

Supporting Information

Copper-Catalyzed spirocyclization-oxytrifluoromethylation of alkynyl-bicyclo[1.1.0]butanes for spirobutyl quinolone synthesis

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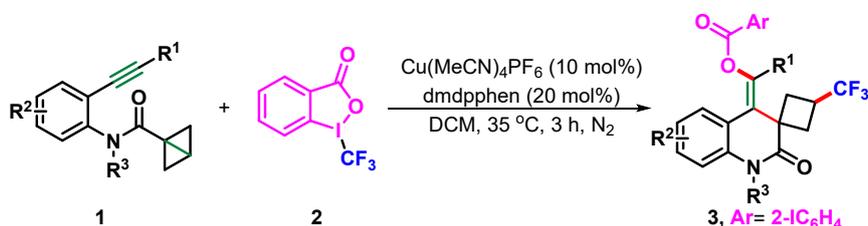
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General Information

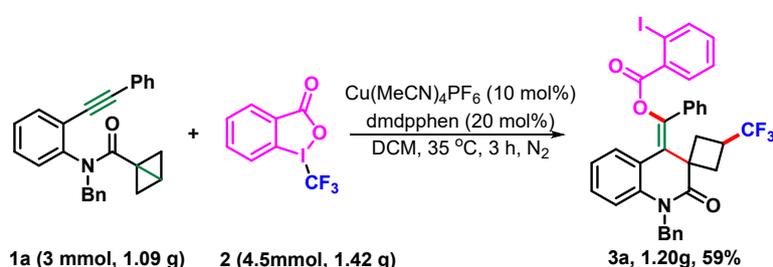
PE refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, as well as DCE refers to dichloroethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated. All reactions were heated by metal sand bath (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. Alkynyl-substituted BCBs **1** was prepared by previous report.¹⁻²

General procedure for the synthesis of compounds **3**



To a Schlenk tube (10 mL) were added alkynyl-substituted BCBs **1** (0.20 mmol, 1.0 equiv.), 1-(trifluoromethyl-1,2-benziodoxol-3(1*H*)-one **2** (1.5 equiv.), Cu(MeCN)₄PF₆ (10 mol%), Bathocuproine (**L1**, 20 mol%) and anhydrous DCM (2.0 mL) under nitrogen protection. The resulting mixture was stirring at 35 °C in metal sand bath for 3 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 **3** was obtained after column chromatography on silica gel (PE/EA=15/1 to 10/1 v/v).

Scale-up experiment for the preparation **3a**



To a Schlenk tube (50 mL) were added alkynyl-substituted BCB (**1a**, 1.09 g, 3.0 mmol, 1.0 equiv.), 1-(trifluoromethyl-1,2-benziodoxol-3(1*H*)-one **2** (1.42 g, 4.5 mmol, 1.5 equiv.), Cu(MeCN)₄PF₆ (112 mg, 10 mol%), Bathocuproine (216 mg, **L1**, 20 mol%) and anhydrous DCM (25 mL) under the protection with nitrogen. The resulting mixture was stirring at 35 °C in metal sand bath for 6 hours. After the

reaction was complete (by TLC), the reaction mixture was cooled to room temperature and diluted with DCM (50 mL) and H₂O (50 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 (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was finally purified by column chromatography on silica gel using a mixture of PE/EA as an eluent to yield the desired product **3a** (1.20 g, 59%).

Crystallographic Data of Compound **3u**

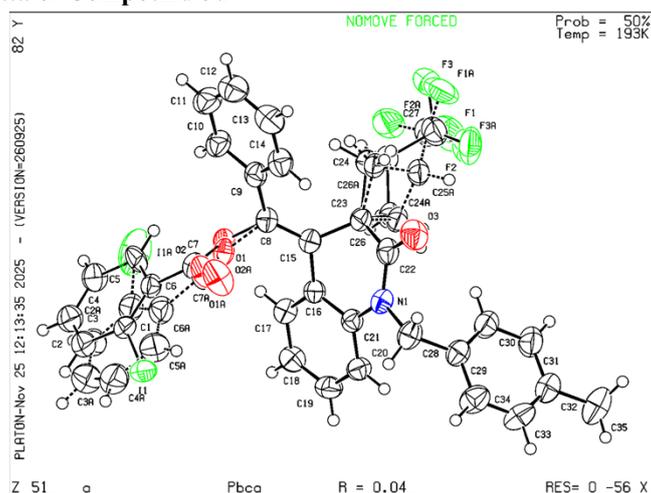


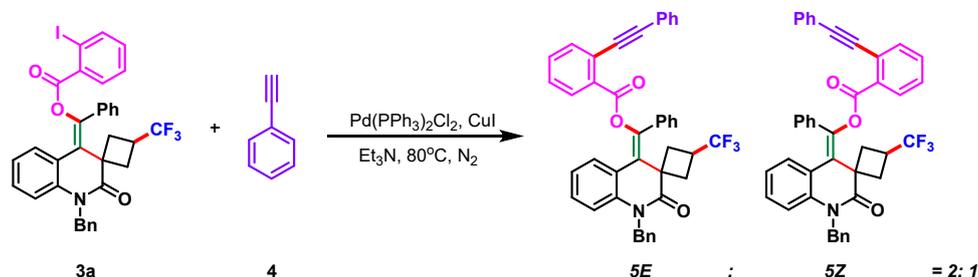
Fig. S1 ORTEP view of X-crystal structure of **3u** (CCDC number 2505747).

Table S1 Crystal data and structure refinement for **A**.

Identification code	A
CCDC	2505747
Empirical formula	C ₃₅ H ₂₇ F ₃ INO ₃
Formula weight	693.47
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	23.0963(5)
b/Å	9.7509(2)
c/Å	26.7974(6)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	6035.0(2)
Z	8
ρ _{calc} /cm ³	1.526
μ/mm ⁻¹	8.808
F(000)	2784.0
Crystal size/mm ³	0.13 × 0.11 × 0.08
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.628 to 136.67
Index ranges	-27 ≤ h ≤ 27, -10 ≤ k ≤ 11, -32 ≤ l ≤ 31
Reflections collected	49730
Independent reflections	5528 [R _{int} = 0.0519, R _{sigma} = 0.0258]
Data/restraints/parameters	5528/549/544
Goodness-of-fit on F ²	1.033
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0413, wR ₂ = 0.1059
Final R indexes [all data]	R ₁ = 0.0474, wR ₂ = 0.1094
Largest diff. peak/hole / e Å ⁻³	0.85/-0.54

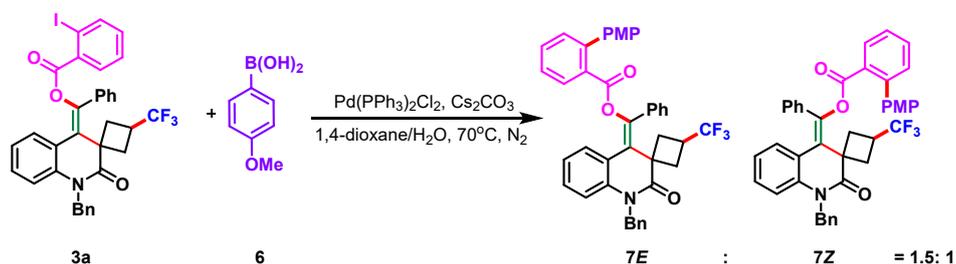
Procedure for recrystallization of compounds **3u**: the hexane was slowly added into the solution of **3u** in dichloromethane (with different concentration), then the dichloromethane was evaporated from the mixed solvent system at room temperature under dark and the crystals were obtained after a few days.

General procedure for the synthesis of compounds **5**



To a Schlenk tube were added **3a** (0.20 mmol, 1.0 equiv.), phenylacetylene **4** (1.2 equiv.), PdCl₂(PPh₃)₂ (2 mol%), CuI (2 mol%) and Et₃N (2.0 mL) under the protection with nitrogen. The resulting mixture was stirring on the heating mantle at 80 °C for 12 h. After the reaction was completed, the solution was concentrated in vacuo and purified by flash chromatography on silica gel (PE/EA= 15/1 v/v) to afford the desired product **5** (87.5 mg, 67% yield) as White solid; m.p:172 °C-173 °C; 87.5 mg, *E/Z*= 2: 1, 67% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.95-7.82 (m, 2H), 7.67-7.62 (m, 1H), 7.57-7.47 (m, 5H), 7.387.30 (m, 9H), 7.24 (s, 2H), 7.19-7.14 (m, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.93-6.87 (m, 2H), 5.42-5.02 (m, 2H), 3.09-2.82 (m, 1H), 2.72-2.59 (m, 1H), 2.39-2.15 (m, 2H), 1.86-1.63 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.9, 171.4, 163.3, 163.0, 143.9, 143.6, 137.9(2), 137.9(5), 137.1, 137.0, 134.3(1), 134.3(6), 134.2, 134.0, 132.5, 132.4, 131.8 (d, *J* = 4.5 Hz), 131.4, 131.0, 130.7, 130.5, 129.8 (d, *J* = 6.0 Hz), 129.0, 128.9 (d, *J* = 7.5 Hz), 128.8, 128.7 (d, *J* = 6.0 Hz), 128.5(4), 128.5(8), 128.4(3), 128.4(6), 128.3(9), 128.3(5), 128.0, 127.2, 127.1, 126.3, 126.2, 125.4, 124.3, 124.2, 124.1(2), 124.1(7), 123.5, 123.3, 123.2(9), 123.2(7), 116.2, 115.9, 95.1, 94.9, 88.8, 88.5, 47.2, 47.1, 44.2, 44.0, 33.9, 31.9 (q, *J* = 31.5 Hz), 30.6 (q, *J* = 30.0 Hz), 26.5; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.1, -73.7; HRMS (ESI) *m/z* calcd for C₄₂H₃₀F₃INNaO₃ [M+Na]⁺ 676.2075, found 676.2075.

General procedure for the synthesis of compounds **7**



To a Schlenk tube were added **3a** (0.20 mmol, 1.0 equiv.), 4-methoxyphenylboronic acid **6** (2.0 equiv.), PdCl₂(PPh₃)₂ (5 mol%), Cs₂CO₃ (10.0 equiv) and 1,4-dioxane/H₂O=4:1 (2.0 mL) under the protection with nitrogen. The resulting mixture was stirring on the heating mantle at 70 °C for 5 h. After the reaction was completed, the solution was concentrated in vacuo and purified by flash chromatography on silica gel (PE/EA= 15/1 v/v) to afford the desired product **7** (87.4 mg, 64% yield) White solid; m.p:176 °C-177

°C; 87.4 mg, *E/Z*= 1.5: 1, 64% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.74-7.55 (m, 2H), 7.50-7.45 (m, 1H), 7.42-7.32 (m, 5H), 7.30 (t, *J* = 5.3 Hz, 3H), 7.23-7.08 (m, 6H), 7.04-6.95 (m, 2H), 6.86-6.76 (m, 2H), 6.65-6.45 (m, 2H), 5.38-5.15 (m, 2H), 3.82-3.65 (m, 3H), 2.98-2.79 (m, 1H), 2.70-2.54 (m, 1H), 2.39-2.04 (m, 2H), 1.62 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.8, 171.3, 170.9, 170.1, 165.7, 165.6, 165.5, 165.4, 159.1, 159.0, 158.8(3), 158.8(1), 143.9, 143.6, 142.5(3), 142.5(0), 138.0, 137.9, 137.0, 136.8, 136.7, 134.0, 133.7, 132.6, 132.5, 132.1, 131.5(3), 131.5(1), 130.9(1), 130.9(7), 130.7 (d, *J* = 6.0 Hz), 130.2, 130.1 (d, *J* = 6.0 Hz), 130.0, 129.8 (d, *J* = 6.0 Hz), 129.7, 129.6 (d, *J* = 3.0 Hz), 129.4(8), 129.4(5), 129.4, 128.9(1), 128.8(5), 128.8, 128.6, 128.5(1), 128.5(9), 128.4(1), 128.4(9), 128.3, 127.9(1), 127.9(4), 127.3, 127.1, 127.0, 126.8, 126.7, 126.6, 126.2, 126.1, 124.9, 124.3, 123.2, 123.0, 122.8, 122.6, 116.1(2), 116.1(9), 116.0, 115.8, 113.7, 113.6, 113.5, 55.0, 54.9, 46.9, 46.7, 46.6, 43.9, 31.0 (q, *J* = 31.5 Hz), 30.5 (q, *J* = 31.5 Hz), 26.4; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₄₃H₃₂F₃INNaO₄ [M+Na]⁺ 706.2181, found 706.2181.

Optical Property-Based Ion Detection Using product 3a

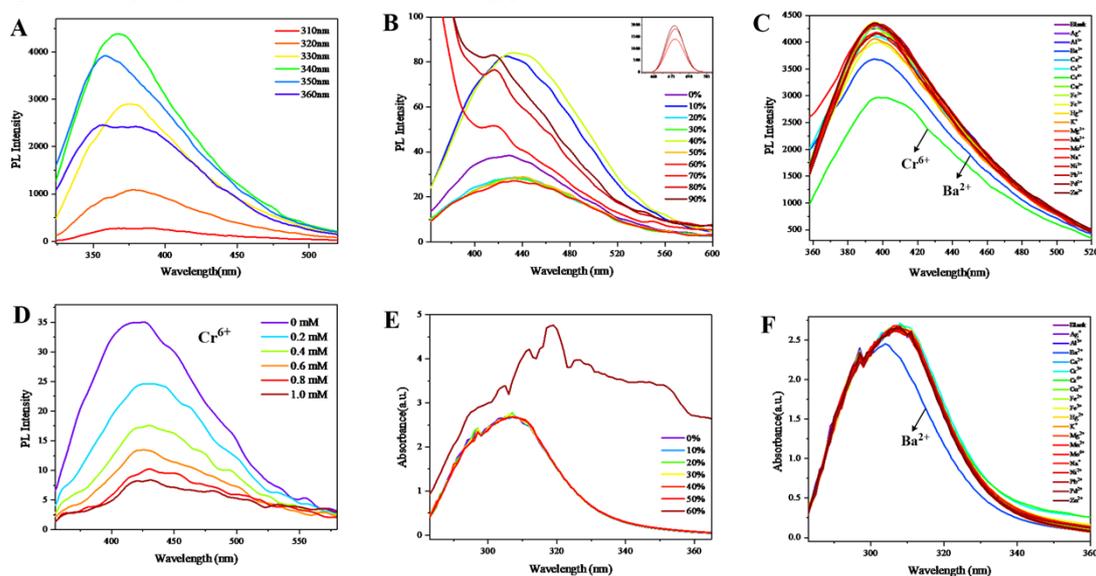


Fig. S2. A. PL spectroscopy of **3a** excited in different wavelengths (0.05mg/mL in THF). B and E. PL spectra and UV spectra of **3a** in different fractions of DI water (0.05mg/mL in THF/DI water mixture, excitation wavelength: 340nm). C and F. PL spectra and UV spectra of **3a** (0.05 mg/mL) in the presence of various metal ion solution (blank, Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Cr³⁺, Cr⁶⁺, Cu²⁺, Fe³⁺, Fe²⁺, Hg²⁺, K⁺, Mg²⁺, Mn²⁺, Mo⁶⁺, Na⁺, Ni²⁺, Pb²⁺, Pd²⁺, Zn²⁺) 10 μL under PBS buffer (20 mM pH 7.4) solution (THF). D. Concentration-dependent fluorescence spectra of **3a** (0.05 mg/mL) on the addition of various amounts of Cr⁶⁺ (0-1.0 mM) in PBS buffer (20 mM, pH 7.4) solution (THF).

As shown in Fig. S2-A, compound **3a** exhibits maximum photoluminescence (PL) intensity at 340 nm. A slight red shift in the emission peak is observed with increasing excitation wavelength. Using 340 nm as the excitation wavelength, the PL spectrum of **3a** and its response toward various metal ions were investigated. The fluorescence results indicate that upon gradual addition of water to the tetrahydrofuran (THF) solution, the PL intensity changes significantly. When the water fraction is between 10% and 30%, the emission intensity decreases noticeably and then stabilizes. As the water content increases to 40%, the strongest emission peak appears at 440 nm, accompanied by maximum PL intensity,

demonstrating characteristic aggregation-induced emission (AIE) behavior. Further increase in water content leads to fluorescence quenching (Fig. S2-B). As depicted in Fig. S2-C, introduction of Ba²⁺ and Cr⁶⁺ into the system of **3a** results in a significant decrease in PL intensity, indicating that both ions exert a fluorescence quenching effect on **3a**, with Cr⁶⁺ showing a more pronounced quenching efficiency. With increasing concentration of Cr⁶⁺, the emission intensity declines progressively (Fig. S2-D), suggesting that **3a** possesses a favorable concentration-dependent response to Cr⁶⁺. When the concentration of Cr⁶⁺ reaches 1.0 mM, the fluorescence quenching efficiency approaches 90%, demonstrating high detection sensitivity.

Fig. S2-E presents the ultraviolet-visible (UV-Vis) absorption spectra of the system under constant **3a** concentration and consistent solvent conditions. When the water fraction varies from 0 to 50%, the spectral profile and absorbance remain highly consistent, showing negligible changes. Upon increasing the water content to 60%, the UV-Vis spectrum alters markedly: the absorbance nearly doubles, and additional absorption peaks emerge. Further ion-selectivity tests via UV-Vis spectroscopy were conducted on **3a**, as shown in Fig. S2-F. After introducing various metal ions, including Ag⁺, Al³⁺, Ca²⁺, Cr³⁺, Cr⁶⁺, Cu²⁺, Fe³⁺, Fe²⁺, Hg²⁺, K⁺, Mg²⁺, Mn²⁺, Mo⁶⁺, Na⁺, Ni²⁺, Pb²⁺, Pd²⁺, and Zn²⁺, the UV-Vis absorption spectra show no substantial changes in either spectral shape or intensity, closely matching those of the blank sample. In contrast, upon addition of Ba²⁺, a distinct red shift in the absorption peak along with a decrease in absorption intensity is observed. This indicates that **3a** exhibits specific recognition toward Ba²⁺, highlighting its potential as a selective optical sensor for Ba²⁺ detection.

Radical inhibition experiments with TEMPO



To a 10 mL Schlenk tube were added **1a** (0.2 mmol, 1.0 equiv), 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one **2** (1.5 equiv), Cu(MeCN)₄PF₆ (10 mol%), Bathocuproine (**L1**, 20 mol%), 2,2,6,6-tetramethylpiperidin-1-yloxy (**TEMPO**) (3.0 equiv) and anhydrous DCM (2.0 mL). The mixture was stirred at 35 °C in a metal sand bath for 3 h. The desired product **3a** was not detected by TLC and the solution was detected by HR-MS analysis, and signal peaks at m/z 248.1238 for the adduct TEMPO-trifluoromethyl was found.

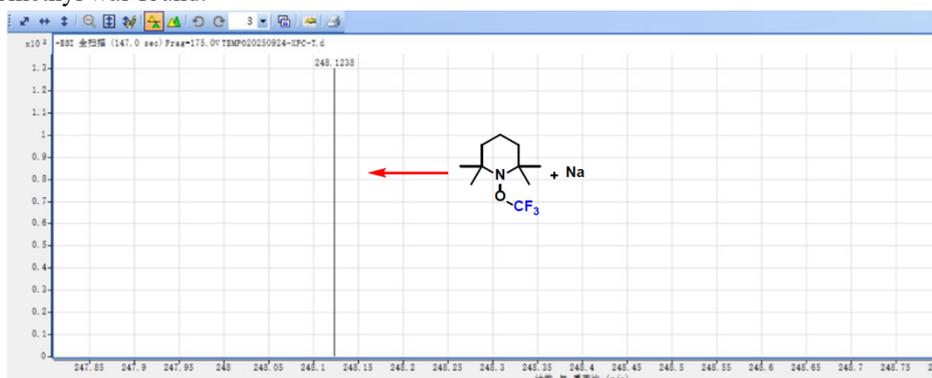
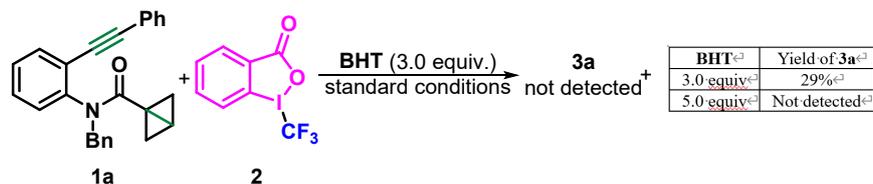


Fig. S2 HR-MS analysis for the adduct **8**

Radical inhibition experiments with BHT



To a 10 mL Schlenk tube were added **1a** (0.2 mmol, 1.0 equiv.), 1-trifluoromethyl-1,2-benziodoxol-3(1*H*)-one **2** (2.0 equiv.), Cu(MeCN)₄PF₆ (10 mol%), Bathocuproine (**L1**) (20 mol%), and 2,6-Di-tert-butylphenol (**BHT**, 5.0 equiv.) were suspended in anhydrous dichloromethane (DCM, 2 mL) under N₂ atmosphere. The resulting mixture was stirring at 35 °C in a metal sand bath for 3 h. The desired product **3a** was not detected by TLC.

*It should be made clear that with the incorporation of 3.0 equivalents of BHT, the alkynyl-substituted BCB **1a** was entirely consumed. The desired product **3a** was isolated at a yield of 29%.*

Radical clock experiment



To a Schlenk tube (10 ml) were added (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 equiv.), 1-TrifluoroMethyl-1,2-benziodoxol-3(1*H*)-one **2** (1.5 equiv.), Cu(MeCN)₄PF₆ (10 mol%), Bathocuproine (**L1**, 20 mol%) and anhydrous DCM (2.0 mL) under nitrogen protection. The resulting mixture was stirring at 35 °C in a metal sand bath for 3 hours. The products **10** was obtained with a 78% total yield after column chromatography on silica gel (PE/EA= 15/1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) (δ, ppm): 7.91 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 6.9 Hz, 1H), 7.27 (d, *J* = 4.4 Hz, 3H), 7.22-7.17 (m, 1H), 7.09-7.06 (m, 1H), 6.00 (t, *J* = 7.3 Hz, 1H), 4.39 (t, *J* = 6.6 Hz, 2H), 3.33-3.25 (m, 2H), 2.71-2.65 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) (δ, ppm): 166.6, 141.6, 141.4, 135.2, 132.7, 130.9 (d, *J* = 7.5 Hz), 128.5, 128.0, 127.6, 126.5, 94.0, 64.5, 34.9 (q, *J* = 30.0 Hz), 28.8; ¹⁹F NMR (282 MHz, CDCl₃) (δ, ppm): -63.5; HRMS (ESI) *m/z* calcd for C₁₉H₁₆F₃INaO₂[M+Na]⁺ 483.0045, found 483.0045.

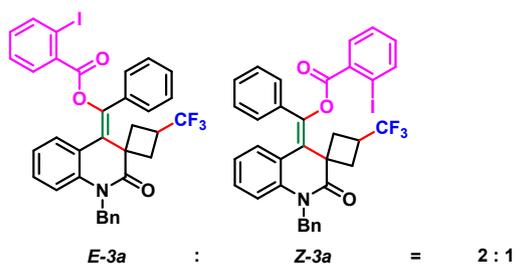
Reference

- X. Zou, Z.-R. Jia, Y.-T. Wang, P.-C. Xu, J.-W. Liu, S.-S. Zhu, and H.-D. Zuo, *Org. Lett.*, 2025, **27**, 13027-13033.
- Y.-T. Wang, X. Zou, P.-C. Xu, S.-H. Yan, Y. Zhang, J.-Y. Wang and H.-D. Zuo, *Chem. Commun.*, 2025, **61**, 19700-19703.

Characterization data

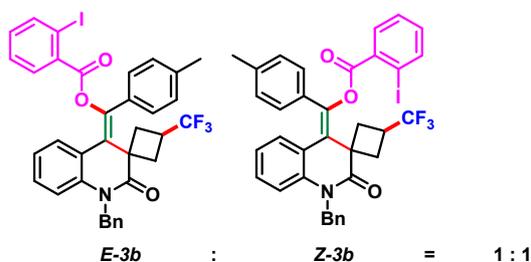
(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-

ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3a)



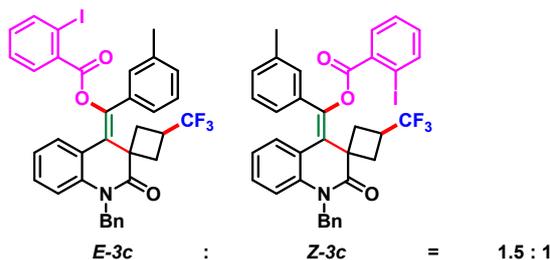
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:178 °C-179 °C; 96.4 mg, *E/Z*= 2: 1, 71% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.93 (d, J = 8.0 Hz, 1H), 7.79-7.72 (m, 1H), 7.68-7.63 (m, 1H), 7.58-7.50 (m, 2H), 7.44-7.40 (m, 3H), 7.39-7.33 (m, 3H), 7.28 (s, 1H), 7.27-7.19 (m, 2H), 7.15-7.09 (m, 2H), 6.98-6.91 (m, 2H), 5.38-5.17 (m, 2H), 3.12-2.81 (m, 1H), 2.71-2.58 (m, 1H), 2.43-2.11 (m, 2H), 1.78-1.59 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.8 , 171.3 , 163.4 , 143.5 , 143.3 , 141.5(7) , 141.5(5) , 137.8 , 137.7 , 137.0 , 136.9 , 134.0 , 133.9 , 133.7 , 133.0 , 131.1 , 131.0 , 130.1 , 129.9 (d, J = 6.0 Hz) , 129.0 (d, J = 6.0 Hz) , 128.9 (d, J = 4.0 Hz) , 128.4 (d, J = 9.0 Hz) , 128.3 , 128.2(0) , 128.2(8) , 127.9(9) , 127.9(8) , 127.1(2) , 127.1(7) , 126.4 , 126.3 , 125.1(1) , 125.1(6) , 124.8 , 123.9 , 123.3 , 123.1 , 116.2 , 116.0 , 94.3(1) , 94.3(9) , 46.9 , 46.8 , 44.1 , 44.0, 33.6, 31.3 (q, J = 32.0 Hz), 30.5 (q, J = 31.0 Hz), 26.5; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.1, -73.6; HRMS (ESI) m/z calcd for C₃₄H₂₅F₃INNaO₃ [M+Na]⁺ 702.0729, found 702.0729.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(p-tolyl)methyl 2-iodobenzoate (syn isomer, 3b)



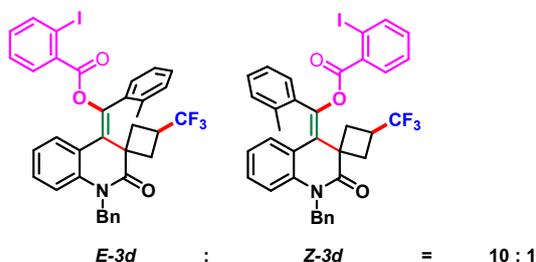
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:163 °C-164 °C; 101.2 mg, *E/Z*= 1: 1, 73% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.95-7.93 (m, 1H), 7.80-7.73 (m, 1H), 7.67-7.61 (m, 1H), 7.44-7.33 (m, 5H), 7.27 (d, J = 8.0 Hz, 2H), 7.24-7.20 (m, 3H), 7.16-7.09 (m, 2H), 6.97-6.92 (m, 2H), 5.37-5.22 (m, 2H), 3.05-2.82 (m, 1H), 2.72-2.61 (m, 1H), 2.39 (s, 3H), 2.25-2.15 (m, 2H), 1.86 1.67 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm) 171.9, 171.3, 163.7, 163.4, 143.7, 143.5, 141.6, 140.1, 140.0, 137.8(2), 137.8(5), 137.0, 136.9, 134.1 (d, J = 9.0 Hz), 133.0, 131.0 (d, J = 13.5 Hz), 130.8, 130.0, 129.2, 129.0, 128.9, 128.7 (d, J = 6.0 Hz), 128.2, 127.9, 127.1 (d, J = 7.5 Hz), 126.4, 126.3, 125.2, 124.6, 124.3, 124.1, 123.3, 123.0, 116.2, 115.9, 94.3, 46.0, 45.8, 44.1, 44.0, 33.6, 31.3 (q, J = 31.5 Hz), 30.5 (q, J = 31.5 Hz), 26.5, 21.5; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm) -73.2, -73.5; HRMS (ESI) m/z calcd for C₃₅H₂₇F₃INNaO₃ [M+Na]⁺ 716.0885, found 716.0884.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(m-tolyl)methyl 2-iodobenzoate (syn isomer, 3c)



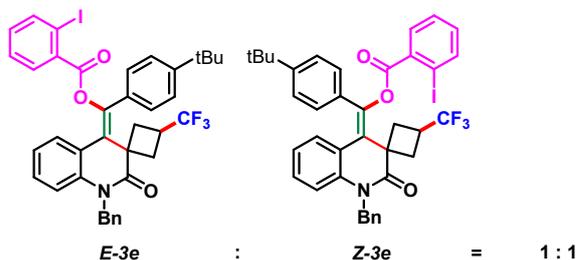
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:168 °C-169 °C; 96.6 mg, *E/Z*= 1.5: 1, 69% yield; ¹H NMR (400 MHz, CDCl₃) *E*+ *Z* isomer (δ, ppm): 7.94 (d, *J* = 8.0 Hz, 1H), 7.81-7.72 (m, 1H), 7.67-7.61 (m, 1H), 7.37-7.32 (m, 5H), 7.28 (s, 2H), 7.24-7.21 (m, 2H), 7.16 – 7.11 (m, 2H), 7.07-7.01 (m, 1H), 6.99-6.88 (m, 2H), 5.29 (d, *J* = 35.4 Hz, 2H), 2.95-2.81 (m, 1H), 2.71-2.61 (m, 1H), 2.40 (s, 3H), 2.26-2.16 (m, 2H), 1.73-1.61 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E*+ *Z* isomer (δ, ppm): 171.8, 171.3, 163.7, 163.4, 143.6, 143.5, 141.6, 141.5, 138.2, 137.9(8), 137.9(6), 137.8, 137.0, 136.9, 134.1, 134.0, 133.8, 133.5, 133.0, 131.0, 130.7 (d, *J* = 9.0 Hz), 128.9(4) (d, *J* = 9.0 Hz), 128.9(6) (d, *J* = 4.5 Hz), 128.8 (d, *J* = 4.5 Hz), 128.5, 128.3, 128.2, 128.1, 127.9(7), 127.9(5), 127.3, 127.2, 127.1(9), 127.1(5), 126.9, 126.8, 126.4, 126.3, 125.1, 124.8, 124.6, 124.0, 123.2, 123.0, 116.2, 115.9, 94.3(9), 94.3(6), 47.0, 46.9, 44.1, 44.0, 33.6, 31.9, 31.0 (q, *J* = 31.5 Hz), 30.1 (q, *J* = 31.5 Hz), 27.2, 21.4; ¹⁹F NMR (282 MHz, CDCl₃) *E*+ *Z* isomer (δ, ppm) -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₅H₂₇F₃INNaO₃ [M+Na]⁺ 716.0885, found 716.0885.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(o-tolyl)methyl 2-iodobenzoate (syn isomer, 3d)



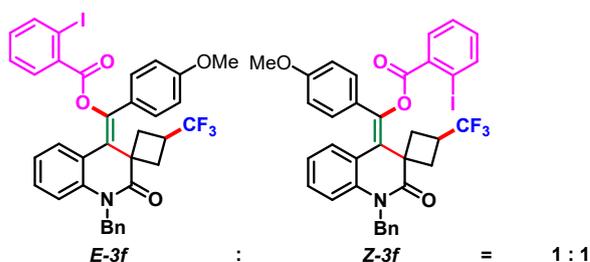
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:176 °C-177 °C; 83.2 mg, *E/Z*= 10: 1, 60% yield; ¹H NMR (400 MHz, CDCl₃) *E*+ *Z* isomer (δ, ppm): 7.96-7.93 (m, 1H), 7.80-7.73 (m, 1H), 7.66-7.60 (m, 1H), 7.47-7.41 (m, 2H), 7.40-7.33 (m, 3H), 7.28 (s, 1H), 7.26-7.20 (m, 2H), 7.16-7.10 (m, 2H), 6.96-6.92 (m, 4H), 5.37-5.21 (m, 2H), 3.84 (s, 3H), 3.03-2.82 (m, 1H), 2.68-2.61 (m, 1H), 2.31-2.12 (m, 2H), 1.87-1.69 (m, 1H); ¹³C NMR *E*+ *Z* isomer (150 MHz, CDCl₃) (δ, ppm): 171.6, 163.1, 143.1, 141.3, 137.7(1), 137.7(8), 137.3, 136.8, 134.5, 132.9, 132.7, 132.4, 130.4, 130.2, 130.0 (d, *J* = 6.0 Hz), 128.9 (d, *J* = 16.5 Hz), 128.5, 128.3, 127.8, 127.1, 126.5, 126.4, 126.3, 125.9, 123.4, 116.1, 115.9, 94.0, 46.7, 46.6, 43.9, 33.8, 31.1 (q, *J* = 31.5 Hz), 25.5, 19.8; ¹⁹F NMR (282 MHz, CDCl₃) *E*+ *Z* isomer (δ, ppm) -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₅H₂₇F₃INNaO₃ [M+Na]⁺ 716.0885, found 716.0885.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(4-(tert-butyl)phenyl)methyl 2-iodobenzoate (syn isomer, 3e)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:193 °C-194 °C; 66.2 mg, *E/Z*= 1: 1, 45% yield; ¹H NMR (400 MHz, CDCl₃) *E+ Z* isomer (δ, ppm): 7.95-7.90 (m, 1H), 7.83-7.75 (m, 1H), 7.66-7.61 (m, 1H), 7.45-7.41 (m, 3H), 7.36-7.31 (m, 3H), 7.28 (s, 1H), 7.24-7.16 (m, 3H), 7.13-7.08 (m, 2H), 6.95-6.90 (m, 2H), 5.35-5.23 (m, 2H), 3.01-2.80 (m, 1H), 2.68-2.59 (m, 1H), 2.39-2.10 (m, 2H), 1.61 (s, 1H), 1.32 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) *E+ Z* isomer (δ, ppm): 171.9, 171.4, 163.7, 163.4, 153.2, 153.1, 143.7, 143.5, 142.3, 142.2, 141.6, 137.8, 137.0, 136.9, 134.1, 134.0, 133.6, 131.2, 131.1, 130.9, 130.7, 129.8 (d, J = 7.5 Hz), 129.7, 129.1, 129.0 (d, J = 9.0 Hz), 128.9(8), 128.9(6), 128.7 (d, J = 6.0 Hz), 128.5, 128.2 (d, J = 6.0 Hz), 127.9, 127.3, 127.1, 127.0, 126.8, 126.6, 126.5, 126.3, 125.5, 125.4, 125.3, 125.2, 125.1, 125.0, 124.7, 124.4, 124.2, 123.3, 123.1, 116.2, 115.9, 94.4, 46.9, 46.7, 44.1, 44.0, 34.9, 31.3, 31.2, 31.0 (q, J = 31.5 Hz), 30.5 (q, J = 31.5 Hz), 26.4; ¹⁹F NMR (282 MHz, CDCl₃) *E+ Z* isomer (δ, ppm): -73.1, -73.5; HRMS (ESI) m/z calcd for C₃₈H₃₃F₃INNaO₃ [M+Na]⁺ 758.1355, found 758.1353.

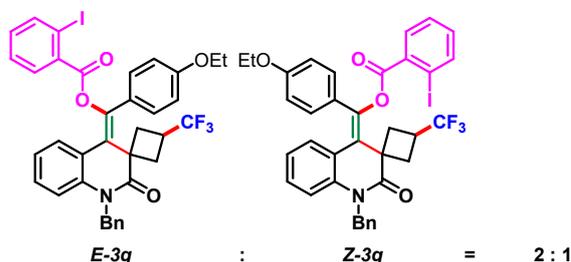
(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(4-methoxyphenyl)methyl 2-iodobenzoate (syn isomer, 3f)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:143 °C-144 °C; 96.4 mg, *E/Z*= 1: 1, 68% yield; ¹H NMR (400 MHz, CDCl₃) *E+ Z* isomer (δ, ppm): 7.97-7.93 (m, 1H), 7.80-7.73 (m, 1H), 7.66-7.61 (m, 1H), 7.49-7.42 (m, 2H), 7.40-7.33 (m, 3H), 7.28 (s, 1H), 7.23 (d, J = 4.6 Hz, 1H), 7.16-7.10 (m, 2H), 6.97-6.91 (m, 4H), 5.38-5.20 (m, 2H), 3.84 (s, 3H), 3.03-2.83 (m, 1H), 2.70-2.61 (m, 1H), 2.34-2.13 (m, 2H), 1.76-1.68 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+ Z* isomer (δ, ppm): 171.9, 171.4, 163.7, 163.5, 160.7, 160.6, 143.4, 143.2, 141.5, 137.8, 137.7, 137.0, 136.9, 134.2, 134.1, 133.0, 131.5, 131.4, 131.0 (d, J = 4.5 Hz), 129.0 (d, J = 10.5 Hz), 128.7 (d, J = 7.5 Hz), 128.2, 127.9, 127.1 (d, J = 7.5 Hz), 126.4, 126.3, 126.1, 126.0, 125.3, 124.2, 124.1, 123.9, 123.2, 123.0, 116.1, 115.9, 113.8, 113.7, 94.2, 55.3, 55.2, 46.9, 46.8, 44.1, 44.0, 33.6, 30.9 (q, J = 31.5 Hz), 30.3 (q, J = 31.5 Hz), 26.4; ¹⁹F NMR (282 MHz, CDCl₃) *E+ Z* isomer (δ, ppm): -73.1, -73.5; HRMS

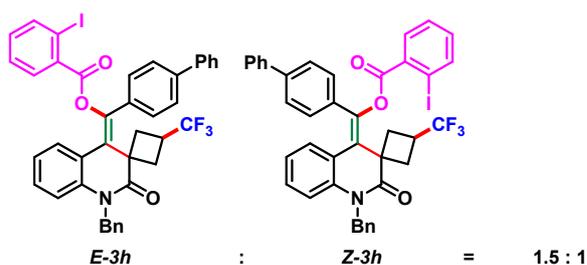
(ESI) m/z calcd for $C_{35}H_{27}F_3INNaO_4$ $[M+Na]^+$ 732.0835, found 732.0835.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(4-ethoxyphenyl)methyl 2-iodobenzoate (syn isomer, 3g)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p: 149 °C-150 °C; 91.1 mg, E/Z = 2: 1, 63% yield; 1H NMR (400 MHz, $CDCl_3$) $E+Z$ isomer (δ , ppm): 7.94 (d, J = 7.9 Hz, 1H), 7.80-7.72 (m, 1H), 7.66-7.60 (m, 1H), 7.48-7.38 (m, 3H), 7.37-7.33 (m, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 7.23 (d, J = 7.0 Hz, 1H), 7.16-7.09 (m, 2H), 6.95-6.89 (m, 4H), 5.37-5.16 (m, 2H), 4.09-4.03 (m, 2H), 3.09-2.81 (m, 1H), 2.69-2.60 (m, 1H), 2.39-2.13 (m, 2H), 1.93-1.69 (m, 1H), 1.45-1.41 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) $E+Z$ isomer (δ , ppm): 171.9, 171.4, 163.7, 163.5, 160.1(2), 160.1(5), 143.5, 143.3, 141.5, 137.8, 137.7, 137.0, 136.9, 134.2, 134.1, 133.0, 131.5, 131.0 (d, J = 4.5 Hz), 128.9(4) (d, J = 9.0 Hz), 128.9(9), 128.7 (d, J = 7.5 Hz), 128.2, 127.9, 127.1 (d, J = 7.5 Hz), 126.4, 126.3, 125.9, 125.8, 125.3, 124.(1)2, 124.1(9), 123.8, 123.2, 123.0, 116.1, 115.9, 114.3, 114.1, 94.2, 63.5, 63.4, 46.9, 46.8, 44.1, 44.0, 33.6, 30.5 (q, J = 31.5 Hz), 30.3 (q, J = 31.5 Hz), 26.5, 22.7, 14.8; ^{19}F NMR (282 MHz, $CDCl_3$) $E+Z$ isomer (δ , ppm): -73.2, -73.6; HRMS (ESI) m/z calcd for $C_{36}H_{29}F_3INNaO_4$ $[M+Na]^+$ 746.0991, found 746.0991.

