Supporting Information for

From byproducts to NLO-active dyes: catalyst-free transfer hydrogenation in the modular synthesis of merocyanines

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1. Computational Details

The preliminary calculations (Table S1) were done at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP level of theory with the Gibbs free energy corrections taken at the B3LYP-D3(BJ)/def2-SVP level. [1–4] The solvent effect of acetic anhydride (ε = 21.0) was taken account by the Polarizable Continuum Model (PCM).[5, 6]

The complete reaction mechanisms and potential energy surfaces (Figure 4, and Figure S1 to S3) were calculated at the B3LYP-D3(BJ)/ma-TZVP level in PCM (acetic anhydride, ε = 21.0).[7] The nature of all stationary points (minima and transition state structures) was confirmed by vibrational frequencies calculations. All calculations were performed using Gaussian 16 quantum chemistry software package.[8]

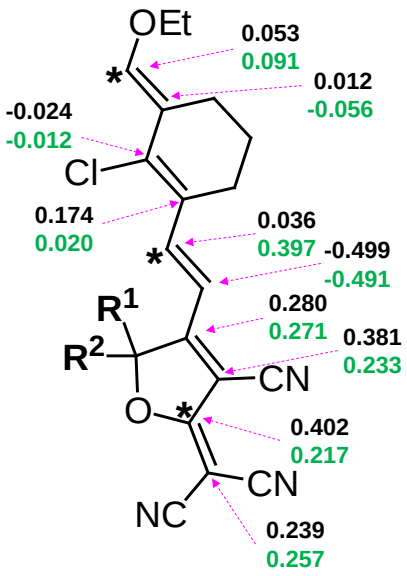
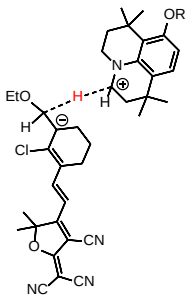
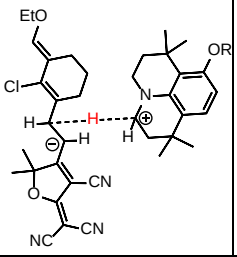
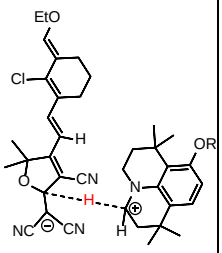
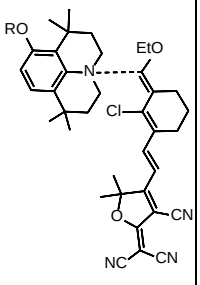
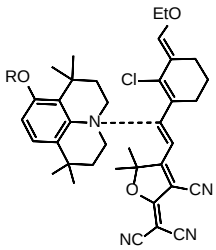
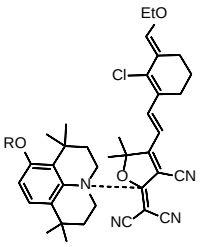


Figure S1. The atomic charges of carbon centers along the polymethine chain of **TCF-A2** (**R**^{1}, **R**^{2} = methyl, in black) and **TCF-A6** (**R**^{1}, **R**^{2} = 4-fluorophenyl, in green) at the B3LYP-D3(BJ)/ma-TZVP level of theory.

Table S1. The activation energy ($\Delta G_{298}^{\ddagger}$, kcal/mol) of the first TS in the initial step of hydride transfer (HT) and nucleophilic addition (NA) pathways, obtained at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP level of theory (Gibbs free energy corrections at the B3LYP-D3(BJ)/def2-SVP level, **R** is -CH_3) and at the B3LYP-D3(BJ)/ma-TZVP level (for both geometrical optimizations and energy corrections). The dielectric constant of 21.0 is used for the solvent of acetic anhydride.

(i) HT pathway			
$\Delta G_{298}^{\ddagger}$ at B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP	**26.5**	**26.3**	**36.5**
$\Delta G_{298}^{\ddagger}$ at B3LYP-D3(BJ)/ma-TZVP	**27.0 (detailed pathway in Figure 4)**	**25.5 (detailed pathway in Figure S3)**	**---**
(ii) NA pathway			
$\Delta G_{298}^{\ddagger}$ at B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP	**37.0**	**not found**	**not found**

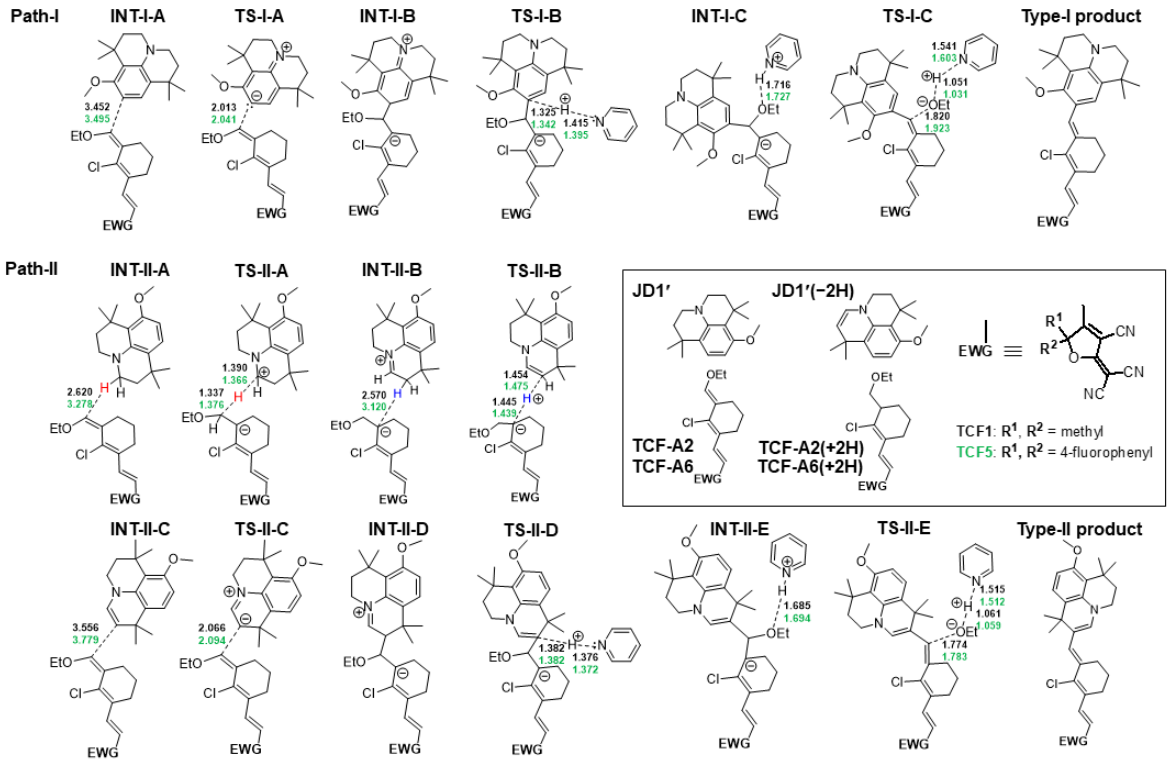


Figure S2. Structures of intermediates (**INT**s) and transition states (**TS**s) for the reactions between 8-methoxyjulolidine (**JD1′**) and two hemicyanine adducts bearing the electron-withdrawing group (EWG) of TCF, namely **TCF-A2** (**TCF1**-based) and **TCF-A6** (**TCF5**-based), by following the **Path I** or **Path II** to form new push-pull chromophores at the B3LYP-D3(BJ)/ma-TZVP level. Bond lengths are in angstrom (Å), black color for **TCF1**-based and green color for **TCF5**-based.

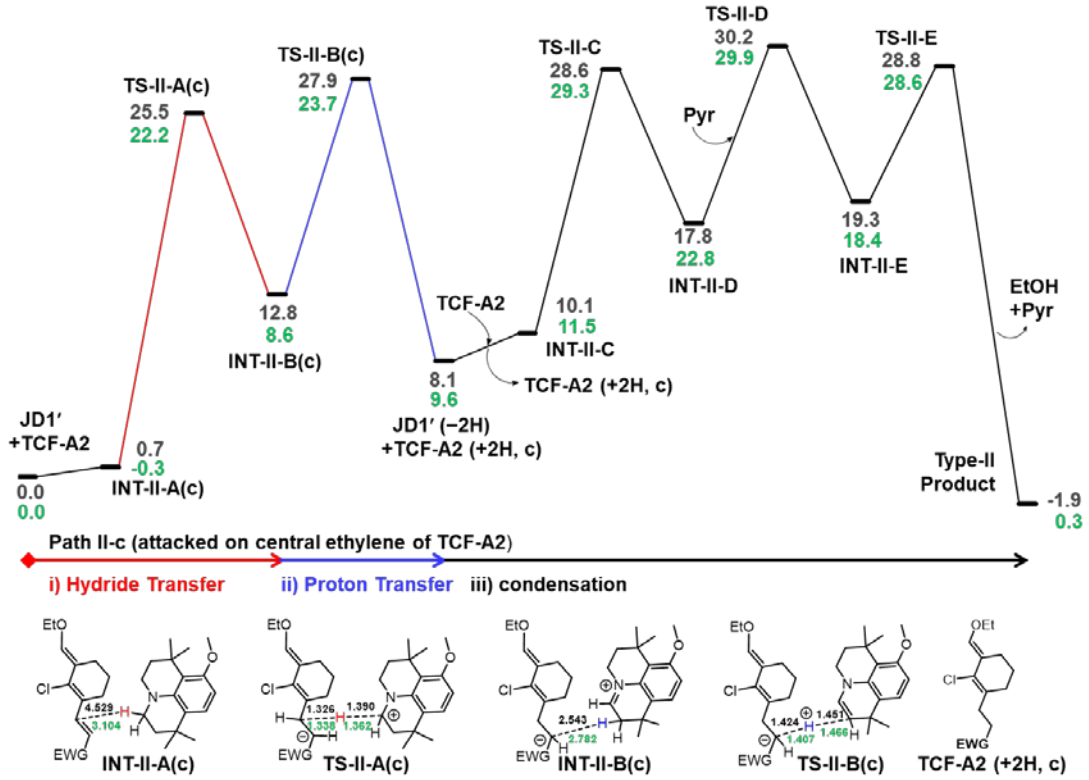


Figure S3. PES and structures of the reactions between 8-methoxyjulolidine (**JD1′**) and π-conjugated TCF acceptor **TCF-A2** (**TCF1**-based) and **TCF-A6** (**TCF5**-based)) by following the **Path II-c** (attacked on central ethylene) to form new push-pull chromophores at the B3LYP-D3(BJ)/ma-TZVP level (ΔG_{298}, kcal/mol). The dielectric constant of 21.0 is used for the solvent of acetic anhydride. The condensation pathway is same as that in Figure 4, except that the PES is elevated by 3.2 kcal/mol for **TCF-A2** and 4.1 kcal/mol for **TCF-A6**, respectively.

2. Synthetic Schemes

2.1 Synthesis of acceptors TCF1-TCF5

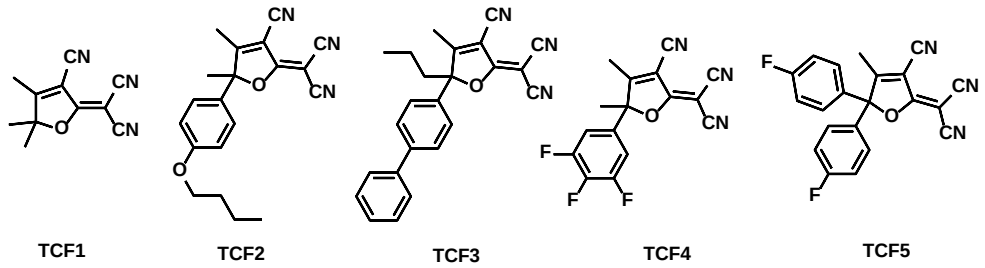
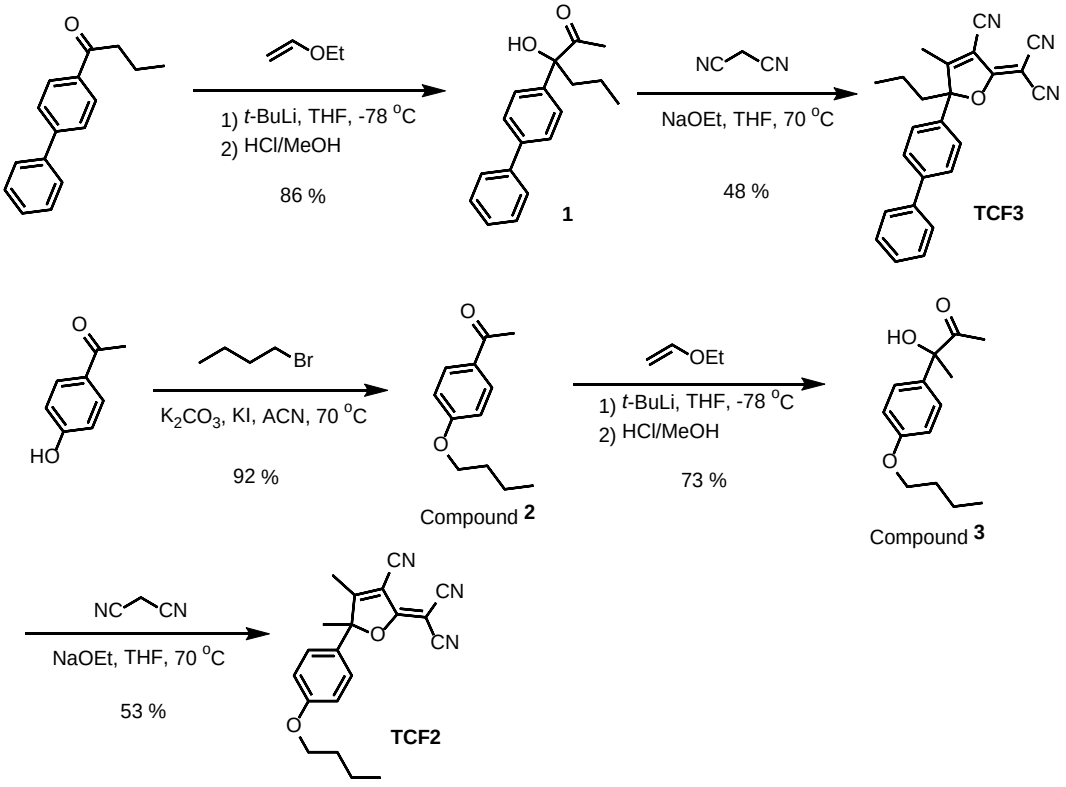


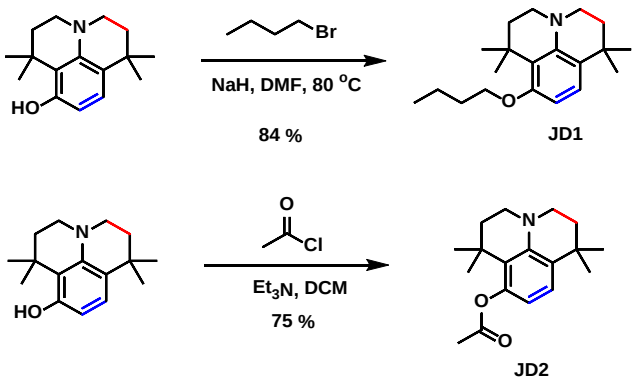
Figure S4. Molecular structures of TCF acceptors **TCF1-TCF5** in this study.

Scheme S1. Synthesis of the **TCF2** and **TCF3** acceptor.



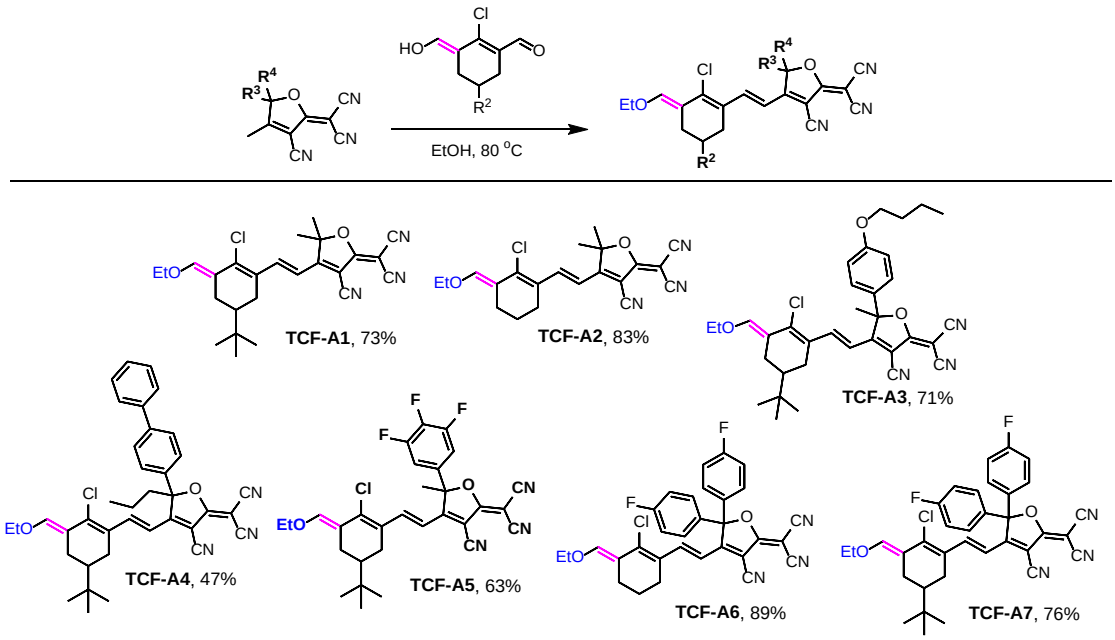
2.2 Synthesis of donor units JD1 and JD2

Scheme S2. Synthesis of the **JD1** and **JD2** donor.



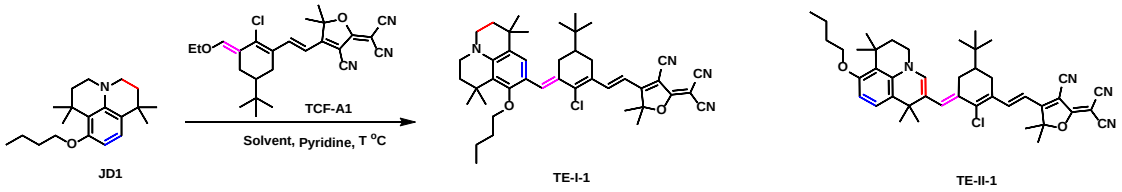
2.3 Synthesis of π-conjugated trienyl precursor with terminal TCF acceptor units TCF-A1 to TCF-A7

Scheme S3. Synthesis of π-conjugated TCF acceptor precursors **TCF-A1** to **TCF-A7**.



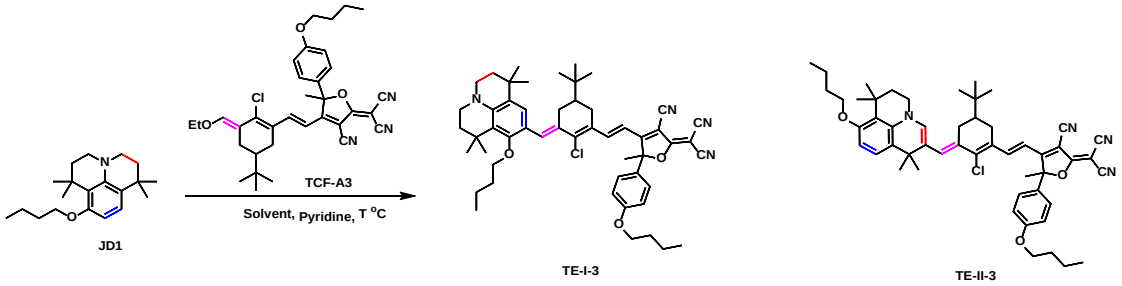
2.4 Optimization reactions of chromophores TE-I-1, TE-I-3 - TE-I-6, TE-II-1, and TE-II-3 - TE-II-6

Table S2. Evaluation of reaction time of **TE-I-1** and **TE-II-1**.



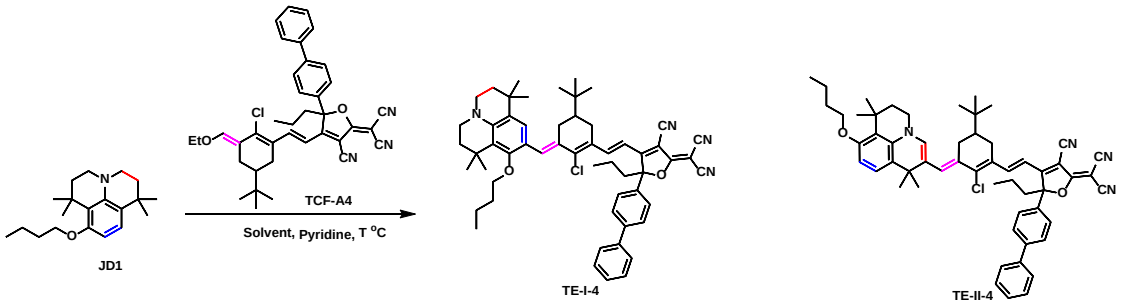
Entry	Solvent	Temperature	Time	**TE-I-1** [%]	**TE-II-1** [%]
1	Ac_2O	80 °C	10 h	-	9
2	Ac_2O	80 °C	14 h	3	27
3	Ac_2O	80 °C	18 h	2	22

Table S3. Evaluation of reaction time of **TE-I-3** and **TE-II-3**.



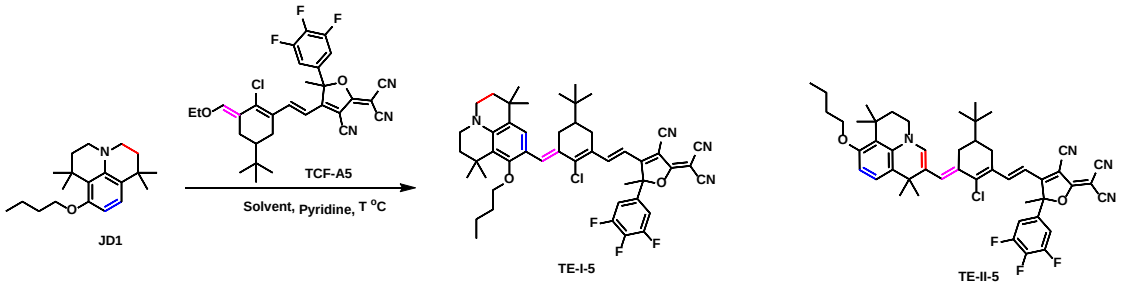
Entry	Solvent	Temperature	Time	**TE-I-3** [%]	**TE-II-3** [%]
1	Ac_2O	80 °C	9.5 h	12	19
2	Ac_2O	80 °C	13.5 h	11	25
3	Ac_2O	80 °C	16 h	6	19

Table S4. Evaluation of reaction time of **TE-I-4** and **TE-II-4**.



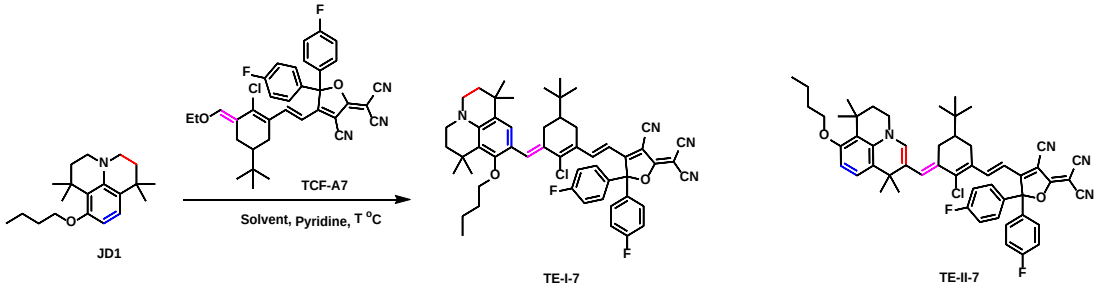
Entry	Solvent	Temperature	Time	**TE-I-4** [%]	**TE-II-4** [%]
1	Ac_2O	80 °C	4 h	10	13
2	Ac_2O	80 °C	6.5 h	19	11
3	Ac_2O	80 °C	15 h	3	4

Table S5. Evaluation of reaction time of **TE-I-5** and **TE-II-5**.



Entry	Solvent	Temperature	Time	**TE-I-5** [%]	**TE-II-5** [%]
1	Ac_2O	80 °C	1h40min	25	4
2	Ac_2O	80 °C	2h	32	5
3	Ac_2O	80 °C	2h20min	8	9

Table S6. Evaluation of reaction time of **TE-I-7** and **TE-II-7**.



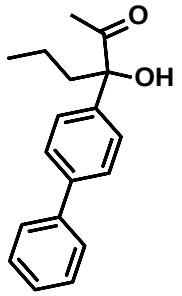
Entry	Solvent	Temperature	Time	**TE-I-7** [%]	**TE-II-7** [%]
1	Ac_2O	80 °C	1 h	26	2
2	Ac_2O	80 °C	1 h 40 min	17	4
3	Ac_2O	80 °C	2 h	21	6

3. Experimental Section

Materials and instruments

All chemicals were purchased from Energy Chemical or Dieckmann, and used as received unless otherwise mentioned. Acceptors **TCF1-TCF5** were synthesized by following the procedure previously reported.[9-11] Donors **JD1** was synthesized by following the procedure previously reported.[12] Hemicyanines **TCF-A1** - **TCF-A7** were synthesized by following the procedure previously reported.[10,13]

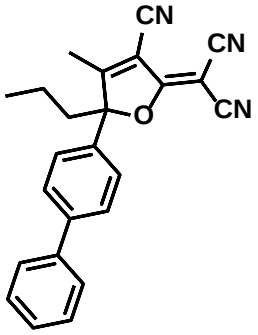
The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 300MHz "AVANCE III HD" Nuclear Magnetic Resonance System (NMR-300), Bruker 400MHz "AVANCE III" Nuclear Magnetic Resonance System (NMR-400) and Bruker 600MHz "AVANCE III HD" Nuclear Magnetic Resonance System (NMR-600). High resolution mass spectrometry (HRMS) was taken at Thermo Scientific Q Exactive mass spectrometer and 4800 Plus MALDI TOF/TOF (SCIEX). For the formulation of EO polymers, the solvent dibromomethane (DBM) and 1,1,2-trichloroethane (TCE) were distilled prior to use. The cyclic voltammetric data were measured by Electrochemical Analyzer (CHI 750) using Ag/AgCl as the reference electrode, the platinum wire as working electrode, platinum gauze (5*5*0.3 mm) as counter electrode and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as the electrolyte in dichloromethane. Films used in absorption spectra and EO measurements were spin-coated on glass or ITO glass substrates with SPIN-PROCESS CONTROLLER. The UV-*vis*-NIR spectra of chromophores were recorded with Ultra-Violet Visible Scanning Spectrophotometer (Shimadzu 1700) and Ultra-Violet Visible Near Infra-red Spectrophotometer with Integrating Sphere (PE Lamda 750).



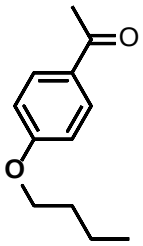
3-([1,1'-biphenyl]-4-yl)-3-hydroxyhexan-2-one (**1**)

To a solution of ethyl vinyl ether (3.0 g, 41.7 mmol) in THF (15 mL) was added 20 mL of *t*-BuLi (1.3 M, 26 mmol) in pentane dropwise at -78 ^{o}C, under nitrogen for 2 h. The solution was warmed on an ice bath and stirred for 1 h. And then cooled to -78 ^{o}C. A solution of 4-phenylbutyrophenone (3.0 g, 13.4 mmol) in THF was added to the lithiated ether solution dropwise at -78 ^{o}C. The resulting mixture was stirred for 1 h at -78 ^{o}C, allowed to warm up to room temperature slowly for 2 h. The reaction was then quenched with 30 ml water, and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over magnesium sulfate. After the solvent was evaporated, the residue was dissolved in 10 mL methanol and 10 mL HCl (aq) (1 M, 10 mmol) was added dropwise at room temperature. After stirring for 2 h, the resulting mixture was neutralized with $NaHCO_3$, concentrated via rotary evaporation, and extracted with CH_2Cl_2. After the solvent was evaporated, the product was purified by chromatogarphy (silica gel, ethyl acetate/hexane) to give a yellow oil (3.1 g, 86 %)

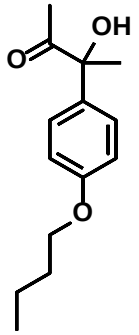
^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.67-7.53 (m, 6H, CH_{Ar}), 7.50-7.41 (m, 2H, CH_{Ar}), 7.41-7.33 (m, 1H, CH_{Ar}), 4.58 (bs, 1H, OH), 2.27-2.17 (m, 2H, CH_2), 2.15 (s, 3H, $COCH_3$), 1.66-1.48 (m, 1H, CH_2), 1.32-1.16 (m, 1H, CH_2), 1.03 (t, *J* = 7.3 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR ($CDCl_3$, 75MHz, ppm): δ 209.59, 140.75, 140.45, 140.03, 128.89, 127.56, 127.37, 127.13, 126.75, 82.64, 38.85, 23.75, 16.69, 14.51.



2-(5-([1,1'-biphenyl]-4-yl)-3-cyano-4-methyl-5-propylfuran-2(*5H*)-ylidene)malononitrile (**TCF3**)
To a solution of compound **1** (5.0 g, 18.7 mmol) and malonitrile (3.7 g, 56.1 mmol) in THF (20 mL) was added 2 mL of a freshly prepared solution of sodium ethoxide (1M, 2 mmol). The reaction mixture was stirred at 70 °C for 24 h, and then purified via flash chromatography on silica gel with a gradient eluent of CH_2Cl_2 to afford a white solid (3.3 g, 48 %).
^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.67 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.61-7.54 (m, 2H, CH_{Ar}), 7.52-7.37 (m, 3H, CH_{Ar}), 7.28 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 2.50 (ddd, *J* = 14.6, 11.7, 4.7 Hz, 1H, CH_2), 2.29 (s, 3H, $COCH_3$), 2.27-2.11 (m, 1H, CH_2), 1.41-1.19 (m, 2H, CH_2), 1.04 (t, *J* = 7.3 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 100MHz, ppm): δ 182.55, 177.13, 142.37, 139.58, 133.54, 129.02, 128.00, 127.74, 126.96, 126.21, 111.41, 110.85, 109.30, 105.10, 104.56, 57.48, 36.86, 16.40, 14.01, 13.19.



1-(4-butoxyphenyl)ethan-1-one (**2**)
A mixture of 1-bromobutane (4.5 g, 33.1 mmol), 4'-hydroxyacetophenone (3.0 g, 22.1 mmol) , potassium carbonate (4.6 g, 33.1 mmol), and KI (0.4 g, 2.2 mmol) was dissolved in acetonitrile (20 mL). The reaction mixture was heated at 75 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into water. The mixture was extracted with CH_2Cl_2 and dried. After the removal of the solvents under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate/hexane) to give a colourless oil. (3.9 g, 92 %).
^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.90-7.80 (m, 2H, CH_{Ar}), 6.88-6.81 (m, 2H, CH_{Ar}), 3.95 (t, *J* = 6.5 Hz, 2H, OCH_2), 2.48 (s, 3H, $COCH_3$), 1.72 (tt, *J* = 12.8, 6.5 Hz, 2H, CH_2), 1.53-1.37 (m, 2H, CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR ($CDCl_3$, 100MHz, ppm): δ 196.61, 163.10, 130.52, 130.04, 114.08, 67.88, 31.11, 26.23, 19.16, 13.78.

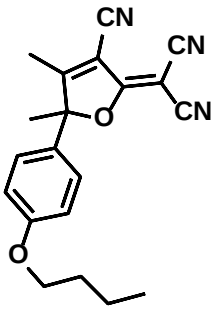


3-(4-butoxyphenyl)-3-hydroxybutan-2-one (**3**)

To a solution of ethyl vinyl ether (2.3 g, 31.2 mmol) in THF (10 mL) was added 16 mL of *t*-BuLi (1.3 M, 20.8 mmol) in pentane dropwise at -78 °C, under nitrogen for 2 h. The solution was warmed on an ice bath and stirred for 1 h. And then cooled to -78 °C. A solution of compund **2** (2.0 g, 10.4 mmol) in THF was added to the lithiated ether solution dropwise at -78 °C. The resulting mixture was stirred for 1h at -78 °C, allowed to warm up to room temperature slowly for 2 h. The reaction was then quenched with 30 ml water, and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over magnesium sulfate. After the solvent was evaporated, the residue was dissolved in 10 mL methanol and 10 mL HCl (aq) (1 M, 10 mmol) was added dropwise at room temperature. After stirring for 2 h, the resulting mixture was neutralized with $NaHCO_3$, concentrated via rotary evaporation, and extracted with CH_2Cl_2. After the solvent was evaporated, the product was purified by chromatogarphy (silica gel, ethyl acetate/hexane) to give a yellow oil (1.8 g, 73 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.33-7.26 (m, 2H, CH_{Ar}), 6.89-6.81 (m, 2H, CH_{Ar}), 4.54 (s, 1H, OH), 3.92 (t, *J* = 6.5 Hz, 2H, OCH_2), 2.03 (s, 3H, $COCH_3$), 1.79-1.63 (m, 5H, CH_2, CH_3), 1.46 (dq, *J* = 14.5, 7.3 Hz, 2H, CH_2), 0.94 (t, *J* = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$, 75MHz, ppm): δ 209.97, 158.91, 133.33, 127.16, 114.53, 79.52, 67.67, 31.28, 24.14, 23.40, 19.23, 13.85.

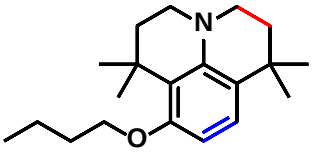


2-(5-(4-butoxyphenyl)-3-cyano-4,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (**TCF2**)

To a solution of compound **3** (1.3 g, 5.5 mmol) and malonitrile (1.1 g, 16.5 mmol) in THF (5 mL) was added 0.5 mL of a freshly prepared solution of sodium ethoxide (1 M, 0.5 mmol). The reaction mixture was stirred at 70 °C for 24 h, and then purified via flash chromatography on silica gel with a gradient eluent of CH_2Cl_2 to afford a white solid (1.0 g, 53 %).

^{1}H NMR ($(CD_3)_2CO$, 300MHz, ppm): δ 7.54-7.36 (m, 2H, CH_{Ar}), 7.10-6.94 (m, 2H, CH_{Ar}), 4.03 (t, *J* = 6.4 Hz, 2H, OCH_2), 2.30 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.82-1.68 (m, 2H, CH_2), 1.56-1.41 (m, 2H, CH_2), 0.96 (t, *J* = 7.4 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR ($(CD_3)_2CO$, 100MHz, ppm): δ 183.25, 176.92, 160.60, 127.60, 125.95, 115.00, 111.54, 110.97, 109.52, 104.96, 102.32, 67.61, 57.02, 31.05, 21.09, 18.96, 13.81, 13.20.

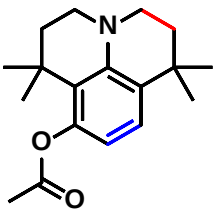


8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinoline (**JD1**)

To a solution of tetramethyljulolidine (3.0 g, 12.2 mmol) and NaH (60 %, dispersion in mineral oil) (0.7 g, 17.5 mmol) in DMF (20 mL) was added 1-bromobutane (2.0 g, 14.6 mmol). The reaction mixture was heated at 80 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into water. The mixture was extracted with CH_2Cl_2 and dried. After the removal of the solvents under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate/hexane) to give a yellow oil. (3.1 g, 84 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.02 (d, *J* = 8.6 Hz, 1H, CH_{Ar}), 6.26 (d, *J* = 8.6 Hz, 1H, CH_{Ar}), 3.95 (t, *J* = 6.4 Hz, 2H, OCH_2), 3.15-2.98 (m, 4H, NCH_2), 1.87-1.73 (m, 6H, CH_2), 1.62-1.49 (m, 2H, CH_2), 1.44 (s, 6H, $C(CH_3)_2$), 1.29 (s, 6H, $C(CH_3)_2$), 1.01 (t, *J* = 7.4 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75MHz, ppm): δ 156.86, 143.47, 124.74, 124.20, 117.93, 100.50, 67.20, 47.74, 47.30, 41.07, 37.59, 32.64, 32.30, 32.23, 31.77, 29.52, 19.77, 13.97.



1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-8-yl acetate (**JD2**)

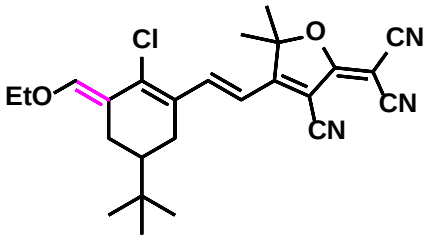
To a solution of tetramethyljulolidine (4.0 g, 16.3 mmol) and Et_3N (3.0 g, 29.4 mmol) in DCM (20 mL) was added acetyl chloride (1.9 g, 24.5 mmol) at 0 °C. The reaction mixture was warmed up to room temperature for 5 h. The reaction mixture was poured into water. The mixture was extracted with CH_2Cl_2 and dried. After the removal of the solvents under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate/hexane) to give a yellow oil. (3.5 g, 75 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.06 (d, *J* = 8.5 Hz, 1H, CH_{Ar}), 6.29 (d, *J* = 8.4 Hz, 1H, CH_{Ar}), 3.16-3.05 (m, 4H, NCH_2), 2.34 (s, 3H, $COCH_3$), 1.84-1.72 (m, 4H, CH_2), 1.37 (s, 6H, $C(CH_3)_2$), 1.30 (s, 6H, $C(CH_3)_2$).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75MHz, ppm): δ 169.93, 148.10, 143.26, 128.40, 124.86, 121.38, 111.21, 47.50, 46.96, 40.09, 37.05, 32.47, 32.20, 31.91, 29.83, 21.90.

General Procedure for the synthesis of compounds TCF-A1 - TCF-A7

Acceptor units **TCF1-TCF5** (2.5 mmol, 1.0 eq) and the bisaldehyde-like precursors (1.5 eq) were mixed in 10 mL EtOH. The reaction mixture was allowed to stir at 80 °C for 12 h and monitored by TLC. The dark red precipitate was collected via filtration.

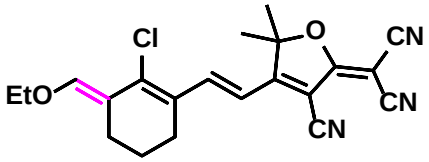


2-(4-((*E*)-2-((*E*)-5-(*tert*-butyl)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (**TCF-A1**).

dark red solid (802 mg, 73 %).

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 8.05 (d, *J* = 15.9 Hz, 1H, =CH), 7.20 (s, 1H, =CH), 6.46 (d, *J* = 15.9 Hz, 1H, =CH), 4.13 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.94 (d, *J* = 15.0 Hz, 1H, CH_2), 2.62 (d, *J* = 15.1 Hz, 1H, CH_2), 2.09 (dd, *J* = 15.7, 12.1 Hz, 1H, CH_2), 1.84 (t, *J* = 14.8 Hz, 1H, CH_2), 1.77 (s, 6H, $C(CH_3)_2$), 1.49-1.40 (m, 1H, CH), 1.38 (t, *J* = 7.1 Hz, 3H, CH_3), 0.99 (s, 9H, $C(CH_3)_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 75MHz, ppm): δ 175.79, 174.52, 153.77, 144.57, 142.93, 128.15, 116.92, 112.91, 112.24, 111.47, 110.63, 97.57, 97.35, 70.62, 56.14, 42.07, 32.33, 27.48, 27.32, 26.95, 26.90, 24.94, 15.49.

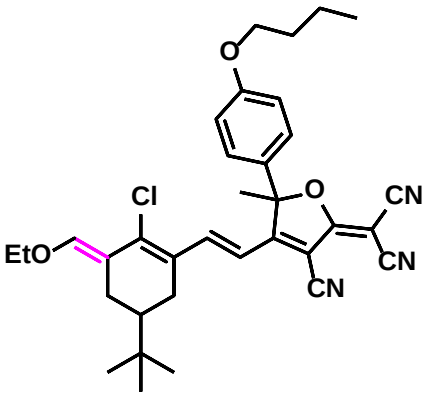


2-(4-((*E*)-2-((*E*)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (**TCF-A2**).

dark red solid (795 mg , 83 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 8.05 (d, *J* = 15.9 Hz, 1H, =CH), 7.20 (s, 1H, =CH), 6.47 (d, *J* = 15.9 Hz, 1H, =CH), 4.12 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.50 (dt, *J* = 9.6, 4.9 Hz, 4H, CH_2), 1.84-1.74 (m, 8H, CH_2, $C(CH_3)_2$), 1.36 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$, 150MHz, ppm): δ 175.78, 174.52, 153.86, 144.36, 142.96, 128.00, 116.22, 113.18, 112.22, 111.44, 110.66, 97.63, 97.37, 70.59, 56.16, 26.85, 26.32, 23.76, 20.45, 15.45.



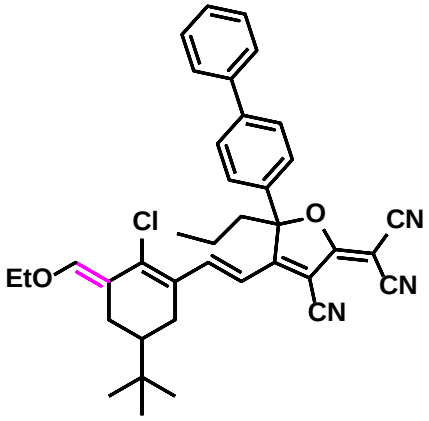
2-(5-(4-butoxyphenyl)-4-((*E*)-2-((*E*)-5-(*tert*-butyl)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5-methylfuran-2(*5H*)-ylidene)malononitrile (**TCF-A3**).

dark red solid (610 mg , 71 %).

^{1}H NMR ($CDCl_3$, 600MHz, ppm): δ 7.58 (dd, *J* = 21.3, 15.8 Hz, 1H, =CH), 7.25-7.18 (m, 2H, CH_{Ar}), 7.09 (s, 1H, =CH), 6.96-6.88 (m, 2H, CH_{Ar}), 6.47 (dd, *J* = 15.7, 2.6 Hz, 1H, =CH), 4.11-4.02 (m, 2H, OCH_2),

4.02-3.91 (m, 2H, OCH_2), 2.86 (d, *J* = 14.9 Hz, 1H, CH_2), 2.52 (dd, *J* = 9.5, 6.4 Hz, 1H, CH_2), 2.11 (d, *J* = 3.0 Hz, 3H, CH_3), 2.02-1.94 (m, 1H, CH_2), 1.82-1.71 (m, 3H, CH_2), 1.52-1.43 (m, 2H, CH_2), 1.38-1.29 (m, 4H, CH, CH_3), 0.99-0.93 (m, 12H, CH_3, $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 150MHz, ppm): δ 175.90, 175.88, 174.32, 174.27, 160.61, 153.50, 153.47, 146.23, 146.13, 142.74, 128.29, 128.26, 127.48, 127.42, 127.36, 127.31, 116.96, 115.25, 115.23, 113.18, 113.13, 112.10, 111.55, 110.56, 98.94, 98.92, 98.18, 98.16, 70.51, 67.94, 56.46, 56.44, 42.07, 41.96, 32.28, 31.15, 27.39, 27.31, 27.28, 24.96, 24.91, 24.88, 19.20, 15.42, 13.83.

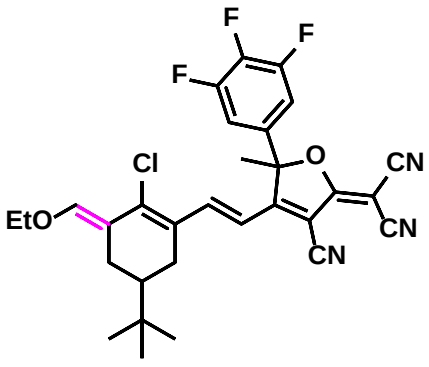


3-(5-([1,1'-biphenyl]-4-yl)-4-((*E*)-2-((*E*)-5-(*tert*-butyl)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5-propylfuran-2(*5H*)-ylidene)malononitrile (**TCF-A4**).

dark red solid (389 mg , 47 %).

^1H NMR ($CDCl_3$, 400MHz, ppm): δ 7.73 (dd, *J* = 15.7, 4.8 Hz, 1H, =CH), 7.68-7.54 (m, 4H, CH_{Ar}), 7.42 (dt, *J* = 17.1, 8.0 Hz, 5H, CH_{Ar}), 7.11 (s, 1H, =CH), 6.50 (dd, *J* = 15.7, 7.0 Hz, 1H, =CH), 4.08 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.88 (d, *J* = 15.0 Hz, 1H, CH_2), 2.77-2.65 (m, 1H, CH_2), 2.58-2.39 (m, 2H, CH_2), 2.02 (dd, *J* = 15.7, 12.1 Hz, 1H, CH_2), 1.78 (t, *J* = 14.6 Hz, 1H, CH_2), 1.39-1.21 (m, 6H, CH, CH_2, CH_3), 1.08-1.00 (m, 3H, CH_3), 0.95 (s, 9H, $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 150MHz, ppm): δ 176.62, 176.57, 172.84, 172.77, 153.72, 153.66, 145.80, 145.65, 143.16, 143.06, 142.03, 139.66, 134.96, 134.88, 129.05, 128.97, 128.43, 128.27, 128.09, 128.03, 127.17, 126.36, 126.30, 126.24, 121.70, 117.02, 116.99, 113.22, 113.19, 112.02, 111.47, 110.52, 110.48, 102.16, 101.37, 101.34, 99.01, 98.84, 70.56, 56.24, 56.21, 43.40, 42.00, 41.92, 39.23, 39.13, 32.43, 32.30, 27.40, 27.29, 26.95, 24.88, 16.58, 16.40, 15.43, 13.99.

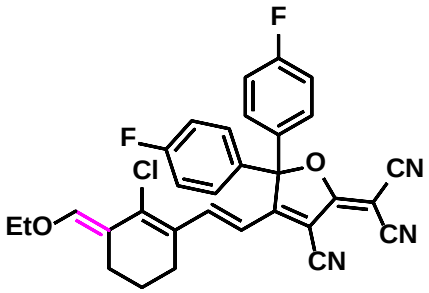


2-(4-((*E*)-2-((*E*)-5-(*tert*-butyl)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5-methyl-5-(3,4,5-trifluorophenyl)furan-2(*5H*)-ylidene)malononitrile (**TCF-A5**)

dark red solid (554 mg , 63 %).

^{1}H NMR ($CDCl_3$, 600MHz, ppm): δ 7.55 (t, *J* = 16.0 Hz, 1H, =CH), 7.18 (s, 1H, =CH), 7.01 (dd, *J* = 12.1, 5.7 Hz, 2H, CH_{Ar}), 6.45 (d, *J* = 15.7 Hz, 1H, =CH), 4.11 (qd, *J* = 7.1, 3.3 Hz, 2H, OCH_2), 2.89 (d, *J* = 14.9 Hz, 1H, CH_2), 2.61-2.49 (m, 1H, CH_2), 2.11 (d, *J* = 3.4 Hz, 3H, CH_3), 2.05-1.97 (m, 1H, CH_2), 1.82-1.75 (m, 1H, CH_2), 1.40-1.31 (m, 4H, CH, CH_3), 0.96 (s, 9H, $C(CH_3)_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 150MHz, ppm): δ 175.19, 171.98, 171.95, 154.66, 154.59, 152.53, 150.76, 146.20, 146.09, 144.13, 132.51, 128.33, 128.29, 117.22, 117.19, 112.47, 111.58, 111.26, 111.22, 111.11, 110.97, 110.19, 98.19, 98.14, 96.50, 70.84, 70.83, 57.68, 42.01, 41.90, 32.29, 27.41, 27.30, 27.27, 24.91, 24.89, 24.83, 24.78, 15.43.

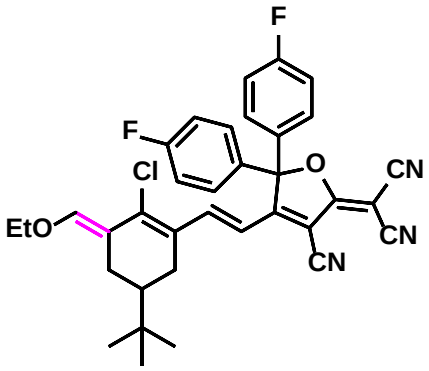


2-(4-((*E*)-2-((*E*)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-bis(4-fluorophenyl)furan-2(*5H*)-ylidene)malononitrile (**TCF-A6**)

dark red solid (672 mg , 89 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.84 (d, *J* = 15.7 Hz, 1H, =CH), 7.28 (dd, *J* = 5.0, 2.0 Hz, 3H, CH_{Ar}), 7.26-7.23 (m, 1H, CH_{Ar}), 7.18-7.11 (m, 5H, =CH, CH_{Ar}), 6.54 (d, *J* = 15.7 Hz, 1H, =CH), 4.09 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.41 (dt, *J* = 11.4, 6.0 Hz, 4H, CH_2), 1.83-1.63 (m, 2H, CH_2), 1.34 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$, 150MHz, ppm): δ 175.28, 170.62, 164.36, 162.69, 154.50, 146.80, 144.07, 132.37, 132.35, 130.25, 130.19, 129.49, 129.43, 128.19, 116.89, 116.74, 116.47, 116.39, 116.24, 114.47, 111.68, 111.05, 110.68, 102.00, 98.41, 70.72, 58.48, 57.35, 26.15, 23.67, 20.29, 18.44, 16.13, 15.41.



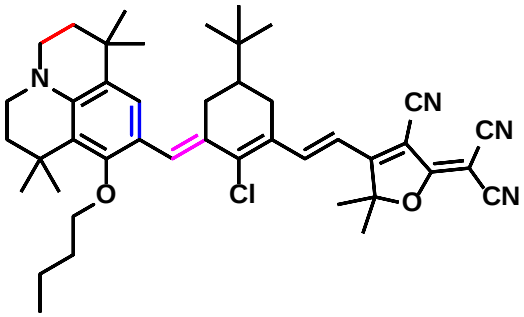
2-(4-((*E*)-2-((*E*)-5-(*tert*-butyl)-2-chloro-3-(ethoxymethylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-bis(4-fluorophenyl)furan-2(*5H*)-ylidene)malononitrile (**TCF-A7**)

dark red solid (633 mg , 76 %).

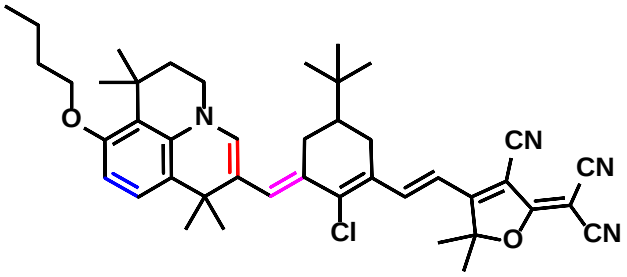
^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.76 (d, *J* = 15.7 Hz, 1H, =CH), 7.32-7.26 (m, 3H, CH_{Ar}), 7.24 (t, *J* = 2.6 Hz, 1H, CH_{Ar}), 7.21-7.08 (m, 5H, =CH, CH_{Ar}), 6.57 (d, *J* = 15.7 Hz, 1H, =CH), 4.09 (q, *J* = 7.1 Hz, 2H,

OCH_2), 2.87 (d, *J* = 14.8 Hz, 1H, CH_2), 2.52 (d, *J* = 14.6 Hz, 1H, CH_2), 1.99 (dd, *J* = 15.9, 12.0 Hz, 1H, CH_2), 1.86-1.70 (m, 1H, CH_2), 1.43-1.27 (m, 4H, CH, CH_3), 0.95 (s, 9H, $C(CH_3)_3$).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100MHz, ppm): δ 175.25, 170.65, 164.74, 162.24, 154.46, 147.23, 144.04, 132.41, 132.38, 132.32, 132.29, 130.35, 130.27, 130.18, 128.38, 117.19, 116.41, 116.39, 116.19, 116.17, 114.22, 111.71, 111.10, 110.58, 102.00, 98.55, 70.76 , 57.26, 41.88, 32.29, 27.30, 27.26, 24.85, 15.45.

General Procedure for the synthesis of Chromophores TE-I-1 - TE-I-9 and TE-II-1 - TE-II-8
Acceptor units **TCF-A1 - TCF-A7** (110 mg, 1.0 eq) and compound **JD1-JD2** (1.1 eq) were mixed in 2 mL of acetic anhydride, and two drops of pyridine was added. The reaction mixture was allowed to stir at 80 ^oC for corresponding reaction time and monitored by TLC. After removal of the solvents, the crude product was purified by flash chromatography eluting with ethyl acetate/hexane to give a dark solid.



