Supporting Information *for*

Synthesis of 4-trifluoromethyl pyridazines *via* annulation of pyridinium ylides with trifluoroacetyl diazoester

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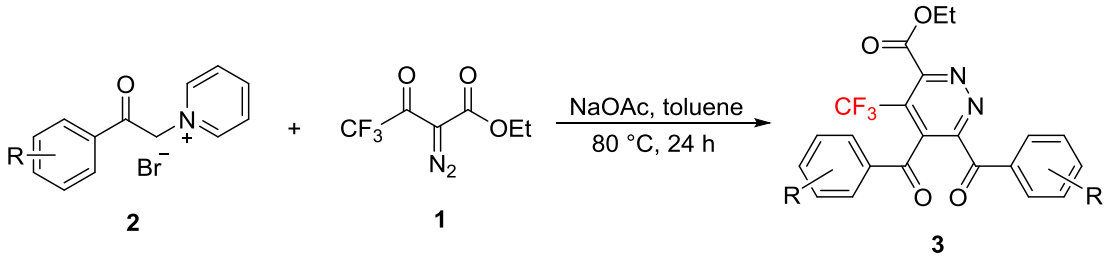
General information

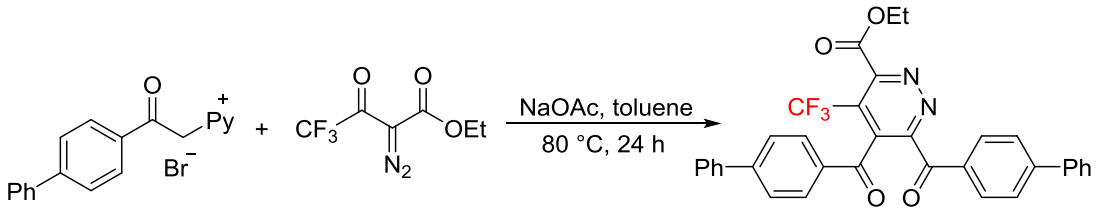
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26), ^{13}C NMR ($CDCl_3$ δ 77.0), ^{1}H NMR (DMSO-d_6 δ 2.50) and ^{13}C NMR (DMSO-d_6 δ 39.50). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate (**1**),[1] ethyl 2-diazo-3-oxobutanoate (**1′**),[2] *N*-(acylmethyl)pyridinium bromides (**2a – 2u**),[3] 2-(2-(4-bromophenyl)-2-oxoethyl)isoquinolin-2-ium bromide (**2s-1**),[4] 2-(4-bromophenyl)-*N*,*N*,*N*-triethyl-2-oxoethan-1-aminium bromide (**2s-2**),[5] and (2-(4-bromophenyl)-2-oxoethyl)dimethylsulfonium bromide (**2s-3**)[6] were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography was performed on silica gel 200–300 mesh obtained from Qingdao Haiyang Chemical.

General procedure of the synthesis of 4-(trifluoromethyl) pyridazines 3a–3u



To an oven-dried 5 mL pressure tube was added *N*-(acylmethyl)pyridinium bromides **2** (0.30 mmol, 1.0 equiv), NaOAc (124.0 mg, 1.50 mmol, 5.0 equiv), ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate **1** (126.0 mg, 0.60 mmol, 3.0 equiv), and toluene (2.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 24 h. The crude mixture was diluted with ethyl acetate (6 mL) and a saturated ammonium chloride solution (4 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting 4-(trifluoromethyl) pyridazine product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

Procedure for gram scale reaction for synthesis of 3c



2c
3.5 g

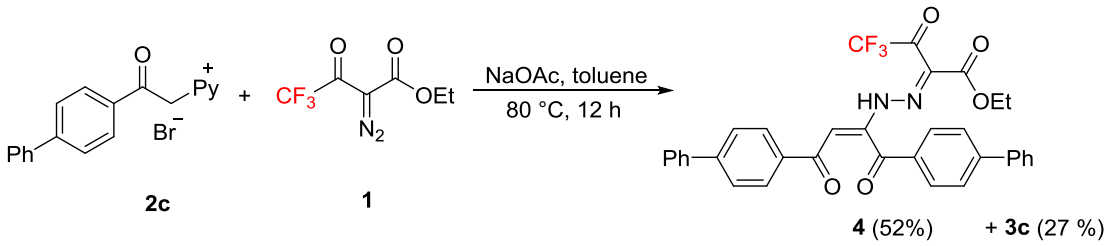
1
4.4 g

3c
2.0 g, 70%

To an oven-dried 100 mL pressure tube was added 1-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)pyridinium bromide **2c** (3.5 g, 10.0 mmol, 1.0 equiv), NaOAc (2.5 g, 30.0 mmol, 5.0 equiv), ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate **1** (4.4 g, 20 mmol, 2.0 equiv), and toluene (30.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 24 h. The crude mixture was diluted with ethyl acetate (50 mL) and a saturated ammonium chloride solution (30 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to give 2.0 g of ethyl 5,6-di([1,1'-biphenyl]-4-carbonyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (**3c**) (70% yield).

Mechanistic studies

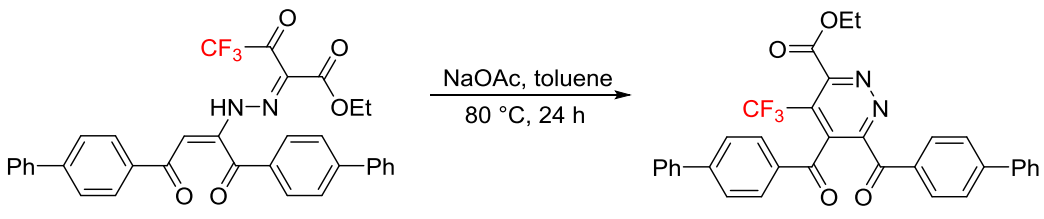
(i) Synthesis of intermediate ethyl-2-(2-(1,4-di([1,1'-biphenyl]-4-yl) -1,4-dioxobut-2-en-2-yl)hydrazineylidene)-4,4,4-trifluoro-3-oxobutanoate (**4**)



2c **1** **4** (52%) + **3c** (27 %)

To an oven-dried 50 mL pressure tube was added 1-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)pyridinium bromide **2c** (212.0 mg, 0.60 mmol, 1.0 equiv), NaOAc (246.0 mg, 3.0 mmol , 5.0 equiv), ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate **1** (252.0 mg, 1.2 mmol, 2.0 equiv), and toluene (10.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 12 h. The crude mixture was diluted with ethyl acetate (25 mL) and a saturated ammonium chloride solution (5 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting trifluoroacetylated hydrazone **4** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

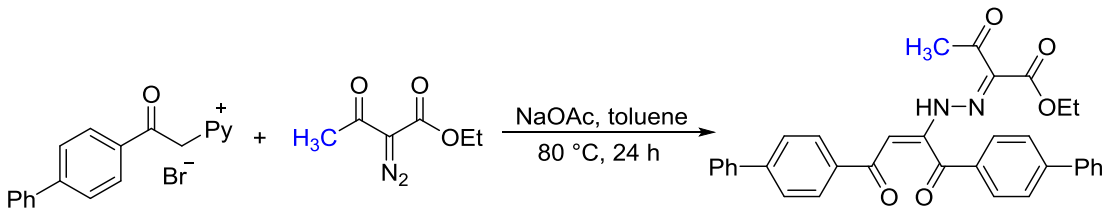
(ii) Intramolecular cyclization of **4**



4 **3c** (87%)

To an oven-dried 5 mL pressure tube was added ethyl (*E*)-2-(2-((*E*)-1,4-di([1,1'-biphenyl]-4-yl)-1,4-dioxobut-2-en-2-yl)hydrazineylidene)-4,4,4-trifluoro-3-oxobutanoate **4** (30.0 mg, 0.05 mmol, 1.0 equiv), NaOAc (21.0 mg, 0.25 mmol , 5.0 equiv), and toluene (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 24 h. The crude mixture was diluted with ethyl acetate (10 mL) and a saturated ammonium chloride solution (5 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to give 25.0 mg of **3c** (87% yield).

(iii) Synthesis of ethyl -2-(2-(1,4-dioxo-1,4-diphenylbut-2-en-2-yl)hydrazineylidene)-3-oxobutanoate (**4′**)

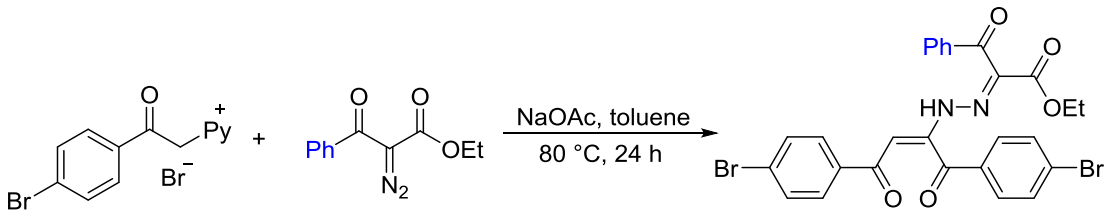


2c **1'** **4'** (40%)

To an oven-dried 50 mL pressure tube was added 1-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)pyridinium bromide **2c** (212.0 mg, 0.60 mmol, 1.0 equiv), NaOAc (246.0 mg, 3.0 mmol, 5.0 equiv), ethyl 2-diazo-3-oxobutanoate **1′** (187.0 mg, 1.2 mmol, 2.0 equiv), and toluene (10.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 24 h. The crude mixture was diluted with ethyl acetate (25 mL) and a saturated ammonium chloride solution (5 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting

intermediate **4′** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

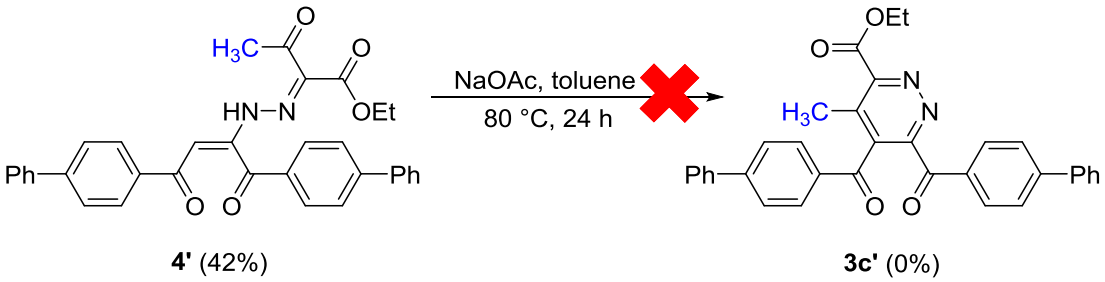
(iv) Synthesis of ethyl (*E*)-2-(2-((*E*)-1,4-bis(4-bromophenyl)-1,4-dioxobut-2-en-2-yl)hydrazineylidene)-3-oxo-3-phenylpropanoate (**4″**)



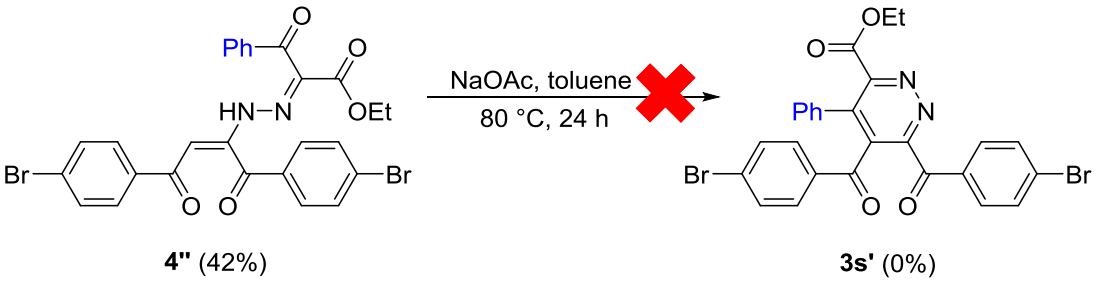
2s **1"** **4"**(81%)

To an oven-dried 50 mL pressure tube was added 1-(2-(4-bromophenyl)-2-oxoethyl)pyridin-1-ium **2s** (355 mg, 1.0 mmol, 1.0 equiv), NaOAc (410.0 mg, 5.0 mmol, 5.0 equiv), ethyl 2-diazo-3-oxo-3-phenylpropanoate **1″** (440.0 mg, 2.0 mmol, 2.0 equiv), and toluene (10.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 24 h. The crude mixture was diluted with ethyl acetate (25 mL) and a saturated ammonium chloride solution (5 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting intermediate **4″** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

(v) Intramolecular cyclization of **4′** or **4″**



4' (42%) **3c'** (0%)

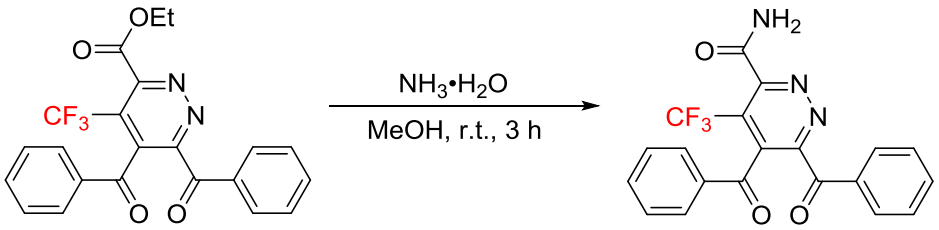


4" (42%) **3s'** (0%)

To an oven-dried 5 mL pressure tube was added **4′** (11.0 mg, 0.20 mmol, 1.0 equiv) or **4″** (12.0 mg, 0.20 mmol, 1.0 equiv), NaOAc (8.0 mg, 1.0 mmol, 5.0 equiv), and toluene (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 80 °C for 24 h. The ^{1}H-NMR indicated no formation of **3c′** or **3s′**.

Synthetic transformation of 3

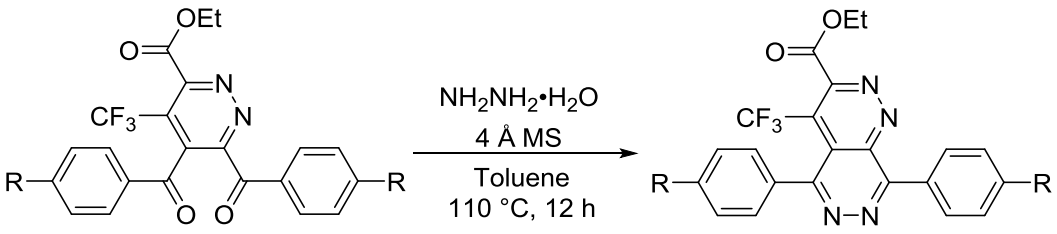
(i) Transformation of **3a** to amide-derivative **5a**



3a **5a** (94%)

To an oven-dried 25 mL pressure tube was added ethyl 5,6-dibenzoyl-4-(trifluoromethyl)pyridazine-3-carboxylate **3a** (43.0 mg, 0.10 mmol, 1.0 equiv), aquous ammonia (14.8 M, 0.14 mL, 1.0 mmol, 10.0 equiv), and MeOH (10.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at room temperature for 3 h. The crude mixture was diluted with ethyl acetate (25 mL) and a saturated ammonium chloride solution (5 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting **5a** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

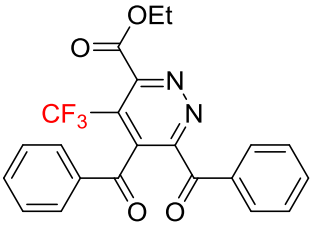
(ii) General procedure of the synthesis of 4-(trifluoromethyl)pyridazino[4,5-*c*]pyridazines **6**



3 **6**

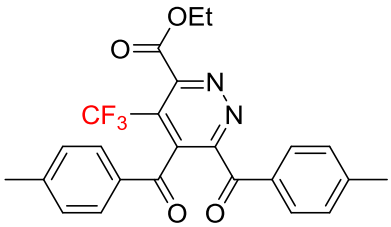
To an oven-dried 5 mL pressure tube was added 4-(trifluoromethyl) pyridazine **3** (0.10 mmol, 1.0 equiv), spherical 4 Å molecular sieve (50 mg), a 85% hydrazine hydrate solution (12 mg, 0.20 mmol, 2.0 equiv), and toluene (2.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 110 °C for 12 h. The crude mixture was diluted with ethyl acetate (6 mL) and a saturated ammonium chloride solution (3 mL). The organic phase was extracted and dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The resulting 4-(trifluoromethyl)pyridazino[4,5-*c*]pyridazine **6** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.

Data for compounds



ethyl 5,6-dibenzoyl-4-(trifluoromethyl)pyridazine-3-carboxylate (3a)

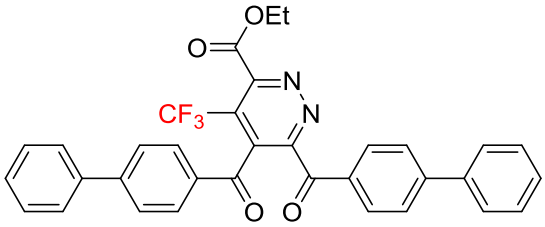
Obtained as a yellow solid in 71% yield (64 mg). Mp: 150–152 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.69 – 7.59 (m, 2H), 7.55 – 7.45 (m, 4H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 189.9, 163.0, 157.2, 151.5 (q, *J* = 1.8 Hz), 138.1 (q, *J* = 2.0 Hz), 135.6, 134.8, 134.7, 134.4, 131.3, 129.3, 129.0, 128.6, 125.5 (q, *J* = 35.5 Hz), 121.3 (q, *J* = 278.3 Hz), 64.0, 13.9. IR (ATR): ν 3063, 2986, 1744, 1671, 1597, 1582, 1519, 1450, 1380, 1360, 1296, 1264, 1224, 1154, 1124, 1098, 1073, 1012, 1001, 984, 956, 934, 878, 861, 842, 817, 756, 729, 708, 686, 675, 632, 615, 588, 537, 492, 456, 423 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{16}F_3N_2O_4$ $[M + H]^+$: 429.1057; found: 429.1057.



ethyl 5,6-bis(4-methylbenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3b)

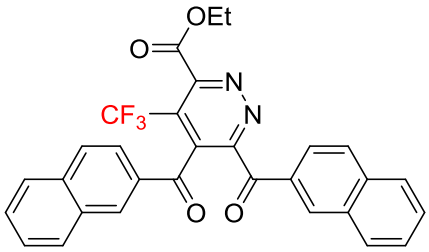
Obtained as a white solid in 72% yield (49 mg). Mp: 176–178 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.23 (m, 4H), 4.63 (q, *J* = 7.3 Hz, 2H), 2.46 (s, 6H), 1.51 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (s, 3F). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 189.6, 189.4, 163.2, 157.7, 151.4, 146.1, 138.1, 133.3, 132.0, 131.5, 129.7, 129.5, 129.4, 128.5, 125.3 (q, *J* = 35.4 Hz), 121.3 (q, *J* = 278.2 Hz), 63.9, 21.9, 13.9. IR (ATR): ν 2959, 2926, 2855, 1747, 1670, 1605, 1572, 1494, 1464, 1409, 1380, 1362, 1297, 1266, 1231, 1211, 1182, 1161, 1124, 1096, 1081, 1019, 960, 881, 849, 820, 754, 745, 700, 610, 587, 527, 496, 460, 429, 421 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{24}H_{20}F_3N_2O_4$ $[M + H]^+$: 457.1370; found: 457.1369.



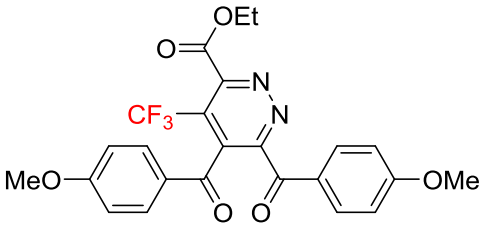
Ethyl 5,6-di([1,1'-biphenyl]-4-carbonyl)-4-(trifluoromethyl)pyridazine-3-carboxy late (3c)

Obtained as a yellow solid in 81% yield (70 mg). Mp: 196–198 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.60. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.70 (m, 4H), 7.69 – 7.60 (m, 4H), 7.58 – 7.36 (m, 6H), 4.66 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 189.4, 163.1, 157.4, 151.5 (q, *J* = 1.6 Hz), 147.5, 139.5, 139.4, 138.1 (q, *J* = 2.1 Hz), 134.4, 133.1, 132.0, 129.9, 129.0, 128.7 (d, *J* = 2.0 Hz), 127.6, 127.4, 127.3, 125.5 (q, *J* = 35.5 Hz), 121.3 (q, *J* = 277.7 Hz), 64.0, 13.9. IR (ATR): ν 3034, 2983, 1747, 1681, 1668, 1602, 1559, 1518, 1486, 1465, 1449, 1407, 1382, 1359, 1314, 1293, 1265, 1233, 1177, 1157, 1124, 1078, 1007, 955, 918, 881, 859, 749, 733, 696, 659, 627, 590, 485 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{34}H_{24}F_3N_2O_4$ $[M + H]^+$: 581.1683; found: 581.1685.



ethyl 5,6-di(2-naphthoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3d)

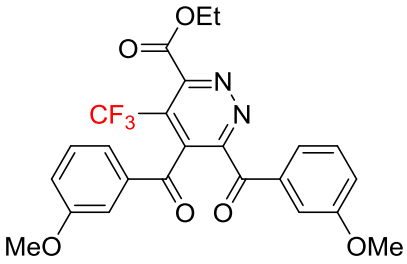
Obtained as a yellow solid in 85% yield (67 mg). Mp: 194–196 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.20 (s, 1H), 8.03 – 7.93 (m, 4H), 7.92 – 7.84 (m, 4H), 7.70 – 7.51 (m, 4H), 4.67 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 189.7, 163.2, 157.7, 151.6, 138.3 (q, *J* = 2.0 Hz), 136.3, 136.2, 135.1, 133.1, 132.4, 132.2, 132.1, 131.7, 130.2, 129.9, 129.6, 129.5, 129.2, 128.7, 128.0, 127.8, 127.3, 127.1, 125.6 (q, *J* = 35.5 Hz), 125.0, 123.6, 121.4 (q, *J* = 278.3 Hz), 64.0, 14.0. IR (ATR): ν 3059, 2984, 1747, 1662, 1625, 1595, 1574, 1507, 1467, 1437, 1384, 1277, 1253, 1219, 1193, 1155, 1134, 1109, 1018, 975, 935, 914, 865, 847, 824, 789, 775, 759, 738, 701, 603, 584, 475 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{30}H_{20}F_3N_2O_4$ $[M + H]^+$: 529.1370; found: 529.1372.



ethyl 5,6-bis(4-methoxybenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3e)

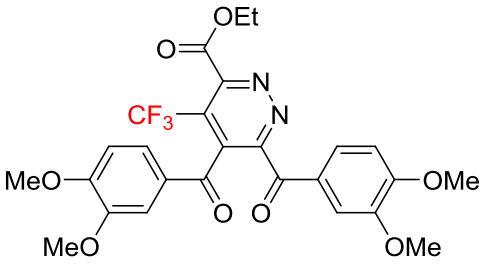
Obtained as a yellow solid in 63% yield (47 mg). Mp: 152–154 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.00 – 6.92 (m, 4H), 4.62 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 188.1, 165.0, 164.8, 163.2, 157.9, 151.3,

138.0, 133.9, 131.9, 128.9, 127.5, 125.1 (q, J = 35.3 Hz), 121.3 (q, J = 276.9 Hz), 114.3, 114.0, 63.9, 55.7, 55.6, 13.9. IR (ATR): ν 2982, 2938, 2843, 1745, 1662, 1594, 1573, 1511, 1463, 1444, 1424, 1402, 1381, 1360, 1317, 1250, 1234, 1166, 1123, 1023, 983, 956, 880, 847, 810, 785, 766, 740, 702, 642, 608, 515, 477, 448, 424, 410 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{24}H_{20}F_3N_2O_6$ $[M + H]^+$: 489.1268; found: 489.1269.



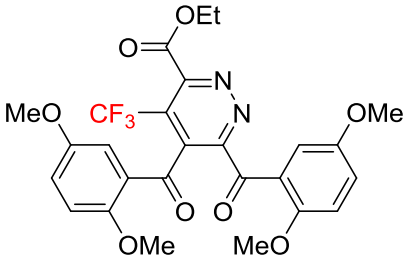
ethyl 5,6-bis(3-methoxybenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3f)

Obtained as a yellow solid in 58% yield (43 mg). Mp: 152–154 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.94 (d, J = 8.5 Hz, 1H), 4.59 (q, J = 7.1 Hz, 2H), 3.68 (s, 3H), 3.55 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 188.0, 163.6, 159.6, 159.5, 156.1, 151.3, 140.0, 136.5, 135.1, 131.3, 130.4, 125.9, 124.9, 123.0 (q, J = 35.8 Hz), 121.8 (q, J = 277.2 Hz), 121.3, 120.8, 112.1, 112.0, 63.5, 55.9, 55.5, 13.9. IR (ATR): ν 2927, 2843, 1746, 1670, 1598, 1582, 1519, 1485, 1466, 1450, 1438, 1402, 1380, 1359, 1282, 1248, 1221, 1159, 1132, 1047, 1017, 987, 958, 879, 861, 841, 796, 754, 729, 709, 687, 671, 651, 588, 535, 523, 495, 442, 427, 414 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{24}H_{20}F_3N_2O_6$ $[M + H]^+$: 489.1268; found: 489.1267.



ethyl 5,6-bis(3,4-dimethoxybenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3g)

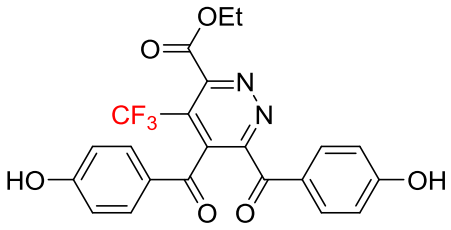
Obtained as a yellow solid in 52% yield (43 mg). Mp: 170–172 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 1H), 7.56 (s, 1H), 7.51 (s, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 4.63 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 3.96 (s, 3H), 3.95 (s, 3H), 3.91 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 188.1, 163.2, 157.9, 155.1, 154.9, 151.3 (q, *J* = 1.6 Hz), 149.5, 149.3, 137.9, 129.0, 128.2, 127.6, 126.1, 125.2 (q, *J* = 35.4 Hz), 121.3 (q, *J* = 277.7 Hz), 111.8, 110.2, 110.1, 109.8, 63.9, 56.3, 56.2, 56.1, 13.9. IR (ATR): ν 2938, 2842, 1745, 1655, 1583, 1512, 1463, 1421, 1382, 1353, 1265, 1243, 1210, 1146, 1116, 1036, 1017, 995, 918, 863, 843, 815, 789, 766, 734, 702, 675, 643, 592, 537, 482, 450, 431 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{26}H_{24}F_3N_2O_8$ $[M + H]^+$: 549.1479; found: 549.1480.



ethyl 5,6-bis(2,5-dimethoxybenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3h)

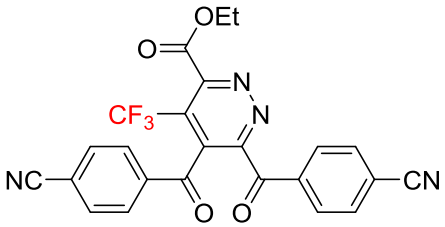
Obtained as a yellow solid in 50% yield (41 mg). Mp: 171–173 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.22 –

7.01 (m, 3H), 6.88 (t, *J* = 9.9 Hz, 2H), 4.58 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H), 3.59 (s, 3H), 3.48 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 187.8, 163.6, 156.2, 154.3, 154.2, 153.9, 153.6, 151.3 (q, *J* = 1.8 Hz), 139.7 (q, *J* = 2.3 Hz), 126.0, 124.9, 124.3, 123.1 (q, *J* = 35.5 Hz), 122.4, 121.7 (q, *J* = 276.5 Hz), 114.1, 113.8, 113.6, 112.0, 63.6, 56.5, 55.9, 55.8, 55.8, 13.9. IR (ATR): ν 2956, 2920, 2852, 2158, 2026, 1973, 1747, 1611, 1582, 1497, 1462, 1419, 1378, 1277, 1227, 1205, 1159, 1106, 1042, 1017, 913, 865, 819, 729, 668 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{26}H_{24}F_3N_2O_8$ $[M + H]^+$: 549.1479; found: 549.1480.



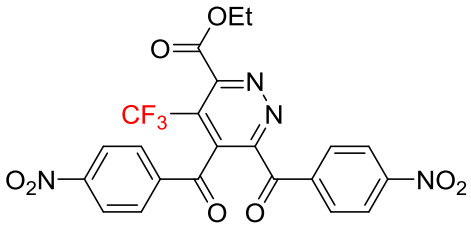
ethyl 5,6-bis(4-hydroxybenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3i)

Obtained as a yellow solid in 67% yield (49 mg). Mp: 152–154 °C. R_f (petroleum ether : ethyl acetate = 3 : 1) = 0.35. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (br s, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.6, 188.2, 164.3, 164.2, 163.7, 157.7, 151.3 (q, *J* = 2.0 Hz), 137.6 (q, *J* = 2.4 Hz), 134.4, 132.9, 127.0, 126.3, 125.3 (q, *J* = 35.4 Hz), 121.8 (q, *J* = 277.4 Hz), 116.0, 115.4, 64.0, 14.2. IR (ATR): ν 3367, 2254, 2188, 1655, 1599, 1455, 1381, 1236, 1170, 1048, 1023, 995, 823, 761, 611, 579, 533, 514, 490, 448 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{15}F_3N_2O_6Na$ $[M + Na]^+$: 483.0774; found: 483.0775.



ethyl 5,6-bis(4-cyanobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3j)

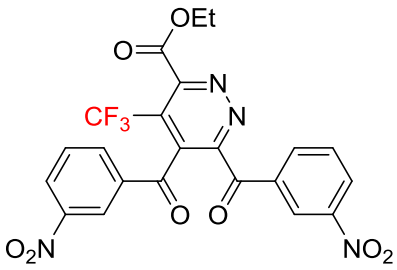
Obtained as a white solid in 80% yield (57 mg). Mp: 180–182 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 2H), 7.97 – 7.76 (m, 6H), 4.64 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 162.5, 155.8, 151.9, 138.3, 137.7, 137.1, 132.9, 132.4, 131.7, 129.3, 125.7 (q, J = 35.7 Hz), 120.9 (q, J = 277.9 Hz), 118.0, 117.9, 117.5, 117.4, 64.3, 13.9. IR (ATR): ν 2986, 2925, 2232, 1746, 1678, 1613, 1582, 1534, 1478, 1442, 1407, 1380, 1350, 1294, 1245, 1223, 1159, 1133, 1094, 1017, 989, 976, 905, 879, 858, 837, 817, 768, 736, 718, 696, 675, 650, 590, 545, 487, 432, 416, 404 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{24}H_{14}O_4N_4F_3$ $[M + H]^+$: 479.0962; found: 479.0963.



ethyl 5,6-bis(4-nitrobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3k)

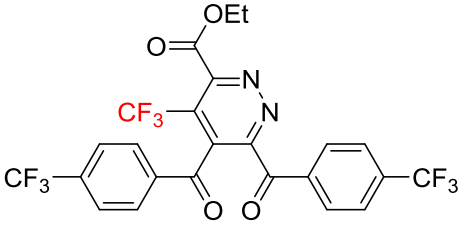
Obtained as a yellow solid in 78% yield (59 mg). Mp: 168–170 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.9 Hz, 2H), 8.38 (d, J = 8.9 Hz, 2H), 8.27 (d, J = 9.0 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 4.66 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 188.4, 162.4, 155.7, 151.9 (q, J = 2.0 Hz), 151.1, 139.7 (q, J = 1.5 Hz), 138.5, 137.7 (q, J = 2.1 Hz), 132.5, 130.0, 125.7 (q, J = 35.7 Hz), 124.4, 123.7, 120.9 (q, J = 277.9 Hz), 64.4, 13.9. IR (ATR): ν 2987, 2926,

2233, 1746, 1678, 1613, 1533, 1478, 1442, 1408, 1380, 1349, 1293, 1245, 1222, 1158, 1133, 1094, 1018, 1001, 990, 975, 905, 879, 857, 816, 768, 735, 718, 696, 675, 650, 589, 545, 489, 437, 417 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{13}F_3N_4O_8$ Na [M + Na]$^+$: 541.0578; found: 541.0582.



ethyl 5,6-bis(3-nitrobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3l)

Obtained as a yellow solid in 75% yield (58 mg). Mp: 165–167 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.62 (s, 1H), 8.57 (d, *J* = 8.2 Hz, 2H), 8.45 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.85 – 7.73 (m, 2H), 4.66 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 162.4, 155.8, 153.1, 152.0, 148.7, 148.3, 137.6 (q, *J* = 2.0 Hz), 136.9 (q, *J* = 1.2 Hz), 136.8, 135.2, 134.3, 130.5, 130.0, 129.0, 128.9, 126.2, 125.8 (q, *J* = 35.4 Hz), 123.5, 121.0 (q, *J* = 278.0 Hz), 64.4, 13.9. IR (ATR): ν 3068, 2966, 2906, 1748, 1676, 1582, 1556, 1516, 1492, 1466, 1383, 1272, 1259, 1238, 1217, 1162, 1137, 1121, 1095, 1082, 1032, 972, 894, 863, 846, 825, 787, 761, 731, 704, 677, 595, 564, 527, 486, 453, 435, 421, 411 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}F_3N_4O_8$ [M + H]$^+$: 519.0758; found: 519.0759.

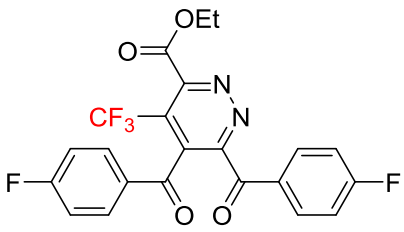


ethyl

4-(trifluoromethyl)-5,6-bis(4-(trifluoromethyl)benzoyl)pyridazine-3-carboxylate

(3m)

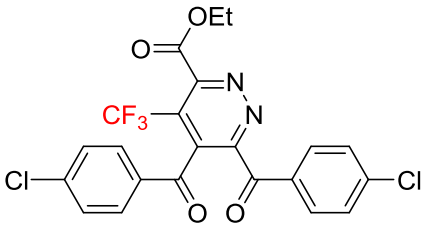
Obtained as a white solid in 73% yield (62 mg). Mp: 162–162 °C. R_f (petroleum ether : ethyl acetate = 8 : 1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.30 (m, 4H), 4.63 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (s, 3F), -57.5 (s, 3F), -57.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 188.3, 162.8, 156.7, 153.9 (q, *J* = 1.6 Hz), 153.7 (q, *J* = 1.6 Hz), 151.6 (q, *J* = 1.9 Hz), 137.8 (q, *J* = 1.9 Hz), 133.7, 133.6, 132.2, 131.3, 125.5 (q, *J* = 35.5 Hz), 120.8 (q, *J* = 278.3 Hz), 120.5, 120.2, 120.2 (q, *J* = 258.3 Hz), 120.1 (q, *J* = 258.3 Hz), 64.1, 13.9. IR (ATR): ν 2988, 1747, 1676, 1602, 1506, 1468, 1414, 1382, 1361, 1303, 1246, 1208, 1155, 1124, 1016, 985, 959, 927, 879, 860, 816, 766, 747, 702, 661, 588, 509, 481, 432 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{24}H_{14}F_9N_2O_4$ $[M + H]^+$: 567.0961; found: 567.0958.



ethyl 5,6-bis(4-fluorobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3n)

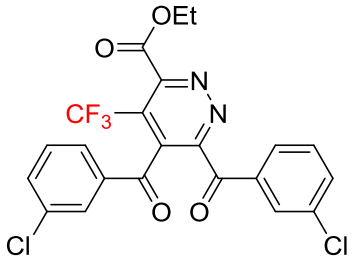
Obtained as a yellow solid in 64% yield (45 mg). Mp: 165–167 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (t, *J* = 6.7 Hz, 2H), 7.80 (t, *J* = 6.7 Hz, 2H), 7.27 – 7.14 (m, 4H), 4.63 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (s, 3F), -100.9 – -101.0 (m, 1F), -101.0 – -101.1 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 188.2, 166.8 (d, *J* = 259.3 Hz), 166.6 (d, *J* = 258.4 Hz), 162.9, 157.0, 151.5 (q, *J* = 2.1 Hz), 137.9 (q, *J* = 2.1 Hz), 134.4 (d, *J* = 10.0 Hz), 132.2, 132.0 (d, *J* = 10.0 Hz), 130.7 (d, *J* = 2.9 Hz), 125.5 (q, *J* = 35.6 Hz), 121.2 (q, *J* = 277.2 Hz), 116.4 (d, *J* = 22.3 Hz), 116.1 (d, *J* =

22.3 Hz), 64.1, 13.9. IR (ATR): ν 2961, 2926, 1746, 1671, 1596, 1507, 1467, 1448, 1414, 1381, 1360, 1299, 1263, 1225, 1153, 1124, 1099, 1082, 1013, 985, 959, 881, 852, 820, 793, 742, 713, 699, 632, 619, 607, 587, 507, 480, 451 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}F_5N_2O_4$ $[M + H]^+$: 465.0868; found: 465.0868.



ethyl 5,6-bis(4-chlorobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3o)

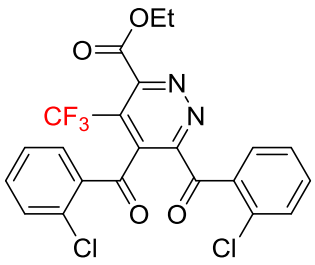
Obtained as a yellow solid in 81% yield (60 mg). Mp: 170–172 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.45 (m, 4H), 4.63 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 188.6, 162.8, 156.8, 151.6, 141.8, 141.6, 137.8 (q, *J* = 2.2 Hz), 134.0 (q, *J* = 1.4 Hz), 132.7, 132.5, 130.5, 129.5, 129.1, 125.4 (q, *J* = 35.2 Hz), 121.1 (q, *J* = 277.7 Hz), 64.1, 13.9. IR (ATR): ν 2985, 1746, 1670, 1586, 1520, 1488, 1466, 1403, 1380, 1359, 1248, 1223, 1157, 1123, 1091, 1013, 985, 958, 878, 844, 800, 758, 737, 716, 703, 691, 656, 625, 586, 556, 526, 496, 476, 404 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Cl_2F_3N_2O_4$ $[M + H]^+$: 497.0277; found: 497.0276.



ethyl 5,6-bis(3-chlorobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3p)

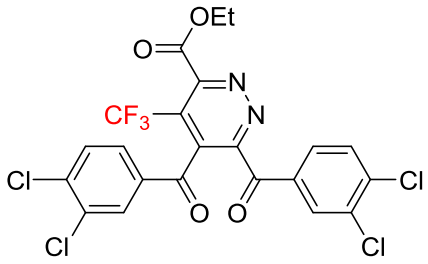
Obtained as a yellow solid in 82% yield (60 mg). Mp: 170–172 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.93

(d, *J* = 7.8 Hz, 1H), 7.81 (s, 1H), 7.69 – 7.60 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.64 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 188.6, 162.8, 156.5, 151.7, 137.7 (q, *J* = 2.2 Hz), 137.0 (q, *J* = 2.2 Hz), 135.7, 135.6, 135.0, 134.8, 131.0, 130.3, 130.0, 129.6, 128.7, 127.5, 125.7 (q, *J* = 35.6 Hz), 121.1 (q, *J* = 277.8 Hz), 64.1, 13.9. IR (ATR): ν 2986, 1746, 1674, 1591, 1571, 1519, 1470, 1428, 1381, 1359, 1280, 1243, 1219, 1159, 1129, 1095, 1076, 1016, 997, 969, 891, 862, 802, 778, 751, 734, 718, 700, 674, 656, 633, 591, 542, 505, 470, 448, 419 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Cl_2F_3N_2O_4$ $[M + H]^+$: 497.0277; found: 497.0276.



