Supporting Information

Photoinduced cascade cyclization of alkynes with NH_4SCN: access to SCN-containing dibenzazepines or dioxodibenzothiazepines

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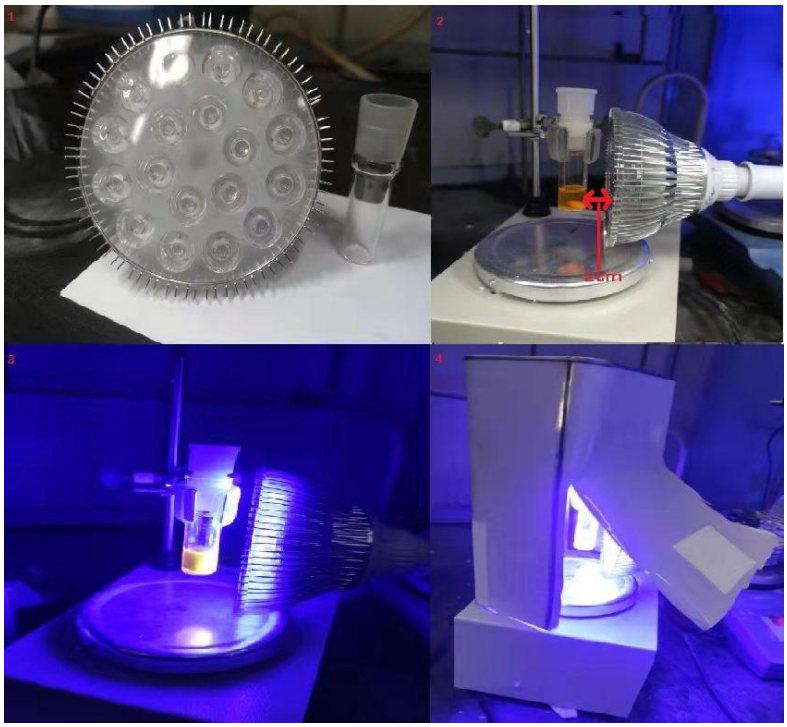
General Information

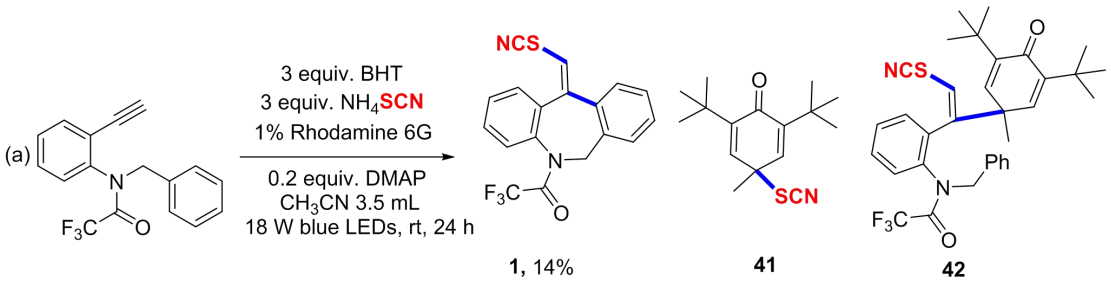
^{1}H and ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker advance Ⅲ 400 or 600 spectrometer in $CDCl_3$ with TMS as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by ^{1}H and ^{13}C NMR, HRMS. The starting materials were purchased from Energy, J&K Chemicals or Aldrich and used without further purification.

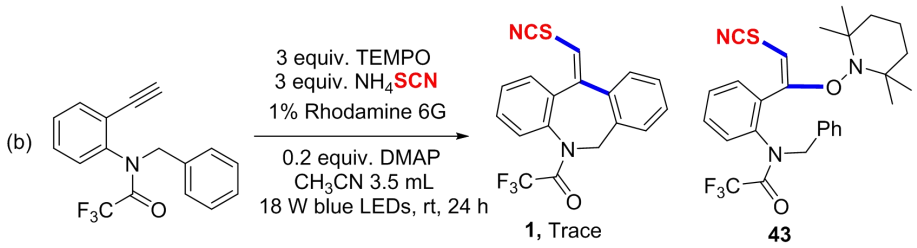
Typical procedure for the reaction



Reaction conditions: A mixture of alkynes (1 equiv., 0.1 mmol), NH_4SCN (3 equiv., 0.3 mmol), rhodamine 6G (0.01 equiv., 0.001 mmol), DMAP (0.2 equiv., 0.02 mmol), CH_3CN (3.5 mL), was added into a 10 mL quartz tube, which was operated with 18 W blue LEDs, rt. When the reaction was finished, the mixture was condensed under vacuum and purified by column chromatography to afford the final product.

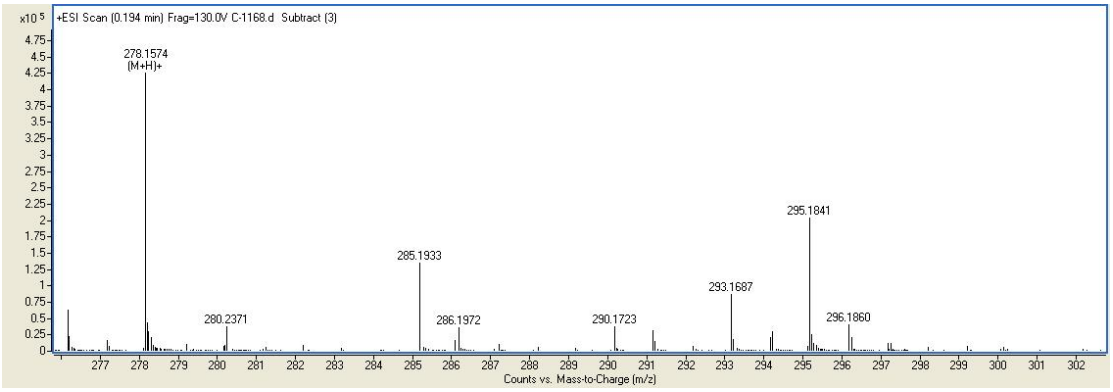
Mechanistic study



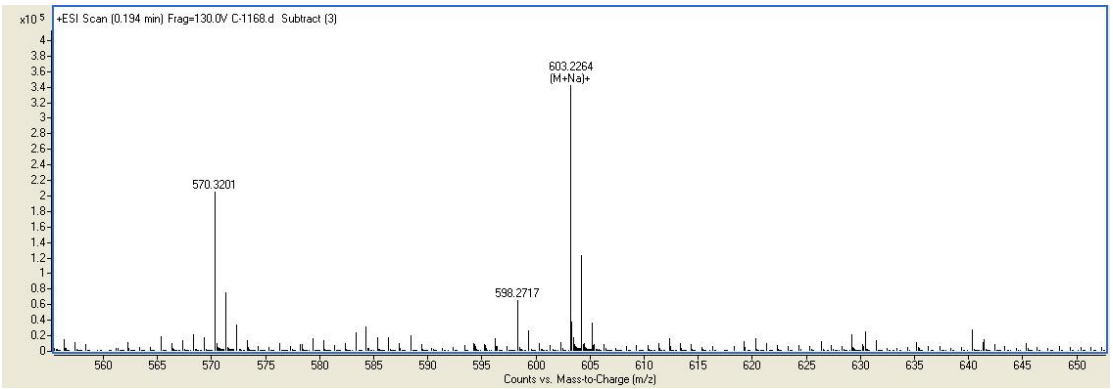


Products **41**, **42**, and **43** all were detected by HRMS

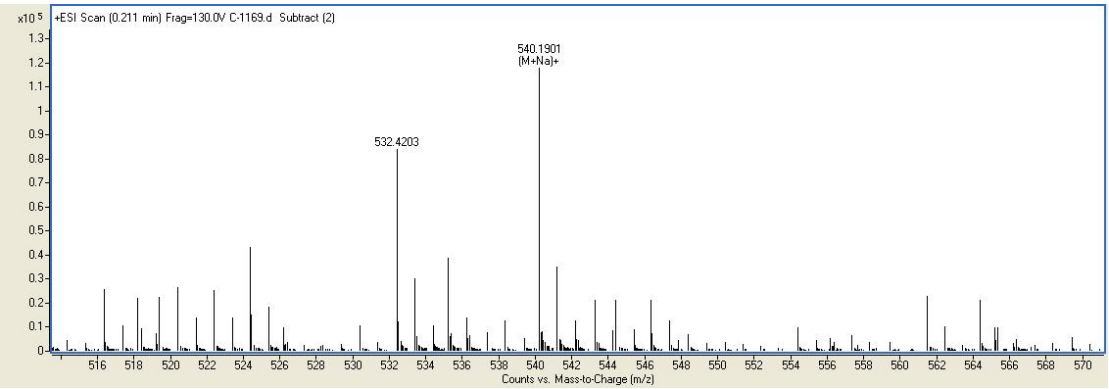
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
41	$C_{16}H_{23}NOS$	$C_{16}H_{24}NOS$	278.1574	278.1573	0.36



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
42	$C_{33}H_{35}F_3N_2O_2S$	$C_{33}H_{35}F_3N_2O_2SNa$	603.2264	603.2264	0



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
43	$C_{27}H_{30}F_3N_3O_2S$	$C_{27}H_{30}F_3N_3O_2SNa$	540.1901	540.1903	0.37



Crystallographic details

Single crystals of $C_{19}H_{13}F_3N_2OS$ [Product **3**] were obtained as follows: A suitable crystal was selected and detected on a "Bruker APEX-II CCD" diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the SHELXL [3] refinement package using Least Squares minimisation. Crystal data and structure refinement parameters are summarized in **Table S1**. CCDC No. 2164051.

[1]. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

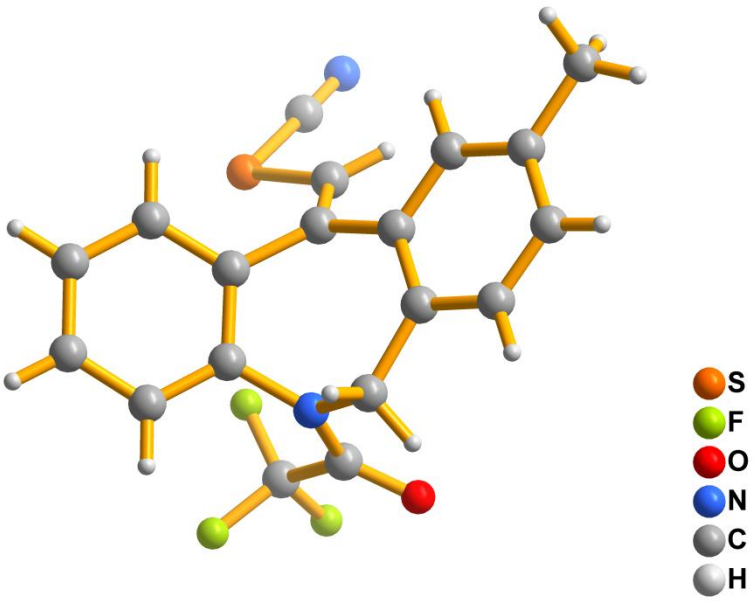
[2]. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

[3]. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table S1. Crystal data and structure refinement for product **3**.

Empirical formula	$C_{19}H_{13}F_3N_2OS$
Formula weight	374.37
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.5655(3)
b/Å	25.6875(12)

c/Å	7.7171(3)
α/°	90
β/°	99.0140(10)
γ/°	90
Volume/Å^3	1676.99(12)
Z	4
ρ_{calc}g/cm^3	1.483
μ/mm^{-1}	0.235
F(000)	768.0
Crystal size/mm^3	0.18 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.816 to 52.788
Index ranges	-10 ≤ h ≤ 10, -32 ≤ k ≤ 27, -8 ≤ l ≤ 9
Reflections collected	12830
Independent reflections	3436 [R_{int} = 0.0640, R_{sigma} = 0.0658]
Data/restraints/parameters	3436/0/236
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.0930
Final R indexes [all data]	R_1 = 0.0929, wR_2 = 0.1122
Largest diff. peak/hole / e Å^{-3}	0.41/-0.31
CCDC	2164051



Physical data and references for the following products

References:

1. C. Wu, L.-H. Lu, A.-Z. Peng, G.-K. Jia, C. Peng, Z. Cao, Z.-L. Tang, W.-M. He and X.-H. Xu, *Green Chem.*, 2018, **20**, 3683.

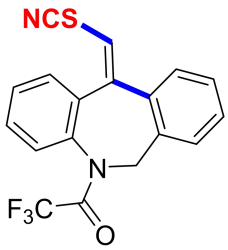
2. C. Xu, Z. He, X. Kang, Q.-L. Zeng, *Green Chem.*, 2021, **23**, 7544.

3. P. Natarajan, Priya and D. Chuskit, *Green Chem.*, 2021, **23**, 4873.

Physical data for the following products:

1. (Z)-2,2,2-trifluoro-1-(11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 22.70 mg, 68% yield. Mp: 129-130 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (t, *J* = 4.0 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.33 (t, *J* = 5.2 Hz, 2H), 7.16 (d, *J* = 6.4 Hz, 1H), 6.67 (s, 1H), 5.87 (d, *J* = 16.8 Hz, 1H), 4.32 (d, *J* = 16.8 Hz, 1H).

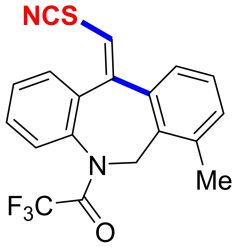
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (q, *J* = 36.3 Hz), 144.7, 137.0, 135.7, 133.8, 133.1, 130.5, 129.9, 129.5, 128.9, 128.6, 128.2, 128.1, 127.6 (q, *J* = 1.7 Hz), 116.7, 116.0 (q, *J* = 286.9 Hz), 110.20, 51.02.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.47 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{11}F_3N_2NaOS$ $(M+Na)^+$ 383.0436, Measured 383.0446.

2. (Z)-2,2,2-trifluoro-1-(7-methyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1). 16.08 mg, 43% yield. Mp: 190-191 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.43 (m, 3H), 7.36 – 7.33 (m, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 10.0 Hz, 2H), 6.65 (s, 1H), 5.90 (d, *J* = 17.2 Hz, 1H), 4.10 (d, *J* = 17.2 Hz, 1H), 2.27 (s, 3H).

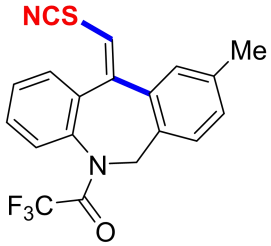
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (q, *J* = 36.3 Hz), 145.6, 136.4, 134.1, 133.4, 131.6, 131.2, 130.6, 130.3, 129.9, 128.1, 127.6, 127.3, 126.0, 116.2 (q, *J* = 287.0 Hz), 115.4, 110.2, 49.1, 19.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.34 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{17}F_3N_3OS$ $(M+NH_4)^+$ 392.1039, Measured 392.1043.

3. (Z)-2,2,2-trifluoro-1-(9-methyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 26.96 mg, 72% yield. Mp: 160-161 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 3.6 Hz, 2H), 7.44 (s, 1H), 7.37 – 7.34 (m, 1H), 7.23 (s, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.66 (s, 1H), 5.83 (d, *J* = 16.8 Hz, 1H), 4.28 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H).

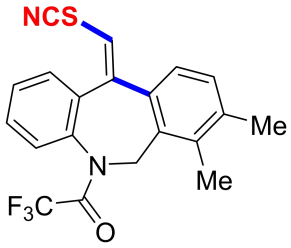
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (q, *J* = 36.3 Hz), 144.9, 137.9, 136.9, 135.7, 133.5, 130.4, 130.3, 130.0, 129.8, 129.4, 128.5, 128.1, 127.5 (q, *J* = 16.6 Hz), 116.2, 116.1 (q, *J* = 287.1 Hz), 110.2, 50.72, 20.86.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.46 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{13}F_3N_2NaOS$ $(M+Na)^+$ 397.0593, Measured 397.0595.

4. (Z)-1-(7,8-dimethyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 23.30 mg, 60% yield. Mp: 173-174 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, *J* = 3.2 Hz, 2H), 7.45 – 7.43 (m, 1H), 7.35 – 7.33 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.93 (d, *J* = 17.2 Hz, 1H), 4.12 (d, *J* = 17.2 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H).

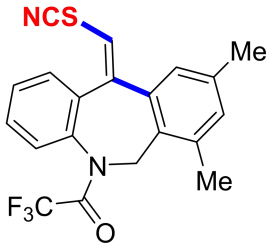
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (q, *J* = 36.0 Hz), 146.0, 138.5, 136.6, 136.4, 134.8, 132.1, 131.0, 130.2, 129.8, 129.3, 128.0, 127.2, 126.7, 116.2 (q, *J* = 287.1 Hz), 114.3, 110.3, 49.7, 20.6, 14.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.34 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{20}H_{19}F_3N_3OS$ $(M+NH_4)^+$ 406.1195, Measured 406.1196.

5. (Z)-1-(7,9-dimethyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 19.03 mg, 49% yield. Mp: 167-168 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, *J* = 3.2 Hz, 2H), 7.45 – 7.44 (m, 1H), 7.35 – 7.33 (m, 1H), 7.08 (s, 1H), 7.01 (s, 1H), 6.65 (s, 1H), 5.86 (d, *J* = 17.2 Hz, 1H), 4.07 (d, *J* = 17.2 Hz, 1H), 2.33 (s, 3H), 2.23 (s, 3H).

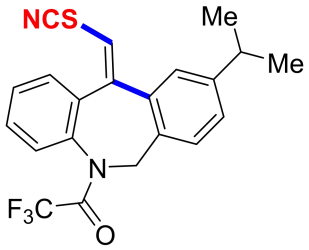
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (q, *J* = 36.3 Hz), 145.8, 137.2, 136.5, 136.4, 136.2, 134.0, 132.4, 130.3, 129.8, 128.2, 128.1, 127.8, 127.3, 116.2 (q, *J* = 287.3 Hz), 115.0, 110.3, 48.9, 20.7, 19.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.31 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{20}H_{19}F_3N_3OS$ $(M+NH_4)^+$ 406.1195, Measured 406.1198.

6. (Z)-2,2,2-trifluoro-1-(9-isopropyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 21.73 mg, 54% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 4.4 Hz, 2H), 7.44 – 7.42 (m, 1H), 7.37 (dd, *J* = 4.4, 2.0 Hz, 1H), 7.24 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 5.84 (d, *J* = 16.8 Hz, 1H), 4.29 (d, *J* = 16.8 Hz, 1H), 2.97 – 2.90 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 6H).

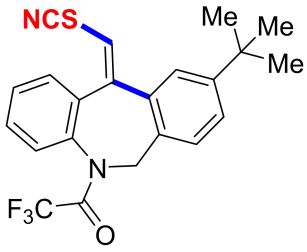
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (q, *J* = 36.0 Hz), 149.0, 145.1, 136.9, 135.8, 133.6, 130.4, 130.2, 129.8, 128.6, 128.2, 127.7, 127.5, 126.9, 116.2, 116.1 (q, *J* = 286.9 Hz), 110.3, 50.8, 33.8, 24.0, 23.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.46 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{21}H_{21}F_3N_3OS$ $(M+NH_4)^+$ 420.1352, Measured 420.1352.

7. (Z)-1-(9-(tert-butyl)-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1). 33.19 mg, 80% yield. Mp: 132-133 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 4.4 Hz, 2H), 7.45 (s, 1H), 7.38 (d, *J* = 6.4 Hz, 3H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.67 (s, 1H), 5.85 (d, *J* = 16.8 Hz, 1H), 4.30 (d, *J* = 16.7 Hz, 1H), 1.35 (s, 9H).

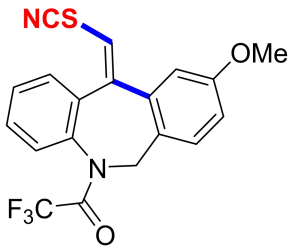
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (q, *J* = 36.3 Hz), 151.2, 145.3, 136.8, 135.8, 133.3, 130.4, 130.0, 129.7, 128.6, 127.9, 127.5 (q, *J* = 2.0 Hz), 126.8, 125.5, 116.1, 116.0 (q, *J* = 287.2 Hz), 110.3, 50.7, 34.6, 31.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.42 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{22}H_{23}F_3N_3OS$ $(M+NH_4)^+$ 434.1508, Measured 434.1511.

8. (Z)-2,2,2-trifluoro-1-(9-methoxy-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 21.84 mg, 56% yield. Mp: 168-169 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 3.6 Hz, 2H), 7.44 (s, 1H), 7.36 – 7.34 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 5.79 (d, *J* = 16.8 Hz, 1H), 4.25 (d, *J* = 16.4 Hz, 1H), 3.84 (s, 3H).

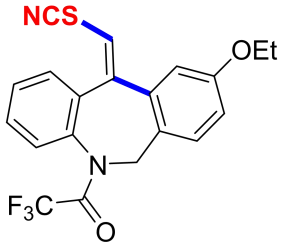
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 156.0 (q, *J* = 36.3 Hz), 144.6, 136.9, 135.4, 134.6, 130.5, 129.8, 129.4, 128.6, 127.6, 124.9, 116.9, 116.1 (q, *J* = 287.2 Hz), 115.3, 113.8, 110.1, 55.5, 50.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.45 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{17}F_3N_3O_2S$ $(M+NH_4)^+$ 408.0988, Measured 408.0987.

9. (Z)-1-(9-ethoxy-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 30.70 mg, 76% yield. Mp: 137-138 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 3.2 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 9.2 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.68 (s, 1H), 5.79 (d, *J* = 16.8 Hz, 1H), 4.25 (d, *J* = 16.4 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 6.8 Hz, 3H).

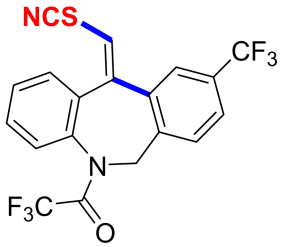
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 115.9 (q, *J* = 36.2 Hz), 144.6, 136.9, 135.4, 134.6, 130.5, 129.8, 129.3, 128.5, 127.5, 124.7, 116.7, 116.1 (q, *J* = 287.2 Hz), 115.7, 114.5, 110.0, 63.7, 50.4, 14.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.44 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{20}H_{19}F_3N_3O_2S$ $(M+NH_4)^+$ 422.1145, Measured 422.1148.

10. (Z)-2,2,2-trifluoro-1-(11-(thiocyanatomethylene)-9-(trifluoromethyl)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 22.68 mg, 53% yield. Mp: 179-180 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.79 (s, 1H), 5.93 (d, *J* = 17.2 Hz, 1H), 4.36 (d, *J* = 17.2 Hz, 1H).

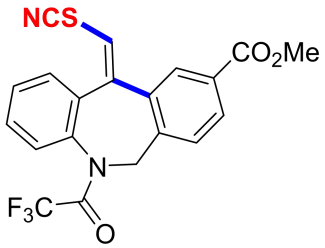
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (q, *J* = 36.6 Hz), 142.8, 137.1, 136.7, 135.0, 134.4, 131.0, 130.7, 130.4, 130.2, 128.9, 128.7, 127.7, 125.9, 120.7 (q, *J* = 270.8 Hz), 119.0, 116.0 (q, *J* = 286.9 Hz), 109.5, 50.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -62.64 (s, 3F), -67.52 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{10}F_6N_2ONaS$ $(M+Na)^+$ 451.0310, Measured 451.0310.

11. methyl (Z)-11-(thiocyanatomethylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5H-dibenzo[b,e]azepine-9-carboxylate

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1). 24.26 mg, 58% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.74 (s, 1H), 7.53 (t, *J* = 3.6 Hz, 2H), 7.37 (dd, *J* = 6.7, 2.4 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 4.36 (d, *J* = 17.2 Hz, 1H), 3.97 (s, 3H).

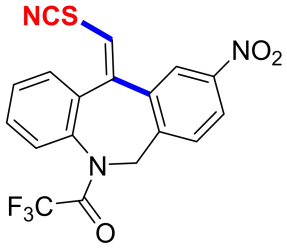
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 156.2 (q, *J* = 36.6 Hz), 143.3, 138.0, 136.7, 135.3, 134.1, 130.8, 130.5, 130.4, 130.1, 130.0, 128.6, 128.5, 127.6, 118.2, 116.0 (q, *J* = 285.5 Hz), 109.7, 52.4, 50.9.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.49 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{20}H_{13}F_3N_2NaO_3S$ $(M+Na)^+$ 441.0491, Measured 441.0492.

12. (Z)-2,2,2-trifluoro-1-(9-nitro-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 20.25 mg, 50% yield. Mp: 178-179 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 2.4 Hz, 1H), 8.17 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 6.8 Hz, 2H), 6.89 (s, 1H), 5.97 (d, *J* = 17.6 Hz, 1H), 4.39 (d, *J* = 17.6 Hz, 1H).

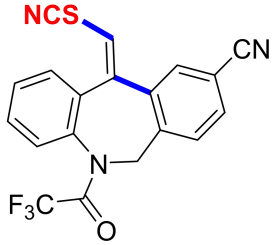
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3 (q, *J* = 36.7 Hz),147.3, 141.6, 140.2, 136.6, 135.2, 134.5, 131.2, 130.4, 129.5, 128.7, 127.8, 123.9, 123.7, 120.5, 116.0 (q, *J* = 287.0 Hz), 109.2, 50.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.52 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}F_3N_3NaO_3S$ $(M+Na)^+$ 428.0287, Measured 428.0285.

13. (Z)-11-(thiocyanatomethylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5H-dibenzo[b,e]azepine -9-carbonitrile.

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1). 15.41 mg, 40% yield. Mp: 235-236 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.34 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 6.8, 3.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 5.92 (d, *J* = 17.6 Hz, 1H), 4.35 (d, *J* = 17.6 Hz, 1H).

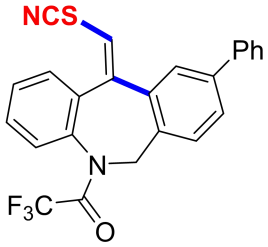
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3 (q, *J* = 36.3 Hz), 141.9, 138.4, 136.6, 135.0, 134.6, 132.6, 132.3, 131.1, 130.3, 129.3, 128.7, 127.8, 120.0, 117.6, 116.0 (q, *J* = 287.1 Hz), 112.4, 109.2, 50.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.52 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{10}F_3N_3NaOS$ $(M+Na)^+$ 408.0389, Measured 408.0389.

14. (Z)-2,2,2-trifluoro-1-(9-phenyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 29.68 mg, 68% yield. Mp: 182-183 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.58 (s, 1H), 7.54 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.51 (d, *J* = 3.6 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 4H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 5.90 (d, *J* = 16.8 Hz, 1H), 4.34 (d, *J* = 16.8 Hz, 1H).

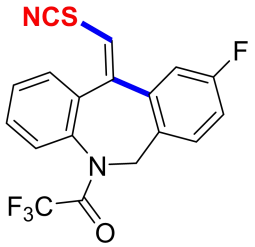
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (q, *J* = 36.2 Hz), 144.6, 141.2, 139.5, 136.9, 135.6, 134.1, 131.9, 130.6, 129.9, 129.0, 128.9, 128.7, 128.6, 128.1, 127.9, 127.5, 127.0, 116.9, 116.1 (q, *J* = 287.1 Hz), 110.0, 50.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.46 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{24}H_{15}F_3N_2NaOS$ $(M+Na)^+$ 459.0749, Measured 459.0752.

15. (Z)-2,2,2-trifluoro-1-(9-fluoro-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1). 26.86 mg, 71% yield. Mp: 141-142 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.51 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.16 – 7.13 (m, 2H), 7.07 – 7.02 (m, 1H), 6.71 (s, 1H), 5.83 (d, *J* = 16.8 Hz, 1H), 4.27 (d, *J* = 16.8 Hz, 1H).

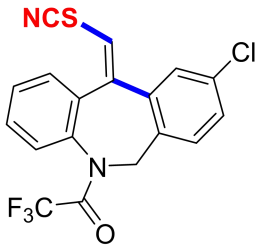
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (d, *J* = 246.8 Hz), 156.1 (q, *J* = 36.5 Hz), 143.2, 136.9, 135.3 (d, *J* = 7.2 Hz), 134.9, 130.8, 130.0 (d, *J* = 7.2 Hz), 128.8 (d, *J* = 3.4 Hz), 128.6, 127.6, 118.4, 116.5 (d, *J* = 21.3 Hz), 116.1 (q, *J* = 287.0 Hz),115.5 (d, *J* = 22.9 Hz), 109.7, 50.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.50 (s, 3F), -113.77 (s, 1F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{14}F_4N_3OS$ $(M+NH_4)^+$ 396.0788, Measured 396.0786.

16. (Z)-1-(9-chloro-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 23.20 mg, 59% yield. Mp: 162-163 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.51 (m, 2H), 7.46 – 7.43 (m, 2H), 7.36 – 7.34 (m, 1H), 7.30 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 5.82 (d, *J* = 16.8 Hz, 1H), 4.27 (d, *J* = 16.8 Hz, 1H).

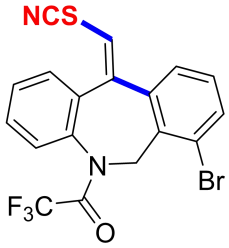
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (q, *J* = 36.3 Hz), 142.9, 136.8, 135.2, 135.0, 133.6, 131.5, 130.8, 130.0, 129.6, 129.4, 128.6, 127.6 (q, *J* = 1.9 Hz), 118.3, 116.0 (q, *J* = 287.0 Hz), 109.7, 50.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.50 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}ClF_3N_2NaOS$ $(M+Na)^+$ 417.0047, Measured 417.0051.

17. (Z)-1-(7-bromo-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 18.50 mg, 42% yield. Mp: 191-192 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.36 (dd, *J* = 14.8, 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 6.03 (d, *J* = 17.6 Hz, 1H), 4.14 (d, *J* = 17.6 Hz, 1H).

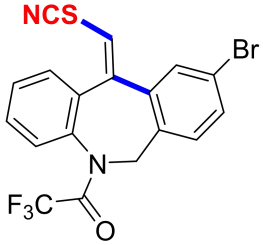
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3 (q, *J* = 36.4 Hz), 143.8, 136.4, 136.3, 135.8, 134.2, 132.1, 130.8, 130.2, 129.0, 128.7, 128.2, 127.6, 124.2, 117.3, 116.2 (q, *J* = 287.1 Hz), 109.9, 52.3.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.33 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}BrF_3N_2NaOS$ $(M+Na)^+$ 460.9542, Measured 460.9543.

18. (Z)-1-(9-bromo-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 18.44 mg, 42% yield. Mp: 165-166 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.54 – 7.51 (m, 2H), 7.45 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.36 – 7.34 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 5.80 (d, *J* = 17.2 Hz, 1H), 4.24 (d, *J* = 17.2 Hz, 1H).

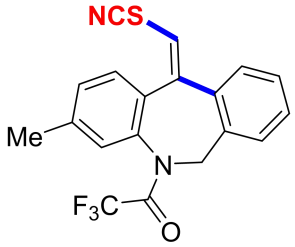
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (q, *J* = 36.2 Hz) , 142.8, 136.7, 135.4, 135.0, 132.2, 132.0, 131.4, 130.8, 130.0, 129.7, 128.6, 127.6 (q, *J* = 1.7 Hz) , 121.5 (d, *J* = 1.5 Hz), 118.3, 116.0 (q, *J* = 287 Hz), 109.7, 50.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.49 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}BrF_3NaN_2OS$ $(M+Na)^+$ 460.9542, Measured 460.9540.

19. (Z)-2,2,2-trifluoro-1-(3-methyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 23.56 mg, 63% yield. Mp: 151-152 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.31 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.28 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.64 (s, 1H), 5.84 (d, *J* = 16.8 Hz, 1H), 4.30 (d, *J* = 16.8 Hz, 1H), 2.43 (s, 3H).

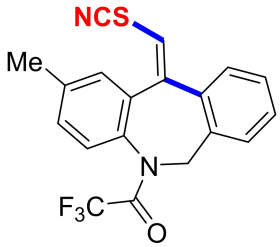
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (q, *J* = 36.1 Hz), 144.6, 141.1, 136.7, 133.9, 133.1, 132.5, 130.4, 129.4, 128.8, 128.3, 128.1, 128.0, 127.9, 116.2 (q, *J* = 287.2 Hz), 116.4, 110.2, 51.0, 21.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.43 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{17}F_3N_3OS$ $(M+NH_4)^+$ 392.1039, Measured 392.1040.

20. (Z)-2,2,2-trifluoro-1-(2-methyl-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 18.72 mg, 50% yield. Mp: 154-155 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.30 (m, 4H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.67 (s, 1H), 5.88 (d, *J* = 16.8 Hz, 1H), 4.32 (d, *J* = 16.8 Hz, 1H), 2.45 (s, 3H).

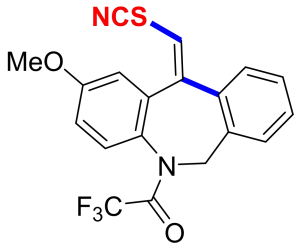
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (q, *J* = 36.0 Hz), 144.8, 140.3, 135.4, 134.2, 133.9, 133.2, 131.0, 129.4, 128.9, 128.8, 128.1, 128.0, 127.30 (q, *J* = 1.7 Hz), 116.3, 116.2 (q, *J* = 287.0 Hz), 110.2, 51.0, 21.2.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.43 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{17}F_3N_3OS$ $(M+NH_4)^+$ 392.1039, Measured 392.1043.

21. (Z)-2,2,2-trifluoro-1-(2-methoxy-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 26.15 mg, 67% yield. Mp: 132-133 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.84 (d, *J* = 2.8 Hz, 1H), 6.65 (s, 1H), 5.84 (d, *J* = 17.2 Hz, 1H), 4.30 (d, *J* = 16.8 Hz, 1H), 3.85 (s, 3H).

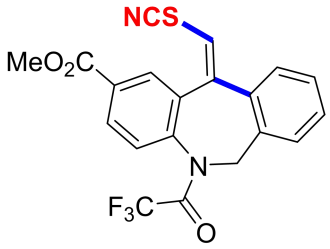
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4 (q, *J* = 35.9 Hz), 160.1, 144.6, 136.8, 133.7, 133.2, 129.4, 129.2, 129.0, 128.8, 128.1, 128.0, 116.5, 116.2 (q, *J* = 287.1 Hz), 115.0, 113.8, 110.1, 55.7, 51.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.47 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{17}F_3N_3O_2S$ $(M+NH_4)^+$ 408.0988, Measured 408.0991.

22. methyl(Z)-11-(thiocyanatomethylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5H-dibenzo[b,e]azepine-2-carboxylate

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 30.93 mg, 74% yield. Mp: 142-143 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 6.8 Hz, 1H), 6.72 (s, 1H), 5.88 (d, *J* = 16.8 Hz, 1H), 4.31 (d, *J* = 17.2 Hz, 1H), 3.96 (s, 3H).

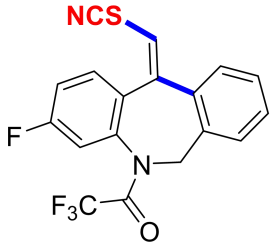
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 155.8 (q, *J* = 36.6 Hz), 143.6, 140.7, 136.0, 133.3, 132.6, 131.7, 131.6, 129.8, 129.7, 128.9, 128.2, 128.1, 127.8, 117.3, 116.0 (q, *J* = 288.5 Hz), 109.6, 52.7, 50.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.47 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{20}H_{13}F_3N_2NaO_3S$ $(M+Na)^+$ 441.0491, Measured 441.0491.

23. (Z)-2,2,2-trifluoro-1-(3-fluoro-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 27.22 mg, 72% yield. Mp: 158-159 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.24 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.69 (s, 1H), 5.84 (d, *J* = 16.8 Hz, 1H), 4.33 (d, *J* = 16.8 Hz, 1H).

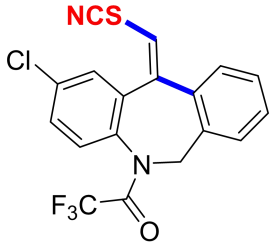
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 251.7 Hz), 155.8 (q, *J* = 36.3 Hz), 143.8, 138.3 (d, *J* = 10.0 Hz), 133.5, 132.7, 131.8 (d, *J* = 3.7 Hz), 130.1 (d, *J* = 9.2 Hz), 129.6, 128.9, 128.2 (d, *J* = 4.5 Hz), 117.2, 117.0, 116.0 (q, *J* = 286.9 Hz), 115.5 (d, *J* = 23.3 Hz), 109.8, 50.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.55 (s, 3F), -108.00 (s, 1F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}F_4N_2NaOS$ $(M+Na)^+$ 401.0342, Measured 401.0339.

24. (Z)-1-(2-chloro-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 32.37 mg, 82% yield. Mp: 151-152 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.40 –7.37 (m, 3H), 7.36 – 7.32(m, 2H), 7.16 (d, *J* = 6.4 Hz, 1H), 6.69 (s, 1H), 5.86 (d, *J* = 16.8 Hz, 1H), 4.30 (d, *J* = 16.8 Hz, 1H).

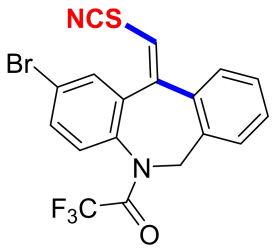
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (q, *J* = 36.3 Hz), 143.4, 137.2, 135.8, 135.4, 133.2, 132.8, 130.5, 129.7, 129.0, 128.6, 128.2, 128.1, 127.6, 117.4, 116.0 (q, *J* = 287.1 Hz), 109.5, 50.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.44 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}ClF_3N_2NaOS$ $(M+Na)^+$ 417.0047, Measured 417.0053.

25. (Z)-1-(2-bromo-11-(thiocyanatomethylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 30.28 mg, 70% yield. Mp: 167-168 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.69 (s, 1H), 5.85 (d, *J* = 16.8 Hz, 1H), 4.30 (d, *J* = 16.8 Hz, 1H).

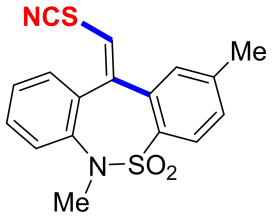
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9 (q, *J* = 36.3 Hz), 143.2, 137.5, 135.9, 133.5, 133.2, 132.8, 131.5, 129.8, 129.2, 129.0, 128.2, 128.1, 123.7, 117.4, 116.0 (q, *J* =286.8 Hz), 109.5, 50.7.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.43 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{10}BrF_3N_2NaOS$ $(M+Na)^+$ 460.9542, Measured 460.9542.

26. (E)-2,6-dimethyl-11-(thiocyanatomethylene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine 5,5-dioxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 19.86 mg, 58% yield. Mp: 193-194 ℃.



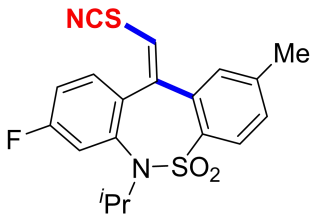
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 3.35 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 143.4, 137.8, 137.0, 135.5, 134.1, 131.5, 130.8, 130.6, 129.3, 129.2, 129.1, 128.1, 119.8, 109.6, 38.8, 21.3.

HRMS (ESI, m/z): Calculated for $C_{17}H_{18}N_3O_2S_2$ $(M+NH_4)^+$ 360.0835, Measured 360.0838.

27. (E)-8-fluoro-6-isopropyl-2-methyl-11-(thiocyanatomethylene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine 5,5-dioxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 20.57 mg, 53% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 6.0 Hz, 1H), 7.15 (t, *J* = 8.8 Hz, 1H), 6.74 (s, 1H), 4.63 – 4.56 (m, 1H), 2.44 (s, 3H), 1.42 – 1.24 (m, 6H).

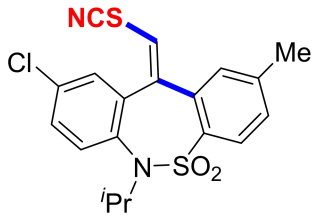
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, *J* = 247.6 Hz), 144.1, 143.0, 137.8, 135.3 (d, *J* = 10.3 Hz), 134.1 (d, *J* = 3.6 Hz), 133.7, 130.8, 130.3 (d, *J* = 9.4 Hz), 129.4, 127.4, 120.1, 119.9, 116.8 (d, *J* = 21.7 Hz), 109.4, 53.8, 26.8, 21.3, 14.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -107.87 (s, 1F).

HRMS (ESI, m/z): Calculated for $C_{19}H_{21}FN_3O_2S_2$ $(M+NH_4)^+$ 406.1054, Measured 406.1060.

28. (E)-9-chloro-6-isopropyl-2-methyl-11-(thiocyanatomethylene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine 5,5-dioxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 22.15 mg, 55% yield. Mp: 171-172 ℃.



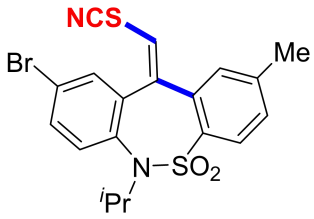
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 9.6 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 2H), 6.75 (s, 1H), 4.63 – 4.56 (m, 1H), 2.44 (s, 3H), 1.49 – 1.02 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 143.0, 139.6, 138.0, 135.3, 134.0, 133.4, 132.0, 131.0, 129.4, 128.9, 127.5, 120.2, 109.2, 53.6, 26.9, 21.3.

HRMS (ESI, m/z): Calculated for $C_{19}H_{21}ClN_3O_2S_2$ $(M+NH_4)^+$ 422.0758, Measured 422.0763.

29. (E)-9-bromo-6-isopropyl-2-methyl-11-(thiocyanatomethylene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine 5,5-dioxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 22.99 mg, 51% yield. Mp: 100-101 ℃.



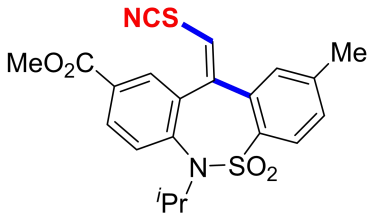
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 10.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 6.75 (s, 1H), 4.63 – 4.56 (m, 1H), 2.44 (s, 3H), 1.43 – 1.25 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 143.1, 139.9, 138.0, 134.3, 134.0, 133.4, 132.6, 131.9, 131.0, 129.4, 127.5, 123.2, 120.2, 109.2, 53.6, 21.3, 14.2.

HRMS (ESI, m/z): Calculated for $C_{19}H_{21}BrN_3O_2S_2$ $(M+NH_4)^+$ 466.0253, Measured 466.0256.

