Manganese-Catalyzed Synthesis of Monofluoroalkenes via C-H Activation and C-F Cleavage

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Supporting Information

Table of Contents

1. General information

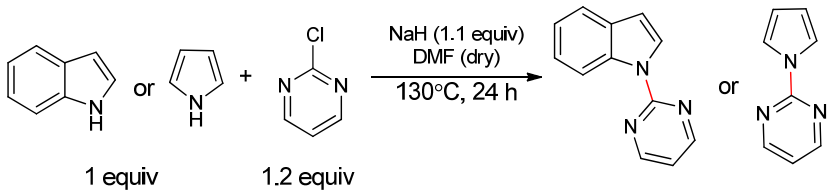
Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. All reactions were carried out under Ar atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on Bruker Advance 400M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.16 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

2. Experimental sections

2.1 Substrate Synthesis

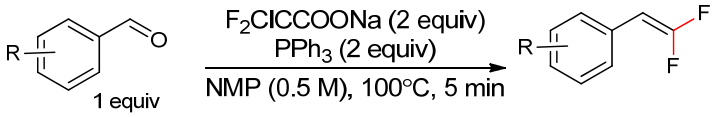
1w was purchased from commercial supplier. Indole derivatives **1p-s**[1a], pyridine derivatives **1u**[3], **1v**[4] were prepared according to the reported methods.

2.1.1 General Method for Synthesis of 1-(Pyrimidin-2-yl)-1*H*-indoles and 1-(Pyrimidin-2-yl)-1*H*-pyrrole



General Method A: Following a previous procedure[1], an oven-dried round-bottom flask was charged with indole (1 equiv, 10 mmol) in DMF (0.5 M), following by portionwise adding of NaH (60% dispersion in mineral oil, 1.1 equiv, 11 mmol) at 0 ºC. After sitrring for 30 min at 0 ºC, 2-chloropyrimidine (1.2 equiv, 12 mmol) was added in. The resulting mixture was stirred at 130 ºC for 24 h. Then the mixture was cooled to room temperature, washed with water and extracted with EtOAc. The layers were separated and the organic layer was dried (Na2SO4), filtered and evaporated. Purification by column chromatography on silica gel or recrystallization using EtOAc/PE as the solvent.

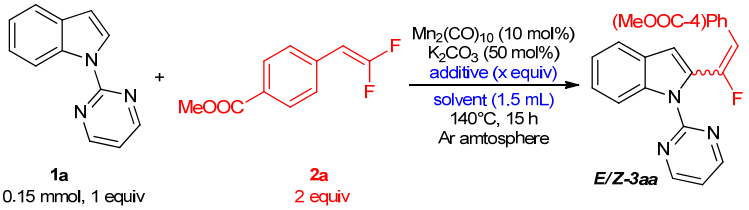
2.1.2 General Method for Synthesis of *gem*-Difluoroalkenes



General Method B: Following a previous procedure[2], to a 100 mL flame-dried round-bottom flask equipped with a stir-bar, (If R = Electron-Donating Group) Sodium 2-chloro-2,2-difluoroacetate (2 equiv, 40 mmol) was added in the mixture of corresponding aldehyde (1 equiv, 20 mmol) and triphenyl phosphine (2 equiv, 40 mmol) in NMP (0.5 M), the reaction was heated at 100 ºC and kepted at this temperature until no further evolution of CO_2 was observed (about 5 min). Then water was added to the reaction slowly and the mixture was extracted with Et_2O or EtOAc, combined the organic layer and 10 mL H_2O_2 (30 wt% in water) was added to washed the organic layer, dried over Na_2SO_4. After evaporating solvent at cooled-water bath or room temperature, the residue was subjected to column chromatography on silica gel to deliver the product. [Note: If R = Electron-Withdrawing Group, $F_2ClCCOONa$ (2 equiv) was portionwise added in the mixture of corresponding aldehyde (1 equiv) and PPh_3 (2 equiv) in NMP (0.5 M) which have heated at 100 ºC.]

2.2 Condition Optimization

2.2.1 Optimization of solvent and additive



1a
0.15 mmol, 1 equiv

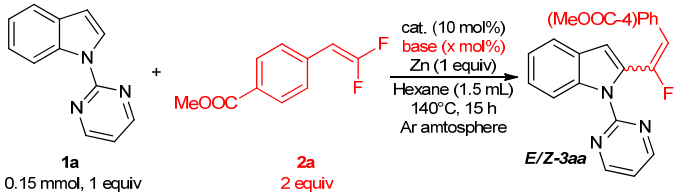
2a
2 equiv

E/Z-3aa

entry	additive	solvent	yield[a](*E*/*Z*)[b]	entry	additive	solvent	yield[a](*E*/*Z*)[b]
1	-	Hexane	67% (73/27)	19	MgO (1.0 equiv)	Hexane	60%(72/28)
2	-	i-Pr_2O	54% (72/28)	**20**	**KPF_6 (0.5 equiv)**	**Hexane**	**83% (73/27)**
3	-	n-Pr_2O	29% (71/29)	21	Zn (1.0 equiv)	Hexane/H_2O (2/1)	trace
4	-	Hexane/i-Pr_2O (2/1)	57% (73/27)	22	Zn (1.0 equiv)	Hexane (0.5 mL)	13%(61/39)
5	-	Hexane/n-Pr_2O (2/1)	52% (73/27)	22	Zn (1.0 equiv)	Hexane (3.0 mL)	53%(75/25)
6	Zn (0.5 equiv)	Hexane	59%(72/28)	23	Zn (1.0 equiv)	Cyclohexane	45% (70/30)
7	**Zn (1.0 equiv)**	**Hexane**	**73% (73/27)**	24	Zn (1.0 equiv)	Pentane	50% (72/28)
8	Zn (1.5 equiv)	Hexane	45%(72/28)	25	Zn (1.0 equiv)	Heptane	32% (70/30)
9	CuOAc (10 mol%)	Hexane	37% (72/28)	26	Zn (1.0 equiv)	HFIP	ndp
10	$Cu(OAc)_2$ (10 mol%)	Hexane	42% (71/29)	27	Zn (1.0 equiv)	MeOH	ndp
11	18-Crown-6 (1.0 equiv)	Hexane	ndp	28	Zn (1.0 equiv)	i-Pr_2O	40% (70/30)
12	Mn (1.0 equiv)	Hexane	42%(73/27)	29	Zn (1.0 equiv)	$MeNO_2$	ndp
13	Fe (1.0 equiv)	Hexane	40%(68/32)	30(c)	KPF_6 (50 mol%)	Hexane	60% (73/27)
14	$ZnBr_2$ (1.0 equiv)	Hexane	22%(35/65)	31(c)	KPF_6 (25 mol%)	Hexane	60% (73/27)
15	Ac-Phe-OH (1.0 equiv)	Hexane	trace	32	KPF_6 (1.2 equiv)	Hexane	71% (74/26)
16	AgOAc (1.0 equiv)	Hexane	trace	33(c)	$AgPF_6$ (25 mol%)	Hexane	33% (73/27)
17	Ag_2CO_3 (0.5 equiv)	Hexane	72%(72/28)	34(d)	KPF_6 (50 mol%)	Hexane	trace
18	Ag_2O (0.5 equiv)	Hexane	66%(73/27)	35(e)	KPF_6 (50 mol%)	Hexane	38% (76/24)

[a]Isolated yield. [b]Determined by ^{1}H NMR after flash column chromatography. [c]K_2CO_3 (25 mol%). [d]Air condition. [e]Run in 120°C.

2.2.2 Optimization of base and catalyst



1a
0.15 mmol, 1 equiv

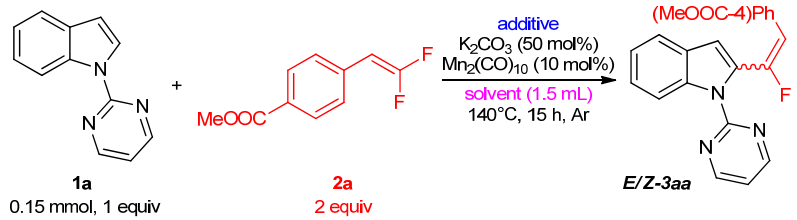
2a
2 equiv

E/Z-3aa

entry	cat.	base	yield[a](*E*/*Z*)[b]	entry	cat.	base	yield[a](*E*/*Z*)[b]
1(c)	-	K_2CO_3 (50 mol%)	nr	10	$Mn_2(CO)_{10}$ (10 mol%)	K_3PO_4 (50mol%)	57% (74/26)
2(d)	$Mn_2(CO)_{10}$ (10 mol%)	-	49% (72/28)	11	$Mn_2(CO)_{10}$ (10 mol%)	$K_3PO_3{\cdot}3H_2O$ (50mol%)	60% (74/26)
3	$Mn_2(CO)_{10}$ (5 mol%)	K_2CO_3 (50 mol%)	49% (74/26)	12	$Mn_2(CO)_{10}$ (10 mol%)	Et_2NH (50 mol%)	26% (66/34)
4	$Mn_2(CO)_{10}$ (15 mol%)	K_2CO_3 (50 mol%)	84% (73/27)	13(e)	$MnBr(CO)_5$ (20 mol%)	K_2CO_3 (50 mol%)	48% (73/27)
5	$Mn_2(CO)_{10}$ (10 mol%)	K_2CO_3 (25 mol%)	78% (73/27)	14	$MnBr(CO)_5$ (20 mol%)	K_2CO_3 (50 mol%)	60% (73/27)
6	$Mn_2(CO)_{10}$ (10 mol%)	K_2CO_3 (200 mol%)	64% (73/27)	15	$MnBr(CO)_5$ (10 mol%)	K_2CO_3 (50 mol%)	40% (74/26)
7	$Mn_2(CO)_{10}$ (10 mol%)	$KHCO_3$ (50 mol%)	68% (73/27)	16(e,f)	$MnBr(CO)_5$ (20 mol%)	K_2CO_3 (50 mol%)	56% (61/39)
8	$Mn_2(CO)_{10}$ (10 mol%)	Na_2CO_3 (50 mol%)	42% (72/28)	17(e,g)	$Re_2(CO)_{10}$ (10 mol%)	K_2CO_3 (50 mol%)	trace
9	$Mn_2(CO)_{10}$ (10 mol%)	NaOAc (50 mol%)	24% (69/31)				

[a]Isolated yield. [b]Determined by ^{1}H NMR after flash column chromatography. [c]No catalyst. [d]No base. [e]No additive (Zn). [f]1.5 equiv Me_2Zn as additive. [g]50 mol% KPF_6 as additive.

2.2.3 Optimization of additive to investigate the role of KPF_6

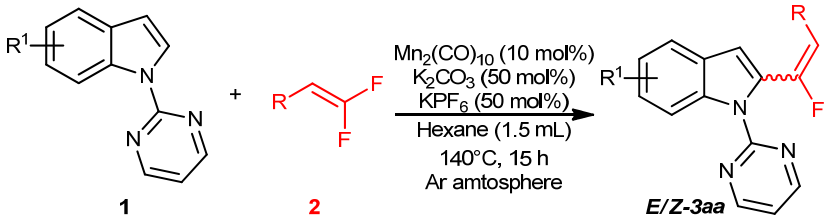


1a 0.15 mmol, 1 equiv + **2a** 2 equiv → ***E/Z-3aa***

entry	additive	solvent	yield[a](*E/Z*)[b]	entry	additive	solvent	yield[a](*E/Z*)[b]
1	KPF_6 (50 mol%)	hexane	83%(73/27)	7	$KHCO_3$ (50 mol%)	hexane	70%(72/28)
2	KPF_6 (50 mol%)	1,4-dioxane	no reaction	8	$LiPF_6$ (50 mol%)	hexane	trace
3	NaOAc (20 mol%)	1,4-dioxane	no reaction	9	$NaPF_6$ (50 mol%)	hexane	46%(76/24)
4	—	hexane	67%(73/27)	10	n-Bu_4PF_6 (50 mol%)	hexane	trace
5(c)	—	hexane	36%(71/29)	11	KBF_4 (50 mol%)	hexane	54%(75/25)
6	KCl (50 mol%)	hexane	68%(72/28)	12	K(OTf) (50 mol%)	hexane	53%(72/28)

[a]Isolated yield. [b]Determined by ^1H NMR after flash column chromatography. [c]no base. (Note: We obtained **3aa** in 20% isolated yield (*E/Z* 8/92) in Ackermann`s reaction conditions (*ACS Catal.*, 2017, **7**, 4209-4213.), but 5 mol% $Mn_2(CO)_{10}$ instead of 10 mol% $MnBr(CO)_5$.)

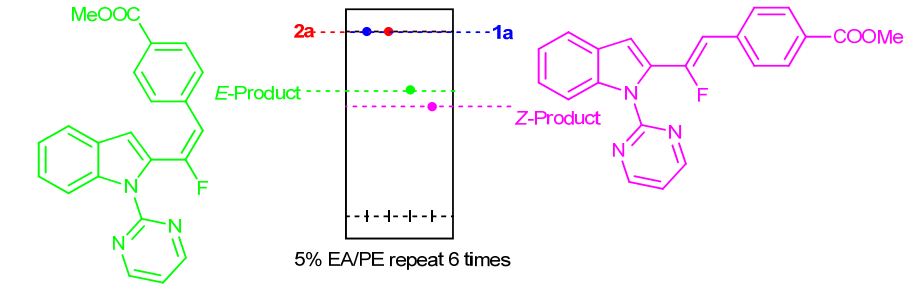
3. General Method for the C-H *α*-fluoroalkenylation of arenes



1 0.15 mmol, 1 equiv + **2** 2 equiv → ***E/Z-3aa***

General Method C: An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1** (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 15 h. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3** (E/Z mixture).

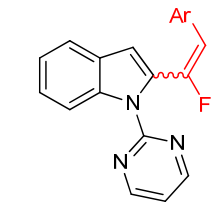
3.1 TLC of Model Reaction as follow:



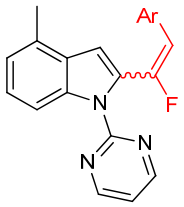
δ_F = -88.20 (dd, *J* = 17.8, 3.5 Hz) **E/Z > 50:50** δ_F = -96.67 (dd, *J* = 35.5, 2.5 Hz)

3.2 Substrate Scope

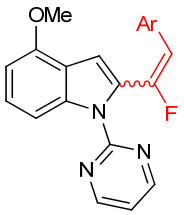
3.2.1 Scope of indole derivatives in the *C–H/C–F* activation reaction



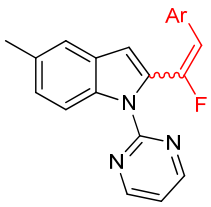
3aa 83%, (*E*/*Z* 73/27)



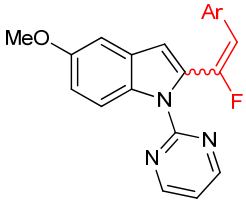
3ba 75% (*E*/*Z* 72/28)



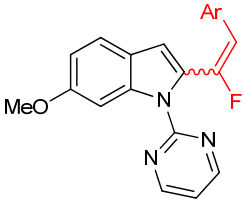
3ca 92% (*E*/*Z* 70/30)



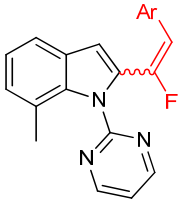
3da 82% (*E*/*Z* 74/26)



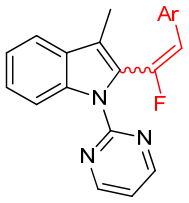
3ea 61% (*E*/*Z* 73/27)



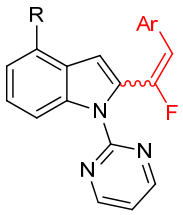
3fa 80% (*E*/*Z* 69/31)



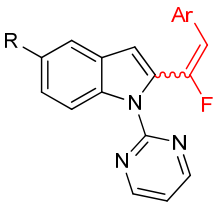
3ga 70% (*E*/*Z* 72/28)



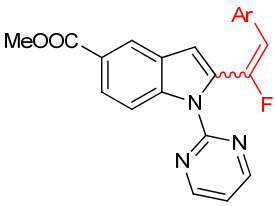
3ha 59% (*E*/*Z* 66/34)



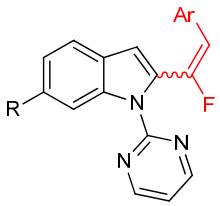
R = Cl, **3ia** 60% (*E*/*Z* 70/30)
R = COOMe, **3ja** 55% (*E*/*Z* 68/32)



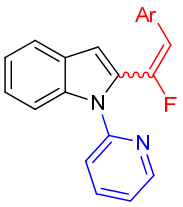
R= F, **3ka** 60% (*E*/*Z* 72/28)
R = Br, **3la** 62% (*E*/*Z* 70/30)



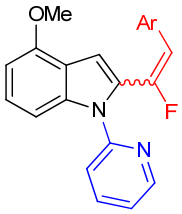
3ma 60% (*E*/*Z* 67/33)



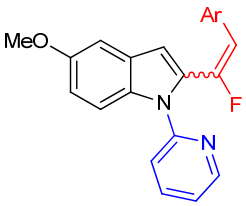
R = F, **3na** 65% (*E*/*Z* 69/31)
R = Br, **3oa** 71% (*E*/*Z* 69/31)



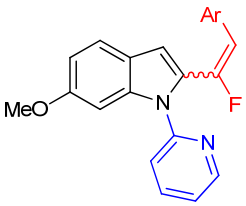
3pa 62%, (*E*/*Z* 61/39)



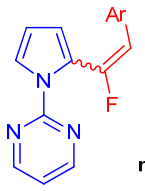
3qa 60%, (*E*/*Z* 68/32)



3ra 63%, (*E*/*Z* 68/32)



3sa 69%, (*E*/*Z* 68/32)



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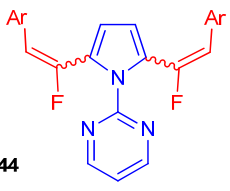
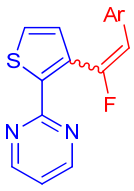


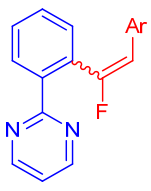
mon:di = 56/44

3ta 39% (*E*/*Z* 75/25)

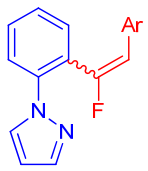
3ta` 31% (ration 7:18:20:55)[c]



3ua 34% (*E*/*Z* 71/29)



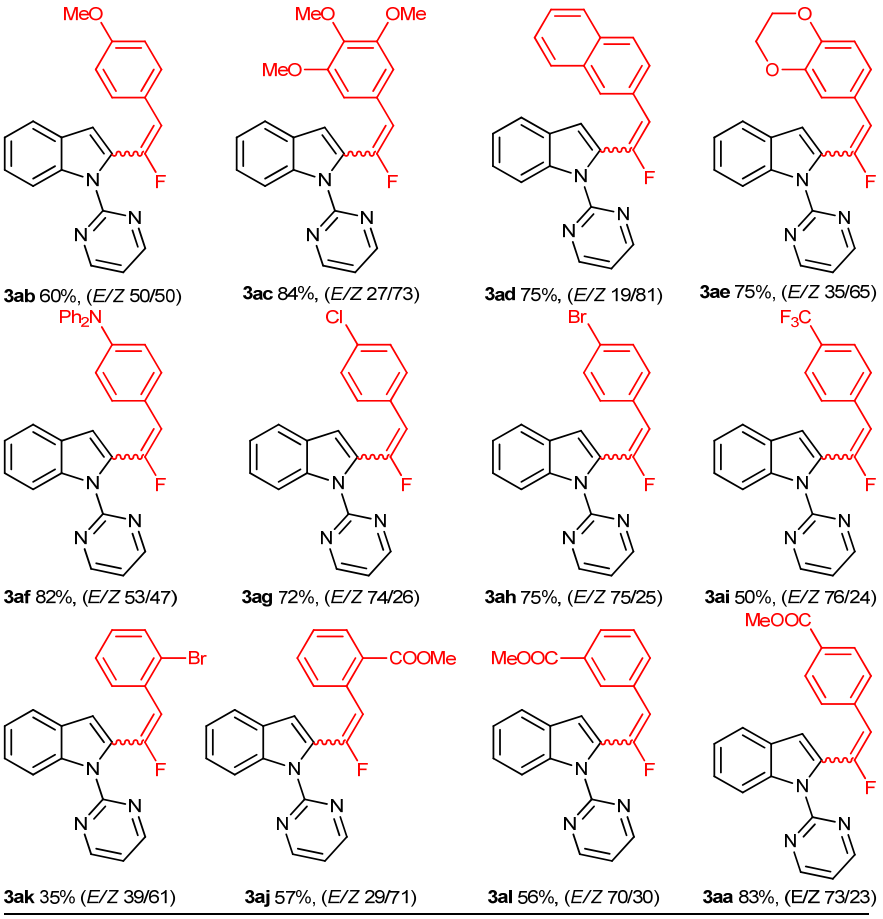
3va 23% (*E*/*Z* 65/35)



3wa 38% (*E*/*Z* 40/60)

[a] Isolated yield. [b] Determined by ^{1}H NMR after flash column chromatography. [c] Isomer ration determined by ^{19}F NMR after flash column chromatography. Ar = (*p*-COOMe)Ph.

3.2.2 Scope of *gem*-difluoroalkene for the *C–H/C–F* activation reaction



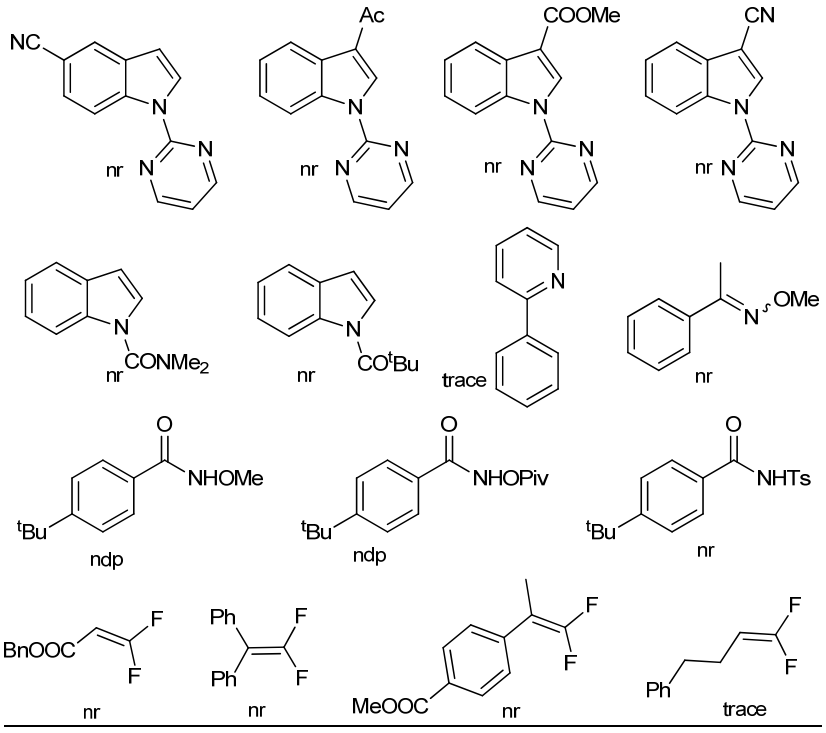
3ab 60%, (*E*/*Z* 50/50) **3ac** 84%, (*E*/*Z* 27/73) **3ad** 75%, (*E*/*Z* 19/81) **3ae** 75%, (*E*/*Z* 35/65)

3af 82%, (*E*/*Z* 53/47) **3ag** 72%, (*E*/*Z* 74/26) **3ah** 75%, (*E*/*Z* 75/25) **3ai** 50%, (*E*/*Z* 76/24)

3ak 35% (*E*/*Z* 39/61) **3aj** 57%, (*E*/*Z* 29/71) **3al** 56%, (*E*/*Z* 70/30) **3aa** 83%, (E/Z 73/23)

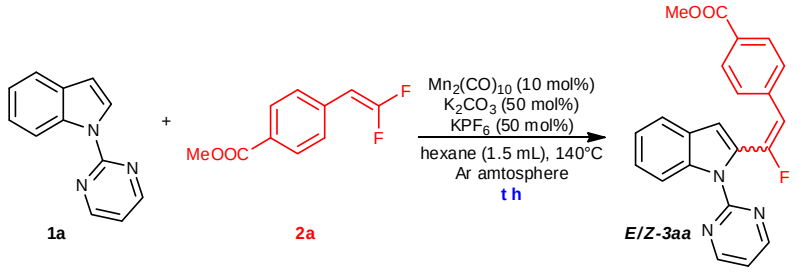
[a] Isolated yield. [b] Determined by ^{1}H NMR after flash column chromatography.

3.2.3 Incompetent substrate



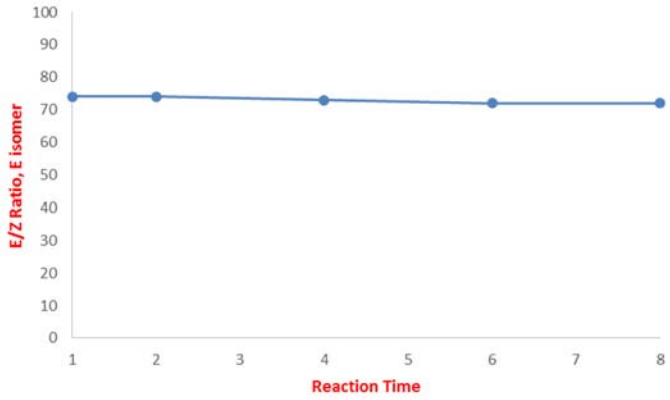
4. Mechanism Study

4.1 The Ration of *E/Z* Isomer Variation with Time

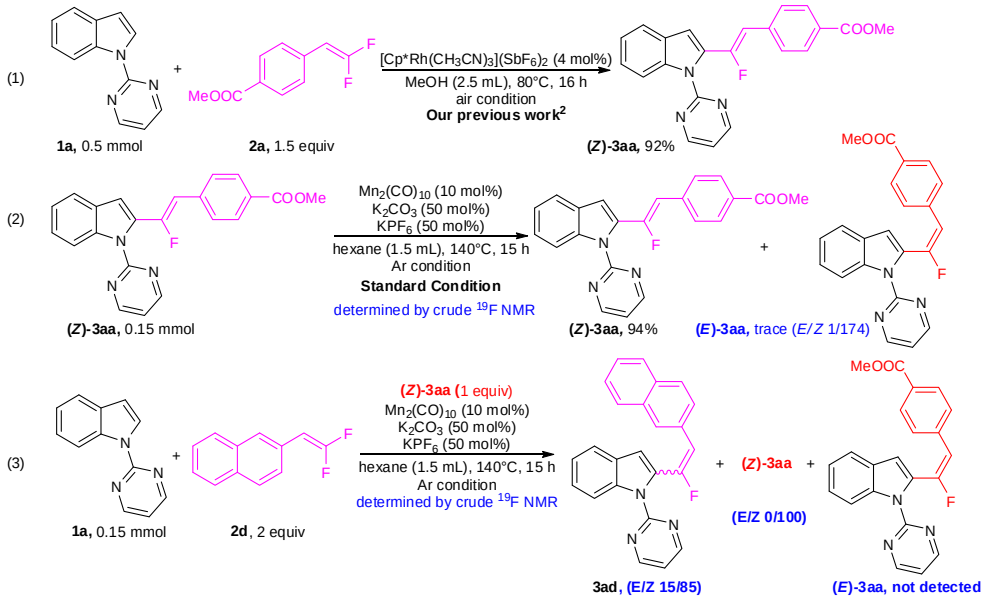


Five parallel reactions of **1a** with **2a** were performed to monitor the ration of E/Z isomer variation with time.

An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a** (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2a** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for especial time (1 h, 2 h, 4 h, 6 h, 8 h). After cooling to room temperature, the mixture was then filtered over silica gel. The filtrate was concentrated under reduced pressure to afford the crude products, the ration of **E/Z isomer** was determined by crude ^{1}H NMR.



4.2 Z isomer encounter standard condition



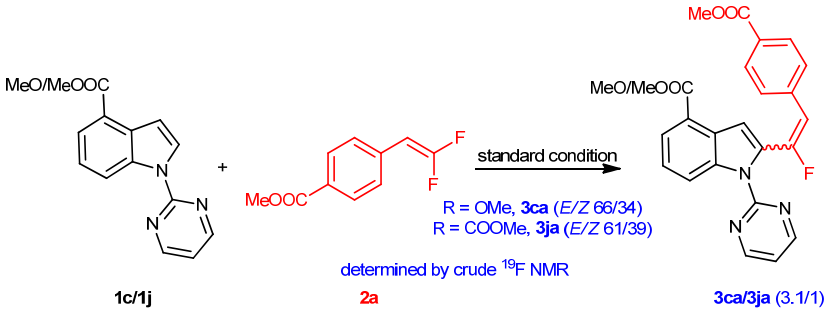
(1) Following our previous procedure[2], an oven-dried 10 ml Schlenk tube was charged with **1a** (0.5 mmol), $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (4% mmol), **2a** (1.5 equiv) in sequence, followed by adding anhydrous MeOH (2.5 ml) through syringe and stirring at 80 °C for 16 h, then removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **Z-3aa** (white solid, 171.8mg, 92%).

(2) An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **Z-3aa** (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 °C for 15 h. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the product and determined by NMR (^{1}H NMR, ^{19}F NMR) found trace **E-3aa** (E/Z 1/174).

(3) An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a** (0.15 mmol, 1 equiv), **2d** (0.3 mmol, 2 equiv), **Z-3aa** (0.15 mmol), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 15 h. After cooling to room temperature, the mixture was then filtered over silica gel. The filtrate was concentrated under reduced pressure to afford the crude products, then determined by NMR (^{1}H NMR, ^{19}F NMR) found **3ad** (E/Z 15/85), **Z-3aa** (E/Z 0/100), **E-3aa** not detected.

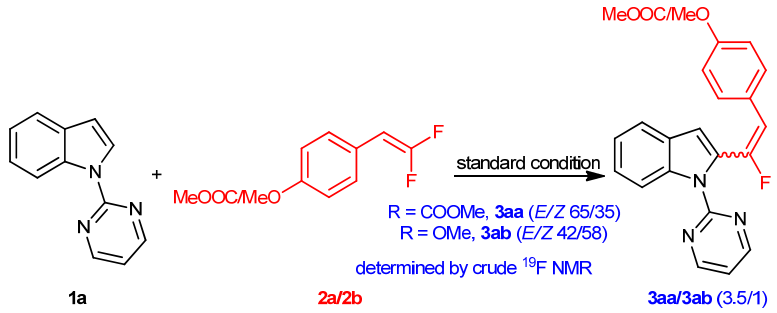
4.3 Intermolecular Competition Experiments

4.3.1 Between Indole Derivatives 1c and 1j



An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1c** (0.15 mmol, 1 equiv), and **1j** (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2a** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 15 h. After cooling to room temperature, the mixture was then filtered over silica gel. The filtrate was concentrated under reduced pressure to afford the crude products, the ration of **3ca**/**3ja** was determined by ^{19}F NMR.

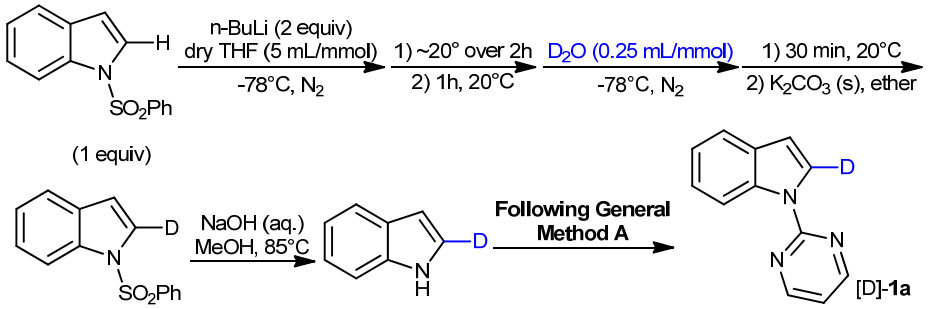
4.3.2 Between *gem*-difluoroalkene 2a and 2b



An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a** (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2a** (0.3 mmol, 2 equiv), **2b** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 °C for 15 h. After cooling to room temperature, the mixture was then filtered over silica gel. The filtrate was concentrated under reduced pressure to afford the crude products, the ration of **3aa/3ab** was determined by ^{19}F NMR.

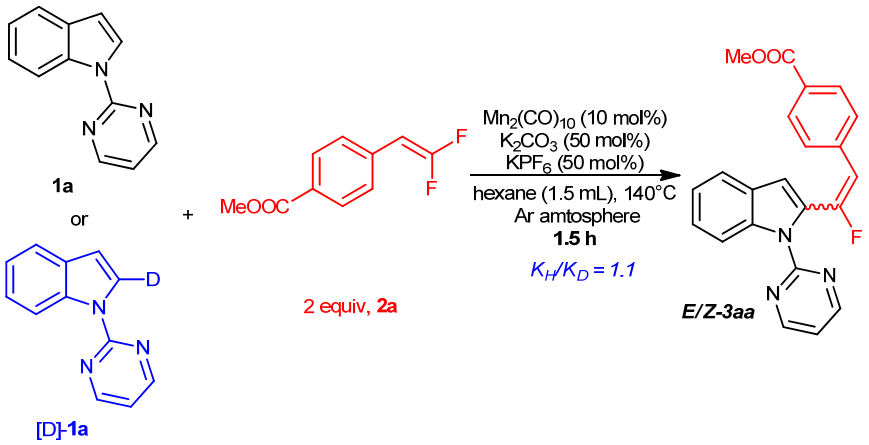
4.4 Kinetic Isotope Effect

4.4.1[5] Preparation of [D]-1a



([D]-1a, 95%D) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (dt, *J* = 8.3, 0.9 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.31 (d, *J* = 3.7 Hz, 0.05H, 0.95D), 7.66 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.38 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.07 (t, *J* = 4.8 Hz, 1H), 6.73 (s, 1H).

4.4.2 Intermolecular KIE by Independent Experiments

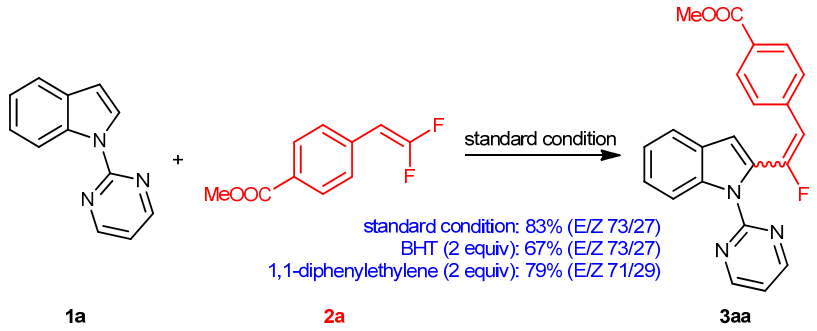


Two parallel reactions of **2a** with **1a** and **[D]-1a** respectively were performed to determine the corresponding KIE value.

An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a** (0.15 mmol, 1 equiv), or

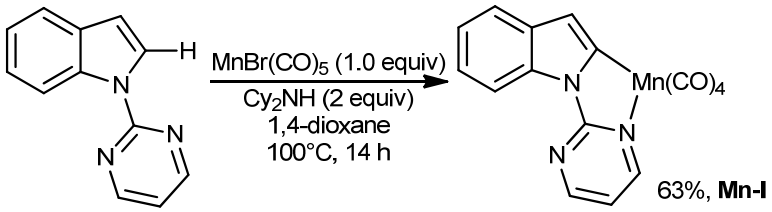
[D]-1a (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2a** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 1.5 h. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3aa** (E/Z mixture).(Note: **1a** as substrate the isolated yield of **3aa** is 27.3 mg; [D]-**1a** as substrate the isolated yield of **3aa** is 25.5 mg)

4.5 Free Radical Scavengers



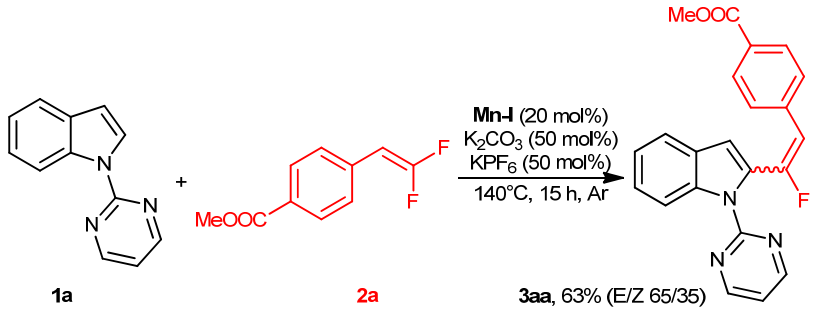
4.6 C-H *α*-fluoroalkenylation of arenes with Cyclometalated Complex Mn-I

4.6.1 Synthesis of Cyclometalated Complex Mn-I[6]



An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **1a** (1 mmol, 1 equiv), $MnBr(CO)_5$ (1 mmol, 1 equiv) in sequence. After refilling with Ar repeated three times, dicyclohexylamine (2 mmol, 2 equiv) and 1,4-dioxane (2.0 mL) was added through syringe in sequence. The mixture was heated in 100 ºC for 14 h. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography (TLC: 15% EtOAc/PE; column: 5%-20% DCM/PE) afforded the desired product **Mn-I** (yellow solid, 227.6 mg, 63%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.72 (s, 1H), 8.64 – 8.45 (m, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 27.8 Hz, 2H), 6.84 (d, *J* = 34.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 218.5, 213.2, 210.8, 162.4, 161.5, 161.0, 160.3, 138.6, 136.2, 123.1, 120.9, 119.5, 117.7, 114.2, 113.8. **HRMS (ESI, m/z):** calcd. for $C_{16}H_8MnN_3O_4H$ $[M+H]^+$ 361.9974, found 361.9981.

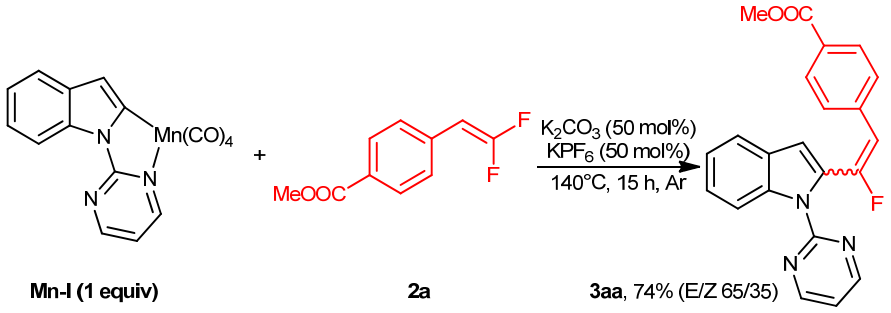
4.6.2 Cyclometalated Complex Mn-I as Catalyst



An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a** (0.15 mmol, 1 equiv), **Mn-I** (0.03 mmol, 20 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2a** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe

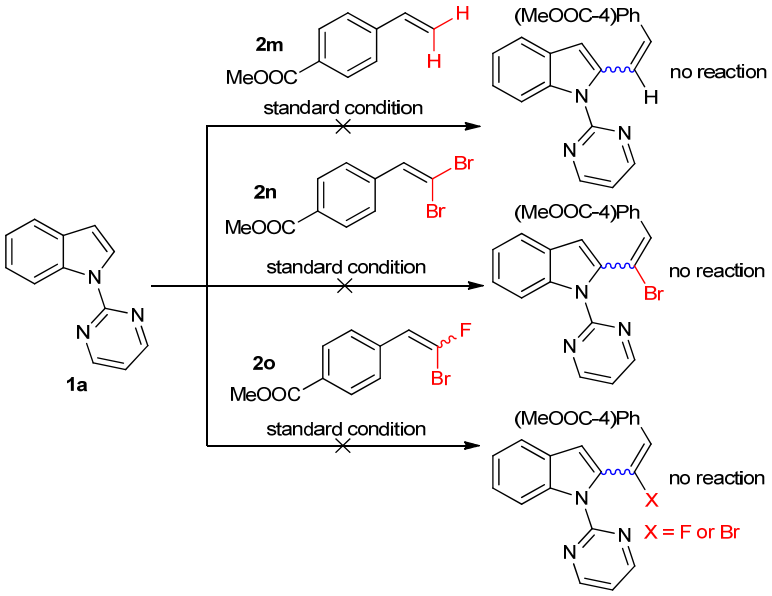
in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 15 h. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3aa** (yellow oil, 35.3 mg, 63%, E/Z 65/35).

4.6.3 Stoichiometric Reaction with Cyclometalated Complex Mn-I



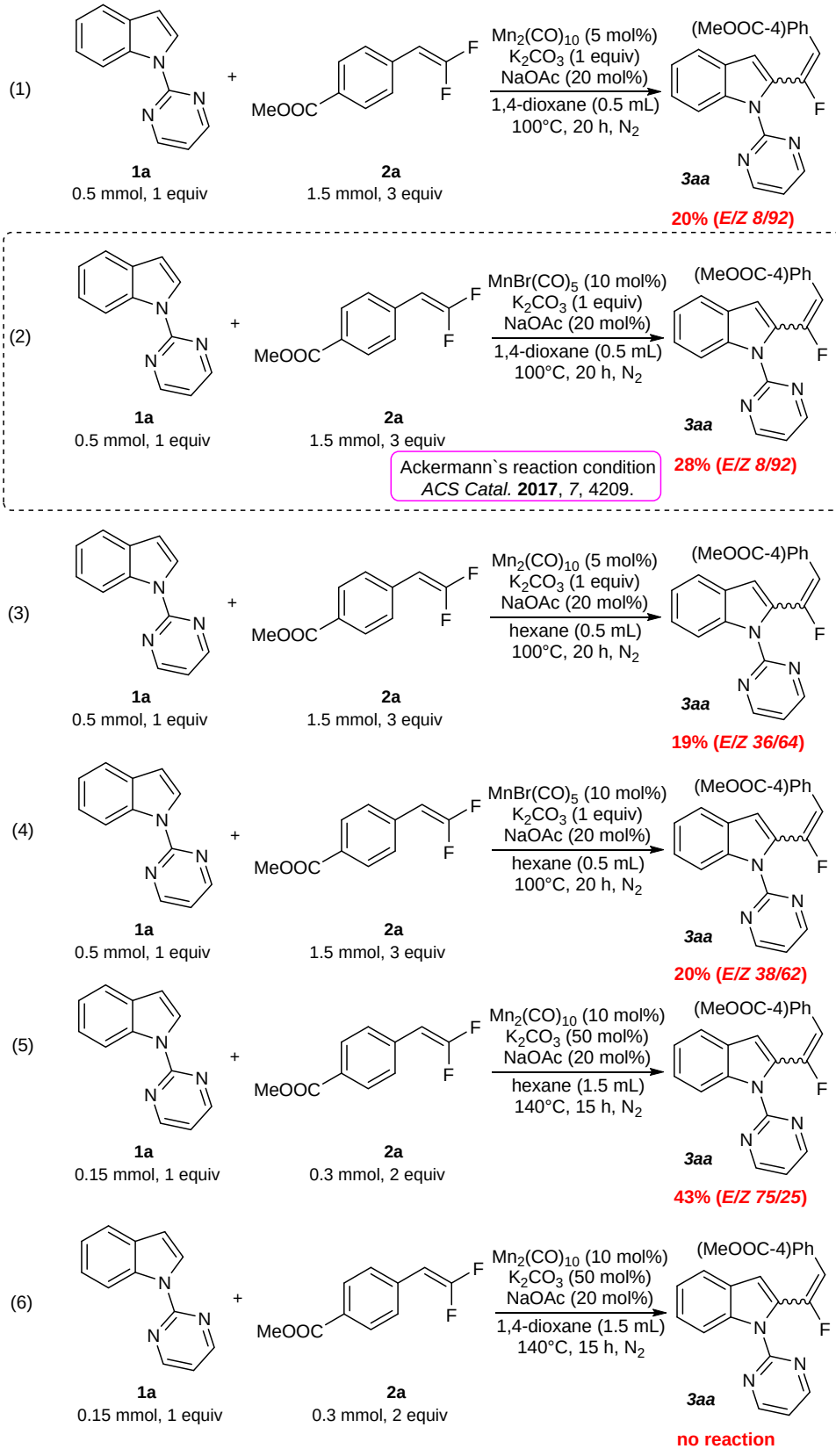
An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **Mn-I** (0.15 mmol, 1 equiv), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2a** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added through syringe in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 15 h. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3aa** (yellow oil, 41.5 mg, 74%, E/Z 65/35).

4.7 Control reactions between 1a and alkene, *gem*-dibromoalkene[7] and terminal bromofluoroolefins[8]



An oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a** (0.15 mmol, 1 equiv), $Mn_2(CO)_{10}$ (0.015 mmol, 10 mol%), K_2CO_3 (0.075 mmol, 50 mol%), KPF_6 (0.075 mmol, 50 mol%) in sequence. After refilling with Ar repeated three times, **2m or 2n or 2o** (0.3 mmol, 2 equiv) and hexane (1.5 mL, 0.1 M) was added in sequence. The mixture was stirred at room temperature about 30 min and then heated in 140 ºC for 15 h. After cooling to room temperature, the mixture was then filtered over silica gel. The filtrate was concentrated under reduced pressure, then determined the target product by TLC and crude ^{1}H NMR.

4.8 Study of the E/Z selectivity of the product



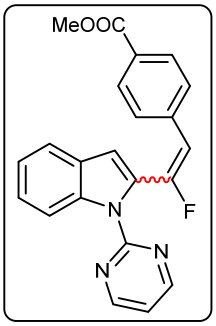
General procedure for the control experiments: an oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with **1a**, $Mn_2(CO)_{10}$/$MnBr(CO)_5$, K_2CO_3, NaOAc in sequence. After refilling with Ar repeated three times, **2a** and solvent was added through syringe in sequence. The mixture was stirred at room temperature about 30

min and then heated in the temperature as indicated in the scheme. After cooling to room temperature, removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3aa**.

As shown above, when the reaction was performed in 1,4-dioxane Z isomer was always the major product with either Mn(0) (eqn 1) or Mn(I) (eqn 2) which is consistent with Ackermann's work. By contrast, the ratio of E isomer increased in the cases of hexane was used as solvent regardless of catalyst and additive (eqn 3 and 4) and the E/Z ratio of product was further improved in diluted solution (eqn 5). However, the choice of the solvent is quite important under less concentrated reaction conditions (eqn 6). In conclusion, the solvent plays a major role for the unusual E/Z selectivity in this reaction.

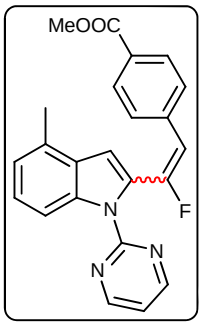
5. Characterization data for compounds

Methyl 4-(2-fluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3aa)



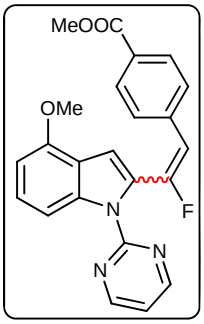
Following General Method C, **3aa** was obtained as yellow oil (0.125 mmol, 46.6 mg, 83%, *E/Z* 73/27) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.70 (d, *J* = 4.8 Hz, 2H), 8.49 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.54 – 7.48 (m, 1H), 7.35 (ddt, *J* = 8.4, 7.2, 1.1 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.76 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.44 (d, *J* = 17.9 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.2, 157.5, 153.9 (d, *J* = 248.8 Hz), 139.2 (d, *J* = 11.0 Hz), 137.2 (d, *J* = 1.7 Hz), 129.7, 129.4, 128.7 (d, *J* = 1.4 Hz), 128.5 (d, *J* = 2.8 Hz), 128.5 (d, *J* = 0.9 Hz), 125.5 (d, *J* = 0.9 Hz), 122.7, 121.7, 117.4, 115.1, 113.3 (d, *J* = 5.9 Hz), 110.8 (d, *J* = 31.8 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.2 (dd, *J* = 17.8, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{16}FN_3O_2H$ $[M+H]^+$ 374.1305, found: 374.1308 ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.36 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.04 – 7.94 (m, 2H), 7.66 – 7.57 (m, 3H), 7.34 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.16 (t, *J* = 4.8 Hz, 1H), 7.00 (dd, *J* = 2.5, 0.8 Hz, 1H), 6.29 (d, *J* = 35.7 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.4, 157.7, 153.8 (d, *J* = 261.1 Hz), 138.6 (d, *J* = 4.5 Hz), 137.9, 132.0 (d, *J* = 25.5 Hz), 129.9, 128.8 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 2.5 Hz), 128.5, 125.4, 122.8, 121.5, 117.8, 114.3, 111.8 (d, *J* = 5.6 Hz), 108.3(d, *J* = 9.7 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.7 (dd, *J* = 35.5, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{16}FN_3O_2H$ $[M+H]^+$ 374.1305, found: 374.1309.

Methyl 4-(2-fluoro-2-(4-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ba)



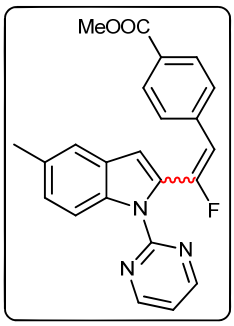
Following General Method , **3ba** was obtained as yellow oil (0.113 mmol, 43.4 mg, 75%, *E/Z* 72/28) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.70 (d, *J* = 4.8 Hz, 2H), 8.31 (d, *J* = 8.5 Hz, 1H), 7.85 – 7.69 (m, 2H), 7.30 – 7.19 (m, 3H), 7.07 (t, *J* = 4.8 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.83 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.44 (d, *J* = 18.0 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.2, 157.5, 154.0 (d, *J* = 249.2 Hz), 139.2, 139.0, 137.1 (d, *J* = 1.9 Hz), 131.3 (d, *J* = 1.0 Hz), 129.7, 129.0 (d, *J* = 28.2 Hz), 128.5, 128.5, 125.6 (d, *J* = 1.1 Hz), 123.0, 117.4, 112.6, 111.7 (d, *J* = 5.8 Hz), 110.7 (d, *J* = 31.5 Hz), 52.1, 18.6. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.5 (dd, *J* = 17.8, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1465. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.73 (d, *J* = 4.9 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.05 – 7.94 (m, 2H), 7.77 – 7.53 (m, 2H), 7.27 – 7.17 (m, 1H), 7.12 (t, *J* = 4.8 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.29 (d, *J* = 35.6 Hz, 1H), 3.88 (s, 3H), 2.54 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.4, 157.7, 154.0 (d, *J* = 262.2 Hz), 138.7 (d, *J* = 4.4 Hz), 137.7, 131.4 (d, *J* = 24.6 Hz), 131.0, 129.9, 128.8 (d, *J* = 8.0 Hz), 128.3, 127.2, 125.6, 123.0, 117.7, 111.8, 110.3 (d, *J* = 6.0 Hz), 108.1 (d, *J* = 10.6 Hz), 52.2, 18.7. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.58 (dd, *J* = 35.9, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1470.

Methyl 4-(2-fluoro-2-(4-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ca)



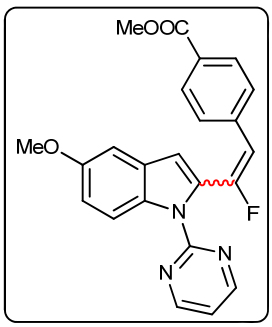
Following General Method C, **3ca** was obtained as a yellow oil of inseparable *E/Z* mixture (0.138 mmol, 55.8 mg, 92%, *E/Z* 70/30) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (dd, *J* = 18.3, 4.8 Hz, 2H), 8.14 – 7.76 (m, 3H), 7.67 – 6.91 (m, 5H), 6.66 (dd, *J* = 10.7, 7.9 Hz, 1H), 6.52 – 6.25 (m, 1H), 4.02 – 3.78 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.4, 158.2, 156.4 (d, *J* = 260.7 Hz, ***Z***), 156.3 (d, *J* = 250.0 Hz, ***E***), 153.7, 153.5, 152.6, 152.5, 139.2 (d, *J* = 10.4 Hz), 138.8 (d, *J* = 4.4 Hz), 138.5 (d, *J* = 1.9 Hz), 130.6 (d, *J* = 25.0 Hz), 129.9, 129.7, 128.8 (d, *J* = 8.1 Hz), 128.6, 128.5 (d, *J* = 2.8 Hz), 128.4 (d, *J* = 1.3 Hz), 128.1 (d, *J* = 28.1 Hz), 126.5 (d, *J* = 1.1 Hz), 126.4, 119.5 (d, *J* = 1.6 Hz), 119.3, 117.8, 117.5, 110.7, 110.5, 110.5, 110.4, 109.0 (d, *J* = 6.0 Hz), 108.0, 107.9, 107.2, 102.6, 102.5, 55.6, 55.5, 52.2, 52.1. ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.6 (dd, *J* = 17.8, 3.7 Hz, 1F). ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** -96.8 (dd, *J* = 35.6, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_3H$ $[M+H]^+$ 404.1410, found: 404.1418.

Methyl 4-(2-fluoro-2-(5-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3da)



Following General Method C, **3da** was obtained as yellow oil (0.123 mmol, 47.4 mg, 82%, *E/Z* 74/26) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.70 (d, *J* = 4.8 Hz, 2H), 8.41 (d, *J* = 8.6 Hz, 1H), 7.84 – 7.71 (m, 2H), 7.31 (dt, *J* = 1.8, 0.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.70 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.45 (d, *J* = 17.8 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.2, 157.5, 154.1 (d, *J* = 248.6 Hz), 139.3 (d, *J* = 10.5 Hz), 135.5 (d, *J* = 2.0 Hz), 132.2, 129.7, 129.5 (d, *J* = 28.0 Hz), 128.9 (d, *J* = 1.6 Hz), 128.5 (d, *J* = 2.9 Hz), 128.4 (d, *J* = 1.0 Hz), 127.1 (d, *J* = 1.2 Hz), 121.4, 117.2, 114.9, 113.1 (d, *J* = 5.7 Hz), 110.5 (d, *J* = 31.8 Hz), 52.1, 21.4. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.8 (dd, *J* = 18.0, 3.7 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1460. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.6 Hz, 1H), 8.08 – 7.96 (m, 2H), 7.70 – 7.60 (m, 2H), 7.25 (s, 1H), 7.21 – 7.13 (m, 2H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.30 (d, *J* = 35.6 Hz, 1H), 3.92 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.3, 157.7, 154.0 (d, *J* = 264.7 Hz), 138.7 (d, *J* = 4.5 Hz), 136.2, 132.2, 132.9 (d, *J* = 24.7 Hz), 129.9, 128.8, 128.8, 128.7, 127.0, 121.2, 117.5, 114.1, 111.7 (d, *J* = 5.6 Hz), 108.1 (d, *J* = 10.5 Hz), 52.2, 21.5. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.3 (dd, *J* = 35.7, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1467.

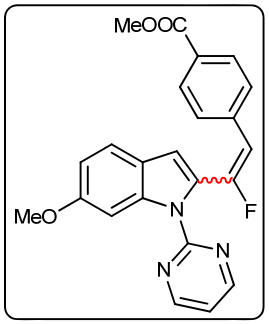
Methyl 4-(2-fluoro-2-(5-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ea)



Following General Method C, **3ea** was obtained as yellow oil (0.092 mmol, 36.8 mg, 61%, *E/Z* 73/27) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.47 (d, *J* = 9.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.20 (m, 2H), 7.10 (t, *J* = 4.8 Hz, 1H), 7.02 (ddd, *J* = 9.1, 2.6, 1.0 Hz, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.72 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.48 (d, *J* = 17.7 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 158.2, 157.4, 155.9, 154.0 (d, *J* = 249.1 Hz), 139.2 (d, *J* = 11.0 Hz), 132.1 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 27.7 Hz), 129.7, 129.4 (d, *J* = 1.4 Hz), 128.5 (d, *J* = 2.8 Hz), 117.2, 116.3, 115.3, 115.3, 113.1 (d, *J* = 5.9 Hz), 110.7 (d, *J* = 31.0 Hz), 103.1, 55.8, 52.1. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.8 (dd, *J* = 17.6, 3.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_3H$ $[M+H]^+$ 404.1410, found: 404.1416. ***Z* isomer: ^{1}H NMR (400**

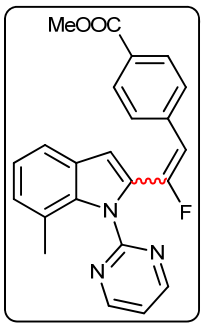
MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 9.1 Hz, 1H), 8.04 – 7.94 (m, 2H), 7.70 – 7.56 (m, 2H), 7.12 (t, *J* = 4.8 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.98 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.27 (d, *J* = 35.5 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.3, 157.6, 156.0, 153.8 (d, *J* = 262.7 Hz), 138.7 (d, *J* = 4.5 Hz), 132.8, 132.4 (d, *J* = 25.0 Hz), 129.9, 129.2, 128.8 (d, *J* = 8.0 Hz), 128.6 (d, *J* = 2.5 Hz), 117.5, 115.5, 115.1, 111.7 (d, *J* = 5.5 Hz), 108.3 (d, *J* = 9.8 Hz), 103.0, 55.8, 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.2 (dd, *J* = 35.5, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_3H$ $[M+H]^+$ 404.1410, found: 404.1410.

Methyl 4-(2-fluoro-2-(6-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3fa)



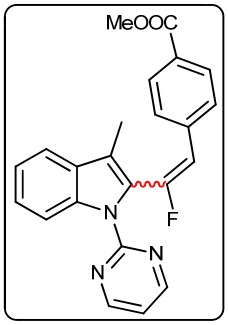
Following General Method C, **3fa** was obtained as yellow oil (0.120 mmol, 48.7 mg, 80%, *E/Z* 69/31) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (d, *J* = 4.8 Hz, 2H), 8.14 (d, *J* = 2.2 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.11 (t, *J* = 4.8 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.75 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.44 (d, *J* = 17.7 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.8, 158.2, 157.6, 154.1 (d, *J* = 249.0 Hz), 139.4 (d, *J* = 10.8 Hz), 138.3 (d, *J* = 1.9 Hz), 129.6, 128.6, 128.5 (d, *J* = 3.0 Hz), 128.3, 122.7 (d, *J* = 1.5 Hz), 122.2, 117.2, 113.5 (d, *J* = 5.8 Hz), 112.3, 110.2 (d, *J* = 32.7 Hz), 99.0, 55.8, 52.1. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.5 (dd, *J* = 17.7, 3.8 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_3H$ $[M+H]^+$ 404.1410, found: 404.1413. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.08 – 7.91 (m, 3H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.18 (t, *J* = 4.8 Hz, 1H), 7.02 – 6.83 (m, 2H), 6.28 (d, *J* = 35.6 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.8, 158.3, 157.8, 154.0 (d, *J* = 262.0 Hz), 139.0, 138.9 (d, *J* = 4.3 Hz), 131.9 (d, *J* = 24.3 Hz), 129.9, 128.7 (d, *J* = 8.1 Hz), 128.5 (d, *J* = 2.5 Hz), 122.6, 122.0, 117.6, 112.4, 112.0 (d, *J* = 5.5 Hz), 107.5 (d, *J* = 10.3 Hz), 98.3, 55.8, 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.2 (dd, *J* = 35.9, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_3H$ $[M+H]^+$ 404.1410, found: 404.1419.

Methyl 4-(2-fluoro-2-(7-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ga)



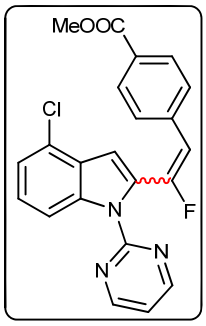
Following General Method C, **3ga** was obtained as yellow oil (0.105 mmol, 40.4 mg, 70%, *E/Z* 72/28) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 10% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.82 (d, *J* = 4.9 Hz, 2H), 7.93 – 7.79 (m, 2H), 7.49 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.35 – 7.24 (m, 3H), 7.22 – 7.10 (m, 2H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.48 (d, *J* = 18.1 Hz, 1H), 3.89 (s, 3H), 2.13 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 158.3, 158.1, 152.5 (d, *J* = 249.6 Hz), 138.3 (d, *J* = 10.9 Hz), 136.6 (d, *J* = 1.6 Hz), 130.7 (d, *J* = 27.3 Hz), 129.7, 128.8 (d, *J* = 1.4 Hz), 128.6 (d, *J* = 1.4 Hz), 128.5 (d, *J* = 3.0 Hz), 127.8, 122.9 (d, *J* = 0.9 Hz), 122.1, 119.8, 119.5, 113.1 (d, *J* = 31.9 Hz), 110.7 (d, *J* = 5.3 Hz), 52.1, 20.6. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.8 (dd, *J* = 18.1, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1469. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.90 (d, *J* = 4.8 Hz, 2H), 8.00 – 7.92 (m, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.42 (t, *J* = 4.9 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.16 (d, *J* = 37.5 Hz, 1H), 3.91 (s, 3H), 1.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 159.5, 158.6, 152.6 (d, *J* = 260.7 Hz), 138.1 (d, *J* = 4.0 Hz), 137.9, 133.0 (d, *J* = 27.7 Hz), 129.9, 128.8, 128.7, 128.4, 127.5, 122.2, 122.0, 120.4, 119.6, 109.0 (d, *J* = 9.3 Hz), 108.5 (d, *J* = 4.8 Hz), 52.2, 19.7. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -102.9 (d, *J* = 37.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1468.

Methyl 4-(2-fluoro-2-(3-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ha)



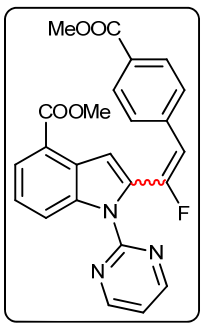
Following General Method C, **3ha** was obtained as yellow oil (0.089 mmol, 34.2 mg, 59%, *E/Z* 66/34) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.63 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.74 (m, 2H), 7.55 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.43 (ddt, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.35 – 7.22 (m, 3H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.62 (d, *J* = 17.2 Hz, 1H), 3.86 (s, 3H), 1.99 (d, *J* = 3.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.2, 157.7, 153.4 (d, *J* = 250.6 Hz), 139.4 (d, *J* = 11.3 Hz), 137.0 (d, *J* = 1.9 Hz), 129.9 (d, *J* = 1.5 Hz), 129.8, 128.3 (d, *J* = 1.4 Hz), 128.0 (d, *J* = 2.7 Hz), 126.4 (d, *J* = 25.4 Hz), 125.8 (d, *J* = 1.4 Hz), 122.3, 120.9 (d, *J* = 7.0 Hz), 120.0 (d, *J* = 1.3 Hz), 116.9, 115.3 (d, *J* = 1.1 Hz), 111.6 (d, *J* = 32.1 Hz), 52.1, 9.5 (d, *J* = 1.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -86.8 (dq, *J* = 17.1, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1464. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (d, *J* = 4.8 Hz, 2H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.11 – 7.98 (m, 2H), 7.67 (dd, *J* = 16.0, 8.1 Hz, 3H), 7.47 – 7.36 (m, 1H), 7.33 – 7.27 (m, 1H), 7.12 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 36.1 Hz, 1H), 3.93 (s, 3H), 2.51 (d, *J* = 2.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 158.2, 157.7, 152.3 (d, *J* = 262.9 Hz), 138.7 (d, *J* = 4.5 Hz), 136.8, 130.0, 128.8 (d, *J* = 8.1 Hz), 128.6 (d, *J* = 2.1 Hz), 128.1, 127.8, 125.8, 122.4, 120.4 (d, *J* = 5.9 Hz), 119.9, 117.1, 114.6, 110.8 (d, *J* = 10.6 Hz), 52.2, 10.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.6 (dt, *J* = 36.1, 3.2 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{18}FN_3O_2H$ $[M+H]^+$ 388.1461, found: 388.1470.

Methyl 4-(2-(4-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-fluorovinyl)benzoate (3ia)



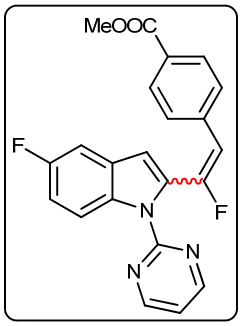
Following General Method C, **3ia** was obtained as a yellow oil of inseparable *E/Z* mixture (0.090 mmol, 36.9 mg, 60%, *E/Z* 70/30) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.76 (dd, *J* = 19.6, 4.8 Hz, 2H), 8.48 – 8.21 (m, 1H), 8.10 – 7.76 (m, 2H), 7.69 – 6.86 (m, 6H), 6.52 (d, *J* = 17.9 Hz, 0.7H, ***E***), 6.38 (d, *J* = 35.7 Hz, 0.3H, ***Z***), 3.92 (s, 0.9H, ***Z***), 3.86 (s, 2.1H, ***E***). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 166.9, 158.5, 158.3, 157.4, 157.2, 153.1 (d, *J* = 261.9 Hz, ***Z***), 153.1 (d, *J* = 248.8 Hz, ***E***), 138.7, 138.6, 138.3, 138.3, 137.7 (d, *J* = 2.0 Hz), 132.6 (d, *J* = 24.5 Hz), 130.2 (d, *J* = 28.7 Hz), 130.0, 129.7, 128.9, 128.9, 128.8, 128.8, 128.7 (d, *J* = 1.1 Hz), 128.5 (d, *J* = 2.9 Hz), 127.5 (d, *J* = 1.5 Hz), 127.4, 126.9 (d, *J* = 1.3 Hz), 126.6, 126.0 (d, *J* = 0.7 Hz), 125.9, 122.4, 118.2, 117.9, 113.7, 112.9, 111.4 (d, *J* = 31.2 Hz), 111.0 (d, *J* = 5.9 Hz), 109.5 (d, *J* = 5.2 Hz), 109.0 (d, *J* = 10.0 Hz), 52.2, 52.1. ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.9 (dd, *J* = 18.0, 3.5 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -97.7 (dd, *J* = 35.7, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}ClFN_3O_2H$ $[M+H]^+$ 408.0915, found: 408.0917.

Methyl 2-(1-fluoro-2-(4-(methoxycarbonyl)phenyl)vinyl)-1-(pyrimidin-2-yl)-1*H*-indole-4- carboxylate (3ja)



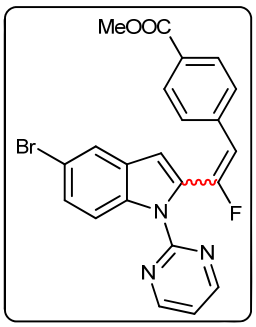
Following General Method C, **3ja** was obtained as a yellow solid of inseparable *E/Z* mixture (0.083 mmol, 35.5 mg, 55%, *E/Z* 68/32) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.95 – 8.51 (m, 3H), 8.07 – 7.97 (m, 1H), 7.86 – 7.37 (m, 4H), 7.28 – 7.14 (m, 3H), 6.60 – 6.37 (m, 1H), 4.14 – 3.65 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.4, 167.2, 167.0, 166.9, 158.5, 158.3, 157.2, 153.4 (d, *J* = 252.2 Hz, ***Z***), 153.2 (d, *J* = 248.9 Hz, ***E***), 138.7, 138.6, 138.4, 137.7 (d, *J* = 1.5 Hz), 131.5, 131.2, 130.0, 129.7, 128.9 (d, *J* = 8.2 Hz), 128.6 (d, *J* = 1.0 Hz), 128.5 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 1.1 Hz), 125.8, 124.7, 124.6, 122.7, 122.3, 119.7, 118.9, 118.2, 117.9, 113.6 (d, *J* = 5.2 Hz), 112.0 (d, *J* = 5.7 Hz), 111.4 (d, *J* = 31.0 Hz), 109.1 (d, *J* = 8.9 Hz), 52.3, 52.1, 52.1. ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.9 (dd, *J* = 18.3, 3.4 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -98.1 (dd, *J* = 35.7, 2.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{18}FN_3O_4H$ $[M+H]^+$ 432.1360, found: 432.1366.

Methyl 4-(2-fluoro-2-(5-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ka)



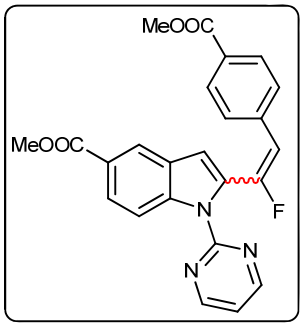
Following General Method C, **3ka** was obtained as yellow oil (0.090 mmol, 35.4 mg, 60%, *E/Z* 72/28) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (d, *J* = 4.8 Hz, 2H), 8.52 (dd, *J* = 9.2, 4.6 Hz, 1H), 7.89 – 7.75 (m, 2H), 7.27 – 7.22 (m, 2H), 7.19 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.74 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.51 (d, *J* = 17.7 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 159.2 (d, *J* = 239.2 Hz), 158.3, 157.3, 153.4 (d, *J* = 249.3 Hz), 139.0 (d, *J* = 10.9 Hz), 133.6 (d, *J* = 1.7 Hz), 131.0 (d, *J* = 28.0 Hz), 129.7, 129.3 (d, *J* = 1.1 Hz), 129.2 (d, *J* = 1.2 Hz), 128.5 (d, *J* = 2.8 Hz), 117.6, 116.5 (d, *J* = 8.8 Hz), 113.6 (d, *J* = 25.3 Hz), 112.8 (m), 111.0 (d, *J* = 30.3 Hz), 106.6 (d, *J* = 24.2 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.8 (dd, *J* = 17.8, 3.5 Hz, 1F), -121.0 (td, *J* = 9.0, 4.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}F_2N_3O_2H$ $[M+H]^+$ 392.1211, found: 392.1218. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.37 (dd, *J* = 9.2, 4.5 Hz, 1H), 8.09 – 7.94 (m, 2H), 7.72 – 7.58 (m, 2H), 7.33 – 7.24 (m, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.10 (td, *J* = 9.1, 2.6 Hz, 1H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 35.6 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 159.3 (d, *J* = 239.1 Hz), 158.4, 157.4, 153.4 (d, *J* = 262.5 Hz), 138.4 (d, *J* = 4.5 Hz), 134.2, 133.4 (d, *J* = 25.1 Hz), 129.9, 129.2 (d, *J* = 10.2 Hz), 128.8 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 2.3 Hz), 117.9, 115.7 (d, *J* = 9.0 Hz), 113.5 (d, *J* = 25.4 Hz), 111.2 (m), 108.8 (d, *J* = 9.3 Hz), 106.4 (d, *J* = 23.8 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -97.0 (dd, *J* = 35.5, 2.5 Hz, 1F), -121.0 (td, *J* = 9.0, 4.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}F_2N_3O_2H$ $[M+H]^+$ 392.1211, found: 392.1213.

Methyl 4-(2-(5-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-fluorovinyl)benzoate (3la)



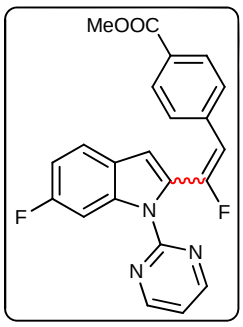
Following General Method C, **3la** was obtained as yellow oil (0.093 mmol, 42.3 mg, 62%, *E/Z* 70/30) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.40 (d, *J* = 9.0 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.43 (ddd, *J* = 9.0, 2.0, 0.9 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.68 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.48 (d, *J* = 17.7 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 158.3, 157.2, 153.2 (d, *J* = 249.2 Hz), 138.9 (d, *J* = 10.4 Hz), 135.8 (d, *J* = 1.6 Hz), 130.7 (d, *J* = 27.6 Hz), 130.3 (d, *J* = 1.3 Hz), 130.0, 129.7, 128.7 (d, *J* = 1.0 Hz), 128.5 (d, *J* = 2.8 Hz), 128.3 (d, *J* = 0.9 Hz), 124.1, 117.7, 116.8, 115.9, 112.2 (d, *J* = 5.7 Hz), 111.3 (d, *J* = 30.8 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.2 (dd, *J* = 17.8, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}BrFN_3O_2H$ $[M+H]^+$ 452.0410, found: 452.0418. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.79 (d, *J* = 4.9 Hz, 2H), 8.29 (d, *J* = 8.9 Hz, 1H), 8.12 – 7.94 (m, 2H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.21 (t, *J* = 4.8 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 35.5 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 158.5, 157.4, 153.2 (d, *J* = 262.7 Hz), 138.4 (d, *J* = 5.4 Hz), 136.5, 133.1 (d, *J* = 25.0 Hz), 130.2, 128.9, 128.9, 128.8, 128.2, 123.9, 118.0, 116.0, 115.9, 110.6 (d, *J* = 5.6 Hz), 108.9 (d, *J* = 9.7 Hz), 52.3. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -97.2 (dd, *J* = 35.6, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}BrFN_3O_2H$ $[M+H]^+$ 452.0410, found: 452.0414.