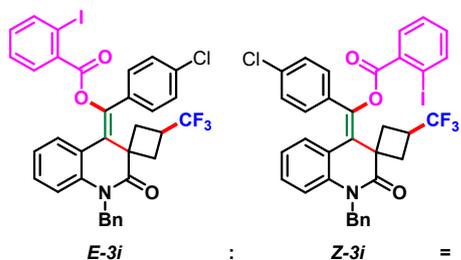
[1,1'-biphenyl]-4-yl(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)methyl 2-iodobenzoate (syn isomer, 3h)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p: 167 °C-168 °C; 29.4 mg, E/Z = 1.5: 1, 39% yield; 1H NMR (400 MHz, $CDCl_3$) $E+Z$ isomer (δ , ppm): 7.98-7.94 (m, 1H), 7.83-7.76 (m, 1H), 7.71-7.54 (m, 7H), 7.46-7.32 (m, 7H), 7.29 (s, 1H), 7.24 (s, 1H), 7.18-7.11 (m, 2H), 7.01-6.93 (m, 2H), 5.39-5.22 (m, 2H), 3.01-2.83 (m, 1H), 2.73-2.64 (m, 1H), 2.35-2.13 (m, 2H), 1.82-1.66 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) $E+Z$ isomer (δ , ppm): 171.8, 171.3, 163.7, 163.5, 143.3, 143.0, 142.6, 142.5, 141.8, 141.6, 140.1(3), 140.1(5), 137.8(3), 137.8(5), 137.0, 136.9, 134.0, 133.1, 132.7(1), 132.7(3), 132.5, 131.1 (d, J = 7.5 Hz), 130.5, 129.0 (d, J = 10.5 Hz), 128.9 (d, J = 3.0 Hz), 128.8, 128.2, 127.9(0), 127.9(2), 127.8 (d, J = 7.5 Hz), 127.2, 127.1(3), 127.1(8), 127.1(6),

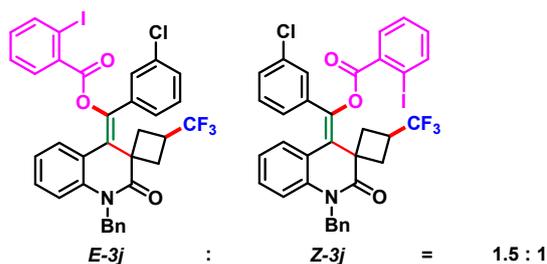
127.0, 126.9, 126.4, 126.3, 125.2, 125.0, 124.0, 123.3, 123.1, 116.2, 116.0, 94.3, 47.0, 46.8, 44.1, 44.0, 32.6, 31.0 (q, $J = 31.5$ Hz), 30.5 (q, $J = 31.5$ Hz), 26.6, 14.1; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.6; HRMS (ESI) m/z calcd for $\text{C}_{40}\text{H}_{29}\text{F}_3\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 778.1042, found 778.1041.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(4-chlorophenyl)methyl 2-iodobenzoate (*syn isomer, 3i*)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:171 °C-172 °C; 106.7 mg, *E/Z*= 1: 1, 75% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.92 (d, $J = 8.0$ Hz, 1H), 7.77-7.70 (m, 1H), 7.66-7.60 (m, 1H), 7.52-7.44 (m, 2H), 7.41-7.36 (m, 3H), 7.35-7.31 (m, 2H), 7.26-7.18 (m, 3H), 7.14-7.09 (m, 2H), 6.98-6.92 (m, 2H), 5.28 (q, $J = 14.3, 12.8$ Hz, 2H), 3.13-2.85 (m, 1H), 2.69-2.60 (m, 1H), 2.40-2.12 (m, 2H), 1.88-1.63 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.6, 171.2, 163.6, 163.4, 142.2, 142.0, 141.7, 137.8 (d, $J = 8.3$ Hz), 136.8 (d, $J = 12.0$ Hz), 136.0 (d, $J = 11.0$ Hz), 133.8 (d, $J = 6.0$ Hz), 133.2, 132.4, 132.2, 131.5, 131.0(3), 131.0(0), 129.1, 129.0, 128.9(4), 128.9(3), 128.9(8), 128.8, 128.7, 128.2, 128.0, 127.2(0), 127.2(5), 126.4, 126.3, 125.9, 125.7, 124.9, 123.7, 123.4, 123.2, 116.3, 116.1, 94.4, 94.3, 47.0, 46.8, 44.1, 44.0, 31.0 (q, $J = 31.0$ Hz), 30.4 (q, $J = 31.0$ Hz), 26.7, 14.2; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.5; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{ClF}_3\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 736.0339, found 736.0339.

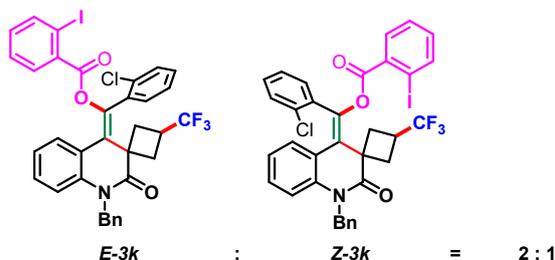
(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(3-chlorophenyl)methyl 2-iodobenzoate (*syn isomer, 3j*)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:189 °C-190 °C; 102.7 mg, *E/Z*= 1.5: 1, 72% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.94 (s, 1H), 7.78-7.70 (m, 1H), 7.65-7.54 (m, 2H), 7.44-7.33 (m, 6H), 7.27 (s, 1H), 7.26-7.20 (m, 2H), 7.18-7.12 (m, 2H), 6.99-6.93 (m, 2H), 5.39-5.18 (m, 2H), 3.08-2.84 (m, 1H), 2.72-2.62 (m, 1H), 2.36-2.11 (m, 2H), 1.62-1.56 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.5, 171.0, 163.6, 163.4, 141.8, 141.6(4), 141.6(1), 141.6(8), 137.8, 137.7, 136.9, 136.7, 135.6, 135.3, 134.5, 134.3, 133.8 (d, $J = 13.5$ Hz), 133.1, 131.0, 130.1 (d, $J = 7.5$ Hz), 129.8, 129.6, 129.1 (d, $J = 7.5$ Hz), 129.0, 128.9,

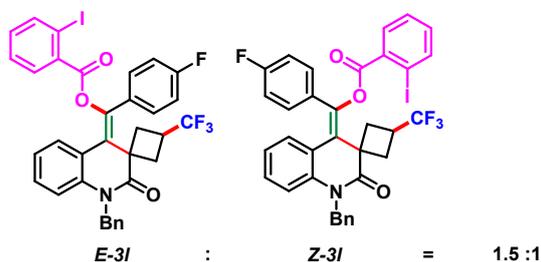
128.1, 128.0, 127.9, 127.1 (d, $J = 6.0$ Hz), 126.4, 126.3, 126.2, 126.1, 124.7, 123.6, 123.3, 116.3, 116.0, 94.3, 94.2, 47.0, 46.9, 44.1, 44.0, 34.7, 30.4 (q, $J = 31.5$ Hz), 30.0 (q, $J = 31.5$ Hz), 26.7; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.6; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{ClF}_3\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 736.0339, found 736.0339.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(2-chlorophenyl)methyl 2-iodobenzoate (syn isomer, 3k)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:176 °C-177 °C; 81.3 mg, *E/Z*= 2: 1, 57% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.95-7.79 (m, 1H), 7.73-7.67 (m, 1H), 7.57-7.43 (m, 2H), 7.39-7.31 (m, 5H), 7.30-7.20 (m, 4H), 7.17-7.08 (m, 2H), 7.07-6.85 (m, 2H), 5.25 (t, $J = 17.7$ Hz, 2H), 3.20-2.89 (m, 1H), 2.88-2.68 (m, 1H), 2.42-2.14 (m, 2H), 1.70-1.51 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.4, 169.8, 163.6, 163.2, 142.0, 141.9, 141.5, 141.4, 137.7, 136.8, 134.2(1), 134.2(9), 134.0, 133.9, 133.6, 133.5, 133.0, 132.8, 132.0 (d, $J = 3.0$ Hz), 131.4(9), 131.4(5), 131.1, 130.4, 129.8, 129.7, 129.6, 129.2, 129.0(4), 129.0(3), 128.9, 128.8(4), 128.8(2), 128.6, 128.5, 128.2 (d, $J = 6.0$ Hz), 128.1, 127.9, 127.8, 127.7, 127.4 (d, $J = 3.0$ Hz), 127.1 (d, $J = 3.0$ Hz), 127.0, 126.9, 126.7, 126.6(4), 126.6(6), 126.5, 126.3, 123.3, 123.1, 122.9, 122.7, 116.1, 115.9(2), 115.9(6), 115.7, 94.9, 94.3, 94.2, 46.9, 46.8, 46.7, 45.6, 44.0, 33.9, 31.4 (q, $J = 31.5$ Hz), 31.0 (q, $J = 31.5$ Hz), 25.9; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.7; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{ClF}_3\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 736.0339, found 736.0339.

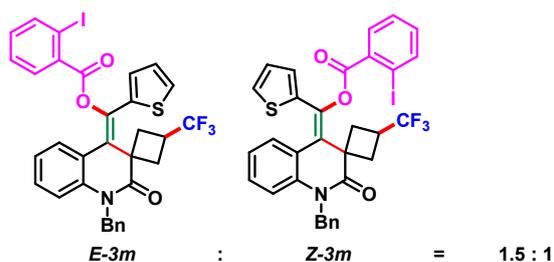
(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(4-fluorophenyl)methyl 2-iodobenzoate (syn isomer, 3l)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:181 °C-182 °C; 97.6 mg, *E/Z*= 1.5: 1, 70% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.95 (d, $J = 8.0$ Hz, 1H), 7.78-7.71 (m, 1H), 7.67-7.61 (m, 1H), 7.57-7.50 (m, 2H), 7.42-7.34 (m, 3H), 7.28 (s, 1H), 7.26-7.20 (m, 2H), 7.17-7.11 (m, 4H), 6.96 (d, $J = 8.0$ Hz, 2H), 5.36-5.18 (m, 2H), 3.08-2.84 (m, 1H), 2.68-2.58 (m, 1H), 2.37-2.13 (m, 2H), 1.83-1.62 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) *E+Z* isomer

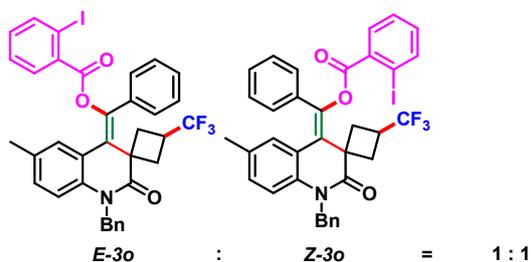
(δ , ppm): 171.6, 171.2, 164.3, 164.2, 163.7, 163.4, 162.6, 142.4, 142.1, 141.6, 137.8, 137.7, 136.9, 136.8, 133.9 (d, $J = 9.0$ Hz), 133.1, 132.1, 130.9 (d, $J = 3.0$ Hz), 130.0 (d, $J = 4.5$ Hz), 129.8 (d, $J = 3.0$ Hz), 129.0, 128.9, 128.2, 127.9, 127.2, 127.1, 126.4, 126.3, 125.5, 125.3, 124.9, 123.7, 123.3(2), 123.3(1), 123.1, 116.3, 116.0, 115.8, 115.6(1), 115.6(9), 115.4, 94.3, 94.2, 47.0, 46.8, 44.1, 44.0, 31.0 (q, $J = 31.5$ Hz), 30.4 (q, $J = 31.5$ Hz), 26.5, 22.7; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.6, -109.7, -109.9; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{F}_4\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 720.0635, found 720.0635.

(1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(thiophen-2-yl)methyl 2-iodobenzoate (syn isomer, 3m)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:165 °C-166 °C; 58.9 mg, *E/Z*= 1.5: 1, 43% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.99-7.95 (m, 1H), 7.82-7.75 (m, 1H), 7.55-7.46 (m, 2H), 7.43 -7.30 (m, 4H), 7.27 (s, 1H), 7.25 (s, 1H), 7.19-7.12 (m, 3H), 7.07-7.03 (m, 1H), 6.96 (t, $J = 7.9$ Hz, 2H), 5.36-5.18 (m, 2H), 2.96-2.84 (m, 1H), 2.79-2.71 (m, 1H), 2.32-2.14 (m, 2H), 1.95-1.81 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.5, 171.0, 164.0, 163.6, 141.7, 137.8, 137.7, 137.0, 136.8, 136.7, 134.4, 134.2, 133.7, 133.6, 133.5, 133.2, 132.1, 131.9, 131.3 (d, $J = 10.5$ Hz), 129.7, 129.1 (d, $J = 7.5$ Hz), 129.0 (d, $J = 3.0$ Hz), 128.9, 128.0 (d, $J = 10.5$ Hz), 127.5, 127.4, 127.2, 126.8, 126.7, 126.4, 126.3, 124.7, 123.6, 123.4, 123.2, 116.2, 115.9, 94.6, 94.5, 47.1, 46.9, 44.6, 44.4, 31.2, 30.8 (q, $J = 31.5$ Hz), 30.6 (q, $J = 31.5$ Hz), 25.8; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.5; HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{23}\text{F}_3\text{INNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 708.0293, found 708.0291.

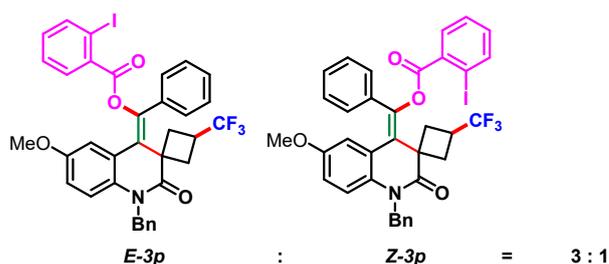
(1'-benzyl-6'-methyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3o)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:177 °C-178 °C; 73.5 mg, *E/Z*= 1: 1, 53% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.96-7.91 (m, 1H), 7.77-7.69 (m, 1H), 7.54-7.48 (m, 2H), 7.45-7.38 (m, 4H), 7.38-7.30 (m, 3H), 7.26-7.19 (m, 3H), 7.15-7.10 (m, 1H), 6.93-6.88 (m, 1H), 6.84-6.80 (m, 1H), 5.24 (d, $J = 22.9$ Hz, 2H), 3.04-2.80

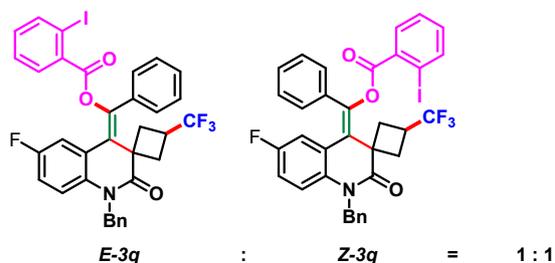
(m, 1H), 2.69-2.58 (m, 1H), 2.46-2.16 (m, 2H), 2.13 (s, 3H), 1.77-1.58 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.9, 171.3, 163.7, 163.4, 143.7, 143.4, 141.6, 141.5, 140.1, 140.0, 137.8, 137.7, 137.0, 136.9, 134.1 (d, *J* = 9.0 Hz), 133.0, 131.1 (d, *J* = 3.0 Hz), 130.8, 130.0, 129.2, 129.0, 128.9, 128.7 (d, *J* = 6.0 Hz), 128.2, 127.9, 127.1 (d, *J* = 6.0 Hz), 126.4, 126.3, 125.2, 124.5, 124.3, 124.0, 123.2, 123.0, 116.1, 115.9, 94.3, 46.9, 46.8, 44.1, 44.0, 33.6, 31.0 (q, *J* = 31.5 Hz), 30.4 (q, *J* = 31.5 Hz), 26.5, 21.5; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₅H₂₇F₃INNaO₃ [M+Na]⁺ 716.0885, found 716.0887.

(1'-benzyl-6'-methoxy-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3p)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:180 °C-181 °C; 63.8 mg, *E/Z*= 3: 1, 45% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.96 (d, *J* = 8.0 Hz, 1H), 7.83-7.78 (m, 1H), 7.52 (d, *J* = 4.0 Hz, 2H), 7.45-7.40 (m, 4H), 7.36-7.33 (m, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.21 (d, *J* = 2.9 Hz, 1H), 7.20-7.12 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.69-6.65 (m, 1H), 5.26 (s, 2H), 3.54 (d, *J* = 2.0 Hz, 3H), 2.97-2.84 (m, 1H), 2.65-2.58 (m, 1H), 2.31-2.17 (m, 2H), 1.66-1.59 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.4, 170.9, 163.4, 163.2, 155.3, 155.2, 143.7, 143.5, 141.6, 137.0, 136.9, 134.1, 133.8, 133.6, 133.1 (d, *J* = 3.0 Hz), 131.2(3), 131.2(6) (d, *J* = 7.5 Hz), 129.9 (d, *J* = 7.5 Hz), 128.9 (d, *J* = 9.0 Hz), 128.5, 128.3, 127.9, 127.1, 127.0, 126.5, 126.3, 125.2, 125.1, 124.9, 117.3, 117.0, 114.9, 114.6, 113.5, 113.2, 94.2, 55.4, 47.0, 46.8, 44.1, 43.9, 33.6, 31.0 (q, *J* = 31.5 Hz), 30.5 (q, *J* = 30.0 Hz), 26.5; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₅H₂₇F₃INNaO₄ [M+Na]⁺ 748.1148, found 748.1142.

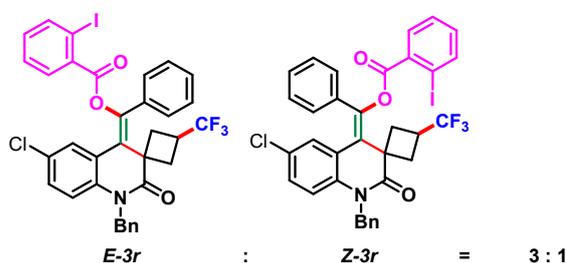
(1'-benzyl-6'-fluoro-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3q)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:193 °C-194 °C; 80.9 mg, *E/Z*= 1: 1, 58% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.95 (d, *J* = 7.9 Hz, 1H), 7.83-7.75 (m, 1H), 7.52 (s, 2H), 7.45-7.39 (m, 5H), 7.39-7.34 (m, 2H), 7.26 (s, 1H),

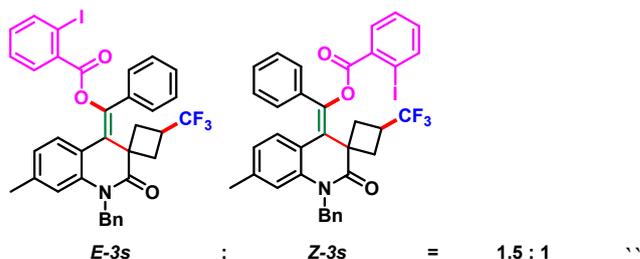
7.24 (d, $J = 10.7$ Hz, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.92-6.81 (m, 2H), 5.28 (s, 2H), 3.09-2.83 (m, 1H), 2.69-2.60 (m, 1H), 2.42-2.15 (m, 2H), 1.74-1.58 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.4, 170.9, 163.5, 163.3, 159.6, 159.5, 157.2, 157.1, 144.4, 144.2, 141.7, 136.6, 136.5, 134.1(8), 134.1(5), 134.0, 133.9, 133.8(3), 133.8(5), 133.5, 133.3, 133.2, 131.0, 130.9, 130.2, 130.1, 130.0, 129.1, 129.0, 128.6(0), 128.6(5), 128.4(3), 128.4(9), 128.3, 128.0 (d, $J = 2.0$ Hz), 127.2 (d, $J = 6.0$ Hz), 126.8 (d, $J = 9.0$ Hz), 126.4, 126.3, 125.6 (d, $J = 8.0$ Hz), 124.2, 124.0, 117.5(4), 117.5(5), 117.3, 117.2, 115.6, 115.5, 115.4, 115.3(4), 115.3(5), 115.2, 94.3, 94.2, 47.1, 47.0, 44.0, 43.8, 31.0 (q, $J = 31.0$ Hz), 30.4 (q, $J = 32.0$ Hz), 26.5, 22.7; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.6, -119.2, -119.4; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{F}_4\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 720.0635, found 720.0633.

(1'-benzyl-6'-chloro-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3r)



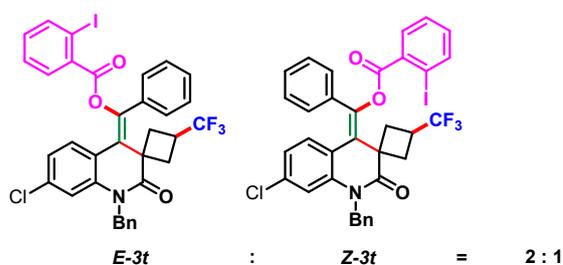
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:189 °C-190 °C; 79.9 mg, *E/Z*= 3: 1, 56% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.94 (d, $J = 7.9$ Hz, 1H), 7.79-7.66 (m, 2H), 7.50 (s, 2H), 7.45-7.40 (m, 4H), 7.38-7.33 (m, 2H), 7.24 (d, $J = 6.8$ Hz, 3H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.11-7.06 (m, 1H), 6.87 (d, $J = 8.7$ Hz, 1H), 5.27 (s, 2H), 3.06-2.81 (m, 1H), 2.68-2.58 (m, 1H), 2.40-2.14 (m, 2H), 1.64 (t, $J = 10.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.5, 171.0, 163.6, 163.4, 144.5, 144.3, 141.5, 136.4, 136.3, 134.2, 134.0, 133.5, 133.3, 133.1, 130.8, 130.2, 130.1, 130.0, 129.1 (d, $J = 6.0$ Hz), 128.7 (d, $J = 6.0$ Hz), 128.6 (d, $J = 5.0$ Hz), 128.4, 128.2, 128.0, 127.3 (d, $J = 6.0$ Hz), 126.6, 126.4, 126.3, 125.4, 123.9, 123.6, 117.4, 117.2, 94.1(8), 94.1(5), 46.9, 46.8, 43.8, 43.7, 31.9, 31.4 (q, $J = 32.0$ Hz), 30.4 (q, $J = 31.0$ Hz), 26.4; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.7; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{ClF}_3\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 736.0339, found 736.0339.

(1'-benzyl-7'-methyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3s)



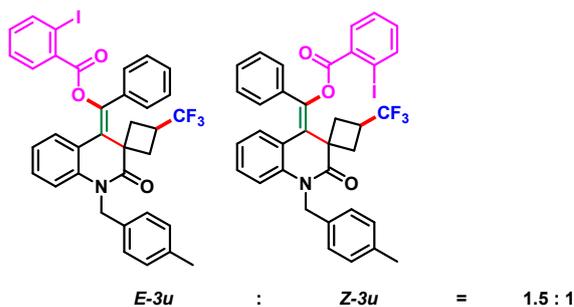
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:173 °C-174 °C; 80.4 mg, *E/Z*= 1.5: 1, 58% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 8.07-7.75 (m, 2H), 7.57-7.49 (m, 2H), 7.47-7.32 (m, 6H), 7.28-7.11 (m, 5H), 6.78-6.48 (m, 2H), 5.35-5.14 (m, 2H), 3.24-2.39 (m, 3H), 2.19 (d, *J* = 6.0 Hz, 3H), 2.16 (s, 1H), 1.59 (d, *J* = 22.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.8, 171.3, 163.7, 163.4, 143.1, 142.9, 142.1, 141.6(2), 141.6(9), 139.0, 138.9, 137.8, 137.7, 137.1, 137.0, 135.0, 134.0, 133.9, 133.8, 133.5, 133.0, 132.0, 131.1, 130.2, 130.1, 129.8 (d, *J* = 7.0 Hz), 129.0, 128.9(1), 128.9(6), 128.7, 128.4, 128.3, 128.1 (d, *J* = 10.0 Hz), 128.0, 127.9, 127.2, 127.0 (d, *J* = 5.0 Hz), 126.7 (d, *J* = 5.0 Hz), 126.4, 126.3, 125.1, 124.9, 124.1, 123.9, 123.8, 122.2, 121.0, 116.9, 116.6, 95.0, 94.4, 47.0, 46.8, 45.2, 44.2, 44.1, 31.0 (q, *J* = 31.0 Hz), 30.5 (q, *J* = 31.0 Hz), 26.5, 21.7; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₅H₂₇F₃INNaO₃ [M+Na]⁺ 716.0885, found 716.0885.

(1'-(benzyl-7'-chloro-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3t)



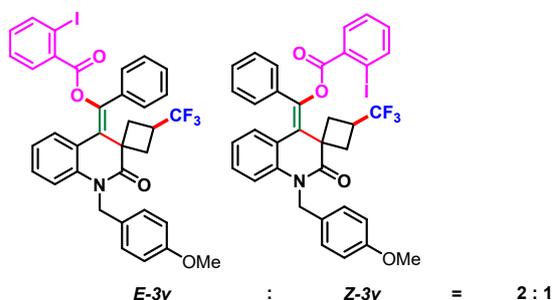
White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:182 °C-183 °C; 47.1 mg, *E/Z*= 2: 1, 33% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.96 (d, *J* = 7.9 Hz, 1H), 7.83-7.75 (m, 1H), 7.63-7.51 (m, 3H), 7.47-7.38 (m, 6H), 7.28 (d, *J* = 8.1 Hz, 3H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.99-6.92 (m, 2H), 5.25 (d, *J* = 21.9 Hz, 2H), 2.99-2.82 (m, 1H), 2.72-2.62 (m, 1H), 2.36-2.13 (m, 2H), 1.74-1.59 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.7, 171.1, 163.5, 163.3, 144.1, 143.9, 141.7(2), 141.7(1), 139.1, 139.0, 136.3, 136.2, 134.5 (d, *J* = 7.5 Hz), 133.8 (d, *J* = 9.0 Hz), 133.7, 133.4, 133.2, 131.8, 130.2, 130.1(1) (d, *J* = 9.0 Hz), 130.1(5), 130.0, 129.2, 129.1(1), 129.1(0), 129.1(5), 128.6, 128.4, 128.3, 128.0, 127.4 (d, *J* = 7.5 Hz), 126.8, 126.4, 126.3(9), 126.3(7), 124.1, 123.9, 123.5, 123.4, 123.1, 122.4, 116.5, 116.3, 94.4(2), 94.4(9), 47.0, 46.9, 44.0, 43.9, 31.3, 31.0 (q, *J* = 31.5 Hz), 30.4 (q, *J* = 31.5 Hz), 26.42; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₄H₂₄ClF₃INNaO₃ [M+Na]⁺ 736.0339, found 736.0339.

(1'-(4-methylbenzyl)-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3u)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:170 °C-171 °C; 76.2 mg, *E/Z*= 1.5: 1, 55% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.94 (d, *J* = 7.9 Hz, 1H), 7.80-7.72 (m, 1H), 7.68-7.62 (m, 1H), 7.59-7.50 (m, 2H), 7.45-7.37 (m, 4H), 7.16 (d, *J* = 12.6 Hz, 6H), 6.99-6.92 (m, 2H), 5.36-5.11 (m, 2H), 3.09-2.81 (m, 1H), 2.70-2.58 (m, 1H), 2.30 (d, *J* = 1.9 Hz, 3H), 2.29-2.05 (m, 2H), 1.74-1.58 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.7, 171.2, 163.7, 163.4, 143.4, 143.2, 141.5, 137.9, 137.8, 136.7, 136.6, 134.1, 134.0, 133.9, 133.8, 133.7, 133.0, 131.0 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 6.0 Hz), 129.6 (d, *J* = 6.0 Hz), 128.8 (d, *J* = 4.0 Hz), 128.5, 128.3, 128.1, 127.9(7), 127.9(5), 126.4, 126.2, 125.1, 125.0, 124.9, 123.8, 123.2, 123.0, 116.2, 115.9, 94.2, 46.7, 46.6, 44.1, 43.9, 33.6, 31.0 (q, *J* = 31.5 Hz), 30.5 (q, *J* = 31.5 Hz), 26.4, 21.1; ¹⁹F NMR (282 MHz, CDCl₃) *E+Z* isomer (δ, ppm): -73.2, -73.6; HRMS (ESI) *m/z* calcd for C₃₅H₂₇F₃INNaO₃ [M+Na]⁺ 716.0885, found 716.0885.

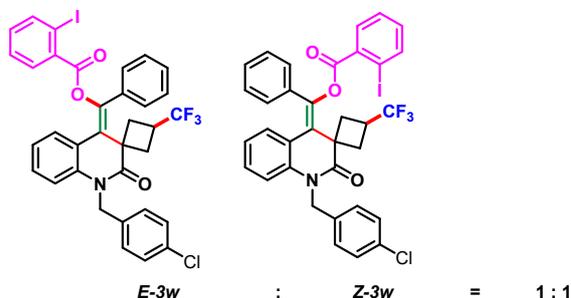
(1'-(4-methoxybenzyl)-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3v)



White solid after purification by column chromatography (petroleum ether/ethyl acetate= 15/1); m.p:175 °C-176 °C; 61.0 mg, *E/Z*= 2: 1, 43% yield; ¹H NMR (400 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 7.97-7.90 (m, 1H), 7.81-7.72 (m, 1H), 7.68-7.61 (m, 1H), 7.57-7.49 (m, 2H), 7.45-7.38 (m, 4H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.17-7.11 (m, 2H), 7.00-6.92 (m, 2H), 6.91-6.85 (m, 2H), 5.28-5.15 (m, 2H), 3.89-3.68 (m, 3H), 2.98-2.79 (m, 1H), 2.63 (d, *J* = 8.8 Hz, 1H), 2.32-2.06 (m, 2H), 1.62 (d, *J* = 10.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) *E+Z* isomer (δ, ppm): 171.8, 171.3, 163.4, 158.7(7), 158.7(5), 143.2, 141.6(8), 141.6(6), 137.8, 137.7, 134.1, 134.0 (d, *J* = 12.0 Hz), 133.7, 133.0, 131.0, 130.2, 130.1, 129.9 (d, *J* = 10.5 Hz), 128.9(1), 128.8(4), 128.8(8) (d, *J* = 6.0 Hz), 128.6, 128.5, 128.4(0), 128.4(5), 128.3, 128.2, 128.1, 128.0, 127.9(9), 127.9(7), 127.7, 127.6, 125.2 (d, *J* = 7.5 Hz), 124.9, 124.0, 123.2, 123.0, 116.3, 116.0, 114.4(4), 114.4(7), 114.3, 55.3, 46.3, 46.2, 44.1, 44.0, 31.0 (q, *J* = 31.5 Hz),

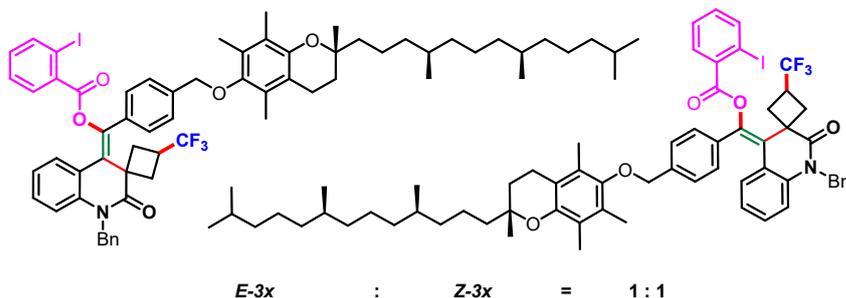
30.5 (q, $J = 31.5$ Hz), 29.7, 26.5; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.6; HRMS (ESI) m/z calcd for $\text{C}_{35}\text{H}_{27}\text{F}_3\text{INNaO}_4$ $[\text{M}+\text{Na}]^+$ 732.0835, found 732.0835.

(1'-(4-chlorobenzyl)-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(phenyl)methyl 2-iodobenzoate (syn isomer, 3w)



White solid after purification by column chromatography (petroleum ether/ethyl acetate = 15/1); m.p: 179 °C-180 °C; 69.9 mg, *E/Z* = 1: 1, 49% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.93 (d, $J = 7.9$ Hz, 1H), 7.81-7.73 (m, 1H), 7.69-7.63 (m, 1H), 7.58-7.48 (m, 2H), 7.45-7.38 (m, 4H), 7.35-7.31 (m, 2H), 7.21 (d, $J = 8.3$ Hz, 2H), 7.13 (t, $J = 7.9$ Hz, 2H), 6.99-6.93 (m, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 5.43-5.11 (m, 2H), 3.08-2.81 (m, 1H), 2.69-2.58 (m, 1H), 2.38-2.09 (m, 2H), 1.82-1.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.8, 171.3, 163.5, 163.3, 143.6, 143.4, 141.6, 137.4, 137.3, 135.3, 135.2, 133.9 (d, $J = 6.0$ Hz), 133.8, 133.6, 133.1, 132.8 (d, $J = 5.0$ Hz), 131.0, 130.0 (d, $J = 7.0$ Hz), 129.2(2), 129.2(5), 128.9 (d, $J = 6.0$ Hz), 128.5, 128.3(3), 128.3(0), 128.0, 127.9, 127.8, 125.3, 125.0, 124.7, 124.2, 123.5, 123.3, 116.1, 115.9, 94.3, 46.0, 45.8, 44.0, 43.9, 32.0, 31.6 (q, $J = 32.0$ Hz), 30.4 (q, $J = 31.0$ Hz), 26.5; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.2, -73.6; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{24}\text{ClF}_3\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 736.0339, found 736.0339.

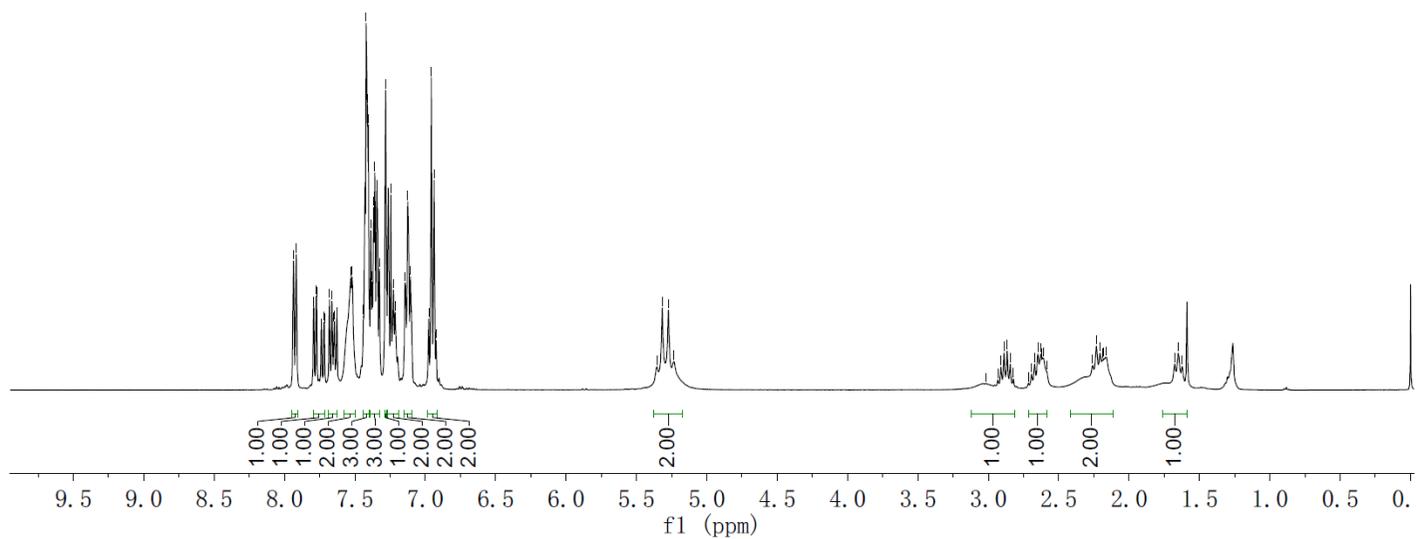
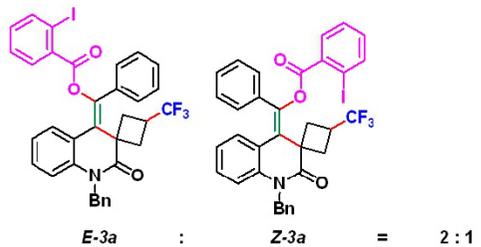
((1*r*,3*r*)-1'-benzyl-2'-oxo-3-(trifluoromethyl)-1',2'-dihydro-4'H-spiro[cyclobutane-1,3'-quinolin]-4'-ylidene)(4-(((*R*)-2,5,7,8-tetramethyl-2-(((*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)methyl 2-iodobenzoate (syn isomer, 3x)



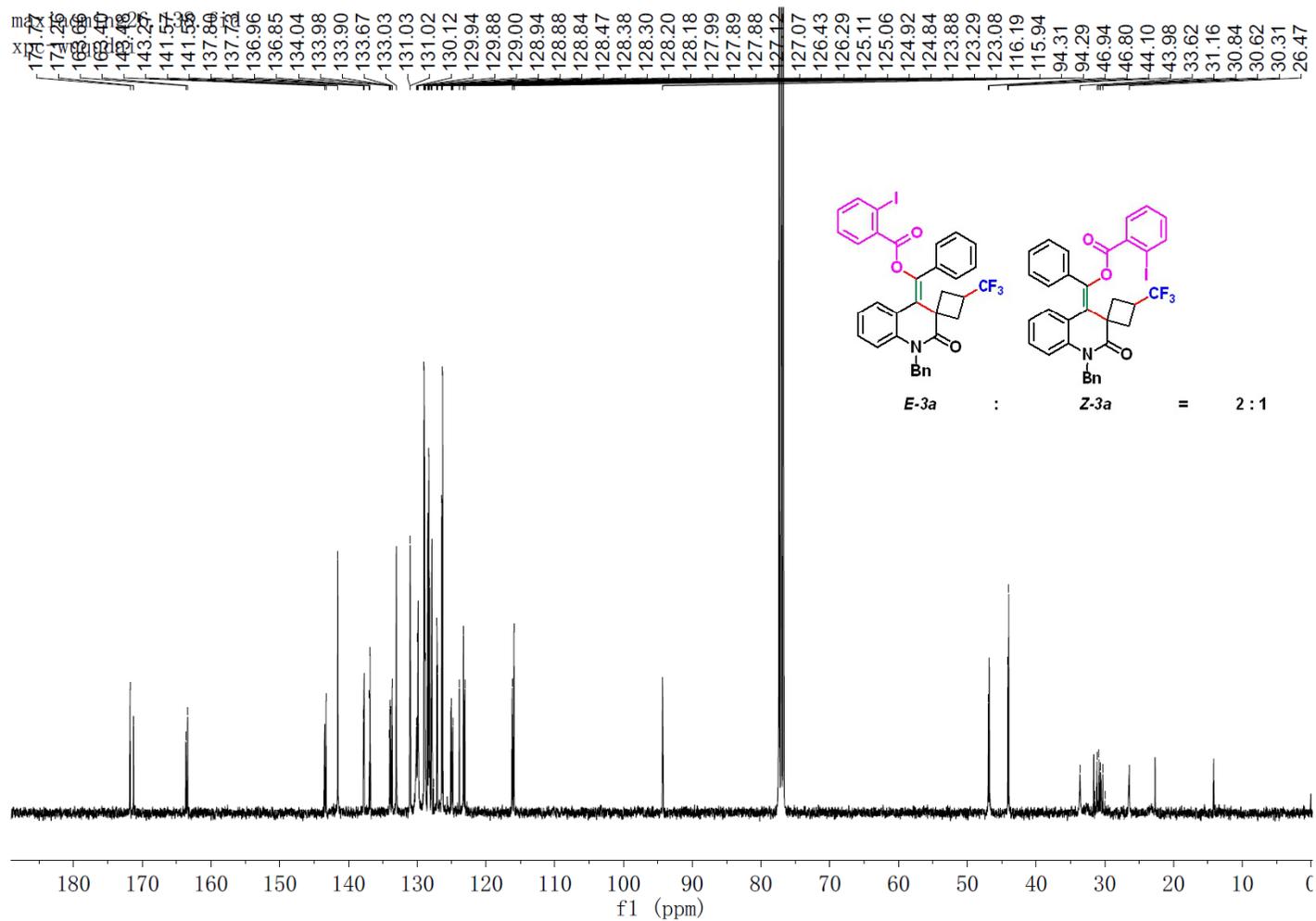
Pale yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 15/1); 100.89 mg, *Z/E* = 1: 1, 45% yield; ^1H NMR (400 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 7.95-7.90 (m, 1H), 7.83-7.75 (m, 1H), 7.68-7.62 (m, 1H), 7.55 (d, $J = 10.2$ Hz, 4H), 7.37-7.31 (m, 3H), 7.28 (s, 2H), 7.23 (s, 1H), 7.12 (t, $J = 7.5$ Hz, 2H), 6.97-6.90 (m, 2H), 5.37-5.21 (m, 2H), 4.67 (d, $J = 49.7$ Hz, 2H), 3.07-2.82 (m, 1H), 2.74-2.64 (m, 1H), 2.58 (t, $J = 6.6$ Hz, 2H), 2.19 (s, 2H), 2.14 (d, $J = 6.1$ Hz, 3H), 2.10 (s, 3H), 1.84-1.70 (m, 3H), 1.58-1.50 (m, 3H), 1.43-1.34 (m, 4H), 1.24 (d, $J = 5.7$ Hz, 10H), 1.13-

1.06 (m, 5H), 0.86 (d, $J = 6.7$ Hz, 13H); ^{13}C NMR (150 MHz, CDCl_3) *E+Z* isomer (δ , ppm): 171.8, 171.3, 163.6, 163.3, 148.1, 148.0, 143.3, 143.1, 141.7, 140.0, 139.9, 137.8(4), 137.8(6), 137.0, 136.9, 134.0, 133.9, 133.1, 131.2(9), 131.2(6), 130.3, 130.2(0), 130.2(8), 129.0, 128.9(3), 128.9(0), 128.9(5), 128.2, 127.9, 127.6, 127.5, 127.4 (d, $J = 4.5$ Hz), 127.3, 127.1 (d, $J = 7.5$ Hz), 126.5, 126.3, 126.0 (d, $J = 6.0$ Hz), 125.2 (d, $J = 4.5$ Hz), 124.0, 123.3, 123.0(4), 123.0(2), 117.7(9), 117.7(7), 116.2, 116.0, 94.4(0), 94.4(9), 74.9, 74.3, 74.2, 47.0, 46.8, 44.1, 44.0, 40.1(3), 40.1(9), 39.4, 37.6(4), 37.6(2), 37.6(5), 37.5(3), 37.5(1), 37.5(6), 37.4(4), 37.4(9), 37.3, 32.8(4), 32.8(2), 32.8(5), 32.7, 30.5 (q, $J = 31.5$ Hz), 31.1 (q, $J = 31.5$ Hz), 24.9, 24.5, 23.9, 22.8, 22.7, 21.1, 20.7, 19.8(2), 19.8(5), 19.7(3), 19.7(9), 19.7(6), 13.0, 12.1, 11.9; ^{19}F NMR (282 MHz, CDCl_3) *E+Z* isomer (δ , ppm): -73.1, -73.4; HRMS (ESI) m/z calcd for $\text{C}_{64}\text{H}_{75}\text{F}_3\text{INNaO}_5$ $[\text{M}+\text{Na}]^+$ 1144.4540, found 1144.4535.