30. methyl (E)-6-isopropyl-2-methyl-11-(thiocyanatomethylene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine-9-carboxylate 5,5-dioxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 22.14 mg, 52% yield.



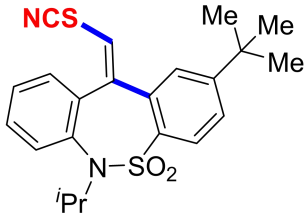
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.84 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 6.77 (s, 1H), 4.64 – 4.57 (m, 1H), 3.94 (s, 3H), 2.45 (s, 3H), 1.30 – 1.25 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 144.1, 143.2, 138.2, 137.9, 133.6, 132.7, 131.9, 131.0, 130.9, 130.4, 129.5, 127.4, 120.3, 109.3, 54.0, 52.6, 26.9, 21.3.

HRMS (ESI, m/z): Calculated for $C_{21}H_{24}N_3O_4S_2$ $(M+NH_4)^+$ 446.1203, Measured 446.1206.

31. (E)-2-(tert-butyl)-6-isopropyl-11-(thiocyanatomethylene)-6,11-dihydrodibenzo[c,f][1,2]thiazepine 5,5-dioxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 25.67 mg, 62% yield. Mp: 116-117 ℃.



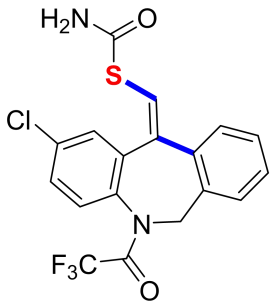
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.69 (s, 1H), 4.65 – 4.58 (m, 1H), 1.50 – 1.18 (m, 6H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 145.7, 138.3, 138.0, 133.7, 133.2, 132.8, 130.9, 129.4, 129.1, 127.4, 127.3, 125.6, 119.2, 109.8, 53.6, 35.1, 31.0, 22.6, 14.1.

HRMS (ESI, m/z): Calculated for $C_{22}H_{28}N_3O_2S_2$ $(M+NH_4)^+$ 430.1617, Measured 430.1619.

32. (Z)-S-((2-chloro-5-(2,2,2-trifluoroacetyl)-5,6-dihydro-11H-dibenzo[b,e]azepin-11-ylidene)methyl) carbamothioate

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1). 24.77 mg, 60% yield. Mp: 139-140 ℃.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.27 (m, 3H), 7.10 (t, *J* = 4.8 Hz, 1H), 5.83 (d, *J* = 16.8 Hz, 1H), 5.62 (s, 2H), 4.28 (d, *J* = 16.8 Hz, 1H).

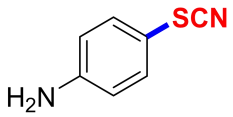
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 156.2 (q, *J* = 36.1 Hz), 140.4, 135.5, 135.3, 135.2, 134.9, 132.2, 129.5, 129.4, 129.3, 128.6, 128.4, 128.0, 127.8, 124.5, 116.2 (q, *J* = 287.3 Hz), 51.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -67.36 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{18}H_{12}ClF_3N_2NaO_2S$ $(M+Na)^+$ 435.0152, Measured 435.0150.

33. 4-thiocyanatoaniline

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). 19.52 mg, 65% yield.



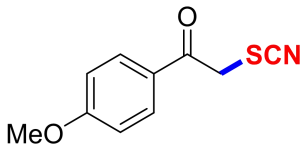
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 148.8, 134.4, 116.1, 112.2, 109.7.

HRMS (ESI, m/z): Calculated for $C_{14}H_{12}N_4NaS_2$ $(2M+Na)^+$ 323.0395, Measured 323.0396.

34. 1-(4-methoxyphenyl)-2-thiocyanatoethan-1-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 124.35 mg, 60% yield.



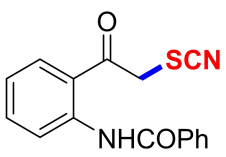
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 9.2 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.71 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.1, 164.8, 130.9, 127.0, 114.3, 112.0, 55.6, 42.8

HRMS (ESI, m/z): Calculated for $C_{20}H_{18}N_2NaO_4S_2$ $(2M+Na)^+$ 437.0600, Measured 437.0596.

35. *N*-(2-(2-thiocyanatoacetyl)phenyl)benzamide

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 7/1). 18.08 mg, 61% yield.



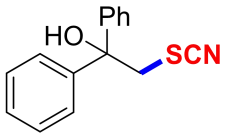
^{1}H NMR (400 MHz, $CDCl_3$): δ 12.10 (s, 1H), 9.04 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 2H), 7.84 (d, *J* = 6.4 Hz, 1H), 7.72 (t, *J* = 8.8 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.21 (t, *J* = 8.4 Hz, 1H), 4.87 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 194.6, 166.2, 142.2, 137.1, 134.3, 132.4, 130.8, 129.0, 127.5, 122.9, 121.5, 119.4, 111.4, 44.0.

HRMS (ESI, m/z): Calculated for $C_{32}H_{24}N_4NaO_4S_2$ $(2M+Na)^+$ 615.1131, Measured 615.1125.

36. 1,1-diphenyl-2-thiocyanatoethan-1-ol

A white liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1). 173.62 mg, 68% yield.



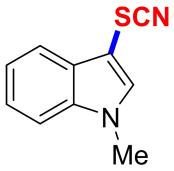
^{1}H NMR (400 MHz,$CDCl_3$): δ 7.43 – 7.37 (m, 6H), 7.33 – 7.31 (m, 4H), 4.01 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 129.1, 129.0, 126.0, 111.1, 72.0, 46.5.

HRMS (ESI, m/z): Calculated for $C_{30}H_{26}KN_2O_2S_2$ $(2M+K)^+$ 549.1067, Measured 549.1062.

37. 1-methyl-3-thiocyanato-1H-indole

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate =10/1). 55.91 mg, 99% yield.



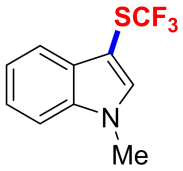
^{1}H NMR (400 MHz,$CDCl_3$): δ 7.76 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.27 (m, 4H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 135.0, 128.3, 123.3, 121.4, 118.7, 111.8, 110.1, 89.6, 33.2.

HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_4NaS_2$ $(2M+Na)^+$ 399.0708, Measured 399.0713.

38. 1-methyl-3-((trifluoromethyl)thio)-1H-indole

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate =20/1). 20.81 mg, 90% yield.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.29 – 7.16 (m, 4H), 3.69 (s, 3H).

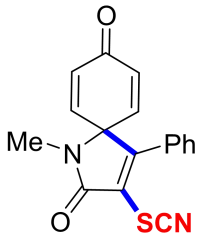
^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.9, 130.2, 129.4 (q, *J* = 308.3 Hz), 122.9, 121.29, 119.3, 109.9, 92.8, 33.1.

^{19}F NMR (565 MHz, $CDCl_3$): δ -44.83 (s, 3F).

HRMS (ESI, m/z): Calculated for $C_{20}H_{20}F_6N_3S_2$ $(2M+NH_4)^+$ 480.0997, Measured 480.0993.

39. 1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate =3/1). 20.66 mg, 67% yield.



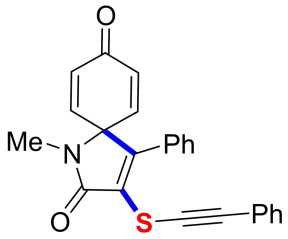
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 6.4 Hz, 2H), 6.53 (s, 4H), 2.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 164.9, 156.9, 143.0, 133.9, 131.1, 129.0, 128.8, 127.7, 122.3, 106.2, 68.3, 26.5

HRMS (ESI, m/z): Calculated for $C_{17}H_{12}N_2NaO_2S$ $(M+Na)^+$ 331.0512, Measured 331.0508.

40. 1-methyl-4-phenyl-3-((phenylethynyl)thio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate =5/1). 32.98 mg, 86% yield.



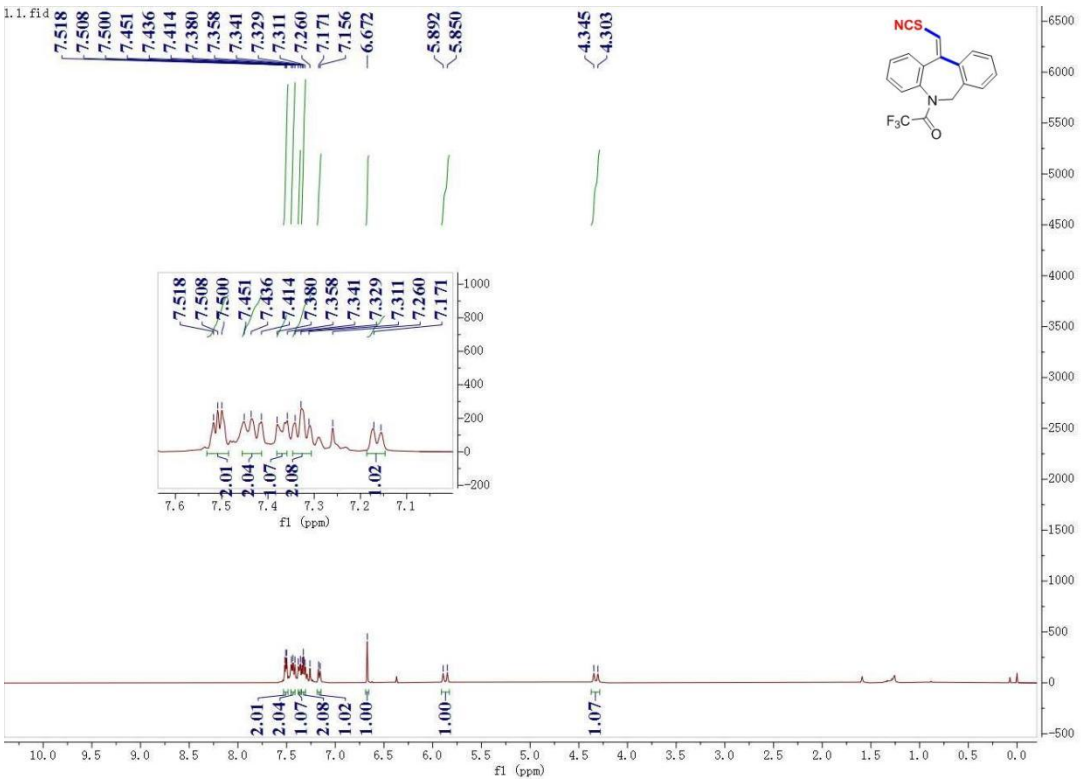
^{1}H NMR (400 MHz,$CDCl_3$): δ 7.34 – 7.31 (m, 2H), 7.30 – 7.28 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 6.4 Hz, 2H), 6.53 (d, *J* = 10.0 Hz, 2H), 6.46 (d, *J* = 10.0 Hz, 2H), 2.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 166.8, 148.9, 144.7, 133.3, 131.6, 129.8, 129.7, 129.0, 128.6, 128.4, 128.2, 127.9, 122.1, 97.7, 71.7, 68.3, 26.2.

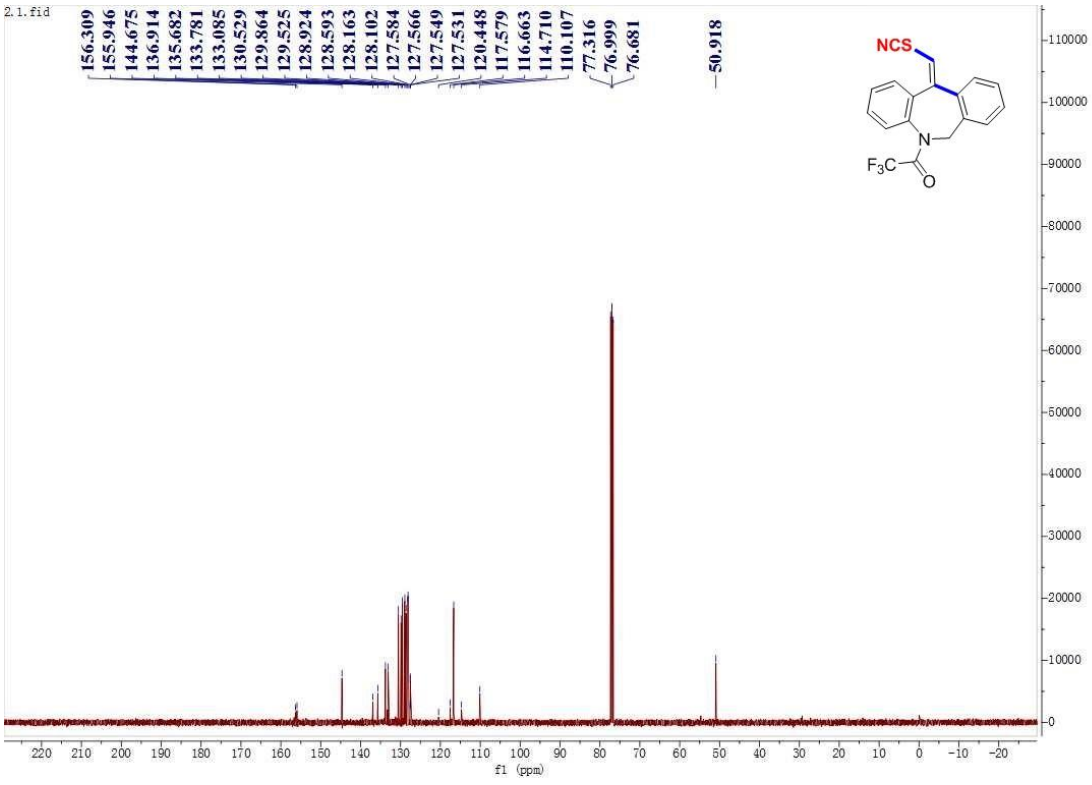
HRMS (ESI, m/z): Calculated for $C_{24}H_{17}KNO_2S$ $(M+K)^+$ 422.0611, Measured 422.0606.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