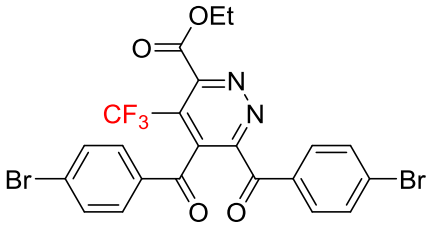
ethyl 5,6-bis(2-chlorobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3q)

Obtained as a yellow solid in 79% yield (59 mg). Mp: 166–168 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.12 (s, 1H), 7.62 – 7.50 (m, 4H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 187.9, 162.9, 154.8, 152.0 (q, *J* = 25.1 Hz), 135.6, 135.1, 134.3, 133.3, 133.0, 132.3, 131.5, 131.1, 130.4, 127.4, 126.9, 124.6 (q, *J* = 35.8 Hz), 121.3 (q, *J* = 277.8 Hz), 63.9, 13.9. IR (ATR): ν 2984, 2964, 1673, 1584, 1556, 1522, 1466, 1436, 1382, 1358, 1259, 1237, 1216, 1158, 1128, 1095, 1060, 1031, 1015, 972, 962, 893, 880, 861, 818, 802, 779, 736, 703, 677, 650, 637, 593, 564, 547, 520, 474, 452, 435 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Cl_2F_3N_2O_4$ $[M + H]^+$: 497.0277; found: 497.0278.



ethyl 5,6-bis(3,4-dichlorobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3r)

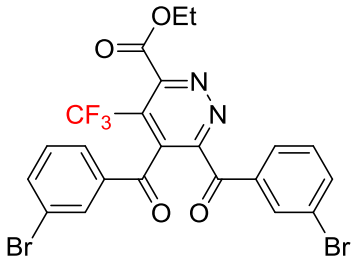
Obtained as a yellow solid in 61% yield (51 mg). Mp: 174–176 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.95 – 7.86 (m, 2H), 7.62 (dt, *J* = 8.4, 2.1 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 1H), 4.64 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 187.6, 162.6, 156.2, 151.8 (q, *J* = 1.8 Hz), 140.0, 139.8, 137.5 (q, *J* = 2.0 Hz), 135.1, 134.2, 133.6, 133.5, 133.1, 131.3, 130.9, 130.5, 130.4, 128.0, 125.7 (q, *J* = 35.6 Hz), 121.0 (q, *J* = 277.7 Hz), 64.2, 13.9. IR (ATR): ν 2966, 2158, 2029, 1748, 1676, 1582, 1556, 1516, 1492, 1466, 1383, 1272, 1258, 1238, 1162, 1137, 1121, 1095, 1082, 1031, 972, 894, 863, 846, 825, 786, 761, 731, 704, 676, 595, 578, 564, 526, 486, 474, 453, 435, 421, 411, 403 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{12}Cl_4F_3N_2O_4$ $[M + H]^+$: 564.9498; found: 564.9500.



ethyl 5,6-bis(4-bromobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3s)

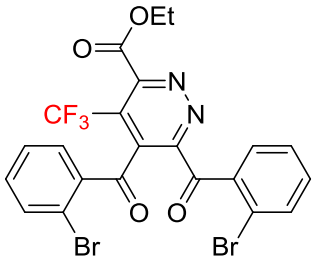
Obtained as a yellow solid in 93% yield (78 mg). Mp: 155–157 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.72 – 7.64 (m, 4H), 7.62 (d, *J* = 8.1 Hz, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 188.8, 162.8, 156.7, 151.6 (q, *J* = 2.1 Hz), 137.8 (q, *J* = 2.1 Hz),

134.4 (q, *J* = 1.2 Hz), 132.9, 132.7, 132.5, 132.1, 130.7, 130.5, 130.4, 125.5 (q, *J* = 35.7 Hz), 121.0 (q, *J* = 276.8 Hz), 64.1, 13.9. IR (ATR): ν 2985, 1745, 1670, 1584, 1519, 1484, 1446, 1399, 1383, 1359, 1295, 1247, 1221, 1155, 1123, 1069, 1011, 984, 957, 977, 841, 796, 756, 737, 703, 683, 654, 634, 623, 587, 545, 495, 475, 456 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Br_2F_3N_2O_4$ $[M + H]^+$: 584.9267; found: 584.9271.



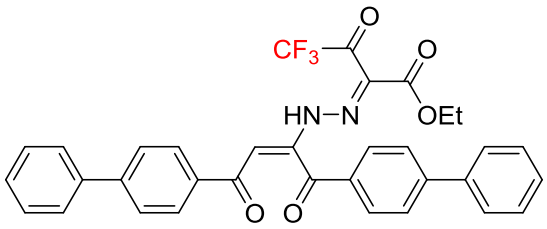
ethyl 5,6-bis(3-bromobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3t)

Obtained as a yellow solid in 89% yield (78 mg). Mp: 154–156 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.01 – 7.91 (m, 2H), 7.81 (t, *J* = 6.9 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 4.64 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 188.5, 162.8, 156.4, 151.7 (q, *J* = 2.1 Hz), 137.7 (q, *J* = 2.1 Hz), 137.2 (q, *J* = 2.1 Hz), 135.9, 133.9, 131.6, 130.6, 130.2, 130.0, 127.9, 125.6 (q, *J* = 35.4 Hz), 123.5, 122.9, 121.0 (q, *J* = 277.2 Hz), 64.1, 13.9. IR (ATR): ν 2984, 1746, 1671, 1589, 1566, 1519, 1470, 1446, 1424, 1380, 1360, 1279, 1241, 1215, 1155, 1127, 1095, 1068, 1014, 998, 966, 886, 861, 842, 799, 772, 732, 696, 672, 646, 632, 590, 541, 486, 463, 428 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Br_2F_3N_2O_4$ $[M + H]^+$: 584.9267; found: 584.9268.



ethyl 5,6-bis(2-bromobenzoyl)-4-(trifluoromethyl)pyridazine-3-carboxylate (3u)

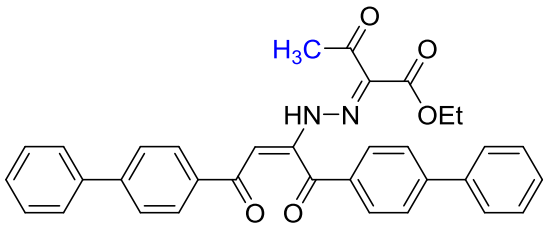
Obtained as a yellow solid in 95% yield (81 mg). Mp: 151–153 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.63 (m, 1H), 7.55 – 7.46 (m, 3H), 7.46 – 7.37 (m, 2H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 188.5, 162.9, 154.8, 151.8 (q, *J* = 1.8 Hz), 138.8, 137.5, 135.3, 135.0, 134.6, 133.5, 133.2, 133.1, 131.2, 127.8, 127.4, 124.9 (q, *J* = 35.5 Hz), 122.8, 121.3 (q, *J* = 277.7 Hz), 121.1, 63.9, 13.9. IR (ATR): ν 2984, 1746, 1671, 1589, 1566, 1519, 1470, 1446, 1424, 1380, 1360, 1279, 1241, 1215, 1155, 1127, 1095, 1068, 1014, 998, 966, 886, 861, 842, 799, 772, 732, 696, 672, 646, 632, 590, 541, 486, 463, 428 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Br_2F_3N_2O_4$ $[M + H]^+$: 584.9267; found: 584.9265.



ethyl

-2-(2-(1,4-di([1,1'-biphenyl]-4-yl)-1,4-dioxobut-2-en-2-yl)hydrazineylidene)-4,4,4-trifluoro-3-oxobutanoate (4)

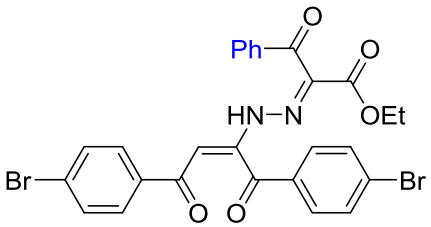
Obtained as a yellow solid in 52% yield (93.0 mg). Mp: 140–142 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.46 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4, Hz, 2H), 7.75 (dd, *J* = 8.5, 2.0 Hz, 4H), 7.67 (d, *J* = 7.6 Hz, 4H), 7.56 – 7.47 (m, 4H), 7.46 – 7.40 (m, 2H), 6.70 (s, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 189.2, 174.9 (q, *J* = 34.7 Hz), 160.4, 153.4, 147.3, 146.3, 139.6, 139.5, 136.2, 133.5, 130.2, 129.1, 129.0, 128.7, 128.5, 127.5, 127.5, 127.4, 127.3, 127.0, 115.7 (q, *J* = 292.6 Hz), 101.5, 62.9, 14.1. IR (ATR): ν 3062, 2988, 2256, 1842, 1725, 1679, 1634, 1600, 1559, 1509, 1452, 1372, 1285, 1253, 1191, 1148, 1044, 1008, 970, 909, 880, 823, 726, 695, 648, 587, 561, 472 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{34}H_{26}O_5N_2F_3$ $[M + H]^+$: 599.1788; found: 599.1785.



ethyl

-2-(2-(1,4-di([1,1'-biphenyl]-4-yl)-1,4-dioxobut-2-en-2-yl)hydrazineylidene)-3-oxo butanoate (4′)

Obtained as a yellow solid in 40% yield (66.0 mg). Mp: 179–181 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.83 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.82 – 7.70 (m, 4H), 7.69 – 7.61 (m, 4H), 7.53 – 7.48 (m, 4H), 7.45 – 7.41 (m, 2H), 6.55 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.90 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 190.7, 190.3, 160.8, 154.4, 147.2, 145.9, 139.8, 139.4, 136.6, 134.0, 133.7, 129.9, 129.1, 129.0, 128.8, 128.7, 128.3, 127.6, 127.4, 127.3, 127.2, 98.5, 62.5, 26.1, 14.1. IR (ATR): ν 3058, 3031, 2982, 2252, 1740, 1679, 1628, 1601, 1582, 1527, 1487, 1447, 1405, 1368, 1357, 1317, 1278, 1226, 1177, 1143, 1077, 1046, 1016, 1005, 971, 945, 907, 884, 855, 810, 790, 769, 755, 726, 695, 647, 610, 579, 545, 506, 476, 455, 435, 426, 414, 404 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{34}H_{29}N_2O_5$ $[M + H]^+$: 545.2071; found: 545.2074.

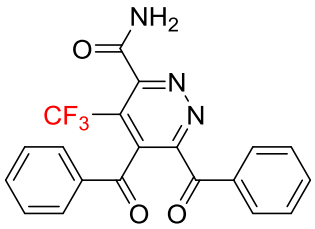


ethyl

2-(2-(1,4-bis(4-bromophenyl)-1,4-dioxobut-2-en-2-yl)hydrazineylidene)-3-oxo-3-p henylpropanoate (4″)

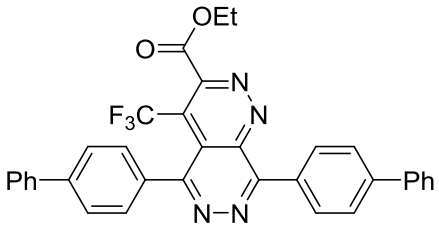
Obtained as a brown solid in 81% yield (244.0 mg). Mp: 148–150 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.99 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 4H), 7.58 – 7.45 (m, 5H), 7.22 (t, *J* = 7.6 Hz,

2H), 6.30 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 189.6, 188.1, 161.0, 154.7, 136.6, 135.2, 134.2, 133.9, 133.2, 132.2, 132.0, 130.5, 129.8, 129.7, 129.6, 128.3, 128.1, 96.9, 62.7, 14.0. IR (ATR): ν 3083, 2845, 2181, 1597, 1557, 1519, 1492, 1441, 1402, 1371, 1348, 1292, 1269, 1243, 1188, 1141, 1073, 1047, 1009, 894, 856, 756, 724, 684, 617, 606, 596, 566, 552, 542, 535, 521, 483, 424, 402 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{27}H_{21}Br_2N_2O_5$ $[M + H]^+$: 610.9817; found: 610.9814.



5,6-dibenzoyl-4-(trifluoromethyl)pyridazine-3-carboxamide (5a)

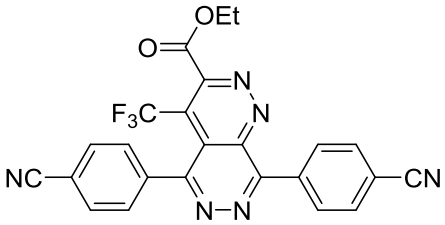
Obtained as a white solid in 94% yield (37.0 mg). Mp: 192–194 °C. R_f (petroleum ether : ethyl acetate = 1 : 1) = 0.23. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (d, J = 7.3 Hz, 2H), 8.46 (s, 1H), 8.19 (s, 1H), 7.71 – 7.65 (m, 3H), 7.35 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.5 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.3, 163.3, 161.2, 152.3, 149.5, 137.6, 132.9, 131.3, 129.8, 129.4, 128.8, 128.8, 125.7, 121.9 (q, J = 276.5 Hz), 121.2 (q, J = 36.1 Hz), 101.1. IR (ATR): ν 3462, 3181, 2924, 2855, 1692, 1593, 1562, 1492, 1451, 1346, 1269, 1184, 1154, 1069, 1022, 976, 952, 920, 860, 770, 729, 693, 656, 624, 543, 483, 454, 420 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{20}H_{13}O_3N_3F_3$ $[M + H]^+$: 400.0903; found: 400.0904.



ethyl

5,8-di([1,1'-biphenyl]-4-yl)-4-(trifluoromethyl)pyridazino[4,5-*c*]pyridazine-3-car boxylate (6c)

Obtained as a yellow solid in 72% yield (41.0 mg). Mp: 220–222 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.86 – 7.70 (m, 7H), 7.56 – 7.50 (m, 4H), 7.49 – 7.42 (m, 3H), 4.66 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 156.0, 155.8, 150.3, 147.9, 143.9, 143.4, 142.5, 140.2, 140.0, 136.5, 132.8, 131.7, 130.3, 129.9, 129.0, 128.1, 127.4, 127.3, 127.2, 127.1, 121.3 (q, J = 277.4 Hz), 120.8 (q, J = 35.4 Hz), 113.7, 64.0, 14.0. IR (ATR): ν 3031, 2926, 1745, 1606, 1487, 1447, 1401, 1370, 1335, 1306, 1255, 1196, 1167, 1145, 1007, 878, 768, 736, 697, 672, 616, 566, 502, 486, 457, 446, 435, 414 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{34}H_{24}F_3N_4O_2$ $[M + H]^+$: 577.1846; found: 577.1844.

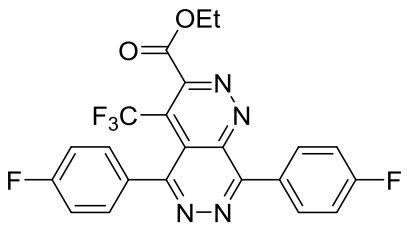


ethyl

5,8-bis(4-cyanophenyl)-4-(trifluoromethyl)pyridazino[4,5-c]pyridazine-3-carboxy late (6j)

Obtained as a yellow solid in 50% yield (24.0 mg). Mp: 215–217 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.0 Hz,

2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 4.66 (q, *J* = 7.2 Hz, 2H), 1.51 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 155.7, 155.6, 150.6, 141.8, 141.0, 132.8, 132.4, 132.2, 130.2, 121.1 (q, *J* = 276.8 Hz), 119.9 (q, *J* = 36.5 Hz), 118.2, 117.9, 116.1, 115.0, 114.7, 113.7, 64.4, 13.9. IR (ATR): ν 3097, 2986, 2359, 2230, 1743, 1609, 1467, 1445, 1401, 1371, 1339, 1306, 1256, 1238, 1194, 1168, 1143, 1112, 1033, 1016, 947, 913, 847, 780, 730, 706, 660, 647, 614, 598, 571, 549, 509, 463, 434, 413, 404 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{24}H_{14}F_3N_6O_2$ $[M + H]^+$: 475.1125; found: 475.1124.



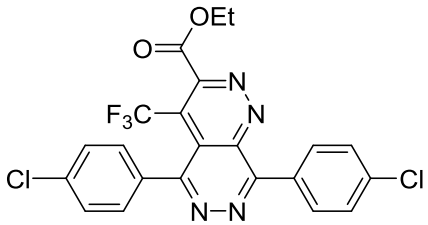
ethyl

5,8-bis(4-fluorophenyl)-4-(trifluoromethyl)pyridazino[4,5-*c*]pyridazine-3-carbox

ylate (6n)

Obtained as a yellow solid in 56% yield (26.0 mg). Mp: 191–193 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.36 (m, 2H), 7.73 – 7.63 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 2H), 4.66 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.1 (s, 3F), -108.5 – -108.4 (m, 1F), -109.3 – -109.2 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0 (d, *J* = 253.0 Hz), 164.2 (d, *J* = 252.0 Hz), 163.4, 155.4 (d, *J* = 8.8 Hz), 150.3 (d, *J* = 2.6 Hz), 142.2, 134.5 (d, *J* = 8.8 Hz), 133.6, 131.6 (d, *J* = 8.6 Hz), 128.9 (d, *J* = 3.4 Hz), 122.5, 121.1 (q, *J* = 278.6 Hz), 120.5 (q, *J* = 36.0 Hz), 116.0, 115.8, 113.7, 64.1, 13.9. IR (ATR): ν 3078, 2986, 1743, 1603, 1514, 1473, 1402, 1371, 1337, 1302, 1255, 1238, 1194, 1160, 1143, 1097, 1032, 1014, 947, 914, 843, 817, 782, 732, 707, 647, 612, 570,

525, 500, 457, 415 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}F_5N_4O_2$ $[M + H]^+$: 461.1031; found: 461.1031.



ethyl

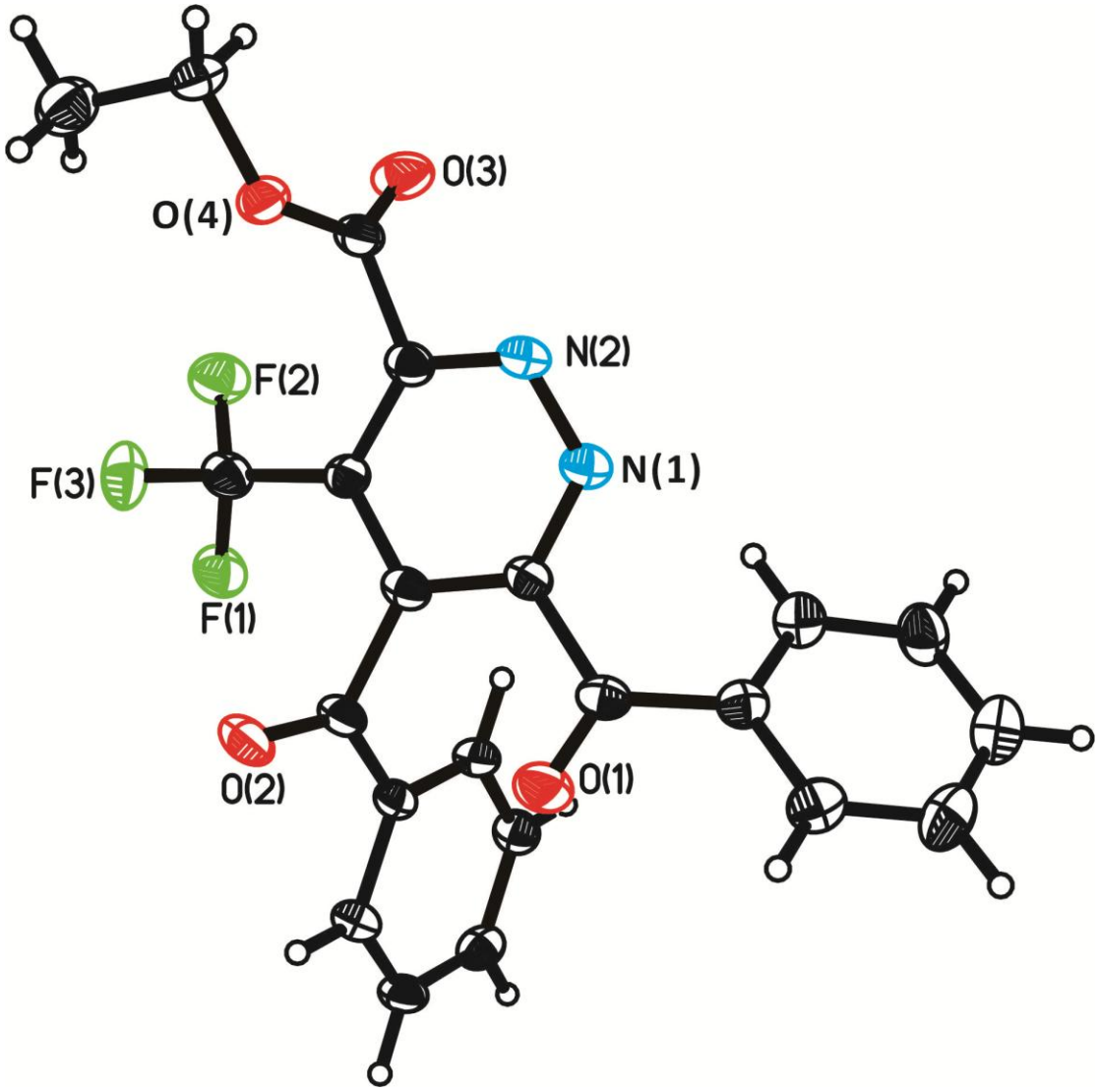
5,8-bis(4-chlorophenyl)-4-(trifluoromethyl)pyridazino[4,5-*c*]pyridazine-3-carbox

ylate (6o)

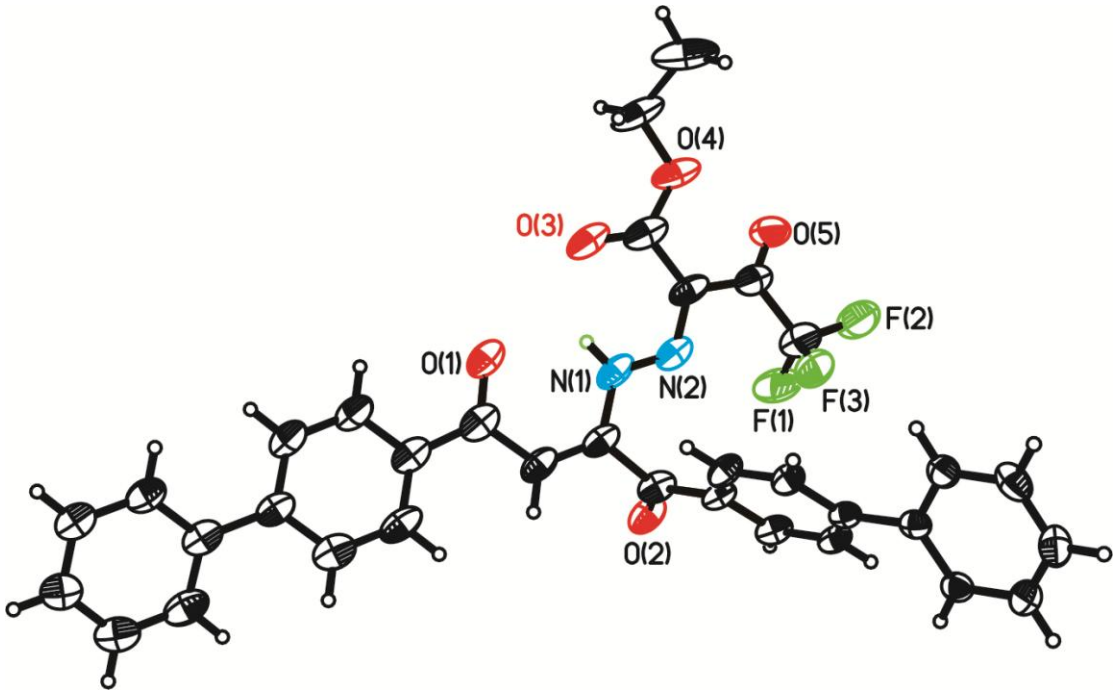
Obtained as a yellow solid in 68% yield (33.0 mg). Mp: 196–198 °C. R_f (petroleum ether : ethyl acetate = 5 : 1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.59 (m, 4H), 7.56 (d, *J* = 8.3 Hz, 2H), 4.65 (q, *J* = 7.2 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 155.5, 155.4, 150.4, 142.1, 138.0, 137.2, 135.8, 133.5, 131.1, 130.8, 129.0, 128.9, 121.1 (q, *J* = 277.8 Hz), 120.4 (q, *J* = 36.2 Hz), 113.6, 64.2, 13.9. IR (ATR): ν 2986, 2359, 2342, 1744, 1684, 1595, 1559, 1540, 1493, 1446, 1400, 1370, 1337, 1303, 1255, 1239, 1195, 1168, 1143, 1093, 1012, 946, 912, 862, 834, 799, 751, 727, 698, 668, 653, 629, 576, 562, 554, 517, 504, 491, 479, 460, 447, 441, 433, 421, 401 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{22}H_{14}Cl_2F_3N_4O_2$ $[M + H]^+$: 493.0440; found: 493.0442.

Crystal structure analyses

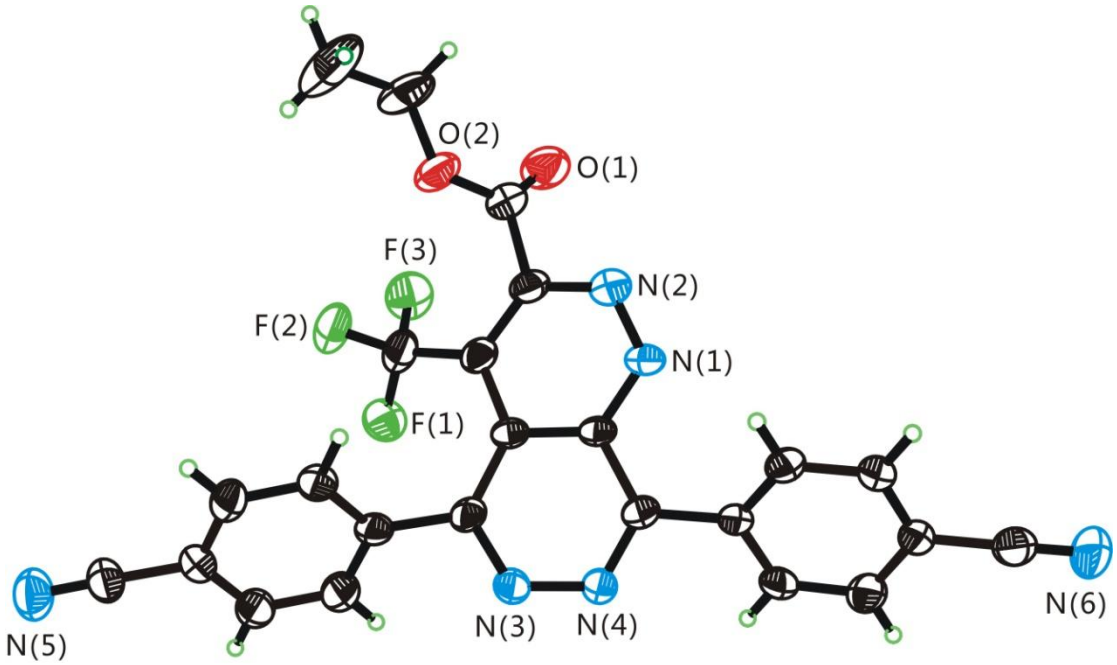
The crystal samples of **3a**, **4**, and **6j** were prepared by slow volatilization in a CH_2Cl_2/$CDCl_3$ (3:1) solvent mixture. The suitable crystals of **3a** (CCDC 2102384), **4** (CCDC 2133310), and **6j** (CCDC 2155007) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ºC, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[7] Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.



ORTEP diagram of compound 3a. Thermal ellipsoids are drawn at 40% probability



ORTEP diagram of compound 4. Thermal ellipsoids are drawn at 40% probability



ORTEP diagram of compound 6j. Thermal ellipsoids are drawn at 40% probability

References

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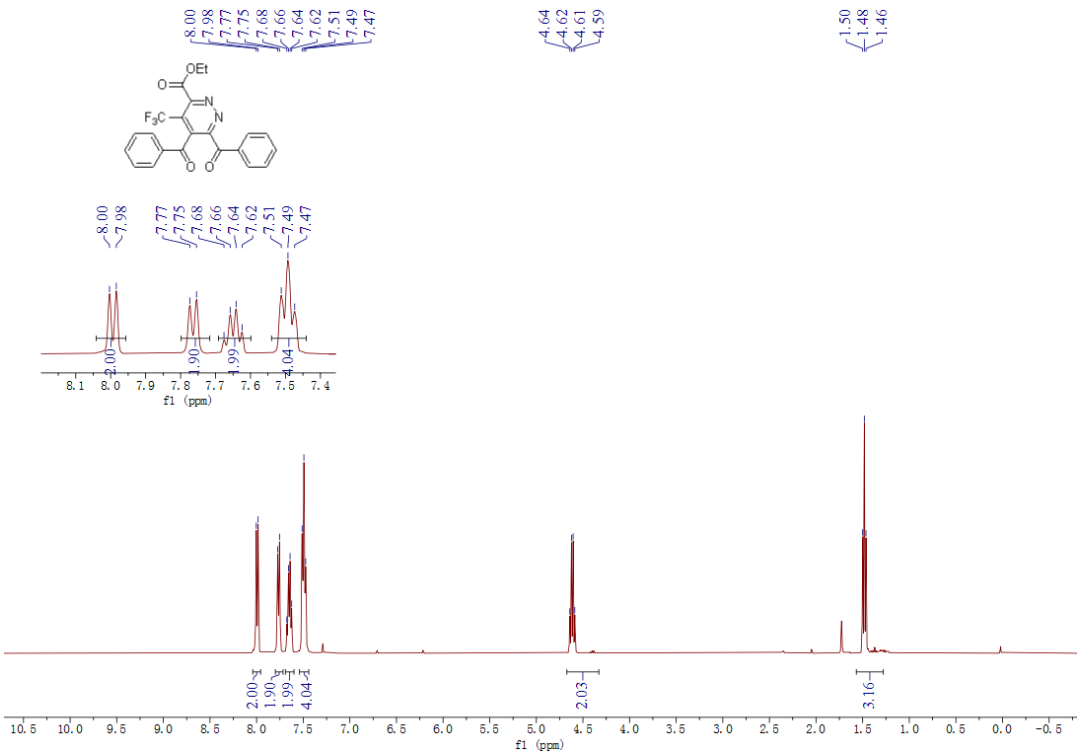
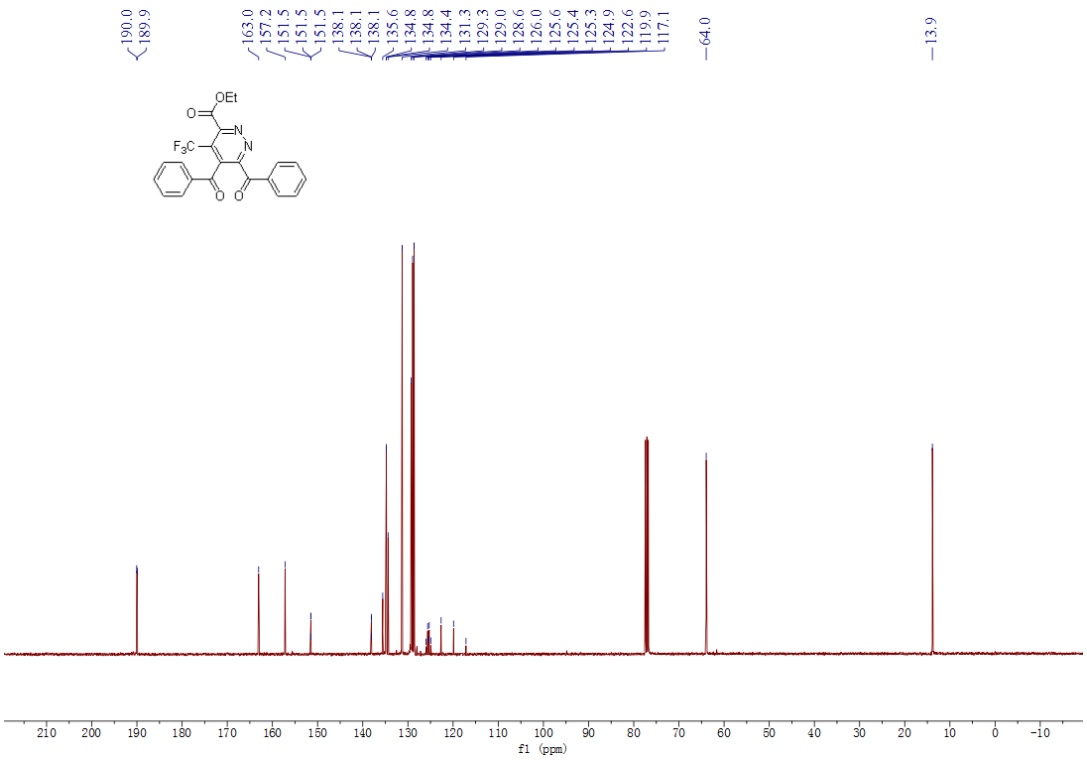
Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

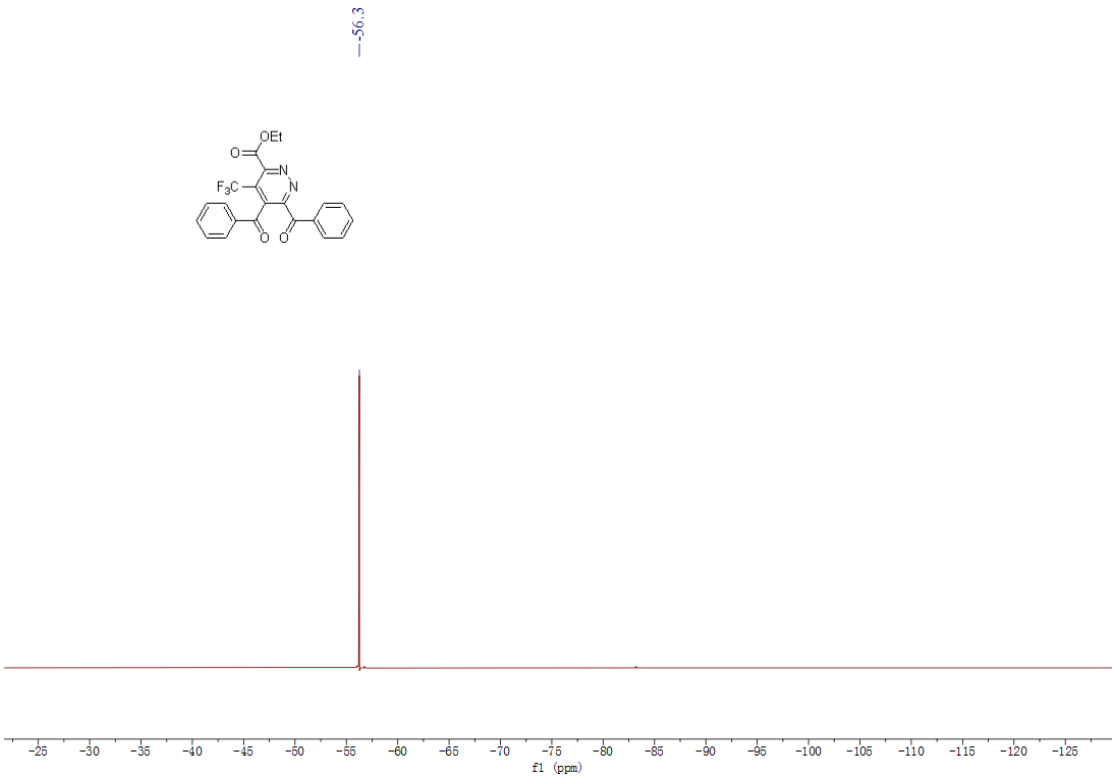
400 MHz ^{1}H NMR spectrum of **3a** in $CDCl_3$



