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Supporting Information

One-pot electrochemical synthesis of *N*-trifluoromethylthio sulfoximines from sulfoximines via *N*-SCN intermediates

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General information:

All products were characterized by ^{1}H NMR and ^{13}C NMR, using TMS as an internal reference (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). HRMS (ESI) data were recorded on a Q-TOF Premier. Flash column chromatography was performed using silica gel (200-300 mesh). All the compounds **1** were synthesized according to the previously reported procedures[1].

Experimental section

Representative procedures for the synthesis of N-thiocyanation sulfoximines (Synthesis of 2a as an example): An undivided cell was equipped with a magnet stirrer, two platinum plates (1.0 x 1.0 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of iminodiphenyl-λ^6-sulfanone **1a** (0.3 mmol, 65.1 mg, 1.0 equiv), NH_4SCN (0.6 mmol, 58.3 mg, 2.0 equiv), NH_4I (0.30 mmol, 43.5 mg, 1.0 equiv), CH_3CN (3.0 mL) was allowed to stir and electrolyze at a constant current condition (7 mA) at room temperature. After the reaction was completed (about 4.3 h), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **2a**. The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Representative procedures for the synthesis of N-trifluoromethylthio sulfoximines (3a as an example): An undivided cell was equipped with a magnet stirrer, two platinum plates (1.0 x 1.0 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of iminodiphenyl-λ^6-sulfanone **1a** (0.3 mmol, 65.1 mg, 1.0 equiv), NH_4SCN (0.6 mmol, 58.3 mg, 2.0 equiv), NH_4I (0.30 mmol, 43.5 mg, 1.0 equiv), CH_3CN (3.0 mL) was allowed to stir and electrolyze at a constant current condition (7 mA) at room temperature. After the reaction was completed (about 4.3 h), $AgSCF_3$ (0.3 mmol, 63.0 mg, 1.0 equiv) was added and stirred for 2 h. Then, the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3a**. The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Cyclic voltammetric (CV) studies:

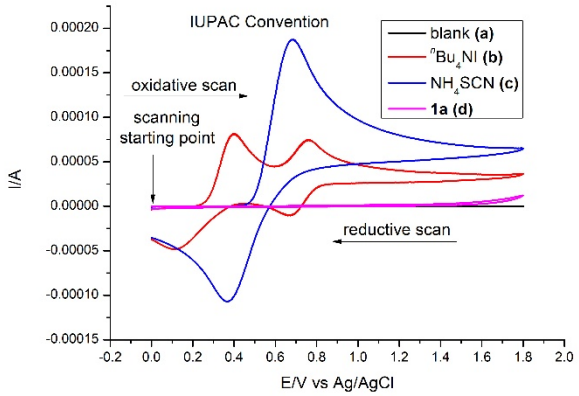


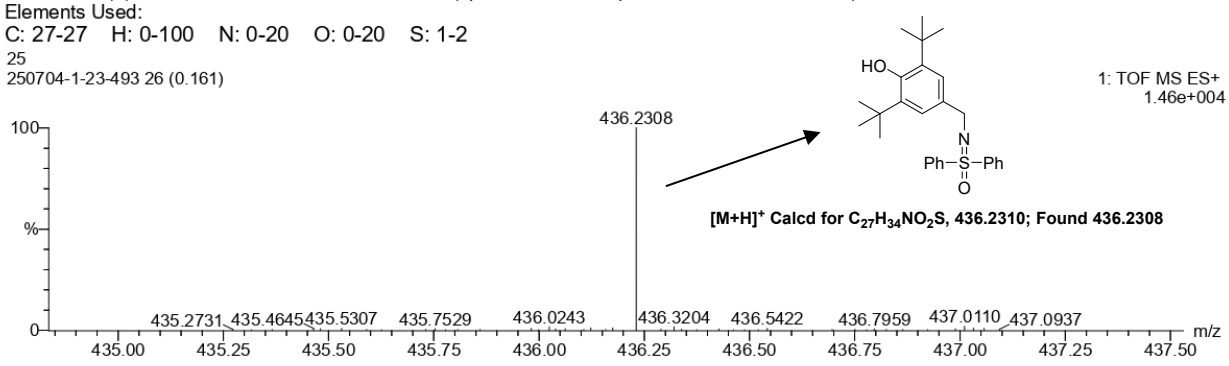
Fig S1 Cyclic voltammogram of 0.1 M NH_4BF_4 in CH_3CN (9.0 mL) using a Pt disk electrode as the working electrode, and Pt wire and Ag/AgCl as the counter and reference electrodes, respectively, at a scan rate of 50 mV/s. (a) background, (b) *n*-Bu_4NI (5 mM), (c) NH_4SCN (5 mM), (d) **1a** (5 mM).

Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
651 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 27-27 H: 0-100 N: 0-20 O: 0-20 S: 1-2



$[M+H]^+$ Calcd for $C_{27}H_{34}NO_2S$, 436.2310; Found 436.2308

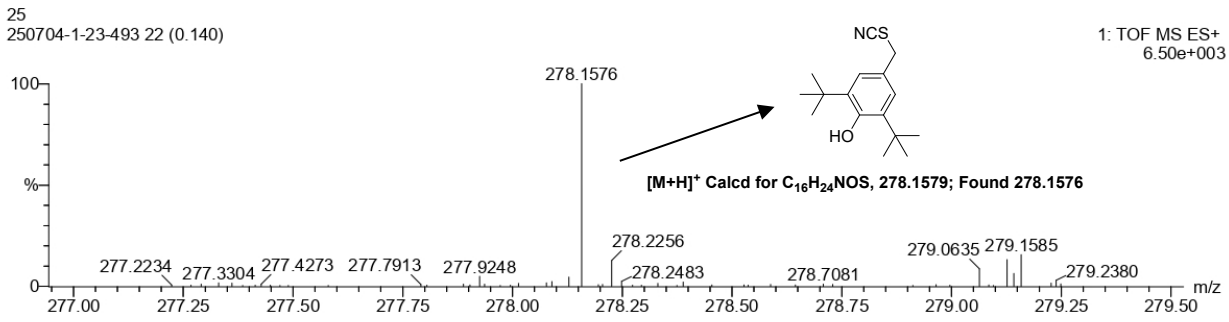
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
436.2308	436.2310	-0.2	-0.5	11.5	198.3	n/a	n/a	C27 H34 N 02 S

Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
267 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 0-100 N: 0-20 O: 0-20 S: 1-2



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
278.1576	278.1579	-0.3	-1.1	5.5	256.4	n/a	n/a	C16 H24 N O S

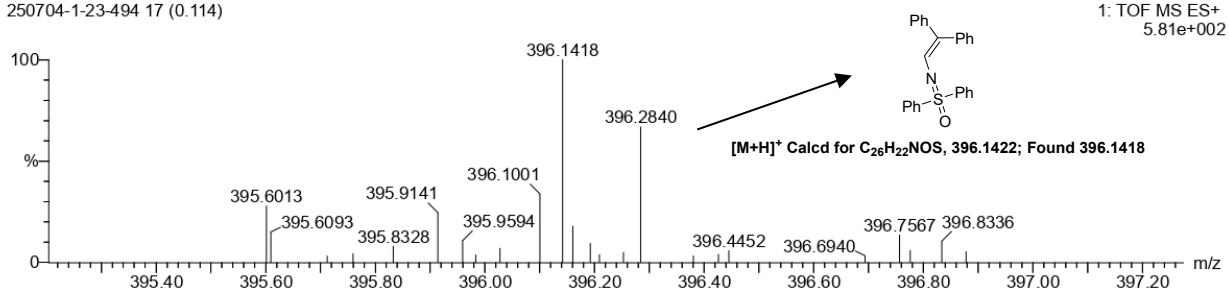
Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
564 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 26-26 H: 0-100 N: 0-20 O: 0-20 S: 1-2

25
250704-1-23-494 17 (0.114)

1: TOF MS ES+
5.81e+002



$[M+H]^+$ Calcd for $C_{26}H_{22}NOS$, 396.1422; Found 396.1418

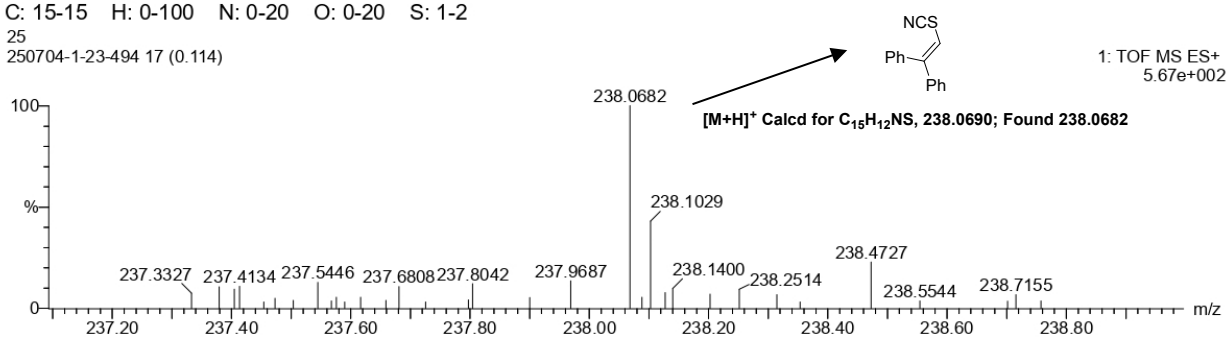
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
396.1418	396.1422	-0.4	-1.0	16.5	120.6	n/a	n/a	C26 H22 N O S

Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
187 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 15-15 H: 0-100 N: 0-20 O: 0-20 S: 1-2

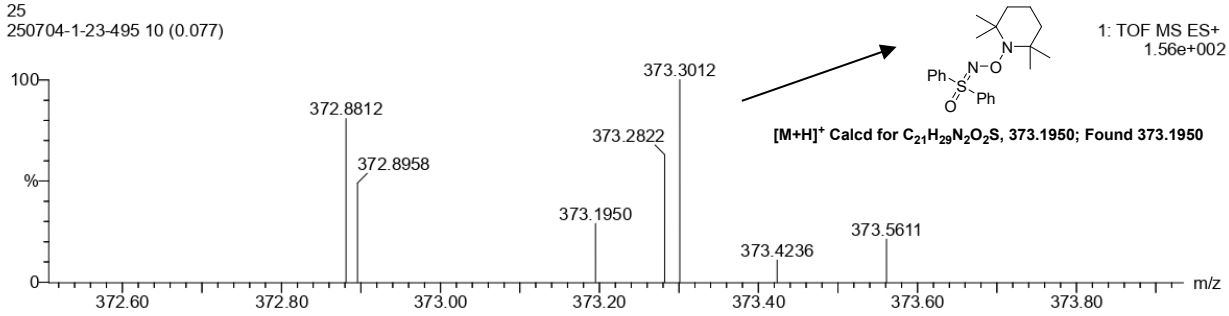


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
238.0682	238.0690	-0.8	-3.4	10.5	119.9	n/a	n/a	C15 H12 N S

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
501 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 21-21 H: 0-100 N: 0-20 O: 0-20 S: 1-2



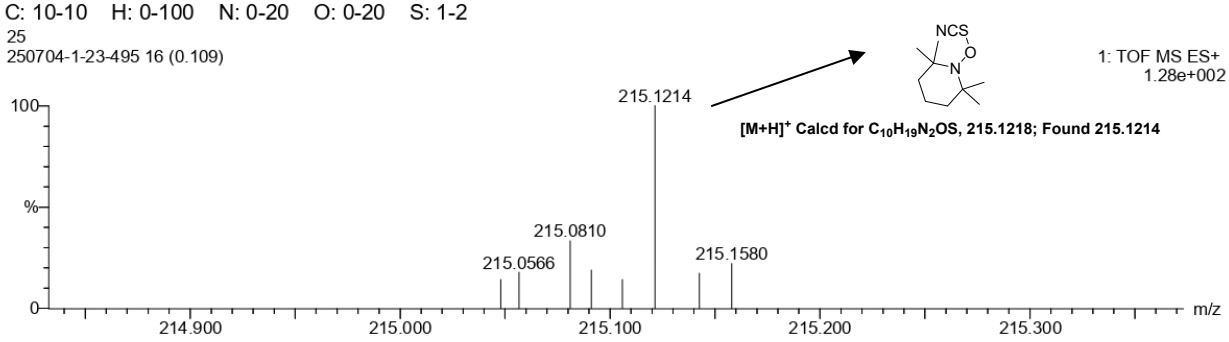
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
373.1950	373.1950	0.0	0.0	8.5	48.1	n/a	n/a	C21 H29 N2 O2 S

Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
148 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 10-10 H: 0-100 N: 0-20 O: 0-20 S: 1-2

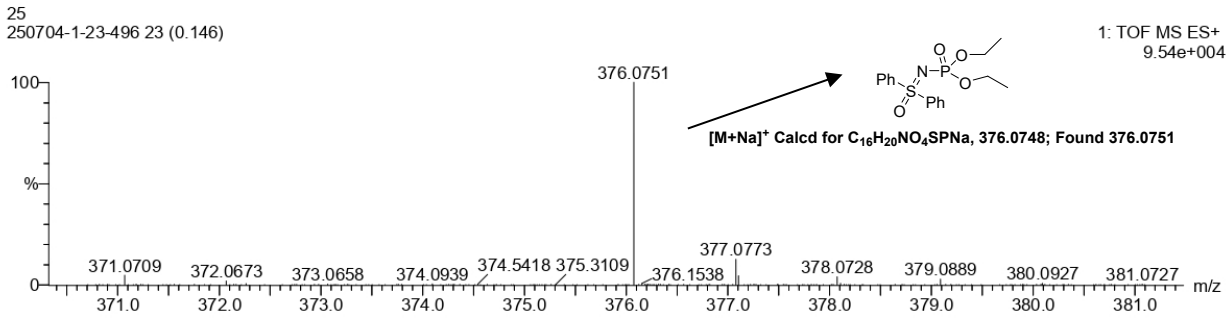


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
215.1214	215.1218	-0.4	-1.9	2.5	30.5	n/a	n/a	C10 H19 N2 O S

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1353 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-16 H: 0-100 N: 0-20 O: 0-20 S: 1-2 P: 0-3 Na: 1-1



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
376.0751	376.0748	0.3	0.8	7.5	511.3	n/a	n/a	C16 H20 N 04 S P Na

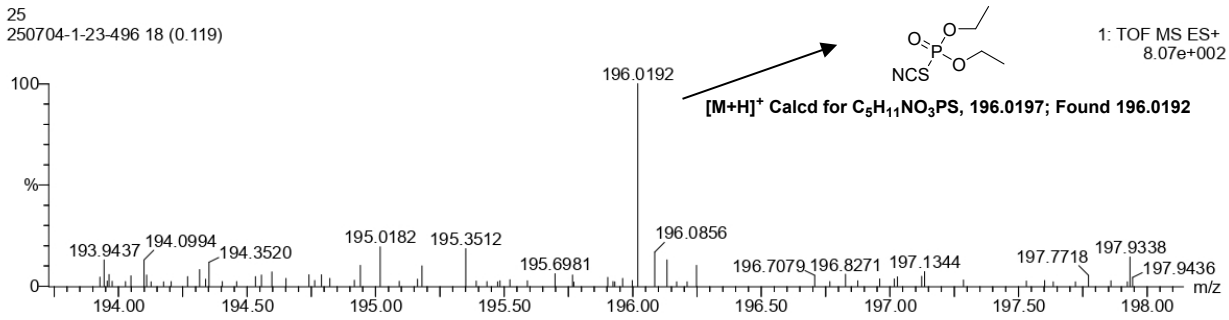
Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
252 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 5-5 H: 0-100 N: 0-20 O: 0-20 P: 0-3 S: 1-2

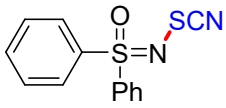
25
250704-1-23-496 18 (0.119)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
196.0192	196.0197	-0.5	-2.6	1.5	176.4	n/a	n/a	C5 H11 N O3 P S

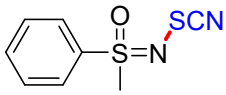
Detail descriptions for products

Diphenyl(thiocyanatoimino)- λ^6-sulfanone (**2a**) [2]



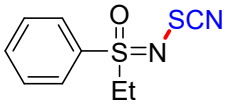
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 88% yield (72.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.98 (d, J = 8.0 Hz, 4H), 7.67-7.64 (m, 2H), 7.58 (t, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 137.7, 134.3, 129.8, 128.6, 115.3.

Methyl(phenyl)(thiocyanatoimino)- λ^6-sulfanone (**2b**) [2]



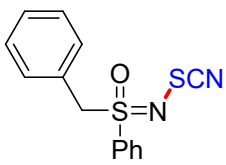
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 66% yield (41.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.94-7.91 (m, 2H), 7.77-7.73 (m, 1H), 7.68-7.64 (m, 2H), 3.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 135.9, 134.9, 130.1, 128.7, 115.4, 43.9.

Ethyl(phenyl)(thiocyanatoimino)- λ^6-sulfanone (**2c**) [2]



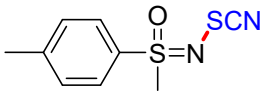
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 64% yield (43.3 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.89-7.86 (m, 2H), 7.76-7.73 (m, 1H), 7.66 (t, J = 8.0 Hz, 1H), 3.51-3.32 (m, 2H), 1.30 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 134.9, 133.9, 130.0, 129.4, 115.6, 50.6, 7.2.

Benzyl(phenyl)(thiocyanatoimino)- λ^6 -sulfanone (**2d**) [2]



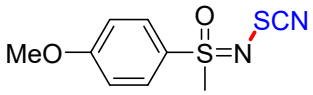
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 65% yield (55.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.70-7.65 (m, 1H), 7.63-7.60 (m, 2H), 7.54-7.50 (m, 2H), 7.35-7.31 (m, 1H), 7.26-7.22 (m, 2H), 7.04-7.01 (m, 2H), 4.65 (d, J = 16.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 134.8, 133.4, 131.3, 129.8, 129.6, 128.8, 126.3, 115.6, 62.5.

Methyl(thiocyanatoimino)(p-tolyl)- λ⁶-sulfanone (**2e**) [2]



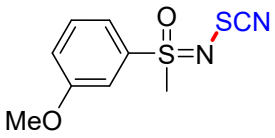
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 95% yield (64.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.78 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 3.28 (s, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 146.2, 132.6, 130.7, 128.7, 115.5, 44.0, 21.8.

(4-Methoxyphenyl)(methyl)(thiocyanatoimino)- λ⁶-sulfanone (**2f**) [2]



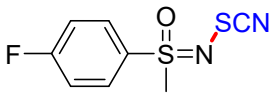
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 84% yield (60.7 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.84-7.81 (m, 2H), 7.12-7.08 (m, 2H), 3.91 (s, 3H), 3.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 164.7, 131.0, 126.4, 115.7, 115.3, 56.0, 44.3.

(3-Methoxyphenyl)(methyl)(thiocyanatoimino)- λ⁶-sulfanone (**2g**) [2]



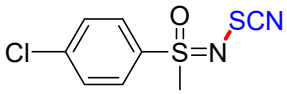
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 51% yield (37.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.56 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.27-7.24 (m, 1H) 3.91 (s, 3H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 160.7, 137.0, 131.1, 121.5, 120.7, 115.4, 113.0, 56.0, 44.0.

(4-Fluorophenyl)(methyl)(thiocyanatoimino)- λ⁶-sulfanone (**2h**) [2]



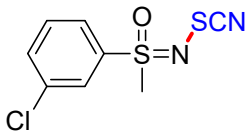
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 81% yield (56.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.97-7.92 (m, 2H), 7.37-7.32 (m, 2H), 3.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 166.6 (d, J = 257.0 Hz), 131.7 (d, J = 9.0 Hz), 131.5 (d, J = 3.0 Hz), 117.6 (d, J = 22.0 Hz), 115.3, 44.1. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = 101.1.

(4-Chlorophenyl)(methyl)(thiocyanatoimino)- λ^6-sulfanone (**2i**) [2]



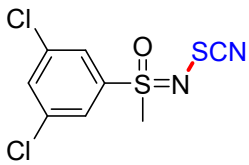
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 80% yield (58.8 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.88-7.84 (m, 2H), 7.65-7.61 (m, 2H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 141.9, 134.3, 130.4, 130.2, 115.2, 44.0.

(3-Chlorophenyl)(methyl)(thiocyanatoimino)- λ^6-sulfanone (**2j**) [2]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 65% yield (48.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.92-7.91 (m, 2H), 7.81-7.79 (m, 1H), 7.73-7.70 (m, 1H), 7.61 (t, J = 8.0 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 137.7, 136.4, 135.1, 131.3, 128.8, 126.8, 115.0, 43.9.

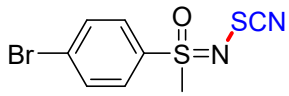
(3,5-Dichlorophenyl)(methyl)(thiocyanatoimino)- λ^6-sulfanone (**2k**) [2]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 83% yield (69.9

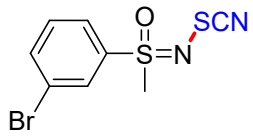
mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.80-7.79 (m, 2H), 7.71-7.70 (m, 1H), 3.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 139.1, 137.2 134.9, 127.0, 114.7, 43.9.

(4-Bromophenyl)(methyl)(thiocyanatoimino)- λ^6-sulfanone (**2l**) [2]



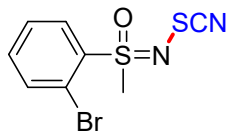
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 77% yield (67.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.82-7.77 (m, 4H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 135.0, 133.5, 130.6, 130.2, 115.2, 44.0.

(3-Bromophenyl)(methyl)(thiocyanatoimino)- λ^6-sulfanone (**2m**) [2]



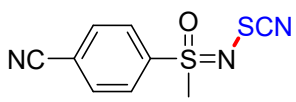
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1) to give the product as a colorless oil in 86% yield (75.5 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.07-8.06 (m, 1H), 7.88-7.83 (m, 2H), 7.54 (t, J = 8.0 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 137.8, 137.9, 131.6, 131.5, 127.2, 124.1, 115.0, 43.9.

(2-Bromophenyl)(methyl)(thiocyanatoimino)- λ^6-sulfanone (**2n**) [2]



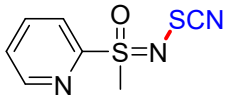
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 79% yield (68.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.28-8.25 (m, 1H), 7.84-7.82 (m, 1H), 7.66-7.56 (m, 2H), 3.55 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 136.2, 136.0, 134.8, 133.5, 128.7, 120.7, 114.3, 42.0.

4-(S-methyl-N-thiocyanatosulfonimidoyl)benzonitrile (**2o**) [2]



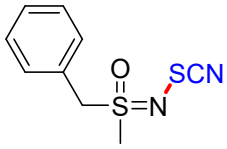
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 51% yield (36.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.07 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 3.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 140.4, 133.7, 129.5, 118.6, 116.9, 114.7, 43.7.

Methyl(pyridin-2-yl)(thiocyanatoimino)-λ^6-sulfanone (**2p**)



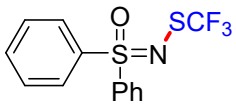
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1) to give the product as a colorless oil in 78% yield (53.3 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.79-8.78 (m, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.09-8.05 (m, 1H), 7.66-7.62 (m, 1H), 3.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 154.1, 150.9, 138.5, 128.3, 124.3, 114.9, 39.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_7H_8N_3OS_2$ 214.0109; Found: 214.0104.

Benzyl(methyl)(thiocyanatoimino)-λ^6-sulfanone (**2q**)



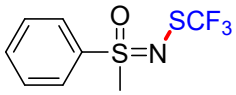
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 56% yield (37.8 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.47-7.40 (m, 5H), 4.62 (d, J = 16.0 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 131.0, 130.1, 129.6, 126.8, 116.4, 60.1, 37.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{11}N_2OS_2$ 227.0313; Found: 227.0263.

Diphenyl(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3a**) [3]



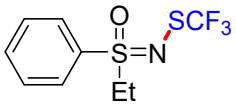
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 58% yield (55.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.98-7.95 (m, 4H), 7.63-7.58 (m, 2H), 7.55-7.52 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 139.0, 133.8, 130.5 (q, J = 311.0 Hz), 129.8, 128.5. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.4.

Methyl(phenyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3b**) [3]



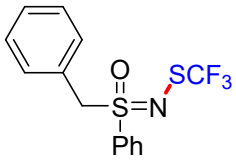
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 56% yield (42.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.91-7.89 (m, 2H), 7.72-7.68 (m, 1H), 7.63-7.59 (m, 2H) , 3.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 137.8, 134.4, 130.5 (q, J = 311.0 Hz), 129.8, 128.4, 43.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.7.

Ethyl(phenyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3c**) [3]



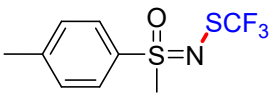
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a pale yellow oil in 41% yield (32.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.86-7.84 (m, 2H), 7.70 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 2H), 3.53-3.43 (m, 1H) , 3.39-3.27 (m, 1H) , 1.29-1.26 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 135.9, 134.3, 133.5 (q, J = 280.0 Hz), 129.8, 129.1, 50.5, 7.5. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.7.

Benzyl(phenyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3d**)



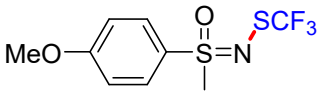
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 41% yield (40.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.64-7.60 (m, 1H), 7.58-7.56 (m, 2H), 7.49-7.45 (m, 2H), 7.32-7.28 (m, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.00-6.98 (m, 2H), 4.70-4.67 (m, 1H), 4.50-4.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 135.1, 134.3, 131.3, 130.5 (q, J = 311.0 Hz), 129.5, 129.3, 128.7, 127.2, 62.3. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}F_3NOS_2$ 332.0391; Found: 332.0381.

Methyl(p-tolyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3e**) [3]



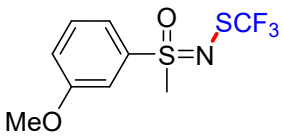
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 43% yield (34.5 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.25 (s, 3H) , 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 145.6, 134.6, 130.5 (q, J = 311.0 Hz), 130.5, 128.4, 43.8, 21.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.7.

(4-Methoxyphenyl)(methyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3f**) [3]



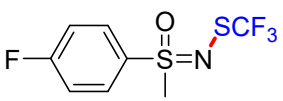
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a colorless oil in 53% yield (45.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.82-7.79 (m, 2H), 7.06-7. 04 (m, 2H), 3.89 (s, 3H) , 3.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 164.3, 130.6, 130.5 (q, J = 310.0 Hz), 128.6, 115.0, 55.9, 44.0. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.7.

(3-Methoxyphenyl)(methyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3g**) [3]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a colorless oil in 42% yield (35.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.51 (t, J = 8.0 Hz, 1H), 7.46-7.44 (m, 1H), 7.39-7.38 (m, 1H) , 7.21-7.19 (m, 1H), 3.88 (s, 3H), 3.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 160.5, 139.0, 130.9, 130.5 (q, J = 310.0 Hz), 120.8, 120.3, 112.9, 55.9, 43.8. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.7.

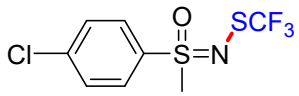
(4-Fluorophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3h**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 63% yield (51.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.95-7.91 (m, 2H), 7.31-7.27 (m, 2H), 3.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 166.3 (d, J = 256.0 Hz), 133.7 (d, J = 3.0 Hz), 131.3 (d, J = 10.0 Hz), 130.4 (q, J = 311.0 Hz), 117.2 (d,

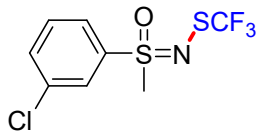
J = 22.0 Hz), 43.9. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.6, -102.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_8F_4NOS_2$ 273.9983; Found: 273.9976.

(4-Chlorophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ⁶-sulfanone (**3i**) [3]



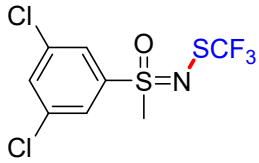
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 43% yield (37.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.85-7.83 (m, 2H), 7.59 (d, J = 8.0 Hz, 2H), 3.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 141.3, 136.3, 130.4 (q, J = 311.0 Hz), 130.2, 129.9, 43.8. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.6.

(3-Chlorophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ⁶-sulfanone (**3j**)



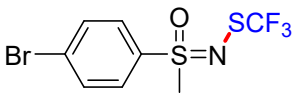
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 63% yield (54.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.91-7.90 (m, 1H), 7.80-7.77 (m, 1H), 7.68-7.66 (m, 1H), 7.58-7.55 (m, 1H), 3.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 139.7, 136.2, 134.5, 131.1, 130.4 (q, J = 310.0 Hz), 128.5, 126.5, 43.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_8ClF_3NOS_2$ 289.9688; Found: 289.9682.

(3,5-Dichlorophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ⁶-sulfanone (**3k**)



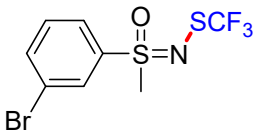
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 46% yield (44.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.78 (s, 2H), 7.67-7.66 (m, 1H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 141.0, 136.9, 134.4, 130.3 (q, J = 311.0 Hz), 126.8, 43.8. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_7Cl_2F_3NOS_2$ 323.9298; Found: 323.9293.

(4-Bromophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ⁶-sulfanone (**3l**)[3]



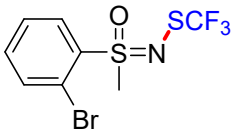
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 58% yield (57.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.76 (s, 4H), 3.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 136.9, 133.2, 130.4 (q, J = 311.0 Hz), 129.9, 129.9, 43.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.6.

(3-Bromophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ⁶-sulfanone (**3m**)[3]



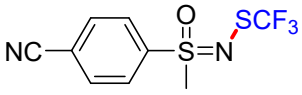
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 59% yield (59.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.05-8.04 (m, 1H), 7.84-7.81 (m, 2H), 7.49 (t, J = 8.0 Hz, 1H), 3.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 139.8, 137.4, 131.3, 131.3, 130.4 (q, J = 311.0 Hz), 126.9, 123.8, 43.8. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.5.

(2-Bromophenyl)(methyl)(((trifluoromethyl)thio)imino)- λ⁶-sulfanone (**3n**)[3]



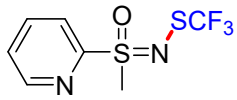
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 53% yield (53.1 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.24-8.22 (m, 1H), 7.82-7.79 (m, 1H), 7.61-7.57 (m, 1H), 7.54-7.51 (m, 1H), 3.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 136.3, 136.0, 135.4, 133.2, 130.3 (q, J = 311.0 Hz), 128.5, 120.7, 41.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.1.

4-(S-methyl-N-((trifluoromethyl)thio)sulfonimidoyl)benzonitrile (**3o**)[3]



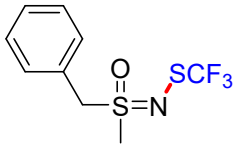
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 50% yield (42.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.06-8.03 (m, 2H), 7.92 (d, J = 8.0 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 142.4, 133.5, 129.2, 130.3 (q, J = 310.0 Hz), 118.1, 117.0, 43.5. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.4.

Methyl(pyridin-2-yl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3p**) [3]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1) to give the product as a colorless oil in 69% yield (52.9mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.76-8.74 (m, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.03-7.98 (m, 1H), 7.60-7.56 (m, 1H), 3.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 155.8, 150.5, 138.2, 130.3 (q, J = 311.0 Hz), 127.8, 123.7, 39.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -50.9.

Benzyl(methyl)(((trifluoromethyl)thio)imino)- λ^6-sulfanone (**3q**) [3]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a colorless oil in 38% yield (30.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.45-7.39 (m, 5H), 4.58-4.55 (m, 1H), 4.42-4.38 (m, 1H) , 2.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 131.0, 129.8, 130.5 (q, J = 310.0 Hz), 129.4, 127.6, 60.4, 37.4. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -51.2.

Reference

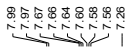
(1) J.-F. Lohier, T. Glachet, H. Marzag, A.-C. Gaumont, V. Reboul. *Chem. Commun*, 2017, **53**, 2064.

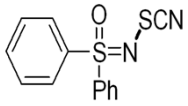
(2) D. Zhang, H. Wang, C. Bolm, *Chem. Commun*, 2018, **54**, 5772.

(3) C. Bohnen, C. Bolm, *Org. Lett*. 2015, **17**, 3011.