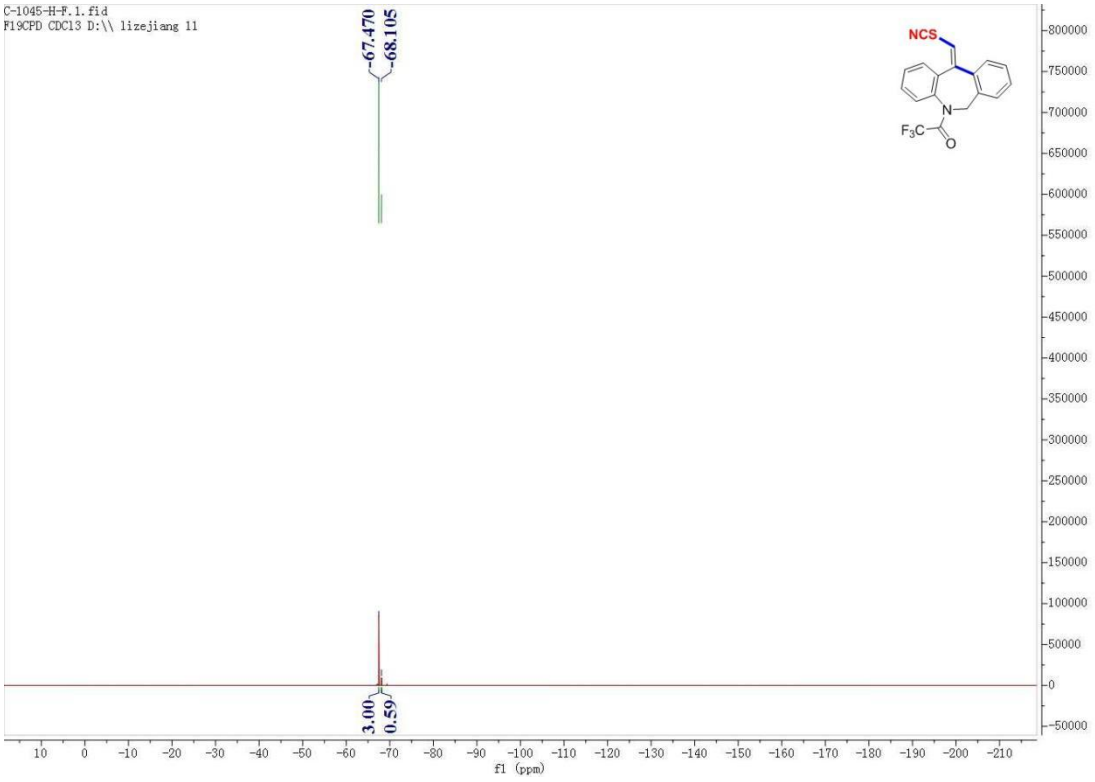
1-^{1}H NMR



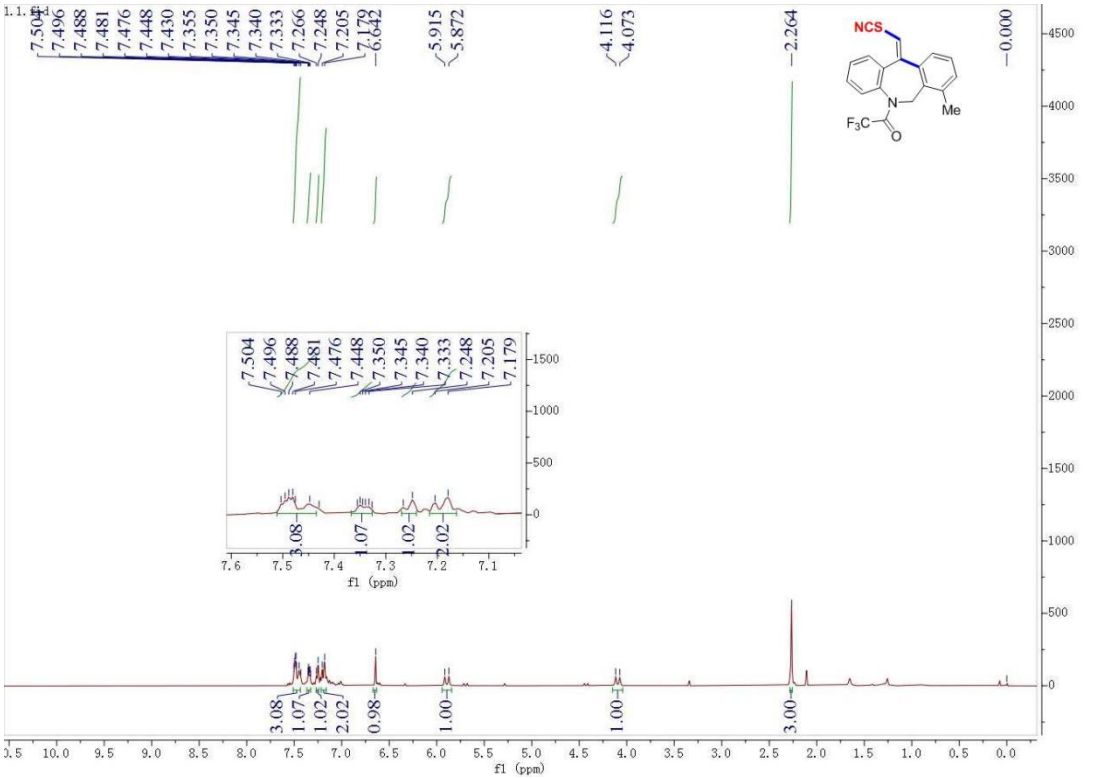
1-^{13}C NMR



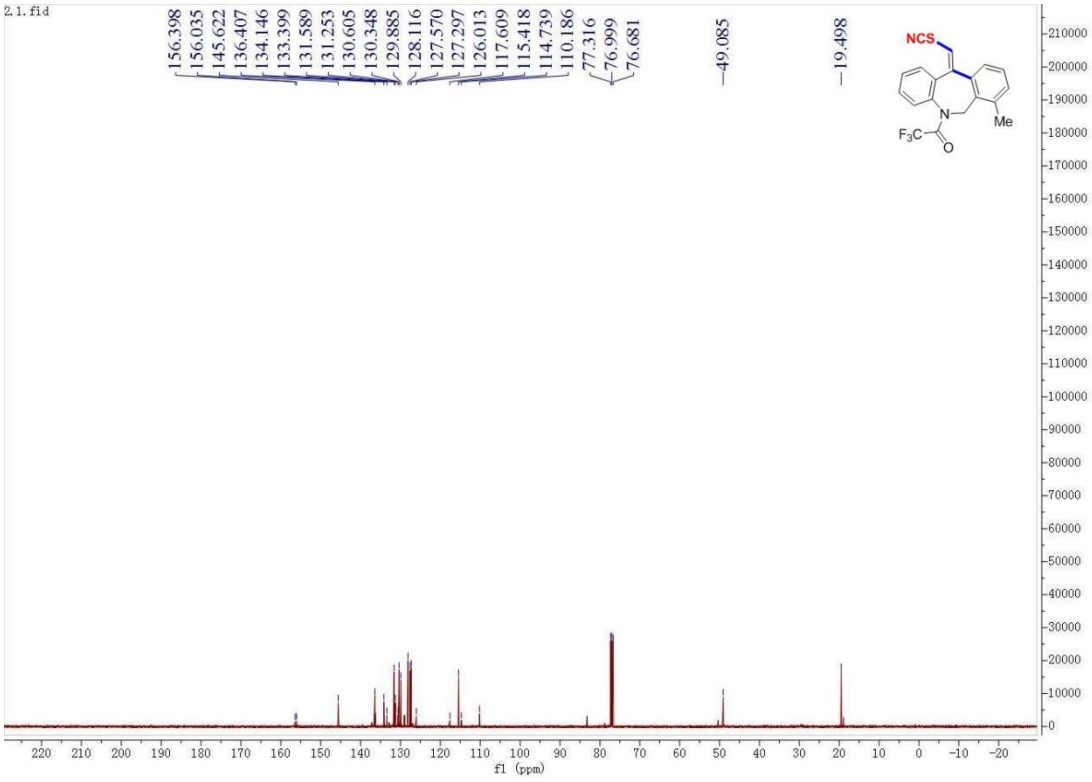
1-^{19}F NMR



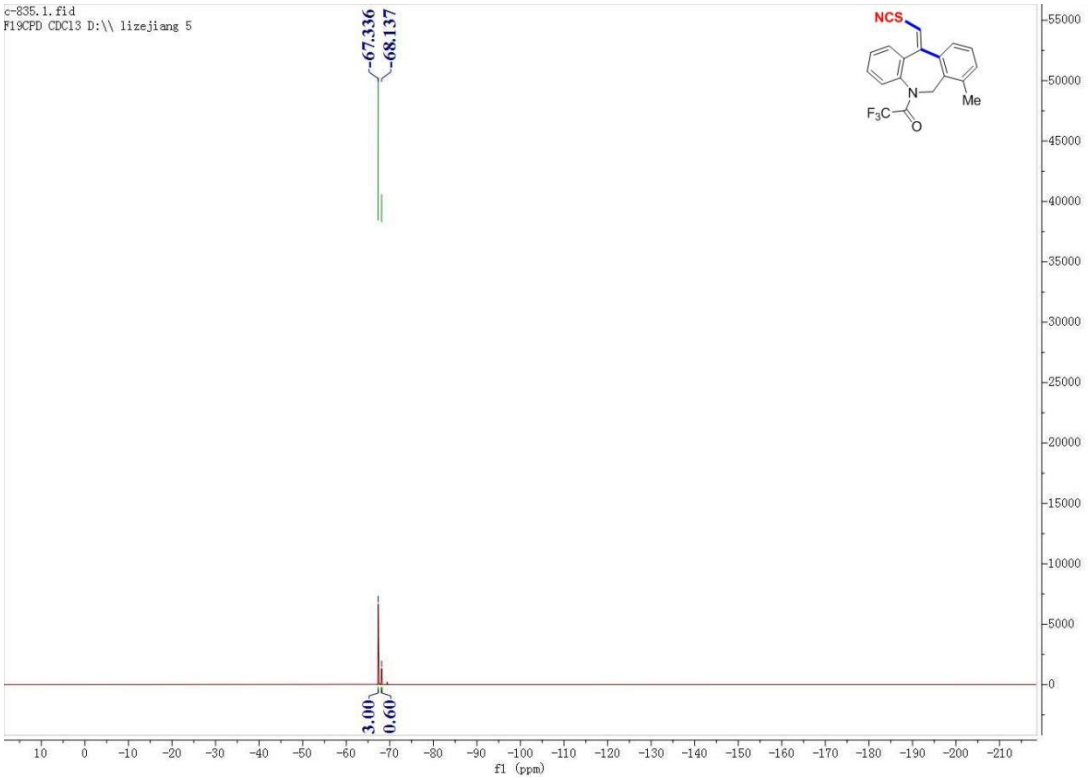
2-^{1}H NMR



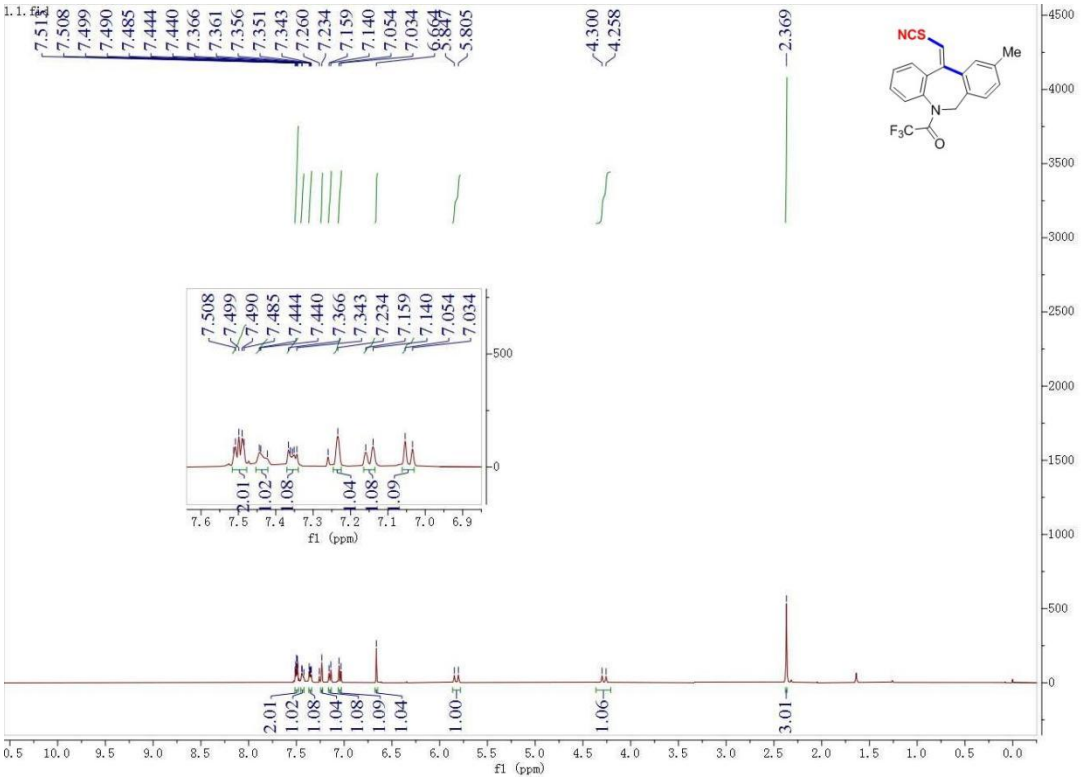
2-^{13}C NMR



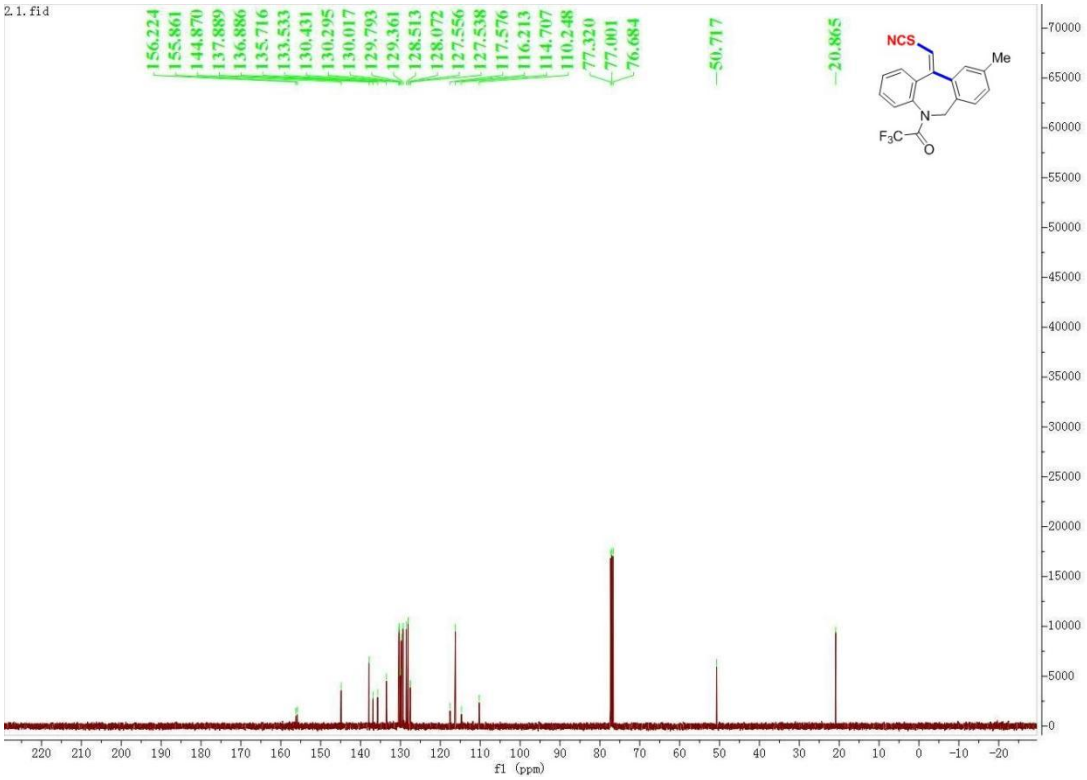
2-^{19}F NMR



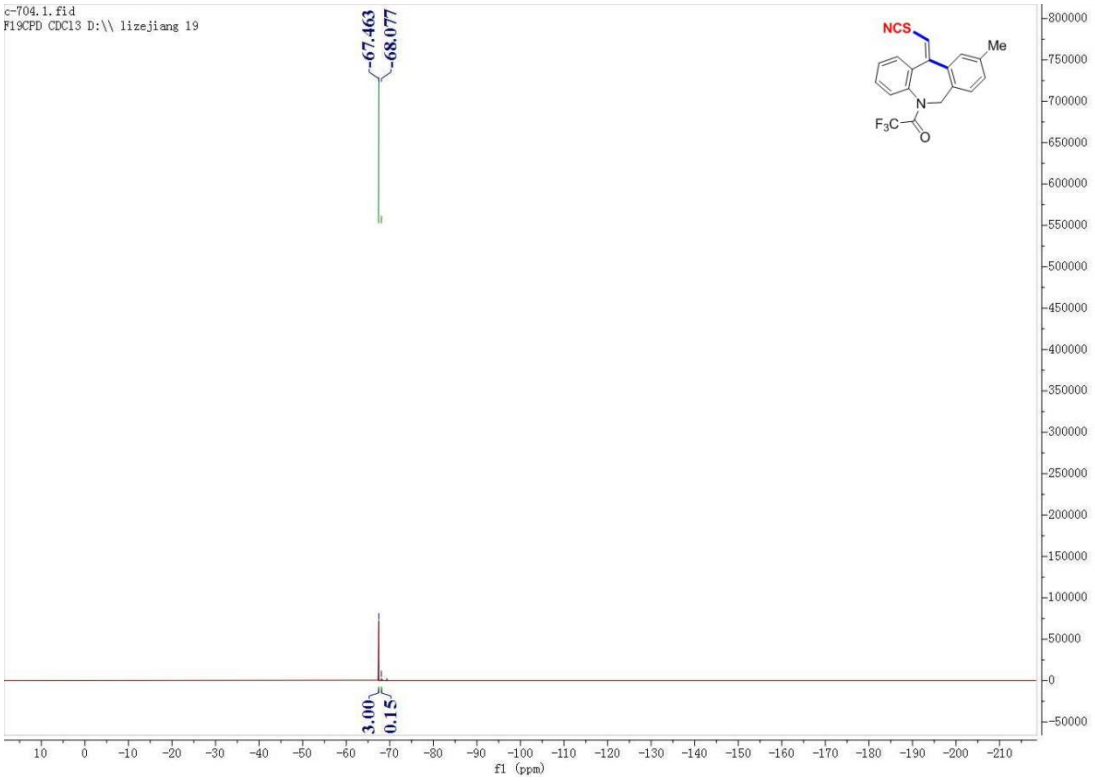
3-^{1}H NMR



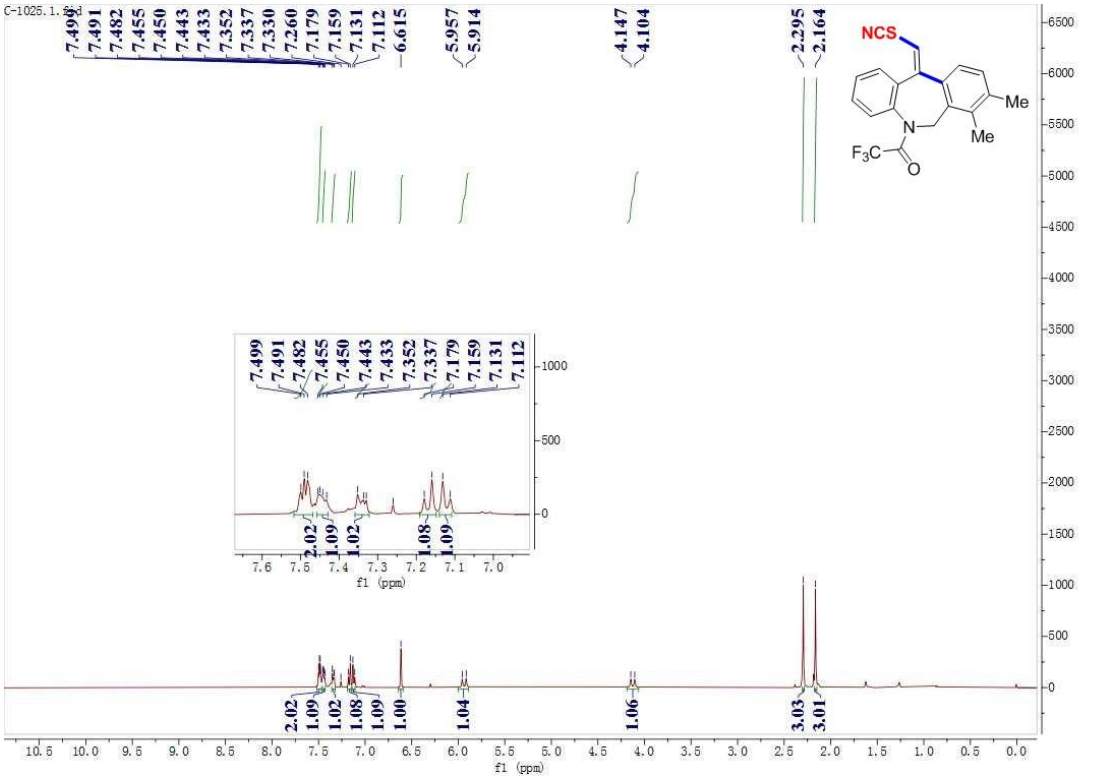
3-^{13}C NMR



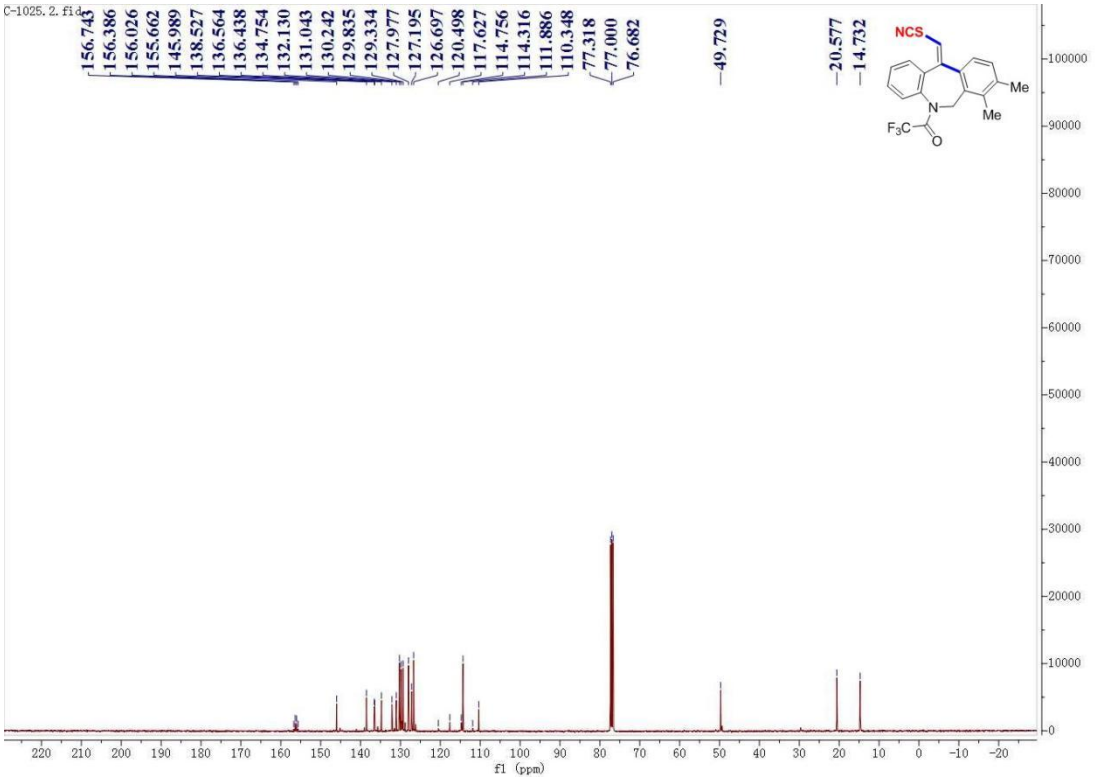
3-^{19}F NMR



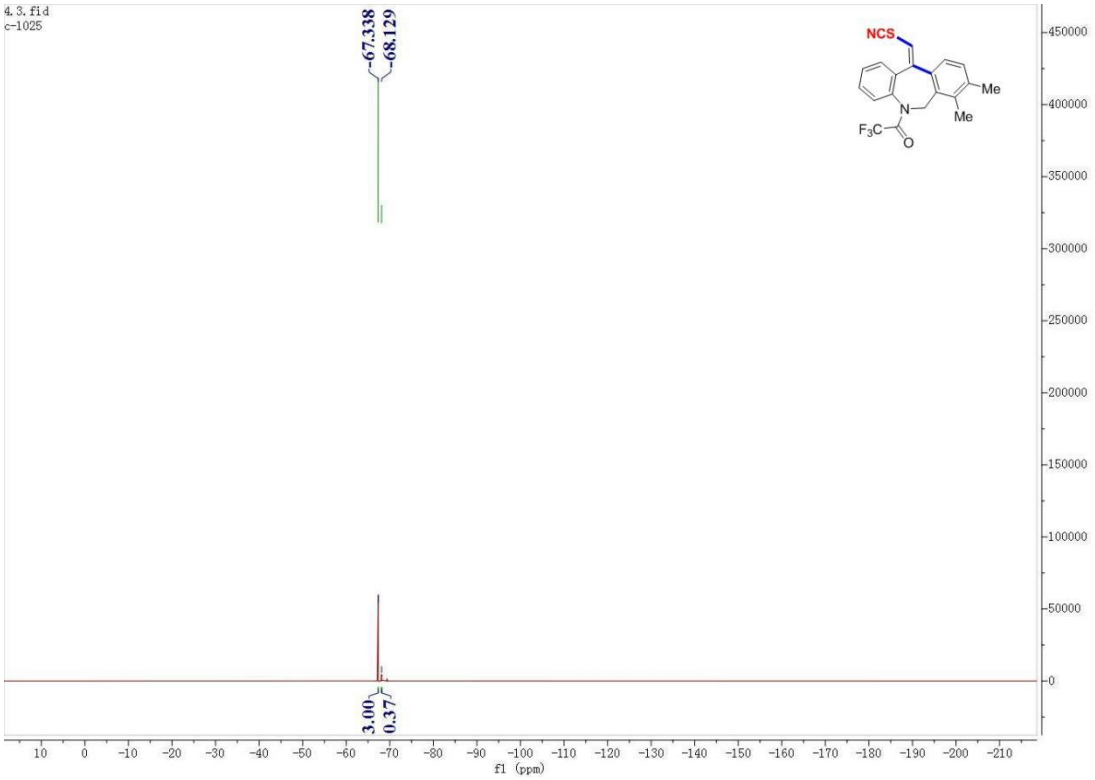
4-^{1}H NMR



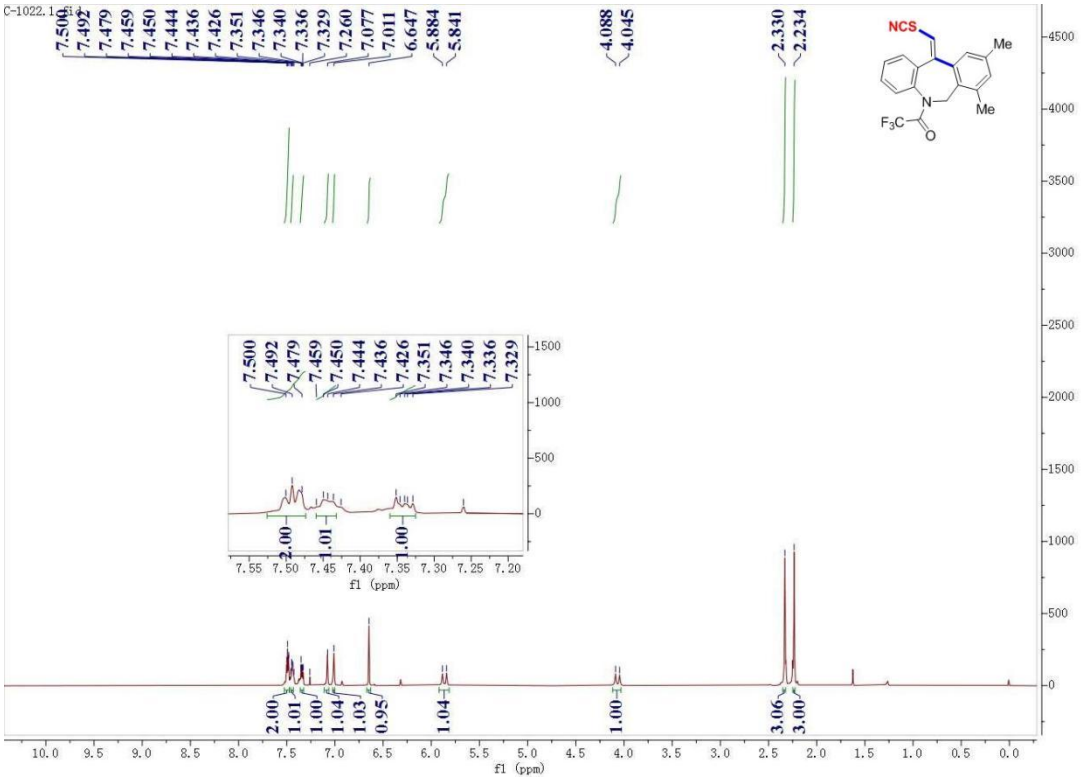
4-^{13}C NMR



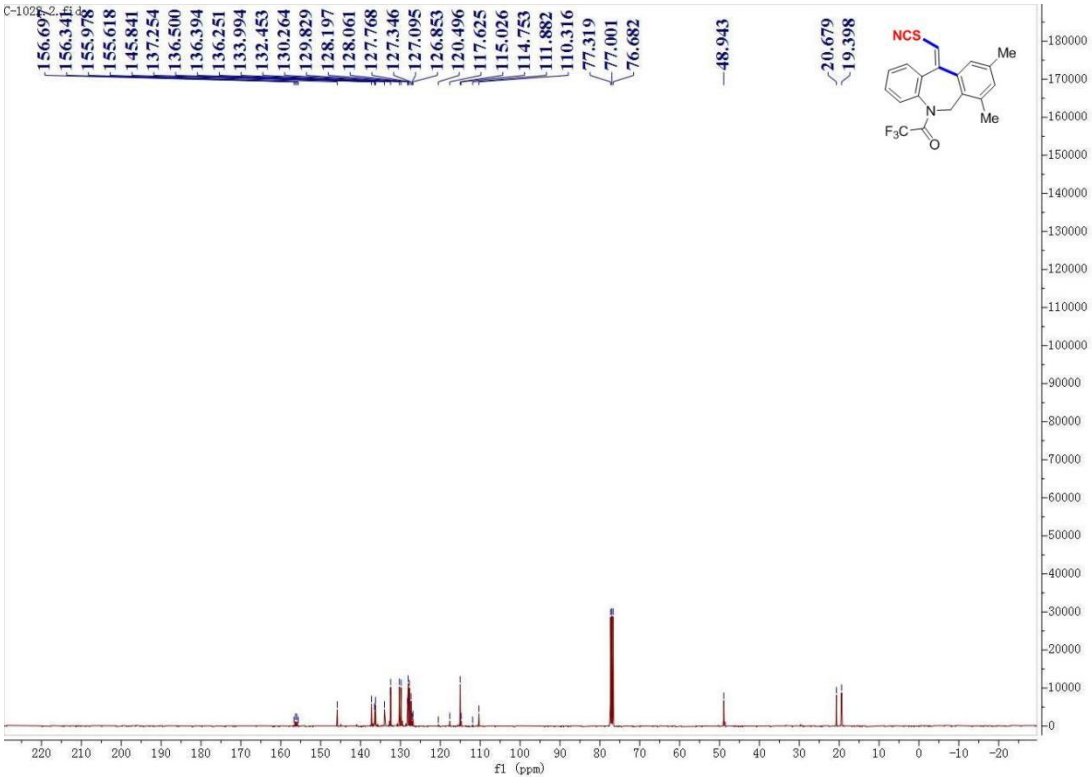
4-^{19}F NMR



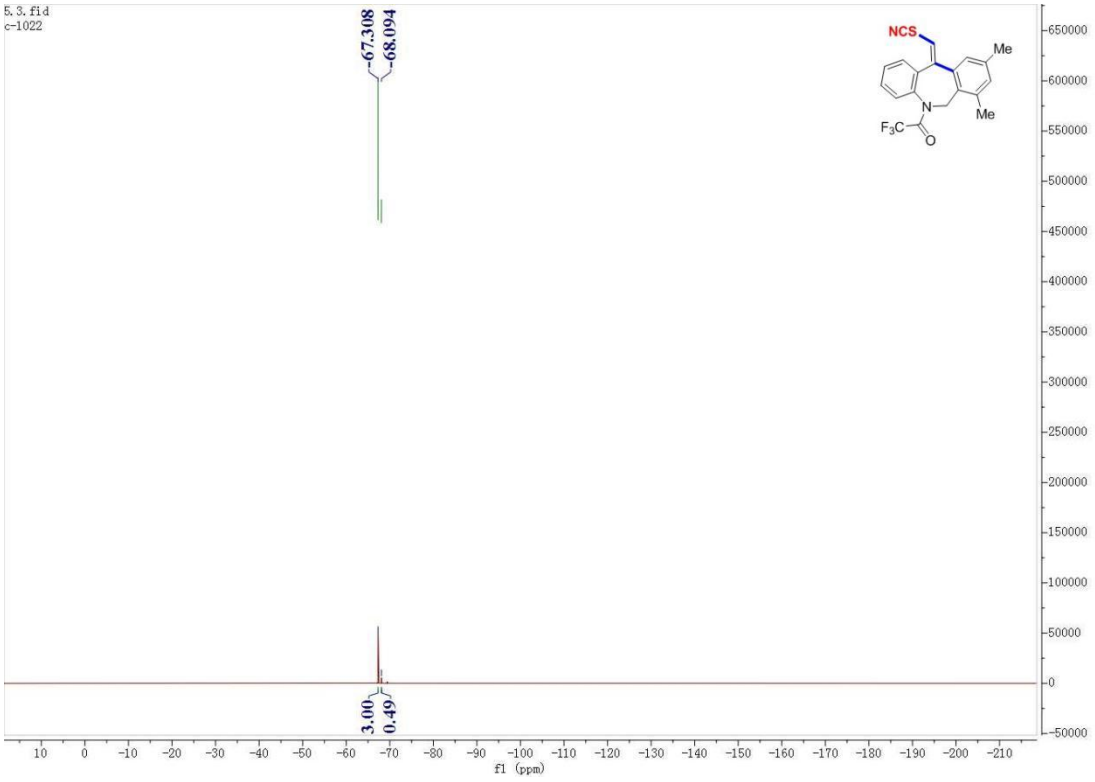
5-^{1}H NMR



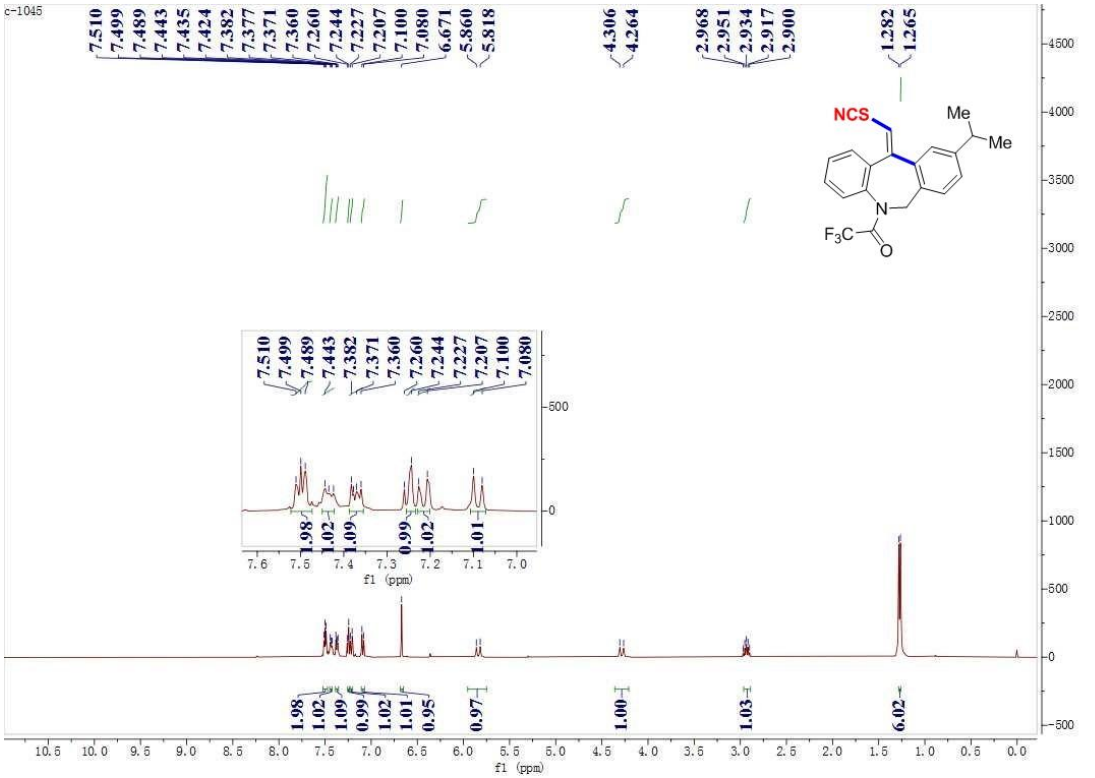
5-^{13}C NMR



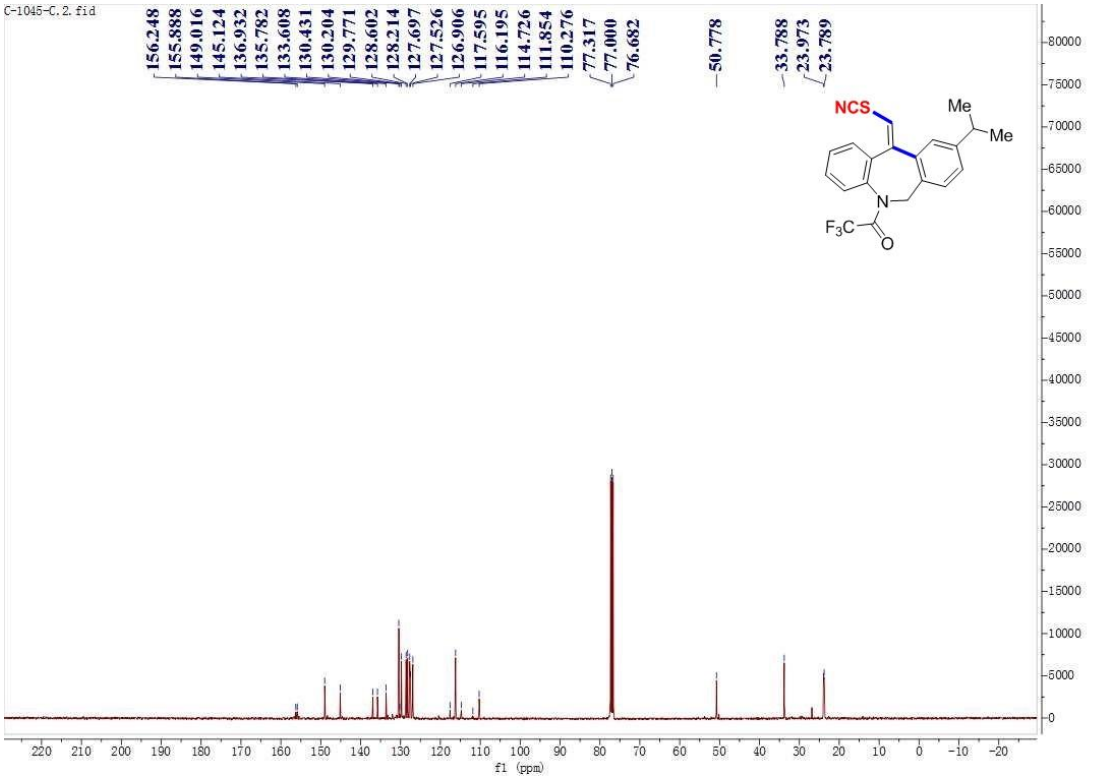
5-^{19}F NMR



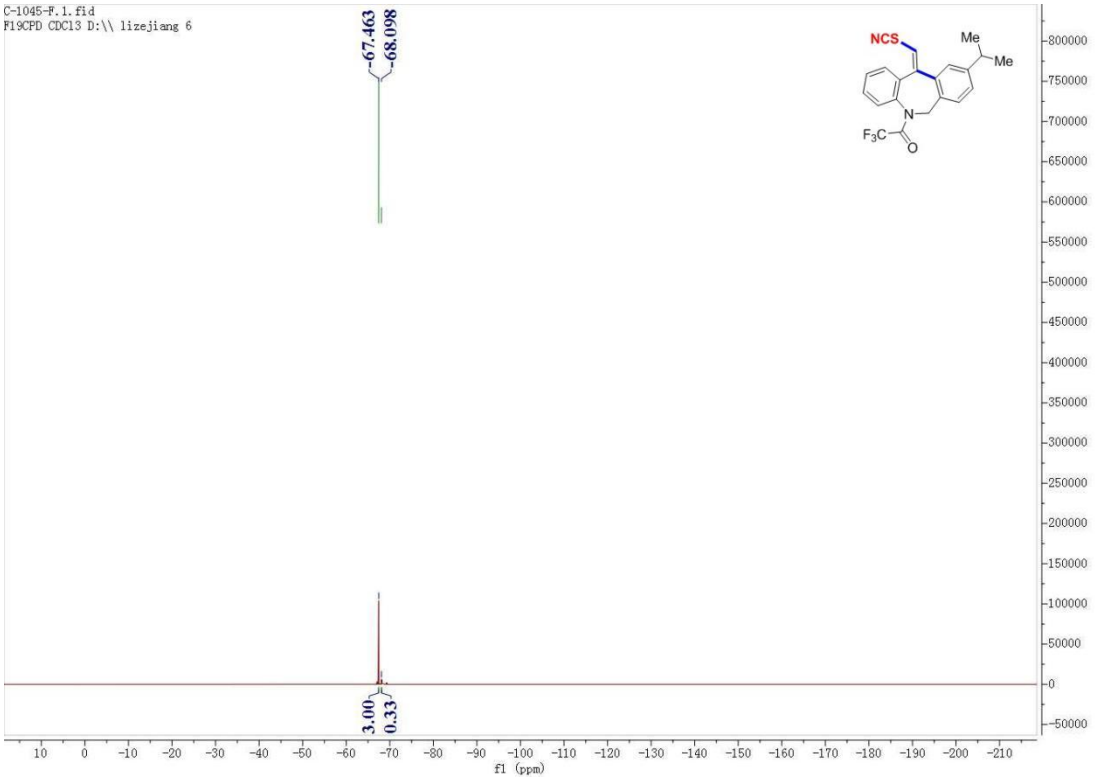
6-^{1}H NMR



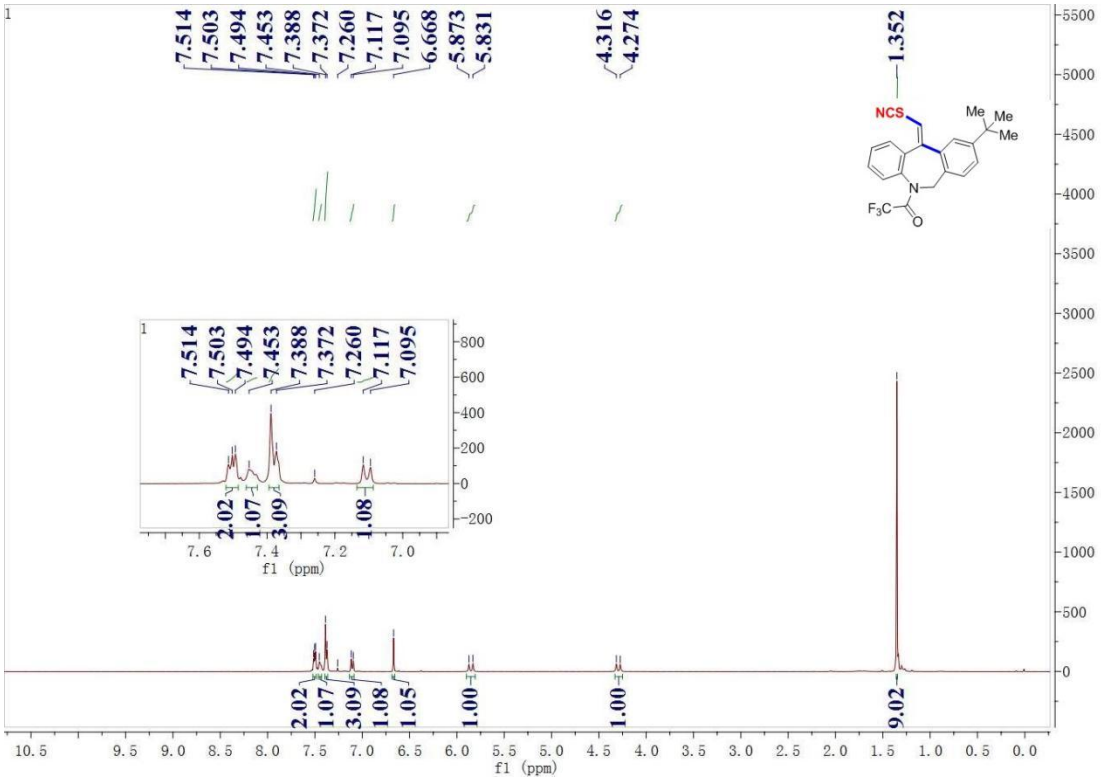
6-^{13}C NMR



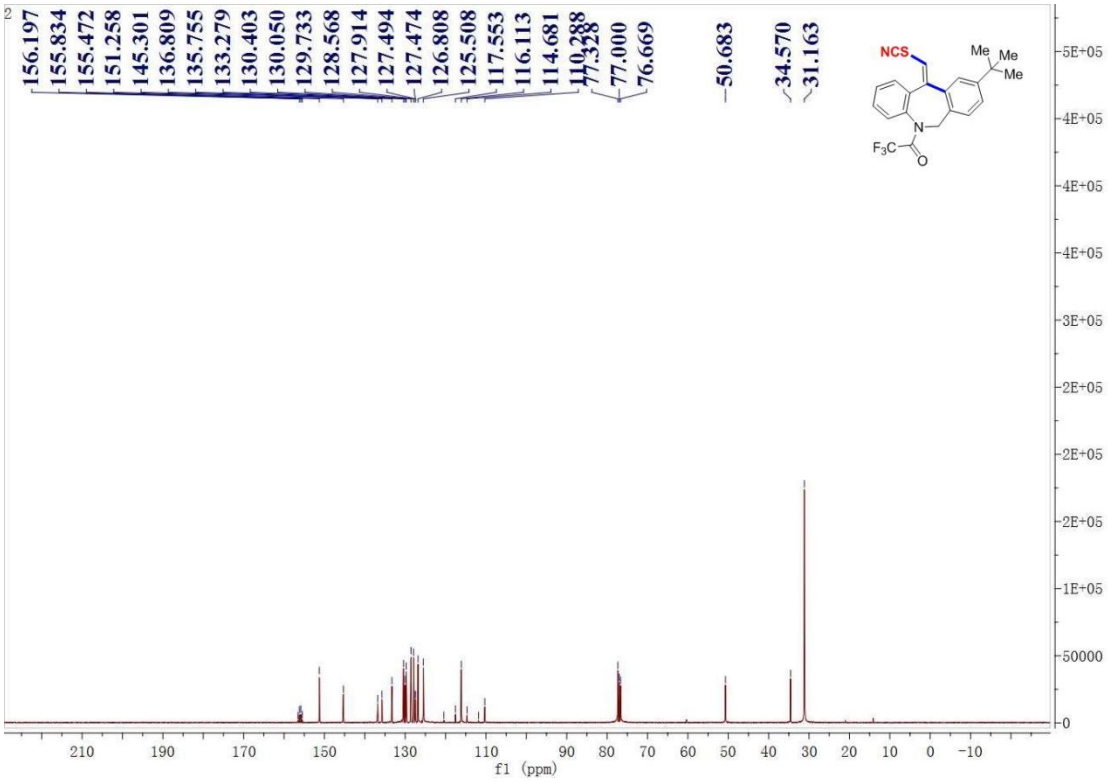
6-^{19}F NMR



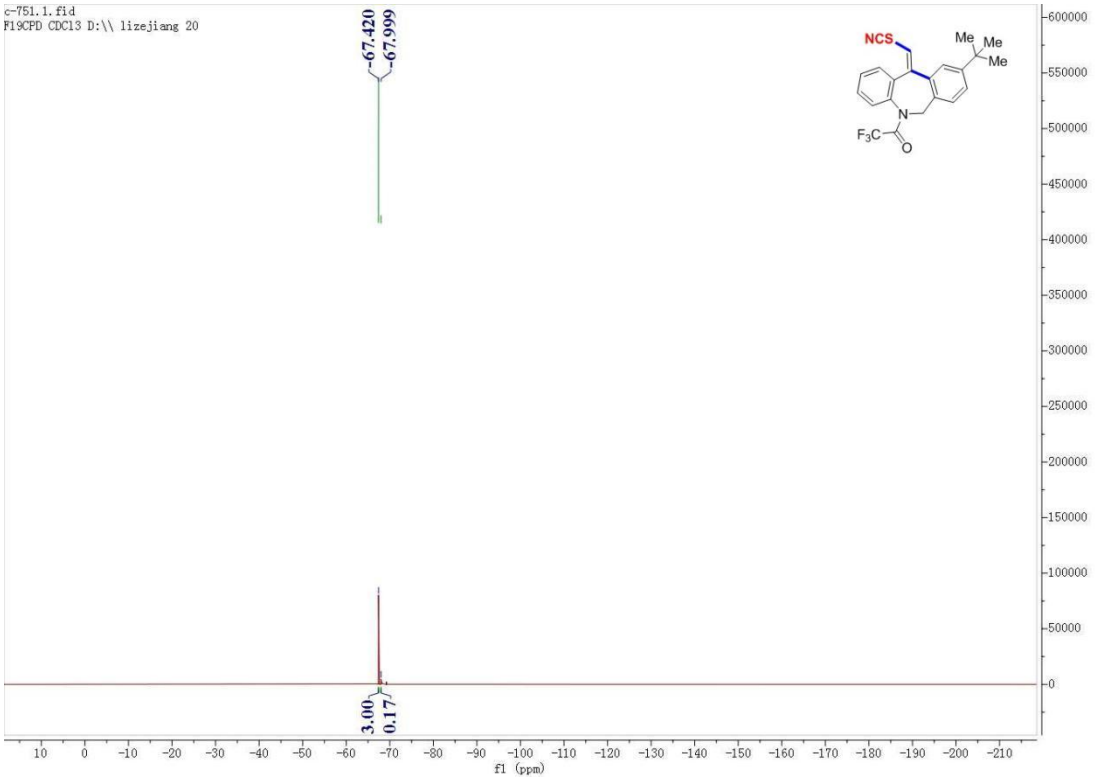
7-^{1}H NMR



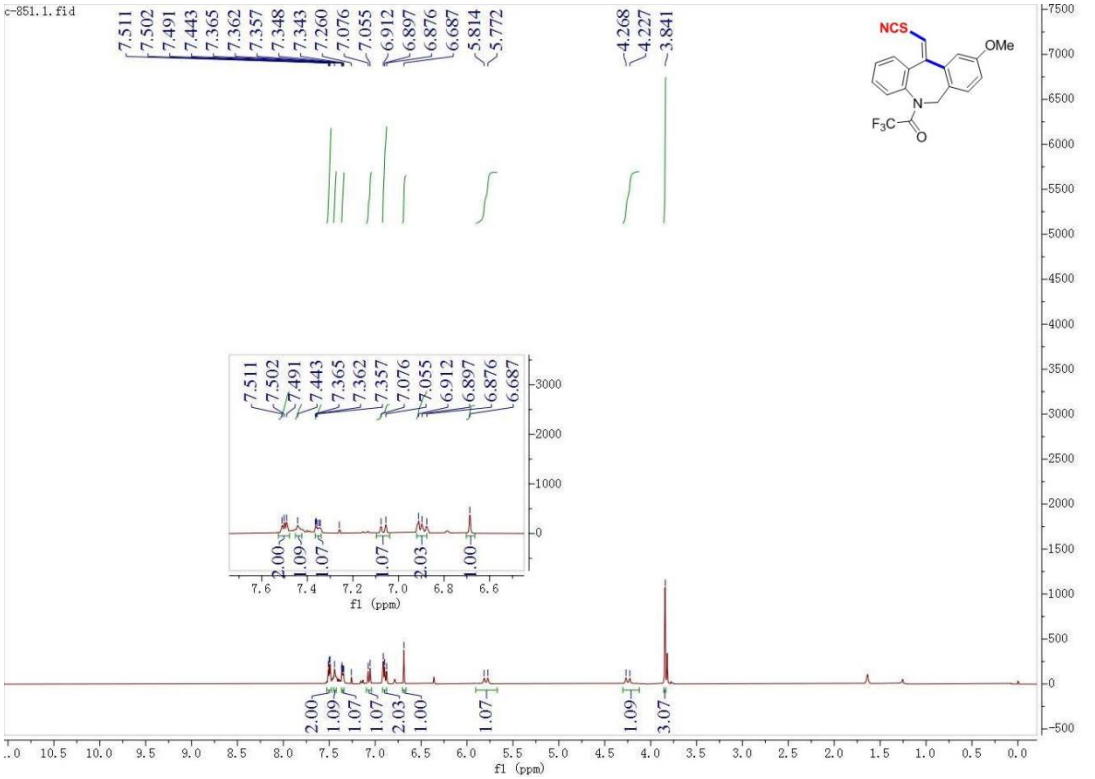
7-^{13}C NMR



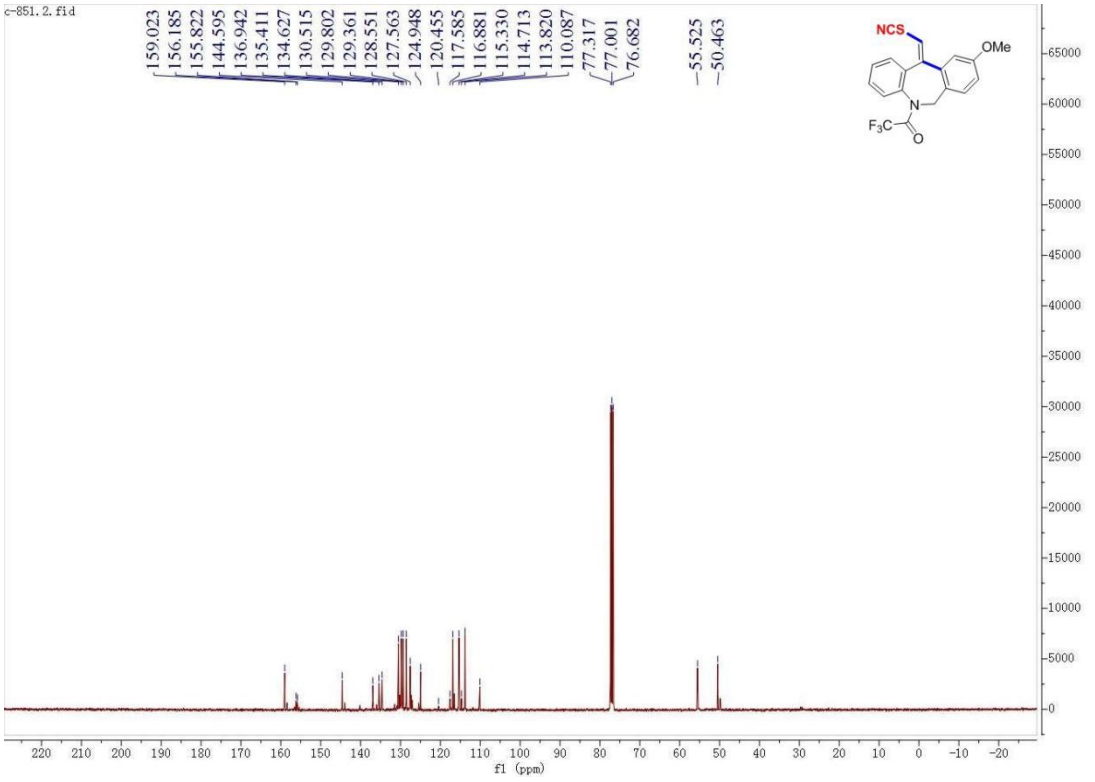
7-^{19}F NMR



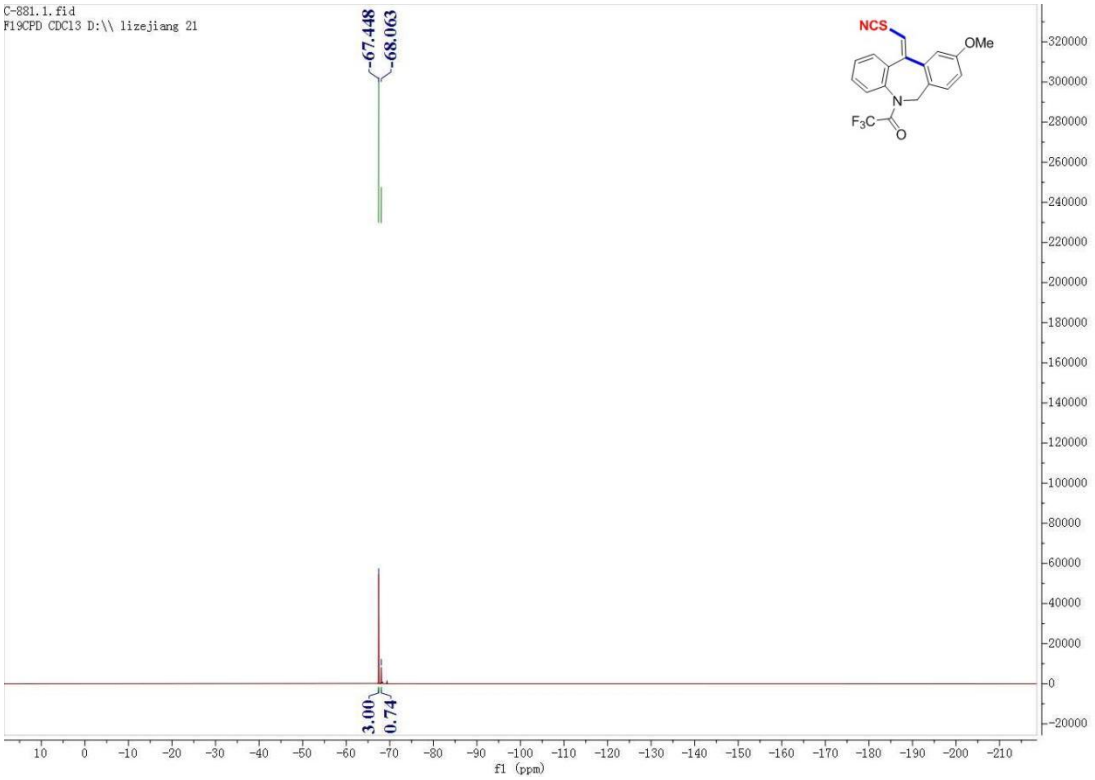
8-^{1}H NMR



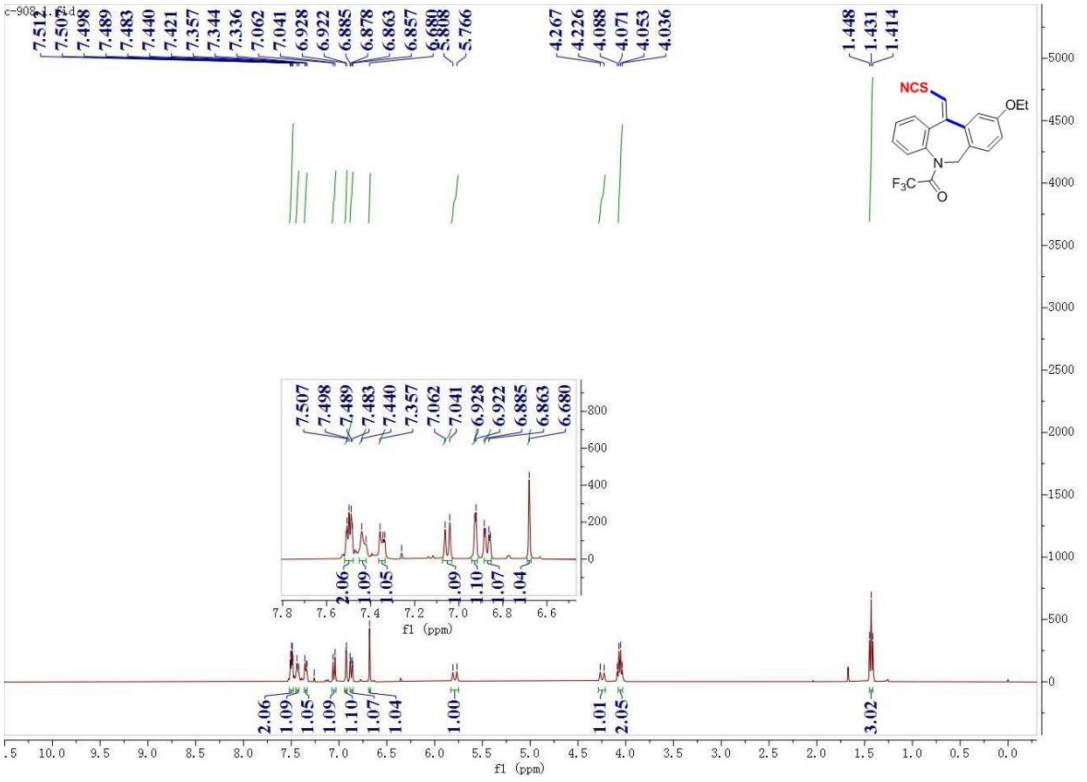
8-^{13}C NMR



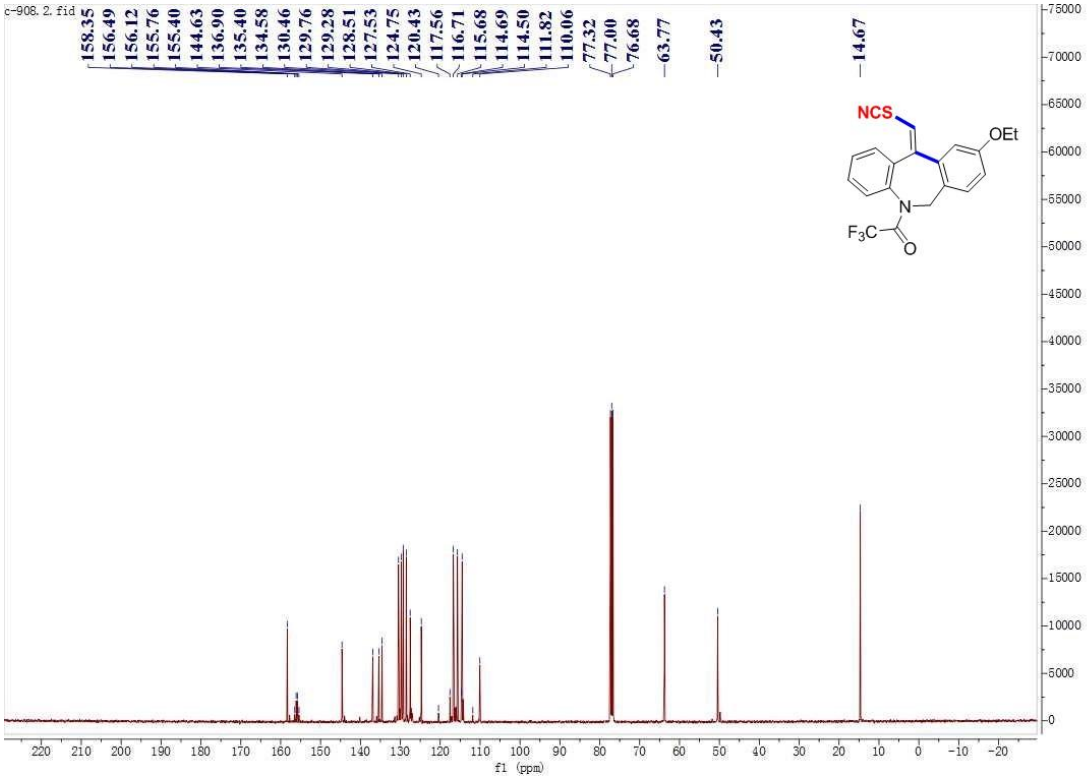
8-^{19}F NMR



9-^{1}H NMR



9-^{13}C NMR



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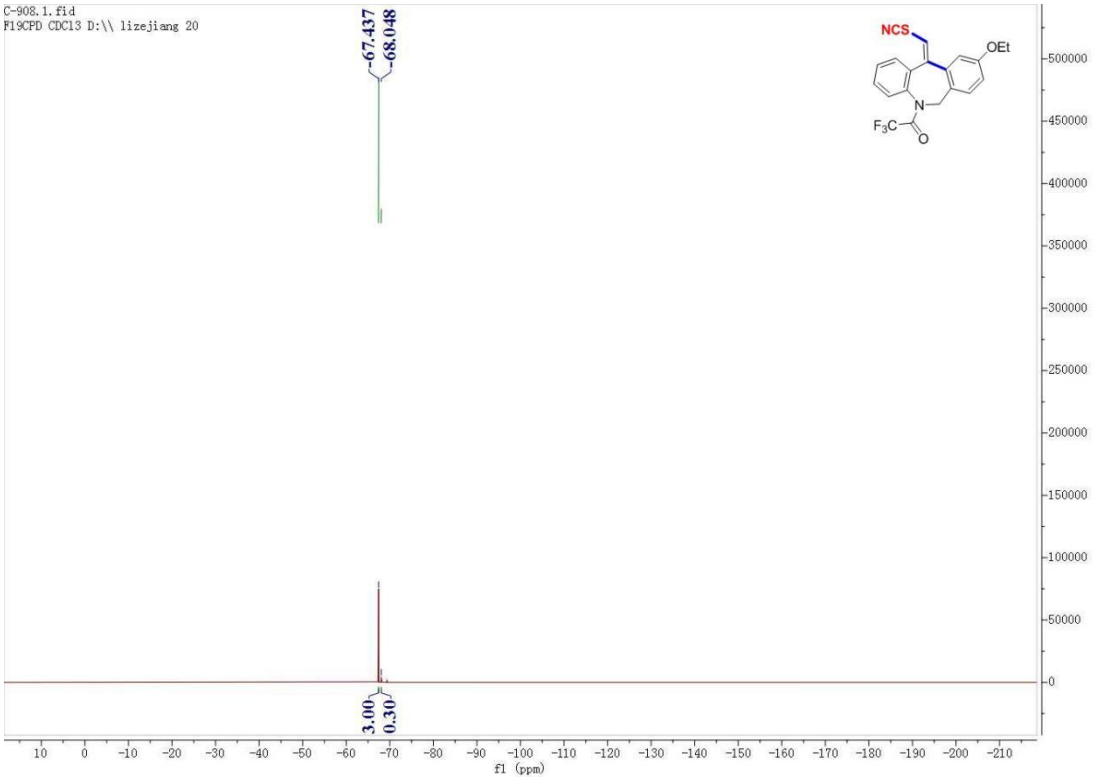
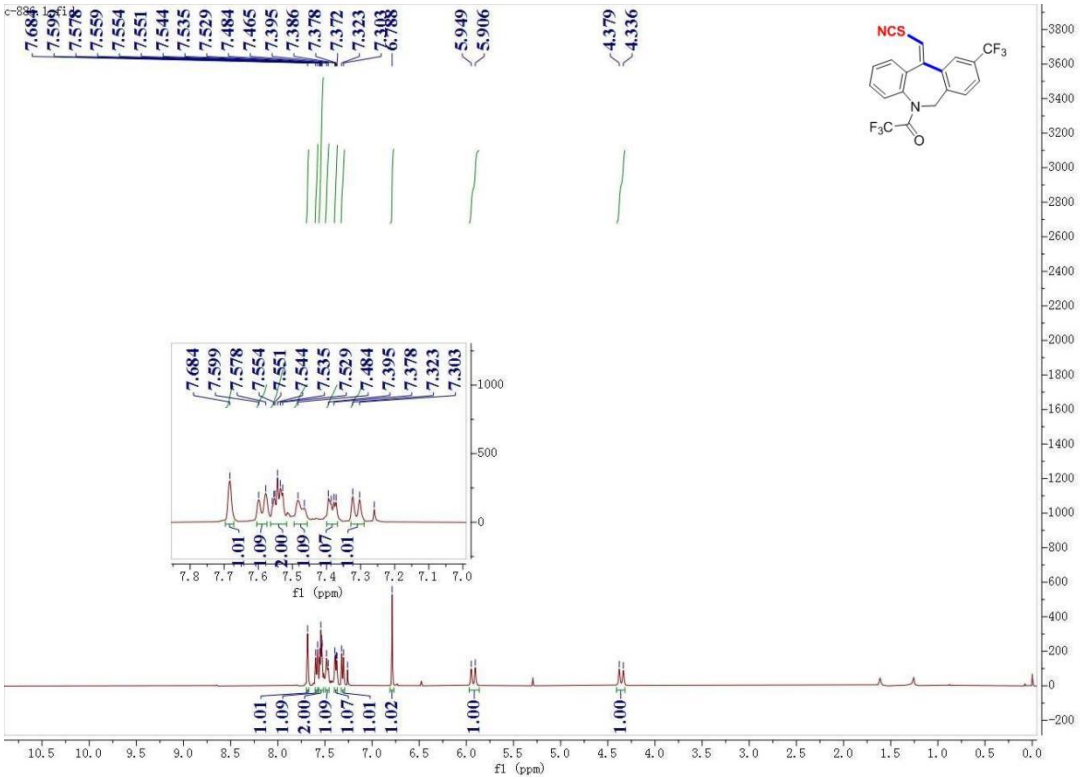
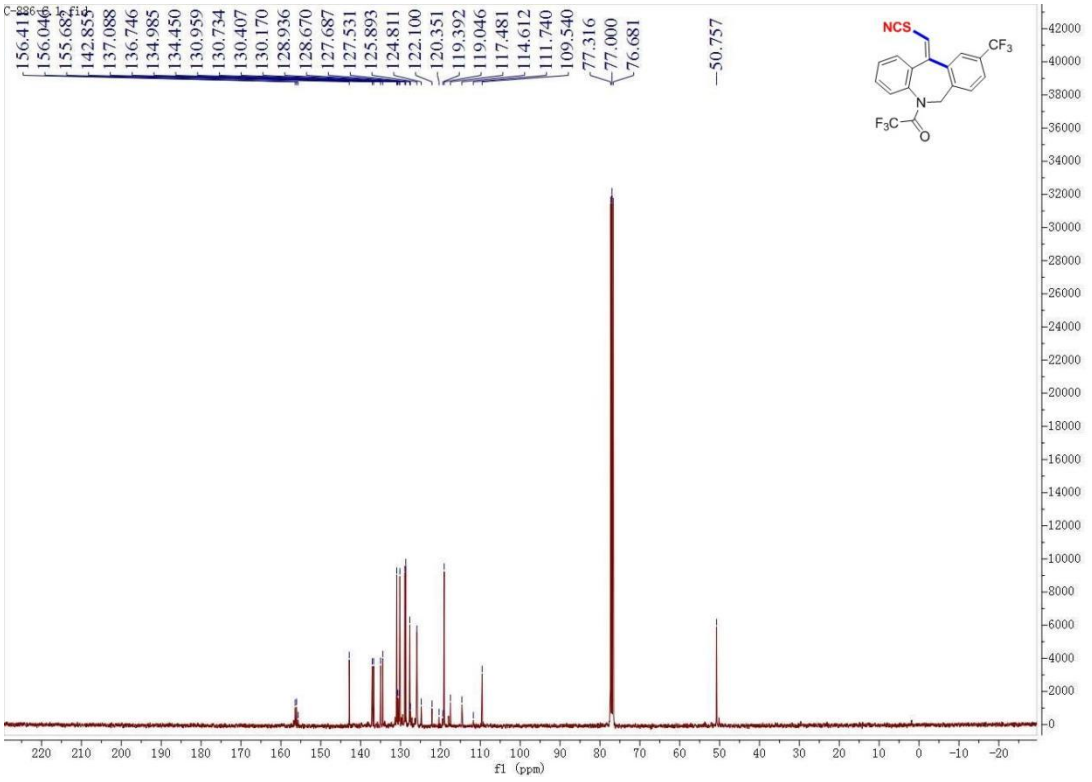