2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-9-yl) methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)ma lononitrile (**TE-I-1**).
14 h, dark solid (5 mg , 3 %).
^1H NMR (CD_2Cl_2, 600MHz, ppm): δ 8.23 (d, *J* = 15.8 Hz, 1H, =CH), 7.60 (s, 1H, =CH), 7.16 (s, 1H, CH_{Ar}), 6.55 (d, *J* = 15.8 Hz, 1H, =CH), 3.87-3.71 (m, 2H, OCH_2), 3.32-3.10 (m, 5H, NCH_2, CH_2), 2.72 (d, *J* = 14.6 Hz, 1H, CH_2), 2.29 (dt, *J* = 15.8, 12.9 Hz, 2H, CH_2), 1.84-1.70 (m, 12H, CH_2, $C(CH_3)_2$), 1.53-1.49 (m, 2H, CH_2), 1.41 (d, *J* = 9.4 Hz, 6H, $C(CH_3)_2$), 1.31-1.22 (m, 7H, CH, $C(CH_3)_2$), 1.02-0.92 (m, 12H, CH_3, $C(CH_3)_3$).
$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150MHz, ppm): 175.94, 174.21, 158.37, 146.13, 145.10, 144.41, 134.40, 130.71, 130.64, 126.66, 125.54, 122.39, 117.00, 113.87, 112.34, 111.73, 110.88, 97.51, 97.44, 75.41, 55.69, 47.34, 46.77, 43.03, 39.90, 36.24, 32.57, 32.26, 32.24, 32.10, 31.15, 30.48, 29.88, 29.73, 27.74, 27.10, 26.67, 26.59, 22.64, 19.44, 13.92, 13.86.
HR-MS calcd for $C_{43}H_{53}ClN_4O_2$ $[M+H]^+$ m/z 693.39298, found m/z 693.39276.



2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-6,7-dihydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-2-yl)methyl ene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)malononit

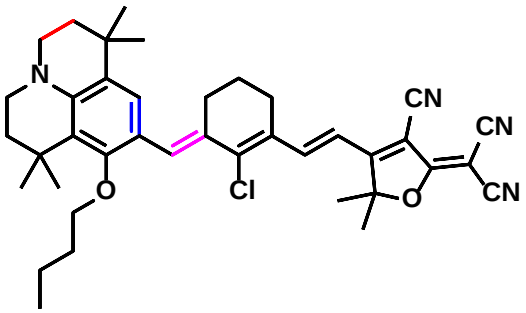
rile (**TE-II-1**).

14 h, dark solid (47 mg, 27 %).

^{1}H NMR (CD_2Cl_2, 600MHz, ppm): δ 8.22 (d, *J* = 15.6 Hz, 1H, =CH), 7.41 (s, 0.25H, =CH), 7.34 (s, 0.74H, =CH), 7.13 (dd, *J* = 13.5, 8.7 Hz, 1H, CH_{Ar}), 6.57 (t, *J* = 9.3 Hz, 1H, CH_{Ar}), 6.54-6.42 (m, 2H, =CH), 3.98 (dt, *J* = 17.0, 6.5 Hz, 2H, OCH_2), 3.65-3.47 (m, 2H, NCH_2), 3.14 (d, *J* = 14.2 Hz, 1H, CH_2), 2.70 (d, *J* = 15.9 Hz, 1H, CH_2), 2.28-2.09 (m, 2H, CH_2), 1.82 (dt, *J* = 9.9, 5.7 Hz, 4H, CH_2), 1.77 (s, 6H, $C(CH_3)_2$), 1.57-1.48 (m, 4H, CH, CH_3), 1.47-1.39 (m, 9H, CH_3, $C(CH_3)_2$), 1.30 (d, *J* = 4.9 Hz, 2H, CH_2), 1.02-0.98 (m, 12H, CH_3, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.20, 173.86, 156.78, 156.25, 146.44, 144.98, 137.71, 136.33, 134.78, 134.16, 133.08, 130.36, 129.40, 125.36, 125.19, 124.72, 124.66, 119.67, 118.61, 117.95, 115.43, 112.70, 112.47, 112.29, 112.09, 111.33, 106.87, 106.51, 100.00, 97.19, 97.14, 95.56, 67.81, 54.58, 47.92, 47.63, 43.11, 43.07, 39.72, 36.68, 36.37, 36.13, 32.65, 32.42, 32.20, 32.11, 31.95, 31.58, 31.56, 31.54, 31.21, 30.96, 30.80, 29.40, 28.17, 28.14, 27.51, 27.13, 26.72, 26.70, 26.64, 26.61, 22.65, 19.72, 19.64, 13.88, 13.63.

HR-MS calcd for $C_{43}H_{51}ClN_4O_2$ $[M+H]^+$ m/z 691.37733, found m/z 691.37701.



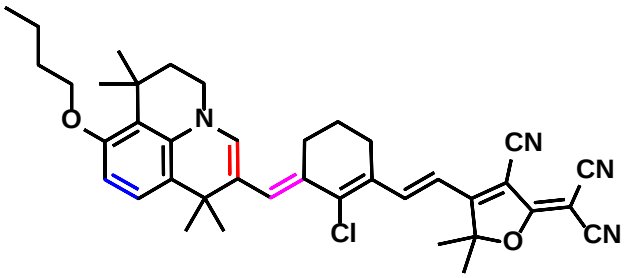
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-9-yl) methylene)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (**TE-I-2**).

14h, dark solid (7 mg , 4 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 8.19 (d, *J* = 15.9 Hz, 1H, =CH), 7.59 (s, 1H, =CH), 7.10 (s, 1H, CH_{Ar}), 6.56 (d, *J* = 15.8 Hz, 1H, =CH), 3.79 (dd, *J* = 8.5, 4.8 Hz, 2H, OCH_2), 3.48-3.02 (m, 4H, NCH_2), 2.83 (dd, *J* = 13.0, 7.6 Hz, 2H, CH_2), 2.61 (t, *J* = 6.0 Hz, 2H, CH_2), 1.91-1.68 (m, 14H, CH_2, $C(CH_3)_2$), 1.49 (dd, *J* = 10.1, 4.9 Hz, 2H, CH_2), 1.42 (d, *J* = 8.5 Hz, 6H, $C(CH_3)_2$), 1.25 (s, 6H, $C(CH_3)_2$), 0.96 (t, *J* = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 175.93, 175.75, 174.28, 174.23, 158.31, 157.47, 146.22, 144.88, 144.76, 144.43, 138.42, 134.70, 133.71, 133.50, 131.90, 131.56, 130.67, 130.27, 128.69, 126.80, 126.69, 125.53, 124.82, 123.21, 122.35, 121.44, 117.02, 115.07, 114.15, 112.32, 111.73, 111.44, 110.89, 110.65, 108.69, 99.99, 97.73, 97.54, 75.37, 75.11, 75.03, 55.70, 47.35, 46.77, 46.06, 45.69, 39.91, 39.79, 36.29, 35.83, 34.07, 33.41, 33.32, 33.17, 32.77, 32.55, 32.27, 32.20, 32.10, 31.58, 30.72, 29.81, 29.54, 29.14, 28.88, 26.70, 26.60, 26.55, 21.75, 21.71, 19.44, 19.39, 13.92.

HR-MS calcd for $C_{39}H_{45}ClN_4O_2$ $[M+H]^+$ m/z 637.33038, found m/z 637.33002.



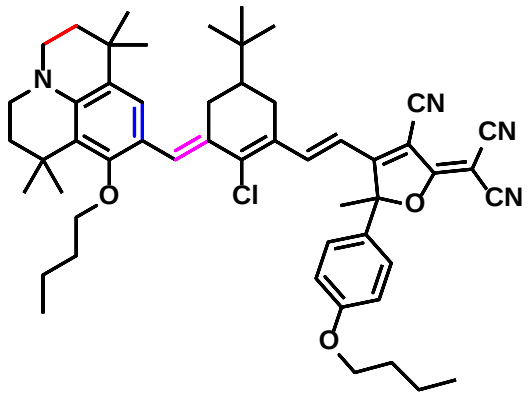
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-6,7-dihydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-2-yl)methylene)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (**TE-II-2**).

14h, dark solid (40 mg , 22 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 8.18 (d, *J* = 15.6 Hz, 1H, =CH), 7.36 (s, 1H, =CH), 7.14 (d, *J* = 8.7 Hz, 1H, CH_{Ar}), 6.51 (dd, *J* = 31.5, 12.0 Hz, 3H, =CH, CH_{Ar}), 3.96 (t, *J* = 6.4 Hz, 2H, OCH_2), 3.60-3.48 (m, 2H, NCH_2), 2.77 (s, 2H, CH_2), 2.57 (t, *J* = 5.7 Hz, 2H, CH_2), 1.89-1.71 (m, 12H, CH_2, $C(CH_3)_2$), 1.60-1.50 (m, 2H, CH_2), 1.43 (d, *J* = 5.3 Hz, 12H, $C(CH_3)_2$), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (CD_2Cl_2, 100MHz, ppm): δ 176.21, 173.81, 156.76, 146.68, 144.78, 136.91, 136.63, 134.01, 129.48, 129.21, 124.77, 124.71, 119.74, 115.53, 112.76, 112.55, 112.15, 111.41, 106.59, 99.99, 97.15, 95.43, 67.80, 54.40, 47.64, 39.68, 36.30, 32.64, 32.24, 32.10, 31.53, 30.87, 29.87, 28.12, 26.66, 26.26, 21.48, 19.72, 19.64, 13.64.

HR-MS calcd for $C_{39}H_{43}ClN_4O_2$ $[M+H]^+$ m/z 635.31473, found m/z 635.31439.



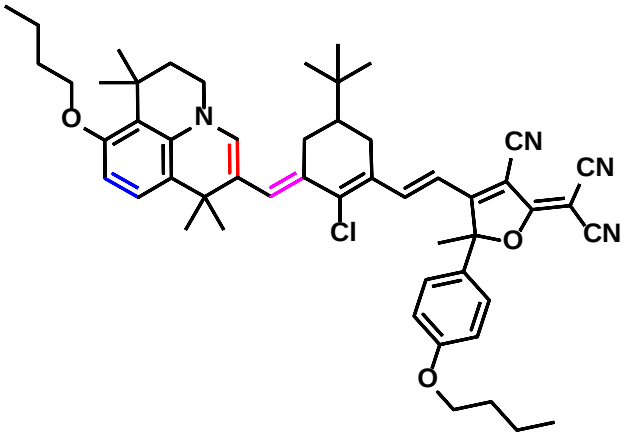
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-9-yl)methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-5-(4-butoxyphenyl)-3-cyano-5-methylfuran-2(*5H*)-ylidene)malononitrile **(TE-I-3)**.

13.5 h, dark solid (17 mg , 11 %).

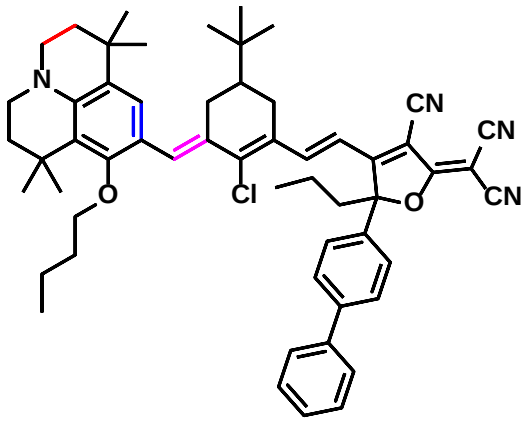
^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.73 (dd, J = 15.7, 6.5 Hz, 1H, =CH), 7.52 (s, 1H, =CH), 7.33 (dd, J = 8.9, 2.9 Hz, 2H, CH_{Ar}), 7.13 (d, J = 5.9 Hz, 1H, CH_{Ar}), 6.99 (dd, J = 8.8, 5.4 Hz, 2H, CH_{Ar}), 6.62 (d, J = 15.7 Hz, 1H, =CH), 4.01 (q, J = 6.1 Hz, 2H, OCH_2), 3.89-3.68 (m, 2H, OCH_2), 3.34-3.10 (m, 5H, NCH_2, CH_2), 2.66 (d, J = 15.4 Hz, 1H, CH_2), 2.36-2.13 (m, 5H, CH_2, CH_3), 1.89-1.68 (m, 8H, CH_2), 1.52 (dd, J = 14.9, 7.5 Hz, 4H, CH_2), 1.43 (d, J = 5.5 Hz, 6H, $C(CH_3)_2$), 1.33-1.21 (m, 7H, CH, $C(CH_3)_2$), 1.06-0.89 (m, 15H, CH_3, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.04, 176.01, 173.88, 173.84, 160.71, 160.69, 158.36, 146.68, 146.52, 146.15, 146.13, 144.41, 134.37, 130.73, 130.71, 127.59, 127.52, 127.45, 126.64, 125.53, 122.35, 116.98, 115.15, 115.12, 114.08, 112.24, 111.80, 110.74, 99.02, 98.05, 75.36, 68.00, 55.97, 55.94, 47.33,

46.76, 43.00, 42.90, 39.89, 36.22, 32.55, 32.22, 32.18, 32.07, 31.16, 31.14, 31.12, 30.44, 29.86, 29.71, 29.69, 27.64, 27.56, 27.07, 24.69, 24.63, 19.41, 19.37, 19.17, 19.15, 13.91, 13.88, 13.58.
HR-MS calcd for $C_{52}H_{63}ClN_4O_3$ $[M+H]^+$ m/z 827.46615, found m/z 827.46582.



2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-6,7-dihydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-2-yl)methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-5-(4-butoxyphenyl)-3-cyano-5-methylfuran-2(*5H*)-ylidene)malononitrile (**TE-II-3**).
13.5 h, dark solid (40 mg , 25 %).
^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.70-7.45 (m, 1H, =CH), 7.22 (dd, *J* = 10.5, 7.7 Hz, 3H, CH_{Ar}, =CH), 7.12 (d, *J* = 8.6 Hz, 1H, CH_{Ar}), 6.92 (dd, *J* = 8.8, 3.7 Hz, 2H, CH_{Ar}), 6.69-6.15 (m, 3H, CH_{Ar}, =CH), 4.12-3.87 (m, 4H, OCH_2), 3.49 (s, 2H, NCH_2), 3.15-2.89 (m, 1H, CH_2), 2.56 (d, *J* = 15.3 Hz, 1H, CH_2), 2.21-1.91 (m, 5H, CH_2, CH_3), 1.71-1.86 (m, 6H, CH_2), 1.58-1.49 (m, 4H, CH_2), 1.45 (t, *J* = 3.4 Hz, 6H, $C(CH_3)_2$), 1.39 (dd, *J* = 10.4, 5.1 Hz, 6H, $C(CH_3)_2$), 1.30 (d, *J* = 2.6 Hz, 1H, CH), 1.05-0.85 (m, 15H, CH_3, $C(CH_3)_3$).
^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.25, 173.53, 160.56, 156.77, 146.48, 146.43, 137.74, 136.43, 136.36, 136.04, 134.07, 130.34, 130.28, 129.47, 127.95, 127.84, 127.62, 127.54, 125.37, 124.71, 124.66, 119.72, 115.52, 115.09, 112.71, 112.62, 112.18, 111.15, 106.56, 98.64, 96.13, 67.99, 67.81, 54.78, 47.66, 43.03, 42.93, 39.68, 36.64, 36.34, 36.10, 32.64, 32.40, 32.14, 32.09, 31.98, 31.90, 31.53, 31.17, 31.15, 30.93, 30.77, 29.40, 28.14, 27.40, 27.28, 27.09, 24.75, 24.69, 19.71, 19.63, 19.16, 13.62, 13.58.
HR-MS calcd for $C_{52}H_{61}ClN_4O_3$ $[M+H]^+$ m/z 825.45050, found m/z 825.45020.



2-(5-([1,1'-biphenyl]-4-yl)-4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H*,*5H*-pyrid

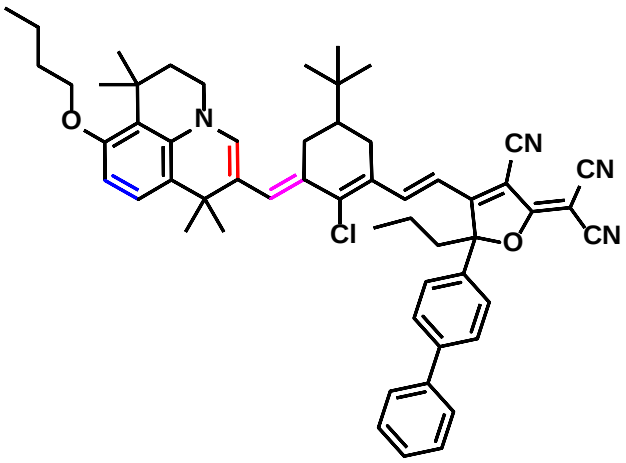
o[3,2,1-*ij*]quinolin-9-yl)methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5-propylfuran-2(*5H*)-ylidene)malononitrile (**TE-I-4**).

6.5h, dark solid (30 mg , 19 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.79 (d, *J* = 15.6 Hz, 1H, =CH), 7.66 (t, *J* = 8.1 Hz, 2H, CH_{Ar}), 7.56 (dd, *J* = 14.8, 7.9 Hz, 3H, CH_{Ar}, =CH), 7.50-7.33 (m, 5H, CH_{Ar}), 7.08 (d, *J* = 7.2 Hz, 1H, CH_{Ar}), 6.59 (dd, *J* = 15.6, 5.7 Hz, 1H, =CH), 3.76 (dd, *J* = 13.1, 6.4 Hz, 2H, OCH_2), 3.18 (t, *J* = 15.5 Hz, 5H, NCH_2, CH_2), 2.73 (dd, *J* = 17.9, 7.7 Hz, 1H, CH_2), 2.54 (dd, *J* = 28.8, 14.7 Hz, 2H, CH_2), 2.16 (dd, *J* = 28.0, 15.3 Hz, 2H, CH_2), 1.78 (d, *J* = 14.5 Hz, 6H, CH_2), 1.52-1.36 (m, 10H, CH_2, $C(CH_3)_2$), 1.23 (dd, *J* = 21.3, 5.5 Hz, 7H, CH, $C(CH_3)_2$), 1.07 (t, *J* = 7.4 Hz, 3H, CH_3), 0.99-0.88 (m, 12H, CH_3, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.72, 176.67, 172.33, 172.29, 158.43, 146.48, 146.28, 146.11, 144.49, 143.04, 143.02, 139.69, 139.67, 135.25, 135.14, 134.60, 130.71, 130.69, 128.91, 128.89, 128.00, 127.94, 127.08, 126.65, 126.49, 126.39, 125.54, 122.35, 116.99, 114.11, 114.08, 112.15, 111.78, 110.72, 110.69, 101.41, 98.78, 98.60, 75.41, 55.72, 55.70, 47.34, 46.76, 42.95, 42.85, 39.86, 39.08, 38.99, 36.19, 32.54, 32.23, 32.19, 32.07, 31.58, 31.09, 30.43, 30.40, 29.84, 29.68, 27.65, 27.54, 27.07, 22.65, 19.41, 19.35, 16.41, 13.90, 13.87, 13.85, 13.69.

HR-MS calcd for $C_{56}H_{63}ClN_4O_2$ $[M+H]^+$ m/z 859.47123, found m/z 859.47076.



2-(5-([1,1'-biphenyl]-4-yl)-4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-6,7-dihydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-2-yl)methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5-propylfuran-2(*5H*)-ylidene)malononitrile (**TE-II-4**).

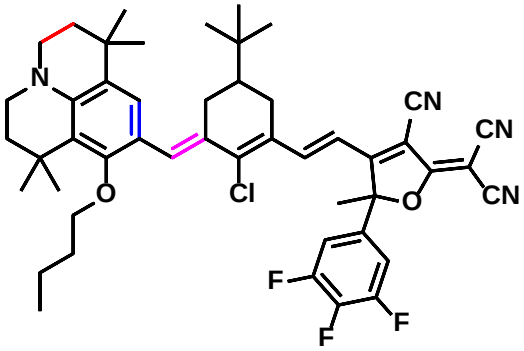
6.5h, dark solid (17 mg , 11 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.85 (d, *J* = 15.4 Hz, 1H, =CH), 7.74 (dd, *J* = 8.5, 3.9 Hz, 2H, CH_{Ar}), 7.66 (t, *J* = 6.0 Hz, 2H, CH_{Ar}), 7.50 (ddd, *J* = 12.0, 6.2, 4.1 Hz, 4H, CH_{Ar}), 7.46-7.40 (m, 1H, CH_{Ar}), 7.33 (d, *J* = 19.3 Hz, 1H, =CH), 7.15 (dd, *J* = 8.7, 2.2 Hz, 1H, CH_{Ar}), 6.68-6.41 (m, 3H, CH_{Ar}, =CH), 4.00 (dd, *J* = 11.8, 5.5 Hz, 2H, OCH_2), 3.55 (dd, *J* = 11.3, 5.2 Hz, 2H, NCH_2), 3.09 (d, *J* = 13.9 Hz, 1H, CH_2), 2.84-2.43 (m, 3H, CH_2), 2.15 (ddd, *J* = 28.6, 18.5, 8.4 Hz, 2H, CH_2), 1.92-1.78 (m, 4H, CH_2), 1.62-1.53 (m, 2H, CH_2), 1.49-1.30 (m, 15H, CH, CH_2, $C(CH_3)_2$), 1.12-0.95 (m, 16H, CH_3, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.92, 171.81, 156.77, 146.82, 145.90, 142.81, 139.71, 138.76, 136.74, 135.55, 134.00, 130.34, 129.42, 128.96, 128.92, 128.05, 127.98, 127.83, 127.09, 126.50, 126.41, 125.40, 124.75, 119.79, 115.72, 112.71, 112.19, 111.15, 106.66, 101.03, 96.82, 67.82, 54.48, 48.02, 47.72, 42.99, 42.90, 42.01, 39.68, 39.19, 36.65, 36.36, 36.10, 32.65, 32.50, 32.16, 32.10, 31.99, 31.59, 31.53, 30.92, 30.77, 29.39, 28.12, 27.29, 27.11, 26.90, 25.44, 22.66, 20.52, 19.71, 19.63, 16.40, 13.89, 13.73,

13.63.

HR-MS calcd for $C_{56}H_{61}ClN_4O_2$ $[M+H]^+$ m/z 857.45558, found m/z 857.45514.



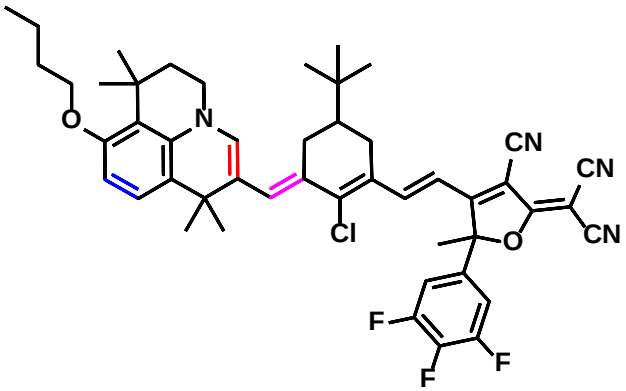
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-9-yl) methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5-methyl-5-(3,4,5-trifluorophenyl)fu ran-2(*5H*)-ylidene)malononitrile (**TE-I-5**).

2h, dark solid (51 mg , 32 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.67 (dd, *J* = 15.6, 3.4 Hz, 1H, =CH), 7.59 (s, 1H, =CH), 7.15 (d, *J* = 3.6 Hz, 1H, CH_{Ar}), 7.10 (t, *J* = 7.2 Hz, 2H, CH_{Ar}), 6.54 (d, *J* = 15.6 Hz, 1H, =CH), 3.75 (dt, J = 8.9, 4.4 Hz, 2H, OCH_2), 3.33-3.09 (m, 5H, CH_2, NCH_2), 2.64 (d, J = 14.3 Hz, 1H, CH_2), 2.36-2.08 (m, 5H, CH_2, CH_3), 1.84-1.68 (m, 6H, CH_2), 1.50-1.44 (m, 2H, CH_2), 1.40 (d, J = 7.0 Hz, 6H, $C(CH_3)_2$), 1.29-1.19 (m, 7H, CH, $C(CH_3)_2$), 0.99-0.91 (m, 12H, CH_3, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 175.42, 171.40, 158.81, 152.41, 150.78, 147.61, 146.60, 146.49, 144.94, 135.66, 130.58, 126.71, 125.71, 122.41, 117.02, 113.10, 111.91, 111.43, 111.35, 111.31, 110.56, 97.41, 97.33, 96.53, 75.75, 75.73, 56.72, 47.39, 46.80, 42.96, 42.87, 39.72, 36.03, 32.53, 32.24, 32.20, 32.06, 31.58, 30.96, 30.58, 30.24, 29.78, 29.58, 27.59, 27.47, 27.08, 24.57, 24.51, 22.65, 19.42, 19.39, 13.88, 13.79.

HR-MS calcd for $C_{48}H_{52}ClF_3N_4O_2$ $[M+H]^+$ m/z 809.38037, found m/z 809.38007.



2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-6,7-dihydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-2-yl)methyl ene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5-methyl-5-(3,4,5-trifluorophenyl)furan-2(*5 H*)-ylidene)malononitrile (**TE-II-5**).

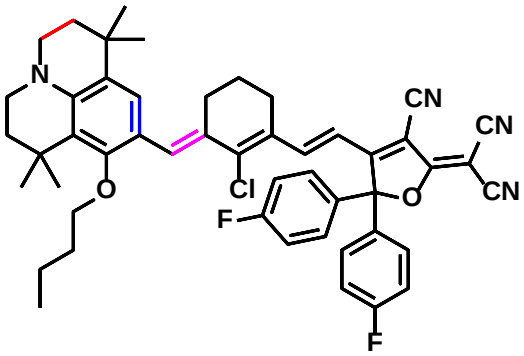
2h, dark solid (8 mg , 5 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.61 (dd, *J* = 15.3, 7.3 Hz, 1H, =CH), 7.42 (d, *J* = 18.8 Hz, 1H, =CH), 7.19-7.03 (m, 3H, CH_{Ar}), 6.62 (dd, *J* = 17.7, 9.5 Hz, 2H, =CH, CH_{Ar}), 6.43 (d, *J* = 15.3 Hz, 1H, =CH), 3.96

(t, *J* = 6.5 Hz, 2H, OCH_2), 3.57 (dt, *J* = 13.6, 6.6 Hz, 2H, NCH_2), 3.03 (d, *J* = 13.9 Hz, 1H, CH_2), 2.63 (d, *J* = 15.7 Hz, 1H, CH_2), 2.19-2.05 (m, 5H, CH_2, CH_3), 1.87-1.75 (m, 4H, CH_2), 1.61-1.49 (m, 2H, CH_2), 1.48-1.28 (m, 13H, CH, $C(CH_3)_2$), 1.02-0.95 (m, 12H, CH_3, $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100MHz, ppm): δ 175.73, 170.58, 156.80, 156.15, 152.78, 150.21, 147.97, 145.97, 145.87, 138.60, 138.29, 138.19, 133.44, 133.39, 130.20, 130.14, 129.29, 129.23, 125.78, 125.58, 125.17, 125.14, 124.93, 120.30, 120.27, 116.97, 116.91, 112.51, 112.02, 111.47, 111.40, 111.29, 111.24, 111.20, 107.79, 107.26, 95.97, 94.51, 67.87, 54.82, 48.55, 48.18, 42.93, 42.82, 39.54, 36.71, 36.45, 36.00, 32.79, 32.70, 32.50, 32.40, 32.14, 31.49, 31.30, 31.24, 30.85, 30.73, 29.66, 28.03, 27.97, 27.27, 27.12, 24.63, 24.58, 19.71, 19.63, 13.89, 13.62.

HR-MS calcd for $C_{48}H_{50}ClF_3N_4O_2$ $[M+H]^+$ m/z 807.36472, found m/z 807.36420.



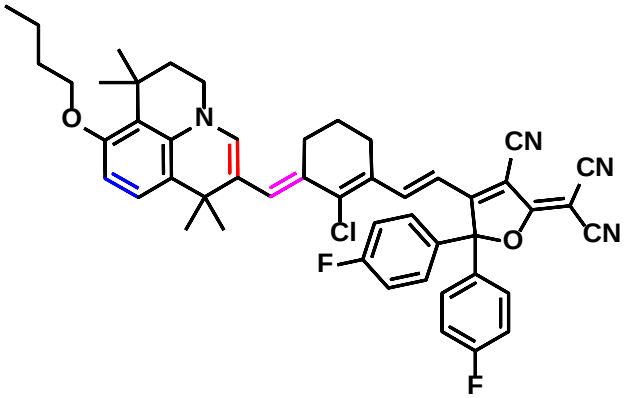
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-9-yl) methylene)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-bis(4-fluorophenyl)furan-2(*5H*)-ylidene)malon onitrile (**TE-I-6**).

3h, dark solid (34 mg , 21 %).

^1H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.96 (d, *J* = 15.6 Hz, 1H, =CH), 7.59 (s, 1H, =CH), 7.37 (ddd, *J* = 8.2, 5.1, 2.6 Hz, 4H, CH_{Ar}), 7.26-7.08 (m, 5H, CH_{Ar}), 6.67 (d, *J* = 15.6 Hz, 1H, =CH), 3.77 (t, *J* = 6.7 Hz, 2H, OCH_2), 3.41-3.08 (m, 4H, NCH_2), 2.88-2.72 (m, 2H, CH_2), 2.54 (t, *J* = 6.0 Hz, 2H, CH_2), 1.90-1.66 (m, 8H, CH_2), 1.50 (dd, *J* = 15.0, 7.4 Hz, 2H, CH_2), 1.42 (s, 6H, $C(CH_3)_2$), 1.26 (s, 6H, $C(CH_3)_2$), 0.97 (t, *J* = 7.4 Hz, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150MHz, ppm): δ 175.46, 170.00, 164.36, 162.70, 158.69, 147.67, 147.20, 144.88, 135.84, 132.61, 132.59, 130.74, 130.43, 130.38, 130.26, 126.72, 125.67, 122.35, 117.07, 116.18, 116.04, 115.14, 111.94, 111.50, 111.02, 101.95, 97.75, 75.62, 56.44, 47.39, 46.79, 39.74, 36.10, 32.51, 32.21, 32.05, 30.51, 29.69, 29.17, 26.43, 21.62, 19.37, 13.86.

HR-MS calcd for $C_{49}H_{47}ClF_2N_4O_2$ $[M+H]^+$ m/z 797.34284, found m/z 797.34247.



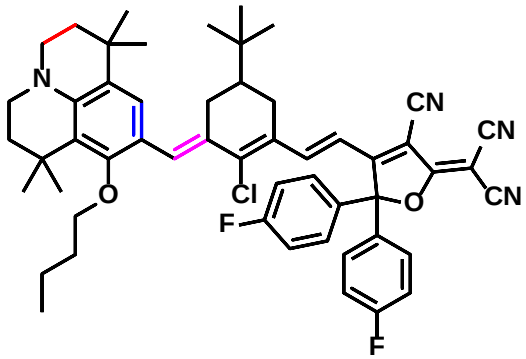
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-9-yl) methylene)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-bis(4-fluorophenyl)furan-2(*5H*)-ylidene)malon onitrile (**TE-II-6**).

3h, dark solid (16 mg , 10 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.89 (d, *J* = 15.2 Hz, 1H, =CH), 7.43 (s, 1H, =CH), 7.37 (ddd, *J* = 8.2, 5.2, 2.6 Hz, 4H, CH_{Ar}), 7.25-7.13 (m, 5H, CH_{Ar}), 6.73 (s, 1H, =CH), 6.63 (d, *J* = 8.8 Hz, 1H, CH_{Ar}), 6.56 (d, *J* = 15.2 Hz, 1H, =CH), 4.00 (t, *J* = 6.5 Hz, 2H, OCH_2), 3.66-3.53 (m, 2H, NCH_2), 2.74 (t, *J* = 5.5 Hz, 2H, CH_2), 2.52 (t, *J* = 5.9 Hz, 2H, CH_2), 1.85 (tt, *J* = 11.1, 5.6 Hz, 6H, CH_2), 1.63-1.53 (m, 2H, CH_2), 1.46 (d, *J* = 12.0 Hz, 12H, $C(CH_3)_2$), 1.03 (t, *J* = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 175.75, 168.96, 164.23, 162.57, 156.80, 156.14, 148.25, 146.62, 140.41, 138.84, 138.60, 137.25, 133.33, 133.12, 133.10, 132.26, 130.41, 130.35, 129.56, 129.21, 125.88, 125.58, 125.27, 124.90, 120.38, 119.41, 117.08, 116.02, 115.87, 113.21, 112.58, 112.15, 111.72, 107.89, 107.37, 101.26, 94.55, 67.88, 54.31, 48.53, 48.16, 39.55, 36.65, 36.40, 36.04, 32.69, 32.61, 32.14, 31.57, 31.50, 31.12, 30.79, 30.34, 30.11, 27.99, 26.02, 22.64, 21.33, 19.69, 19.61, 13.86, 13.60.

HR-MS calcd for $C_{49}H_{45}ClF_2N_4O_2$ $[M+H]^+$ m/z 795.32719, found m/z 795.44165.



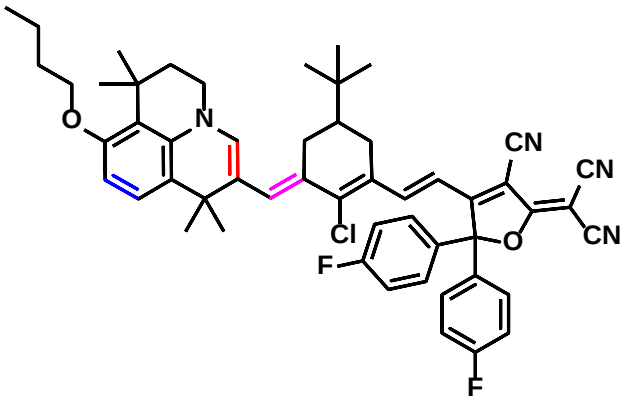
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-9-yl) methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-bis(4-fluorophenyl)furan-2(*5H*)-ylidene)malononitrile (**TE-I-7**).

1h, dark solid (41 mg , 26 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.87 (d, *J* = 15.6 Hz, 1H, =CH), 7.55 (s, 1H, =CH), 7.40-7.28 (m, 4H, CH_{Ar}), 7.18 (ddd, *J* = 13.3, 6.1, 3.9 Hz, 5H, CH_{Ar}), 6.66 (d, *J* = 15.6 Hz, 1H, =CH), 3.73 (dd, *J* = 11.2, 6.7 Hz, 2H, OCH_2), 3.32-3.08 (m, 5H, CH_2, NCH_2), 2.62 (d, *J* = 14.4 Hz, 1H, CH_2), 2.33-2.07 (m, 2H, CH_2), 1.82-1.65 (m, 6H, CH_2), 1.46 (dd, *J* = 15.1, 7.4 Hz, 2H, CH_2), 1.39 (d, *J* = 6.3 Hz, 6H, $C(CH_3)_2$), 1.23 (d, *J* = 19.6 Hz, 7H, CH, $C(CH_3)_2$), 1.00-0.88 (m, 12H, CH_3, $C(CH_3)_3$).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150MHz, ppm): δ 175.44, 169.98, 164.37, 164.35, 162.71, 162.69, 158.75, 147.54, 147.50, 144.88, 135.55, 132.66, 132.63, 132.59, 132.57, 130.76, 130.70, 130.52, 130.46, 130.43, 130.37, 126.71, 125.69, 122.39, 117.04, 116.17, 116.02, 114.91, 111.96, 111.52, 110.94, 101.93, 97.82, 75.66, 56.39, 47.38, 46.80, 42.86, 39.73, 36.05, 32.53, 32.21, 32.19, 32.06, 30.97, 30.54, 30.26, 29.77, 29.60, 27.52, 27.06, 19.38, 13.87.

HR-MS calcd for $C_{53}H_{55}ClF_2N_4O_2$ $[M+H]^+$ m/z 853.40544, found m/z 853.40521.



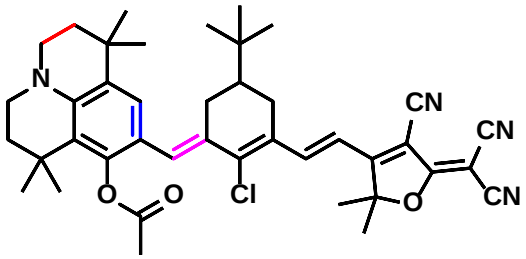
2-(4-((*E*)-2-((*E*)-3-((8-butoxy-1,1,7,7-tetramethyl-6,7-dihydro-*1H*,*5H*-pyrido[3,2,1-**ij**]quinolin-2-yl)methylene)-5-(*tert*-butyl)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-bis(4-fluorophenyl)furan-2(*5H*)-ylidene)malononitrile (**TE-II-7**).

1h, dark solid (3 mg , 2 %).

^{1}H NMR (CD_2Cl_2, 300MHz, ppm): δ 7.80 (d, *J* = 15.2 Hz, 1H, =CH), 7.40-7.27 (m, 5H, =CH, CH_{Ar}), 7.22-7.08 (m, 5H, CH_{Ar}), 6.67-6.51 (m, 3H, =CH, CH_{Ar}), 3.96 (t, *J* = 6.5 Hz, 2H, OCH_2), 3.65-3.46 (m, 2H, NCH_2), 3.01 (d, *J* = 13.7 Hz, 1H, CH_2), 2.61 (d, *J* = 14.2 Hz, 1H, CH_2), 2.19-2.03 (m, 2H, CH_2), 1.88-1.74 (m, 4H, CH_2), 1.59-1.49 (m, 2H, CH_2), 1.47-1.36 (m, 13H, CH, $C(CH_3)_2$), 1.03-0.91 (m, 12H, CH_3, $C(CH_3)_3$).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150MHz, ppm): δ 175.70, 169.10, 164.24, 162.60, 162.58, 156.80, 156.16, 147.94, 146.94, 138.45, 138.04, 133.47, 133.11, 133.09, 133.00, 132.98, 130.49, 130.43, 130.40, 130.35, 129.44, 125.73, 125.55, 125.12, 124.90, 120.27, 116.88, 116.03, 115.88, 113.20, 112.52, 112.09, 111.54, 107.73, 107.24, 101.34, 95.04, 67.88, 54.55, 48.48, 48.14, 42.85, 39.56, 36.44, 36.03, 32.73, 32.69, 32.36, 32.13, 31.50, 31.20, 30.85, 30.72, 28.04, 27.99, 27.19, 27.10, 19.69, 19.62, 13.87, 13.61.

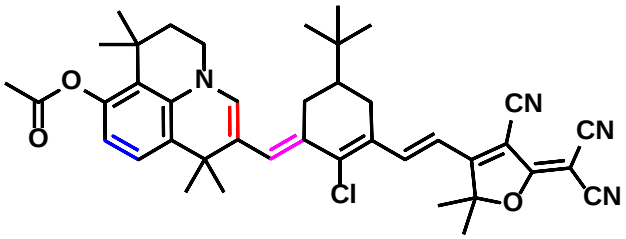
HR-MS calcd for $C_{53}H_{53}ClF_2N_4O_2$ $[M+H]^+$ m/z 851.38979, found m/z 851.38934.



2-((*E*)-(5-(*tert*-butyl)-2-chloro-3-((*E*)-2-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)cyclohex-2-en-1-ylidene)methyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-8-yl acetate (**TE-I-8**).

A peak at 679.38776 suggests the formation of **TE-I-8**.

HR-MS calcd for $C_{41}H_{47}ClN_4O_3$ M^+ m/z 679.34095, found m/z 679.38776.



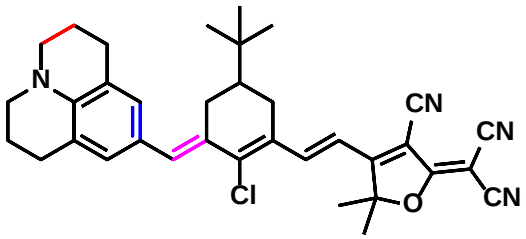
2-((*E*)-(5-(*tert*-butyl)-2-chloro-3-((*E*)-2-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)cyclohex-2-en-1-ylidene)methyl)-1,1,7,7-tetramethyl-6,7-dihydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-8-yl acetate (**TE-II-8**).

15h, dark solid (19 mg , 11 %).

^{1}H NMR (CD_2Cl_2, 400MHz, ppm): δ 8.19 (d, *J* = 15.8 Hz, 1H, =CH), 7.26 (d, *J* = 6.0 Hz, 1H, =CH), 7.17 (t, *J* = 8.5 Hz, 1H, CH_{Ar}), 6.57 (t, *J* = 8.5 Hz, 1H, CH_{Ar}), 6.49 (dd, *J* = 15.7, 3.7 Hz, 1H, =CH), 6.35 (d, *J* = 24.8 Hz, 1H, =CH), 3.60-3.45 (m, 2H, NCH_2), 3.15 (d, *J* = 14.4 Hz, 1H, CH_2), 2.67 (d, *J* = 14.4 Hz, 1H, CH_2), 2.33-2.06 (m, 5H, CH_2, $COCH_3$), 1.87-1.80 (m, 2H, CH_2), 1.74 (d, *J* = 14.4 Hz, 6H, $C(CH_3)_2$), 1.50-1.38 (m, 6H, $C(CH_3)_2$), 1.38-1.27 (m, 7H, CH, $C(CH_3)_2$), 0.99 (s, 9H, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.05, 174.09, 169.53, 169.41, 148.13, 147.84, 145.82, 145.03, 135.89, 135.08, 134.95, 134.90, 133.78, 131.43, 131.29, 129.99, 129.85, 129.69, 129.05, 125.19, 124.66, 123.23, 122.53, 117.87, 117.48, 115.81, 114.92, 113.27, 113.20, 112.46, 111.86, 111.06, 97.39, 96.70, 55.28, 47.53, 47.01, 43.21, 43.14, 38.87, 36.72, 36.32, 35.78, 32.46, 32.28, 32.22, 32.08, 31.58, 31.42, 30.90, 30.77, 30.70, 30.64, 29.85, 28.72, 28.58, 27.65, 27.10, 26.93, 26.66, 26.57, 22.64, 21.55, 21.49, 13.87.

HR-MS calcd for $C_{41}H_{45}ClN_4O_3$ $[M+H]^+$ m/z 677.32530, found m/z 677.32489.



2-(4-((*E*)-2-((*E*)-5-(*tert*-butyl)-2-chloro-3-((2,3,6,7-tetrahydro-*1H,5H*-pyrido[3,2,1-*ij*]quinolin-9-yl)methylene)cyclohex-1-en-1-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (**TE-I-9**).

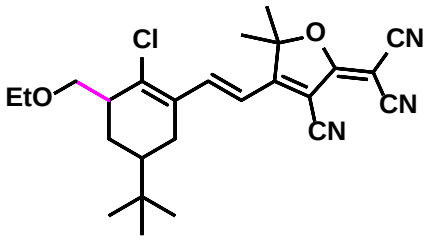
15h, dark solid (77 mg , 54 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 8.10 (d, *J* = 15.9 Hz, 1H, =CH), 7.36 (s, 1H, =CH), 6.97 (s, 2H, CH_{Ar}), 6.54 (d, *J* = 15.9 Hz, 1H, =CH), 3.27 (dd, *J* = 11.4, 5.7 Hz, 5H, CH_2, NCH_2), 2.81-2.59 (m, 5H, CH_2), 2.20 (dd, *J* = 27.2, 12.0 Hz, 2H, CH_2), 2.01 (dd, *J* = 11.6, 6.0 Hz, 4H, CH_2), 1.80 (s, 6H, $C(CH_3)_2$), 1.55-1.43 (m, 1H, CH), 1.00 (s, 9H, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 150MHz, ppm): δ 176.04, 174.14, 146.12, 145.13, 144.09, 137.78, 130.58, 130.52, 130.27, 123.35, 121.09, 113.48, 112.44, 111.83, 111.01, 97.45, 96.88, 55.38, 49.96, 43.02, 32.25, 30.10, 27.79, 27.56, 27.11, 26.64, 26.58, 21.62.

HR-MS calcd for $C_{35}H_{37}ClN_4O$ $[M+H]^+$ m/z 565.27287, found m/z 565.27295.

HRMS/HPLC experiment to identify the formation of INT-b



INT-b

HR-MS analysis of reaction with **JD1** and **TCF-A1** in Ac_2O at 80 °C for 2 days:

Products were separated on a J&K Scientific HPLC C18-H column (10 μm, 21.2 x 250 mm) with a linear gradient using a combination of solvent A (acetonitrile, 1% FA) and solvent B (water, 1% FA) at a flow rate of 6 mL/minute. Gradient protocol in minutes: 0 (5% A); 5 (10% A); 55 (95% A), 55-60 (95% A). High-resolution spectra for the reaction product **INT-b** at elution time of 43 -46 min. A peak at 439.29248 suggest the formation of **INT-b**.

HR-MS calcd for $C_{25}H_{30}ClN_3O_2$ M^+ m/z 439.20265, found m/z 439.29248.

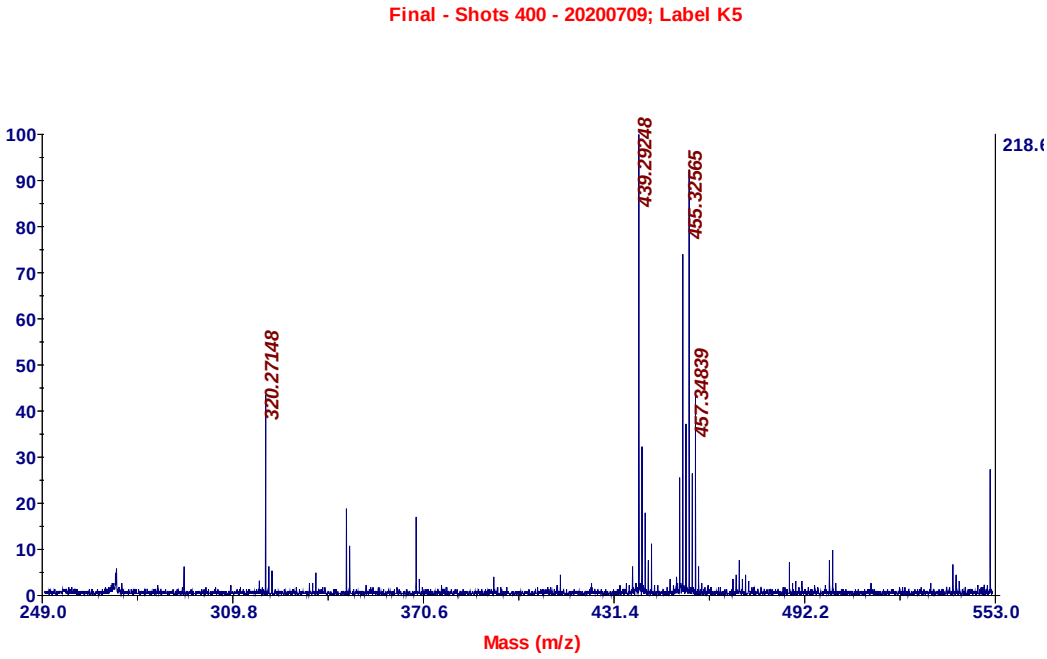


Figure S5. HRMS spectrum of compound **TCF-A1(+2H)**.

4. Spectra

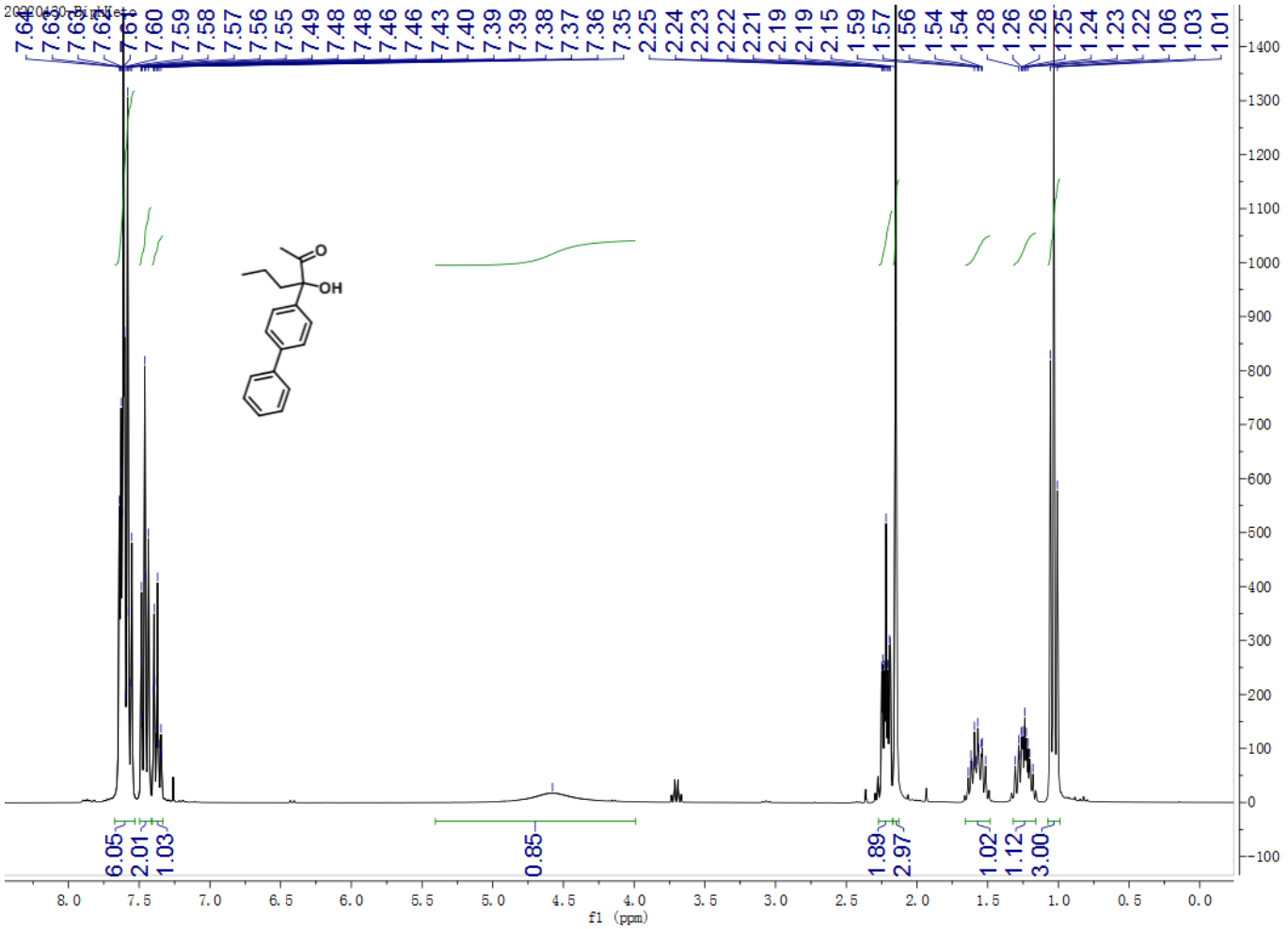


Figure S6. ^{1}H NMR spectrum of compound **1**.