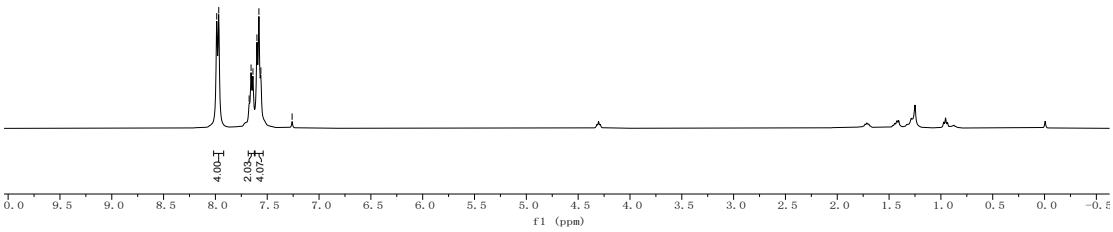
NMR Spectra of products

2a-^{1}H NMR

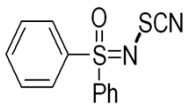




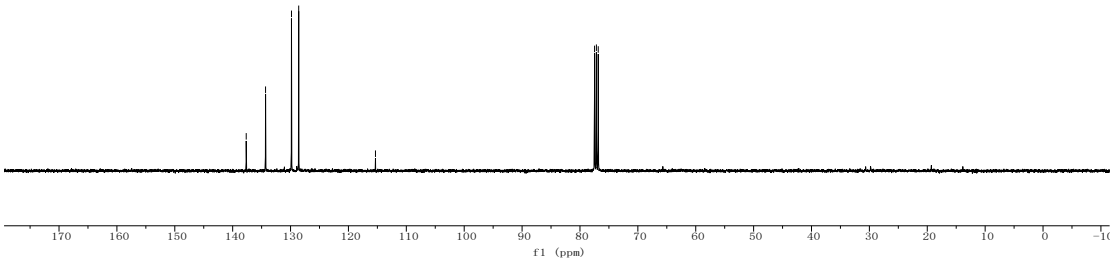
400 MHz, $CDCl_3$



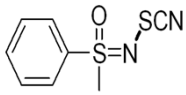
2a-^{13}C NMR



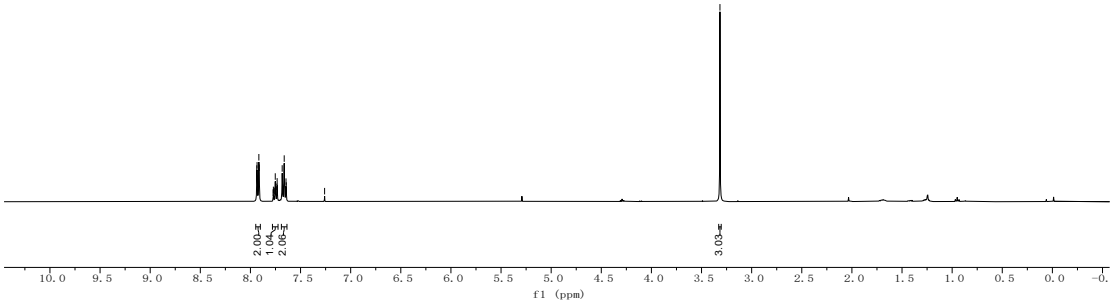
100 MHz, $CDCl_3$



2b-^{1}H NMR



400 MHz, $CDCl_3$



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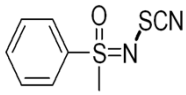
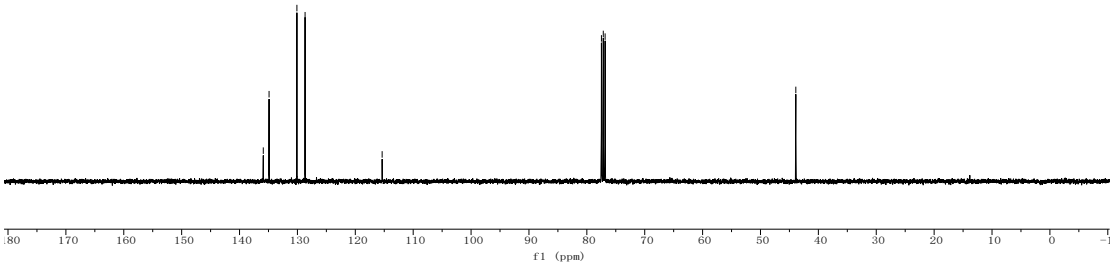
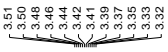
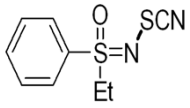


100 MHz, $CDCl_3$

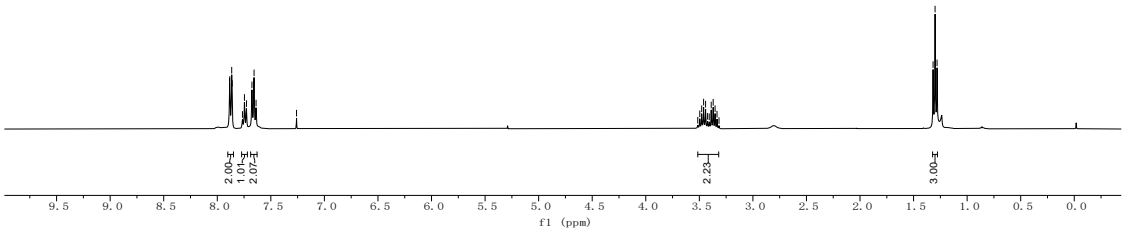


2c-^{1}H NMR

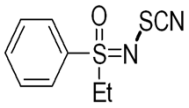




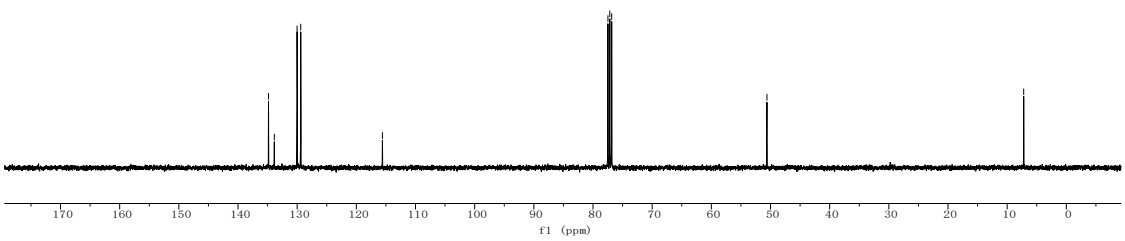
400 MHz, $CDCl_3$



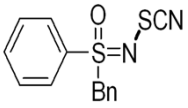
2c-^{13}C NMR



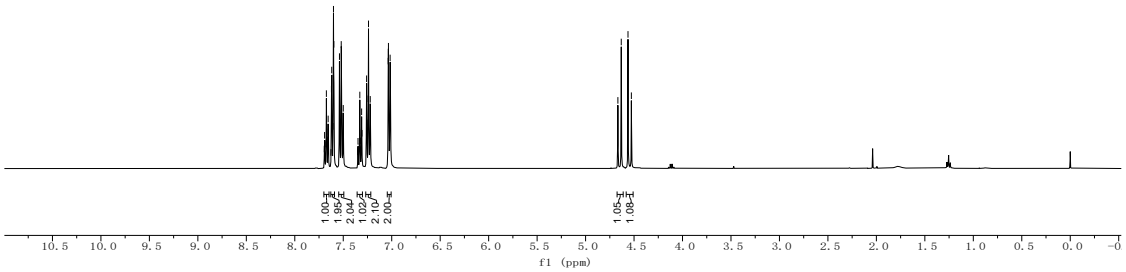
100 MHz, $CDCl_3$



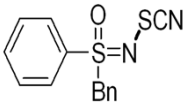
2d-^{1}H NMR



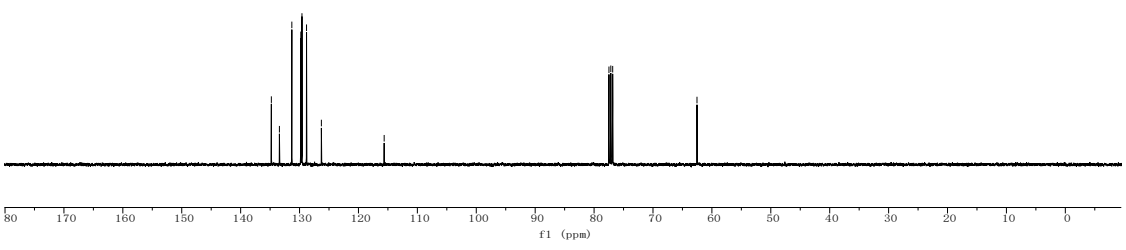
400 MHz, $CDCl_3$



2d -^{13}C NMR



100 MHz, $CDCl_3$



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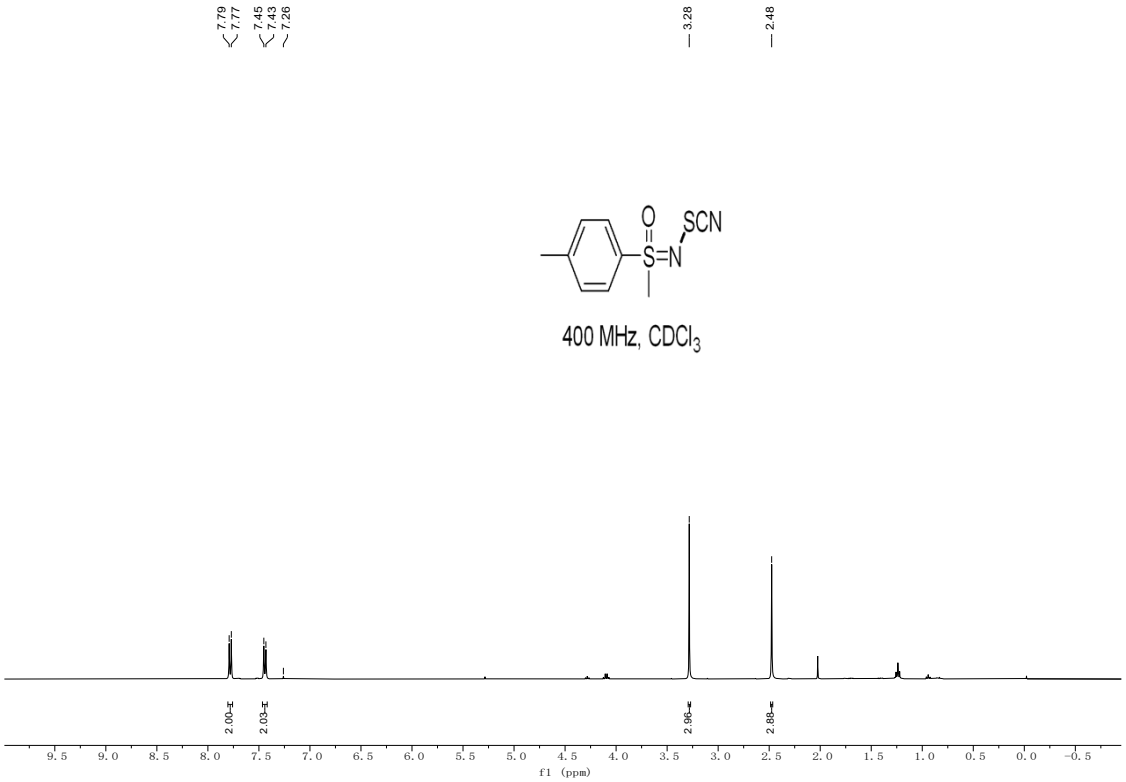
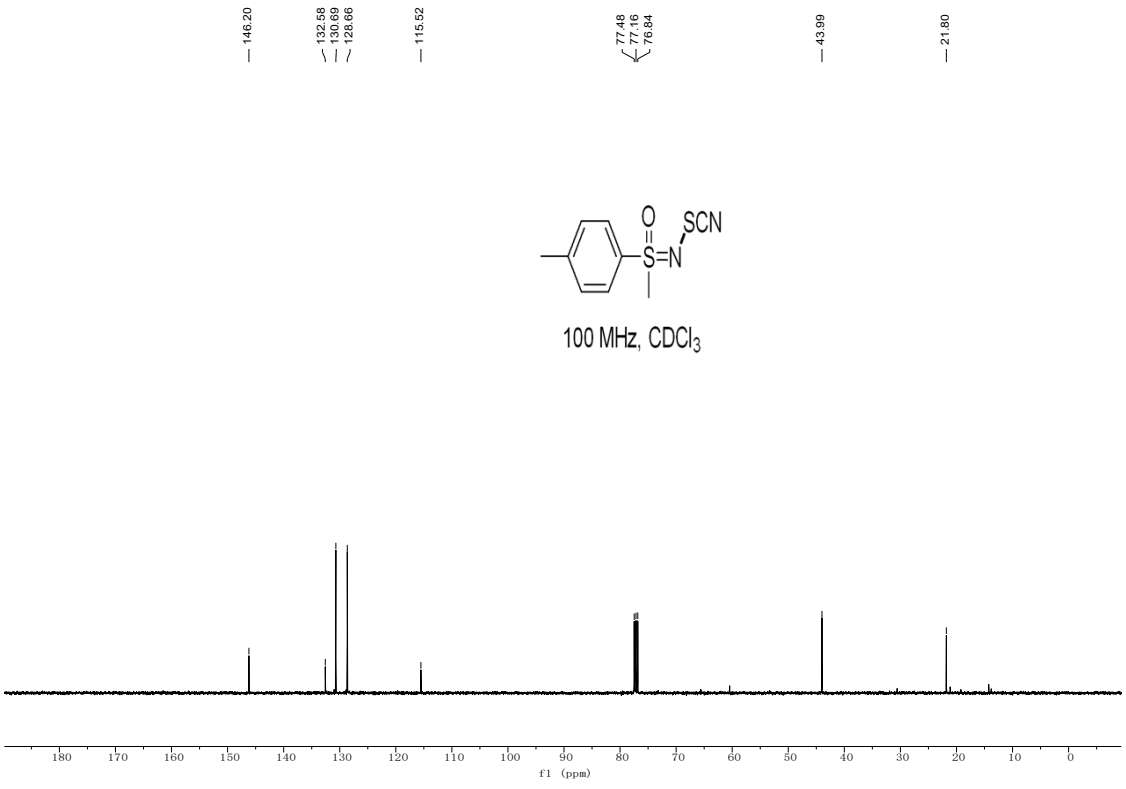
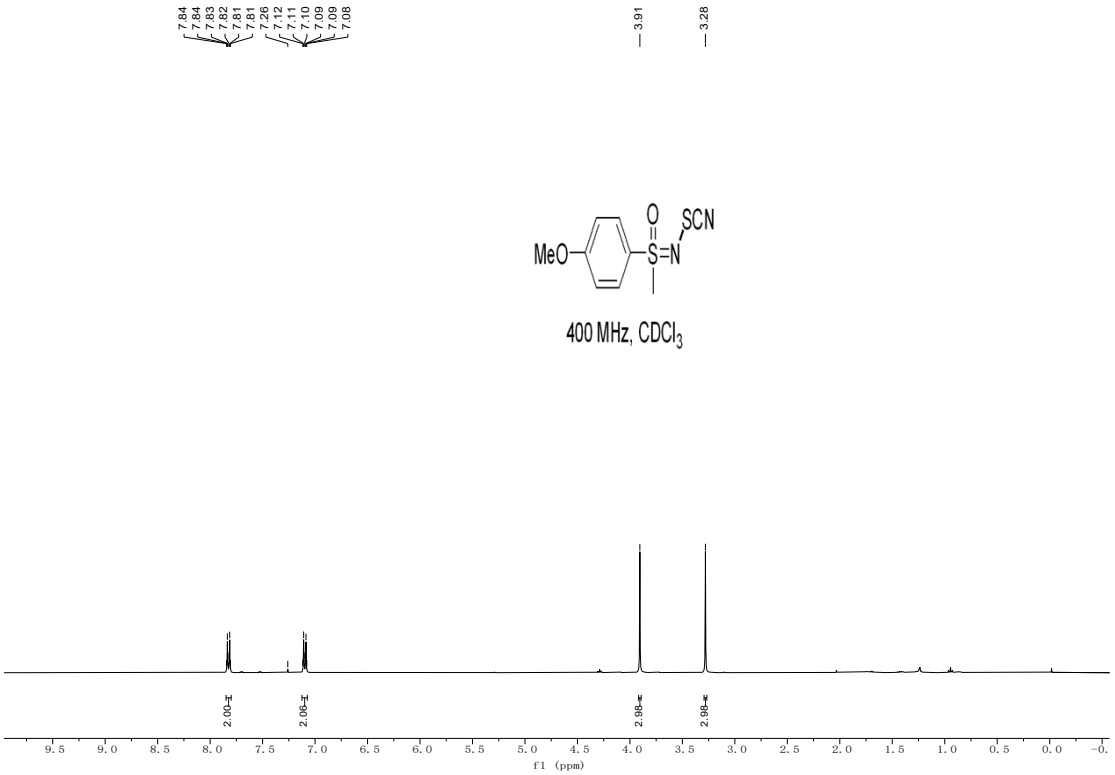