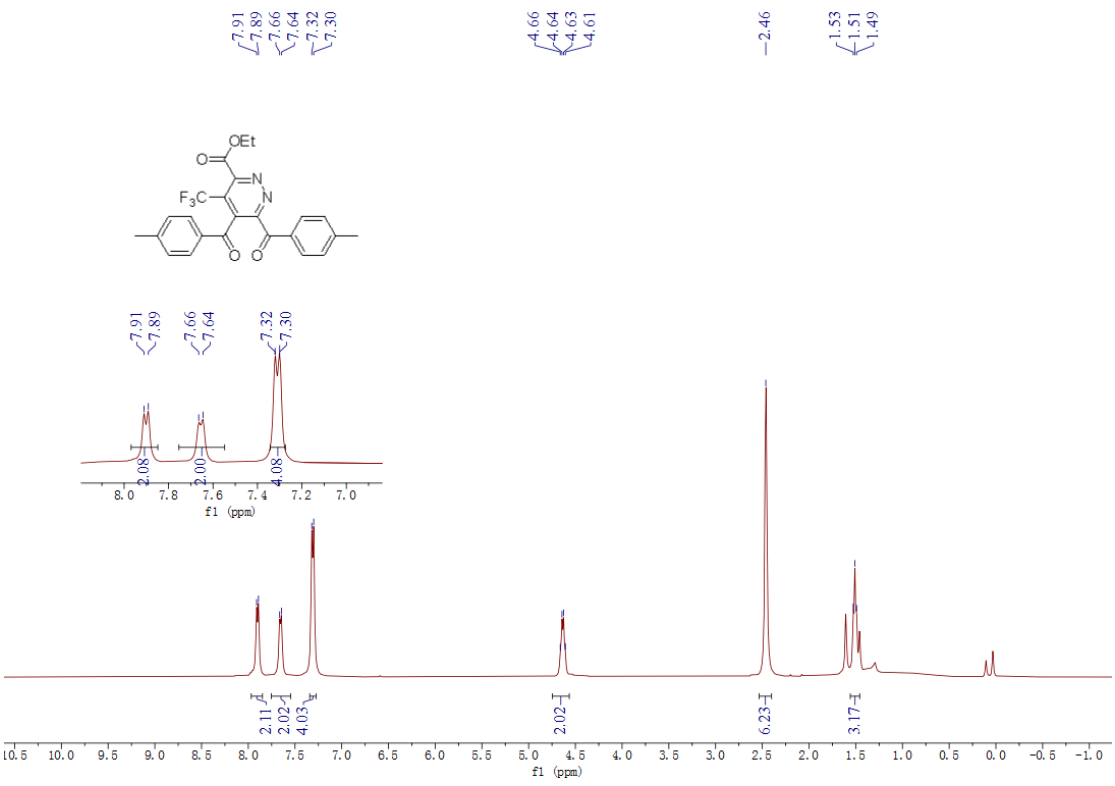
101 MHz ^{13}C NMR spectrum of **3a** in $CDCl_3$



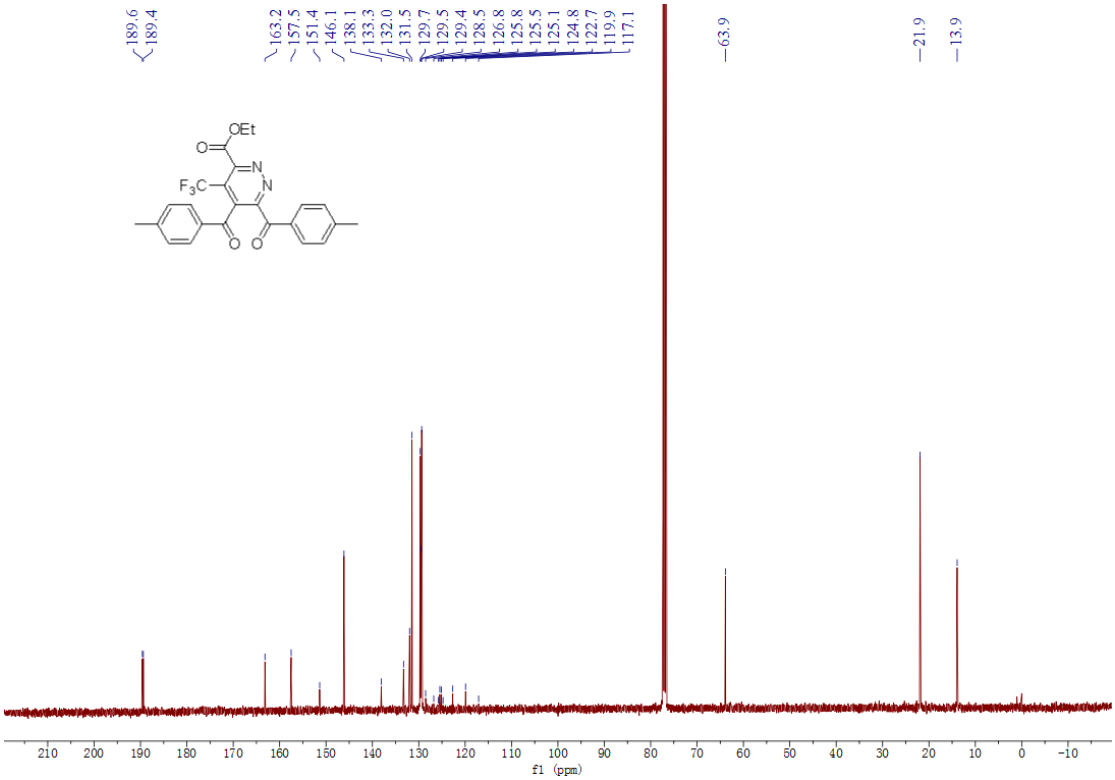
376 MHz ^{19}F NMR spectrum of **3a** in $CDCl_3$



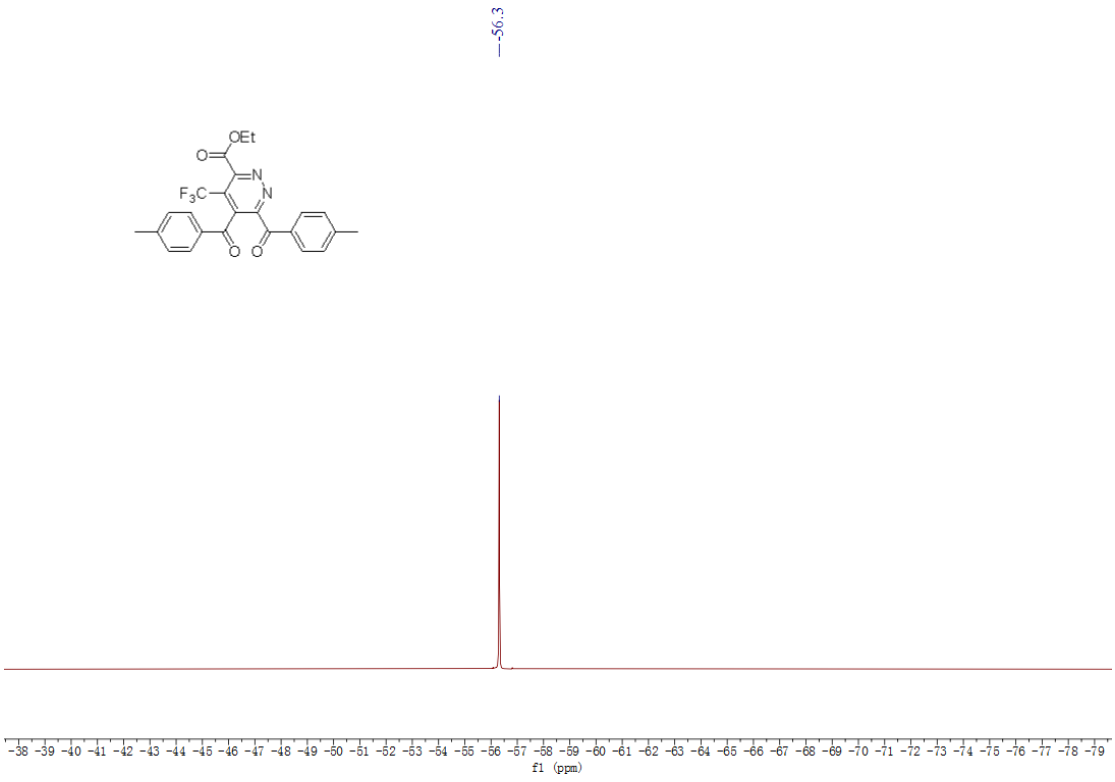
400 MHz ^{1}H NMR spectrum of **3b** in $CDCl_3$



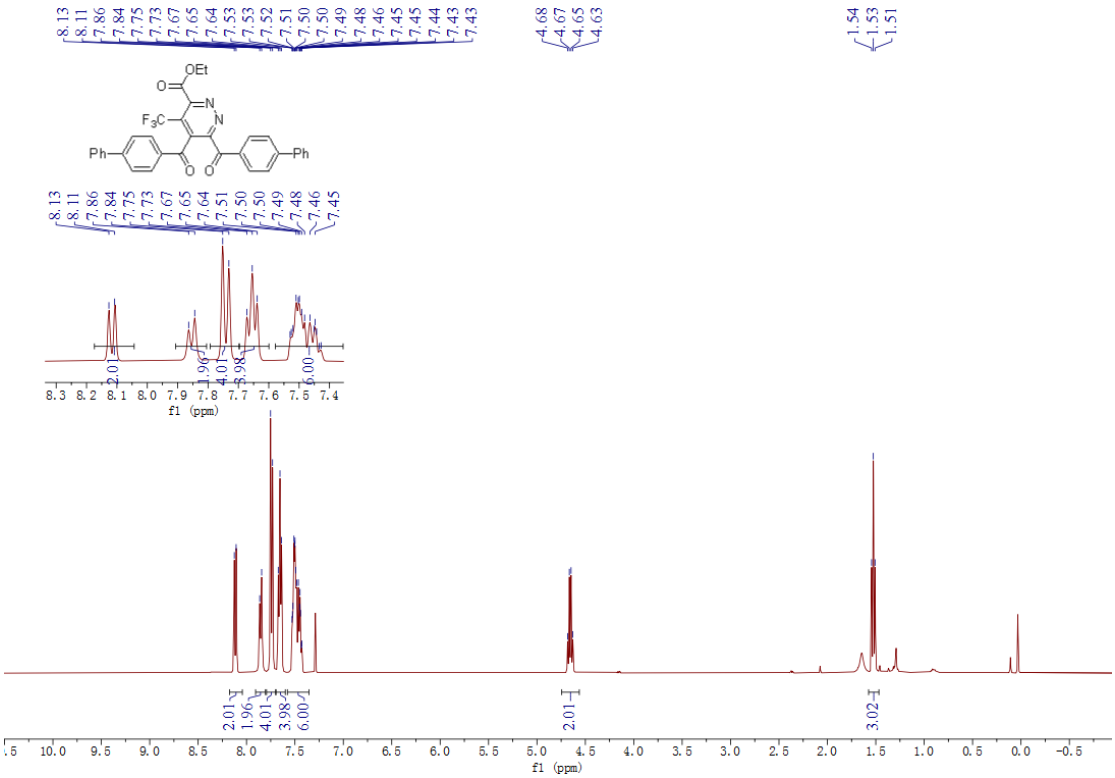
101 MHz ^{13}C NMR spectrum of **3b** in $CDCl_3$



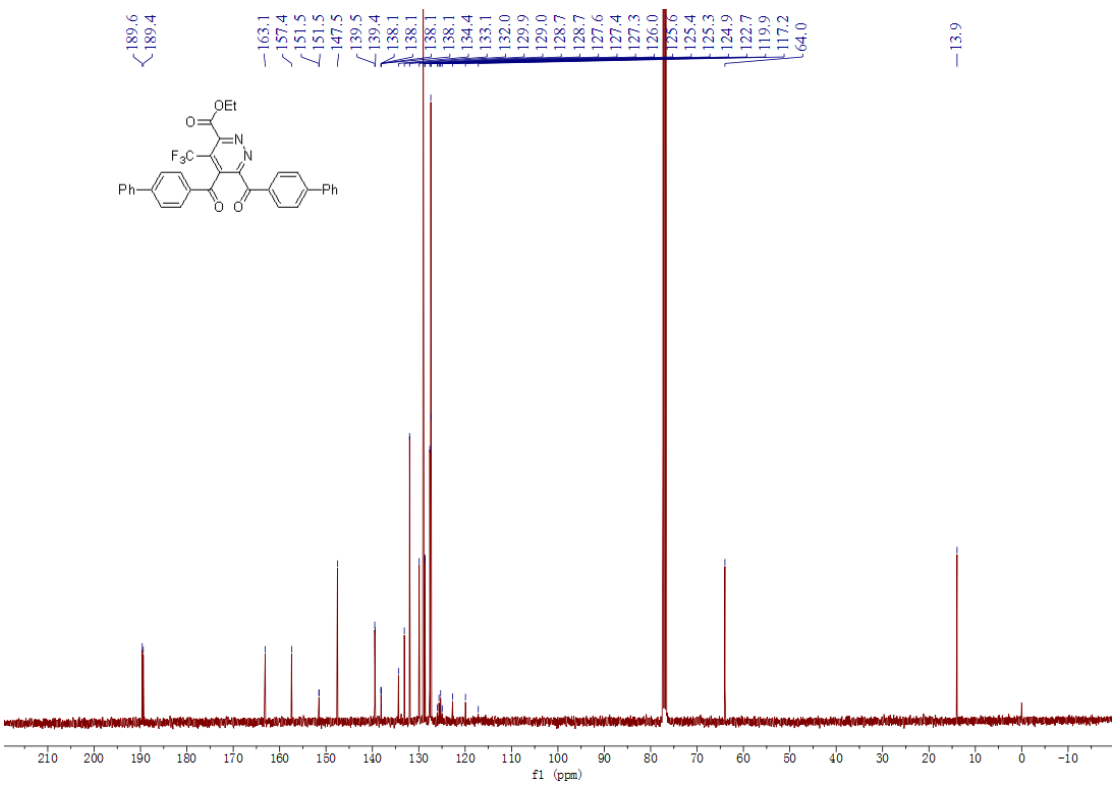
376 MHz ^{19}F NMR spectrum of **3b** in $CDCl_3$



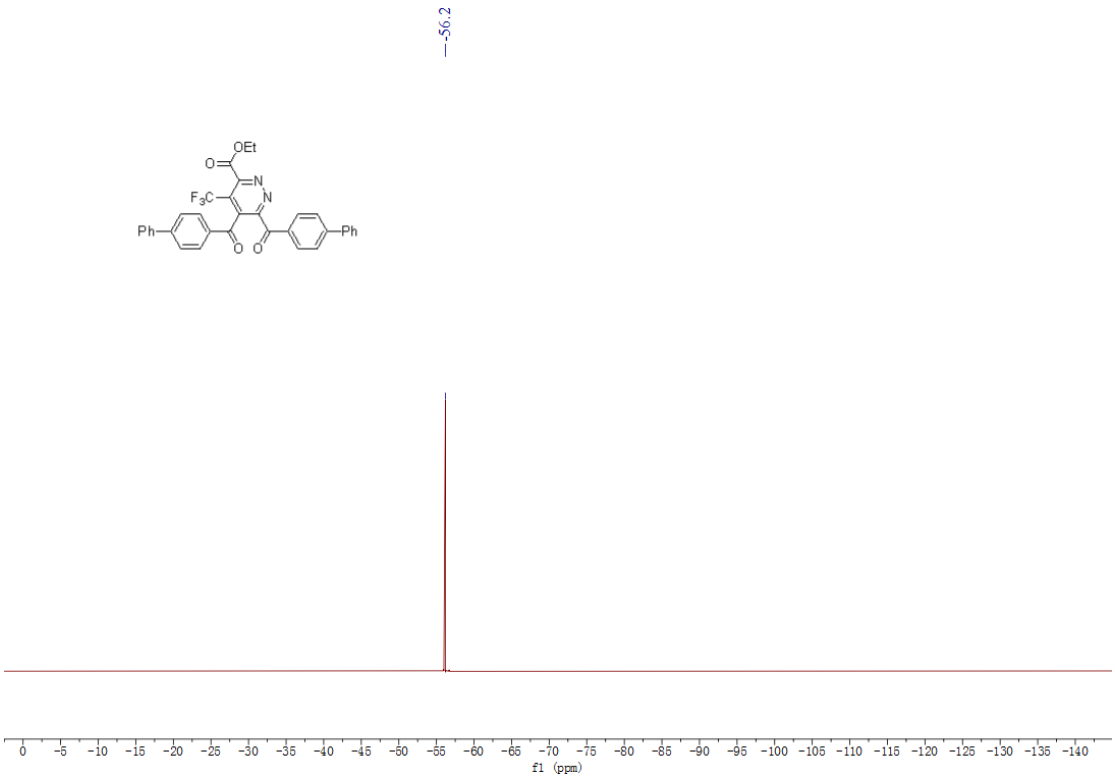
400 MHz ^{1}H NMR spectrum of **3c** in $CDCl_3$



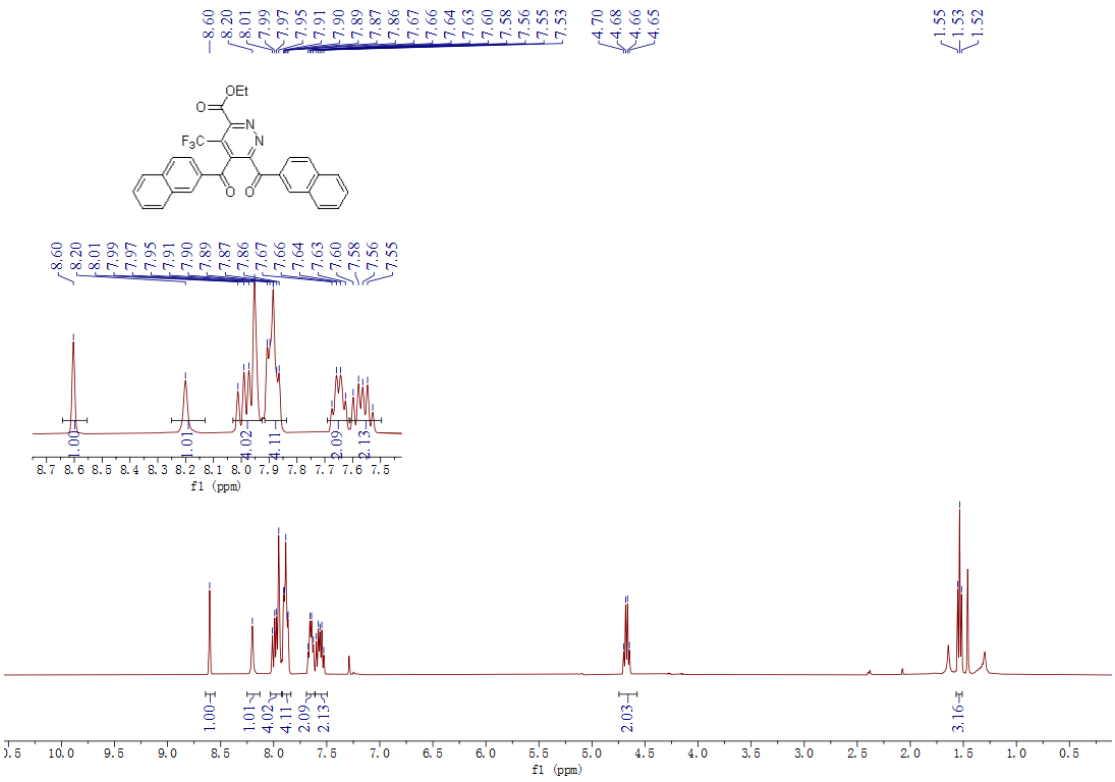
101 MHz ^{13}C NMR spectrum of **3c** in $CDCl_3$



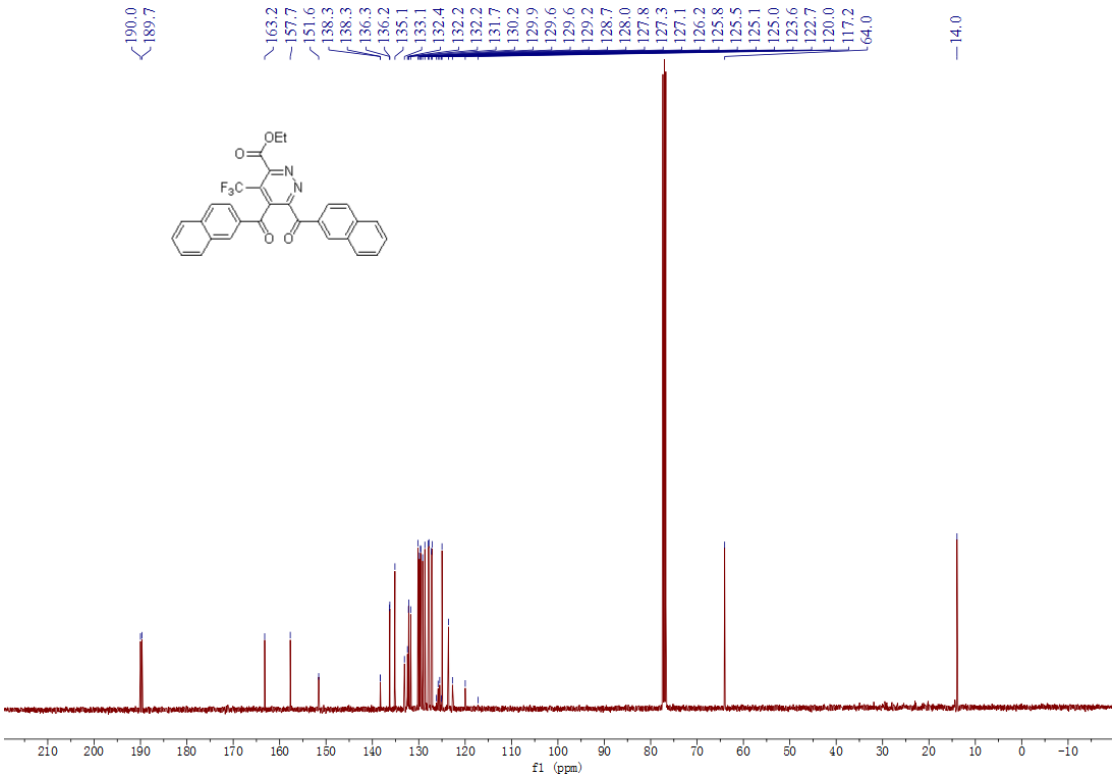
376 MHz ^{19}F NMR spectrum of **3c** in $CDCl_3$



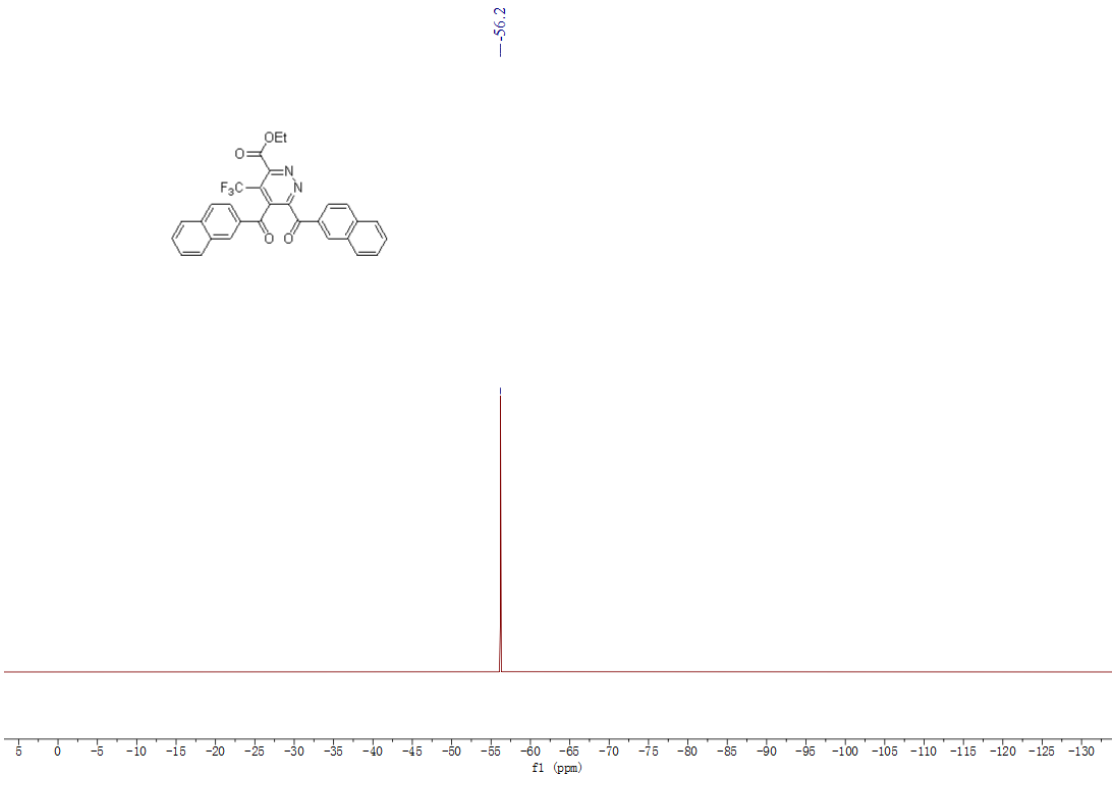
400 MHz ^{1}H NMR spectrum of **3d** in $CDCl_3$



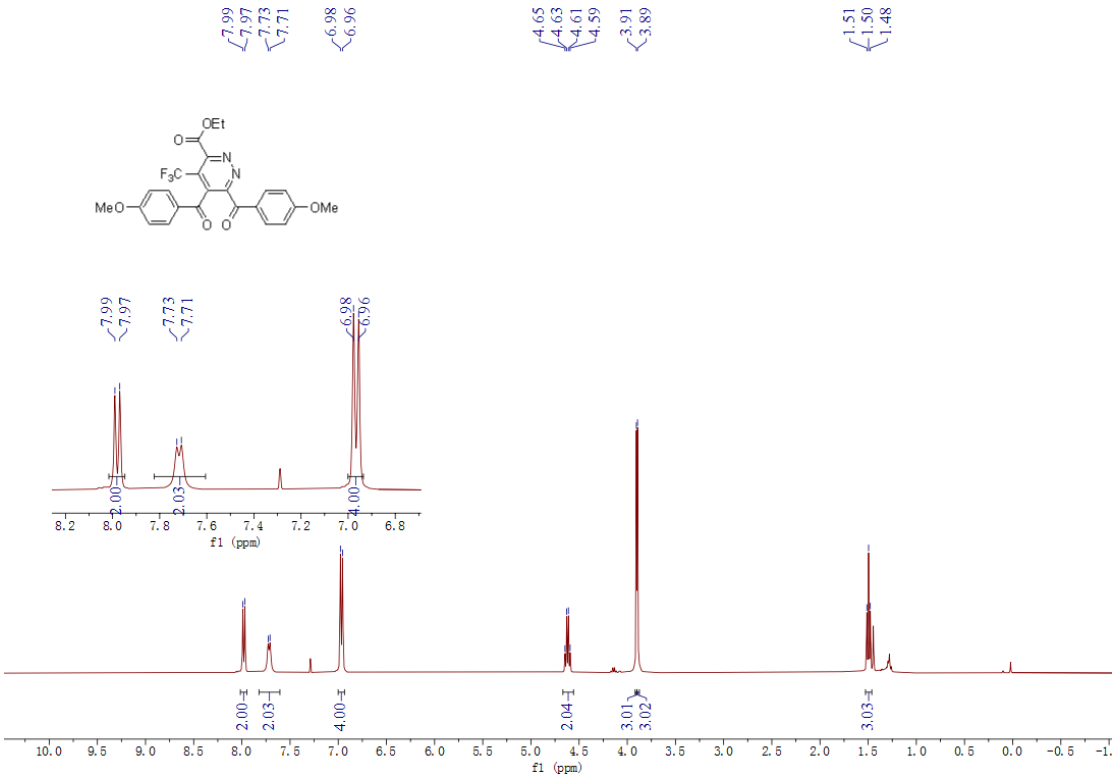
101 MHz ^{13}C NMR spectrum of **3d** in $CDCl_3$



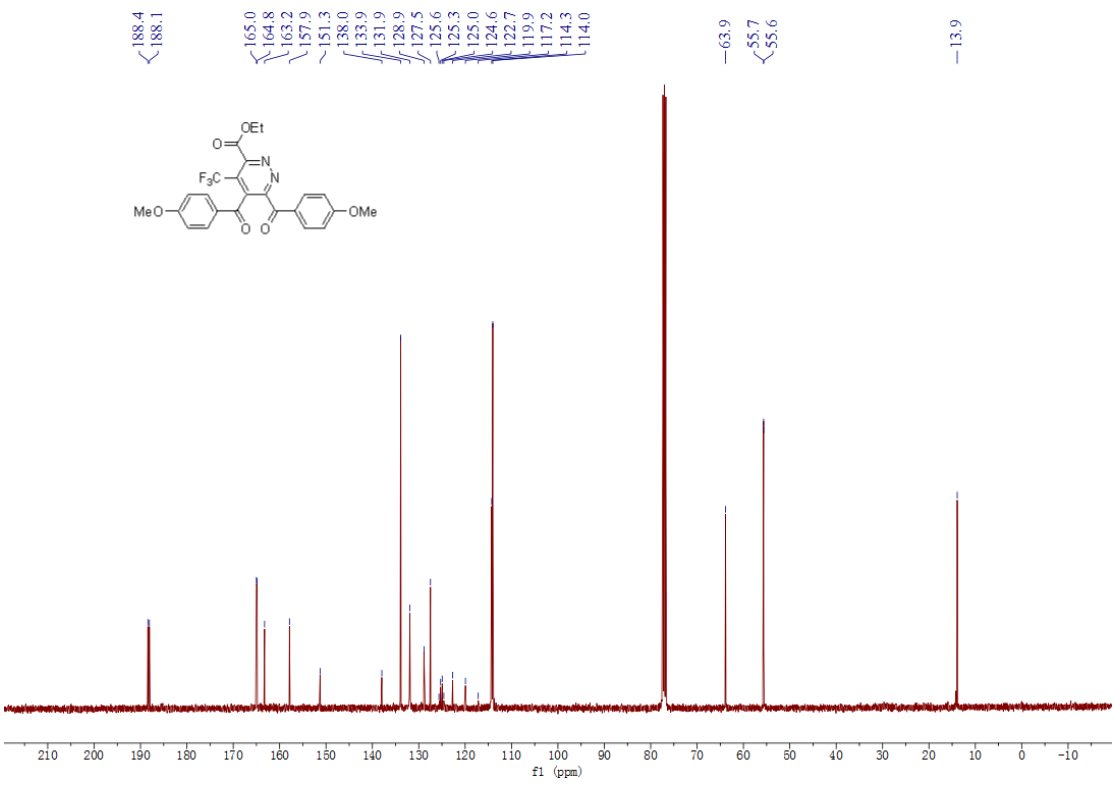
376 MHz ^{19}F NMR spectrum of **3d** in $CDCl_3$



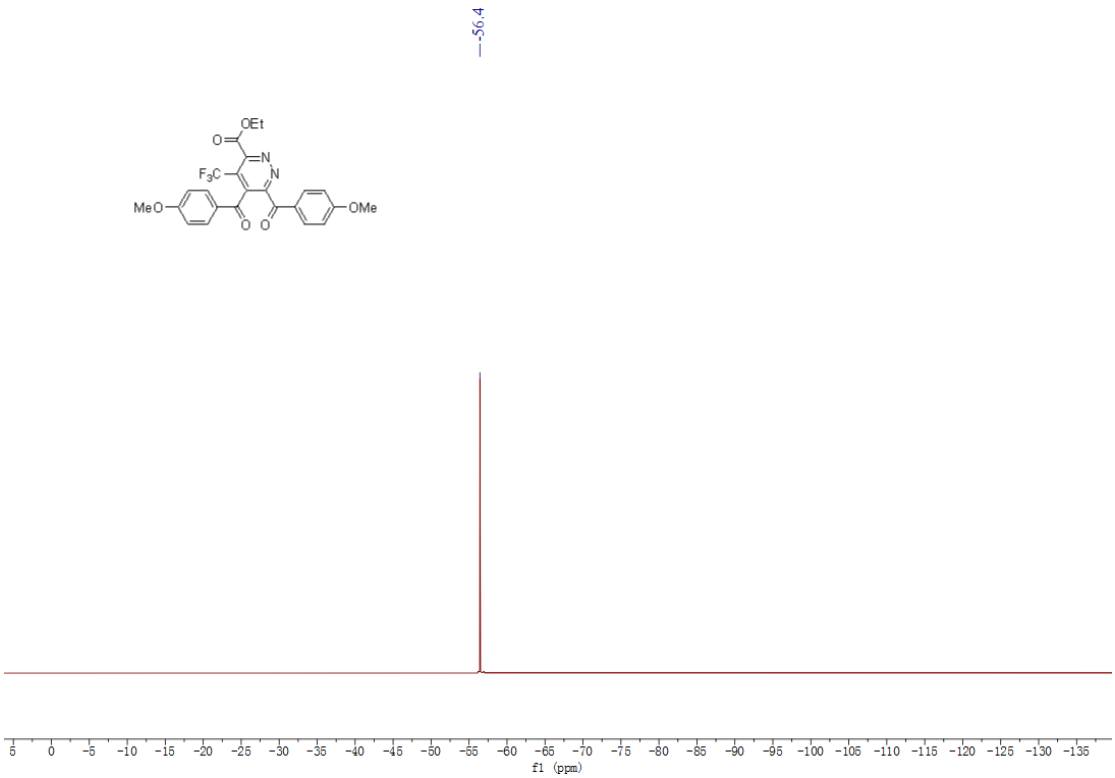
400 MHz ^{1}H NMR spectrum of **3e** in $CDCl_3$



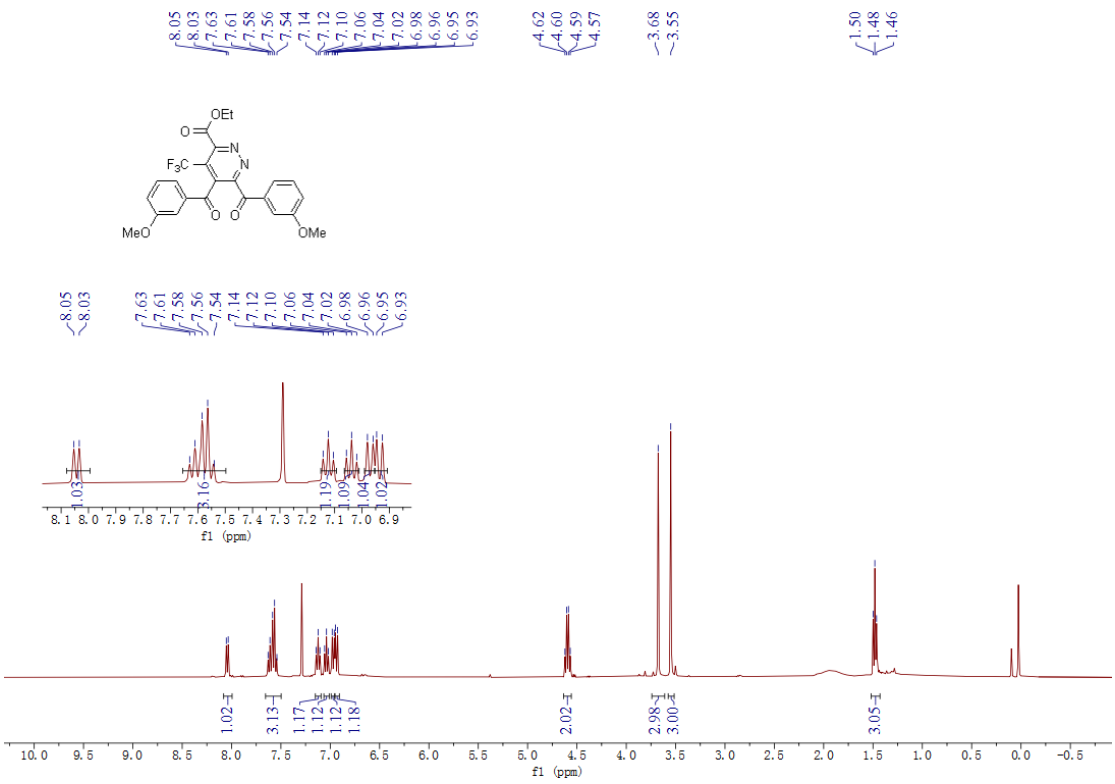
101 MHz ^{13}C NMR spectrum of **3e** in $CDCl_3$