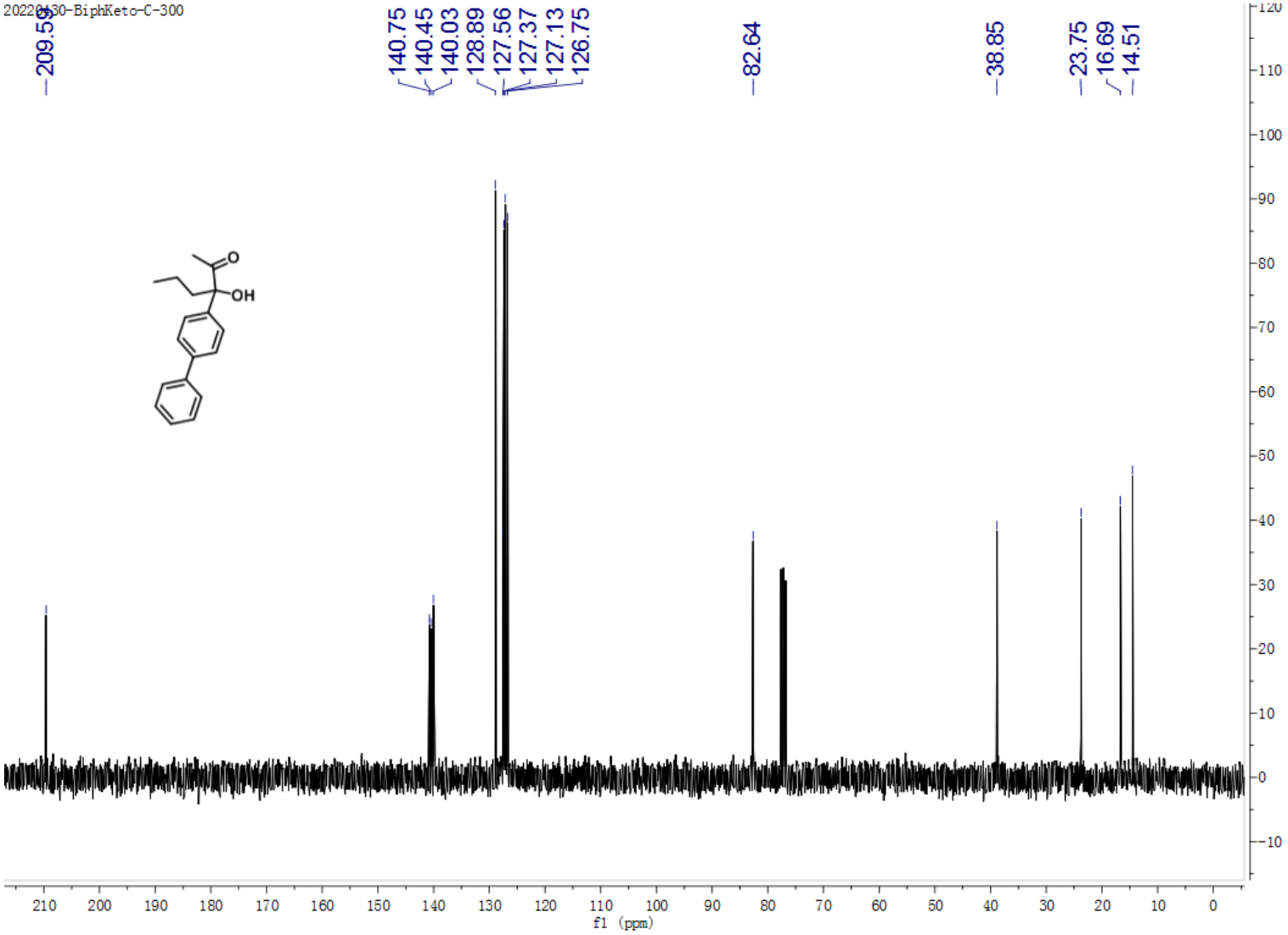


Figure S7. ^{13}C NMR spectrum of compound **1**.

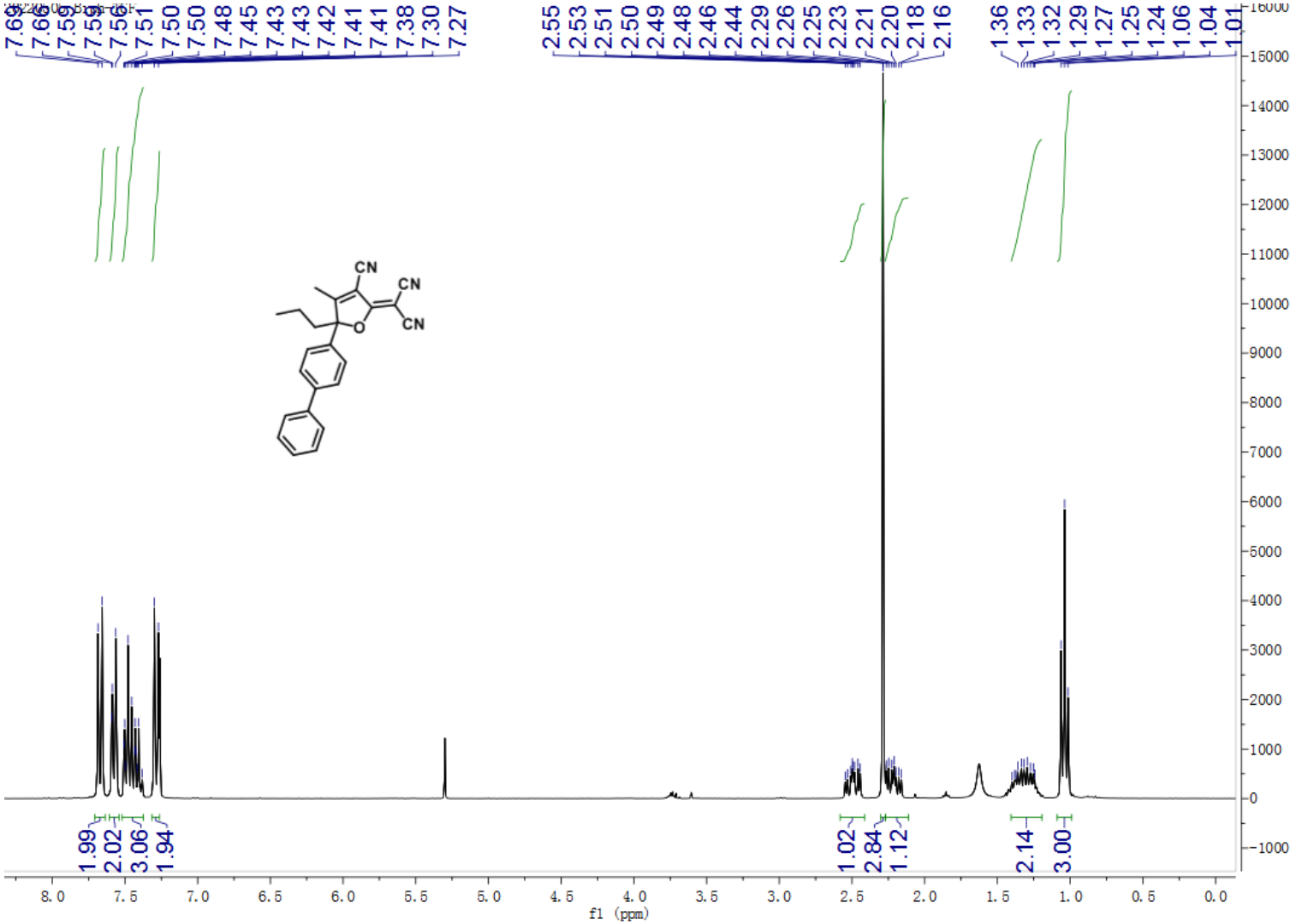


Figure S8. ^{1}H NMR spectrum of compound **TCF3**.

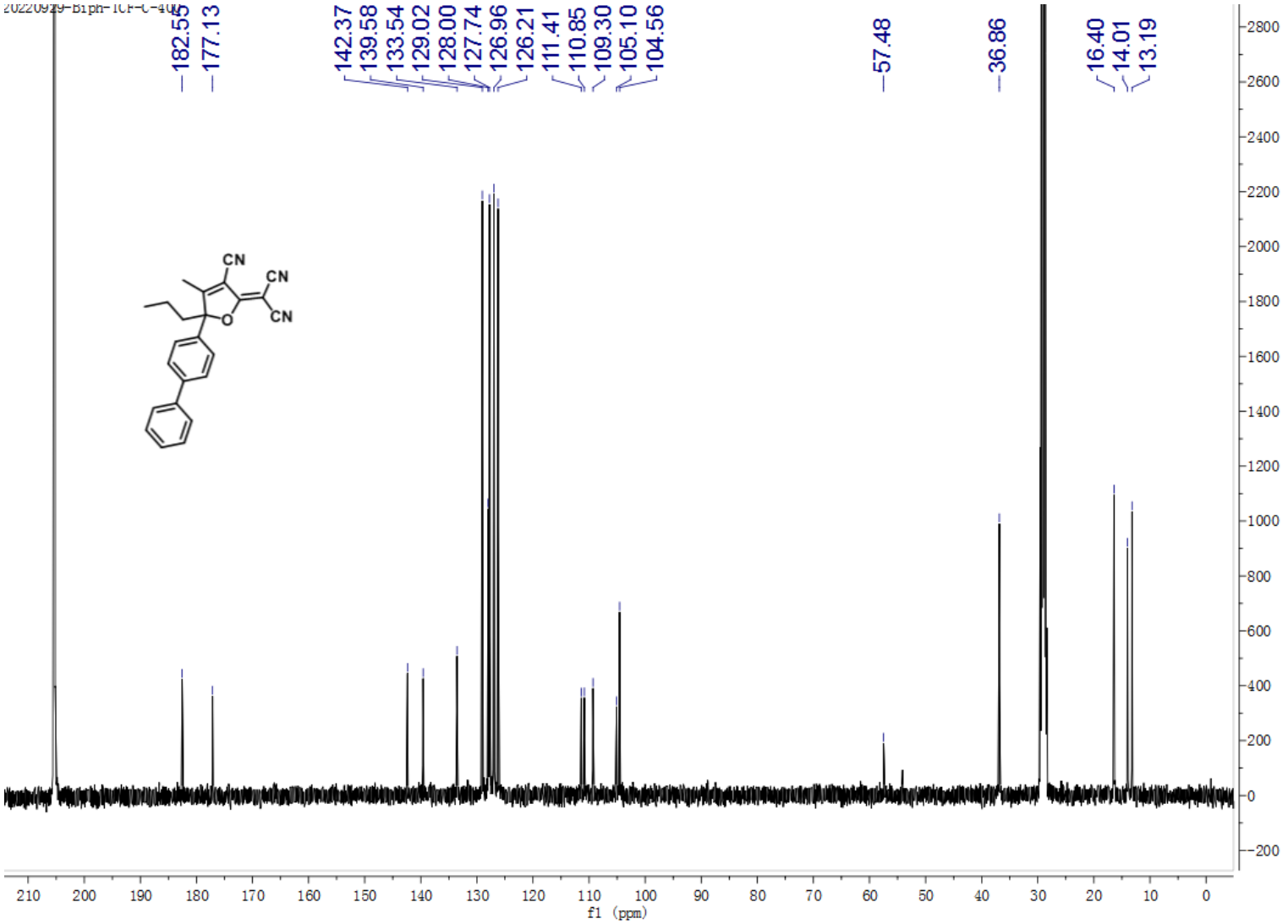


Figure S9. ^{13}C NMR spectrum of compound **TCF3**.

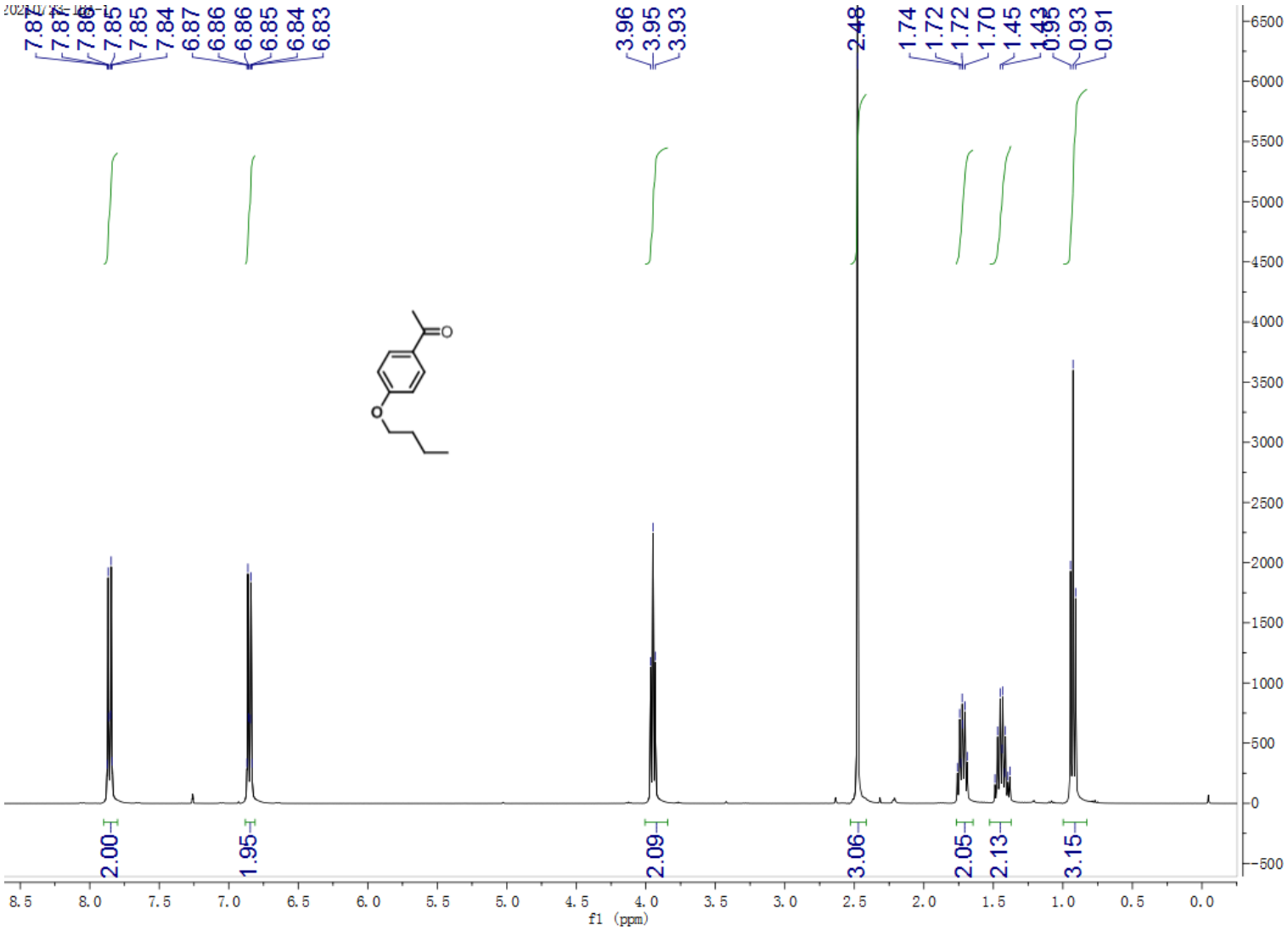


Figure S10. ^{1}H NMR spectrum of compound **2**.

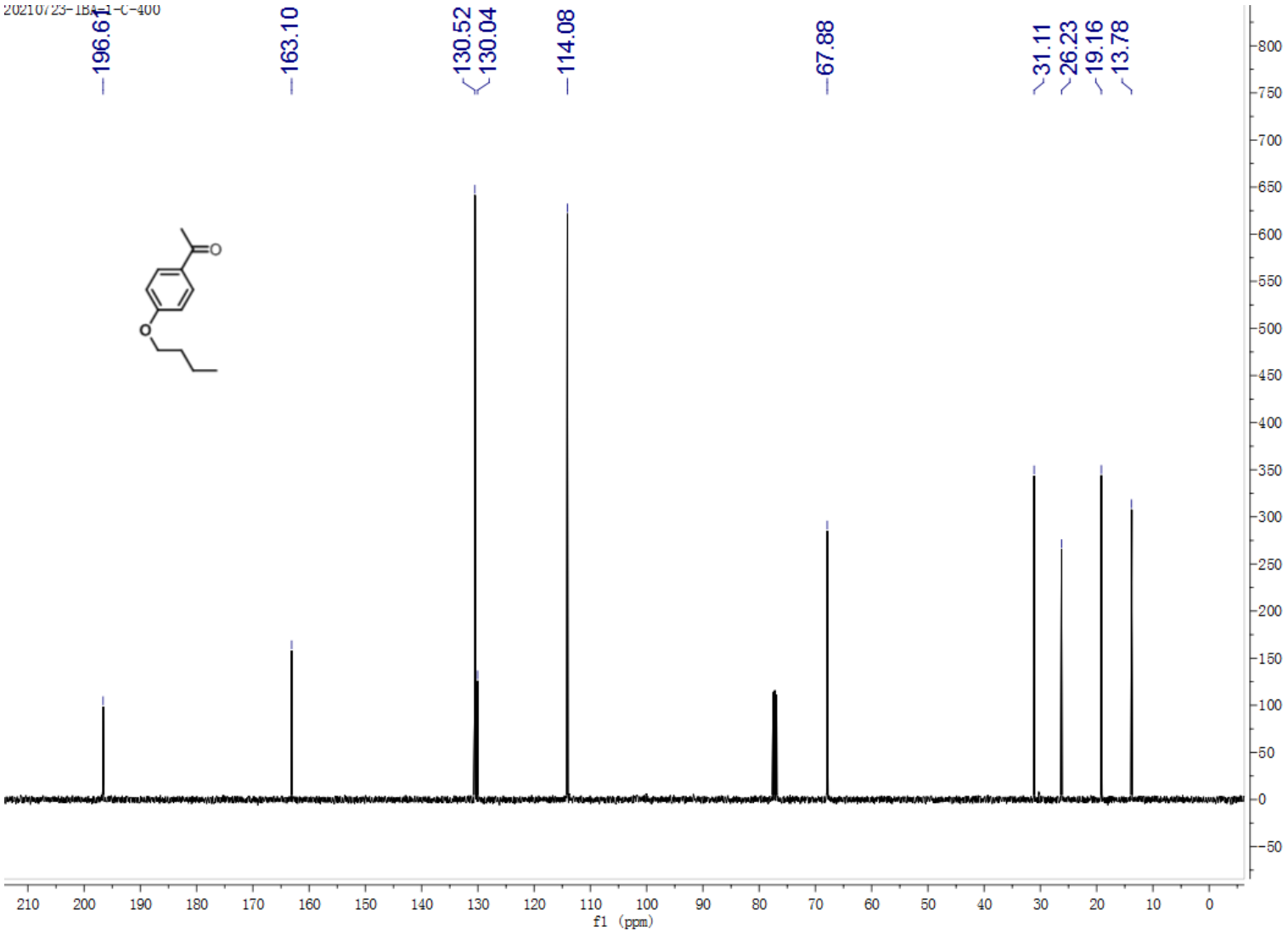


Figure S11. ^{13}C NMR spectrum of compound **2**.

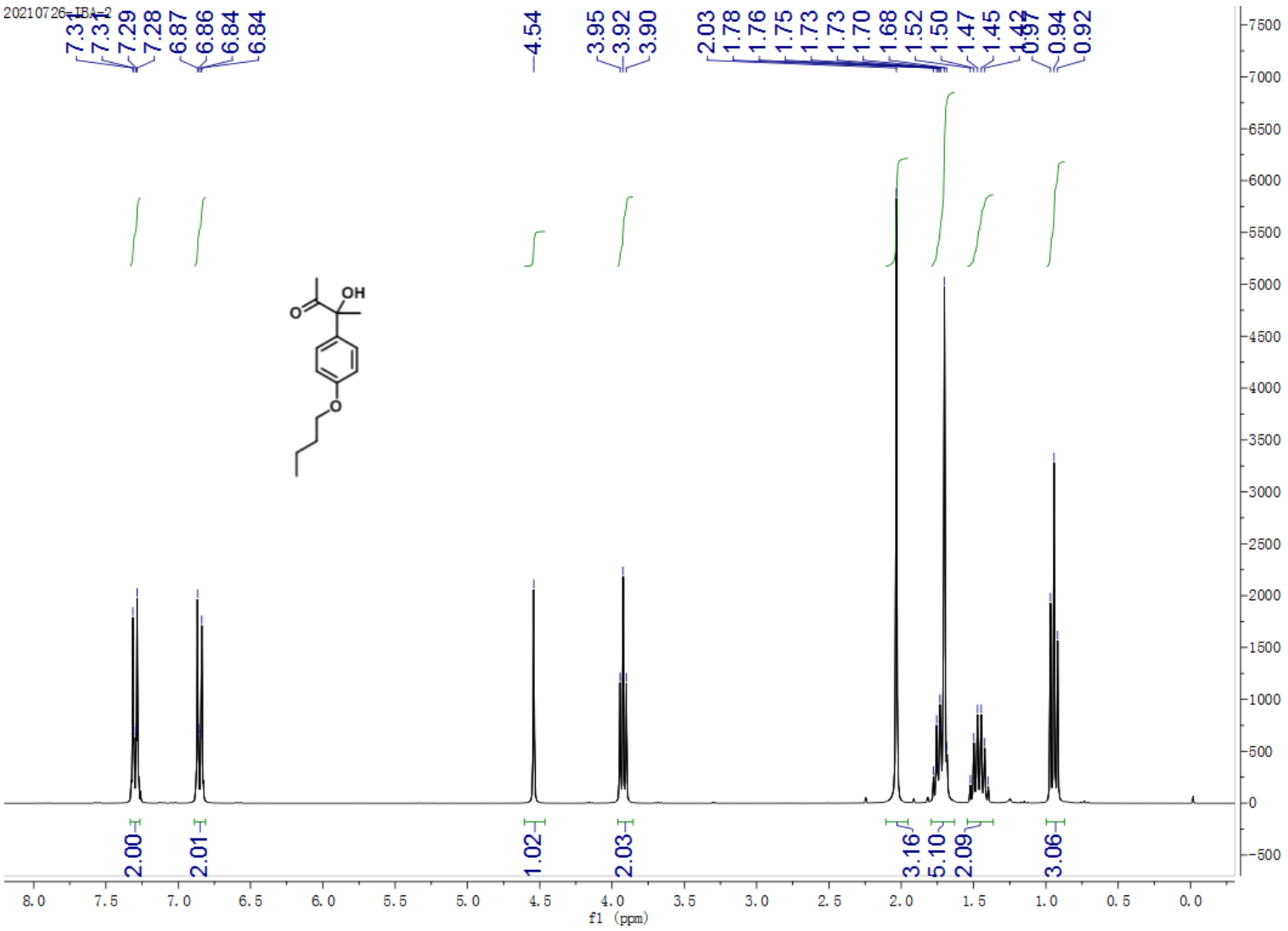


Figure S12. ^{1}H NMR spectrum of compound **3**.

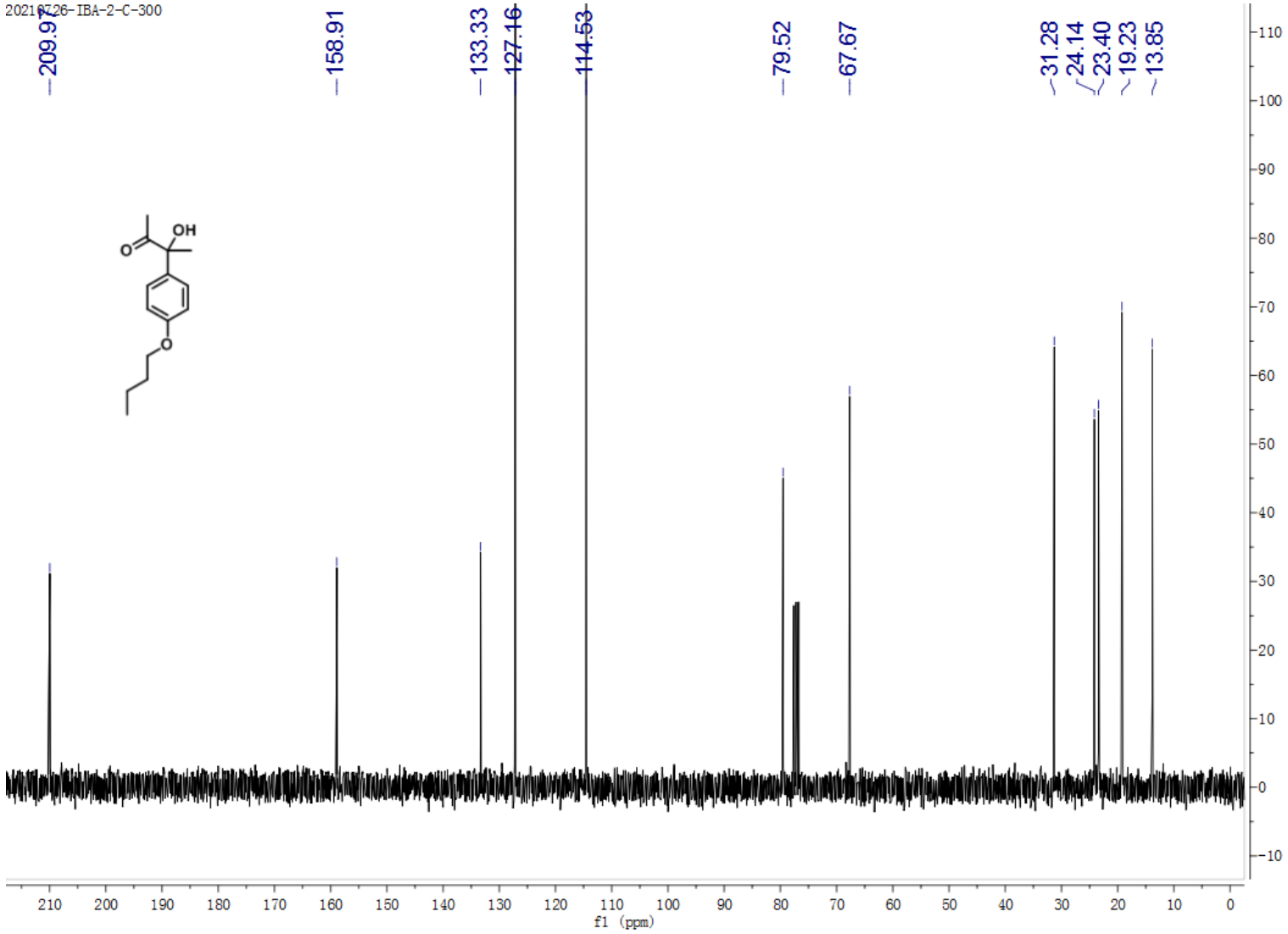


Figure S13. ^{13}C NMR spectrum of compound **3**.

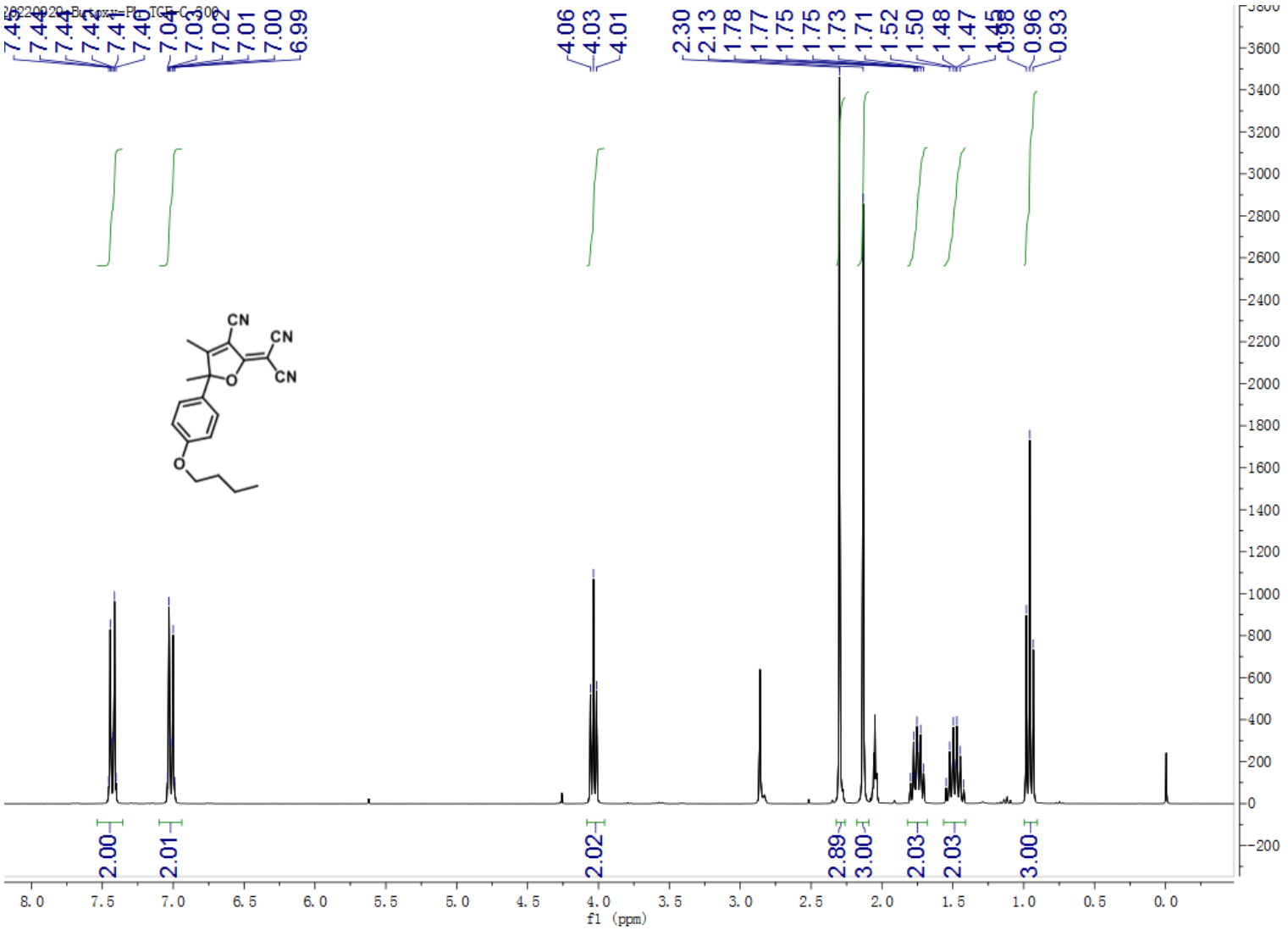


Figure S14. ^{1}H NMR spectrum of compound **TCF2**.

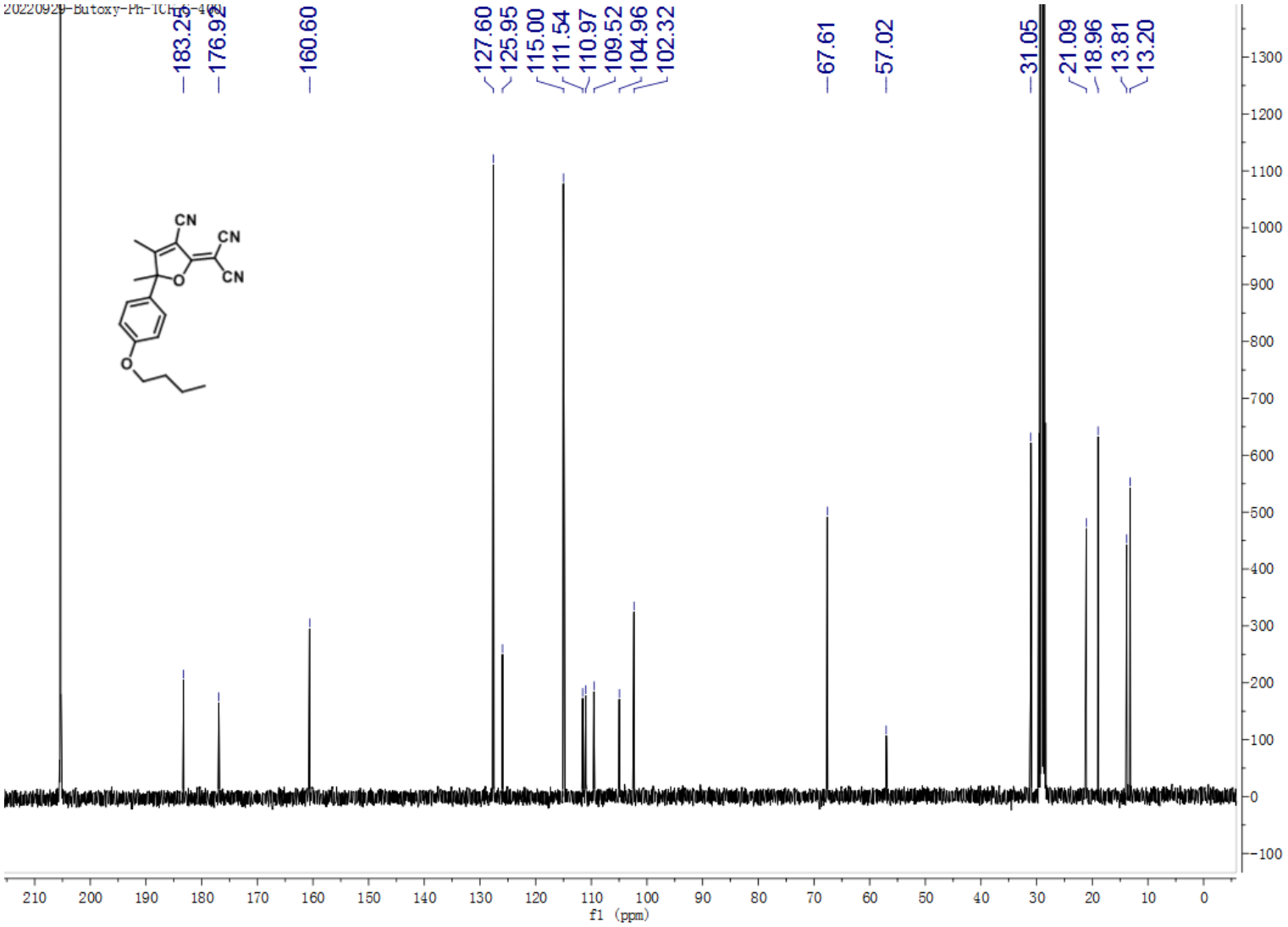


Figure S15. ^{13}C NMR spectrum of compound **TCF2**.

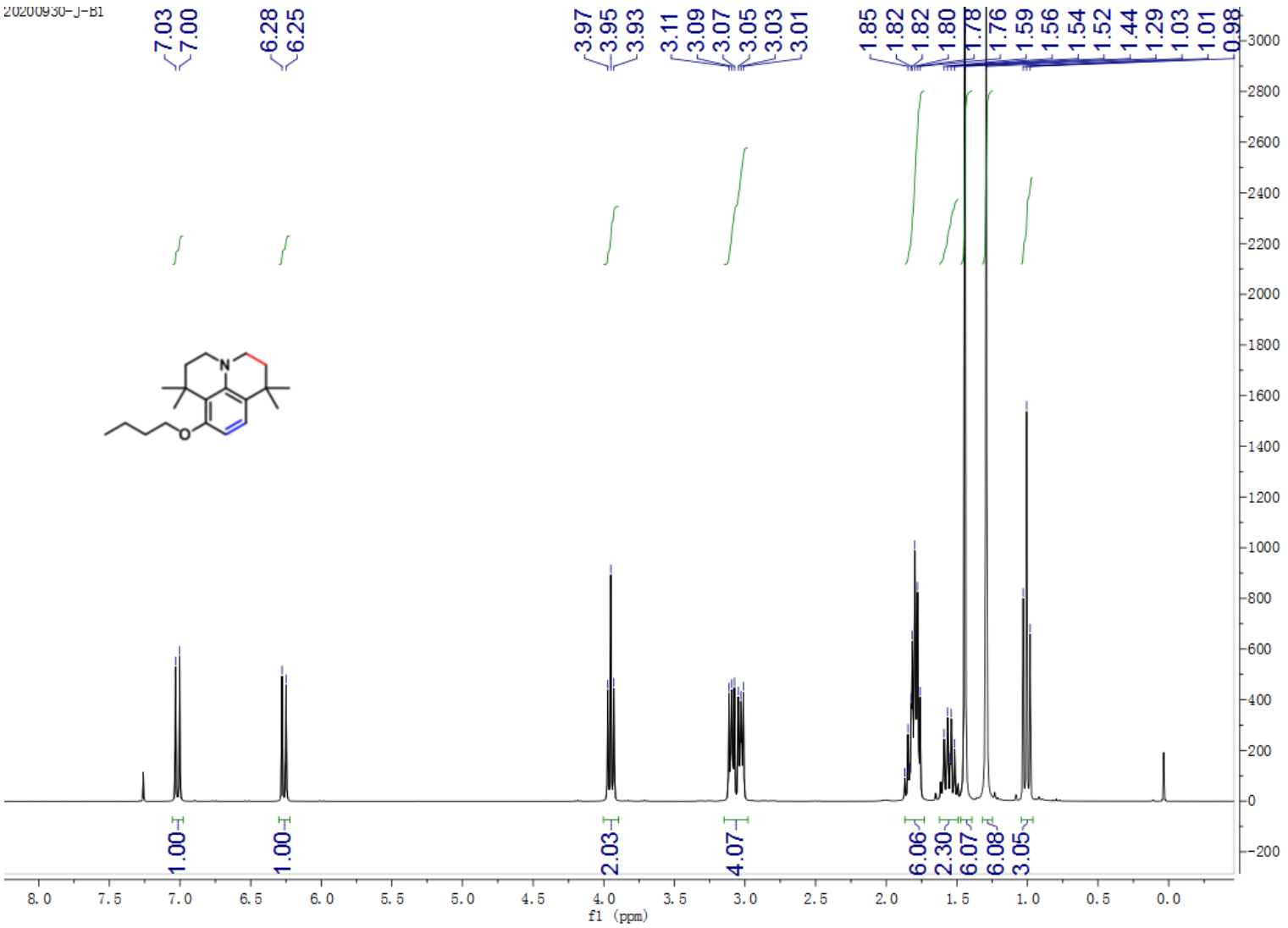


Figure S16. ^{1}H NMR spectrum of compound **JD1**.

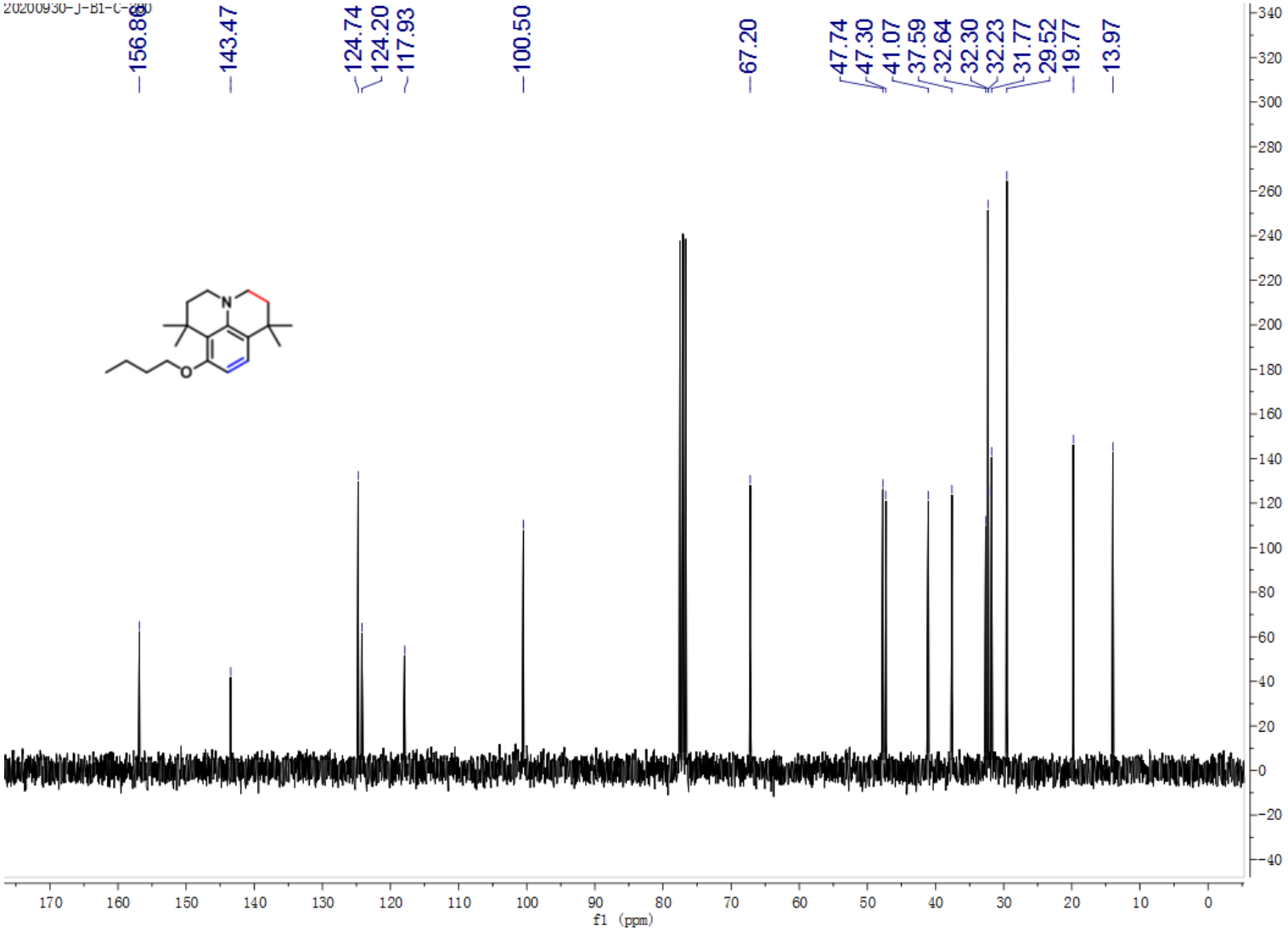


Figure S17. ^{13}C NMR spectrum of compound **JD1**.

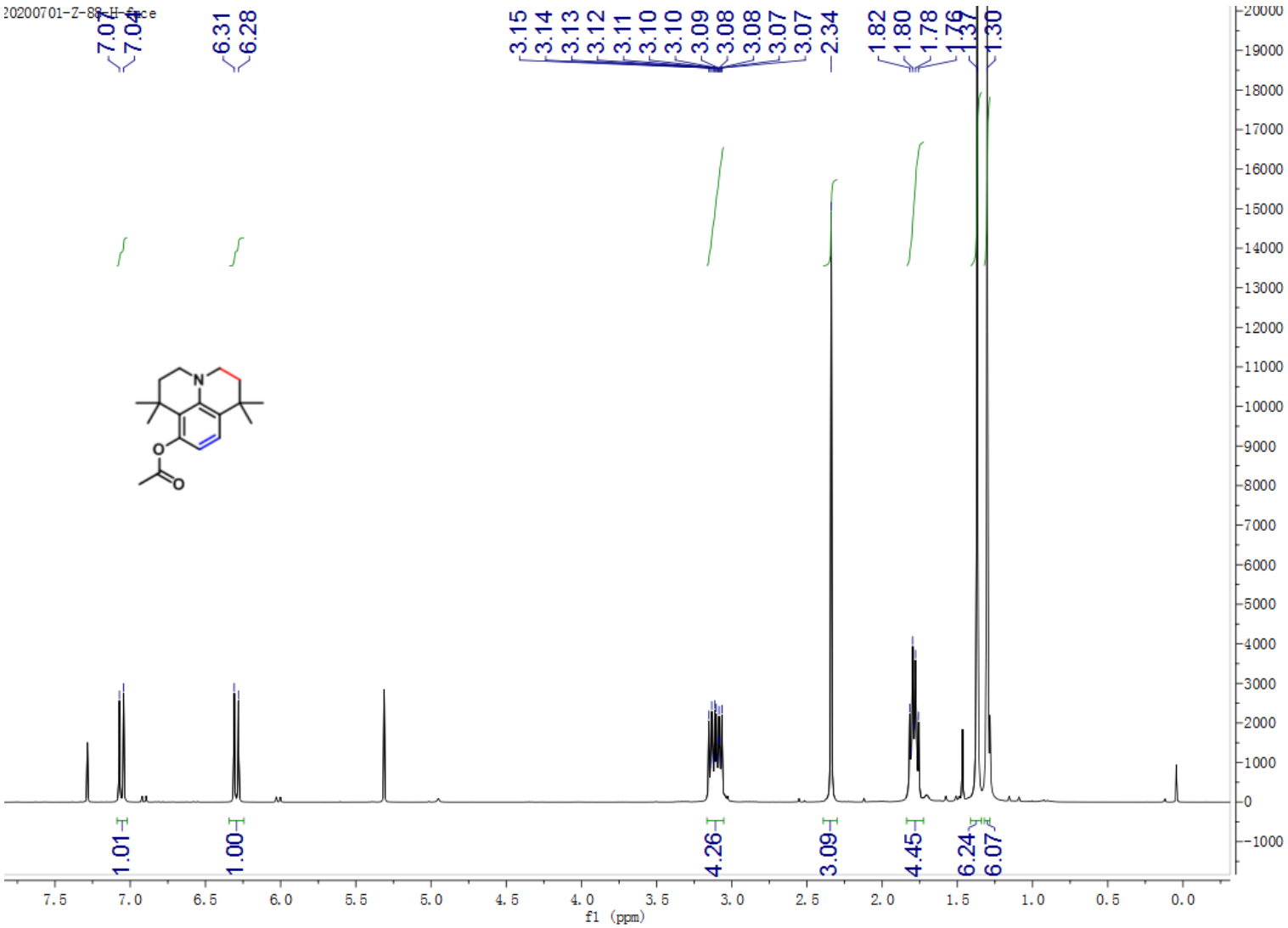


Figure S18. ^{1}H NMR spectrum of compound **JD2**.

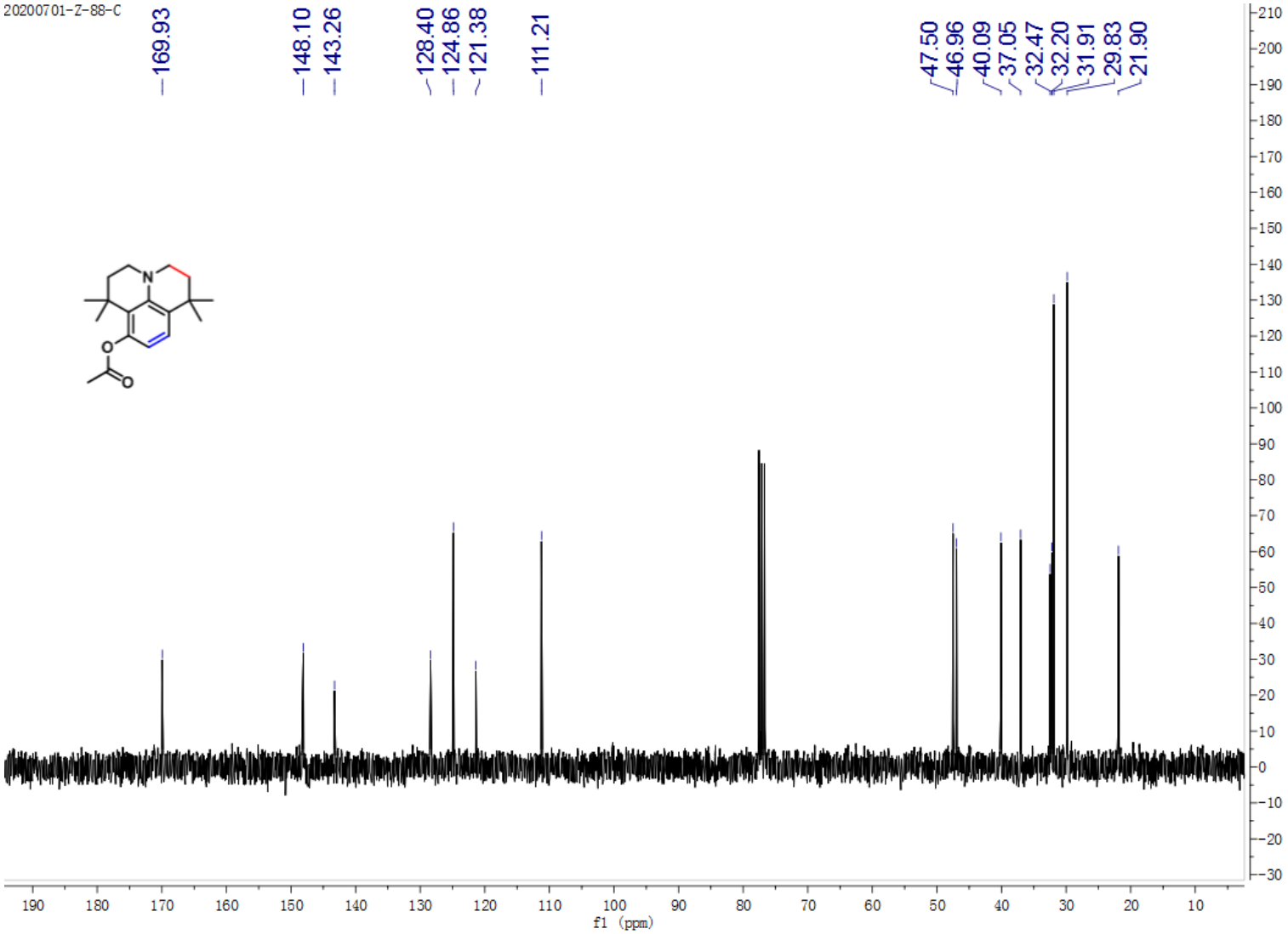


Figure S19. ^{13}C NMR spectrum of compound **JD2**.

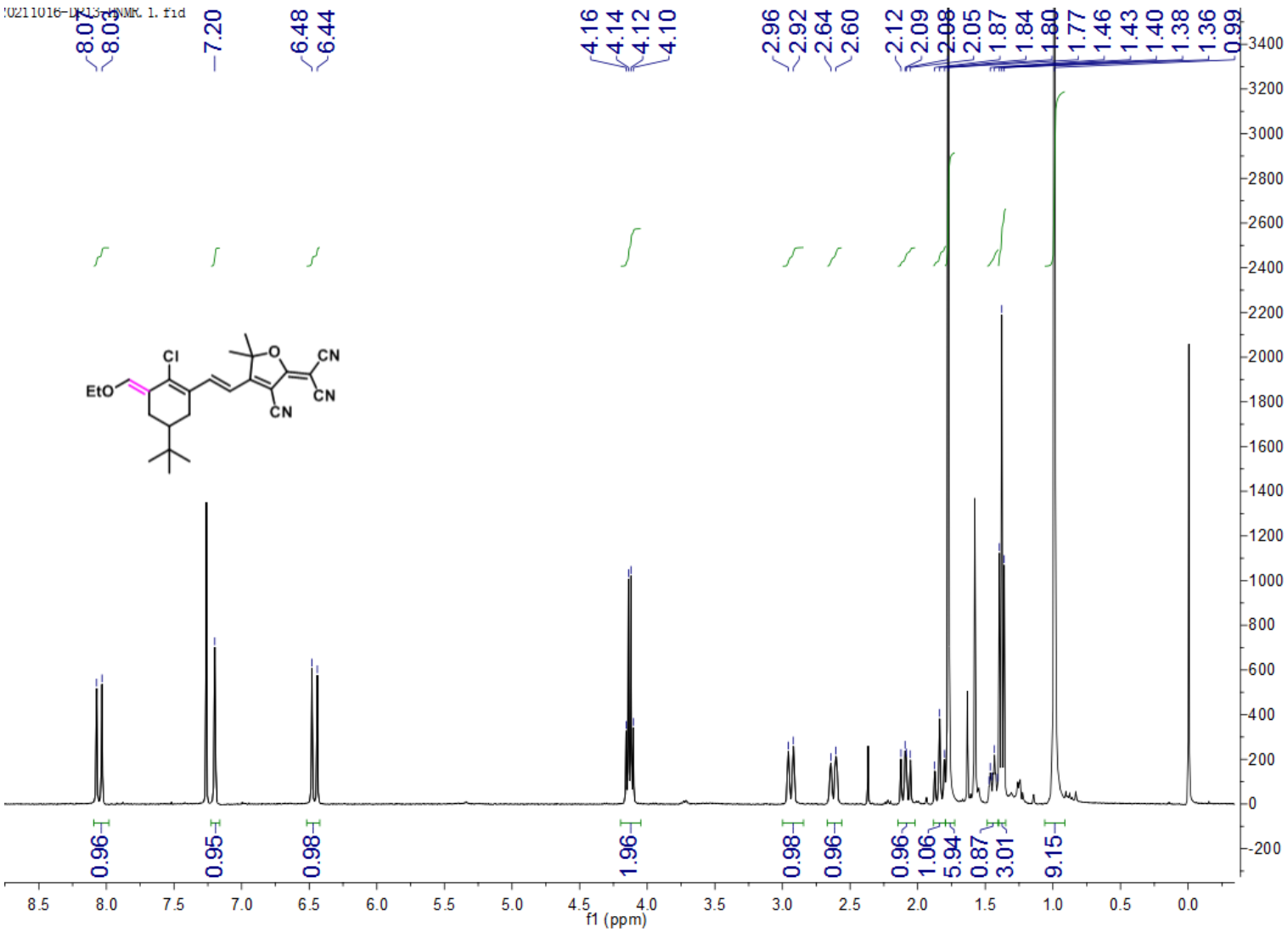


Figure S20. ^{1}H NMR spectrum of compound **TCF-A1**.