Methyl 2-(1-fluoro-2-(4-(methoxycarbonyl)phenyl)vinyl)-1-(pyrimidin-2-yl)-1*H*-indole-5-carboxylate (3ma)



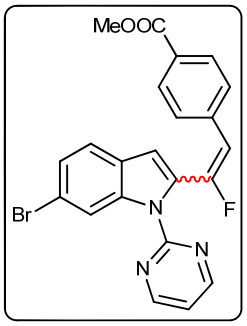
Following General Method C, **3ma** was obtained as yellow oil (0.090 mmol, 38.9 mg, 60%, *E*/*Z* 67/33) using EA/PE (5%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.53 (d, *J* = 8.9 Hz, 1H), 8.30 (d, *J* = 1.6 Hz, 1H), 8.07 (dt, *J* = 8.9, 1.1 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 (t, *J* = 4.8 Hz, 1H), 6.86 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.53 (d, *J* = 17.8 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.5, 166.9, 158.4, 157.2, 153.1 (d, *J* = 251.4 Hz), 139.6 (d, *J* = 1.5 Hz), 138.8 (d, *J* = 10.9 Hz), 131.1 (d, *J* = 29.8 Hz), 129.7, 128.7 (d, *J* = 0.7 Hz), 128.6 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 1.3 Hz), 126.5, 124.7, 124.2, 118.0, 114.8, 113.6 (d, *J* = 6.0 Hz), 111.4 (d, *J* = 30.5 Hz), 52.2, 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.5 (dd, *J* = 17.8, 3.5 Hz). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{18}FN_3O_4H$ $[M+H]^+$ 432.1360, found: 432.1364. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.82 (d, *J* = 4.9 Hz, 2H), 8.45 – 8.35 (m, 2H), 8.11 – 7.98 (m, 3H), 7.75 – 7.58 (m, 2H), 7.24 (d, *J* = 4.8 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.36 (d, *J* = 35.6 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.6, 166.9, 158.6, 157.3, 153.1 (d, *J* = 261.4 Hz), 140.2, 138.3 (d, *J* = 4.6 Hz), 133.4 (d, *J* = 25.2 Hz), 130.0, 128.9, 128.8, 128.2, 126.5, 124.8, 124.0, 118.3, 114.0, 111.9 (d, *J* = 5.3 Hz), 109.0 (d, *J* = 9.5 Hz), 52.3, 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -97.6 (dd, *J* = 35.9, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{18}FN_3O_4H$ $[M+H]^+$ 432.1360, found: 432.1370.

Methyl 4-(2-fluoro-2-(6-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3na)



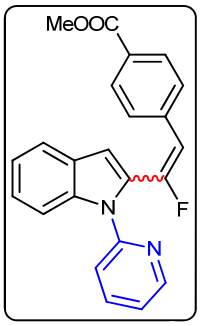
Following General Method C, **3na** was obtained as yellow oil (0.098 mmol, 38.4 mg, 65%, *E*/*Z* 69/31) using EA/PE (5%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.32 (dd, *J* = 10.9, 2.4 Hz, 1H), 7.88 – 7.75 (m, 2H), 7.47 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 7.01 (td, *J* = 8.9, 2.4 Hz, 1H), 6.76 (dd, *J* = 3.7, 0.8 Hz, 1H), 6.49 (d, *J* = 17.6 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 161.7 (d, *J* = 241.2 Hz), 158.3, 157.3, 153.6 (d, *J* = 248.9 Hz), 139.1 (d, *J* = 11.0 Hz), 137.4 (dd, *J* = 13.2, 1.6 Hz), 130.2 (d, *J* = 4.6 Hz), 129.9 (d, *J* = 4.6 Hz), 129.7, 128.5 (d, *J* = 2.8 Hz), 125.0, 122.5 (d, *J* = 10.0 Hz), 117.6, 113.1 (dd, *J* = 6.0, 1.0 Hz), 111.5 (d, *J* = 24.9 Hz), 110.8 (d, *J* = 31.1 Hz), 102.5 (d, *J* = 28.9 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.2 (dt, *J* = 17.7, 3.0 Hz, 1F), -113.18 – -119.34 (m, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}F_2N_3O_2H$ $[M+H]^+$ 392.1211, found: 392.1217. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.17 (dd, *J* = 10.7, 2.4 Hz, 1H), 8.08 – 7.97 (m, 2H), 7.69 – 7.60 (m, 2H), 7.56 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.09 – 6.94 (m, 2H), 6.29 (d, *J* = 35.5 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 161.7 (d, *J* = 241.2 Hz), 158.4, 157.5, 153.5 (d, *J* = 262.3 Hz), 138.6 (d, *J* = 4.4 Hz), 138.1 (d, *J* = 129.1 Hz), 130.0, 129.7, 128.8, 128.7, 124.9 (d, *J* = 1.1 Hz), 122.3 (d, *J* = 10.2 Hz), 117.9, 111.6 (m), 111.4, 108.3 (d, *J* = 9.4 Hz), 101.8 (d, *J* = 28.3 Hz), 52.3. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.4 (dd, *J* = 35.6, 2.6 Hz, 1F), -115.6 (td, *J* = 9.9, 5.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}F_2N_3O_2H$ $[M+H]^+$ 392.1211, found: 392.1214.

Methyl 4-(2-(6-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2-fluorovinyl)benzoate (3oa)



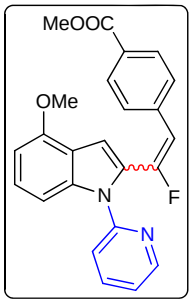
Following General Method C, **3oa** was obtained as yellow oil (0.107 mmol, 48.2 mg, 71%, *E*/*Z* 69/31) using EA/PE (5%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.77 (d, *J* = 4.8 Hz, 3H), 7.87 – 7.77 (m, 2H), 7.45 – 7.32 (m, 2H), 7.30 – 7.21 (m, 2H), 7.17 (t, *J* = 4.8 Hz, 1H), 6.75 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.51 (d, *J* = 17.8 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.9, 158.4, 157.2, 153.3 (d, *J* = 248.7 Hz), 138.9 (d, *J* = 10.8 Hz), 137.7 (d, *J* = 1.8 Hz), 130.2 (d, *J* = 28.3 Hz), 129.7, 128.6 (d, *J* = 0.9 Hz), 128.5 (d, *J* = 3.0 Hz), 127.4 (d, *J* = 1.2 Hz), 126.1, 122.8, 119.4 (d, *J* = 1.5 Hz), 118.3, 117.8, 112.9 (d, *J* = 5.9 Hz), 111.1 (d, *J* = 30.7 Hz), 52.2. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -88.87 – -89.30 (m, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}BrFN_3O_2H$ $[M+H]^+$ 452.0410, found: 452.0414. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.69 – 8.52 (m, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.22 (t, *J* = 4.8 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 35.5 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 167.0, 158.5, 157.3, 153.3 (d, *J* = 262.7 Hz), 138.4 (d, *J* = 5.5 Hz), 132.6 (d, *J* = 24.7 Hz), 130.0, 129.7, 128.9 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 2.4 Hz), 127.4, 126.1, 122.5, 119.1, 118.1, 117.5, 111.4 (d, *J* = 5.6 Hz), 108.8 (d, *J* = 9.7 Hz), 52.3. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -97.1 (dd, *J* = 35.5, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{15}BrFN_3O_2H$ $[M+H]^+$ 452.0410, found: 452.0416.

Methyl 4-(2-fluoro-2-(1-(pyridin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3pa)



Following General Method C, **3pa** was obtained as a colourless oil of inseparable *E*/*Z* mixture (0.093 mmol, 34.4 mg, 62%, *E*/*Z* 61/39) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 – 8.45 (m, 1H), 8.04 – 7.85 (m, 1H), 7.82 – 7.43 (m, 5H), 7.40 – 7.26 (m, 2H), 7.24 – 6.90 (m, 4H), 6.56 – 5.91 (m, 1H), 3.89 (d, *J* = 16.5 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.9, 152.7 (d, *J* = 260.1 Hz, ***Z* isomer**), 152.4 (d, *J* = 248.1 Hz, ***E* isomer**), 151.7, 150.8, 149.7, 149.4, 138.9, 138.6, 138.2, 138.1, 138.1, 138.1, 137.5 (d, *J* = 1.9 Hz), 131.9 (d, *J* = 30.4 Hz), 129.9, 129.7, 129.5 (d, *J* = 31.4 Hz), 128.8, 128.8, 128.7, 128.5 (d, *J* = 2.9 Hz), 127.9 (d, *J* = 1.3 Hz), 127.8, 124.8, 124.8, 122.7, 121.9, 121.8, 121.6, 120.8, 119.7, 112.5, 112.1, 111.7, 111.3, 110.0 (d, *J* = 4.4 Hz), 109.1 (d, *J* = 9.5 Hz), 108.3 (d, *J* = 4.7 Hz), 52.2, 52.2. ***(E* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -89.1 (dd, *J* = 18.0, 2.8 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -102.9 (d, *J* = 37.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{17}FN_2O_2H$ $[M+H]^+$ 373.1352, found: 373.1360.

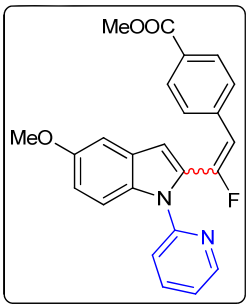
Methyl 4-(2-fluoro-2-(4-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3qa)



Following General Method C, **3qa** was obtained as a yellow oil of inseparable *E*/*Z* mixture (0.090 mmol, 36.5 mg, 60%, *E*/*Z* 68/32) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.74 – 8.65 (m, 0.32H, ***Z* isomer**), 8.53 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 0.68H, ***E* isomer**), 8.02 – 7.97 (m, 0.67H, ***Z* isomer**), 7.91 (td, *J* = 7.8, 2.0 Hz, 0.33H, ***Z* isomer**), 7.84 – 7.78 (m, 1.33H, ***E* isomer**), 7.74 (td, *J* = 7.8, 1.9 Hz, 0.67H, ***E* isomer**), 7.51 (dd, *J* = 22.8, 8.2 Hz, 1H), 7.41 – 7.04 (m, 6H), 6.67 – 6.59 (m, 1H), 6.45 (d, *J* = 17.9 Hz, 0.68H, ***E* isomer**), 6.08 (d, *J* = 37.5 Hz, 0.32H, ***Z* isomer**), 4.01 (s, 1H, ***Z* isomer**), 3.97 (s, 2H, ***E* isomer**), 3.93 (s, 1H, ***Z* isomer**), 3.89 (s, 2H, ***E* isomer**). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.9, 150.4, 153.8, 152.8 (d, *J* = 260.9 Hz, ***Z* isomer**), 152.5 (d, *J* = 248.6 Hz, ***E* isomer**), 151.7, 150.8, 149.6, 149.3, 140.2, 138.8 (d, *J* = 1.9 Hz), 138.7, 138.3, 138.1, 138.1, 129.9, 129.7, 128.7 (d, *J* = 8.1 Hz), 128.6, 128.4 (d, *J* = 2.9 Hz), 128.0 (d, *J* = 32.1 Hz), 125.8, 125.8, 122.7, 121.9, 120.9, 119.8, 118.9 (d, *J* = 1.2 Hz), 112.1 (d, *J* = 32.0 Hz), 108.6 (d, *J* = 9.0 Hz), 107.5 (d, *J* = 4.4 Hz), 105.7 (d, *J* = 4.6 Hz), 104.8, 104.4, 101.4, 101.4, 55.6 (***Z* isomer**), 55.5 (***E* isomer**),

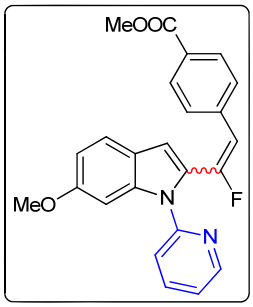
52.2 (***Z isomer***), 52.2 (***E isomer***). ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.6 (dd, *J* = 17.9, 2.9 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -102.9 (d, *J* = 37.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{19}FN_2O_3H$ $[M+H]^+$ 403.1458, found: 403.1460.

Methyl 4-(2-fluoro-2-(5-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ra)



Following General Method C, **3ra** was obtained as yellow oil (0.095 mmol, 38.2 mg, 63%, *E/Z* 68/32) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 – 8.62 (m, 0.33H, ***Z isomer***), 8.59 – 8.48 (m, 0.67H, ***E isomer***), 8.00 (d, *J* = 8.3 Hz, 0.66H, ***Z isomer***), 7.90 (td, J = 7.7, 1.9 Hz, 0.32H, ***Z isomer***), 7.85 – 7.77 (m, 1.34H, ***E isomer***), 7.74 (td, *J* = 7.8, 1.9 Hz, 0.68H, ***E isomer***), 7.62 – 7.42 (m, 2H), 7.40 – 6.82 (m, 6H), 6.47 (d, *J* = 18.0 Hz, 0.68H, ***E isomer***), 6.07 (d, J = 37.5 Hz, 0.32H, ***Z isomer***), 3.95 – 3.87 (m, 6H).). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.8, 155.5, 155.4, 152.7 (d, *J* = 259.8 Hz, ***Z isomer***), 152.4 (d, *J* = 248.5 Hz, ***E isomer***), 151.7, 150.8, 149.5, 149.2, 138.6, 138.2, 138.1, 138.1, 134.1, 132.6 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 29.9 Hz), 129.9, 129.6, 129.5 (d, *J* = 32.0 Hz), 128.7, 128.6, 128.4, 128.4, 128.3, 122.5, 121.7, 120.5, 119.4, 115.4, 115.1, 112.8, 112.3, 112.3, 112.0, 109.7 (d, *J* = 4.6 Hz), 108.9 (d, *J* = 9.0 Hz), 108.0 (d, *J* = 5.1 Hz), 102.7, 102.5, 55.8 (***Z isomer***), 55.8 (***E isomer***), 52.2 (***Z isomer***), 52.1 (***E isomer***). ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.1 (dd, *J* = 17.7, 2.8 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -102.8 (d, *J* = 37.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{19}FN_2O_3H$ $[M+H]^+$ 403.1458, found: 403.1456. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.51 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.73 (td, *J* = 7.8, 1.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.28 (s, 1H), 7.20 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.96 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.85 (d, *J* = 2.6 Hz, 1H), 6.46 (d, *J* = 18.0 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H).

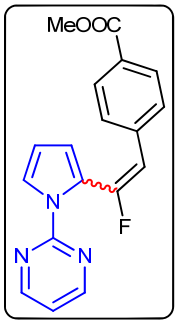
Methyl 4-(2-fluoro-2-(6-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3sa)



Following General Method C, **3sa** was obtained as yellow oil (0.104 mmol, 41.8 mg, 69%, *E/Z* 68/32) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer.

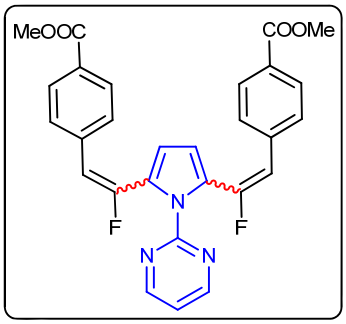
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 – 8.65 (m, 0.33H, ***Z isomer***), 8.61 – 8.47 (m, 0.67H, ***E isomer***), 8.01 – 7.96 (m, 0.67H, ***Z isomer***), 7.91 (td, *J* = 7.8, 2.0 Hz, 0.33H, ***Z isomer***), 7.86 – 7.78 (m, 1.34H, ***E isomer***), 7.76 (td, *J* = 7.8, 1.9 Hz, 0.7H, ***E isomer***), 7.60 – 7.43 (m, 2H), 7.42 – 7.09 (m, 4H), 7.06 – 6.85 (m, 2H), 6.43 (d, *J* = 18.0 Hz, 0.68H, ***E isomer***), 5.99 (d, *J* = 37.6 Hz, 0.32H, ***Z isomer***), 3.94 – 3.82 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.8, 158.5, 158.5, 152.8 (d, *J* = 259.7 Hz, ***Z isomer***), 152.5 (d, *J* = 248.9 Hz, ***E isomer***), 151.8, 150.9, 149.6, 149.2, 140.0, 138.7, 138.5 (d, *J* = 2.0 Hz), 138.3, 138.2, 138.2, 138.1, 130.7 (d, *J* = 30.5 Hz), 129.9, 129.6, 128.6, 128.5 (d, *J* = 2.5 Hz), 128.5, 128.3 (d, *J* = 3.0 Hz), 128.0, 122.6, 122.5, 122.2, 122.0 (d, *J* =1.3 Hz), 121.9, 121.8, 120.7, 119.6, 112.1, 112.0, 111.8 (d, *J* =31.0 Hz), 110.2 (d, *J* = 4.7 Hz), 108.6 (d, *J* = 4.7 Hz), 108.1 (d, *J* = 9.4 Hz), 95.0 (***E isomer***), 94.7, 55.7(***Z isomer and E isomer overlap***), 52.2 (***Z isomer***), 52.1 (***E isomer***). ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.5 (dd, *J* = 18.1, 2.9 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -102.9 (d, *J* = 37.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{19}FN_2O_3H$ $[M+H]^+$ 403.1458, found: 403.1459. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.55 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.76 (td, *J* = 7.8, 1.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.23 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 7.19 – 7.11 (m, 3H), 6.93 – 6.86 (m, 2H), 6.43 (d, *J* = 17.9 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H).

Methyl 4-(2-fluoro-2-(1-(pyrimidin-2-yl)-1*H*-pyrrol-2-yl)vinyl)benzoate (3ta)



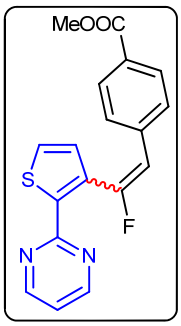
Following General Method C, **3ta** was obtained as a colourless oil of inseparable *E/Z* mixture (0.059 mmol, 19 mg, 39%, *E/Z* 75/25) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.66 (dd, *J* = 8.7, 4.8 Hz, 2H), 8.06 – 7.74 (m, 3H), 7.70 – 7.62 (m, 0.5H), 7.18 – 7.08 (m, 2.5H), 6.66 – 6.06 (m, 3H), 3.89 (d, *J* = 25.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.1, 167.0, 158.5, 158.5, 156.6, 156.4, 153.9 (d, *J* = 250.3 Hz, ***E* isomer**), 153.7 (d, *J* = 264.2 Hz, ***Z* isomer**), 139.5 (d, *J* = 10.9 Hz), 139.1 (d, *J* = 4.8 Hz), 129.9, 129.6, 128.7 (d, *J* = 8.1 Hz), 128.4 (d, *J* = 3.0 Hz), 128.2 (d, *J* = 1.3 Hz), 128.2 (d, *J* = 2.9 Hz), 126.1 (d, *J* = 25.7 Hz), 124.4 (d, *J* = 1.5 Hz), 123.7 (d, *J* = 3.7 Hz), 123.3 (d, *J* = 29.8 Hz), 118.8 (d, *J* = 5.2 Hz), 118.1 (d, *J* = 5.5 Hz), 118.1, 118.0, 111.3 (d, *J* = 2.0 Hz), 110.8 (d, *J* = 33.7 Hz), 110.9, 107.7 (d, *J* = 12.0 Hz), 52.2, 52.1. ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -83.4 (dt, *J* = 16.9, 3.2 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.6 (dd, *J* = 34.8, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{18}H_{14}FN_3O_2H$ $[M+H]^+$ 324.1148, found: 324.1151.

Dimethyl 4,4'-((1-(pyrimidin-2-yl)-1*H*-pyrrole-2,5-diyl)bis(2-fluoroethene-2,1-diyl))dibenzoate (3ta`)



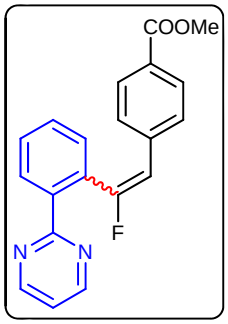
Following General Method C, **3ta`** was obtained as a yellow oil of inseparable *isomer (EE/EZ/ZZ)* mixture (0.047 mmol, 23.2 mg, 31%, *isomer ration 7/8/20/55*) using EA/PE (15%-40%) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.93 – 8.50 (m, 2H), 8.04 – 7.80 (m, 4H), 7.58 – 7.35 (m, 1H), 7.25 – 7.12 (m, 4H), 6.74 – 5.99 (m, 4H), 3.98 – 3.79 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 166.9, 166.9, 158.8, 158.6, 158.3, 156.7, 156.1, 152.3 (d, *J* = 251.0 Hz), 152.0 (d, *J* = 247.3 Hz), 138.7, 138.6, 138.6, 138.6, 138.5, 138.4, 138.3, 138.3, 129.9, 129.7, 129.7, 128.7, 128.7, 128.7, 128.5, 128.4, 128.4, 126.9, 126.6, 126.6, 119.6, 119.1, 116.2, 115.8, 115.8, 114.7, 114.6, 112.1, 111.8, 111.7, 111.5, 111.4, 108.2, 108.1, 77.5, 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.1 (dd, *J* = 17.3, 2.8 Hz, 1F), -88.4 (d, *J* = 15.5 Hz, 1F), -99.1 (d, *J* = 36.6 Hz, 1F), -100.7 (d, *J* = 36.8 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{28}H_{21}F_2N_3O_4H$ $[M+H]^+$ 502.1578, found: 502.1573. **Note:** (1) *isomer ration determined by ^{19}F NMR after column.* (2) *^{13}C NMR can not affiliation clearly.*

Methyl 4-(2-fluoro-2-(2-(pyrimidin-2-yl)thiophen-3-yl)vinyl)benzoate (3ua)



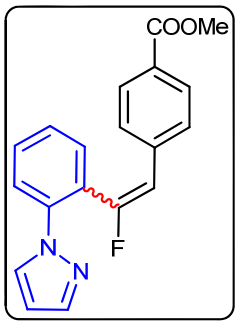
Following General Method C, **3ua** was obtained as a yellow oil (0.051 mmol, 17.4 mg, 34%, *E/Z* 71/29) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 15% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.63 (d, *J* = 4.9 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 5.1 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.90 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.48 (d, *J* = 18.4 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 160.9, 157.2, 155.7 (d, *J* = 252.1 Hz), 143.1, 138.9 (d, *J* = 12.3 Hz), 132.4 (d, *J* = 28.6 Hz), 131.1 (d, *J* = 2.3 Hz), 129.6, 129.2, 128.4 (d, *J* = 1.4 Hz), 128.2 (d, *J* = 3.0 Hz), 119.0, 110.5 (d, *J* = 30.1 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -84.5 (d, *J* = 18.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{18}H_{13}FN_2O_2SH$ $[M+H]^+$ 341.0760, found: 341.0765. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (d, *J* = 4.9 Hz, 2H), 8.12 – 7.94 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.16 (t, *J* = 4.9 Hz, 1H), 6.27 (d, *J* = 37.0 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.0, 161.3, 157.2, 155.5 (d, *J* = 266.3 Hz), 140.9, 138.6 (d, *J* = 3.9 Hz), 134.1 (d, *J* = 134.1 Hz), 130.5 (d, *J* = 4.7 Hz), 129.9, 128.9 (d, *J* = 8.2 Hz), 128.6 (d, *J* = 2.5 Hz), 128.5, 118.9, 109.3 (d, *J* = 9.3 Hz), 52.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -93.3 (d, *J* = 37.0 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{18}H_{13}FN_2O_2SH$ $[M+H]^+$ 341.0760, found: 341.0769.

Methyl 4-(2-fluoro-2-(2-(pyrimidin-2-yl)phenyl)vinyl)benzoate (3va)



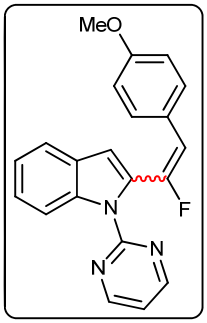
Following General Method C, **3va** was obtained as yellow oil (0.035 mmol, 11.5 mg, 23%, *E/Z* 65/35) using EA/PE (5%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 15% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.75 (d, *J* = 4.9 Hz, 2H), 8.08 (dq, *J* = 7.9, 0.9 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.63 – 7.51 (m, 1H), 7.48 – 7.38 (m, 2H), 7.17 (t, *J* = 4.9 Hz, 1H), 7.06 – 6.94 (m, 2H), 6.36 (d, *J* = 19.3 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 167.0, 165.5, 160.8 (d, *J* = 256.5 Hz), 157.1, 139.0 (d, *J* = 12.5 Hz), 138.7 (d, *J* = 0.7 Hz), 131.8 (d, *J* = 3.1 Hz), 131.4 (d, *J* = 26.2 Hz), 131.0 (d, *J* = 1.5 Hz), 130.5 (d, *J* = 2.4 Hz), 130.1 (d, *J* = 1.1 Hz), 129.6, 128.5 (d, *J* = 2.9 Hz), 128.2 (d, *J* = 1.1 Hz), 119.2, 109.2 (d, *J* = 30.4 Hz), 52.1. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -83.1 (d, *J* = 19.1 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{15}FN_2O_2H$ $[M+H]^+$ 335.1196, found: 335.1199. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.83 (d, *J* = 4.9 Hz, 2H), 7.96 (dd, *J* = 23.6, 7.9 Hz, 3H), 7.68 – 7.49 (m, 5H), 7.24 (d, *J* = 4.9 Hz, 1H), 6.10 (d, *J* = 37.0 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 167.0, 165.3, 160.6 (d, *J* = 267.4 Hz), 157.2, 138.8 (d, *J* = 4.0 Hz), 137.9, 132.8 (d, *J* = 25.2 Hz), 131.1, 130.1, 130.0 (d, *J* = 4.8 Hz), 129.9, 129.7, 128.7 (d, *J* = 8.1 Hz), 128.5 (d, *J* = 2.6 Hz), 119.2, 108.5 (d, *J* = 9.7 Hz), 52.2. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -91.7 (d, *J* = 37.1 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{15}FN_2O_2H$ $[M+H]^+$ 335.1196, found: 335.1206.

Methyl 4-(2-(2-(1*H*-pyrazol-1-yl)phenyl)-2-fluorovinyl)benzoate (3wa)



Following General Method C, **3wa** was obtained as a colourless oil of inseparable *E/Z* mixture (0.057 mmol, 18.4 mg, 38%, *E/Z* 40/60) using EA/PE (5%-20%) as eluent. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.00 – 7.60 (m, 5H), 7.58 – 7.48 (m, 3H), 7.47 – 7.34 (m, 1H), 7.20 – 6.78 (m, 1H), 6.49 – 5.50 (m, 2H), 3.88 (d, *J* = 20.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.9, 166.8, 157.4 (d, *J* = 254.0 Hz, ***E isomer***), 156.2 (d, *J* = 263.5 Hz, ***Z isomer***), 141.3, 141.2, 139.8, 138.4 (d, *J* = 2.0 Hz), 138.0 (d, *J* = 3.5 Hz), 137.7 (d, *J* = 11.7 Hz), 132.0 (d, *J* = 2.1 Hz), 131.6 (d, *J* = 2.4 Hz), 130.6, 129.9, 129.8 (d, *J* = 1.7 Hz), 129.7, 129.5 (d, *J* = 5.9 Hz), 129.0 (d, *J* = 8.2 Hz), 129.0 (d, *J* = 2.3 Hz), 128.7 (d, *J* = 1.5 Hz), 128.6, 128.3 (d, *J* = 2.9 Hz), 128.0 (d, *J* = 1.5 Hz), 127.2, 126.7, 126.0 (d, *J* = 26.5 Hz), 125.7 (d, *J* = 1.1 Hz), 111.3 (d, *J* = 30.4 Hz), 109.9 (d, *J* = 8.6 Hz), 107.5 (d, *J* = 8.1 Hz), 52.2, 52.2. ***(E* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -85.9 (d, *J* = 18.9 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -101.0 (d, *J* = 38.8 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{19}H_{15}FN_2O_2H$ $[M+H]^+$ 323.1196, found: 323.1201.

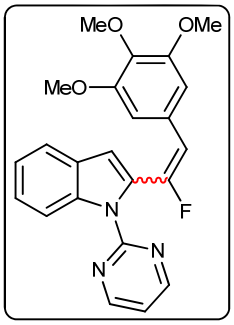
2-(1-fluoro-2-(4-methoxyphenyl)vinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3ab)



Following General Method C, 3**ab** was obtained as colourless oil (0.090 mmol, 31.1 mg, 60%, *E/Z* 50/50) using EA/PE (2%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 10 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.73 (d, *J* = 4.8 Hz, 2H), 8.48 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.36 (ddt, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.13 – 7.07 (m, 3H), 6.81 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.70 – 6.64 (m, 2H), 6.42 (d, *J* = 18.9 Hz, 1H), 3.71 (s, 3H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.7 (d, *J* = 0.8 Hz), 158.2, 157.6, 151.1 (d, *J* = 242.3 Hz), 137.1 (d, *J* = 1.8 Hz), 130.4 (d, *J* = 28.2 Hz), 129.7 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 1.6 Hz), 126.4 (d, *J* = 10.3 Hz), 125.1 (d, *J* = 0.8 Hz), 122.5, 121.6 (d, *J* = 1.1 Hz), 117.4, 115.0, 113.9, 112.5 (d, *J* = 5.8 Hz), 111.2 (d, *J* = 30.5 Hz), 55.3. **^{19}F NMR (376 MHz, CDCl3):** δ -94.1 (dd, *J* = 19.0, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{21}H_{16}FN_3OH$ $[M+H]^+$ 346.1356, found: 346.1360. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.40 – 8.24 (m, 1H), 7.62 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.32 (ddd, *J* = 8.4, 7.2,

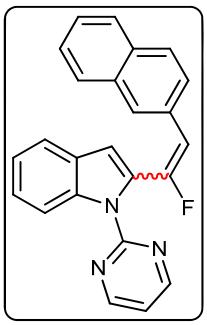
1.3 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.94 (dd, *J* = 2.5, 0.8 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.21 (d, *J* = 36.7 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 159.0 (d, *J* = 3.1 Hz), 158.4, 157.8, 150.8 (d, *J* = 256.1 Hz), 137.7, 132.7 (d, *J* = 25.4 Hz), 130.4 (d, *J* = 7.4 Hz), 128.7, 126.8 (d, *J* = 4.1 Hz), 124.9, 122.6, 121.2, 117.7, 114.1, 114.1, 110.6 (d, *J* = 5.4 Hz), 108.8 (d, *J* = 10.6 Hz), 55.43. **^{19}F NMR (376 MHz, CDCl3):** δ -103.7 (dd, *J* = 36.7, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{21}H_{16}FN_3OH$ $[M+H]^+$ 346.1356, found: 346.1359.

2-(1-fluoro-2-(3,4,5-trimethoxyphenyl)vinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3ac)



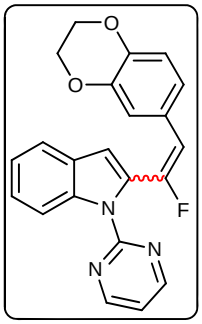
Following General Method C, **3ac** was obtained as colourless oil (0.126 mmol, 51.3 mg, 84%, *E*/*Z* 27/73) using EA/PE (5%-40%) as eluent. *E*/*Z* single isomer isolated by PTLC using 15% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.66 (d, *J* = 4.8 Hz, 2H), 8.39 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.19 – 7.14 (m, 1H), 7.04 (t, *J* = 4.8 Hz, 1H), 6.87 (d, *J* = 3.4 Hz, 1H), 6.32 (d, *J* = 18.1 Hz, 1H), 6.19 (s, 2H), 3.69 (s, 3H), 3.43 (s, 6H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.2, 157.4, 153.0, 151.8 (d, *J* = 245.8 Hz), 137.1 (d, *J* = 1.1 Hz), 136.9 (d, *J* = 2.1 Hz), 130.0 (d, *J* = 32.0 Hz), 129.2 (d, *J* = 11.0 Hz), 128.7 (d, *J* = 1.8 Hz), 125.3 (d, *J* = 1.0 Hz), 122.6, 121.6 (d, *J* = 1.1 Hz), 117.4, 114.9, 112.5 (d, *J* = 4.7 Hz), 112.0 (d, *J* = 31.6 Hz), 105.4 (d, *J* = 2.7 Hz), 61.0, 55.9. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -91.5 (dd, *J* = 18.1, 3.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{20}FN_3O_3H$ $[M+H]^+$ 406.1567, found: 406.1569. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.78 (d, J = 4.8 Hz, 2H), 8.35 (dd, J = 8.4, 0.9 Hz, 1H), 7.62 (dt, J = 7.8, 1.0 Hz, 1H), 7.34 (ddd, J = 8.5, 7.1, 1.3 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.17 (t, J = 4.8 Hz, 1H), 6.96 (dd, J = 2.5, 0.7 Hz, 1H), 6.83 (s, 2H), 6.19 (d, J = 35.7 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 6H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.4, 157.7, 153.2, 151.8 (d, *J* = 257.9 Hz), 137.7, 132.4 (d, *J* = 24.9 Hz), 129.6 (d, *J* = 4.3 Hz), 128.6, 125.1, 122.6, 121.3, 117.7, 114.2, 111.2 (d, *J* = 5.5 Hz), 109.2 (d, *J* = 10.1 Hz), 106.3 (d, *J* = 8.3 Hz), 61.1, 56.2. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -101.4 (dd, *J* = 35.7, 2.7 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{23}H_{20}FN_3O_3H$ $[M+H]^+$ 406.1567, found: 406.1581.

2-(1-fluoro-2-(naphthalen-2-yl)vinyl)-1-(pyrimidin-2-yl)-1H-indole (3ad)



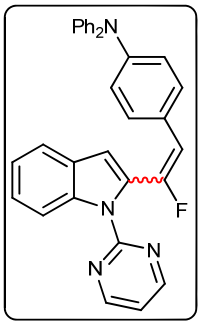
Following General Method C, **3ad** was obtained as yellow oil (0.113 mmol, 41.3 mg, 75%, *E*/*Z* 19/81) using EA/PE (2%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.54 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.75 – 7.65 (m, 3H), 7.55 (t, *J* = 8.4 Hz, 2H), 7.44 – 7.32 (m, 4H), 7.26 – 7.21 (m, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.84 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.65 (d, *J* = 18.7 Hz, 1H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.2, 157.6, 152.7 (d, *J* = 244.2 Hz), 137.2 (d, *J* = 1.6 Hz), 133.5, 132.5, 131.7 (d, *J* = 10.7 Hz), 130.3, 130.0, 128.8 (d, *J* = 1.1 Hz), 128.0 (d, *J* = 7.0 Hz), 127.8 (d, *J* = 4.1 Hz), 127.7, 126.4 (d, *J* = 1.8 Hz), 126.2, 125.9, 125.3 (d, *J* = 0.9 Hz), 122.5, 121.7, 117.4, 115.0, 113.2 (d, *J* = 5.6 Hz), 111.7 (d, *J* = 31.1 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -91.7 (dd, *J* = 18.8, 3.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{16}FN_3H$ $[M+H]^+$ 366.1407, found: 366.1400. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 1.6 Hz, 1H), 7.88 – 7.72 (m, 4H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.46 (tt, *J* = 5.7, 4.6 Hz, 2H), 7.37 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 36.3 Hz, 1H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.4, 157.8, 152.4 (d, *J* = 259.3 Hz), 137.8, 133.6, 132.7, 132.7, 132.4, 131.6 (d, *J* = 4.4 Hz), 128.7, 128.3, 128.1, 128.1, 127.7, 127.0 (d, *J* = 8.0 Hz), 126.3 (d, *J* = 15.0 Hz), 125.1, 122.7, 121.4, 117.7, 114.2, 111.2 (d, *J* = 5.4 Hz), 109.3 (d, *J* = 10.2 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -100.2 (dd, *J* = 36.2, 2.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{24}H_{16}FN_3H$ $[M+H]^+$ 366.1407, found: 346.1405.

2-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3ae)



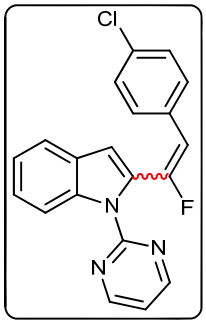
Following General Method C, **3ae** was obtained as a colourless oil of inseparable *E/Z* mixture (0.113 mmol, 41.9 mg, 75%, *E/Z* 35/65) using EA/PE (2%-20%) as eluent. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 (dd, *J* = 13.7, 4.8 Hz, 2H), 8.43 (ddd, *J* = 71.7, 8.5, 0.9 Hz, 1H), 7.70 – 7.51 (m, 1H), 7.41 – 7.31 (m, 1H), 7.30 – 7.18 (m, 2H), 7.14 (dt, *J* = 20.4, 4.8 Hz, 1H), 7.09 – 6.93 (m, 1H), 6.89 – 6.82 (m, 1H), 6.79 – 6.61 (m, 1H), 6.45 – 6.07 (m, 1H), 4.31 – 4.11 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.4, 158.2, 157.8, 157.6, 151.5 (d, *J* = 243.2 Hz, ***E***), 151.1 (d, *J* = 256.2 Hz, ***Z***), 143.5, 143.3, 143.2 (d, *J* = 2.9 Hz), 142.8 (d, *J* = 1.0 Hz), 137.7, 137.1 (d, *J* = 1.8 Hz), 132.7 (d, *J* = 25.4 Hz), 130.2 (d, *J* = 29.1 Hz), 128.8 (d, *J* = 1.6 Hz), 128.7, 127.6 (d, *J* = 4.1 Hz), 127.4 (d, *J* = 10.6 Hz), 125.1 (d, *J* = 1.1 Hz), 124.9, 122.7, 122.6, 122.5, 122.4, 122.0 (d, *J* = 2.8 Hz), 121.6 (d, *J* = 1.1 Hz), 121.3, 117.7, 117.7, 117.6, 117.4, 117.3, 117.2, 115.0, 114.1, 112.7 (d, *J* = 5.7 Hz), 111.1, 110.8, 110.7 (d, *J* = 5.7 Hz), 108.7 (d, *J* = 10.2 Hz), 64.6, 64.5, 64.5, 64.3. ***(E* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -93.2 (dd, *J* = 19.0, 3.6 Hz, 1F). ***(Z* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** -102.7 (dd, *J* = 36.2, 2.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{16}FN_3O_2H$ $[M+H]^+$ 374.1305, found: 374.1310.

4-(2-fluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)-*N,N*-diphenylaniline (3af)



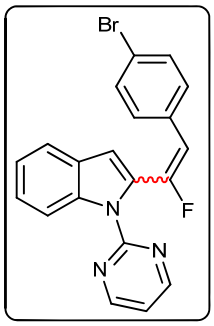
Following General Method C, **3af** was obtained as yellow solid (0.123 mmol, 59.5 mg, 82%, *E/Z* 53/47) using EA/PE (2%-20%) as eluent. *E/Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer, but *E* isomer convert to *Z* isomer slowly even though at -10 °C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.78 (dd, *J* = 20.7, 4.8 Hz, 2H), 8.43 (dd, *J* = 62.8, 8.3 Hz, 1H), 7.63 (dd, *J* = 14.3, 7.8 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.36 (q, *J* = 8.1 Hz, 1H), 7.31 – 7.16 (m, 6H), 7.13 (d, *J* = 7.7 Hz, 3H), 7.10 – 6.96 (m, 6H), 6.95 – 6.80 (m, 1H), 6.52 – 6.12 (m, 1H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.4, 158.2, 157.8, 157.6, 151.3 (d, *J* = 243.2 Hz, ***E***), 151.2 (d, *J* = 256.7 Hz, ***Z***), 147.6, 147.6, 147.1 (d, *J* = 2.9 Hz), 146.7 (d, *J* = 0.9 Hz), 137.7, 137.1 (d, *J* = 1.7 Hz), 132.8 (d, *J* = 27.3 Hz), 130.4 (d, *J* = 29.0 Hz), 129.9 (d, *J* = 8.0 Hz), 129.4, 129.3, 129.2 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 1.4 Hz), 128.7, 128.1 (d, *J* = 4.4 Hz), 127.7 (d, *J* = 10.3 Hz), 125.1, 124.9, 124.7, 124.6, 123.4, 123.2, 123.2, 123.1, 122.6, 122.5, 121.6, 121.2, 117.7, 117.3, 115.0, 114.1, 112.6 (d, *J* = 5.6 Hz), 111.4 (d, *J* = 31.0 Hz), 110.7 (d, *J* = 4.8 Hz), 108.9 (d, *J* = 10.4 Hz). ***(E* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -93.0 (dd, *J* = 19.0, 3.7 Hz, 1F). ***(Z* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -102.7 (dd, *J* = 36.7, 2.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{32}H_{23}FN_4H$ $[M+H]^+$ 483.1985, found: 483.1990. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.34 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.35 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.15 – 7.10 (m, 4H), 7.08 – 7.01 (m, 4H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.24 (d, *J* = 36.7 Hz, 1H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.4, 157.8, 151.1 (d, *J* = 258.7 Hz), 147.6, 147.0 (d, *J* = 2.9 Hz), 137.7, 132.8, 132.6, 129.9 (d, *J* = 8.0 Hz), 129.4, 128.7, 128.1 (d, *J* = 4.6 Hz), 124.9, 124.7, 123.3 (d, *J* = 14.0 Hz), 122.6, 121.2, 117.7, 114.0, 110.7 (d, *J* = 5.0 Hz), 108.8 (d, *J* = 10.6 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -102.7 (dd, *J* = 36.7, 2.4 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{32}H_{23}FN_4H$ $[M+H]^+$ 483.1985, found: 483.1986.

2-(2-(4-chlorophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3ag)



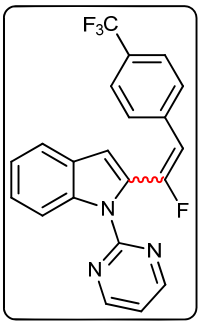
Following General Method C, **3ag** was obtained as yellow oil (0.108 mmol, 37.8 mg, 72%, *E*/*Z* 74/26) using EA/PE (2%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.74 (d, *J* = 4.8 Hz, 2H), 8.51 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.38 (ddt, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.18 – 7.06 (m, 5H), 6.79 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.41 (d, *J* = 18.1 Hz, 1H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.3, 157.5, 152.7 (d, *J* = 246.2 Hz), 137.1 (d, *J* = 1.8 Hz), 132.7, 132.7 (d, *J* = 1.4 Hz), 132.6 (d, *J* = 10.8 Hz), 129.9 (d, *J* = 3.0 Hz), 128.7 (d, *J* = 1.6 Hz), 128.6, 125.4 (d, *J* = 1.1 Hz), 122.6, 121.7 (d, *J* = 1.1 Hz), 117.4, 115.0, 112.9 (d, J = 6.0 Hz), 110.3 (d, *J* = 31.0 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -90.8 (dd, *J* = 18.0, 3.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{13}ClFN_3H$ $[M+H]^+$ 350.0860, found: 350.0874. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.37 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.39 – 7.30 (m, 3H), 7.28 – 7.23 (m, 1H), 7.18 (t, *J* = 4.8 Hz, 1H), 7.00 (dd, *J* = 2.6, 0.8 Hz, 1H), 6.24 (d, *J* = 35.7 Hz, 1H). **^{13}C NMR (400 MHz, CDCl$_3$):** δ 158.4, 157.7, 152.6 (d, *J* = 259.4 Hz), 137.7, 133.0 (d, *J* = 3.4 Hz), 132.5 (d, *J* = 4.2 Hz), 132.1 (d, *J* = 25.3 Hz), 130.2, 132.0, 128.8, 125.3, 122.7, 121.4, 117.7, 114.2, 111.4 (d, *J* = 5.6 Hz), 108.1 (d, *J* = 10.2 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -99.5 (dd, *J* = 35.5, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{13}ClFN_3H$ $[M+H]^+$ 350.0860, found: 350.0863.

2-(2-(4-bromophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3ah)



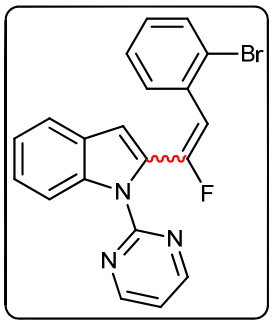
Following General Method C, **3ah** was obtained as yellow oil (0.113 mmol, 44.1 mg, 75%, *E*/*Z* 75/25) using EA/PE (5%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.75 (d, J = 4.8 Hz, 2H), 8.52 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.39 (ddt, J = 8.4, 7.2, 1.1 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.13 (t, J = 4.8 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.80 (d, J = 3.5 Hz, 1H), 6.40 (d, J = 18.0 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.2, 157.5, 152.8 (d, *J* = 246.5 Hz), 137.2 (d, *J* = 1.8 Hz), 133.2 (d, *J* = 10.5 Hz), 131.6, 130.2 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 27.9 Hz), 128.7 (d, *J* = 1.5 Hz), 125.4 (d, *J* = 1.1 Hz), 122.7, 121.7, 120.9 (d, *J* = 1.1 Hz), 117.4, 115.0, 112.9 (d, *J* = 6.0 Hz), 110.4 (d, *J* = 31.0 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -90.5 (dd, J = 18.1, 3.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{13}BrFN_3H$ $[M+H]^+$ 394.0355, found: 394.0356. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.37 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.54 – 7.41 (m, 4H), 7.36 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.31 – 7.21 (m, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.00 (dd, *J* = 2.5, 0.8 Hz, 1H), 6.23 (d, *J* = 35.7 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.4, 157.7, 152.7 (d, *J* = 258.8 Hz), 137.8, 132.9 (d, *J* = 4.3 Hz), 132.2 (d, *J* = 25.4 Hz), 131.8, 130.5 (d, *J* = 8.2 Hz), 128.6, 125.3, 122.7, 121.4, 121.2 (d, *J* = 3.5 Hz), 117.7, 114.3, 111.4 (d, *J* = 6.1 Hz), 108.1 (d, *J* = 10.0 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -99.2 (dd, *J* = 36.1, 2.7 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{13}BrFN_3H$ $[M+H]^+$ 394.0355, found: 394.0375.

2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3ai)



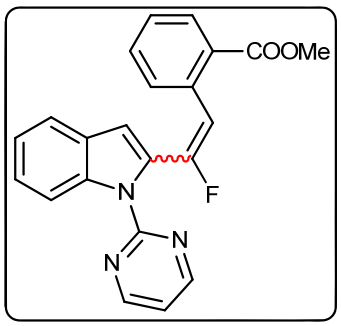
Following General Method C, **3ai** was obtained as yellow oil (0.075 mmol, 28.9 mg, 50%, *E*/*Z* 76/24) using EA/PE (2%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 2% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.56 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.41 (dd, *J* = 8.5, 7.1 Hz, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.82 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.50 (d, *J* = 17.7 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.3, 157.5, 153.9 (d, *J* = 251.8 Hz), 138.1 (d, *J* = 1.4 Hz), 138.0 (d, *J* = 1.4 Hz), 137.2 (d, *J* = 1.6 Hz), 129.5 (d, *J* = 28.0 Hz), 129.0 (d, *J* = 1.1 Hz), 128.8 (d, *J* = 3.0 Hz), 128.7 (d, *J* = 1.7 Hz), 125.6 (q, *J* = 2.3 Hz), 125.4 (q, *J* = 4.0 Hz), 122.7, 121.8 (d, *J* = 1.2 Hz), 117.5, 115.2, 113.3 (d, *J* = 6.0 Hz), 110.3 (d, *J* = 31.1 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.6 (s, 3F), δ -88.3 (dd, *J* = 17.8, 3.7 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{21}H_{13}F_4N_3H$ $[M+H]^+$ 384.1124, found: 384.1134. ***Z* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.41 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.73 – 7.57 (m, 5H), 7.39 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.32 – 7.24 (m, 1H), 7.18 (t, *J* = 4.8 Hz, 1H), 7.04 (dd, *J* = 2.5, 0.8 Hz, 1H), 6.32 (d, *J* = 35.3 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.4, 157.7, 153.8 (d, *J* = 263.0 Hz), 137.9, 137.6 (m), 131.9 (d, *J* = 25.0 Hz), 129.2 (d, *J* = 2.7 Hz), 129.1 (d, *J* = 8.2 Hz), 128.9 (d, *J* = 2.6 Hz), 128.5, 125.6 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.3 Hz), 122.8, 121.5, 117.7, 114.4, 111.8 (d, *J* = 5.5 Hz), 107.9 (d, *J* = 9.6 Hz). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.5 (s, 3F), δ -97.0 (dd, *J* = 35.4, 2.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{21}H_{13}F_4N_3H$ $[M+H]^+$ 384.1124, found: 384.1129.

2-(2-(2-bromophenyl)-1-fluorovinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3aj)



Following General Method C, **3aj** was obtained as a colourless oil of inseparable *E*/*Z* mixture (0.053 mmol, 20.9 mg, 35%, *E*/*Z* 39/61) using EA/PE (2%-20%) as eluent. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 (dd, *J* = 22.1, 4.8 Hz, 2H), 8.39 (ddd, *J* = 14.3, 8.5, 0.9 Hz, 1H), 7.95 – 7.14 (m, 6H), 7.13 – 6.74 (m, 3H), 6.68 – 6.51 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.4, 158.2, 157.7, 157.4, 153.4 (d, *J* = 248.9 Hz),153.0 (d, *J* = 260.3 Hz), 137.9, 137.3 (d, *J* = 1.7 Hz), 134.7 (d, *J* = 11.4 Hz), 133.6 (d, *J* = 4.4 Hz), 133.0, 132.3, 132.1 (d, *J* = 26.3 Hz), 131.1 (d, *J* = 1.1 Hz), 130.6 (d, *J* = 12.9 Hz), 129.7 (d, *J* = 30.0 Hz), 128.7 (d, *J* = 1.8 Hz), 128.6, 128.6, 127.5, 127.4, 125.3 (d, *J* = 3.3 Hz), 124.2 (d, *J* = 4.3 Hz), 123.8 (d, *J* = 1.4 Hz), 122.7, 122.5, 121.6 (d, *J* = 0.7 Hz), 121.5, 117.7, 117.4, 114.7, 114.3, 113.0 (d, *J* = 5.0 Hz), 111.7 (d, *J* = 5.0 Hz), 110.7 (d, *J* = 32.0 Hz), 107.6 (d, *J* = 9.0 Hz). ***(E* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ -92.4 (dd, *J* = 17.2, 3.1 Hz, 1F), ***(Z* isomer) ^{19}F NMR (376 MHz, CDCl$_3$):** δ-100.6 (dd, *J* = 35.4, 2.3 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{20}H_{13}BrFN_3H$ $[M+H]^+$ 394.0355, found: 394.0360.

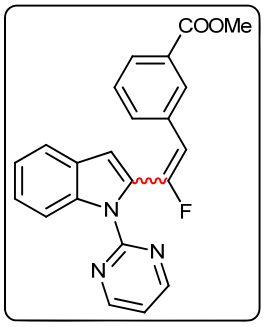
Methyl 2-(2-fluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3ak)



Following General Method C, **3ak** was obtained as yellow oil (0.086 mmol, 32.1 mg, 57%, *E*/*Z* 29/81) using EA/PE (5%-20%) as eluent. *E*/*Z* single isomer isolated by PTLC using 5% EtOAc/PE as eluent (repeat 6 times) to get the single isomer. ***E* isomer: ^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.42 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.91 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.33 (ddt, *J* = 8.2, 7.1, 1.0 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.14 (t, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 17.6 Hz, 1H), 6.61 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 167.6, 158.2, 157.6, 152.6 (d, *J* = 246.2 Hz), 137.2 (d, *J* = 1.1 Hz), 136.1 (d, *J* = 11.4 Hz), 132.2, 131.7 (d, *J* = 1.2 Hz), 130.5, 130.0, 129.0 (d, *J* = 3.6 Hz), 128.7, 127.0, 125.1, 122.4, 121.6, 117.4, 114.6, 113.3 (d, *J* = 5.4 Hz), 111.4 (d, *J* = 31.8 Hz), 52.2. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -94.3 (dd, *J* = 17.7, 3.2 Hz, 1F). **HRMS (ESI, m/z):** calcd.

for $C_{22}H_{16}FN_3O_2H$ $[M+H]^+$ 374.1305, found: 374.1318. ***Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.83 – 8.70 (m, 2H), 8.41 – 8.28 (m, 1H), 8.01 – 7.83 (m, 2H), 7.67 – 7.57 (m, 1H), 7.48 (td, *J* = 7.7, 1.5 Hz, 1H), 7.30 (dtd, *J* = 16.7, 7.4, 1.3 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.14 (t, *J* = 4.8 Hz, 1H), 7.09 – 7.05 (m, 1H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.9, 158.3, 157.8, 152.4 (d, *J* = 259.3 Hz), 137.8, 134.6 (d, *J* = 3.4 Hz), 132.5 (d, *J* = 26.7 Hz), 132.0, 130.8, 130.7 (d, *J* = 11.0 Hz), 128.8, 128.7, 127.1 (d, *J* = 0.9 Hz), 125.1, 122.6, 121.4, 117.6, 114.3, 111.6 (d, *J* = 5.5 Hz), 106.8 (d, *J* = 8.0 Hz), 52.3. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -102.28 (dd, *J* = 35.7, 2.6 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{16}FN_3O_2H$ $[M+H]^+$ 374.1305, found: 374.1309.

Methyl 3-(2-fluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)vinyl)benzoate (3al)



Following General Method C, **3al** was obtained as a yellow oil of inseparable *E/Z* mixture (0.084 mmol, 31.5 mg, 56%, *E/Z* 70/30) using EA/PE (2%-20%) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (dd, *J* = 17.5, 4.8 Hz, 2H), 8.54 – 8.16 (m, 1H), 7.96 – 7.72 (m, 2H), 7.67 – 7.49 (m, 1H), 7.46 – 7.31 (m, 2H), 7.28 – 7.06 (m, 3H), 6.88 (ddd, *J* = 89.5, 3.0, 0.8 Hz, 1H), 6.48 (d, *J* = 17.8 Hz, 0.7H, *E* isomer), 6.30 (d, *J* = 35.6 Hz, 0.3H, *Z* isomer), 3.90 (s, 0.9H, *Z* isomer), 3.80 (s, 2.1H, *E* isomer). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.1, 167.0 (*E*), 158.4, 158.2 (*E*), 157.7, 157.5 (*E*), 153.2 (d, *J* = 274.5 Hz, *E*), 153.0 (d, *J* = 260.1 Hz, *Z*), 137.8, 137.2 (d, *J* = 1.7 Hz), 134.6 (d, *J* = 10.5 Hz), 134.4 (d, *J* = 4.1 Hz), 133.2 (d, *J* = 8.8 Hz), 132.7 (d, *J* = 2.2 Hz), 132.1 (d, *J* = 25.2 Hz), 130.6, 130.4, 130.1 (d, *J* = 7.7 Hz), 130.0 (d, *J* = 3.3 Hz), 129.7 (d, *J* = 28.5 Hz), 128.8, 128.7 (d, *J* = 1.7 Hz), 128.6, 128.5, 128.4 (d, *J* = 2.1 Hz), 128.1 (d, *J* = 1.0 Hz), 125.4 (d, *J* = 1.0 Hz), 125.3, 122.7, 122.6, 121.7 (d, *J* = 0.9 Hz), 121.4, 117.7, 117.4, 115.1, 114.3, 113.1 (d, *J* = 5.4 Hz), 111.5 (d, *J* = 5.5 Hz), 110.6 (d, *J* = 32.0 Hz), 108.3 (d, *J* = 10.2 Hz), 52.3, 52.2 (*E*). ***(E* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.4 (dd, *J* = 17.8, 3.5 Hz, 1F). ***(Z* isomer) ^{19}F NMR (376 MHz, $CDCl_3$):** -98.9 (d, *J* = 35.5 Hz, 1F). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{16}FN_3O_2H$ $[M+H]^+$ 374.1305, found: 374.1314.