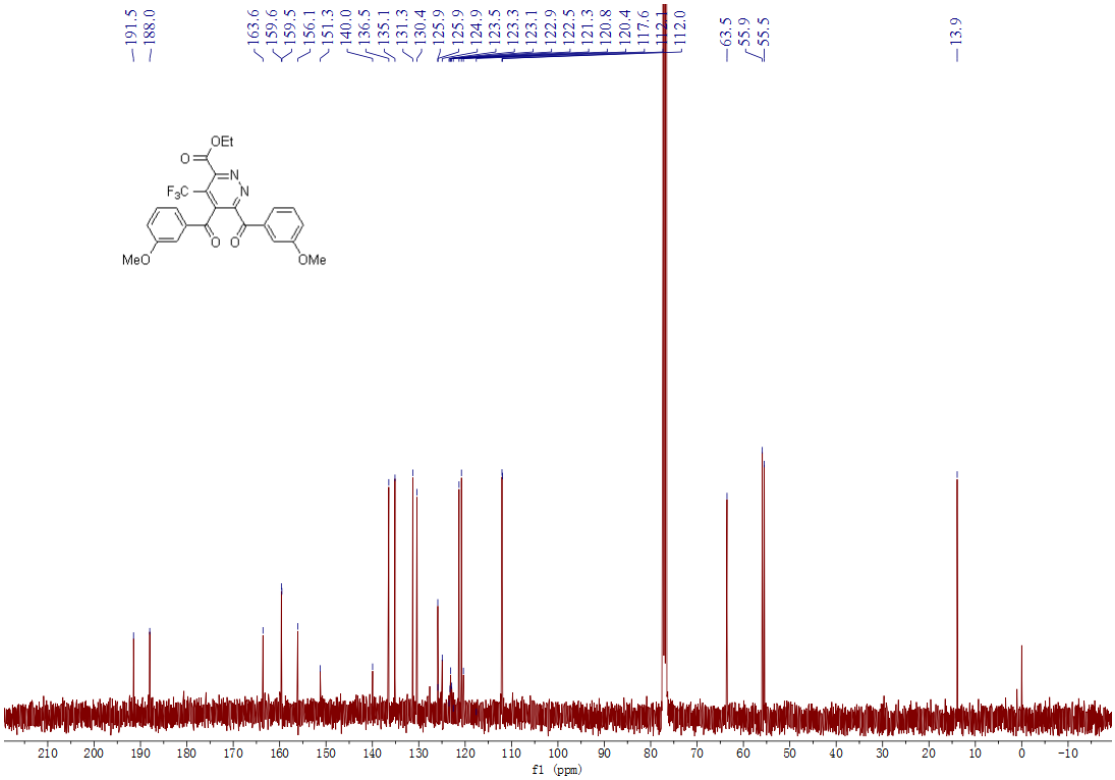
376 MHz ^{19}F NMR spectrum of **3e** in $CDCl_3$



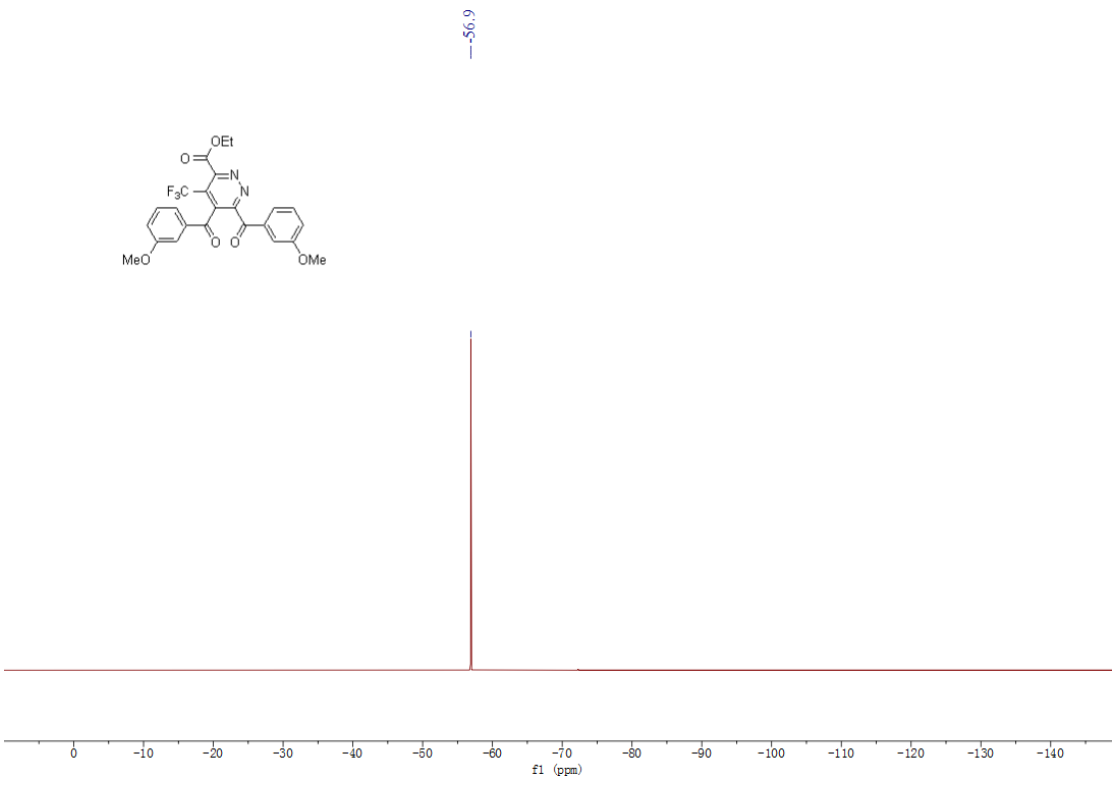
400 MHz ^{1}H NMR spectrum of **3f** in $CDCl_3$



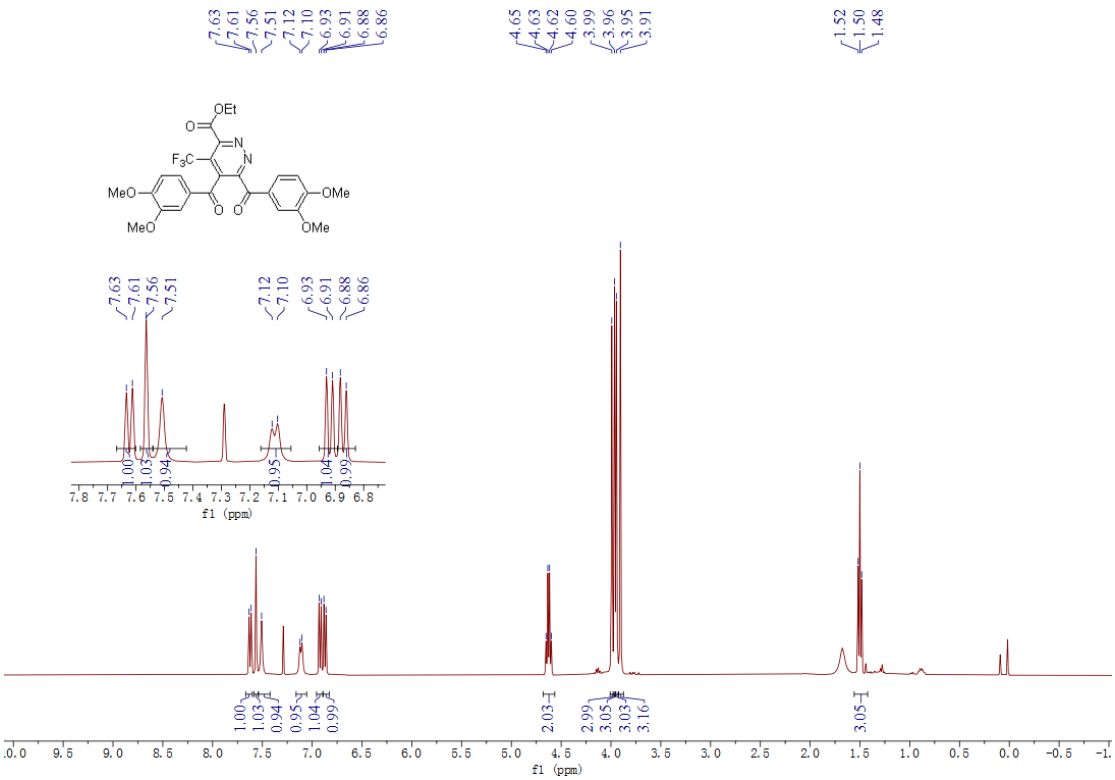
101 MHz ^{13}C NMR spectrum of **3f** in $CDCl_3$



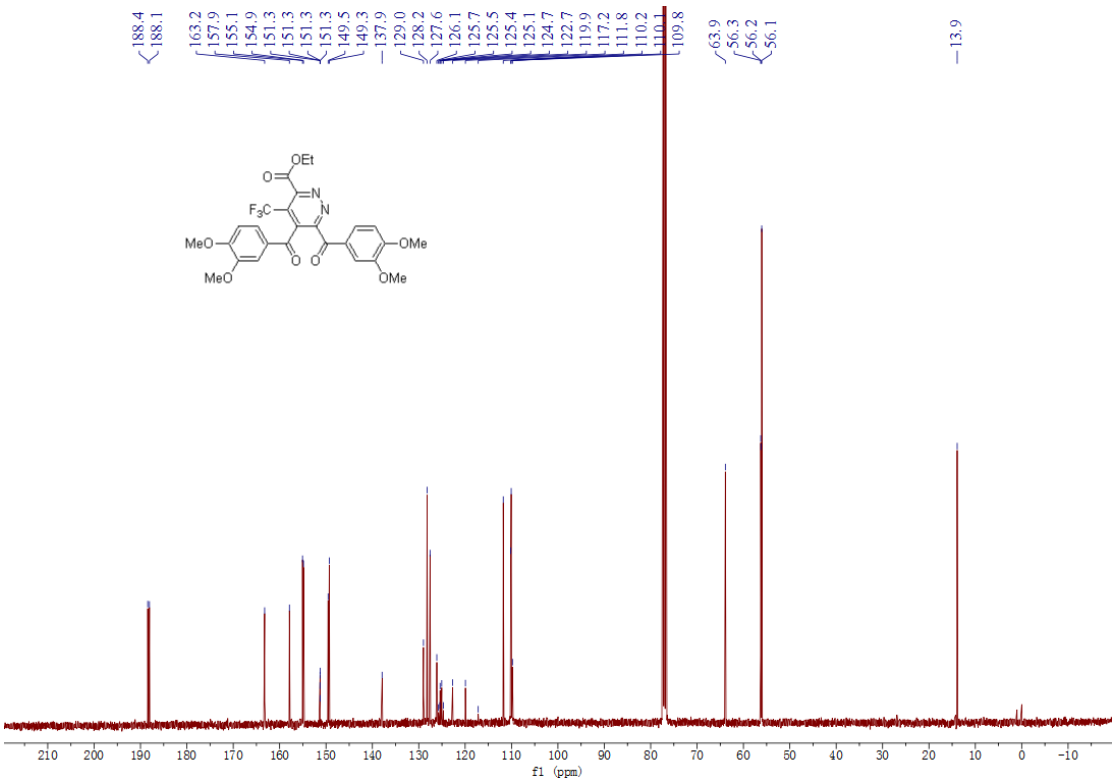
376 MHz ^{19}F NMR spectrum of **3f** in $CDCl_3$



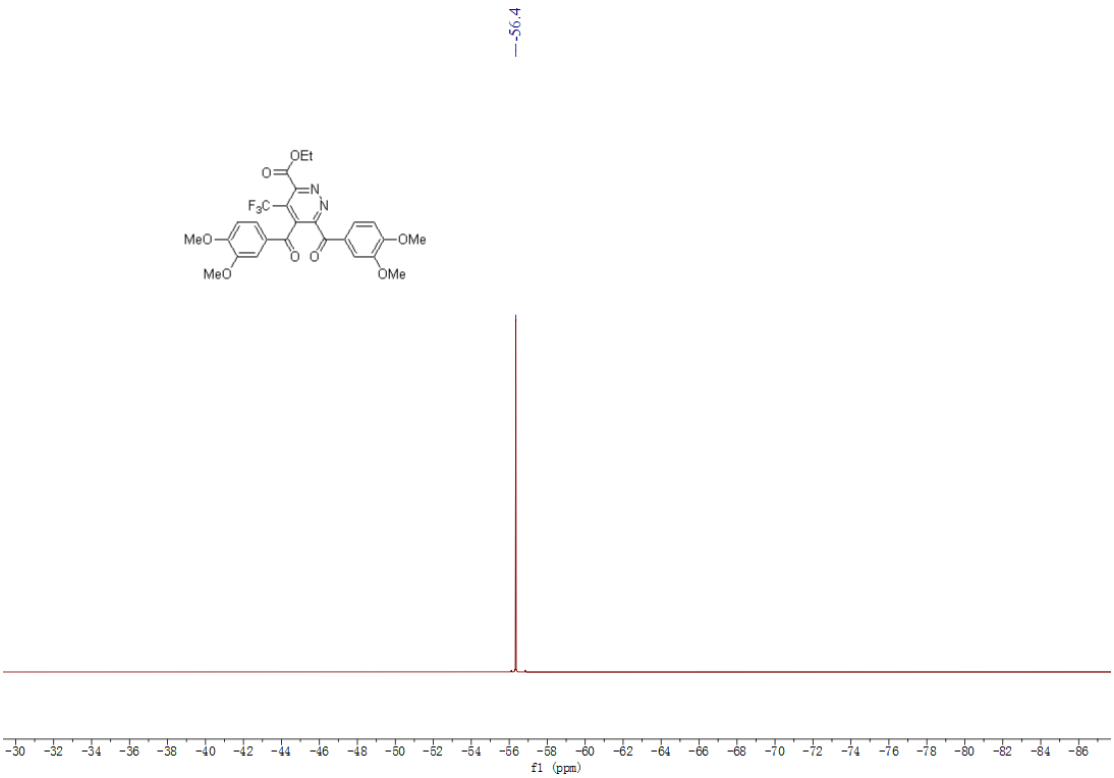
400 MHz ^{1}H NMR spectrum of **3g** in $CDCl_3$



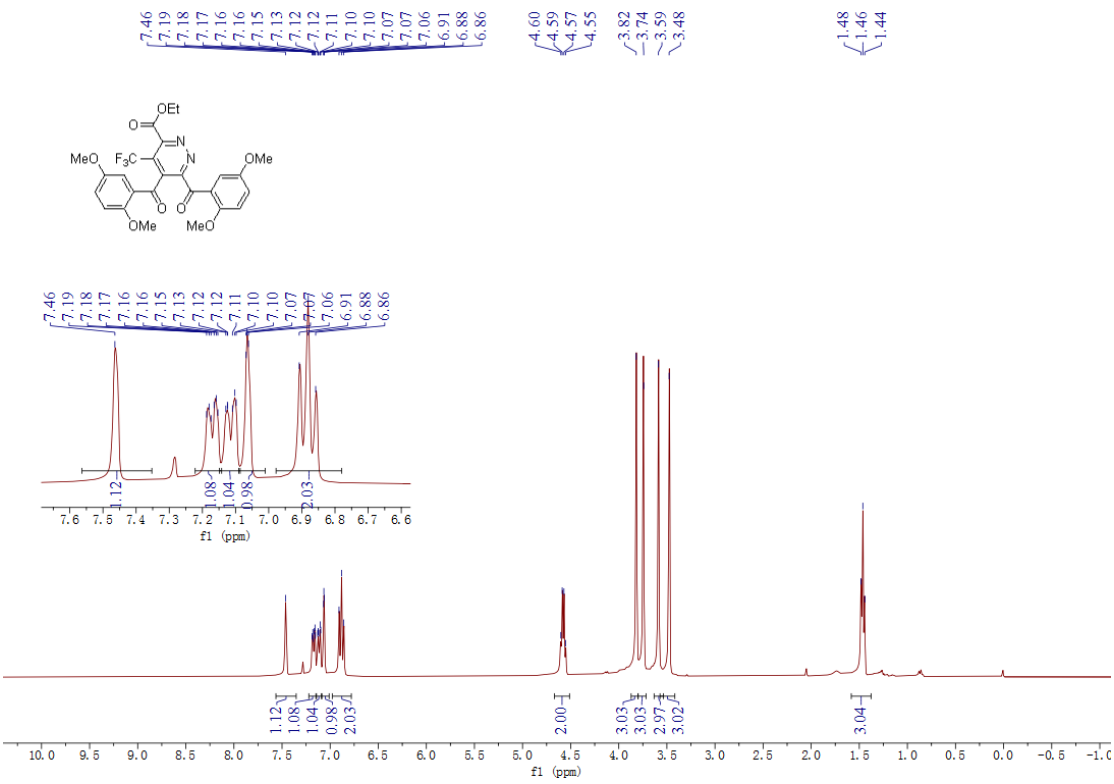
101 MHz ^{13}C NMR spectrum of **3g** in $CDCl_3$



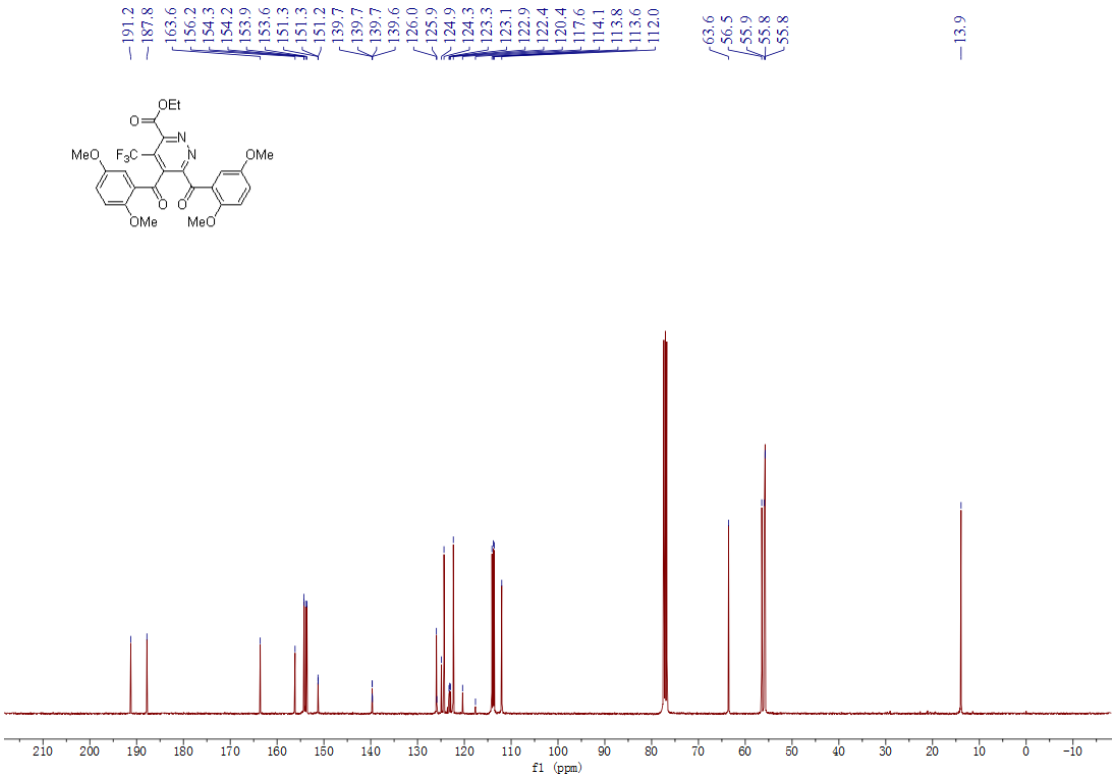
376 MHz ^{19}F NMR spectrum of **3g** in $CDCl_3$



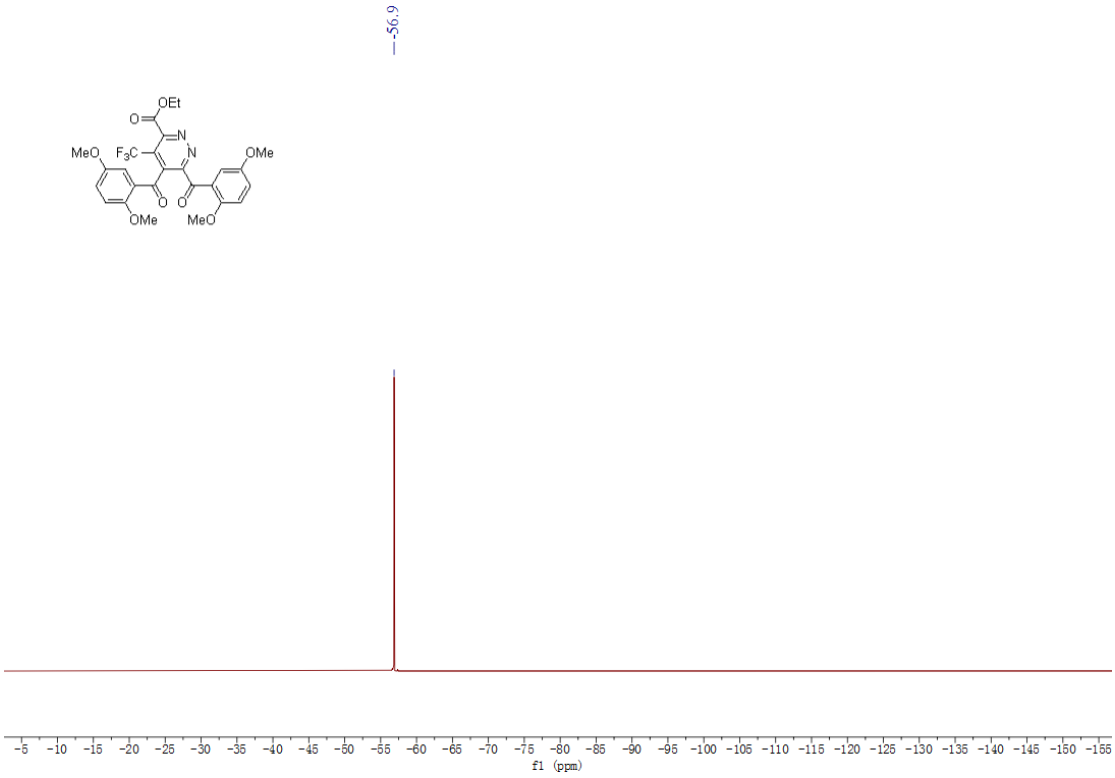
400 MHz ^{1}H NMR spectrum of **3h** in $CDCl_3$



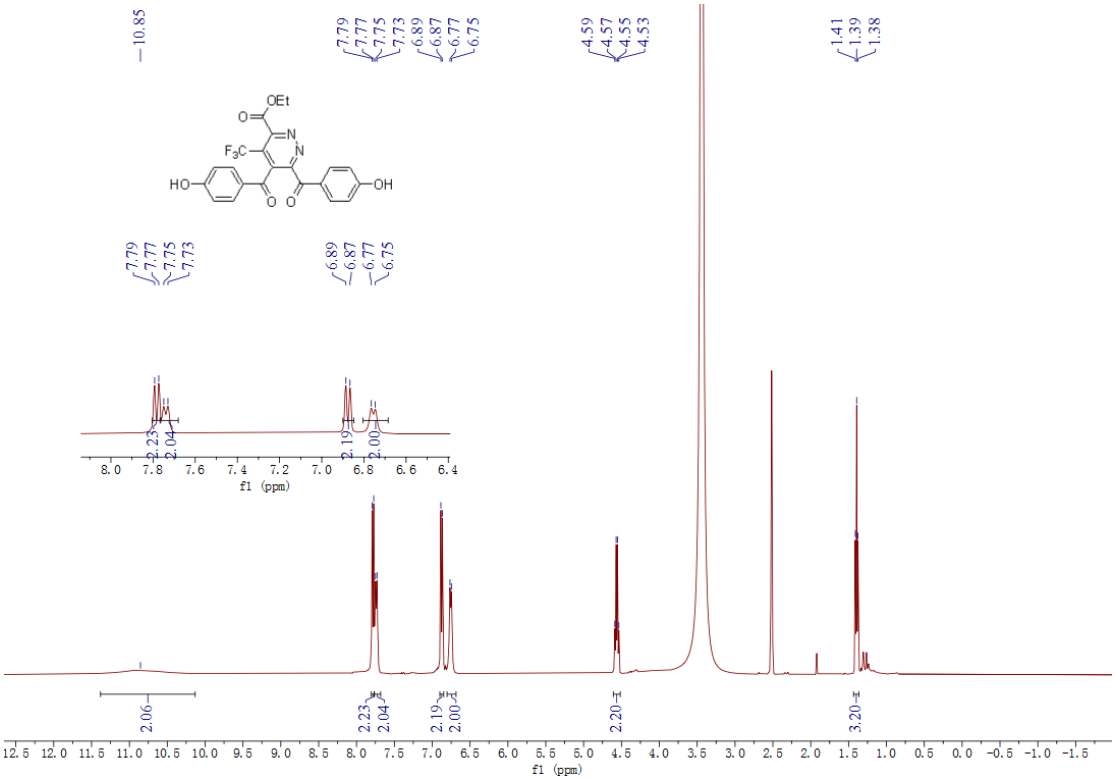
101 MHz ^{13}C NMR spectrum of **3h** in $CDCl_3$



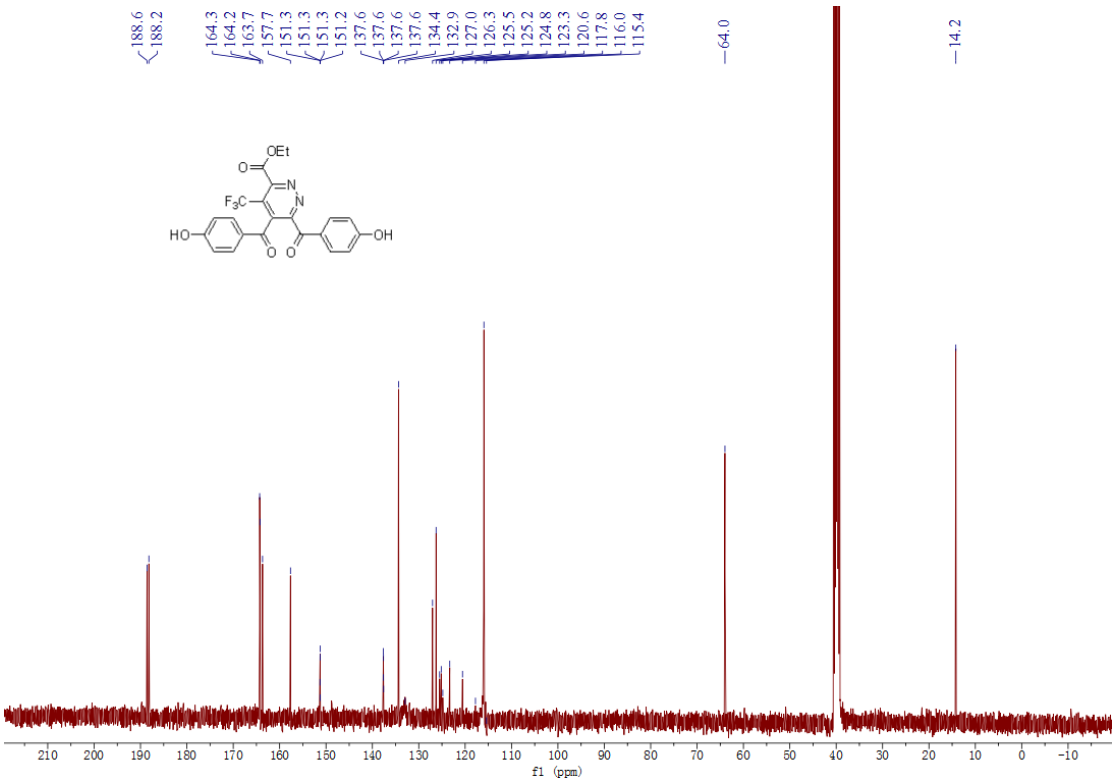
376 MHz ^{19}F NMR spectrum of **3h** in $CDCl_3$



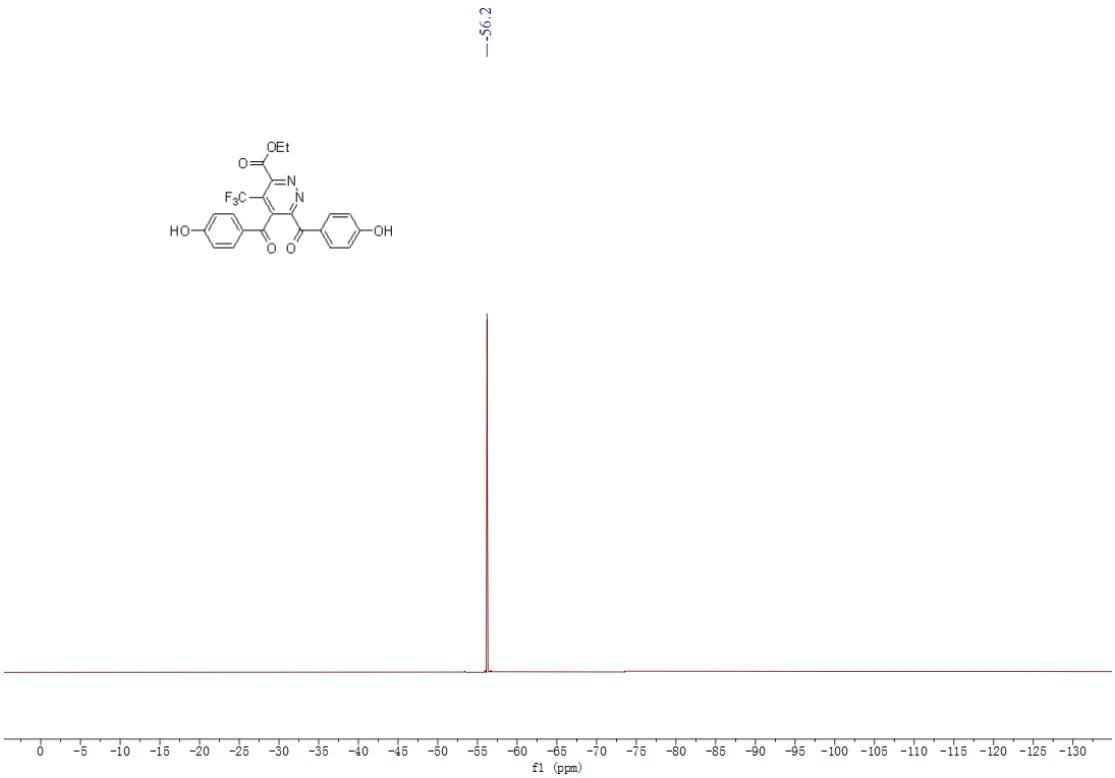
400 MHz ^{1}H NMR spectrum of **3i** in DMSO-d_6



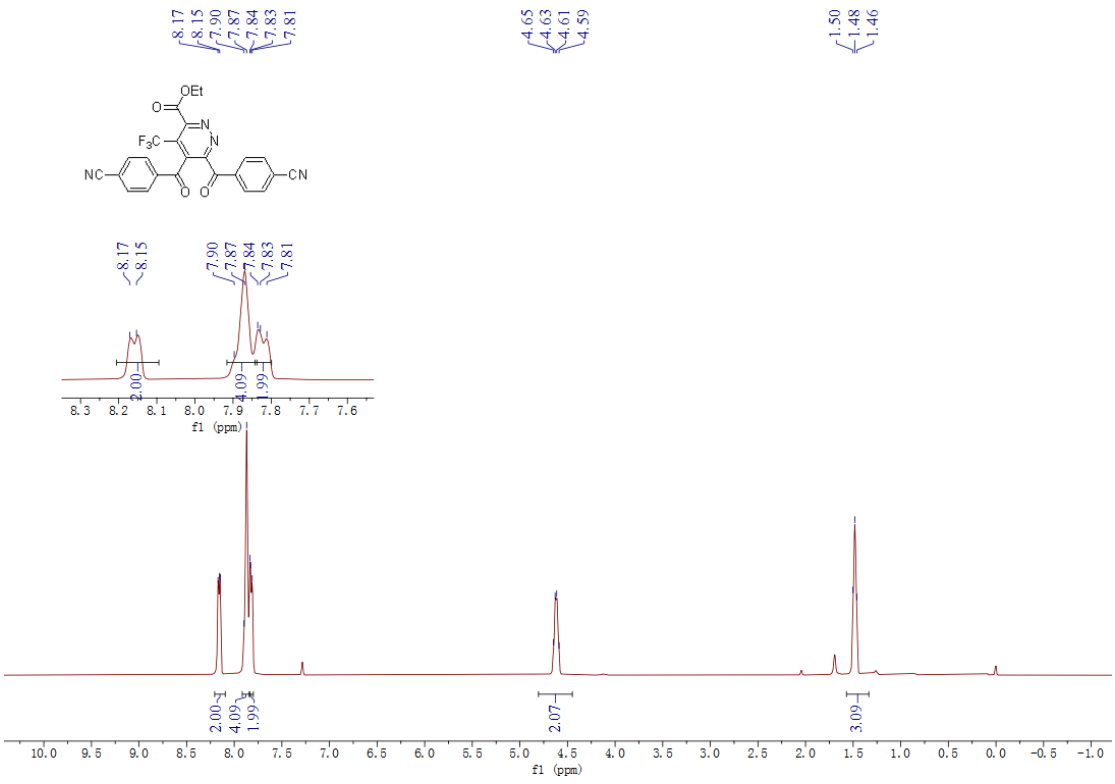
101 MHz ^{13}C NMR spectrum of **3i** in DMSO-d_6



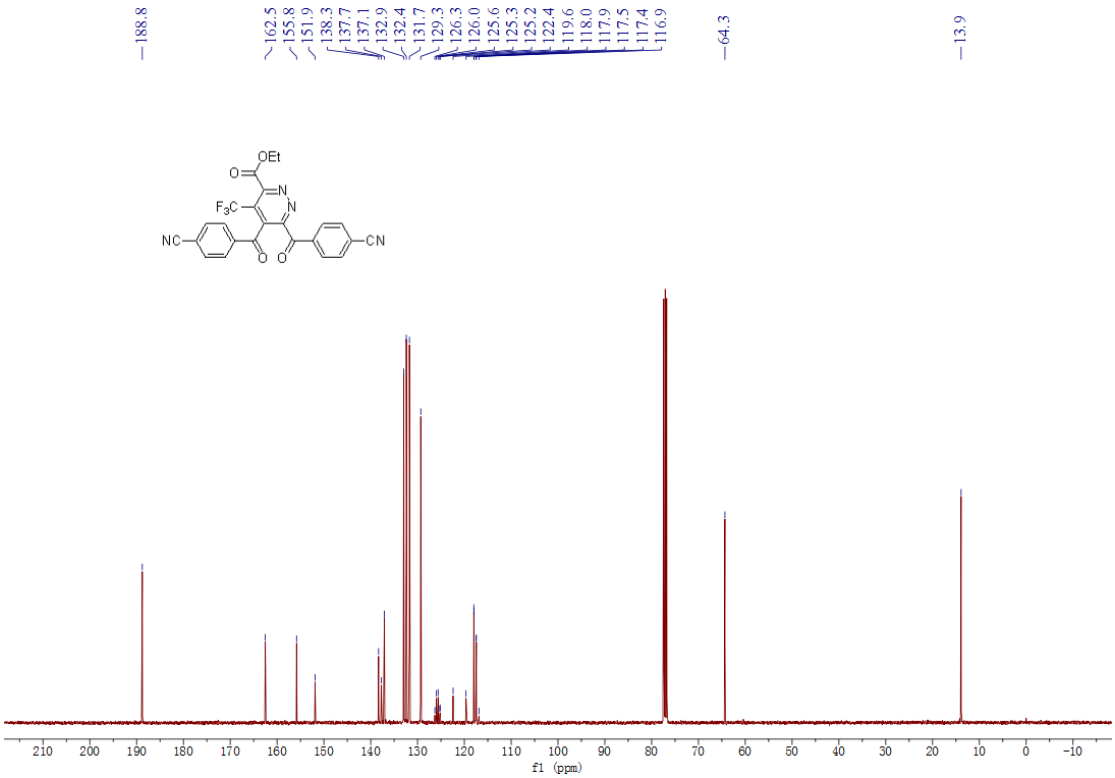
376 MHz ^{19}F NMR spectrum of **3i** in DMSO-d_6



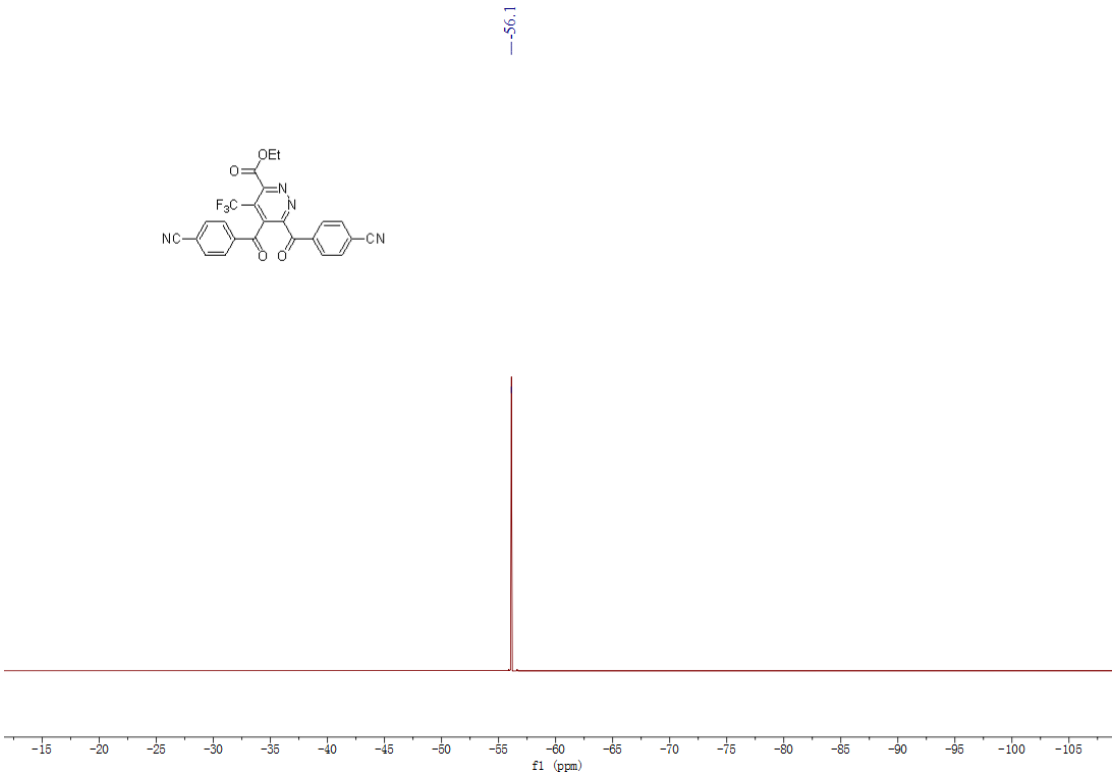
400 MHz ^{1}H NMR spectrum of **3j** in $CDCl_3$