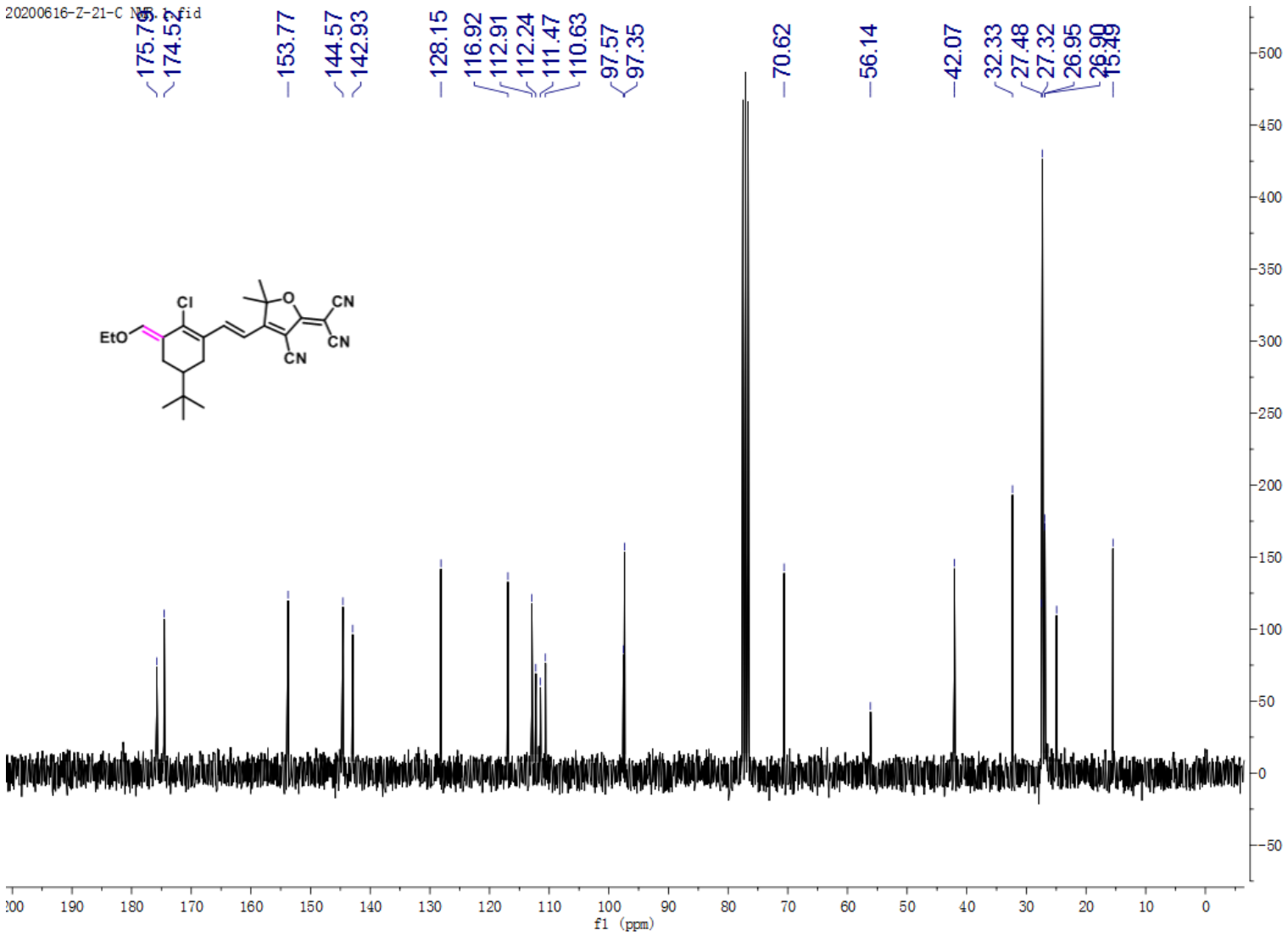


Figure S21. ^{13}C NMR spectrum of compound **TCF-A1**.

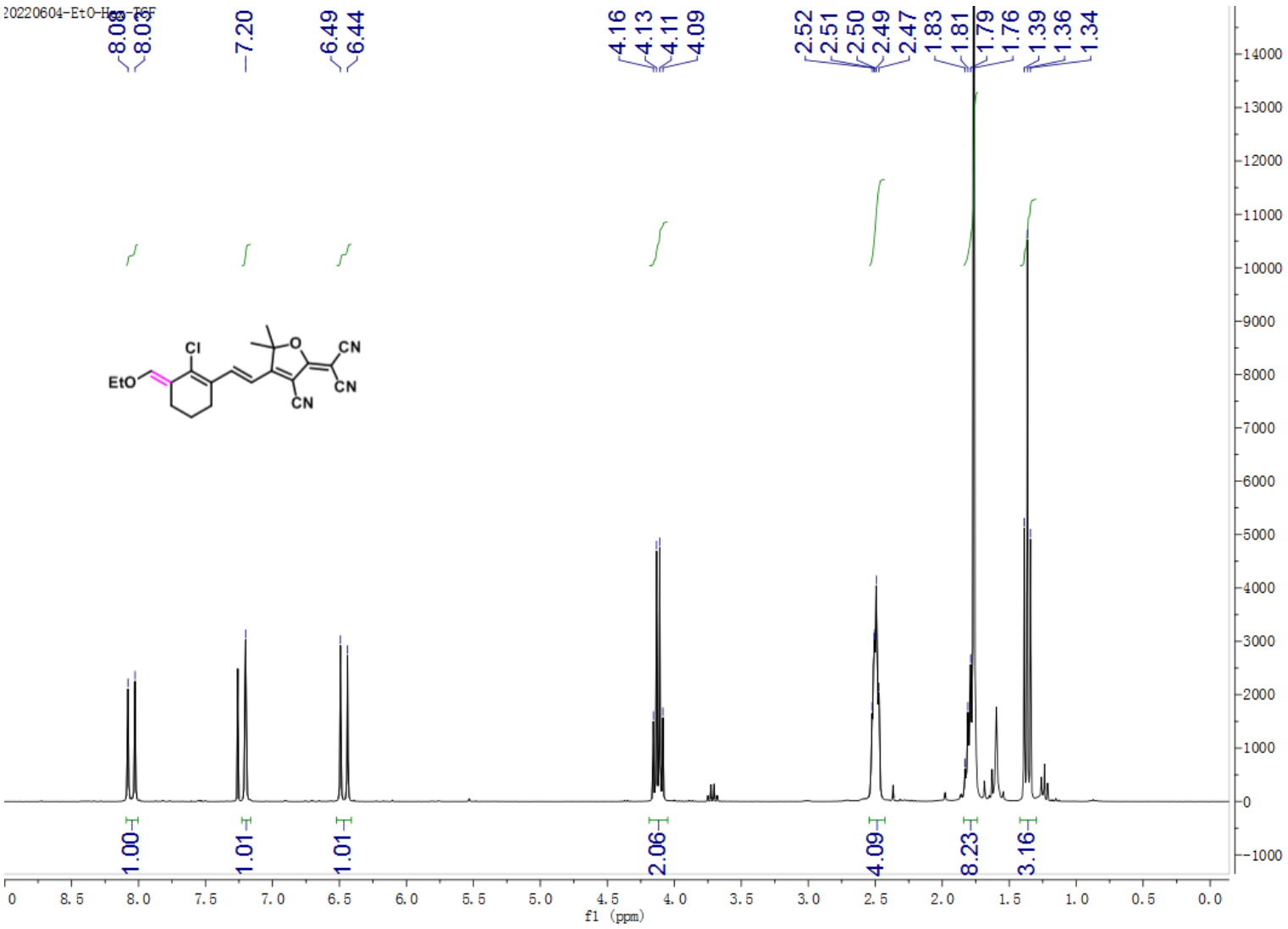


Figure S22. ^{1}H NMR spectrum of compound **TCF-A2**.

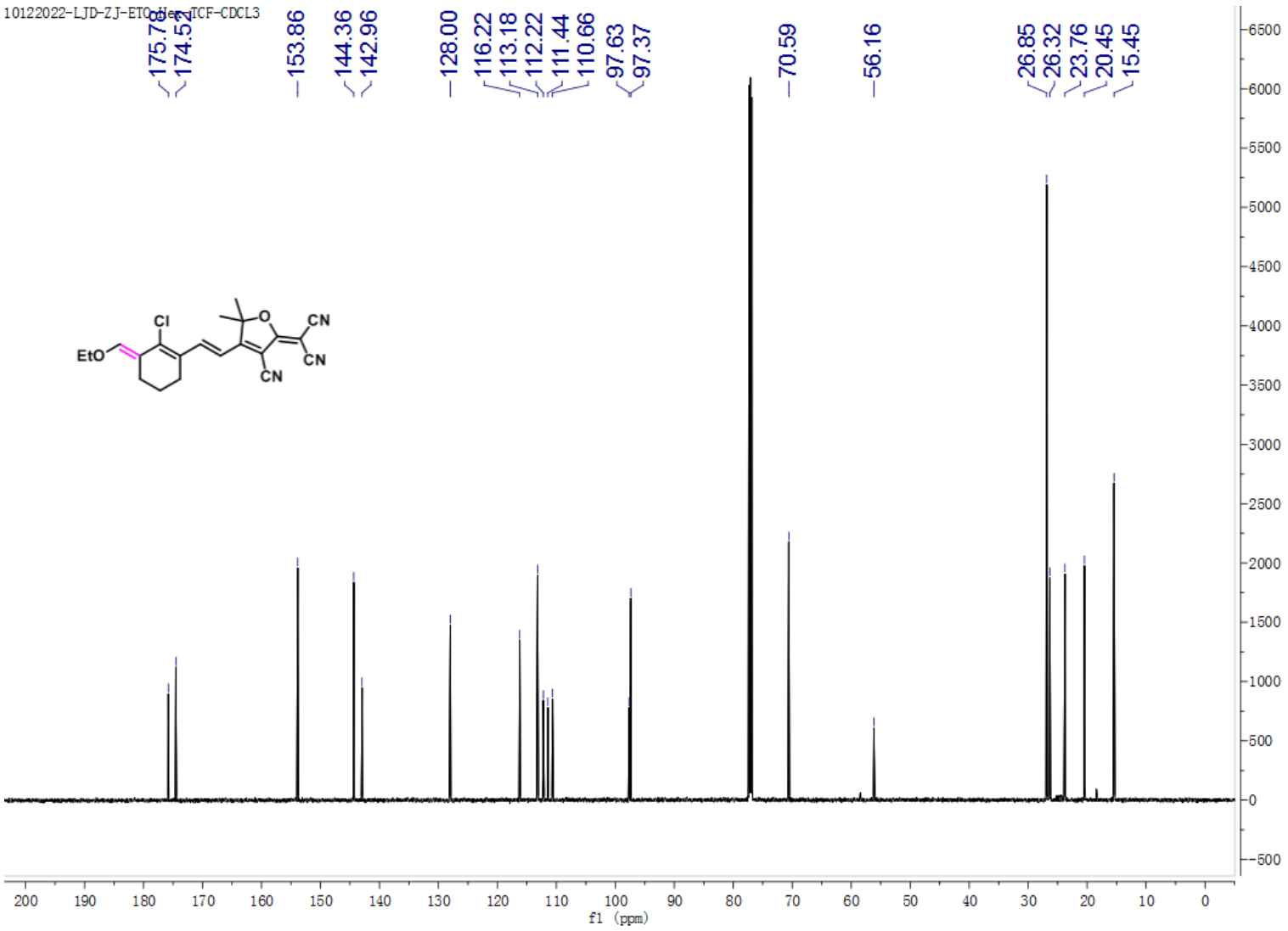


Figure S23. ^{13}C NMR spectrum of compound **TCF-A2**.

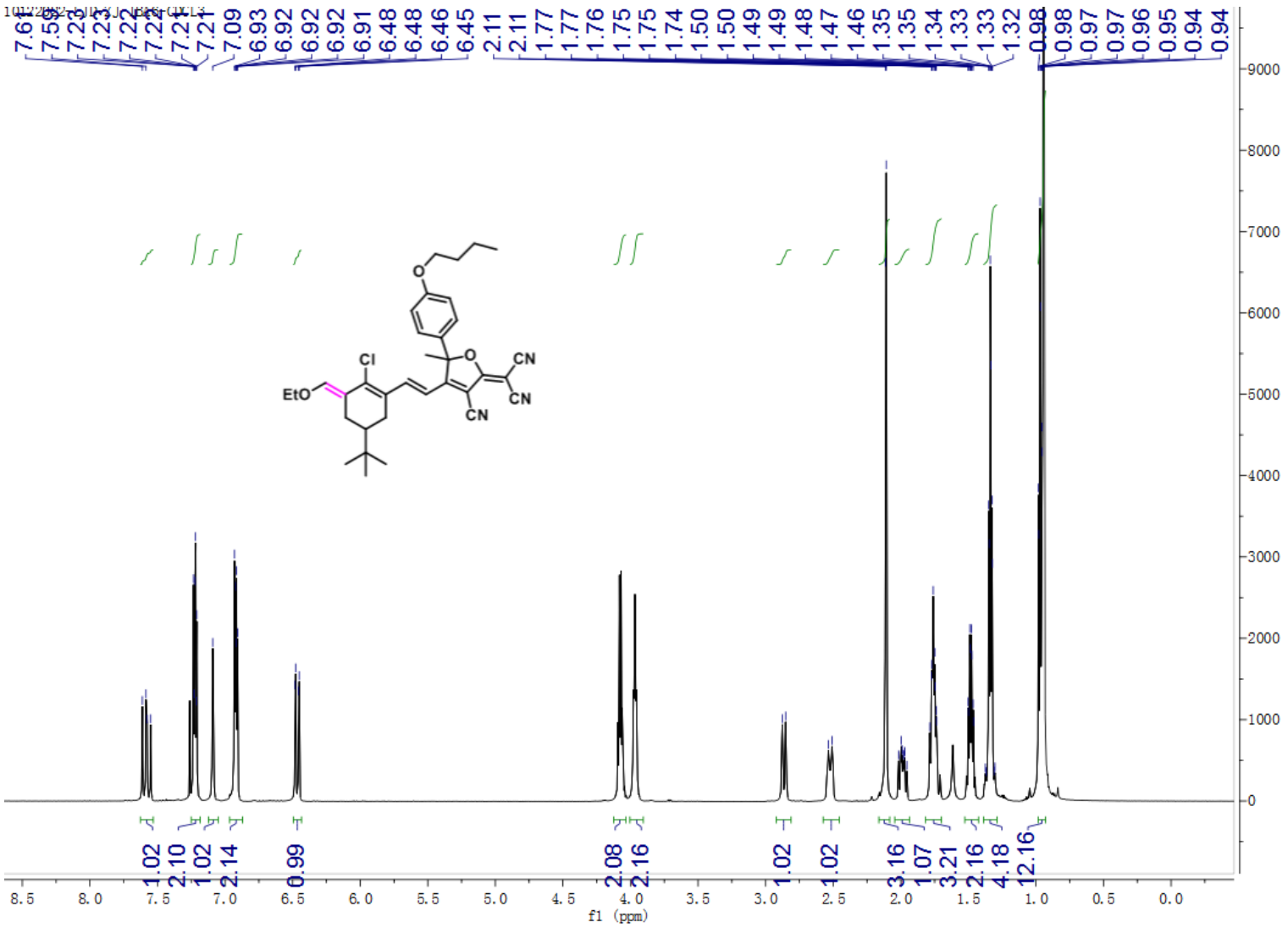


Figure S24. ^{1}H NMR spectrum of compound **TCF-A3**.

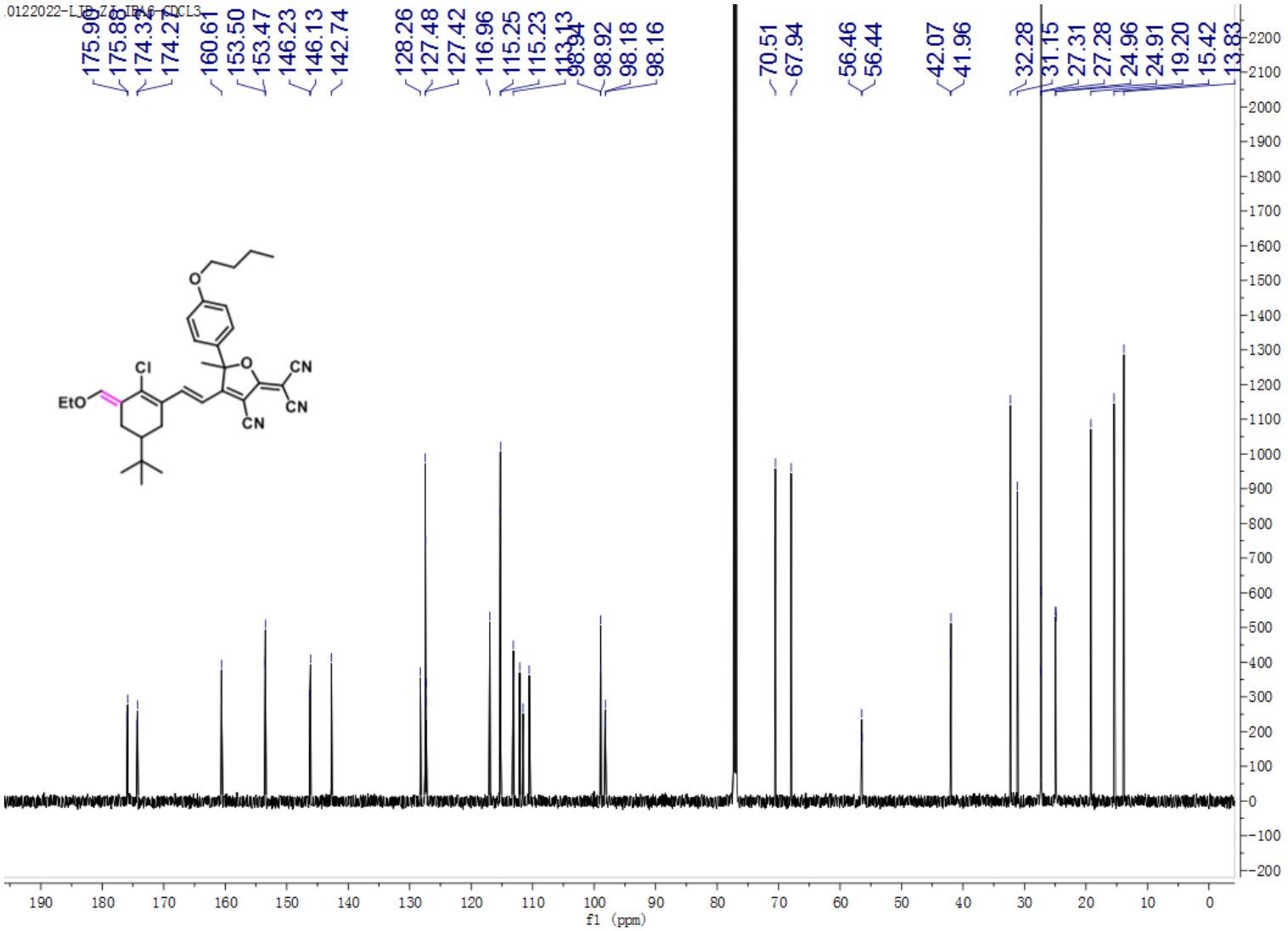


Figure S25. ^{13}C NMR spectrum of compound **TCF-A3**.

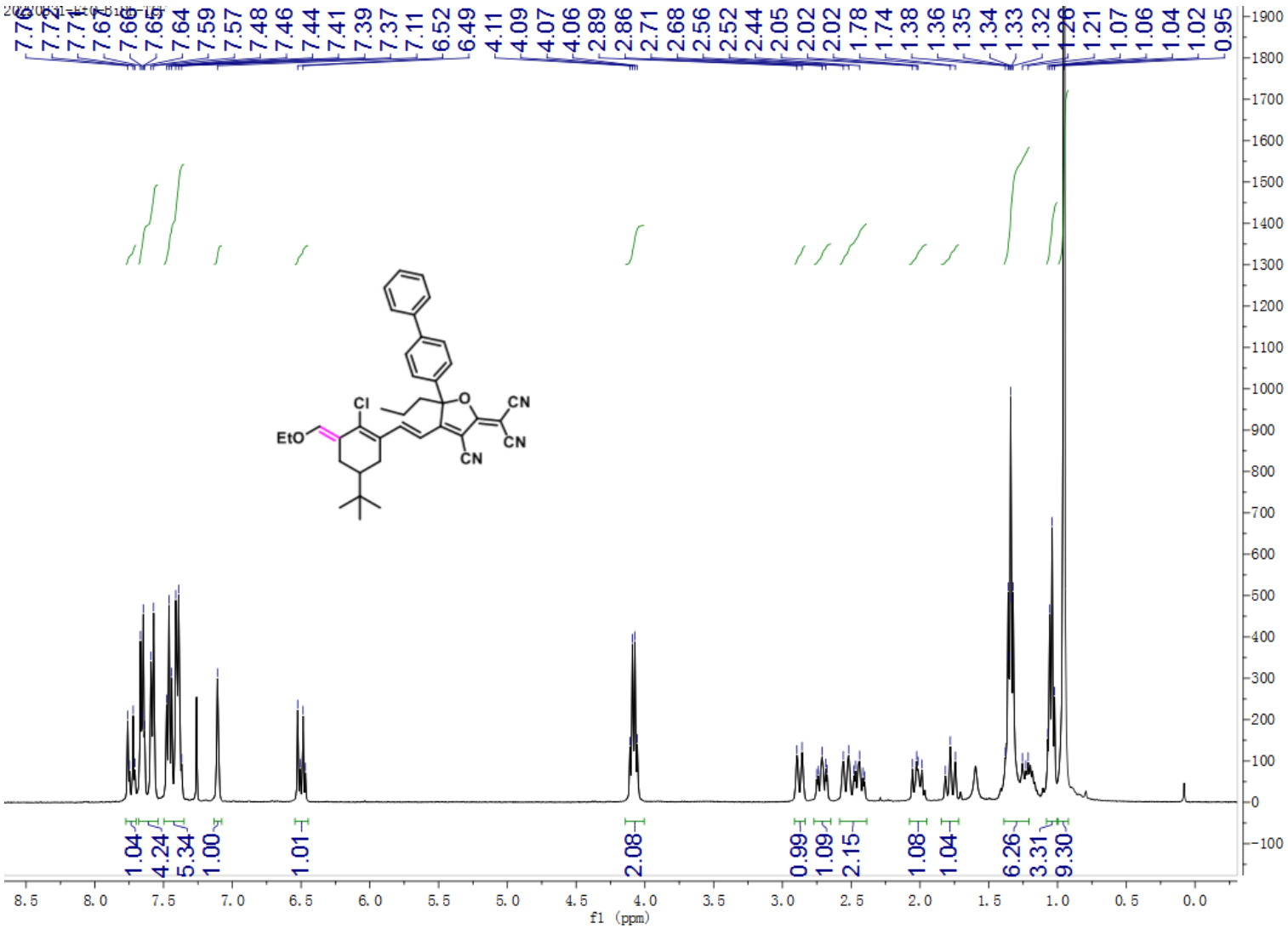


Figure S26. ^{1}H NMR spectrum of compound **TCF-A4**.

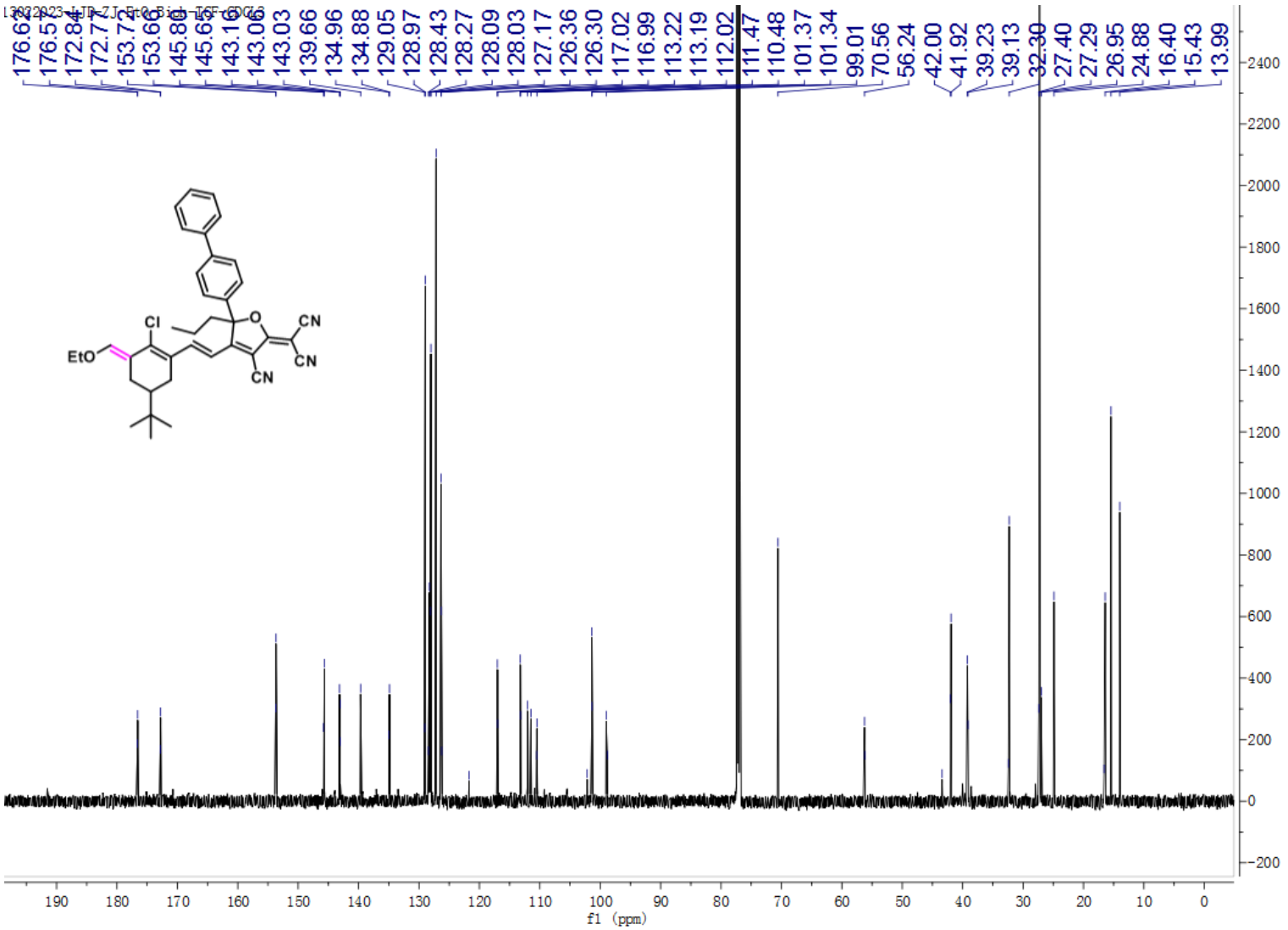


Figure S27 ^{13}C NMR spectrum of compound **TCF-A4**.

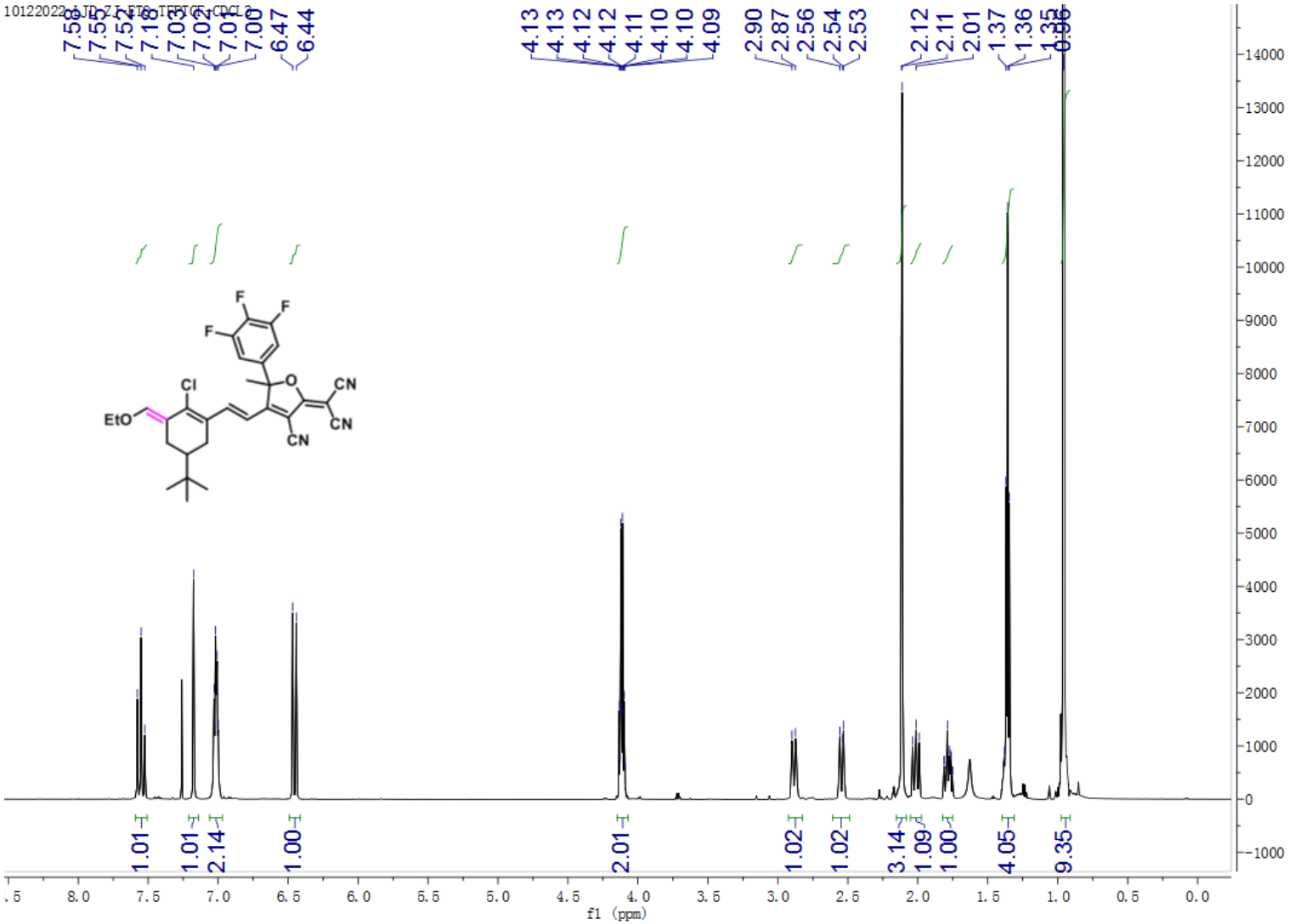


Figure S28. ^{1}H NMR spectrum of compound **TCF-A5**.

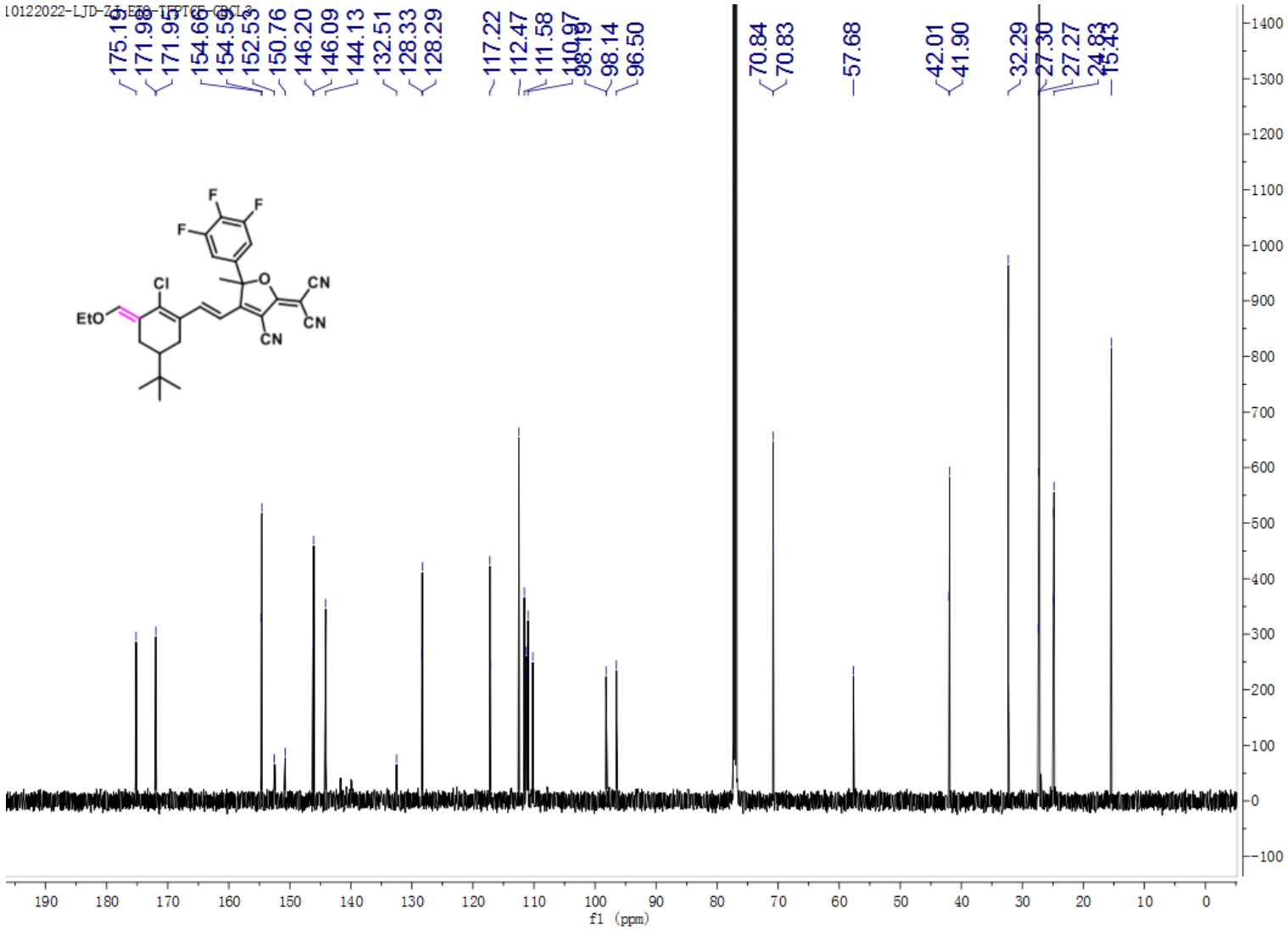


Figure S29. ^{13}C NMR spectrum of compound **TCF-A5**.

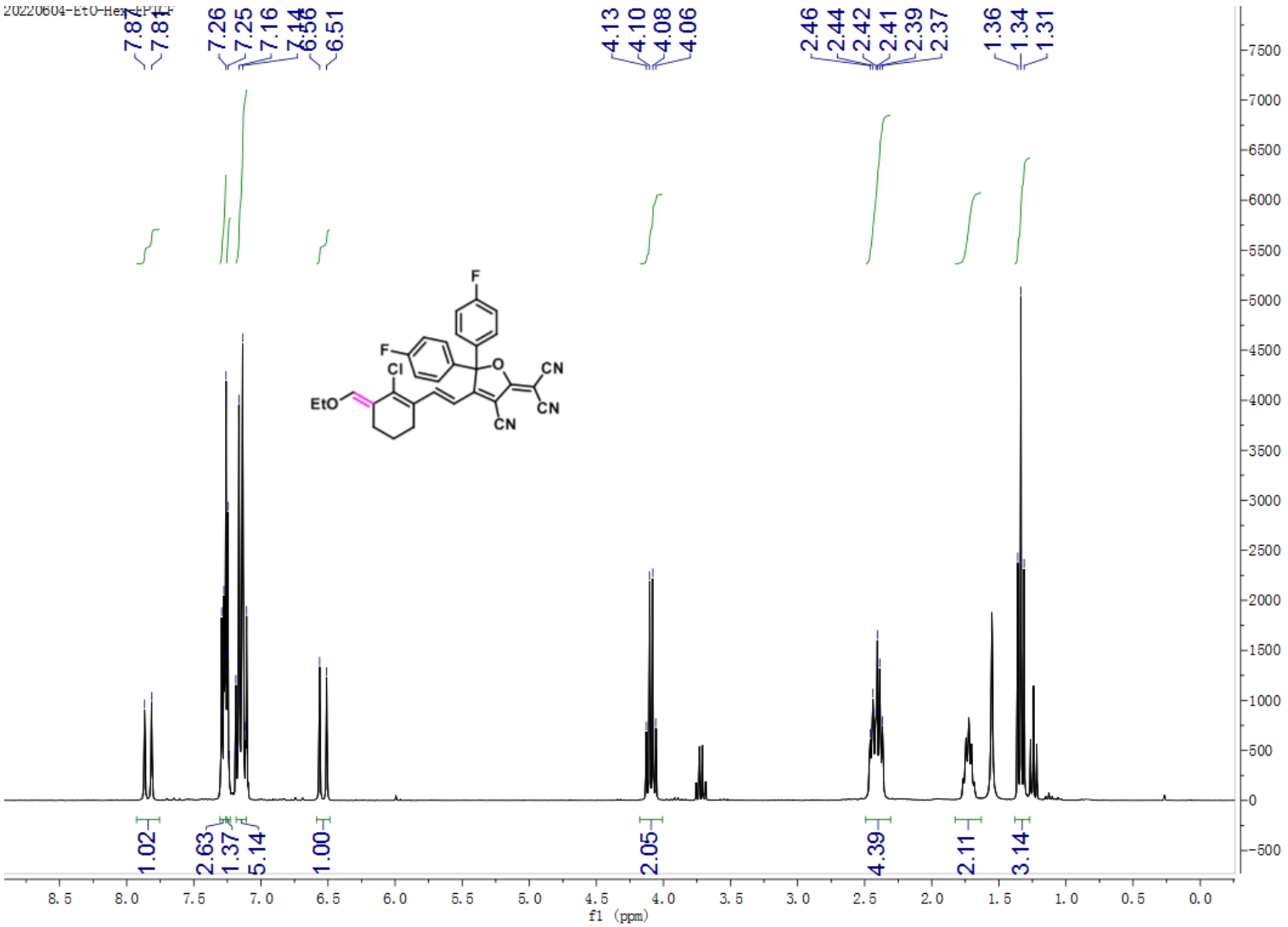


Figure S30. ^{1}H NMR spectrum of compound **TCF-A6**.

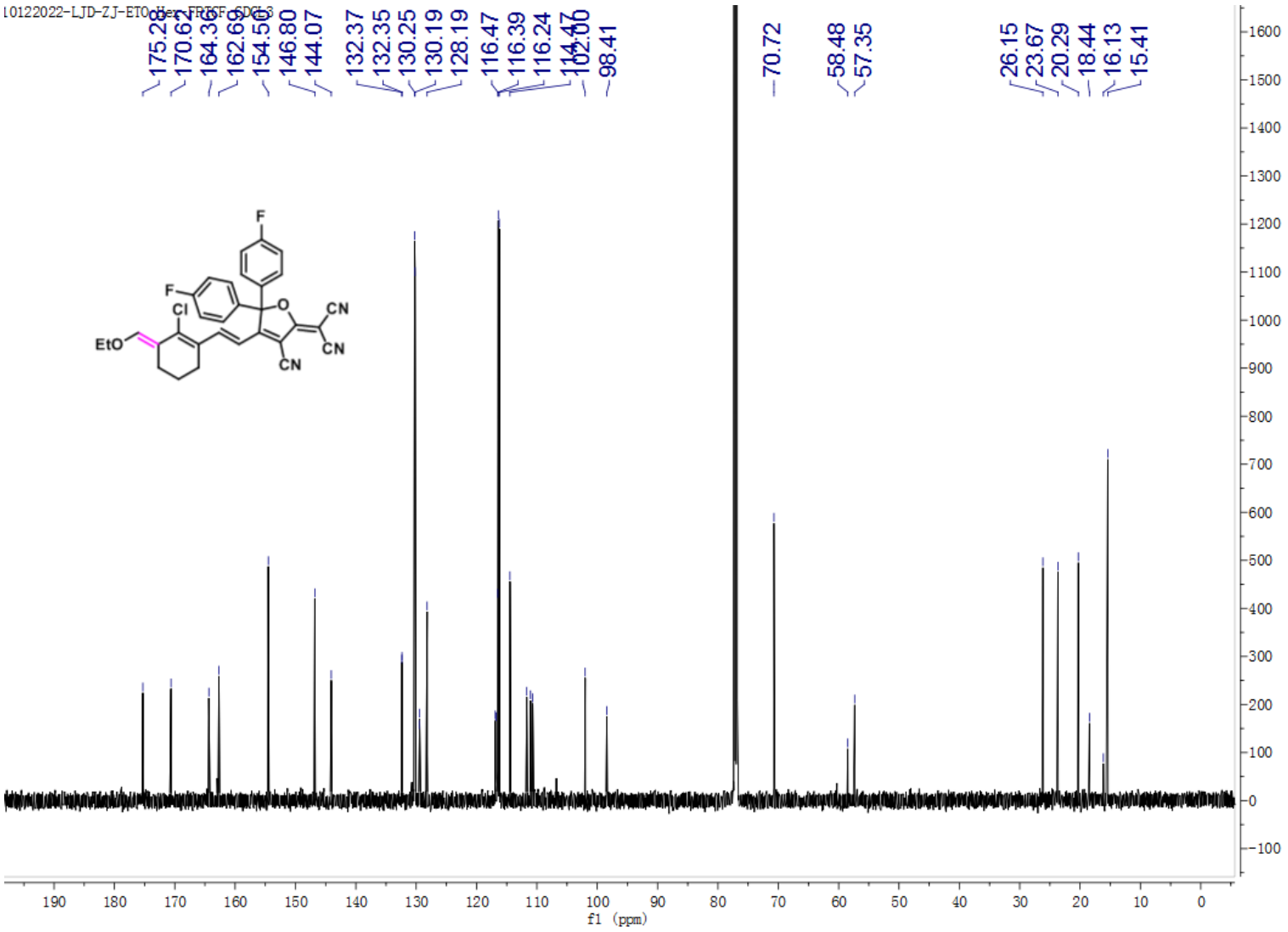


Figure S31. ^{13}C NMR spectrum of compound **TCF-A6**.

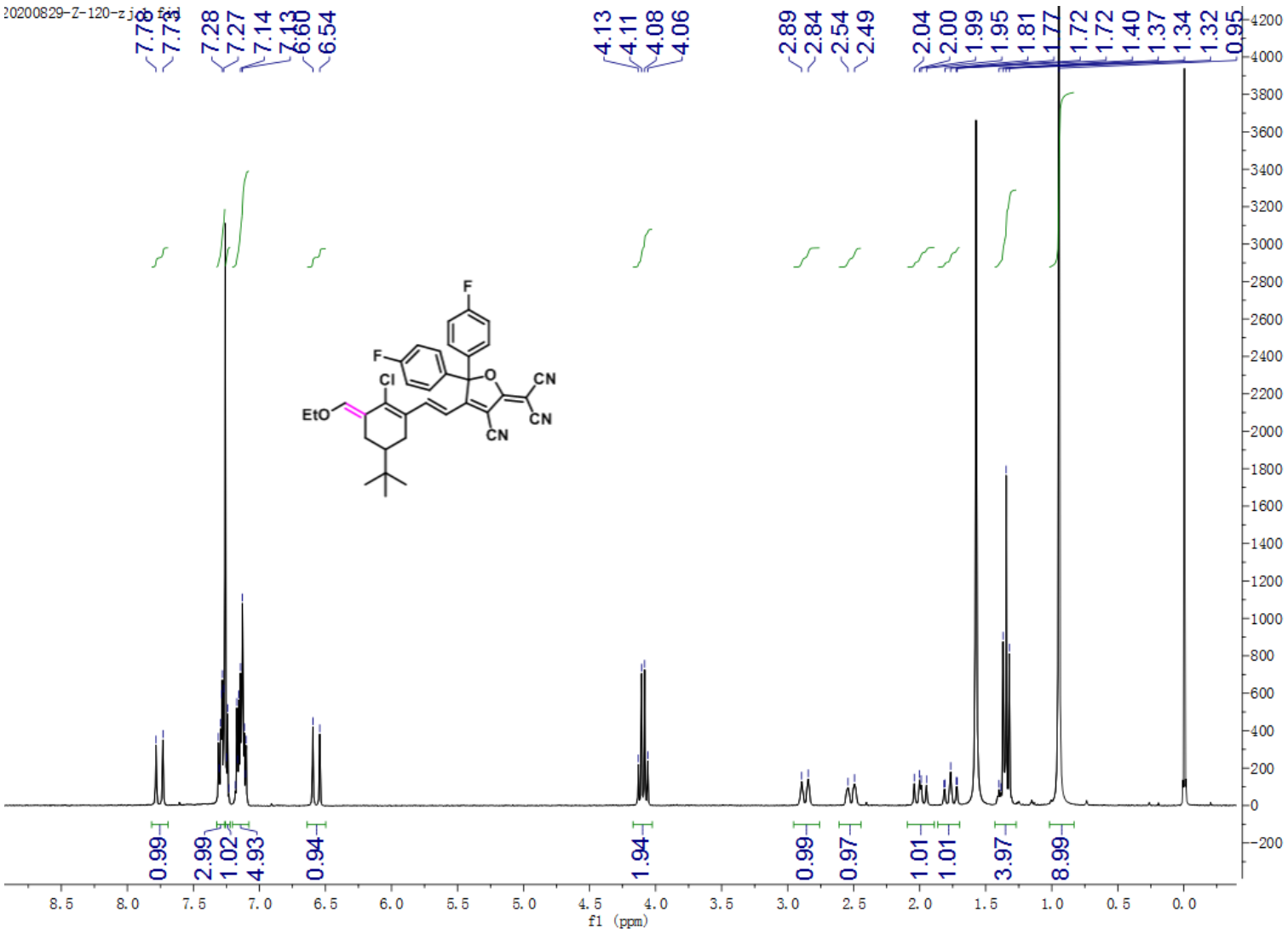


Figure S32. ^{1}H NMR spectrum of compound **TCF-A7**.

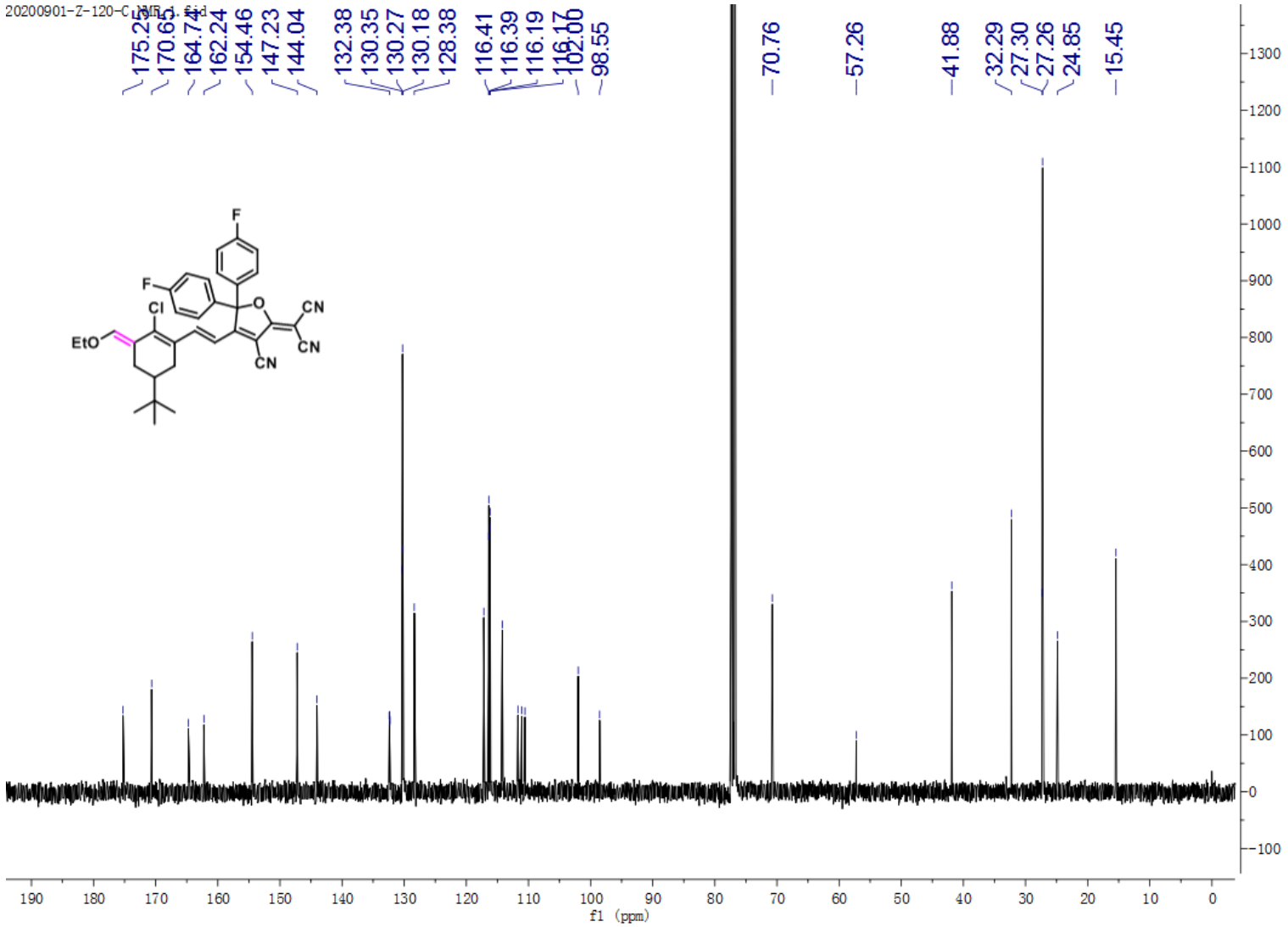


Figure S33. ^{13}C NMR spectrum of compound **TCF-A7**.

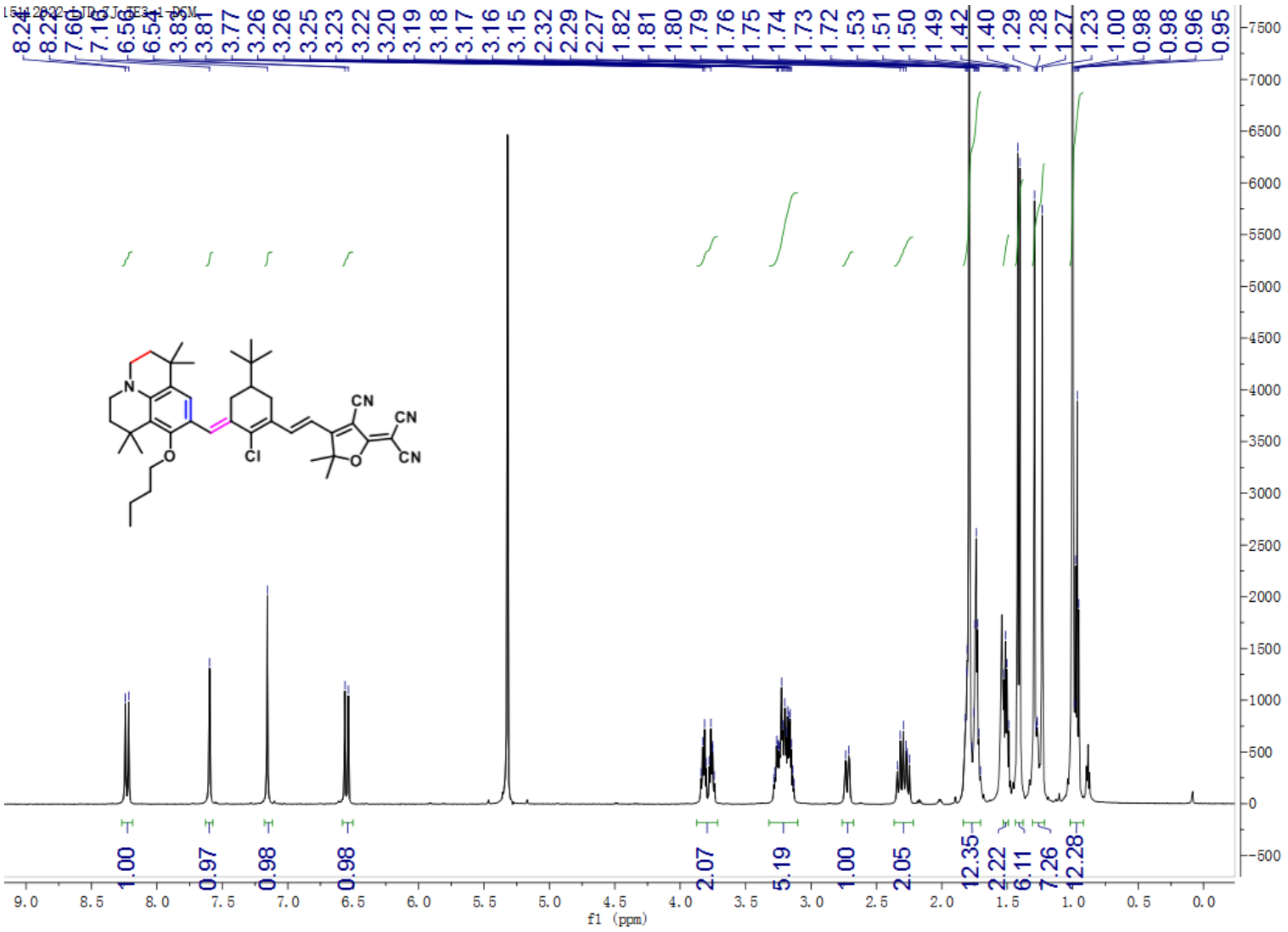


Figure S34. ^{1}H NMR spectrum of compound **TE-I-1**.

