Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Catalyst-free Direct C-H Trifluoromethylation of Arene in Water–Acetonitrile

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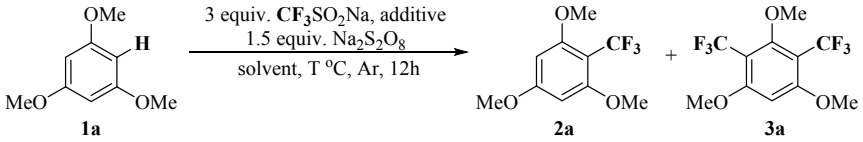
1. General information

Preparative thin-layer chromatography was performed for product purification using Sorbent Silica Gel 60 F254 TLC plates and visualized with ultraviolet light. IR spectra were recorded on a new Fourier transform infrared spectroscopy. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 400, 100, 377 MHz NMR spectrometer using $CDCl_3$ as solvent unless otherwise stated. HRMS were made by means of ESI. Melting points were measured on micro melting point apparatus and uncorrected. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were carried out in a sealed tube under an atmosphere of argon. Unless otherwise noted, all reagents were purchased on the net, and used without further purifications.

2. Selected optimization results

Table S1 Selected optimization results.[a]



Entry[b]	Additive (mol%)	Solevent(mL)	Yield(%)[c]
1	—	MeCN/H_2O(0.5/0.5)	25
2	—	CH_3CN (1.0)	trace
3	—	H_2O (1.0)	1
4	—	THF (1.0)	0
5	—	C_2H_5OH (1.0)	0
6	—	EtOAc (1.0)	trace
7	—	DCE (1.0)	trace
8	—	MeCN/H_2O (0.99/0.01)	trace
9	—	MeCN/H_2O (0.9/0.1)	14
10	—	MeCN/H_2O (0.6/0.4)	16
11	—	MeCN/H_2O (0.55/0.45)	16
12	—	MeCN/H_2O (0.4/0.6)	23
13	—	MeCN/H_2O (0.3/0.7)	17
14	—	MeCN/H_2O (0.2/0.8)	10
15	—	MeCN/H_2O (0.1/0.9)	trace
16	—	THF/H_2O (0.5/0.5)	0
17	—	DMSO/H_2O (0.5/0.5)	5(4/1)
18	—	DMF/H_2O (0.5/0.5)	5
19	—	NMP/H_2O (0.5/0.5)	3
20	—	Actone/H_2O (0.5/0.5)	1
21	KF (1)	MeCN/H_2O (0.5/0.5)	27
22	KH_2PO_4 (1)	MeCN/H_2O (0.5/0.5)	41(40/1)
23	LiF (1)	MeCN/H_2O (0.5/0.5)	23
24	NaF (1)	MeCN/H_2O (0.5/0.5)	23
25	CH_3COOH (1.5)	MeCN/H_2O (0.5/0.5)	30(28/2)
26	CF_3COOH (1.5)	MeCN/H_2O (0.5/0.5)	23(22/1)
28	H_2TiF_6 (1.5)	MeCN/H_2O (0.5/0.5)	40(39/1)
29	HPF_6 (1.5)	MeCN/H_2O (0.5/0.5)	50(49/1)
30	K_3PO_4 (5)	MeCN/H_2O (0.5/0.5)	64(60/4)
31	$HCONH_2$ (5)	MeCN/H_2O (0.5/0.5)	67(65/2)
32	Na_2HPO_4 (5)	MeCN/H_2O (0.5/0.5)	70(68/2)
33	CH_3COONH_4 (5)	MeCN/H_2O (0.5/0.5)	57(54/3)
34	CF_3COOLi (5)	MeCN/H_2O (0.5/0.5)	28
35	CF_3COOK (5)	MeCN/H_2O (0.5/0.5)	27
36	CF_3COONa (5)	MeCN/H_2O(0.5/0.5)	28
37	$(C_2H_5)_3N$ (5)	MeCN/H_2O (0.5/0.5)	68(66/2)
38	$(C_2H_5)_2NH$ (5)	MeCN/H_2O (0.5/0.5)	62(65/3)

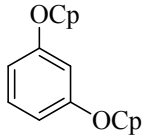
39	DIPEA (5)	MeCN/H_2O (0.5/0.5)	74(70/4)
40	HBF_4 (1.5)	MeCN/H_2O (0.5/0.5)	80(74/6)
41	NH_4NO_3 (5)	MeCN/H_2O (0.5/0.5)	82(77/5)
42	(n-C_4H_9)$_4$NBr (5)	MeCN/H_2O (0.5/0.5)	82(79/3)
43	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	76(73/3)
44	DIPEA (5)	MeCN/H_2O (0.5/0.5)	77(73/4)
45	HBF_4 (1.5)	MeCN/H_2O (0.5/0.5)	81(77/4)
46	NH_4NO_3 (5)	MeCN/H_2O (0.5/0.5)	77(73/4)
47	(n-C_4H_9)$_4$NBr (5)	MeCN/H_2O (0.5/0.5)	88(82/6)
48	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	98(84/14)(98)[d]
49	NH_4NO_3 (6)	MeCN/H_2O (0.5/0.5)	80(76/4)
50[e]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	50(44/6)
51[f]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	88(82/6)
52[g]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	76(73/3)
53[h]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	83(78/5)
54[i]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	61(59/2)
55[j]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	58(56/2)
56k	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	79(74/5)
57[l]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	65(62/3)
58[m]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	85(80/5)
59[n]	H_3PO_4 (1.5)	MeCN/H_2O (0.5/0.5)	17

[a] Unless otherwise noted, all reactions were conducted on a 0.1 mmol scale with 3 equiv. of CF_3SO_2Na, 1.5 equiv. $Na_2S_2O_8$ and additive in a sealed tube in solvent under an atmosphere of argon for 12 h. [b] Entries 1-43, react temperature is 25 ^oC; entries 44-59, react temperature is 30 ^oC. [c] Yields are detected by GC-MS using naphthalene as internal standard. [d] Isolated yield. [e] 1.5 equiv. t-BuOOH was used as initiator. [f] 1.5 equiv. $K_2S_2O_8$ was used as initiator. [g] 1.5 equiv. $NH_4S_2O_8$ was used as initiator. [h] 2 equiv. CF_3SO_2Na was used. [i] 1.5 equiv. CF_3SO_2Na was used. [j] 1 equiv. CF_3SO_2Na was used. [k] 1.2 equiv. $Na_2S_2O_8$ was used. [l] 1 equiv. $Na_2S_2O_8$ was used. [m] under an atmosphere of air. [n] under an atmosphere of oxygen. DIPEA = *N,N-di*isopropylethylamine.

3. Preparation of substrates

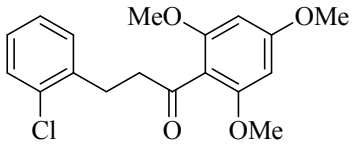
Compounds **1c**, **1d**, **1e, 1f, 1j, 1l, 1m, 1n, 1o, 1p, 1za** and **1zb** were synthesized according to literature methods. [lit.[1-4]]

1,3-Bis(cyclopentyloxy)benzene (1f)



^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, J = 8 Hz, 1H), 6.46-6.38 (m, 3H), 4.75-4.68 (m, 2H), 1.96-1.40 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.44 (s), 129.75 (s), 107.59 (s), 103.45 (s), 79.29 (s), 33.02 (s), 24.18 (s).

3-(2-Chlorophenyl)-1-(2,4,6-trimethoxyphenyl)propan-1-one (1zb)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 2H), 7.20-7.05 (m, 2H), 6.08 (s, 2H), 3.80 (s, 3H), 3.74 (s, 6H), 3.20-2.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.18 (s), 162.43 (s), 158.35 (s), 139.23 (s), 134.04 (s), 130.74 (s), 129.39 (s), 127.42 (s), 126.81 (s), 113.38 (s), 90.71 (s), 55.85 (s), 55.49 (s), 44.32 (s), 28.13 (s).

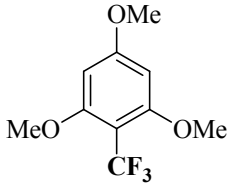
4. Experimental procedure and characterization data for products

A typical experimental procedure: A solution of arene (0.2 mmol), $Na_2S_2O_8$ (1.5 equiv.), CF_3SO_2Na (3.0 equiv), and H_3PO_4 (1.5 mol%) in a water–acetonitrile mixture (1 mL:1 mL) was stirred in a sealed tube under an atmosphere of argon at 30 °C for 12 h. The reaction mixture was then extracted with ethyl acetate. Afterward, the combined organic phase was dried with Na_2SO_4, and the solvent was evaporated in *vacuo*. The residue was purified by preparative thin-layer chromatography on silica gel with petroleum ether and diethyl ether to achieve the pure product.

Gram-scale synthesis of 1,3,5-trimethoxy-2-(trifluoromethyl)benzene (2a)

A solution of 1,3,5-trimethoxybenzene (1g, 5.8 mmol), $Na_2S_2O_8$ (2.08g, 8.7 mmol), CF_3SO_2Na (2.96g, 17.4 mmol), and H_3PO_4 (1.5 mol%) in a water–acetonitrile mixture (1 mL:1 mL) was stirred in a sealed tube under an atmosphere of argon at 30 °C for 72 h. The reaction mixture was CH_2Cl_2 and washed with brine. Afterward, the combined organic phase was dried with Na_2SO_4, and the solvent was evaporated in *vacuo*. The residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/4) to give 1,3,5-trimethoxy-2-(trifluoromethyl)benzene (**2a**) as a white solid (1.33g, 91% yield).

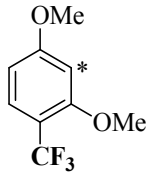
1,3,5-Trimethoxy-2-(trifluoromethyl)benzene (2a)



Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.7; White solid; Yield 89%; Mp. 51-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 3.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.66 (s), 160.58 (s), 124.48 (q, J = 272 Hz), 100.61

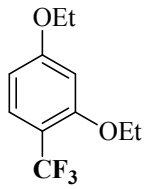
(q, J = 30 Hz), 91.44 (s), 56.40 (s), 55.51 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.13 (s); IR (neat) 2960, 1590, 1470, 1290, 1210, 1090, 925, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}F_3O_3$ 237.0733, found [M+H] 237.0735.

1,3-Dimethoxy-4-(trifluoromethyl)benzene (2b) and **1,3-dimethoxy-2-(trifluoromethyl)benzene (2b*)**



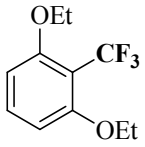
Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.7; Light yellow liquid; Yield 85% (2b:2b* = 60:25); ^{1}H NMR for the mixture (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8 Hz, 1H, major), 7.38 (t, J = 8 Hz, 1H, minor), 6.61 (d, J = 8 Hz, 2H, minor), 6.51 (s, 1H, major), 6.49 (d, J = 9 Hz, 1H, major), 3.87 (s, 3H, major), 3.86 (s, 6H, minor), 3.84 (s, 3H, major); ^{13}C NMR for the mixture (100 MHz, $CDCl_3$) δ 163.79 (s), 159.43 (s), 158.99 (s), 133.13 (s), 128.40 (q, J = 5 Hz), 124.24 (q, J = 273 Hz), 124.12 (q, J = 269 Hz), 111.67 (q, J = 31 Hz), 107.37 (q, J = 29 Hz), 104.95 (s), 103.85 (s), 99.50 (s), 56.46 (s), 55.95 (s), 55.64 (s); ^{19}F NMR for the mixture (377 MHz, $CDCl_3$) δ -54.87 (s, minor), -61.27 (s, major); IR (neat) 2940, 2850, 1600, 1480, 1320, 1210, 1100, 829 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_{10}F_3O_2$ 207.0627, found [M+H] 207.0639.

1,3-Diethoxy-4-(trifluoromethyl)benzene (2c)



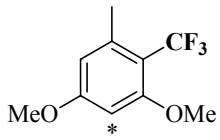
Purified by TLC (dichloromethane/petroleum ether = 1:4, v:v), R_f = 0.7; Light yellow solid; Yield 49%; Mp. 40-42 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 9 Hz, 1H), 6.49 (s, 1H), 6.45 (d, J = 9 Hz, 1H), 4.10-4.02 (m, 4H), 1.45-1.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163 (s), 158.37 (d, J = 2 Hz), 124.16 (q, J = 270 Hz), 128.28 (q, J = 5 Hz), 111.80 (q, J = 31 Hz), 104.25 (s), 100.71 (s), 64.49 (s), 63.89 (s), 14.82 (s), 14,67 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.25 (s); IR (neat) 2980, 1610, 1510, 1280, 1100, 1030, 917, 812 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}F_3O_4$ 279.0839, found [M+HCO_2] 279.0848.

1,3-Diethoxy-2-(trifluoromethyl)benzene (2c*)



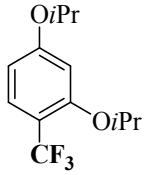
Purified by TLC (dichloromethane/petroleum ether = 1:4, v:v), R_f = 0.6; Light yellow liquid; Yield 25%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8Hz, 1H), 6.57 (d, *J* = 8 Hz, 2H), 4.06 (q, *J* = 8Hz, 4H), 1.42 (t, *J* = 6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.88 (s), 132.89 (s), 124.27 (q, *J* = 273 Hz), 128.29(q, *J* = 30 Hz) , 106.10 (s), 65.20 (s), 14.81 (s);^{19}F NMR (377 MHz, $CDCl_3$) δ -54.80 (s); IR (neat) 2990, 2940, 1600, 1470, 1320, 1110, 1040, 785 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{14}F_3O_2$ 235.0940, found [M+H] 235.0934.

1,5-Dimethoxy-3-methyl-2-(trifluoromethyl)benzene (2d) and **1,3-dimethoxy-5-methyl-2-(trifluoromethyl)benzene (2d*)**



Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.6; Colorless liquid; Yield 82% (2d:2d* = 62:20); ^{1}H NMR for the mixture (400 MHz, $CDCl_3$) δ 6.42 (s, 2H, minor), 6.37 (s, 1H, major), 6.32 (s, 1H, major), 3.84 (s, 3H, mixture), 3.82 (s, 3H, major), 2.44 (q, *J* = 4 Hz, 3H), 2.36 (s, 3H, minor); ^{13}C NMR for the mixture (100 MHz, $CDCl_3$) δ 162.27 (s), 160.27 (d, *J* = 2 Hz), 159.19 (d, *J* = 1 Hz), 143.95 (s), 140.20 (d, *J* = 2 Hz), 125.46(q, *J* = 272 Hz), 124.4 (q, *J* = 272 Hz), 110.54 (q, *J* = 29 Hz), 108.78 (s), 105.81 (s), 104.68 (q, *J* = 29 Hz), 97.28 (s), 56.38 (s), 56.28 (s), 55.43 (s), 22.31 (s), 22.07 (q, *J* = 5 Hz); ^{19}F NMR for the mixture (377 MHz, $CDCl_3$) δ -53.83 (s, major), -54.57 (s, minor); IR (neat) 2940, 2850, 1610, 1470, 1280, 1210, 1110, 834 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}F_3O_2$ 221.0784, found [M+H] 221.0782.

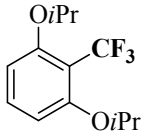
1,3-*Di*isopropoxy-4-(trifluoromethyl)benzene (2e)



Purified by TLC (dichloromethane/petroleum ether = 1:4, v:v), R_f = 0.7; Light yellow liquid; Yield 46%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8 Hz, 1H), 6.48 (s, 1H),

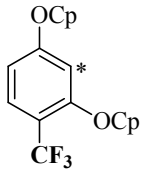
6.43 (dd, J = 8,2 Hz, 1H), 4.61-4.53 (m, 2H), 1.37-1.33 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.94 (t, J = 1 Hz), 157.81-157.41 (m), 128.31 (q, J = 5 Hz), 124.18 (q, J = 269 Hz), 112.53 (q, J = 30 Hz), 105.40 (d, J = 4Hz), 102.98 (d, J = 2Hz), 71.32 (d, J = 1 Hz), 70.30 (d, J = 1 Hz), 22.09 (s), 22.02 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.07 (s); IR (neat) 2980, 2920, 1620, 1510, 1290, 1120, 1010, 802 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{18}F_3O_2$ 263.1253, found [M+H] 263.1256.

1,3-Diisopropoxy-2-(trifluoromethyl)benzene (2e*)



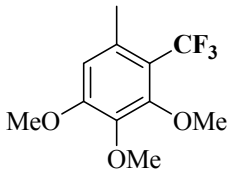
Purified by TLC (dichloromethane/petroleum ether = 1:4, v:v), R_f = 0.6; Light yellow liquid; Yield 23%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 8 Hz, 1H), 6.57 (d, J = 8 Hz, 2H), 4.60-4.51 (m, 2H), 1.34 (d, J =4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.10 (s), 132.49 (s), 124.22 (q, J = 274 Hz), 110.35 (q, J = 28 Hz), 107.55 (d, J = 2 Hz), 71.99 (s), 22.10 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.50 (s); IR (neat) 2980, 2940, 1600, 1480, 1310, 1110, 1060, 903 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{18}F_3O_2$ 263.1253, found [M+H] 263.1247.

1,3-Bis-cyclopentyloxy-4-(trifluoromethyl)benzene (2f) and **1,3-bis-cyclopentyloxy-2-(trifluoromethyl)benzene (2f*)**



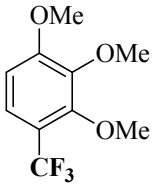
Purified by TLC (dichloromethane/petroleum ether = 1:2, v:v), R_f = 0.7; Light yellow liquid; Yield 71% (2f:2f* = 47:24); ^{1}H NMR for the mixture (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8 Hz, 1H, major), 7.29 (t, J = 8 Hz, 1H, minor), 6.53 (d, J = 8 Hz, 1H, major), 6.45 (s, 1H, major), 6.41 (d, J = 8 Hz, 2H, minor), 4.82-4.74 (m, 2H, mixture), 1.95-1.58 (m, 16H, mixture); ^{13}C NMR for the mixture (100 MHz, $CDCl_3$) δ 162.04 (s), 158.03 (s), 157.45 (s), 132.38 (s), 128.18 (q, J = 5 Hz), 124.37(q, J = 274 Hz), 124.27 (q, J = 270 Hz), 111.85 (q, J = 30 Hz), 108.75 (q, J = 29 Hz), 106.30 (s), 105.15 (s), 102.33 (s), 80.56 (s), 80.11 (s), 79.75 (s), 32.99 (s), 32.94 (s), 32.87 (s), 24.20 (s), 23.97 (s); ^{19}F NMR for the mixture (377 MHz, $CDCl_3$) δ -54.72 (s, minor), -61.27 (s, major); IR (neat) 2960, 2870, 1600, 1470, 1310, 1120, 1070, 840 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{22}F_3O_2$ 315.1566, found [M+H] 315.1568.

1,2,3-Trimethoxy-5-methyl-4-(trifluoromethyl)benzene (2g)



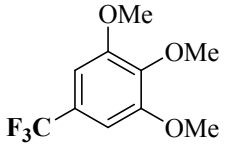
Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.7; Colorless liquid; Yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.27 (s), 153.52 (d, *J* = 2 Hz), 141.05 (s), 133.25 (d, *J* = 2 Hz), 125.01 (q, *J* = 273 Hz), 115.59 (q, *J* = 29 Hz), 110.84 (s), 61.88 (s), 60.95 (s), 56.05 (s), 21.70 (q, *J* = 4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.26 (s); IR (neat) 2940, 1600, 1470, 1300, 1110, 1010, 838 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{14}F_3O_3$ 251.0890, found [M+H] 251.0889.

1,2,3-Trimethoxy-4-(trifluoromethyl)benzene (2h)



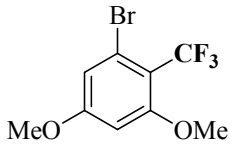
Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.7; Light yellow liquid; Yield 31%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9 Hz, 1H), 6.69 (d, *J* = 9 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H),3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.91 (s), 152.41 (d, *J* = 2 Hz), 143.05 (s), 123.78 (q, *J* = 270 Hz), 121.65 (q, *J* = 5 Hz), 117.14 (q, *J* = 31 Hz), 106.49 (s), 61.77 (s), 60.97 (s), 56.22 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.86 (s); IR (neat) 2940, 2840, 1600, 1470, 1320, 1120, 1010, 876, 806 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}F_3O_3$ 237.0733, found [M+H] 237.0727.

1,2,3-Trimethoxy-5-(trifluoromethyl)benzene (2h*)



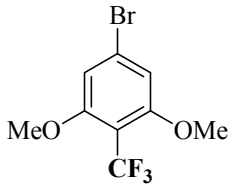
Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.8; White solid; Yield 20%; Mp. 62-64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 3.91 (s, 6H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.55 (s), 140.73 (s), 125.86 (q, *J* = 33 Hz), 124.19 (q, *J* = 270 Hz), 102.69 (q, *J* = 4 Hz), 61.04 (s), 56.42 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.07 (s); IR (neat) 2930, 2850, 1600, 1470, 1350, 1170, 1100, 992, 842 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}F_3O_3$ 237.0733, found [M+H] 237.0735.

1-Bromo-3,5-dimethoxy-2-(trifluoromethyl)benzene (2i)



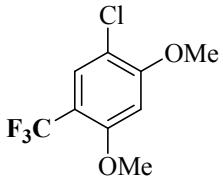
Purified by TLC (ethyl acetate/petroleum ether = 1:8, v:v), R_f = 0.5; Light yellow liquid; Yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, *J* = 4 Hz, 1H), 6.46 (d, *J* = 4 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.55 (s), 160.80 (s), 123.51 (q, *J* = 273 Hz), 122.05 (d, *J* = 2 Hz), 112 (s), 111.72 (q, *J* = 31 Hz), 99.20 (s), 56.58 (s), 55.83 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.57 (s); IR (neat) 3010, 2940, 1600, 1410, 1280, 1160, 1040, 818 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_8BrF_3O_2$ 284.9733, found [M+H] 284.9736.

1-Bromo-3,5-dimethoxy-4-(trifluoromethyl)benzene (2i*)



Purified by TLC (ethyl acetate/petroleum ether = 1:8, v:v), R_f = 0.6; White solid; Yield 17%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.71 (s), 127.20 (s), 123.89 (q, *J* = 273 Hz), 108.80 (s), 106.60 (q, *J* = 29 Hz), 56.73 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.20 (s); IR (neat) 3080, 2970, 1580, 1410, 1300, 1150, 1030, 821 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_8BrF_3O_2$ 284.9733, found [M+H] 284.9739.

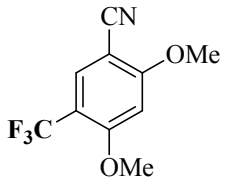
1-Chloro-2,4-dimethoxy-5-(trifluoromethyl)benzene (2j)



Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.5; White solid; Yield 62%; Mp. 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 6.54 (s, 1H), 3.96 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.61 (s), 157.74 (s), 128.54 (q, *J* = 5 Hz), 123.30 (q, *J* = 270 Hz), 113.40 (s), 111.83 (q, *J* = 31 Hz), 97.08 (s), 56.49 (s), 56.42 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.17 (s); IR (neat) 2920,

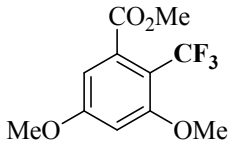
1610, 1400, 1330, 1210, 1080, 1020, 894, 822 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_9ClF_3O_4$ 285.0136, found [M+HCO_2H-H] 285.0133.

2,4-Dimethoxy-5-(trifluoromethyl)benzonitrile (2k)



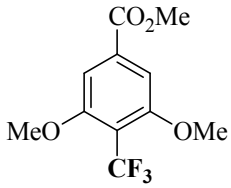
Purified by TLC (ethyl acetate/petroleum ether = 1:2, v:v), R_f = 0.4; Brown solid; Yield 44%; Mp. 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 6.53 (s, 1H), 4.01 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.63 (s), 162.60 (d, *J* = 1 Hz), 132.79 (q, *J* = 6 Hz), 122.76 (q, *J* = 270 Hz), 115.70 (s), 112.38 (q, *J* = 33 Hz), 95.72 (s), 93.28 (s), 56.60 (s), 56.48 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.17 (s); IR (neat) 2950, 2230, 1620, 1480, 1320, 1130, 1020, 916, 841 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_9F_3NO_2$ 232.0580, found [M+H] 232.0577.

Methyl 3,5-dimethoxy-2-(trifluoromethyl)benzoate (2l)



Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.4; White solid; Yield 64%; Mp. 83-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.50 (s, 1H), 3.89 (s, 6H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.89 (s), 163.09 (s), 159.66 (d, *J* = 1 Hz), 135.37 (q, *J* = 3 Hz), 123.50 (q, *J* = 271 Hz), 108.69 (q, *J* = 31 Hz), 103.96 (s), 100.91 (s), 56.43 (s), 55.84 (s), 53.08 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.34 (s); IR (neat) 2960, 2580, 1730, 1590, 1430, 1290, 1110, 863 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}F_3O_4$ 265.0682, found [M+H] 265.0683.

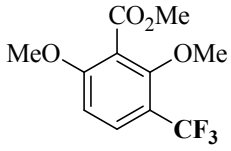
Methyl 3,5-dimethoxy-4-(trifluoromethyl)benzoate (2l*)



Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.5; White solid; Yield 21%; Mp. 113-114 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.24 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.05 (s), 159.37 (d, *J* = 1 Hz), 134.42 (s), 123.68 (q, *J* = 273 Hz), 111.07 (q, *J* = 30 Hz), 105.85 (s), 56.69 (s), 52.77

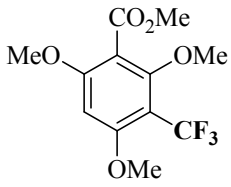
(s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.70 (s); IR (neat) 2960, 1720, 1580, 1410, 1230, 1100, 1030, 860 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}F_3O_4$ 263.0537, found [M-H] 263.0534.

Methyl 2,6-dimethoxy-3-(trifluoromethyl)benzoate (2m)



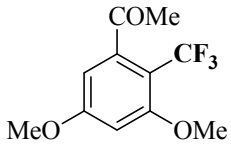
Purified by TLC (ethyl acetate/petroleum ether = 1:4, v:v), R_f = 0.6; Light yellow liquid; Yield 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8 Hz, 1H), 6.72 (d, *J* = 8 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.98 (s), 160.31 (s), 156.79 (d, *J* = 2 Hz), 129.39 (q, *J* = 5 Hz), 123.54 (q, *J* = 270 Hz), 119.28 (s), 116.81 (q, *J* = 31 Hz), 106.02 (s), 63.51 (d, *J* = 1 Hz), 56.42 (s), 52.93 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.38 (s); IR (neat) 2950, 2850, 1740, 1600, 1490, 1290, 1100, 969, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}F_3O_4$ 265.0682, found [M+H] 265.0682.

Methyl 2,4,6-trimethoxy-3-(trifluoromethyl)benzoate (2n)



Purified by TLC (ethyl acetate/petroleum ether = 1:3, v:v), R_f = 0.3; White solid; Yield 84%; Mp. 65-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (s, 1H), 3.91 (s, 6H), 3.88 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.98 (s), 161.31 (d, *J* = 1 Hz), 160.50 (s), 158.40 (d, *J* = 2 Hz), 123.61 (q, *J* = 272 Hz), 112.31 (s), 105.27 (q, *J* = 30 Hz), 92.07 (s), 64.13 (d, *J* = 2 Hz), 56.54 (s), 56.17 (s), 52.72 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.89 (s); IR (neat) 2950, 1720, 1610, 1410, 1250, 1080, 980, 815 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}F_3NaO_5$ 317.0607, found [M+Na] 317.0607.

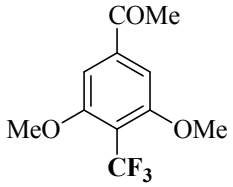
1-(3,5-Dimethoxy-2-(trifluoromethyl)phenyl)ethanone (2o)



Purified by TLC (ethyl acetate/petroleum ether = 1:2, v:v), R_f = 0.7; White solid; Yield 70%; Mp. 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, *J* = 1 Hz, 1H), 6.26 (d, *J* = 2 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

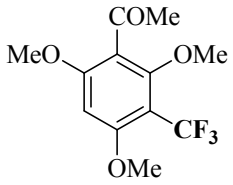
δ 202.98 (s), 163.44 (s), 159.68 (d, *J* = 2 Hz), 144.55 (q, *J* = 2 Hz), 123.88 (q, *J* = 271 Hz), 107.10 (q, *J* = 32 Hz), 101.76 (s), 99.87 (s), 56.38 (s), 55.81 (s), 31.43 (q, *J* = 3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.42 (s); IR (neat) 2950, 1700, 1590, 1360, 1290, 1110, 1030, 830 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}F_3O_3$ 249.0733, found [M+H] 249.0733.

1-(3,5-Dimethoxy-4-(trifluoromethyl)phenyl)ethanone (2o*)



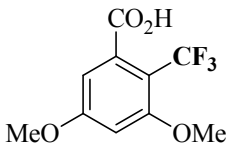
Purified by TLC (ethyl acetate/petroleum ether = 1:2, v:v), R_f = 0.7; White solid; Yield 23%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 3.93 (s, 6H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.04 (d, *J* = 4 Hz), 159.72 (d, *J* = 2 Hz), 140.82 (s), 123.63 (q, *J* = 274 Hz), 111.22 (q, *J* = 30Hz), 104.54 (s), 56.68 (s), 26.83 (d, *J* = 3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.35 (s); IR (neat) 2950, 1700, 1590, 1420, 1280, 1220, 1100, 829 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}F_3O_3$ 249.0733, found [M+H] 249.0735.

1-(2,4,6-Trimethoxy-3-(trifluoromethyl)phenyl)ethanone (2p)



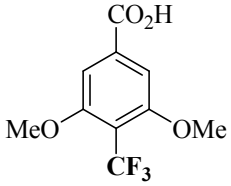
Purified by TLC (dichloromethane), R_f = 0.8; White solid; Yield 83%; Mp. 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.98 (s), 161.31 (d, *J* = 1 Hz), 160.50 (s), 158.40 (d, *J* = 2 Hz), 123.61 (q, *J* = 272 Hz), 112.31 (s), 105.27 (q, *J* = 30 Hz), 92.07 (s), 64.13 (d, *J* = 2 Hz), 56.54 (s), 56.17 (s), 52.72 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.77 (s); IR (neat) 2920, 1690, 1600, 1470, 1310, 1210, 1090, 917, 816 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}F_3KO_4$ 317.0398, found [M+K] 317.0397.

3,5-Dimethoxy-2-(trifluoromethyl)benzoic acid (2q)



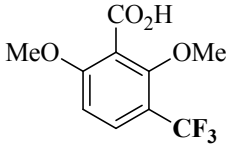
Purified by TLC (formic acid/dichloromethane = 1:100, v:v), R_f = 0.3; White solid; Yield 62%; Mp. 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62(s, 1H), 6.61(s, 1H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.63 (s), 163.16 (s), 159.81 (s), 134.50 (s), 123.44 (q, *J* = 271 Hz), 108.75 (q, *J* = 31 Hz), 104.16 (s), 101.38 (s), 56.52 (s), 55.93 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -56.79 (s); IR (neat) 2950, 1700, 1590, 1460, 1270, 1110, 1030, 911, 828 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{10}F_3O_4$ 251.0526, found [M+H] 251.0528.

3,5-Dimethoxy-4-(trifluoromethyl)benzoic acid (2q*)



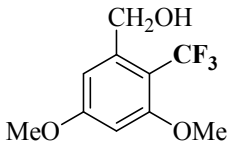
Purified by TLC (formic acid/dichloromethane = 1:100, v:v), R_f = 0.2; White solid; Yield 16%; sublimation at 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H), 3.94 (s, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 168.34 (s), 160.61 (s), 136.86 (s), 125.05 (q, *J* = 273 Hz), 111.49 (q, *J* = 30 Hz), 106.83 (s), 56.96 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.83 (s); IR (neat) 2970, 2850, 1690, 1580, 1410, 1230, 1110, 924, 867 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{10}F_3O_4$ 251.0526, found [M+H] 251.0533.

2,6-Dimethoxy-3-(trifluoromethyl)benzoic acid (2r)



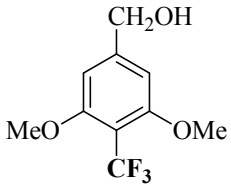
Purified by TLC (formic acid/dichloromethane = 1:100, v:v), R_f = 0.2; White solid; Yield 52%; Mp. 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9 Hz, 1H), 6.78 (d, *J* = 9 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.27 (s), 160.49 (s), 157.39 (d, *J* = 2 Hz), 130.07 (q, *J* = 5 Hz), 123.50 (q, *J* = 270 Hz), 118.30 (s), 117.23 (q, *J* = 31 Hz), 106.36 (s), 64.05 (s), 56.60 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.41 (s); IR (neat) 2920, 1720, 1650, 1590, 1420, 1280, 1090, 877, 815 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{10}F_3O_4$ 251.0526, found [M+H] 251.0525.

(3,5-Dimethoxy-2-(trifluoromethyl)phenyl)methanol (2s)



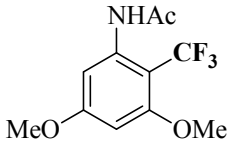
Purified by TLC (ethyl acetate/petroleum ether = 1:1, v:v), R_f = 0.7; White solid; Yield 46%; Mp. 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, *J* = 2 Hz, 1H), 6.44 (d, *J* = 2 Hz, 1H), 4.80 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.91 (s), 160.10 (d, *J* = 2 Hz), 142.88 (s), 125.20 (q, *J* = 272 Hz), 108.36 (q, *J* = 31 Hz), 104.50 (s), 98.39 (s), 62.69 (q, *J* = 6 Hz), 56.26 (s), 55.43 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.03 (s); IR (neat) 3300, 2950, 1590, 1460, 1290, 1090, 1030, 835 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}F_3O_3$ 237.0733, found [M+H] 237.0732.

(3,5-Dimethoxy-4-(trifluoromethyl)phenyl)methanol (2s*)



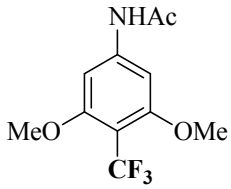
Purified by TLC (ethyl acetate/petroleum ether = 1:1, v:v), R_f = 0.6; White solid; Yield 15%; Mp. 79-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 2H), 4.69 (s, 2H), 3.86 (s, 6H), 2.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.55 (d, *J* = 1 Hz), 146.70 (s), 124.16 (q, *J* = 273 Hz), 106.23 (q, *J* = 30 Hz), 102.77 (s), 64.85 (s), 56.48 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.86 (s); IR (neat) 3280, 2920, 1590, 1420, 1330, 1240, 1090, 825 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{12}F_3O_3$ 237.0733, found [M+H] 237.0731.

***N*-(3,5-Dimethoxy-2-(trifluoromethyl)phenyl)acetamide (2t)**



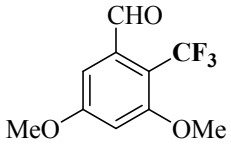
Purified by TLC (dichloromethane), R_f = 0.4; White solid; Yield 52%; Mp. 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.42 (s, 1H), 6.32 (s, 1H), 3.84 (d, *J* = 4 Hz, 6H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.65 (s), 163.12 (s), 159.98 (d, *J* = 1 Hz), 138.08 (d, *J* = 1 Hz), 125.03 (q, *J* = 272 Hz), 101.67 (d, *J* = 32 Hz), 100.77 (s), 96.59 (s), 56.37 (s), 55.67 (s), 25.10 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -52.78 (s); IR (neat) 3260, 1660, 1590, 1530, 1280, 1200, 1090, 834 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{13}F_3NO_3$ 264.0842, found [M+H] 264.0841.

***N*-(3,5-Dimethoxy-4-(trifluoromethyl)phenyl)acetamide (2t*)**



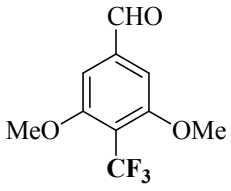
Purified by TLC (dichloromethane), R_f = 0.3; White solid; Yield 21%; Mp. 148-149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 6.87 (s, 2H), 3.82 (s, 6H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.95 (s), 159.91 (s), 142.49 (s), 124.15 (q, *J* = 272 Hz), 103.07 (d, *J* = 30 Hz), 96.09 (s), 56.43 (s), 24.91 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.47 (s); IR (neat) 3280, 2940, 1670, 1600, 1280, 1100, 1020, 827 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}F_3NNaO_3$ 286.0661, found [M+Na] 286.0653.

3,5-Dimethoxy-2-(trifluoromethyl)benzaldehyde (2u)



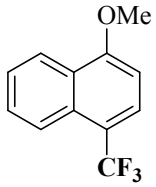
Purified by TLC (ethyl acetate/petroleum ether = 1:3, v:v), R_f = 0.6; White solid; Yield 38%; Mp. 75-77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (q, *J* = 2 Hz, 1H), 6.99 (d, *J* = 2 Hz, 1H), 6.73 (d, *J* = 2 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.67 (q, *J* = 5 Hz), 163.14 (s), 159.77 (d, *J* = 2 Hz), 138.35 (s), 124.60 (q, *J* = 273 Hz), 111.73 (q, *J* = 31 Hz), 104.26 (s), 103.97 (s), 56.67 (s), 55.94 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -51.40 (s); IR (neat) 3100, 2920, 2850, 1690, 1590, 1470, 1280, 1070, 847 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{10}F_3O_3$ 235.0577, found [M+H] 235.0581.

3,5-Dimethoxy-4-(trifluoromethyl)benzaldehyde (2u*)



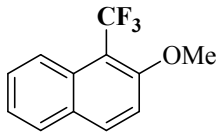
Purified by TLC (ethyl acetate/petroleum ether = 1:3, v:v), R_f = 0.5; White solid; Yield 10%; Mp. 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.12 (s, 2H), 3.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.17 (s), 160.09 (s), 139.69 (s), 123.50 (q, *J* = 274 Hz), 112.29 (q, *J* = 30 Hz), 105.49 (s), 56.74 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.87 (s); IR (neat) 3020, 2920, 2850, 1700, 1590, 1470, 1240, 1100, 1030, 835 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_8F_3O_3$ 233.0431, found [M-H] 233.0426.

1-Methoxy-4-(trifluoromethyl)naphthalene (2v)



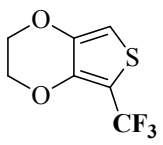
Purified by TLC (ethyl acetate/petroleum ether = 1:8, v:v), R_f = 0.7; Light yellow liquid; Yield 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8 Hz, 1H), 8.12 (d, *J* = 8 Hz, 1H), 7.78 (d, *J* = 8 Hz, 1H), 7.62 (t, *J* = 8 Hz, 1H), 7.55 (t, *J* = 7 Hz, 1H), 6.77 (d, *J* = 8 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.58 (s), 130.24 (s), 128.15 (s), 126.07 (s), 126.01 (s), 125.84 (q, *J* = 6 Hz), 124.13 (q, *J* = 2 Hz), 122.80 (s), 118.45 (q, *J* = 30 Hz), 104.63 (s), 101.82 (s), 55.90 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.96 (s); IR (neat) 2940, 2850, 1590, 1470, 1260, 1110, 998, 820 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}F_3O$ 227.0678, found [M+H] 227.0680.

2-Methoxy-1-(trifluoromethyl)naphthalene (2w)



Purified by TLC (ethyl acetate/petroleum ether = 1:8, v:v), R_f = 0.7; White solid; Yield 55%; Mp. 50-52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9 Hz, 1H), 7.98 (d, *J* = 9 Hz, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.56 (t, *J* = 8 Hz, 1H), 7.41 (t, *J* = 8 Hz, 1H), 7.31 (d, *J* = 9 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.08 (d, *J* = 2 Hz), 134.48 (s), 131.16 (s), 129.14 (s), 128.77 (s), 128.29 (s), 126.91 (s), 124.34 (s), 124.08 (q, *J* = 5 Hz), 114.23 (s), 111.18 (q, *J* = 29 Hz), 57.38 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -52.54 (s); IR (neat) 2950, 2850, 1630, 1510, 1340, 1240, 1060, 811 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}F_3O$ 227.0678, found [M+H] 227.0680.

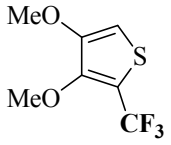
5-(Trifluoromethyl)-2,3-dihydro-thieno[3,4-*b*][1,4]dioxine (2x)



Purified by TLC (ethyl acetate/petroleum ether = 1:8, v:v), R_f = 0.7; Light yellow liquid; Yield 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 1H), 4.29-4.33 (m, 2H), 4.19-4.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.13 (d, *J* = 3 Hz), 141.48 (s), 122.39 (q, *J* = 267 Hz), 104.56 (q, *J* = 39 Hz), 102.25 (s), 65.08 (s), 64.39 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.36 (s); IR (neat) 3120, 2940, 1710, 1600, 1510, 1310,

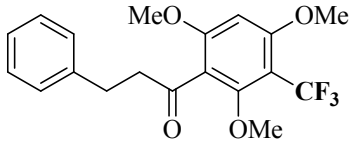
1170, 1070, 940 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_7H_4F_3O_2S$ 208.9890, found [M-H] 208.9890.

3,4-Dimethoxy-2-(trifluoromethyl)thiophene (2y)



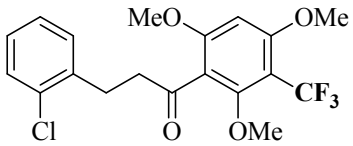
Purified by TLC (ethyl acetate/petroleum ether = 1:8, v:v), R_f = 0.6; Light yellow liquid; Yield 84%; ^1H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 3.94 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.67 (s), 147.62-147.48 (m), 122.35 (q, *J* = 268 Hz), 113.08 (q, *J* = 38 Hz), 99.95-96.84 (m), 61.23 (s), 57.66 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.59 (s); IR (neat) 3120, 2940, 1510, 1410, 1310, 1120, 1030, 883 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_8H_8F_3O_4S$ 257.0090, found [M+HCO_2H-H] 257.0085.

3-Phenyl-1-(2,4,6-trimethoxy-3-(trifluoromethyl)phenyl)propan-1-one (2za)



Purified by TLC (dichloromethane/petroleum ether = 2:1, v:v), R_f = 0.8; Light yellow liquid; Yield 39%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.05 (m, 5H), 6.28 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.66 (s, 3H), 3.15-2.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.66 (s), 160.99 (s), 159.88 (s), 157.71 (s), 141.16 (s), 128.61 (s), 128.48 (s), 126.10 (s), 123.68 (q, *J* = 272 Hz), 119.66 (s), 105.50 (q, *J* = 30 Hz), 92.27 (s), 64.81 (d, *J* = 2 Hz), 56.59 (s), 55.97 (s), 46.45 (s), 29.72 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.79 (s); IR (neat) 2950, 2840, 1700, 1600, 1310, 1210, 1100, 922, 814 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{18}F_3O_4$ 367.1163, found [M-H] 367.1164.

3-(2-Chlorophenyl)-1-(2,4,6-trimethoxy-3-(trifluoromethyl)phenyl)propan-1-one (2zb)



Purified by TLC (dichloromethane/petroleum ether = 2:1, v:v), R_f = 0.8; Light yellow solid; Yield 48%; Mp. 110-112 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 2H), 7.21-7.10 (m, 2H), 6.29 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.69 (s, 3H), 3.15-3.07 (m,

4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.32 (s), 161.03 (s), 159.97 (s), 157.73 (s), 138.74 (s), 134.09 (s), 130.88 (s), 129.55 (s), 127.69 (s), 126.92 (s), 123.68 (q, J = 272 Hz), 119.53 (s), 105.51 (q, J = 30 Hz), 92.25 (s), 64.81 (s), 56.58 (s), 55.97 (s), 44.47 (s), 27.82 (s); ^{19}F NMR (377 MHz, $CDCl_3$) δ -55.79 (s); IR (neat) 2960, 1700, 1580, 1410, 1280, 1100, 921, 821 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}ClF_3O_6$ 447.0817, found [M+HCO_2H-H] 447.0818.