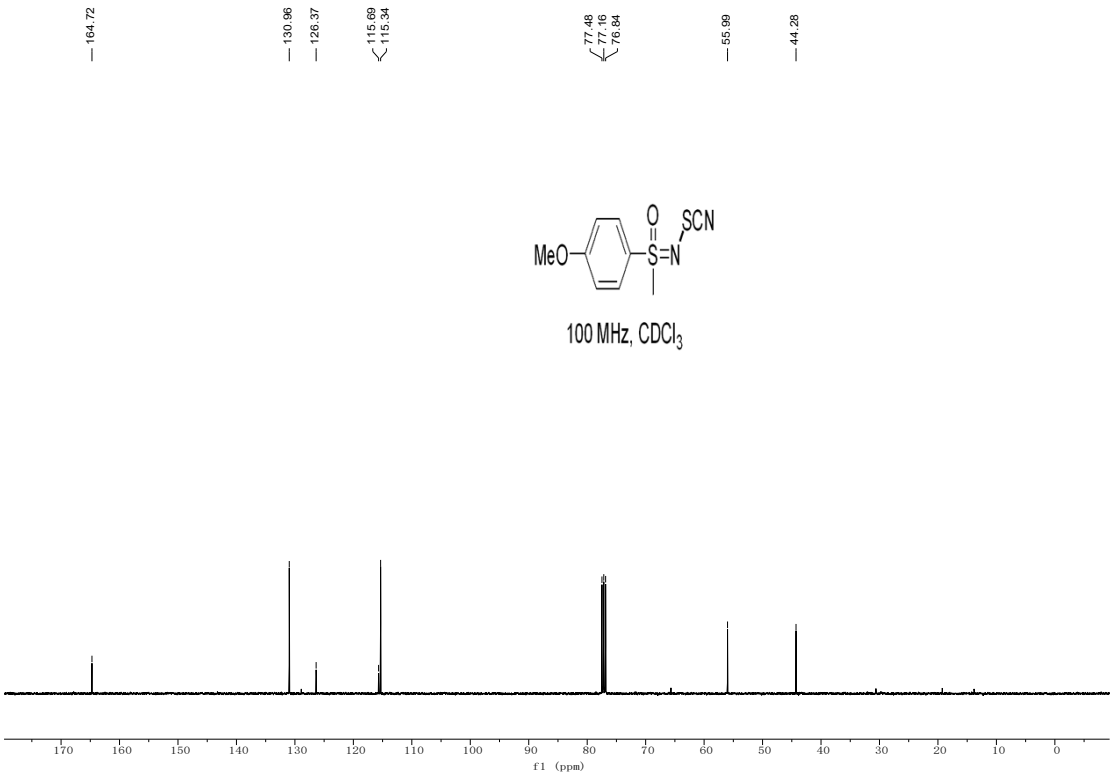
2e-^{13}C NMR



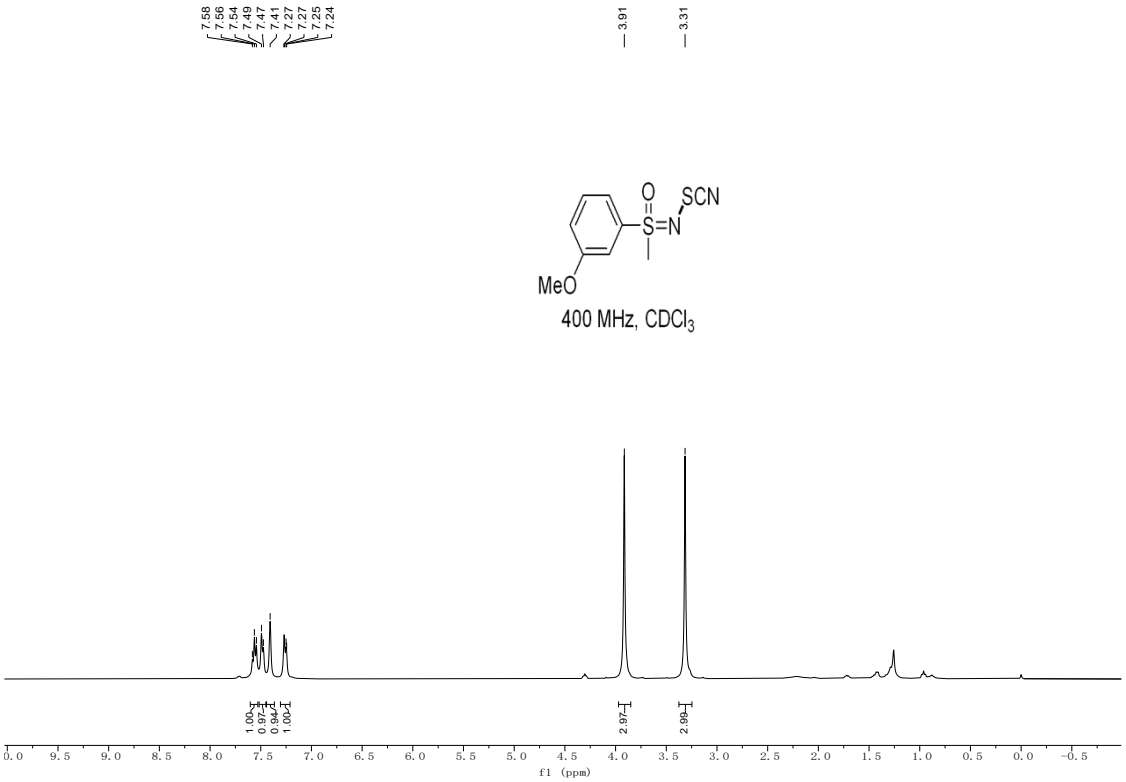
2f-^{1}H NMR



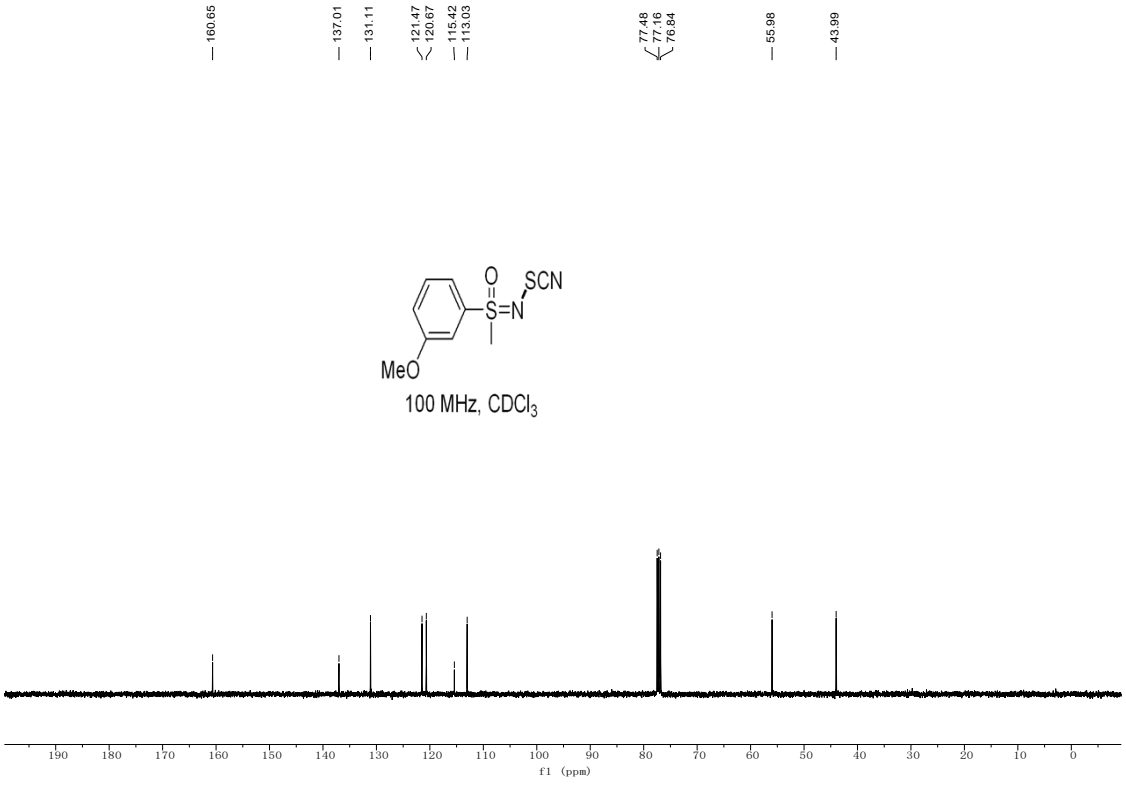
2f -^{13}C NMR



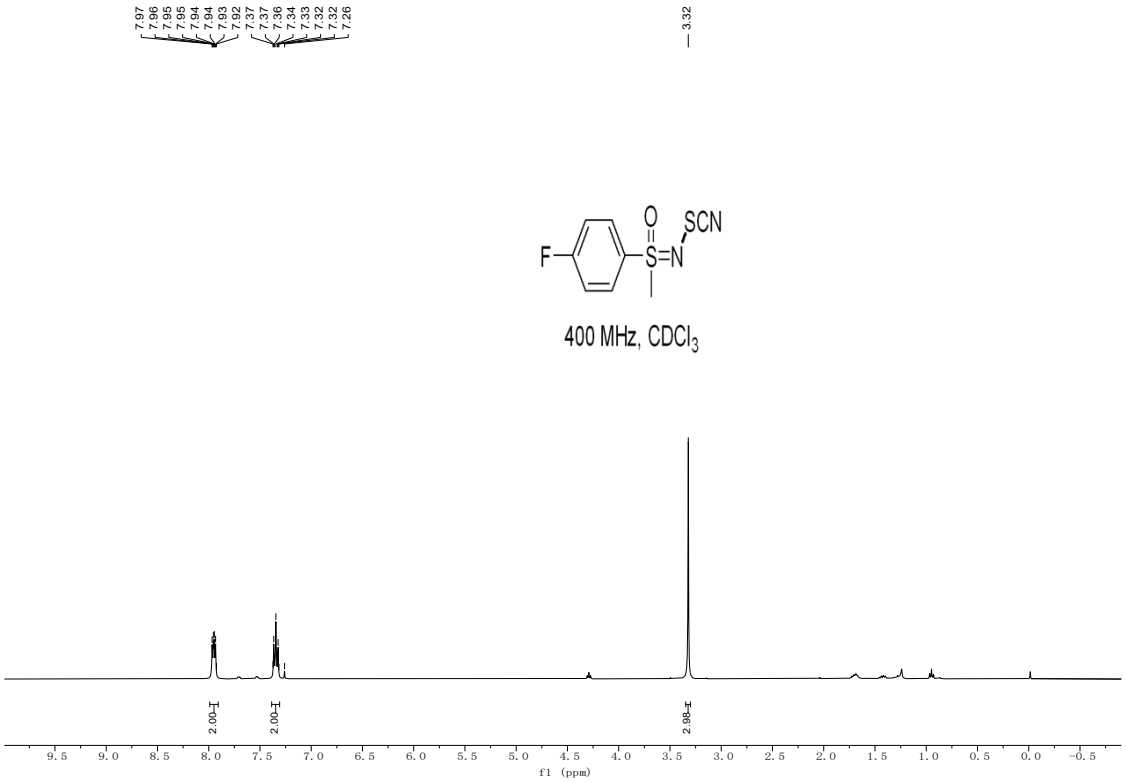
2g-^{1}H NMR



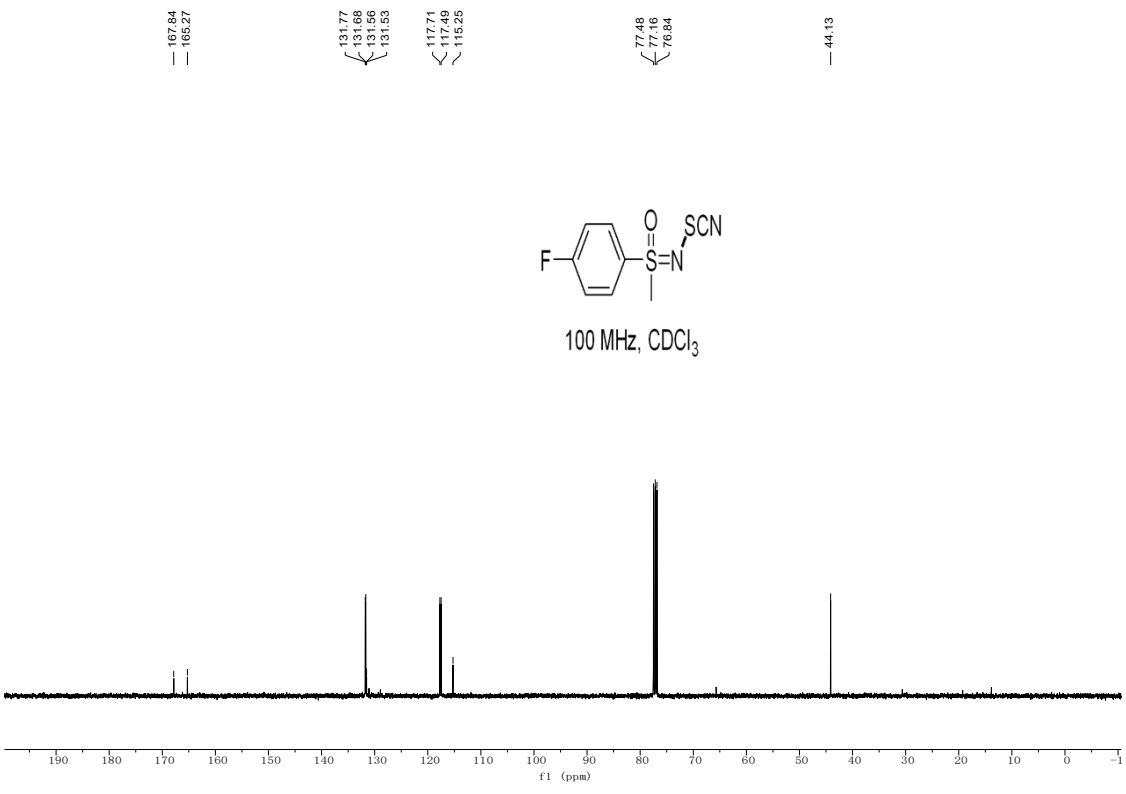
2g -^{13}C NMR



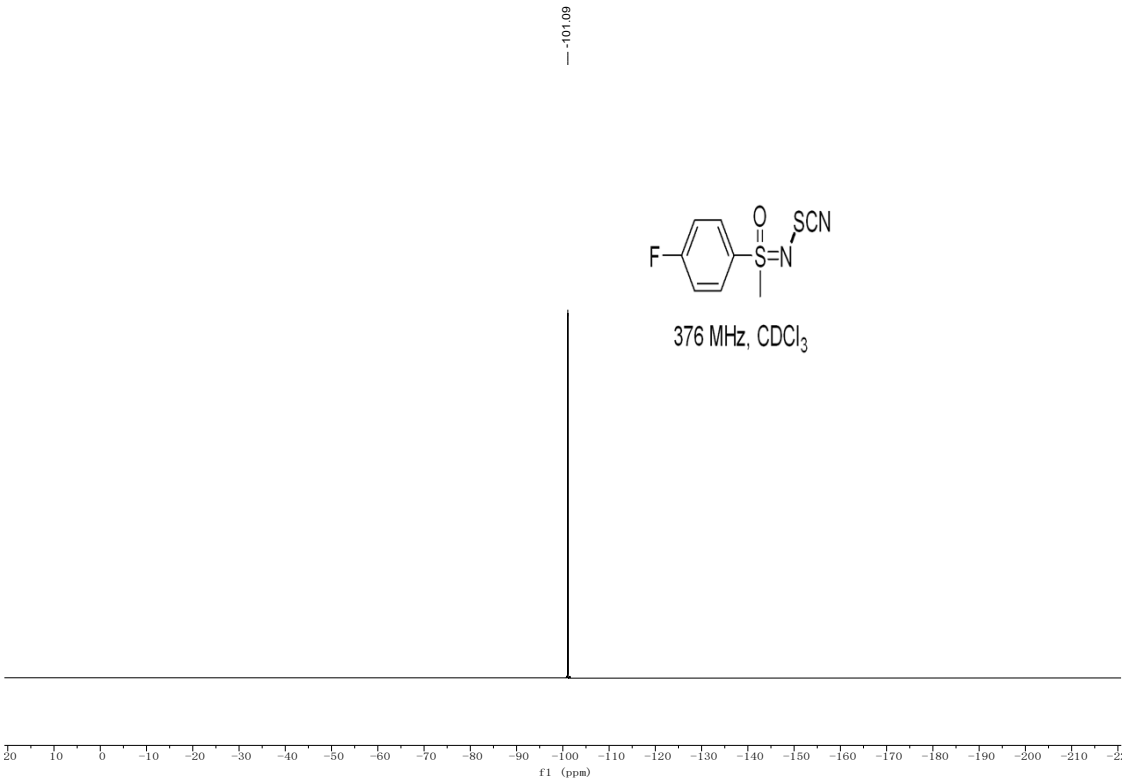
2h-^{1}H NMR



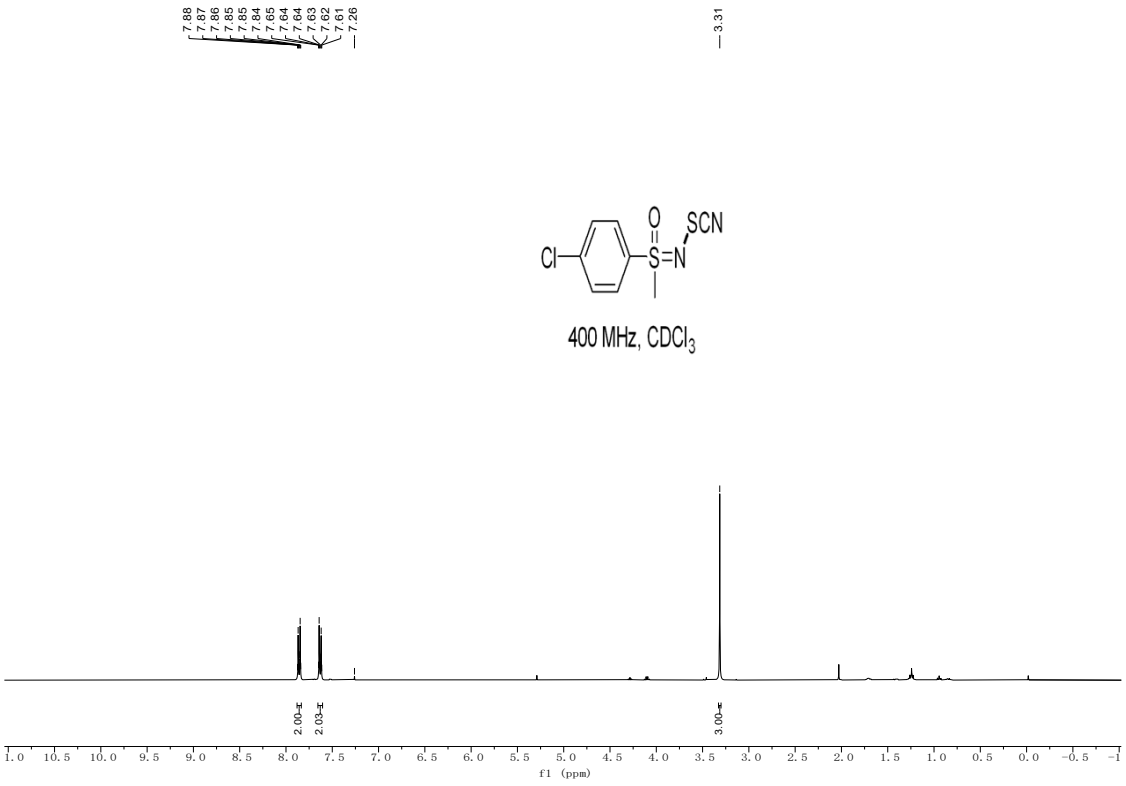
2h -^{13}C NMR



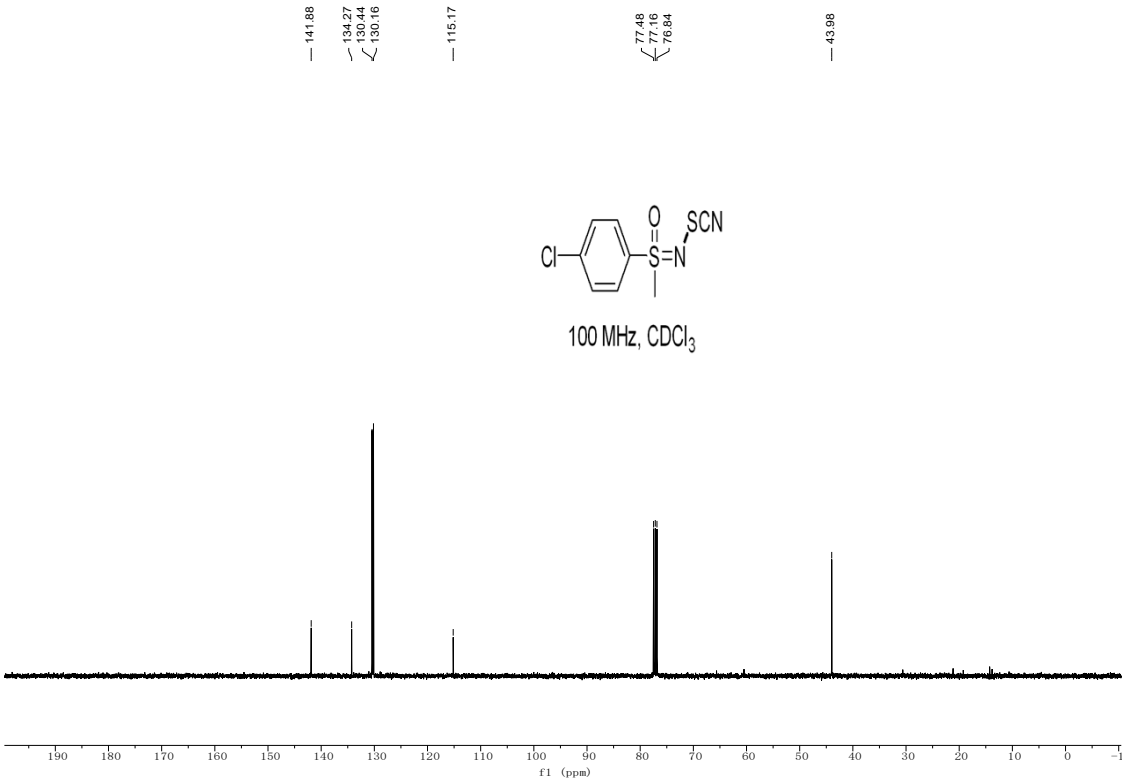
2h -^{19}F NMR



2i-^{1}H NMR



2i -^{13}C NMR



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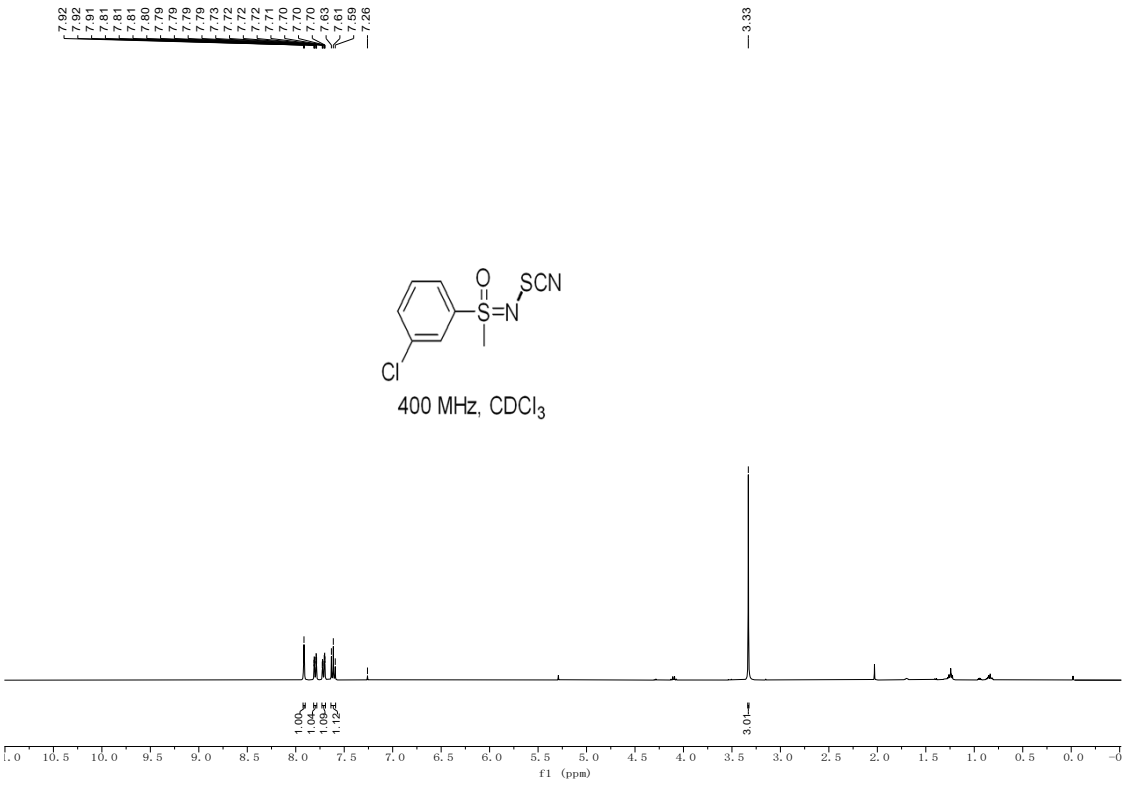

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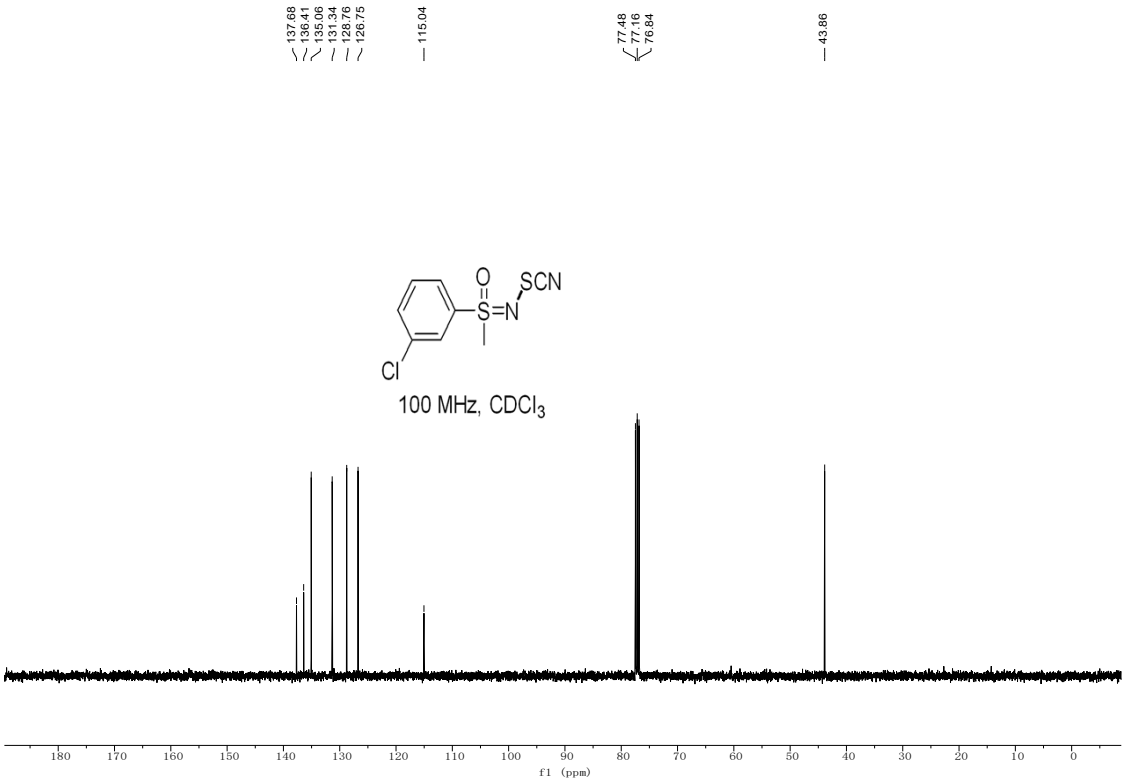
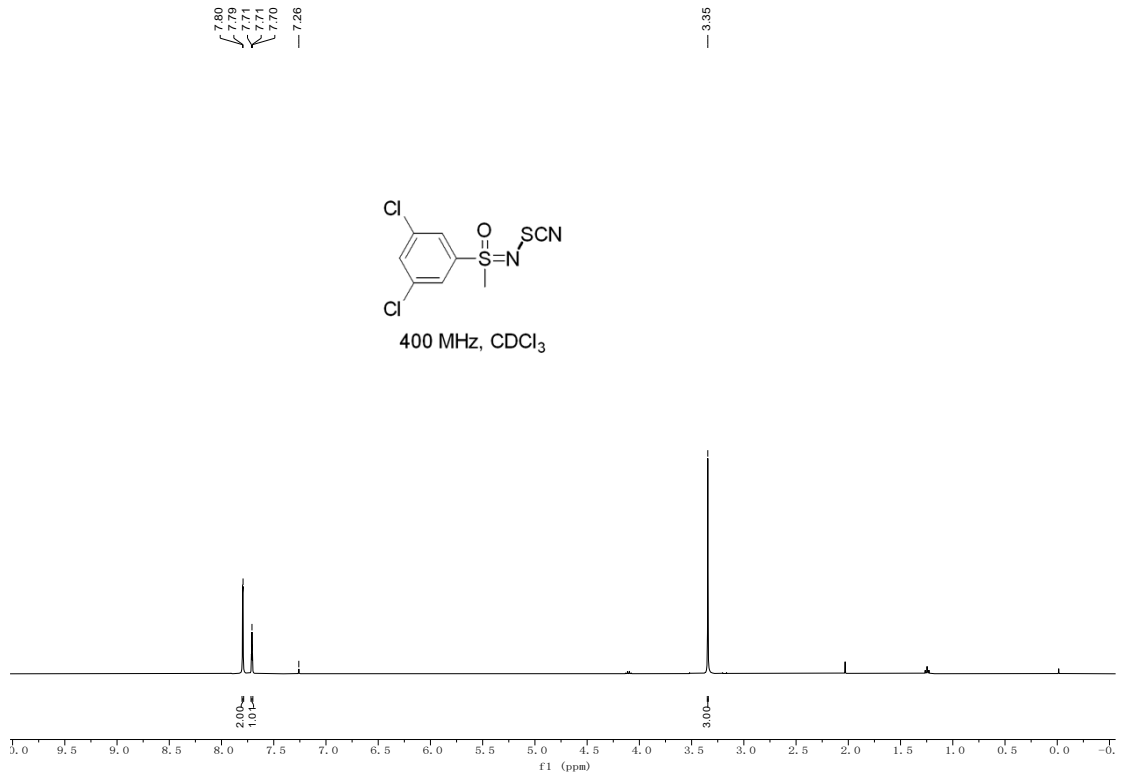


2k-^{1}H NMR



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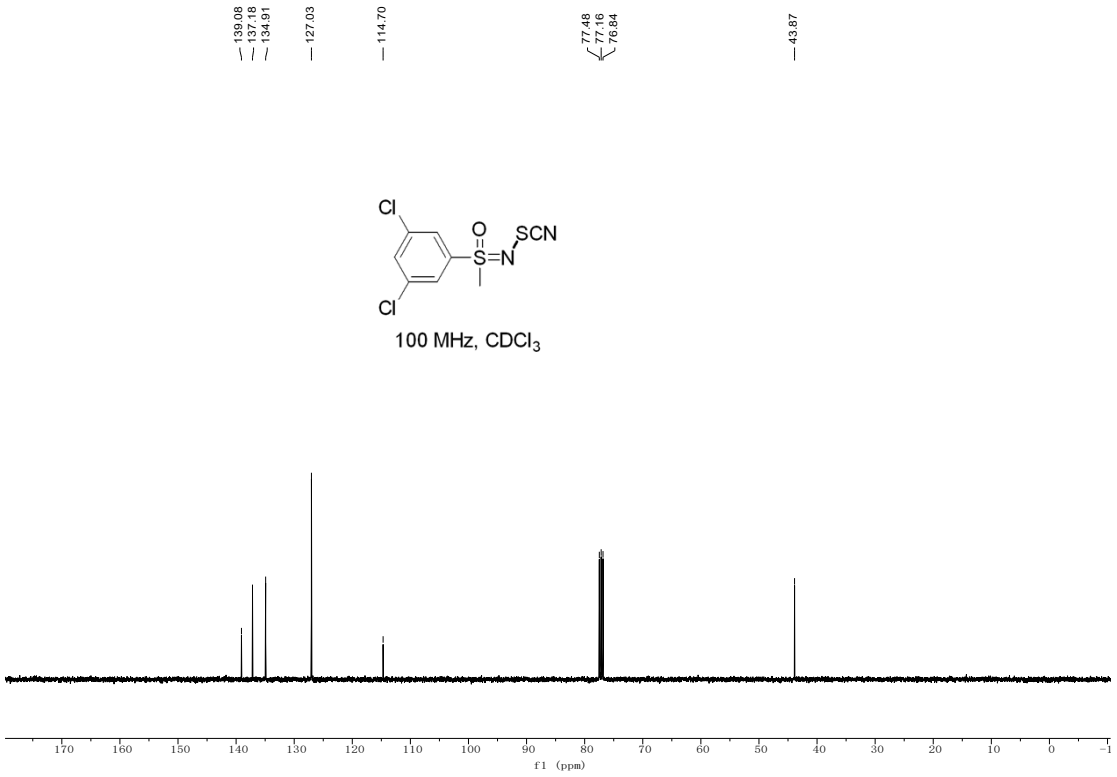

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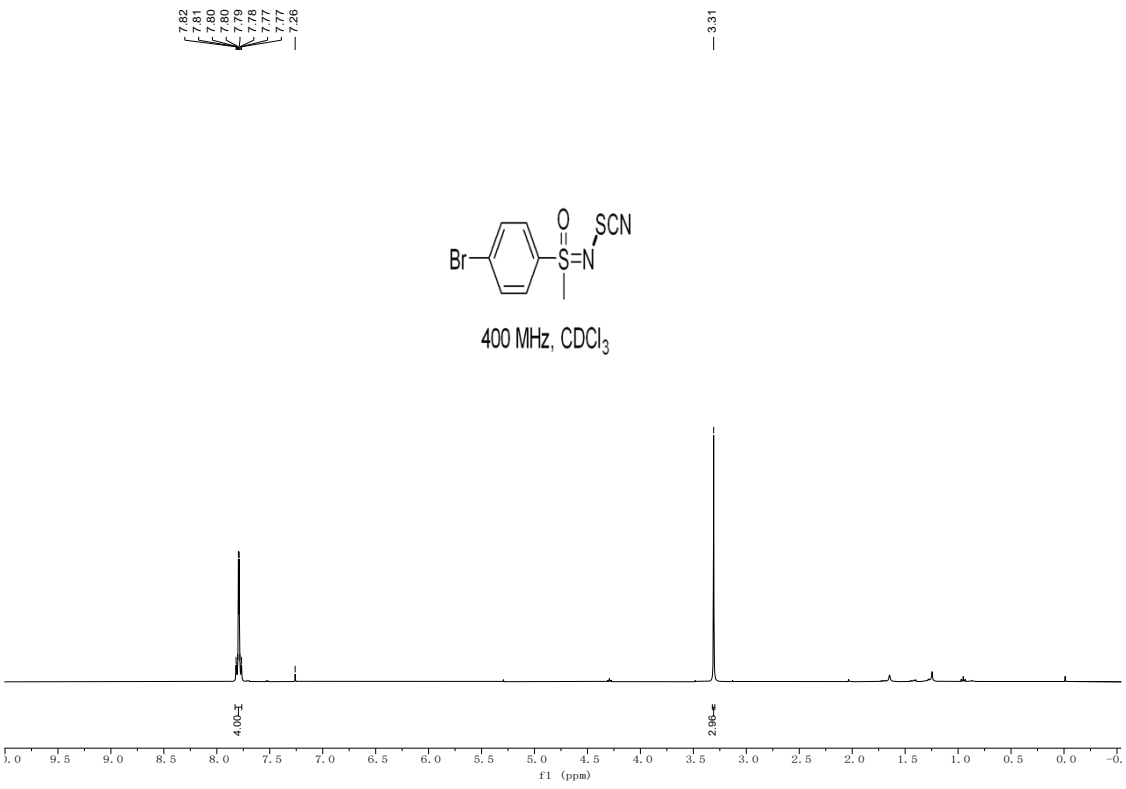

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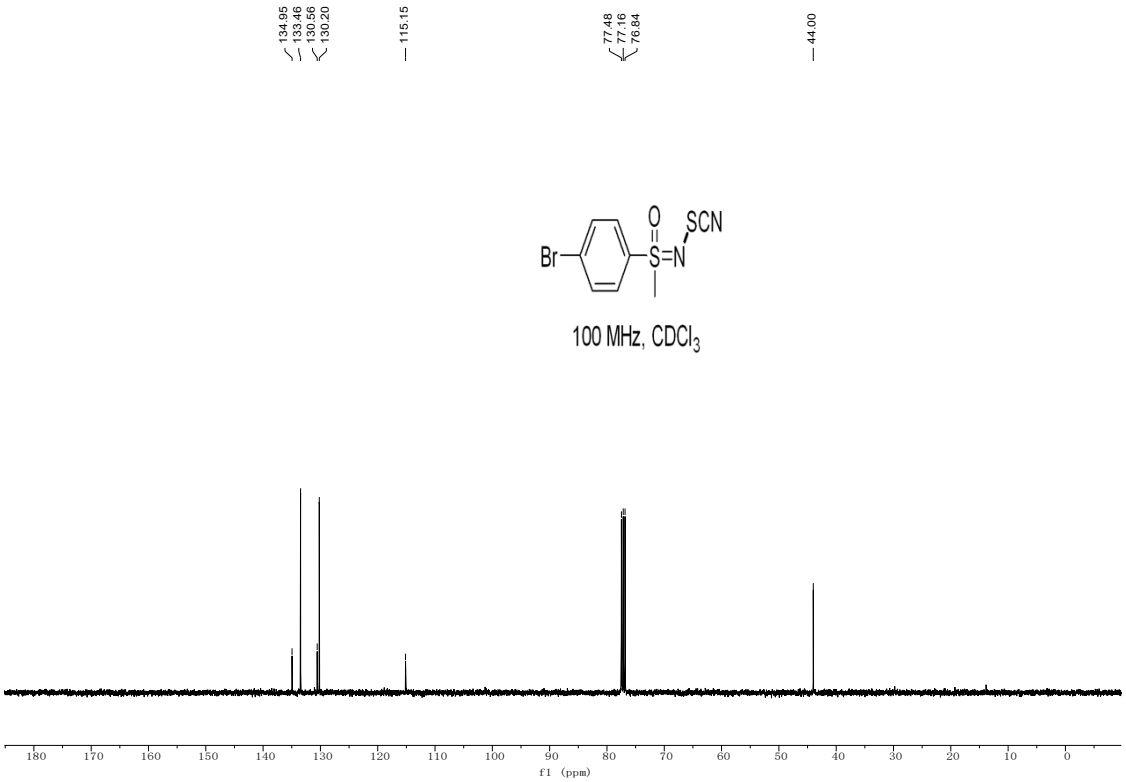
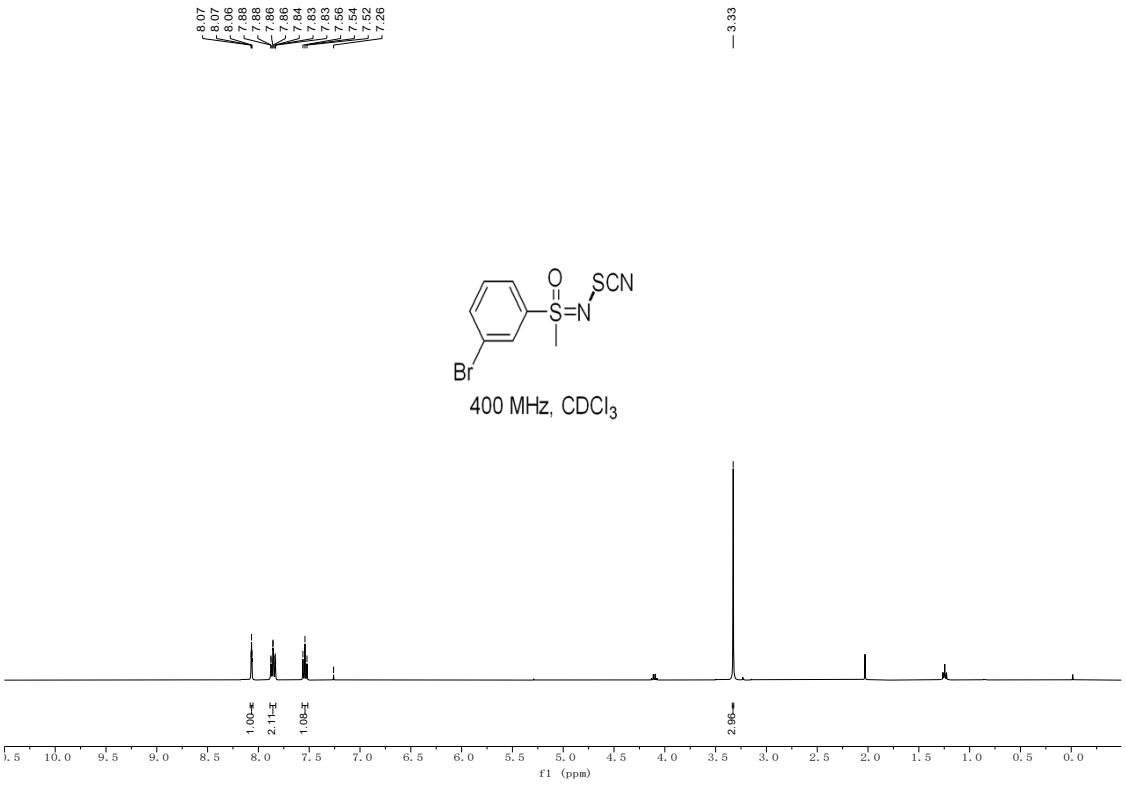


2m-^{1}H NMR



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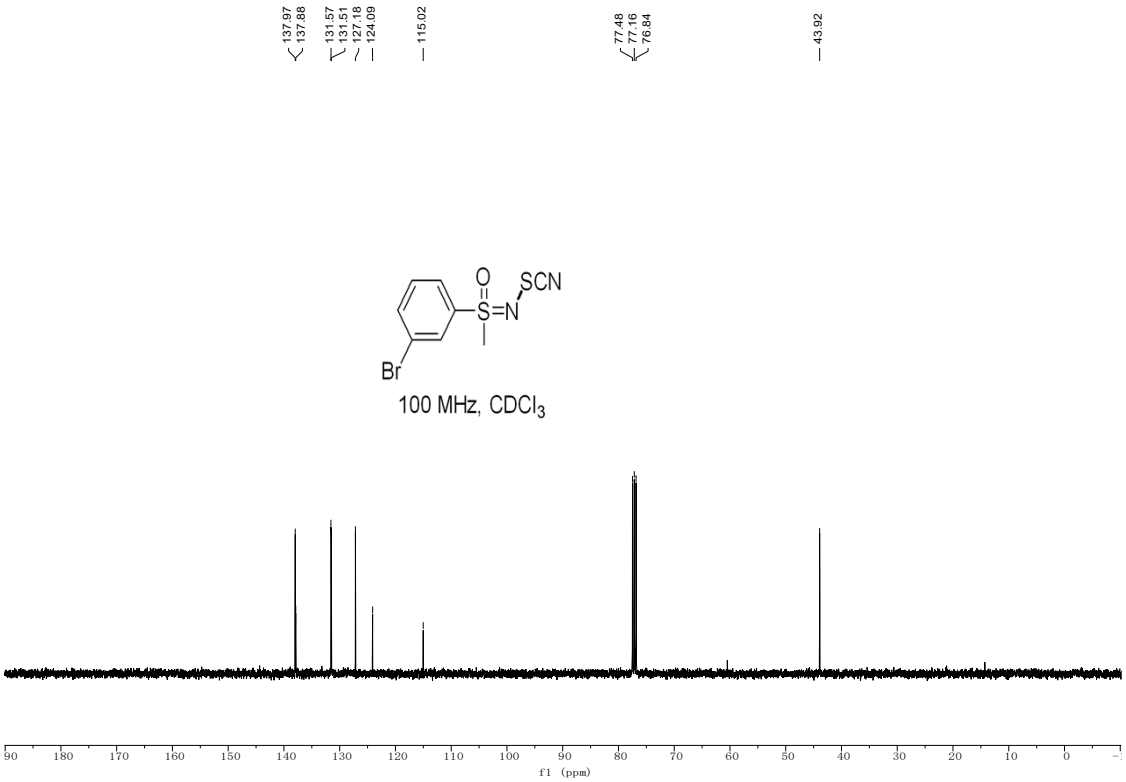
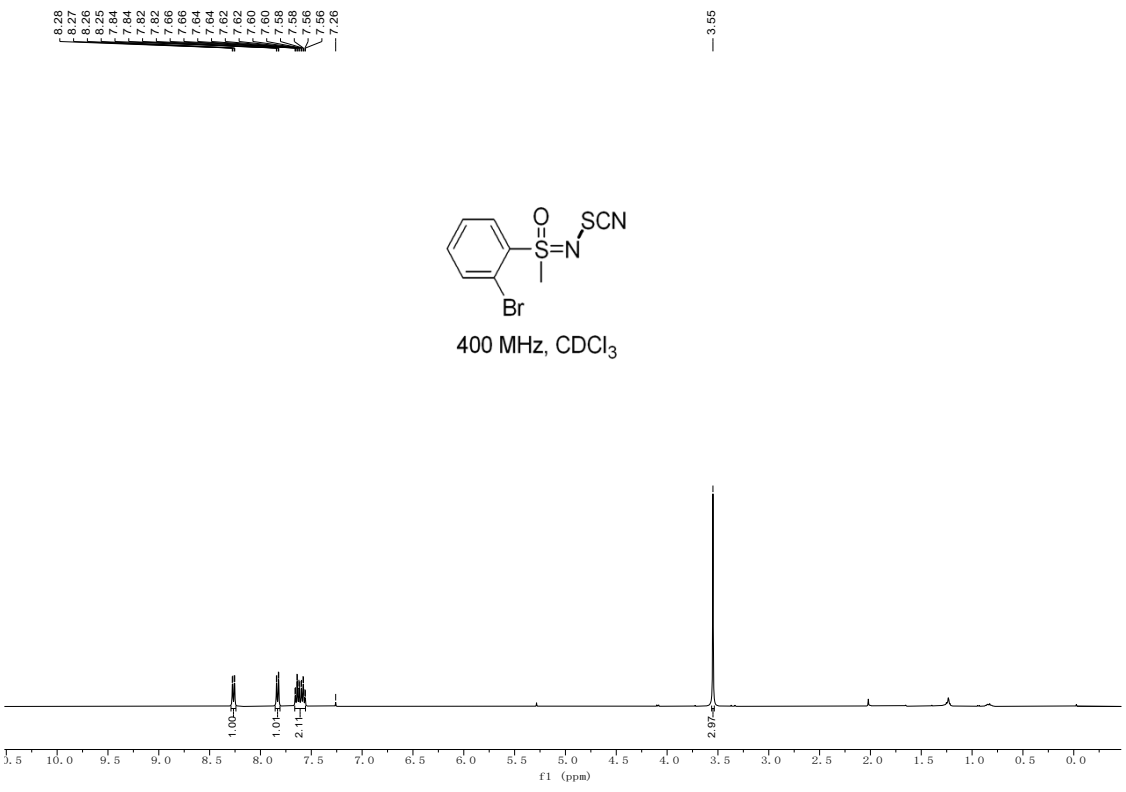
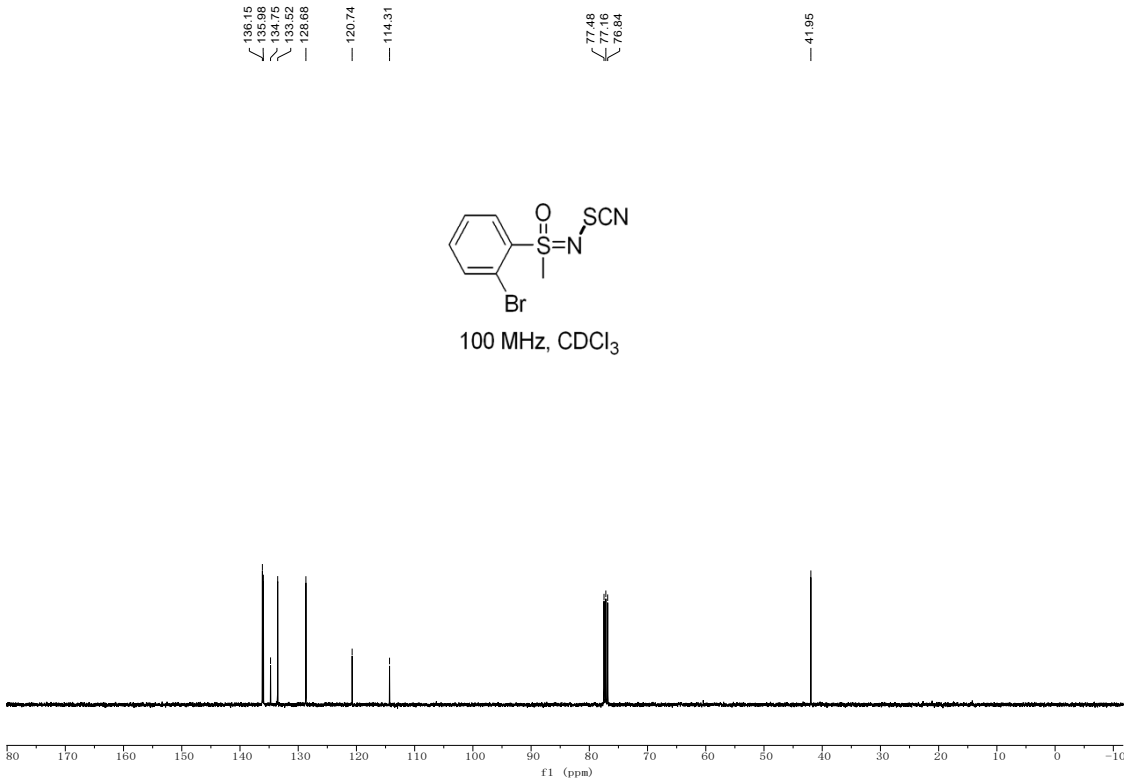


