Supporting Information

Pd(II)-Catalyzed Intramolecular Oxidative Heck Dearomative Reaction: Approach to Thiazloes Fused Pyrrolidinones with a C2-Azaquarternary Center

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1. General Information

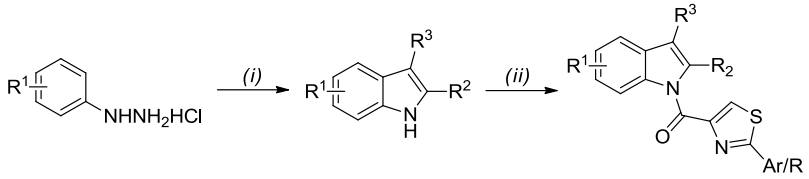
Melting point (m.p.) was measured on a microscopic melting point apparatus. ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.0 ppm). Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer; absorptions are reported in reciprocal centimeters. High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source.

2. Materials

Palladium(II) catalysts, oxidants and additives are commercially available. Unless otherwise indicated, all other reagents and solvents were obtained from commercial suppliers and used without further purification.

3. Experimental Section

3.1 General procedure for the synthesis of *N*-acylindole



Scheme S1. Preparation of *N*-acylindole substrates.
Reaction Conditions: (i) Ketone, AcOH, 100 °C; (ii) substituted thiazole-4-carbonyl chloride, 55% NaH, DMF, 0 °C to r.t., overnight

As shown in **Scheme S1**, *N*-acylindole substrates were synthesized from corresponding phenylhydrazine hydrochlorides as starting materials *via* Fisher indole synthesis followed by a *N*-acylation according to literatures.[1, 2]

The suspension of substituted phenylhydrazine hydrochloride (40 mmol) in AcOH (40 mL) was heated in 50 °C for half an hour, then butan-2-one (80 mmol, 2 equiv) was added in one portion and the reaction mixture was refluxed for 3 hours. After cooling to room temperature, AcOH was removed under vacum and the residue was dissolved in ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give gray residue, which was purified by flash chromatography on silica gel to afford the 2,3-disubstituted indoles.

To the suspension of NaH (55% dispersion in mineral oil, 1.2 equiv) in 10 mL anhydrous DMF (fresh distilled from CaH_2) under argon, 2,3-disubstituted indoles (10 mmol) in anhyrous DMF (5 mL)was added slowly at 0 °C. Then the reaction mixture was allowed to stir for half an hour at room temperature. Substituted thiazole-4-carbonyl chloride (10 mmol) in anhydrous DMF (5~10 mL) was added dropwise. The reaction mixture was stirred at room temperature overnight and quenched by adding 10 mL 1 N HCl solution. DMF was removed under vacum and the residue was dissolved in ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel to afford the *N*-acylindole.

3.2 General Procedure for the Synthesis of the Thiazole Fused Indolines

A reaction tube was charged with *N*-acylindole **1** (0.5 mmol, 1 equiv), $Pd(OAc)_2$ (0.05 mmol, 10 mol %), AgOAc (1 mmol, 2 equiv) and CH_3CN/DMSO (3.96 mL/0.04 mL). The reaction mixture was vigorously stirred at 130 °C (oil temperature) under air for 15 hours. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a Cetile pad. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel to afford the products **2**.

3.3 Gram-scale reaction of compound 1e

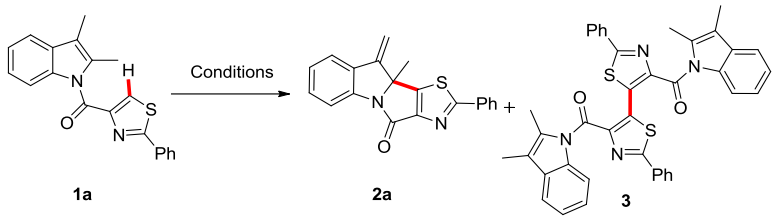
A reaction tube was charged with **1e** (6 mmol, 2.17 g, 1 equiv), $Pd(OAc)_2$ (0.6 mmol, 135 mg, 10 mol %), AgOAc (12 mmol, 2.0 g, 2 equiv) and CH_3CN/DMSO (48 mL, 99:1, *v/v*). The reaction mixture was vigorously stirred at 130 °C (oil temperature) under air for 20 hours. After cooling to room temperature, diluted with ethyl acetate and filtered through a Cetile pad. The filtrate was

concentrated *in vacuo* directly to give dark residue, which was purified by flash chromatography on silica gel to afford 1.55 g faint yellow solid in 72% yield.

A reaction tube was charged with **1e** (6 mmol, 2.17 g, 1 equiv), $Pd(OAc)_2$ (0.3 mmol, 68 mg, 5mol %), AgOAc (12 mmol, 2.0 g, 2 equiv) and CH_3CN/DMSO (48 mL, 99:1, *v/v*). The reaction mixture was vigorously stirred at 130 °C (oil temperature) under air for 24 hours. After cooling to room temperature, diluted with ethyl acetate and filtered through a Cetile pad. The filtrate was concentrated *in vacuo* directly to give dark residue, which was purified by flash chromatography on silica gel to afford 1.16 g faint yellow solid in 54% yield.

3.4 The effect of the ratios of CH_3CN/DMSO on the reaction

Table S1 Screening the ratio of CH_3CN/DMSO [a]

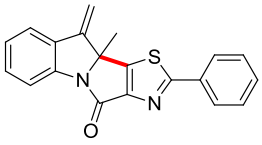


Entry	$Pd(OAc)_2$ (mol %)	Solvent (mL, v/v)	Yield(%)[b] (**2a**/**3**)
1	10	CH_3CN:DMSO(1.6:0.4)	55/20
2	10	CH_3CN:DMSO(1.8:0.2)	74/10
3	10	CH_3CN:DMSO(1.98:0.02)	77/8
4	10	CH_3CN:DMSO:AcOH(1.9:0.05:0.05)	55/3
5	10	CH_3CN:DMSO:PivOH(1.9:0.05:0.05)	52/21
6	**10**	**CH_3CN:DMSO(3.96:0.04)**	**86(84[c])/7**

[a] Reaction conditions: **1a** (0.5 mmol), $Pd(OAc)_2$ (10 mol %) and AgOAc (1 mmol) in solvent under air at 130 °C for 15 h. [b] ^1H NMR yields using dibromomethane (δ = 4.80) as an internal standard. [c] Isolated yield.

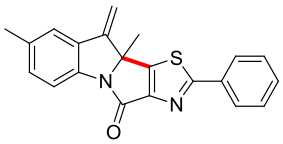
3.5 Characterization of the Title Compounds

10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2a)



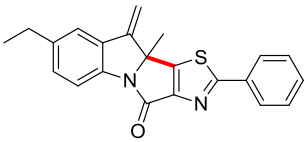
Faint yellow solid, m.p. 138-140 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 6.9, 2.6 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.58 - 7.32 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.63 (s, 1H), 5.20 (s, 1H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 164.0, 154.6, 153.3, 146.2, 142.1, 133.0, 131.9, 131.3, 130.7, 129.2, 127.1, 125.0, 121.9, 117.5, 104.4, 72.5, 30.4 ppm; IR (KBr) 1717, 1460, 1400, 1331, 1295, 1129, 890, 788, 745, 693 cm^{-1}; HRMS(ESI) calcd for $[C_{20}H_{14}N_2OS+H]^+$ 331.0900, found 331.0906.

8,10a-dimethyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2b)



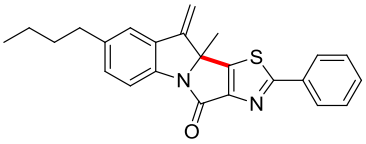
Faint yellow solid, m.p. 178-180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.29 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 5.61 (s, 1H), 5.17 (s, 1H), 2.36 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 163.5, 153.9, 152.8, 145.8, 139.4, 134.2, 132.5, 131.3, 131.0, 130.7, 128.6, 126.5, 121.7, 116.7, 103.5, 72.1, 29.8, 20.7 ppm; IR (KBr) 3126, 1717, 1647, 1478, 1400, 1326, 1287, 892, 759, 686 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{16}N_2OS+H]^+$ 345.1056, found 345.1064.

8-ethyl-10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one(2c)



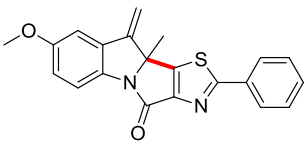
Faint yellow solid, m.p. 121-123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.31 (s, 1H), 7.23 (dd, *J* = 8.1, 1.0 Hz, 1H), 5.62 (s, 1H), 5.17 (s, 1H), 2.65 (q, J = 7.6 Hz, 2H), 1.81 (s, 3H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 164.0, 154.5, 153.3, 146.4, 141.2, 140.1, 133.0, 131.9, 131.2, 130.5, 129.1, 127.0, 121.0, 117.3, 104.0, 72.7, 30.3, 28.7, 15.8 ppm; IR (KBr) 3132, 1717, 1647, 1478, 1400, 1326, 1287, 1141, 892, 759, 686 cm^{-1}; HRMS(ESI) calcd for $[C_{22}H_{18}N_2OS+H]^+$ 359.1213, found 359.1220.

8-butyl-10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2d)



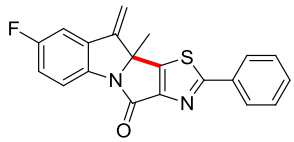
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 7.93 (m, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 5.0 Hz, 3H), 7.29 (s, 1H), 7.22 (d, J = 8.1 Hz, 1H), 5.62 (s, 1H), 5.17 (s, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.82 (s, 3H), 1.65 – 1.54 (m, 2H), 1.43 – 1.29 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 164.0, 154.5, 153.3, 146.4, 140.1, 139.9, 133.0, 131.8, 131.2, 131.0, 129.1, 127.0, 121.5, 117.2, 103.9, 72.7, 35.4, 33.8, 30.3, 22.3, 13.9 ppm; IR (KBr) 3133, 2924, 2853, 1715, 1441, 1400, 1336, 1154, 875, 809, 694, 640 cm^{-1}; HRMS(ESI) calcd for $[C_{24}H_{22}N_2OS+H]^+$ 387.1526, found 387.1533.

8-methoxy-10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2e)



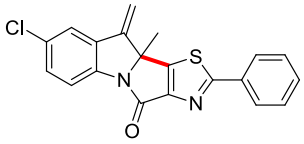
Faint yellow solid, m.p. 152-154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.45 (dd, *J* = 7.0, 3.7 Hz, 3H), 7.10 – 6.89 (m, 2H), 5.61 (s, 1H), 5.19 (s, 1H), 3.81 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 164.2, 157.6, 154.3, 153.4, 146.4, 136.0, 133.0, 133.0, 131.3, 129.2, 127.0, 118.3, 116.8, 106.8, 104.6, 72.9, 55.89, 30.3 ppm; IR (KBr) 3127, 2924, 2853, 1718, 1481, 1460, 1400, 1277, 1218, 1063, 809, 762, 728, 686 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{16}N_2O_2S+Na]^+$ 383.0849, found 383.0840.

8-fluoro-10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2f)



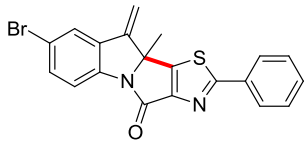
Faint yellow solid, m.p. 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.68 (dd, *J* = 8.6, 4.6 Hz, 1H), 7.48 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.21 – 7.04 (m, 2H), 5.64 (s, 1H), 5.26 (s, 1H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 164.1, 162.2, 159.0, 154.5, 153.2, 145.9, 138.3, 133.6, 133.5, 132.9, 131.4, 129.3, 127.1, 126.9, 118.7, 118.6, 117.8, 117.5, 109.0, 108.7, 105.9, 73.0, 30.3 ppm; IR (KBr) 3128, 2924, 2854, 1717, 1481, 1400, 1318, 1153, 1087, 903, 818, 757, 684 cm^{-1}; HRMS(ESI) calcd for $[C_{20}H_{13}FN_2OS+H]^+$ 349.0805, found 349.0810.

8-chloro-10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2g)



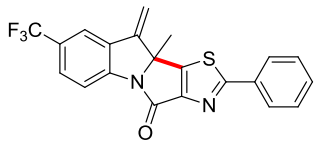
Faint yellow solid, m.p. 151-153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.65 (s, 1H), 5.26 (s, 1H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 163.7, 154.5, 153.1, 145.4, 140.6, 133.4, 132.8, 131.4, 130.6, 130.6, 129.2, 127.0, 122.0, 118.5, 105.8, 72.8, 30.3 ppm; IR (KBr) 3126, 1717, 1647, 1464, 1400, 1328, 1149, 889, 759, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{13}ClN_2OS+H]^+$ 365.0510, found 365.0517.

8-bromo-10a-methyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2h)



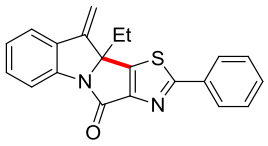
Faint yellow solid, m.p. 143-145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.67 – 7.55 (m, 2H), 7.48 (tt, *J* = 6.2, 3.0 Hz, 4H), 5.65 (s, 1H), 5.25 (s, 1H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 163.7, 154.6, 153.1, 145.2, 141.1, 133.8, 133.5, 132.8, 131.4, 129.2, 127.1, 125.0, 118.9, 118.1, 106.0, 72.7, 30.4 ppm; IR (KBr) 3126, 1717, 1637, 1464, 1400, 1328, 1133, 889, 817, 759, 686 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{13}BrN_2OS+H]^+$ 409.0005, found 409.0006.

10a-methyl-10-methylene-2-phenyl-8-(trifluoromethyl)-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2i)



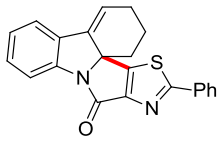
Faint yellow solid, m.p. 81-83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 7.92 (m, 2H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.73 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.38 (m, 3H), 5.76 (d, *J* = 1.4 Hz, 1H), 5.33 (d, *J* = 1.3 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 163.5, 155.0, 152.9, 145.2, 144.6, 132.8, 132.4, 131.5, 129.3, 128.0, 127.9, 127.5, 127.1, 126.0, 122.4, 119.2, 119.1, 118.1, 117.5, 106.5, 72.9, 30.5 ppm; IR (KBr) 3127, 1721, 1615, 1400, 1340, 1329, 1269, 1134, 889, 833, 761, 678 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{13}F_3N_2OS+H]^+$ 399.0773, found 399.0780.

10a-ethyl-10-methylene-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2j)



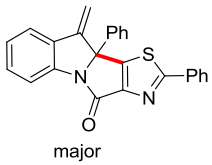
Faint yellow solid, m.p. 99-101 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.67 (s, 1H), 5.18 (s, 1H), 2.07 (ddt, *J* = 21.3, 14.0, 7.1 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 164.3, 153.8, 153.1, 145.2, 142.6, 132.9, 132.5, 131.3, 130.6, 129.2, 127.0, 124.8, 121.6, 117.3, 104.8, 76.0, 35.6, 8.2 ppm; IR (KBr) 2966, 2930, 1721, 1646, 1600, 1463, 1380, 1273, 1128, 883, 836, 765, 751, 688, 650 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{16}N_2OS+H]^+$ 345.1056, found 345.1062.

6-phenyl-3,4-dihydrothiazolo[5',4':3,4]pyrrolo[2,1-k]carbazol-8(2H)-one (2k)



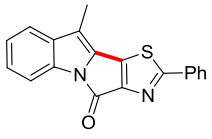
Brown solid, m.p. 129-131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 - 7.91 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.37 (m, 4H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.09 (td, *J* = 7.5, 0.7 Hz, 1H), 6.26 (dd, *J* = 6.5, 4.0 Hz, 1H), 2.66 – 2.60 (m, 2H), 2.24 – 1.87 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 168.6, 157.1, 152.9, 144.2, 138.4, 132.9, 131.3, 130.3, 129.4, 129.2, 127.1, 124.7, 120.5, 119.1, 116.6, 76.7, 72.9, 35.8, 22.5, 15.1 ppm. IR(KBr) 2938, 1728, 1593, 1461, 1440, 1129, 751, 689 cm^{-1}; HRMS(ESI) calcd for $[C_{22}H_{16}N_2OS+H]^+$ 357.1056, found 357.1054.

10-methylene-2,10a-diphenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2l)



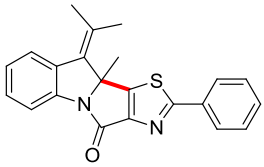
Faint yellow solid, m.p. 203-205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.1 Hz, 0.21H), 8.17 – 7.86 (m, 2.4H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.62-7.54 (m, 2.7H), 7.61-7.23 (m, 11.9H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.78 (s, 1H), 5.45 (s, 1H), 2.50 (s, 0.62H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 165.8, 163.9, 160.8, 154.2, 153.2, 146.3, 145.0, 142.1, 140.4, 139.8, 136.6, 133.4, 132.8, 132.8, 132.4, 131.8, 131.3, 131.0, 130.8, 130.4, 129.8, 129.1, 129.0, 128.6, 127.4, 127.0, 126.3, 125.4, 125.3, 124.1, 121.8, 121.0, 118.6, 117.5, 115.7, 107.5, 77.0, 11.9 ppm. IR(KBr) 2939, 2902, 2857, 1687, 1442, 1364, 1190, 1132, 841, 759, 687 cm^{-1}. HRMS(ESI) calcd for $[C_{25}H_{16}N_2OS+H]^+$ 393.1056, found 393.1053.

10-methyl-2-phenyl-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2m)



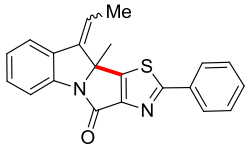
Brown solid, m.p. 224-226 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.42 (m, 3H), 7.31 (dd, *J* = 8.0, 3.4 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 156.5, 155.0, 137.3, 134.9, 133.9, 132.9, 131.1, 130.0, 129.2, 128.1, 126.8, 123.5, 120.7, 118.8, 112.6, 10.0 ppm. IR(KBr) 2909, 1721, 1443, 1331, 1136, 806, 760, 742 cm^{-1}; HRMS(ESI) calcd for $[C_{19}H_{12}N_2OS+H]^+$ 317.0743, found 317.0742.

10a-methyl-2-phenyl-10-(propan-2-ylidene)-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2n)



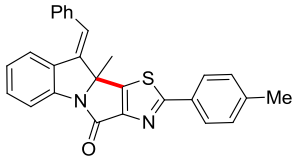
Faint yellow solid, m.p. 154-156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.05 (m, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 162.5, 154.4, 154.0, 140.7, 133.4, 132.9, 131.8, 131.2, 129.5, 129.1, 128.3, 127.0, 125.4, 124.5, 117.0, 73.3, 28.7, 24.5, 22.4 ppm; IR (KBr) 2927, 1711, 1461, 1441, 1392, 1337, 1300, 748, 729, 686, 632 cm^{-1}; HRMS(ESI) calcd for $[C_{22}H_{18}N_2OS+H]^+$ 359.1213, found 359.1217.

10-ethylidene-10a-methyl-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2o)



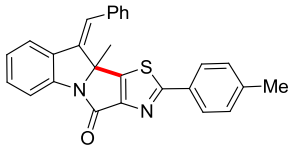
Z/E = 1.3:1, inseparable. Faint yellow solid, m.p. 159-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 3.2 Hz, 3.7H), 7.72 (t, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.27 (m, 9H), 7.17-7.06 (m, 2H), 6.11 (q, *J* = 7.3 Hz, 1H), 5.76 (q, *J* = 7.1 Hz, 0.8H), 2.10 (d, 7.3Hz, 3H), 2.05 (d, 7.3Hz, 2.5H), 1.83 (s, 3H), 1.77(s, 2.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 174.2, 163.4, 163.3, 154.9, 153.9, 153.8, 153.2, 141.9, 140.3, 138.0, 137.4, 132.9, 132.8, 132. 7, 132.1, 131.1, 131.1, 129.4, 129.2, 129.0, 126.8, 125.4, 124.7, 120.4, 119.8, 117.4, 116.9, 116.4, 72.8, 71.8, 30.3, 28.5, 14.8, 14.0 ppm. IR(KBr) 2975, 2918, 2857, 1718, 1462, 763, 688 cm^{-1}. HRMS(ESI) calcd for $[C_{21}H_{16}N_2OS+H]^+$ 345.1056, found 345.1059.

(E)-10-benzylidene-10a-methyl-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (E-2p)



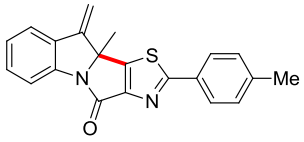
White solid, m.p. 171-173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.25 (m, 9H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 2.40 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 163.6, 154.6, 153.4, 142.8, 141.9, 139.3, 135.8, 130.7, 130.6, 130.4, 129.9, 128.8, 128.4, 128.1, 127.1, 125.0, 124.4, 123.6, 117.8, 73.3, 30.6, 21.6 ppm. IR(KBr) 2923, 2852, 1716, 1461, 1299, 1144, 812, 750, 707 cm^{-1}. HRMS(ESI) calcd for $[C_{27}H_{20}N_2OS+H]^+$ 421.1369, found 421.1366.

(Z)-10-benzylidene-10a-methyl-2-phenyl-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (Z-2p)



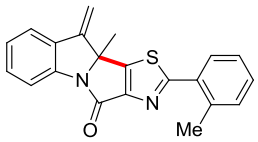
White solid, m.p. 184-186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.46 (m, 3H), 7.41 – 7.35 (m, 3H), 7.20 – 7.14 (m, 4H), 2.35 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 162.8, 154.0, 151.4, 141.5, 140.5, 139.0, 135.9, 133.5, 130.4, 130.3, 129.7, 129.3, 129.0, 128.3, 126.8, 124.9, 122.4, 121.3, 117.1, 72.4, 31.8, 21.6 ppm. IR(KBr) 2922, 2853, 1715, 1458, 1151, 1118, 750, 729 cm^{-1}. HRMS(ESI) calcd for $[C_{27}H_{20}N_2OS+H]^+$ 421.1369, found 421.1365.

10a-methyl-10-methylene-2-(p-tolyl)-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2q)



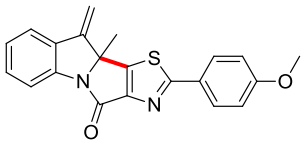
Faint yellow solid, m.p. 168-170 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 5.63 (s, 1H), 5.19 (s, 1H), 2.39 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 164.0, 154.3, 153.2, 146.4, 142.2, 141.8, 131.9, 130.7, 130.4, 129.9, 127.0, 124.9, 121.9, 117.6, 104.4, 72.5, 30.4, 21.6 ppm; IR (KBr) 3126, 1715, 1646, 1462, 1401, 1332, 1292, 1128, 1004, 889, 772, 745, 662 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{16}N_2OS+H]^+$ 345.1046, found 345.1056.

10a-methyl-10-methylene-2-(o-tolyl)-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2r)



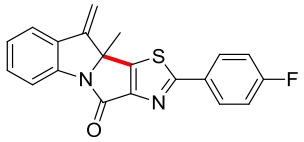
Faint yellow solid, m.p. 218-220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.44 - 7.23 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.65 (s, 1H), 5.21 (s, 1H), 2.63 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 164.1, 155.4, 152.9, 146.4, 142.3, 137.3, 132.2, 131.9, 131.8, 130.8, 130.5, 130.3, 126.3, 124.9, 121.9, 117.6, 104.4, 72.5, 30.5, 21.7 ppm; IR (KBr) 2812, 2858, 1717, 1643, 1600, 1462, 1295, 1129, 890, 774, 766, 745, 694, 656 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{16}N_2OS+H]^+$ 345.1056, found 345.1053.

2-(4-methoxyphenyl)-10a-methyl-10-methylene-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2s)



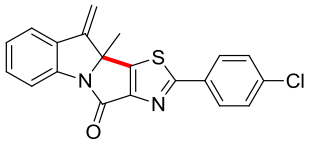
Faint yellow solid, m.p. 126-128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 1H), 5.18 (s, 1H), 3.85 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 164.1, 162.2, 154.0, 153.1, 146.4, 142.2, 131.9, 130.7, 128.7, 125.9, 124.9, 121.9, 117.6, 114.6, 104.3, 72.5, 55.6, 30.4 ppm; IR(KBr) 3138, 2920, 1714, 1607, 1573, 1461, 1291, 1257, 1127, 884, 835, 772, 671 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{16}N_2O_2S+H]^+$ 361.1005, found 361.1011.

2-(4-fluorophenyl)-10a-methyl-10-methylene-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2t)



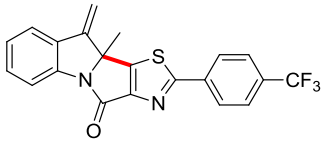
Faint yellow solid, m.p. 87-89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.68 (dd, *J* = 8.6, 4.6 Hz, 1H), 7.46 (dd, *J* = 7.3, 3.8 Hz, 3H), 7.23 – 7.04 (m, 2H), 5.64 (s, 1H), 5.26 (s, 1H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 164.1, 162.3, 159.0, 154.6, 153.2, 146.0, 138.4, 133.6, 133.0, 131.4, 129.3, 127.2, 118.7, 118.6, 117.8, 117.5, 109.0, 108.7, 105.8, 73.0, 30.4 ppm; IR (KBr) 3126, 1720, 1647, 1475, 1400, 1327, 1265, 1139, 862, 806, 766, 688 cm^{-1}; HRMS(ESI) calcd for $[C_{20}H_{13}FN_2OS+H]^+$ 349.0805, found 349.0801.

2-(4-chlorophenyl)-10a-methyl-10-methylene-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2u)



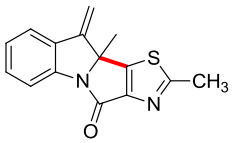
Faint yellow solid, m.p. 142-144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 13.0, 7.6 Hz, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.65 (s, 1H), 5.20 (s, 1H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 163.7, 154.7, 153.4, 146.1, 142.0, 137.4, 131.8, 131.4, 130.8, 129.5, 128.2, 125.0, 121.9, 117.5, 104.5, 72.5, 30.4 ppm; IR(KBr) 3132, 2920, 2850, 1713, 1602, 1462, 1400, 1293, 1225, 1127, 1093, 1081, 897, 823, 732, 628 cm^{-1}; HRMS(ESI) calcd for $[C_{20}H_{13}ClN_2OS+H]^+$ 365.0510, found 365.0504.

10a-methyl-10-methylene-2-(4-(trifluoromethyl)phenyl)-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2v)



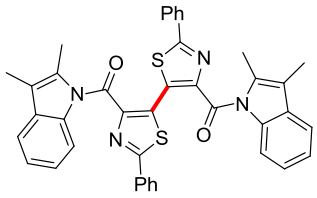
Faint yellow solid, m.p. 101-103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.11 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.73 (s, 1H), 5.66 (s, 1H), 5.22 (s, 1H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 163.5, 155.3, 153.6, 146.0, 141.9, 136.0, 132.9, 132.4, 132.0, 131.7, 130.7, 129.1, 127.3, 126.2, 126.2, 126.1, 125.5, 125.1, 121.9, 117.5, 104.6, 72.5, 30.3 ppm; IR (KBr) 3125, 1721, 1615, 1463, 1400, 1340, 1328, 1269, 1115, 1054, 889, 833, 760, 687 cm^{-1}; HRMS(ESI) calcd for $[C_{21}H_{13}F_3N_2OS+H]^+$ 399.0773, found 399.0767.

2,10a-dimethyl-10-methylene-10,10a-dihydro-4H-thiazolo[5',4':3,4]pyrrolo[1,2-a]indol-4-one (2w)



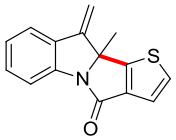
Faint yellow solid, m.p. 99-101 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.38 (dd, *J* = 11.0, 4.4 Hz, 1H), 7.14 (dd, *J* = 10.9, 4.2 Hz, 1H), 5.61 (s, 1H), 5.13 (s, 1H), 2.82 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 163.8, 155.4, 146.4, 142.2, 132.0, 130.8, 124.9, 121.9, 117.6, 104.3, 72.5, 30.4, 20.3 ppm; IR (KBr) 3108, 2924, 2854, 2360, 1714, 1601, 1395, 882, 739, 709 cm^{-1}; HRMS(ESI) calcd for $[C_{15}H_{12}N_2OS+H]^+$ 269.0743, found 269.0750.

(2,2'-diphenyl-[5,5'-bithiazole]-4,4'-diyl)bis((2,3-dimethyl-1H-indol-1-yl)methanone) (3)



Yellow solid, m.p. 218-220 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.34 (m, 4H), 7.21 – 7.09 (m, 2H), 2.16 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 162.7, 136.3, 132.5, 132.3, 131.5, 131.3, 129.2, 127.9, 127.0, 124.1, 123.5, 118.0, 116.7, 115.1, 13.1, 8.9 ppm; IR(KBr) 3233, 2962, 2922, 2850, 1685, 1670, 1618, 1221, 818, 754, 684, 614 cm^{-1}; HRMS(ESI) calcd for $[C_{40}H_{30}N_4O_2S_2+H]^+$ 663.1883, found 663.1882.