7.837
 7.817
 7.795
 7.775
 7.753
 7.740
 7.736
 7.721
 7.717
 7.684
 7.680
 7.663
 7.650
 7.646
 7.630
 7.627
 7.530
 7.521
 7.440
 7.420
 7.411
 7.404
 7.388
 7.377
 7.366
 7.359
 7.344
 7.340
 7.326
 7.282
 7.245
 7.226
 7.214
 7.144
 7.138
 7.125
 7.105
 7.099
 6.975
 6.957
 6.937
 6.925
 5.317
 5.273
 5.234
 2.888
 2.866
 2.671
 2.648
 2.627
 2.619
 2.606
 2.232
 2.206
 2.189
 2.179
 2.164
 1.650



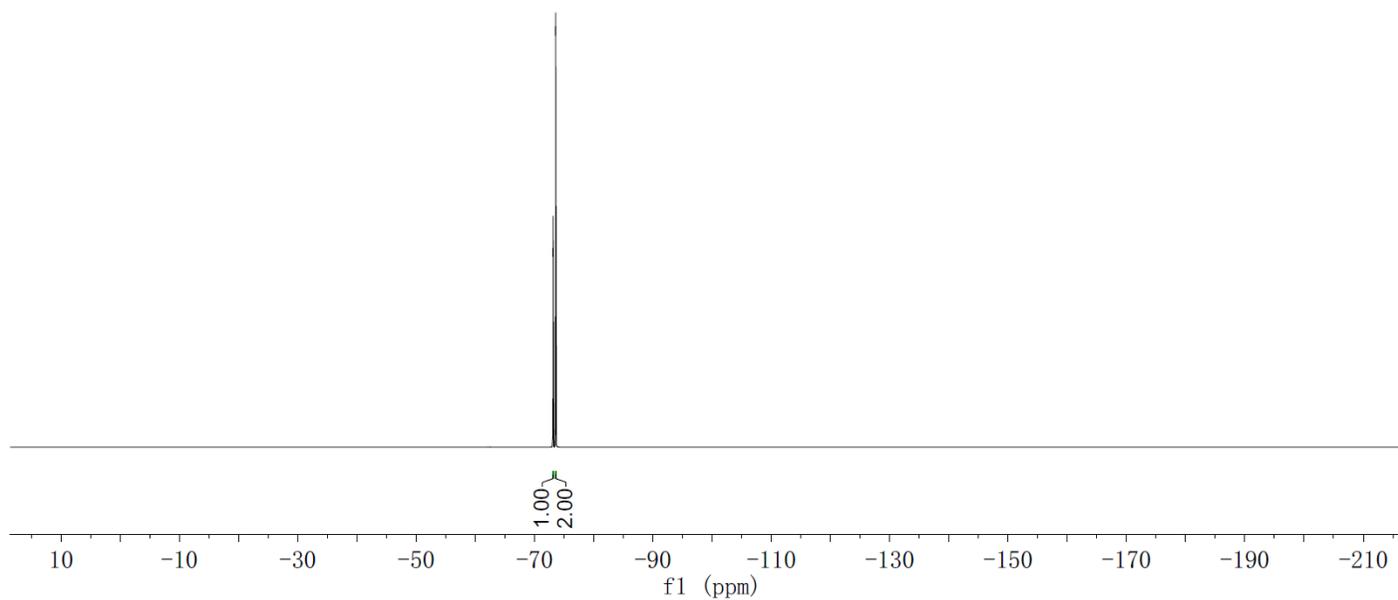
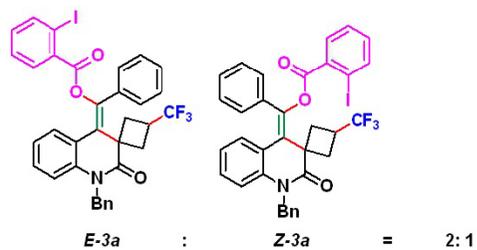
¹H NMR Spectrum of Compound 3a (400 MHz, CDCl₃)



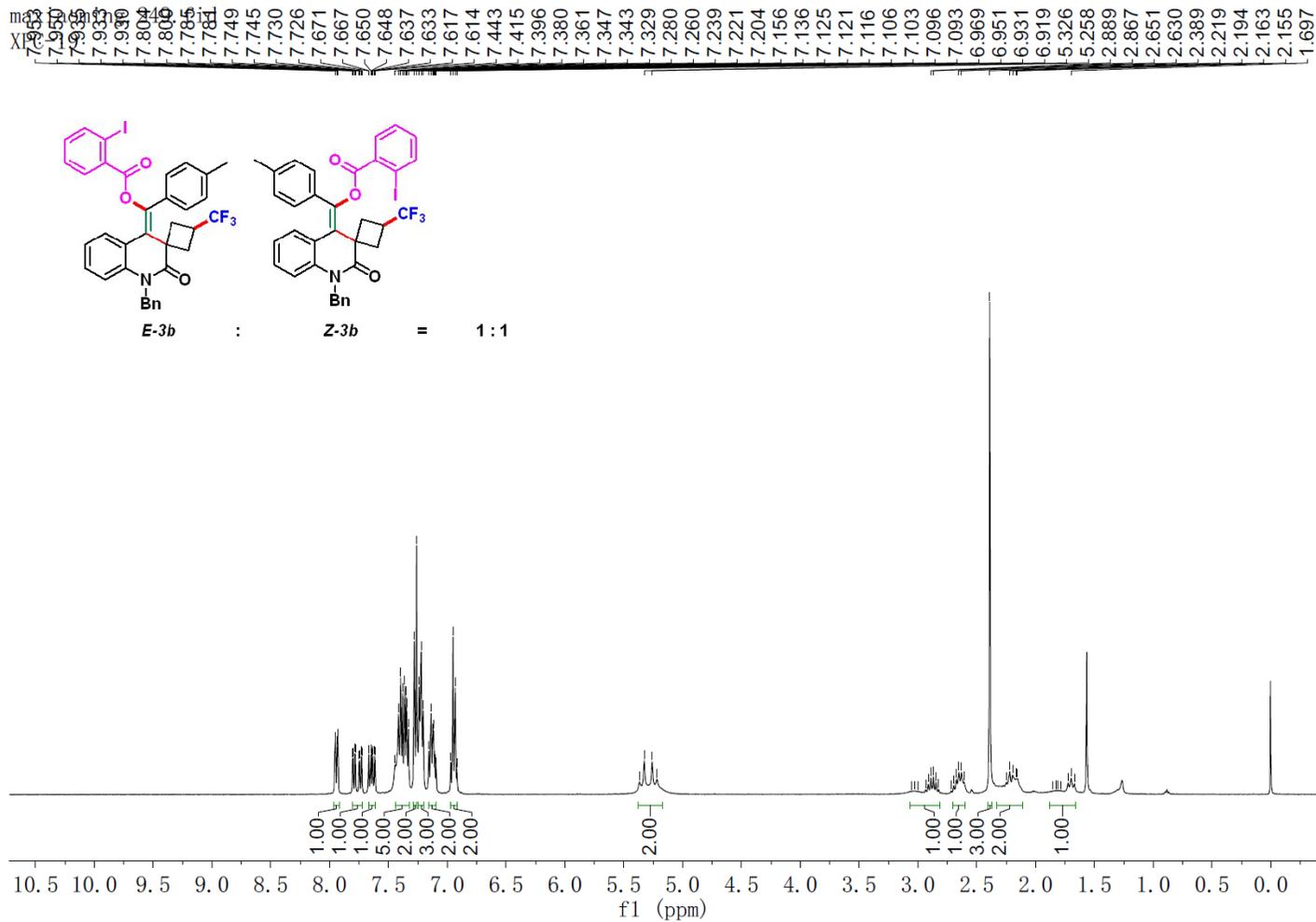
¹³C NMR Spectrum of Compound 3a (100 MHz, CDCl₃)

3maxiaoming02.680.fid
wuqudai

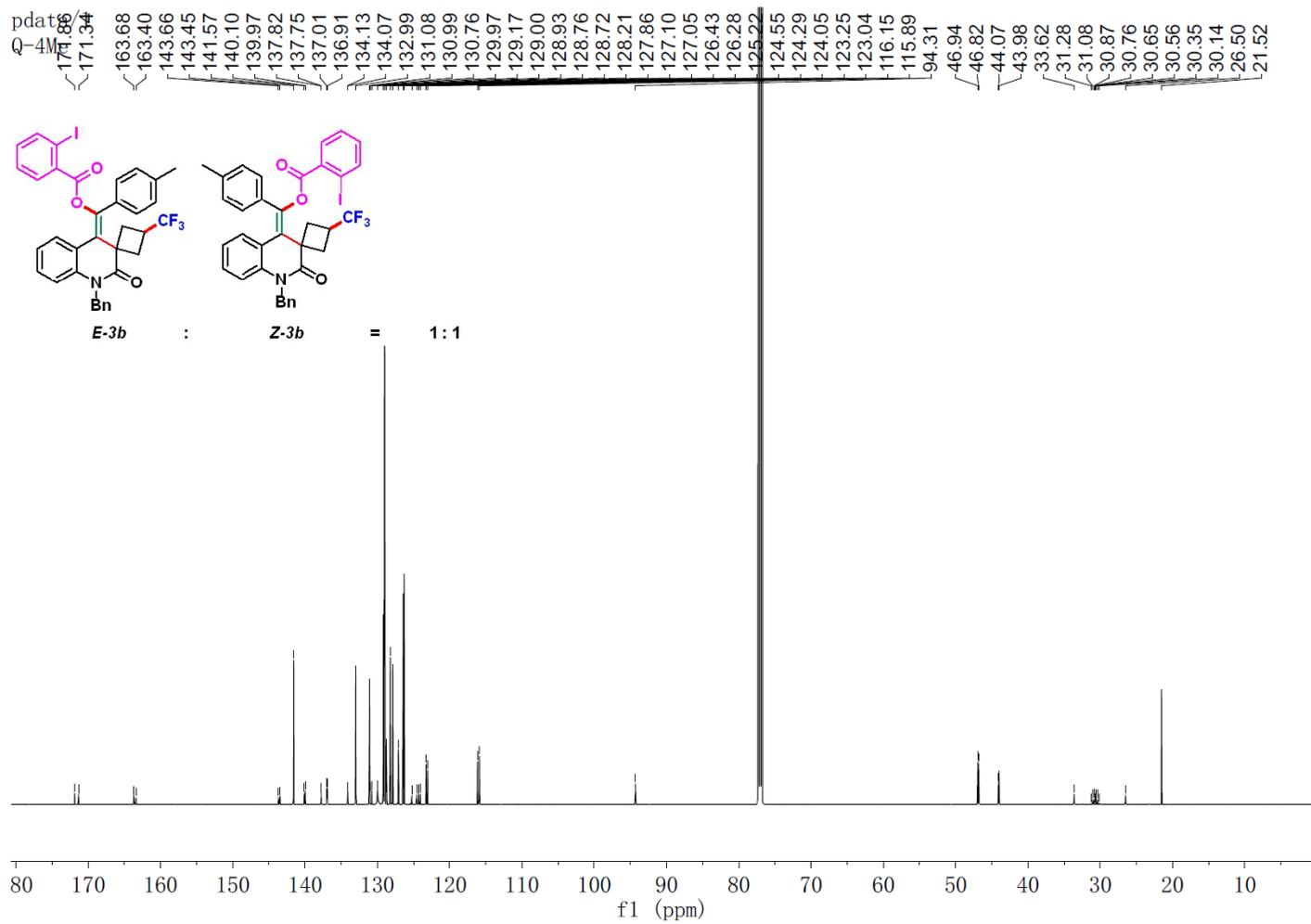
-73.14
-73.58



¹⁹F NMR Spectrum of Compound 3a (282 MHz, CDCl₃)



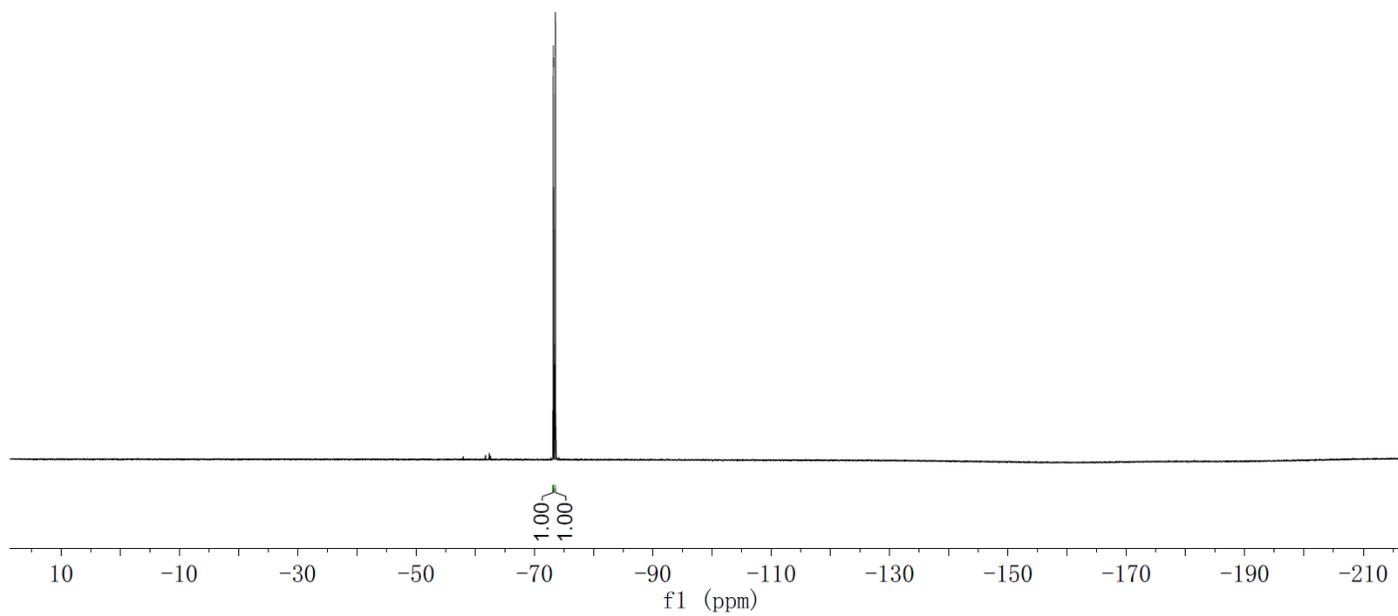
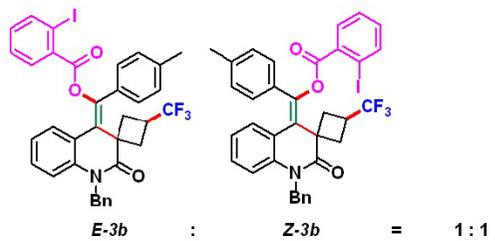
¹H NMR Spectrum of Compound 3b (400 MHz, CDCl₃)



¹³C NMR Spectrum of Compound 3b (150 MHz, CDCl₃)

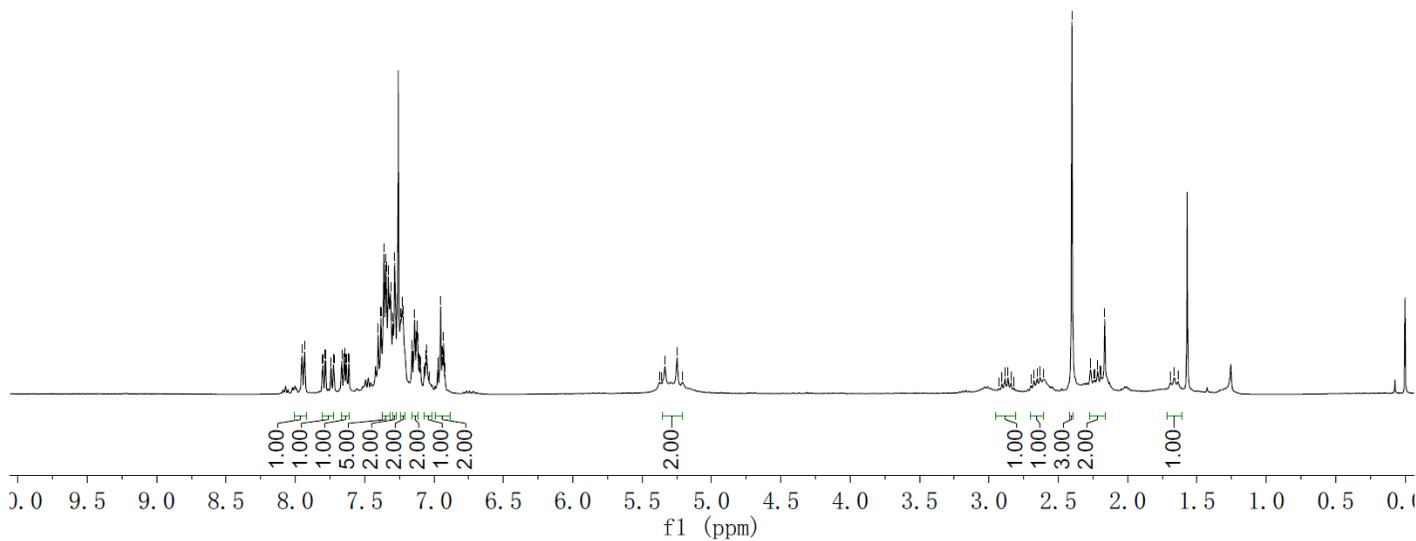
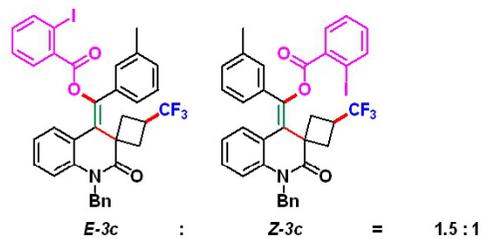
3maxiaoming02.640.fid
19

73.16
73.54

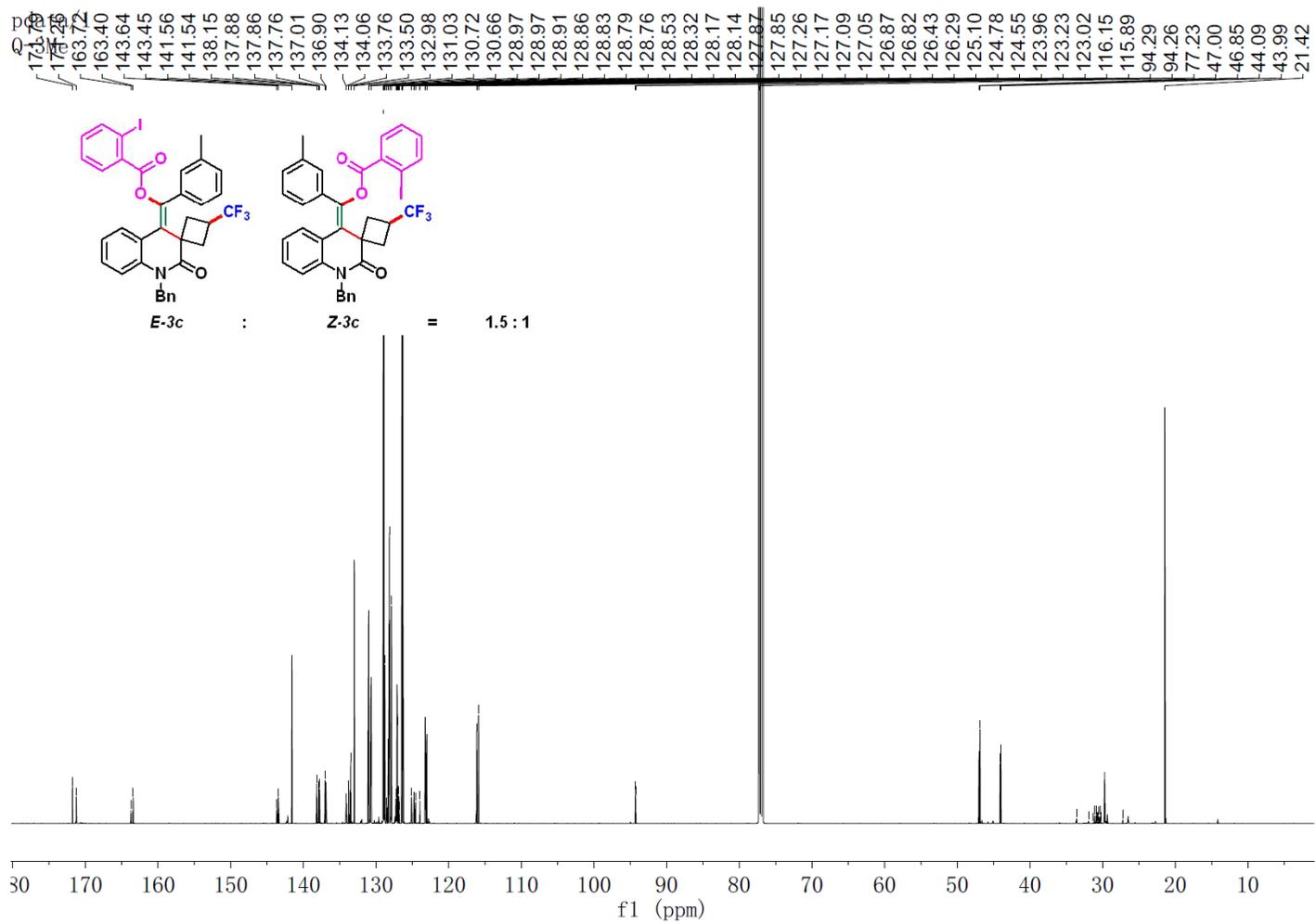


¹⁹F NMR Spectrum of Compound 3b (282 MHz, CDCl₃)

7.963
7.933
7.805
7.801
7.785
7.784
7.744
7.740
7.725
7.721
7.665
7.648
7.646
7.635
7.631
7.615
7.612
7.403
7.383
7.382
7.362
7.348
7.345
7.330
7.313
7.298
7.283
7.241
7.232
7.223
7.163
7.159
7.156
7.144
7.140
7.127
7.125
7.121
7.118
7.109
7.105
7.100
7.096
7.068
7.059
7.053
7.044
6.973
6.971
6.952
6.941
6.932
6.923
5.336
5.247
2.401
2.268
2.216
2.165

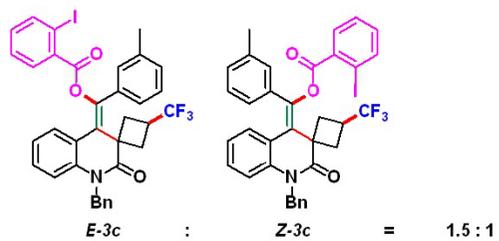


¹H NMR Spectrum of Compound 3c (400 MHz, CDCl₃)

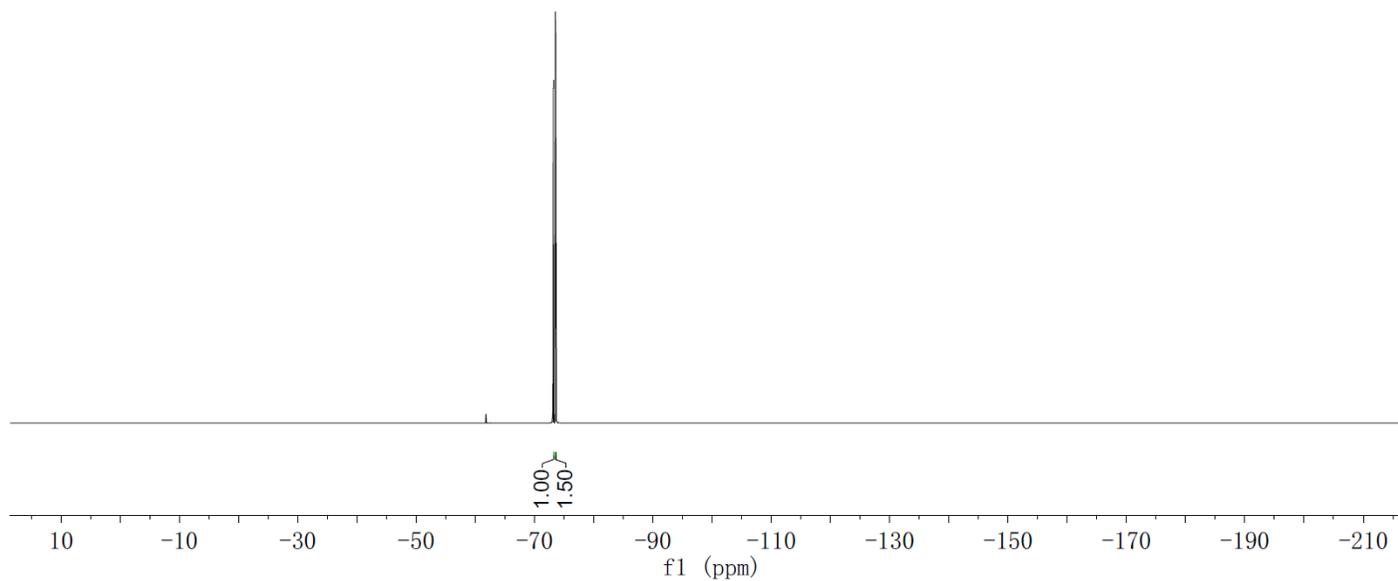


¹³C NMR Spectrum of Compound 3c (150 MHz, CDCl₃)

3maxiaoming02.830.fid
Q-3Me



-73.17
-73.56

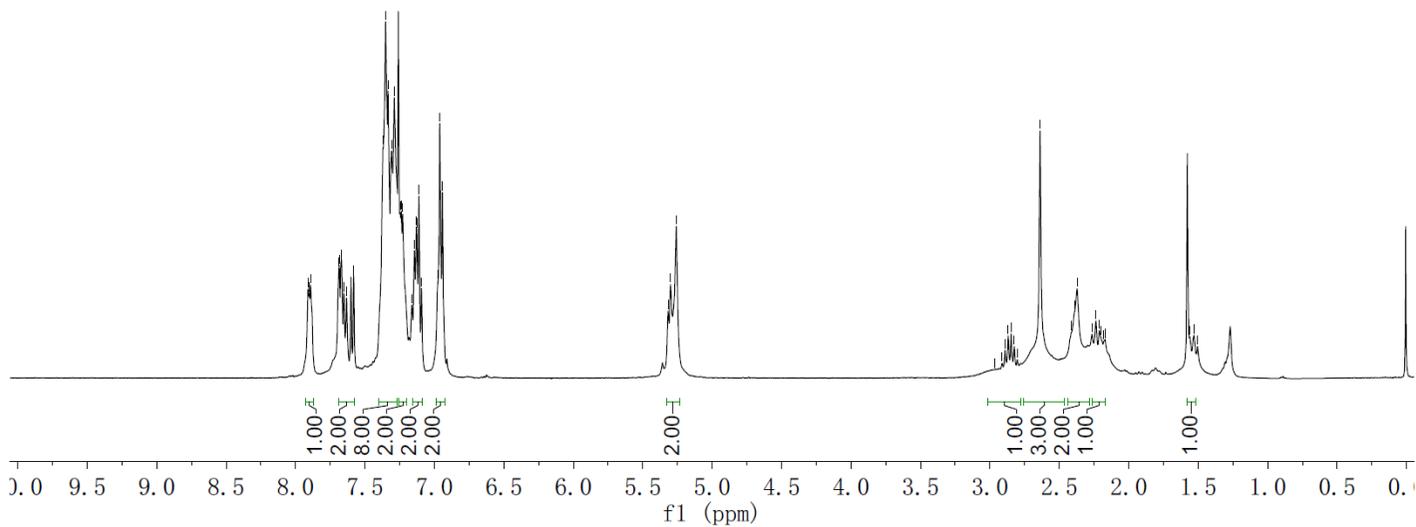
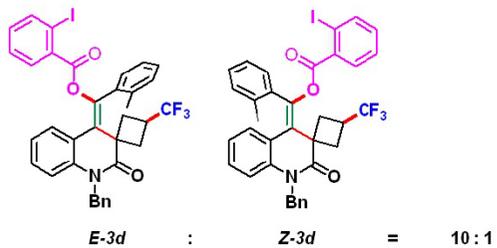


¹⁹F NMR Spectrum of Compound 3c (282 MHz, CDCl₃)

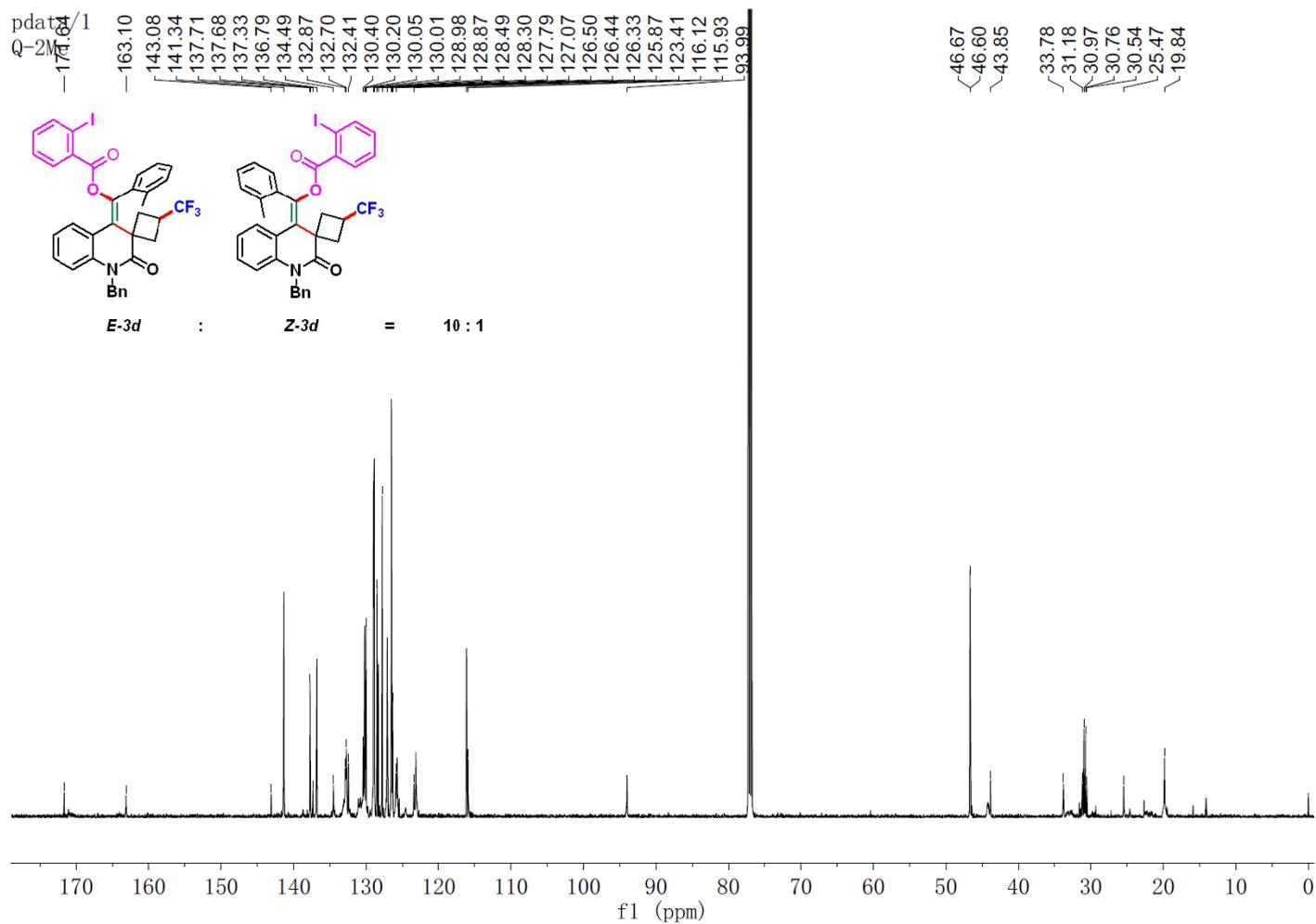
max
XP

7.911
7.895
7.887
7.885
7.873
7.868
7.802
7.595
7.583
7.580
7.370
7.352
7.334
7.309
7.289
7.247
7.239
7.229
7.144
7.130
7.127
7.112
7.093
6.975
6.962
6.947
5.300
5.259

2.967
2.912
2.890
2.868
2.846
2.824
2.802
2.639
2.411
2.391
2.372
2.265
2.236
2.211
2.203
2.179
2.172
1.560
1.531
1.504

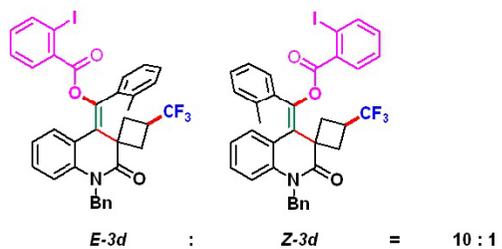


¹H NMR Spectrum of Compound 3d (400 MHz, CDCl₃)

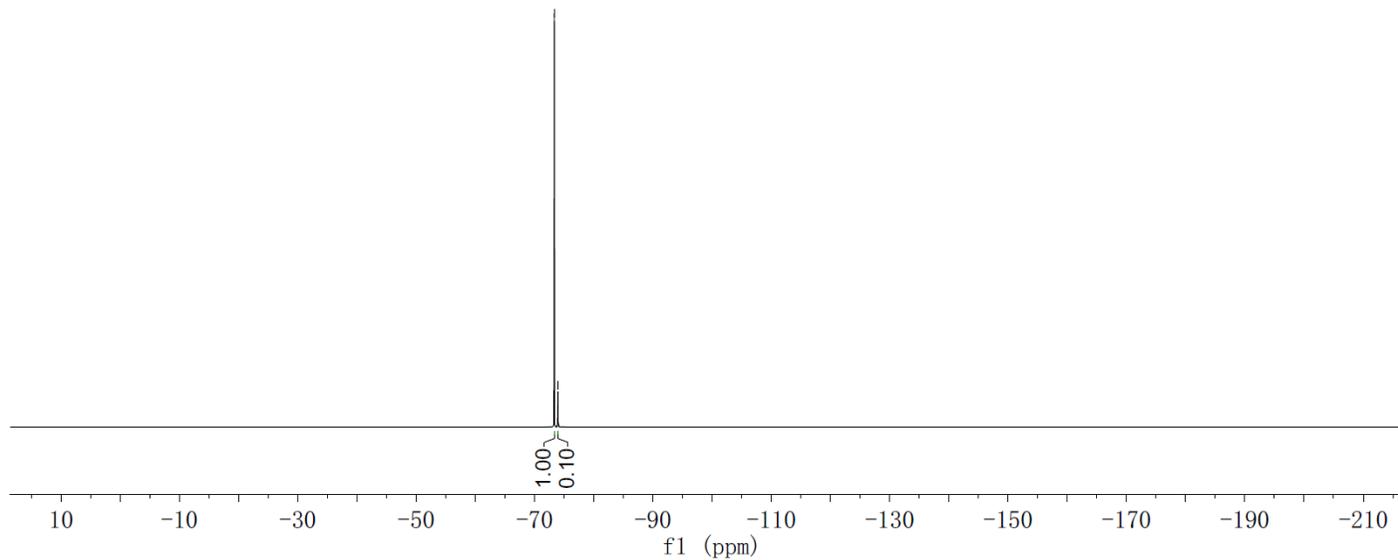


¹³C NMR Spectrum of Compound 3d (150 MHz, CDCl₃)

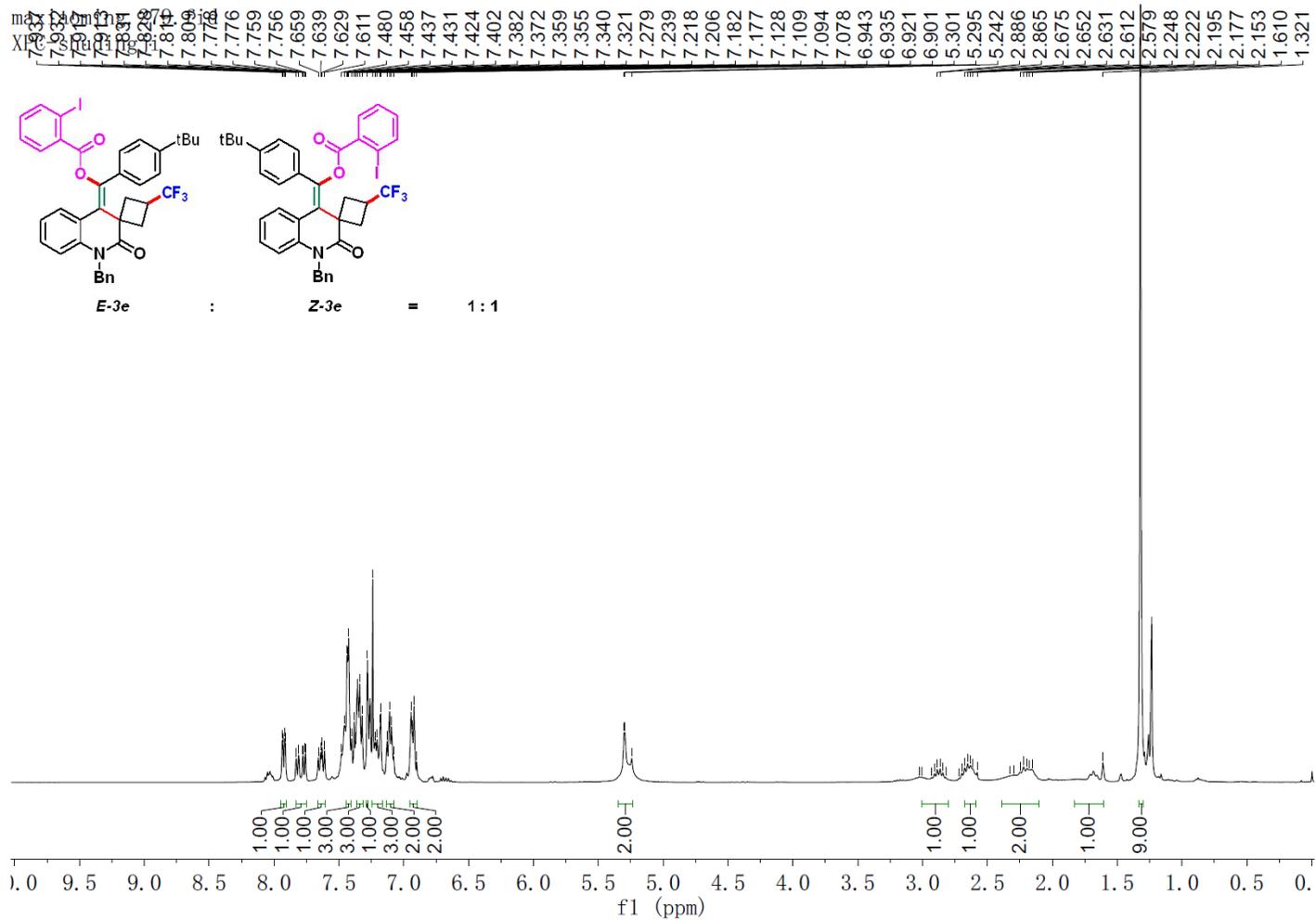
3maxiaoming02.780.fid
que-2Me



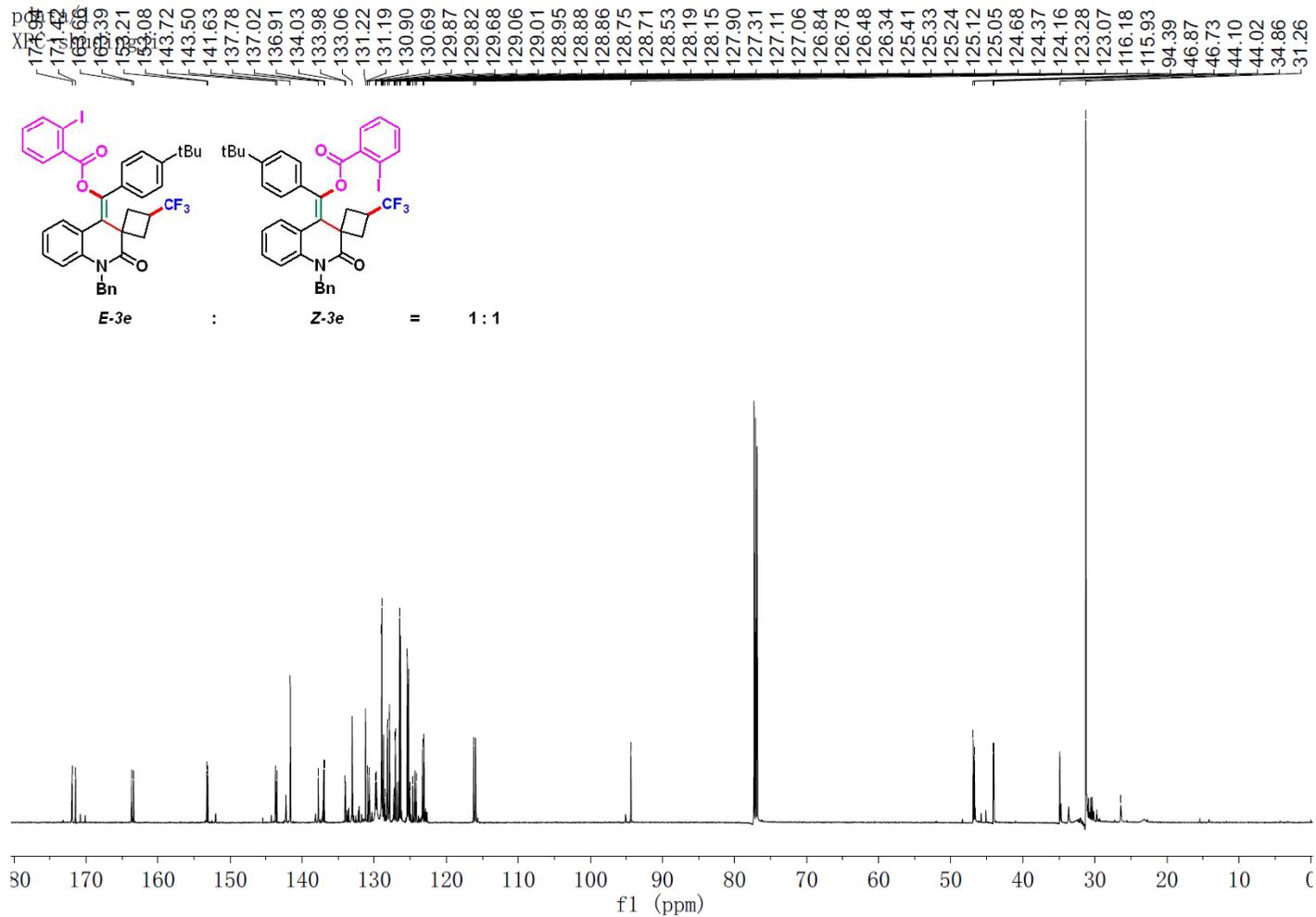
73.34
73.97



¹⁹F NMR Spectrum of Compound 3d (282 MHz, CDCl₃)