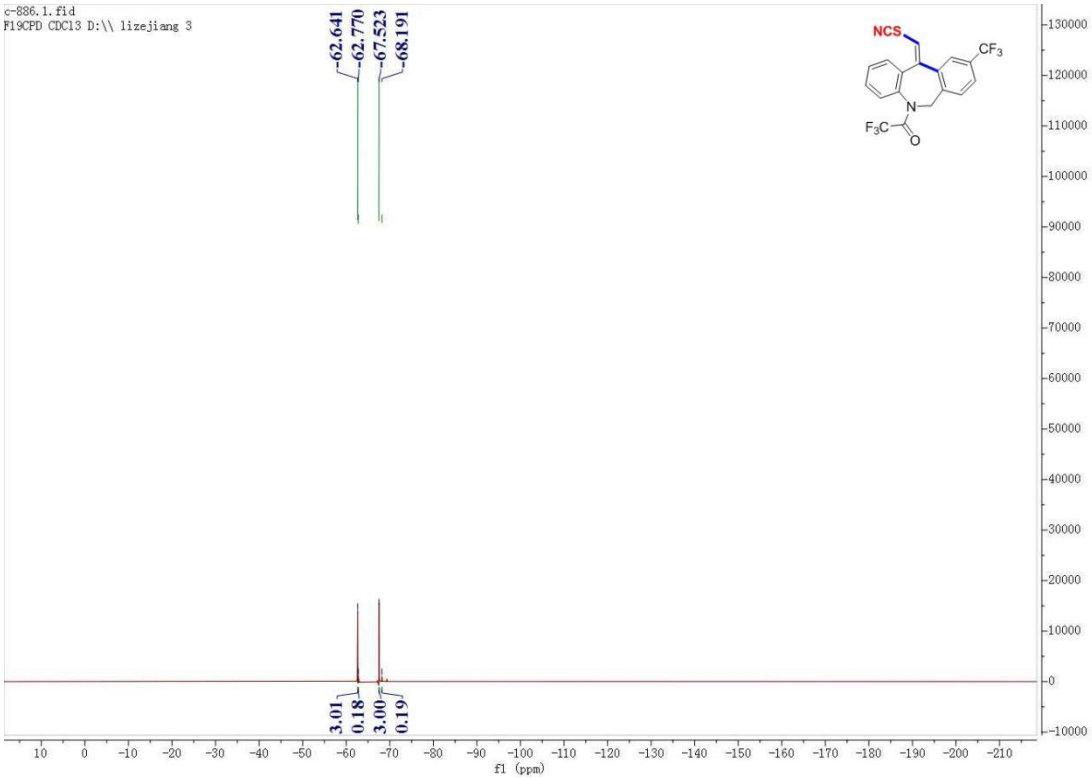
10-^{1}H NMR



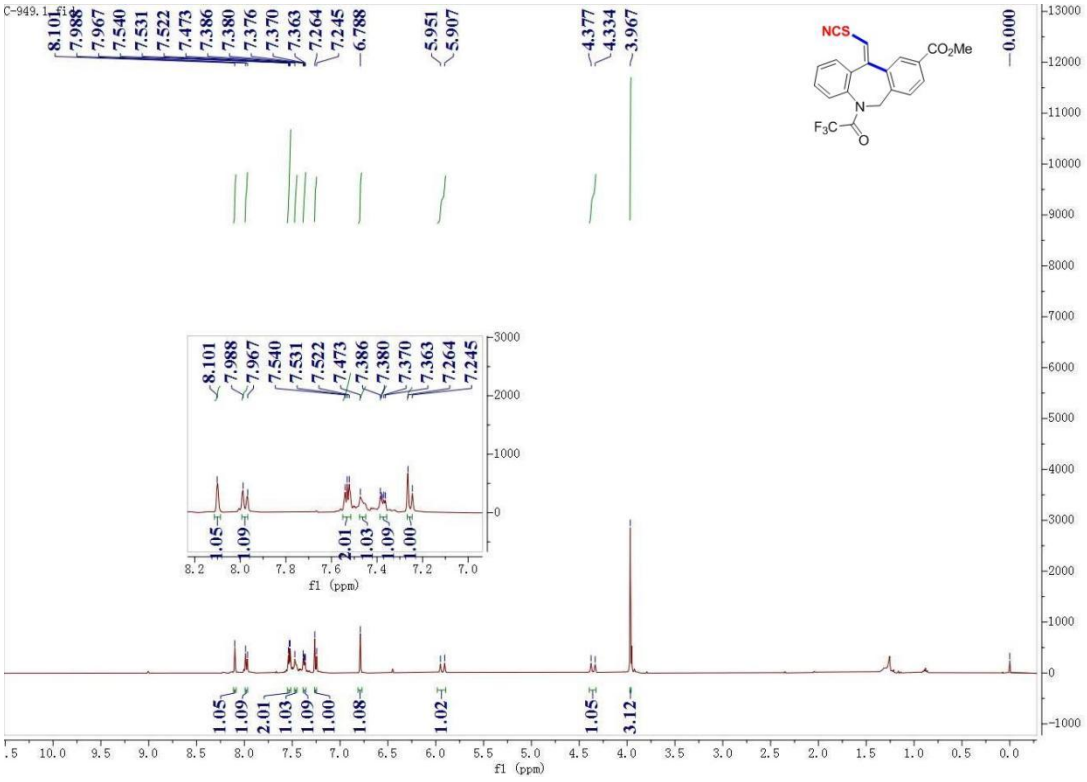
10-^{13}C NMR



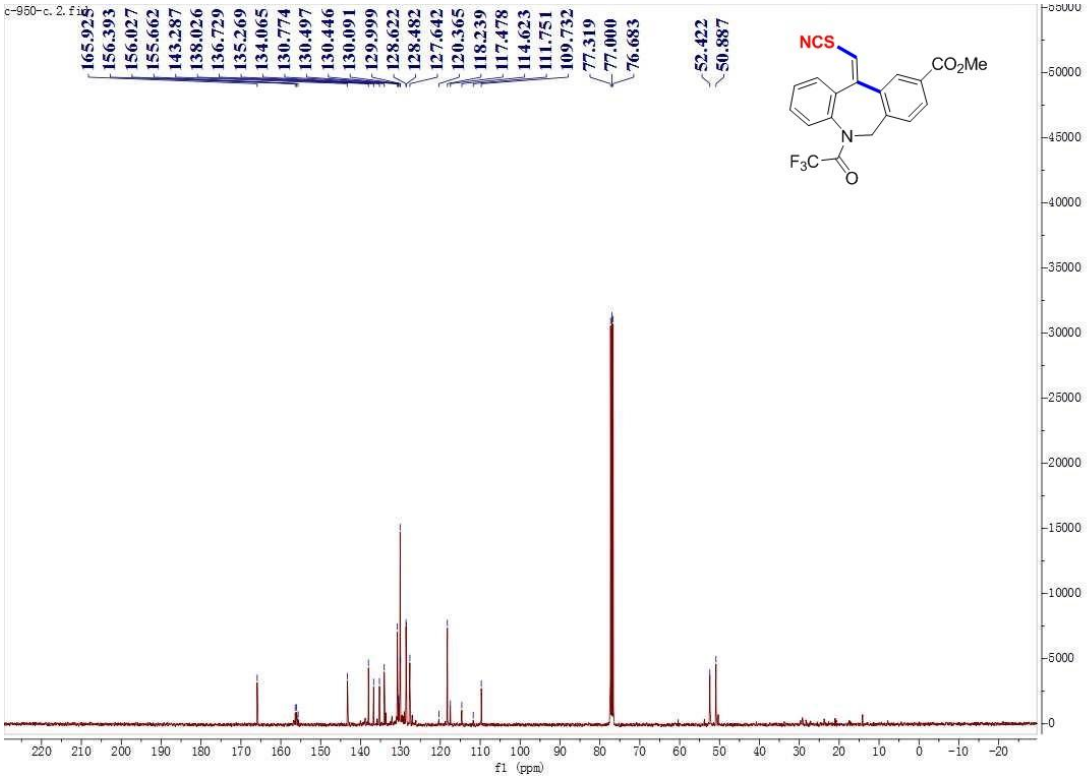
10-^{19}F NMR



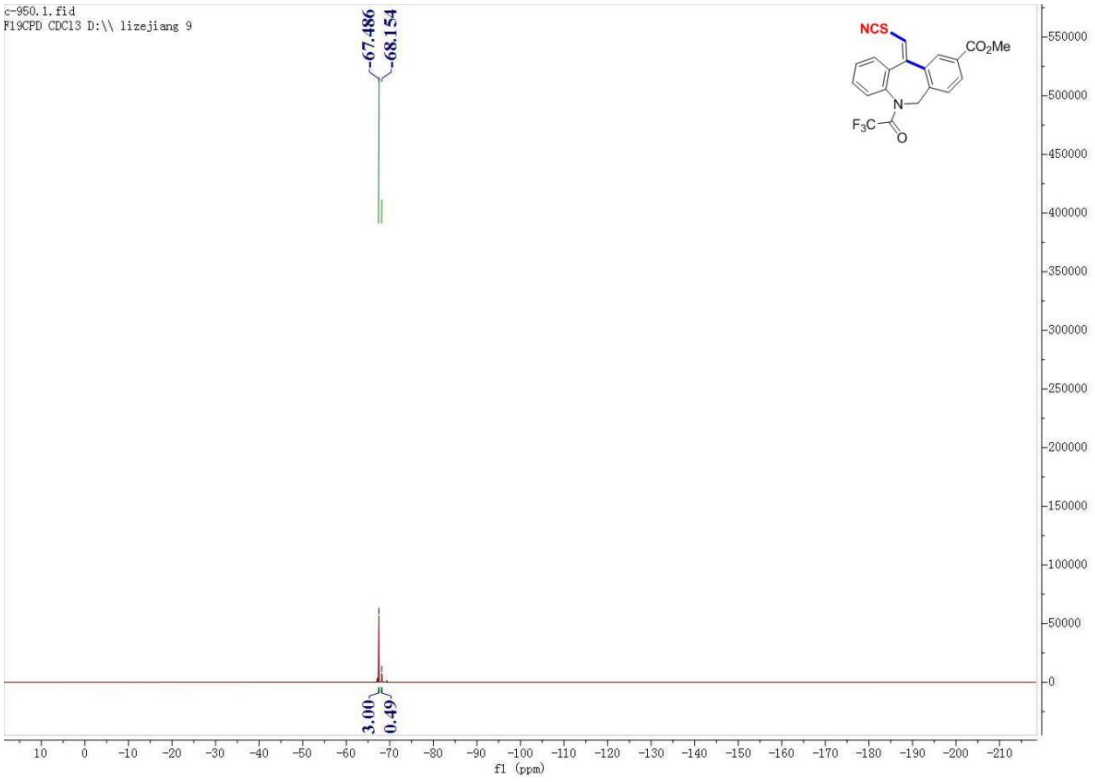
11-^{1}H NMR



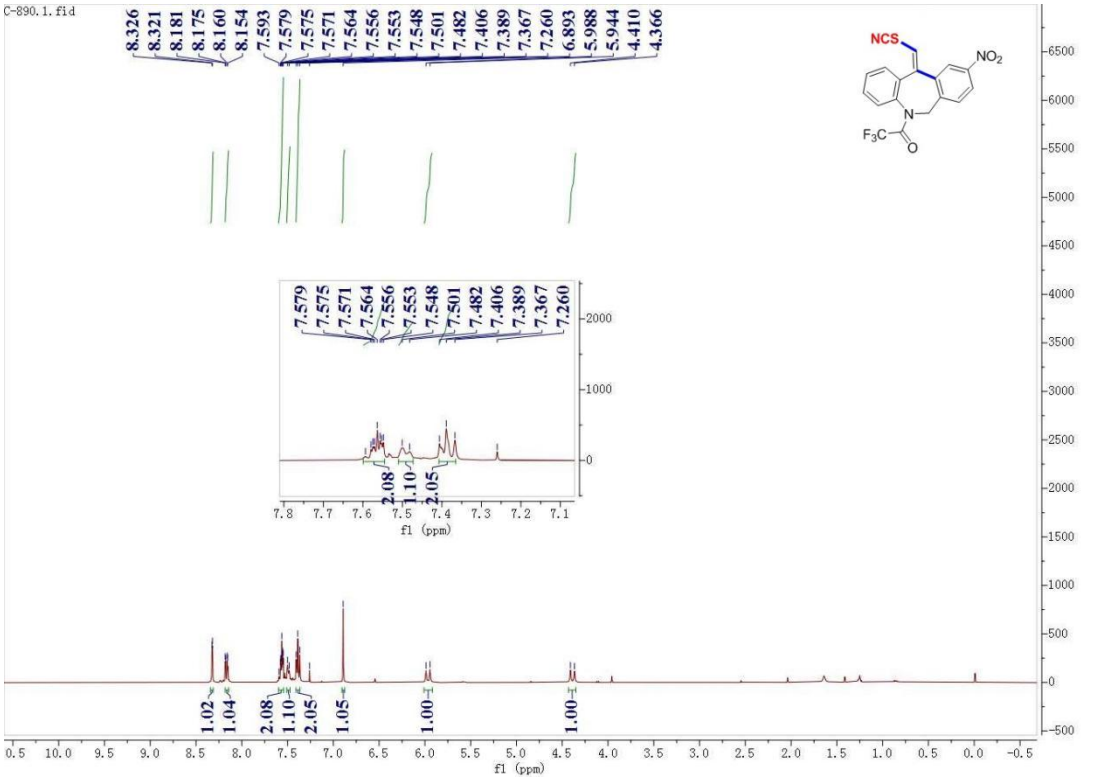
11-^{13}C NMR



11-^{19}F NMR



12-^{1}H NMR



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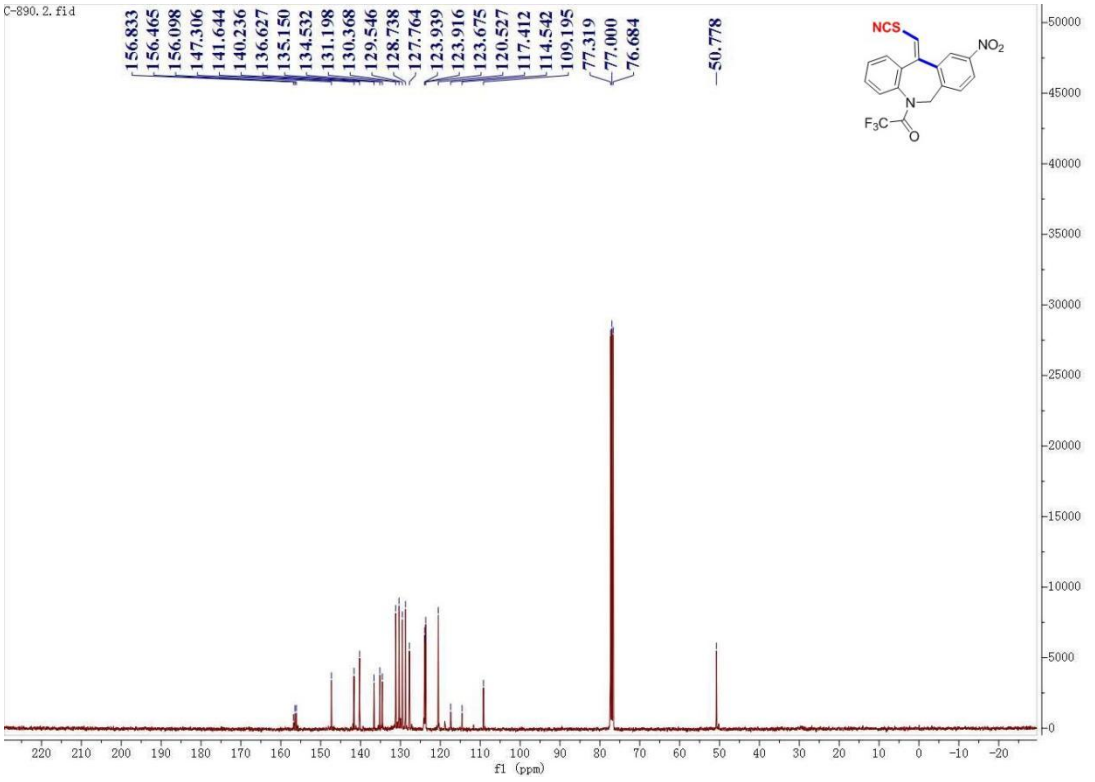

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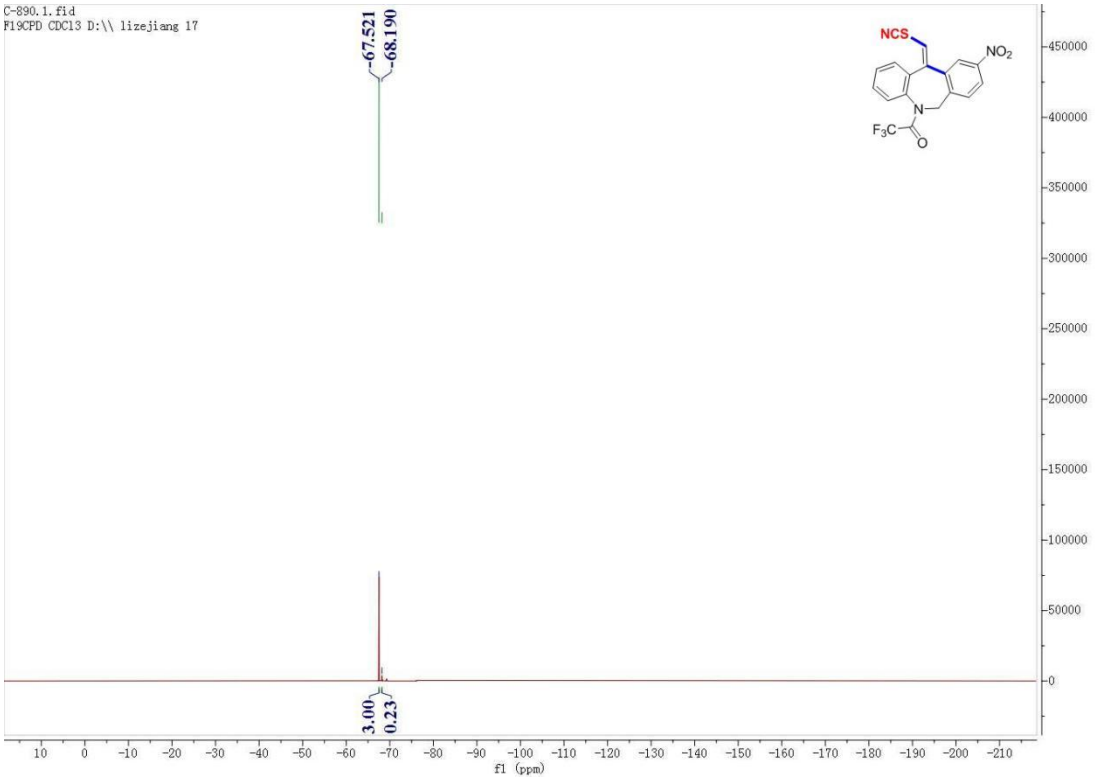
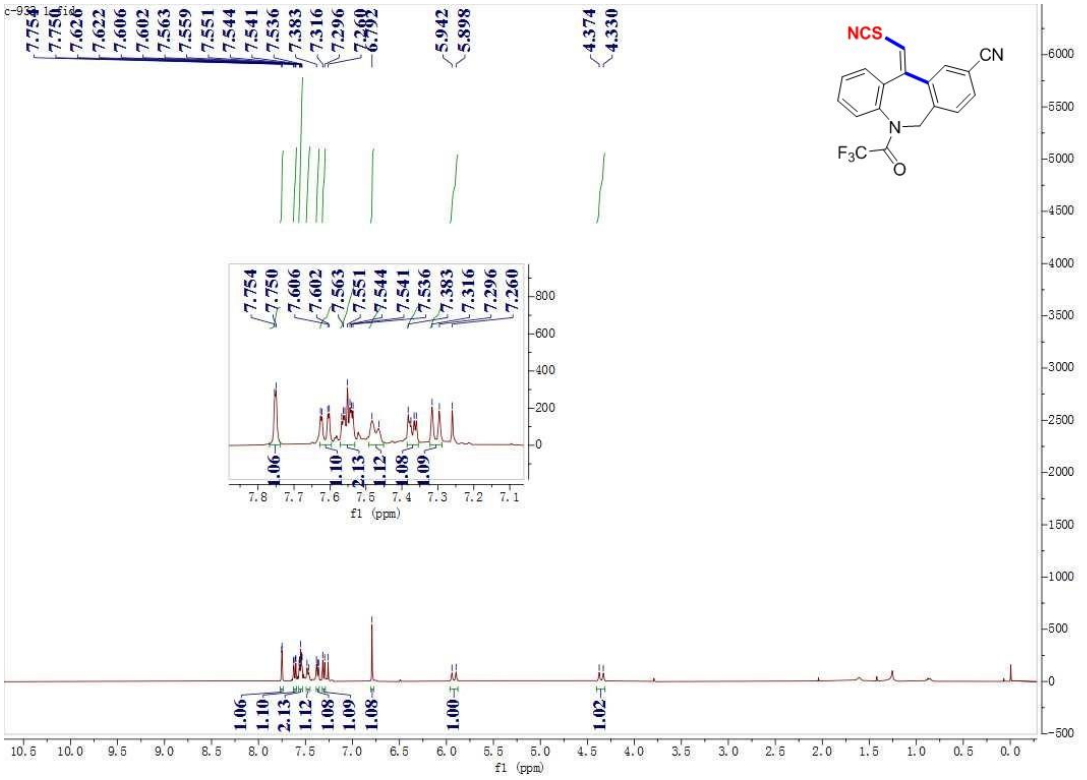
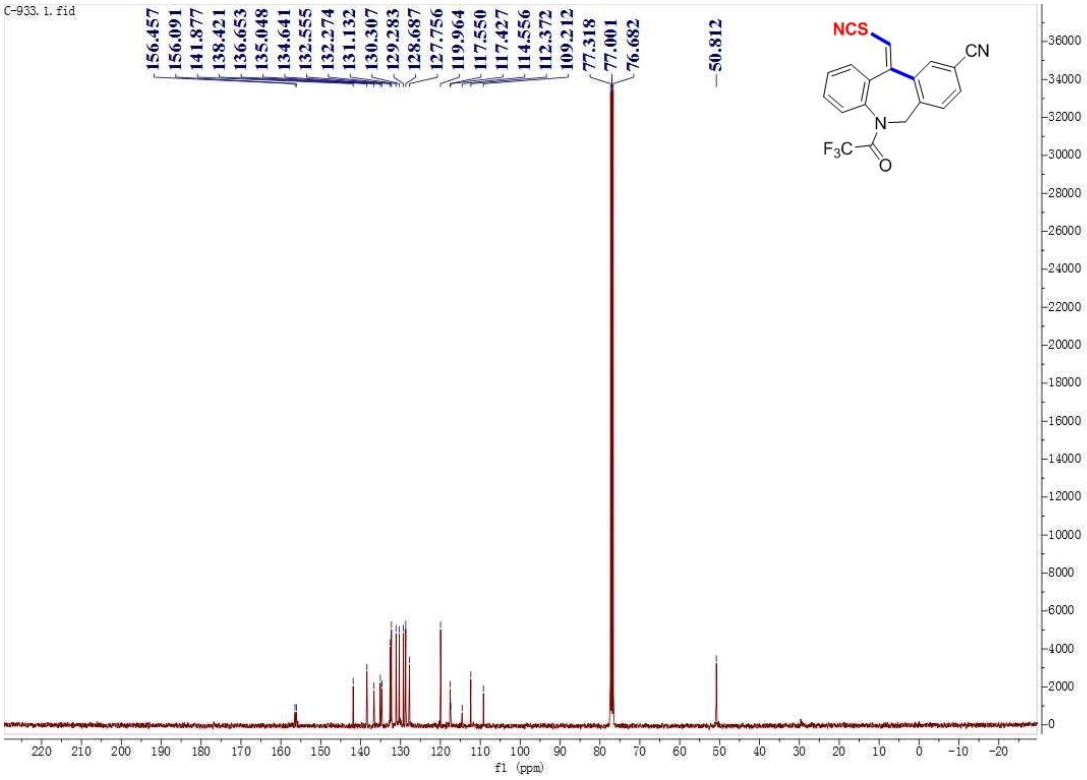


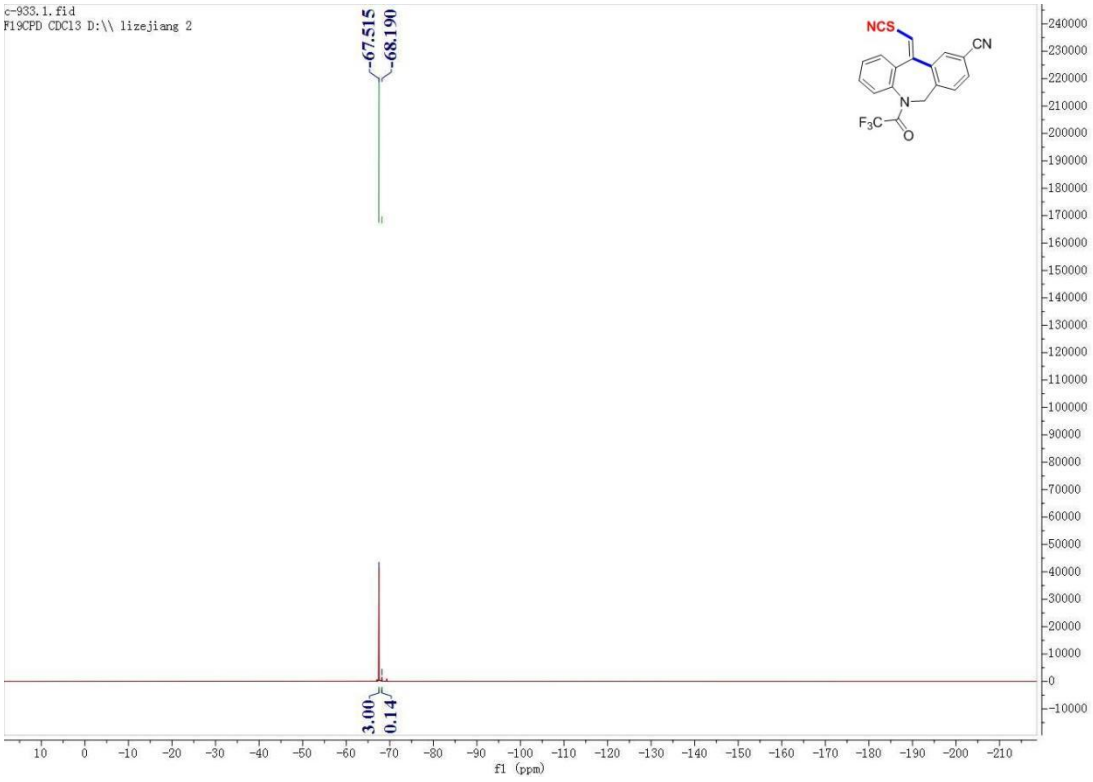
13-^{1}H NMR



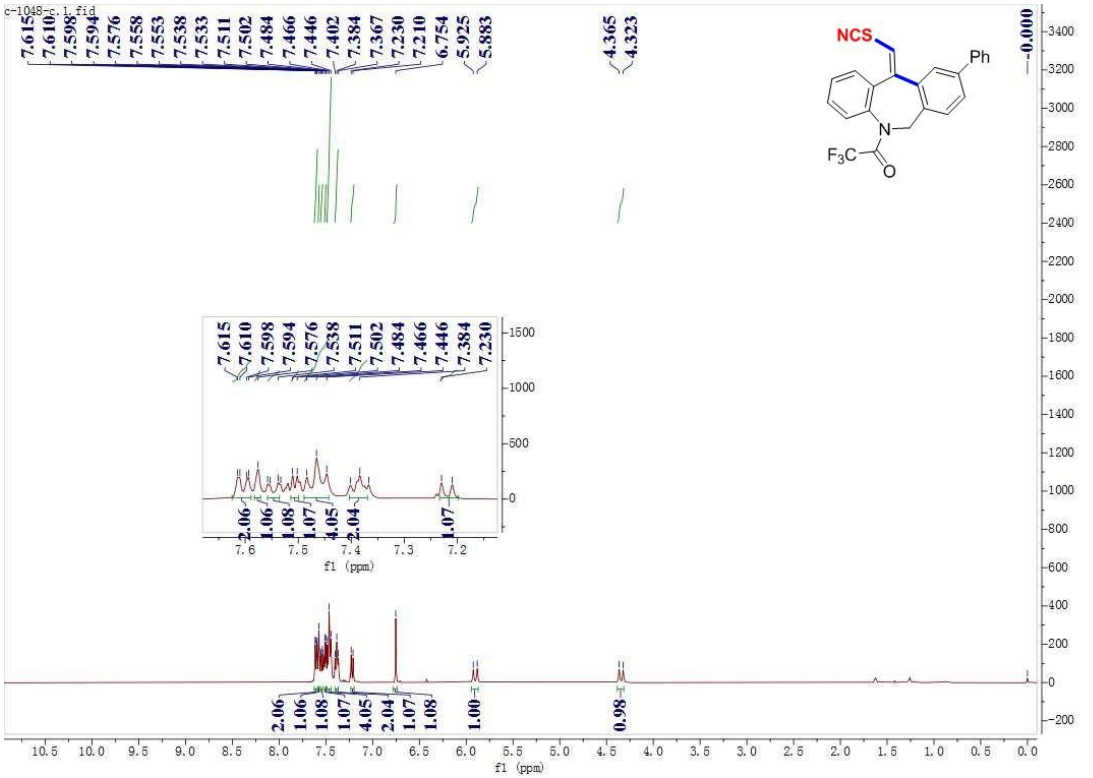
13-^{13}C NMR



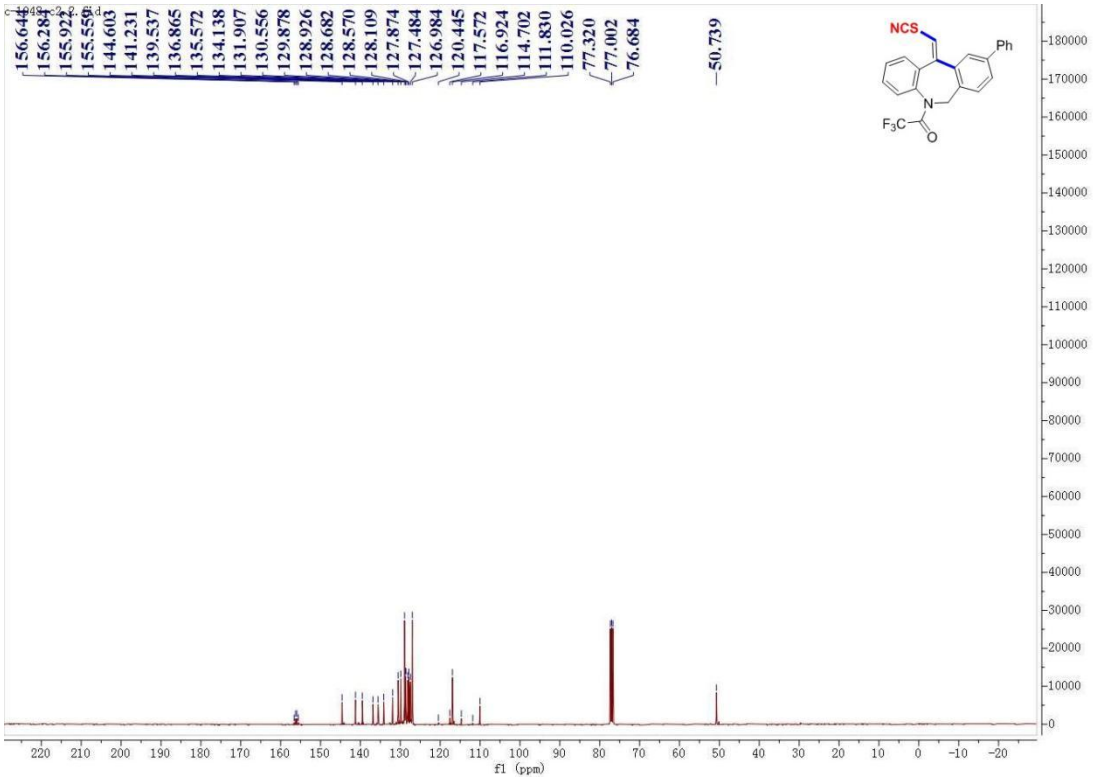
13-^{19}F NMR



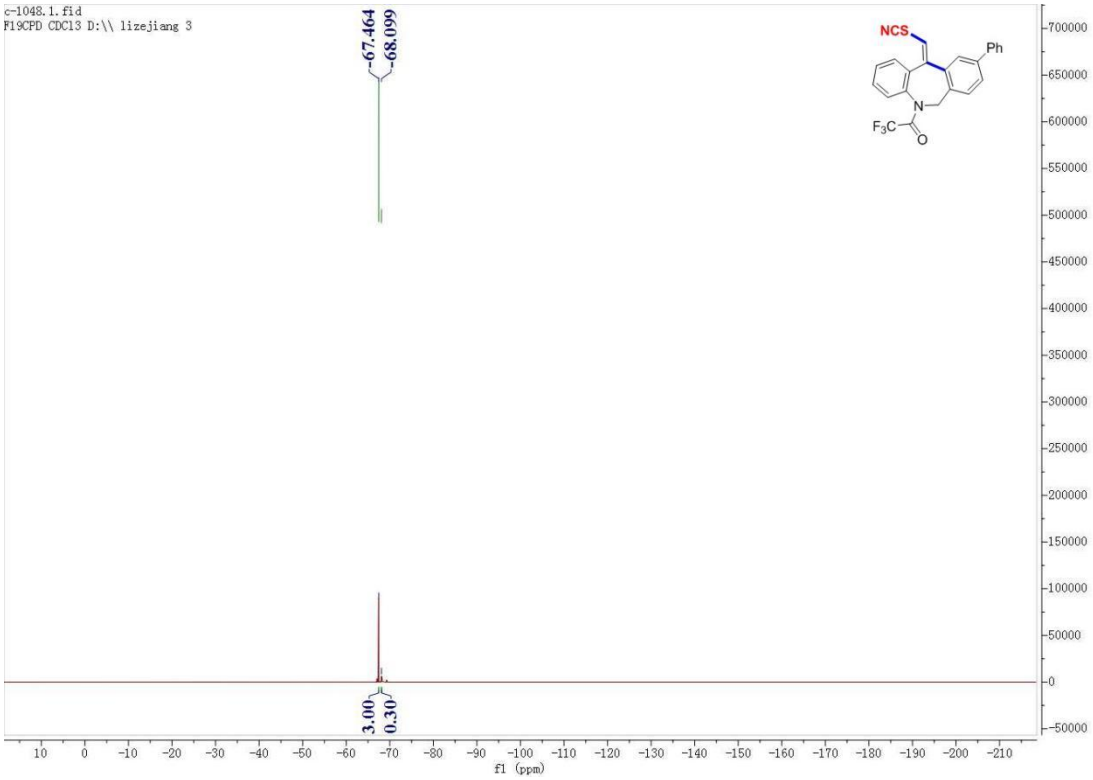
14-^{1}H NMR



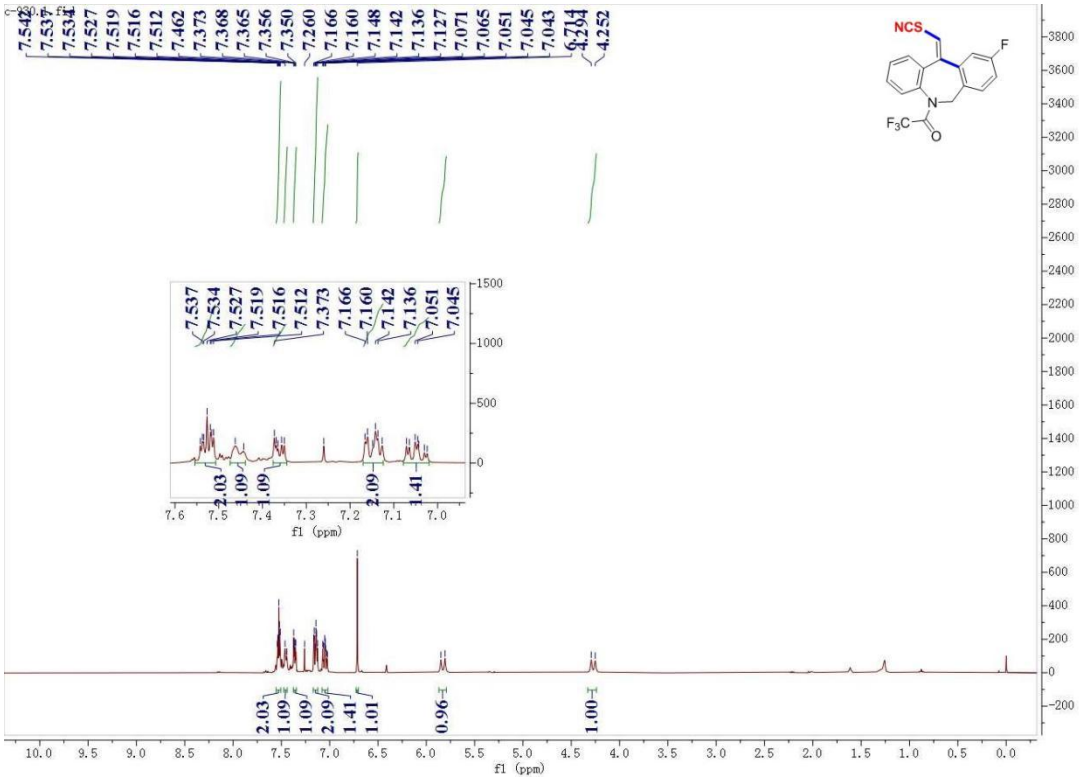
14-^{13}C NMR



14-^{19}F NMR



15-^{1}H NMR



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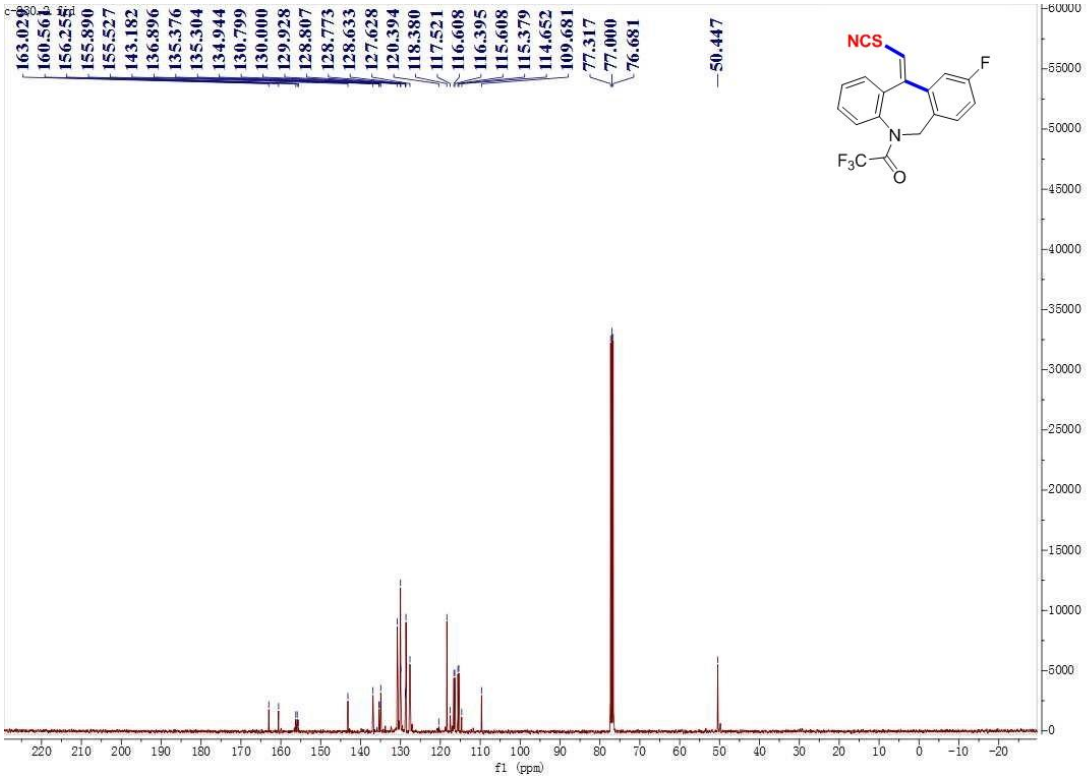
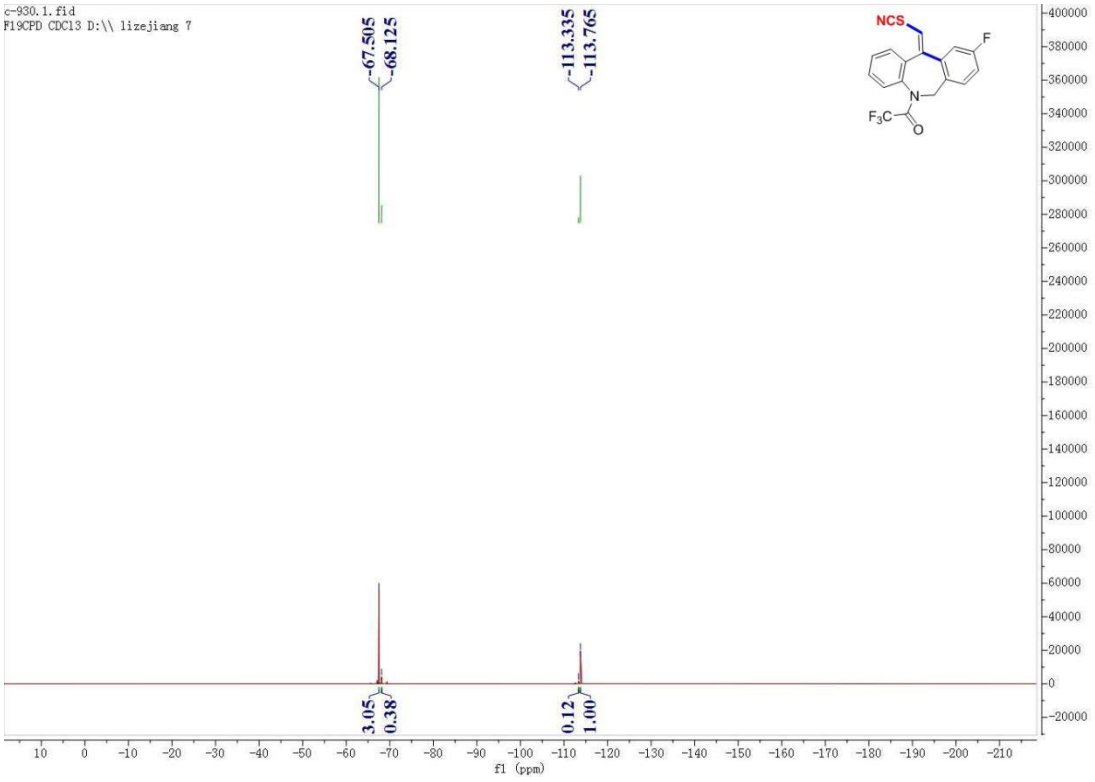
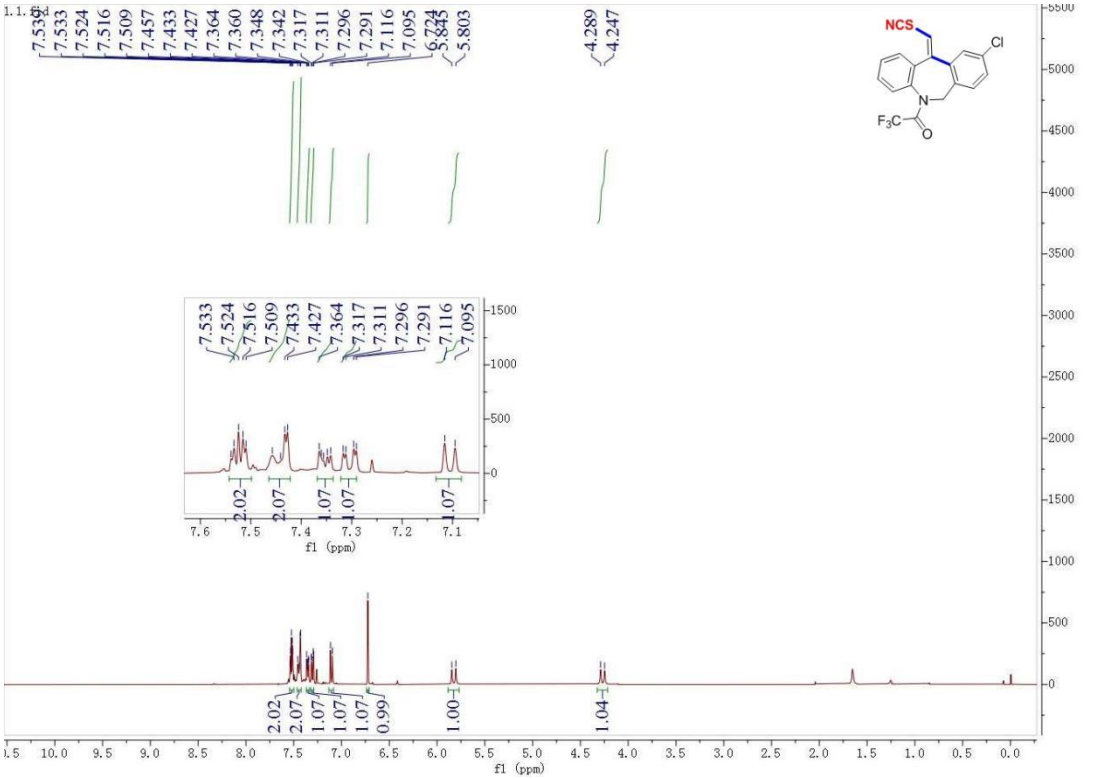