10a-methyl-10-methylene-10,10a-dihydro-4H-thieno[2',3':3,4]pyrrolo[1,2-a]indol-4-one (4)



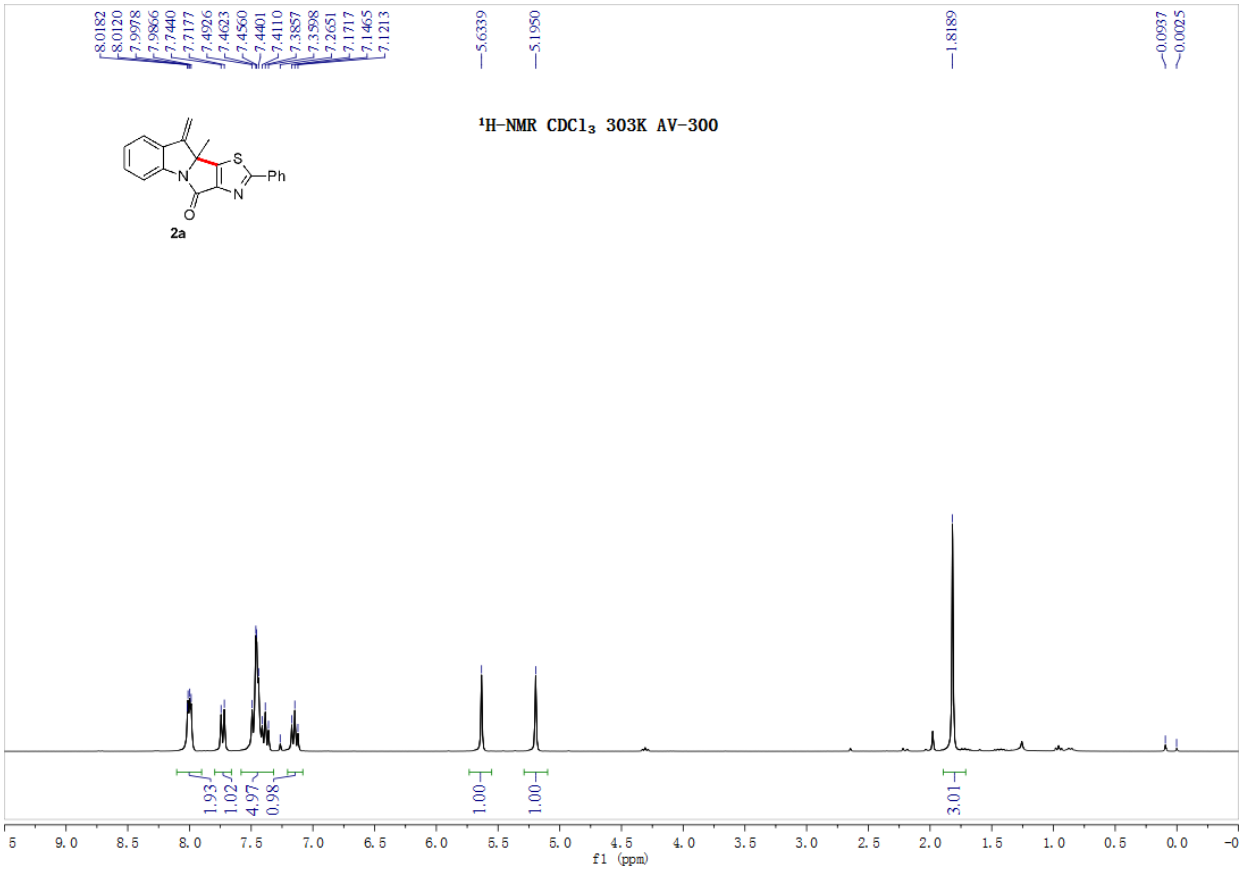
Brown solid, m.p. 102-104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 9.6, 4.8 Hz, 2H), 7.20 (d, *J* = 5.0 Hz, 1H), 7.13 (dd, *J* = 7.8, 7.3 Hz, 1H), 5.61 (d, *J* = 0.7 Hz, 1H), 5.22 (d, *J* = 0.7 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 161.1, 146.8, 142.3, 138.8, 132.1, 130.8, 130.4, 124.6, 121.8, 120.8, 117.2, 103.9, 73.7, 30.6 ppm. IR(KBr) 2918, 2853, 1670, 1458, 1387, 1327, 810, 746, 620 cm^{-1}; HRMS(ESI) calcd for $[C_{15}H_{11}NOS+H]^{+}$ 254.0634, found 254.0633.

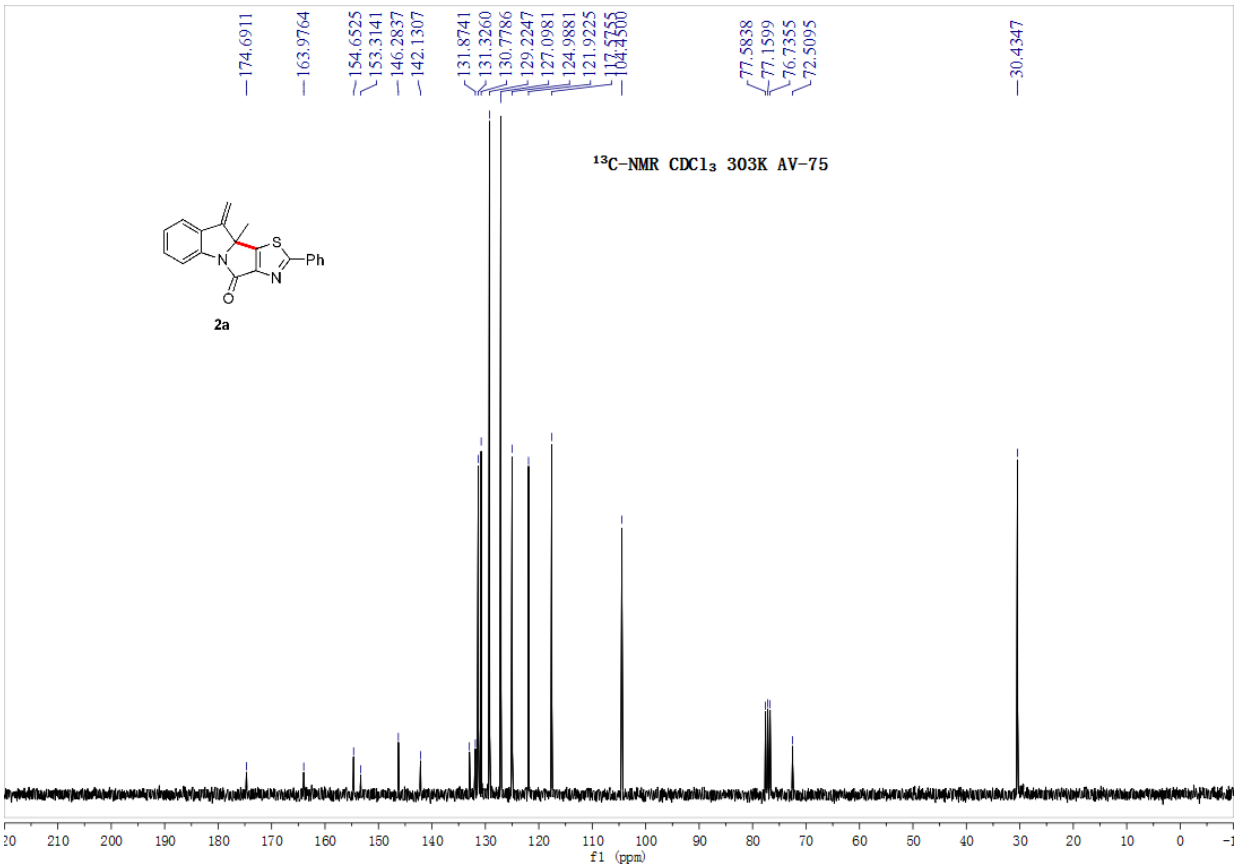
References

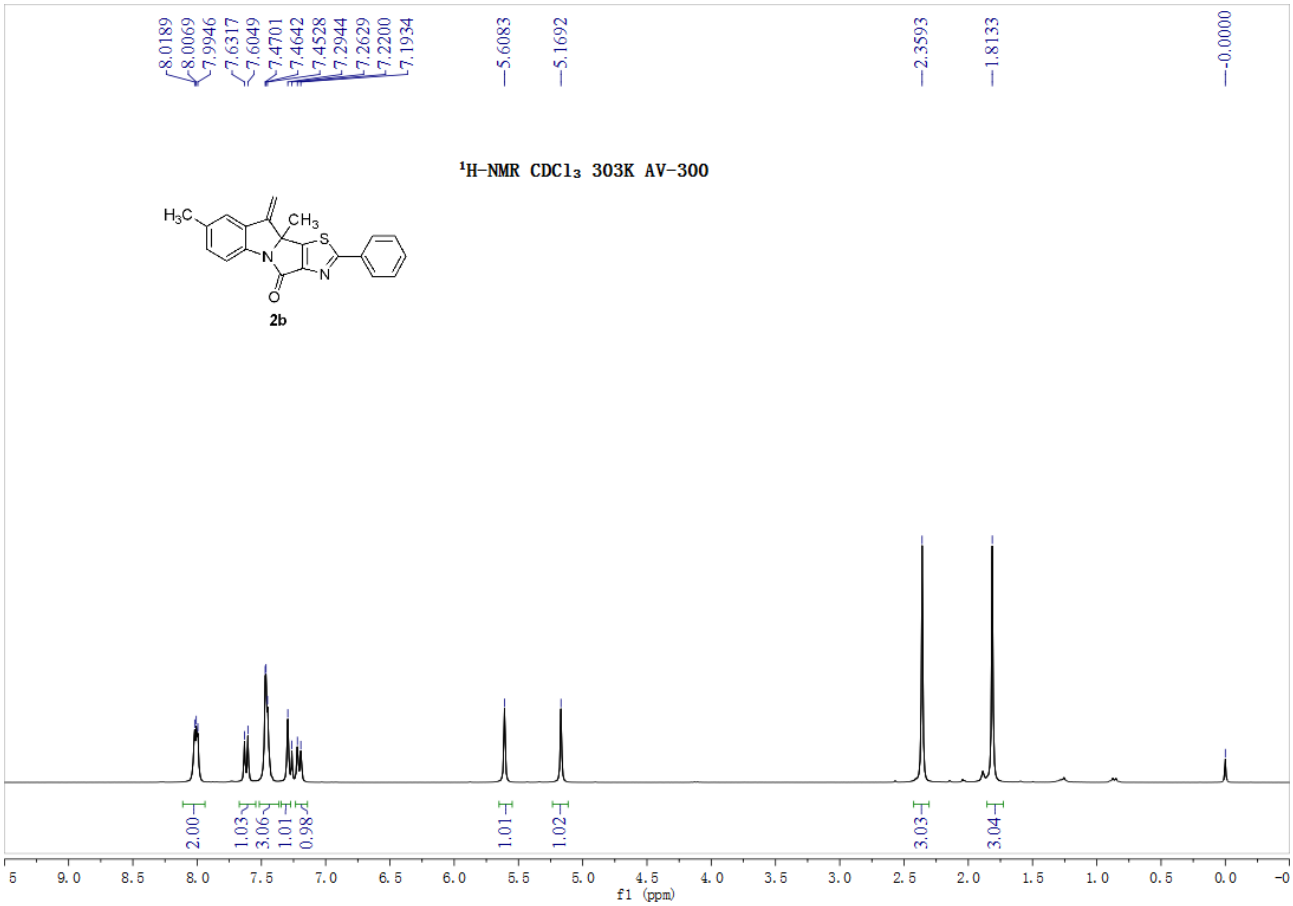
1. For examples of Fisher indole synthesis, see: (a) H. Illy and L. Funderburk, *J. Org. Chem.* 1968, **33**, 4283-4285; (b) P. Fludzinski, L. A. Wittenarer, K. W. Schenck and M. L. Cohen, *J. Med. Chem.* 1986, **29**, 2415-2418; (c) K. G. Liu, A. J. Robichaud, J. R. Lo, J. F. Mattes and Y. Cai, *Org. Lett.* 2006, **8**, 5769-5771.

2. For acylation on *NH* of indole, see: (a) E. V. Angerer and J. Strohmeier, *J. Med. Chem.* 1987, **30**, 131-136; (b) B. Saroja and P. C. Srinivasan, *Tetrahedron Lett.* 1984, **25**, 5429-5430; (c) J. H. Markgraf, A. A. Dowst, L. A. Hensley, C. E. Jakobsche, C. J. Kaltner, P. J. Webb and P. W. Zimmerman, *Tetrahedron* 2005, **61**, 9102-9110.