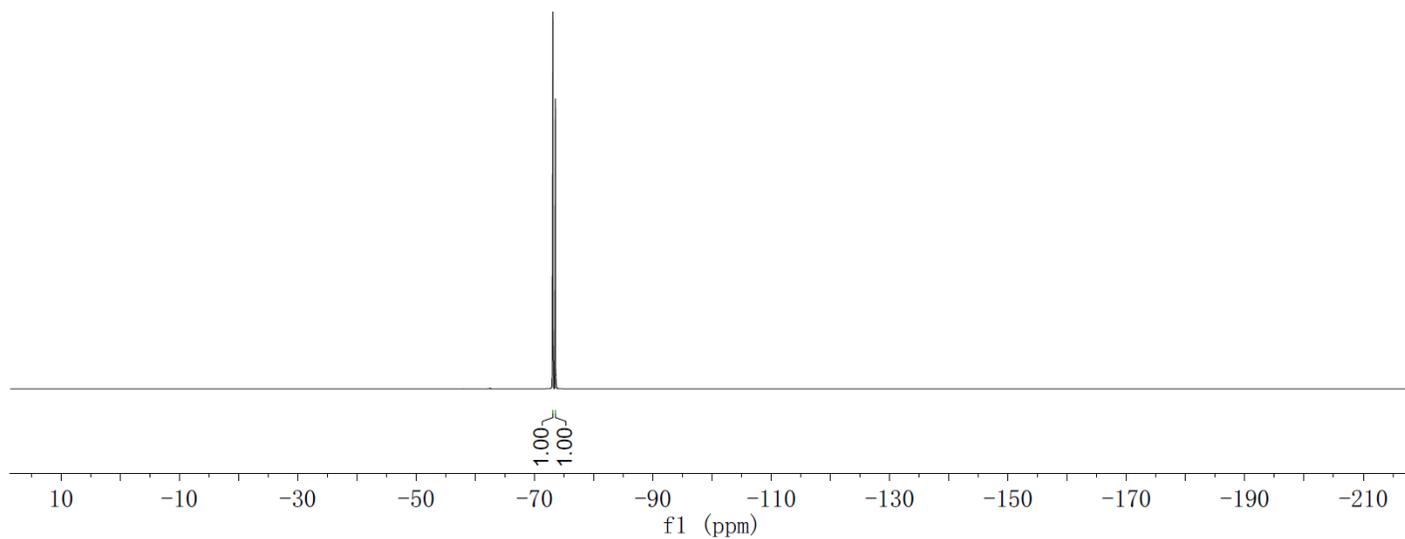
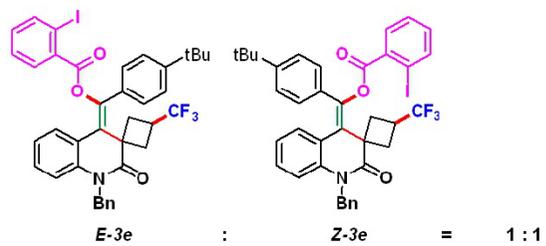
¹H NMR Spectrum of Compound 3e (400 MHz, CDCl₃)



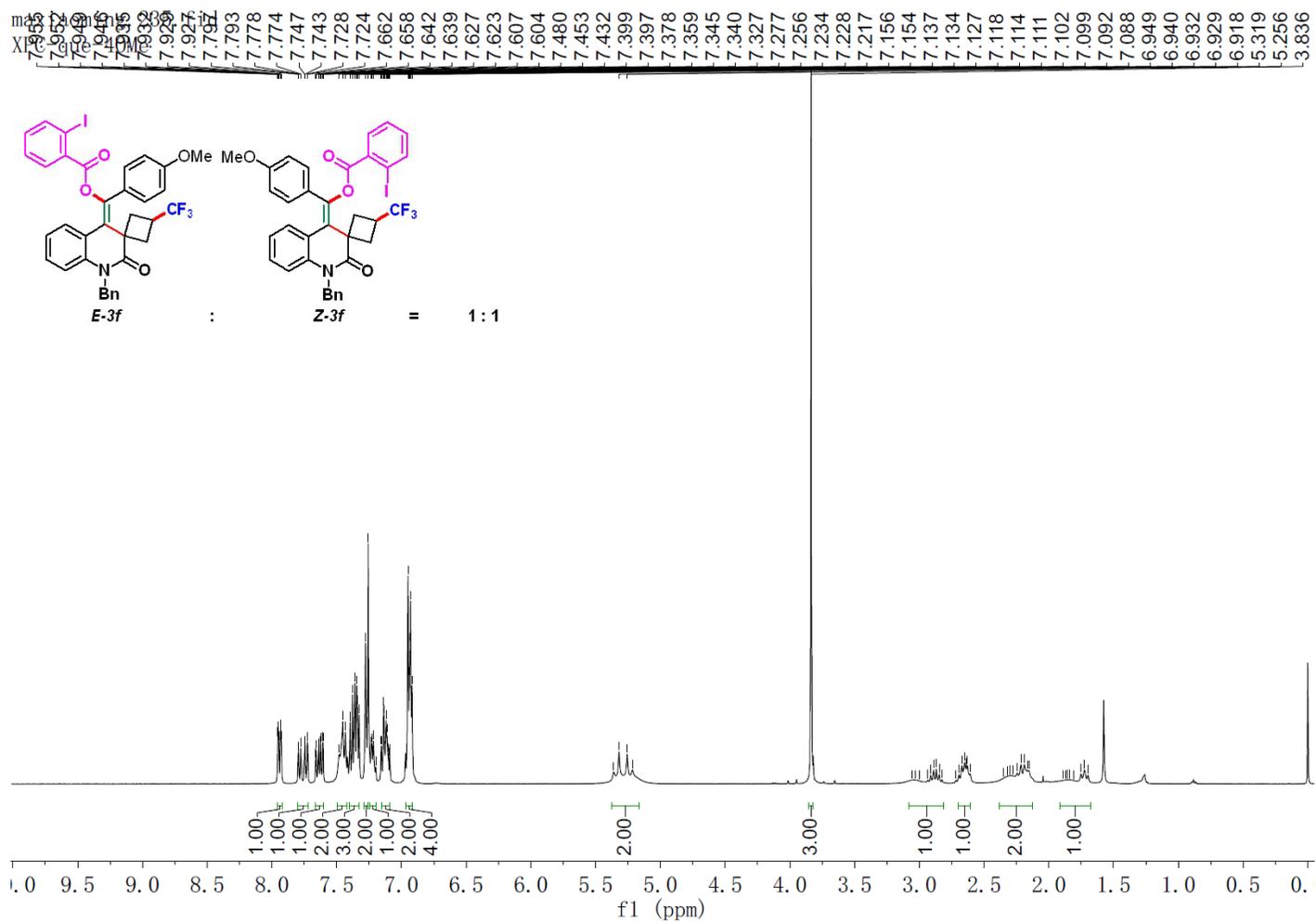
¹³C NMR Spectrum of Compound 3e (150 MHz, CDCl₃)

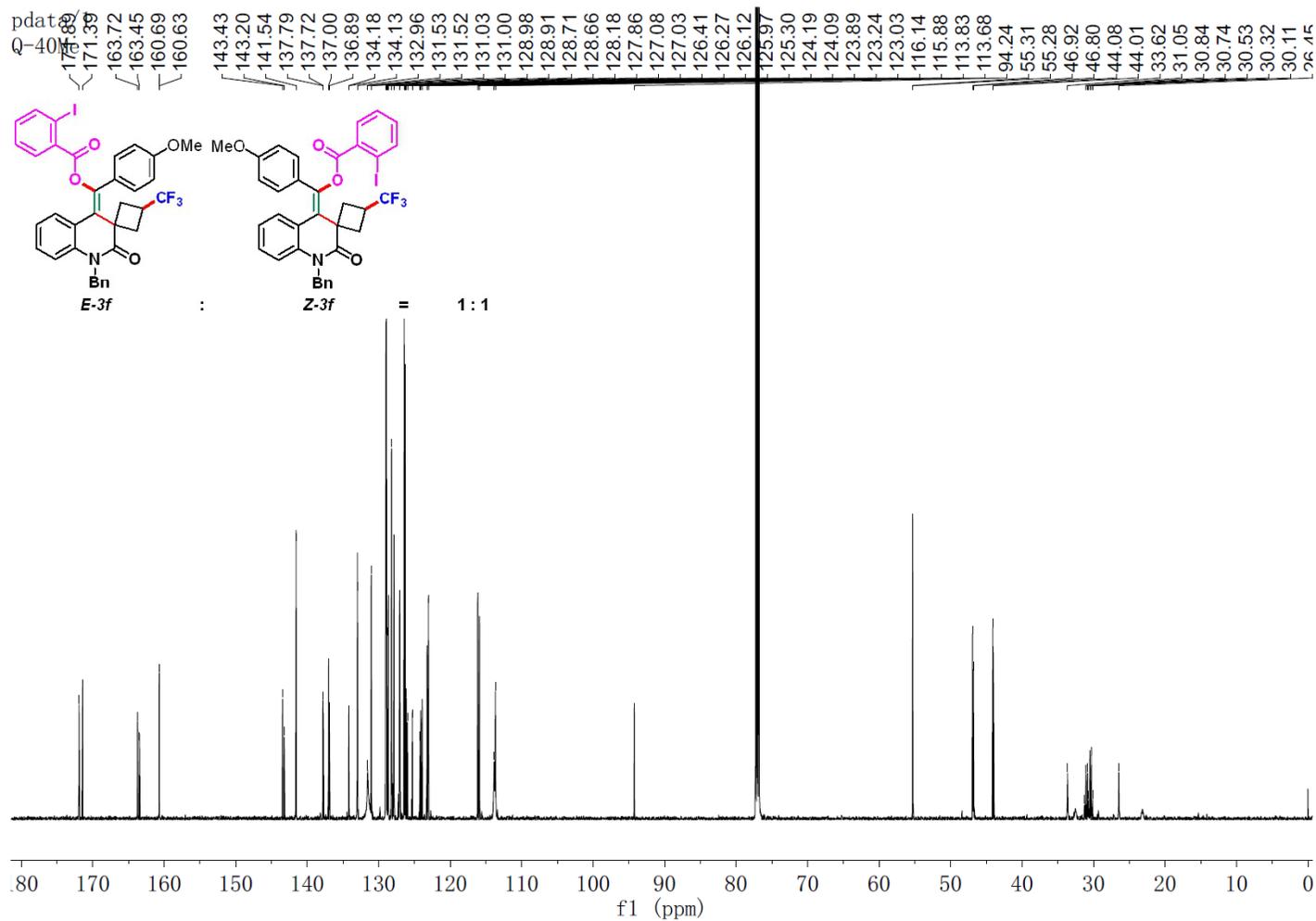
3maxiaoming02.860.fid
XPC-shudingji

-73.10
-73.53



¹⁹F NMR Spectrum of Compound 3e (282 MHz, CDCl₃)

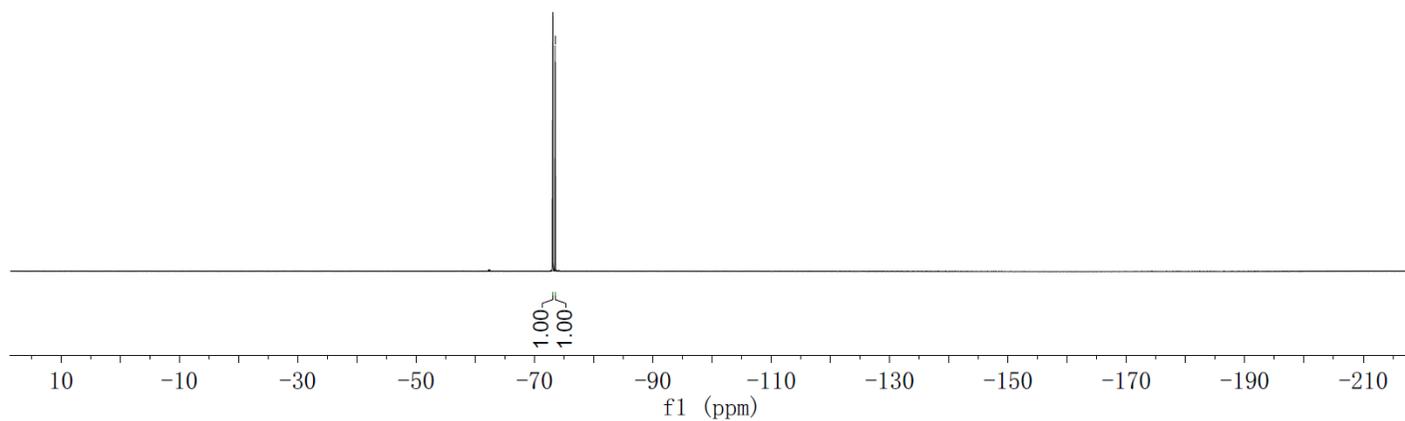
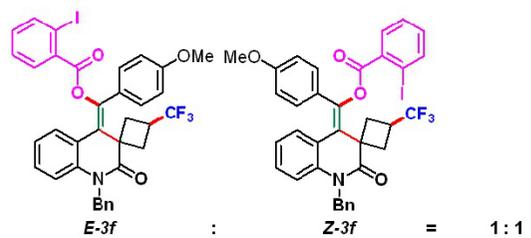




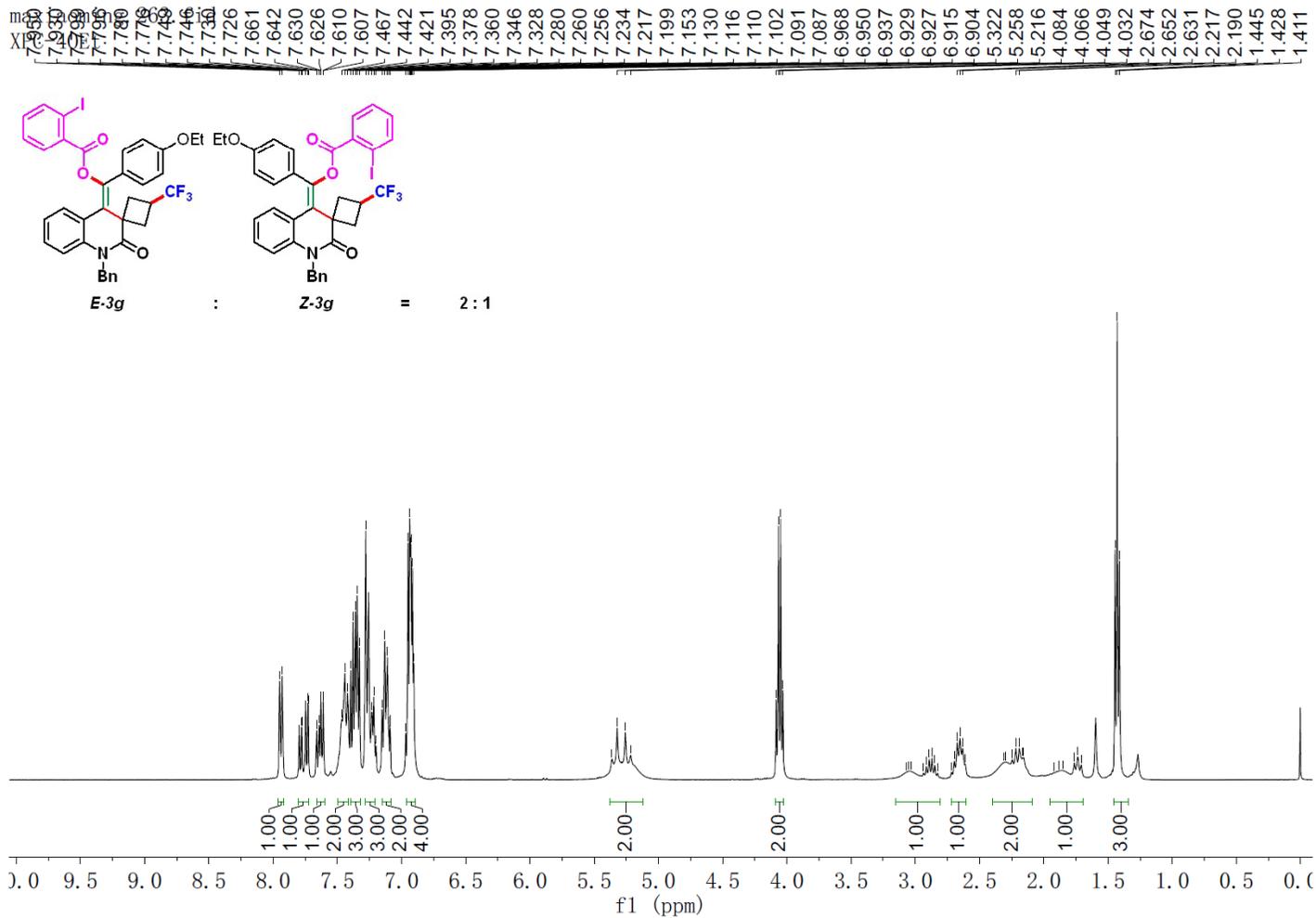
¹³C NMR Spectrum of Compound 3f (150 MHz, CDCl₃)

3maxiaoming02.810.fid
que-40Me

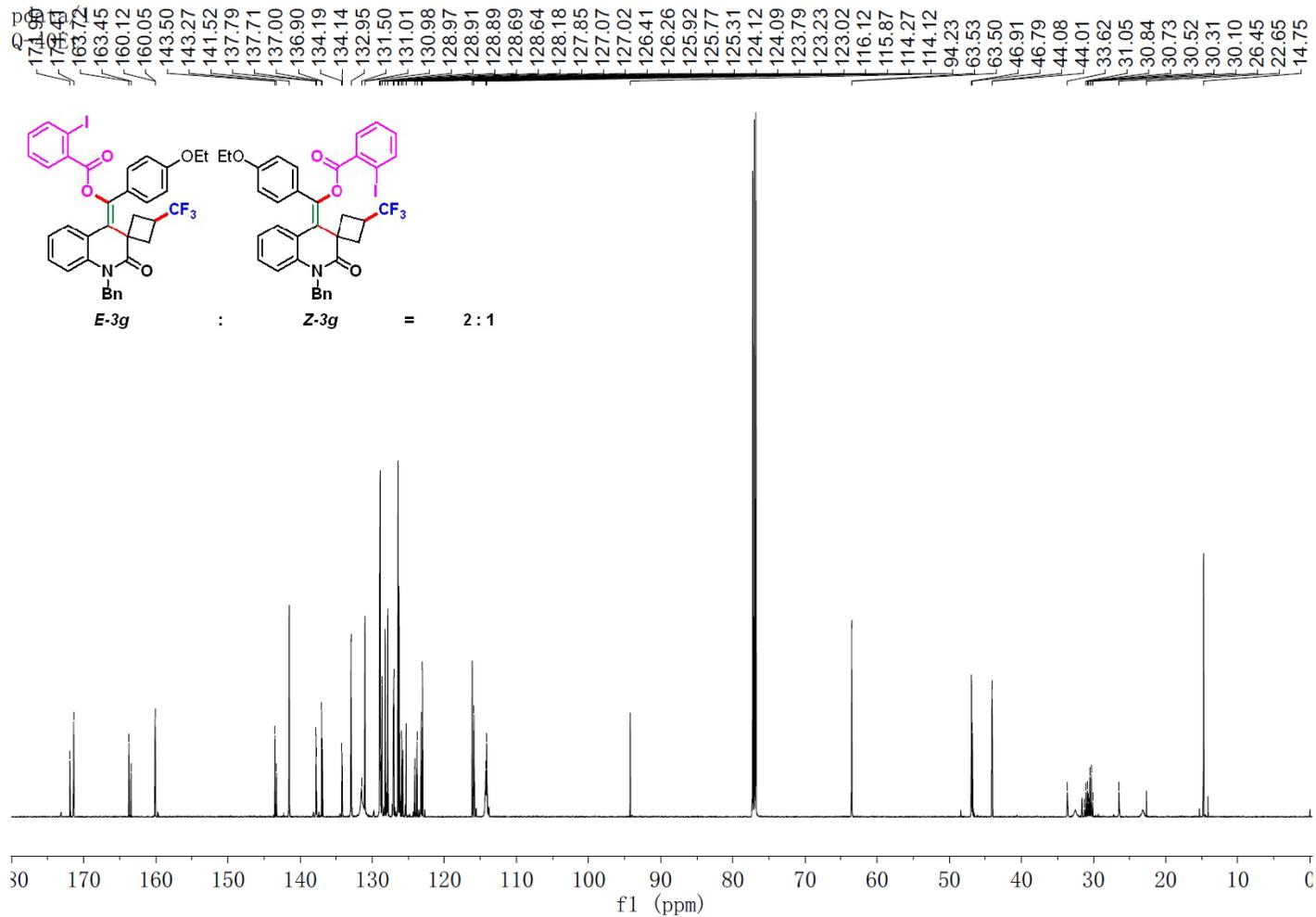
-73.09
-73.48



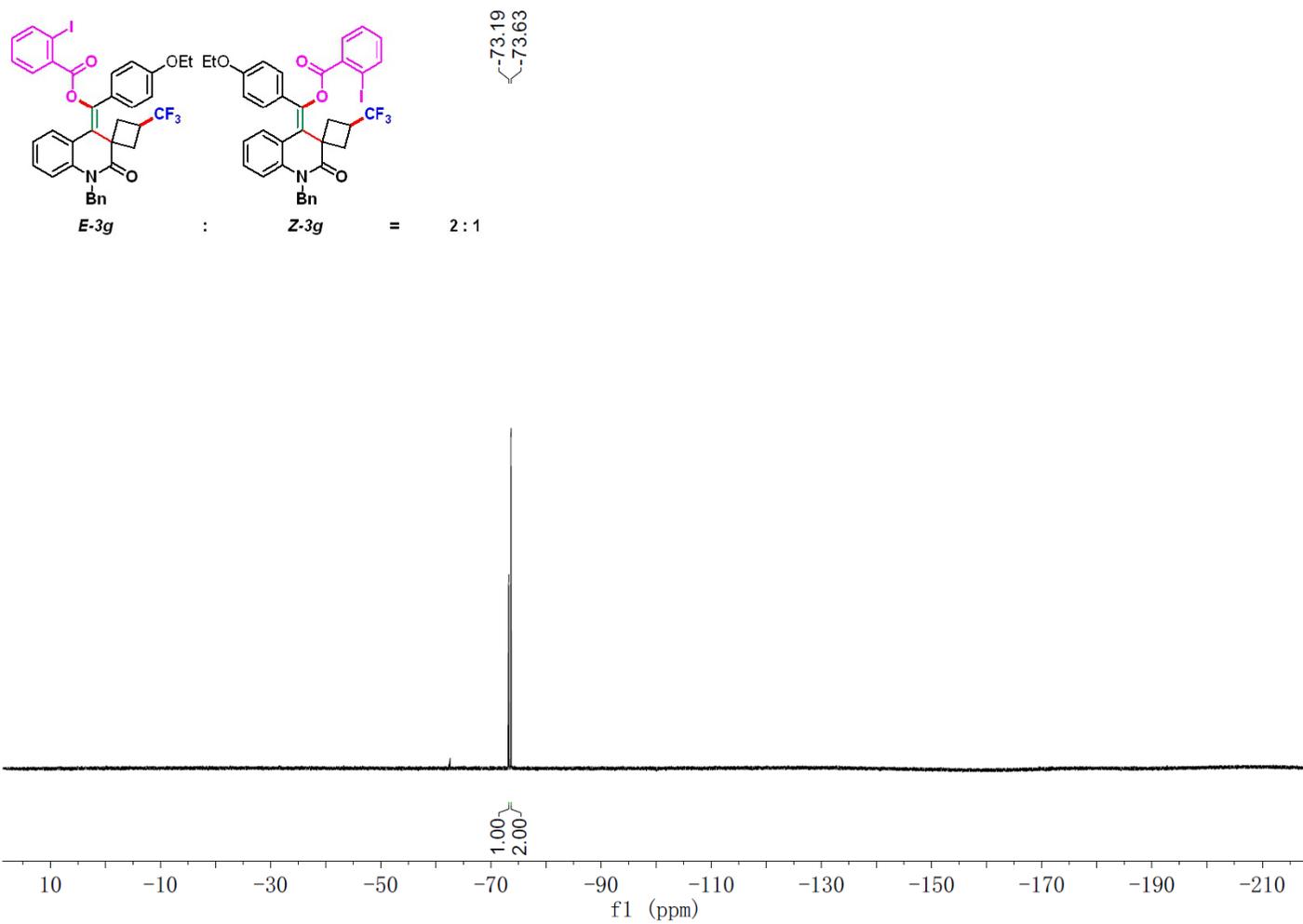
¹⁹F NMR Spectrum of Compound 3f (282 MHz, CDCl₃)



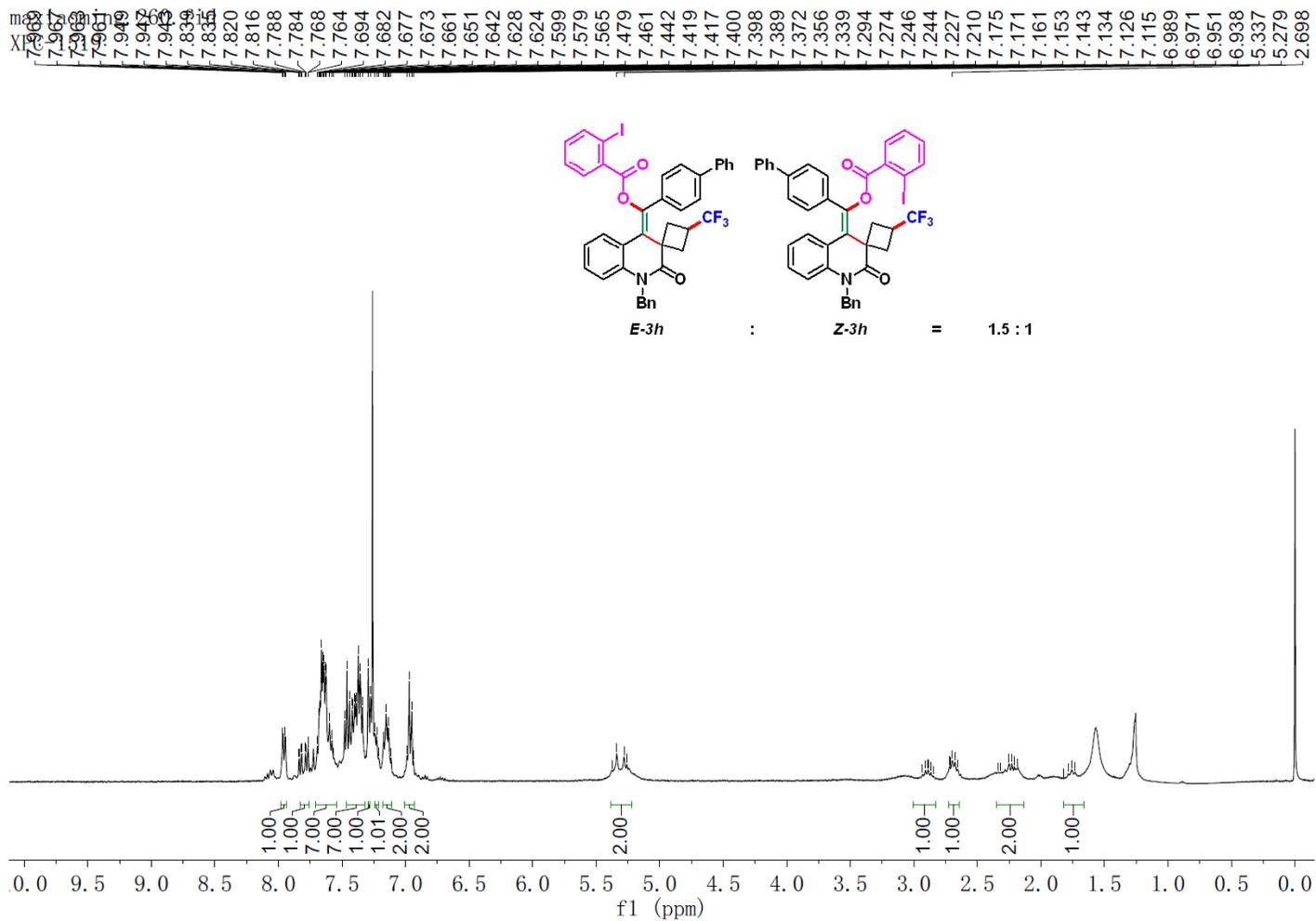
^1H NMR Spectrum of Compound 3g (400 MHz, CDCl_3)



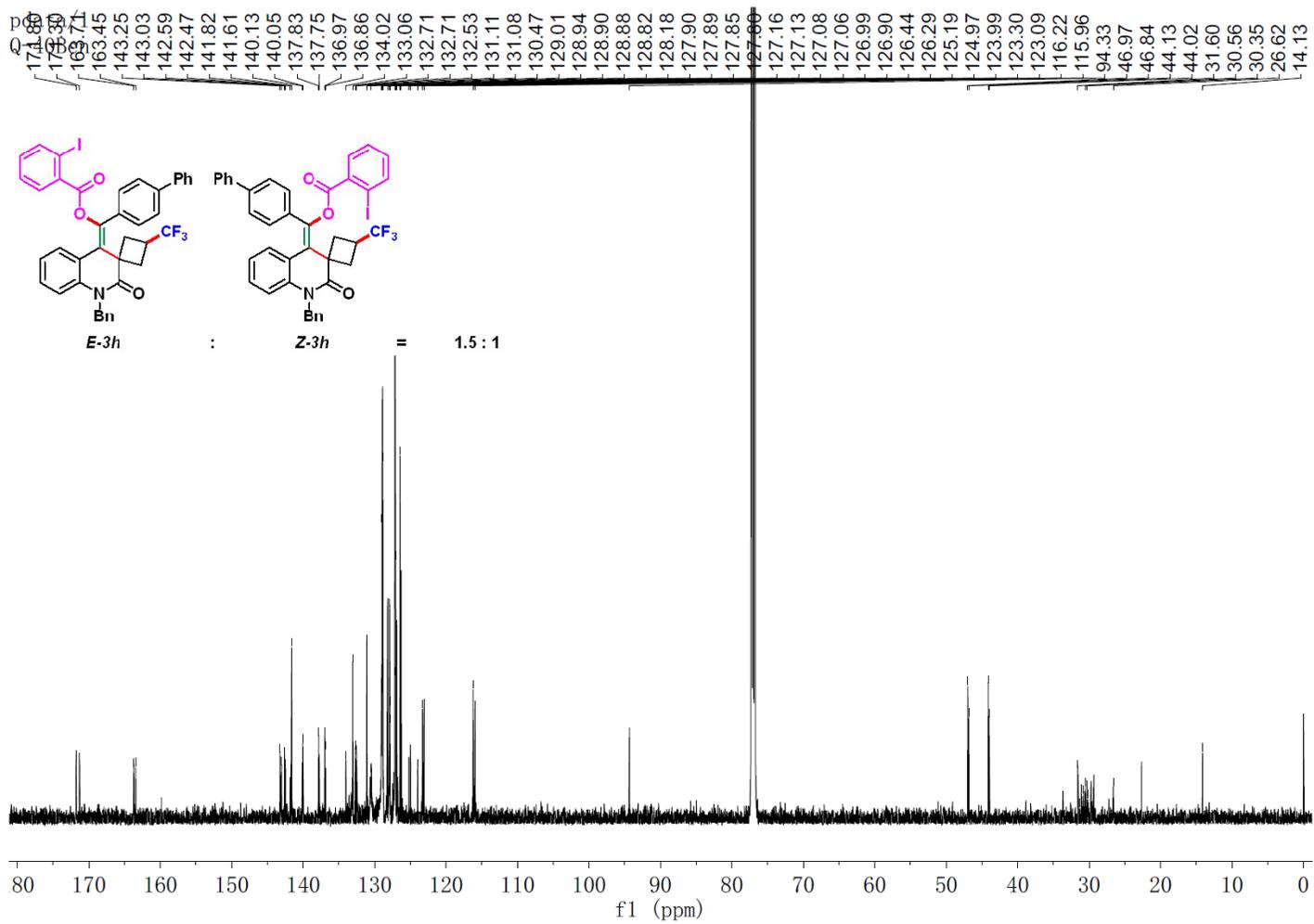
¹³C NMR Spectrum of Compound 3g (150 MHz, CDCl₃)



¹⁹F NMR Spectrum of Compound 3g (282 MHz, CDCl₃)



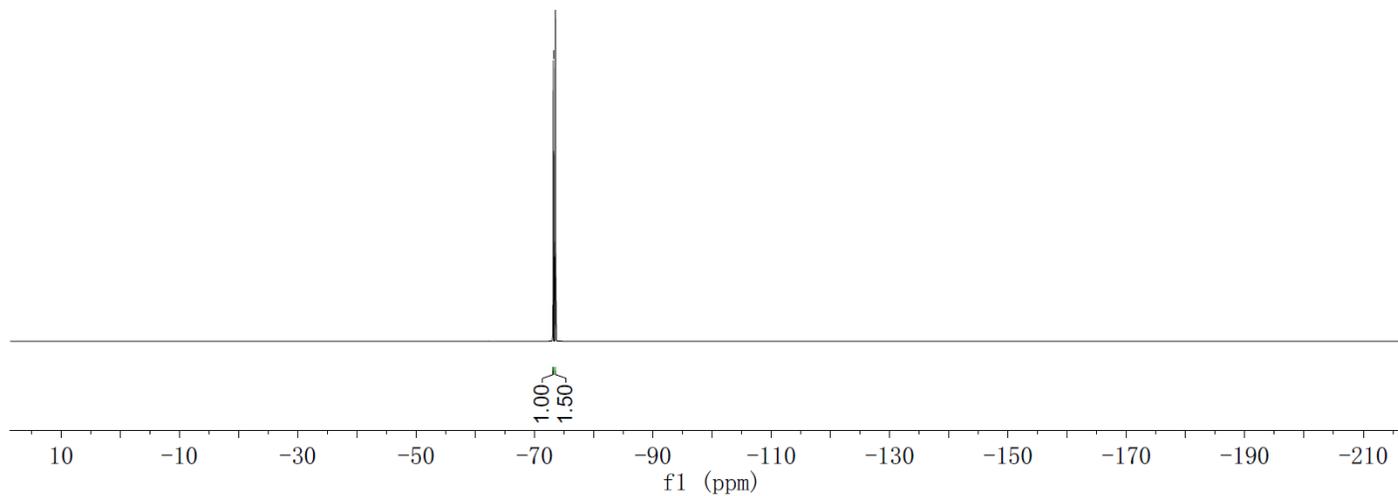
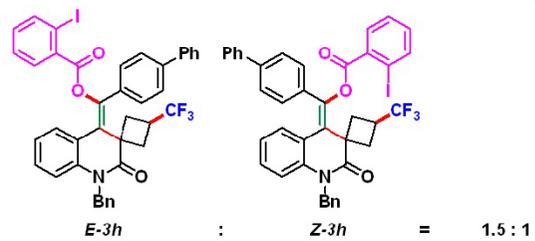
¹H NMR Spectrum of Compound 3h (400 MHz, CDCl₃)



¹³C NMR Spectrum of Compound 3h (150 MHz, CDCl₃)

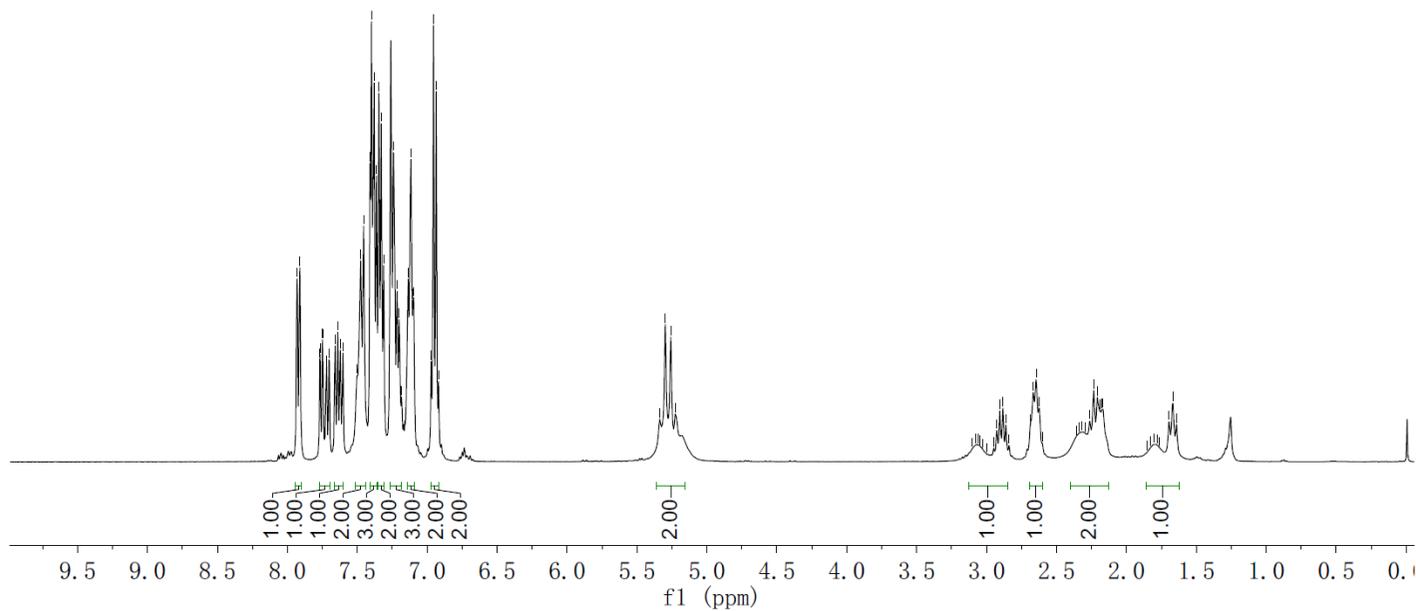
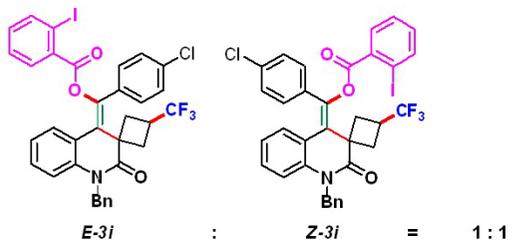
3maxiaoming02.910.fid
Q-BEN

-73.16
-73.55

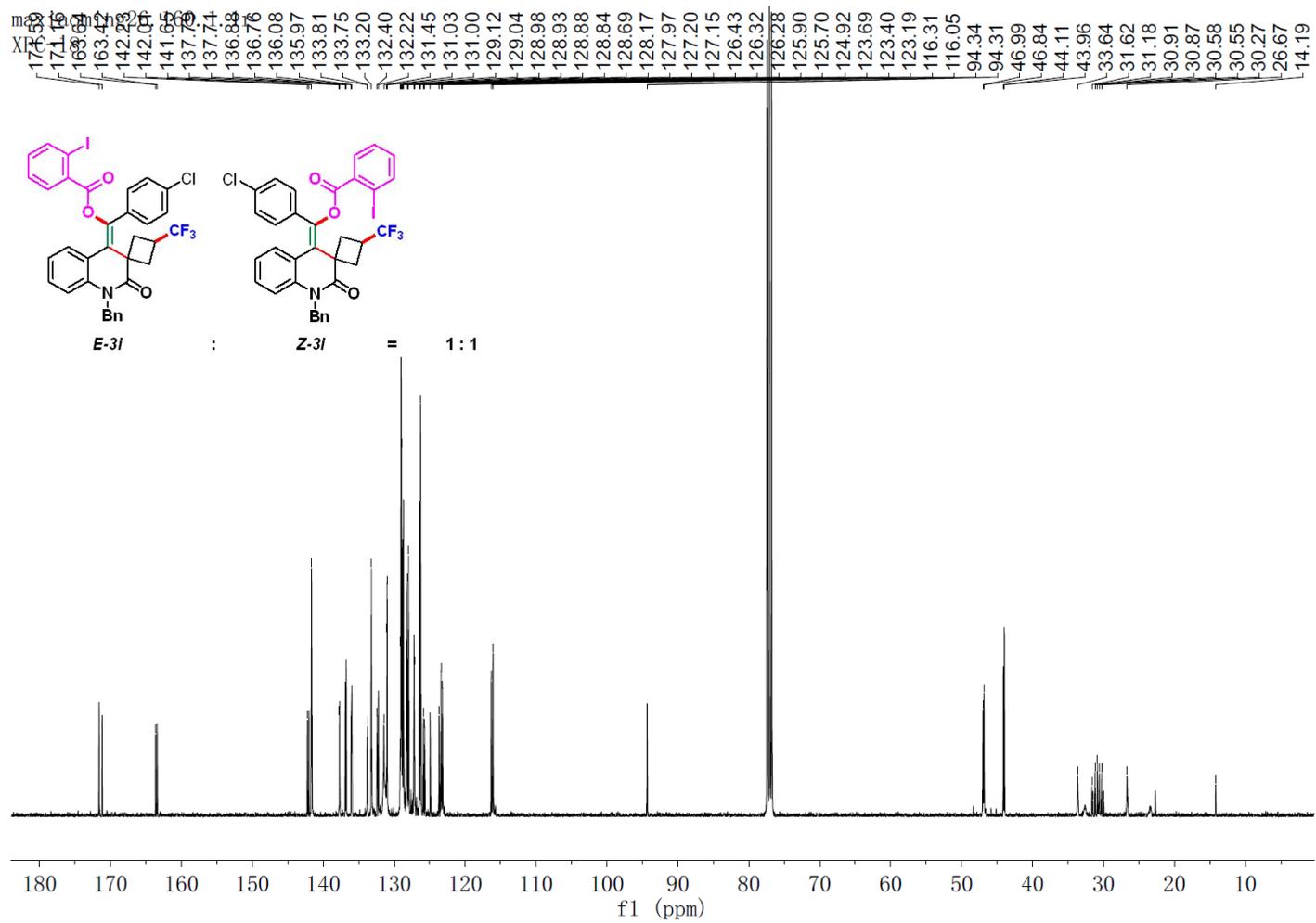


¹⁹F NMR Spectrum of Compound 3h (282 MHz, CDCl₃)

7.930
7.911
7.898
7.765
7.749
7.748
7.722
7.719
7.705
7.700
7.658
7.639
7.621
7.602
7.501
7.475
7.455
7.408
7.399
7.386
7.379
7.363
7.345
7.329
7.312
7.241
7.215
7.201
7.184
7.135
7.116
7.102
7.096
6.971
6.955
6.936
6.919
5.337
5.297
5.258
5.226
2.927
2.905
2.884
2.862
2.688
2.667
2.646
2.624
2.319
2.262
2.234
2.208
2.186
2.176
2.168
1.695
1.669
1.642