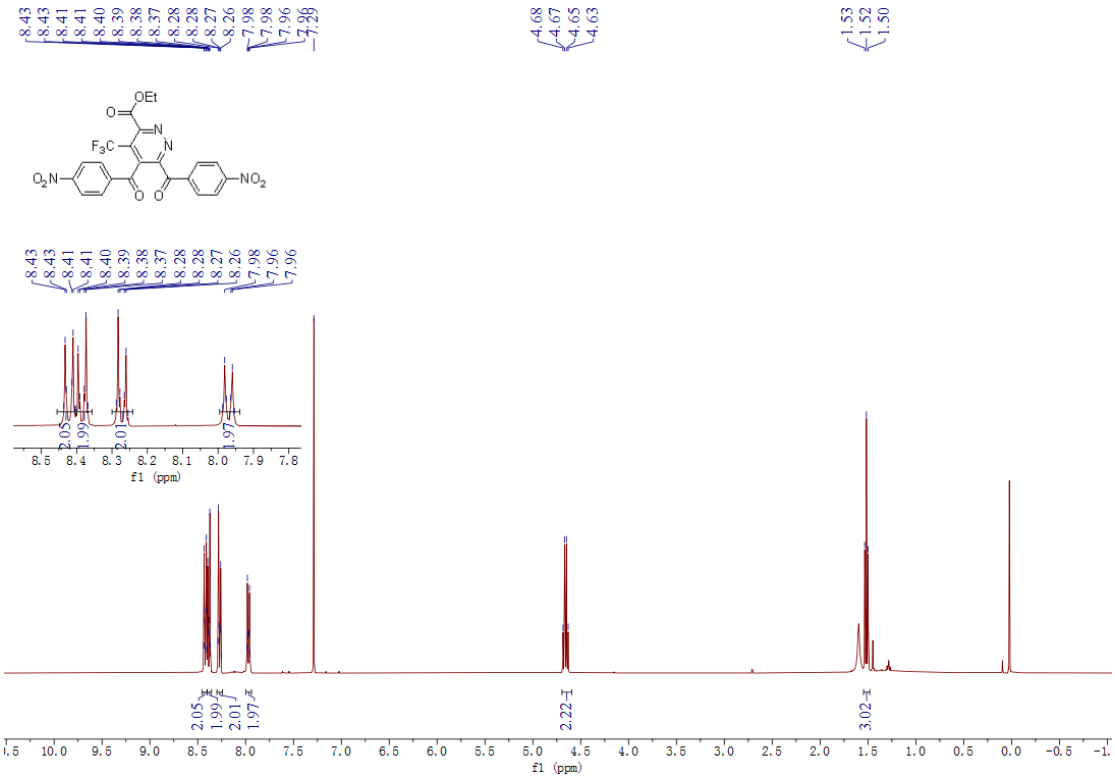
101 MHz ^{13}C NMR spectrum of **3j** in $CDCl_3$



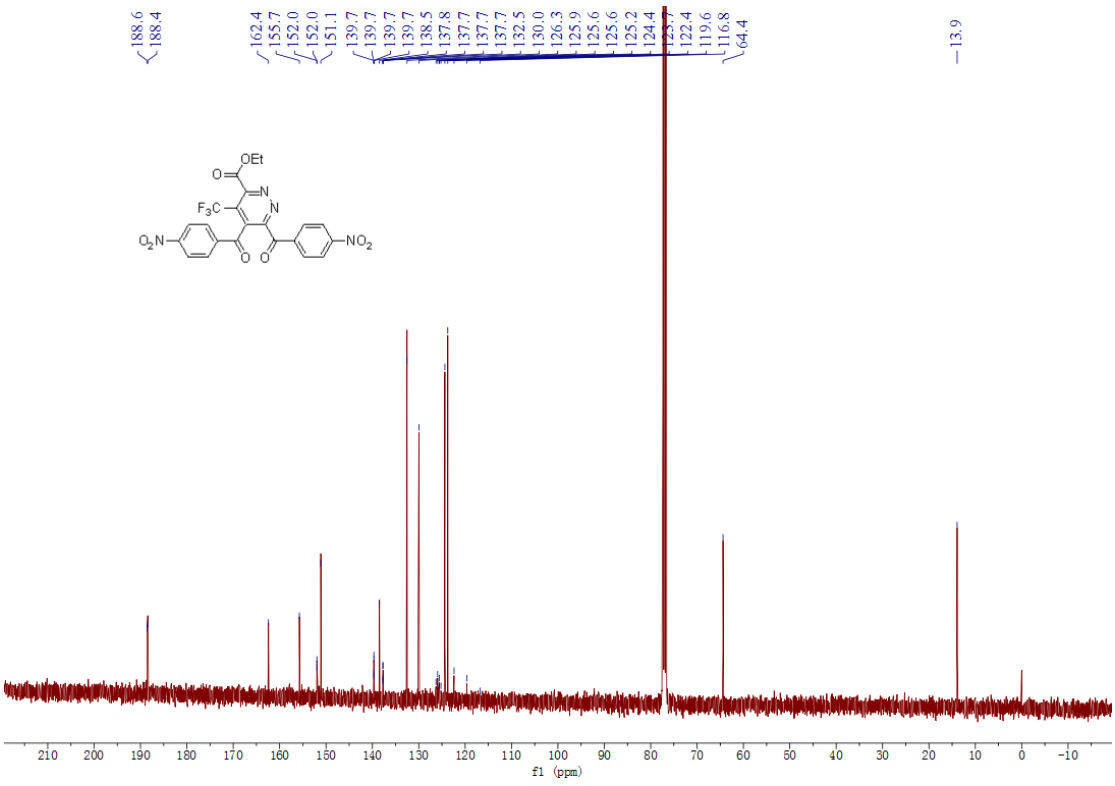
376 MHz ^{19}F NMR spectrum of **3j** in $CDCl_3$



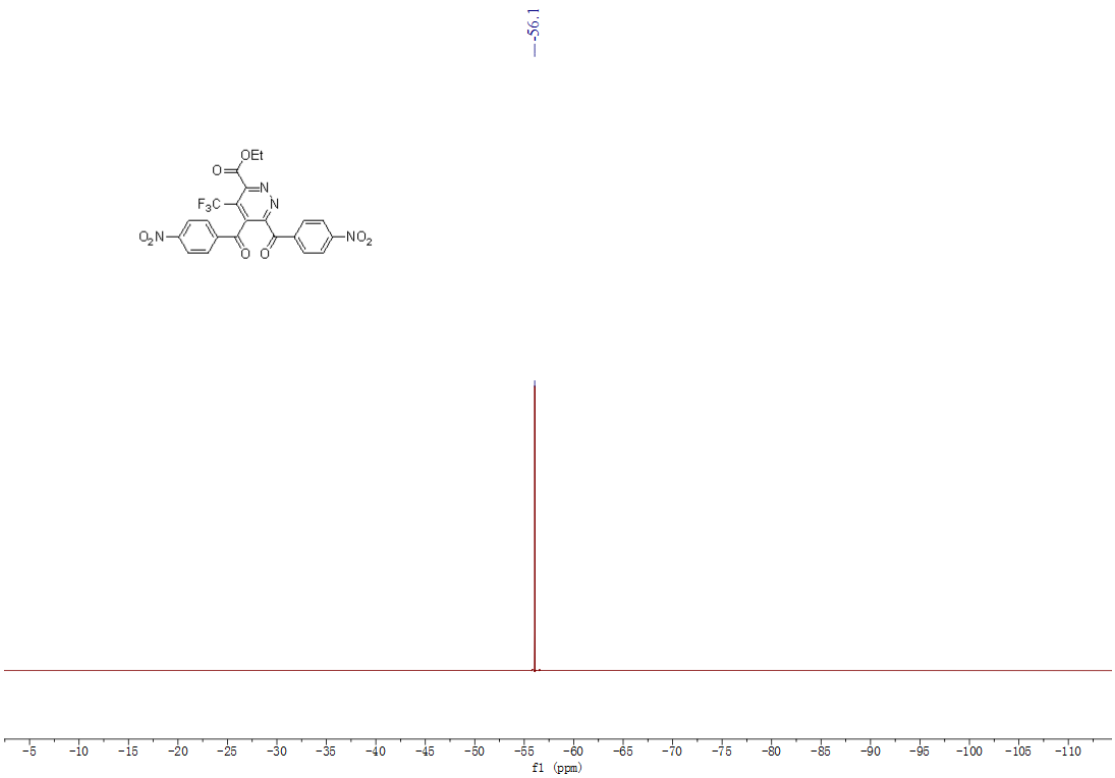
400 MHz ^{1}H NMR spectrum of **3k** in $CDCl_3$



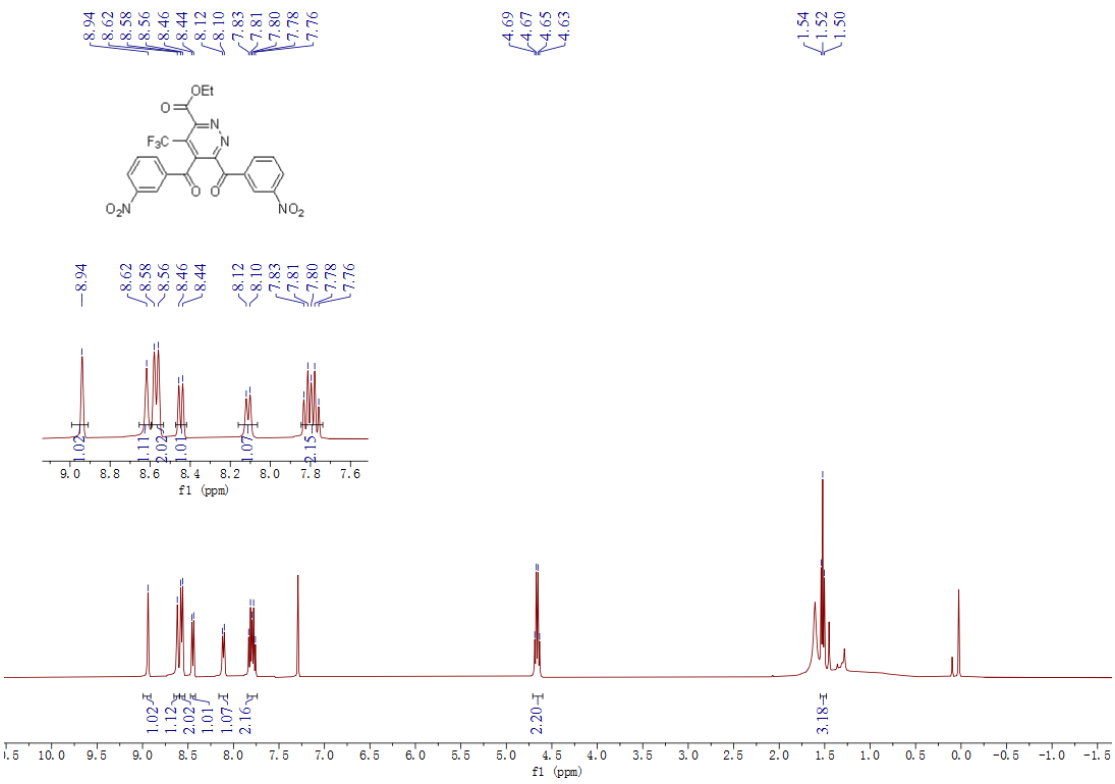
101 MHz ^{13}C NMR spectrum of **3k** in $CDCl_3$



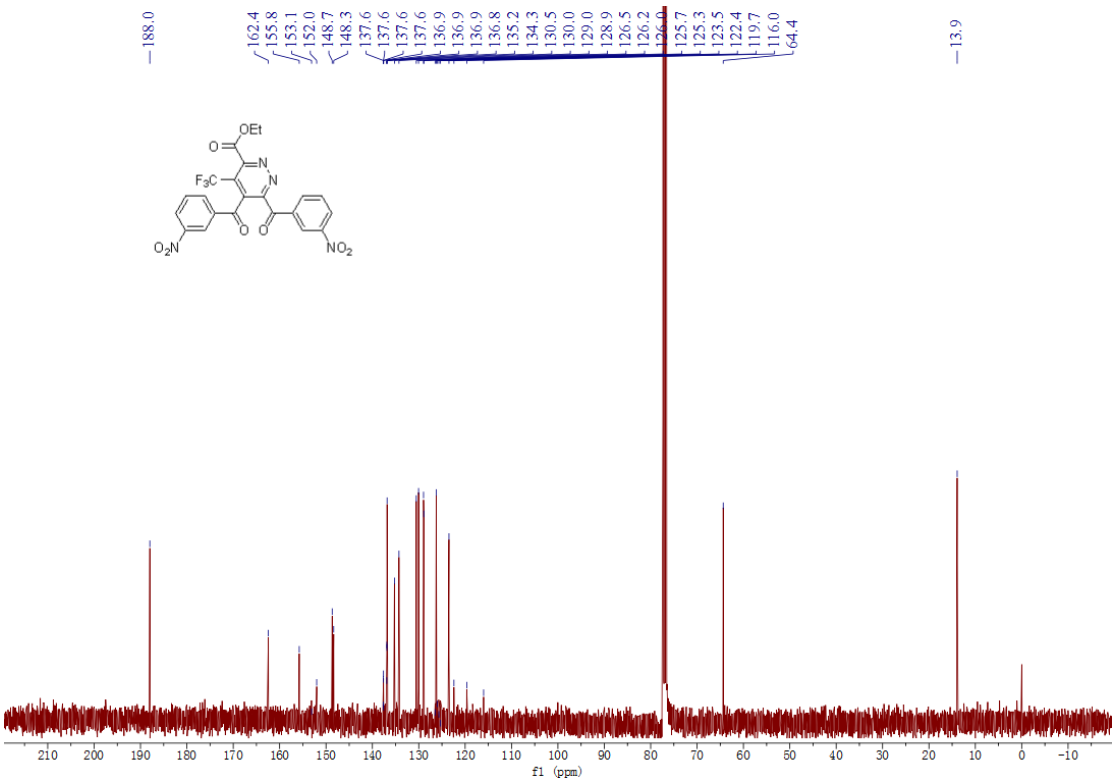
376 MHz ^{19}F NMR spectrum of **3k** in $CDCl_3$



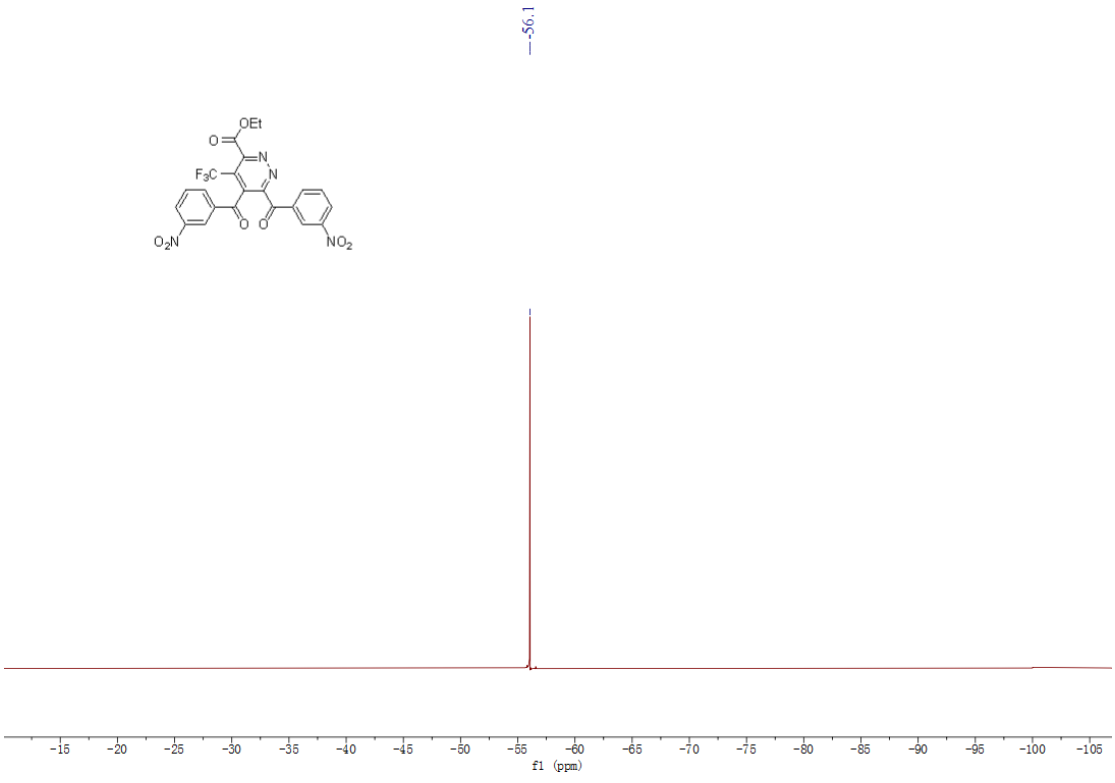
400 MHz ^{1}H NMR spectrum of **3l** in $CDCl_3$



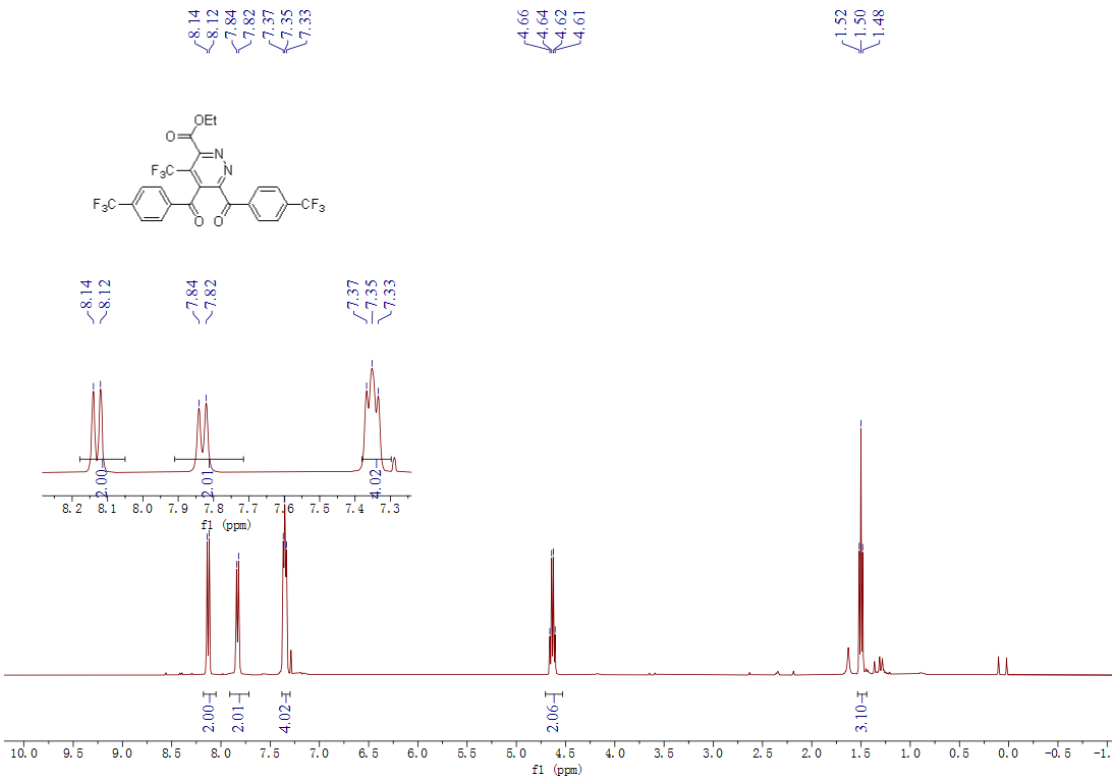
101 MHz ^{13}C NMR spectrum of **3l** in $CDCl_3$



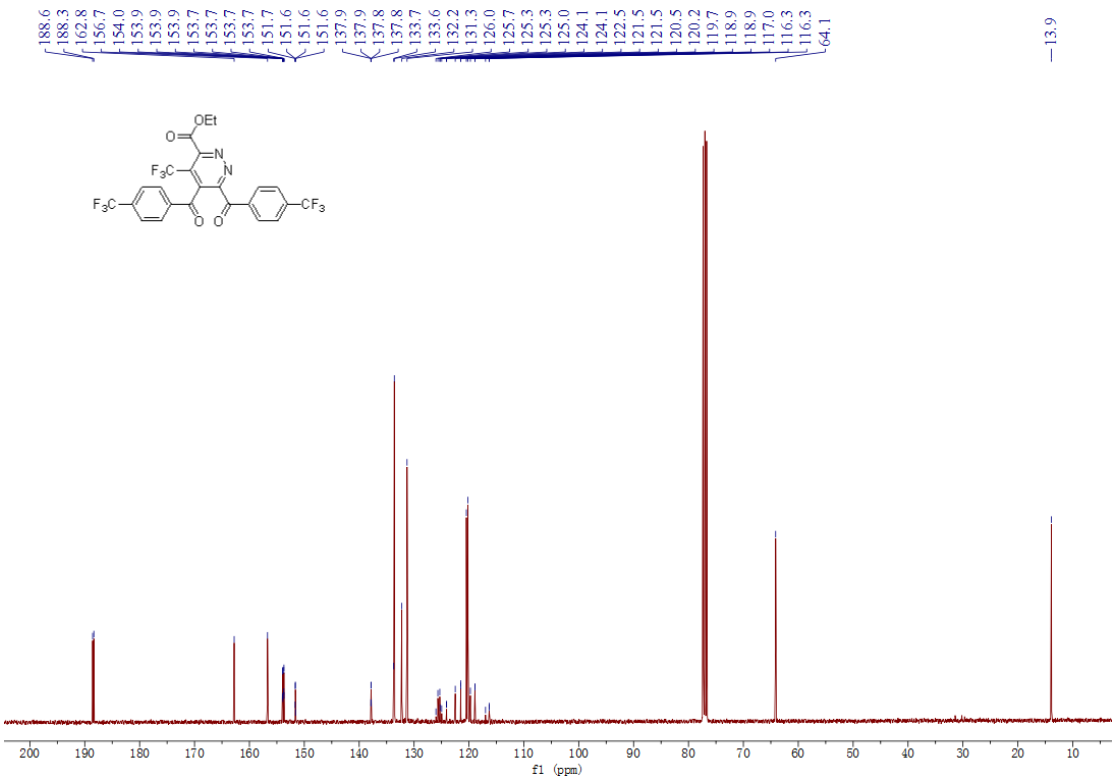
376 MHz ^{19}F NMR spectrum of **3l** in $CDCl_3$



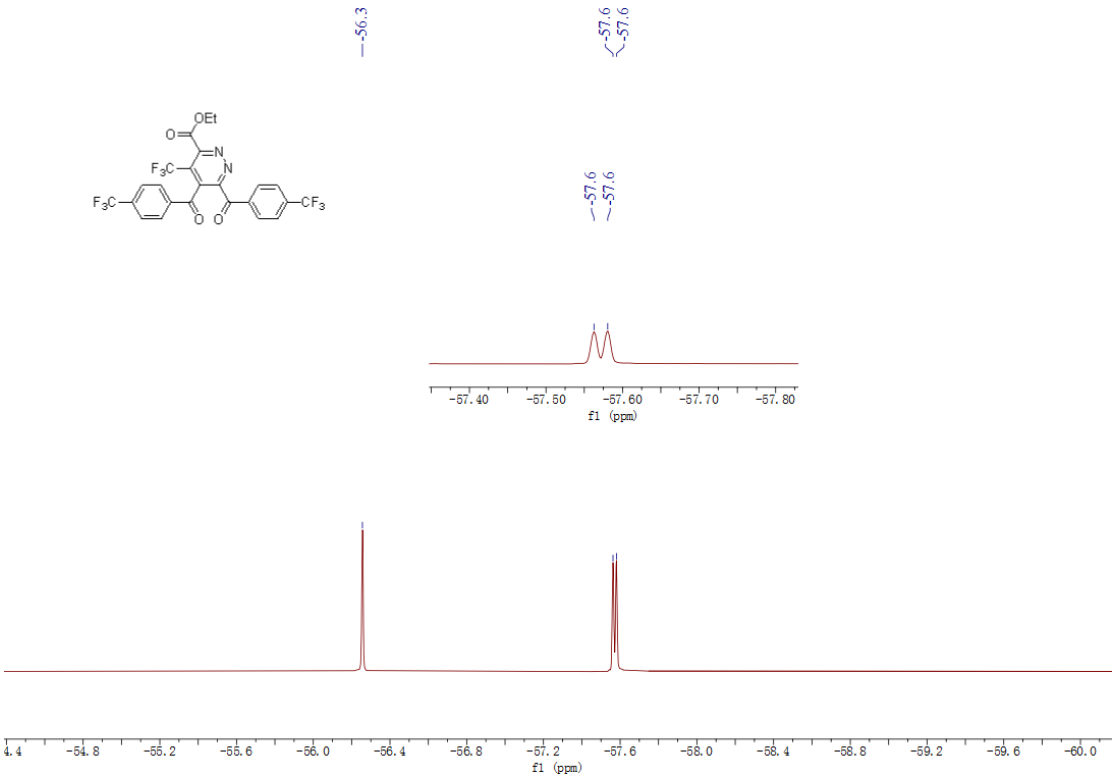
400 MHz ^{1}H NMR spectrum of **3m** in $CDCl_3$



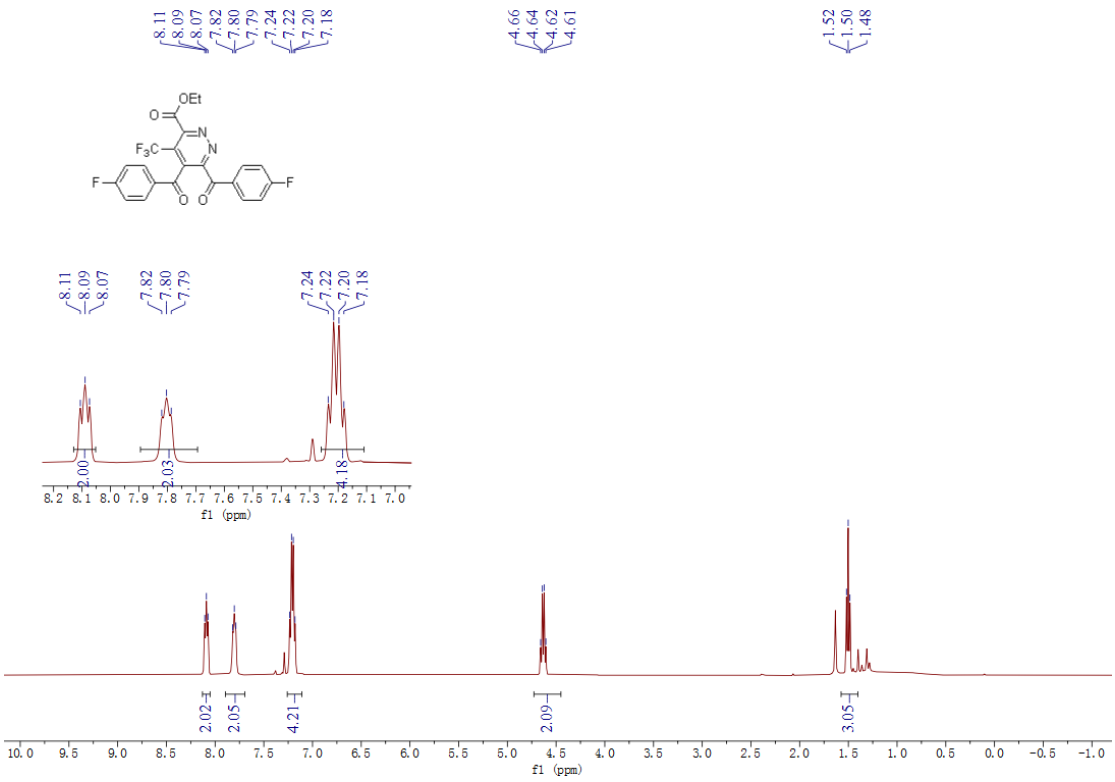
101 MHz ^{13}C NMR spectrum of **3m** in $CDCl_3$



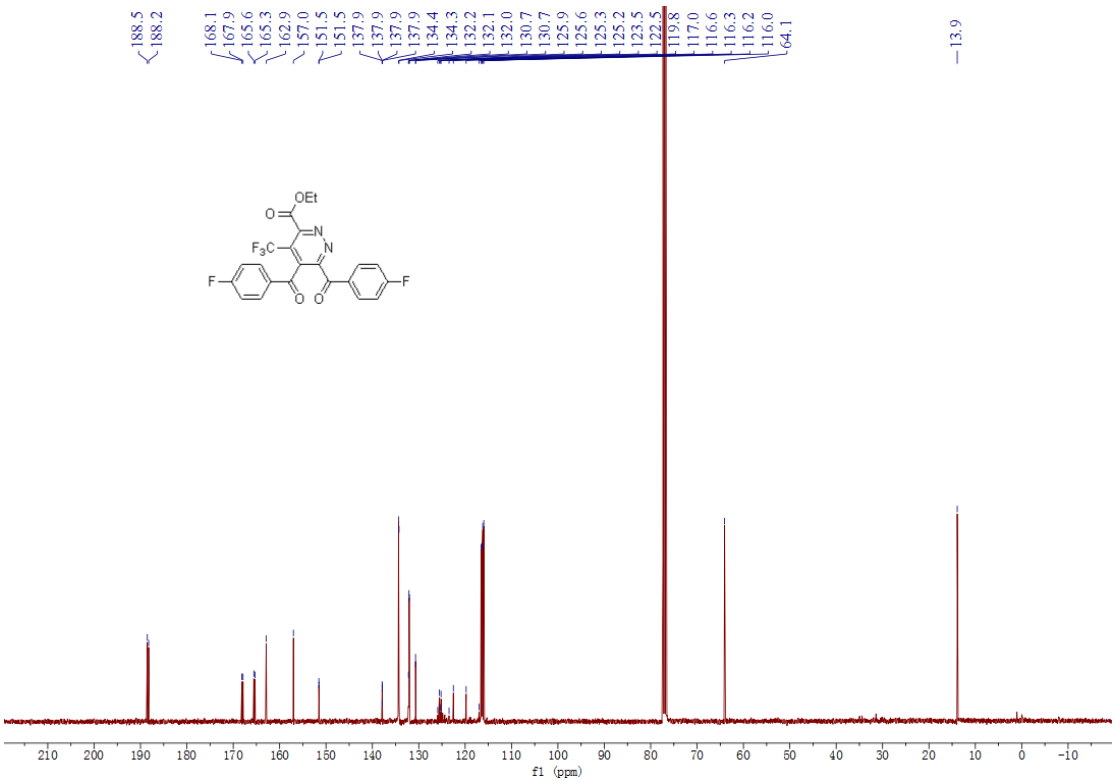
376 MHz ^{19}F NMR spectrum of **3m** in $CDCl_3$



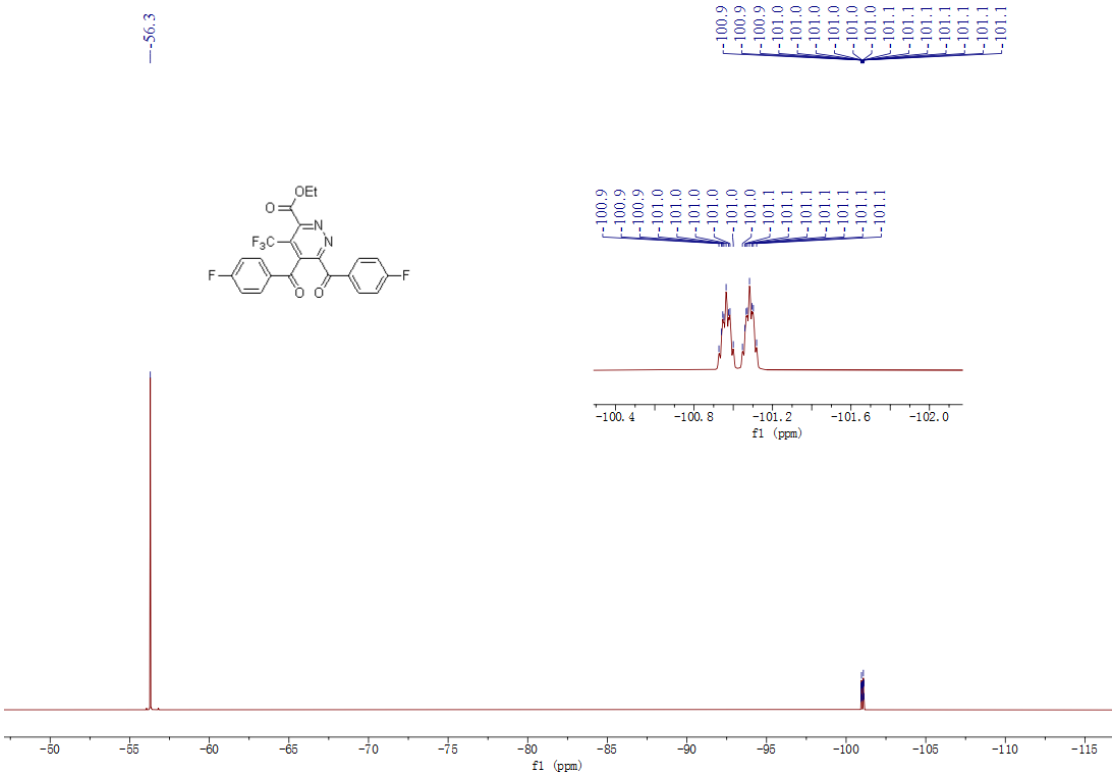
400 MHz ^{1}H NMR spectrum of **3n** in $CDCl_3$



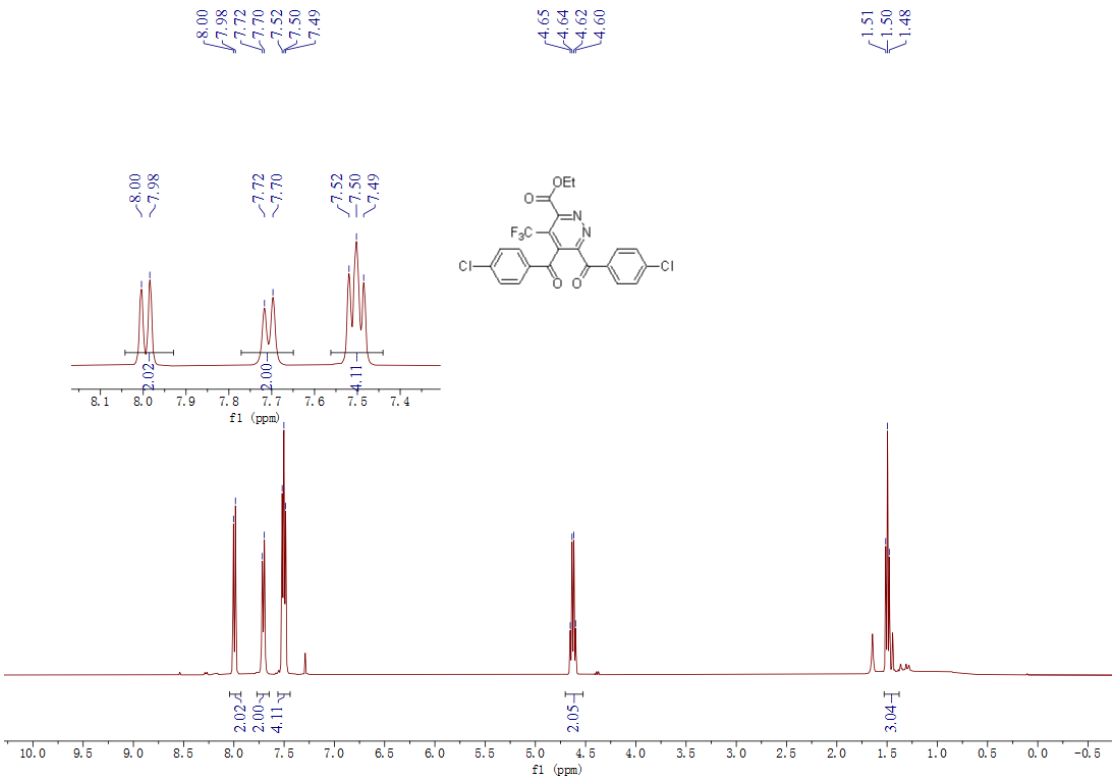
101 MHz ^{13}C NMR spectrum of **3n** in $CDCl_3$



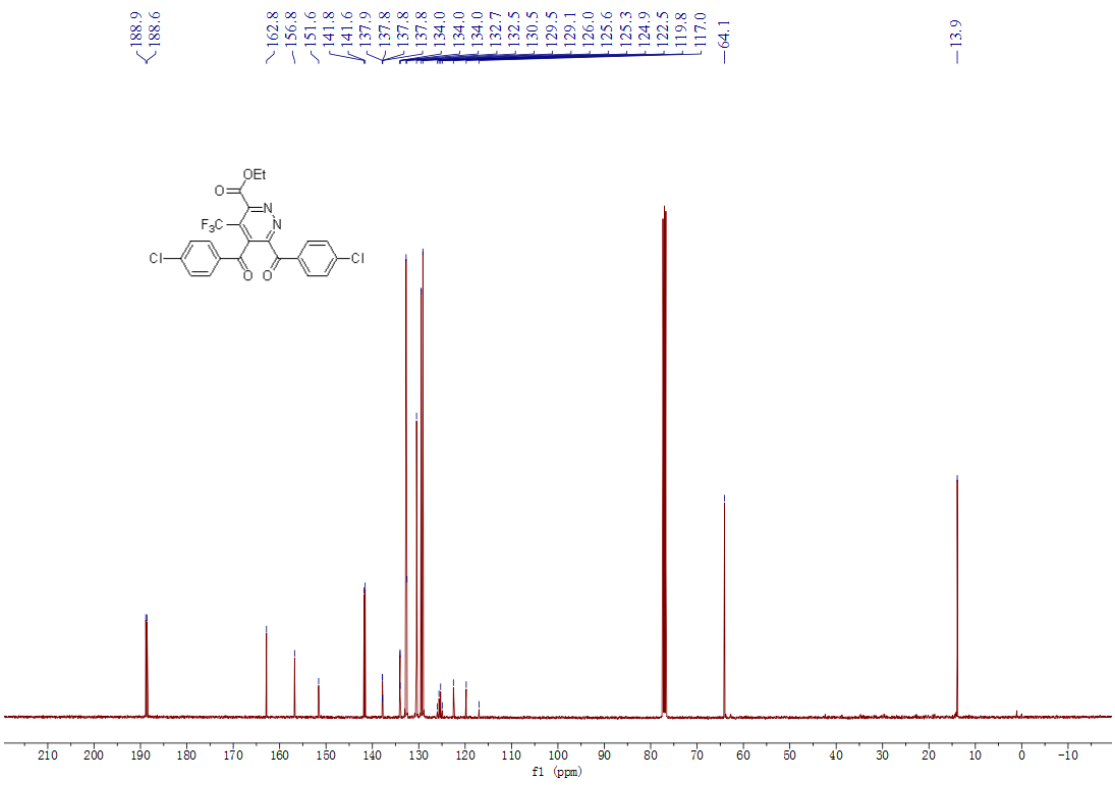
376 MHz ^{19}F NMR spectrum of **3n** in $CDCl_3$