^{1}H NMR and ^{13}C NMR Spectra of Title Compounds

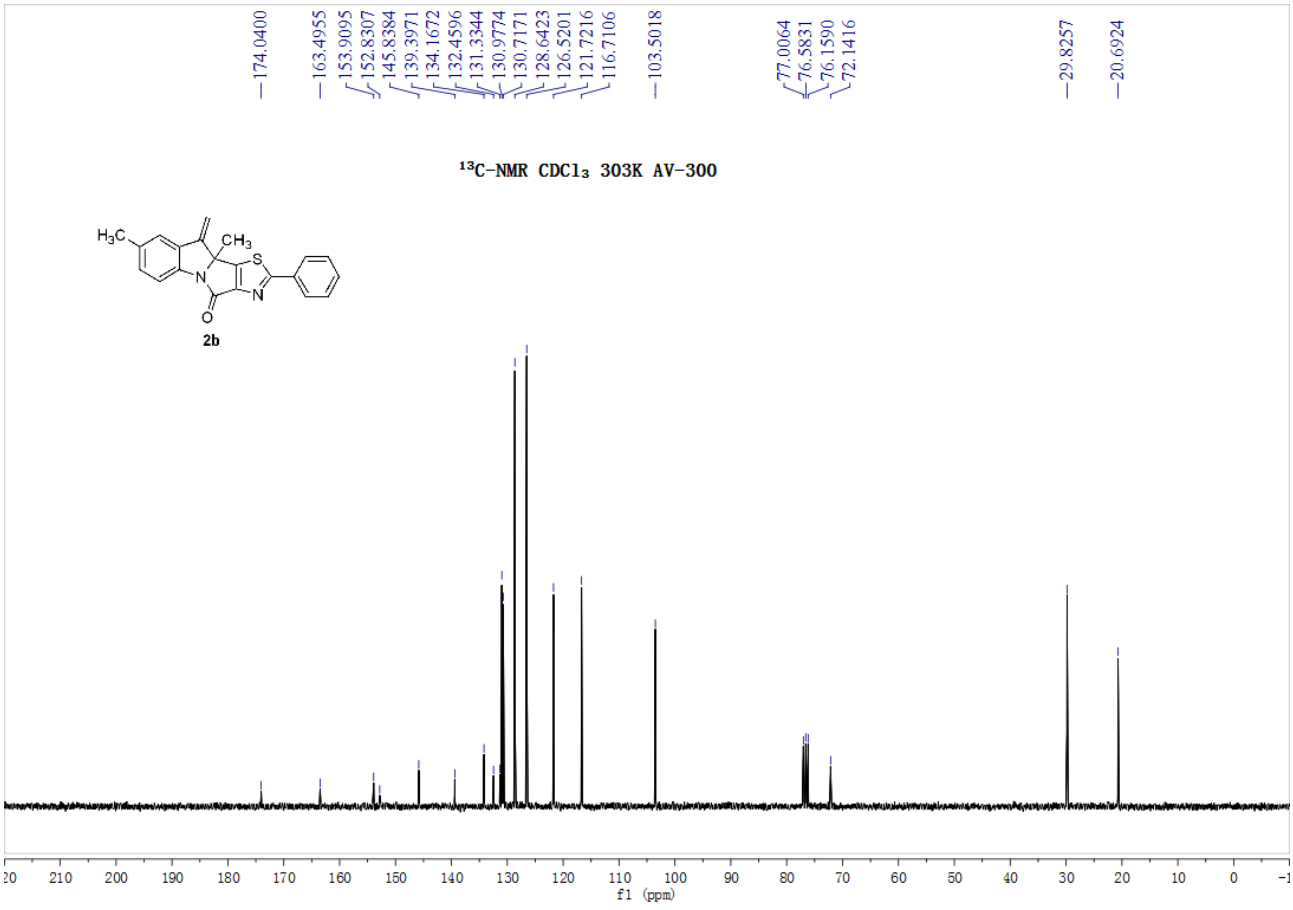






^{1}H-NMR CDCl$_3$ 303K AV-300

2b



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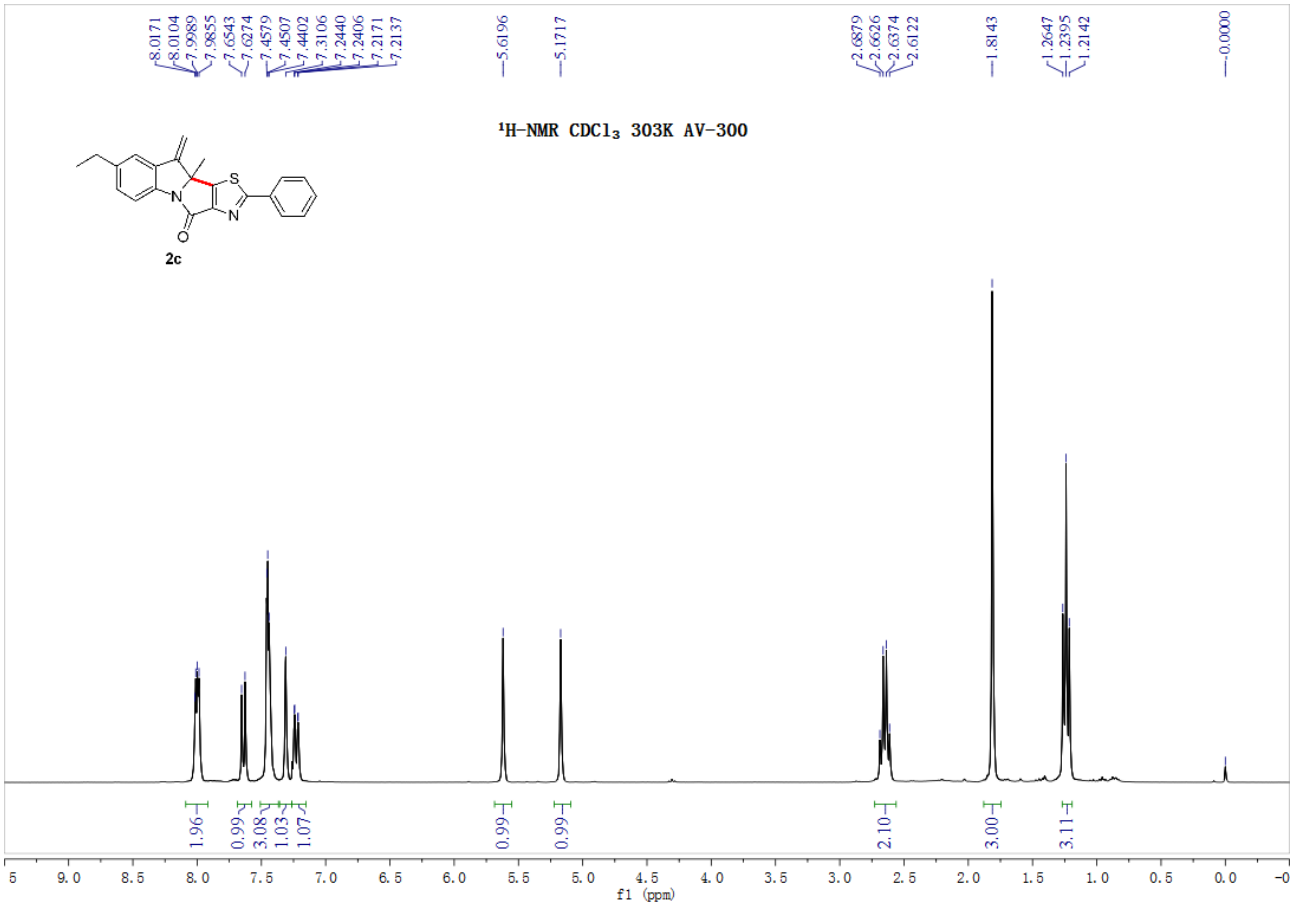
2b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7.2440
7.2406
7.2171
7.2137
5.6196
5.1717
2.6879
2.6626
2.6374
2.6122
1.8143
1.2647
1.2395
1.2142
0.0000
1H-NMR CDCl3 303K AV-300
2c
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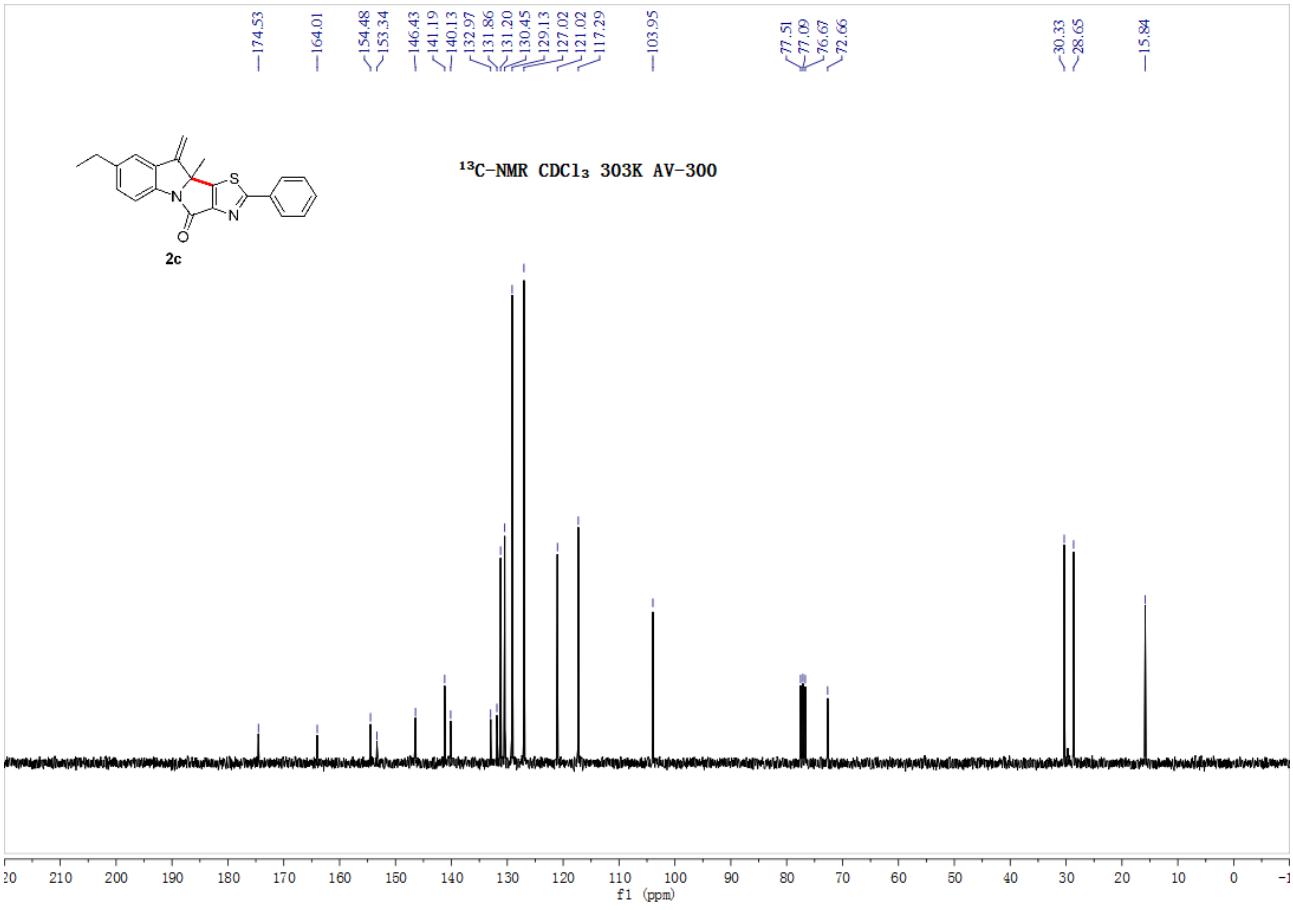
3.08
1.03
1.07
0.99
0.99
2.10
3.00
3.11
f1 (ppm)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127.02
121.02
117.29
103.95
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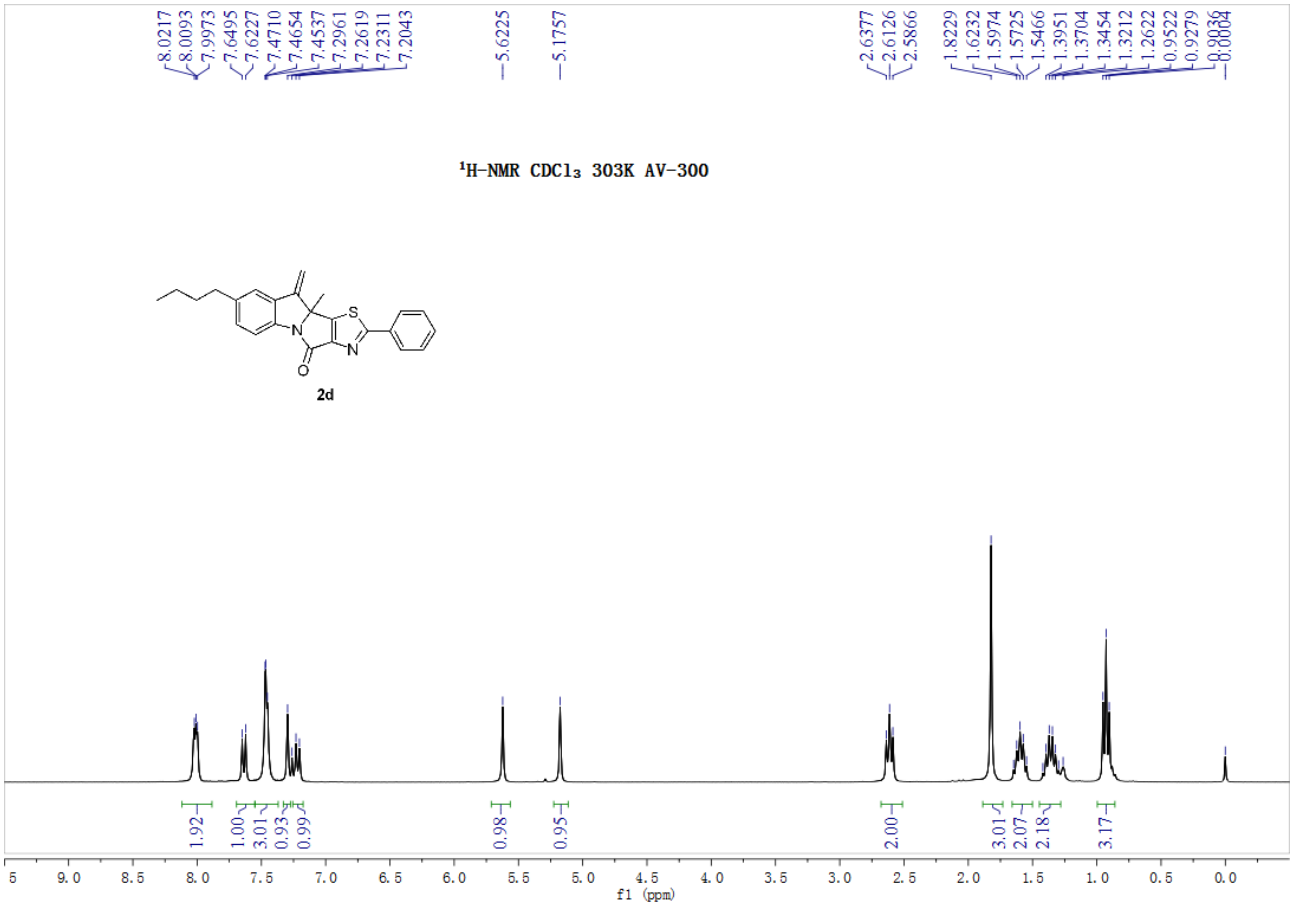
76.67
72.66
30.33
28.65
15.84
13C-NMR CDCl3 303K AV-300
2c
f1 (ppm)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2.6377
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2.5866
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1.5466
1.3951
1.3704
1.3454
1.3212
1.2622
0.9522
0.9279
0.0836
0.0804
1H-NMR CDCl3 303K AV-300
2d
1.92
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0.95
2.00
3.01
2.07
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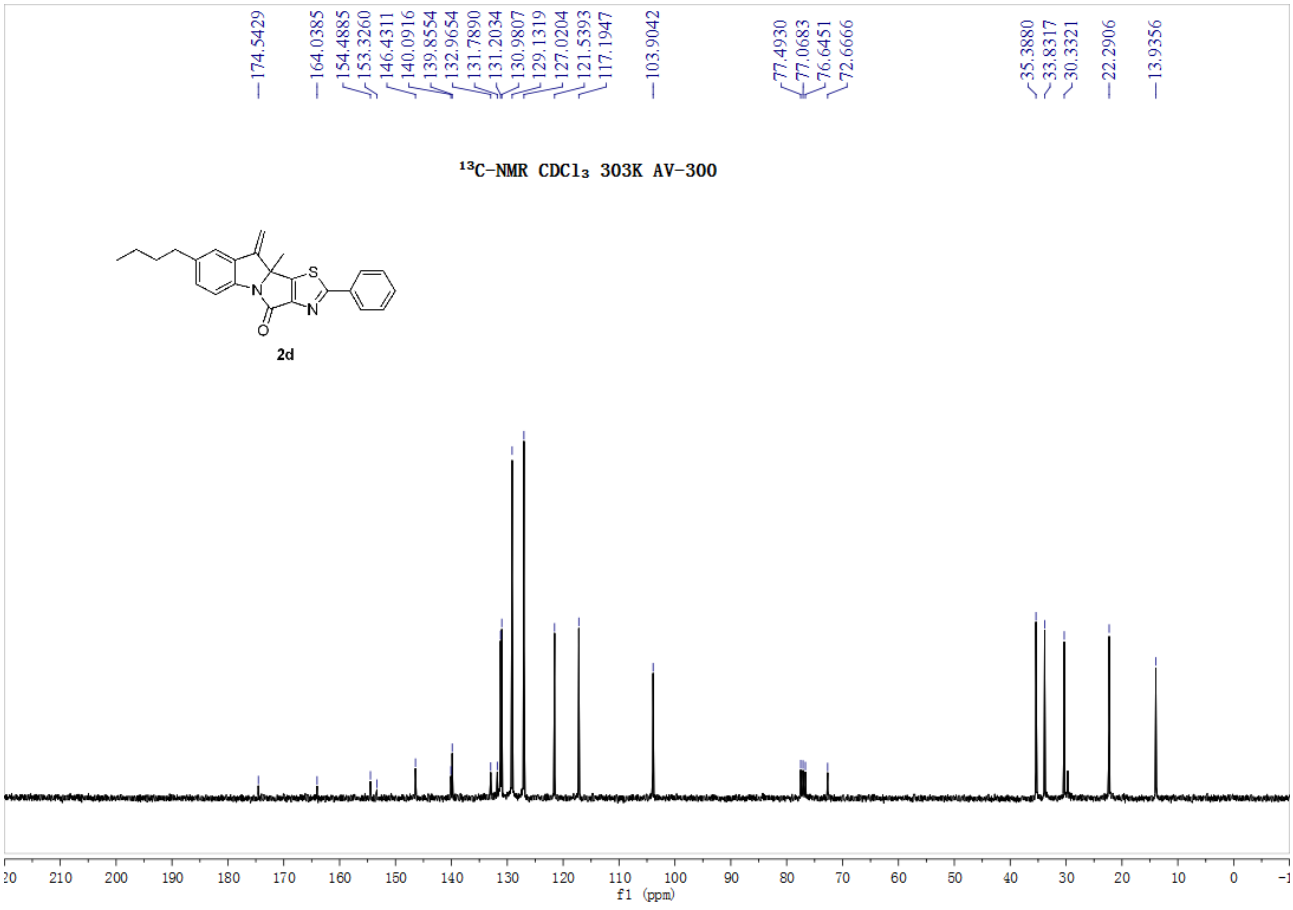
3.17
f1 (ppm)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130.9807
129.1319
127.0204
121.5393
117.1947
103.9042
77.4930
77.0683
76.6451
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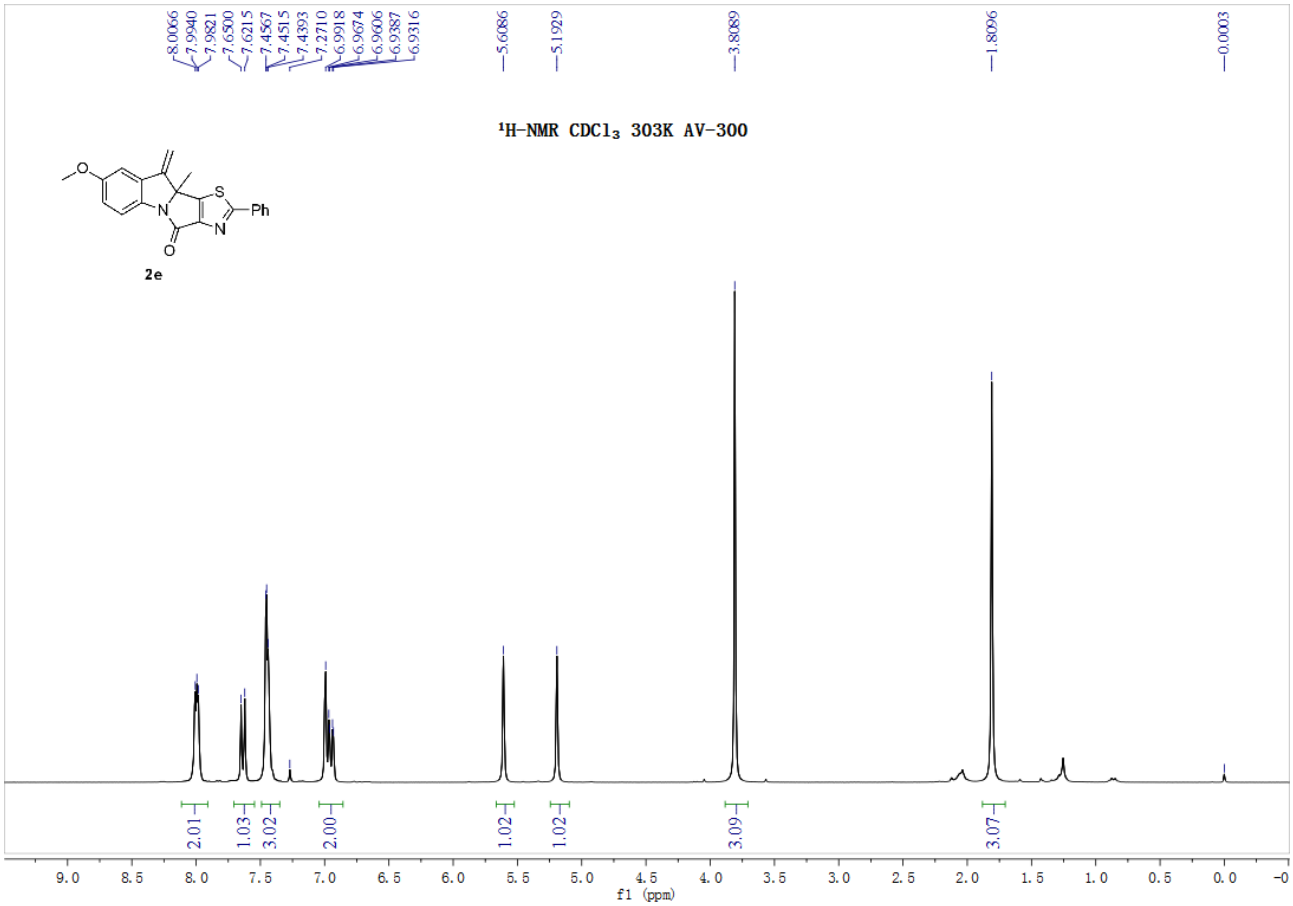
13C-NMR CDCl3 303K AV-300
2d
f1 (ppm)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¹H-NMR CDCl₃ 303K AV-300
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3.02
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1.02
1.02
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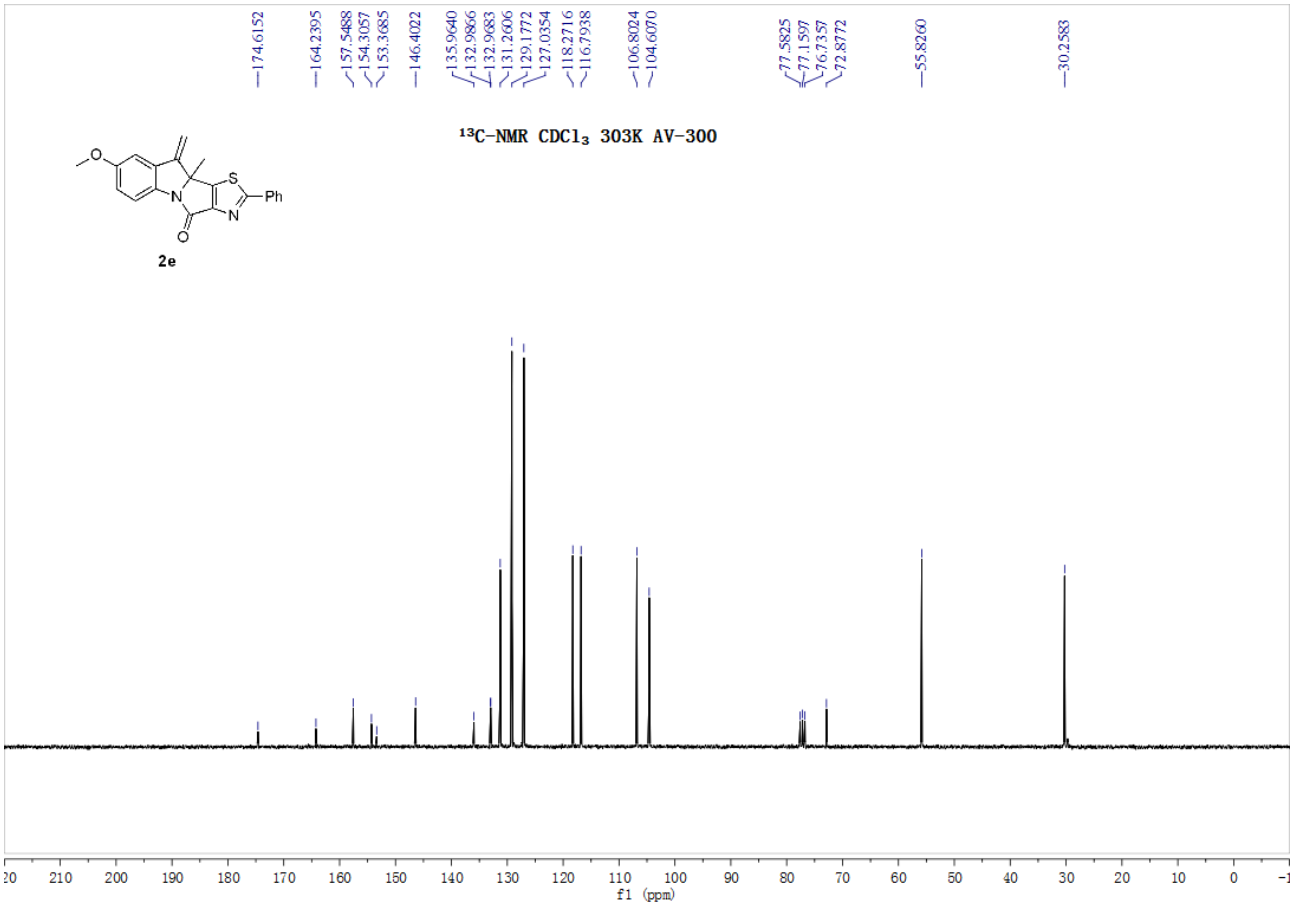
3.07
f1 (ppm)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127.0354
118.2716
116.7938
106.8024
104.6070
77.5825
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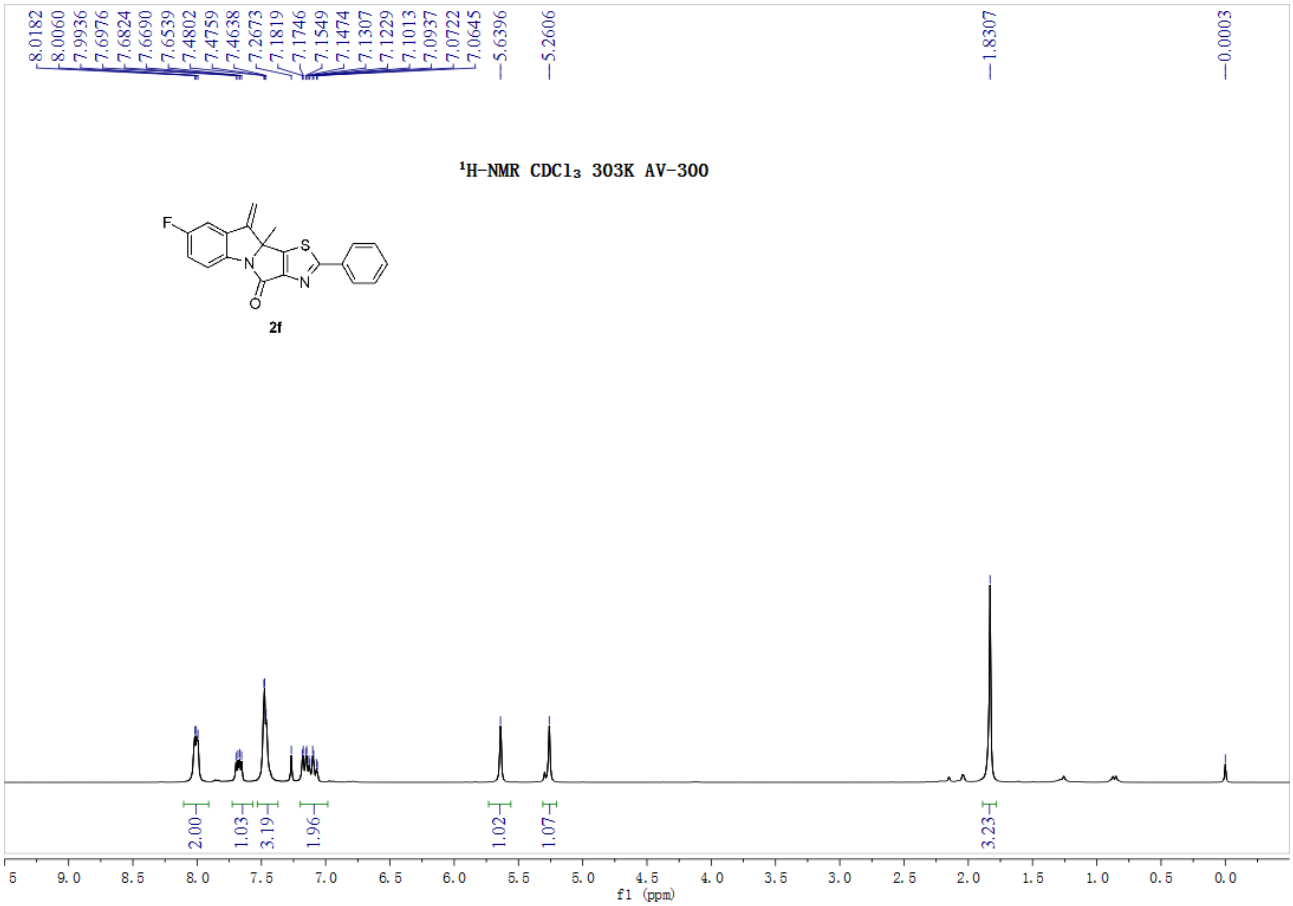
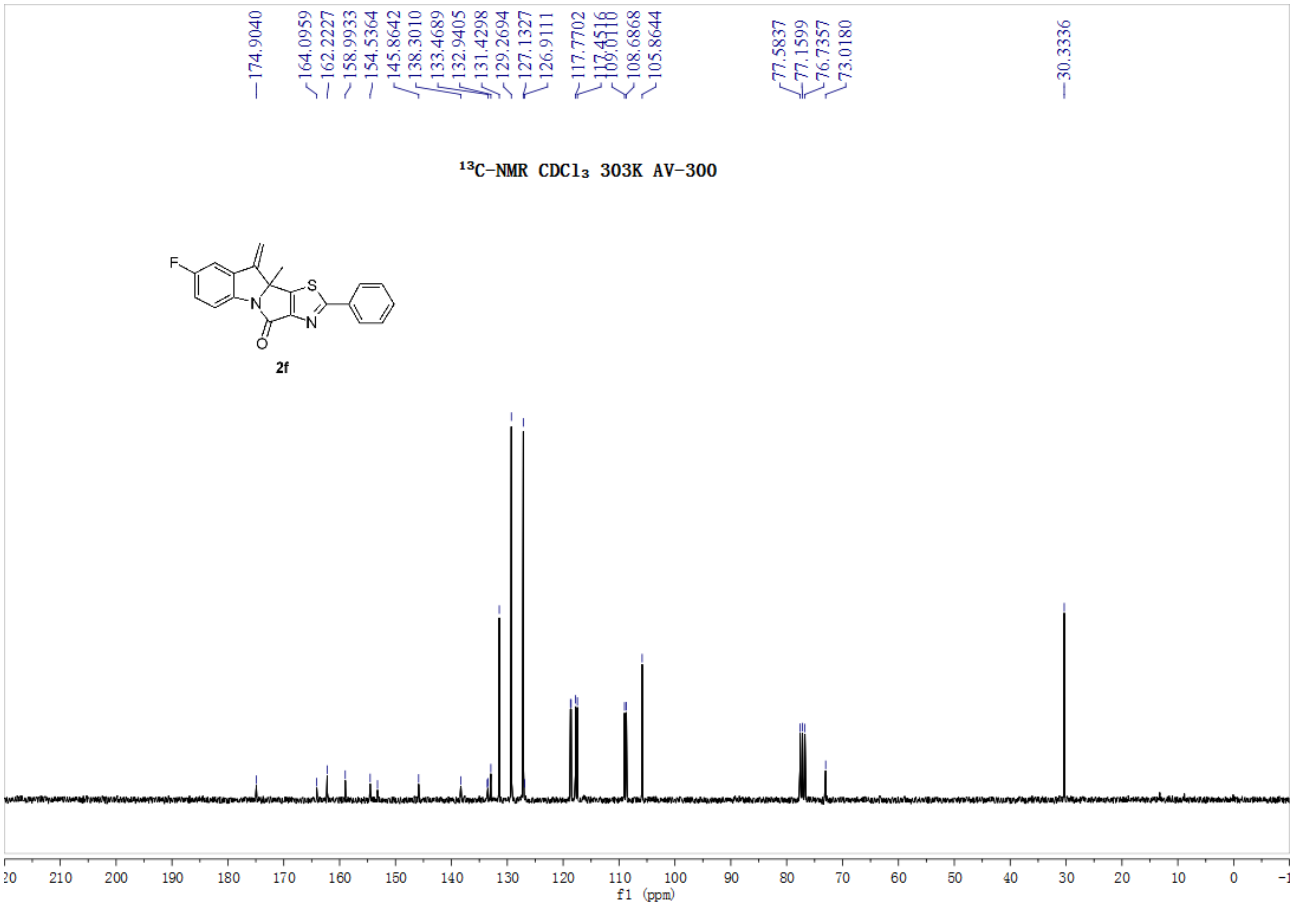
Ph
O
2e
f1 (ppm)



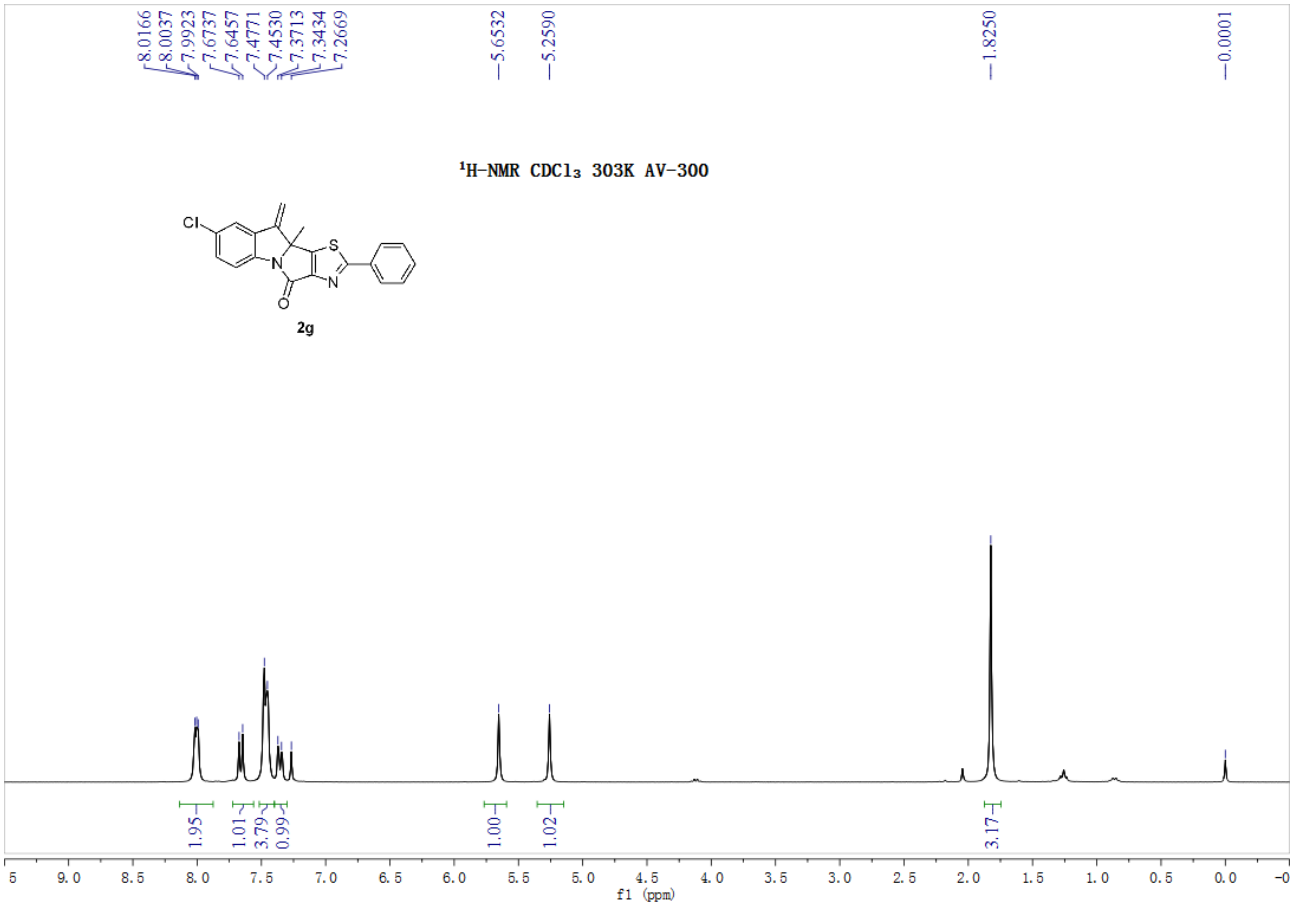
^{1}H-NMR CDCl$_3$ 303K AV-300

2f



^{13}C-NMR CDCl$_3$ 303K AV-300

2f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5.6532
5.2590
1.8250
0.0001
1H-NMR CDCl3 303K AV-300
Cl
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N
O
2g
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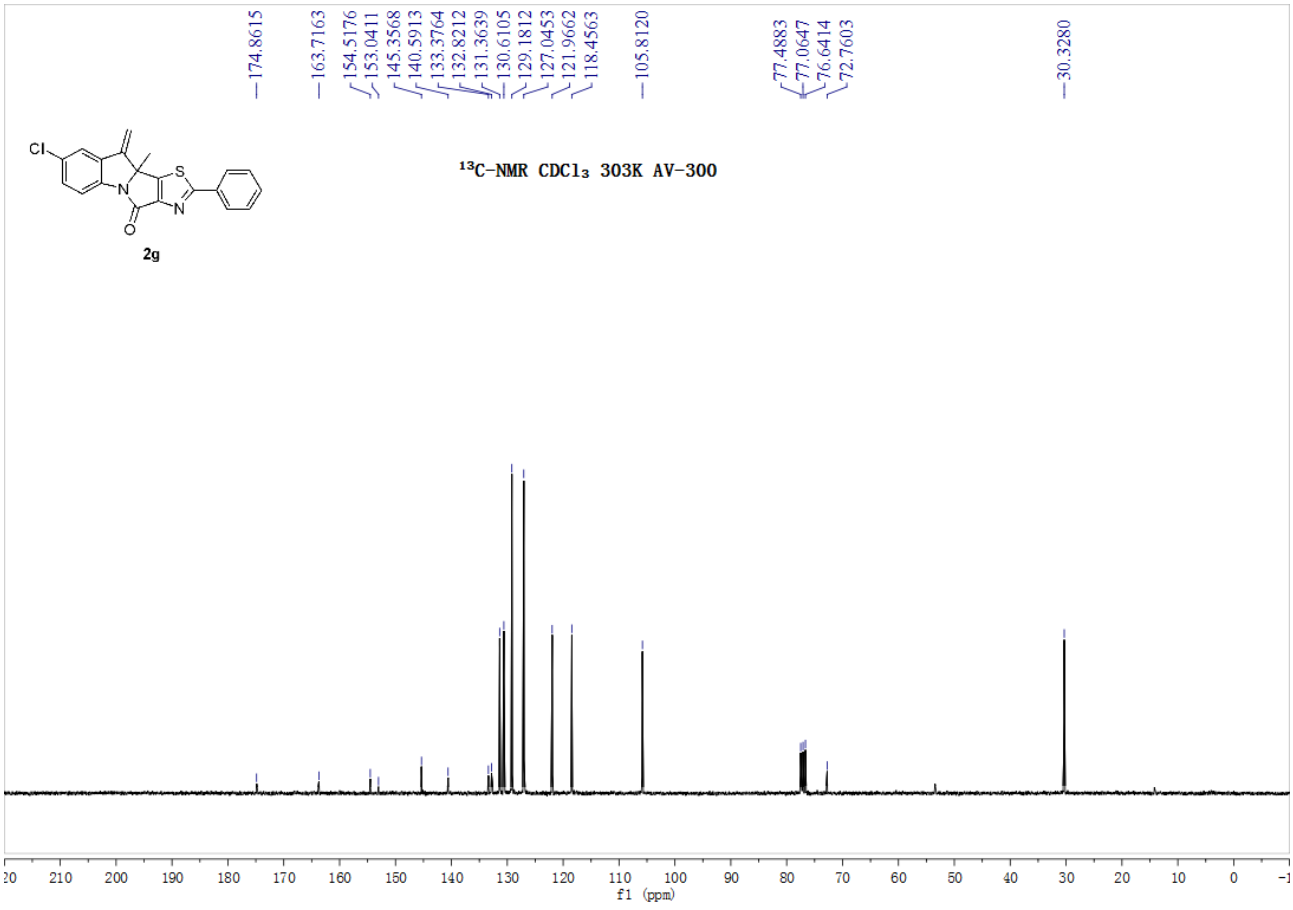
1.01
3.79
0.99
1.00
1.02
3.17
f1 (ppm)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77.0647
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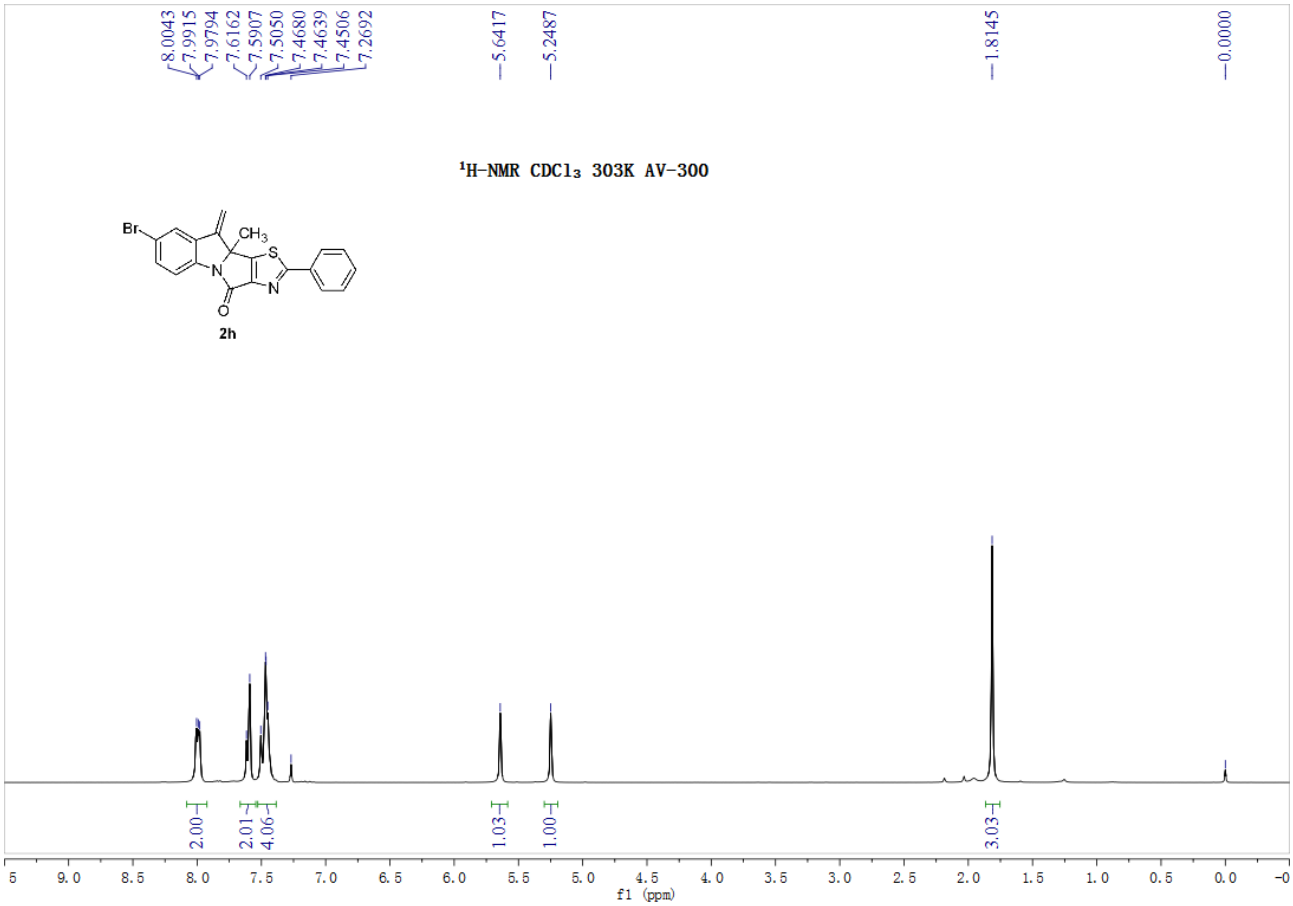
13C-NMR CDCl3 303K AV-300
Cl
S
N
N
O
2g
f1 (ppm)