6. References

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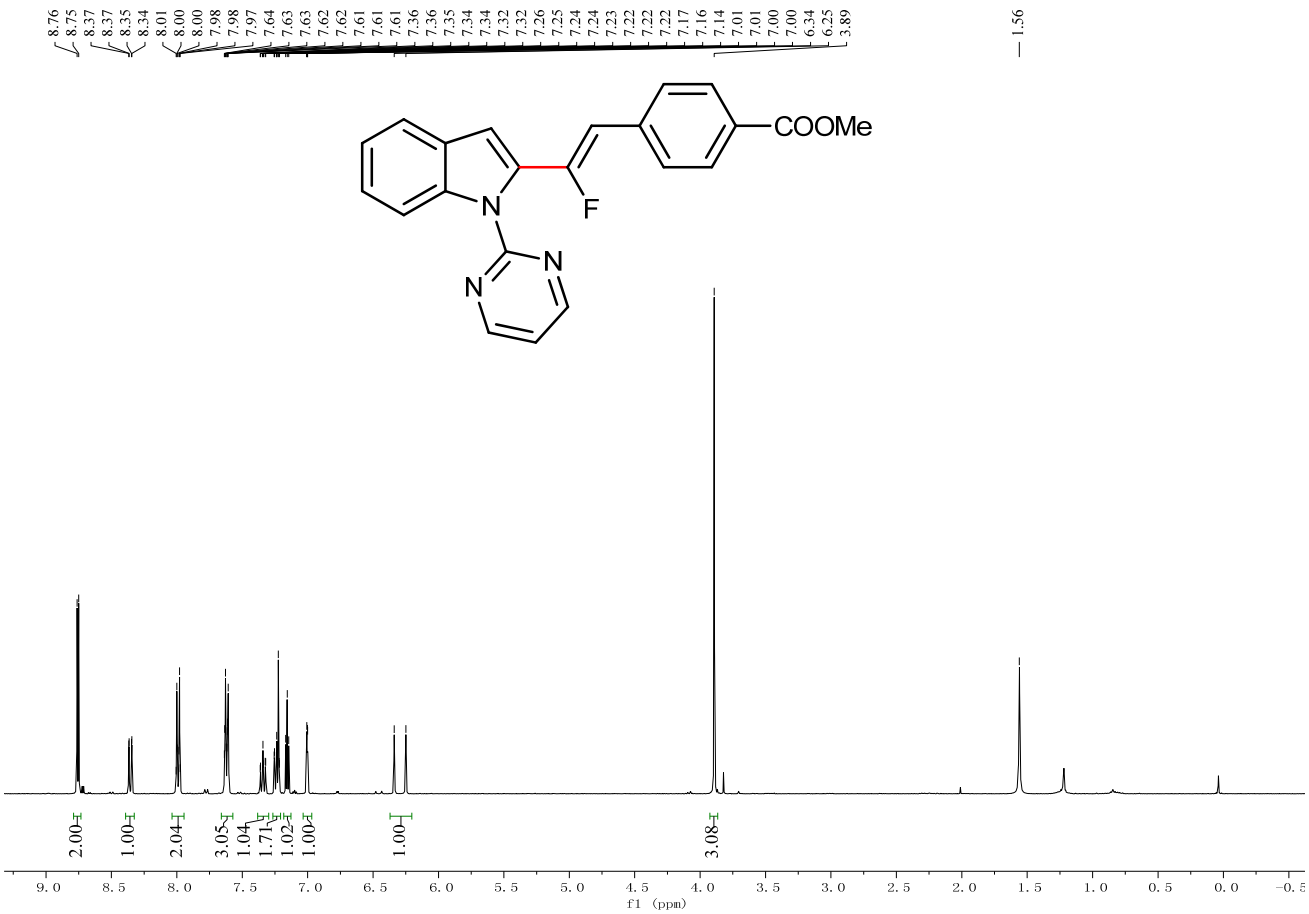
7. ^{1}H and ^{13}C NMR spectra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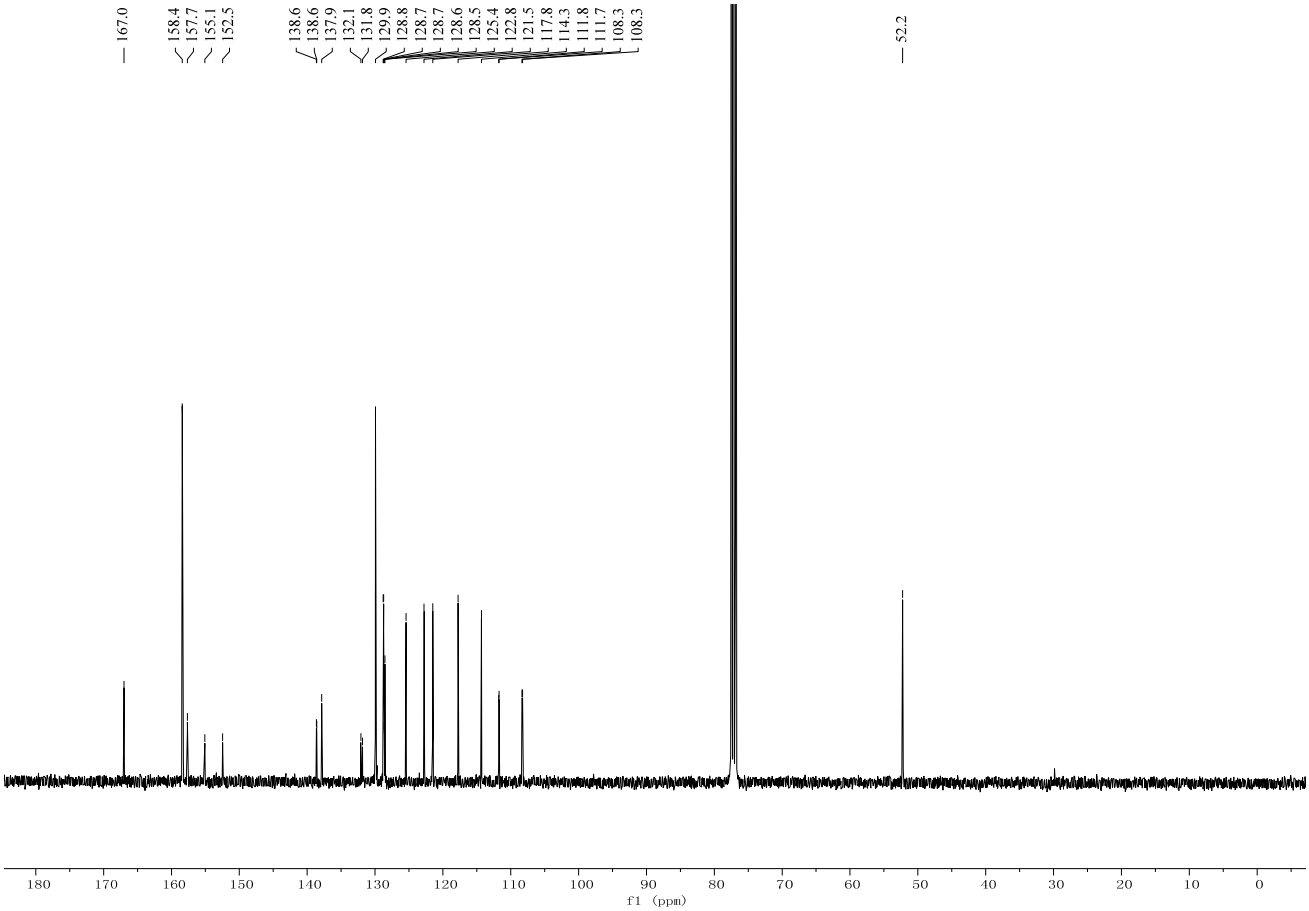
f1 (ppm)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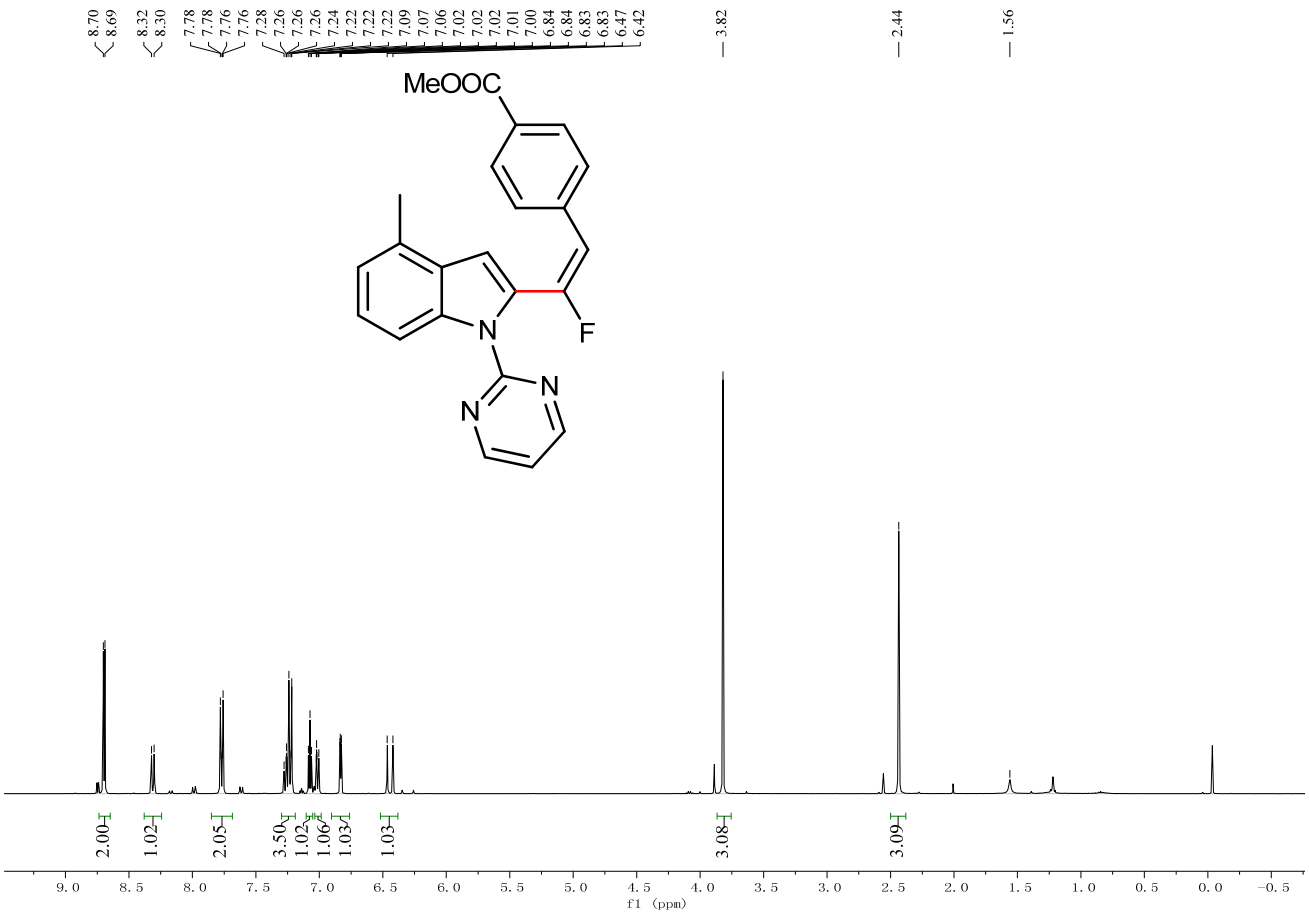
f1 (ppm)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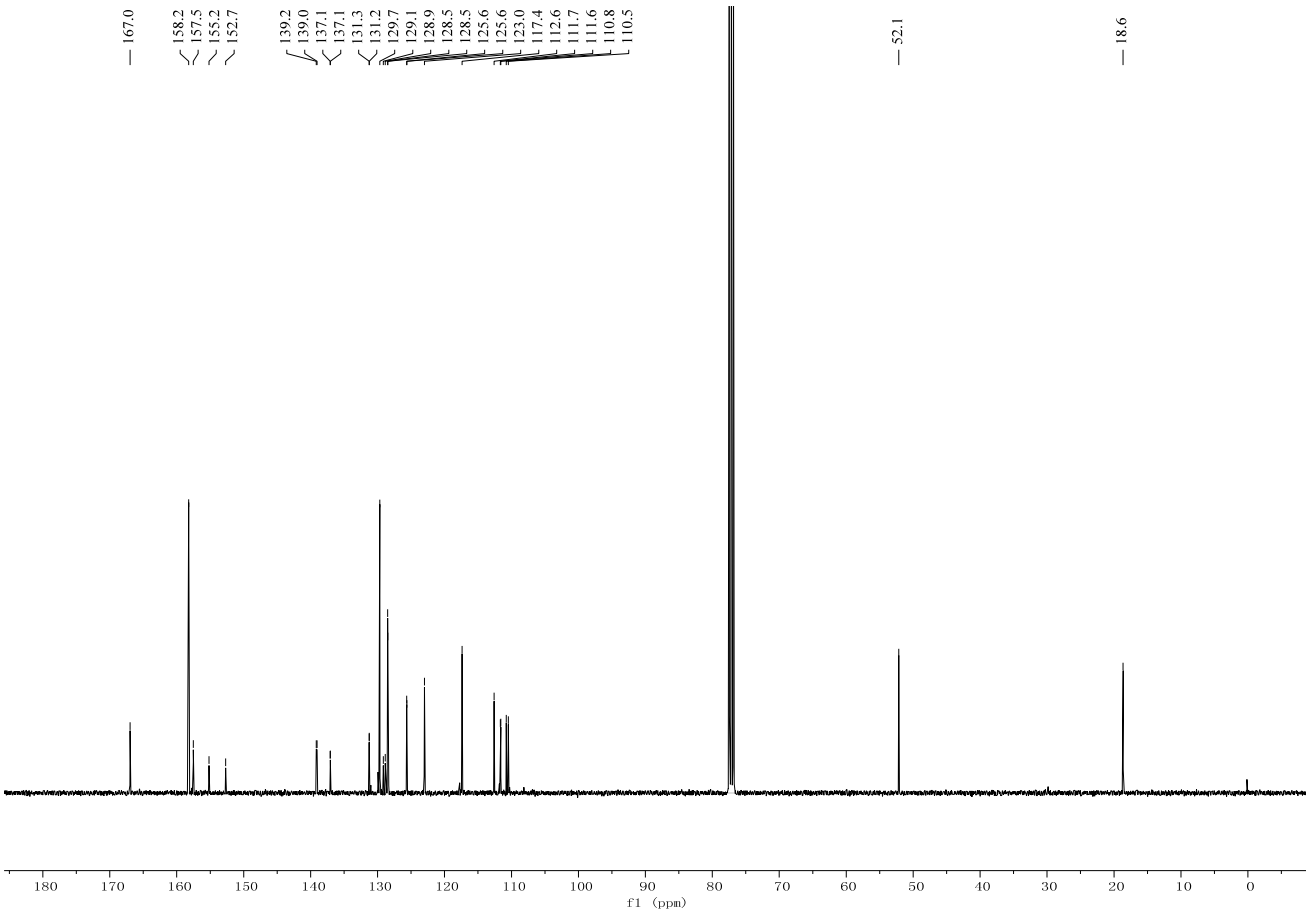
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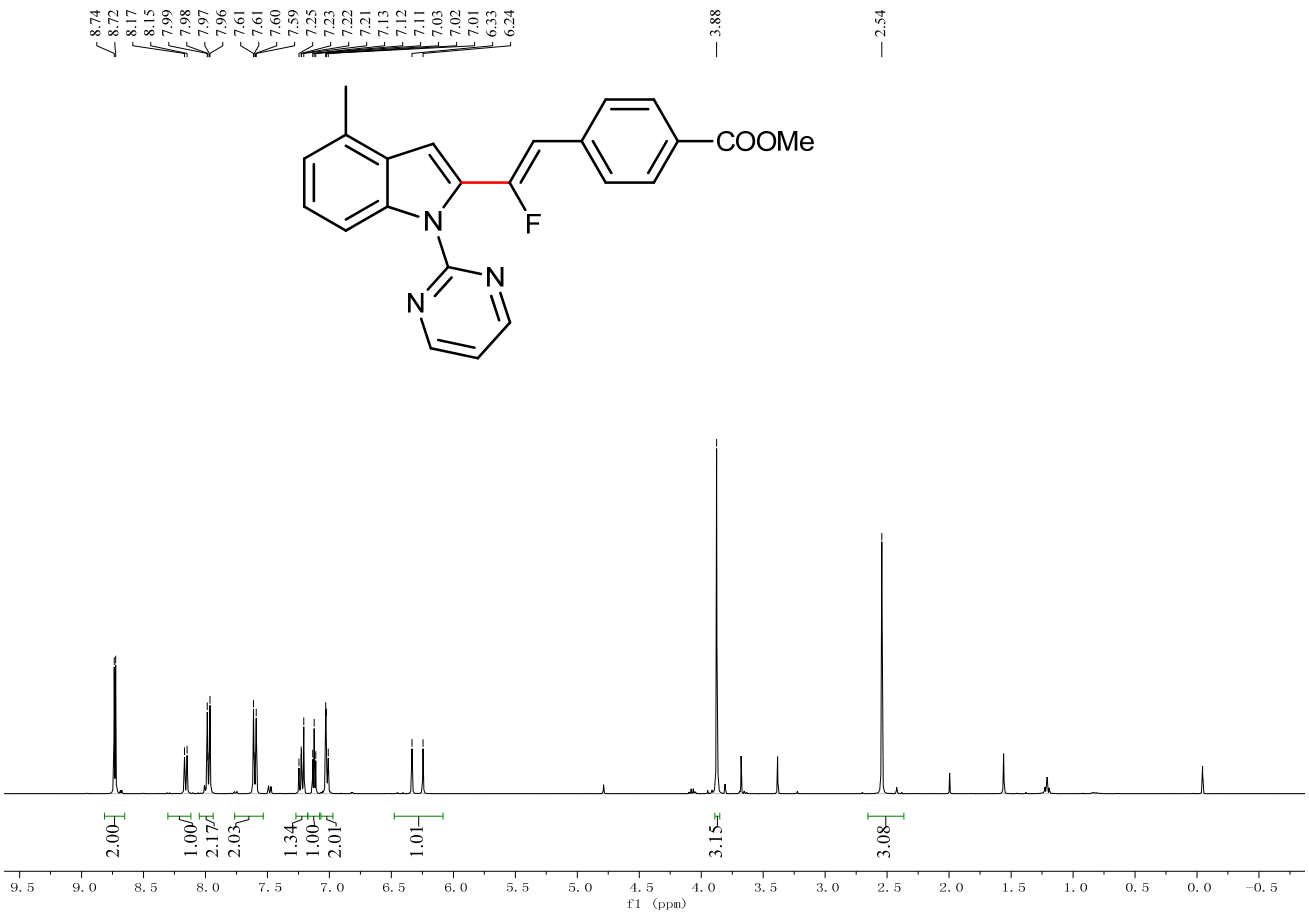
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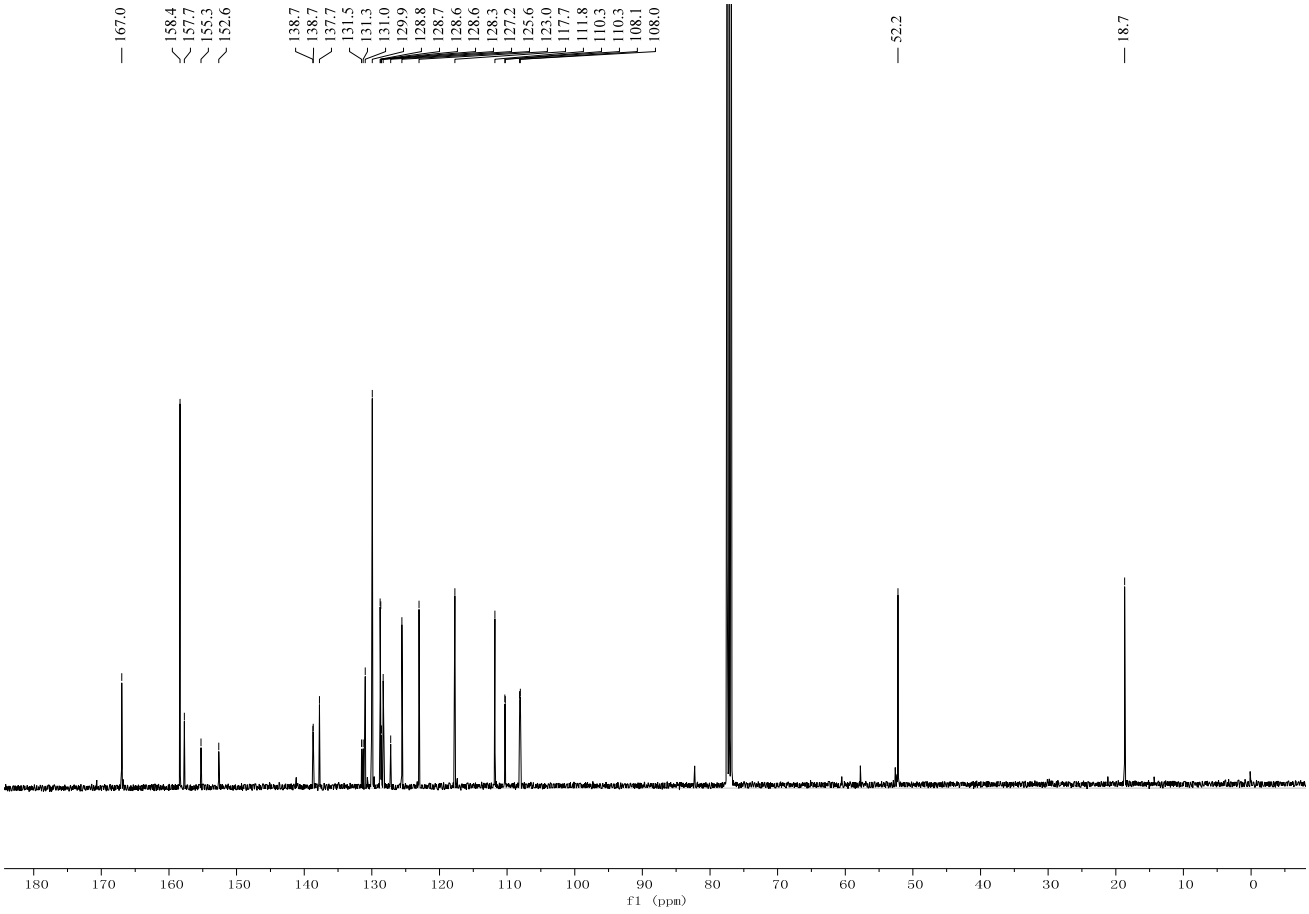
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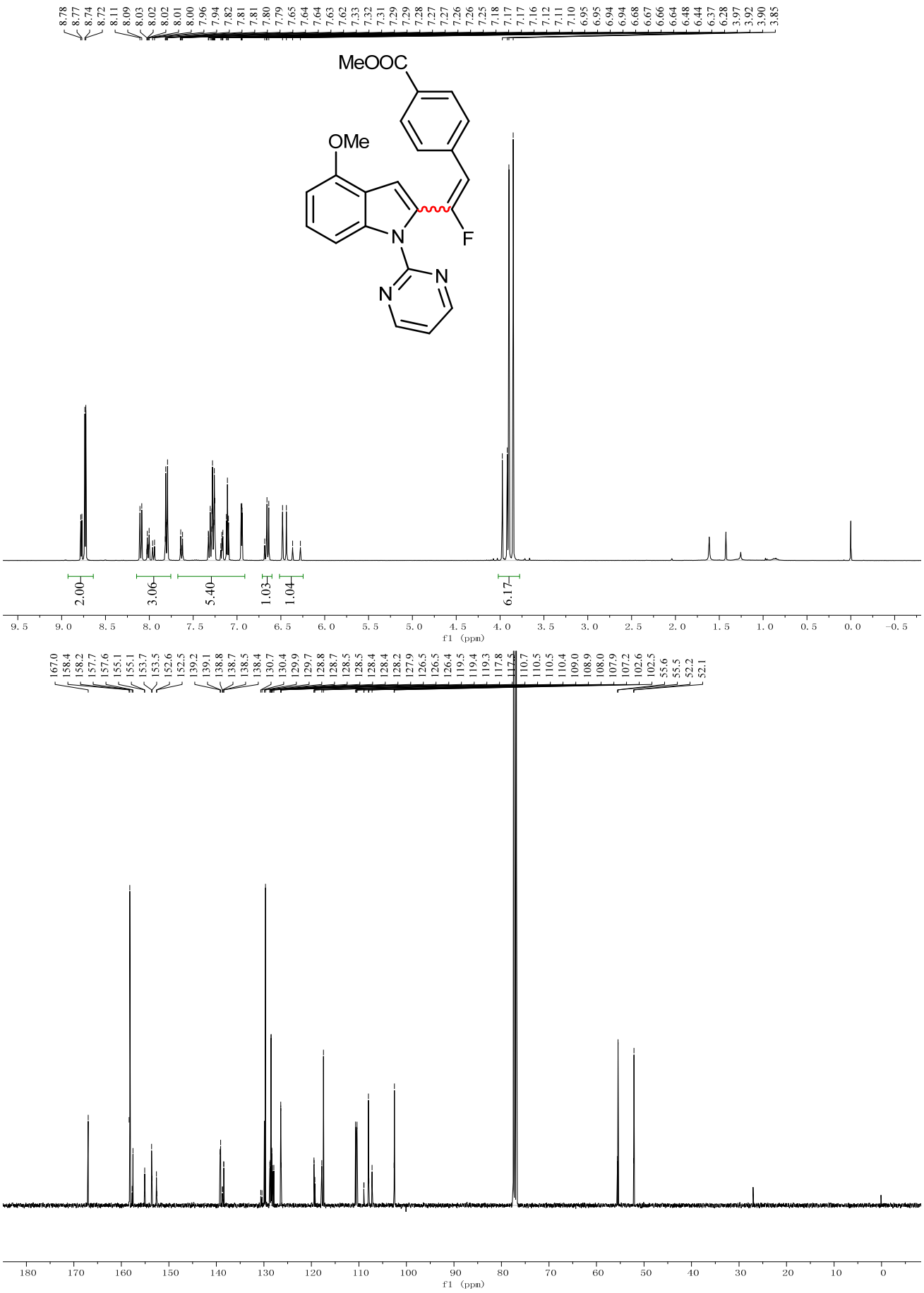
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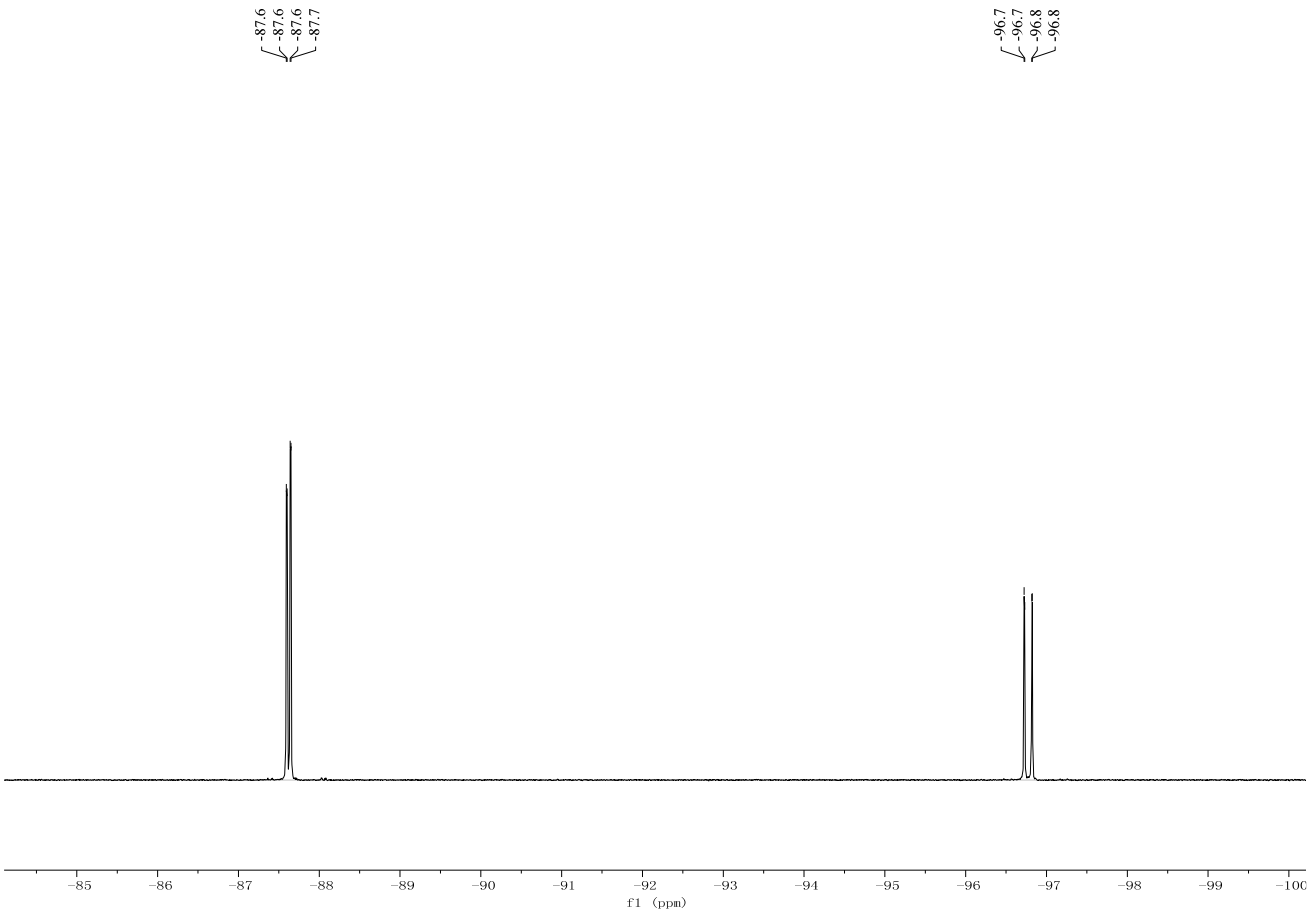
f1 (ppm)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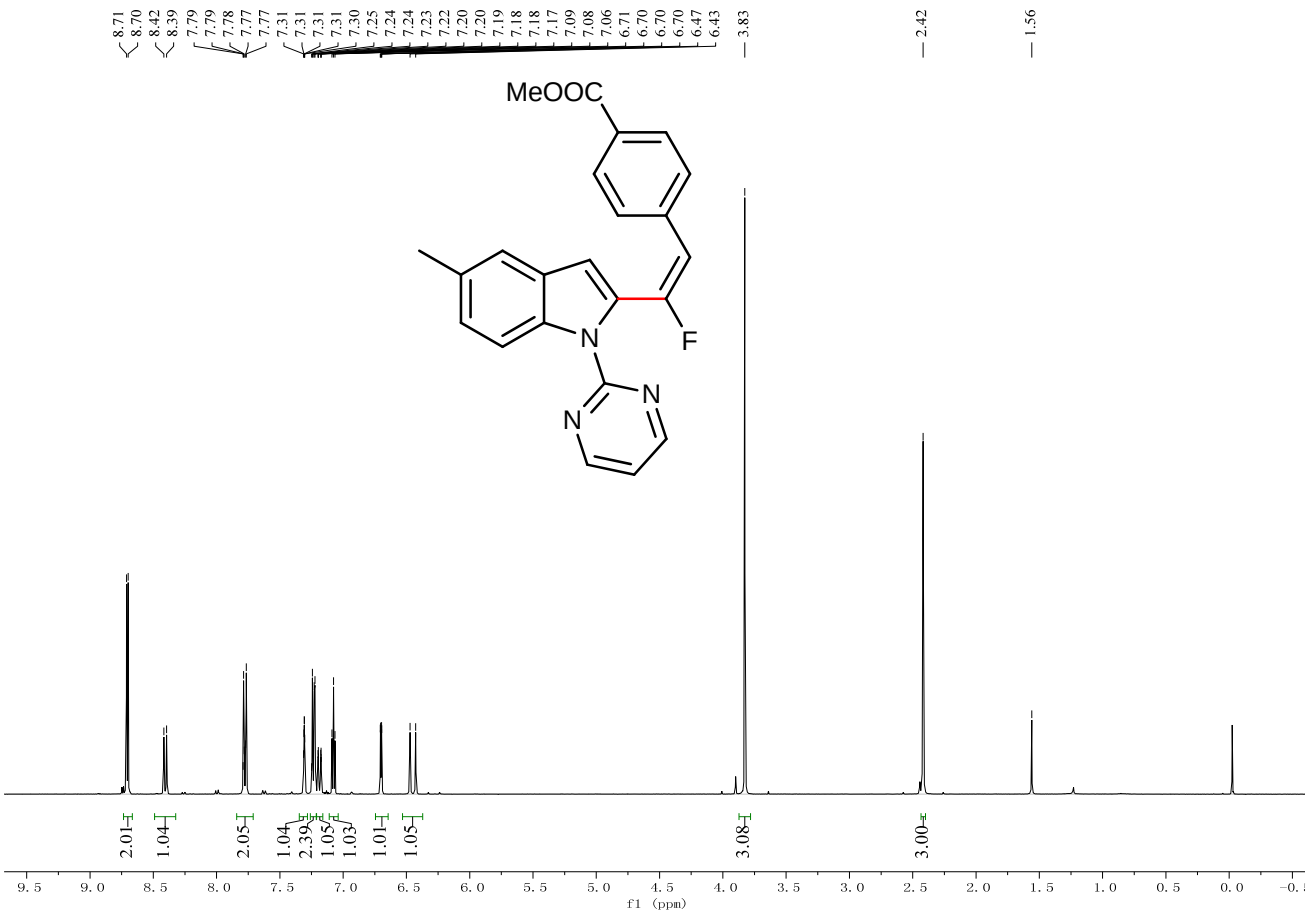
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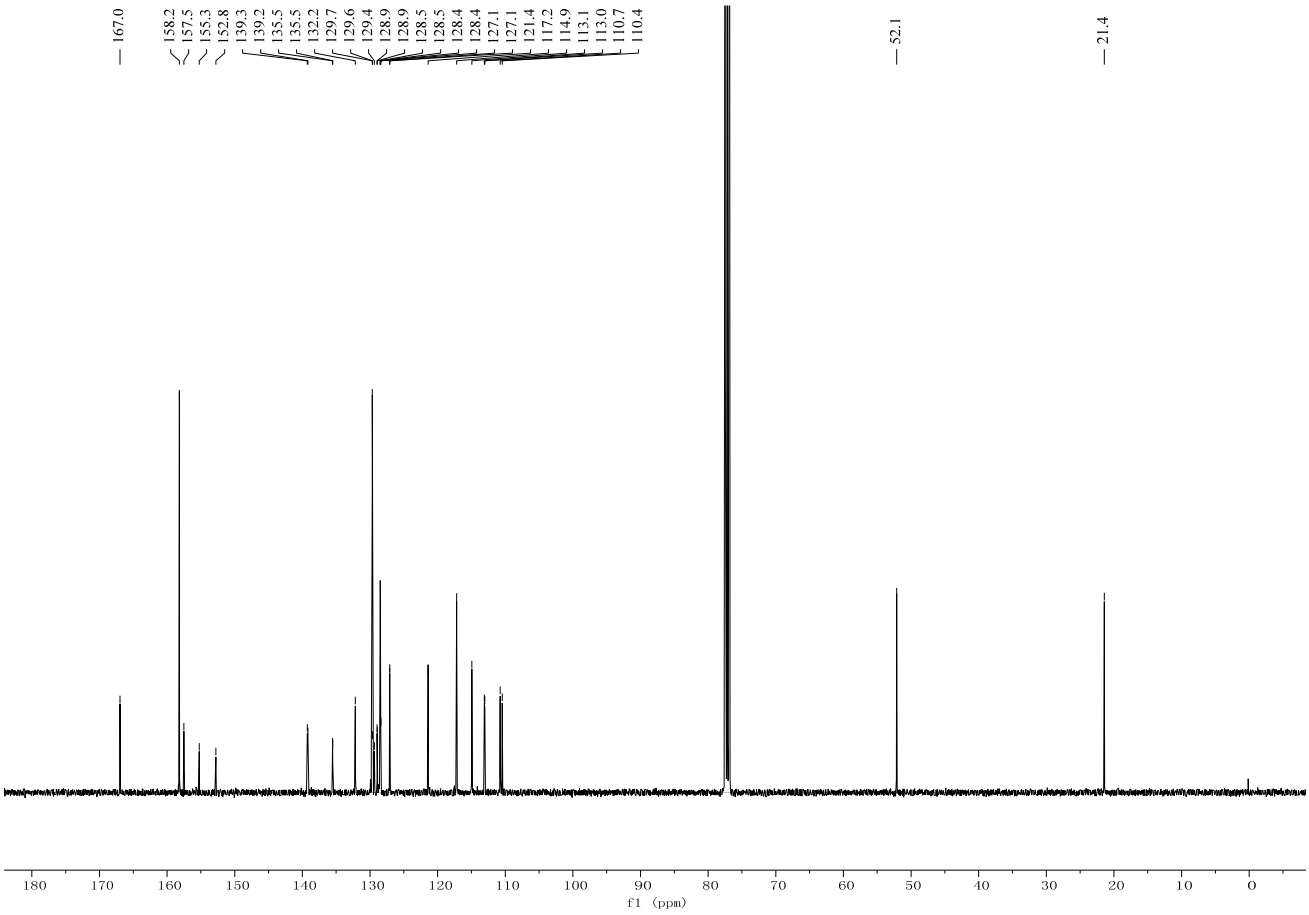
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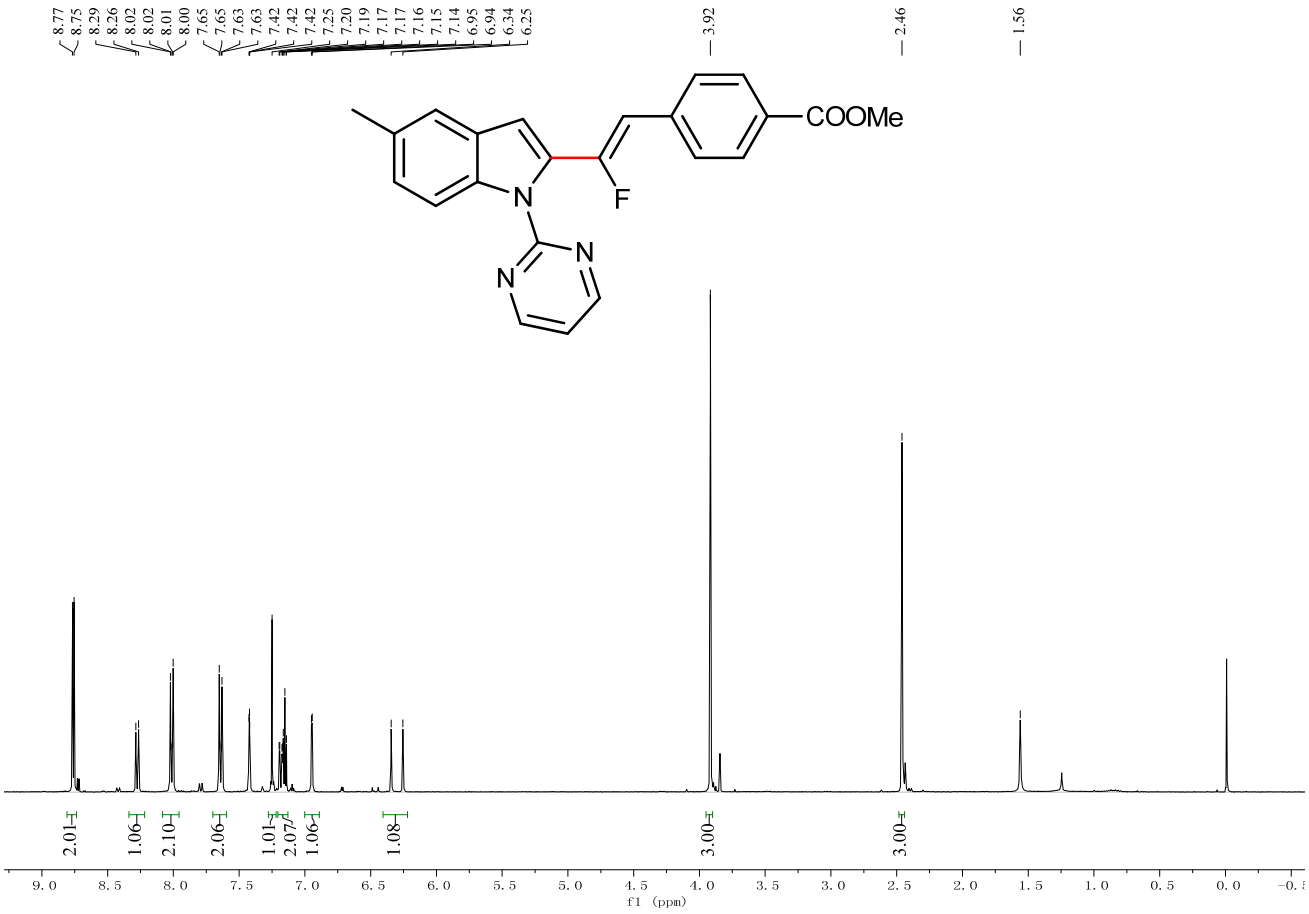
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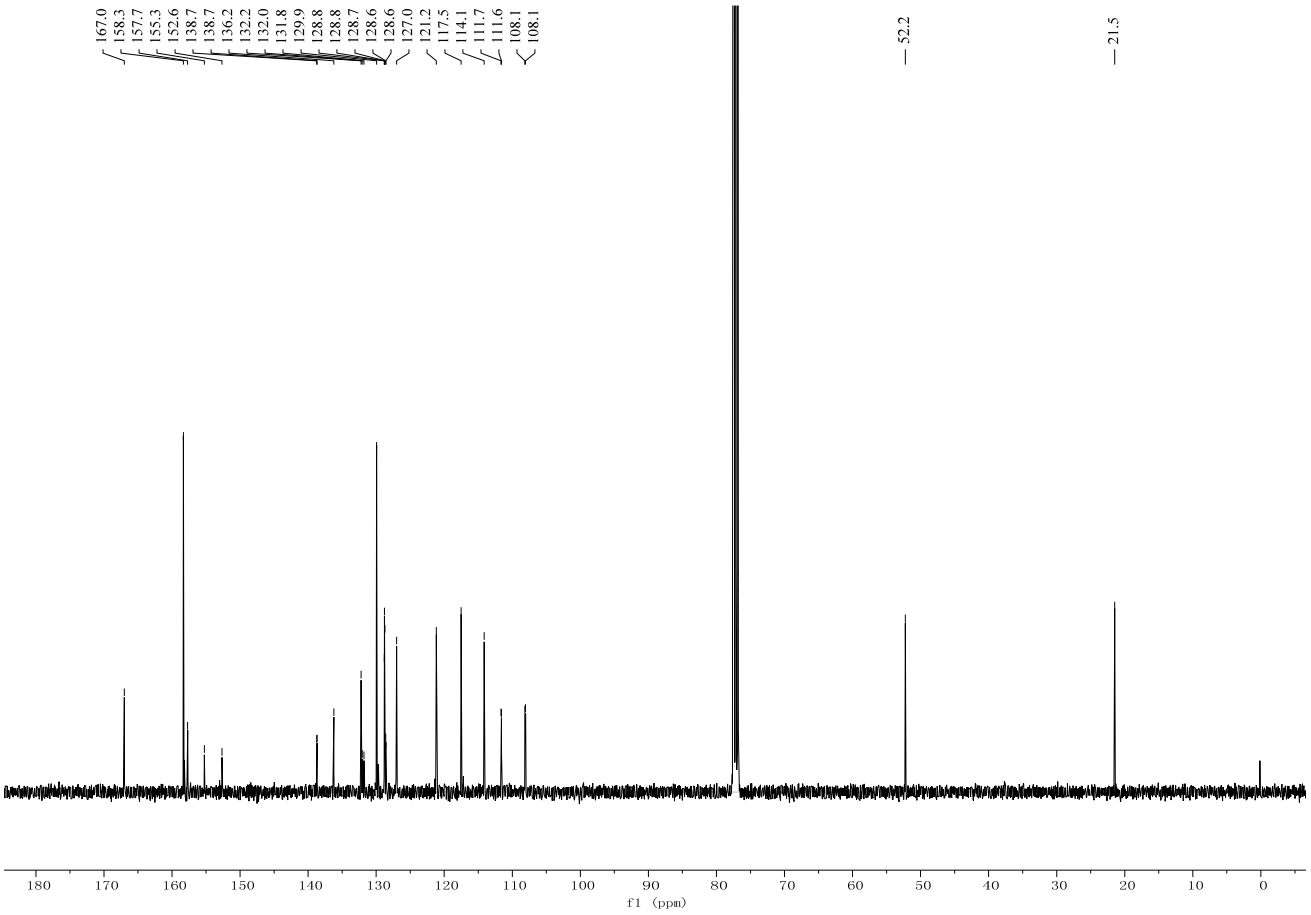
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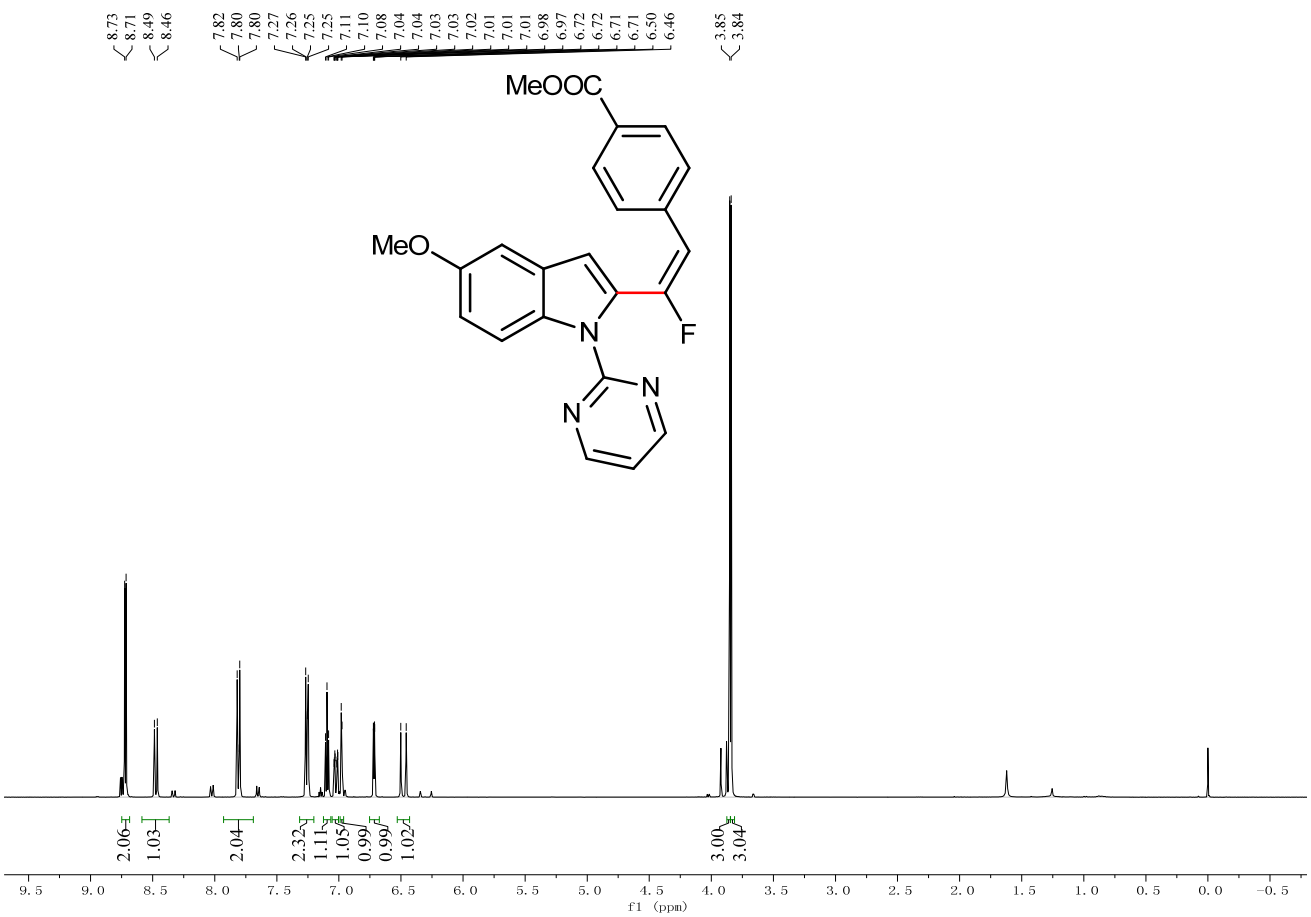
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7.01
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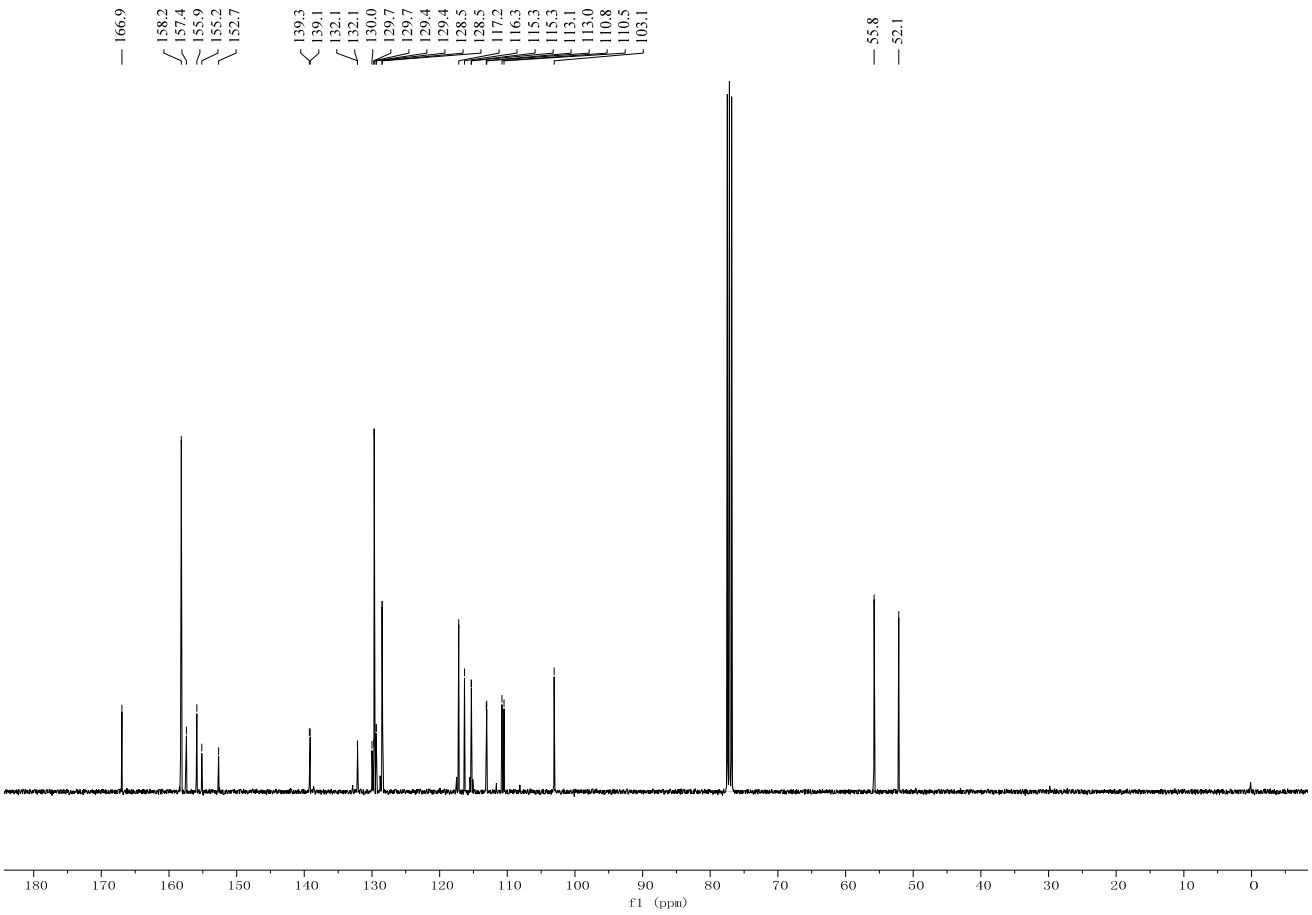
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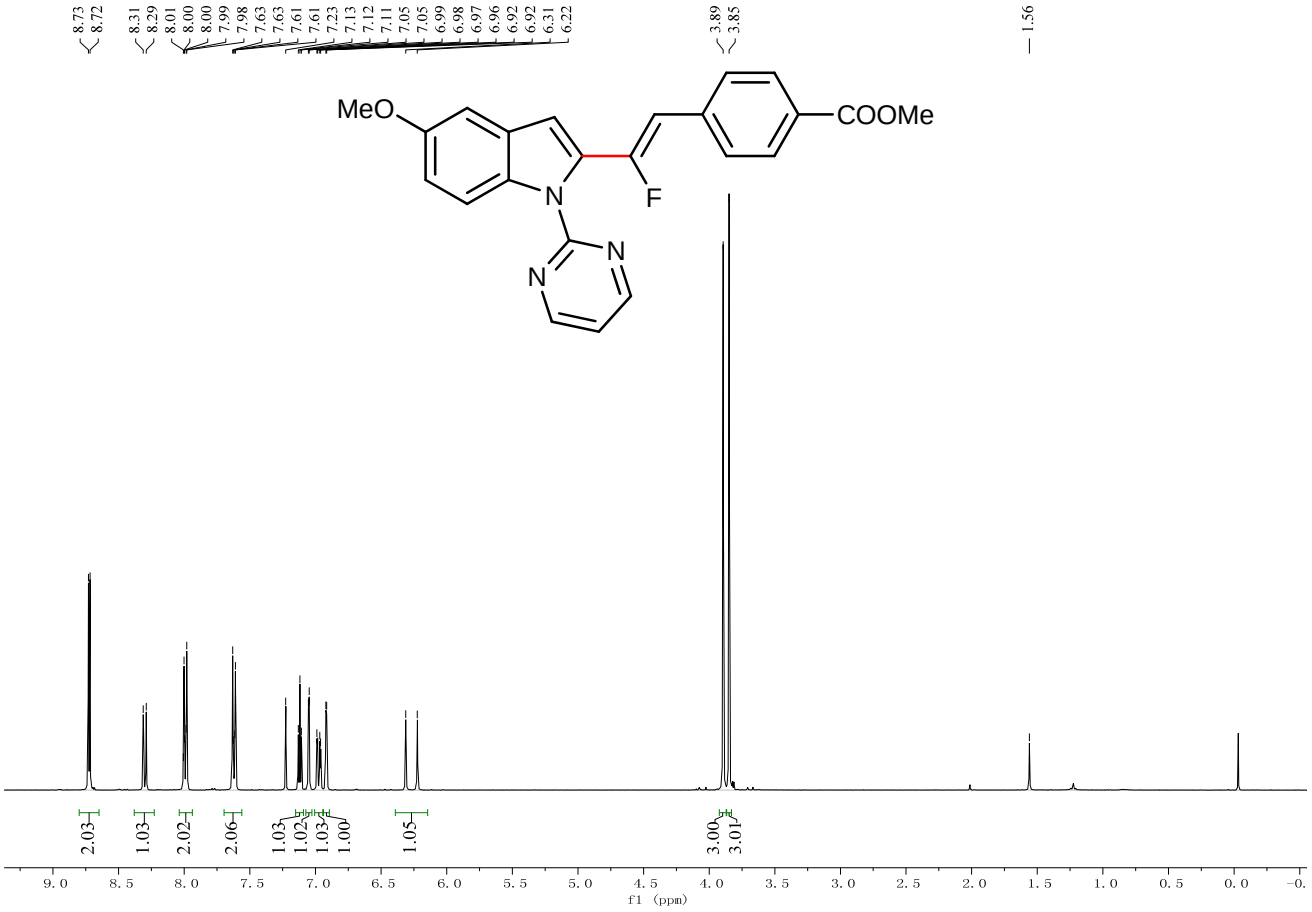
55.8
52.1
f1 (ppm)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7.05
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6.97
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6.92
6.92
6.31
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1.56
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COOMe
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N
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1.03
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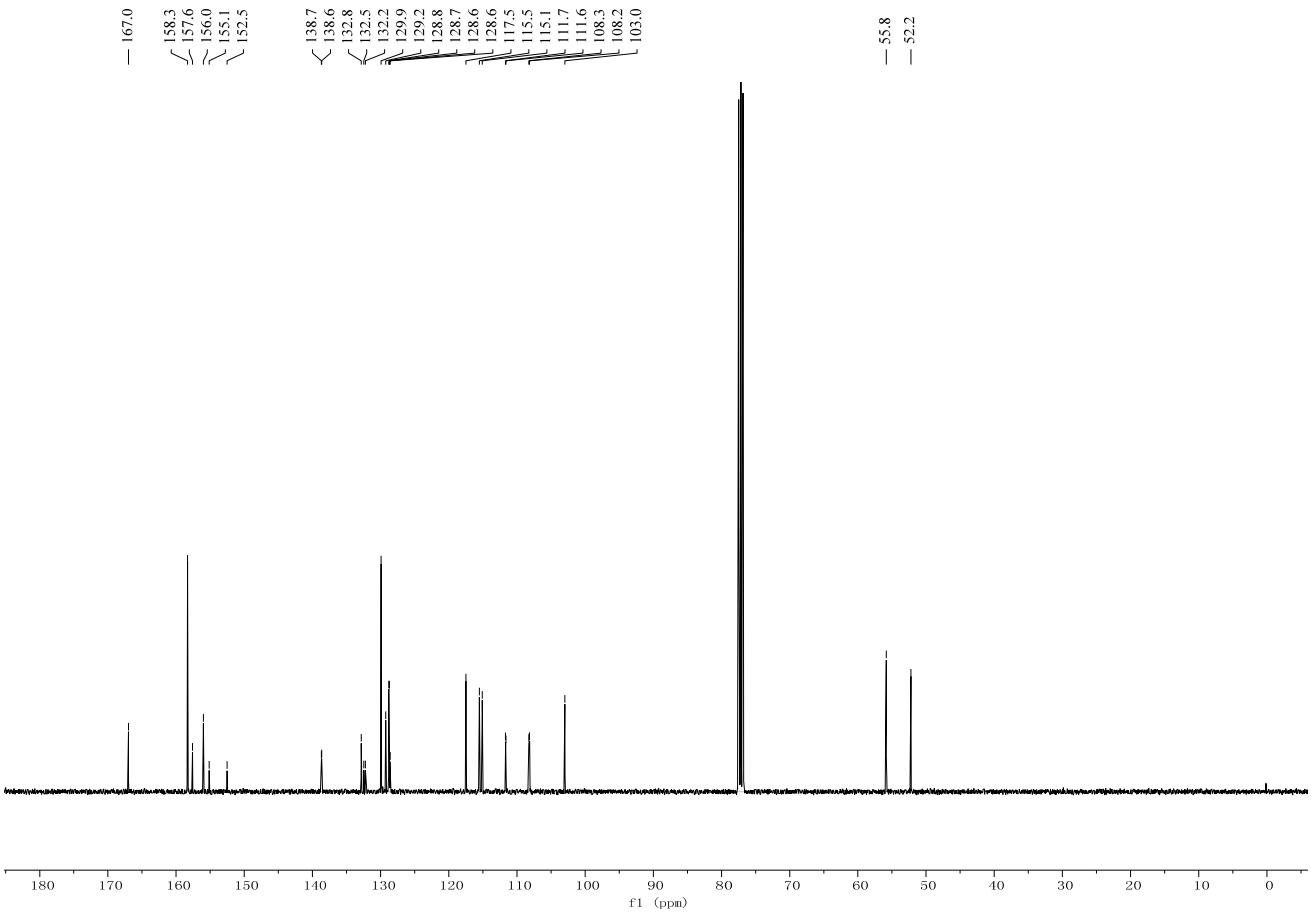
1.02
1.03
1.00
1.05
3.00
3.01
f1 (ppm)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128.7
128.6
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115.1
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111.6
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108.2
103.0
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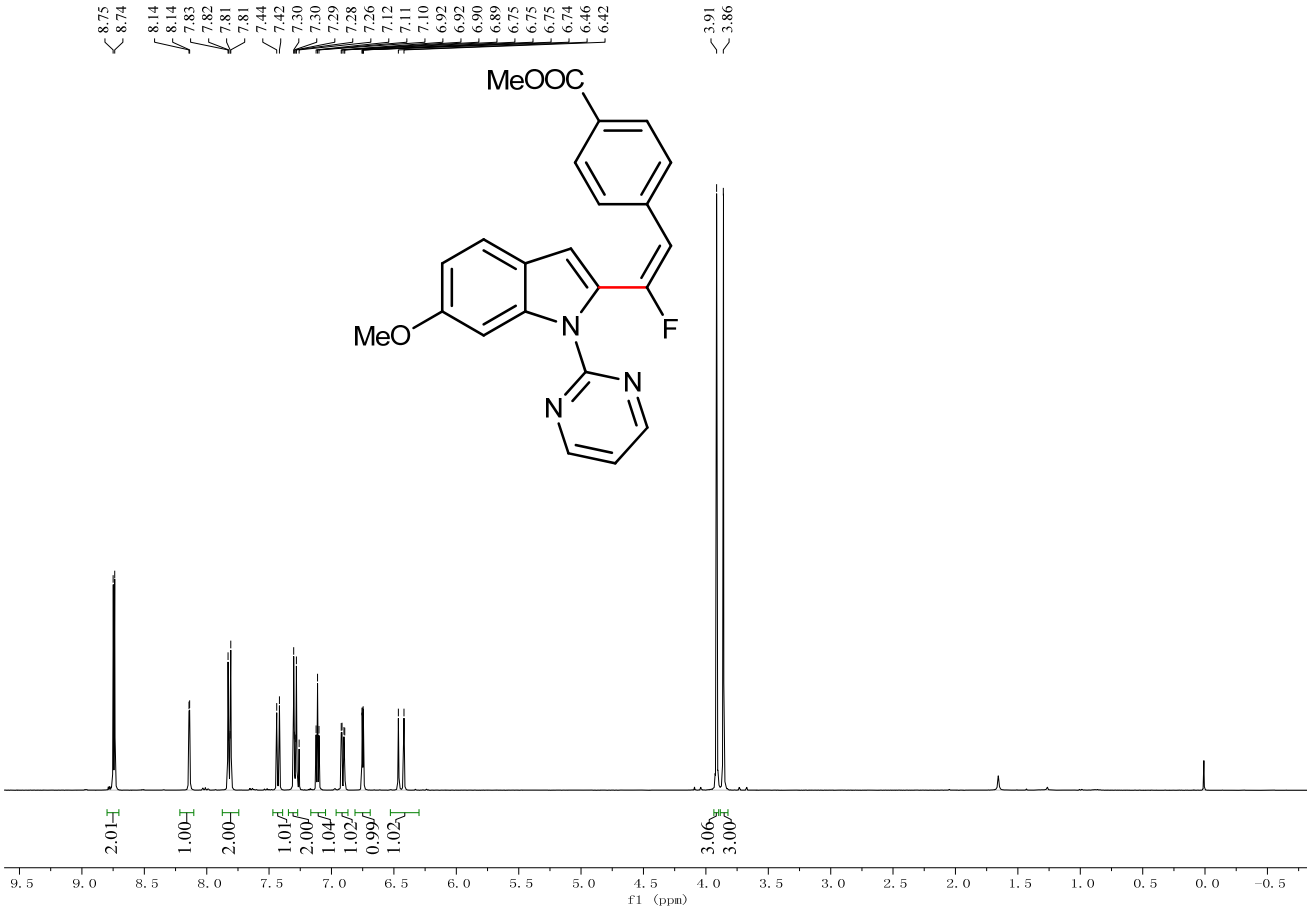
52.2
f1 (ppm)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6.92
6.92
6.90
6.89
6.75
6.75
6.75
6.74
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3.91
3.86
MeOOC
MeO
N
F
N
N
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1.00
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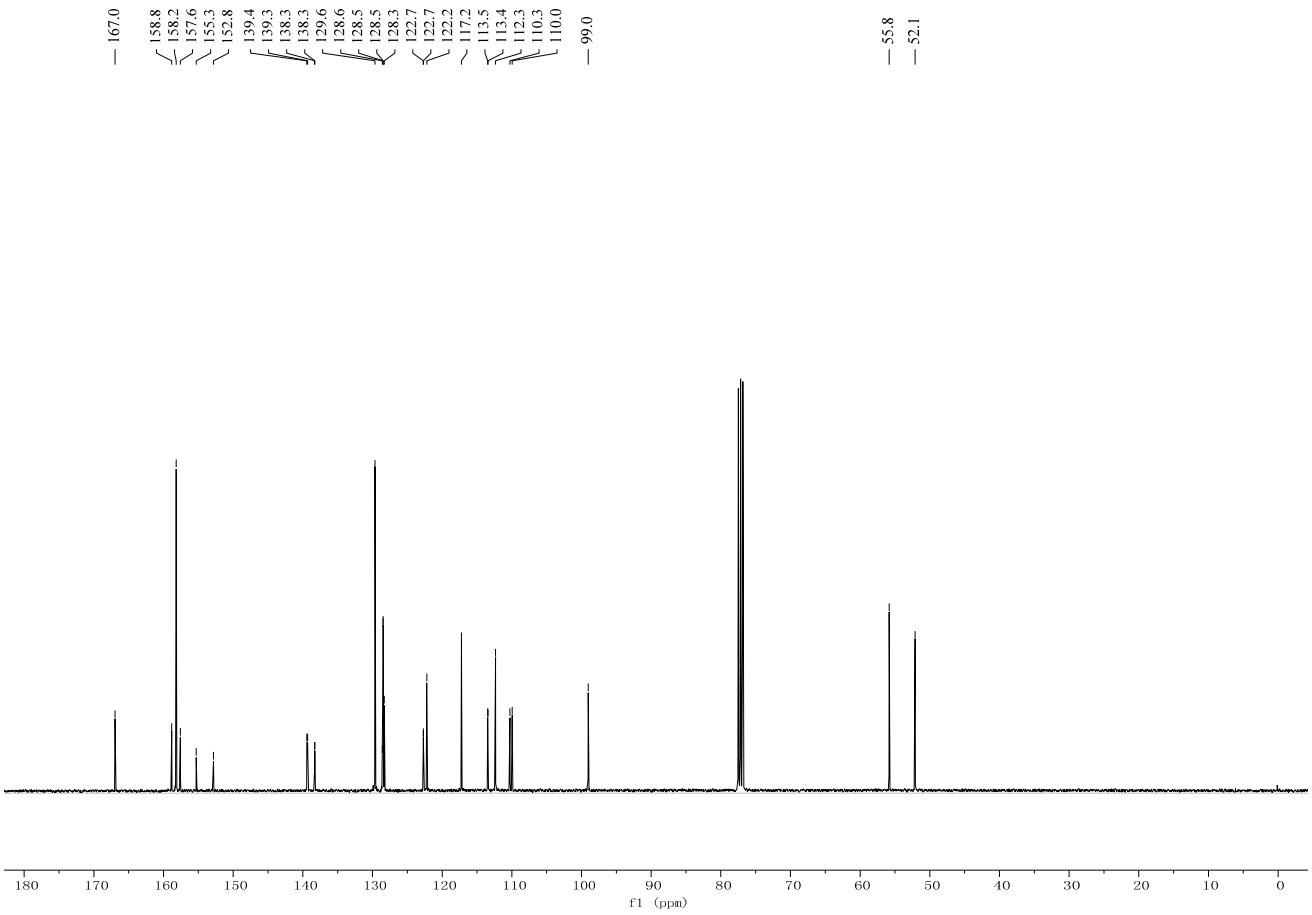
1.01
2.00
1.04
1.02
0.99
1.02
3.06
3.00
f1 (ppm)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122.7
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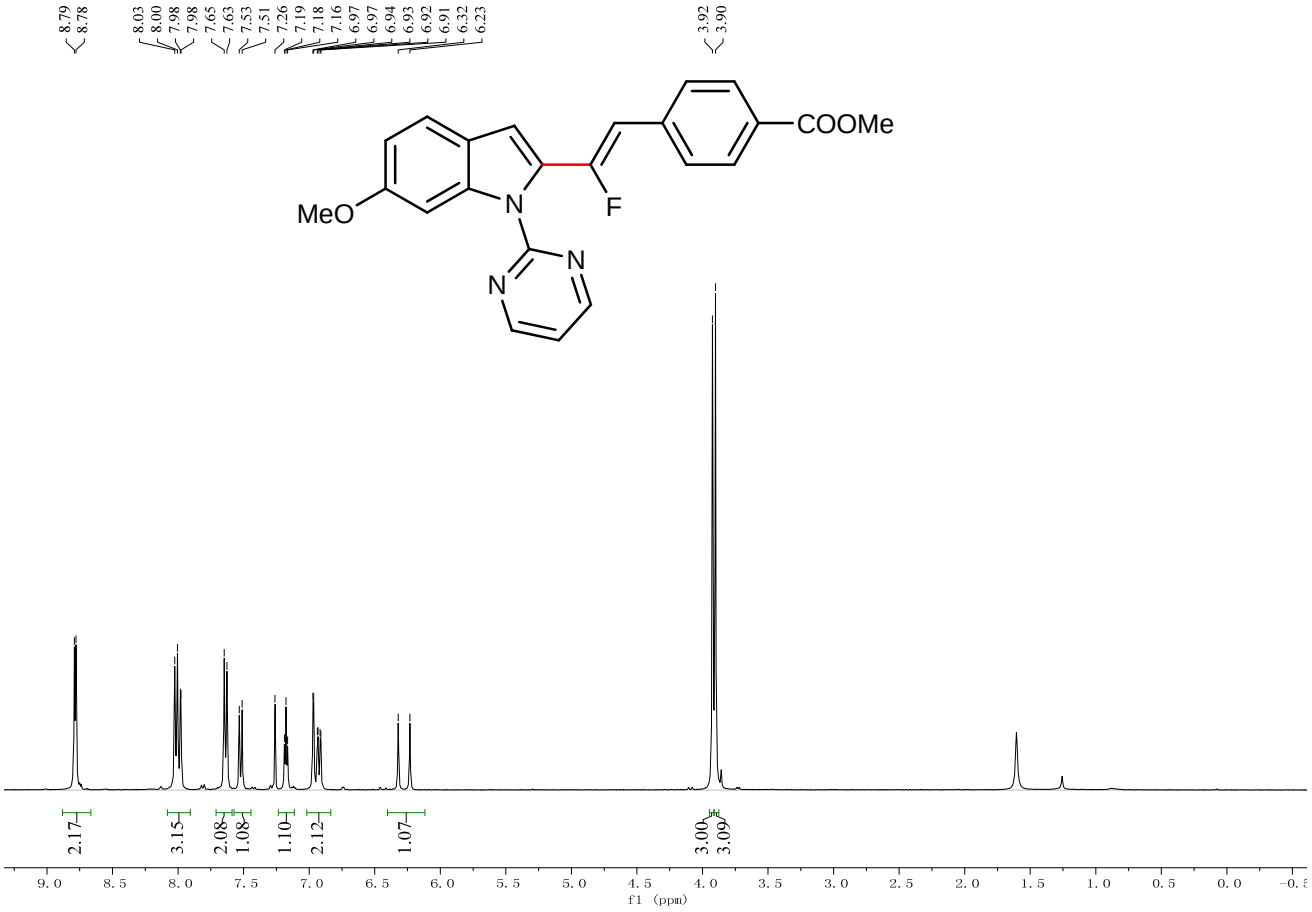
52.1
f1 (ppm)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6.91
6.32
6.23
3.92
3.90
COOMe
MeO
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1.08
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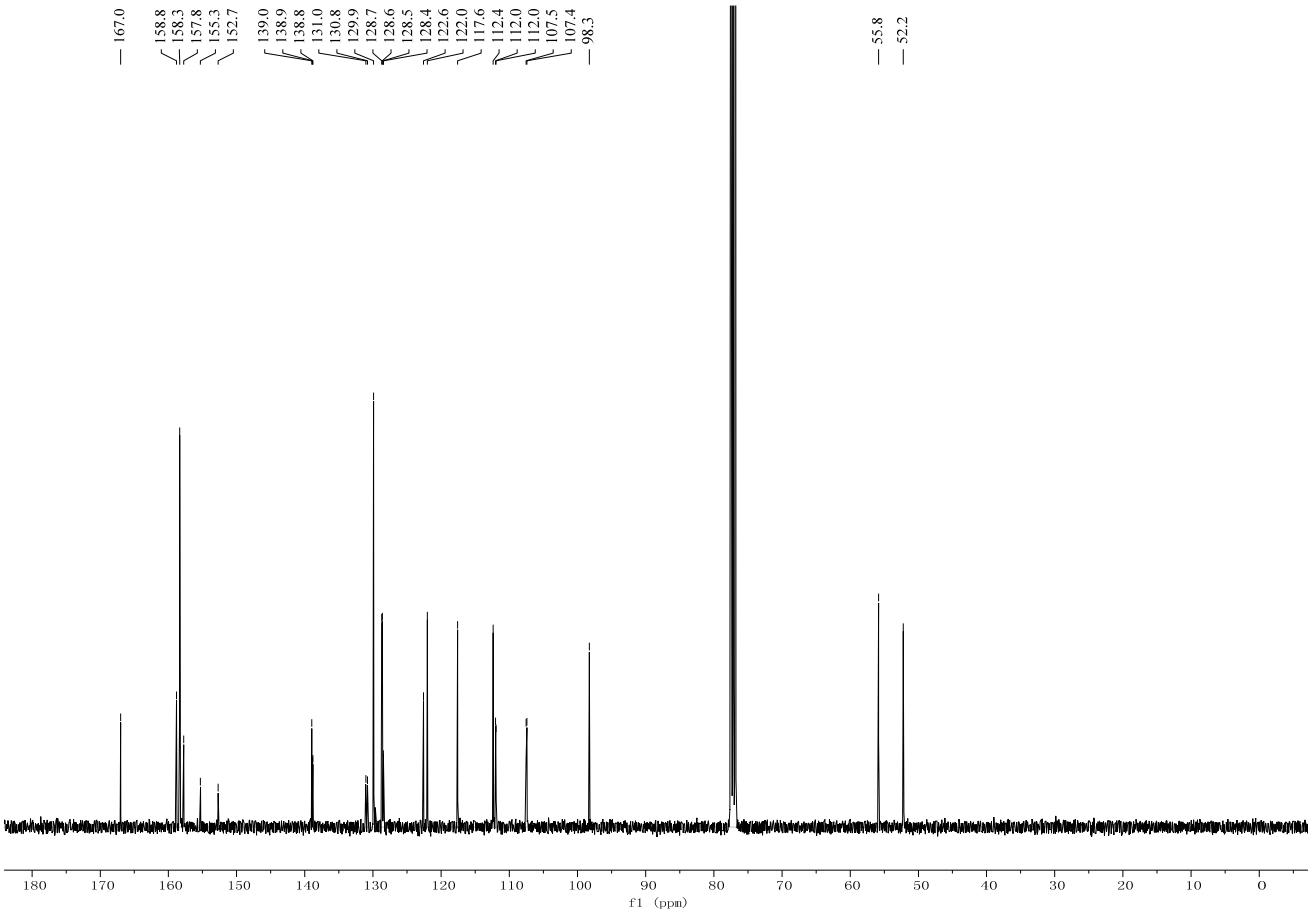
3.09
f1 (ppm)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128.5
128.4
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112.0
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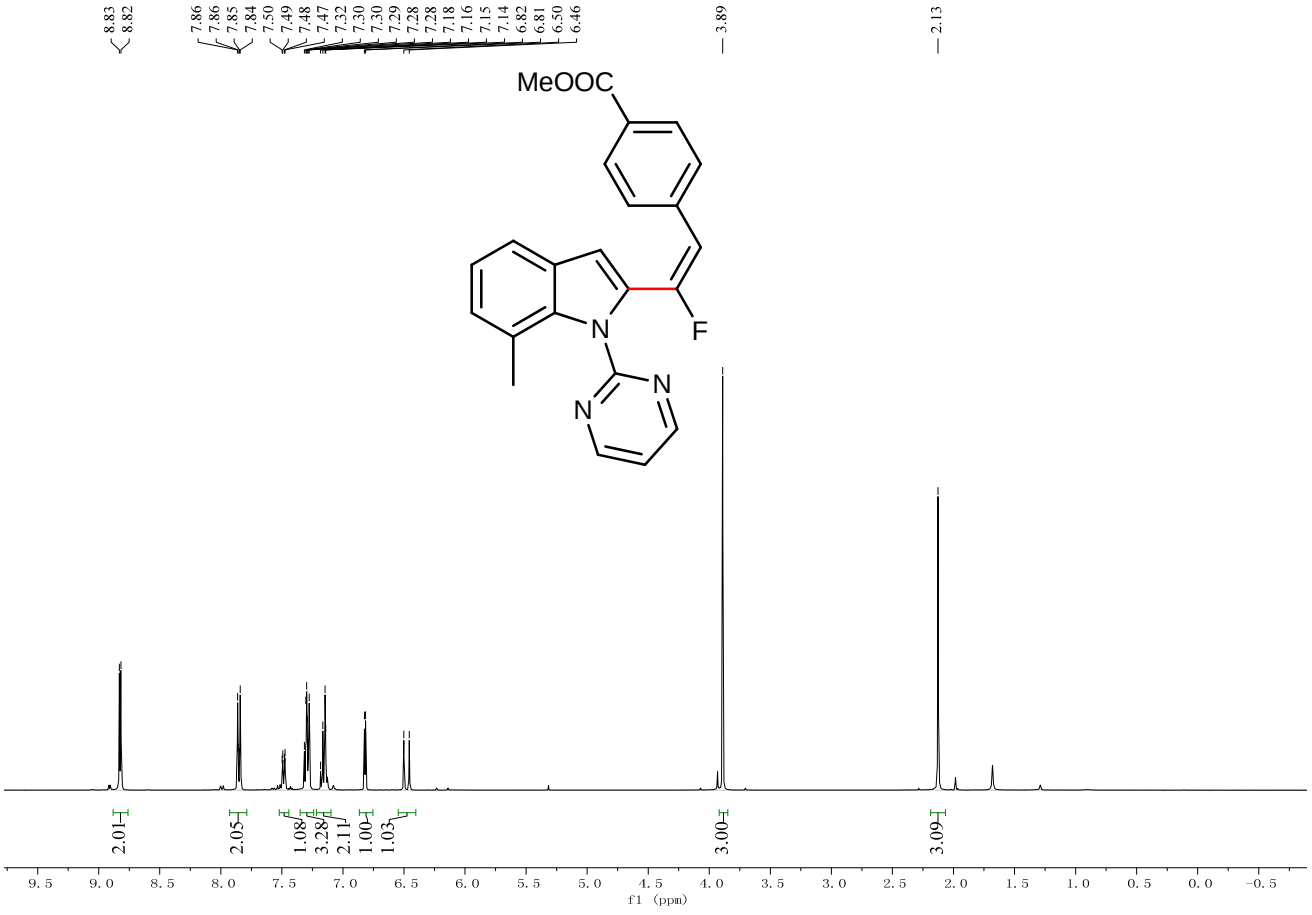
55.8
52.2
f1 (ppm)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3.89
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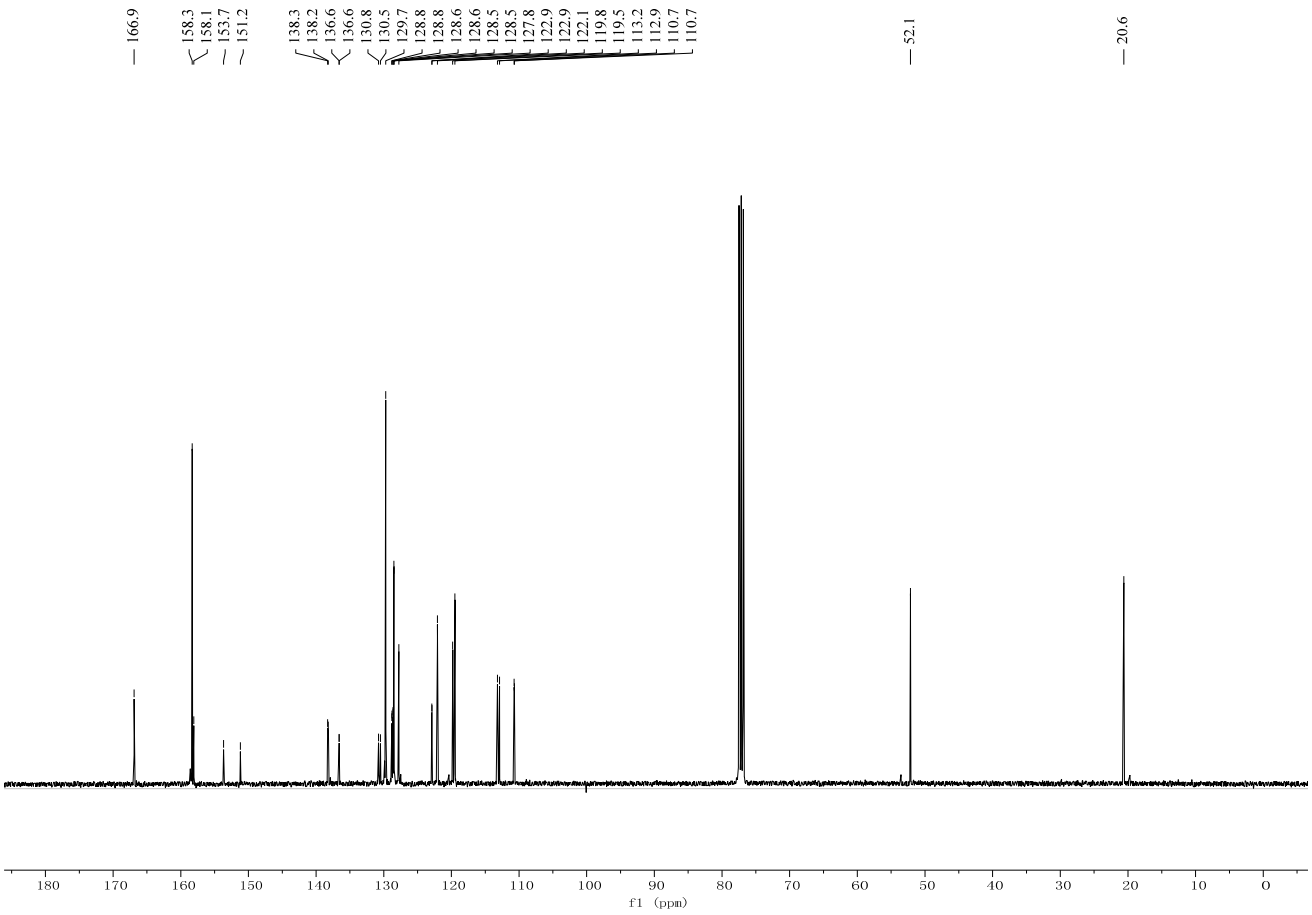
3.09
f1 (ppm)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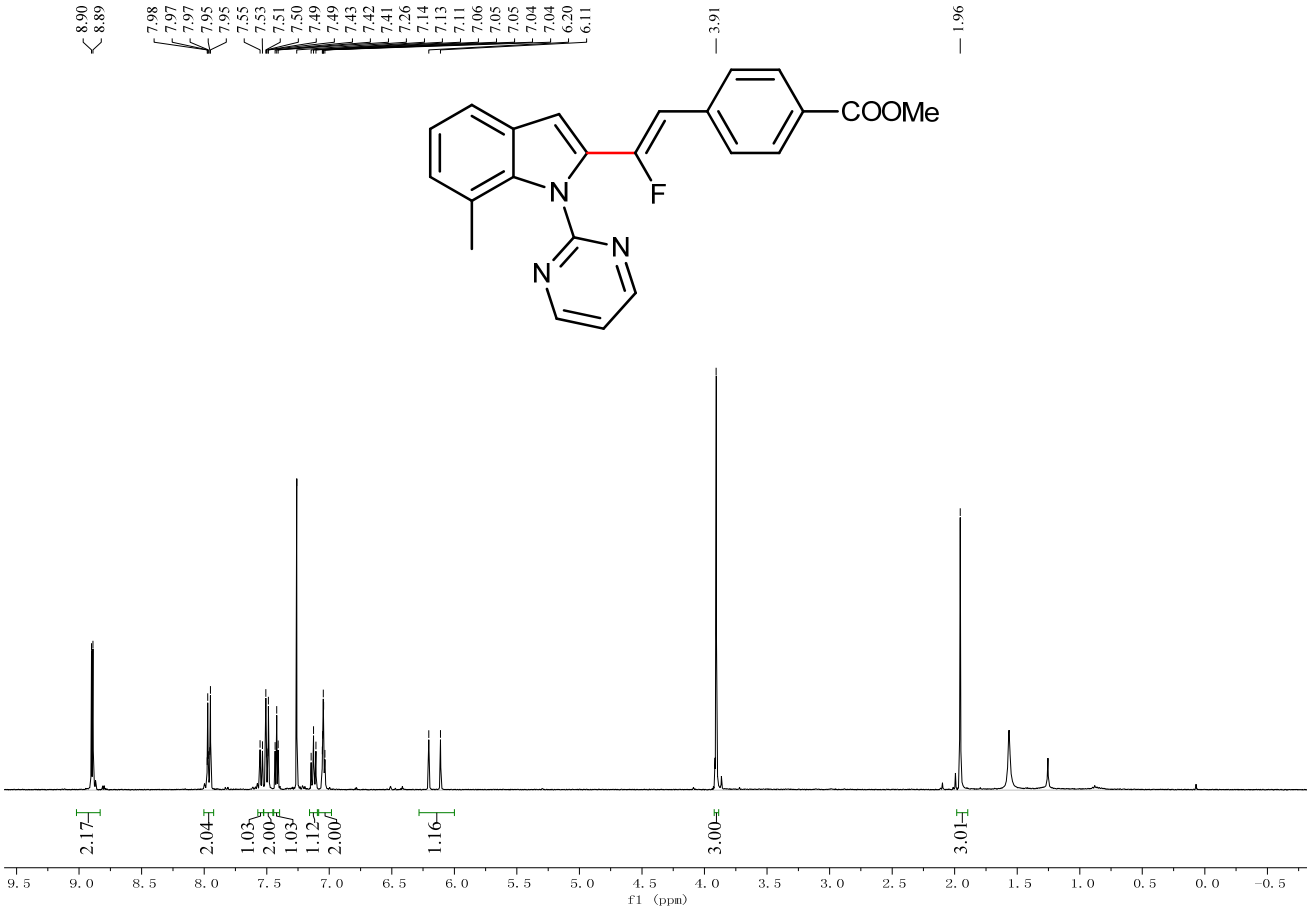
20.6
f1 (ppm)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7.04
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6.11
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COOMe
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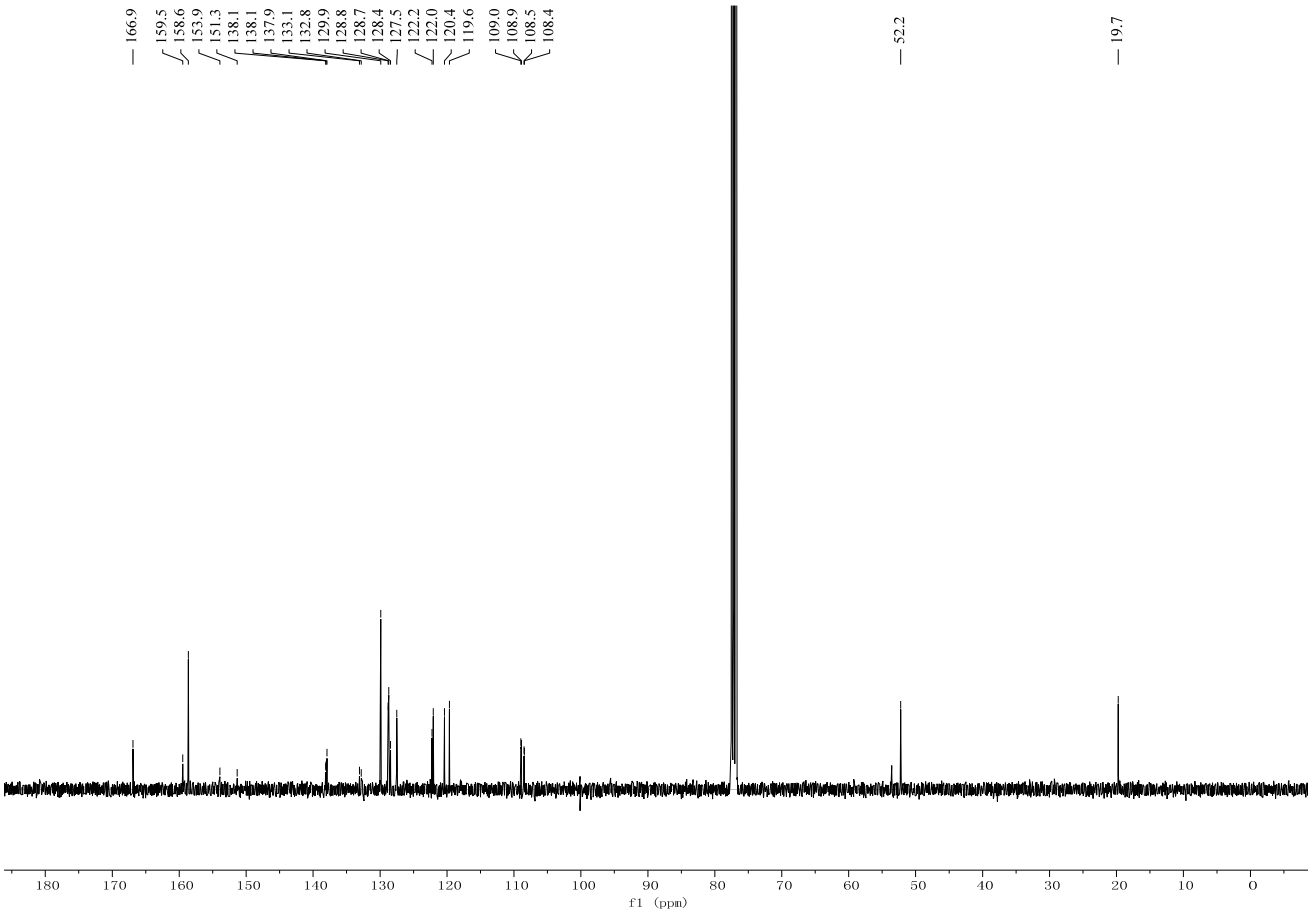
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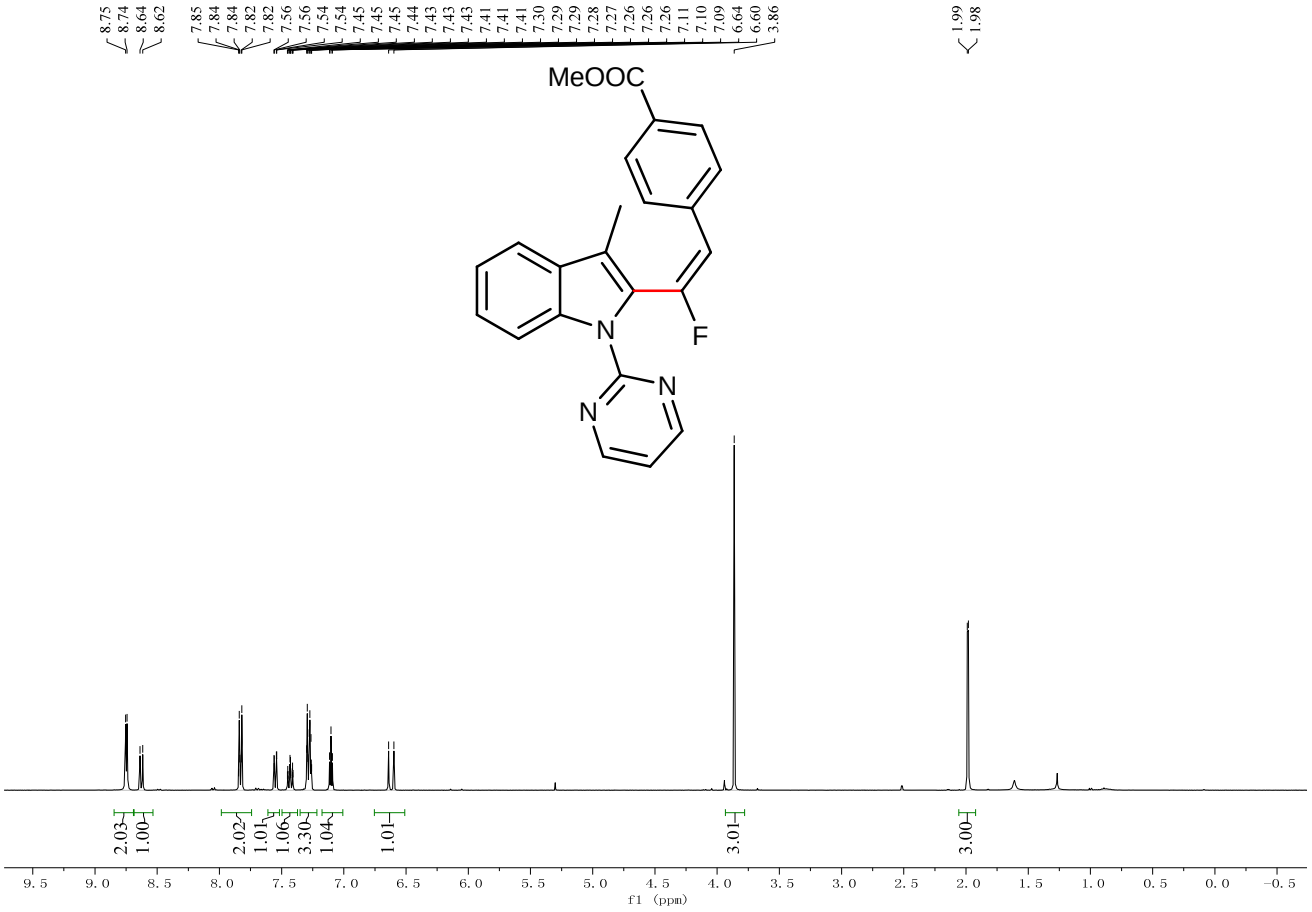
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7.26
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6.60
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1.98
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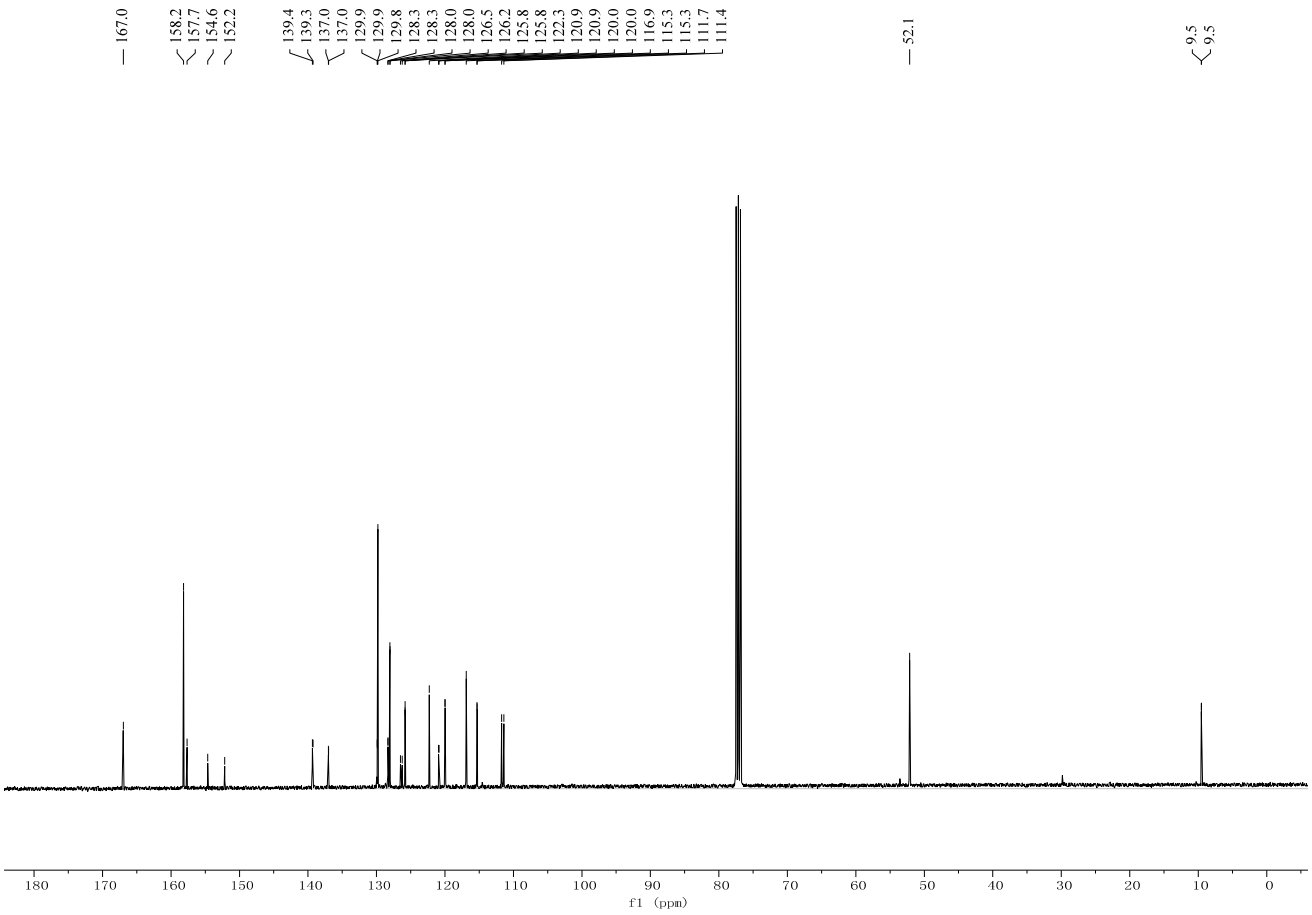
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9.5