5. References

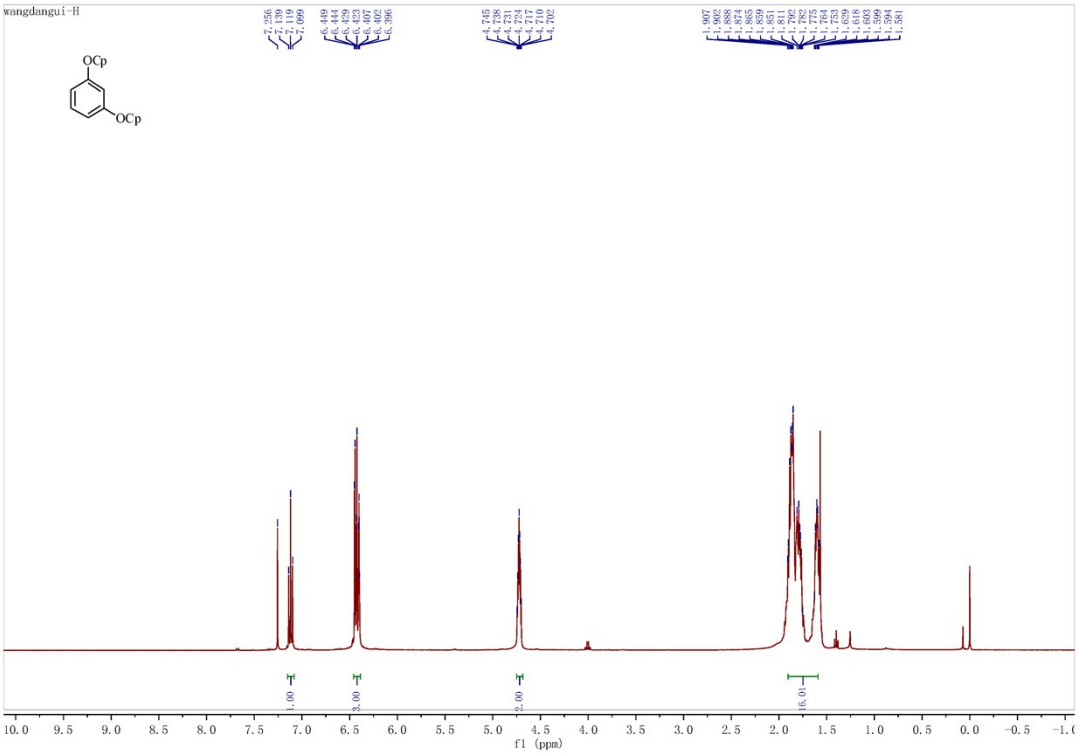
[1] M. Iwasaki, T. Watanabe, T. Ishikawa, S. Chansakaow, Y. Higuchi, S. Tahara, *Heterocycles.* **2004**, *63*, 1375-1392.

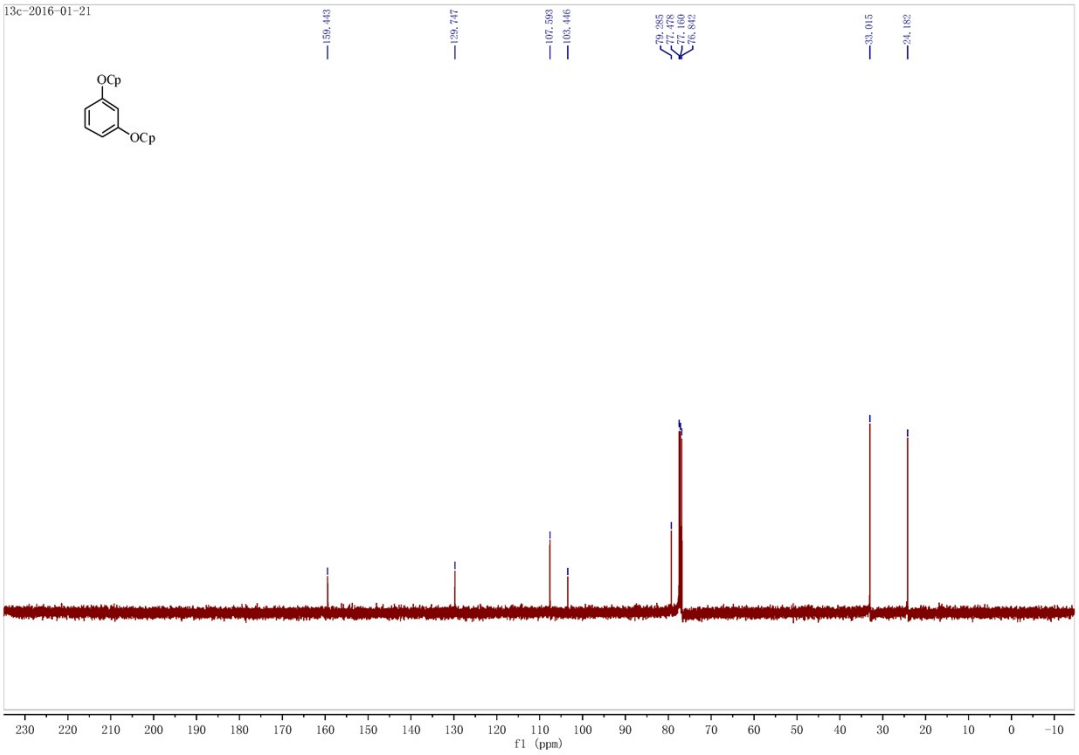
[2] A. A. Beharry, O. Sadovski, G. A. Woolley Beharry, A. Andrew, O. Sadovski, G. A. Woolley, *J. Am. Chem. Soc.* **2011,** *133*, 19684-19687.

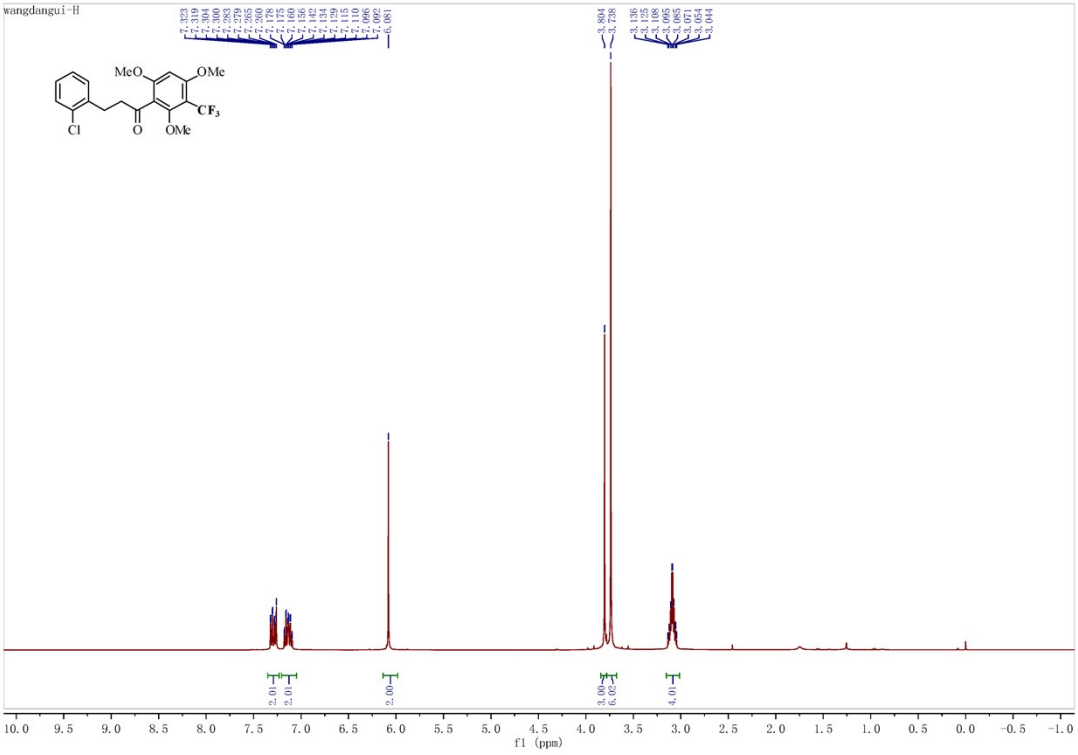
[3] L. D. Chiaradia, R. D. Santos, C. E. Vitor, A. A. Vieira, P. C. Leal, R. J. Nunes, J. B. Calixto, R. A. Yunes, *Bioorg. Med. Chem.* **2008**, *16*, 658-667.

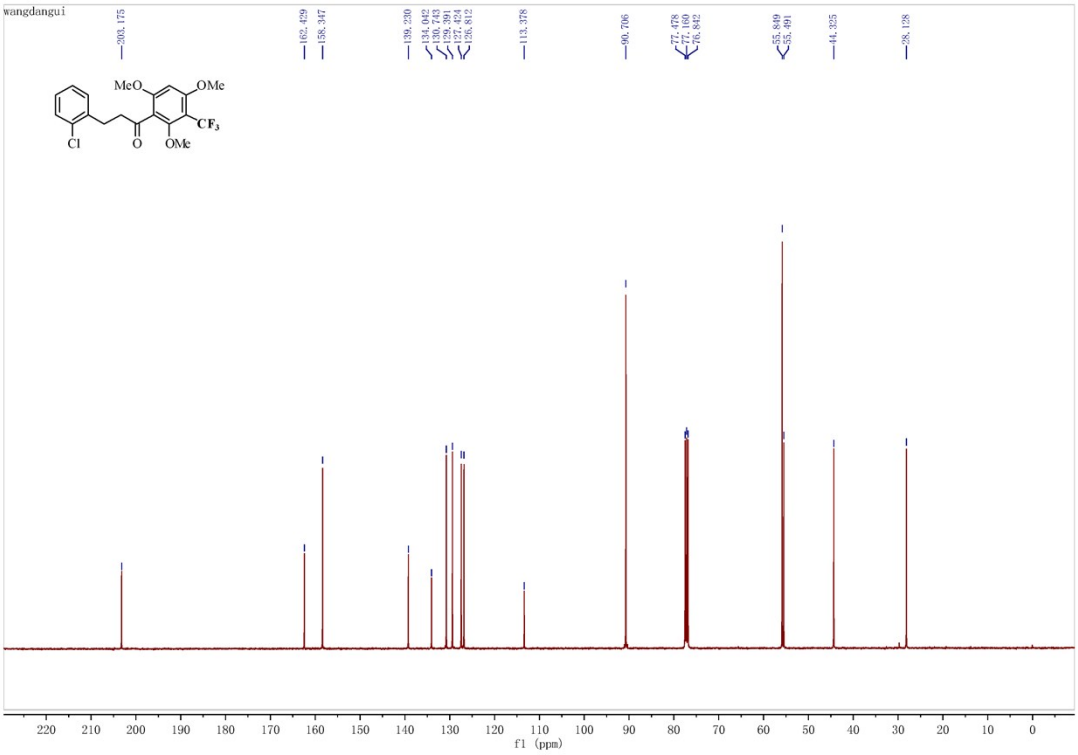
[4] H. Y. Lee, M. An*, Tetrahedron Lett.* **2003**, *44*, 2775-2778.

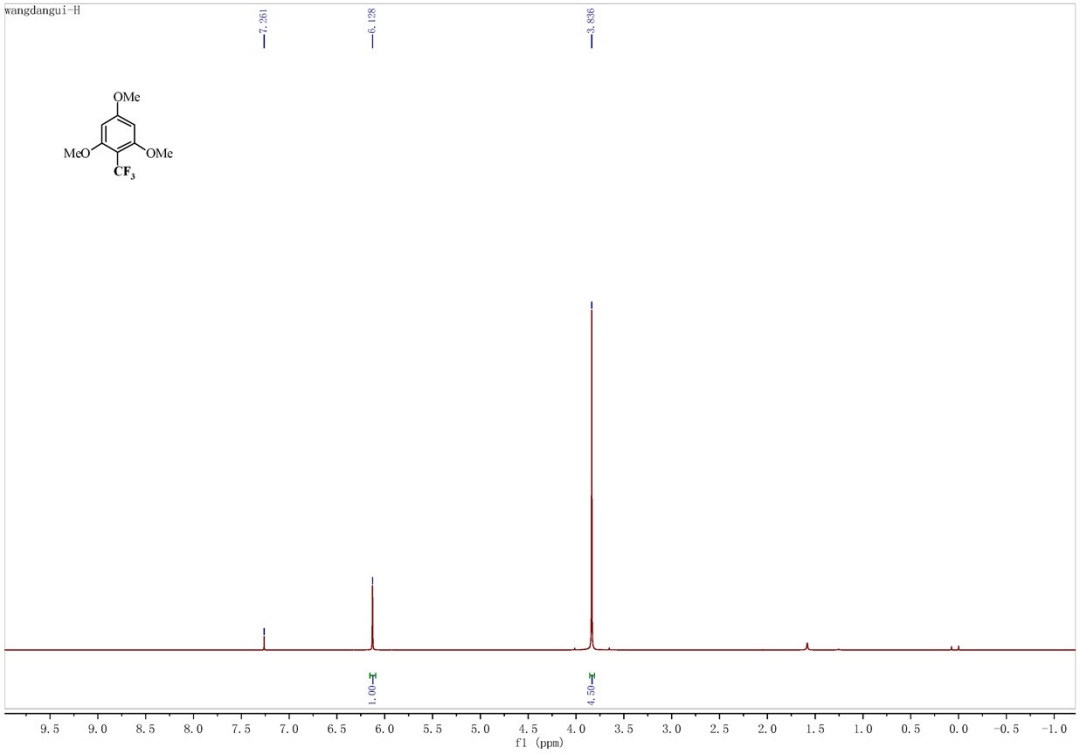
6. Copies of ^{1}H, ^{19}F and ^{13}C NMR spectra

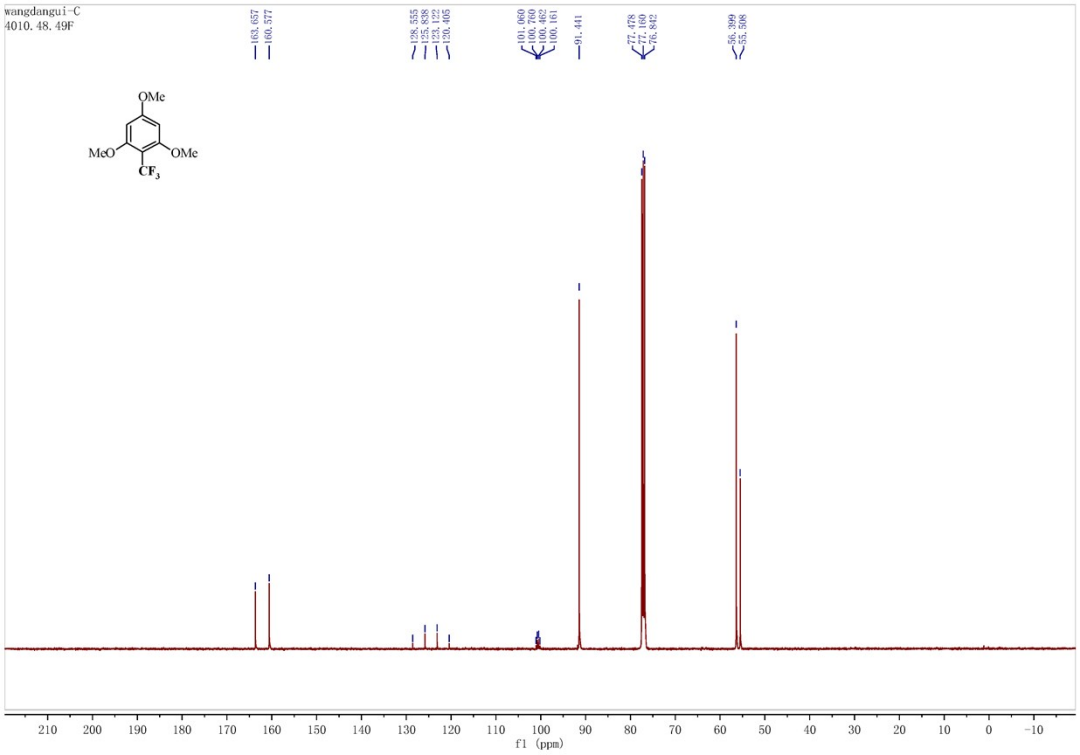


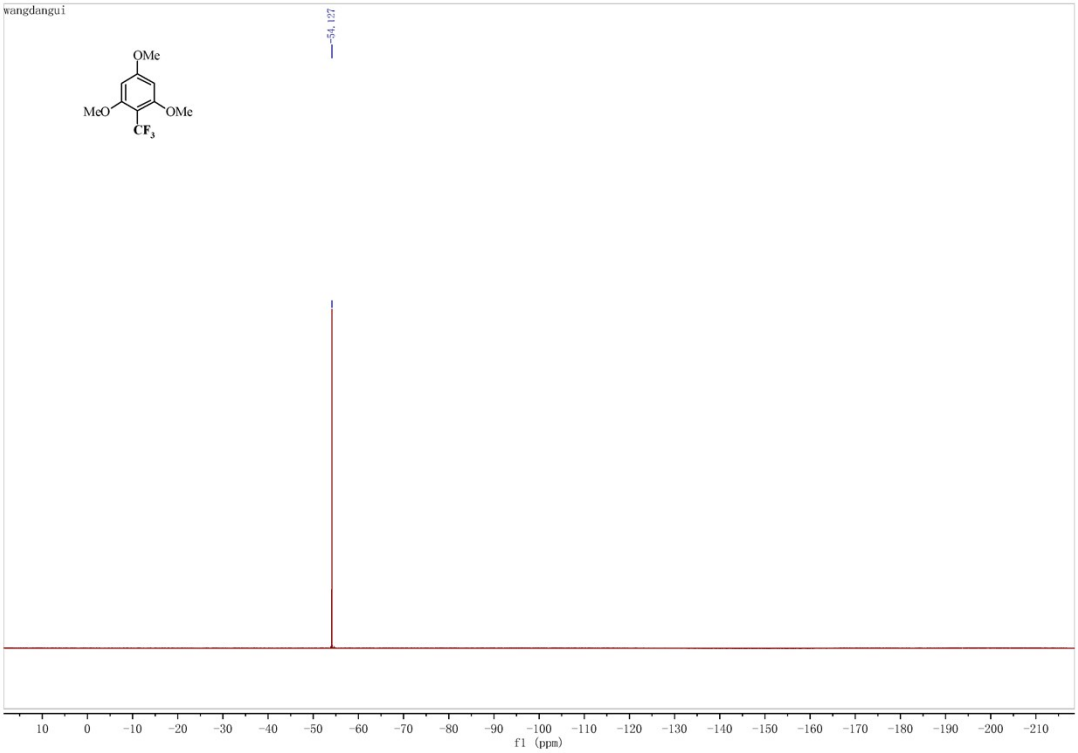


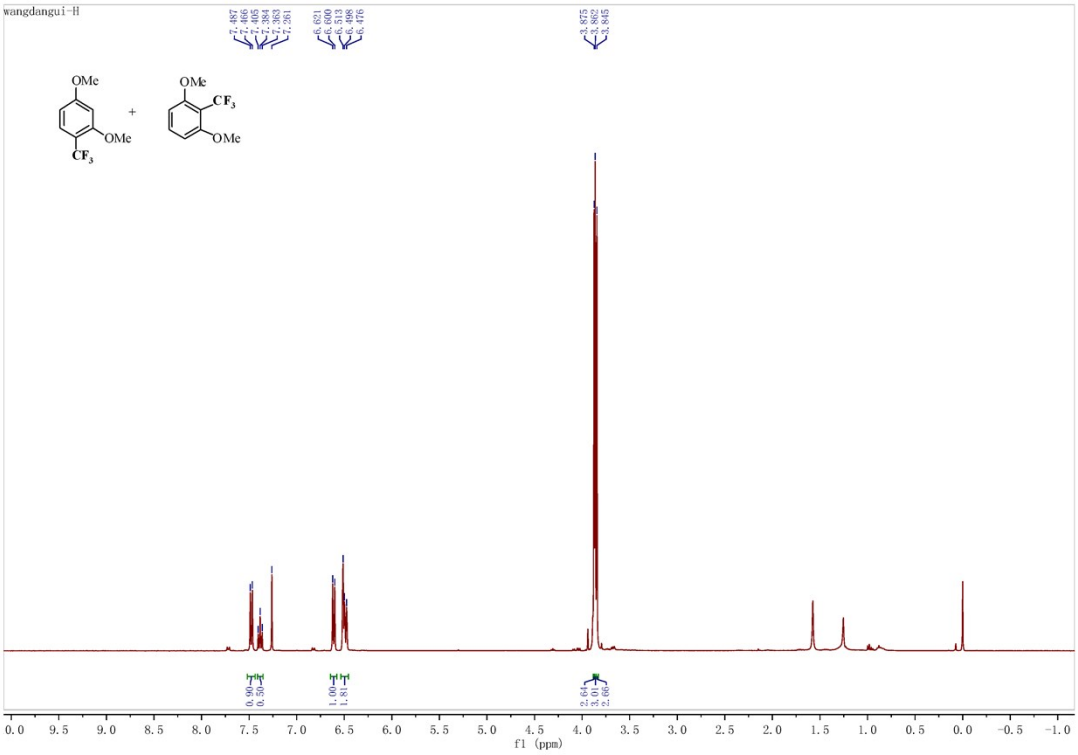

wangdangui-H
MeO
OMe
CF3
Cl
O
OMe
f1 (ppm)

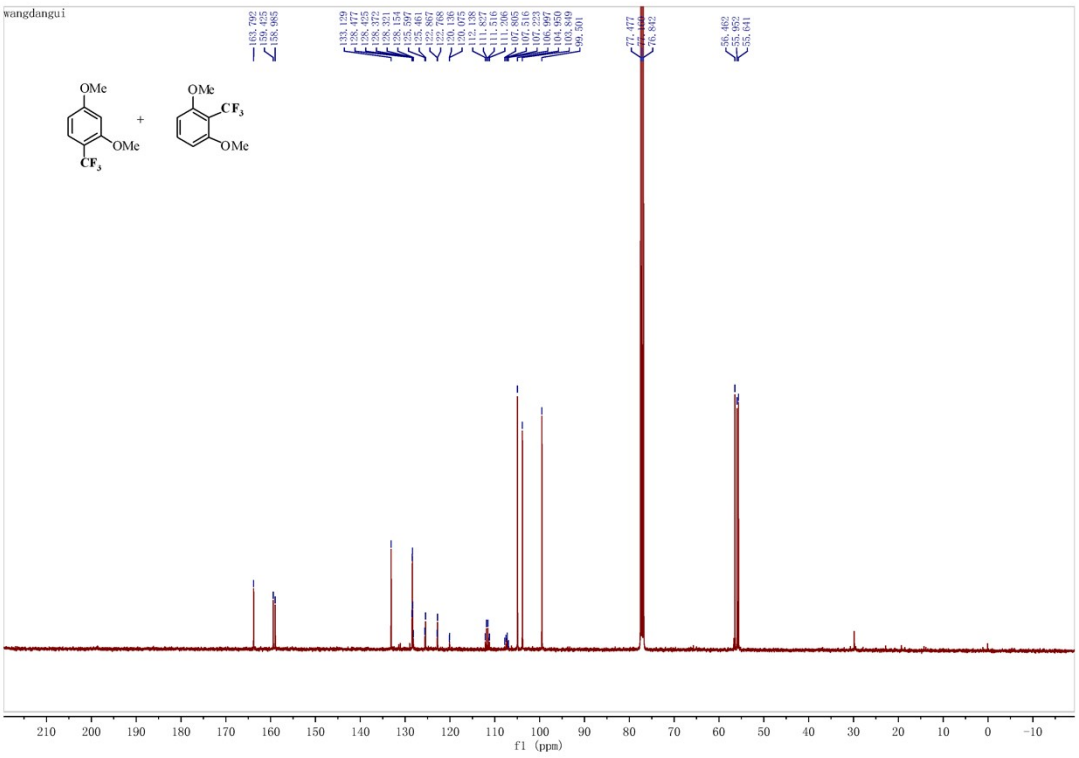

wangdangui
MeO
OMe
CF3
Cl
O
OMe
f1 (ppm)


wangdangui-H
7.261
6.128
3.836
OMe
MeO
OMe
CF3
1.00
4.50
f1 (ppm)


wangdangui-C
4010.48.49F
163.657
160.577
128.535
125.838
123.122
120.465
101.060
100.780
100.482
100.161
91.441
77.478
77.160
76.842
56.399
55.508
OMe
MeO
OMe
CF3
f1 (ppm)


wangdangui
-54.127
OMe
MeO
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


wangdangui-H
7.487
7.466
7.405
7.384
7.383
7.361
6.621
6.600
6.513
6.498
6.476
3.875
3.862
3.845
OMe
OMe
CF3
+
OMe
CF3
OMe
0.90
0.50
1.00
1.81
2.64
3.00
2.86
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui
163.792
159.455
158.985
133.129
128.477
128.425
128.372
128.321
128.154
125.597
125.461
122.867
122.768
120.136
120.075
119.198
111.827
111.516
111.206
107.965
107.516
107.223
106.997
104.959
104.849
99.501
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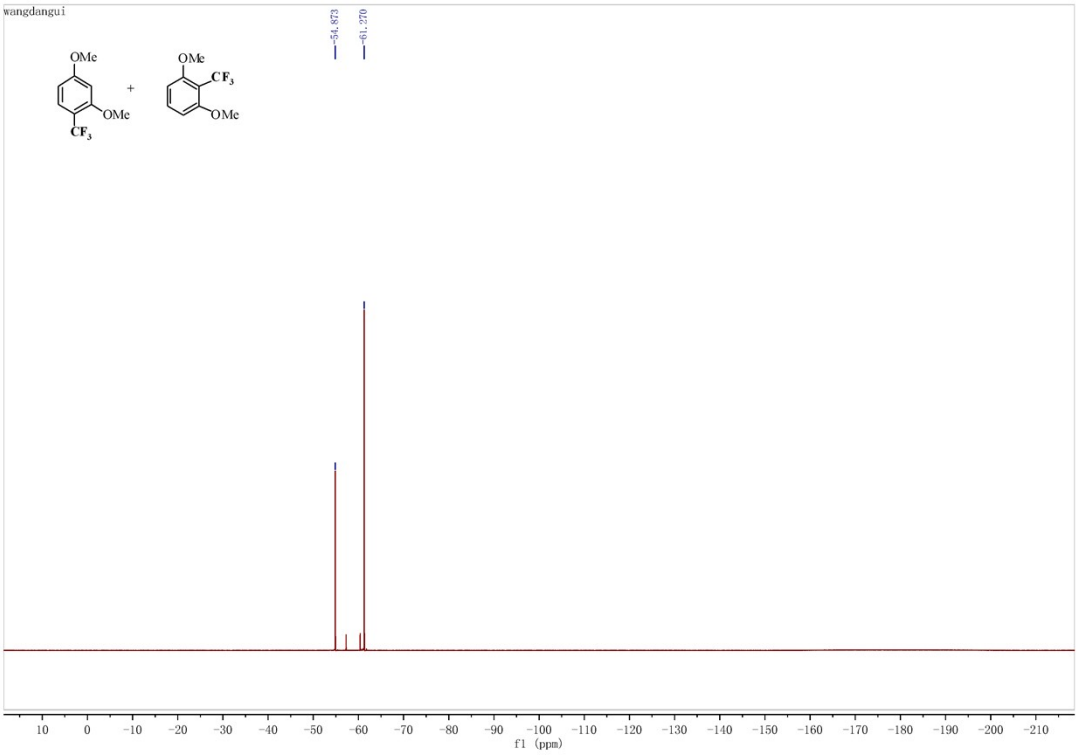
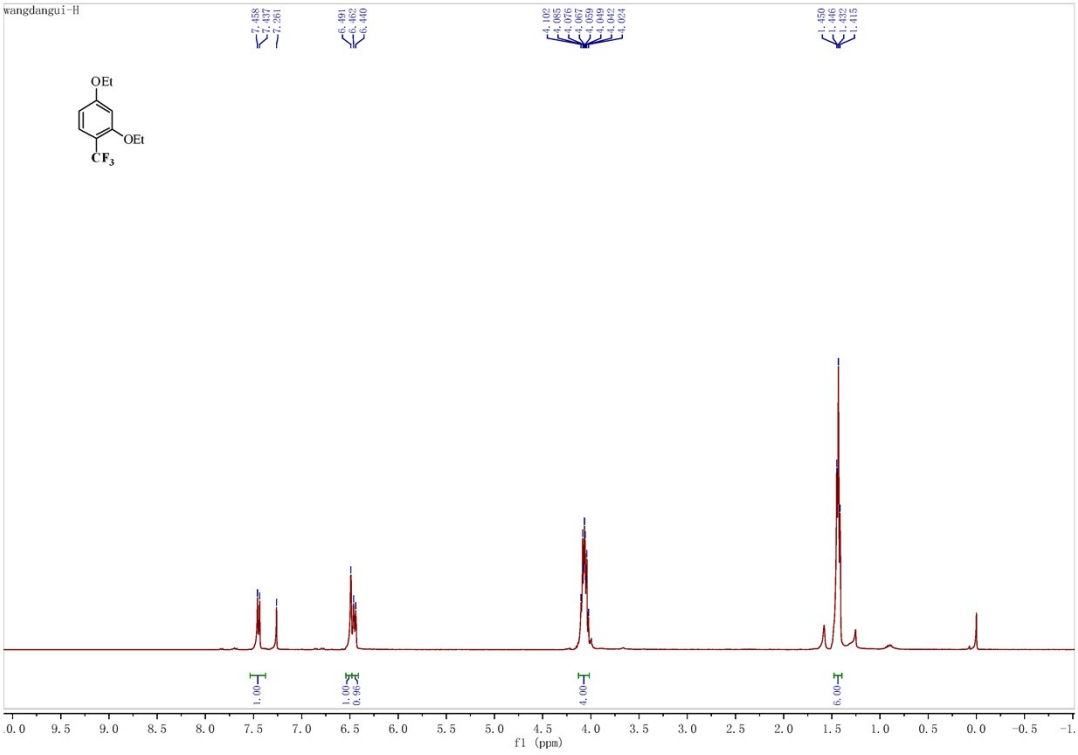
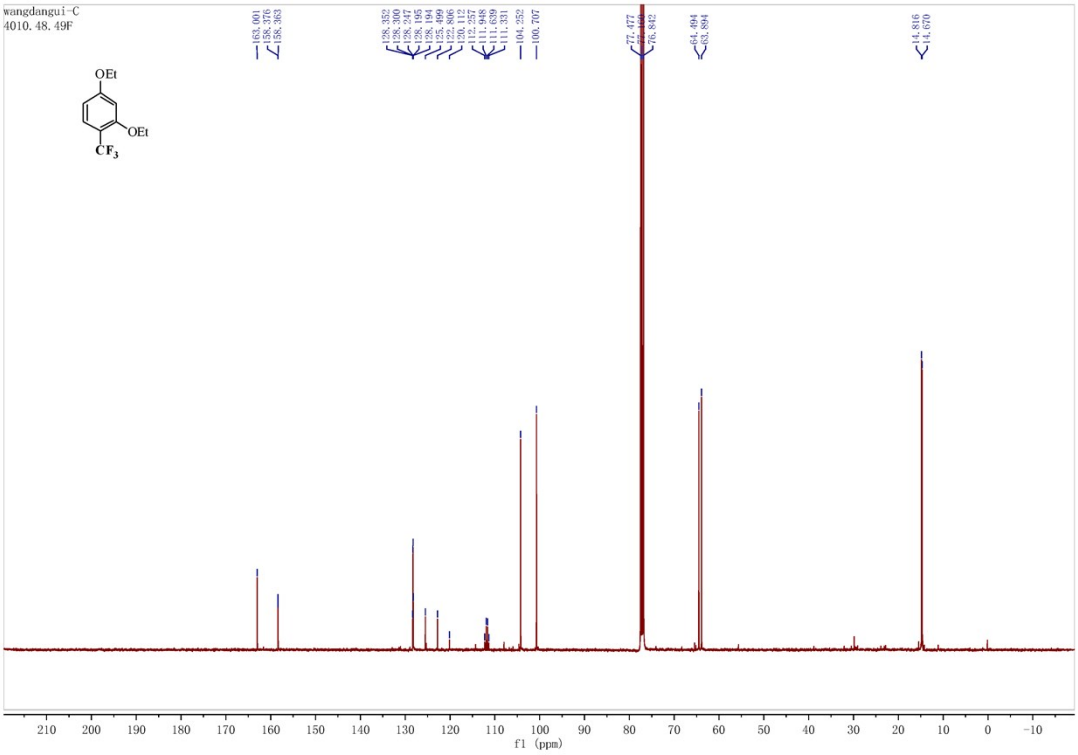
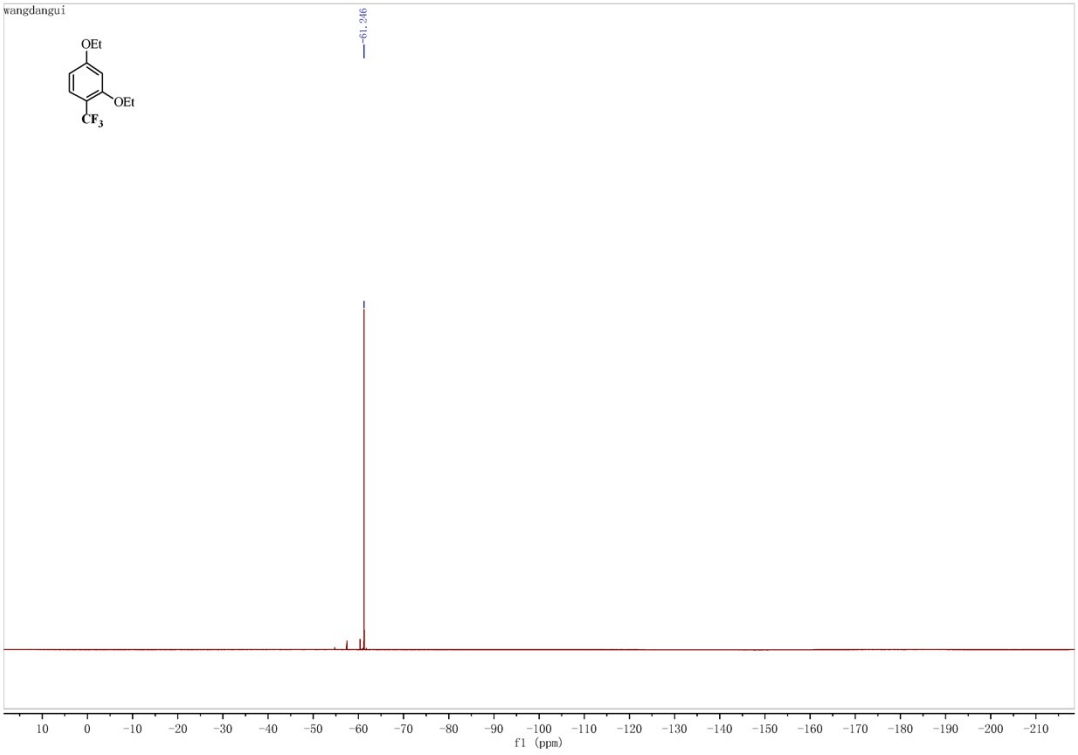
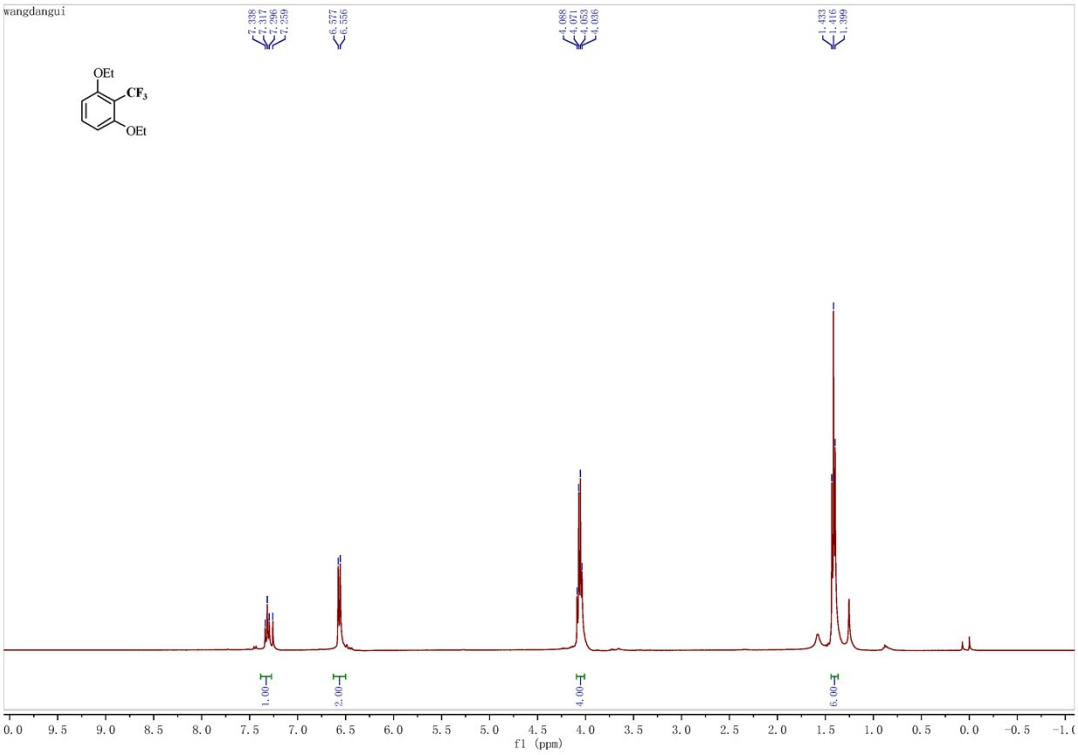
OMe
CF3
OMe
OMe
CF3
f1 (ppm)

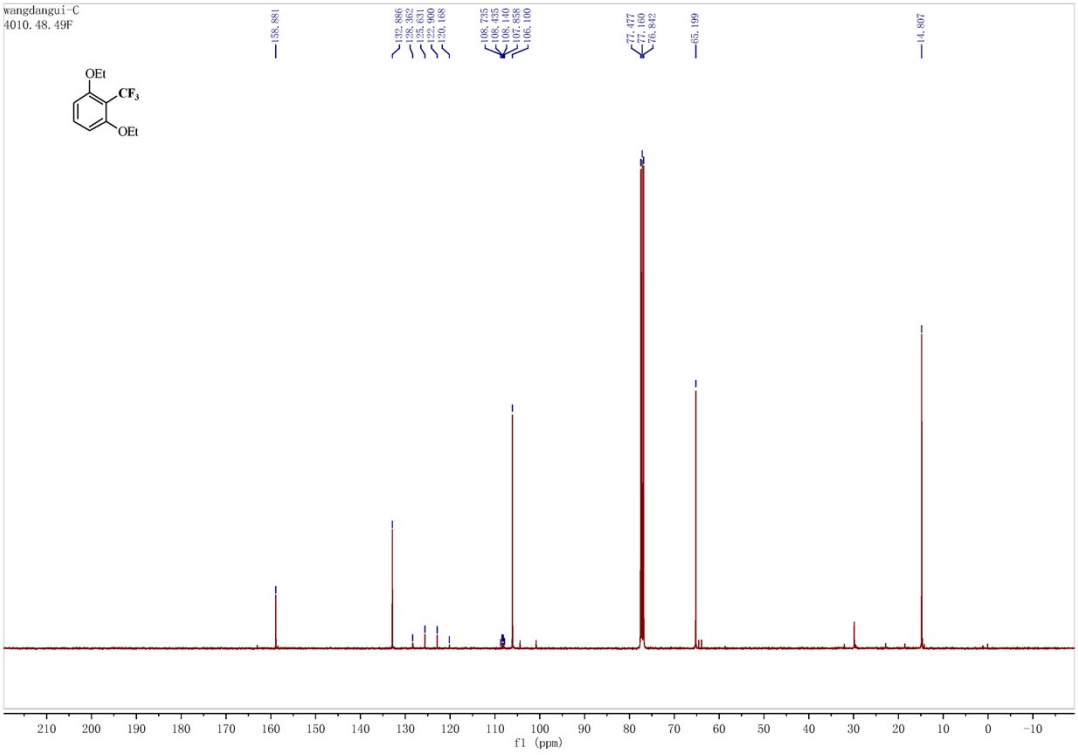

wangdangui
-54.873
-61.270
OMe
OMe
CF3
OMe
OMe
CF3
f1 (ppm)

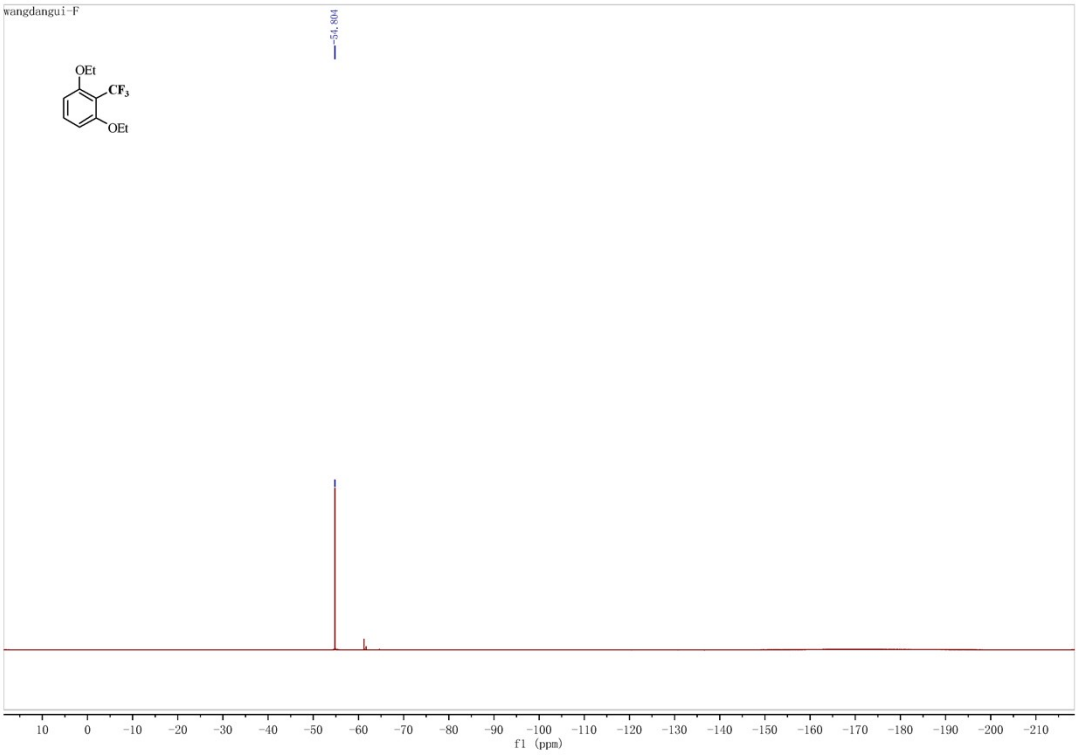

wangdangui-H
7.458
7.437
7.361
6.491
6.462
6.440
4.102
4.085
4.076
4.067
4.059
4.049
4.042
4.024
1.450
1.446
1.432
1.415
OEt
OEt
CF3
1.00
1.00
0.96
4.00
6.00
f1 (ppm)

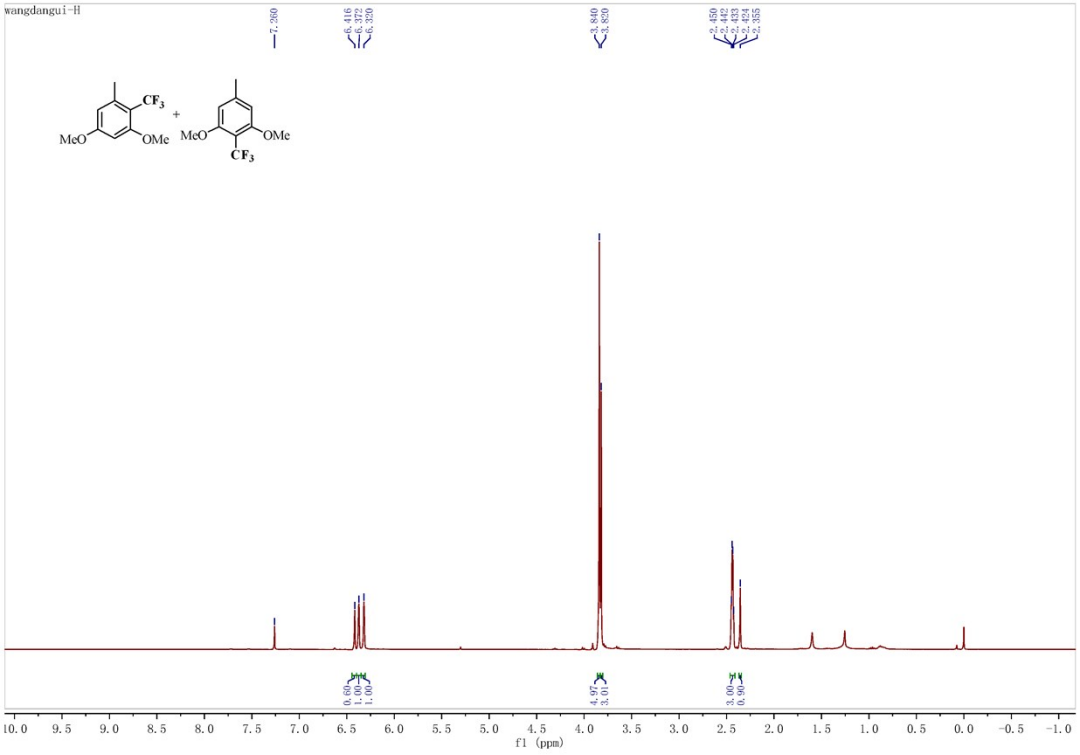

wangdangui-C
4010.48.49F
163.001
158.376
158.363
128.352
128.309
128.247
128.195
128.144
125.499
122.806
120.112
117.425
111.948
111.639
111.331
104.352
100.707
77.477
77.164
76.842
64.494
63.894
14.816
14.670
OEt
OEt
CF3
f1 (ppm)