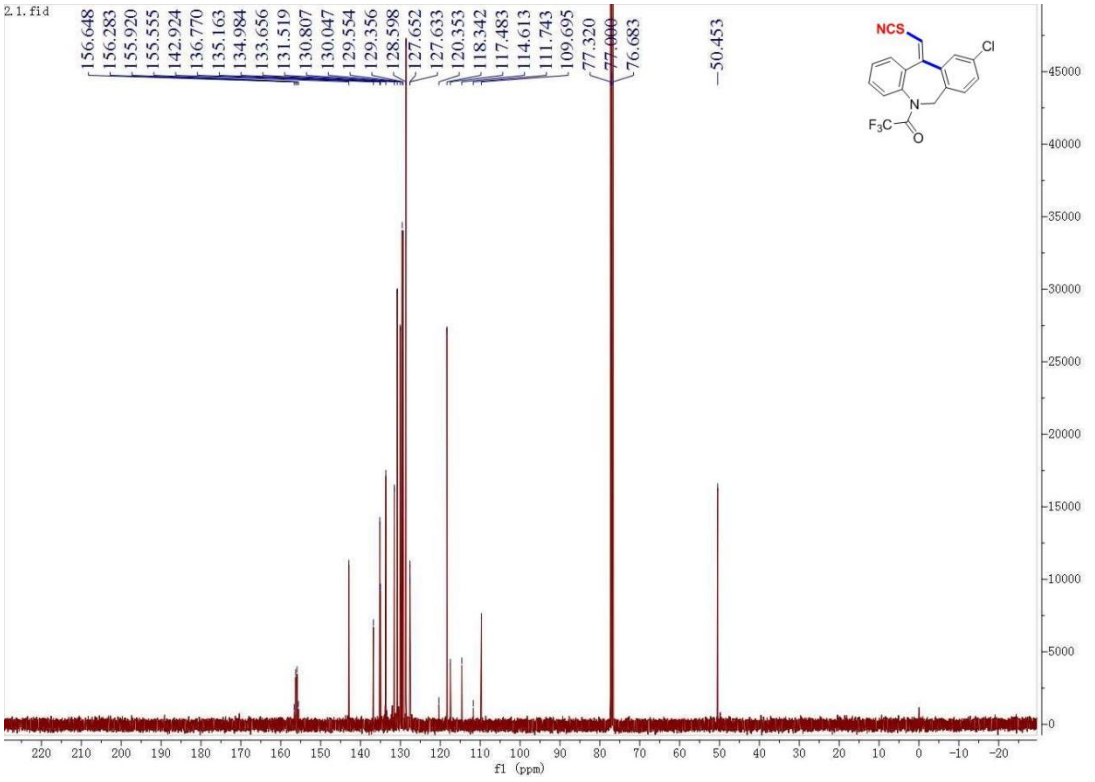
15-^{19}F NMR



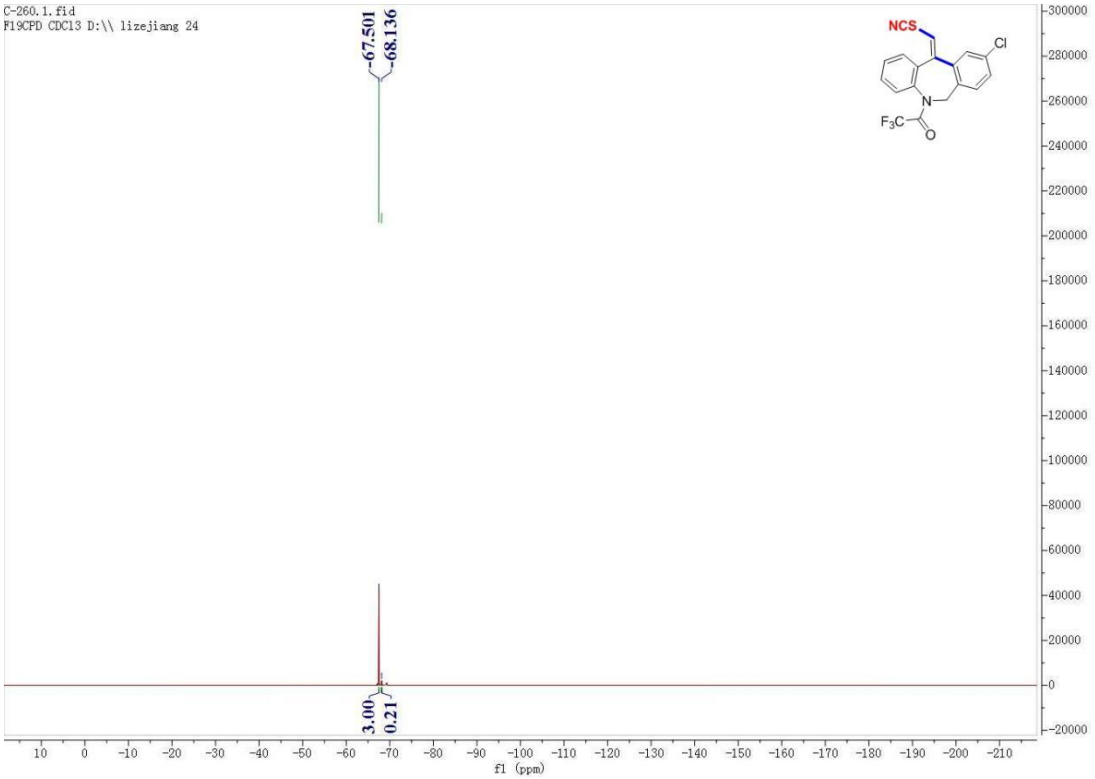
16-^{1}H NMR



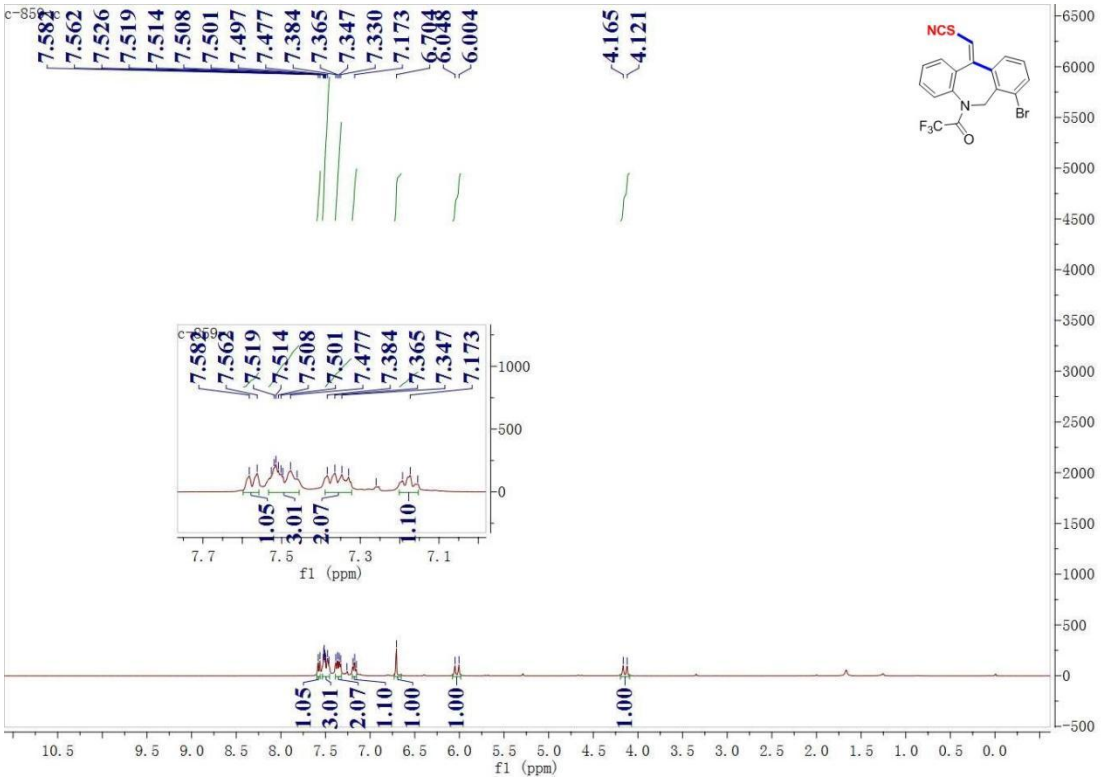
16-^{13}C NMR



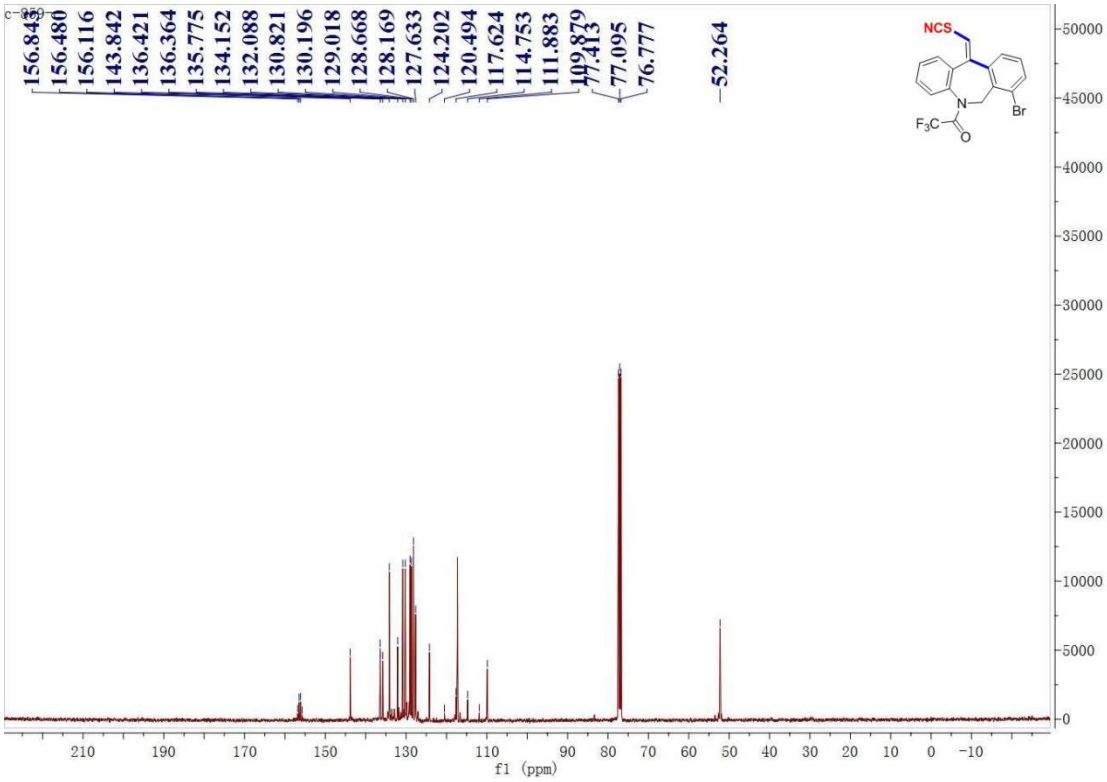
16-^{19}F NMR



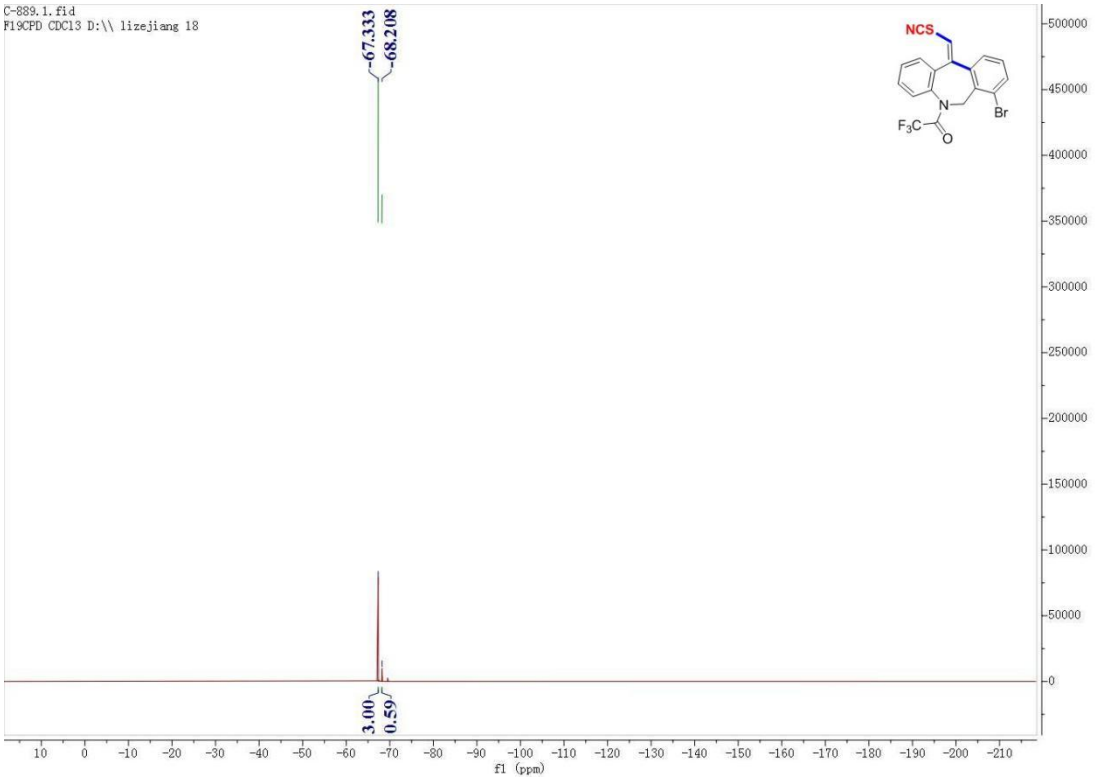
17-^{1}H NMR



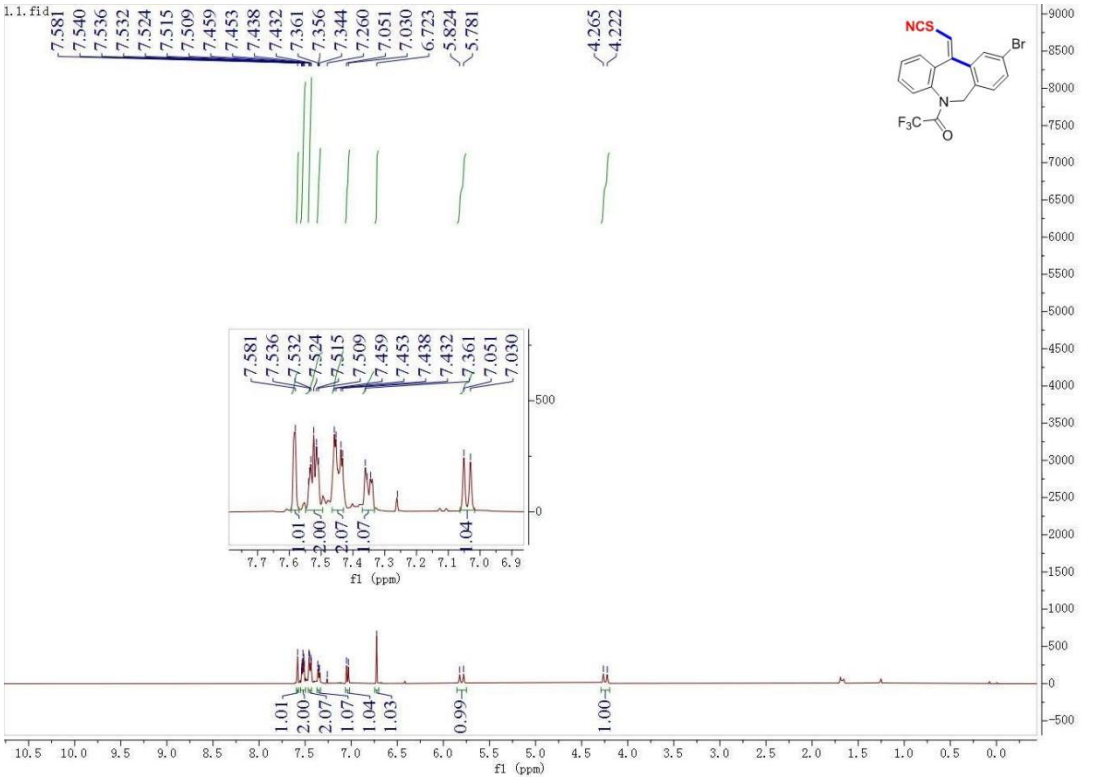
17-^{13}C NMR



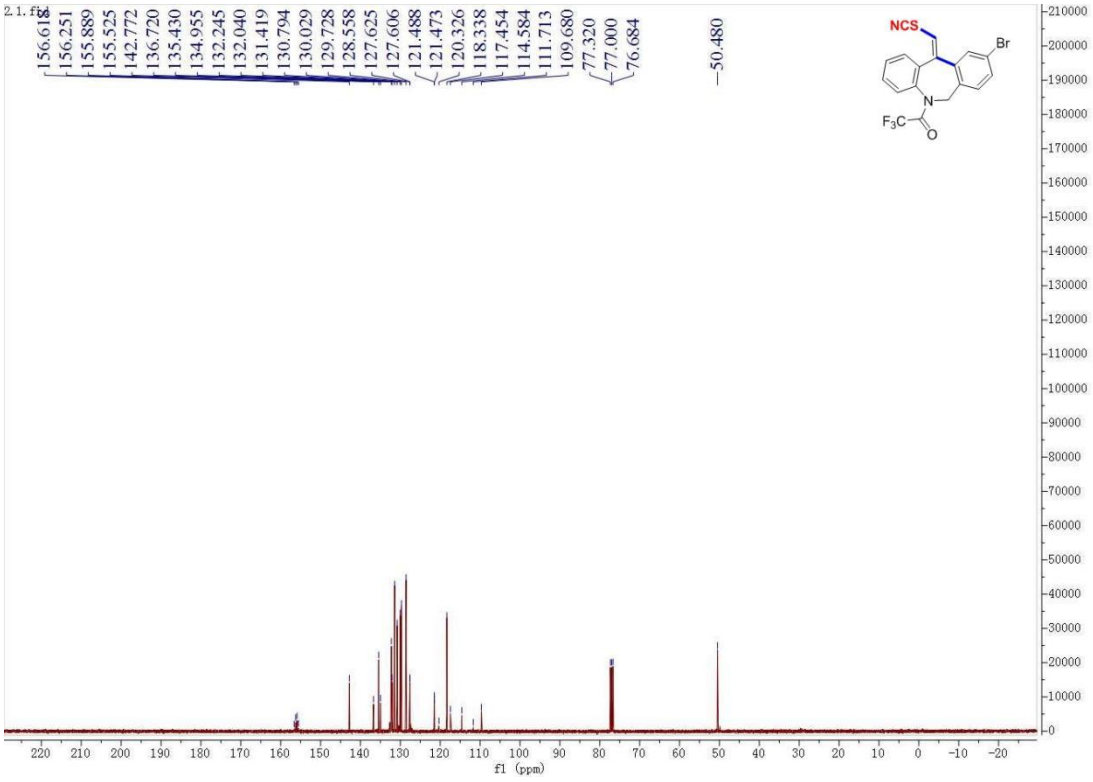
17-^{19}F NMR



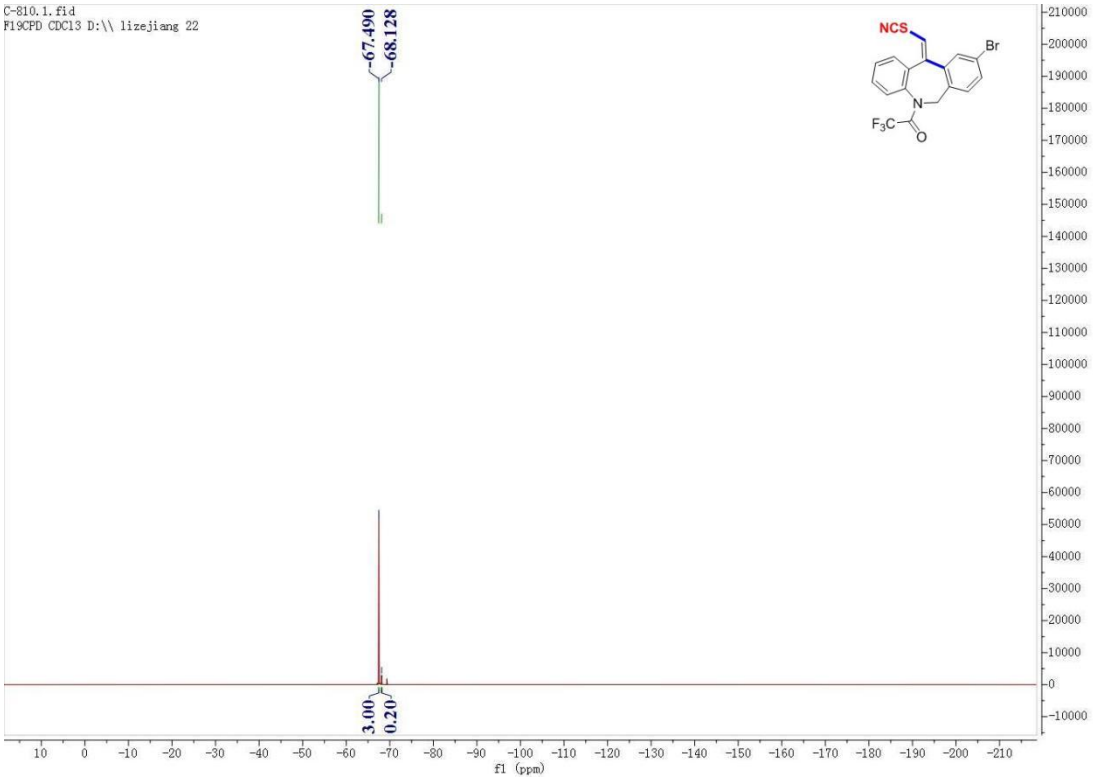
18-^{1}H NMR



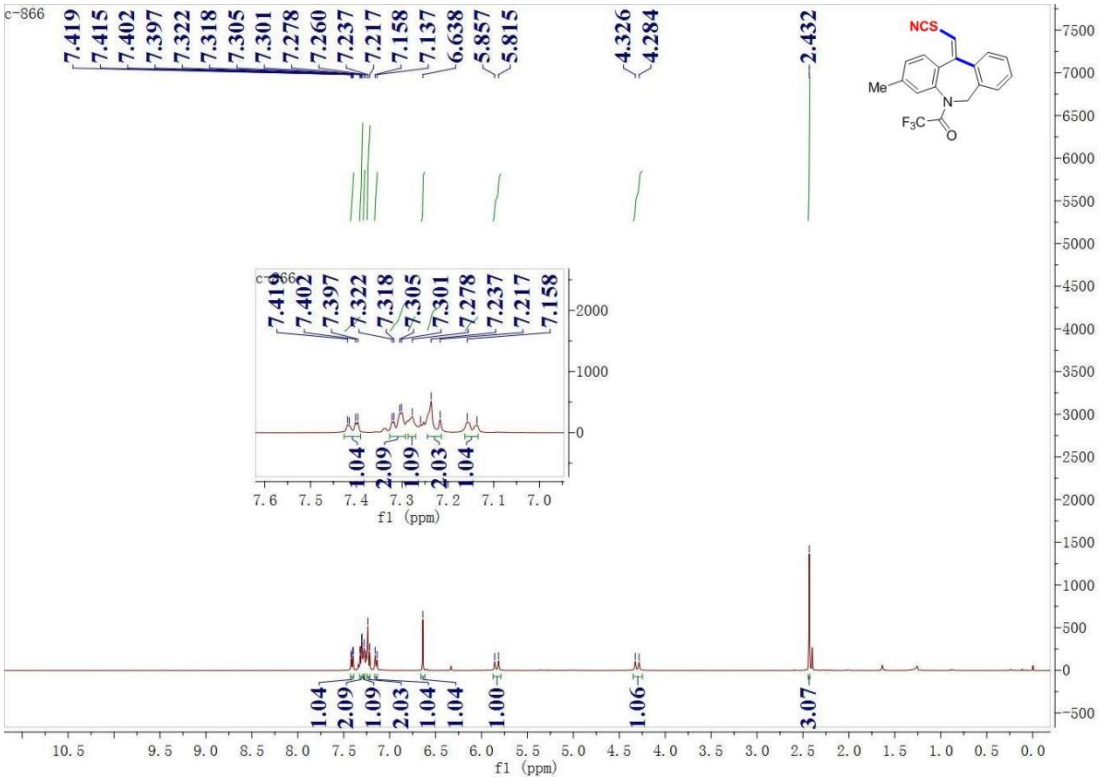
18-^{13}C NMR



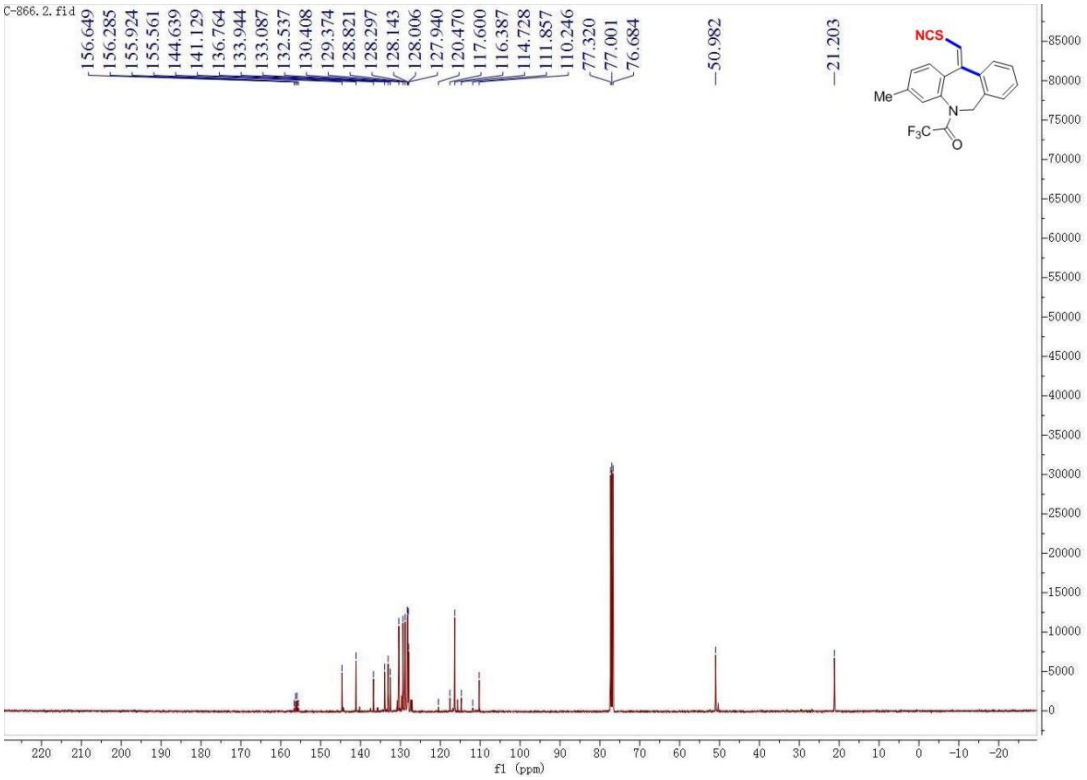
18-^{19}F NMR



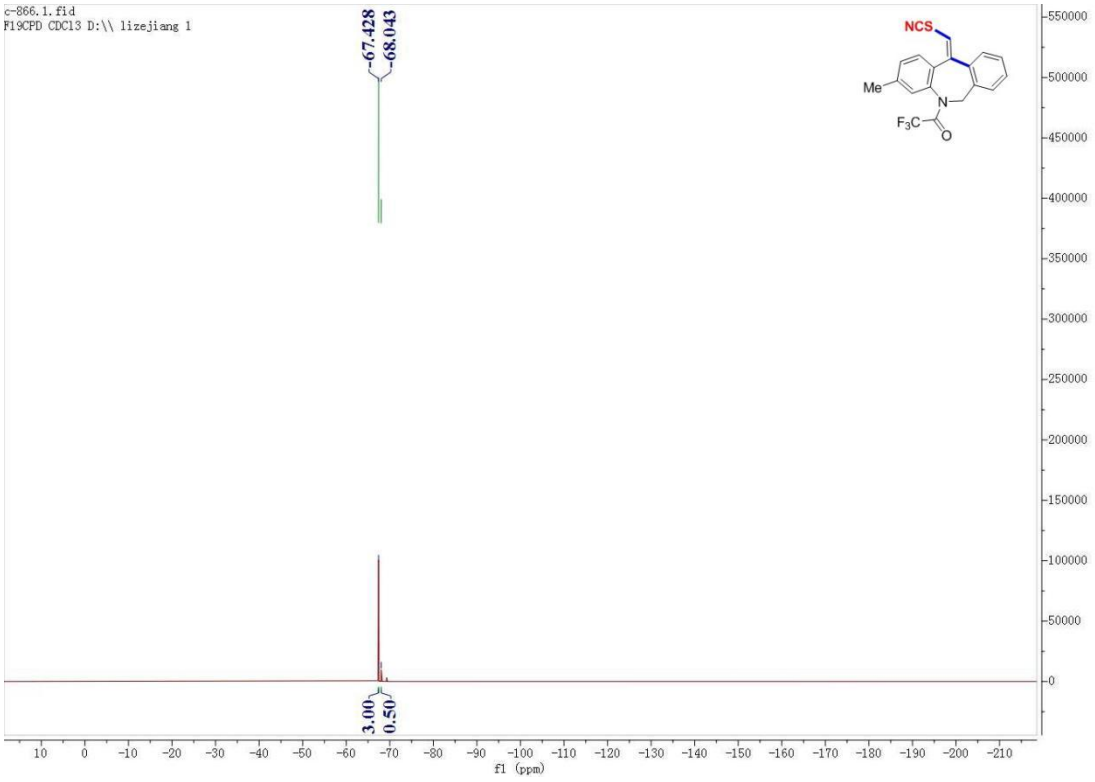
19-^{1}H NMR



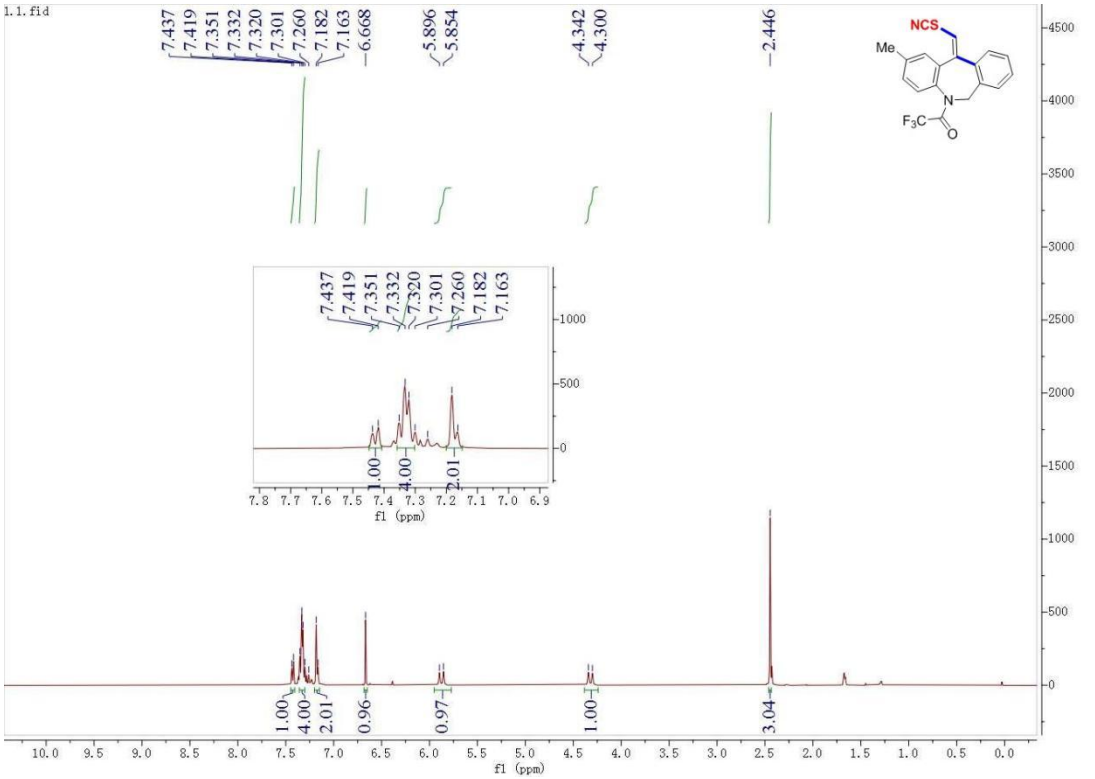
19-^{13}C NMR



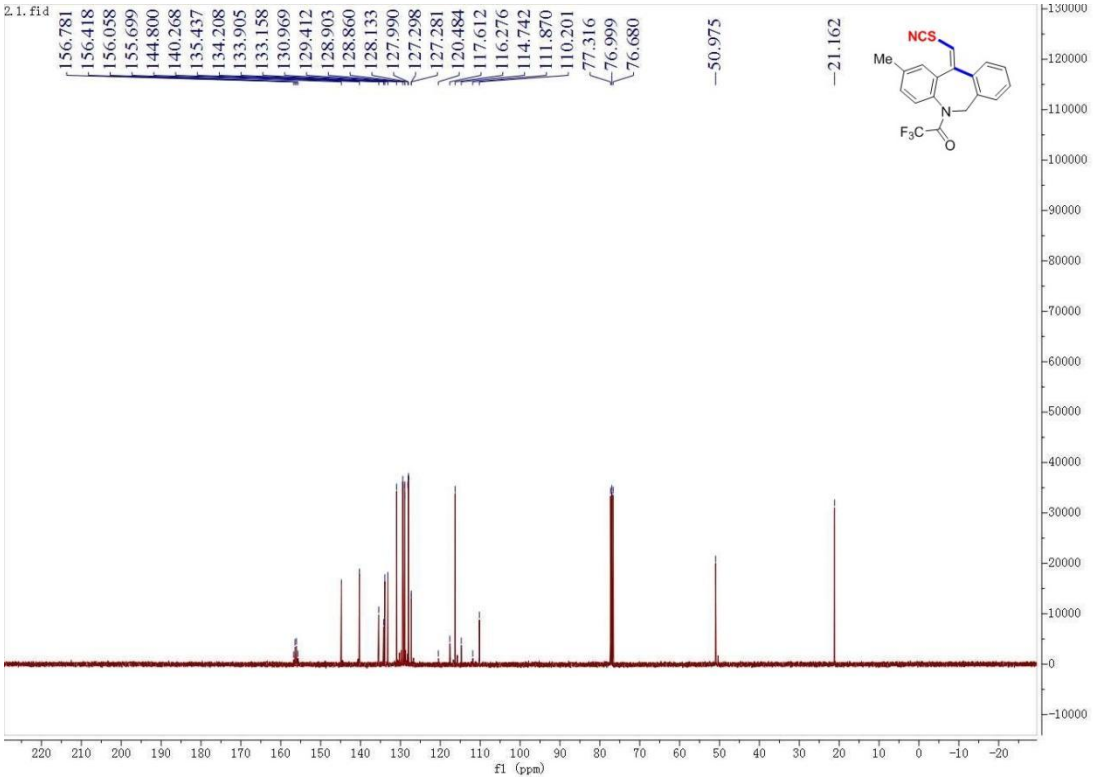
19-^{19}F NMR



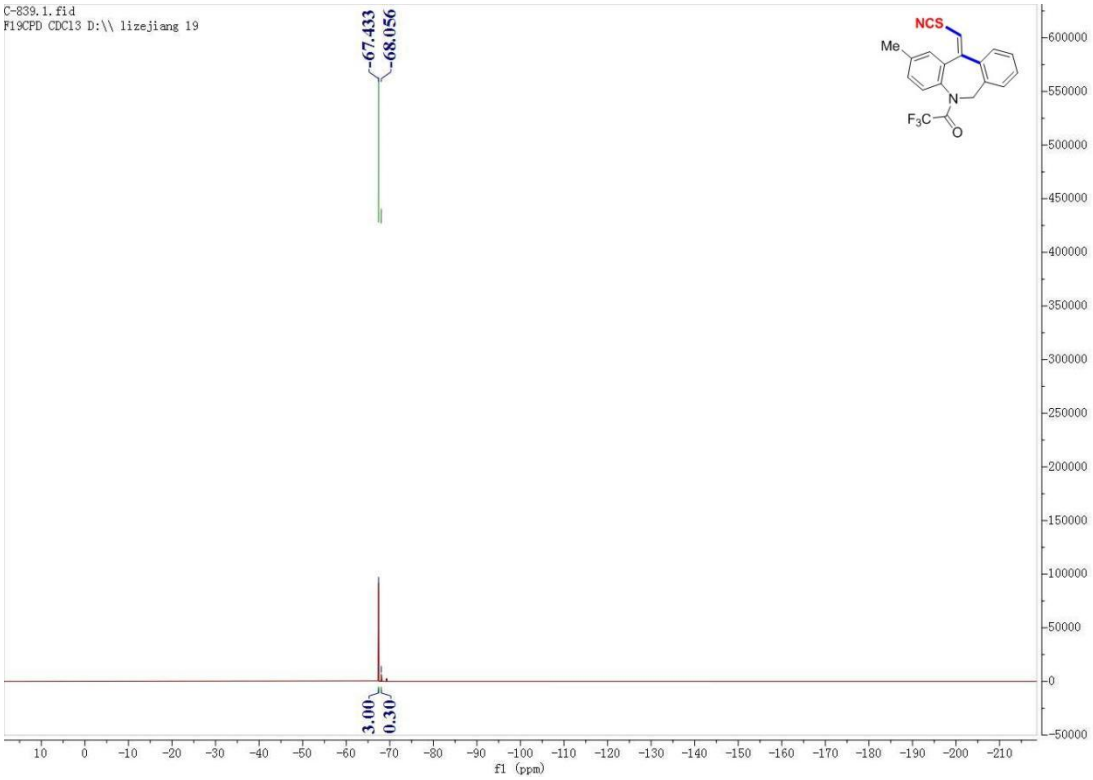
20-^{1}H NMR



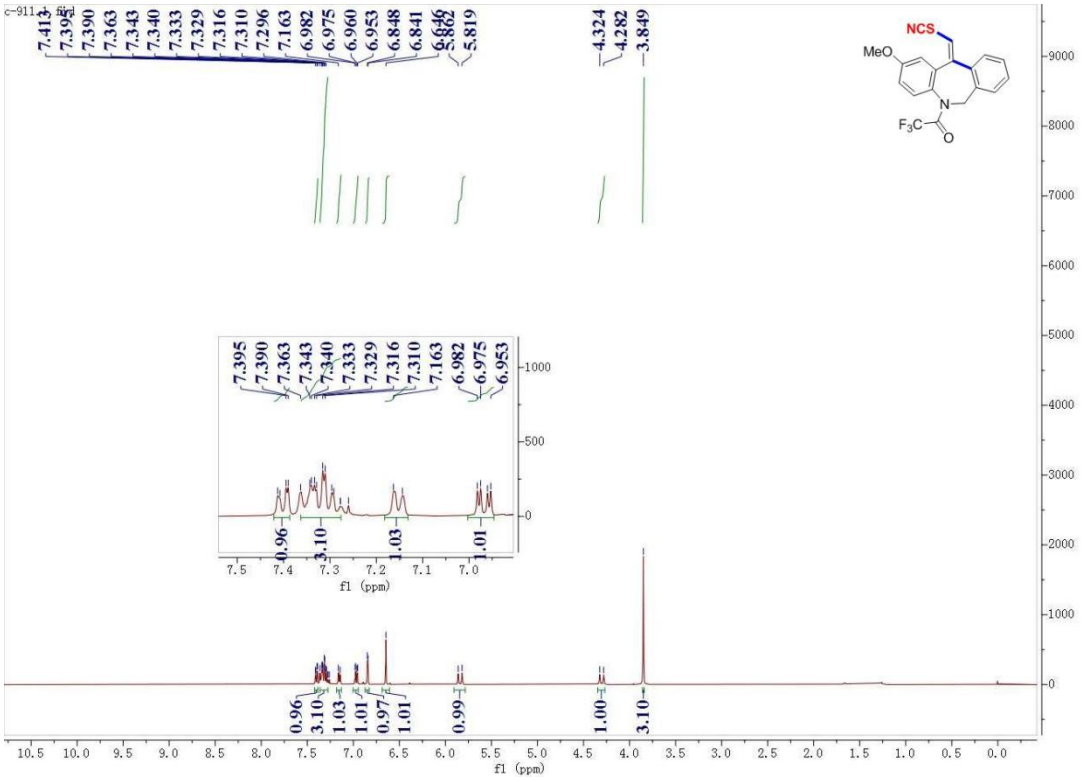
20-^{13}C NMR



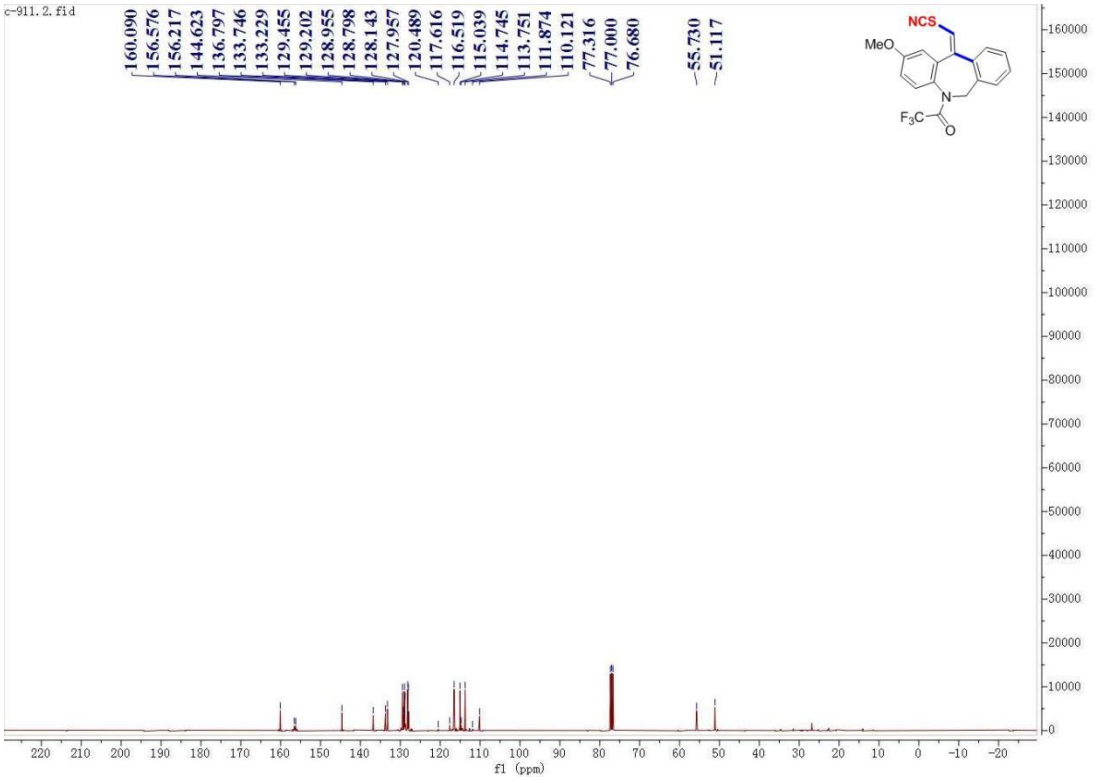
