Supporting Information

Synthesis of Isothiazoles through *N*-Propargylsulfinylamide: TFA-Promoted Sulfinyl Group-Involved Intramolecular Cyclization

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1. General information

All the commercial reagents including solvents were used directly without further purification. All the experiments were monitored by thin layer chromatography (TLC) with UV light. The TLC employed 0.25 mm silica gel coated on glass plates. Purification of products was carried out by silica gel 60 F-254 TLC plates of 20 cm × 20 cm. Melting points were recorded without correction on RY-1G of Tianjin Xintianguang instrument company. NMR spectra were recorded on Bruker 400 MHz and 600 MHz spectrometers. High resolution mass spectra (HRMS) were measured on Agilent 6210 ESI/TOF MS instrument. The X-ray data were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Mo at Zero equipped with an AtlasS2 CCD using Mo Kα radiation.

2. General procedure for the intramolecular cycloaddition

Into a flask were taken amine **1** (0.1 mmol), TFA (1.3 mL, 18 mmol), DCM/toluene (5 mL), and the mixture was stirred at room temperature for 4 h. Then, Et_3N was added to neutralize the acid, followed by H_2O (15 mL). The organic layer was taken and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product **2**. Further purification was carried out by TLC plate of 20 cm × 20 cm using petroleum ether/ethyl acetate (8:1, v/v) as eluent.

3. Procedure for the nucleophilic addition of 2a with benzaldehyde

Into an oven-dried flask flushed with N_2 were taken isothiazole **2a** (0.1 mmol) and anhydrous THF (2 mL). After cooling to -78 ºC, *n*-BuLi (1.6 M in hexane, 0.1 mL) was added dropwise with stirring.

Then, benzaldehyde (0.15 mmol) dissolved in anhydrous THF (1 mL) was added dropwise and stirring was continued at -78 °C for 2 h. The reaction was quenched with saturated NH_4Cl (2 mL), followed by H_2O (10 mL) and the mixture was brought to room temperature. The organic layer was taken and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed in vacuum. Product **5** was purified by TLC plate of 20 cm × 20 cm with petroleum ether/ethyl acetate (8:1, v/v) as eluent.

4. Procedure for the reaction of 1a in the presence of DBU

Into a flask were taken amine **1a** (0.1 mmol) and DCM (5 mL). DBU (0.1 mmol) was added dropwise and the mixture was stirred at room temperature for 1 h, followed by H_2O (15 mL). The organic layer was taken and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product **6**, which was purified by TLC plate of 20 cm × 20 cm using petroleum ether/ethyl acetate (10:1, v/v) as eluent.

5. Large scale synthesis

Into a 250 mL flask were taken amine **1a** (2.0 mmol, 666.7 mg), dichloromethane (100 mL), TFA (27 mL, 360 mmol), and the mixture was stirred at room temperature for 5 h. Then, Et_3N was added to neutralize the acid, followed by H_2O (100 mL). The organic layer was taken and the aqueous layer was extracted with DCM (3 × 150 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product **2a**. Purification by column using petroleum ether/ethyl acetate (8:1, v/v) as eluent gave **2a** (404.1 mg, 78% yield).

6. X-ray crystallography of 2a

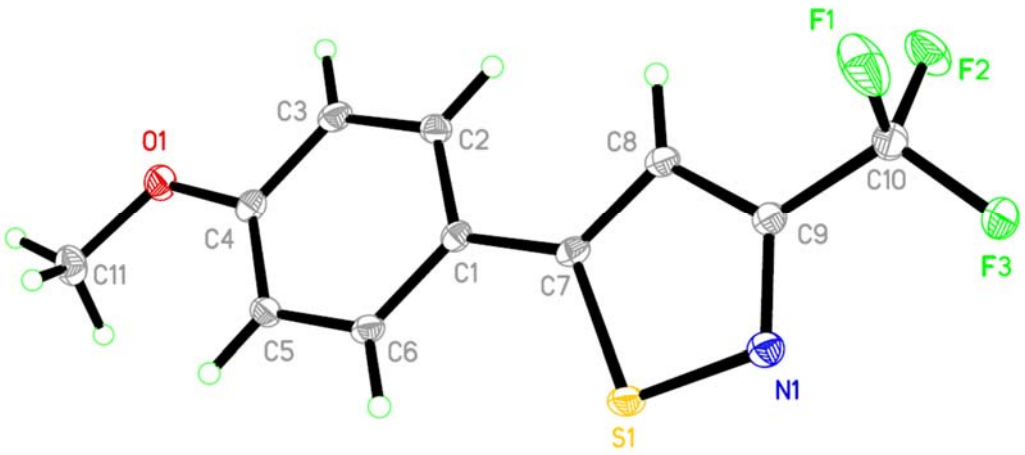


Figure S1. ORTEP diagram showing of **2a** (ellipsoid contour 30% probability, CCDC number 2086110).

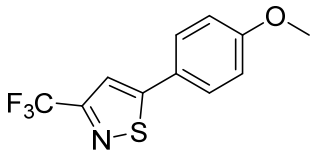
The single crystals for compound **2a** were prepared via slowly evaporating the solution of the compounds in ethyl acetate and hexane.

Table S1. Crystal parameters.

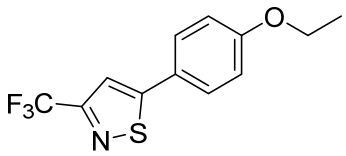
space_group_crystal_system	orthorhombic
space_group_IT_number	60
space_group_name_H-M_alt	P b c n
space_group_name_Hall	-P 2n 2ab
cell_length_a	13.2986(6)
cell_length_b	11.5969(5)
cell_length_c	13.9831(7)
cell_angle_alpha	90
cell_angle_beta	90
cell_angle_gamma	90
cell_volume	2156.51(17)
cell_formula_units_Z	8
cell_measurement_reflns_used	4958
cell_measurement_temperature	100.0(2)
cell_measurement_theta_max	28.9940
cell_measurement_theta_min	2.7120

absorpt_coefficient_mu	0.323
absorpt_correction_T_max	1.00000
absorpt_correction_T_min	0.81568
absorpt_correction_type	multi-scan
absorpt_process_details	CrysAlisPro 1.171.38.43f (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm

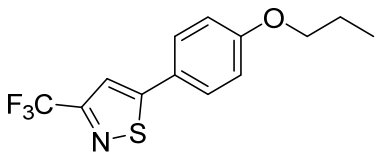
7. Characterization data for product 2, 4, 5, 6



Compound **2a**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 18.7 mg, 72% yield, yellow solid, mp 40-41 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.54 (m, 3H), 7.02 (d, *J* = 8.68 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 161.4, 158.5 (q, *J* = 36.8 Hz), 128.1, 122.3, 121.0 (d, *J* = 271.2), 116.5, 114.9, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.4 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_9F_3NOS^+$ 260.0351, found 260.0362.

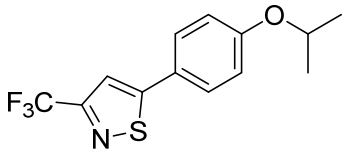


Compound **2b**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 21.9 mg, 80% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 3H), 7.00 (d, *J* = 8.76 Hz, 2H), 4.14 (q, *J* = 6.96 Hz, 2H), 1.49 (t, *J* = 6.96 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 160.8, 158.4 (q, *J* = 36.6 Hz), 128.1, 122.1, 121.0 (d, *J* = 271.1), 116.4, 115.3, 63.8, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.4 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}F_3NOS^+$ 274.0508, found 274.0517.

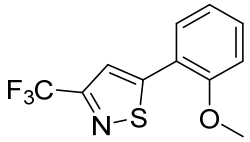


Compound **2c**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 15.2 mg, 53% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 3H), 7.00 (d, *J* = 8.52 Hz, 2H), 4.01 (t, *J* = 6.48 Hz, 2H), 1.91-1.82 (m, 2H), 1.10 (t, *J* = 7.40 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 161.0, 158.1 (d, *J* = 36.9 Hz), 128.1, 122.1, 121.0 (d, *J* = 271.4), 116.4, 115.3, 69.8, 22.5,

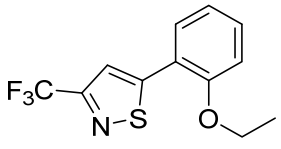
10.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.4 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NOS^+$ 288.0664, found 288.0669.



Compound **2d**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 14.4 mg, 50% yield, yellow oil. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.55-7.53 (m, 3H), 6.98 (d, *J* = 8.76 Hz, 2H), 4.67-4.61 (m, 1H), 1.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.0, 159.8, 158.2 (q, *J* = 36.7 Hz), 128.1, 121.9, 120.6 (d, *J* = 271.4), 116.4, 116.3, 70.2, 21.9. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -64.4 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NOS^+$ 288.0664, found 288.0664.

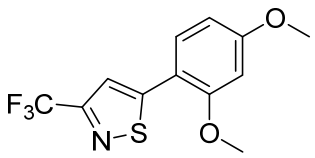


Compound **2e**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 18.6 mg, 72% yield, colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.81 (d, *J* = 7.74 Hz, 1H), 7.47-7.44 (m, 1H), 7.13-7.09 (m, 2H), 4.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 156.0, 155.6 (d, *J* = 36.9 Hz), 131.4, 126.9, 121.5 (d, *J* = 271.5), 121.3, 119.2, 116.4, 111.6, 55.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -64.1 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_9F_3NOS^+$ 260.0351, found 260.0359.

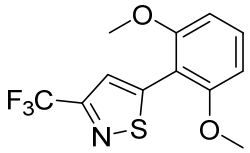


Compound **2f**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 16.3 mg, 60% yield, white solid, mp 68-69 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.81 (d, *J* = 7.88 Hz, 1H), 7.44-7.40 (m, 1H), 7.12-7.05 (m, 2H), 4.35 (q, *J* = 6.96 Hz, 2H), 1.66 (t, *J* = 6.88 Hz, 3H). ^{13}C NMR

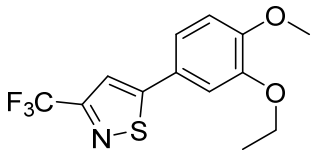
(150 MHz, $CDCl_3$): δ = 164.9, 155.4 (d, *J* = 36.3 Hz), 155.3, 131.3, 126.8, 121.2, 121.1 (d, *J* = 271.3 Hz), 119.3, 116.2, 112.1, 65.1, 14.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -64.1 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}F_3NOS^+$ 274.0508, found 274.0519.



Compound **2i**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 19.4 mg, 67%, yellow solid, mp 66-67 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.70 (m, 2H), 6.65 (dd, *J* = 2.40, 8.64 Hz, 1H), 6.60 (d, *J* = 2.36 Hz, 1H), 4.05 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.0, 162.4, 157.4, 155.9 (q, *J* = 36.8 Hz), 127.9, 124.2 (q, *J* = 271.1 Hz), 115.1, 112.6, 106.1, 98.5, 55.7, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.1 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}F_3NO_2S^+$ 290.0457, found 290.0468.

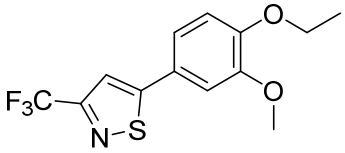


Compound **2j**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 19.6 mg, 68% yield, white solid, mp 98-100 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.40-7.36 (m, 1H), 6.76 (d, *J* = 8.40 Hz, 2H), 4.05 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0, 157.4, 155.4 (q, *J* = 35.9 Hz), 130.8, 123.2 (q, *J* = 271.4 Hz), 120.3, 109.1, 104.2, 55.9. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -64.0 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}F_3NO_2S^+$ 290.0457, found 290.0466.

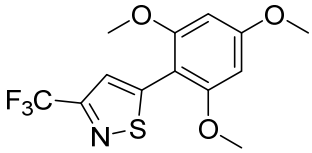


Compound **2k**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 17.0 mg, 56% yield, white solid, mp 67-68 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.22 (d, *J* = 8.32 Hz, 1H),

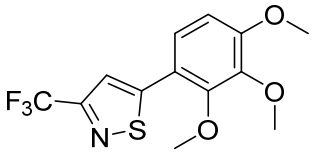
7.08 (s, 1H), 6.96 (d, J = 8.32 Hz, 1H), 4.21 (q, J = 6.96 Hz, 2H), 3.95 (s, 3H), 1.55 (t, J = 6.96 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 158.4 (q, J = 36.7 Hz), 151.3, 149.0, 123.7 (q, J = 271.1 Hz), 122.4, 119.8, 116.6, 111.8, 110.9, 64.7, 56.1, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.3 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO_2S^+$ 304.0614, found 304.0624.



Compound **2l**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 16.7 mg, 55% yield, yellow solid, mp 75-77 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.20 (d, J = 8.20 Hz, 1H), 7.07 (s, 1H), 6.95 (d, J = 8.28 Hz, 1H), 4.20 (q, J = 6.92 Hz, 2H), 3.96 (s, 3H), 1.53 (t, J = 6.96 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 158.4 (q, J = 36.8 Hz), 150.5, 149.8, 123.7 (q, J = 271.9 Hz), 122.3, 119.8, 116.6, 112.7, 109.7, 64.5, 56.1, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.4 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO_2S^+$ 304.0614, found 324.0627.

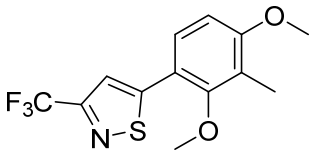


Compound **2m**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 24.2 mg, 76% yield, white solid, mp 138-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 6.26 (s, 2H), 4.02 (s, 6H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 161.4, 158.5, 155.5 (q, J = 35.8 Hz), 121.8 (d, J = 271.2 Hz), 118.8, 102.8, 90.8, 55.9, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.0 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO_3S^+$ 320.0563, found 320.0575.

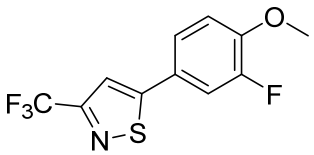


Compound **2n**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 23.1 mg, 72% yield,

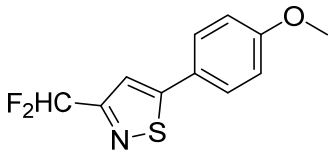
yellow solid, mp 59-60 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.48 (d, *J* = 8.76 Hz, 1H), 6.80 (d, *J* = 8.82 Hz, 1H), 4.08 (s, 3H), 3.95 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.9, 156.0 (q, *J* = 36.7 Hz), 155.3, 151.0, 142.1, 122.8 (q, *J* = 271.7 Hz), 121.2, 117.1, 115.8, 107.9, 60.9, 60.5, 56.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -64.3 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO_3S^+$ 320.0563, found 320.0576.



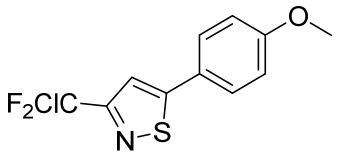
Compound **2o**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 13.6 mg, 45% yield, white solid, mp 50-51 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.59 (d, *J* = 8.70 Hz, 1H), 6.77 (d, *J* = 8.76 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.5, 160.5, 156.6, 156.2 (q, *J* = 36.5 Hz), 124.7, 122.8 (q, *J* = 271.1 Hz), 120.2, 116.6, 115.9, 106.8, 60.5, 55.8, 9.47. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -64.3 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO_2S^+$ 304.0614, found 304.0626.



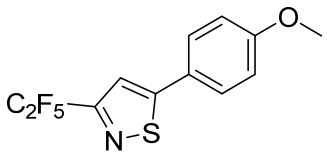
Compound **2p**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 10.3 mg, 37% yield, yellow solid, mp 77-79 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.39-7.34 (m, 2H), 7.08-7.04 (m, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 158.6 (q, *J* = 37.0 Hz), 153.7 (d, *J* = 247.1 Hz), 149.6 (d, *J* = 10.2 Hz), 123.1 (d, *J* = 3.6 Hz), 122.6 (d, *J* = 7.2 Hz), 120.9 (d, *J* = 271.5 Hz), 117.1, 114.6 (d, *J* = 19.6 Hz), 113.9 (d, *J* = 2.7 Hz), 56.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -64.4 (s, 3F), -133.0 (s, 1F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_8F_4NOS^+$ 278.0257, found 278.0261.



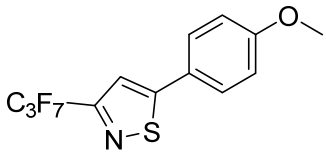
Compound **2q**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 13.0 mg, 54% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 2H), 7.53 (s, 1H), 7.02-6.98 (m, 2H), 6.84 (t, *J* = 54.9 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.9, 163.6 (t, *J* = 28.4 Hz), 161.1, 128.1, 122.8, 116.0, 114.8, 112.7 (t, *J* = 237.8 Hz), 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -113.3 (s, 2F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{10}F_2NOS^+$ 242.0446, found 242.0457.



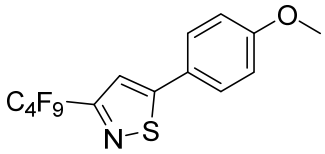
Compound **2r**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 3.9 mg, 14% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.68 Hz, 2H), 7.53 (s, 1H), 7.01 (d, *J* = 8.64 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 162.3 (t, *J* = 31.0 Hz), 161.4, 128.1, 122.4, 122.0, 115.9, 114.8, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -50.3 (s, 2F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_9ClF_2NOS^+$ 276.0056, found 276.0063.



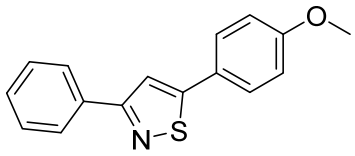
Compound **2t**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 23.9 mg, 77% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 3H), 7.02 (d, *J* = 8.64 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.9, 161.4, 157.3 (t, *J* = 27.9 Hz), 128.2, 122.2, 119.6, 117.6, 114.9, 109.9, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.6 (s, 3F), -113.4 (s, 2F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_9F_5NOS^+$ 310.0320, found 310.0331.



Compound **2u**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 26.9 mg, 75% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 3H), 7.03-6.99 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.8, 161.4, 157.2 (t, *J* = 27.6 Hz), 128.2, 122.2, 119.0-116.6 (m), 117.8, 113.7-111.5 (m), 110.3-108.2 (m), 114.9, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.2--80.3 (m, 3F), -111.2 - -111.3 (m, 2F), -126.6 (s, 2F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9F_7NOS^+$ 360.0288, found 360.0299.

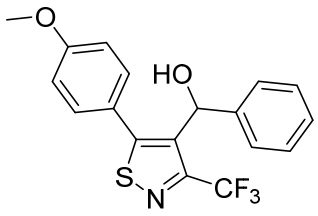


Compound **2v**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 33.7 mg, 82% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.56 (m, 3H), 7.02-6.99 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 161.4, 157.4 (t, *J* = 27.3 Hz), 128.2, 122.2, 119.2-118.5 (m), 117.9, 116.3-115.7 (m), 114.9, 112.9-112.2 (m), 110.3-108.6 (m), 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.9--81.0 (m, 3F), -110.5--110.6 (m, 2F), -123.0--123.1 (m, 2F), -125.7--125.8 (m, 2F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_9F_9NOS^+$ 410.0256, found 410.0268.

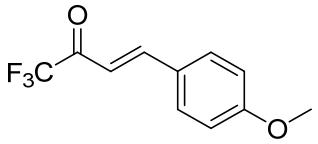


Compound **4**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 5.7 mg, 21% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.76 Hz, 2H), 7.69 (s, 1H), 7.63 (d, *J* = 8.84 Hz, 2H), 7.51-7.42 (m, 3H), 7.01 (d, *J* = 8.88 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.3, 168.1, 160.7, 135.0, 129.2, 128.8, 128.0, 126.9, 123.7, 116.7, 114.6, 55.4. HRMS

(ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NOS^+$ 268.0791, found 268.0795.



Compound **5**: purified by TLC plate (petroleum ether/ethyl acetate = 8:1, v/v), 26.0 mg, 71% yield, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.29-7.23 (m, 5H), 7.20 (d, *J* = 7.38 Hz, 2H), 6.88 (d, *J* = 8.34 Hz, 2H), 6.25 (d, *J* = 2.94 Hz, 1H), 3.83 (s, 3H), 2.73 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.4, 160.9, 155.9 (q, *J* = 36.1 Hz), 141.6, 134.8, 130.7, 128.2, 127.4, 125.7, 122.7 (q, *J* = 272.5 Hz), 121.2, 114.3, 68.0, 55.4. ^{19}F NMR (565 MHz, $CDCl_3$): δ = -61.4 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO_2S^+$ 366.0770, found 366.0783.

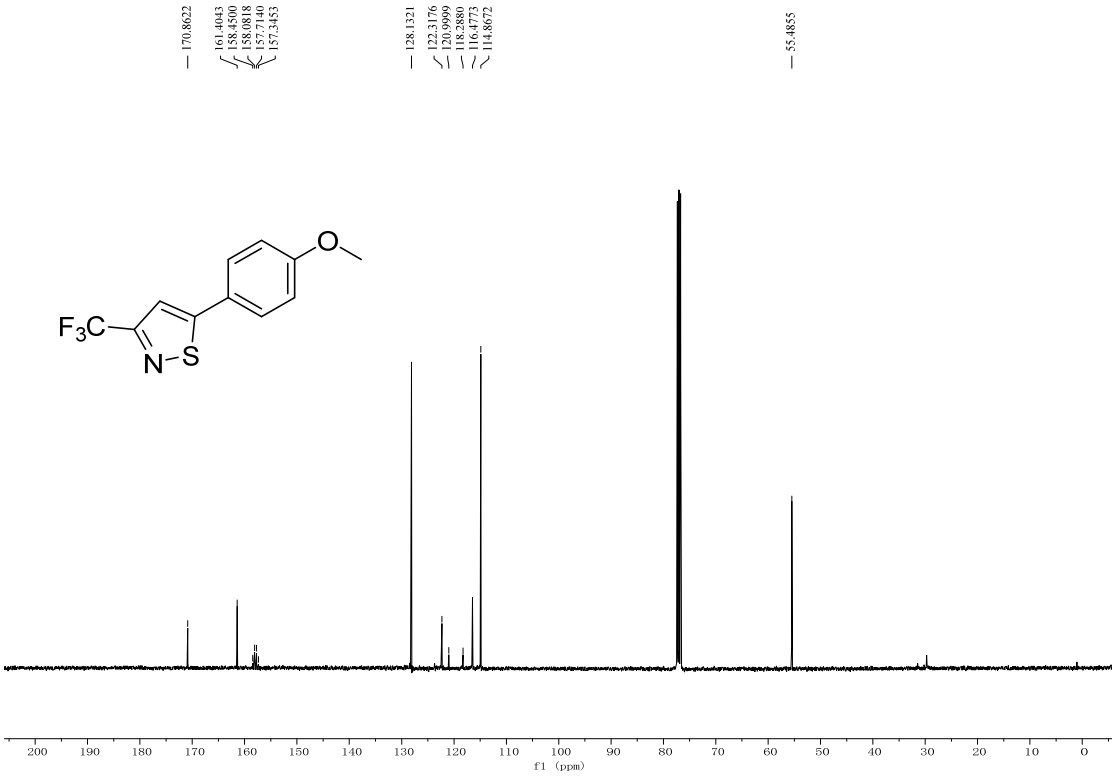


Compound **6**: purified by TLC plate (petroleum ether/ethyl acetate = 10:1, v/v), 13.3 mg, 58% yield, white solid, mp 43-44 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 15.72 Hz, 1H), 7.64 (d, *J* = 8.36 Hz, 2H), 6.99 (d, *J* = 8.36 Hz, 2H), 6.93 (d, *J* = 15.84 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.4 (q, *J* = 34.9 Hz), 163.2, 150.0, 131.4, 126.2, 120.9 (q, *J* = 288.9 Hz), 114.8, 114.1, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -77.5 (s, 3F). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{10}F_3O_2^+$ 231.0627, found 231.0633.