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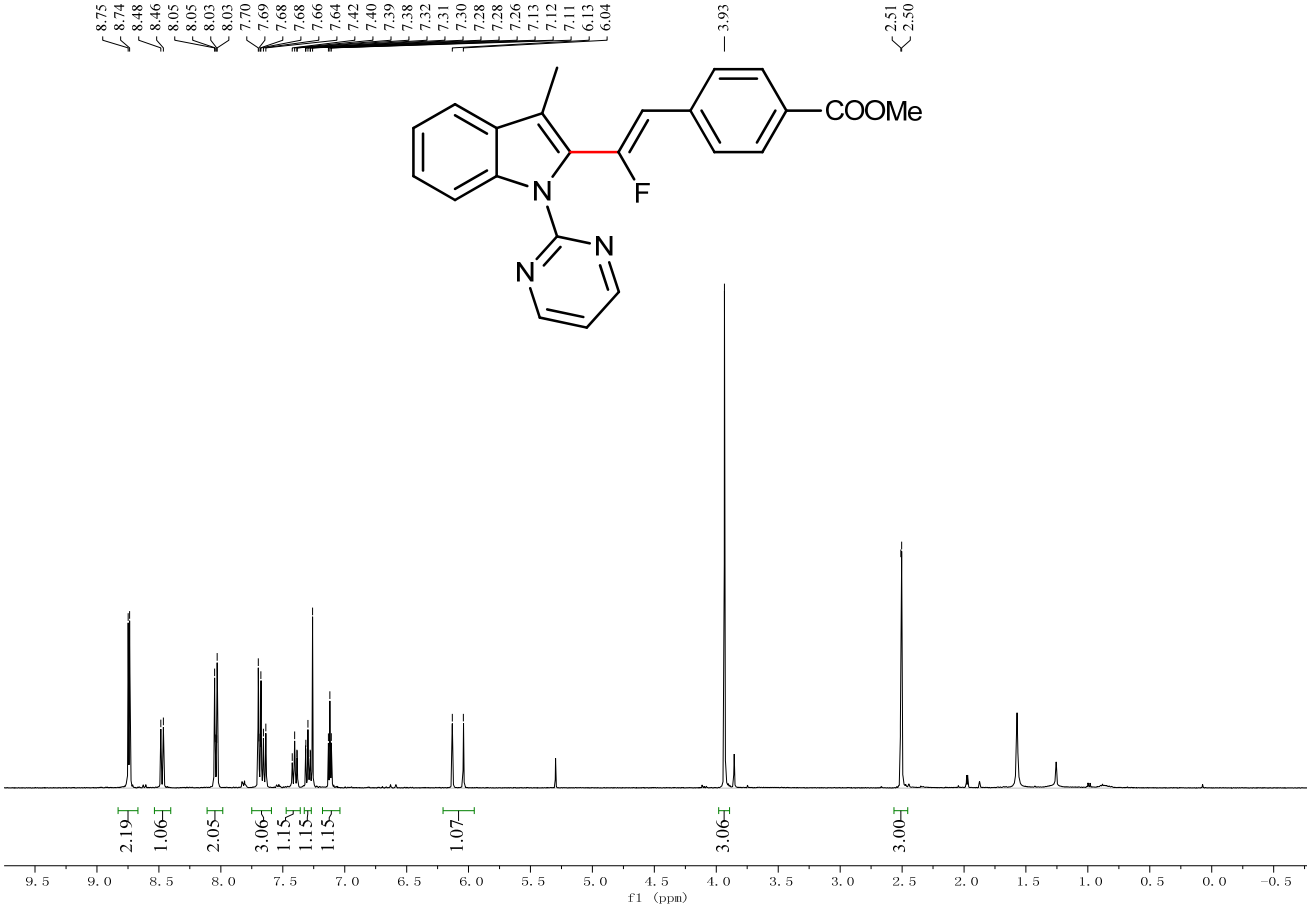
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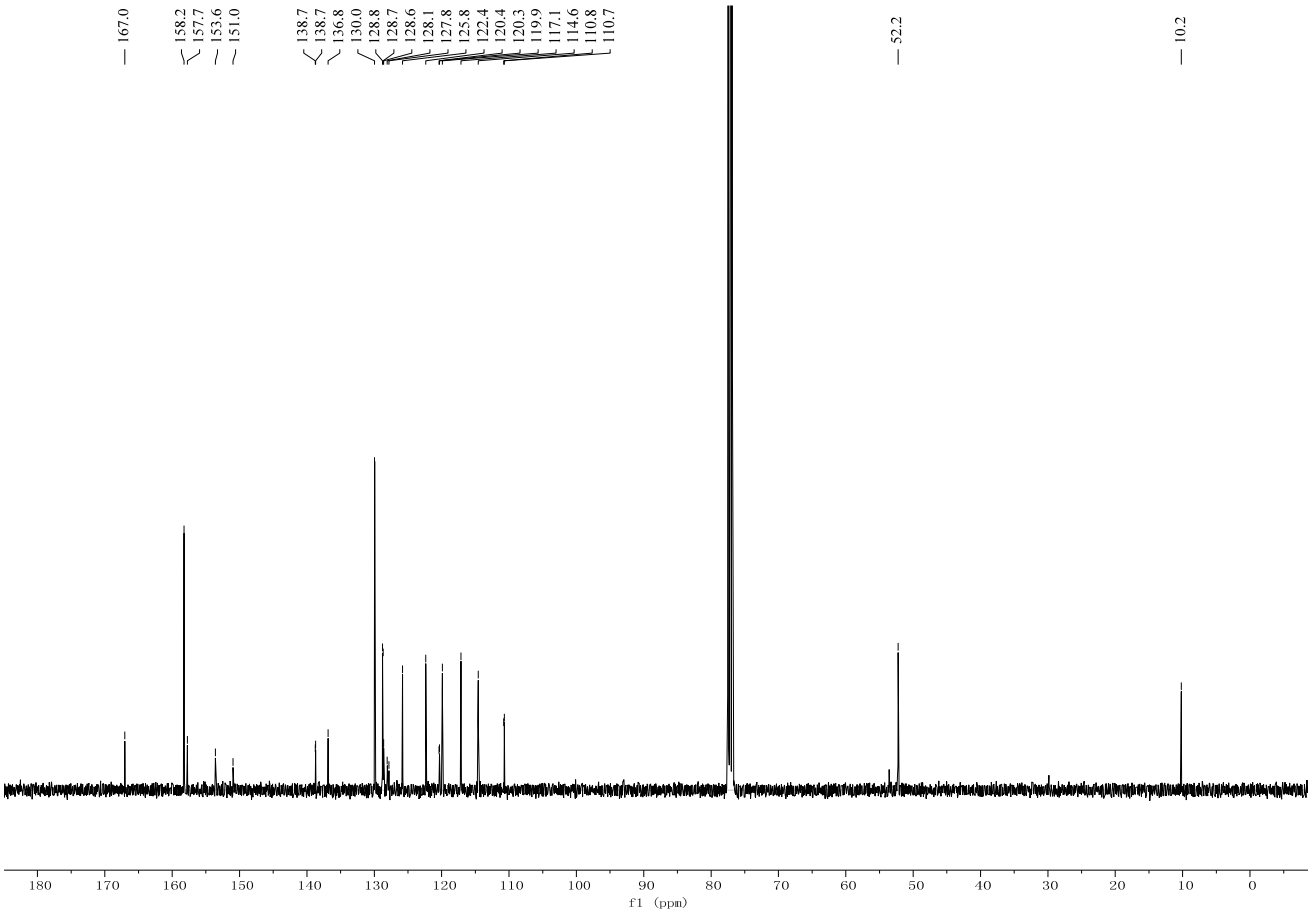
3.00
f1 (ppm)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128.1
127.8
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110.7
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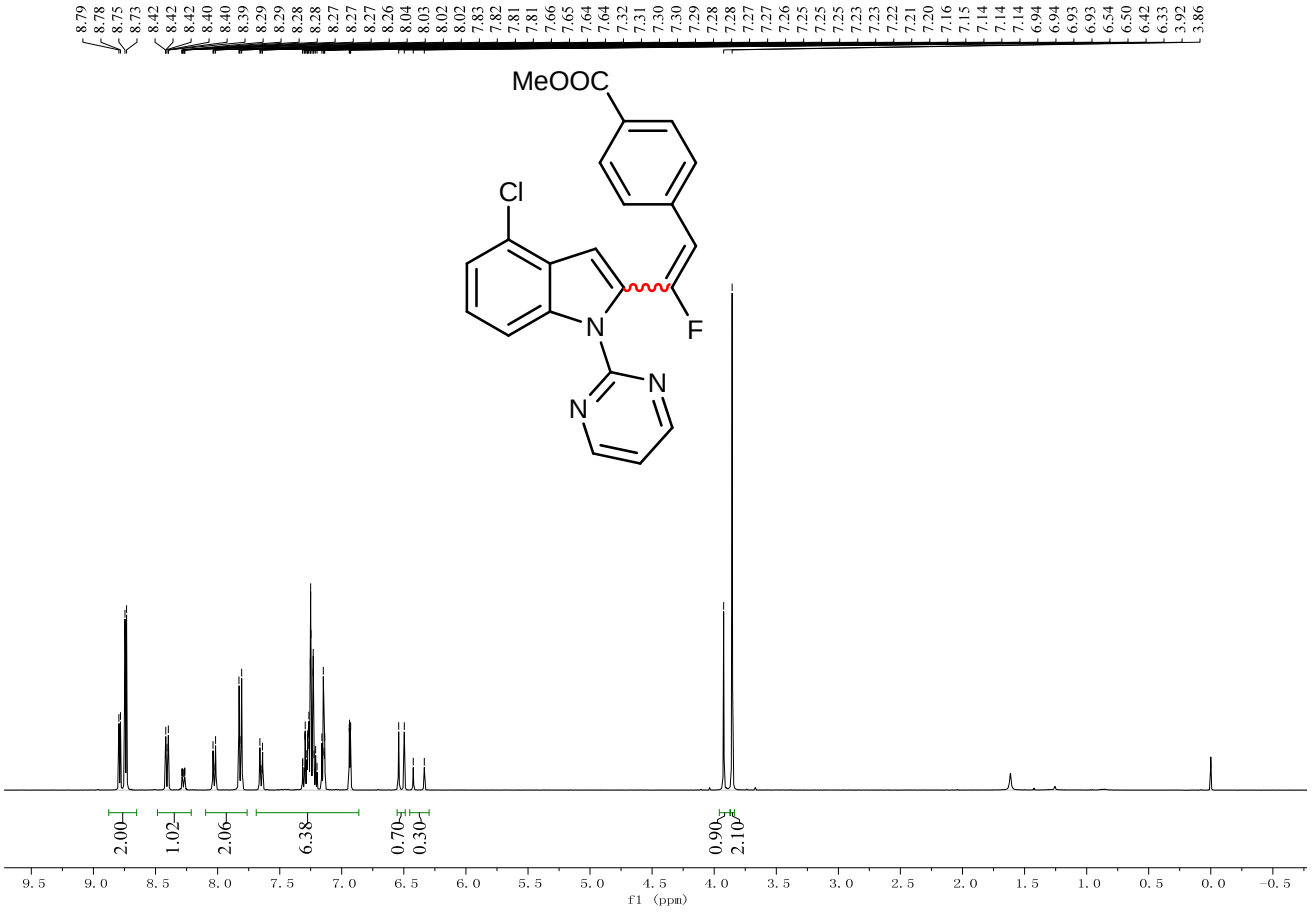
10.2
f1 (ppm)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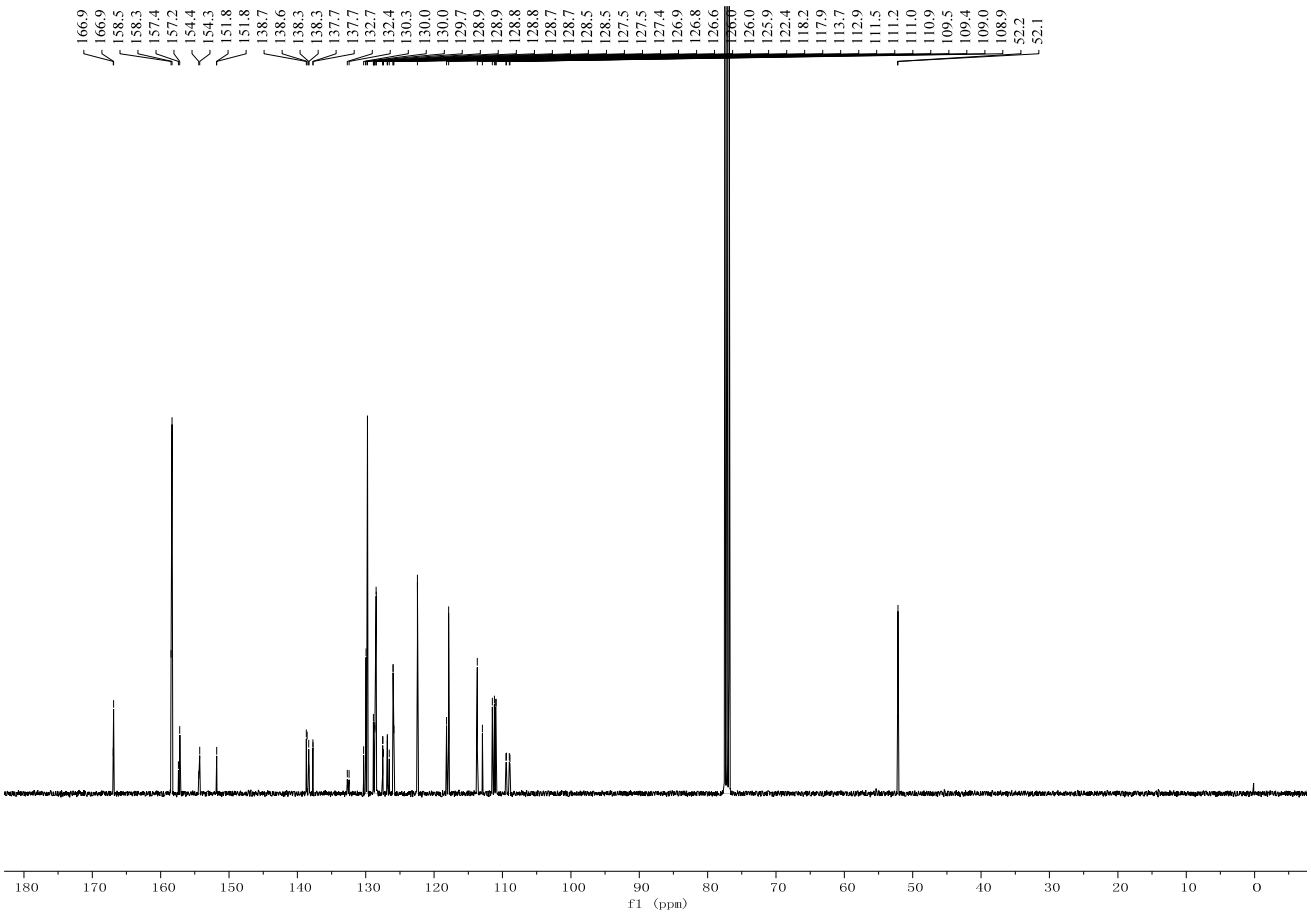
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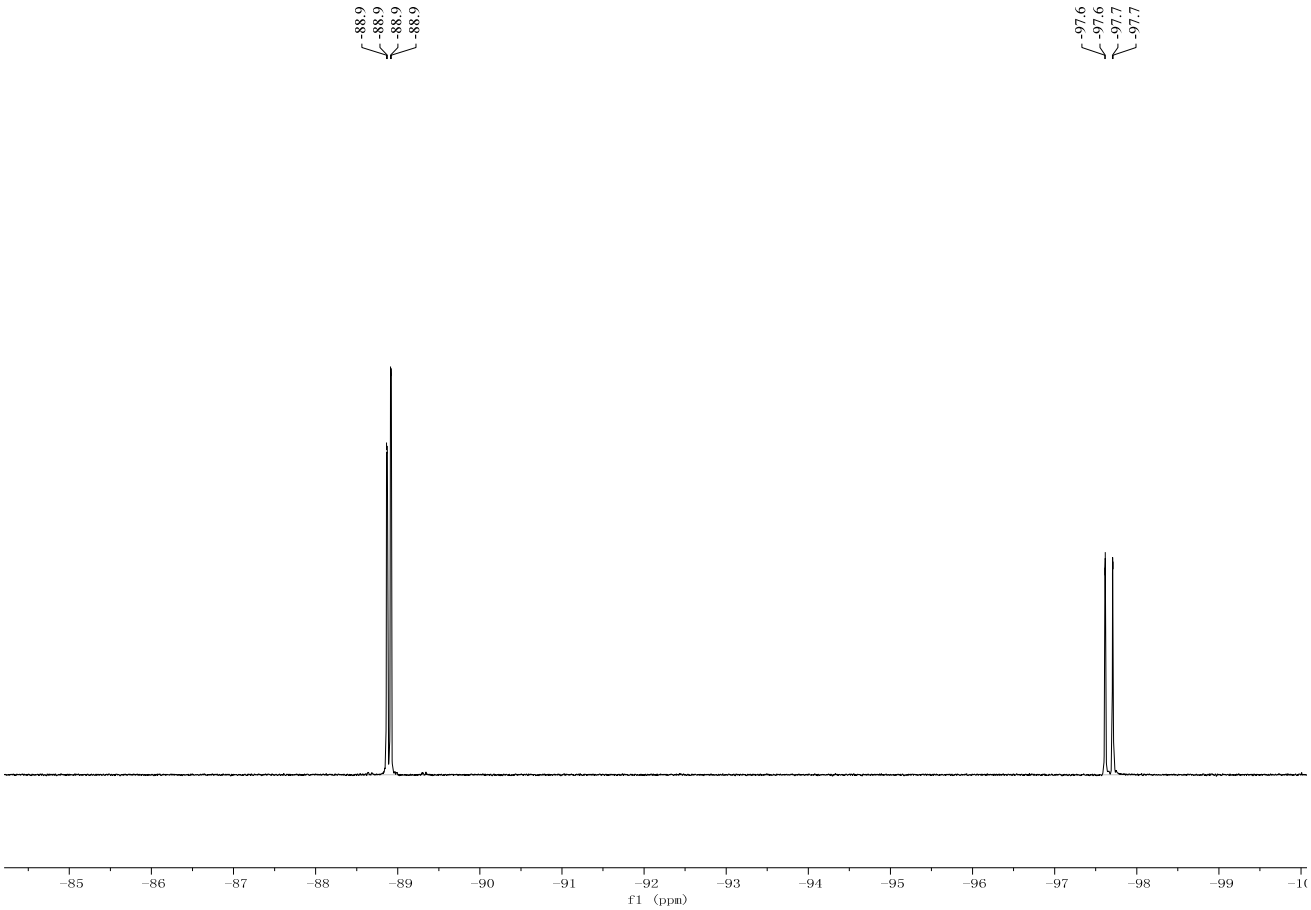
f1 (ppm)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−92
−93
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−96
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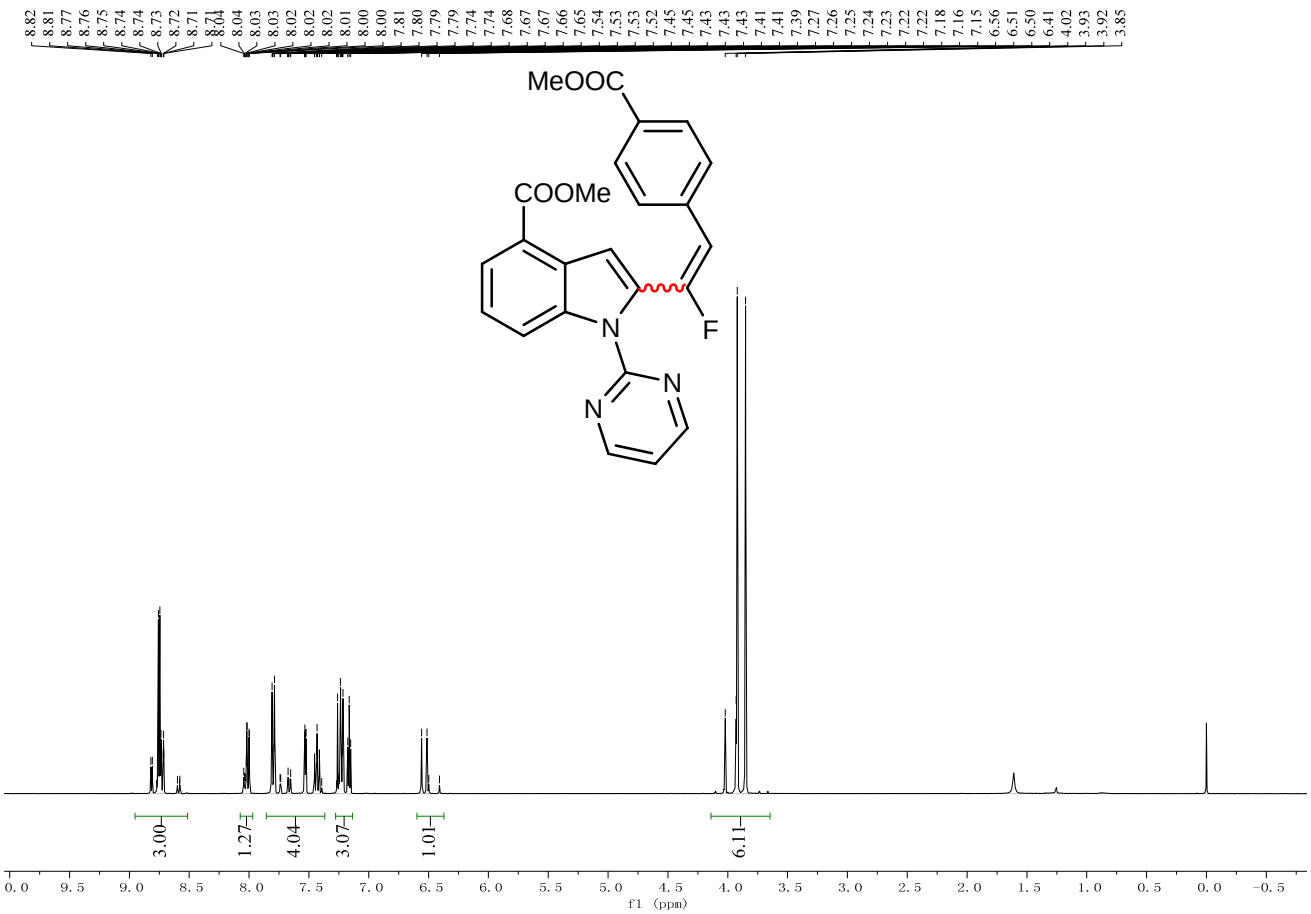
−99
f1 (ppm)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COOMe
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1.27
4.04
3.07
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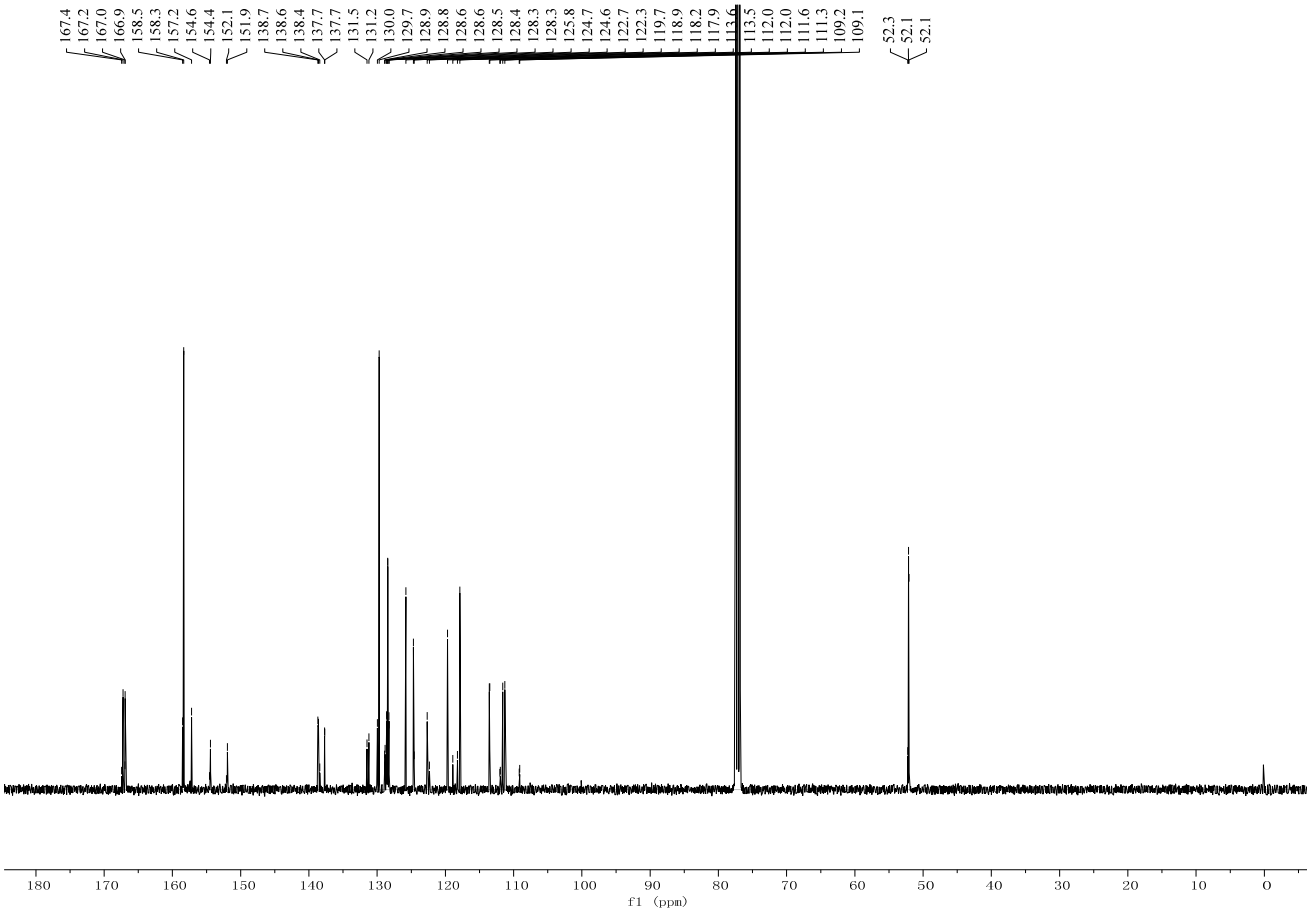
6.11
f1 (ppm)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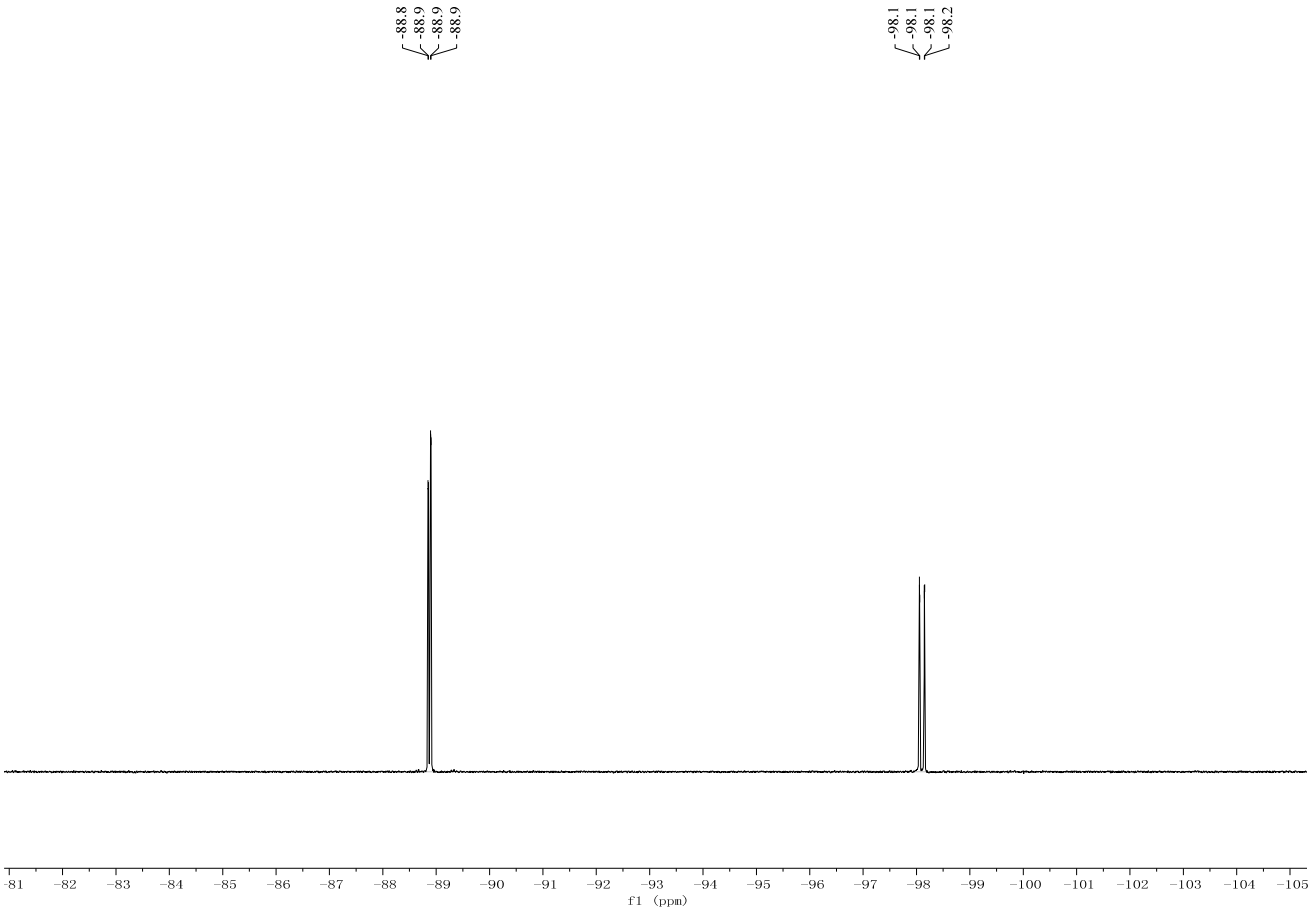
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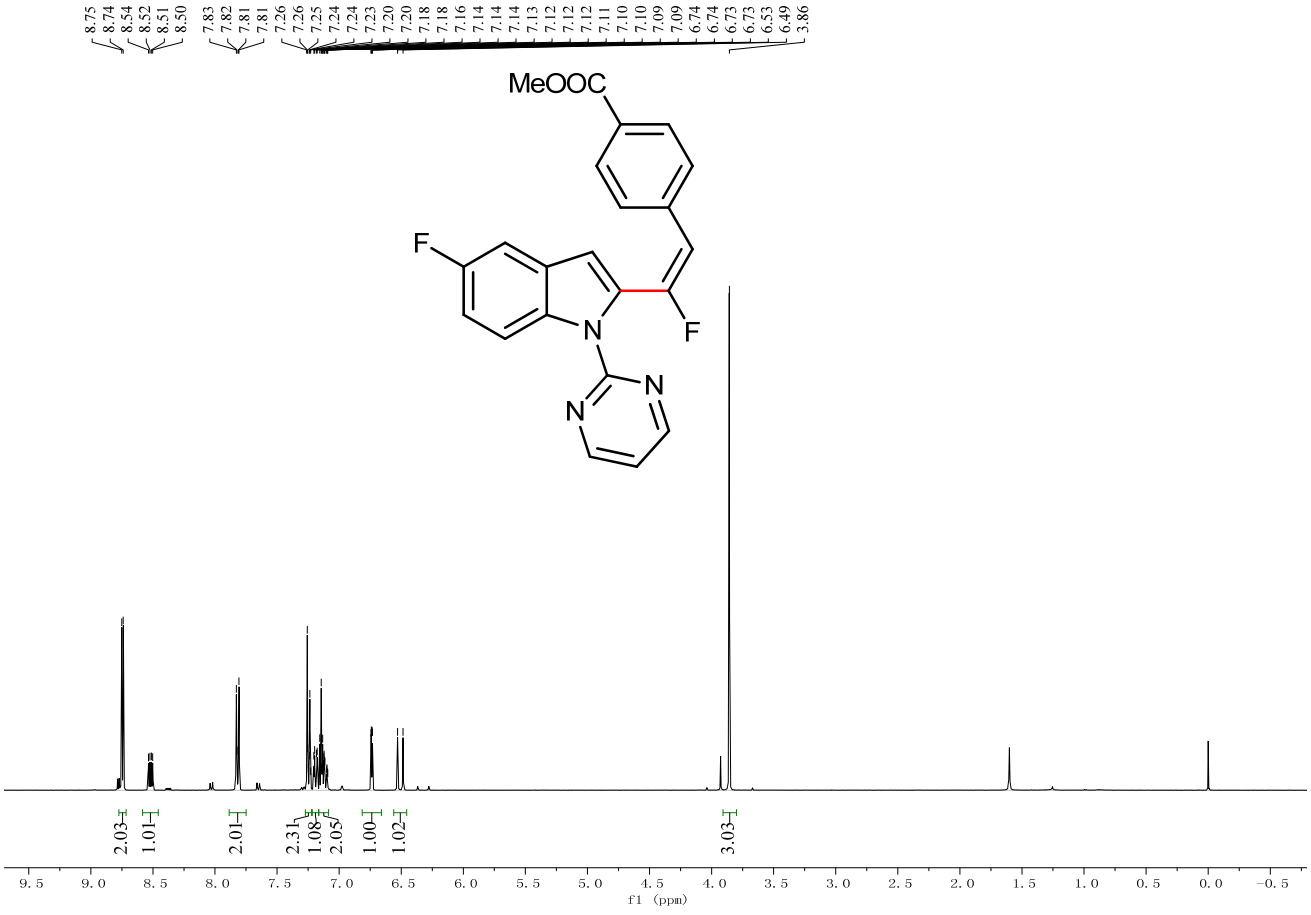
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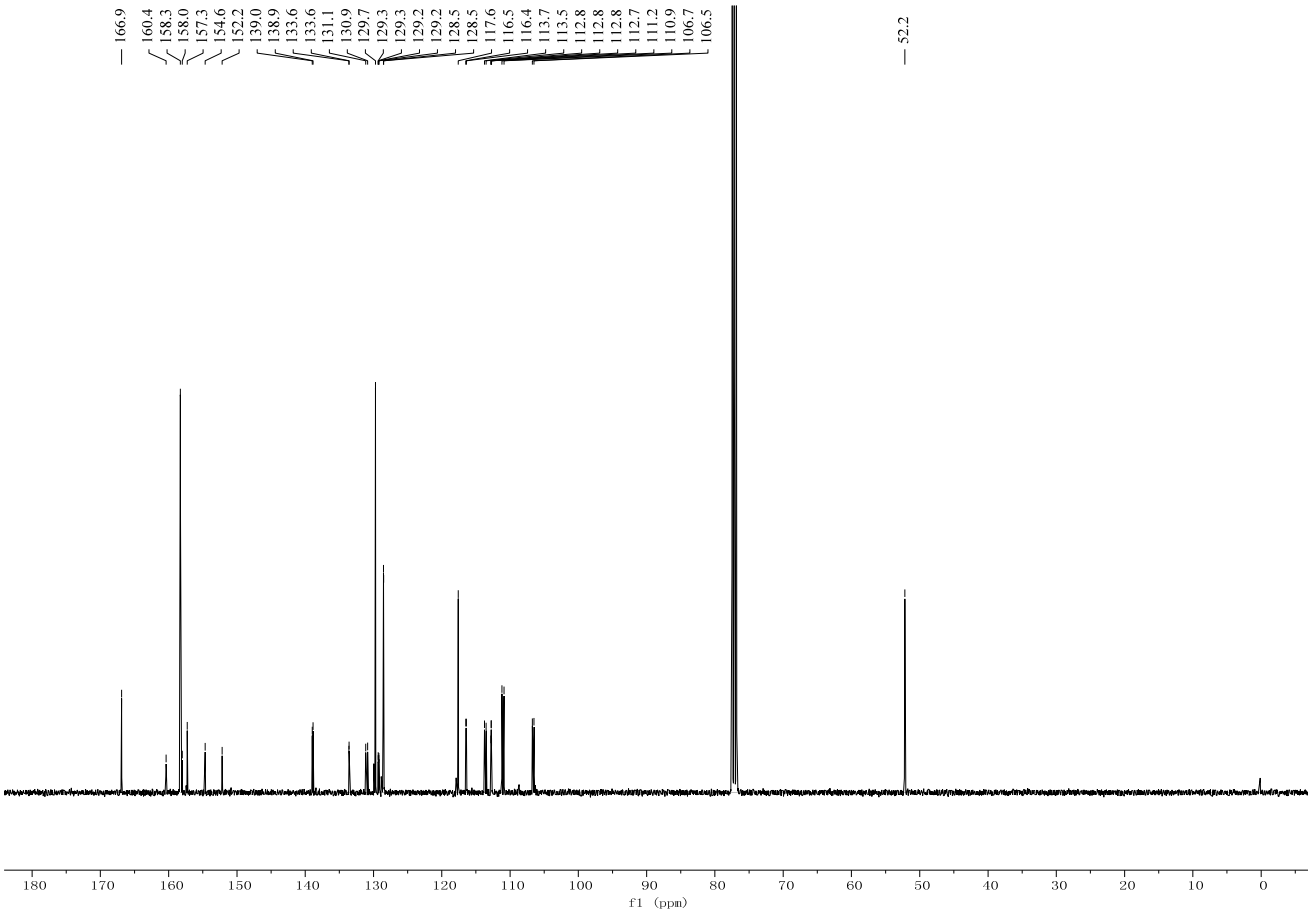
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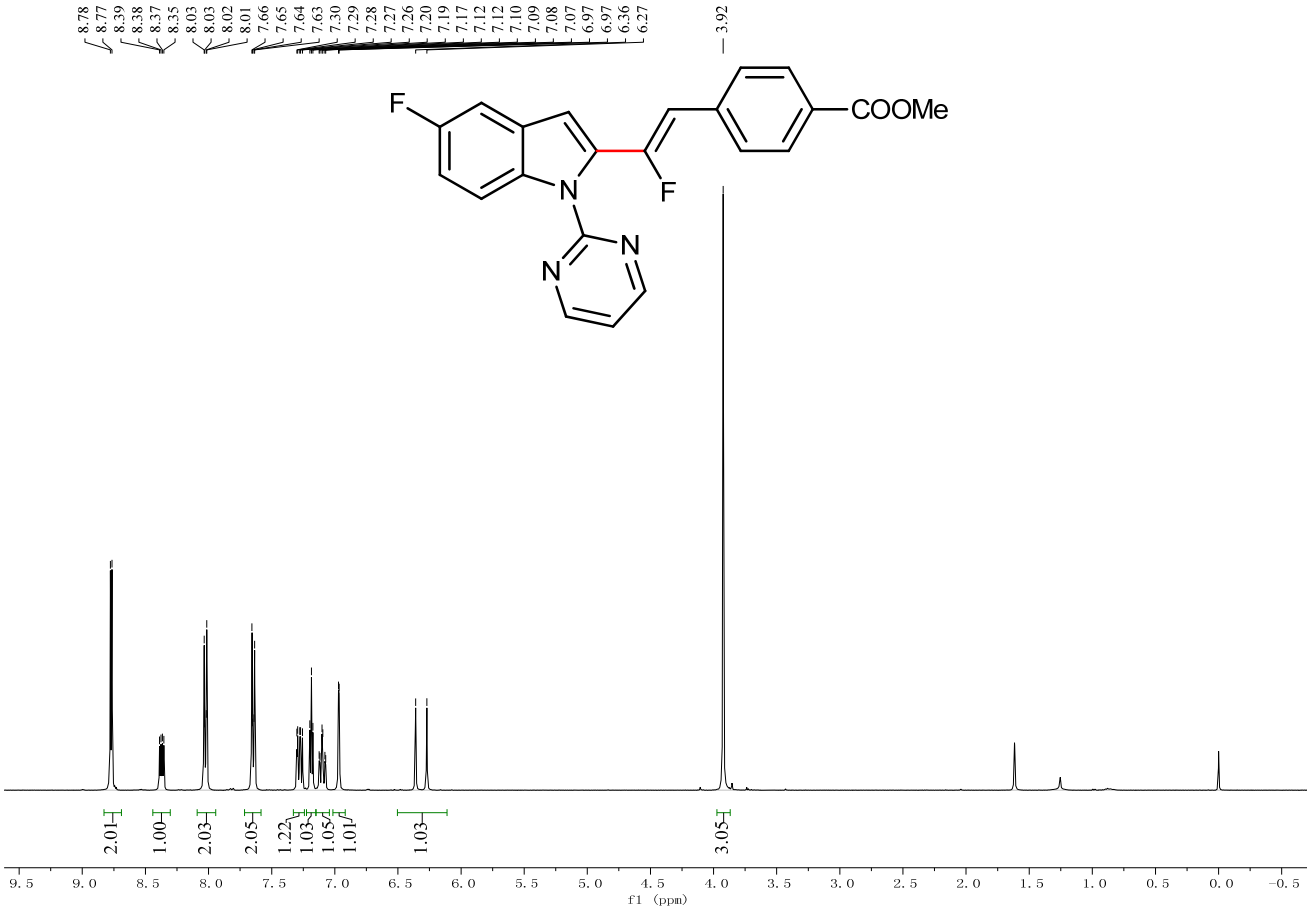
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6.97
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6.27
3.92
F
COOMe
F
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3.05
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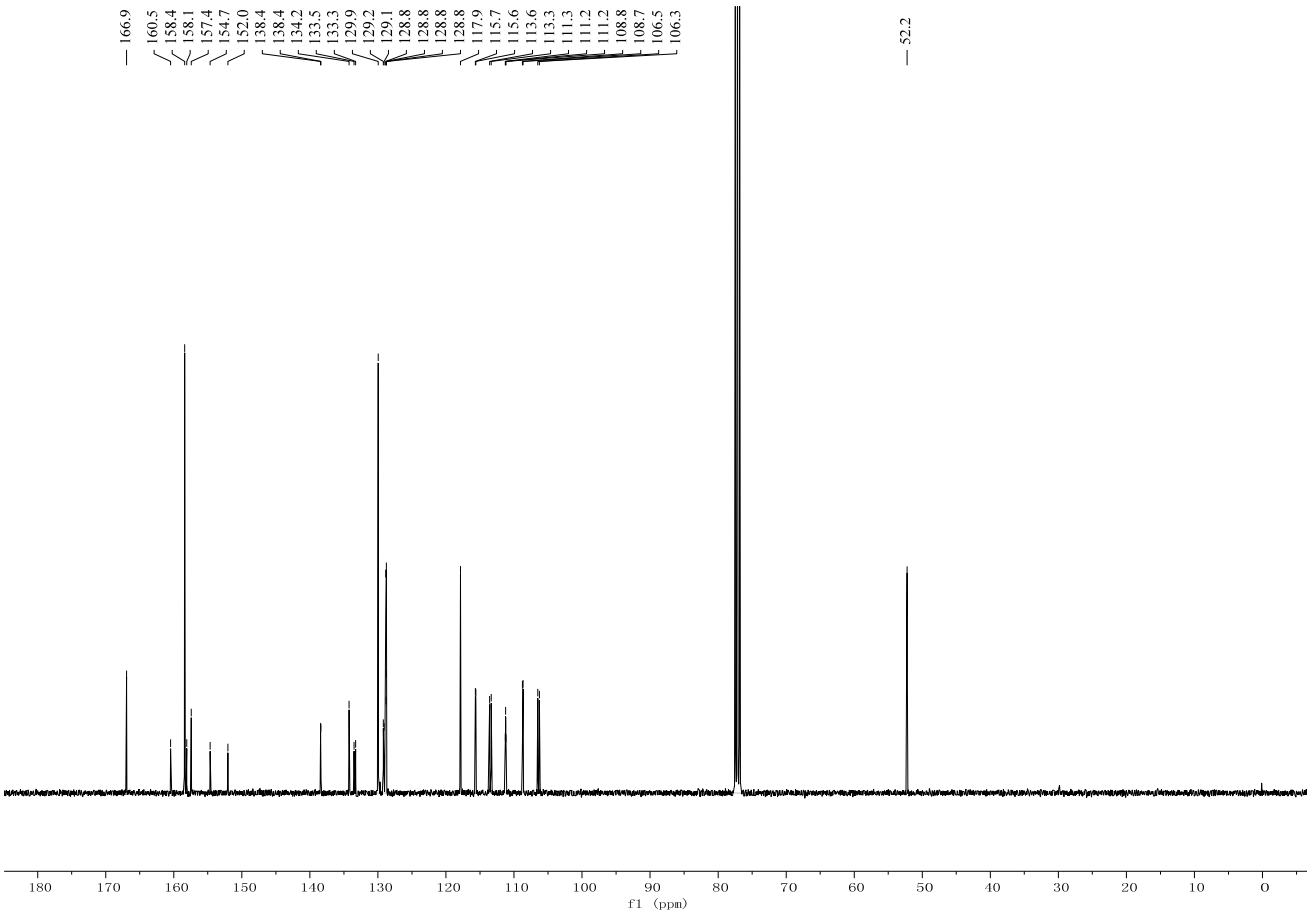
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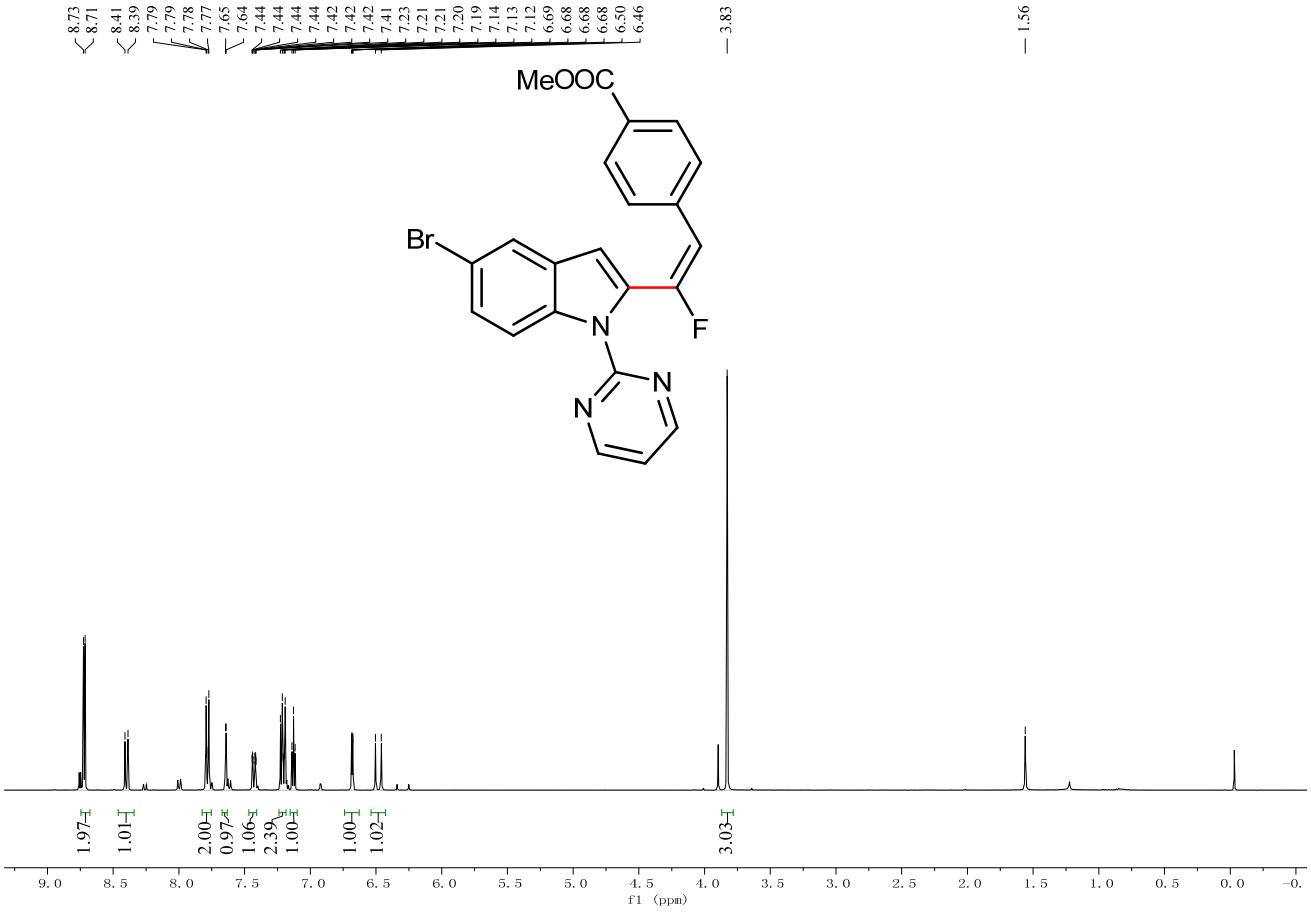
52.2
f1 (ppm)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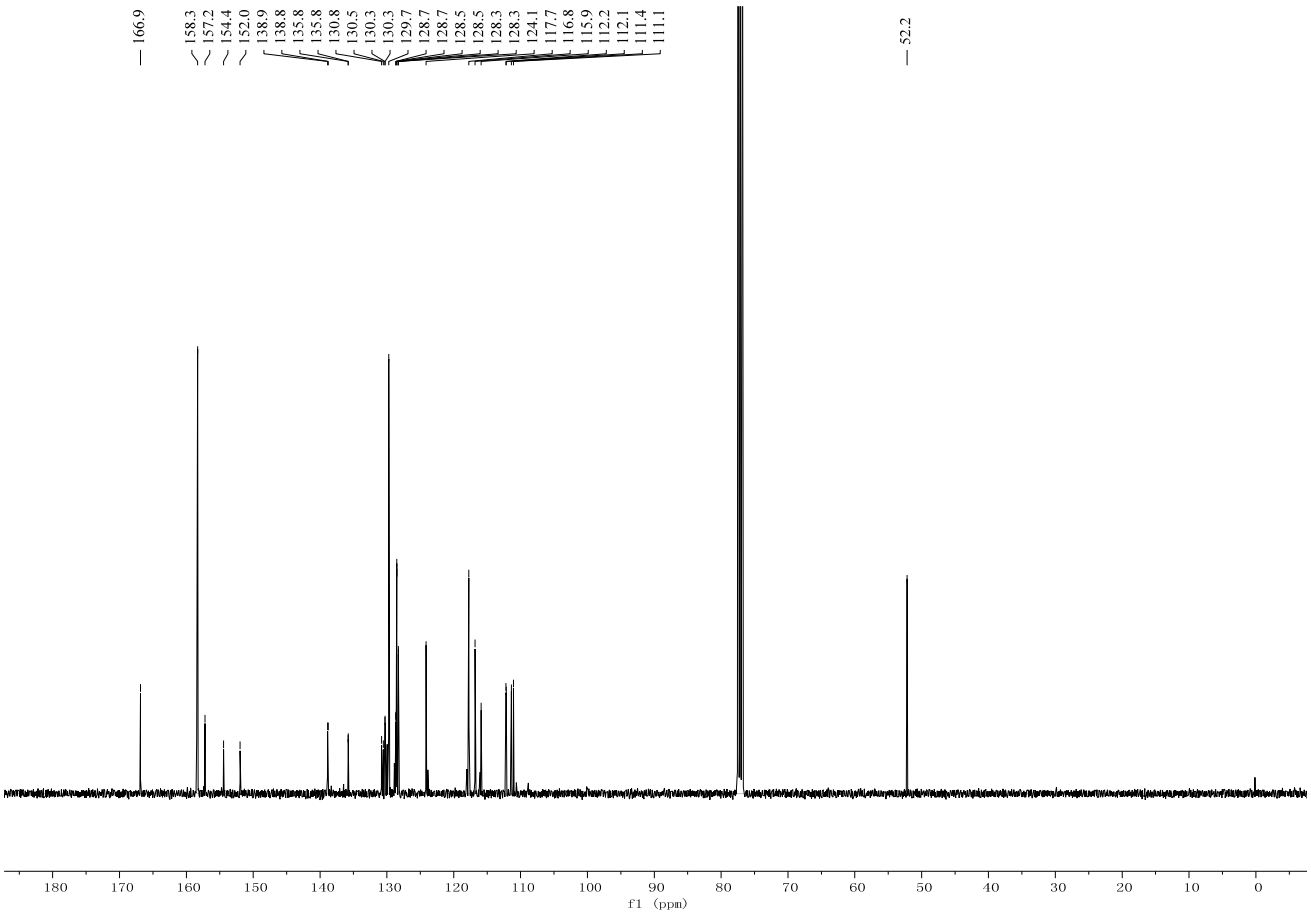
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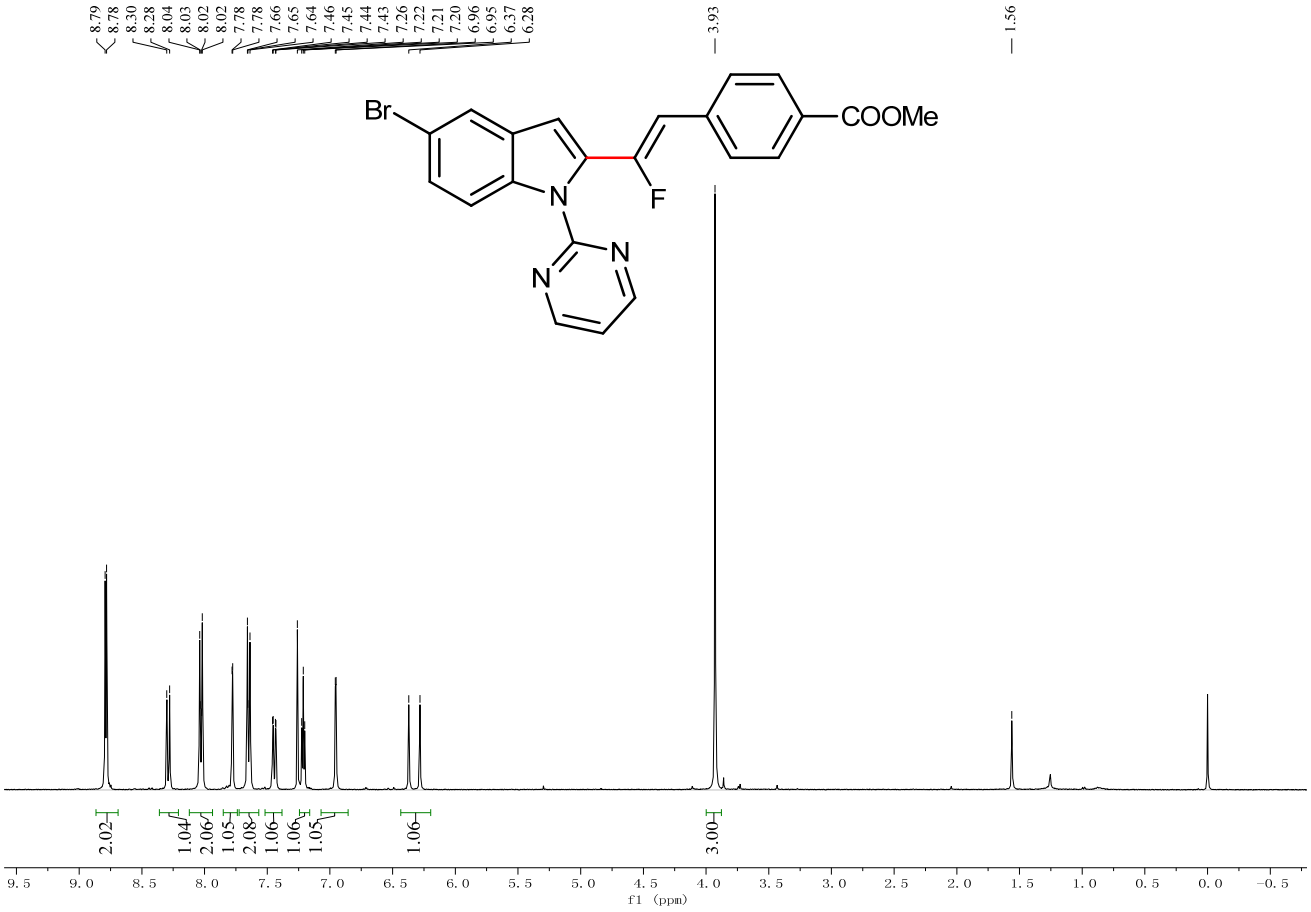
52.2
f1 (ppm)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7.43
7.26
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7.21
7.20
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6.95
6.37
6.28
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Br
COOMe
F
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1.06
1.06
1.05
1.06
3.00
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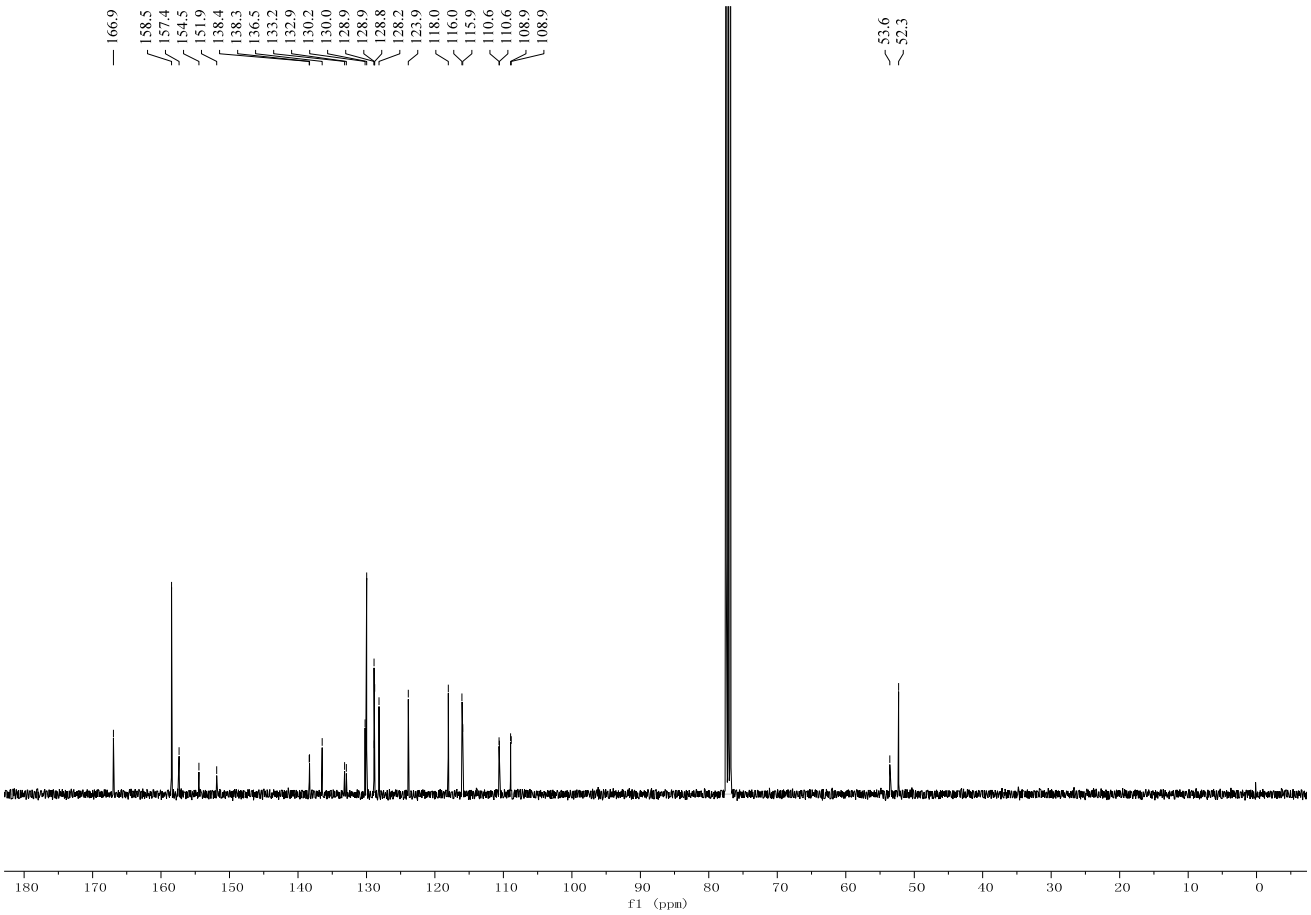
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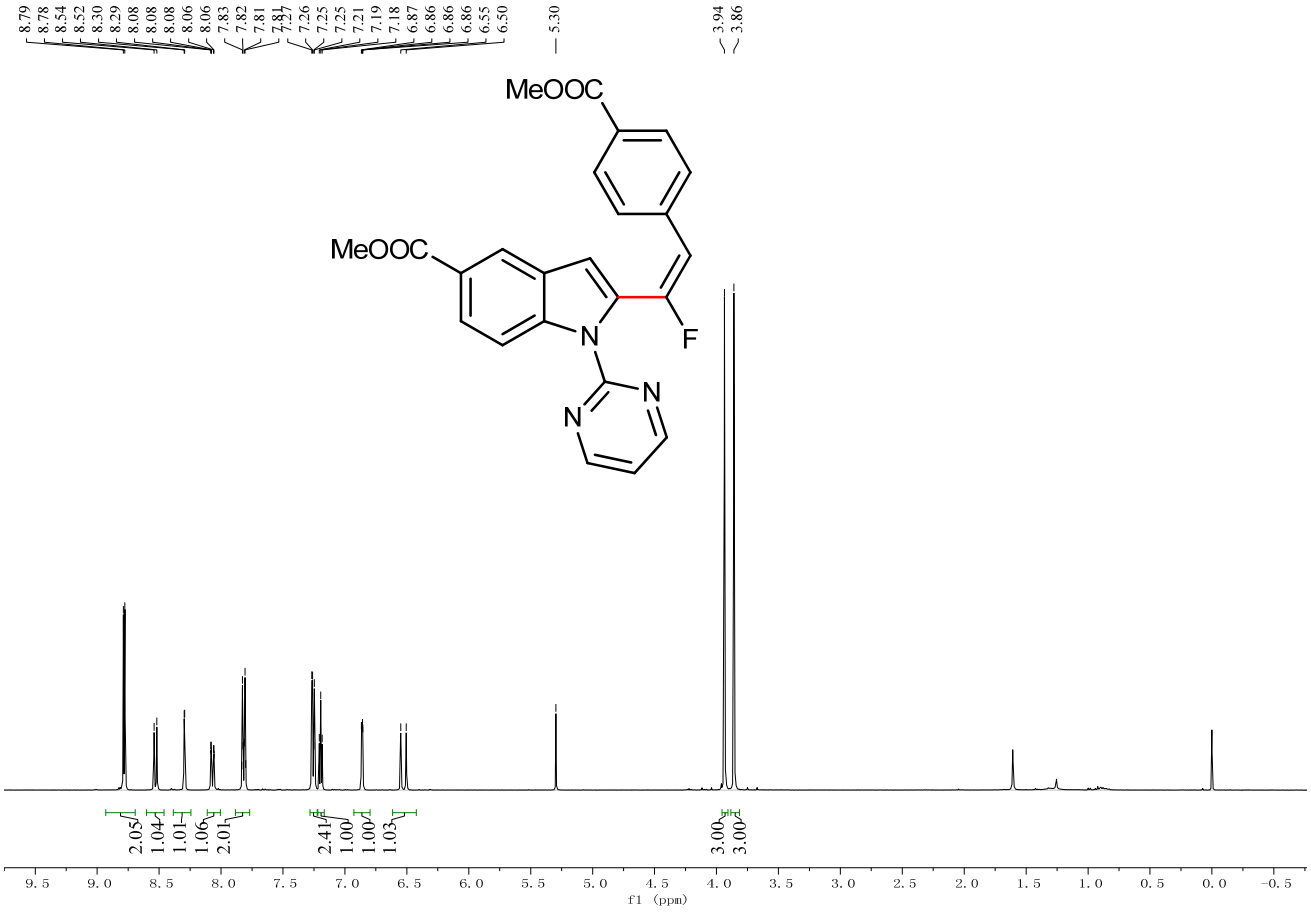
52.3
f1 (ppm)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6.86
6.86
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3.86
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MeOOC
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F
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N
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3.00
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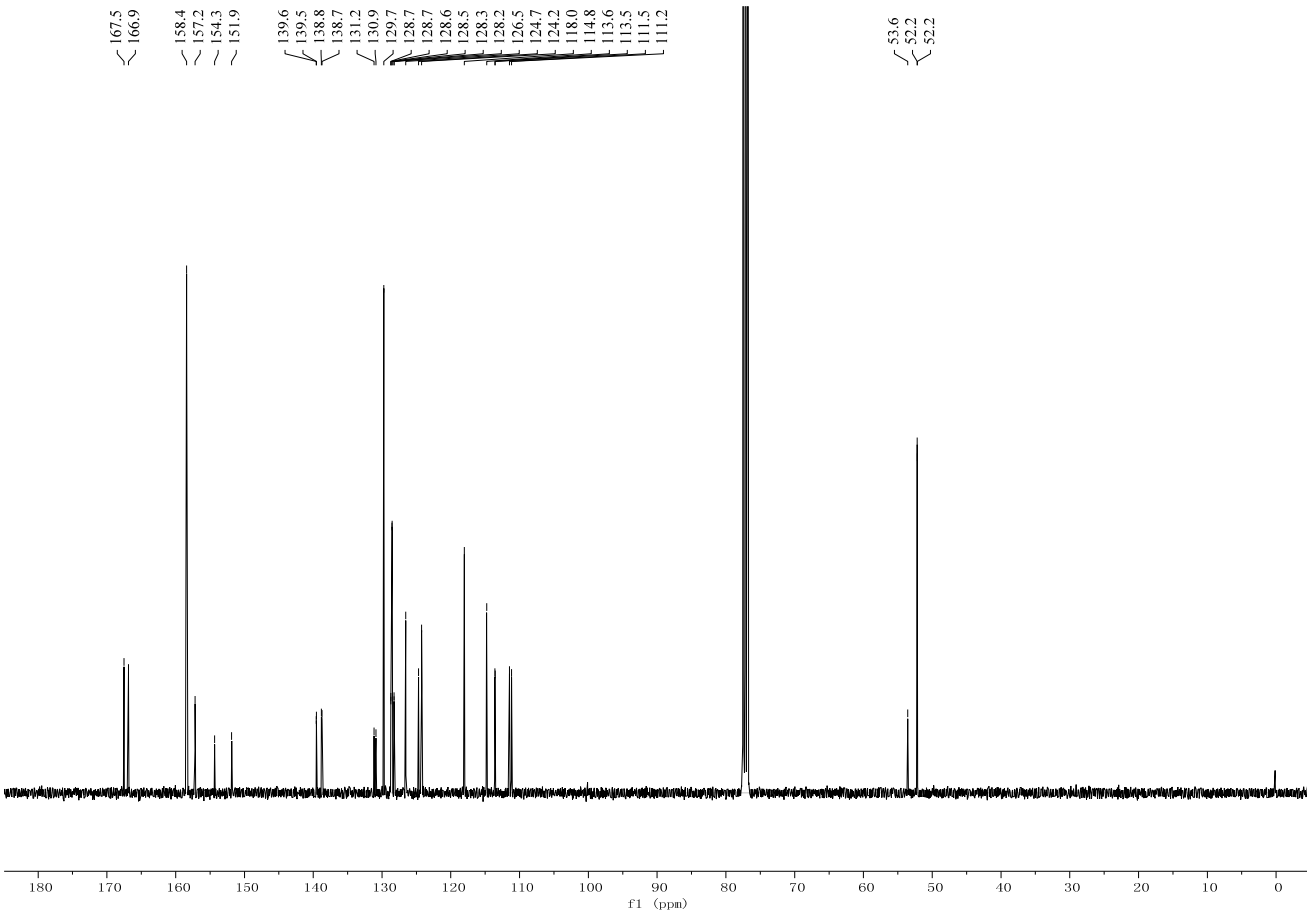
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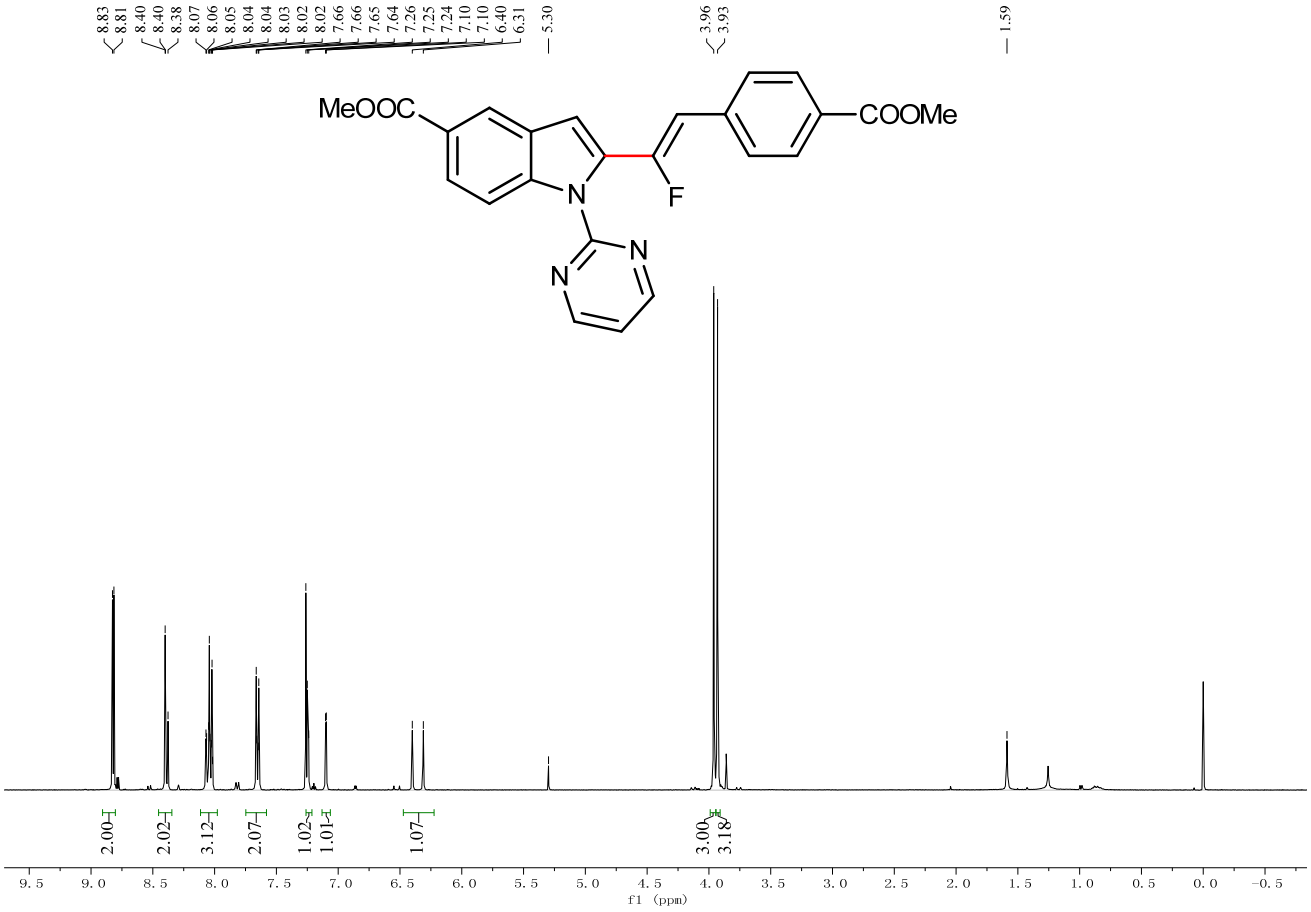
52.2
f1 (ppm)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COOMe
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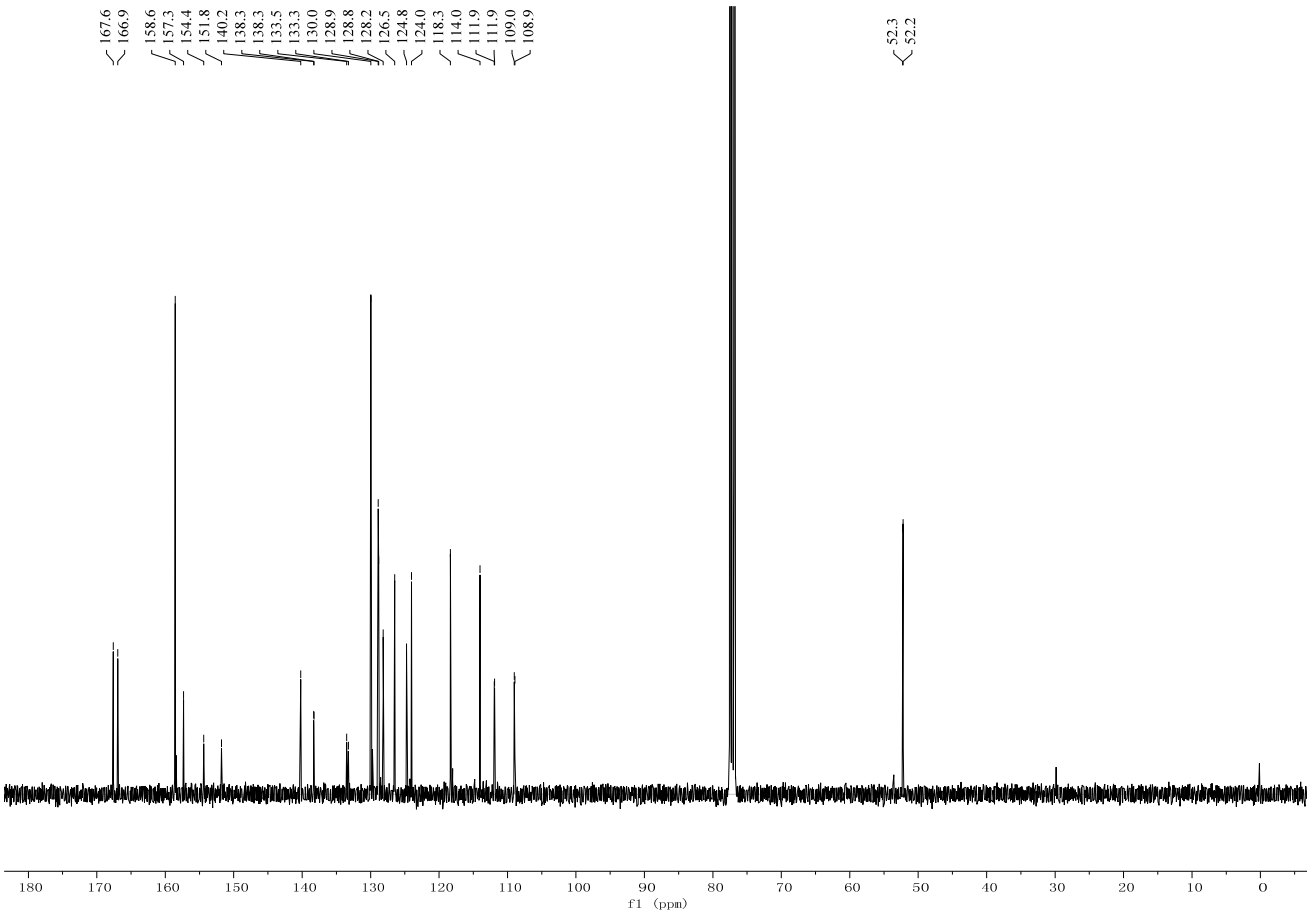
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128.2
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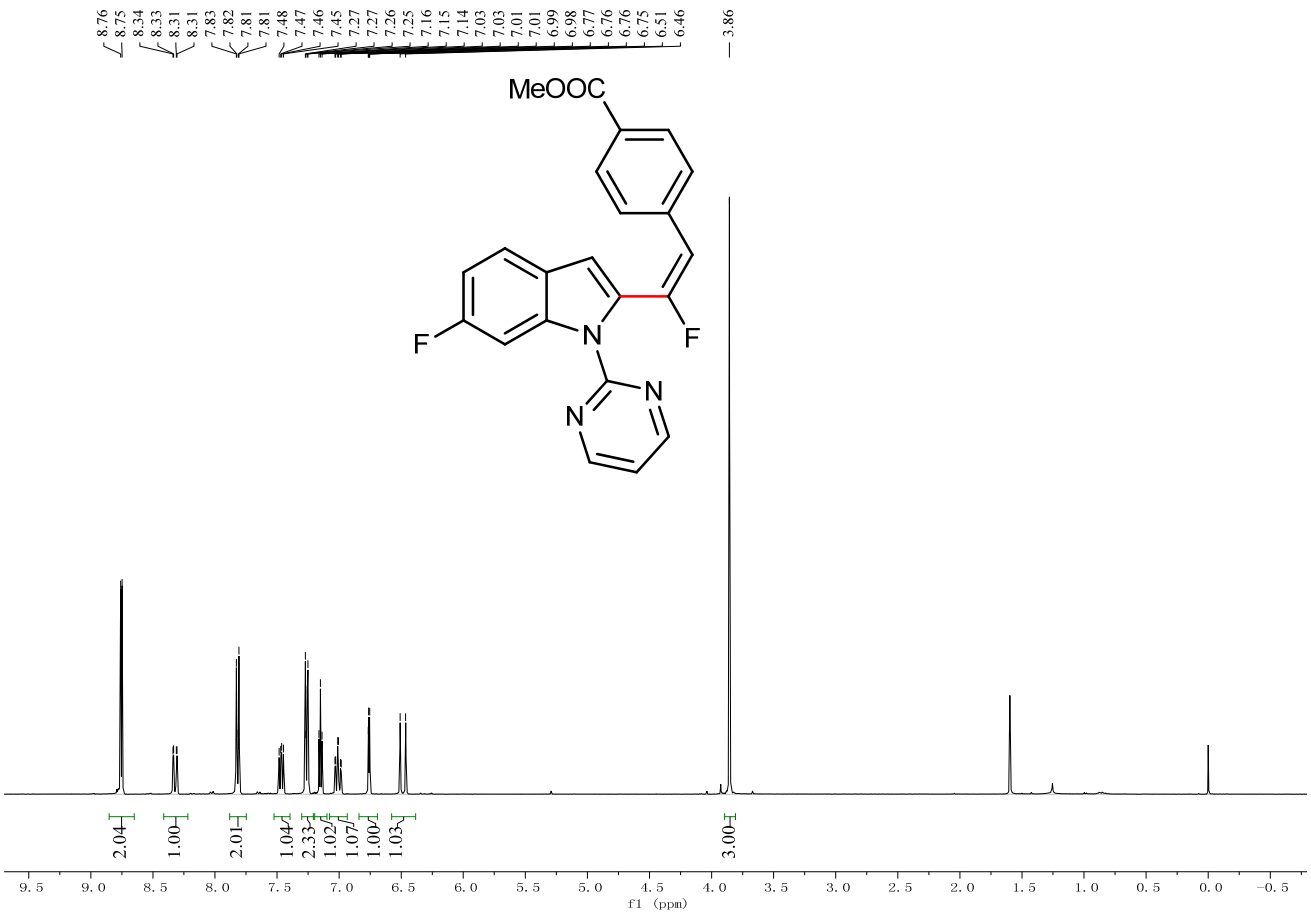
f1 (ppm)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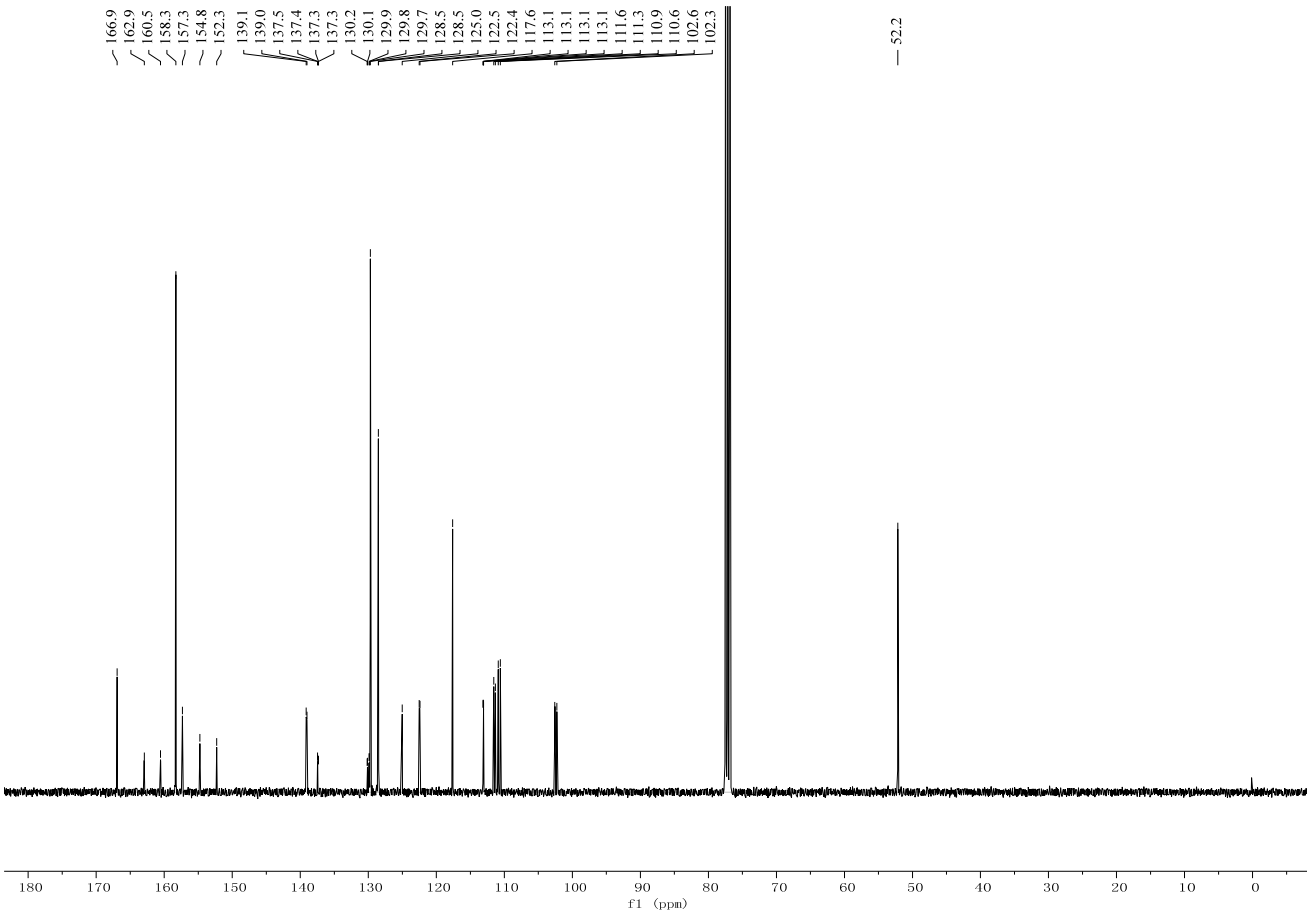
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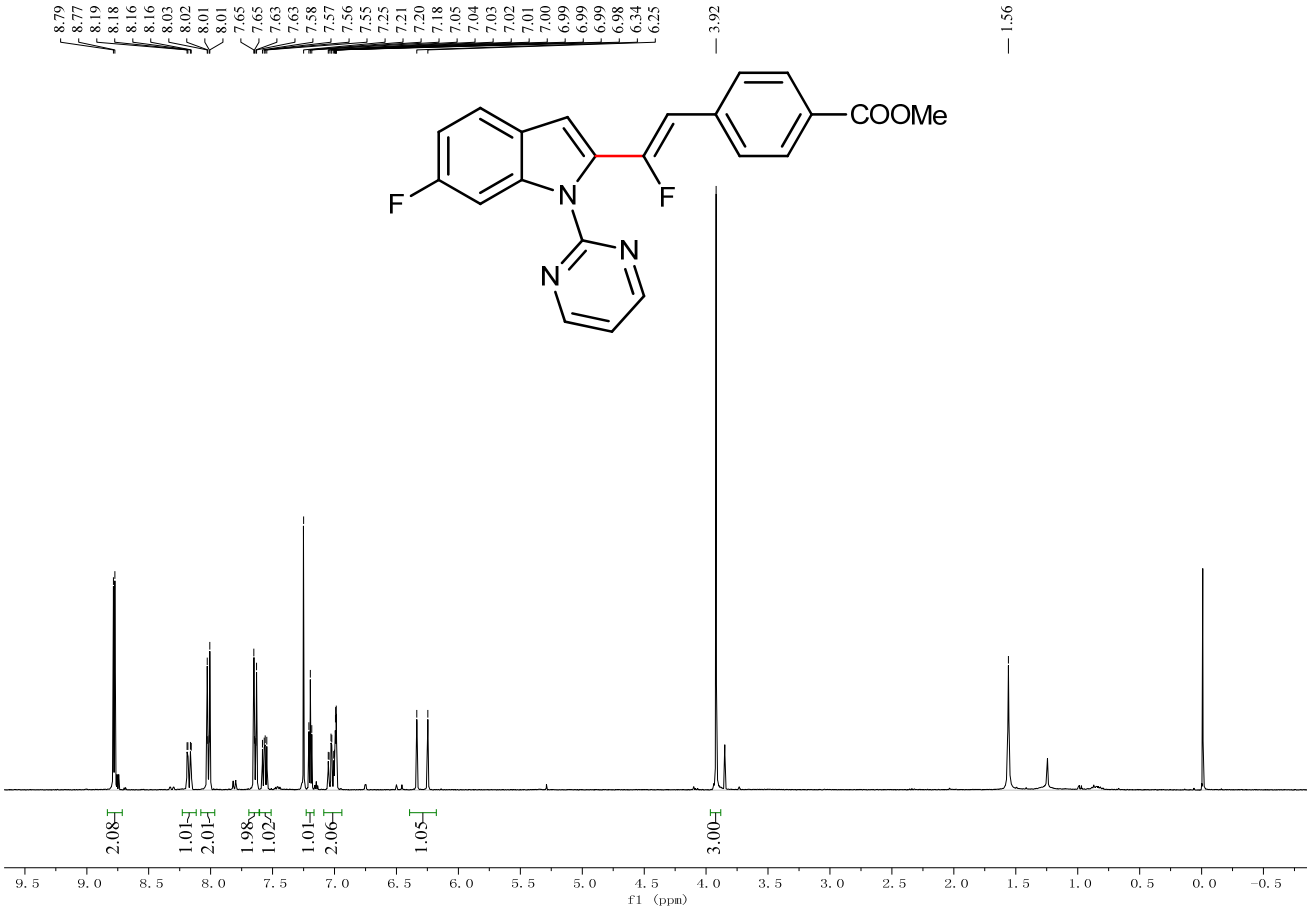
52.2
f1 (ppm)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COOMe
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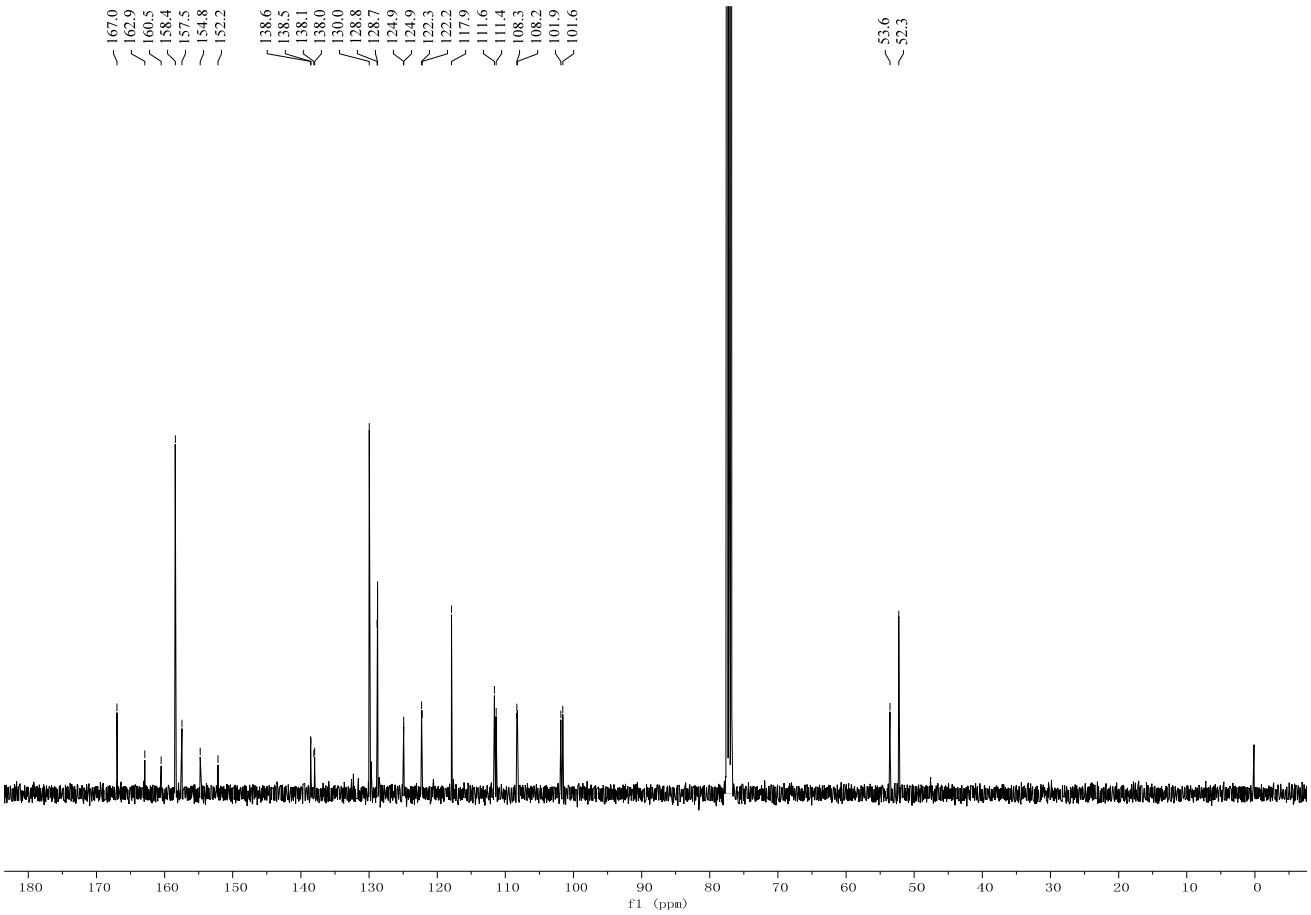
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124.9
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111.4
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108.2
101.9
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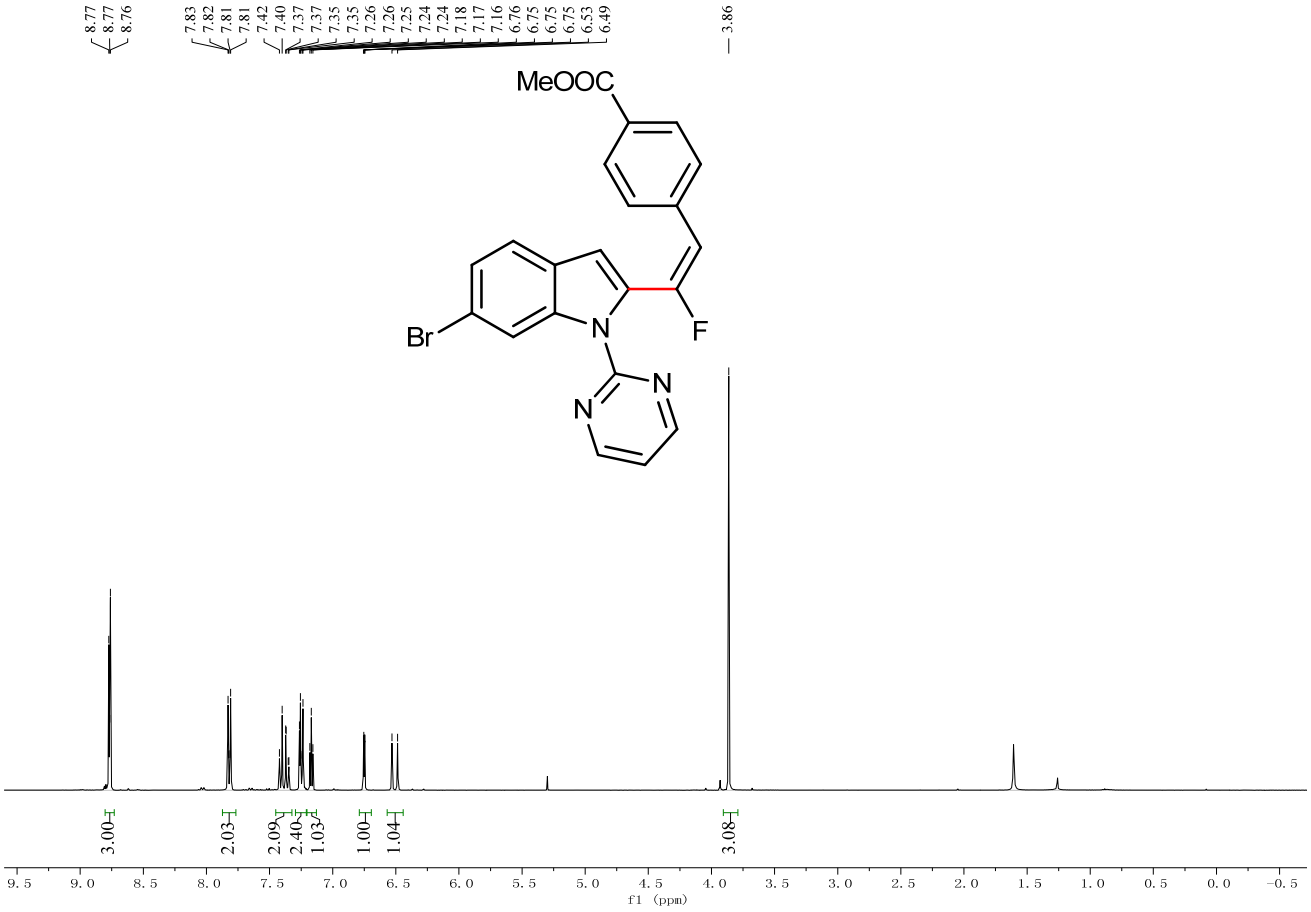
52.3
f1 (ppm)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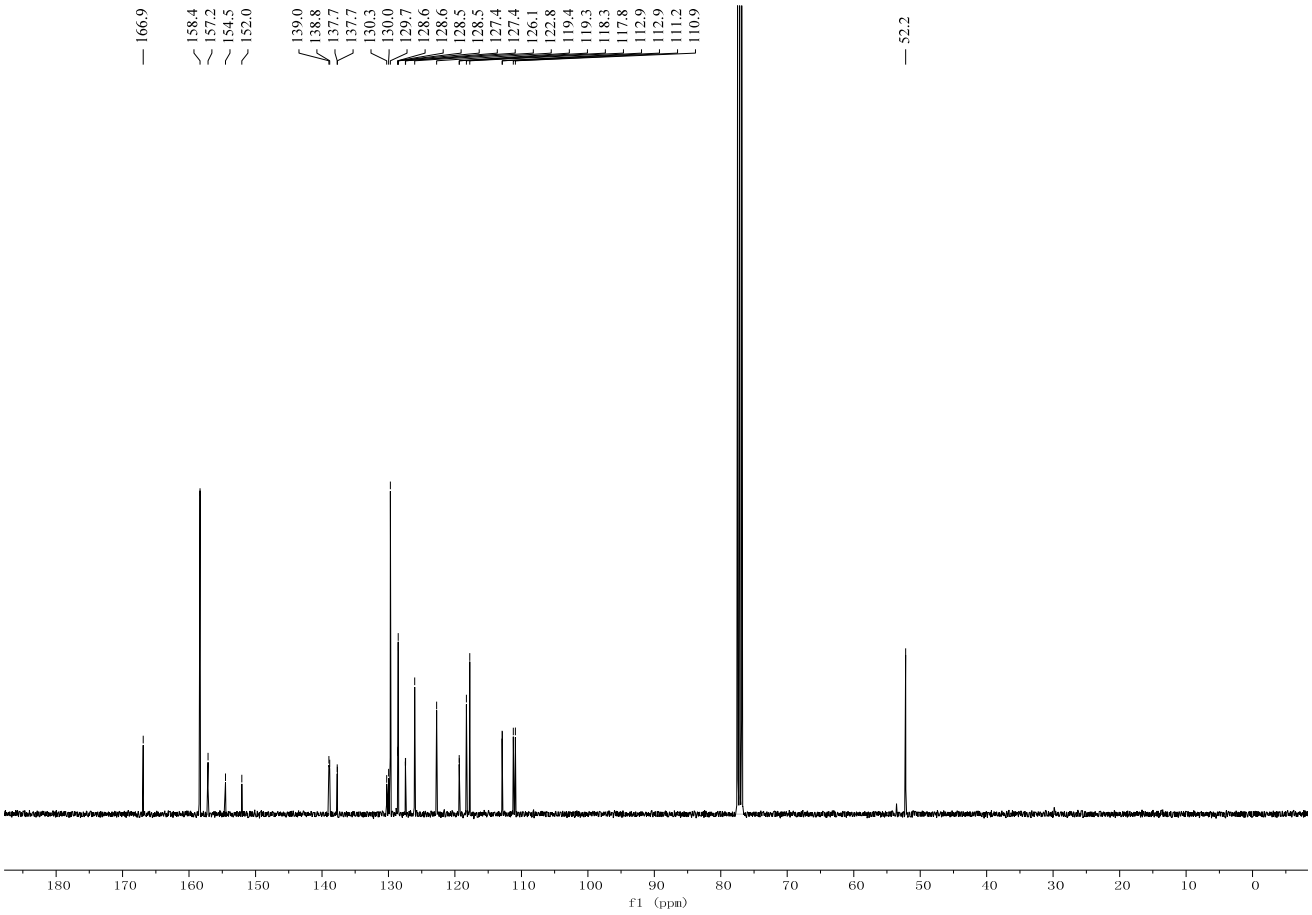
1.00
1.04
3.08
f1 (ppm)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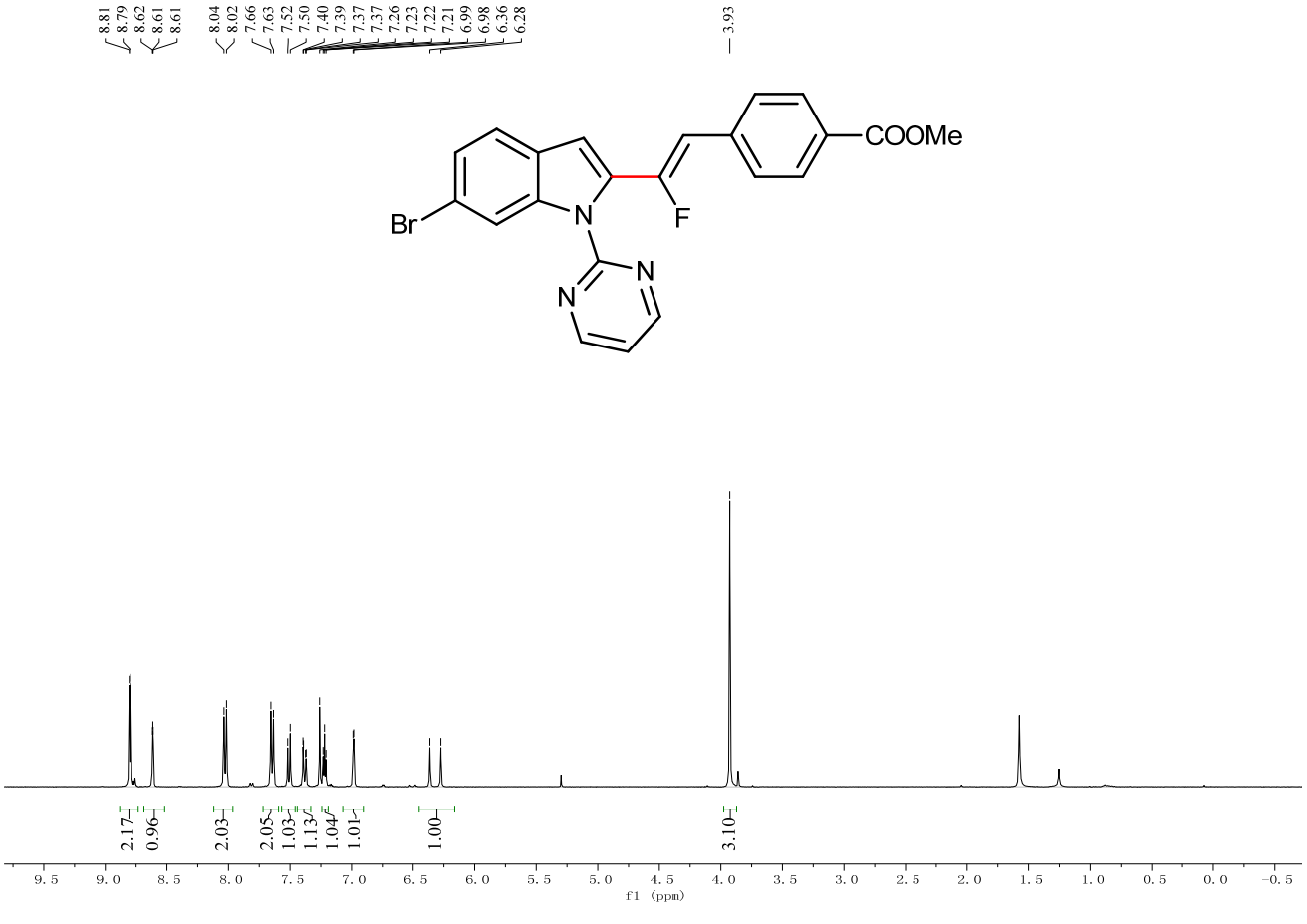
f1 (ppm)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6.28
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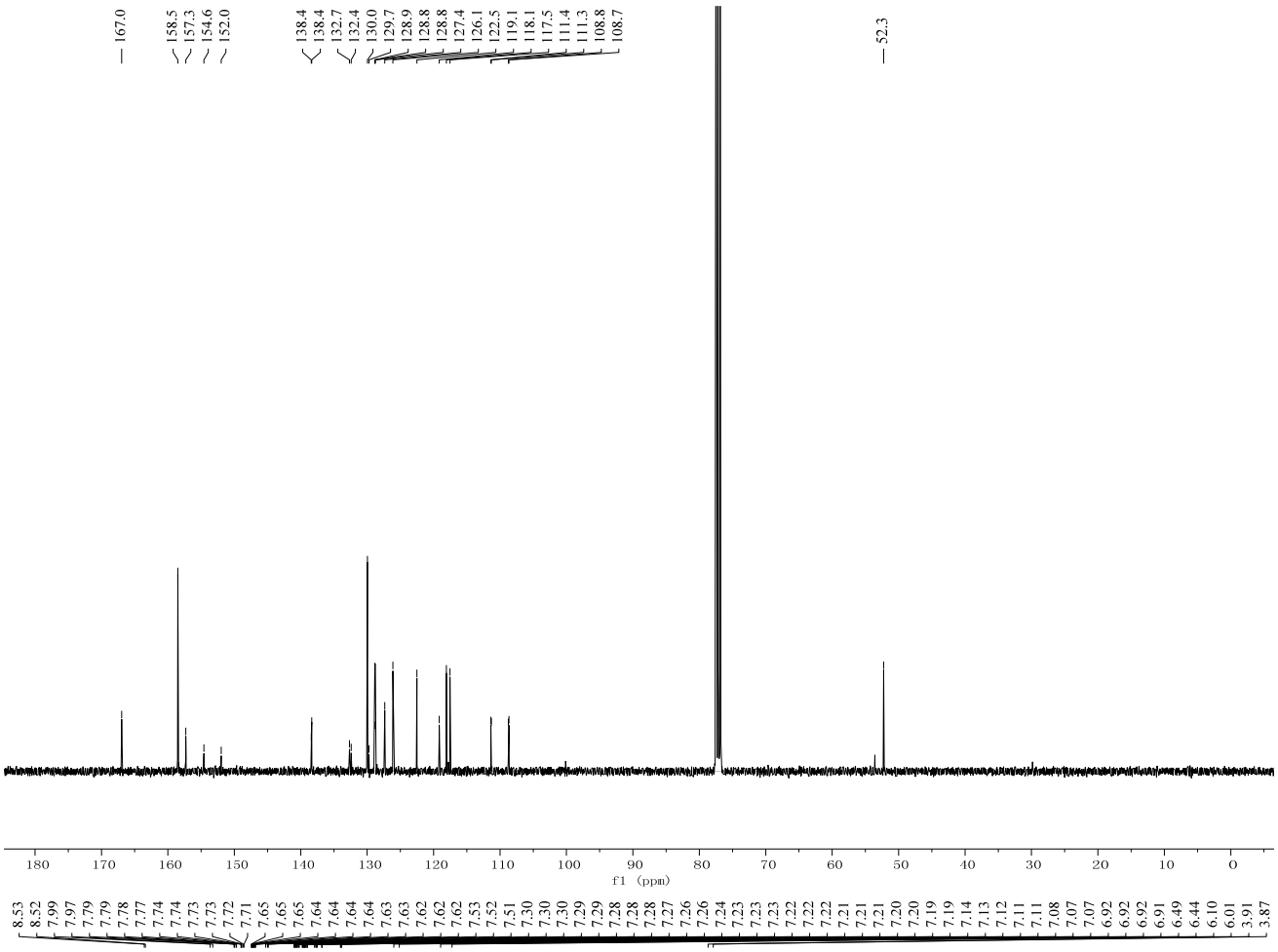
1.04
1.01
1.00
3.10
f1 (ppm)