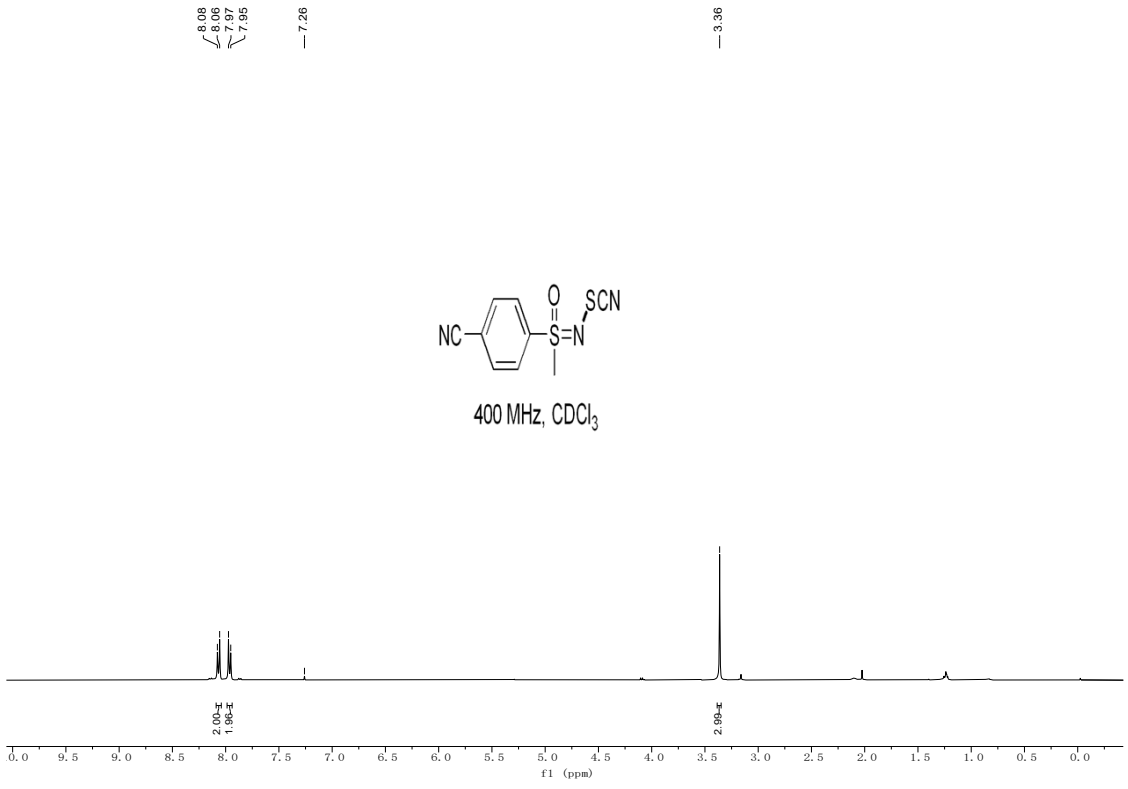
2n-^{1}H NMR



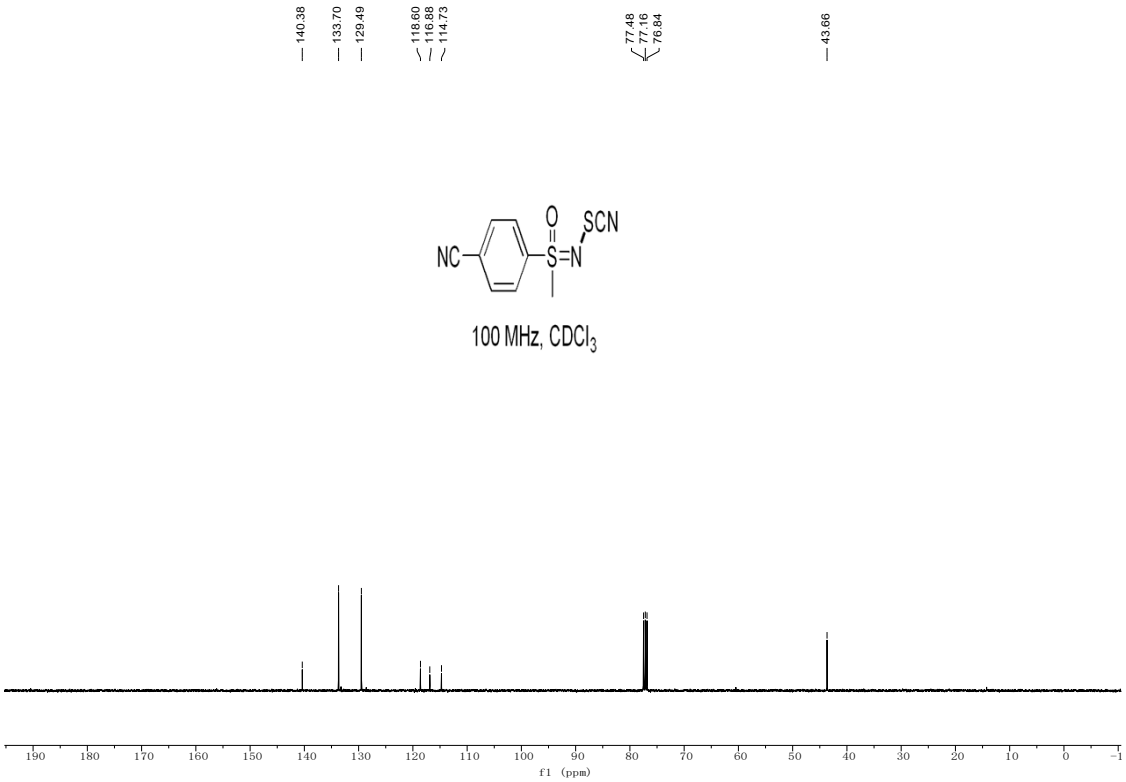
2n -^{13}C NMR



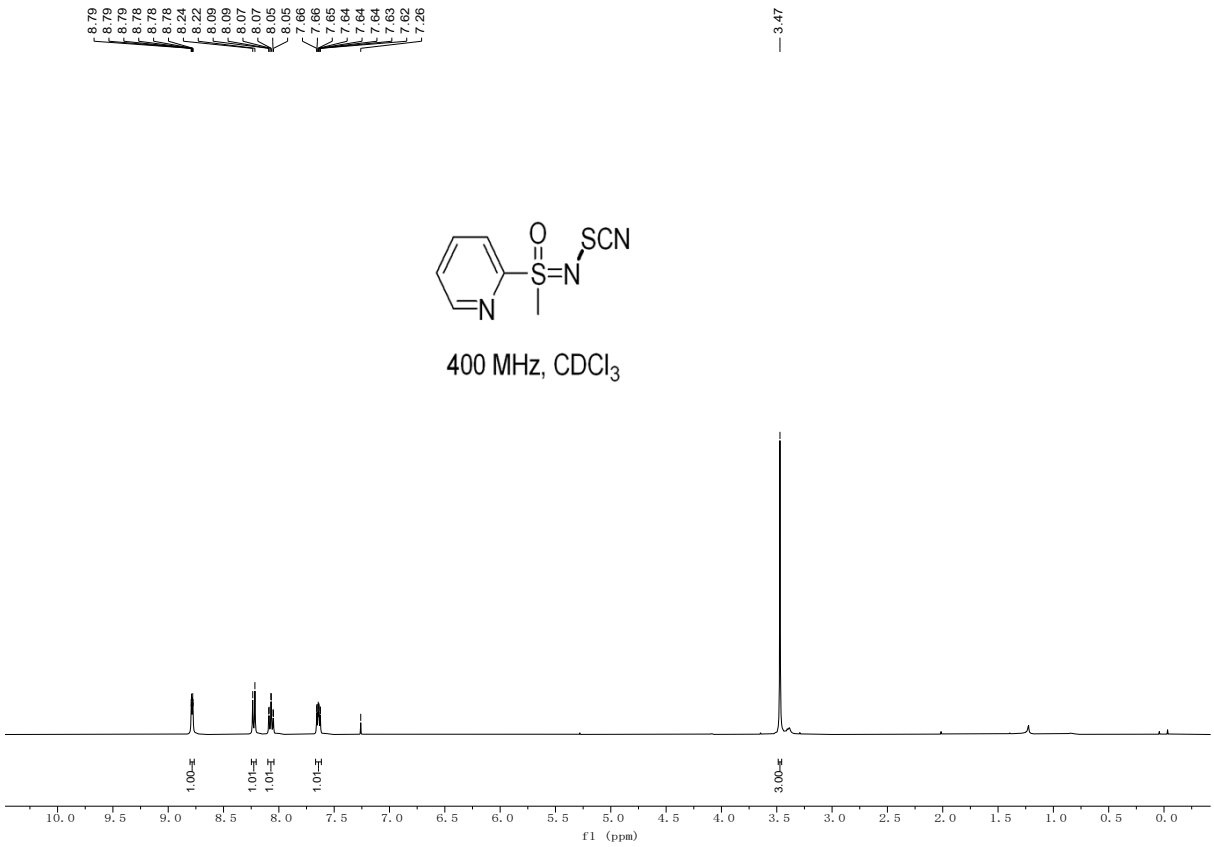
2o-^{1}H NMR



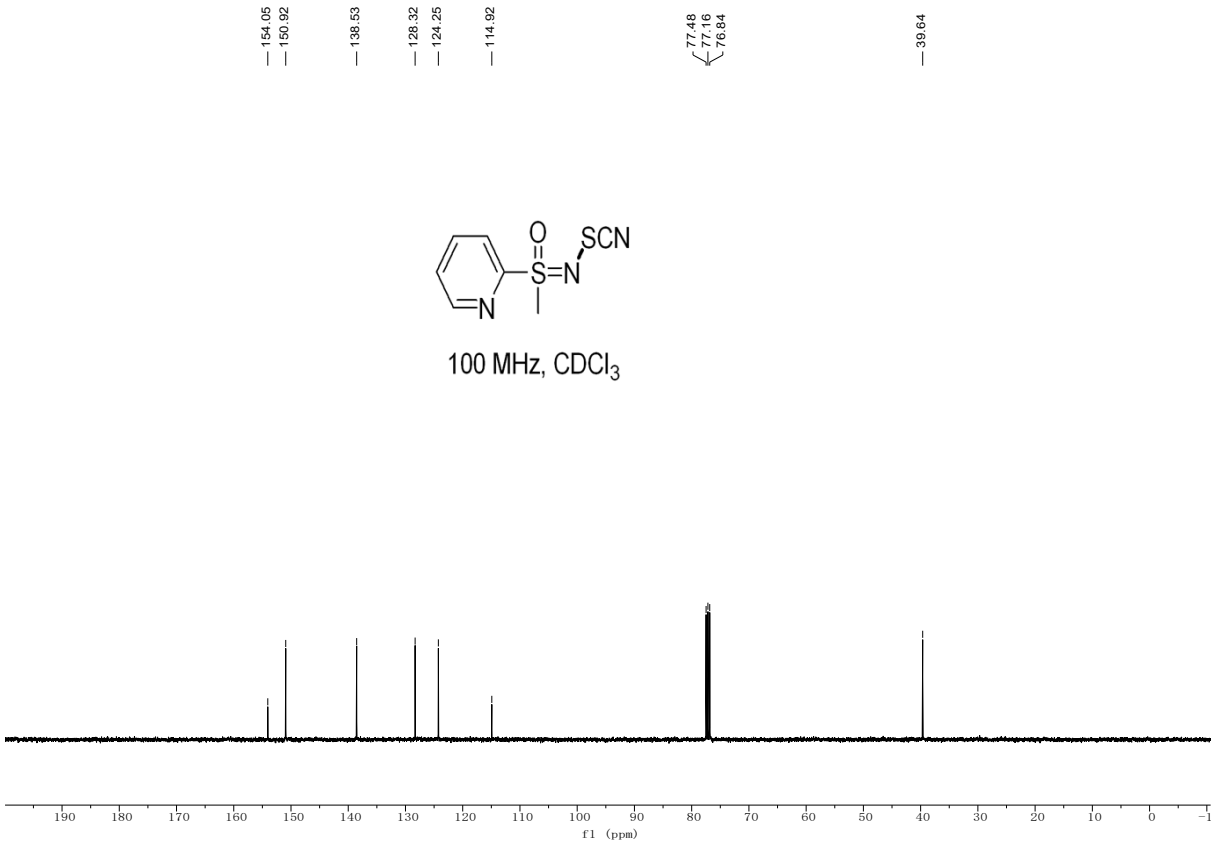
2o -^{13}C NMR



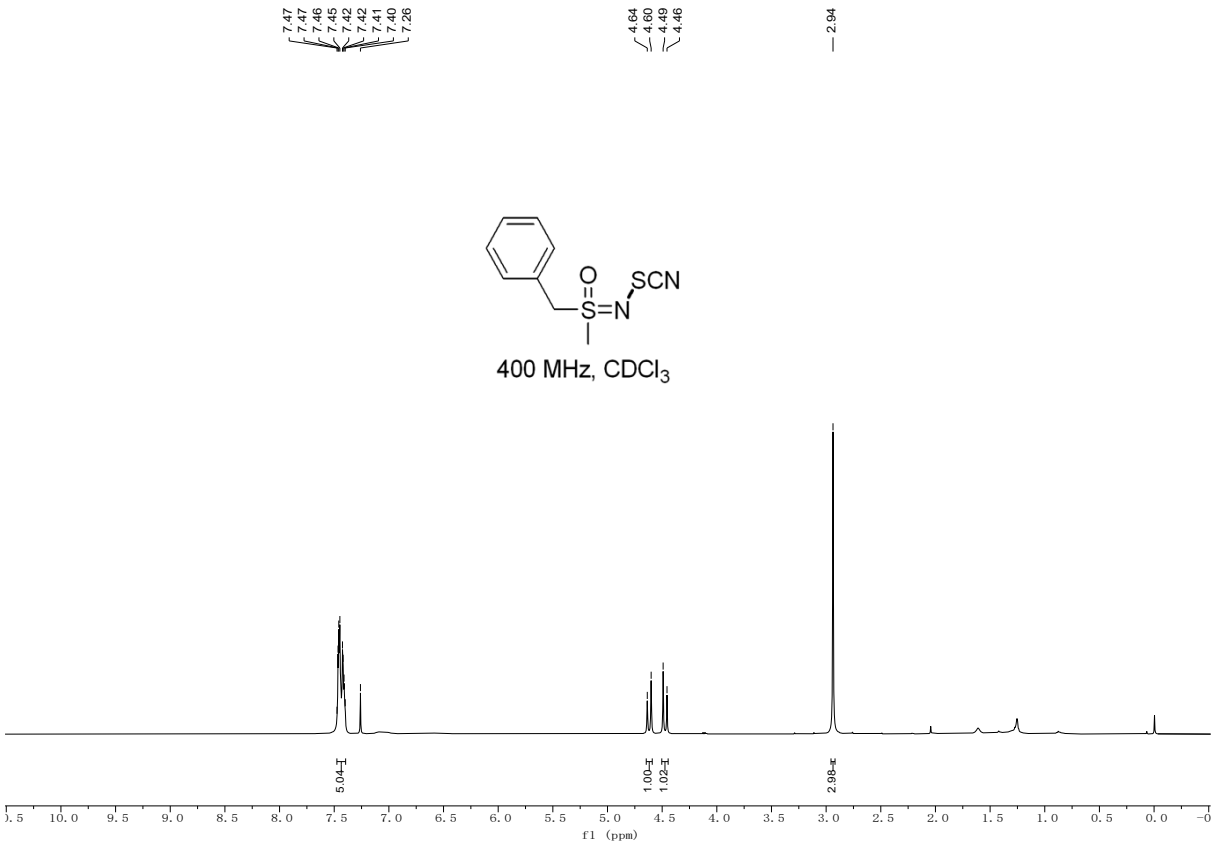
2p-^{1}H NMR



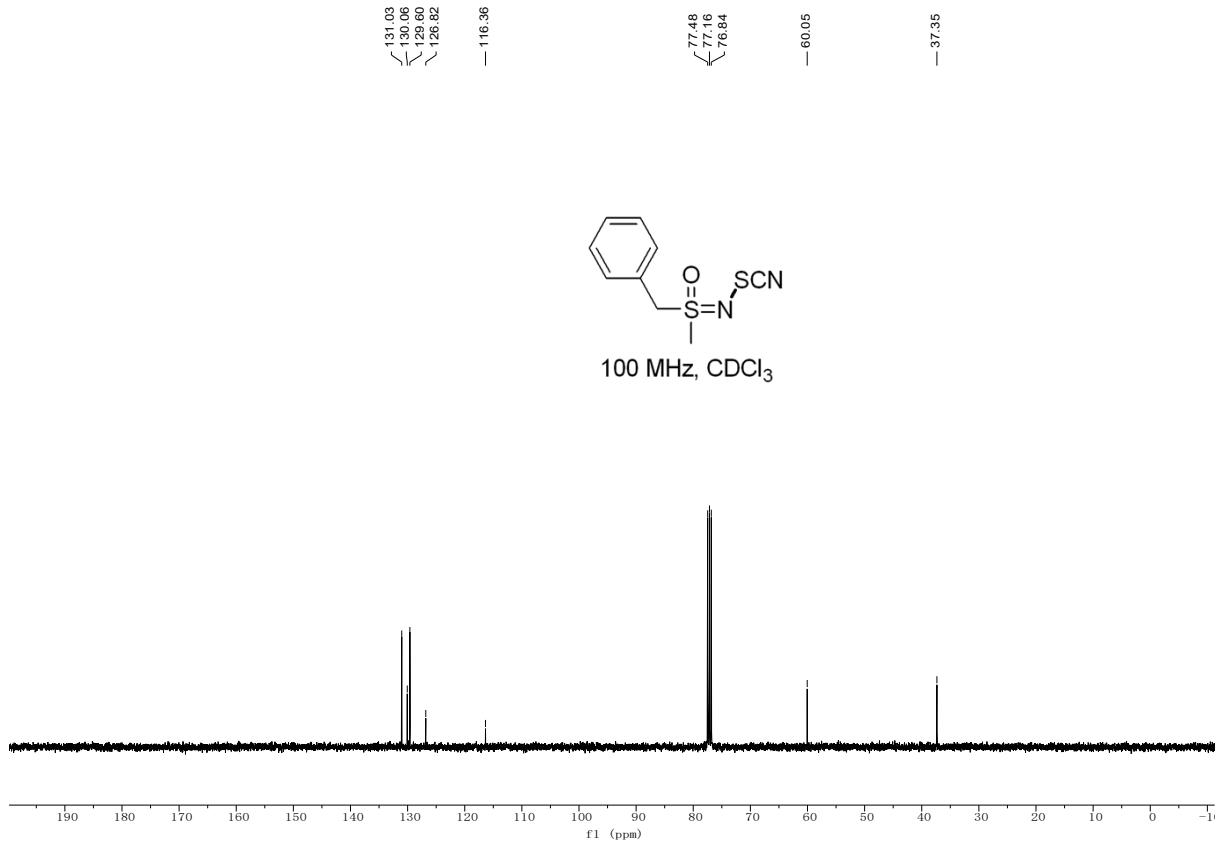
2p -^{13}C NMR



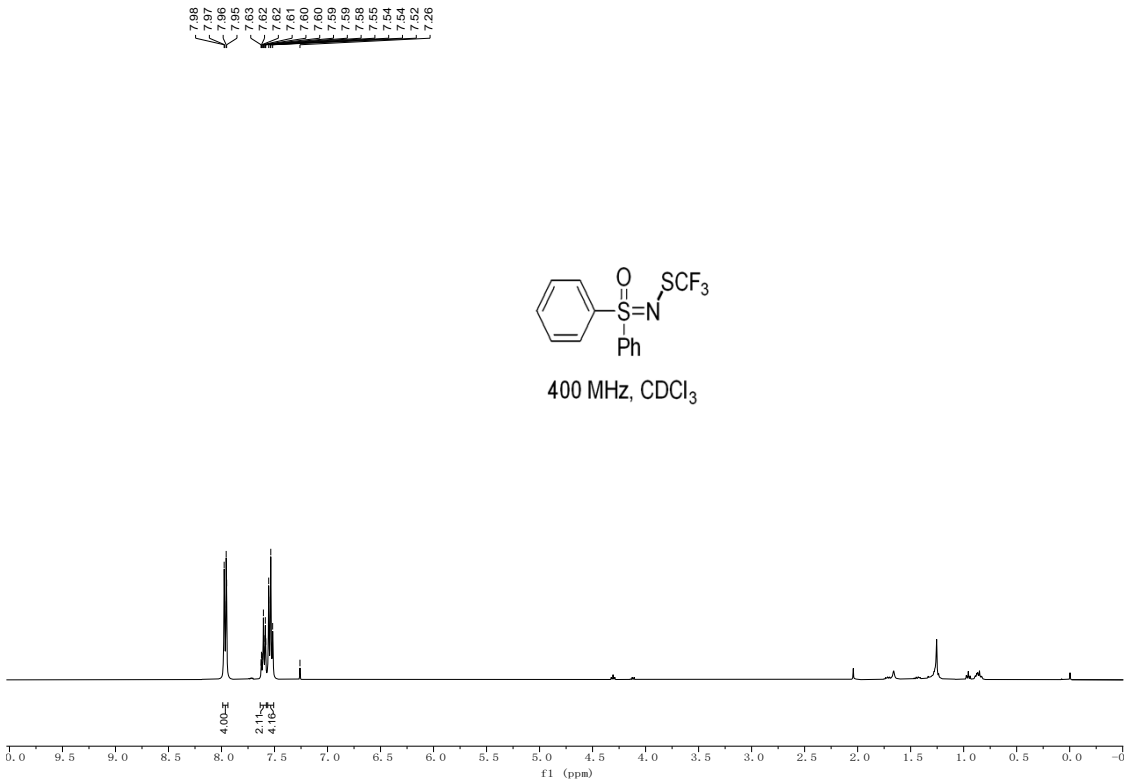
2q-^{1}H NMR



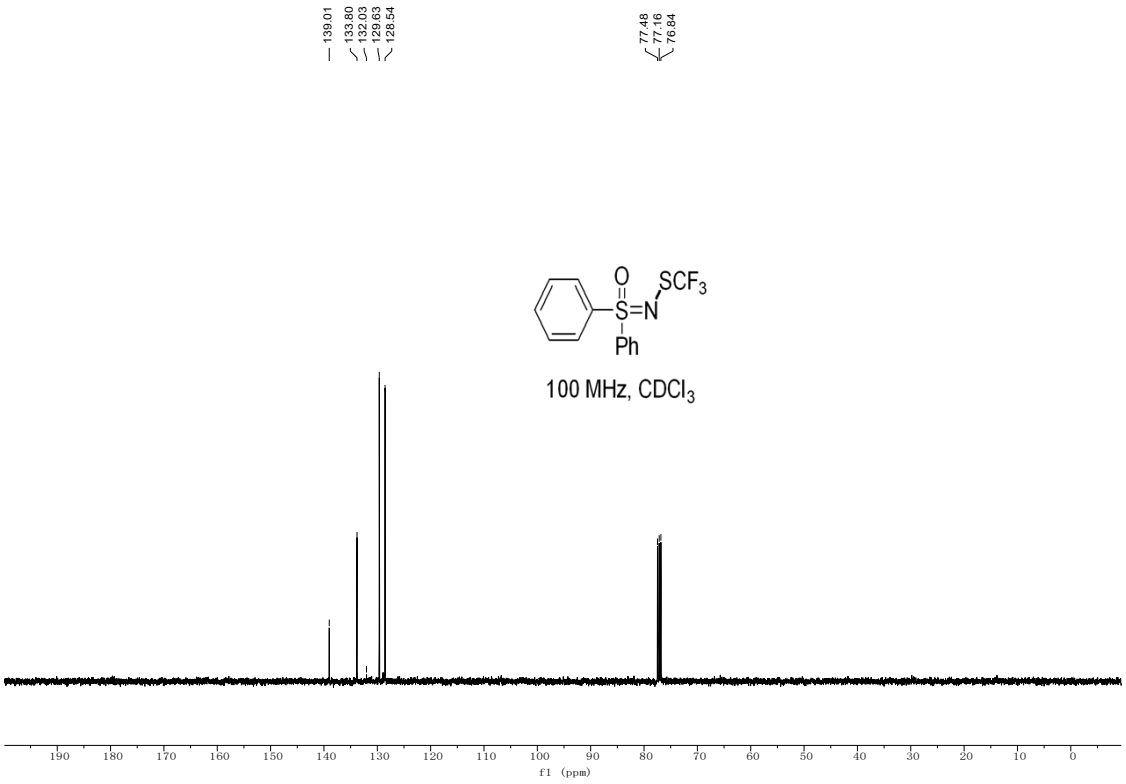
2q -^{13}C NMR



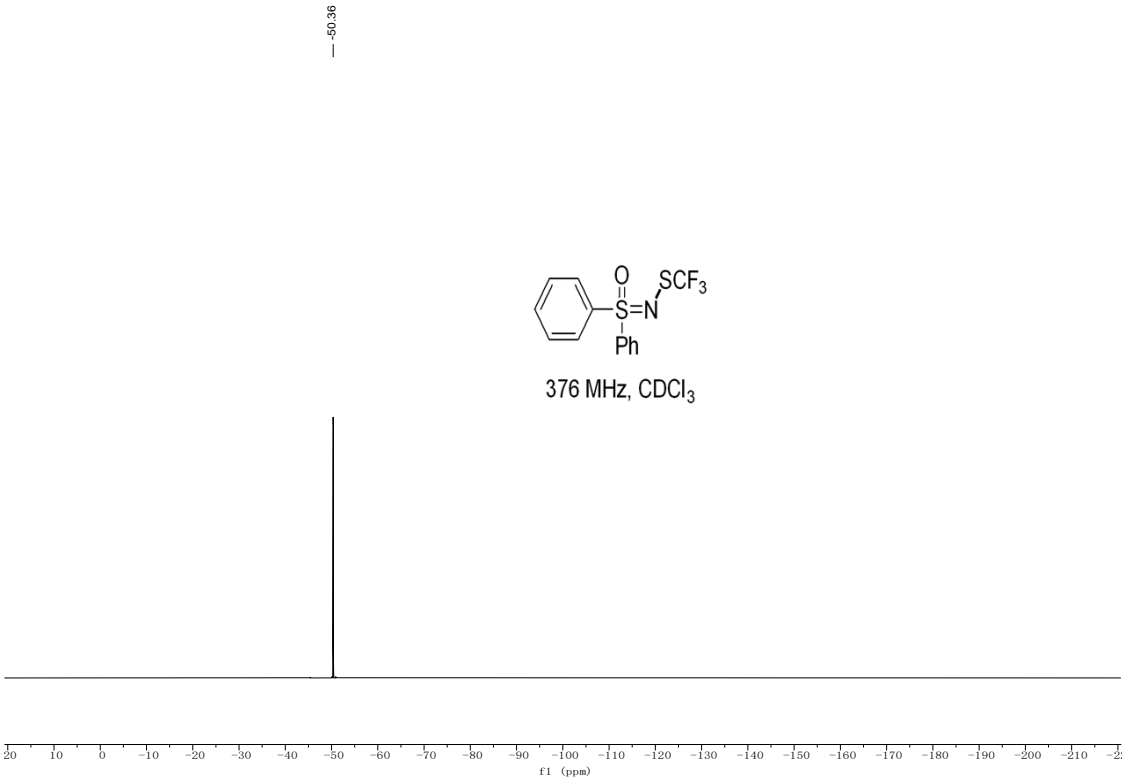
3a-^{1}H NMR



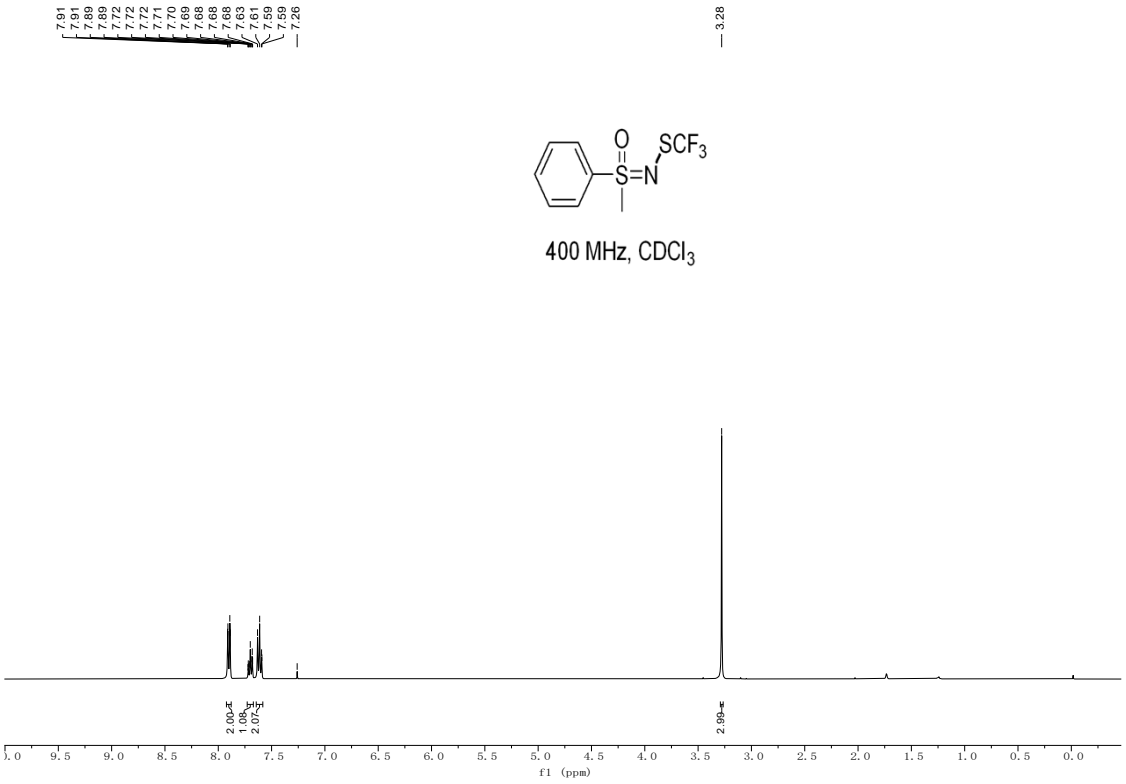
3a -^{13}C NMR



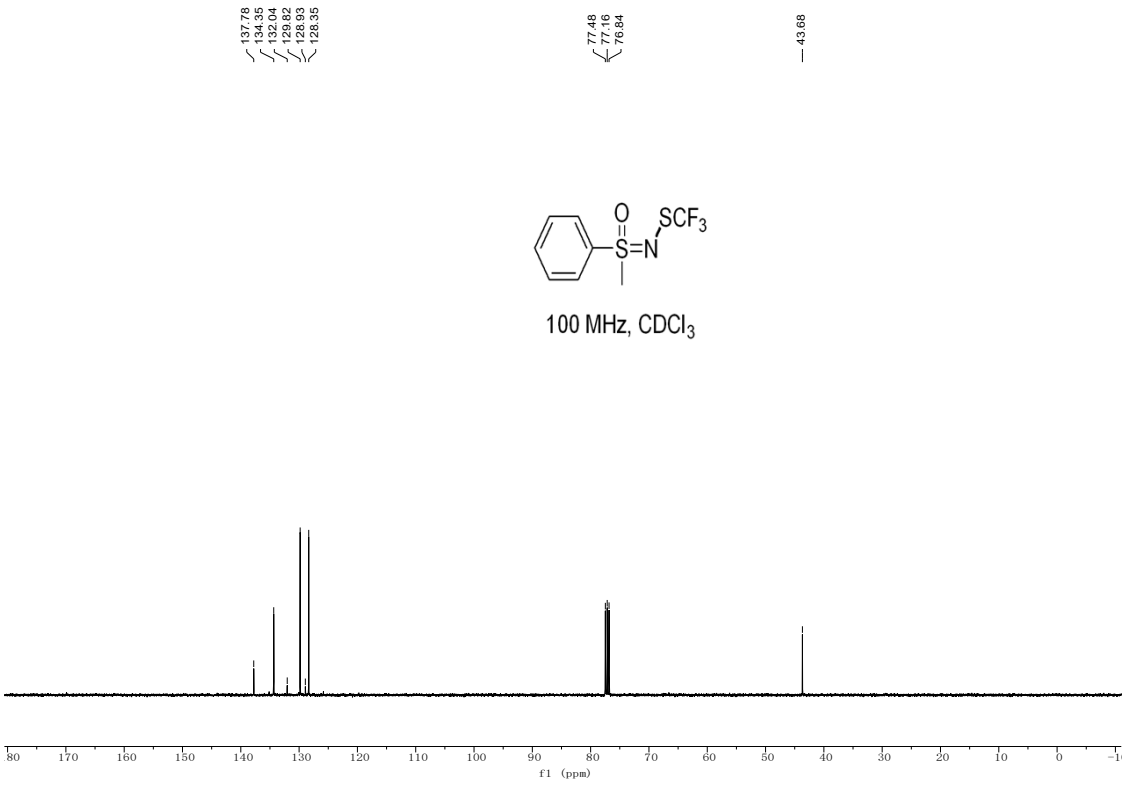
3a -^{19}F NMR



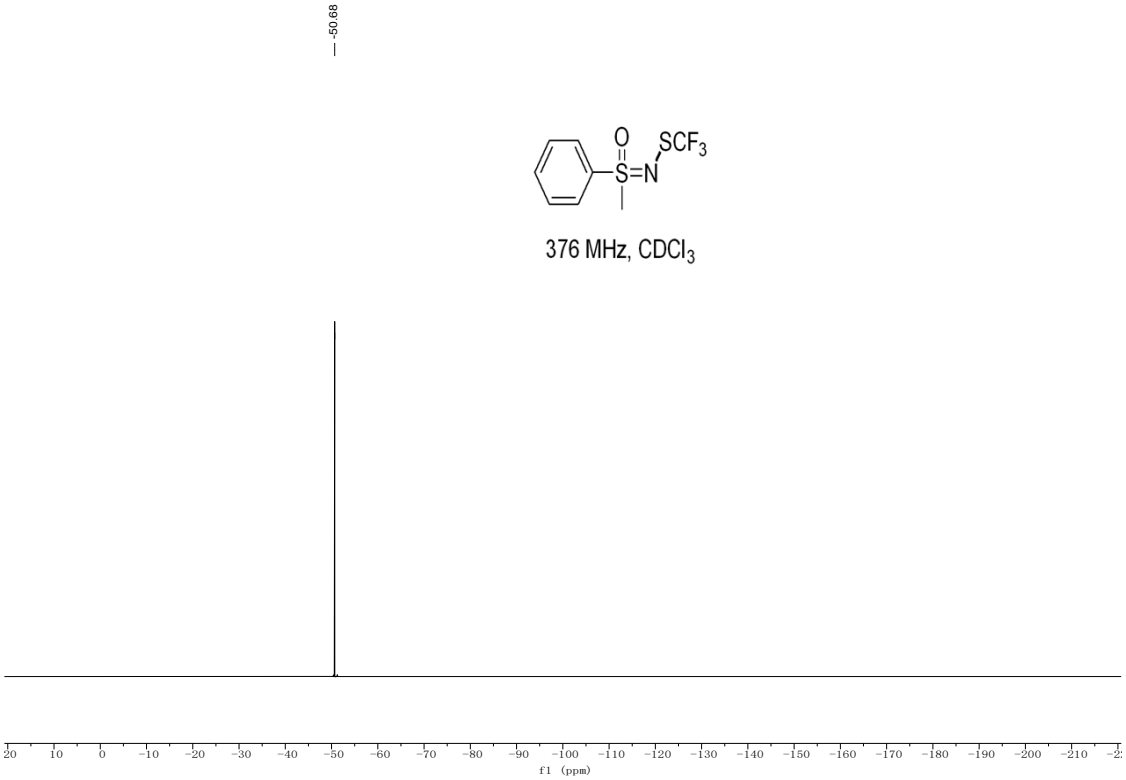
3b-^{1}H NMR



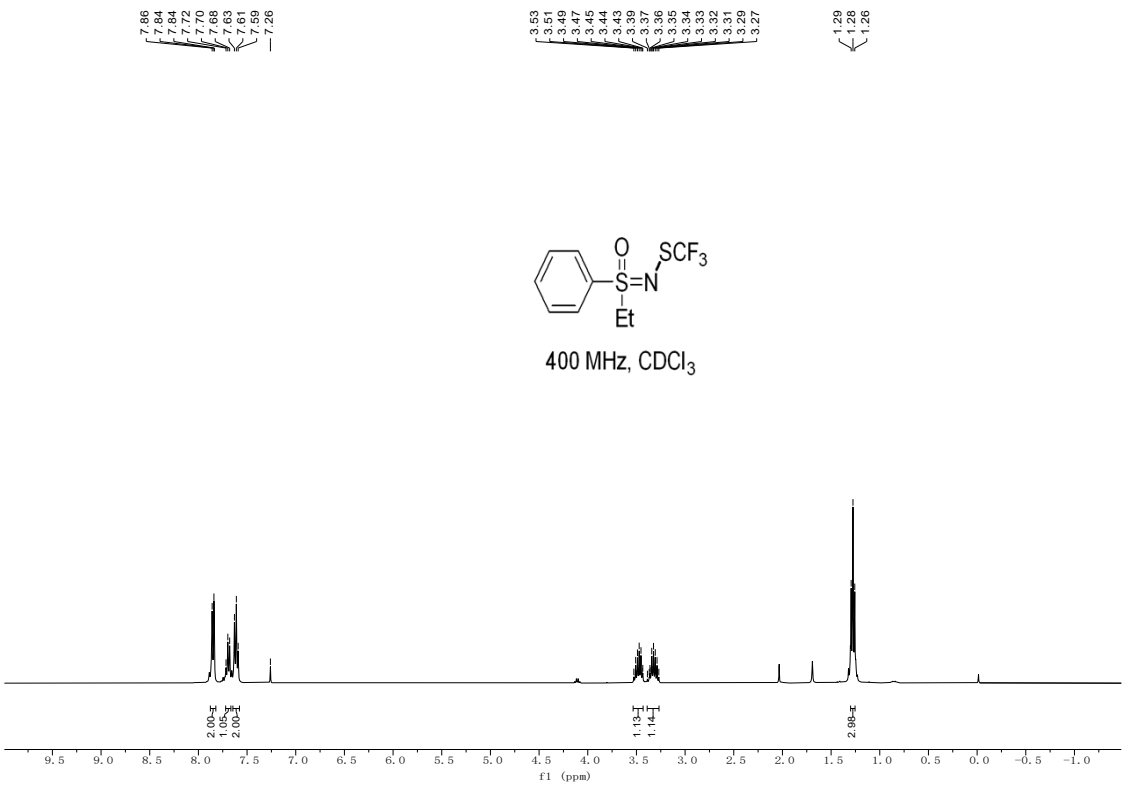
3b -^{13}C NMR



