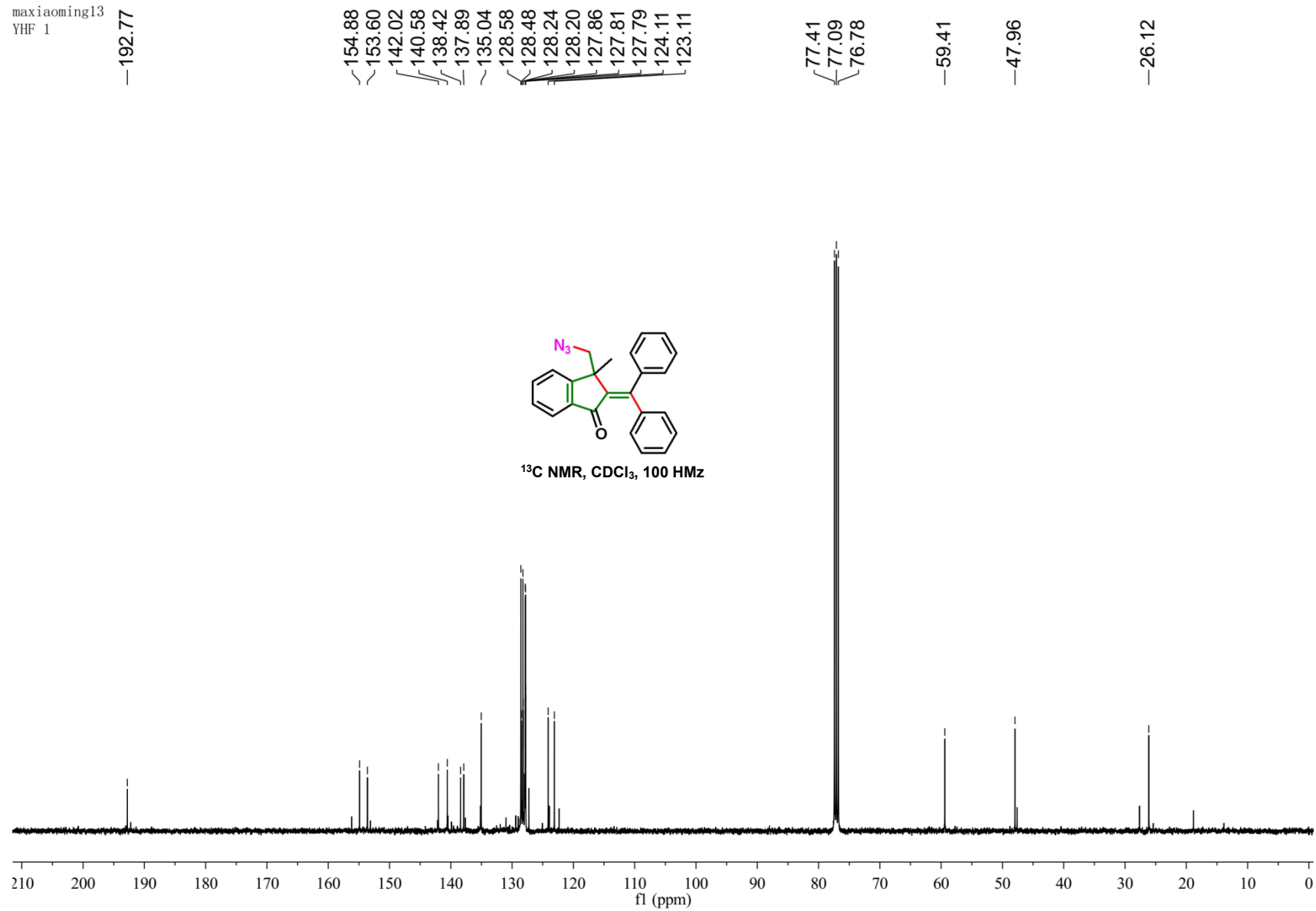


¹H NMR, CDCl₃, 400 HMz



¹H NMR Spectrum of Compound 7

maxiaoming13
YHF 1



¹³C NMR Spectrum of Compound 7