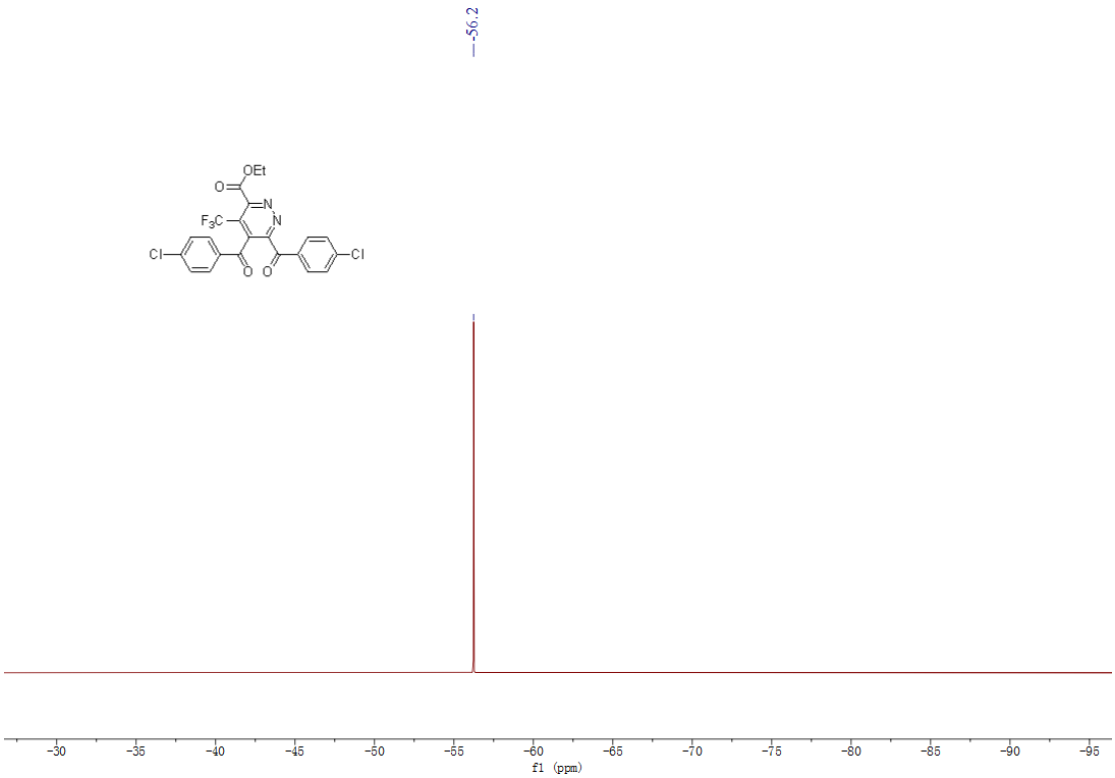
400 MHz ^{1}H NMR spectrum of **3o** in $CDCl_3$



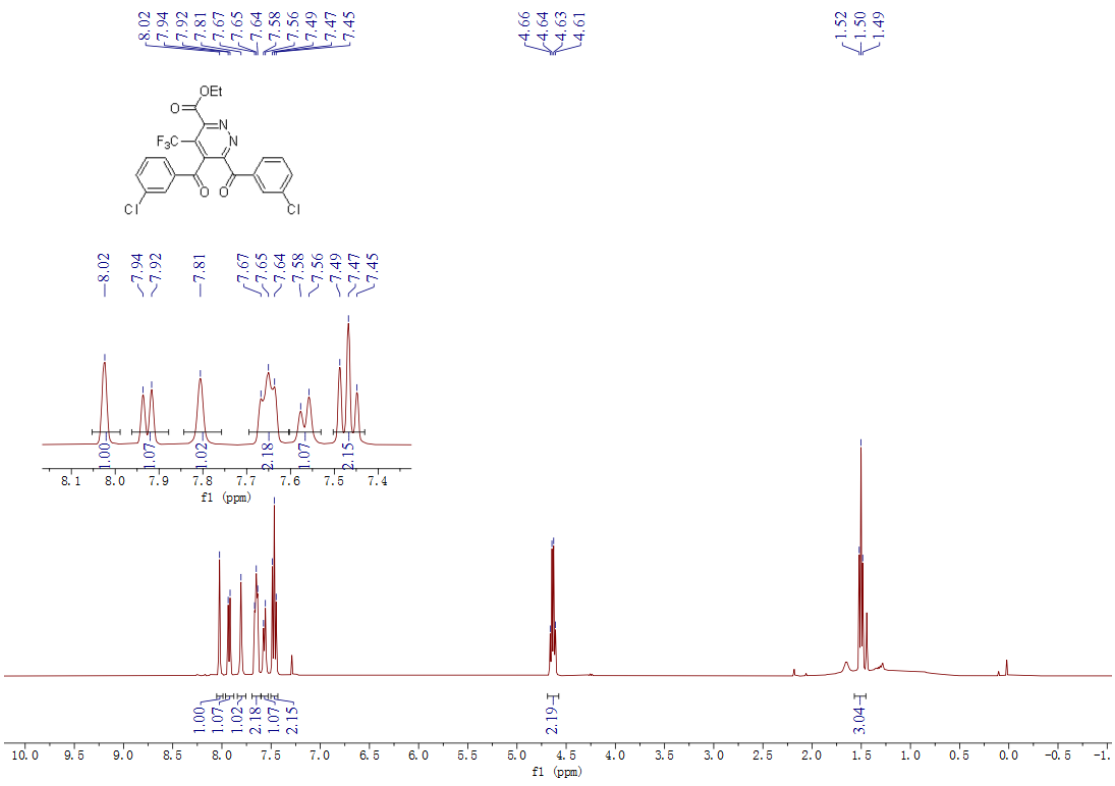
101 MHz ^{13}C NMR spectrum of **3o** in $CDCl_3$



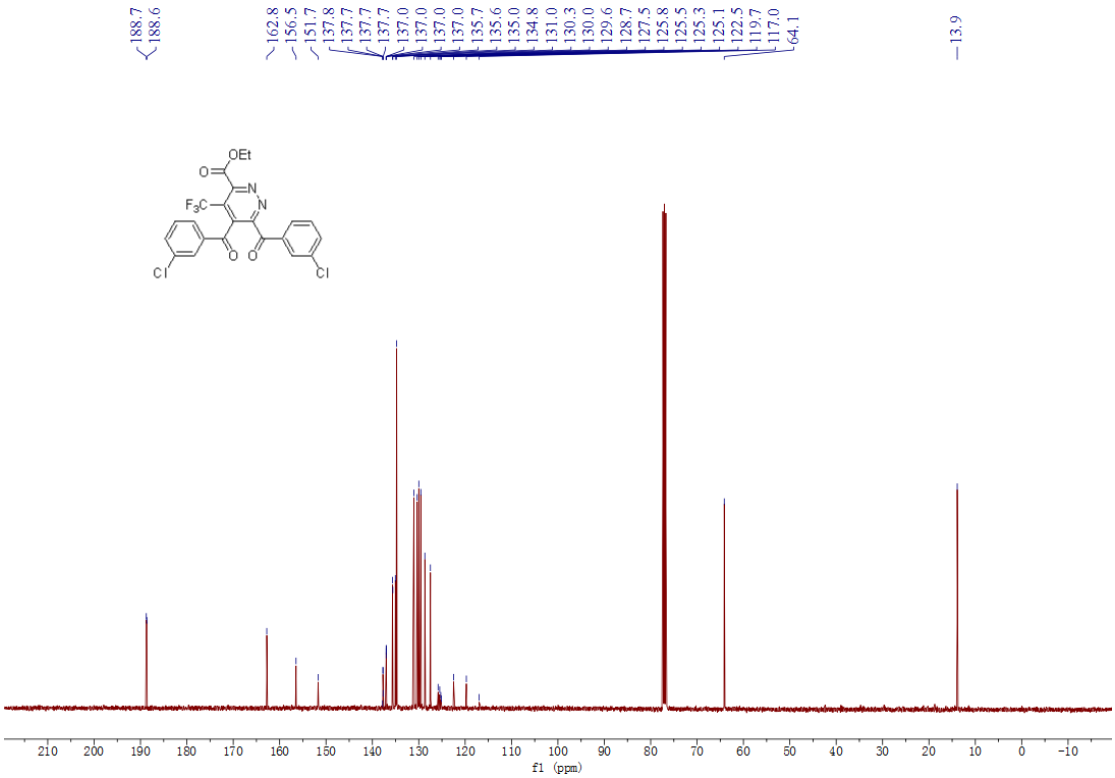
376 MHz ^{19}F NMR spectrum of **3o** in $CDCl_3$



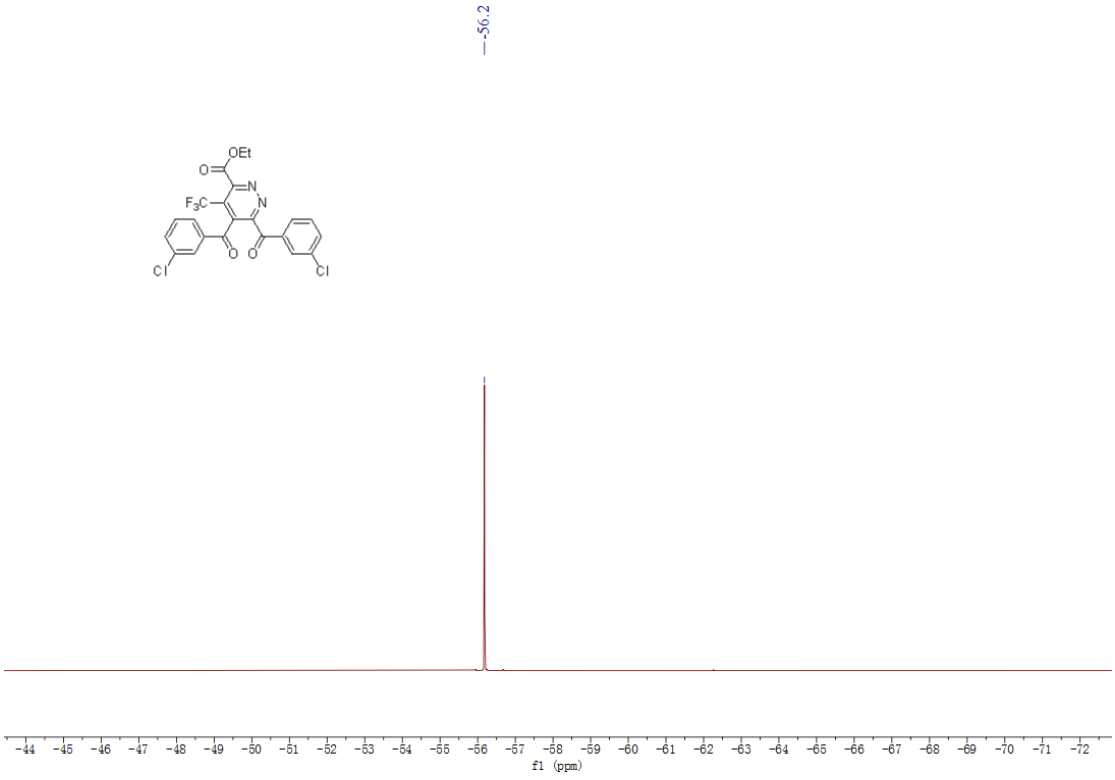
400 MHz ^{1}H NMR spectrum of **3p** in $CDCl_3$



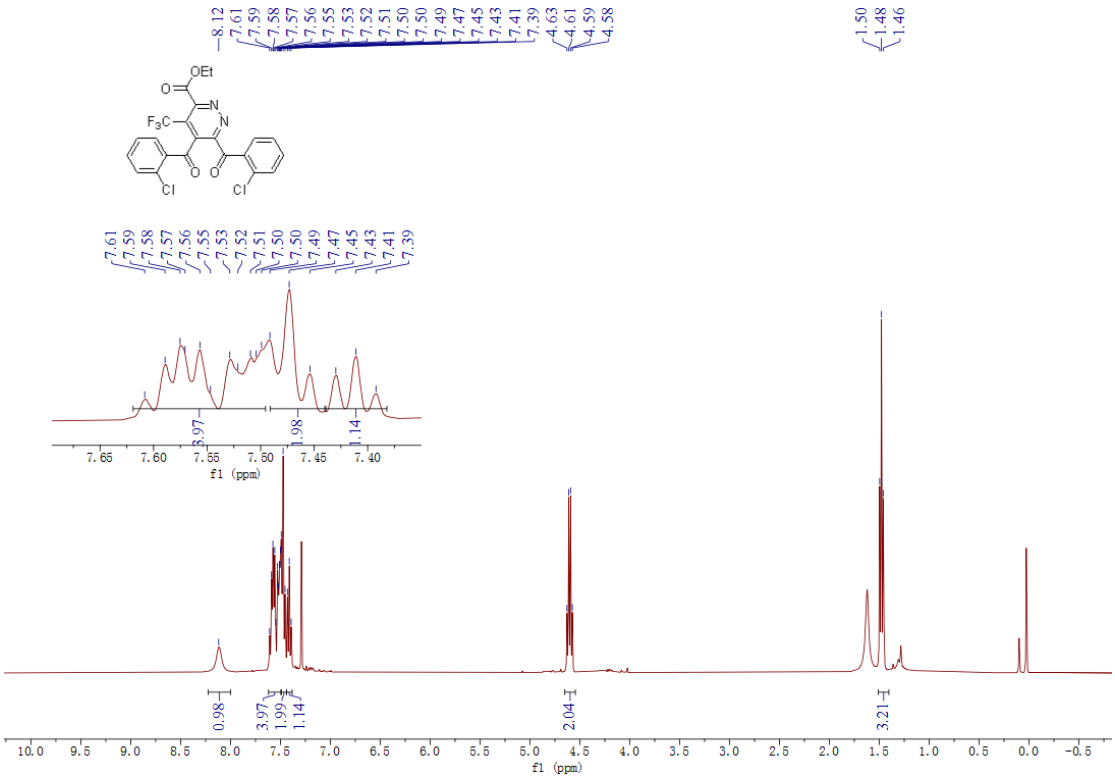
101 MHz ^{13}C NMR spectrum of **3p** in $CDCl_3$



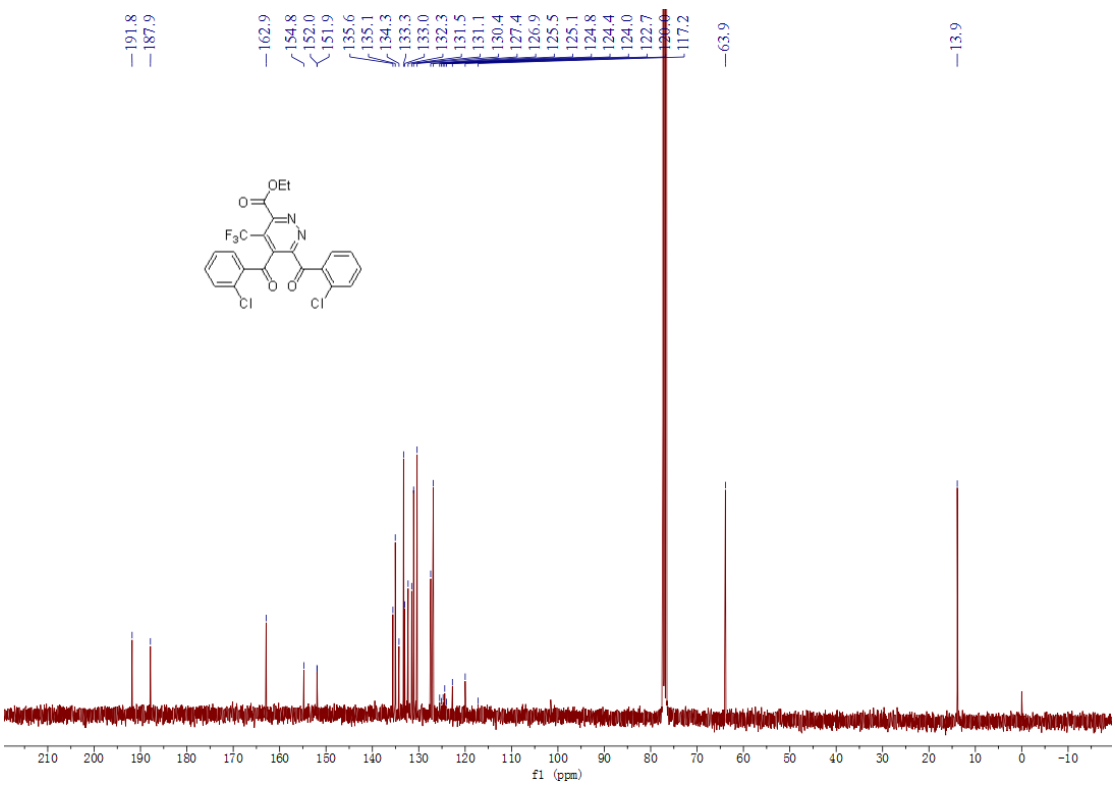
376 MHz ^{19}F NMR spectrum of **3p** in $CDCl_3$



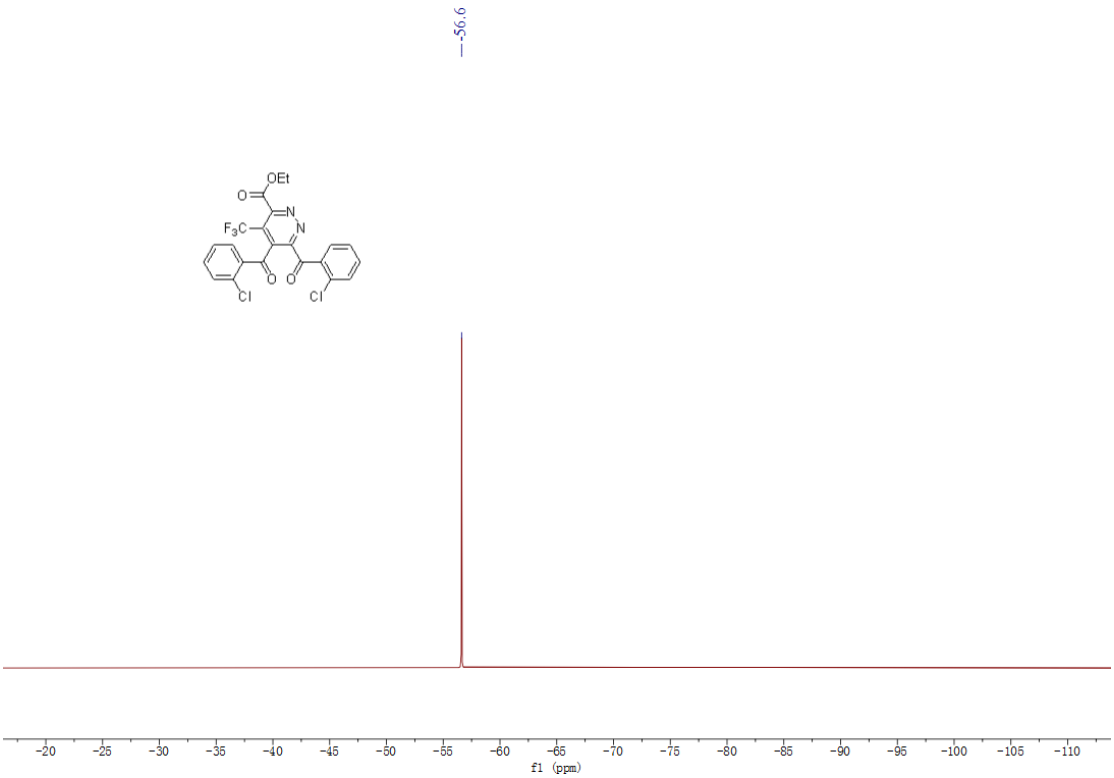
400 MHz ^{1}H NMR spectrum of **3q** in $CDCl_3$



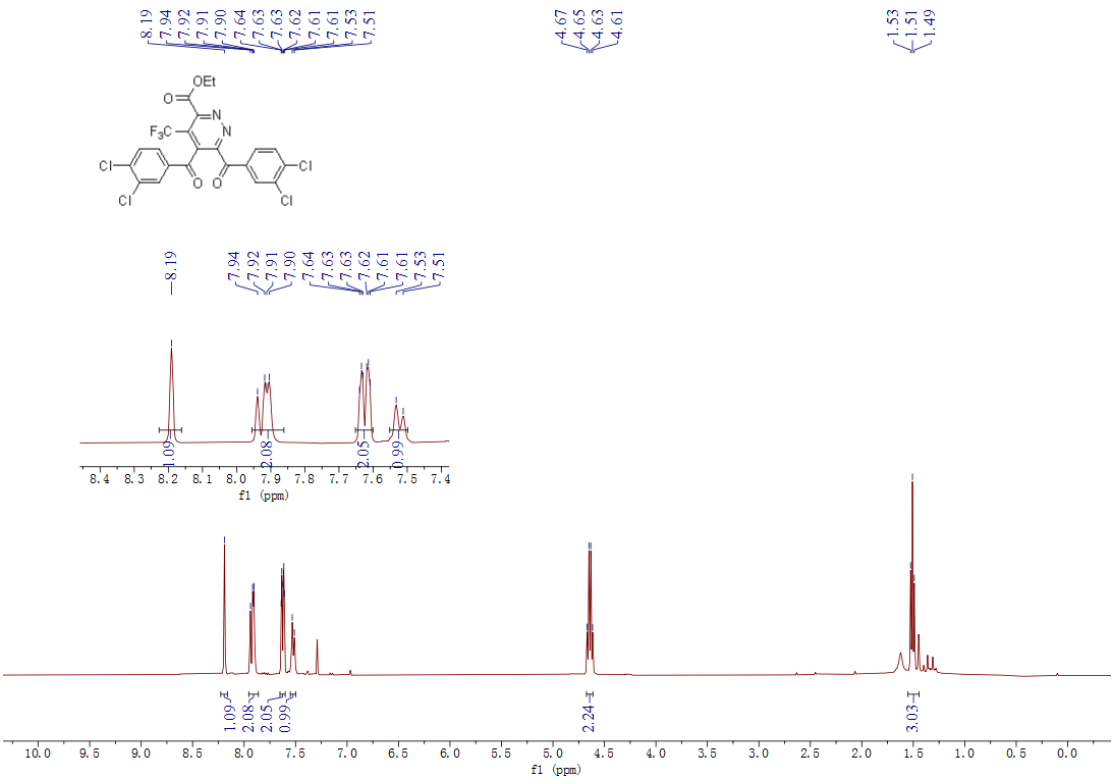
101 MHz ^{13}C NMR spectrum of **3q** in $CDCl_3$



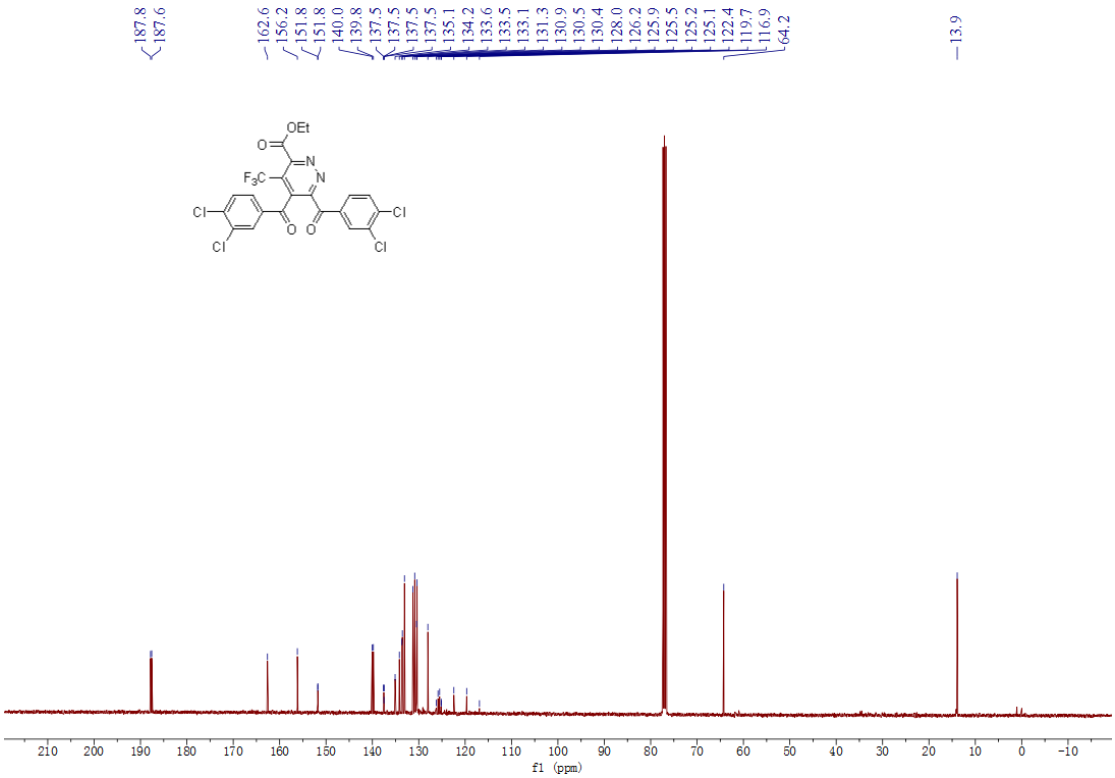
376 MHz ^{19}F NMR spectrum of **3q** in $CDCl_3$



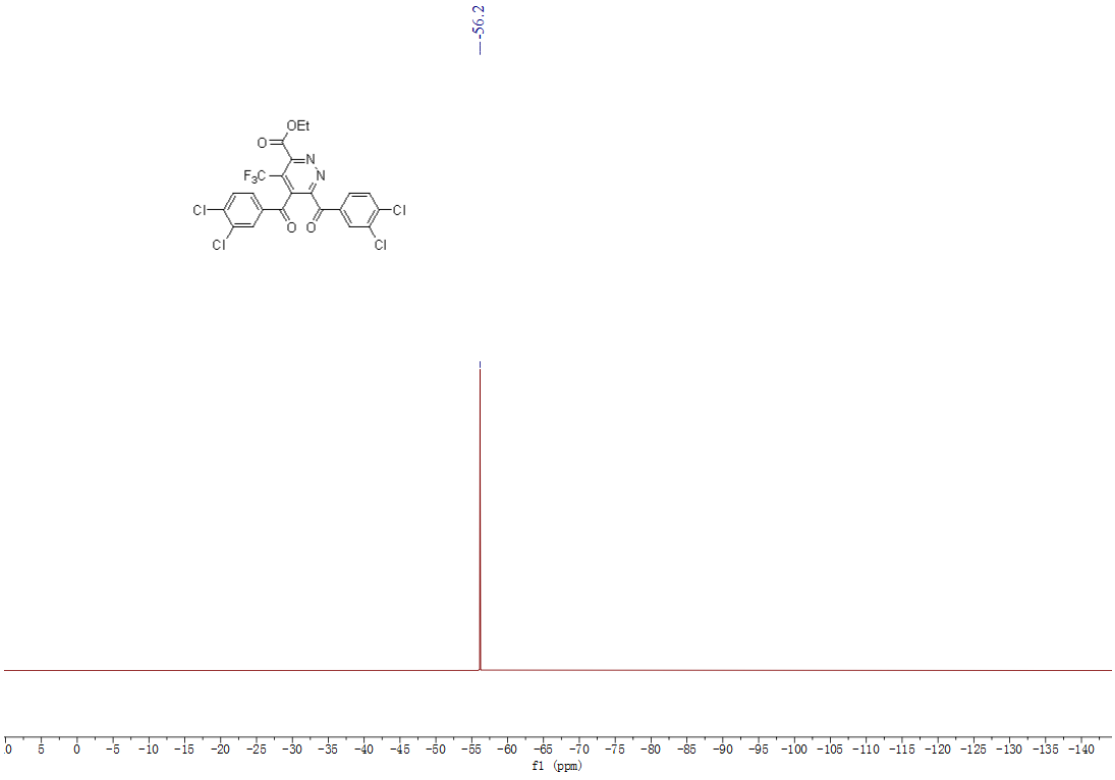
400 MHz ^{1}H NMR spectrum of **3r** in $CDCl_3$



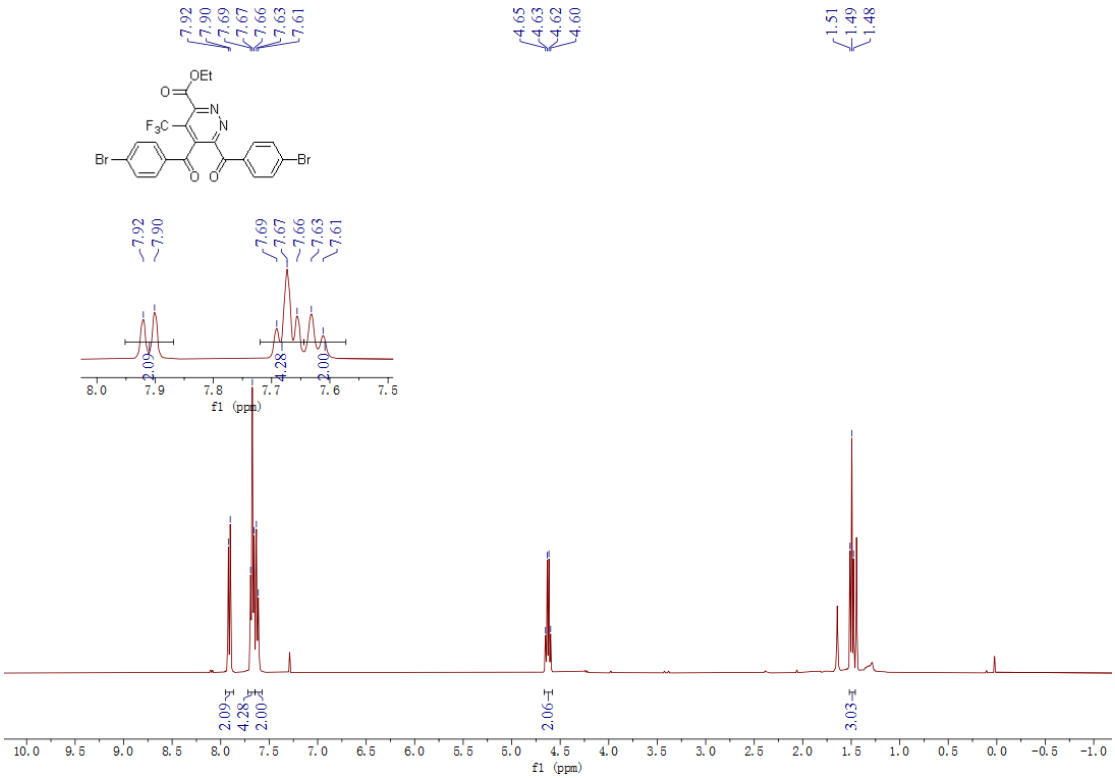
101 MHz ^{13}C NMR spectrum of **3r** in $CDCl_3$



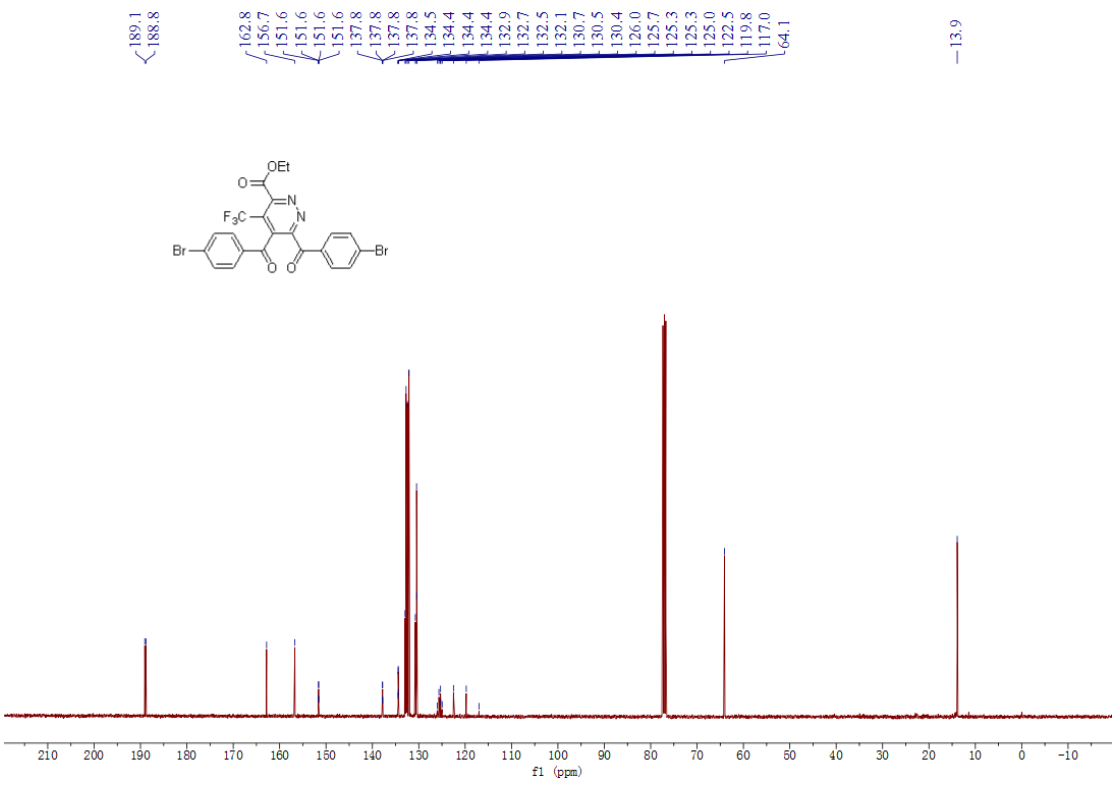
376 MHz ^{19}F NMR spectrum of **3r** in $CDCl_3$



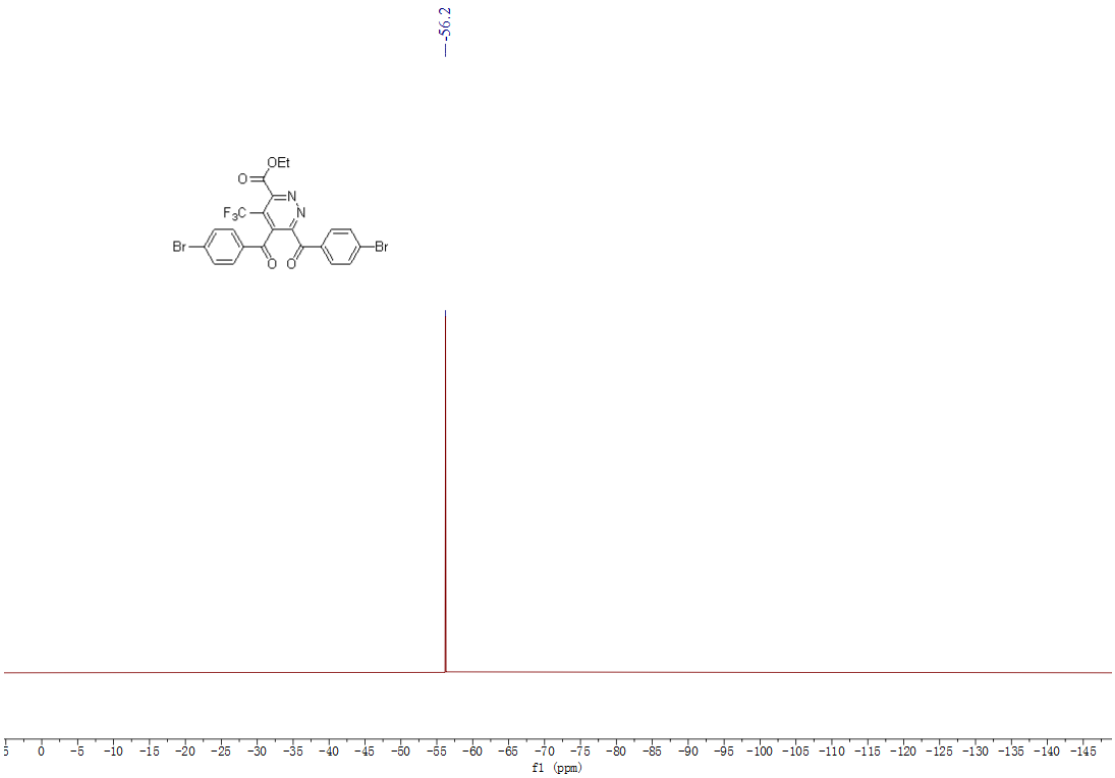
400 MHz ^{1}H NMR spectrum of **3s** in $CDCl_3$