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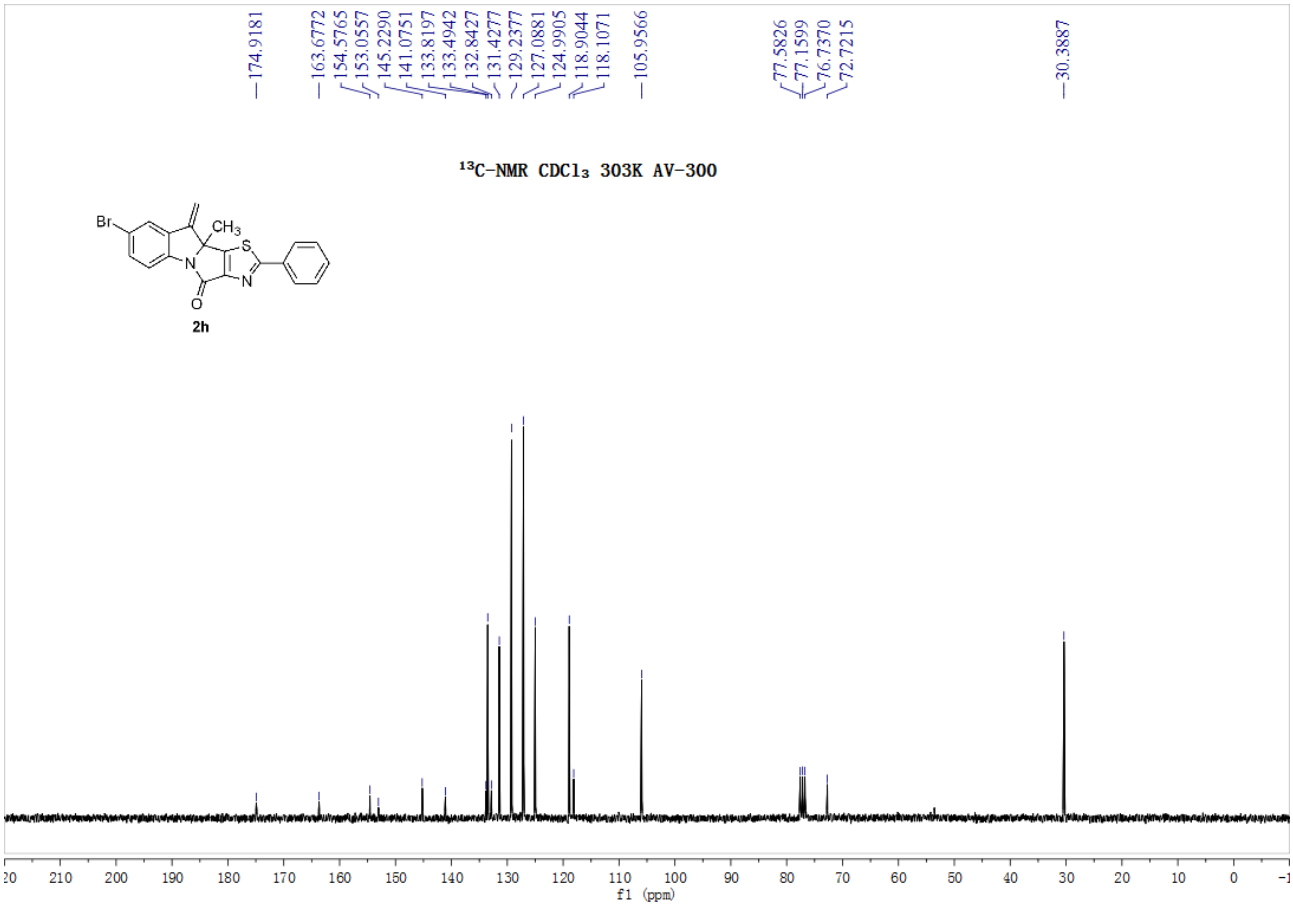

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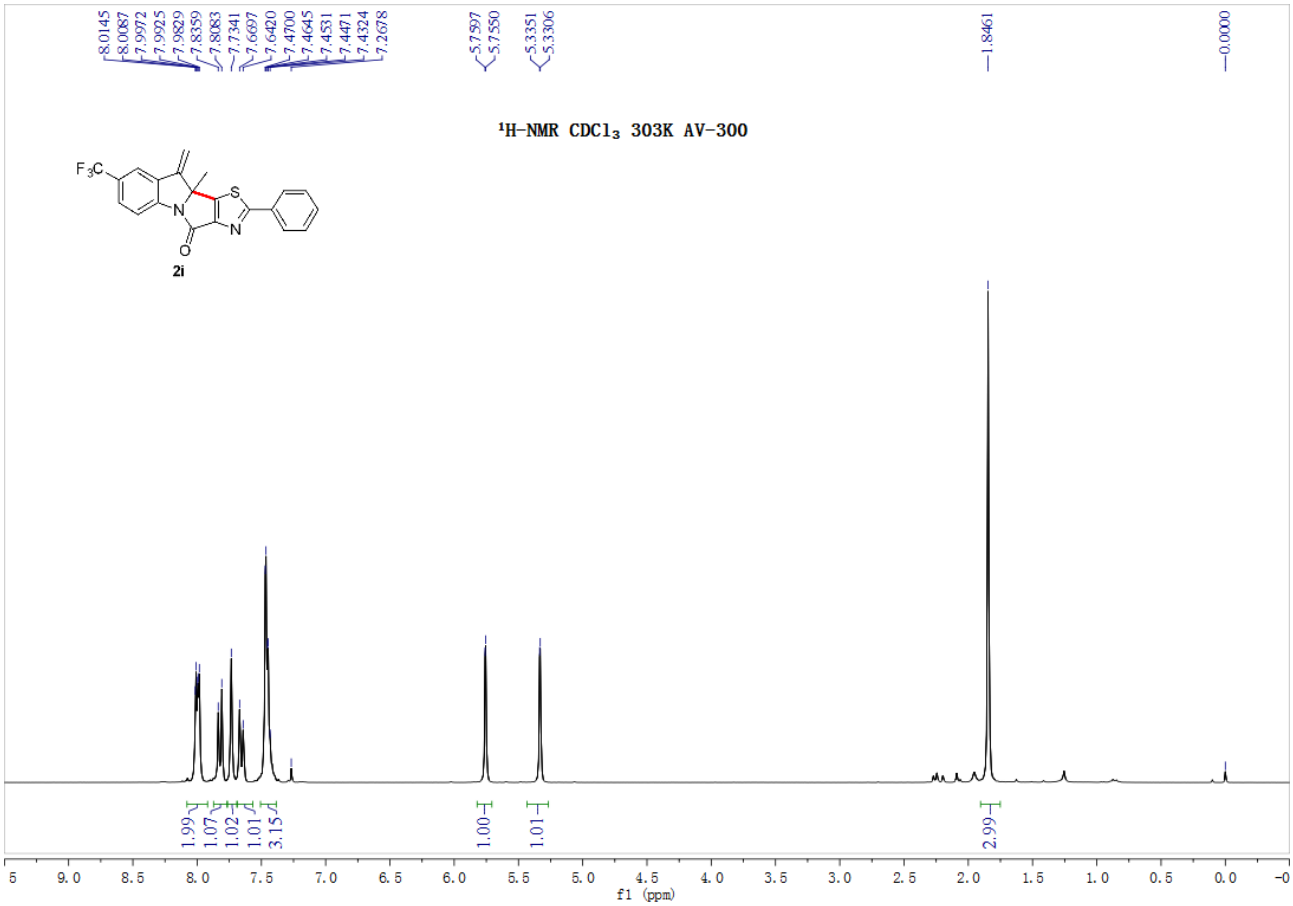
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7.4324
7.2678
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5.7550
5.3351
5.3306
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0.0000
1H-NMR CDCl3 303K AV-300
F3C
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N
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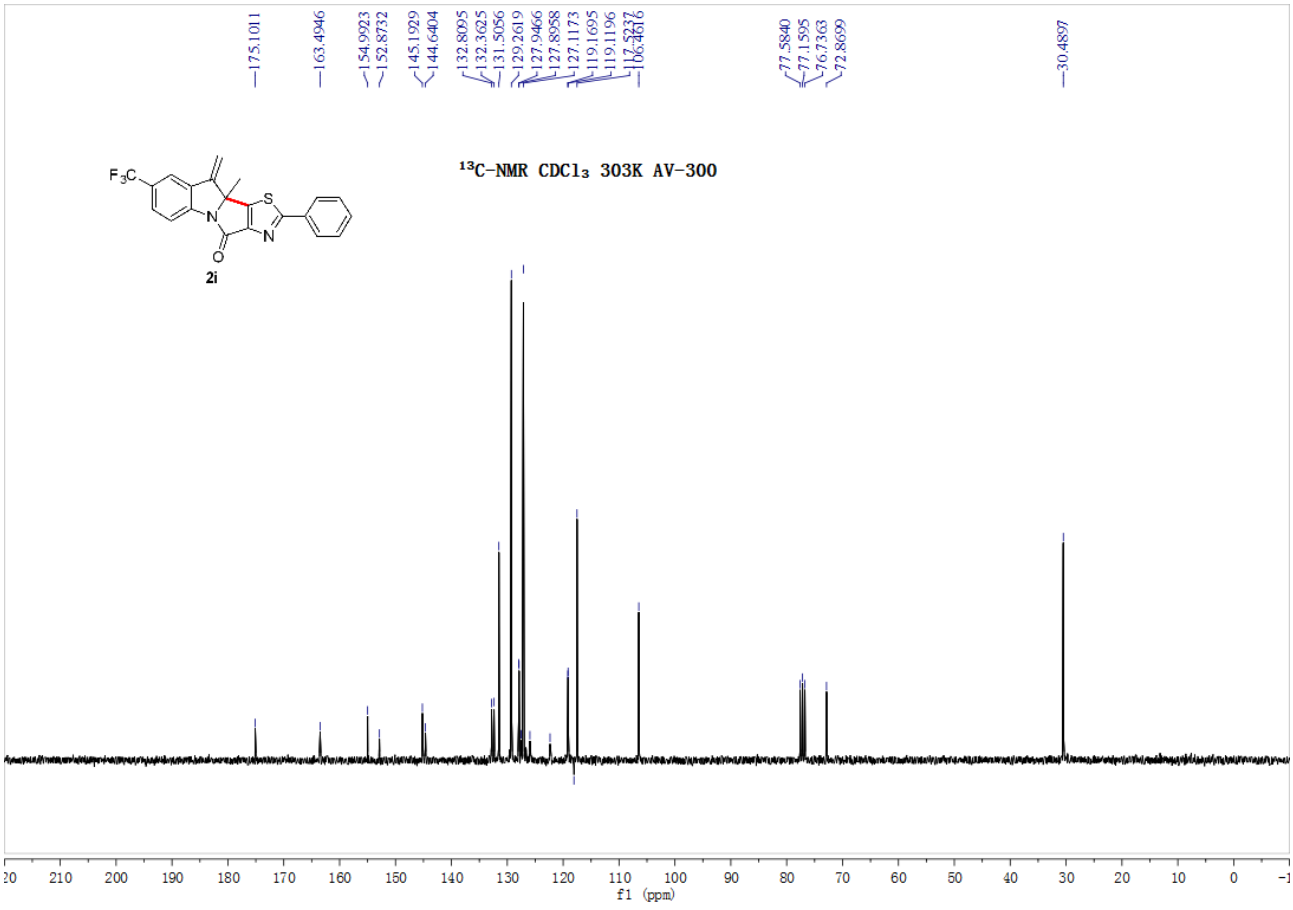
2.99
f1 (ppm)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106.4616
77.5840
77.1595
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13C-NMR CDCl3 303K AV-300
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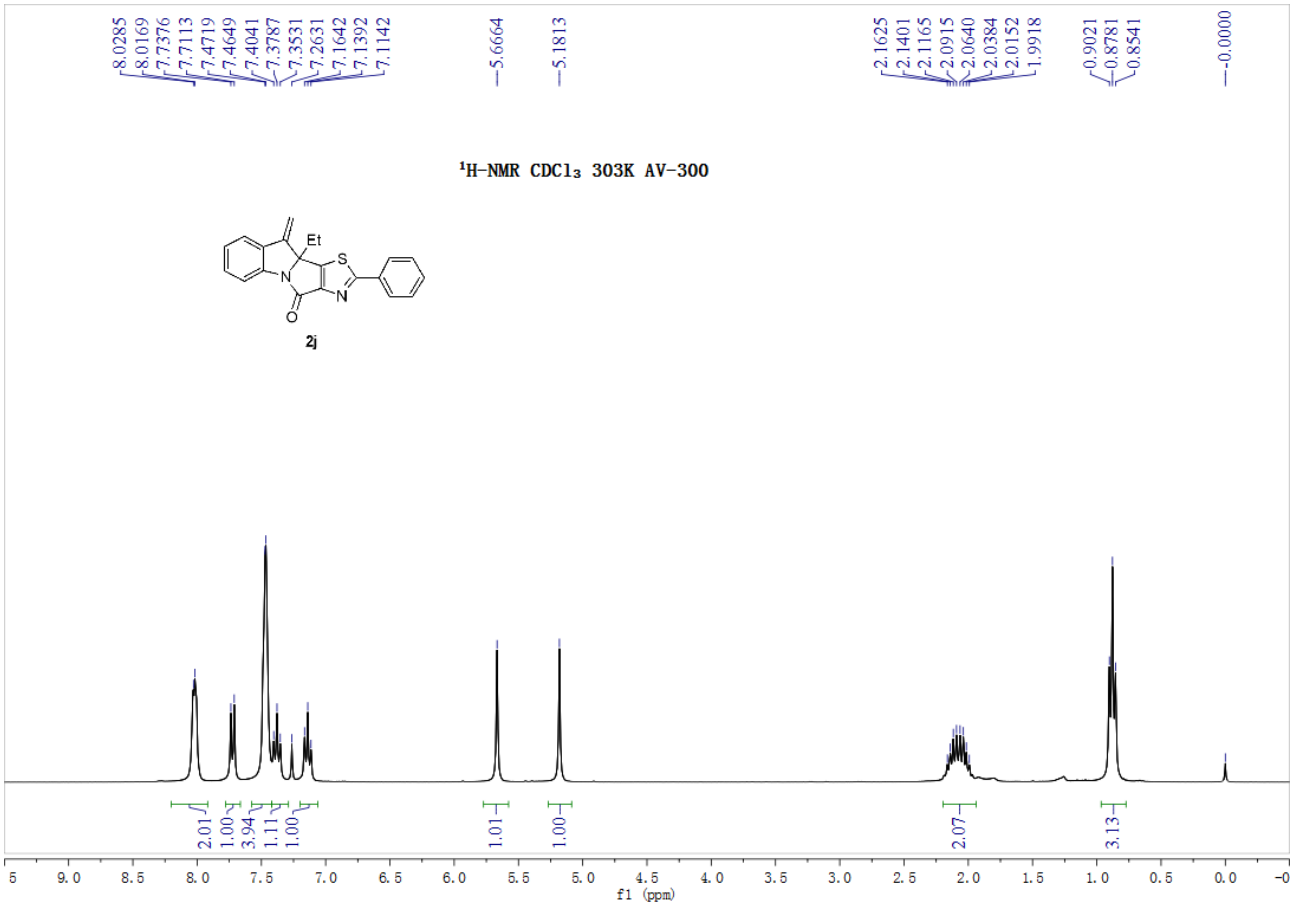
S
N
N
O
2i
f1 (ppm)



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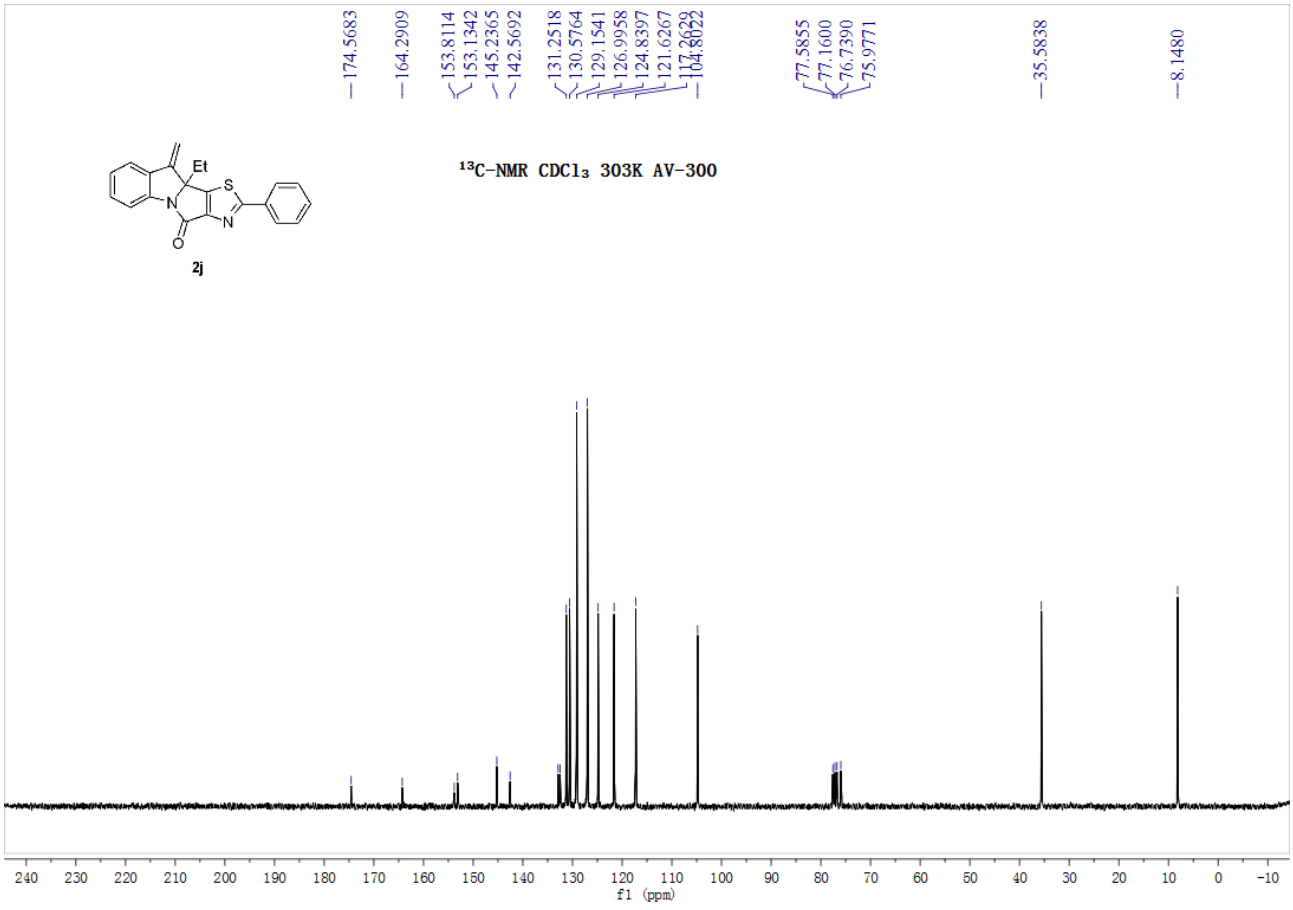