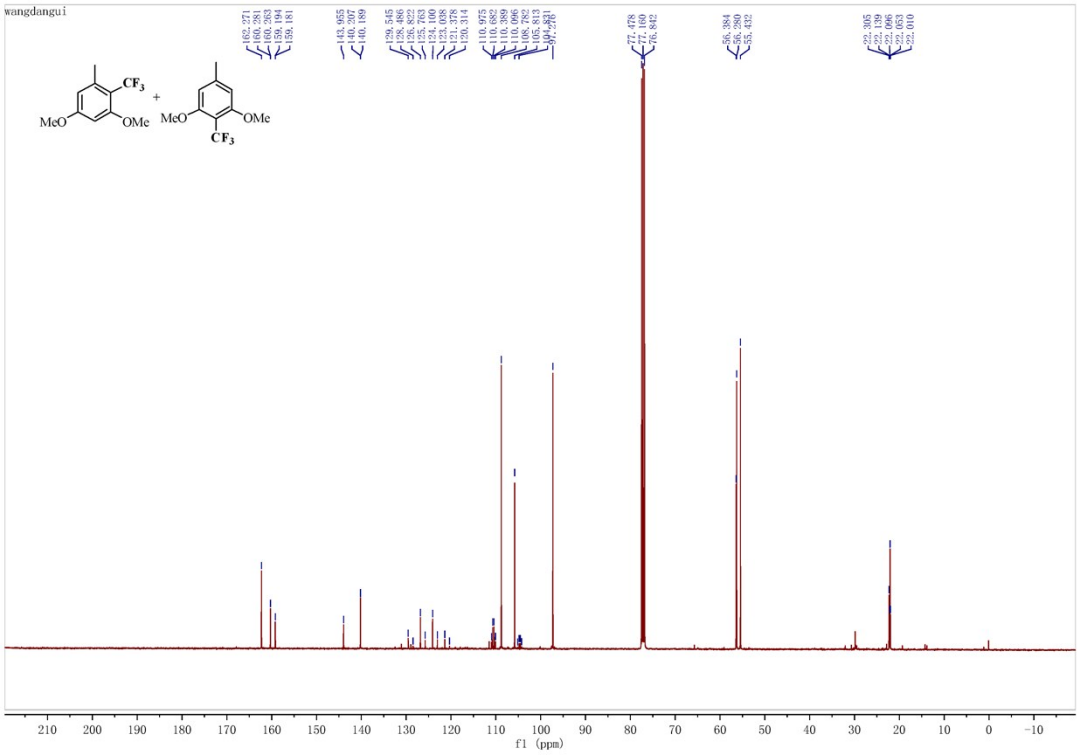

wangdangui
OEt
OEt
CF3
-61.246
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

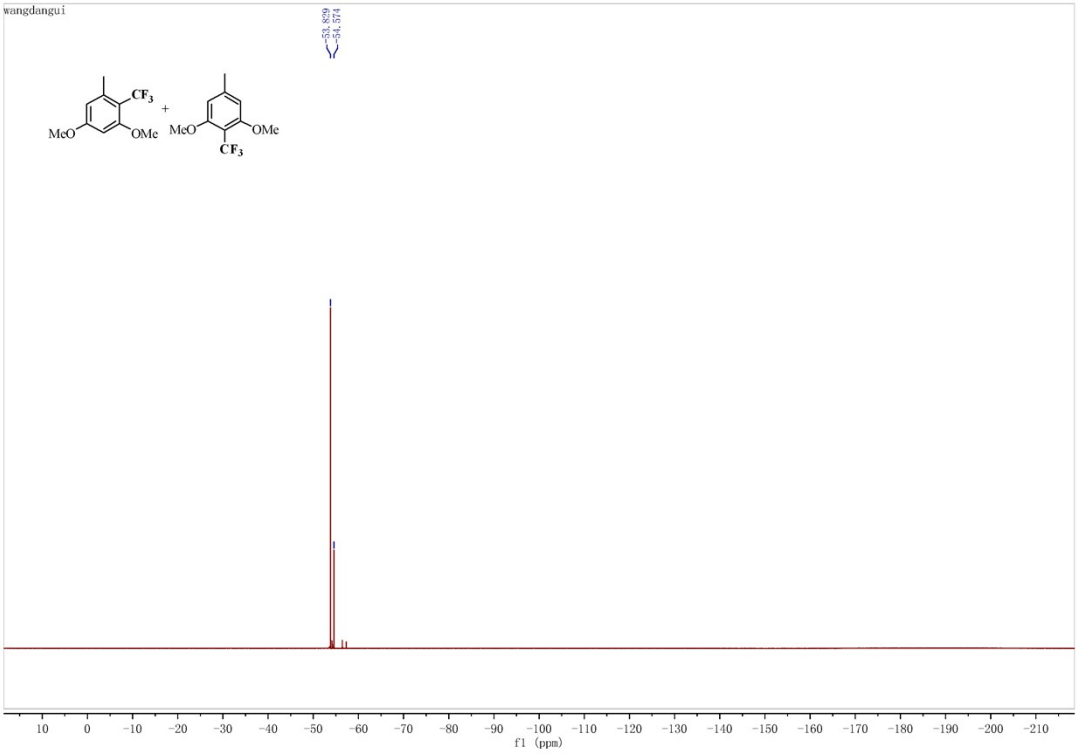

wangdangui
7.338
7.317
7.296
7.259
6.577
6.556
4.088
4.071
4.053
4.036
1.433
1.416
1.399
OEt
CF3
OEt
1.00
2.00
4.00
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

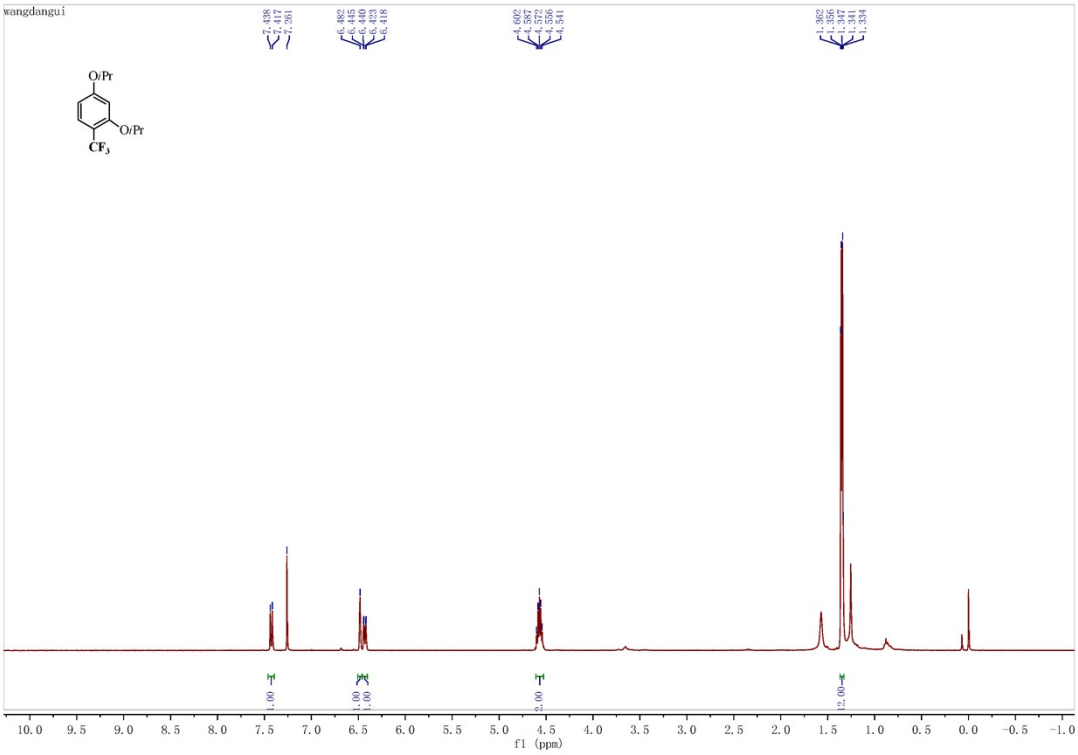

wangdangui-C
4010.48.49F
158.881
132.886
128.362
125.631
122.960
120.168
108.735
108.435
108.140
107.858
106.100
77.477
77.160
76.842
65.199
14.807
OEt
CF3
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

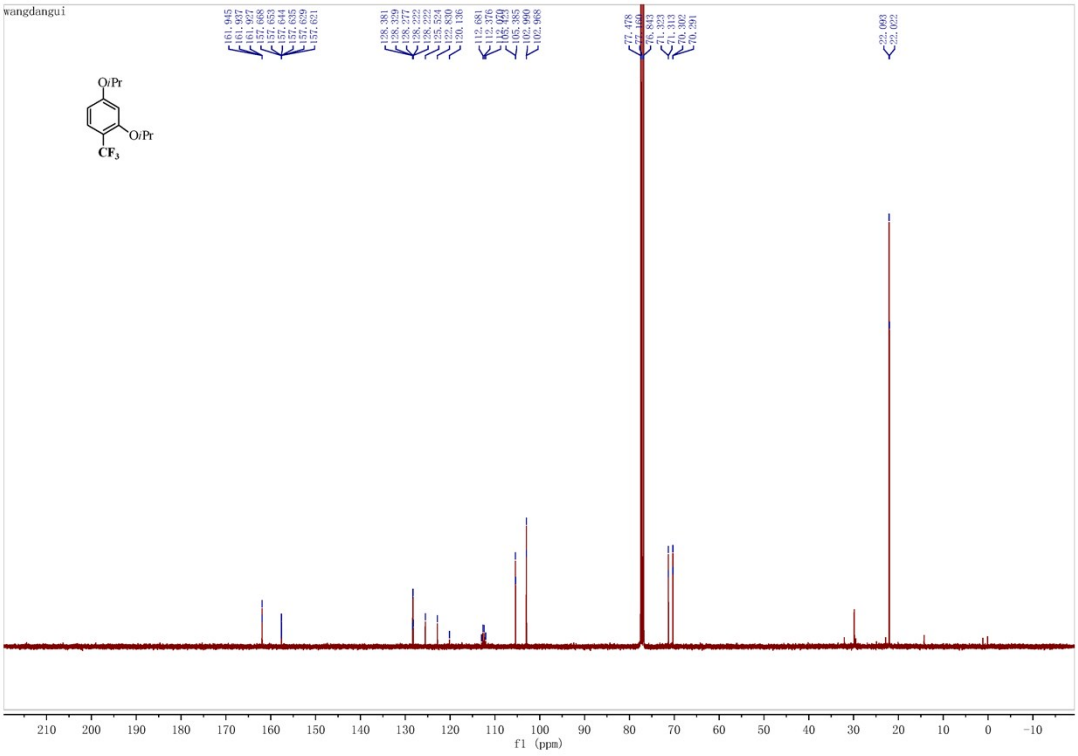

wangdangui-F
-54.804
OEt
CF3
OEt
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

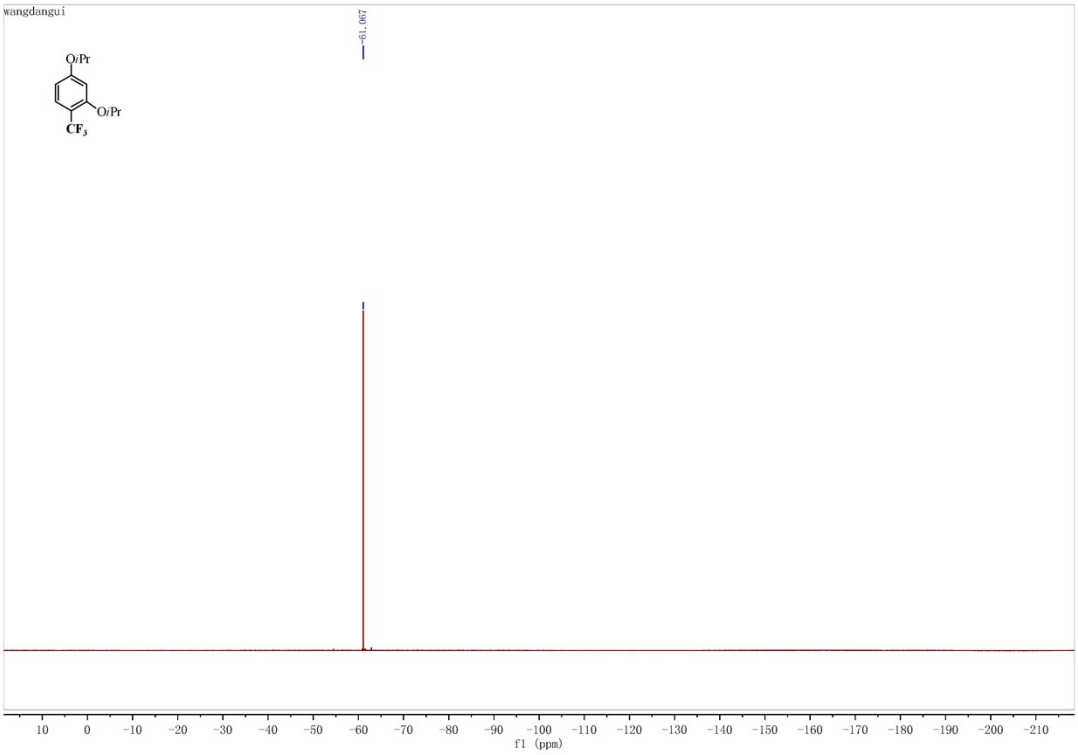

wangdangui-H
MeO
OMe
CF3
f1 (ppm)

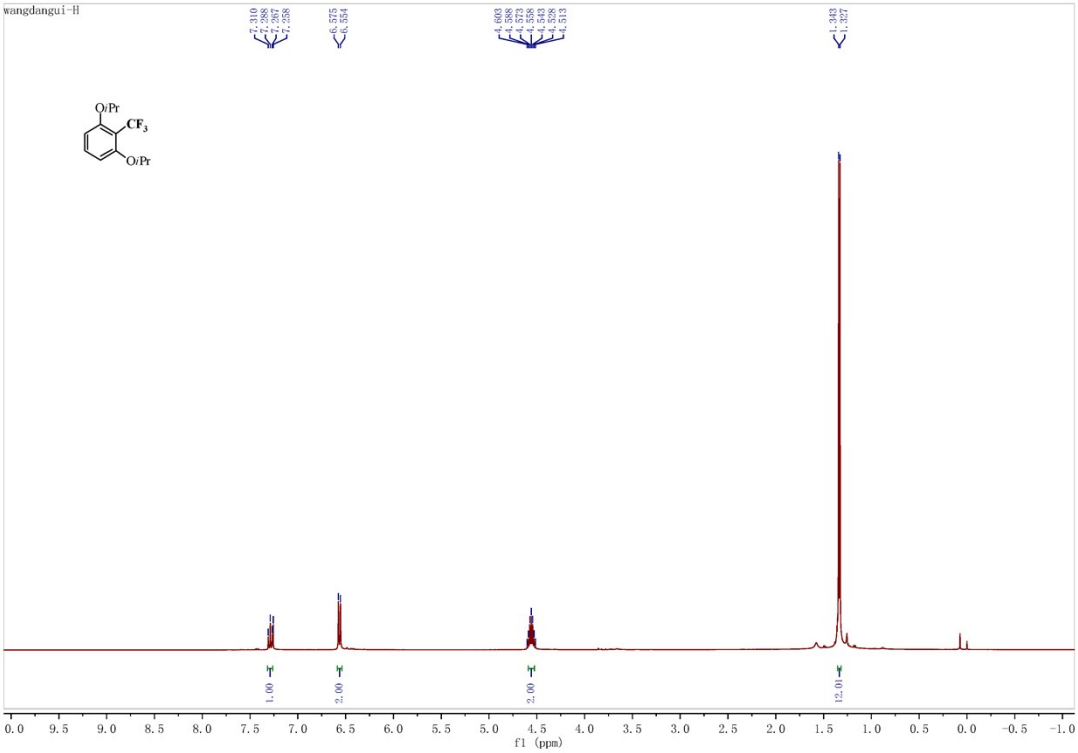

wangdangui
MeO
OMe
CF3
f1 (ppm)

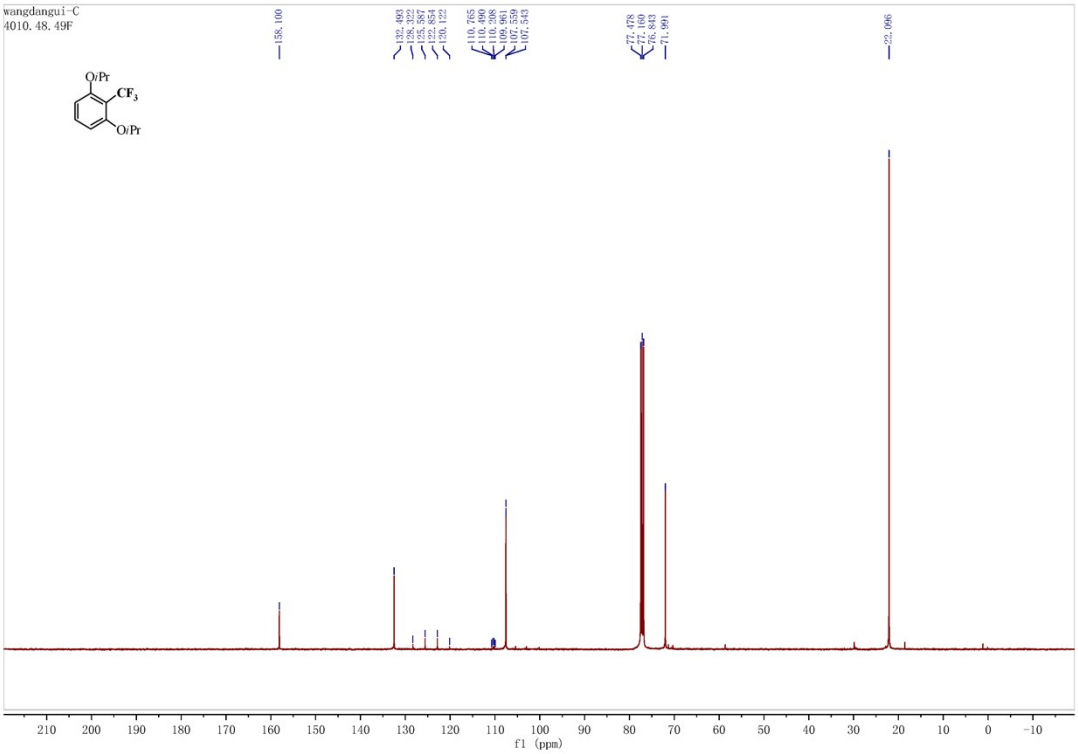

wangdangui
-53.829
-54.574
CF3
MeO
OMe
MeO
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


wangdangui
7.438
7.417
7.401
6.482
6.445
6.440
6.423
6.418
4.602
4.587
4.572
4.556
4.541
1.382
1.356
1.347
1.341
1.334
O/Pr
O/Pr
CF3
1.00
1.00
1.00
2.00
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui
O/Pr
O/Pr
CF3
f1 (ppm)


wangdangui
O/Pr
O/Pr
CF3
f1 (ppm)


wangdangui-H
7.310
7.298
7.287
7.258
6.575
6.554
4.603
4.588
4.573
4.558
4.543
4.528
4.513
1.343
1.327
O/Pr
CF3
O/Pr
1.00
2.00
2.00
12.01
f1 (ppm)


wangdangui-C
4010.48.49F
158.100
132.493
128.322
125.587
122.454
120.122
110.265
110.490
110.308
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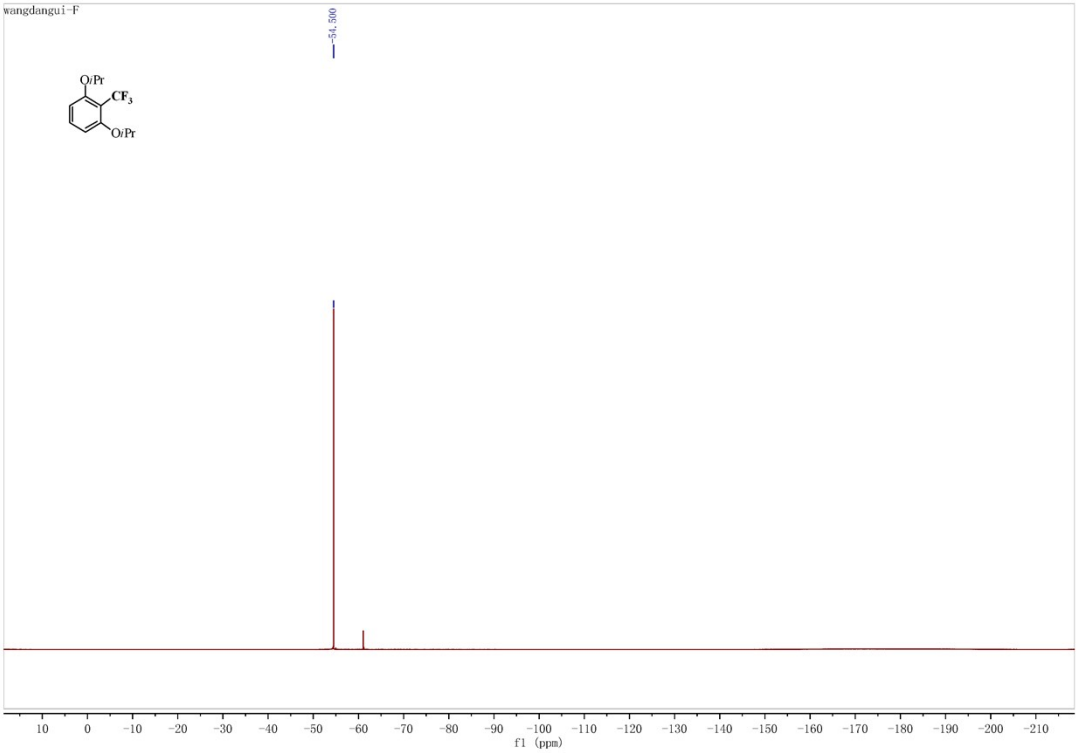
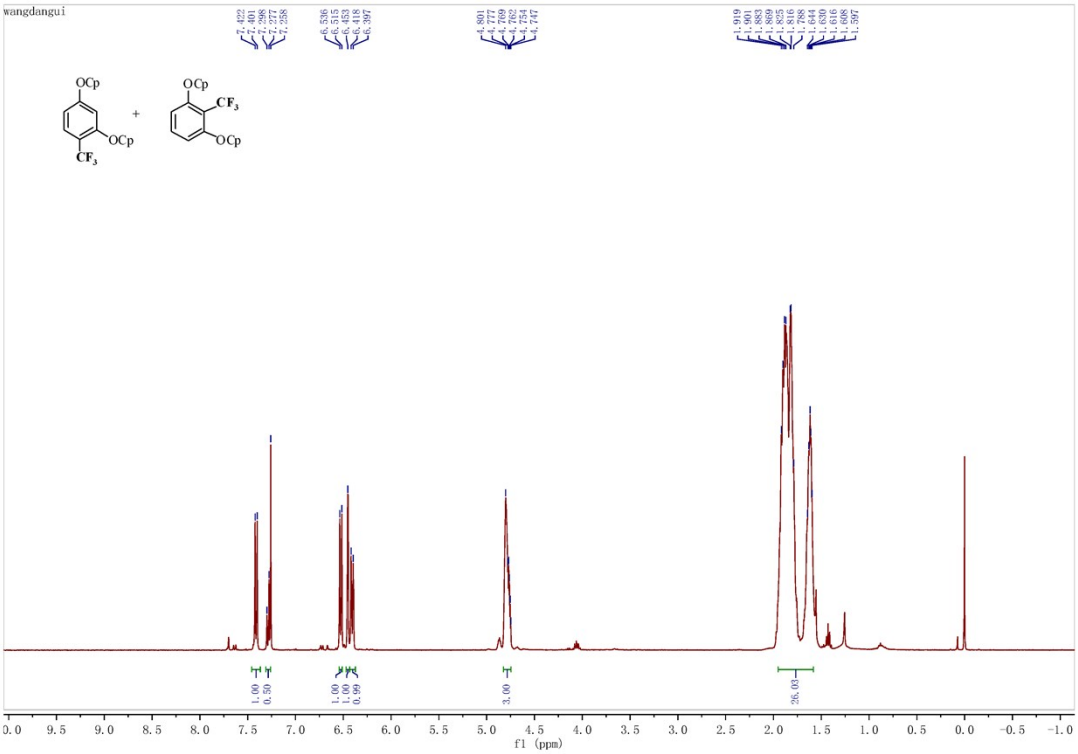
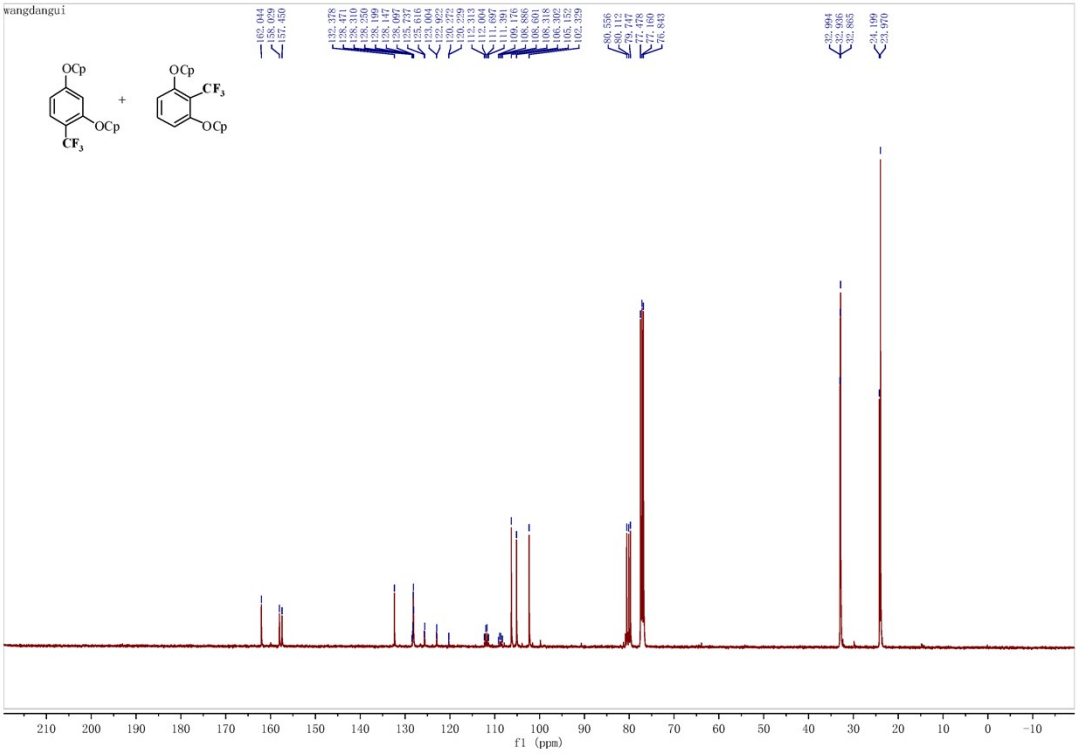
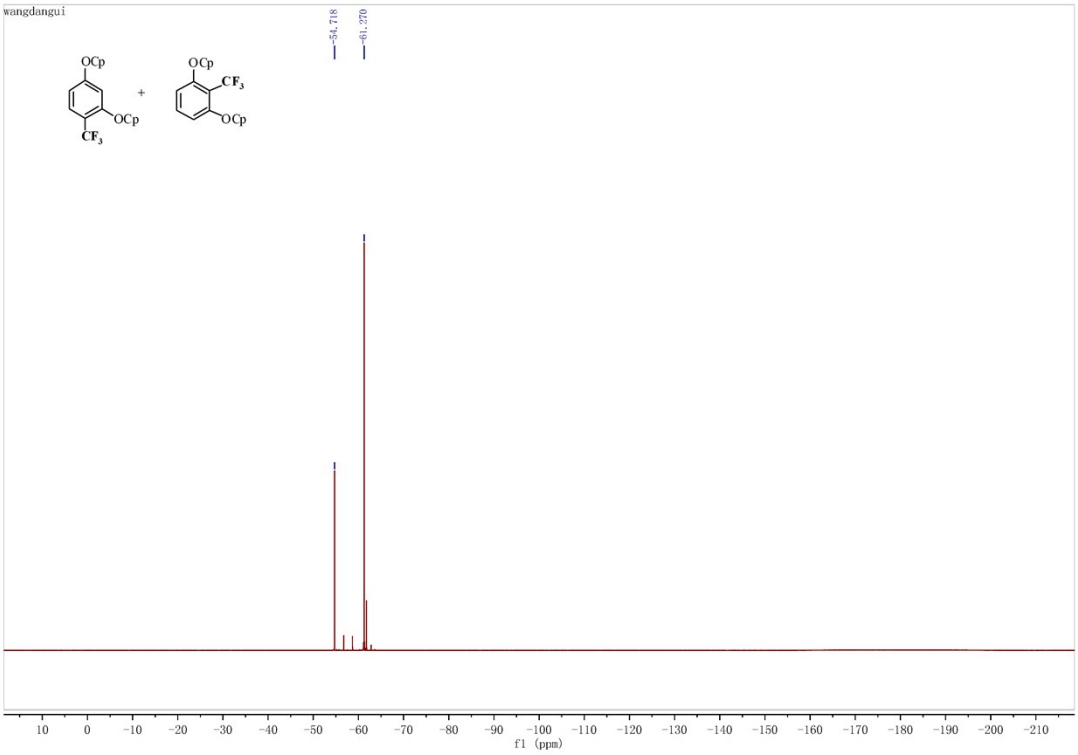
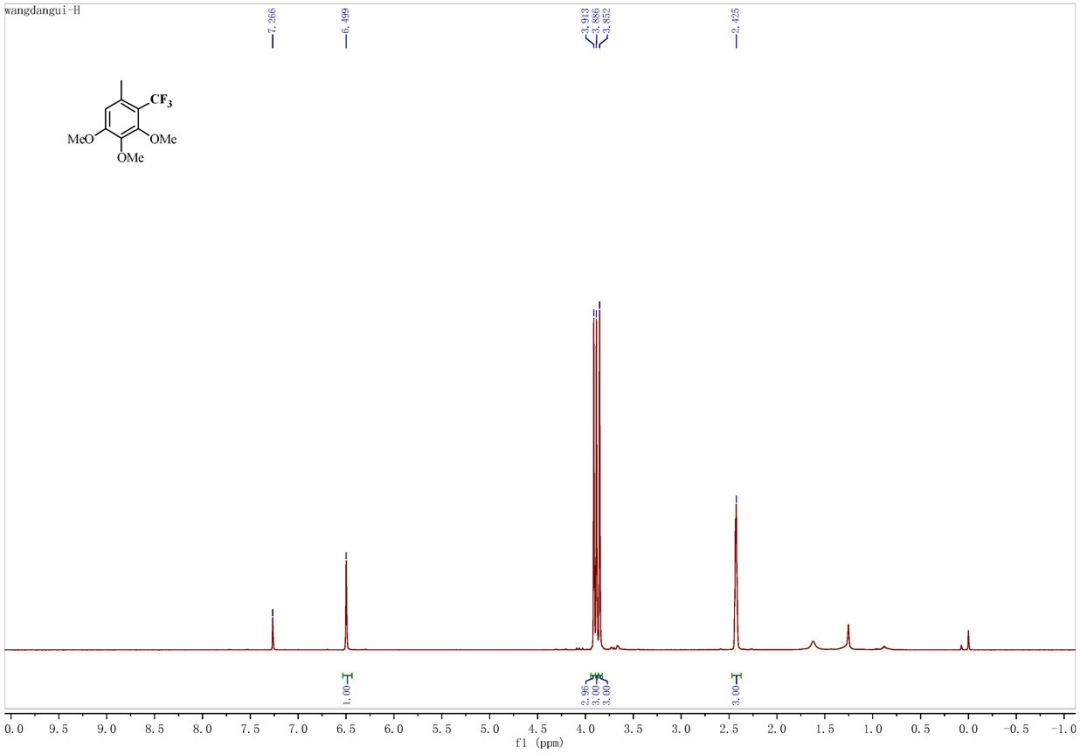
76.843
71.991
23.006
O/Pr
CF3
O/Pr
f1 (ppm)

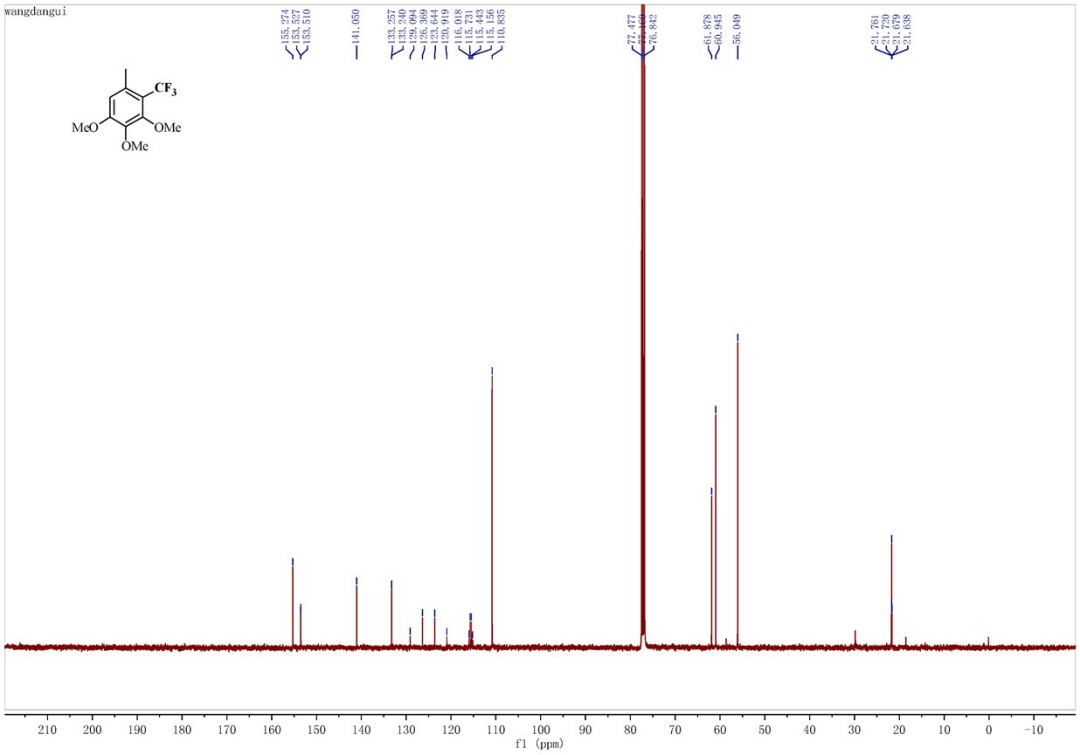

wangdangui-F
-54.500
O/Pr
CF3
O/Pr
f1 (ppm)

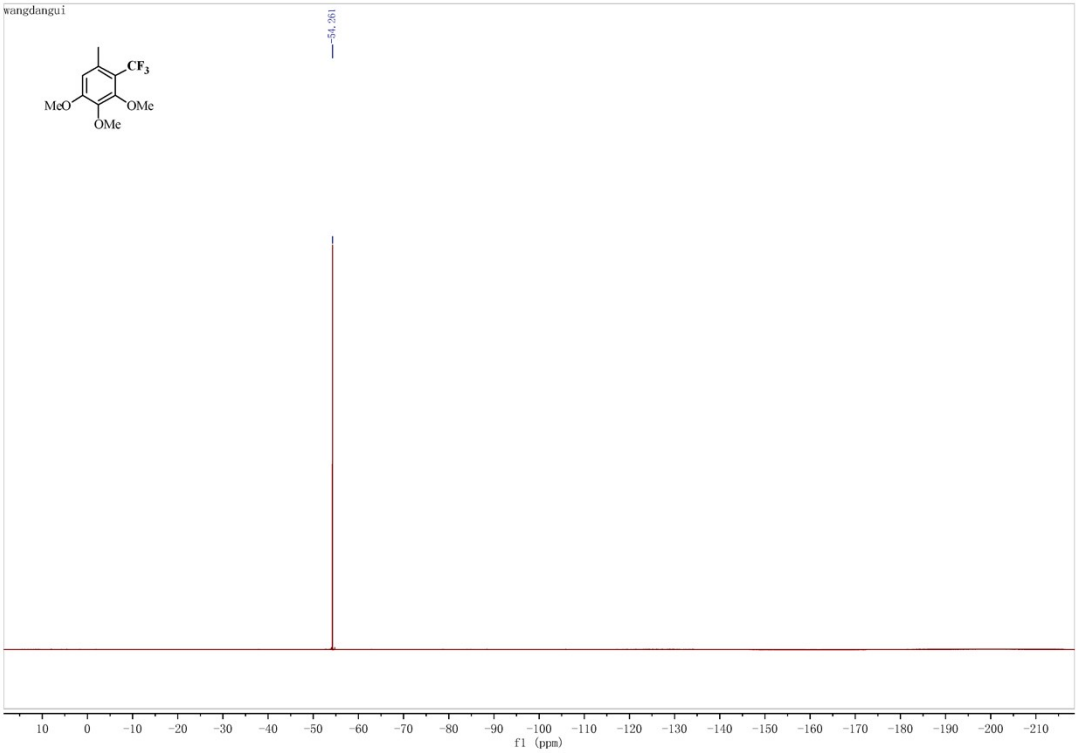

wangdangui
OCp
CF3
OCp
f1 (ppm)

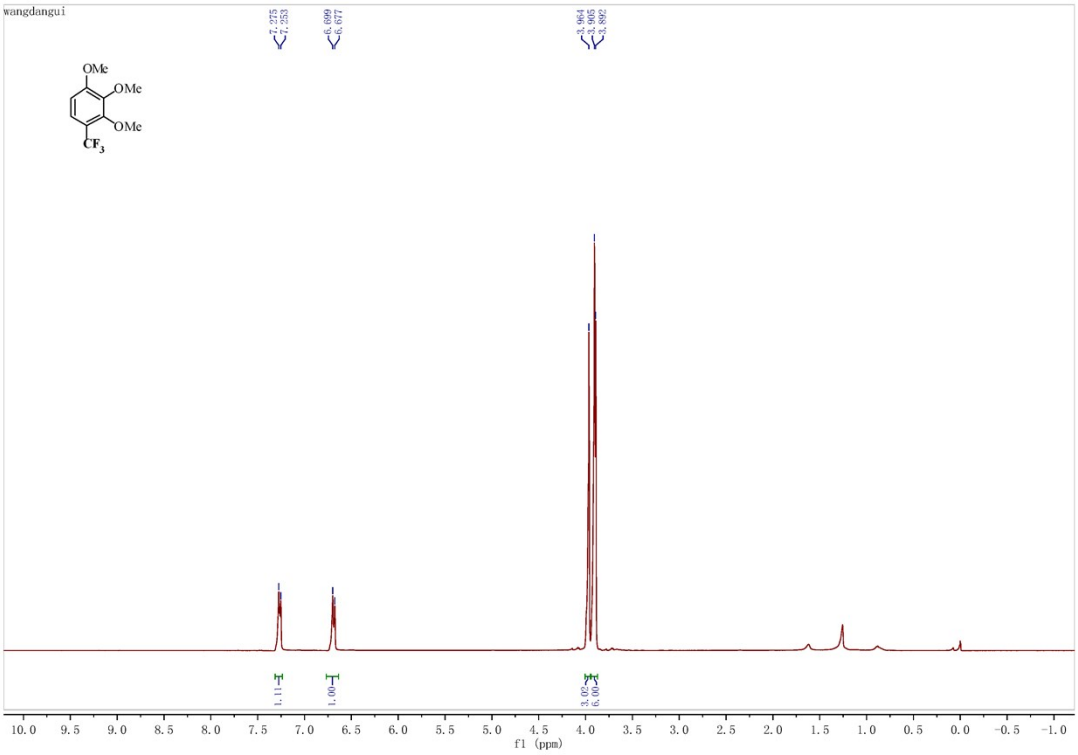

wangdangui
162.044
158.059
157.450
132.378
128.471
128.310
128.250
128.169
128.147
128.097
125.737
125.616
123.004
122.922
120.272
120.239
117.313
112.004
111.697
111.391
109.175
108.886
108.601
108.318
106.909
105.152
102.329
80.556
80.112
79.747
77.428
77.160
76.843
32.994
32.908
32.865
24.199
23.970
OCp
OCp
CF3
OCp
OCp
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

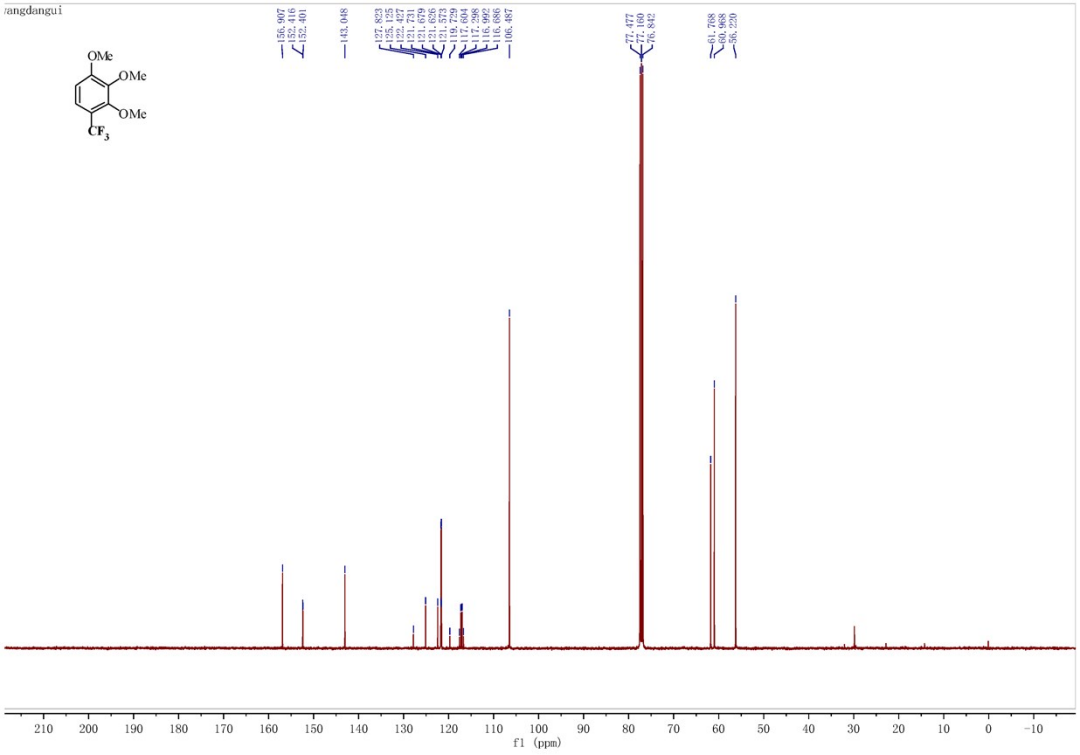

wangdangui
-54.718
-61.270
OCp
OCp
CF3
OCp
OCp
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