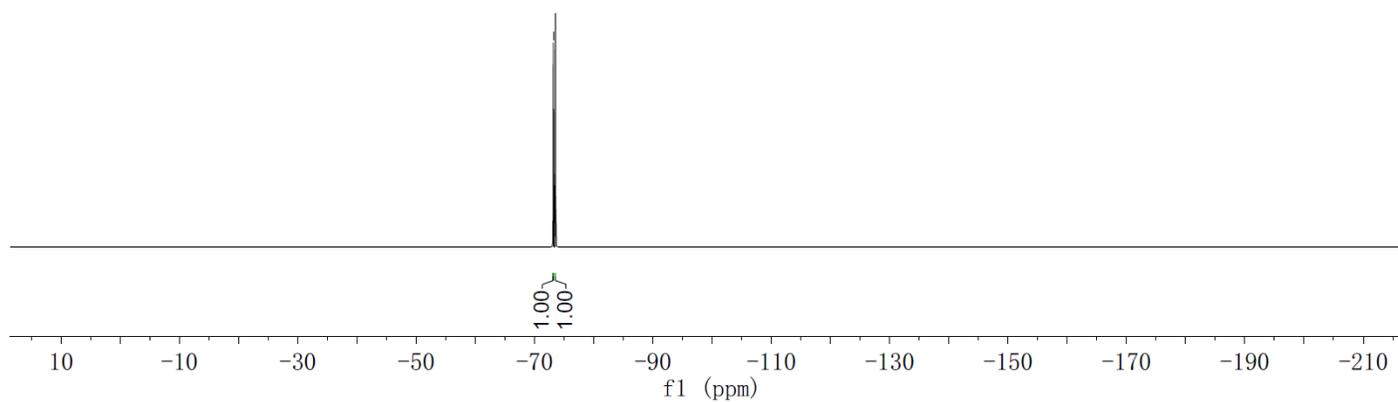
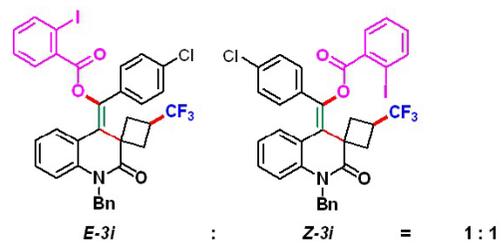
¹H NMR Spectrum of Compound 3i (400 MHz, CDCl₃)



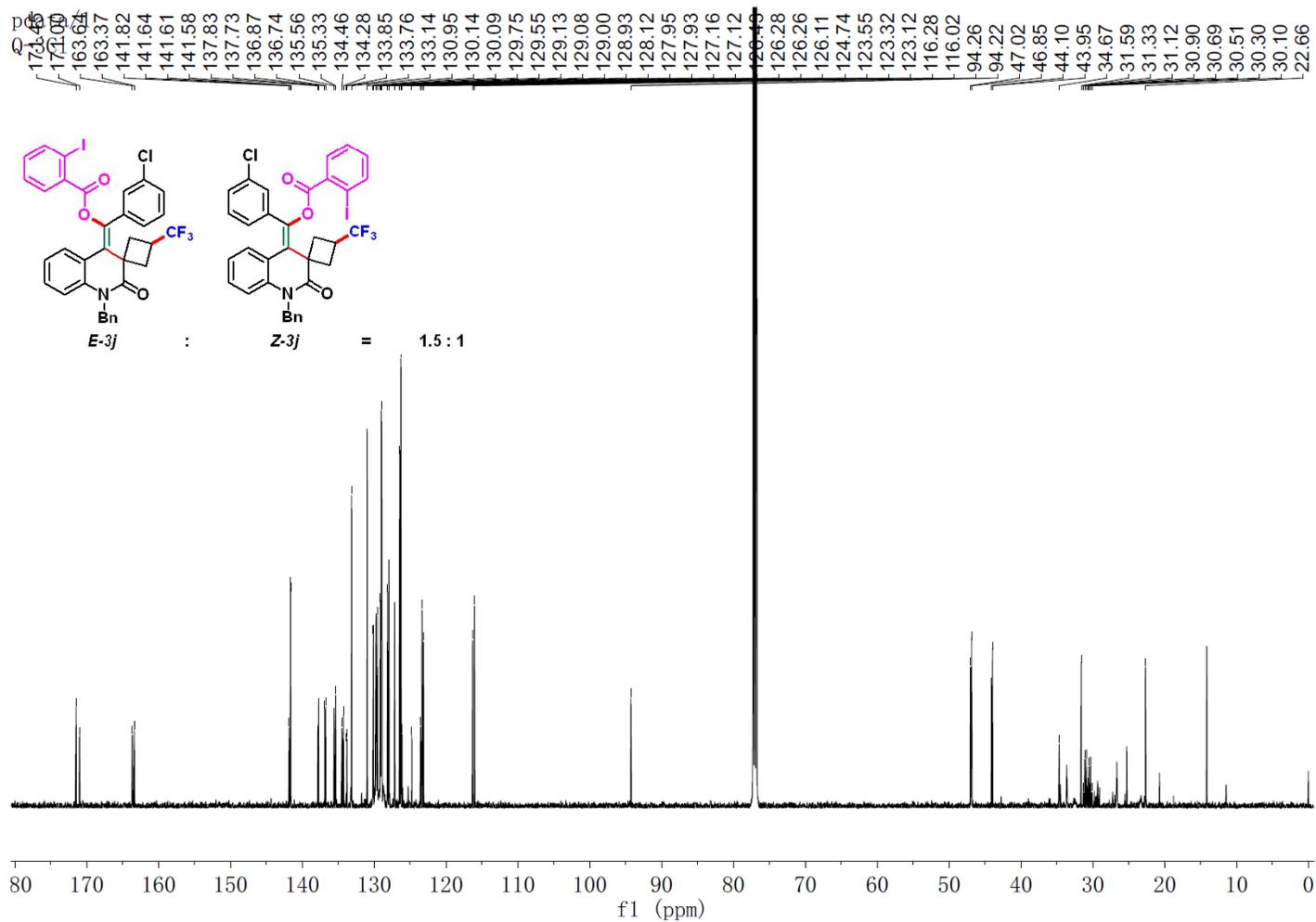
¹³C NMR Spectrum of Compound 3i (100 MHz, CDCl₃)

3maxiaoming02.640.fid
19

73.16
73.54

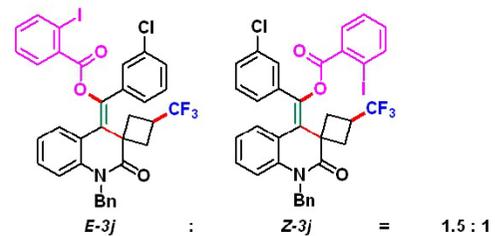


¹⁹F NMR Spectrum of Compound 3i (282 MHz, CDCl₃)

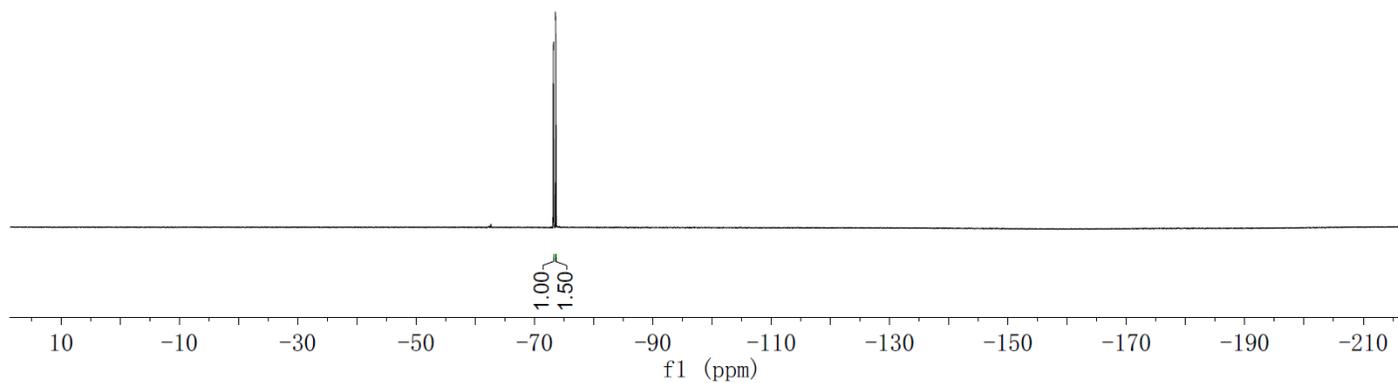


¹³C NMR Spectrum of Compound 3j (150 MHz, CDCl₃)

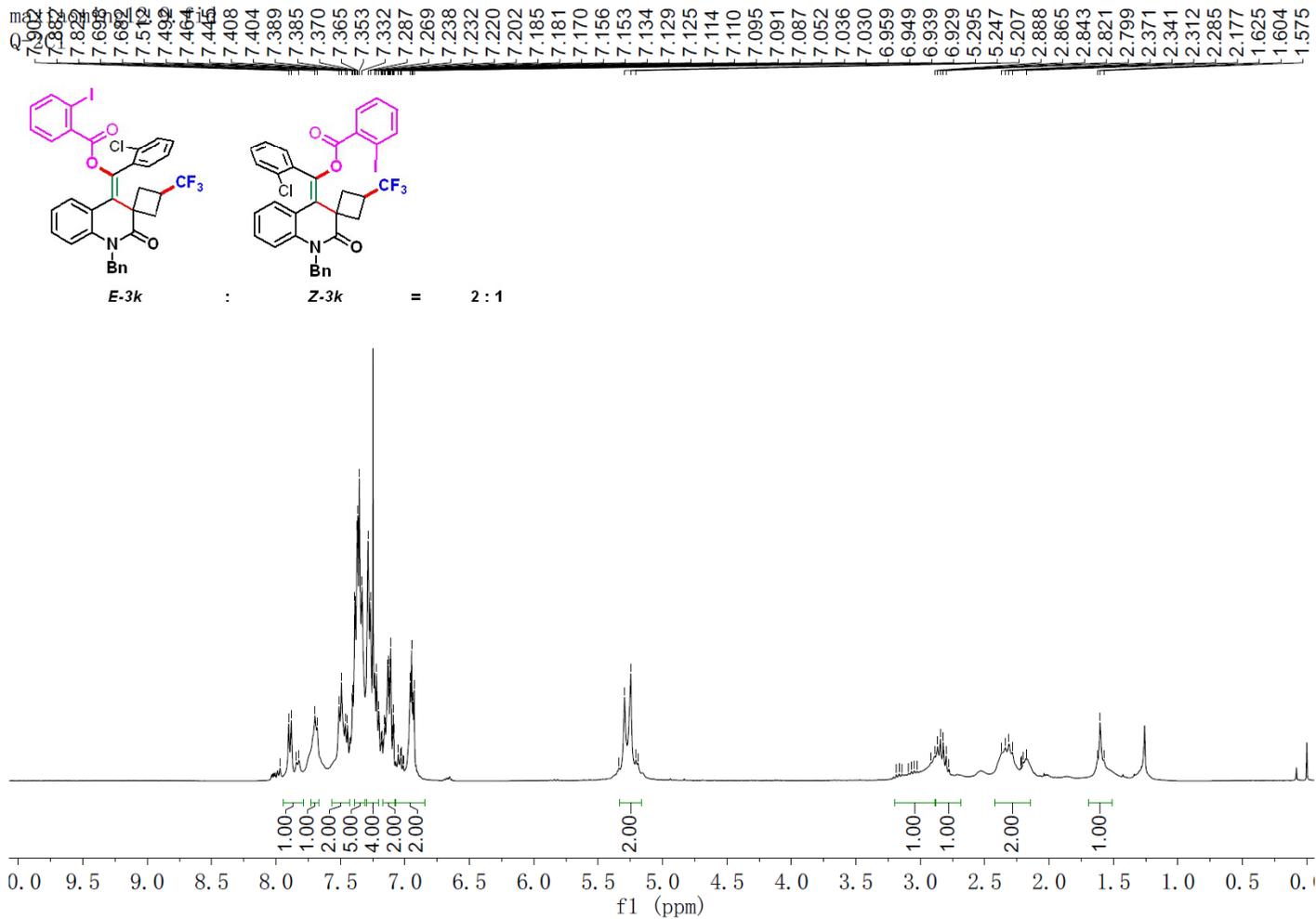
3maxiaoming02.650.fid
20



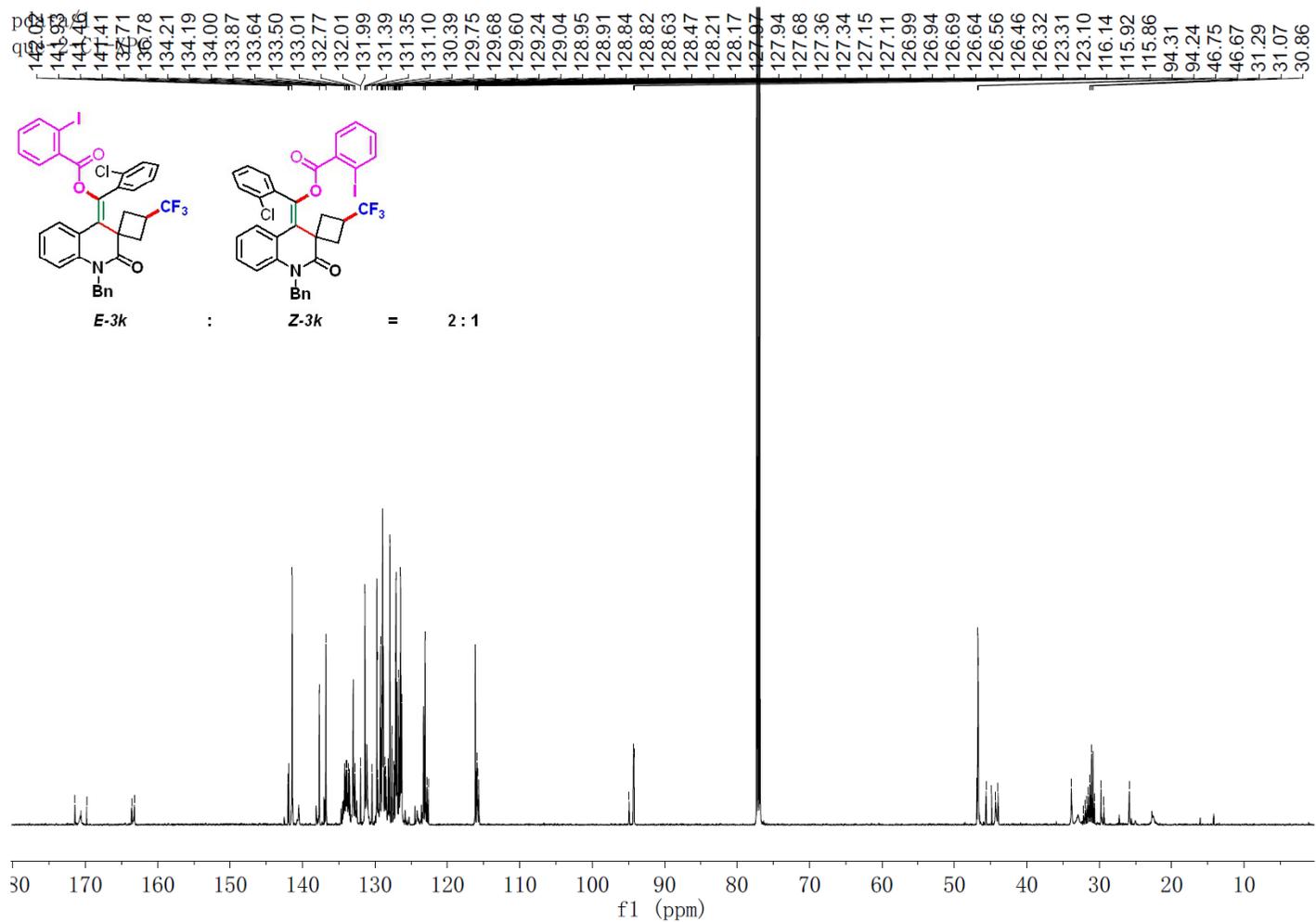
-73.17
-73.59



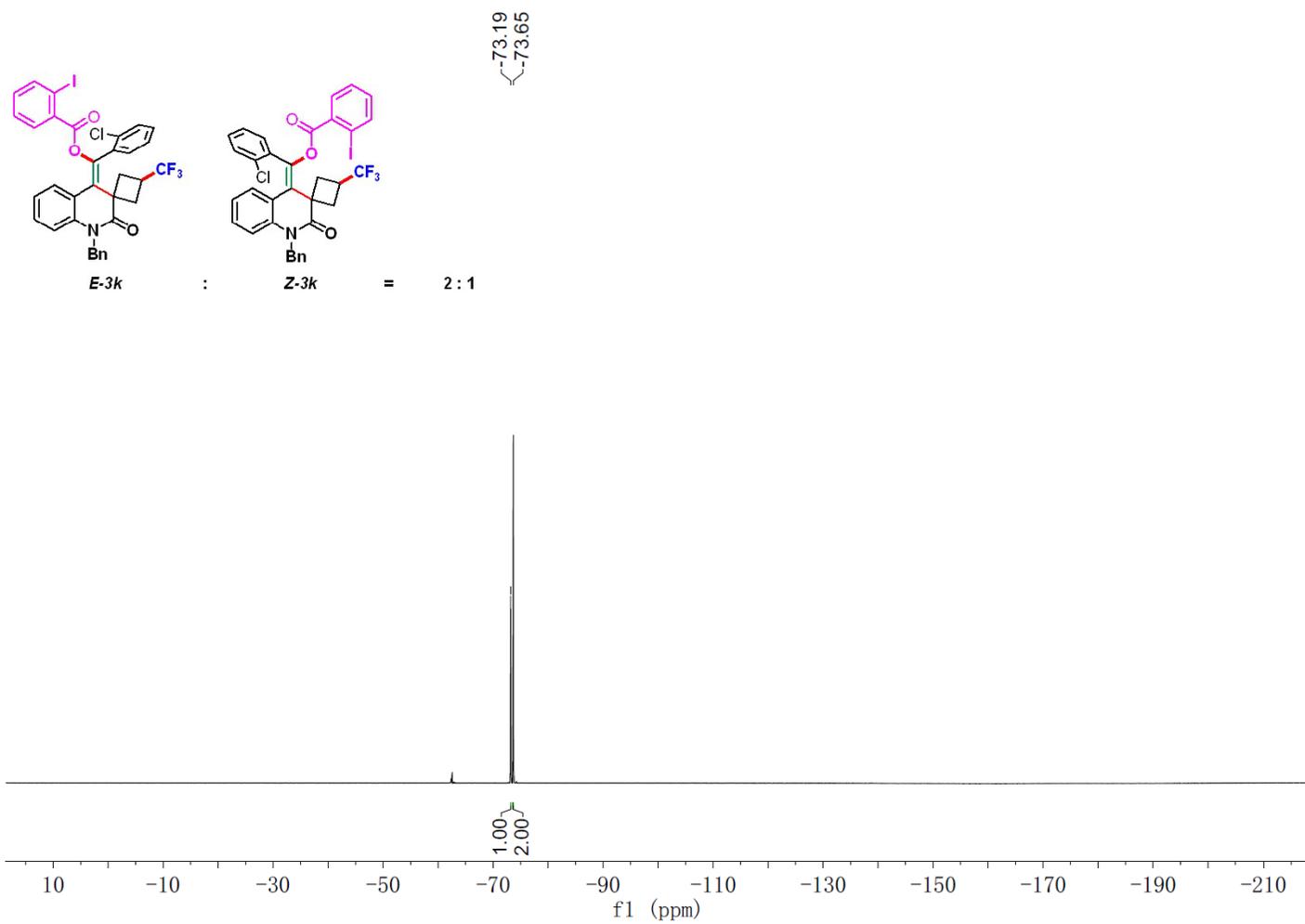
¹⁹F NMR Spectrum of Compound 3j (282 MHz, CDCl₃)



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

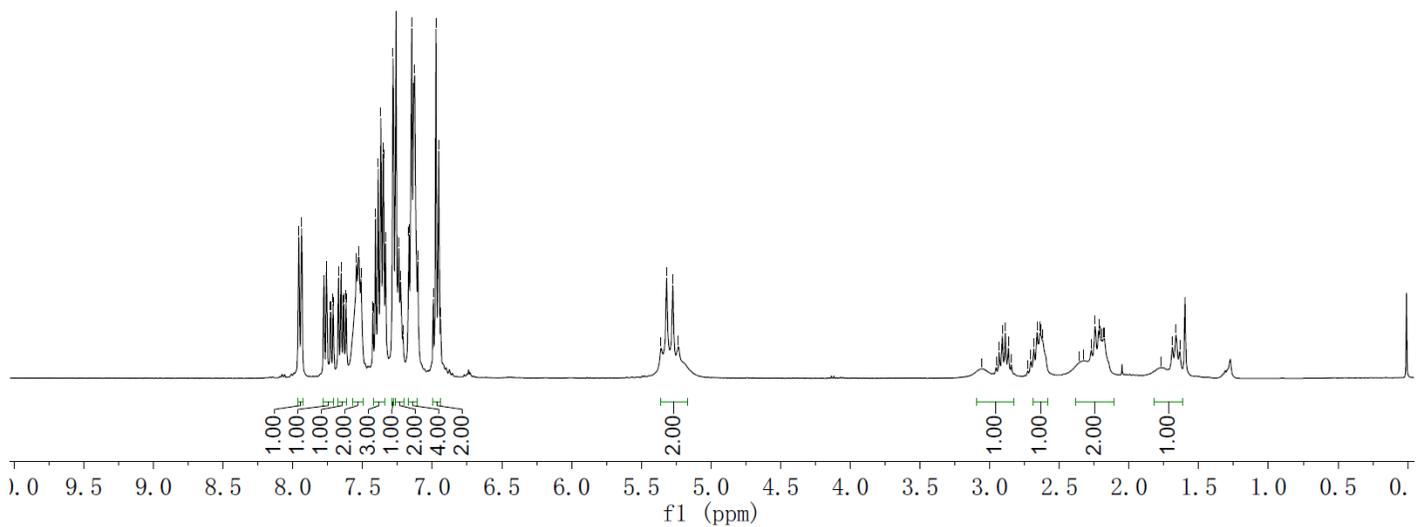
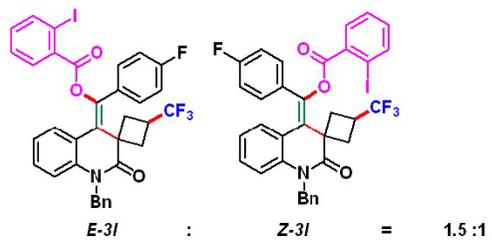


¹³C NMR Spectrum of Compound 3k (150 MHz, CDCl₃)

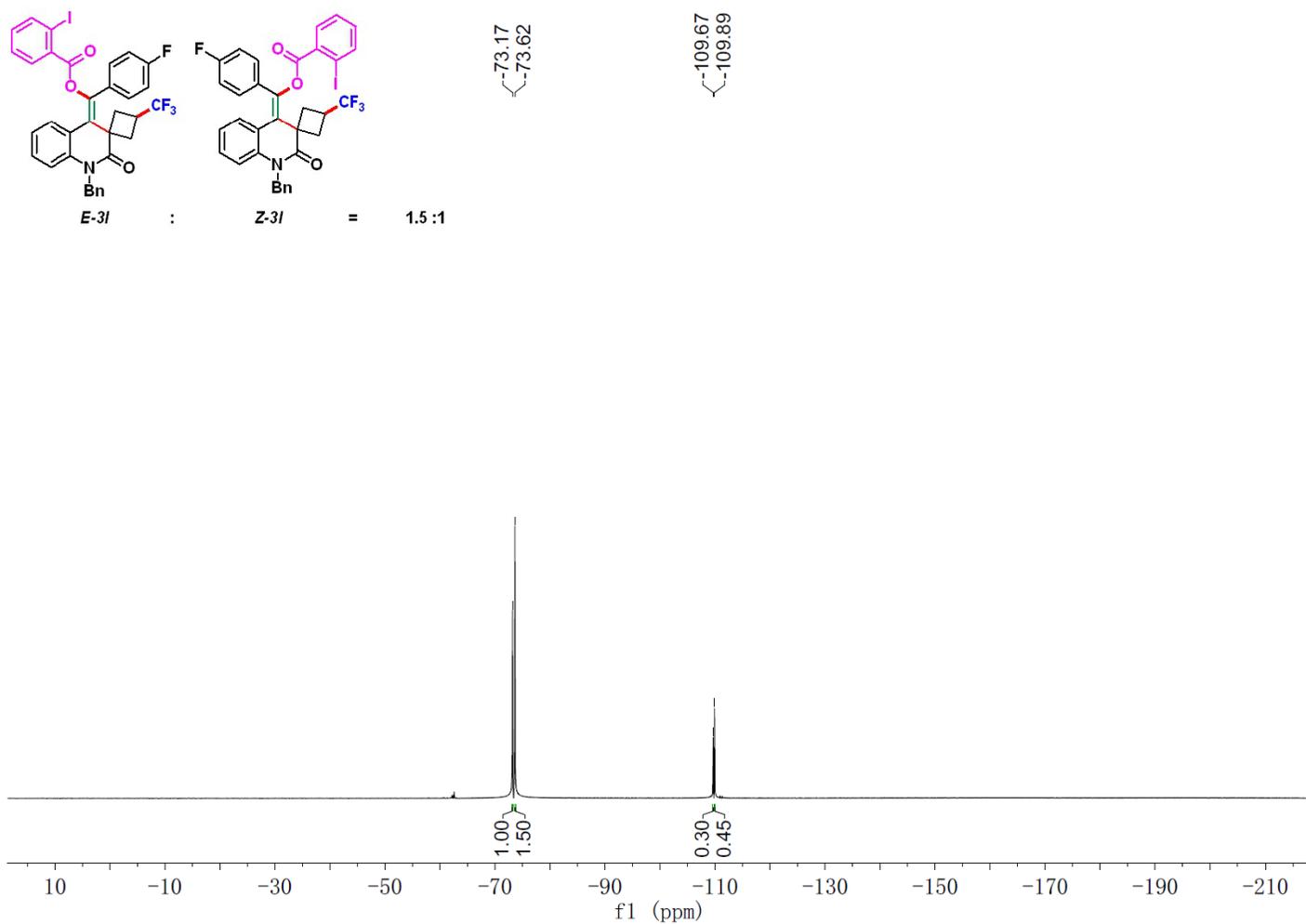


¹⁹F NMR Spectrum of Compound 3k (282 MHz, CDCl₃)

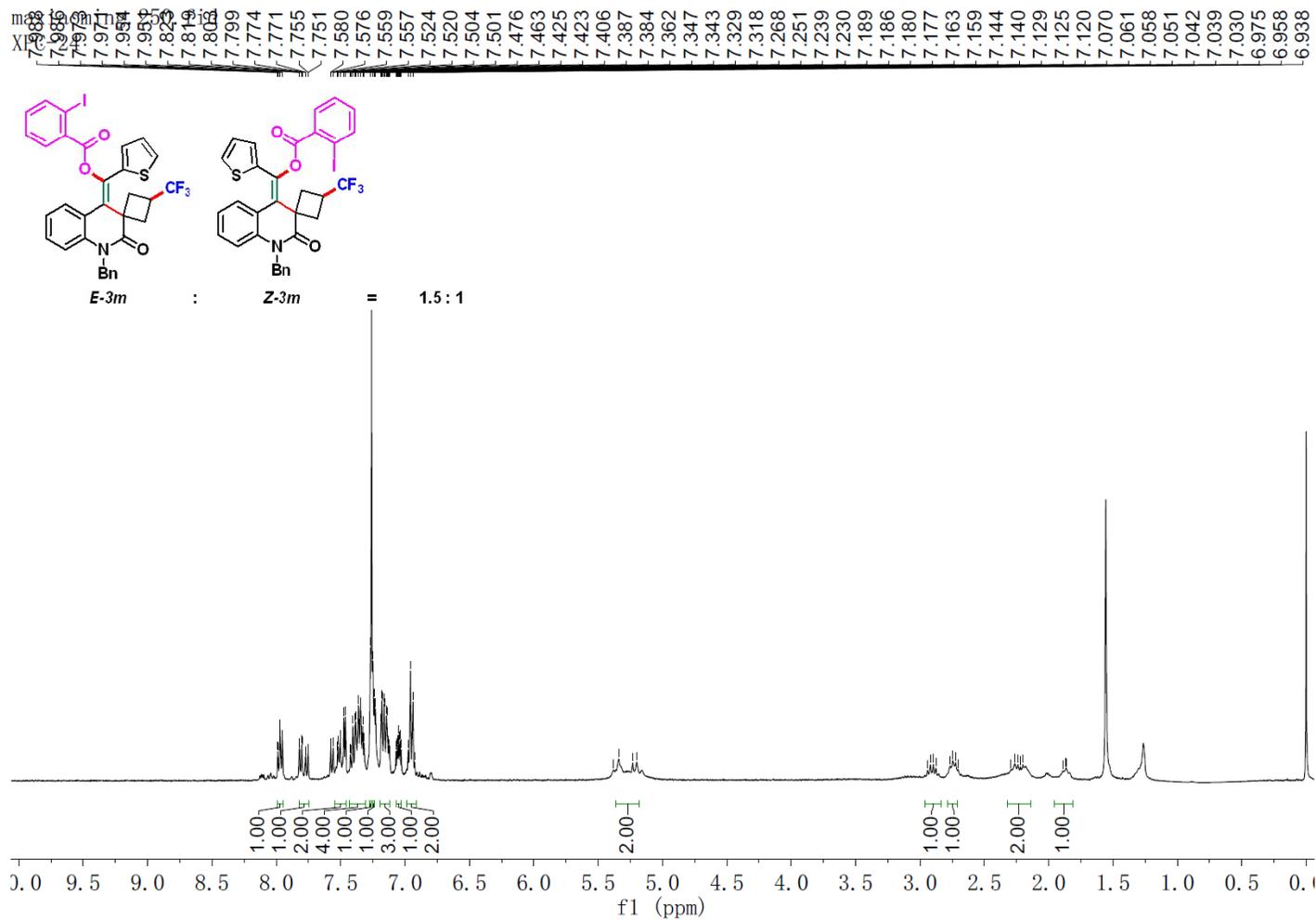
7.967
 7.937
 7.779
 7.775
 7.760
 7.756
 7.734
 7.727
 7.712
 7.708
 7.672
 7.653
 7.639
 7.635
 7.619
 7.616
 7.543
 7.530
 7.525
 7.511
 7.426
 7.424
 7.407
 7.388
 7.368
 7.353
 7.349
 7.335
 7.281
 7.239
 7.227
 7.210
 7.169
 7.166
 7.146
 7.133
 7.130
 7.126
 7.102
 6.992
 6.973
 6.954
 6.941
 5.318
 5.274
 5.233
 2.910
 2.888
 2.660
 2.638
 2.630
 2.619
 2.243
 2.217
 2.209
 2.197
 2.184
 2.177
 1.663



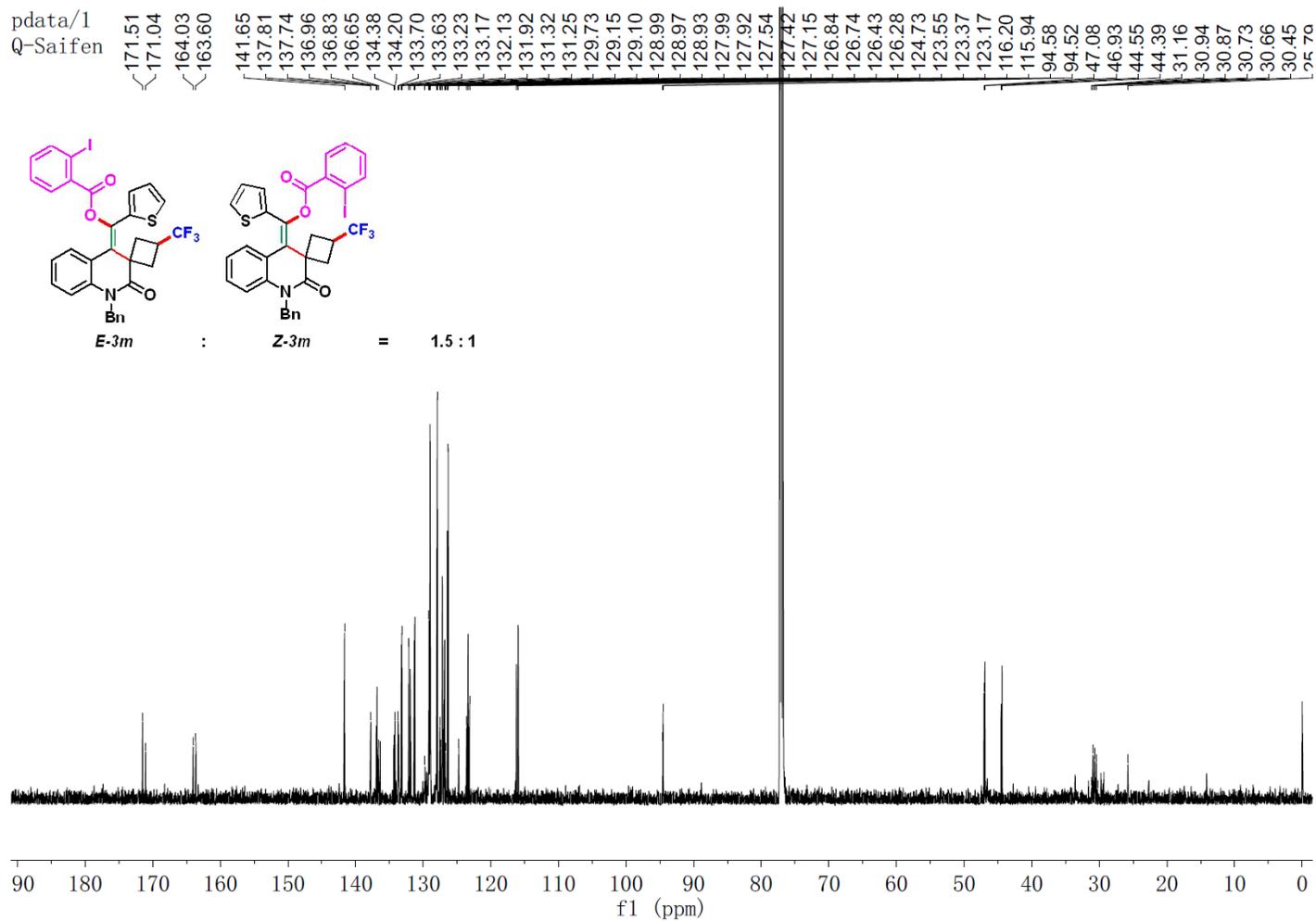
¹H NMR Spectrum of Compound 31 (400 MHz, CDCl₃)



¹⁹F NMR Spectrum of Compound 31 (282 MHz, CDCl₃)



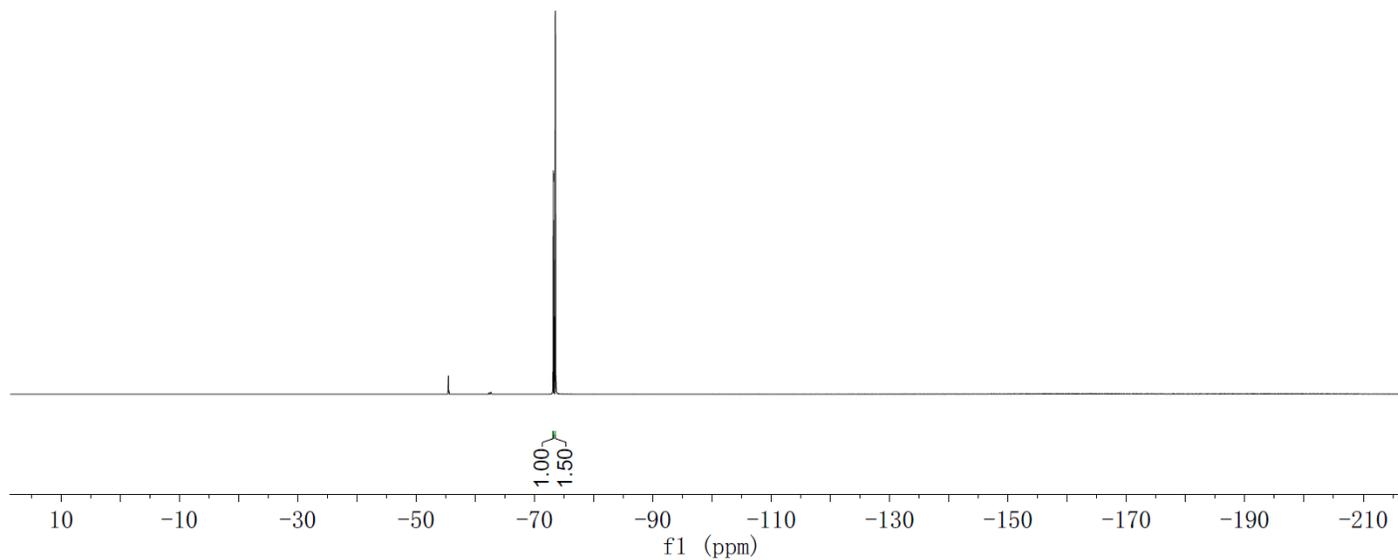
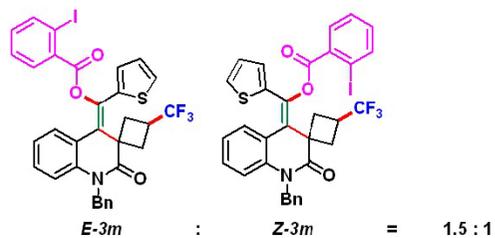
¹H NMR Spectrum of Compound 3m (400 MHz, CDCl₃)



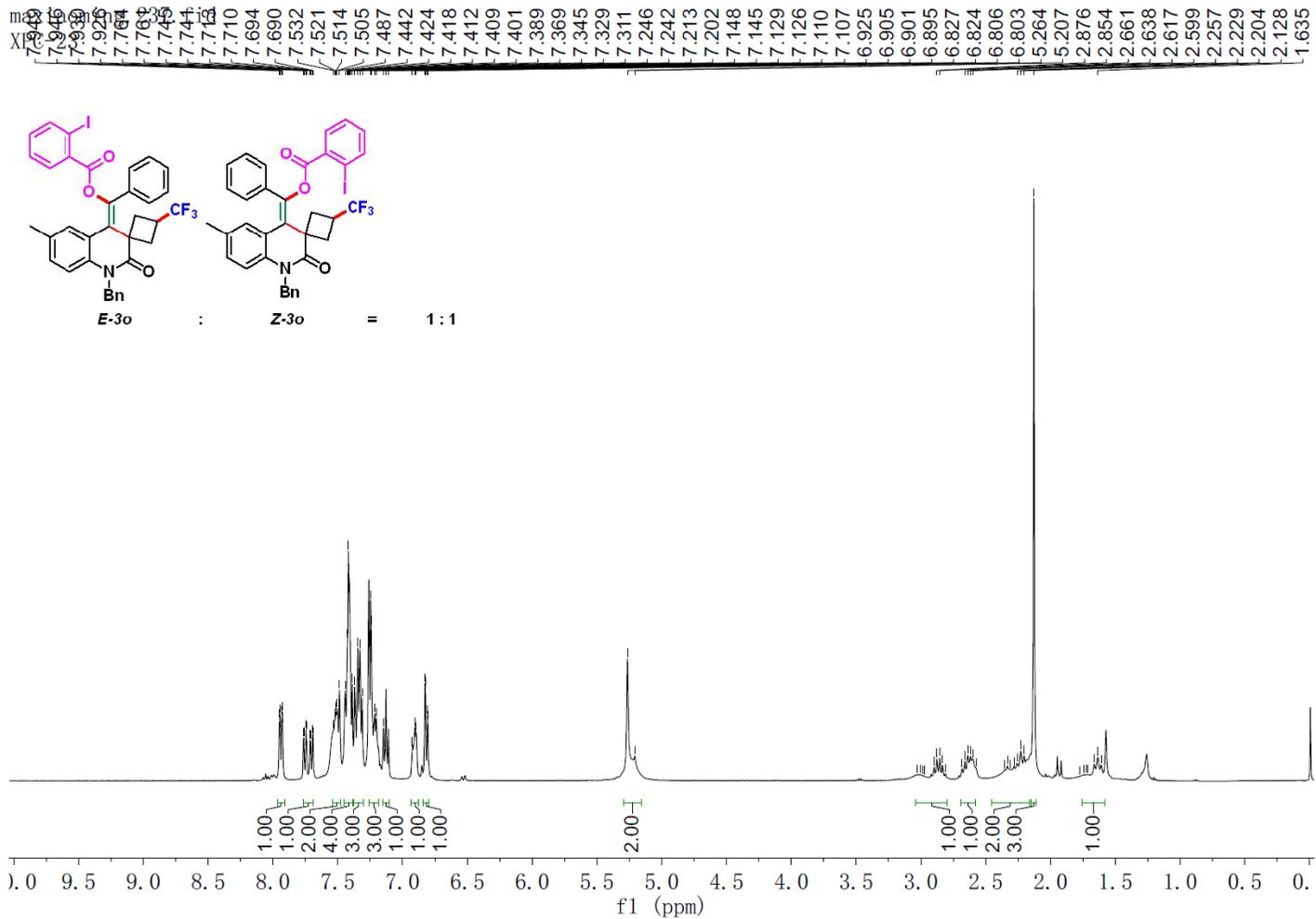
¹³C NMR Spectrum of Compound 3m (150 MHz, CDCl₃)