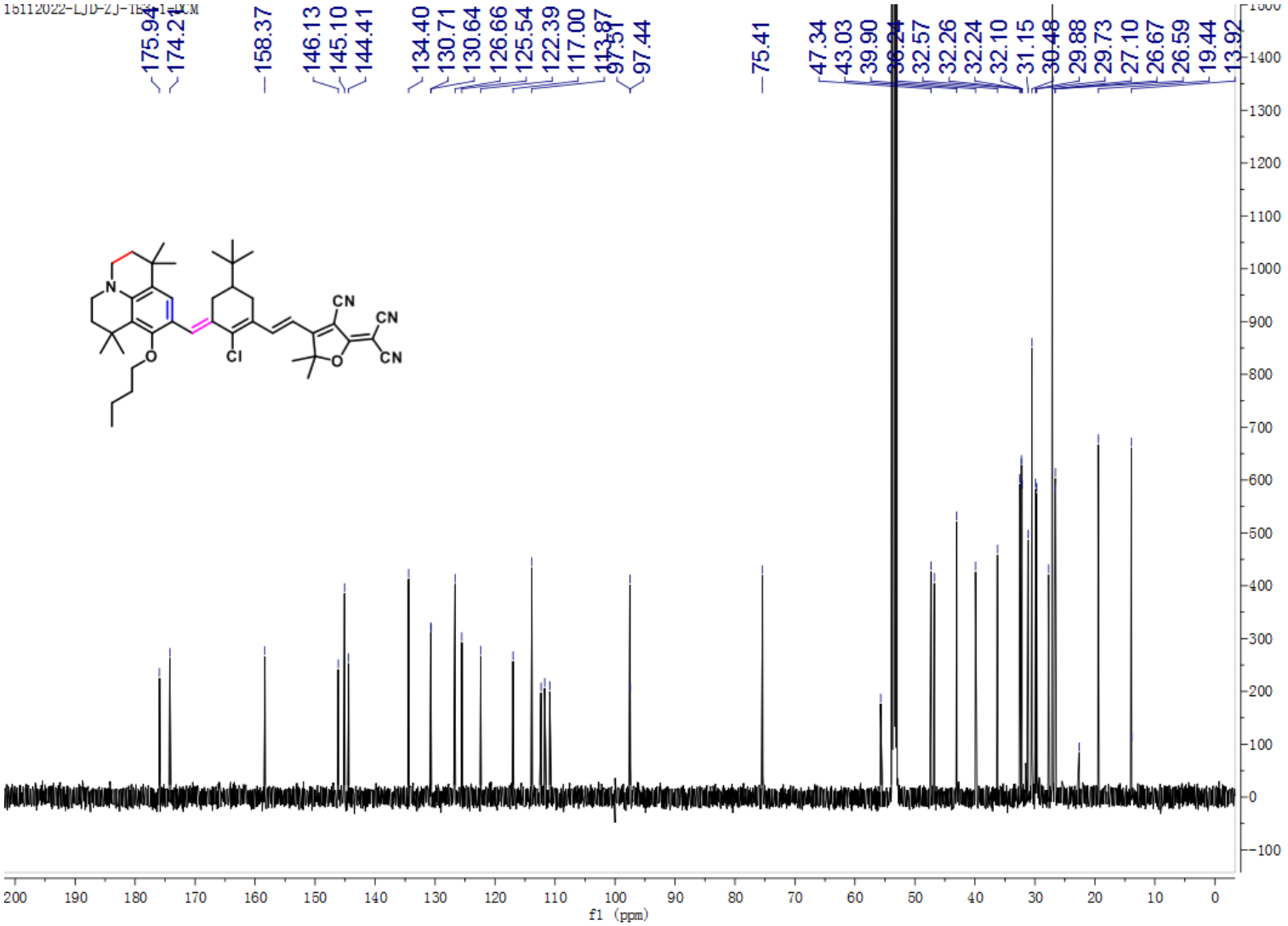


Figure S35. ^{13}C NMR spectrum of compound **TE-I-1**.

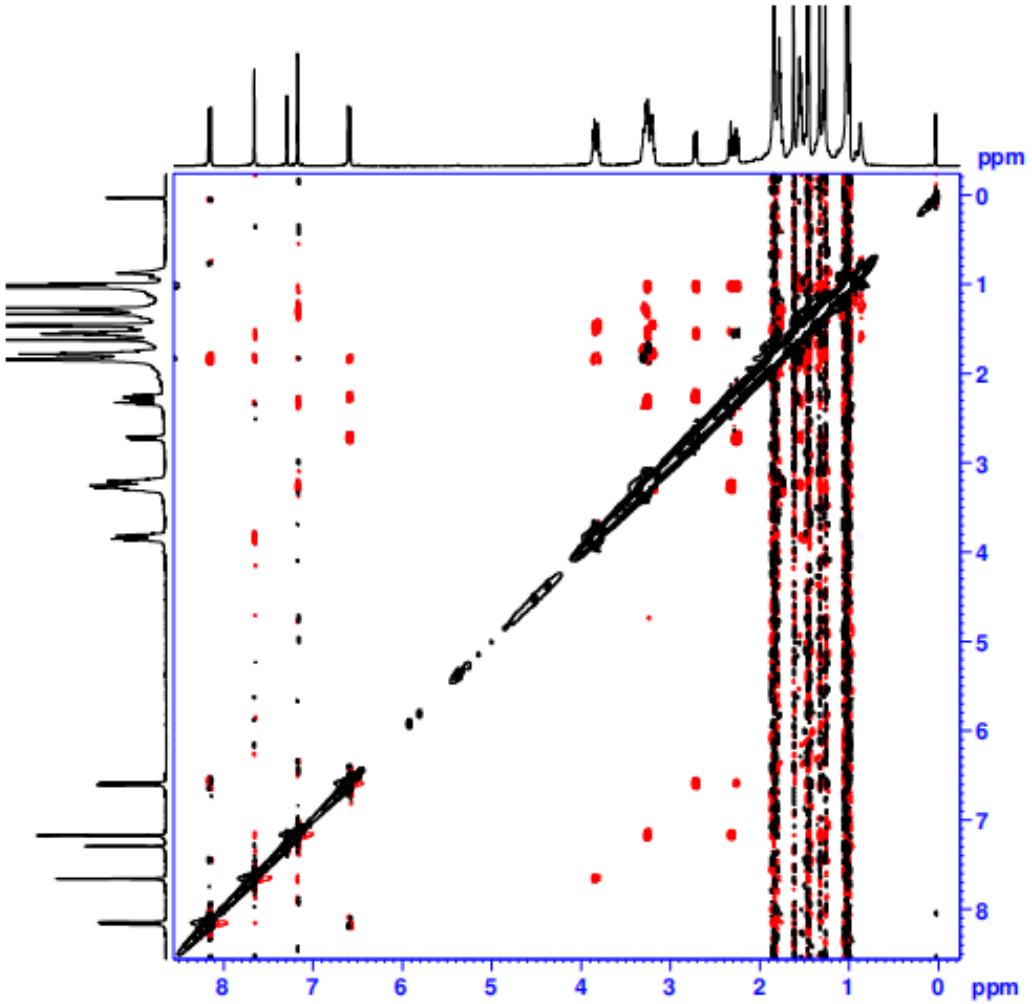


Figure S36. ROESY spectrum of compound **TE-I-1**.

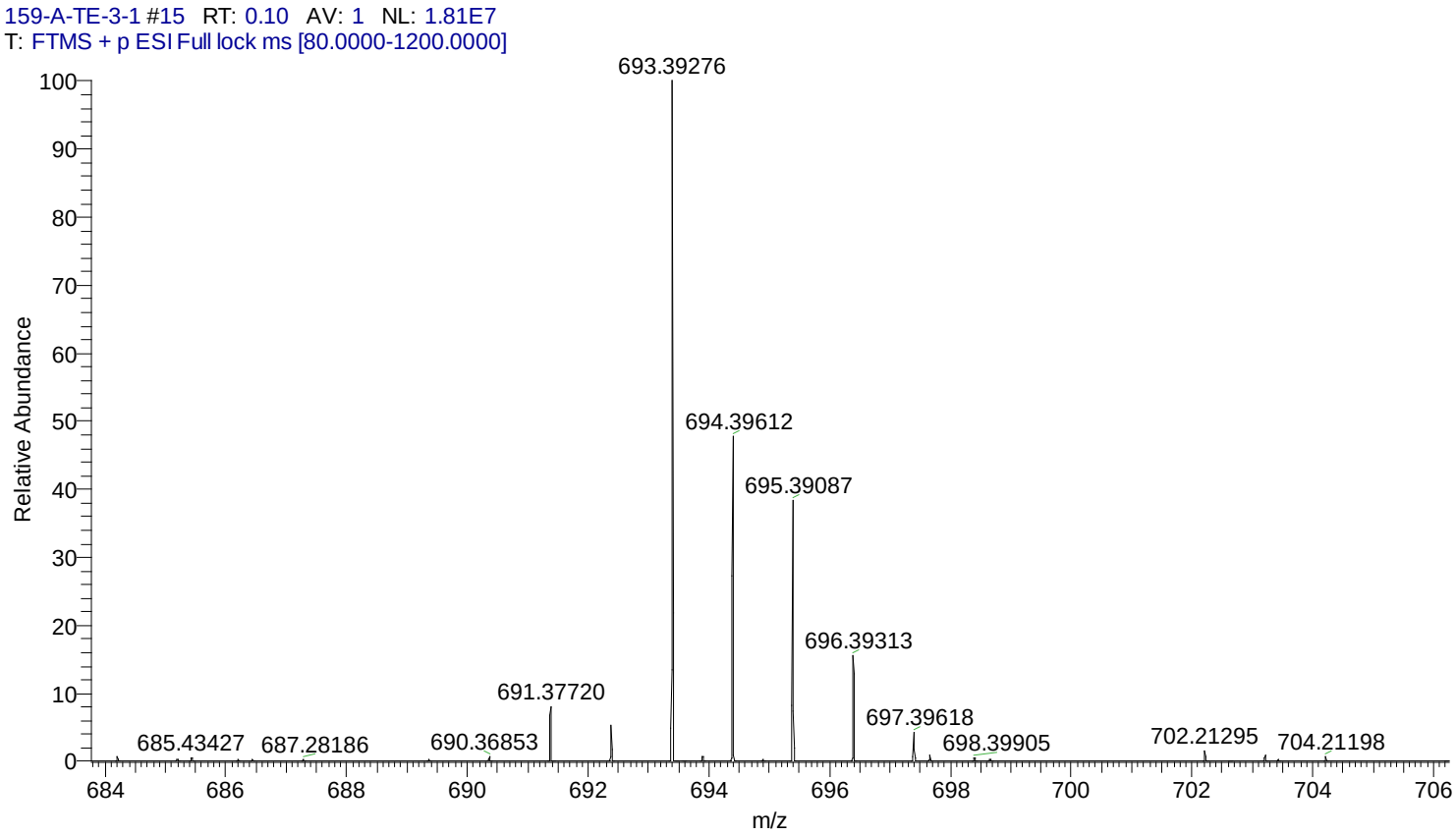


Figure S37. HRMS spectrum of compound **TE-I-1**.

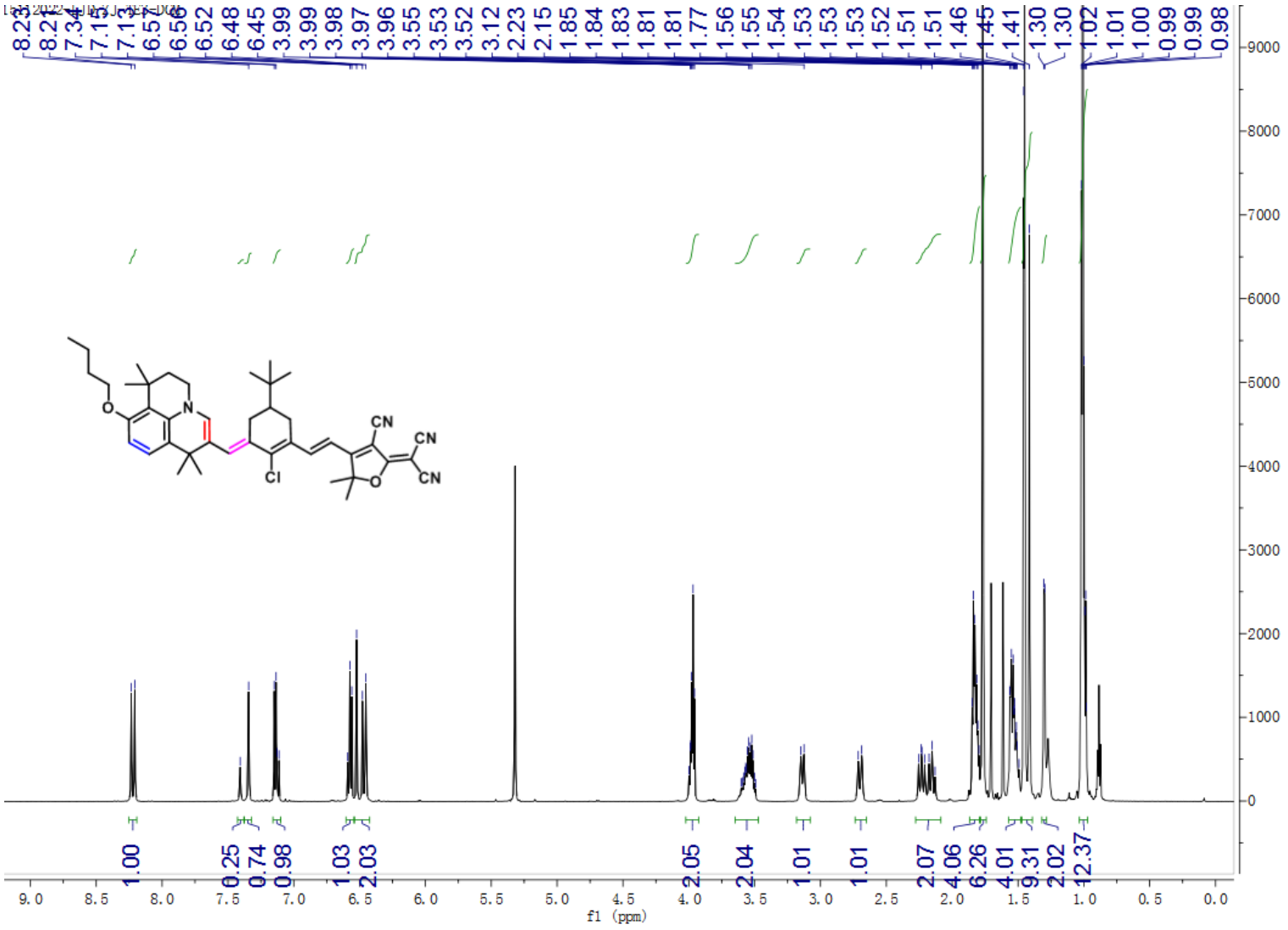


Figure S38. ^{1}H NMR spectrum of compound **TE-II-1**.

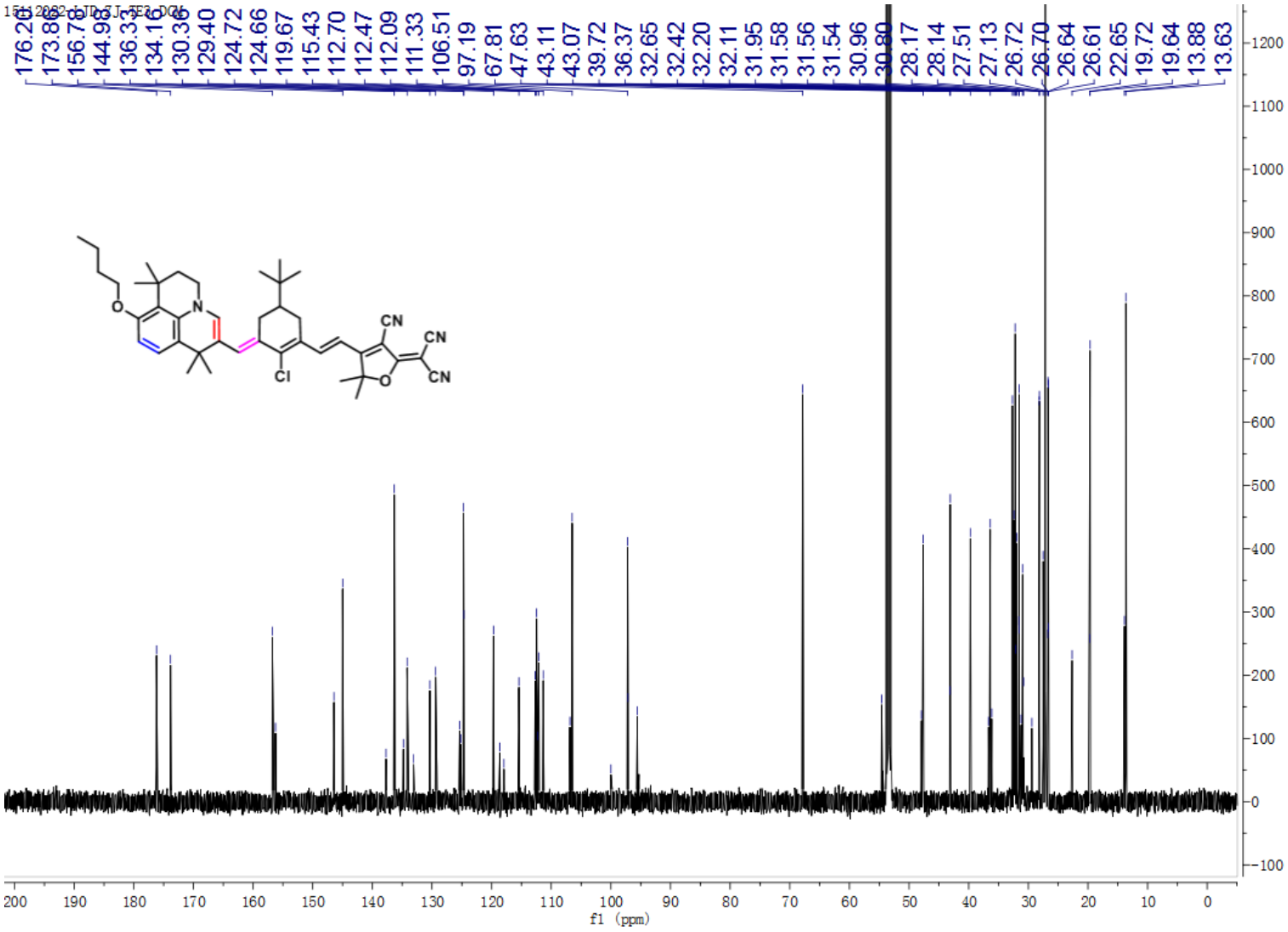


Figure S39. ^{13}C NMR spectrum of compound **TE-II-1**.

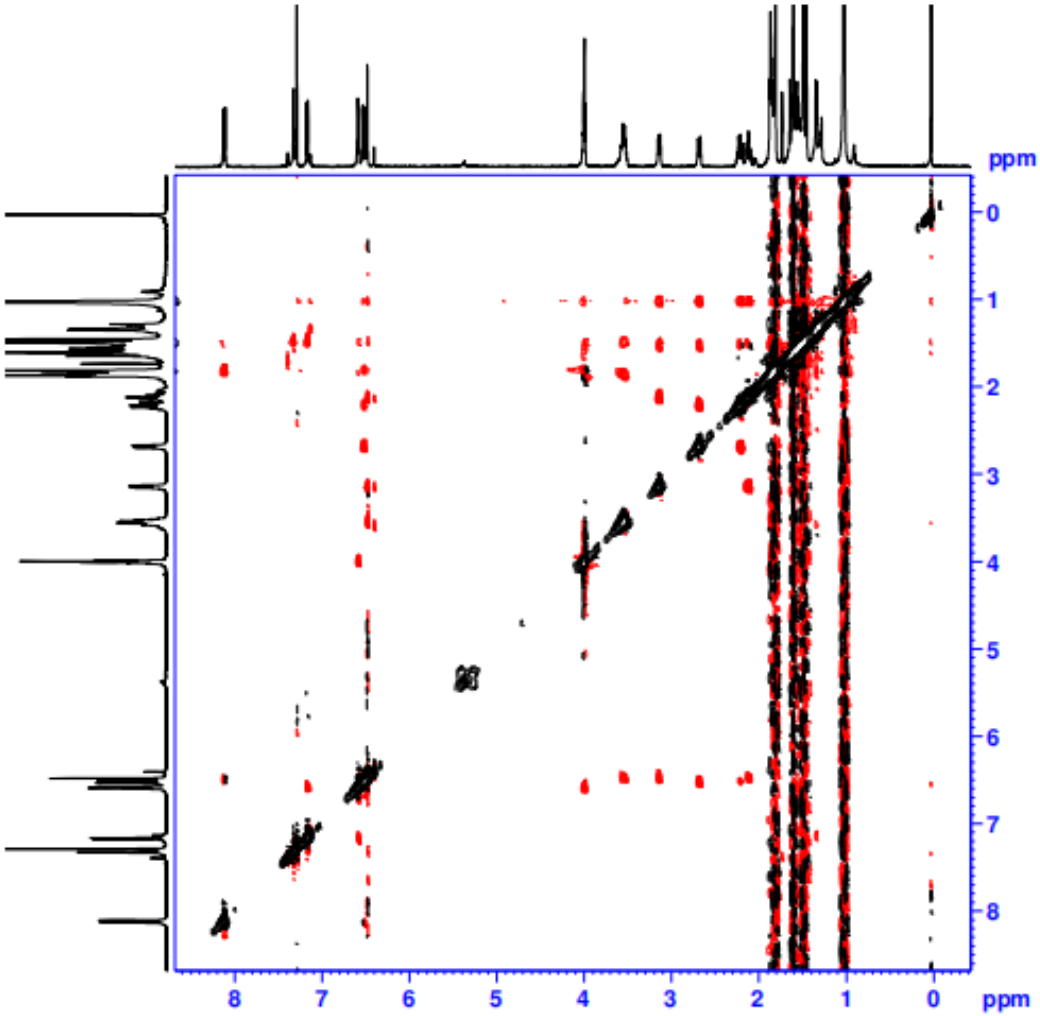


Figure S40 ROESY spectrum of compound **TE-II-1**.

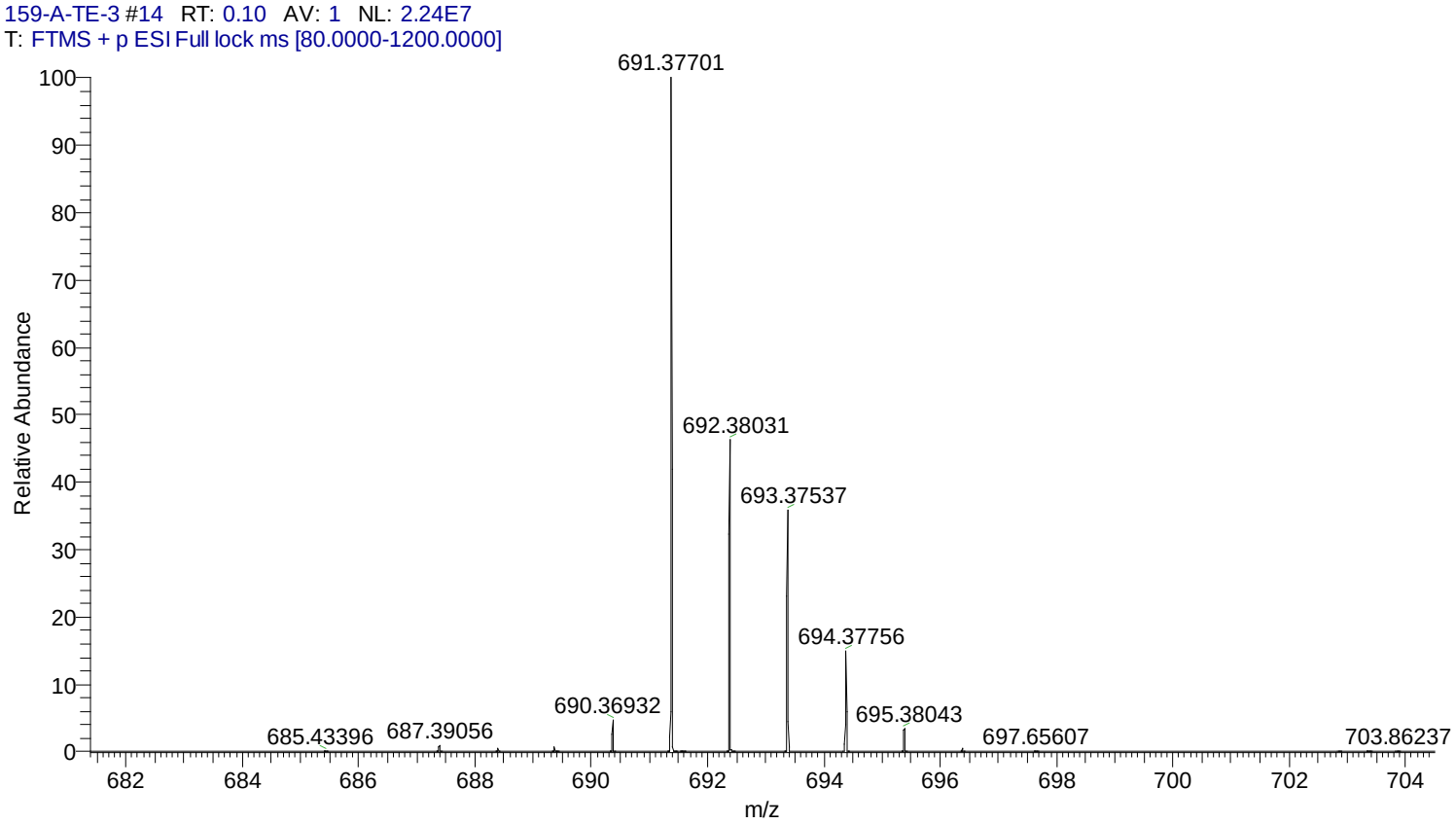


Figure S41. HRMS spectrum of compound **TE-II-1**.

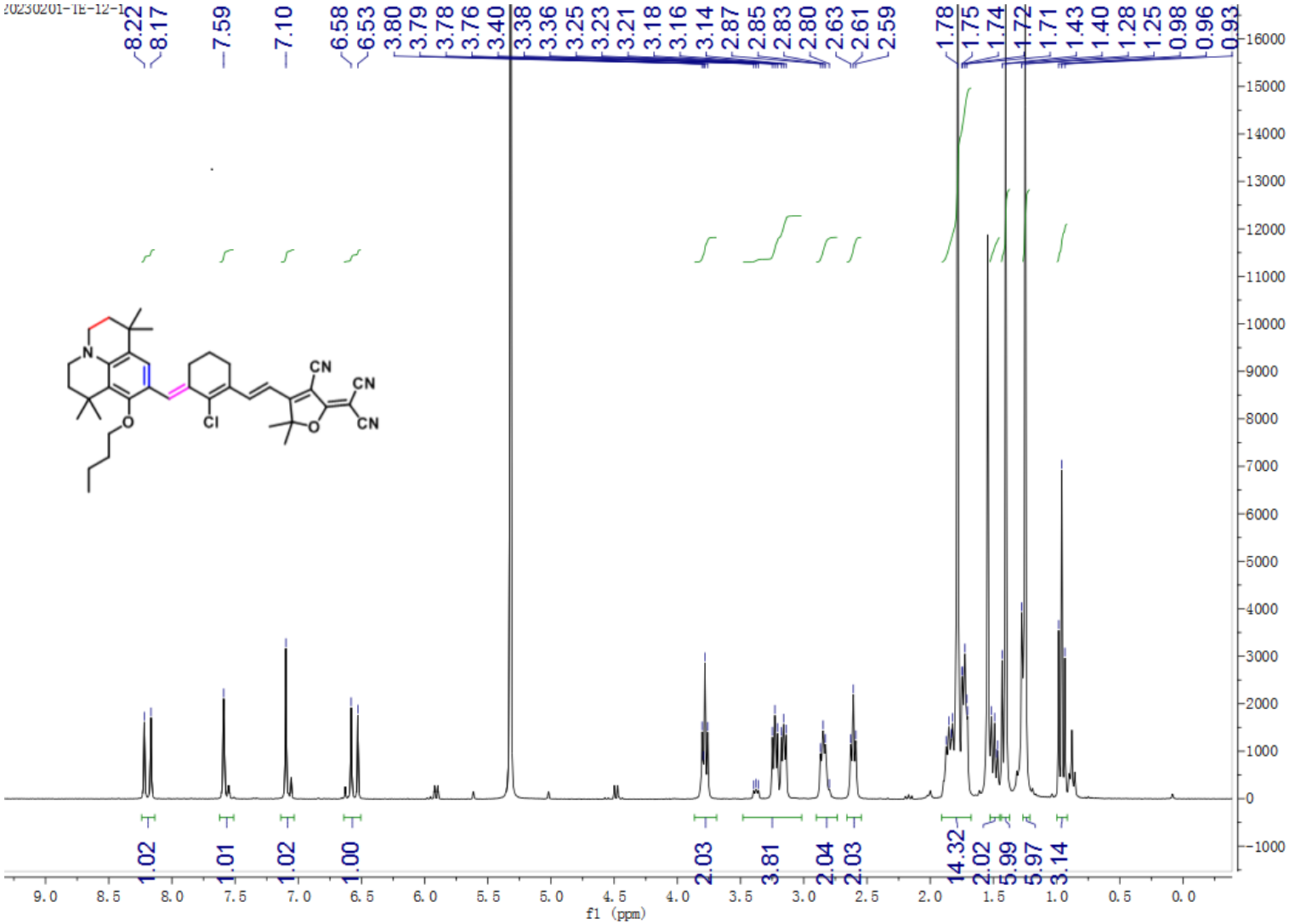


Figure S42. ^{1}H NMR spectrum of compound **TE-I-2**.

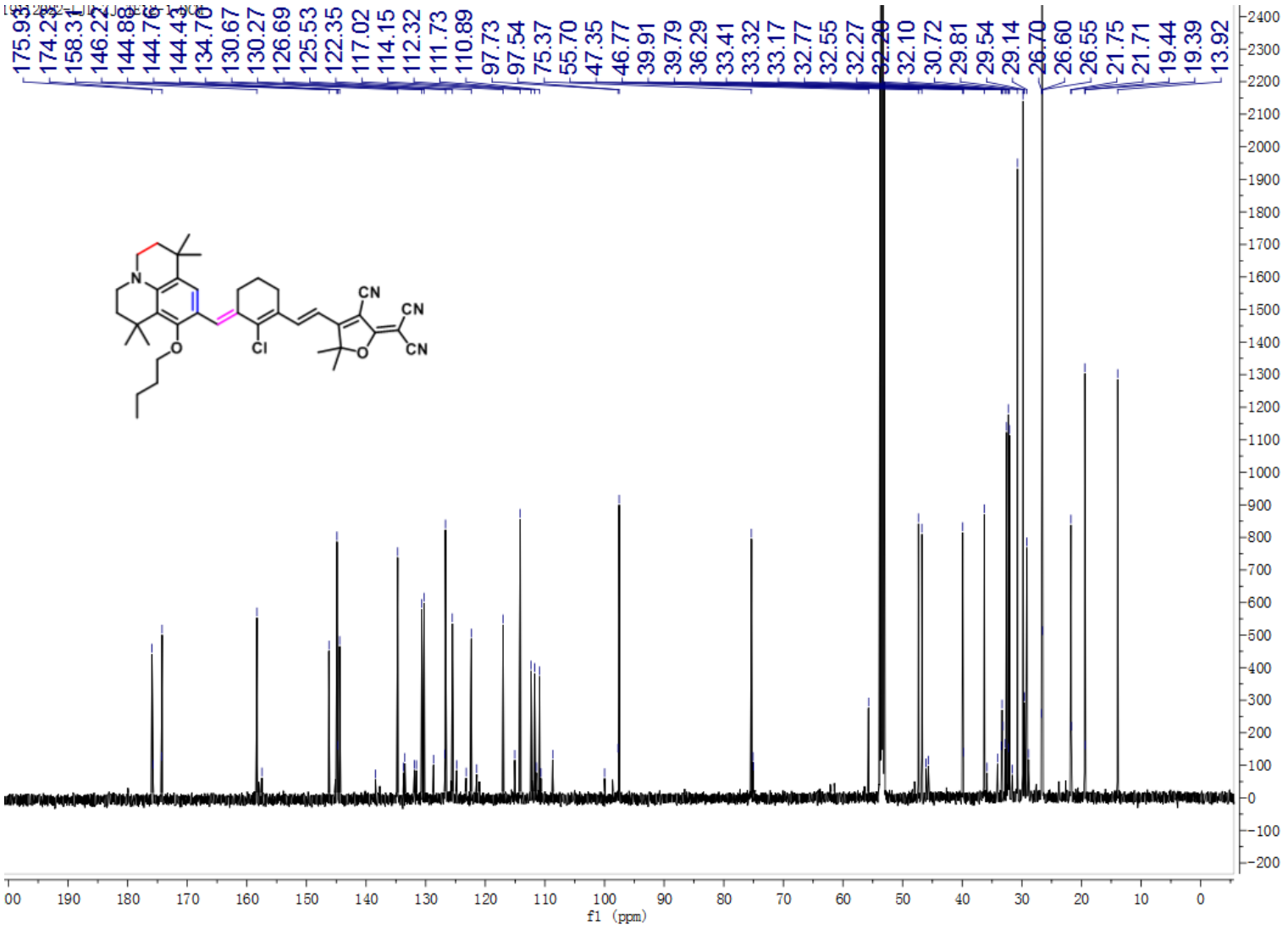


Figure S43. ^{13}C NMR spectrum of compound **TE-I-2**.

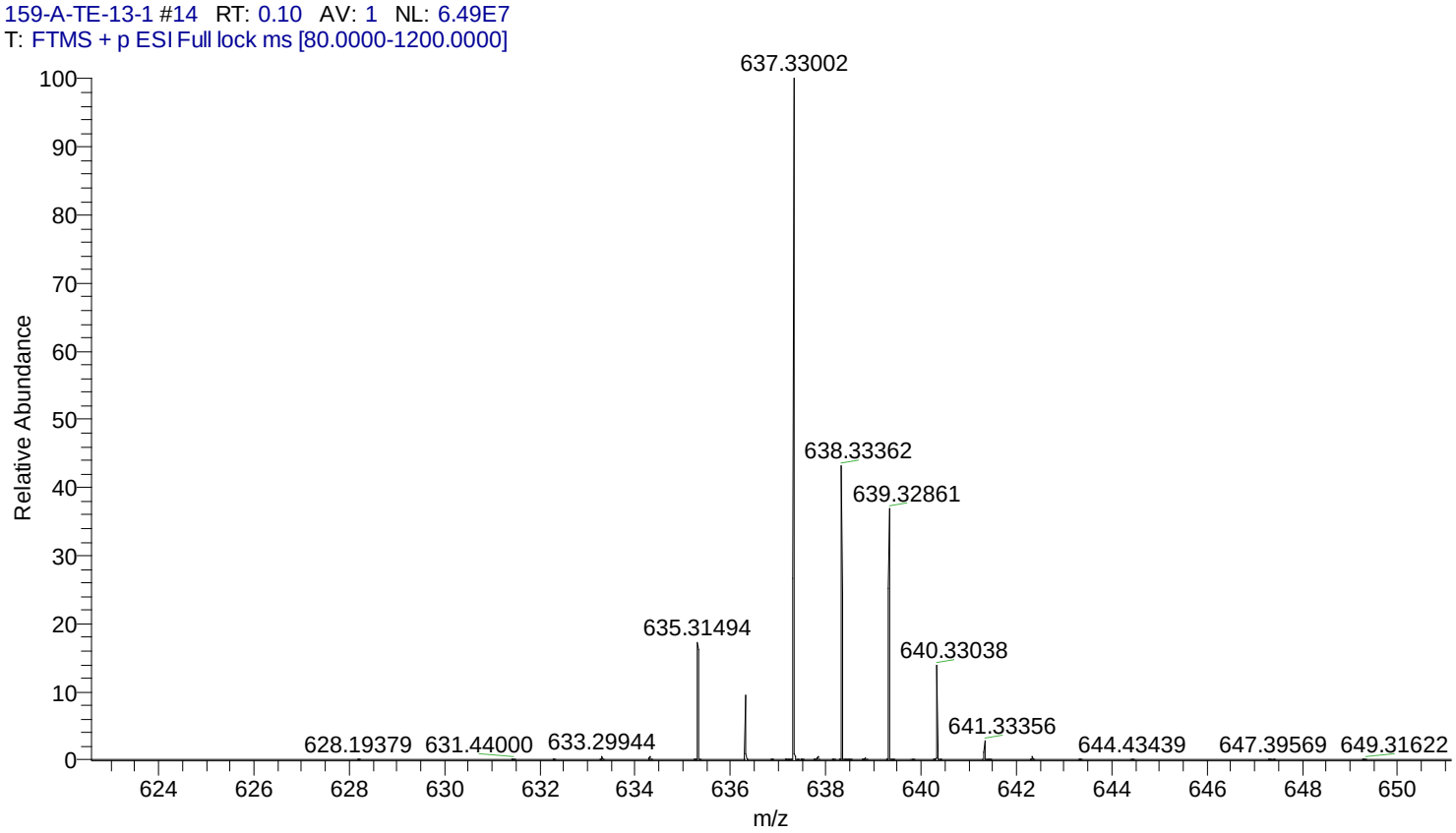


Figure S44. HRMS spectrum of compound **TE-I-2**.

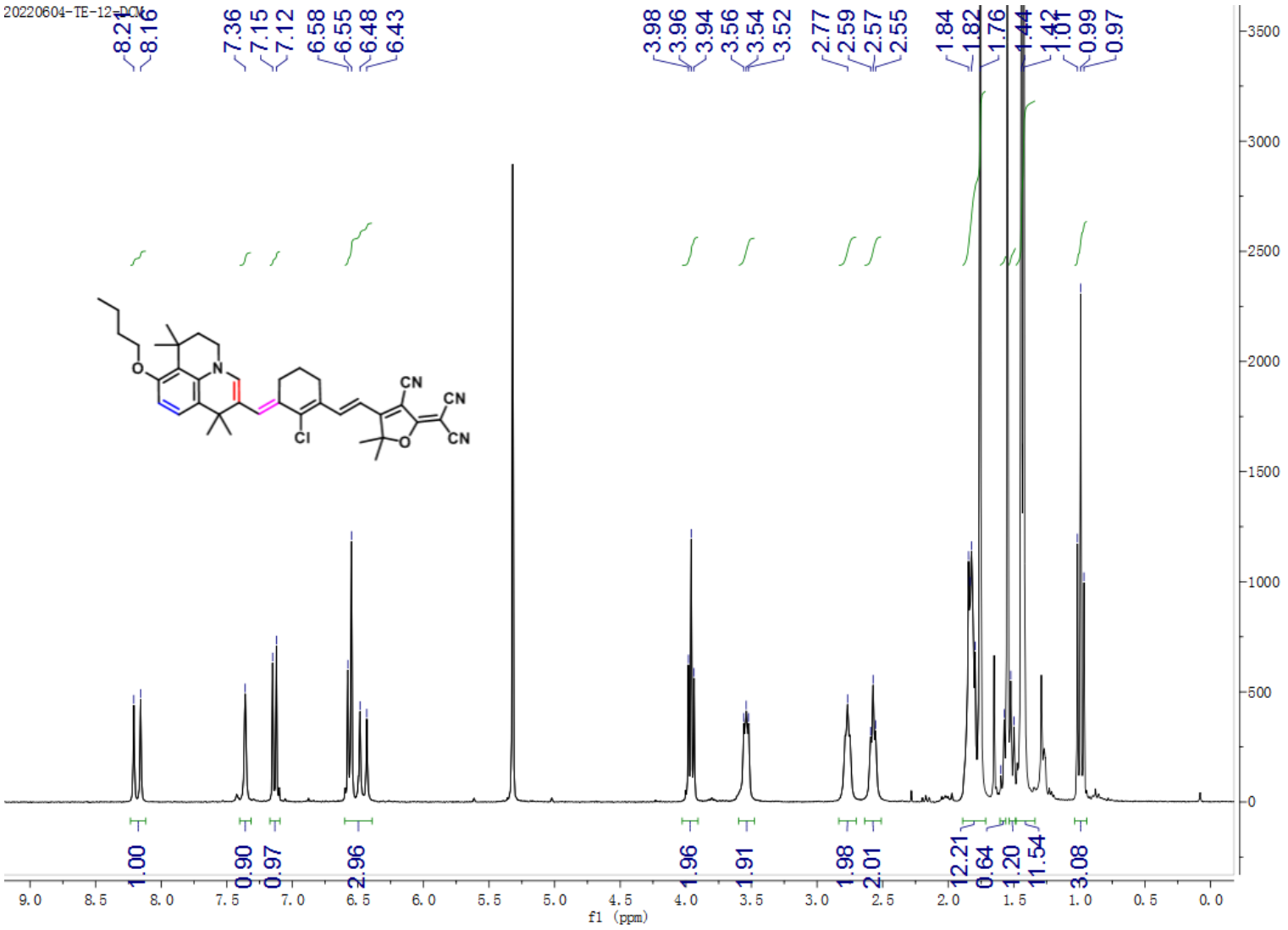


Figure S45. [1]H NMR spectrum of compound **TE-II-2**.

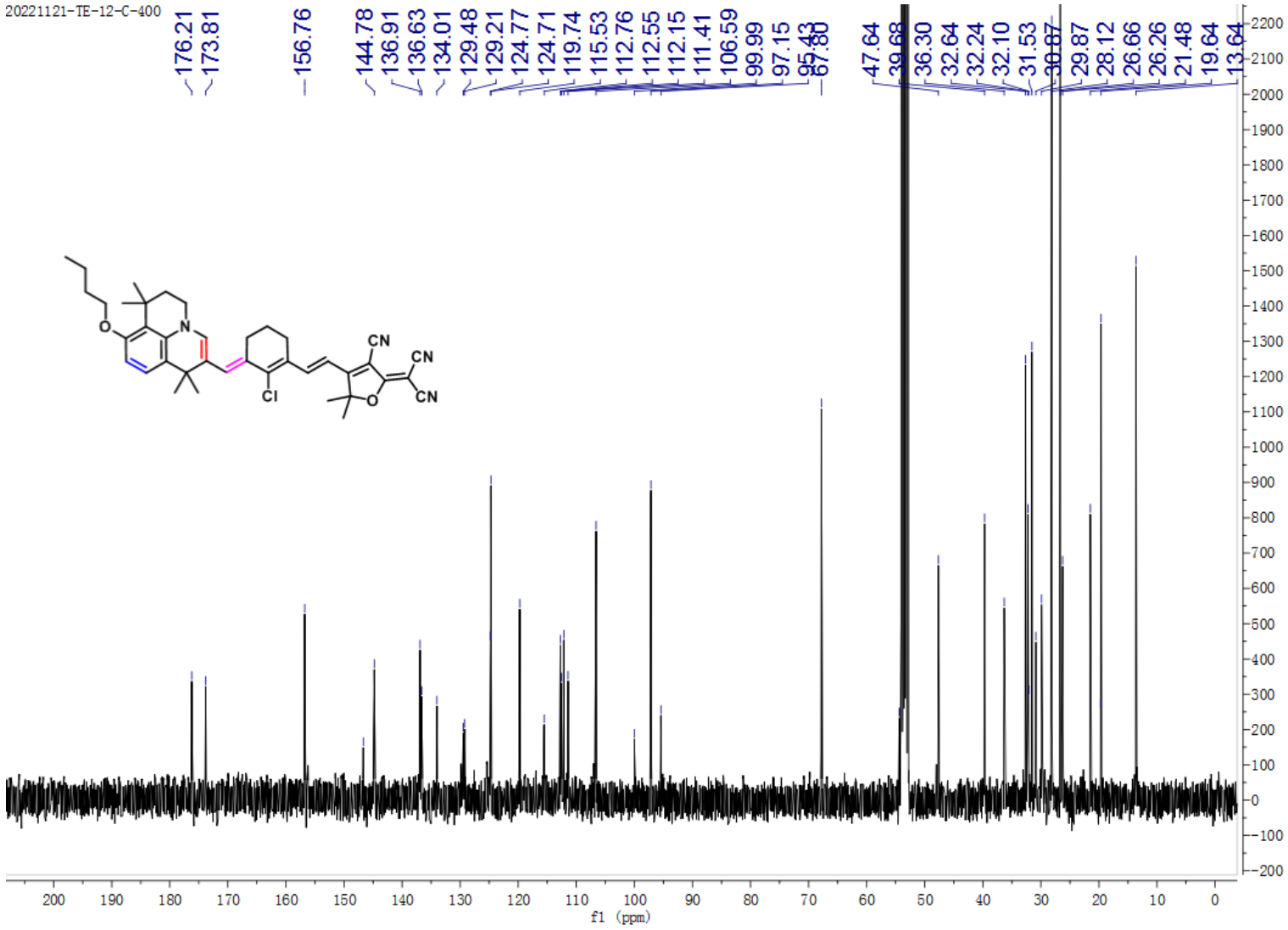


Figure S46. ^{13}C NMR spectrum of compound **TE-II-2**.

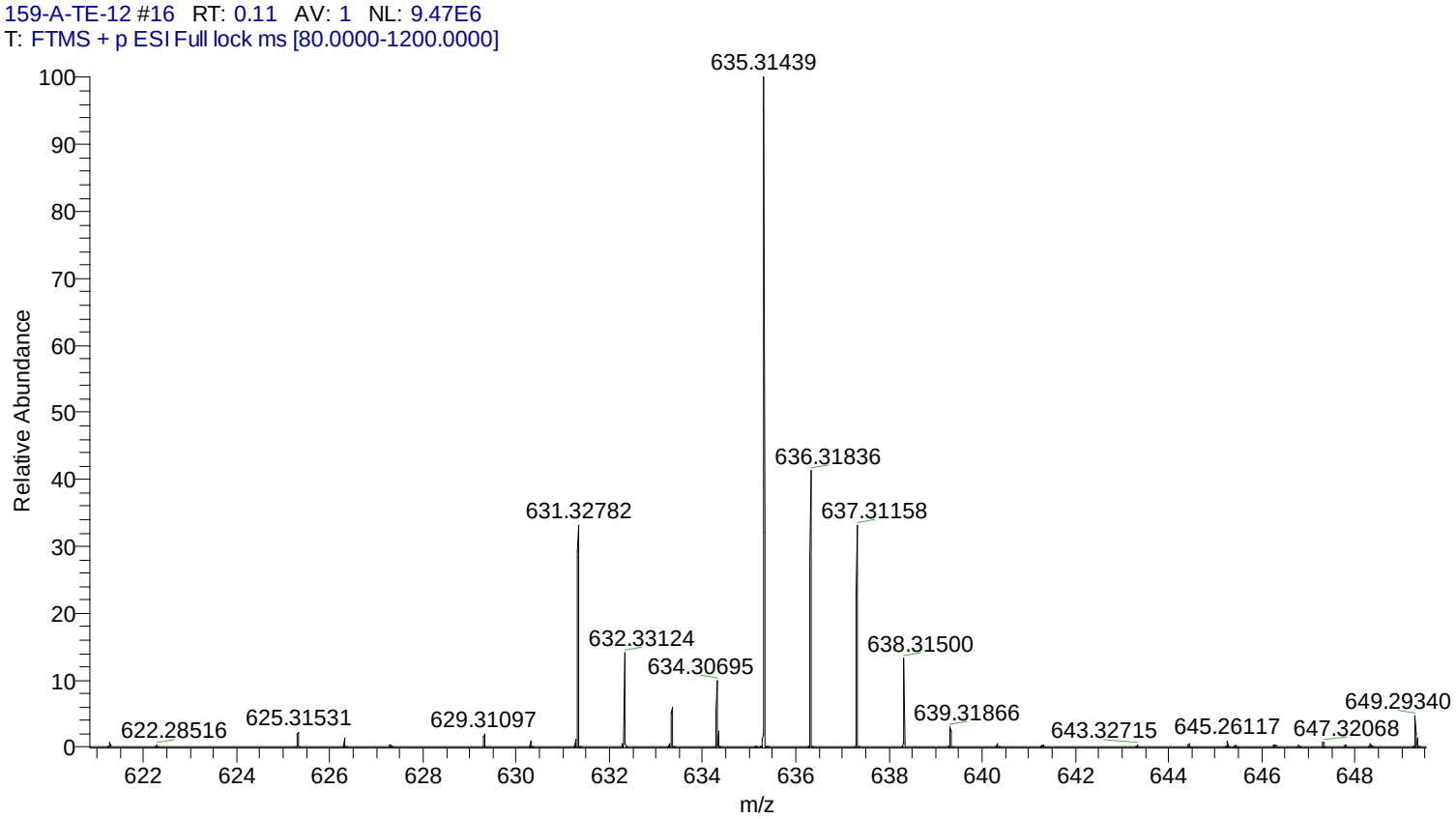


Figure S47. HRMS spectrum of compound **TE-II-2**.

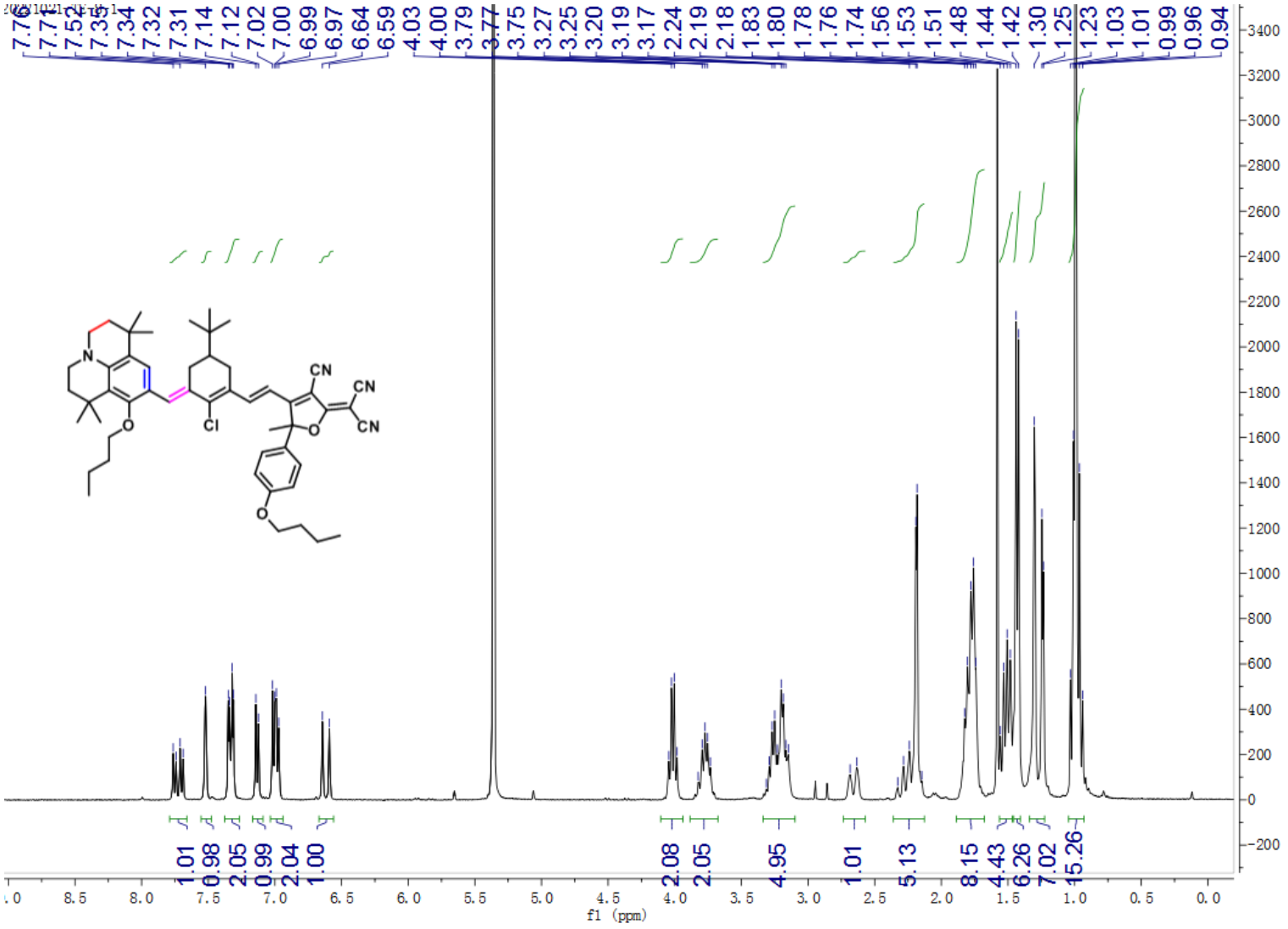


Figure S48. ^{1}H NMR spectrum of compound **TE-I-3**.