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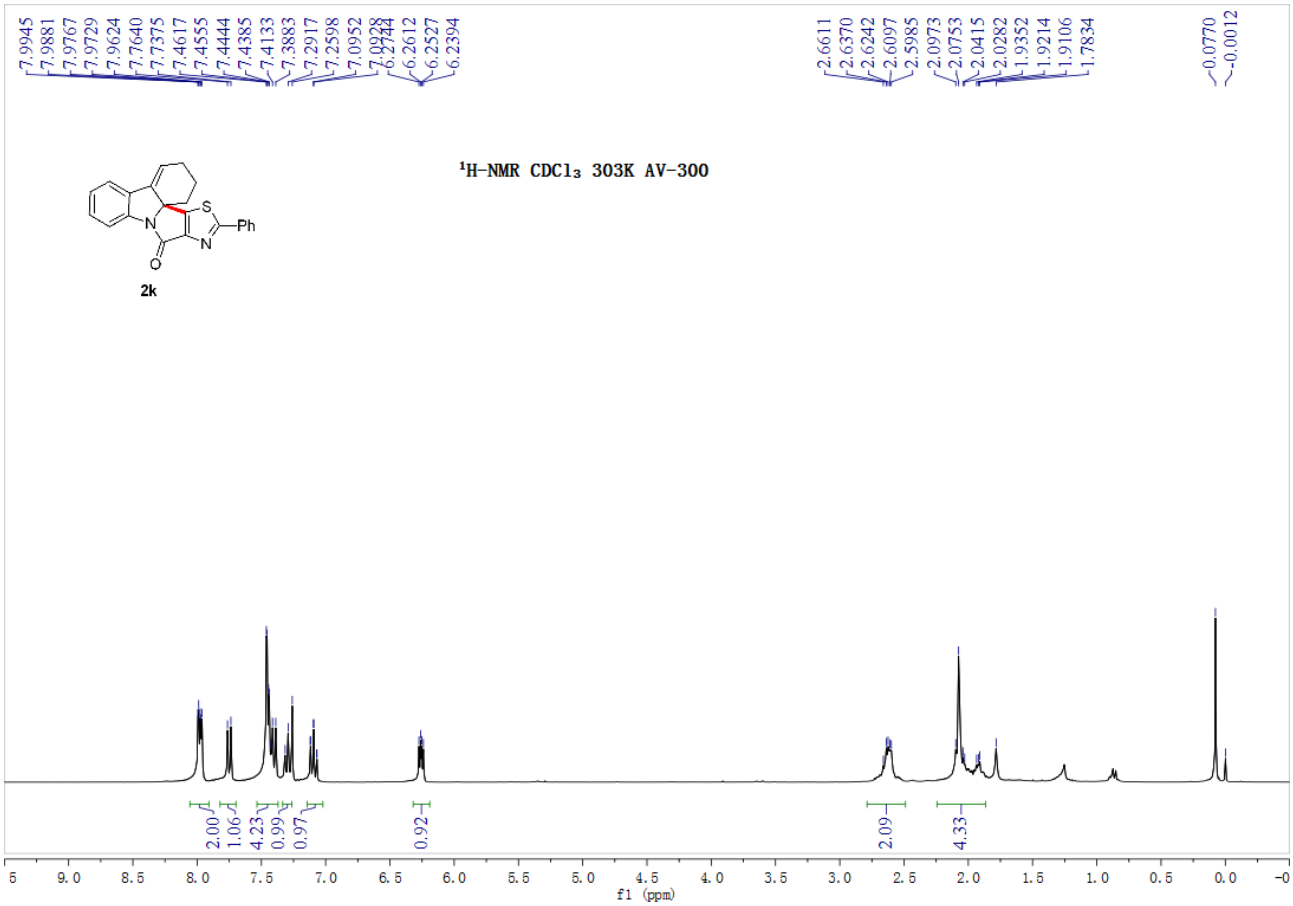
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2.5985
2.0973
2.0753
2.0415
2.0282
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1.9214
1.9106
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1H-NMR CDCl3 303K AV-300
S
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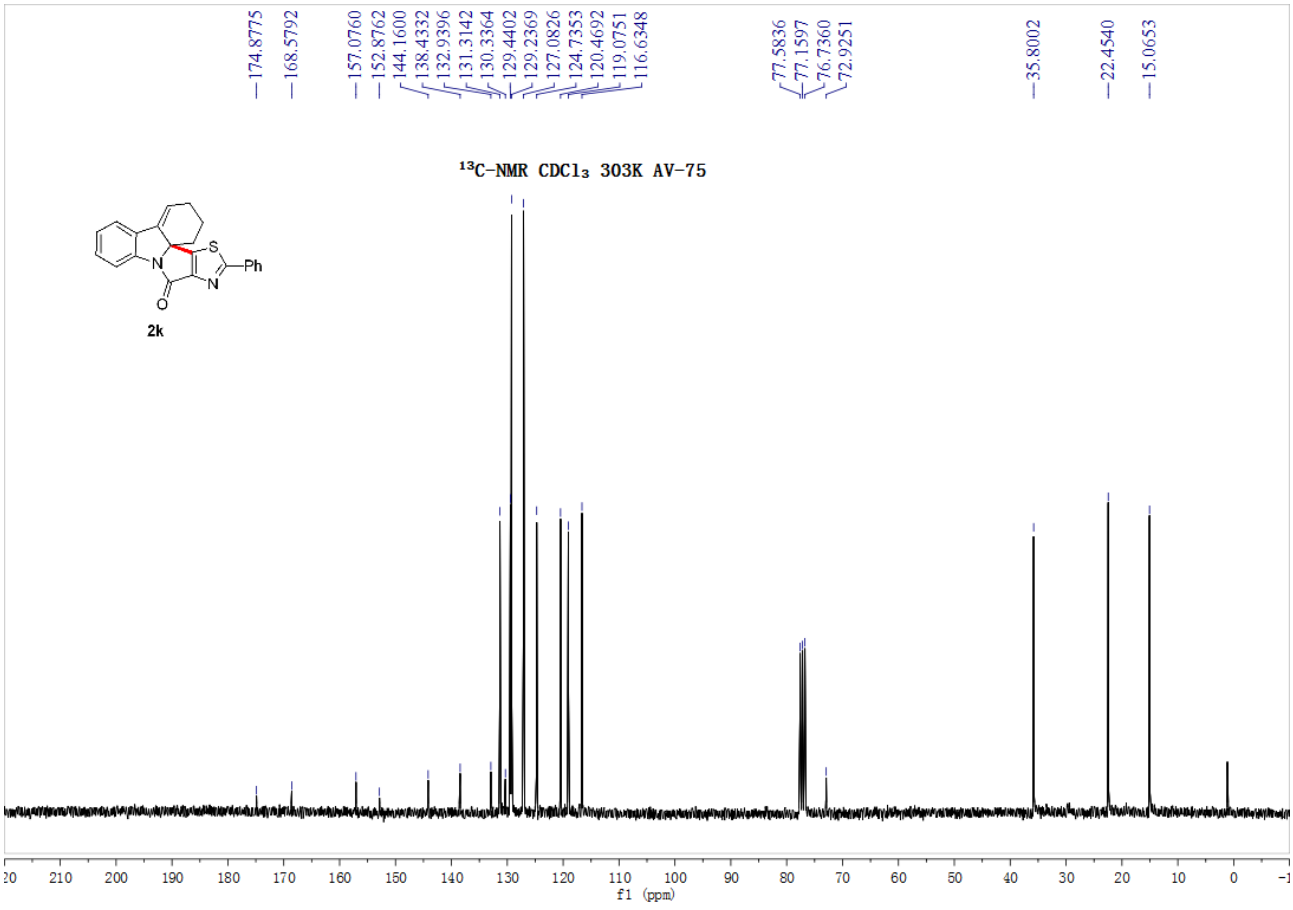
f1 (ppm)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Ph
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O
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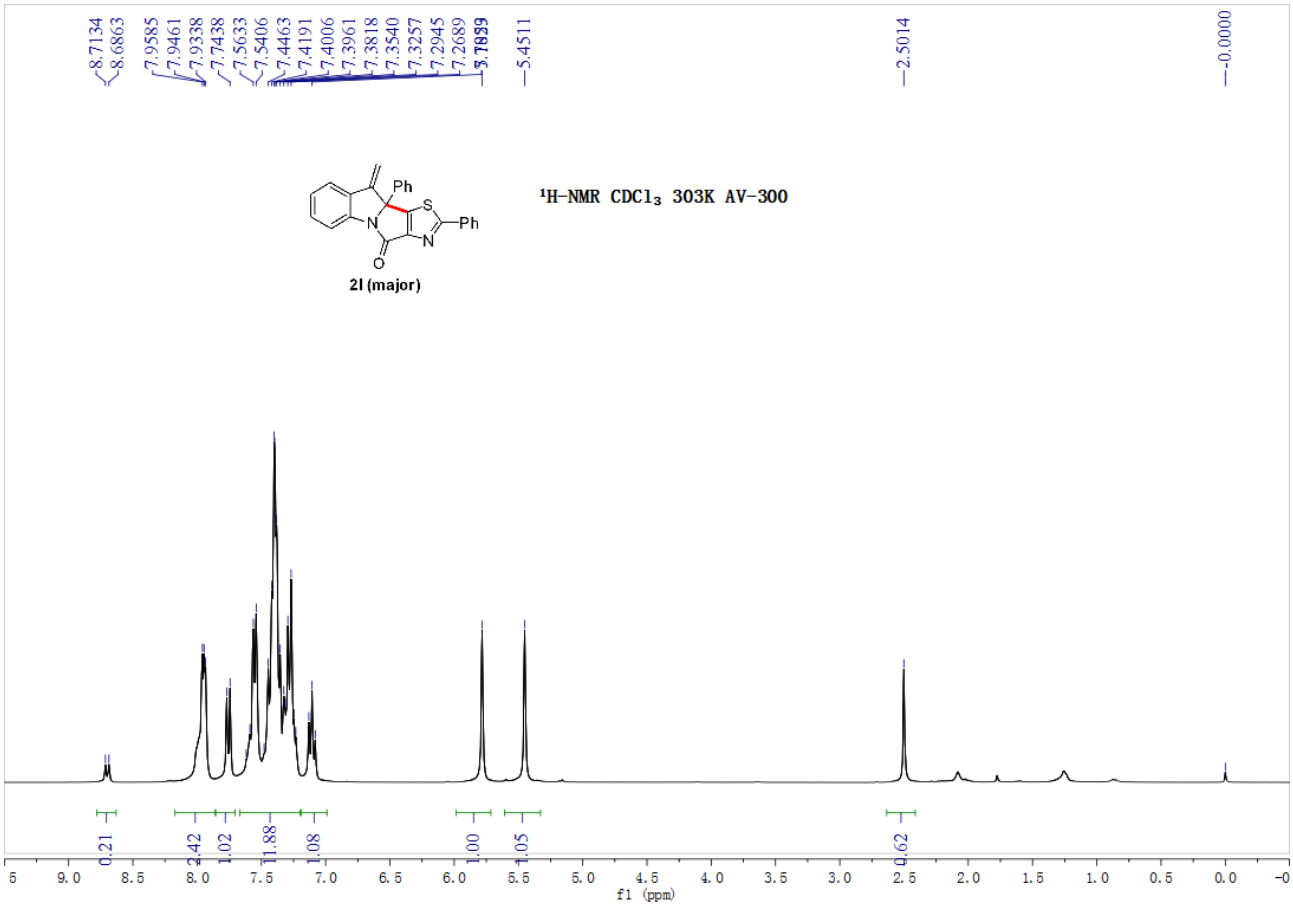
f1 (ppm)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S
N
Ph
N
O
2l (major)
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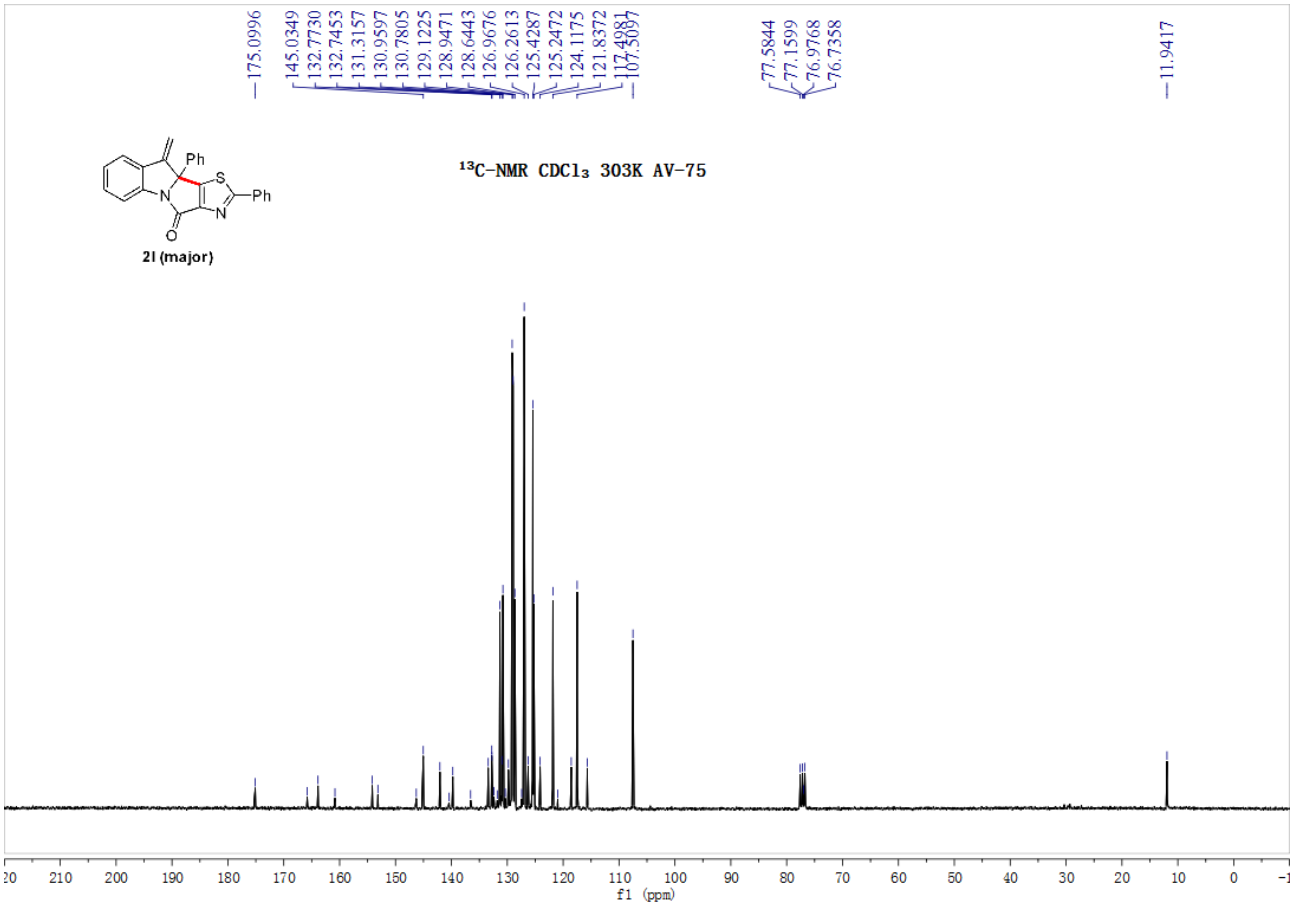
f1 (ppm)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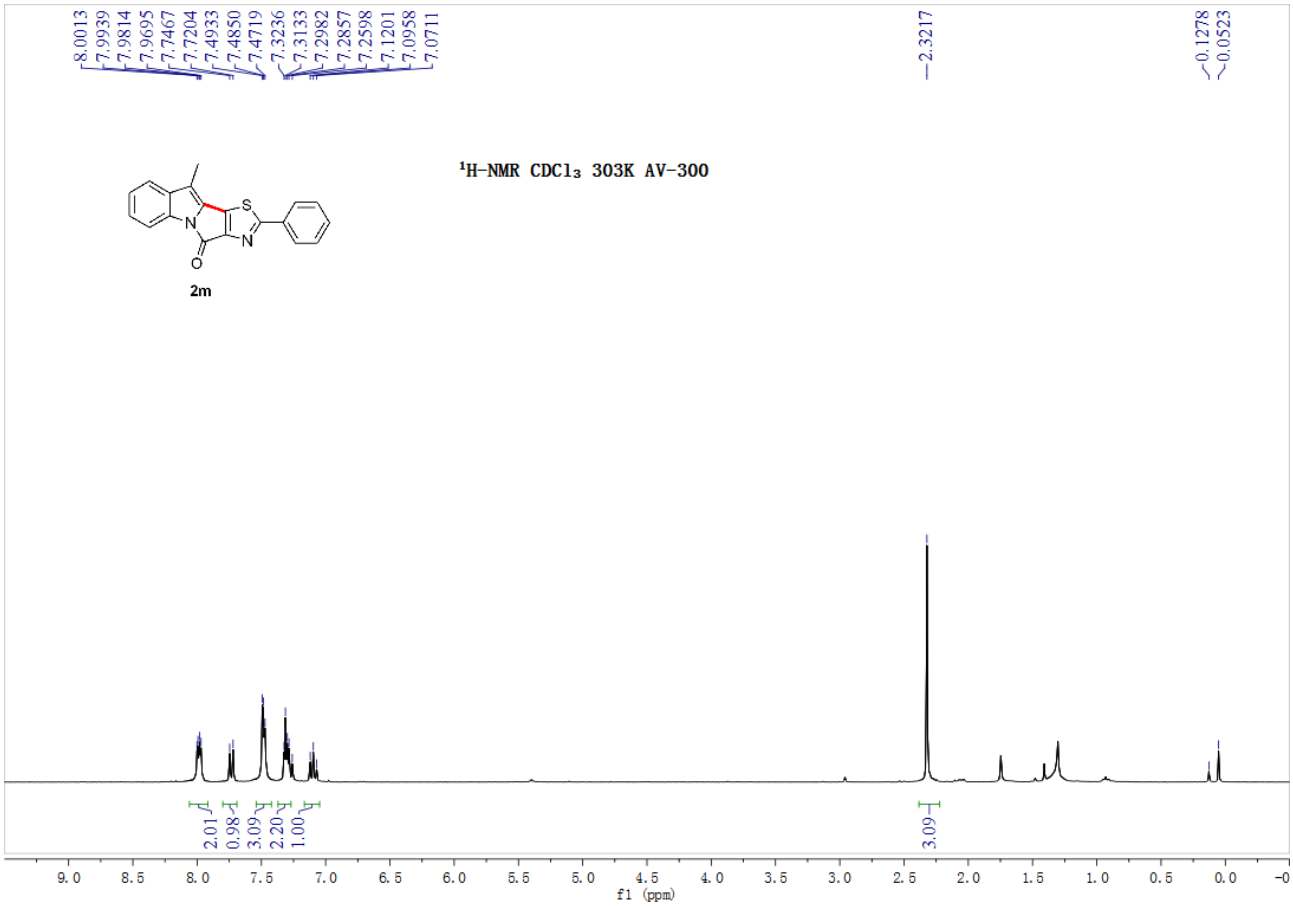
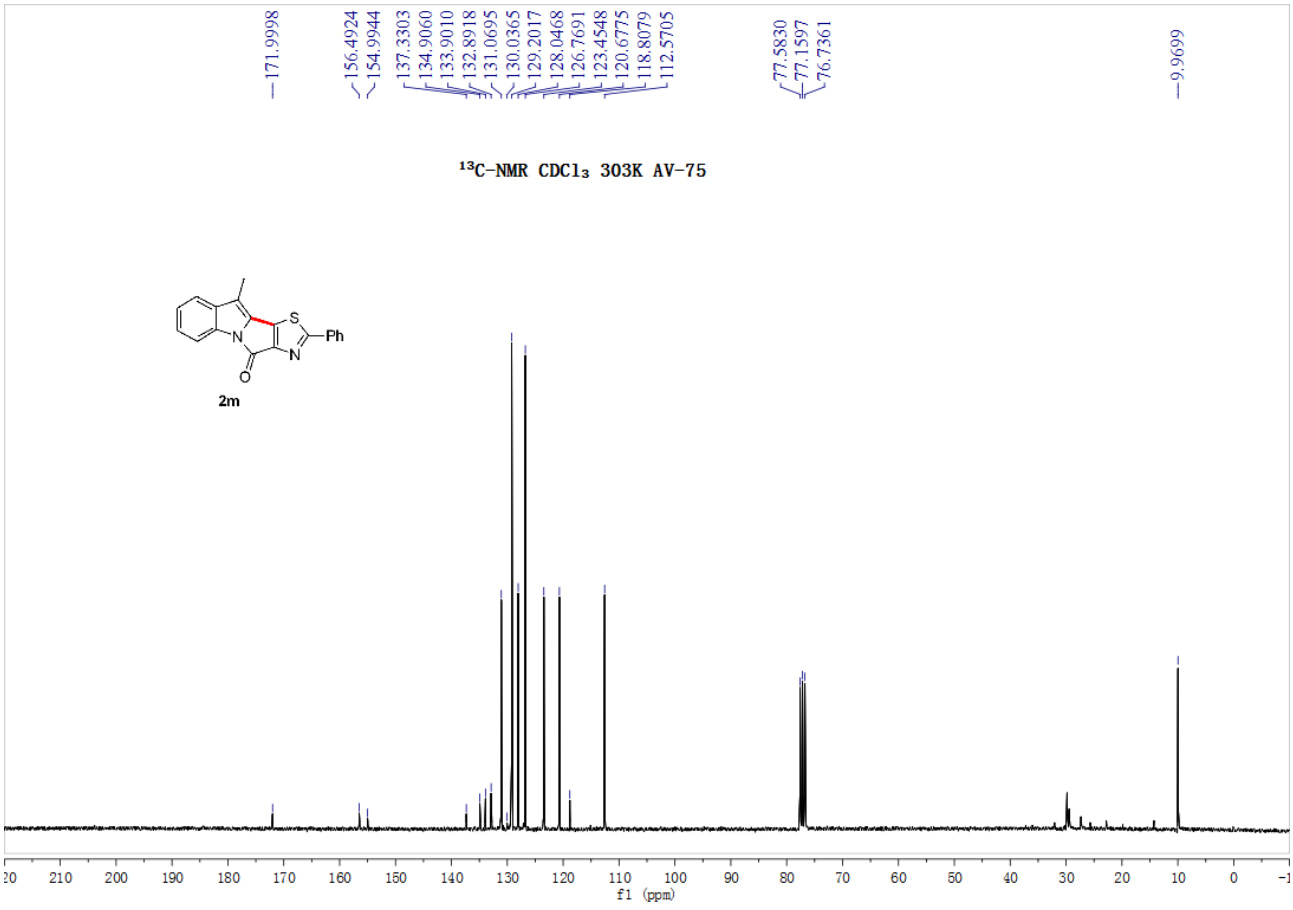
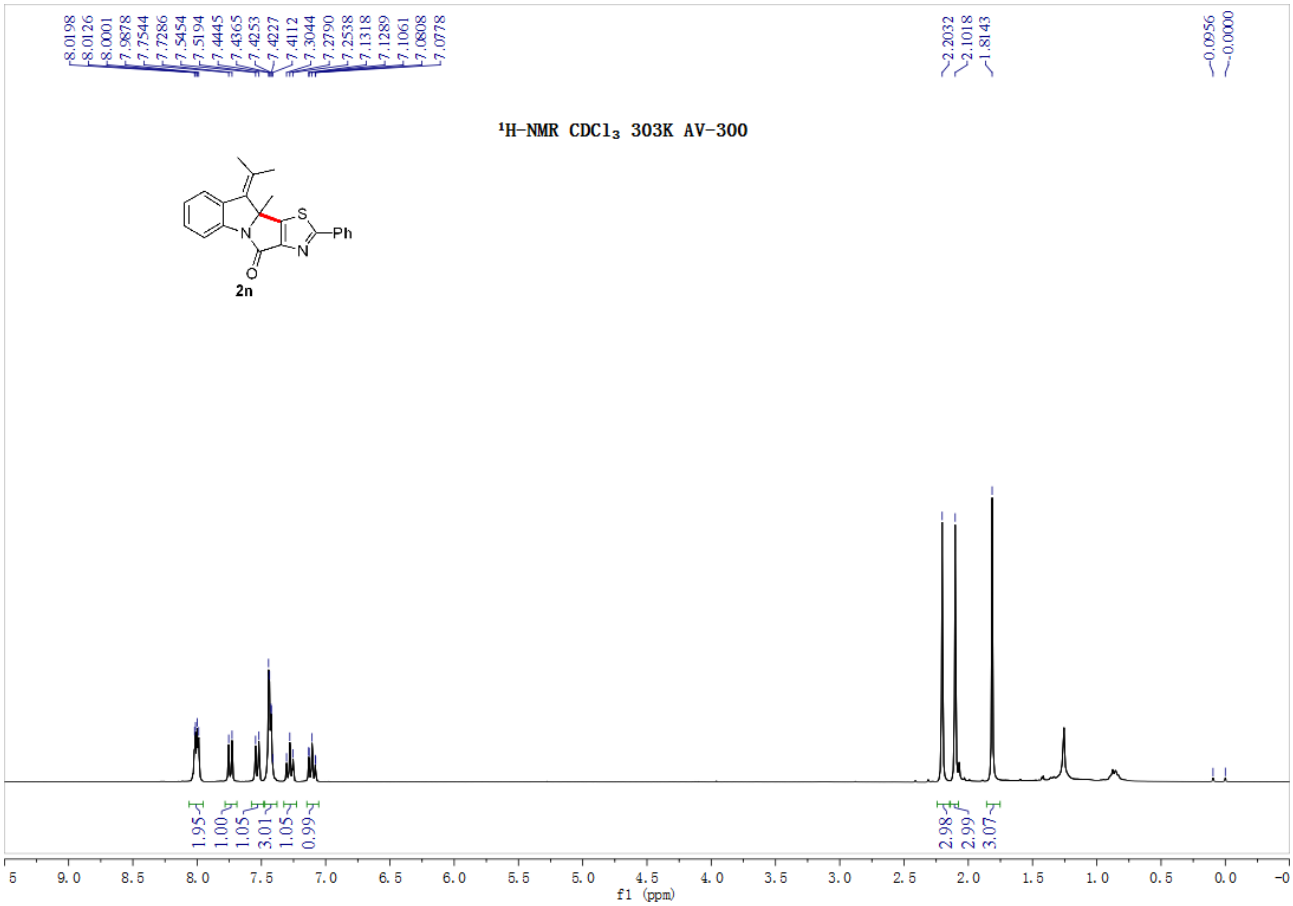
¹³C-NMR CDCl₃ 303K AV-75
f1 (ppm)



^{1}H-NMR CDCl$_3$ 303K AV-300



^{13}C-NMR CDCl$_3$ 303K AV-75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7.3044
7.2790
7.2538
7.1318
7.1289
7.1061
7.0808
7.0778
2.2032
2.1018
1.8143
-0.0956
-0.0000
1H-NMR CDCl3 303K AV-300
S
N
Ph
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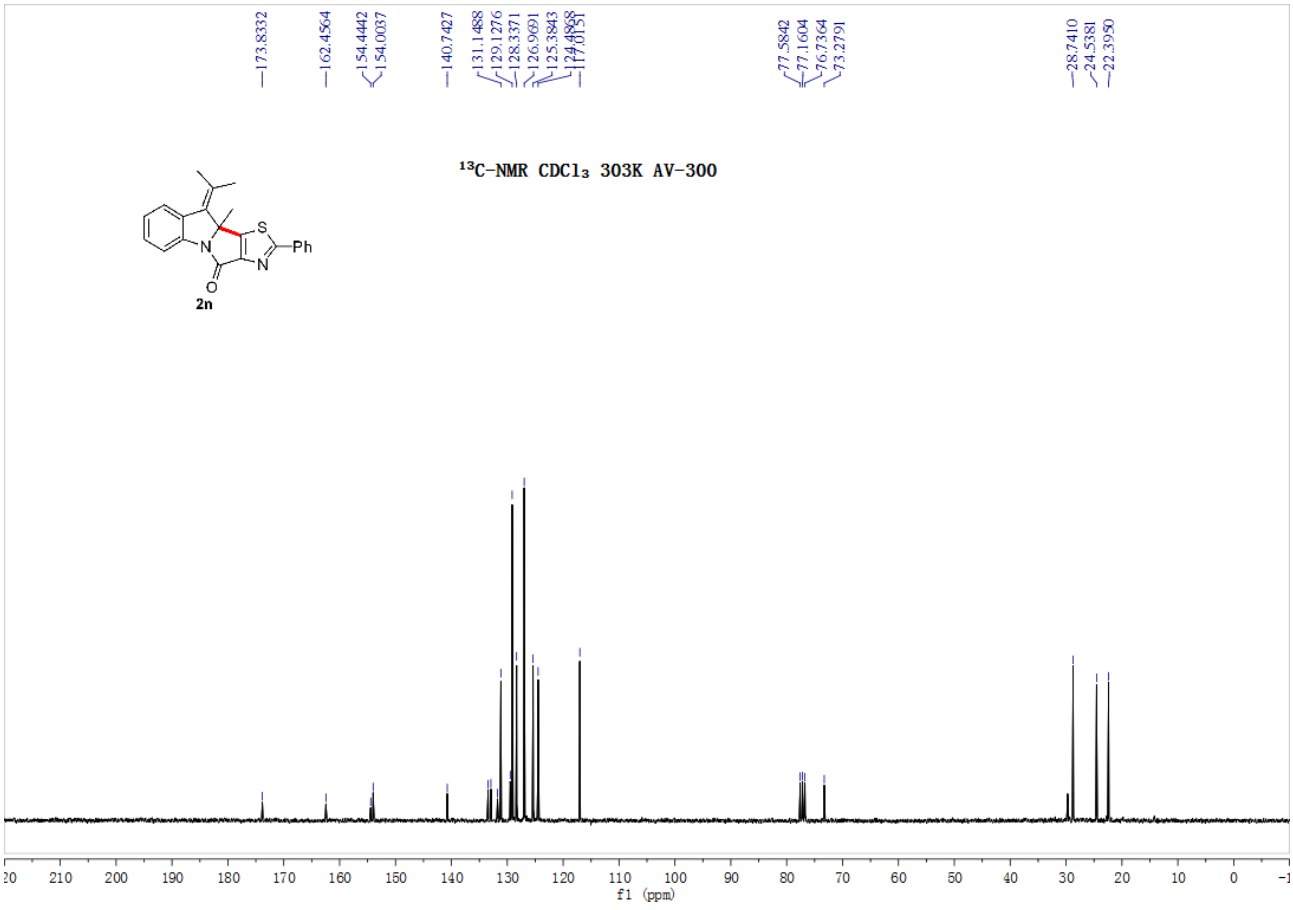
f1 (ppm)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77.1604
76.7364
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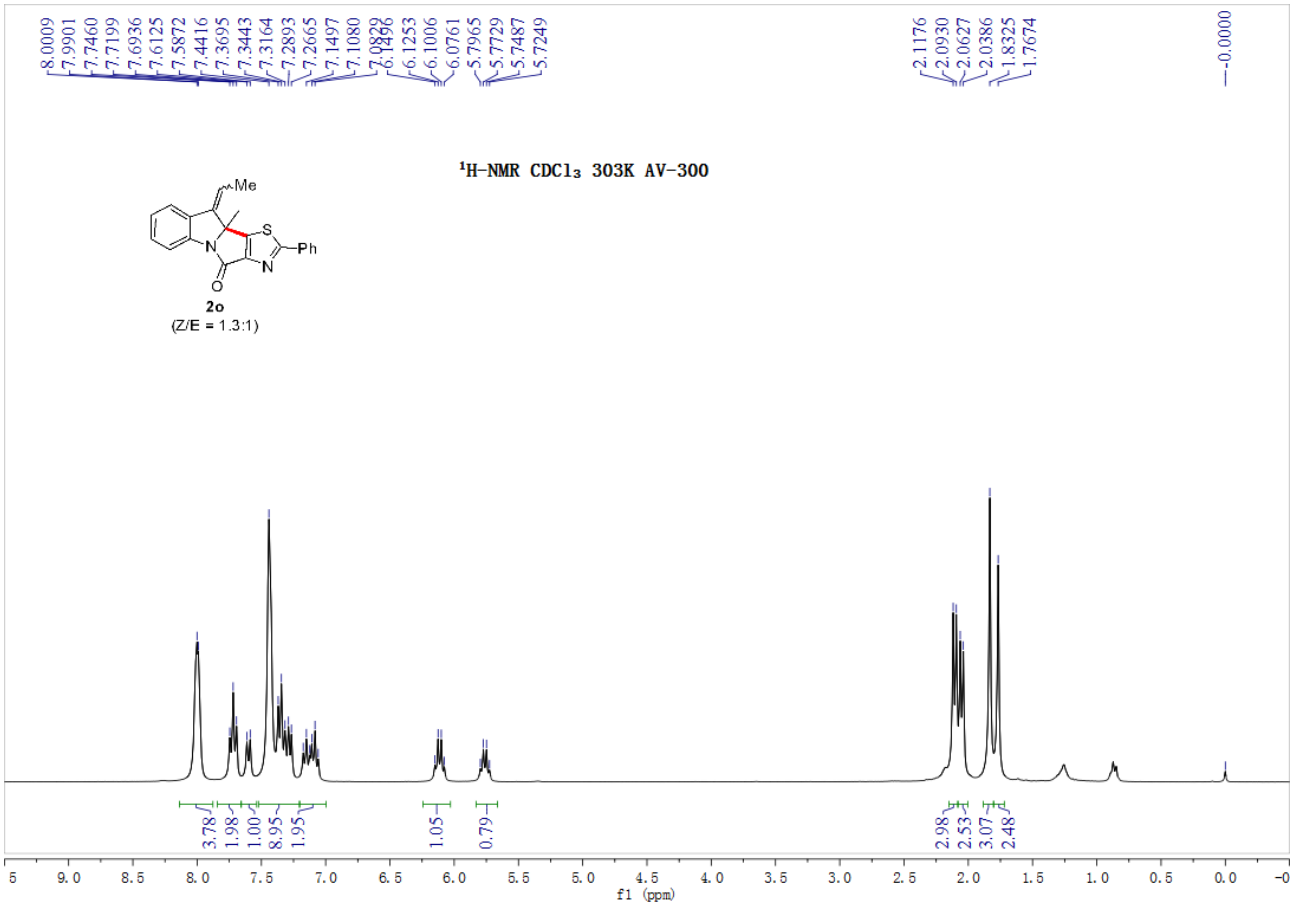
13C-NMR CDCl3 303K AV-300
S
N
Ph
O
2n
f1 (ppm)



^{1}H-NMR CDCl$_3$ 303K AV-300

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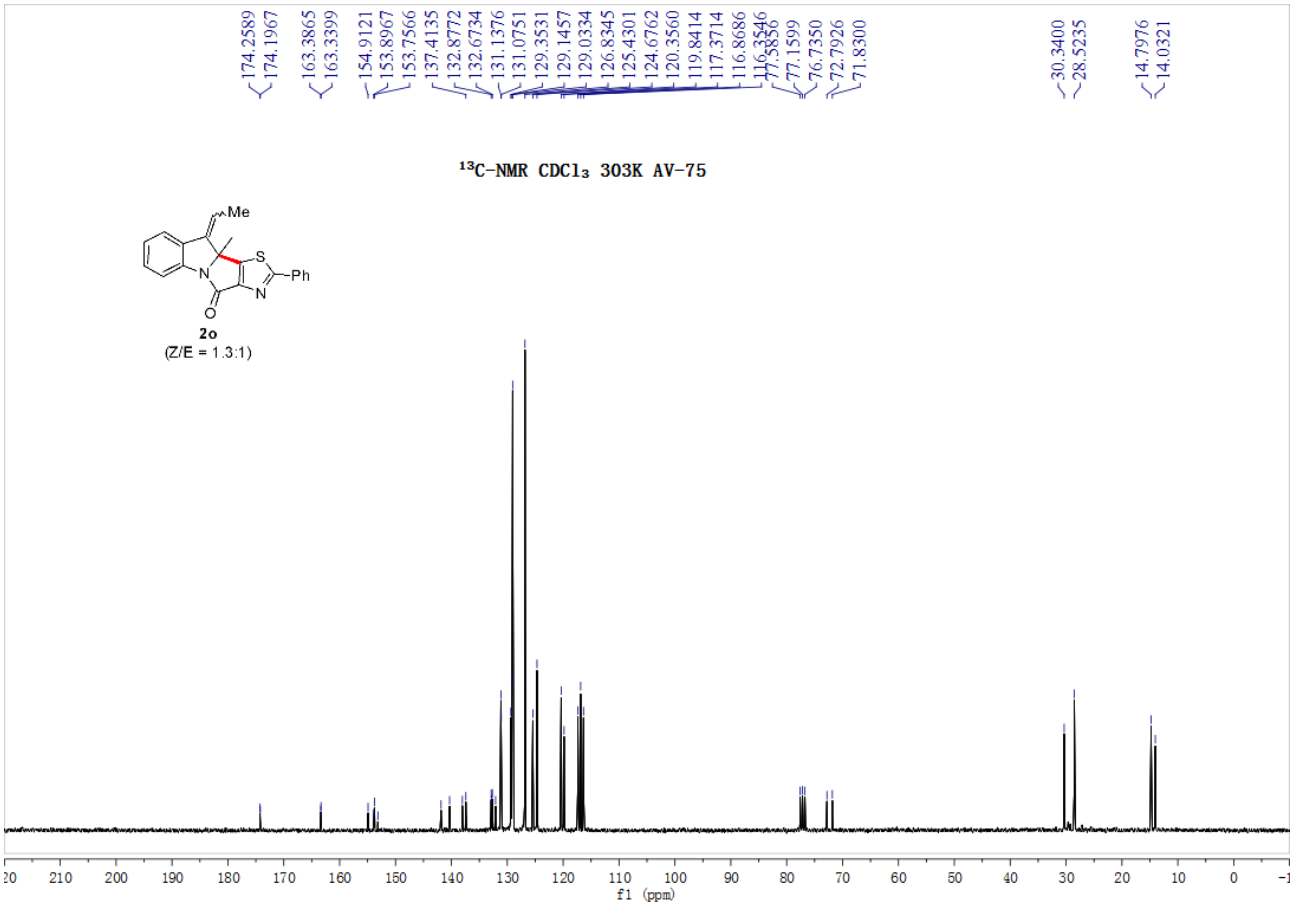
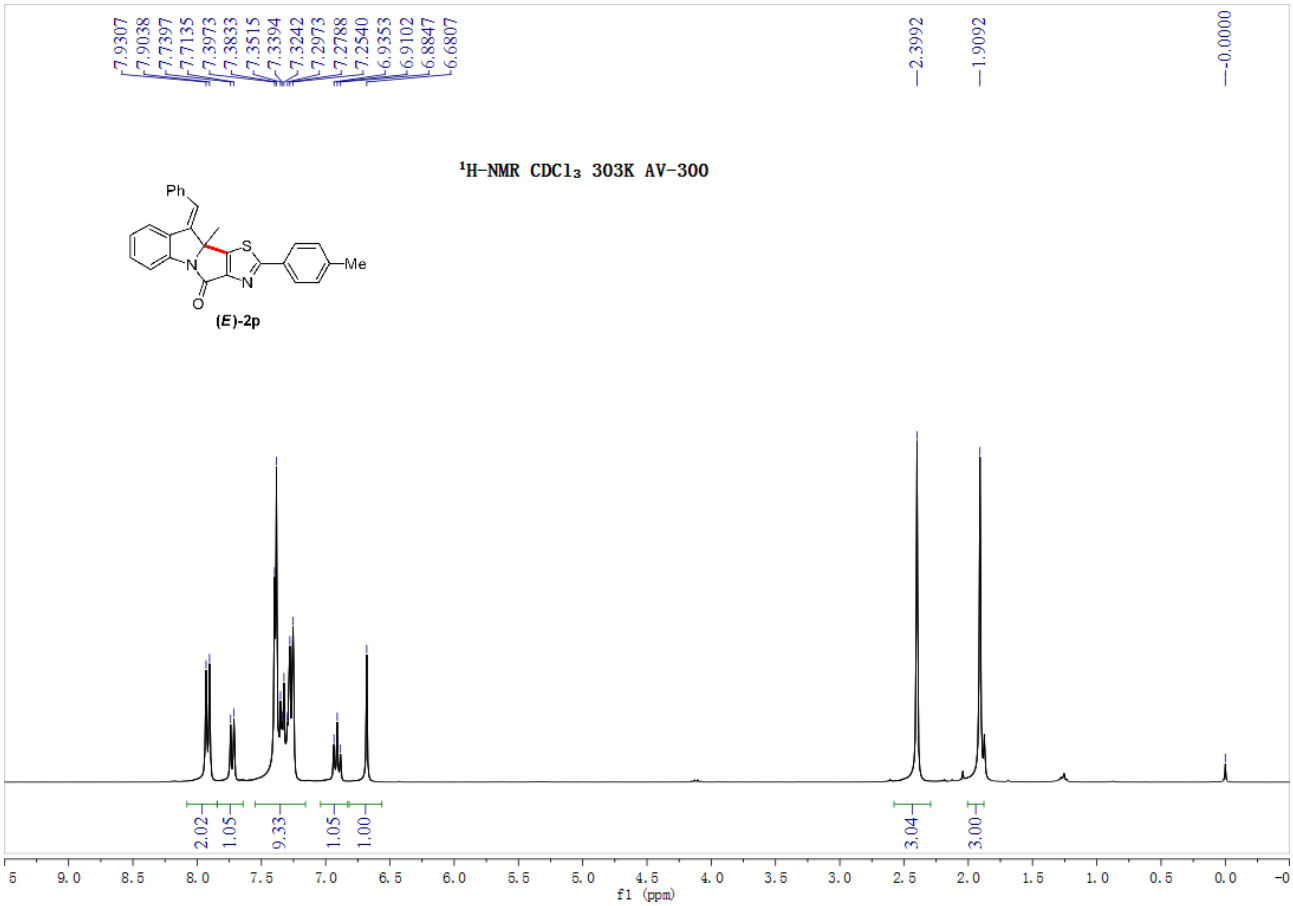