COOMe
Br
N
F
N
N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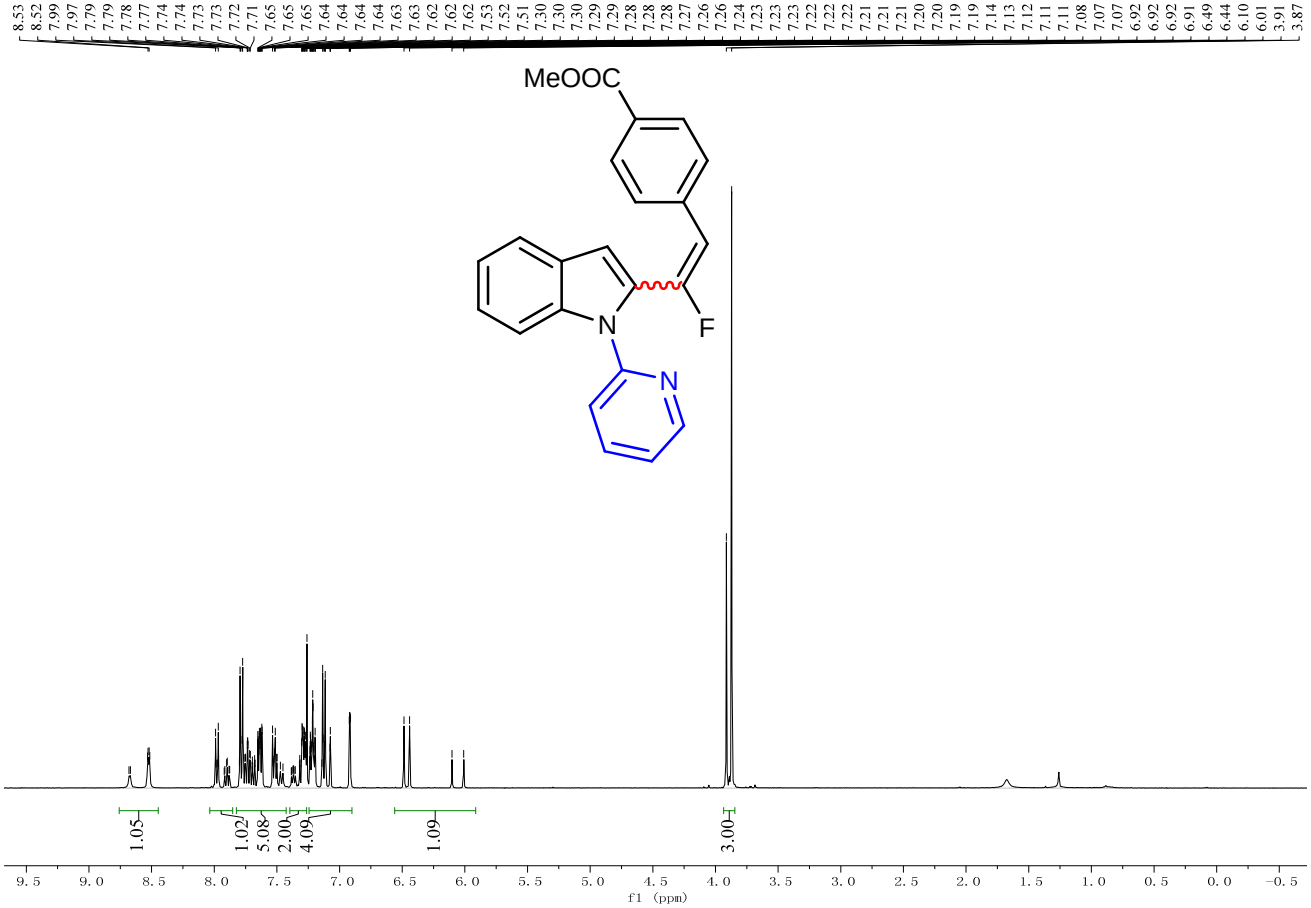
52.3
f1 (ppm)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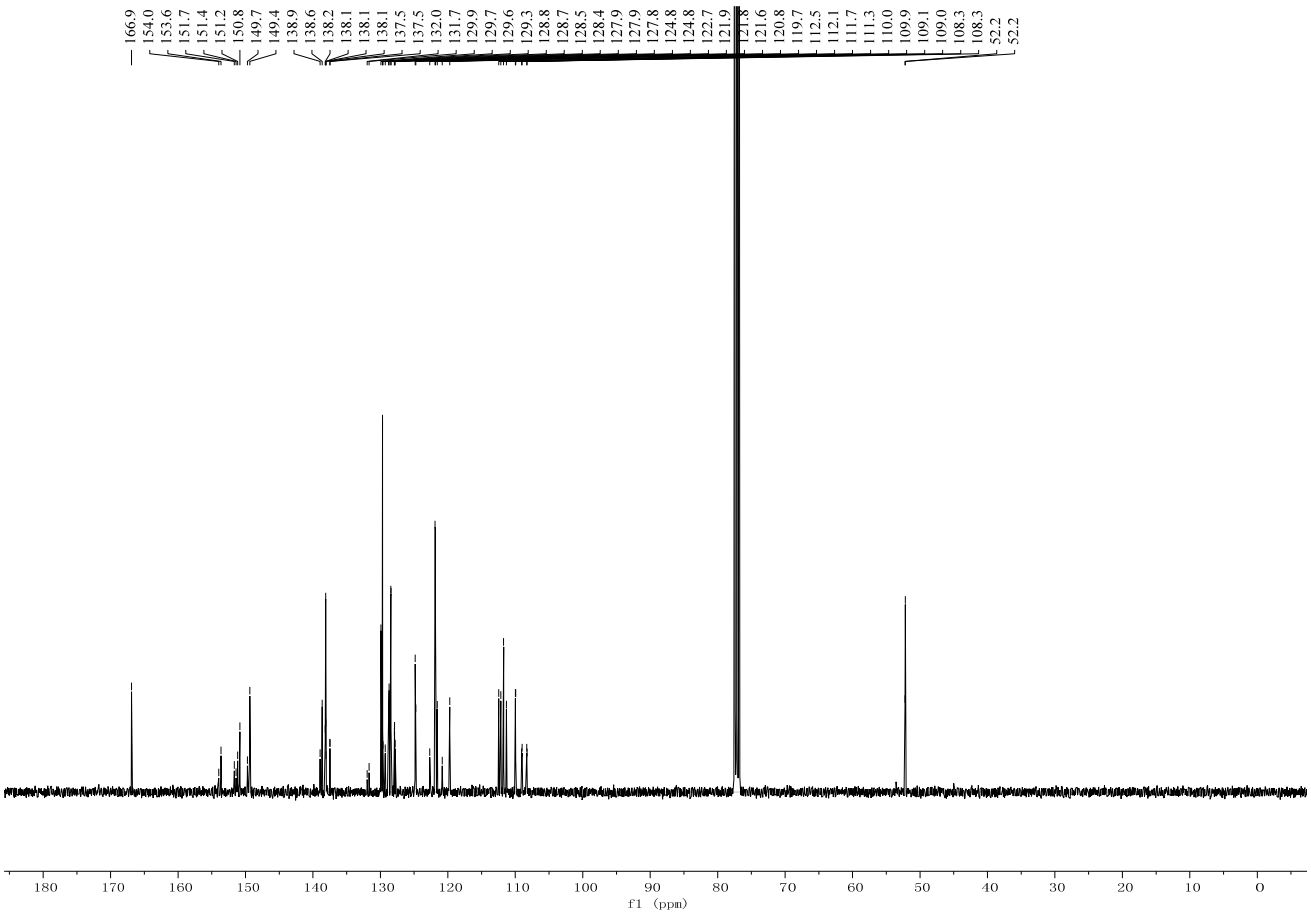
f1 (ppm)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52.2
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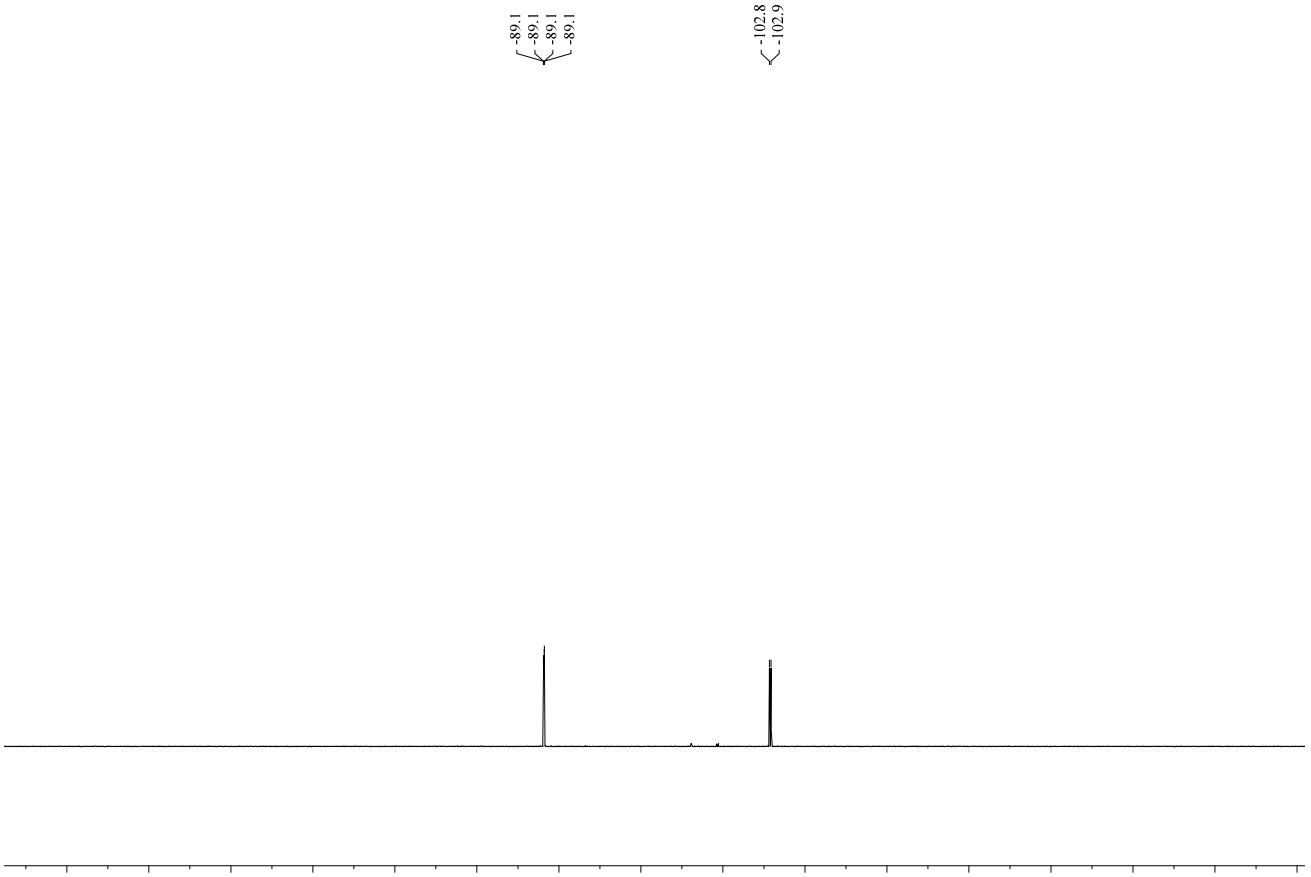
f1 (ppm)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-89.1
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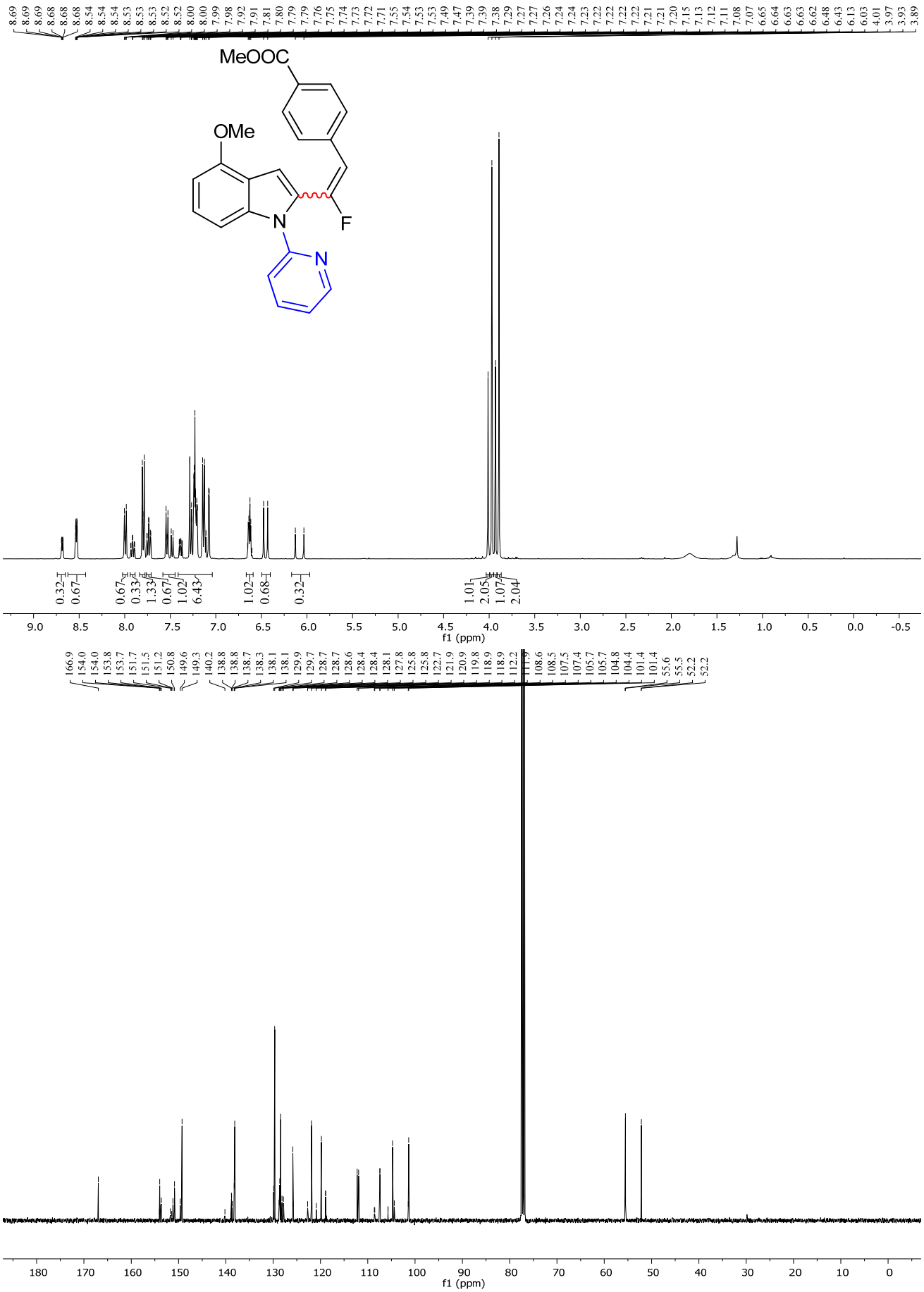
-102.9
−60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130
f1 (ppm)


MeOOC
OMe
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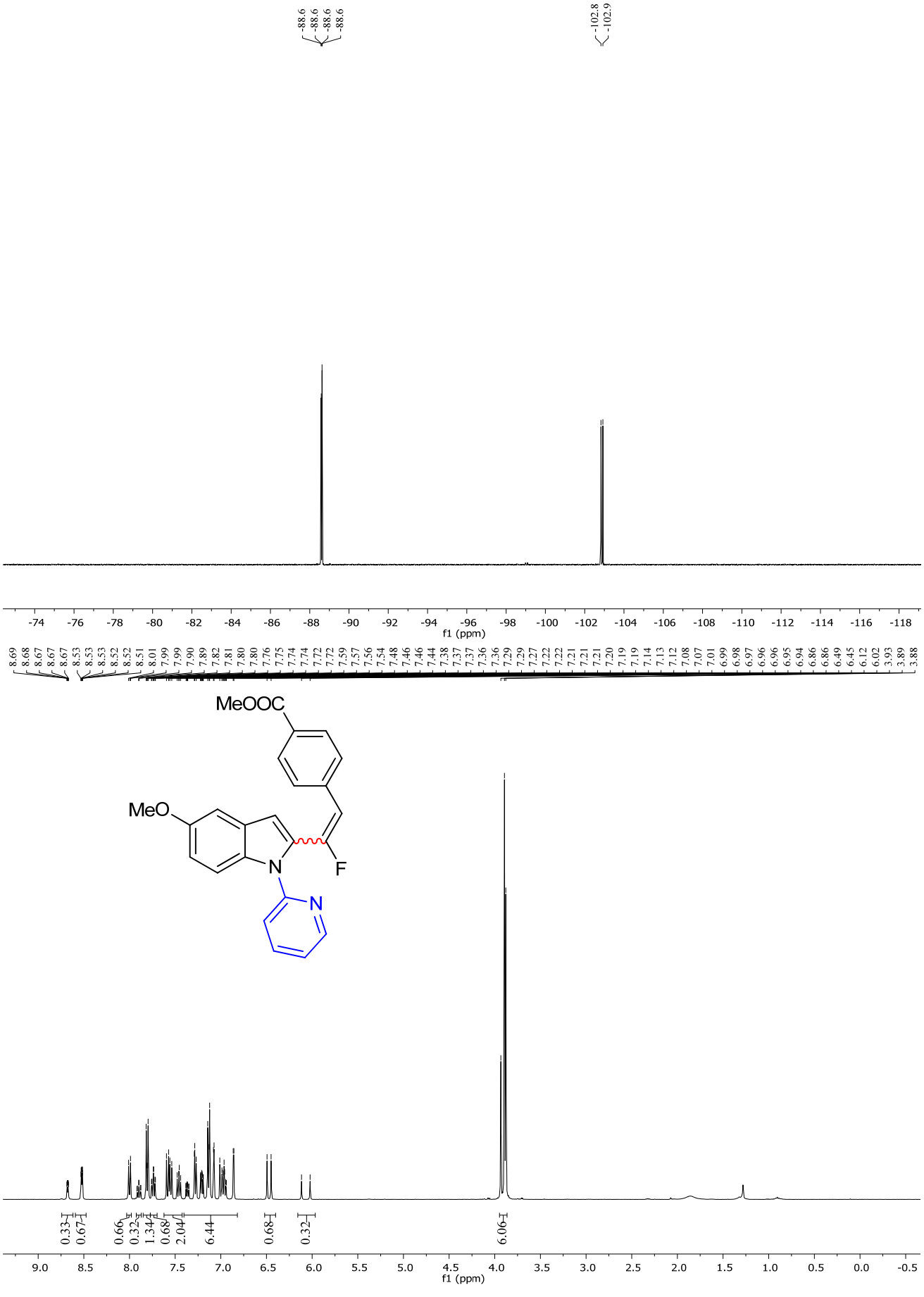
F
N
f1 (ppm)
f1 (ppm)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-88.6
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-102.9
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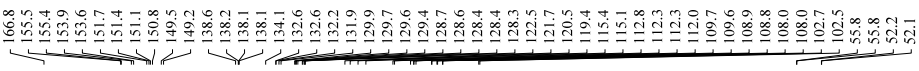
MeO
N
F
N
f1 (ppm)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155.4
153.9
153.6
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151.4
151.1
150.8
149.5
149.2
138.6
138.2
138.1
138.1
134.1
132.6
132.6
132.2
131.9
129.9
129.7
129.6
129.4
128.7
128.6
128.4
128.4
128.3
122.5
121.7
120.5
119.4
115.4
115.1
112.8
112.3
112.3
112.0
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108.8
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108.0
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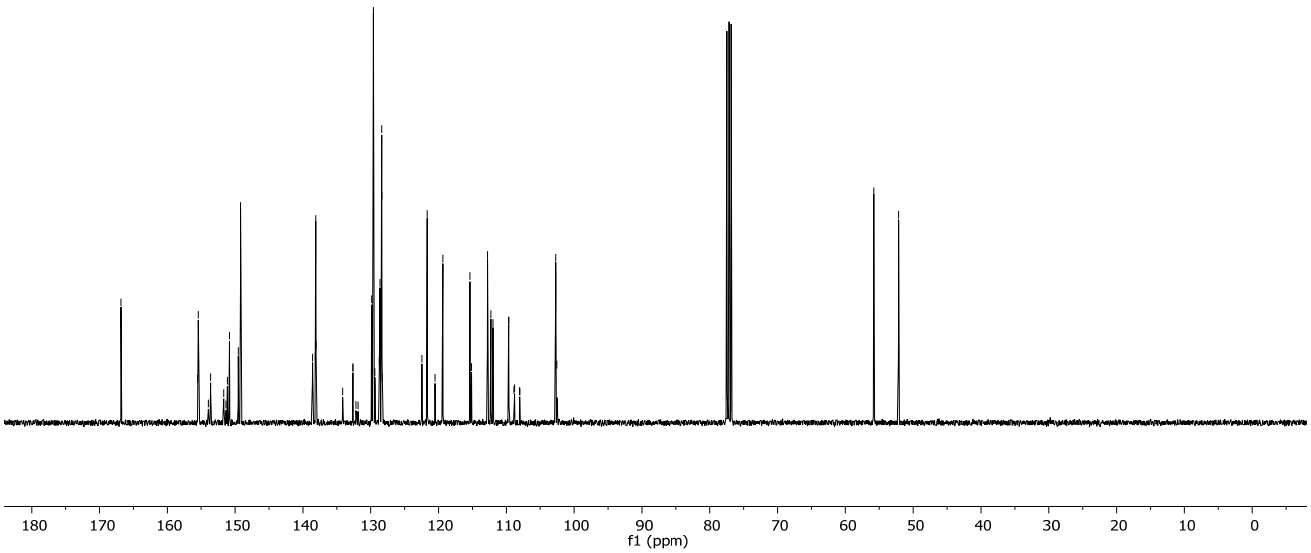
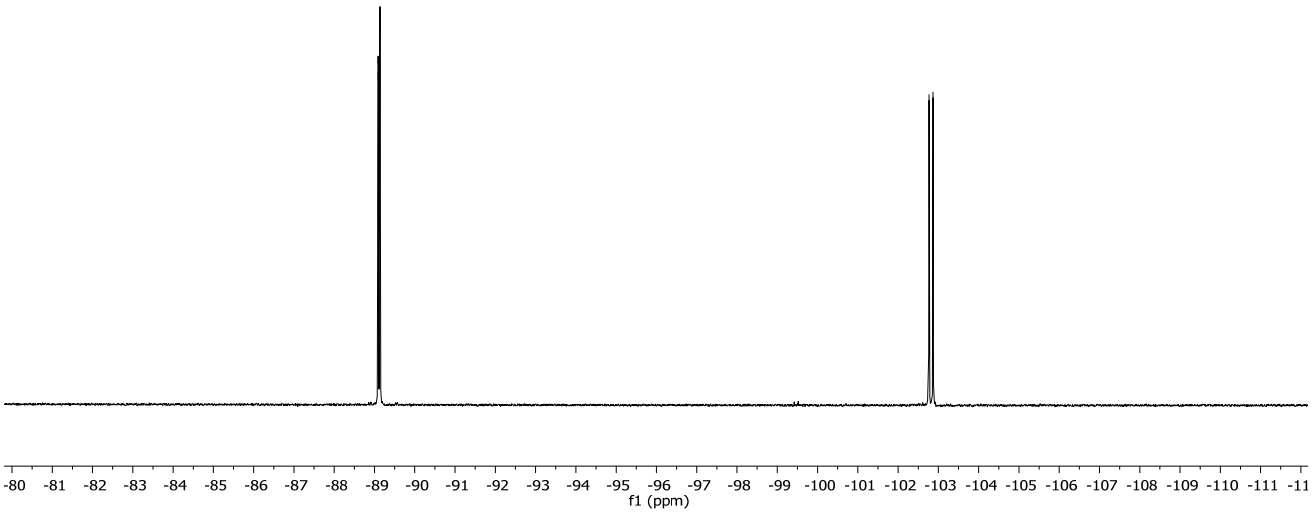
102.5
55.8
55.8
52.2
52.1


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-89.1
-89.1
-89.1
-89.1
-102.8
-102.9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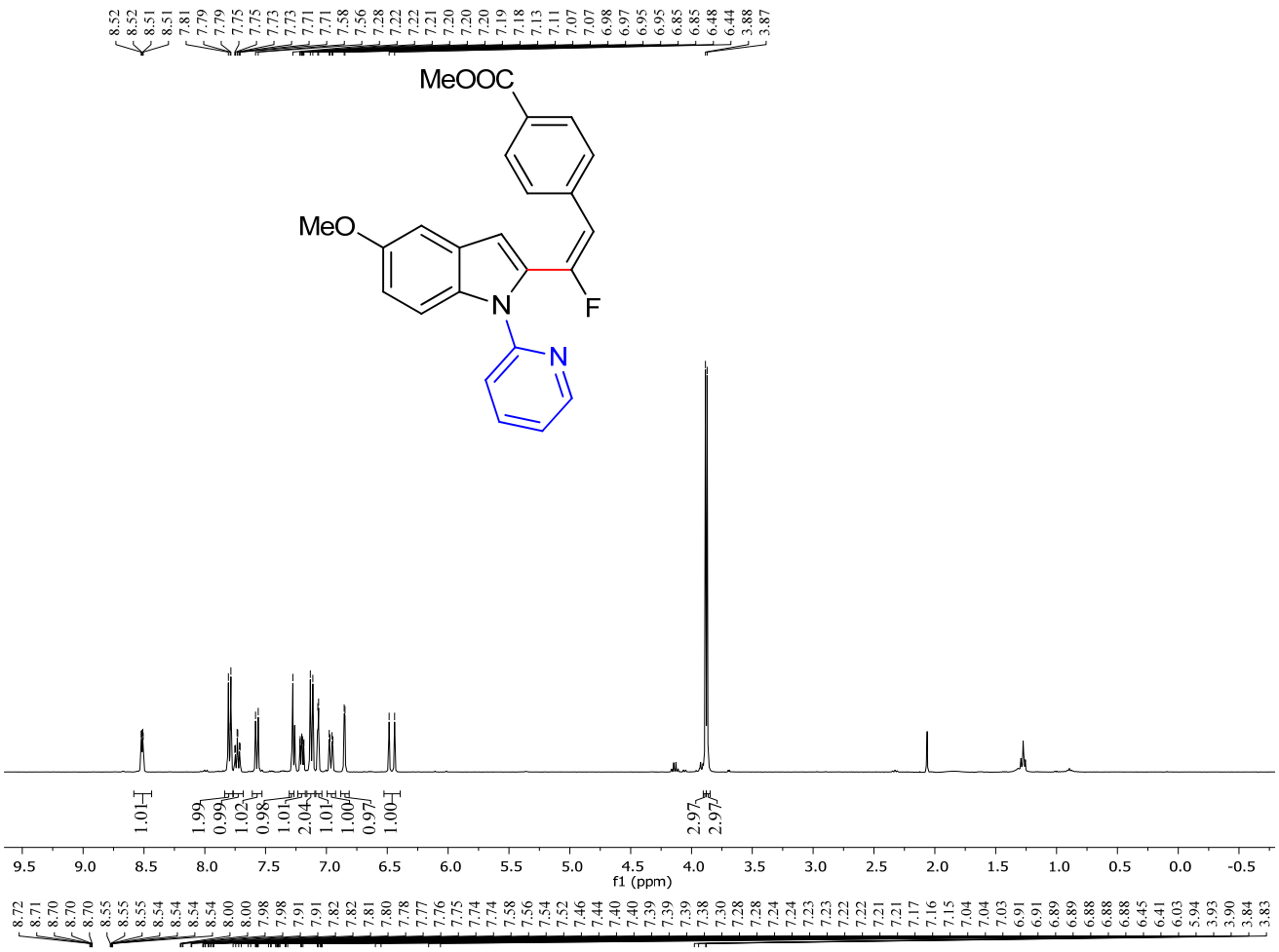
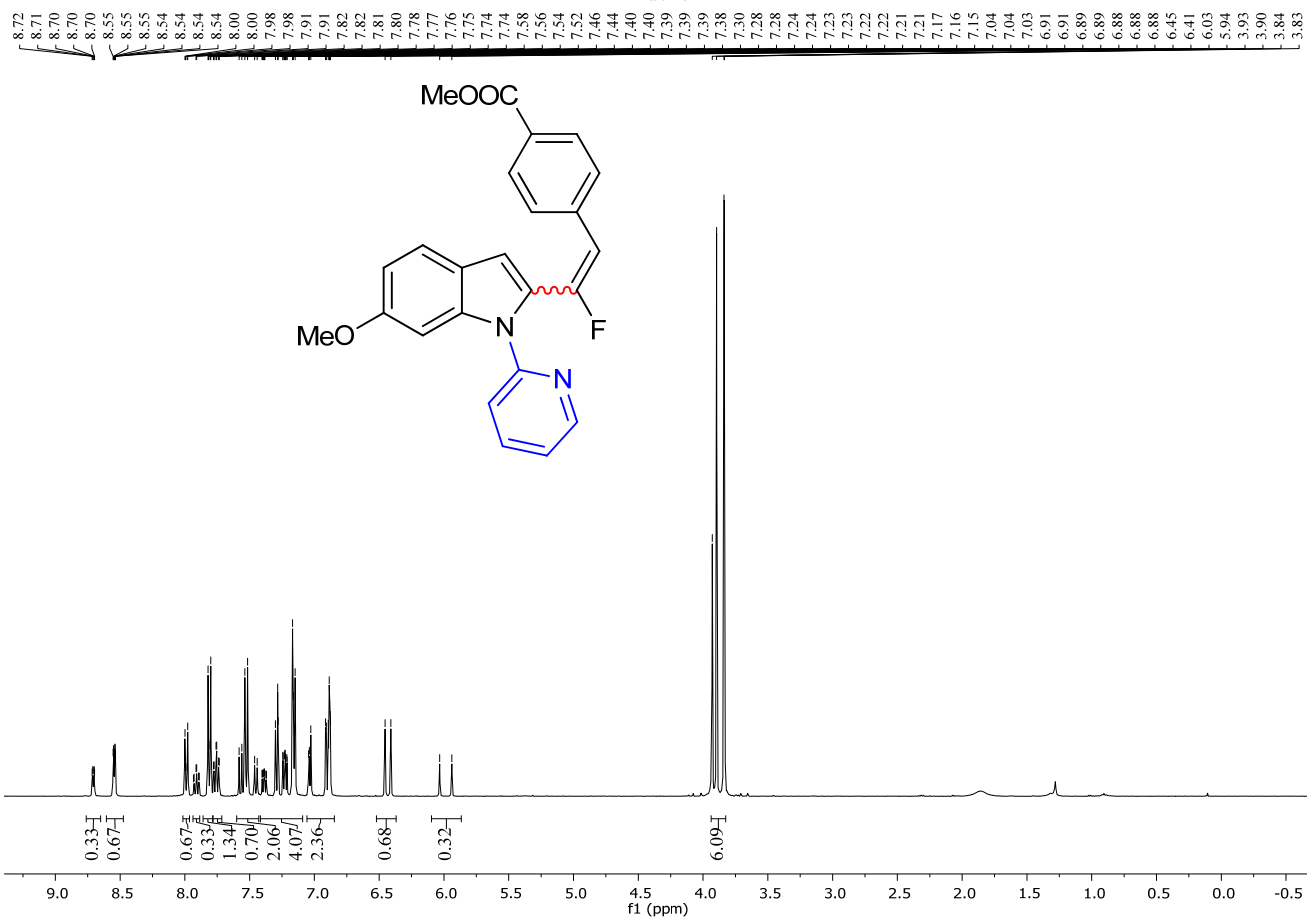
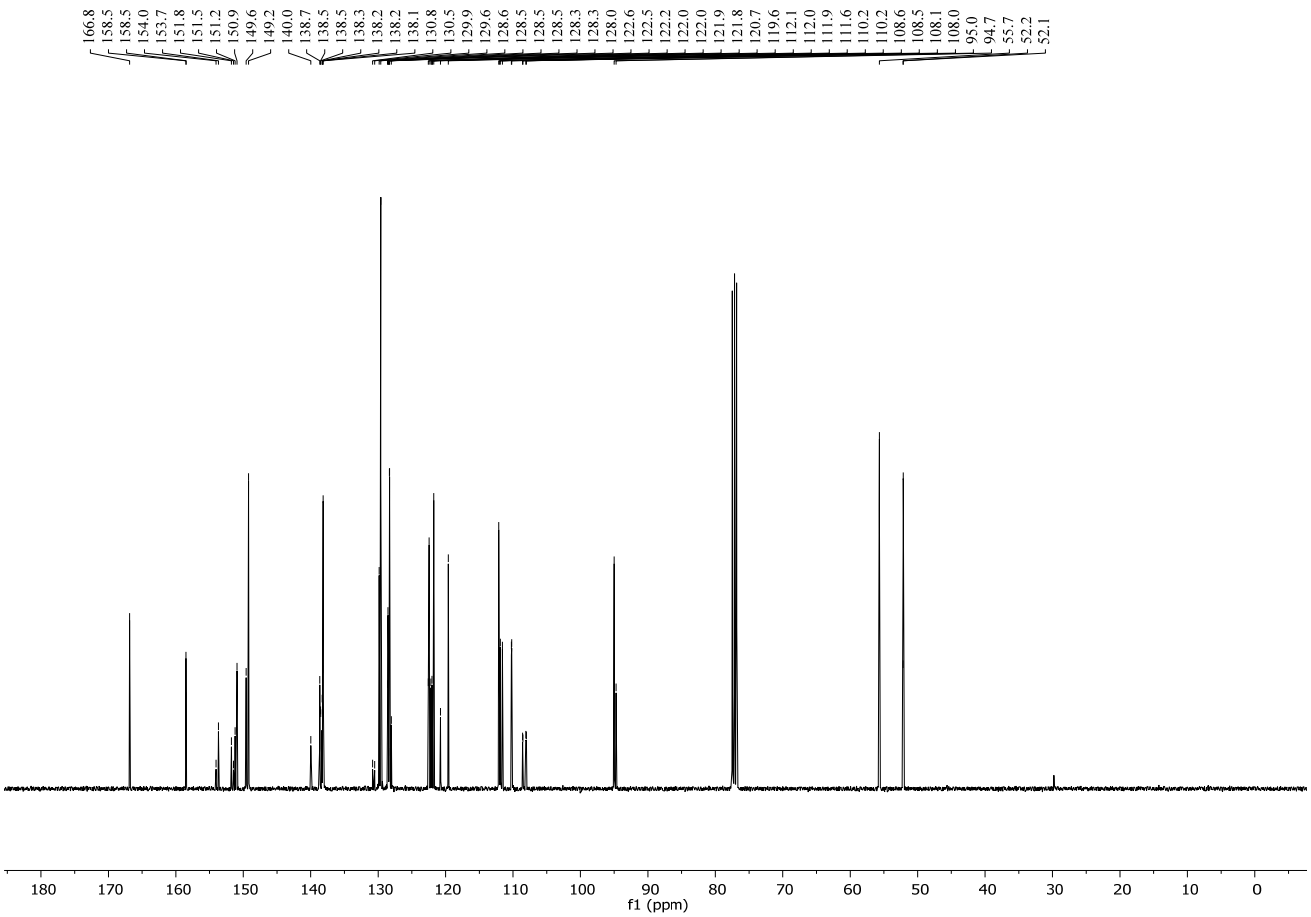
-95
-96
-97
-98
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
f1 (ppm)


MeOOC
MeO
N
F
N
f1 (ppm)