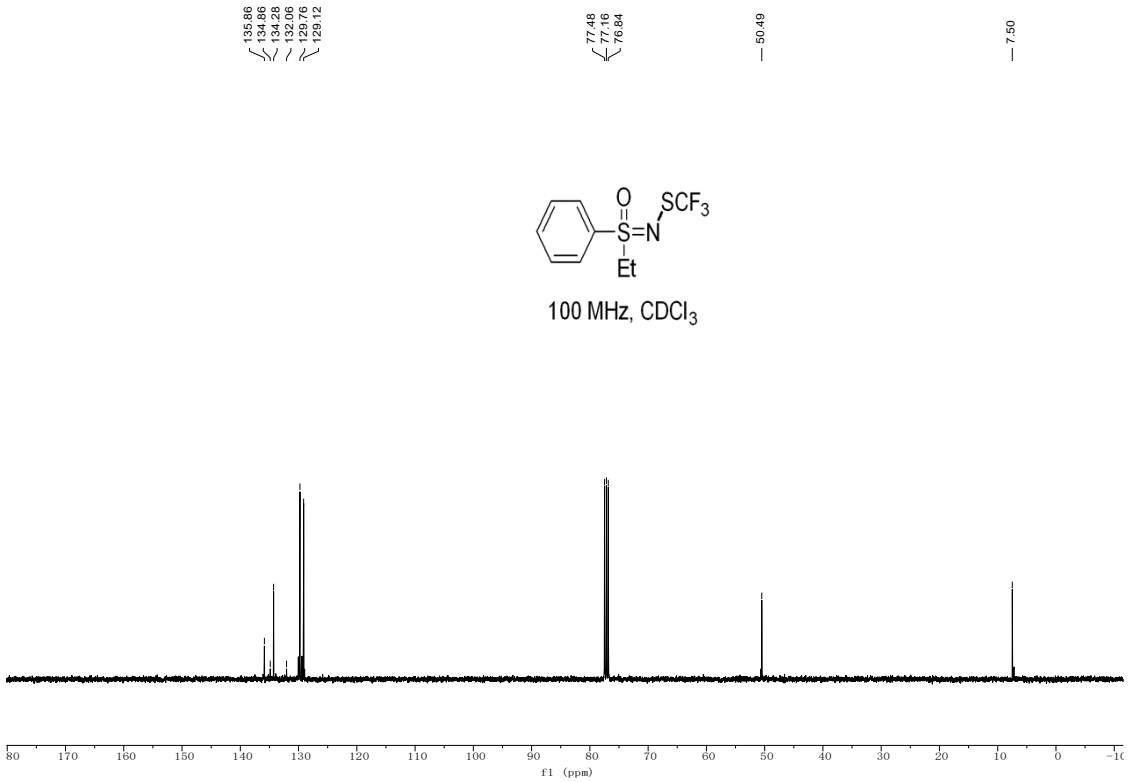
3b -^{19}F NMR



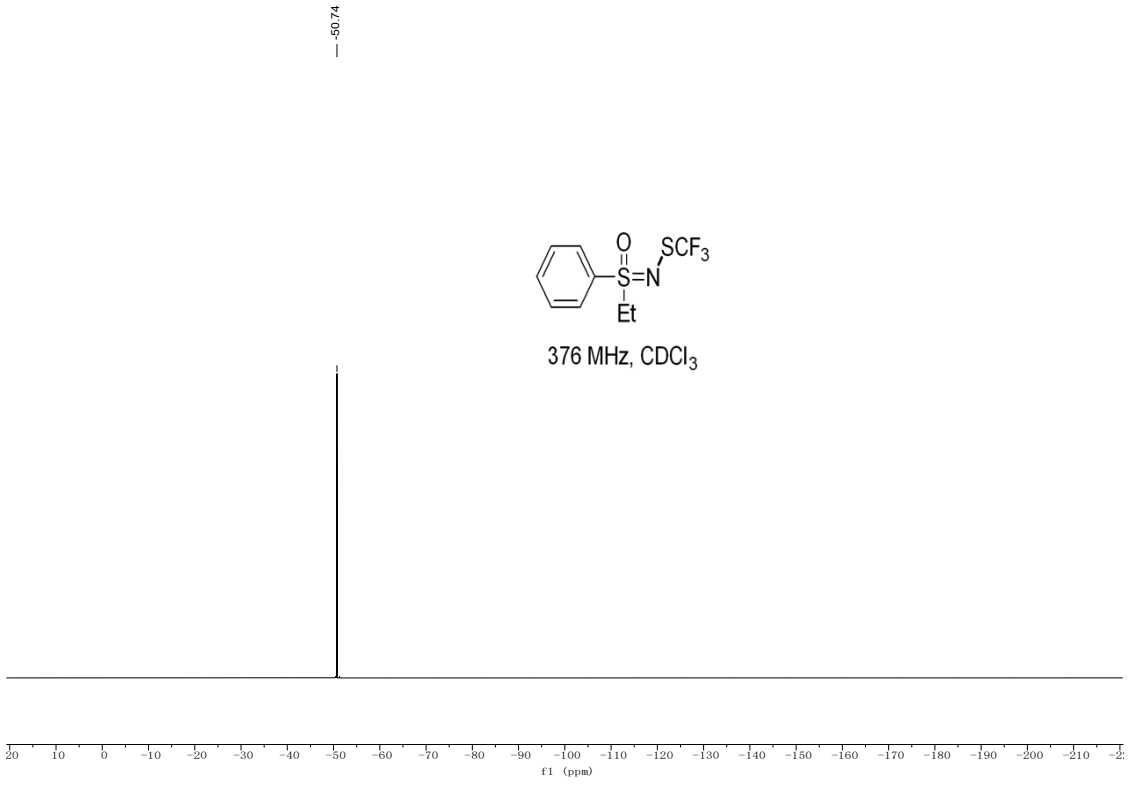
3c-^{1}H NMR



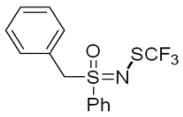
3c -^{13}C NMR



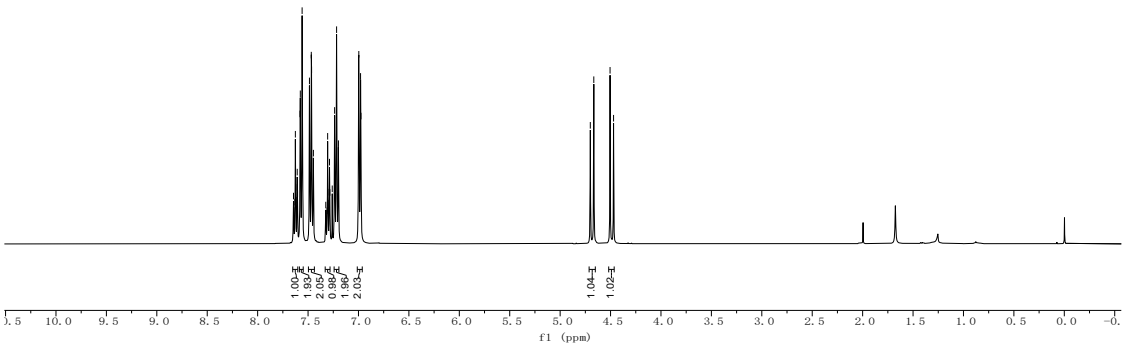
3c -^{19}F NMR



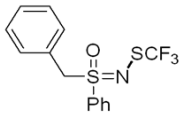
3d-^{1}H NMR



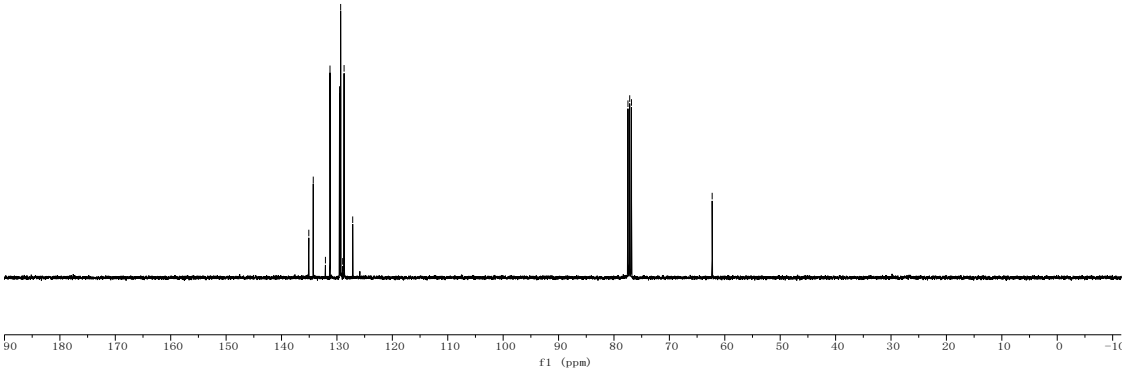
400 MHz, $CDCl_3$



3d -^{13}C NMR



100 MHz, $CDCl_3$



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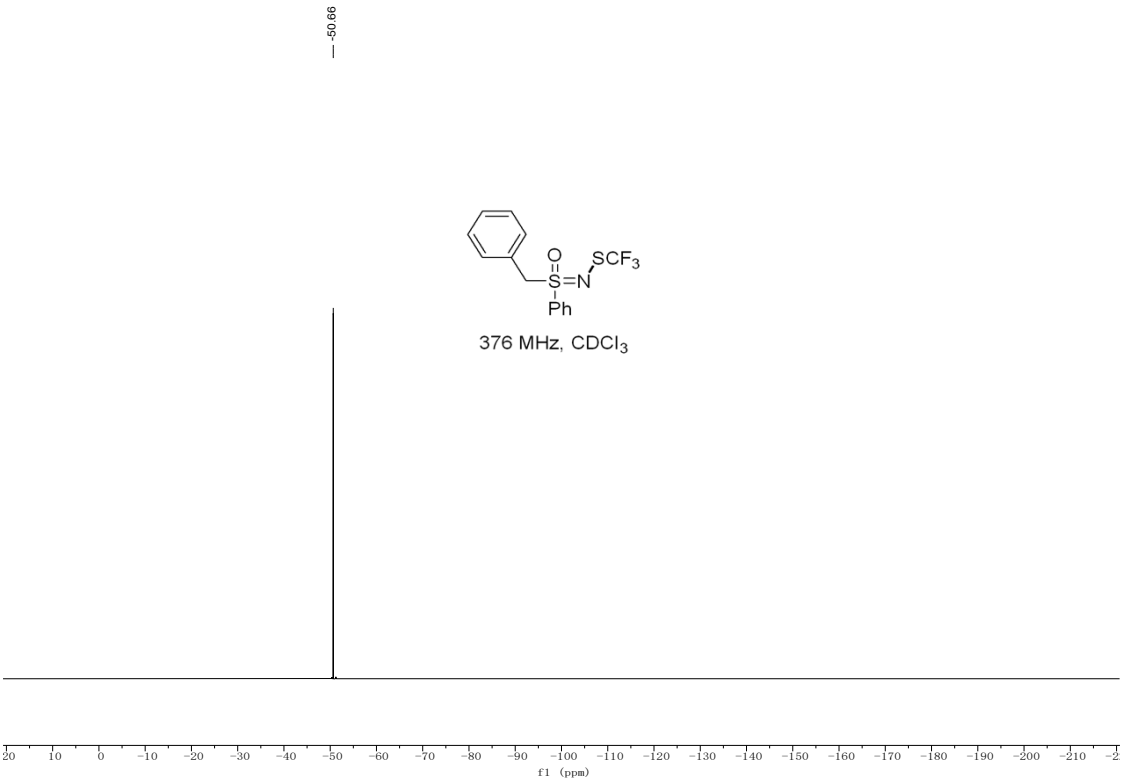
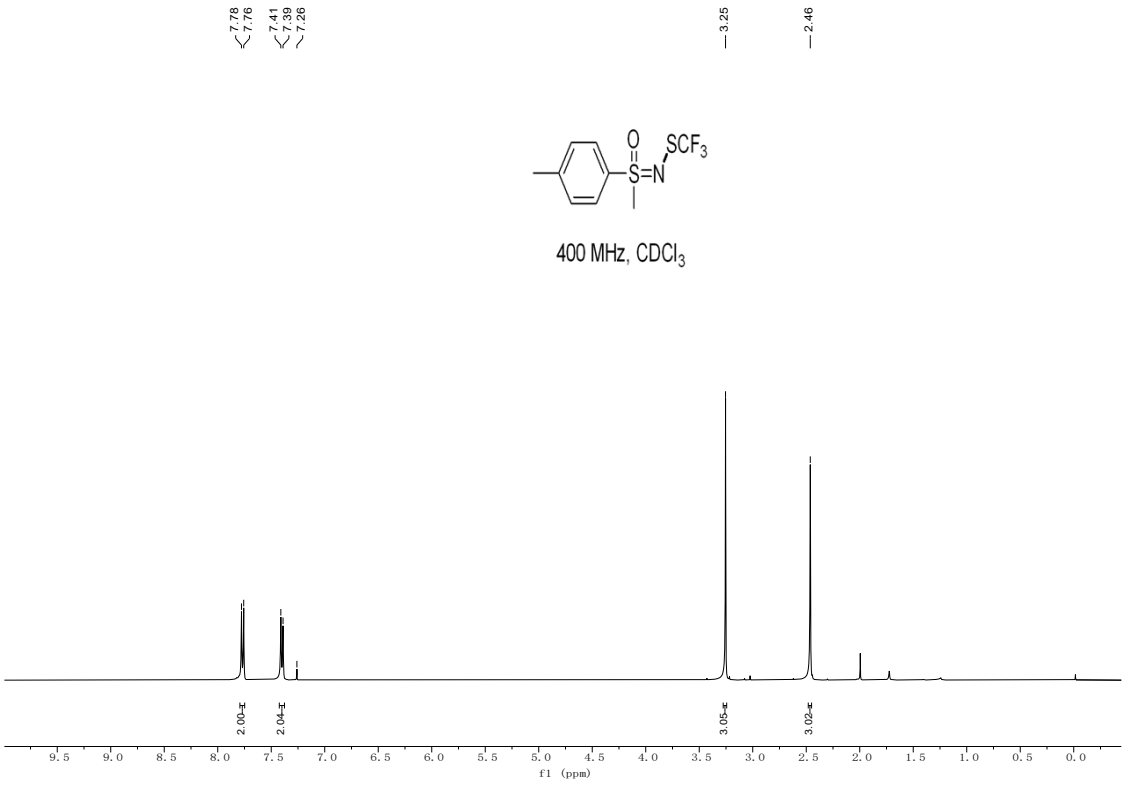


3e-^{1}H NMR



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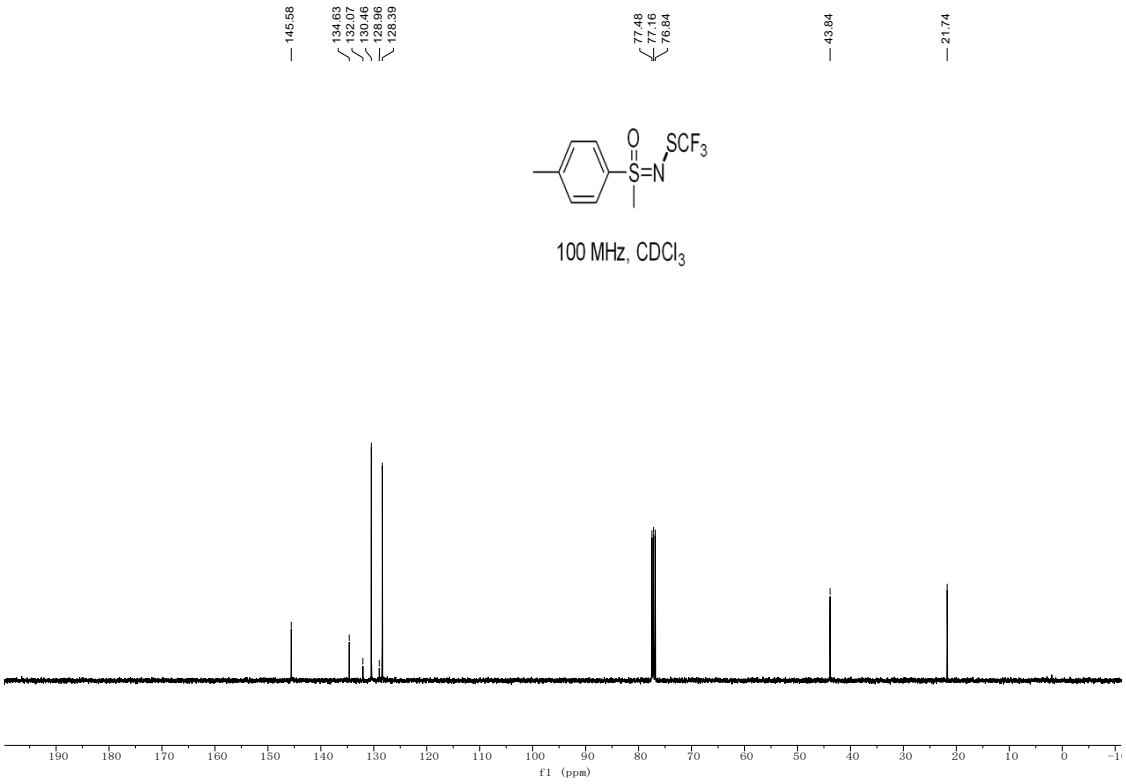

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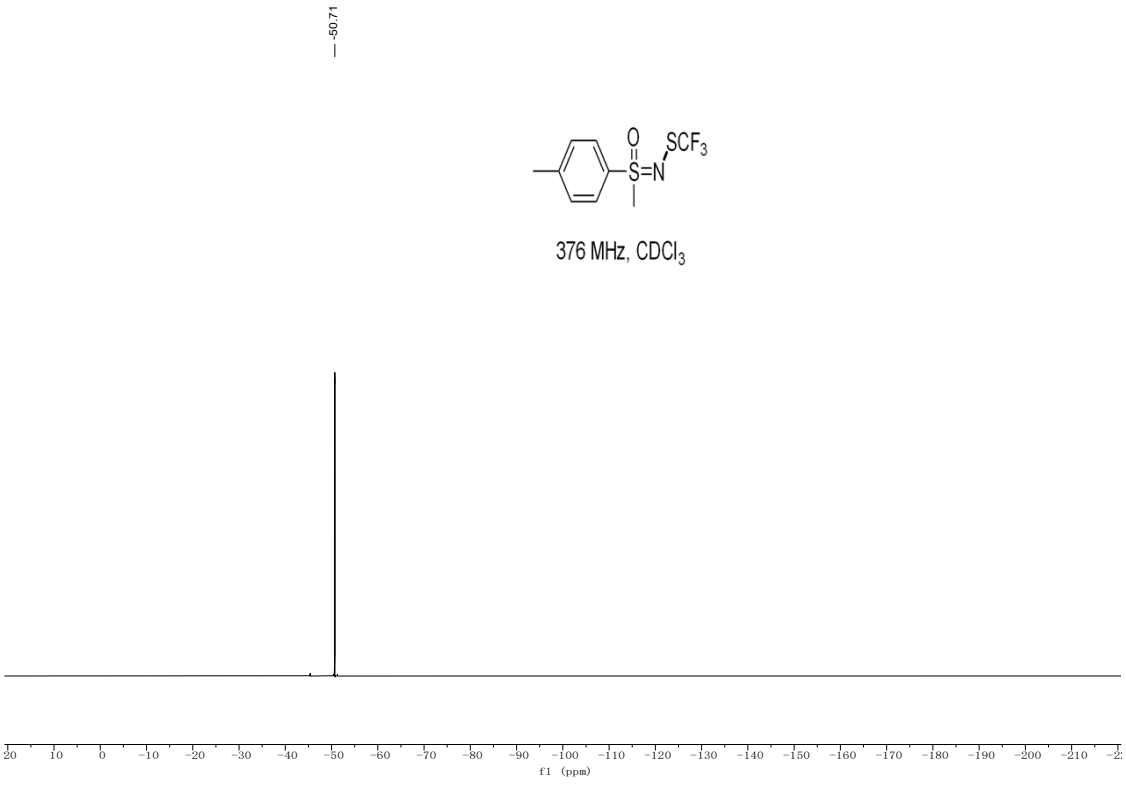
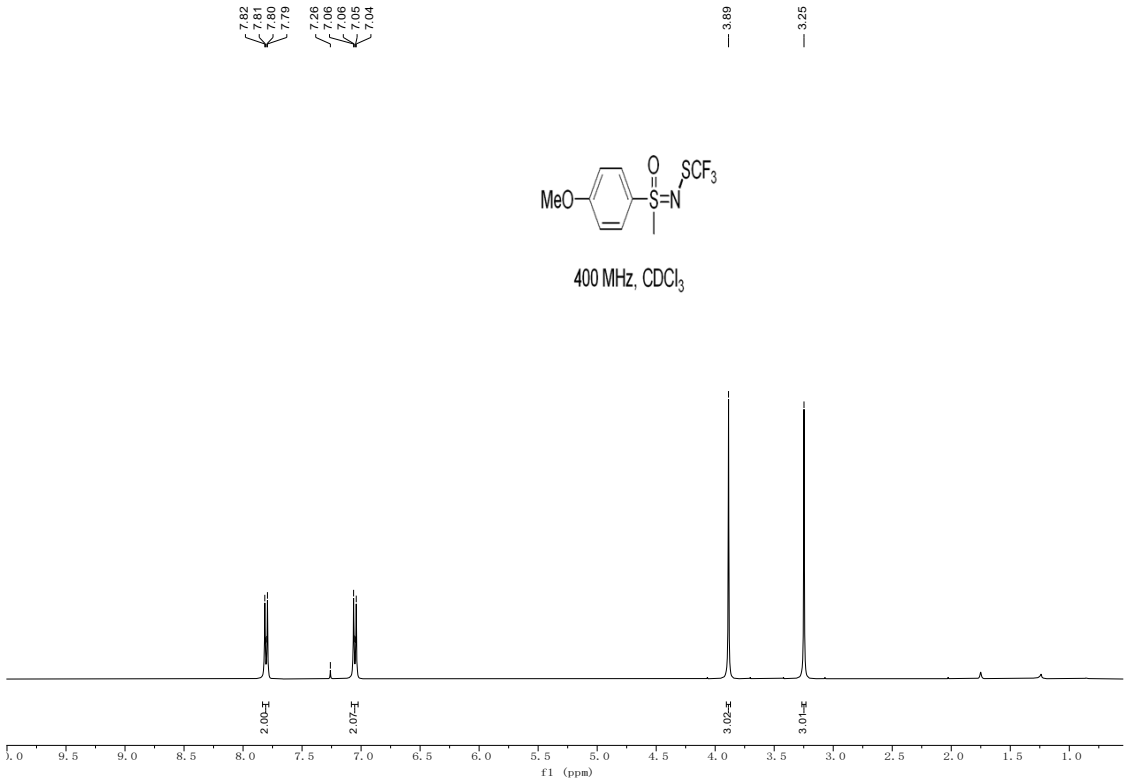