20-^{19}F NMR



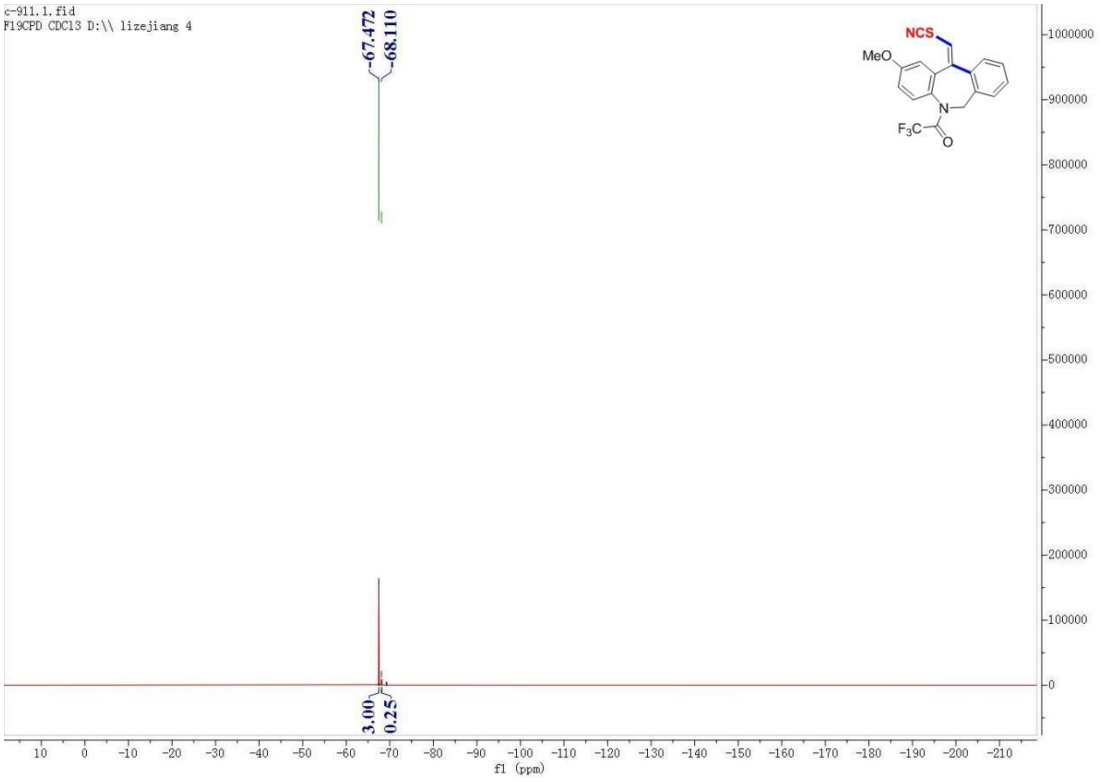
21-^{1}H NMR



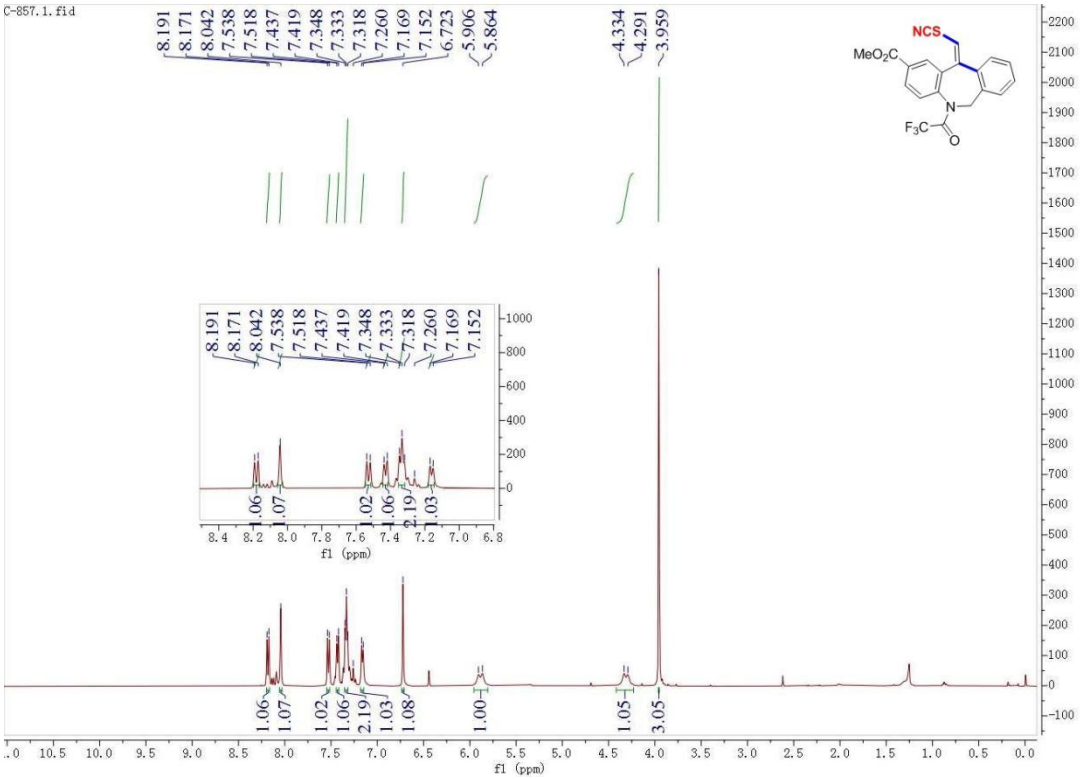
21-^{13}C NMR



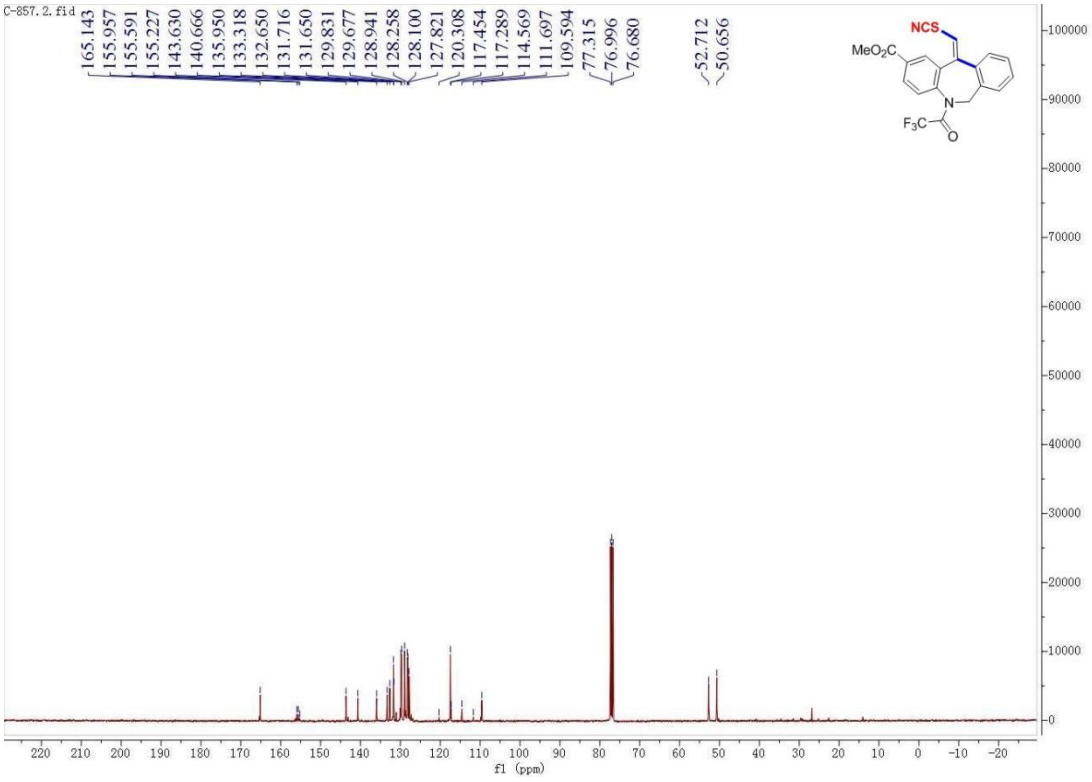
21-^{19}F NMR



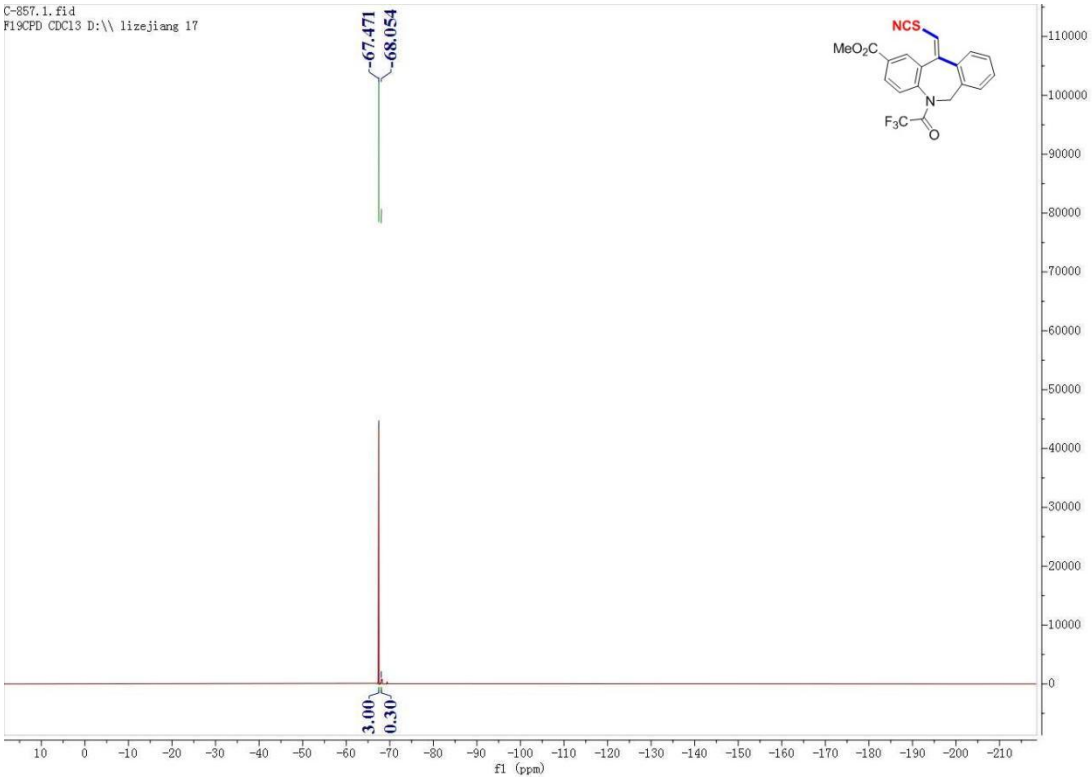
22-^{1}H NMR



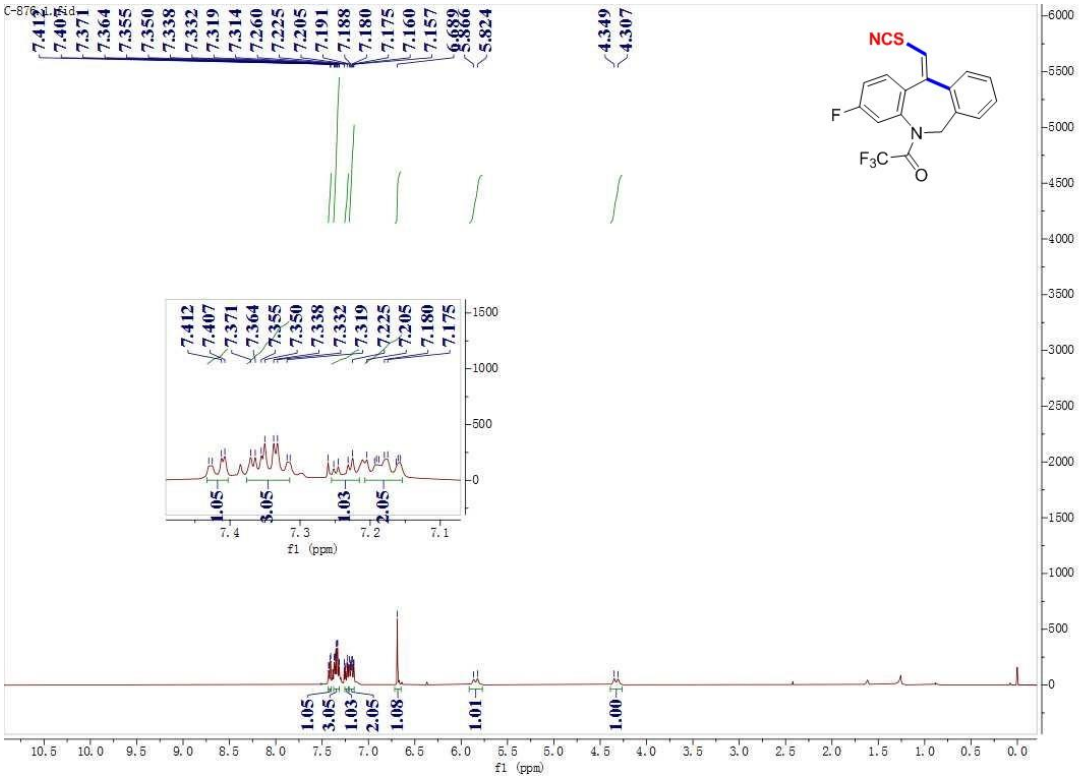
22-^{13}C NMR



22-^{19}F NMR



23-^{1}H NMR



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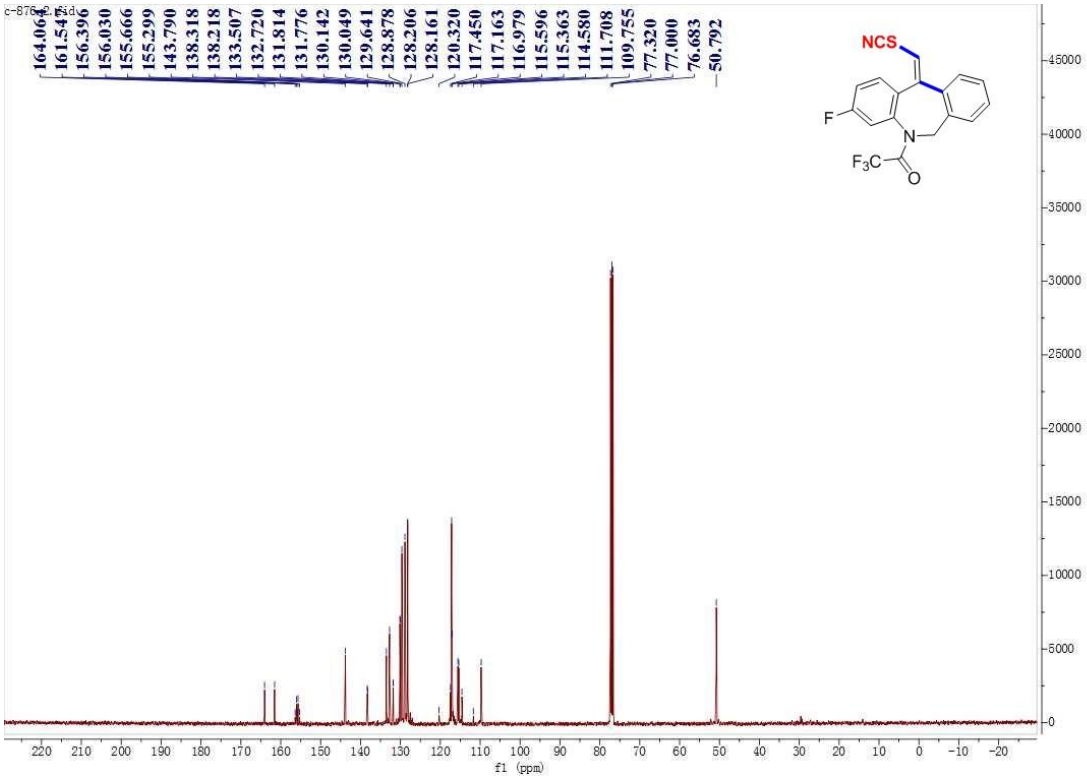
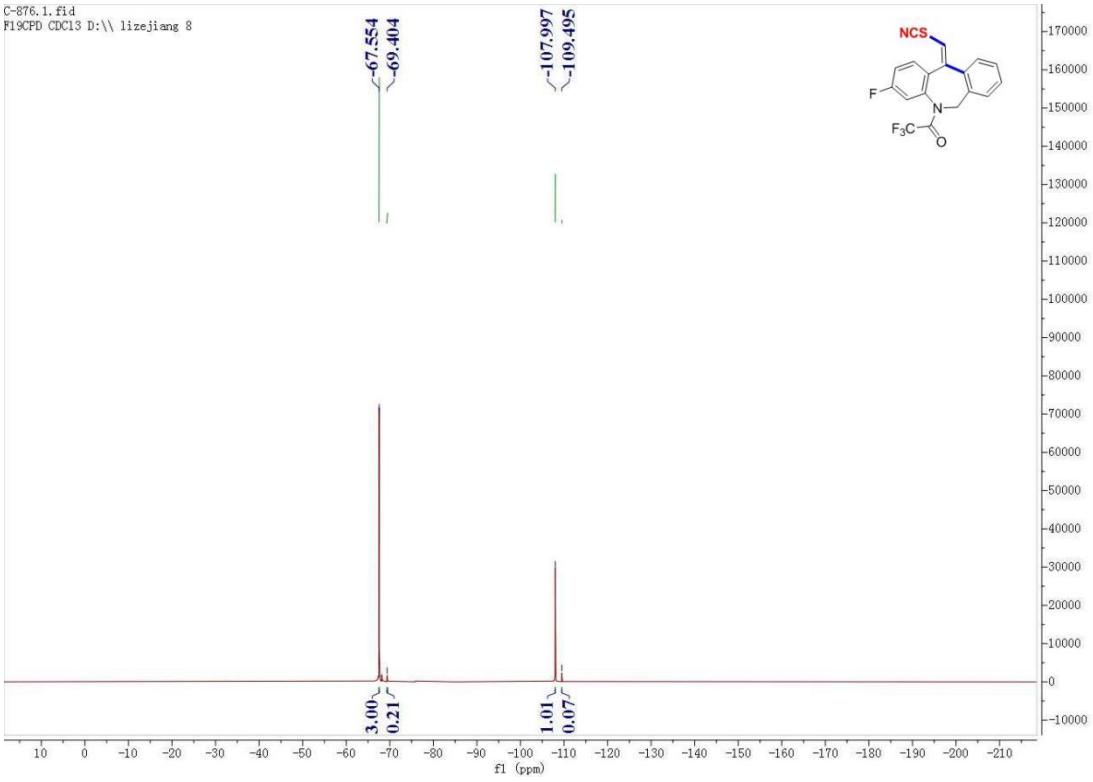
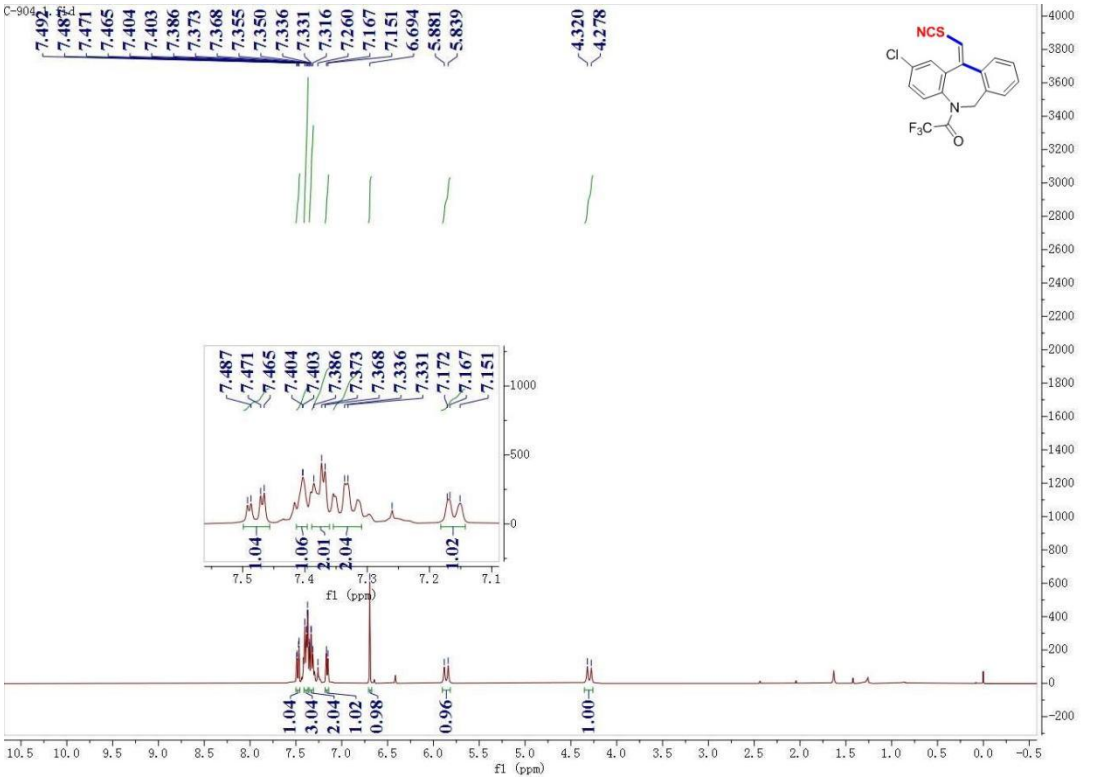


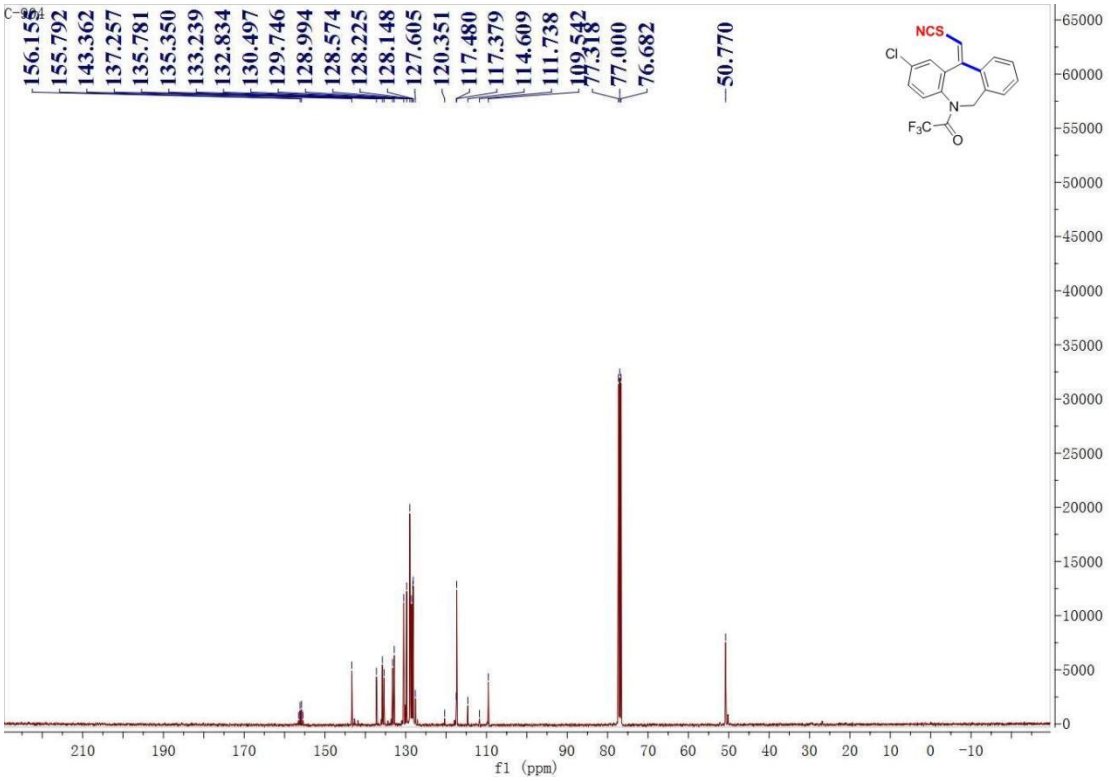
23-^{19}F NMR



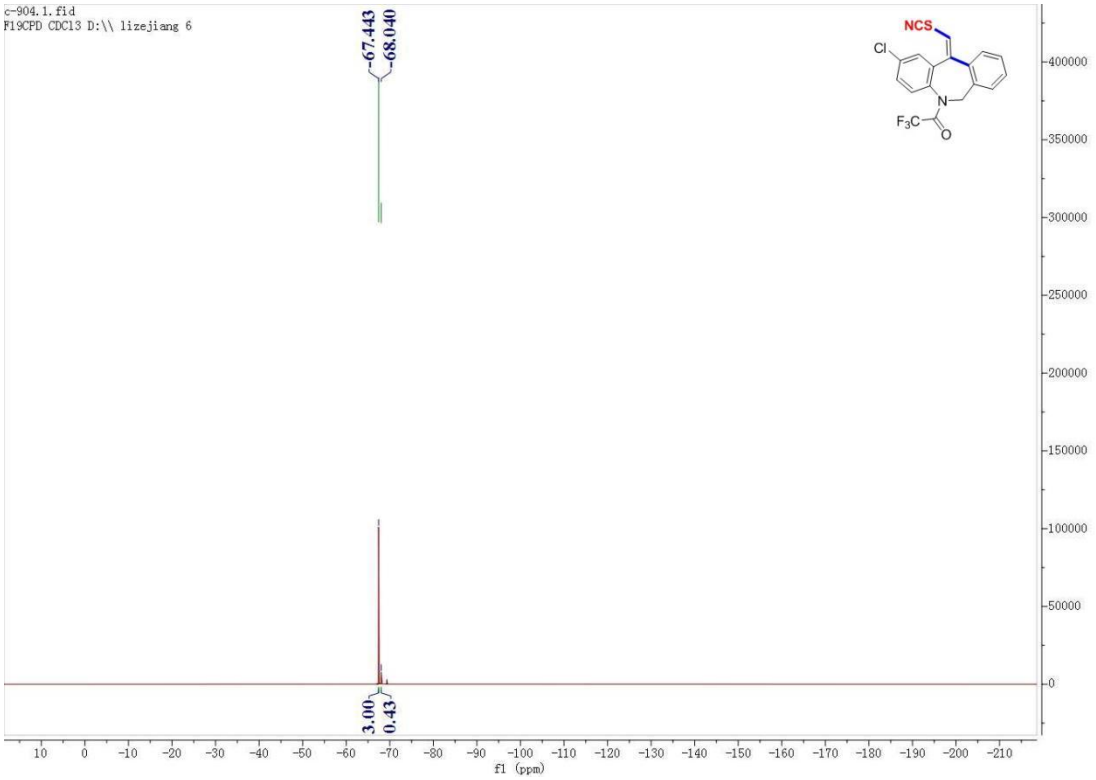
24-^{1}H NMR



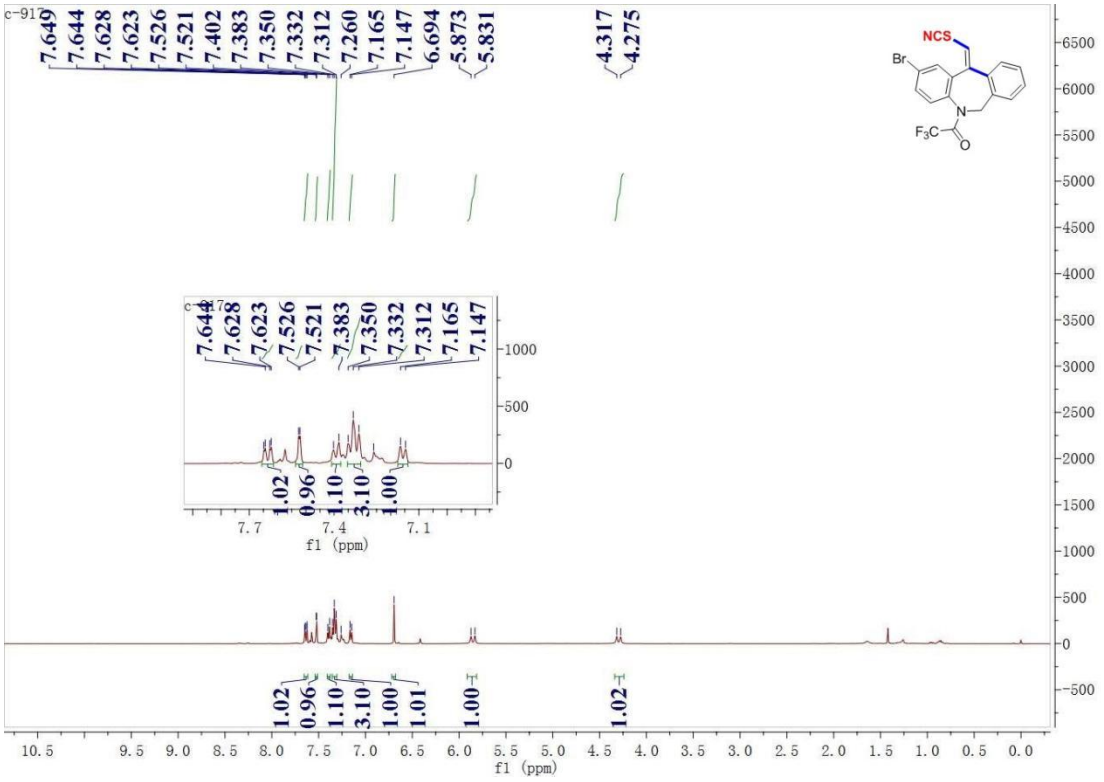
24-^{13}C NMR



24-^{19}F NMR



25-^{1}H NMR



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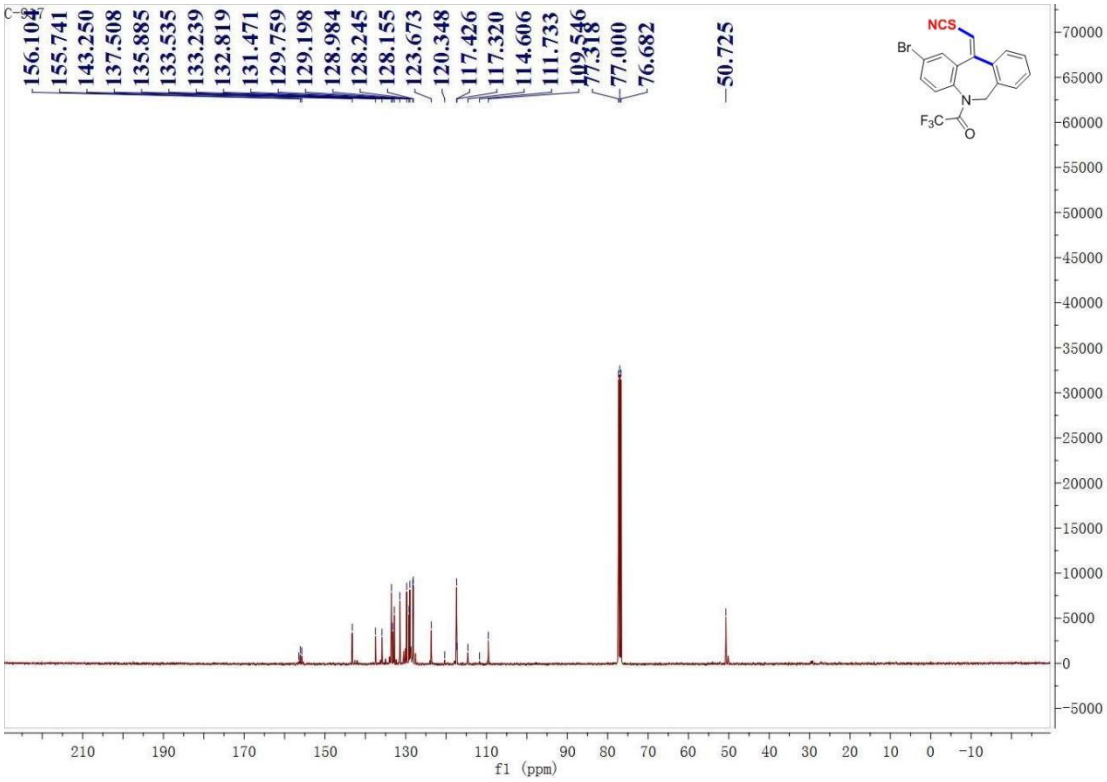
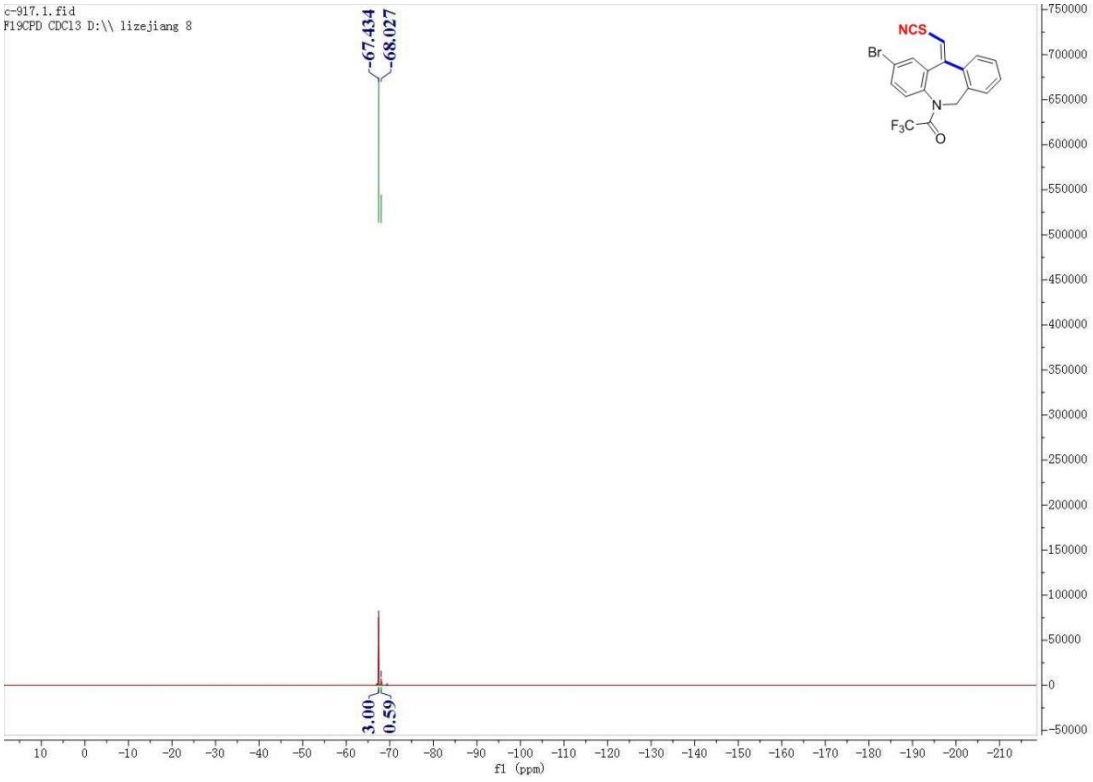
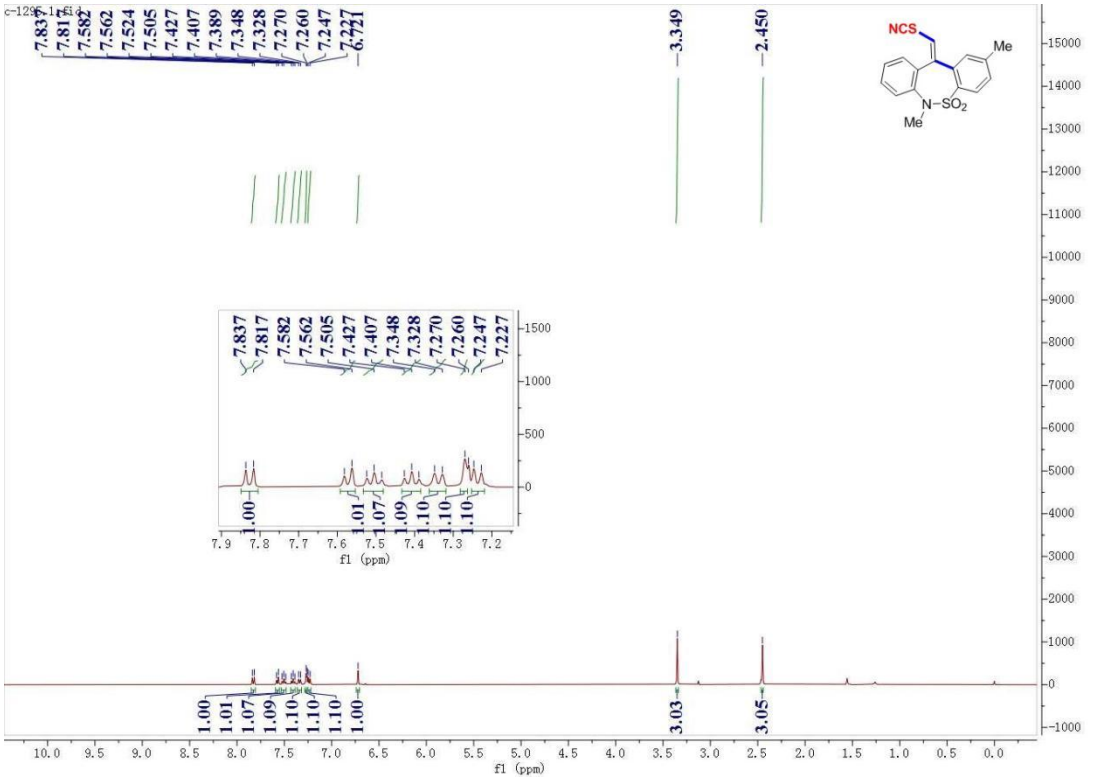