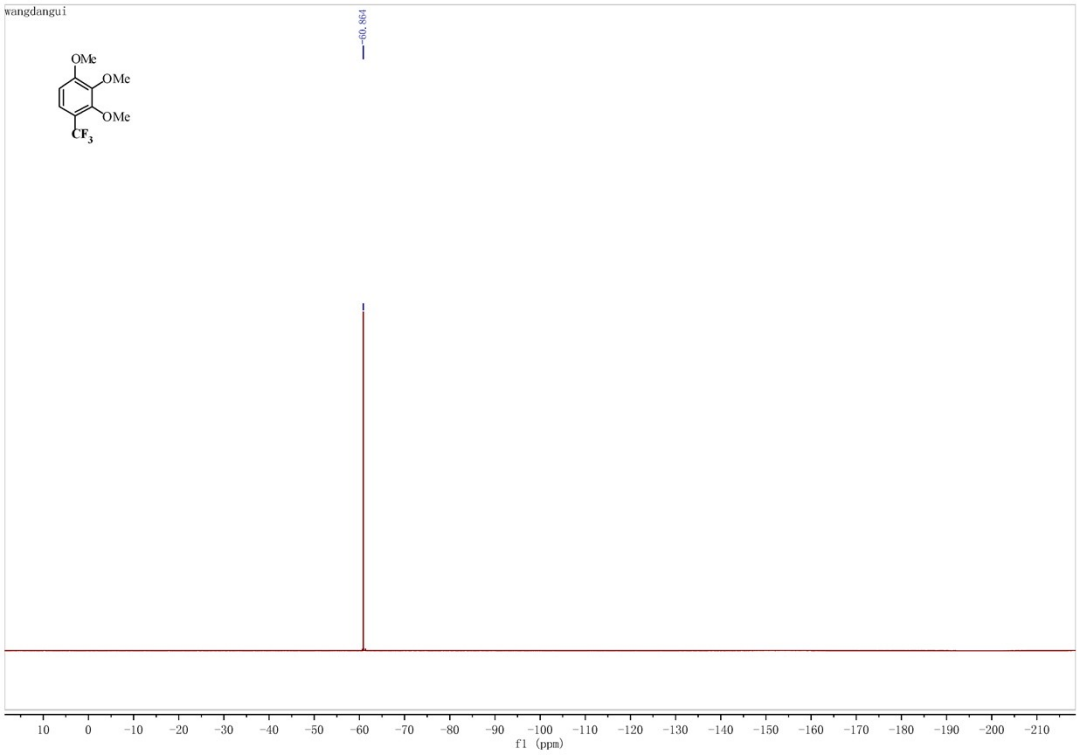

wangdangui-H
7.266
6.499
3.913
3.886
3.852
2.425
CF3
MeO
OMe
OMe
1.00
2.96
3.00
3.00
3.00
f1 (ppm)


wangdangui
155.274
153.827
153.510
141.050
133.257
132.940
129.094
126.369
123.644
120.919
116.018
115.731
115.443
115.156
110.935
77.477
77.164
76.852
61.878
60.945
56.049
21.761
21.720
21.679
21.638
CF3
MeO
OMe
OMe
f1 (ppm)


wangdangui
-54.261
CF3
MeO
OMe
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


wangdangui
7.475
7.353
6.699
6.677
3.964
3.905
3.892
OMe
OMe
OMe
CF3
1.11
1.00
3.07
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui
OMe
OMe
OMe
CF3
156.907
152.416
152.401
143.048
127.823
125.175
122.427
121.731
121.679
121.626
121.573
119.729
117.694
117.598
116.962
116.686
106.487
77.477
77.160
76.842
61.708
60.468
56.229
f1 (ppm)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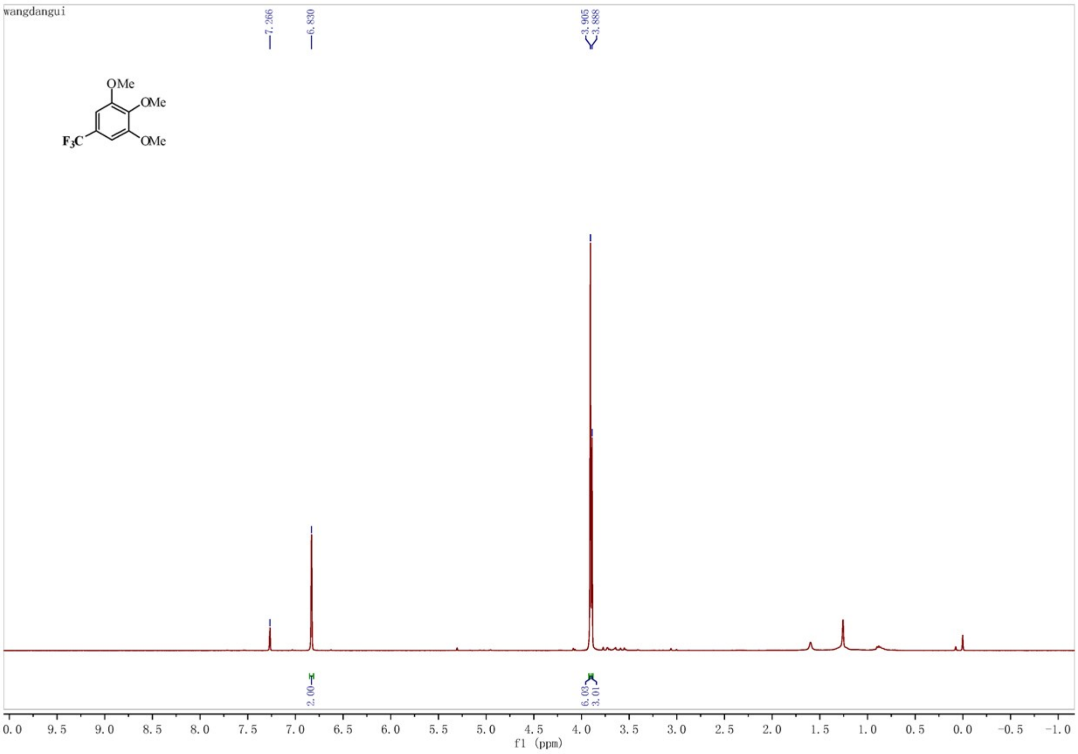
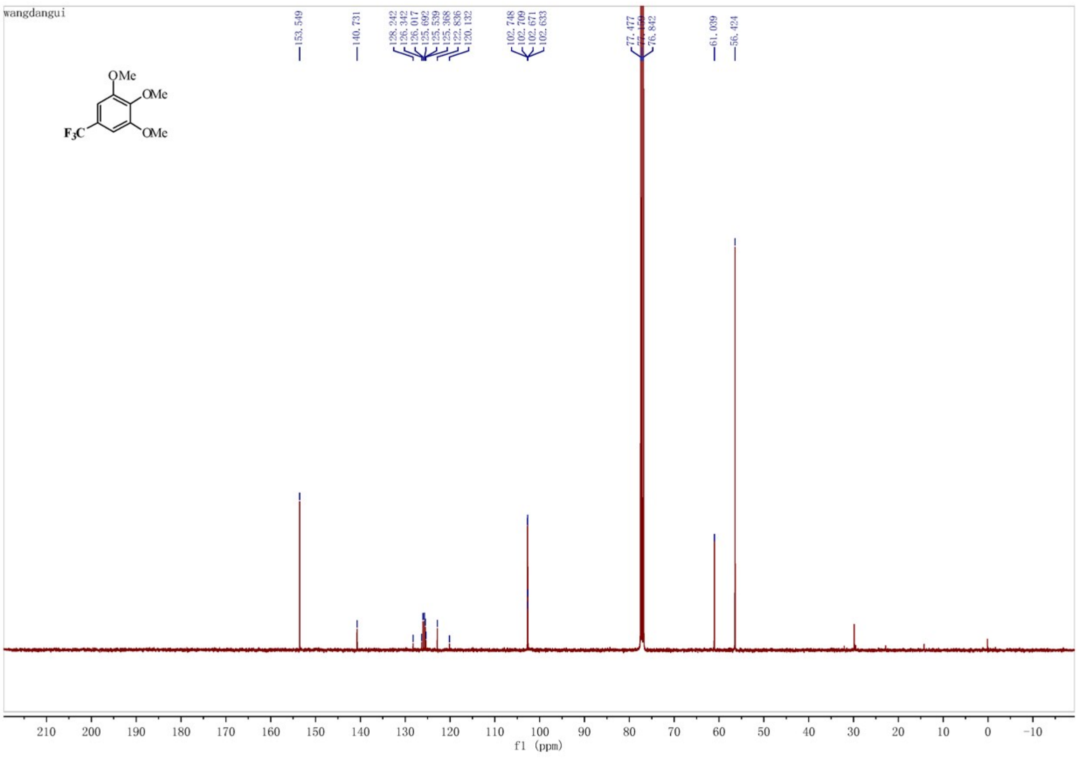
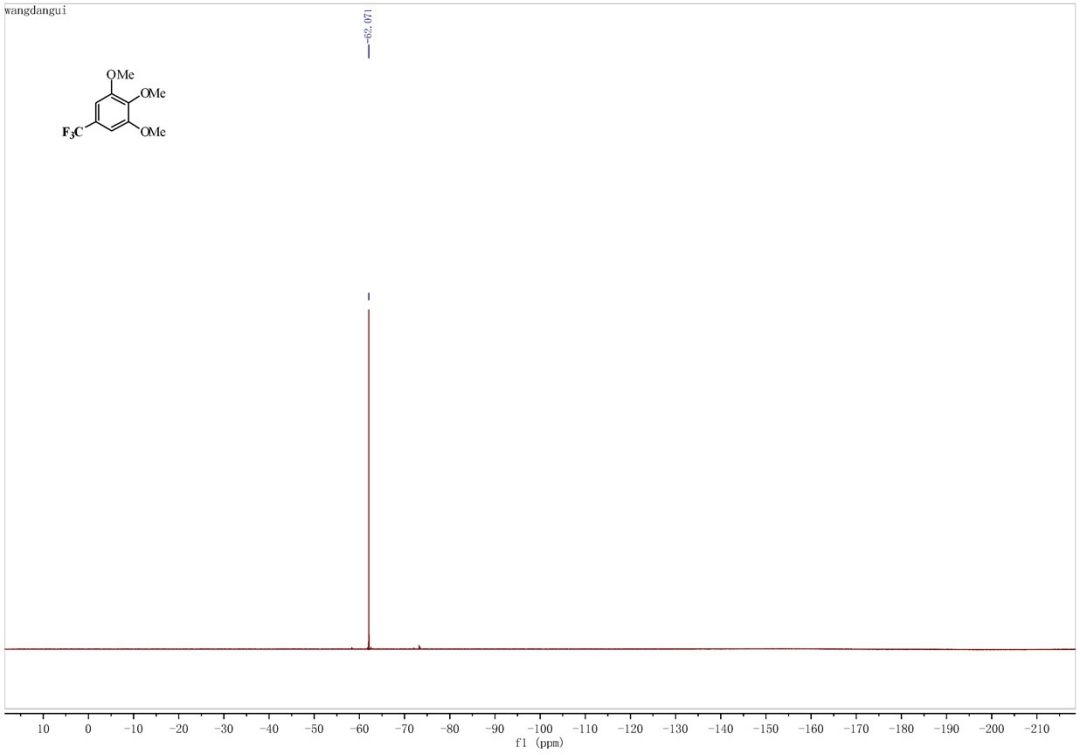
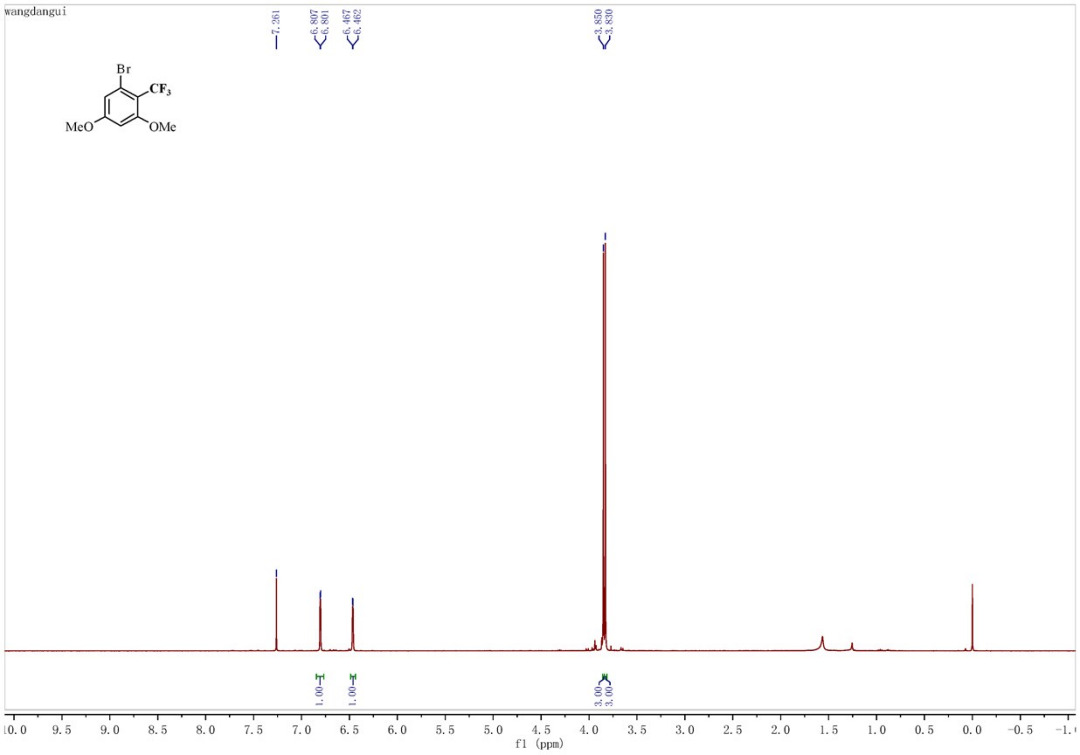
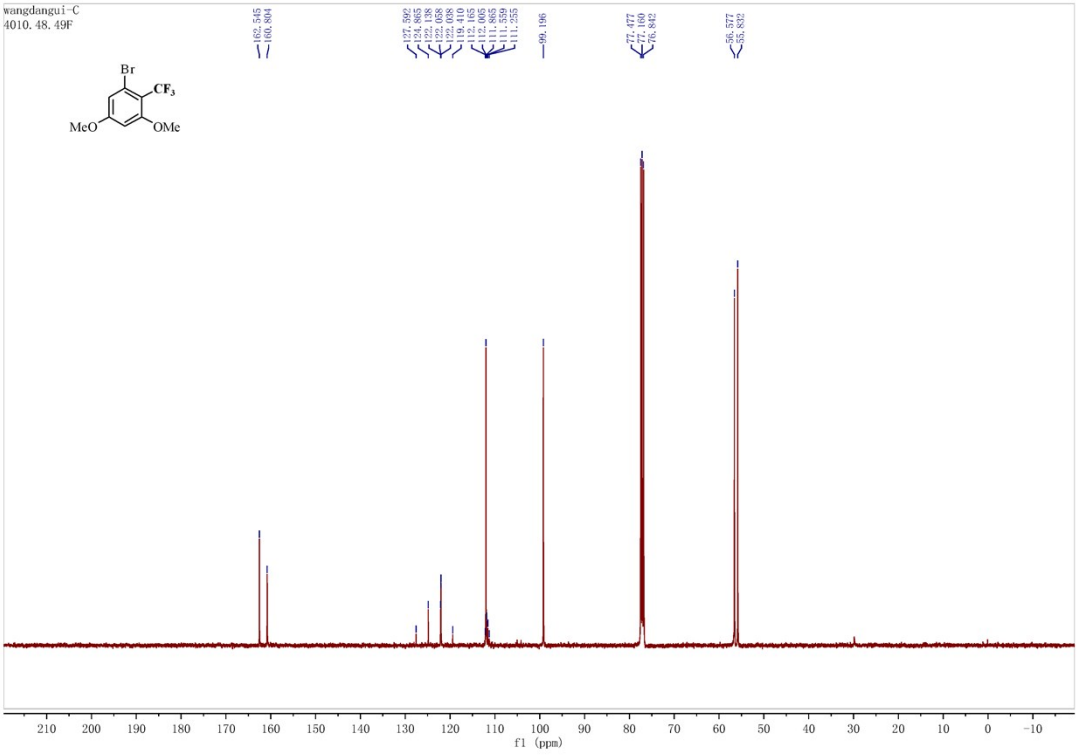
OMe
OMe
OMe
CF3
-60.864
f1 (ppm)

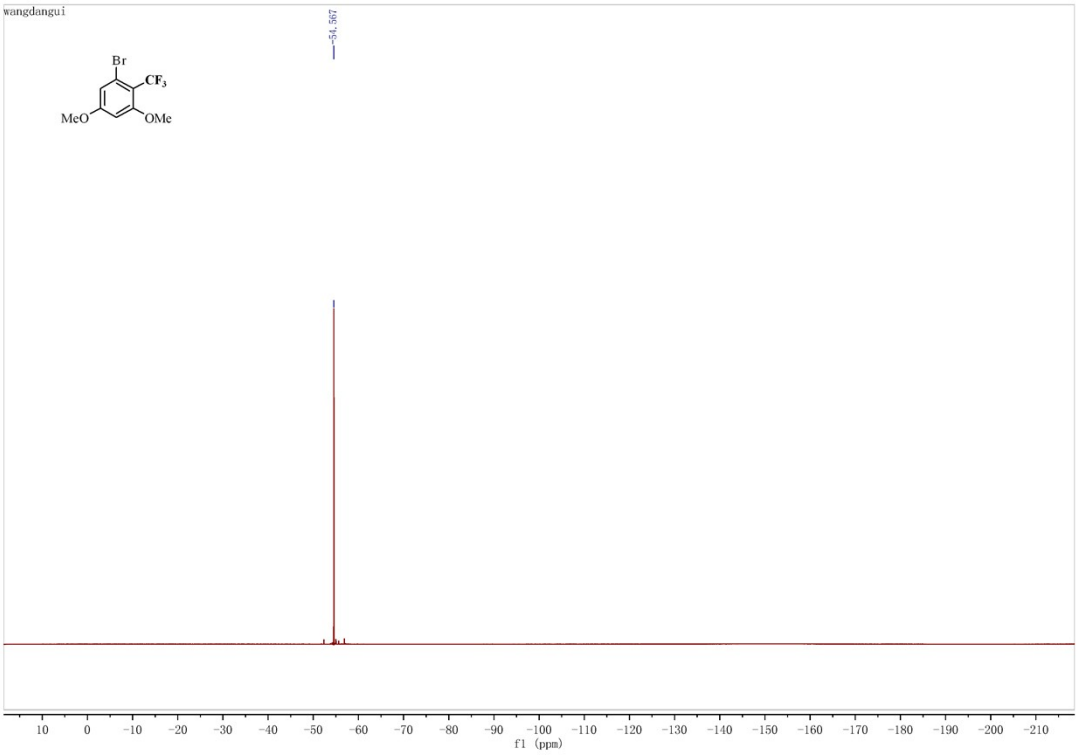

wangdangui
7.266
6.830
3.905
3.888
OMe
OMe
F3C
OMe
2.00
6.03
3.01
f1 (ppm)

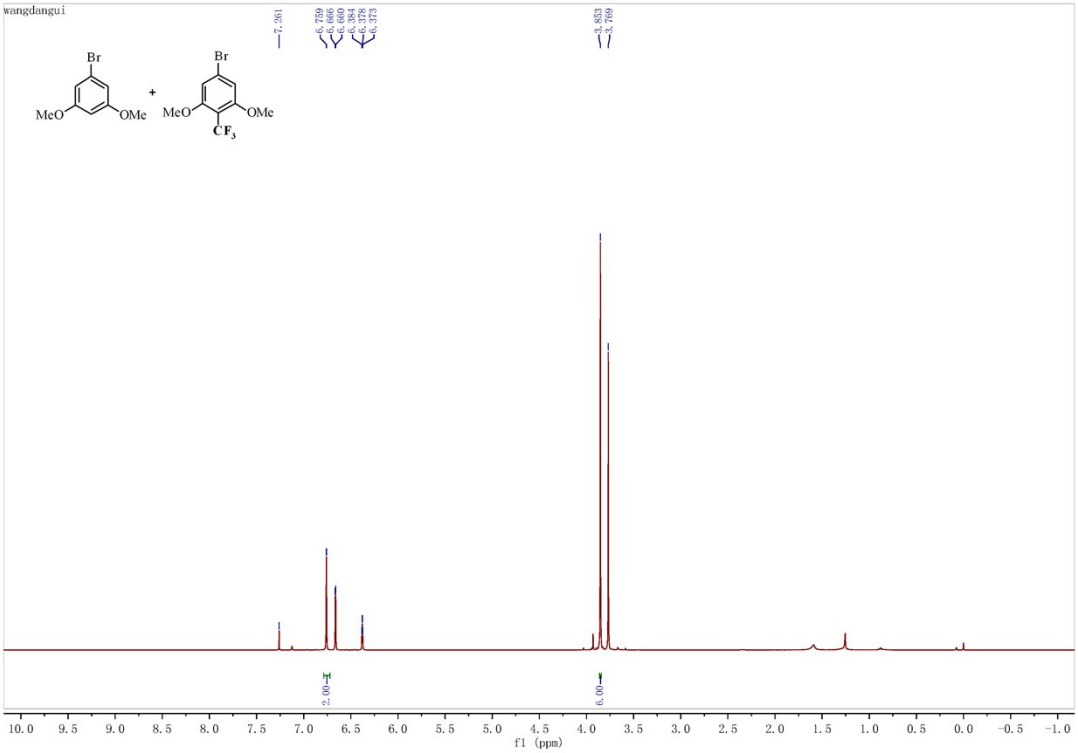

wangdangui
153.549
140.731
128.242
126.342
126.017
125.692
125.539
125.368
122.836
120.132
102.748
102.709
102.671
102.633
77.477
76.842
61.039
56.424
OMe
OMe
F3C
OMe
f1 (ppm)

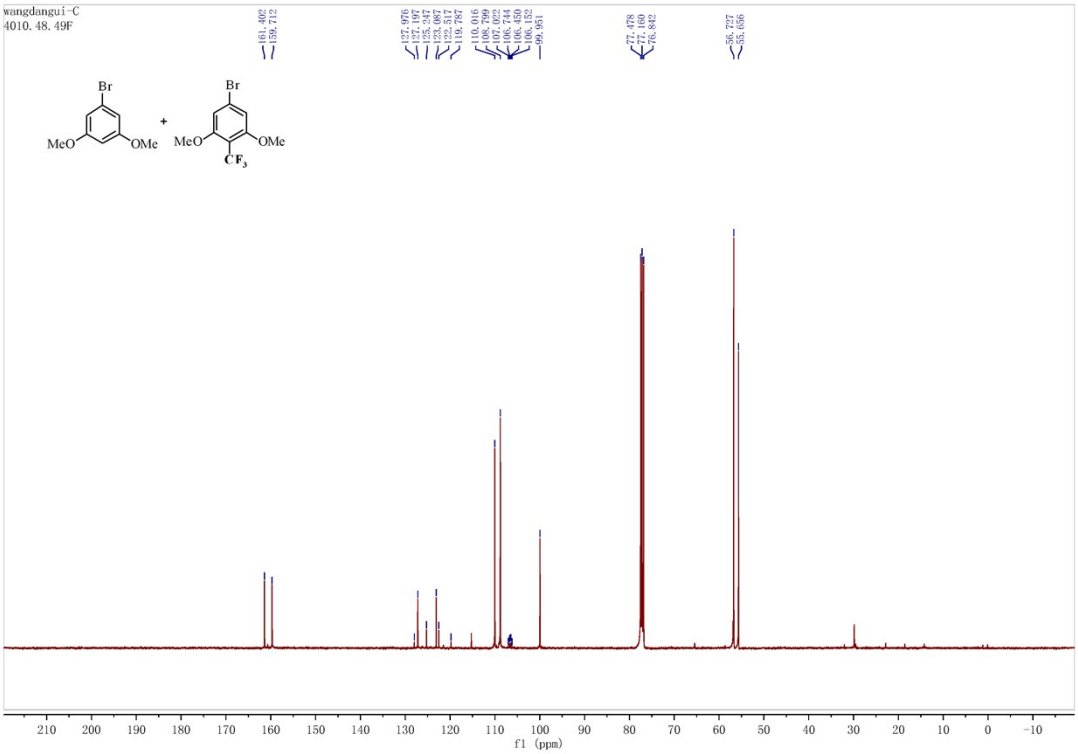

wangdangui
-62.071
OMe
OMe
OMe
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

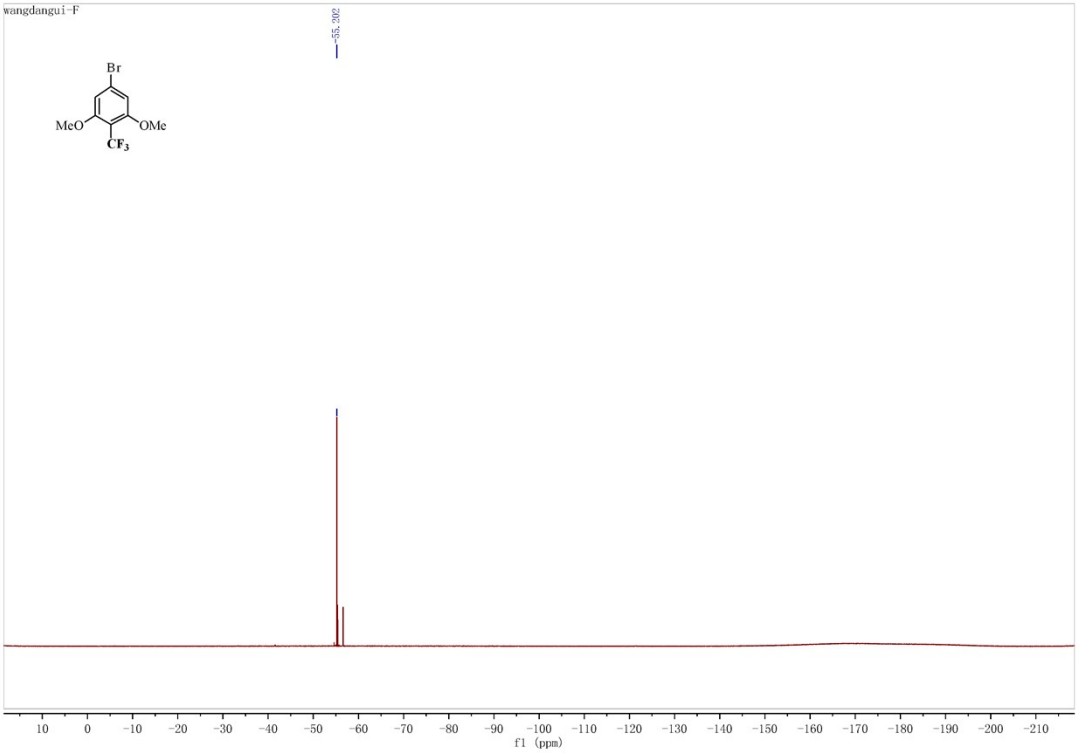

wangdangui
7.361
6.807
6.801
6.467
6.462
3.850
3.830
Br
CF3
MeO
OMe
1.00
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


wangdangui-C
4010.48.49F
162.545
160.804
127.592
124.965
122.135
122.058
122.038
119.410
117.165
112.005
111.865
111.559
111.355
99.196
77.477
77.160
76.842
56.577
55.832
Br
CF3
MeO
OMe
f1 (ppm)


wangdangui
-54.567
Br
CF3
MeO
OMe
f1 (ppm)


wangdangui
7.361
6.759
6.666
6.660
6.384
6.378
6.373
3.853
3.769
Br
MeO
OMe
+
Br
MeO
OMe
CF3
2.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui-C
4010.48.49F
161.402
159.712
127.976
127.597
125.547
123.087
122.517
119.757
110.916
108.909
107.022
106.744
106.450
106.153
99.951
77.478
77.160
76.842
56.727
55.656
Br
MeO
OMe
+
Br
MeO
OMe
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


wangdangui-F
-55.202
Br
MeO
OMe
CF3
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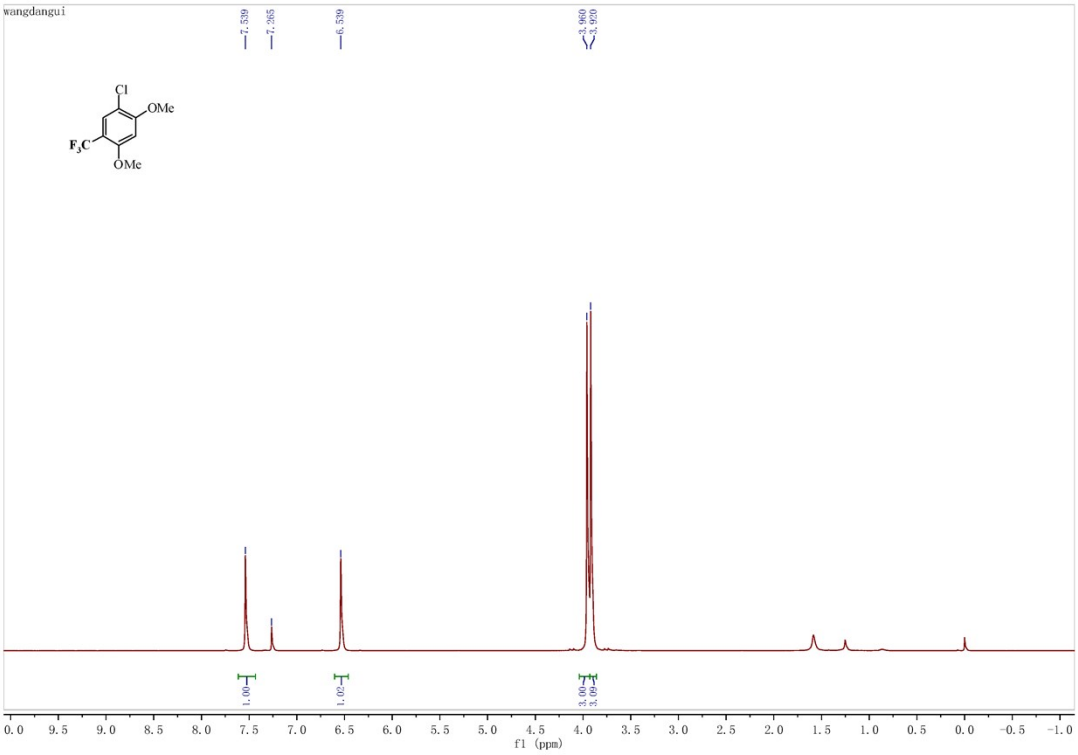
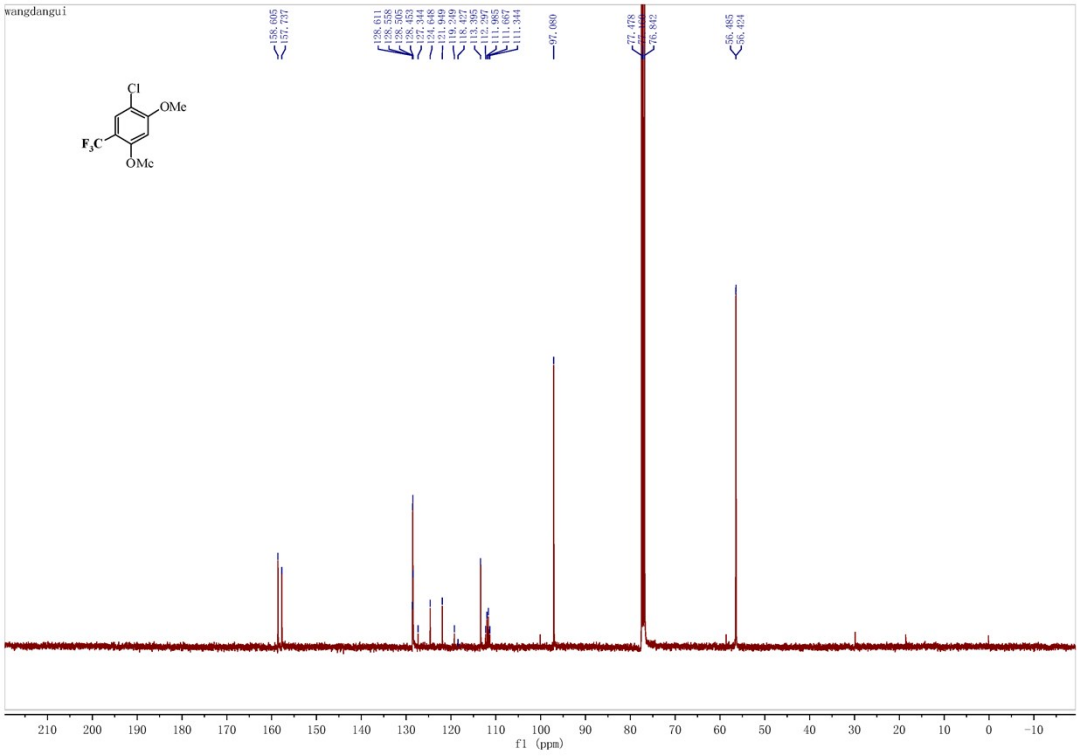
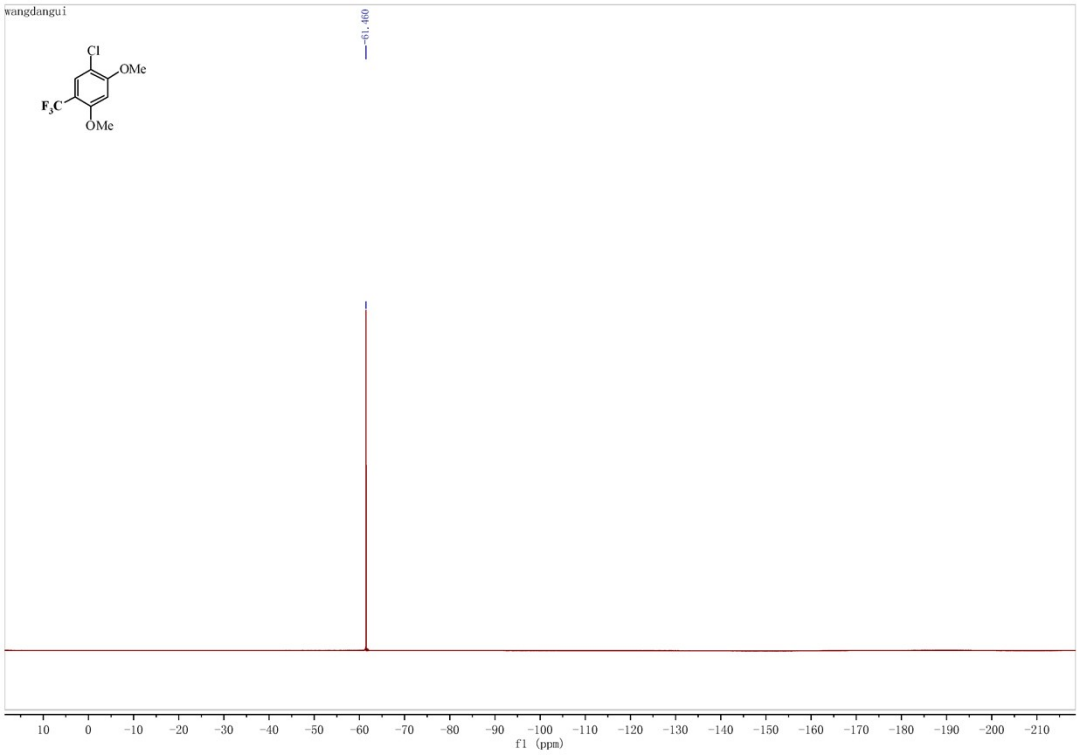
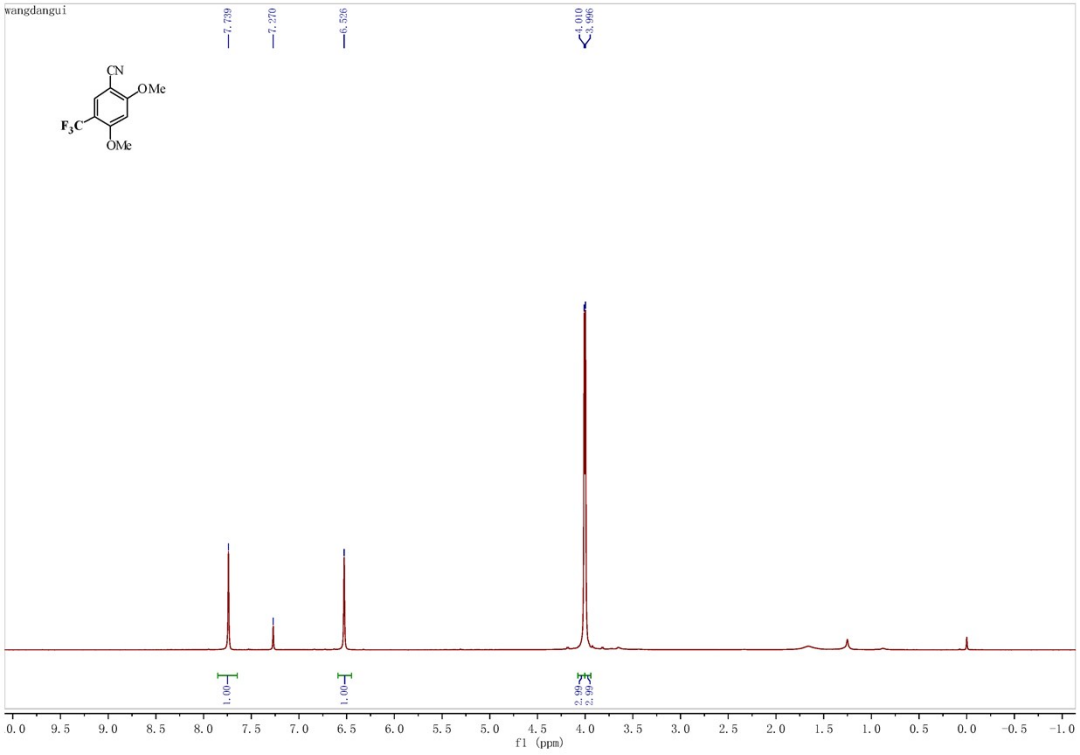
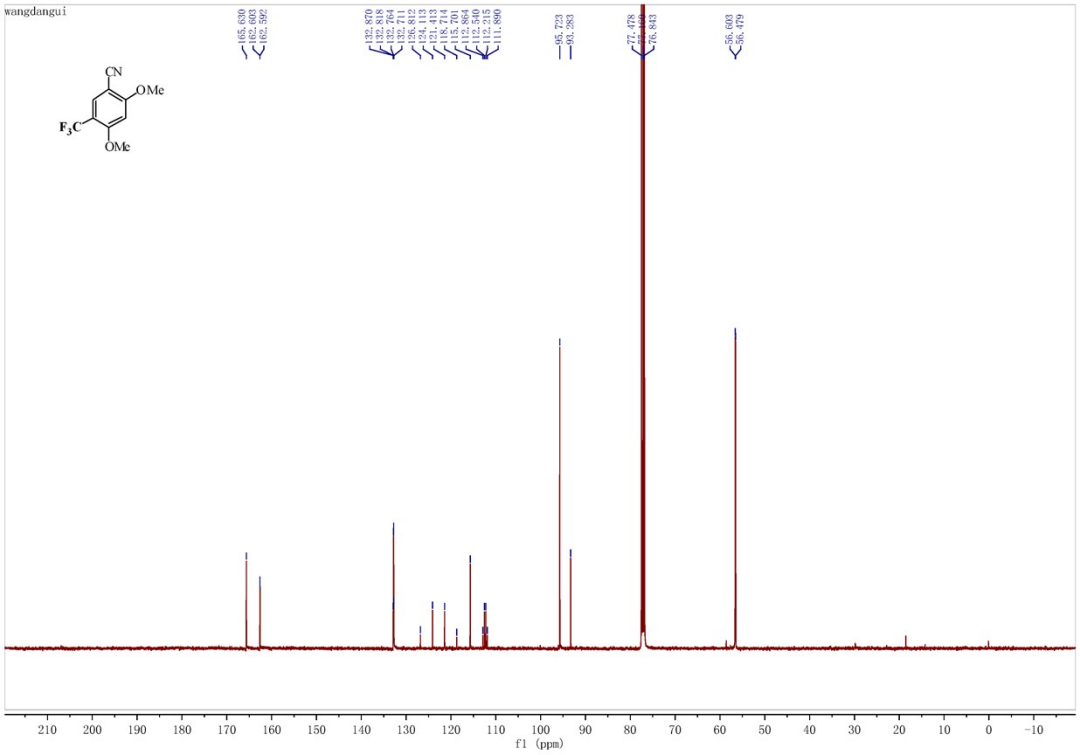
f1 (ppm)

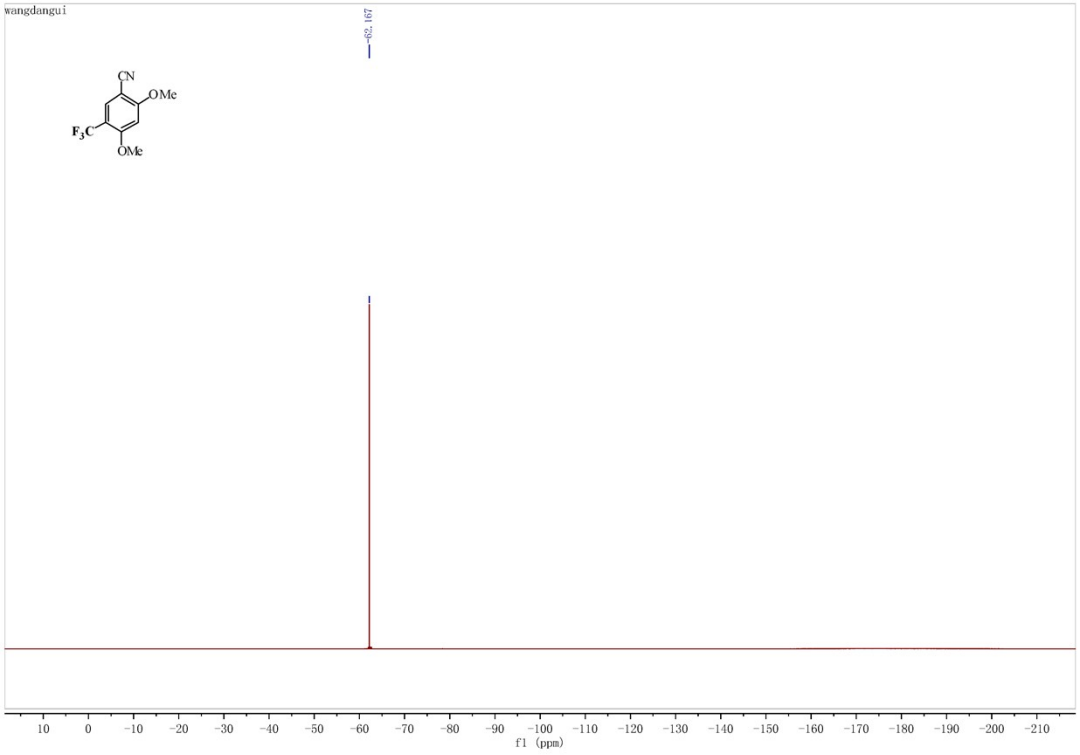

wangdangui
7.539
7.365
6.539
3.960
3.920
Cl
OMe
F3C
OMe
1.00
1.02
3.00
3.09
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

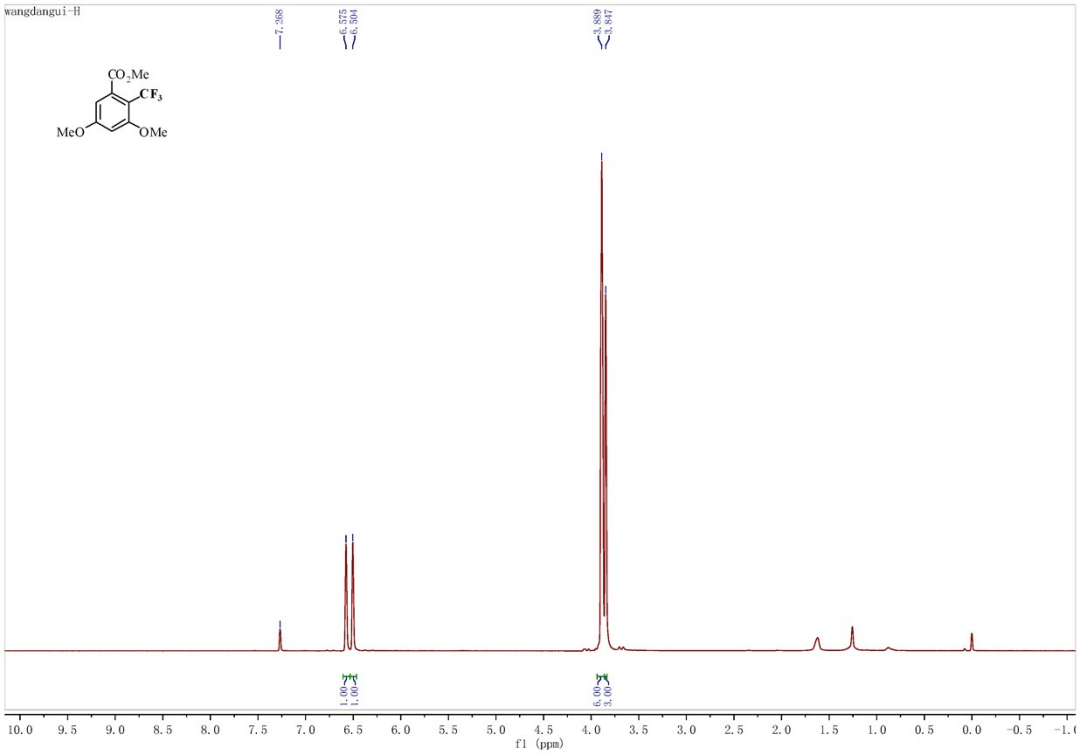

wangdangui
158.605
157.737
128.611
128.558
128.505
128.453
127.344
124.648
121.949
119.249
118.427
113.995
112.297
111.965
111.667
111.344
97.080
77.478
77.160
76.842
56.485
56.424
Cl
OMe
F3C
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