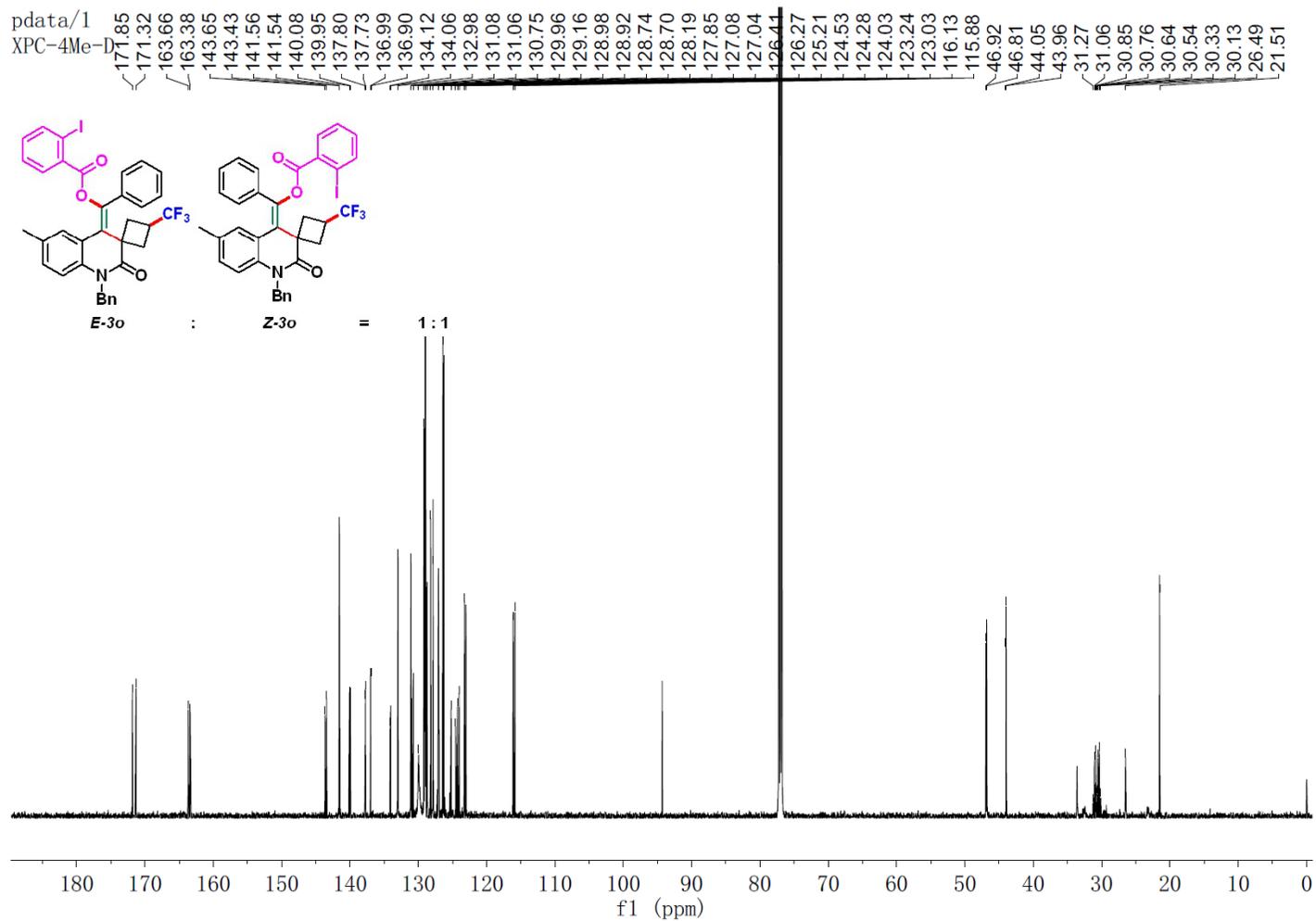
3maxiaoming02.800.fid
24

-73.17
-73.52

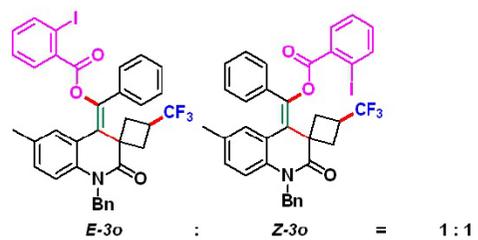


¹⁹F NMR Spectrum of Compound 3m (282 MHz, CDCl₃)

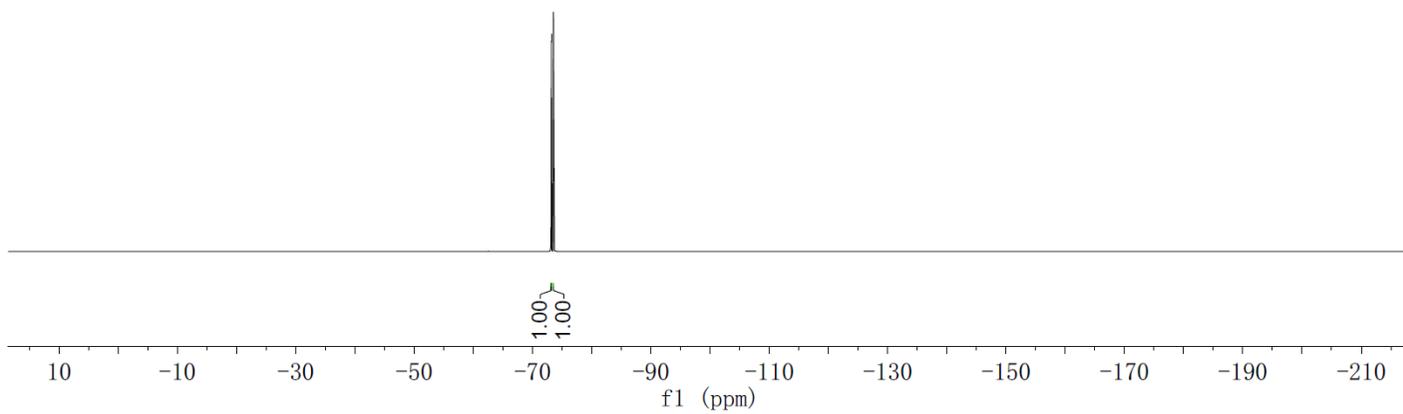




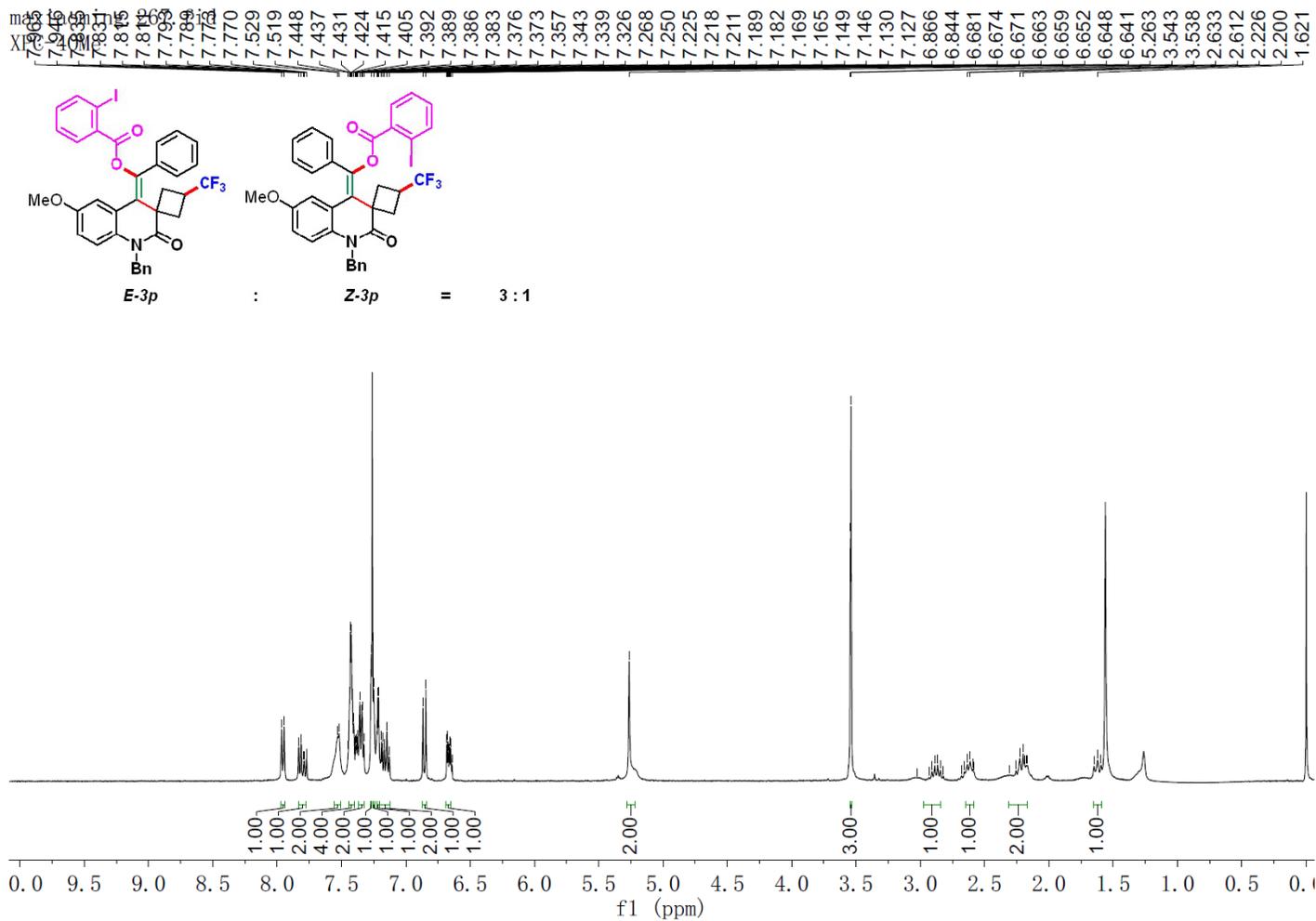
¹³C NMR Spectrum of Compound 3o (150 MHz, CDCl₃)



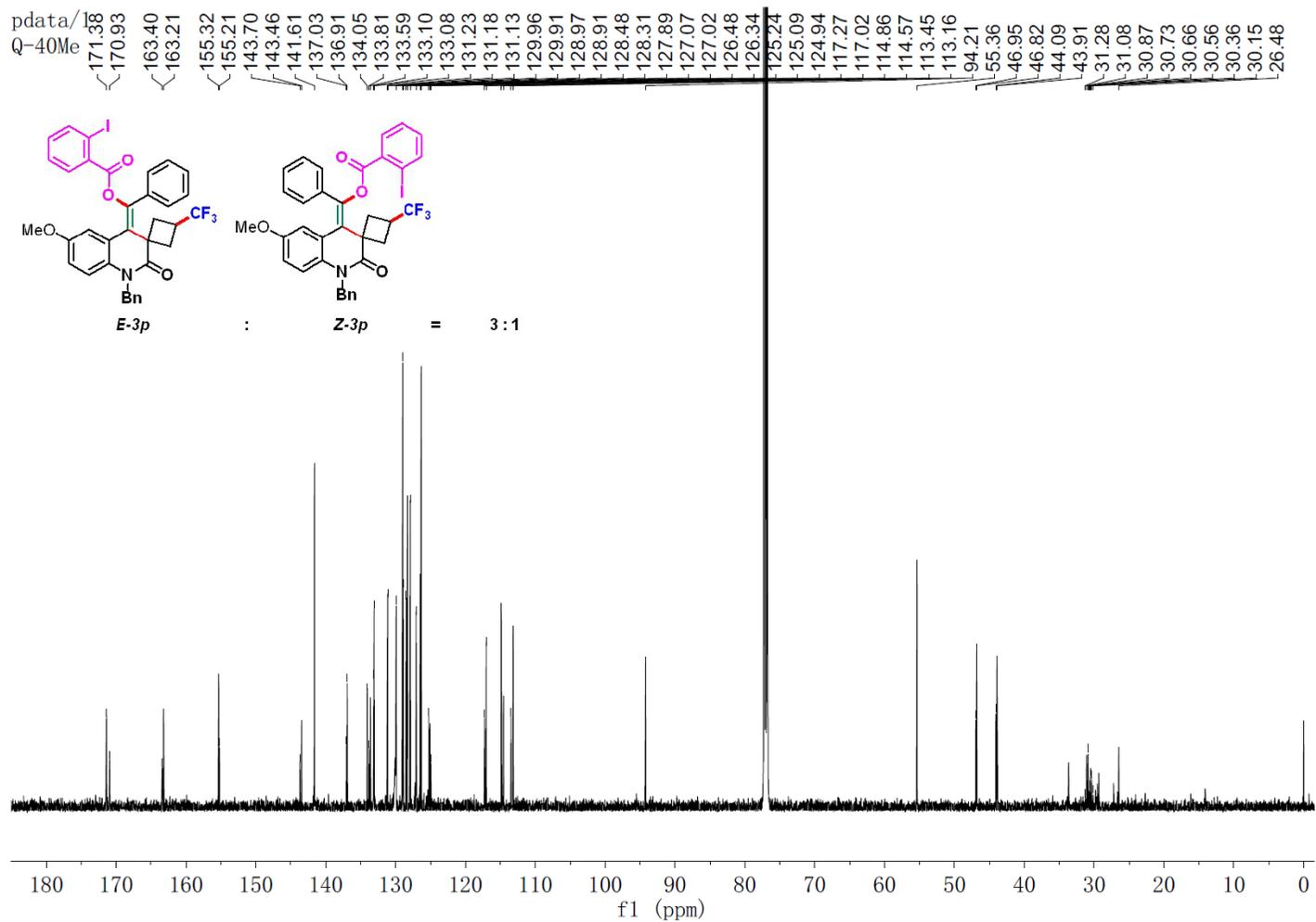
δ -73.17
 δ -73.55



^{19}F NMR Spectrum of Compound 3o (282 MHz, CDCl_3)



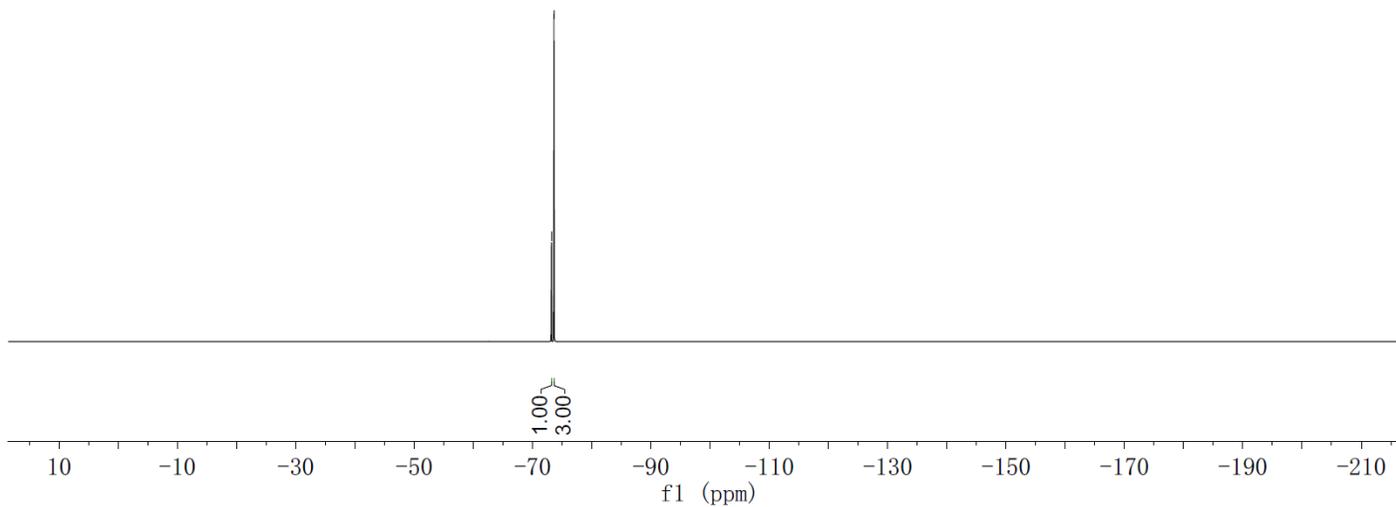
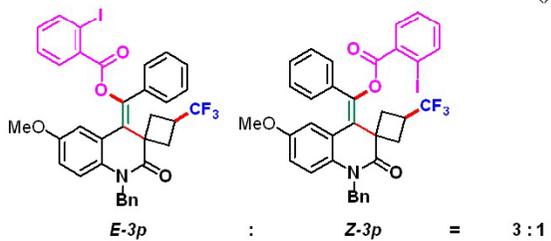
^1H NMR Spectrum of Compound 3p (400 MHz, CDCl_3)



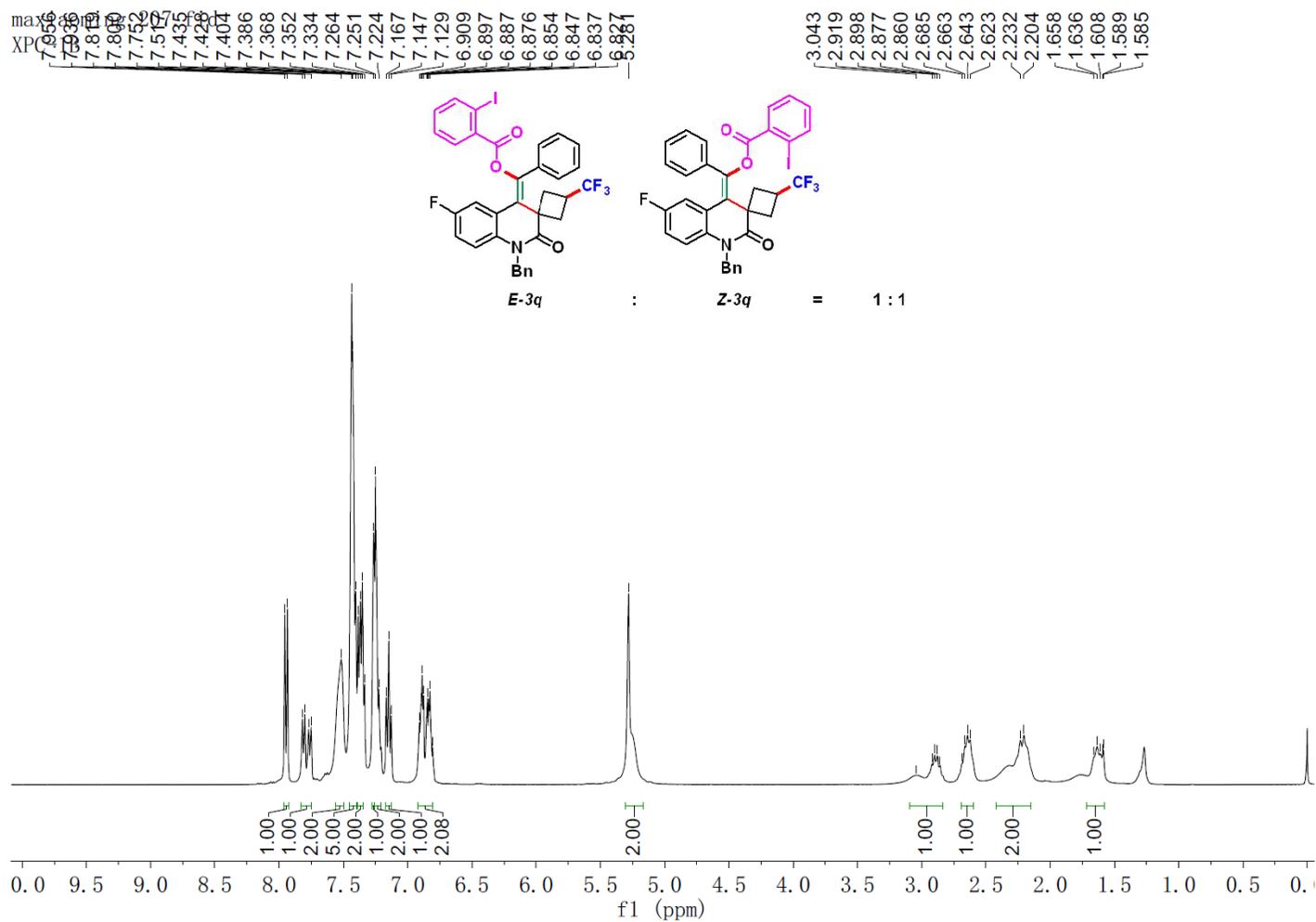
^{13}C NMR Spectrum of Compound 3p (150 MHz, CDCl_3)

3maxiaoming02.750.fid
dianben-40Me

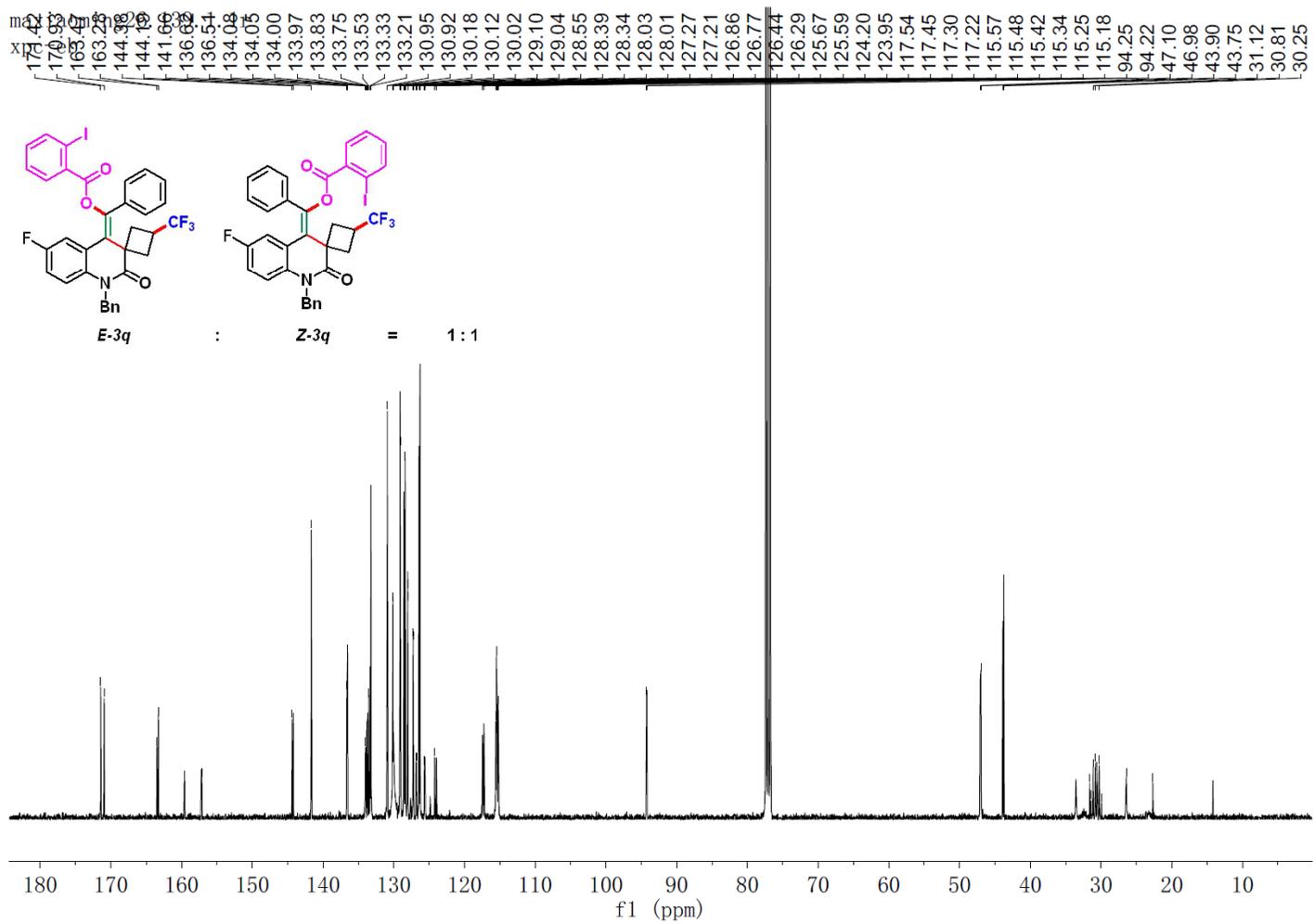
73.20
73.63



¹⁹F NMR Spectrum of Compound 3p (282 MHz, CDCl₃)

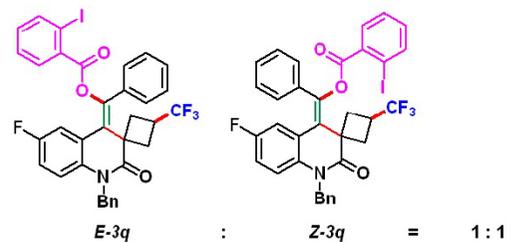


¹H NMR Spectrum of Compound 3q (400 MHz, CDCl₃)



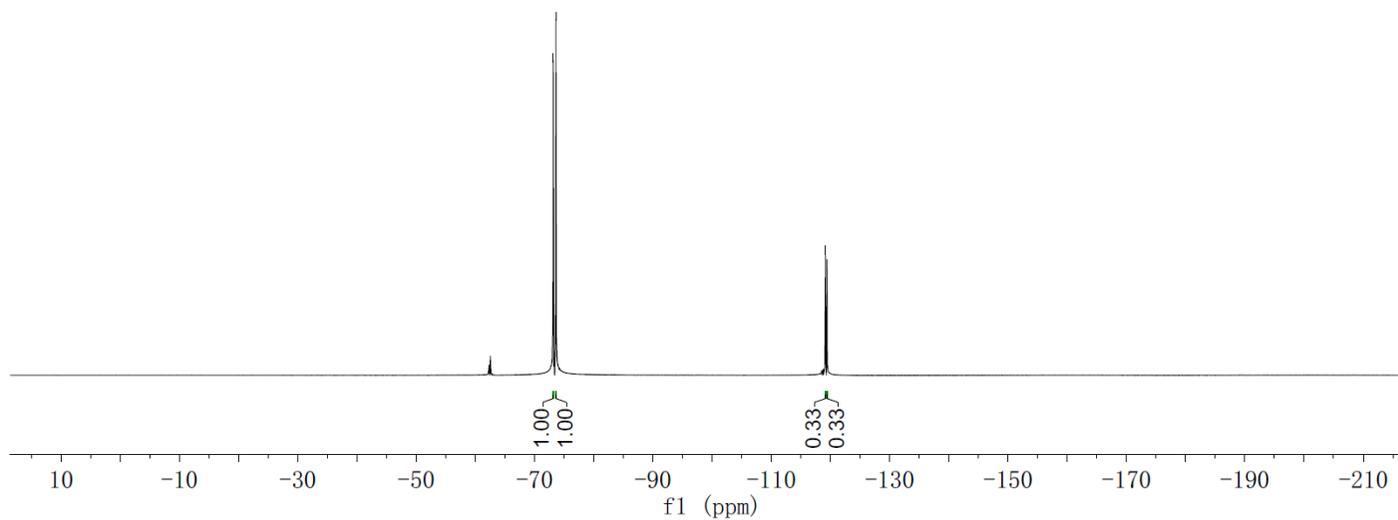
¹³C NMR Spectrum of Compound 3q (100 MHz, CDCl₃)

3maxiaoming02.620.fid
1b

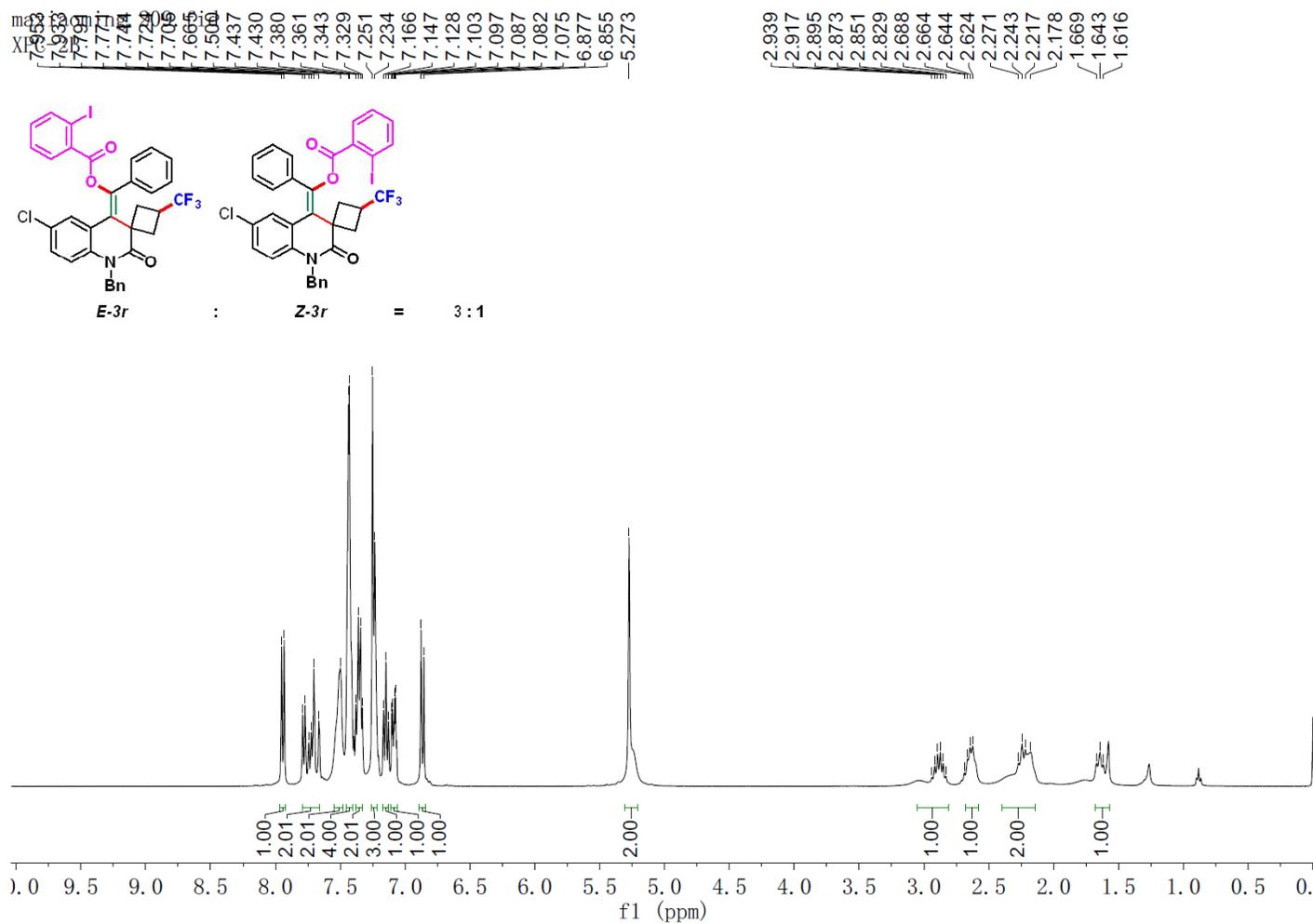


-73.15
-73.62

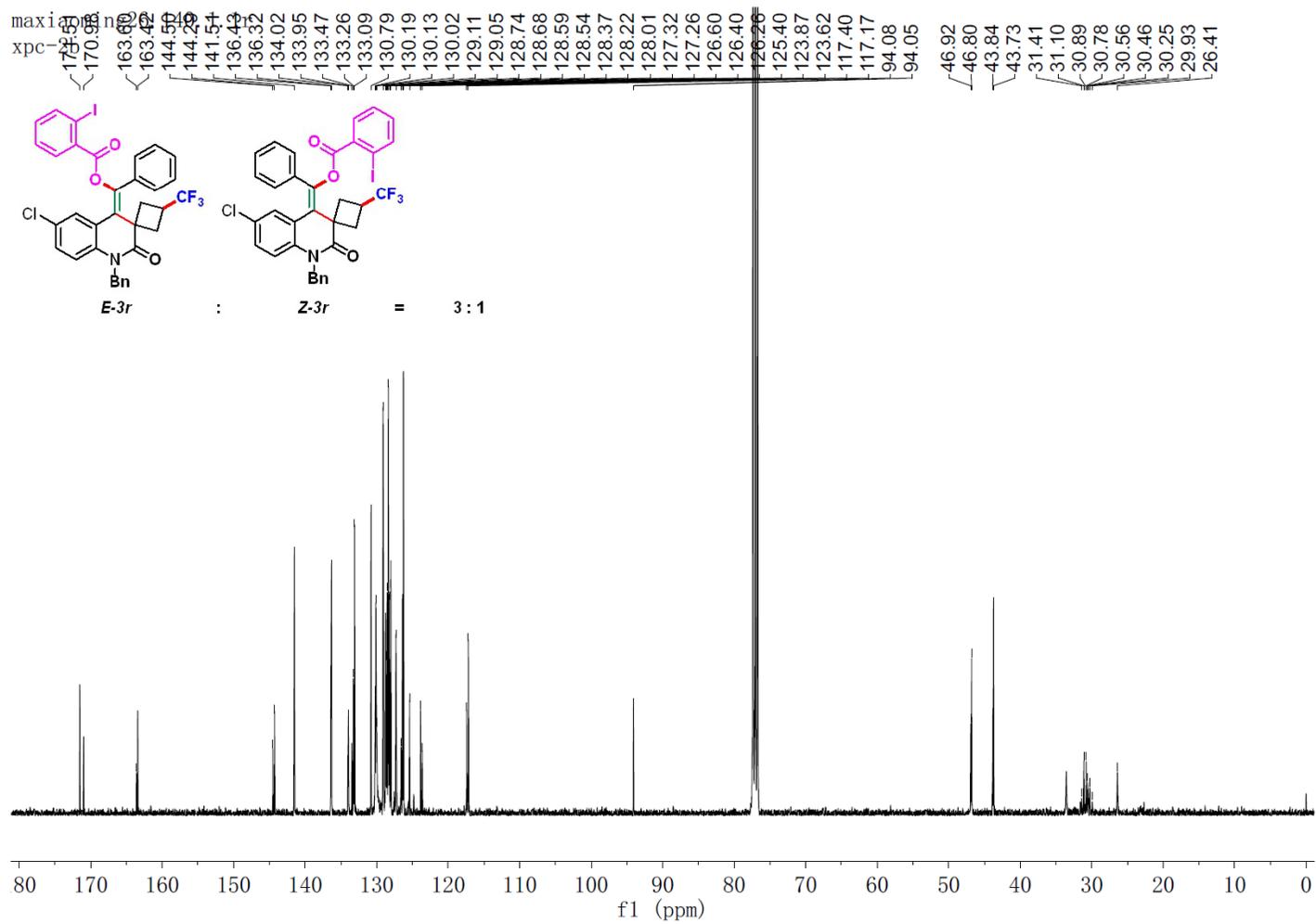
-119.15
-119.40



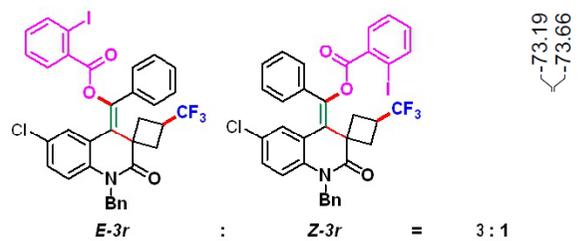
¹⁹F NMR Spectrum of Compound 3q (282 MHz, CDCl₃)



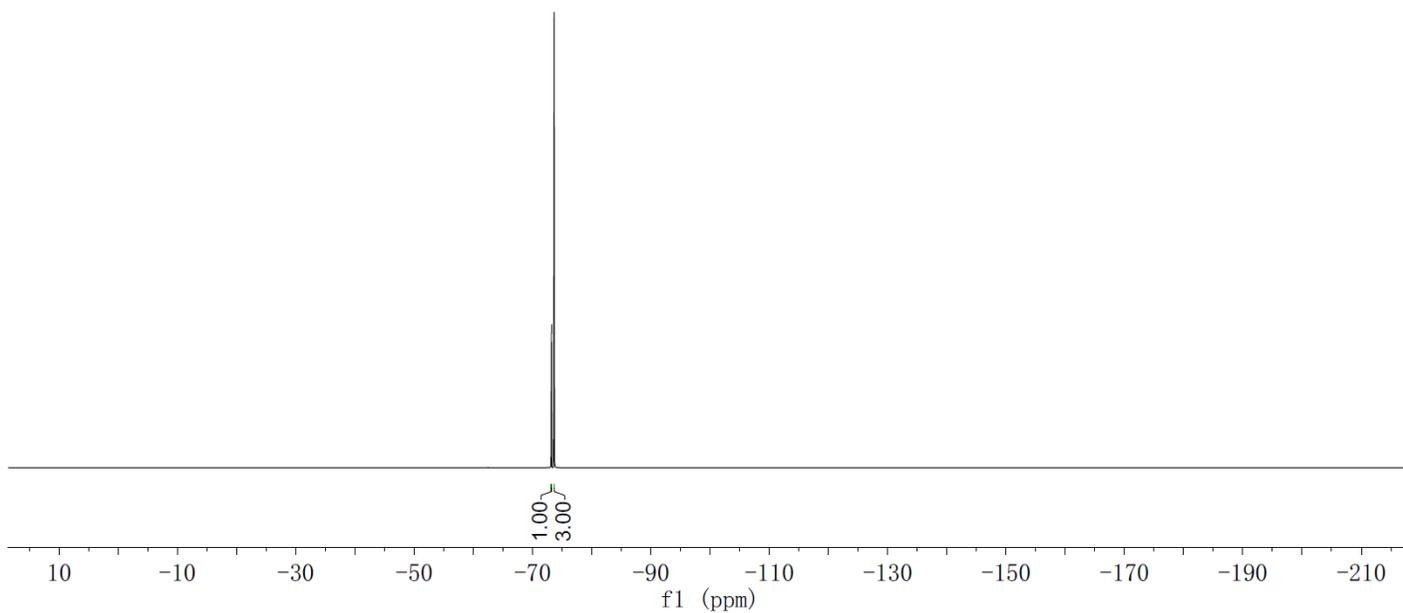
¹H NMR Spectrum of Compound 3r (400 MHz, CDCl₃)



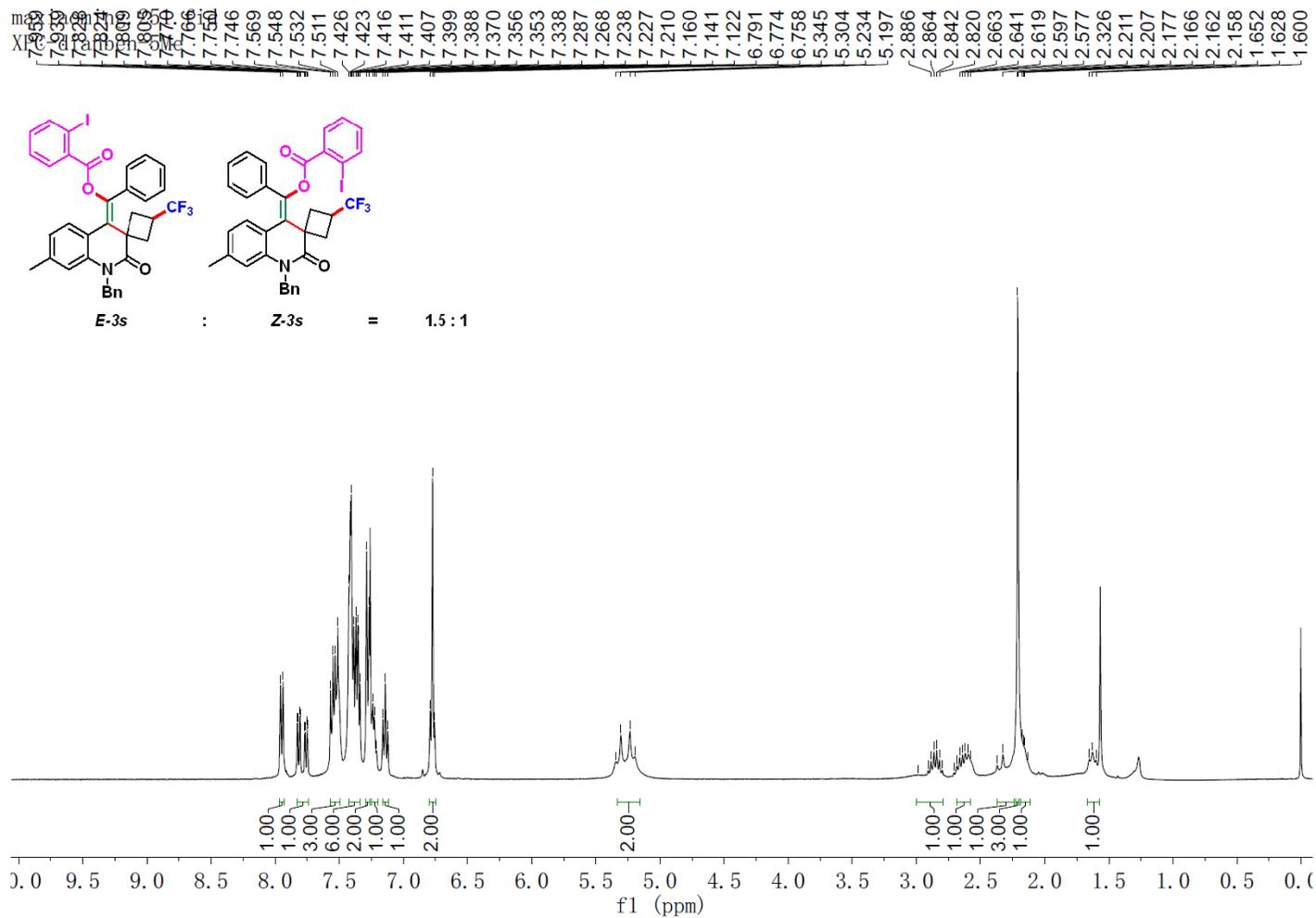
¹³C NMR Spectrum of Compound 3r (100 MHz, CDCl₃)