^{13}C-NMR CDCl$_3$ 303K AV-75

2o
(Z/E = 1.3:1)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7.2540
6.9353
6.9102
6.8847
6.6807
2.3992
1.9092
0.0000
^{1}H-NMR CDCl$_3$ 303K AV-300
Ph
S
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N
O
Me
(E)-2p
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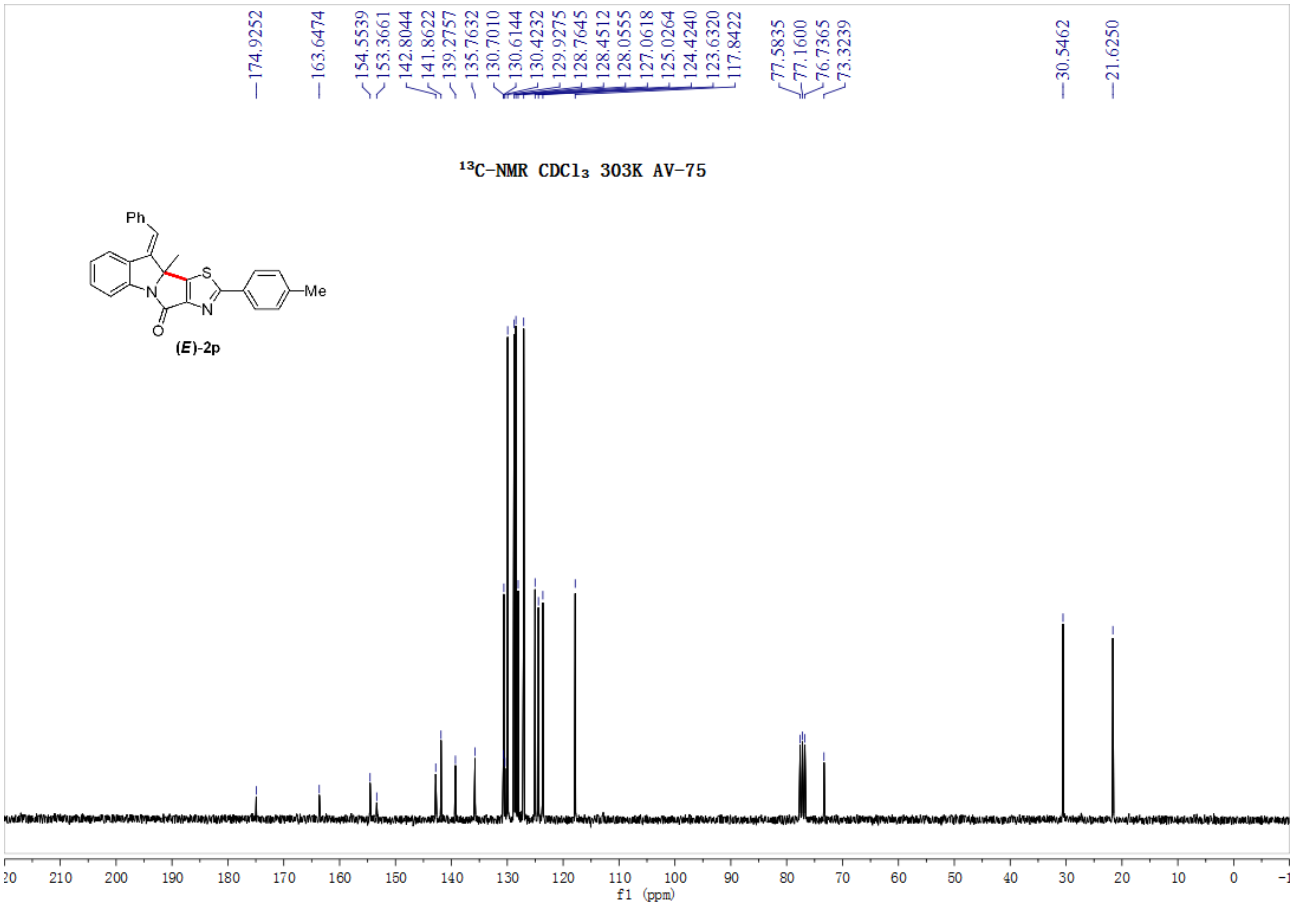
3.00
f1 (ppm)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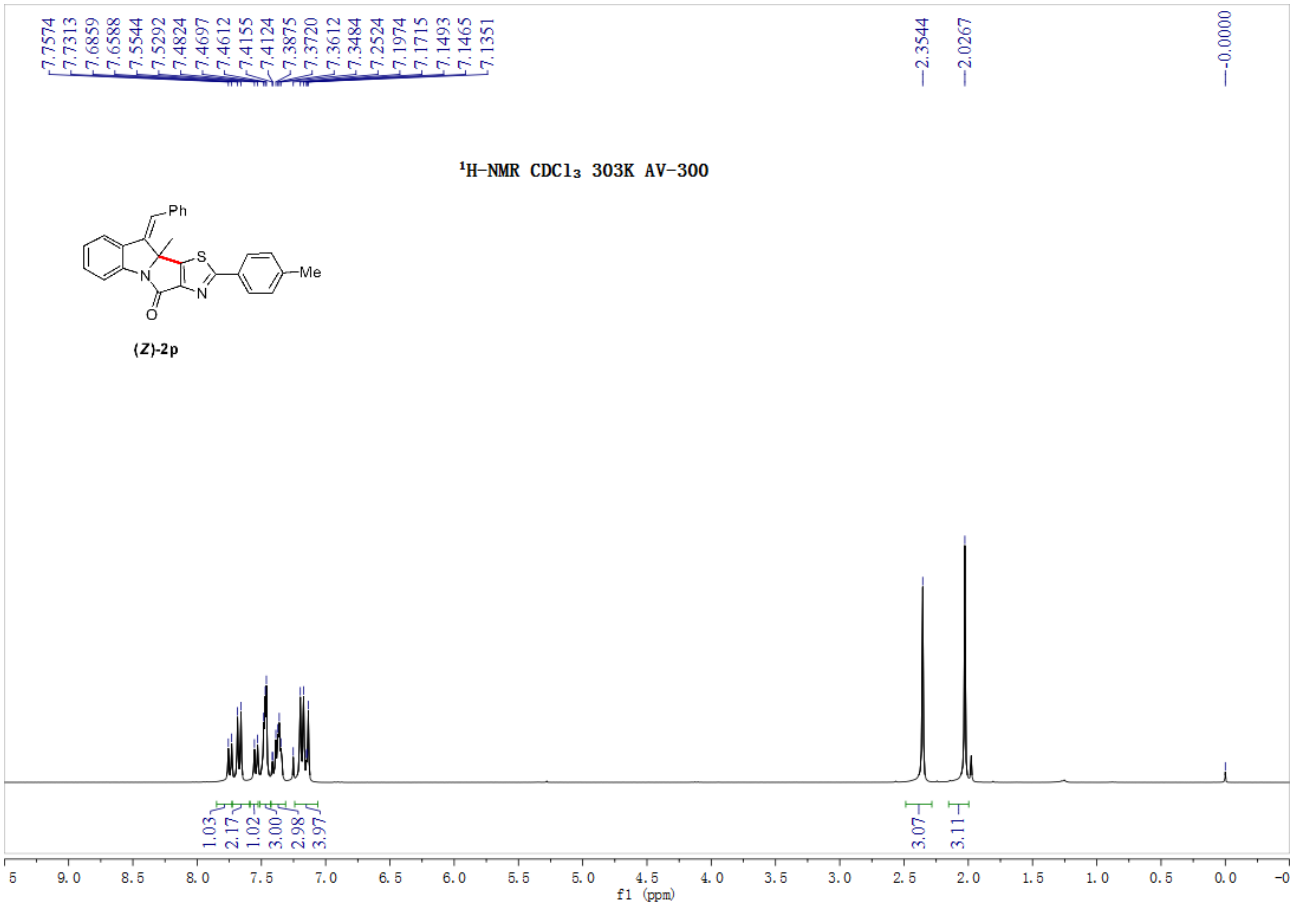
128.0555
127.0618
125.0264
124.4240
123.6320
117.8422
77.5835
77.1600
76.7365
73.3239
30.5462
21.6250
^{13}C-NMR CDCl$_3$ 303K AV-75
Ph
S
N
N
O
Me
(E)-2p
f1 (ppm)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7.4824
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7.4612
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7.4124
7.3875
7.3720
7.3612
7.3484
7.2524
7.1974
7.1715
7.1493
7.1465
7.1351
2.3544
2.0267
0.0000
1H-NMR CDCl3 303K AV-300
Ph
S
N
Me
O
(Z)-2p
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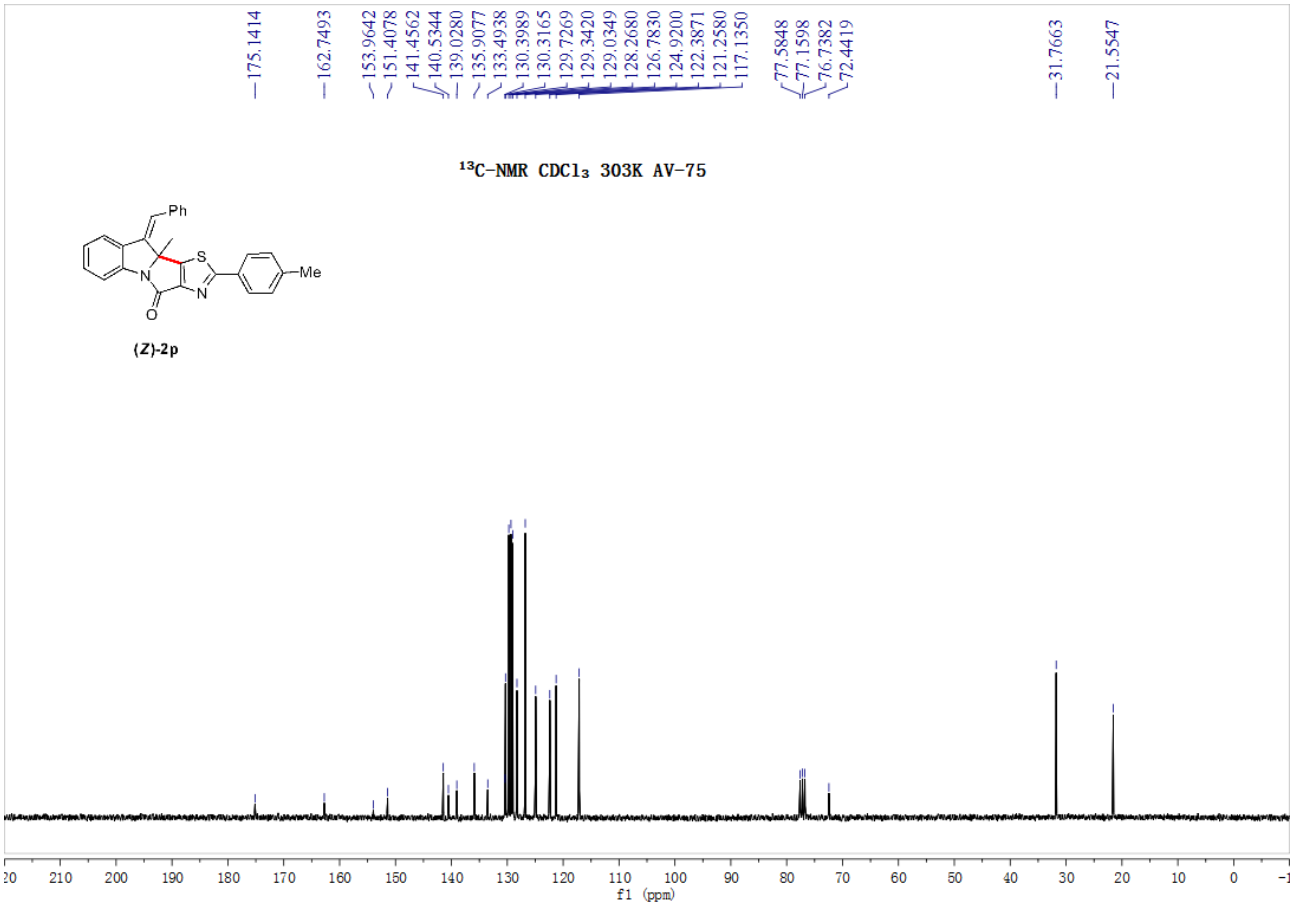
2.17
1.02
3.00
2.98
3.97
3.07
3.11
f1 (ppm)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153.9642
151.4078
141.4562
140.5344
139.0280
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133.4938
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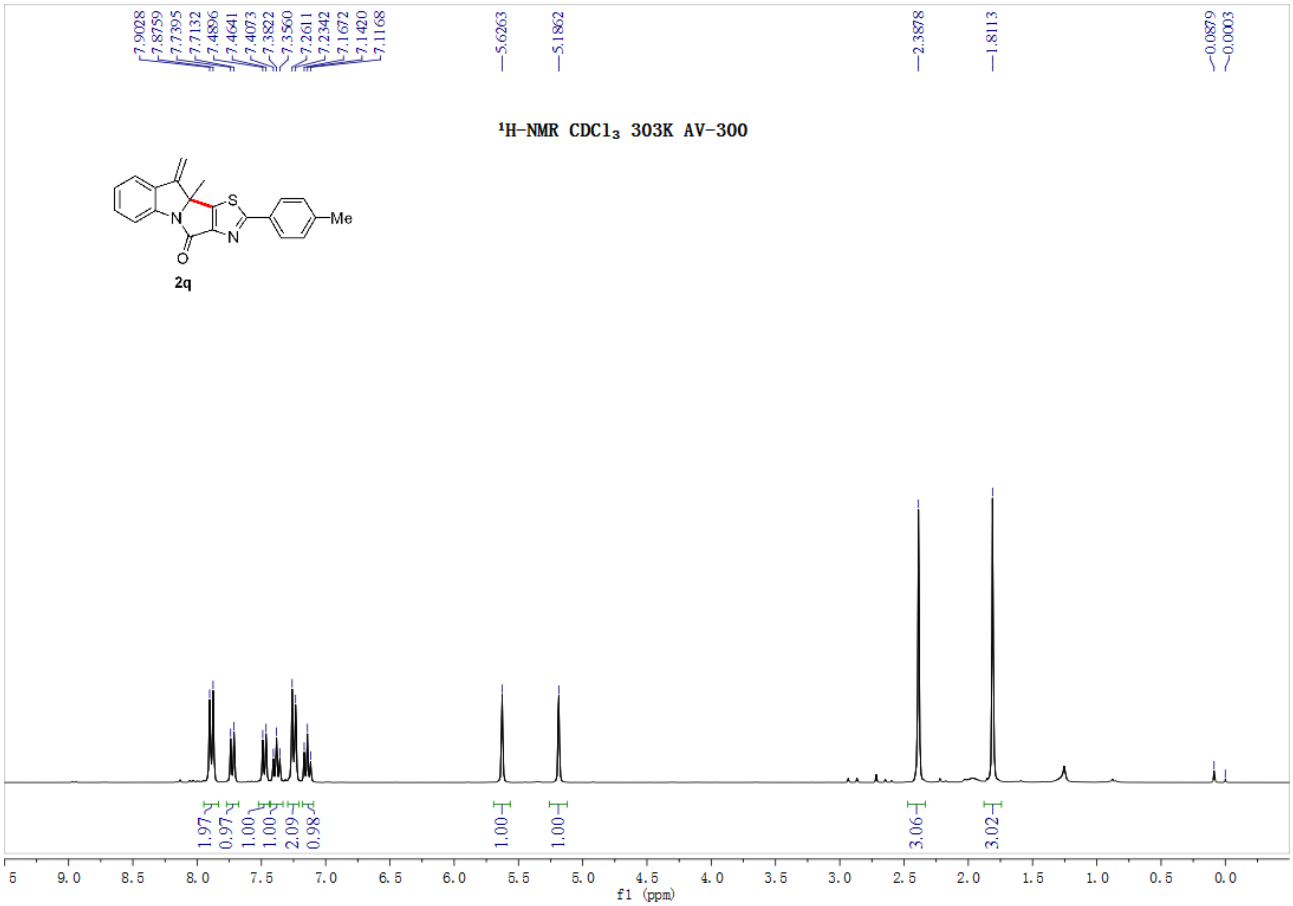
130.3165
129.7269
129.3420
129.0349
128.2680
126.7830
124.9200
122.3871
121.2580
117.1350
77.5848
77.1598
76.7382
72.4419
31.7663
21.5547
13C-NMR CDCl3 303K AV-75
Ph
S
N
Me
O
(Z)-2p
f1 (ppm)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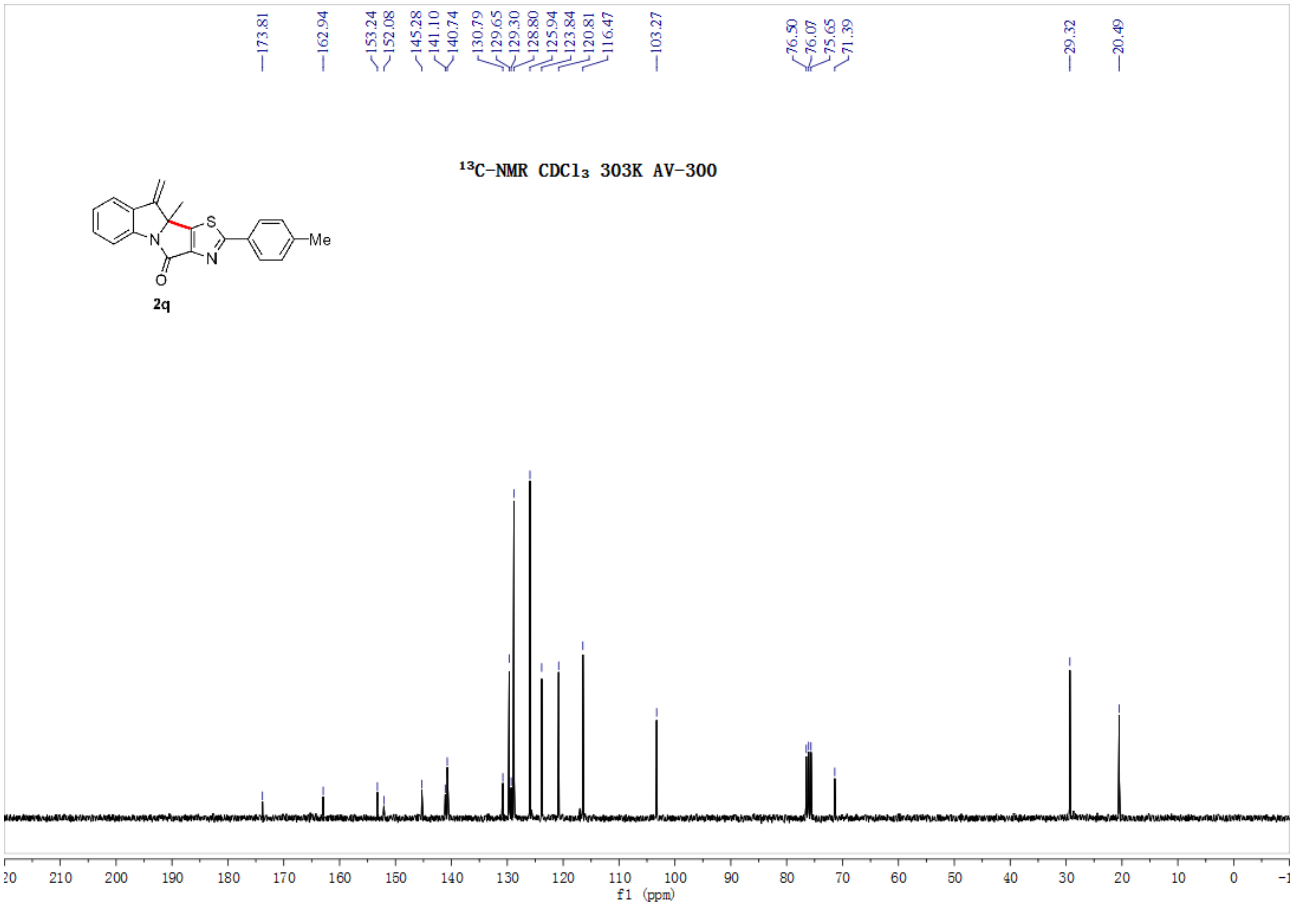
7.7395
7.7132
7.4896
7.4641
7.4073
7.3822
7.3560
7.2611
7.2342
7.1672
7.1420
7.1168
5.6263
5.1862
2.3878
1.8113
0.0879
0.0003
1H-NMR CDCl3 303K AV-300
Me
2q
1.97
0.97
1.00
1.00
2.09
0.98
1.00
1.00
3.06
3.02
f1 (ppm)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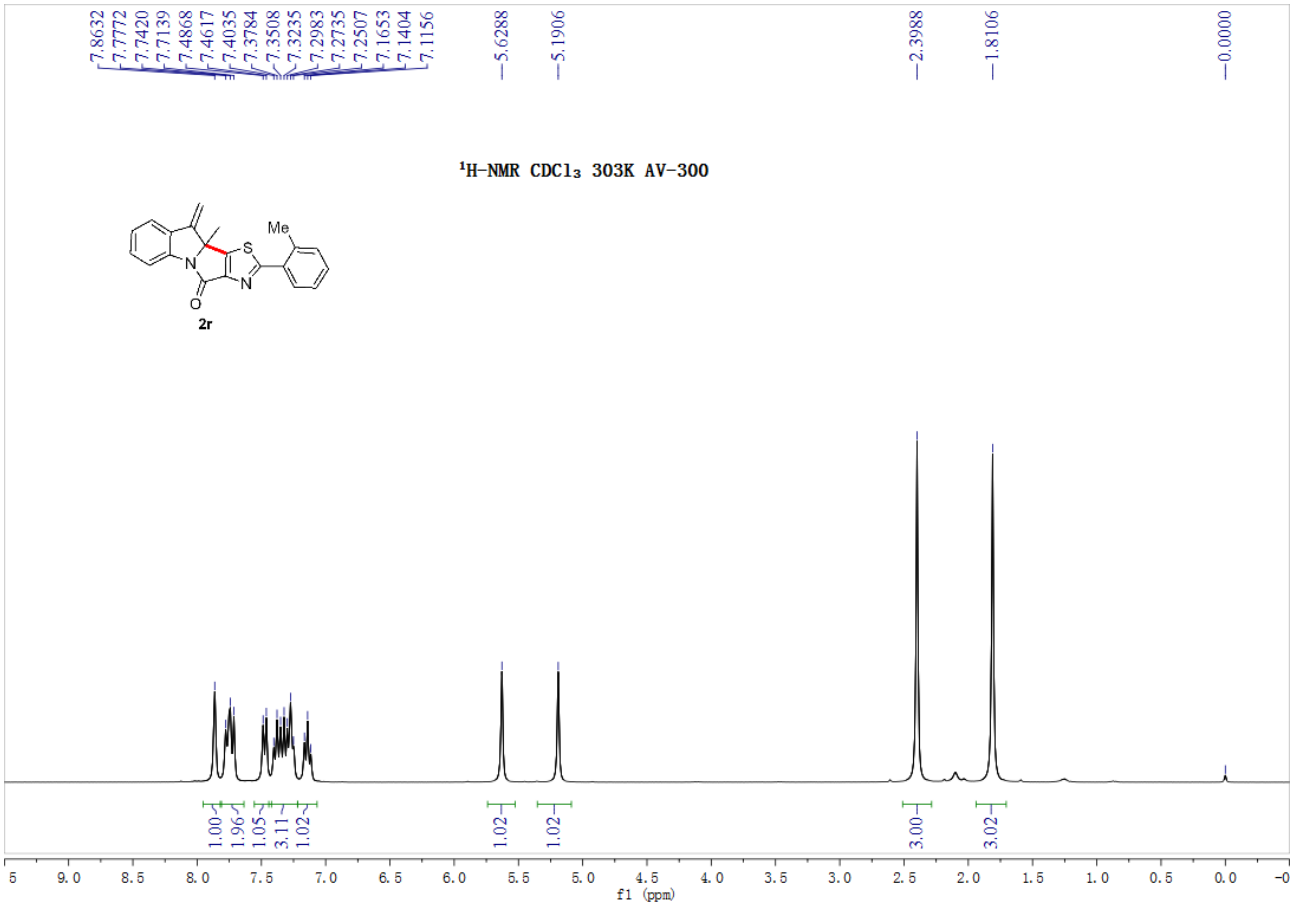
162.94
153.24
152.08
145.28
141.10
140.74
130.79
129.65
129.30
128.80
125.94
123.84
120.81
116.47
103.27
76.50
76.07
75.65
71.39
29.32
20.49
13C-NMR CDCl3 303K AV-300
Me
2q
f1 (ppm)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7.7420
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7.4868
7.4617
7.4035
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7.3508
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7.2983
7.2735
7.2507
7.1653
7.1404
7.1156
5.6288
5.1906
2.3988
1.8106
0.0000
1H-NMR CDCl3 303K AV-300
Me
S
N
N
O
2r
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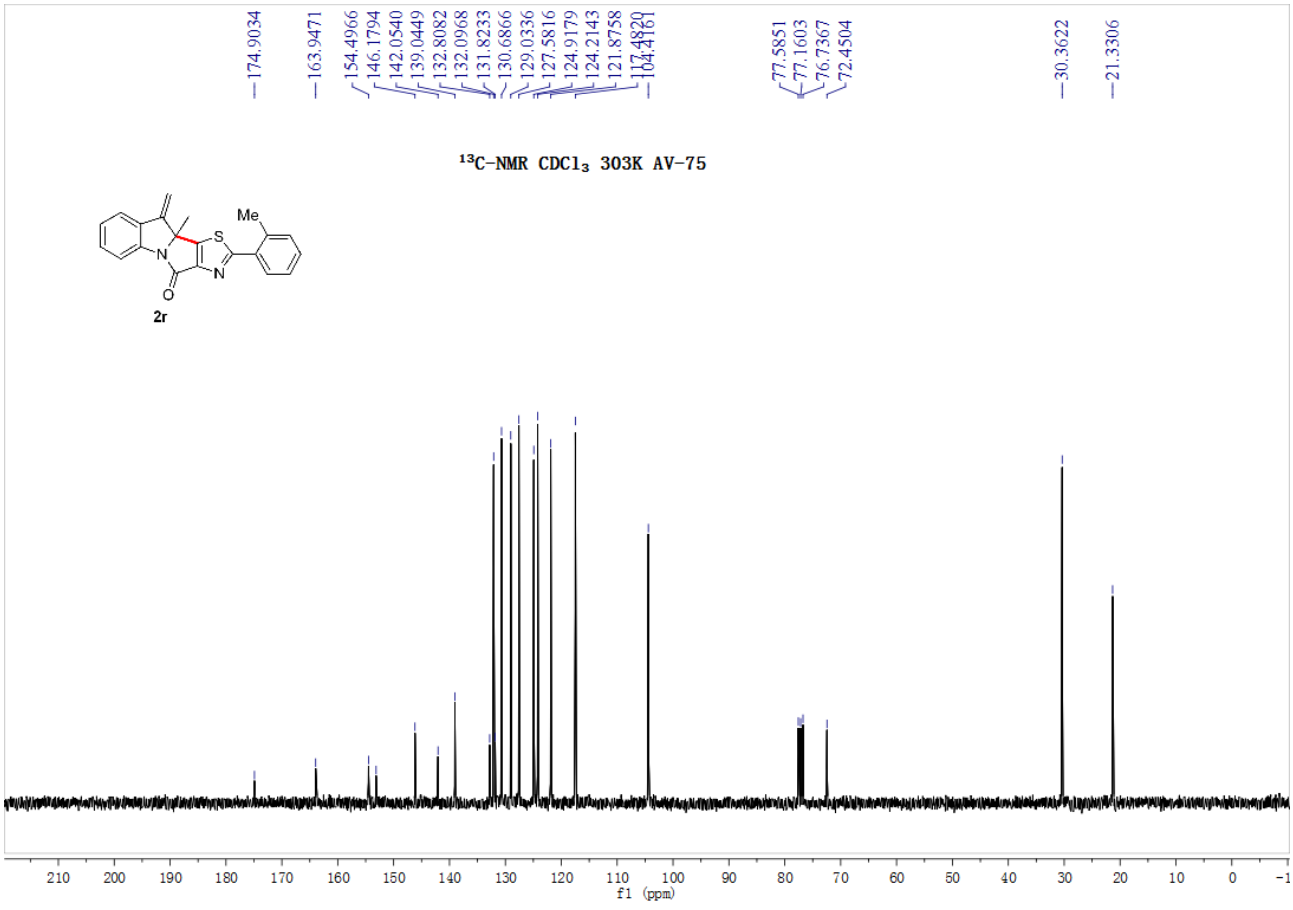
1.96
1.05
3.11
1.02
1.02
1.02
3.00
3.02
f1 (ppm)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129.0336
127.5816
124.9179
124.2143
121.8758
117.4820
104.4161
77.5851
77.1603
76.7367
72.4504
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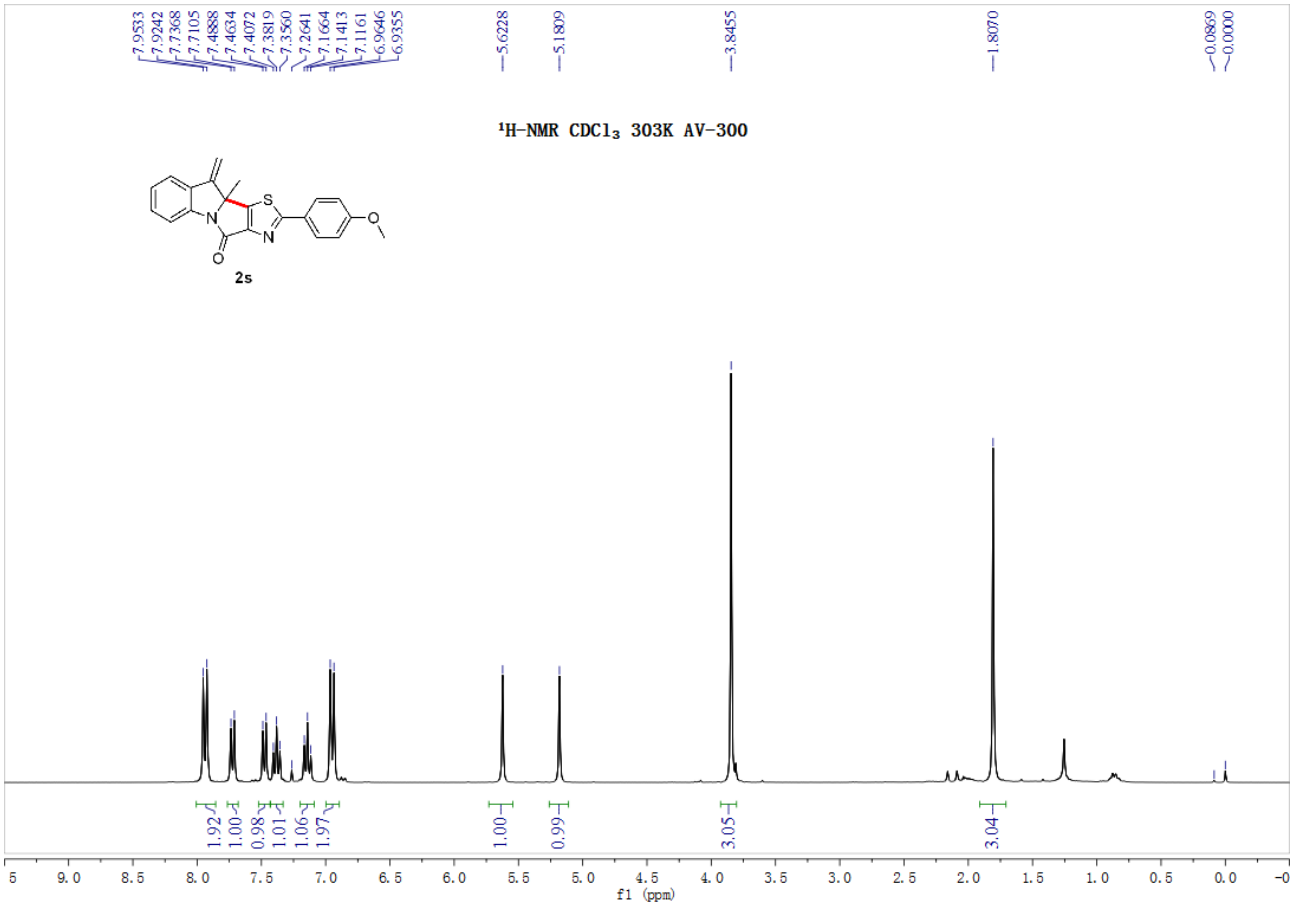
21.3306
13C-NMR CDCl3 303K AV-75
Me
S
N
N
O
2r
f1 (ppm)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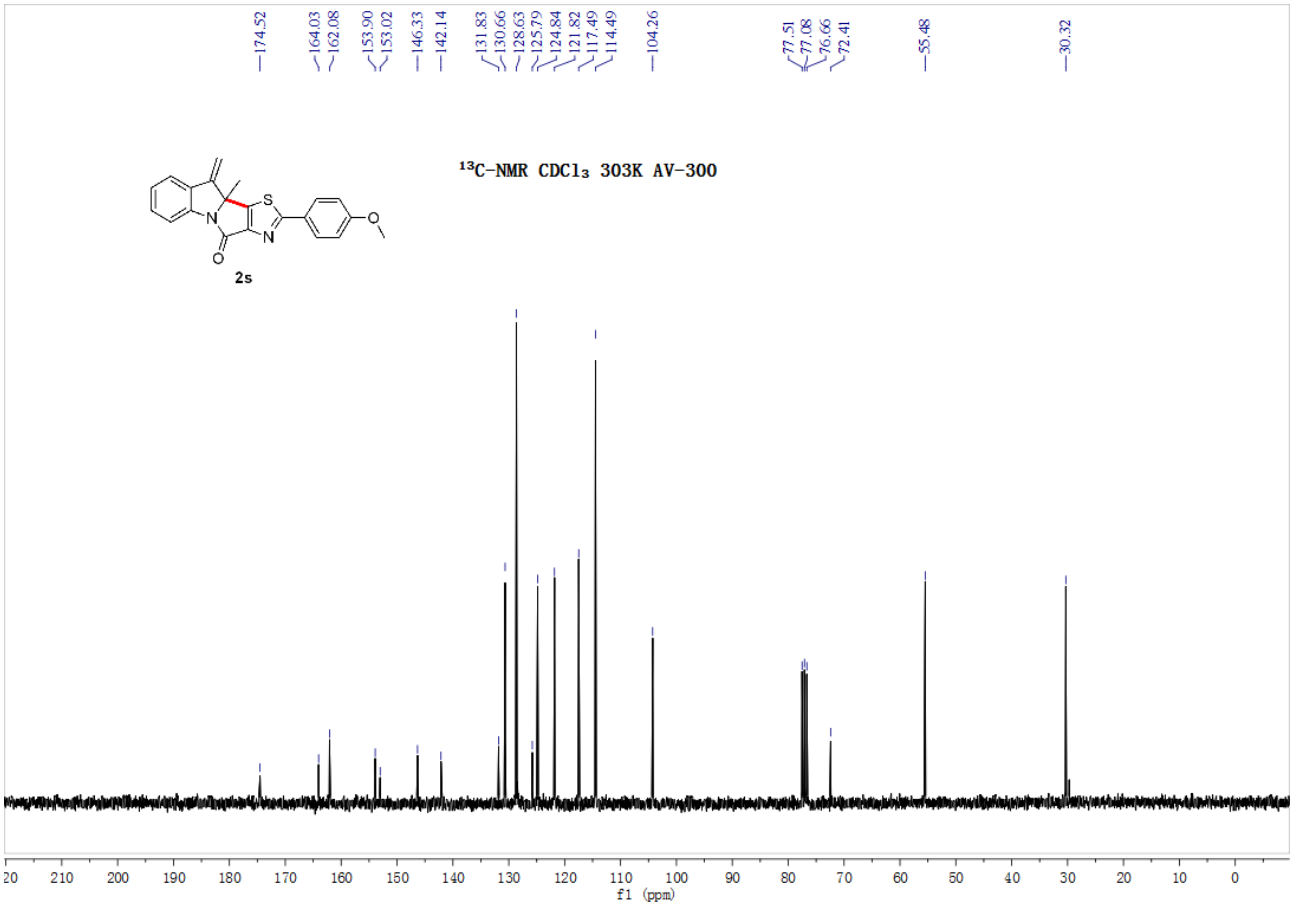
7.7368
7.7105
7.4888
7.4634
7.4072
7.3819
7.3560
7.2641
7.1664
7.1413
7.1161
6.9646
6.9355
5.6228
5.1809
3.8455
1.8070
0.0869
0.0000
1H-NMR CDCl3 303K AV-300
2s
1.92
1.00
0.98
1.01
1.06
1.97
1.00
0.99
3.05
3.04
f1 (ppm)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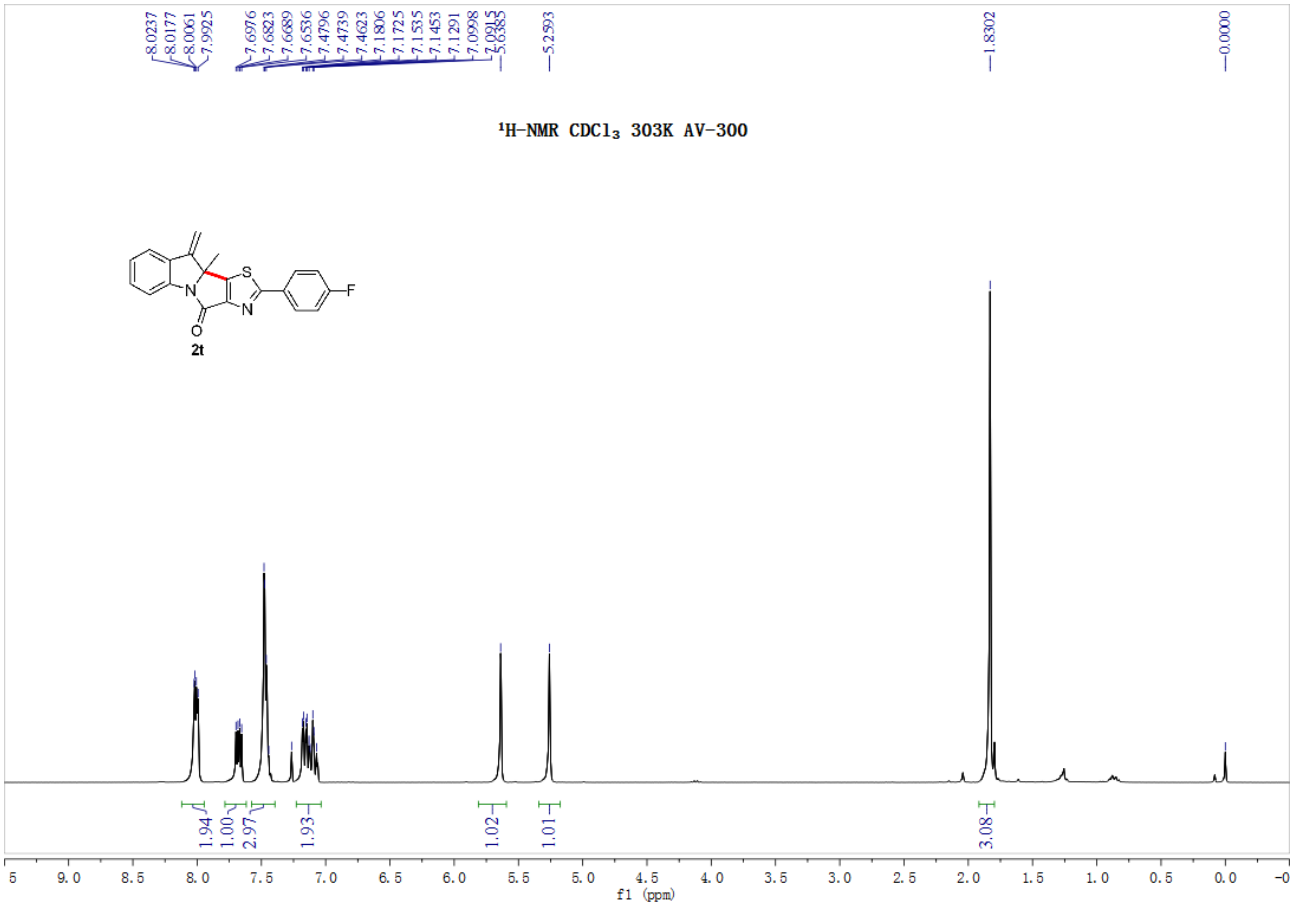
162.08
153.90
153.02
146.33
142.14
131.83
130.66
128.63
125.79
124.84
121.82
117.49
114.49
104.26
77.51
77.08
76.66
72.41
55.48
30.32
13C-NMR CDCl3 303K AV-300
2s
f1 (ppm)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8.0061
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7.6689
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7.4796
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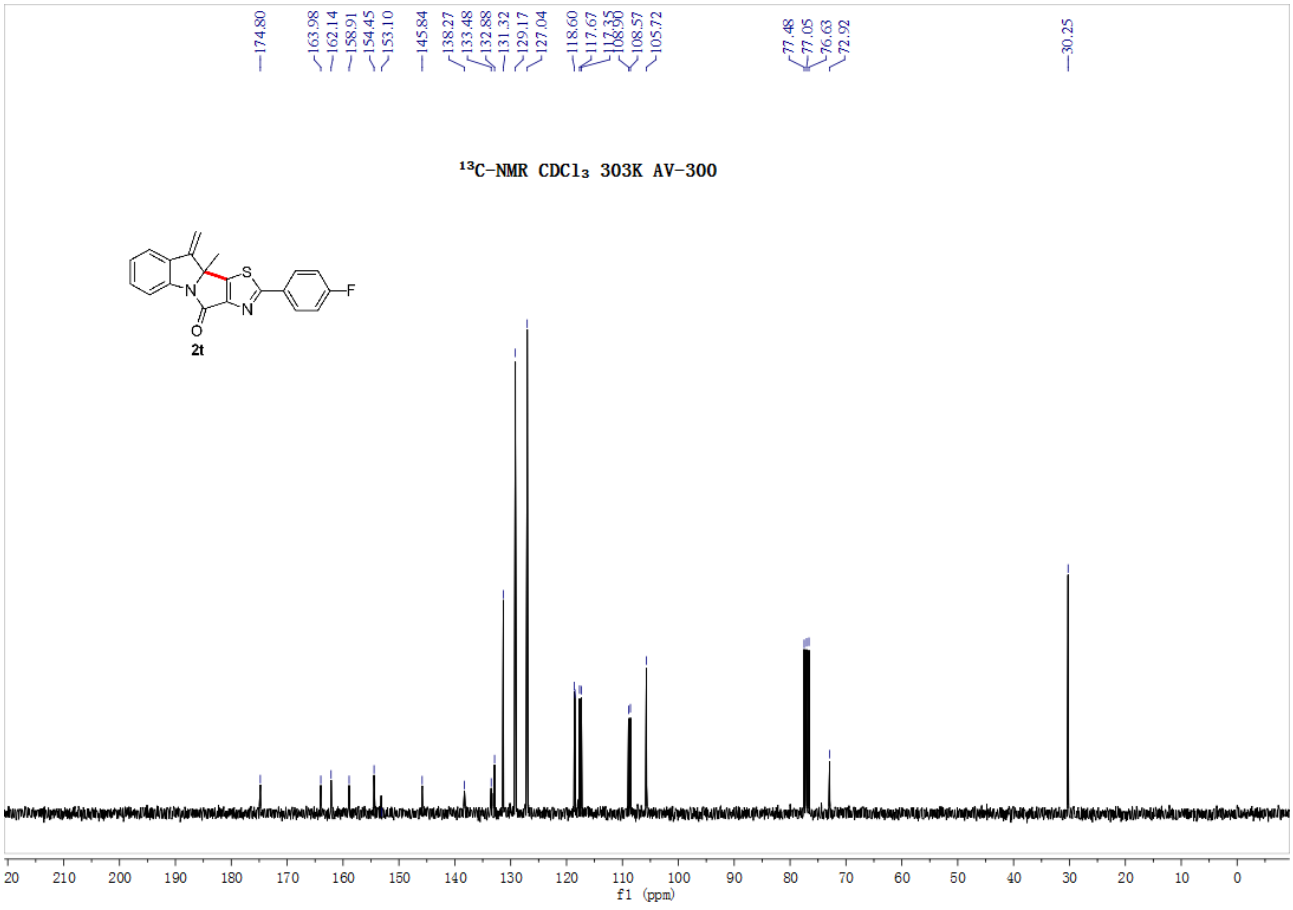
7.4623
7.1806
7.1725
7.1535
7.1453
7.1291
7.0998
7.0915
5.6385
5.2593
1.8302
0.0000
1H-NMR CDCl3 303K AV-300
F
O
2t
1.94
1.00
2.97
1.93
1.02
1.01
3.08
f1 (ppm)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162.14
158.91
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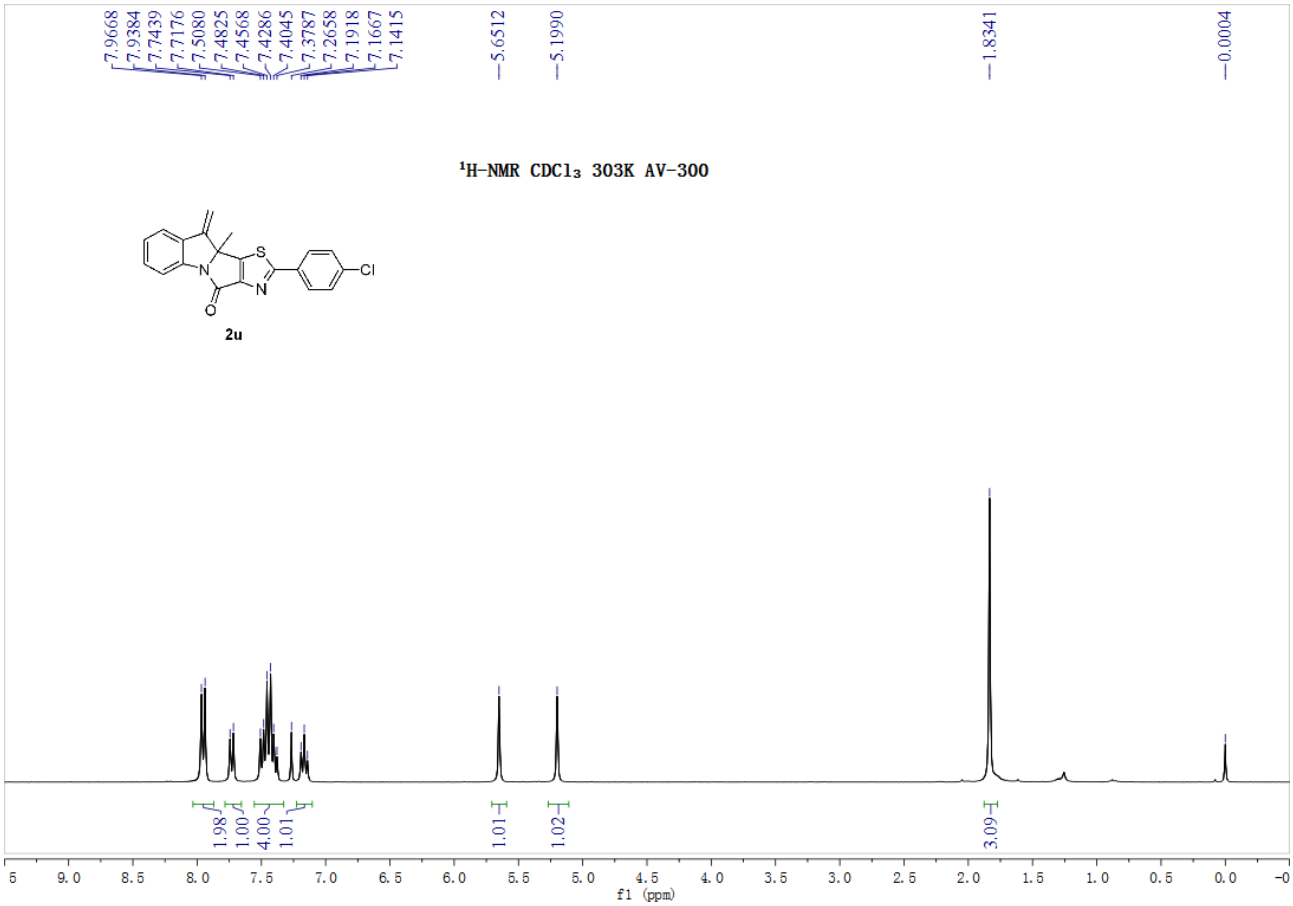
153.10
145.84
138.27
133.48
132.88
131.32
129.17
127.04
118.60
117.67
117.35
108.90
108.57
105.72
77.48
77.05
76.63
72.92
30.25
13C-NMR CDCl3 303K AV-300
F
O
2t
f1 (ppm)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7.7439
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7.5080
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7.4568
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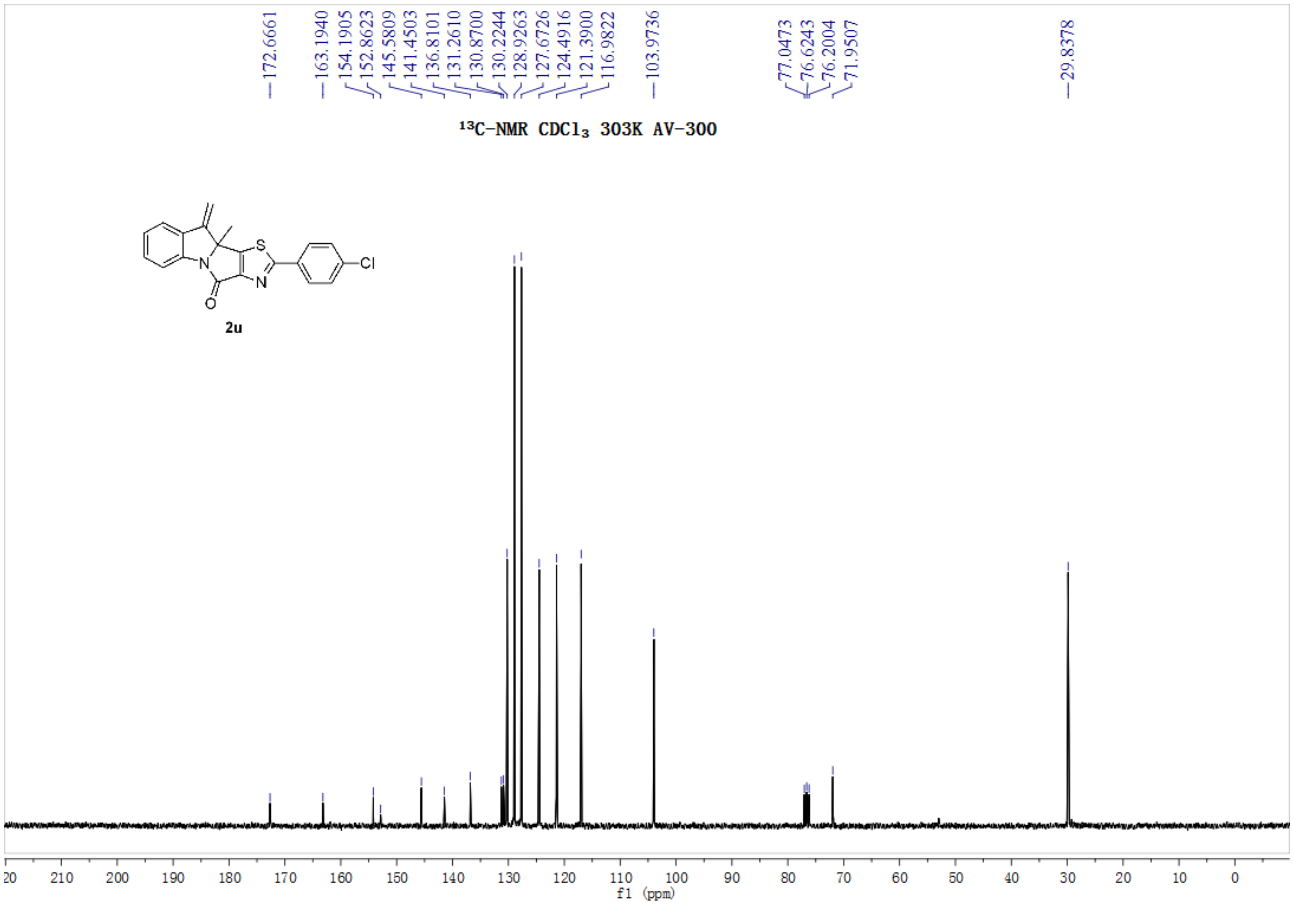
7.4045
7.3787
7.2658
7.1918
7.1667
7.1415
5.6512
5.1990
1.8341
0.0004
1H-NMR CDCl3 303K AV-300
Cl
2u
1.98
1.00
4.00
1.01
1.01
1.02
3.09
f1 (ppm)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128.9263
127.6726
124.4916
121.3900
116.9822
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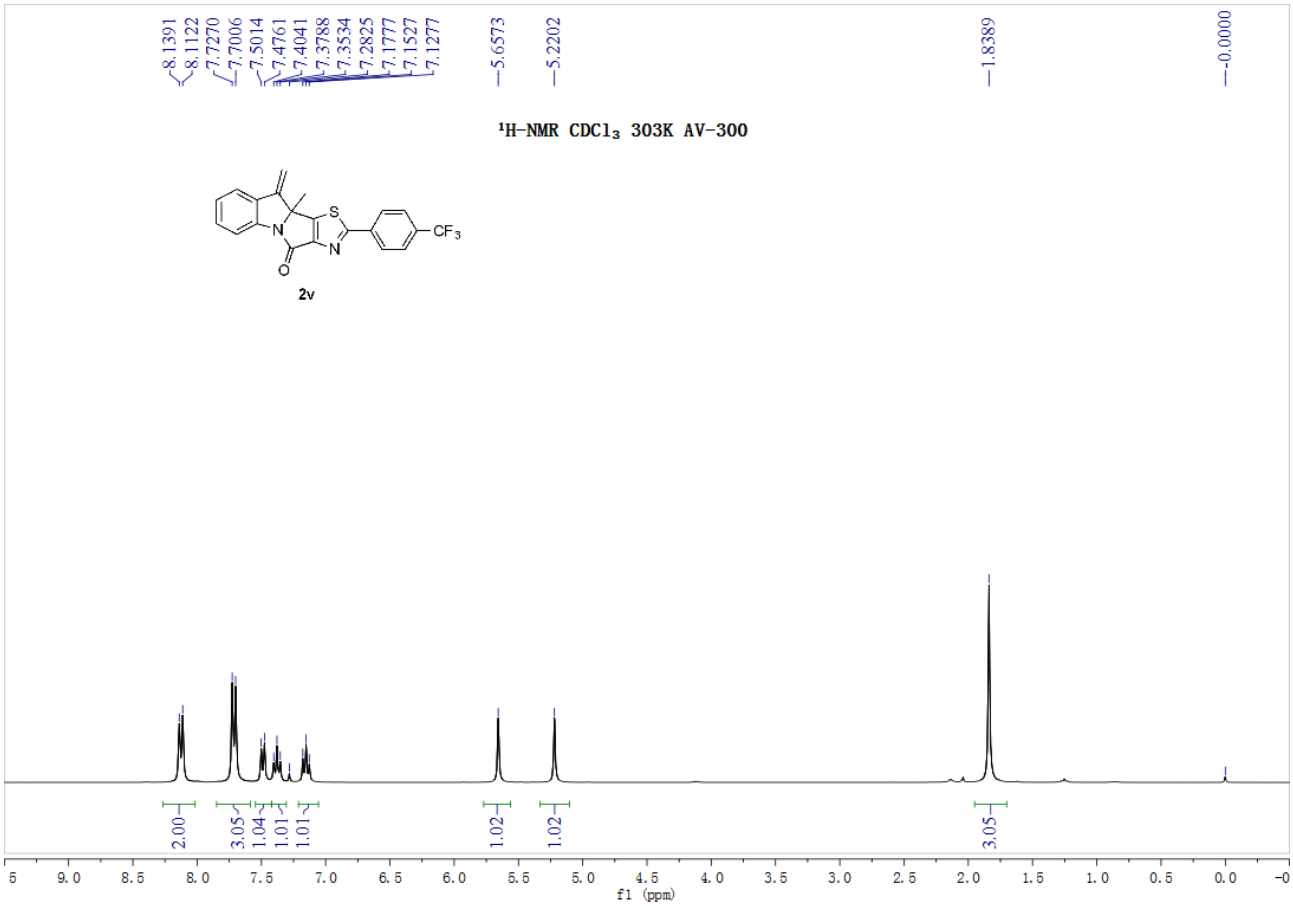
76.6243
76.2004
71.9507
29.8378
13C-NMR CDCl3 303K AV-300
Cl
2u
f1 (ppm)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7.7006
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7.4041
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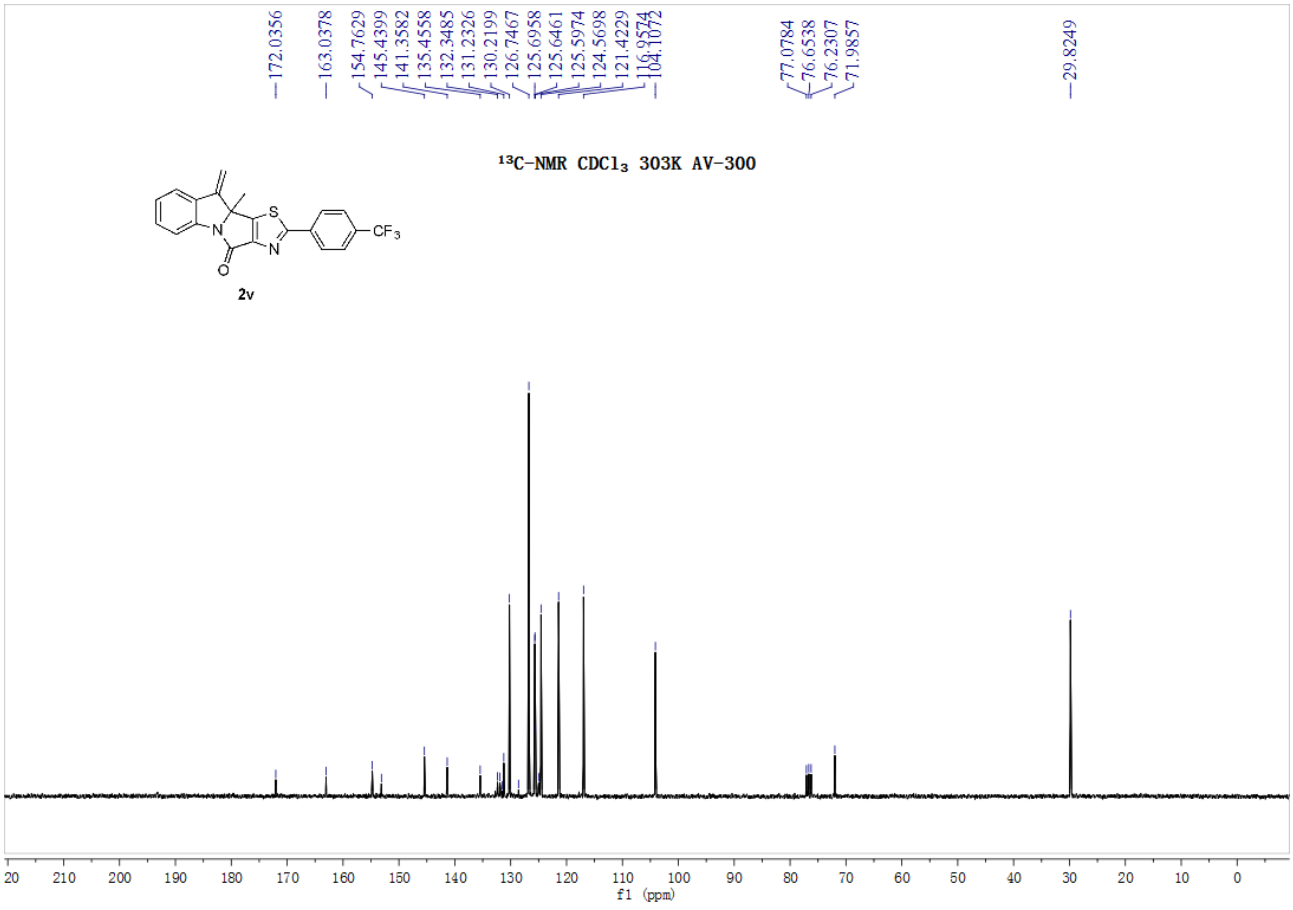
7.3534
7.2825
7.1777
7.1527
7.1277
5.6573
5.2202
1.8389
0.0000
¹H-NMR CDCl₃ 303K AV-300
CF₃
2v
2.00
3.05
1.04
1.01
1.01
1.02
1.02
3.05
f1 (ppm)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125.6958
125.6461
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124.5698
121.4229
116.9574
104.1072
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71.9857
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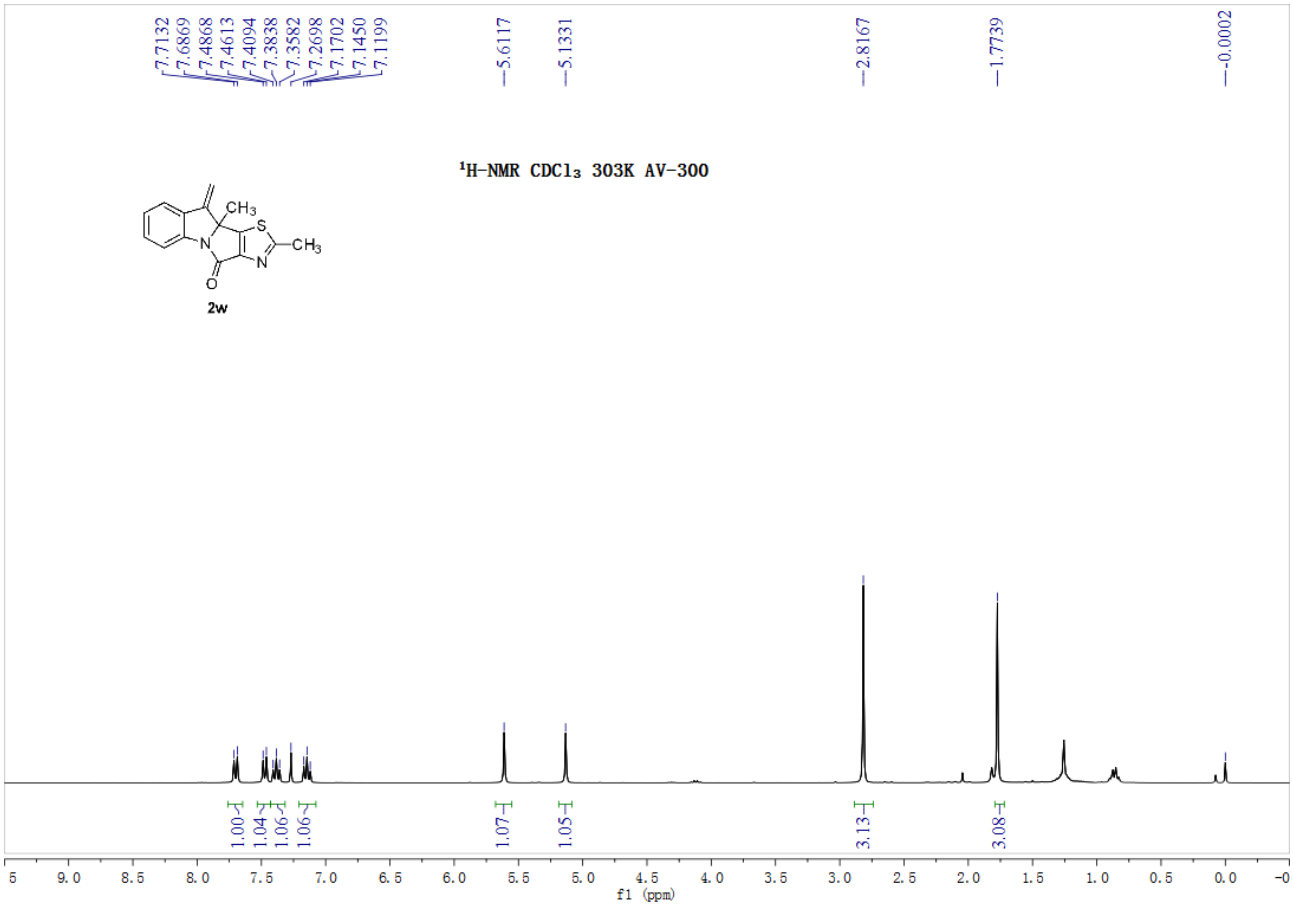
¹³C-NMR CDCl₃ 303K AV-300
CF₃
2v
f1 (ppm)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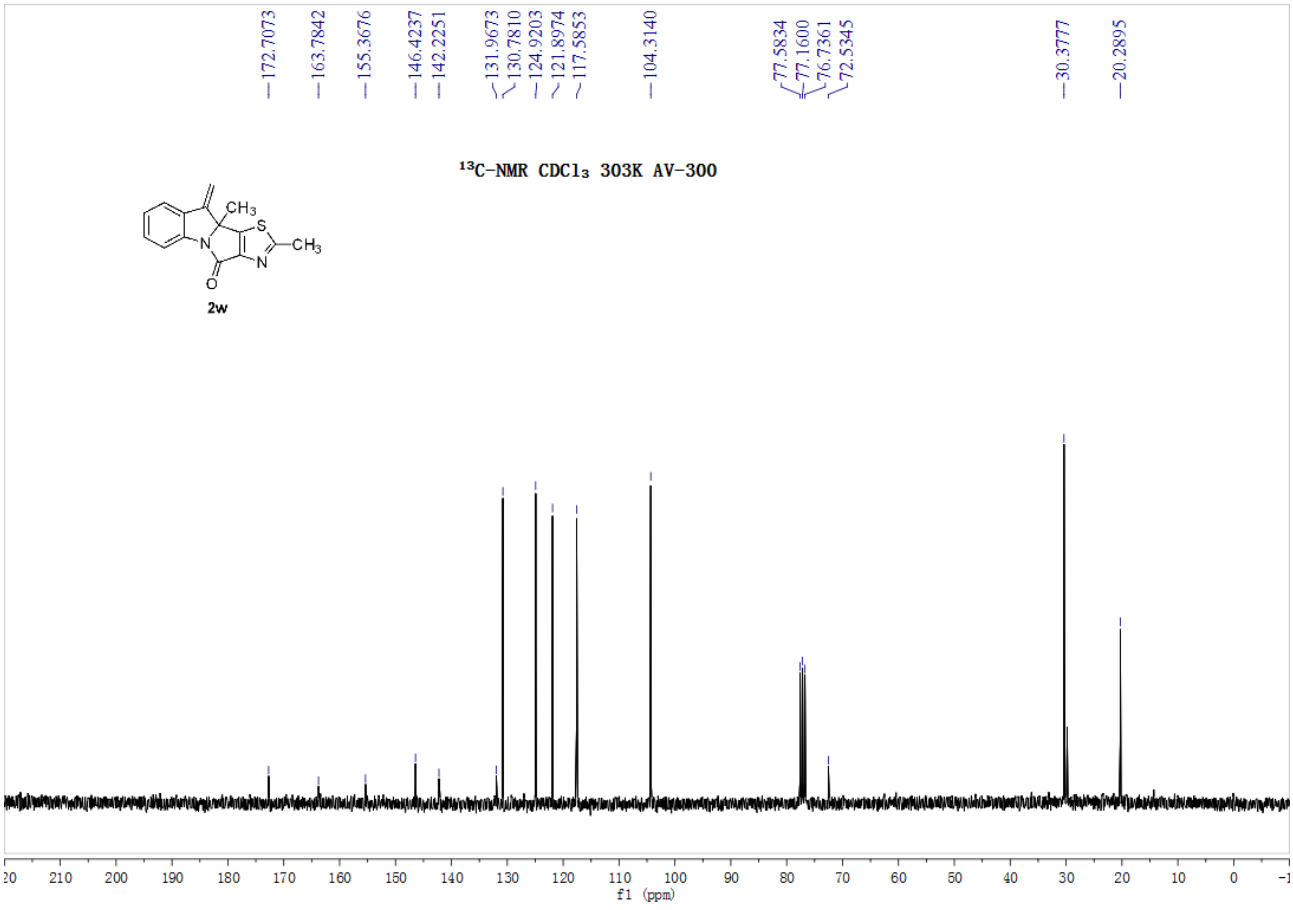
7.4868
7.4613
7.4094
7.3838
7.3582
7.2698
7.1702
7.1450
7.1199
5.6117
5.1331
2.8167
1.7739
0.0002
1H-NMR CDCl3 303K AV-300
CH3
S
CH3
N
N
O
2w
1.00
1.04
1.06
1.06
1.07
1.05
3.13
3.08
f1 (ppm)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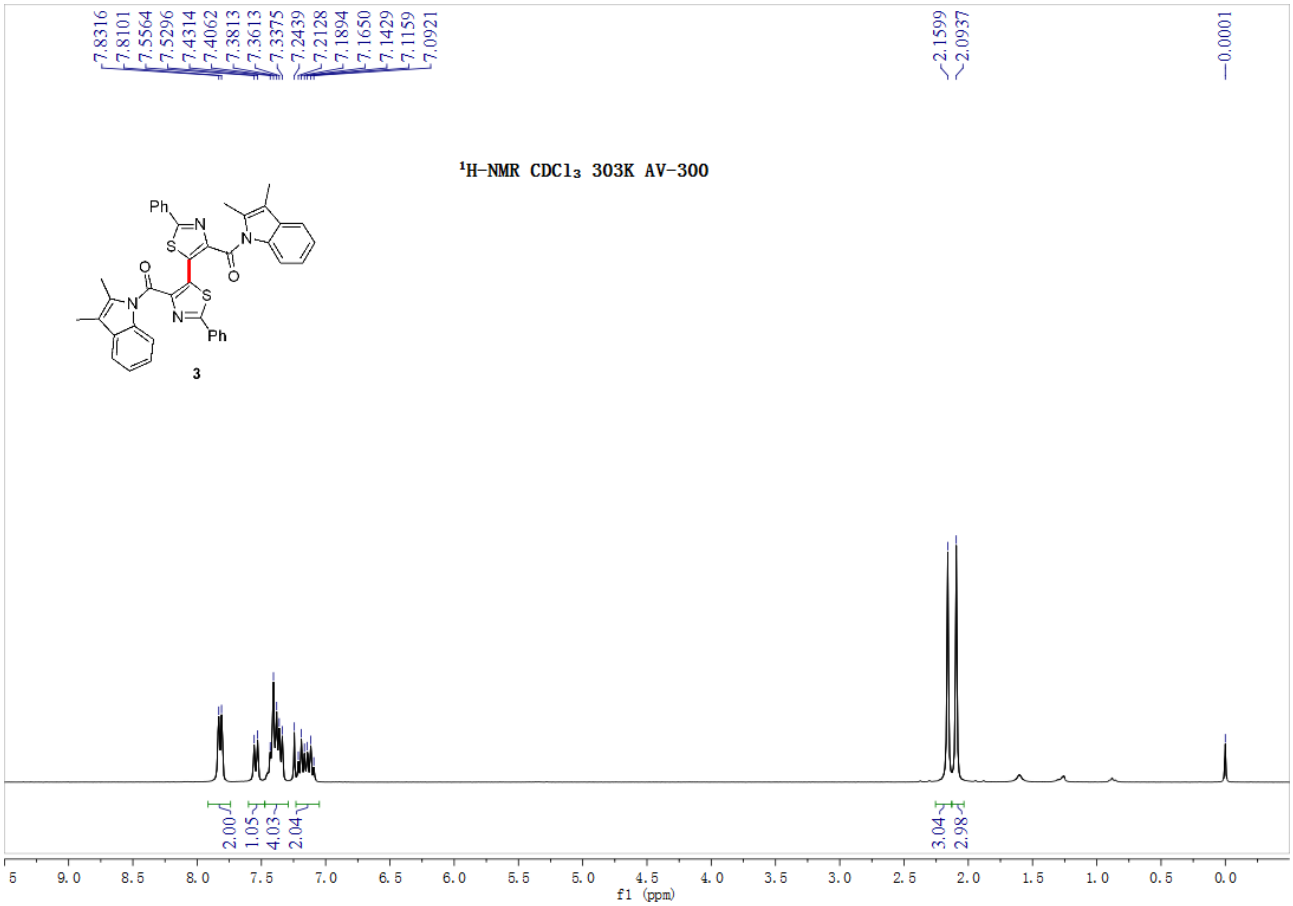
104.3140
77.5834
77.1600
76.7361
72.5345
30.3777
20.2895
13C-NMR CDCl3 303K AV-300
CH3
S
CH3
N
N
O
2w
f1 (ppm)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7.3375
7.2439
7.2128
7.1894
7.1650
7.1429
7.1159
7.0921
2.1599
2.0937
0.0001
¹H-NMR CDCl₃ 303K AV-300
Ph
N
S
O
N
O
S
N
Ph
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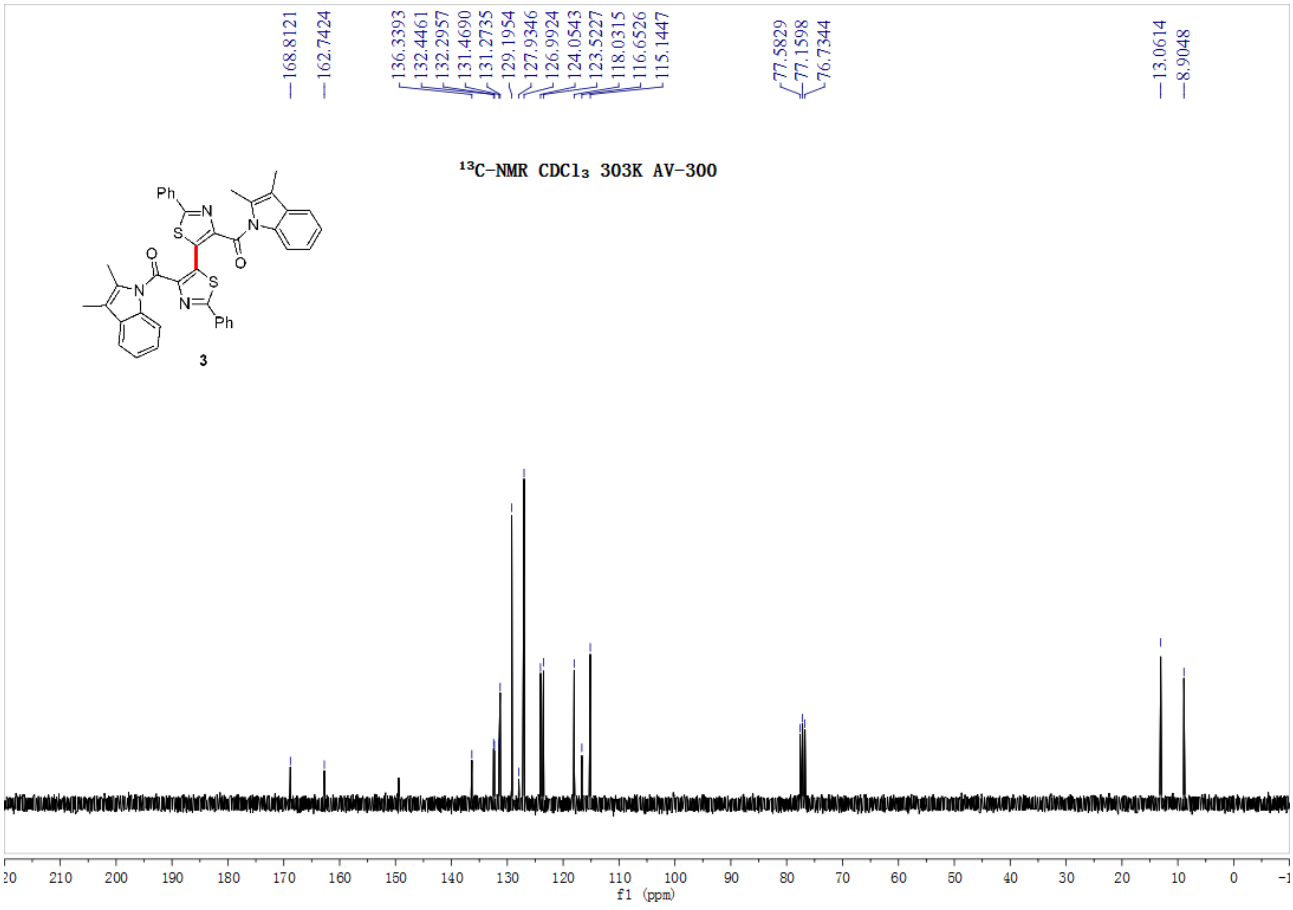
2.04
3.04
2.98
f1 (ppm)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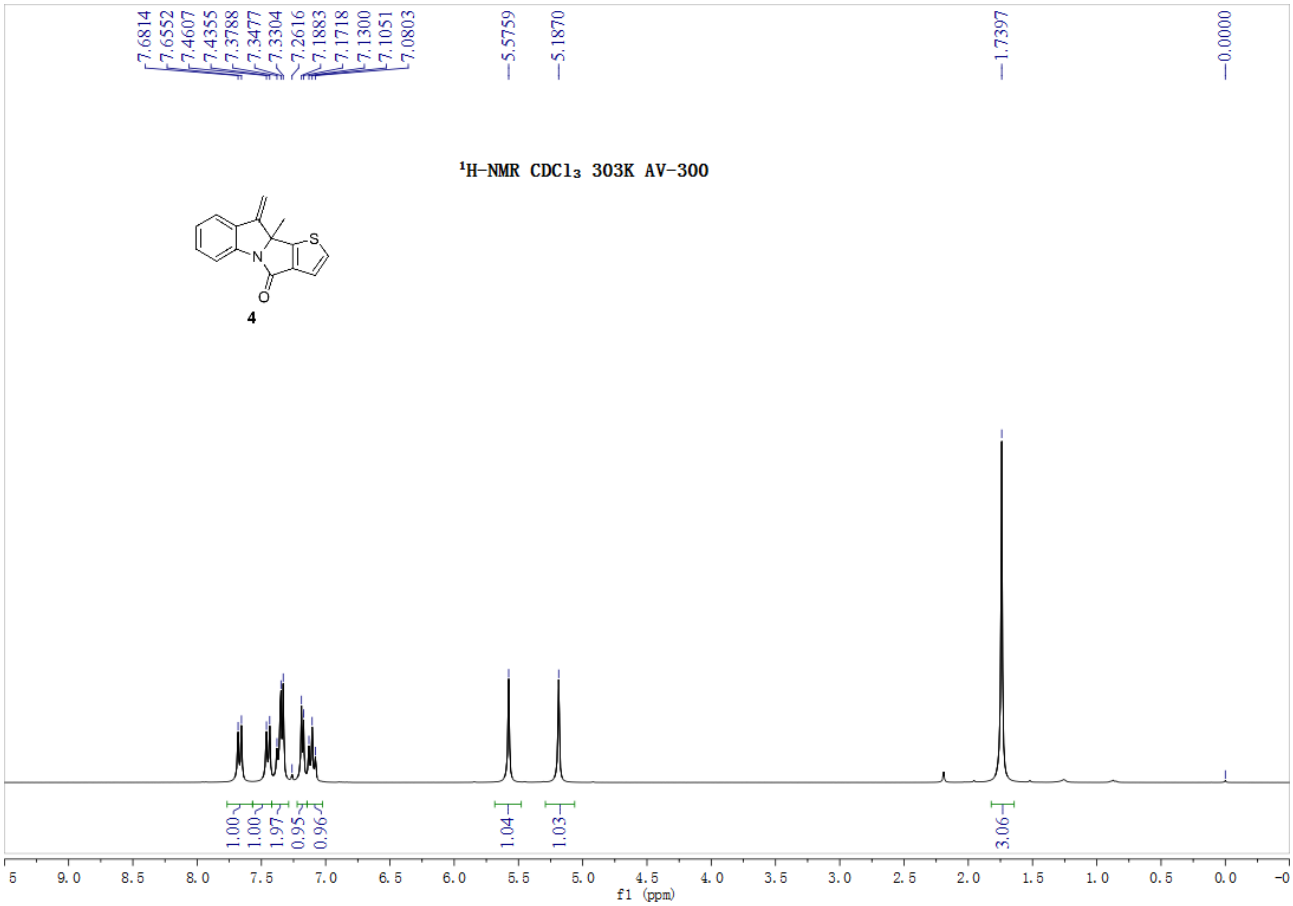
123.5227
118.0315
116.6526
115.1447
77.5829
77.1598
76.7344
13.0614
8.9048
¹³C-NMR CDCl₃ 303K AV-300
Ph
N
S
O
N
O
S
N
Ph
3
f1 (ppm)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7.3788
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7.3304
7.2616
7.1883
7.1718
7.1300
7.1051
7.0803
5.5759
5.1870
1.7397
0.0000
1H-NMR CDCl3 303K AV-300
4
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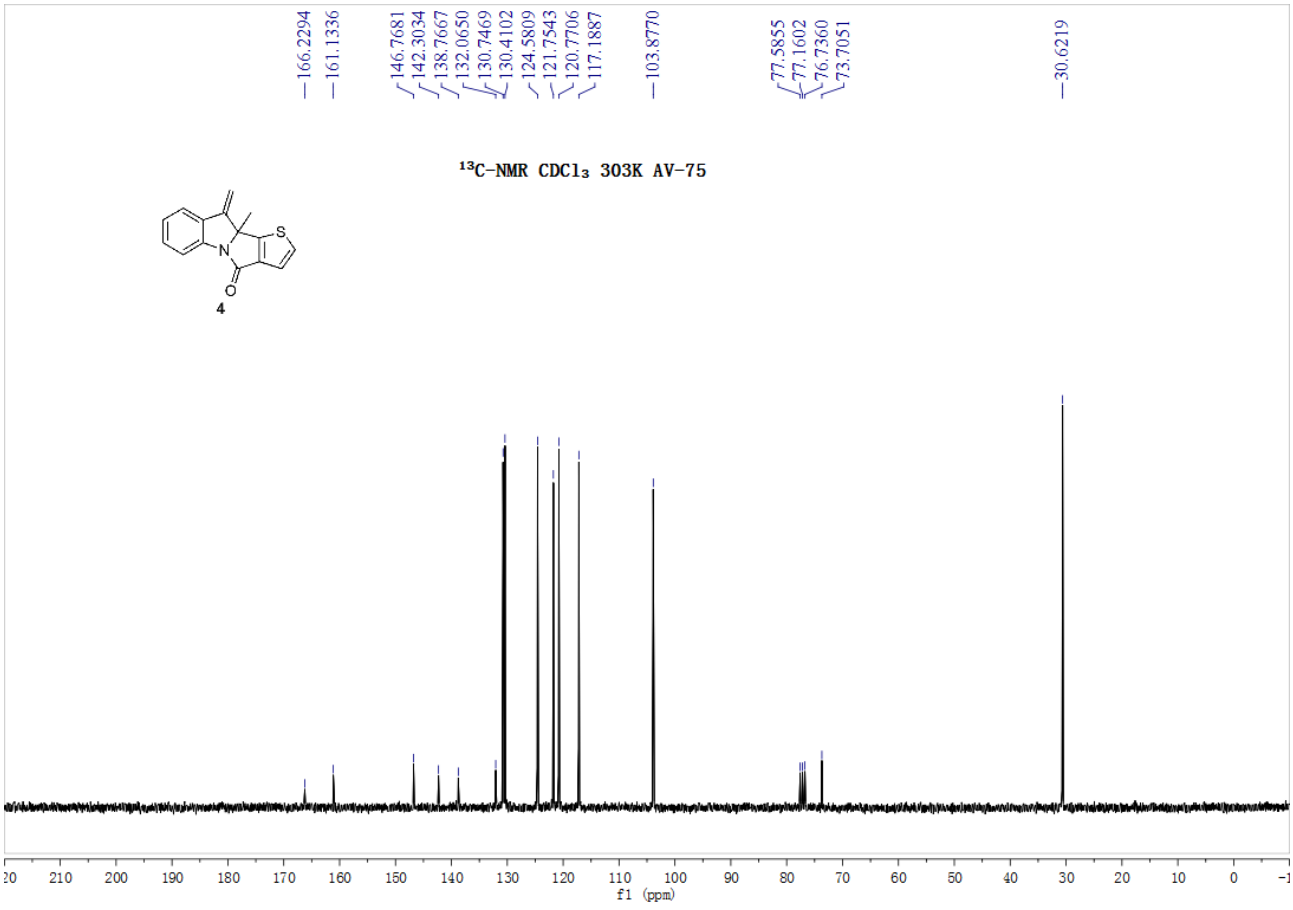
1.00
1.97
0.95
0.96
1.04
1.03
3.06
f1 (ppm)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117.1887
103.8770
77.5855
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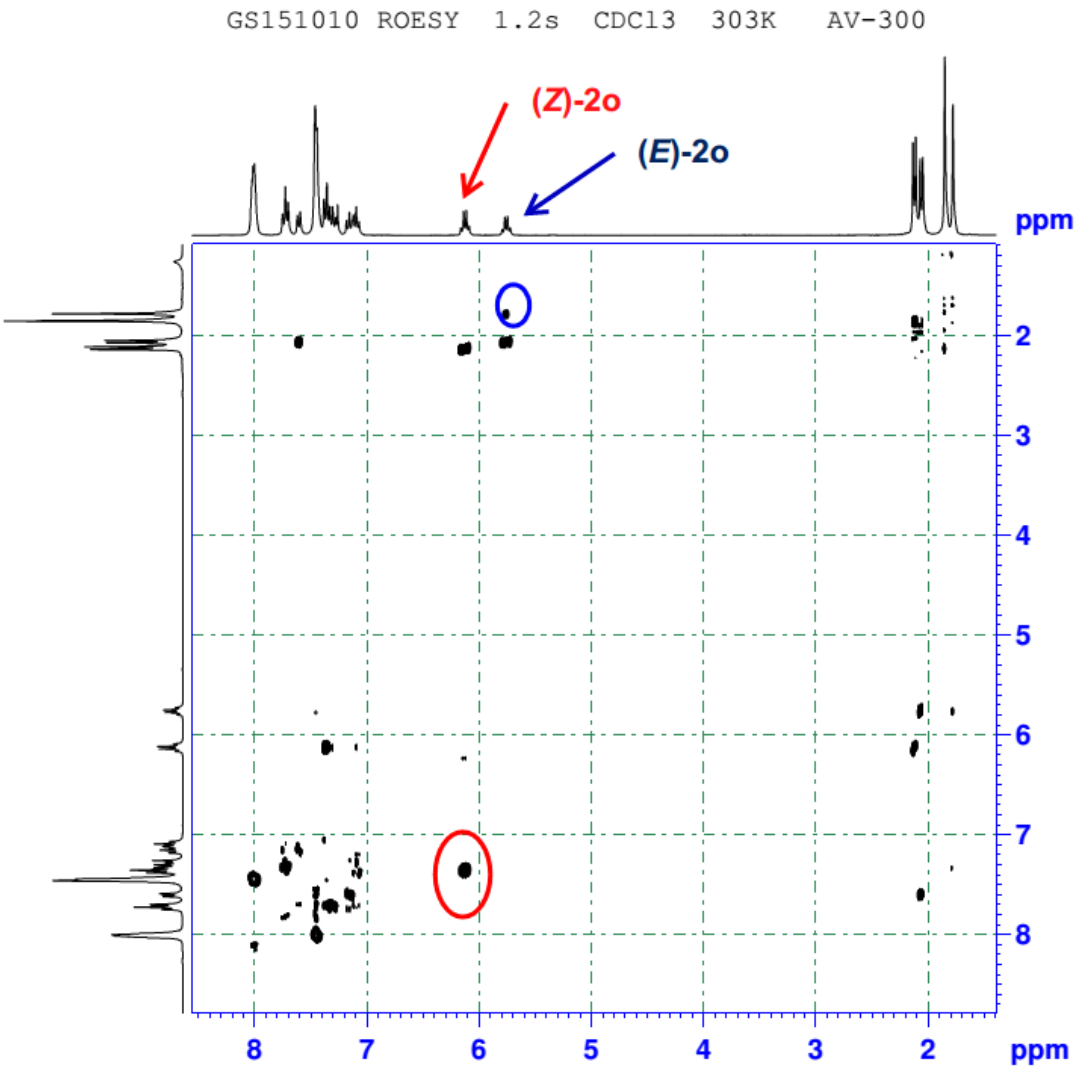
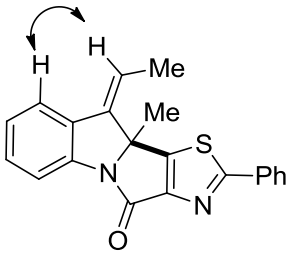
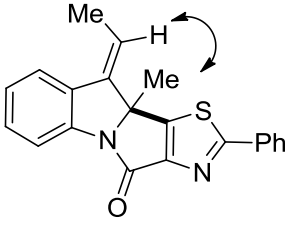
73.7051
30.6219
13C-NMR CDCl3 303K AV-75
4
f1 (ppm)

ROESY spectra of compound 2o





(*Z*)-2o



(*E*)-2o