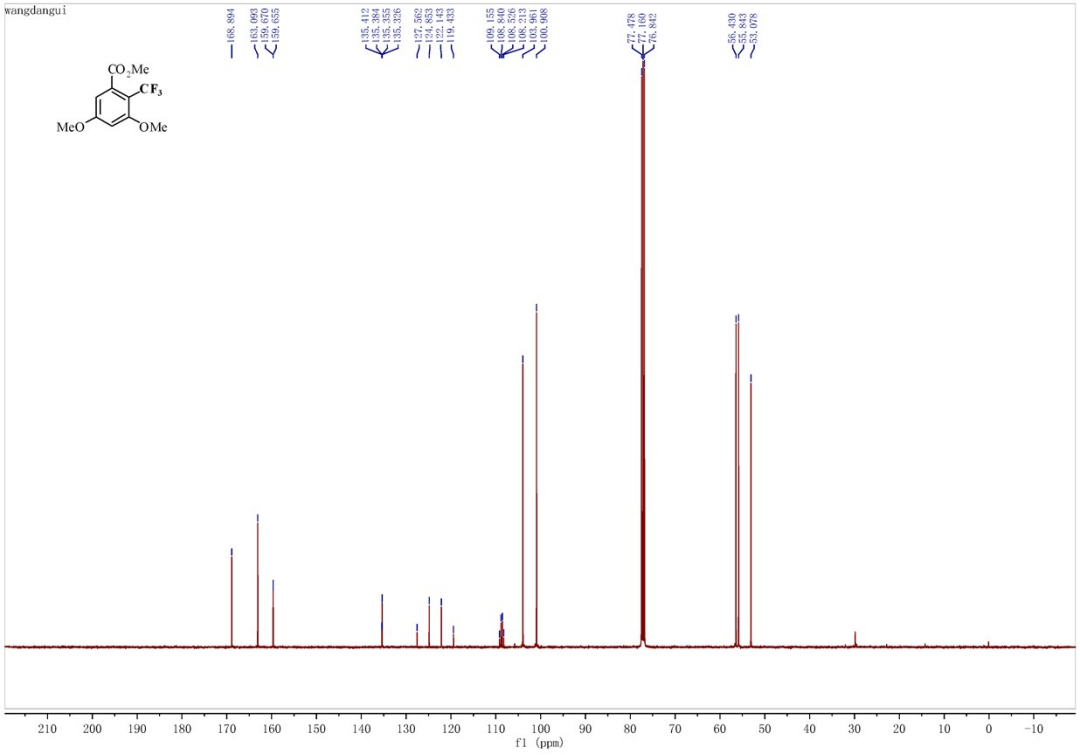

wangdangui
-61.460
Cl
OMe
F3C
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

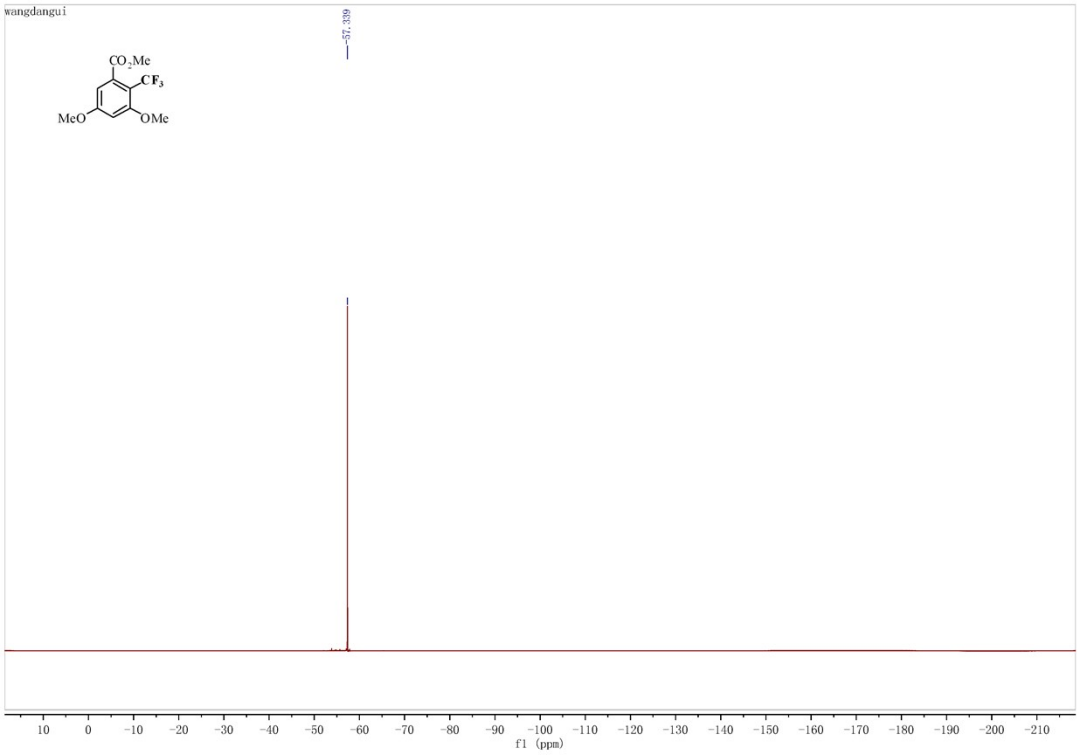

wangdangui
7.739
7.270
6.526
4.010
3.996
CN
OMe
F3C
OMe
1.00
1.00
2.99
2.99
f1 (ppm)

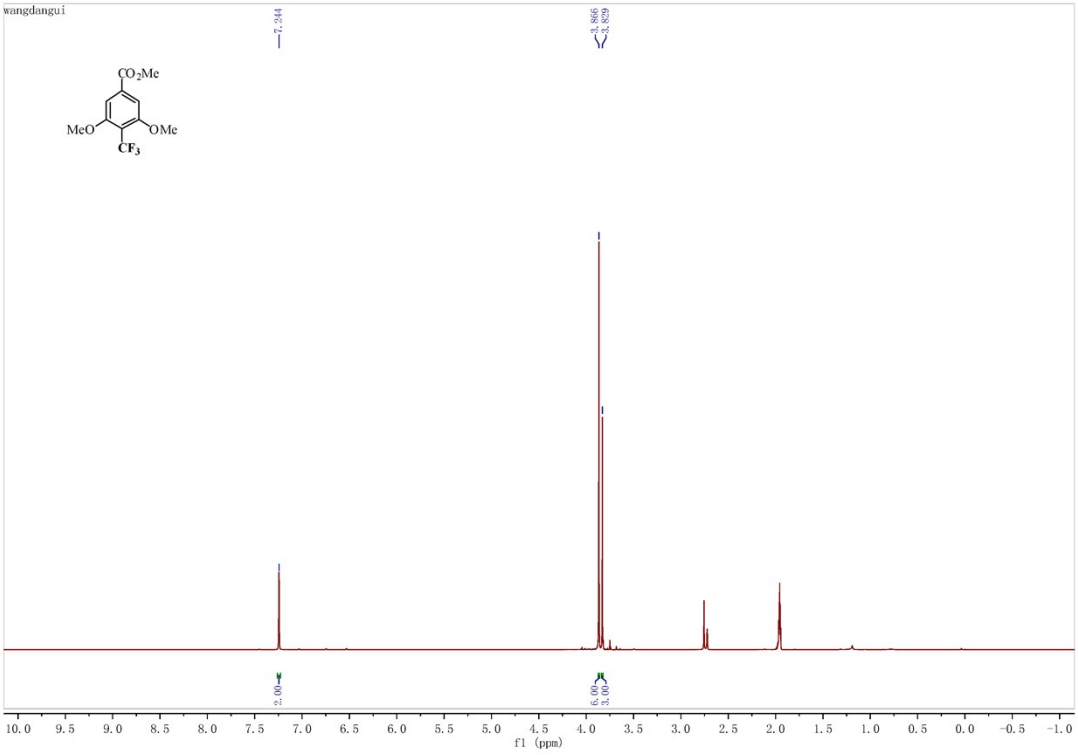

wangdangui
165.630
162.803
162.992
132.870
132.818
132.764
132.711
126.812
124.113
121.413
118.714
115.701
112.864
112.540
112.215
111.889
85.723
83.593
77.478
77.160
76.843
56.603
56.479
CN
OMe
F3C
OMe
f1 (ppm)

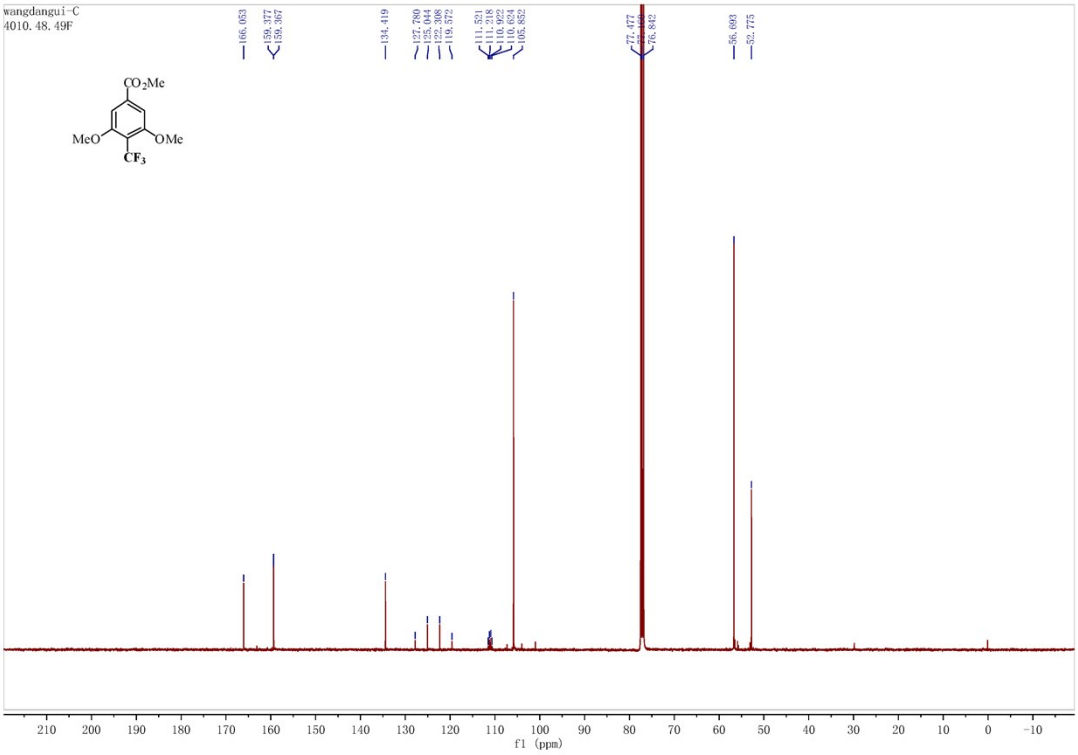

wangdangui
-62.167
CN
OMe
F3C
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

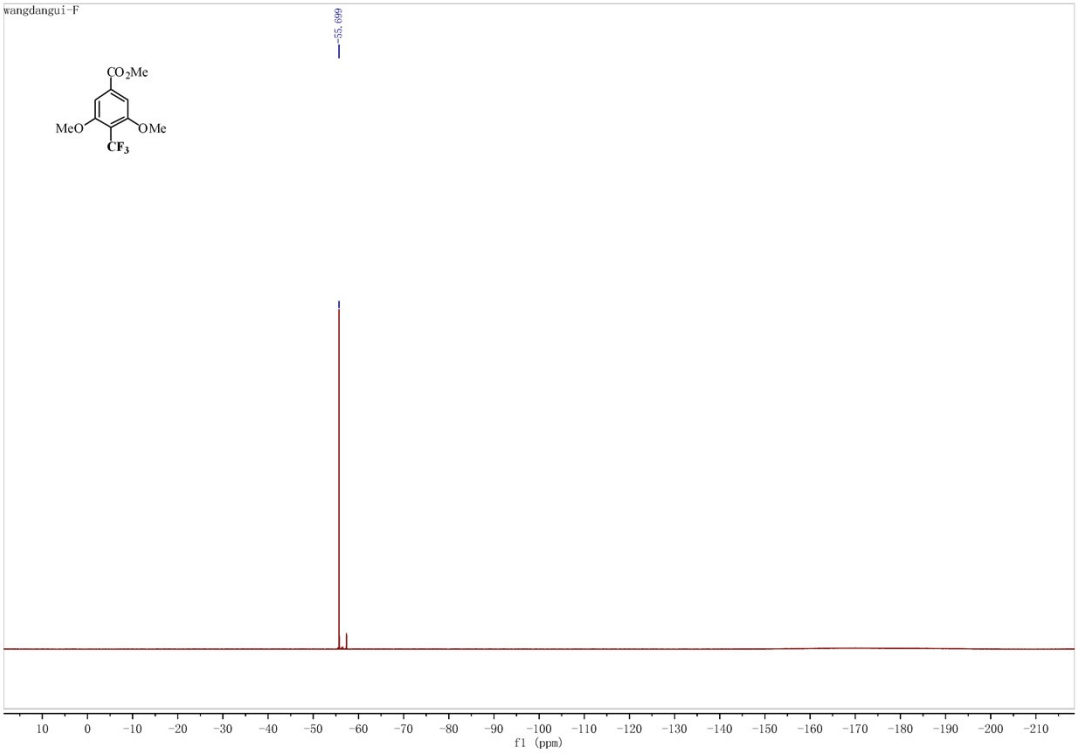

wangdangui-H
7.398
6.575
6.504
3.889
3.847
CO2Me
CF3
MeO
OMe
1.00
1.00
6.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

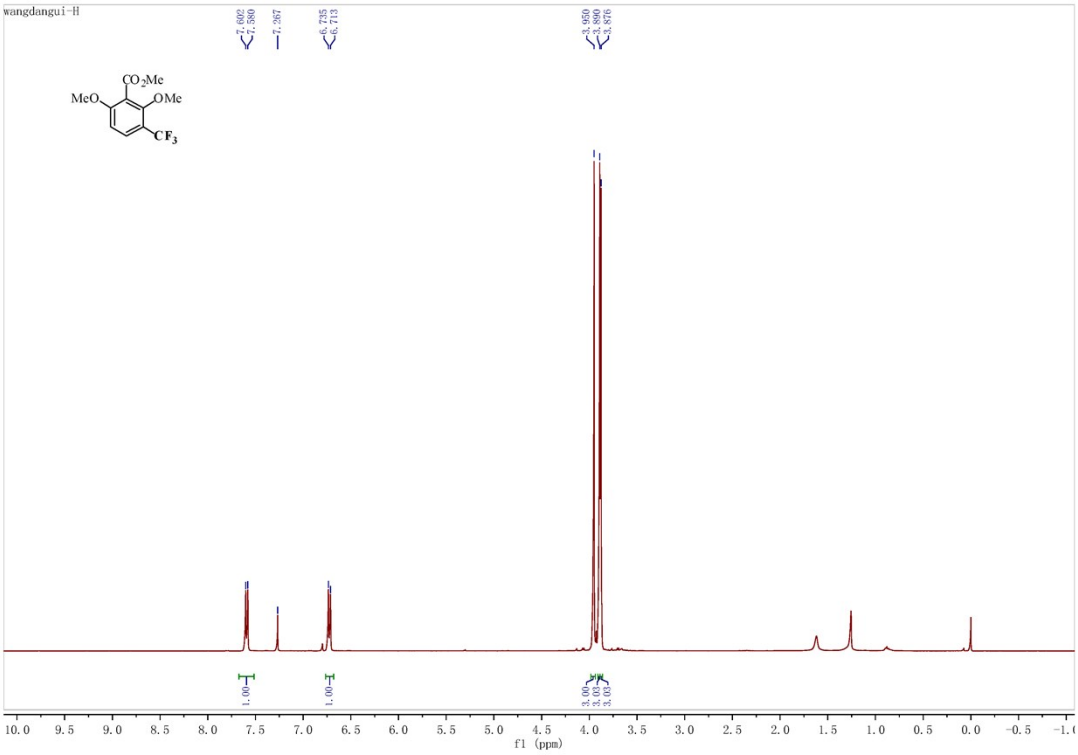

wangdangui
168.894
163.093
159.670
158.695
135.412
135.364
135.355
135.326
127.562
124.853
122.143
119.433
109.155
108.840
108.526
108.213
103.961
100.908
77.478
77.160
76.842
56.430
53.843
53.676
MeO
OMe
f1 (ppm)

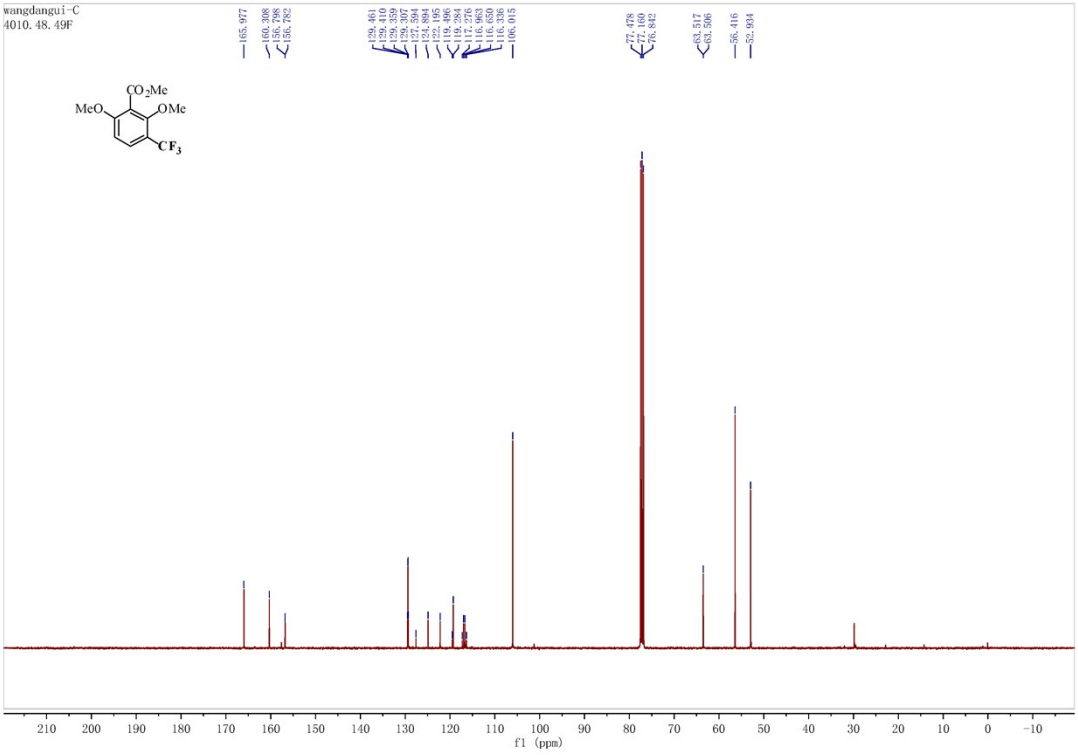

wangdangui
-57.339
MeO
OMe
f1 (ppm)

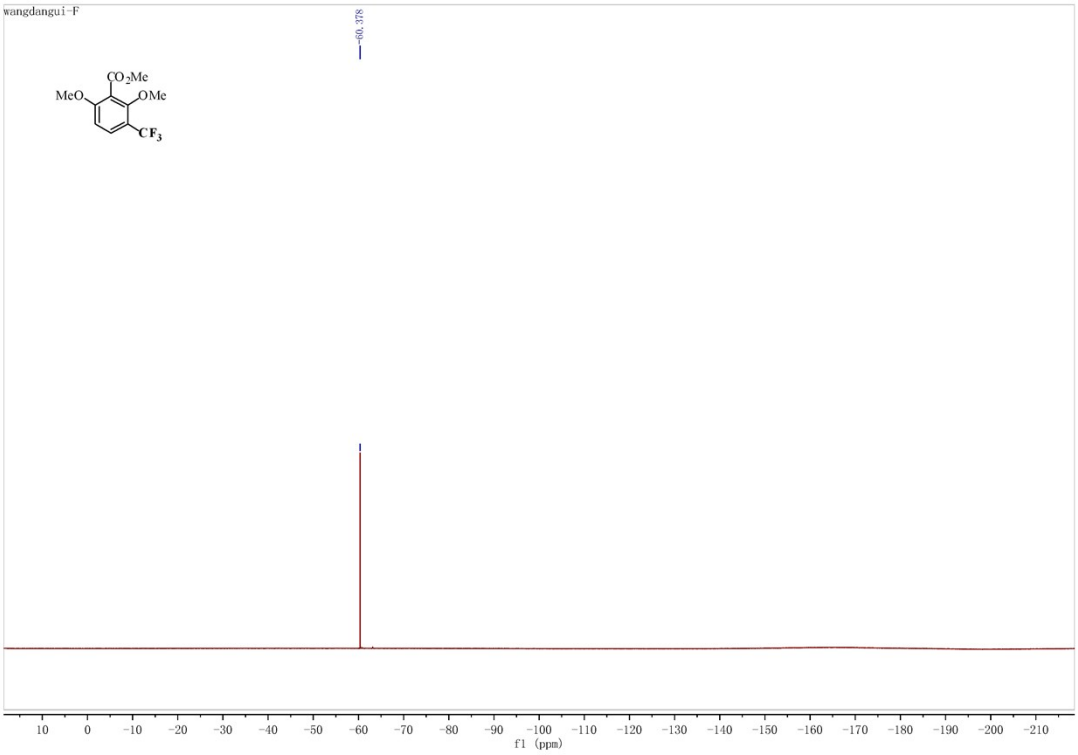

wangdangui
7.244
3.866
3.829
CO2Me
MeO
OMe
CF3
2.00
6.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

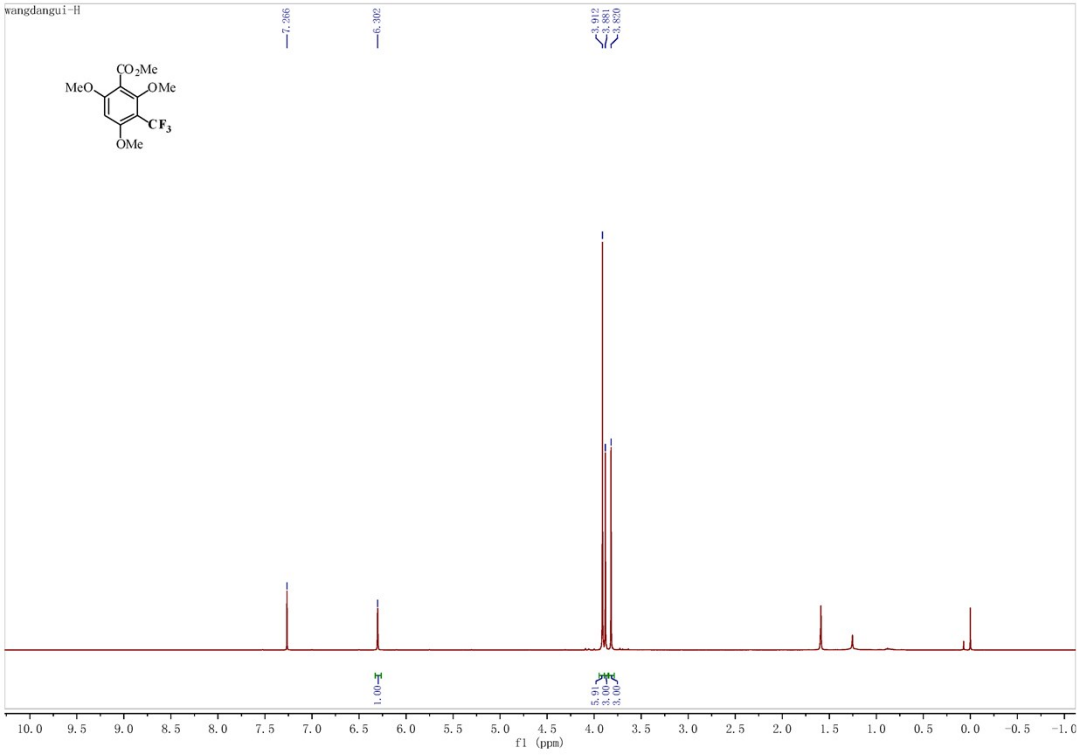

wangdangui-C
4010.48.49F
166.653
159.477
159.367
134.419
127.789
125.044
122.308
119.572
111.521
111.238
110.977
110.824
105.852
77.477
77.164
76.842
56.693
52.775
CO2Me
MeO
OMe
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

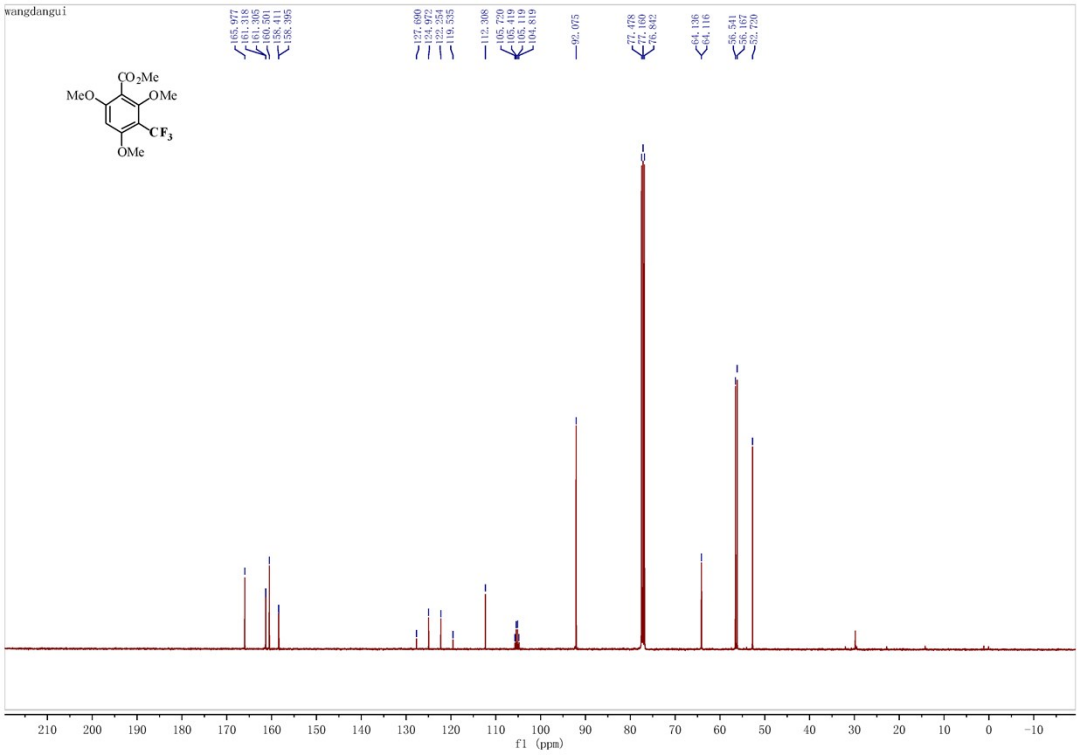

wangdangui-F
-55.699
CO2Me
MeO
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

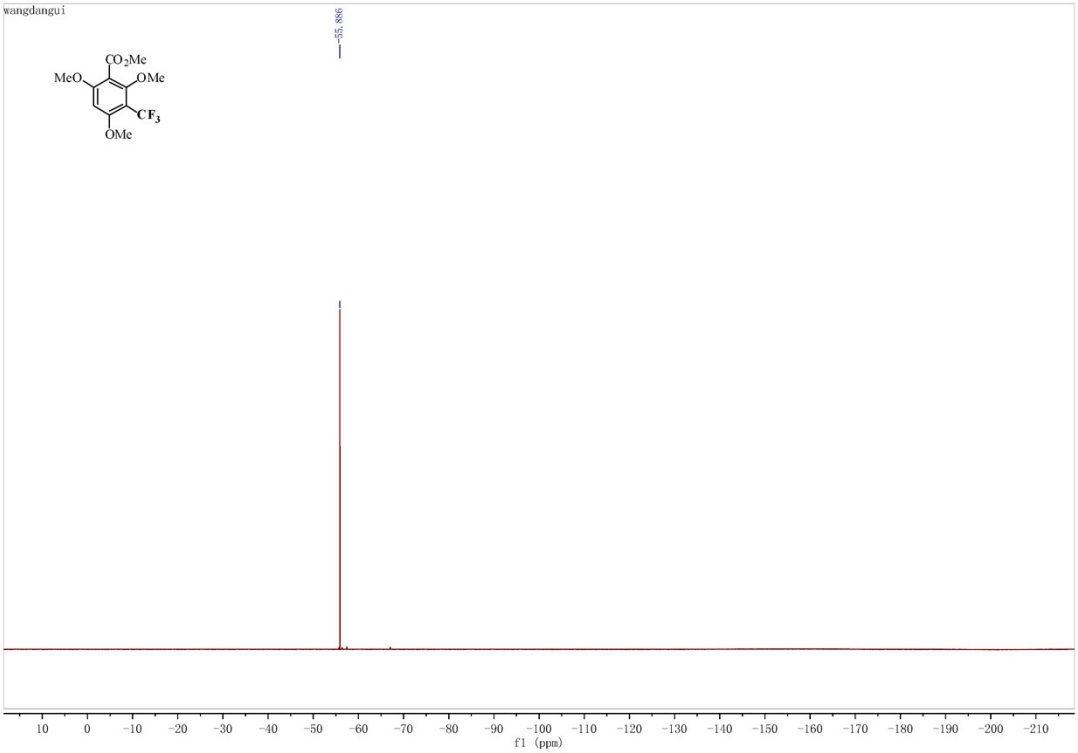

wangdangui-H
7.602
7.580
7.367
6.735
6.713
3.959
3.900
3.876
CO2Me
MeO
OMe
CF3
1.00
1.00
3.00
3.02
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

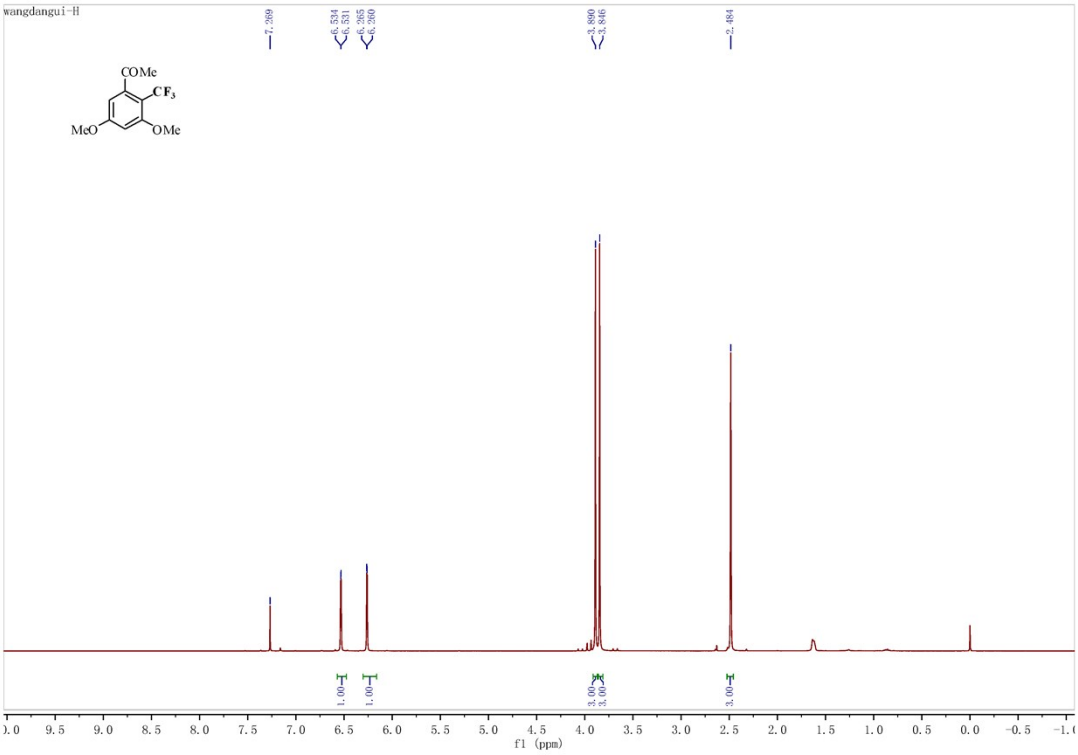

wangdangui-C
4010.48.49F
165.977
160.308
155.708
156.782
129.461
129.410
129.359
129.307
125.594
124.894
122.195
119.496
118.984
117.276
116.963
116.650
116.336
106.015
77.478
77.160
76.842
63.517
63.506
56.416
52.934
CO2Me
MeO
OMe
CF3
f1 (ppm)

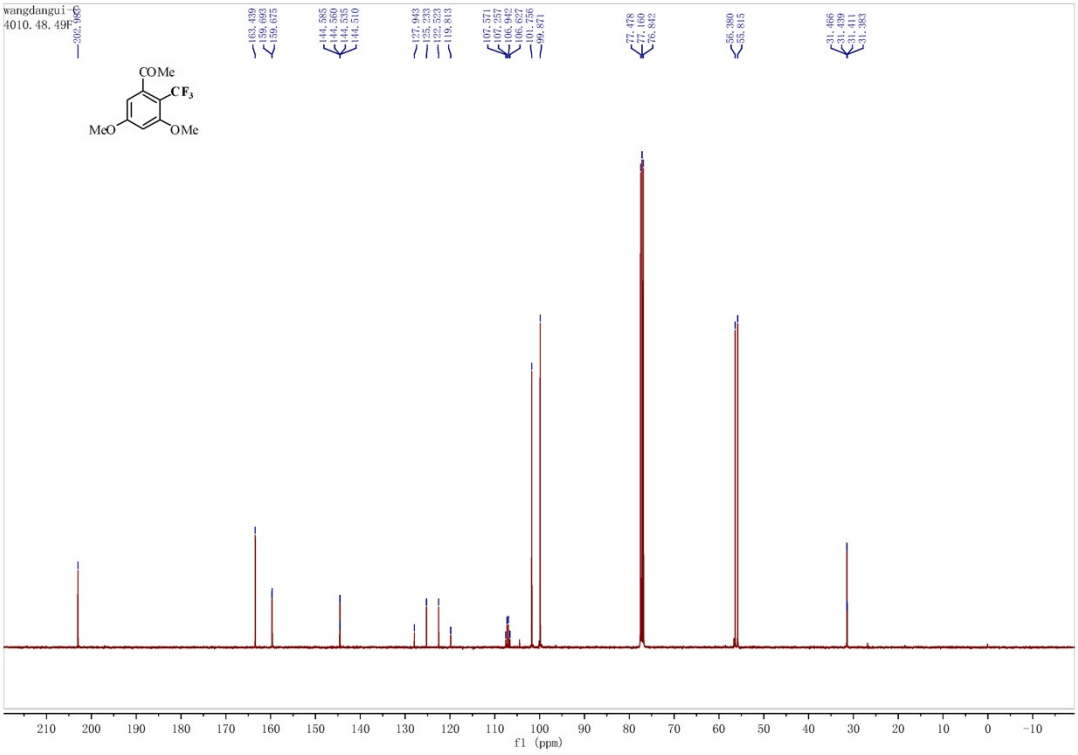

wangdangui-F
-60.378
CO2Me
MeO
OMe
CF3
f1 (ppm)

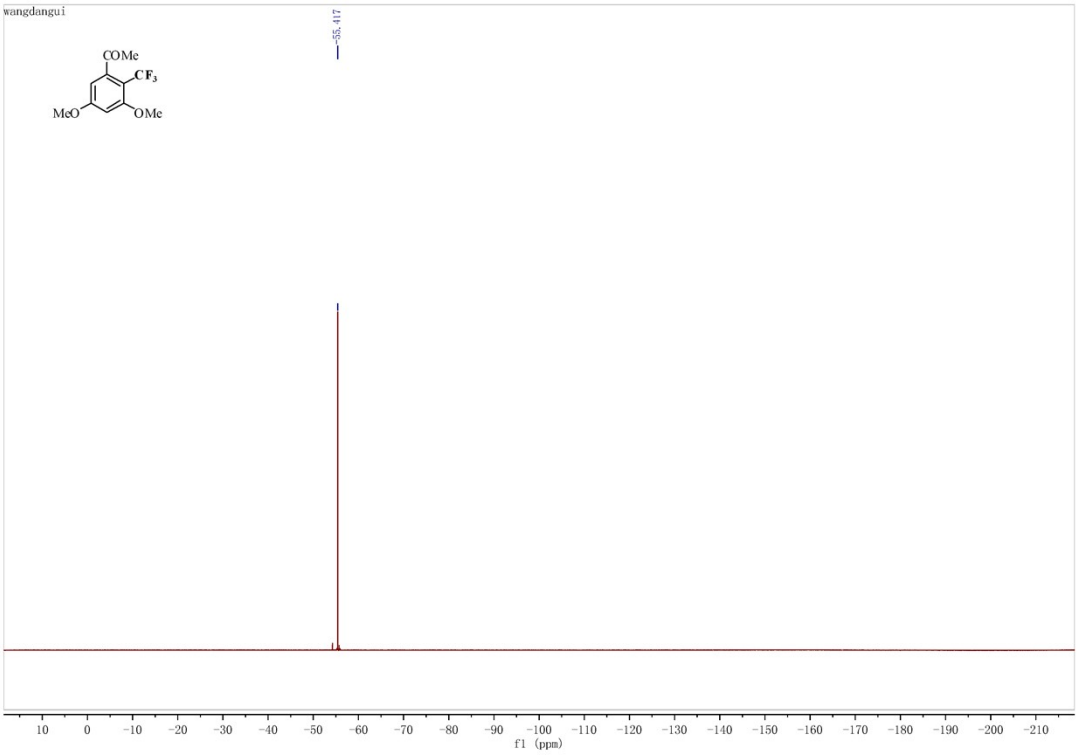

wangdangui-H
7.266
6.302
3.912
3.881
3.830
CO2Me
MeO
OMe
CF3
OMe
1.00
5.91
3.00
3.00
f1 (ppm)

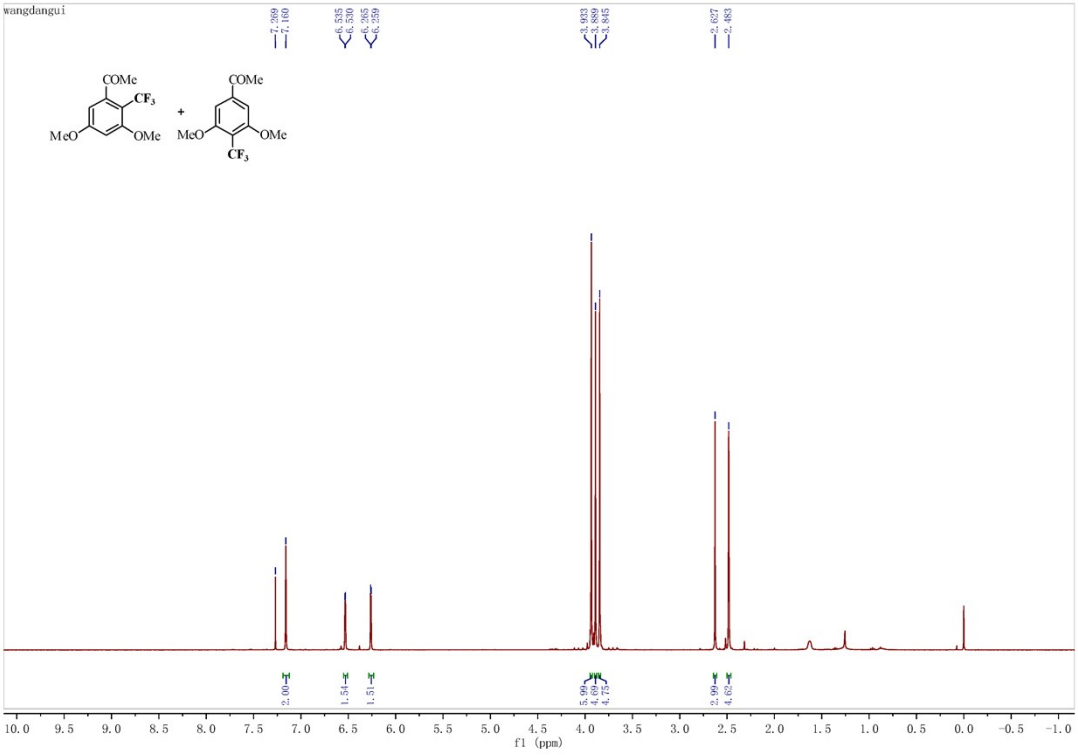

wangdangui
165.977
161.318
161.305
160.301
158.411
158.305
127.690
124.972
122.354
119.535
112.308
105.729
105.419
105.119
104.819
92.075
77.478
77.160
76.842
64.136
64.116
56.541
56.167
52.750
CO2Me
MeO
OMe
CF3
OMe
f1 (ppm)

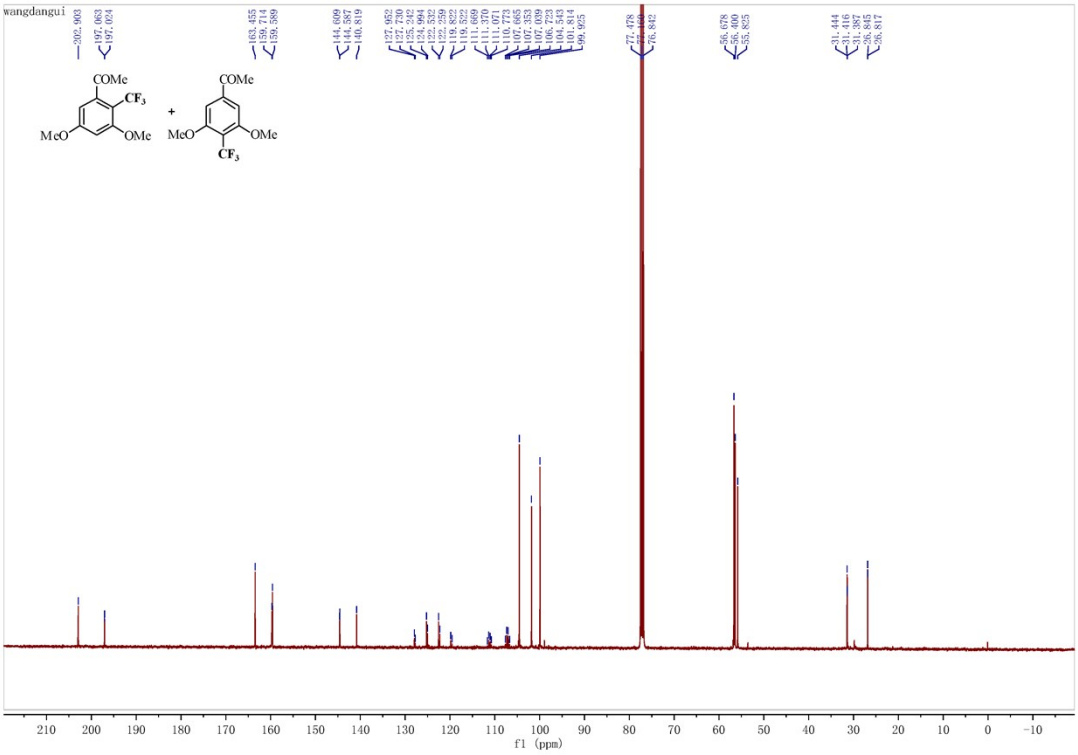

wangdangui
-55.886
CO2Me
MeO
OMe
CF3
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