MeOOC
MeO
N
F
N
f1 (ppm)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158.5
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151.5
151.2
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149.2
140.0
138.7
138.5
138.5
138.3
138.2
138.2
138.1
130.8
130.5
129.9
129.6
128.6
128.5
128.5
128.5
128.3
128.3
128.0
122.6
122.5
122.2
122.0
122.0
121.9
121.8
120.7
119.6
112.1
112.0
111.9
111.6
110.2
110.2
108.6
108.5
108.1
108.0
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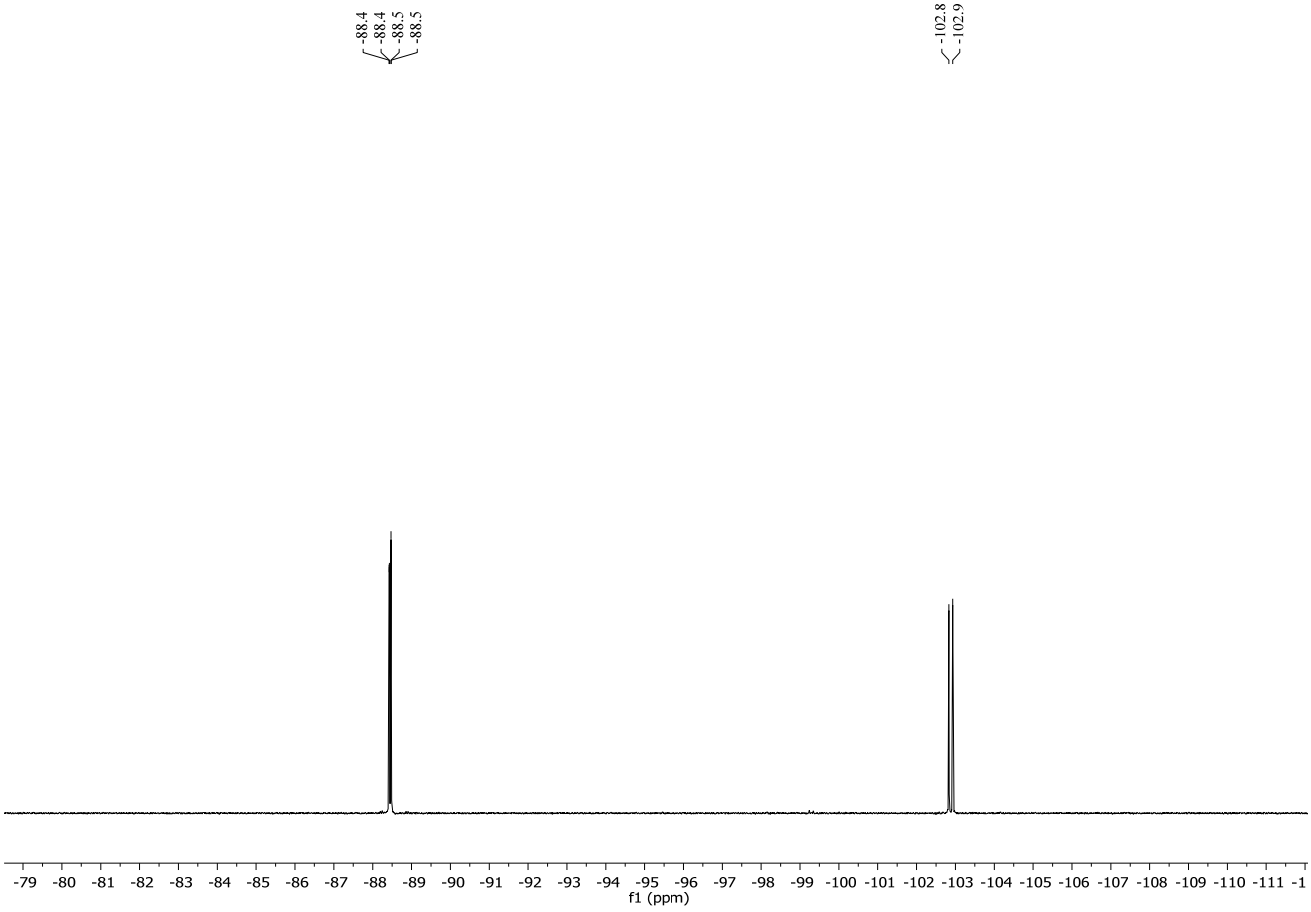
94.7
55.7
52.2
52.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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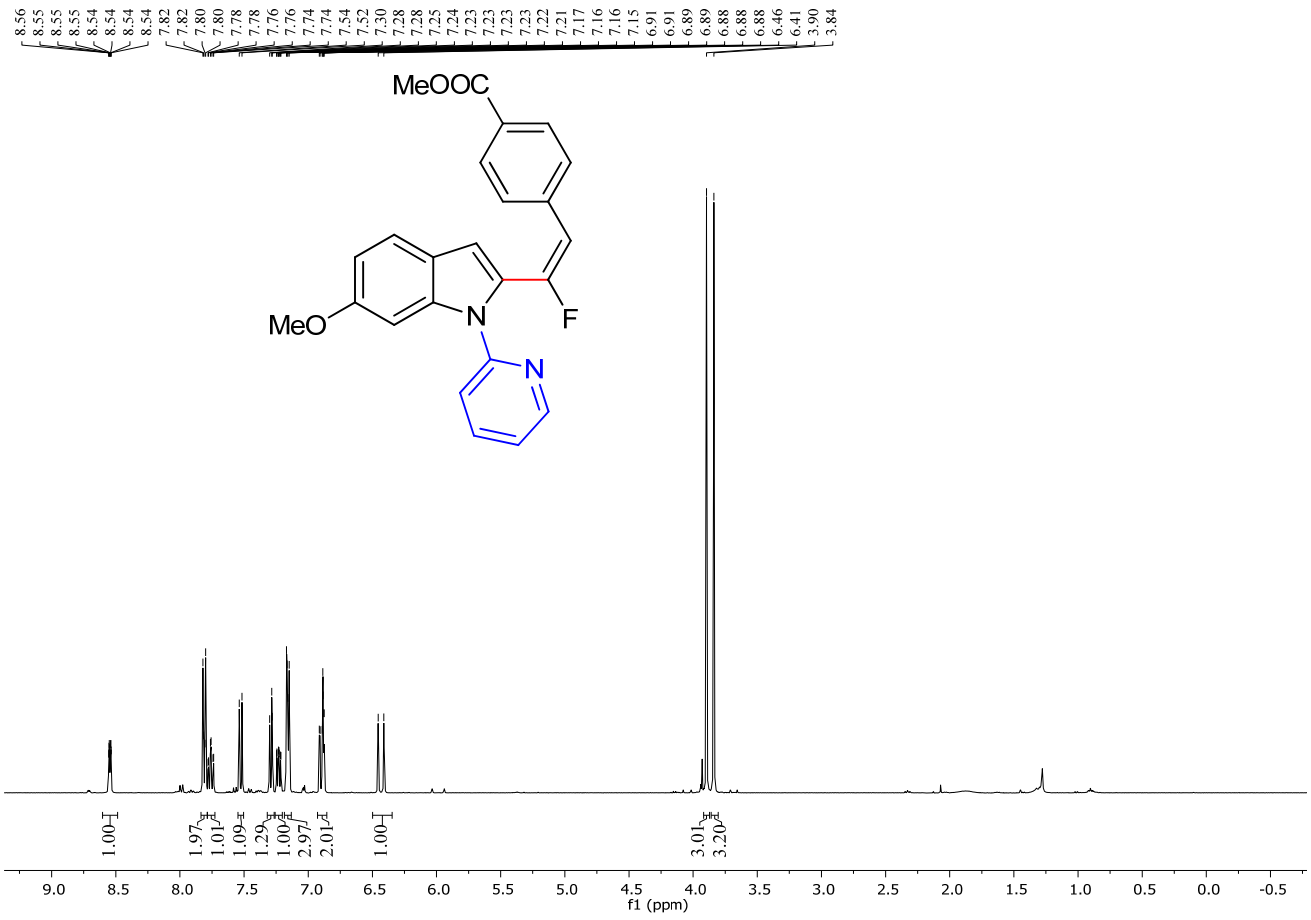
-88.5
-88.5
-102.8
-102.9
-79 -80 -81 -82 -83 -84 -85 -86 -87 -88 -89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -1
f1 (ppm)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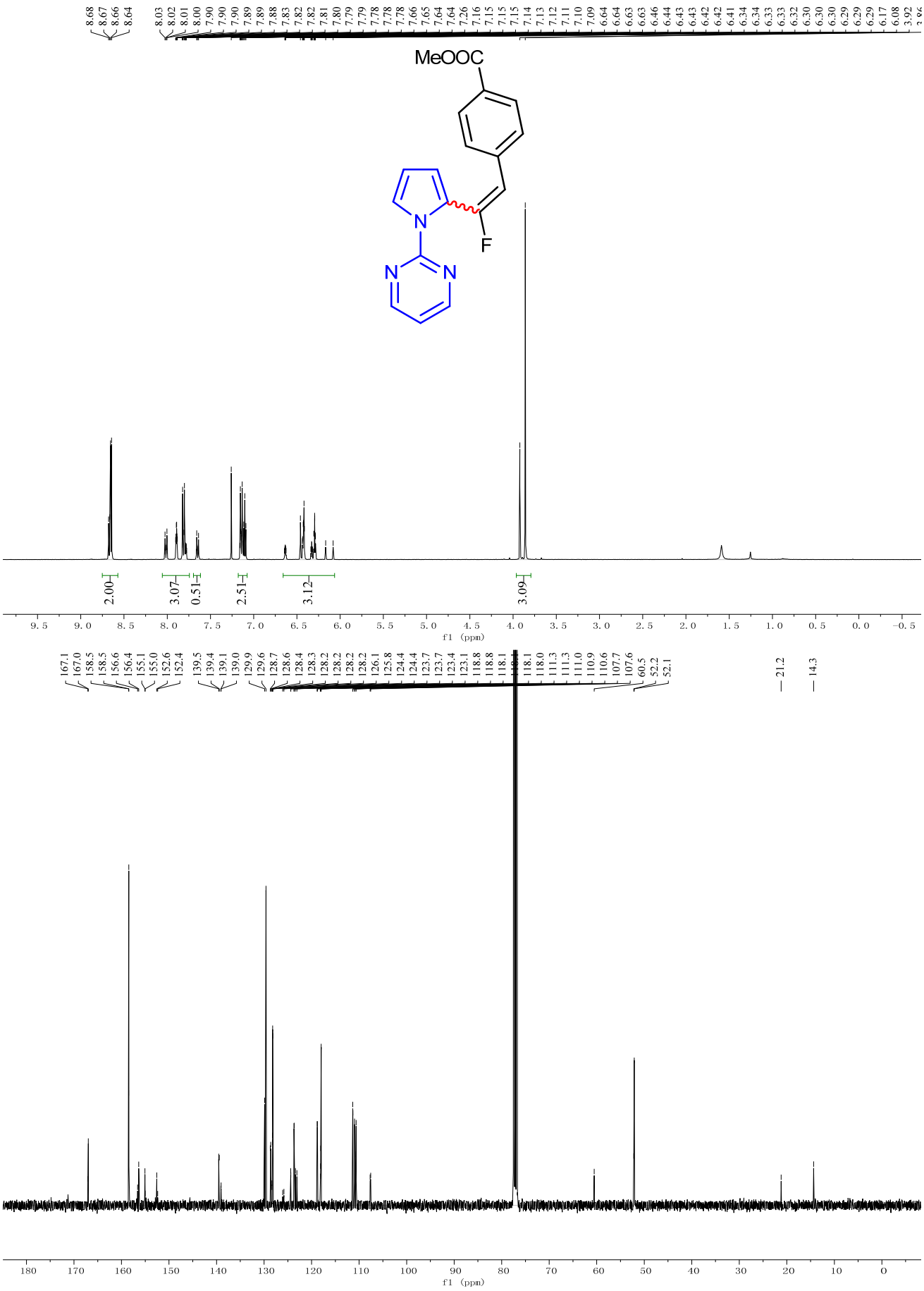
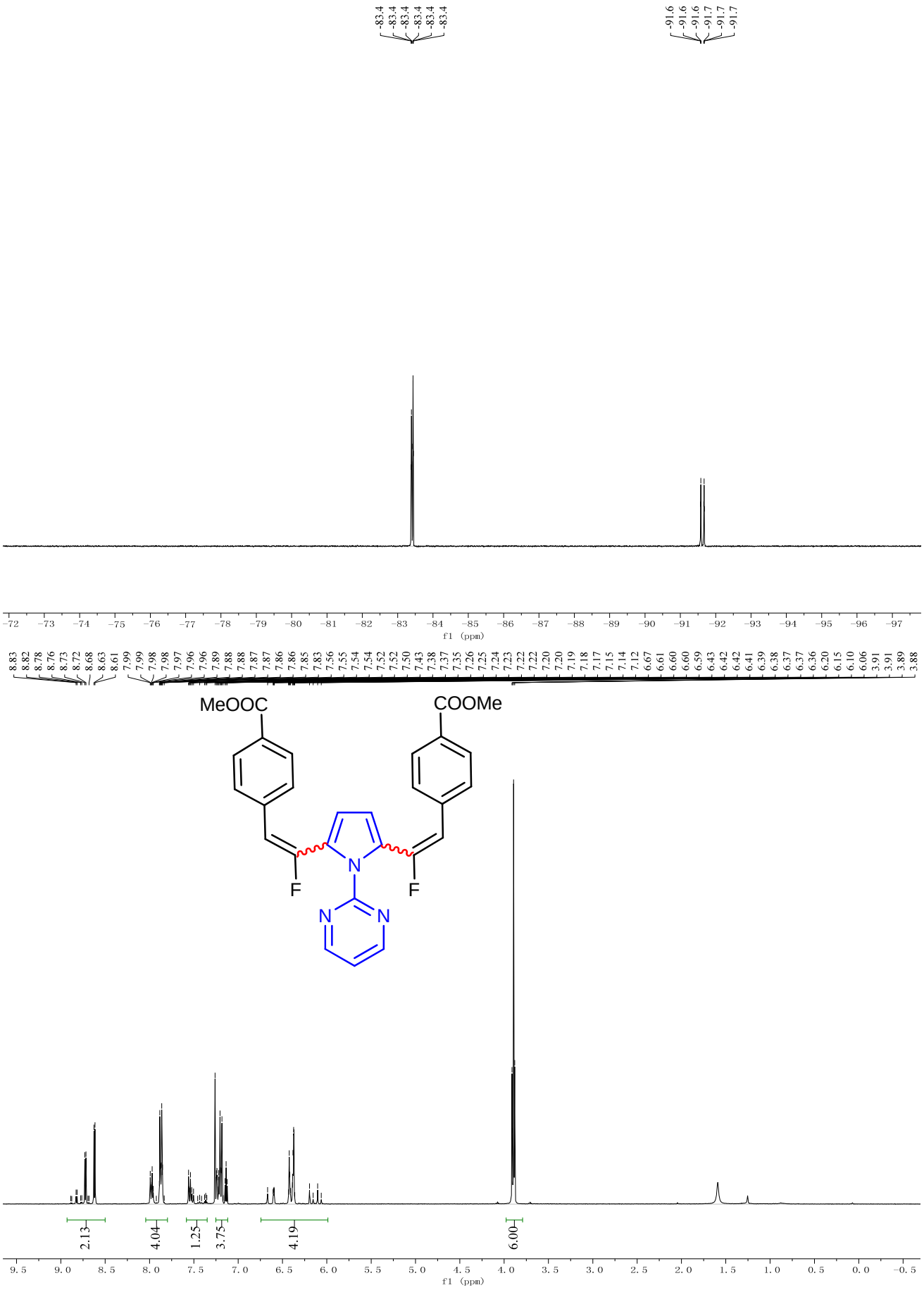
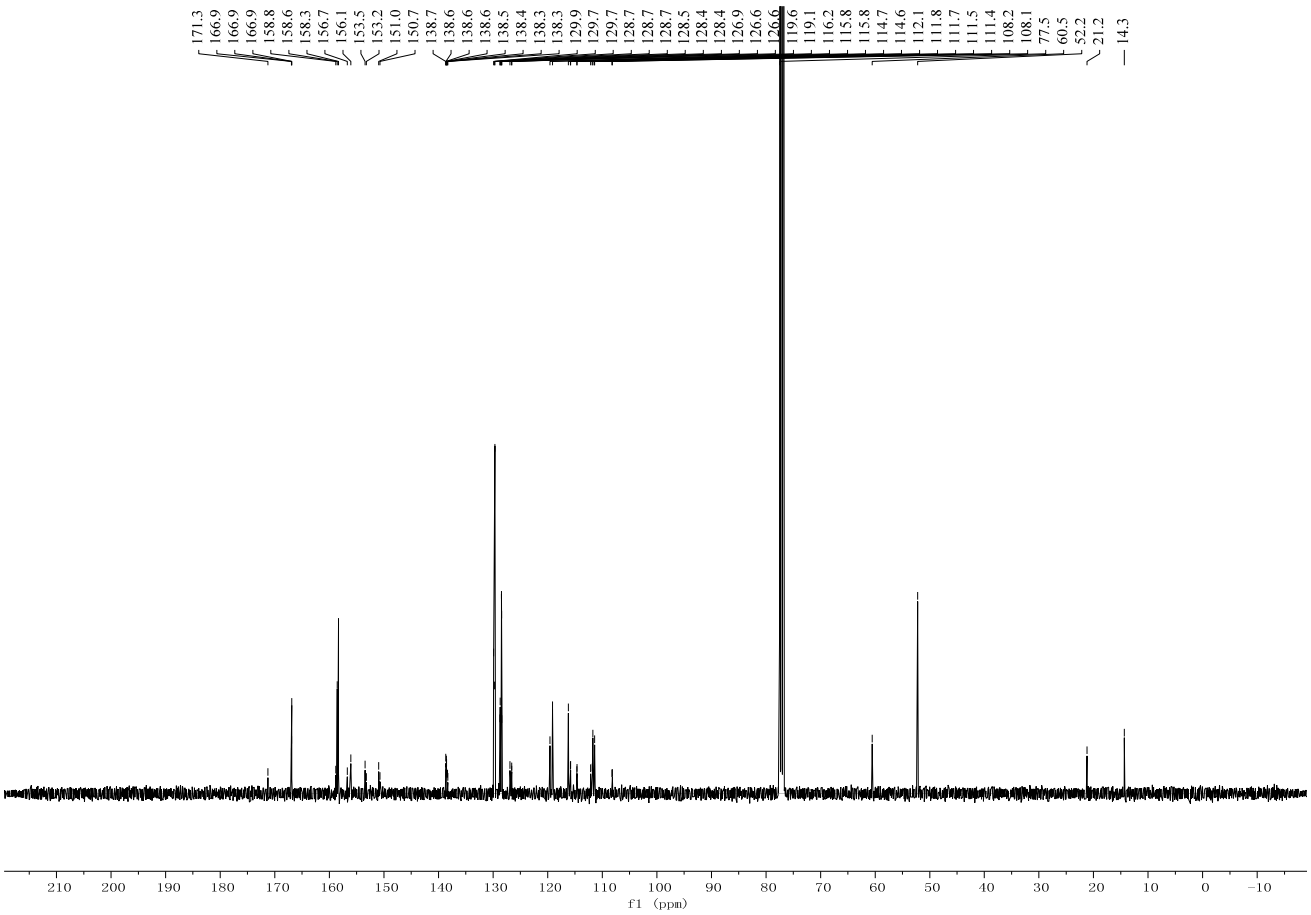
MeOOC
MeO
N
F
N
1.00 1.97 1.01 1.09 1.29 1.00 2.97 2.01 1.00 3.01 3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


MeOOC
N
F
N
N
2.00
3.07
0.51
2.51
3.12
3.09
f1 (ppm)
— 21.2
— 14.3
f1 (ppm)


-83.4
-91.6
-91.7
f1 (ppm)
MeOOC
COOMe
F
F
N
N
N
2.13
4.04
1.25
3.75
4.19
6.00
f1 (ppm)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166.9
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158.3
156.7
156.1
153.5
153.2
151.0
150.7
138.7
138.6
138.6
138.6
138.5
138.4
138.3
138.3
129.9
129.7
129.7
128.7
128.7
128.7
128.5
128.4
128.4
126.9
126.6
126.6
119.6
119.1
116.2
115.8
115.8
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114.6
112.1
111.8
111.7
111.5
111.4
108.2
108.1
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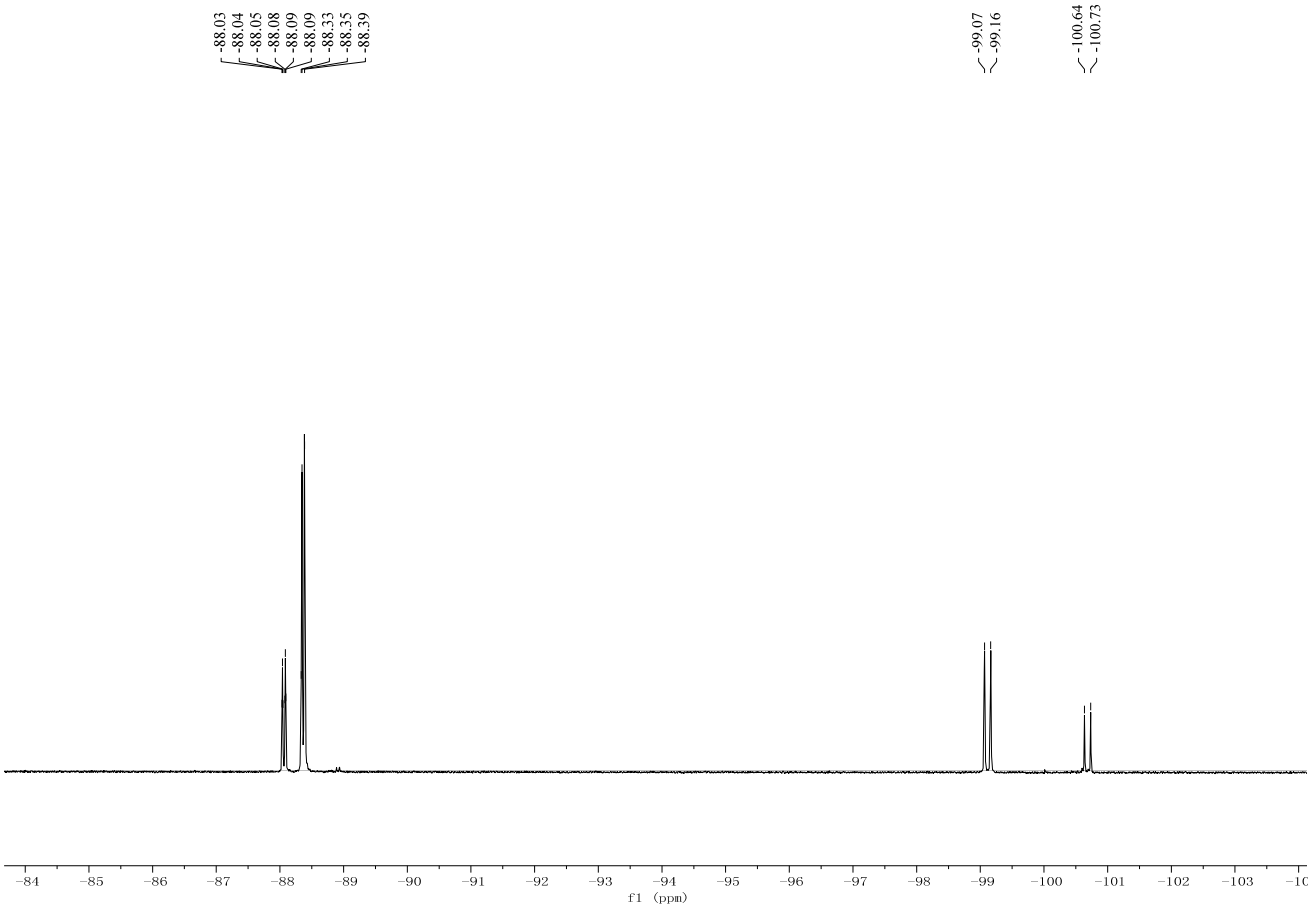
52.2
21.2
14.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-88.04
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-88.09
-88.09
-88.33
-88.35
-88.39
-99.07
-99.16
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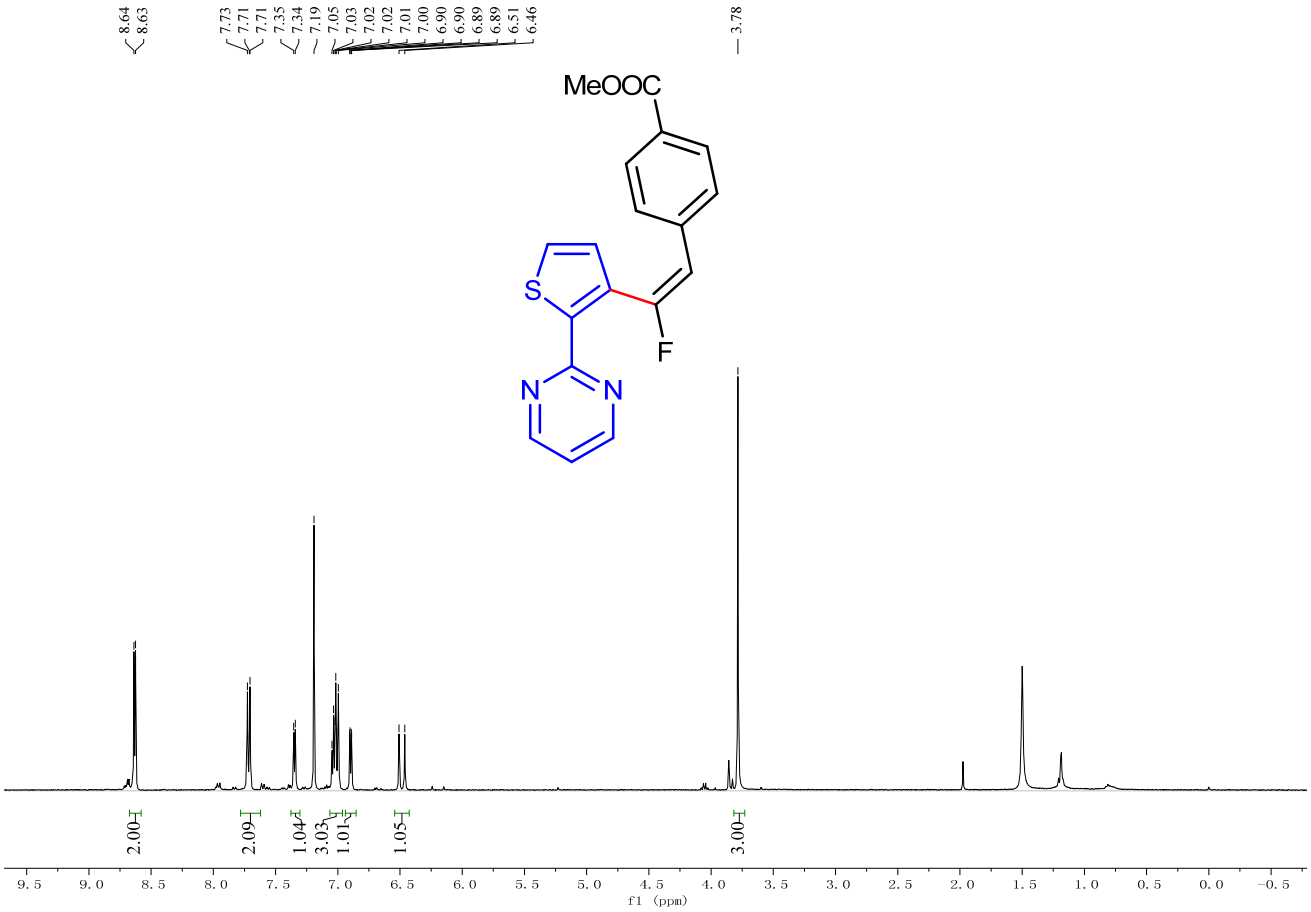
-100.73
-84 -85 -86 -87 -88 -89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -10
f1 (ppm)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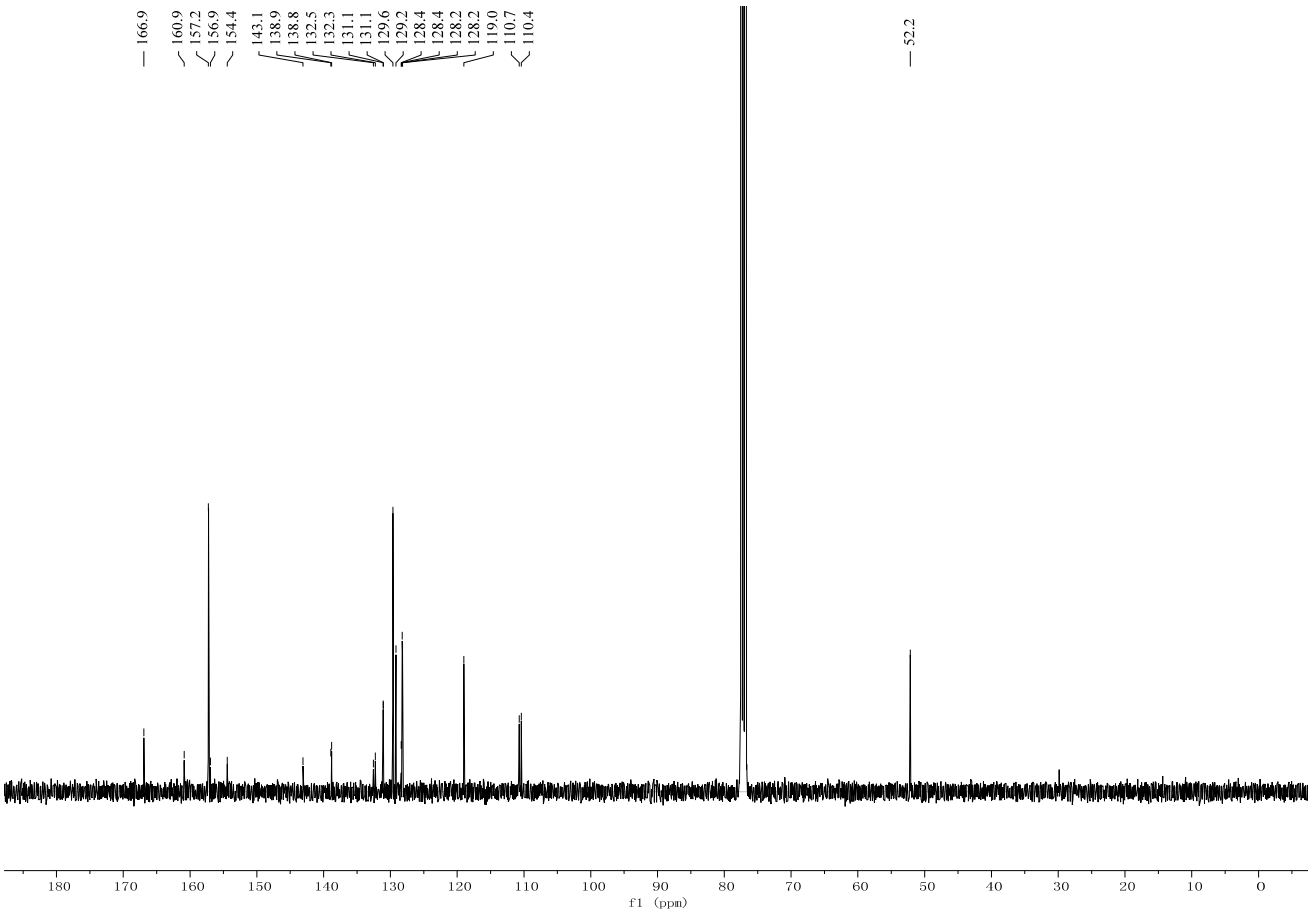
7.34
7.19
7.05
7.03
7.02
7.02
7.01
7.00
6.90
6.90
6.89
6.89
6.51
6.46
3.78
MeOOC
S
F
N
N
2.00
2.09
1.04
3.03
1.01
1.05
3.00
f1 (ppm)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156.9
154.4
143.1
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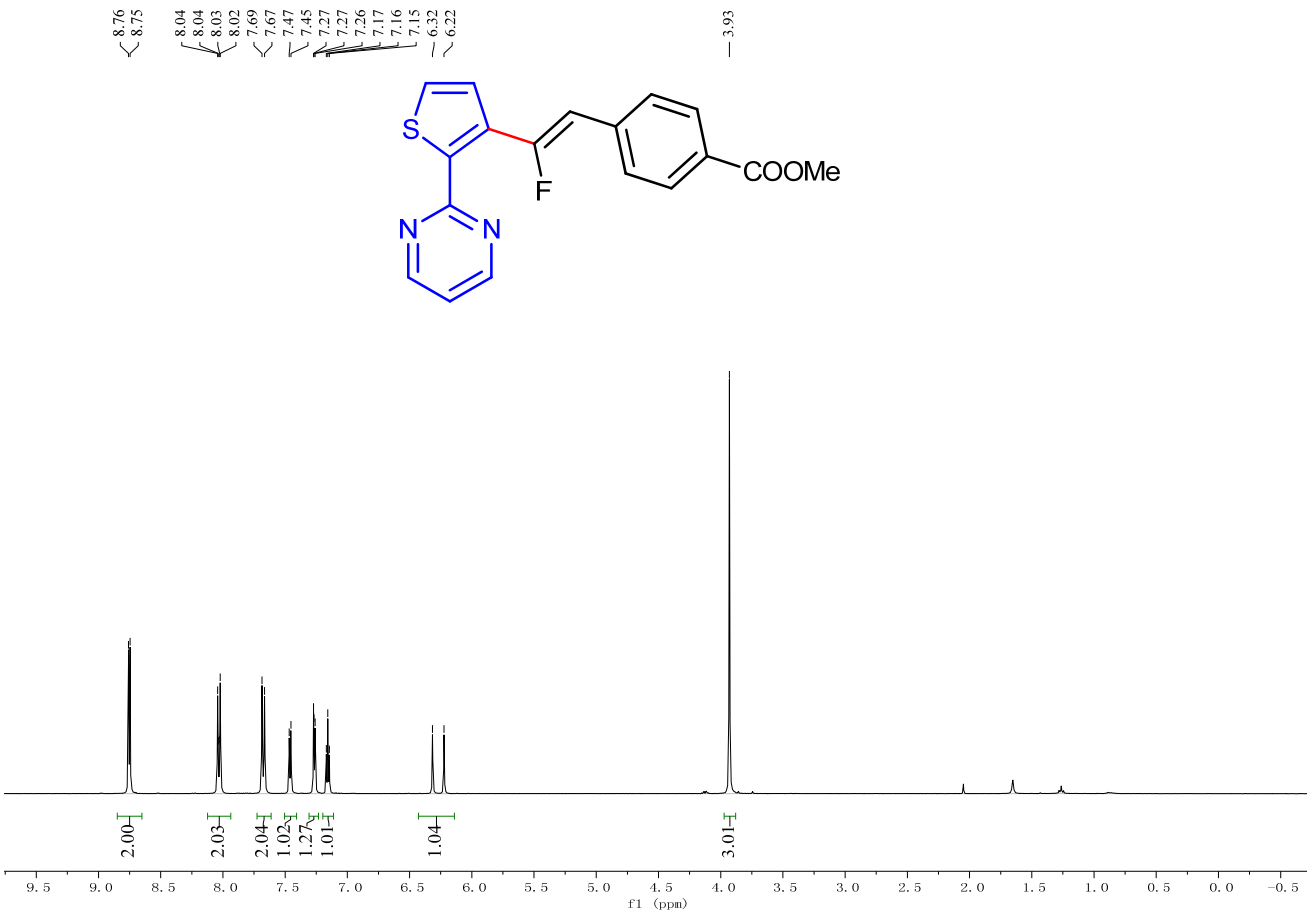
138.8
132.5
132.3
131.1
131.1
129.6
129.2
128.4
128.4
128.2
128.2
119.0
110.7
110.4
52.2
f1 (ppm)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8.04
8.03
8.02
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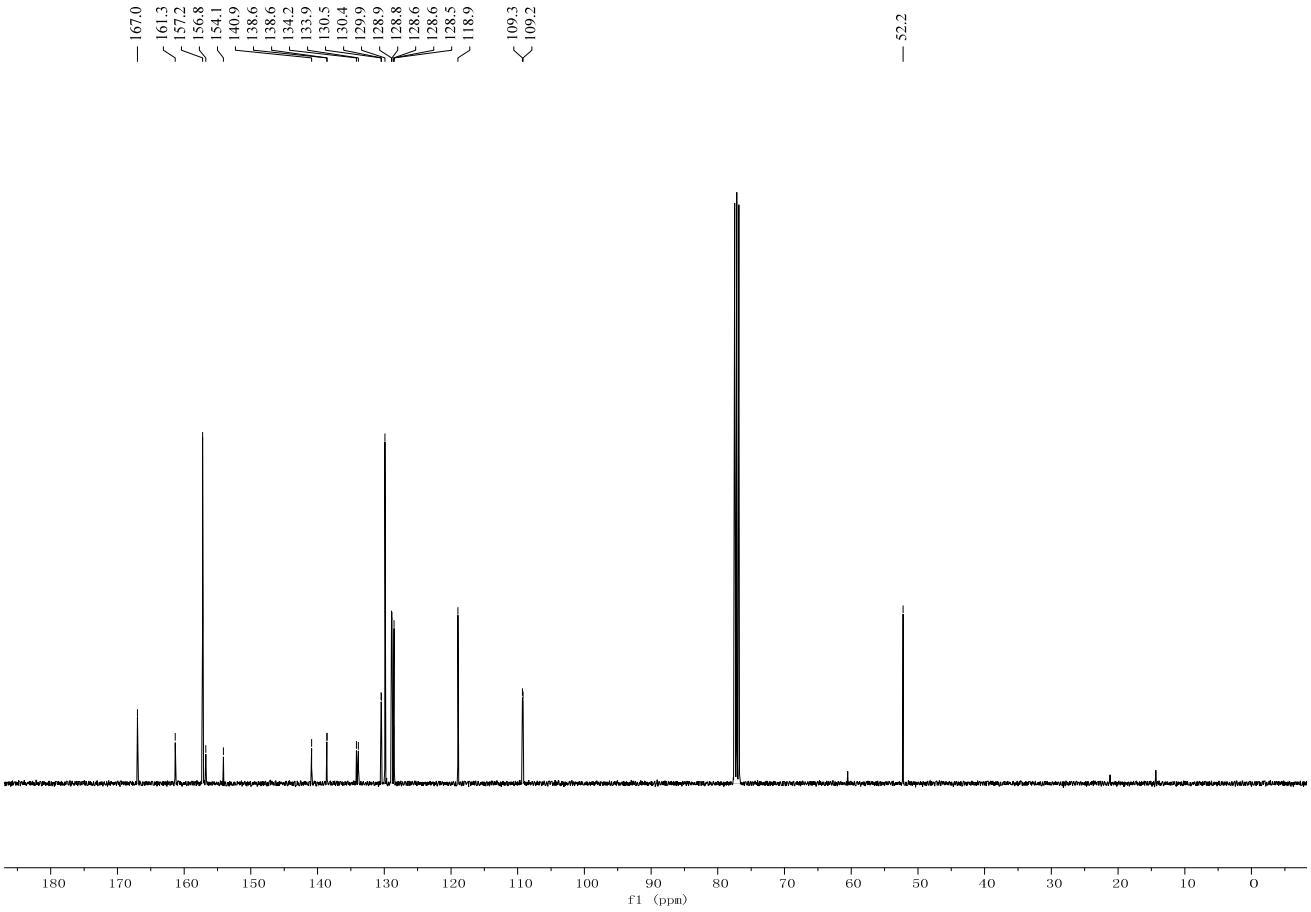
7.67
7.47
7.45
7.27
7.27
7.26
7.17
7.16
7.15
6.32
6.22
3.93
S
F
COOMe
N
N
2.00
2.03
2.04
1.02
1.27
1.01
1.04
3.01
f1 (ppm)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157.2
156.8
154.1
140.9
138.6
138.6
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133.9
130.5
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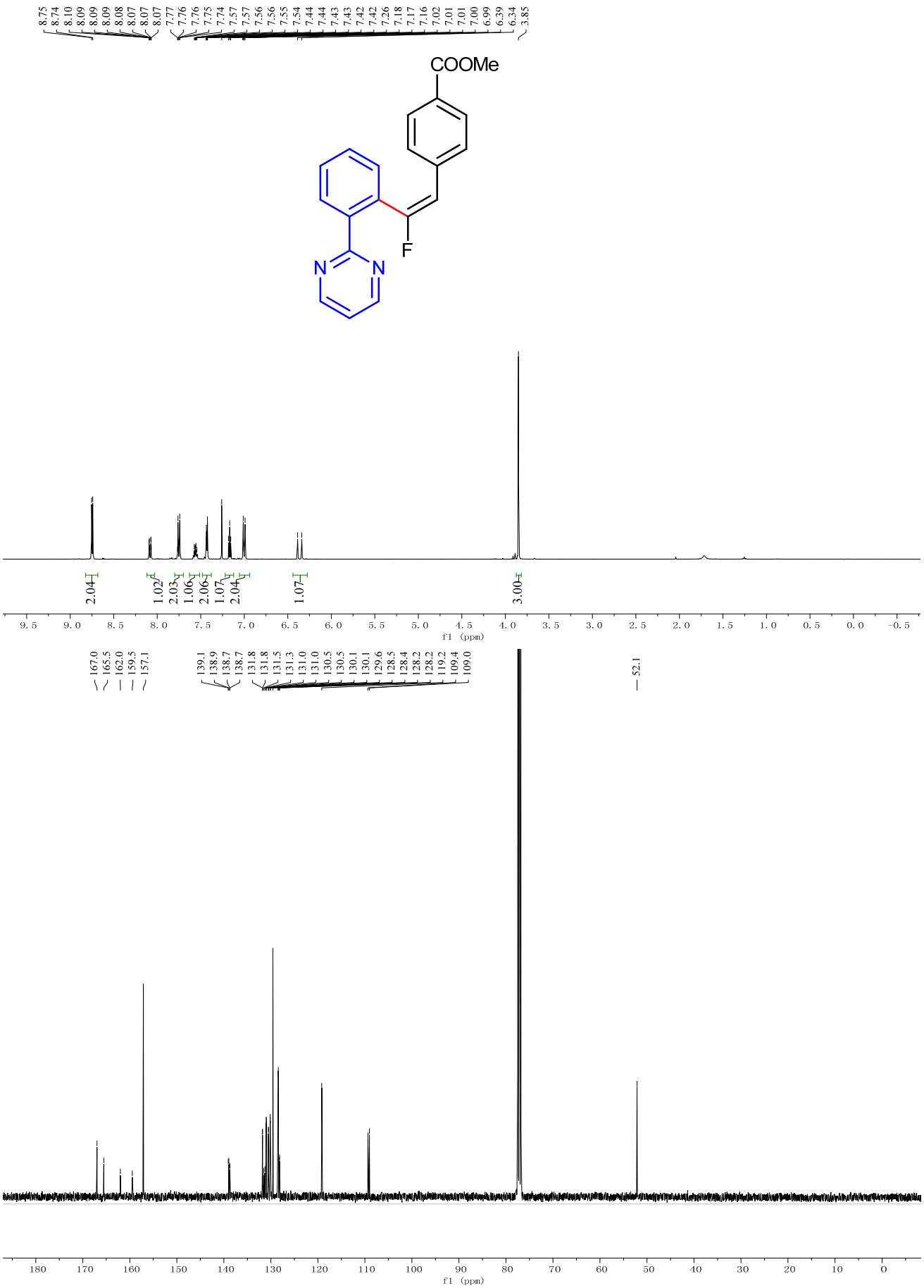
128.8
128.6
128.6
128.5
118.9
109.3
109.2
52.2
f1 (ppm)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8.07
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7.76
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7.75
7.74
7.57
7.57
7.56
7.56
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7.54
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7.43
7.42
7.42
7.26
7.18
7.17
7.16
7.02
7.01
7.01
7.00
6.99
6.39
6.34
3.85
COOMe
F
N
N
2.04
1.02
2.03
1.06
2.06
1.07
2.04
1.07
3.00
f1 (ppm)
167.0
165.5
162.0
159.5
157.1
139.1
138.9
138.7
138.7
131.8
131.8
131.5
131.3
131.0
131.0
130.5
130.5
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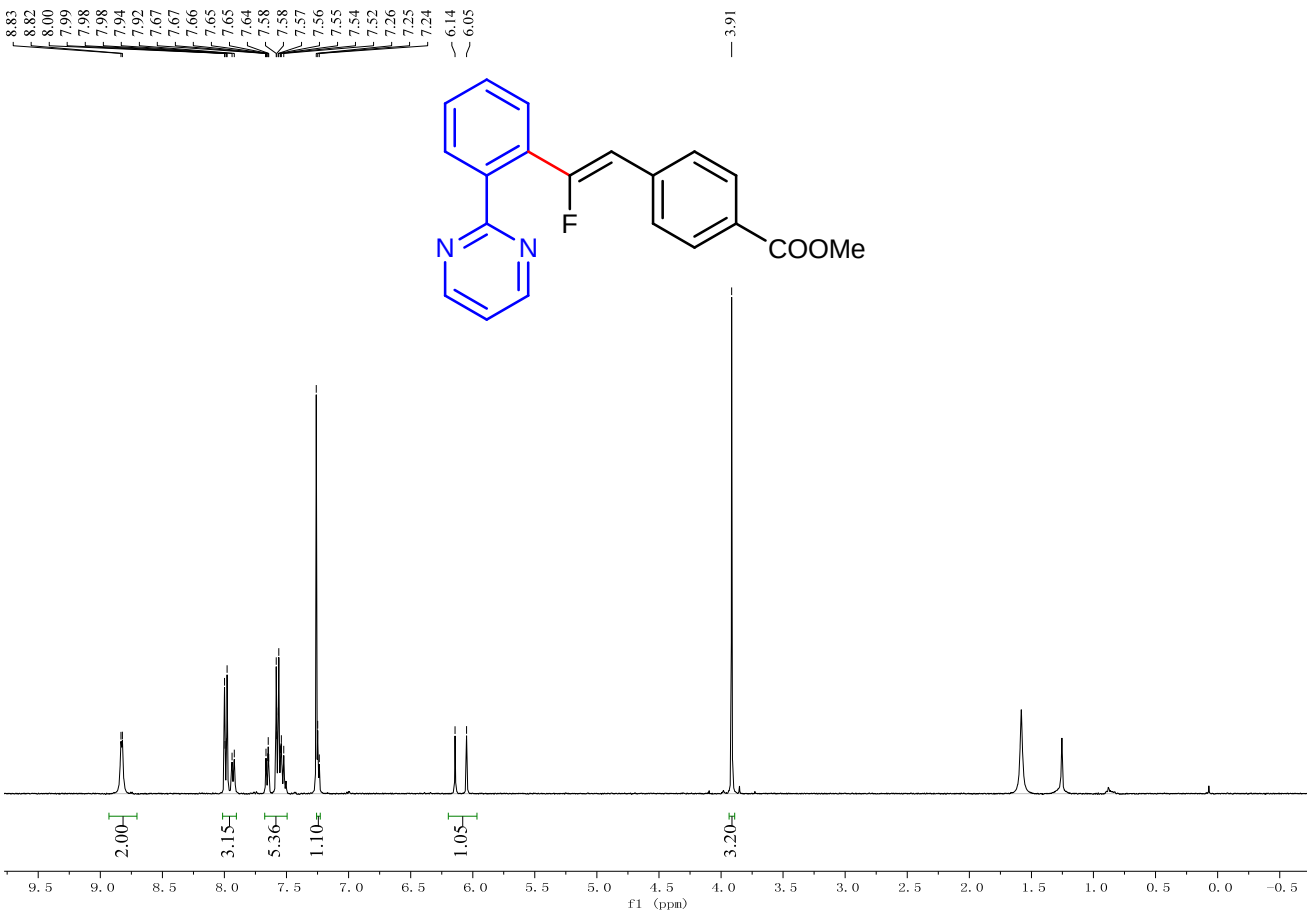
128.2
128.2
119.2
109.4
109.0
52.1
f1 (ppm)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7.52
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7.25
7.24
6.14
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N
COOMe
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1.10
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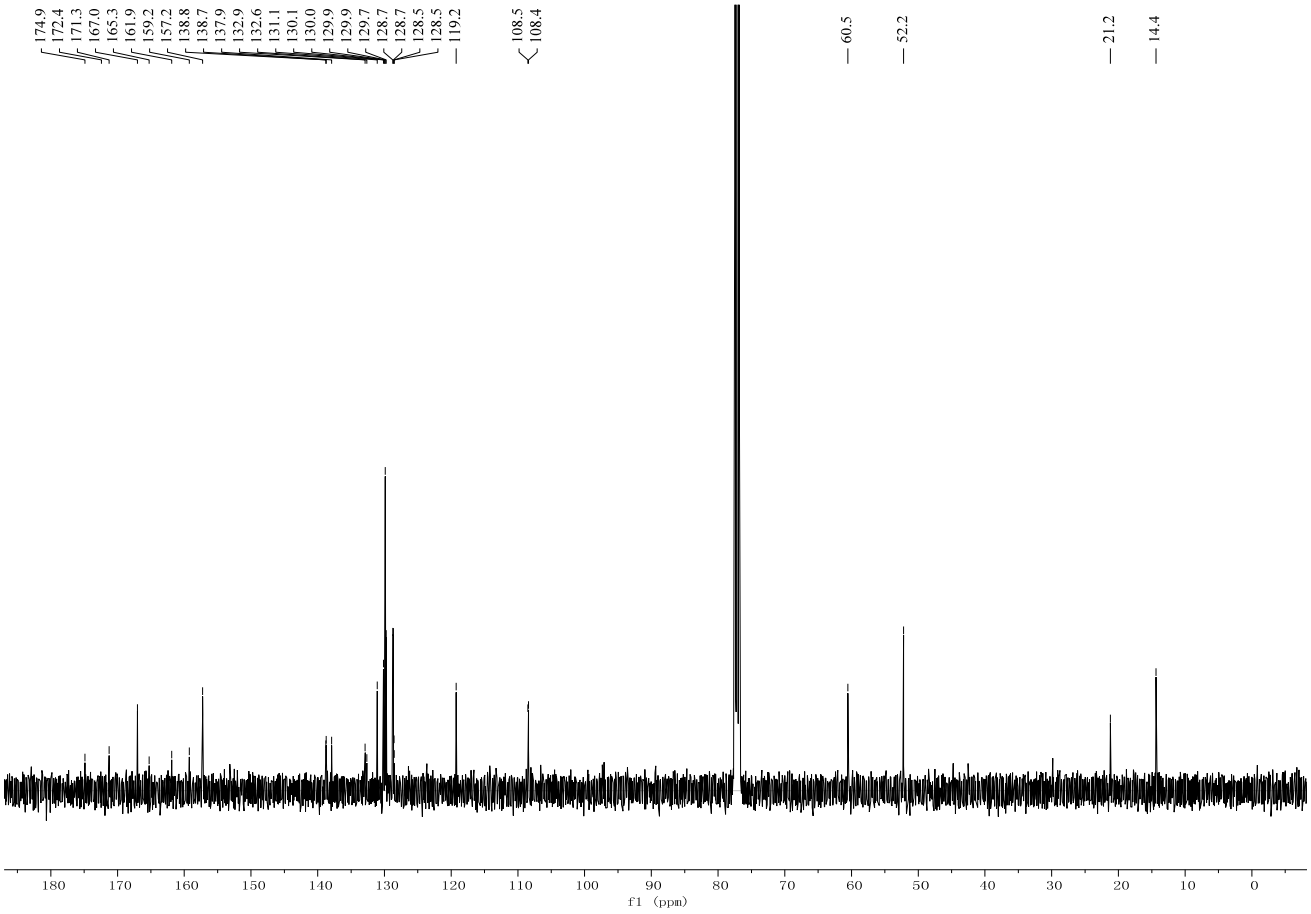
3.20
f1 (ppm)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132.9
132.6
131.1
130.1
130.0
129.9
129.9
129.7
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128.7
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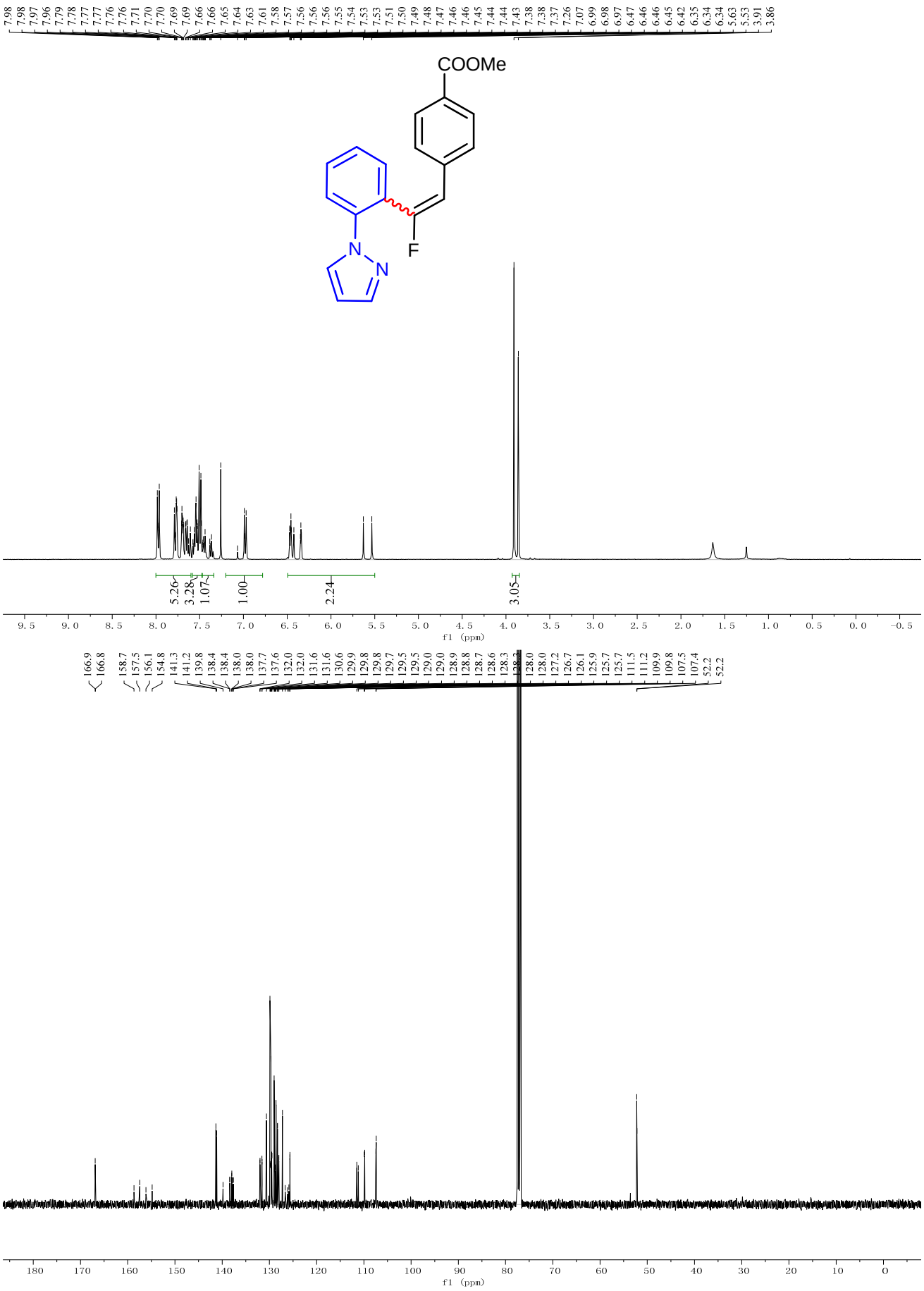
128.5
119.2
108.5
108.4
60.5
52.2
21.2
14.4
f1 (ppm)