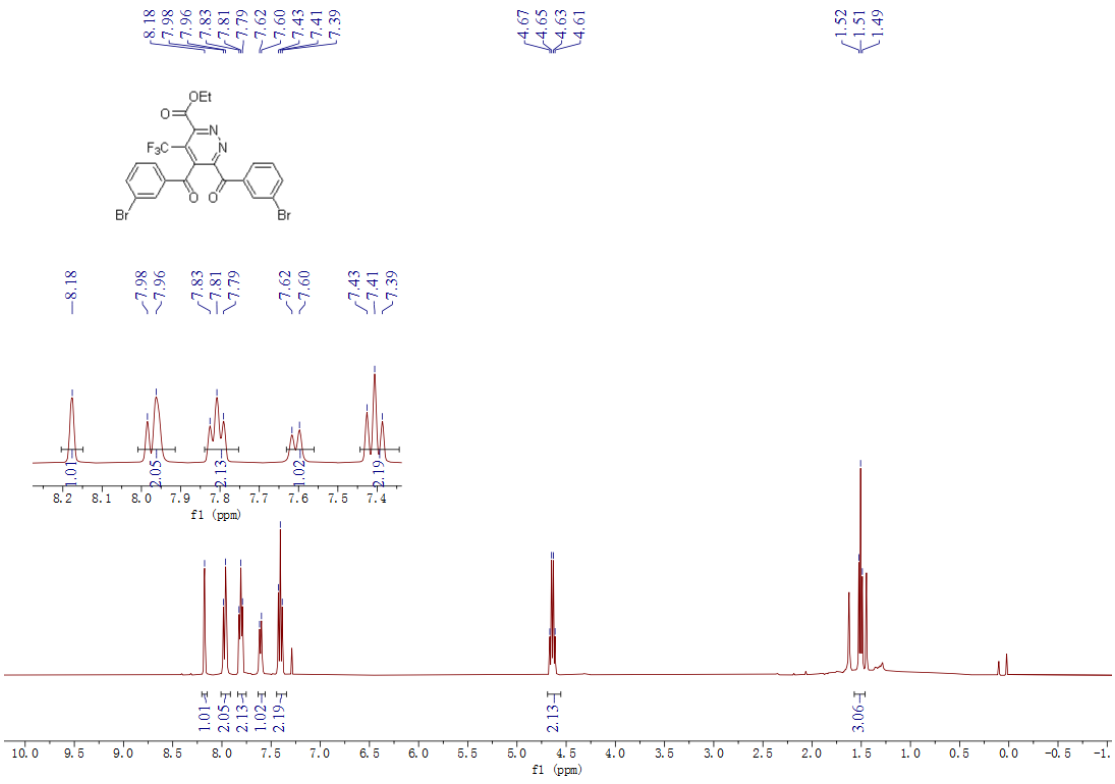
101 MHz ^{13}C NMR spectrum of **3s** in $CDCl_3$



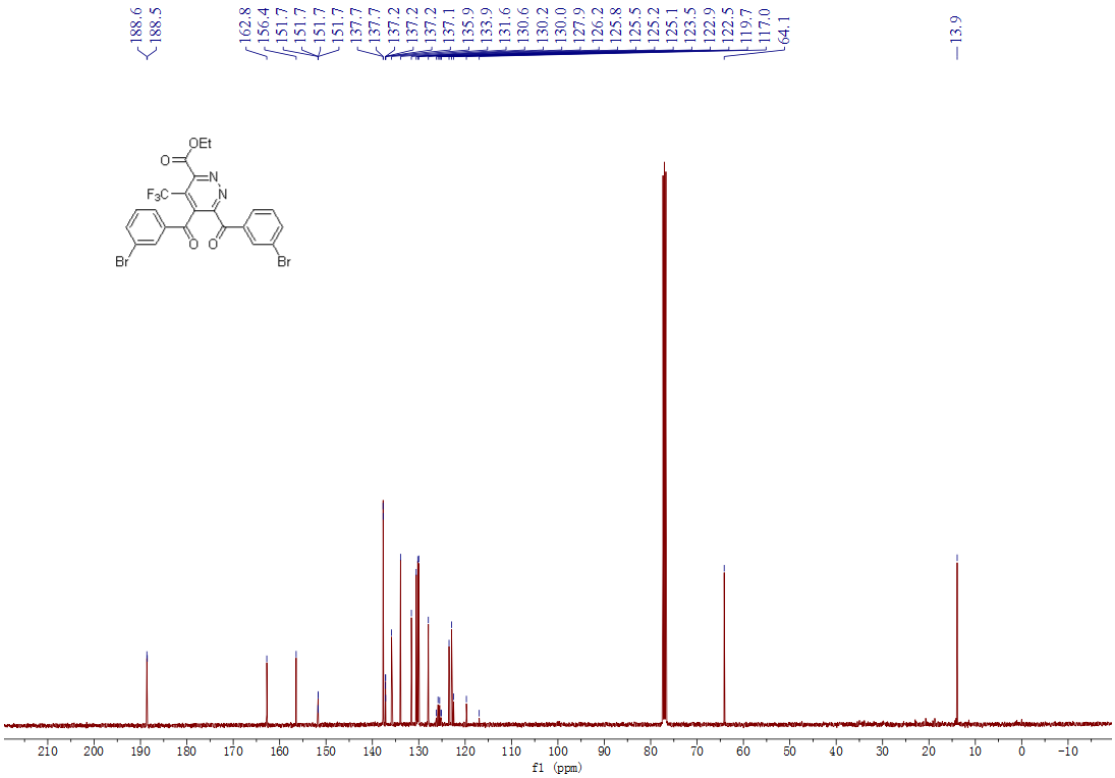
376 MHz ^{19}F NMR spectrum of **3s** in $CDCl_3$



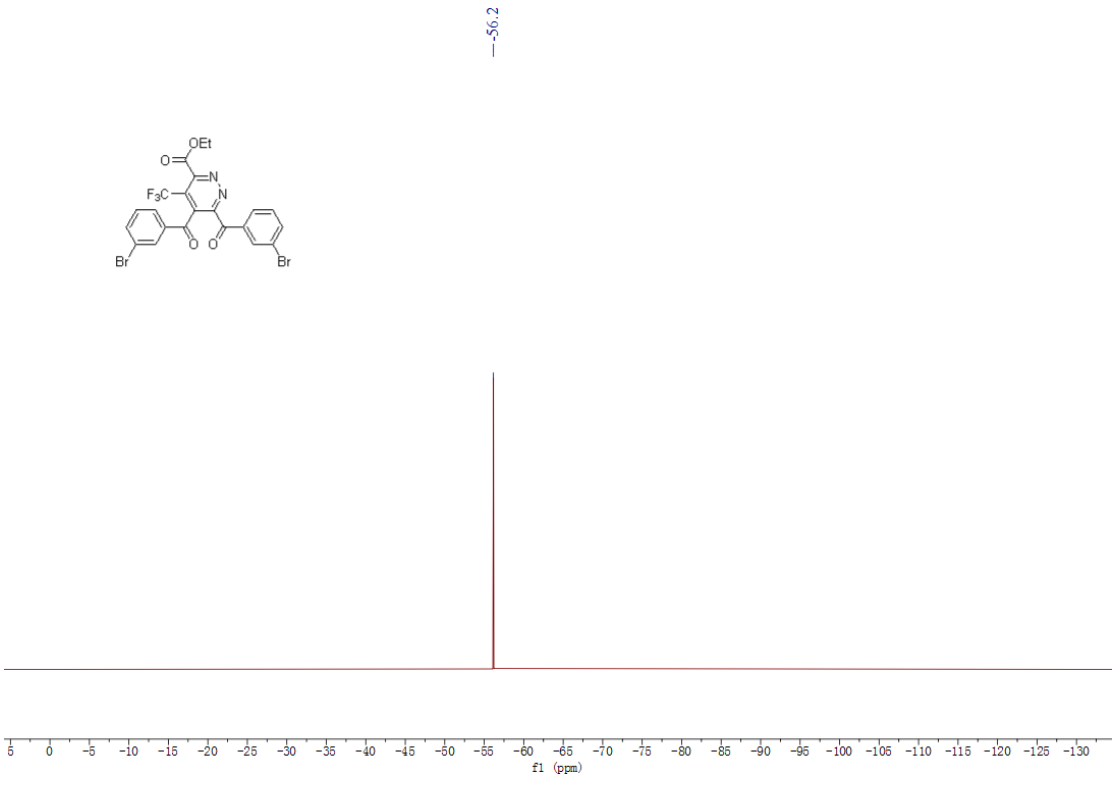
400 MHz ^{1}H NMR spectrum of **3t** in $CDCl_3$



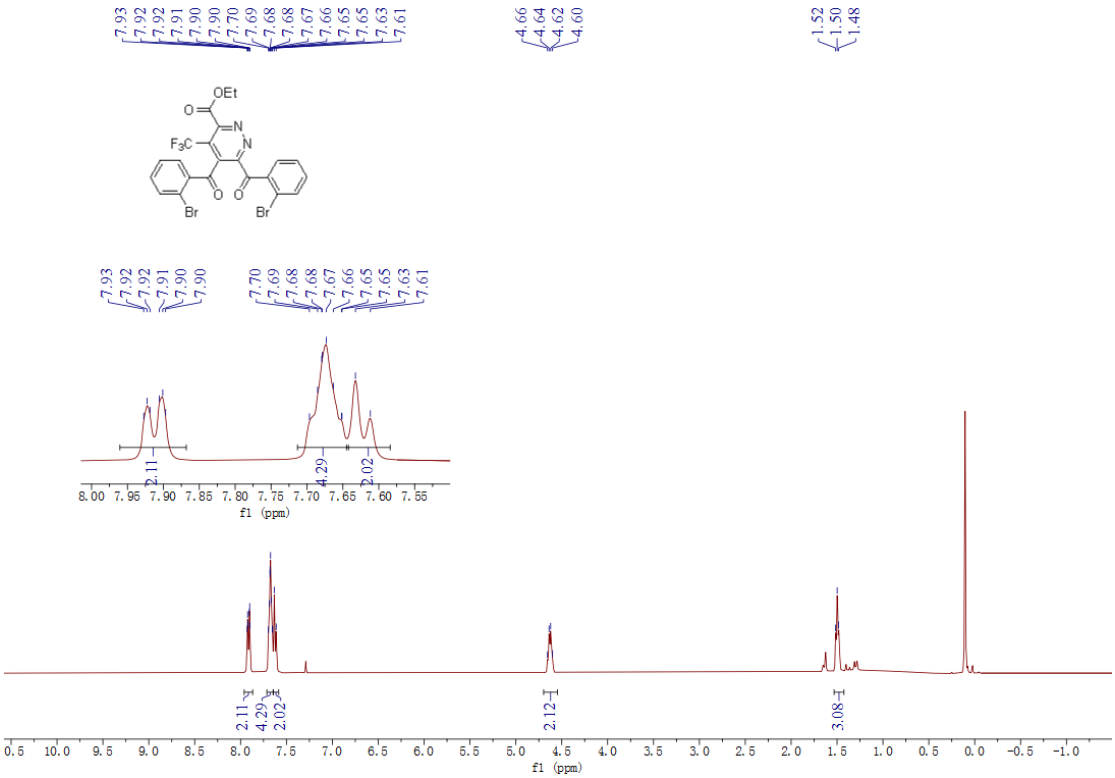
101 MHz ^{13}C NMR spectrum of **3t** in $CDCl_3$



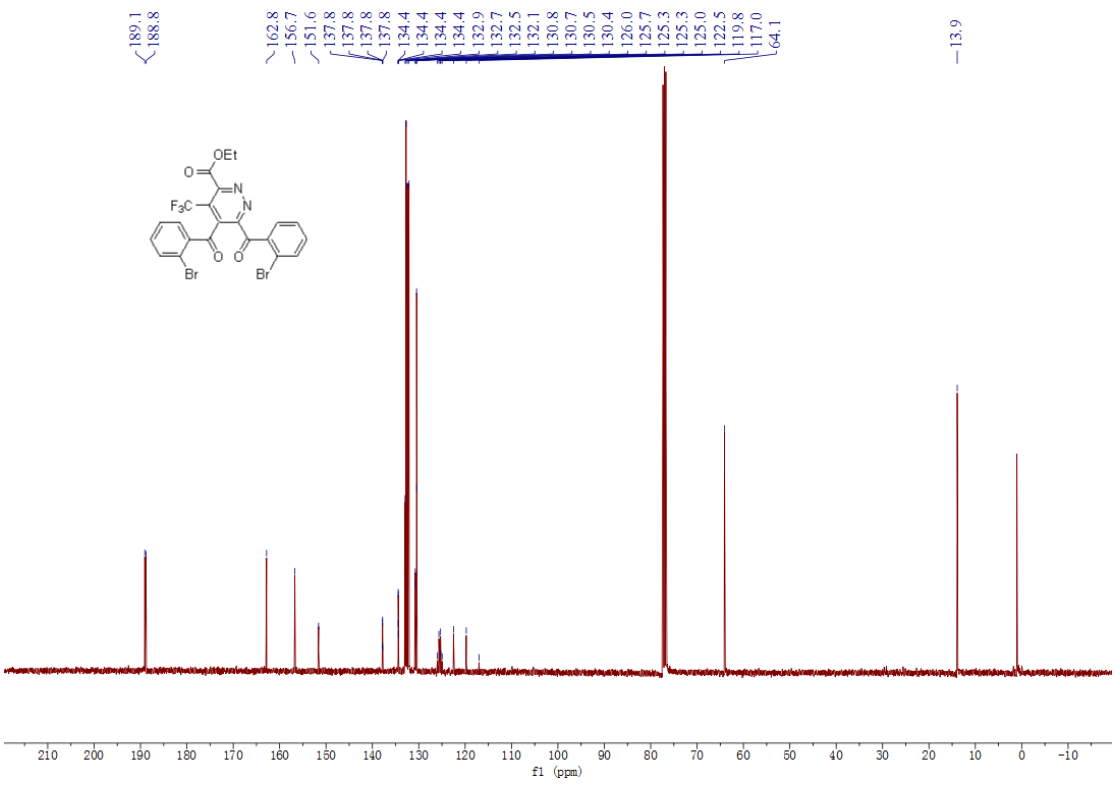
376 MHz ^{19}F NMR spectrum of **3t** in $CDCl_3$



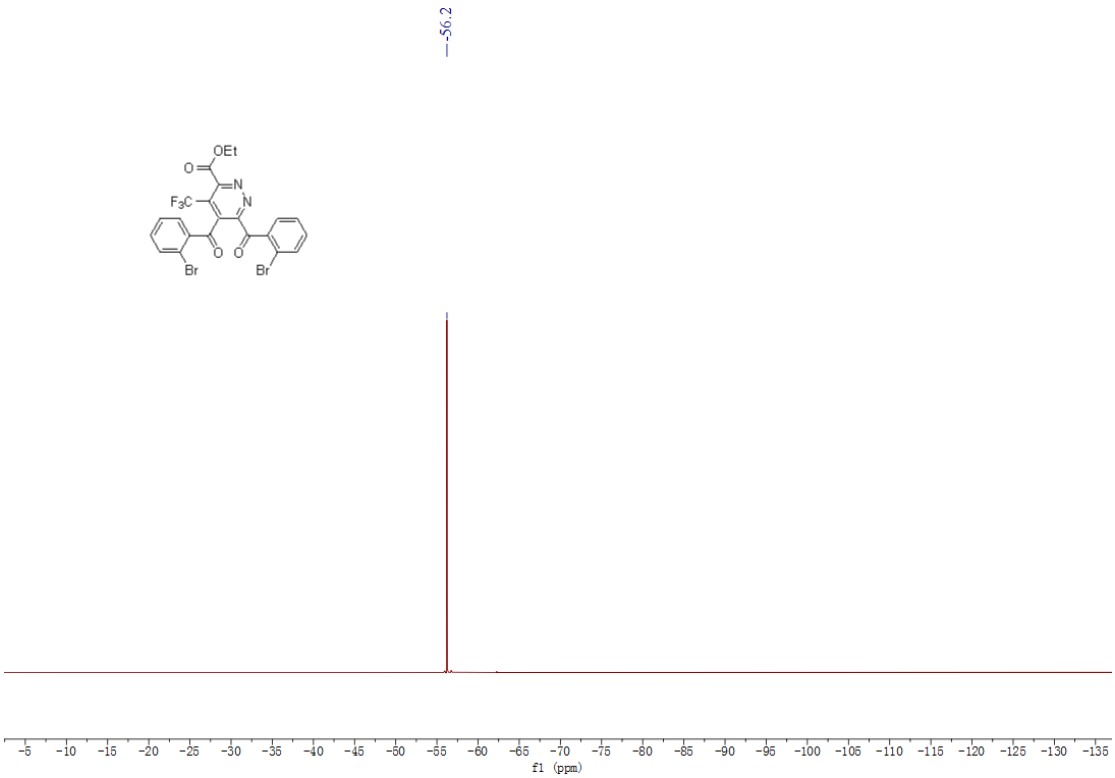
400 MHz ^{1}H NMR spectrum of **3u** in $CDCl_3$



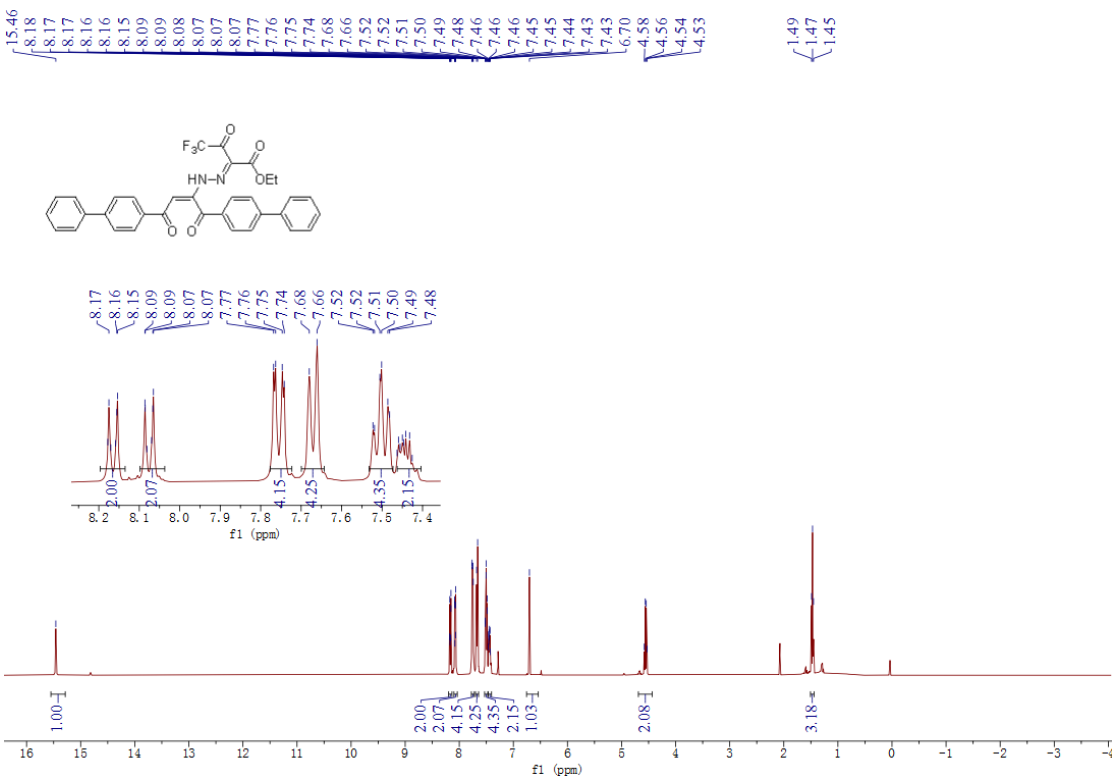
101 MHz ^{13}C NMR spectrum of **3u** in $CDCl_3$



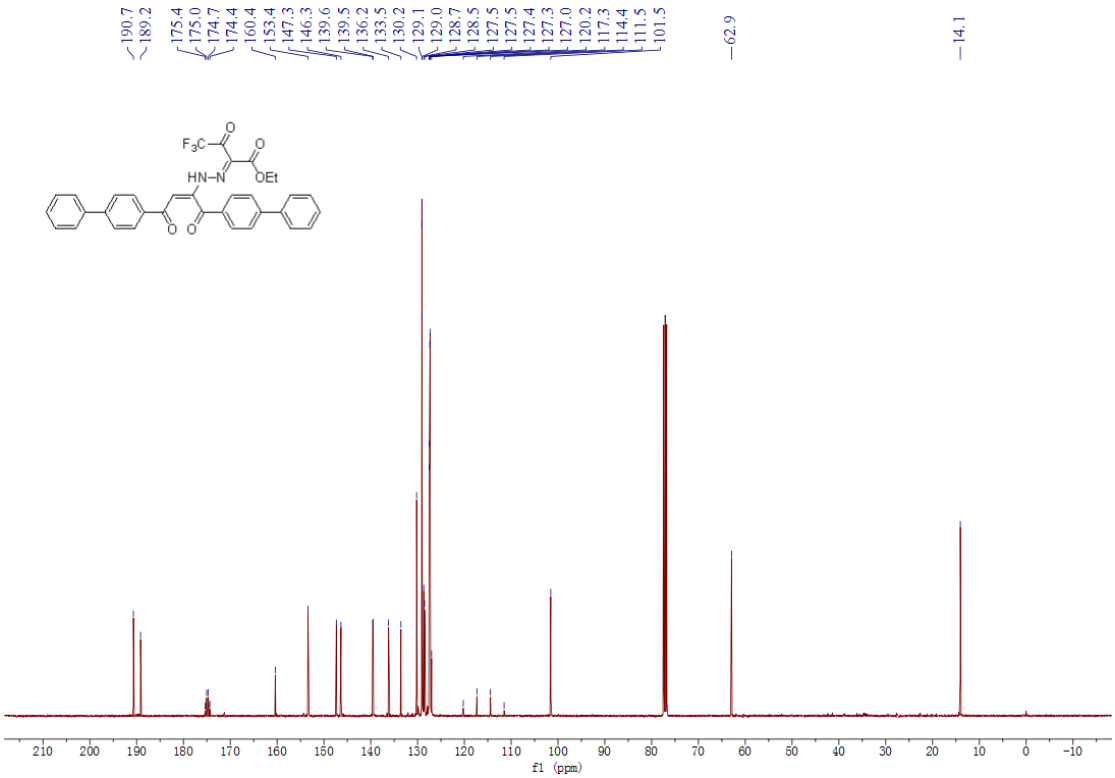
376 MHz ^{19}F NMR spectrum of **3u** in $CDCl_3$



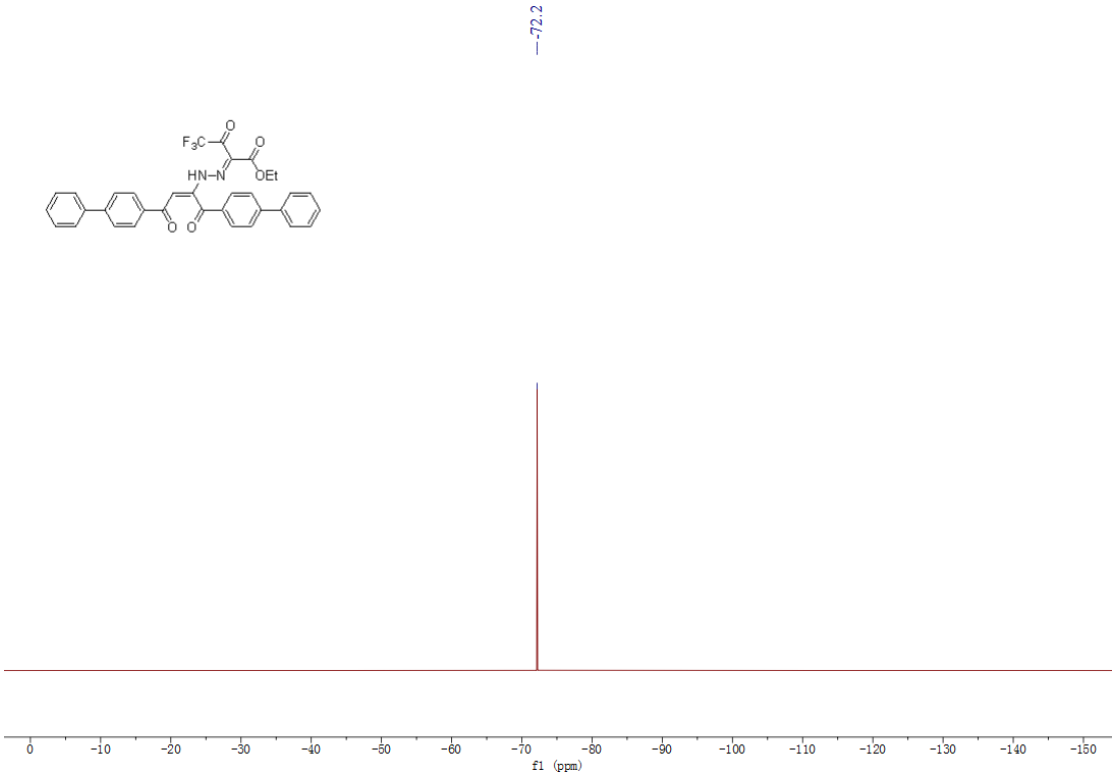
400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$



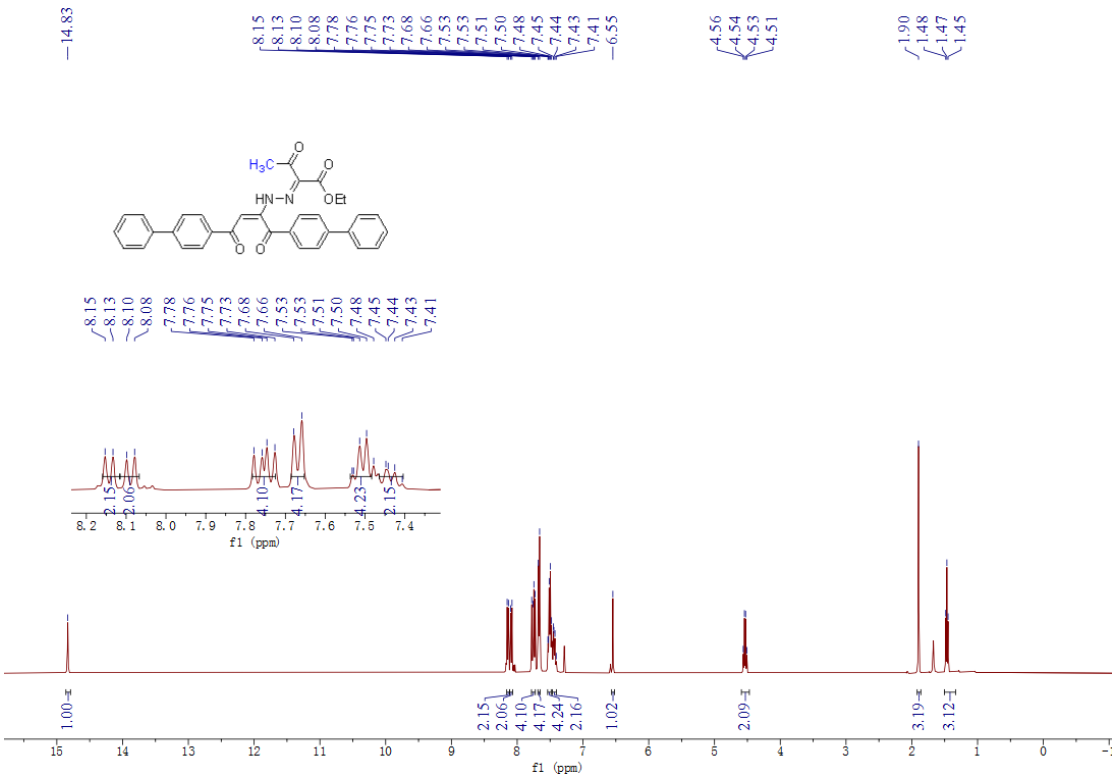
101 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$



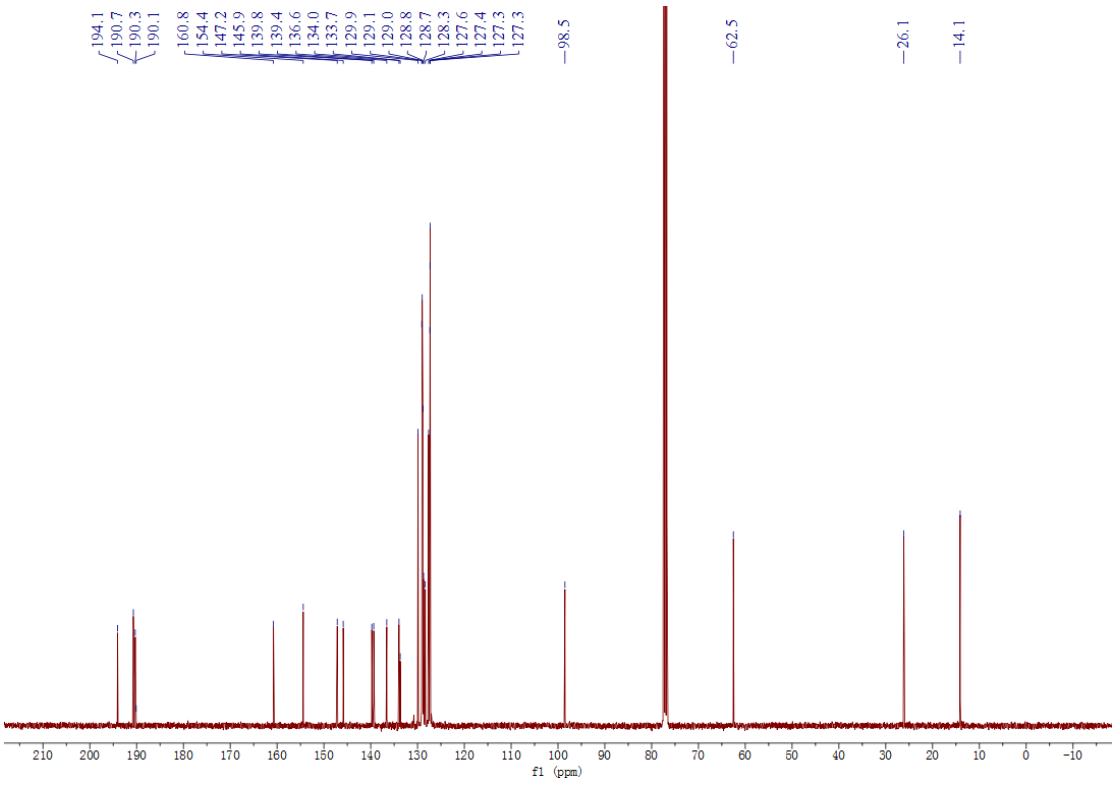
376 MHz ^{19}F NMR spectrum of **4** in $CDCl_3$



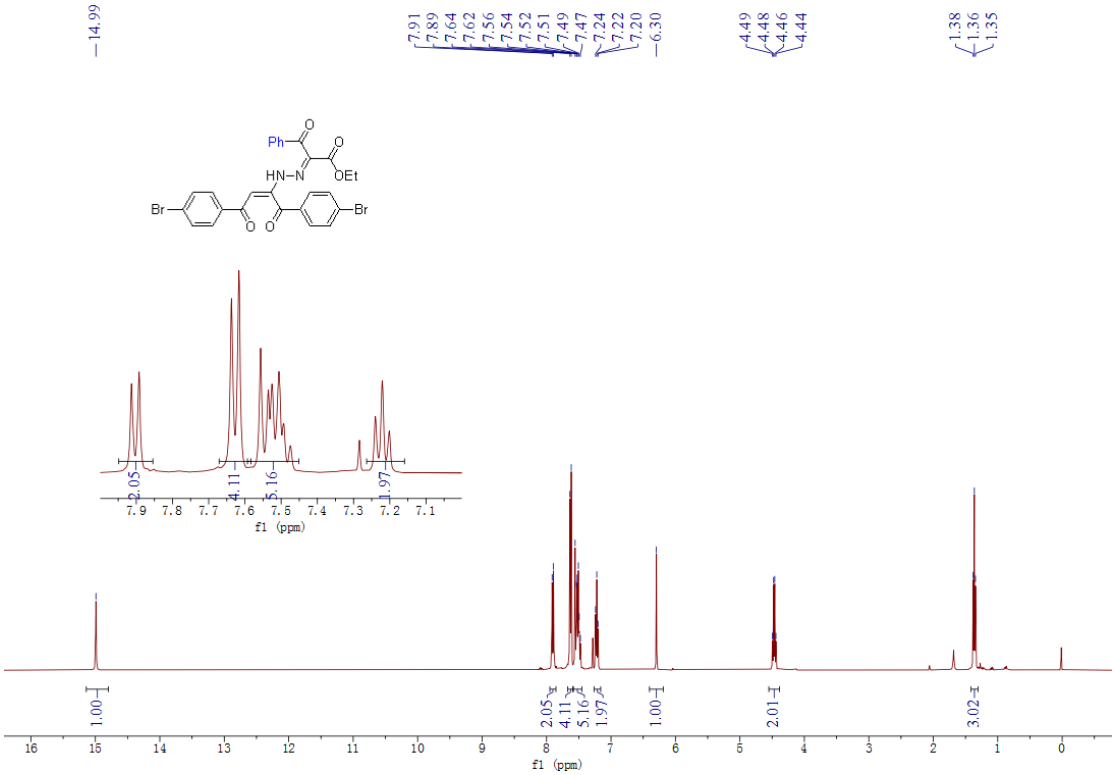
400 MHz ^{1}H NMR spectrum of **4′** in $CDCl_3$



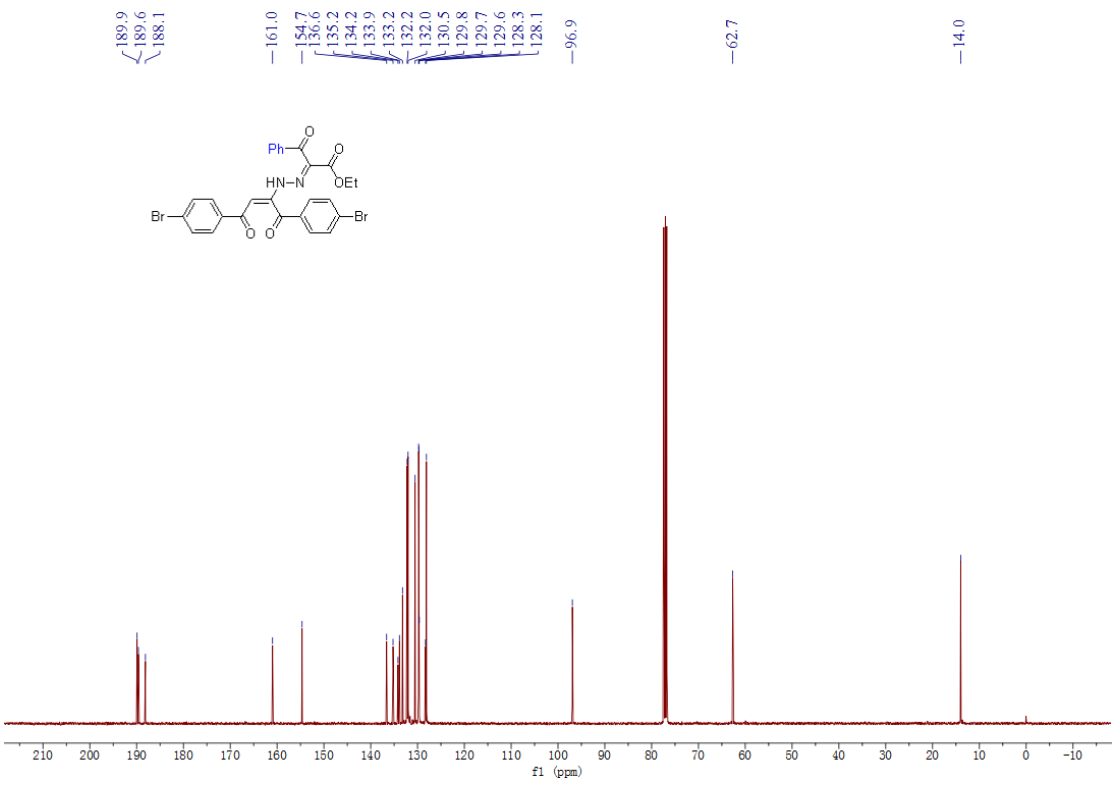
101 MHz ^{13}C NMR spectrum of **4′** in $CDCl_3$



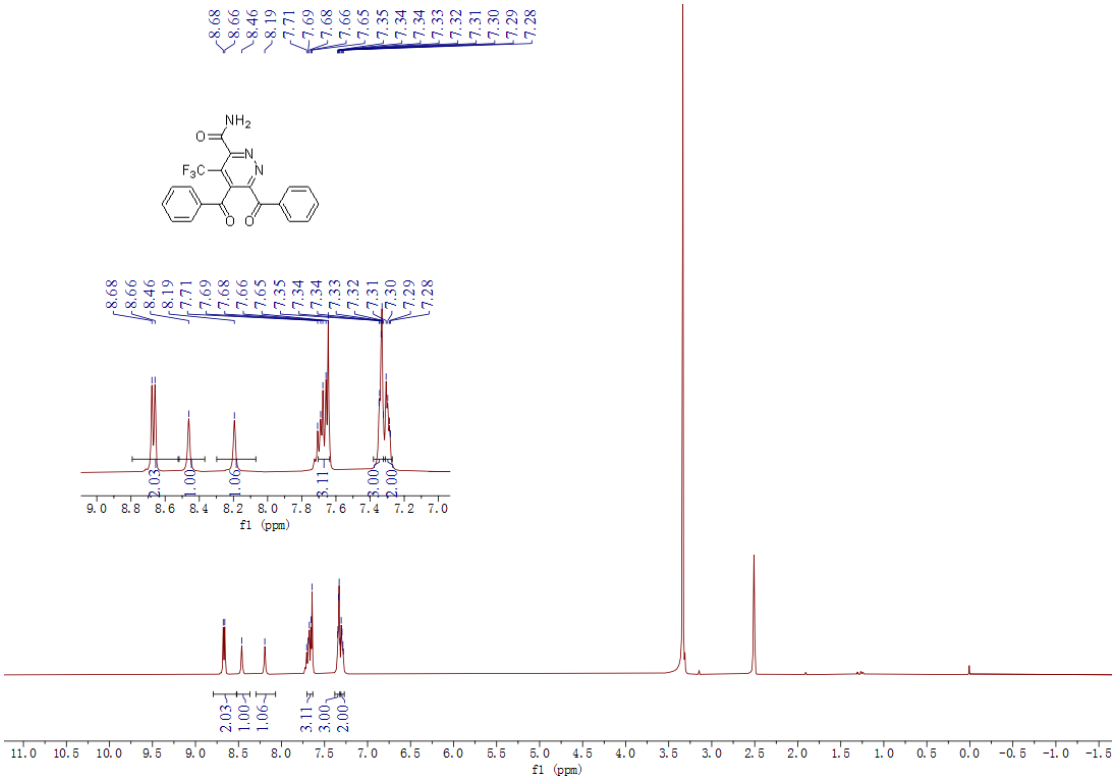
400 MHz ^{1}H NMR spectrum of **4″** in $CDCl_3$