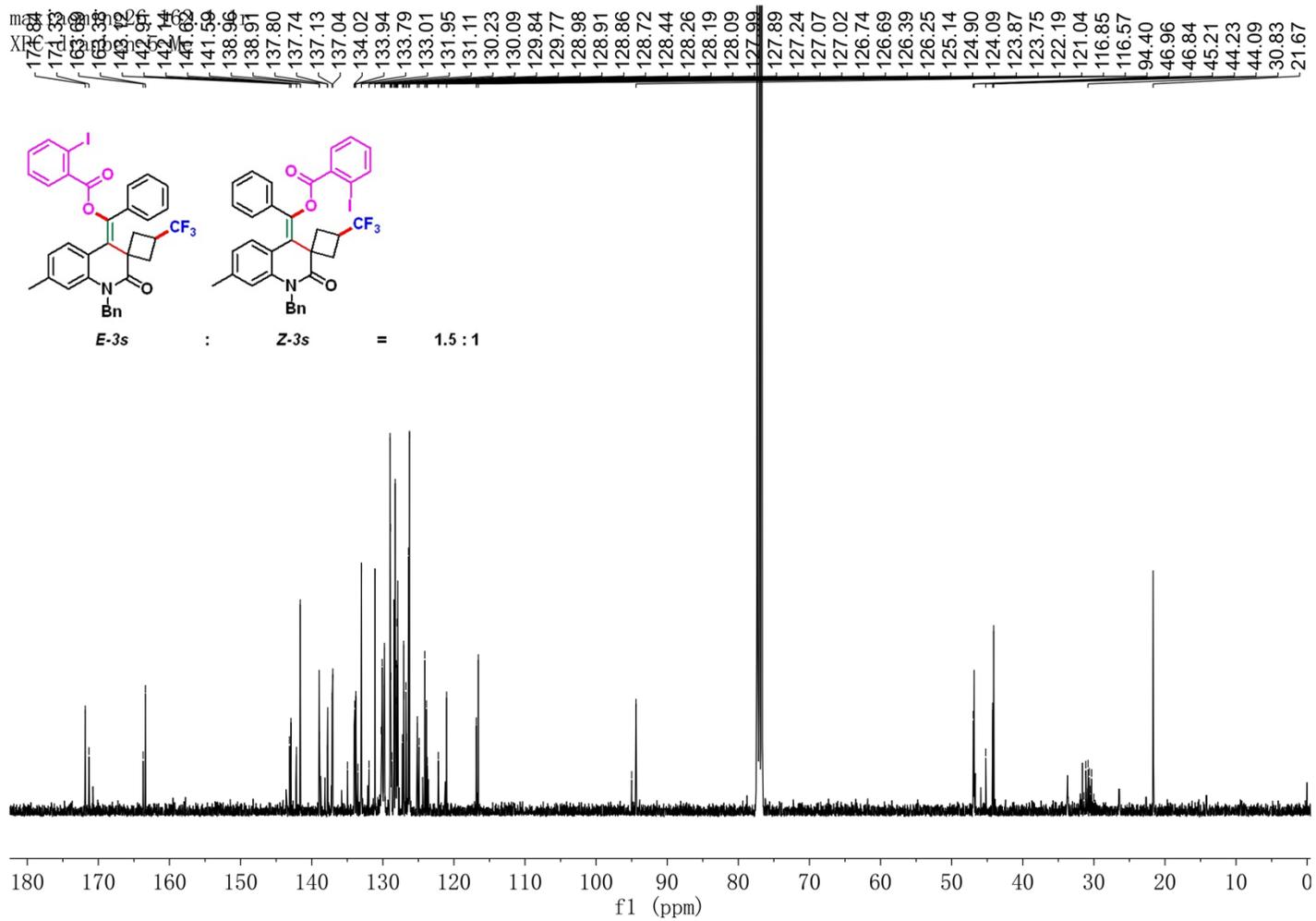
-73.19
 -73.66



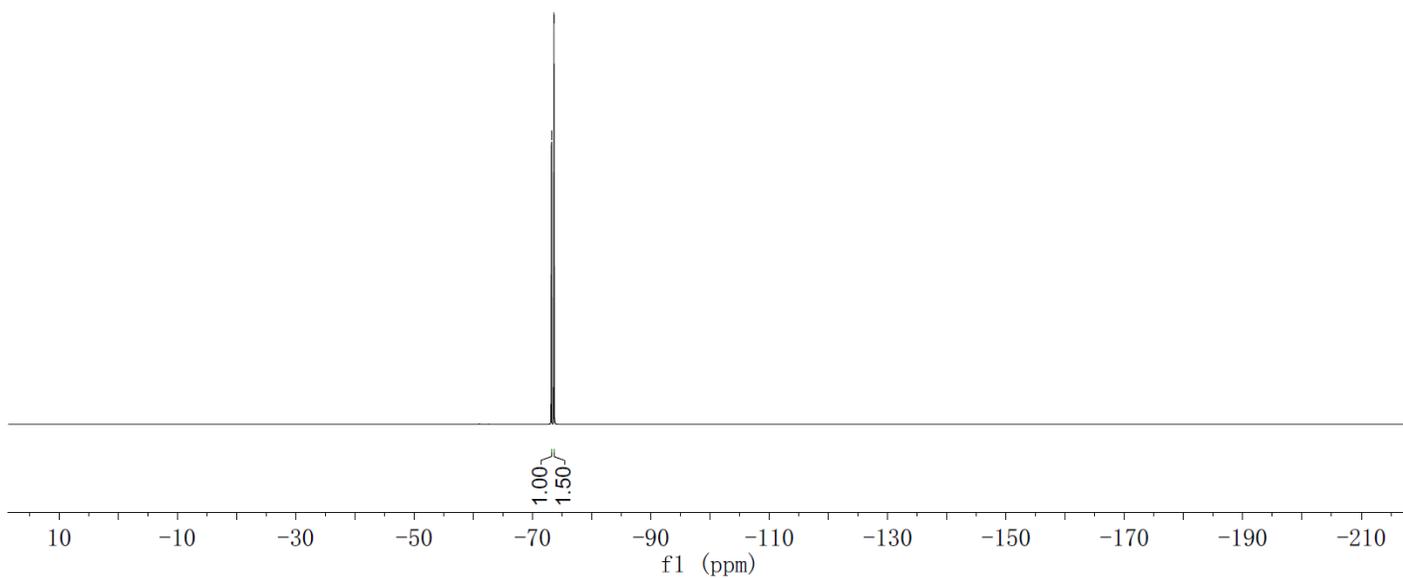
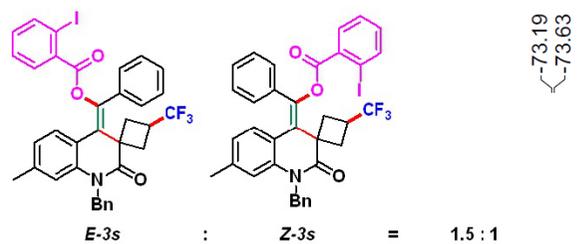
^{19}F NMR Spectrum of Compound 3r (282 MHz, CDCl_3)



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

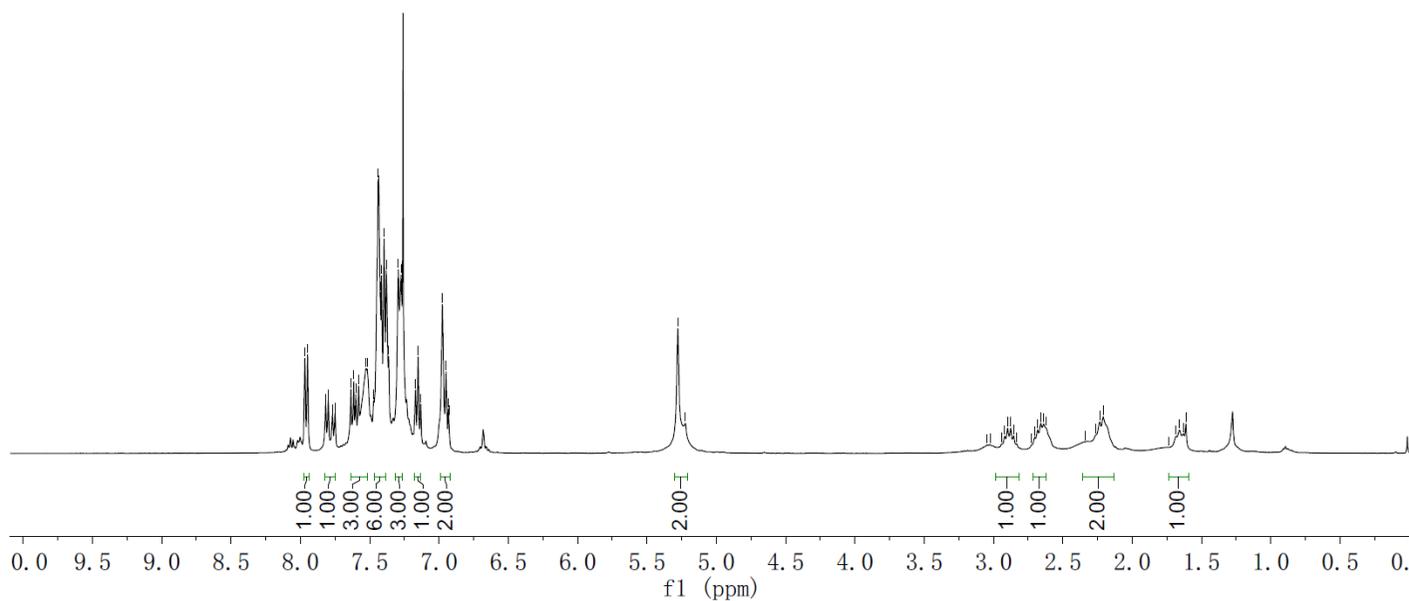
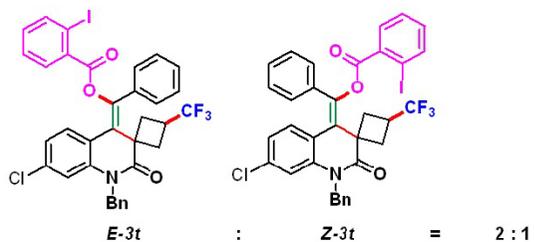


¹³C NMR Spectrum of Compound 3s (100 MHz, CDCl₃)

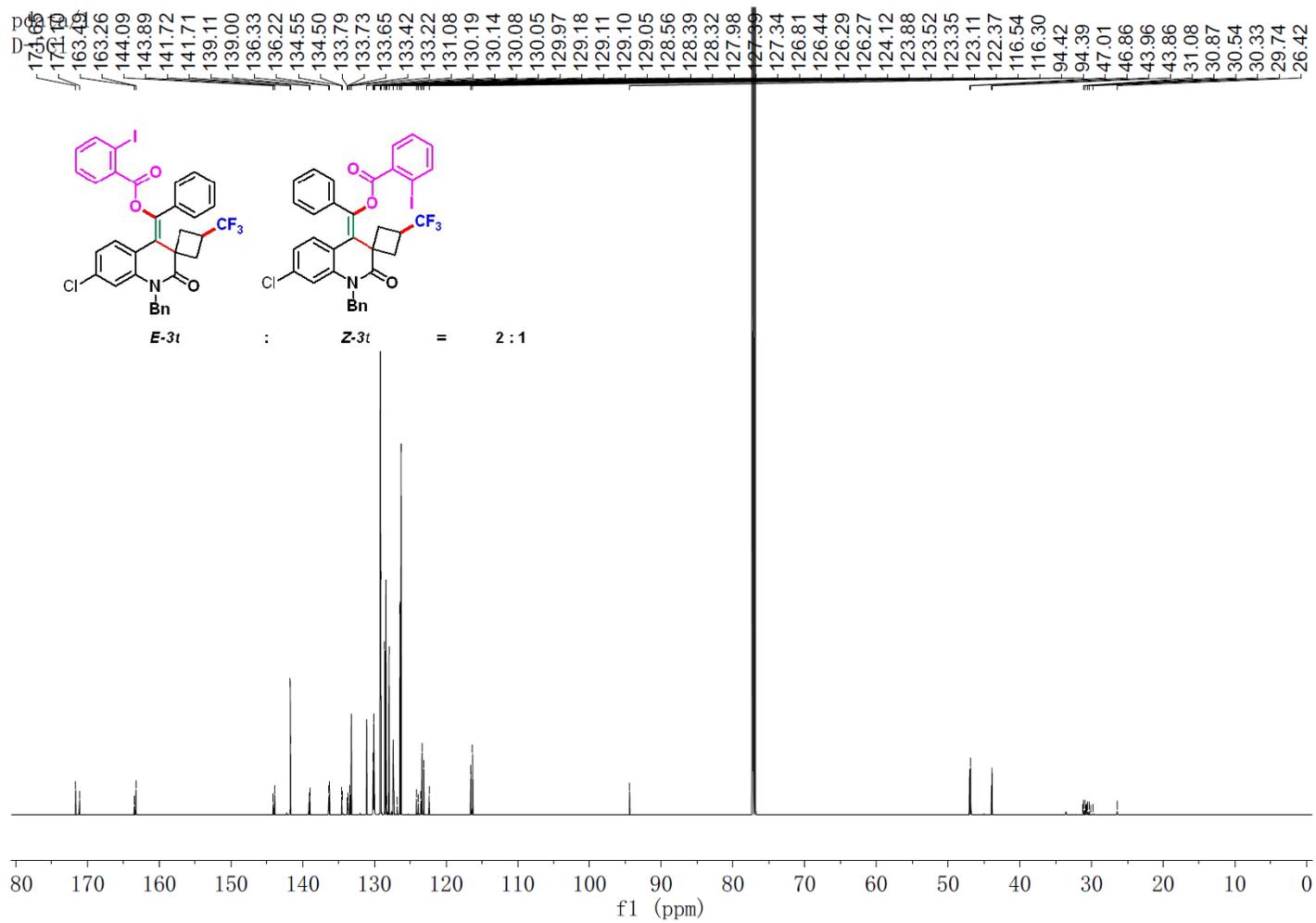


^{19}F NMR Spectrum of Compound 3s (282 MHz, CDCl_3)

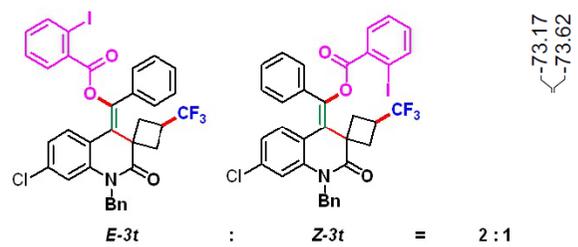
max 7.968
 XP 7.949
 7.881
 7.876
 7.800
 7.798
 7.635
 7.615
 7.600
 7.580
 7.527
 7.519
 7.471
 7.439
 7.434
 7.423
 7.415
 7.396
 7.381
 7.363
 7.294
 7.274
 7.170
 7.151
 7.132
 6.975
 6.953
 6.949
 5.278
 3.025
 2.941
 2.919
 2.898
 2.876
 2.855
 2.832
 2.725
 2.703
 2.681
 2.659
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 2.233
 2.209
 1.737
 1.683
 1.660
 1.630
 1.613



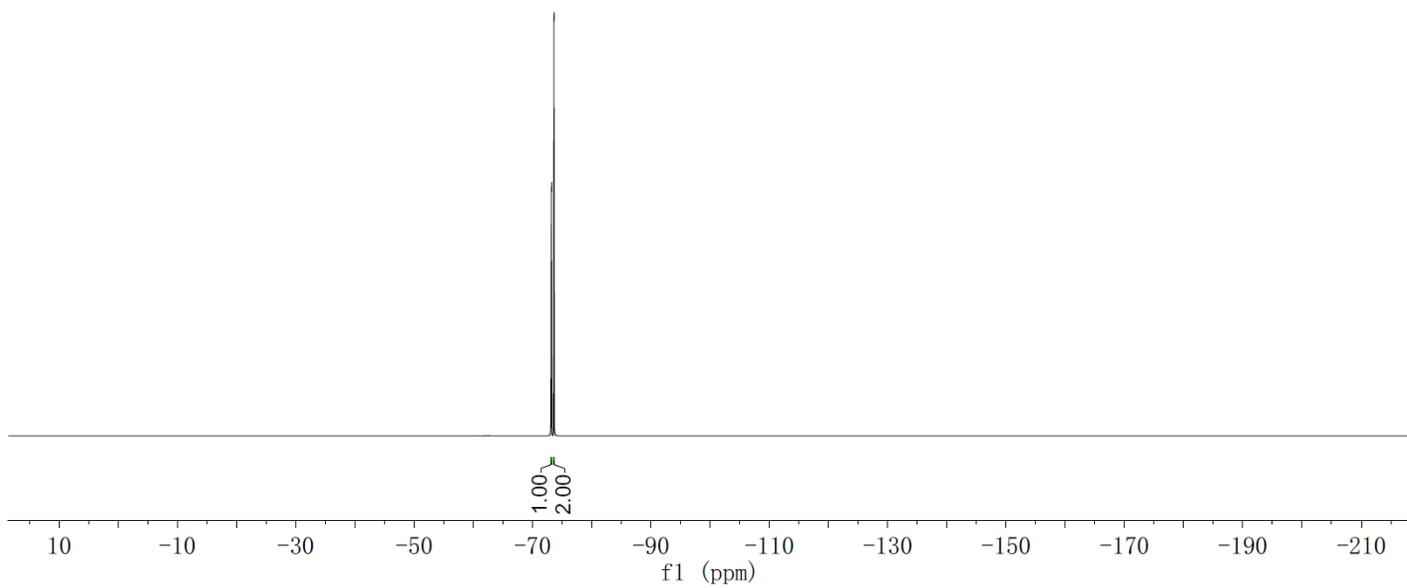
¹H NMR Spectrum of Compound 3t (400 MHz, CDCl₃)



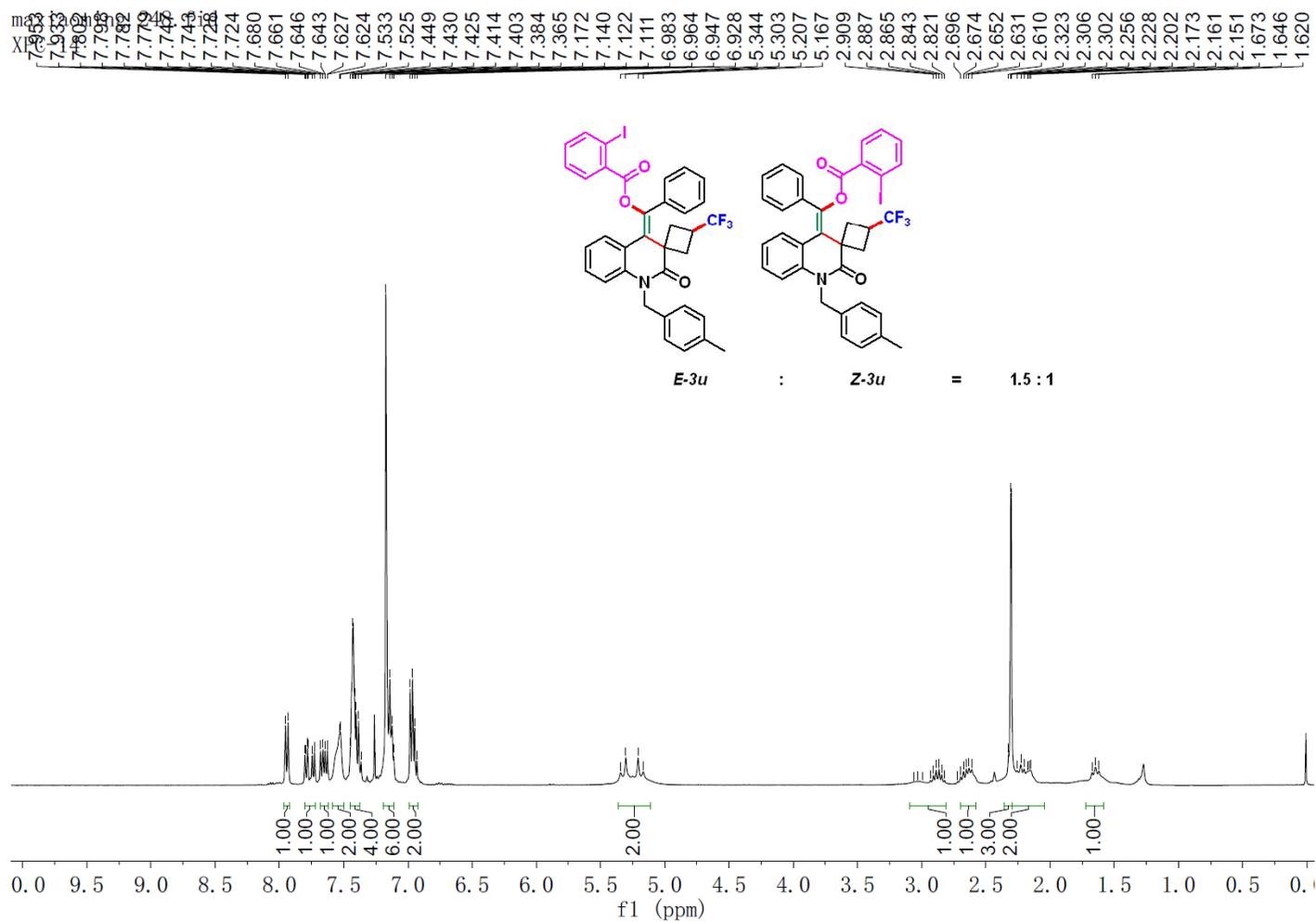
¹³C NMR Spectrum of Compound 3t (150 MHz, CDCl₃)



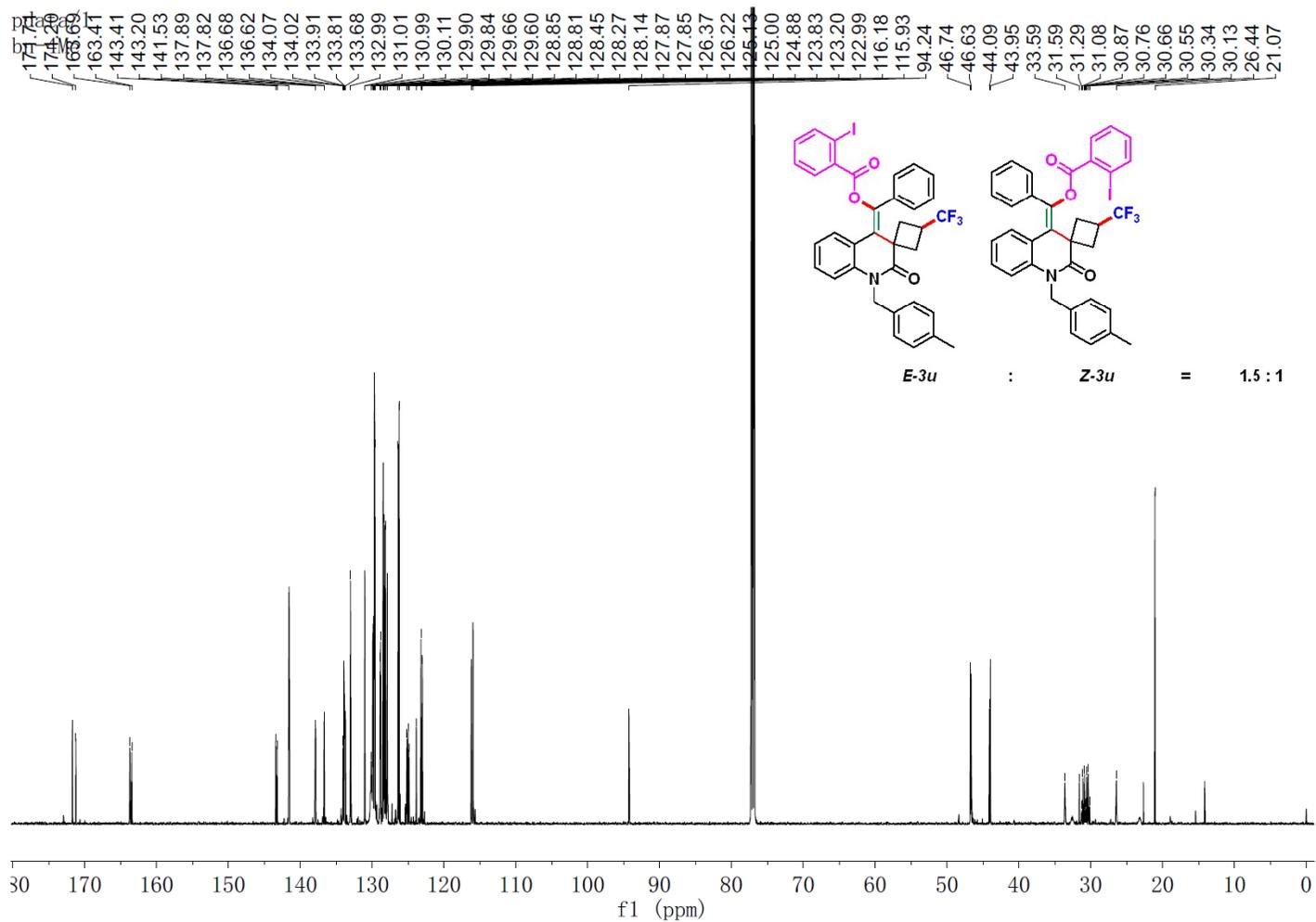
δ -73.17
 δ -73.62



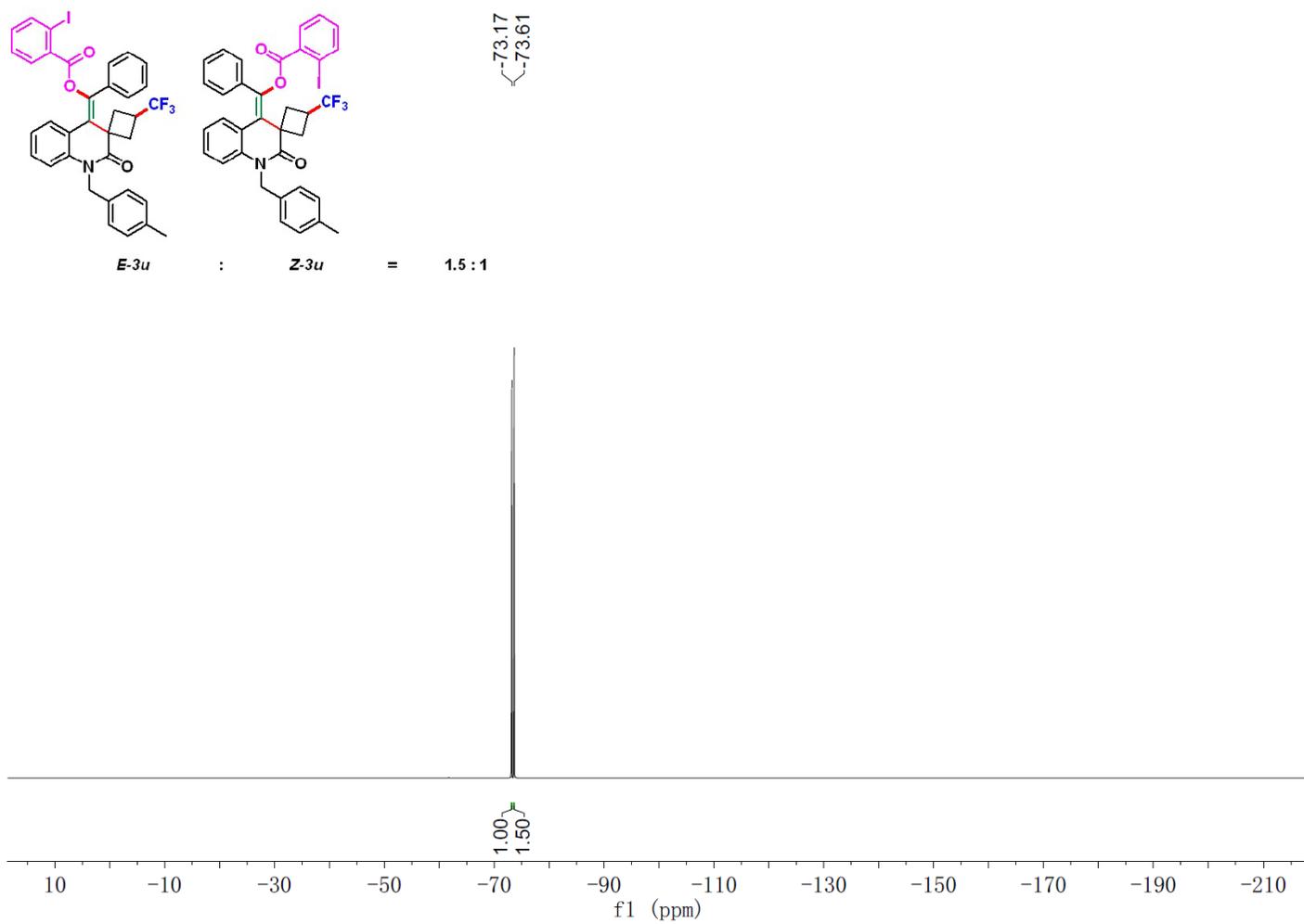
^{19}F NMR Spectrum of Compound 3t (282 MHz, CDCl_3)



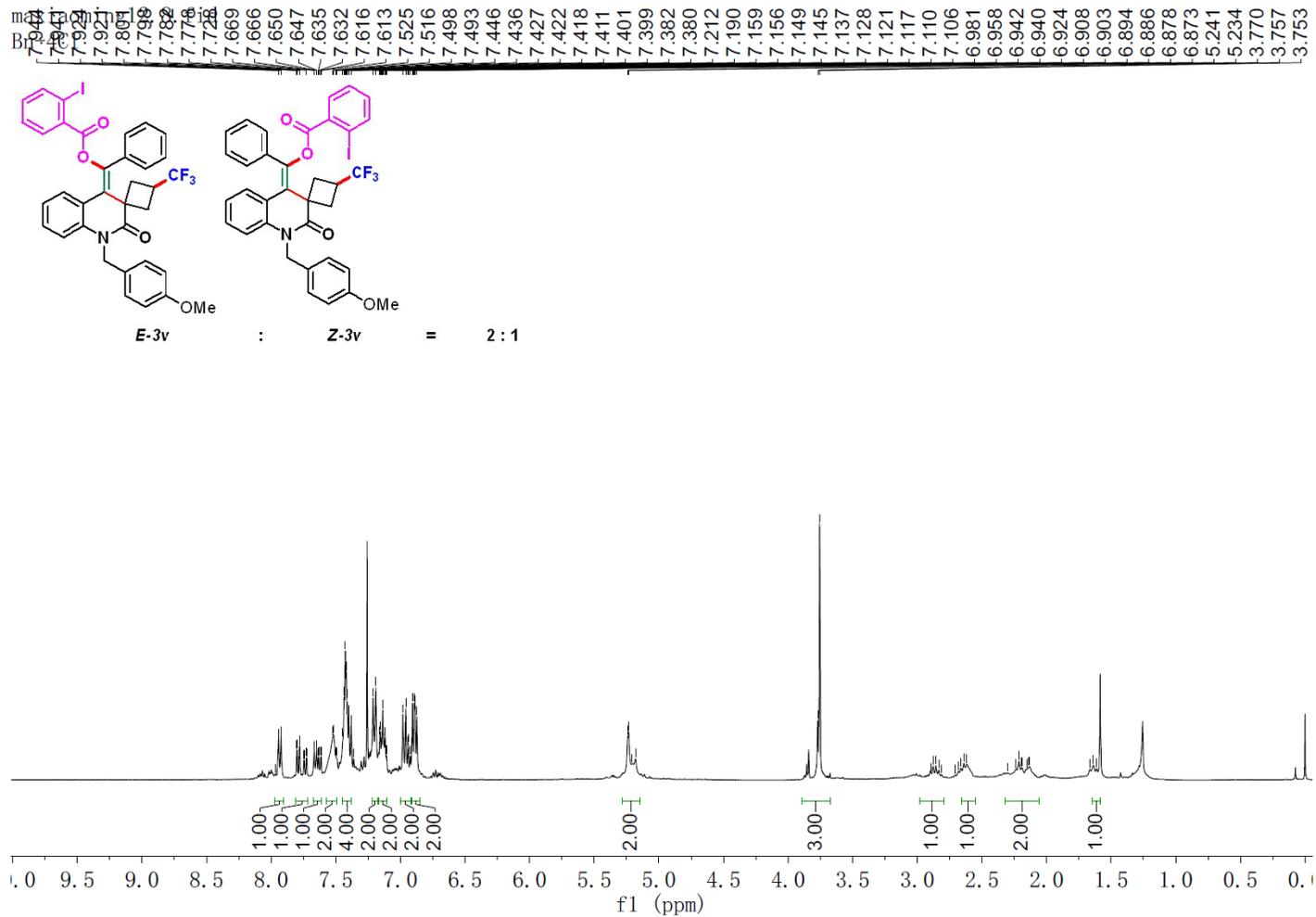
¹H NMR Spectrum of Compound 3u (400 MHz, CDCl₃)



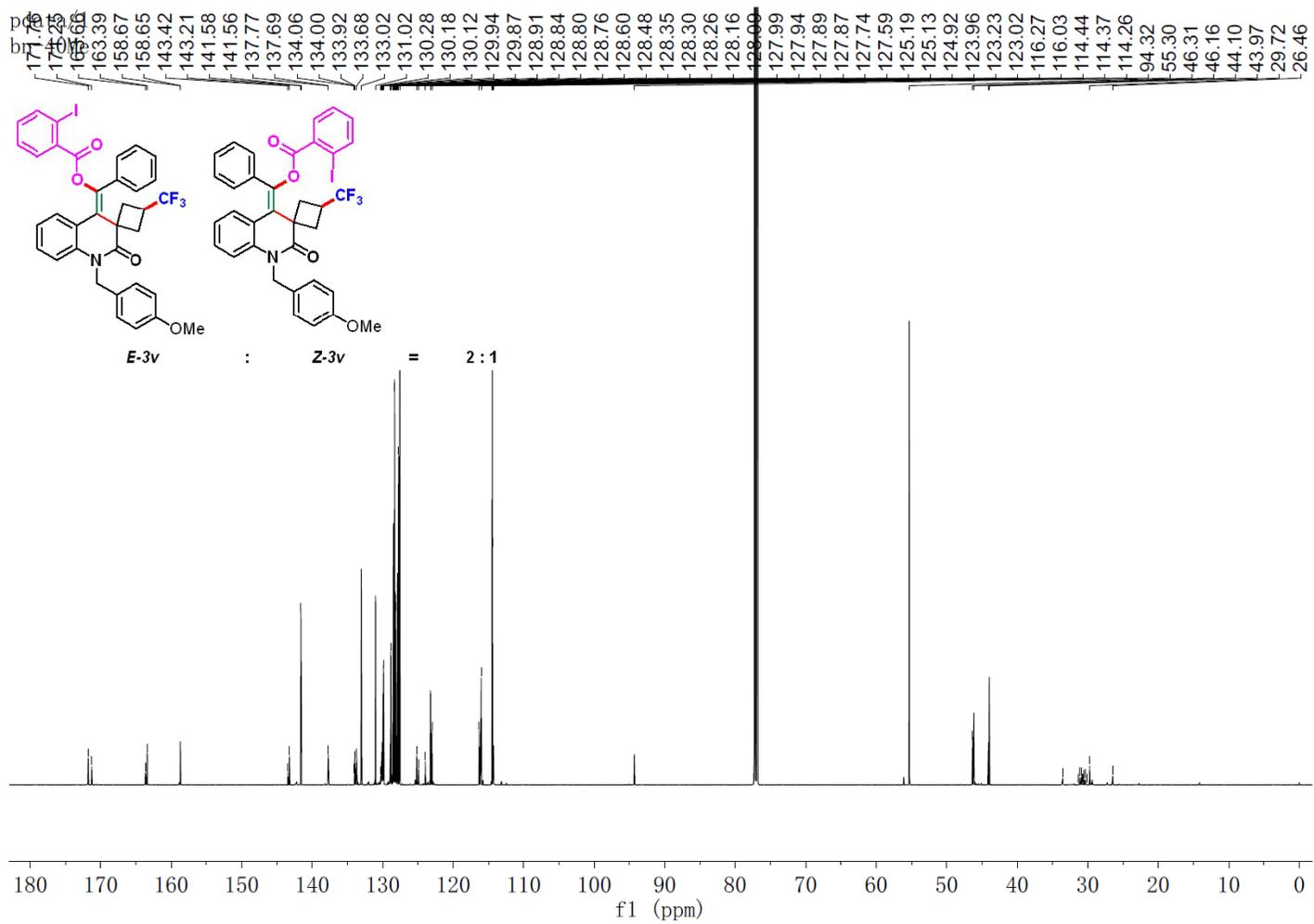
^{13}C NMR Spectrum of Compound 3u (150 MHz, CDCl_3)



¹⁹F NMR Spectrum of Compound 3u (282 MHz, CDCl₃)



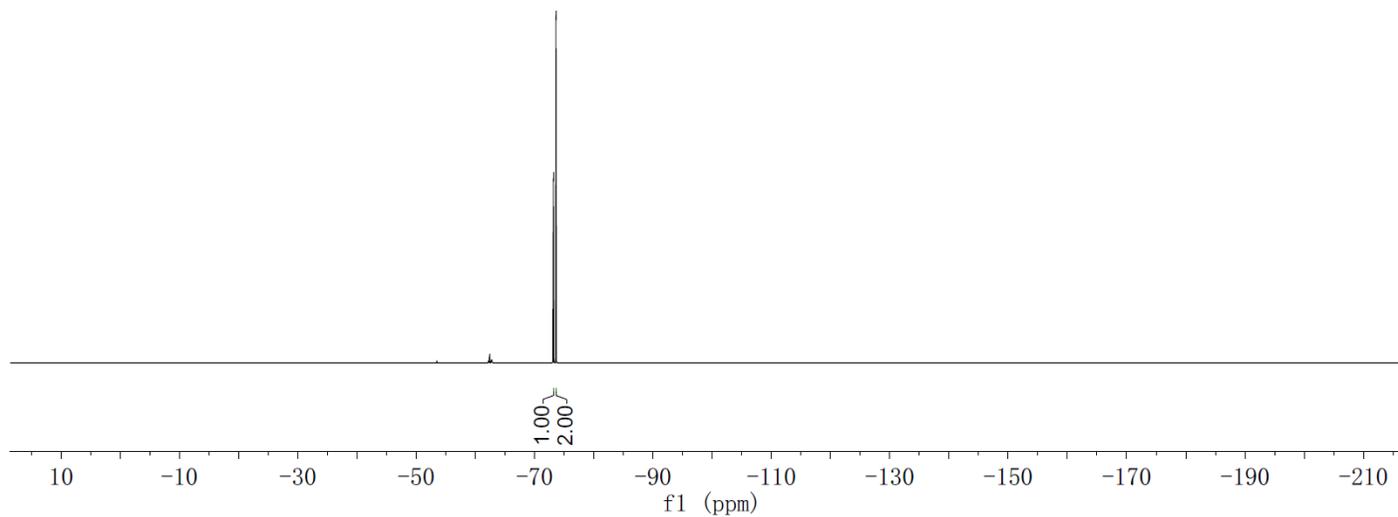
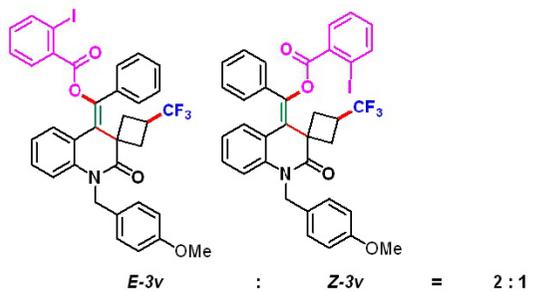
¹H NMR Spectrum of Compound 3v (400 MHz, CDCl₃)



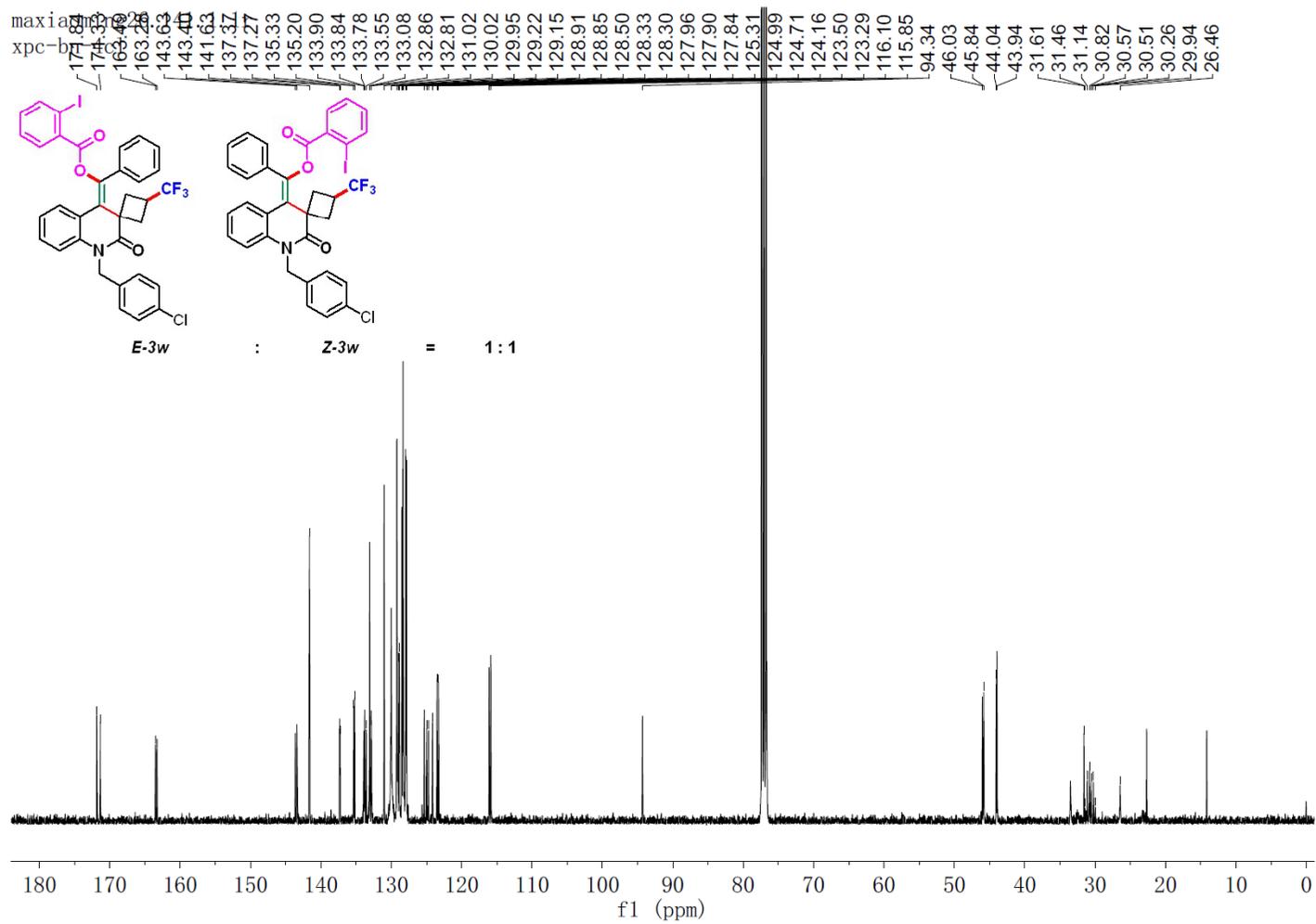
¹³C NMR Spectrum of Compound 3v (150 MHz, CDCl₃)