3f-^{1}H NMR



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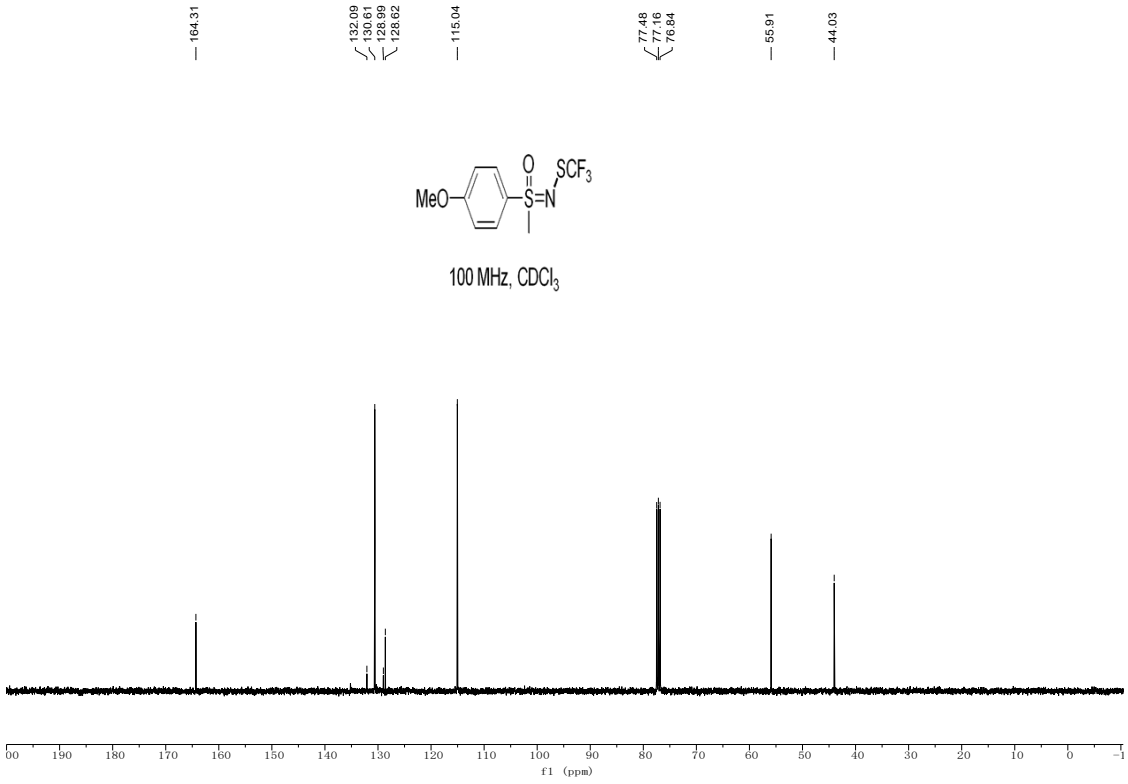
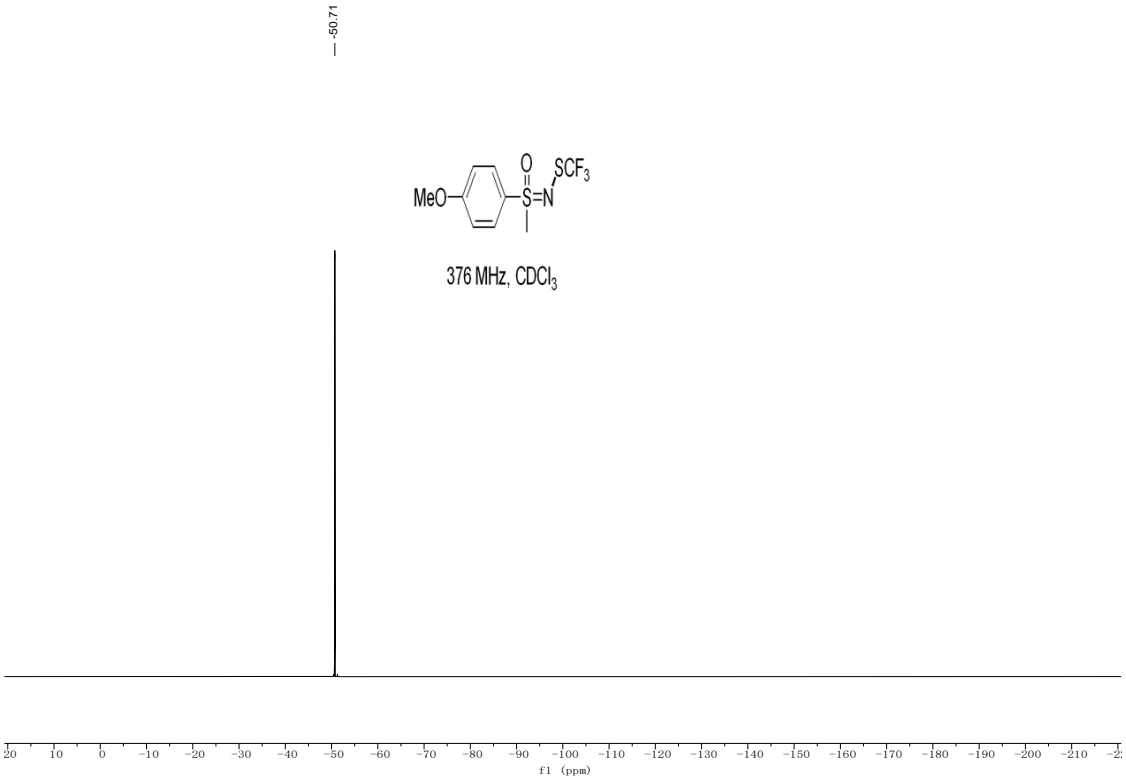
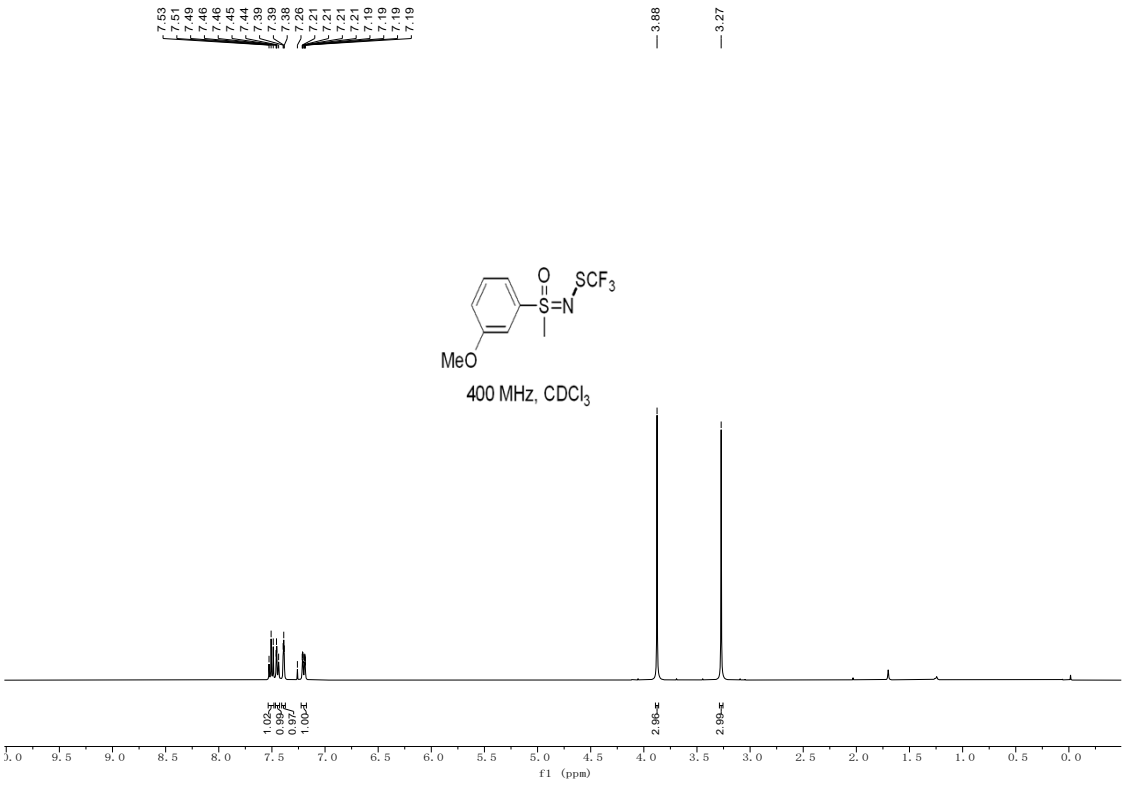


3f -^{19}F NMR



3g-^{1}H NMR



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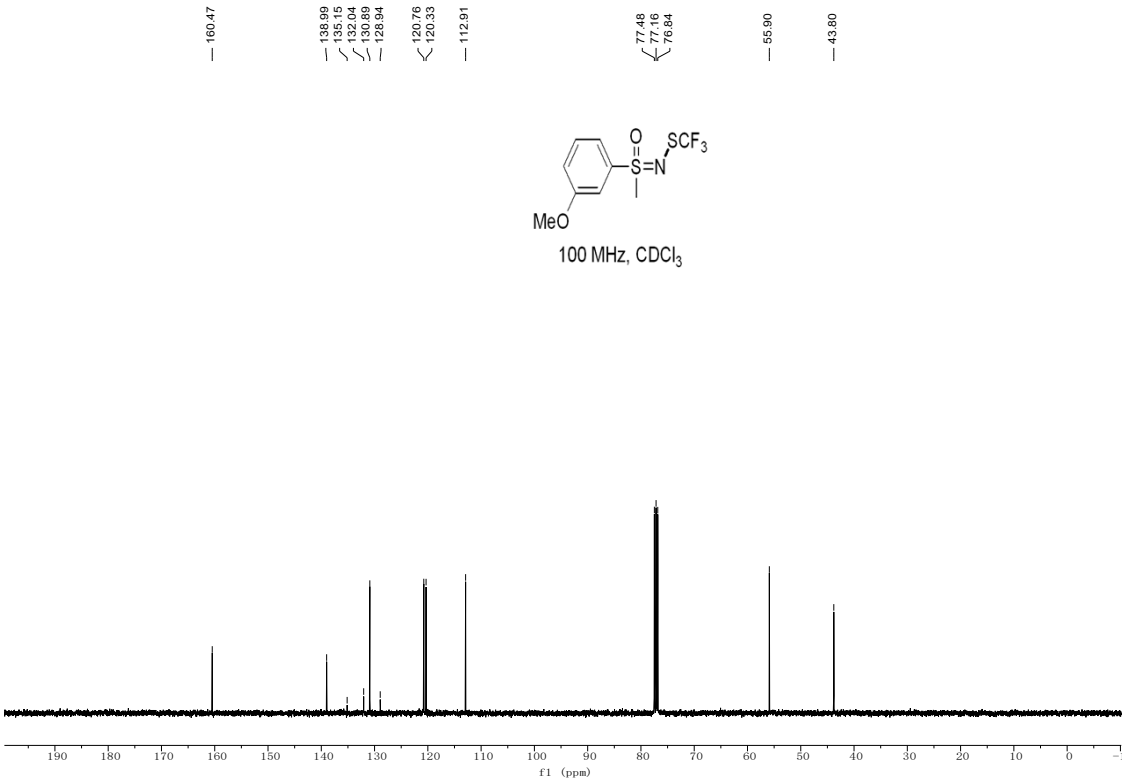
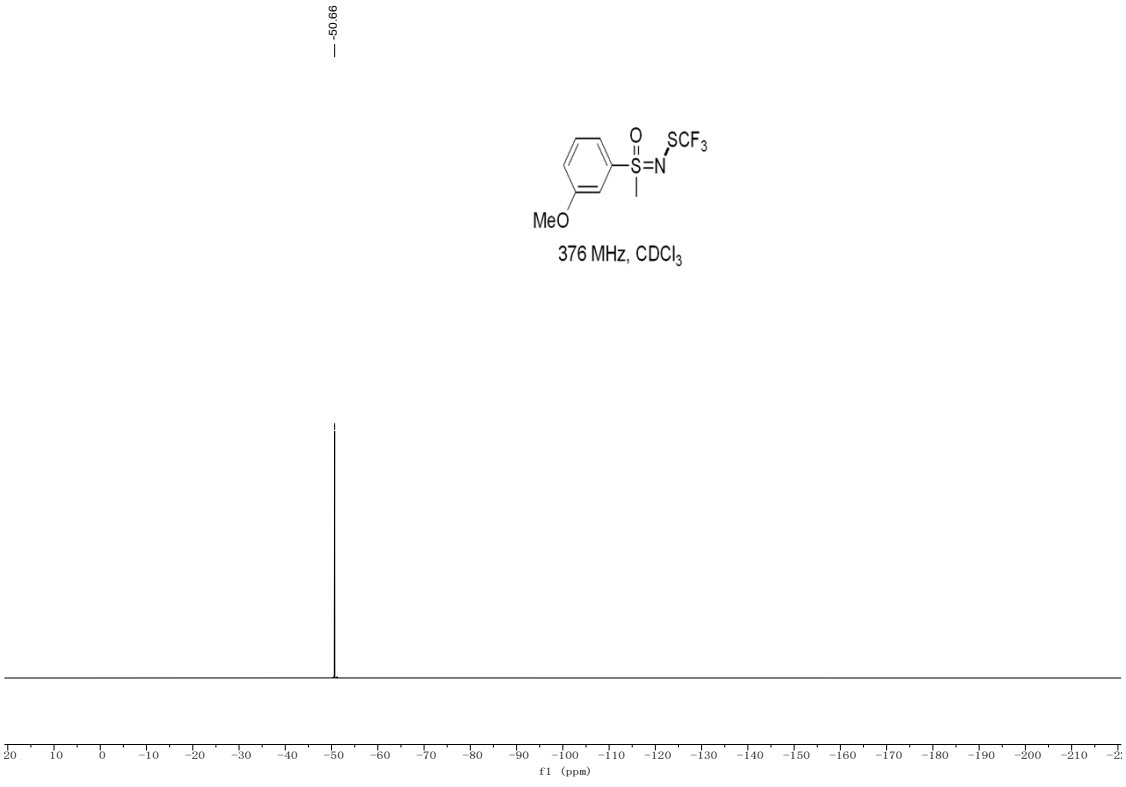
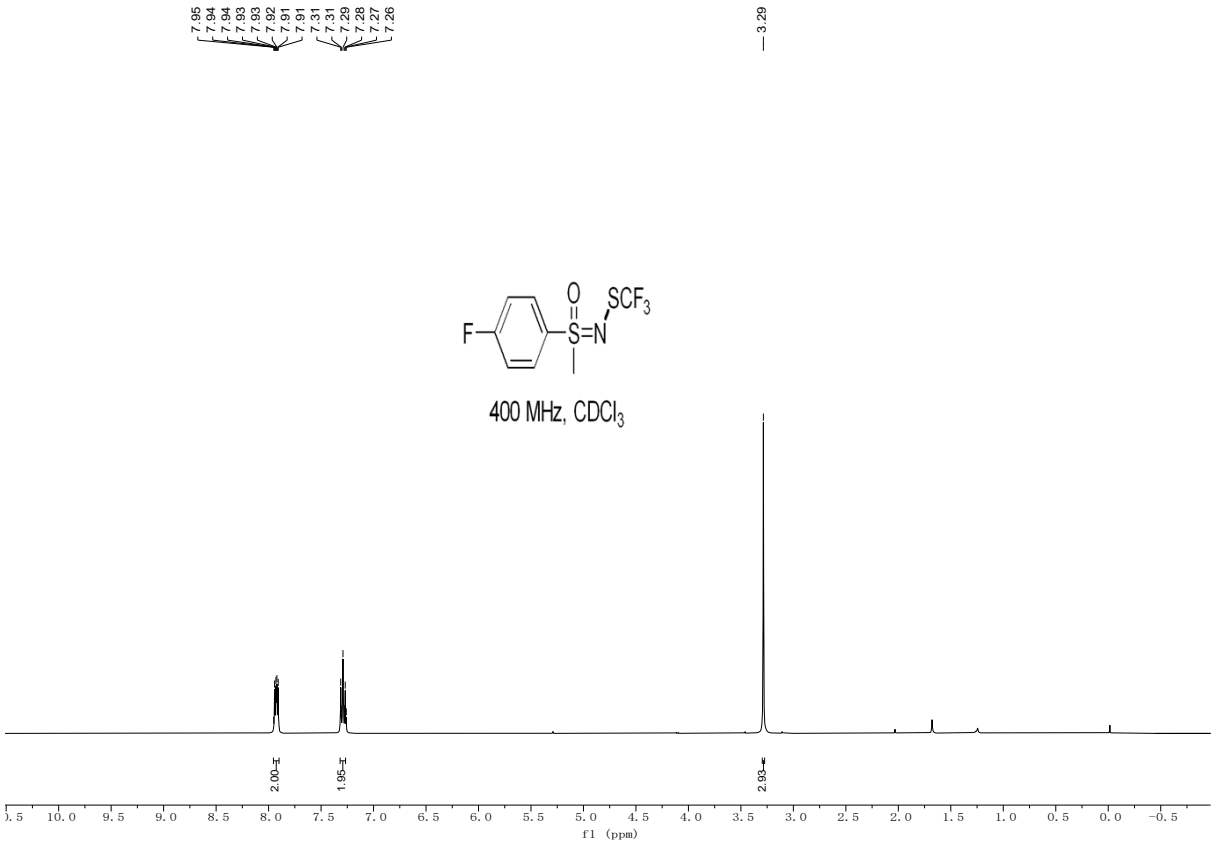


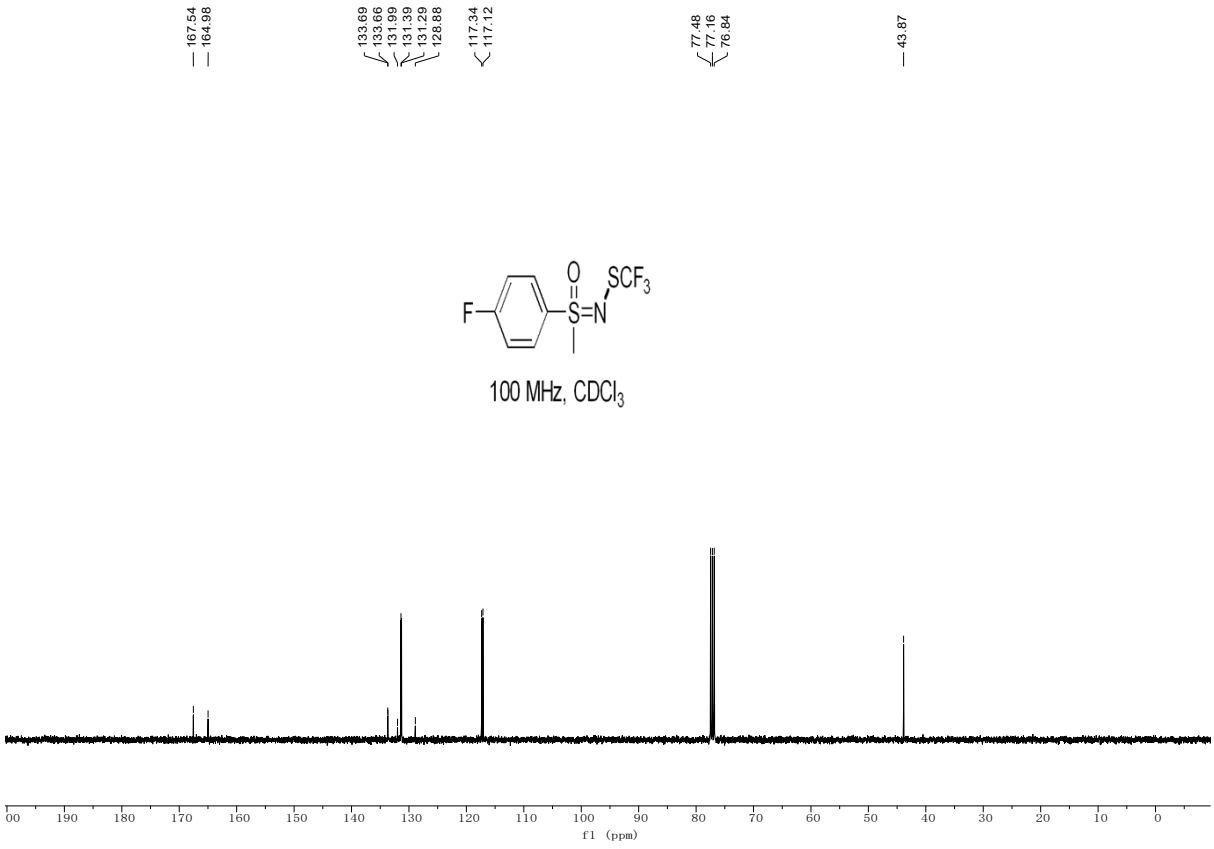
3g -^{19}F NMR



3h-^{1}H NMR



3h -^{13}C NMR



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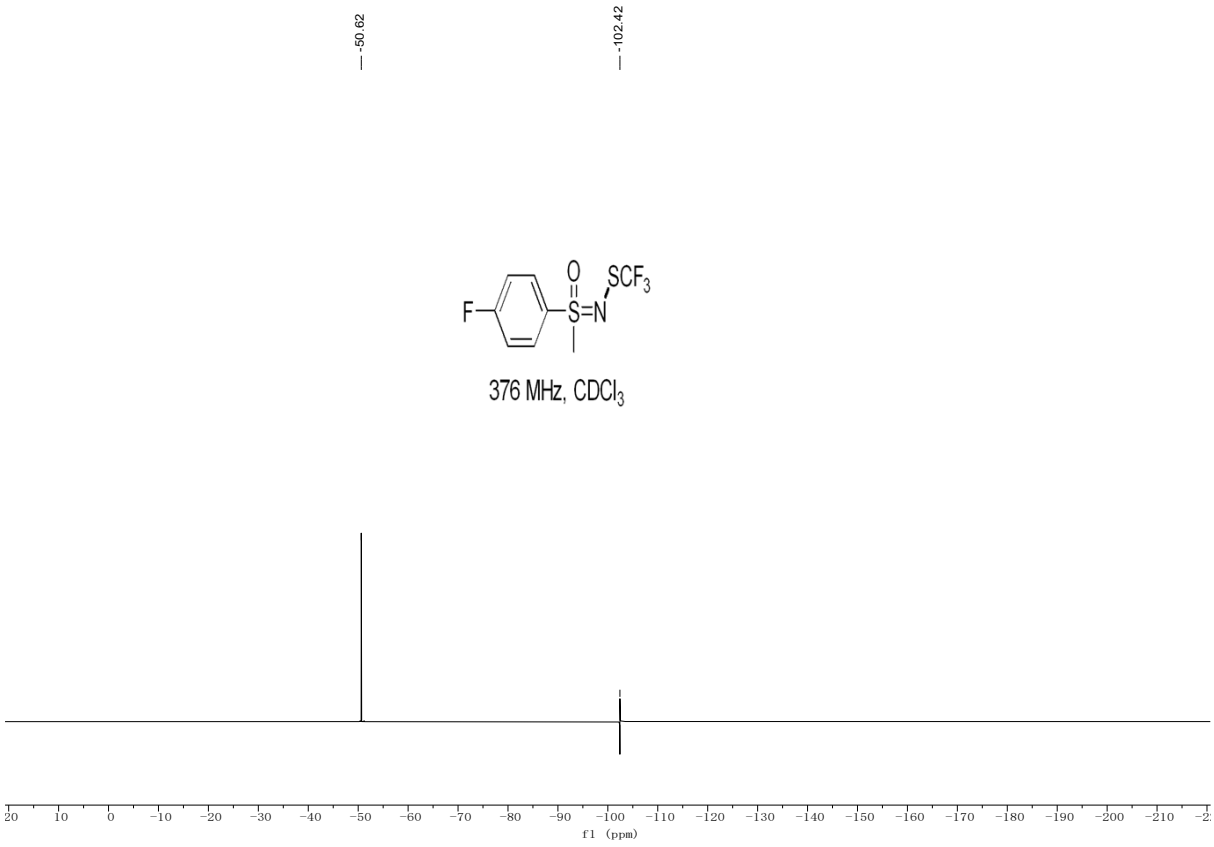
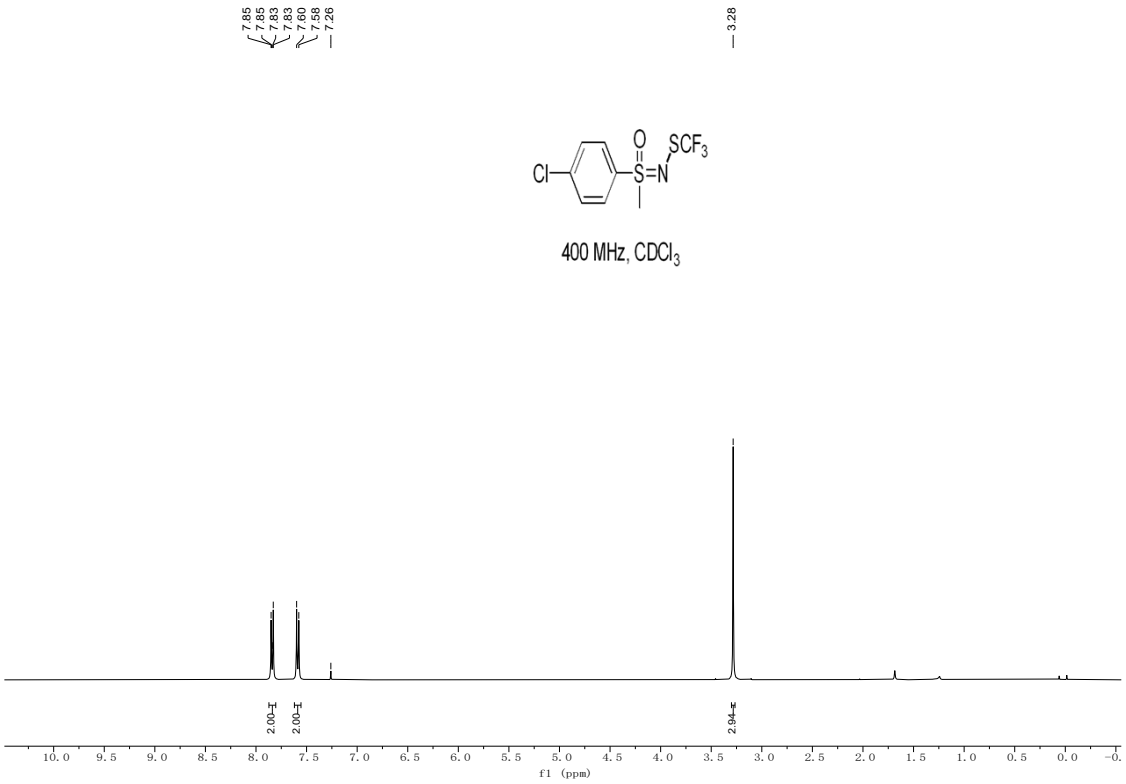


3i-^{1}H NMR



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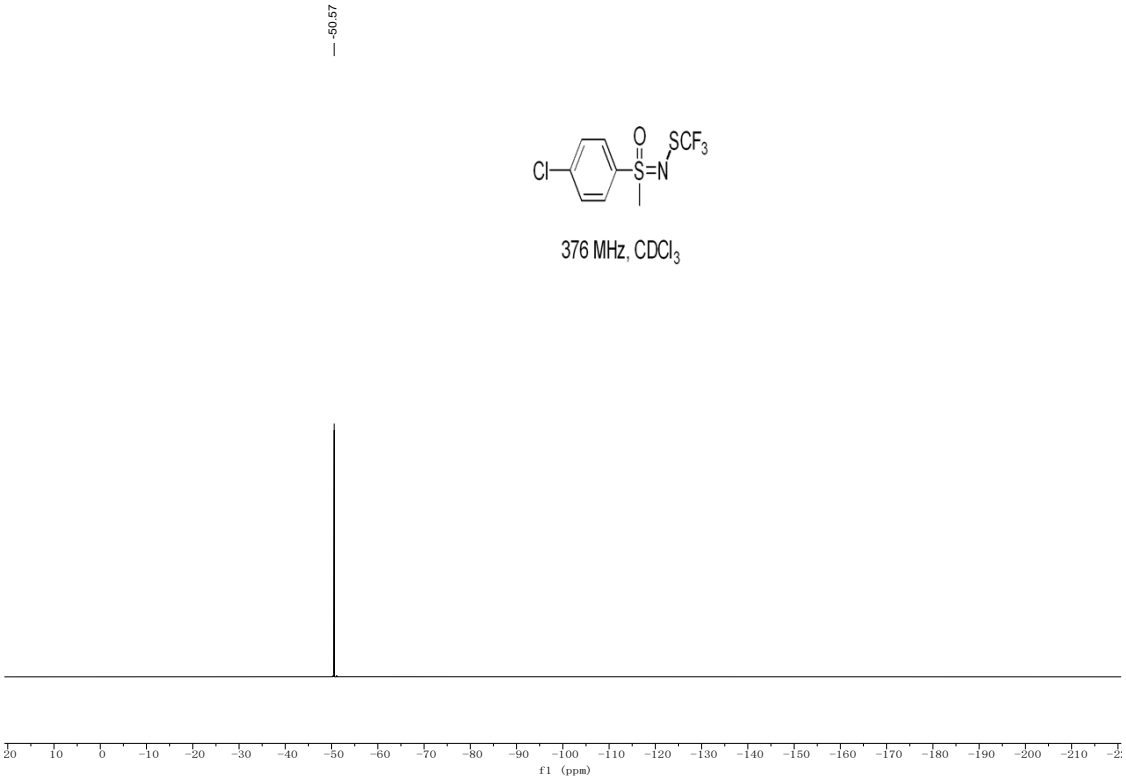

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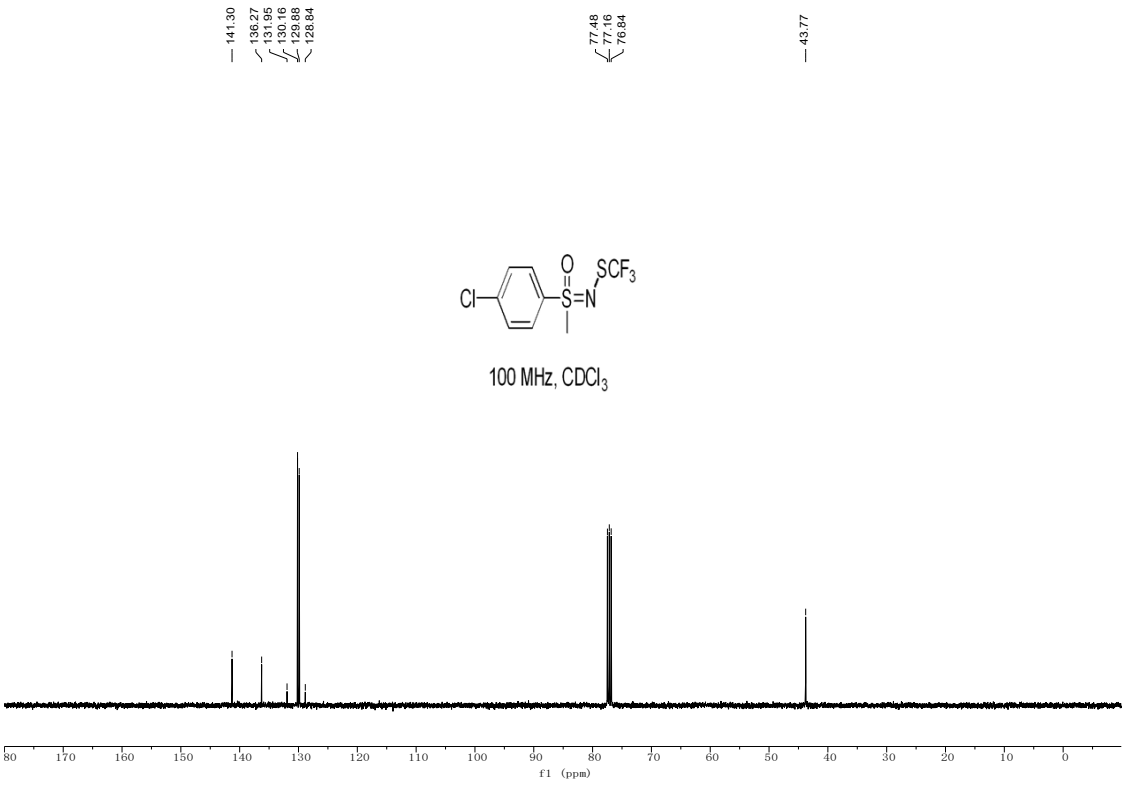
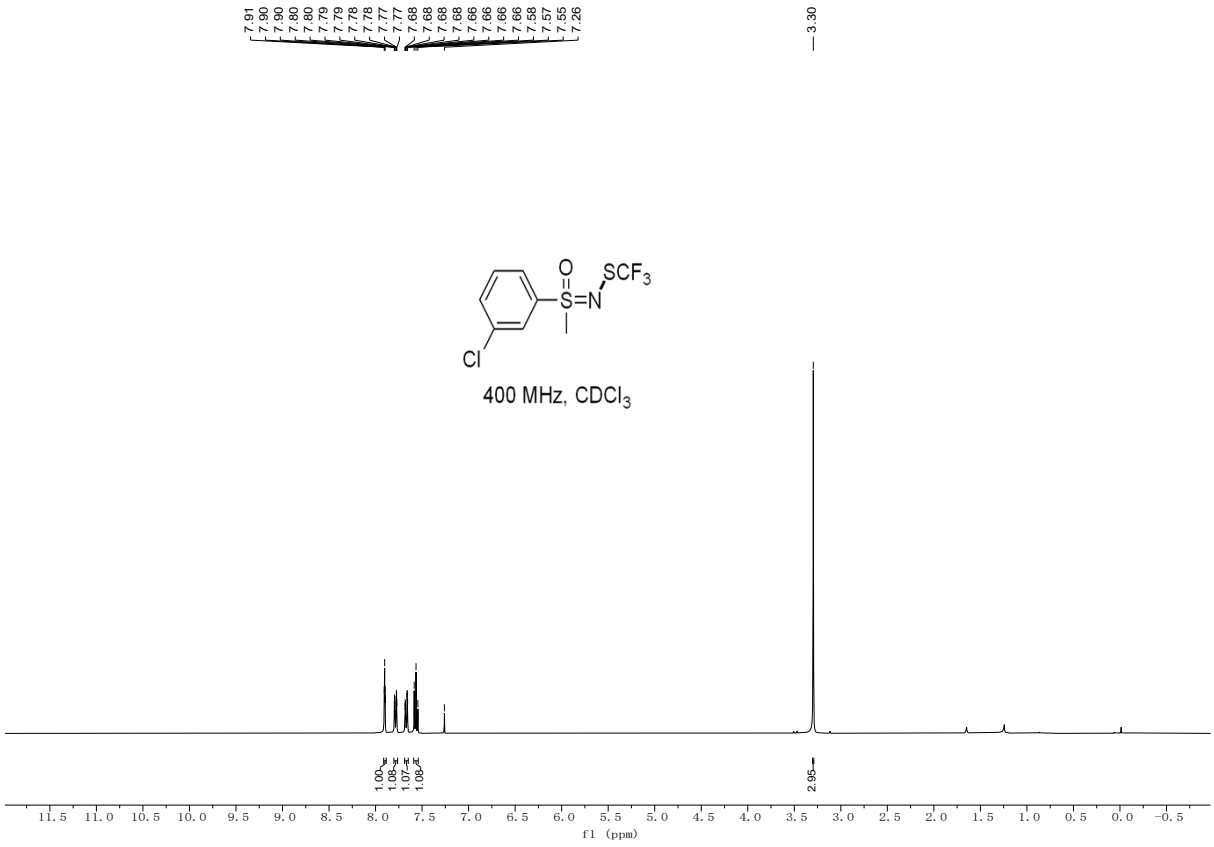