COOMe
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N
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1.00
2.24
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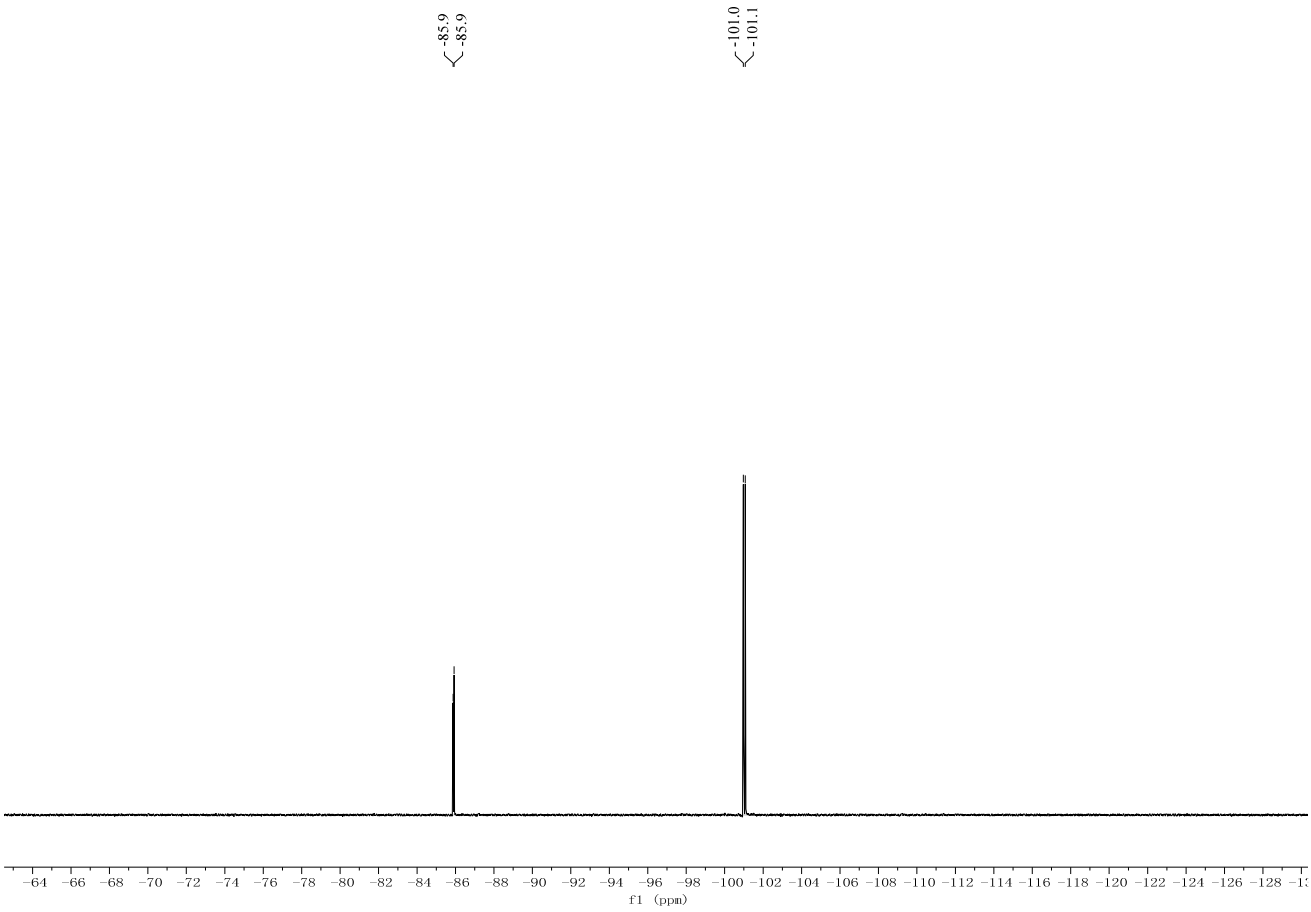
f1 (ppm)
f1 (ppm)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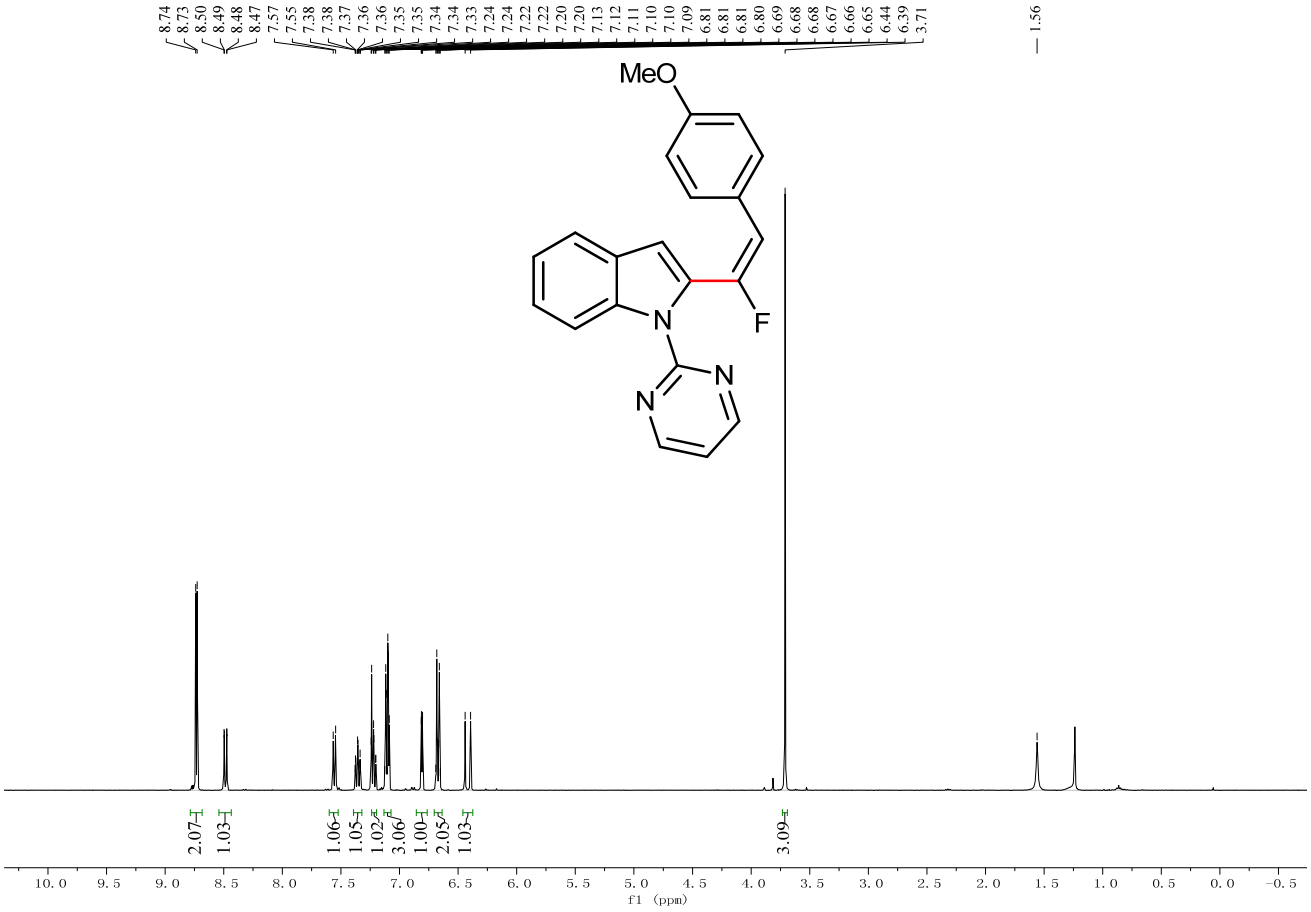
f1 (ppm)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7.24
7.22
7.22
7.20
7.20
7.13
7.12
7.11
7.10
7.10
7.09
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6.81
6.80
6.69
6.68
6.68
6.67
6.66
6.65
6.44
6.39
3.71
1.56
MeO
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1.06
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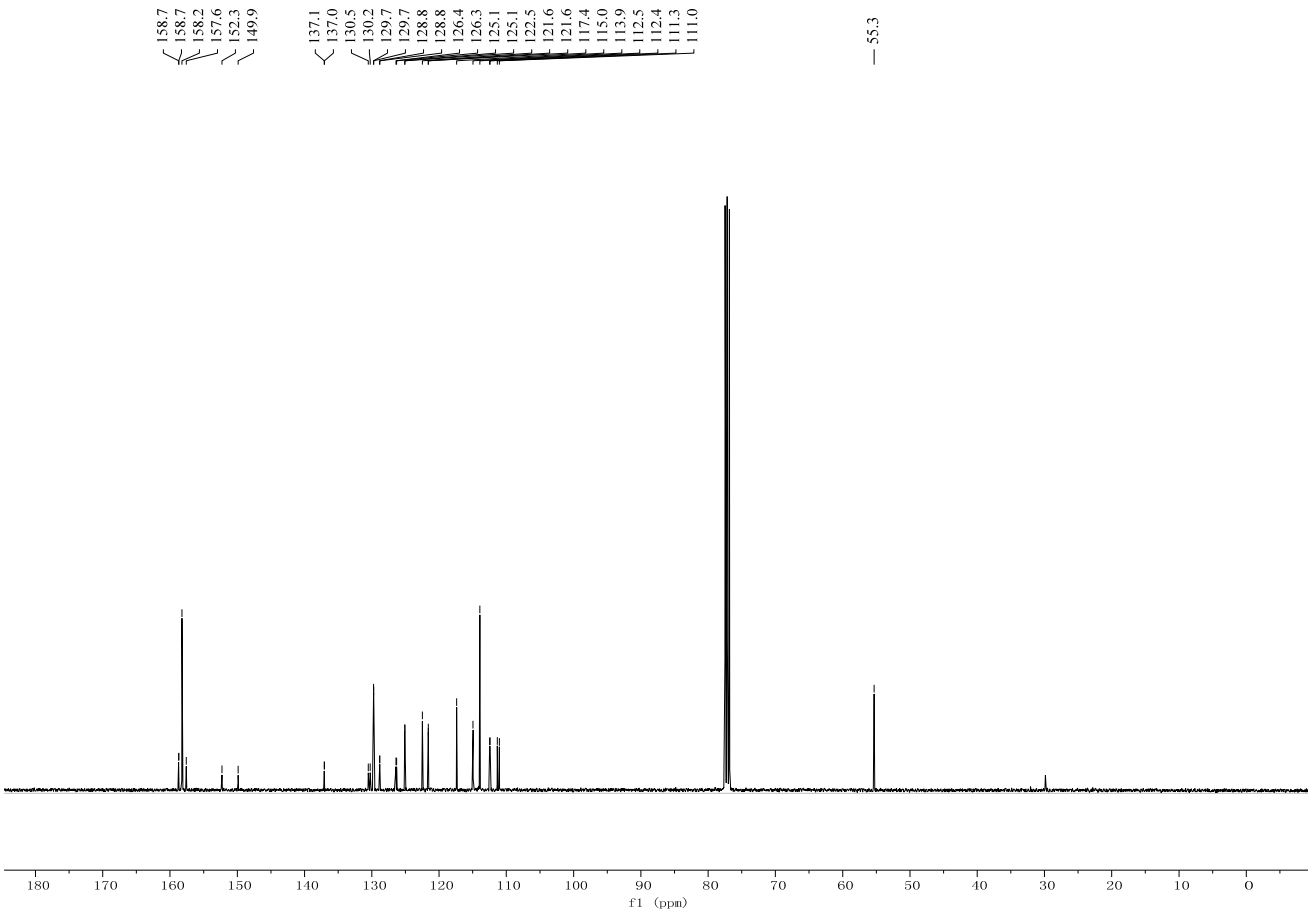
1.02
3.06
1.00
2.05
1.03
3.09
f1 (ppm)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137.0
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128.8
128.8
126.4
126.3
125.1
125.1
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117.4
115.0
113.9
112.5
112.4
111.3
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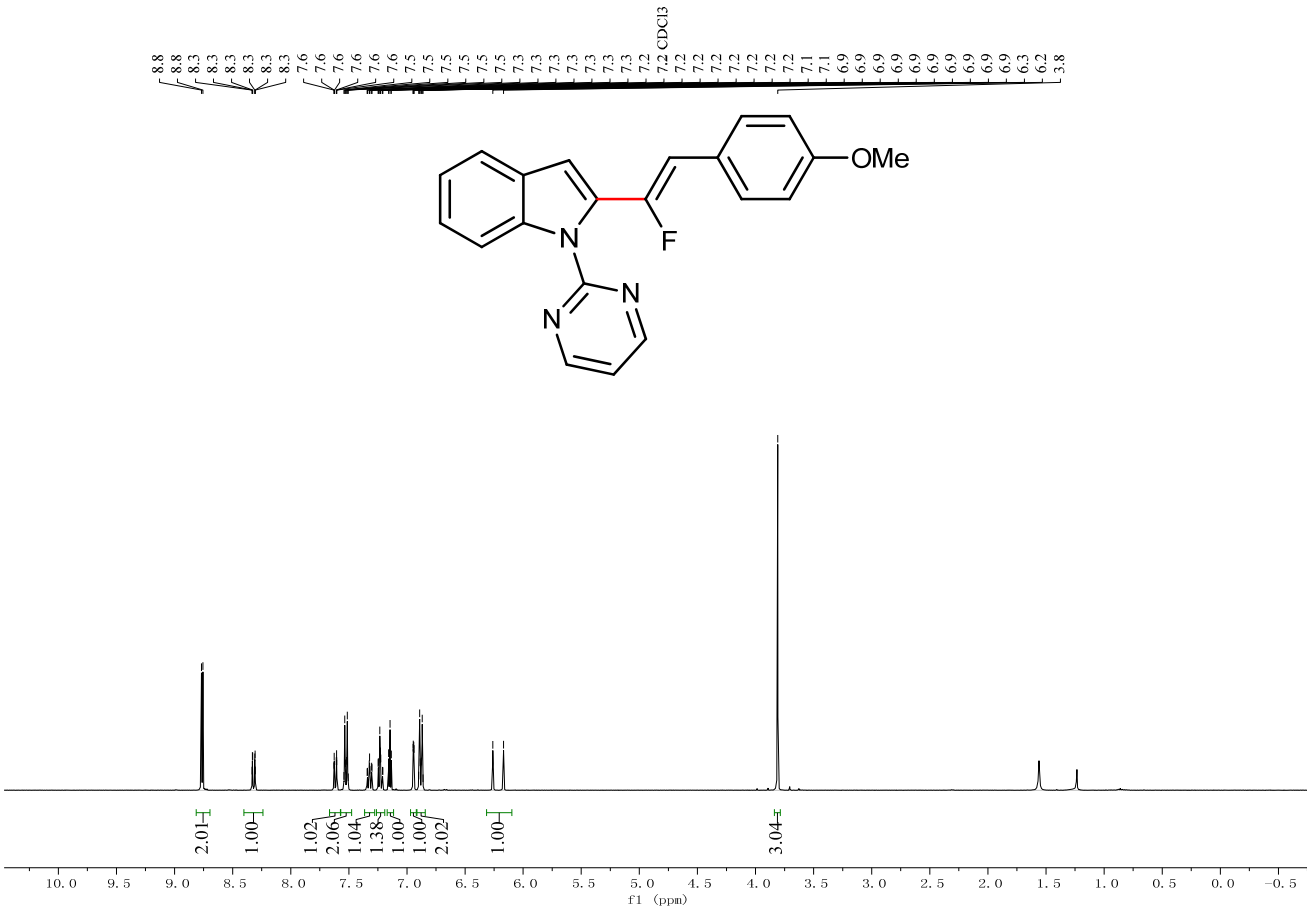
55.3
f1 (ppm)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6.2
3.8
OMe
F
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N
N
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1.38
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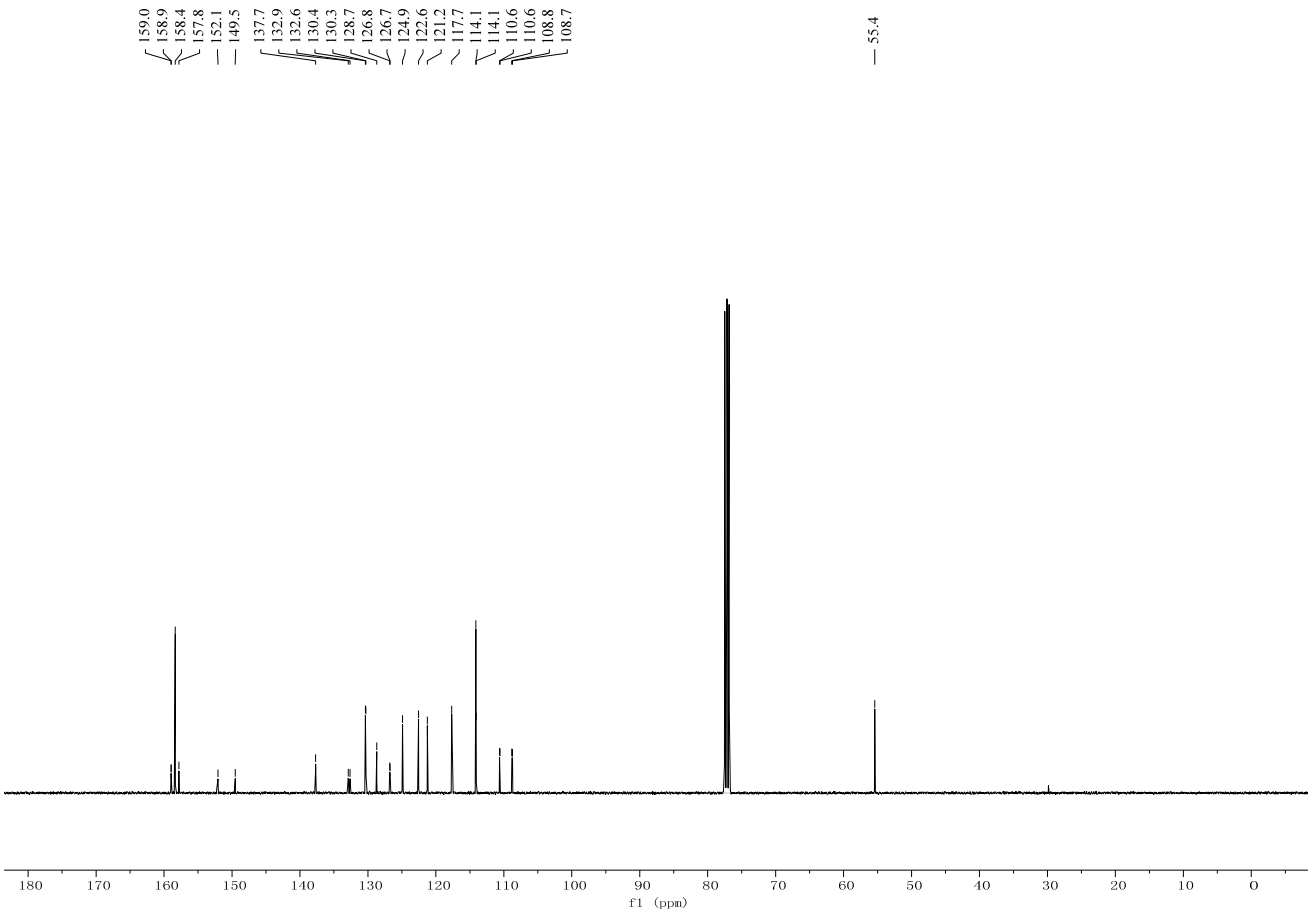
1.00
2.02
1.00
3.04
f1 (ppm)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149.5
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132.9
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130.3
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126.8
126.7
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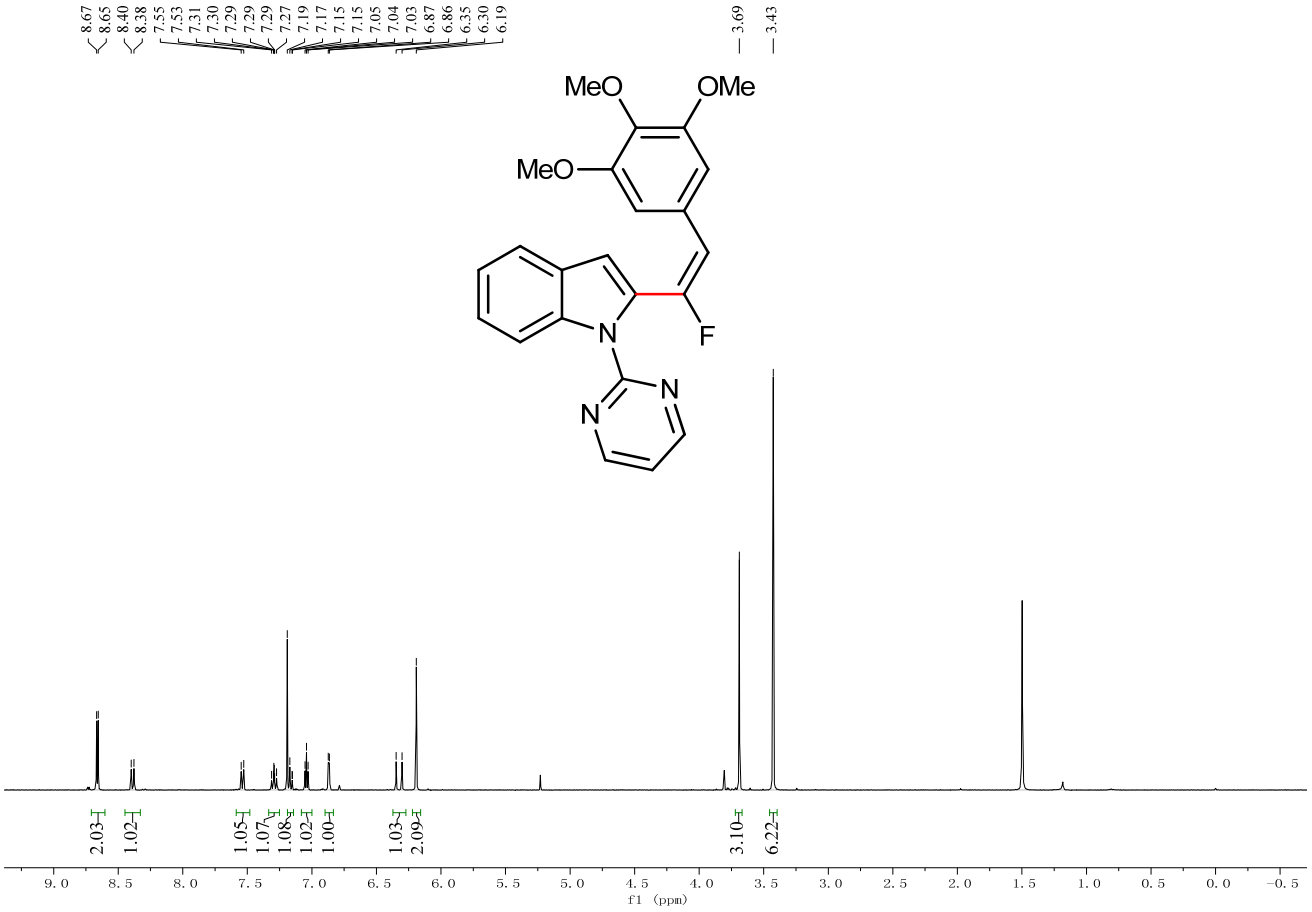
122.6
121.2
117.7
114.1
114.1
110.6
110.6
108.8
108.7
55.4
f1 (ppm)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7.15
7.05
7.04
7.03
6.87
6.86
6.35
6.30
6.19
3.69
3.43
MeO
OMe
MeO
N
F
N
N
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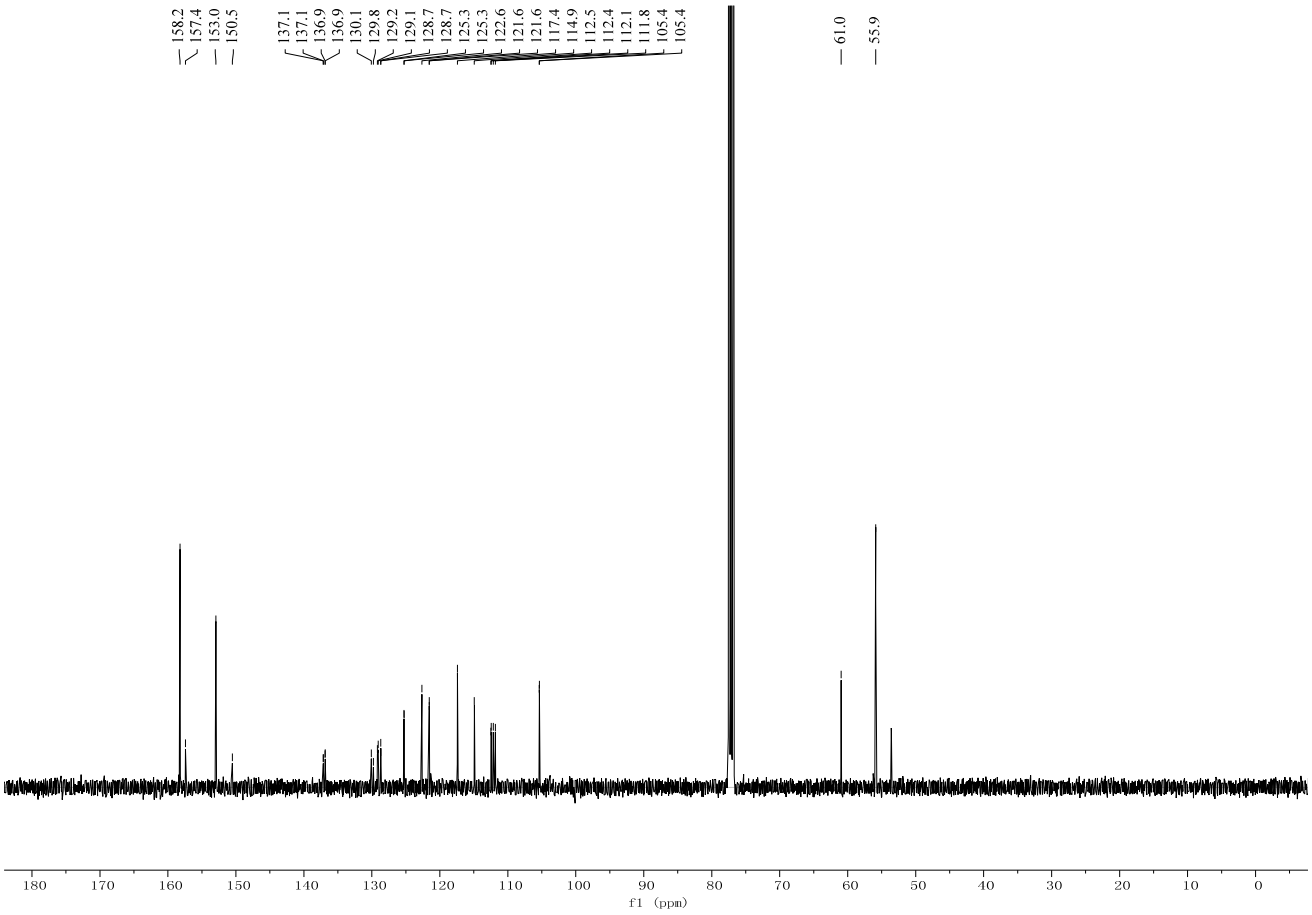
1.07
1.08
1.02
1.00
1.03
2.09
3.10
6.22
f1 (ppm)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117.4
114.9
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112.4
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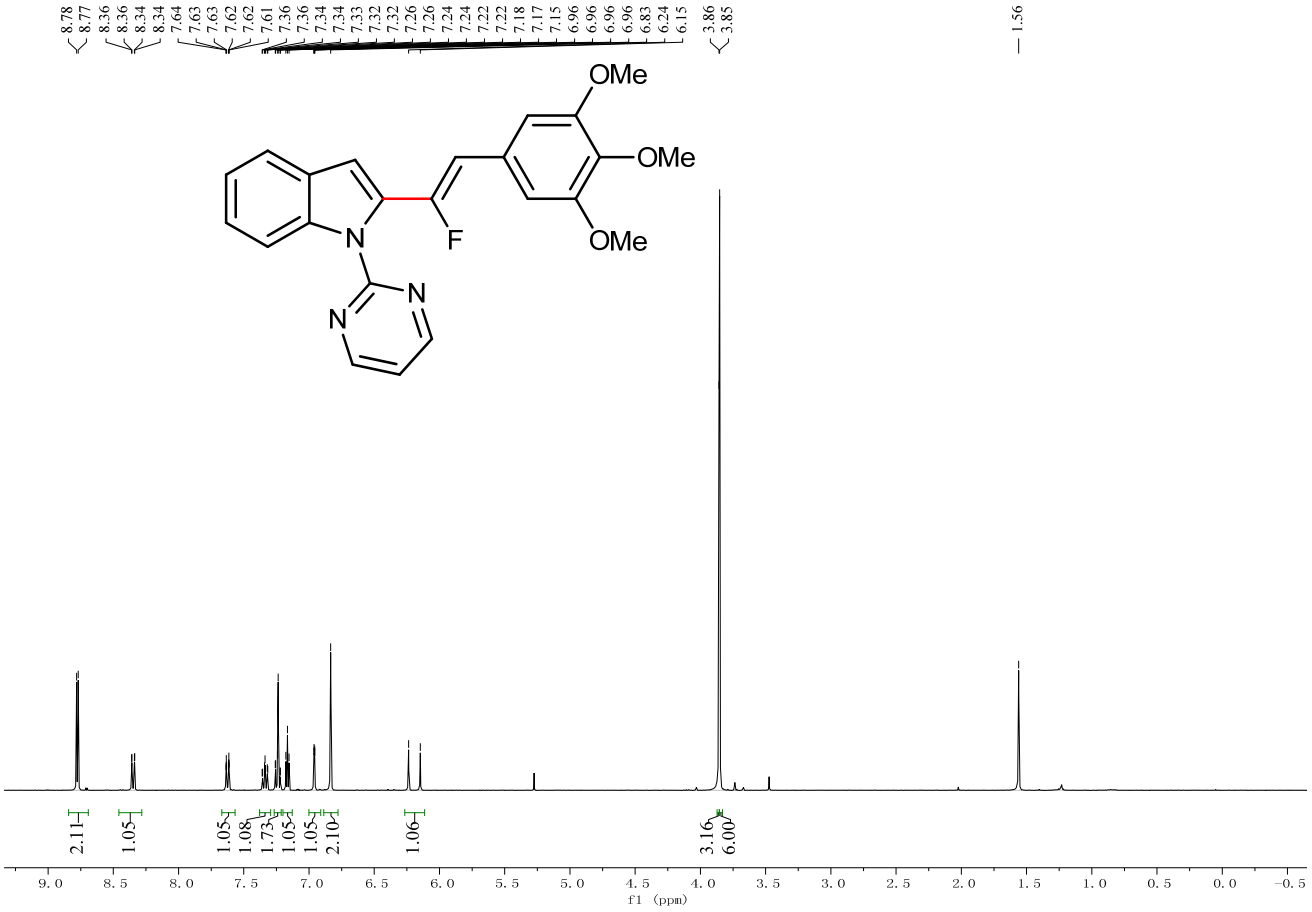
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OMe
OMe
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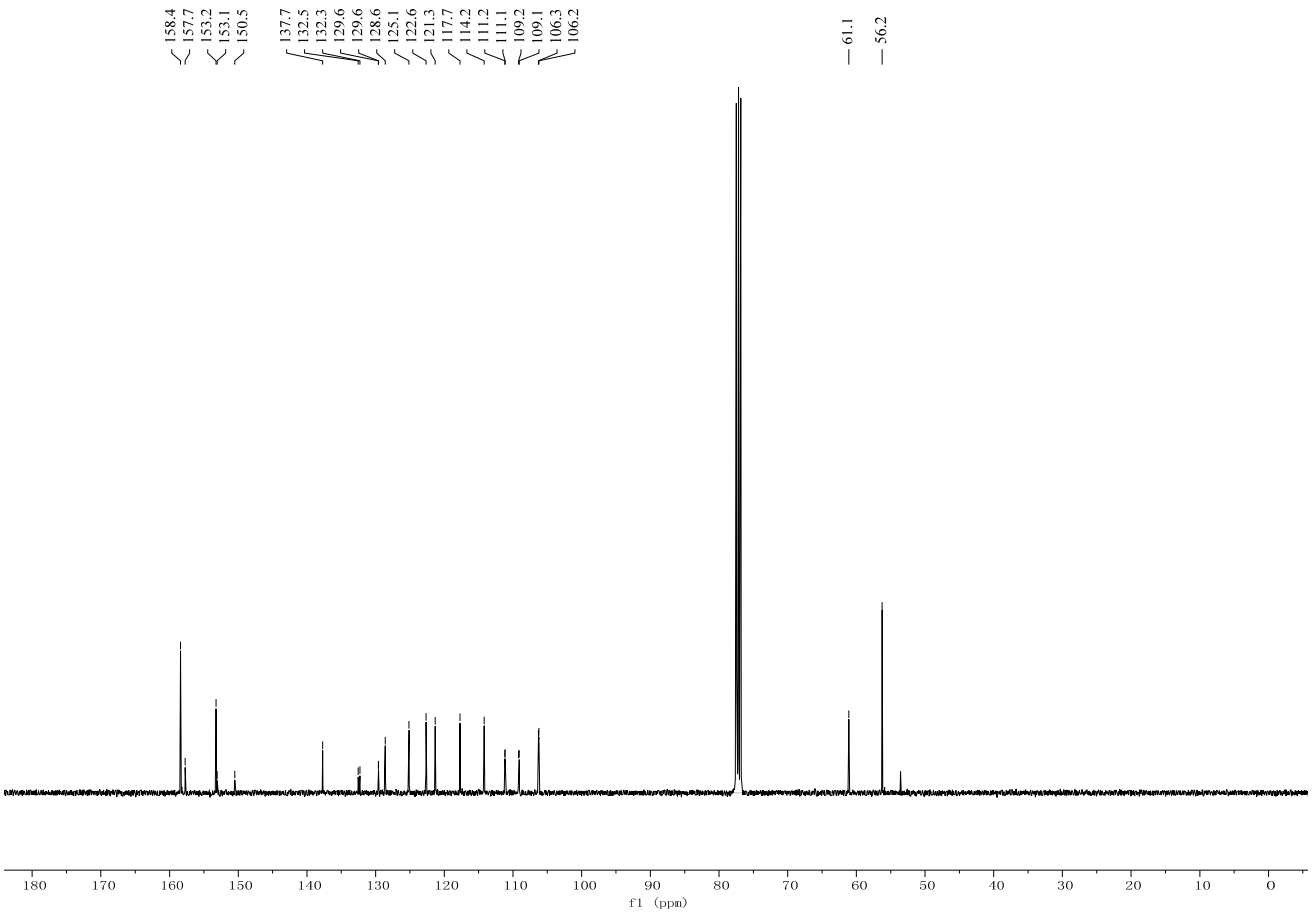
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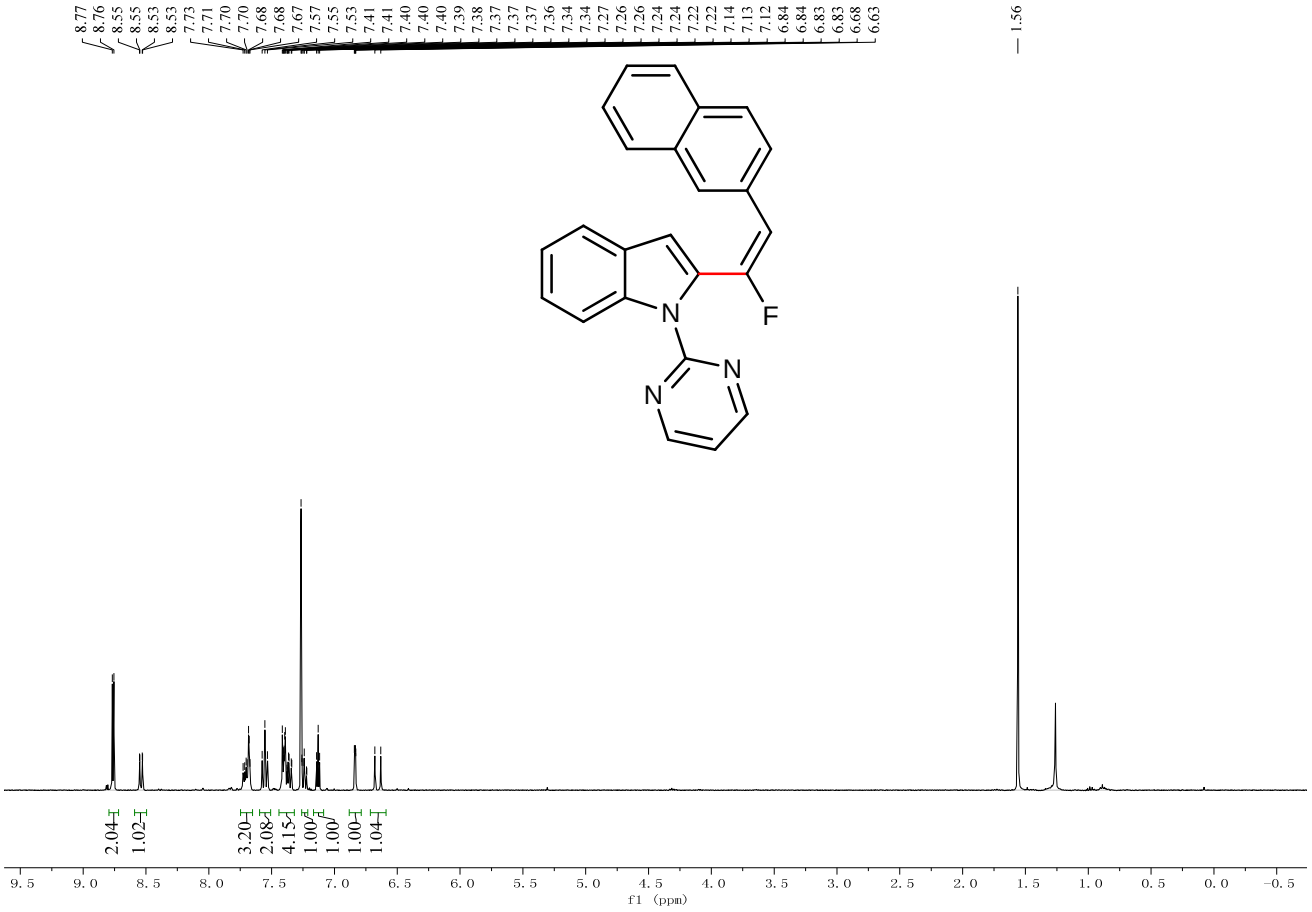
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3.20
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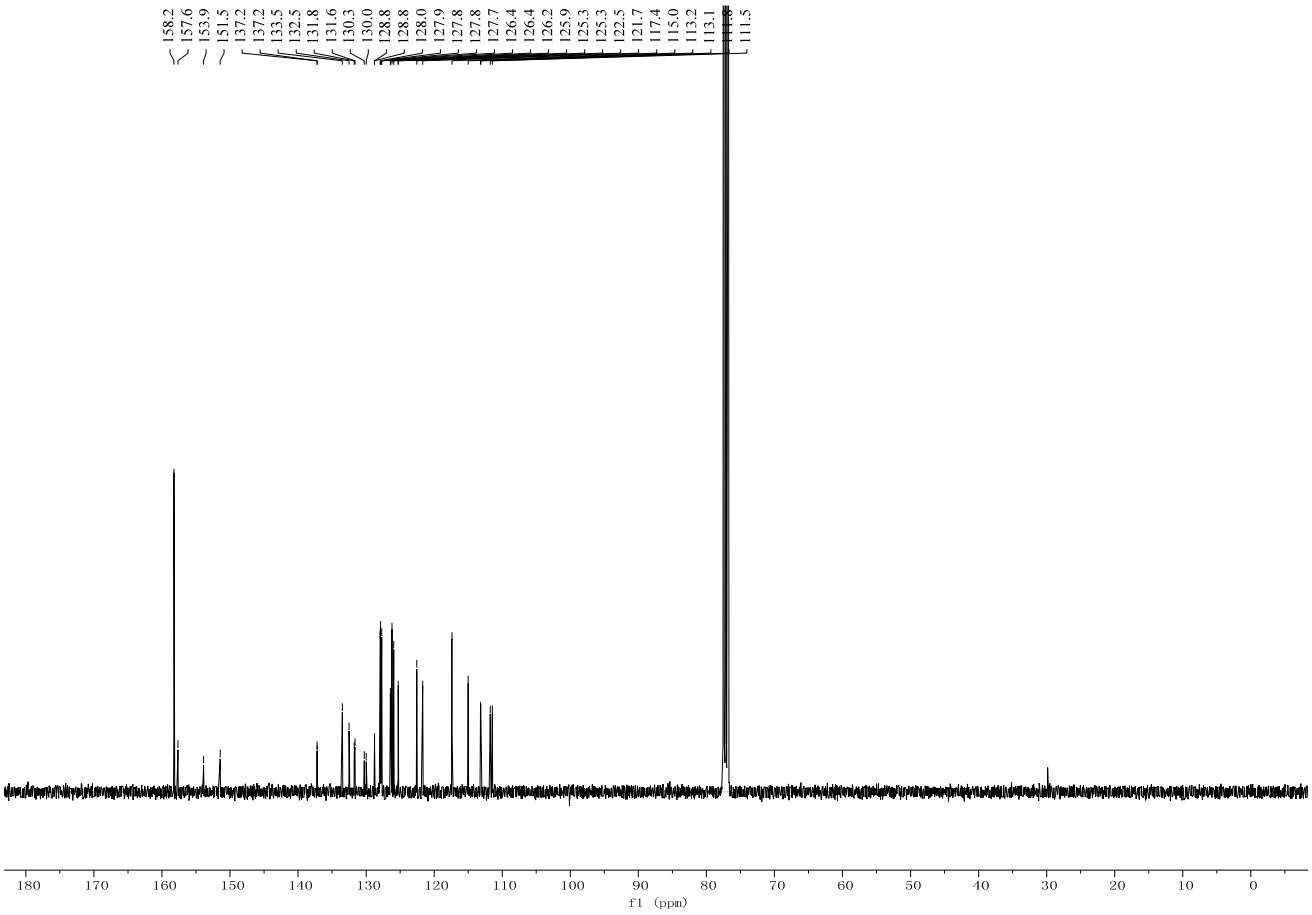
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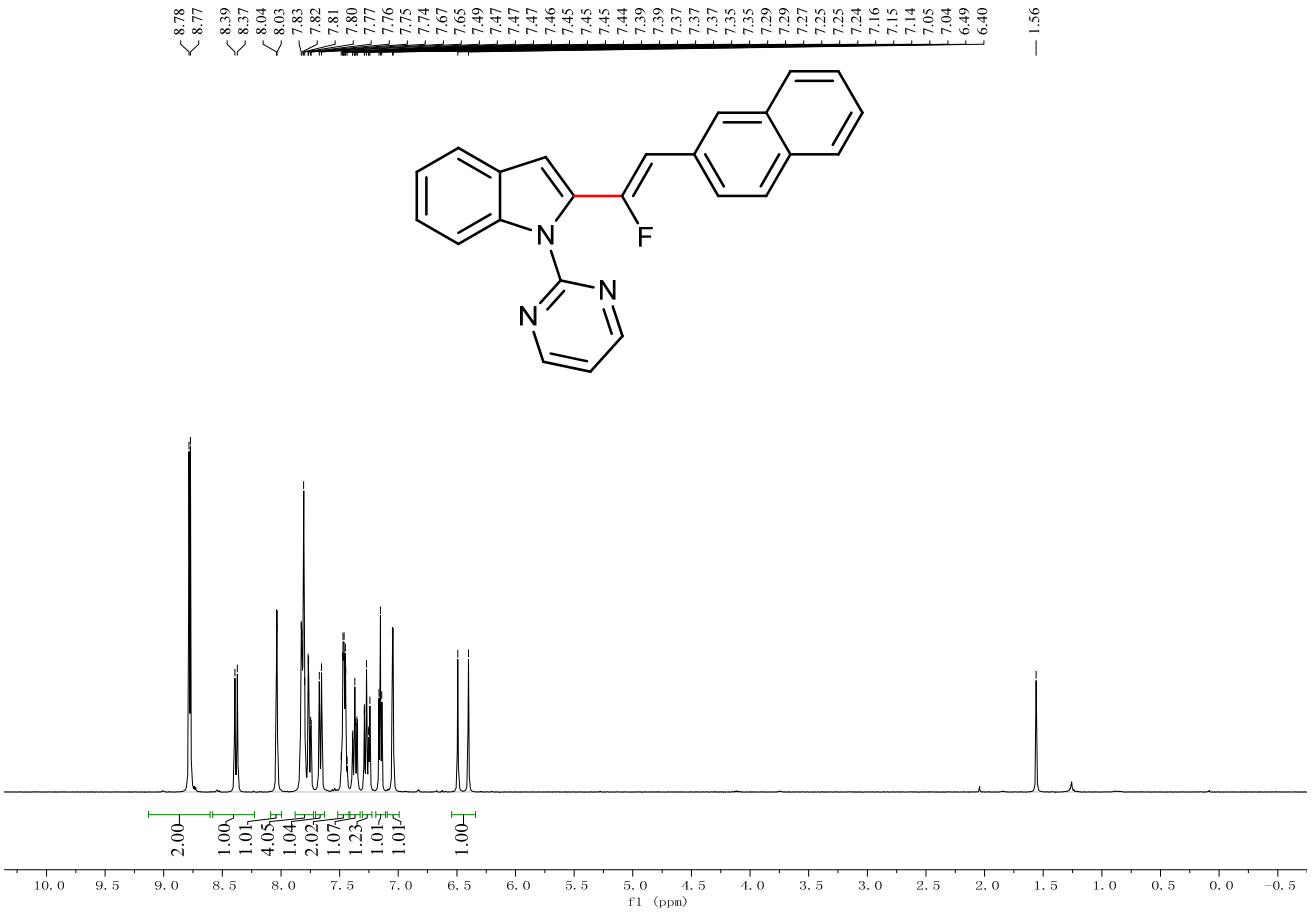
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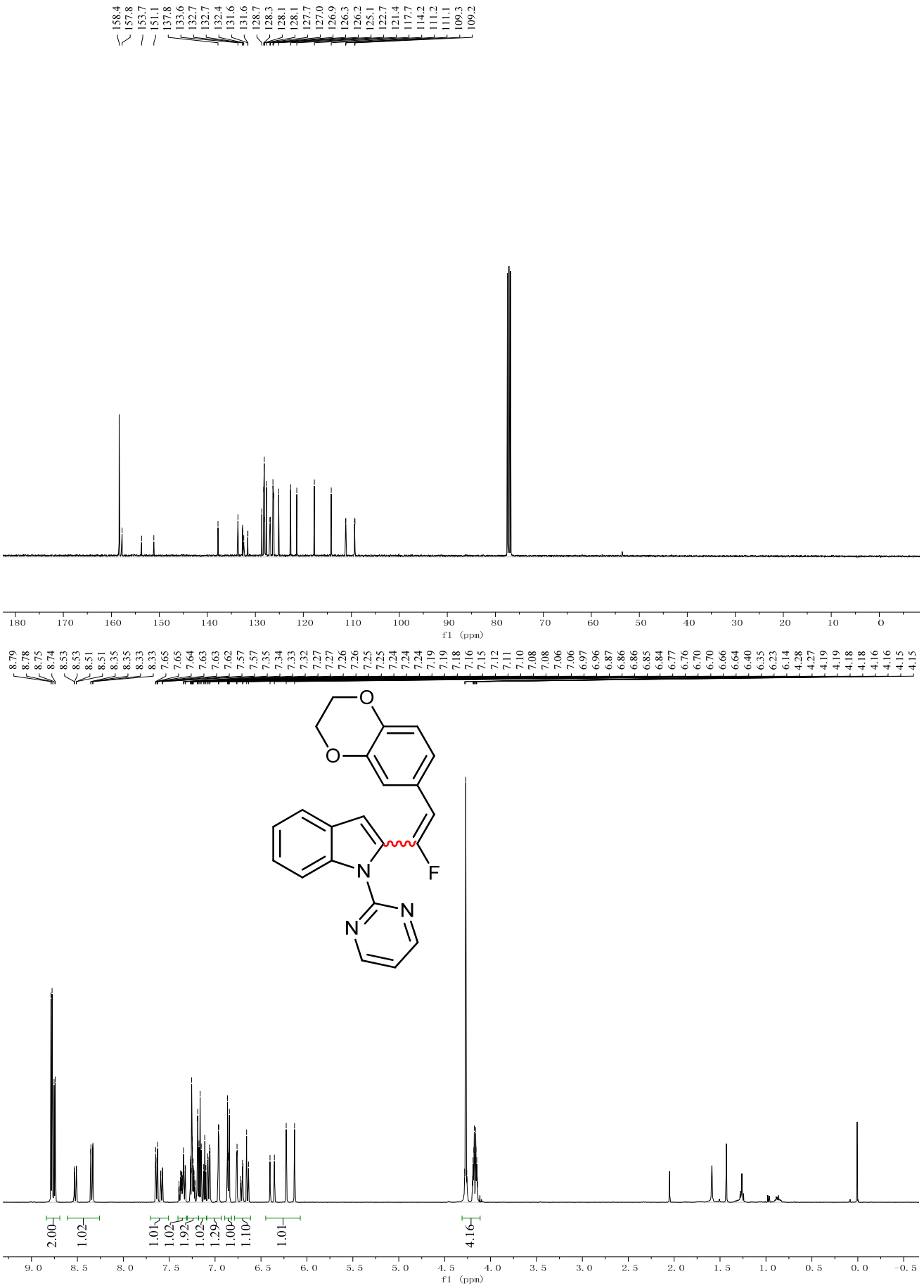
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109.2
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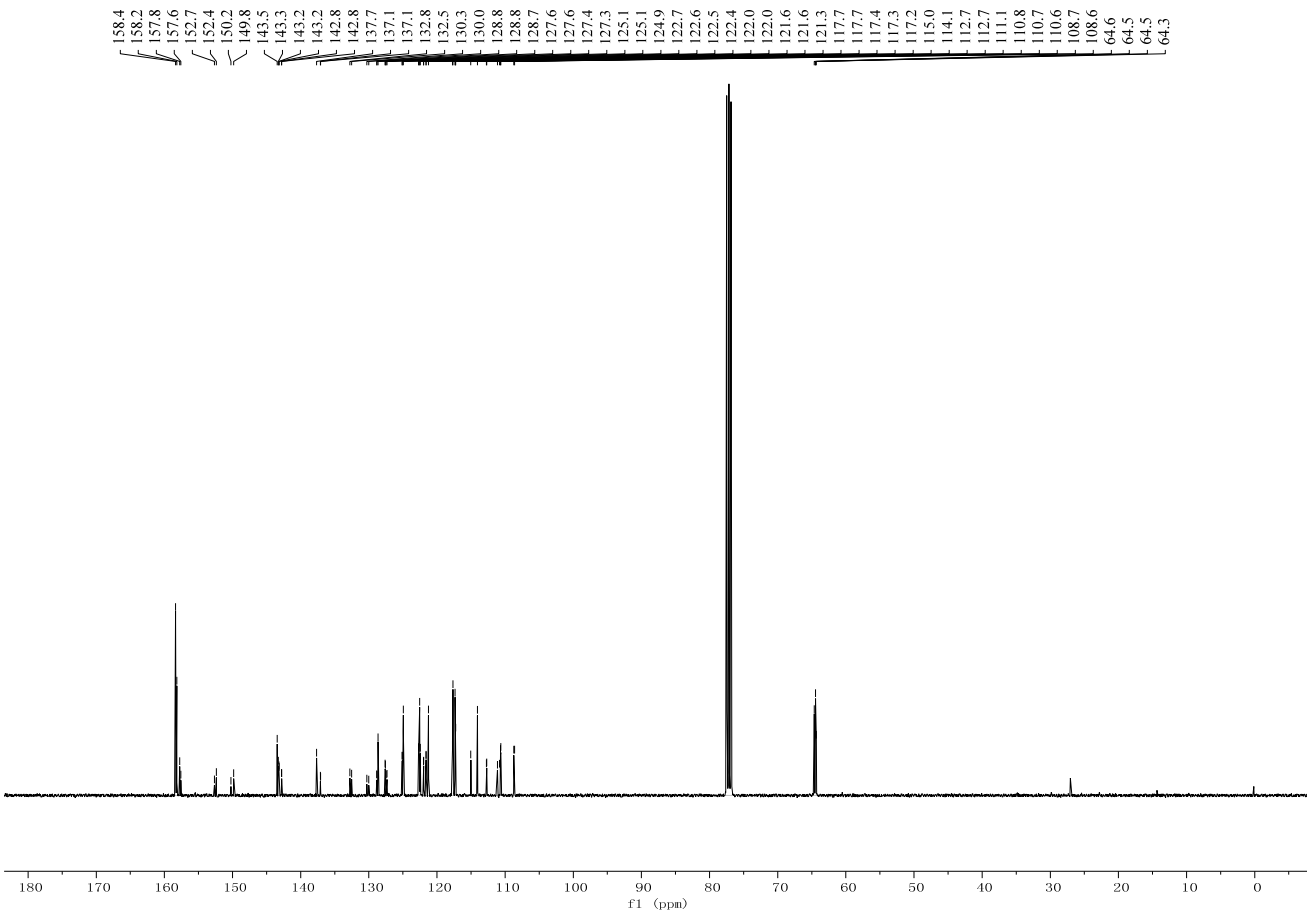
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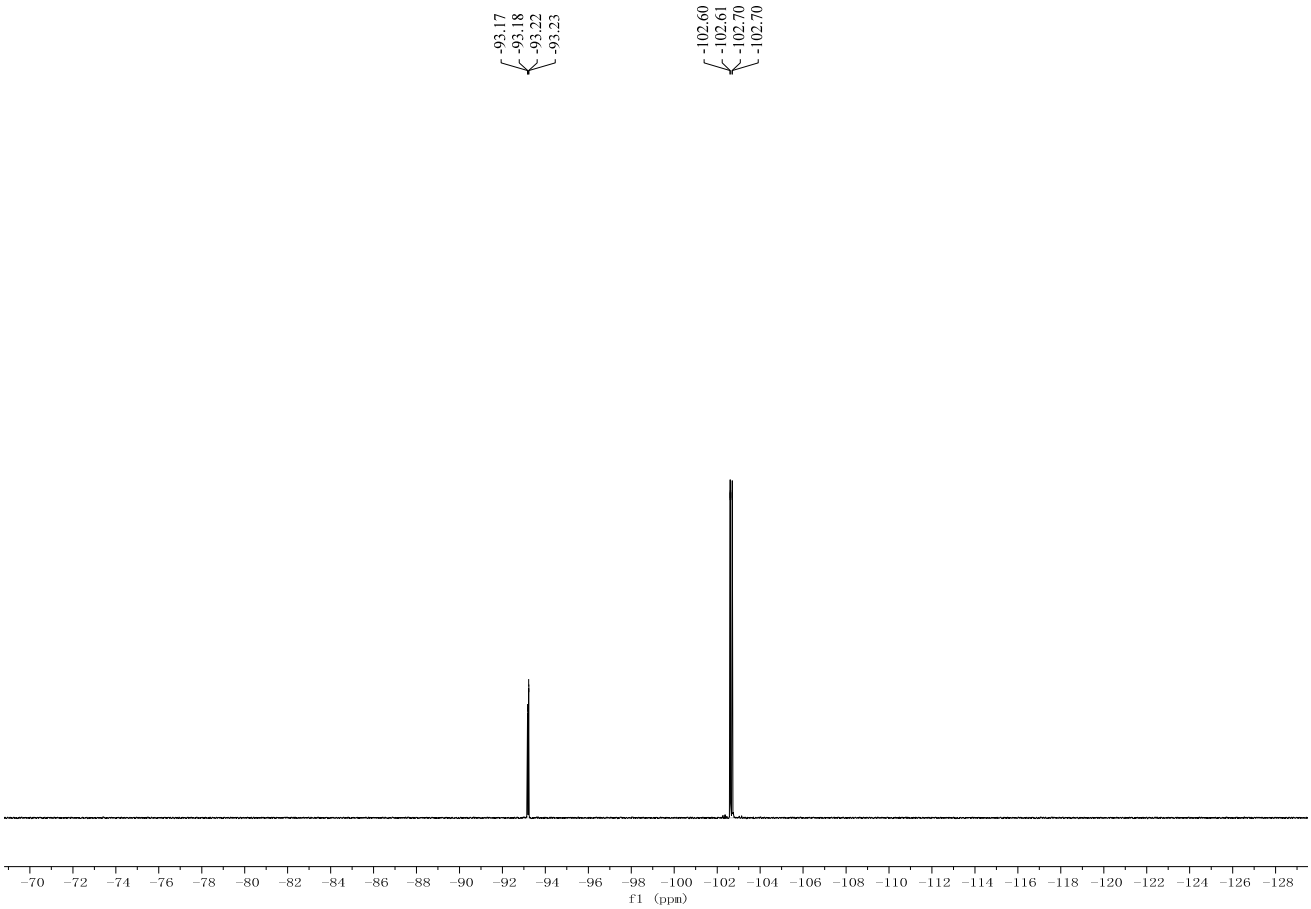
f1 (ppm)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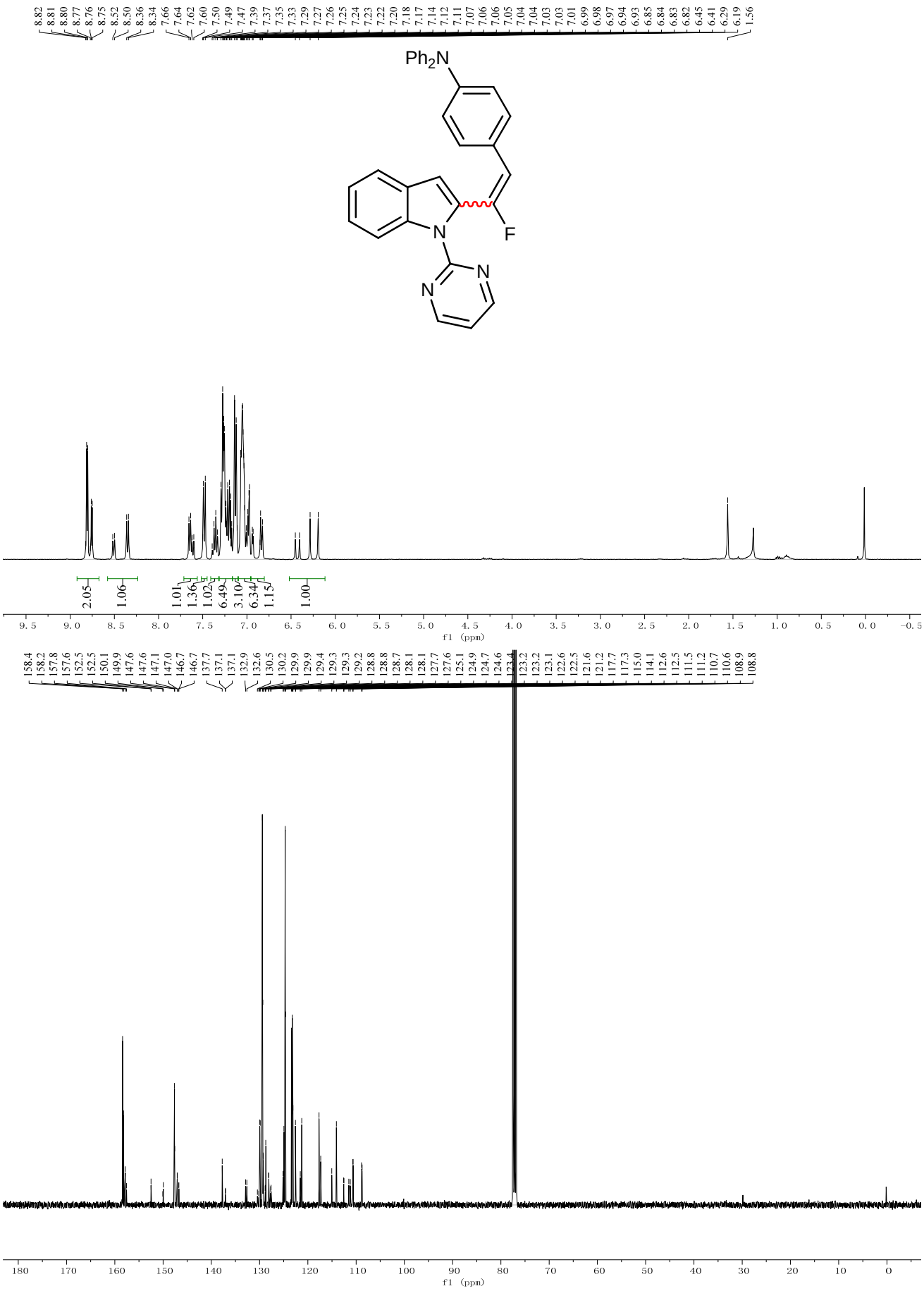
f1 (ppm)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Ph2N
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f1 (ppm)
158.4 158.2 157.8 157.6 152.5 152.5 150.1 149.9 147.6 147.6 147.1 147.0 146.7 146.7 137.7 137.1 137.1 132.9 132.6 130.5 130.2 129.9 129.9 129.4 129.3 129.3 129.2 128.8 128.8 128.7 128.1 128.1 127.7 127.6 125.1 124.9 124.7 124.6 123.4 123.2 123.2 123.1 122.6 122.5 121.6 121.2 117.7 117.3 115.0 114.1 112.6 112.5 111.5 111.2 110.7 110.6 108.9 108.8
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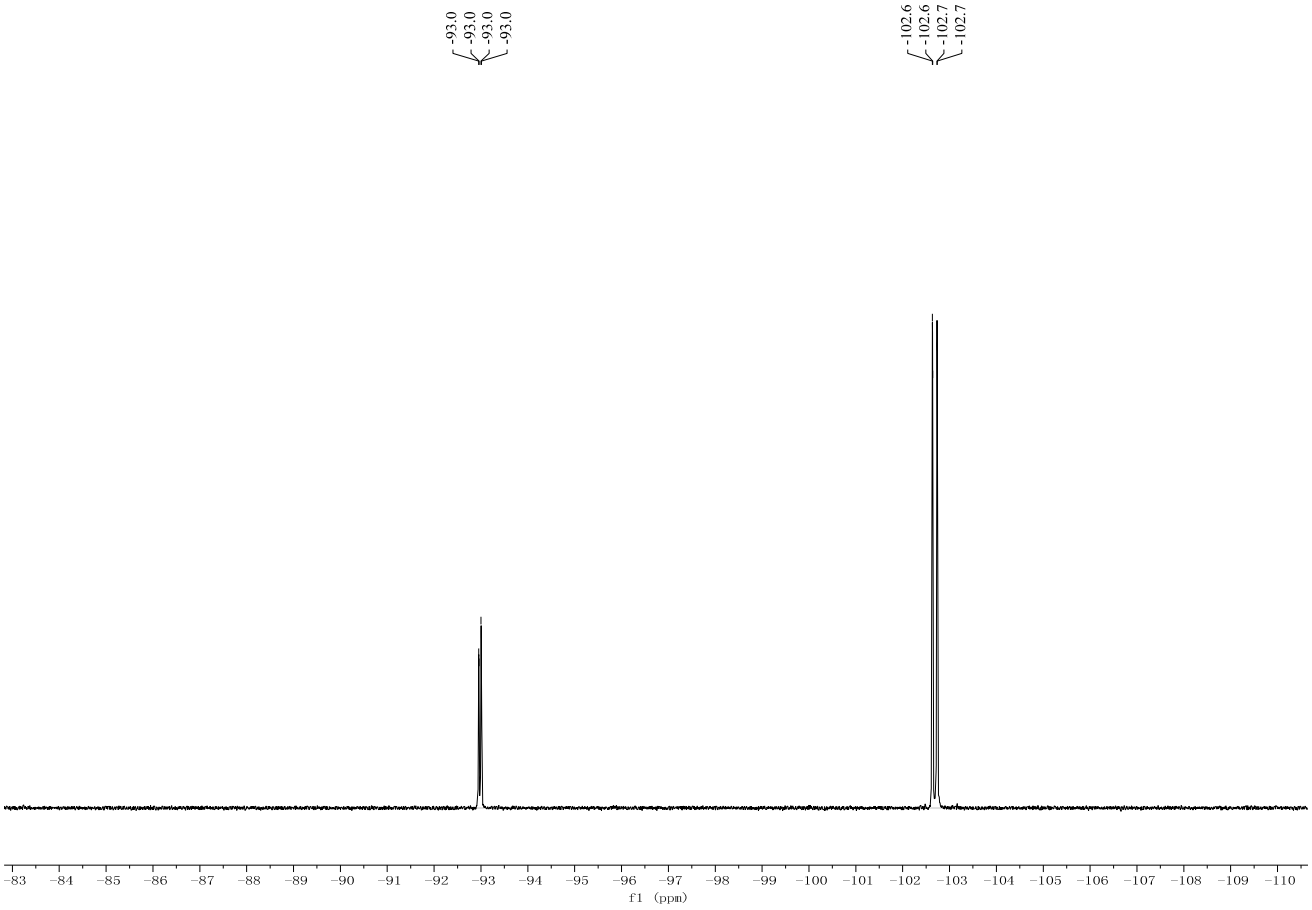
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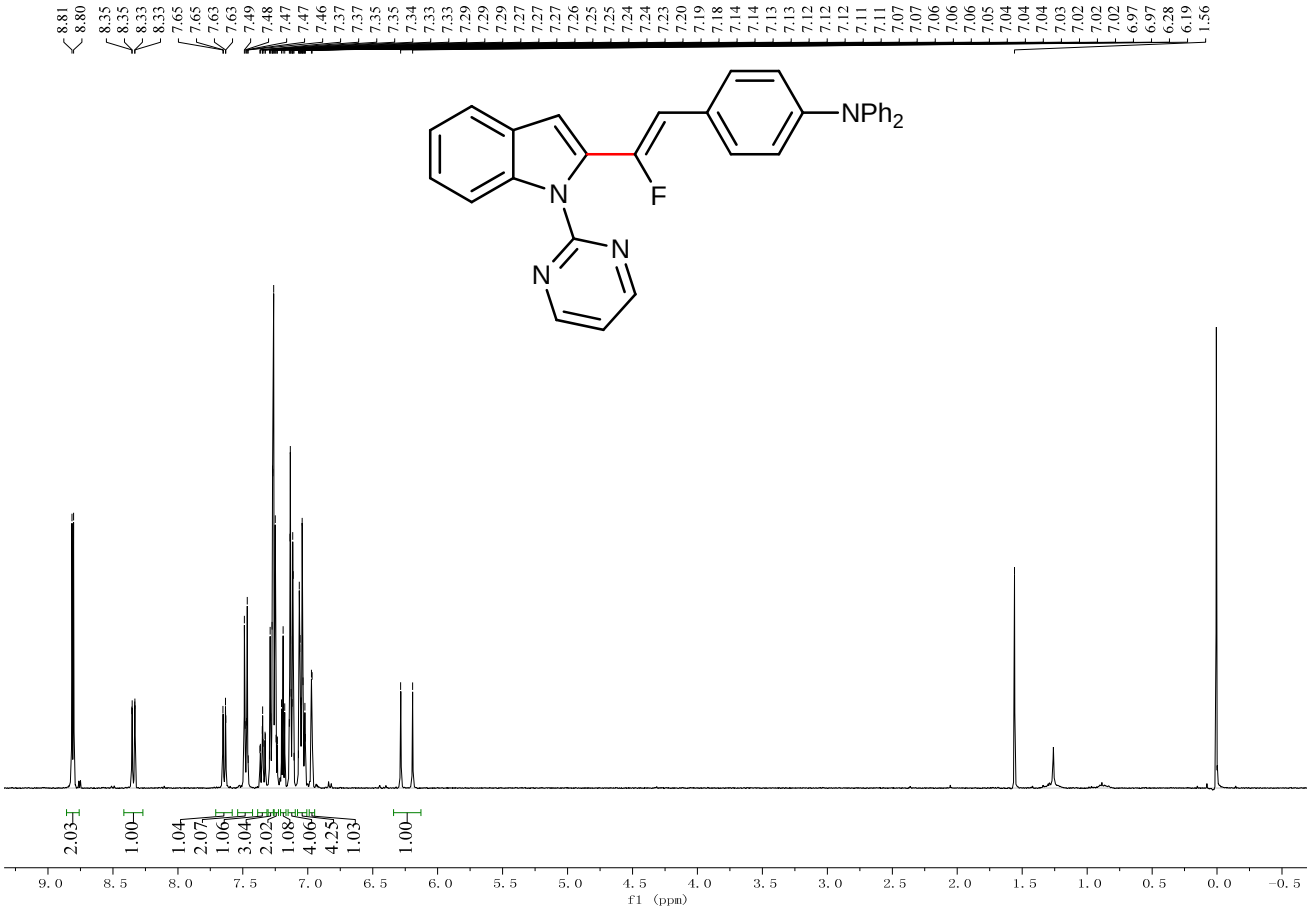
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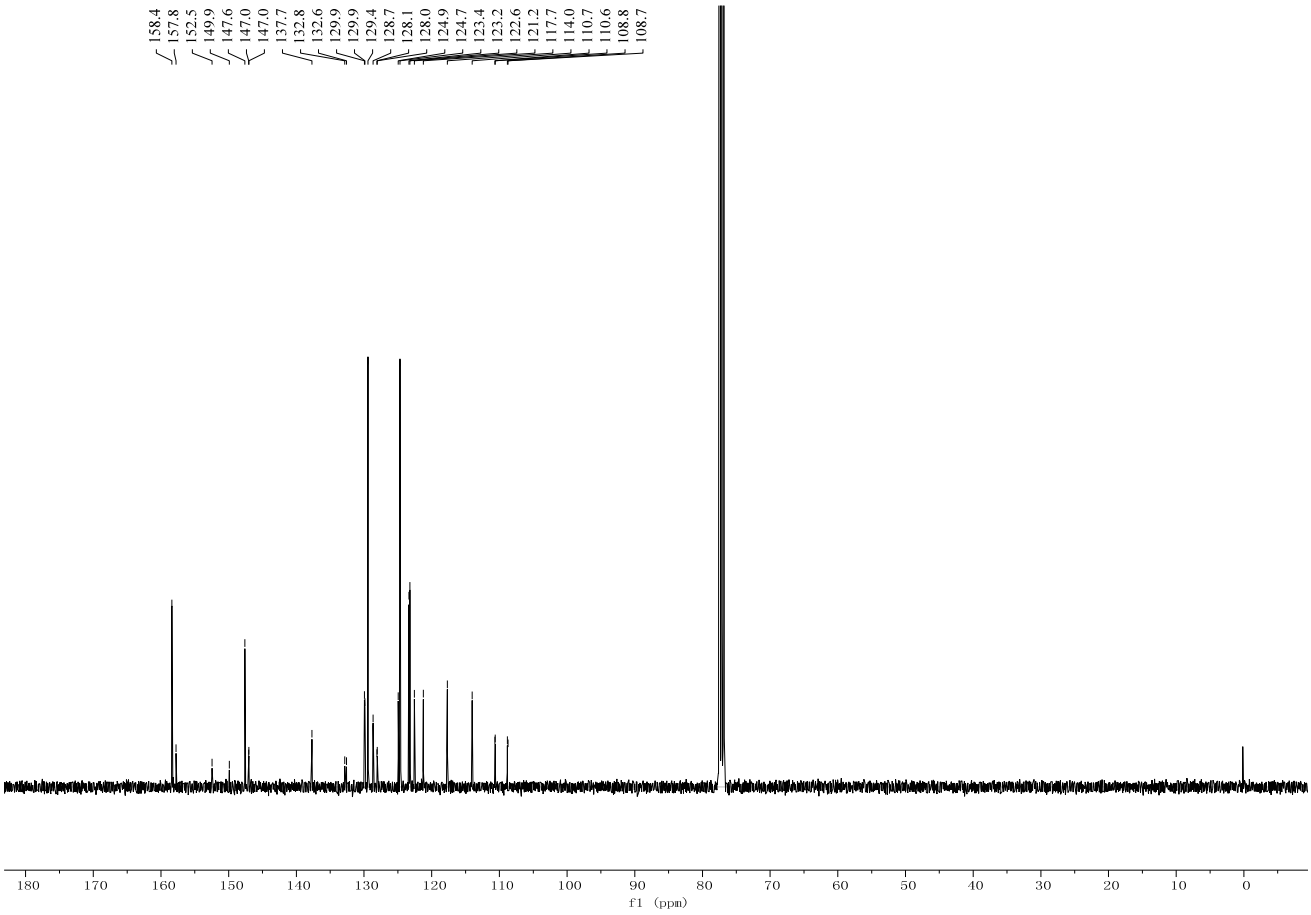
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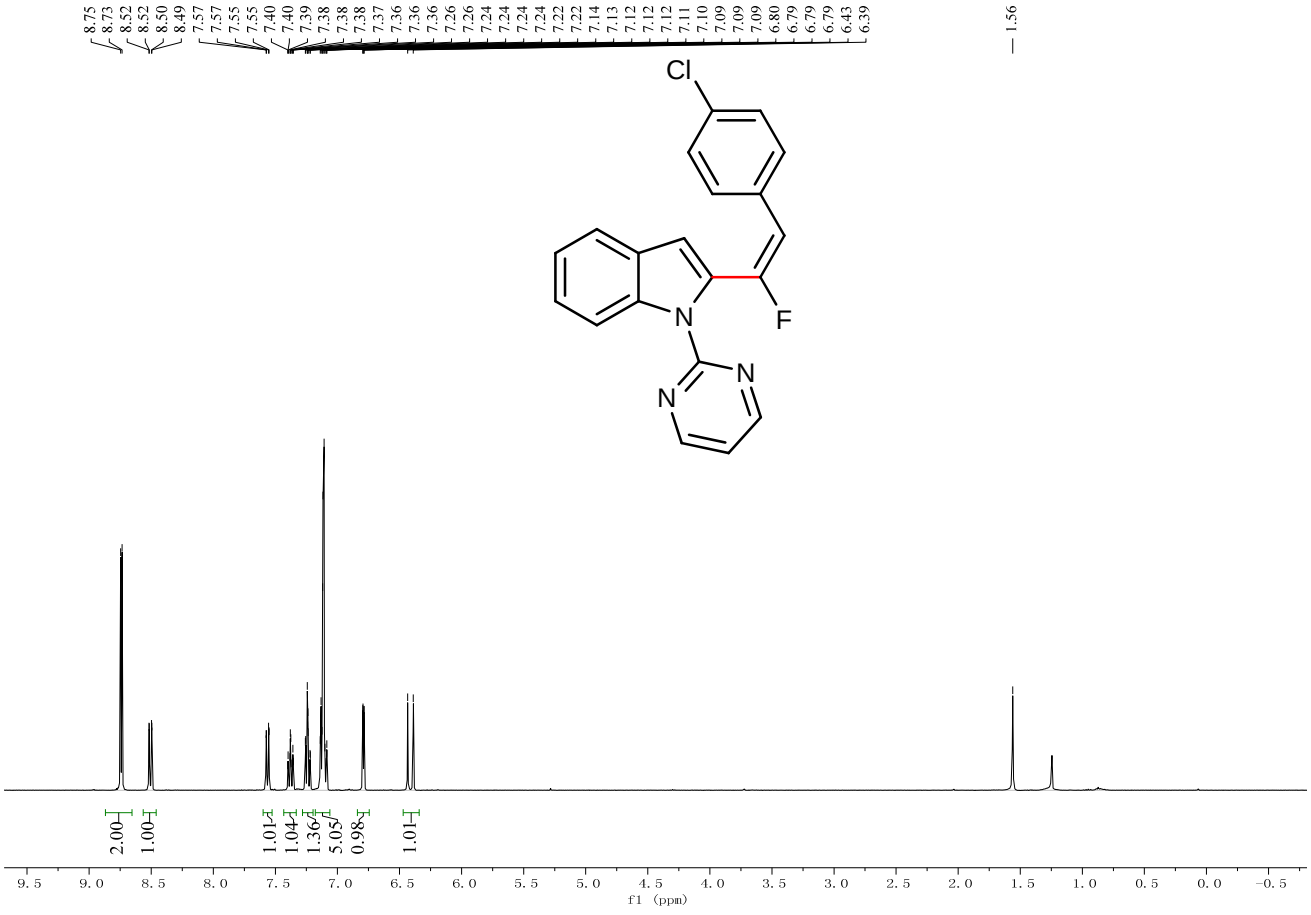
f1 (ppm)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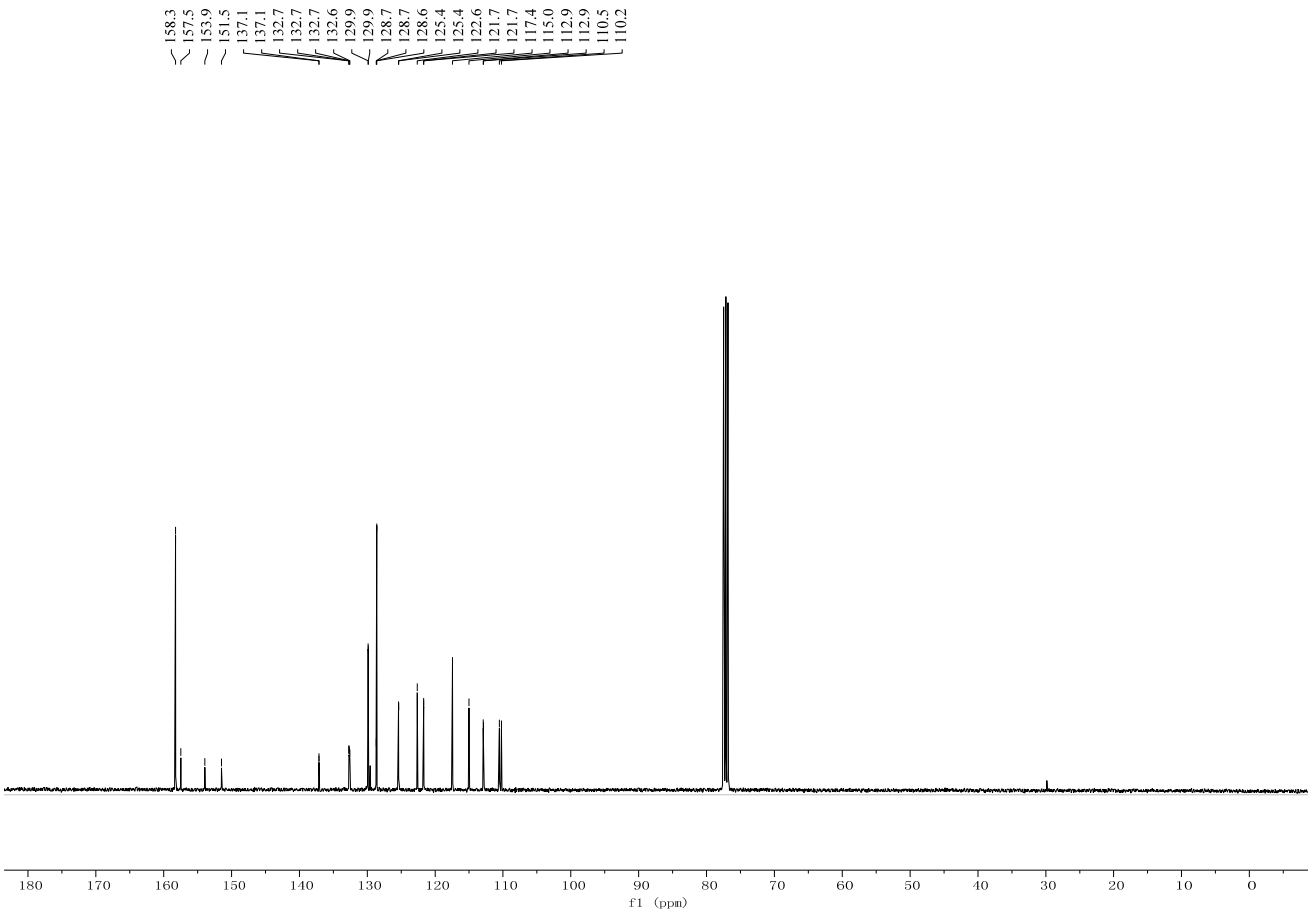
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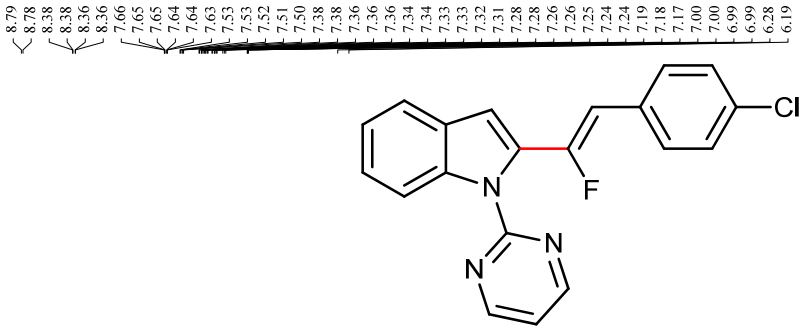
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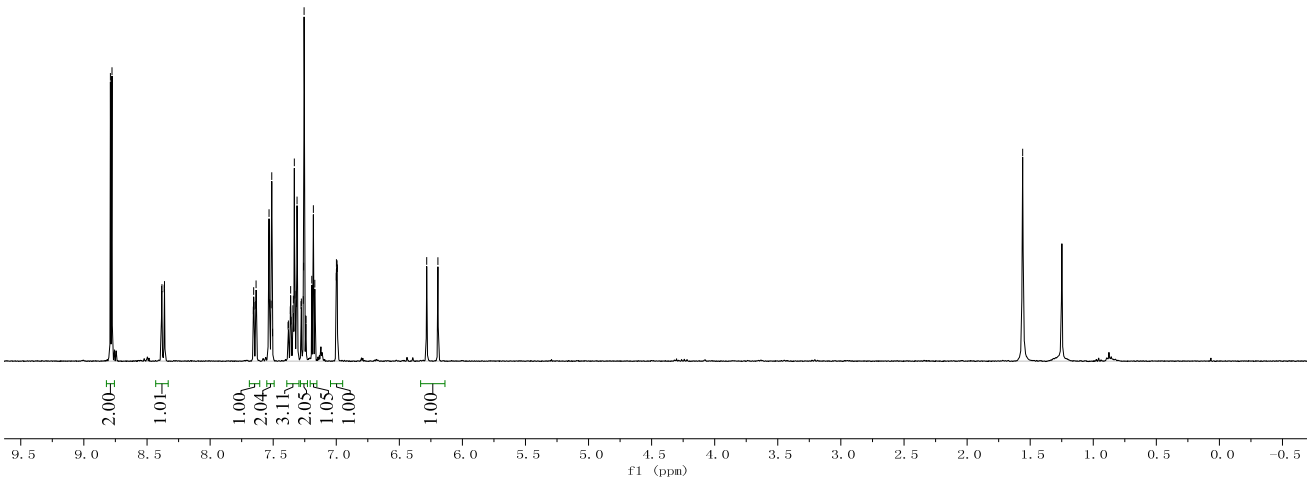
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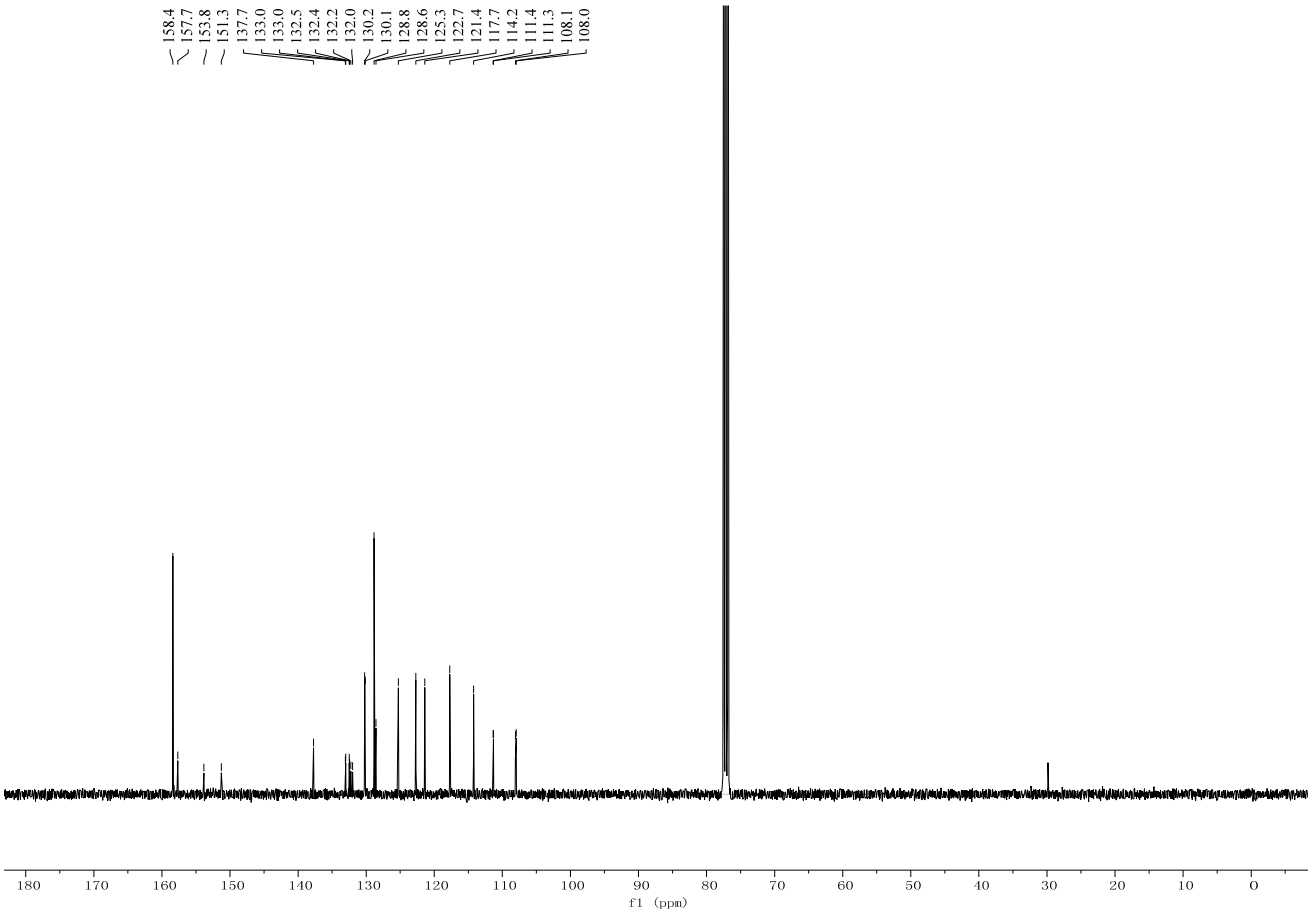
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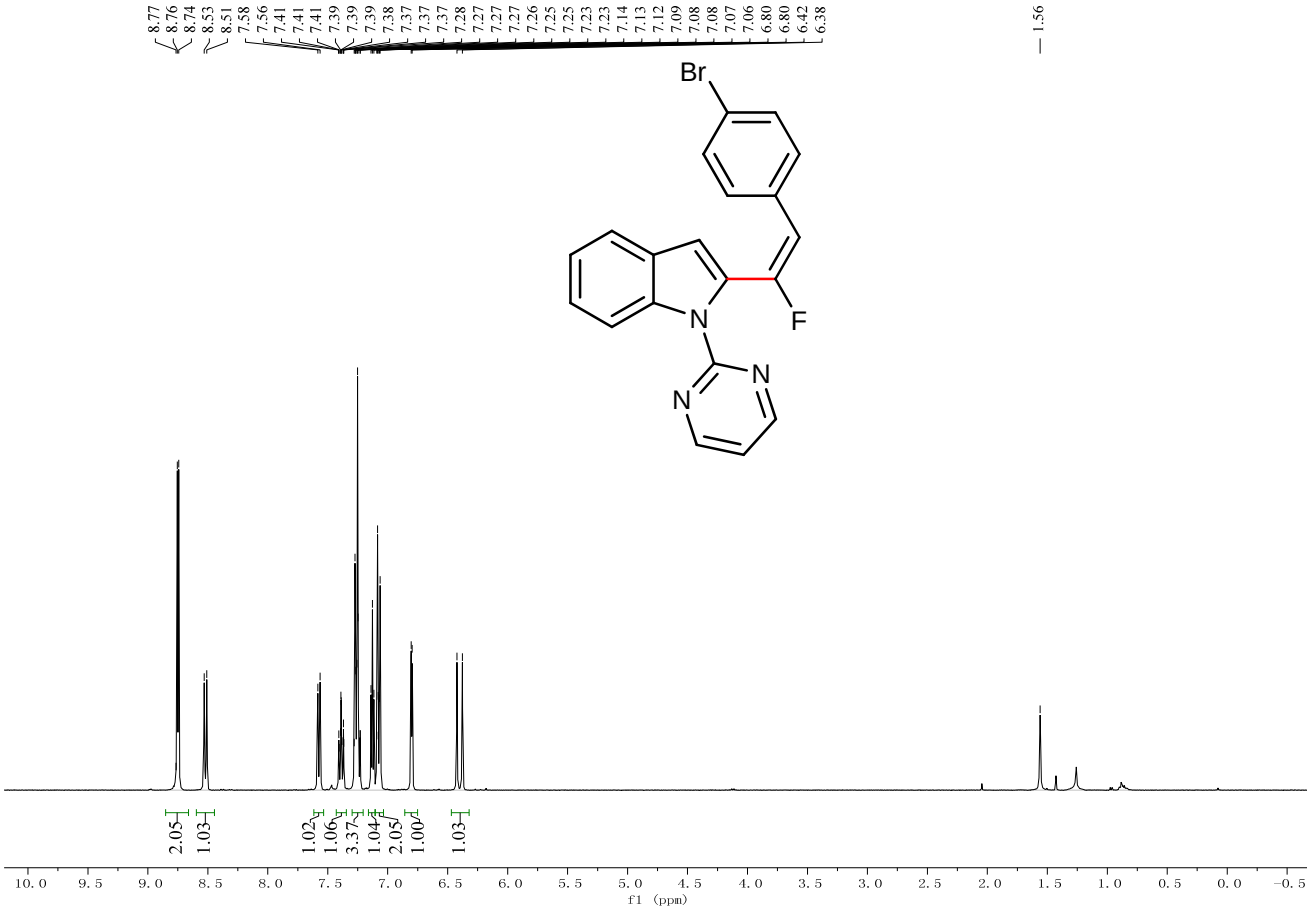
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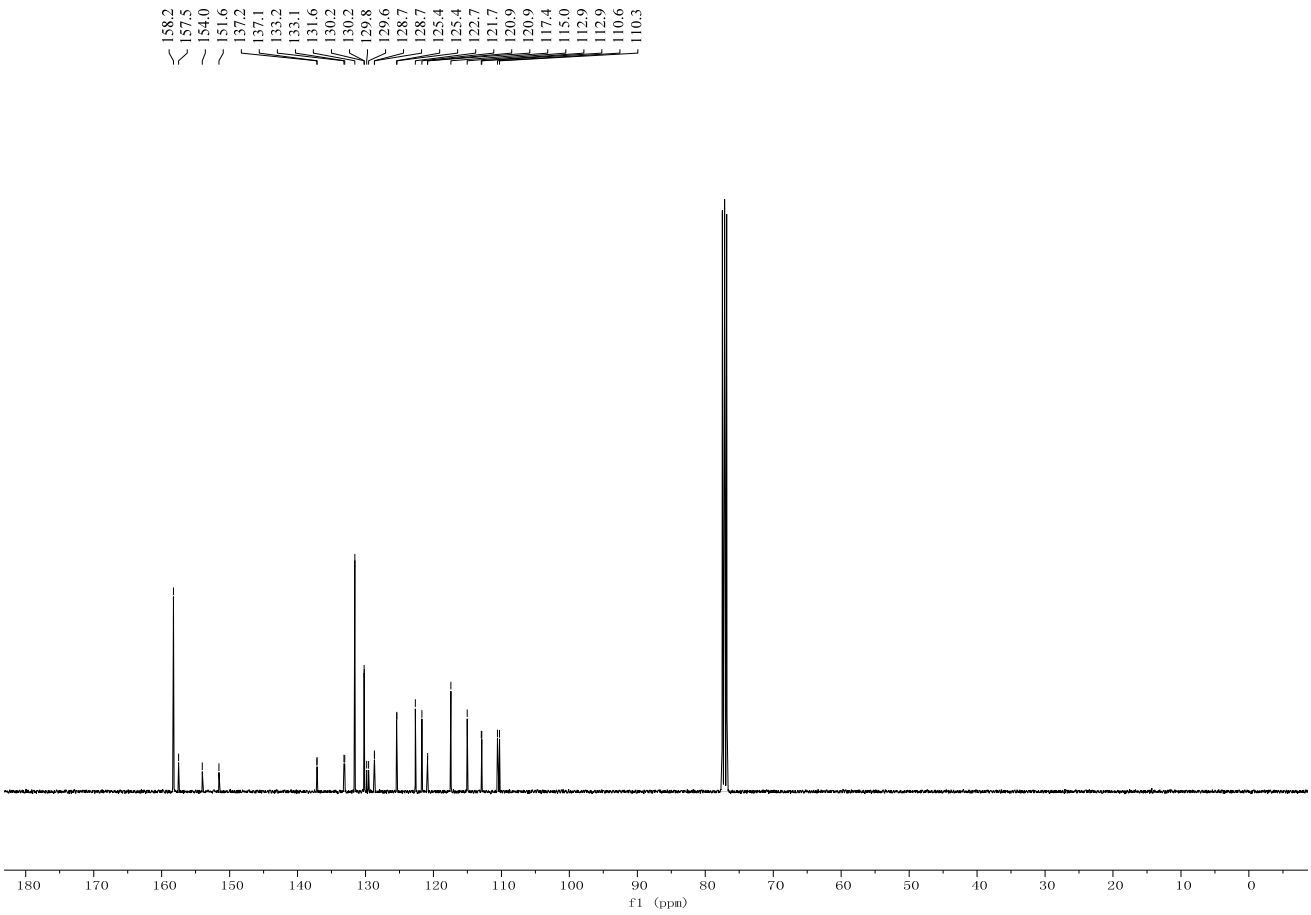
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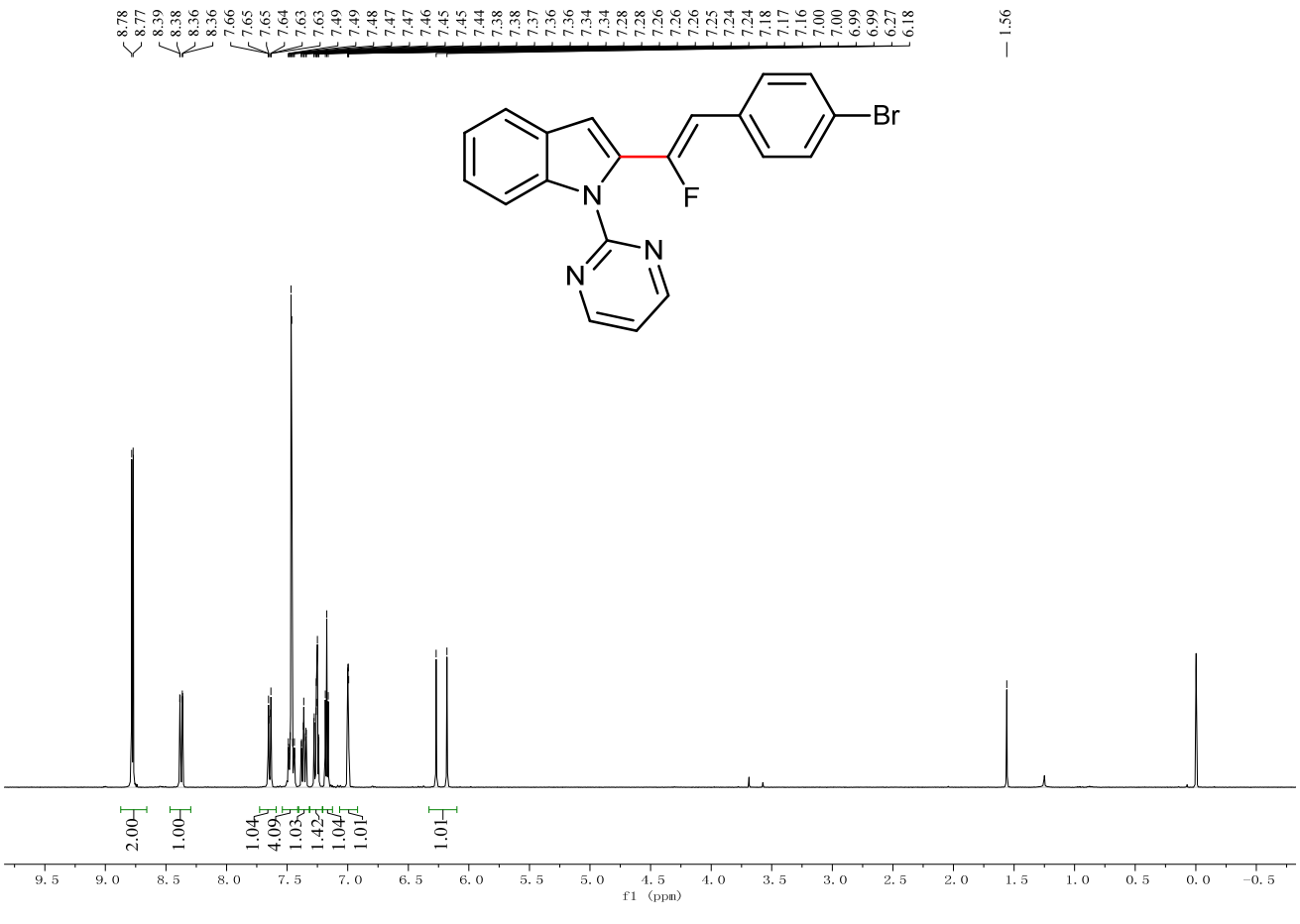
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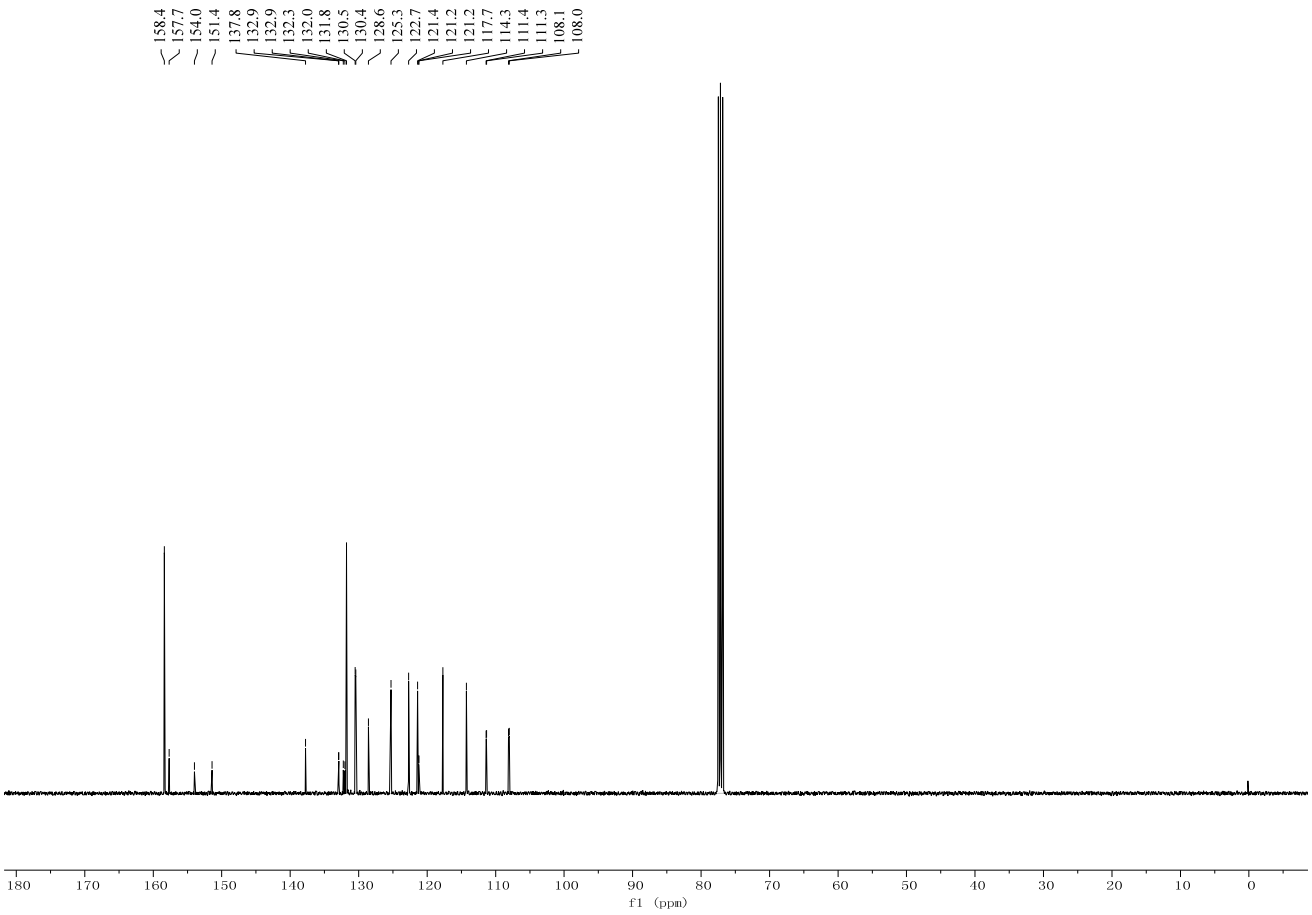
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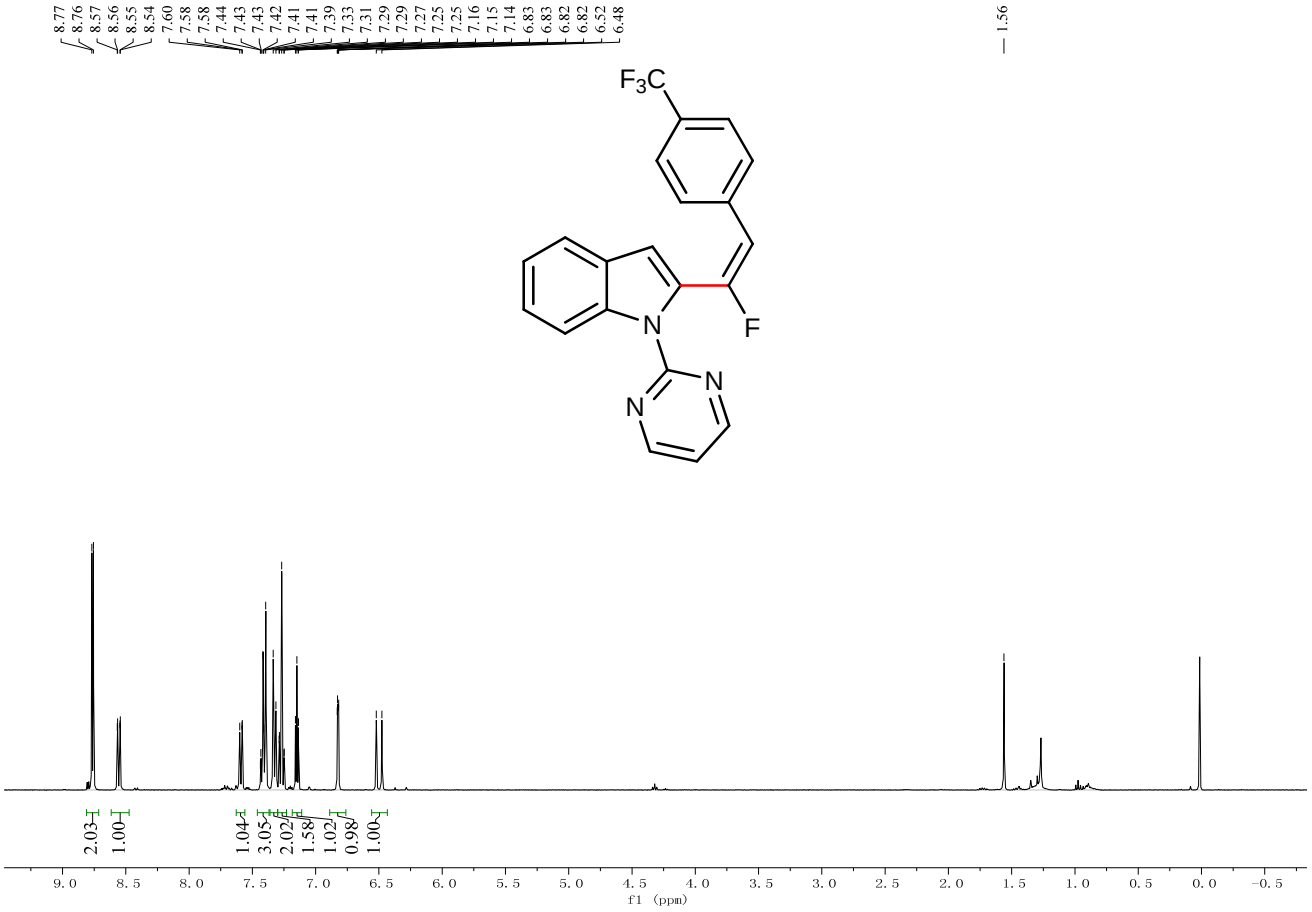
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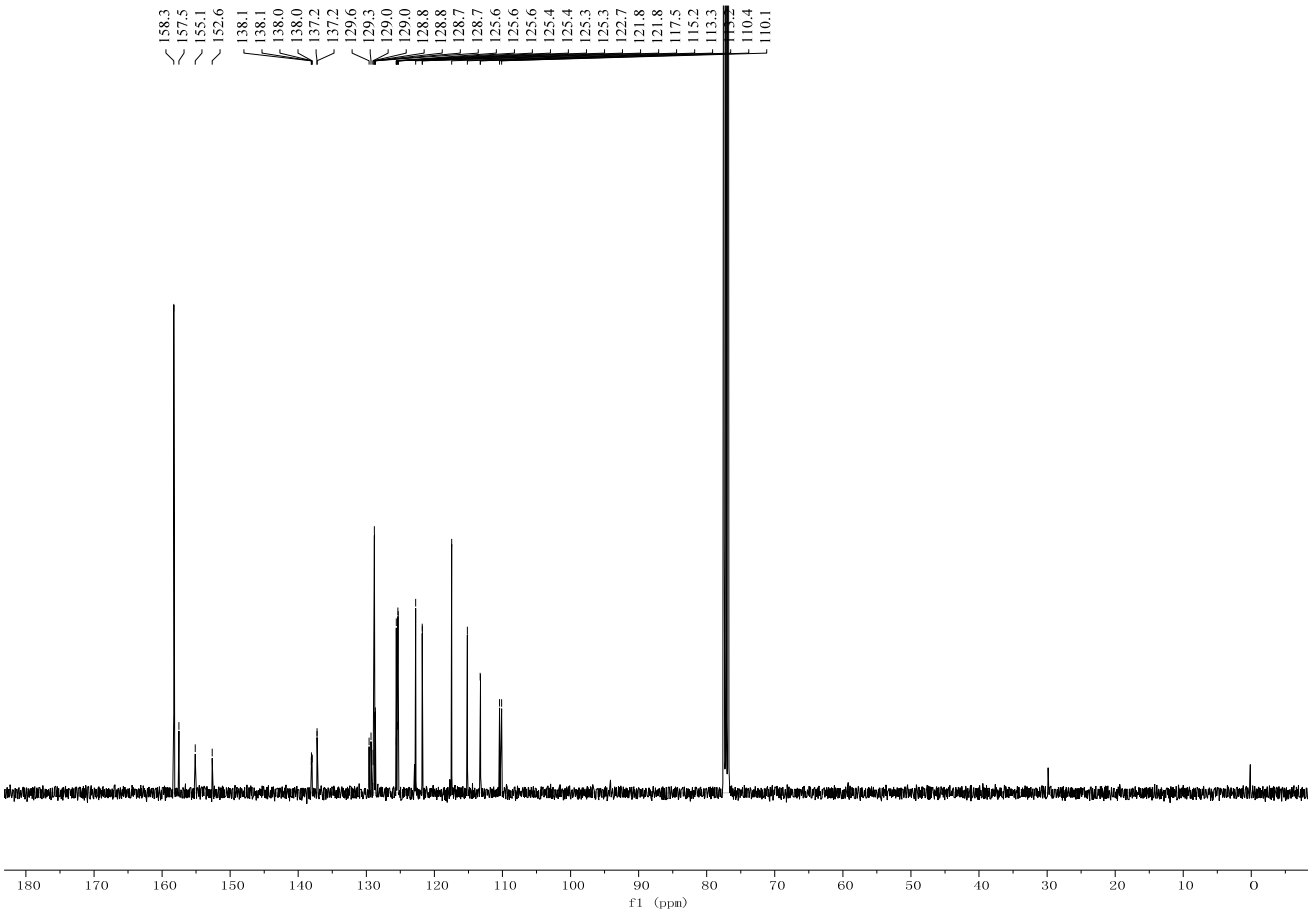
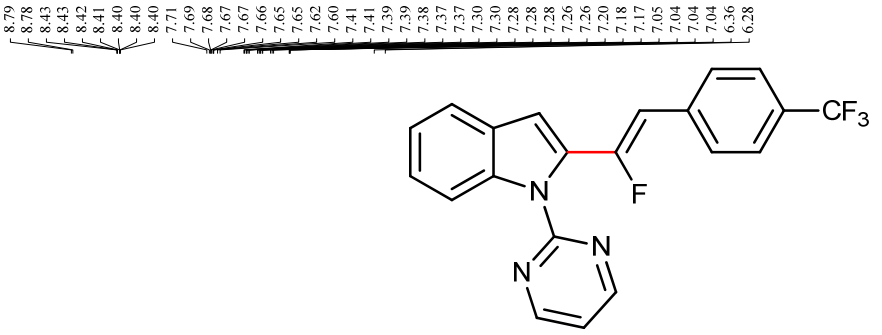
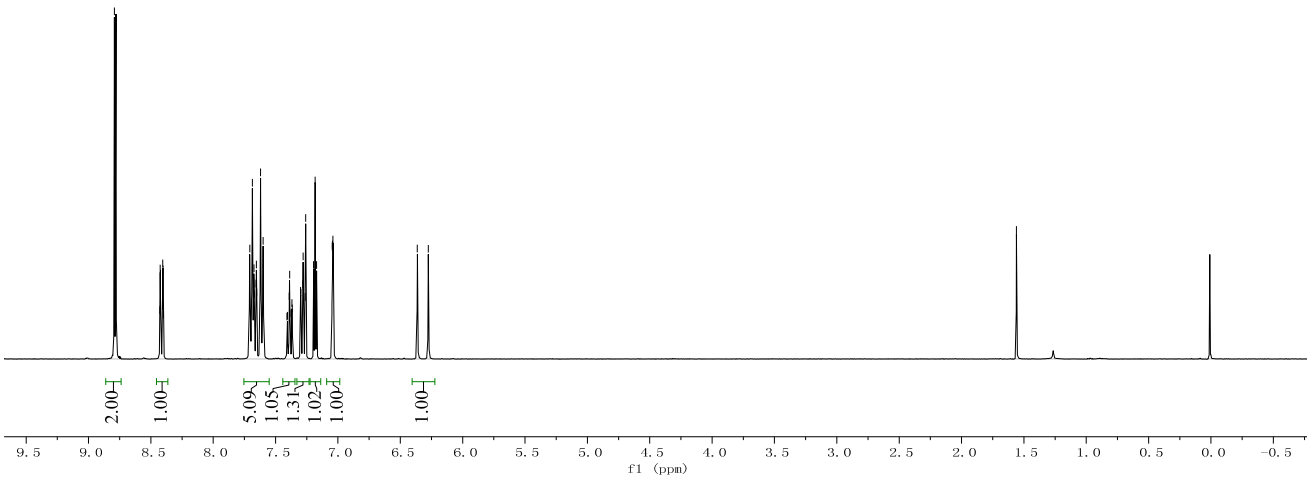
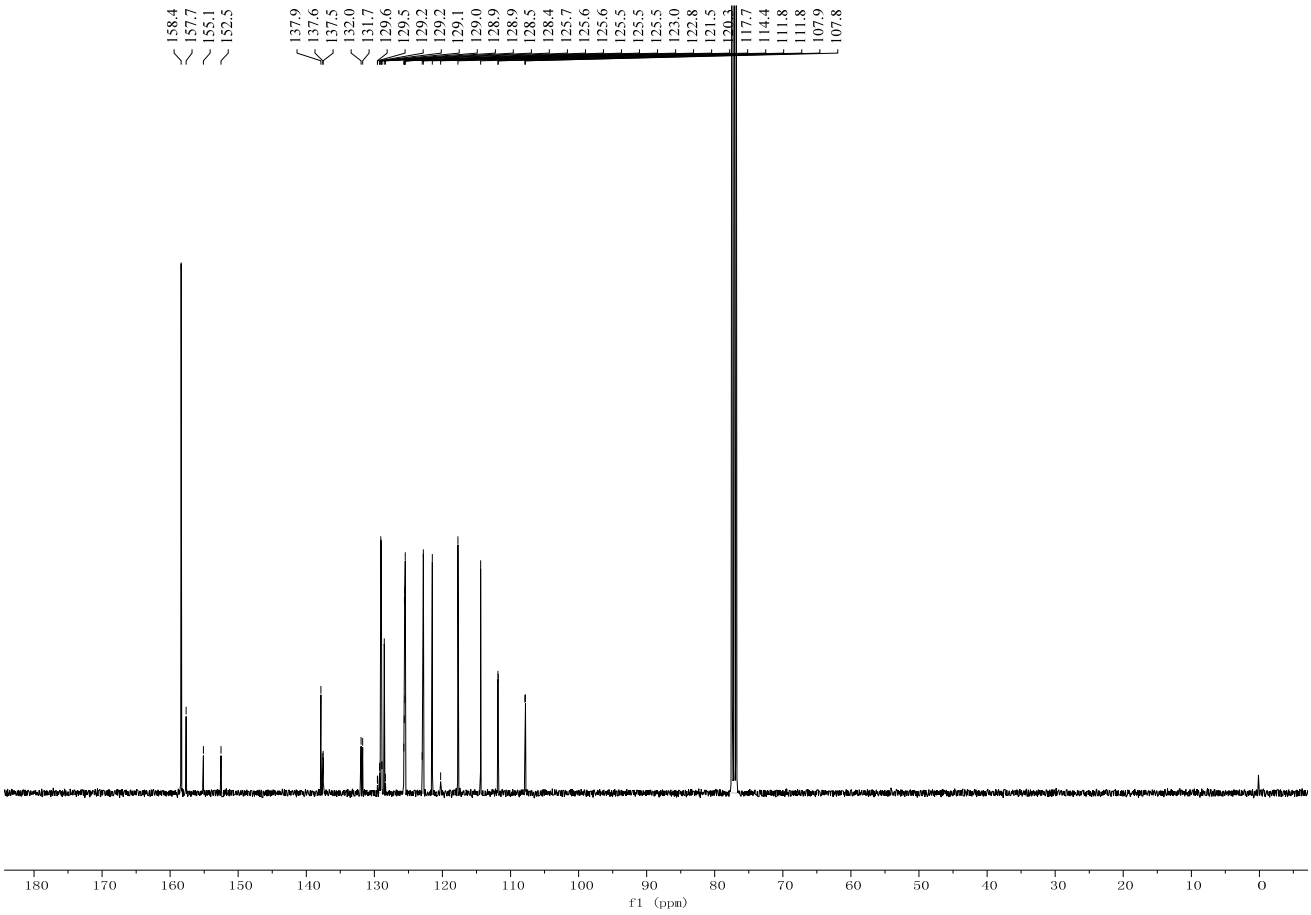
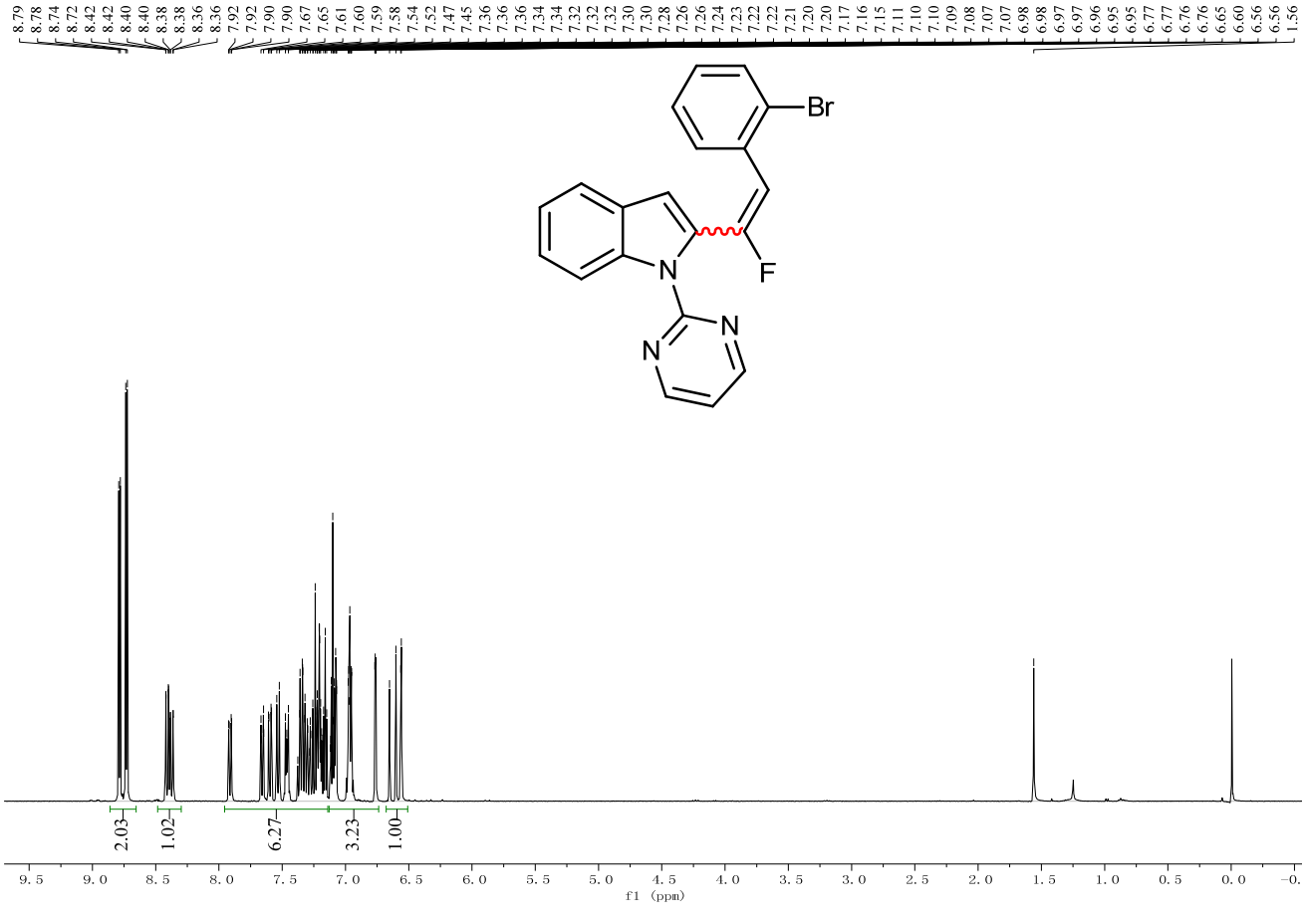
7.31
7.29
7.29
7.27
7.25
7.25
7.16
7.15
7.14
6.83
6.83
6.82
6.52
6.48
1.56
F3C
F
N
N
N
2.03
1.00
1.04
3.05
2.02
1.58
1.02
0.98
1.00
f1 (ppm)