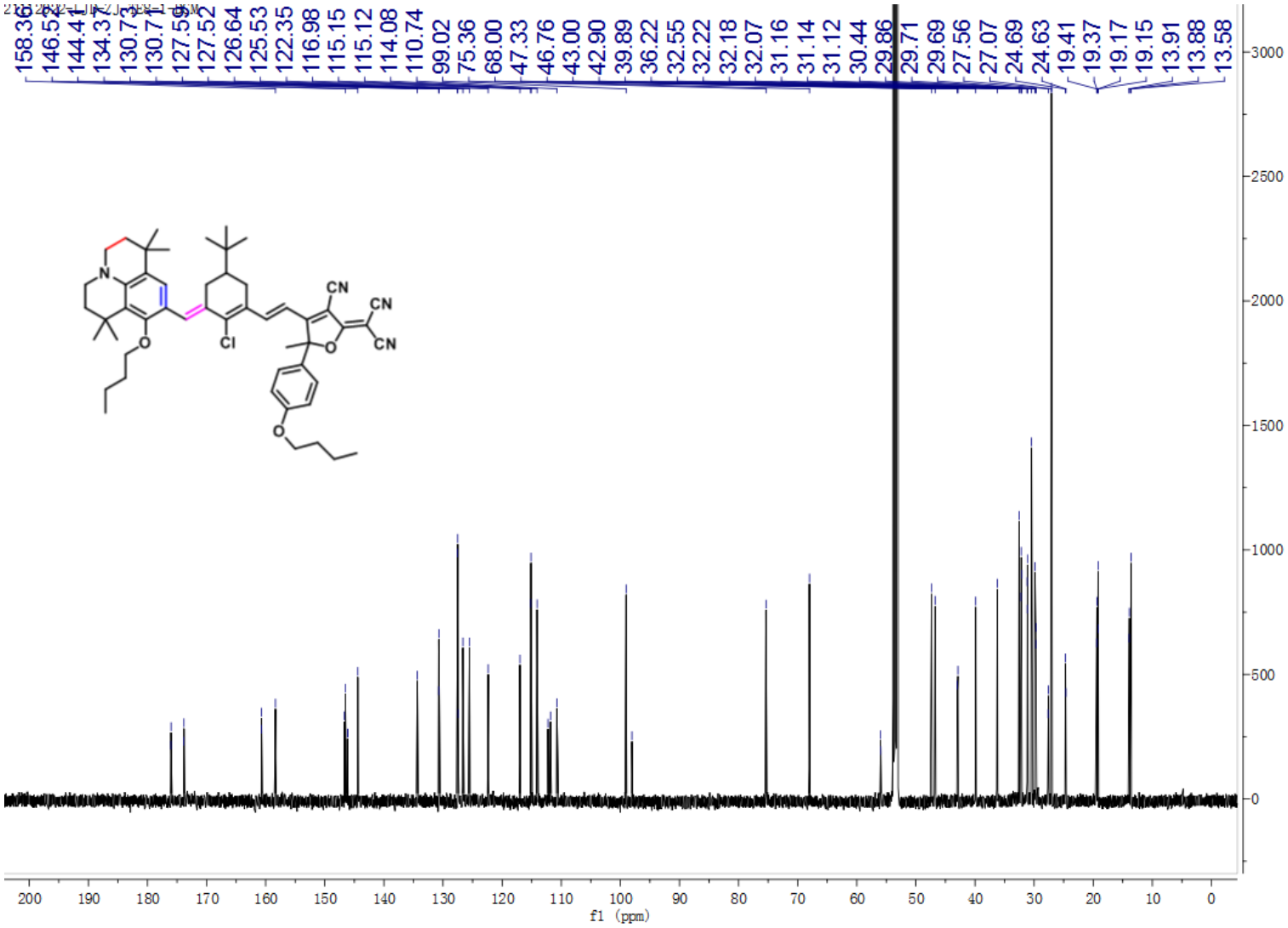


Figure S49. ^{13}C NMR spectrum of compound **TE-I-3**.

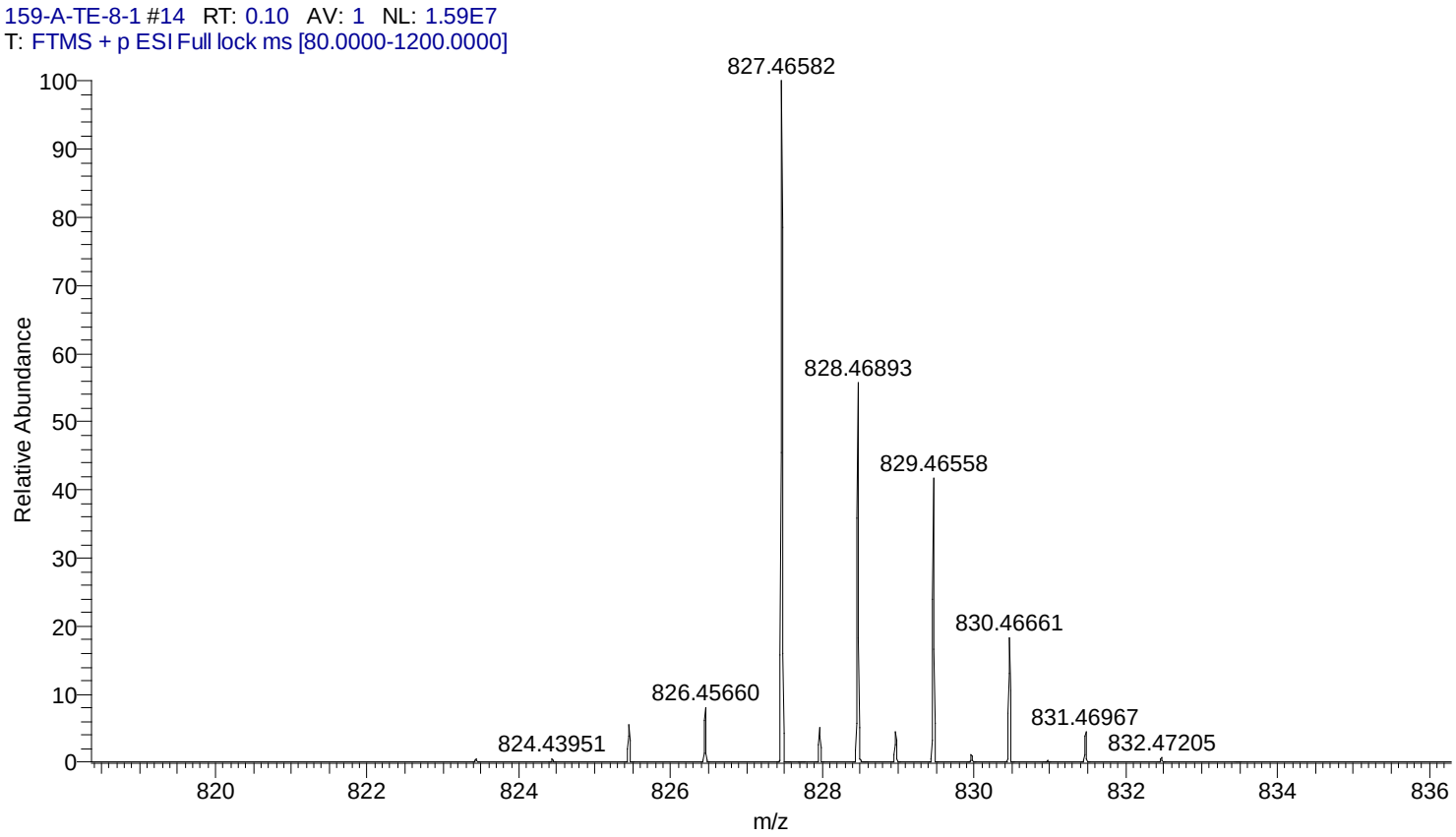


Figure S50. HRMS spectrum of compound **TE-I-3**.

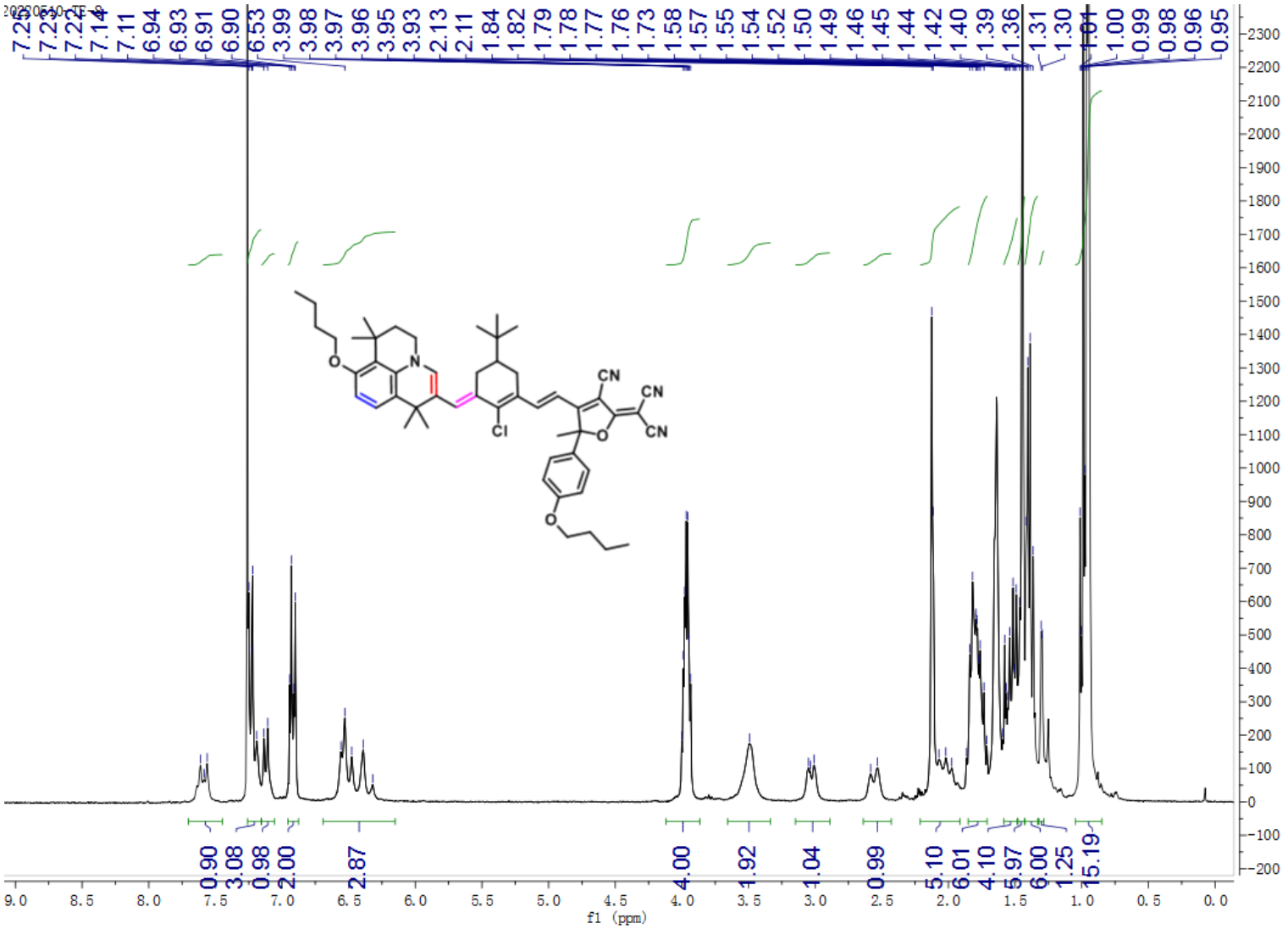


Figure S51. [1]H NMR spectrum of compound **TE-II-3**.

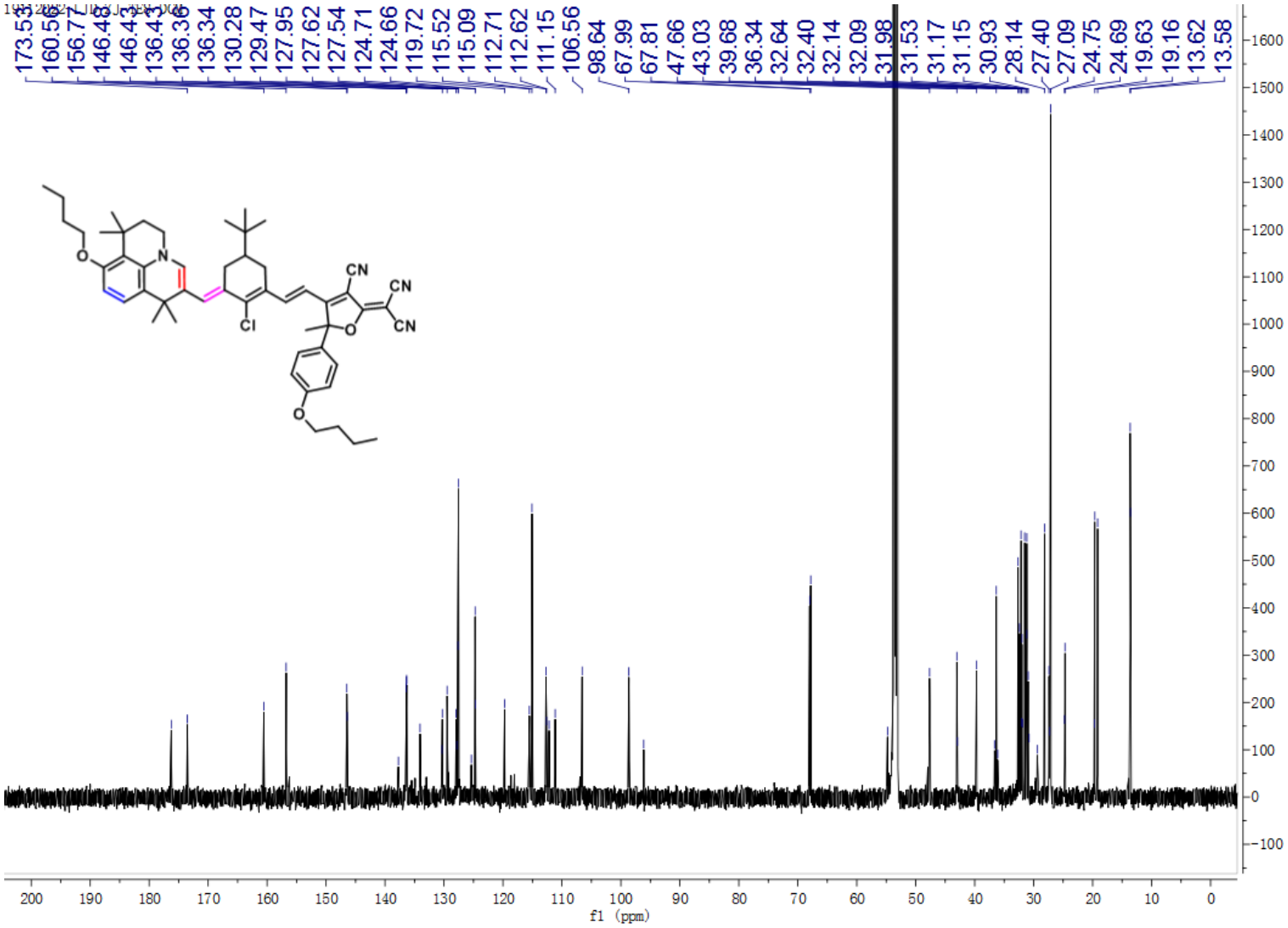


Figure S52. ^{13}C NMR spectrum of compound **TE-II-3**.

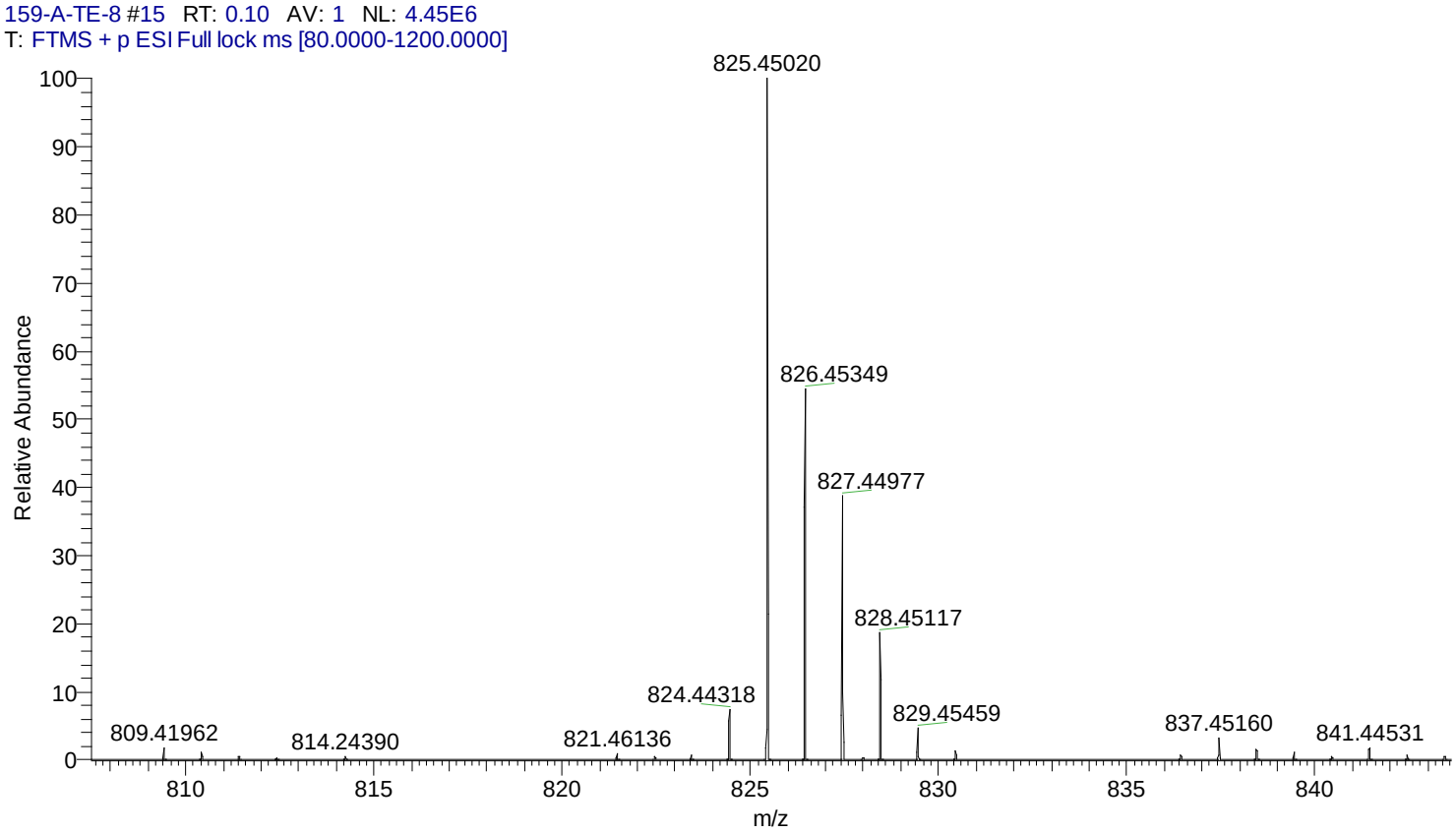


Figure S53. HRMS spectrum of compound **TE-II-3**.

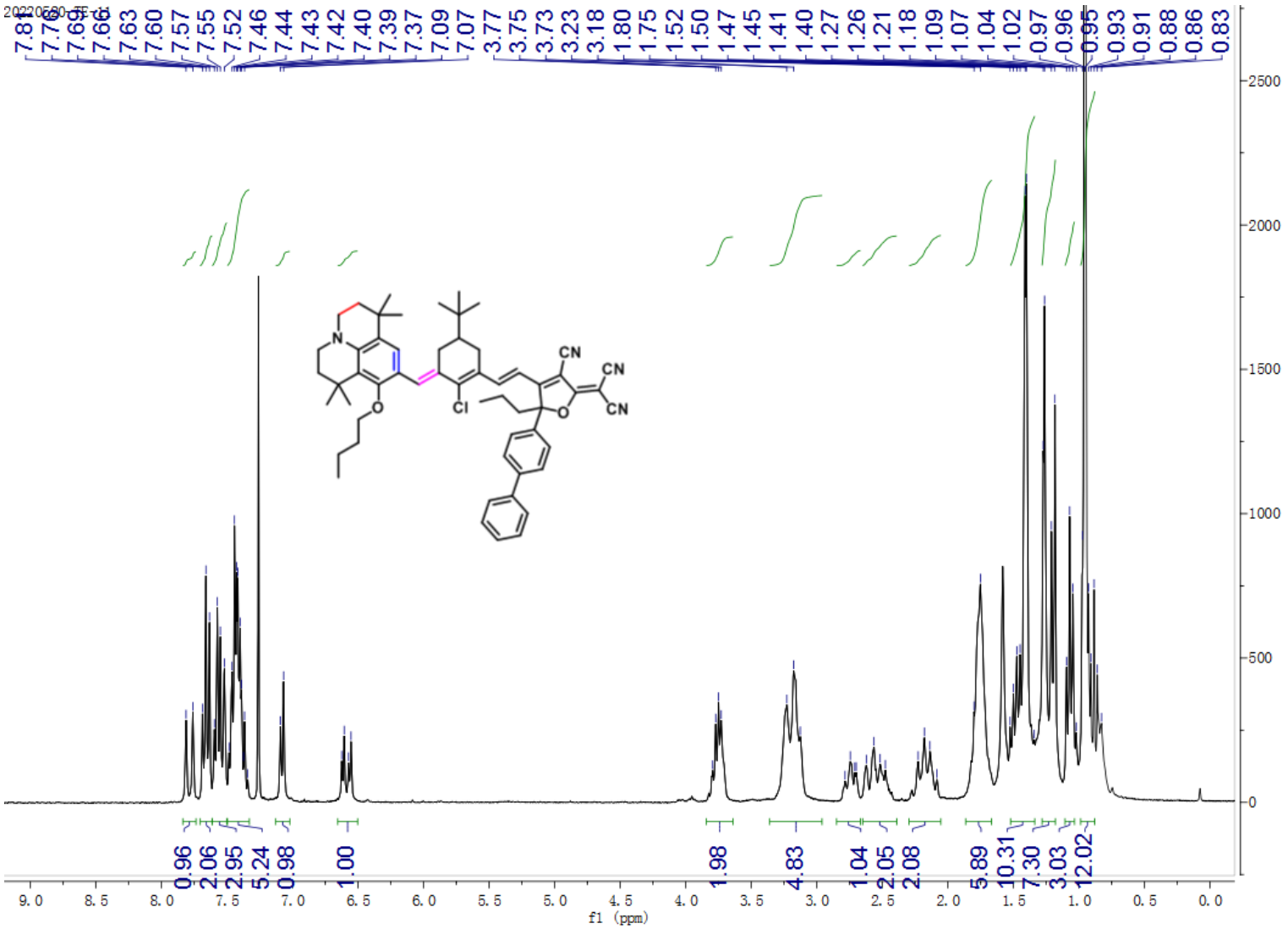


Figure S54. ^{1}H NMR spectrum of compound **TE-I-4**.

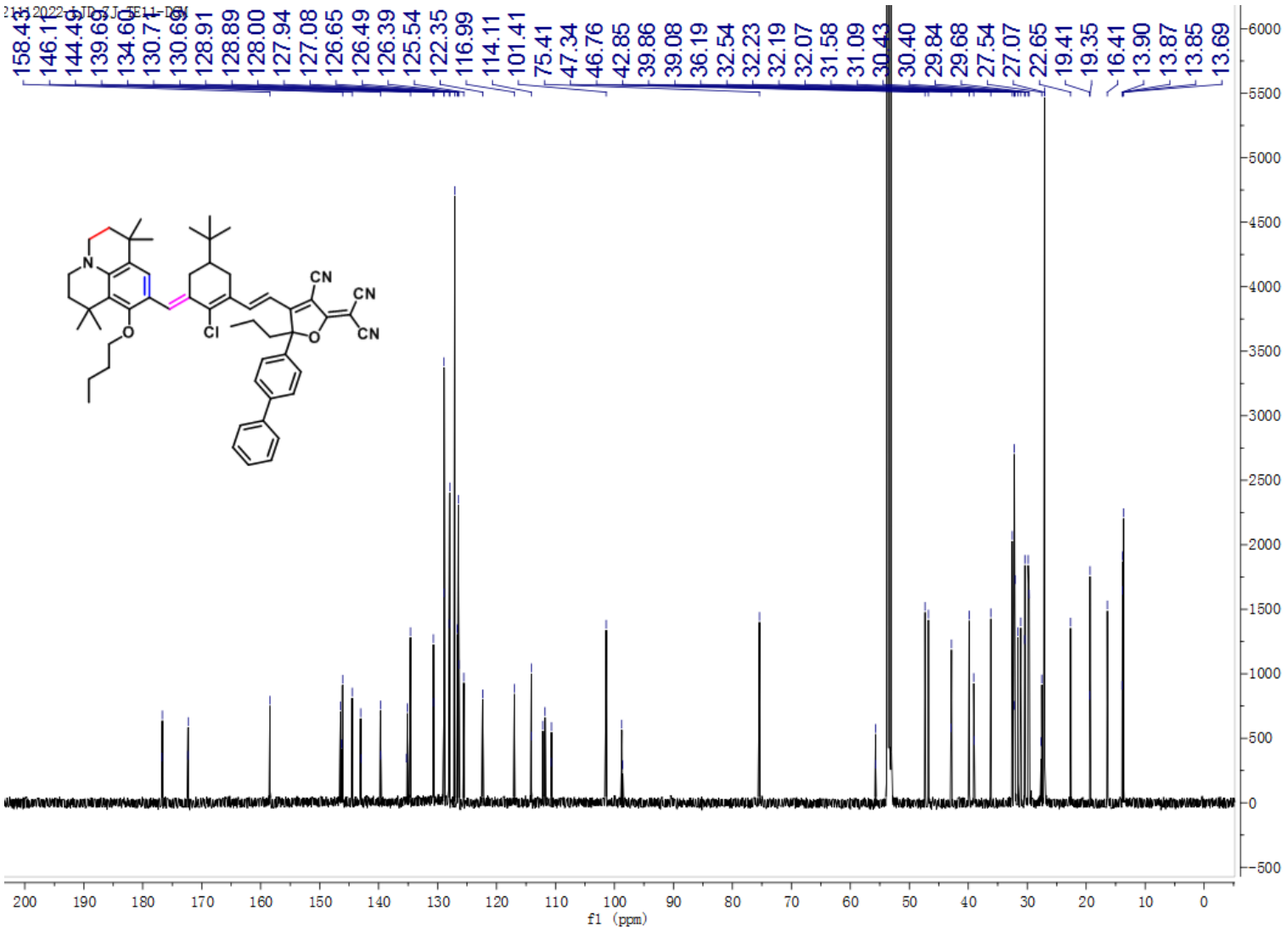


Figure S55. ^{13}C NMR spectrum of compound **TE-I-4**.

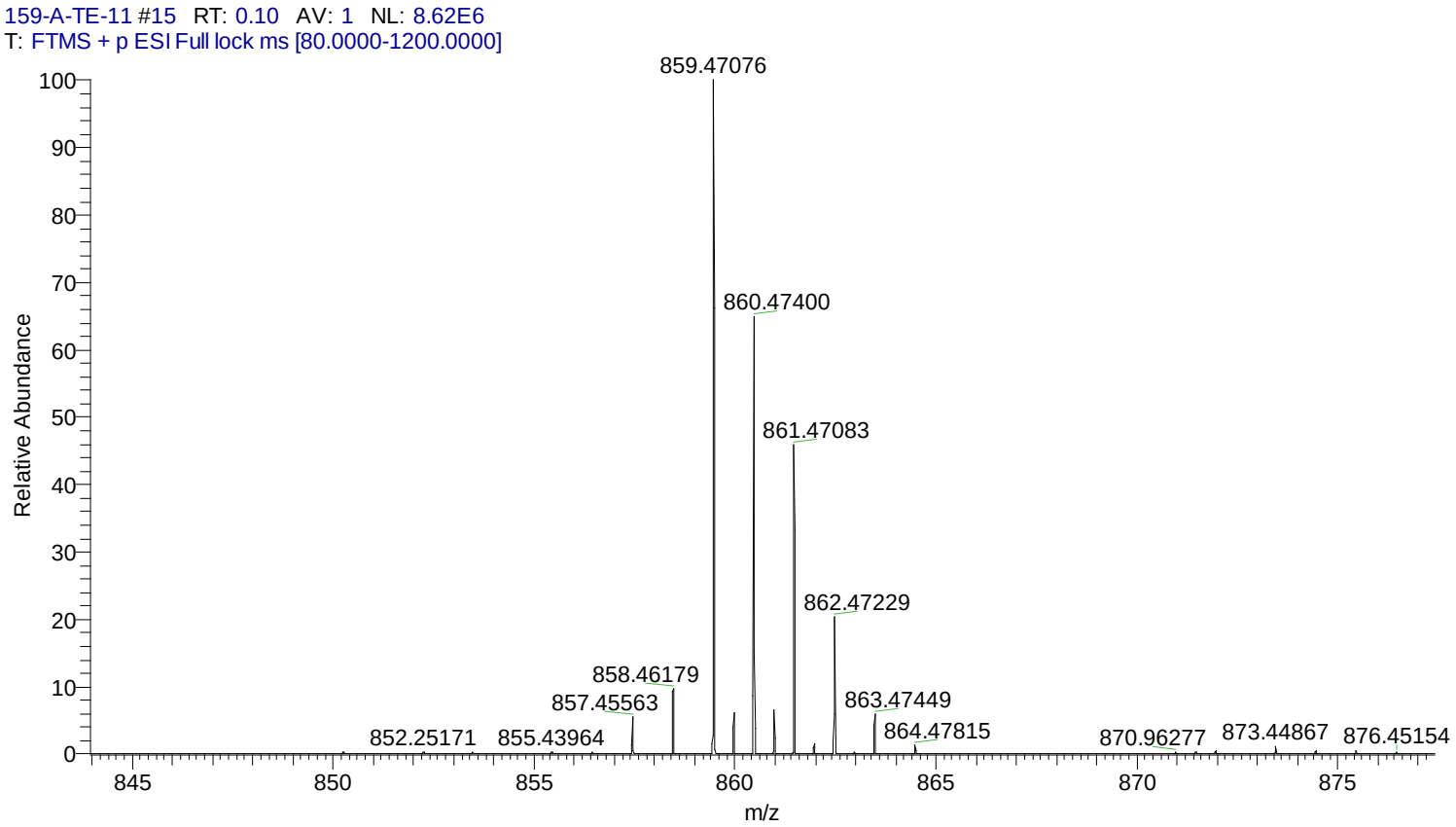


Figure S56. HRMS spectrum of compound **TE-I-4**.

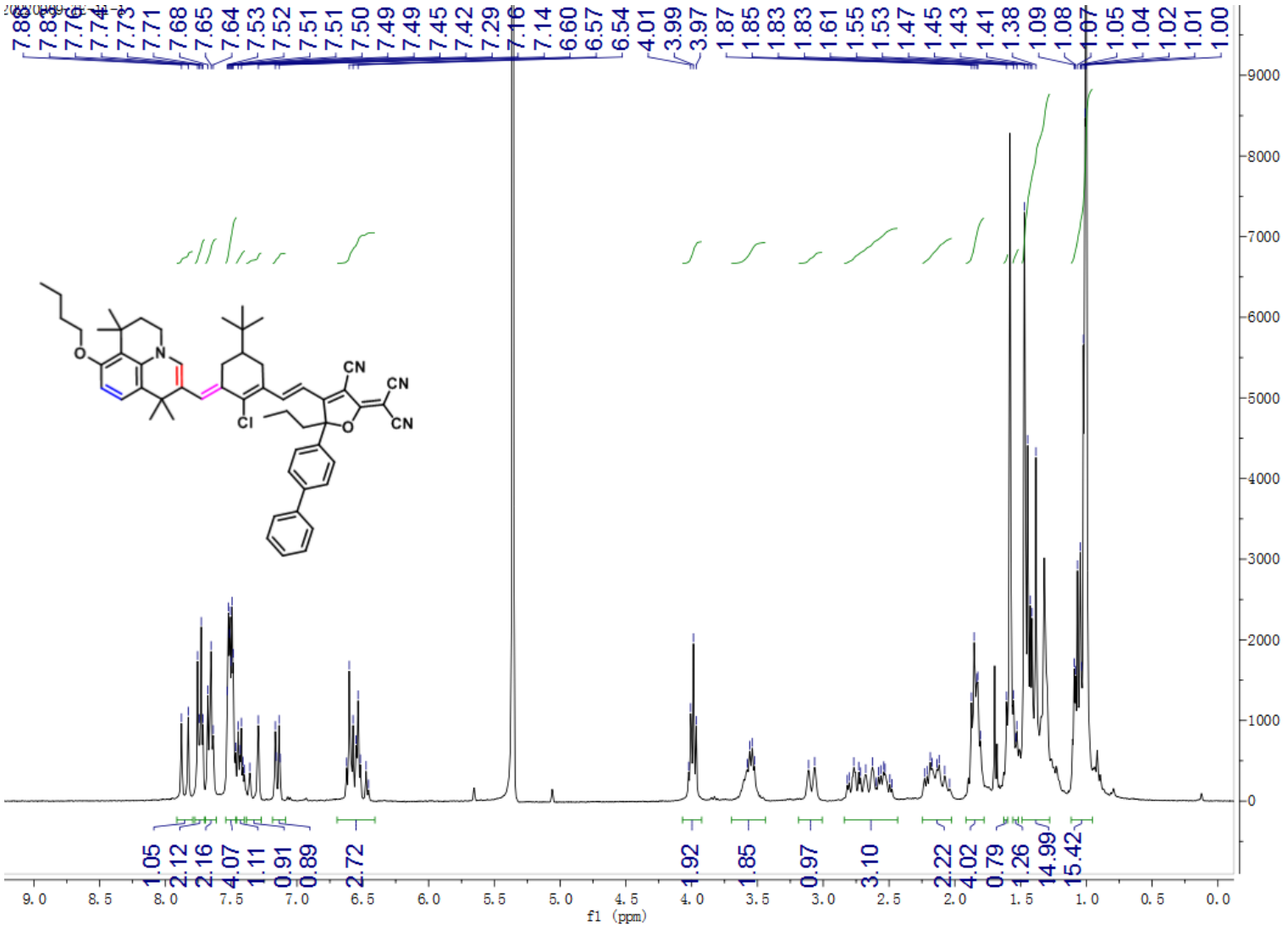


Figure S57. ^{1}H NMR spectrum of compound **TE-II-4**.

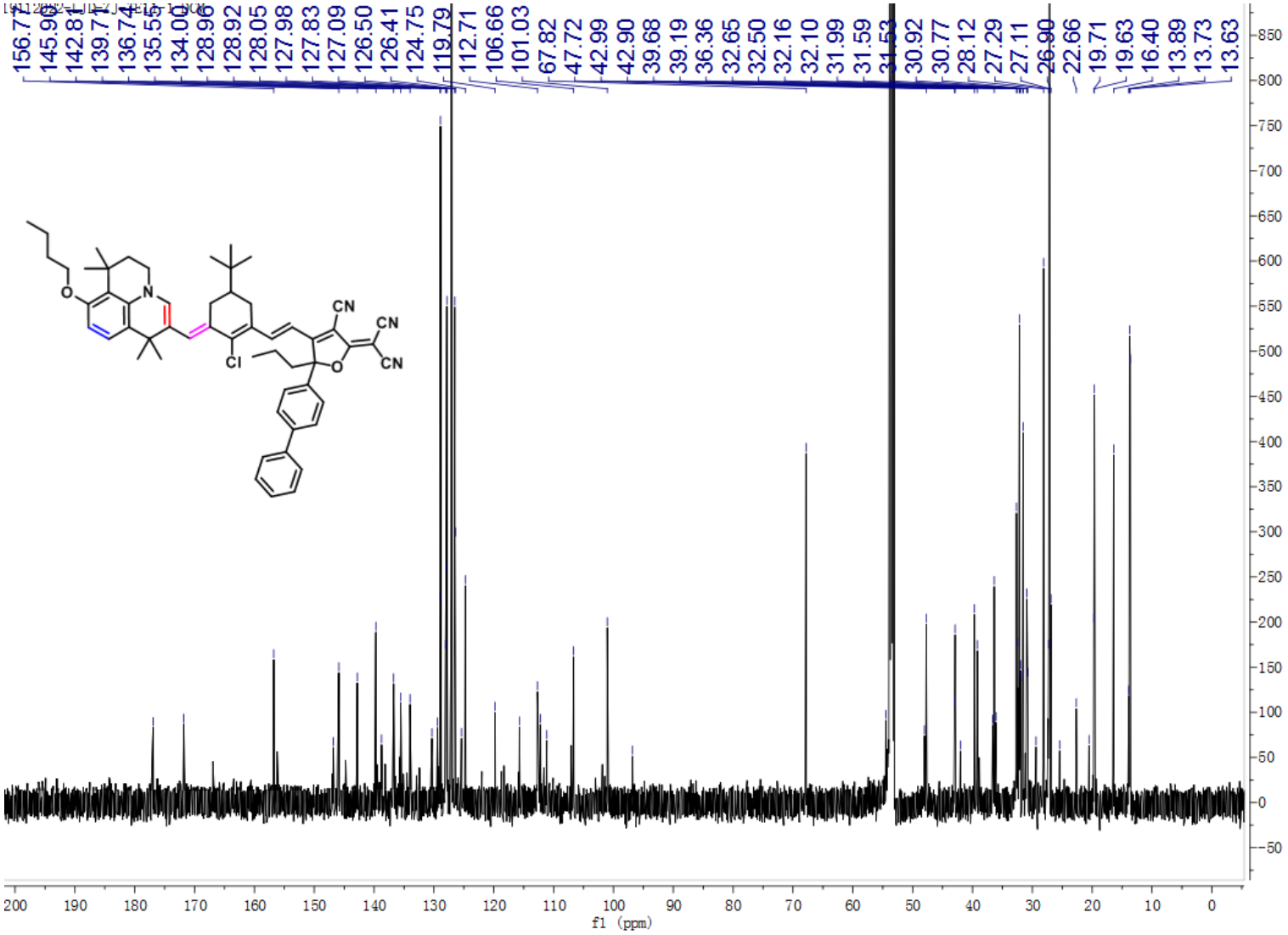


Figure S58. ^{13}C NMR spectrum of compound **TE-II-4**.

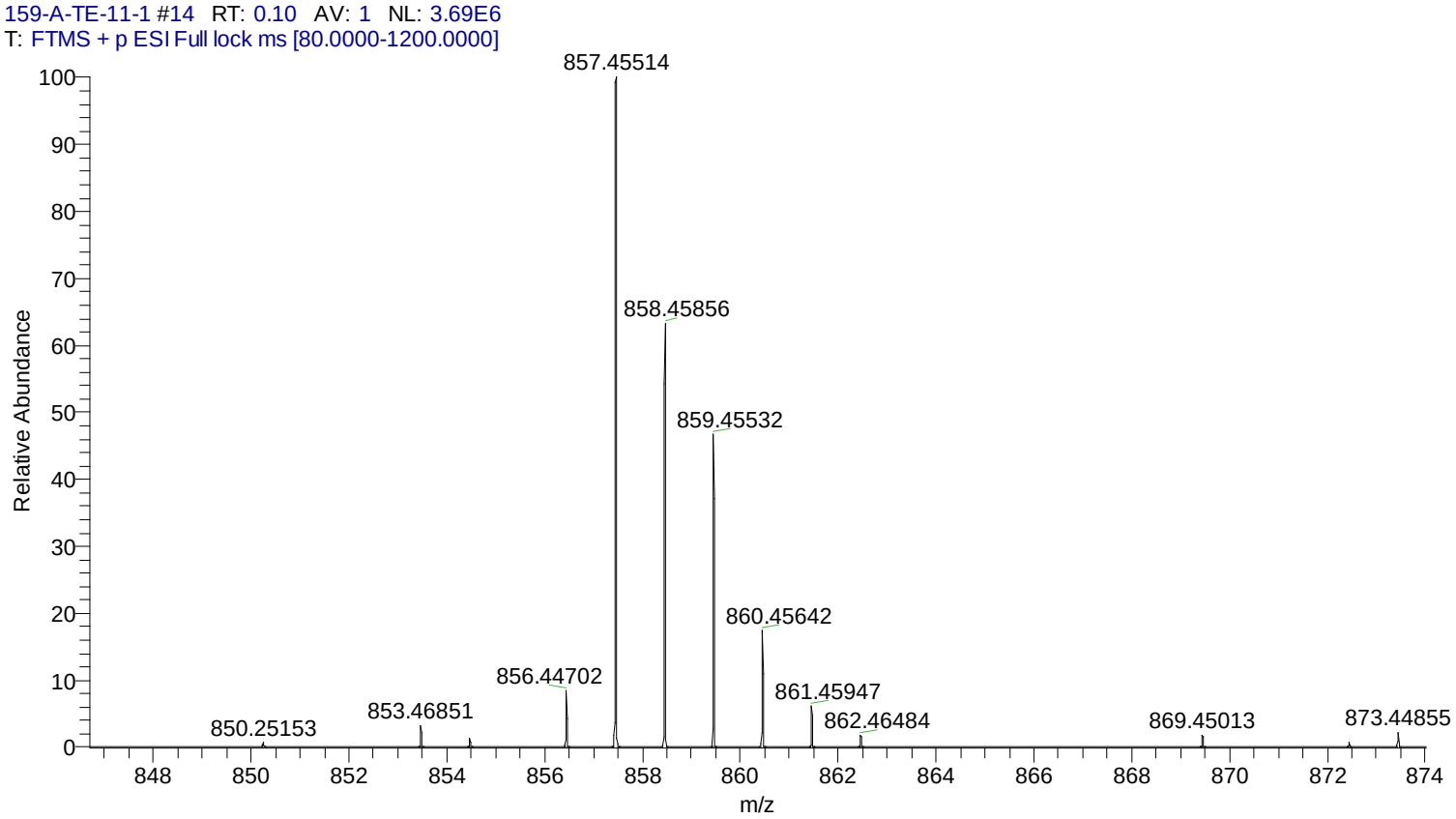


Figure S59. HRMS spectrum of compound **TE-II-4**.

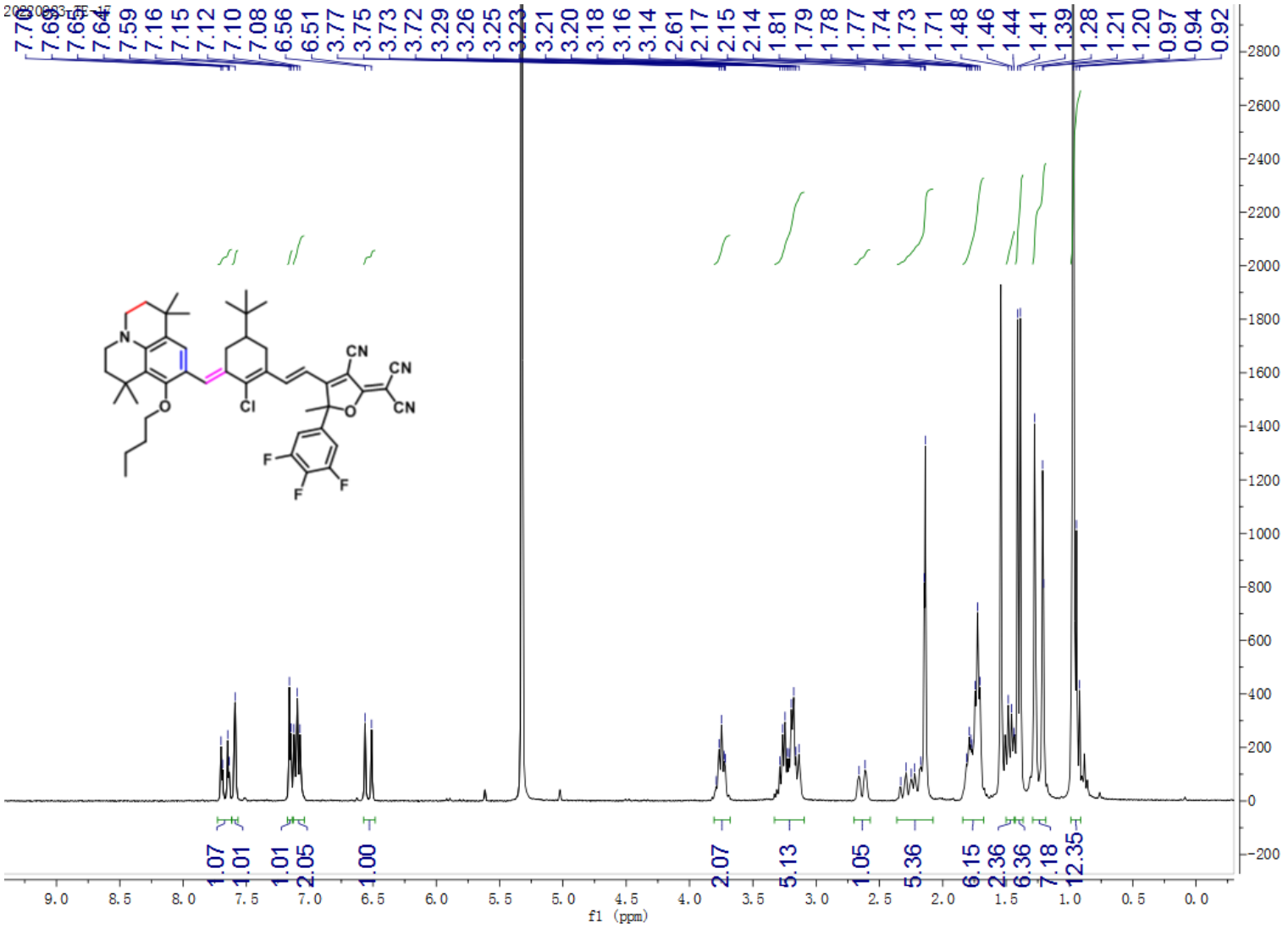


Figure S60. ^{1}H NMR spectrum of compound **TE-I-5**.

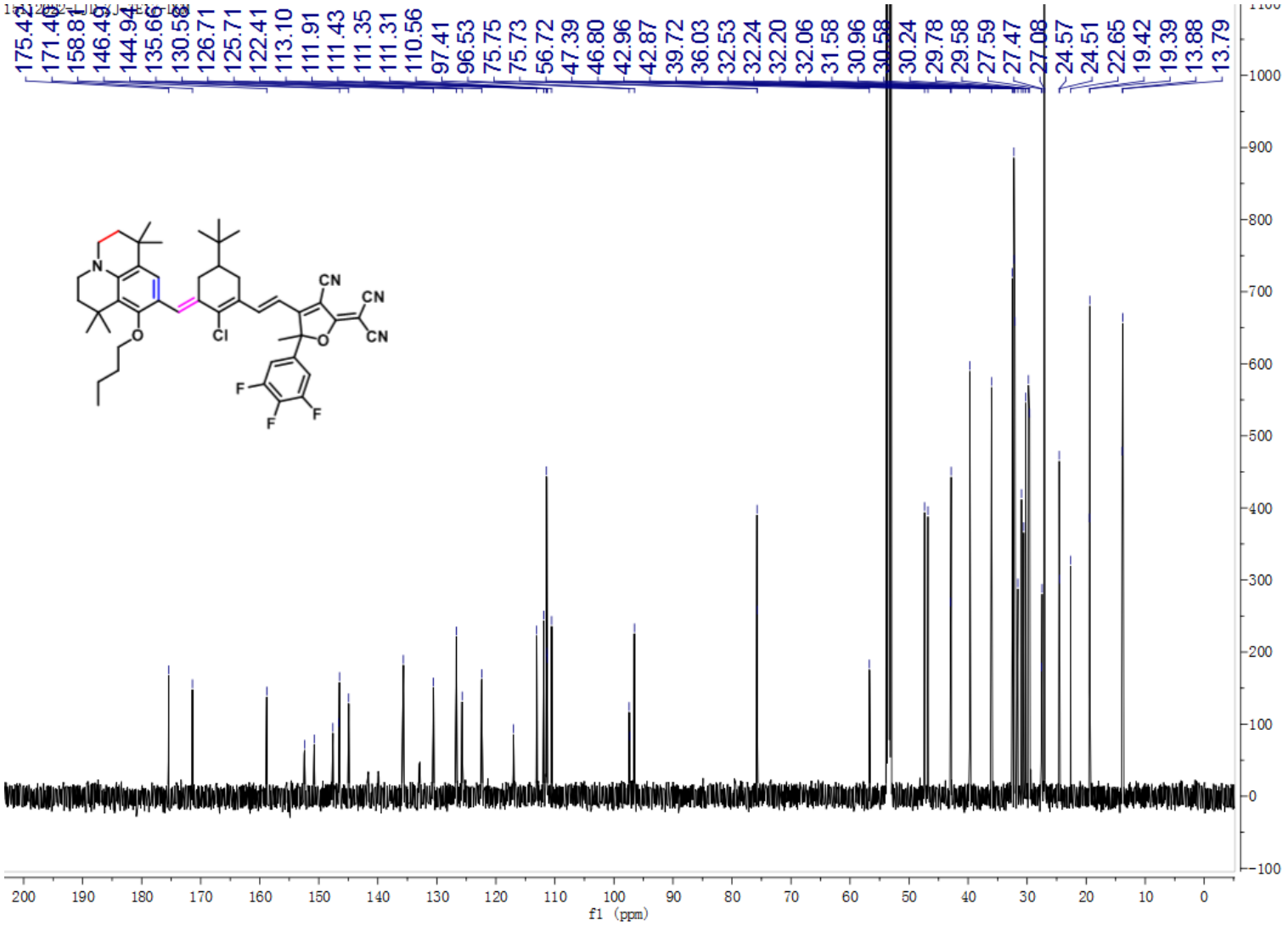


Figure S61. ^{13}C NMR spectrum of compound **TE-I-5**.