3j-^{1}H NMR



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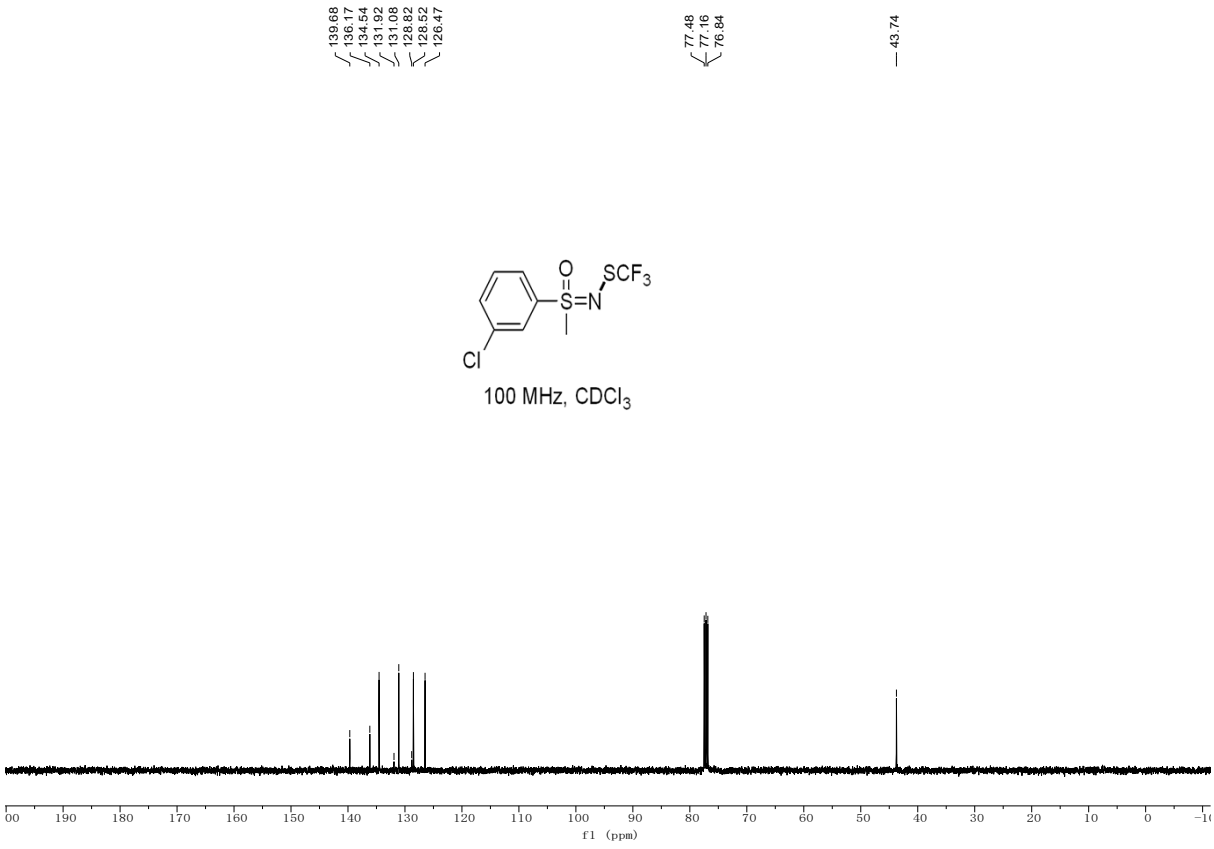

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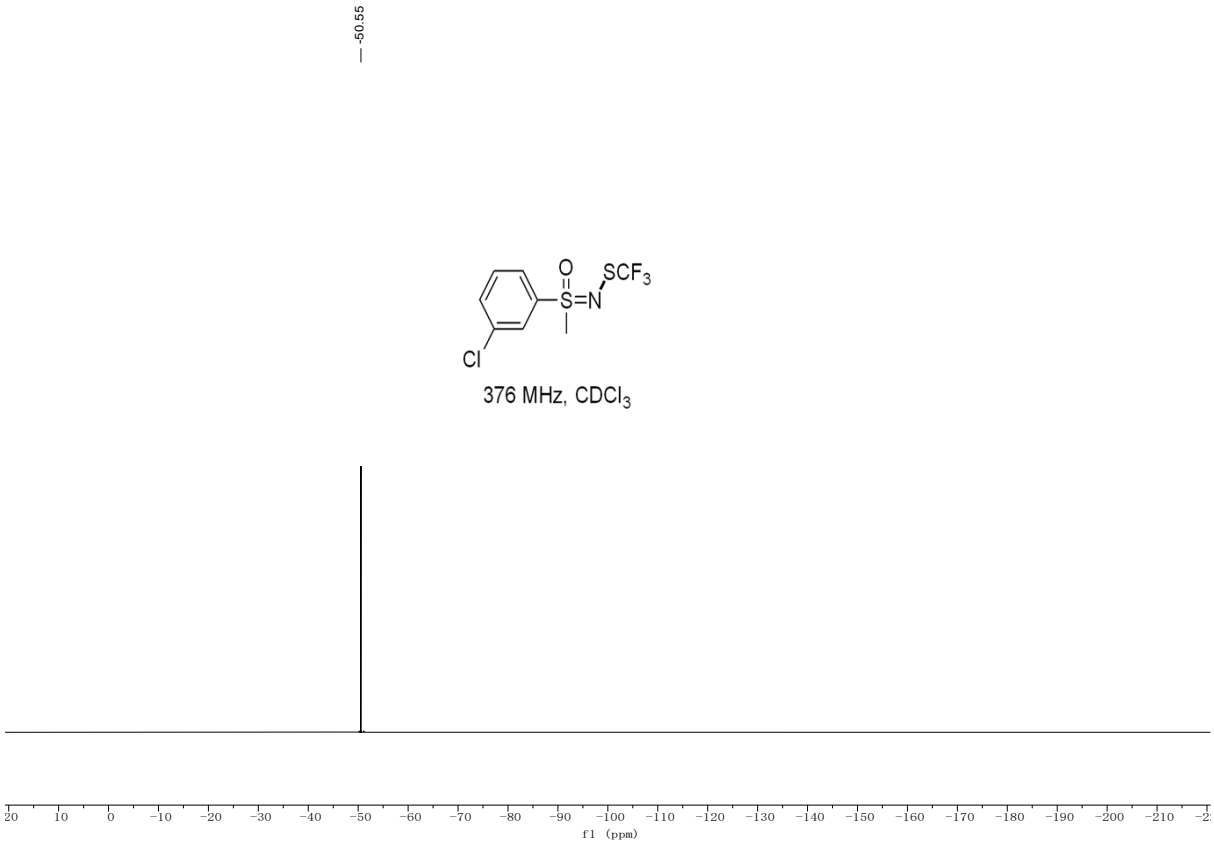
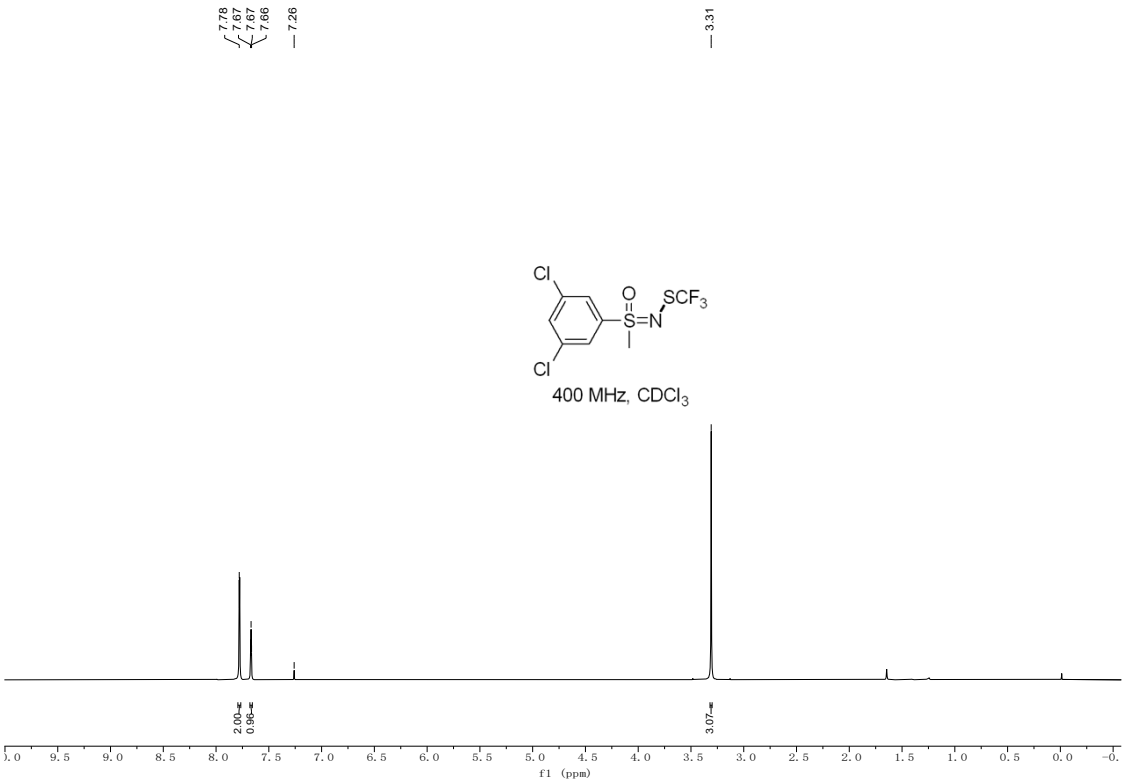


3k-^{1}H NMR



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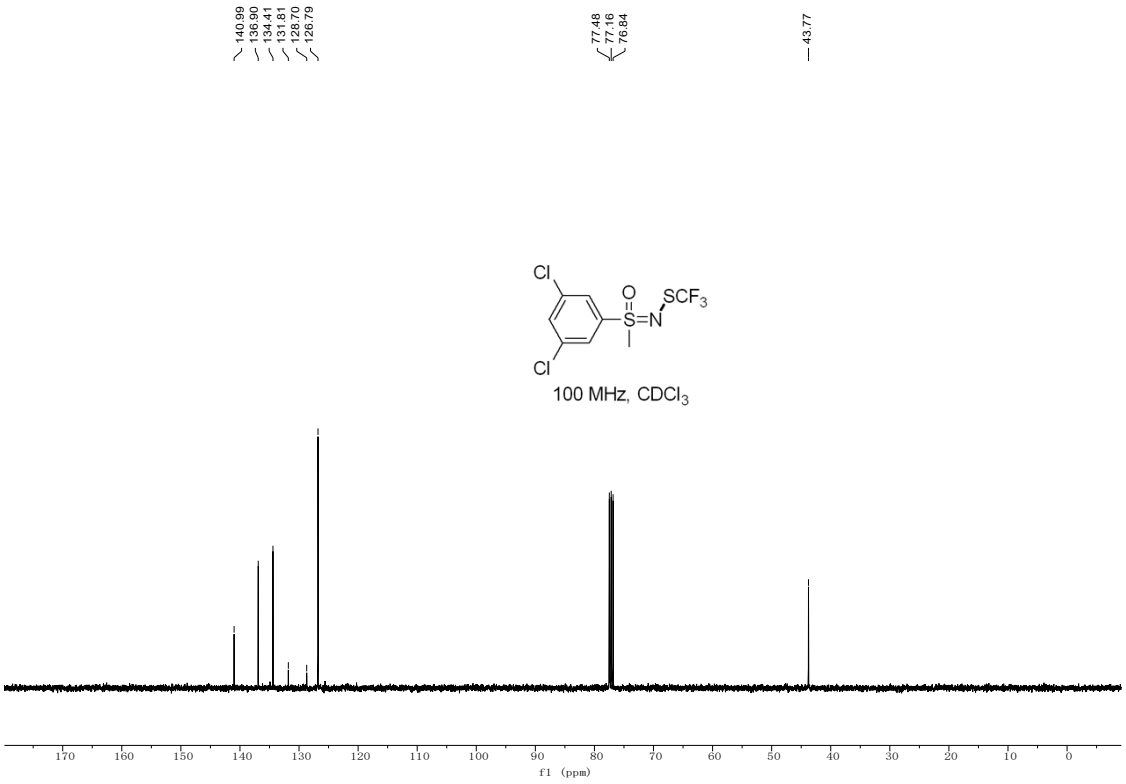

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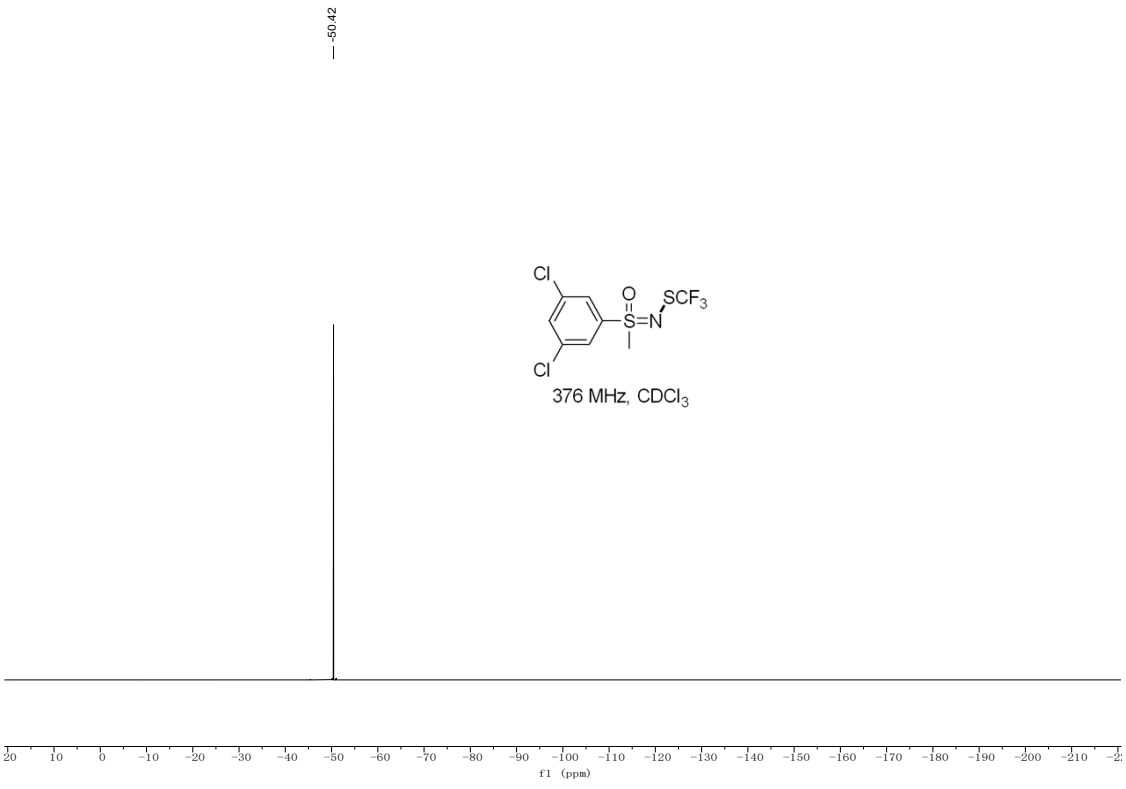

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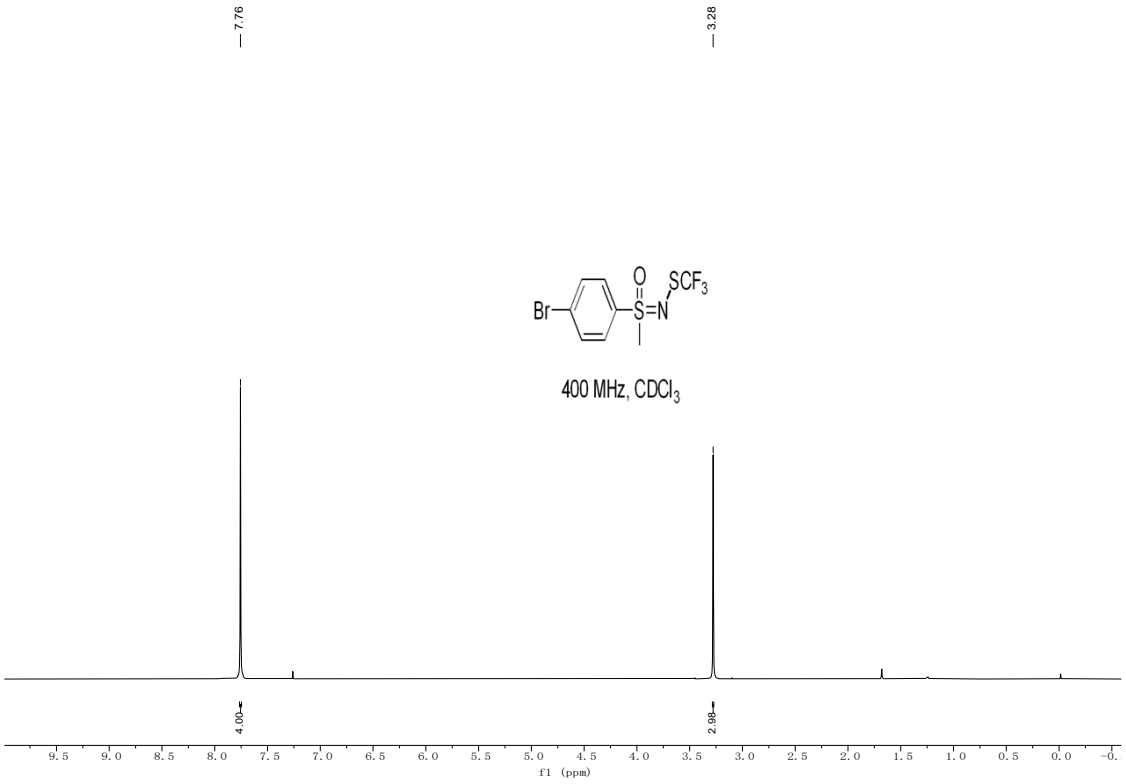

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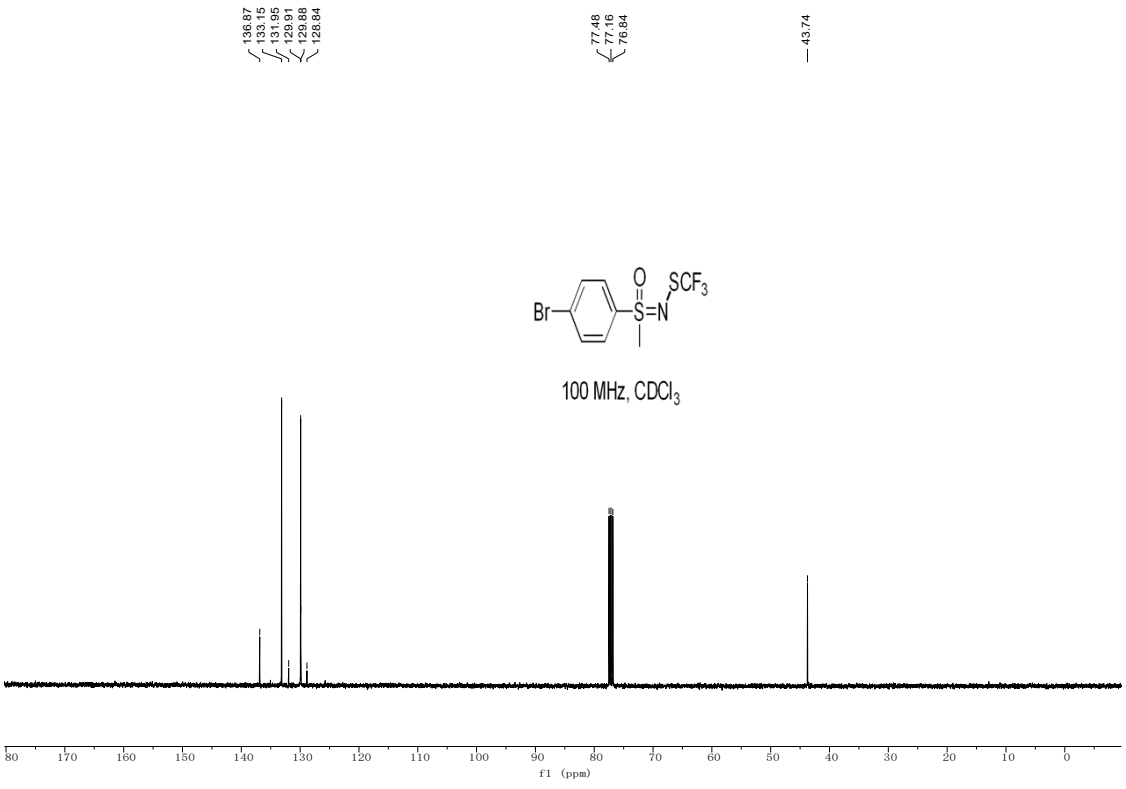
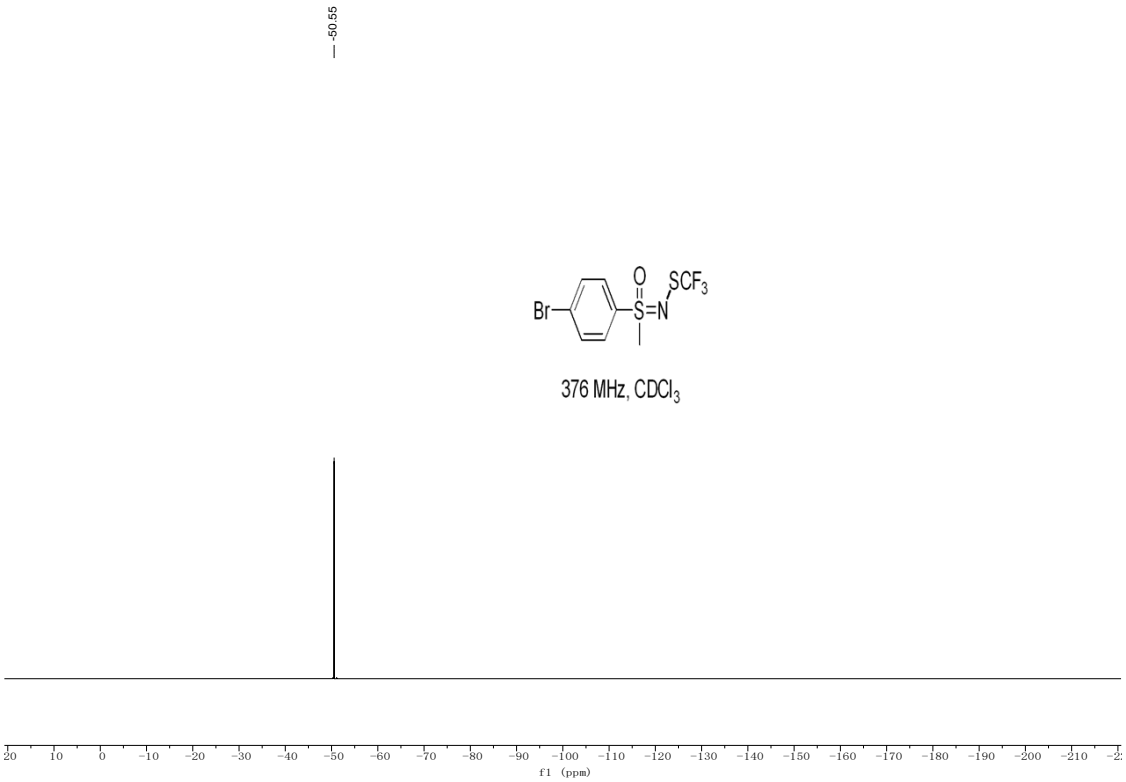
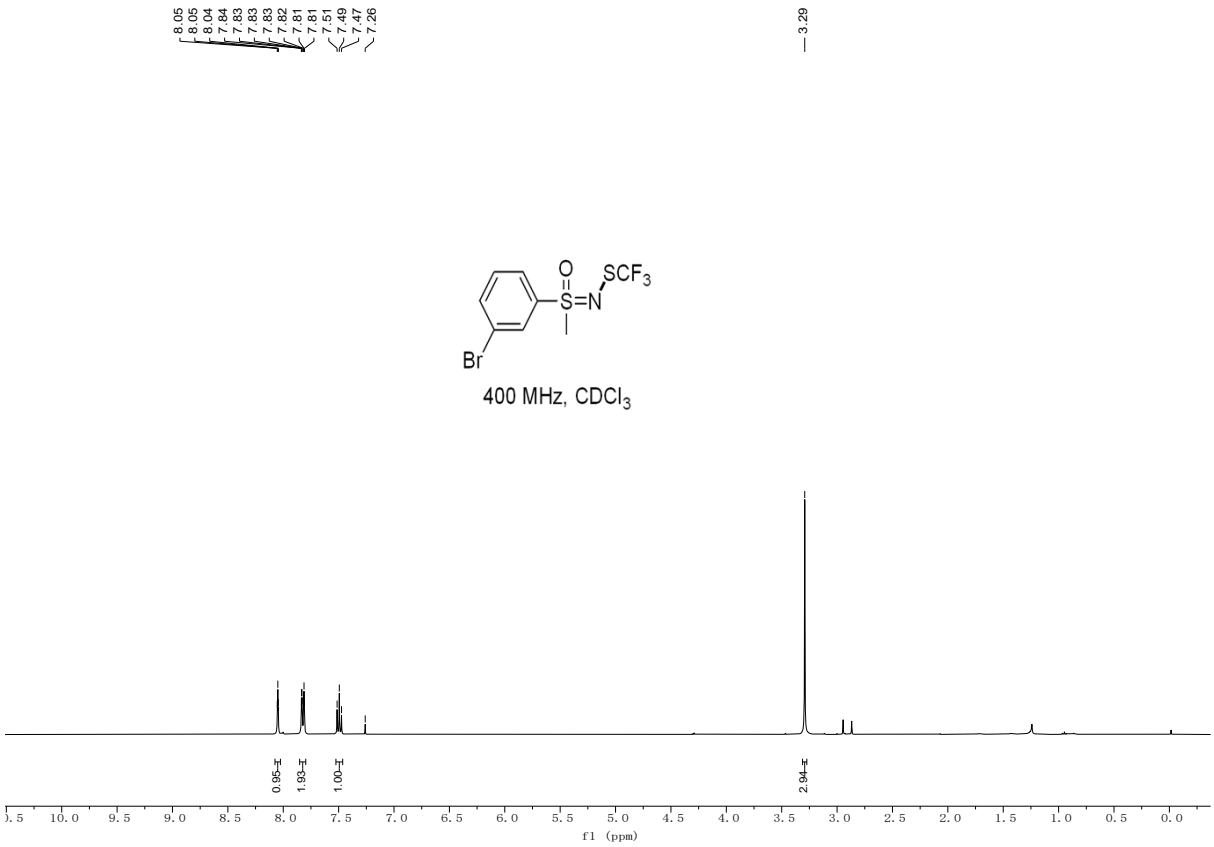


3l -^{19}F NMR



3m-^{1}H NMR



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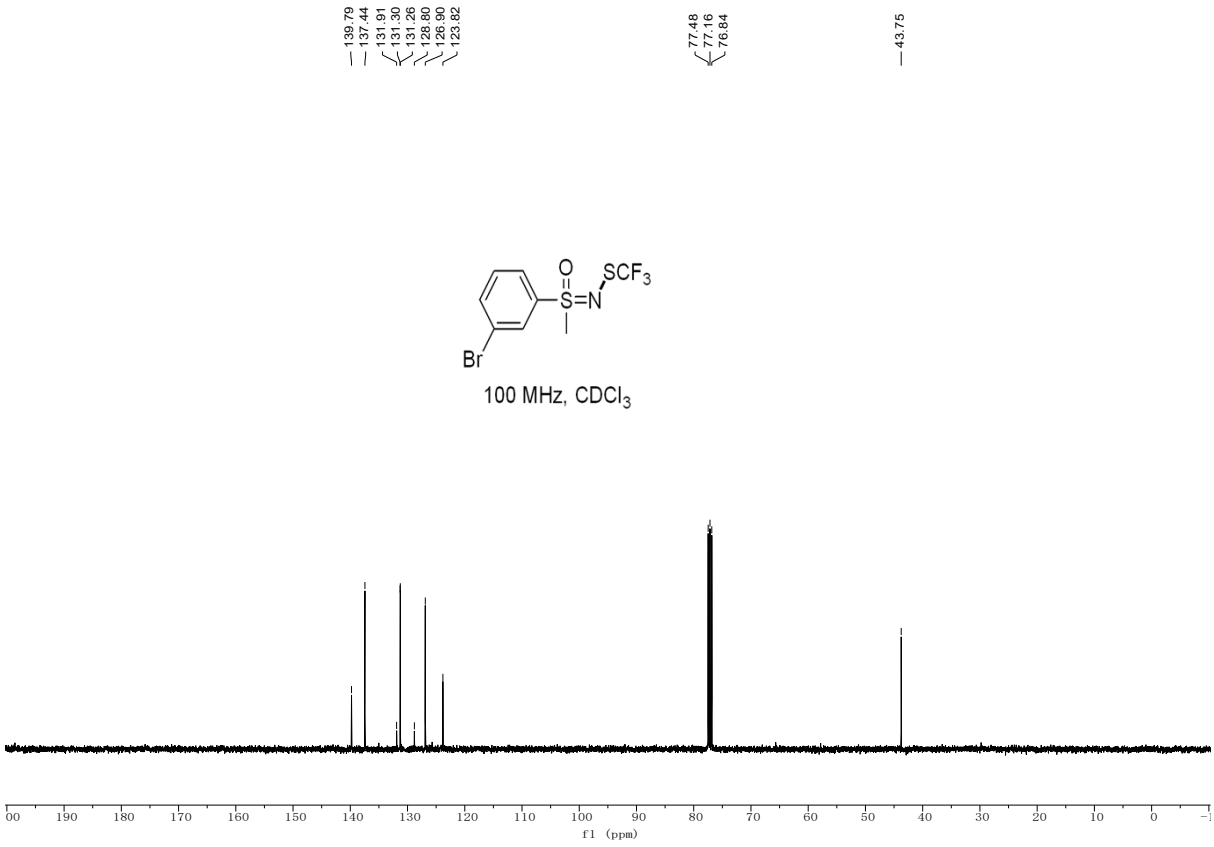