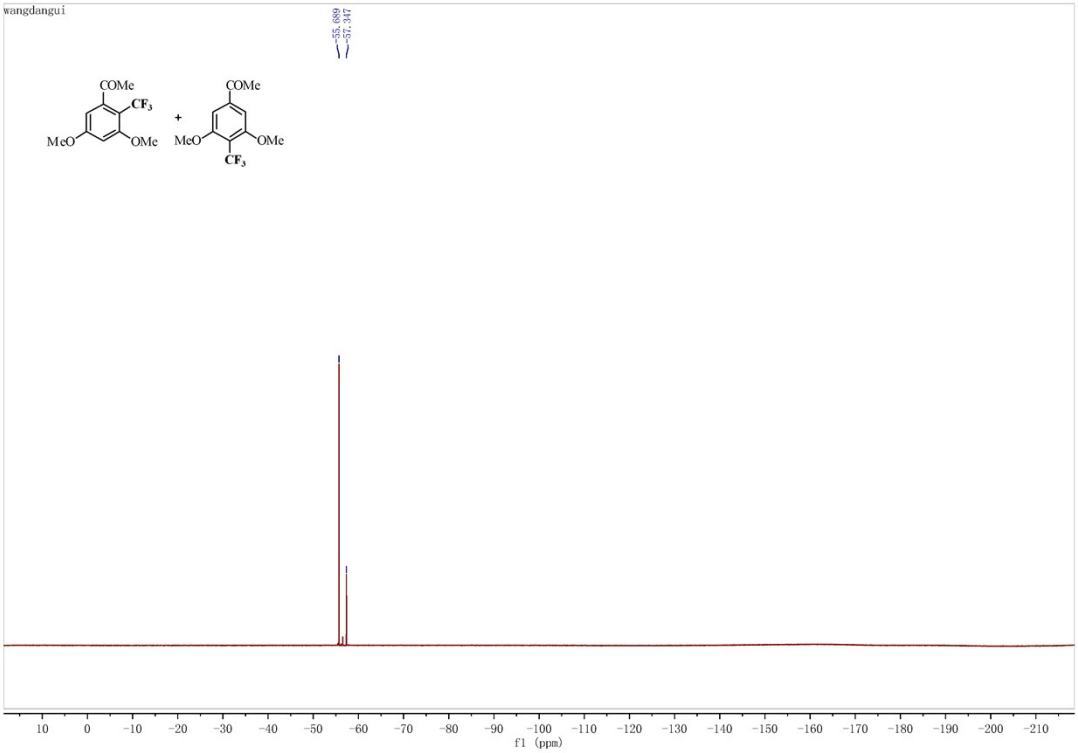

wangdangui-H
7.399
6.534
6.371
6.305
6.269
3.890
3.846
2.484
COMe
CF3
MeO
OMe
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

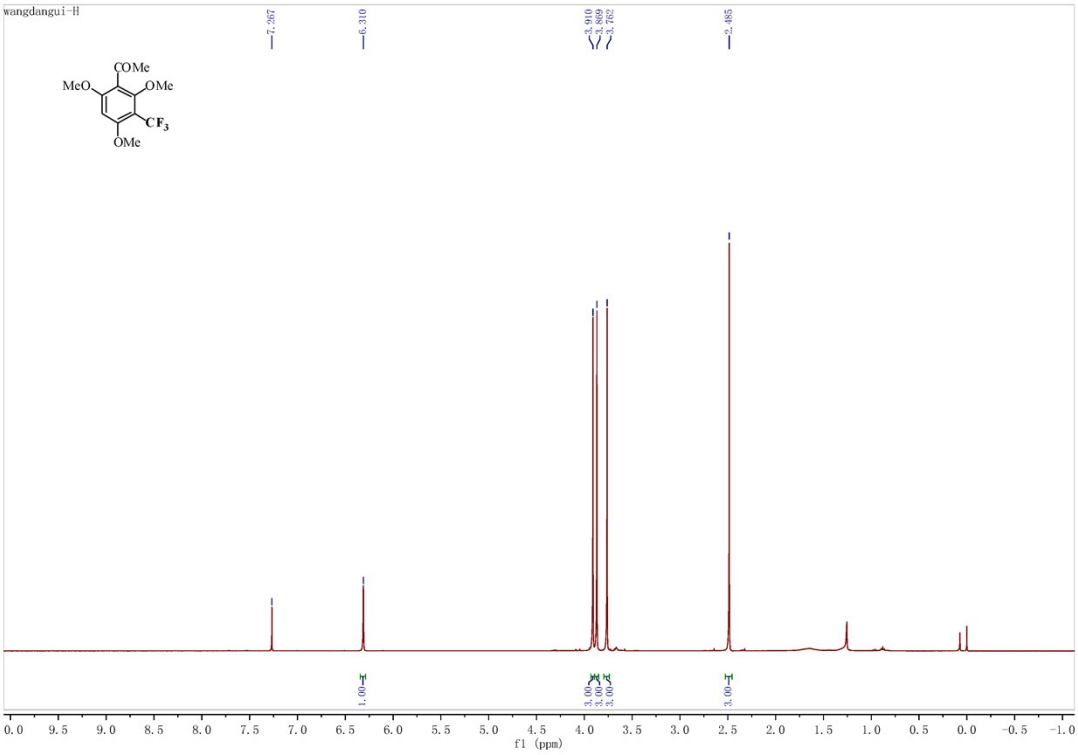

wangdangui
4010.48.495
202.966
163.439
159.675
144.585
144.510
127.943
125.233
122.523
119.813
107.571
107.257
106.942
106.627
101.756
101.476
94.871
77.478
77.160
76.842
56.380
55.815
31.466
31.439
31.141
31.383
COMe
CF3
MeO
OMe
f1 (ppm)

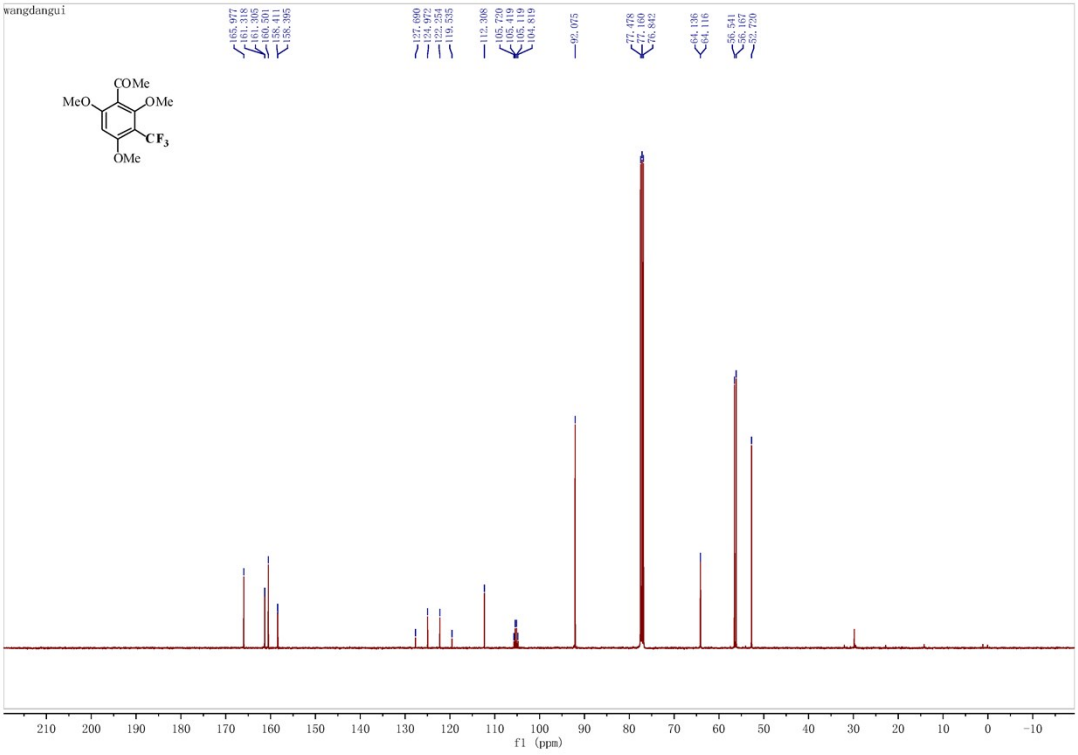

wangdangui
55.417
COMe
CF3
MeO
OMe
f1 (ppm)

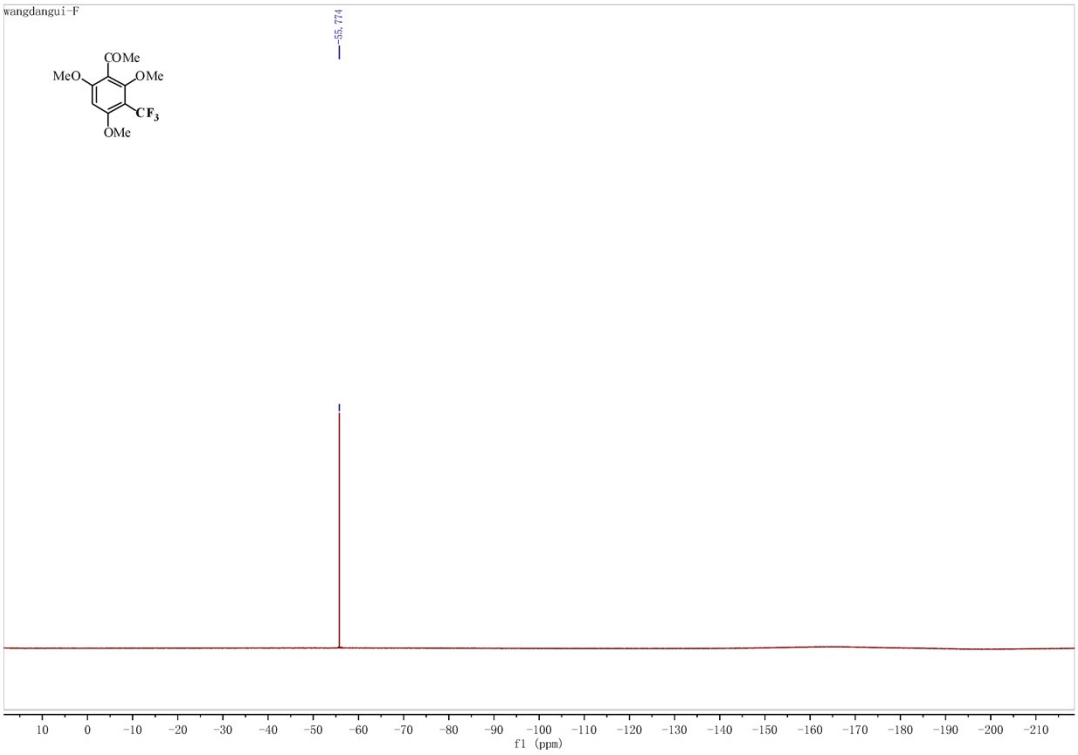

wangdangui
7.299
7.160
6.535
6.530
6.265
6.259
3.933
3.889
3.845
2.627
2.483
COMe
CF3
MeO
OMe
+
COMe
MeO
OMe
CF3
2.00
1.54
1.51
5.99
4.69
4.75
2.99
4.62
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

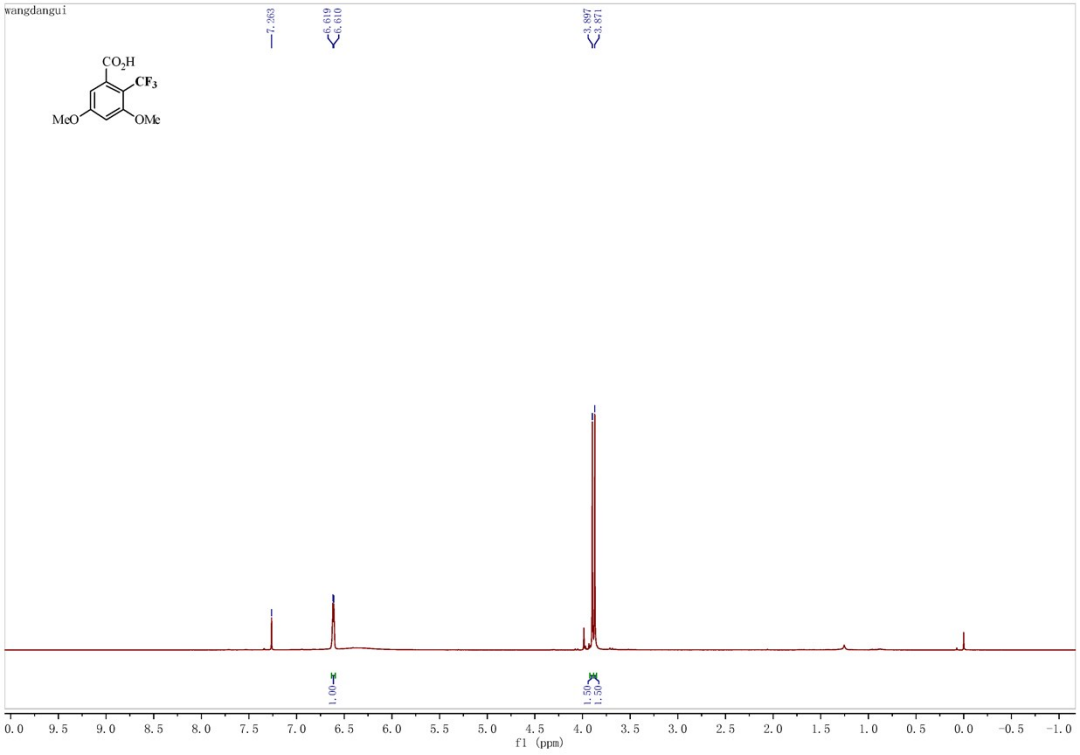

wangdangui
202.903
197.063
197.024
163.455
159.414
158.589
144.609
140.897
140.819
127.652
127.230
125.342
124.994
123.232
122.239
119.822
119.522
111.669
111.370
111.071
110.773
107.955
107.653
107.039
106.723
104.343
101.944
99.905
77.478
77.160
76.842
56.678
56.400
55.835
31.444
31.416
31.387
26.845
26.817
COMe
CF3
MeO
OMe
+
COMe
MeO
OMe
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

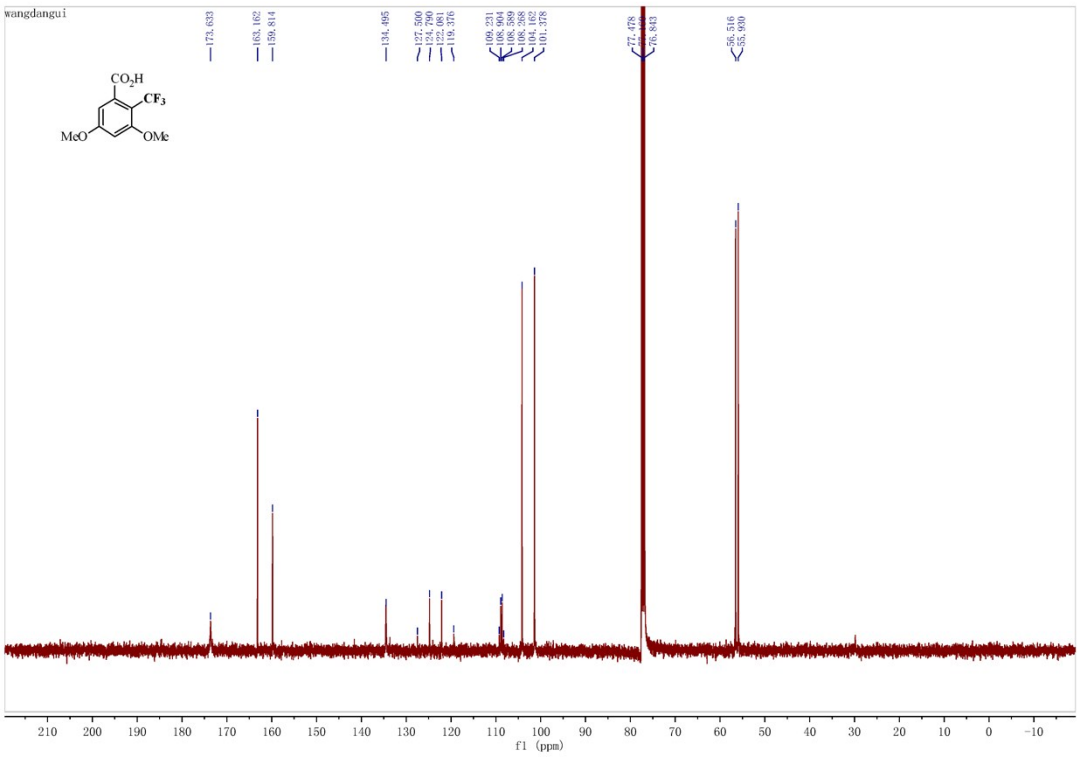

wangdangui
-55.889
-57.347
COMe
CF3
MeO
OMe
+
COMe
MeO
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

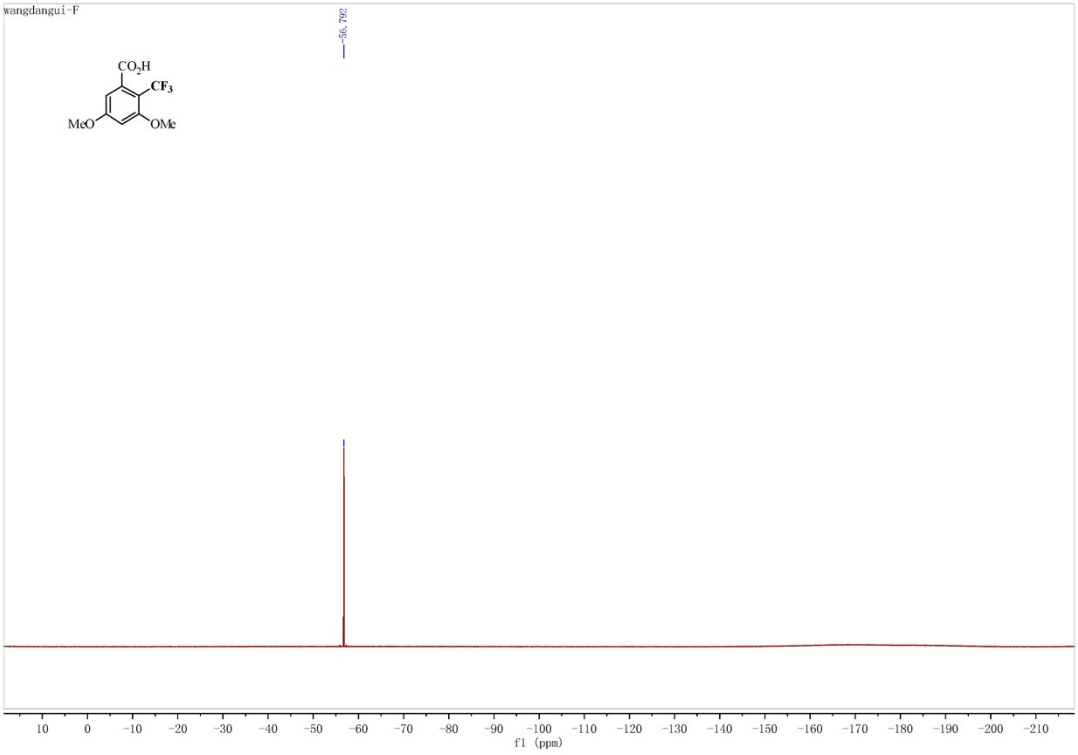

wangdangui-H
7.387
6.310
3.910
3.900
3.892
2.485
COMe
MeO
OMe
CF3
OMe
1.00
3.00
3.00
3.00
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

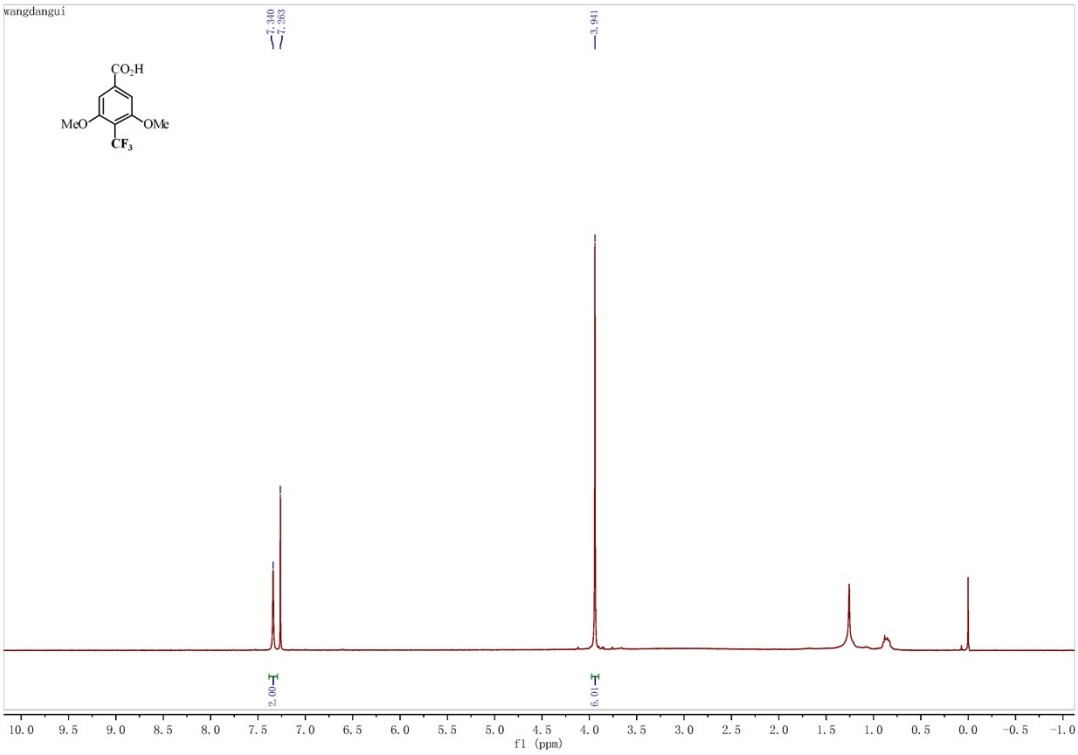

wangdangui
165.977
161.318
161.305
160.301
158.411
158.395
127.690
124.972
122.254
119.535
112.308
105.739
105.419
105.119
104.819
92.075
77.478
77.160
76.842
64.136
64.116
56.541
56.167
52.720
COMe
MeO
OMe
CF3
OMe
f1 (ppm)

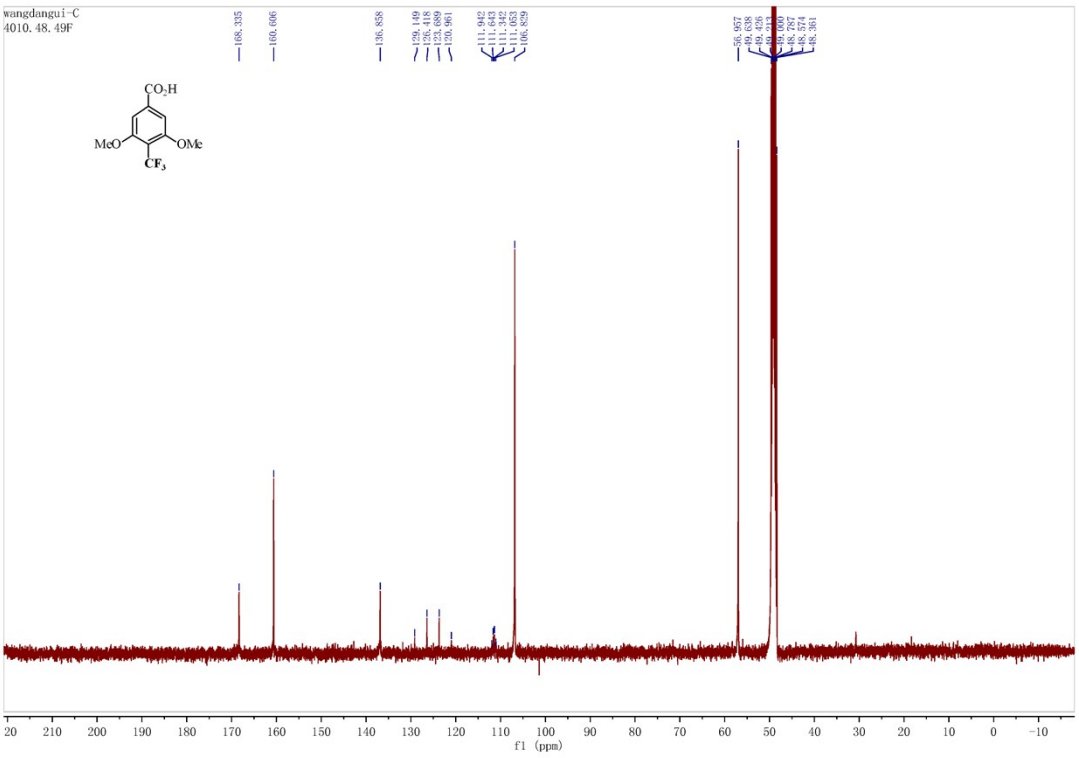

wangdangui-F
-55.774
COMe
MeO
OMe
CF3
OMe
f1 (ppm)

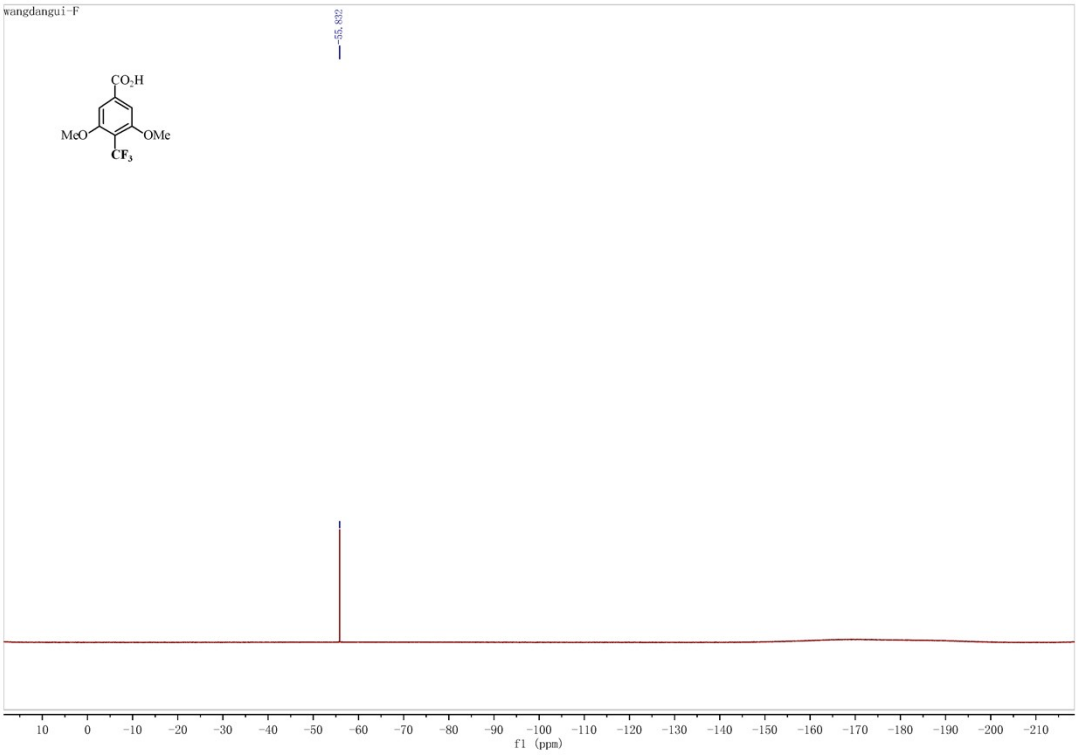

wangdangui
7.263
6.619
6.610
3.897
3.871
CO2H
CF3
MeO
OMe
1.00
1.50
1.50
f1 (ppm)

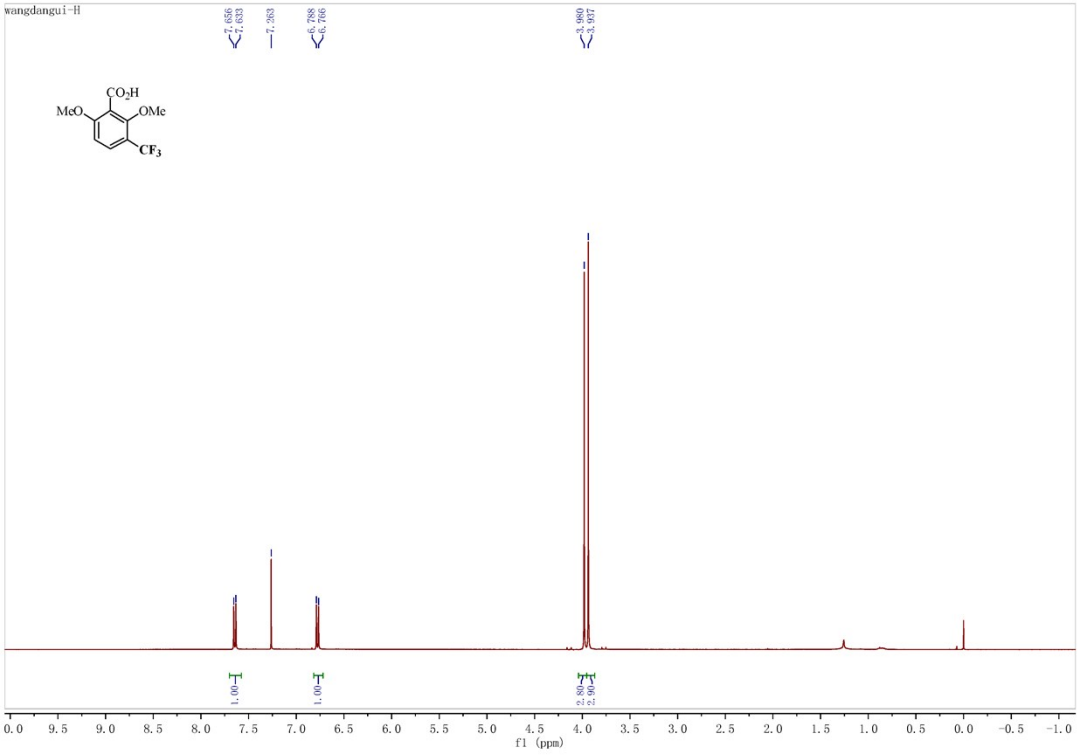

wangdangui
173.633
163.162
159.814
134.495
127.500
124.790
122.081
119.576
109.921
108.804
108.389
108.288
104.162
101.976
77.478
76.843
56.516
55.990
CO2H
CF3
MeO
OMe
f1 (ppm)

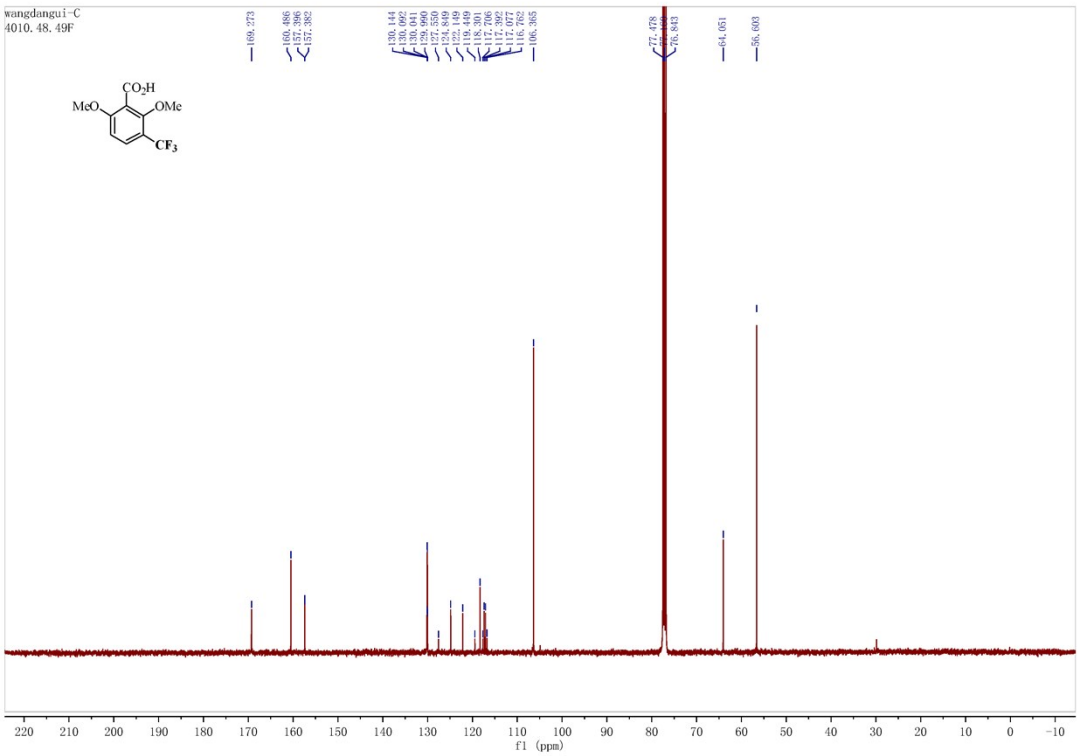

wangdangui-F
-56.792
CO2H
CF3
MeO
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

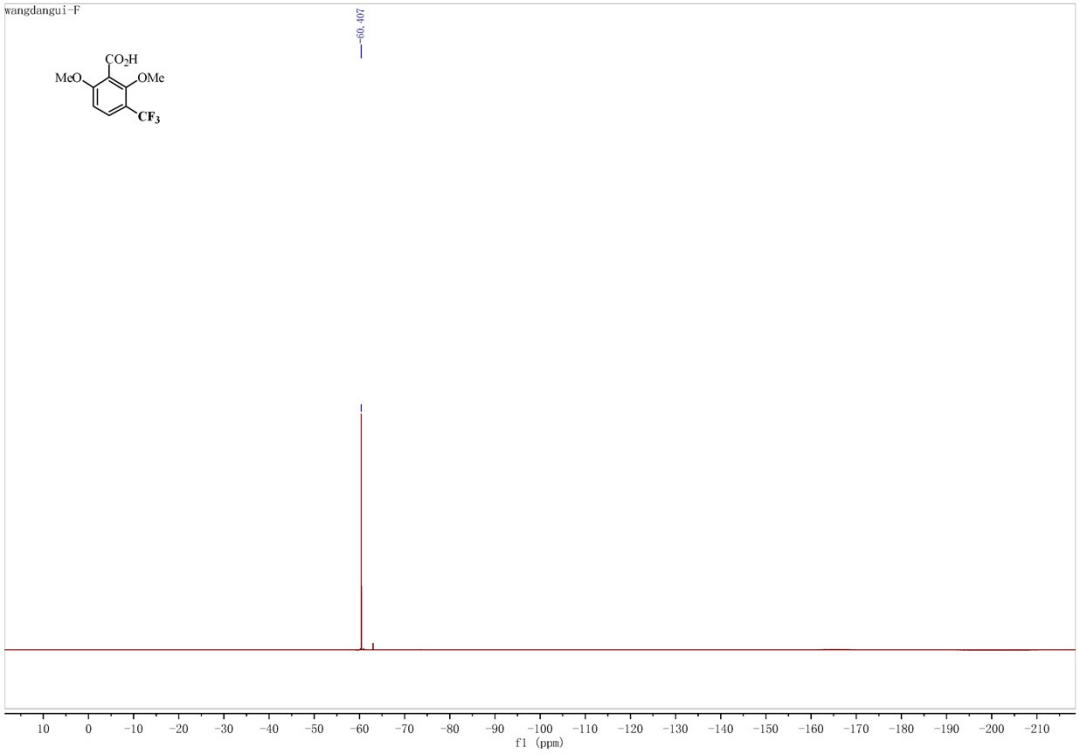

wangdangui
7.340
7.383
3.941
CO2H
MeO
OMe
CF3
2.00
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

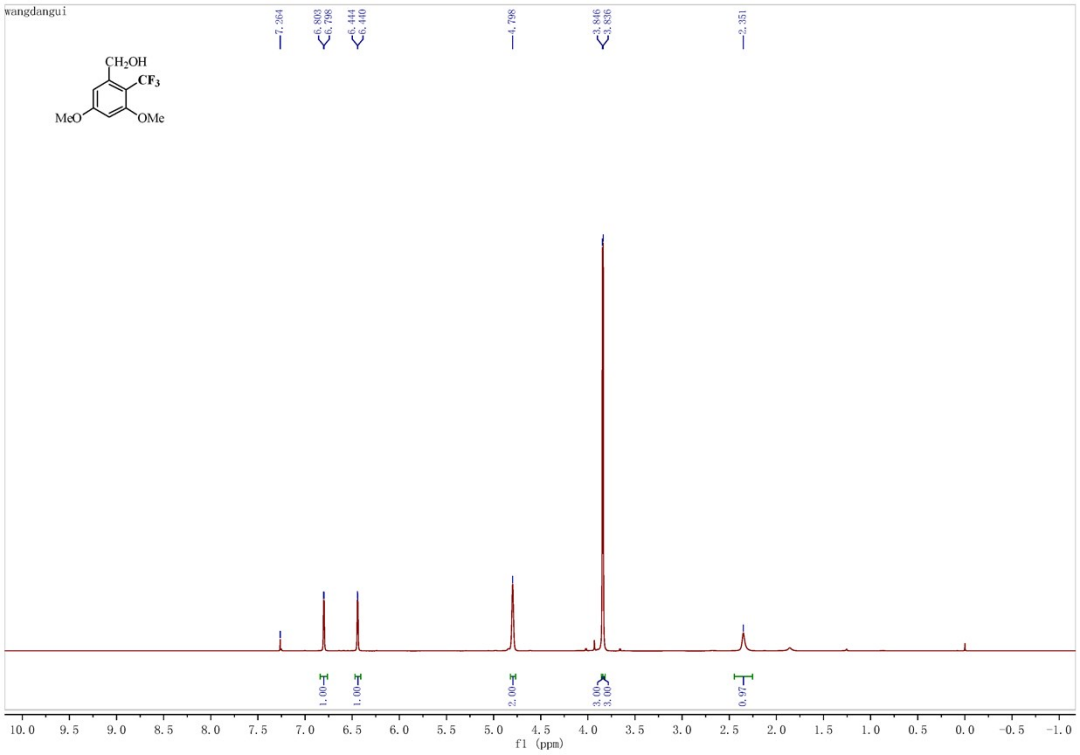

wangdangui-C
4010.48.49F
168.335
160.606
136.858
129.149
125.418
123.689
120.961
111.942
111.643
111.342
111.053
106.829
56.957
49.638
49.426
49.215
48.797
48.574
48.361
CO2H
MeO
OMe
CF3
f1 (ppm)

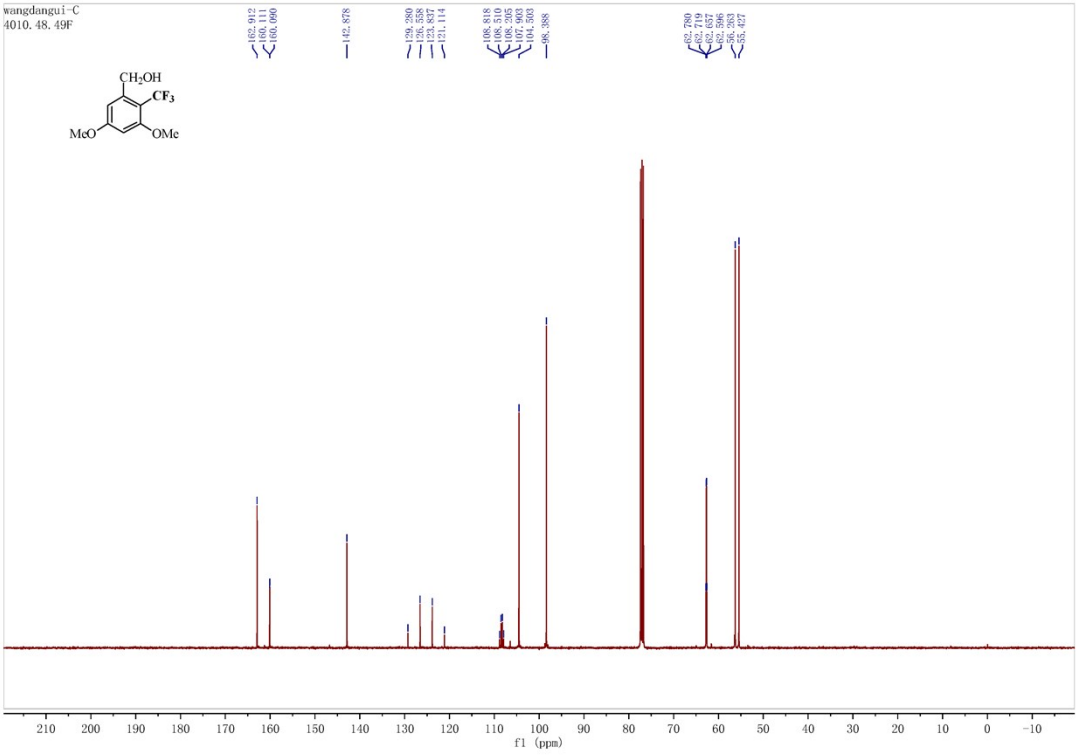

wangdangui-F
-55.832
CO2H
MeO
OMe
CF3
f1 (ppm)

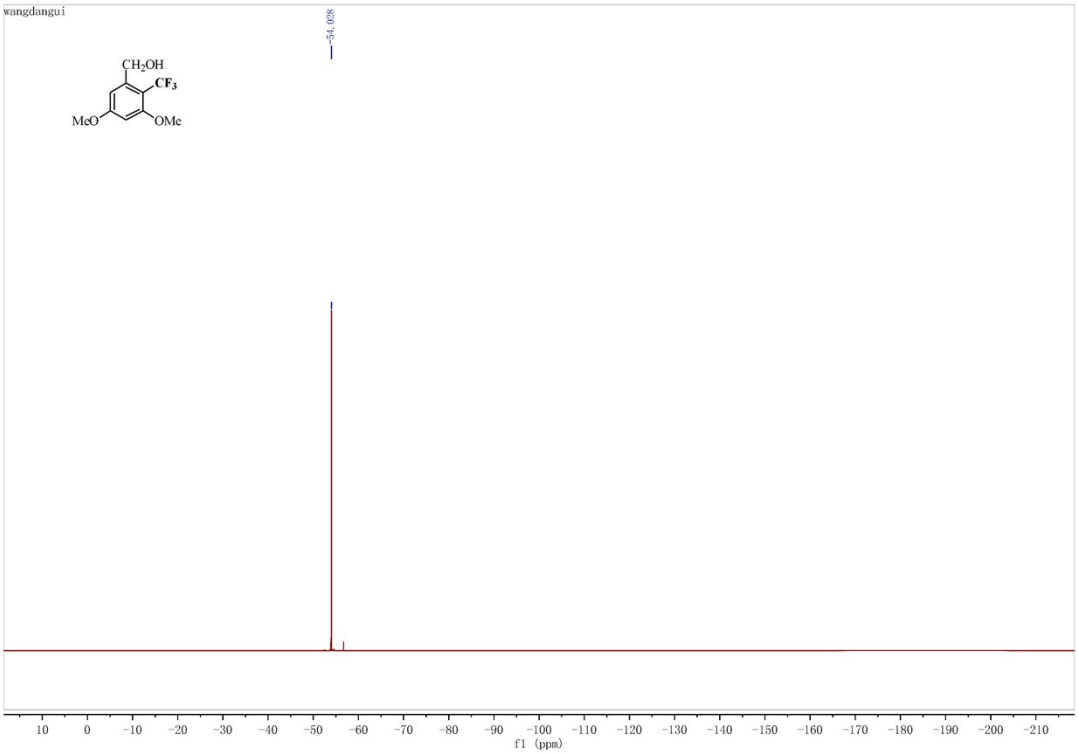

wangdangui-H
7.656
7.633
7.263
6.788
6.766
3.980
3.937
CO2H
MeO
OMe
CF3
1.00
1.00
2.89
2.90
f1 (ppm)