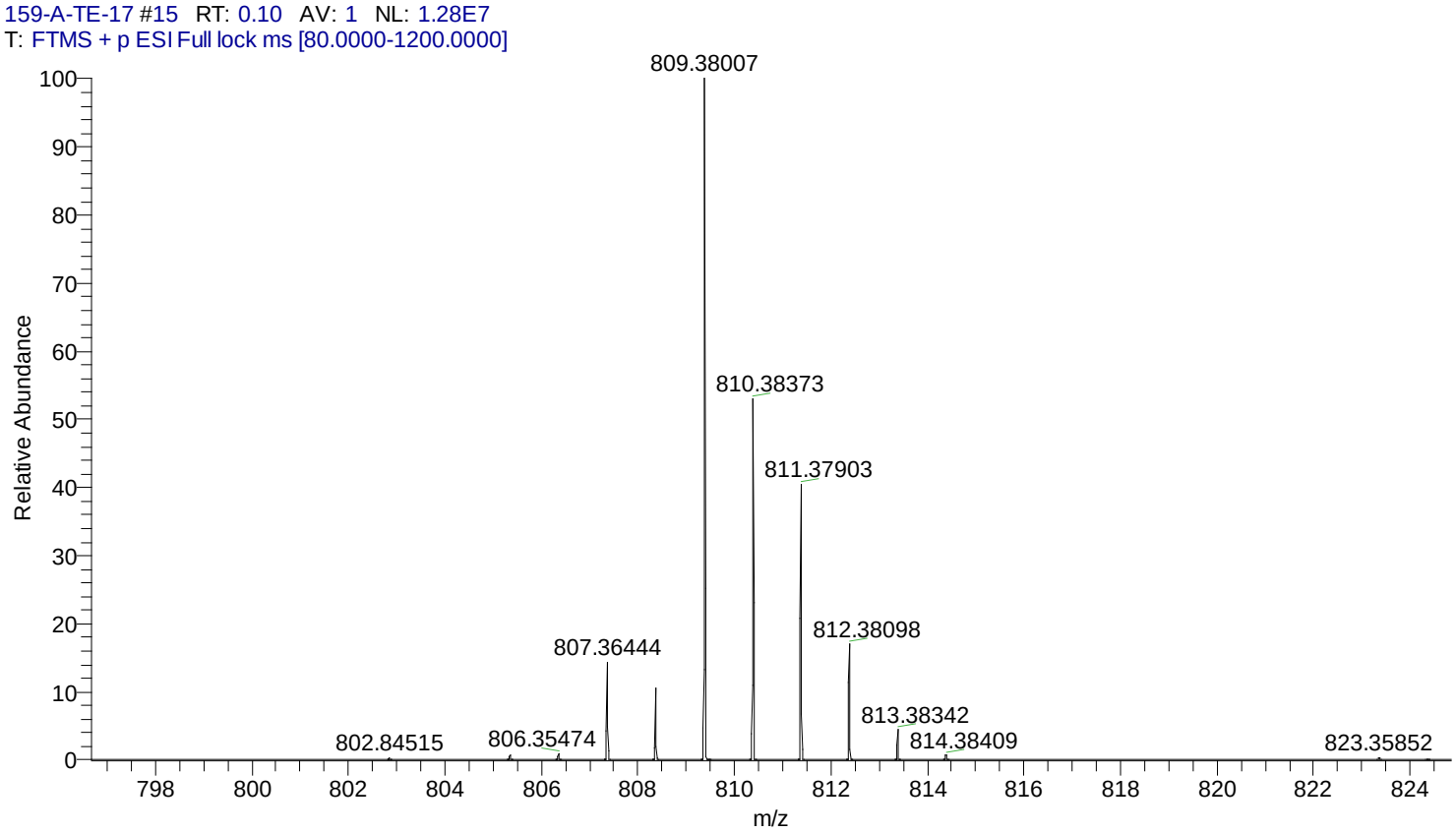


Figure S62. HRMS spectrum of compound **TE-I-5**.

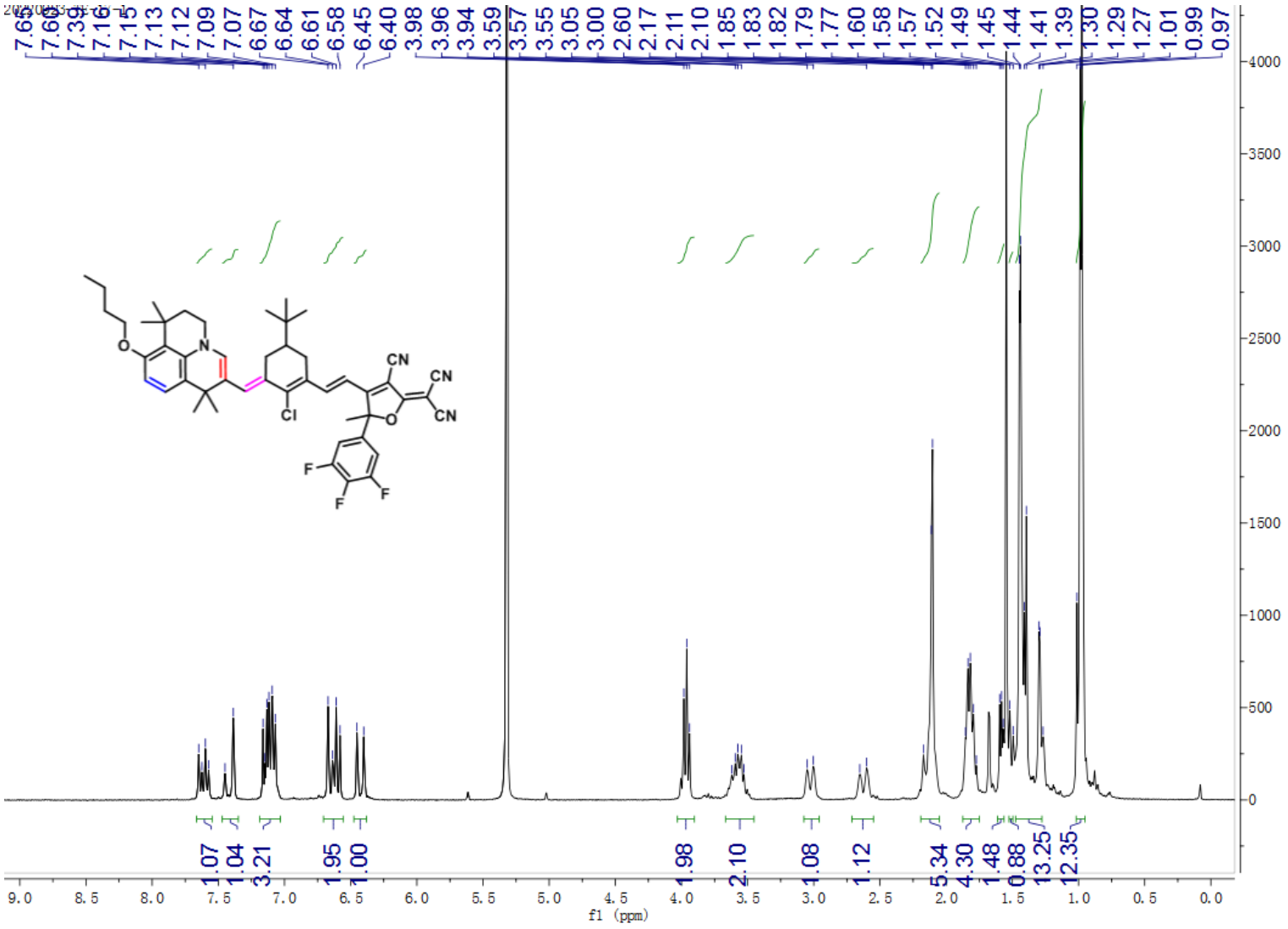


Figure S63. ^{1}H NMR spectrum of compound **TE-II-5**.

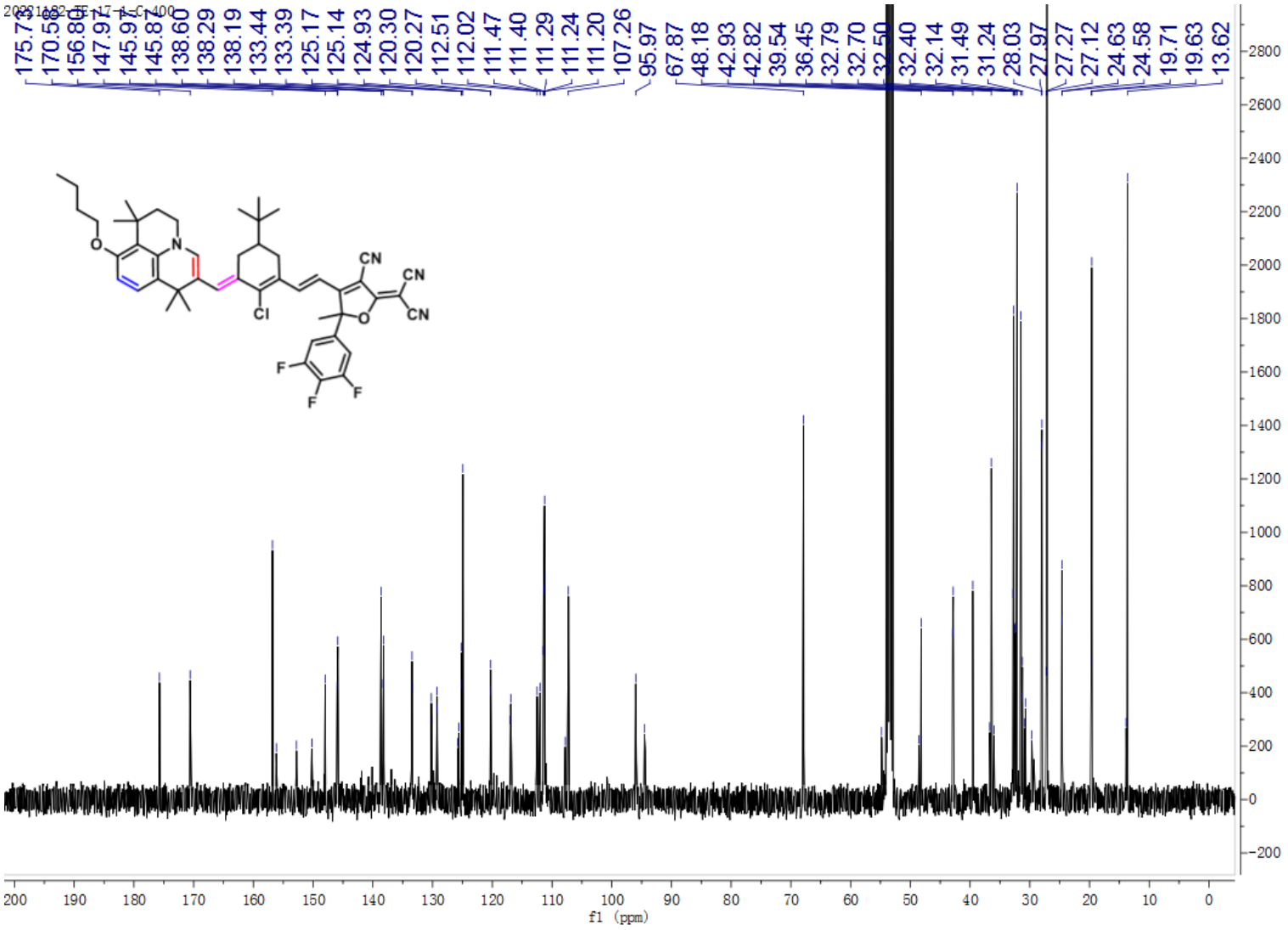


Figure S64. ^{13}C NMR spectrum of compound **TE-II-5**.

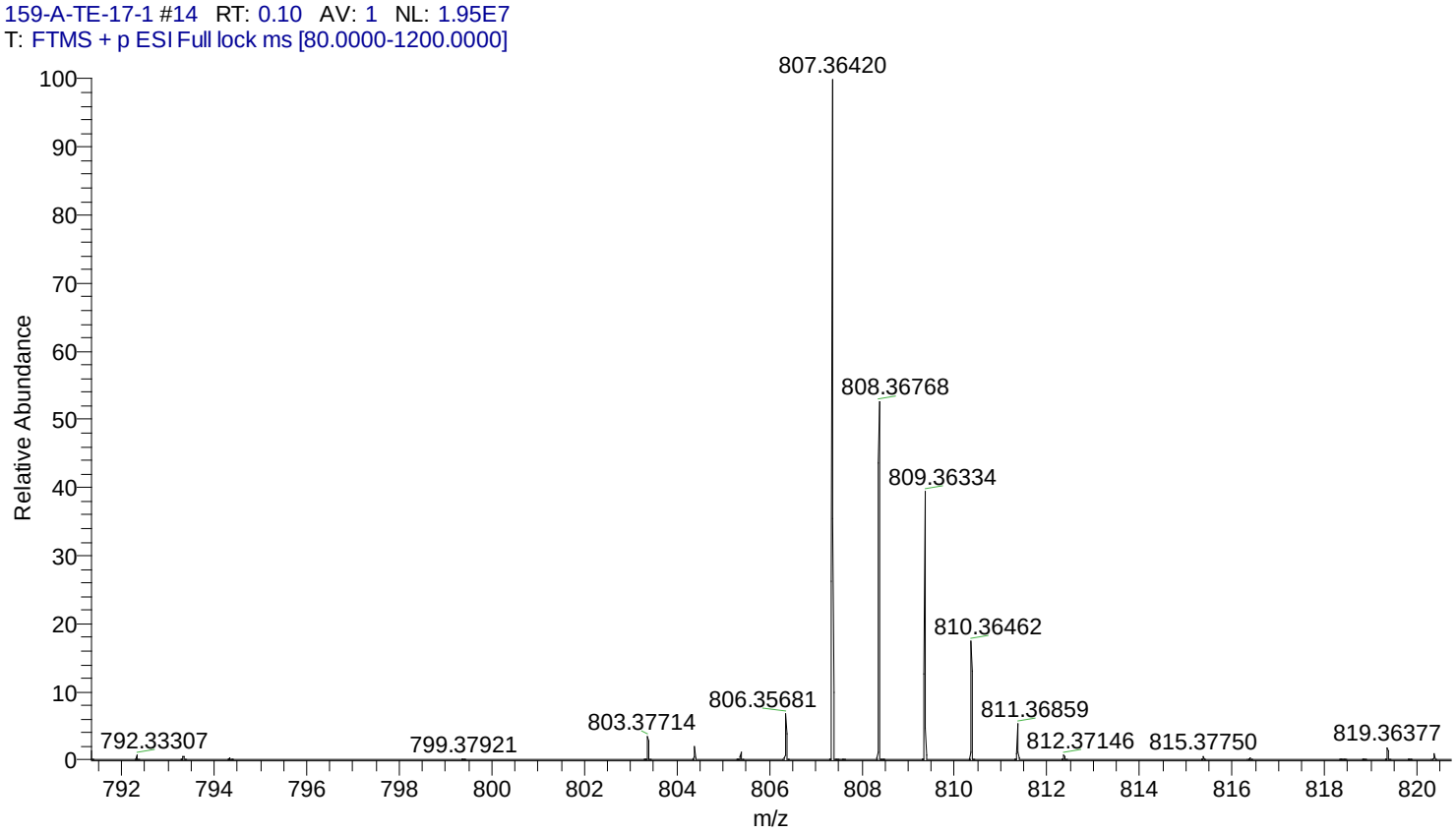


Figure S65. HRMS spectrum of compound **TE-II-5**.

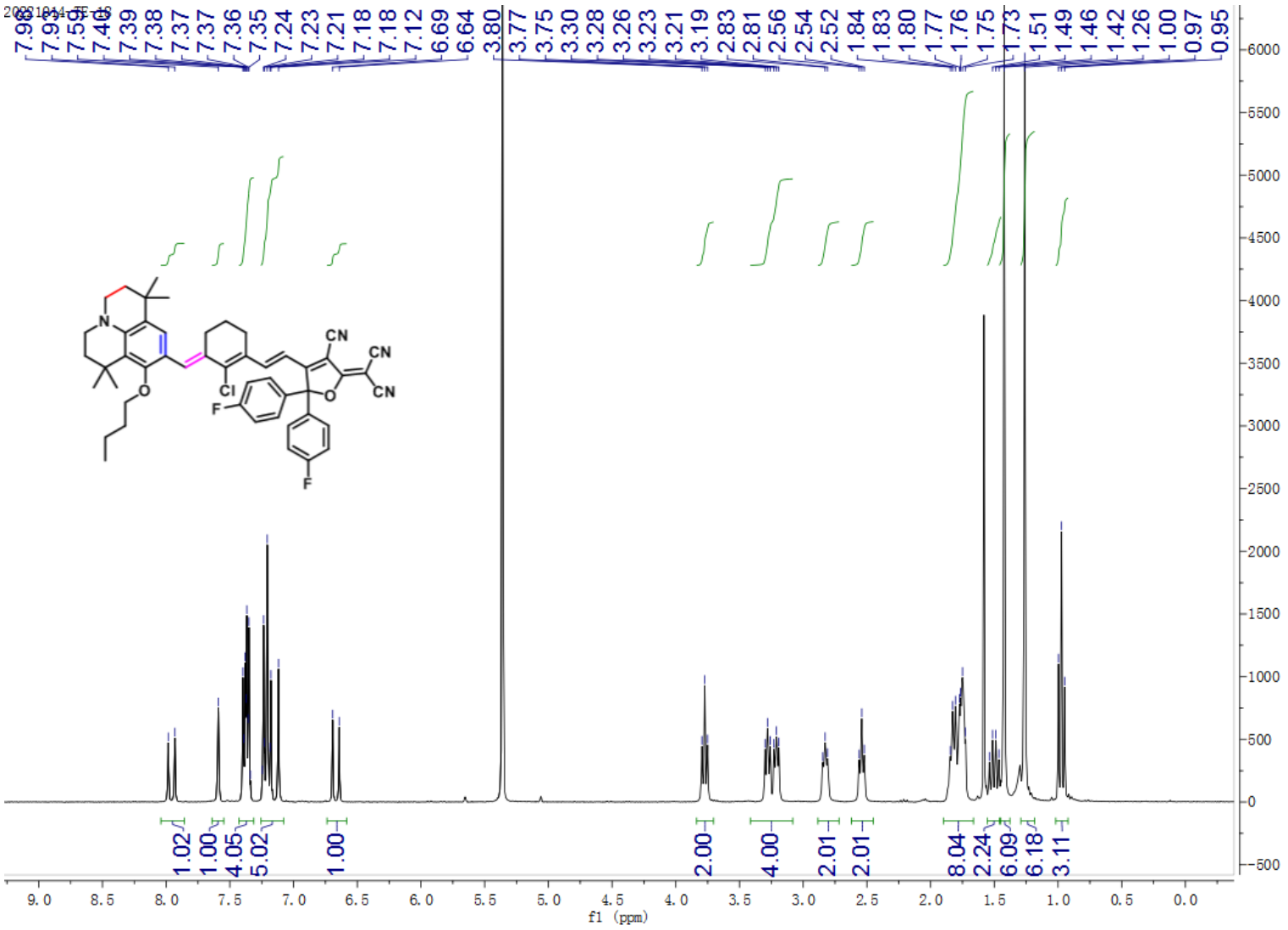


Figure S66. ^{1}H NMR spectrum of compound **TE-I-6**.

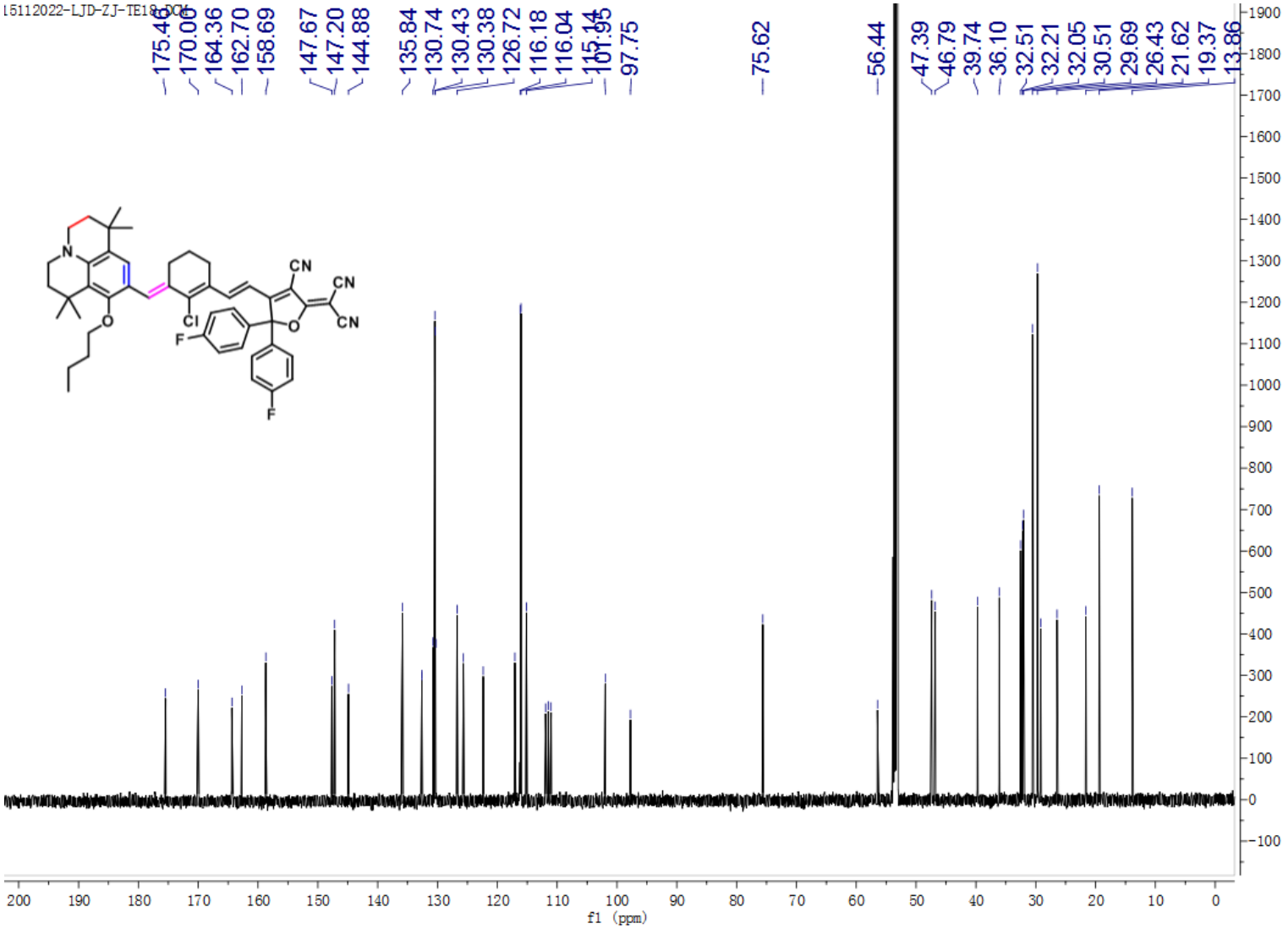


Figure S67. ^{13}C NMR spectrum of compound **TE-I-6**.

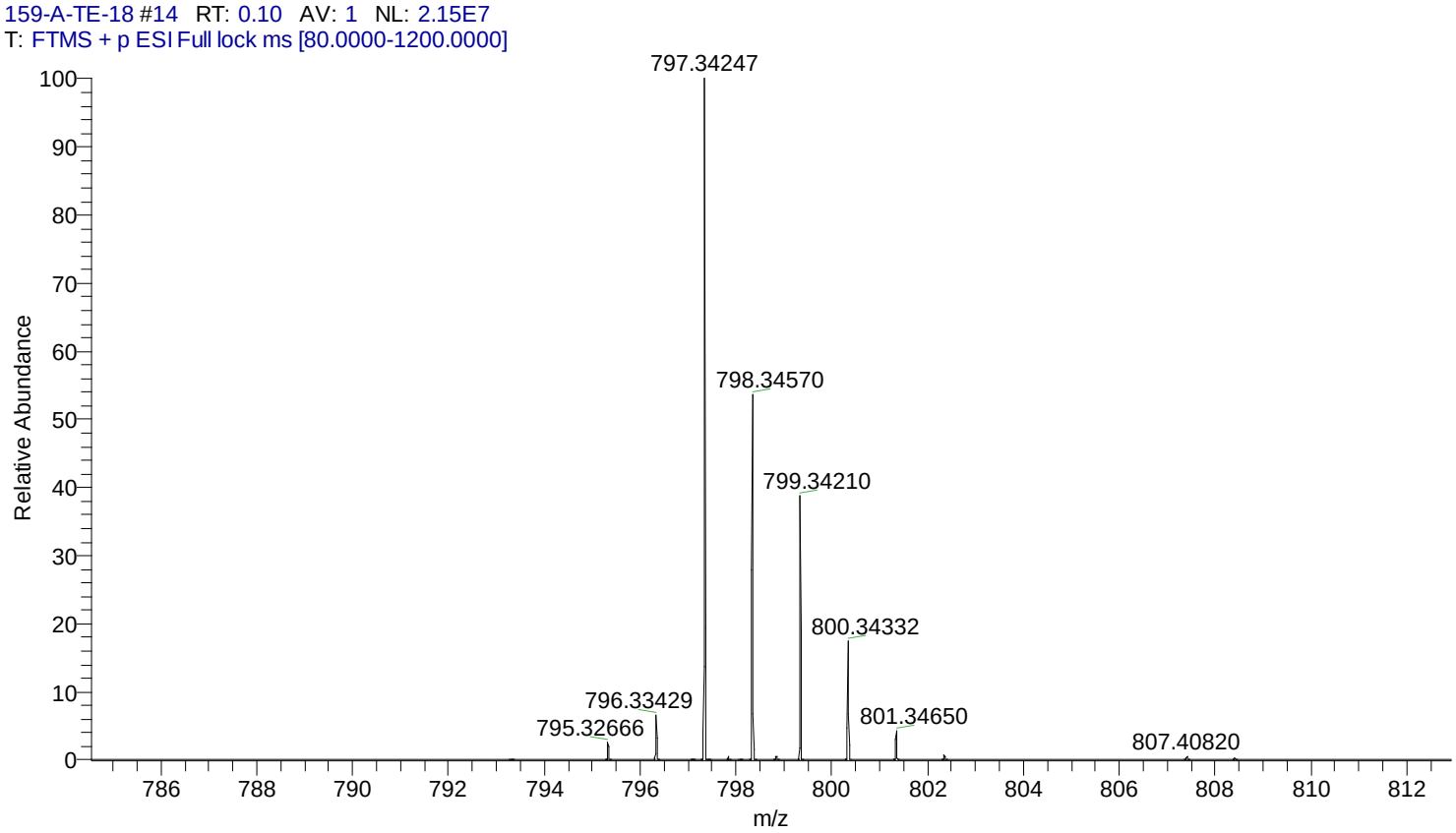


Figure S68. HRMS spectrum of compound **TE-I-6**.

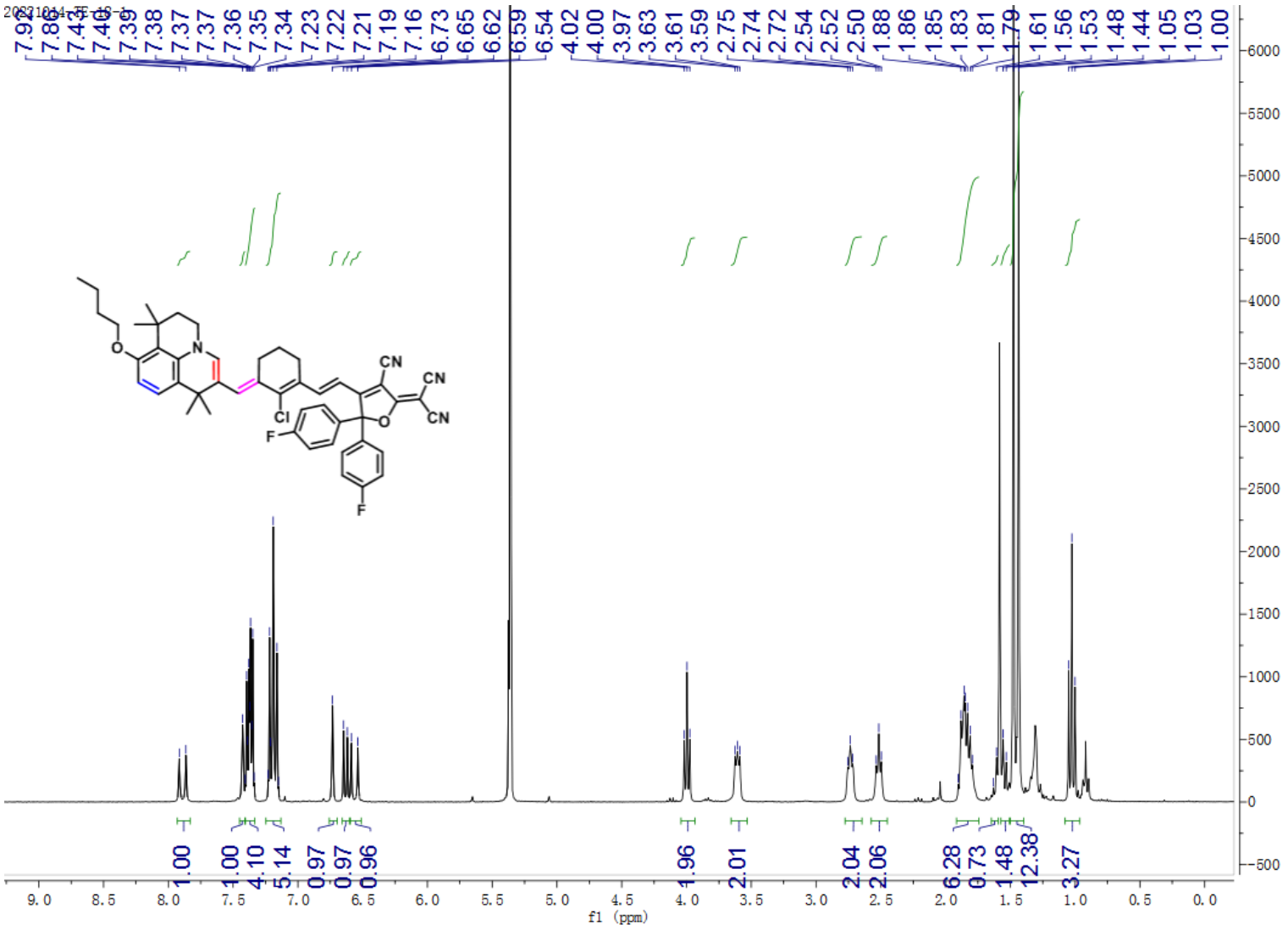


Figure S69. ^{1}H NMR spectrum of compound **TE-II-6**.

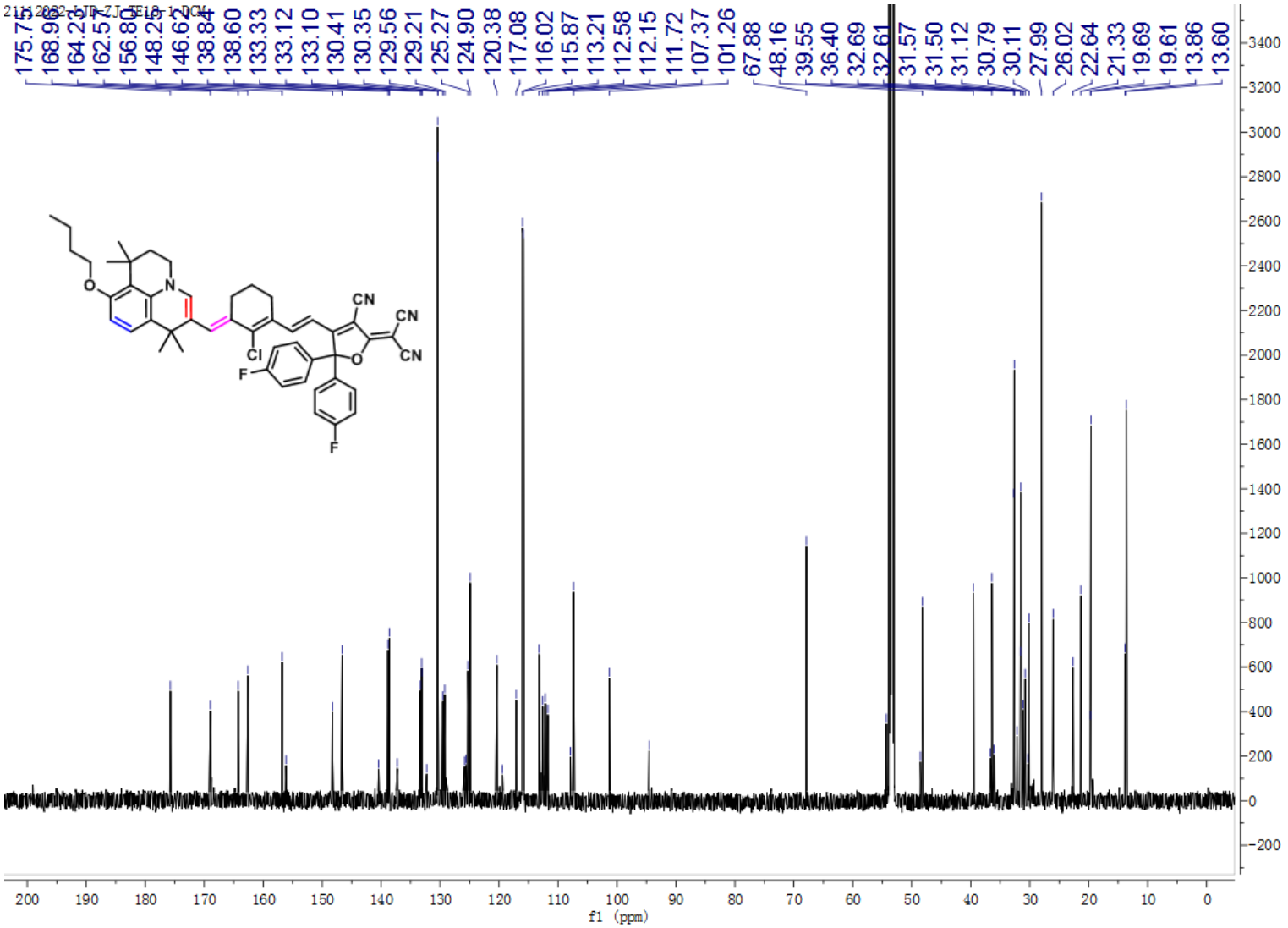


Figure S70. ^{13}C NMR spectrum of compound **TE-II-6**.

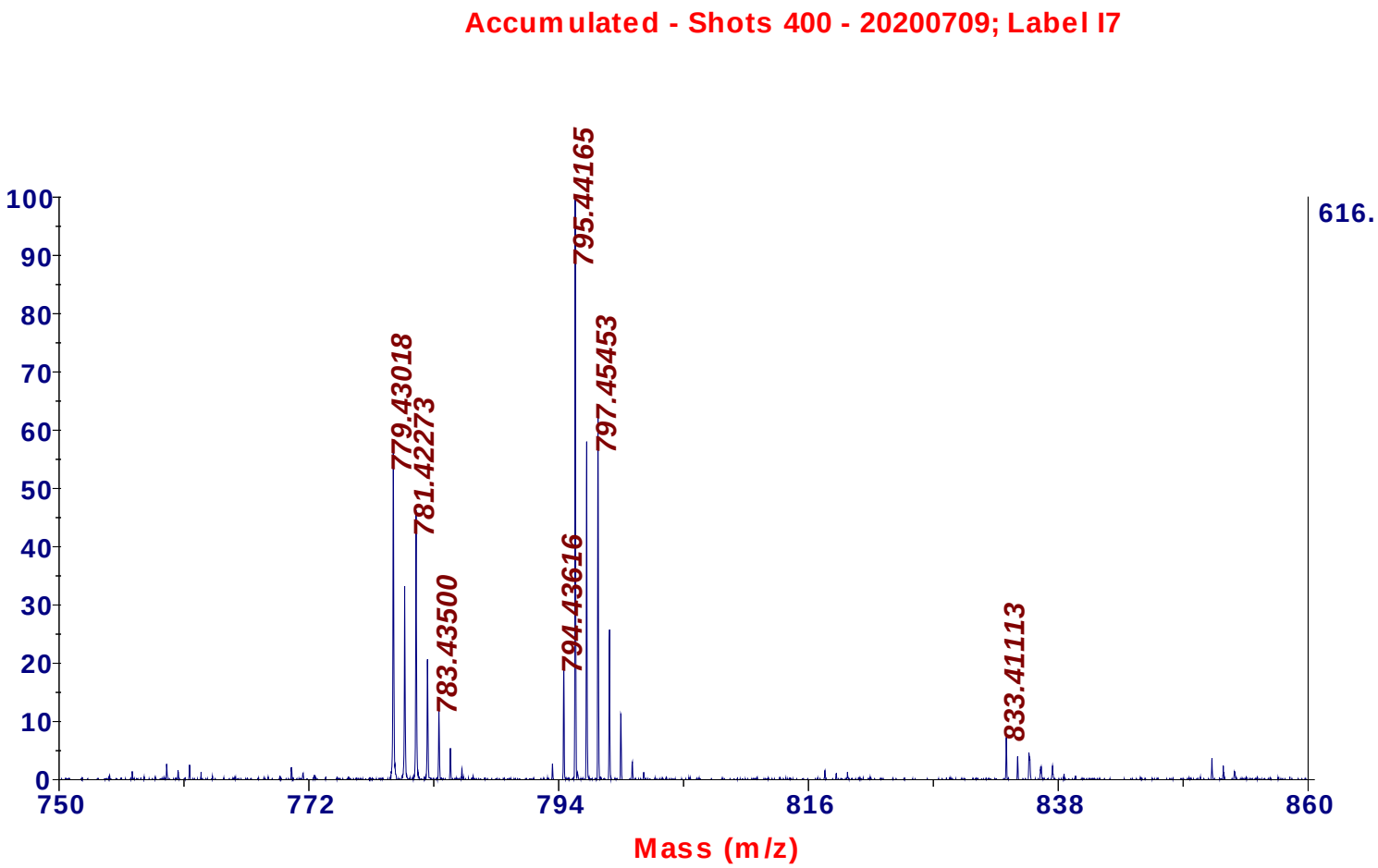


Figure S71. HRMS spectrum of compound **TE-II-6**.

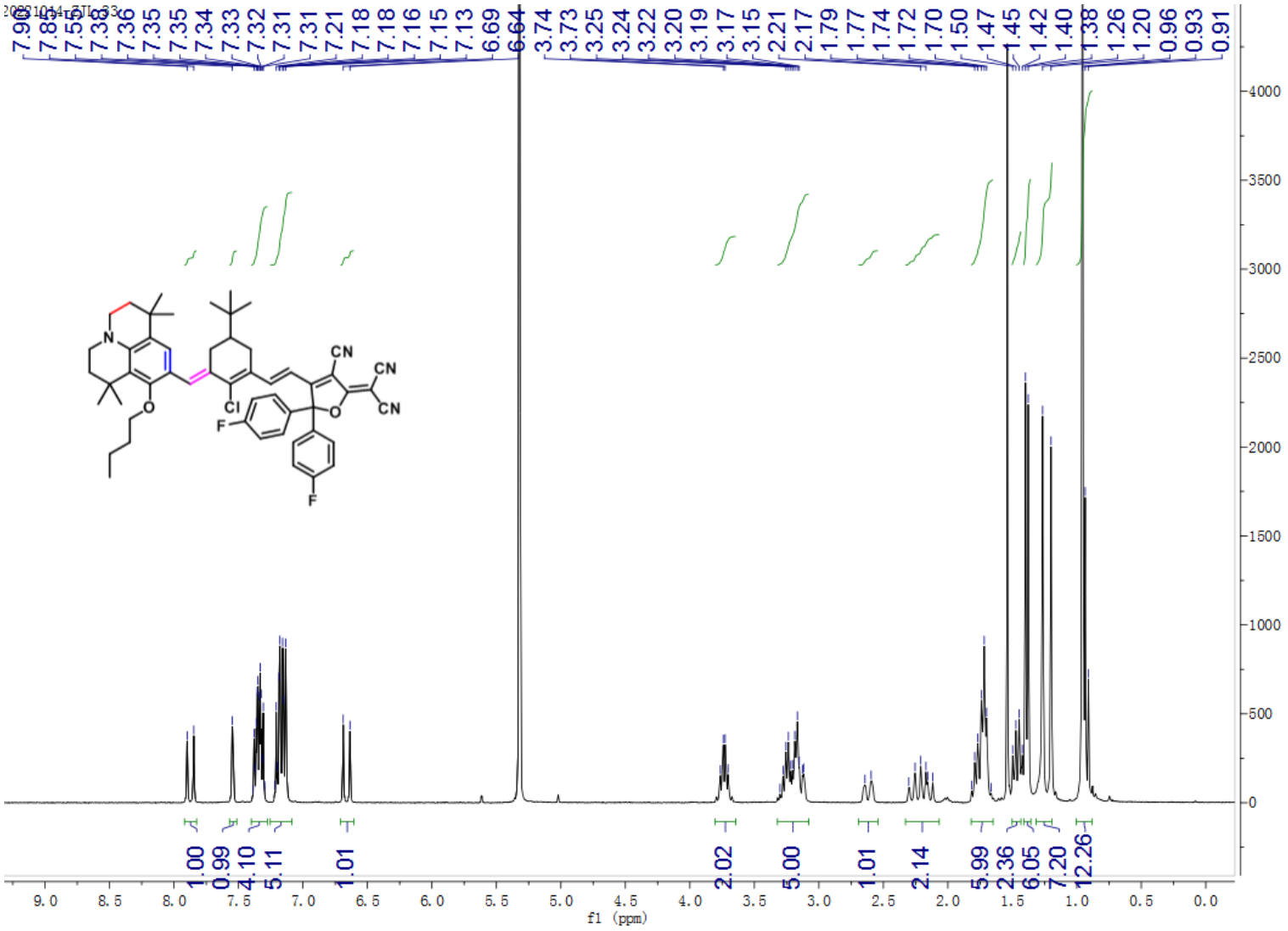


Figure S72. ^{1}H NMR spectrum of compound **TE-I-7**.

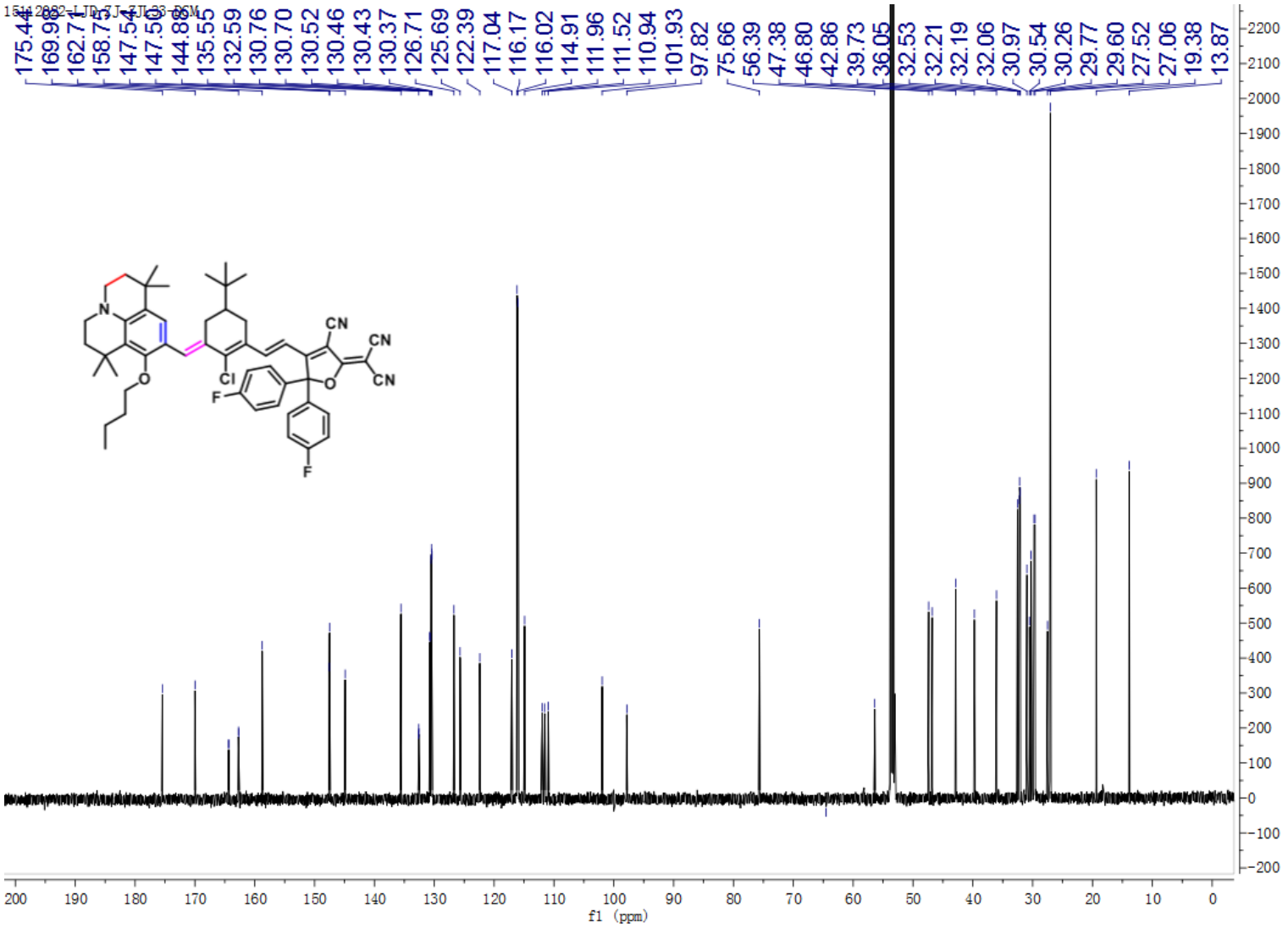


Figure S73. ^{13}C NMR spectrum of compound **TE-I-7**.

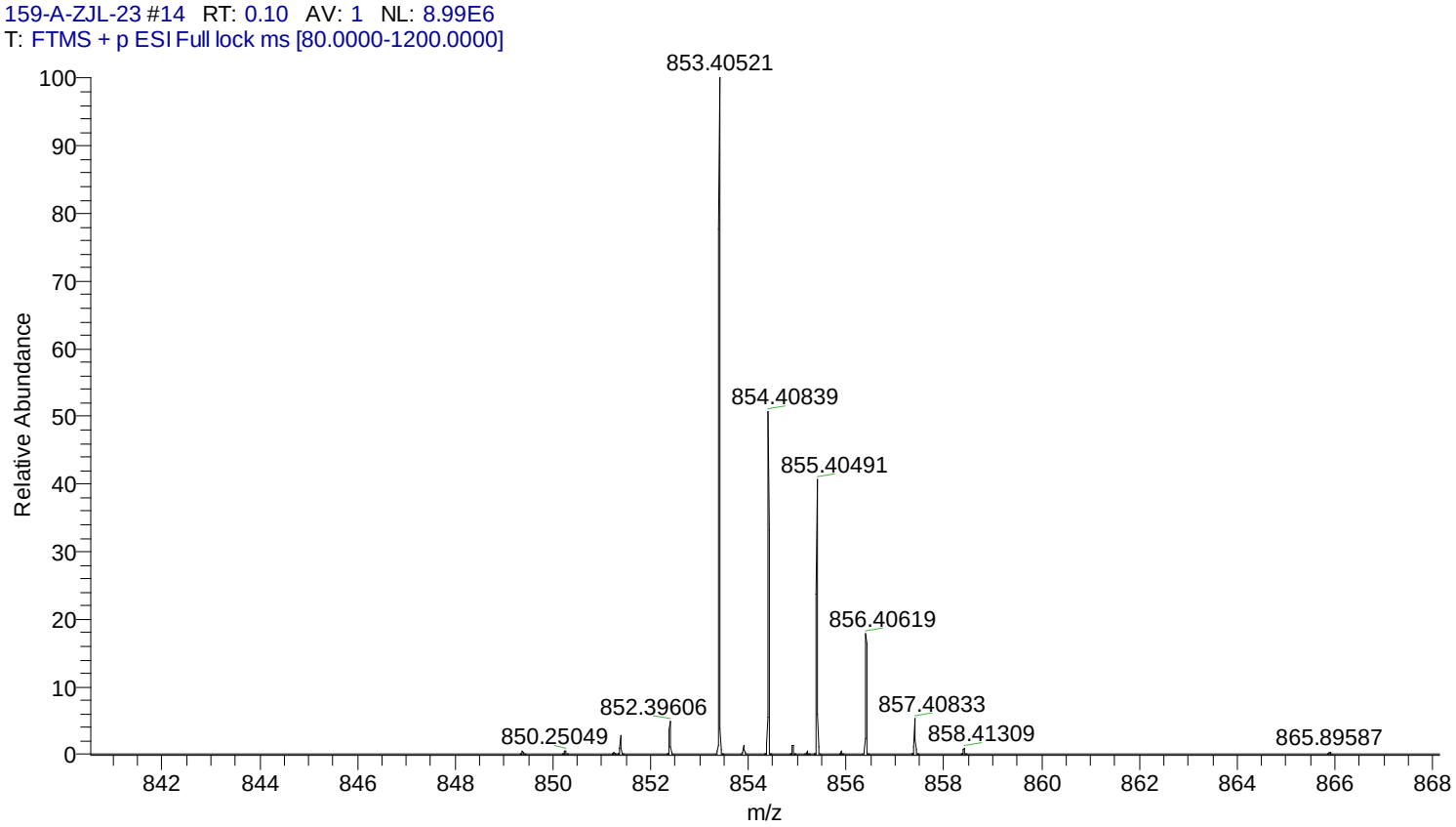


Figure S74. HRMS spectrum of compound **TE-I-7**.

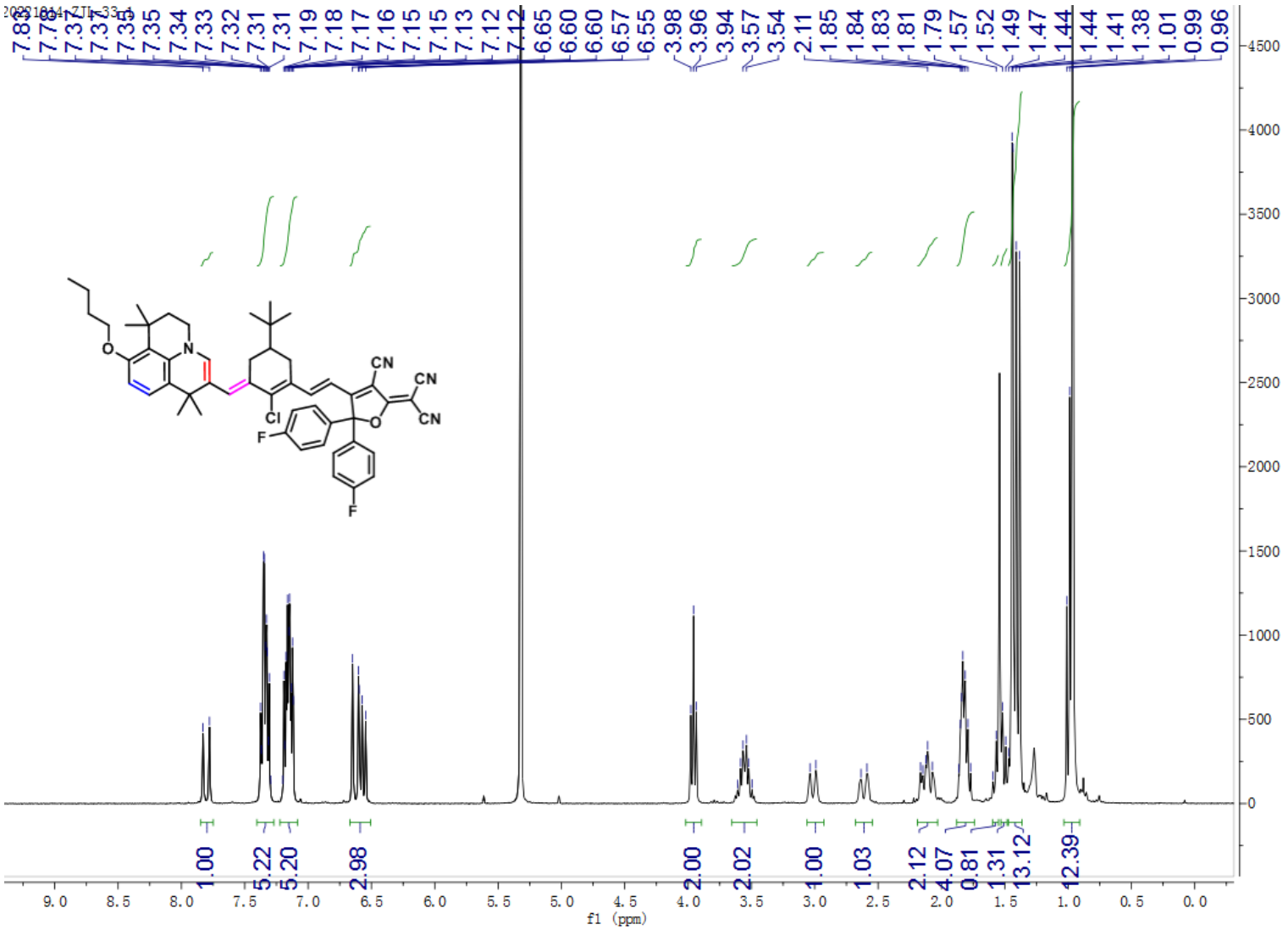


Figure S75. ^{1}H NMR spectrum of compound **TE-II-7**.