3maxiaoming02.940.1.1r
XPC-Bn-OMe

-73.17
-73.62



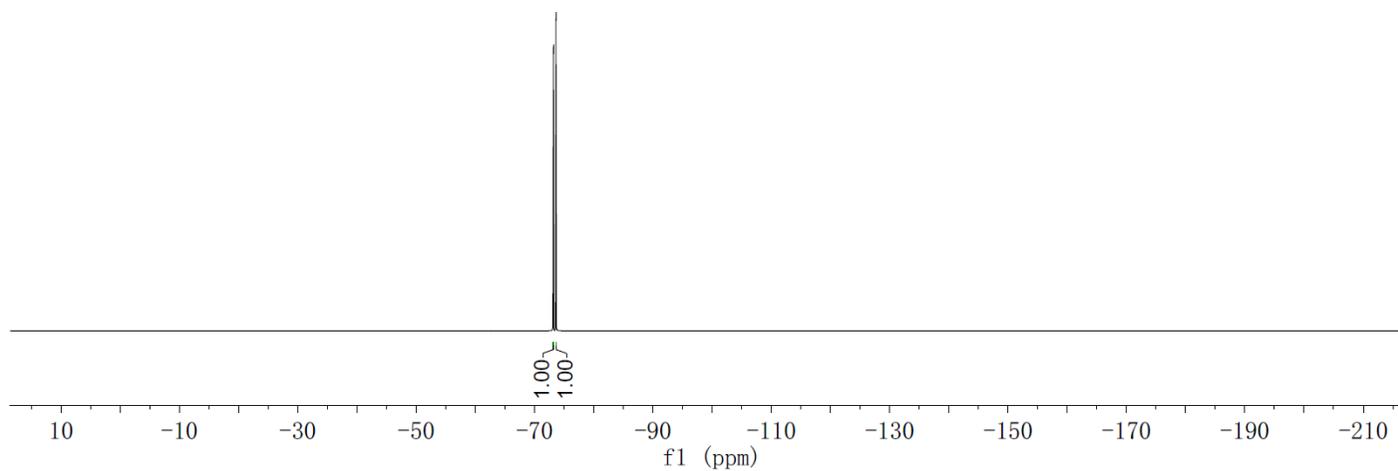
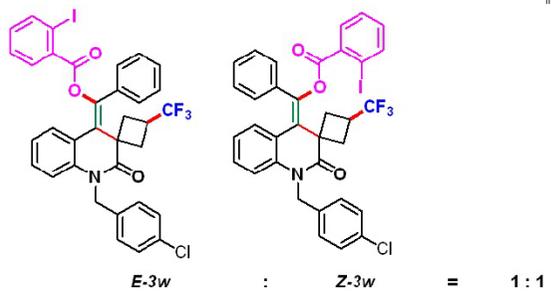
¹⁹F NMR Spectrum of Compound 3v (282 MHz, CDCl₃)



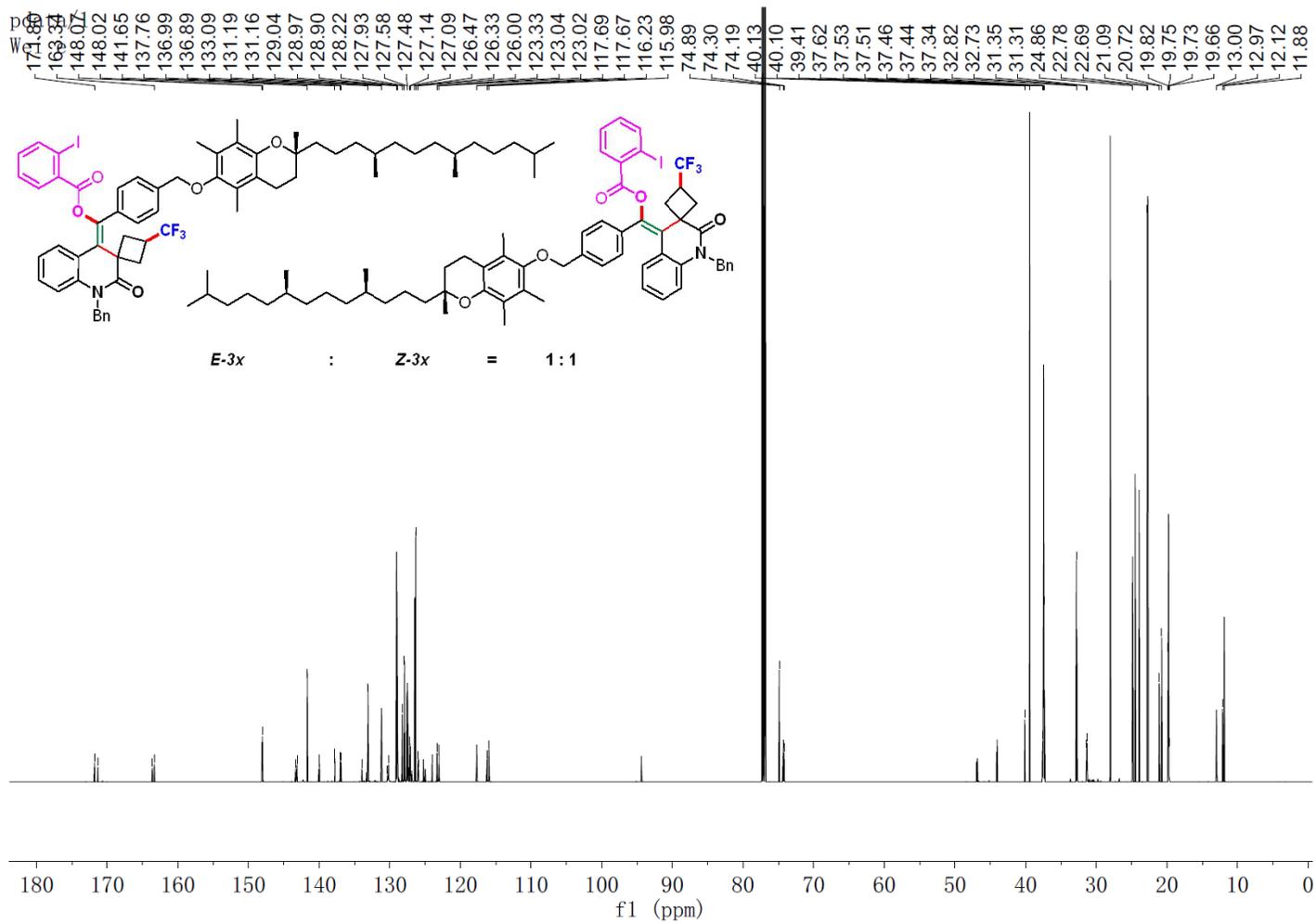
¹³C NMR Spectrum of Compound 3w (150 MHz, CDCl₃)

3maxiaoming02.760.fid
Bn-4Cl

-73.19
-73.62

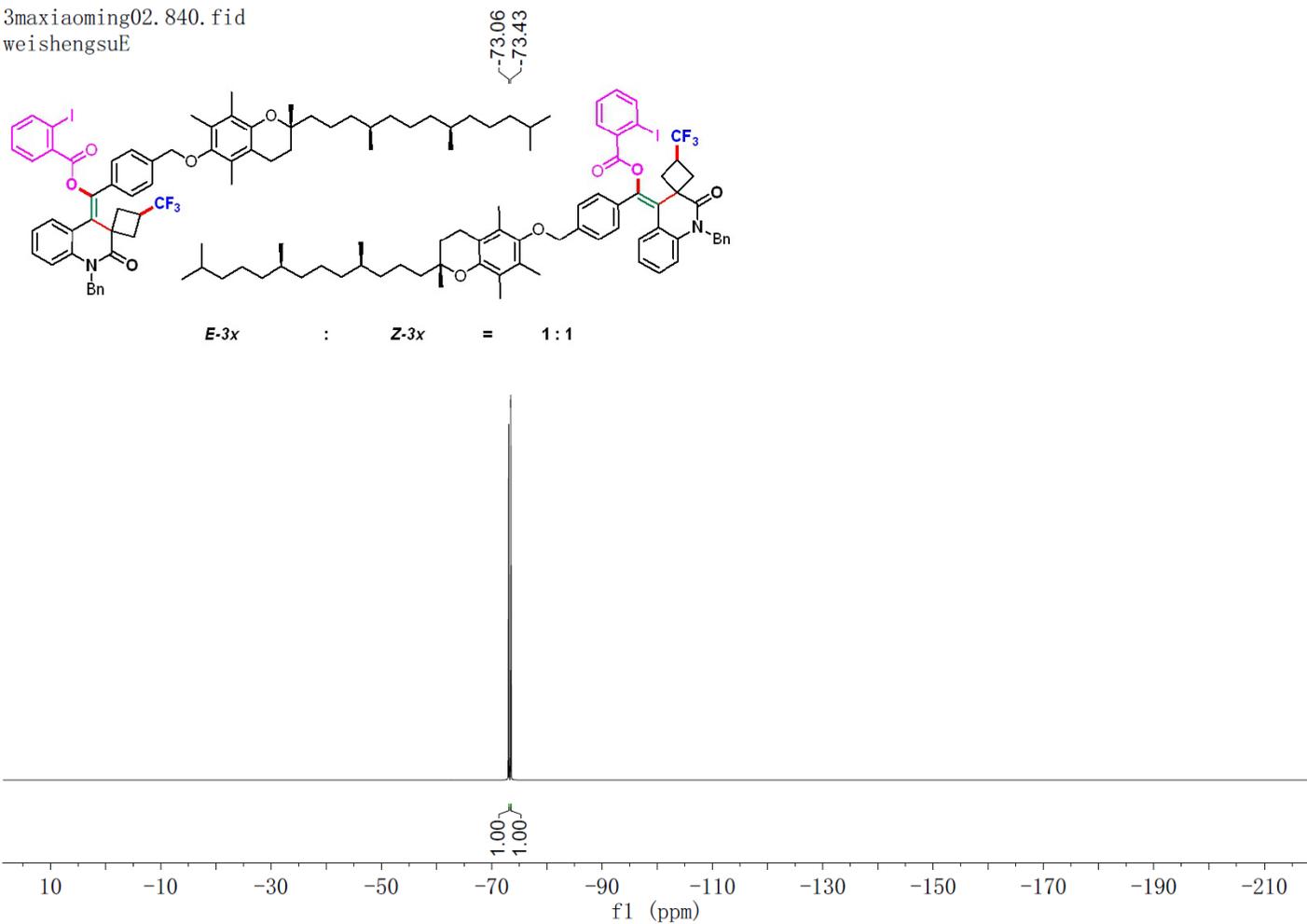


¹⁹F NMR Spectrum of Compound 3w (282 MHz, CDCl₃)

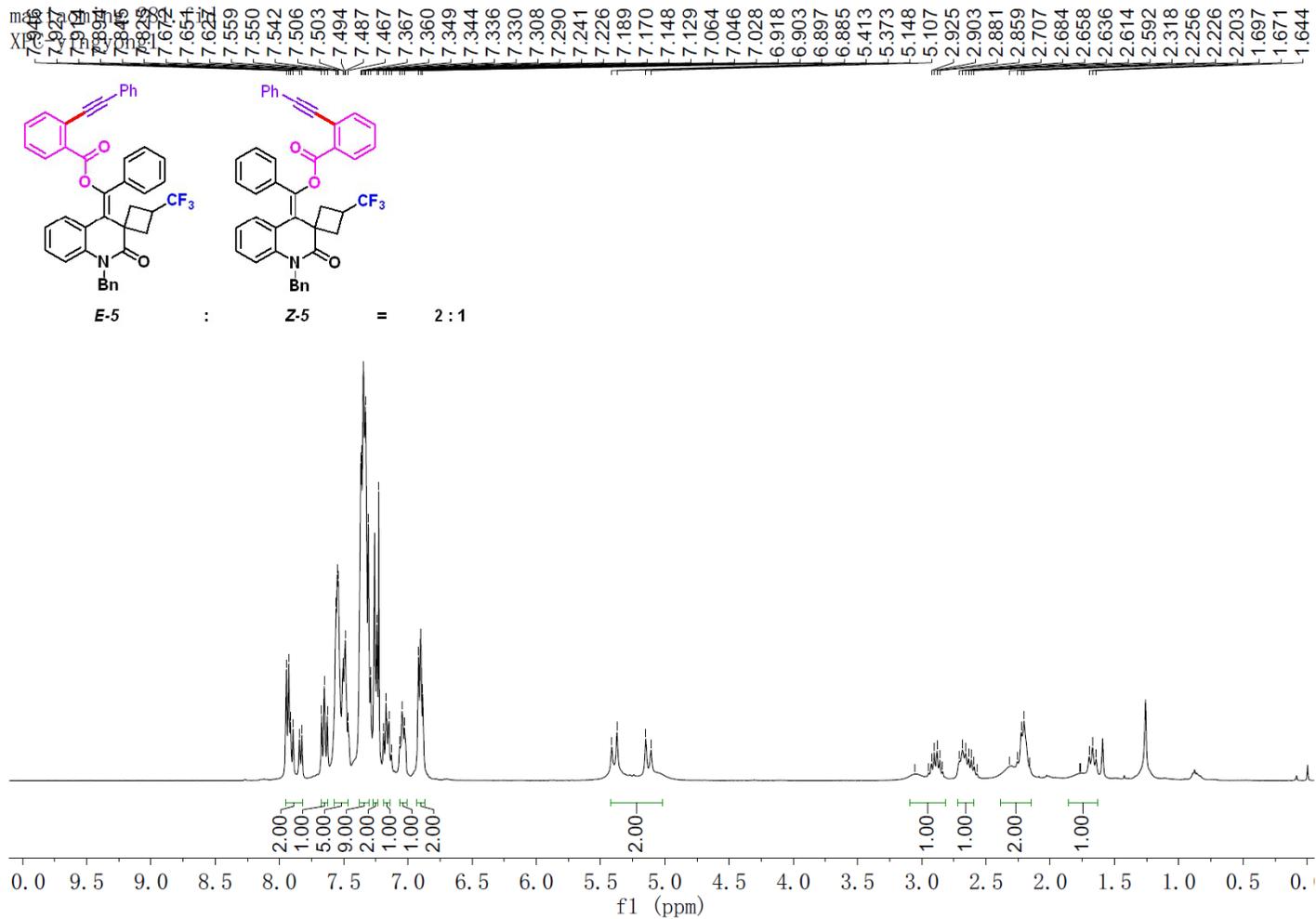


¹³C NMR Spectrum of Compound 3x (150 MHz, CDCl₃)

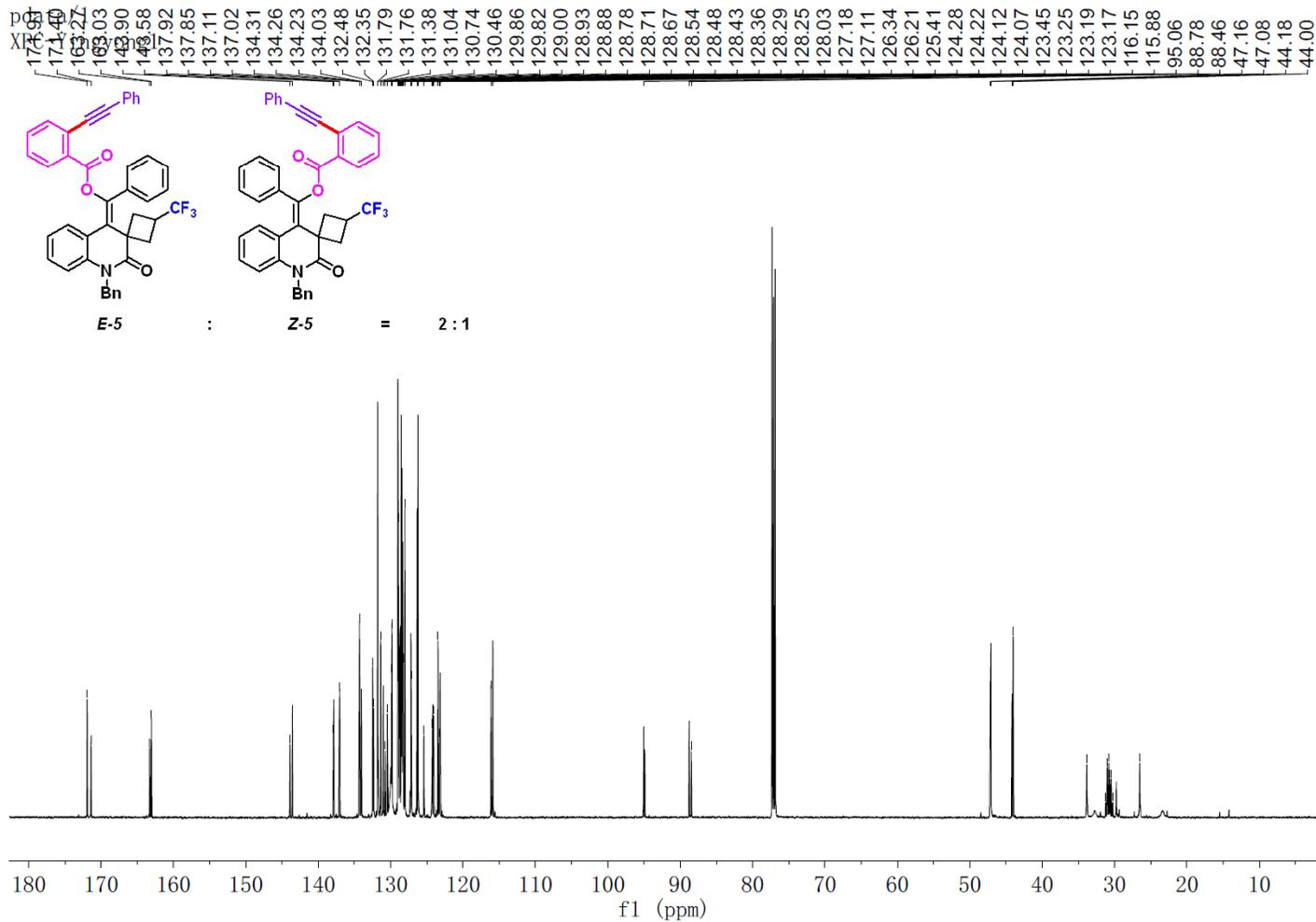
3maxiaoming02.840.fid
weishengsuE



^{19}F NMR Spectrum of Compound 3x (282 MHz, CDCl_3)



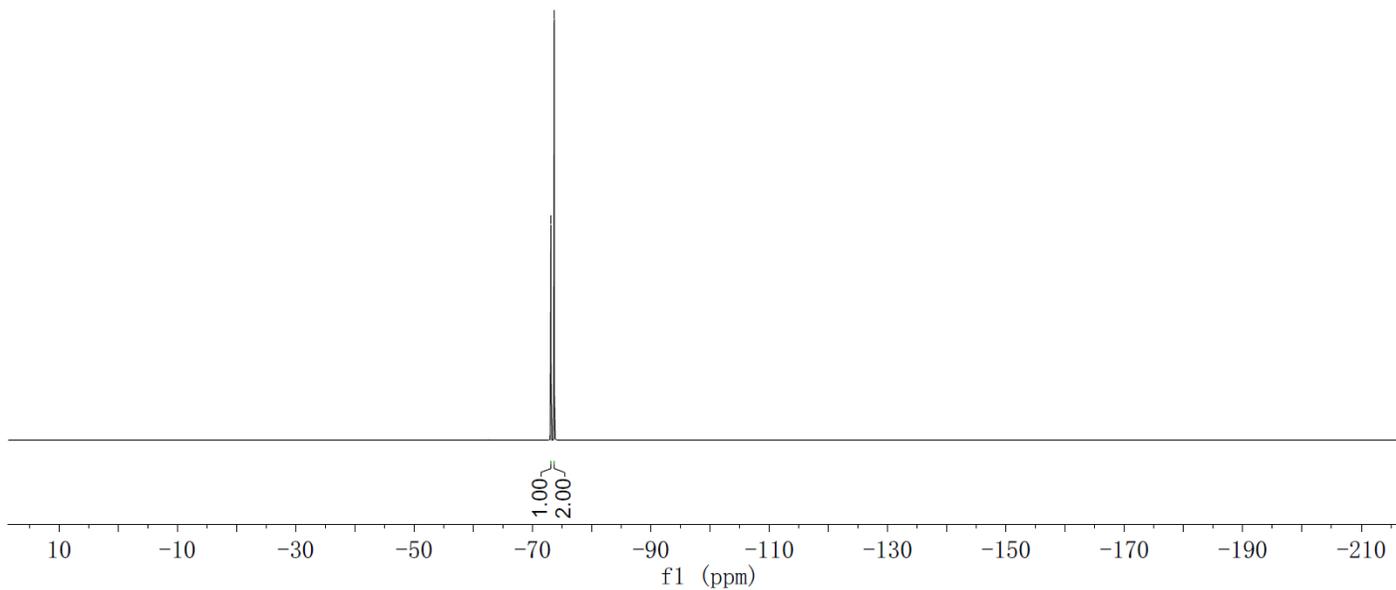
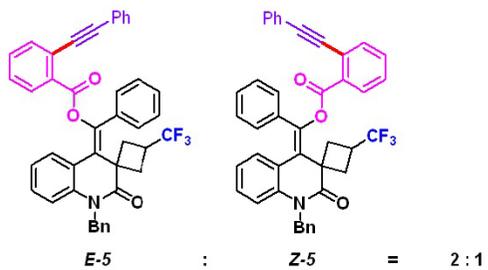
¹H NMR Spectrum of Compound 5 (400 MHz, CDCl₃)



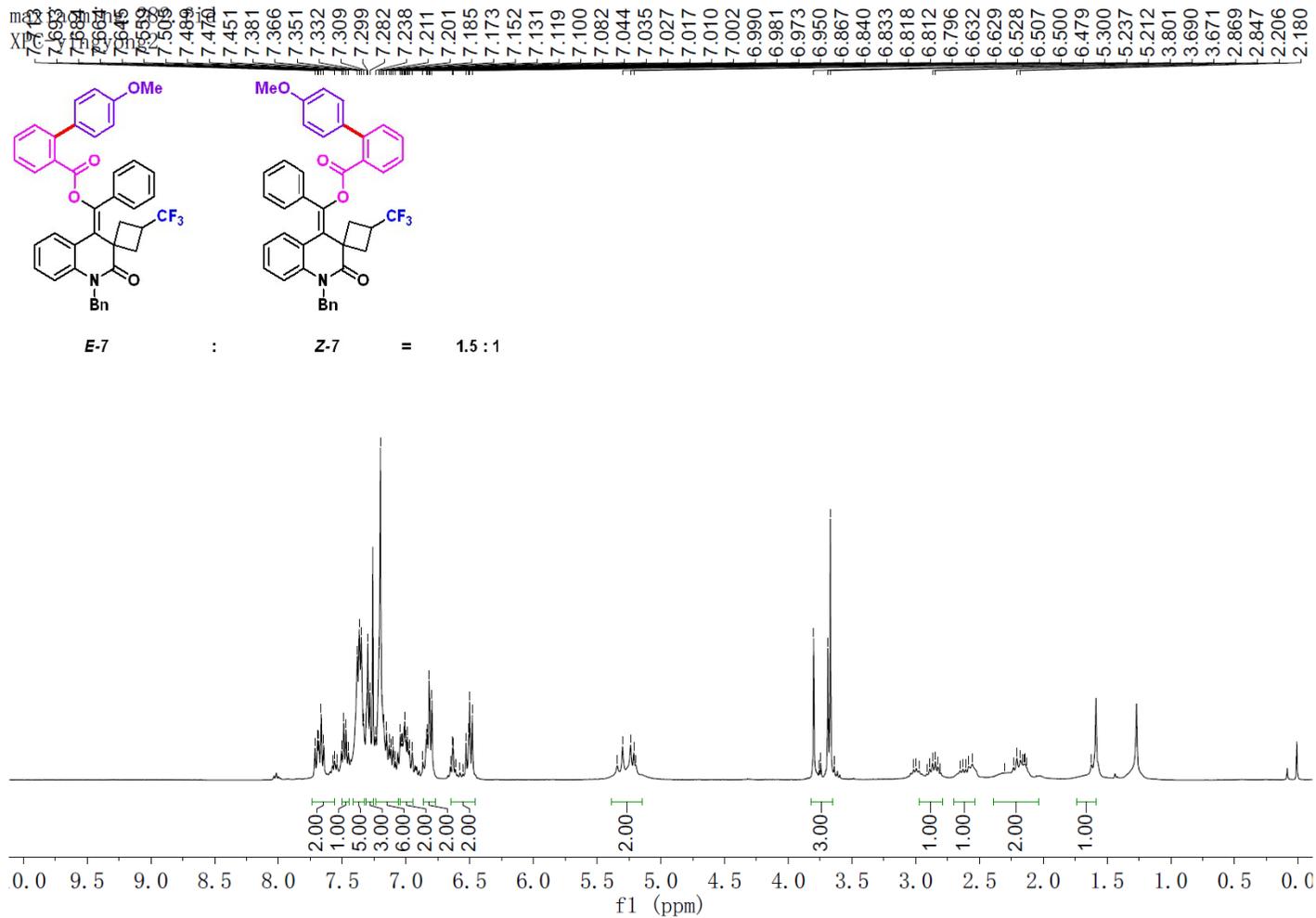
¹³C NMR Spectrum of Compound 5 (150 MHz, CDCl₃)

3maxiaoming02.870.fid
XPC-yingyong1

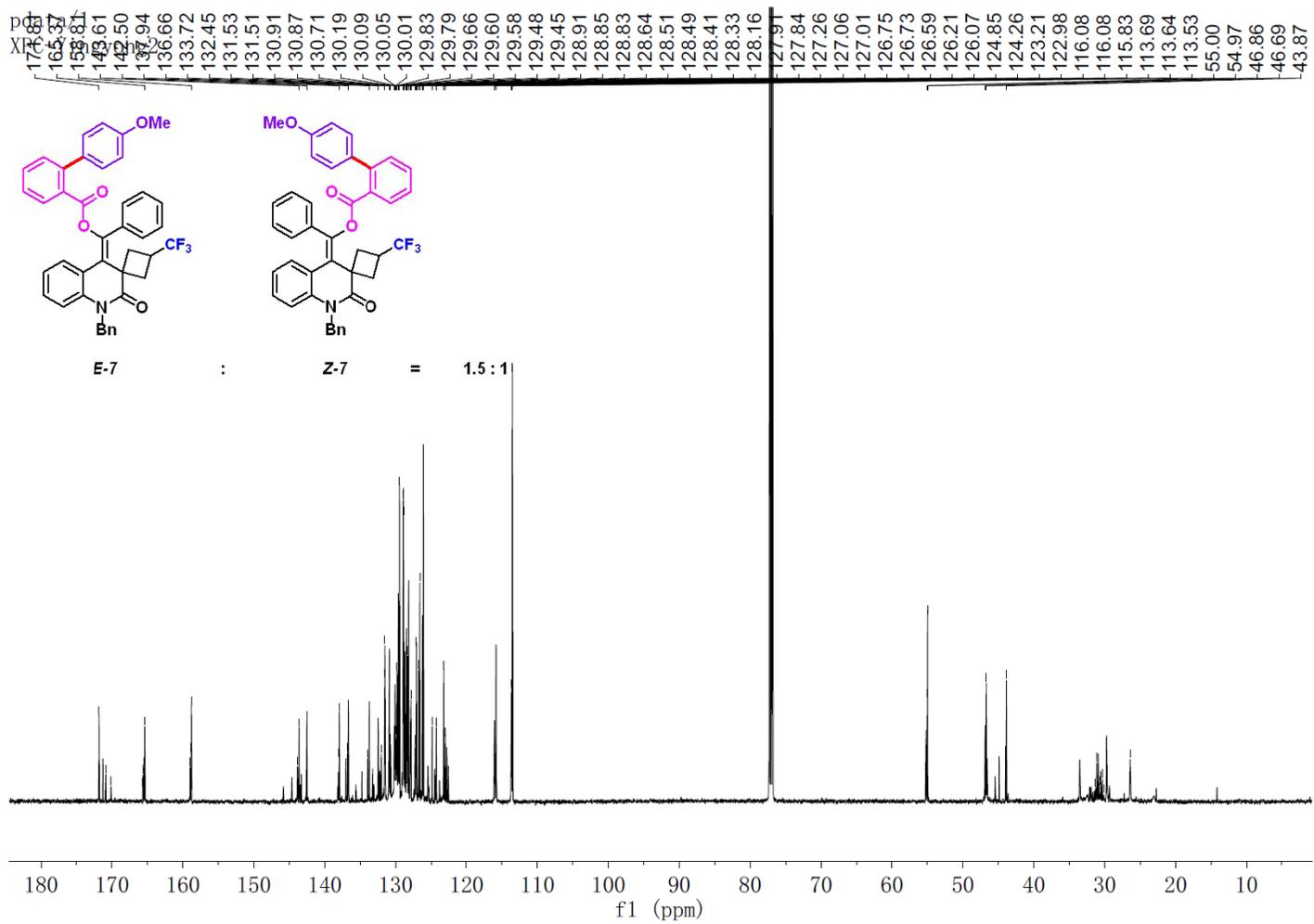
-73.10
-73.67



¹⁹F NMR Spectrum of Compound 5 (282 MHz, CDCl₃)

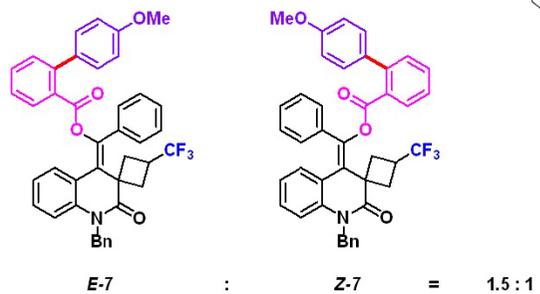


¹H NMR Spectrum of Compound 7 (400 MHz, CDCl₃)

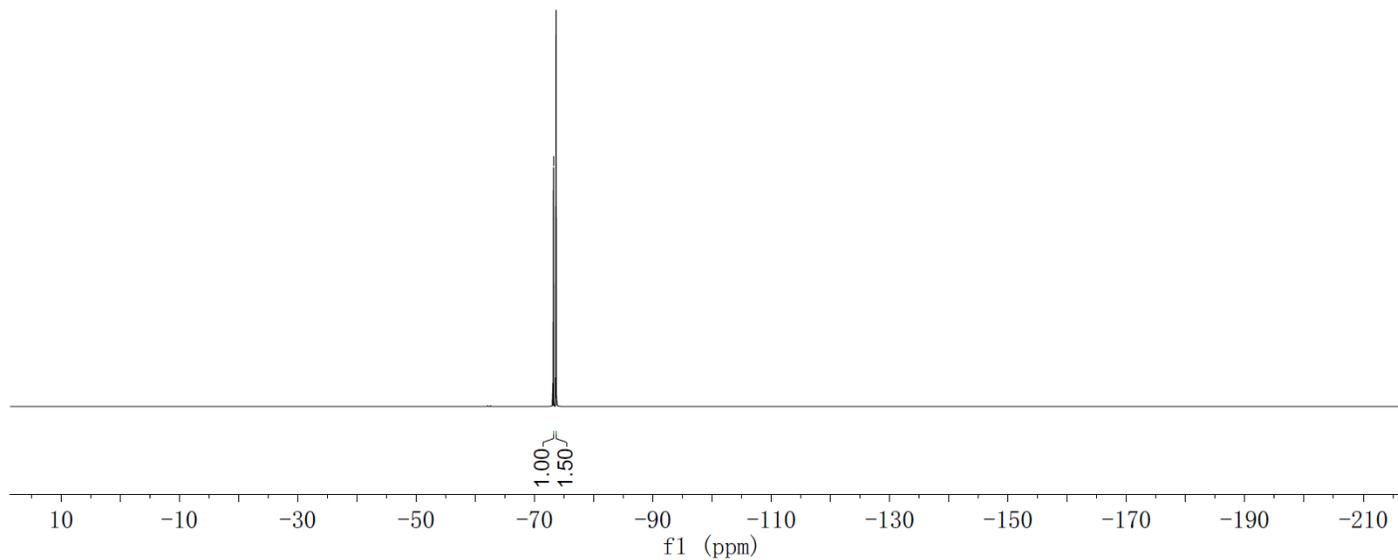


¹³C NMR Spectrum of Compound 7 (150 MHz, CDCl₃)

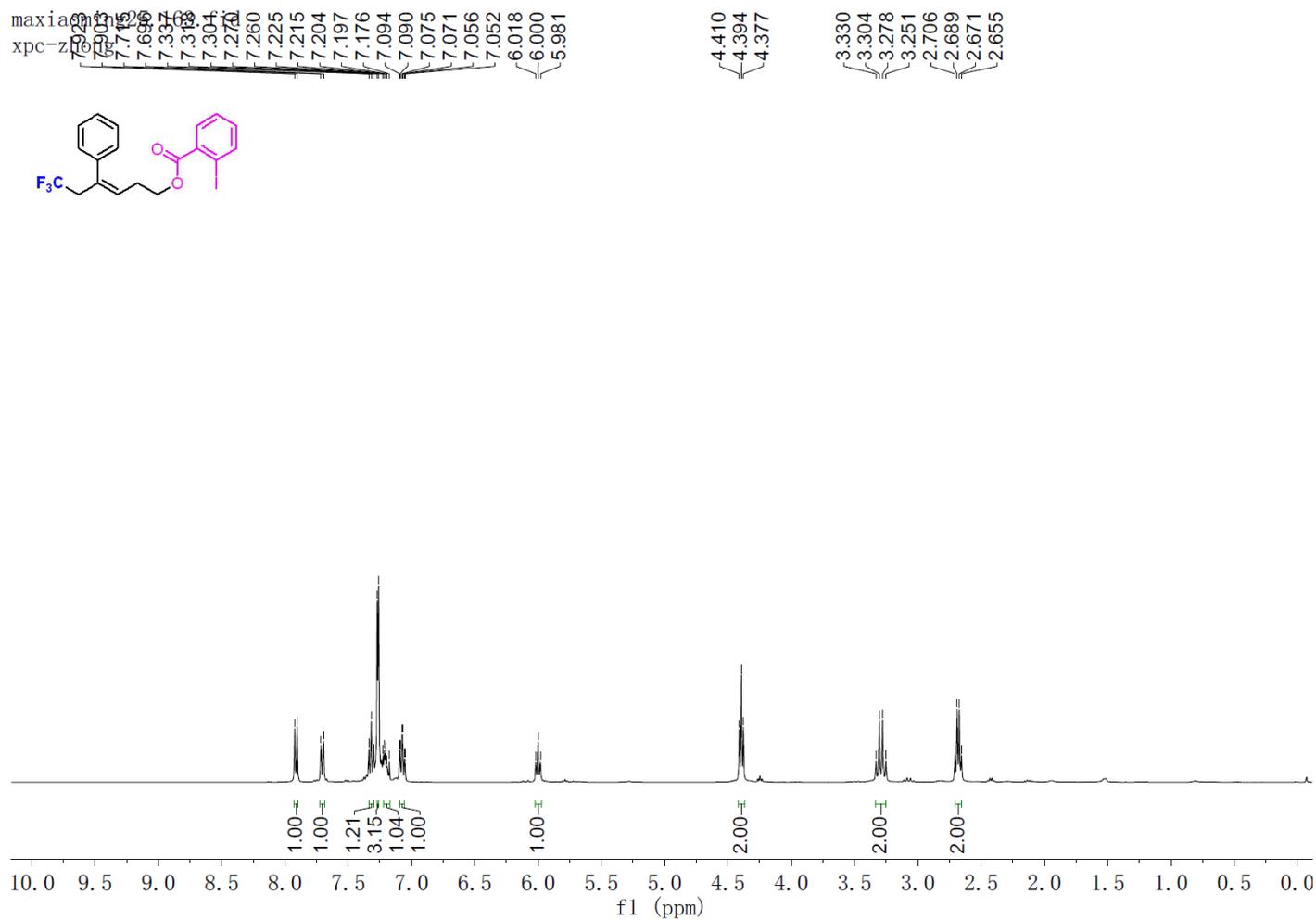
3maxiaoming02.880.fid
XPC-yingyong2



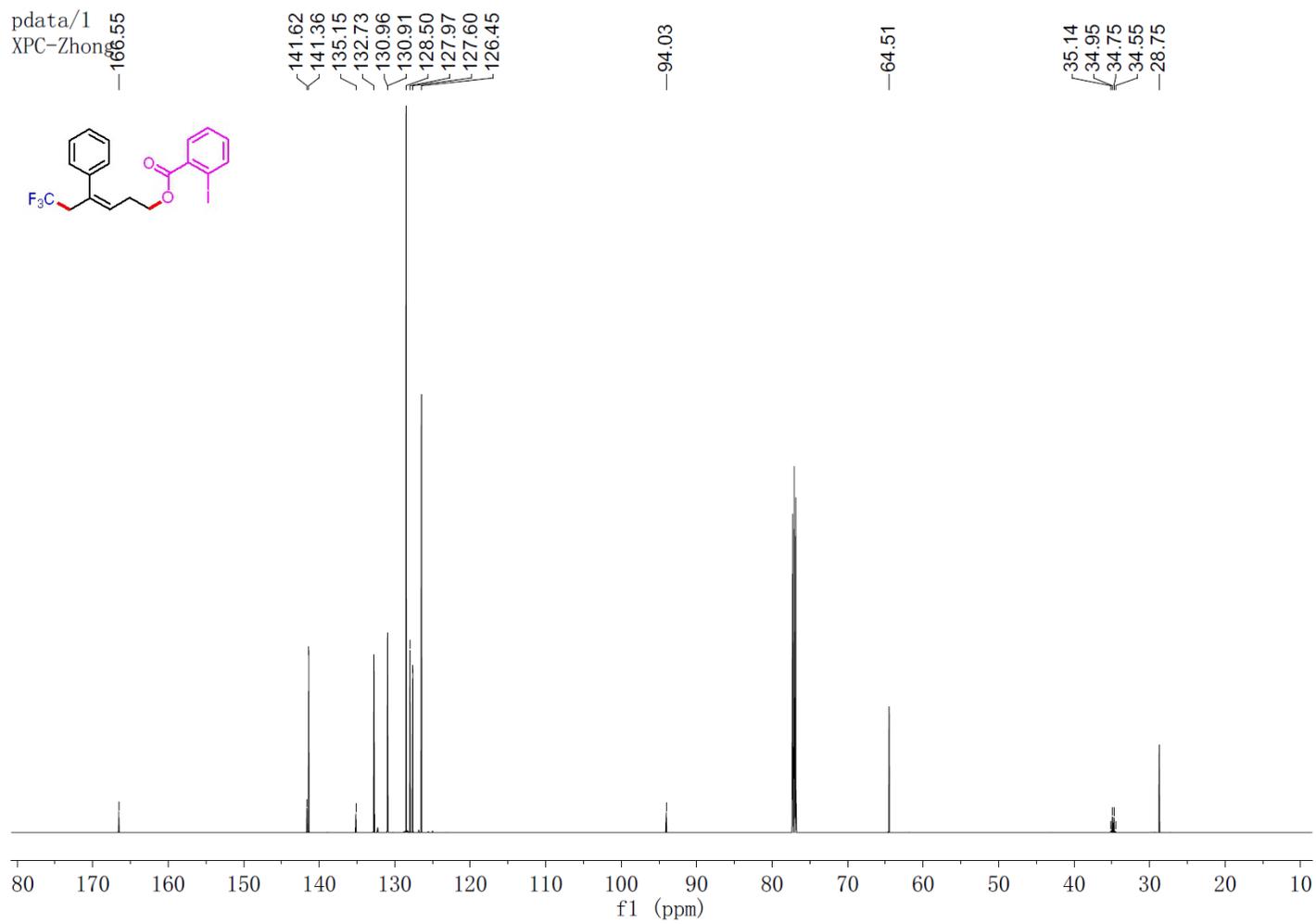
-73.20
-73.64



¹⁹F NMR Spectrum of Compound 7 (282 MHz, CDCl₃)



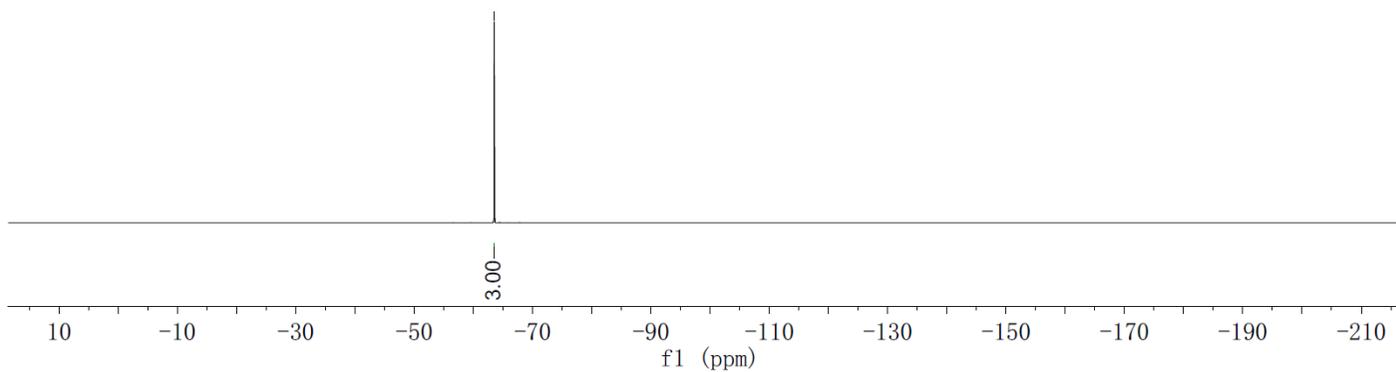
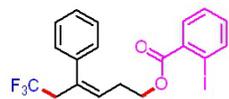
¹H NMR Spectrum of Compound 10 (400 MHz, CDCl₃)



¹³C NMR Spectrum of Compound 10 (150 MHz, CDCl₃)

3maxiaoming02.770.fid
ziyoujizhong

---63.54



¹⁹F NMR Spectrum of Compound 10 (282 MHz, CDCl₃)