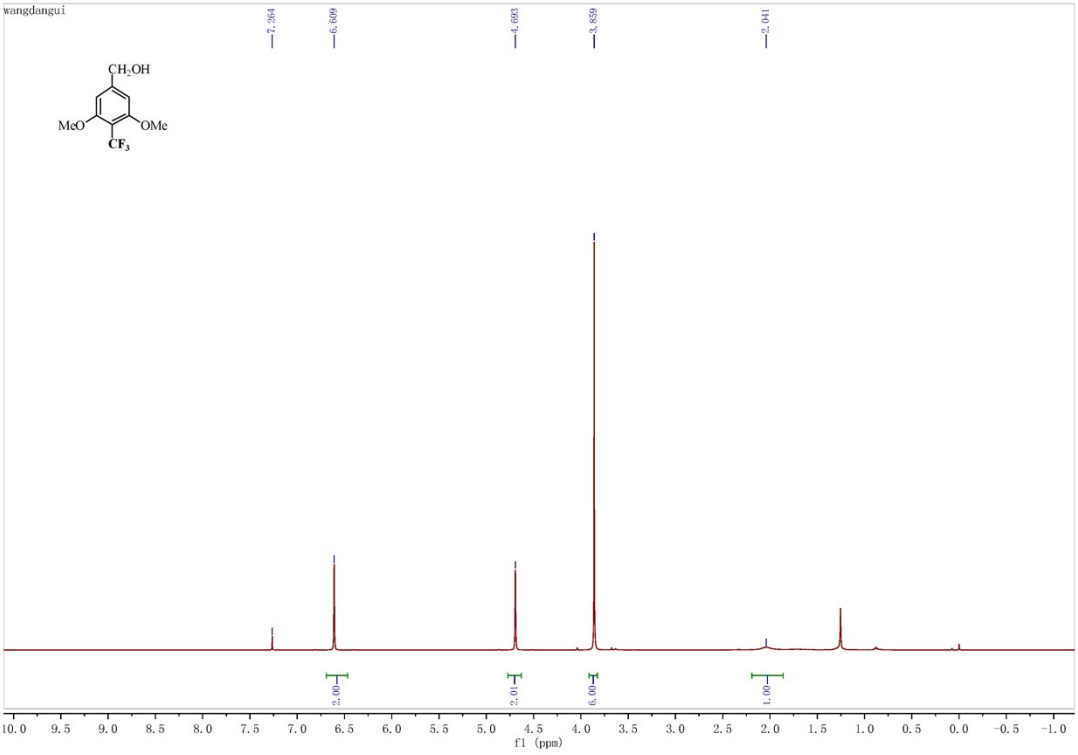

wangdangui-C
4010.48.49F
169.273
160.486
157.396
157.382
130.444
130.097
130.041
129.990
127.550
124.948
122.149
119.449
118.301
117.786
117.492
117.077
116.762
106.365
77.478
76.843
64.051
56.603
CO2H
MeO
OMe
CF3
f1 (ppm)

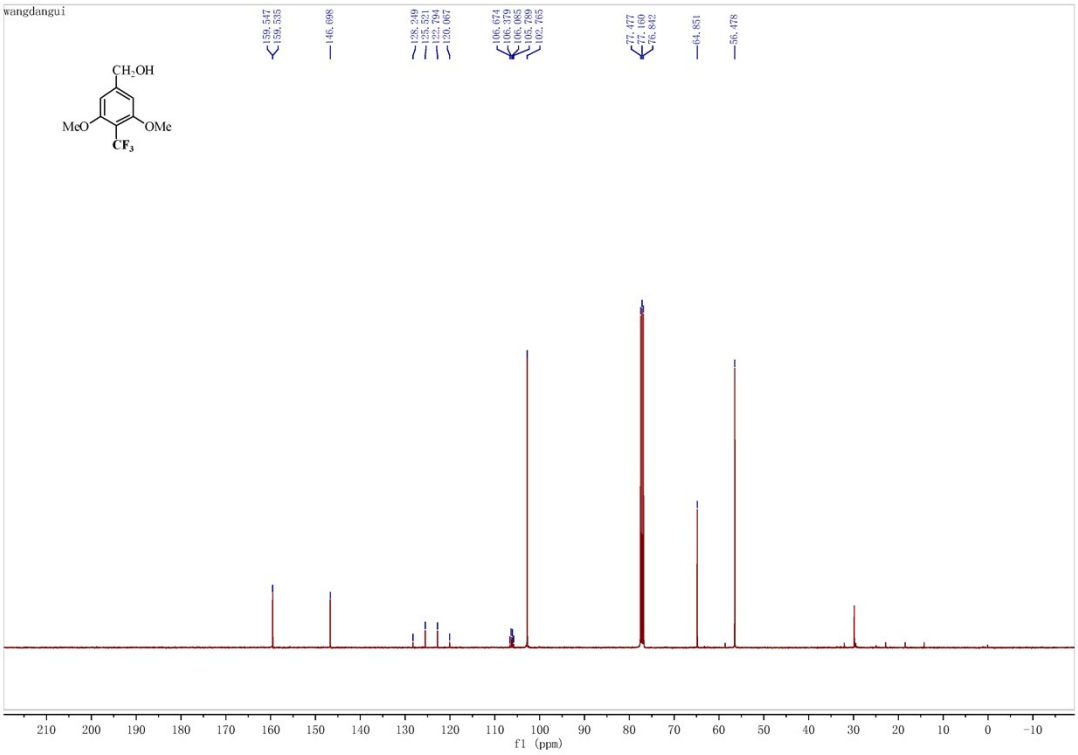

wangdangui-F
-60.407
CO2H
MeO
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

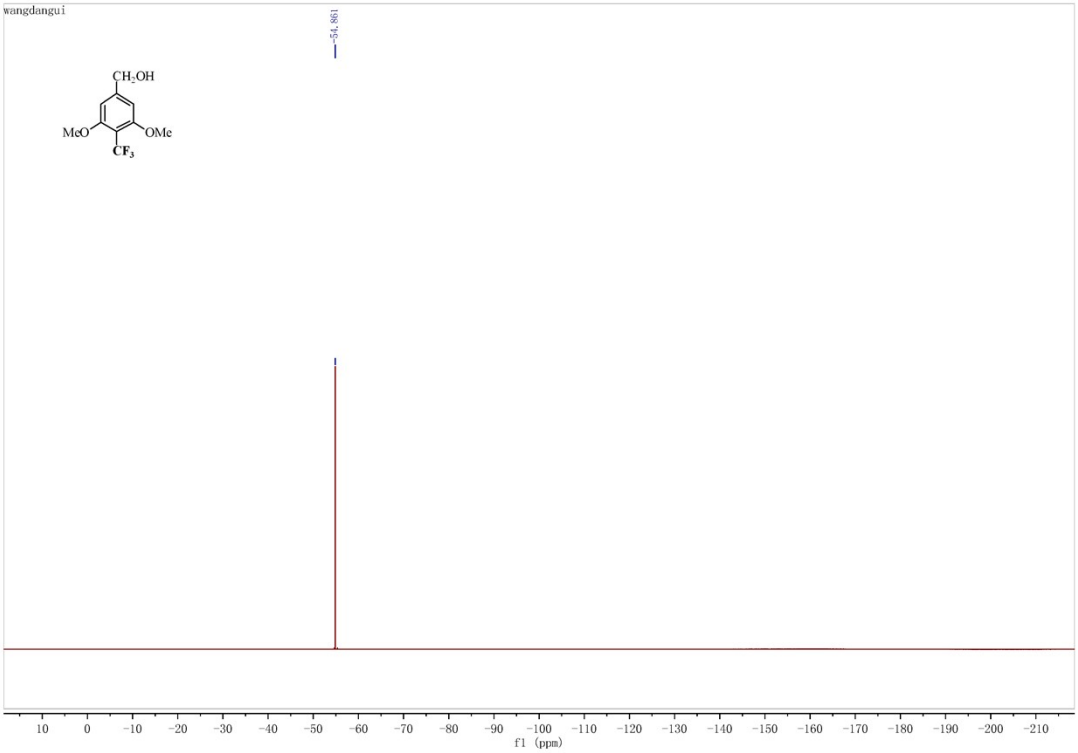

wangdangui
7.264
6.803
6.798
6.444
6.440
4.798
3.846
3.836
2.351
CH2OH
CF3
MeO
OMe
1.00
1.00
2.00
3.00
3.00
0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

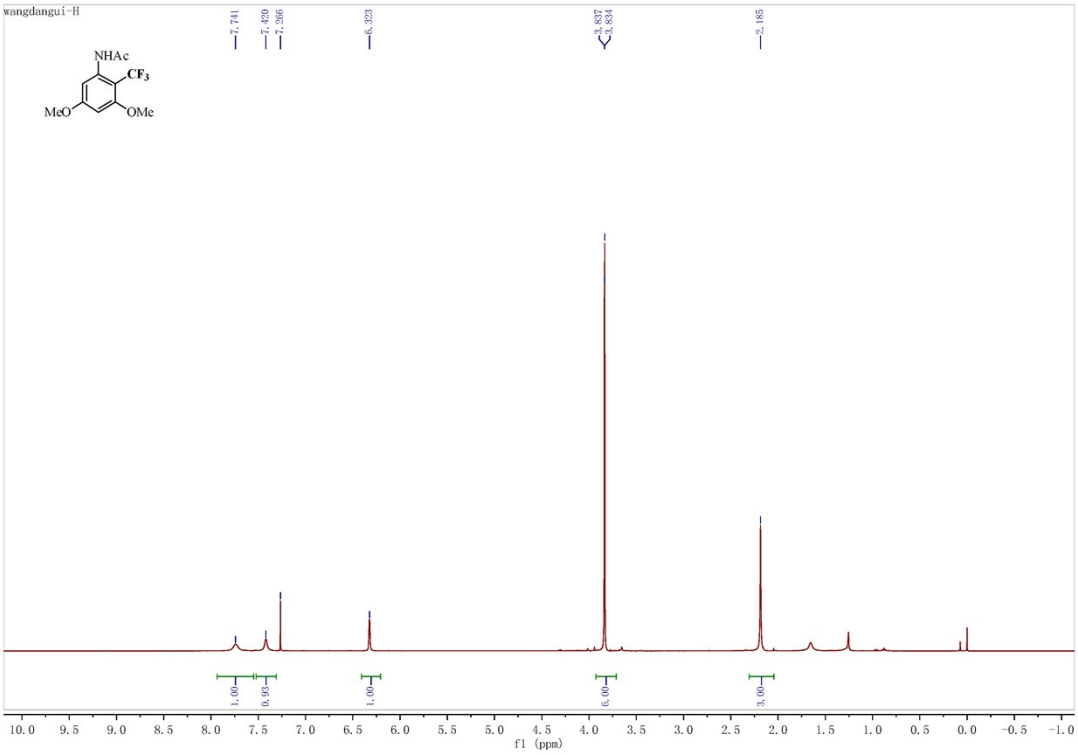

wangdangui-C
4010.48.49F
162.912
160.111
160.090
142.878
129.280
126.358
123.847
121.114
108.818
108.510
108.205
107.903
104.303
98.388
62.780
62.719
62.657
62.596
56.283
55.427
CH2OH
CF3
MeO
OMe
f1 (ppm)

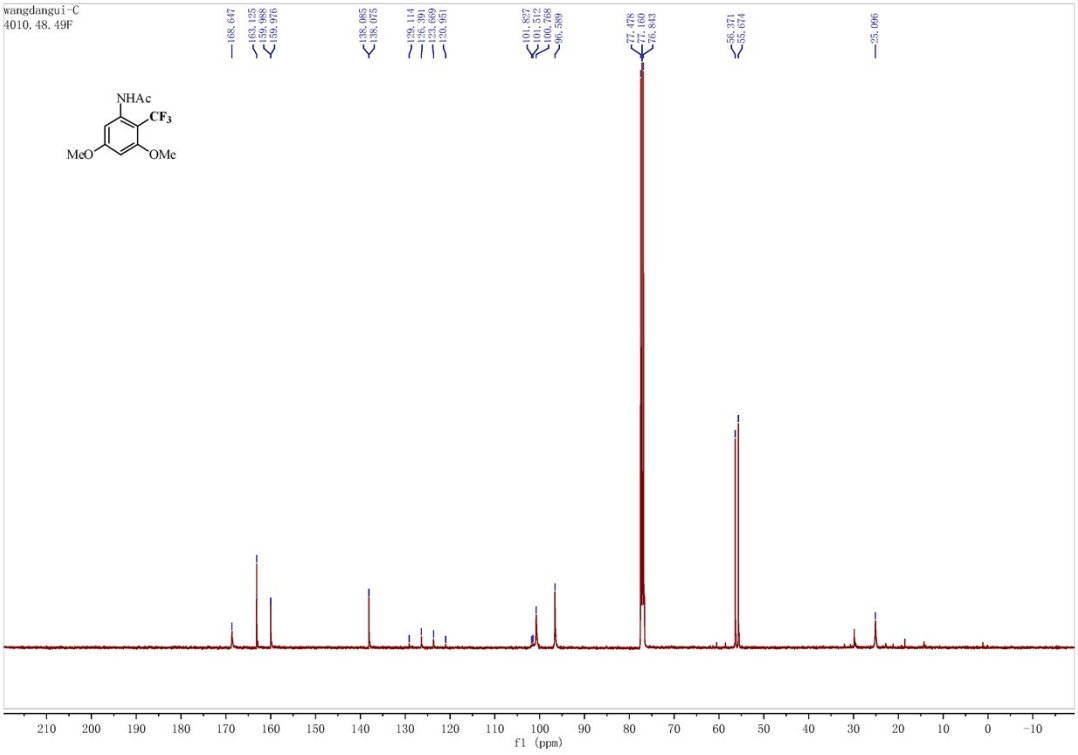

wangdangui
-54.028
CH2OH
CF3
MeO
OMe
f1 (ppm)

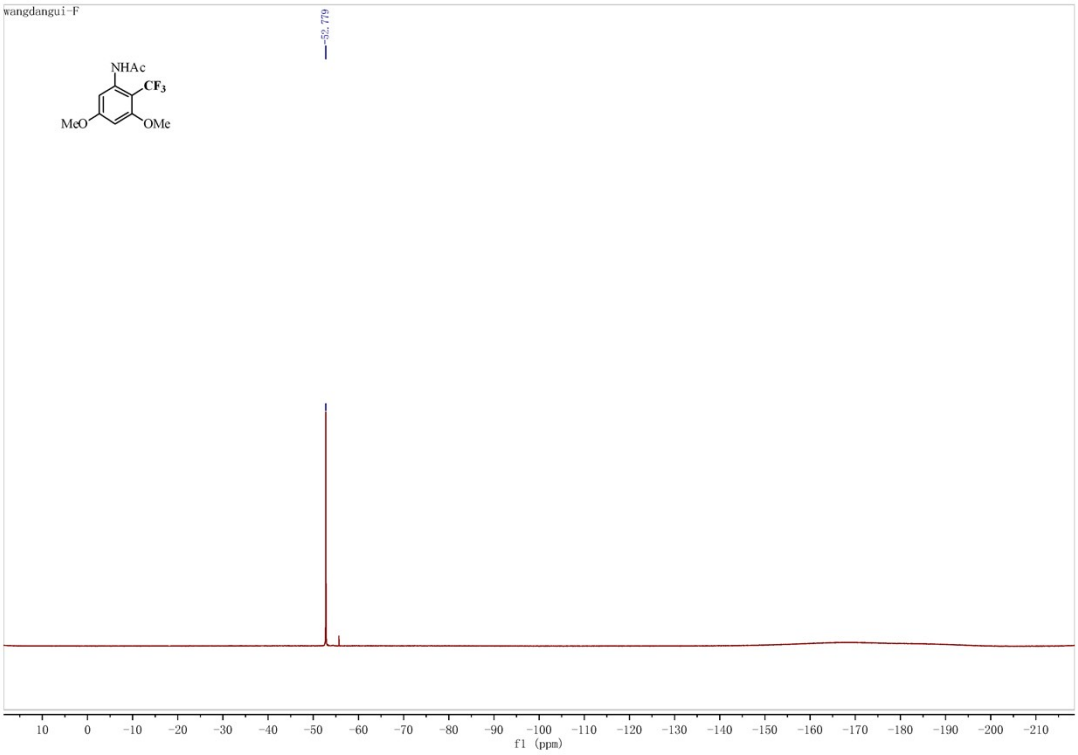

wangdangui
7.264
6.609
4.693
3.859
2.041
CH2OH
MeO
OMe
CF3
2.00
2.01
6.00
1.00
f1 (ppm)

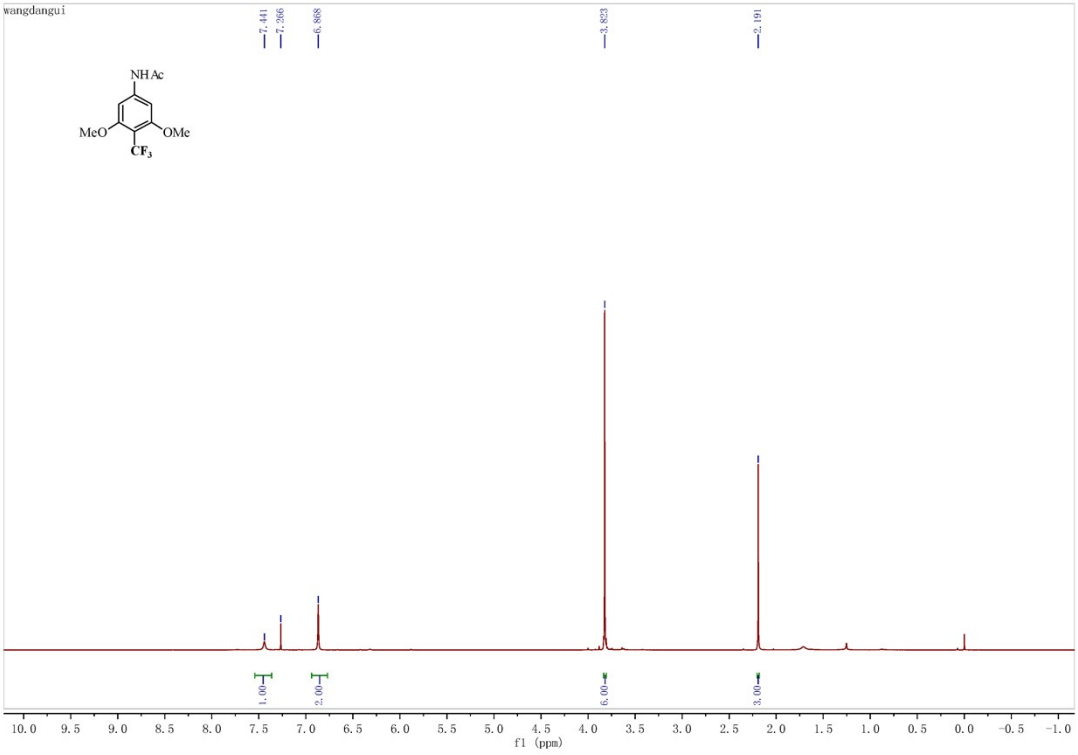

wangdangui
159.547
159.535
146.698
128.349
125.321
122.794
120.067
106.674
106.379
106.085
105.789
102.765
77.477
77.160
76.842
64.851
56.478
CH2OH
MeO
OMe
CF3
f1 (ppm)

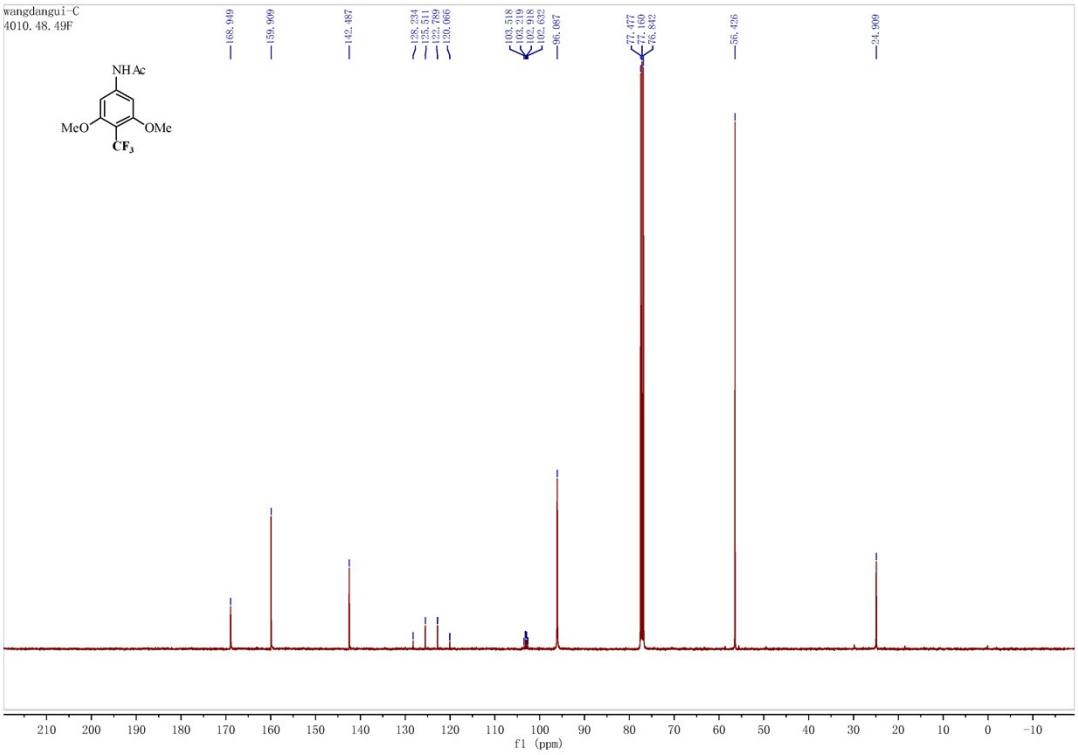

wangdangui
-54.861
CH2OH
MeO
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

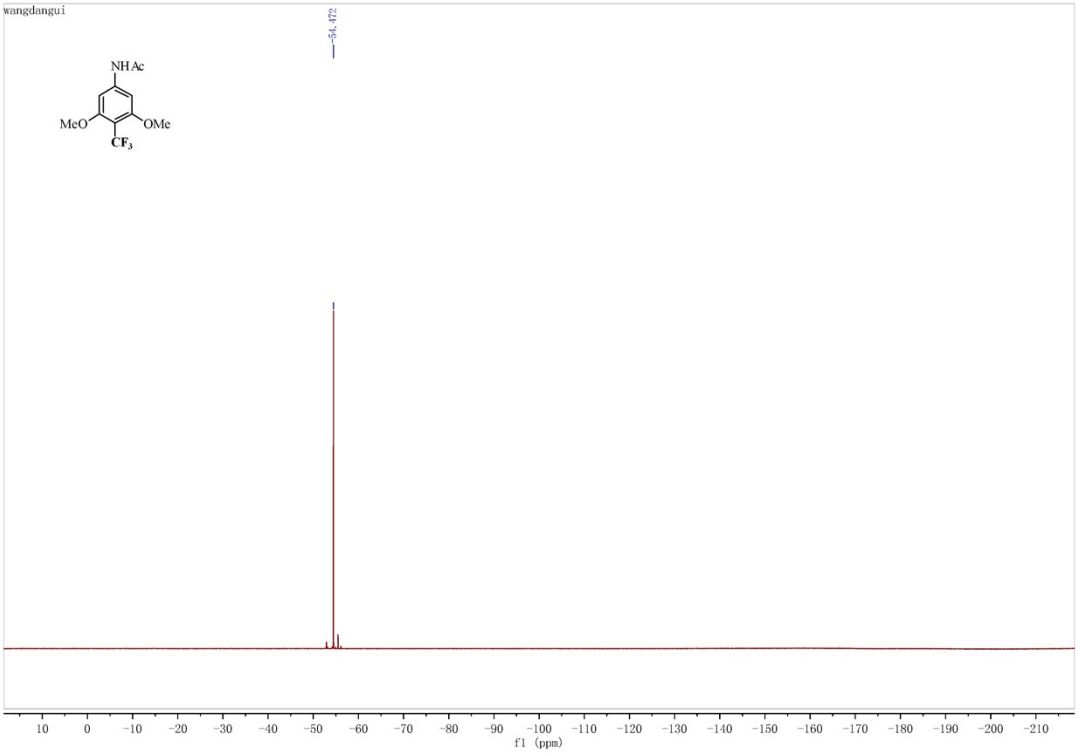

wangdangui-H
7.741
7.420
7.396
6.323
3.837
3.834
2.185
NHAc
CF3
MeO
OMe
1.00
0.93
1.00
6.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui-C
4010.48.49F
168.647
163.125
159.976
138.085
138.075
129.114
126.391
123.669
110.951
101.827
101.512
100.768
96.389
77.478
77.160
76.843
56.371
55.674
25.066
NHAc
CF3
MeO
OMe
f1 (ppm)


wangdangui-F
-32.779
NHAc
CF3
MeO
OMe
f1 (ppm)


wangdangui
7.441
7.266
6.868
3.823
2.191
NH Ac
MeO
OMe
CF3
1.00
2.00
6.00
3.00
f1 (ppm)


wangdangui-C
4010.48.49F
168.949
159.909
142.487
128.234
125.511
122.789
120.066
103.518
103.219
102.918
102.622
96.067
77.477
77.160
76.842
56.436
24.909
NH Ac
MeO
OMe
CF3
f1 (ppm)


wangdangui
-54.472
NHAc
MeO
OMe
CF3
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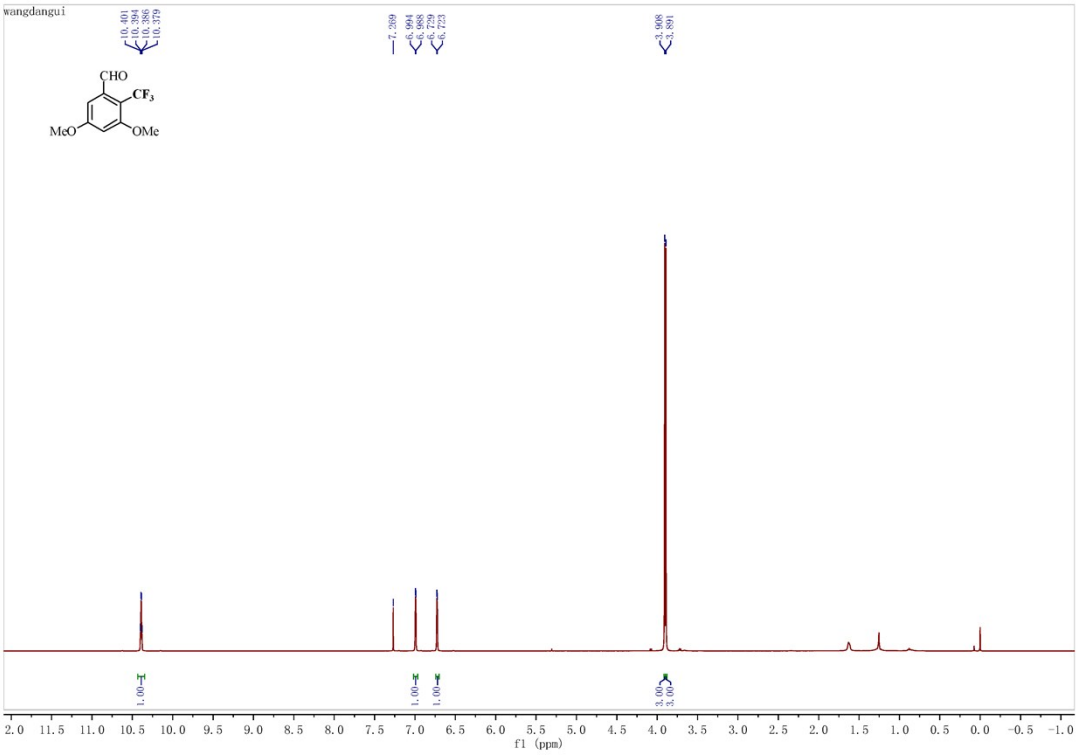
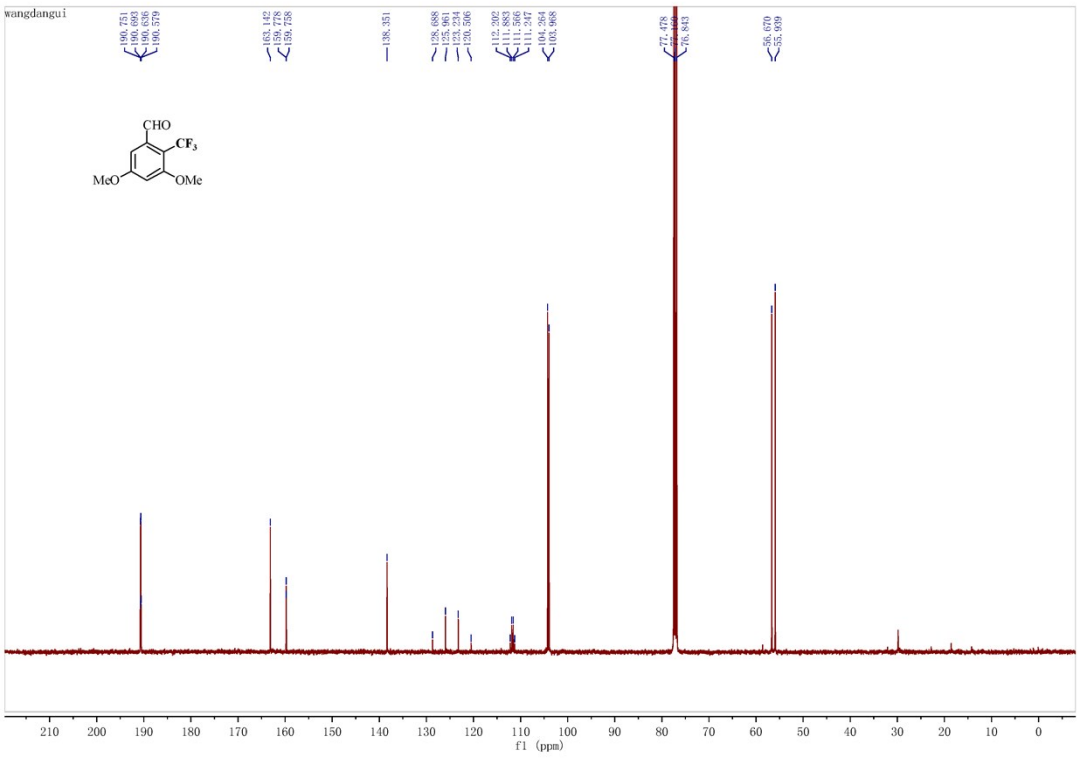
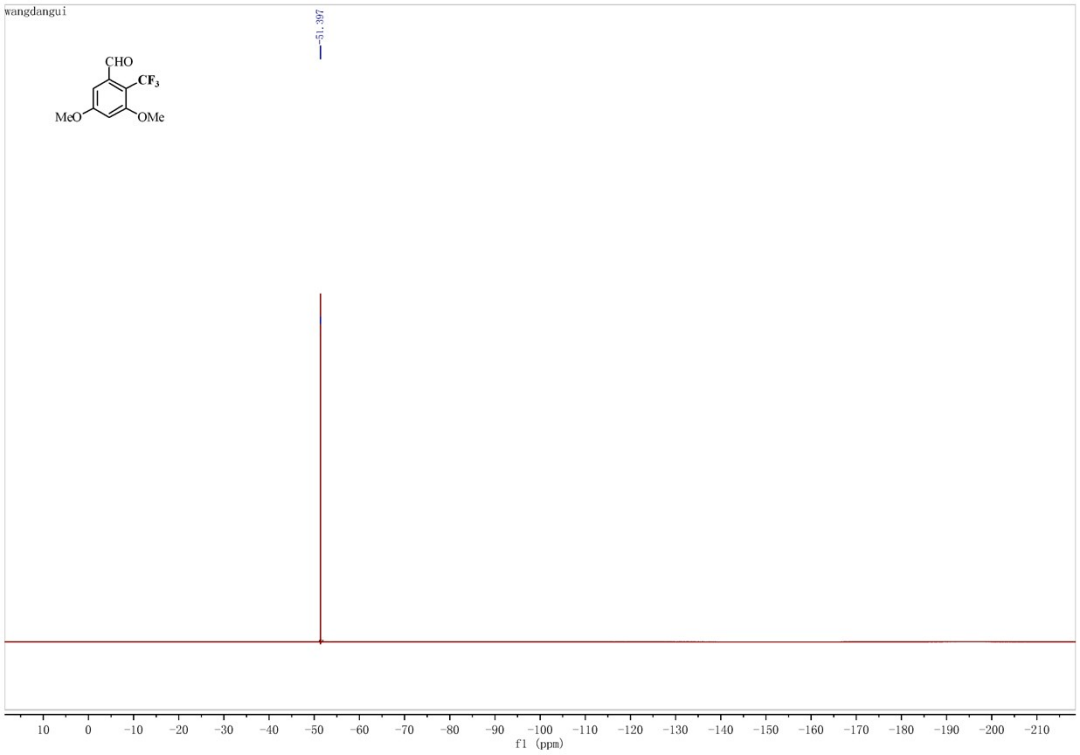
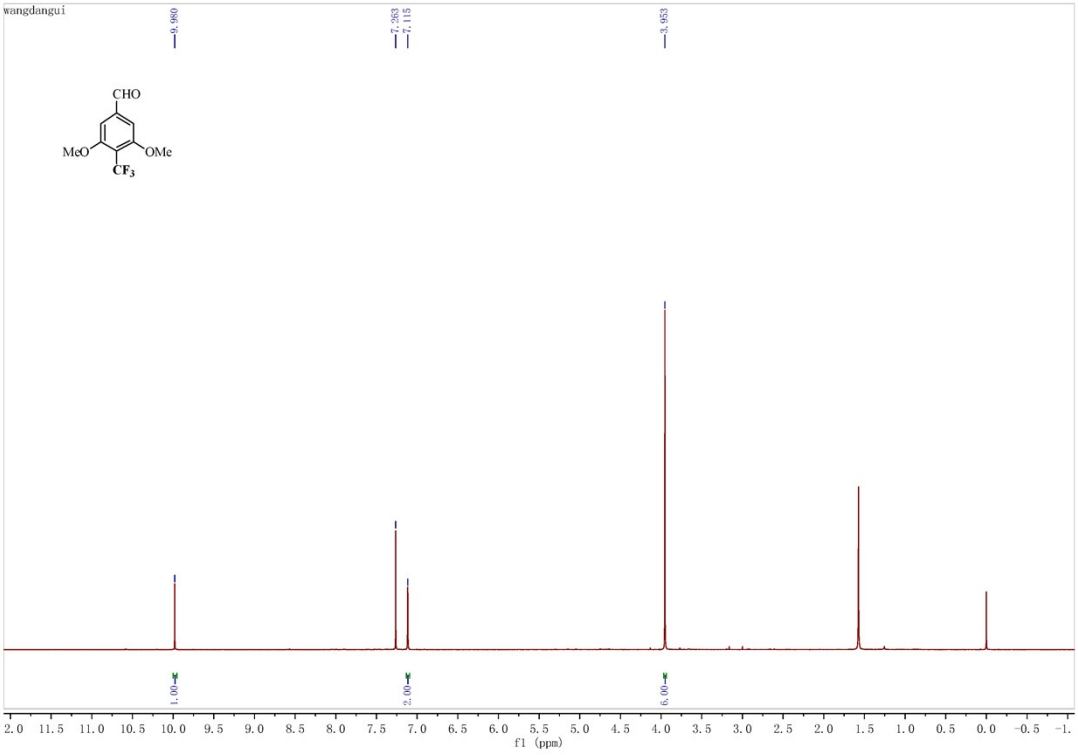
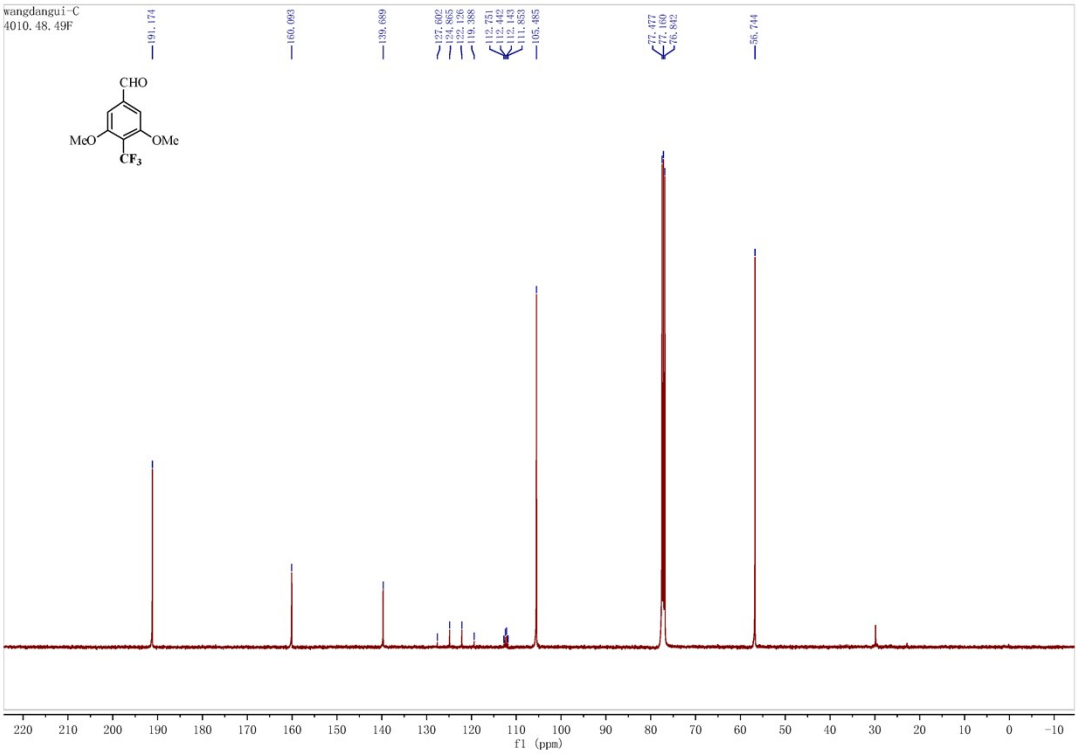
f1 (ppm)

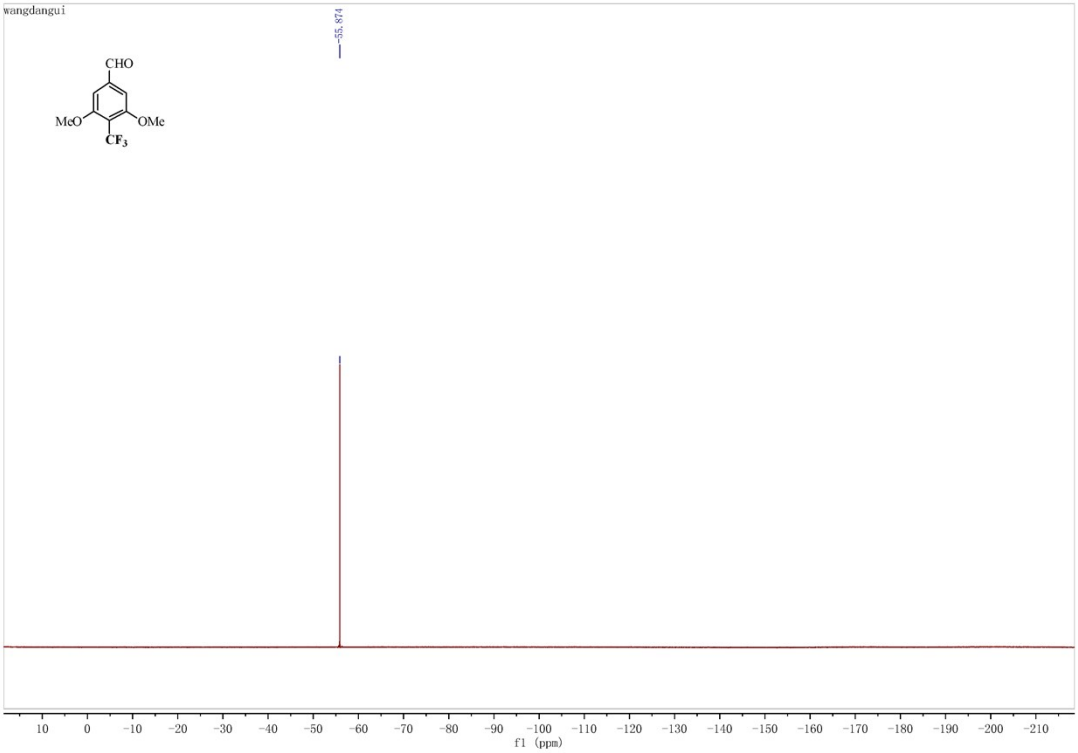

wangdangui
10.401
10.394
10.386
10.379
7.269
6.994
6.988
6.729
6.723
3.908
3.891
CHO
CF3
MeO
OMe
1.00
1.00
1.00
3.00
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui
190.751
190.693
190.636
190.579
163.142
159.758
159.758
138.351
128.688
125.961
123.234
120.506
112.202
111.883
111.566
111.247
104.264
103.968
77.478
77.160
76.843
56.670
55.939
CHO
CF3
MeO
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


wangdangui
-51.397
CHO
CF3
MeO
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


wangdangui
9.980
7.263
7.115
3.953
CHO
MeO
OMe
CF3
1.00
2.00
6.00
f1 (ppm)


wangdangui-C
4010.48.49F
191.174
160.993
139.889
137.602
124.865
122.138
118.988
112.731
112.472
112.143
111.853
105.485
77.477
77.160
76.842
56.744
CHO
MeO
OMe
CF3
f1 (ppm)