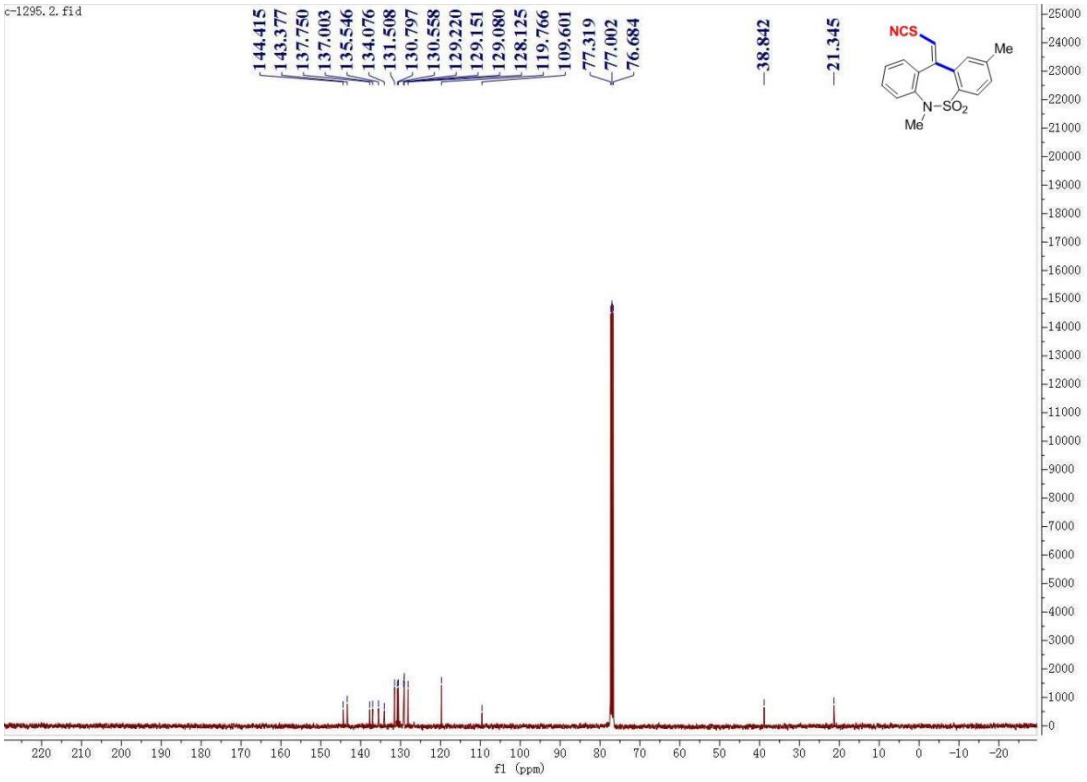
25-^{19}F NMR



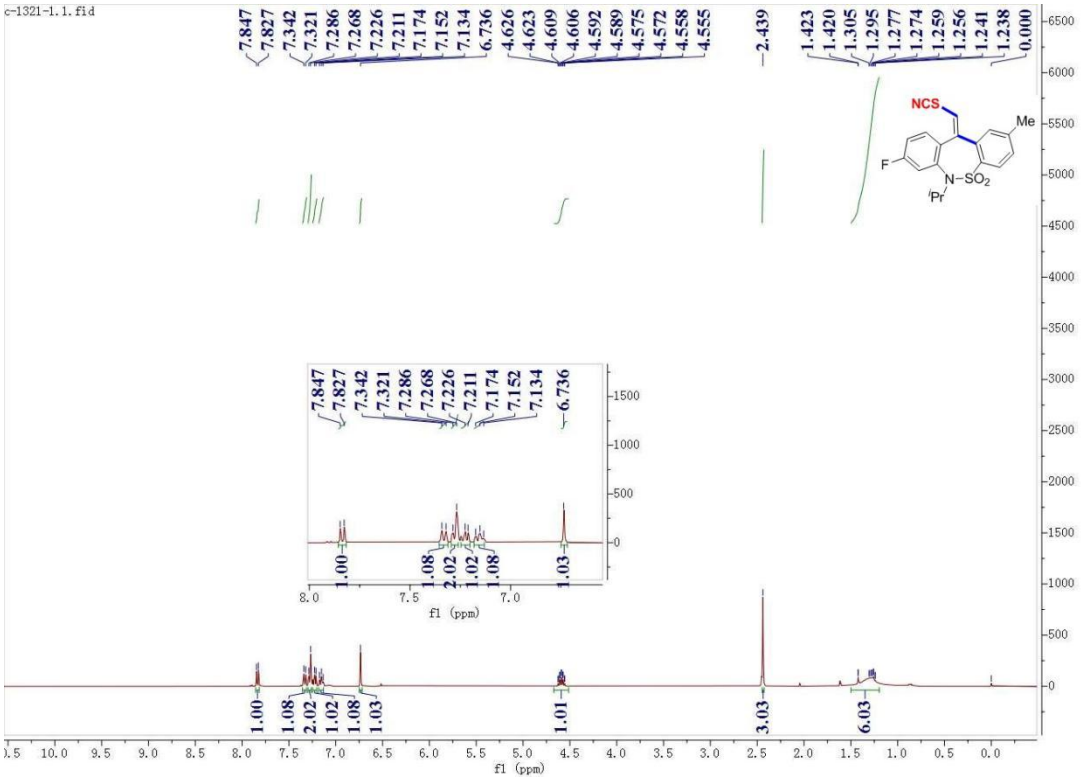
26-^{1}H NMR



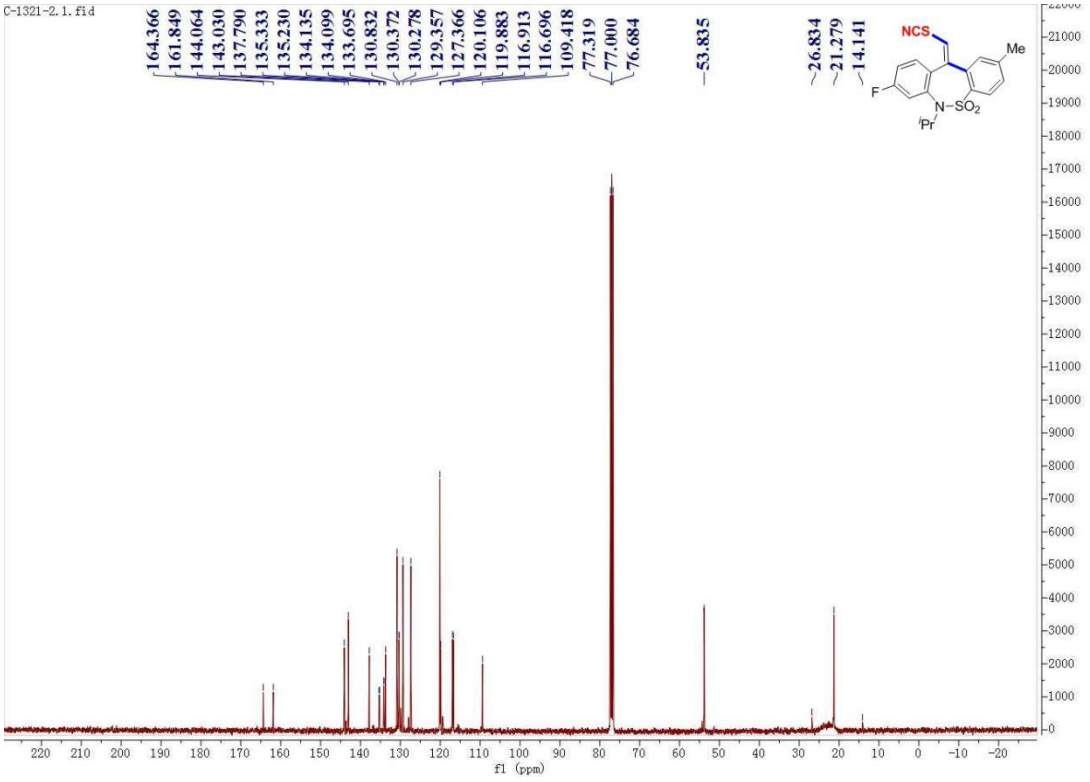
26-^{13}C NMR



27-^{1}H NMR



27-^{13}C NMR



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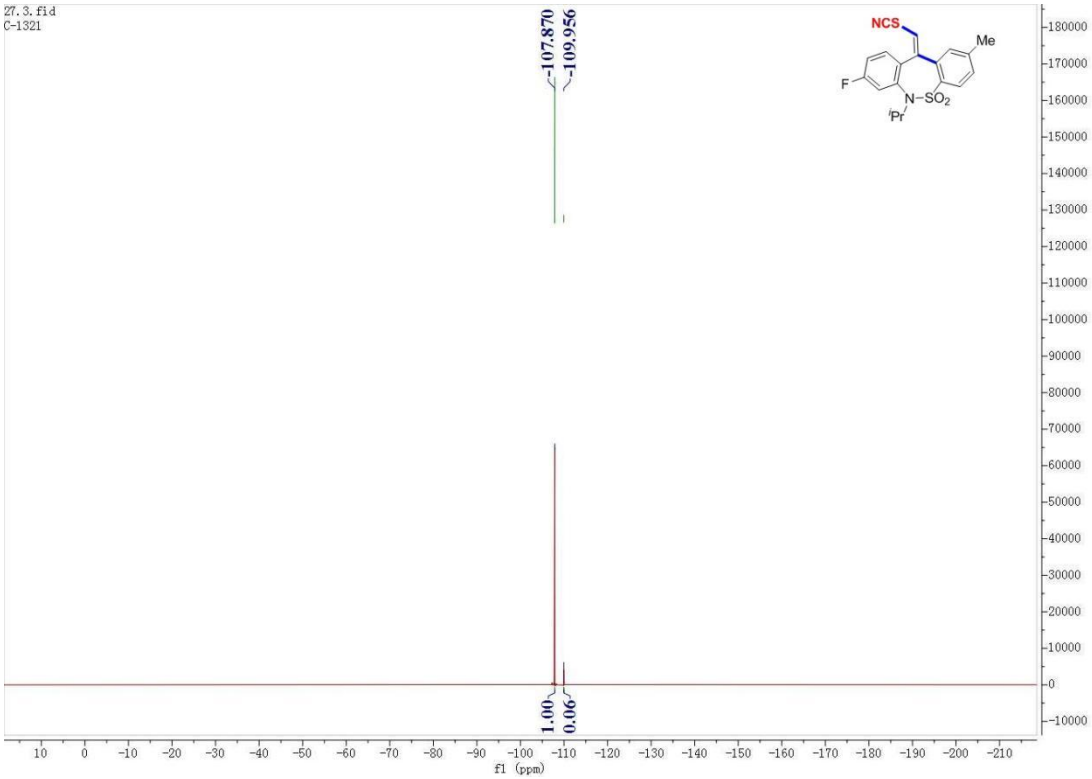
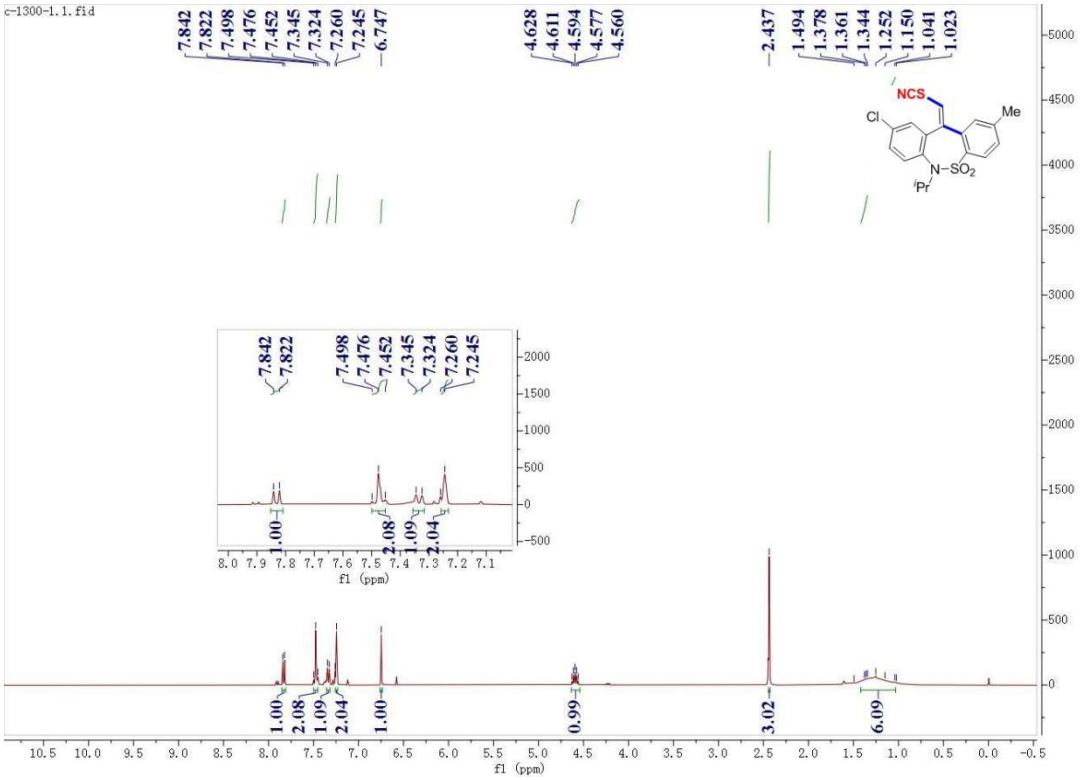
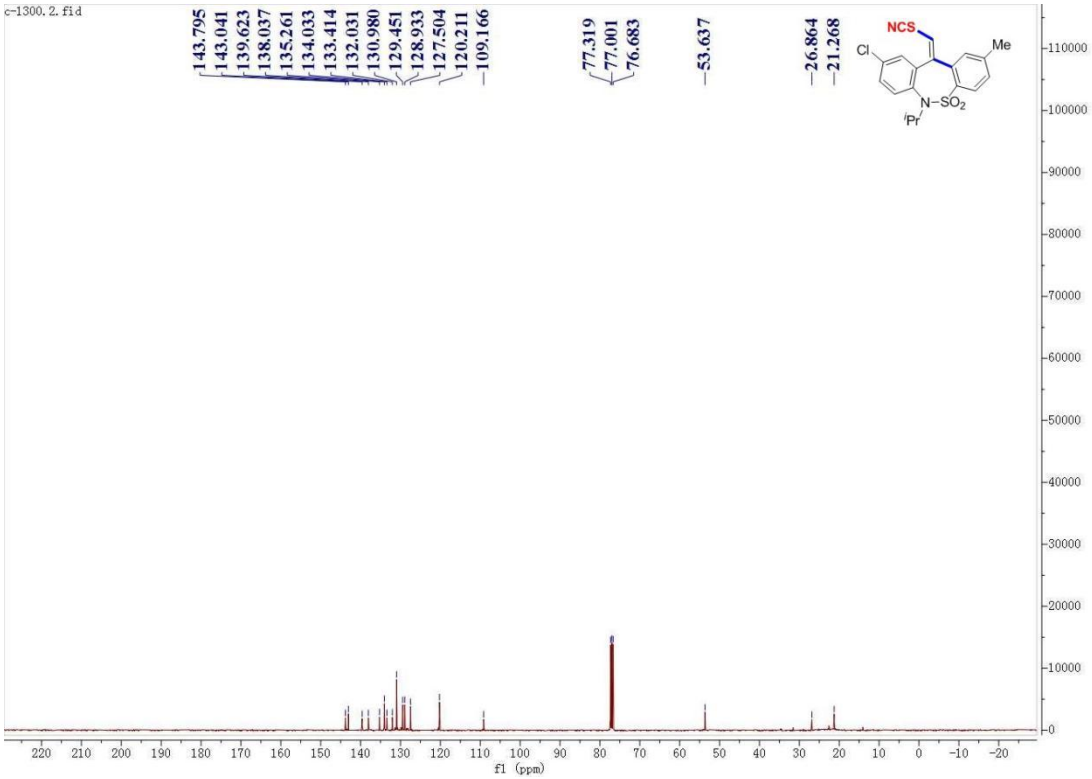