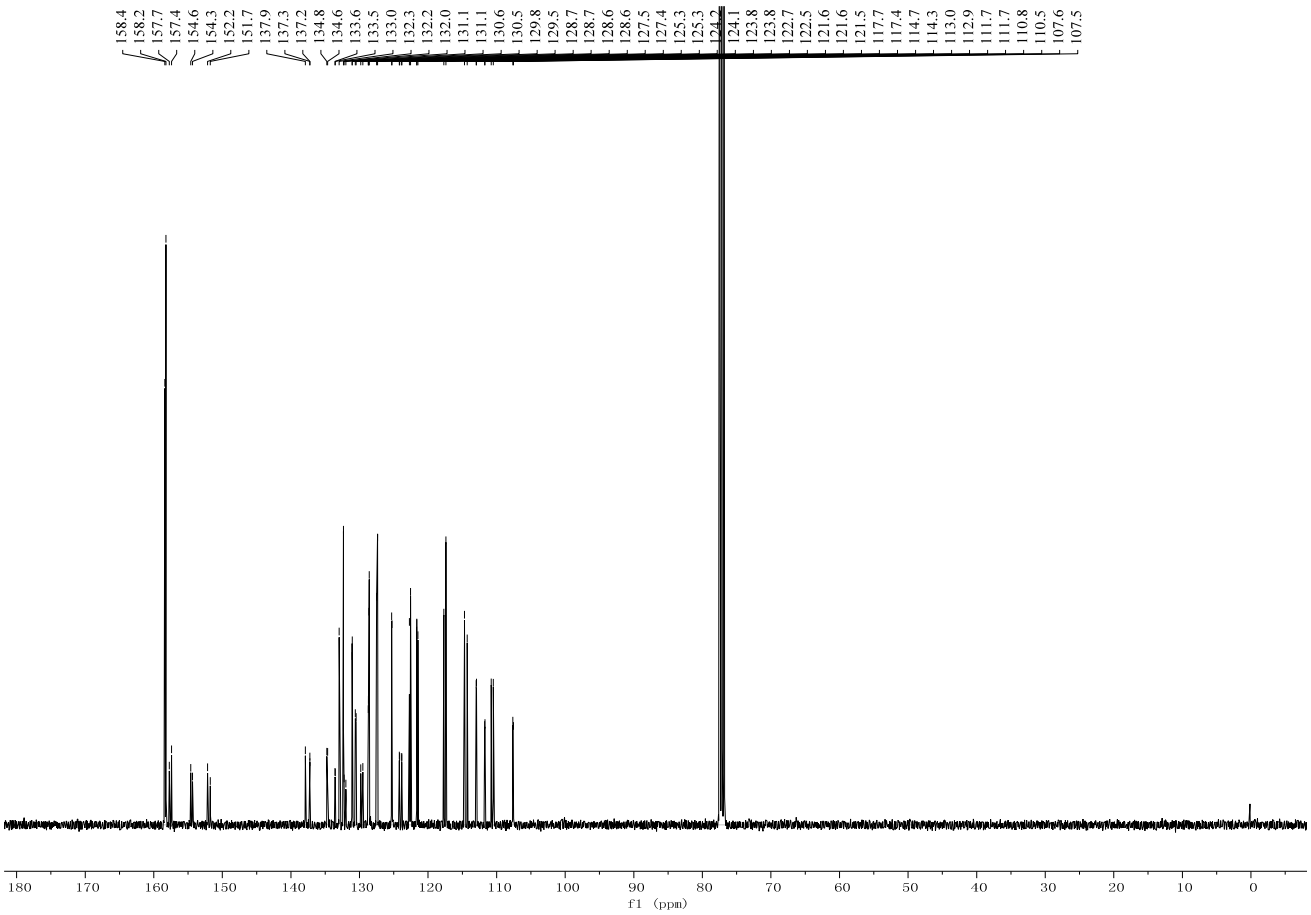

158.3
157.5
155.1
152.6
138.1
138.1
138.0
138.0
137.2
137.2
129.6
129.3
129.0
129.0
128.8
128.8
128.7
128.7
125.6
125.6
125.6
125.4
125.4
125.3
125.3
122.7
121.8
121.8
117.5
115.2
113.3
110.4
110.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

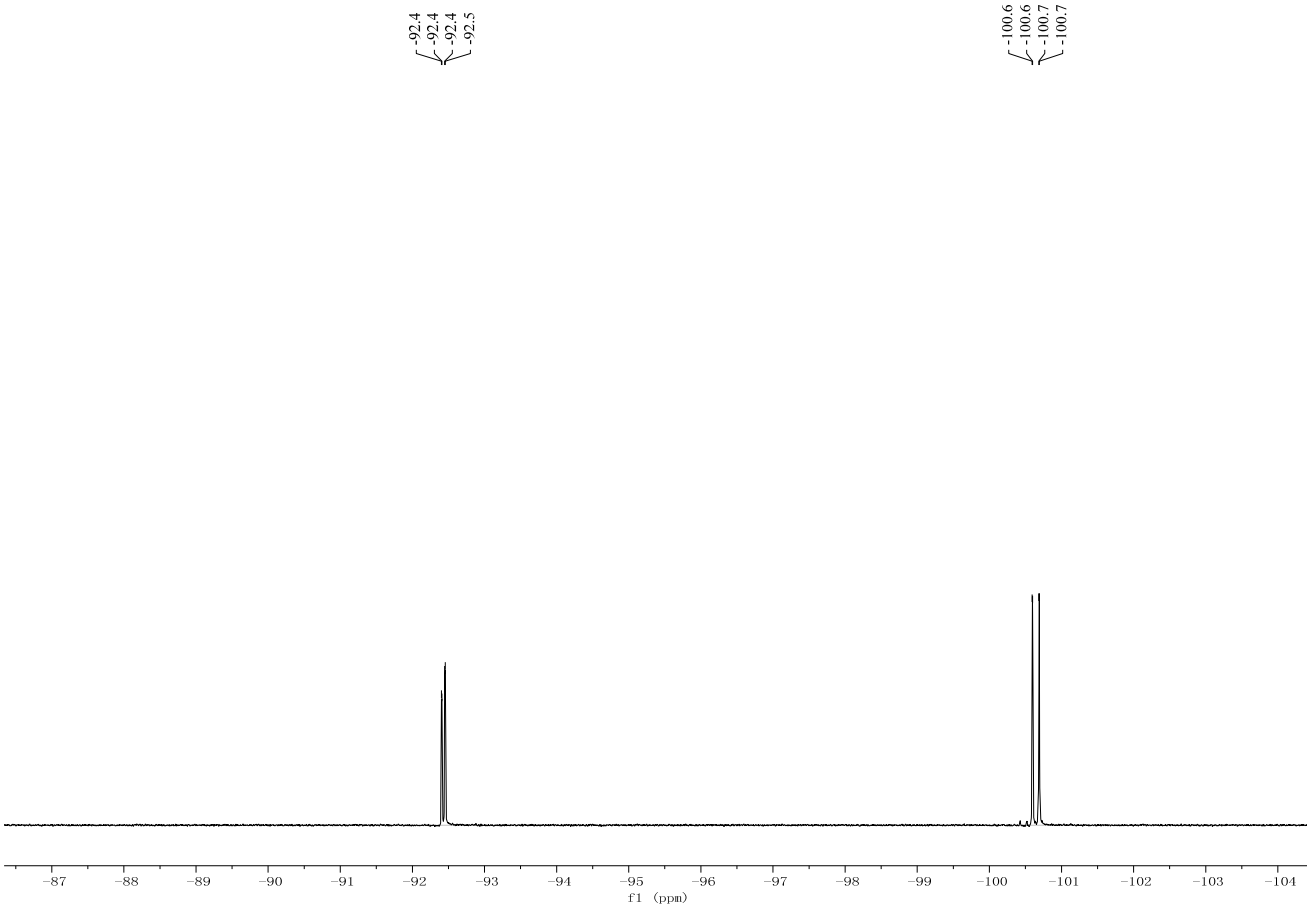

8.79
8.78
8.43
8.43
8.42
8.41
8.40
8.40
8.40
7.71
7.69
7.68
7.67
7.67
7.66
7.65
7.65
7.62
7.60
7.41
7.41
7.39
7.39
7.38
7.37
7.37
7.30
7.30
7.28
7.28
7.28
7.26
7.26
7.20
7.18
7.17
7.05
7.04
7.04
7.04
6.36
6.28
1.56
CF3
F
N
N
N

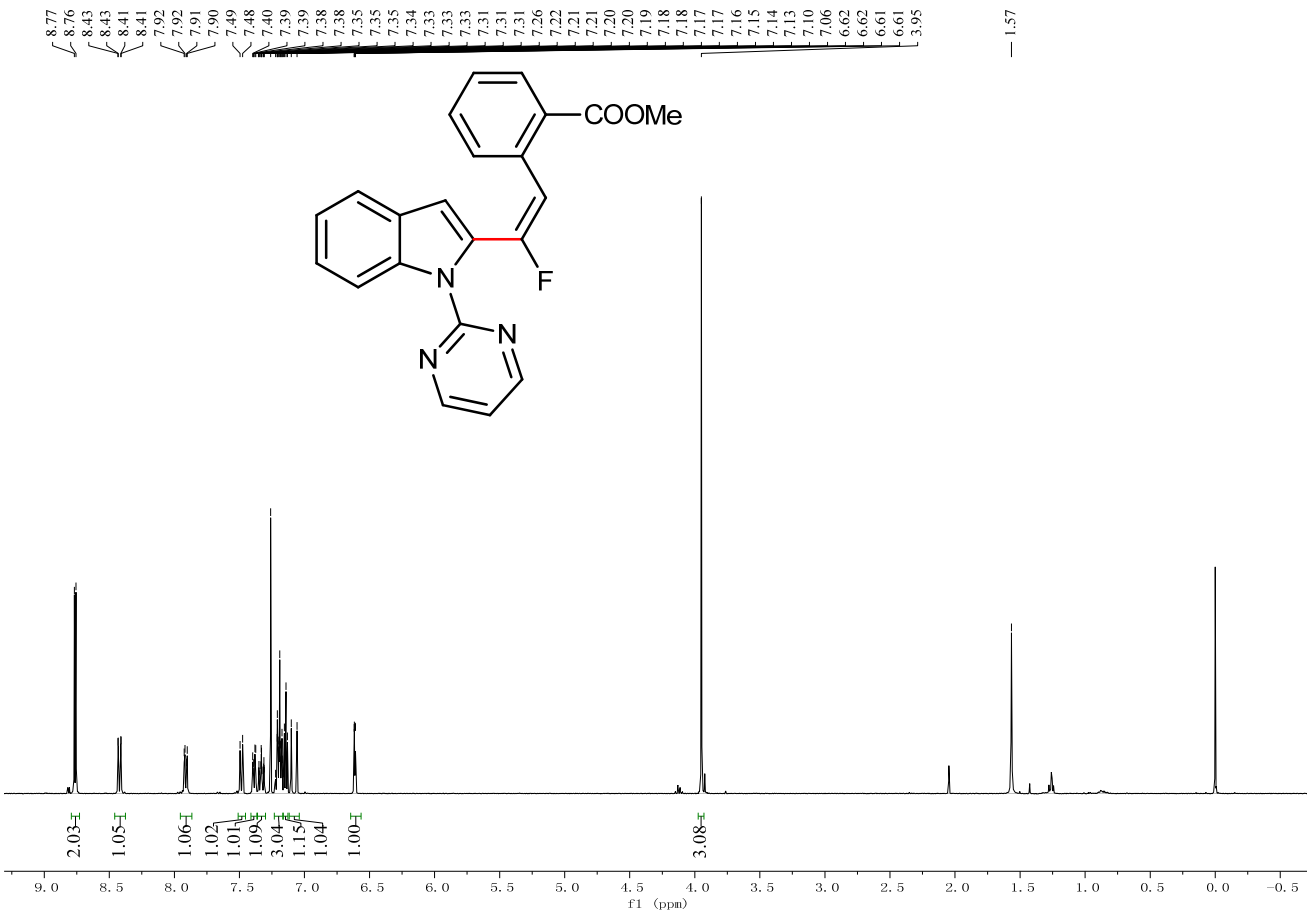

2.00
1.00
5.09
1.05
1.31
1.02
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

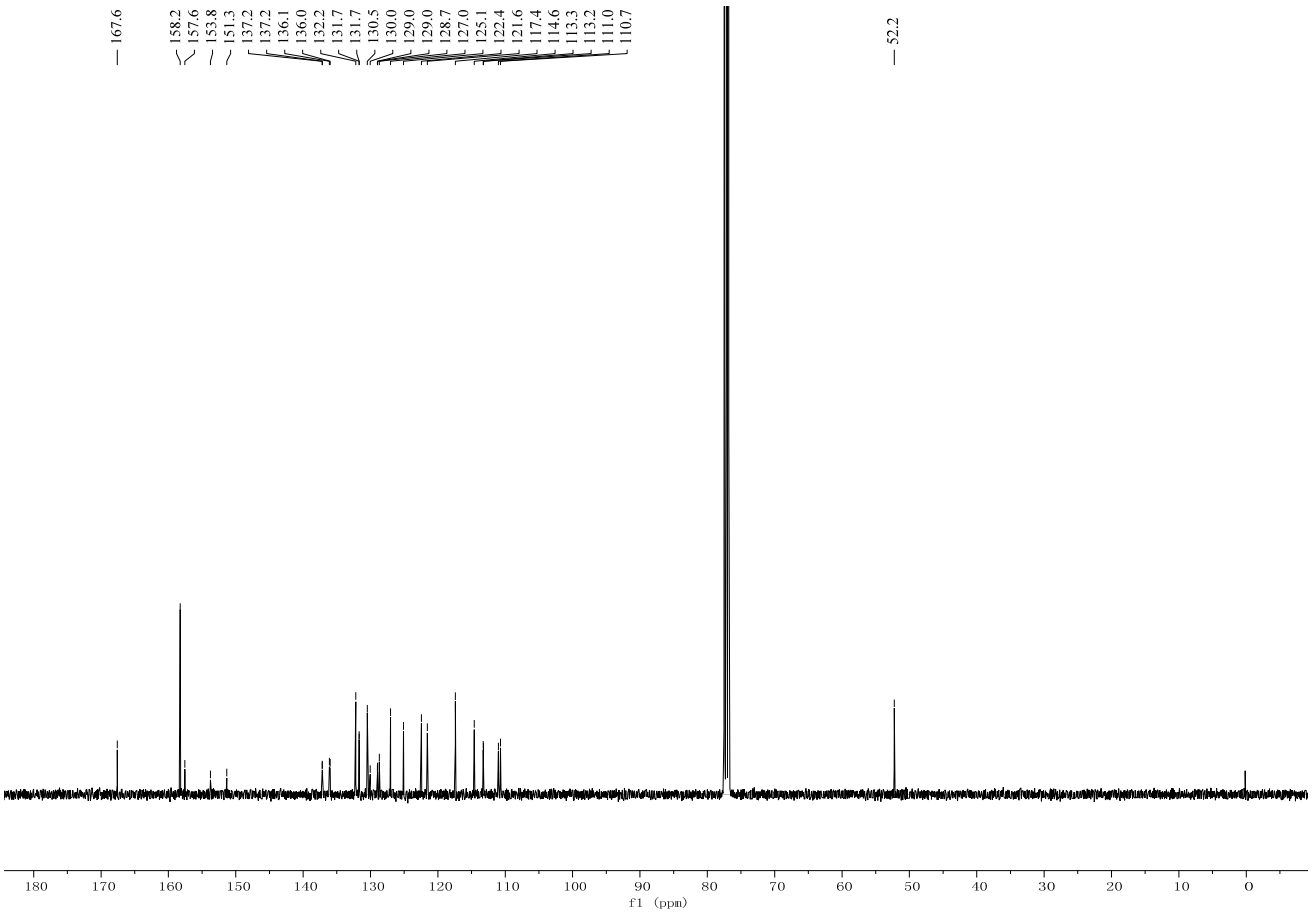

158.4
157.7
155.1
152.5
137.9
137.6
137.5
132.0
131.7
129.6
129.5
129.2
129.2
129.1
129.0
128.9
128.9
128.5
128.4
125.7
125.6
125.6
125.5
125.5
125.5
123.0
122.8
121.5
120.3
117.7
114.4
111.8
111.8
107.9
107.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

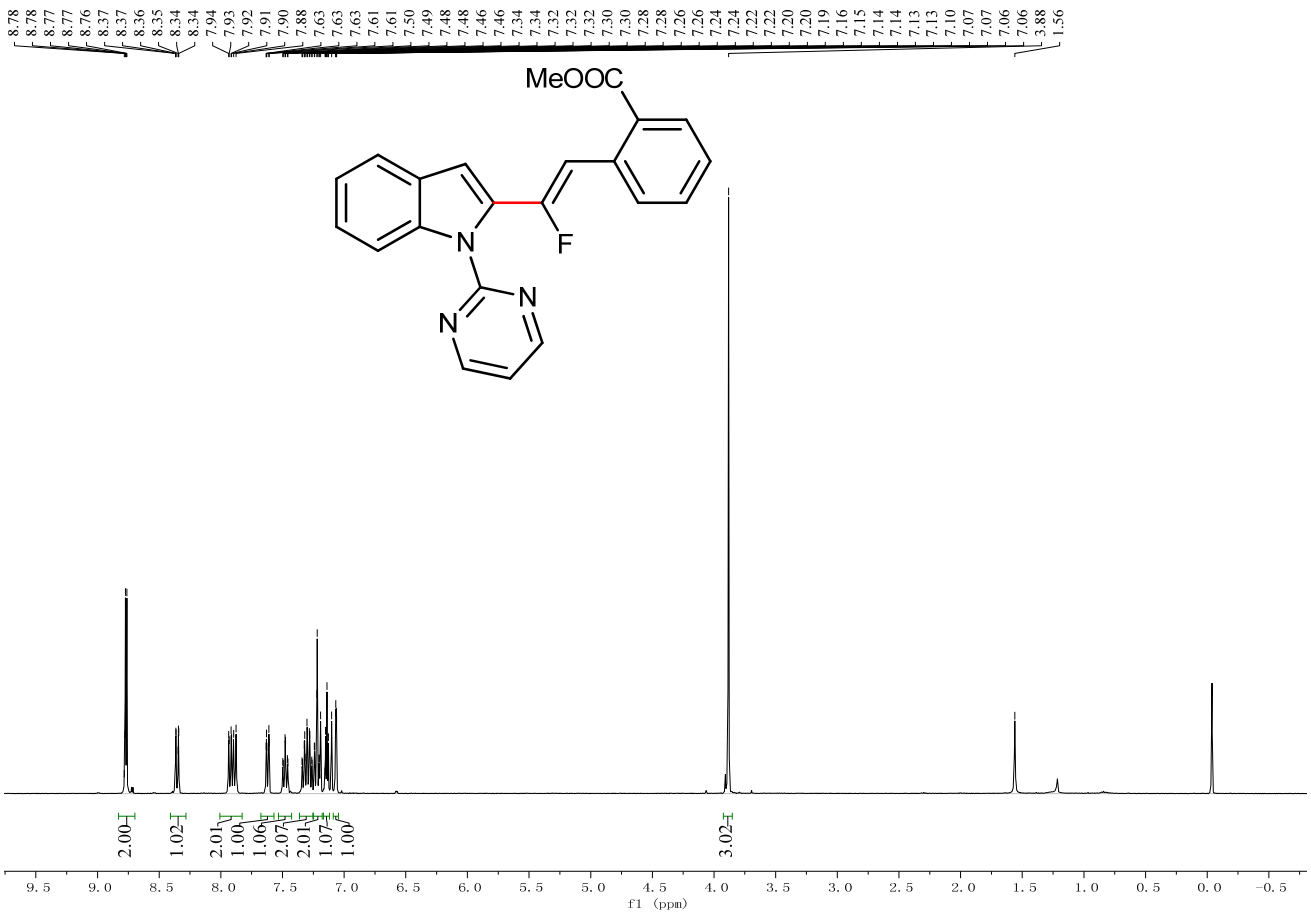

8.79
8.78
8.74
8.72
8.42
8.42
8.40
8.40
8.38
8.38
8.36
8.36
7.92
7.92
7.90
7.90
7.67
7.65
7.61
7.60
7.59
7.58
7.54
7.52
7.47
7.45
7.36
7.36
7.36
7.34
7.34
7.32
7.32
7.32
7.30
7.30
7.28
7.26
7.26
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.17
7.16
7.15
7.11
7.10
7.10
7.09
7.08
7.07
7.07
6.98
6.98
6.97
6.97
6.96
6.95
6.95
6.77
6.76
6.76
6.65
6.60
6.56
6.56
1.56
Br
F
N
N
N
2.03
1.02
6.27
3.23
1.00
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.
f1 (ppm)


158.4
158.2
157.7
157.4
154.6
154.3
152.2
151.7
137.9
137.3
137.2
134.8
134.6
133.6
133.5
133.0
132.3
132.2
132.0
131.1
131.1
130.6
130.5
129.8
129.5
128.7
128.7
128.6
128.6
127.5
127.4
125.3
125.3
124.2
124.1
123.8
123.8
122.7
122.5
121.6
121.6
121.5
117.7
117.4
114.7
114.3
113.0
112.9
111.7
111.7
110.8
110.5
107.6
107.5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

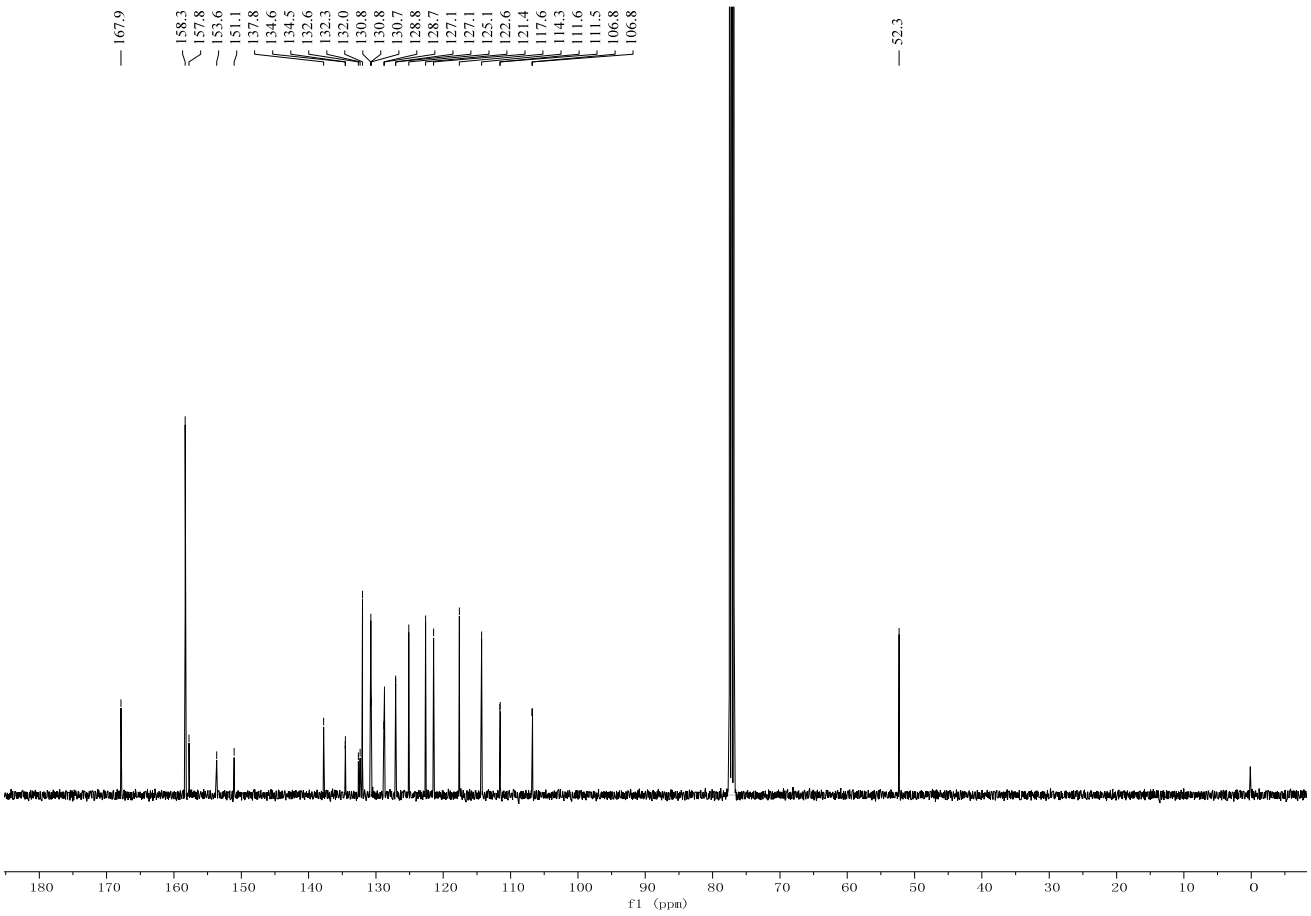

-92.4
-92.4
-92.4
-92.5
-100.6
-100.6
-100.7
-100.7
−87 −88 −89 −90 −91 −92 −93 −94 −95 −96 −97 −98 −99 −100 −101 −102 −103 −104
f1 (ppm)

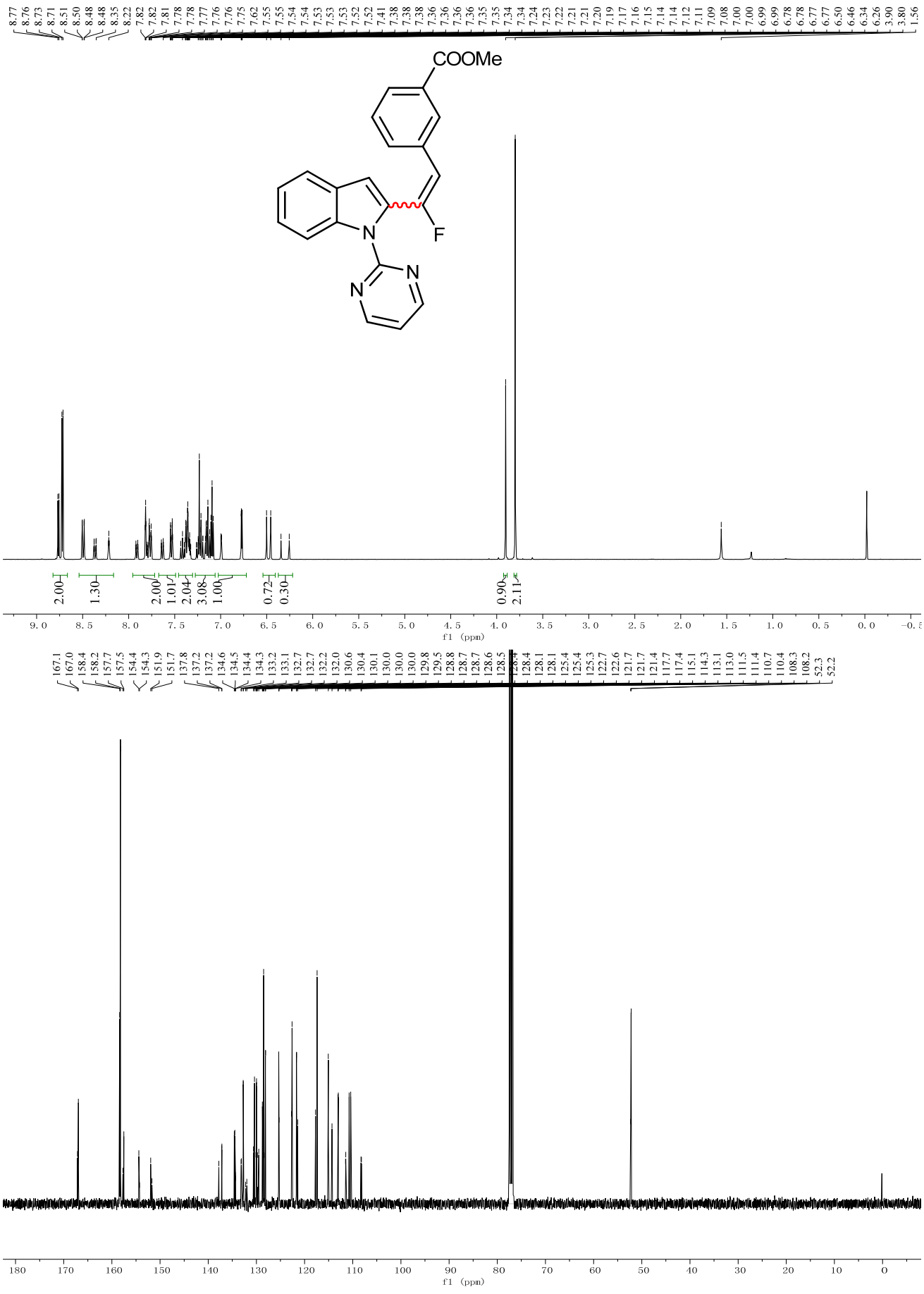

8.77
8.76
8.43
8.43
8.41
8.41
7.92
7.92
7.91
7.90
7.49
7.48
7.40
7.39
7.39
7.38
7.38
7.35
7.35
7.35
7.34
7.33
7.33
7.31
7.31
7.31
7.26
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.15
7.14
7.13
7.10
7.06
6.62
6.61
6.61
3.95
1.57
COOMe
F
N
N
N
2.03
1.05
1.06
1.02
1.01
1.09
3.04
1.15
1.04
1.00
3.08
f1 (ppm)

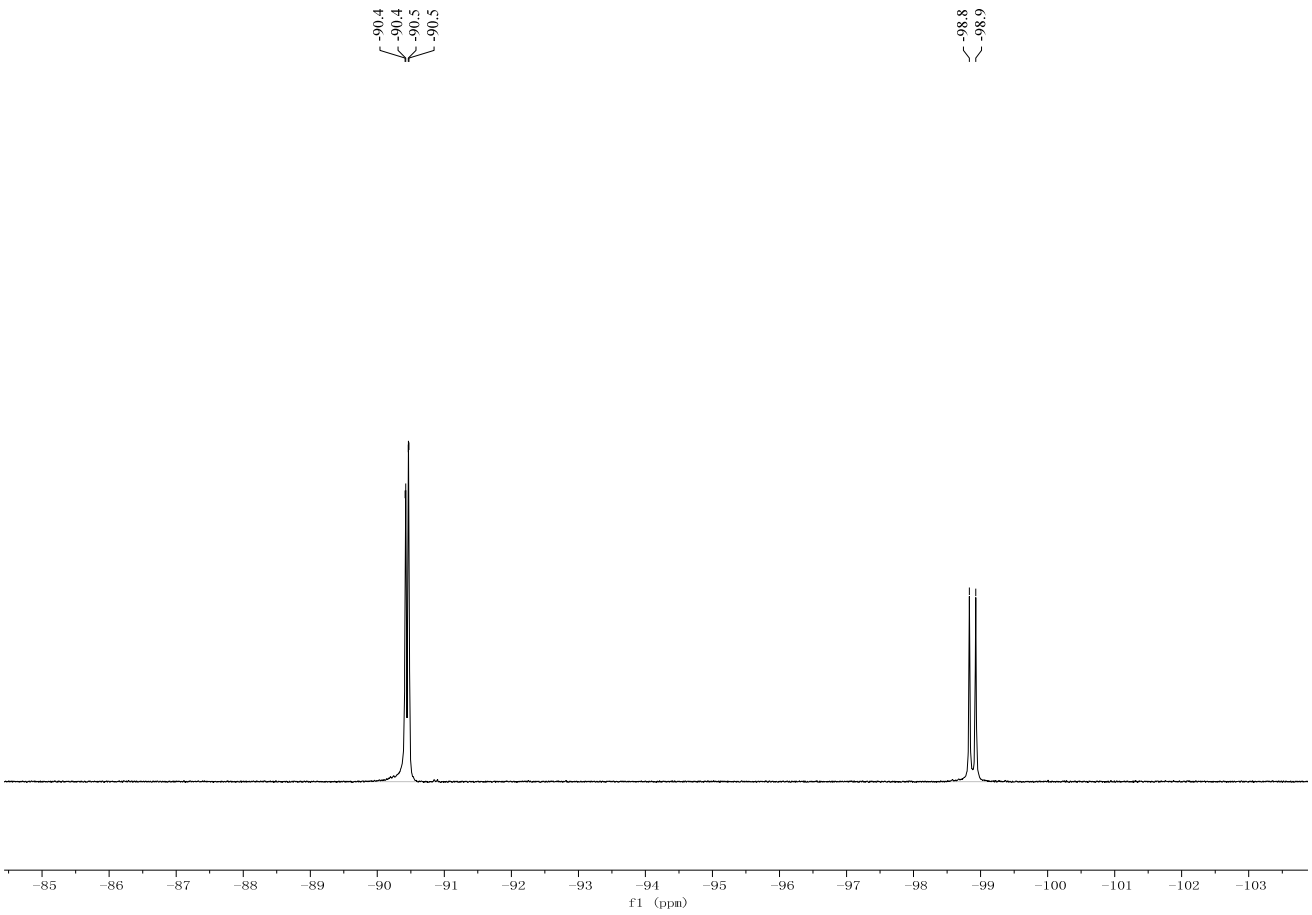

167.6
158.2
157.6
153.8
151.3
137.2
137.2
136.1
136.0
132.2
131.7
131.7
130.5
130.0
129.0
129.0
128.7
127.0
125.1
122.4
121.6
117.4
114.6
113.3
113.2
111.0
110.7
52.2
f1 (ppm)

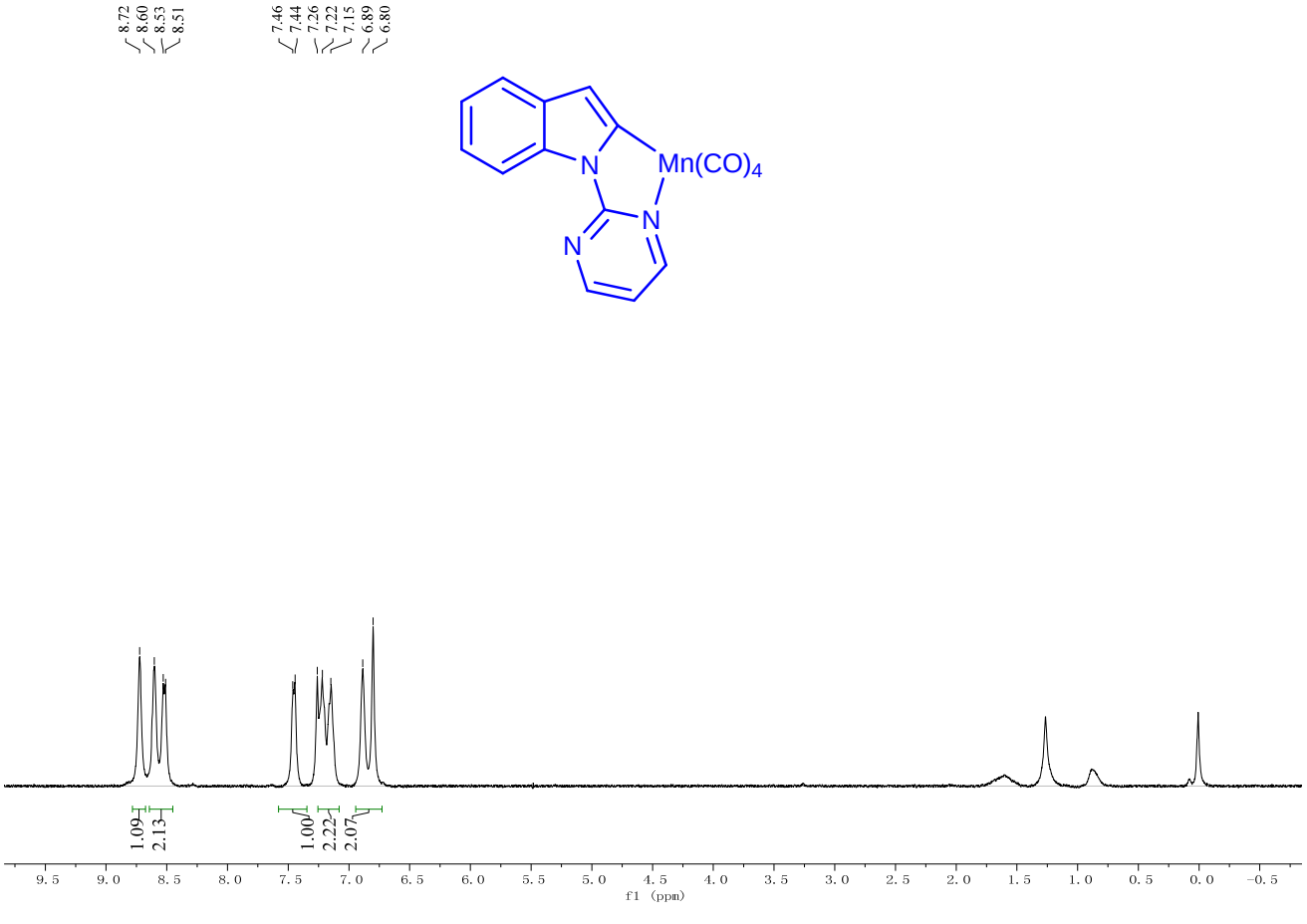

MeOOC
F
N
N
N

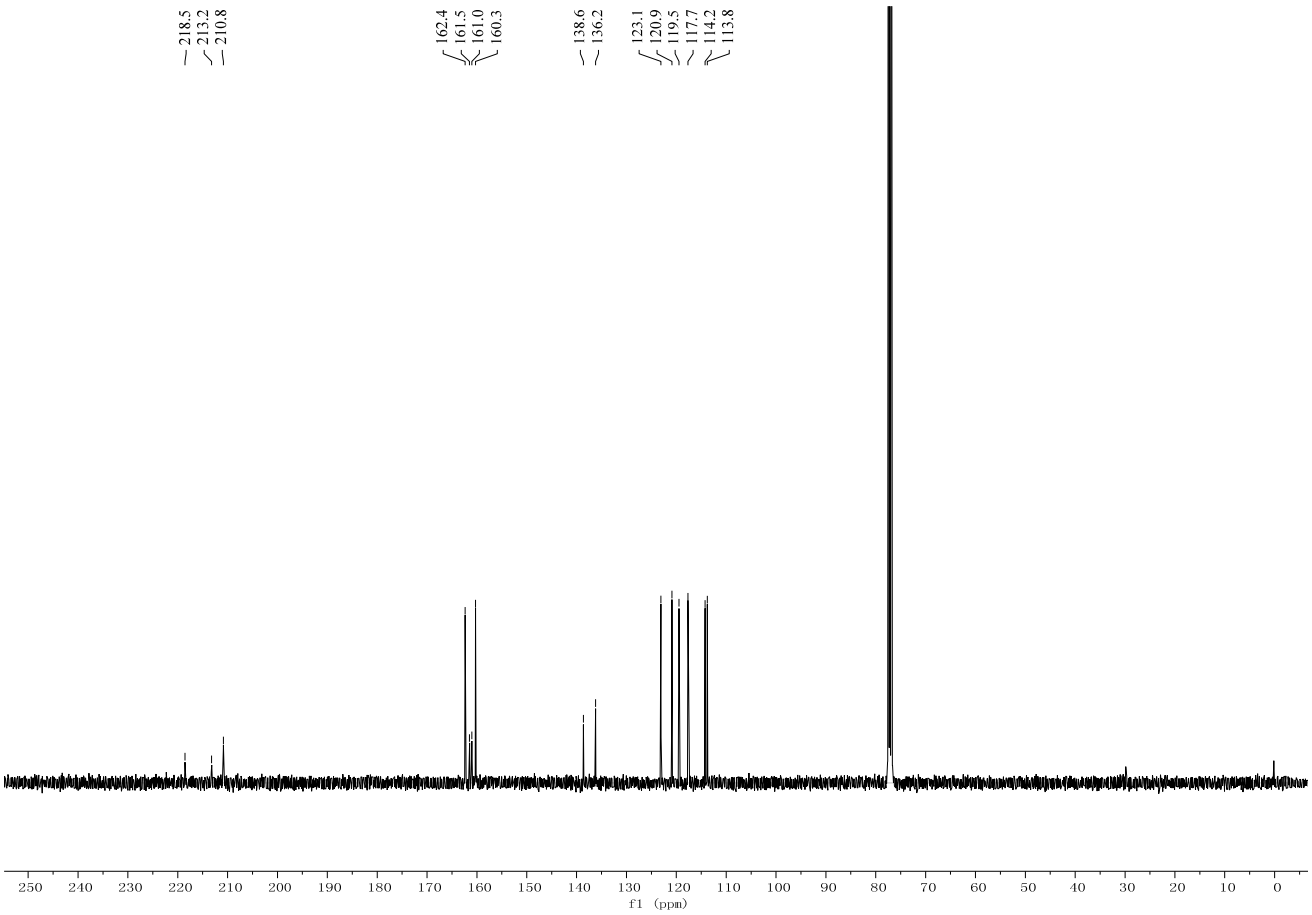
8.78 8.78 8.77 8.77 8.76 8.37 8.37 8.36 8.35 8.34 8.34 7.94 7.93 7.92 7.91 7.90 7.88 7.63 7.63 7.61 7.61 7.50 7.49 7.48 7.48 7.46 7.46 7.34 7.34 7.32 7.32 7.32 7.30 7.30 7.28 7.28 7.26 7.26 7.24 7.24 7.22 7.22 7.20 7.20 7.19 7.16 7.15 7.14 7.14 7.13 7.13 7.10 7.07 7.07 7.06 7.06 3.88 1.56
2.00 1.02 2.01 1.00 1.06 2.07 2.01 1.07 1.00 3.02
f1 (ppm)


167.9 158.3 157.8 153.6 151.1 137.8 134.6 134.5 132.6 132.3 132.0 130.8 130.8 130.7 128.8 128.7 127.1 127.1 125.1 122.6 121.4 117.6 114.3 111.6 111.5 106.8 106.8 52.3
f1 (ppm)


COOMe
F
N
N
N
f1 (ppm)
f1 (ppm)


-90.4
-90.4
-90.5
-90.5
-98.8
-98.9
−85 −86 −87 −88 −89 −90 −91 −92 −93 −94 −95 −96 −97 −98 −99 −100 −101 −102 −103
f1 (ppm)


8.72
8.60
8.53
8.51
7.46
7.44
7.26
7.22
7.15
6.89
6.80
Mn(CO)4
N
N
N
1.09
2.13
1.00
2.22
2.07
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)


218.5
213.2
210.8
162.4
161.5
161.0
160.3
138.6
136.2
123.1
120.9
119.5
117.7
114.2
113.8
f1 (ppm)
8.86
8.86
8.85
8.84
8.84
8.83
8.74
8.72
8.31
8.30
7.67
7.67
7.67
7.65
7.65
7.65
7.40
7.40
7.38
7.38
7.38
7.36
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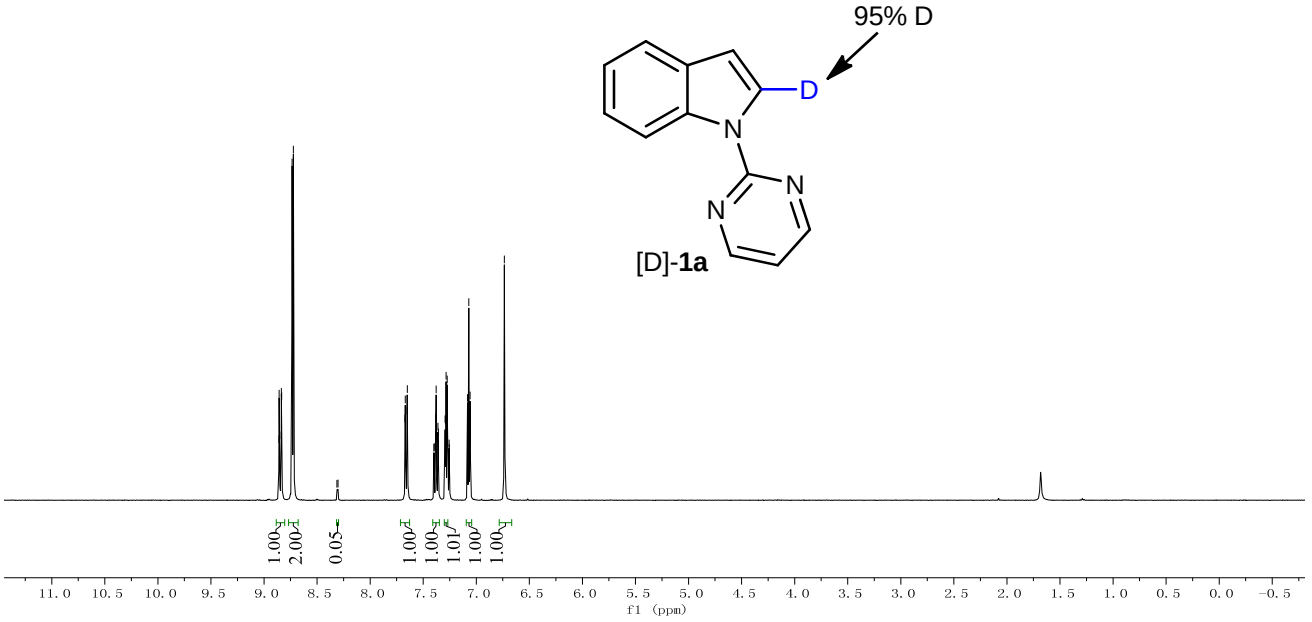
7.26
7.25
7.08
7.07
7.06
6.73


95% D
D
N
N
N
[D]-1a
1.00
2.00
0.05
1.00
1.00
1.01
1.00
1.00
f1 (ppm)