wangdangui
-55.874
CHO
MeO
OMe
CF3
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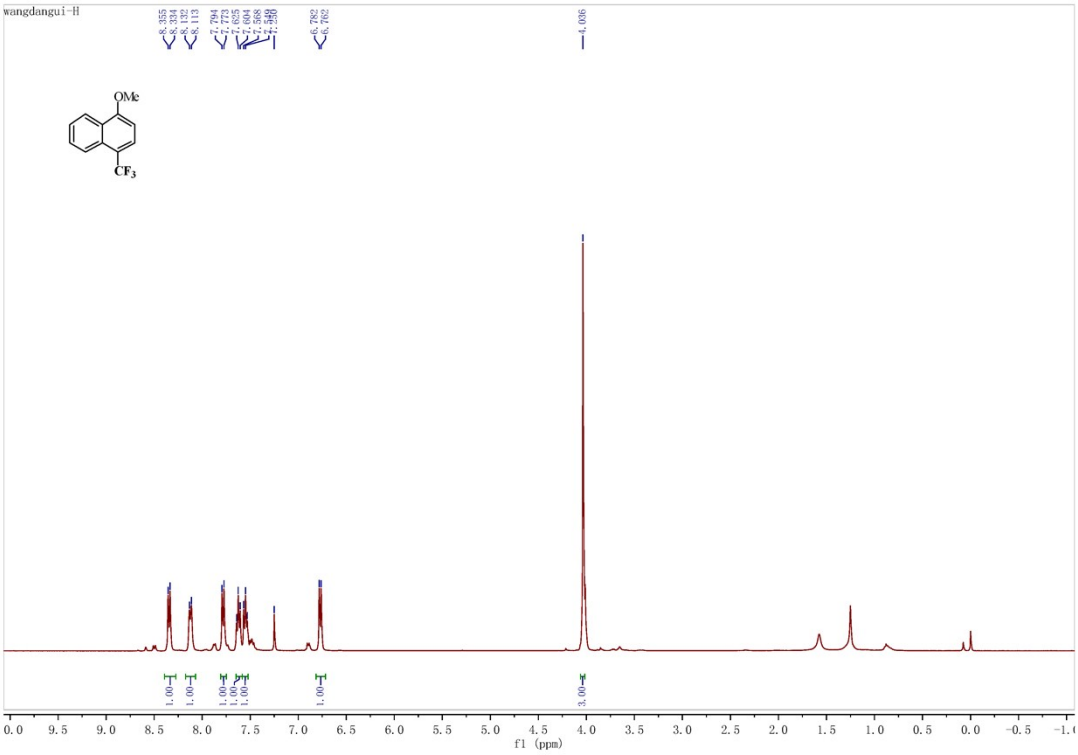
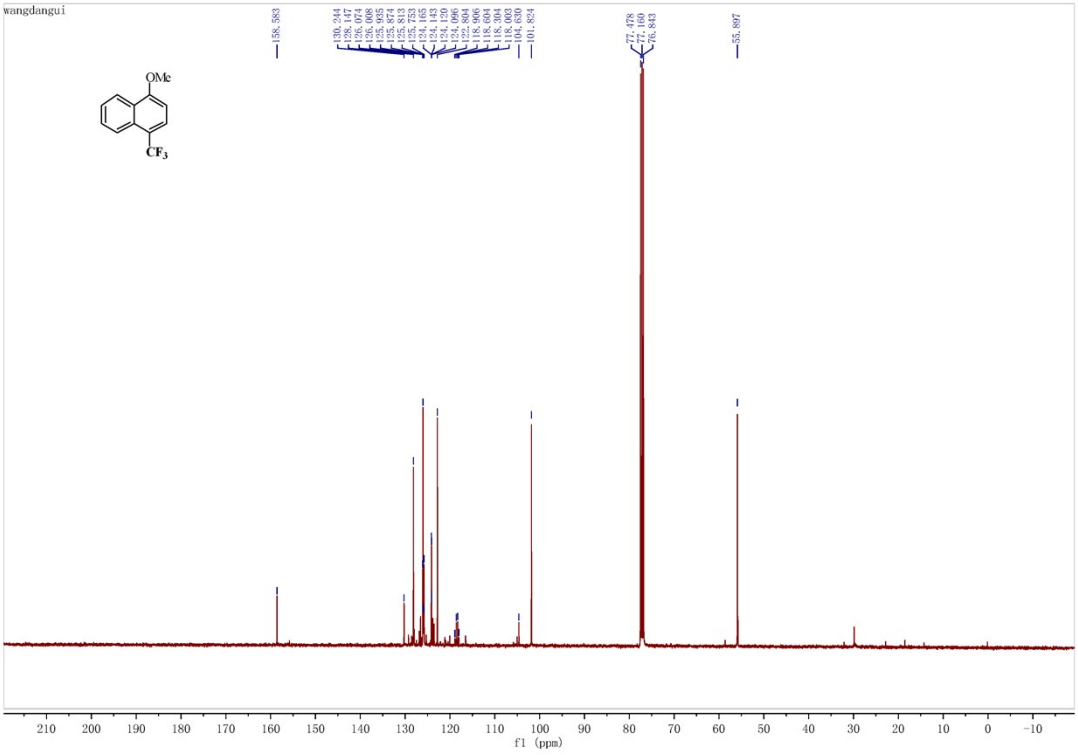
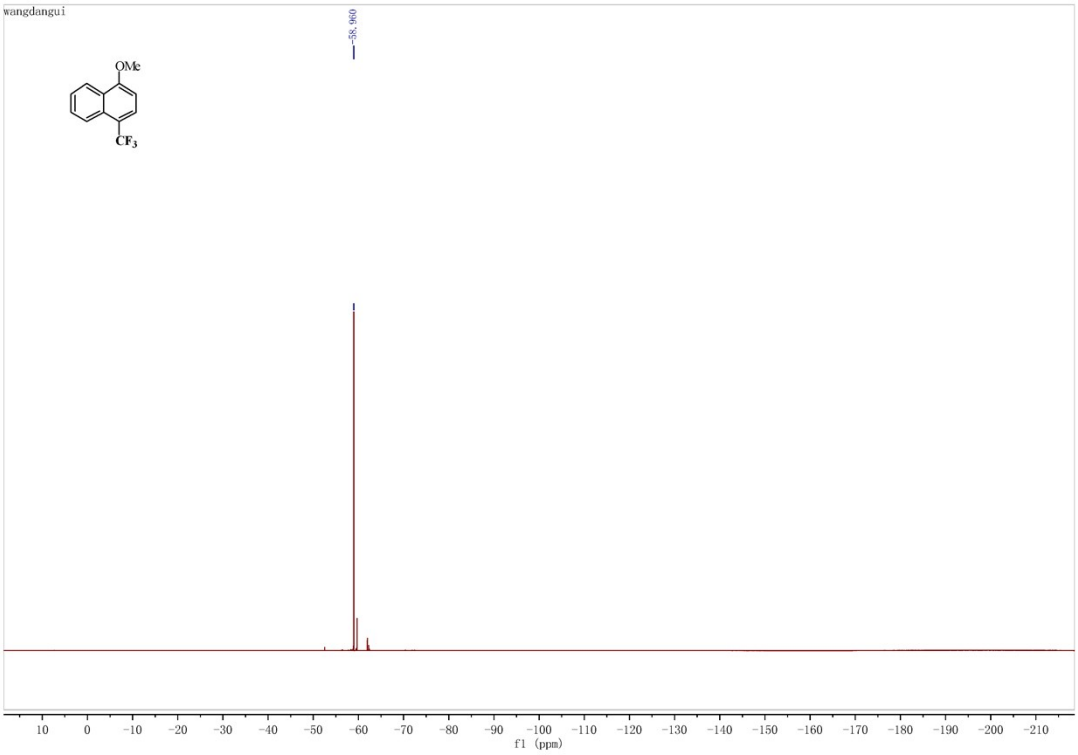
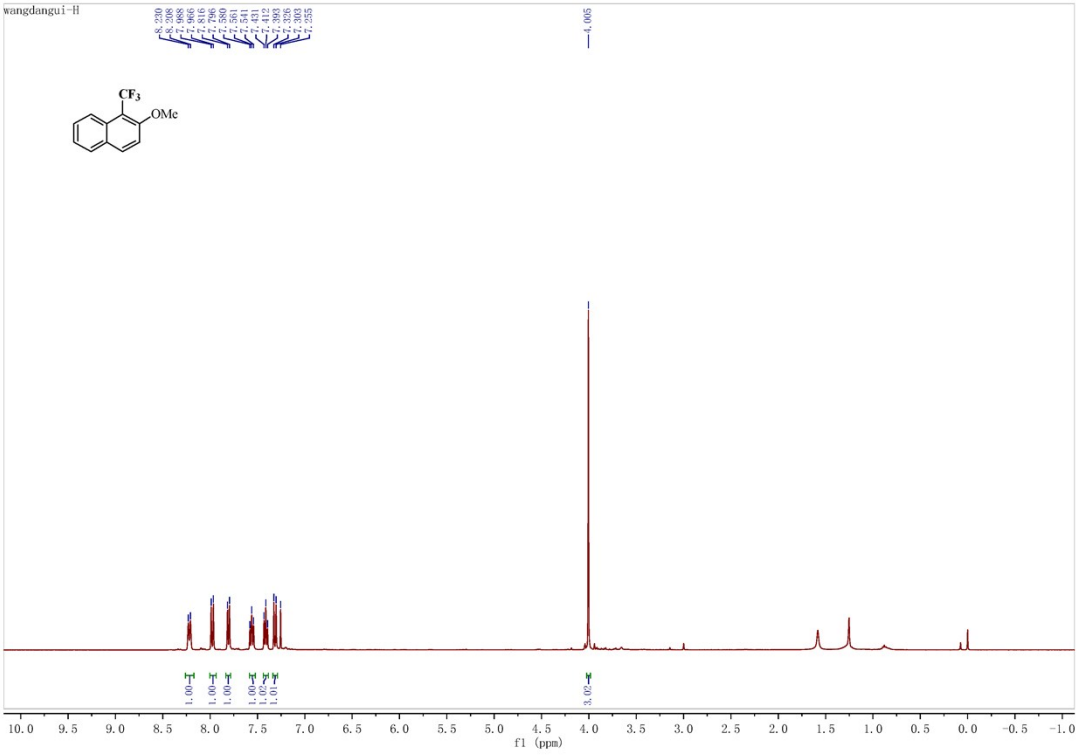
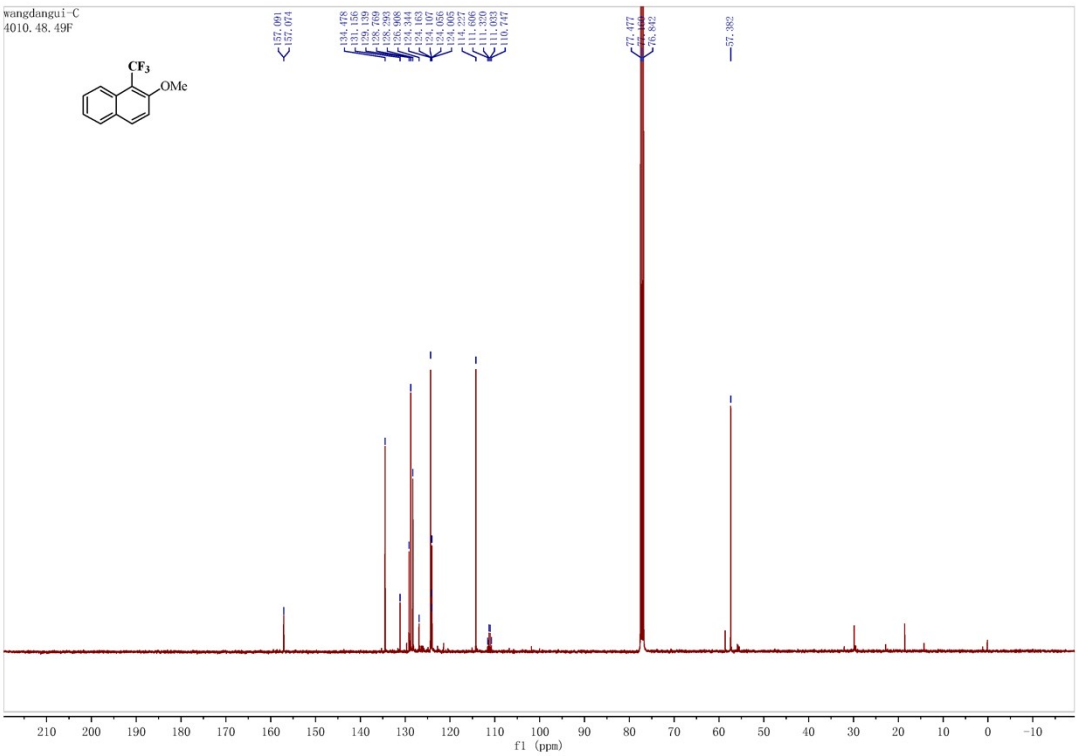
f1 (ppm)

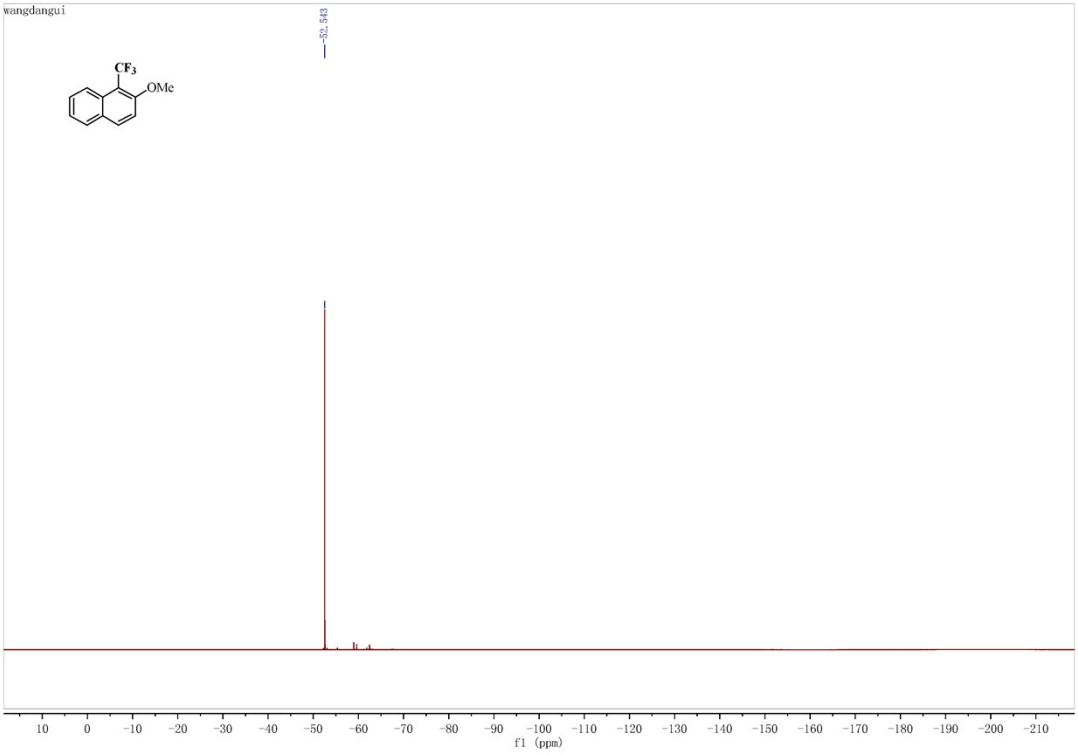

wangdangui-H
8.355
8.334
8.132
8.113
7.794
7.773
7.695
7.674
7.568
7.549
6.782
6.762
4.036
OMe
CF3
1.00
1.00
1.00
1.00
1.00
1.00
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

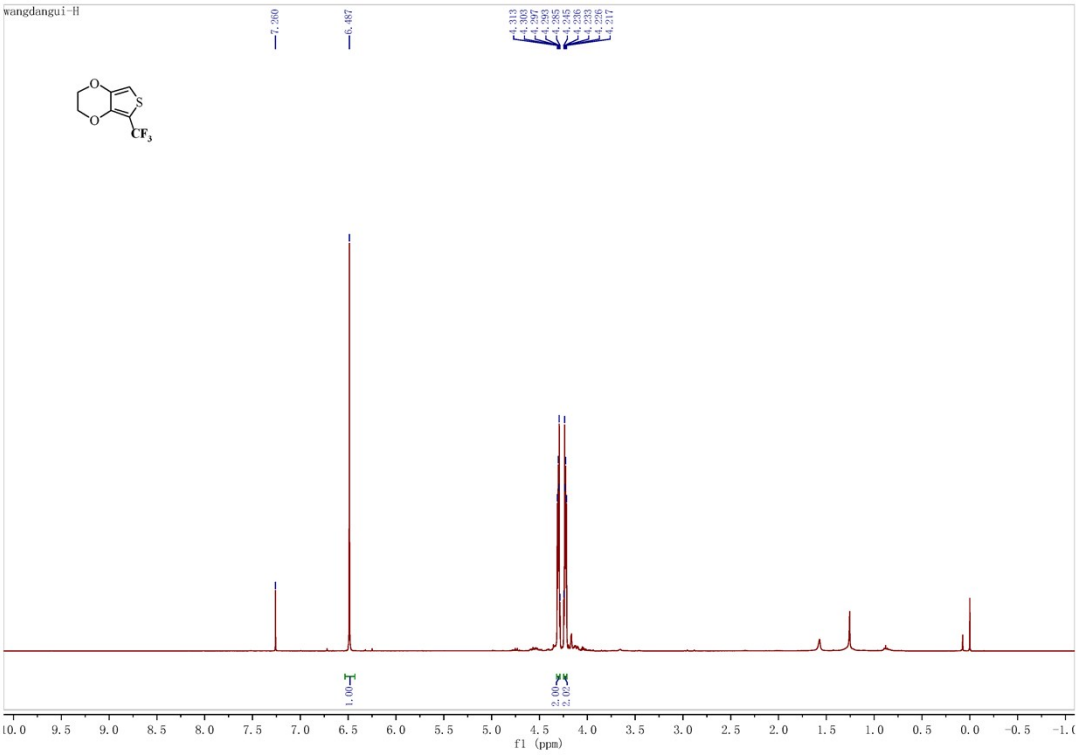

wangdangui
158.583
130.244
128.147
126.174
126.008
125.935
125.874
125.813
125.753
124.165
124.143
124.120
124.096
122.894
118.906
118.604
118.304
118.003
104.630
101.824
77.478
77.160
76.843
55.897
OMe
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

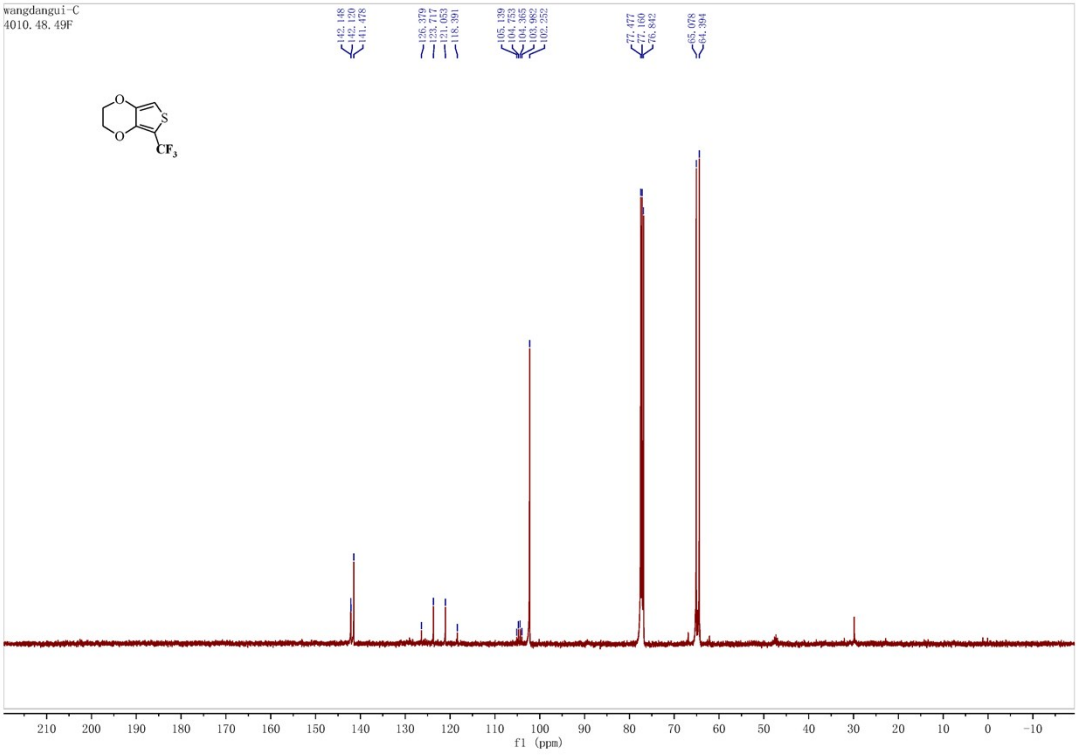

wangdangui
-58.860
OMe
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

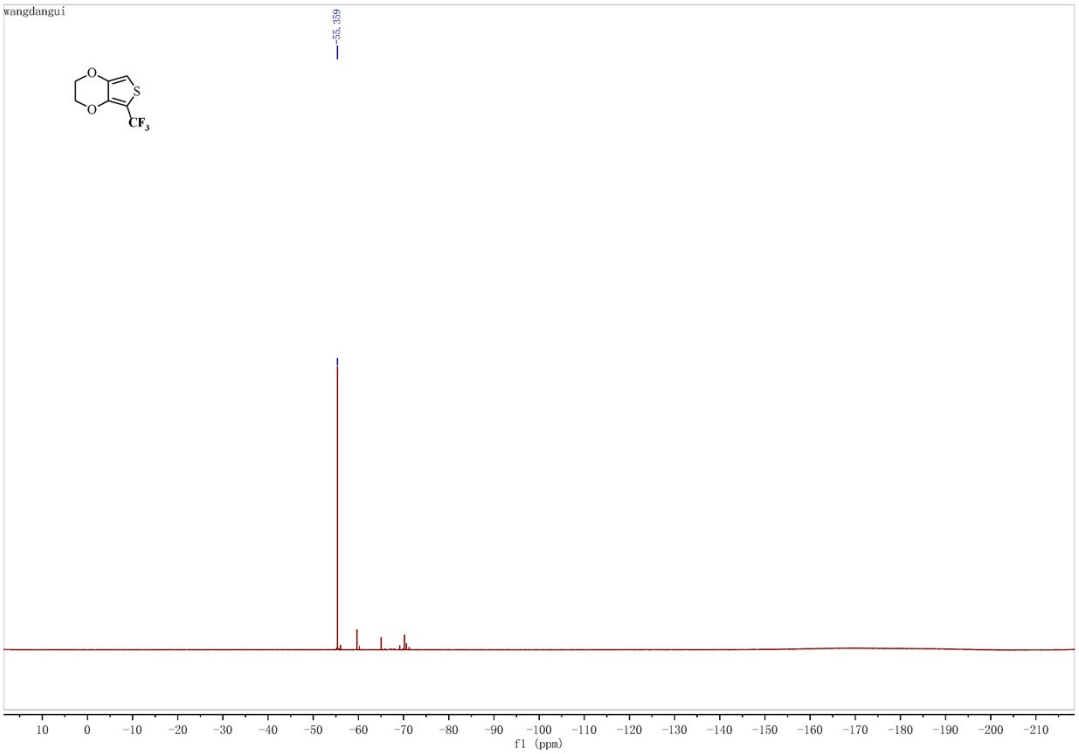

wangdangui-H
8.230
8.208
7.966
7.816
7.796
7.580
7.561
7.541
7.431
7.412
7.398
7.326
7.303
7.255
4.005
CF3
OMe
1.00
1.00
1.00
1.00
1.05
1.01
3.02
f1 (ppm)

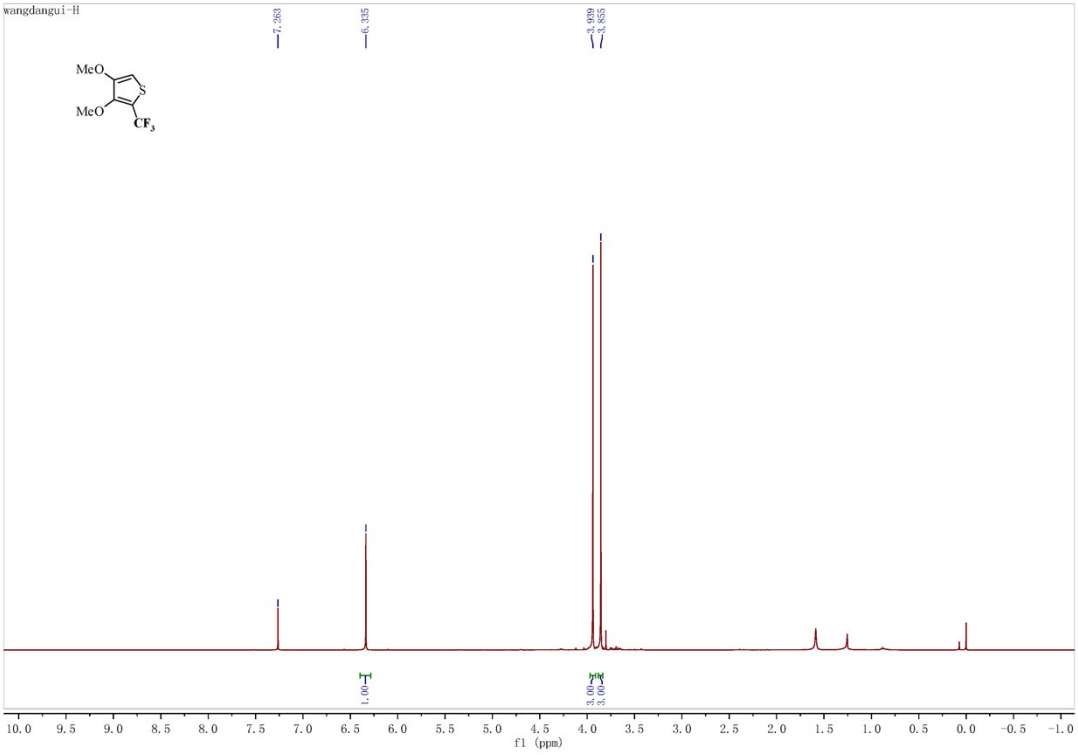

wangdangui-C
4010.48.49F
157.091
157.074
134.478
131.156
129.139
128.789
128.595
126.908
124.344
124.163
124.107
124.056
124.005
114.257
111.566
111.320
111.033
110.747
77.477
77.160
76.842
57.382
CF3
OMe
f1 (ppm)

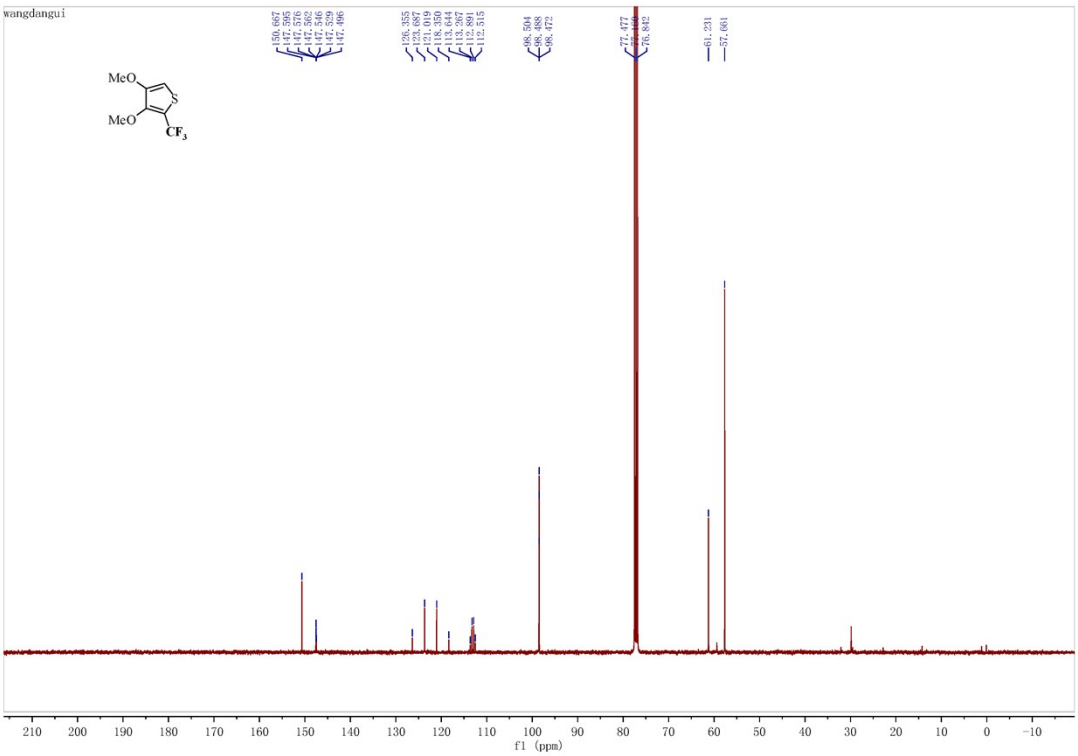

wangdangui
-52.543
CF3
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

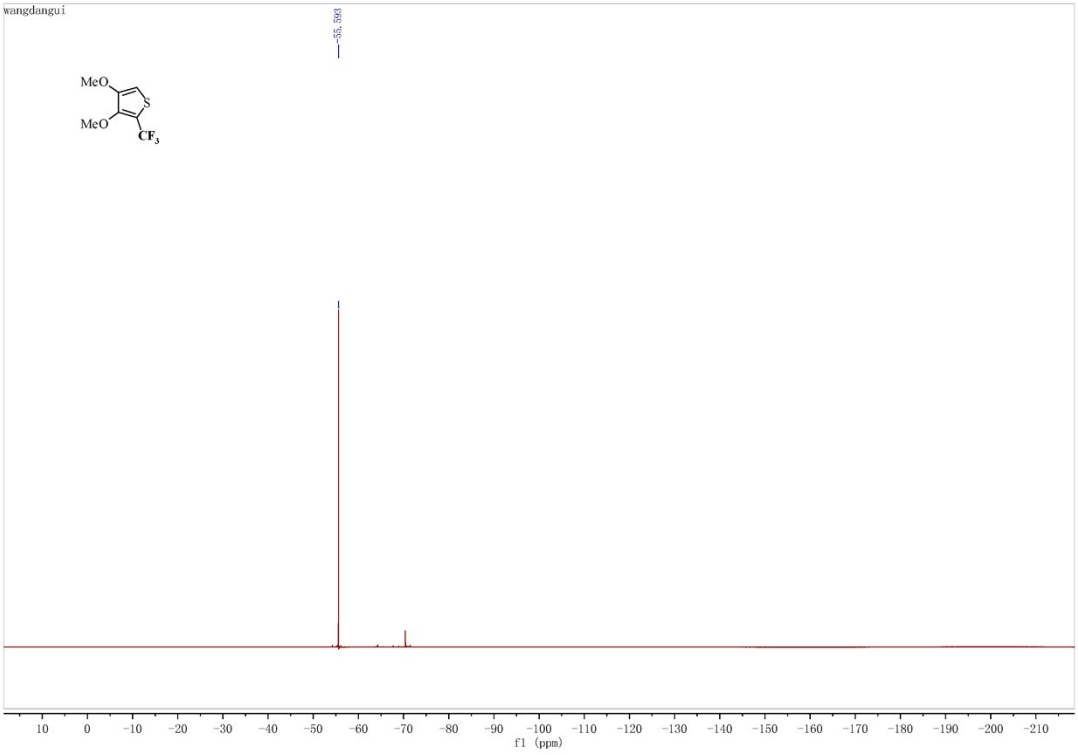

wangdangui-H
7.260
6.487
4.313
4.303
4.297
4.293
4.285
4.245
4.236
4.233
4.226
4.217
O
O
S
CF3
1.00
2.00
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

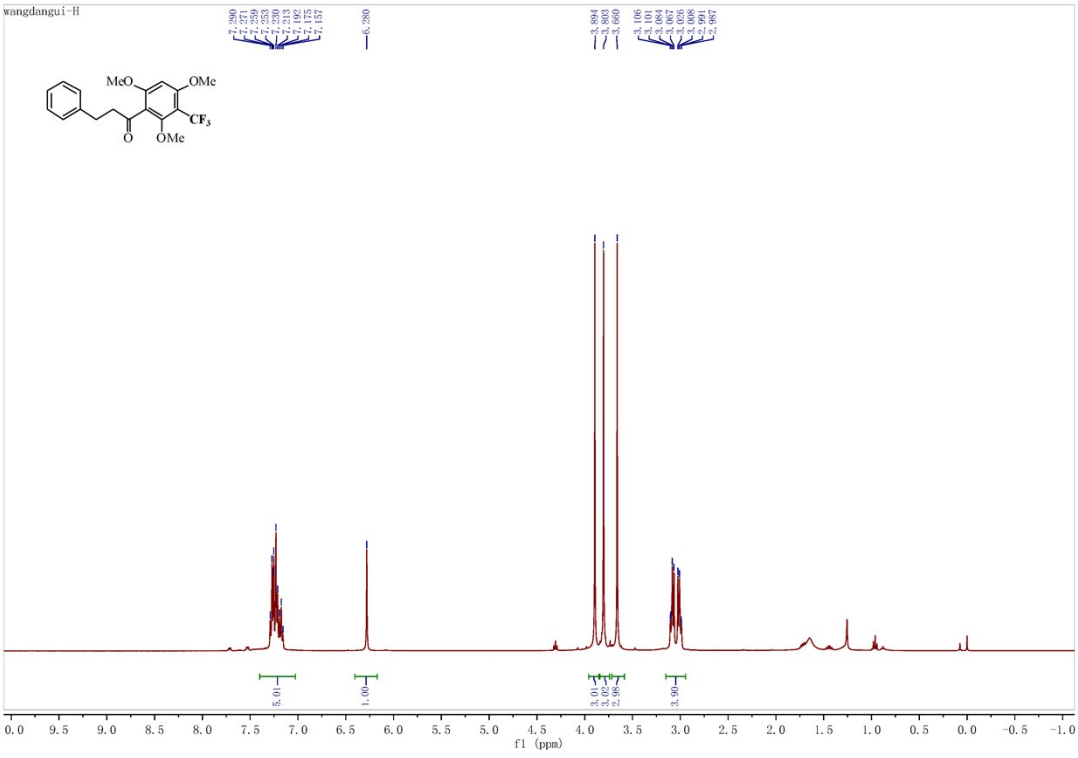

wangdangui-C
4010.48.49F
142.148
142.120
141.478
126.379
123.717
121.053
118.391
105.139
104.753
104.365
103.982
102.232
77.477
77.160
76.842
65.078
64.394
O
O
S
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

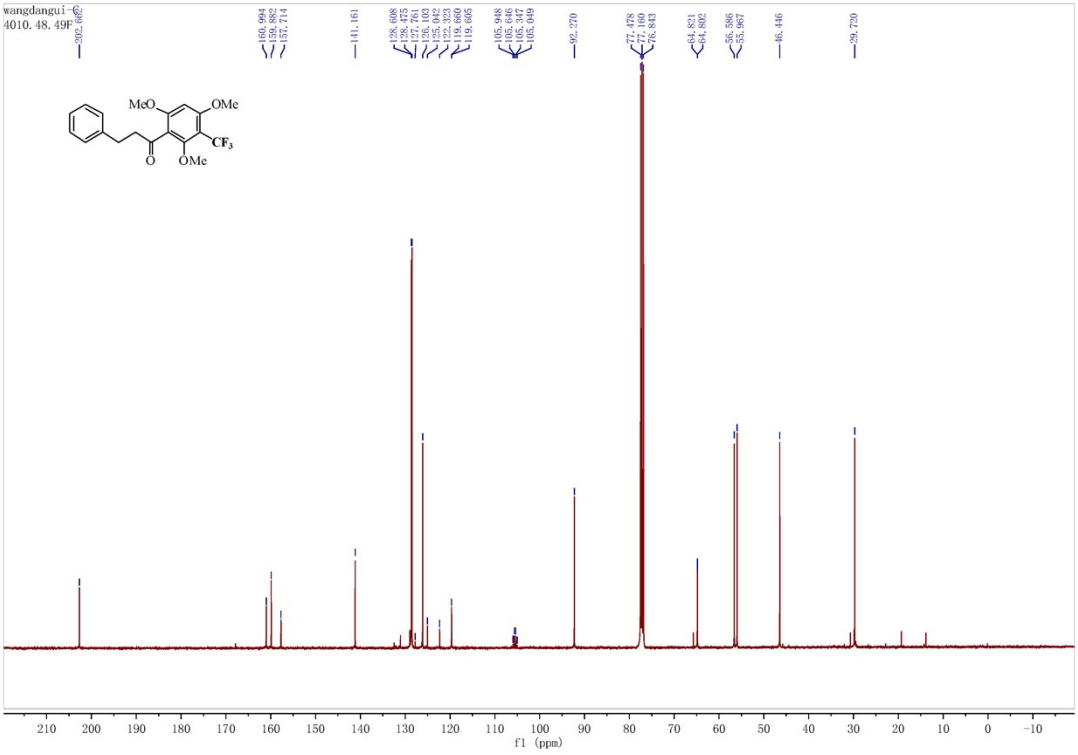

wangdangui
-55.359
O
O
S
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

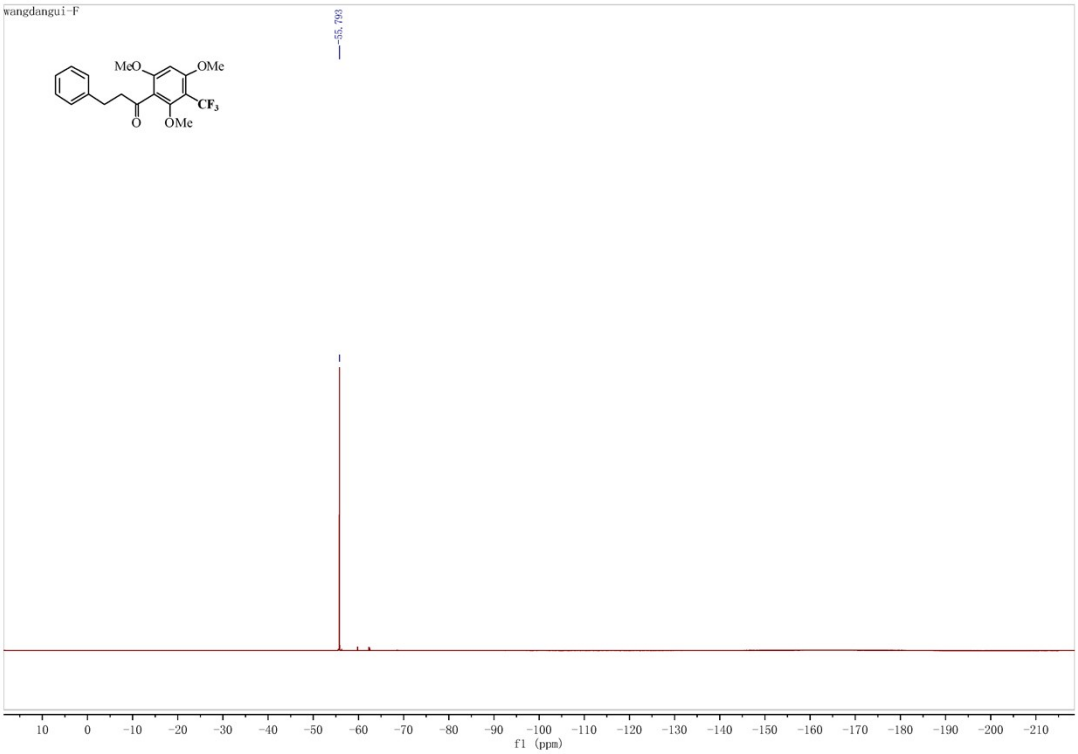

wangdangui-H
7.263
6.335
3.939
3.855
MeO
MeO
S
CF3
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

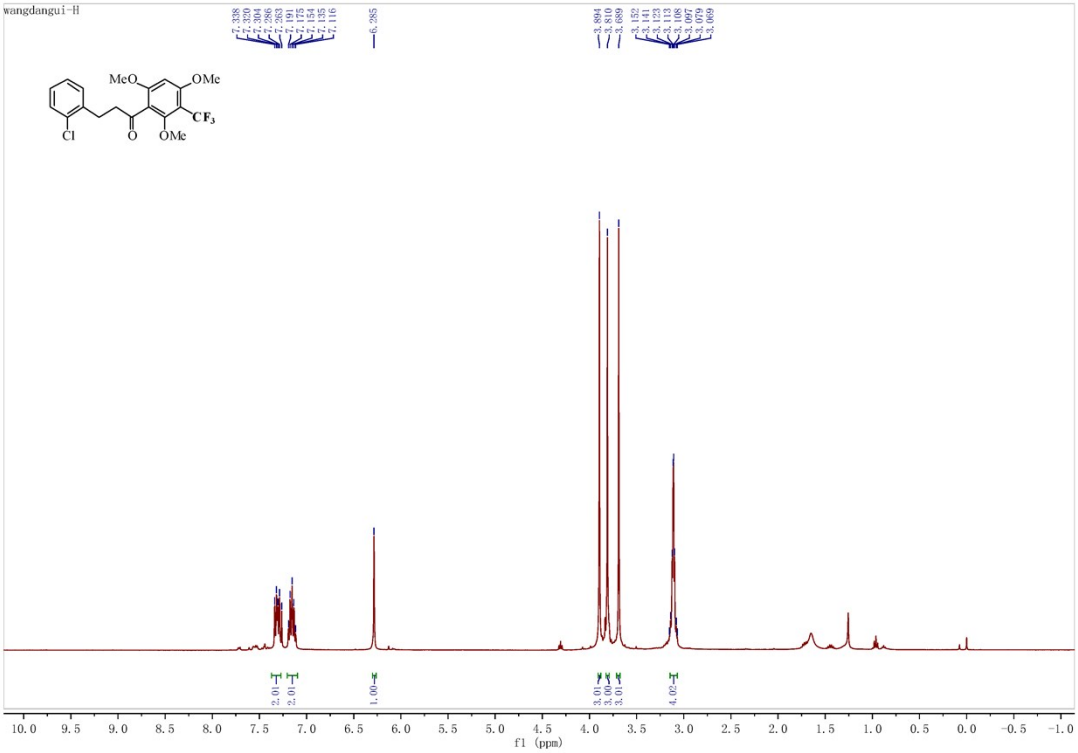

wangdangui
150.667
147.595
147.576
147.562
147.546
147.529
147.496
120.355
118.657
121.019
118.350
113.644
113.357
112.891
112.515
98.504
98.488
98.472
77.477
77.160
76.842
61.231
57.661
MeO
MeO
S
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

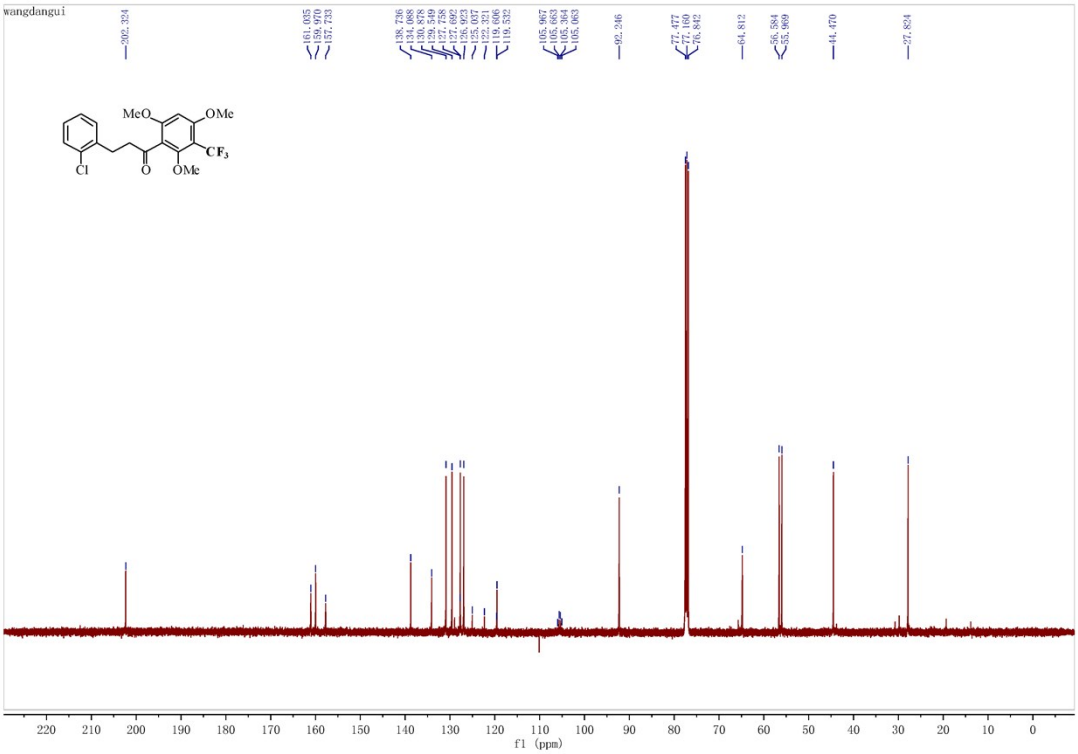

wangdangui
-55.593
MeO
MeO
S
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

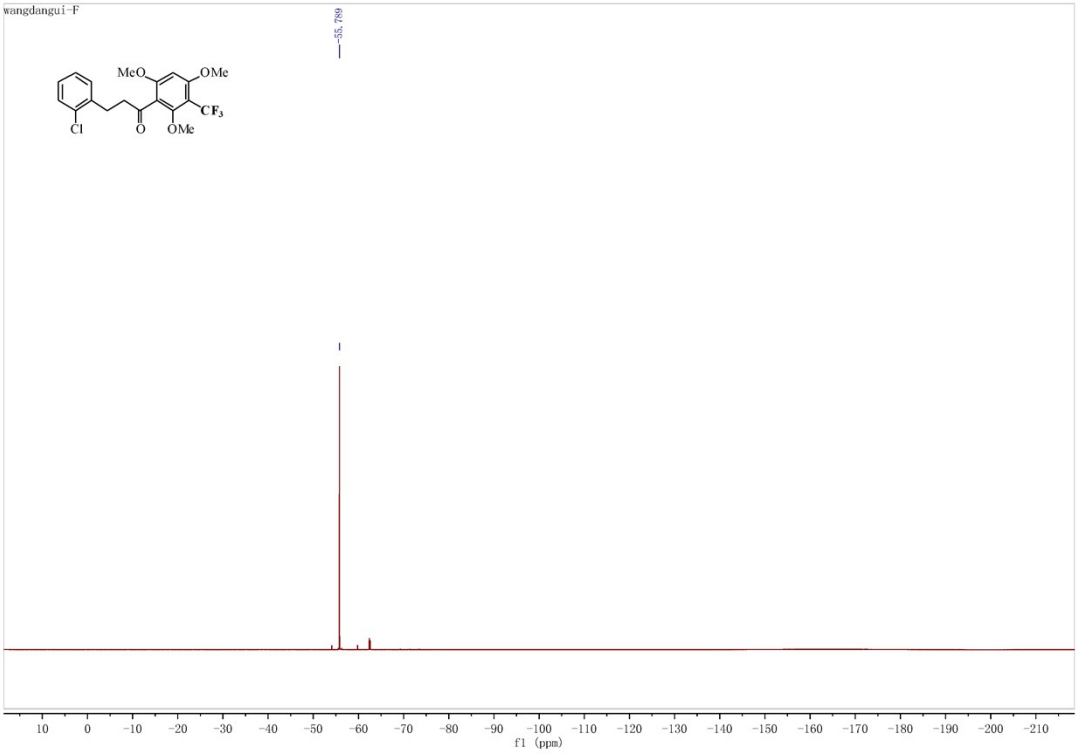

wangdangui-H
7.290
7.271
7.259
7.253
7.238
7.213
7.192
7.175
7.157
6.280
3.894
3.803
3.660
3.106
3.101
3.084
3.057
3.035
3.008
2.991
2.987
MeO
OMe
CF3
O
OMe
5.01
1.00
3.01
3.02
2.98
3.90
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wangdangui-C
4010.48.49F
202.662
160.994
159.882
157.714
141.161
128.608
128.475
127.751
126.103
125.042
122.323
119.660
119.605
105.948
105.646
105.347
105.049
92.270
77.478
77.160
76.843
64.821
64.802
56.586
55.967
46.446
29.720
MeO
OMe
CF3
O
OMe
f1 (ppm)


wangdangui-F
-55.793
MeO
OMe
CF3
O
OMe
f1 (ppm)


wangdangui-H
MeO
OMe
CF3
Cl
O
OMe
f1 (ppm)


wangdangui
MeO
OMe
CF3
Cl
O
OMe
f1 (ppm)


wangdangui-F
-55.789
MeO
OMe
CF3
Cl
O
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)