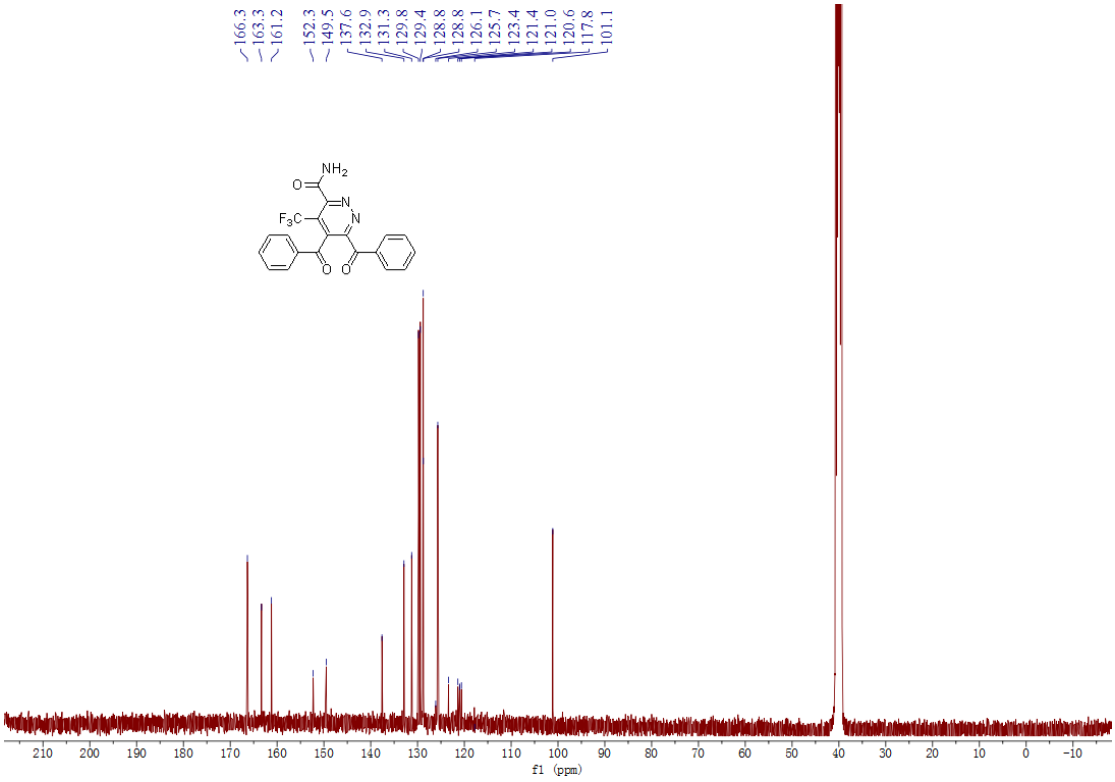
101 MHz ^{13}C NMR spectrum of **4″** in $CDCl_3$



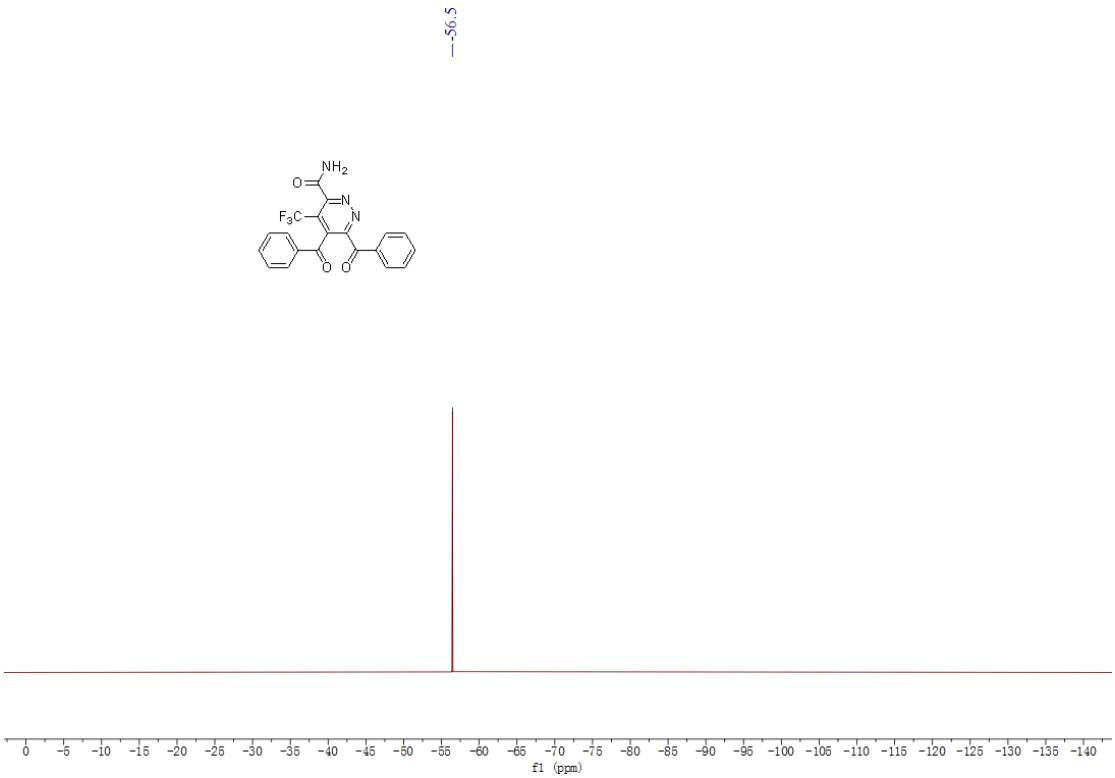
400 MHz ^{1}H NMR spectrum of **5a** in DMSO-d_6



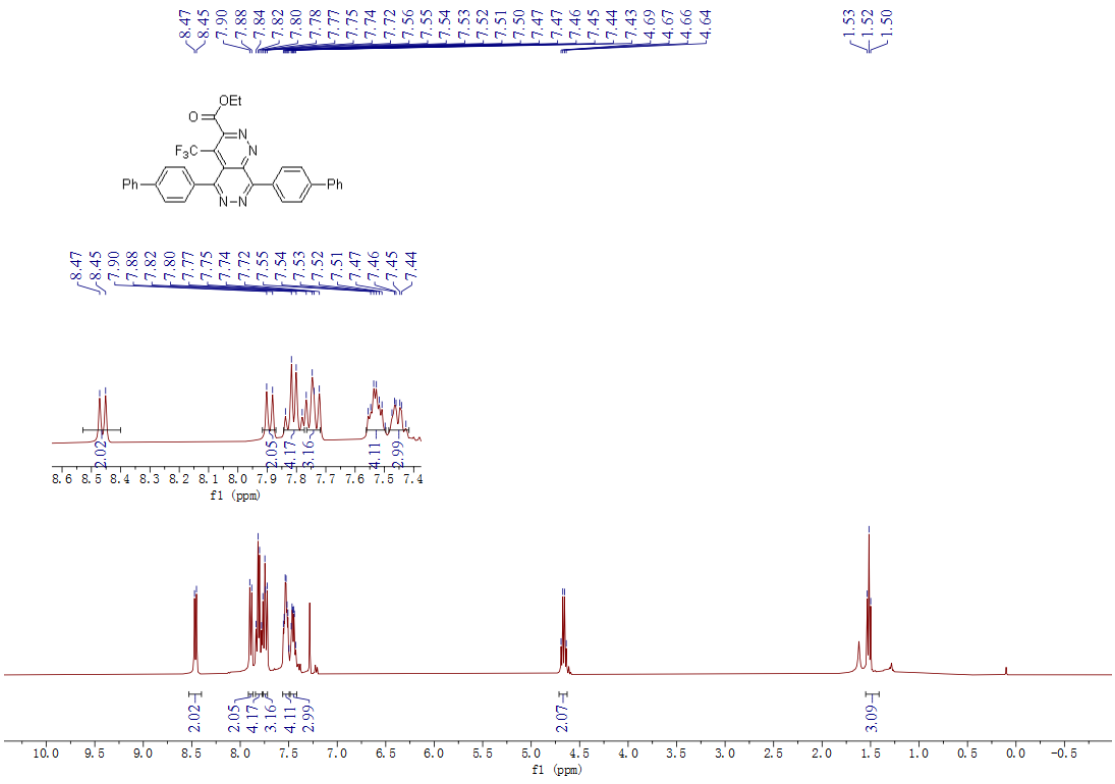
101 MHz ^{13}C NMR spectrum of **5a** in DMSO-d_6



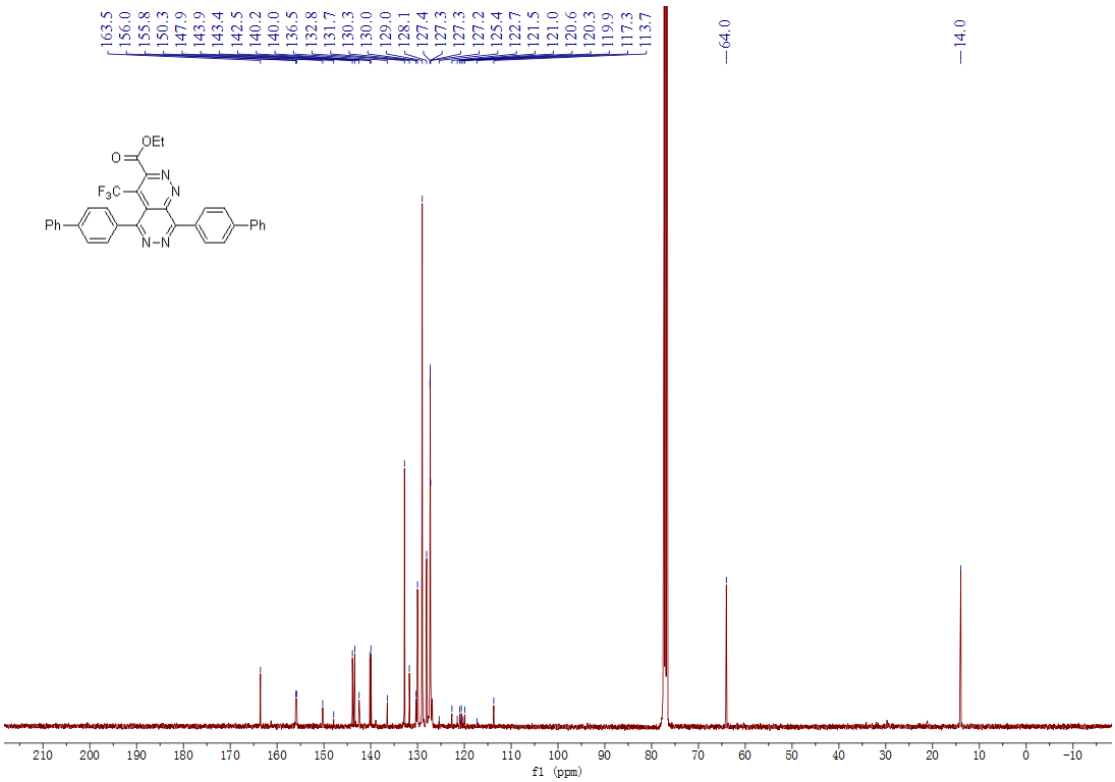
376 MHz ^{19}F NMR spectrum of **5a** in DMSO-d_6



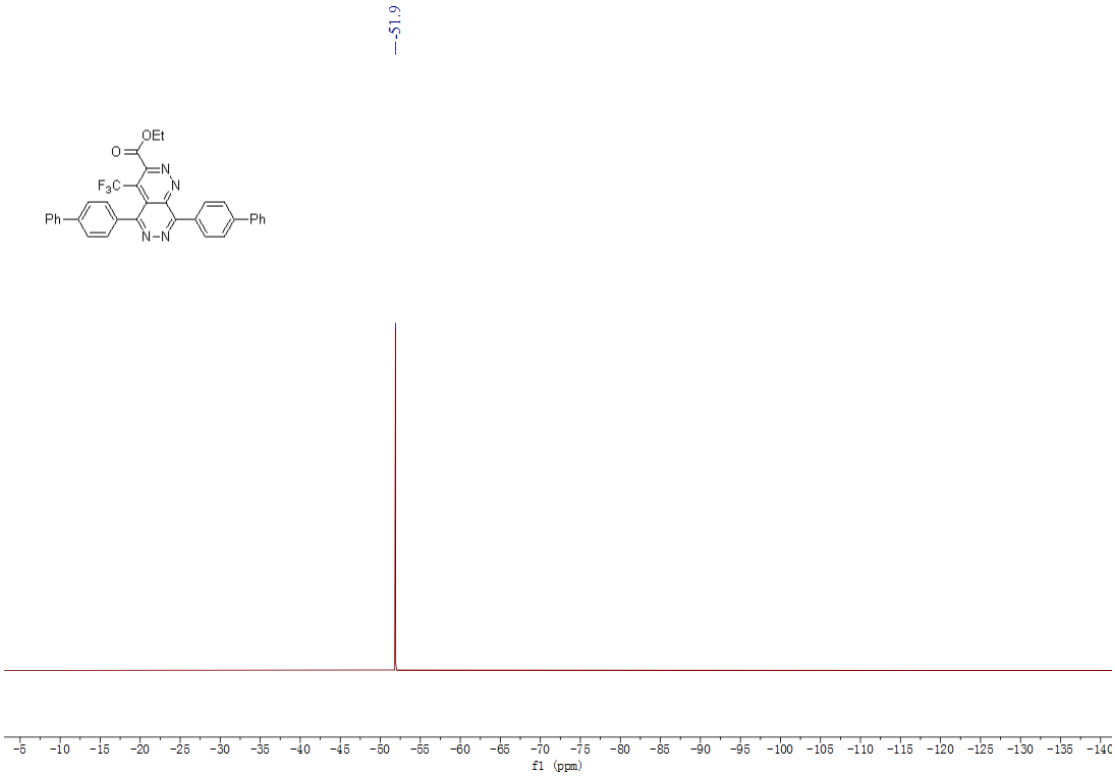
400 MHz ^{1}H NMR spectrum of **6c** in $CDCl_3$



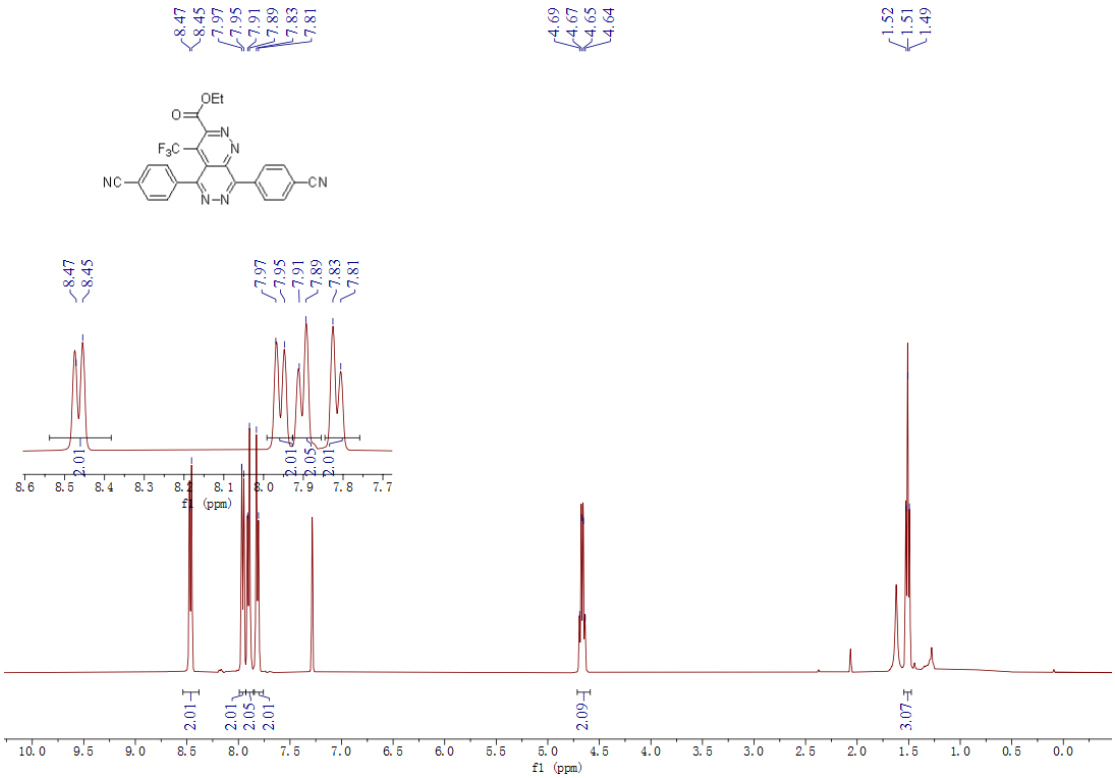
101 MHz ^{13}C NMR spectrum of **6c** in $CDCl_3$



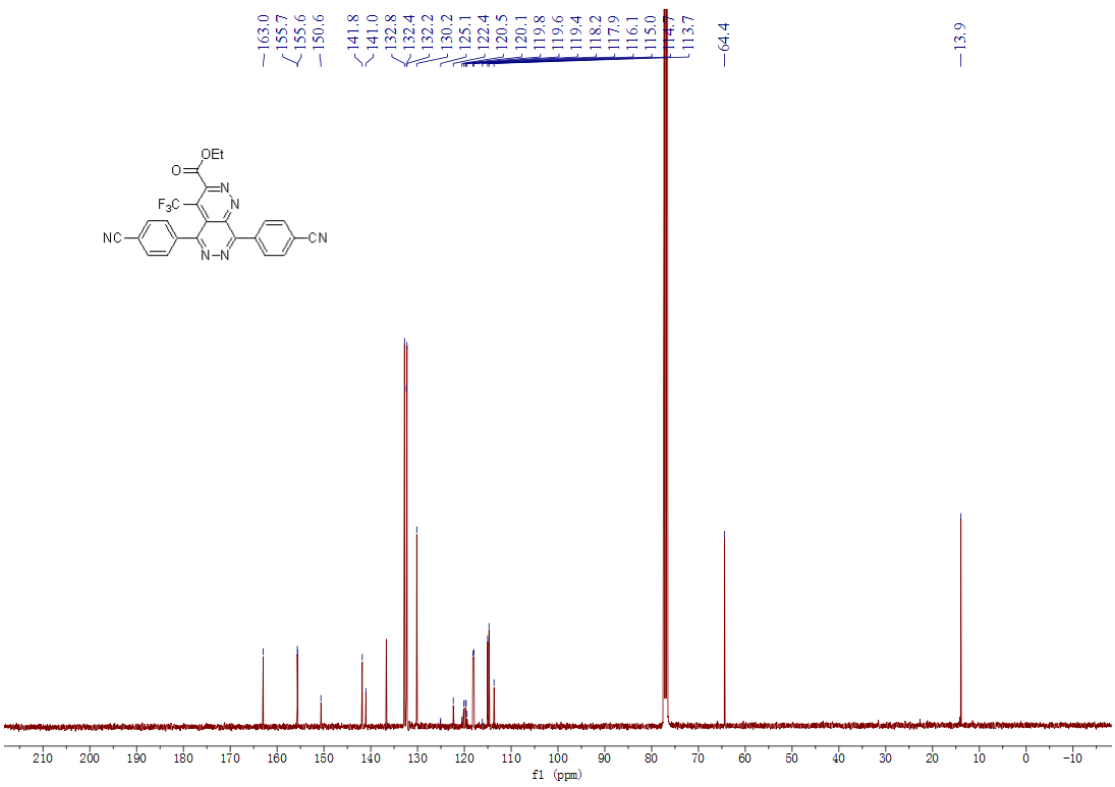
376 MHz ^{19}F NMR spectrum of **6c** in $CDCl_3$



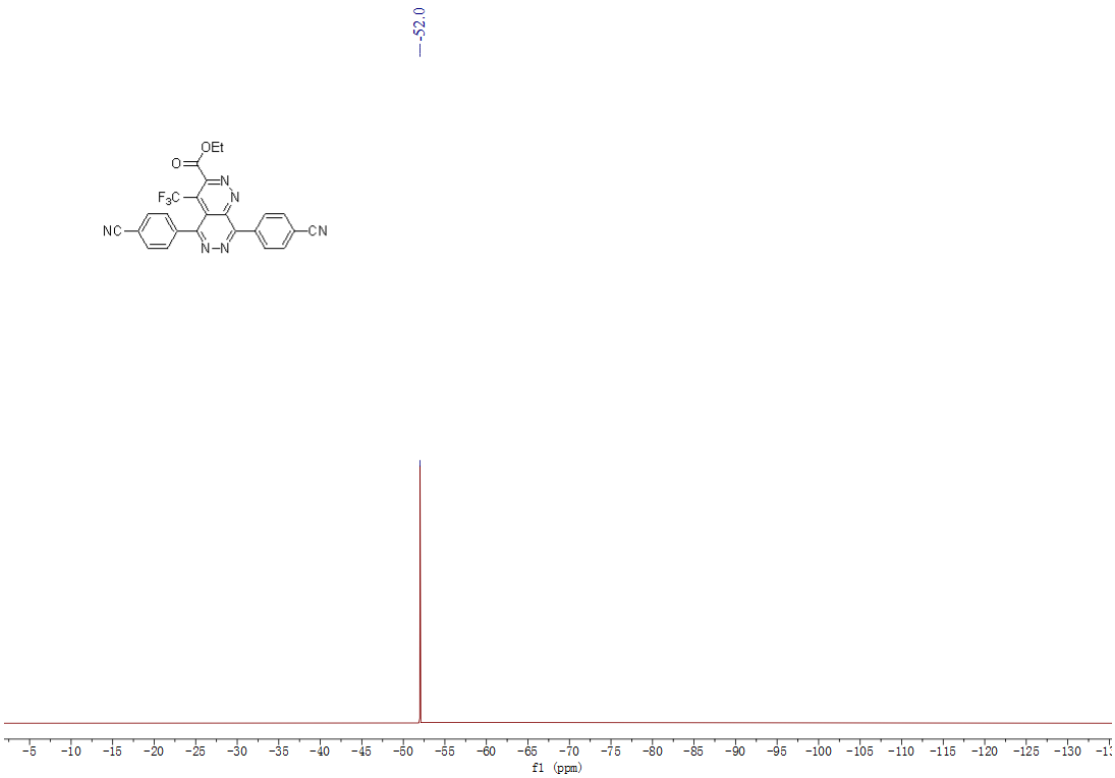
400 MHz ^{1}H NMR spectrum of **6j** in $CDCl_3$



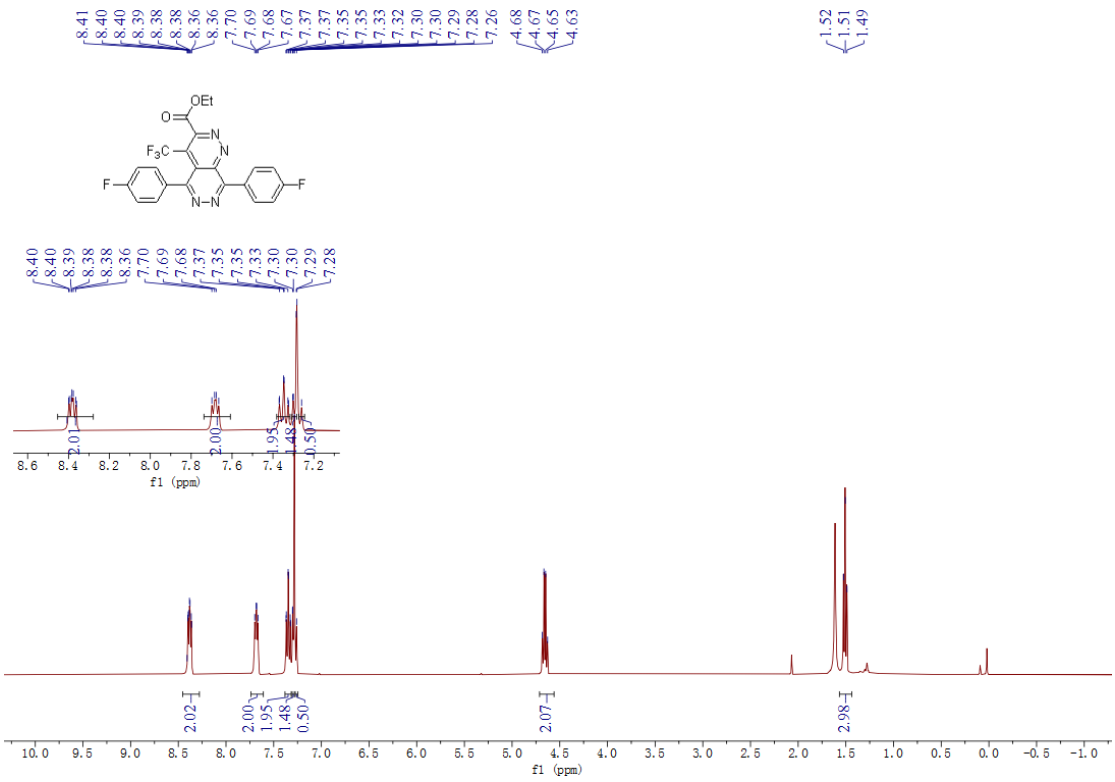
101 MHz ^{13}C NMR spectrum of **6j** in $CDCl_3$



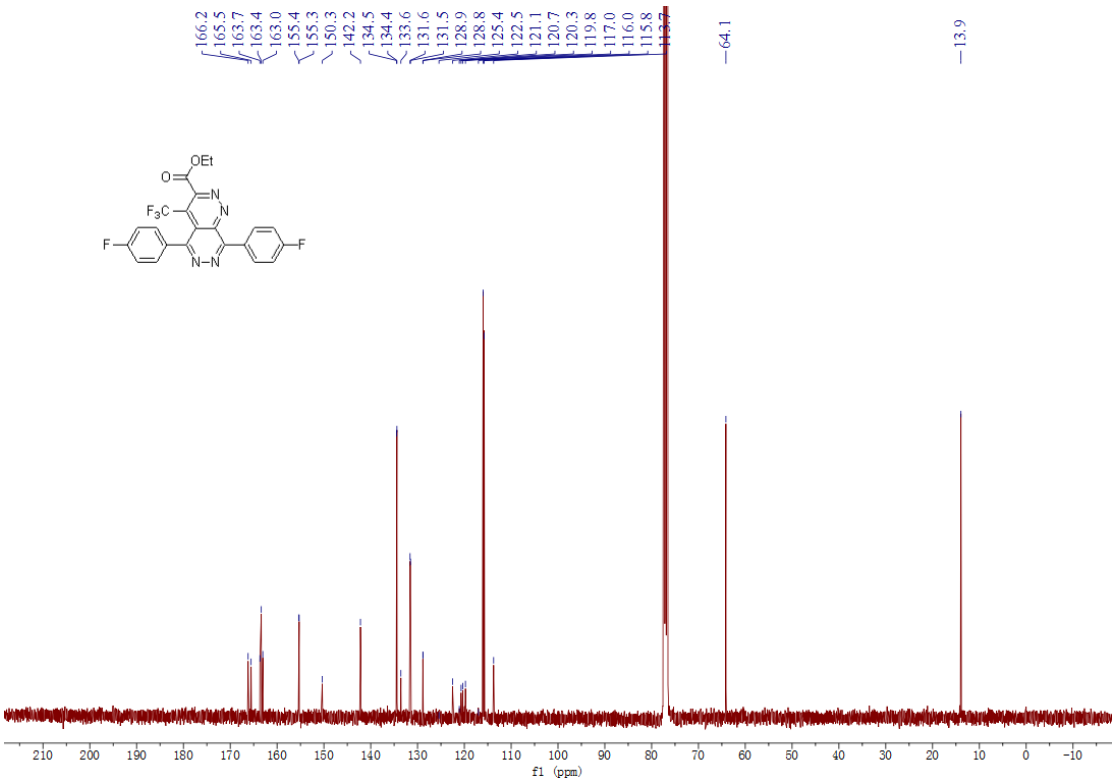
376 MHz ^{19}F NMR spectrum of **6j** in $CDCl_3$



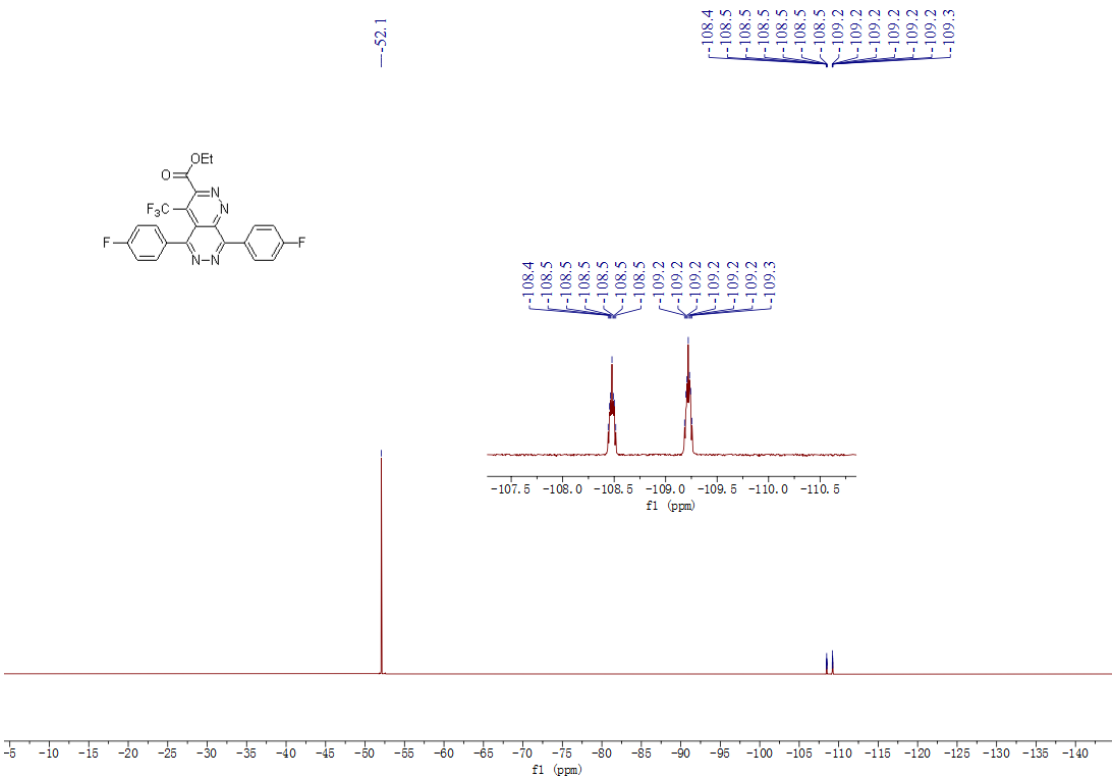
400 MHz ^{1}H NMR spectrum of **6n** in $CDCl_3$



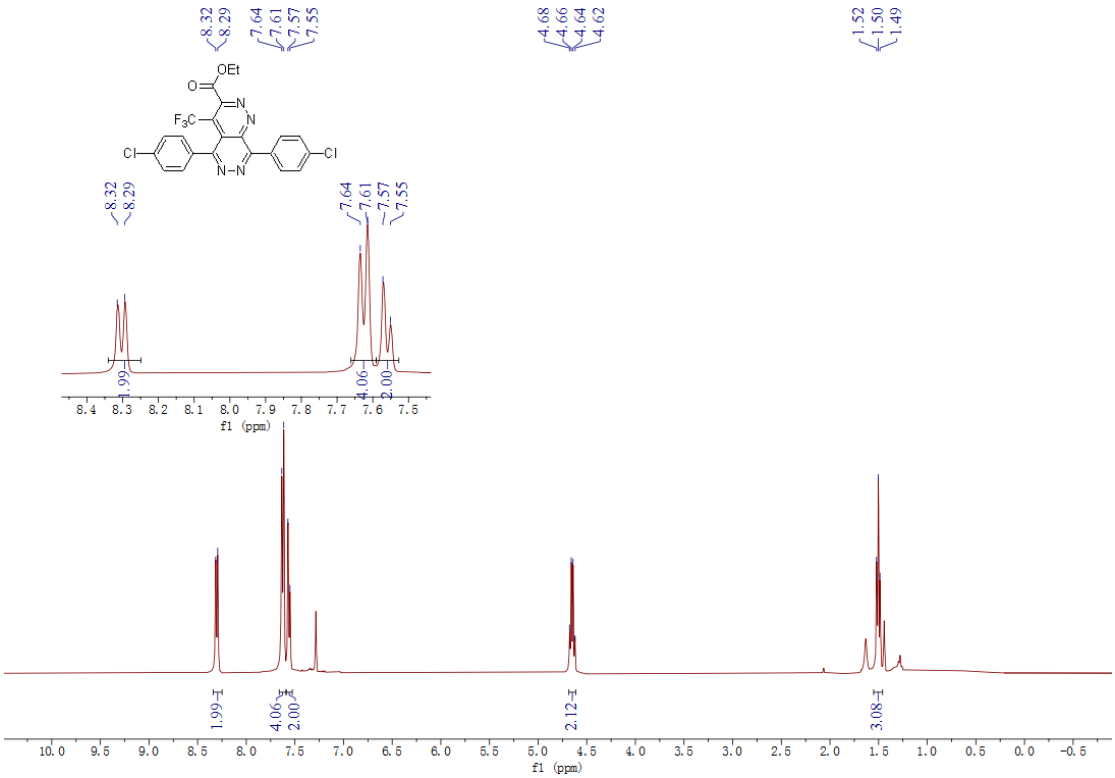
101 MHz ^{13}C NMR spectrum of **6n** in $CDCl_3$



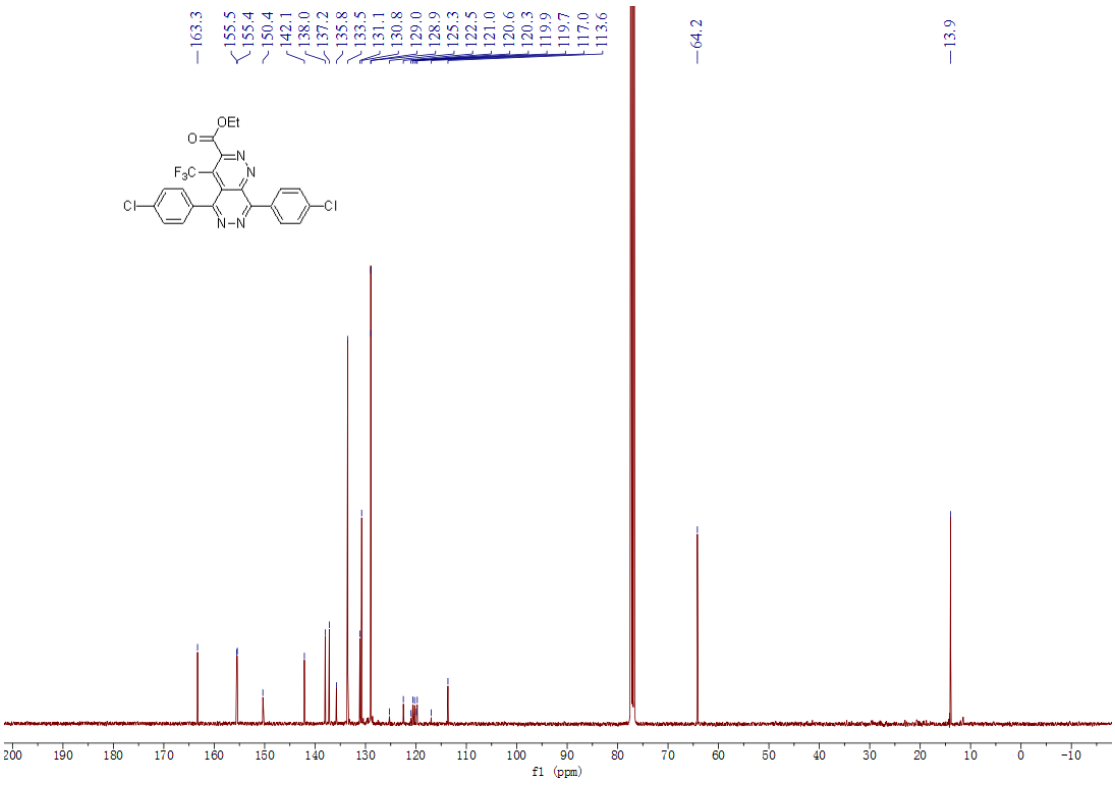
376 MHz ^{19}F NMR spectrum of **6n** in $CDCl_3$



400 MHz ^{1}H NMR spectrum of **6o** in $CDCl_3$



101 MHz ^{13}C NMR spectrum of **6o** in $CDCl_3$



376 MHz ^{19}F NMR spectrum of **6o** in $CDCl_3$