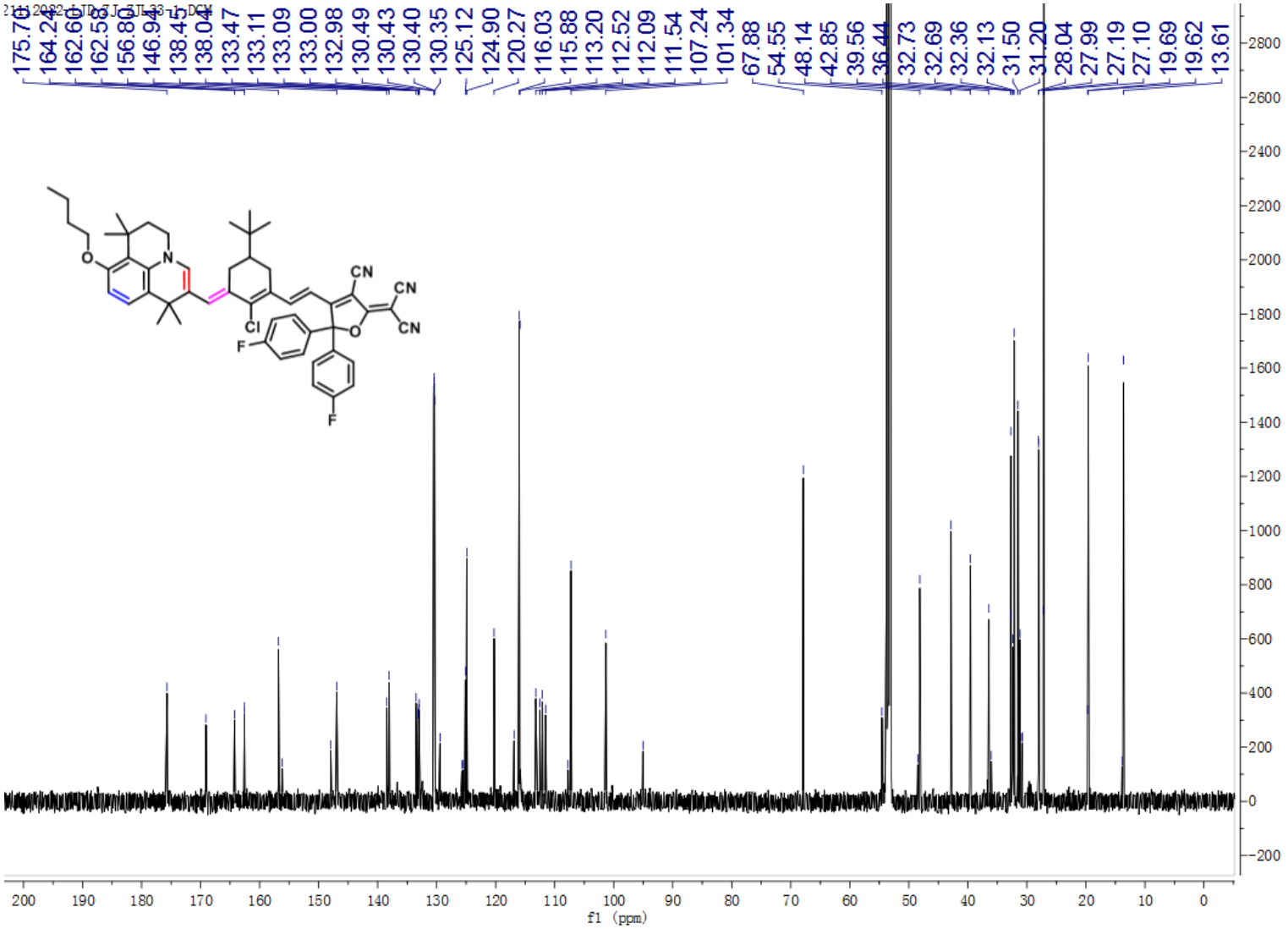


Figure S76. ^{13}C NMR spectrum of compound **TE-II-7**.

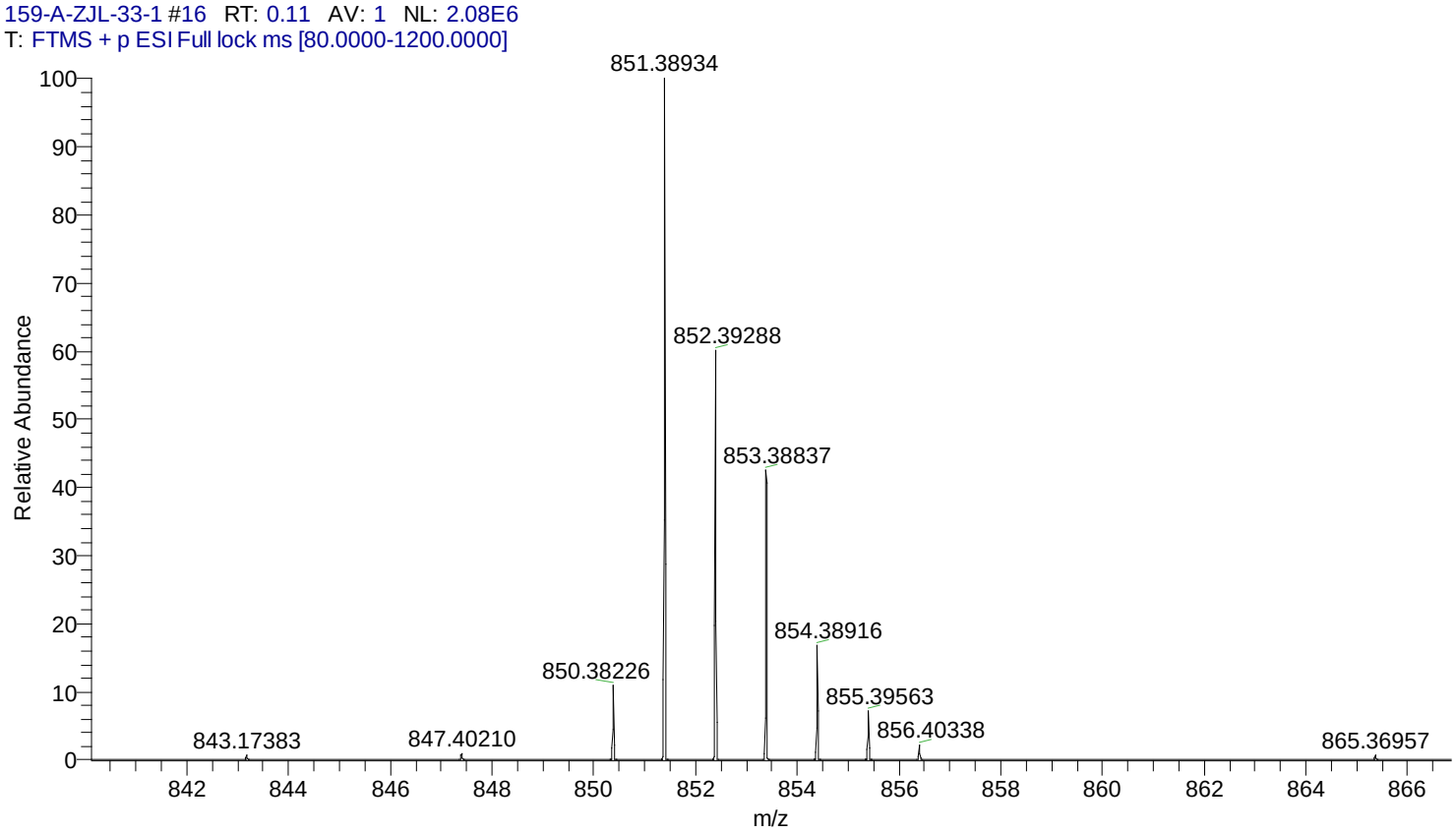


Figure S77. HRMS spectrum of compound **TE-II-7**.

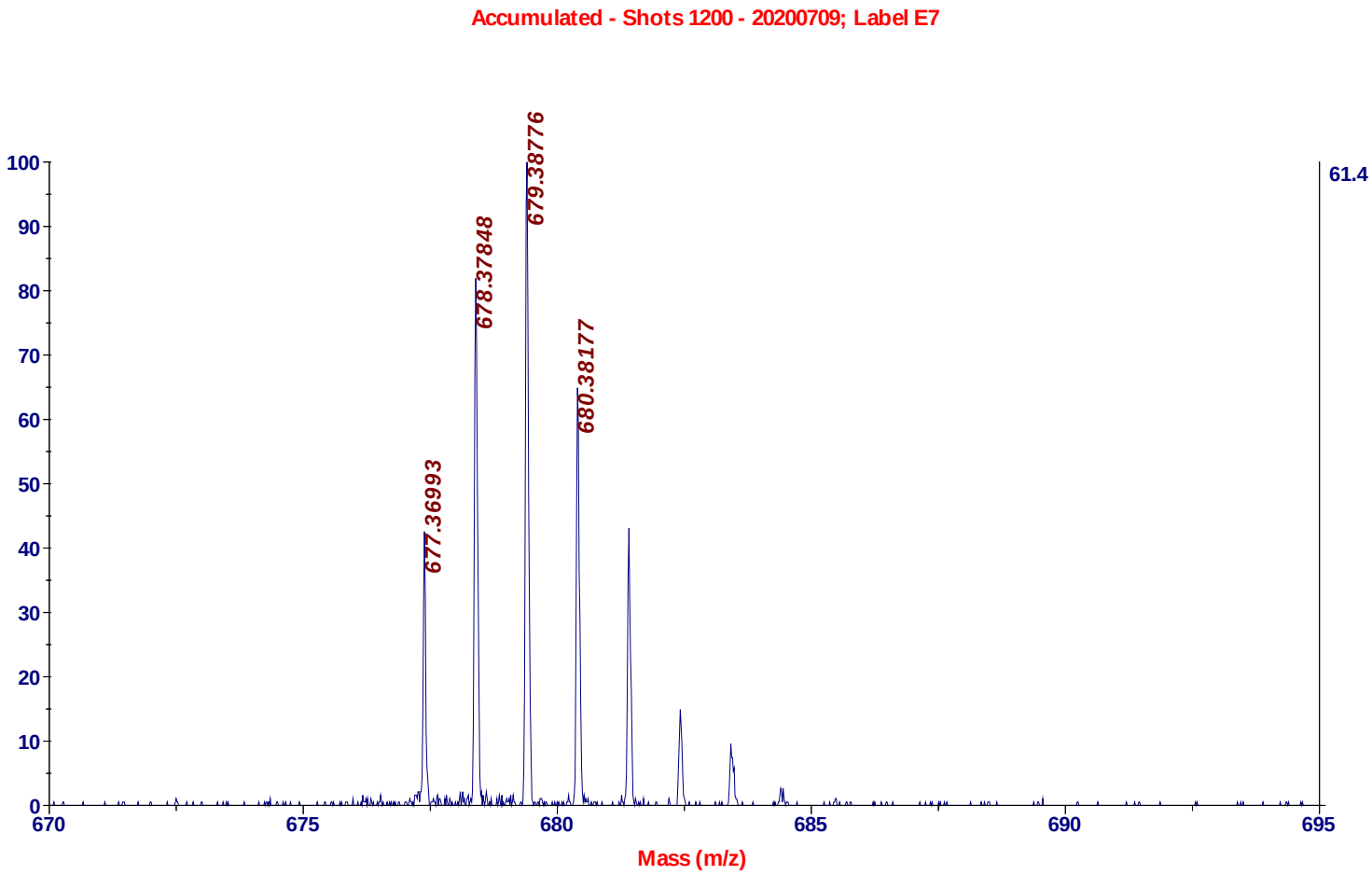


Figure S78. HRMS spectrum of compound **TE-I-8**.

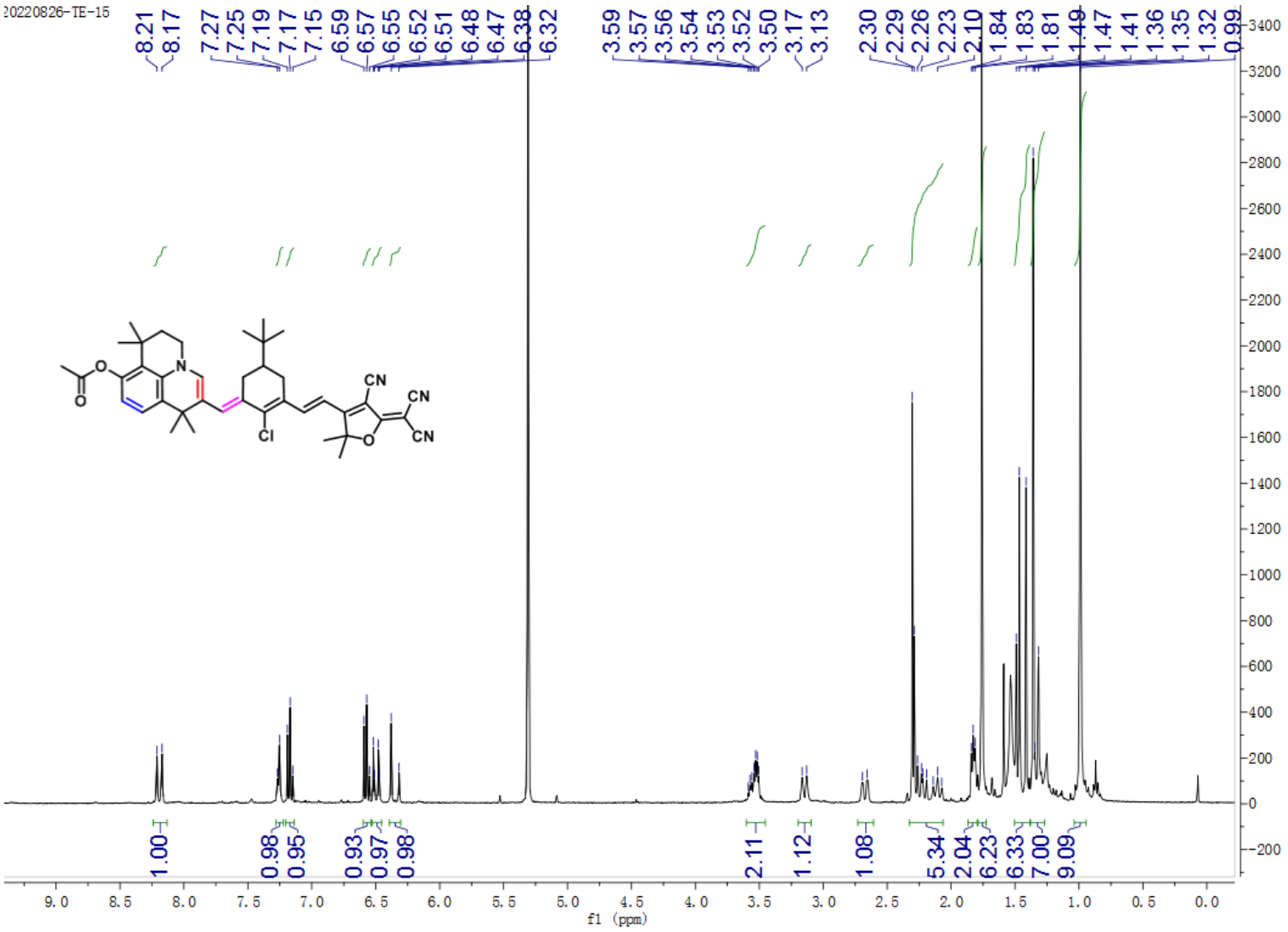


Figure S79. ^{1}H NMR spectrum of compound **TE-II-8**.

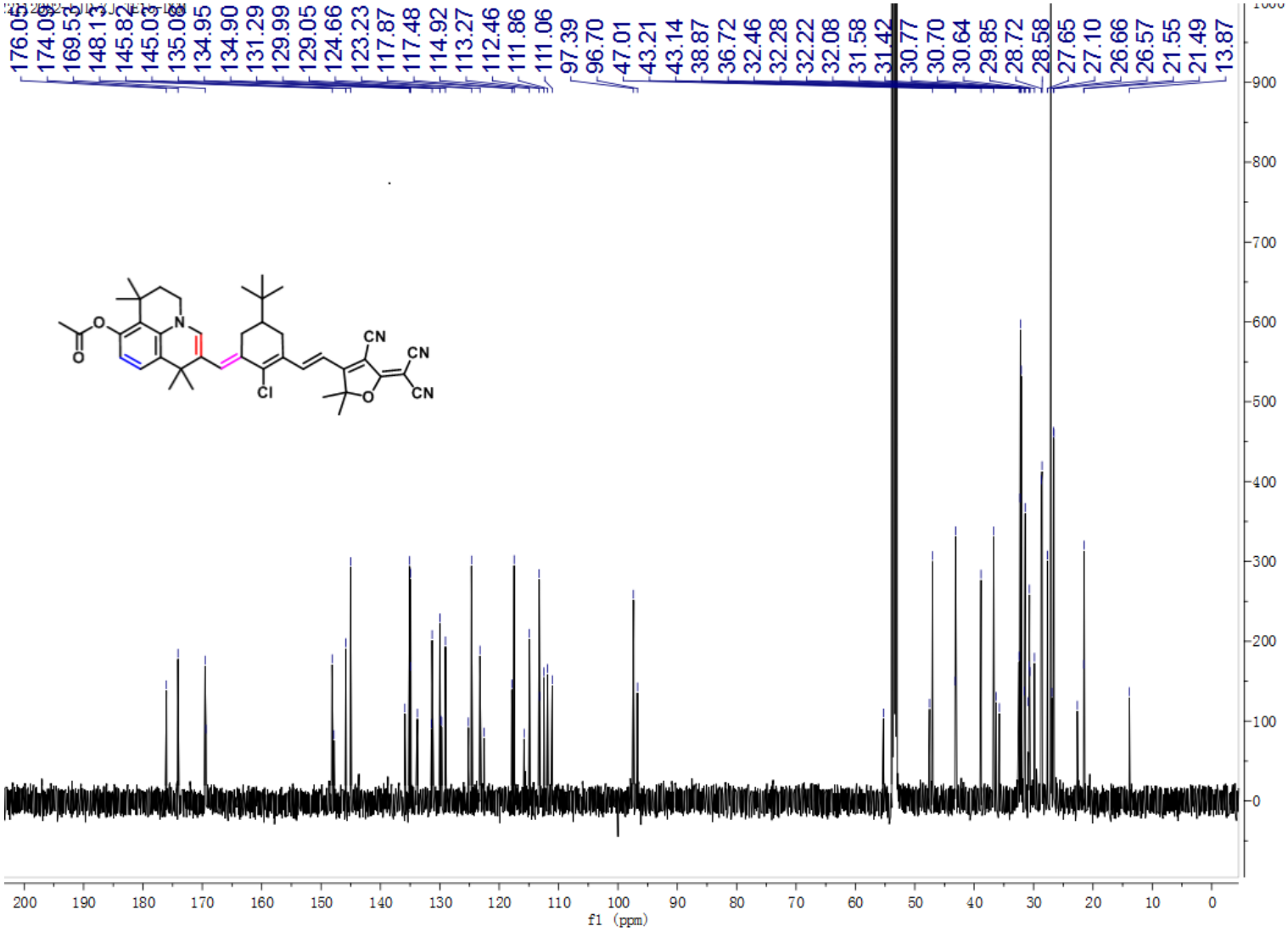


Figure S80. ^{13}C NMR spectrum of compound **TE-II-8**.

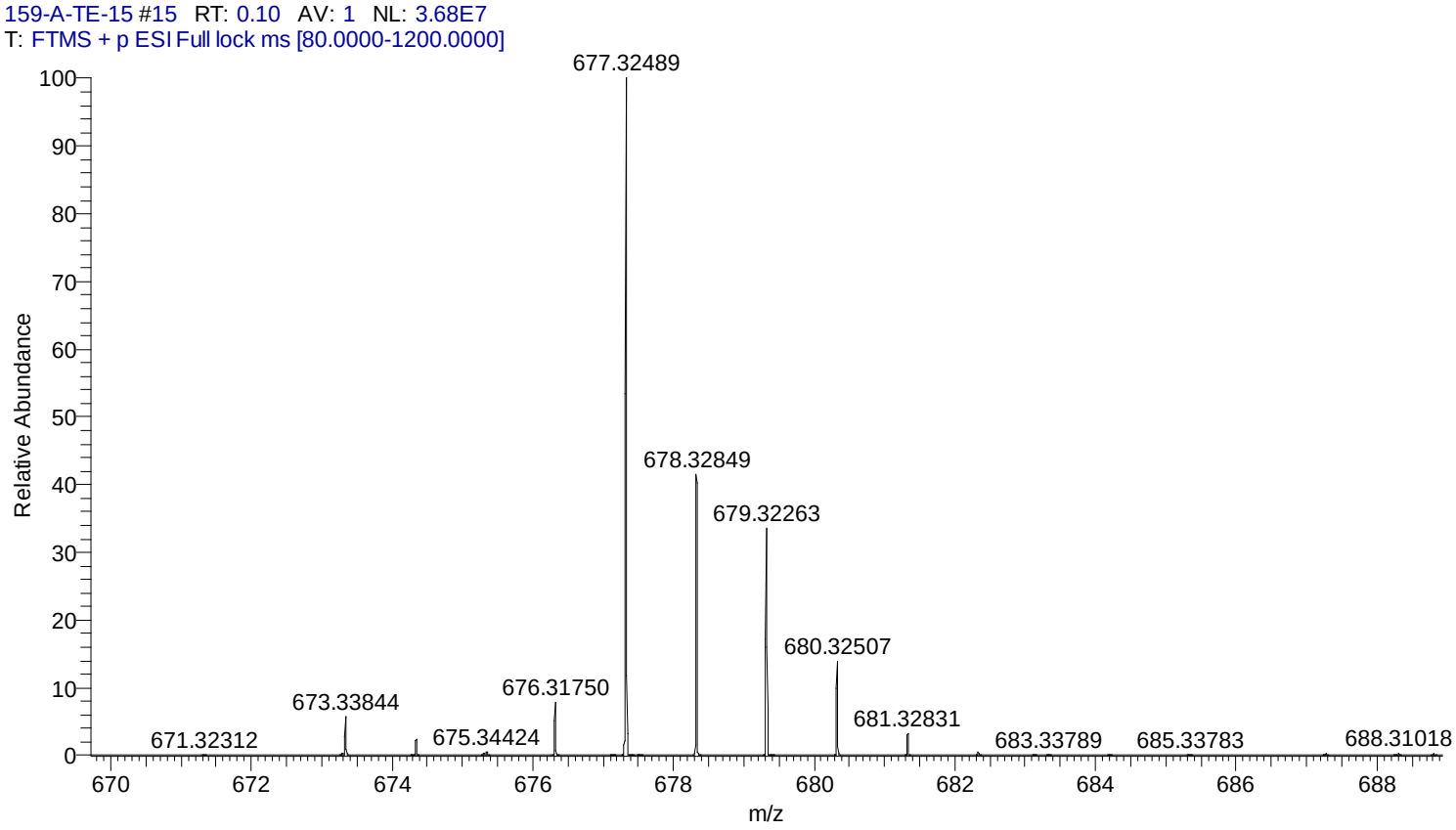


Figure S81. HRMS spectrum of compound **TE-II-8**.

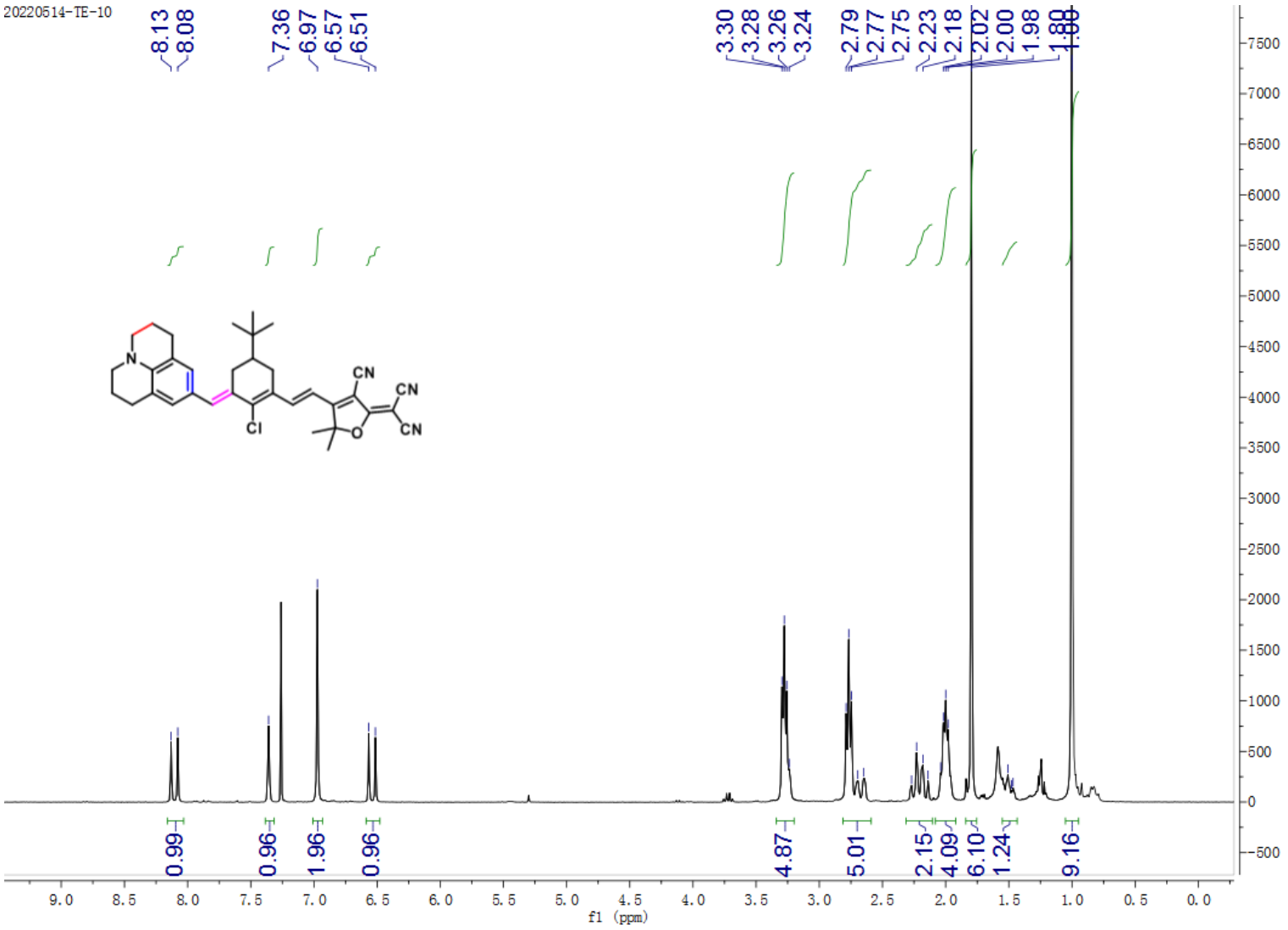


Figure S82. ^{1}H NMR spectrum of compound **TE-I-9**.

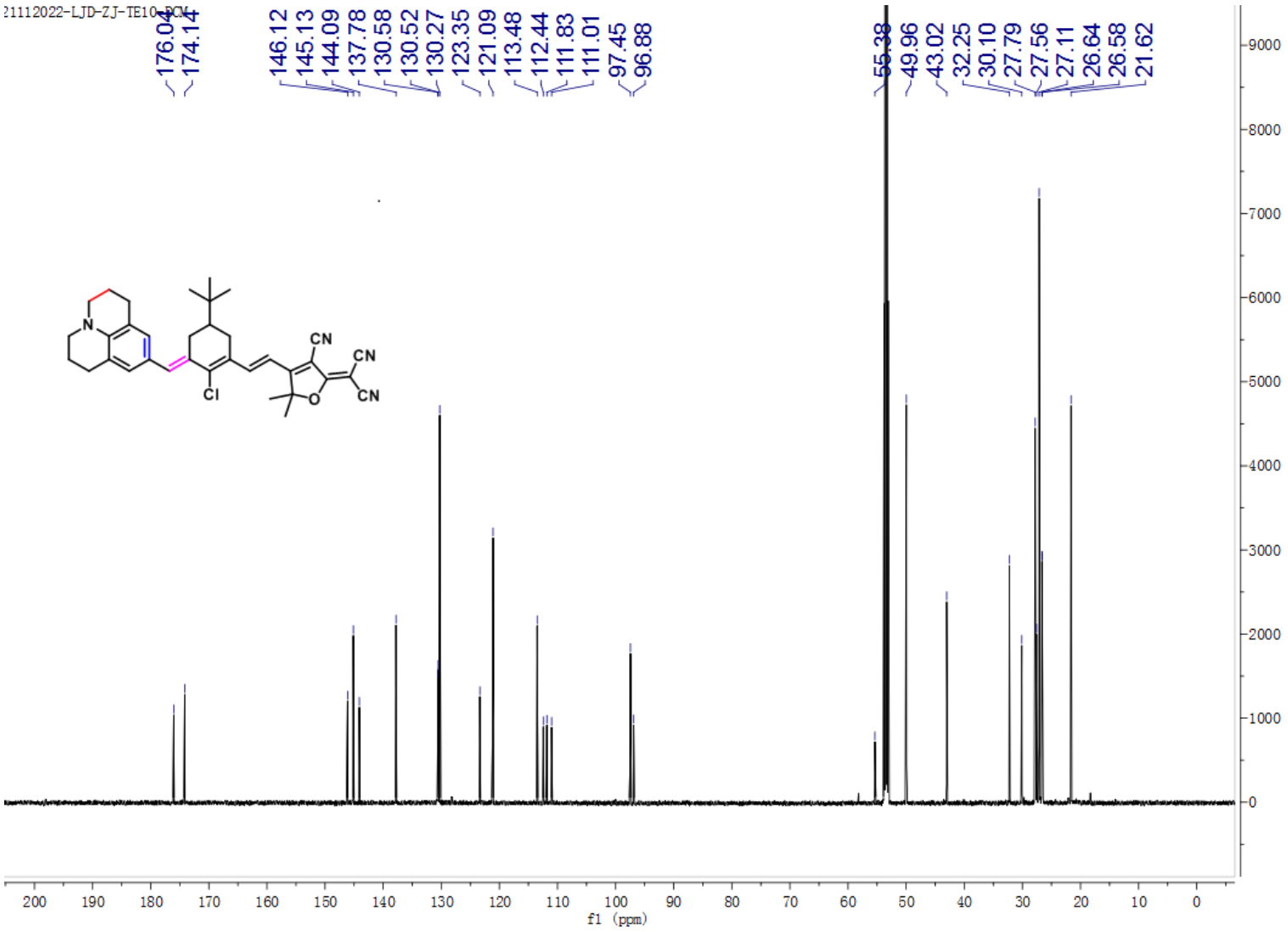


Figure S83. ^{13}C NMR spectrum of compound **TE-I-9**.

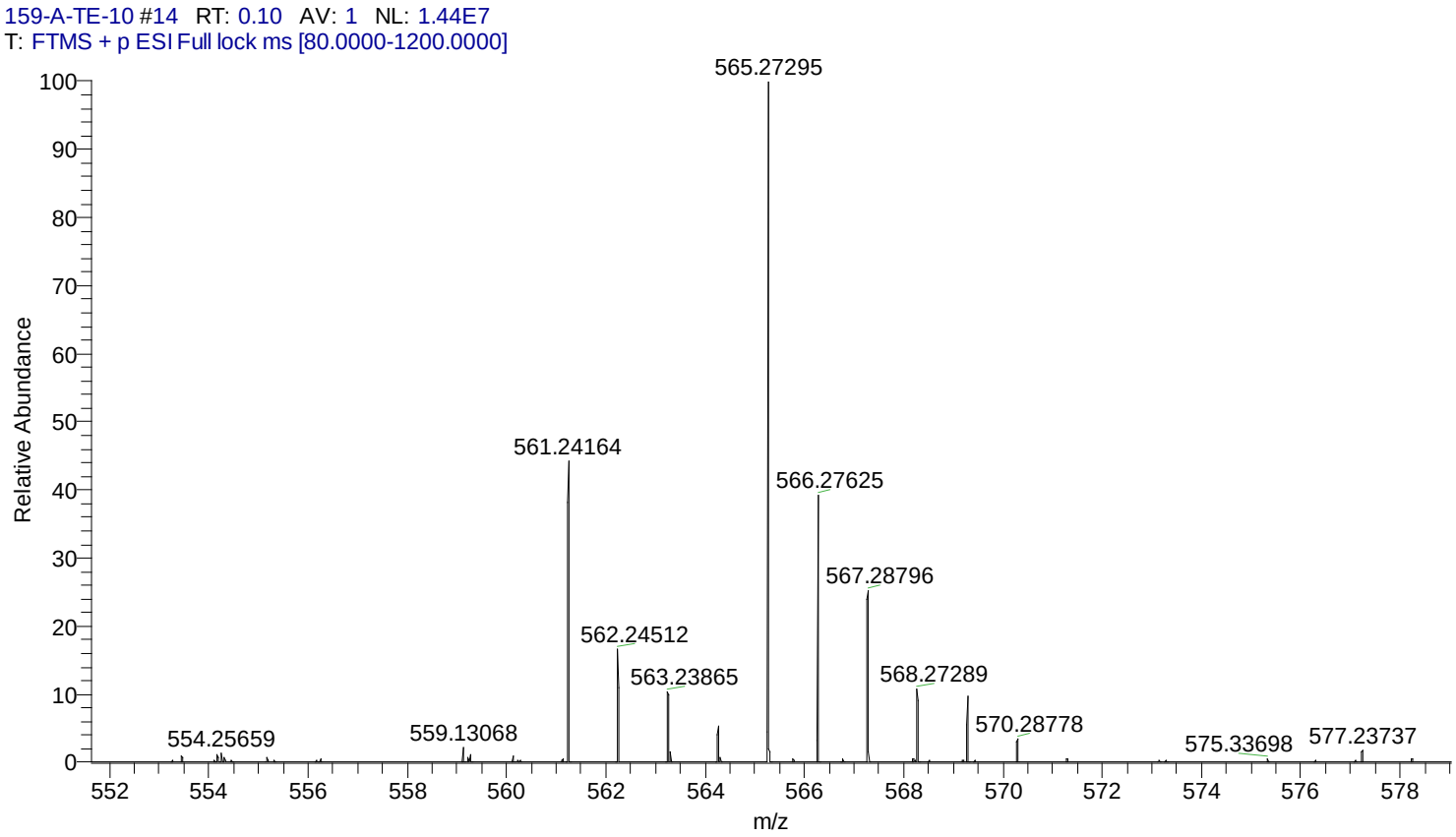


Figure S84. HRMS spectrum of compound **TE-I-9**.

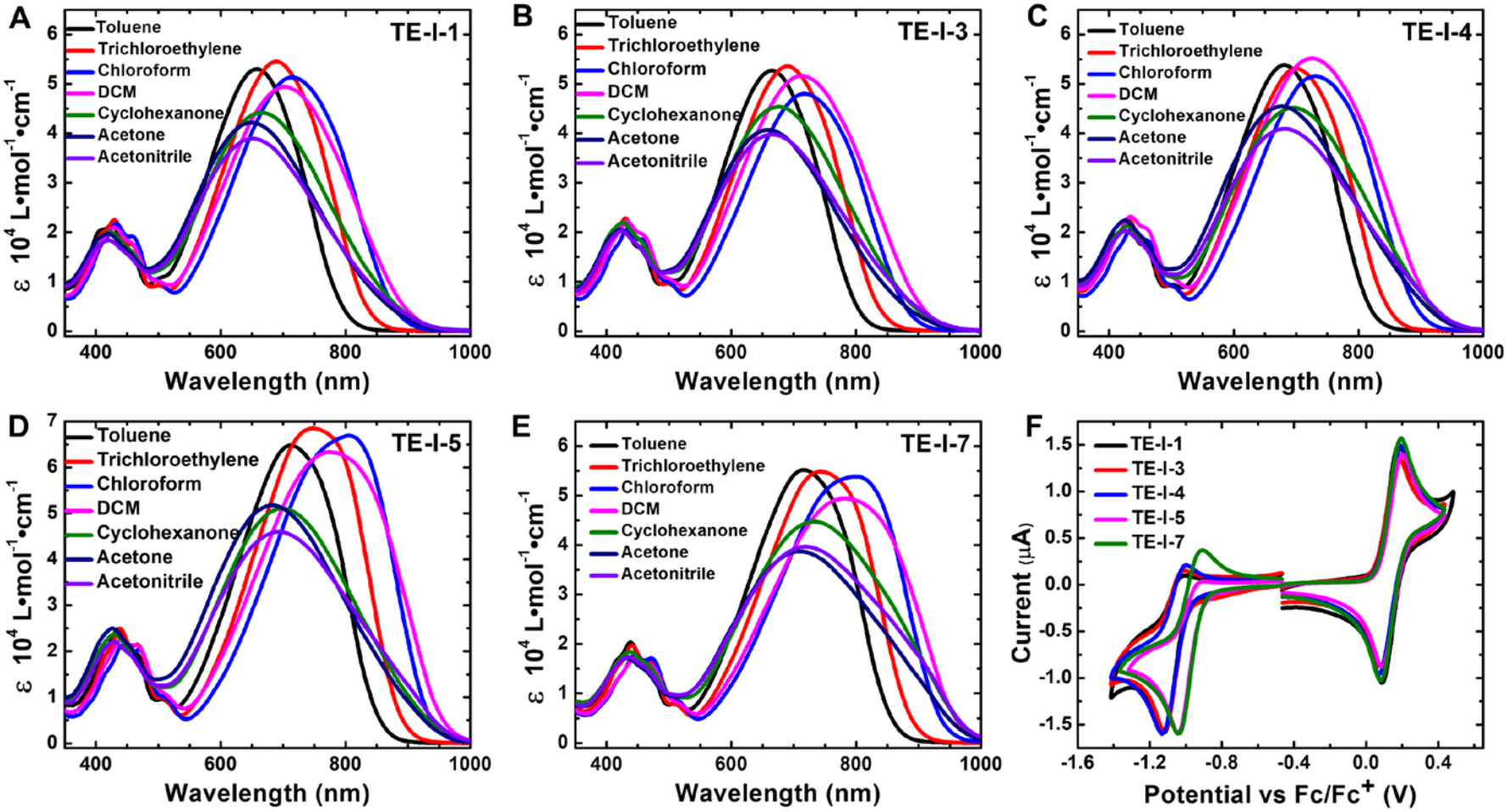


Figure S85. A-E, UV-vis-NIR spectra of Type-I chromophores recorded in solvents of different polarities. **F**, Cyclic voltammograms of Type-I chromophores in degassed anhydrous DCM solutions containing 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF) as the supporting electrolyte.

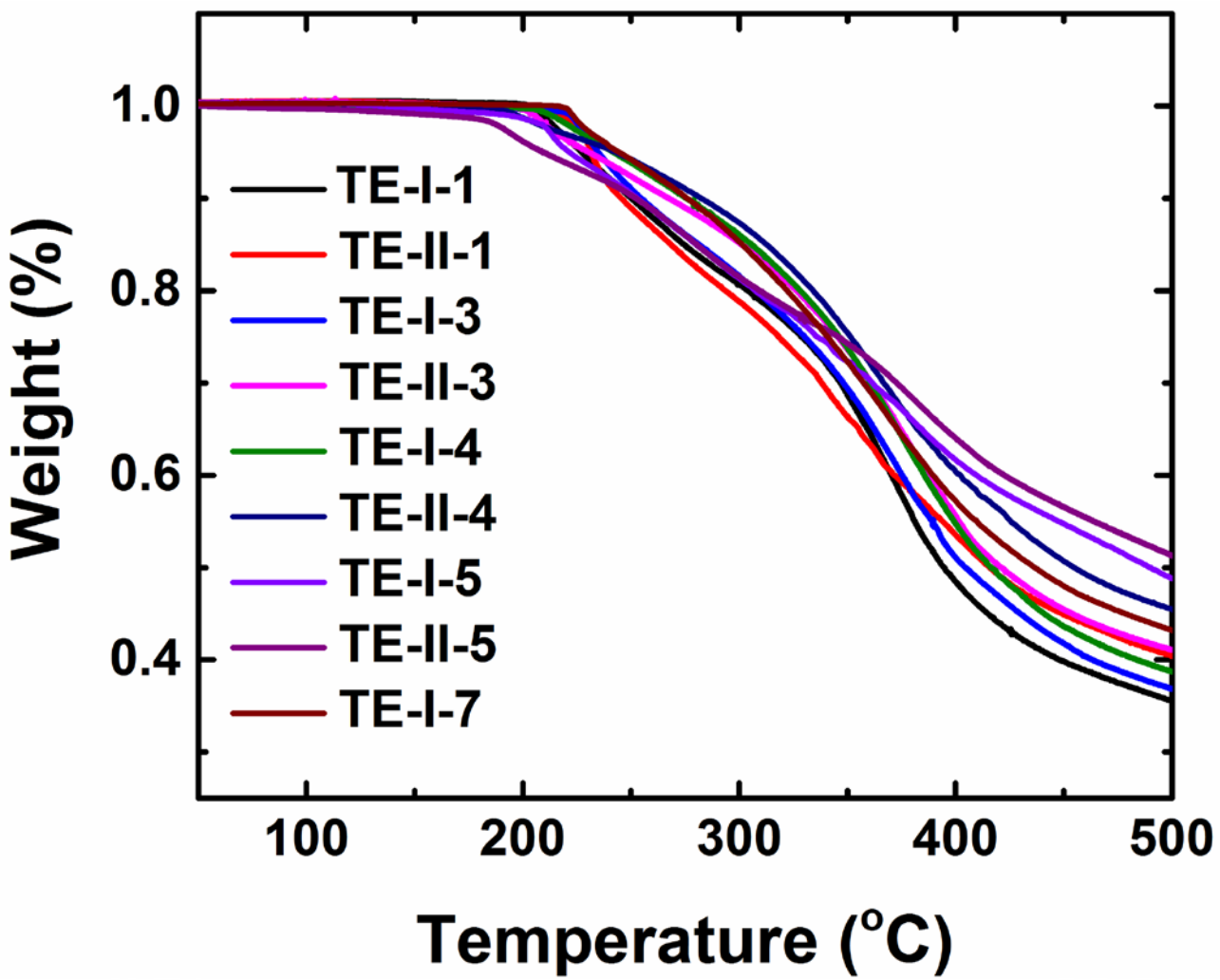


Figure S86. Thermogravimetric analysis of chromophores **TE-I-1**, **TE-II-1**, **TE-I-3**, **TE-II-3**, **TE-I-4**, **TE-II-4**, **TE-I-5**, **TE-II-5**, and **TE-I-7**.

5. X-ray crystallography

X-ray reflections were collected on the 4-circle kappa diffractometer (Oxford GEMINI S Ultra) with a 92 nm diagonal Sapphire CCD detector and co-mounted Enhance (Mo) and Enhance (Cu) X-ray sources. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for apsorption effects using the Multi-Scan method (SADABS). The structure was solved and refined using the Bruker SHELXTL software Package.

The crystal for **TE-II-1** has been grown by slow evaporation of $CHCl_3$ and EtOH.

Table S7. Crystallographic Data for Chromophore **TE-II-1**.

Compound	**TE-II-1**
Chemical formula	$C_{43}H_{51}ClN_4O_2$
Formula weight	691.32 g/mol
Temperature	173(2) K
Crystal system	monoclinic
Space group	C 1 2/c 1
Unit cell dimension	
a	30.3974(8) Å
b	15.2528(4) Å
c	22.3991(9) Å
α	90°
β	131.8510(10)°
γ	90°
Volume	7735.8(4) $Å^3$
Z	8
Density (calculated)	1.187 g/cm^3
Absorption coefficient	1.183 mm^{-1}
θ range for data collection	3.49-74.55°
Reflections collected	32612
Independent reflections	7878 (R_{int} = 0.0987)
Data/restraints/parameters	7878/168/498
Goodness of fit on F^2	1.143
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0974, wR_2 = 0.2699
R indices (all data)	R_1 = 0.1141, wR_2 = 0.2964

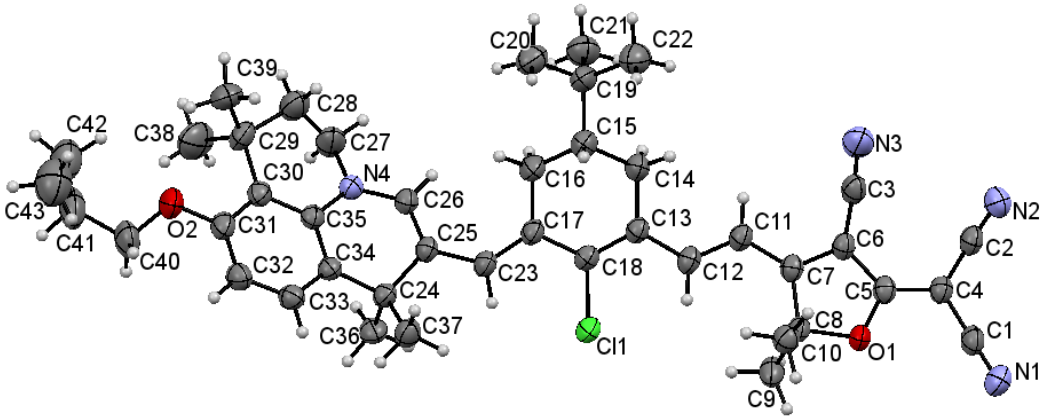


Figure S87. ORTEP drawings of chromophores **TE-II-1**. Ellipsoid contour percent probability level is 50%.

The crystal for **TE-II-2** has been grown by slow evaporation of $CHCl_3$ and EtOH.

Table S8. Crystallographic Data for Chromophore **TE-II-2**.

Compound	**TE-II-2**
Chemical formula	$C_{40}H_{44}Cl_4N_4O_2$
Formula weight	754.59 g/mol
Temperature	213(2) K
Crystal system	triclinic
Space group	P -1
Unit cell dimension	
a	9.0000(2) Å
b	10.1845(2) Å
c	22.4129(5) Å
α	102.5470(10)°
β	92.9080(10)°
γ	106.7020(10)°
Volume	1906.59(7) $Å^3$
Z	2
Density (calculated)	1.314 g/cm^3
Absorption coefficient	3.135 mm^{-1}
θ range for data collection	2.03-74.65°
Reflections collected	25539
Independent reflections	7731 (R_{int} = 0.0888)
Data/restraints/parameters	7731/132/505
Goodness of fit on F^2	1.008
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0857, wR_2 = 0.2457
R indices (all data)	R_1 = 0.1103, wR_2 = 0.2803

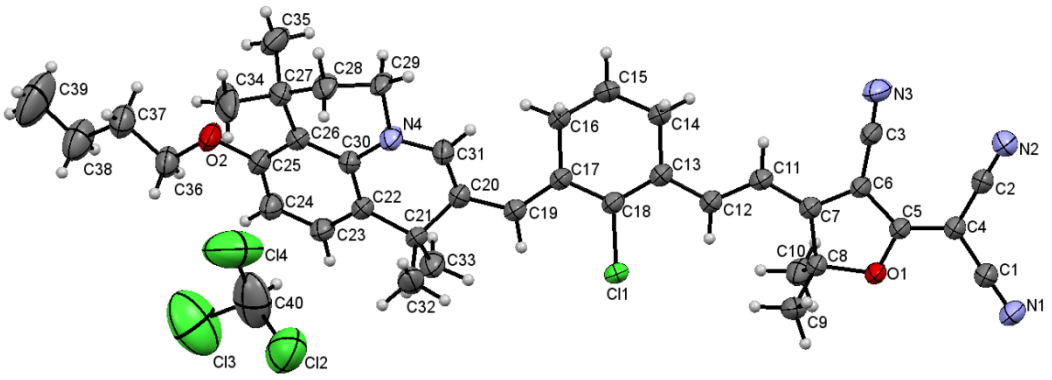


Figure S88. ORTEP drawings of chromophores **TE-II-2**. Ellipsoid contour percent probability level is 50%.

The crystal for **TE-I-6** has been grown by slow evaporation of $CHCl_3$ and EtOH.

Table S9. Crystallographic Data for Chromophore **TE-I-6**.

Compound	**TE-I-6**
Chemical formula	$C_{50}H_{48}Cl_4F_2N_4O_2$
Formula weight	916.72 g/mol
Temperature	233(2) K
Crystal system	triclinic
Space group	P -1
Unit cell dimension	
a	9.9554(11) Å
b	15.264(2) Å
c	15.9425(19) Å
α	76.061(5)°
β	83.579(4)°
γ	84.782(5)°
Volume	2331.4(5) $Å^3$
Z	2
Density (calculated)	1.306 g/cm^3
Absorption coefficient	0.306 mm^{-1}
θ range for data collection	2.35-26.43°
Reflections collected	29614
Independent reflections	9556 (R_{int} = 0.0926)
Data/restraints/parameters	9556/213/640
Goodness of fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0666, wR_2 = 0.1564
R indices (all data)	R_1 = 0.1268, wR_2 = 0.1953

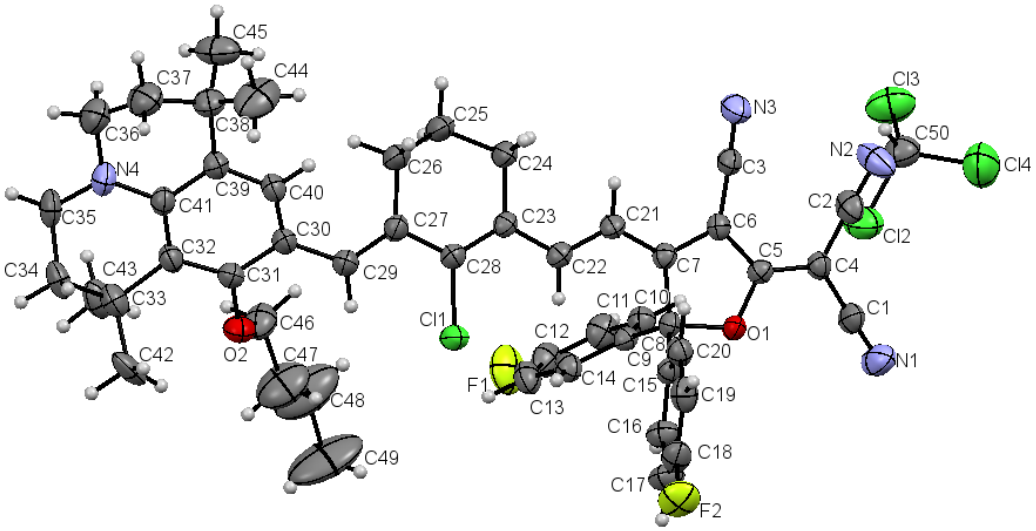


Figure S89. ORTEP drawings of chromophores **TE-I-6**. Ellipsoid contour percent probability level is 50%.

The crystal for **TE-II-6** has been grown by slow evaporation of $CHCl_3$ and EtOH.

Table S10. Crystallographic Data for Chromophore **TE-II-6**.

Compound	**TE-II-6**
Chemical formula	$C_{49}H_{45}ClF_2N_4O_2$
Formula weight	795.34 g/mol
Temperature	218(2) K
Crystal system	monoclinic
Space group	C 1 2/c 1
Unit cell dimension	
a	30.7033(7) Å
b	26.4439(6) Å
c	11.6452(3) Å
α	90°
β	111.3770(10)°
γ	90°
Volume	8804.4(4) Å^3
Z	8
Density (calculated)	1.200 g/cm^3
Absorption coefficient	1.179 mm^{-1}
θ range for data collection	3.09-74.73°
Reflections collected	58974
Independent reflections	9041 (R_{int} = 0.0532)
Data/restraints/parameters	9041/372/603
Goodness of fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0533, wR_2 = 0.1636
R indices (all data)	R_1 = 0.0594, wR_2 = 0.1715

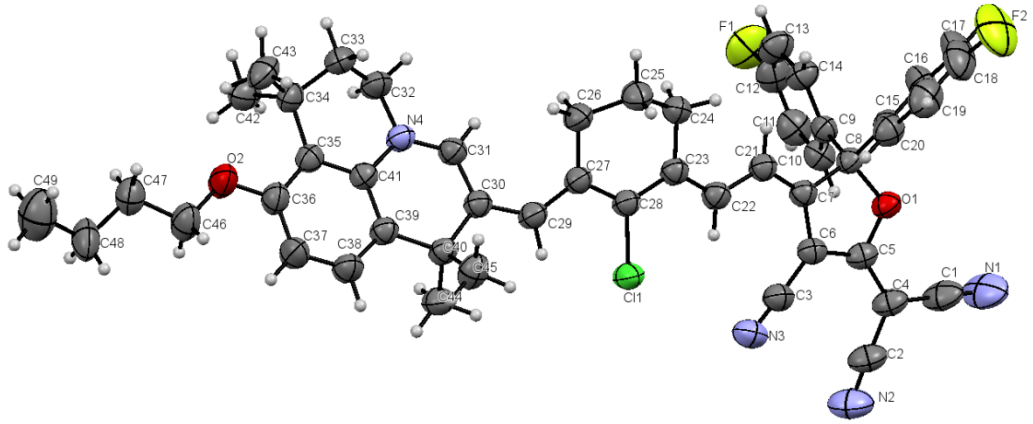


Figure S90. ORTEP drawings of chromophores **TE-II-6**. Ellipsoid contour percent probability level is 50%.

6. References

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