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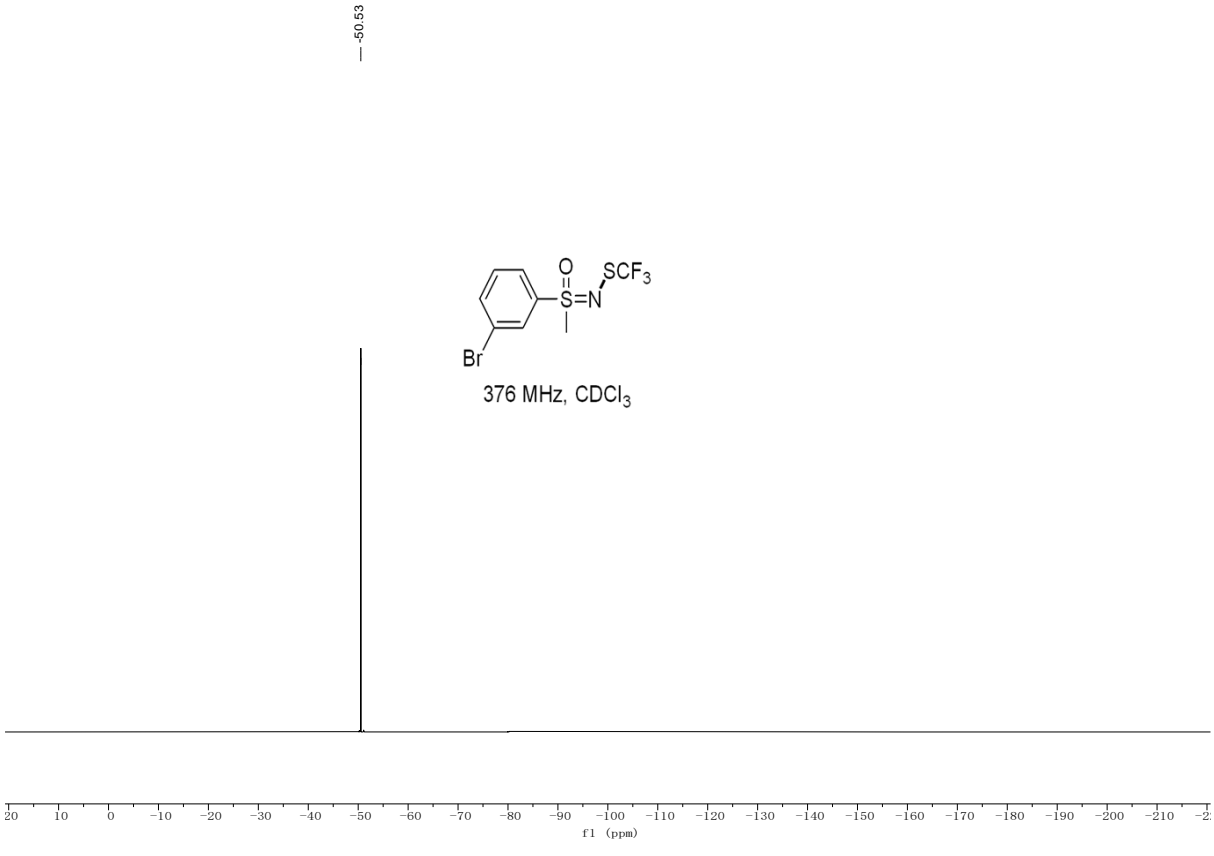

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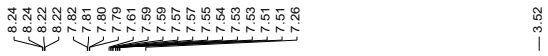
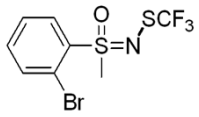
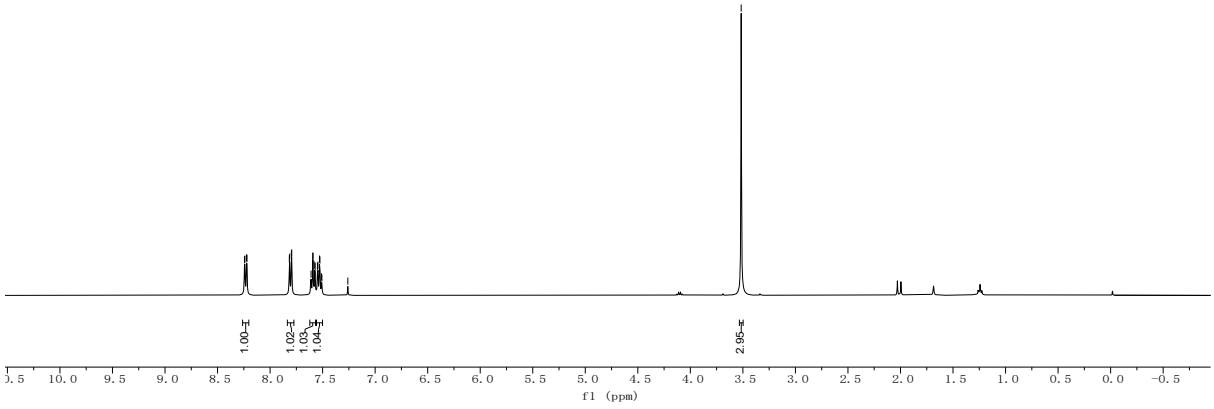
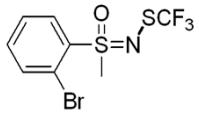




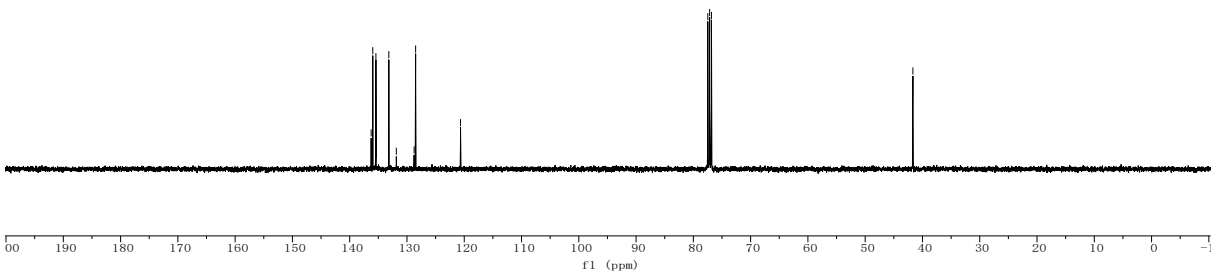
400 MHz, $CDCl_3$



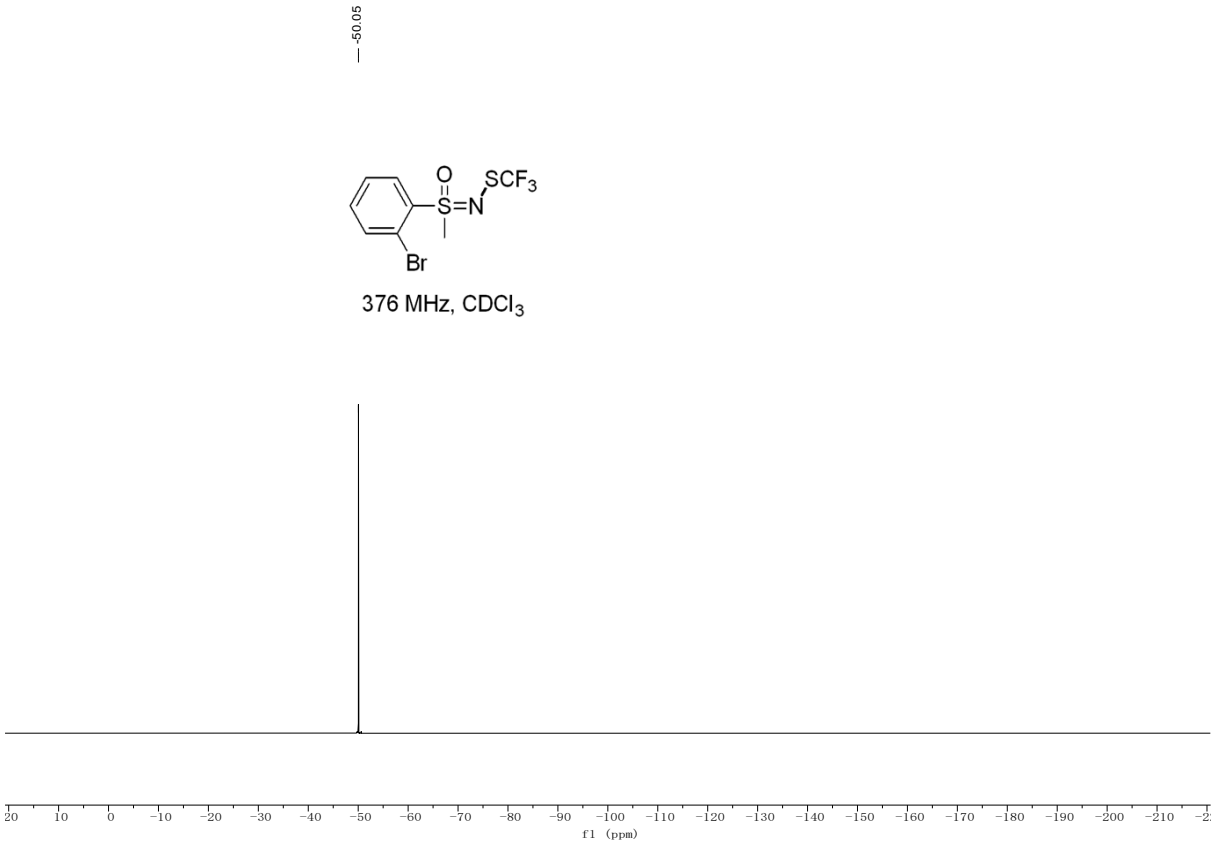
3n -^{13}C NMR



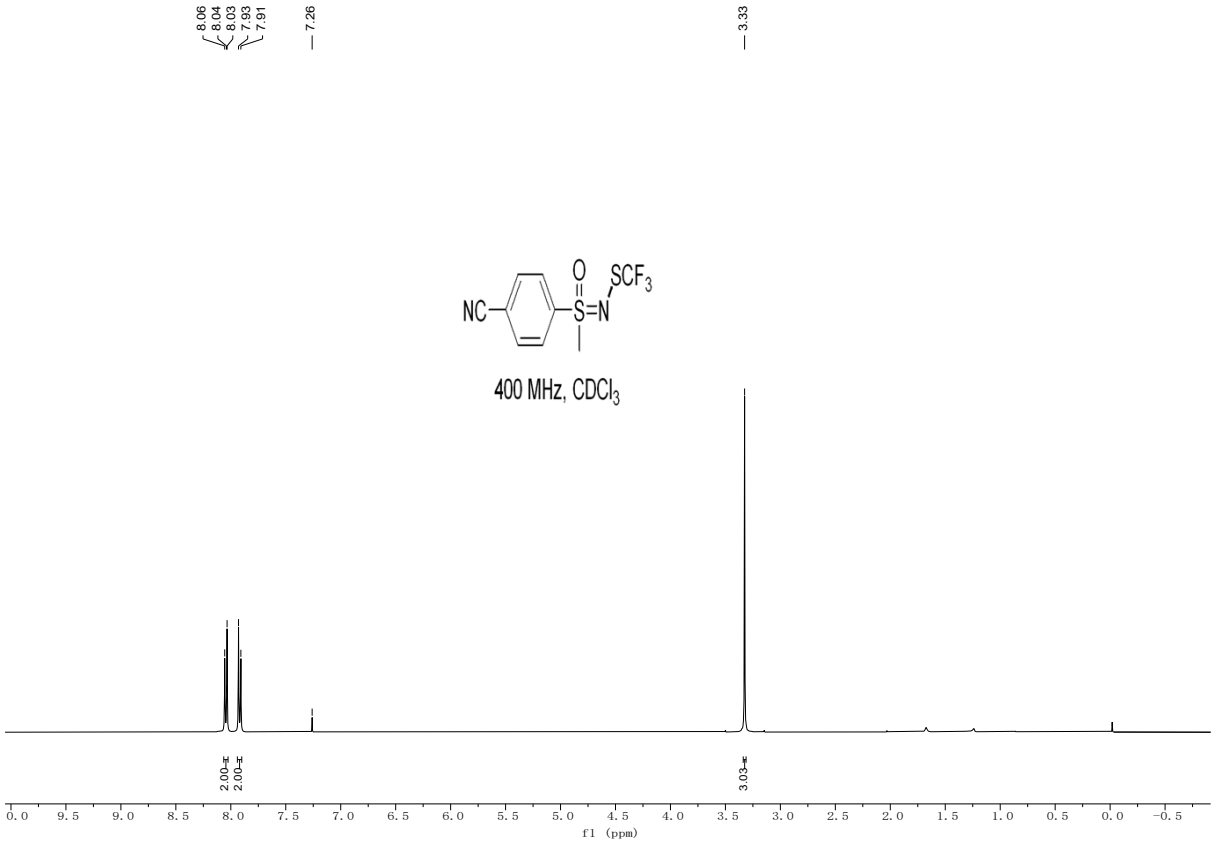
100 MHz, $CDCl_3$



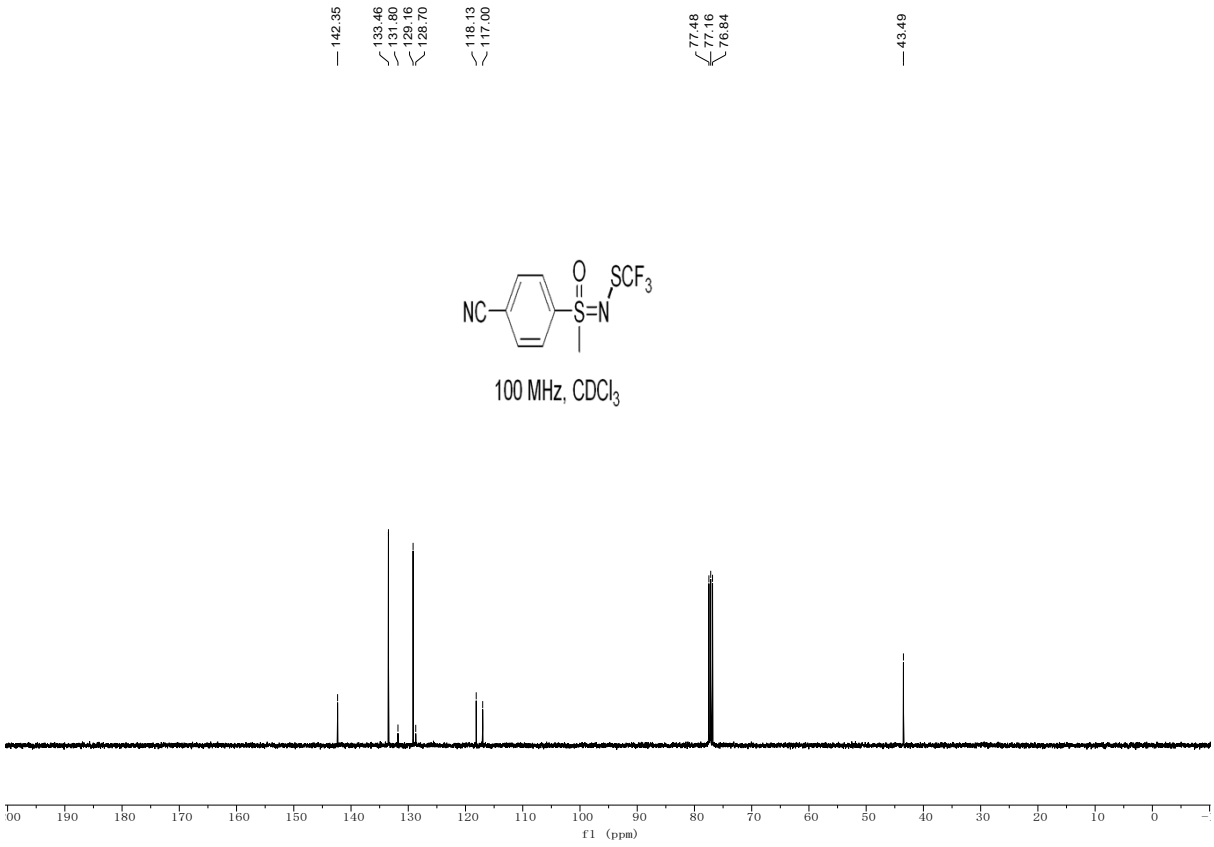
3n -^{19}F NMR



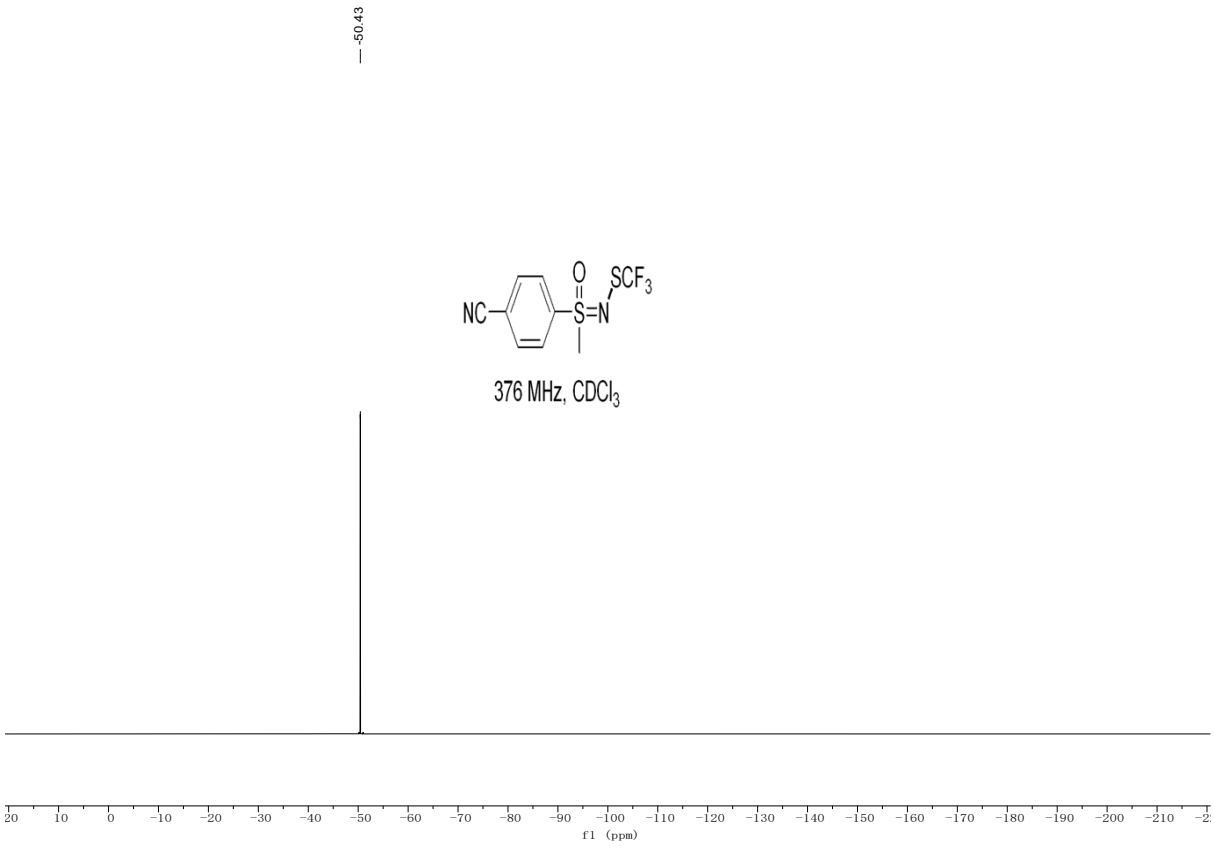
3o-^{1}H NMR



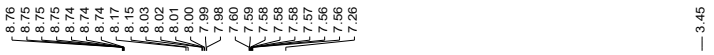
3o -^{13}C NMR

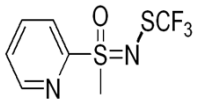


3o -^{19}F NMR

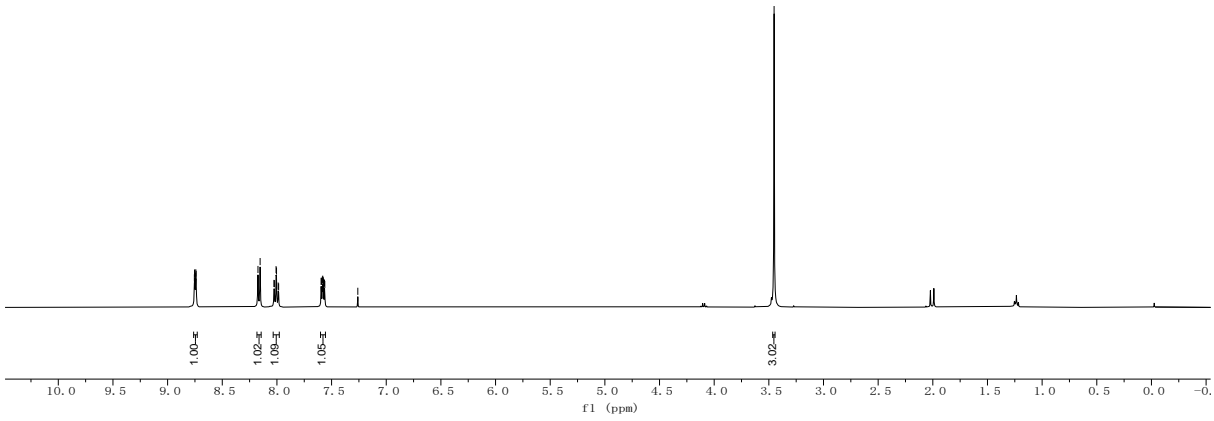


3p-^{1}H NMR

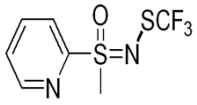




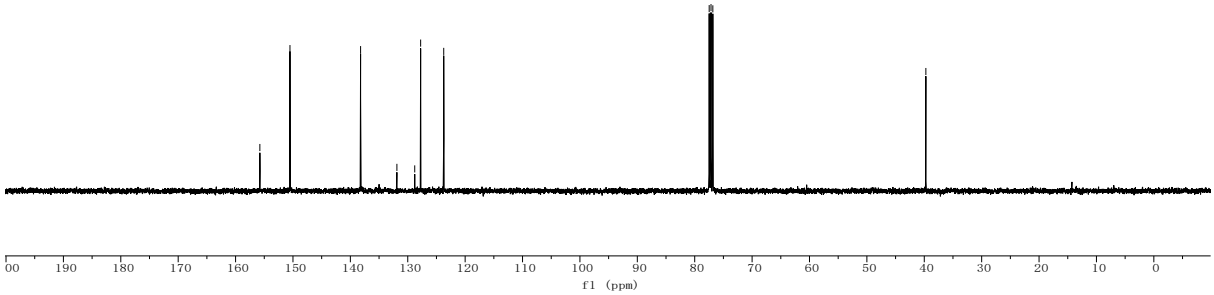
400 MHz, $CDCl_3$



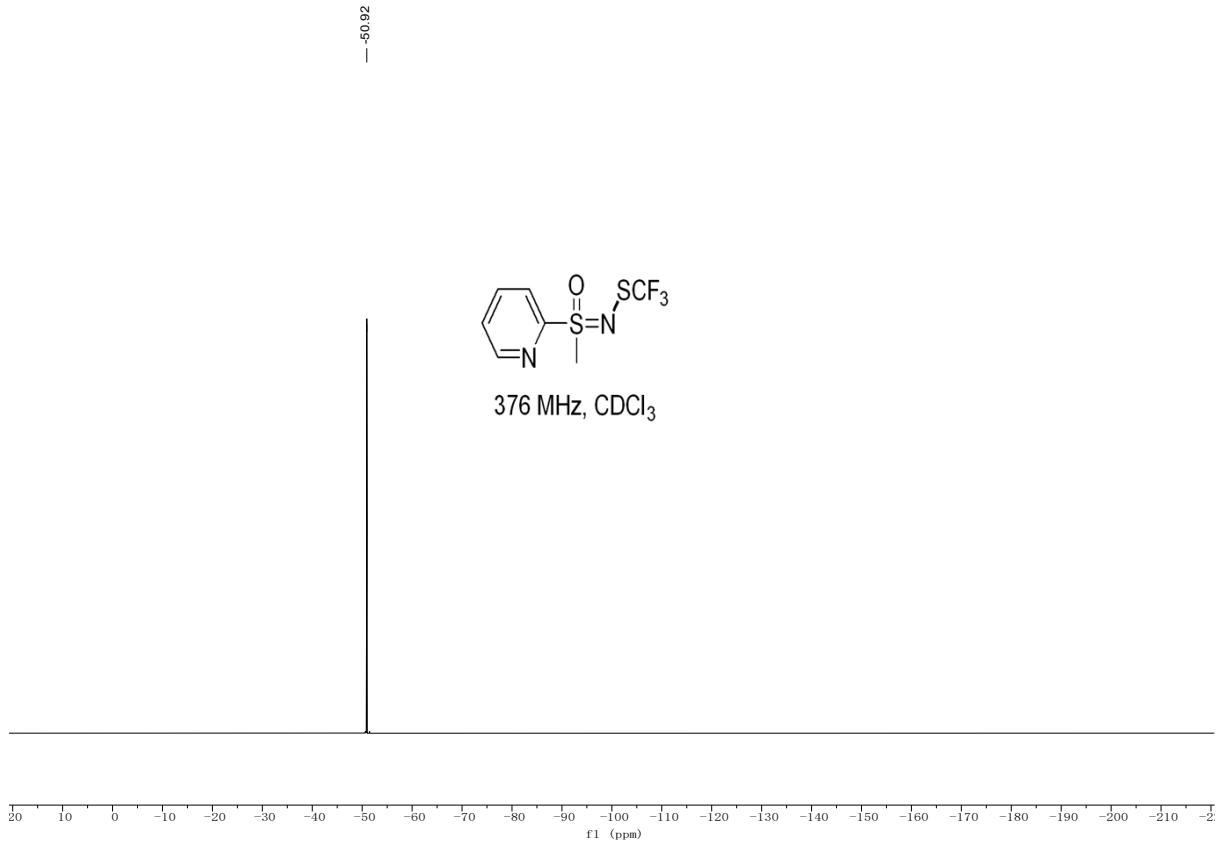
3p -^{13}C NMR



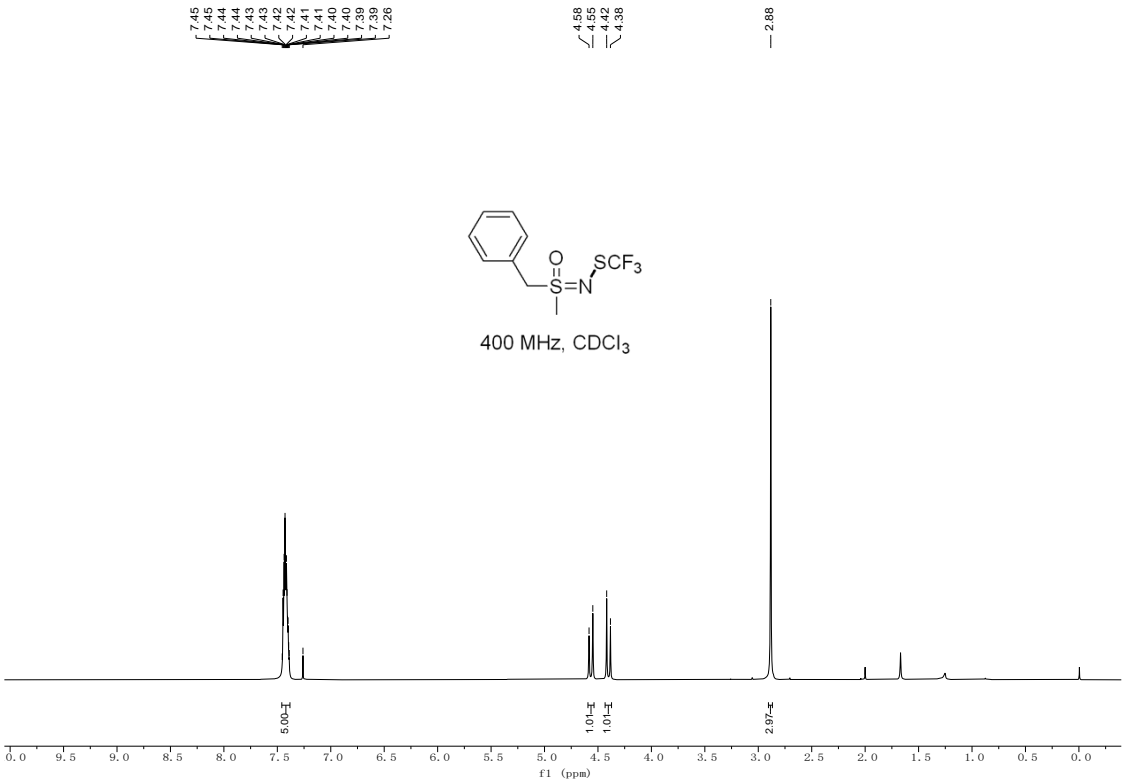
100 MHz, $CDCl_3$



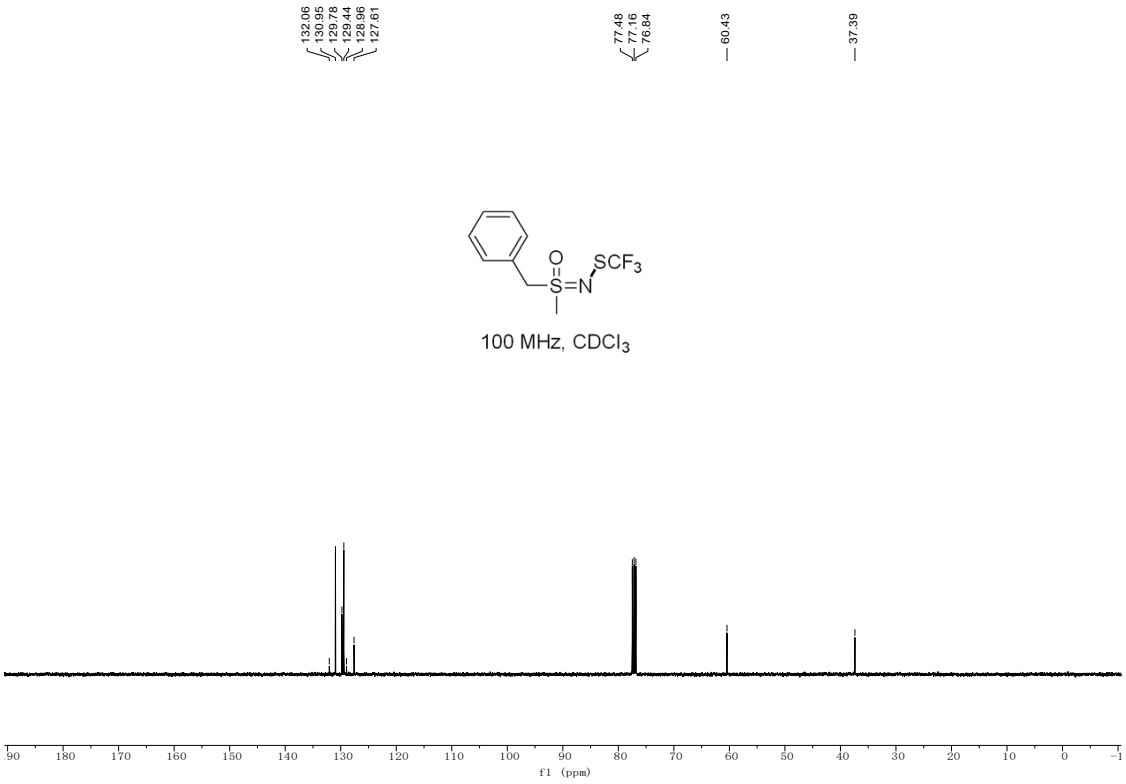
3p -^{19}F NMR



3q-^{1}H NMR



3q -^{13}C NMR



3q -^{19}F NMR