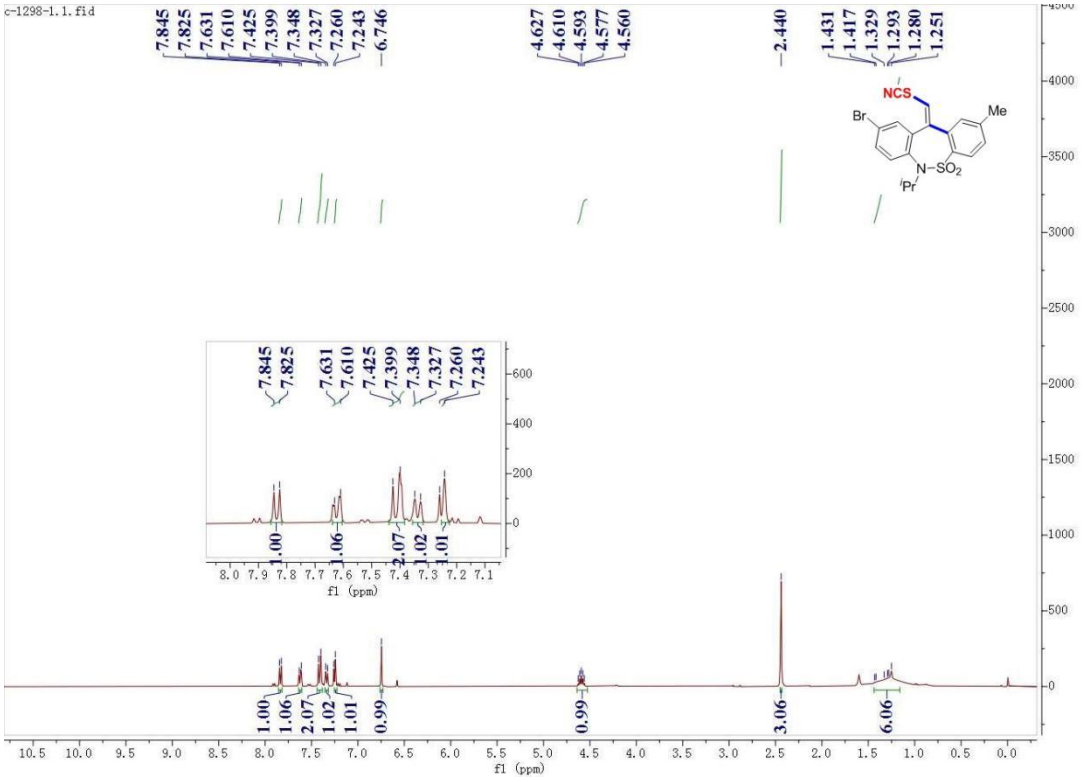
28-^{1}H NMR



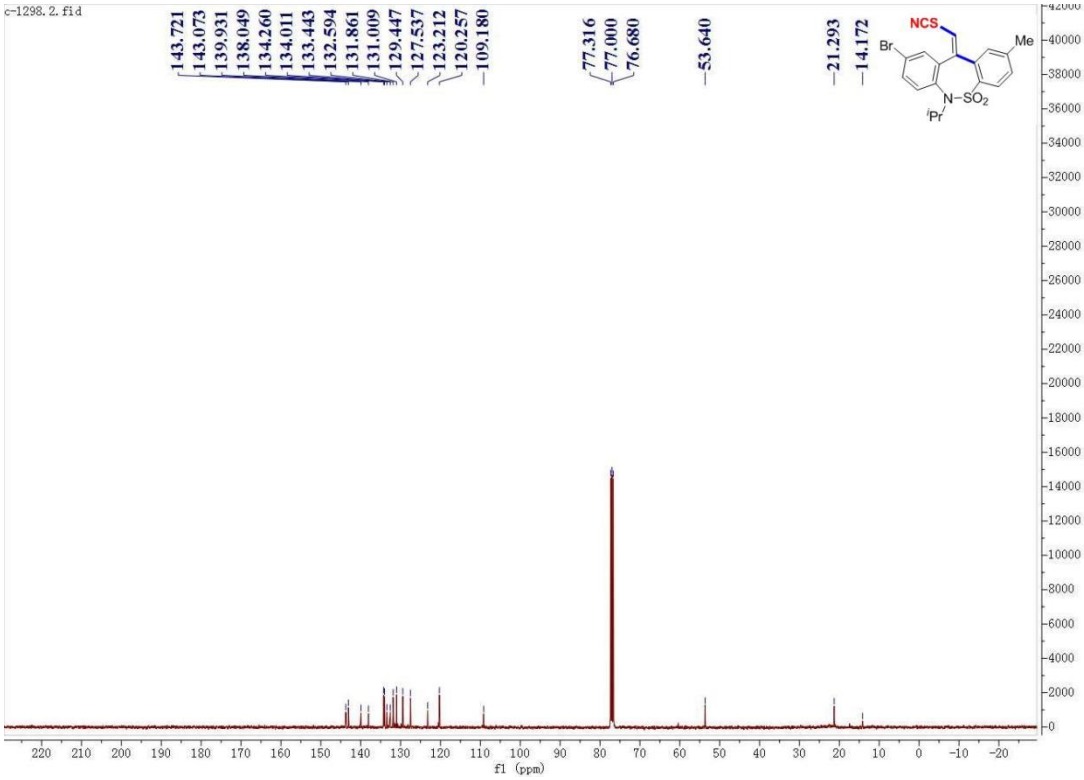
28-^{13}C NMR



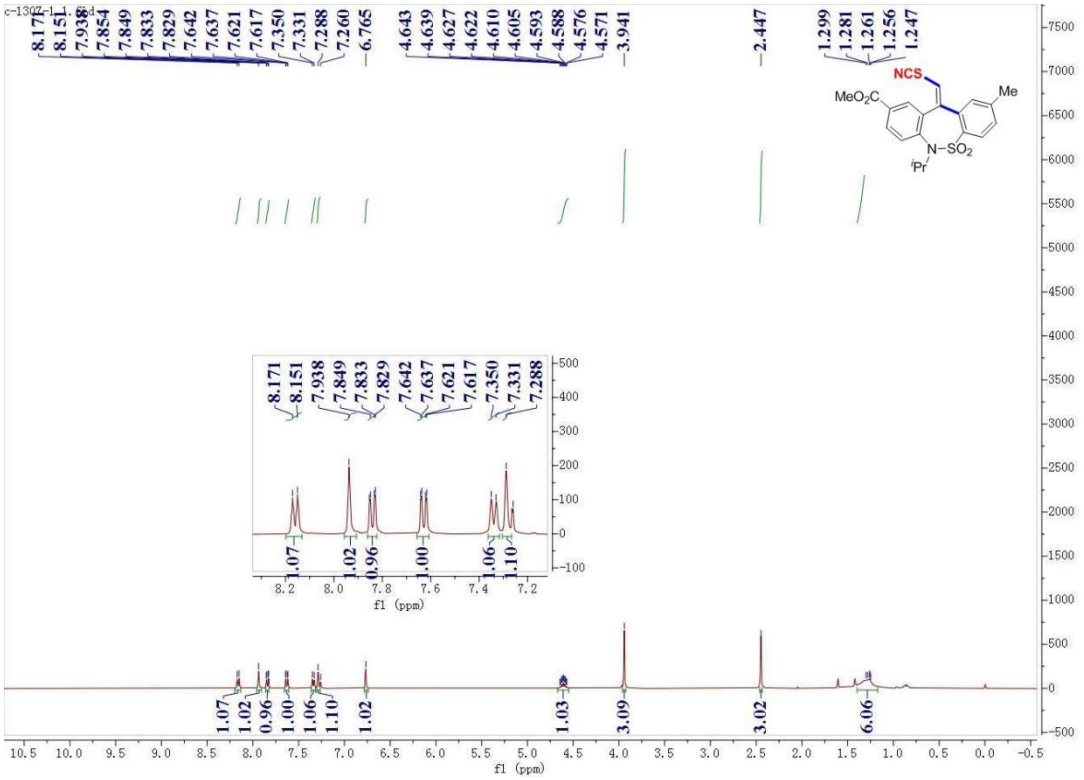
29-^{1}H NMR



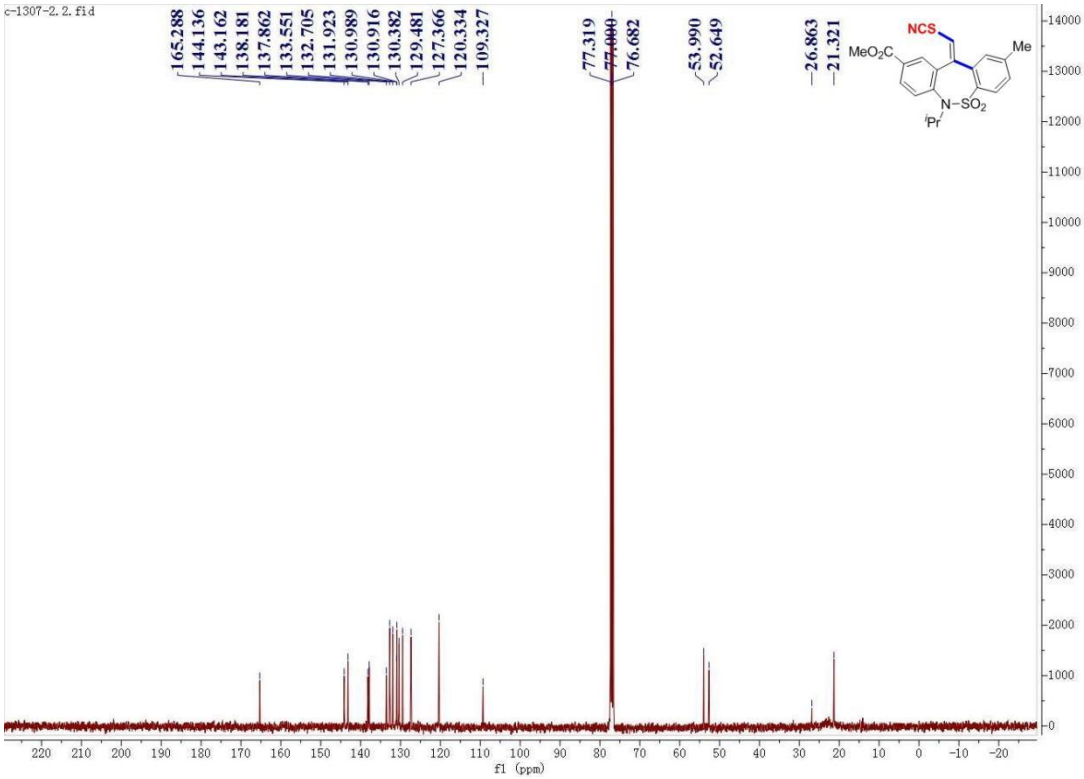
29-^{13}C NMR



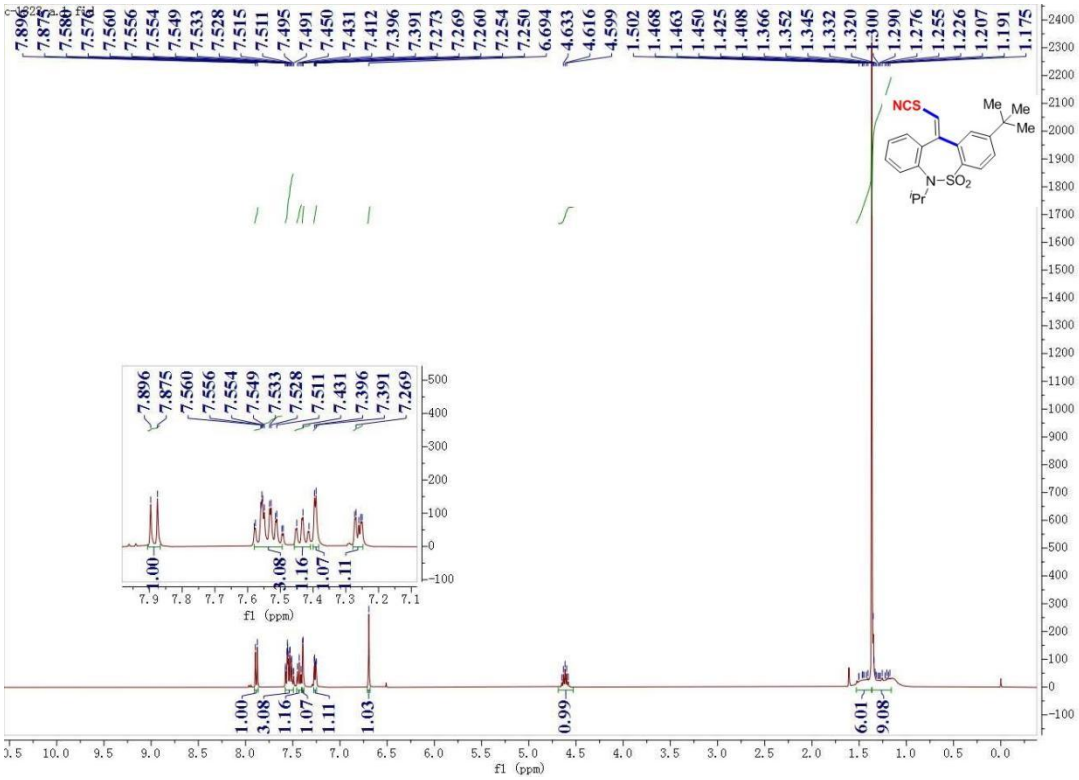
30-^{1}H NMR



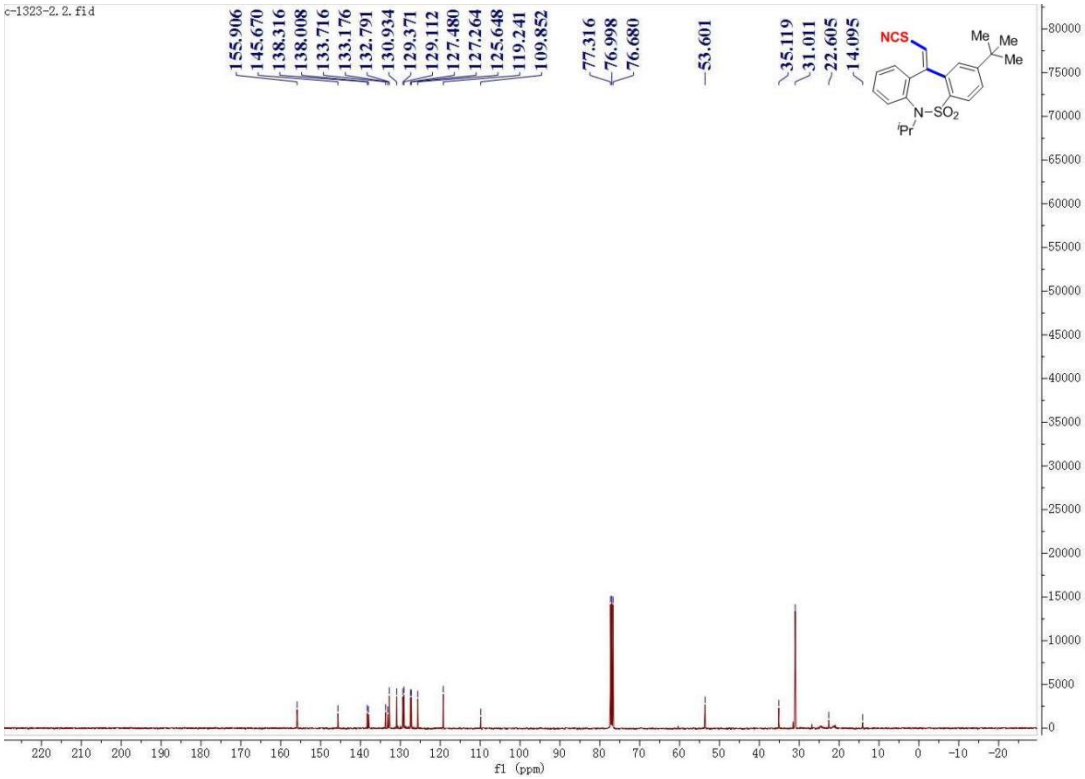
30-^{13}C NMR



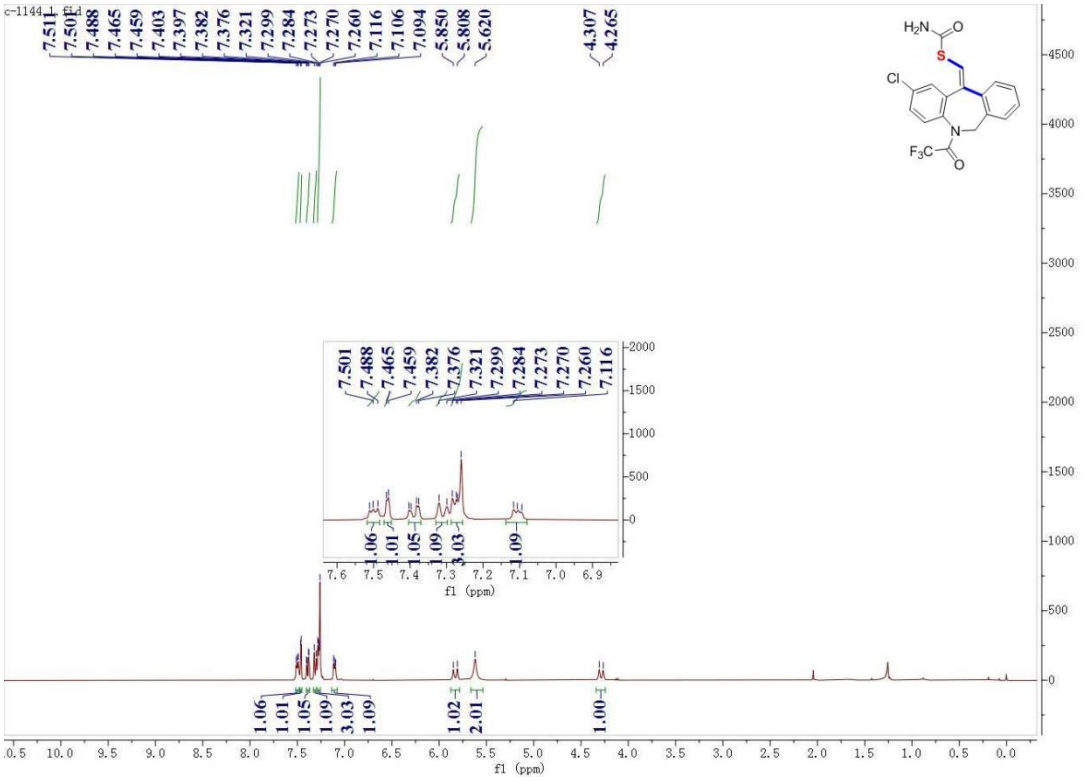
31-^{1}H NMR



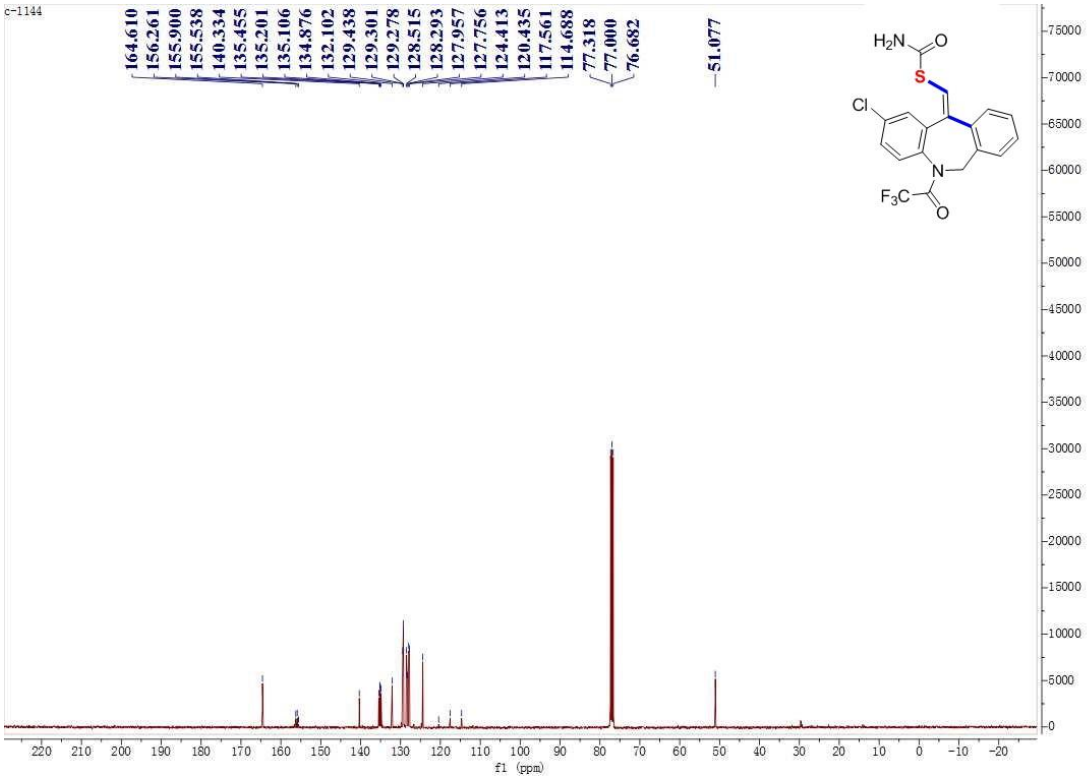
31-^{13}C NMR



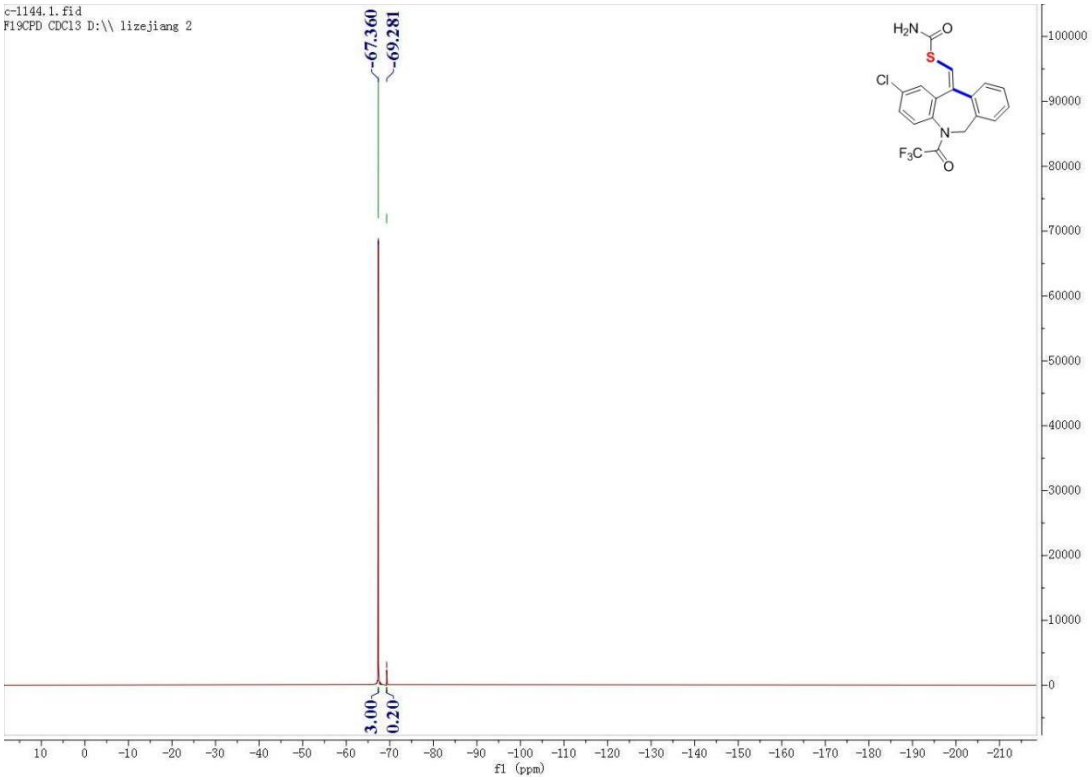
32-^{1}H NMR



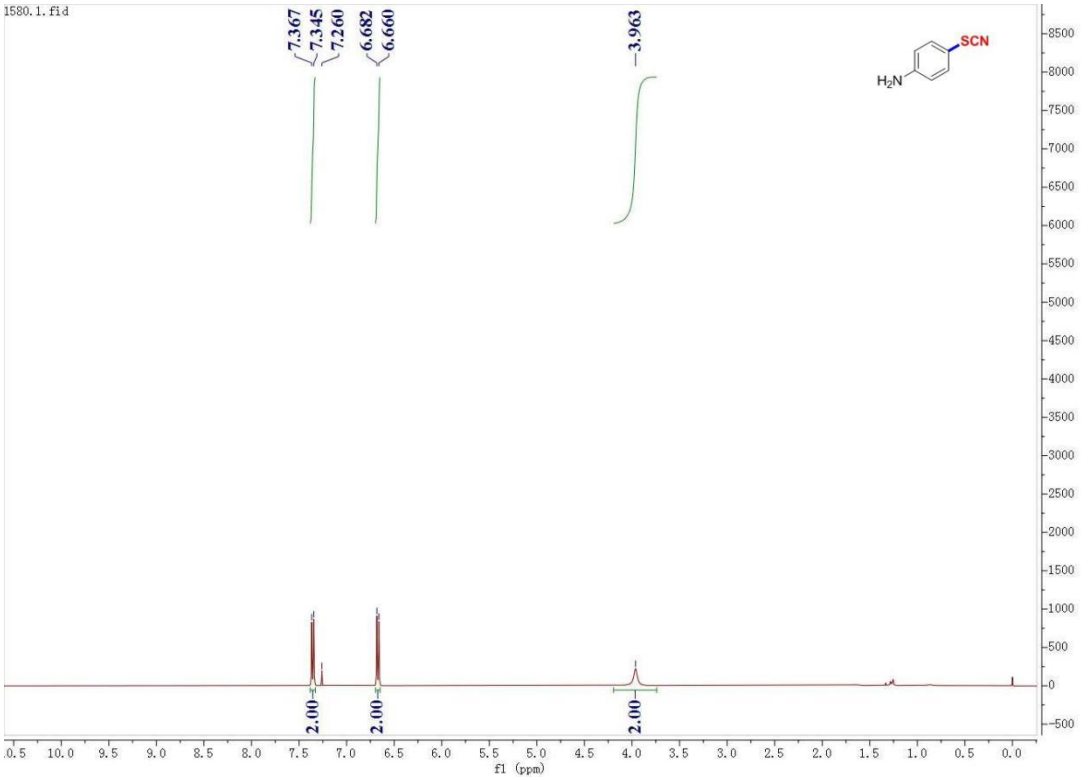
32-^{13}C NMR



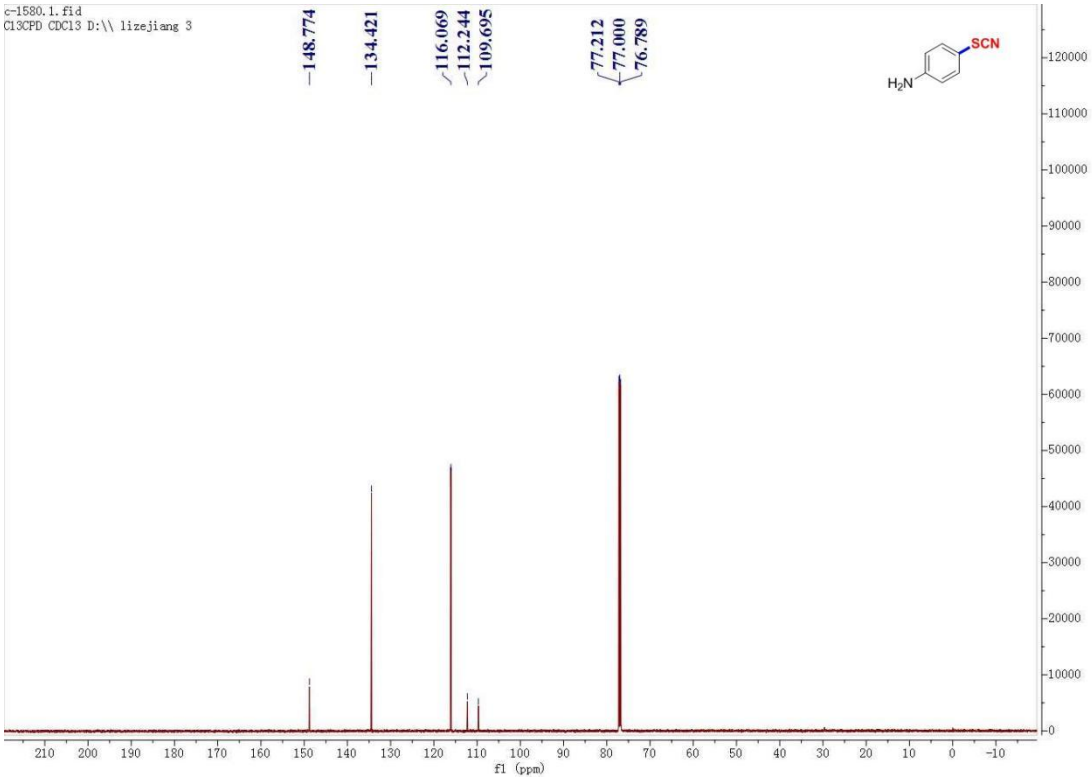
32-^{19}F NMR



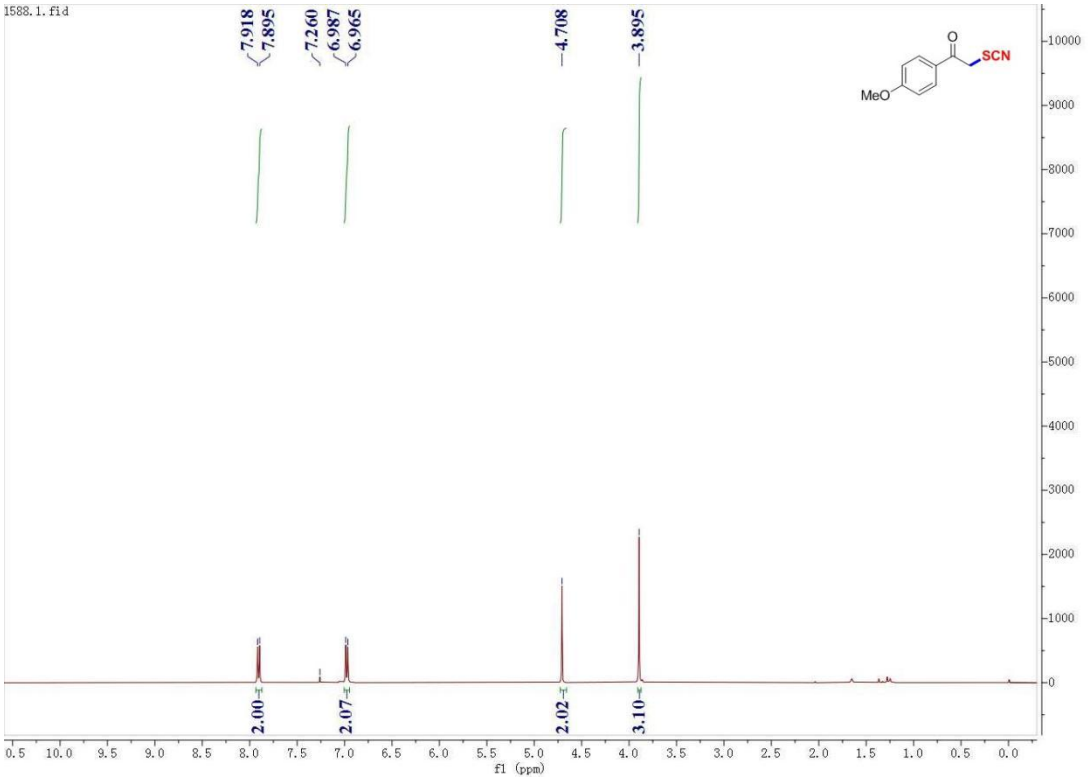
33-^{1}H NMR



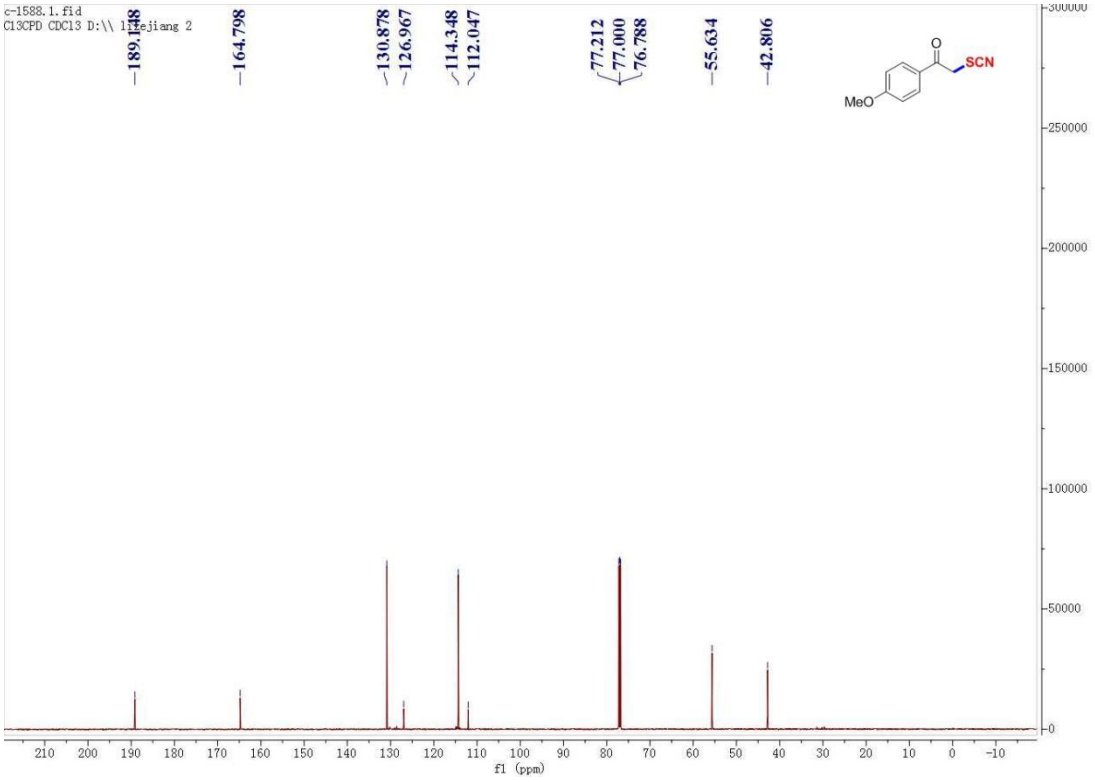
33-^{13}C NMR



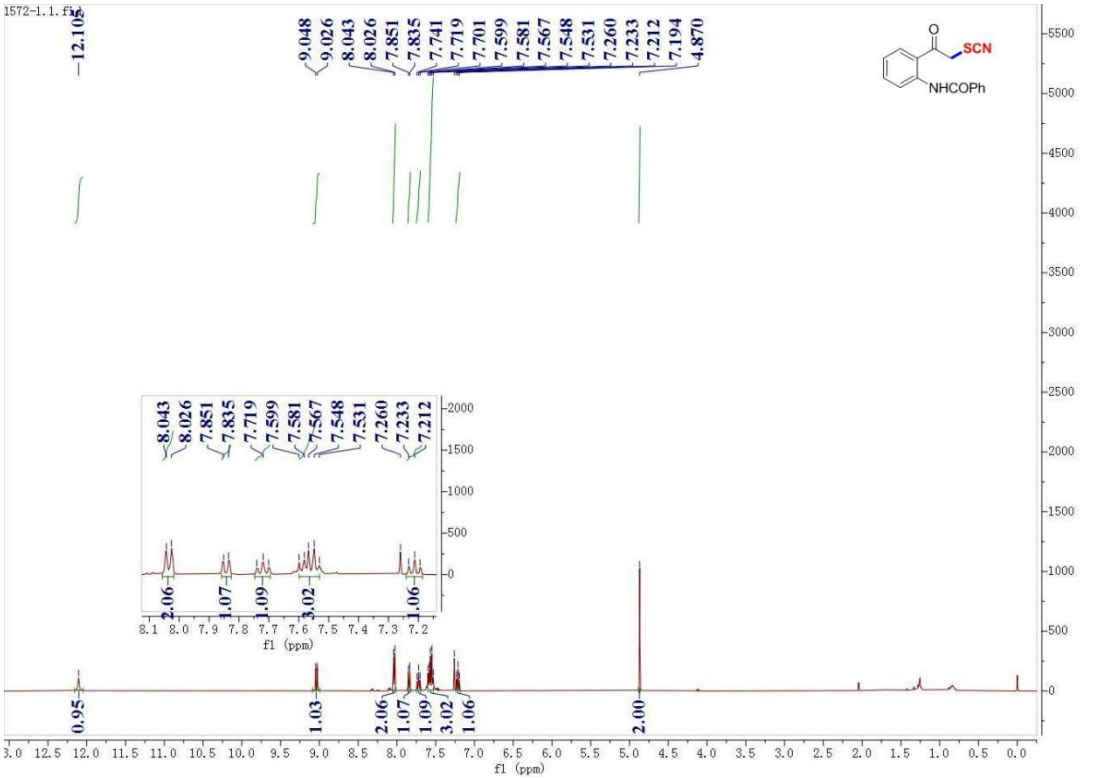
34-^{1}H NMR



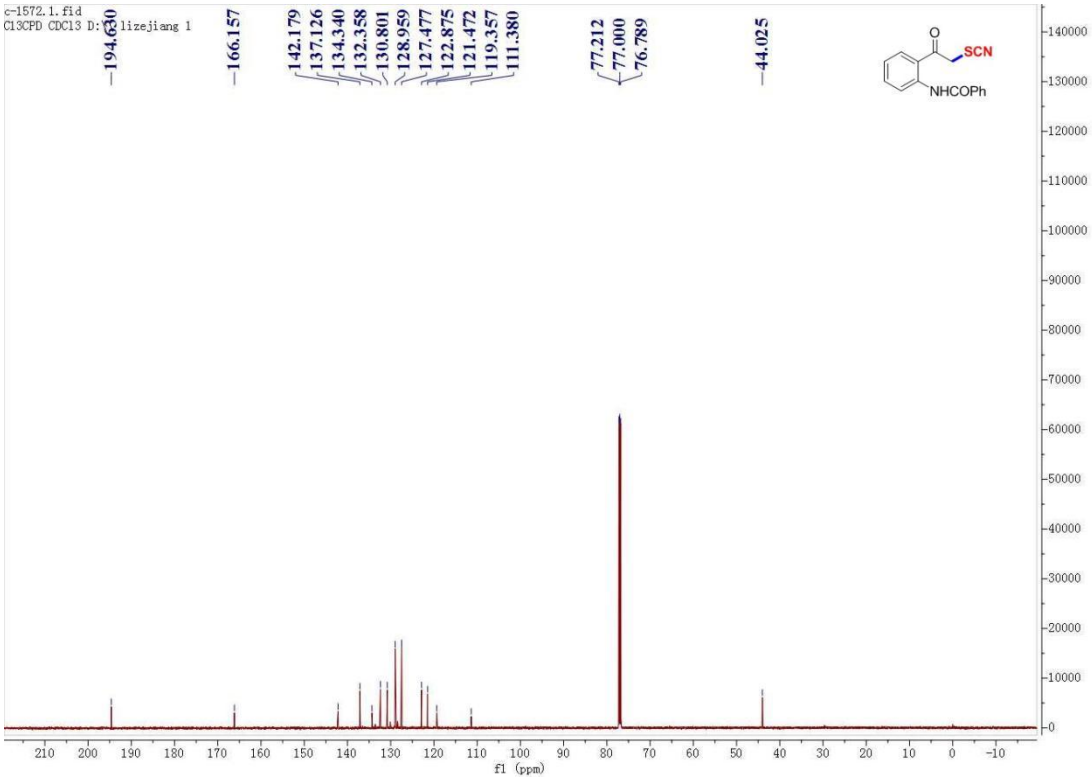
34-^{13}C NMR



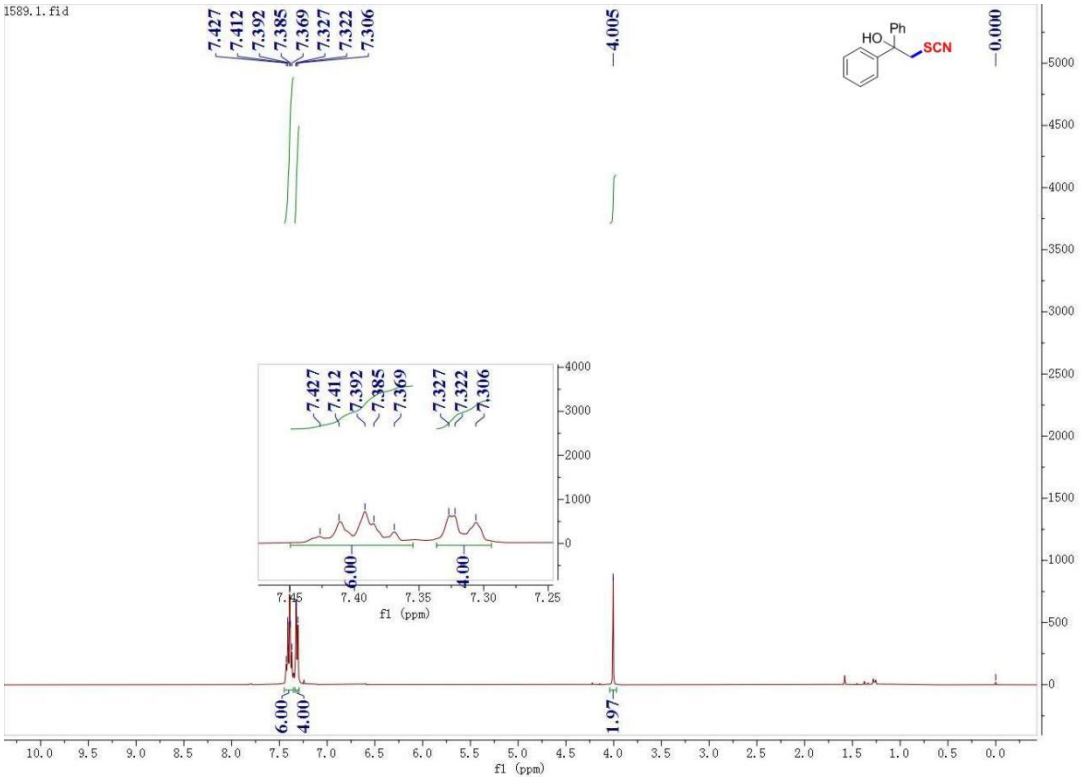
35-^{1}H NMR



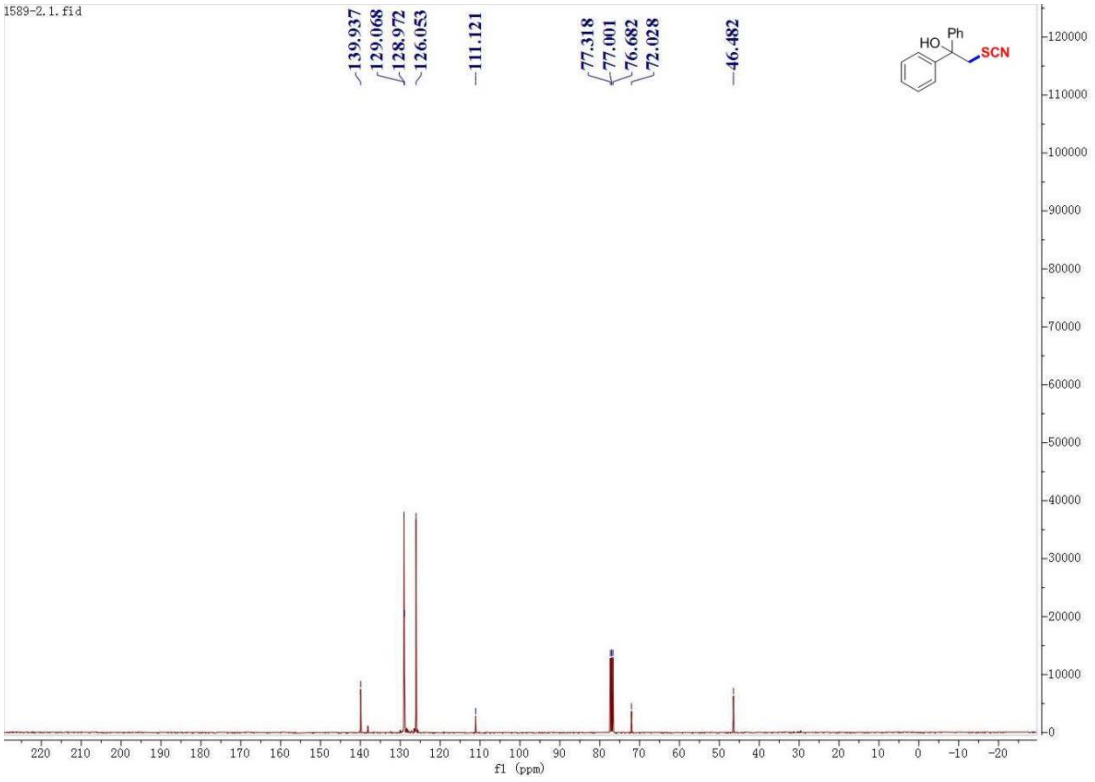
35-^{13}C NMR



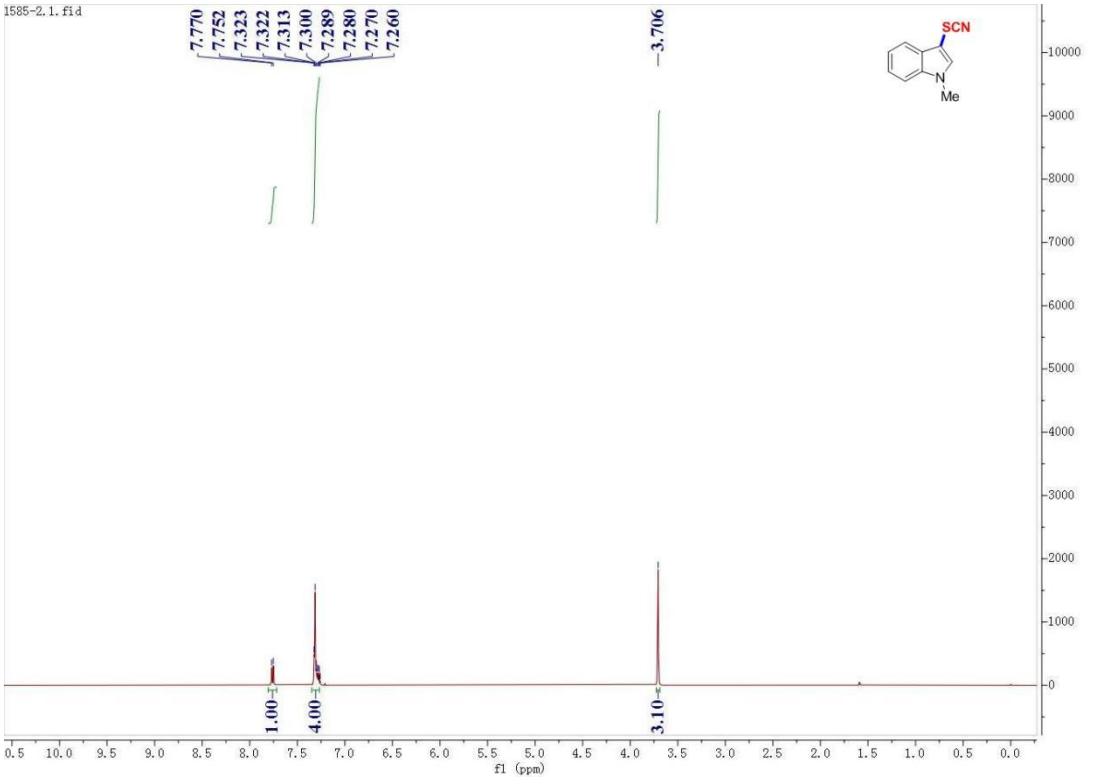
36-^{1}H NMR



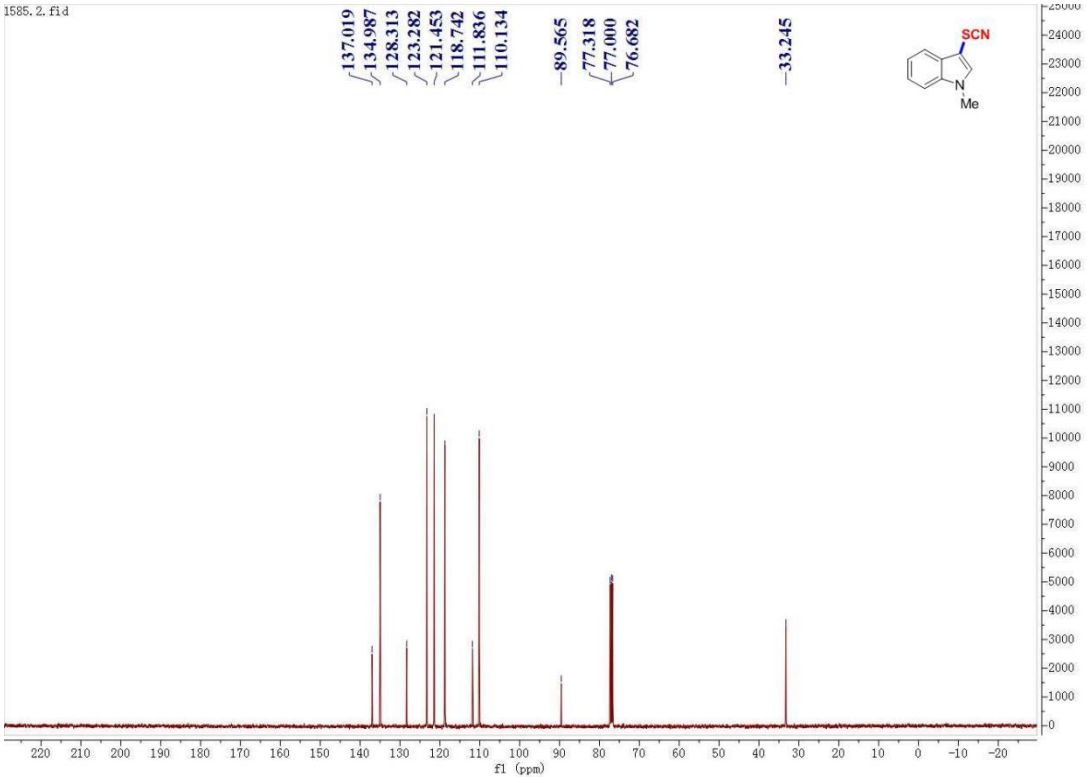
36-^{13}C NMR



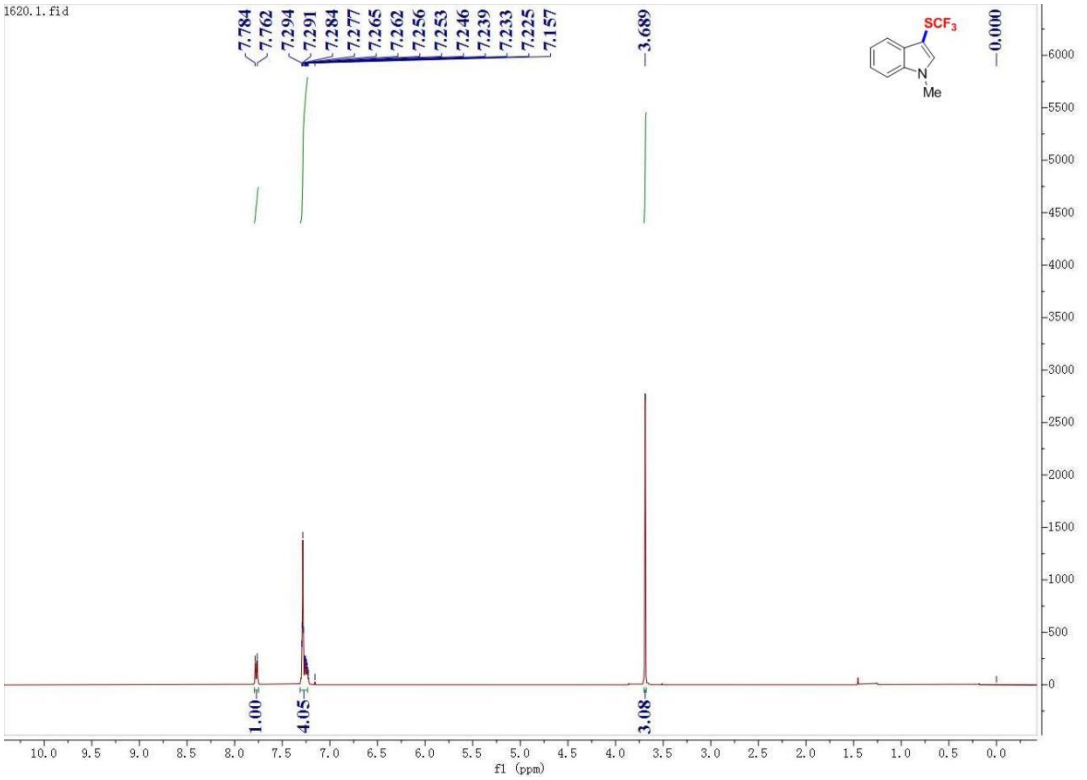
37-^{1}H NMR



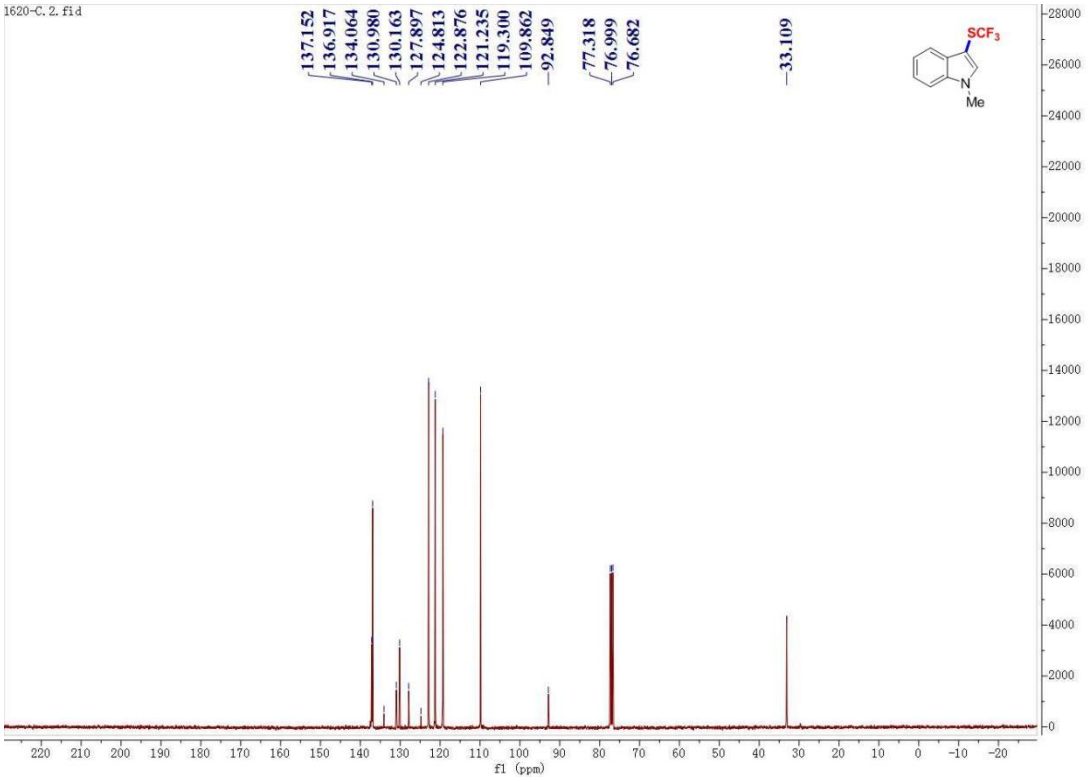
37-^{13}C NMR



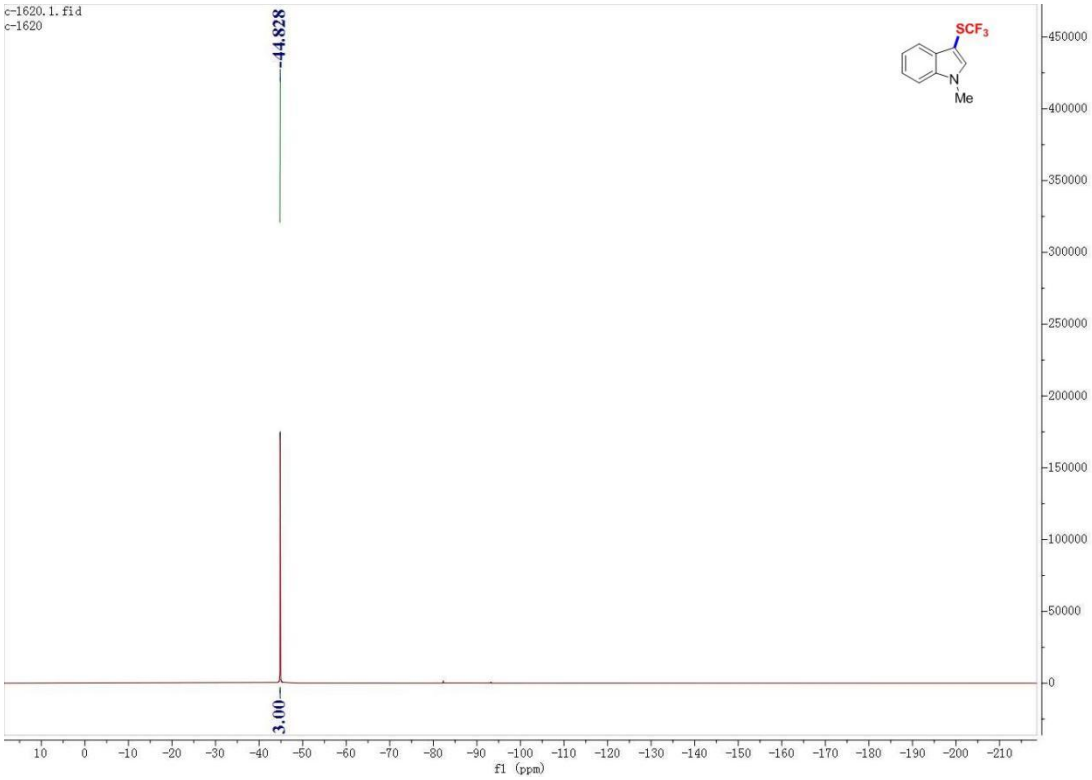
38-^{1}H NMR



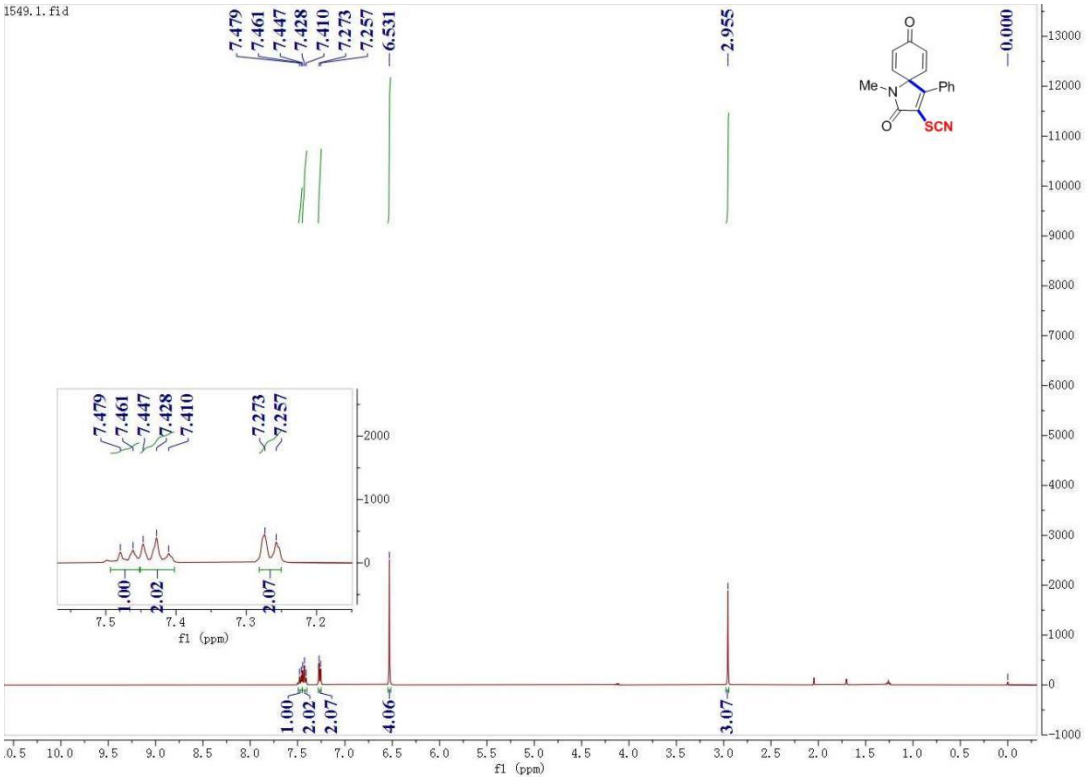
38-^{13}C NMR



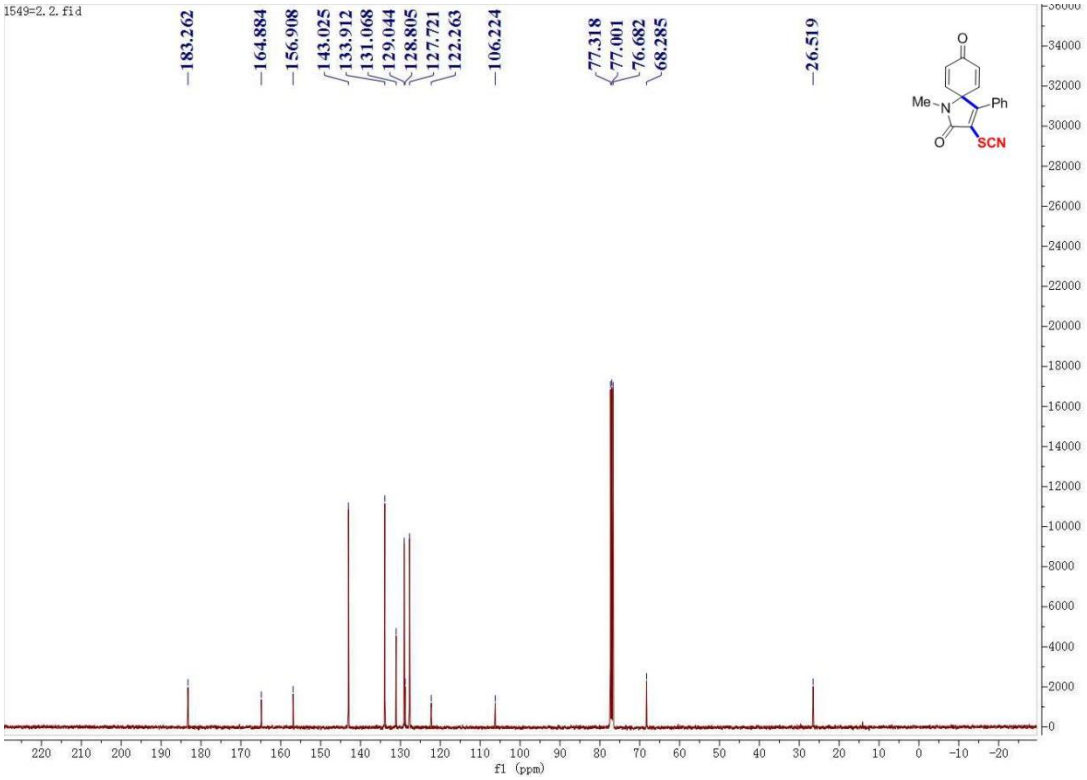
38-^{19}F NMR



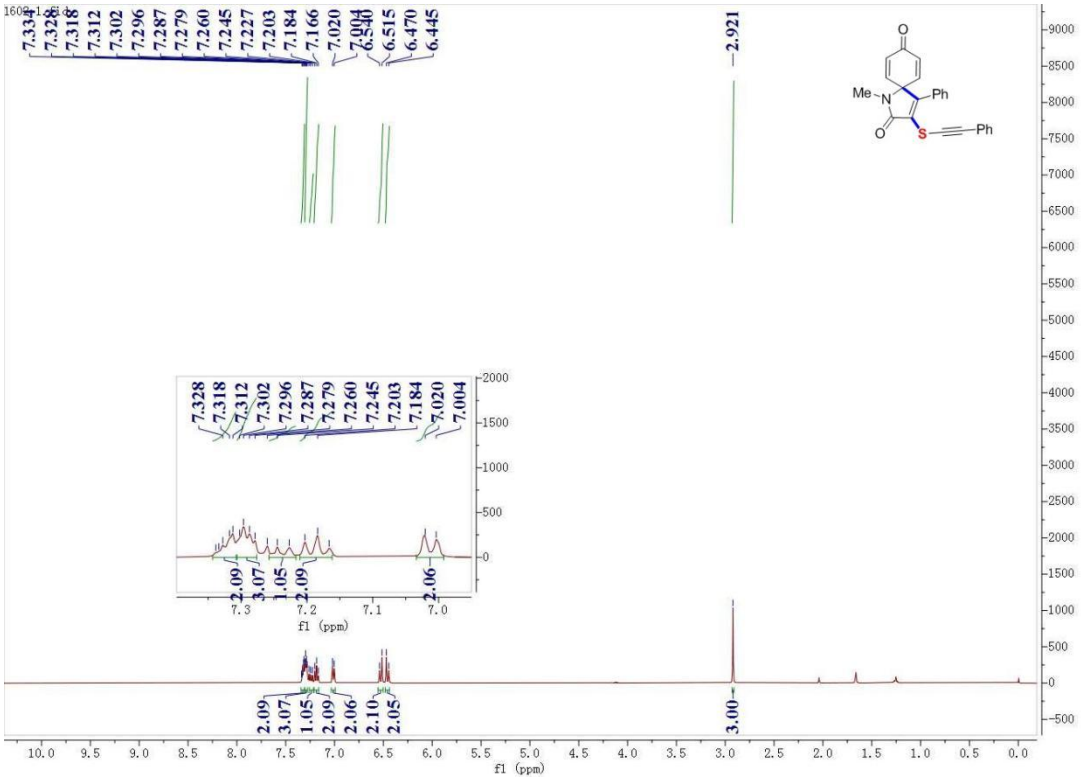
39-^{1}H NMR



39-^{13}C NMR



40-^{1}H NMR



40-^{13}C NMR