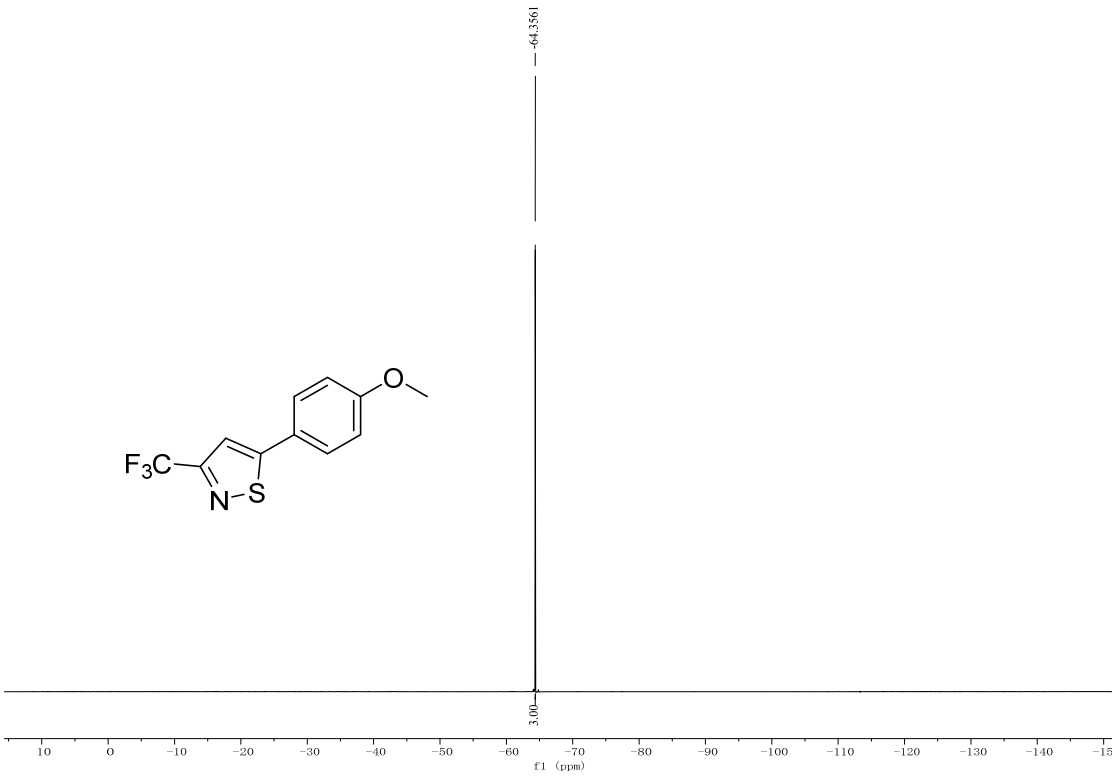
8. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra

^{1}H NMR (400 MHz, $CDCl_3$) of **2a**:

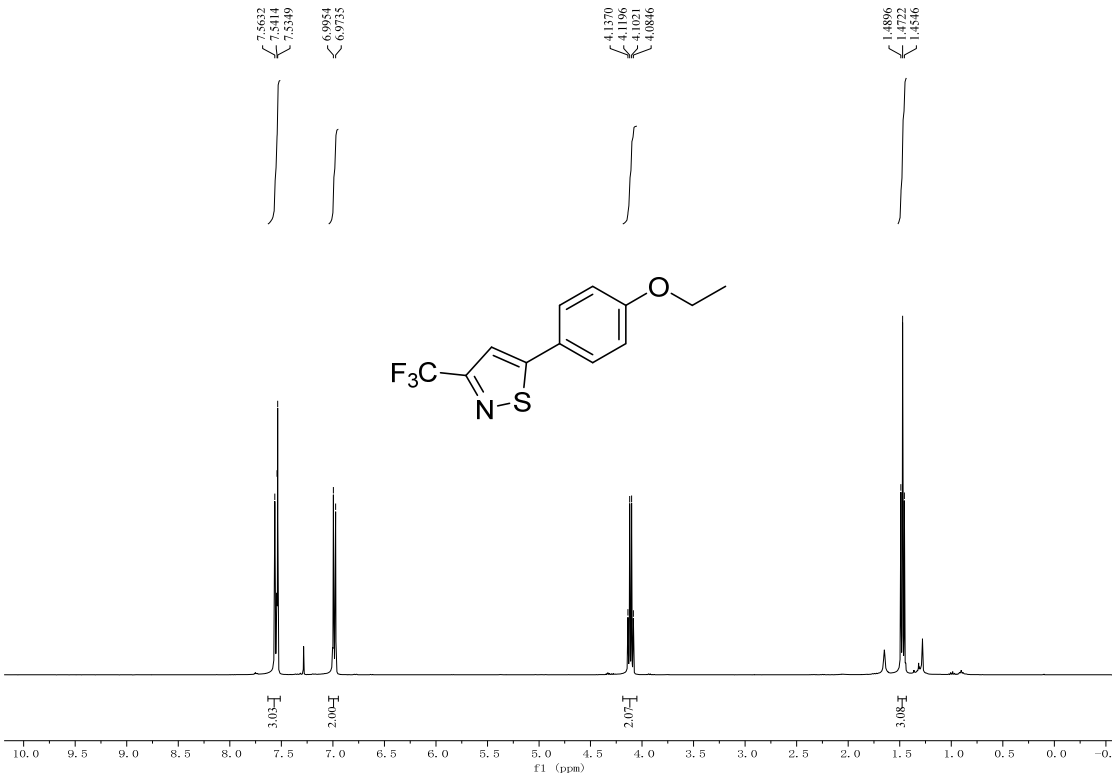
^{13}C NMR (100 MHz, $CDCl_3$) of **2a**:



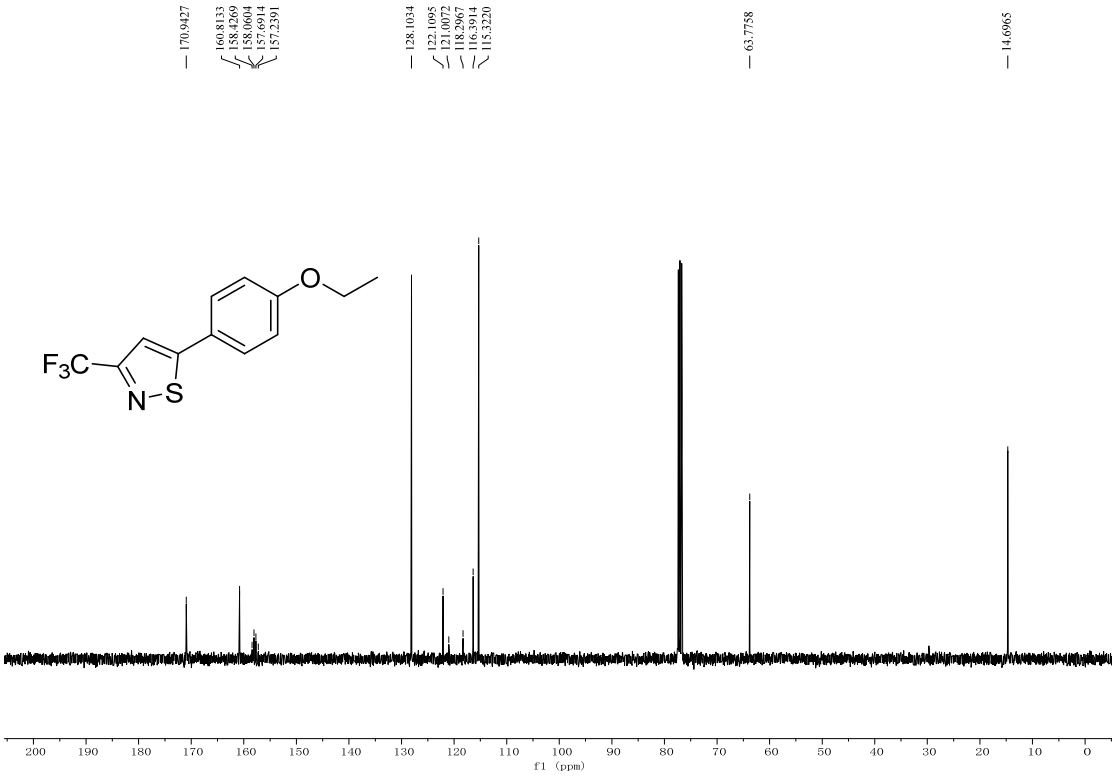
^{19}F NMR (376 MHz, $CDCl_3$) of **2a**:



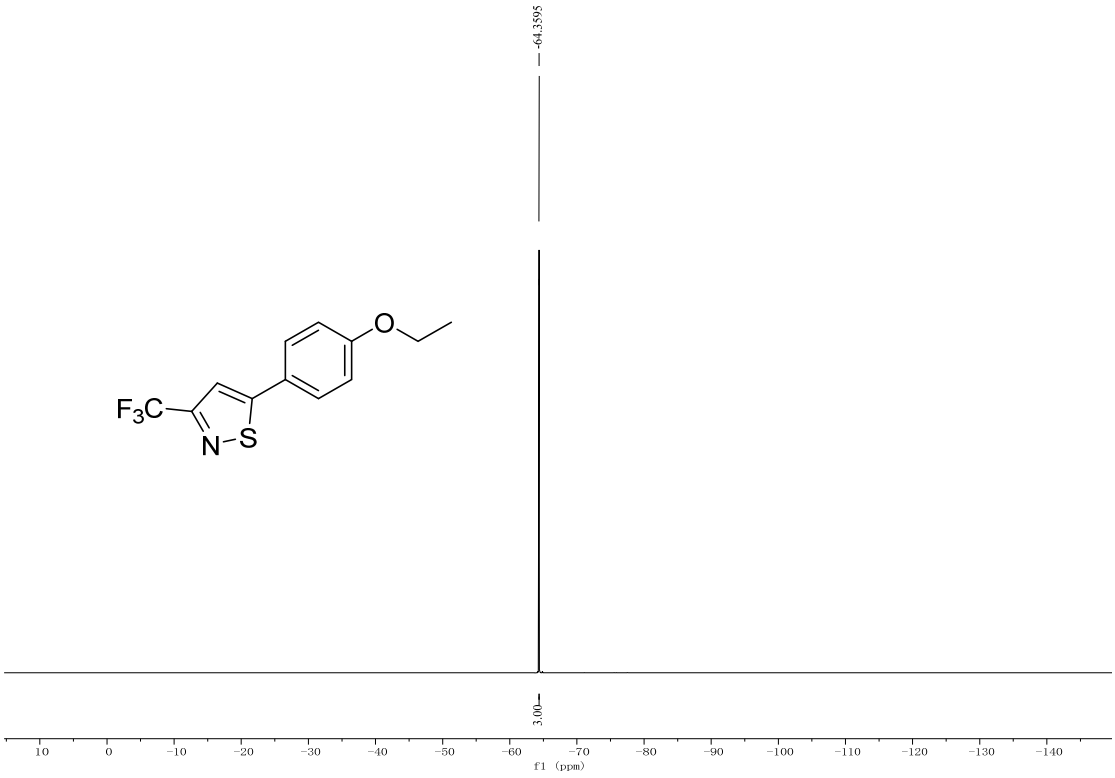
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**:



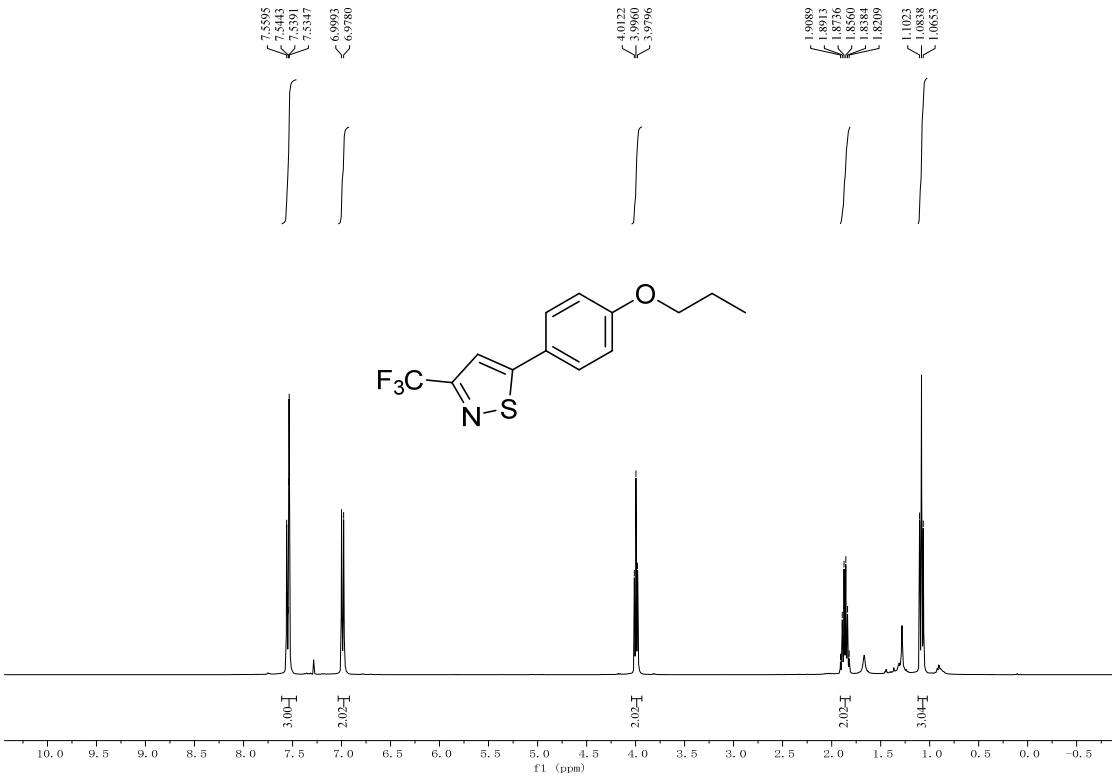
^{13}C NMR (100 MHz, $CDCl_3$) of **2b**:



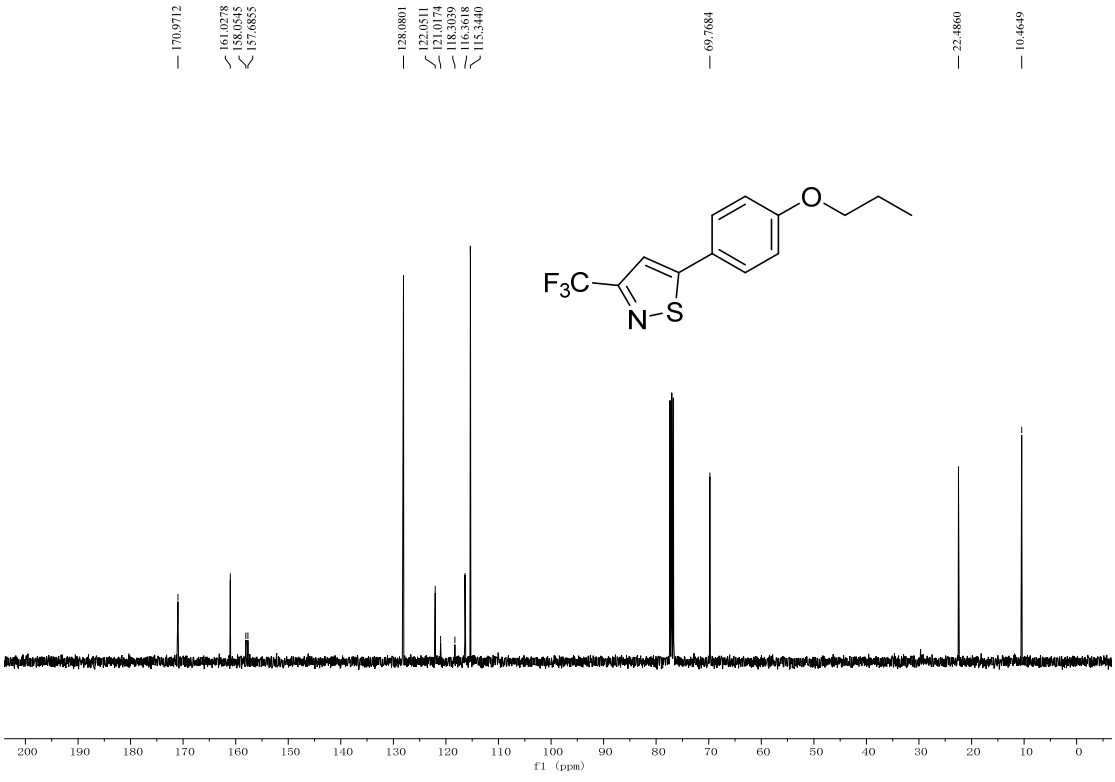
^{19}F NMR (376 MHz, $CDCl_3$) of **2b**:



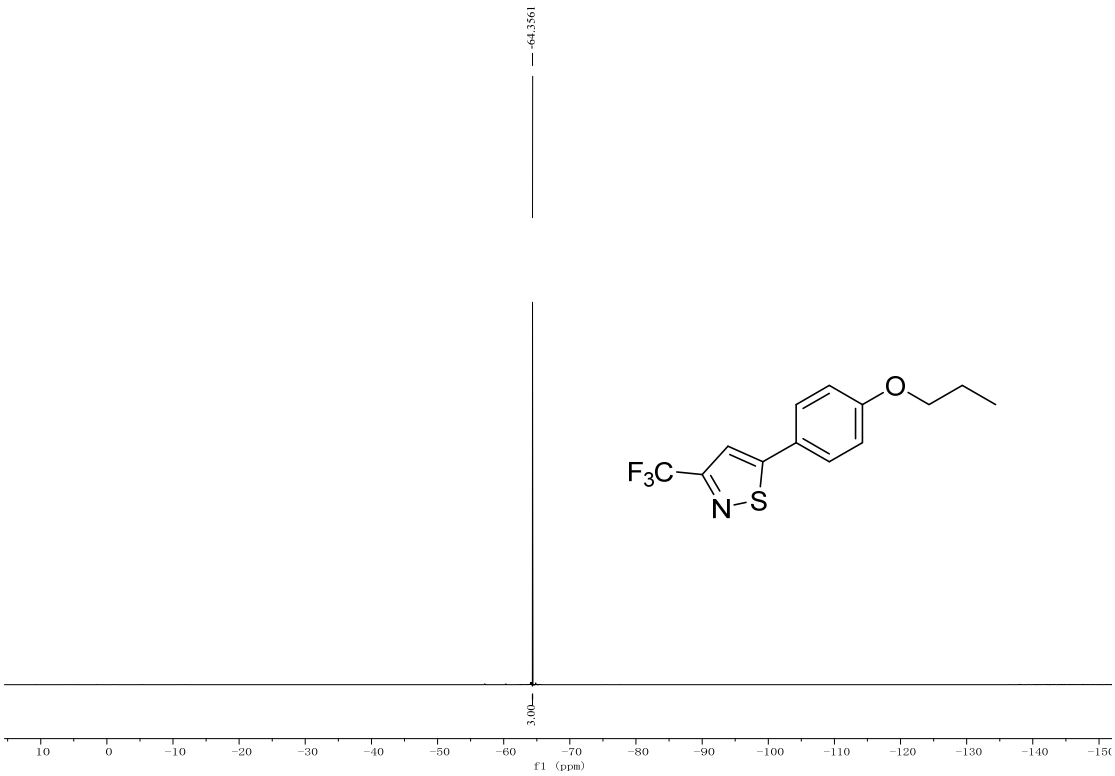
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**:



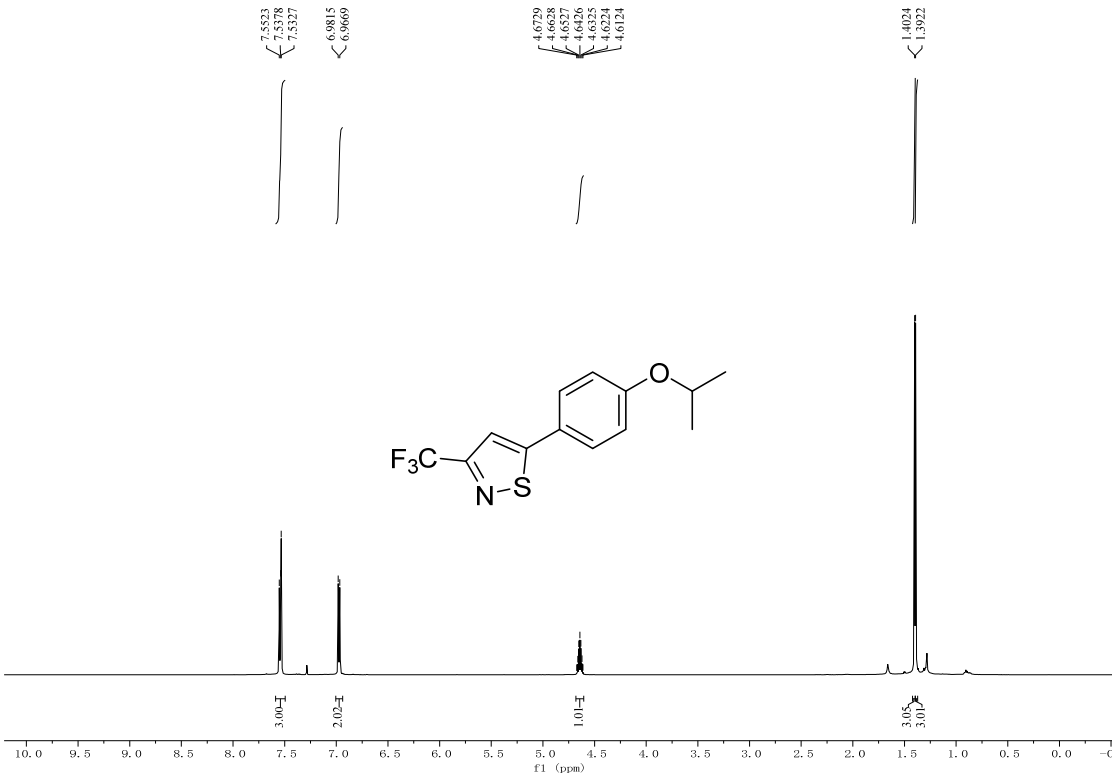
^{13}C NMR (100 MHz, $CDCl_3$) of **2c**:



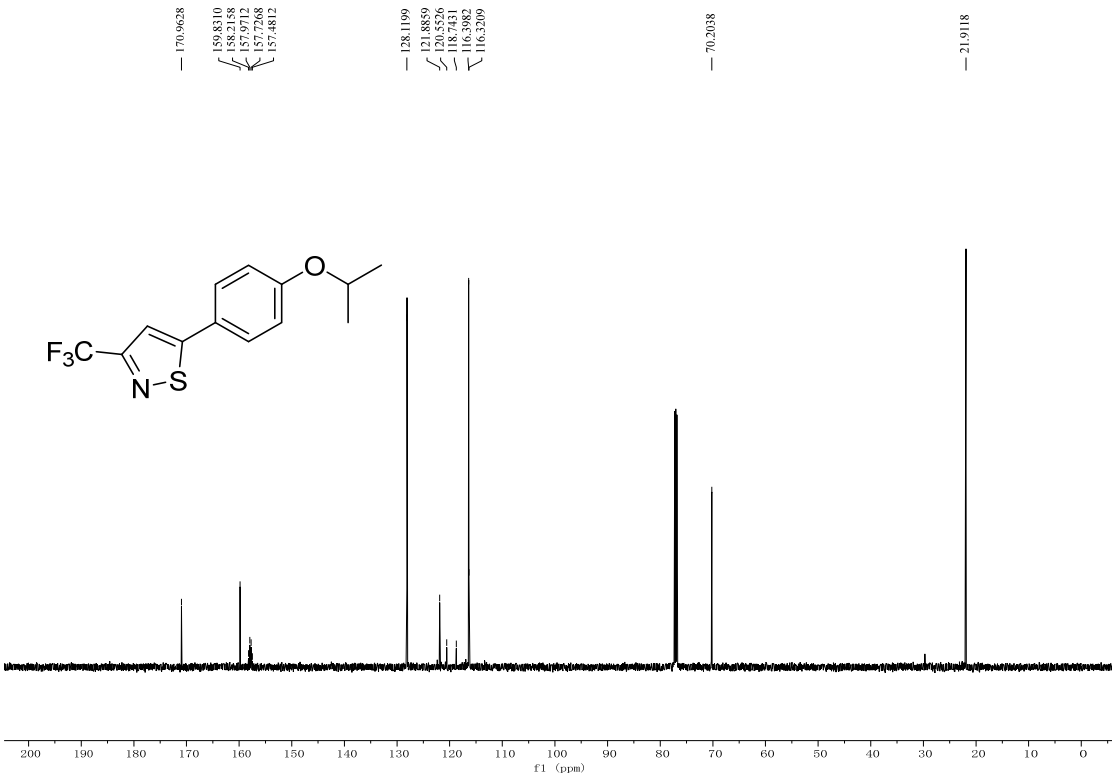
^{19}F NMR (376 MHz, $CDCl_3$) of **2c**:



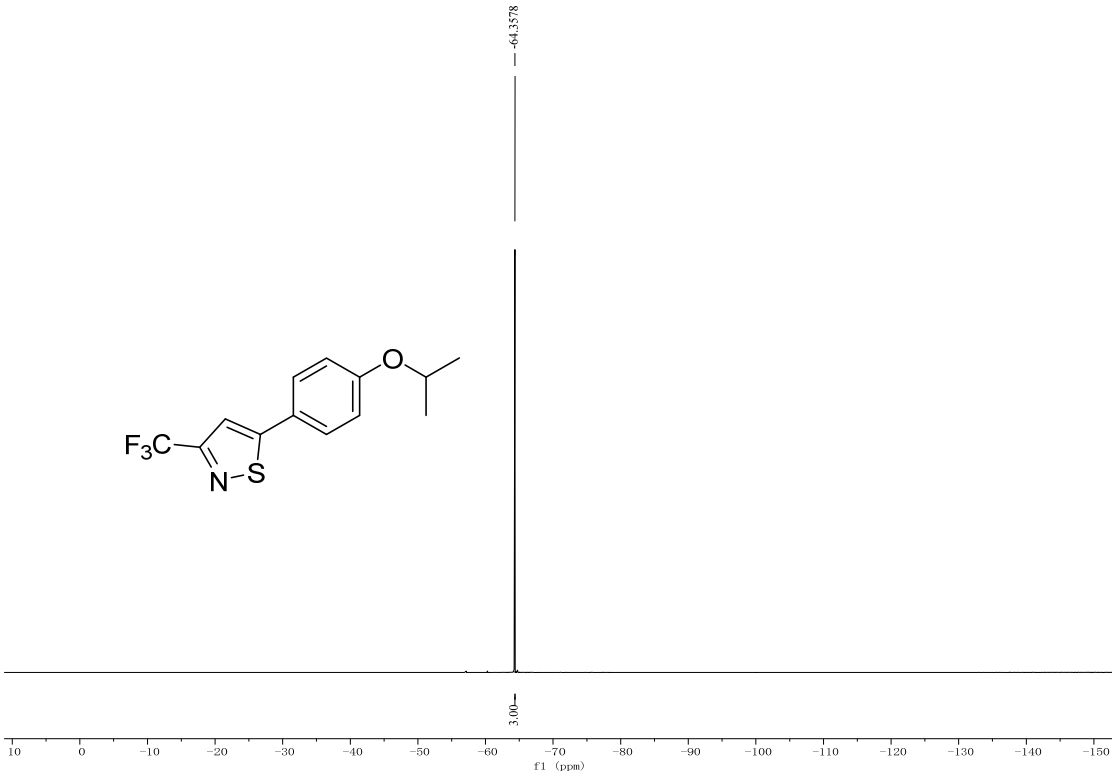
^{1}H NMR (600 MHz, $CDCl_3$) of **2d**:



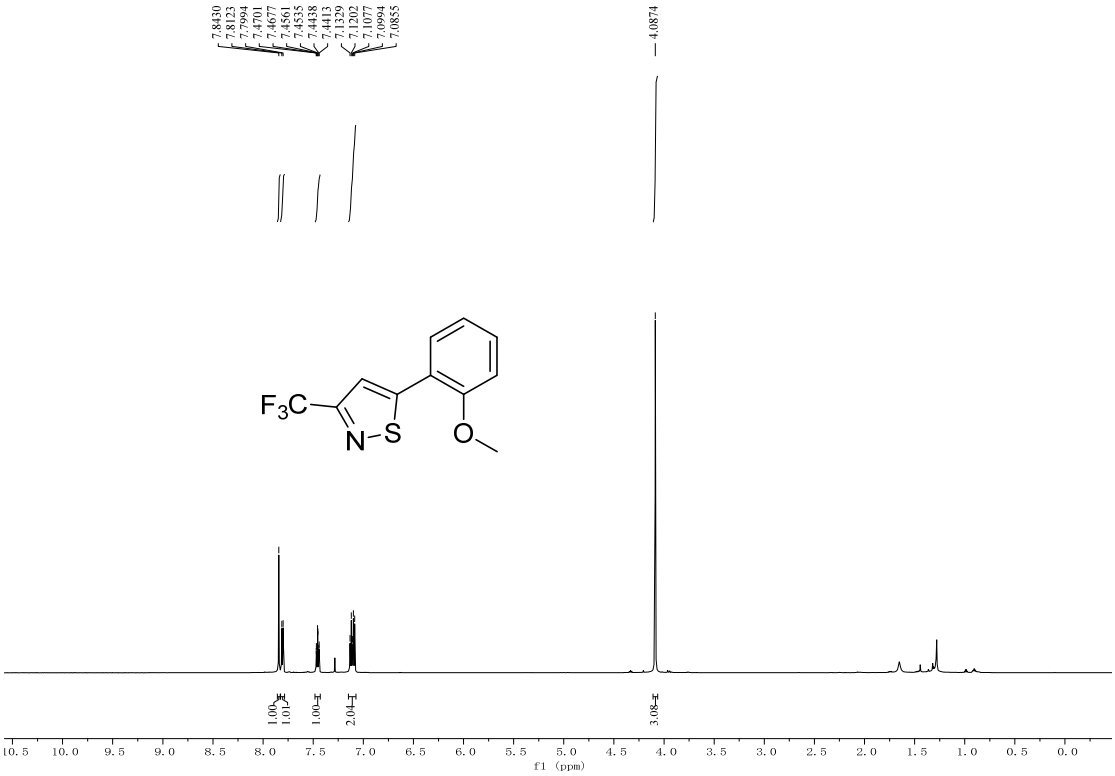
^{13}C NMR (150 MHz, $CDCl_3$) of **2d**:



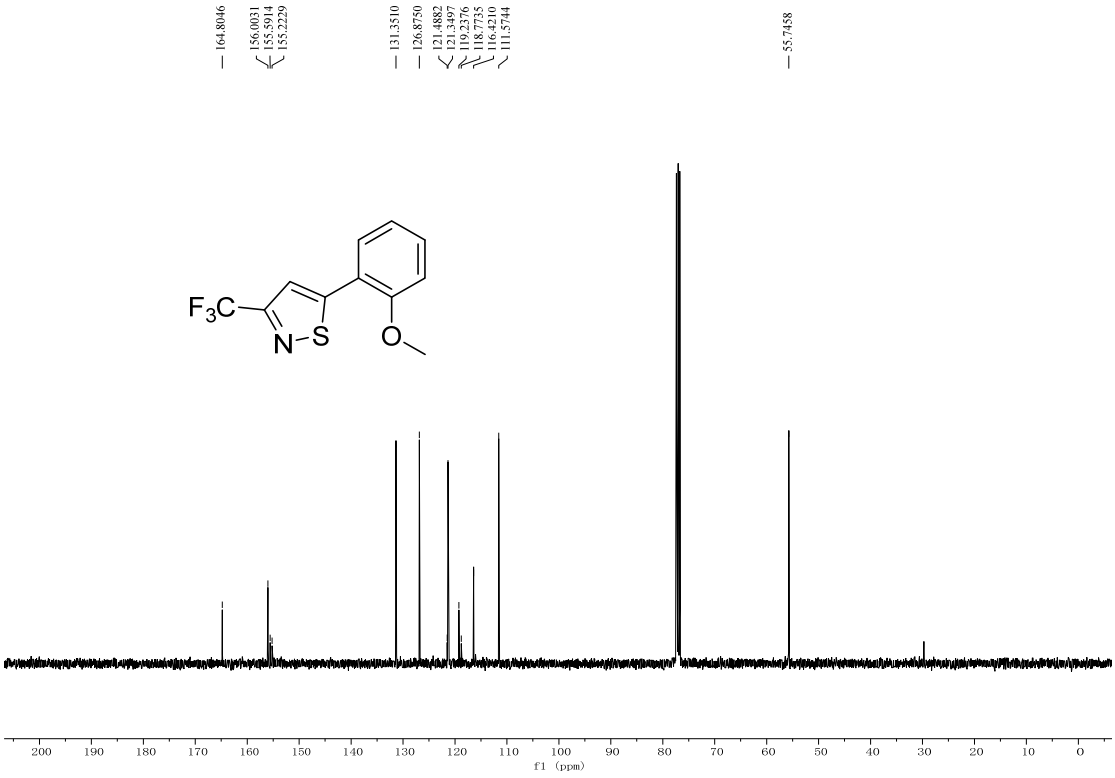
^{19}F NMR (565 MHz, $CDCl_3$) of **2d**:



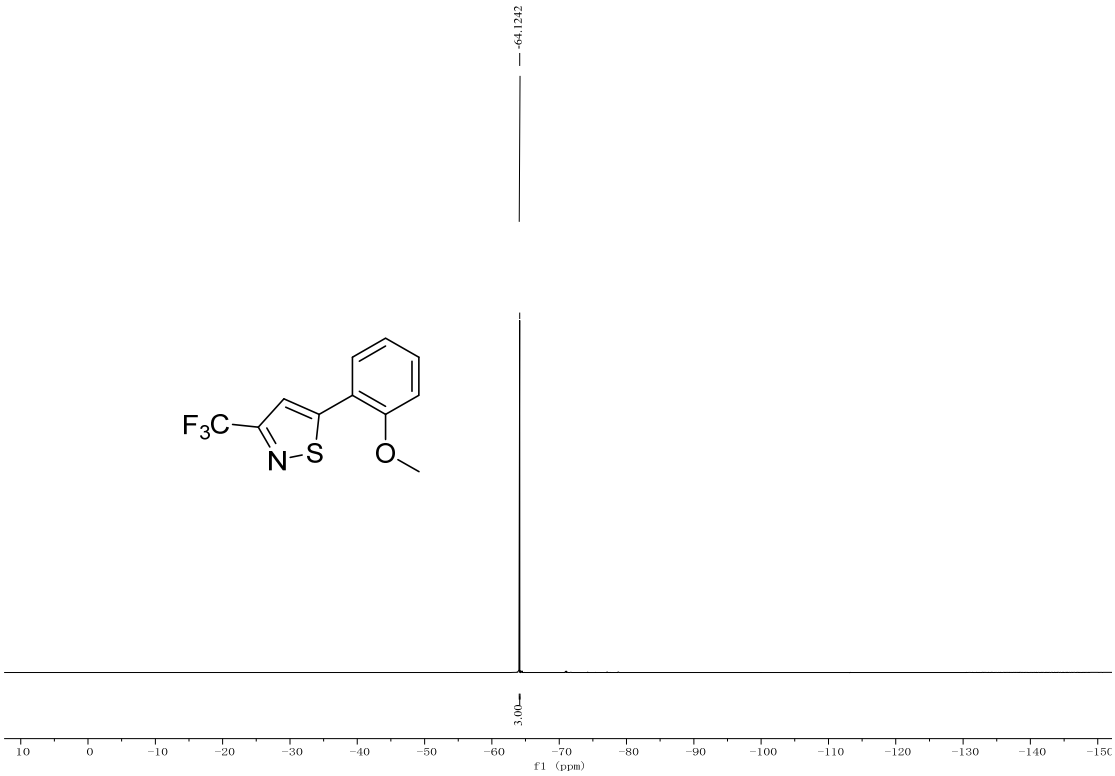
^{1}H NMR (600 MHz, $CDCl_3$) of **2e**:



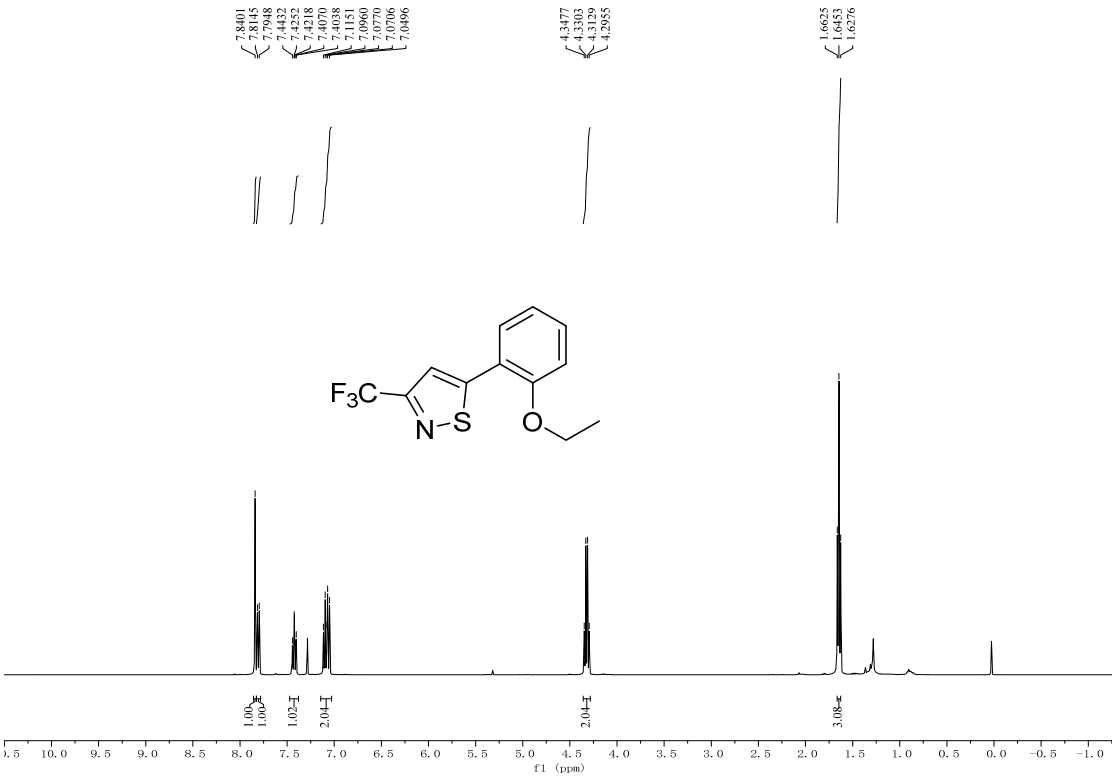
^{13}C NMR (100 MHz, $CDCl_3$) of **2e**:



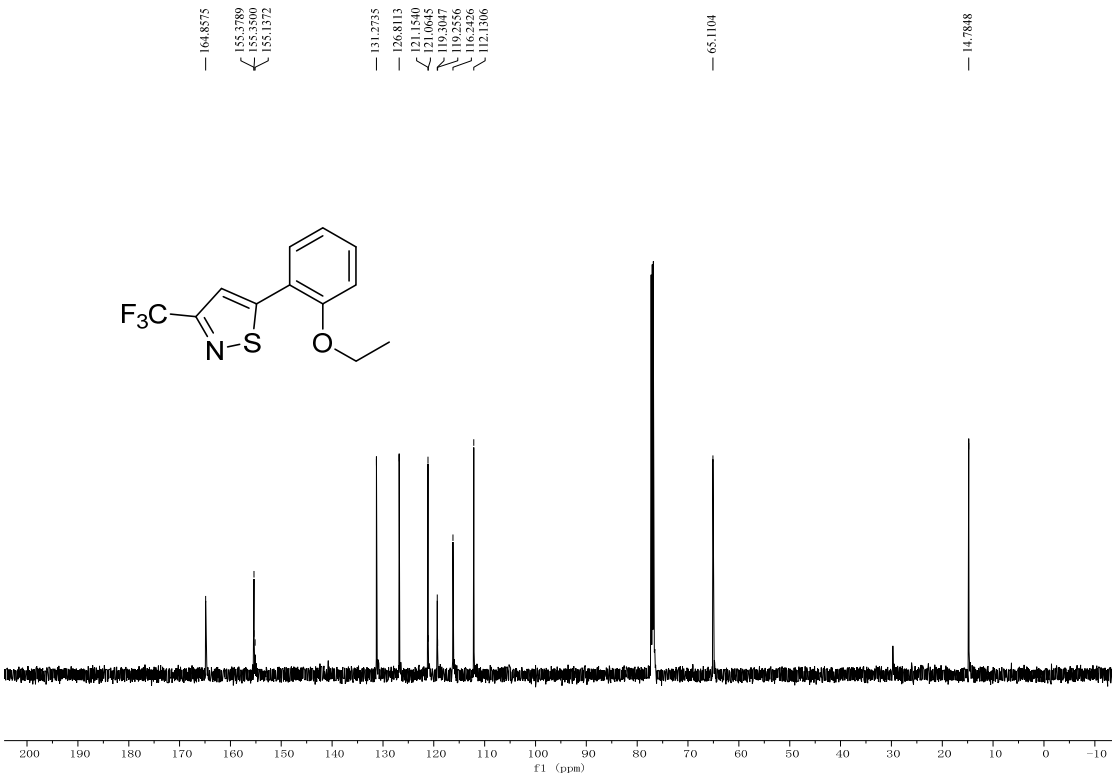
^{19}F NMR (565 MHz, $CDCl_3$) of **2e**:



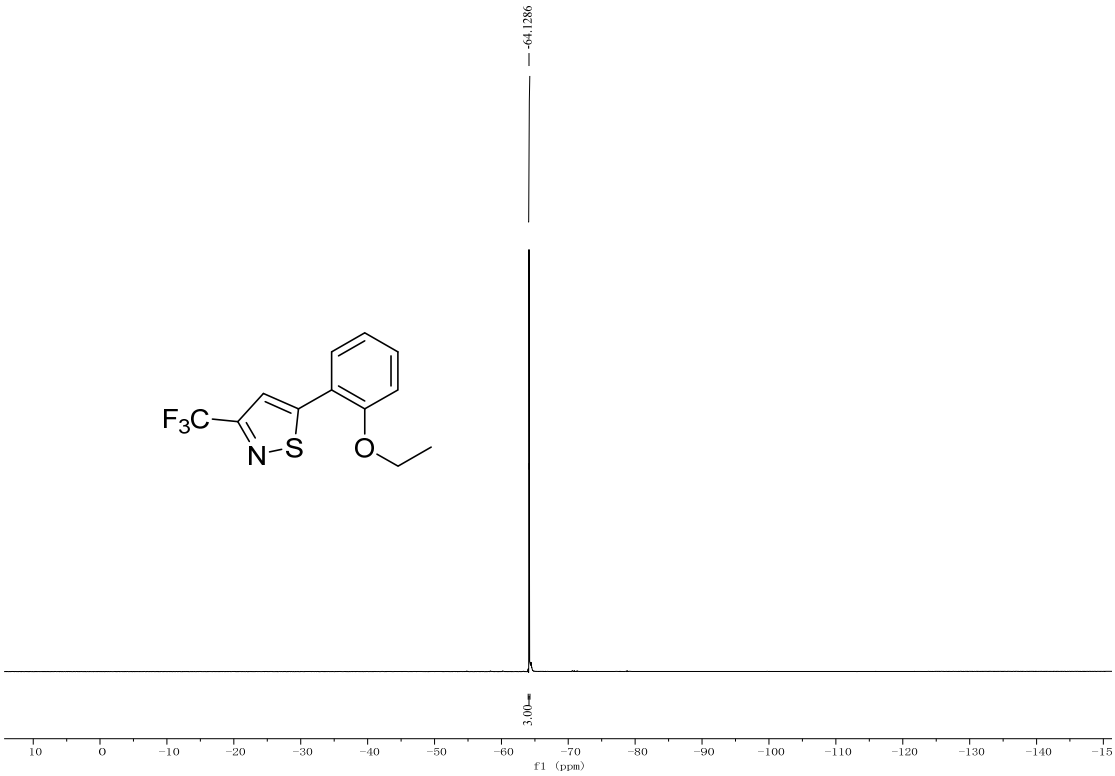
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**:



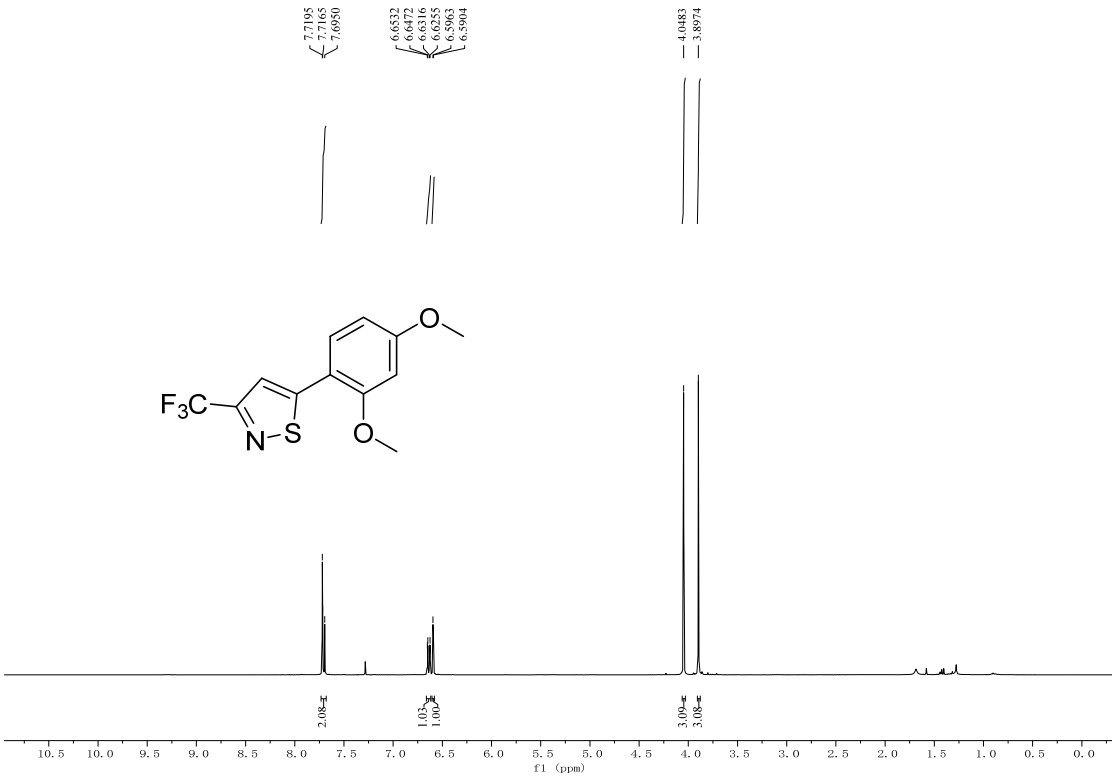
^{13}C NMR (150 MHz, $CDCl_3$) of **2f**:



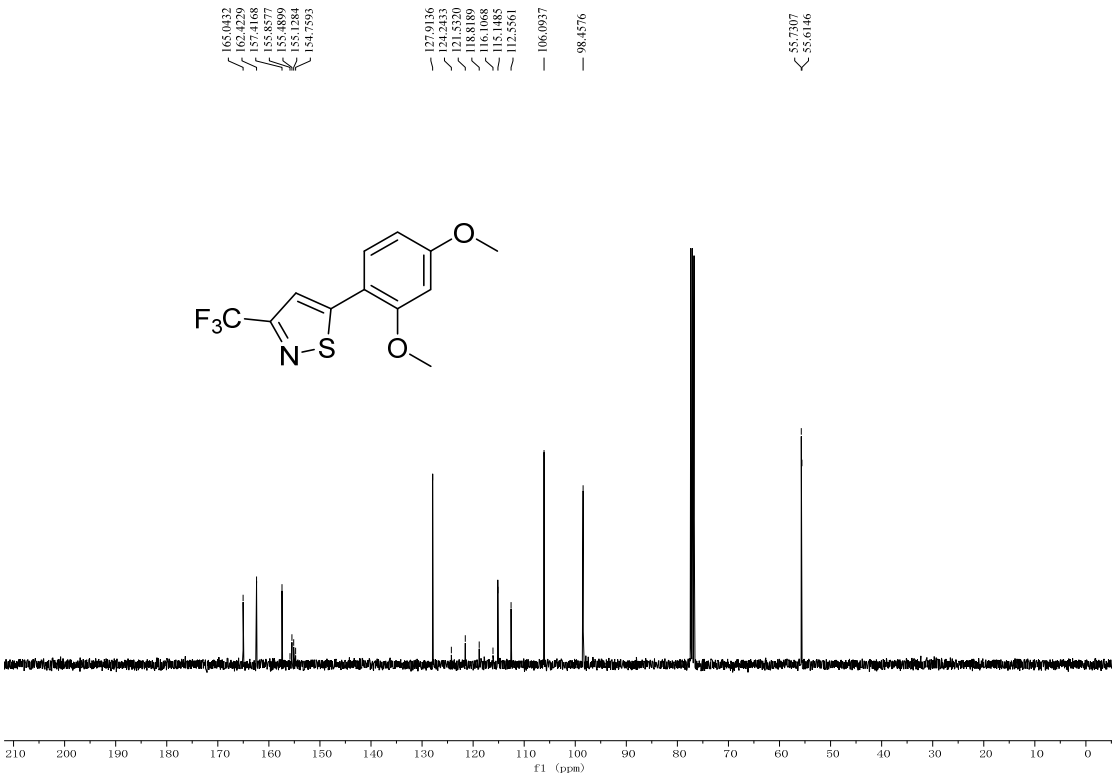
^{19}F NMR (565 MHz, $CDCl_3$) of **2f**:



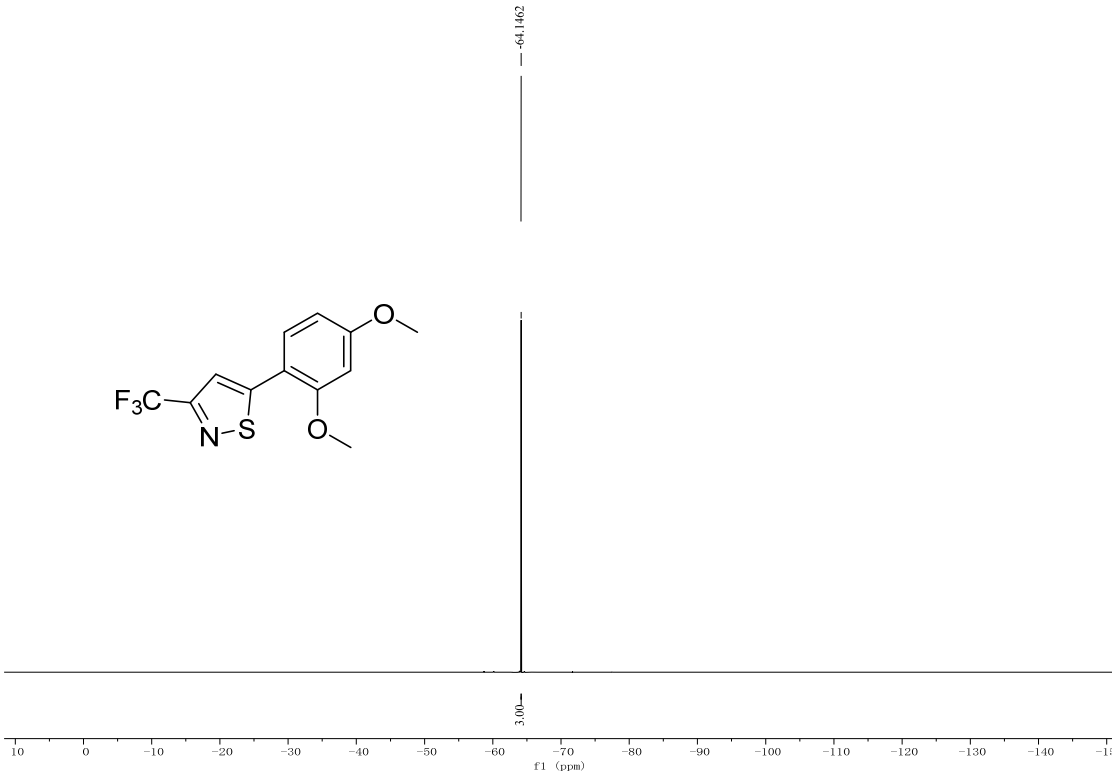
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**:



^{13}C NMR (100 MHz, $CDCl_3$) of **2i**:

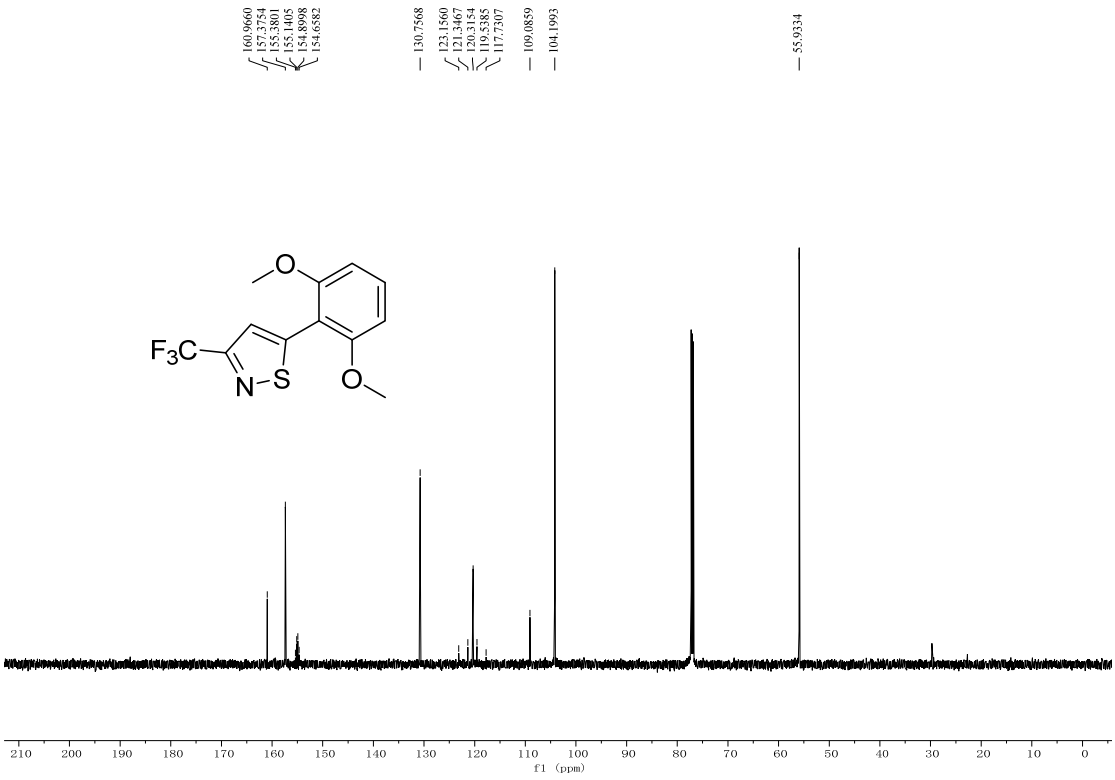


^{19}F NMR (376 MHz, $CDCl_3$) of **2i**:

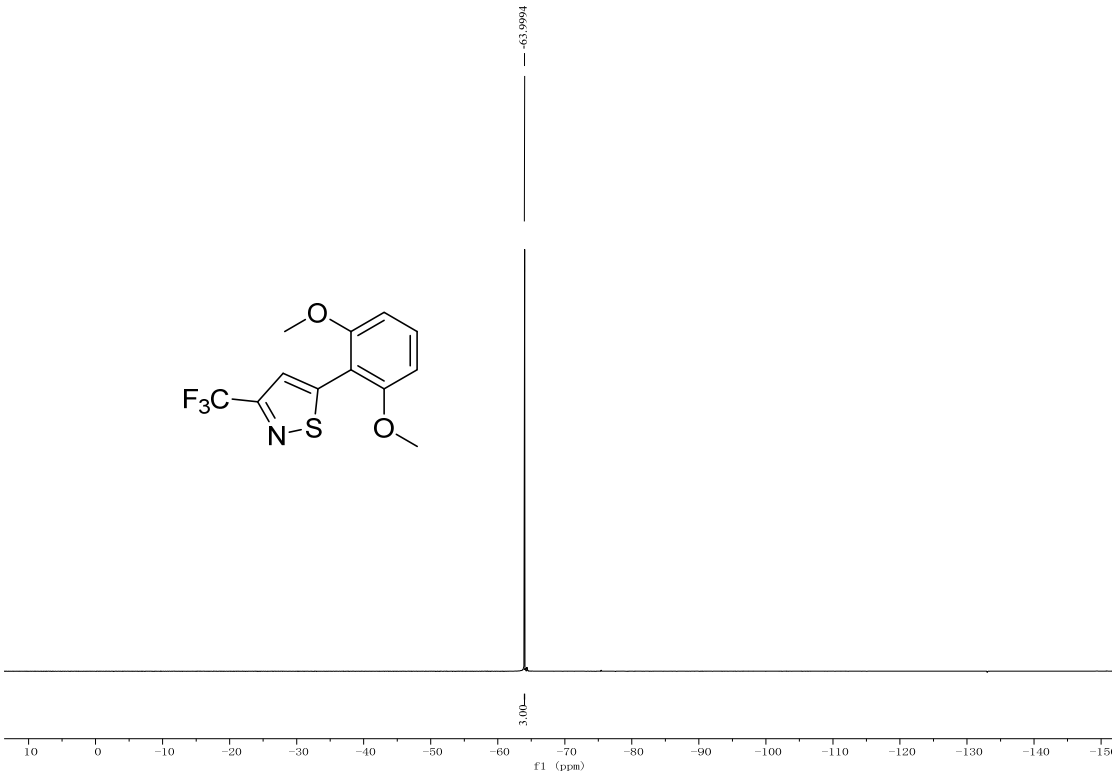


^{1}H NMR (400 MHz, $CDCl_3$) of **2j**:

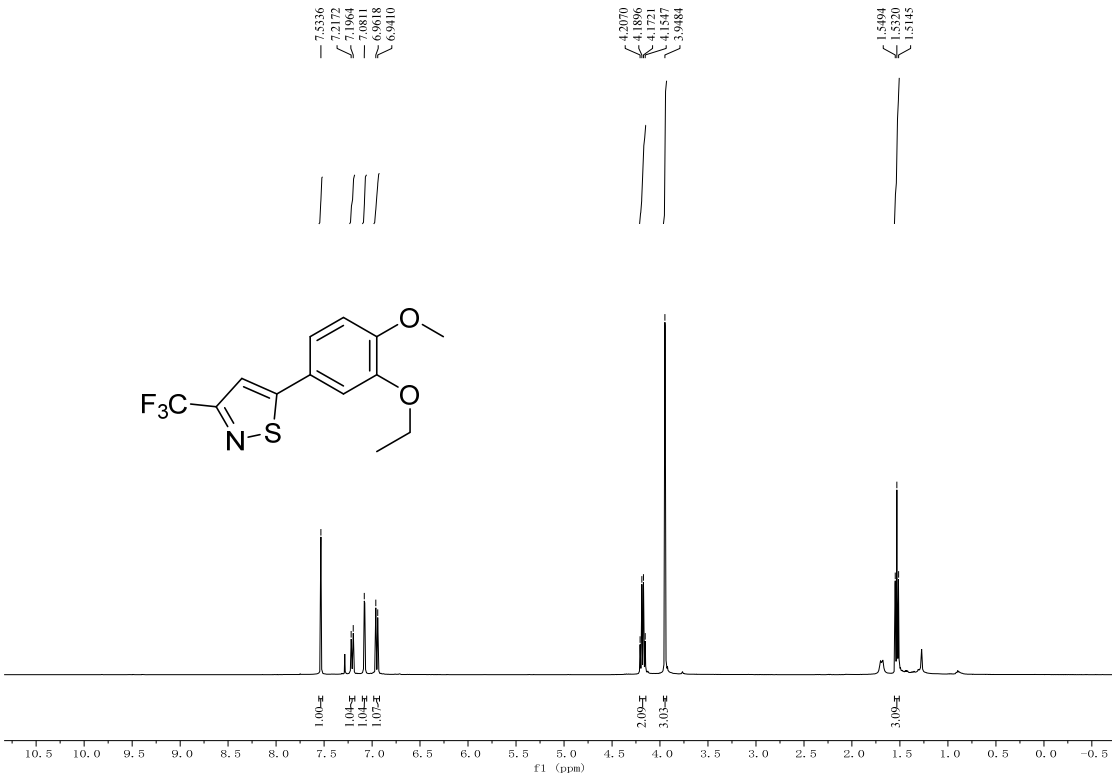
^{13}C NMR (150 MHz, $CDCl_3$) of **2j**:



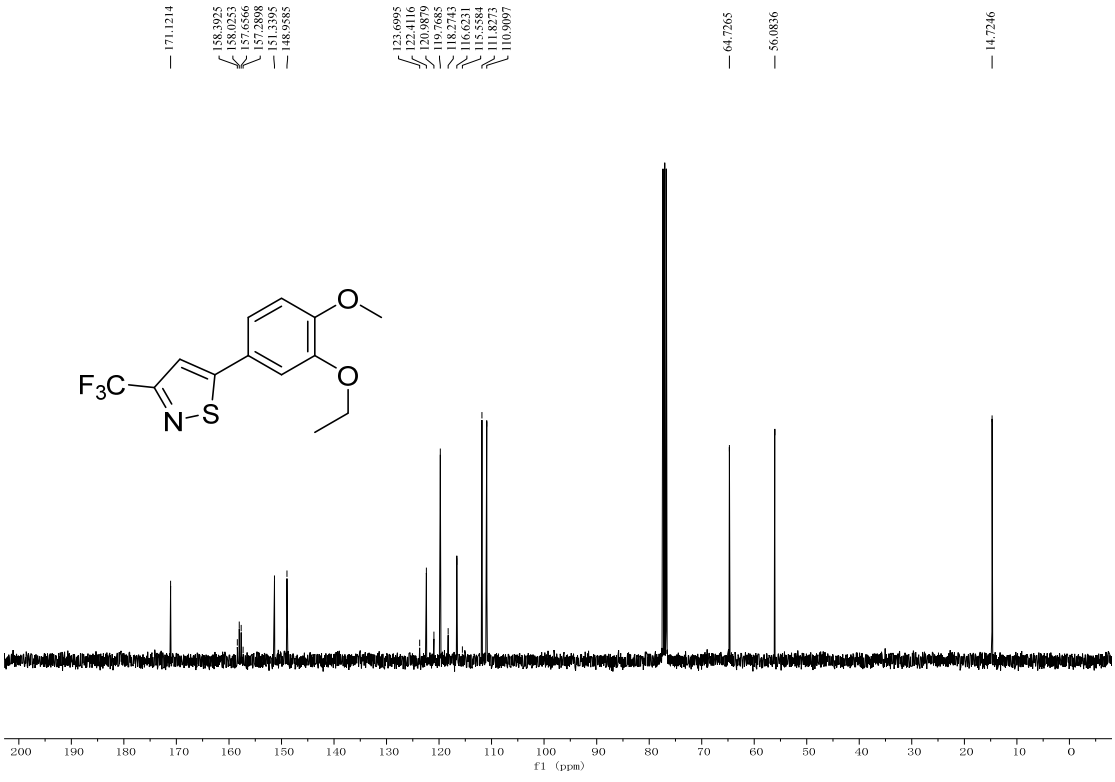
^{19}F NMR (565 MHz, $CDCl_3$) of **2j**:



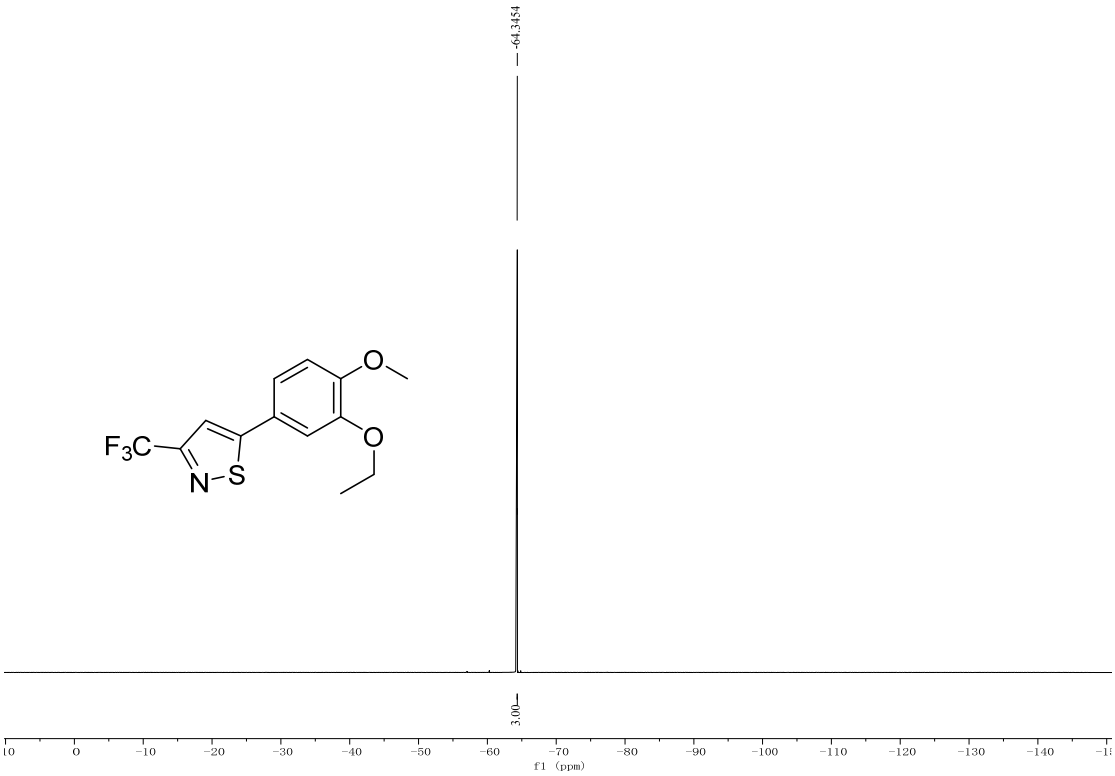
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**:



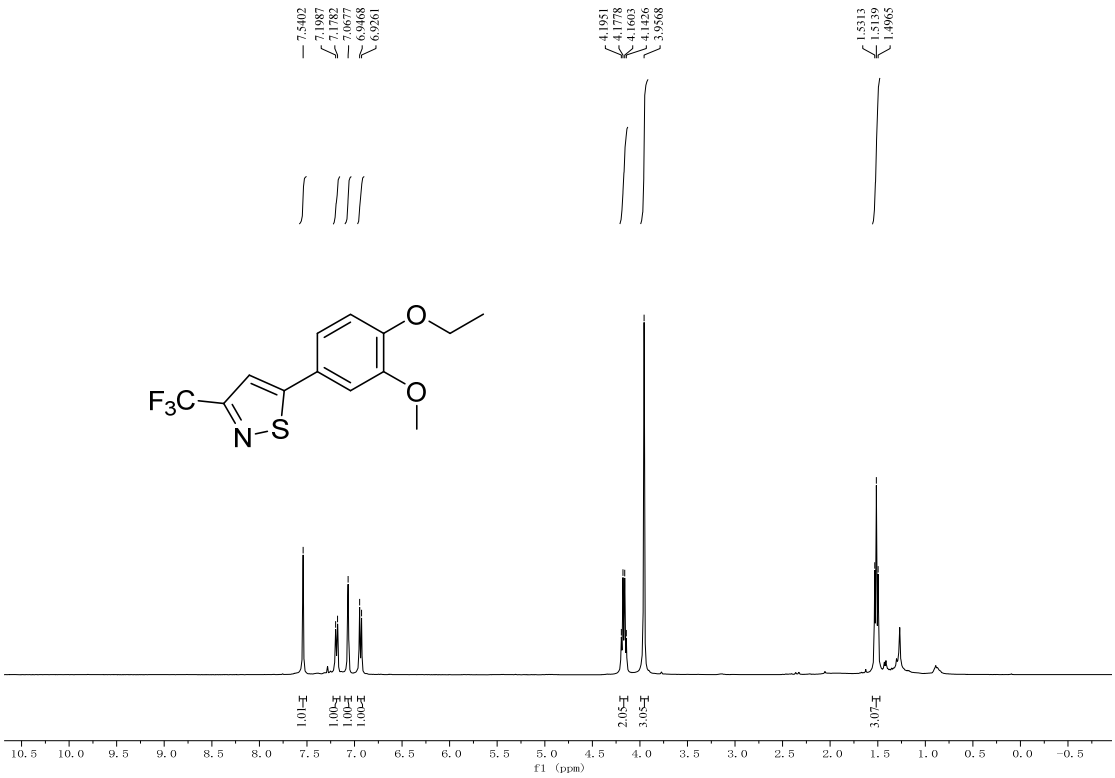
^{13}C NMR (100 MHz, $CDCl_3$) of **2k**:



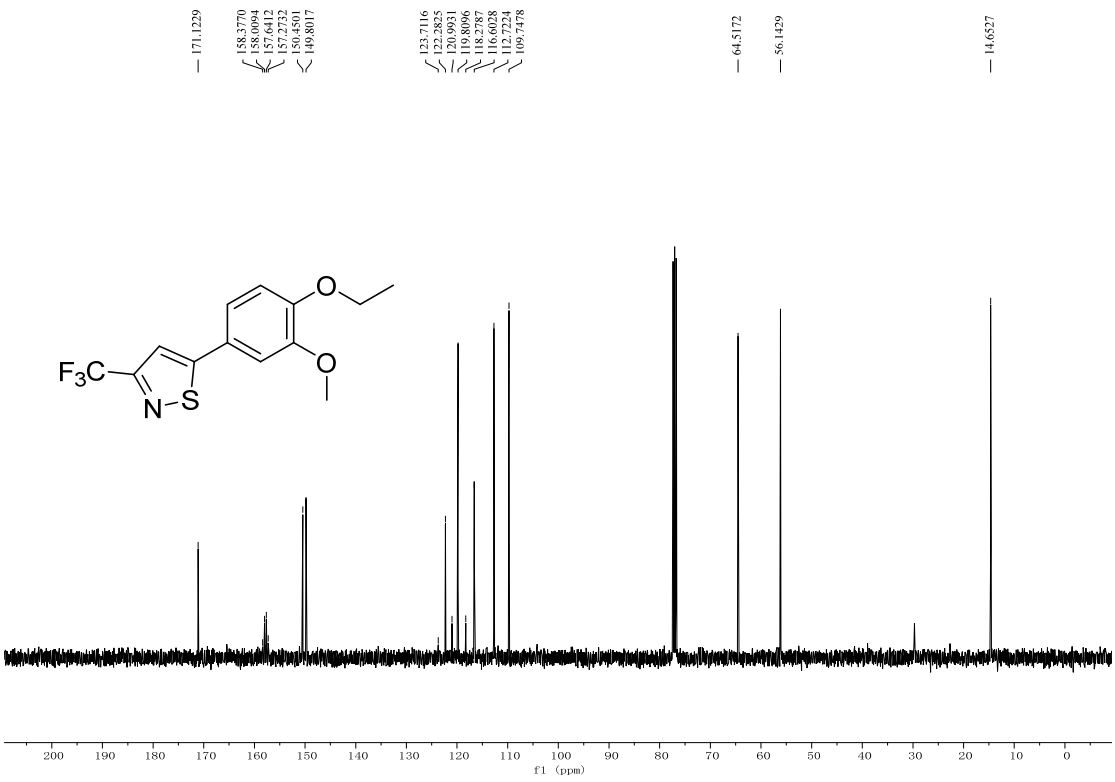
^{19}F NMR (376 MHz, $CDCl_3$) of **2k**:



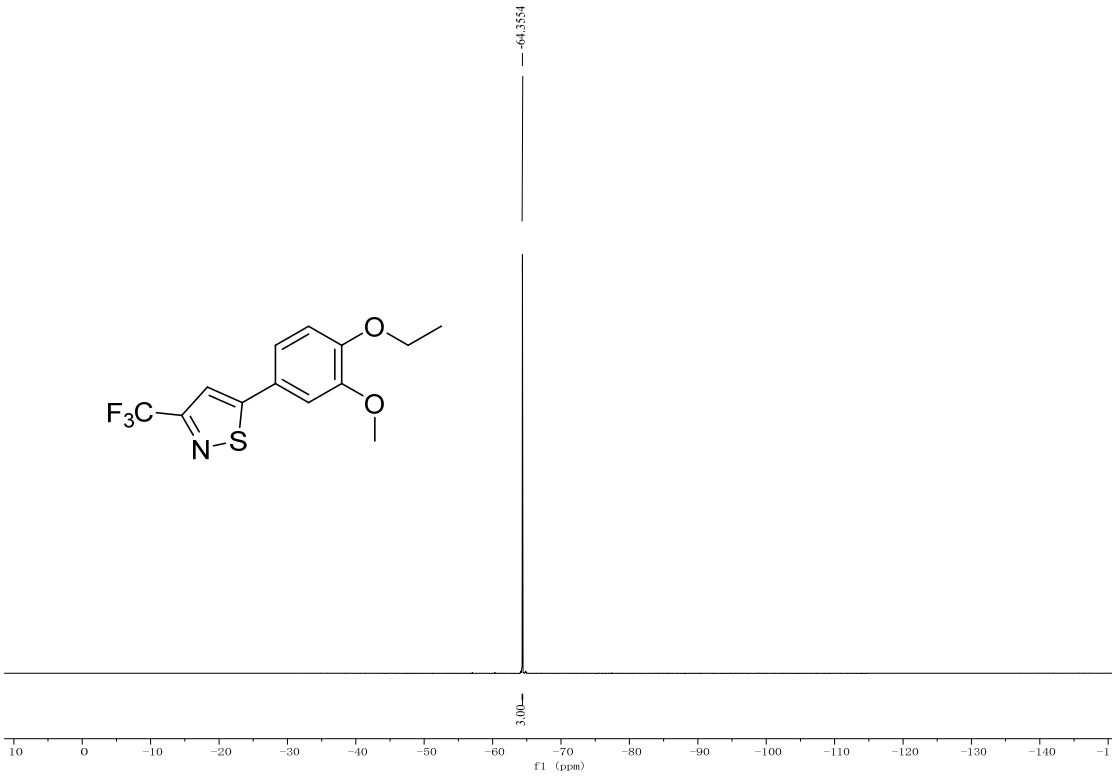
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**:



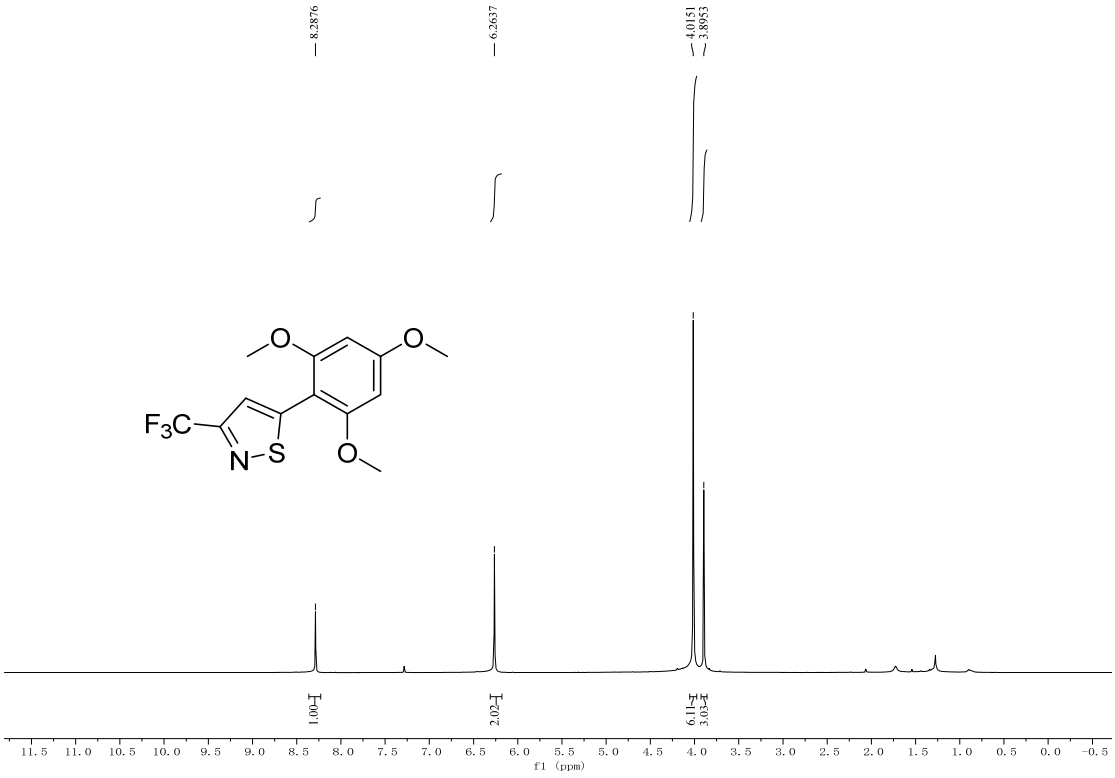
^{13}C NMR (100 MHz, $CDCl_3$) of **2l**:



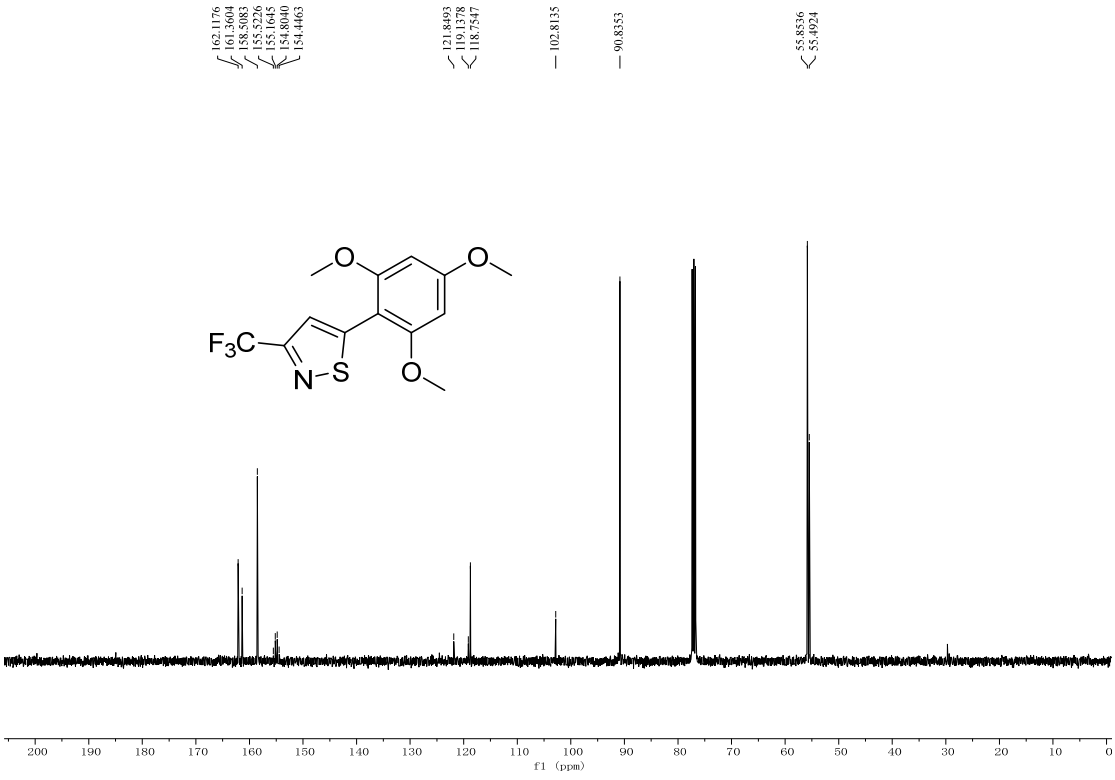
^{19}F NMR (376 MHz, $CDCl_3$) of **2l**:



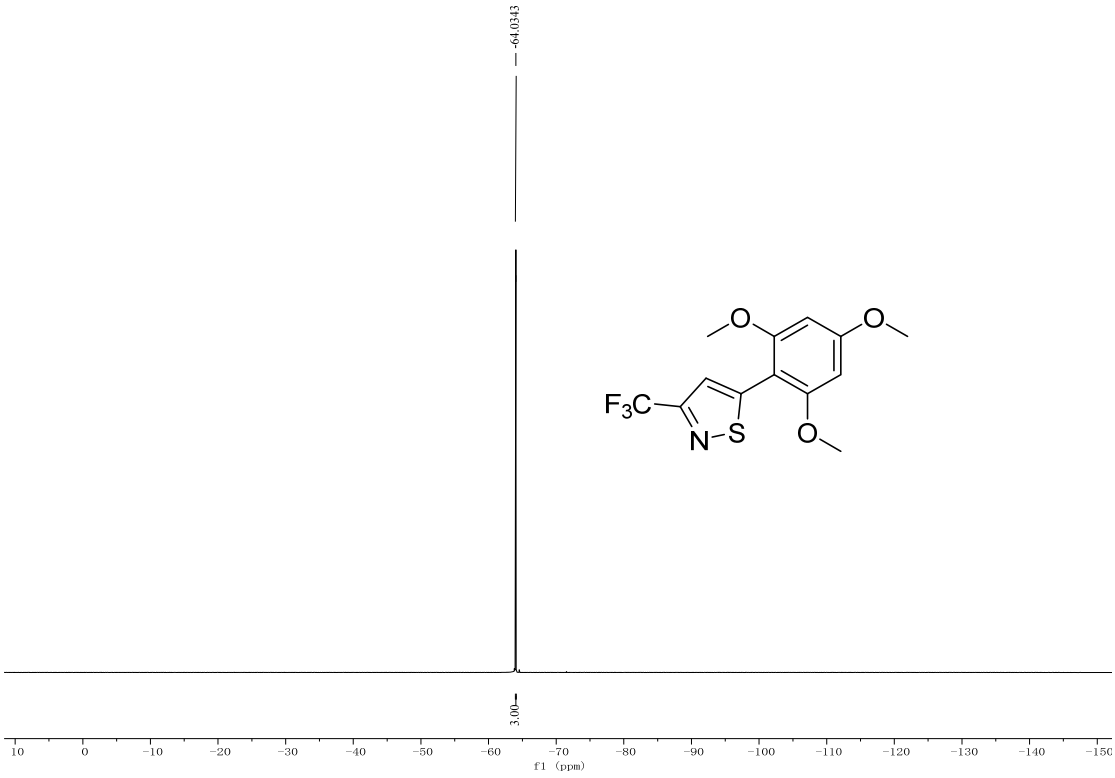
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**:



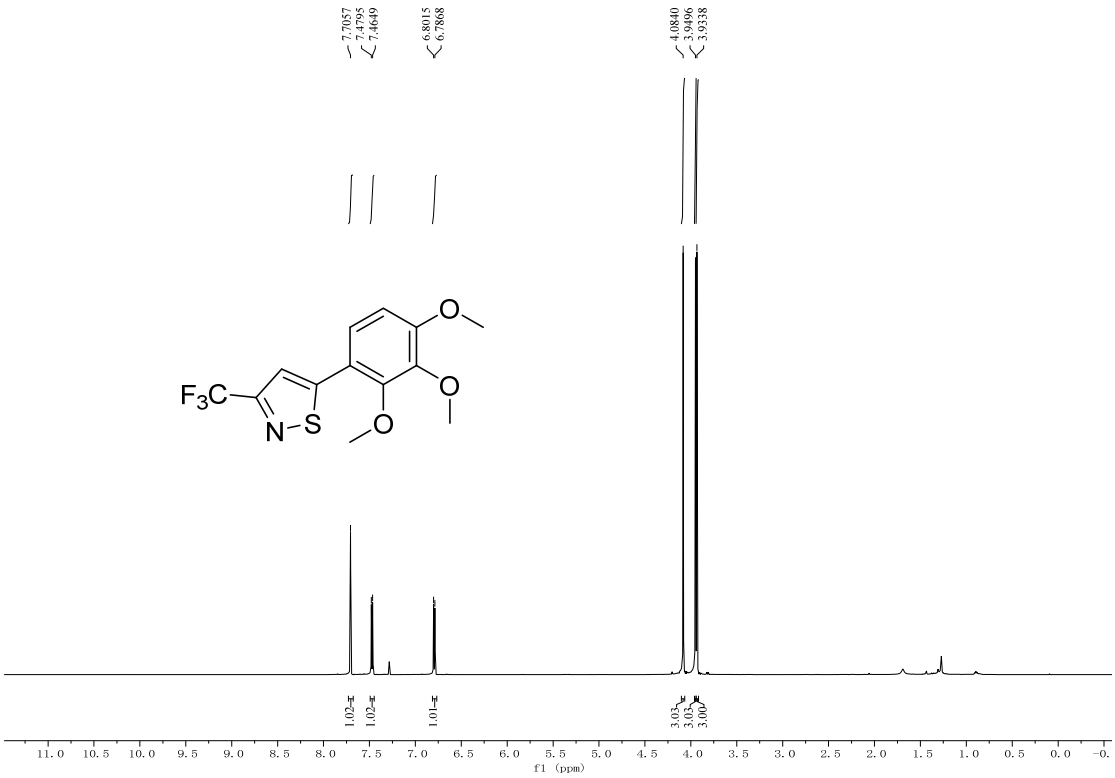
^{13}C NMR (100 MHz, $CDCl_3$) of **2m**:



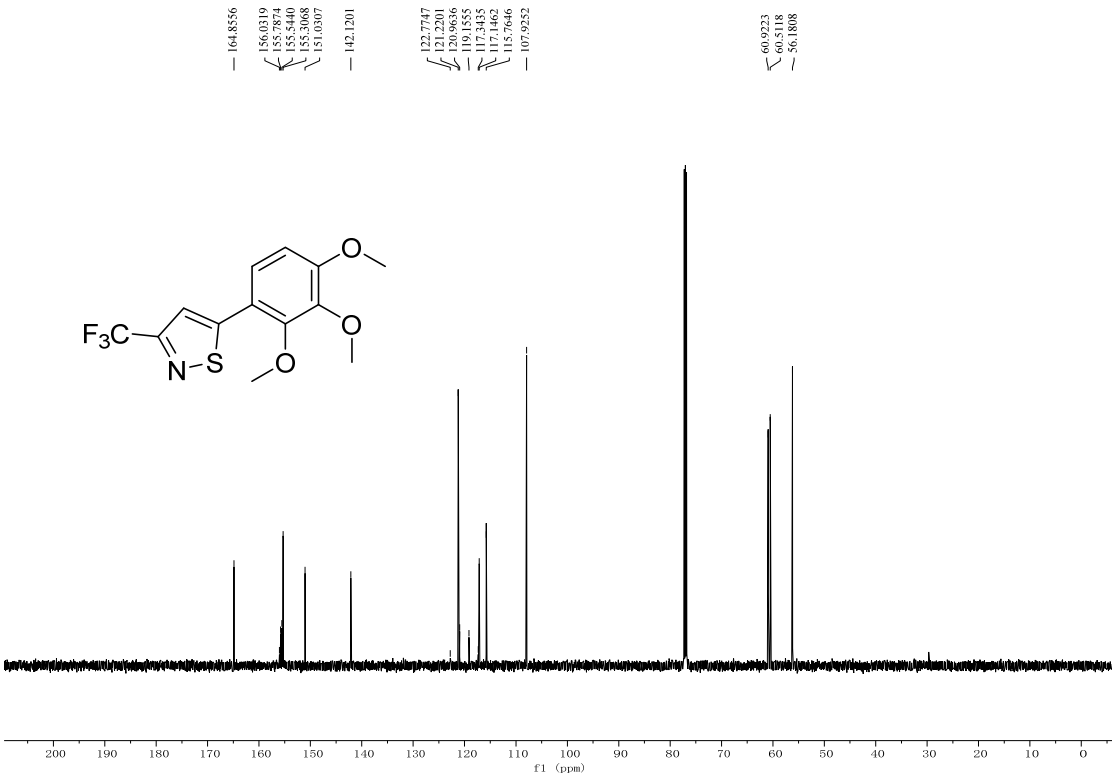
^{19}F NMR (376 MHz, $CDCl_3$) of **2m**:



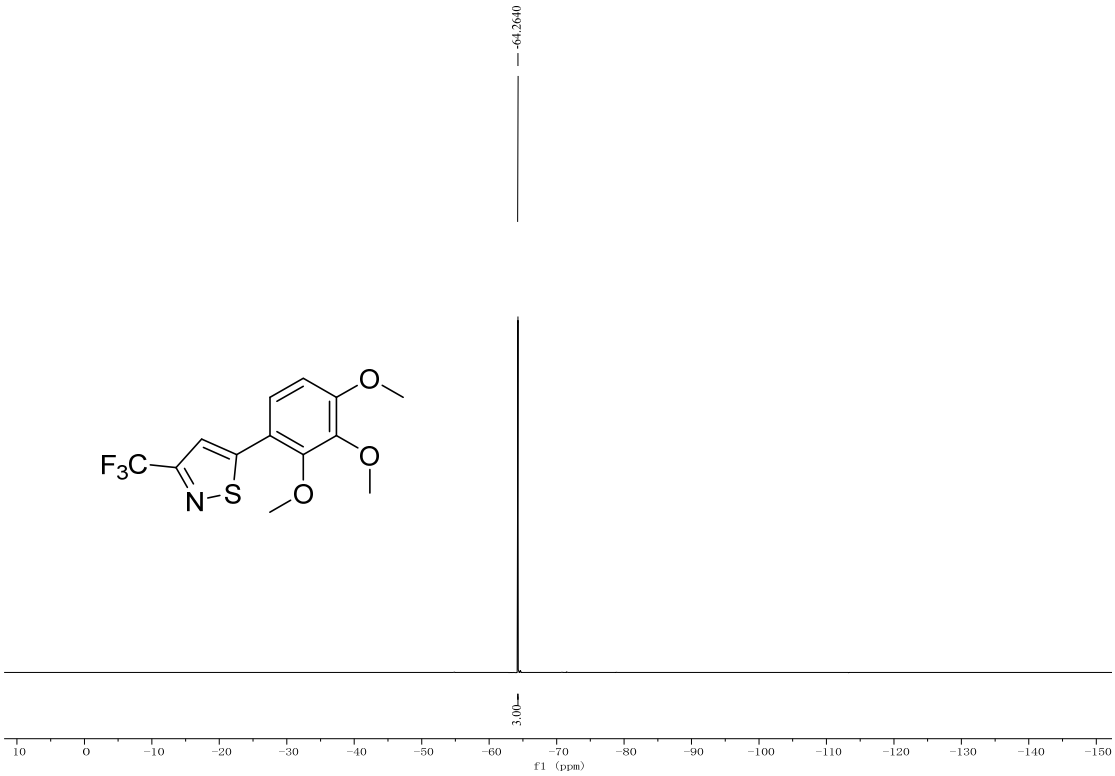
^{1}H NMR (600 MHz, $CDCl_3$) of **2n**:



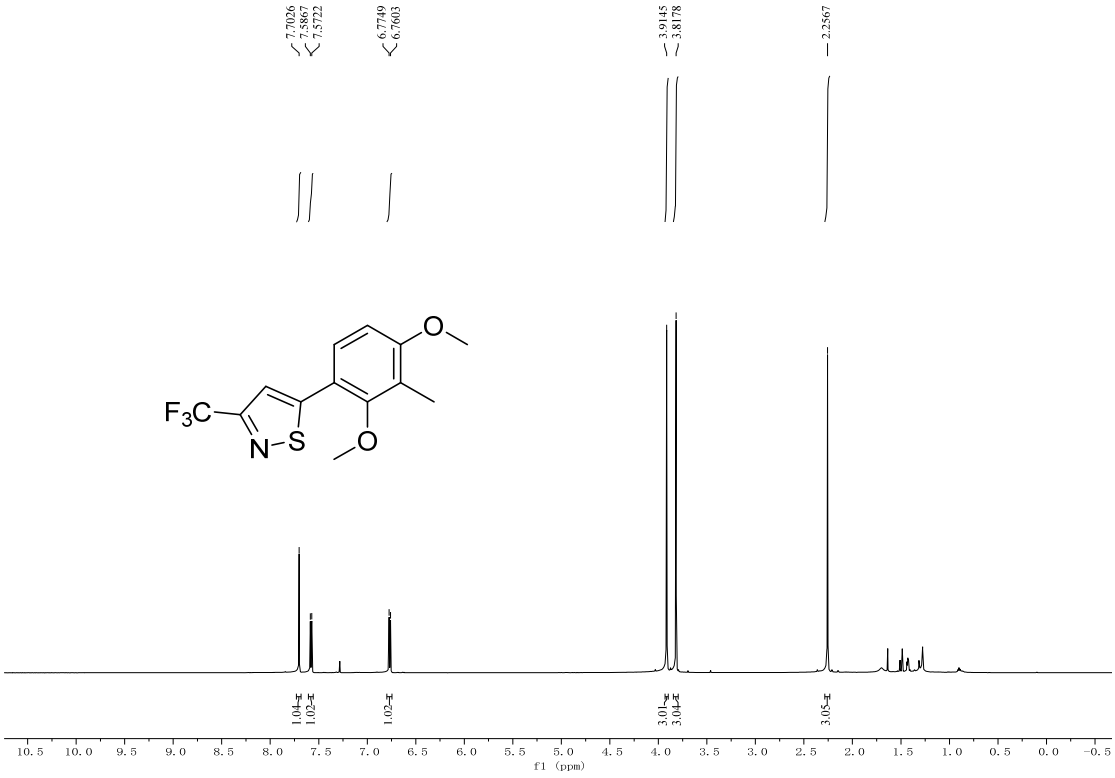
^{13}C NMR (150 MHz, $CDCl_3$) of **2n**:



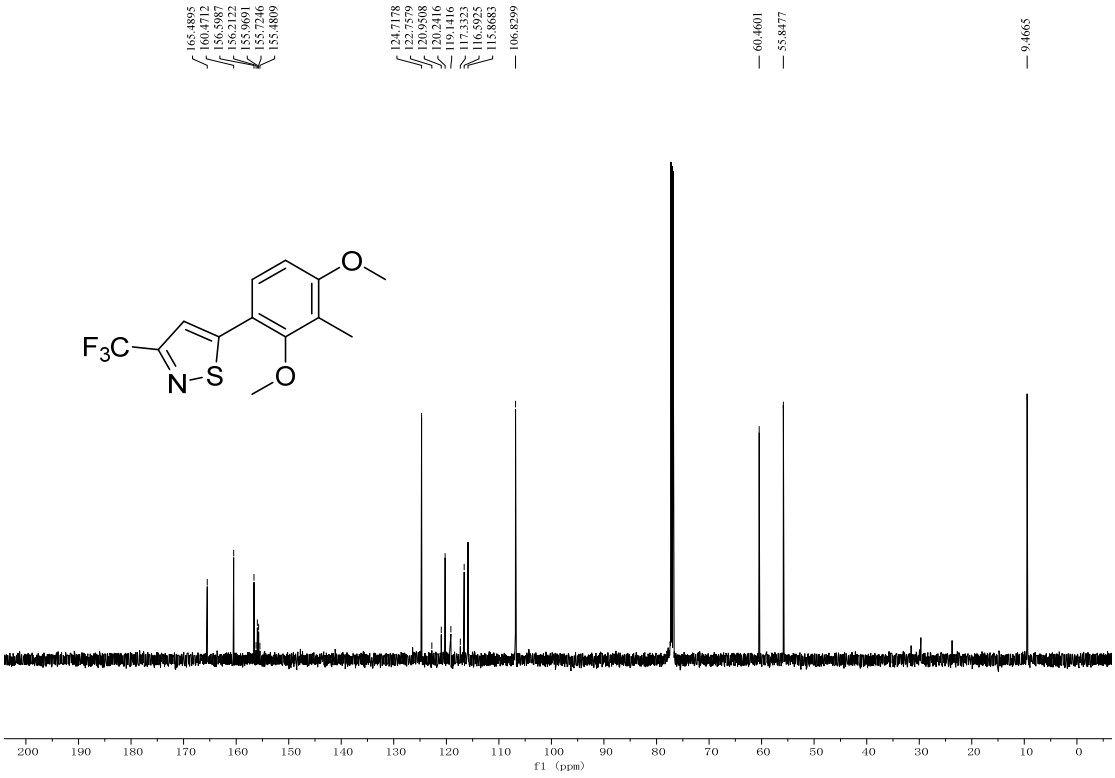
^{19}F NMR (565 MHz, $CDCl_3$) of **2n**:



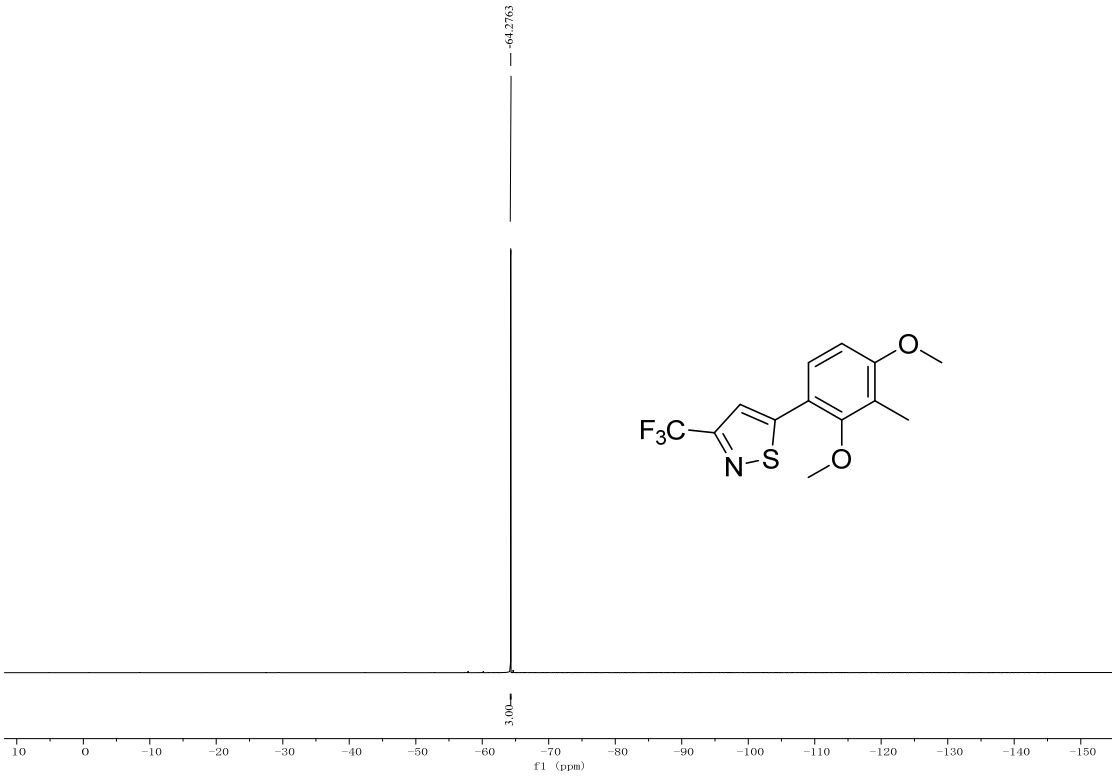
^{1}H NMR (600 MHz, $CDCl_3$) of **2o**:



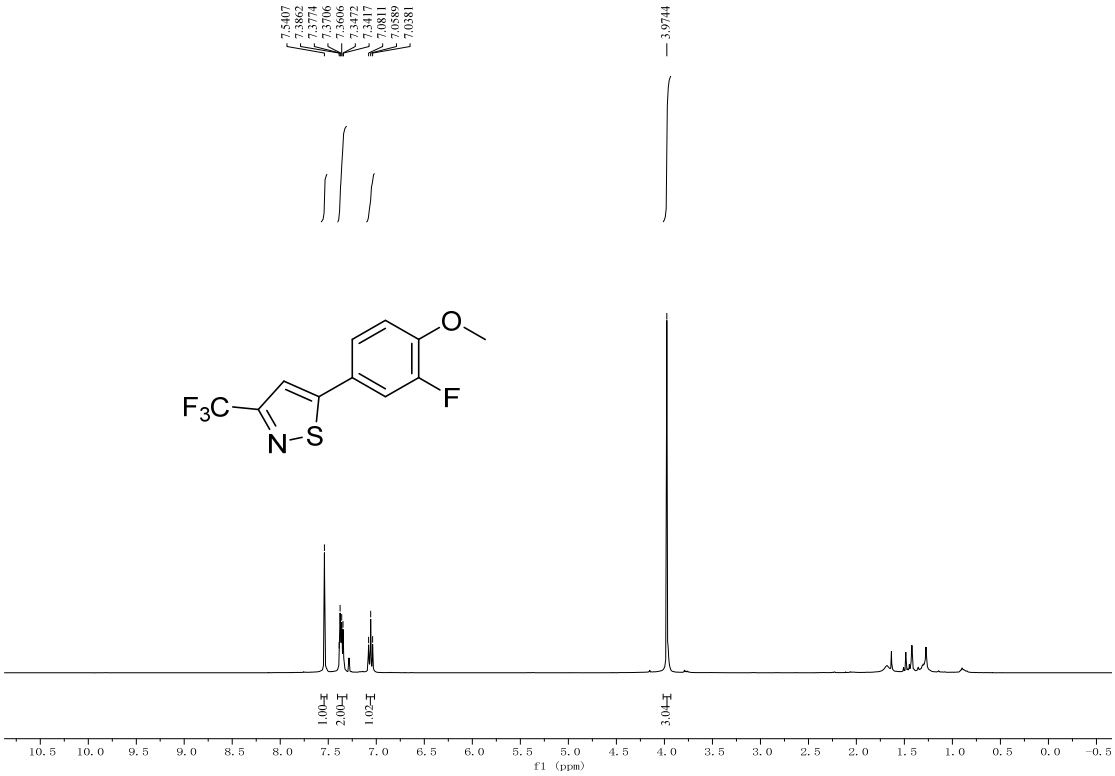
^{13}C NMR (150 MHz, $CDCl_3$) of **2o**:



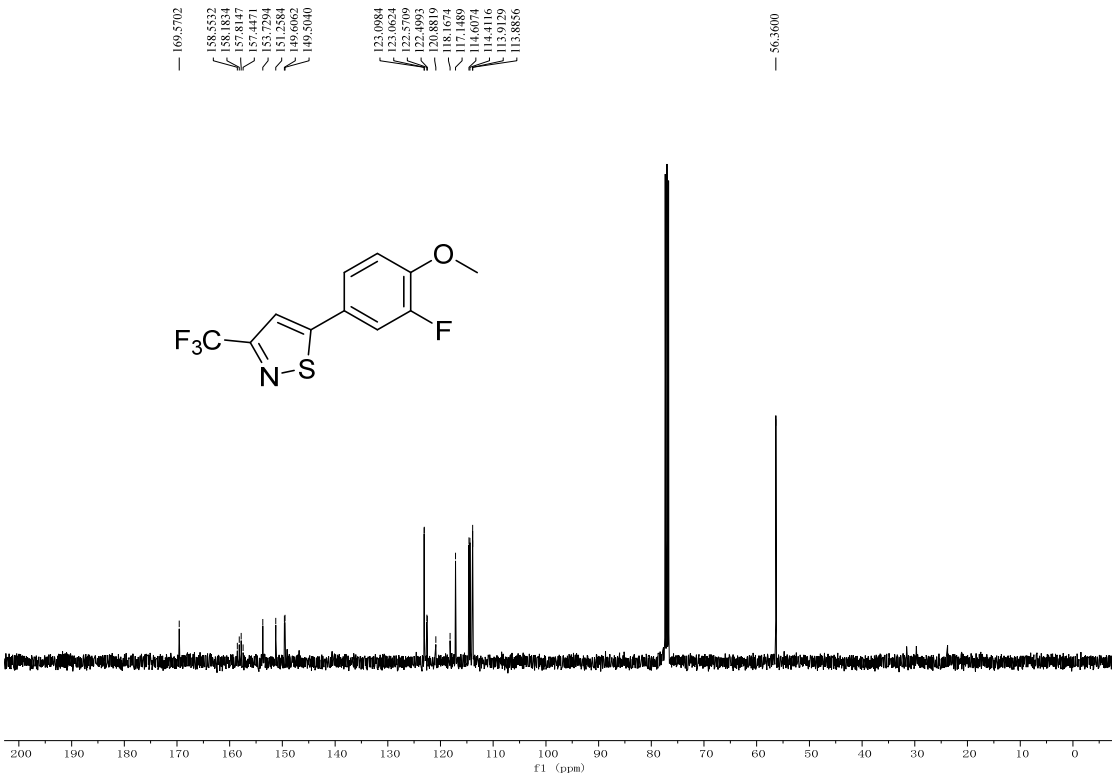
^{19}F NMR (565 MHz, $CDCl_3$) of **2o**:



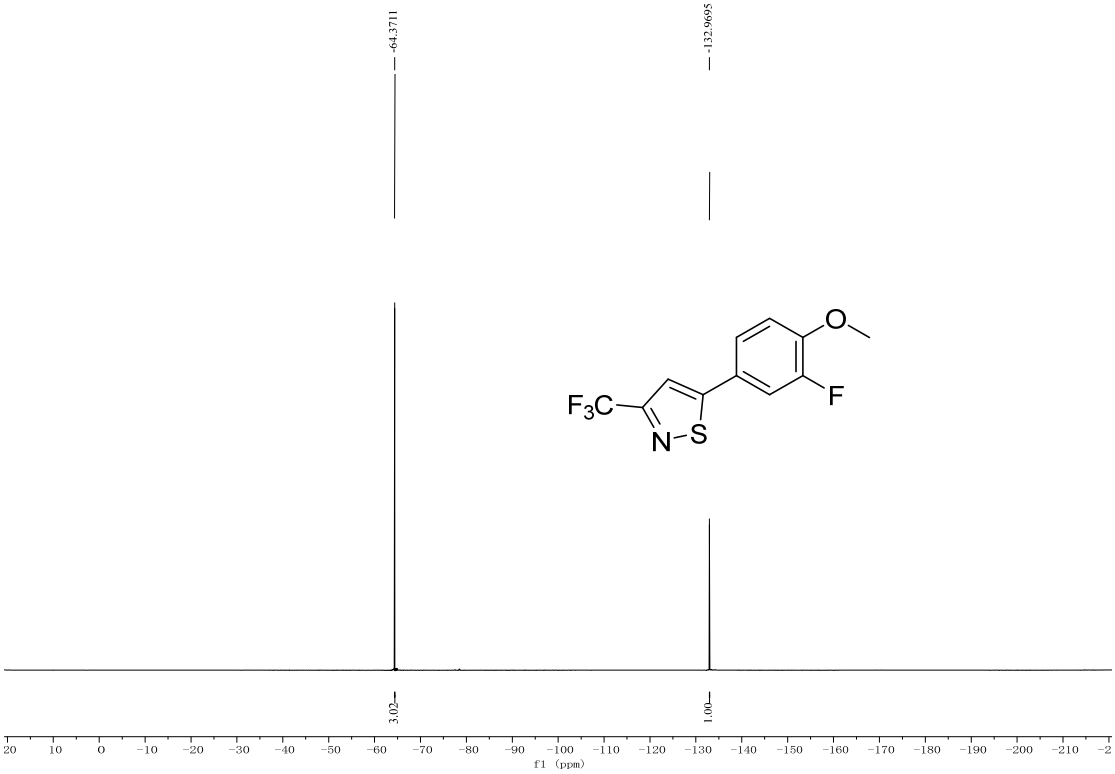
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**:



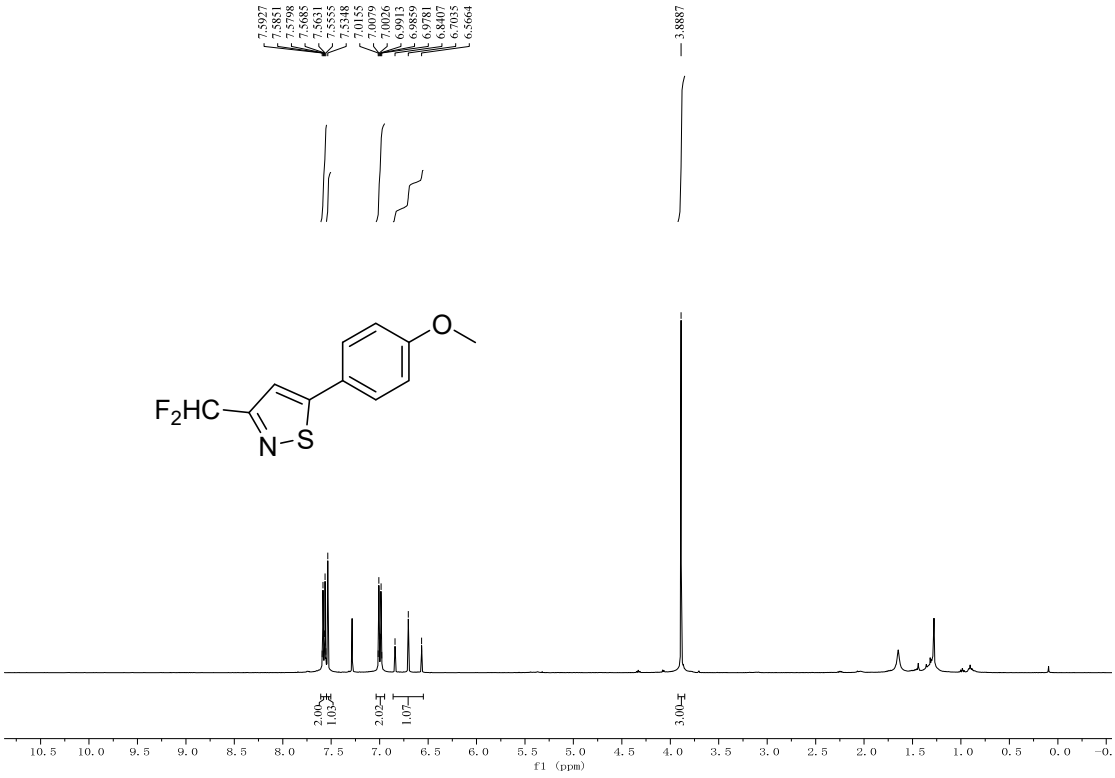
^{13}C NMR (100 MHz, $CDCl_3$) of **2p**:



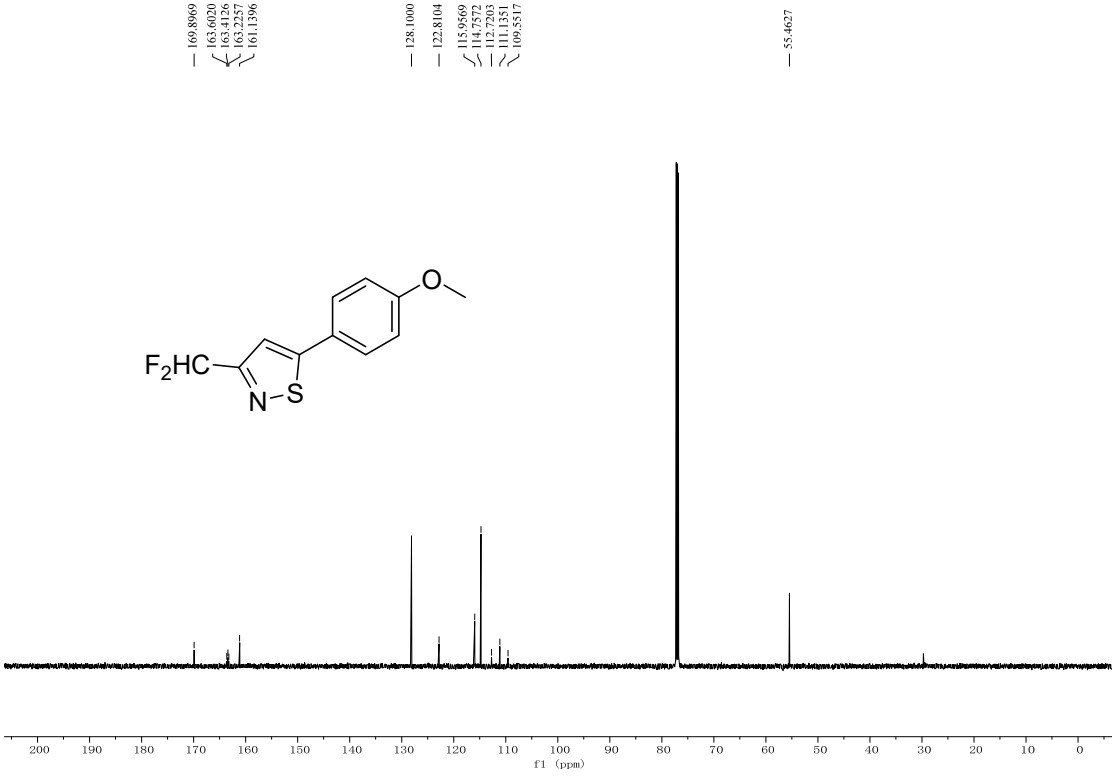
^{19}F NMR (376 MHz, $CDCl_3$) of **2p**:



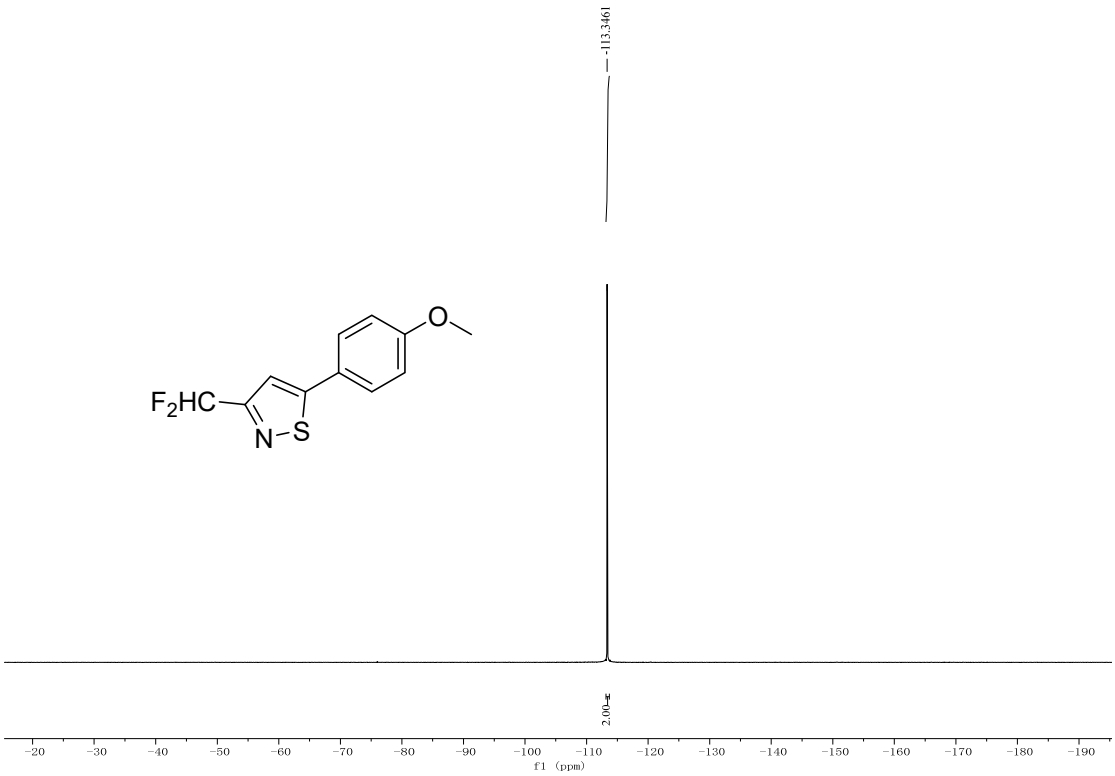
^{1}H NMR (400 MHz, $CDCl_3$) of **2q**:



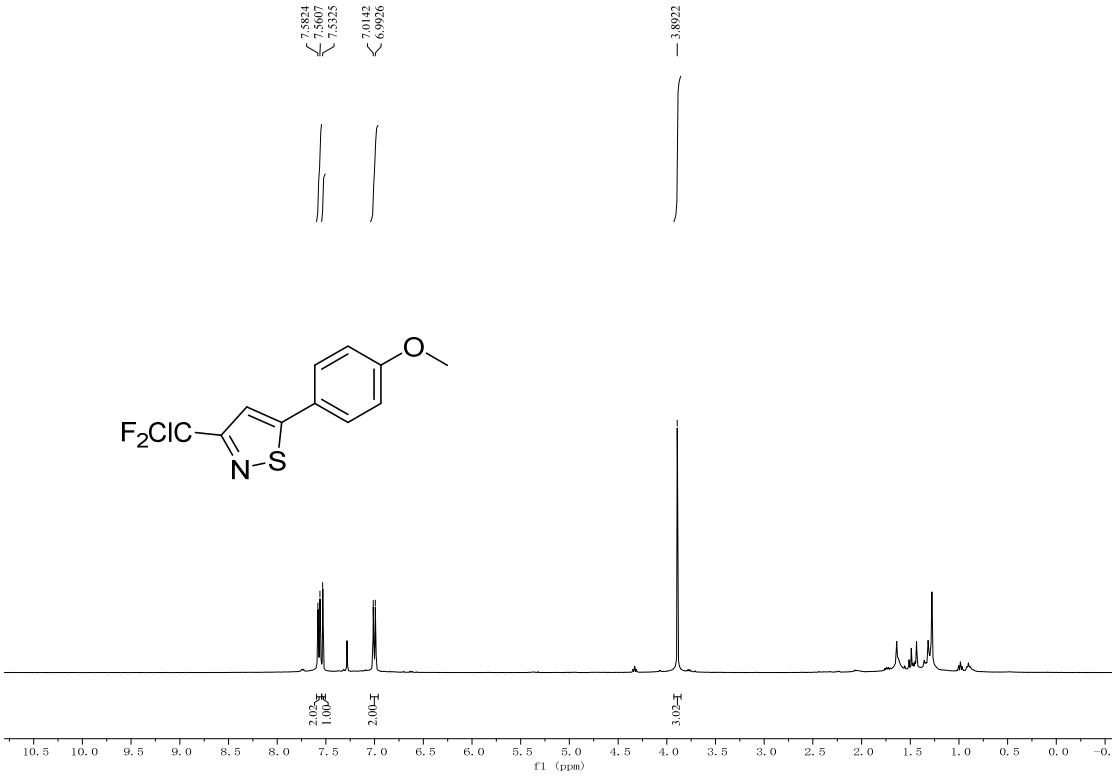
^{13}C NMR (150 MHz, $CDCl_3$) of **2q**:



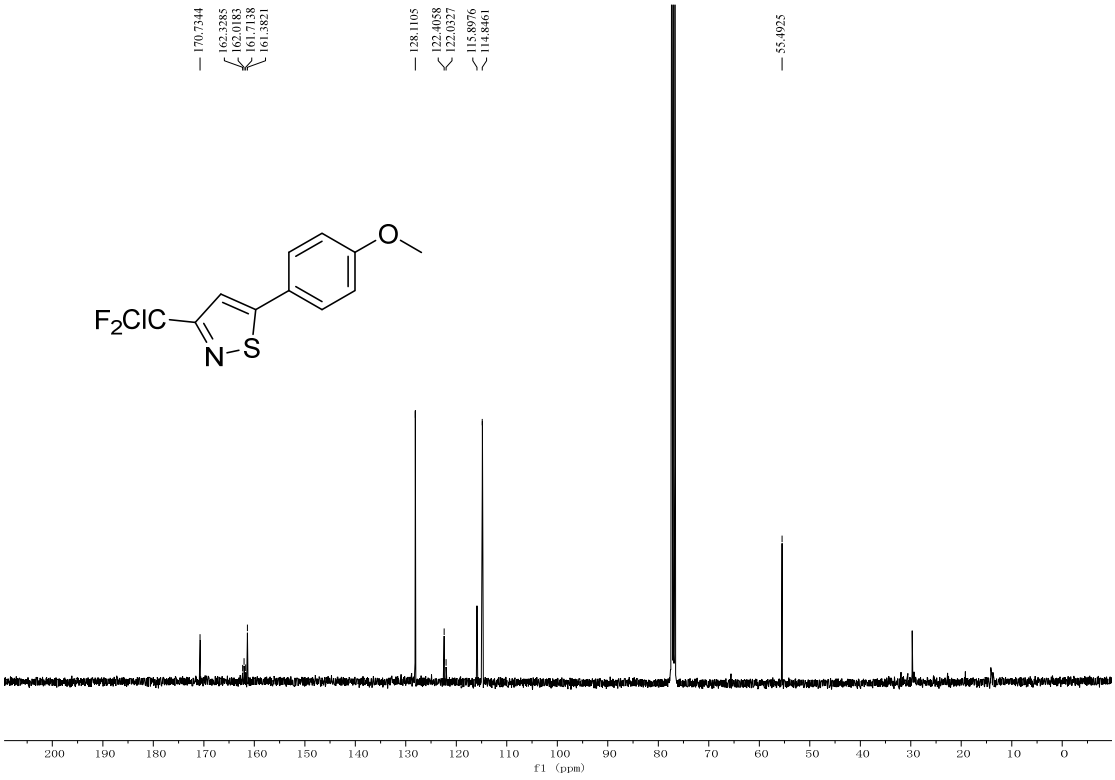
^{19}F NMR (376 MHz, $CDCl_3$) of **2q**:



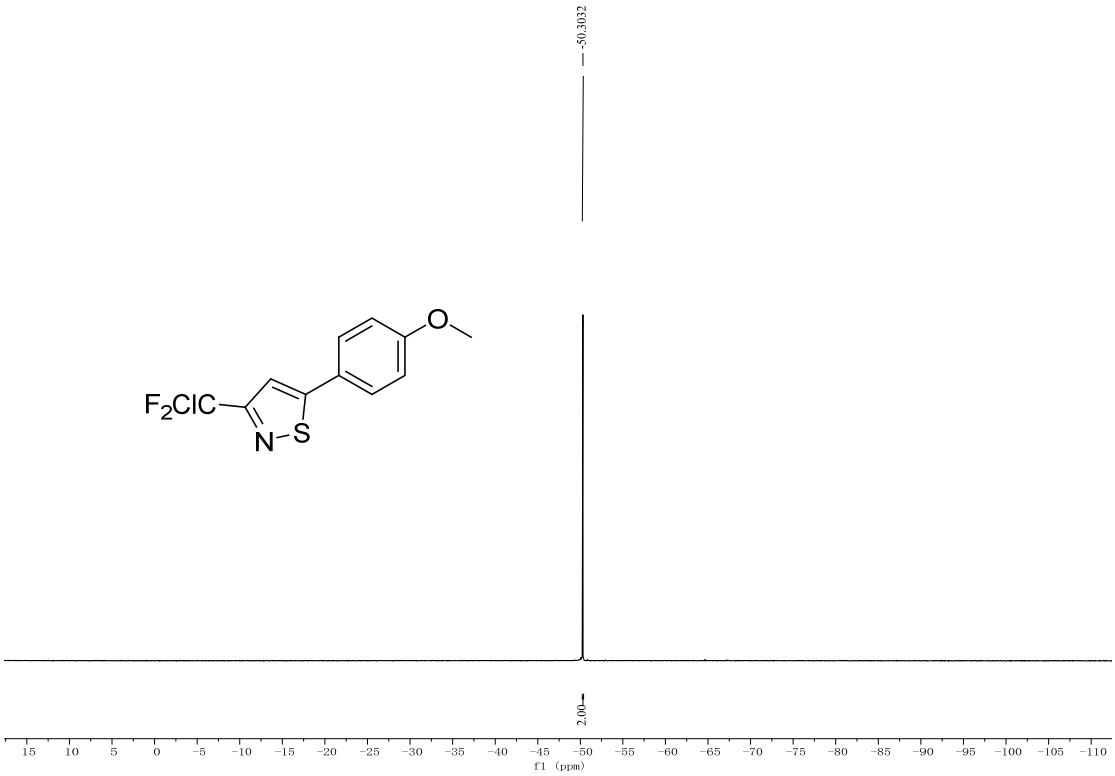
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**:



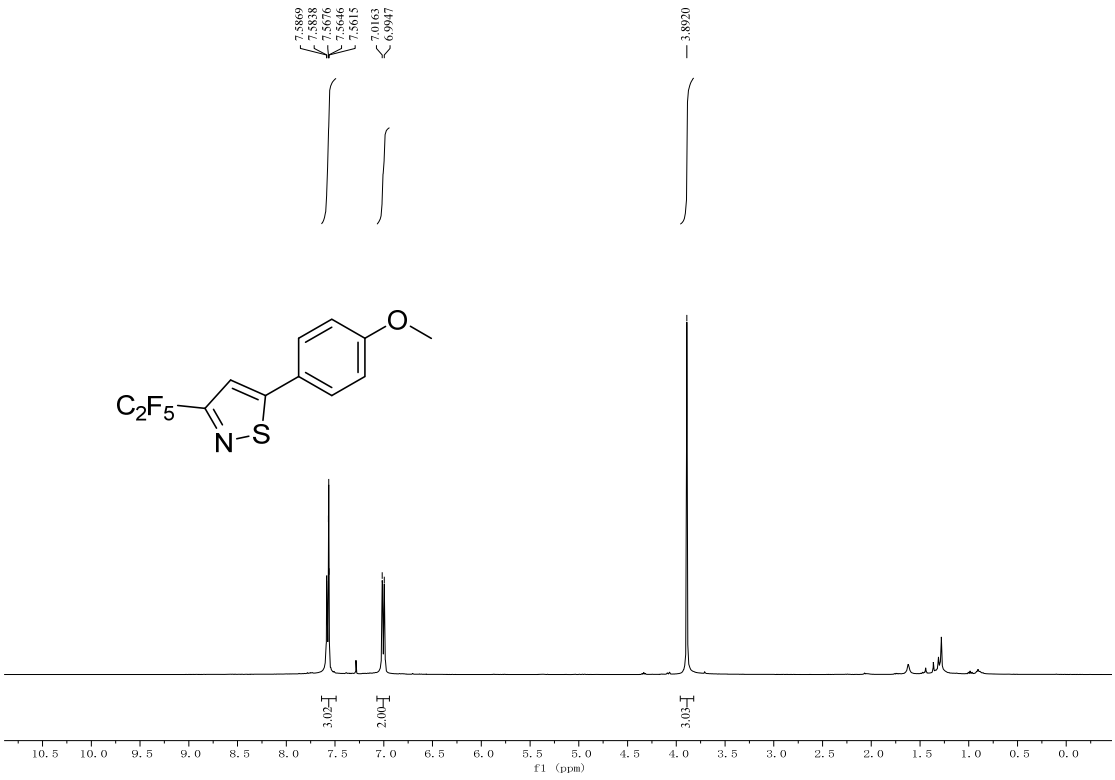
^{13}C NMR (100 MHz, $CDCl_3$) of **2r**:



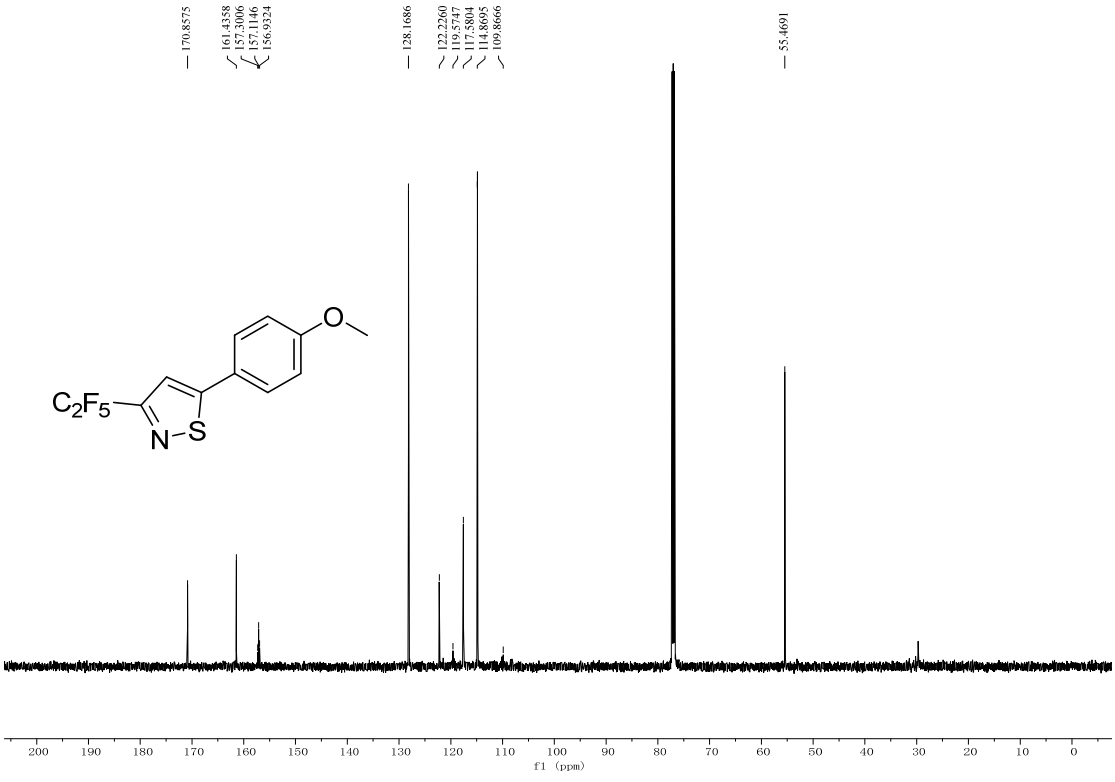
^{19}F NMR (376 MHz, $CDCl_3$) of **2r**:



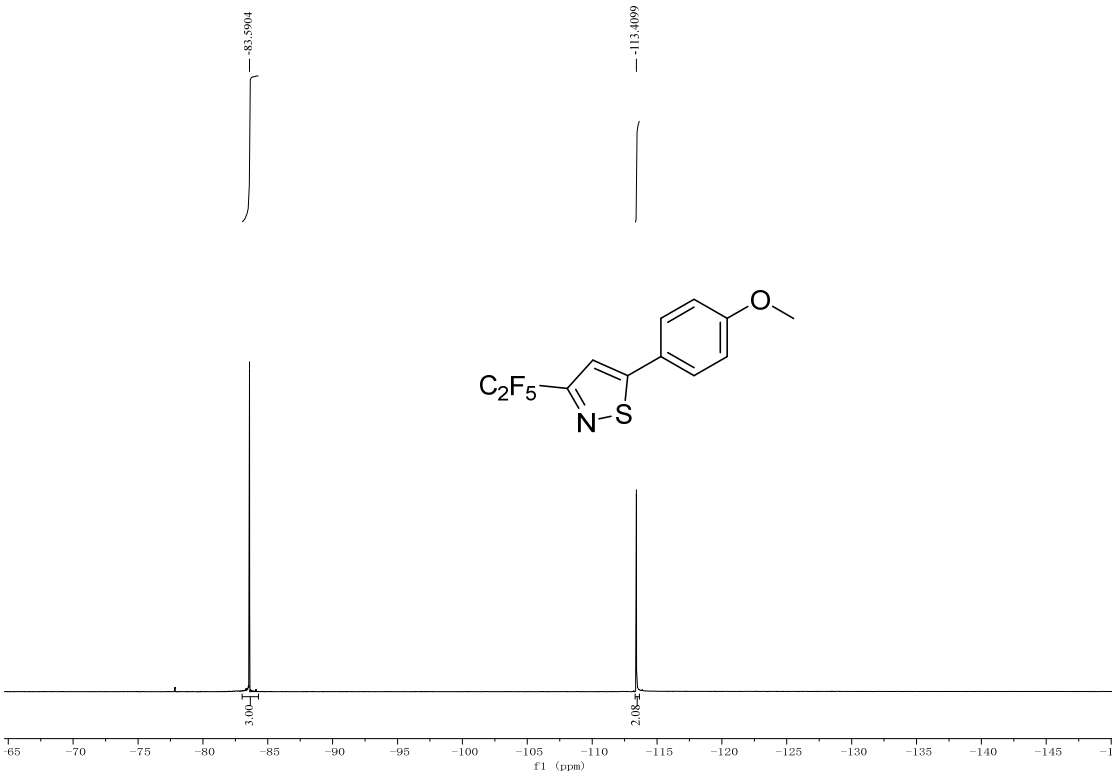
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**:



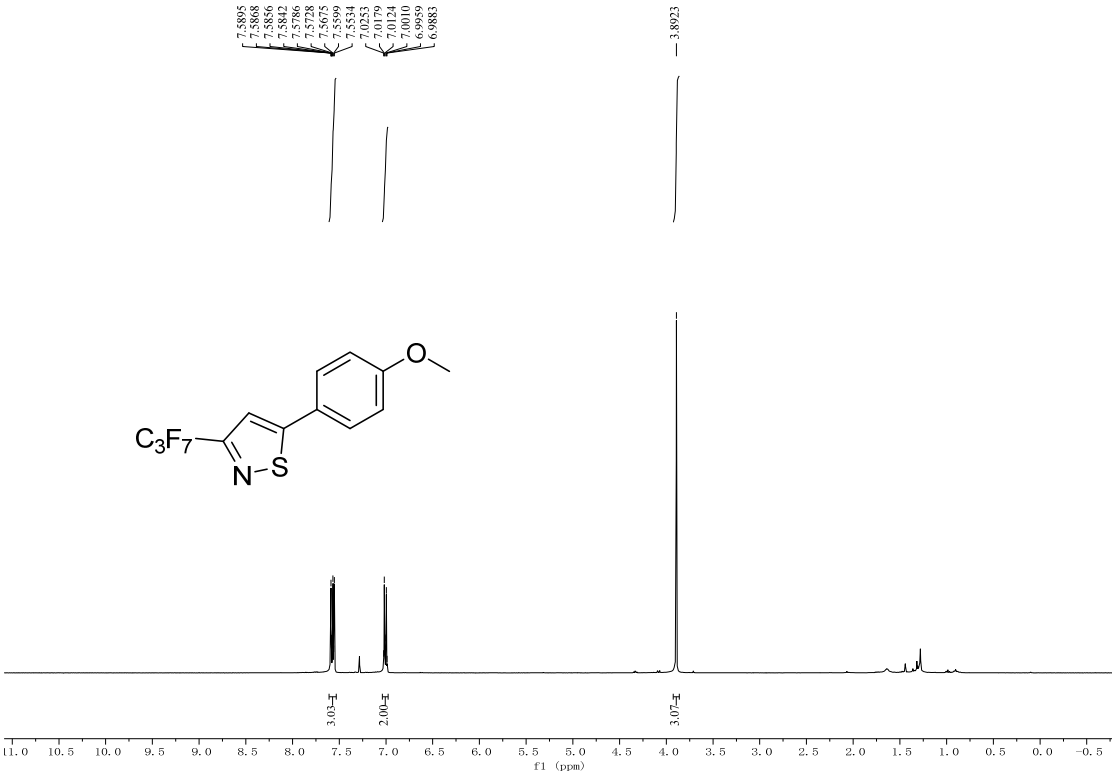
^{13}C NMR (150 MHz, $CDCl_3$) of **2t**:



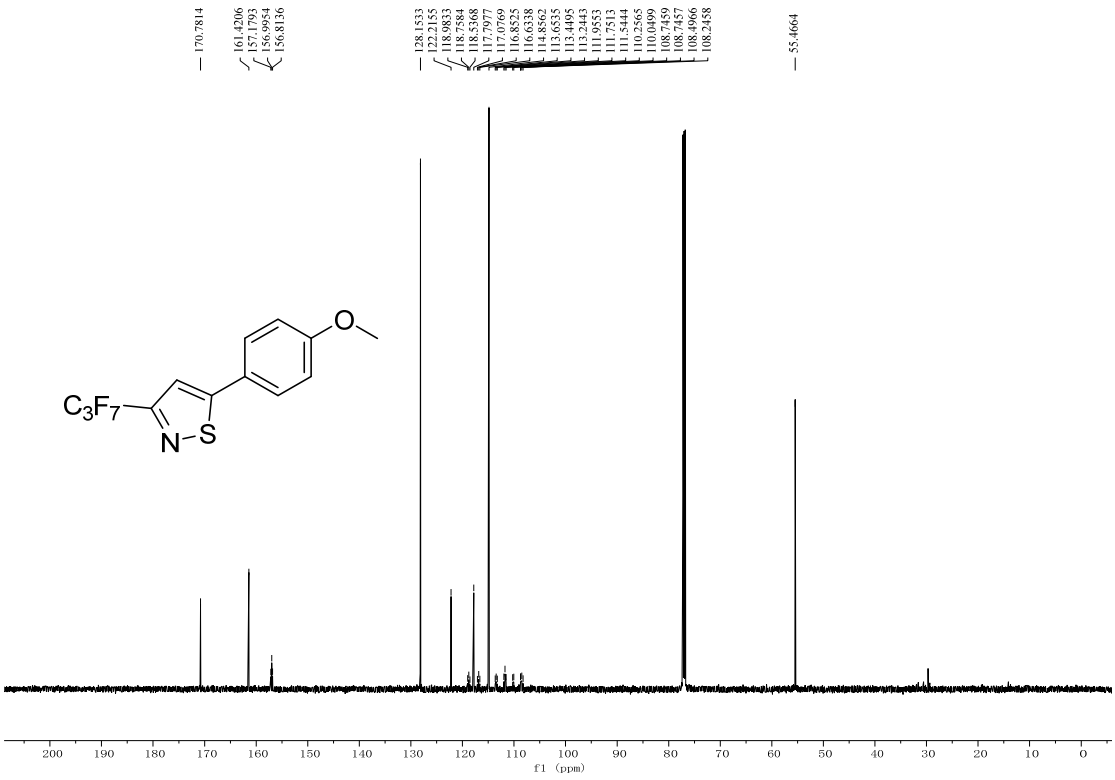
^{19}F NMR (376 MHz, $CDCl_3$) of **2t**:



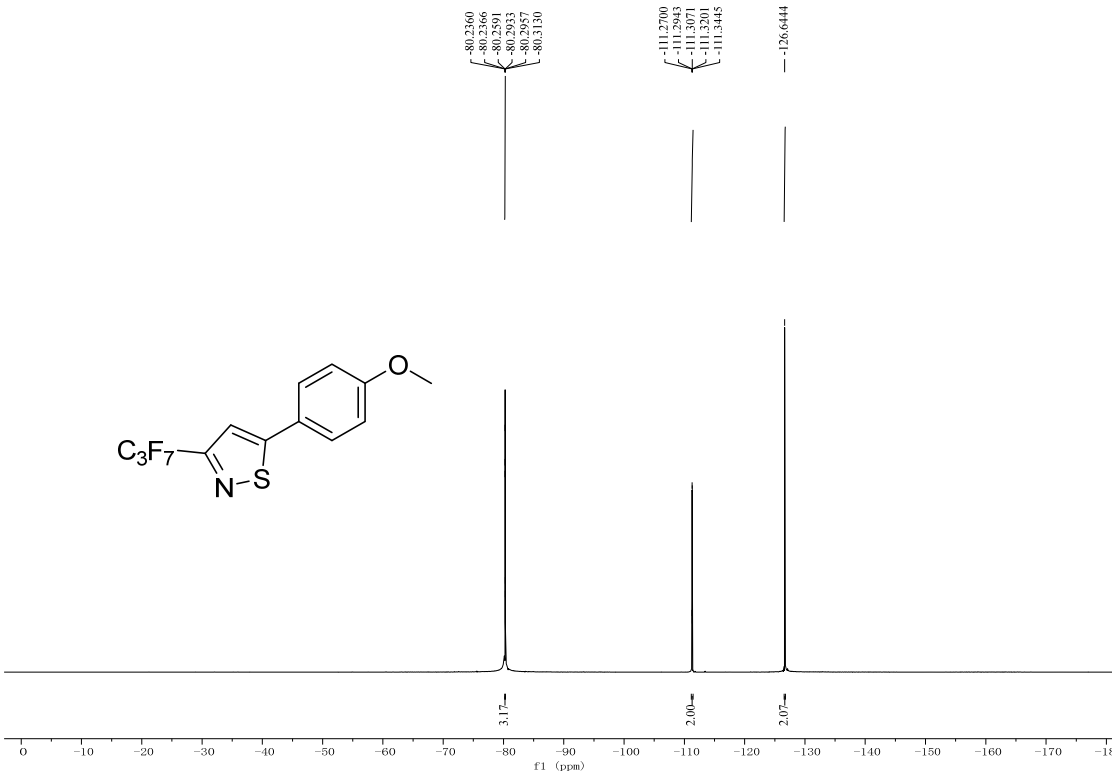
^{1}H NMR (400 MHz, $CDCl_3$) of **2u**:



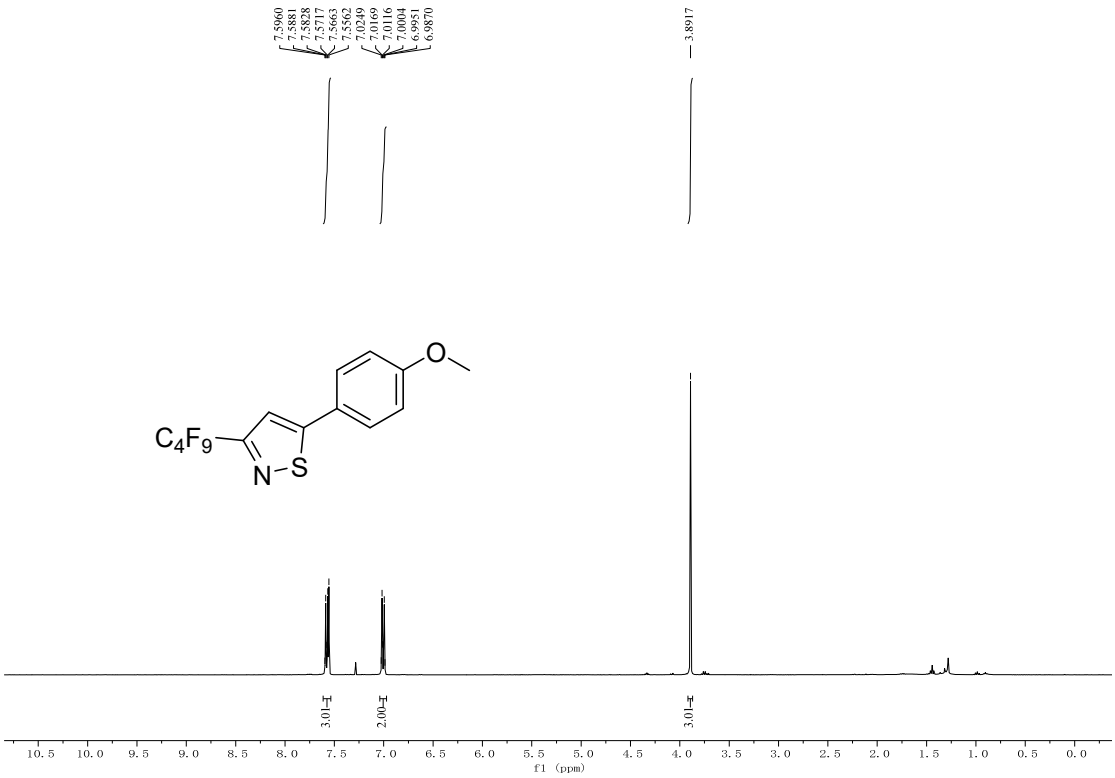
^{13}C NMR (150 MHz, $CDCl_3$) of **2u**:



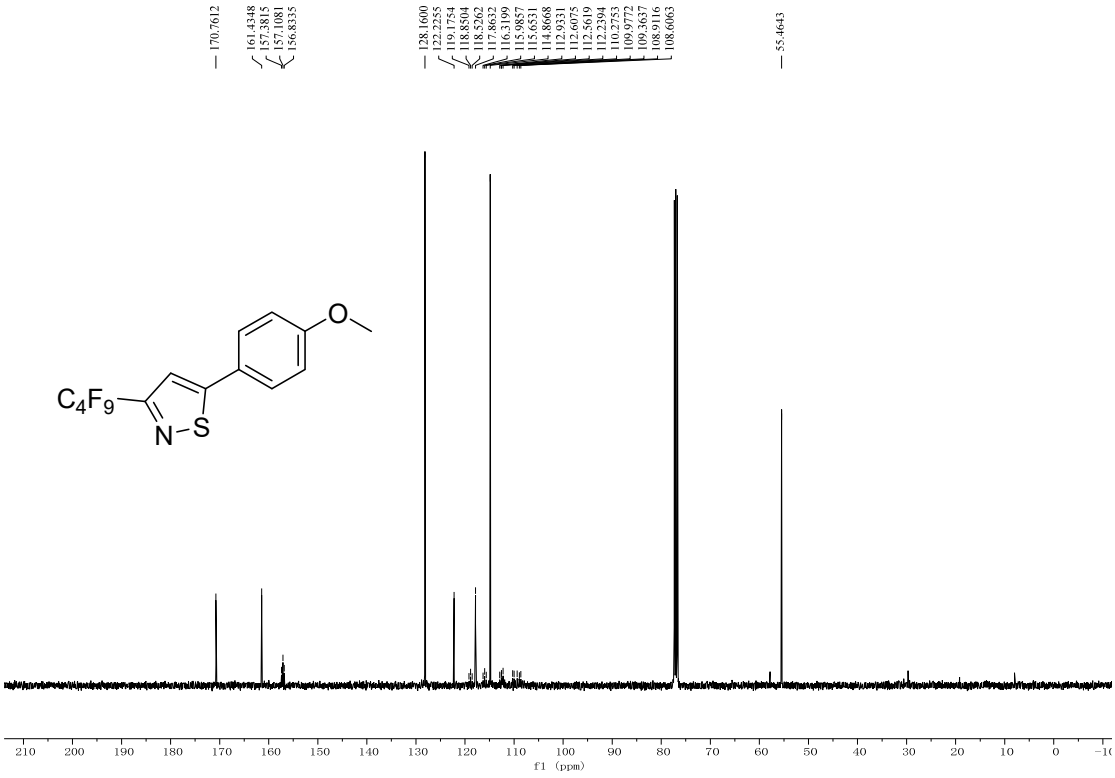
^{19}F NMR (376 MHz, $CDCl_3$) of **2u**:



^{1}H NMR (400 MHz, $CDCl_3$) of **2v**:

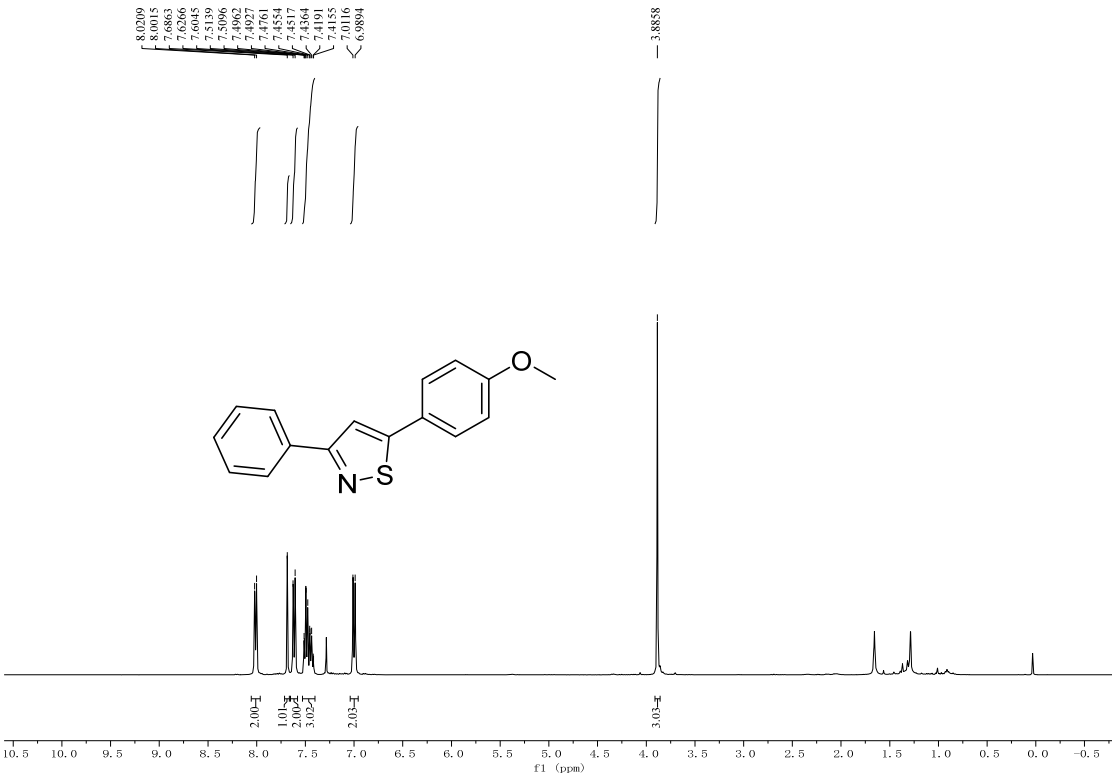


^{13}C NMR (100 MHz, $CDCl_3$) of **2v**:

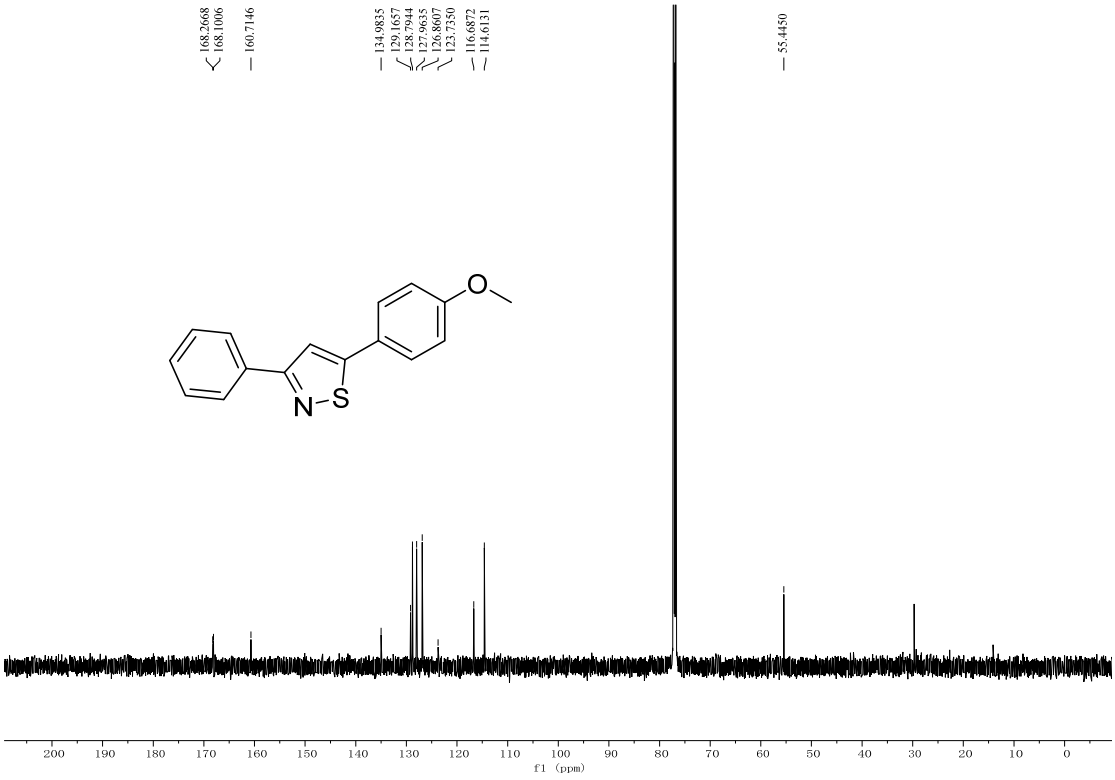


^{19}F NMR (376 MHz, $CDCl_3$) of **2v**:

^{1}H NMR (400 MHz, $CDCl_3$) of **4**:

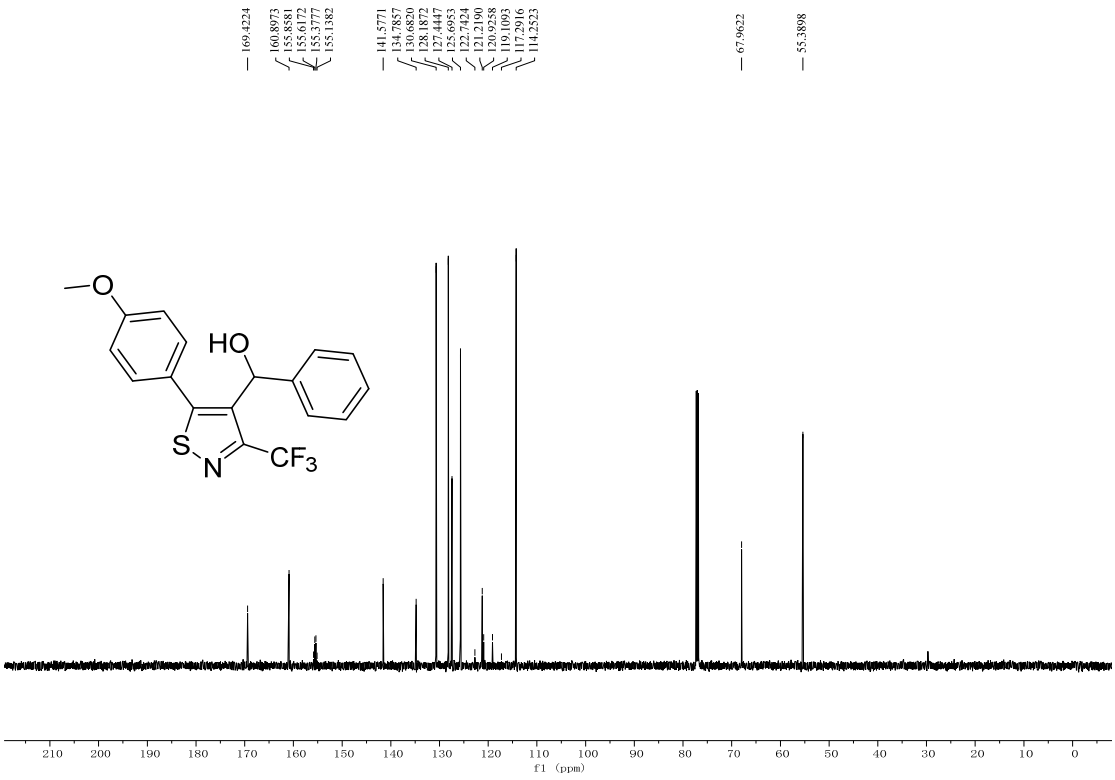


^{13}C NMR (150 MHz, $CDCl_3$) of **4**:

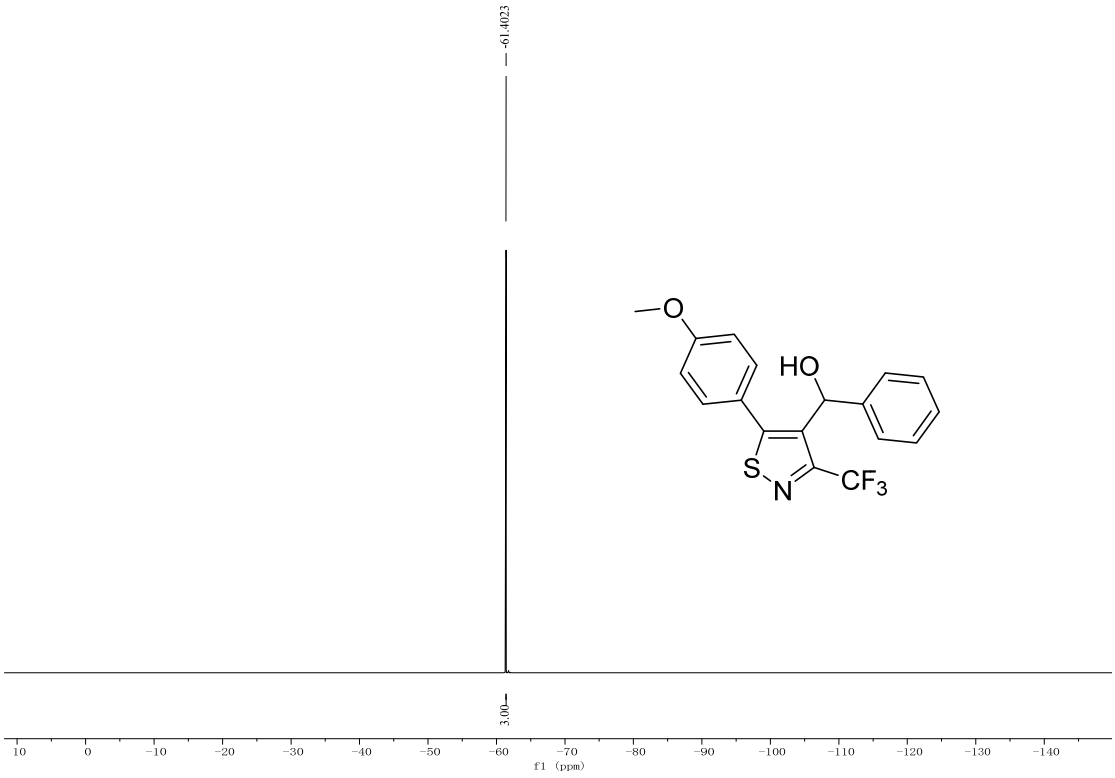


^{1}H NMR (600 MHz, $CDCl_3$) of **5**:

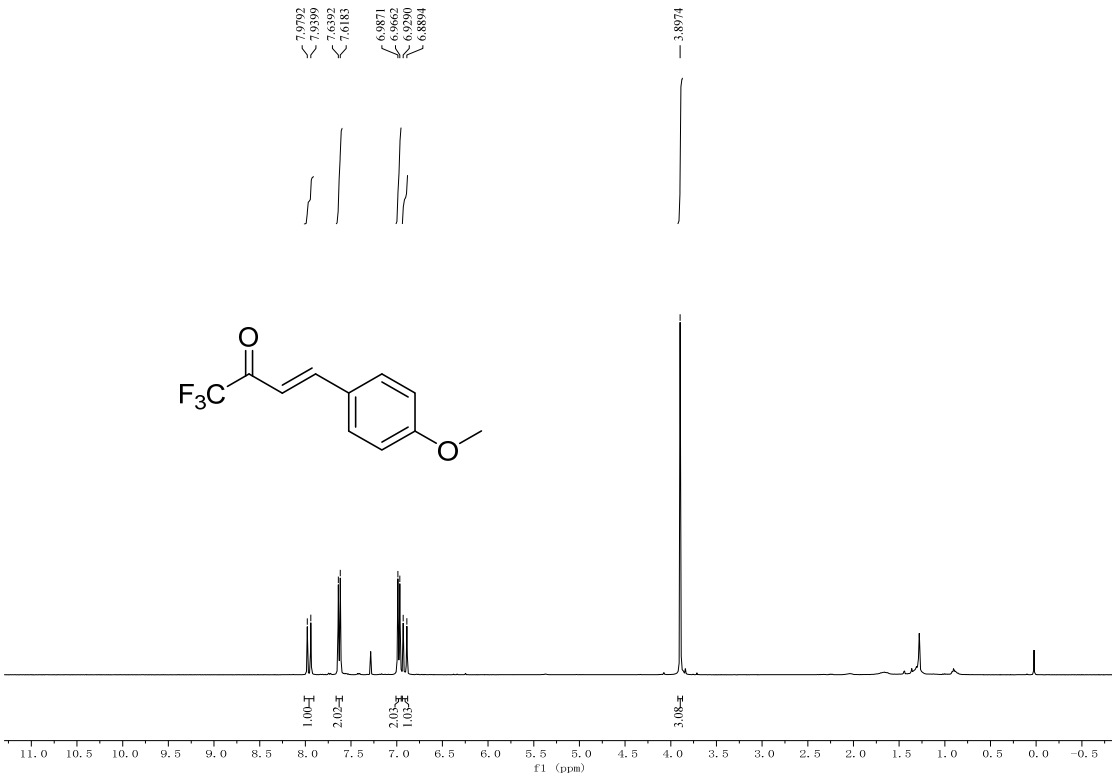
^{13}C NMR (150 MHz, $CDCl_3$) of **5**:



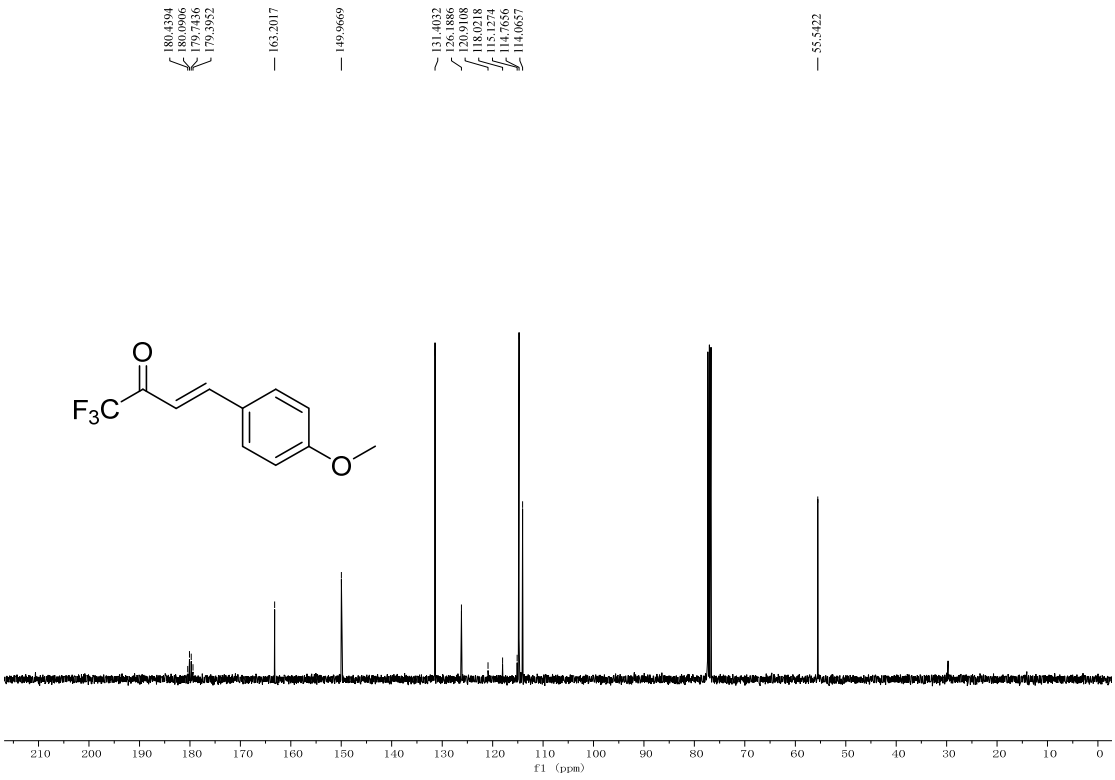
^{19}F NMR (565 MHz, $CDCl_3$) of **5**:



^{1}H NMR (400 MHz, $CDCl_3$) of **6**:



^{13}C NMR (100 MHz, $CDCl_3$) of **6**:



^{19}F NMR (376 MHz, $CDCl_3$) of **6**: