Selective Single C−F Bond Arylation of Trifluoromethylalkene Derivatives

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General Information

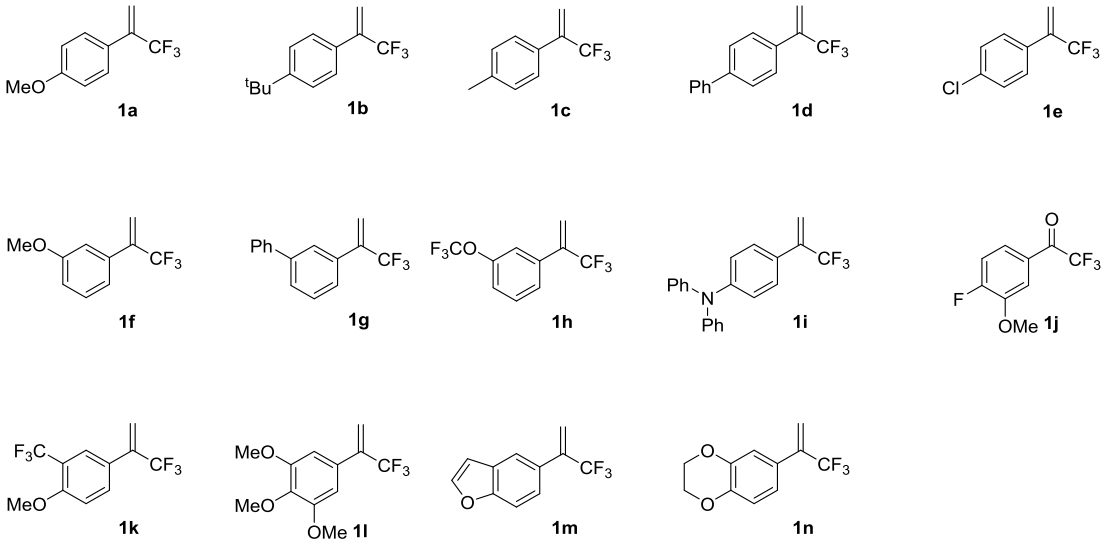
$Pd(PPh_3)_4$ was purchased from Chemical Service and used as received. Cs_2CO_3, K_2CO_3, anhydrous 1,4-dioxane, Et_2O, $CuBr{\cdot}Me_2S$, $P(4\text{-}CF_3Ph)_3$, C^nBuLi, MeOTf, hexahydroazine, phenylboronic acid, (4-methoxyphenyl)boronic acid, (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)boronic acid, naphthalen-2-ylboronic acid, (9-phenyl-9H-carbazol-3-yl)boronic acid, cyclohex-1-en-1-ylboronic acid, benzofuran-5-ylboronic acid *et al*. were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were carried out under air without extra protection unless otherwise noted. Reactions were monitored by thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate as stain. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q–TOF Permier Spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ^1H 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 7.26, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplet) and *etc*.

Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) 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 77.00, triplet).

Experimental Section

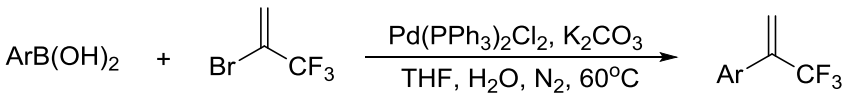
Substrate synthesis

Trifluoromethylalkenes 1 examined:



Trifluoromethylalkenes 1 were prepared according to the reported methods[1].

General reaction scheme for 1 synthesis:



Synthetic procedure:

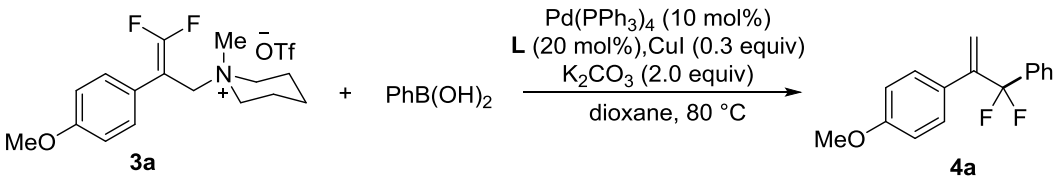
To a Schlenk tube equipped with a magnetic stir bar were added aqueous K_2CO_3 (2.0 M, 40 mL), THF (60 mL), arylboronic acid (20 mmol), 2-bromo-3,3,3-trifluoropropene (7.00 g, 40 mmol) and $PdCl_2(PPh_3)_2$ (0.14 g,

0.2 mmol). The resulting solution was stirred at 60 ℃ for 24 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3×20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

Optimization of reaction conditions

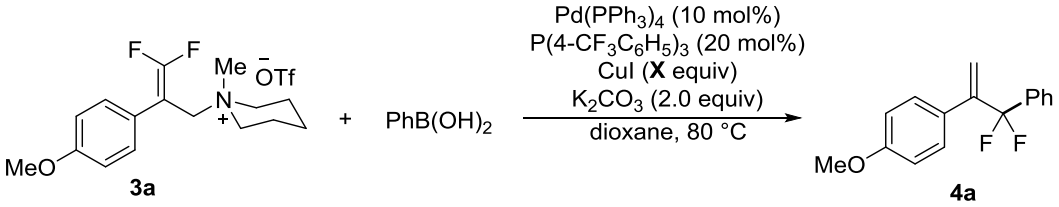
To a Schlenk tube equipped with a magnetic stir bar were added base, Pd salt, ligand, Cu salt, 5Å molecular sieve, phenylboronic acid (2 equiv), **3a** (1 equiv) and 1,4-dioxane. The resulting solution was stirred at 80 ℃ for 20 h. After the reaction mixture was cooled to room temperature, the yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc. The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography to give the pure **4a**.

Table S1. Screening of ligand.



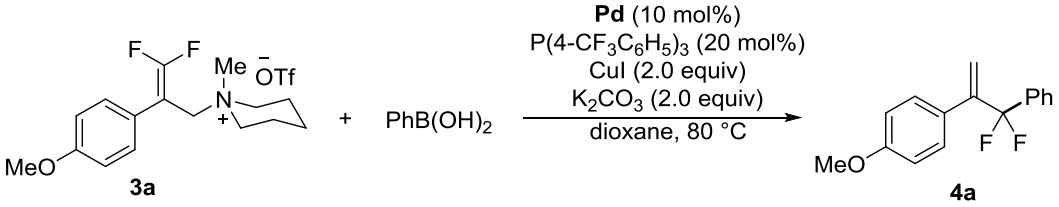
entry	ligand	yield (%)
1	X-Phos	41
2	$P(4\text{-}CF_3C_6H_5)_3$	50
3	$P(C_6F_5)_3$	39
4	Cphos	32
5	TTMPP	46

Table S2. Screening of the stoichiometry of CuI.



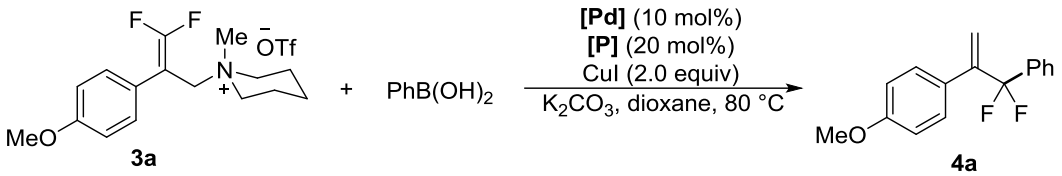
entry	CuI (X equiv)	yield (%)
1	0	trace
2	0.1	5
3	0.3	50
4	0.5	56
5	1.0	72
6	2.0	80
7	2.5	80
8	3.0	80

Table S3. Screening of Pd species.



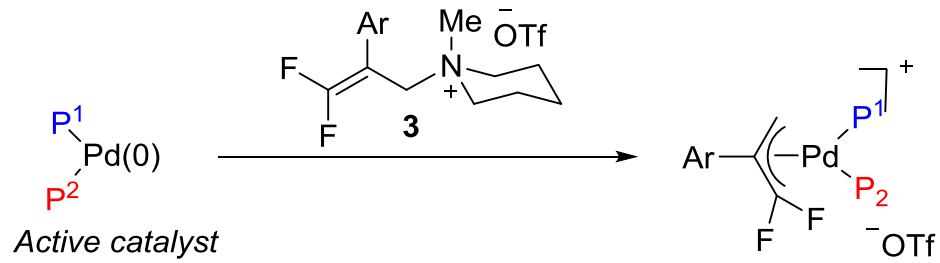
entry	Pd	yield (%)
1	$Pd_2(dba)_3$	68
2	$Pd(PPh_3)_2Cl_2$	64
3	$PdCl_2$	11
4	$Pd(TFA)_2$	33
5	$Pd[(t\text{-}Bu)_3P]_2$	60
6	$[Pd(allyl)Cl]_2$	49

Table S4. Screening of Pd species and assisting ligand.



entry	[Pd]	[P]	yield (%)
1	$Pd(PPh_3)_4$	$P(4\text{-}CF_3C_6H_5)_3$	80
2	$Pd(PPh_3)_4$	-	72
3	$Pd_2(dba)_3$	$P(4\text{-}CF_3C_6H_5)_3$	68
4	$Pd_2(dba)_3$	PPh_3	60
5	$Pd_2(dba)_3$	X-phos	26
6	$Pd_2(dba)_3$	Cphos	26
7	$Pd_2(dba)_3$	TTMPP	74
8	$Pd_2(dba)_3$	Xantphos	trace
9	$Pd_2(dba)_3$	PPh_3(10 mol%) + $P(4\text{-}CF_3C_6H_5)_3$(10 mol%)	79

We have examined the Pd source and ancillary ligands. From these results, we could clearly see that the combination of $Pd_2(dba)_3$ 5 mol% ([Pd] 10 mol%) and PPh_3 10 mol%, $(4\text{-}CF_3C_6H_5)_3$ 10 mol% led to the formation of desired product **4a** in a yield that is equal to the optimal catalyst composition ($Pd(PPh_3)_4$ 10 mol%, $(4\text{-}CF_3C_6H_5)_3$ 20 mol%), whereas the employment of other type of tertiary phosphines as the single assisting ligands was revealed to be inferior. Therefore, it is quite reasonable to inferring the active catalyst in the optimal conditions is a heteroleptic diphosphine Pd(0) complex {$Pd(PPh_3)(4\text{-}CF_3C_6H_5)$}.

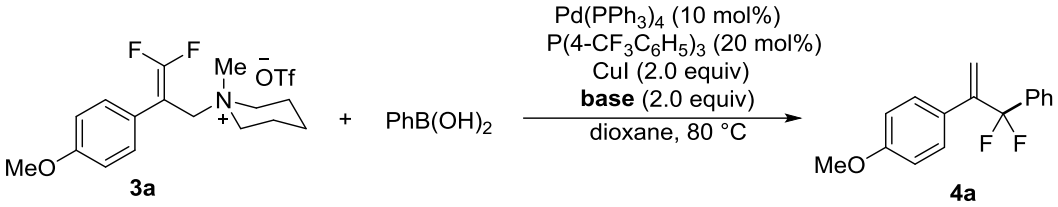


Active catalyst

Heteroleptic diphosphine Pd(0) complex

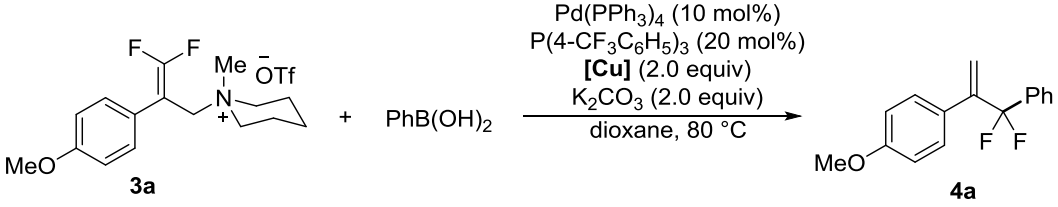
$P^1 = PPh_3$, $P^2 = P(4\text{-}CF_3C_6H_5)_3$

Table S5. Screening of base.



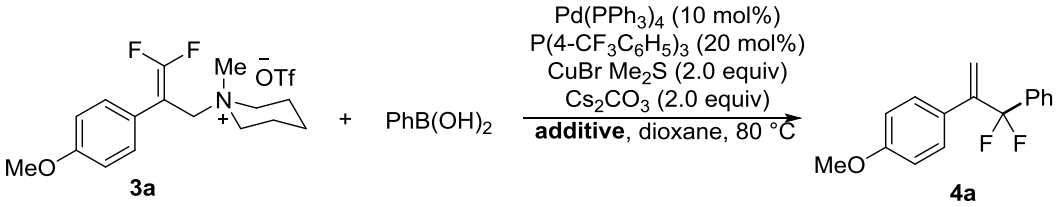
entry	Pd	yield (%)
1	Cs_2CO_3	83
2	NaO*t*-Bu	47
3	KH_2PO_4	30
4	$NaHCO_3$	58
5	Na_2CO_3	78
6	NaOH	55
7	CH_3OK	32
8	NaOEt	55
9	NaH	76

Table S6. Screening of Cu salt.



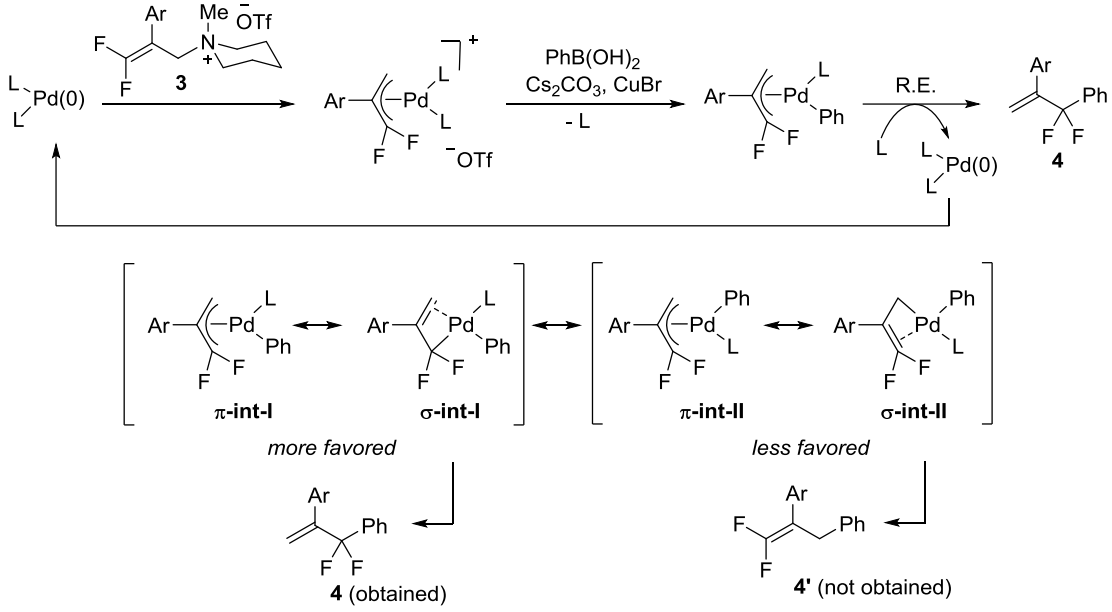
entry	[Cu]	yield (%)
1	$Cu(MeCN)_4PF_6$	56
2	$Cu(MeCN)_4BF_4$	58
3	Cu_2O	trace
4	CuCNS	trace
5	$CuBr{\cdot}Me_2S$	85
6	CuTc	31
7	CuBr	53
8	CuCl	61
9	CuOAc	29
10	CuCN	48

Table S7. Screening of additive.



entry	additive	yield (%)
1	3Å (100 mg)	92
2	4Å (100 mg)	77
3	5Å (100 mg)	99
4	H_2O (20 μL)	trace
5	1-methyl-piperidin (2 eq.)	70

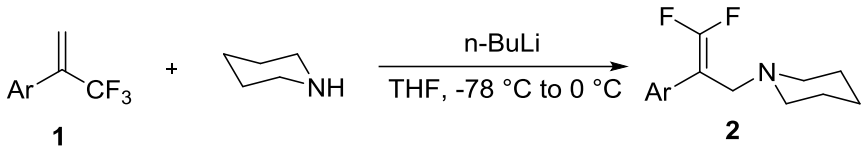
Proposed reaction mechanism.



The reaction mechanism of the final step is similar with the work of Zhang (*J. Am. Chem. Soc.* 2014, 136, 1230), however, the exact reason for the high selectivity with respect to reductive elimination of allyl aryl palladium complex is not very clear at this stage. We surmise that the larger trans-effect of phosphine ligand than that of phenyl substituent would make the

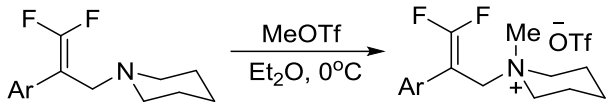
π-int-I and σ-int-I relative more stable compared with π-int-II and σ-int-II. Therefore, the reductive elimination from σ-int-I would guarantee the selective formation of the desired product.

General procedure for the reaction



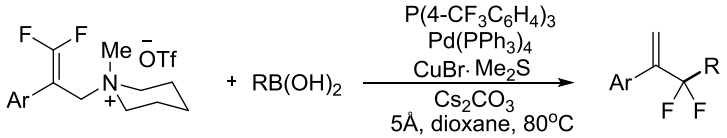
Experiment procedure A[2]**:** In a flame-dried flask equipped with a stirbar, rubber septum, and N_2 inlet needle were added piperidine (0.4888 g, 5.75 mol, 1.15 equiv) and anhydrous THF (50 mL, 0.10 M in the olefin). The flask was cooled to −78 °C via a dry ice/acetone bath and, after cooling for 10 min, a 2.5 M solution of n-BuLi (2.3 mL, 5.75 mmol, 1.15 equiv) in hexanes was added dropwise to the flask over 5 min. The solution was stirred at −78 °C for 1 h and gradually became cloudy and white. After this time, **1** (5 mmol, 1 equiv) was added to the flask dropwise over 5 min. The solution was stirred at −78 °C for 1 h and after this time was warmed to 0 °C in an ice−water bath. The solution was stirred at 0 °C for 1 h and then was poured into a separatory funnel containing saturated aqueous NH_4Cl (~100 mL). The biphasic mixture was diluted with EtOAc (~50mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers were washed with deionized water (~50 mL), followed by brine (~75 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced

pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.



2 **3**

Experiment procedure B: To a Schlenk tube equipped with a magnetic stir bar were added **2** (3 mmol 1 equiv) and Et_2O (3 ml). The flask was cooled to 0 °C via an ice−water bath, after cooling for 5 min, the MeOTf (0.6396 g, 3.9 mmol, 1.3 equiv) was added dropwise to the flask over 5 min. The solution was stirred at 0 °C for 30 min and gradually became cloudy and white. The solution was filtrated and washed with Et_2O (3 × 10 mL). The pure products **3** were got.

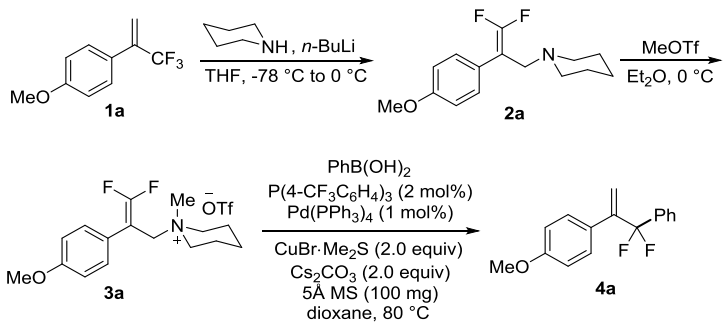


3 **4**

Experiment procedure C: To a Schlenk tube equipped with a magnetic stir bar were added aqueous Cs_2CO_3 (65.2 mg, 2 equiv), $Pd(PPh_3)_4$ (1.2 mg, 1 mol%), $P(4\text{-}CF_3C_6H_4)_3$ (0.9 mg, 2 mol%), $CuBr{\cdot}Me_2S$ (41.2 mg, 2 equiv), 5Å molecular sieve (100 mg), arylboronic acid (0.2 mmol, 2 equiv), **3** (0.1 mmol, 1 equiv) and1,4-dioxane (1mL). The resulting solution was stirred at 80 ℃ for 20 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3×20 mL). The combined organic

layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

Gram-scale reaction



Experiment procedure: 1) In a flame-dried flask equipped with a stirbar, rubber septum, and N_2 inlet needle were added piperidine (1.955 g, 23 mol, 1.15 equiv) and anhydrous THF (100 mL, 0.2 M in the olefin). The flask was cooled to −78 °C via a dry ice/acetone bath and, after cooling for 10 min, a 2.5 M solution of n-BuLi (9.2 mL, 23 mmol, 1.15 equiv) in hexanes was added dropwise to the flask over 5 min. The solution was stirred at −78 °C for 1 h and gradually became cloudy and white. After this time, **1a** (20 mmol, 1 equiv) was added to the flask dropwise over 5 min. The solution was stirred at −78 °C for 1 h and after this time was warmed to 0 °C in an ice−water bath. The solution was stirred at 0 °C for 1 h and then was poured into a separatory funnel containing saturated aqueous NH_4Cl (~200 mL). The biphasic mixture was diluted with EtOAc (~100 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3

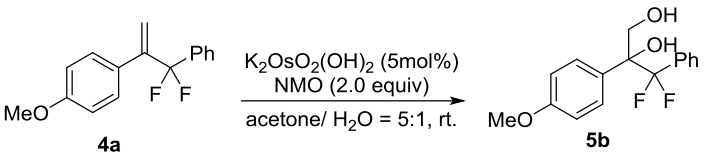
× 50 mL) and the combined organic layers were washed with deionized water (~100 mL), followed by brine (~150 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography to give the pure **2a** (3.204 g, 60% yield)

2) To a Schlenk tube equipped with a magnetic stir bar were added **2a** (12 mmol 1 equiv) and Et_2O (12 ml). The flask was cooled to 0 °C via an ice−water bath, after cooling for 5 min, the MeOTf (2.558 g, 15.6 mmol, 1.3 equiv) was added dropwise to the flask over 5 min. The solution was stirred at 0 °C for 30 min and gradually became cloudy and white. The solution was filtrated and washed with Et_2O (3 × 50 mL). The pure products **3a** were got in 99% yield (5.126 g).

3) To a Schlenk tube equipped with a magnetic stir bar were added aqueous Cs_2CO_3 (7.824 g, 24 mmol, 2 equiv), $Pd(PPh_3)_4$ (0.139g, 0.12 mmol, 1 mol%), $P(4\text{-}CF_3C_6H_4)_3$ (12.000 g, 0.24 mmol, 2 mol%), $CuBr{\cdot}Me_2S$ (4.944 g, 24 mmol, 2 equiv), 5Å molecular sieve (1.200 g), phenylboronic acid (2.928 g, 24 mmol, 2 equiv), **3a** (11.9 mmol, 1 equiv) and1,4-dioxane (120 mL). The resulting solution was stirred at 80 ℃ for 20 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3×100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product

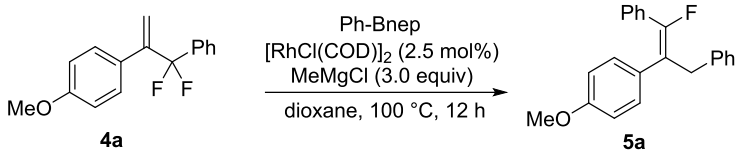
material was purified by flash chromatography to give the pure **4a** (2.869 g, 93% yield).

Synthetic transformation of *gem*-difluoroallylarene 4a



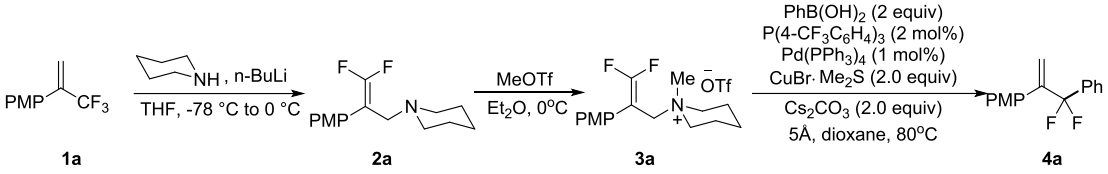
Experiment procedure E: In a 10 mL one-neck round-bottom flask were added **4a** (26.0 mg, 0.1 mmol, 1 equiv), acetone (1 mL), and deionized water (0.2 mL). The flask was cooled to 0 °C in an ice bath. After cooling for 10 min, 50% w/w NMO in H_2O (46.8 mg, 0.2 mmol, 2 equiv) was added to the flask followed by $K_2Os_2(OH)_2$ (Caution! Toxic!) (8.8 mg, 0.01 mmol, 0.1 equiv). Five minutes after this addition, the ice bath was removed and the solution was stirred at room temperature overnight. After 24 h, the reaction appeared to have stalled and an additional loading of NMO (46.8 g, 0.2 mmol, 2 equiv) and $K_2Os_2(OH)_2$ (8.8 mg, 0.01 mmol, 0.1 equiv) was added. The reaction mixture was stirred for an additional 24 h and after this time was judged to be complete. The solution was transferred to a separatory funnel and diluted with deionized water (~100 mL) and EtOAc (~10 mL). The phases were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (~15 mL) and dried with Na_2SO_4. The solvent was removed in vacuo to give the crude diol as a thick, dark brown oil. The resultant crude product material was purified by flash chromatography to

give pure product **5b** (48% yield).



Experiment procedure D: To a Schlenk tube equipped with a magnetic stir bar were added **4a** (26.0 mg, 0.1 mmol, 1 equiv), Ph-Bnep (57.0 mg, 0.3 mmol, 3 equiv), $[RhCl(COD)]_2$ (1.2 Mg, 0.025 mmol, 2.5 mol%), MeMgCl (0.3 mL, 0.3 mmol, 3 equiv) and1,4-dioxane (1 mL). The resulting solution was stirred at 100 ℃ for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography to give the pure **5b** (15.7g, 48% yield).

Synthesis of 4a by one-pot reaction



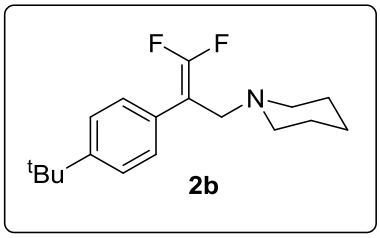
Experiment procedure: n a flame-dried flask equipped with a stirbar, rubber septum, and N_2 inlet needle were added piperidine (97.8 mg, 1.15 mol, 1.15 equiv) and anhydrous THF (10 mL, 0.2 M in the olefin). The flask was cooled to −78 °C via a dry ice/acetone bath and, after cooling for 10 min, a 2.5 M solution of n-BuLi (0.46 mL, 1.15 mmol, 1.15 equiv) in hexanes was added dropwise to the flask over 5 min. The solution was

stirred at −78 °C for 1 h and gradually became cloudy and white. After this time, **1a** (202.0 mg,1 mmol, 1 equiv) was added to the flask dropwise over 5 min. The solution was stirred at −78 °C for 1 h and after this time was warmed to 0 °C in an ice−water bath. The solution was stirred at 0 °C for 1 h and then was poured into a separatory funnel containing saturated aqueous NH_4Cl (∼20 mL). The biphasic mixture was diluted with EtOAc (∼10 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with deionized water (∼10 mL), followed by brine (∼15 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. 2) To a Schlenk tube equipped with a magnetic stir bar were added crud product **2a** (1 equiv) and Et_2O (1 ml). The flask was cooled to 0 °C via an ice−water bath, after cooling for 5 min, the MeOTf (213.2 mg, 1.3 mmol, 1.3 equiv) was added dropwise to the flask over 5 min. The solution was stirred at 0 °C for 30 min and gradually became cloudy and white. The solution was removed under reduced pressure. 3) To a Schlenk tube equipped with a magnetic stir bar were added aqueous Cs_2CO_3 (652.0 mg, 2 mmol, 2 equiv), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 1 mol%), $P(4\text{-}CF_3C_6H_4)_3$ (11.2 mg, 0.024 mmol, 2 mol%), $CuBr{\cdot}Me_2S$ (412.0 mg, 2 mmol, 2 equiv), 5Å molecular sieve (1.000 g), phenylboronic acid (244.0 mg, 2 mmol, 2 equiv), **3a** (1 equiv) and1,4-dioxane (10 mL). The resulting solution was stirred at 80 ℃ for 20 h. After the reaction mixture

was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3×100 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography to give the pure **4a** (110.0 mg, 42% yield).

Characterization of structurally novel compounds

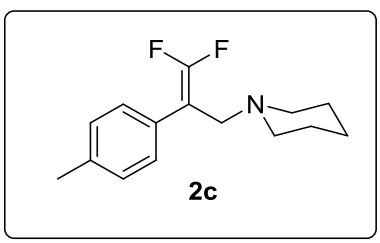
1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene



Following the experiment procedure **A**, **2b** was obtained in 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 1.6 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 3.24 (dd, *J* = 1.8, 3.0 Hz, 2H), 2.40 (s, 4H), 1.58-1.52 (m, 4H), 1.44-1.39 (m, 2H), 1.33 (s, 9H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.76 (d, *J* = 36.50 Hz, 1F), -88.92 (d, *J* = 36.77 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.5, 26.1, 31.4, 34.6, 54.1, 56.3, 89.4 (dd, *J* = 11.8, 17.9 Hz), 125.3, 128.1, 131.3, 150.1, 155.3(dd, *J* = 288.1, 291.8 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 294.2033, found: 294.2033.

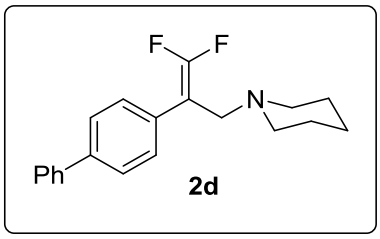
1-(3,3-difluoro-2-(p-tolyl)allyl)piperidine



Following the experiment procedure **A**, **2c** was obtained in 59% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 6.9 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.26 (dd, *J* = 1.7, 3.0 Hz, 2H), 2.39 (s, 4H), 2.36 (s, 3 H), 1.57-1.51 (m, 4H), 1.43-1.38 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.18 (d, *J* = 37.71 Hz, 1F), -89.40 (d, *J* = 37.71 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.2, 24.3, 26.0, 54.0, 56.2 (d, *J* = 3.7 Hz), 89.5 (dd, *J* = 11.7, 18.3 Hz), 128.2 (t, *J* = 3.5 Hz), 129.0, 131.2 (t, *J* = 3.3 Hz), 136.9, 155.1(dd, *J* = 287.4, 291.0 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 252.1564, found: 252.1563.

4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl

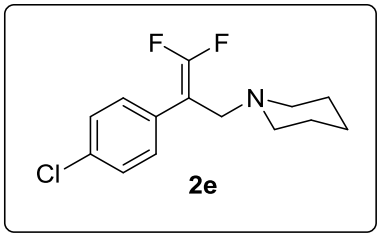


2d

Following the experiment procedure **A**, **2d** was obtained in 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.59 (m, 6 H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.0 Hz, 2H), 3.30-3.29 (m, 2H), 2.42 (s, 4H), 2.36 (s, 3 H), 1.58-1.53 (m, 4H), 1.45-1.39 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.14 (d, *J* = 35.32 Hz, 1F), -88.29 (d, *J* = 35.87 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.4, 26.0, 54.0, 56.1 (d, *J* = 3.6 Hz), 89.4 (dd, *J* = 11.8, 18.0 Hz), 126.9, 127.0, 127.3, 128.7 (t, *J* = 3.4 Hz), 128.8, 133.2 (t, *J* = 2.9 Hz), 139.9, 140.7, 155.3 (dd, *J* = 288.2, 291.4 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 314.1720, found: 314.1718.

1-(2-(4-chlorophenyl)-3,3-difluoroallyl)piperidine

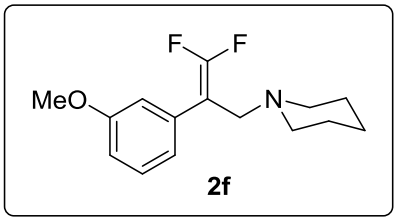


2e

Following the experiment procedure **A**, **2e** was obtained in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 1.3, 8.5 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 3.22 (dd, *J* = 1.7, 3.2 Hz, 2H), 2.38 (s, 4H), 1.56-1.51 (m, 4H), 1.44-1.39 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.96 (d, *J* = 35.04 Hz, 1F), -88.30 (d, *J* = 35.50 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 26.0, 54.0, 56.0 (d, *J* = 3.6 Hz), 89.0 (dd, *J* = 11.0, 19.1 Hz), 128.4, 129.7 (t, *J* = 3.5 Hz), 132.6 (t, *J* = 3.6 Hz), 133.0, 155.1 (dd, *J* = 288.1, 291.9 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 272.1018, found: 272.1016.

1-(3,3-difluoro-2-(3-methoxyphenyl)allyl)piperidine



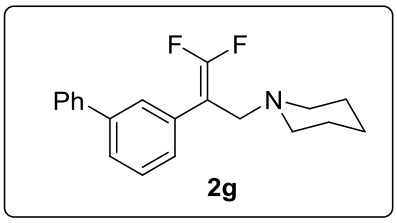
2f

Following the experiment procedure **A**, **2f** was obtained in 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 8.0 Hz, 1H), 7.16 (s, 2H), 7.07 (dd, *J* = 1.4, 7.9 Hz, 1H), 6.81 (dd, *J* = 1.7, 8.2 Hz, 1H), 3.81 (s, 3H), 3.24 (dd, *J* = 1.7, 3.1 Hz, 2H), 2.39 (s, 4H), 1.56-1.51 (m, 4H), 1.43-1.37 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.11 (d, *J* = 35.57 Hz, 1F), -

88.69 (d, J = 35.55 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 26.0, 53.9, 55.2, 56.2 (d, J = 4.1 Hz), 89.6 (dd, J = 10.9, 19.0 Hz), 122.7, 114.2 (t, J = 3.5 Hz), 120.8 (t, J = 3.0 Hz), 129.1, 135.7 (t, J = 3.6 Hz), 155.2 (dd, J = 287.4, 291.9 Hz), 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 268.1513, found: 268.1514.

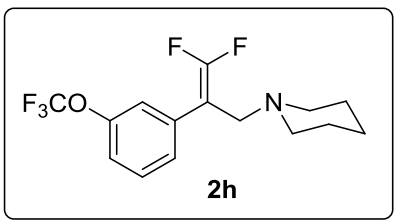
1-(2-([1,1'-biphenyl]-3-yl)-3,3-difluoroallyl)piperidine



2g

Following the experiment procedure **A**, **2g** was obtained in 53% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (s, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.16 (s, 2H), 7.51-7.41 (m, 5H), 7.37 (q, J = 7.1, 14.6 Hz, 1H), 3.30 (s, 2H), 2.42 (s, 4H), 1.57-1.52 (m, 4H), 1.47-1.38 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.36 (d, J = 35.81 Hz, 1F), -88.70 (d, J = 36.53 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 26.0, 54.0, 56.2 (d, J = 4.2 Hz), 89.7 (dd, J = 8.7, 17.2 Hz), 126.0, 127.2, 127.3 (t, J = 3.4 Hz), 128.6, 128.8, 134.5, 134.7, 141.1, 155.3 (dd, J = 287.3, 291.8 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 314.1720, found: 314.1722.

1-(3,3-difluoro-2-(3-(trifluoromethoxy)phenyl)allyl)piperidine

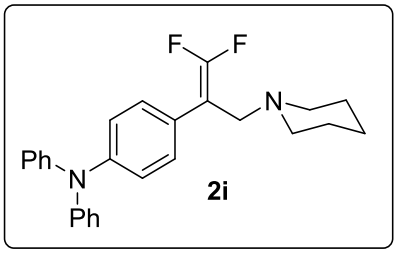


2h

Following the experiment procedure **A**, **2h** was obtained in 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.45 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.11 (dt, *J* = 1.0, 8.0 Hz, 1H), 3.22 (dd, J = 1.7, 2.9 Hz, 2H), 2.40 (s, 4H), 1.58-1.52 (m, 4H), 1.45-1.40 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -57.82, -87.12 (d, *J* = 32.72 Hz, 1F), -87.64 (d, *J* = 30.42 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 25.9, 53.9, 56.0 (d, *J* = 3.9 Hz), 88.9 (dd, *J* = 10.7, 19.8 Hz), 119.5, 120.5 (q, J = 255.4, 511.2 Hz), 121.0 (t, *J* = 3.7 Hz), 126.7 (q, *J* = 2.7, 4.4 Hz), 129.4, 136.2 (t, *J* = 3.9 Hz), 149.2, 155.3 (dd, *J* = 288.3, 292.8 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 322.1230, found: 322.1223.

4-(1,1-difluoro-3-(piperidin-1-yl)prop-1-en-2-yl)-N,N-diphenylaniline



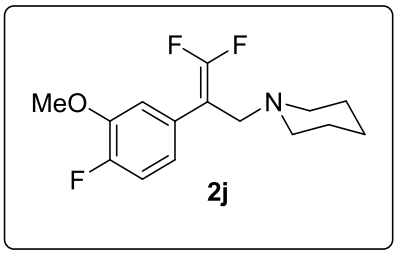
2i

Following the experiment procedure **A**, **2i** was obtained in 64% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 4H), 7.16 (d, *J* = 7.6 Hz, 4H), 7.09-7.04 (m, 4H), 3.27 (s, 2H), 2.46 (s, 4H), 1.63-1.57 (m, 4H), 1.49-1.44 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.55 (d, *J* = 37.61 Hz, 1F), -88.96 (d, *J* = 37.15 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.4, 26.1, 54.1, 56.3 (d, *J* = 3.9 Hz), 89.2 (dd, *J* = 11.1, 18.5 Hz), 123.0, 123.1, 124.6, 128.0 (t, *J* = 3.5 Hz), 129.1, (*J* = 3.5 Hz), 129.3, 146.7, 147.7, 155.2 (dd, *J* = 287.2, 291.8 Hz) ppm;

HRMS (ESI, m/z): calculated for $[M+H]^+$: 405.2142, found: 405.2137.

1-(3,3-difluoro-2-(4-fluoro-3-methoxyphenyl)allyl)piperidine

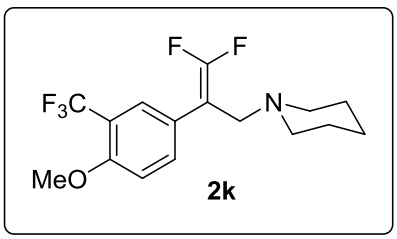


2j

Following the experiment procedure **A**, **2j** was obtained in 68% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 3.88 (s, 3H), 3.19 (dd, *J* = 1.6, 3.1 Hz, 2H), 2.41 (s, 4H), 1.58-1.53 (m, 4H), 1.46-1.40 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.49 (d, *J* = 37.06 Hz, 1F), -89.34 (d, *J* = 36.46 Hz, 1F), 136.93 (dd, *J* = 8.22, 15.89 Hz) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 26.1, 53.9, 56.0, 56.4 (d, *J* = 4.1 Hz), 89.0 (dd, *J* = 11.4, 19.4 Hz), 113.9 (q, *J* = 2.6, 4.7 Hz), 115.5 (d, *J* = 18.2 Hz), 121.0-120.9 (m), 130.5 (q, *J* = 4.0, 7.7 Hz), 147.2 (*J* = 10.9 Hz), 151.5 (d, *J* = 244.9 Hz), 155.2 (dd, *J* = 287.2, 290.7 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 286.1419, found: 286.1414.

1-(3,3-difluoro-2-(4-methoxy-3-(trifluoromethyl)phenyl)allyl) piperidine

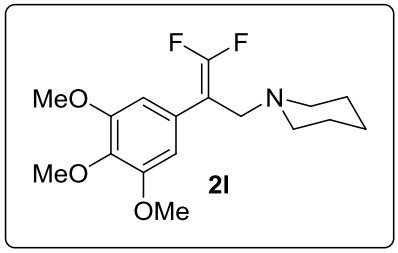


2k

Following the experiment procedure **A**, **2k** was obtained in 56% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 1.5 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.20 (dd, *J* = 1.8, 3.2 Hz, 2H), 2.40 (s, 4H), 1.58-1.53 (m, 4H), 1.45-1.40 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.50, -88.79 (d, *J* = 37.18 Hz, 1F), -89.26 (d, *J* = 36.96 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.3, 26.0, 54.0, 55.9, 56.1 (d, *J* = 3.8 Hz), 88.5 (dd, *J* = 11.5, 19.6 Hz), 111.7, 118.4 (q, *J* = 30.5, 61.0 Hz), 123.7 (q, *J* = 271.0, 541.7 Hz), 126.0 (t, *J* = 3.7 Hz), 127.4-127.2 (m), 133.2, 155.2 (dd, *J* = 287.9, 291.5 Hz), 156.5 ppm. **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 336.1387, found: 336.1382.

1-(3,3-difluoro-2-(3,4,5-trimethoxyphenyl)allyl)piperidine

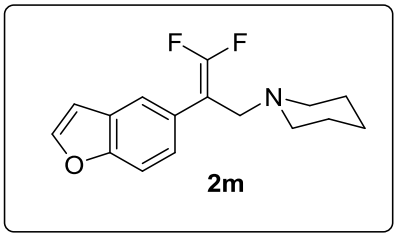


2l

Following the experiment procedure **A**, **2l** was obtained in 48% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (s, 2H), 3.84 (s, 9H), 3.17 (dd, *J* = 1.3, 3.1 Hz, 2H), 2.41 (s, 4H), 1.57-1.52 (m, 4H), 1.44-1.39 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -88.13 (d, *J* = 37.26 Hz, 1F), -89.37 (d, *J* = 37.30 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.4, 26.2, 53.9, 56.0, 56.5 (d, *J* = 4.2 Hz), 60.8, 89.4 (dd, *J* = 11.0, 19.0 Hz), 105.7 (t, *J* = 3.6 Hz), 129.8 (t, *J* = 3.7 Hz), 137.1, 152.8, 155.2 (dd, *J* = 287.3, 291.7 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 328.1724, found: 328.1721.

1-(2-(benzofuran-5-yl)-3,3-difluoroallyl)piperidine

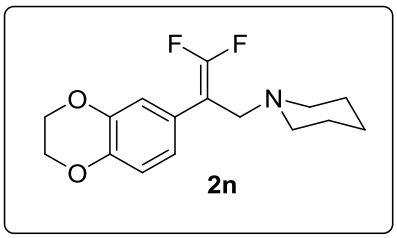


2m

Following the experiment procedure **A**, **2m** was obtained in 64% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.63 (d, *J* = 2.1 Hz, 1H), 7.48 (dd, *J* = 8.4, 20.9 Hz, 2H), 6.78 (dd, *J* = 0.8, 2.2 Hz, 1H), 3.33 (t, *J* = 2.3 Hz, 2H), 2.44 (s, 4H), 1.60-1.55 (m, 4H), 1.46-1.41 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.76 (d, *J* = 38.57 Hz, 1F), -89.90 (d, *J* = 39.13 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.4, 26.0, 54.1, 56.8 (d, *J* = 3.0 Hz), 89.9 (dd, *J* = 12.9, 18.2 Hz), 106.7, 111.1, 121.3 (t, *J* = 3.3 Hz), 125.0 (t, *J* = 2.9 Hz), 127.5, 128.9 (t, *J* = 2.7 Hz), 145.3, 154.2, 155.2 (dd, *J* = 287.3, 289.5 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 278.1356, found: 278.1355

1-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-difluoroallyl) piperidine



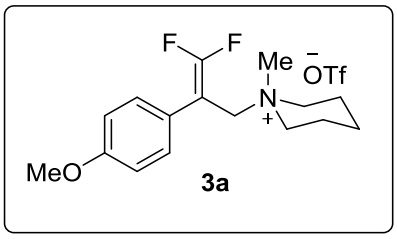
2n

Following the experiment procedure **A**, **2n** was obtained in 63% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.98 (dt, *J* = 1.5, 9.9 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1 H), 4.26 (s, 4 H), 3.20 (dd, *J* = 1.7, 3.1 Hz, 2H), 2.38

(s, 4H), 1.57-1.51 (m, 4H), 1.43-1.37 (m, 2H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.02 (d, *J* = 38.04 Hz, 1F), -89.47 (d, *J* = 37.87 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 24.4, 26.0, 54.0, 56.3 (d, *J* = 3.7 Hz), 64.3, 64.4, 89.0 (dd, *J* = 11.6, 19.4 Hz), 117.0, 117.3 (t, *J* = 3.6 Hz), 121.6 (t, *J* = 3.4 Hz), 127.4 (t, *J* = 3.6 Hz), 142.7, 143.1, 155.1 (dd, *J* = 286.7, 291.0 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 296.1462, found: 296.1460.

1-(3,3-difluoro-2-(4-methoxyphenyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

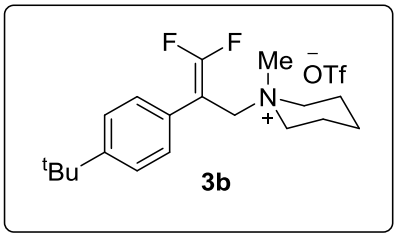


3a

Following the experiment procedure **B**, **3a** was obtained in 97% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.49 (s, 2 H), 3.79 (s, 3H), 3.37-3.34 (m, 4H), 2.95 (s, 3H), 1.83-1.77 (m, 4H), 1.74-1.68 (m, 1H), 1.64-1.56 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.50, -79.41 (d, *J* = 14.63 Hz, 1F), -80.54 (d, *J* = 13.97 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.5, 55.4, 61.3, 62.2, 84.4 (dd, *J* = 17.3, 20.4 Hz), 115.0, 120.7 (q, *J* = 318.6, 636.6 Hz), 122.4 (t, *J* = 2.8 Hz), 129.6 (t, *J* = 2.8 Hz), 157.2 (t, *J* = 296.6 Hz), 159.9 ppm. **HRMS (ESI, m/z):** calculated for $[M-OTf]^+$: 282.1669, found: 282.1669.

1-(2-(4-(tert-butyl)phenyl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

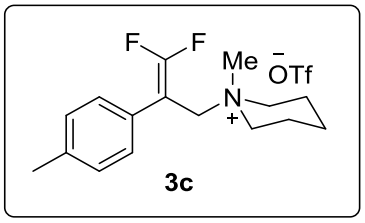


3b

Following the experiment procedure **B**, **3b** was obtained in 98% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 4.53 (s, 2 H), 3.38 (t, *J* = 5.4 Hz, 4H), 2.95 (s, 3H), 1.84-1.78 (m, 4H), 1.76-1.70 (m, 1H), 1.66-1.58 (m, 1H), 1.29 (s, 9H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.48, -78.56 (d, *J* = 12.87 Hz, 1F), -79.84 (d, *J* = 12.80 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 31.2, 34.7, 47.7, 61.3, 62.0, 84.7 (dd, *J* = 16.8, 20.3 Hz), 120.7 (q, *J* = 318.0, 636.1 Hz), 126.5, 127.5 (t, *J* = 2.9 Hz), 127.9 (t, *J* = 2.8 Hz), 152.3, 157.3 (t, *J* = 297.3 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 308.2190, found: 308.2188.

1-(3,3-difluoro-2-(p-tolyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



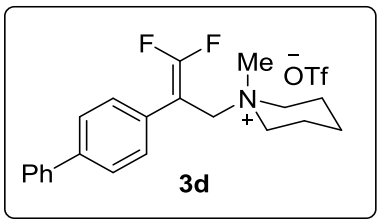
3c

Following the experiment procedure **B**, **3c** was obtained in 95% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.38 (d, *J* = 8.1

Hz, 2H), 4.51 (s, 2 H), 3.36 (t, *J* = 6.0 Hz, 4H), 2.95 (s, 3H), 2.33 (s, 3H), 1.82-1.77 (m, 4H), 1.74-1.68 (m, 1H), 1.64-1.56 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.50, -78.81 (d, *J* = 12.54 Hz, 1F), -80.00 (d, *J* = 12.61 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 21.2, 47.6, 61.3, 62.0, 84.7 (dd, *J* = 16.9, 20.0 Hz), 120.7 (q, *J* = 318.0, 636.6 Hz), 127.6 (t, *J* = 2.8 Hz), 128.2 (t, *J* = 2.3 Hz), 130.2, 139.2, 157.3 (t, *J* = 297.2 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 266.1720, found: 266.1721.

1-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



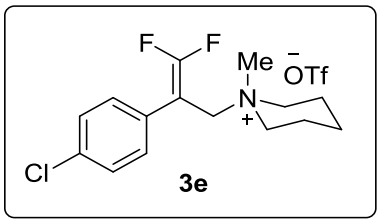
3d

Following the experiment procedure **B**, **3d** was obtained in 93% yield

^{1}H NMR (400 MHz, $(CD_3)SO$): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.74-7.70 (m, 4H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 4.53 (s, 2 H), 3.37-3.26 (m, 4H), 2.94 (s, 3H), 2.33 (s, 3H), 1.76-1.68 (m, 4H), 1.58-1.51 (m, 1H), 1.48-1.39 (m, 1H) ppm; **^{19}F NMR (376 MHz, $(CD_3)SO$):** δ -77.78, -78.74 (d, *J* = 14.24 Hz, 1F), -80.52 (d, *J* = 14.41 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $(CD_3)SO$):** δ 19.7, 20.9, 46.8, 60.5, 61.4, 84.9 (dd, *J* = 18.4, 18.7 Hz), 121.2 (q, *J* = 320.2, 640.7 Hz), 127.2, 127.4, 128.3, 129.5, 129.7, 131.3 (t, *J* = 3.1 Hz), 139.6, 140.4, 157.2 (t, *J* = 294.0 Hz) ppm; **HRMS**

(ESI, m/z): calculated for $[M\text{-}OTf]^+$: 328.1877, found: 328.1874.

1-(2-(4-chlorophenyl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

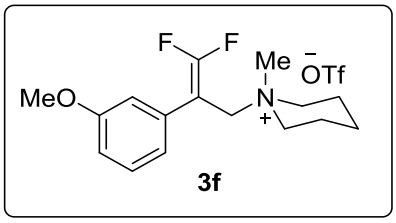


3e

Following the experiment procedure **B**, **3e** was obtained in 97% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 6.9 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.53 (s, 2 H), 3.36 (t, *J* = 5.5 Hz, 4H), 2.95 (s, 3H), 2.33 (s, 3H), 1.86-1.76 (m, 4H), 1.75-1.69 (m, 1H), 1.64-1.54 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ-77.29 (d, *J* = 9.91 Hz, 1F), -78.52 (d, *J* = 9.85 Hz, 1F), -78.54 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.1, 61.3, 62.2, 84.1 (dd, *J* = 17.8, 19.3 Hz), 120.7 (q, *J* = 318.1, 636.5 Hz), 129.3 (t, *J* = 3.0 Hz), 129.8, 129.9 (t, *J* = 2.8 Hz), 135.0, 157.5 (t, *J* = 297.7 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 286.1774, found: 286.1778.

1-(3,3-difluoro-2-(3-methoxyphenyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



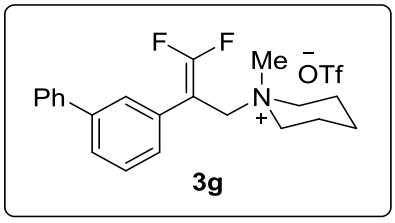
3f

Following the experiment procedure **B**, **3f** was obtained in 99% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.9

Hz, 2H), 6.99 (s, 1H), 6.88 (dd, *J* = 2.5, 8.3 Hz, 1H), 4.51 (s, 2 H), 3.83 (s, 3H), 3.36 (t, *J* = 5.2 Hz, 4H), 2.96 (s, 3H), 1.83-1.77 (m, 4H), 1.75-1.68 (m, 1H), 1.64-1.56 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ-78.10 (d, *J* = 10.90 Hz, 1F), -78.73 (d, *J* = 10.72 Hz, 1F), -78.56 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.5, 55.5, 61.3, 62.1, 84.8 (dd, *J* = 17.5, 20.4 Hz), 113.6 (t, *J* = 2.6 Hz), 115.0, 120.5 (t, *J* = 1.8 Hz), 120.7 (q, *J* = 317.8, 635.8 Hz), 130.6, 132.0 (t, *J* = 2.3 Hz), 157.4 (t, *J* = 297.3 Hz), 160.3 ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 282.1669, found: 282.1665.

1-(2-([1,1'-biphenyl]-3-yl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



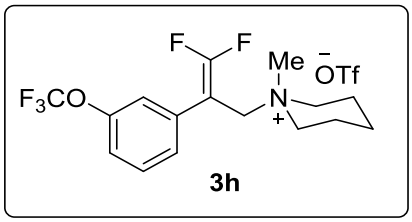
3g

Following the experiment procedure **B**, **3g** was obtained in 98% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.50-7.41 (m, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 4.51 (s, 2 H), 3.36 (t, *J* = 4.7 Hz, 4H), 2.92 (s, 3H), 1.75-1.71 (m, 4H), 1.67-1.61 (m, 1H), 1.58-1.49 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ-77.86 (d, *J* = 10.54 Hz, 1F), -79.06 (d, *J* = 10.67 Hz, 1F), -78.48 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 19.9, 20.4, 47.5, 61.3, 62.1, 84.8 (dd, *J* = 17.4, 20.1 Hz), 120.7 (q, *J* = 318.1, 636.1 Hz), 126.8 (t, *J* = 2.9 Hz), 127.2, 127.7, 127.9,

129.0, 130.1, 131.5 (t, J = 2.9 Hz), 139.7, 142.3, 157.5 (t, J = 297.0 Hz) ppm. **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 328.1877, found: 328.1872.

1-(3,3-difluoro-2-(3-(trifluoromethoxy)phenyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

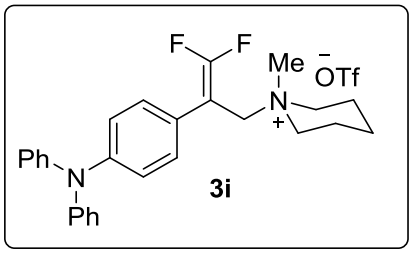


3h

Following the experiment procedure **B**, **3h** was obtained in 94% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.35 (s, 1H), 7.22 (d, J = 7.9 Hz, 1H), 4.56 (s, 2 H), 3.38 (t, J = 1.4 Hz, 4H), 2.96 (s, 3H), 1.84-1.77 (m, 4H), 1.74-1.67 (m, 1H), 1.65-1.54 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -57.97, -76.48 (d, J = 7.68 Hz, 1F), -77.76 (d, J = 7.93 Hz, 1F), -78.68 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.4, 47.3, 61.3, 61.9, 84.0 (t, J = 18.9 Hz), 120.3 (q, J = 256.4, 513.0 Hz), 120.7 (q, J = 318.1, 636.0 Hz), 121.1, 121.3, 127.0, 131.2, 132.9 (t, J = 3.4 Hz), 149.6 (d, J = 1.4 Hz), 157.7 (t, J = 298.3 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 336.1387, found: 336.1378.

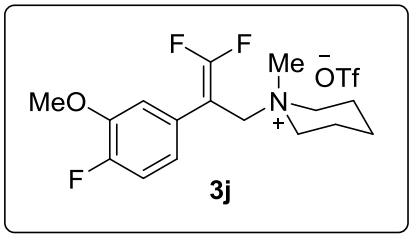
1-(2-(4-(diphenylamino)phenyl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



Following the experiment procedure **B**, **3i** was obtained in 85% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25 (m, 6H), 7.07 (dd, *J* = 8.2, 18.4 Hz, 8H), 4.46 (s, 2 H), 3.39 (t, *J* = 5.6 Hz, 4H), 2.99 (s, 3H), 1.86-1.80 (m, 4H), 1.78-1.61 (m, 1H), 1.67-1.57 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.51, -78.99 (d, *J* = 13.69 Hz, 1F), -78.03 (d, *J* = 13.87 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.8, 61.3, 61.8, 84.5 (dd, *J* = 17.0, 20.2 Hz), 120.6 (q, *J* = 318.0, 635.0 Hz), 122.2, 122.7, 123.9, 125.3, 129.0, 129.5, 146.9, 148.4, 157.3 (t, *J* = 297.1 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 419.2299, found: 419.2292.

1-(3,3-difluoro-2-(4-fluoro-3-methoxyphenyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

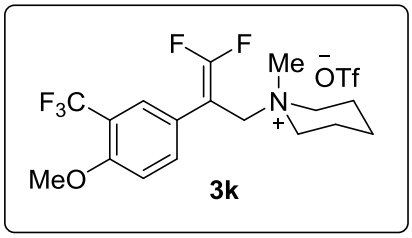


Following the experiment procedure **B**, **3j** was obtained in 93% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.3, 10.8 Hz, 1H), 7.00-6.96 (m, 1H), 4.52 (s, 2 H), 3.94 (s, 3H), 3.36 (t, *J* = 5.6 Hz, 4H), 2.96 (s, 3H), 1.84-1.79 (m, 4H), 1.76-1.70 (m, 1H), 1.65-1.54 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.26 (d, *J* = 11.90 Hz, 1F), -

78.73 (d, J = 11.13 Hz, 1F), -78.59, -133.6- -133.7(m) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.1, 56.6, 61.3, 62.5, 84.4 (dd, J = 17.6, 20.0 Hz), 113.6, 116.8 (d. J = 18.5 Hz), 120.7 (q, J = 318.0, 636.2 Hz), 120.9 (d, J = 6.6 Hz), 127.1 (d, J = 3.4 Hz), 148.6 (d, J = 10.9 Hz), 148.6 (d, J = 10.9 Hz), 152.3 (d, J = 248.0 Hz), 157.5 (t, J = 297.2 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 300.1575, found: 300.1571.

1-(3,3-difluoro-2-(4-methoxy-3-(trifluoromethyl)phenyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

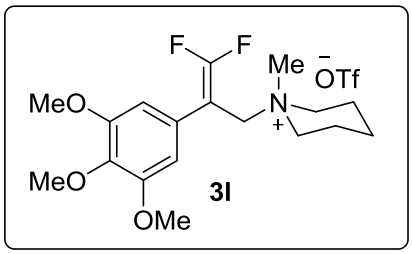


3k

Following the experiment procedure **B**, **3k** was obtained in 95% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 2.2, 8.6 Hz, 1H), 7.61 (s, 1H), 7.12 (d, J = 8.9 Hz, 1H), 4.53 (s, 2 H), 3.90 (s, 3H), 3.37 (t, J = 5.6 Hz, 4H), 2.96 (s, 3H), 1.85-1.79 (m, 4H), 1.76-1.70 (m, 1H), 1.65-1.55 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.59, -77.79 (d, J = 10.99 Hz, 1F), -78.17 (d, J = 10.88 Hz, 1F), -78.61 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.1, 56.1, 61.3, 62.3, 83.7 (t, J = 19.3 Hz), 113.3, 119.3 (d. J = 30.9 Hz), 120.7 (q, J = 318.4, 636.5 Hz), 122.3 (t, J = 3.1 Hz), 123.1 (q, J = 271.4, 542.3 Hz), 126.9 (d, J = 3.2 Hz), 133.8, 157.6 (t, J = 297.5 Hz), 157.7 ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 350.1543, found: 350.1541.

1-(3,3-difluoro-2-(3,4,5-trimethoxyphenyl)allyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate

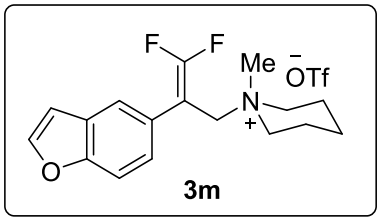


3l

Following the experiment procedure **B**, **3l** was obtained in 95% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (s, 2H), 4.51 (s, 2 H), 3.89 (s, 6H), 3.83 (s, 3H), 3.41-3.32 (m, 4H), 2.96 (s, 3H), 1.85-1.81 (m, 4H), 1.76-1.69 (m, 1H), 1.64-1.54 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.57, -78.63 (d, J = 12.16 Hz, 1F), -78.68 (d, J = 12.52 Hz, 1F), -78.61 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.1, 56.5, 60.9, 61.3, 62.5, 85.0 (dd, J = 18.2, 19.4 Hz), 105.5, 120.7 (q, J = 318.1, 636.1 Hz), 126.1, 138.2, 157.6 (t, J = 297.5 Hz), 153.9, 157.4 (t, J = 296.8 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 342.1881, found: 342.1884.

1-(2-(benzofuran-5-yl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



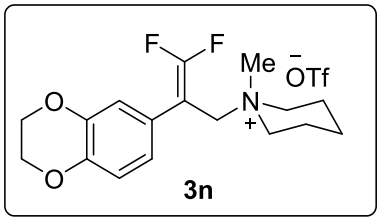
3m

Following the experiment procedure **B**, **3m** was obtained in 99% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.64 (d, J = 2.1 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 6.81 (dd, J = 0.6, 2.1 Hz, 1H),

4.57 (s, 2 H), 3.35 (t, *J* = 1.0 Hz, 4H), 2.94 (s, 3H), 1.79-1.73 (m, 4H), 1.71-1.63 (m, 1H), 1.61-1.50 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.46, -78.96 (d, *J* = 13.37 Hz, 1F), -80.18 (d, *J* = 13.32 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.5, 61.3, 62.6, 85.0 (dd, *J* = 16.9, 20.4 Hz), 106.9, 112.5, 120.7 (q, *J* = 318.2, 636.1 Hz), 121.7 (t, *J* = 2.8 Hz), 124.5 (t, *J* = 2.7 Hz), 125.2 (t, *J* = 2.8 Hz), 128.6, 146.4, 154.7, 157.4 (t, *J* = 296.6 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$: 292.1513, found: 292.1511.

1-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-difluoroallyl)-1-methylpiperidin-1-ium trifluoromethanesulfonate



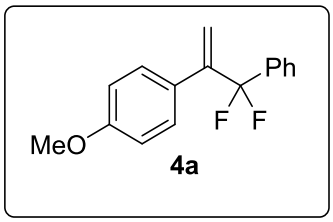
3n

Following the experiment procedure **B**, **3n** was obtained in 99% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, *J* = 8.1 Hz, 1H), 6.90 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.41 (s, 2 H), 4.23 (s, 4H), 3.33 (t, *J* = 5.4 Hz, 4H), 2.94 (s, 3H), 1.83-1.77 (m, 4H), 1.74-1.66 (m, 1H), 1.63-1.53 (m, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -78.55, -78.94 (d, *J* = 12.64 Hz, 1F), -79.89 (d, *J* = 13.29 Hz, 1F) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.0, 20.5, 47.6, 61.3, 62.1, 64.3, 64.4, 84.3 (dd, *J* = 17.4, 20.4 Hz), 117.2, 118.4, 120.6 (q, *J* = 317.8, 635.8 Hz), 121.4, 123.5 (t, *J* = 2.7 Hz),144.1, 141.2, 157.3 (t, *J* = 296.6 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M\text{-}OTf]^+$:

310.1619, found: 310.1615.

1-(3,3-difluoro-3-phenylprop-1-en-2-yl)-4-methoxybenzene

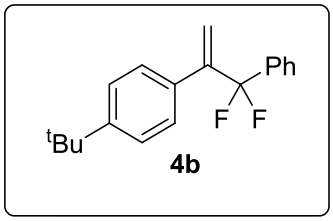


4a

Following the experiment procedure **C**, **4a** was obtained in 92% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.42-7.38 (m, 3H), 7.30 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.67 (s, 1H), 5.61 (s, 1H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.92 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 118.2 (t, *J* = 8.0 Hz), 120.6 (t, *J* = 241.1 Hz), 125.9 (t, *J* = 5.4 Hz), 128.3, 128.8, 129.4, 129.9 (t, *J* = 1.9 Hz), 136.5 (t, *J* = 27.2 Hz), 144.8 (t, *J* = 26.2 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 261.1091, found: 261.1097.

1-(tert-butyl)-4-(3,3-difluoro-3-phenylprop-1-en-2-yl)benzene



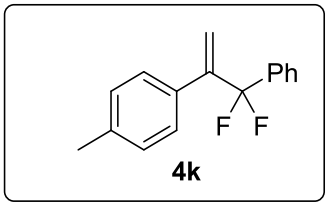
4b

Following the experiment procedure **C**, **4b** was obtained in 73% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.38-7.32 (m, 3H), 7.24-7.21 (m, 4H), 5.60 (s, 1H), 5.59 (s, 1H), 1.24 (s, 9H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.43 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 31.2, 34.5, 119.0, 120.7 (t, *J* = 240.7 Hz), 125.1, 126.0 (t, *J* = 5.3 Hz), 127.7,

128.3, 129.9 (t, J = 2.3 Hz), 133.3, 136.5 (t, J = 27.0 Hz), 145.1 (t, J = 26.2 Hz), 151.1 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 287.1611, found: 287.1613.

1-(3,3-difluoro-3-phenylprop-1-en-2-yl)-4-methylbenzene

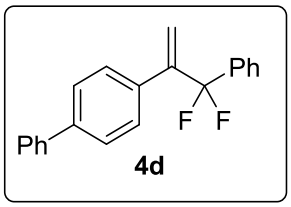


4k

Following the experiment procedure **C**, **4c** was obtained in 62% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.40-7.38 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.7 Hz, 1H), 5.67 (s, 1H), 5.61 (s, 1H), 2.32 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.95 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.1, 118.8 (t, J = 8.0 Hz), 120.5 (t, J = 240.7 Hz), 125.9 (t, J = 5.8 Hz), 128.0, 128.3, 128.9, 129.9 (t, J = 1.4 Hz), 133.5, 136.4 (t, J = 27.1 Hz), 138.0, 145.2 (t, J = 26.2 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 245.1142, found: 245.1140.

4-(3,3-difluoro-3-phenylprop-1-en-2-yl)-1,1'-biphenyl



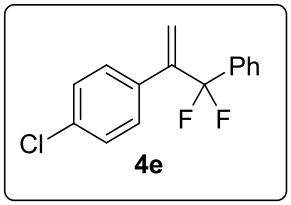
4d

Following the experiment procedure **C**, **4d** was obtained in 72% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.55 (m, 4H), 7.52 (d, J = 8.6 Hz, 2H), 7.45-7.41 (m, 7H), 7.35 (t, J = 7.2 Hz, 1H), 5.73 (s, 1H), 5.71 (s, 1H)

ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.72 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 119.4, 120.6 (t, J = 241.0 Hz), 126.0 (t, J = 5.8 Hz), 126.9, 127.0, 127.5, 128.4, 128.6, 128.8, 130.0 (t, J = 1.7 Hz), 135.3, 136.3 (t, J = 27.1 Hz), 140.5, 140.9, 145.0 (t, J = 26.3 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 307.1298, found: 307.1298.

1-chloro-4-(3,3-difluoro-3-phenylprop-1-en-2-yl)benzene

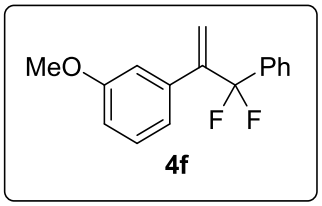


4e

Following the experiment procedure **C**, **4e** was obtained in 61% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.42-7.37 (m, 3H), 7.25 (s, 4H), 5.71 (s, 1H), 5.61 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.48 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 119.8 (t, J = 8.0 Hz), 120.3 (t, J = 241.3 Hz), 125.8 (t, J = 5.7 Hz), 128.4, 129.6, 130.0 (t, J = 1.5 Hz), 134.2, 134.8, 136.0 (t, J = 27.1 Hz), 144.5 (t, J = 26.3 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 265.0596, found: 265.0591.

1-(3,3-difluoro-3-phenylprop-1-en-2-yl)-3-methoxybenzene



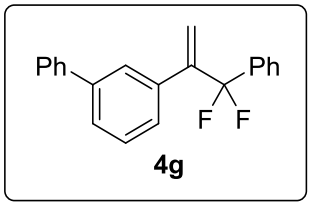
4f

Following the experiment procedure **C**, **4f** was obtained in 68% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.42-7.36 (m, 3H),

7.19 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.85-6.82 (m, 2H), 5.72 (s, 1H), 5.64 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.14 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 113.9, 118.0 (t, J = 241.3 Hz), 119.4 (t, J = 8.1 Hz), 120.7, 125.9 (t, J = 5.8 Hz), 128.3, 129.1, 129.9, 136.3 (t, J = 27.1 Hz), 137.8, 145.3 (t, J = 26.2 Hz), 159.2 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 261.1091, found: 261.1090.

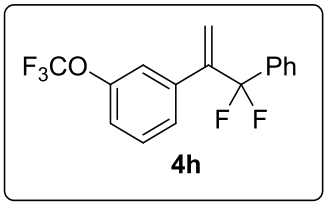
3-(3,3-difluoro-3-phenylprop-1-en-2-yl)-1,1'-biphenyl



4g

Following the experiment procedure **C**, **4g** was obtained in 90% yield **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55-7.52 (m, 6H), 7.45-7.40 (m, 5H), 7.38-7.34 (m, 2H), 7.30 (d, J = 8.0 Hz, 1H), 5.76 (s, 1H), 5.69 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.24 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 119.6, 120.5 (t, J = 241.3 Hz), 126.0 (t, J = 5.7 Hz), 127.0, 127.1, 127.2, 127.4, 128.4, 128.6, 128.8, 130.0, 136.3 (t, J = 27.0 Hz), 136.9, 140.8, 141.1, 145.5 (t, J = 26.2 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 307.1298, found: 307.1299.

1-(3,3-difluoro-3-phenylprop-1-en-2-yl)-3-(trifluoromethoxy)benzene

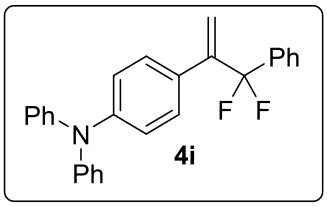


4h

Following the experiment procedure **C**, **4h** was obtained in 30% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.42-7.37 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.75 (s, 1H), 5.65 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -57.85, -91.63 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 120.0 (t, *J* = 241.0 Hz), 120.4 (q, *J* = 255.6, 511.2 Hz), 120.5 (t, *J* = 7.9 Hz), 120.6, 120.9, 125.8 (t, *J* = 5.5 Hz), 126.7, 128.4, 129.5, 130.1, 135.8 (t, *J* = 27.1 Hz), 138.3, 144.3 (t, *J* = 26.9 Hz), 148.9 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 315.0808, found: 315.0803.

4-(3,3-difluoro-3-phenylprop-1-en-2-yl)-N,N-diphenylaniline

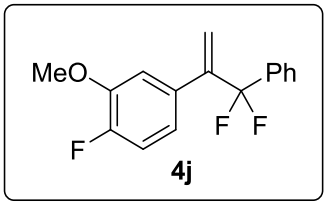


4i

Following the experiment procedure **C**, **4i** was obtained in 66% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 2H), 7.45-7.42 (m, 3H), 7.30-7.22 (m, 6H), 7.11 (d, *J* = 7.6 Hz, 4H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 5.68 (s, 1H), 5.64 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.33 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 118.2 (t, *J* = 8.1 Hz), 120.7 (t, *J* = 241.3 Hz), 122.4, 123.2, 124.8, 126.0 (t, *J* = 5.3 Hz), 128.3, 128.8, 129.3, 129.7, 129.9, 136.5 (t, *J* = 27.1 Hz), 144.7 (t, *J* = 25.8 Hz), 147.4, 147.7 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 398.1720, found: 398.1719

4-(3,3-difluoro-3-phenylprop-1-en-2-yl)-1-fluoro-2-methoxybenzene

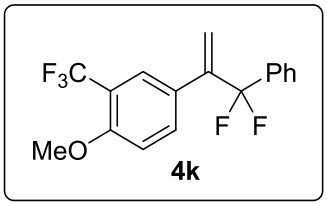


4j

Following the experiment procedure **C**, **4j** was obtained in 73% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.42-7.39 (m, 3H), 6.96 (dd, *J* = 8.3, 11.3, 1H), 6.87 (dd, *J* = 1.9, 8.3 Hz, 1H), 6.84-6.81 (m, 1H), 5.71 (s, 1H), 5.59 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.82, -135.77- -135.84 (m) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 56.1, 113.6, 115.7 (t, *J* = 18.2 Hz), 120.3 (t, *J* = 241.0 Hz), 121.1 (d, *J* = 6.7 Hz), 125.8 (t, *J* = 5.8 Hz), 126.4, 128.0, 128.4, 130.0, 136.5 (t, *J* = 29.2 Hz), 144.8 (t, J = 26.4 Hz), 147.0 (d, *J* = 10.7 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 279.0997, found: 279.0998.

4-(3,3-difluoro-3-phenylprop-1-en-2-yl)-1-methoxy-2-(trifluoromethyl)benzene



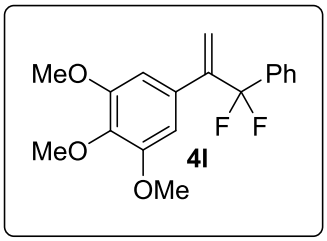
4k

Following the experiment procedure **C**, **4k** was obtained in 87% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 1.4 Hz, 1H), 7.50-7.37 (m, 6H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.68 (s, 1H), 5.60 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.59, -91.51 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):**

δ 56.0, 111.6, 118.4 (q, *J* = 31.0, 61.8 Hz), 119.5 (t, *J* = 7.6 Hz), 120.4 (t, *J* = 240.6 Hz), 123.4 (q, *J* = 215.8, 652.7 Hz), 125.8 (t, *J* = 5.6 Hz), 127.0 (q, *J* = 4.6, 10.2 Hz), 128.3, 128.4, 130.0 (t, *J* = 1.8 Hz), 133.0, 135.9 (t, *J* = 27.2 Hz), 144.0 (t, *J* = 26.7 Hz), 157.3 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 329.0965, found: 329.0956.

5-(3,3-difluoro-3-phenylprop-1-en-2-yl)-1,2,3-trimethoxybenzene

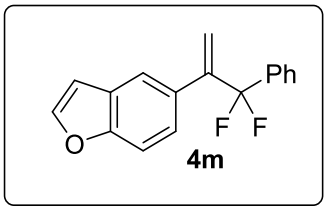


4l

Following the experiment procedure **C**, **4l** was obtained in 75% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.43-7.38 (m, 3H), 6.48 (s, 2H), 5.70 (s, 1H), 5.61 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.53 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 54.9, 59.8, 104.5, 118.0 (t, *J* = 7.9 Hz), 119.3 (t, *J* = 241.4 Hz), 124.8 (t, *J* = 5.4 Hz), 127.3, 128.9, 130.9, 135.3 (t, *J* = 27.3 Hz), 136.9, 144.3 (t, *J* = 26.4 Hz), 151.6 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 321.1302, found: 321.1295.

5-(3,3-difluoro-3-phenylprop-1-en-2-yl)benzofuran



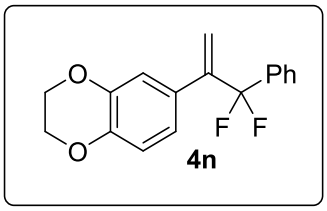
4m

Following the experiment procedure **C**, **4m** was obtained in 73% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 2.1 Hz, 1H), 7.56 (s, 1H),

7.52-7.50 (m, 2H), 7.40-7.34 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.71 (dd, *J* = 0.8, 2.1 Hz, 1H), 5.73 (s, 1H), 5.61 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.31 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 106.8, 111.0, 119.4 (t, *J* = 7.9 Hz), 120.6 (t, *J* = 240.8 Hz), 121.2, 124.9, 125.9 (t, *J* = 5.8 Hz), 127.3, 128.3, 129.9 (t, *J* = 2.0 Hz), 131.4, 136.4 (t, *J* = 27.7 Hz), 145.5, 145.7 (t, *J* = 26.2 Hz), 154.7 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 271.0934, found: 271.0927.

6-(3,3-difluoro-3-phenylprop-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine

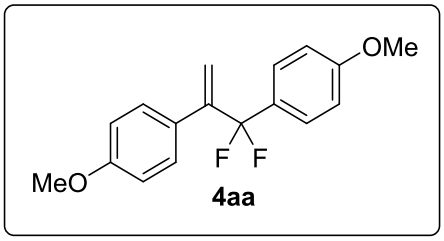


4n

Following the experiment procedure **C**, **4n** was obtained in 58% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.40-7.36 (m, 2H), 6.88 (d, *J* = 1.8 Hz, 1H), 6.82 (dd, *J* = 1.9, 8.6 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.63 (s, 1H), 5.59 (s, 1H), 4.23 (s, 4H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.73 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 64.3, 64.4, 116.9, 117.2, 118.6 (t, *J* = 8.0 Hz), 120.5 (t, *J* = 240.7 Hz), 121.4, 125.9 (t, *J* = 5.8 Hz), 128.3, 129.7, 129.9, 136.4 (t, *J* = 27.1 Hz), 143.0, 143.6, 144.5 (t, *J* = 26.0 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 289.1040, found: 289.1038.

4,4'-(1,1-difluoroprop-2-ene-1,2-diyl)bis(methoxybenzene)

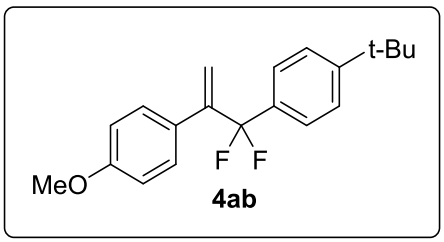


4aa

Following the experiment procedure **C**, **4aa** was obtained in 88% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.65 (s, 1H), 5.58 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.28 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 55.3, 113.5, 113.6, 117.8 (t, *J* = 7.7 Hz), 120.7 (t, *J* = 240.0 Hz), 127.5 (t, *J* = 5.7 Hz), 128.8 (t, *J* = 27.9 Hz), 129.0, 129.3, 144.9 (t, *J* = 26.3 Hz), 159.4, 160.7 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 291.1197, found: 297.1194.

1-(tert-butyl)-4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzene



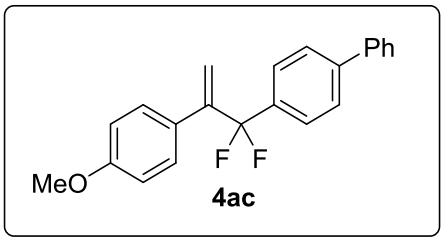
4ab

Following the experiment procedure **C**, **4ab** was obtained in 99% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 8.7, 19.2 Hz, 4H), 7.31 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.63 (s, 1H), 5.60 (s, 1H), 3.79 (s, 3H), 1.33 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.74 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 31.2, 34.7, 55.2, 113.6, 118.1 (t, *J* = 8.0 Hz), 120.8 (t, *J* = 239.9 Hz), 125.2, 125.7 (t, *J* = 5.6 Hz), 129.0, 129.4, 133.6 (t,

J = 27.6 Hz), 144.9 (t, J = 26.3 Hz), 153.0, 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 317.1717, found: 317.1709.

4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-1,1'-biphenyl

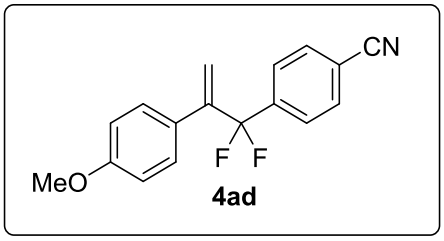


4ac

Following the experiment procedure **C**, **4ac** was obtained in 85% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, J = 8.7, 14.0 Hz, 6H), 7.46 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 5.70 (s, 1H), 5.62 (s, 1H), 3.79 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.56 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 118.2 (t, J = 7.8 Hz), 120.7 (t, J = 240.7 Hz), 126.4 (t, J = 5.2 Hz), 127.0, 127.2, 127.8, 128.8, 128.9, 129.4, 135.4 (t, J = 27.5 Hz), 140.2, 142.7, 144.7 (t, J = 26.1 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 337.1404, found: 337.1406.

4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzonitrile



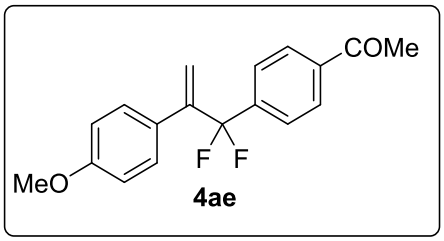
4ad

Following the experiment procedure **C**, **4ad** was obtained in 62% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 5.69 (s, 1H),

5.60 (s, 1H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -92.87 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.7, 113.9 (t, *J* = 1.9 Hz), 118.1, 118.7 (t, *J* = 8.5 Hz), 119.5 (t, *J* = 242.8 Hz), 126.7 (t, *J* = 5.8 Hz), 128.0, 129.4, 132.2, 141.1 (t, *J* = 27.8 Hz), 144.0 (t, *J* = 24.9 Hz), 159.8 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 286.1043, found: 286.1045.

1-(4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)phenyl)ethan-1-one

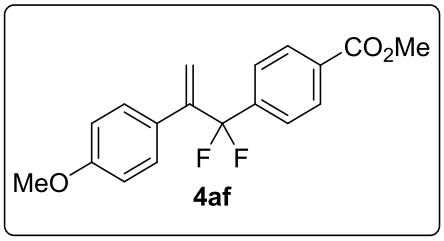


4ae

Following the experiment procedure **C**, **4ae** was obtained in 58% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.68 (s, 1H), 5.58 (s, 1H), 3.71 (s, 3H), 2.60 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -92.20 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 26.8, 55.2, 113.6, 118.5 (t, *J* = 8.0 Hz), 120.0 (t, *J* = 241.5 Hz), 126.2 (t, *J* = 5.3 Hz), 128.3, 128.5, 129.4, 138.1, 140.9 (t, *J* = 27.7 Hz), 144.3 (t, *J* = 25.2 Hz), 159.6, 197.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 303.1197, found: 303.1192.

methyl 4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzoate

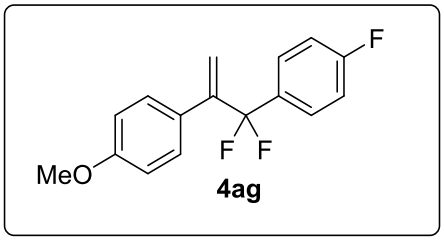


4af

Following the experiment procedure **C**, **4af** was obtained in 58% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 5.67 (s, 1H), 5.59 (s, 1H), 3.92 (s, 3H), 3.77 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -92.26 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 52.4, 55.2, 113.6, 118.4 (t, *J* = 8.0 Hz), 120.0 (t, *J* = 241.4 Hz), 126.0 (t, *J* = 5.7 Hz), 128.4, 129.4, 129.6, 131.5, 140.8 (t, *J* = 27.5 Hz), 144.4 (t, *J* = 25.6 Hz), 159.6, 166.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 319.1146, found: 319.1138.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-4-fluorobenzene



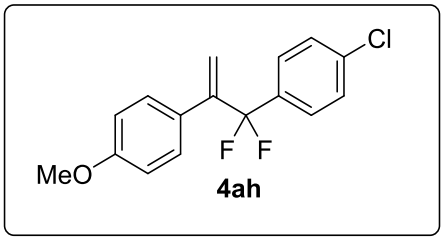
4ag

Following the experiment procedure **C**, **4ag** was obtained in 39% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 5.7, 8.4 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.65 (s, 1H), 5.58 (s, 1H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.14, -111.02- -111.09 (m) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 115.4 (d, *J* = 21.8 Hz), 118.2 (t, *J* = 8.1 Hz), 120.2 (t, *J* = 241.5 Hz),

128.0 (t, J = 5.7 Hz), 128.1 (t, J = 5.5 Hz), 128.6, 128.8, 129.4, 135.0 (t, J = 27.9 Hz), 144.6 (t, J = 25.7 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 279.0997, found: 279.0996.

1-chloro-4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzene

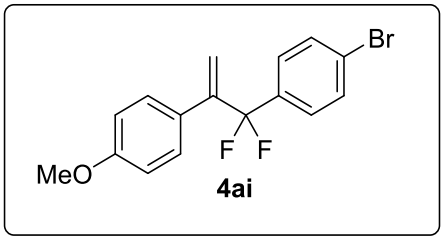


4ah

Following the experiment procedure **C**, **4ah** was obtained in 76% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 5.65 (s, 1H), 5.57 (s, 1H), 3.77 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.03 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 118.2 (t, J = 8.1 Hz), 120.1 (t, J = 241.3 Hz), 127.4 (t, J = 5.2 Hz), 128.5, 128.6, 129.4, 135.0 (t, J = 27.9 Hz), 136.0 (t, J = 2.0 Hz), 144.4 (t, J = 25.5 Hz), 159.6 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 295.0701, found: 295.0702.

1-bromo-4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzene



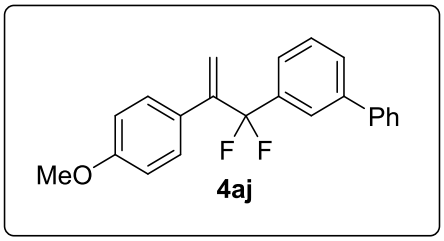
4ai

Following the experiment procedure **C**, **4ai** was obtained in 64% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.65 (s, 1H),

5.57 (s, 1H), 3.77 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.25 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 118.3 (t, *J* = 8.0 Hz), 120.1 (t, *J* = 241.2 Hz), 124.3 (t, *J* = 2.1 Hz), 127.6 (t, *J* = 5.7 Hz), 128.4, 129.4, 131.6, 135.5 (t, *J* = 27.8 Hz), 144.3 (t, *J* = 25.5 Hz), 159.6 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 339.0196, found: 339.0192.

3-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-1,1'-biphenyl

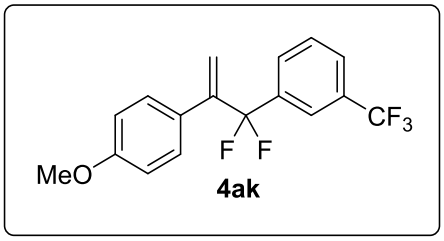


4aj

Following the experiment procedure **C**, **4aj** was obtained in 60% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 1.4 Hz, 1H), 7.55 (s, 1H), 7.50-7.43 (m, 4H), 7.37 (tt, *J* = 1.2, 8.5 Hz, 1H), 7.30 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.69 (s, 1H), 5.61 (s, 1H), 3.79 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.93 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 118.4 (t, *J* = 8.0 Hz), 120.6 (t, *J* = 241.3 Hz), 124.7 (t, *J* = 5.7 Hz), 124.8 (t, *J* = 5.2 Hz), 127.2, 127.7, 128.6, 128.8, 128.9, 129.4, 137.0 (t, *J*=27.6 Hz), 140.4, 141.3, 144.7 (t, *J* = 26.1 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 337.1404, found: 337.1401.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-3-(trifluoromethyl)benzene

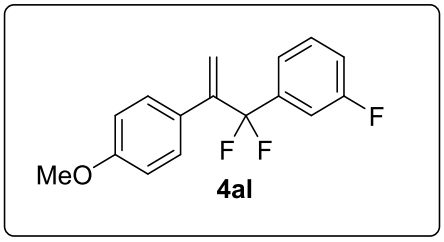


4ak

Following the experiment procedure **C**, **4ak** was obtained in 75% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.66 (s, 1H), 5.61 (s, 1H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.73, -91.62 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.7, 118.8 (t, *J* = 8.2 Hz), 119.8 (t, *J* = 241.8 Hz), 122.9 (q, *J* = 7.8, 9.6 Hz), 126.7, 127.5 (q, *J* = 445.1, 587.7 Hz), 129.0, 129.3 (t, *J* = 5.4 Hz), 130.4, 130.7 (t, *J* = 27.3 Hz), 131.0, 137.5 (t, *J* = 28.3 Hz), 144.2 (t, *J* = 25.7 Hz), 159.7 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 329.0965, found: 329.0970.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-3-fluorobenzene



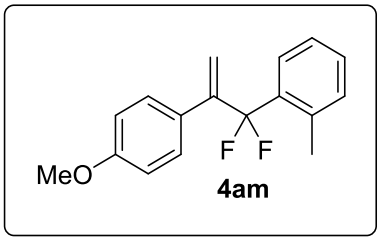
4al

Following the experiment procedure **C**, **4al** was obtained in 55% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 7.9, 13.5 Hz, 1H), 7.26 (t, *J* = 2.2 Hz, 3H), 7.21 (d, *J* = 9.7 Hz, 1H), 7.09 (td, *J* = 2.1, 8.5 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.66 (s, 1H), 5.59 (s, 1H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -91.24, -112.00- -112.07(m) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.3 (dt, *J* = 6.0, 23.8 Hz), 113.6, 116.9 (d, *J* =

21.2 Hz), 118.4 (t, J = 8.3 Hz), 119.8 (t, J = 241.4 Hz), 121.6-121.8 (m), 128.4, 129.4, 130.1 (d, J = 8.0 Hz), 138.8 (td, J = 6.8, 27.9 Hz), 144.3 (t, J = 25.5 Hz), 159.6, 162.5 (d, J = 245.3 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 279.0997, found: 279.0996.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-2-methylbenzene

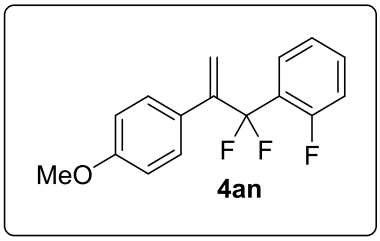


4am

Following the experiment procedure **C**, **4am** was obtained in 27% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 8.6 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.7 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.54 (s, 1H), 5.38 (s, 1H), 3.80 (s, 3H), 2.38 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -89.04 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.4, 55.2, 113.5, 119.3 (t, J = 7.4 Hz), 125.5, 126.8 (t, J =8.2 Hz), 128.9, 129.4, 129.9, 131.0, 131.7, 134.3 (t, J = 25.2 Hz), 136.5, 144.9 (t, J = 26.6 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 275.1247, found: 275.1242.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-2-fluorobenzene

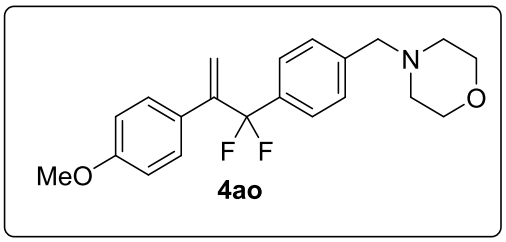


4an

Following the experiment procedure **C**, **4an** was obtained in 13% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 8.2 Hz, 1H), 7.42-7.36 (m, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 10.0 Hz, 1H), 6.81 (d, J = 8.9 Hz, 2H), 5.62 (s, 1H), 5.55 (s, 1H), 3.78 (s, 3H), ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –90.75 (d, *J* = 11.4 Hz), -112.69- 112.81(m) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.5, 116.4 (d, *J* = 21.1 Hz), 118.7 (td, *J* = 1.1, 7.2 Hz), 119.0 (t, *J* = 241.3 Hz), 123.8 (d, *J* = 3.7 Hz), 127.8 (td, *J* = 1.4, 6.4 Hz), 128.6, 129.4, 132.0 (d, *J* = 8.1 Hz), 144.2 (t, *J* = 25.1 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 279.0997, found: 279.0993.

4-(4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzyl)morpholine

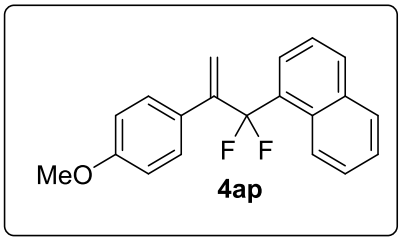


4ao

Following the experiment procedure **C**, **4ao** was obtained in 72% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 1H), 5.58 (s, 1H), 3.78 (s, 3H), 3.70 (t, *J* = 4.6 Hz, 4H), 3.50 (s, 2H), 2.43 (s, 4H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –90.41 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 53.6, 55.2, 63.0, 67.0, 113.5, 118.2 (t, *J* = 8.0 Hz), 120.6 (t, *J* = 240.7 Hz), 125.9 (t, *J* = 5.7 Hz), 128.8, 129.0, 129.4, 135.4(t, *J* = 27.2 Hz), 139.7, 144.7 (t, *J* = 25.8 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 360.1775, found: 360.1771.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)naphthalene

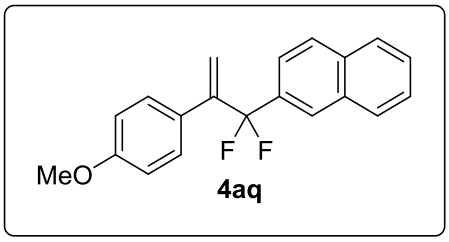


4ap

Following the experiment procedure **C**, **4ap** was obtained in 71% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (m, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89-7.87 (m, 1H), 7.82 (d, *J* = 6.9 Hz, 1H), 7.54-7.50(m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.60 (s, 1H), 5.45 (s, 1H), 3.80 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –86.35 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 120.0 (t, *J* = 7.5 Hz), 121.8 (t, *J* = 260.3 Hz), 124.4, 125.5 (t, *J* = 8.7 Hz), 125.8 (t, *J* = 3.0 Hz), 125.9, 126.6, 128.7, 128.9, 129.5, 130.0 (t, *J* = 2.2 Hz), 131.1, 131.8 (t, *J* = 25.0 Hz), 134.0, 145.5 (t, *J* = 26.1 Hz), 159.6 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 311.1247, found: 311.1251.

2-(1,1-difluoro-2-(4-methoxyphenyl)allyl)naphthalene



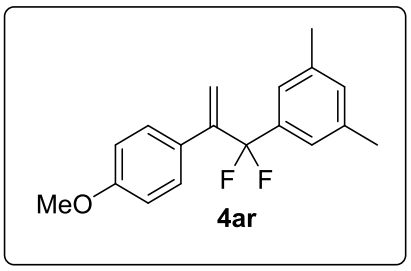
4aq

Following the experiment procedure **C**, **4aq** was obtained in 30% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.87-7.85 (m, 3H), 7.58-7.52 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.71 (s, 1H), 5.64 (s, 1H), 3.76 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –90.53

ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 113.6, 118.4 (t, *J* = 7.7 Hz), 120.8 (t, *J* = 241.2 Hz), 123.0 (t, *J* = 4.6 Hz), 125.8 (t, *J* = 6.4 Hz), 126.6, 127.2, 127.7, 128.3, 128.7,128.8, 129.4, 132.5, 133.7 (t, *J* = 27.0 Hz), 133.8, 144.7 (t, *J* = 26.3 Hz), 159.5 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 311.1247, found: 311.1239.

1-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-3,5-dimethylbenzene

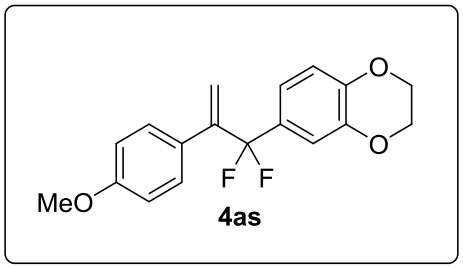


4ar

Following the experiment procedure **C**, **4ar** was obtained in 76% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.9 Hz, 2H), 7.13 (s, 2H), 7.03 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 5.58 (s, 1H), 3.78 (s, 3H), 2.32 (s, 6H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –90.29 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.3, 55.2, 113.5, 118.1 (t, *J* = 8.0 Hz), 120.8 (t, *J* = 240.7 Hz), 123.6 (t, *J* = 5.8 Hz), 128.9, 129.3, 131.5, 136.3 (t, *J* = 27.0 Hz), 138.0, 144.8 (t, *J* = 26.2 Hz), 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 289.1404, found: 289.1410.

6-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-2,3-dihydrobenzo[b][1,4]dioxine

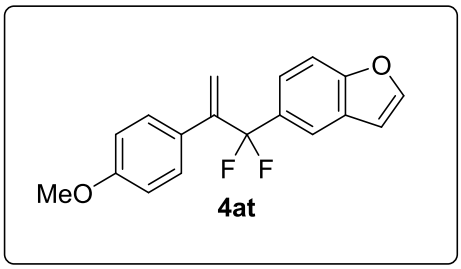


4as

Following the experiment procedure **C**, **4as** was obtained in 79% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 2.1 Hz, 1H), 6.98 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.65 (s, 1H), 5.58 (s, 1H), 4.25 (s, 4H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –89.25 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 64.2, 64.4, 113.5, 115.4 (t, *J* = 5.7 Hz), 117.2, 117.9 (t, *J* = 27.9 Hz), 119.3 (t, *J* = 5.5 Hz), 120.3 (t, *J* = 240.6 Hz), 128.8, 129.3, 129.7 (t, *J* = 27.9 Hz), 143.2, 144.6 (t, *J* = 26.2 Hz), 144.8, 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 319.1146, found: 319.1142.

5-(1,1-difluoro-2-(4-methoxyphenyl)allyl)benzofuran



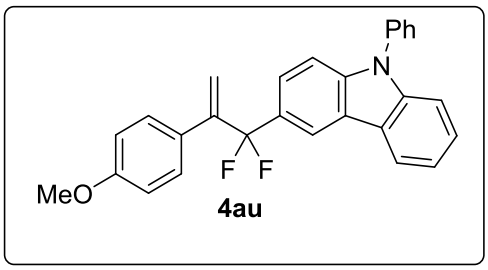
4at

Following the experiment procedure **C**, **4at** was obtained in 33% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.80-6.78(m, 2H), 5.68 (s, 1H), 5.61 (s, 1H), 4.25 (s, 3H), 3.77 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –88.62 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):**

δ 55.2, 106.9, 111.3, 113.5, 118.0 (t, J = 7.9 Hz), 119.3 (t, J = 6.1 Hz), 120.9 (t, J = 240.9 Hz), 121.3, 122.4 (t, J = 5.3 Hz), 127.2, 128.9, 129.3, 131.1 (t, J = 27.2 Hz), 145.0 (t, J = 26.4 Hz), 146.0, 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$:301.1040, found: 301.1042.

3-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-9-phenyl-9H-carbazole

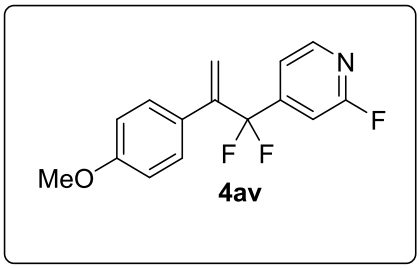


4au

Following the experiment procedure **C**, **4au** was obtained in 45% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.15 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H), 7.56-7.53 (m, 3H), 7.51-7.46 (m, 1H), 7.44-7.42 (m, 2H), 7.38 (d, J = 8.6 Hz, 1H), 7.34-7.29 (m, 3H), 6.80 (d, J = 8.7 Hz, 2H), 5.76 (s, 1H), 5.66 (s, 1H), 3.76 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –87.77 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 109.6, 110.0, 113.5, 118.0 (t, J = 7.9 Hz), 118.3 (t, J = 6.0 Hz), 120.4, 120.5, 121.4 (t, J = 241.2 Hz), 123.0, 123.1, 123.9 (t, J = 5.4 Hz), 126.5, 127.1, 127.8, 128.1 (t, J = 27.5 Hz), 129.1, 129.4, 129.9, 130.0, 137.3, 141.4, 145.2 (t, J = *26.1* Hz), 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 426.1669, found: 426.1675.

4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-2-fluoropyridine

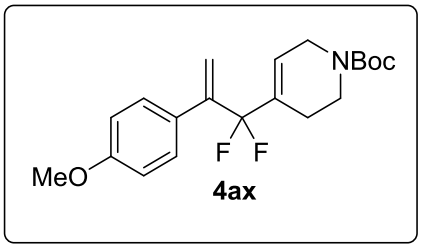


4av

Following the experiment procedure **C**, **4av** was obtained in 50% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 5.1 Hz, 1H), 7.23-7.18 (m, 3H), 6.98 (s, 1H), 6.79 (d, J = 8.8 Hz, 2H), 5.69 (s, 1H), 5.59 (s, 1H), 3.76 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -65.90, –94.36 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 107.0 (dt, *J* = 5.9, 39.4 Hz), 113.8, 118.3 (dd, *J* = 4.7, 9.5 Hz), 118.5 (d, *J* = 3.4 Hz), 119.1 (t, *J* = 8.2 Hz), 127.5, 129.4, 143.3 (t, *J* = 24.5 Hz), 148.3 (d, *J* = 14.6 Hz), 150.3 (d, J = 7.6 Hz), 159.9, 163.7 (d, *J* = 238.4 Hz) ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 280.0949, found: 280.0942.

tert-butyl 4-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-3,6-dihydropyridine-1(2H)-carboxylate



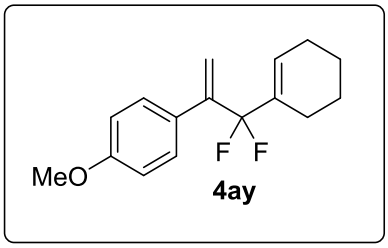
4ax

Following the experiment procedure **C**, **4ax** was obtained in 34% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H) , 6.04 (s, 1H), 5.66 (s, 1H), 5.56 (s, 1H), 3.92 (s, 2H), 3.81 (s, 3H), 3.45 (t, *J* = 5.6 Hz, 2H), 2.15 (s, 2H), 1.45 (s, 9H) ppm; **^{19}F NMR (376**

MHz, $CDCl_3$): δ –97.35 (d, *J* = 82.94 Hz) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 15.2, 23.5, 28.4, 29.7, 55.3, 79.9, 113.6, 118.2 (t, *J* = 7.5 Hz), 120.0 (t, *J* = 240.6 Hz), 128.7, 129.2, 129.5, 132.1 (t, *J* = 9.8 Hz)143.0 (t, *J* = 25.2 Hz), 154.8, 159.6 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 366.1881, found: 366.1888.

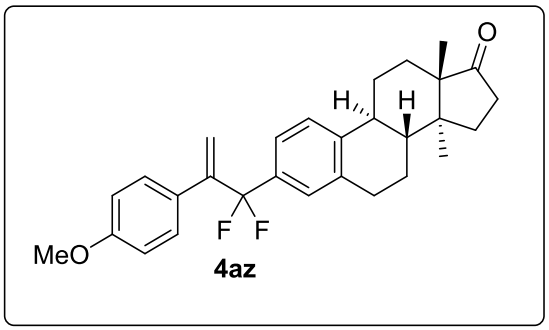
1-(3-(cyclohex-1-en-1-yl)-3,3-difluoroprop-1-en-2-yl)-4-methoxybenzene



4ay

Following the experiment procedure **C**, **4ay** was obtained in 56% yield **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H) , 6.09 (s, 1H), 5.64 (s, 1H), 5.53 (s, 1H), 3.81 (s, 3H), 2.04 (s, 4H), 1.64-1.51 (m, 4H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –96.75 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 22.0, 23.0, 24.7, 55.2, 113.4, 117.6 (t, *J* = 8.1 Hz), 120.9 (t, *J* = 237.1 Hz), 128.6 (t, *J* = 9.0 Hz), 129.2, 129.3, 133.0 (t, *J* = 25.1 Hz), 143.6 (t, *J* = 26.2 Hz), 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 265.1404, found: 265.1397.

(8R,9S,13S,14S)-3-(1,1-difluoro-2-(4-methoxyphenyl)allyl)-13,14-dimethyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthrene-17-one

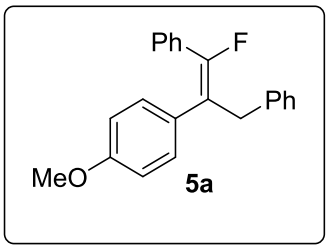


4az

Following the experiment procedure **C**, **4az** was obtained in 57% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 3H), 7.25 (ds, 2H) , 6.81 (d, *J* = 8.8 Hz, 2H), 5.63 (s, 1H), 5.59 (s, 1H), 3.78 (s, 3H), 2.91 (dd, *J* = 4.4, 9.1 Hz, 2H), 2.51 (dd, *J* = 9.2, 19.5 Hz, 1H), 2.44-2.39 (m, 1H), 2.30 (t, *J* = 10.1 Hz, 1H), 2.20-1.95 (m, 4H), 1.66-1.42 (m, 8H), 0.91 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –89.86 ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 13.8, 21.6, 25.6, 26.4, 29.4, 31.5, 35.9, 37.9, 44.4, 47.9, 50.5, 55.2, 113.5, 118.1 (t, *J* = 7.9 Hz), 120.7 (t, *J* = 240.6 Hz), 123.3 (t, *J* = 5.5 Hz), 125.3, 126.4 (t, *J* = 5.5 Hz), 128.9, 129.3, 133.9 (t, *J* = 27.0 Hz), 136.6, 141.6, 144.6 (t, J = 25.9 Hz), 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 437.2292, found: 437.2293

(E)-(1-fluoro-2-(4-methoxyphenyl)prop-1-ene-1,3-diyl)dibenzene



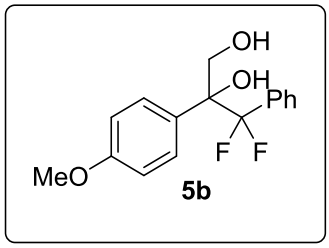
5a

Following the experiment procedure **D**, **5a** was obtained in 48% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.40-7.36 (m, 5H), 7.26-7.22 (m, 2H), 7.19-7.13 (m, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.89 (s,

2H), 3.78 (s, 3H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –99.75 (d, *J* = 82.94 Hz) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 37.3 (d, *J* = 3.5 Hz), 55.2, 113.6, 117.1 (d, *J* = 15.4 Hz), 126.1, 128.1 (d, *J* = 4.4 Hz), 128.3 (d, *J* = 1.2 Hz), 128.5, 129.0, 129.1 (d, *J* = 1.2 Hz), 130.0 (d, *J* = 4.3 Hz), 113.0 (d, *J* = 29.2 Hz), 139.4 (d, *J* = 3.5 Hz), 154.6 (d, *J* = 246.7 Hz), 158.6 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 319.1498, found: 319.1503.

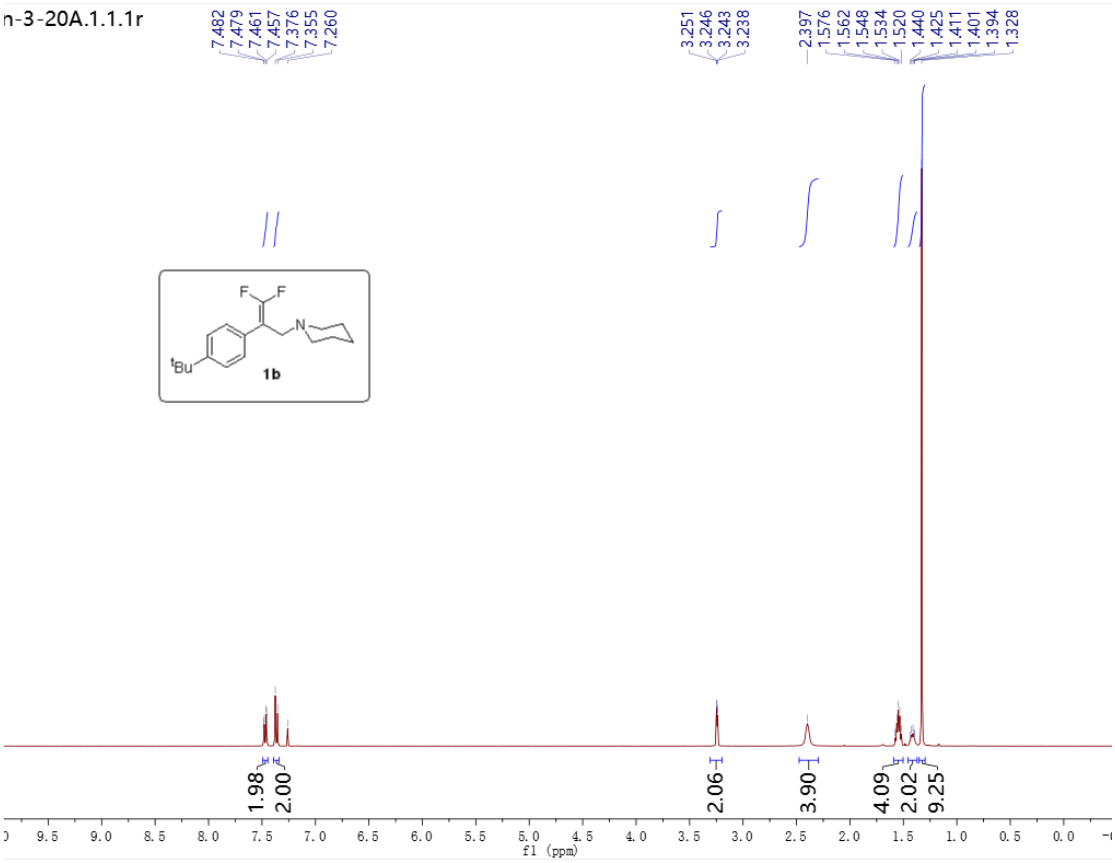
3,3-difluoro-2-(4-methoxyphenyl)-3-phenylpropane-1,2-diol



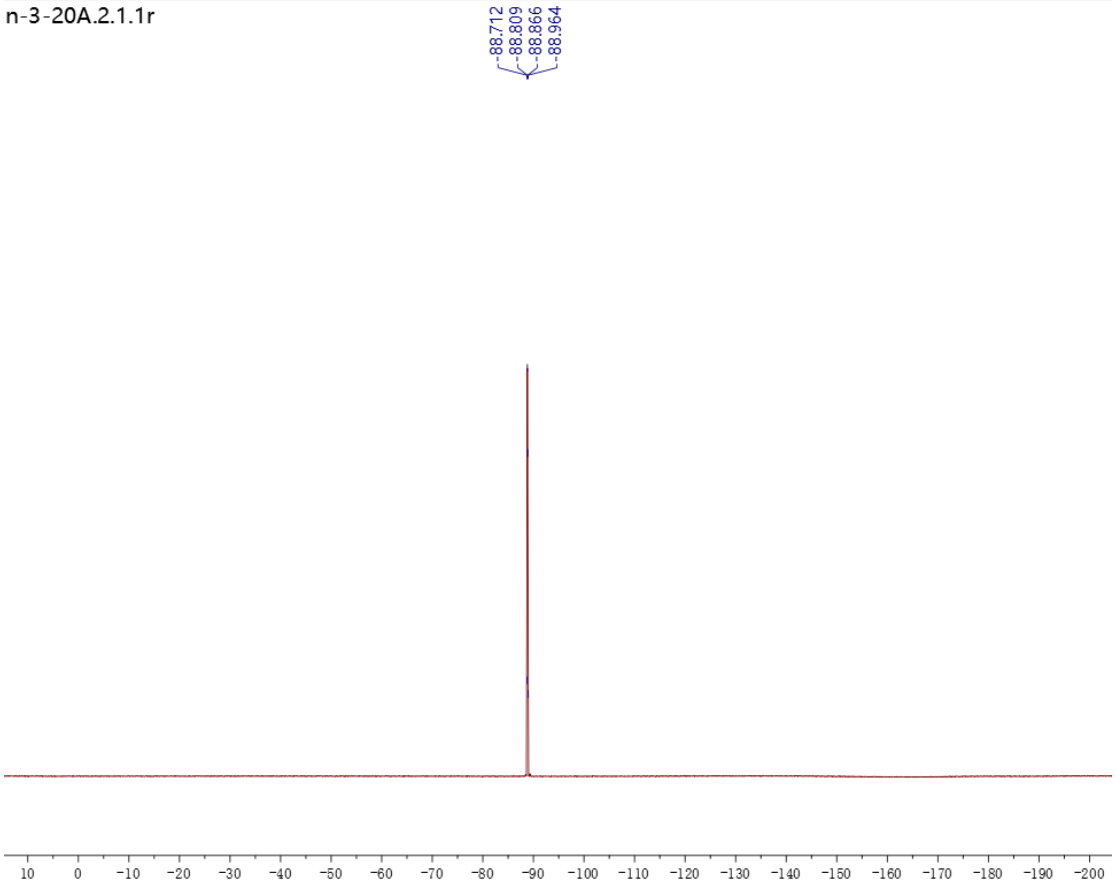
5b

Following the experiment procedure **E**, **5b** was obtained in 48% yield **^{1}H NMR (400 MHz, $CDCl_3$):** 7.34 (t, *J* = 7.0 Hz, 1H), 7.23 (dd, *J* = 8.2, 16.4 Hz, 4H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.04 (d, *J* = 11.6 Hz, 1H), 3.78 (s, 3H), 3.48 (s, 1H) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –105.04 (d, *J* = 246.48 Hz), –106.83 (d, *J* = 246.53 Hz) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.2, 65.0 (t, *J* = 2.7 Hz), 78.0 (dd, J = 25.8, 29.4 Hz), 113.4, 122.6 (t, *J* = 251.0 Hz), 126.9 (t, *J* = 6.5 Hz), 127.4, 128.1, 129.3 (d, *J* = 3.6 Hz), 129.7, 133.6 (t, *J* = 25.8 Hz), 159.4 ppm; **HRMS (ESI, m/z):** calculated for $[M+H]^+$: 295.1146, found: 295.1141.

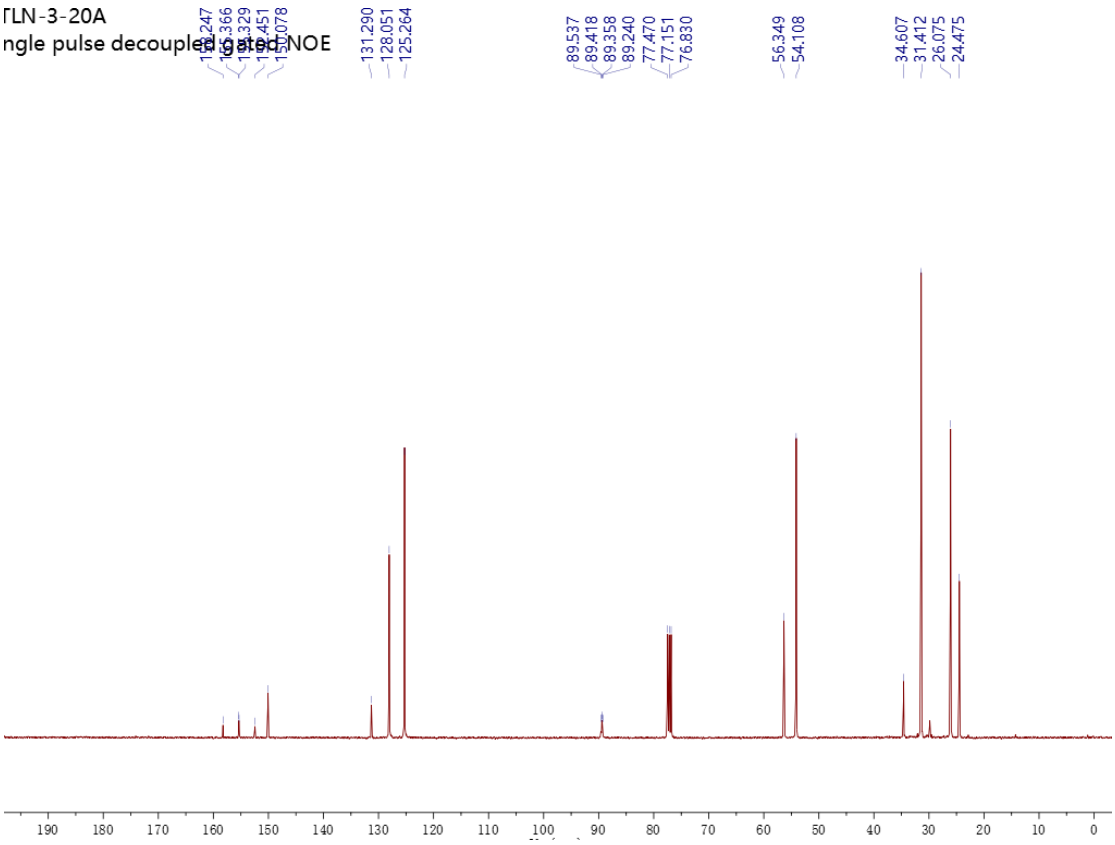
n-3-20A.1.1.1r



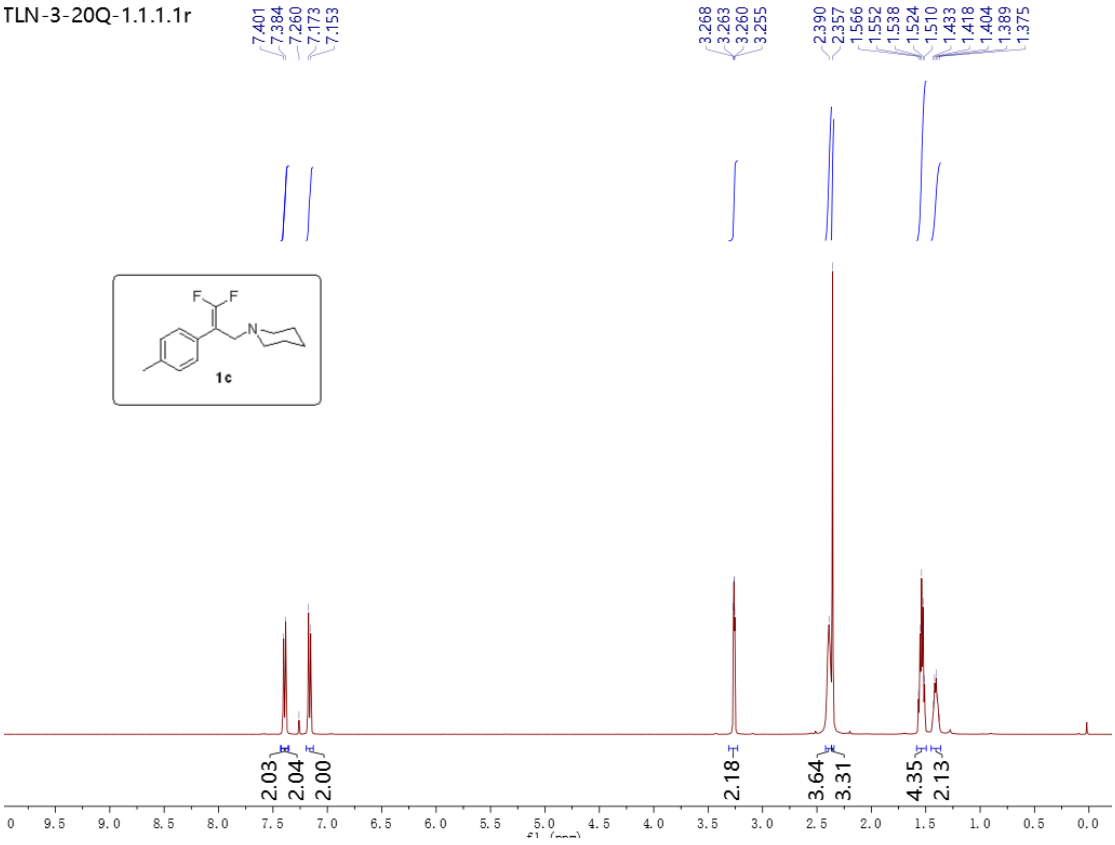
n-3-20A.2.1.1r



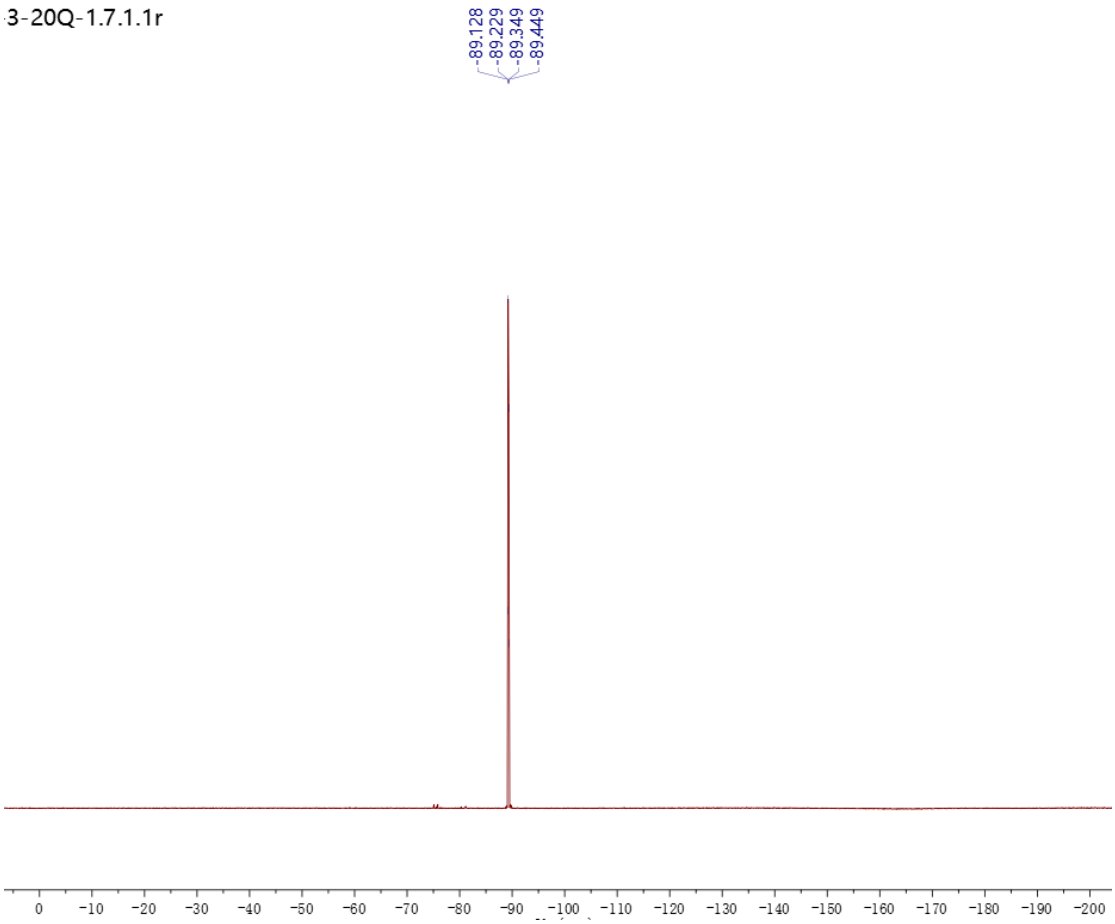
TLN-3-20A
ngle pulse decoupled gated NOE



TLN-3-20Q-1.1.1.1r



3-20Q-1.7.1.1r



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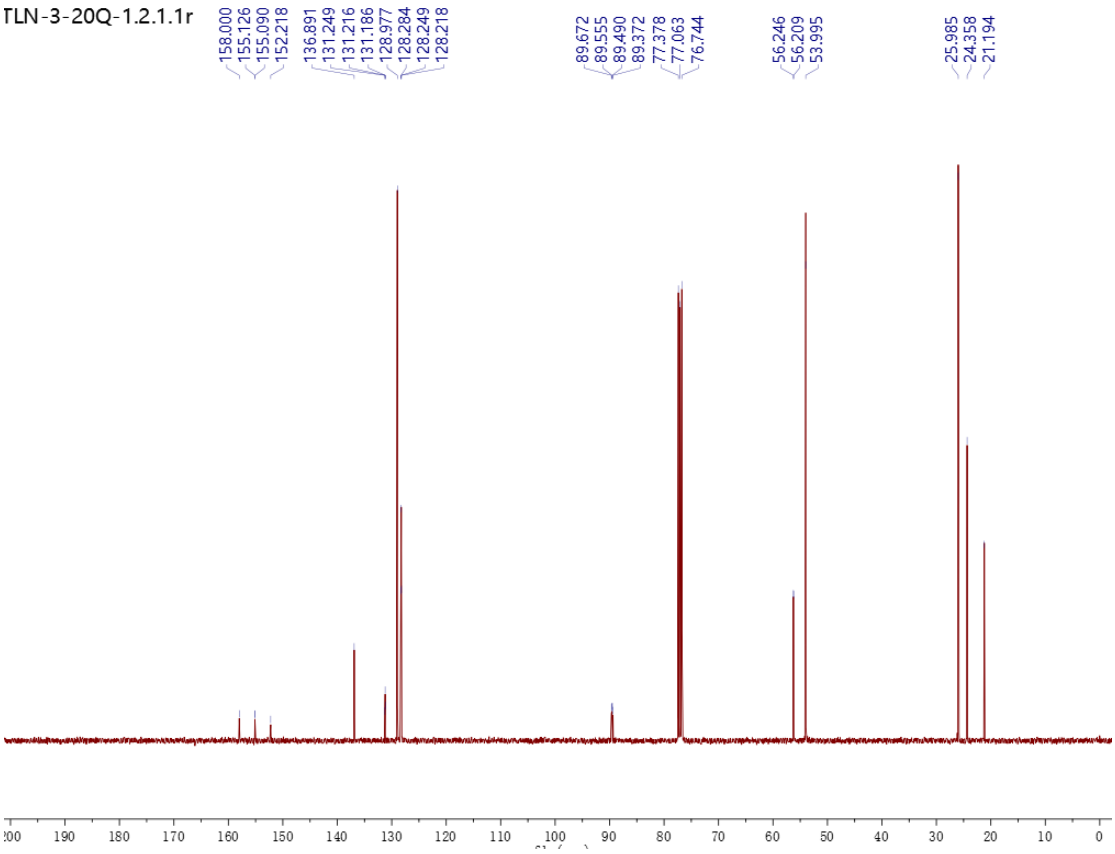

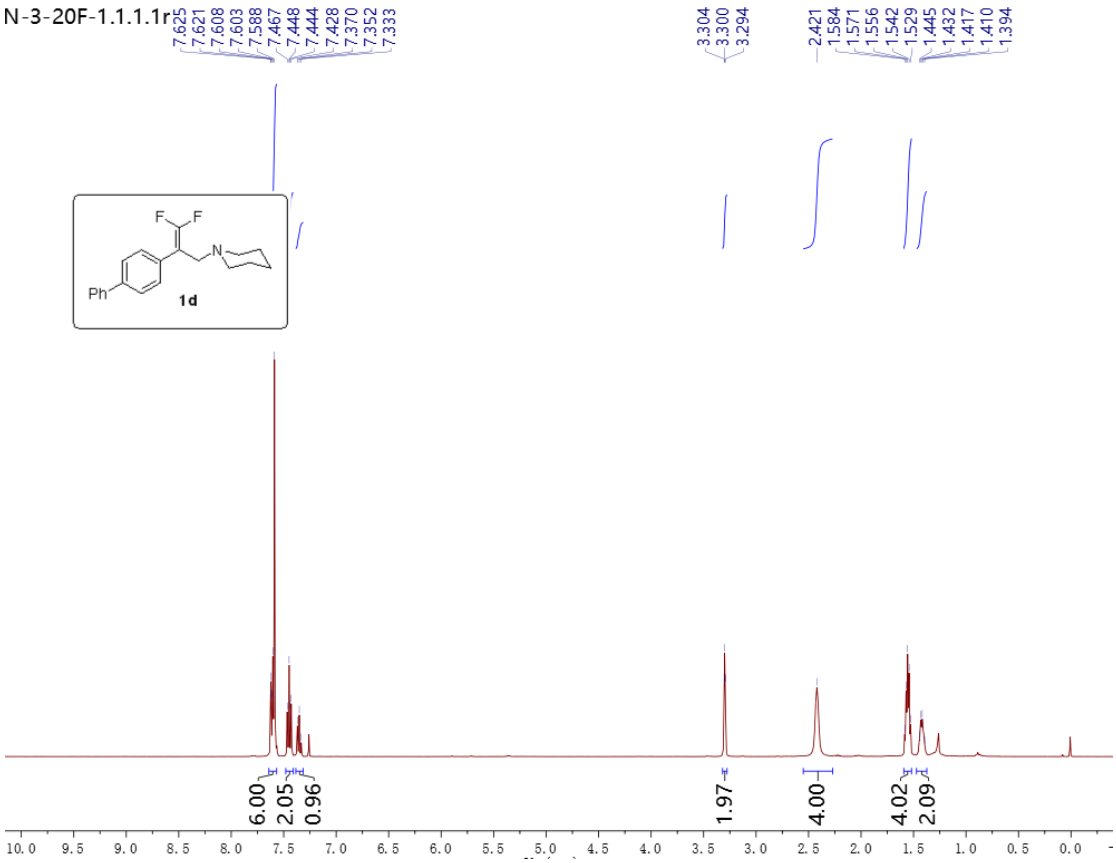
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7.444
7.428
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7.333
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1.542
1.529
1.445
1.432
1.417
1.410
1.394
F
F
N
Ph
1d
6.00
2.05
0.96
1.97
4.00
4.02
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
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2.0
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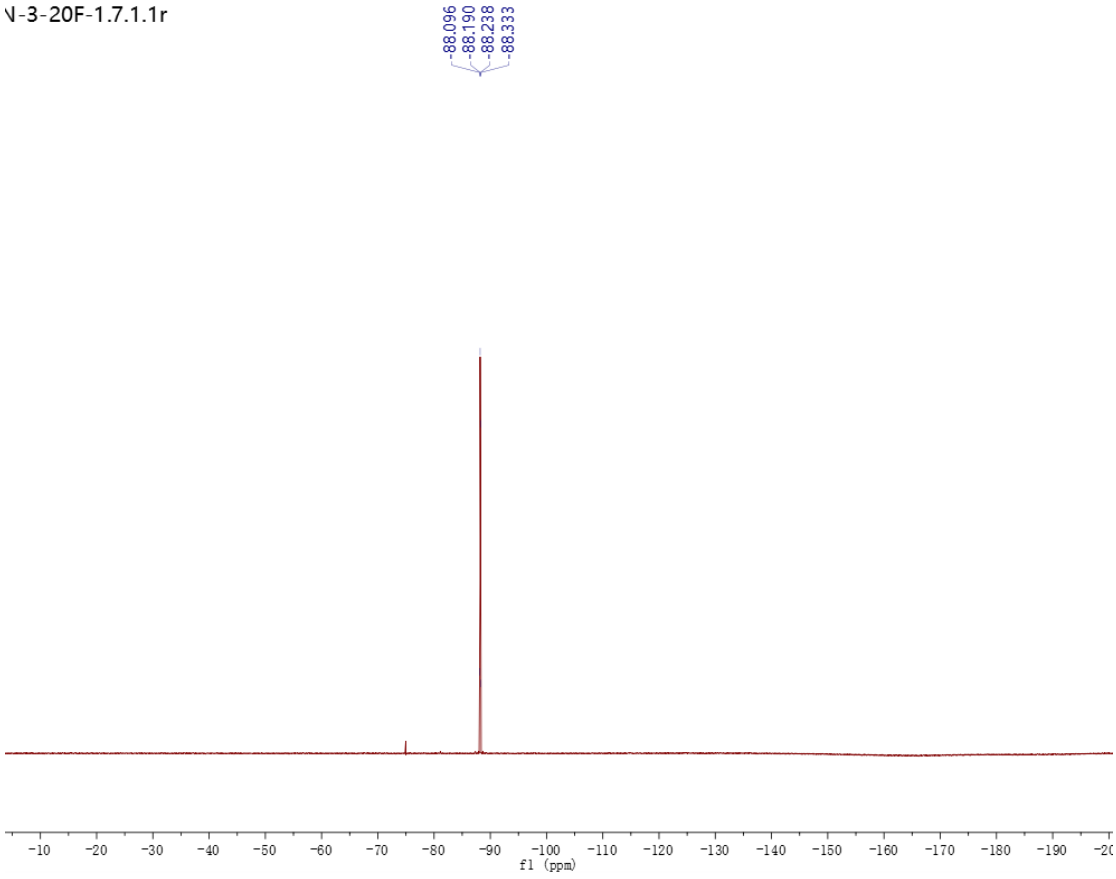
0.0


N-3-20F-1.7.1.1r
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-30
-40
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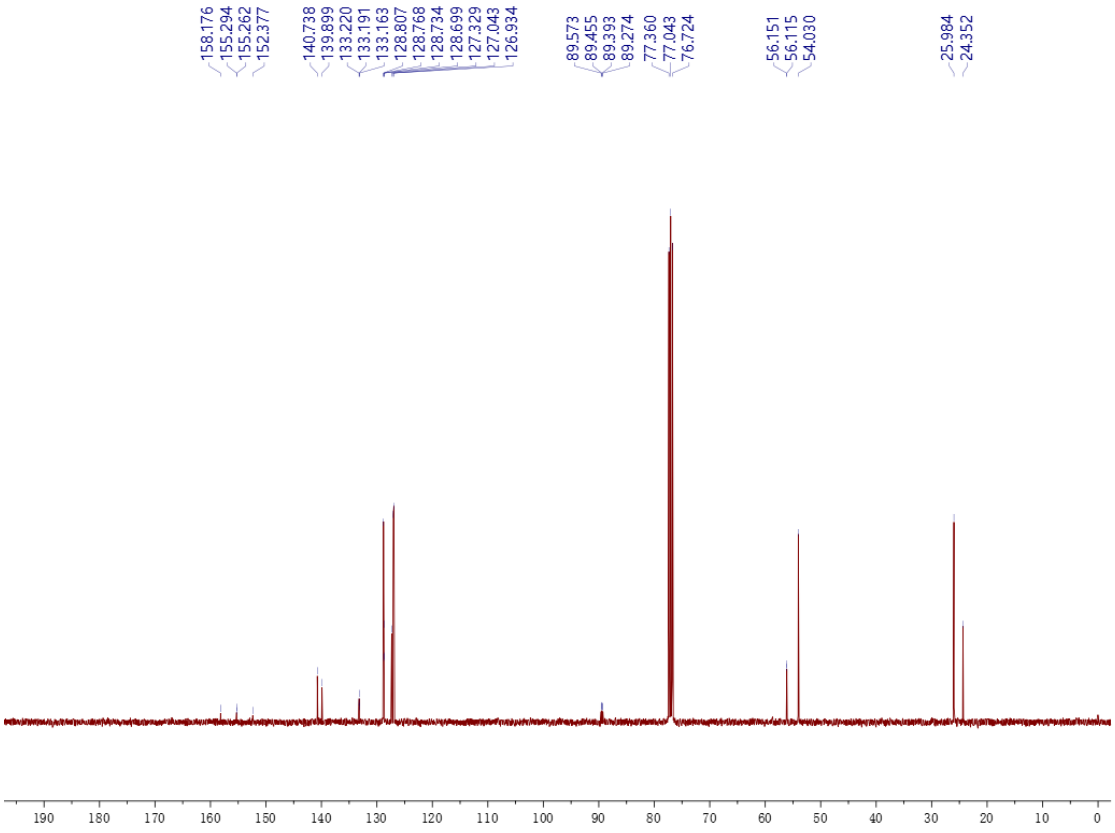
-150
-160
-170
-180
-190
f1 (ppm)


158.176
155.294
155.262
152.377
140.738
139.899
133.220
133.191
133.163
128.807
128.768
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128.699
127.329
127.043
126.934
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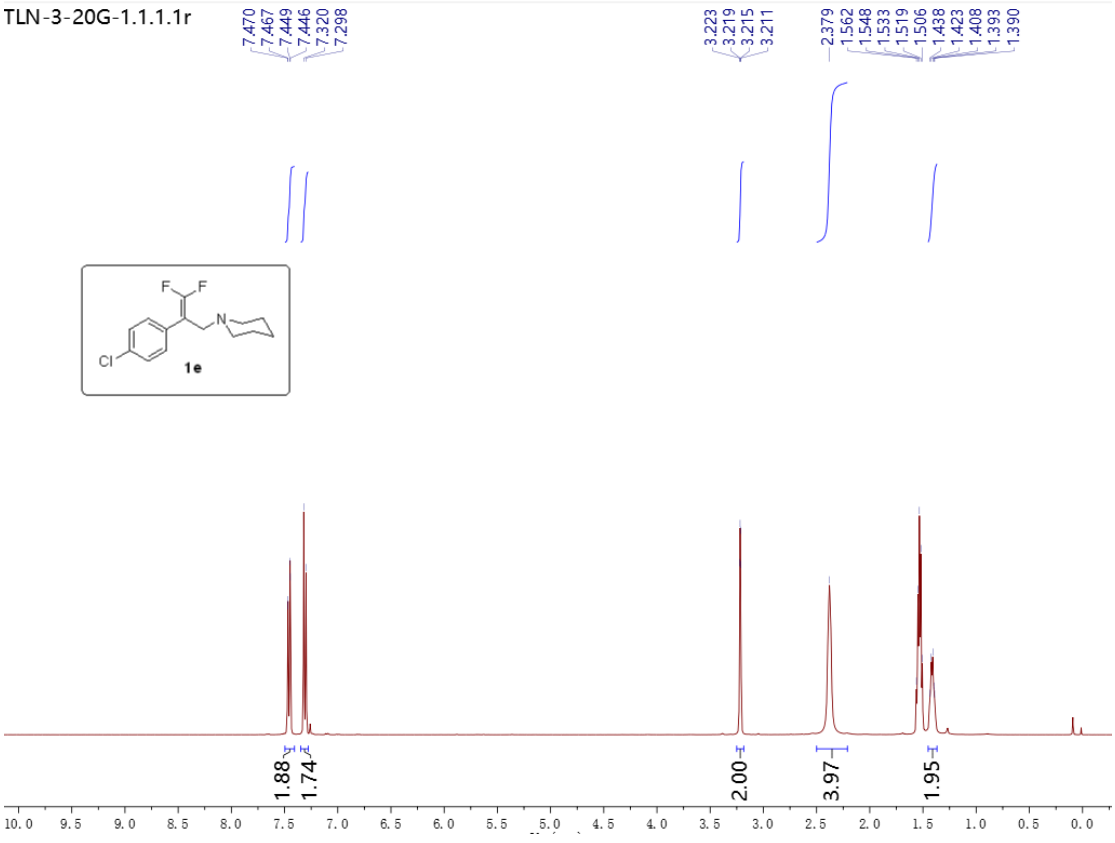
56.115
54.030
25.984
24.352


TLN-3-20G-1.1.1.1r
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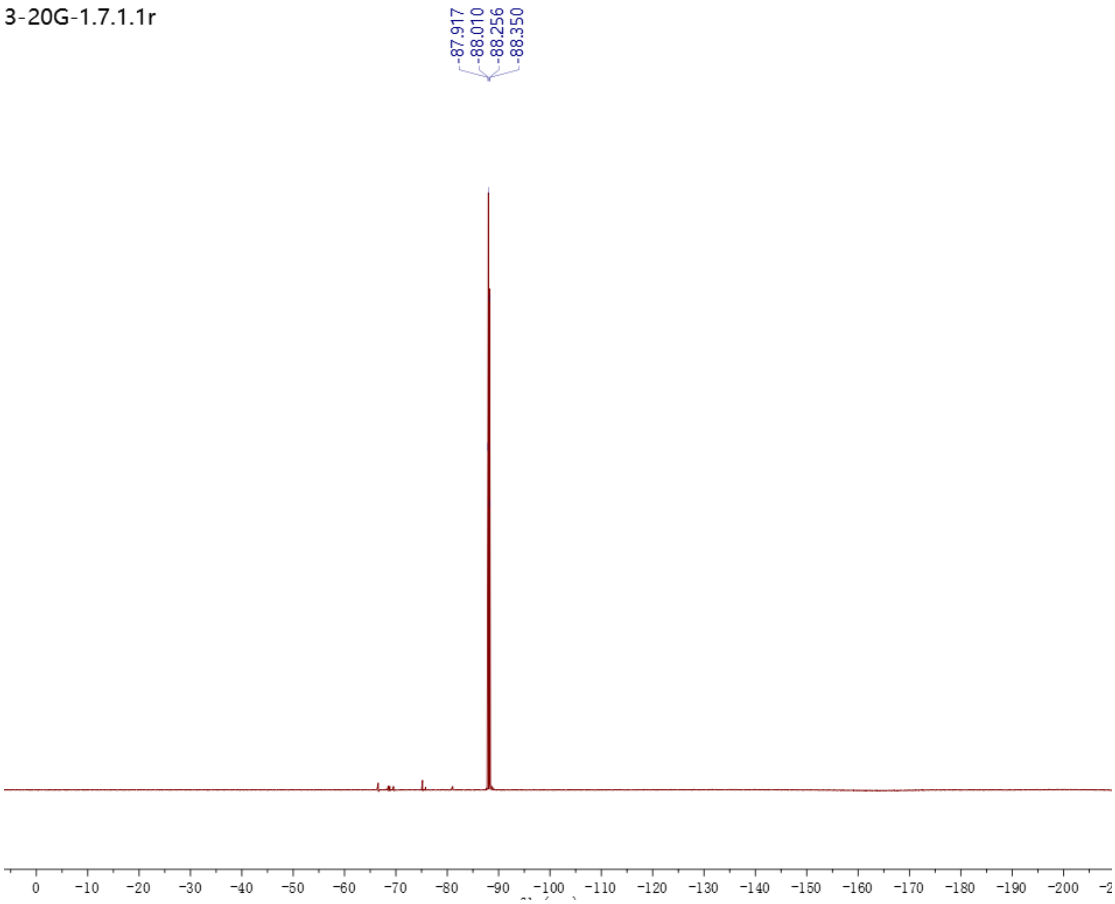
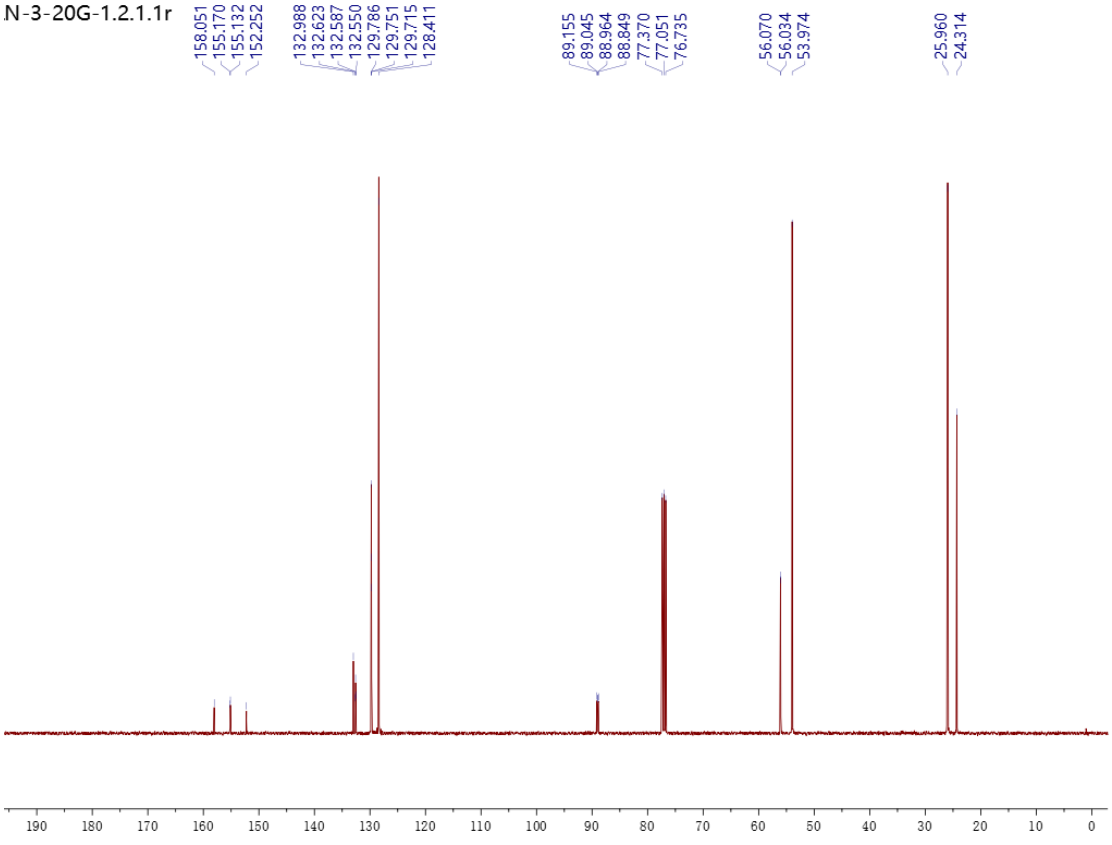
3.219
3.215
3.211
2.379
1.562
1.548
1.533
1.519
1.506
1.438
1.423
1.408
1.393
1.390
F
F
N
Cl
1e
1.88
1.74
2.00
3.97
1.95

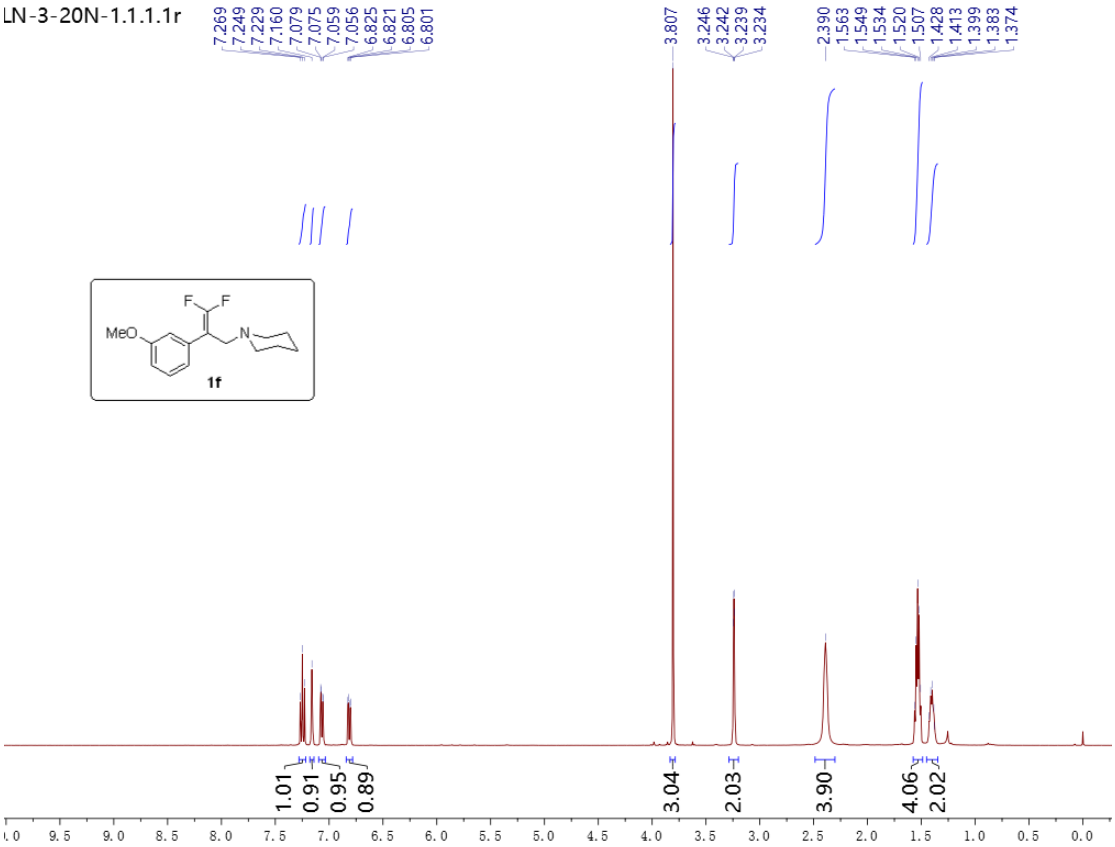
3-20G-1.7.1.1r



N-3-20G-1.2.1.1r



LN-3-20N-1.1.1.1r



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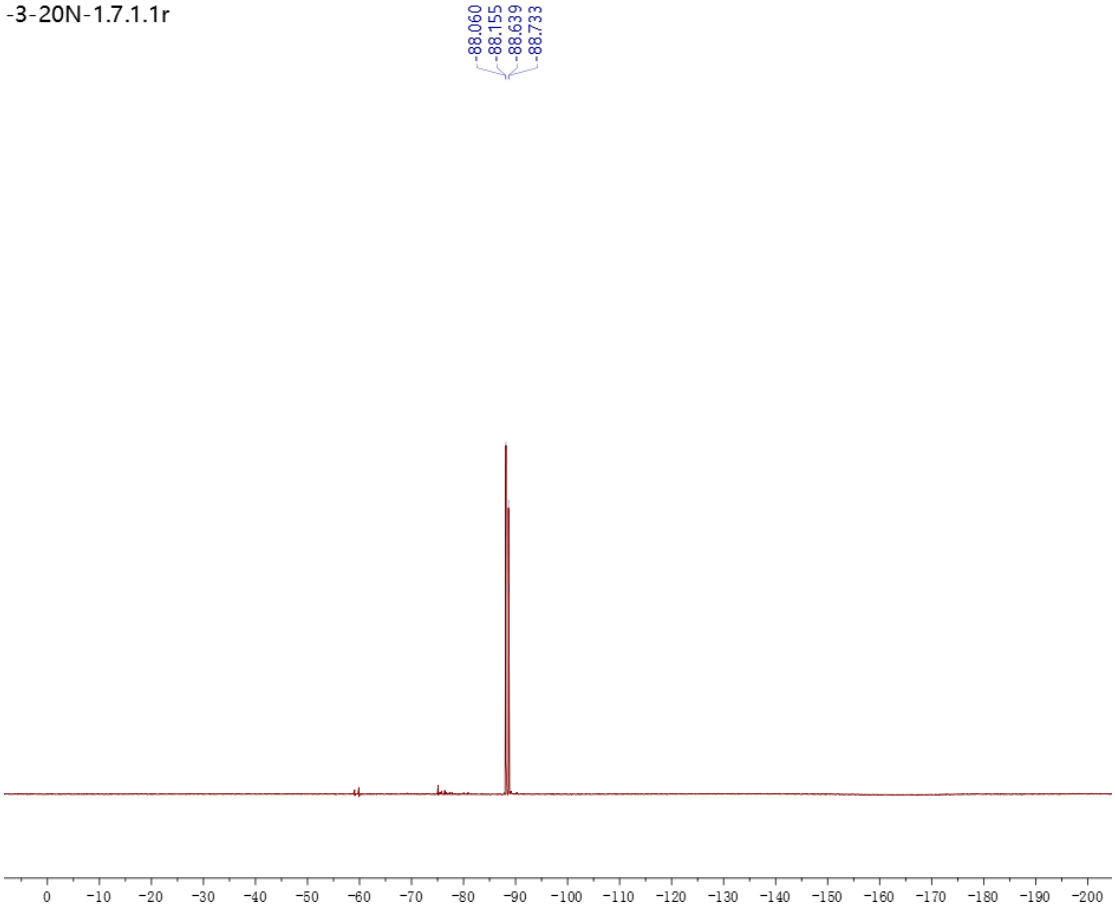

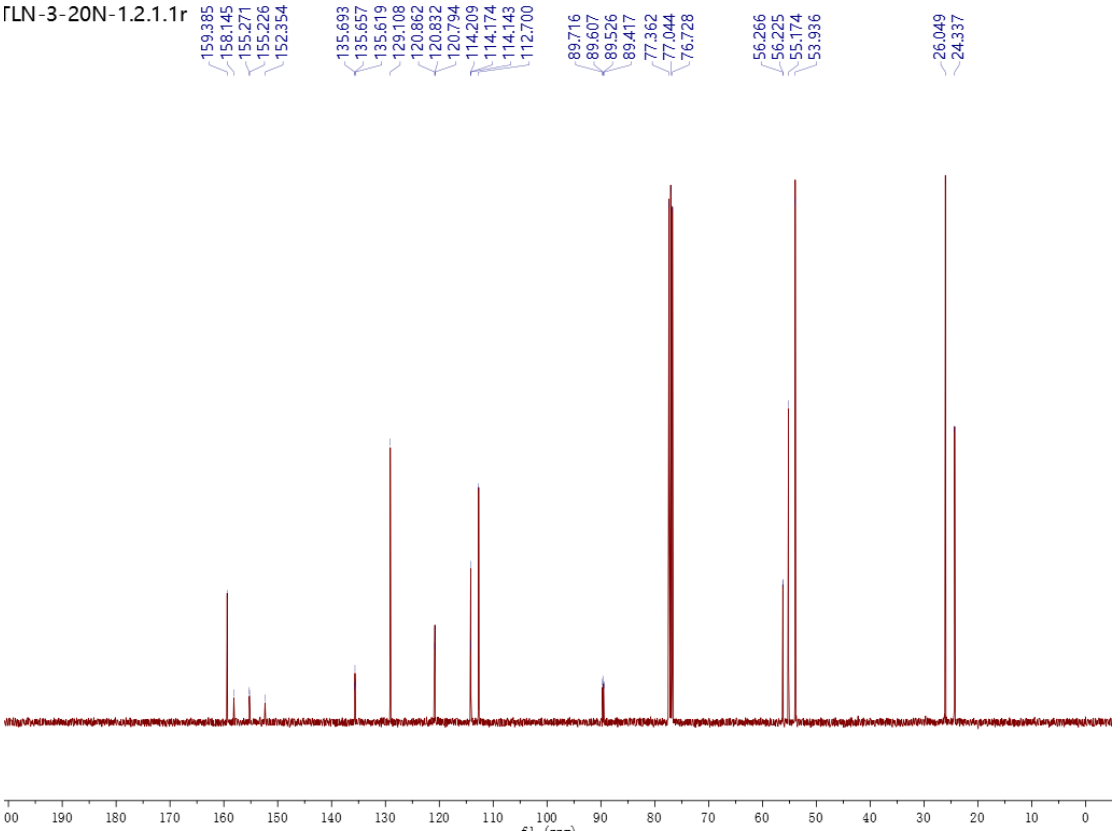
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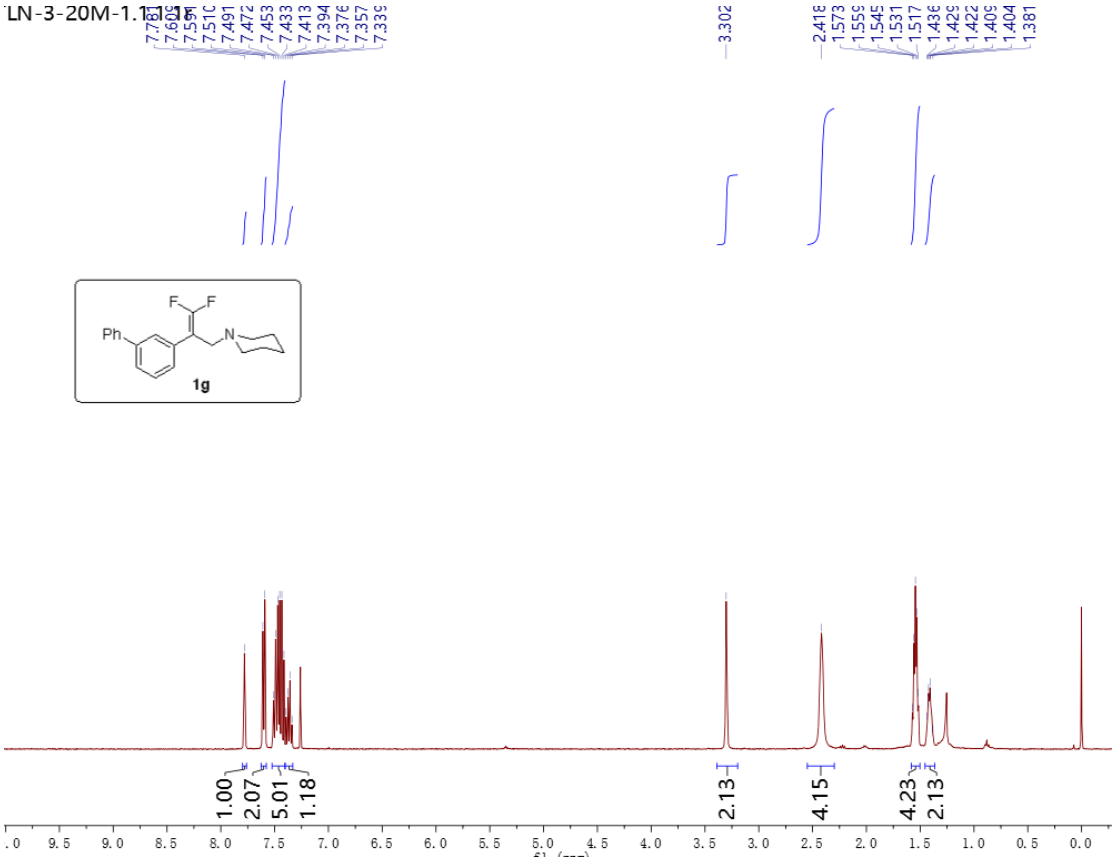
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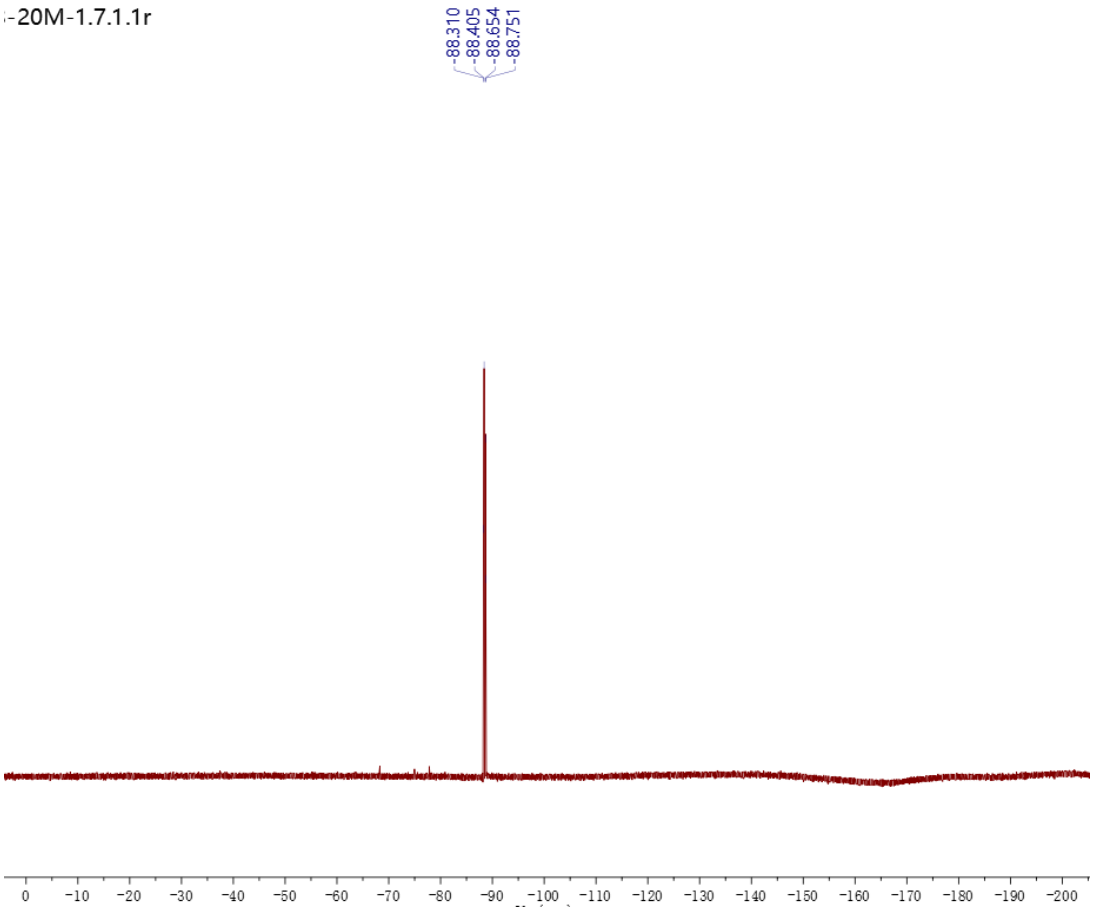
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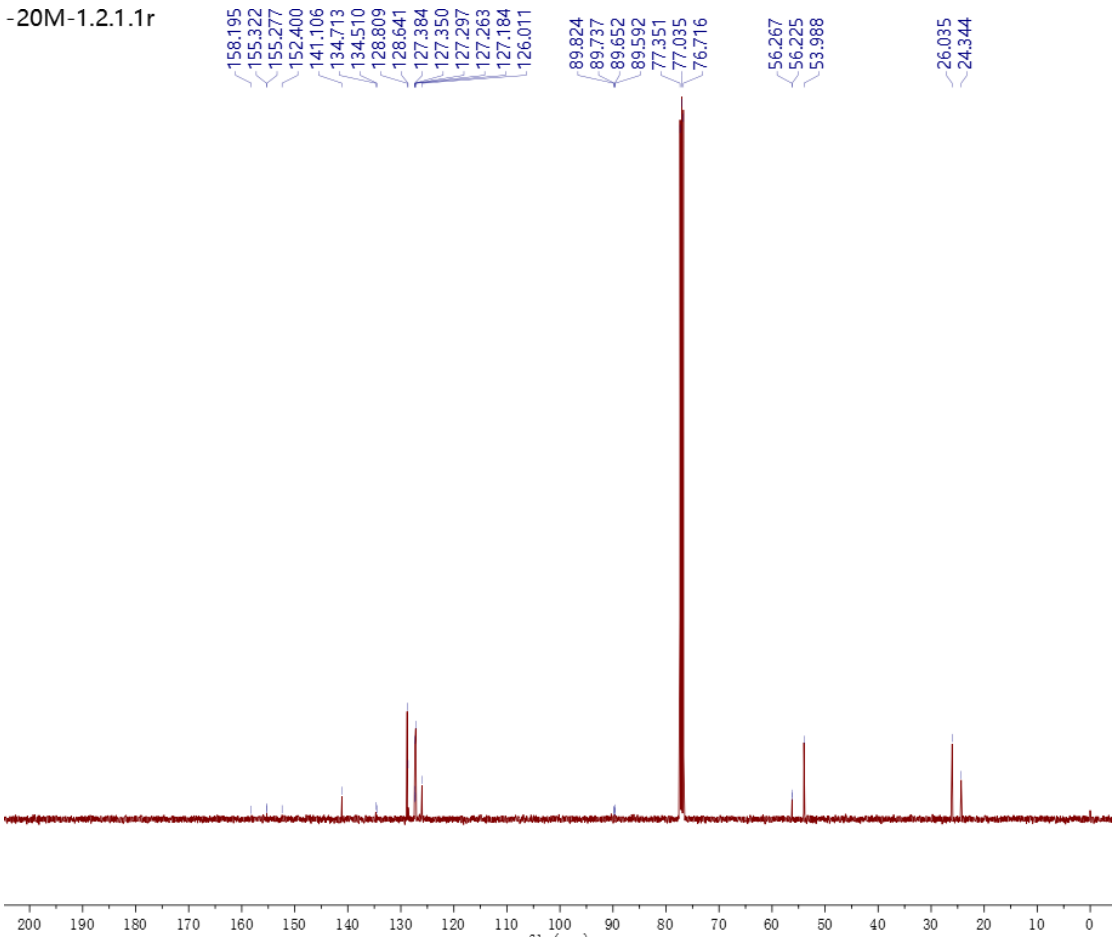
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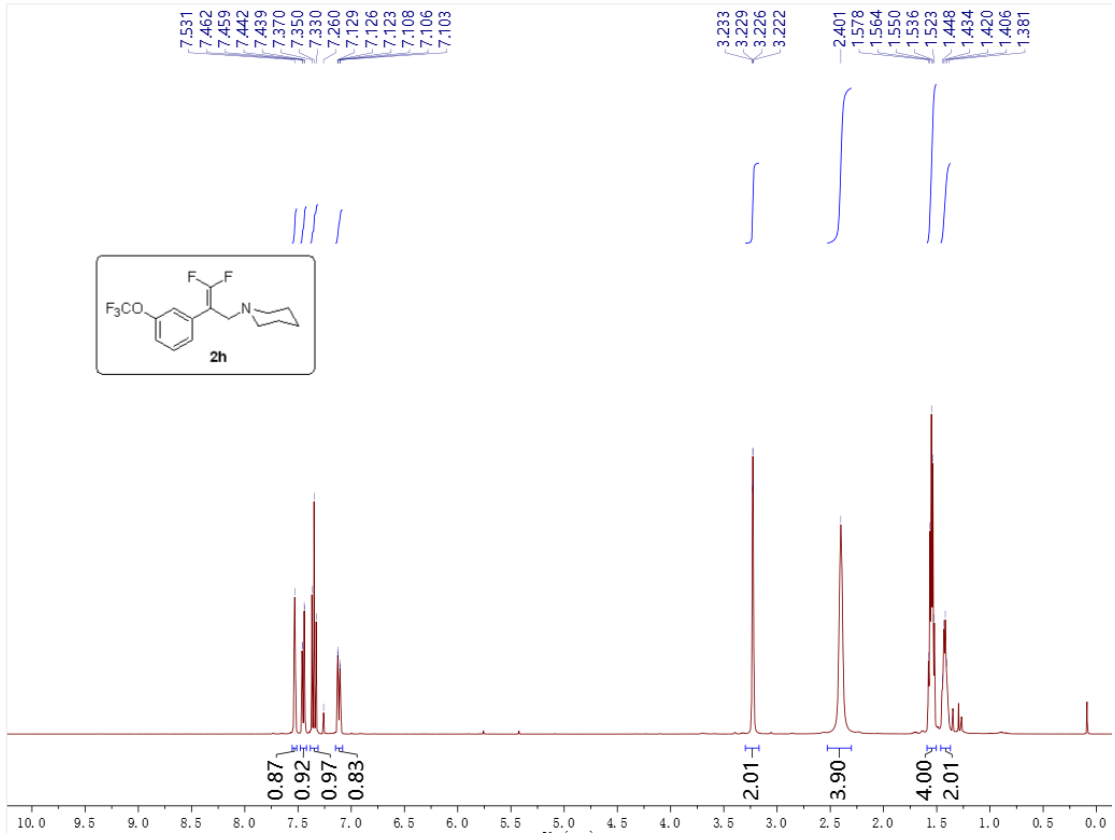
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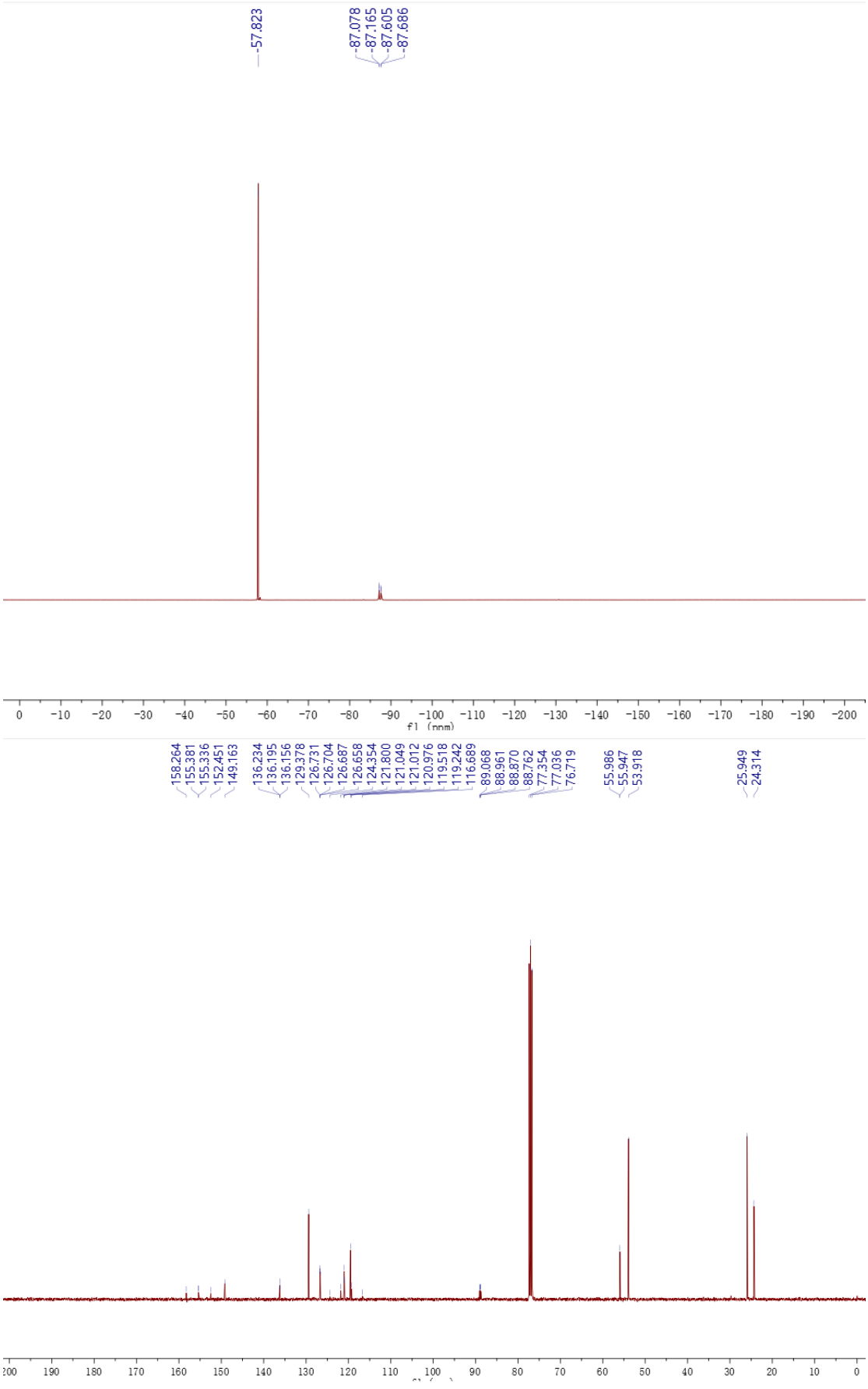
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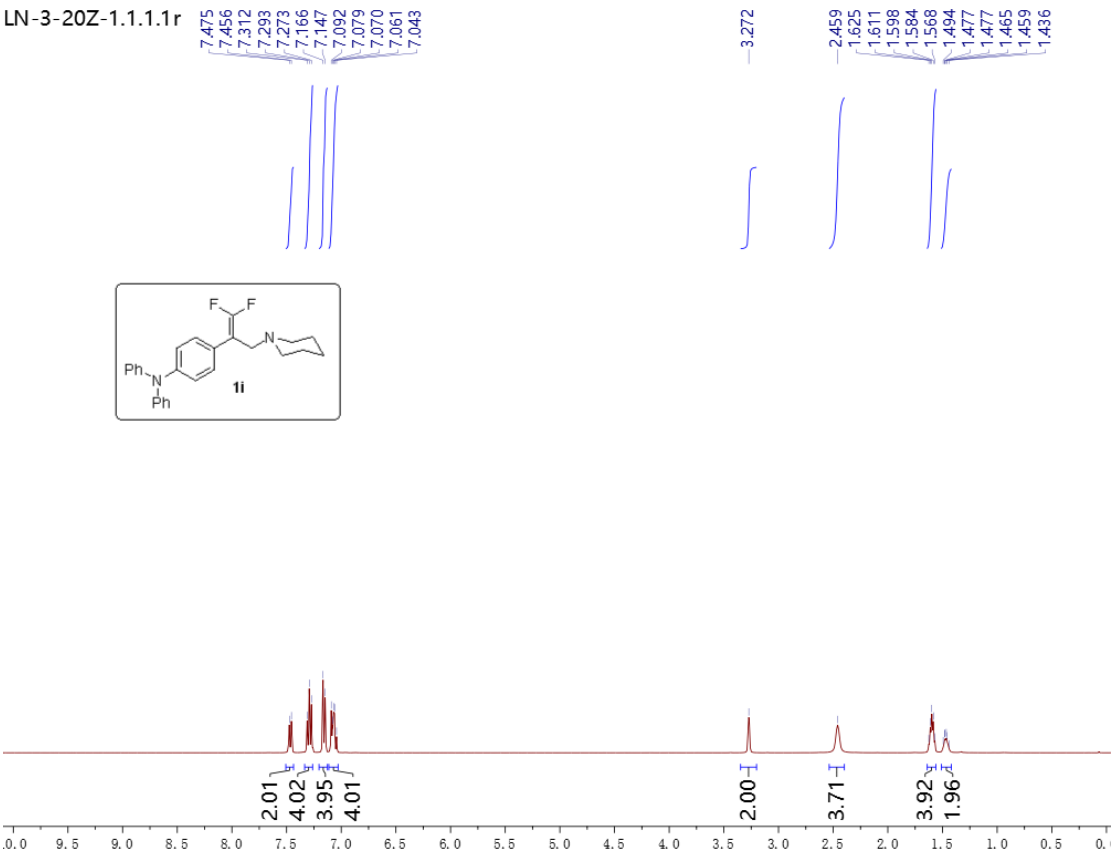
LN-3-20Z-1.1.1.1r



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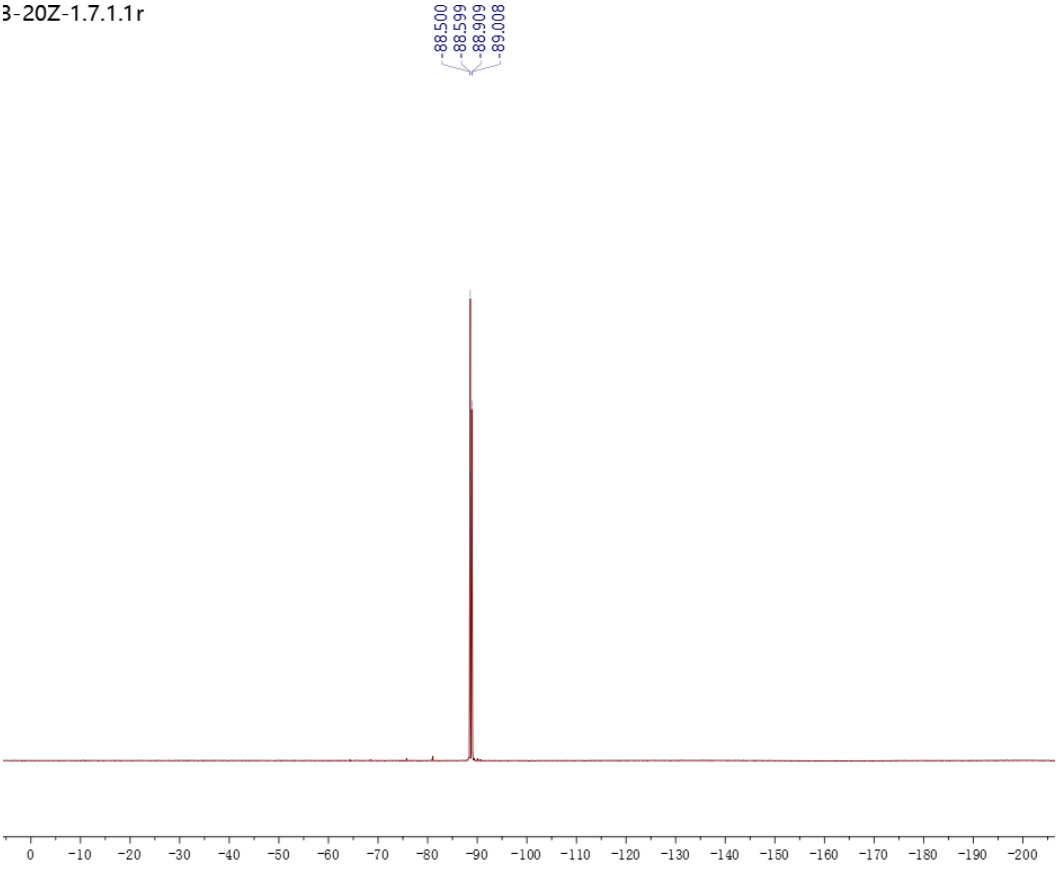

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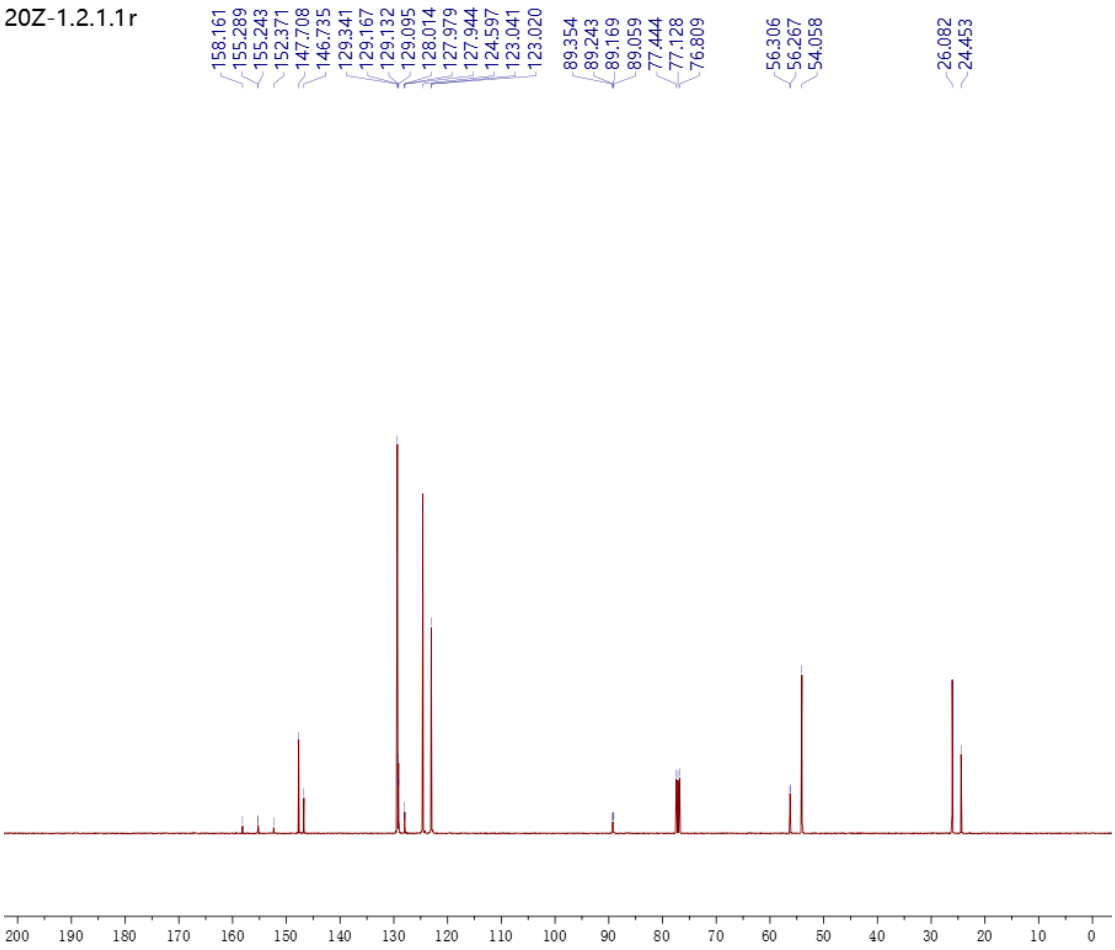
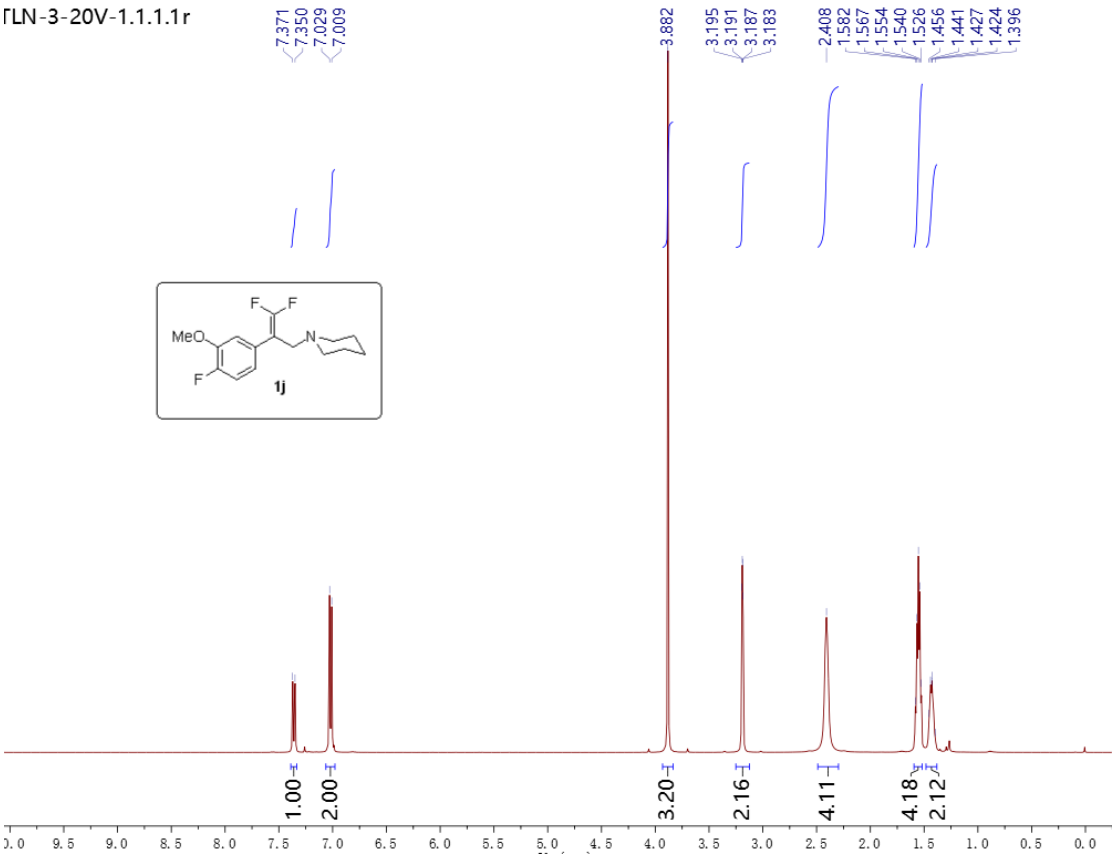


ΓLN-3-20V-1.1.1.1r



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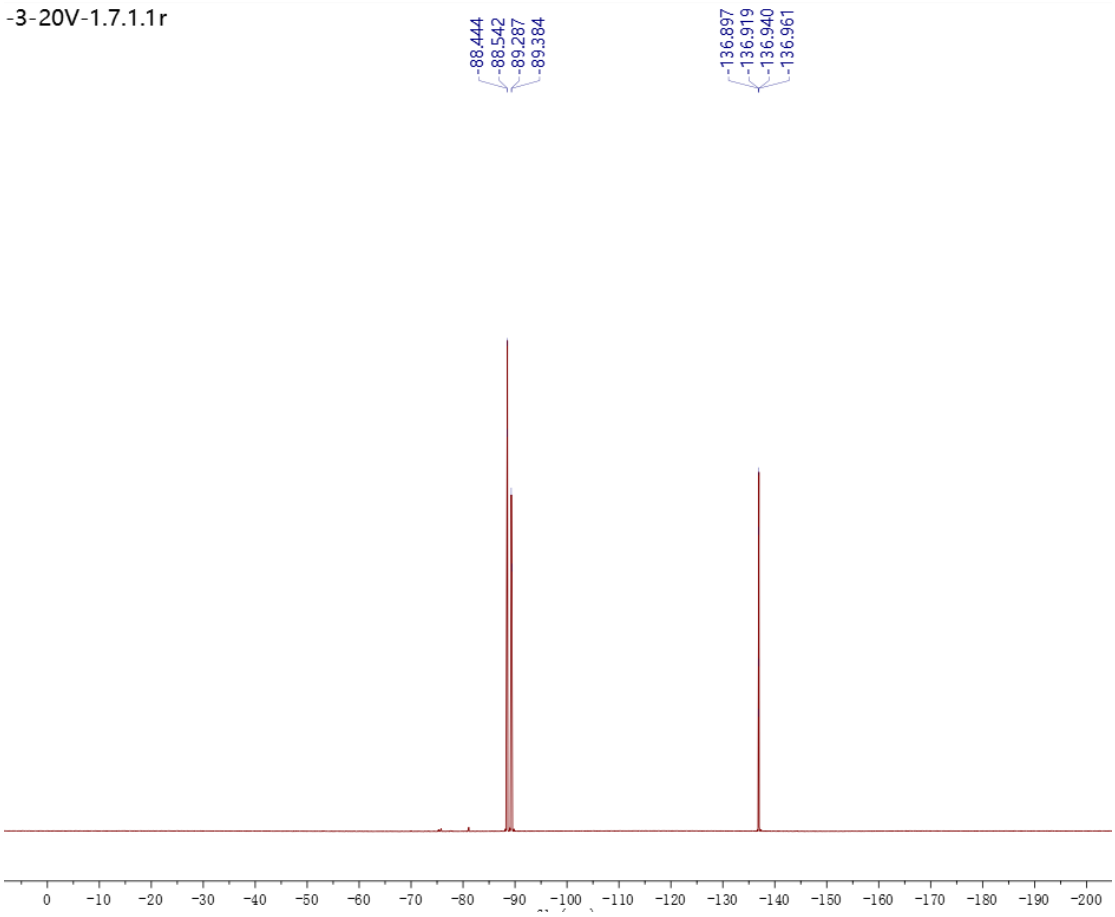

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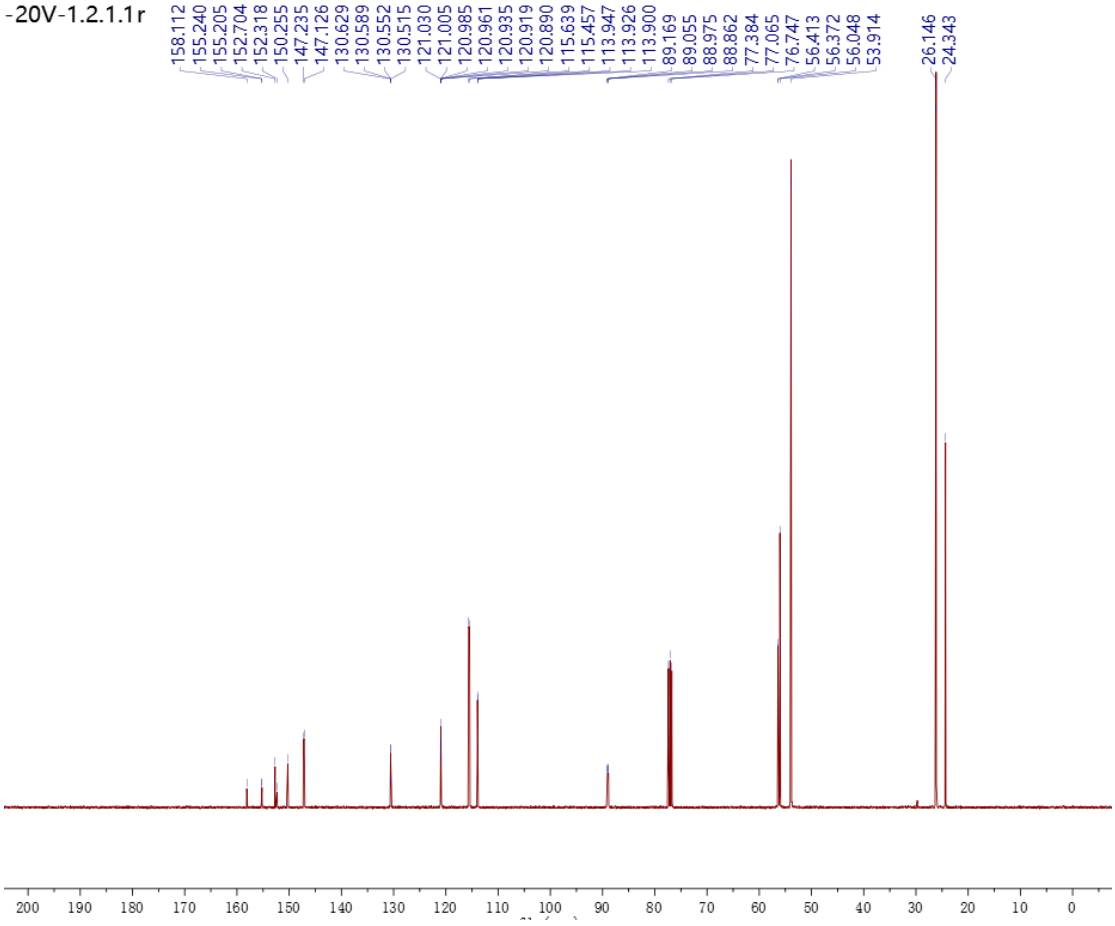

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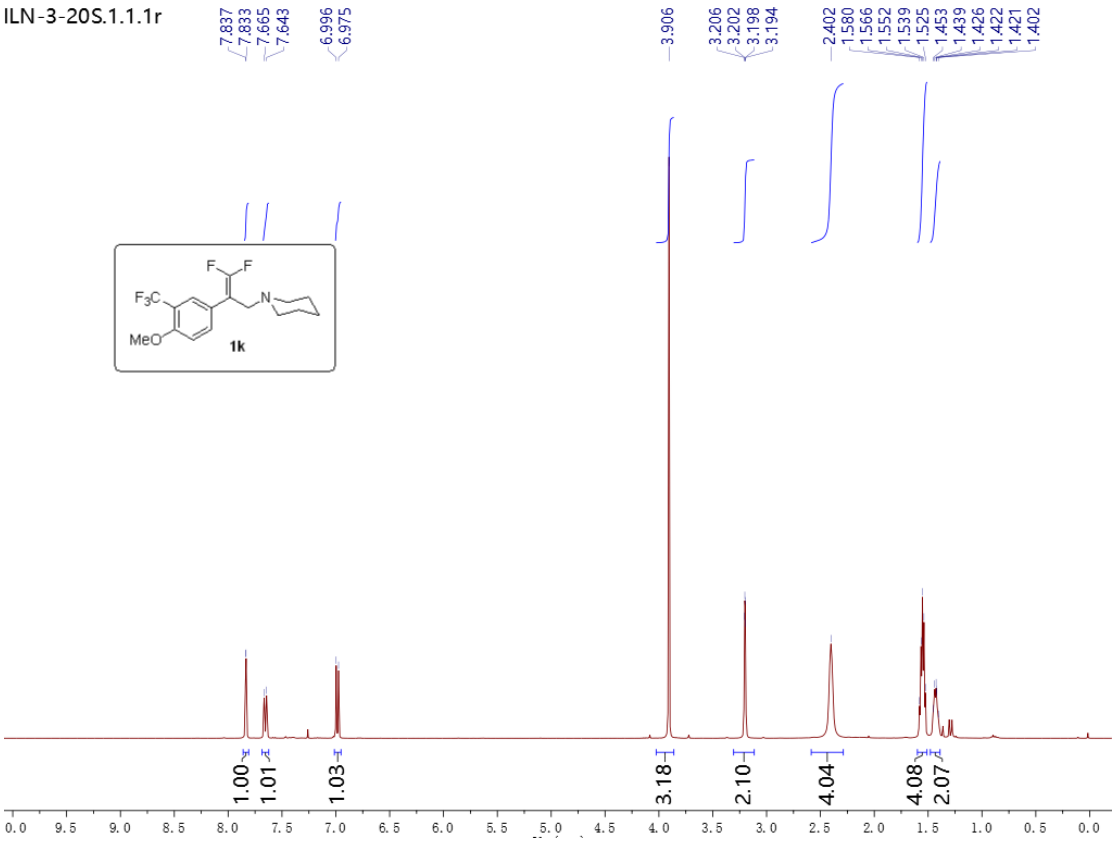

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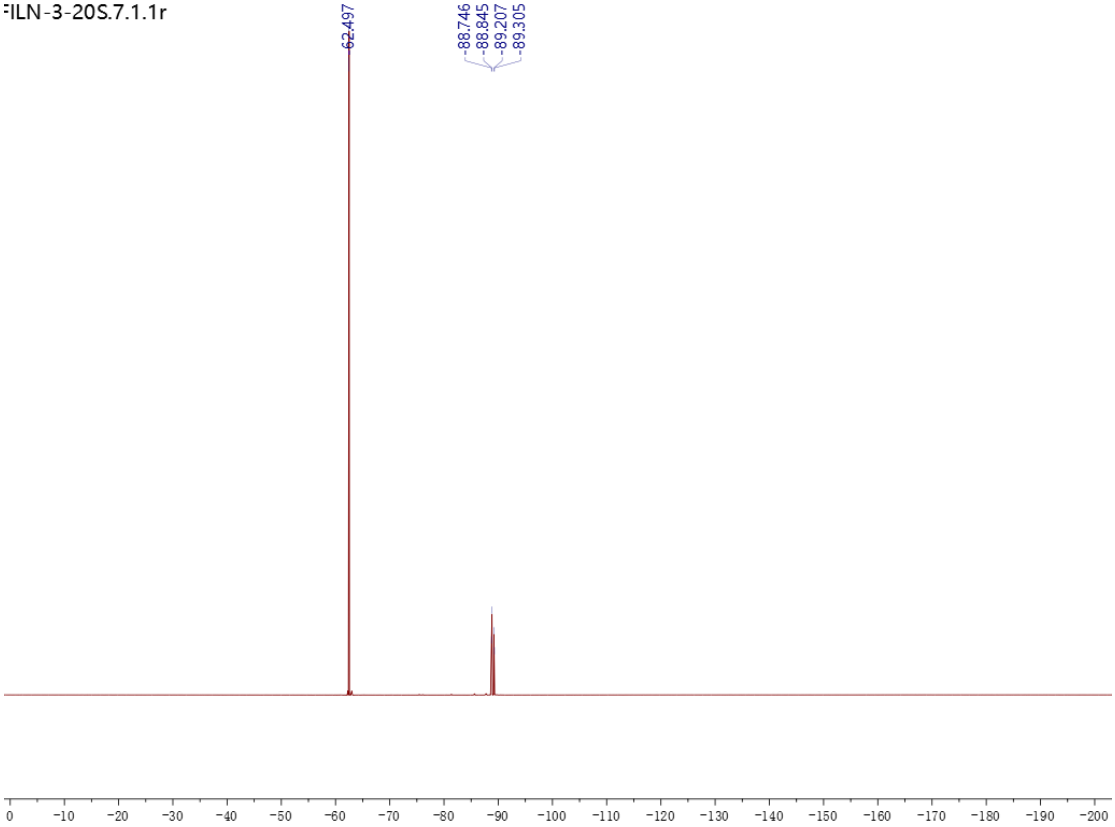

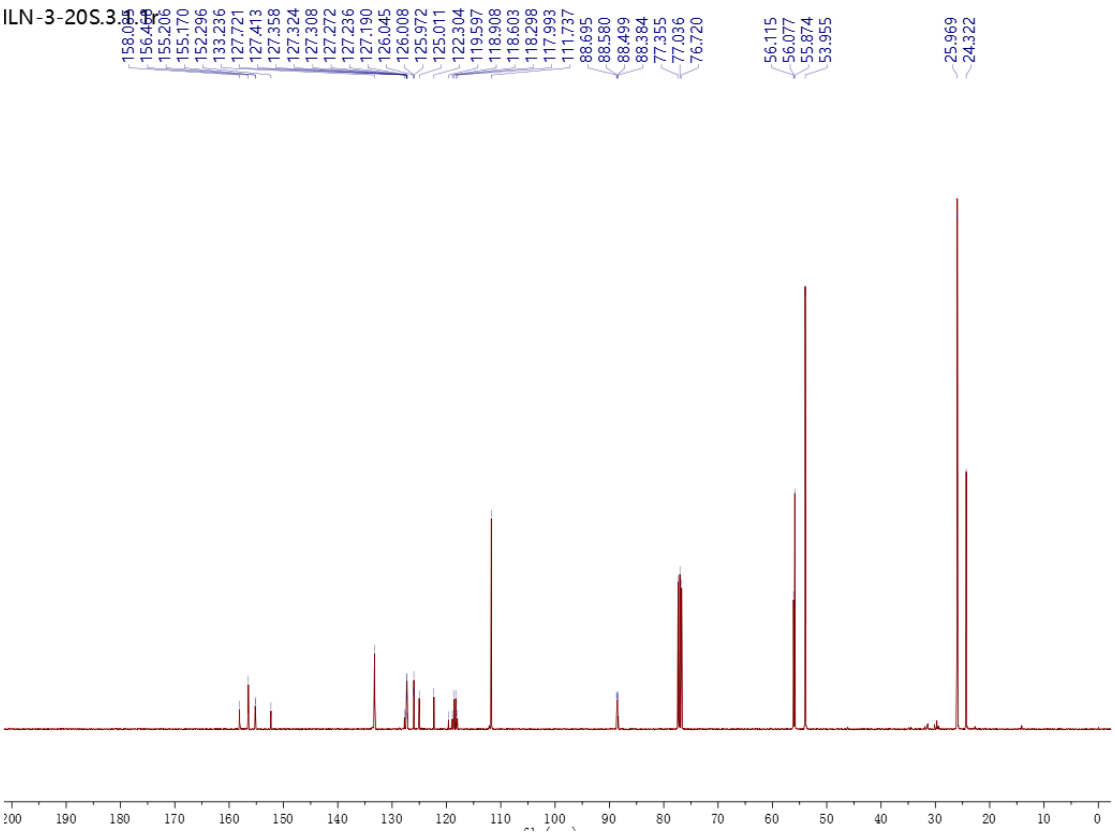
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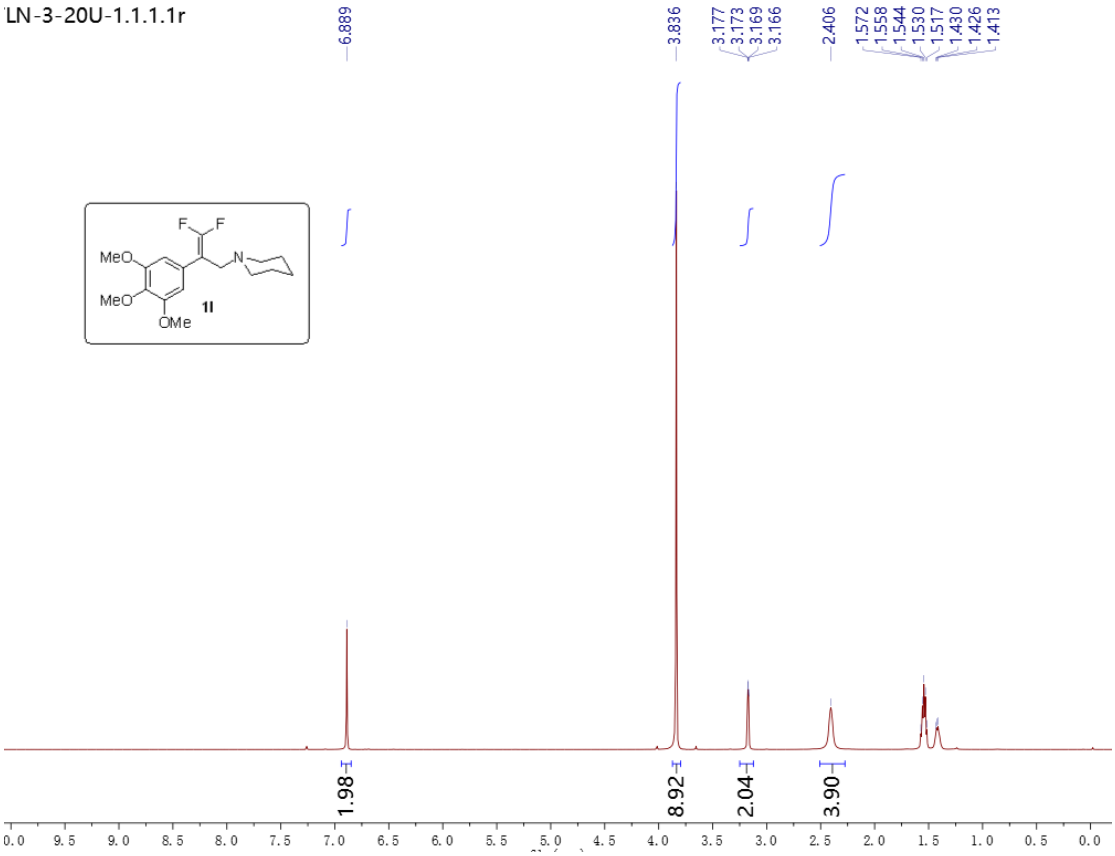
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1.517
1.430
1.426
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MeO
OMe
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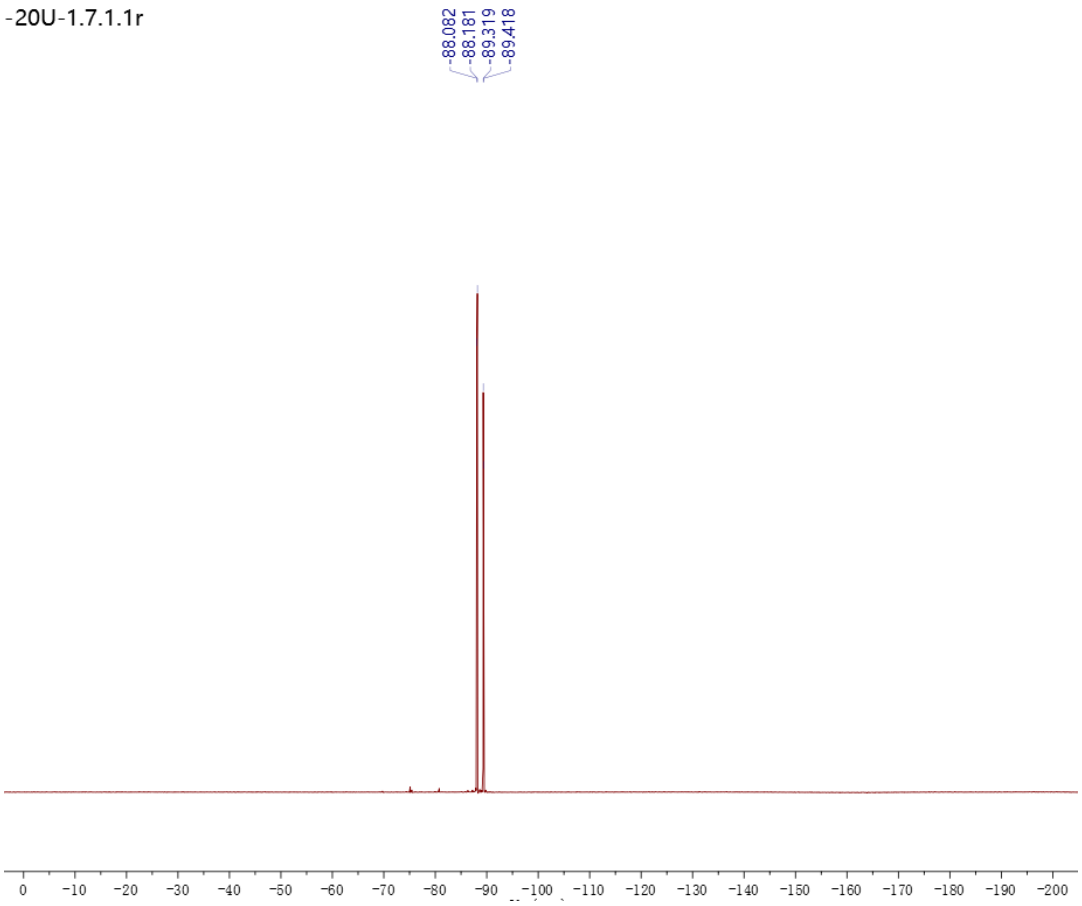
2.04
3.90

-20U-1.7.1.1r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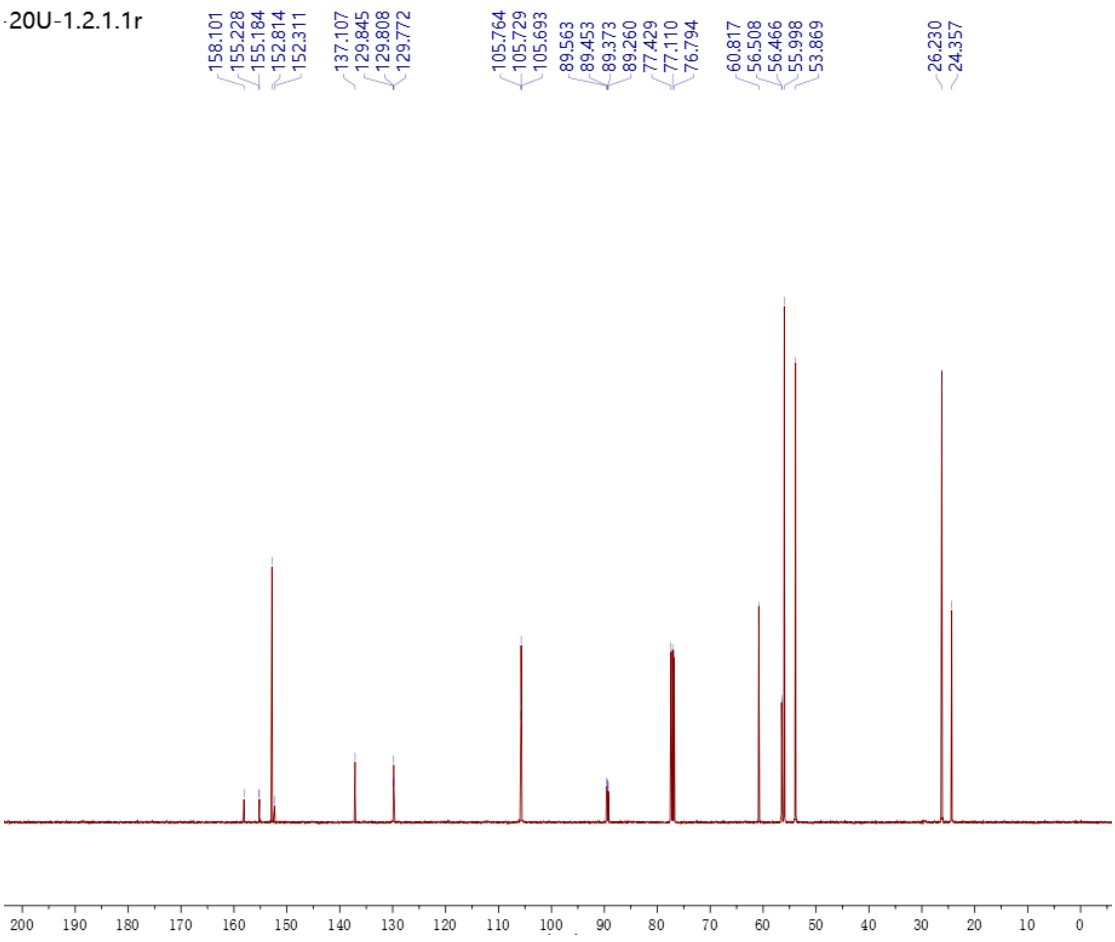
-200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76.794
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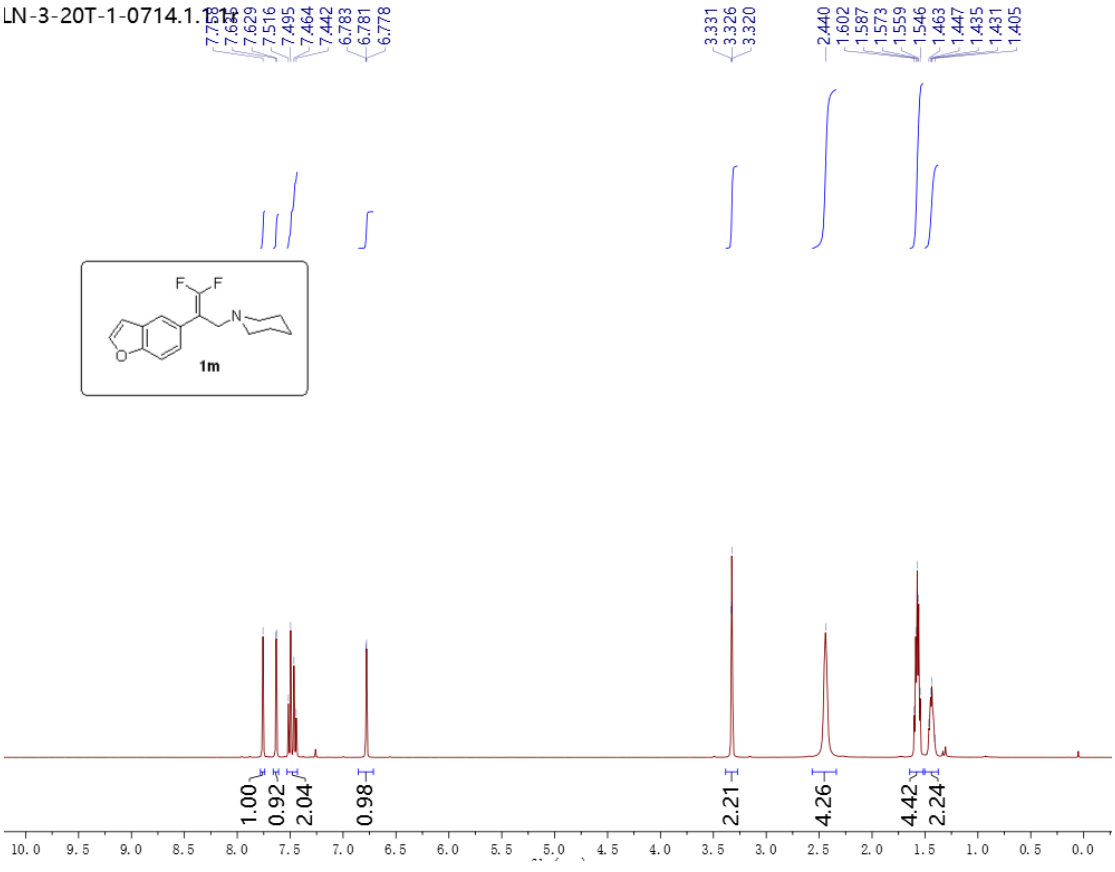
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1.587
1.573
1.559
1.546
1.463
1.447
1.435
1.431
1.405
F
F
N
O
1m
1.00
0.92
2.04
0.98
2.21
4.26
4.42
2.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

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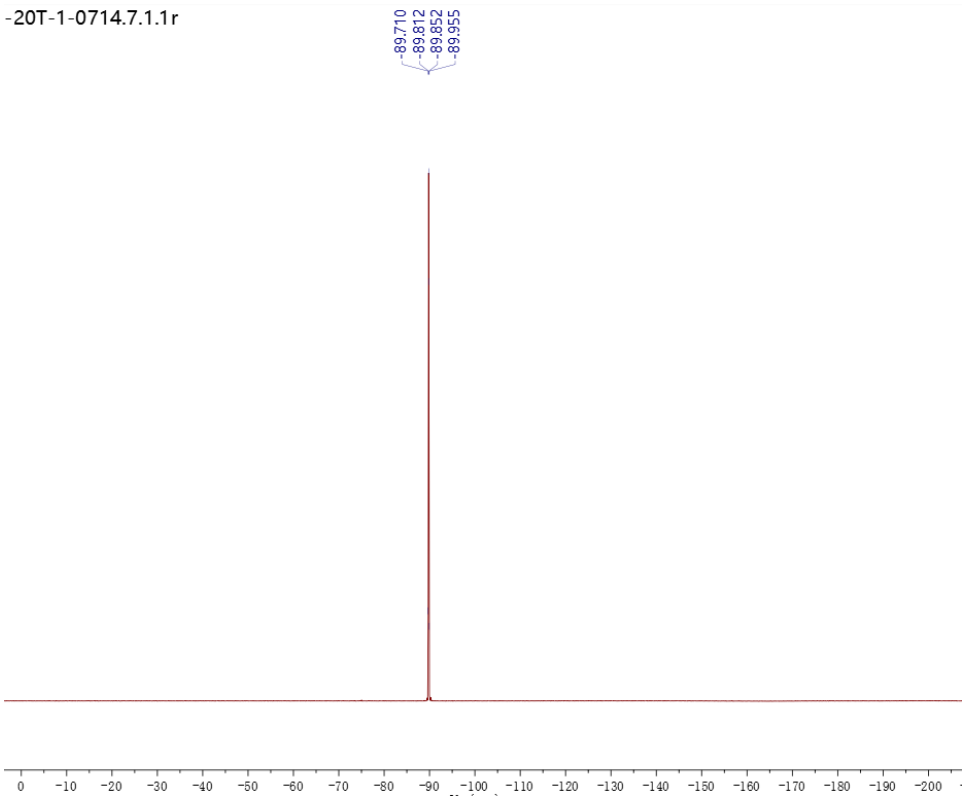

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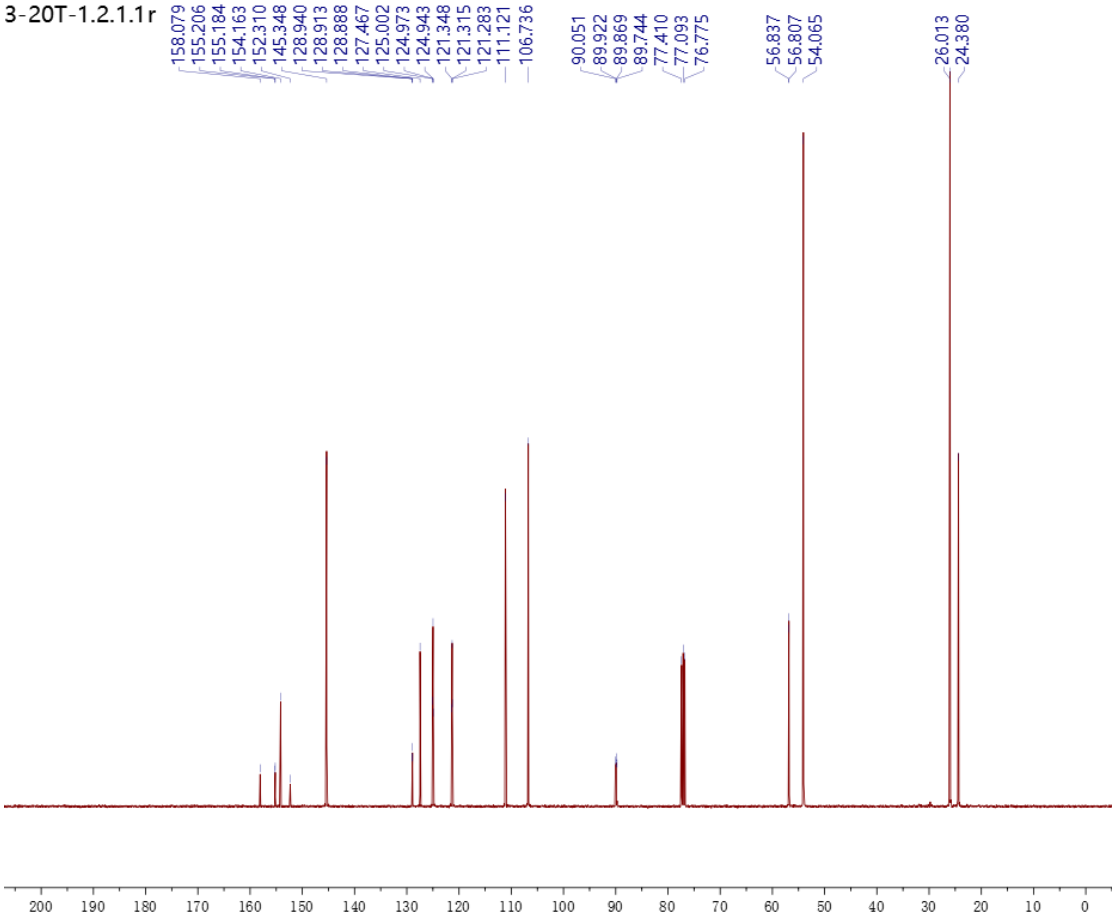

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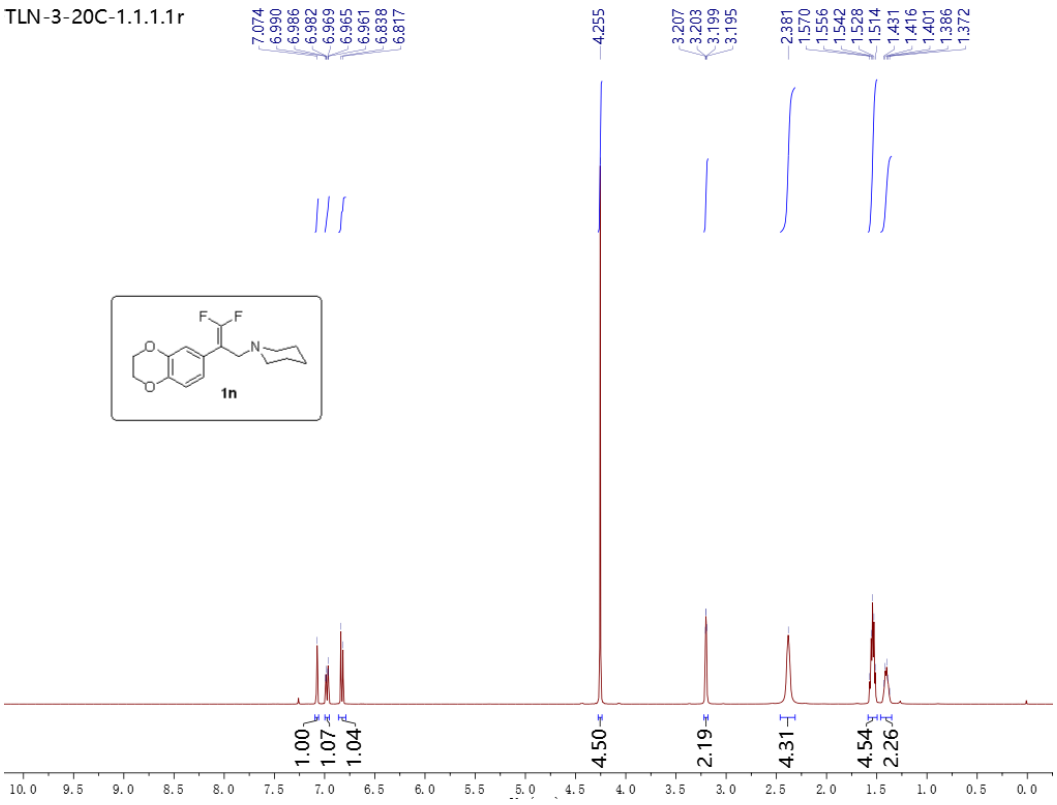

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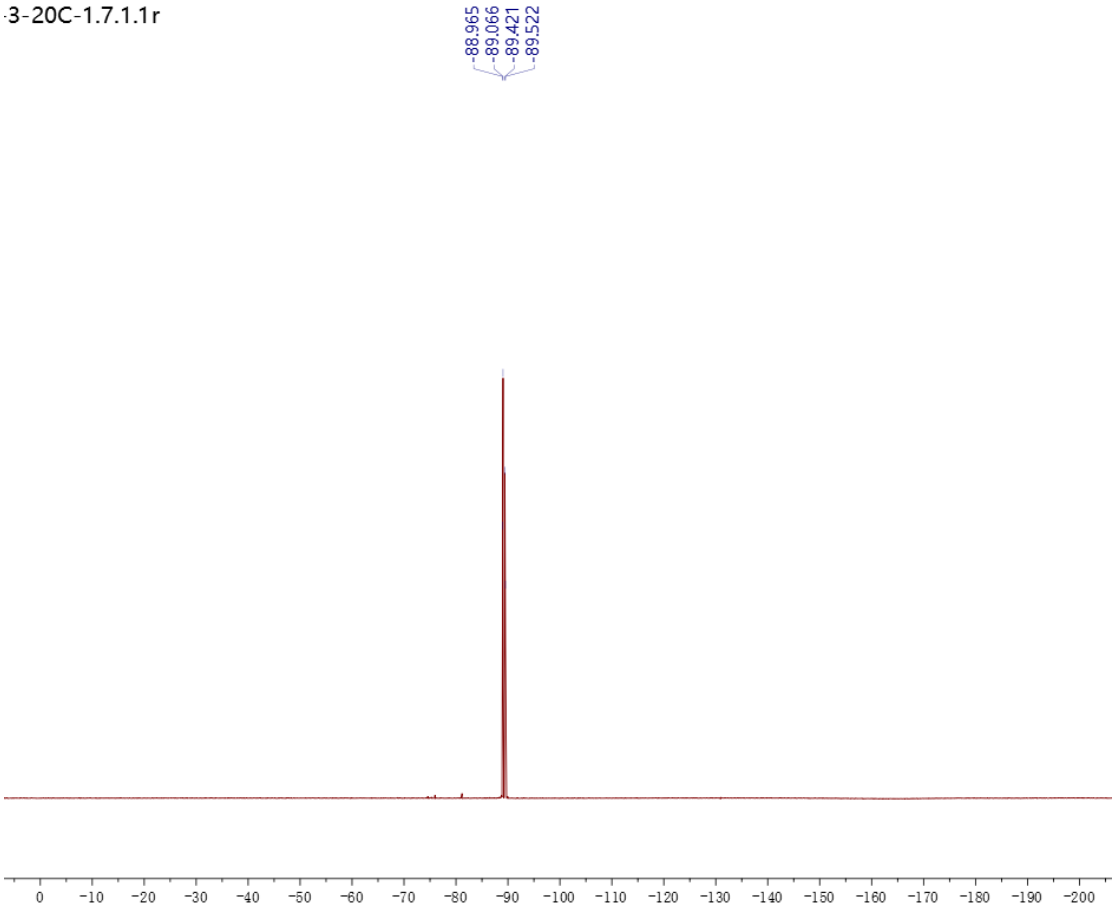

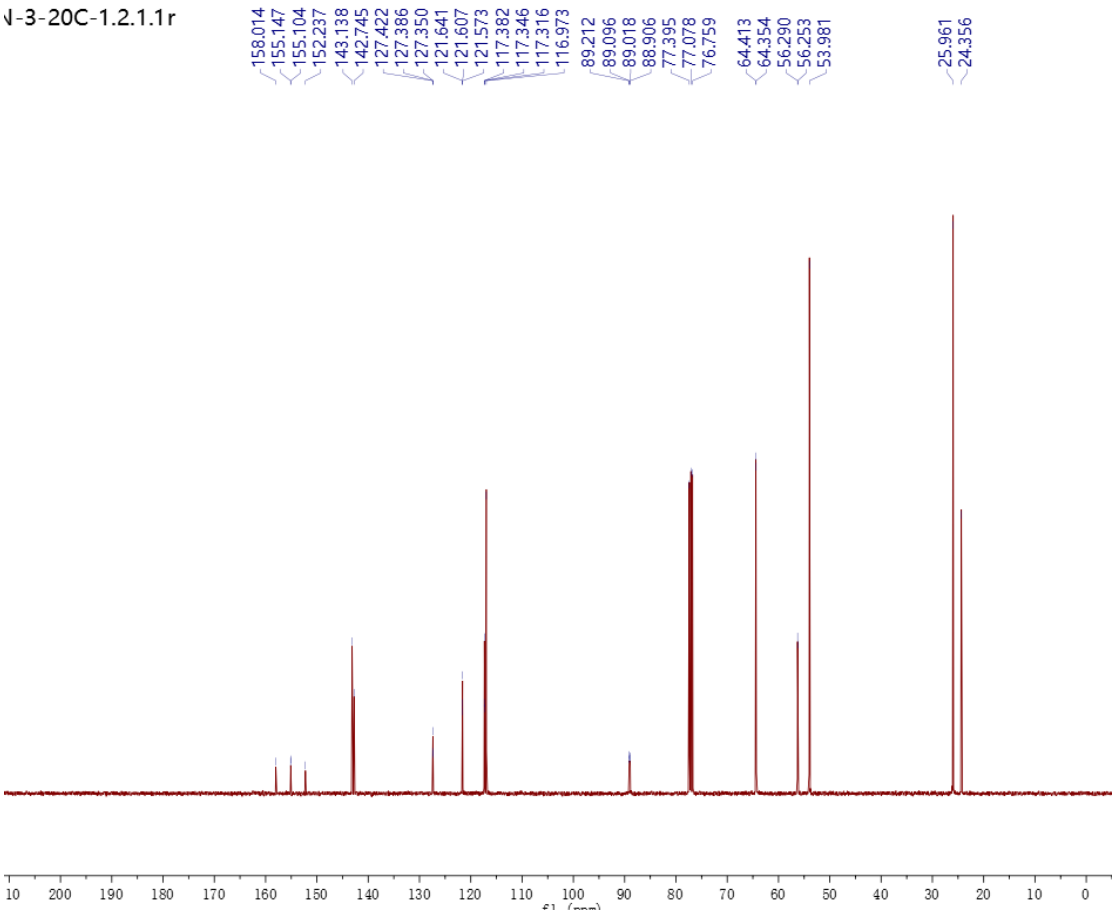
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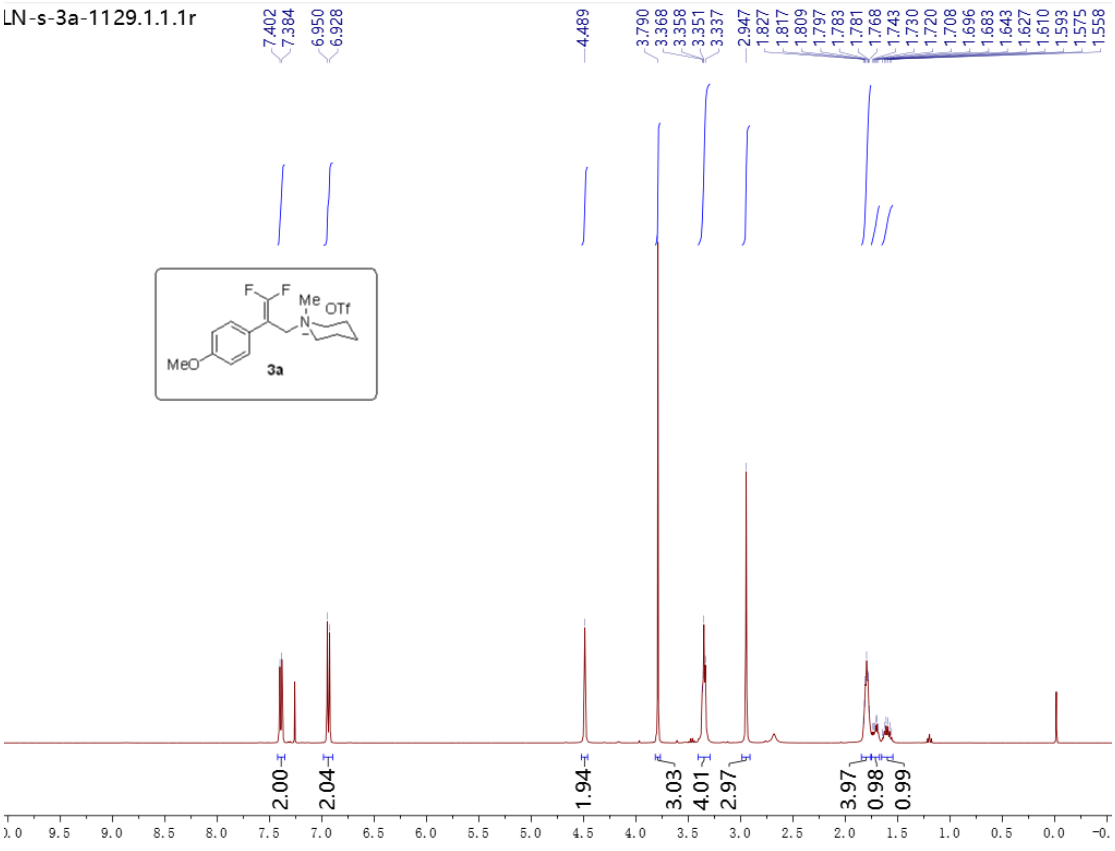
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1.593
1.575
1.558
F
F
Me
OTf
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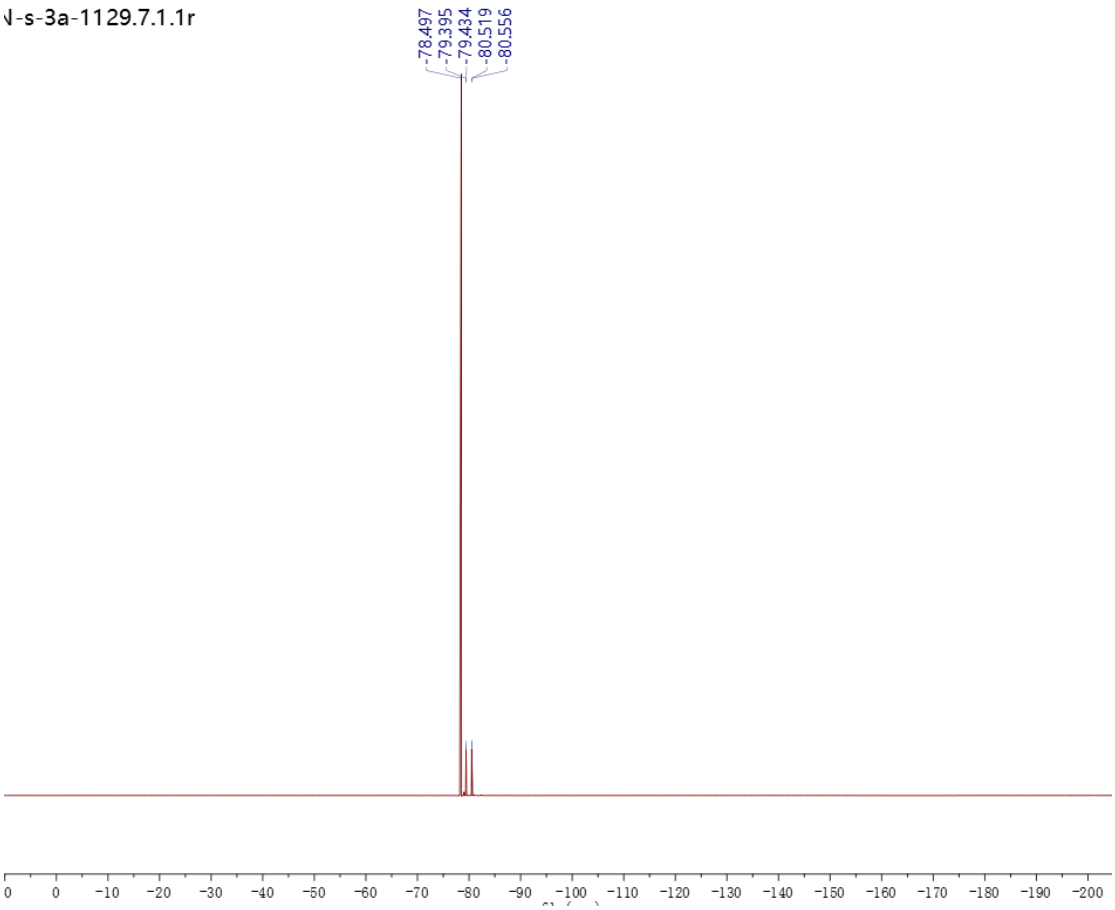
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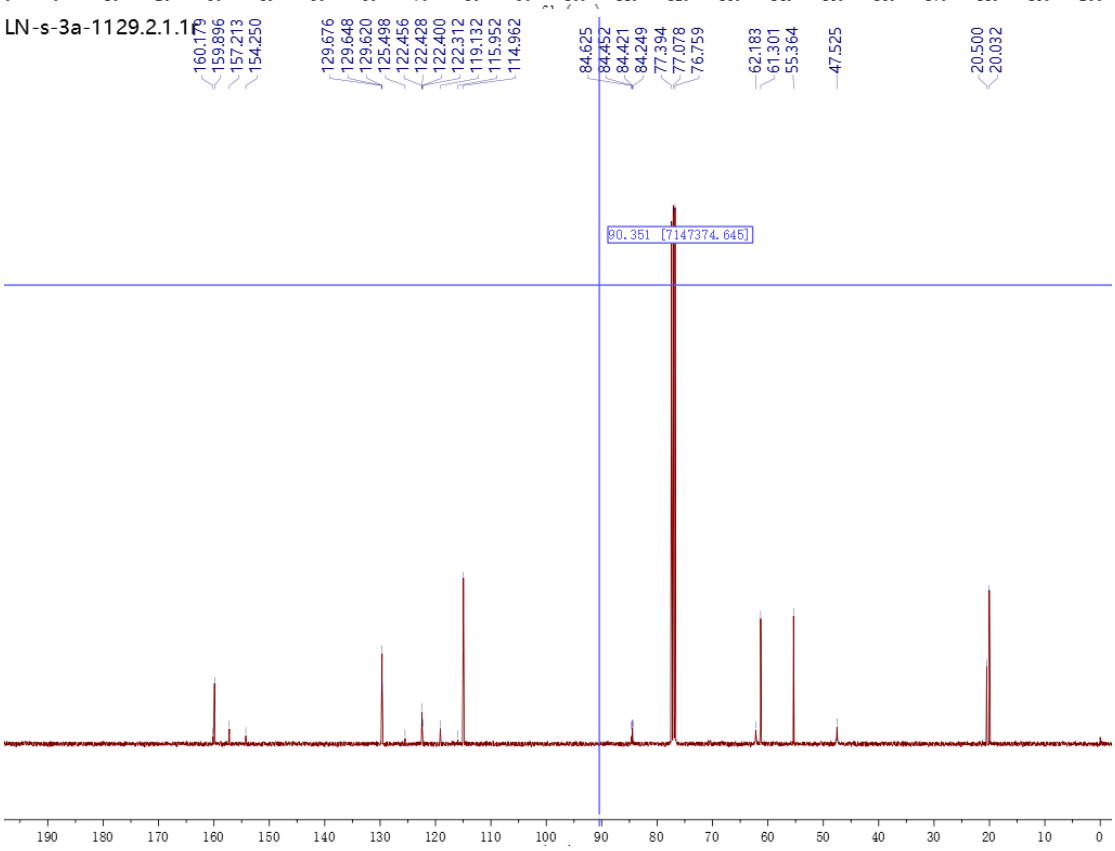
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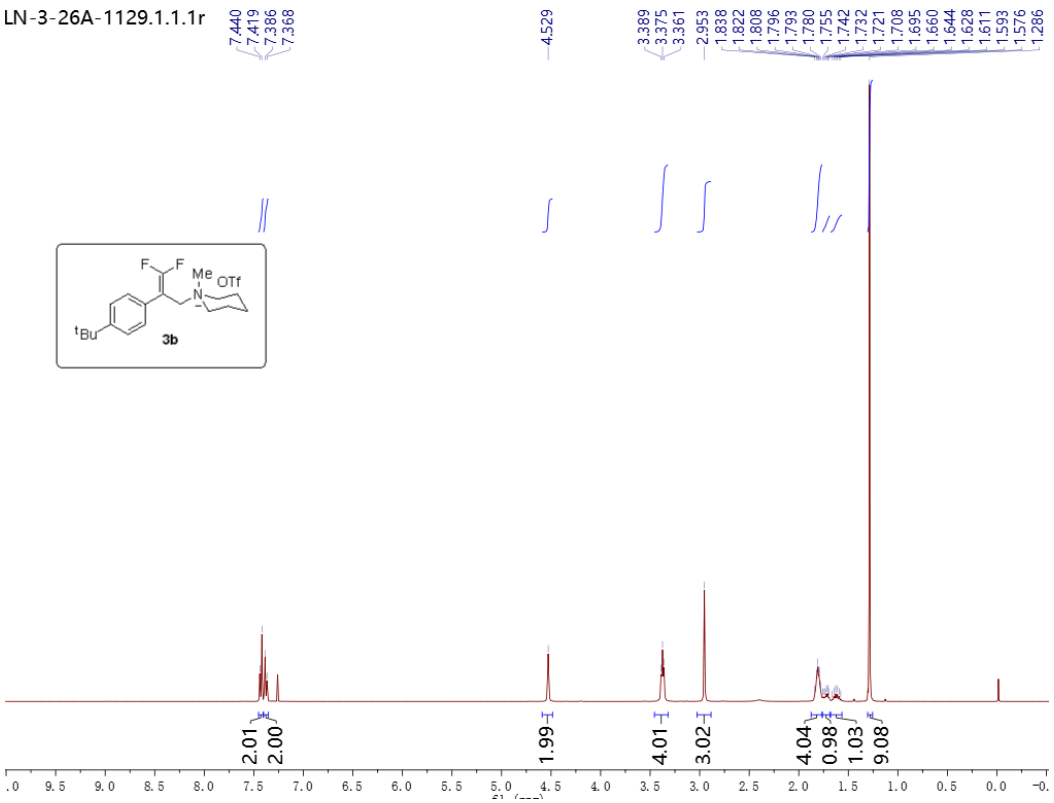
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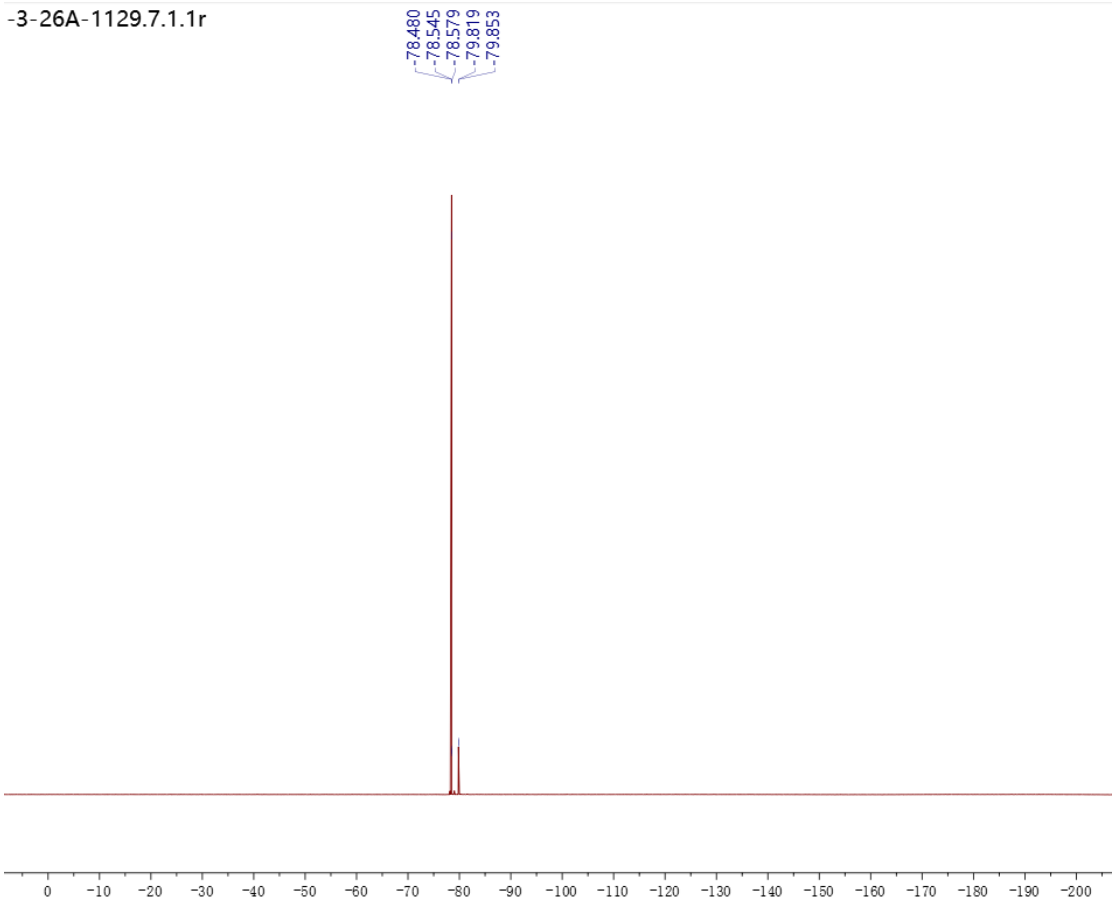

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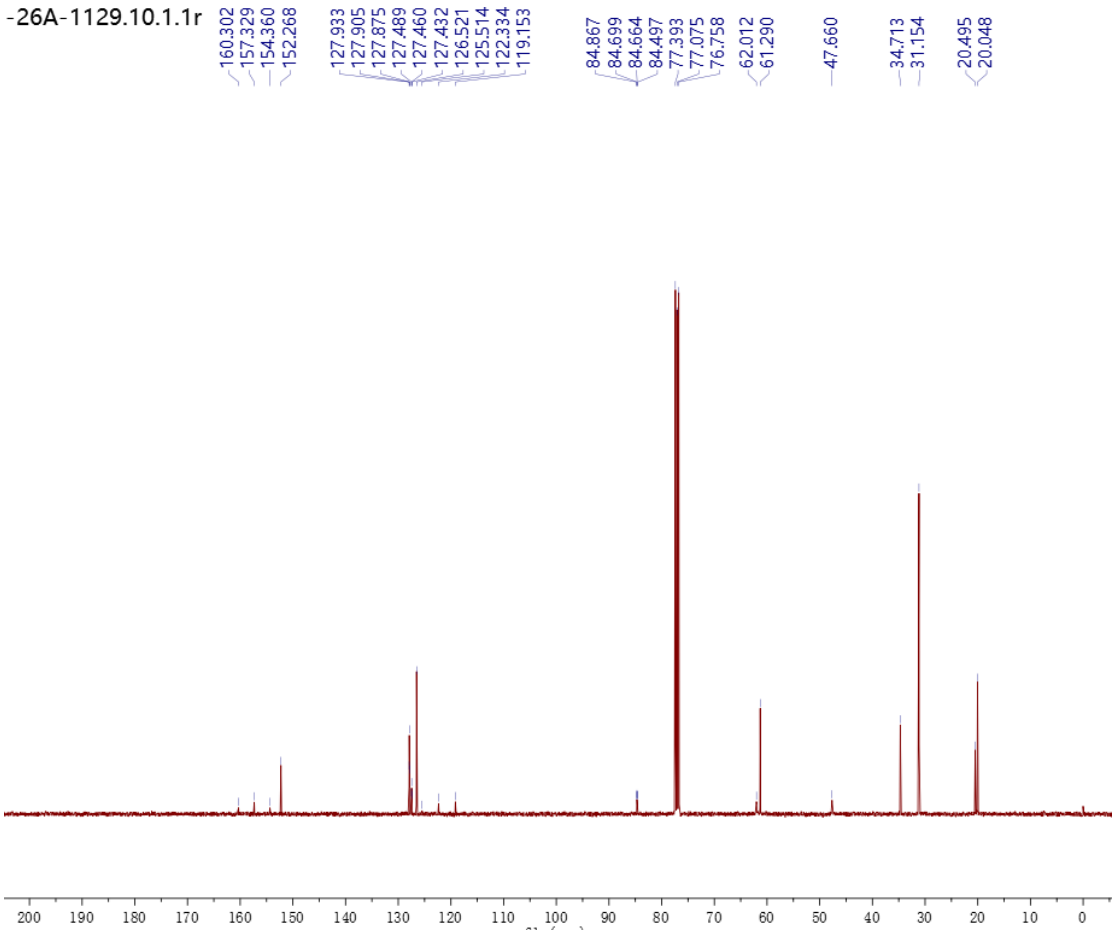

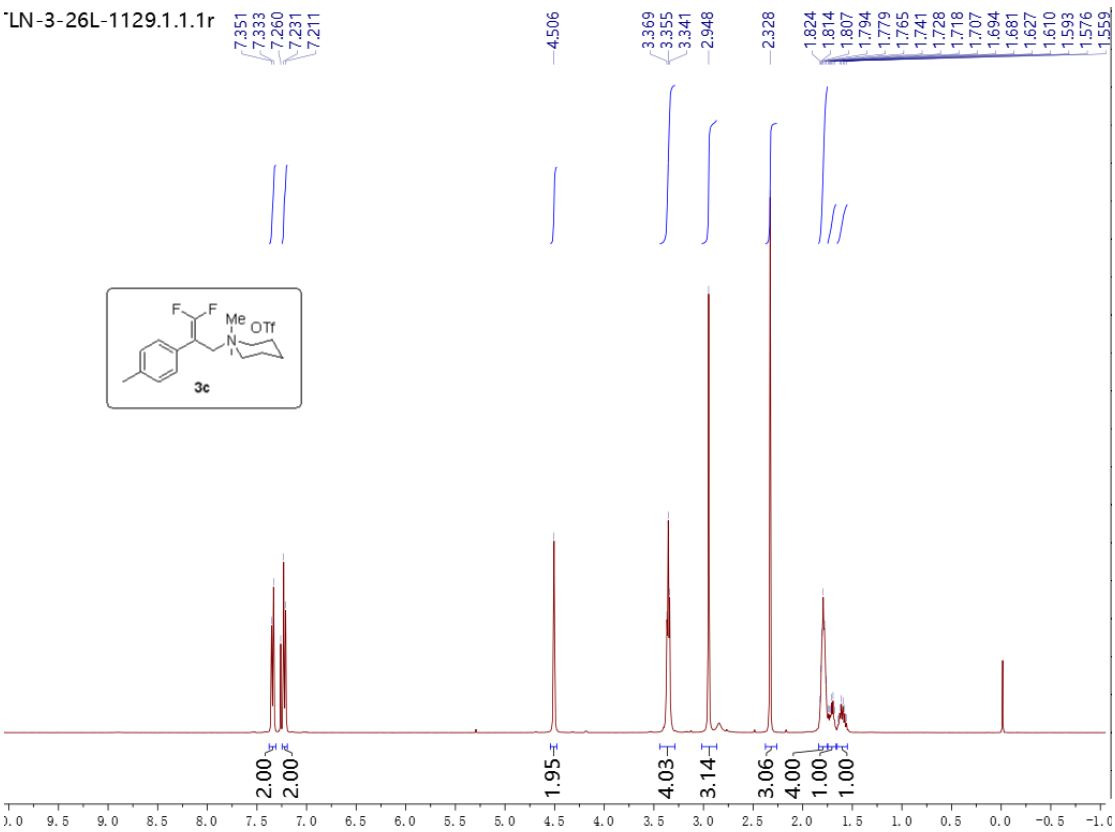
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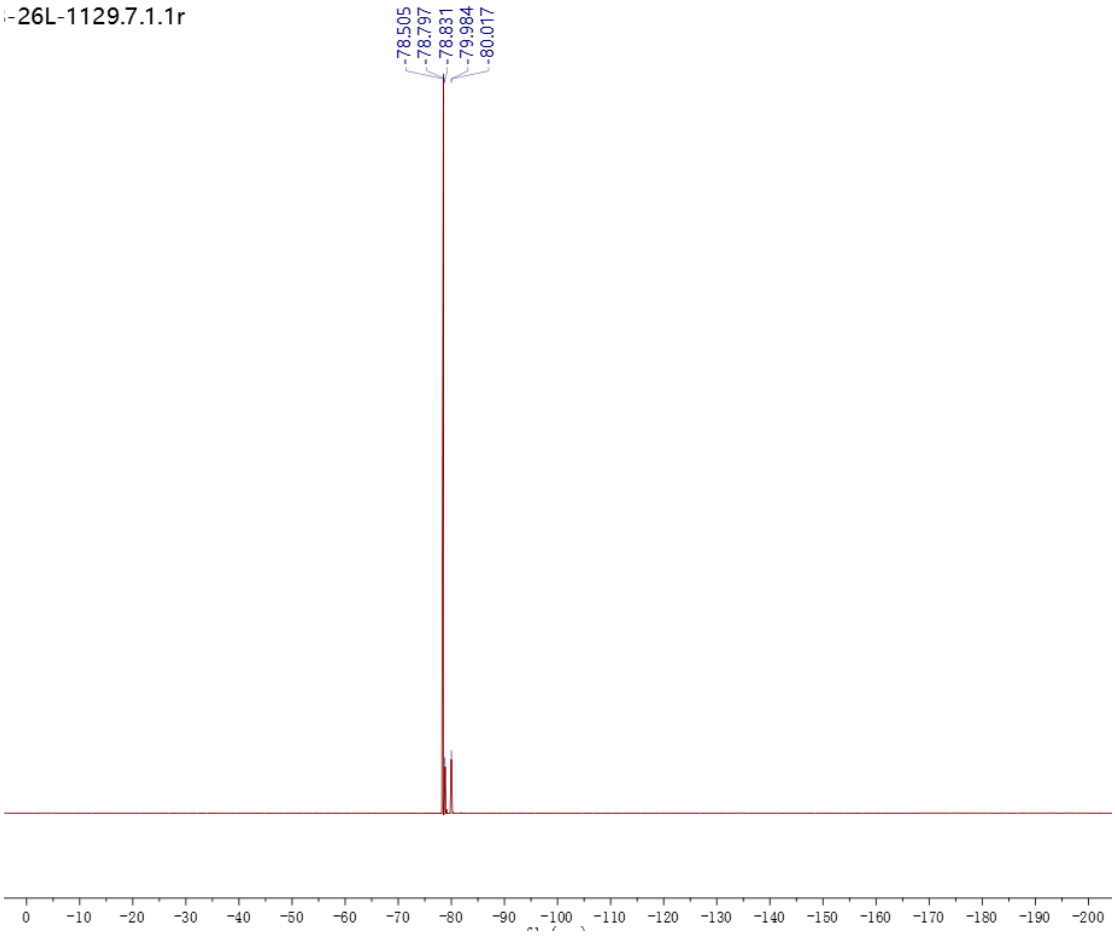
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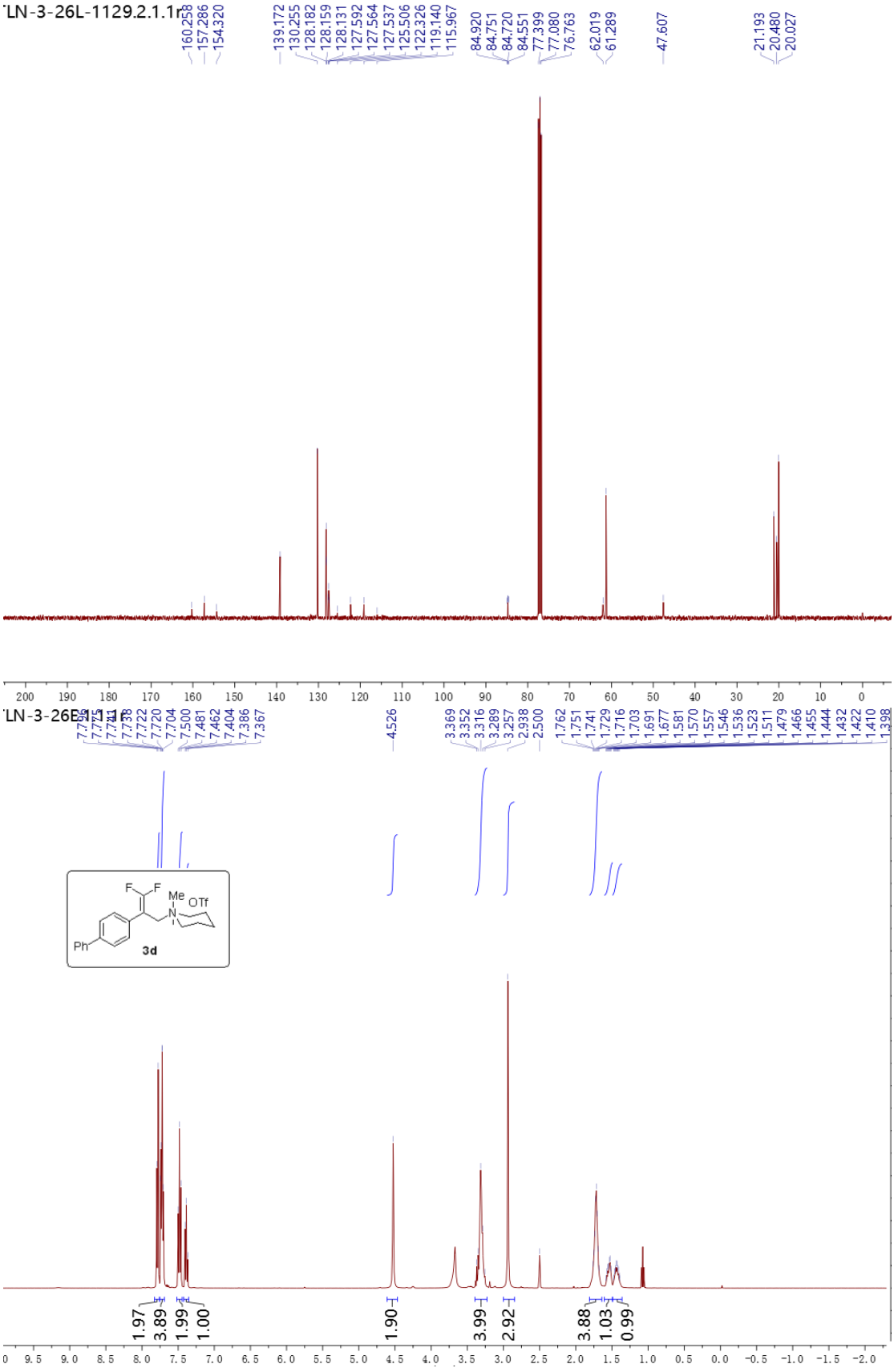
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F
Me
OTf
N
Ph
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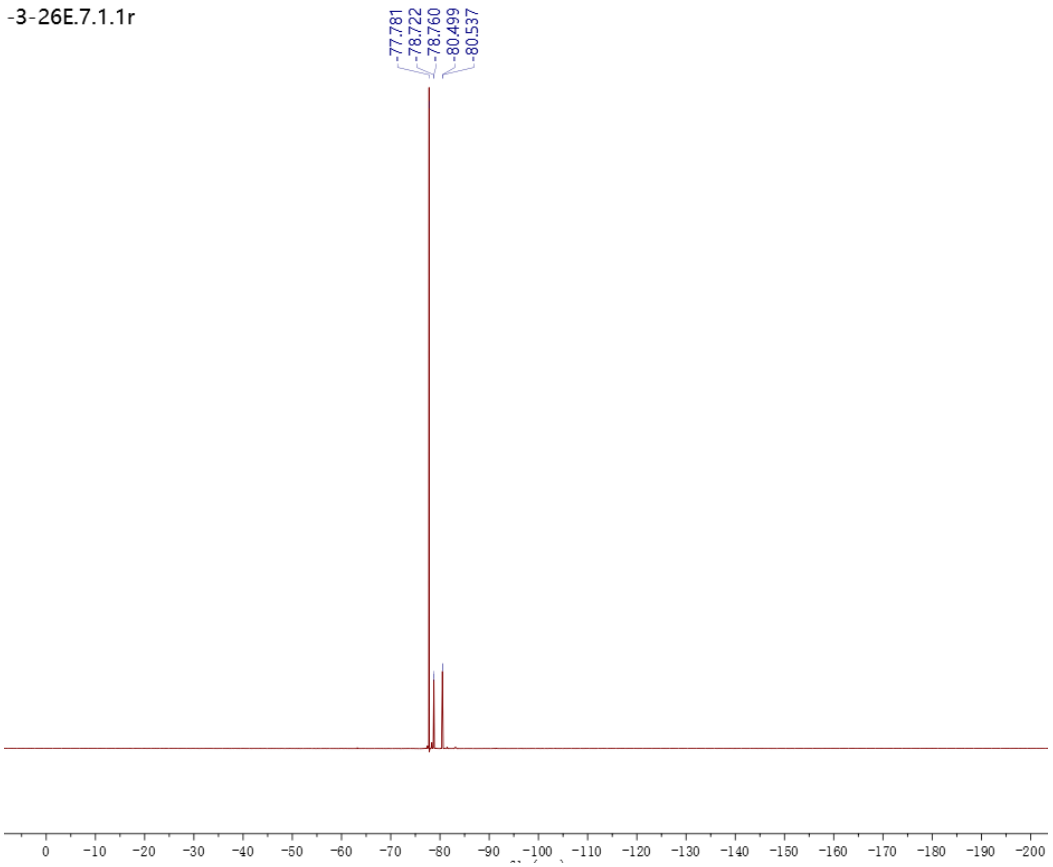

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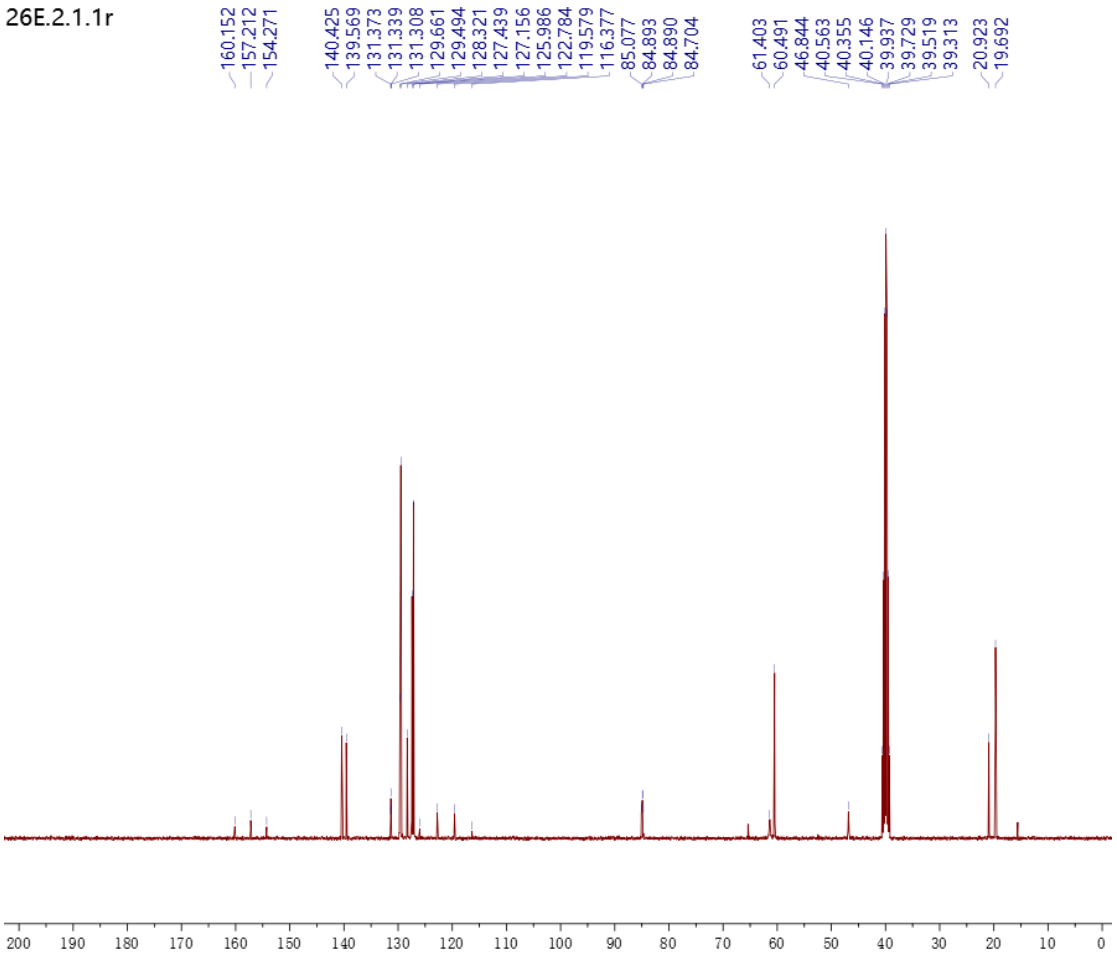

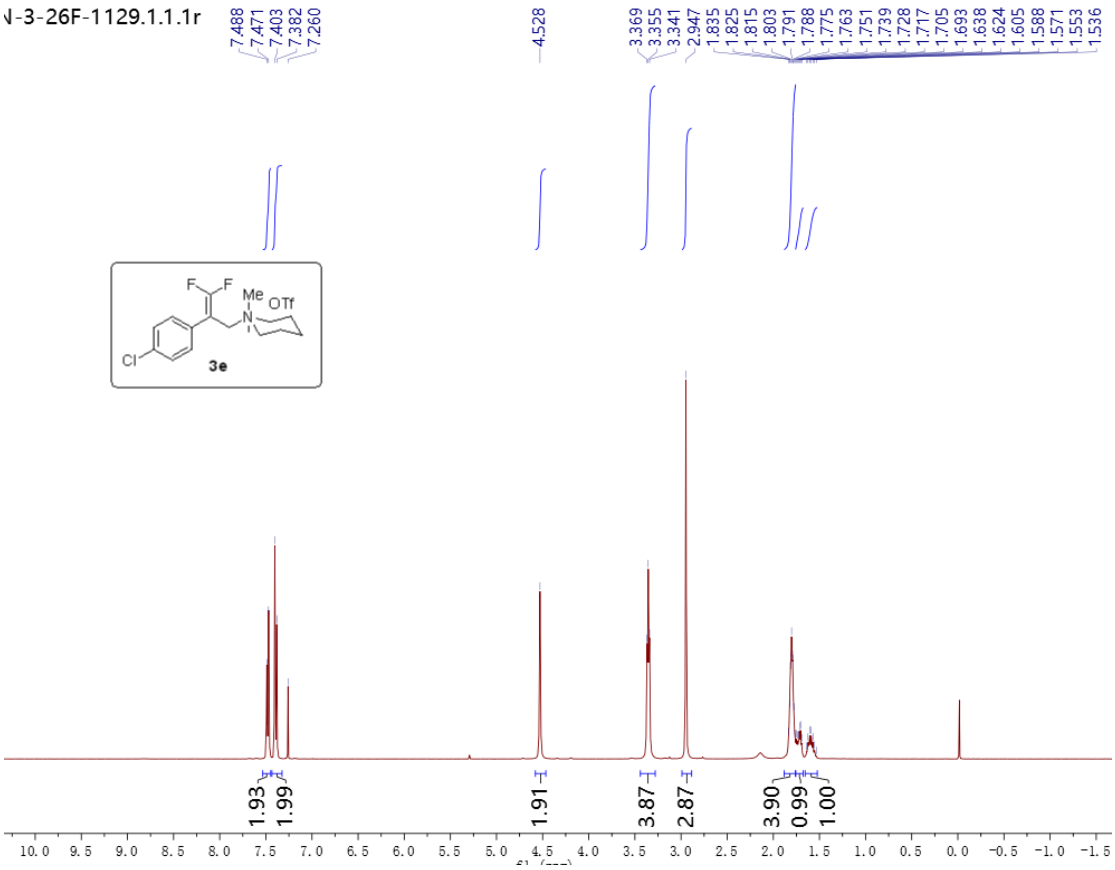
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F
F
Me
OTf
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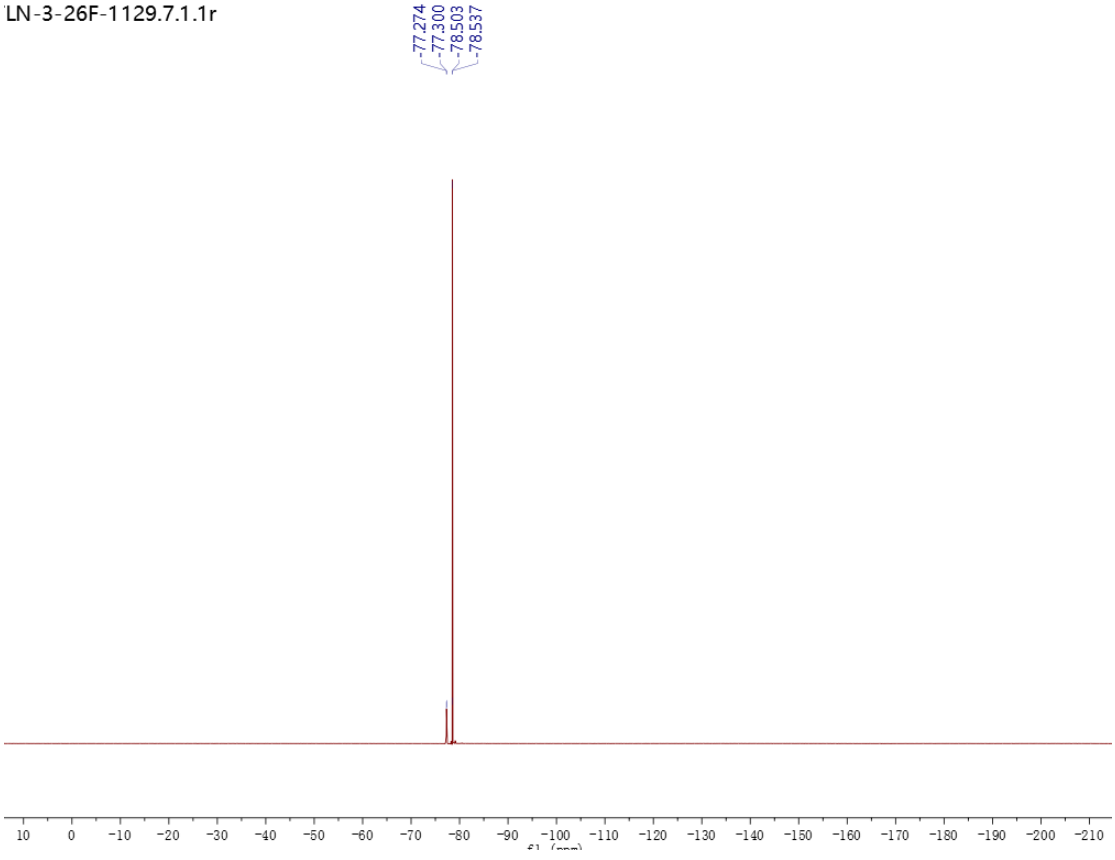
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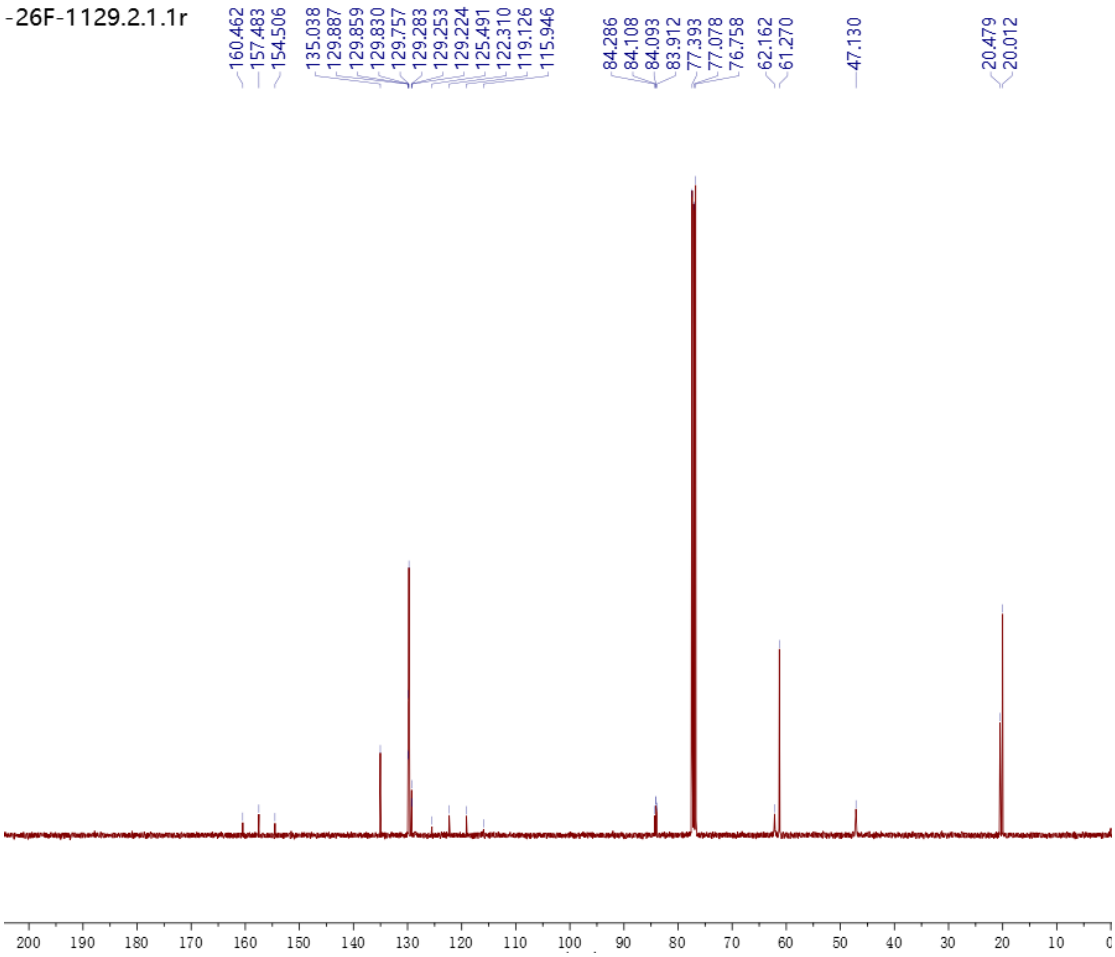
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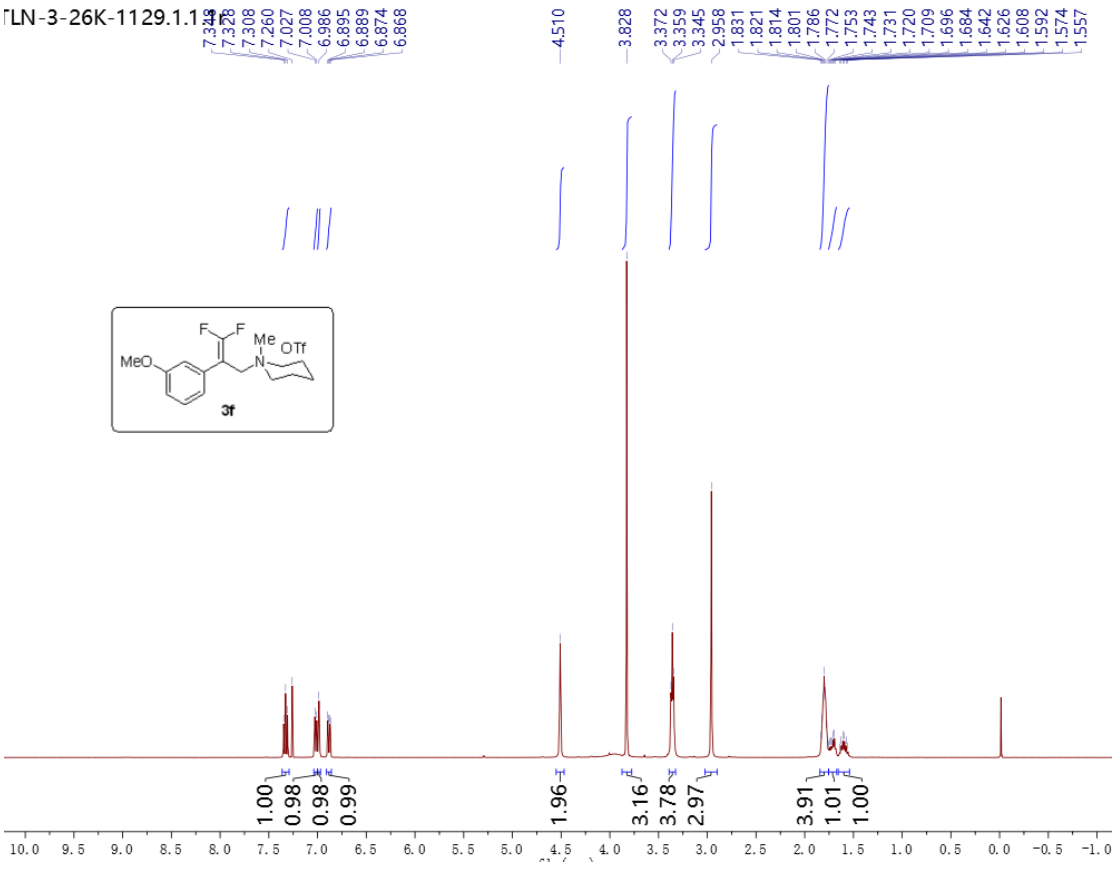
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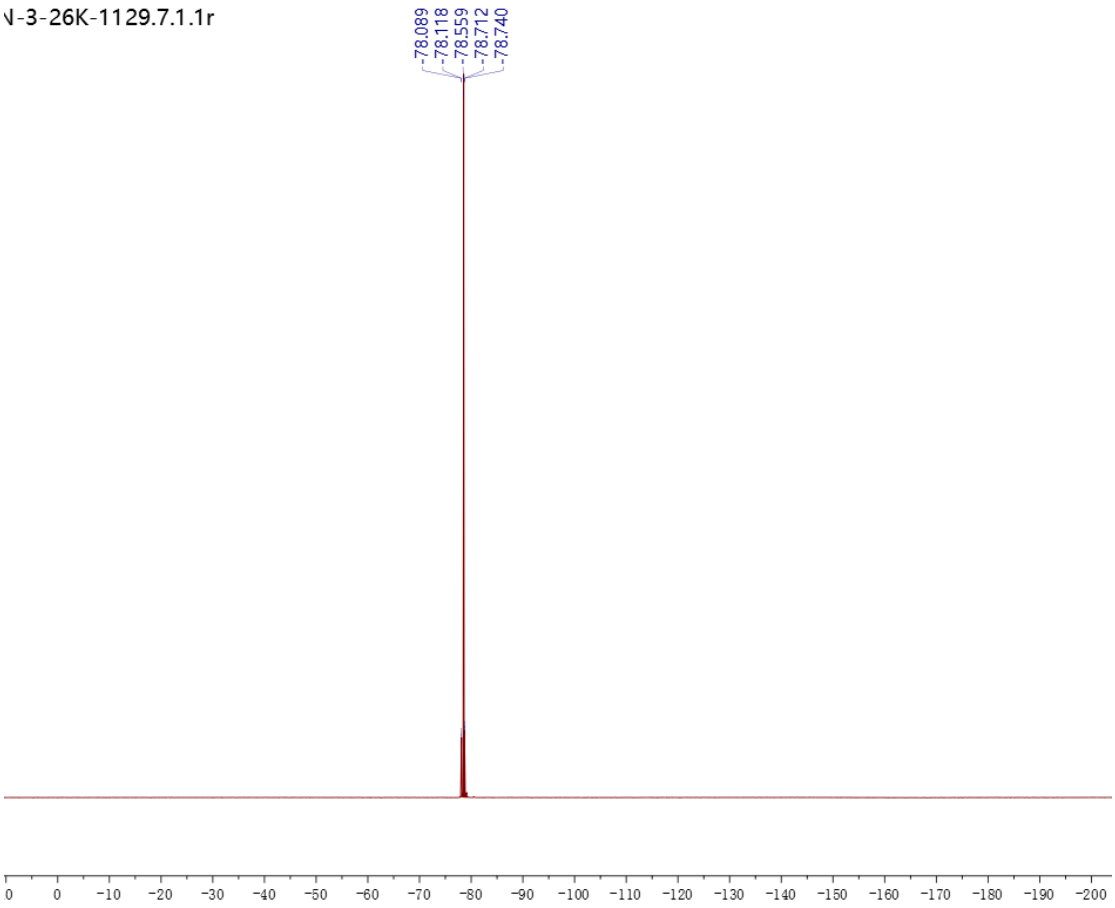
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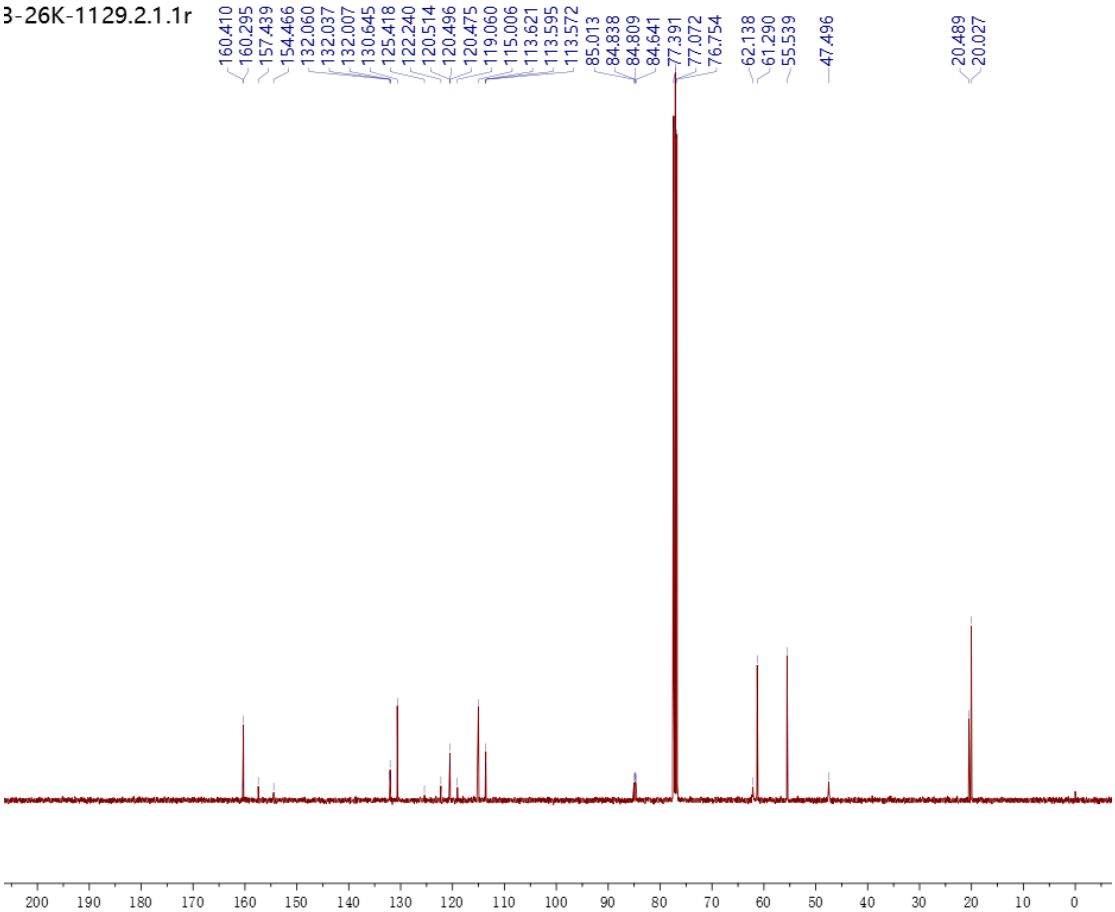
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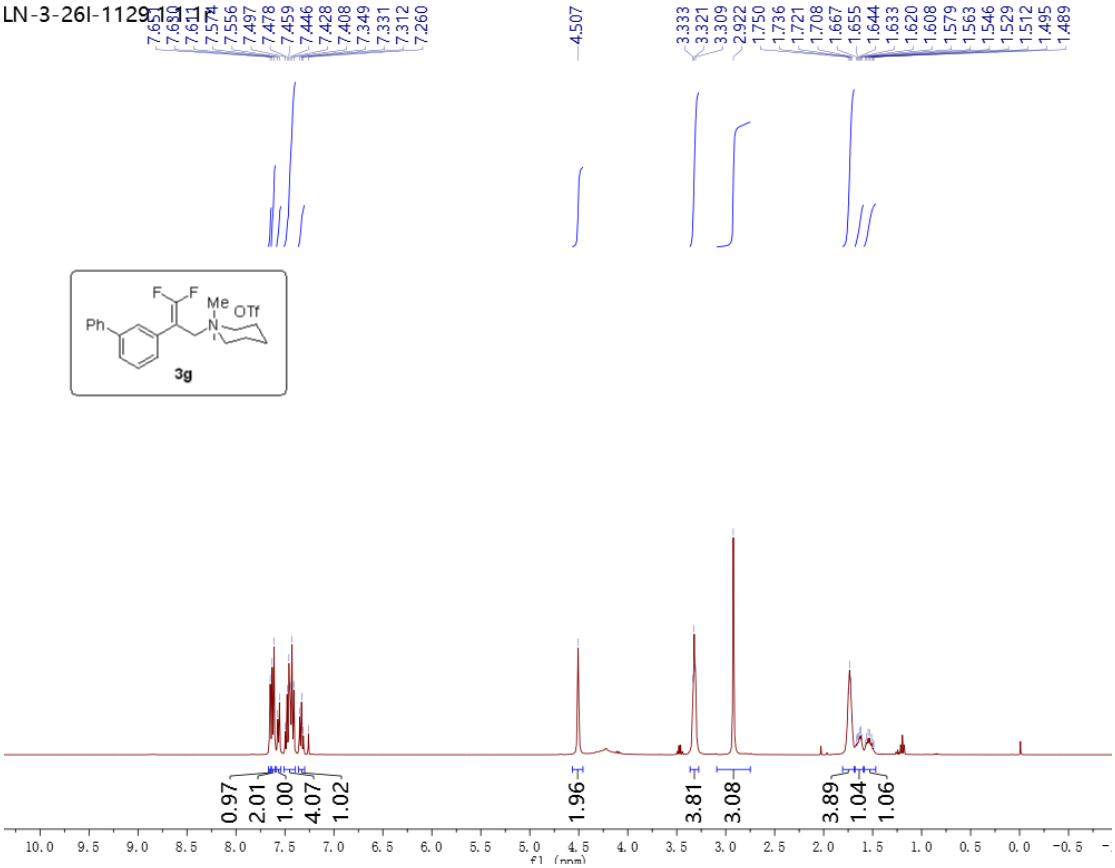
LN-3-26l-1129.1.1r



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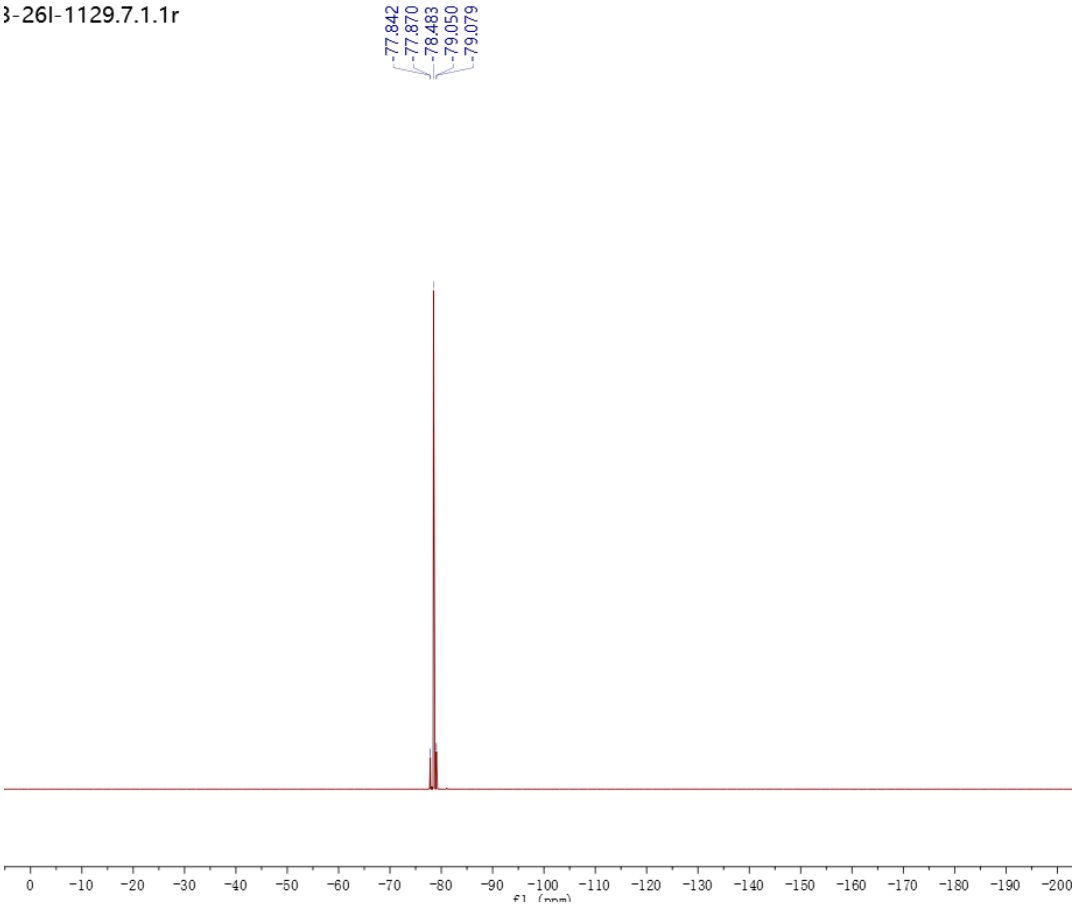

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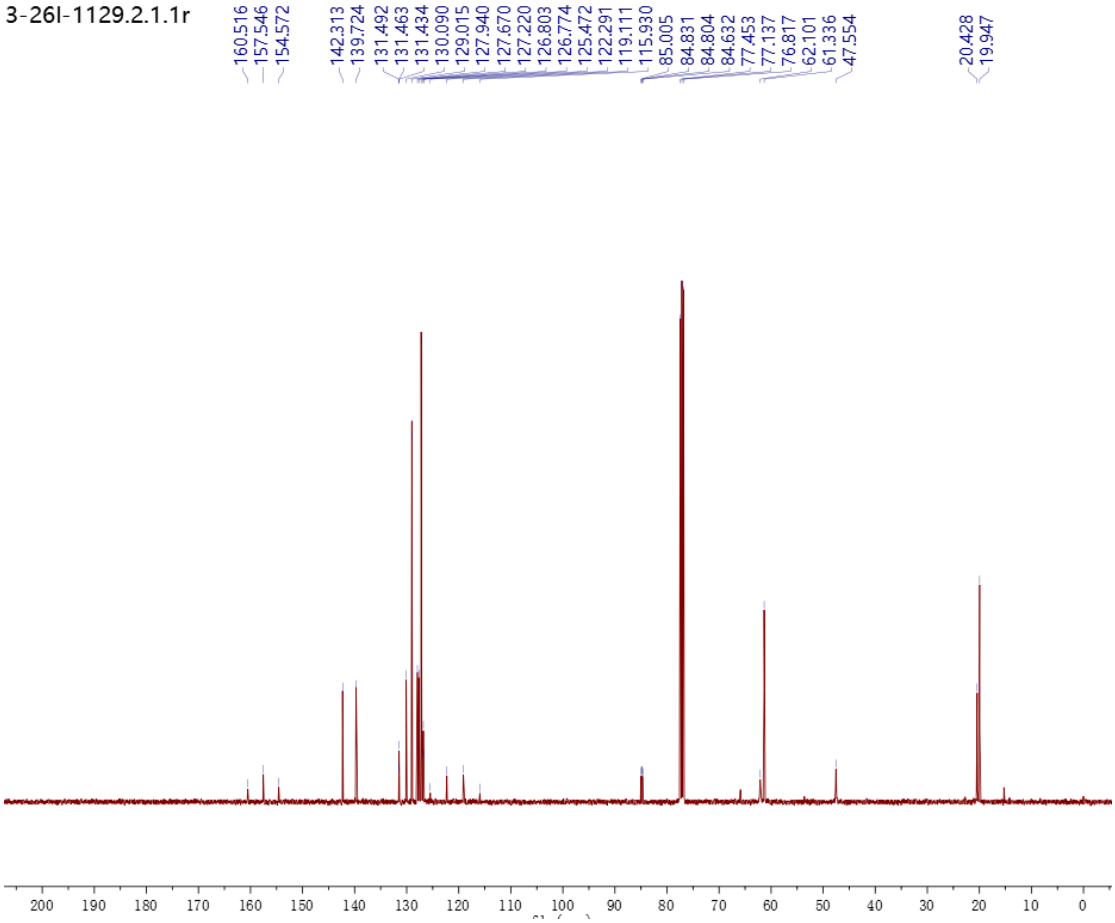

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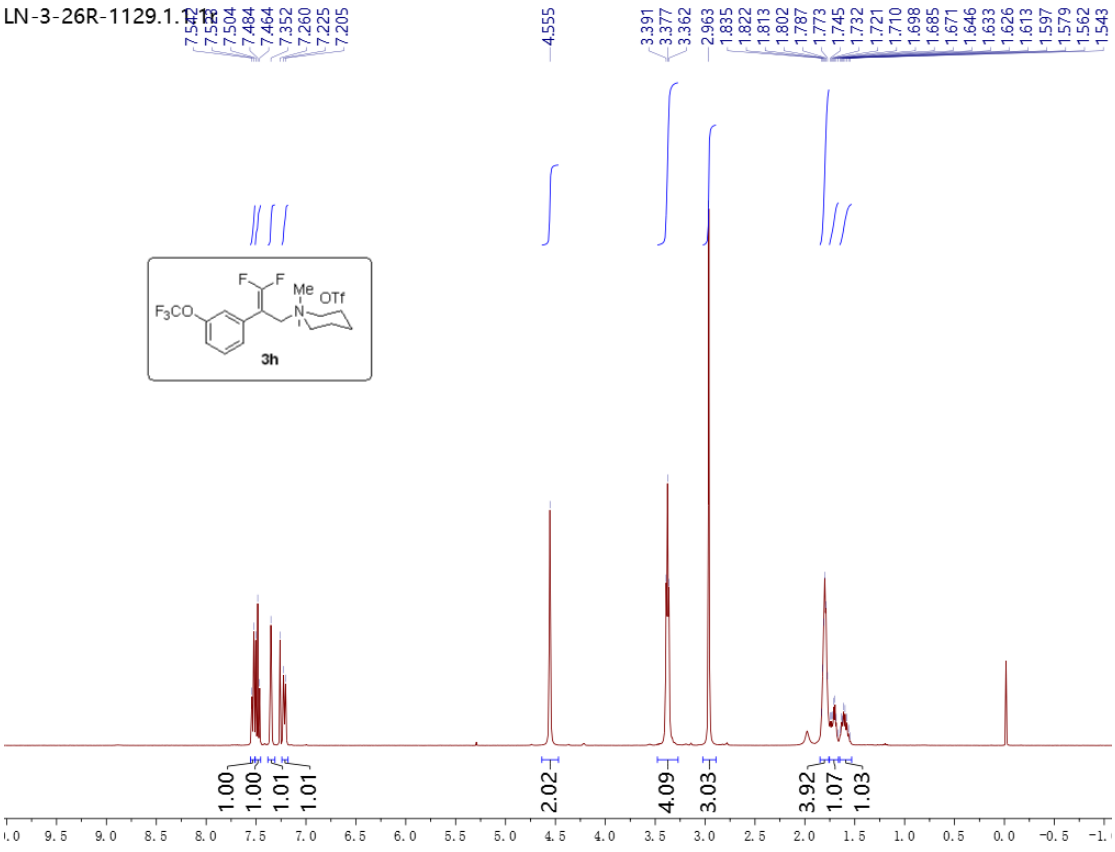

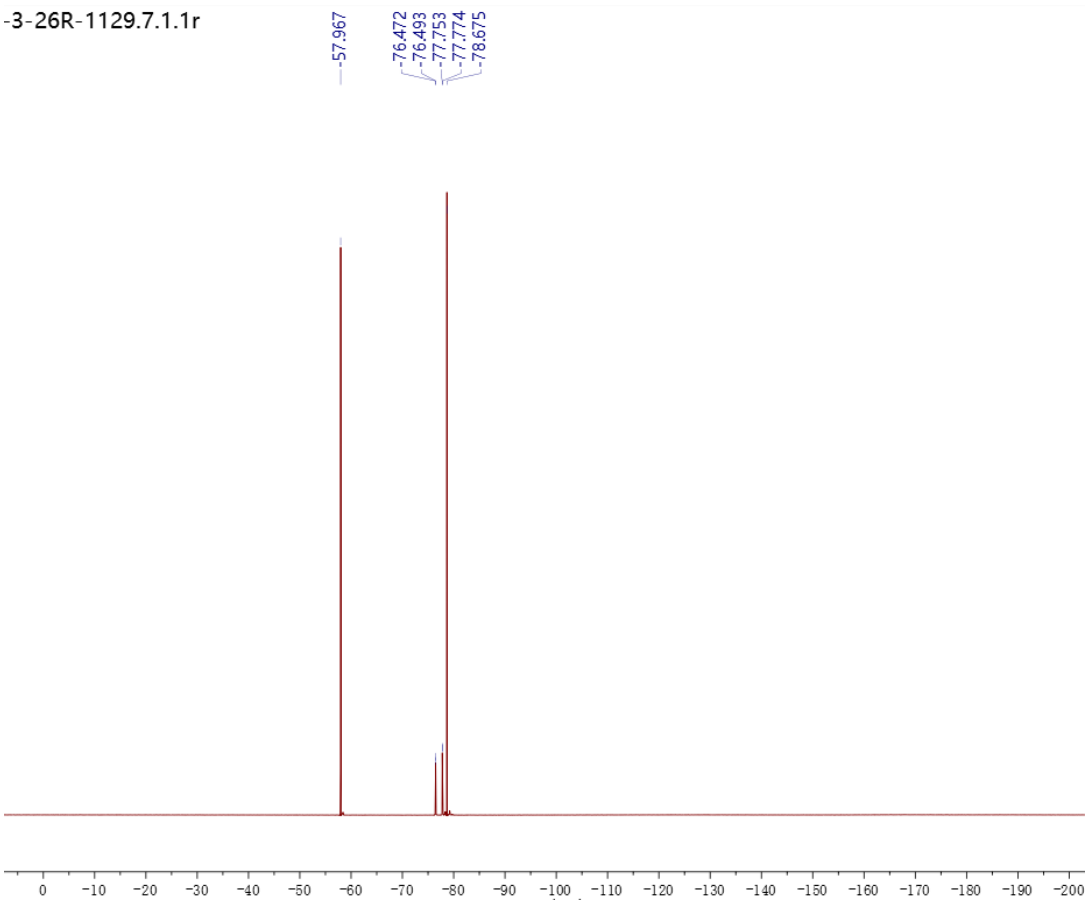
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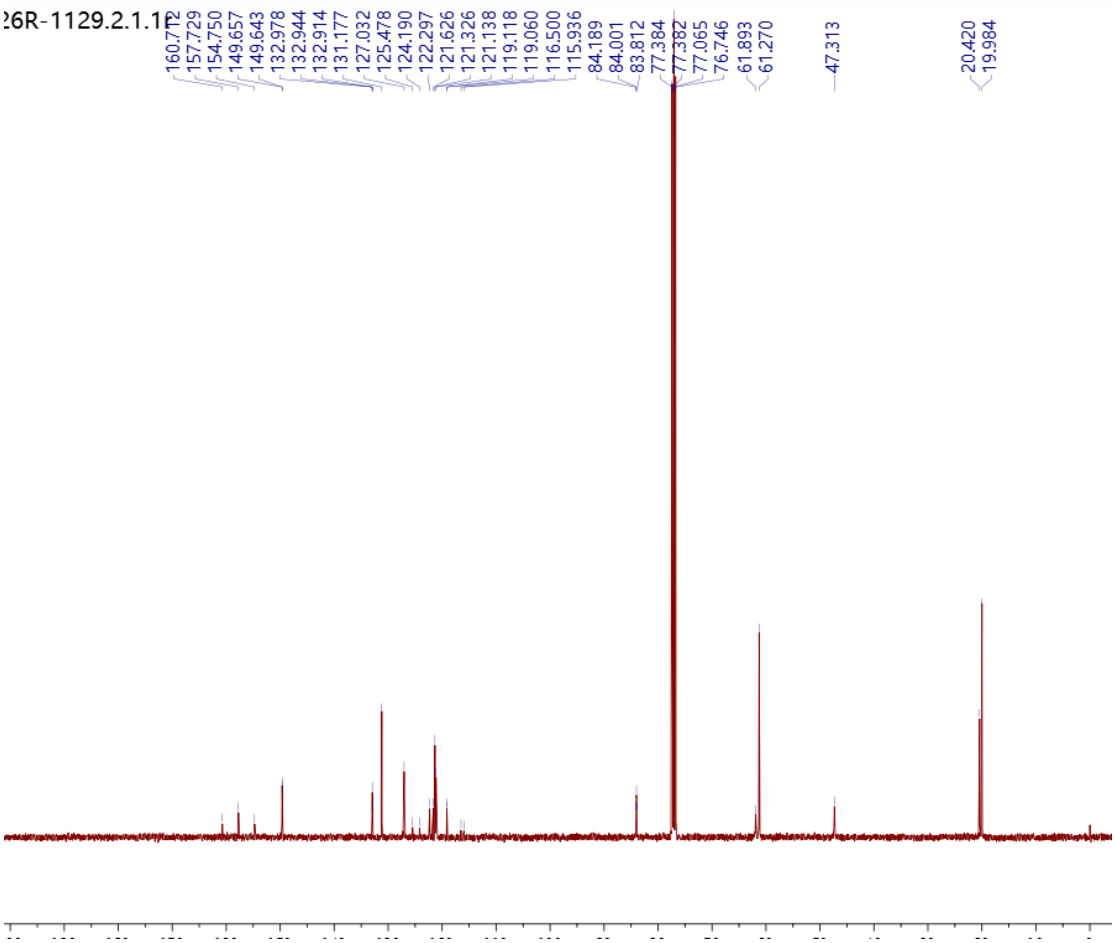
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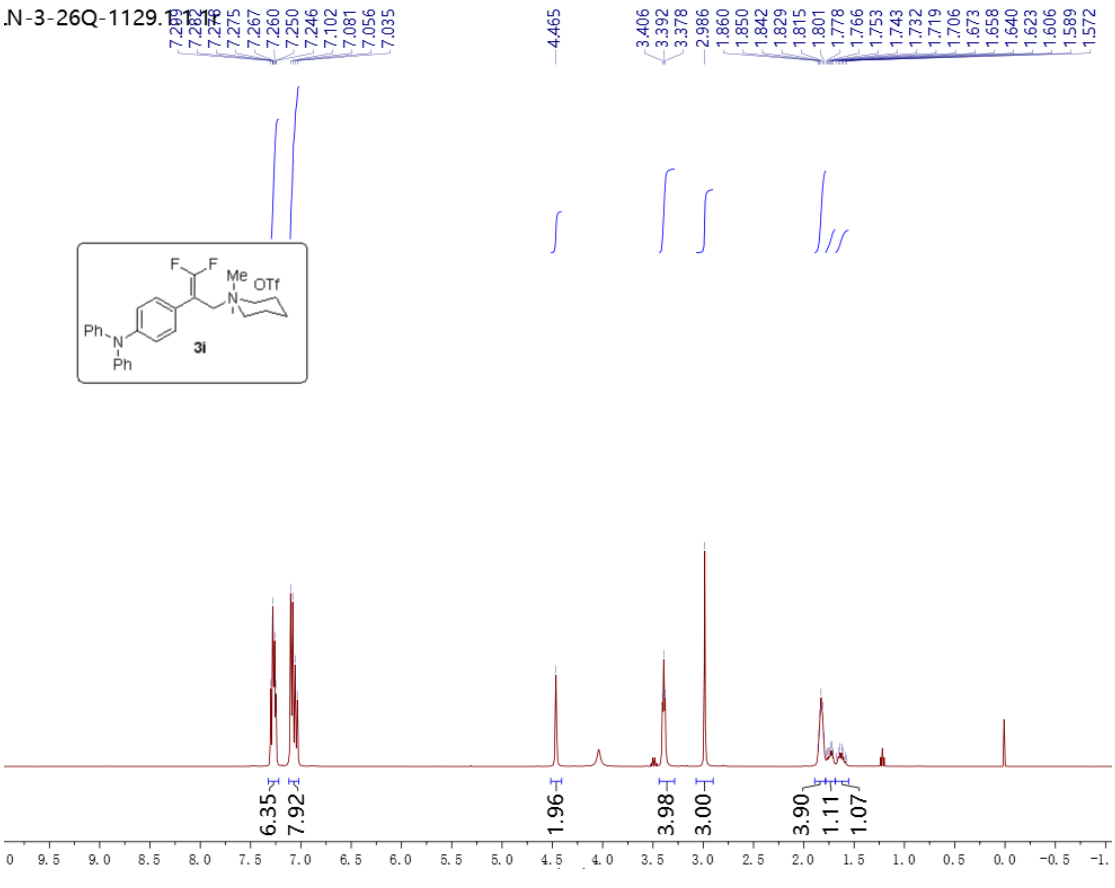
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1.572
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Me
OTf
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Ph
N
Ph
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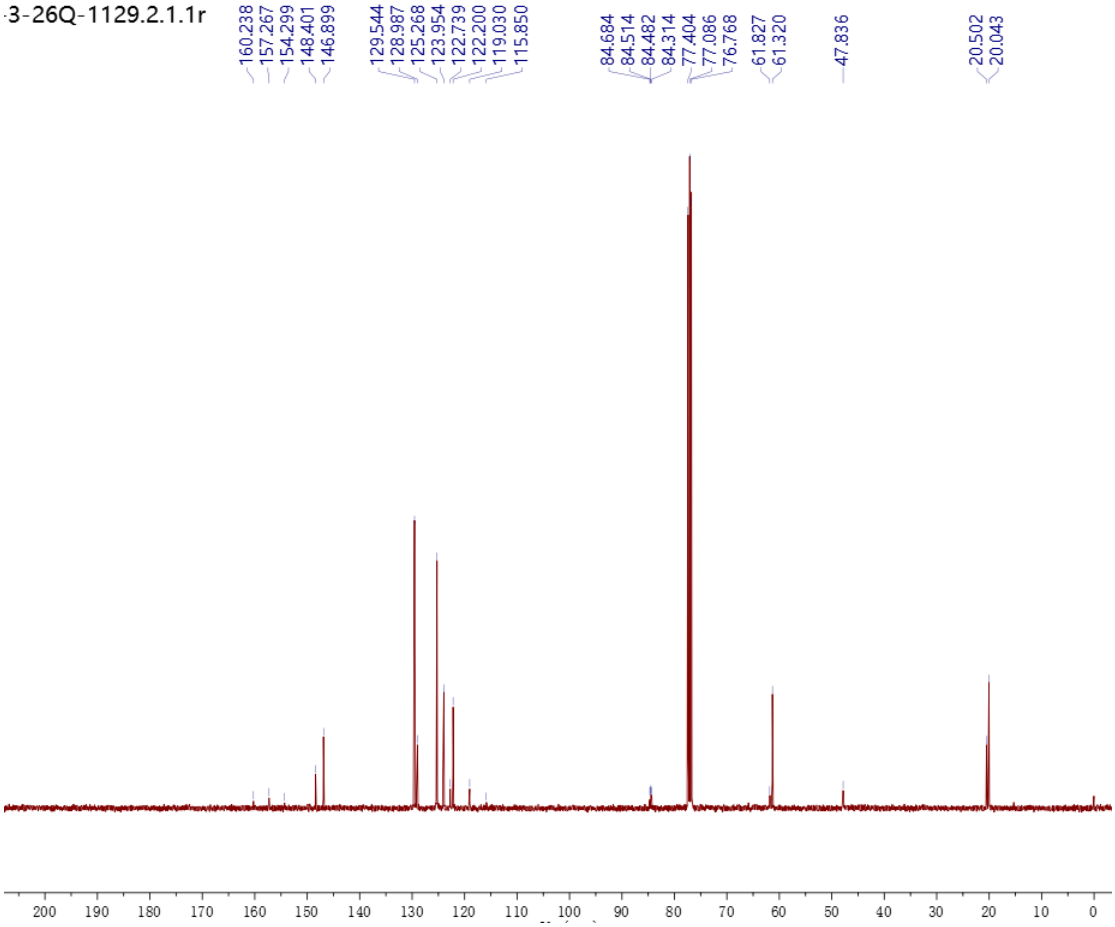
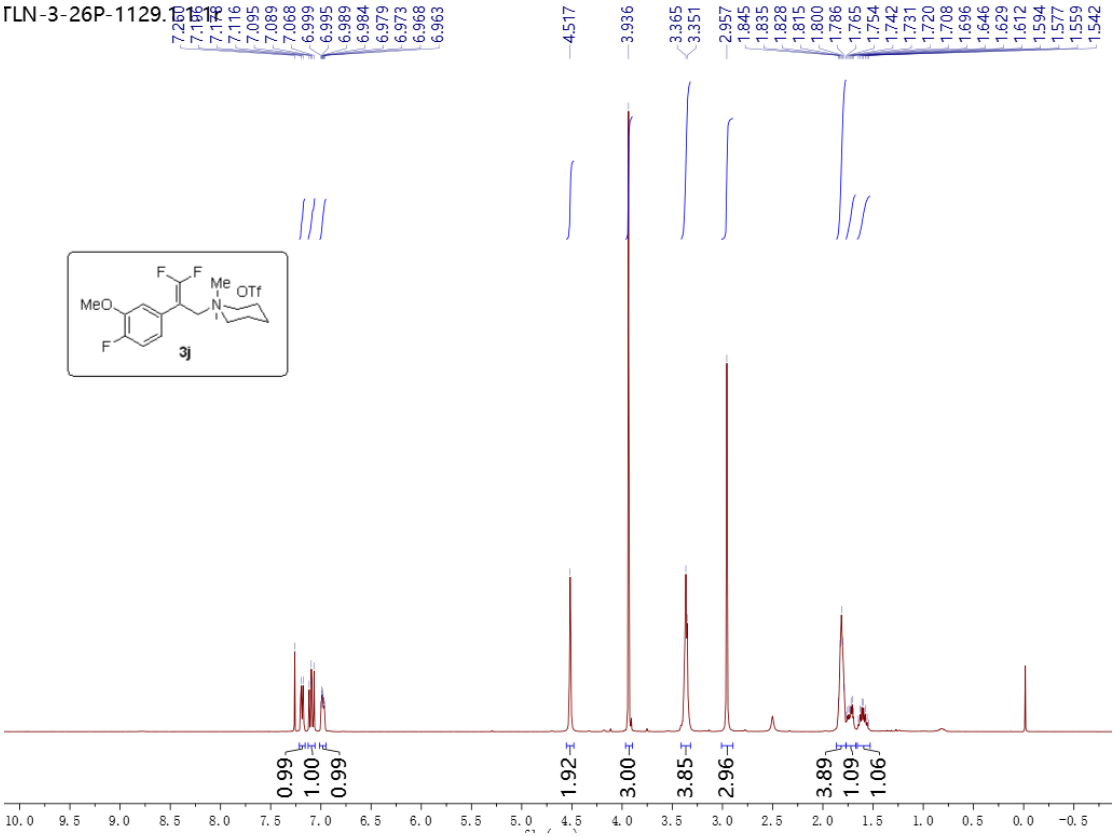
-3-26Q-1129.2.1.1r





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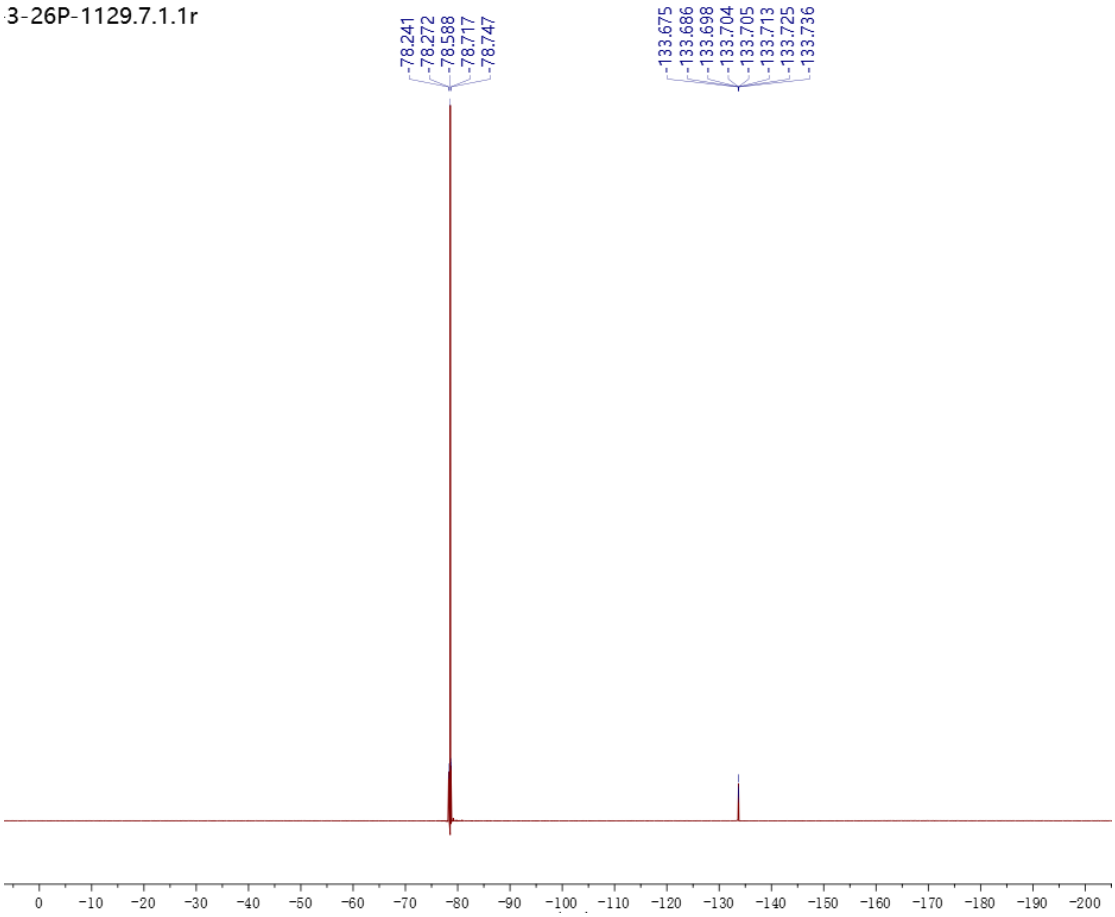

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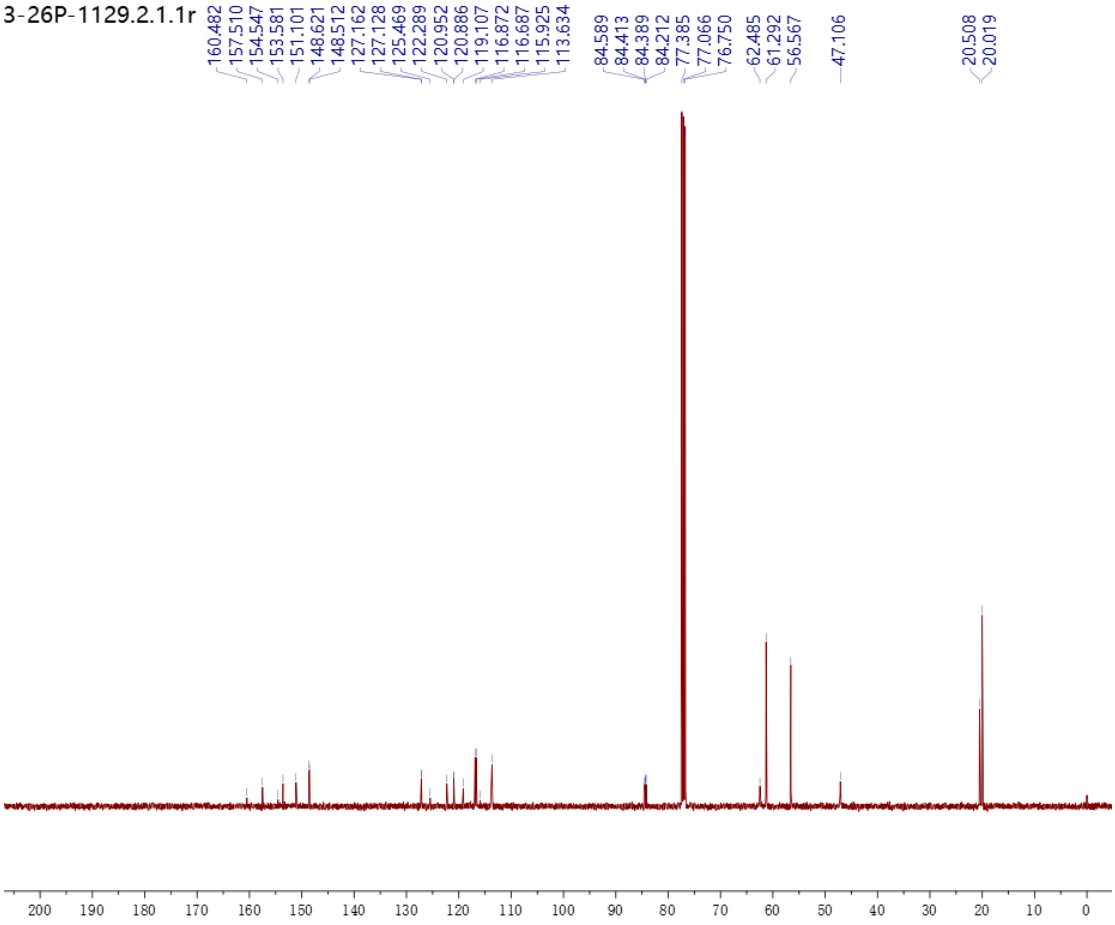

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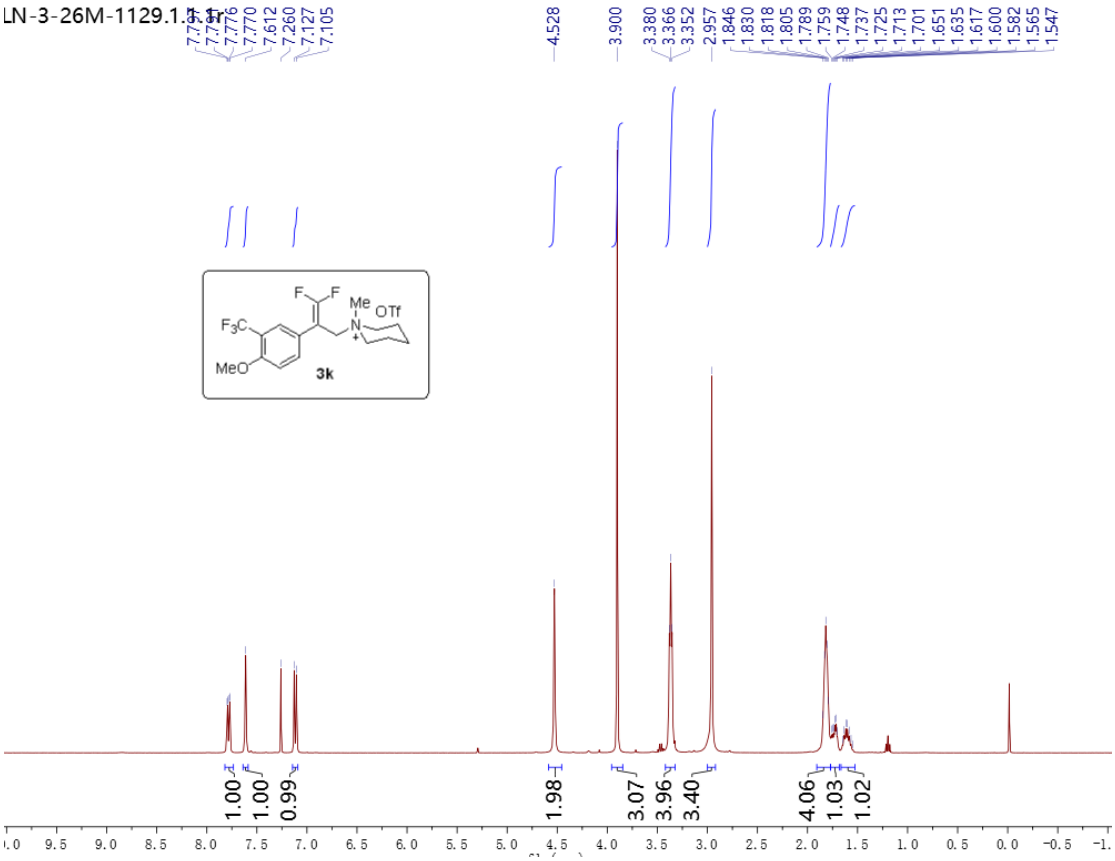

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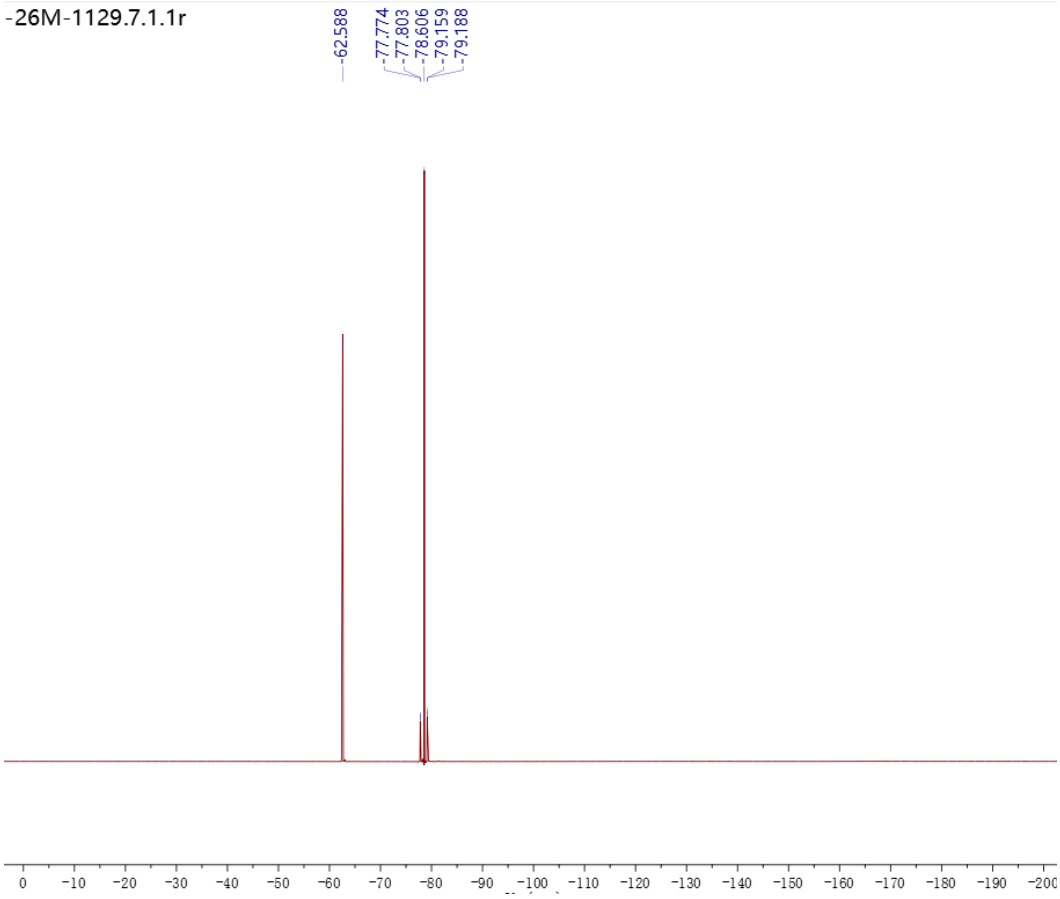

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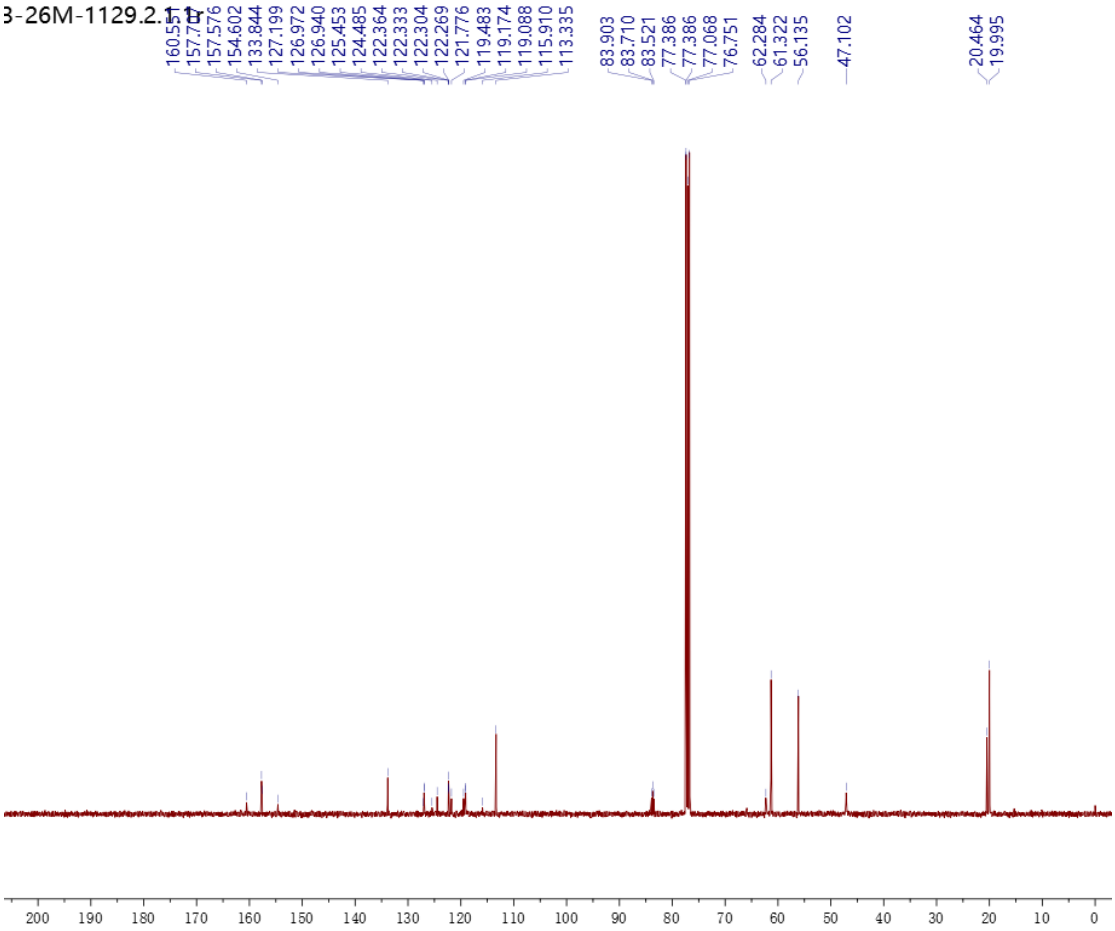

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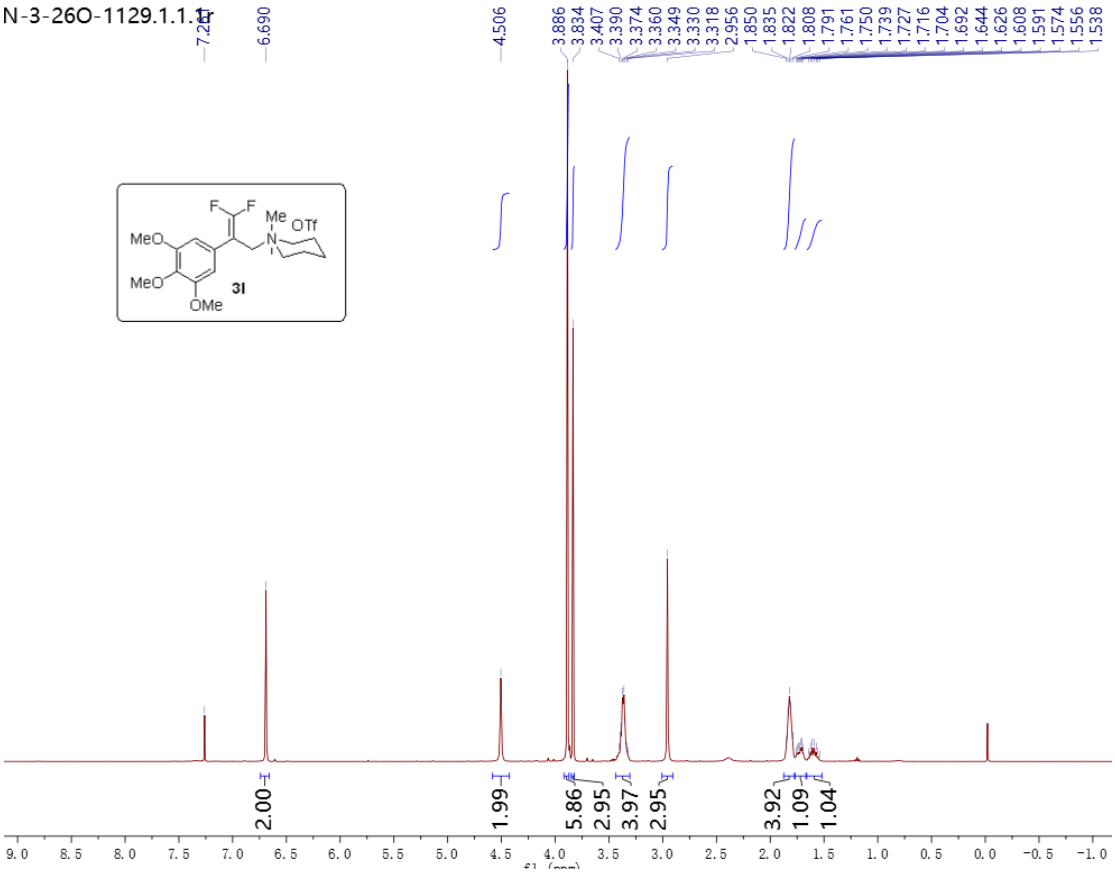

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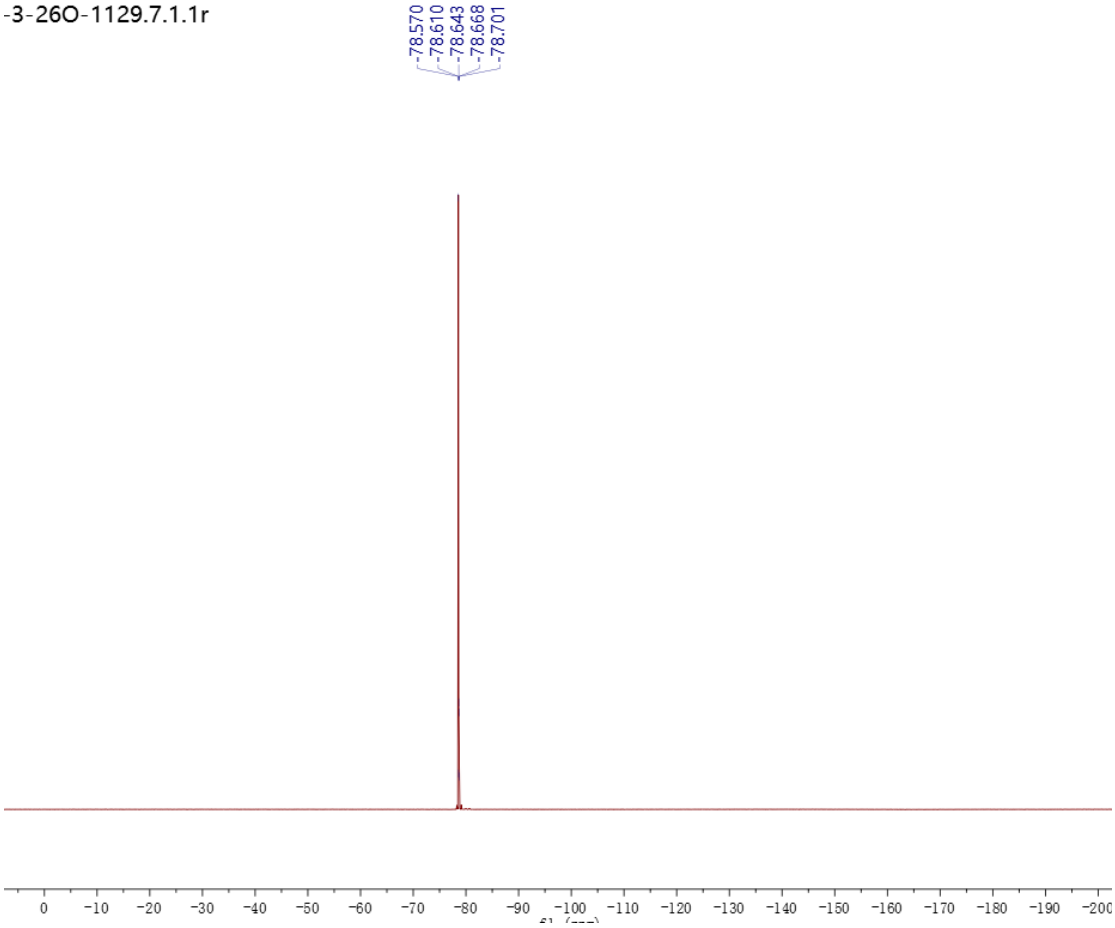

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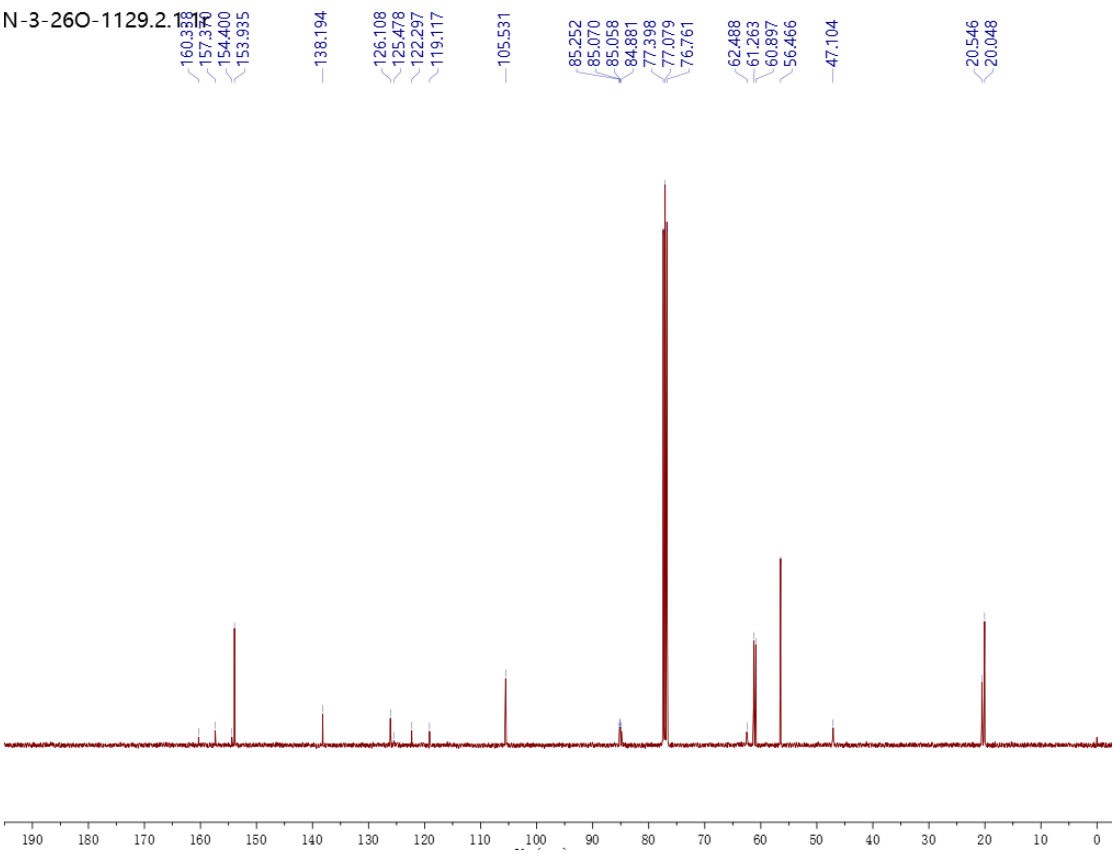

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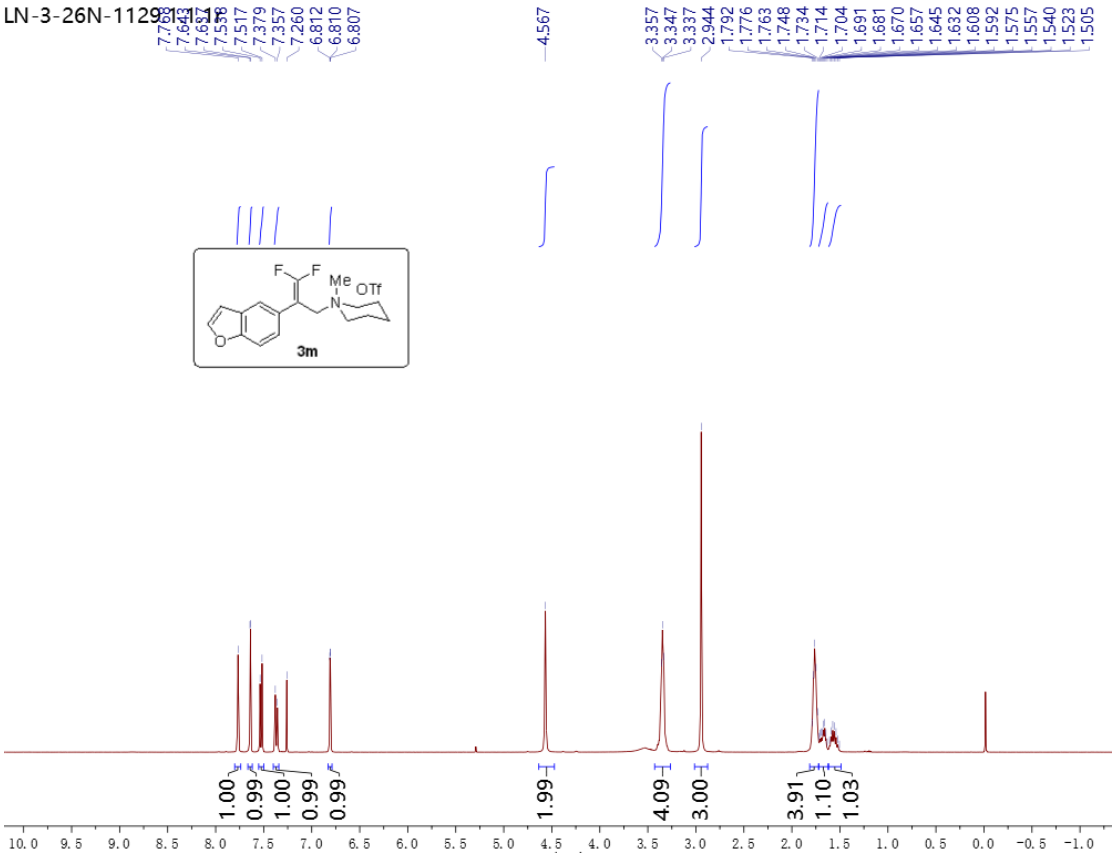

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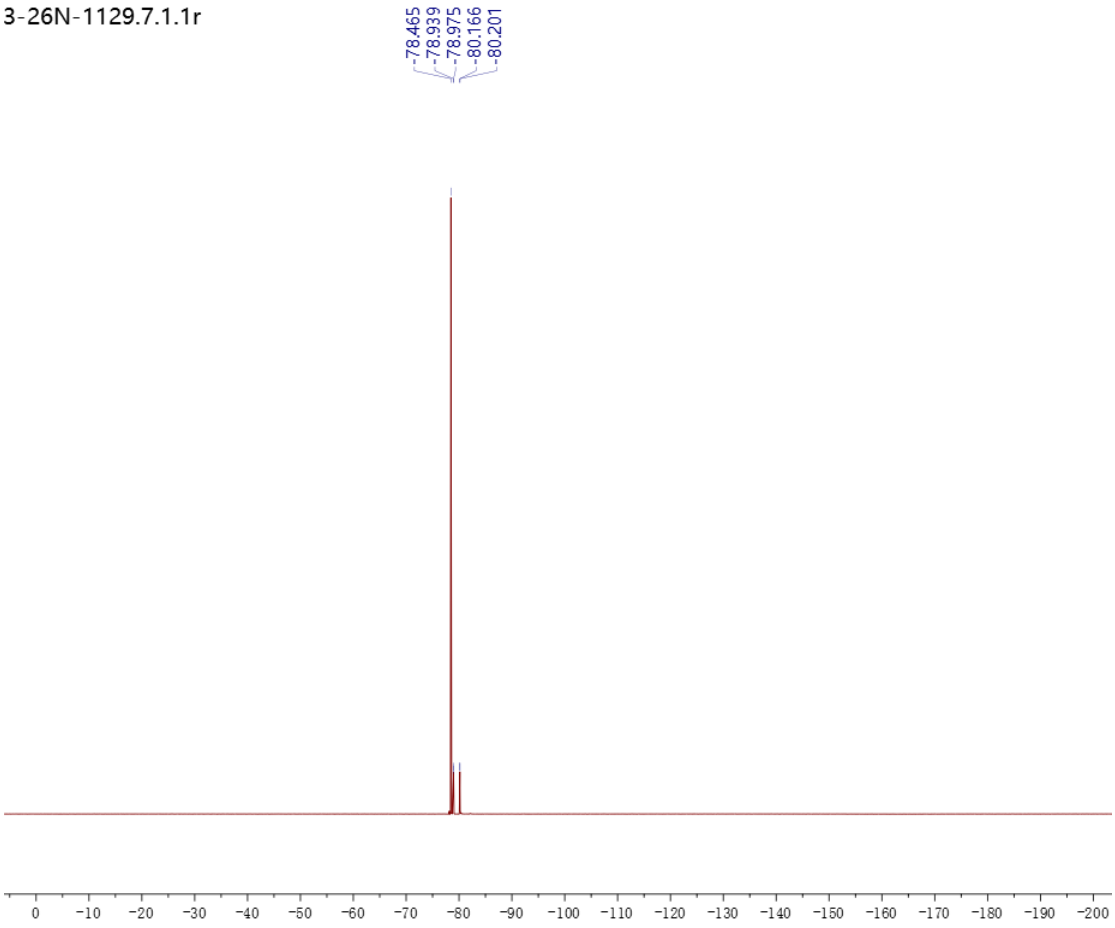

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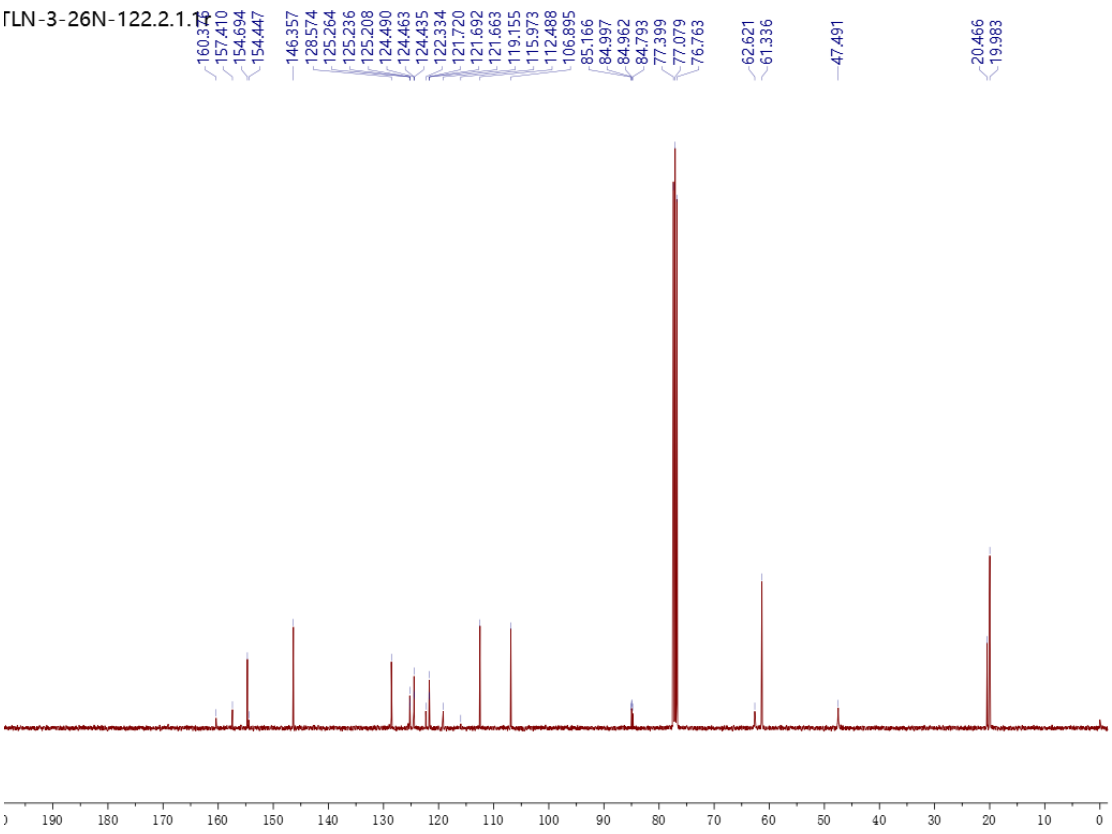

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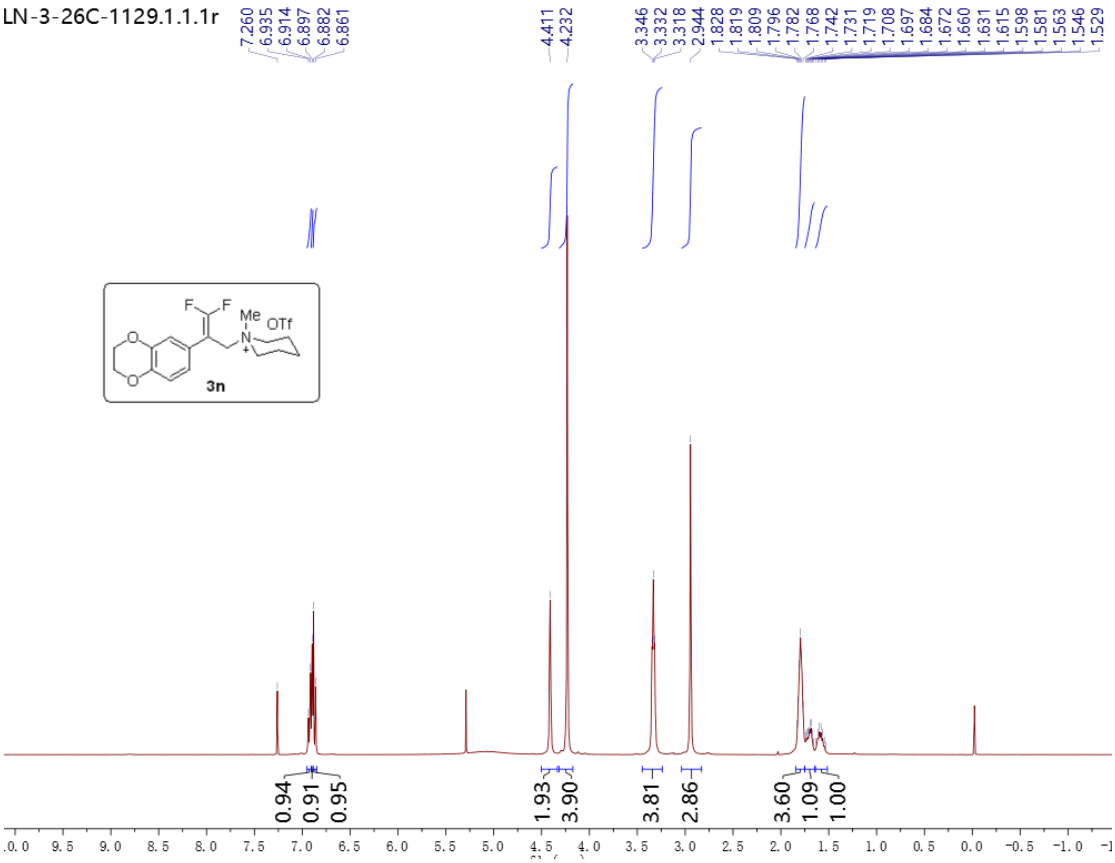

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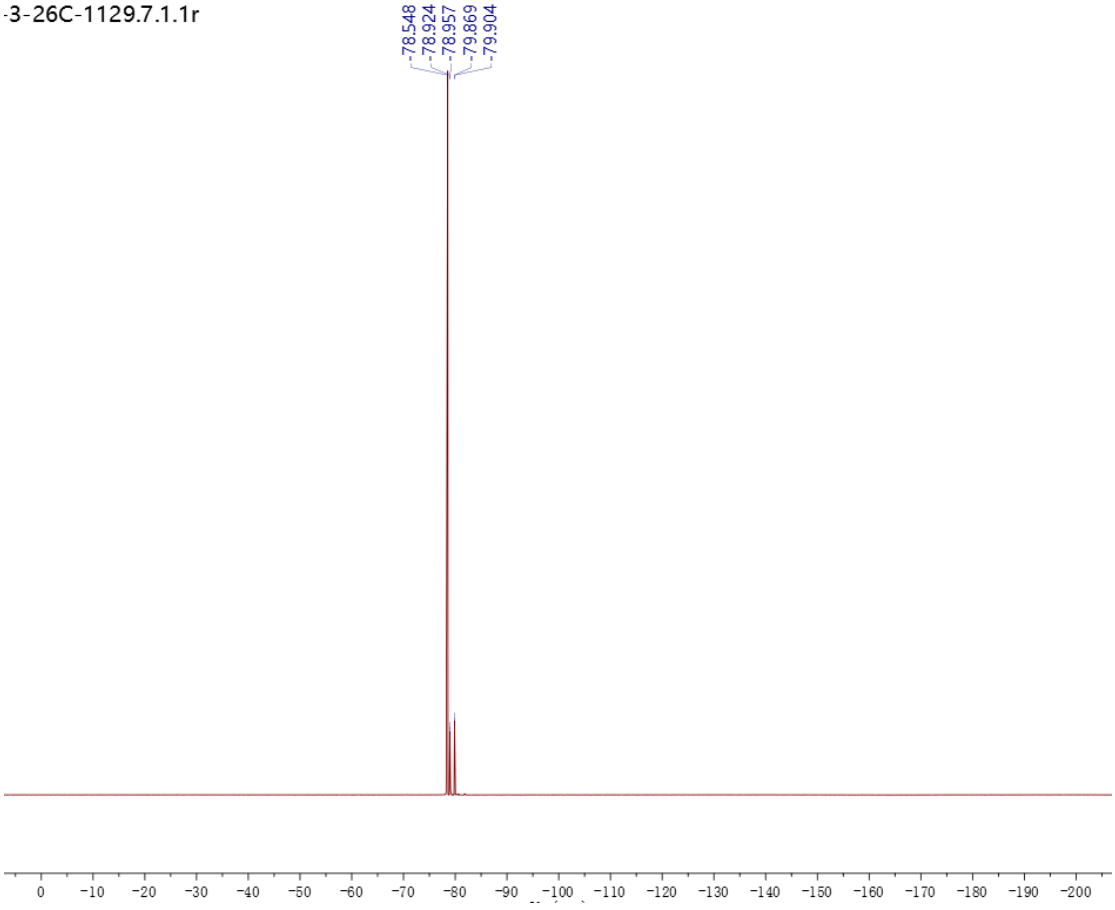

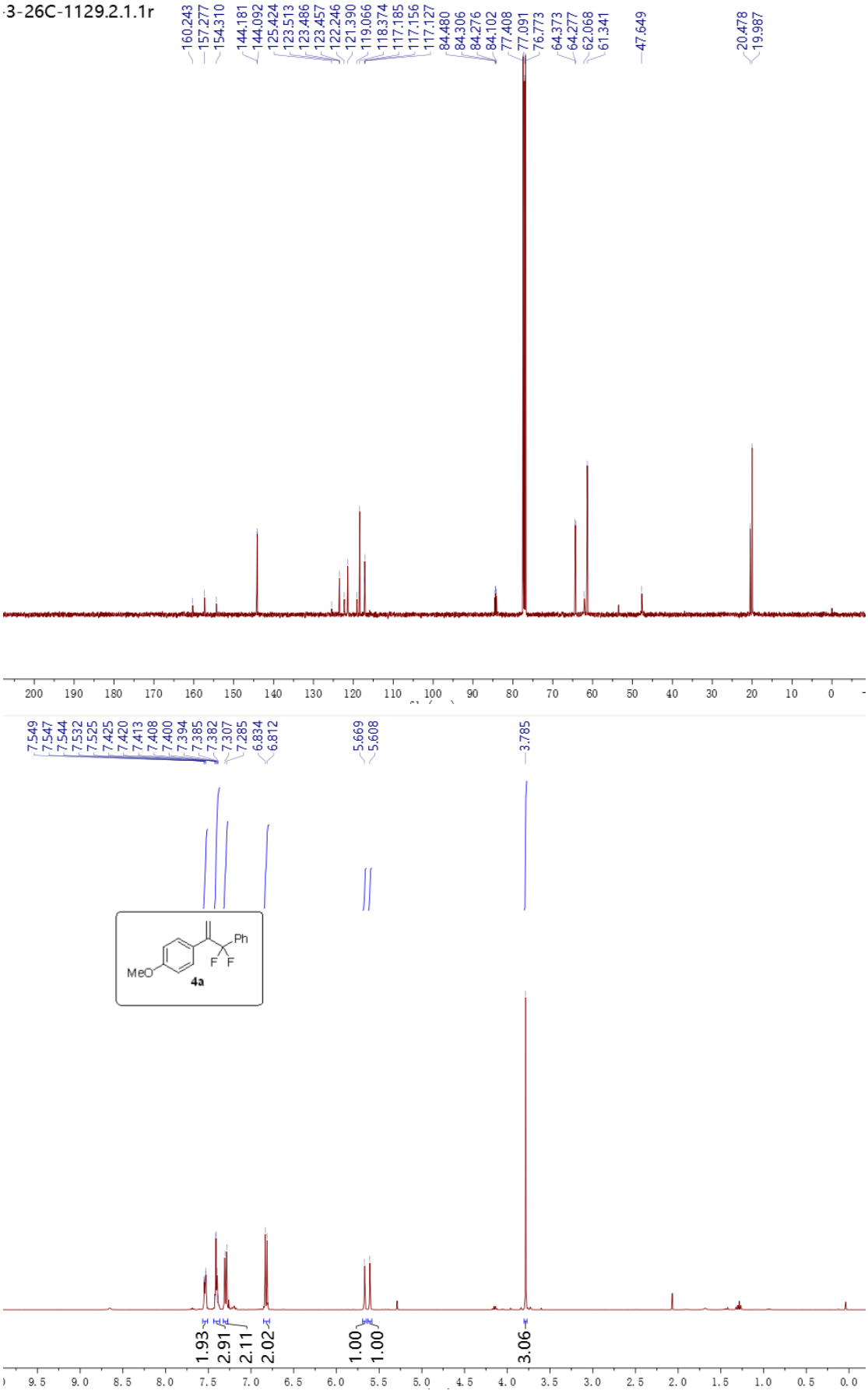
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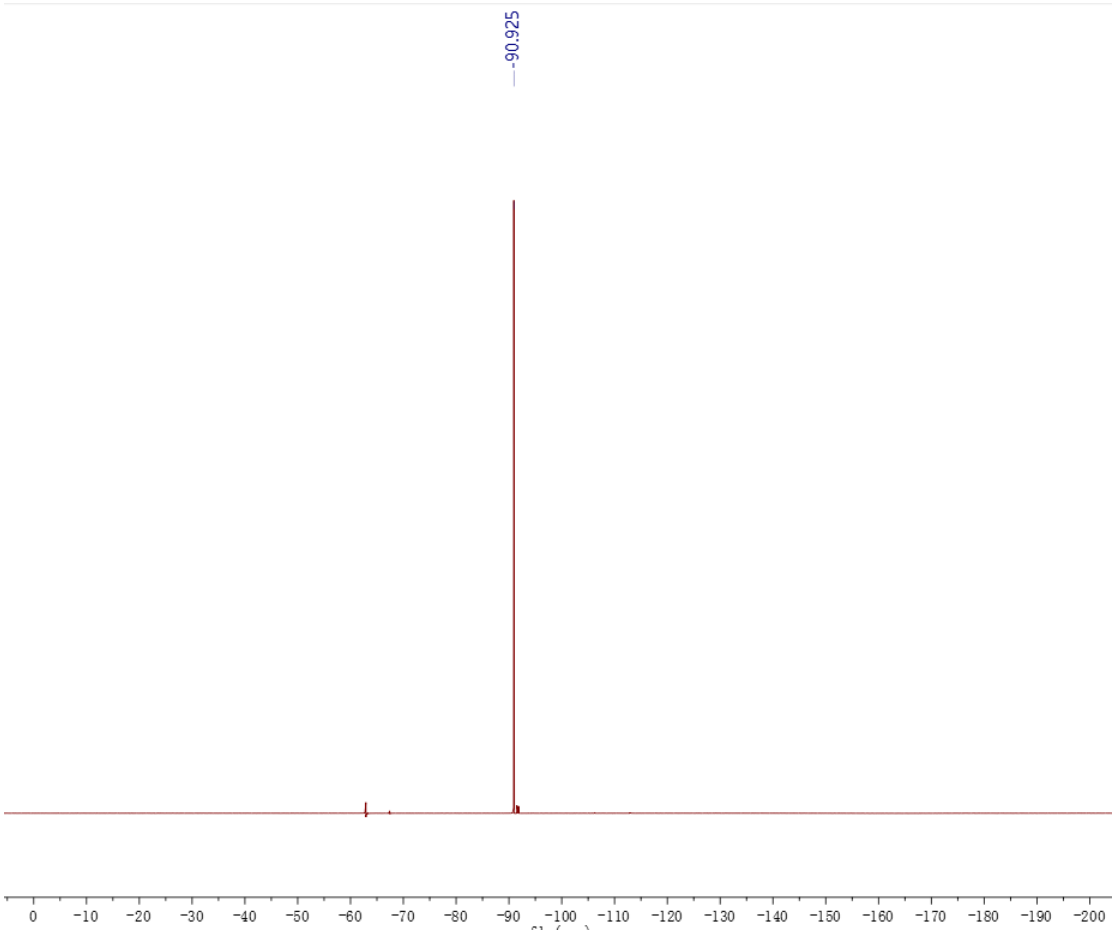
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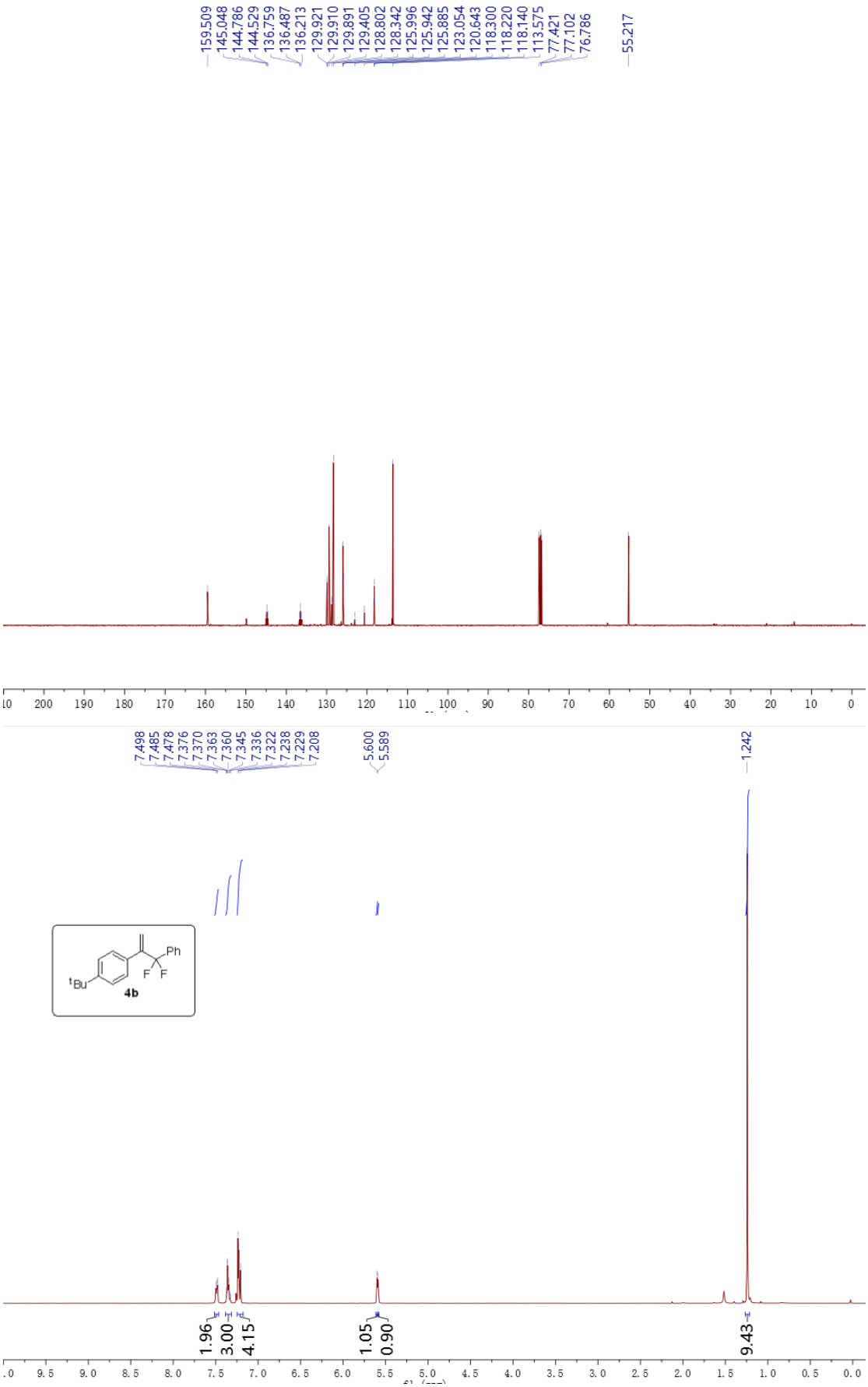
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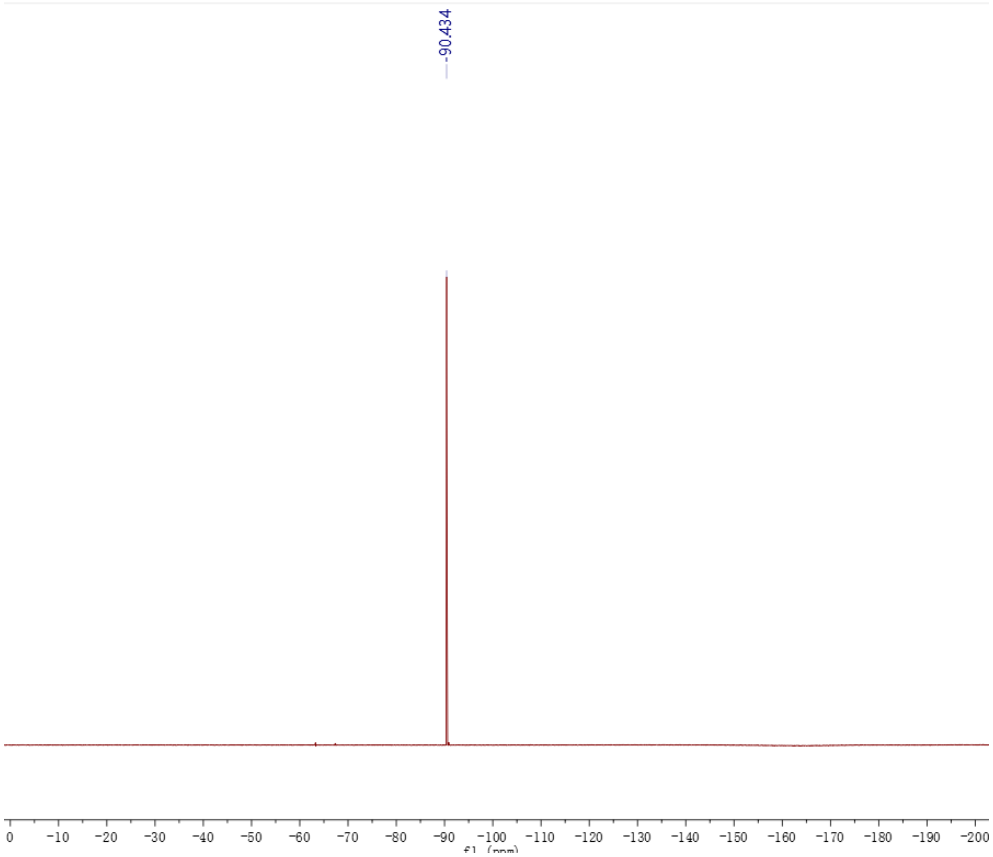
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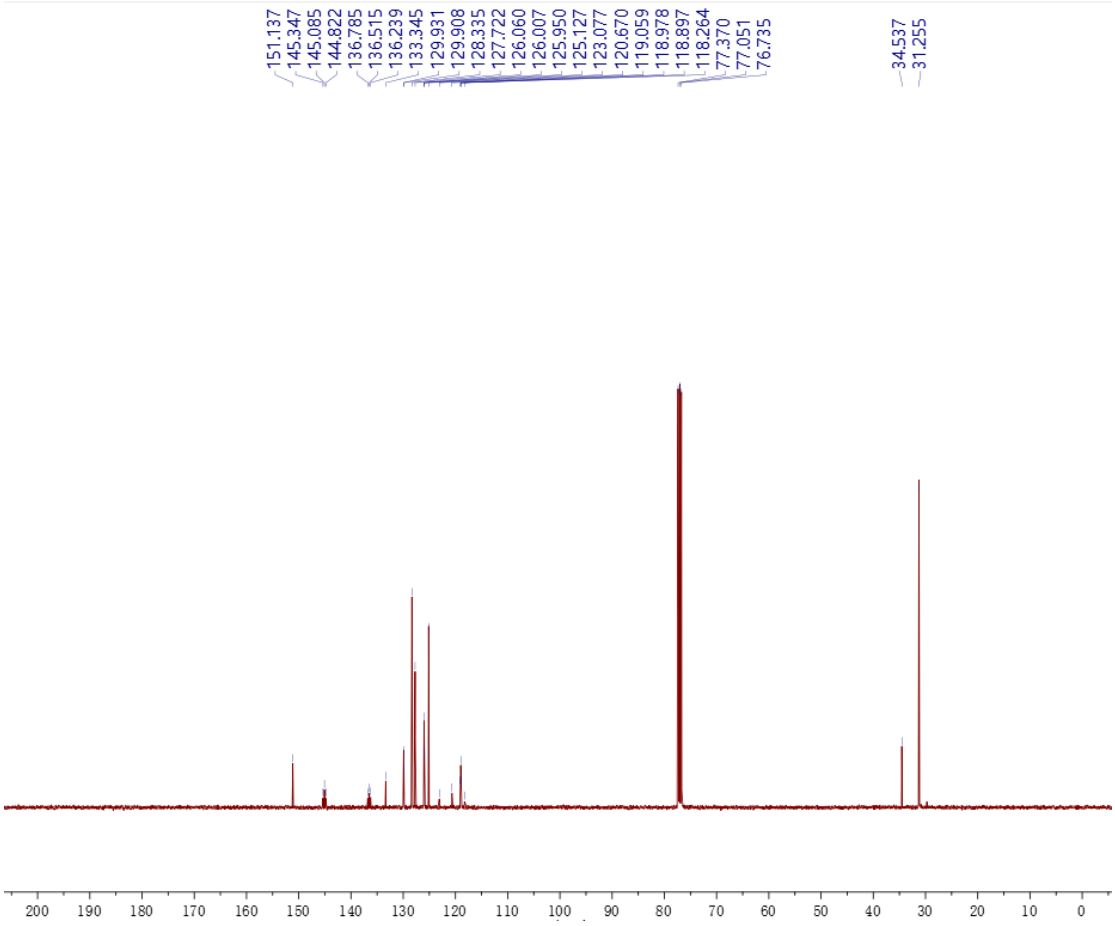
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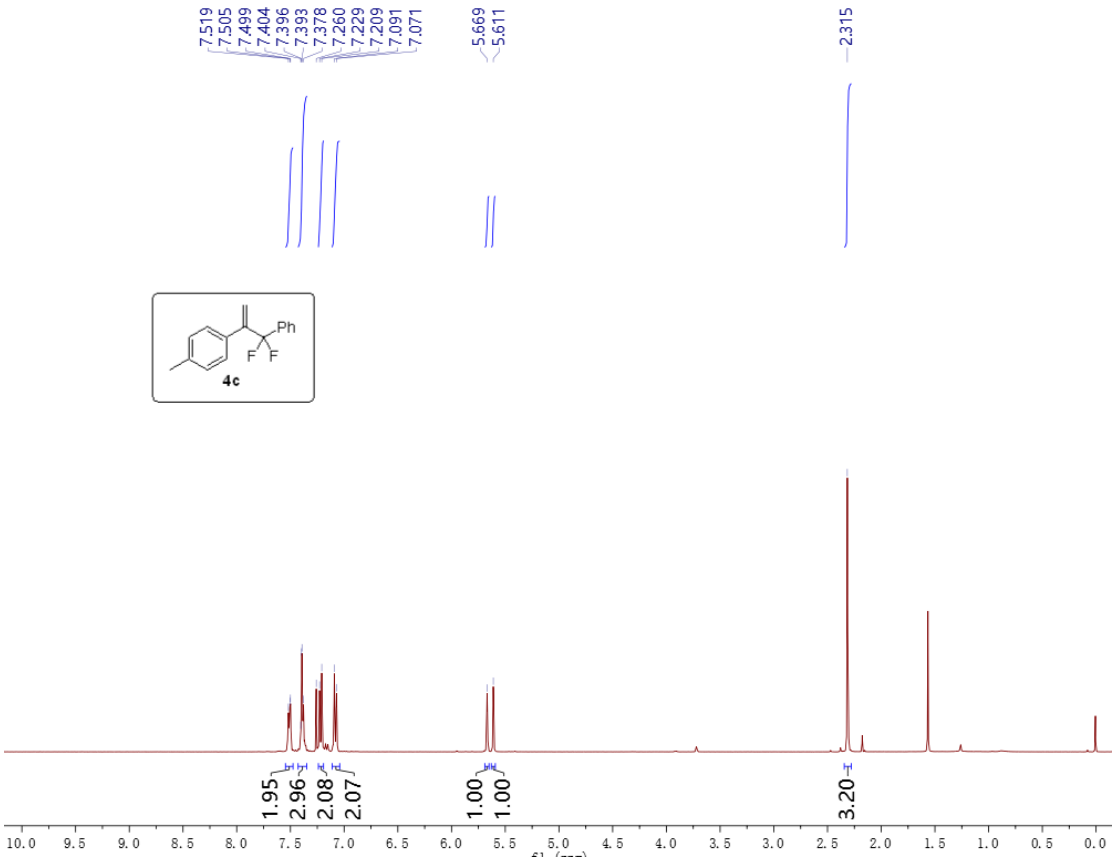
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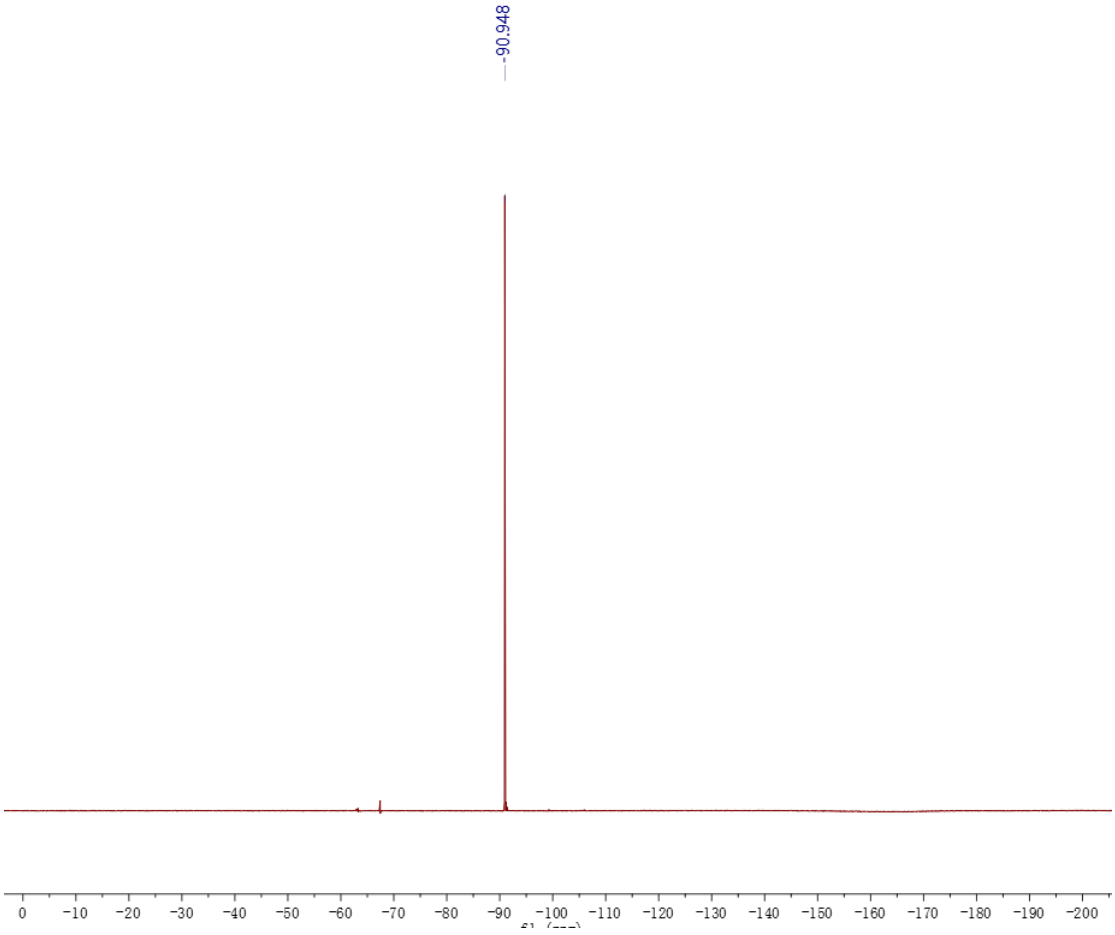
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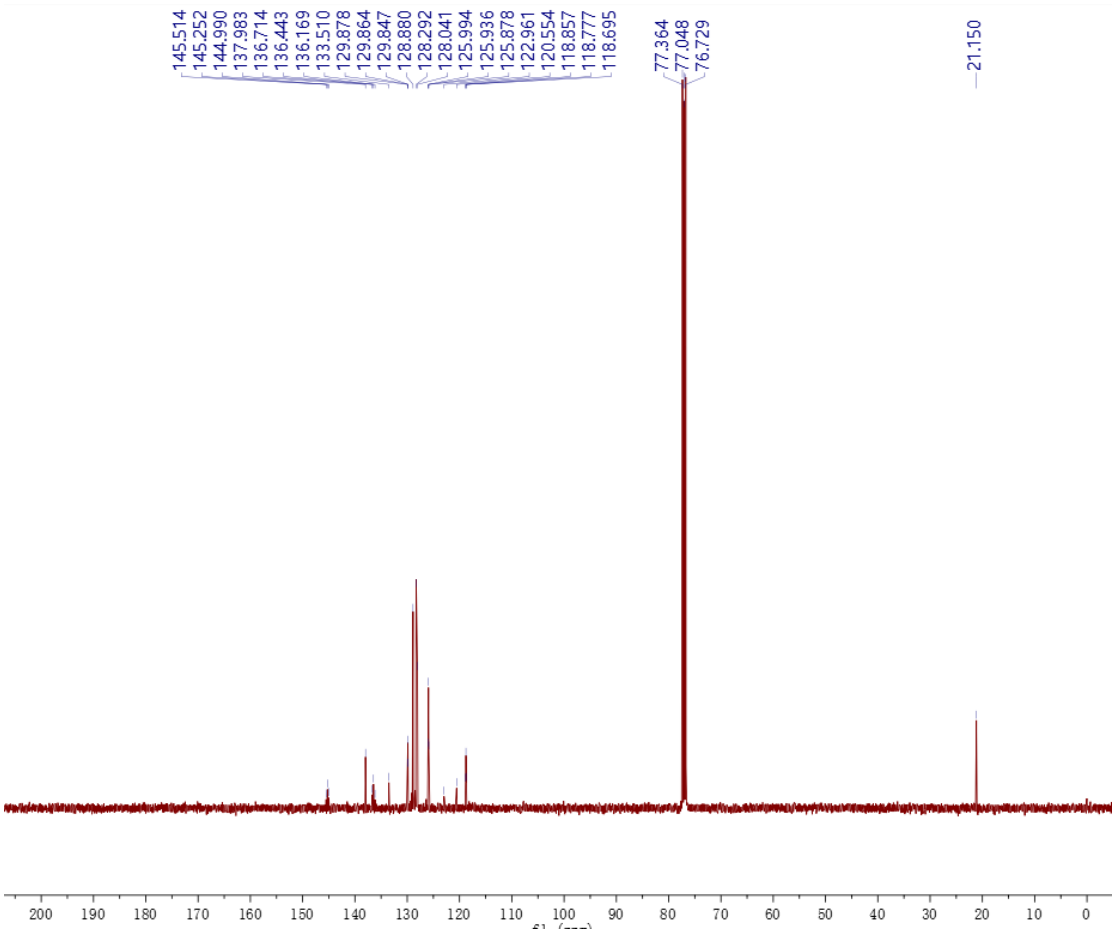
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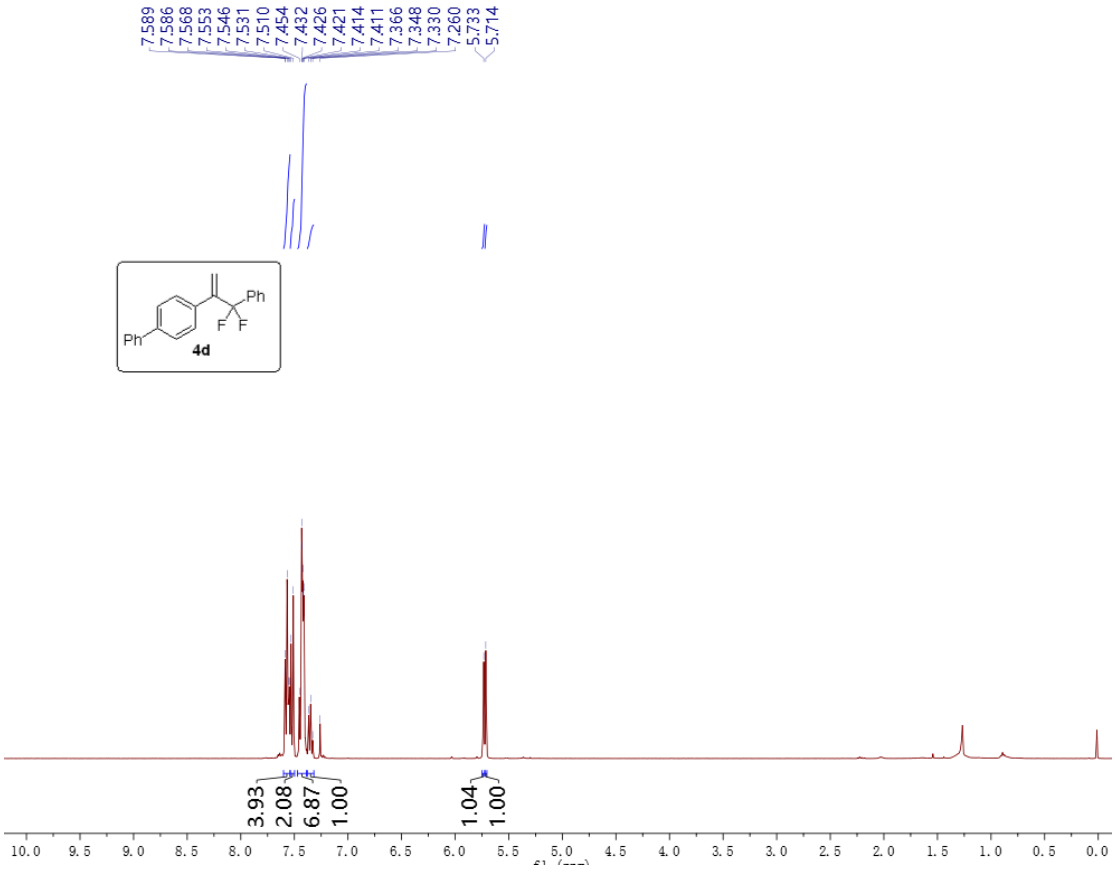
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F
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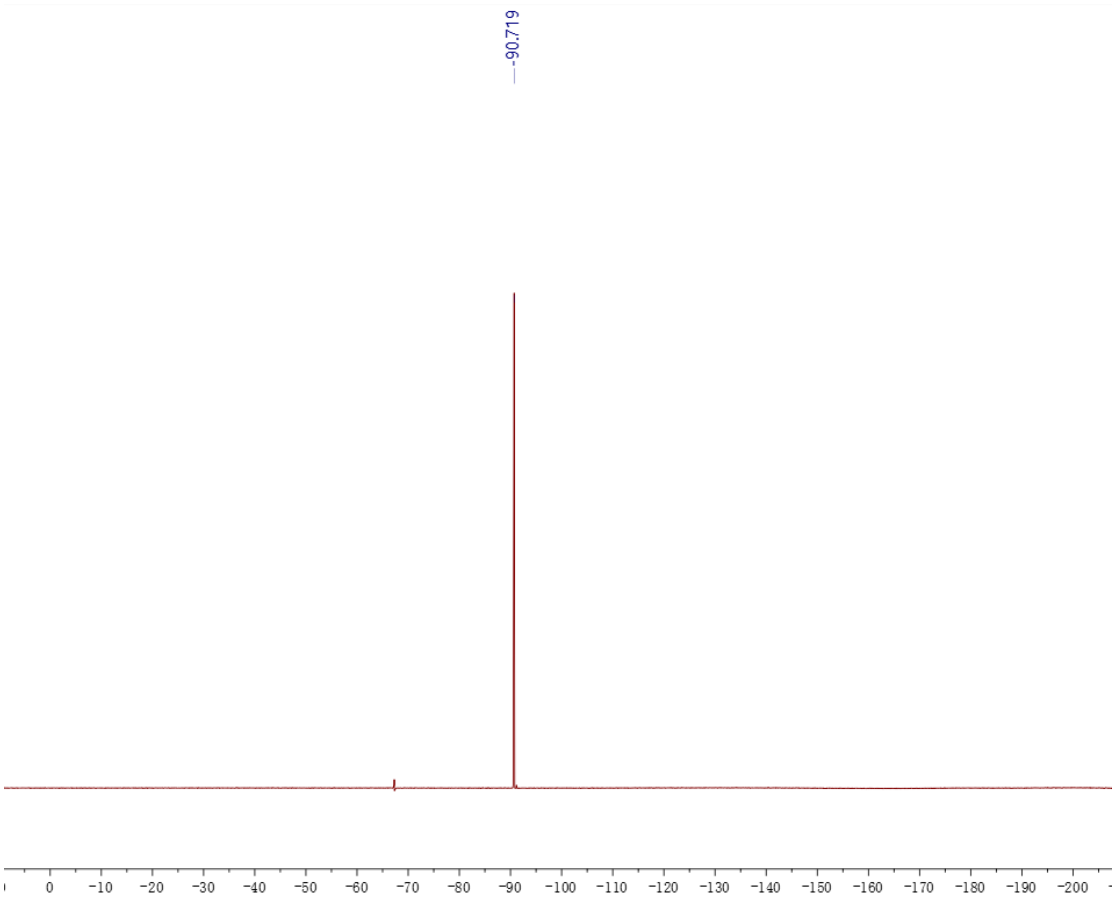
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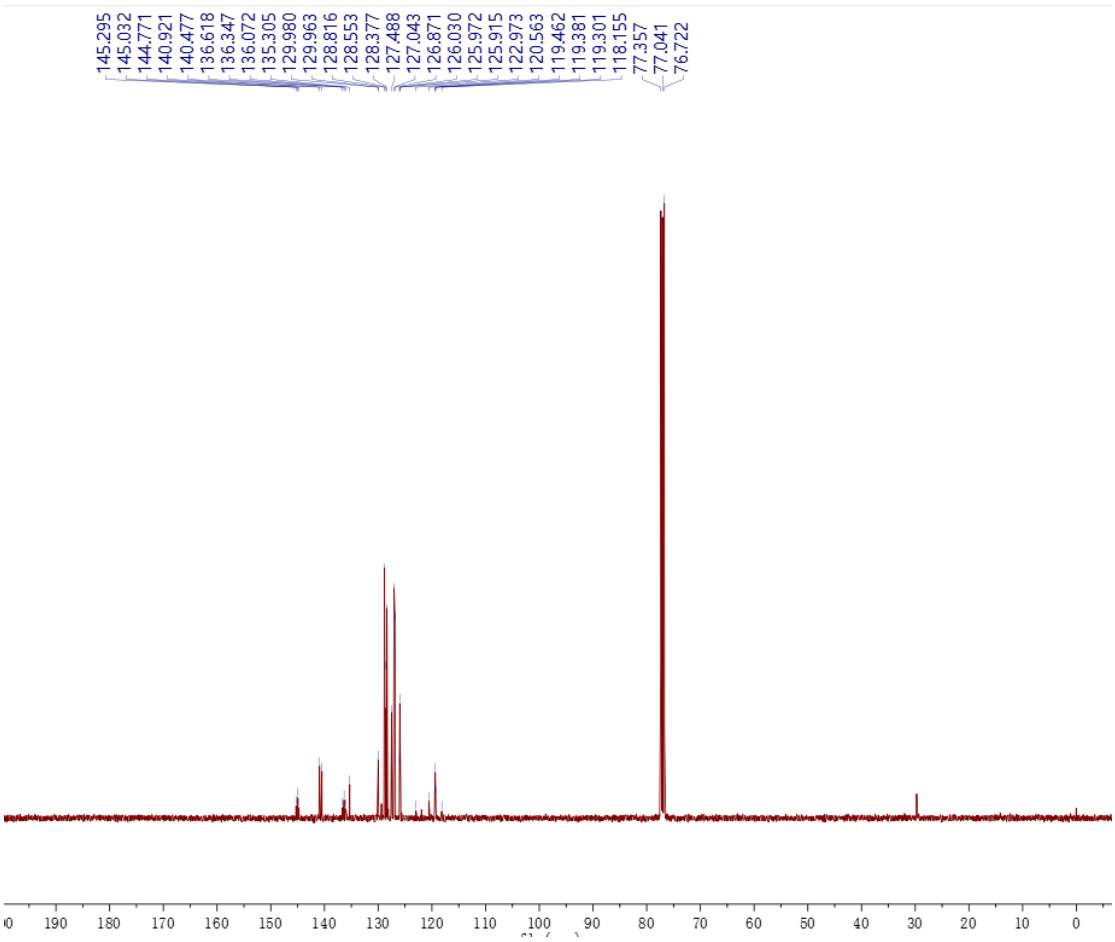
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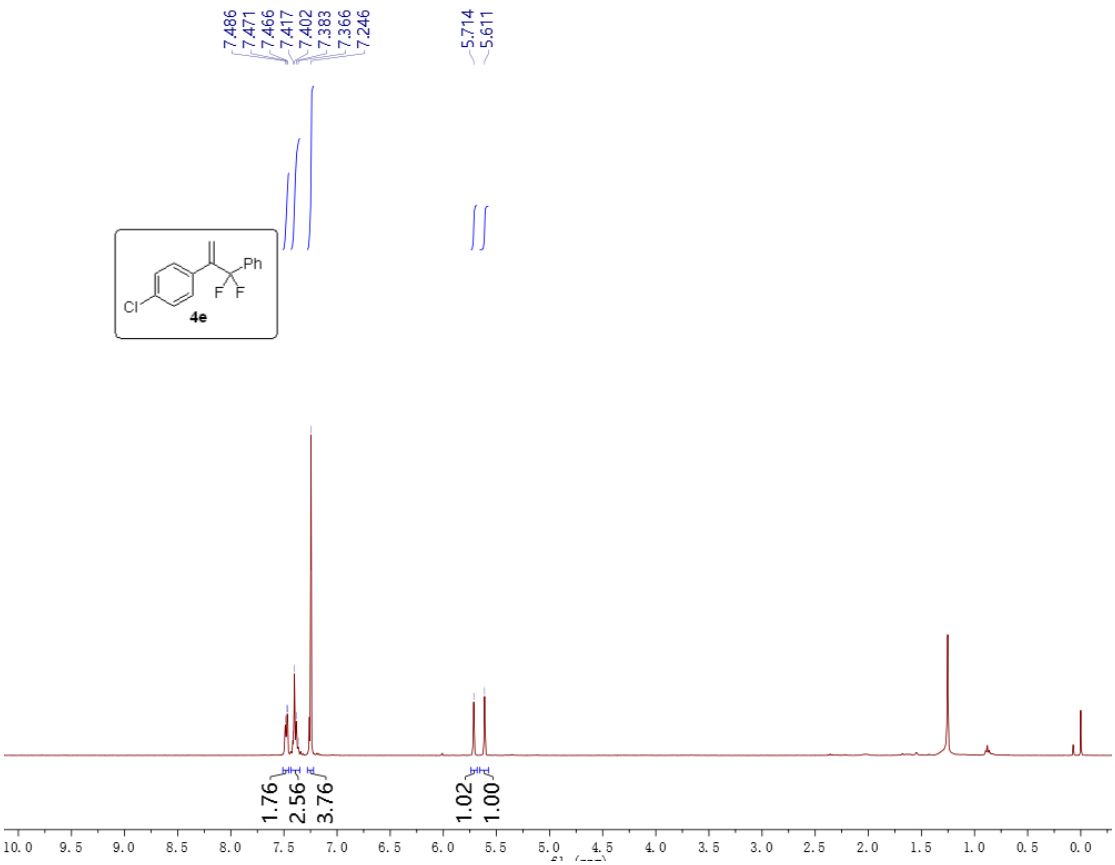
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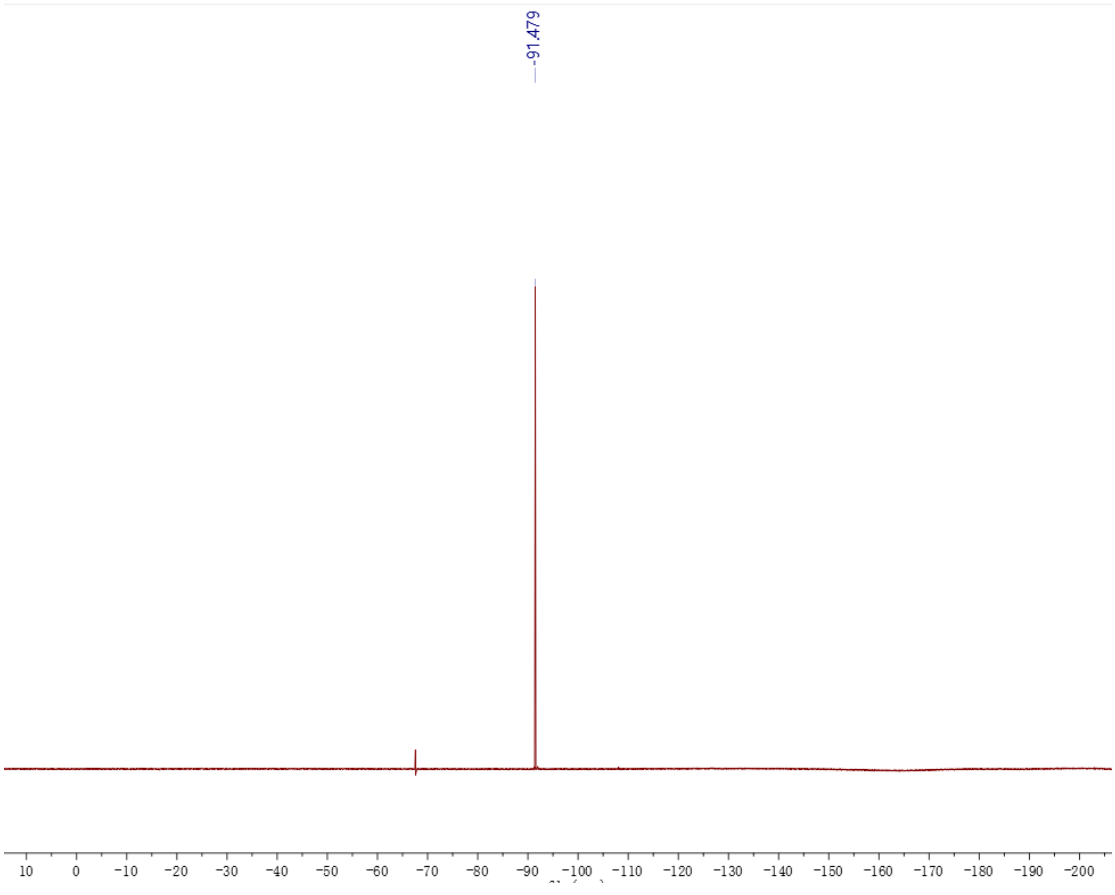
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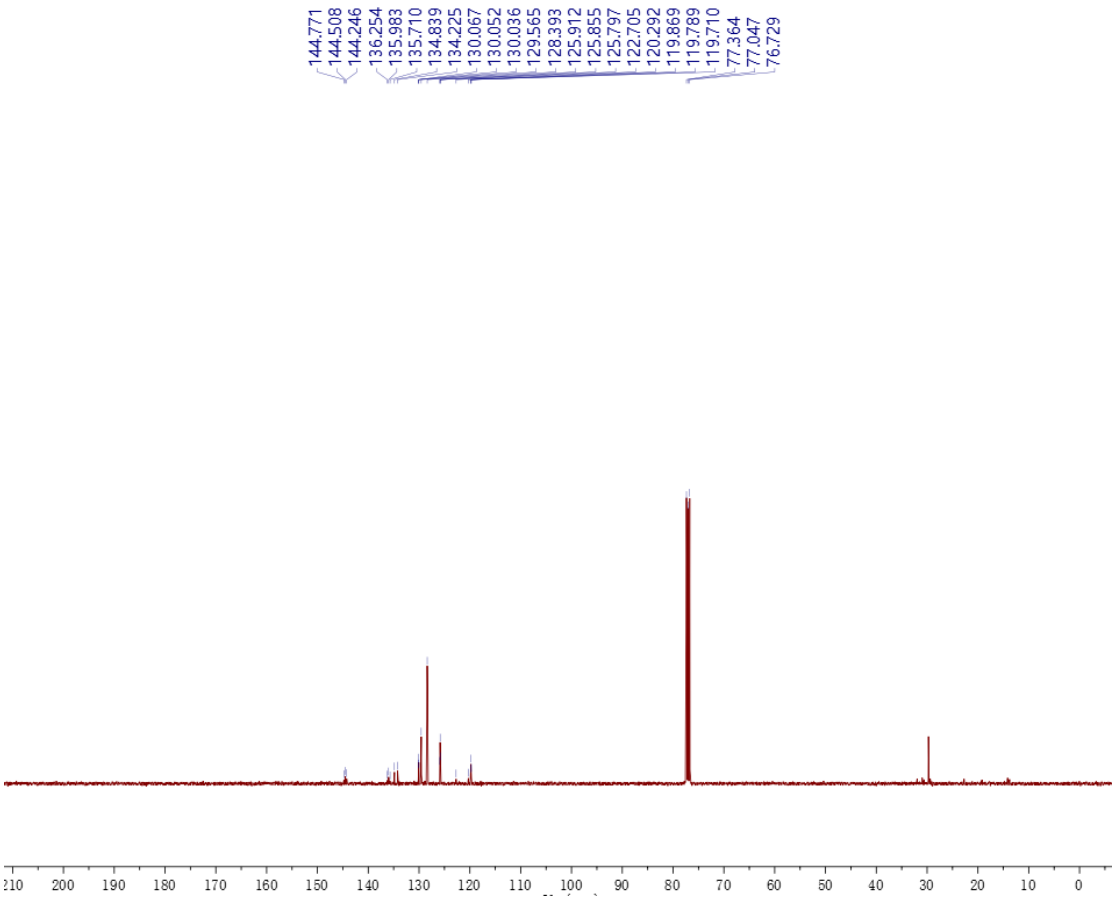
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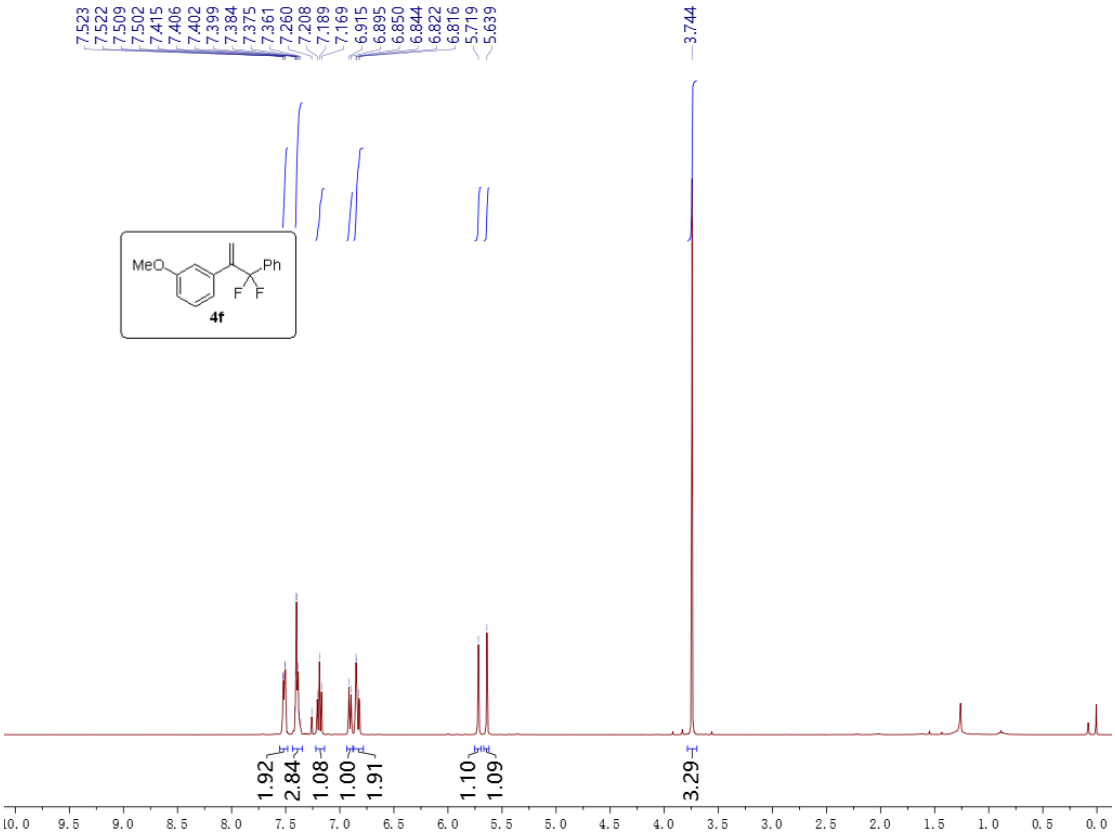
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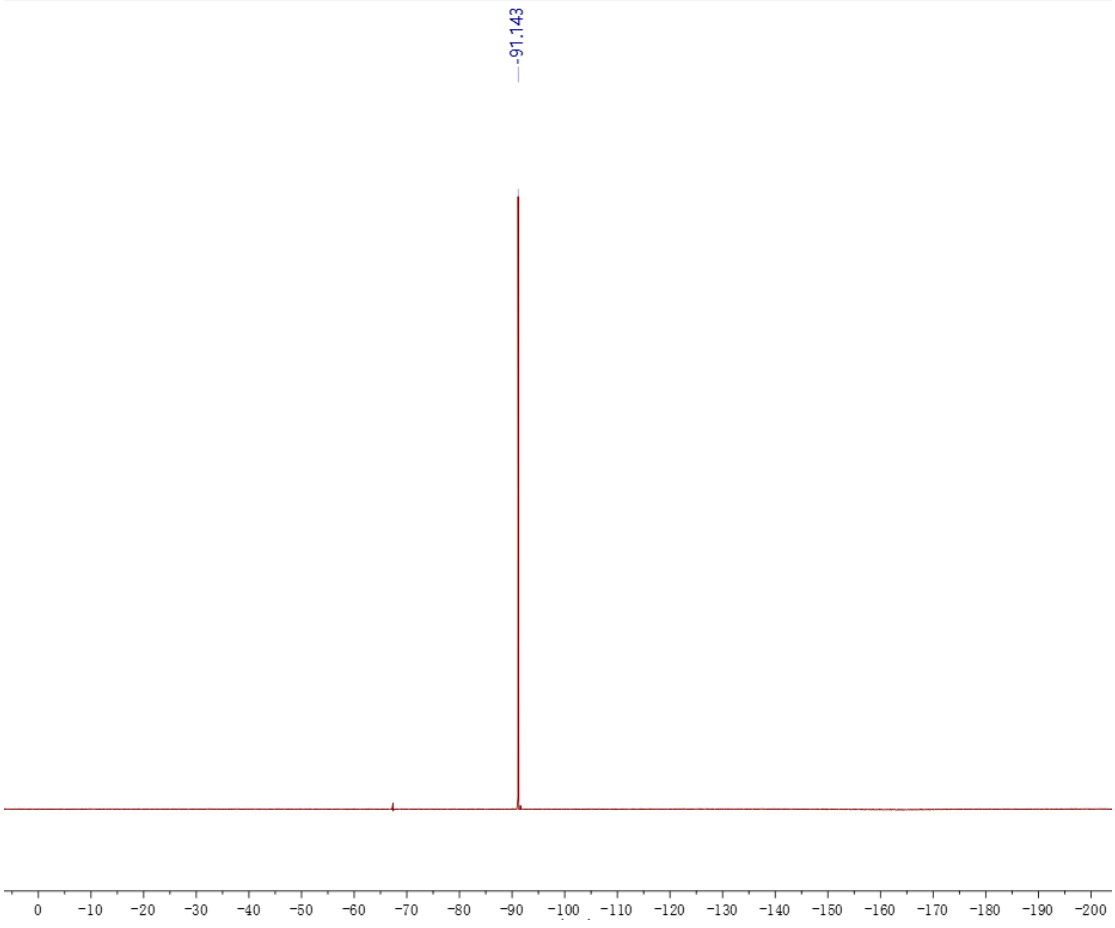
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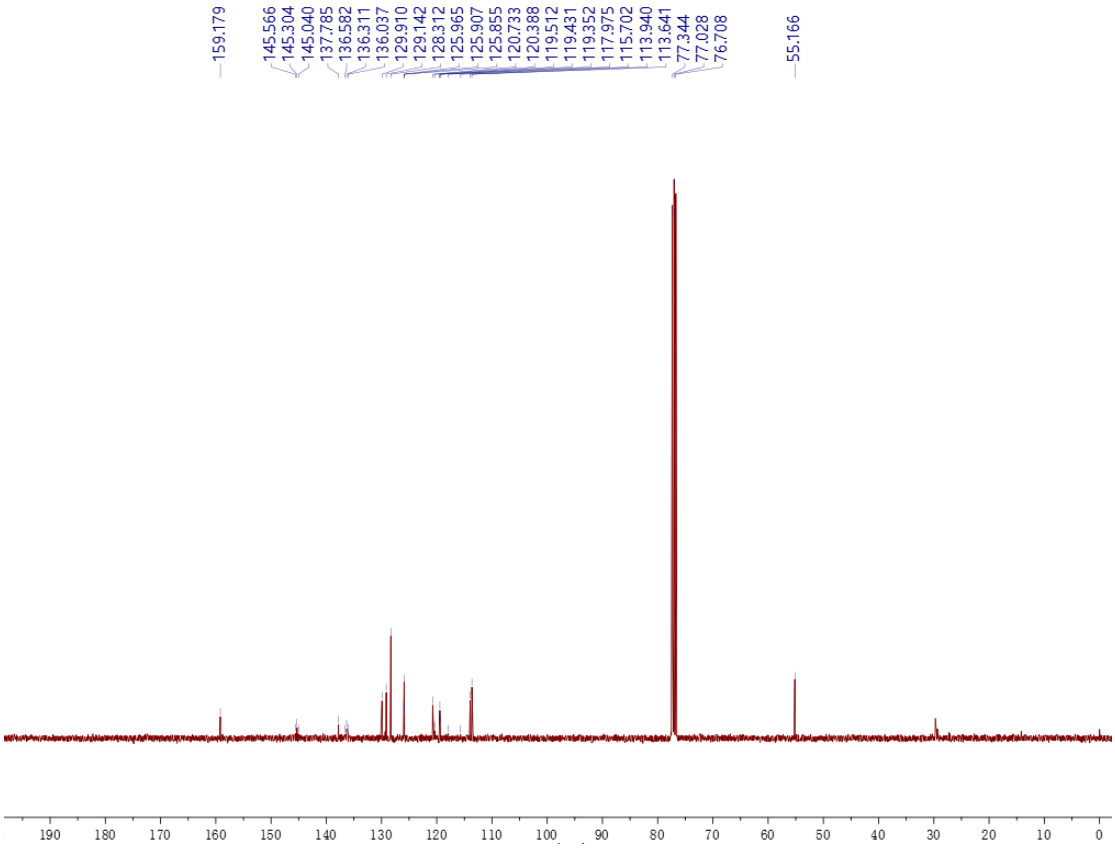
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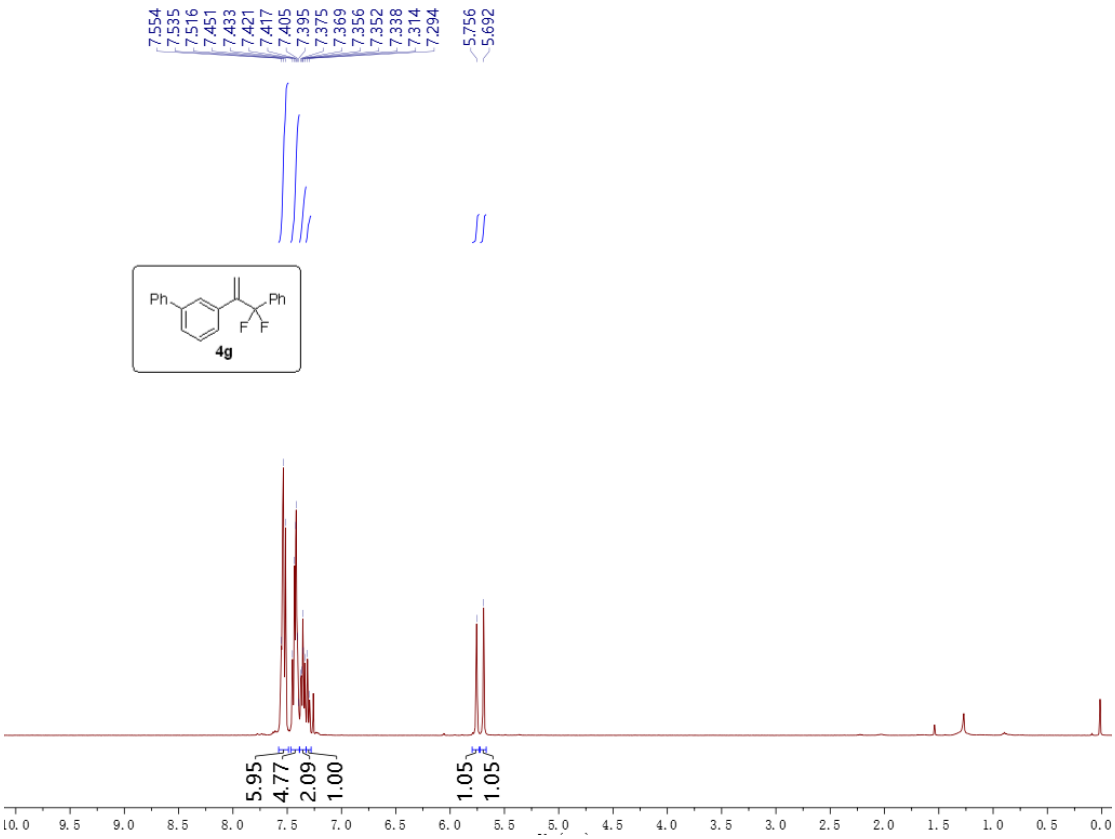
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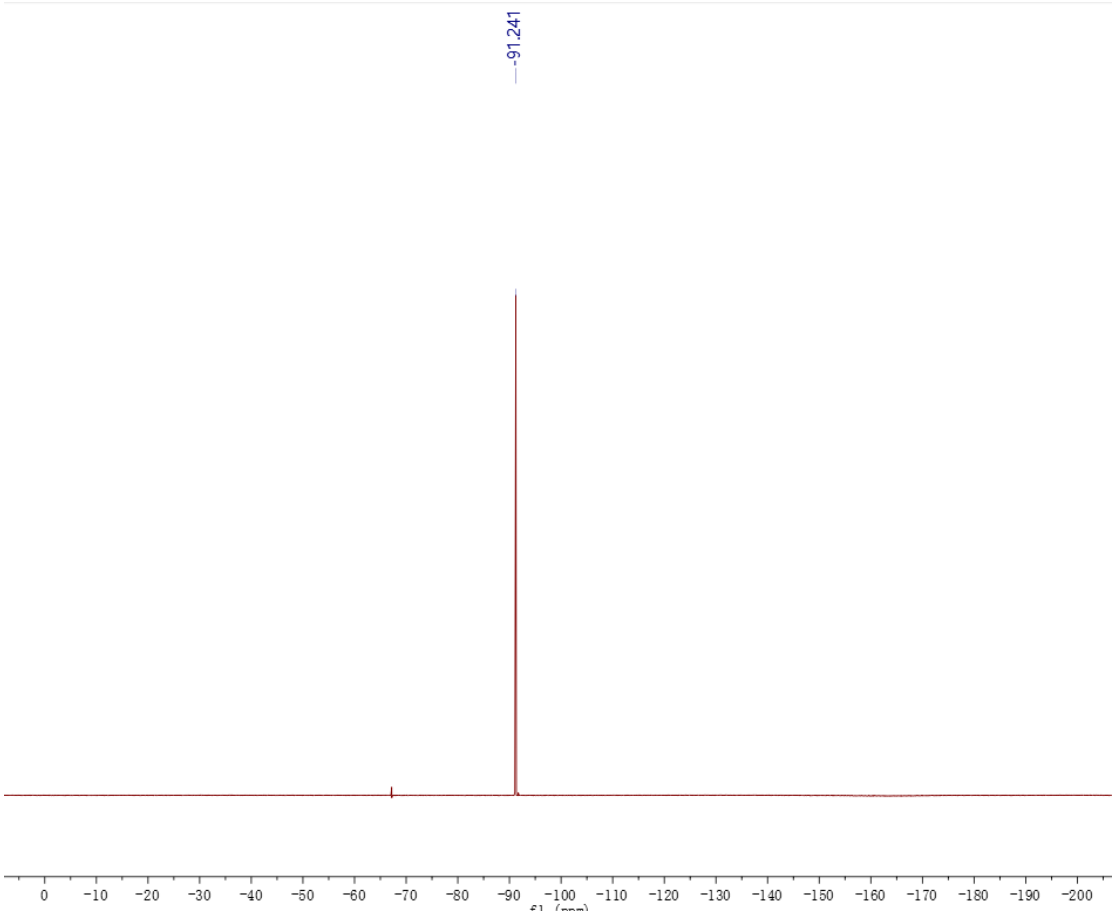
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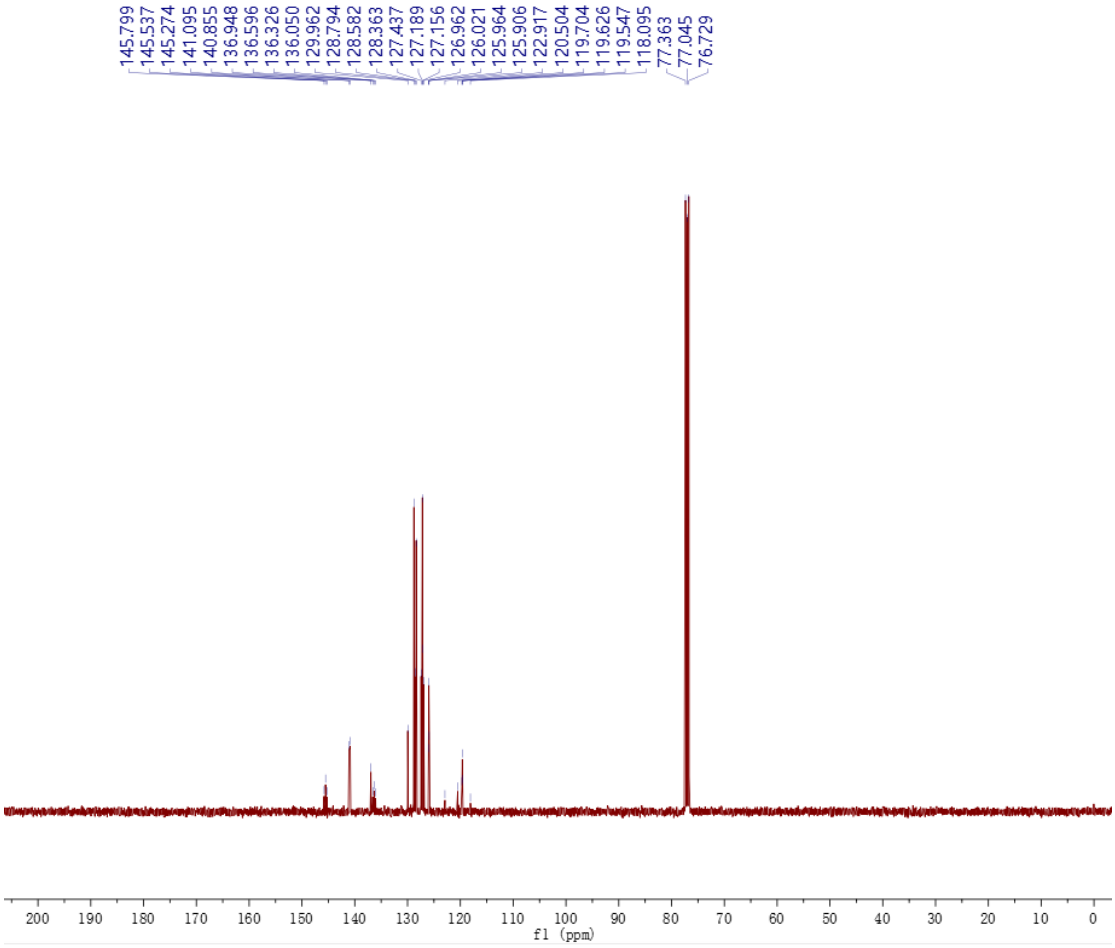
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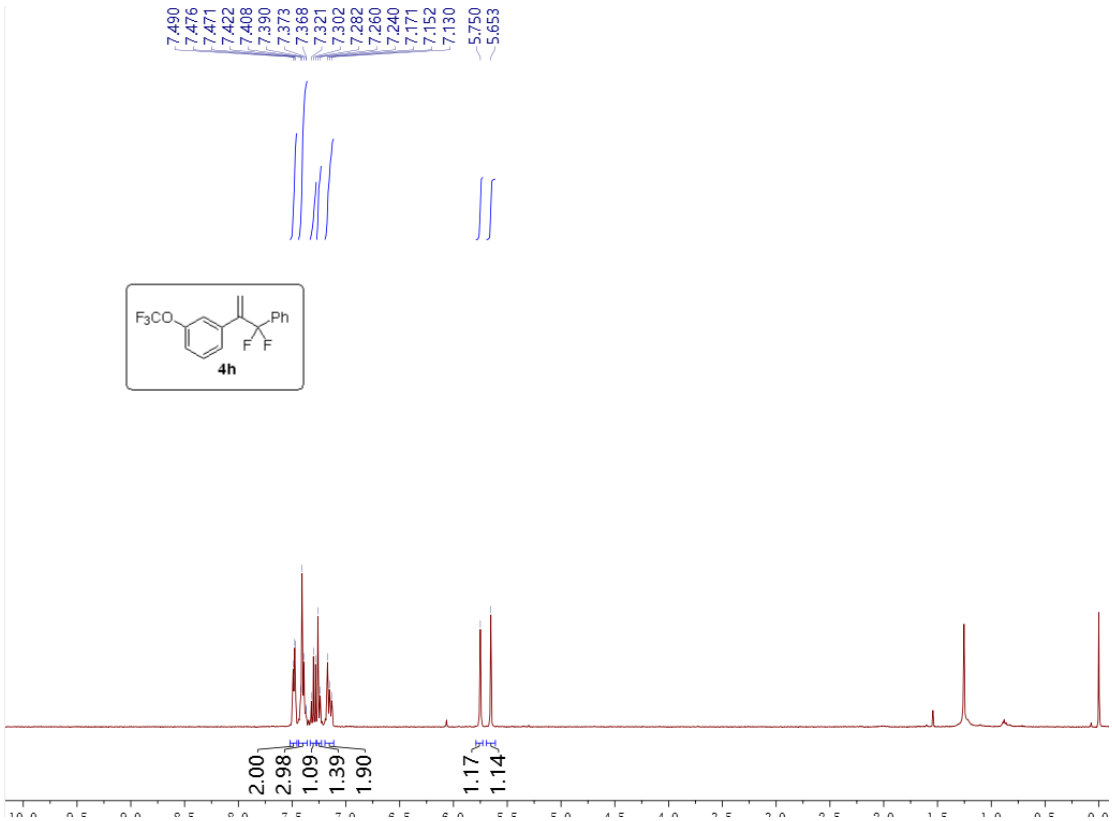
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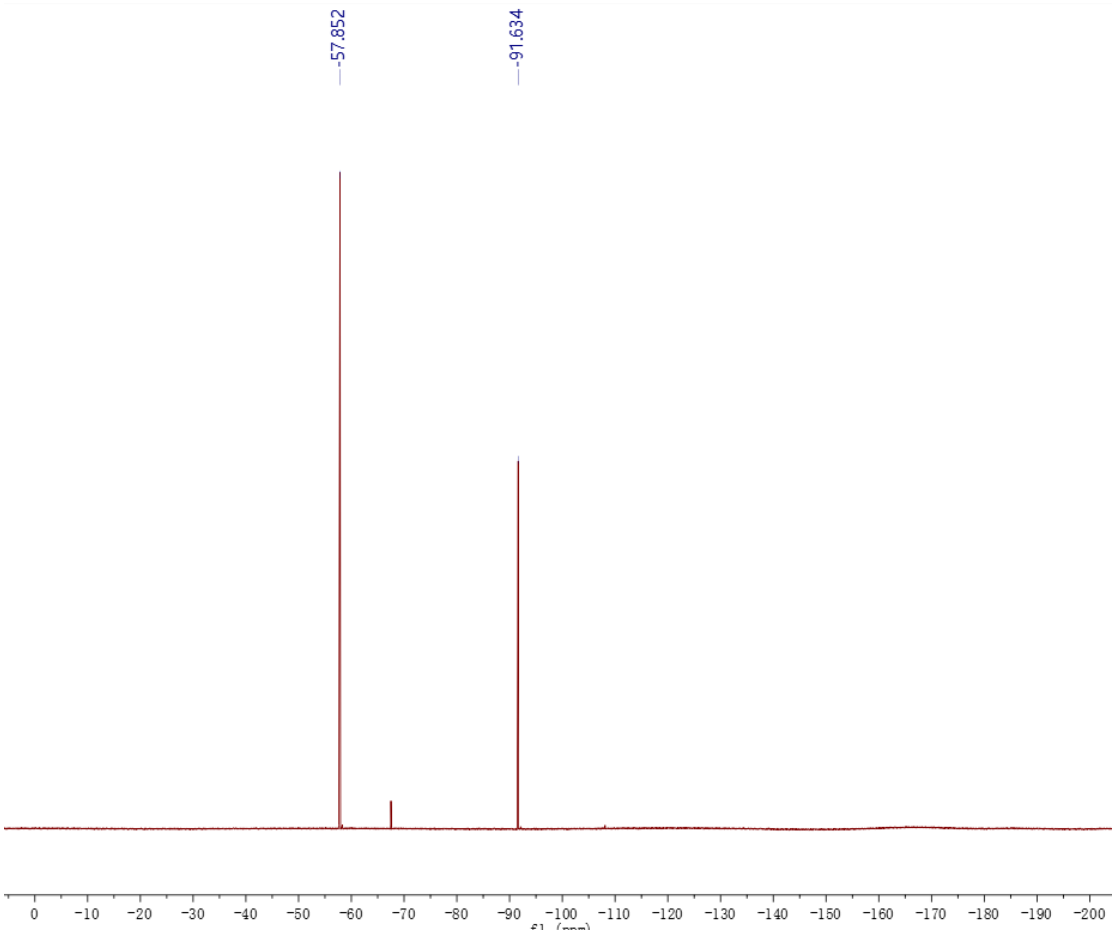
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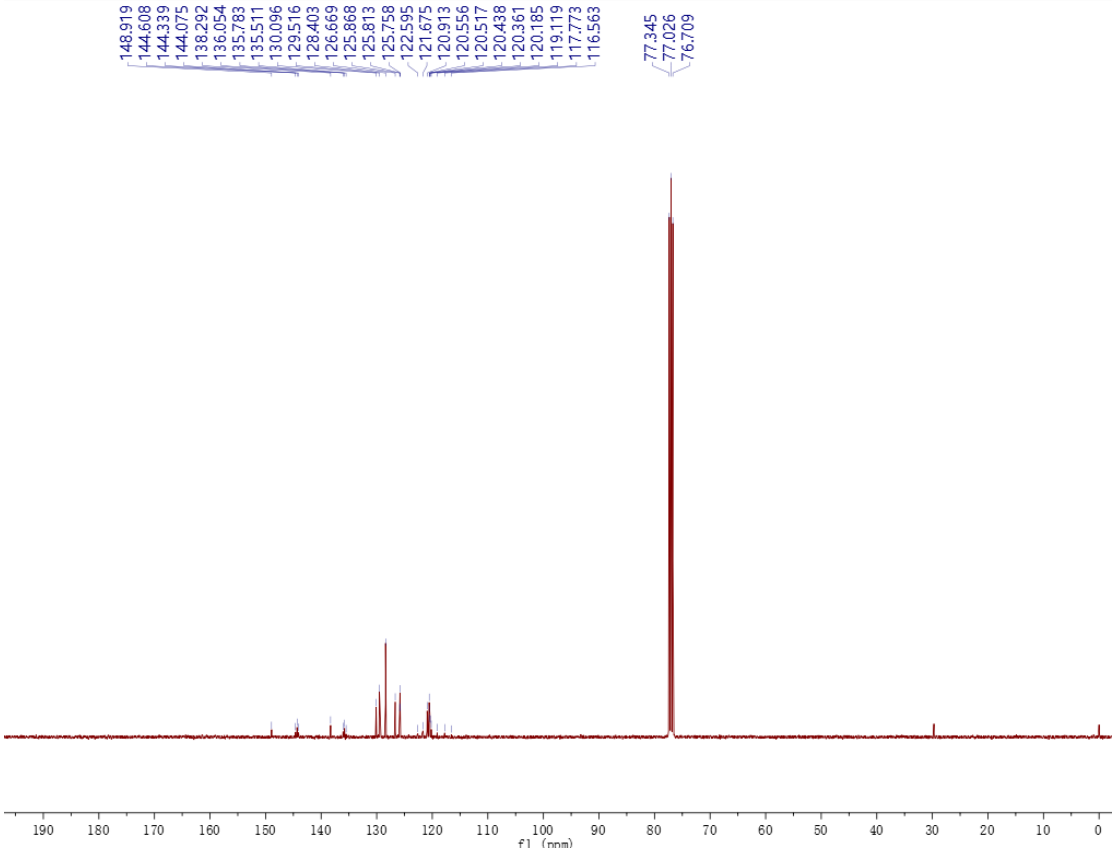
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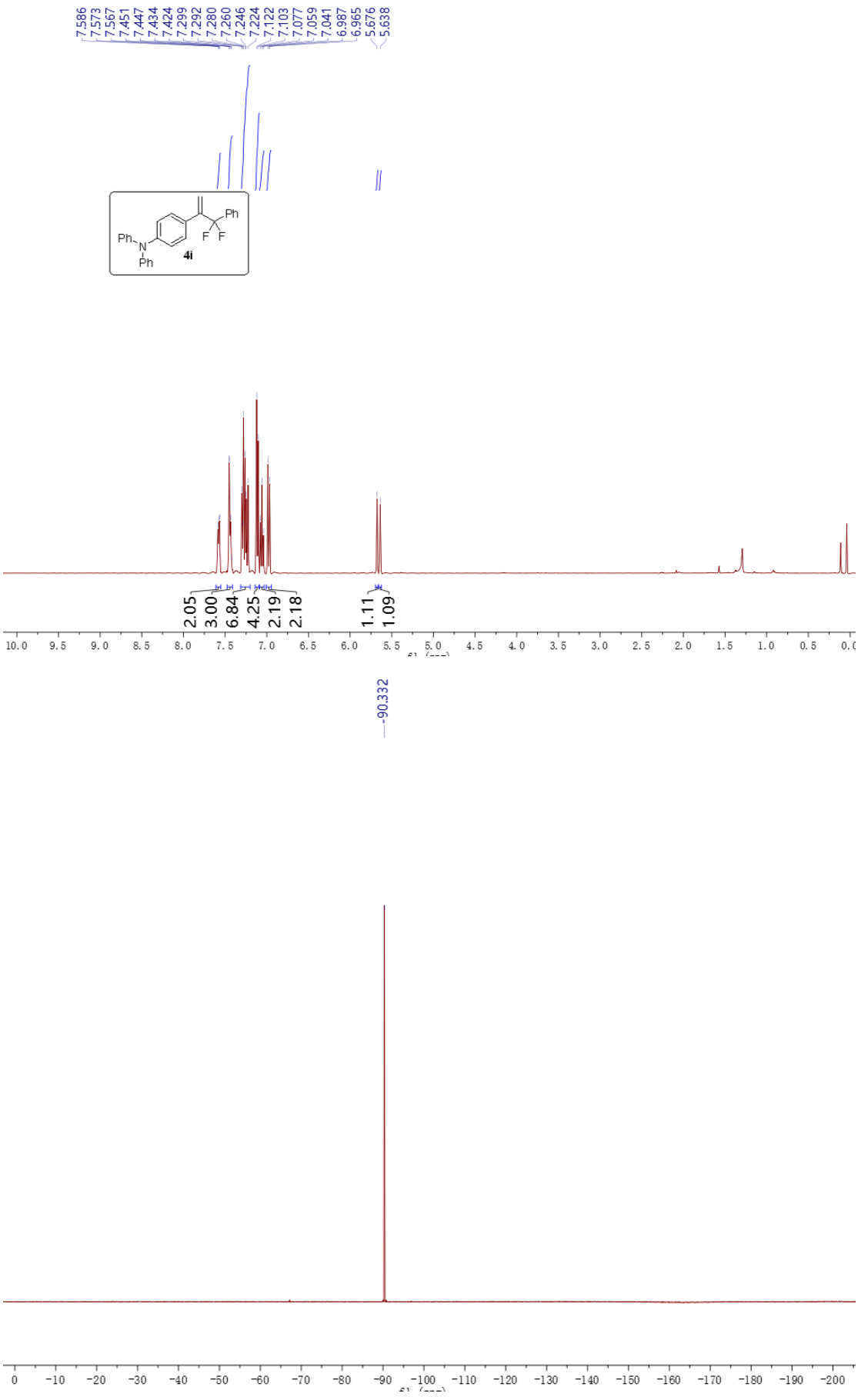
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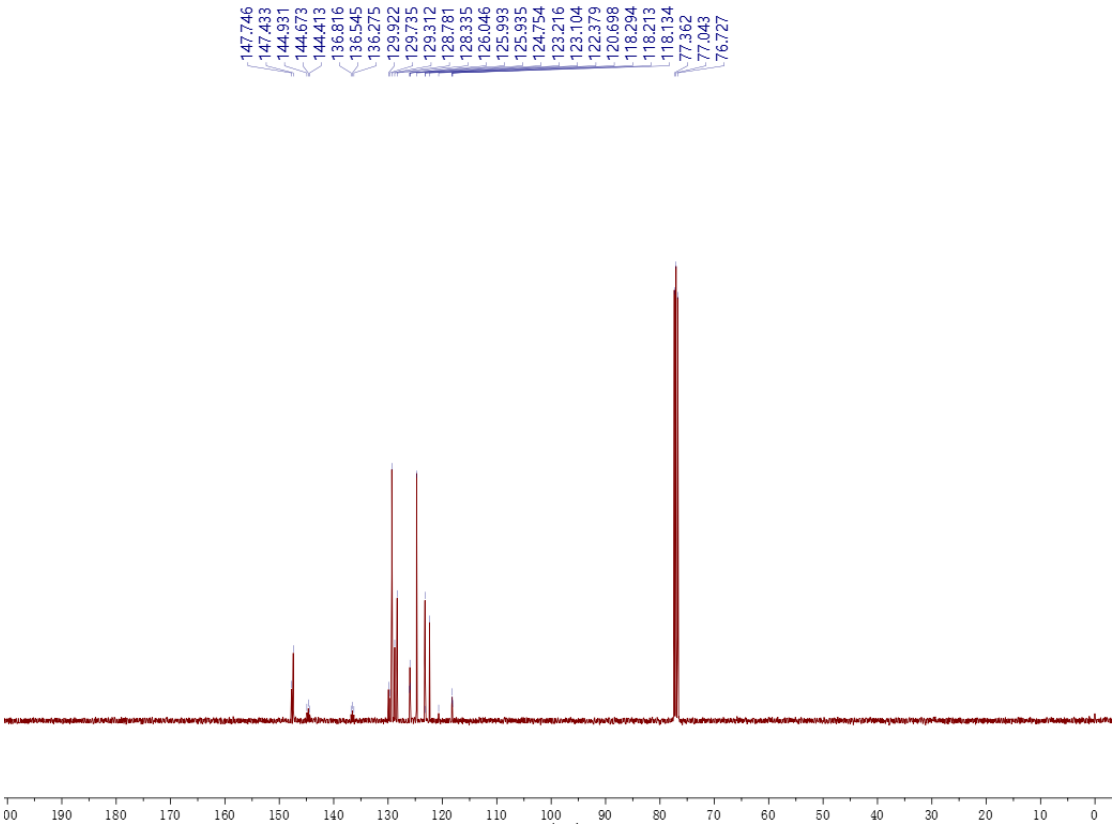
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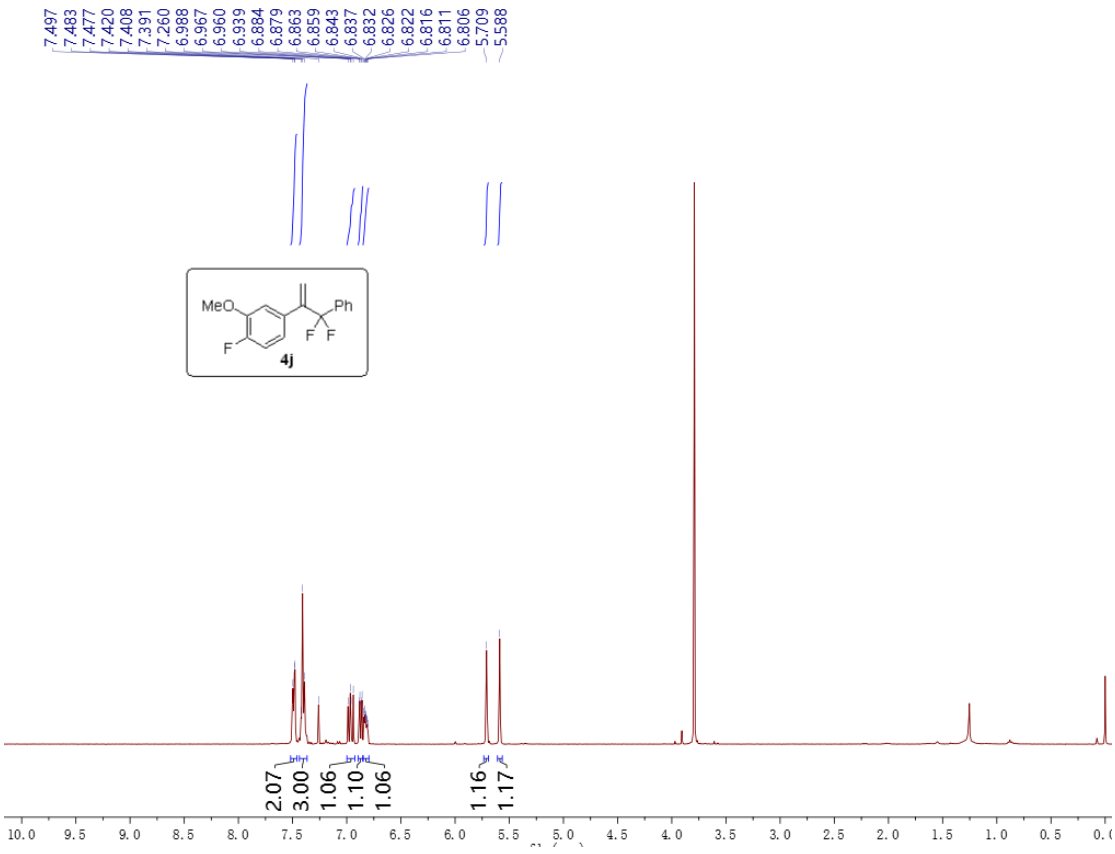
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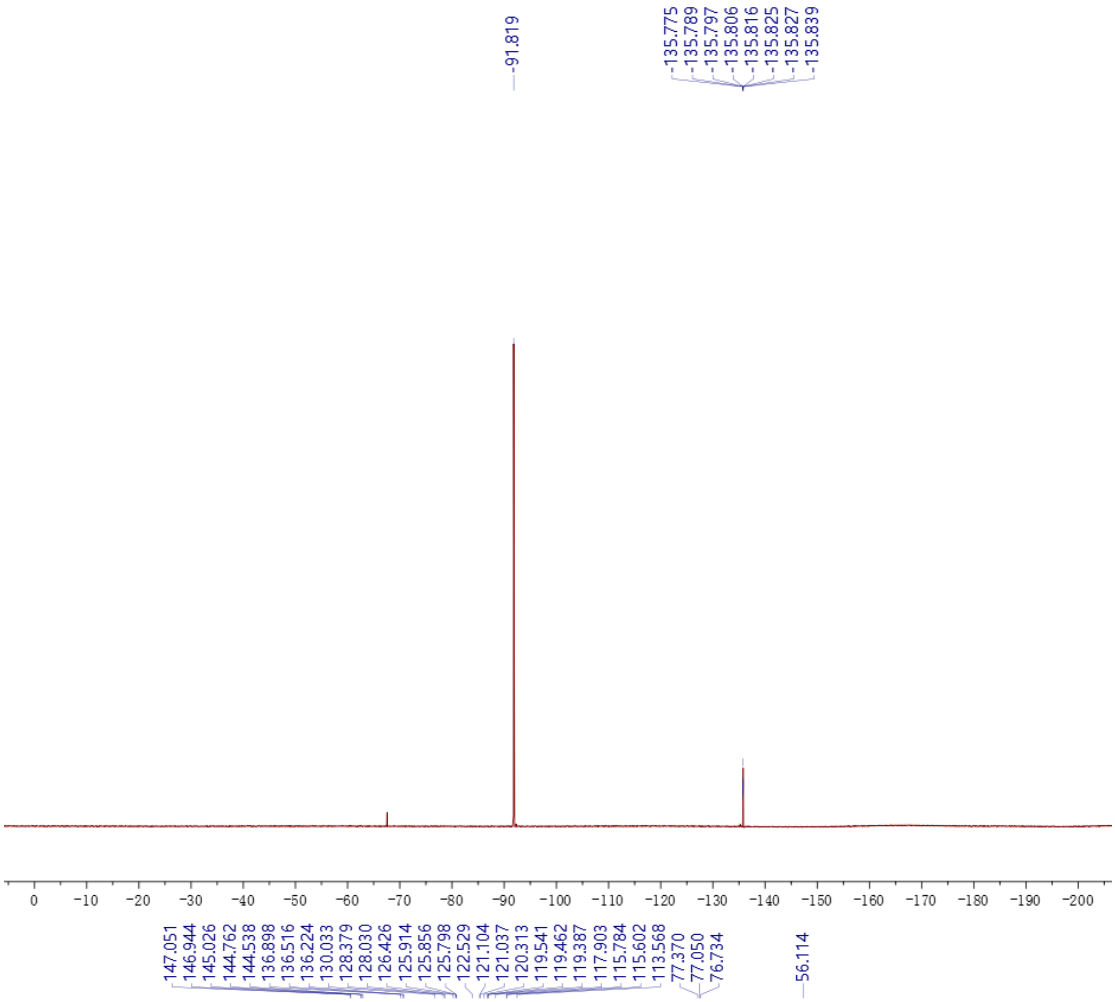
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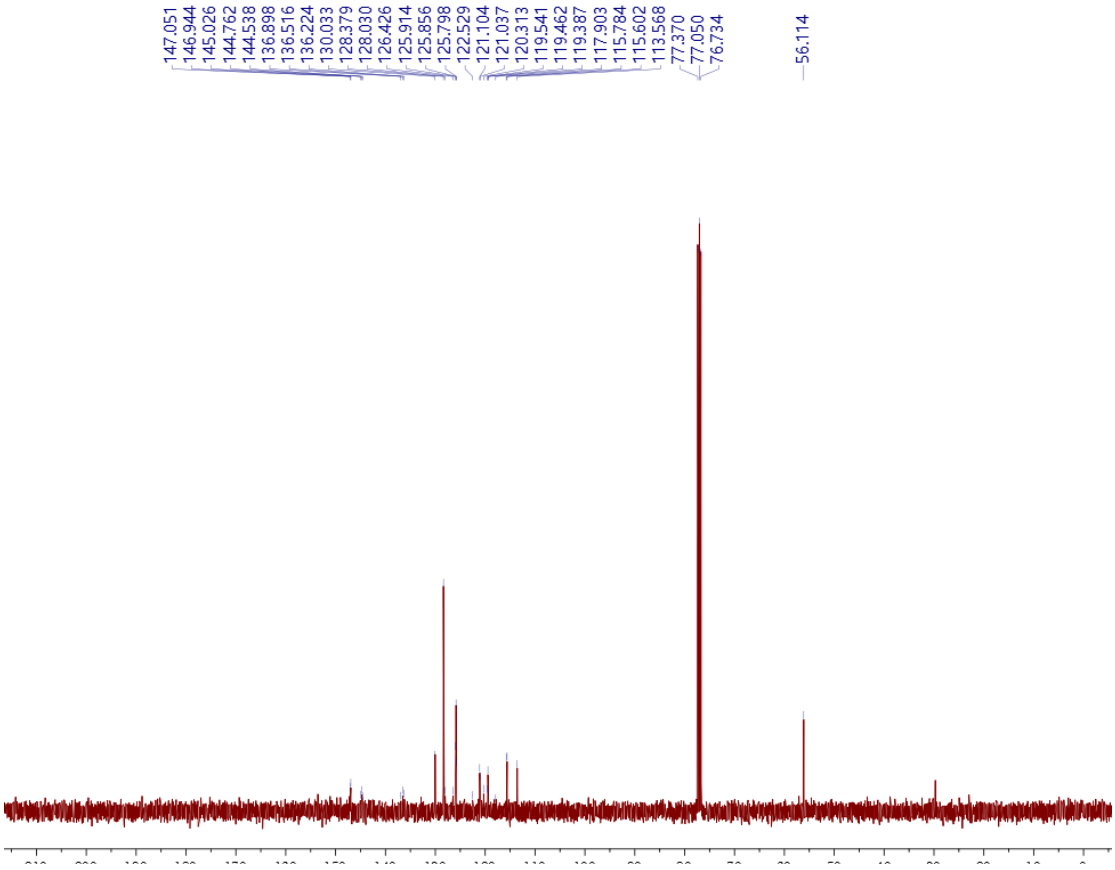
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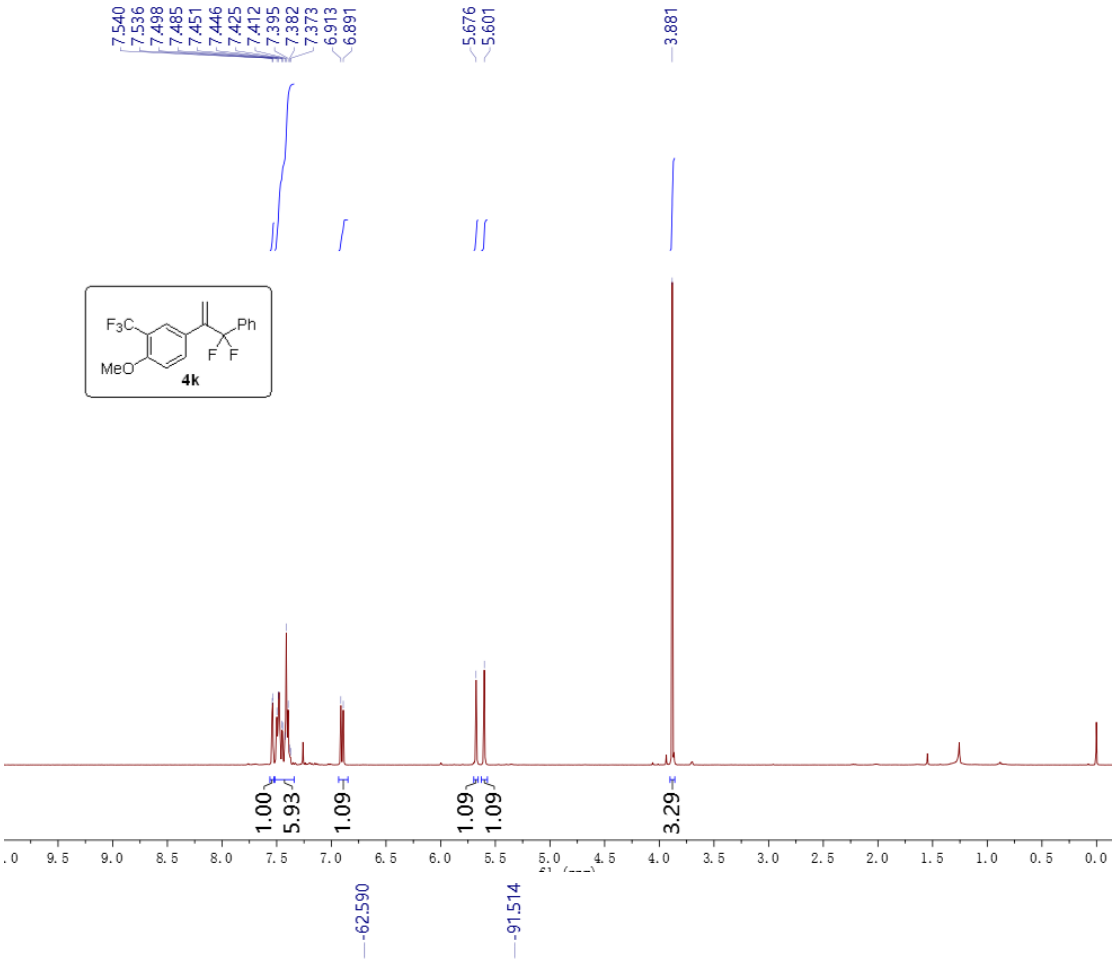
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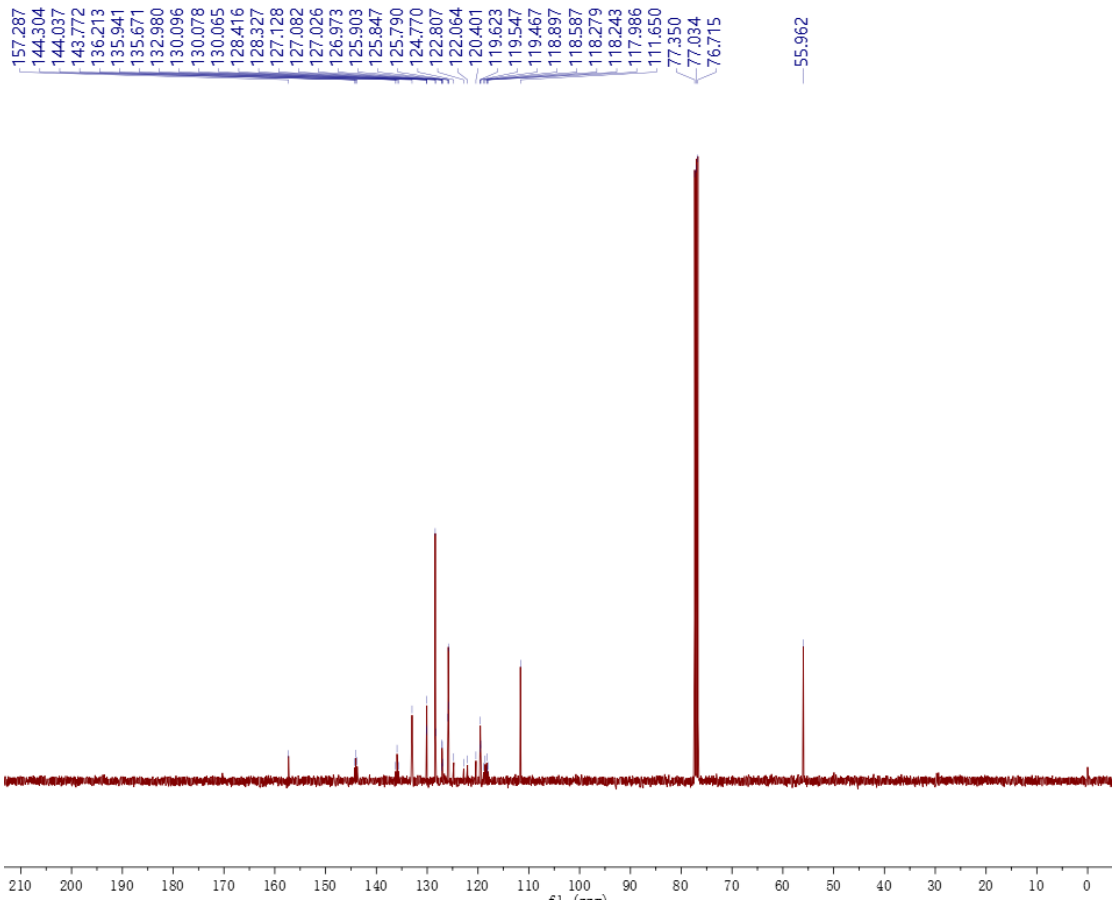
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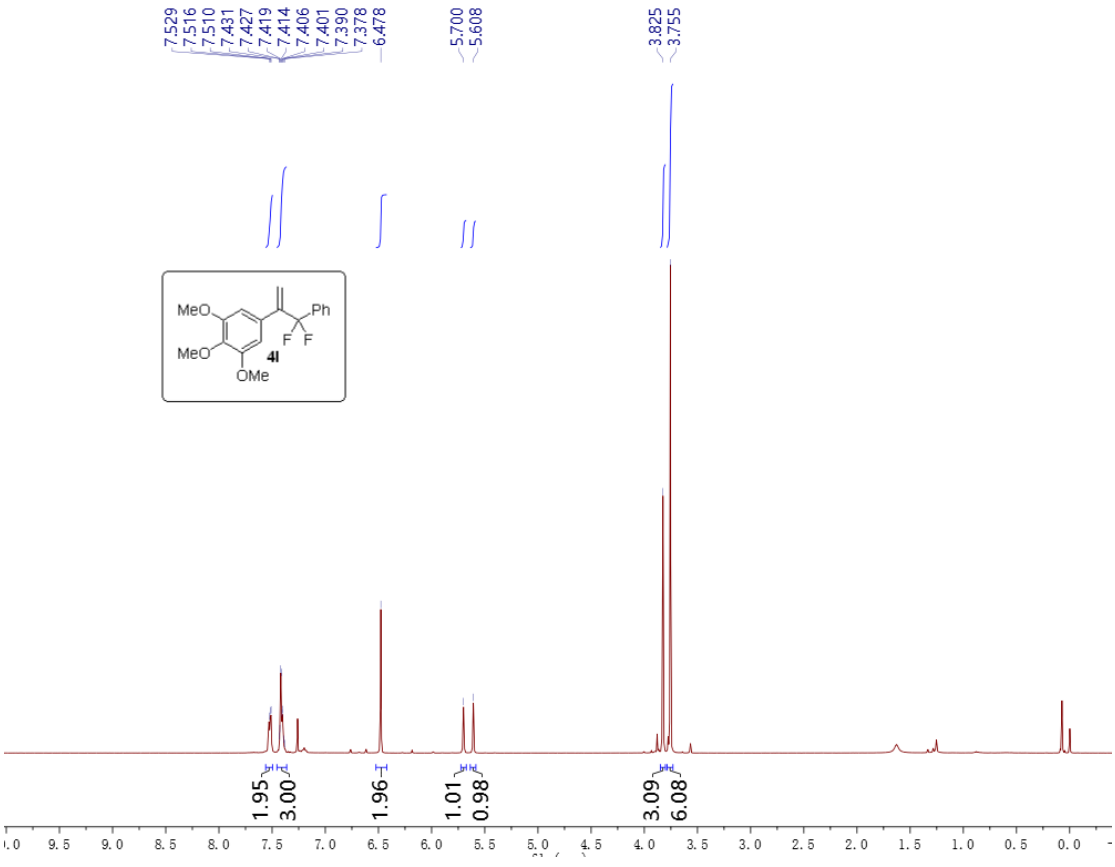
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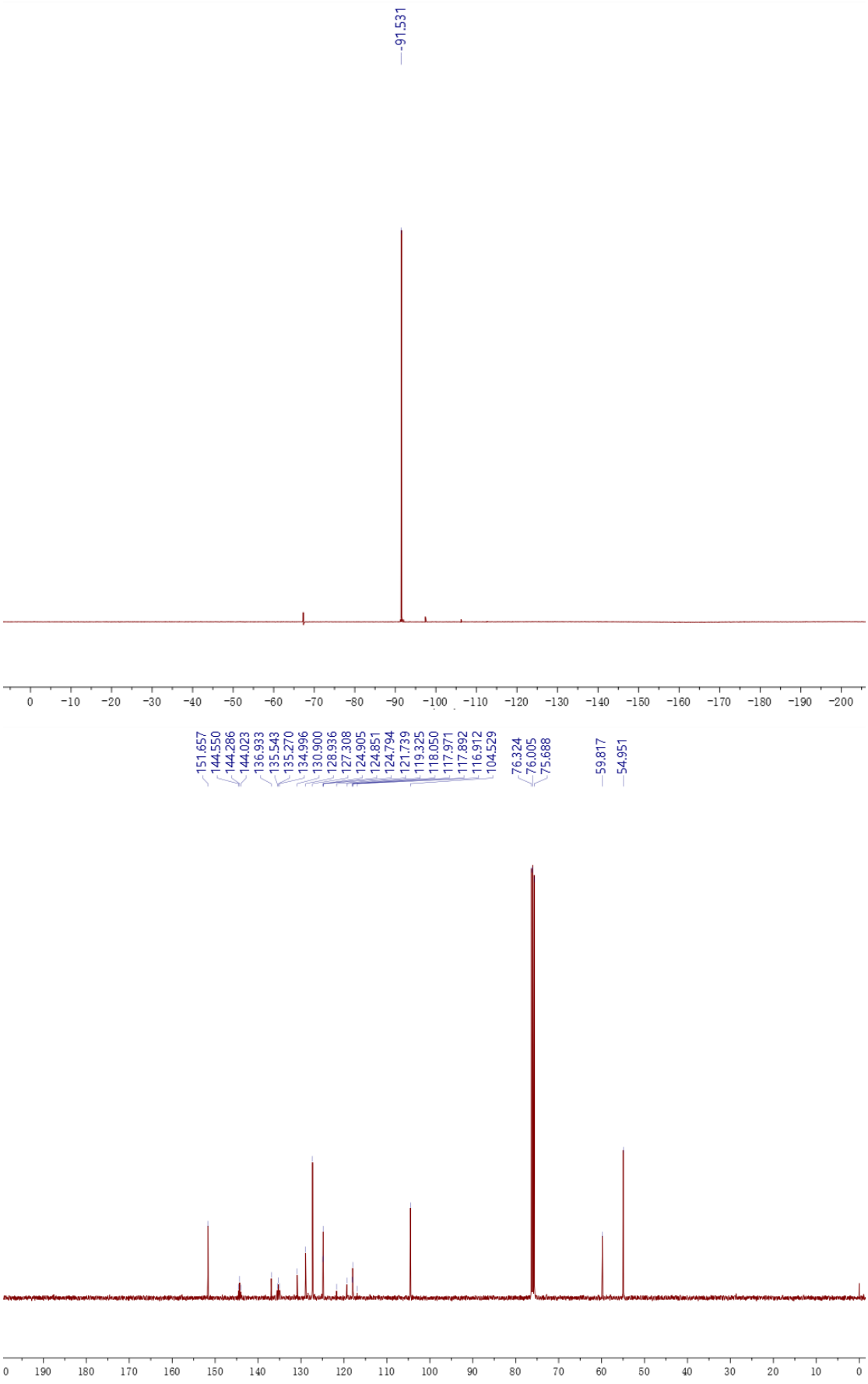
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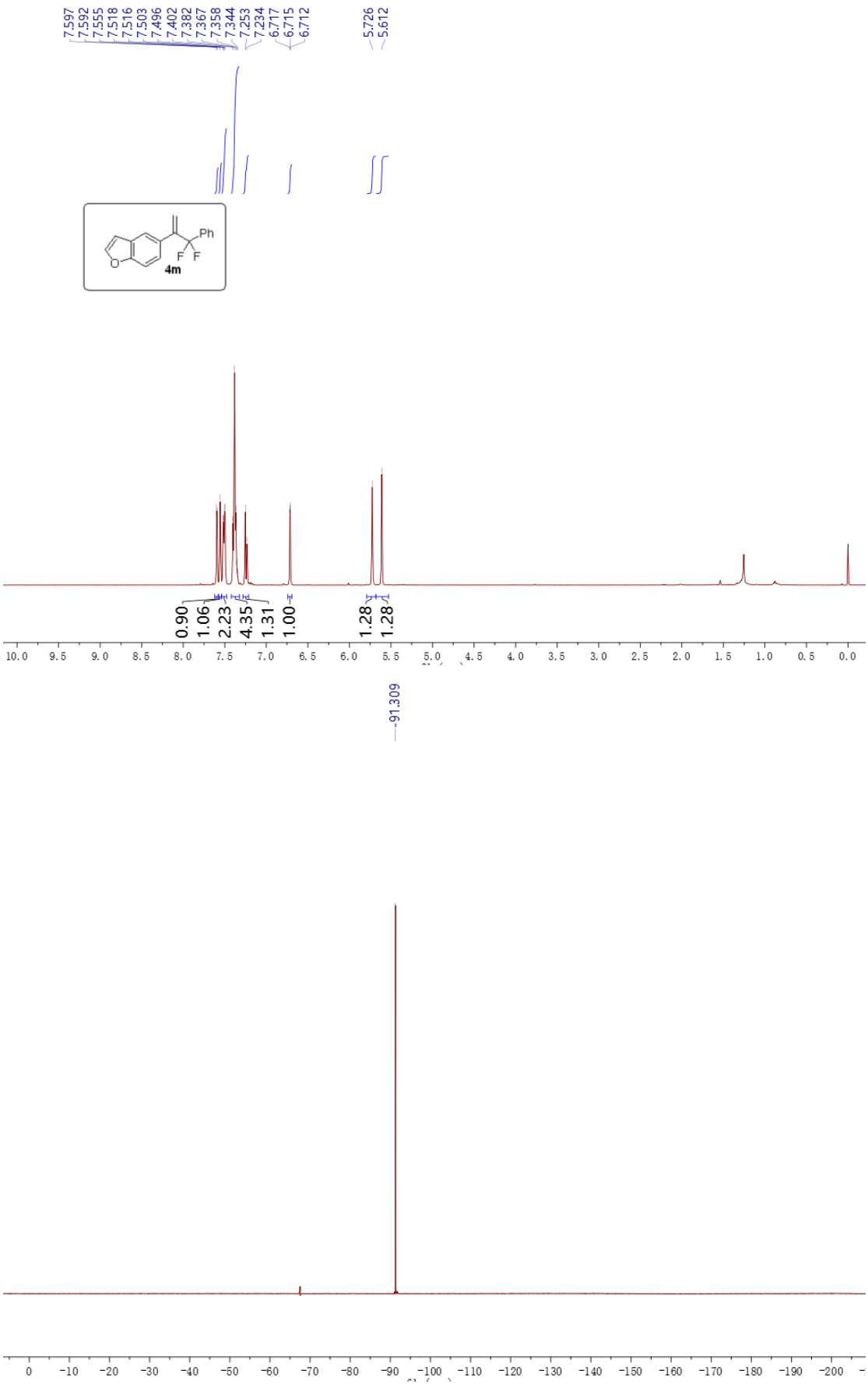
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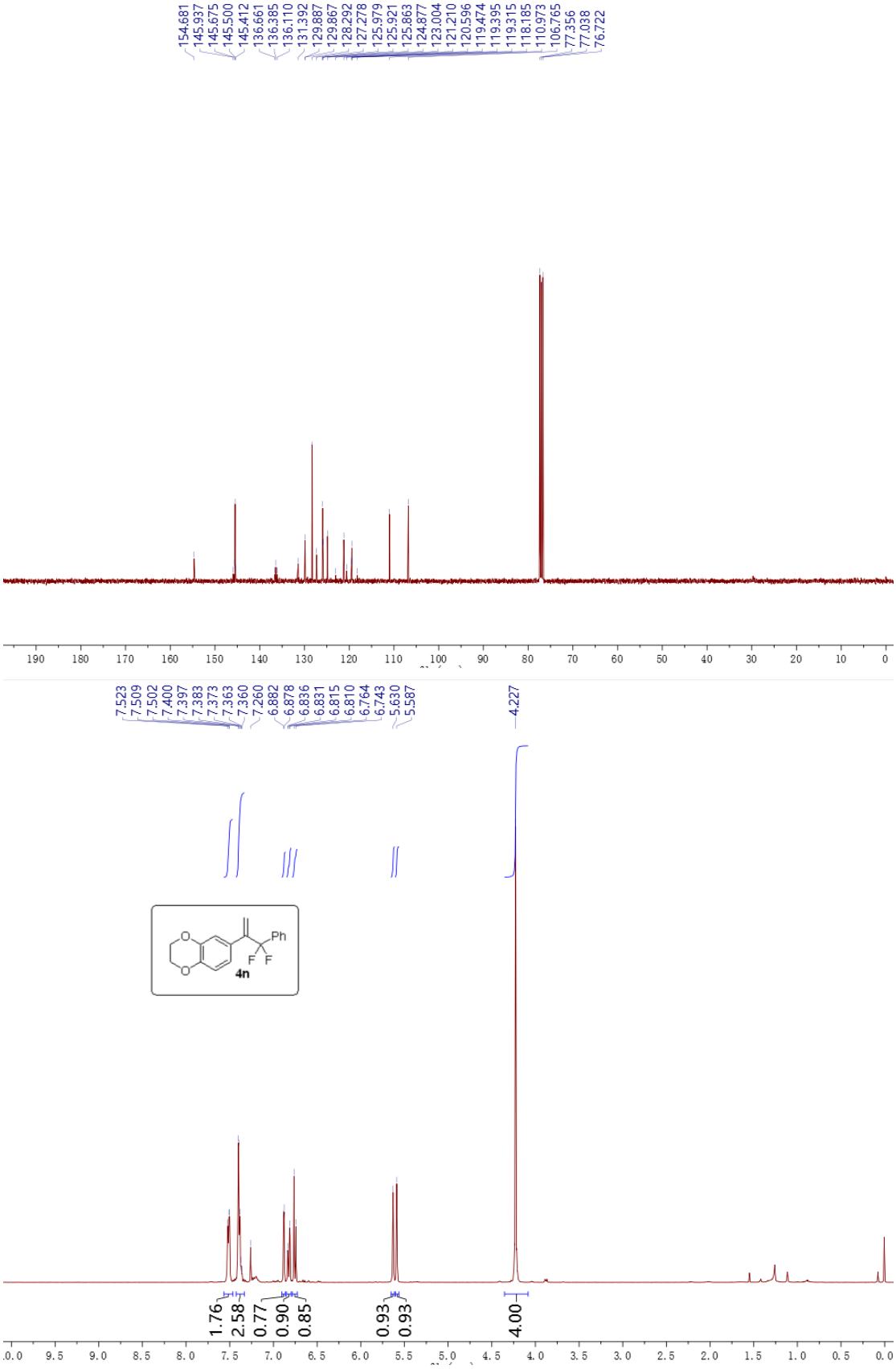
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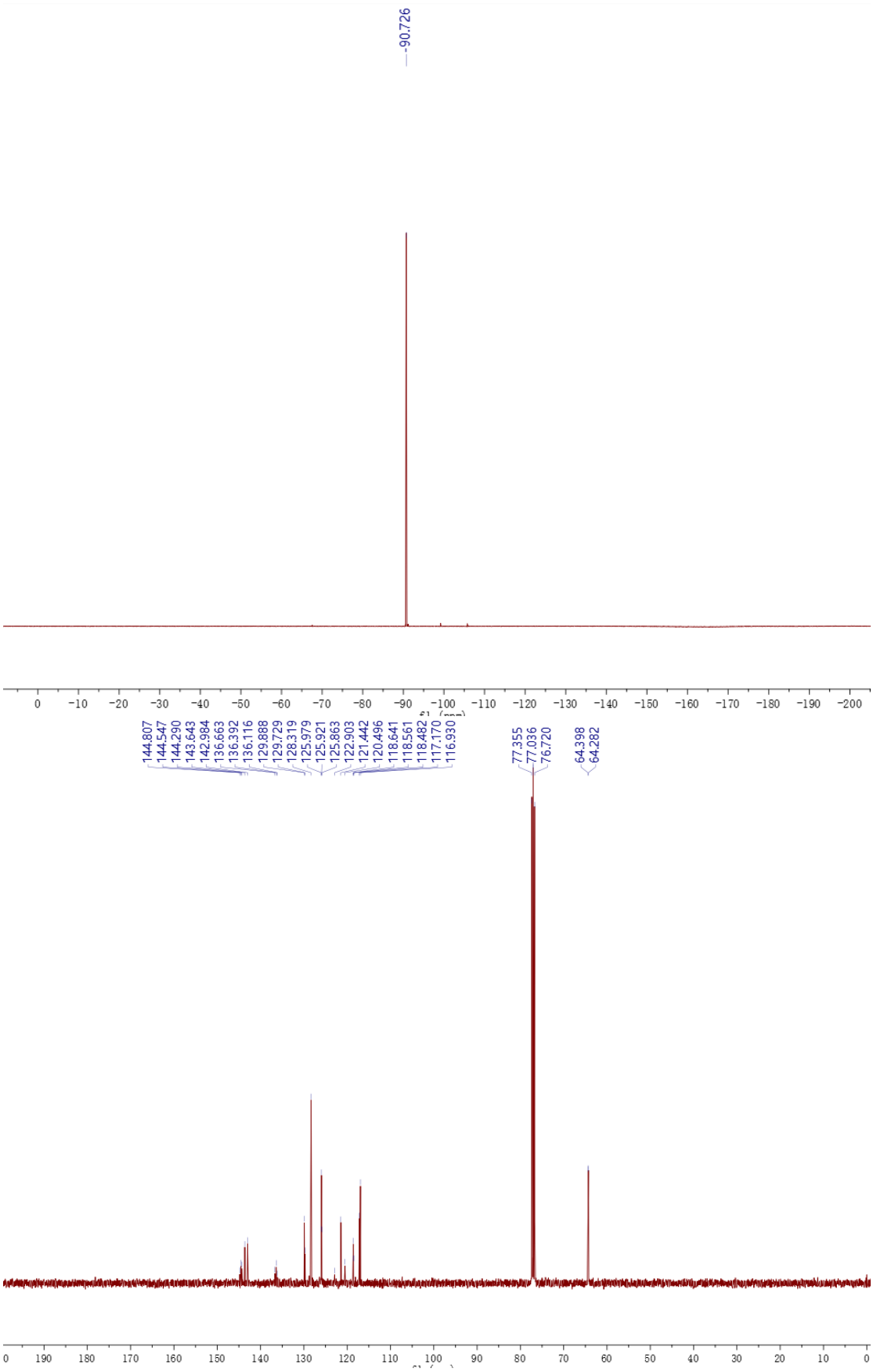
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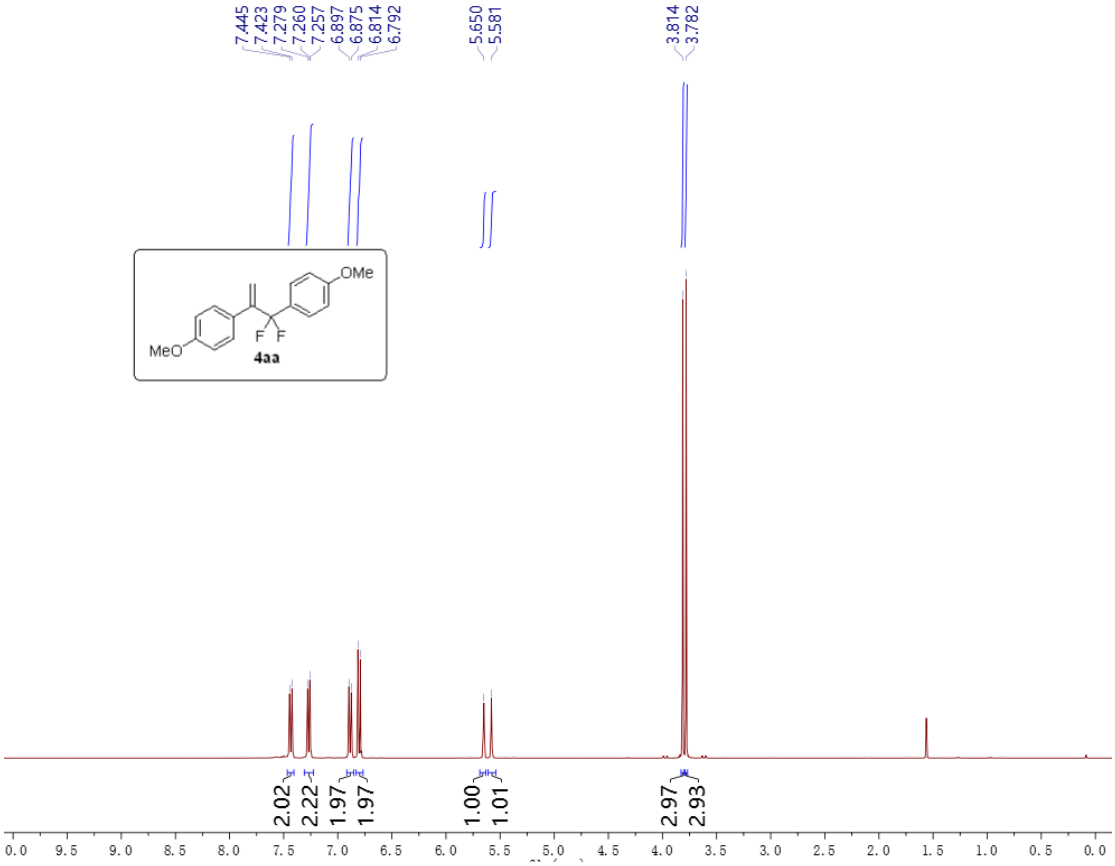
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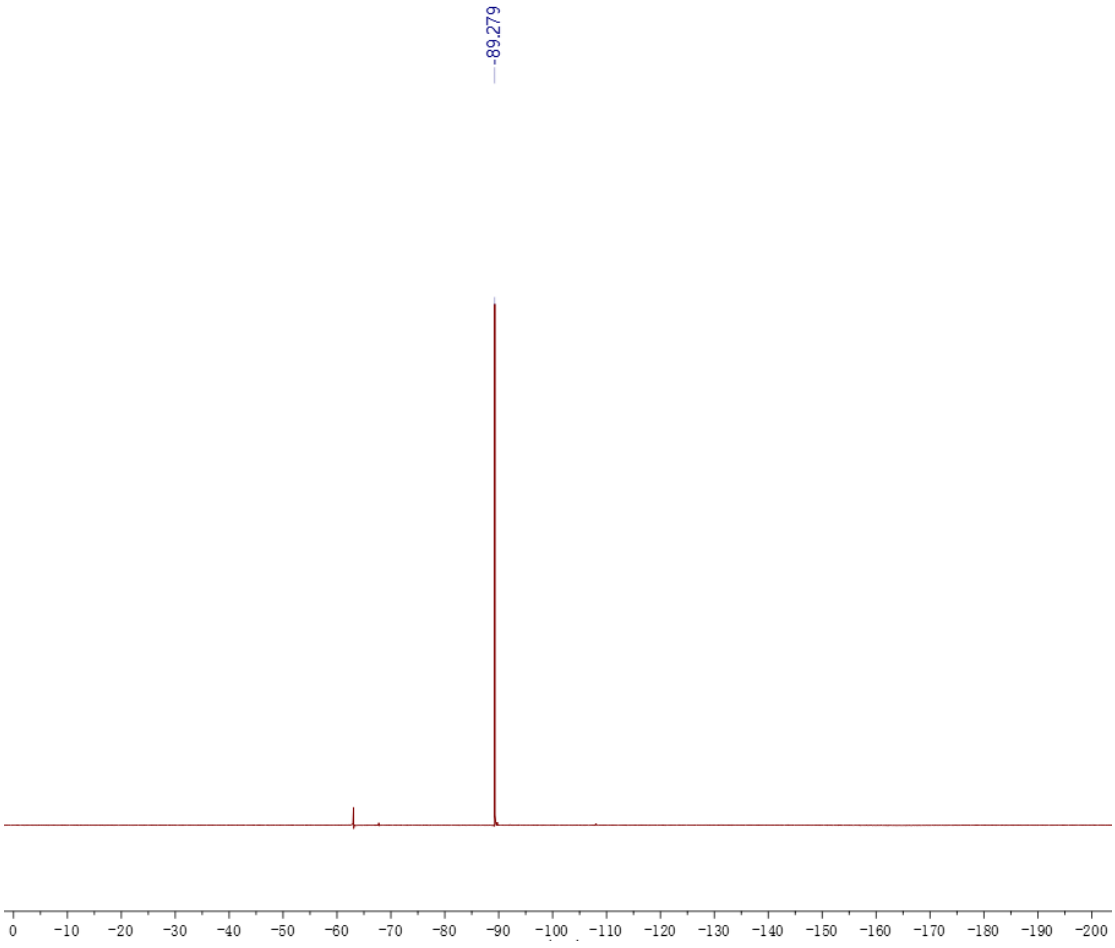
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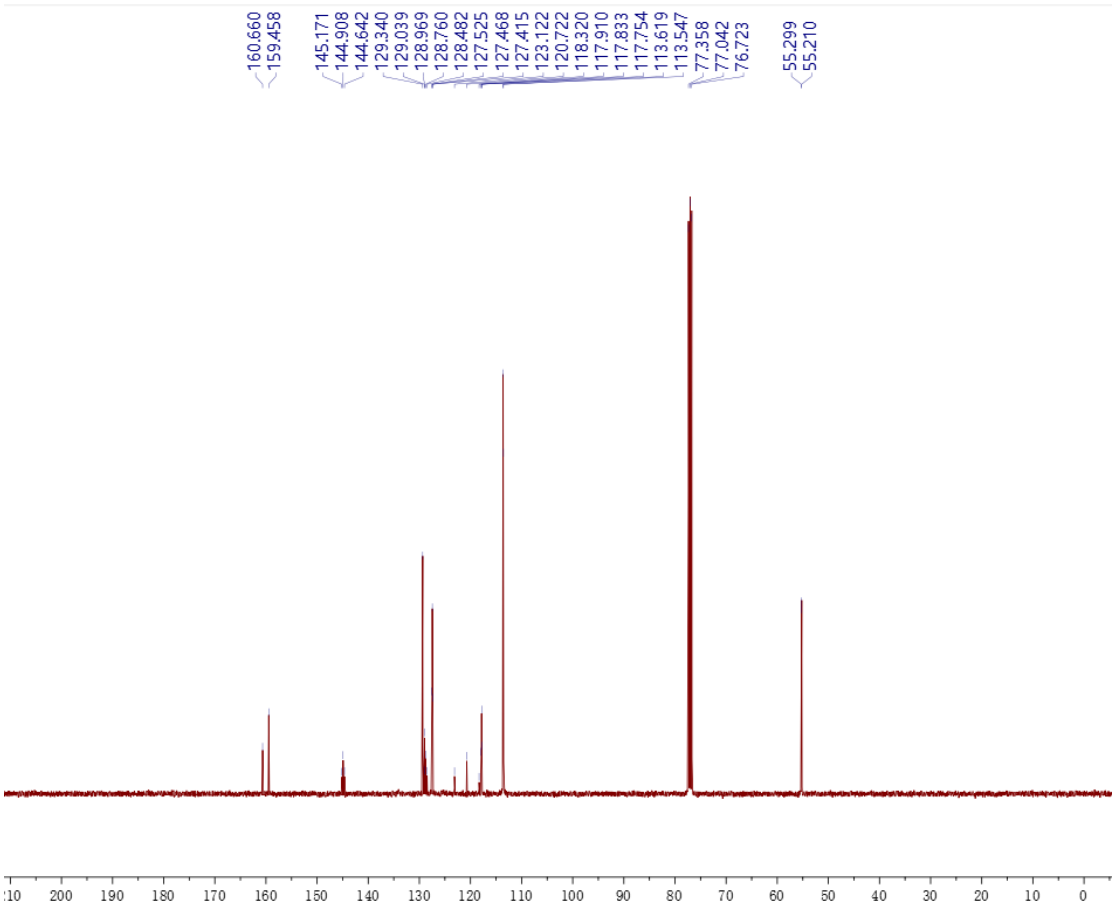
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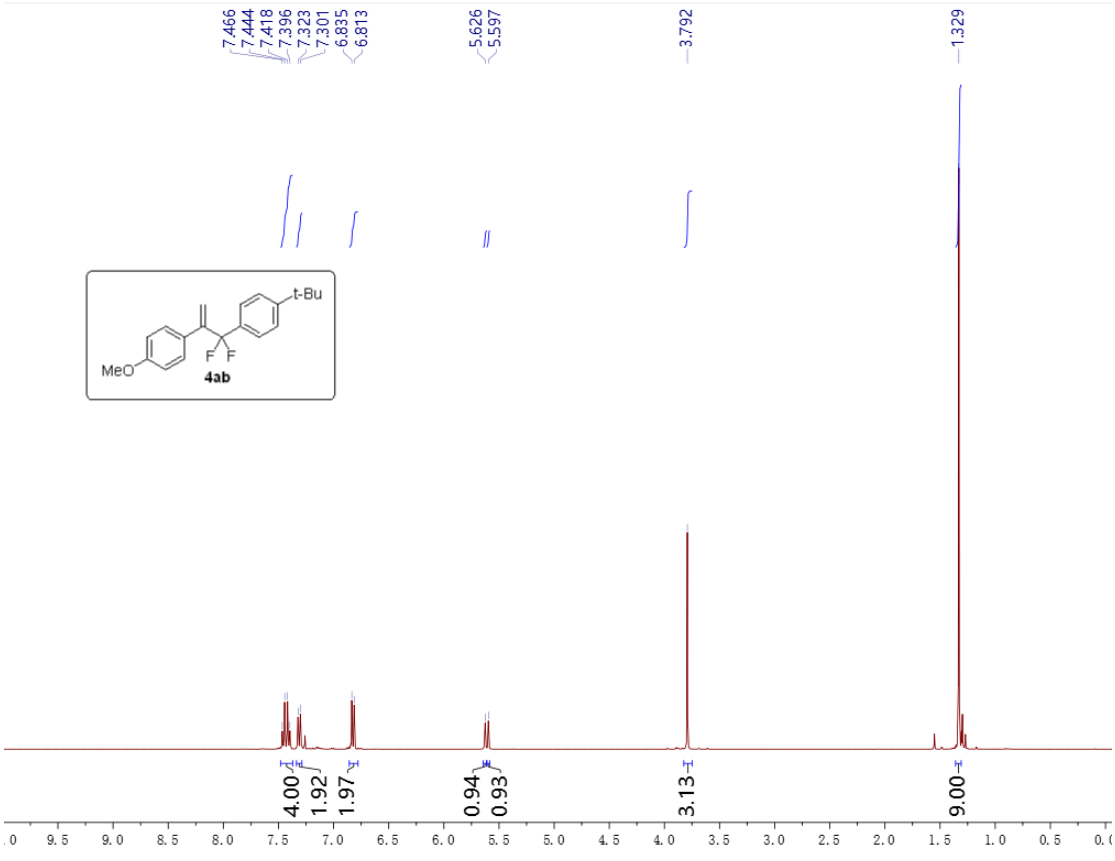
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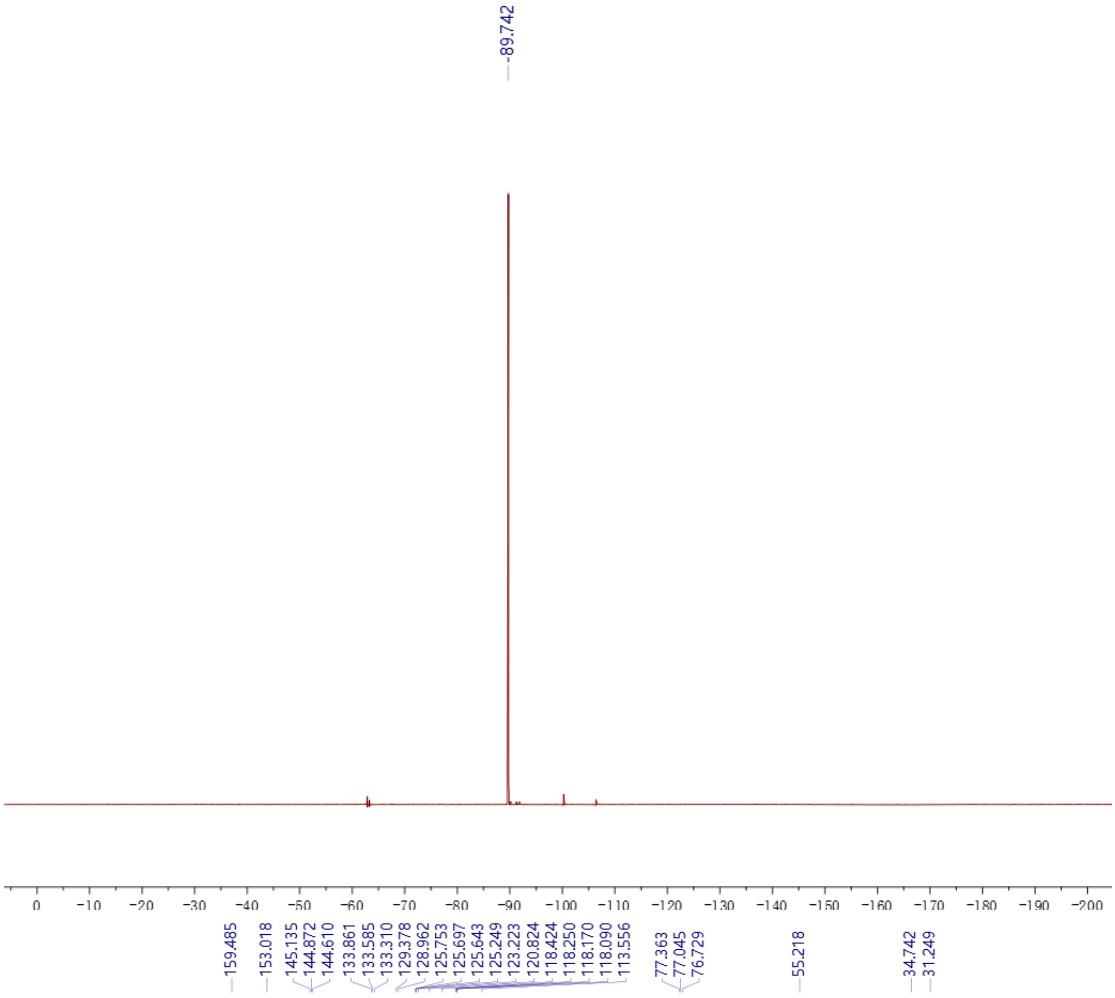
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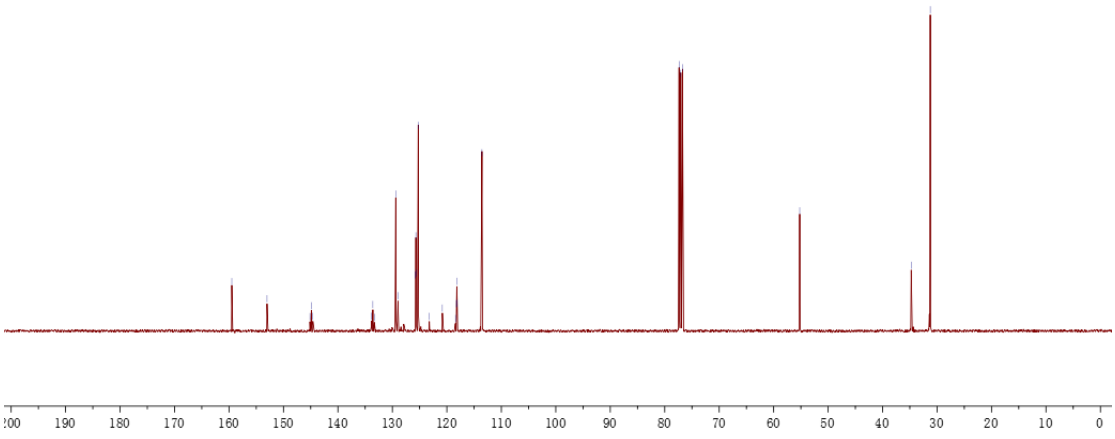
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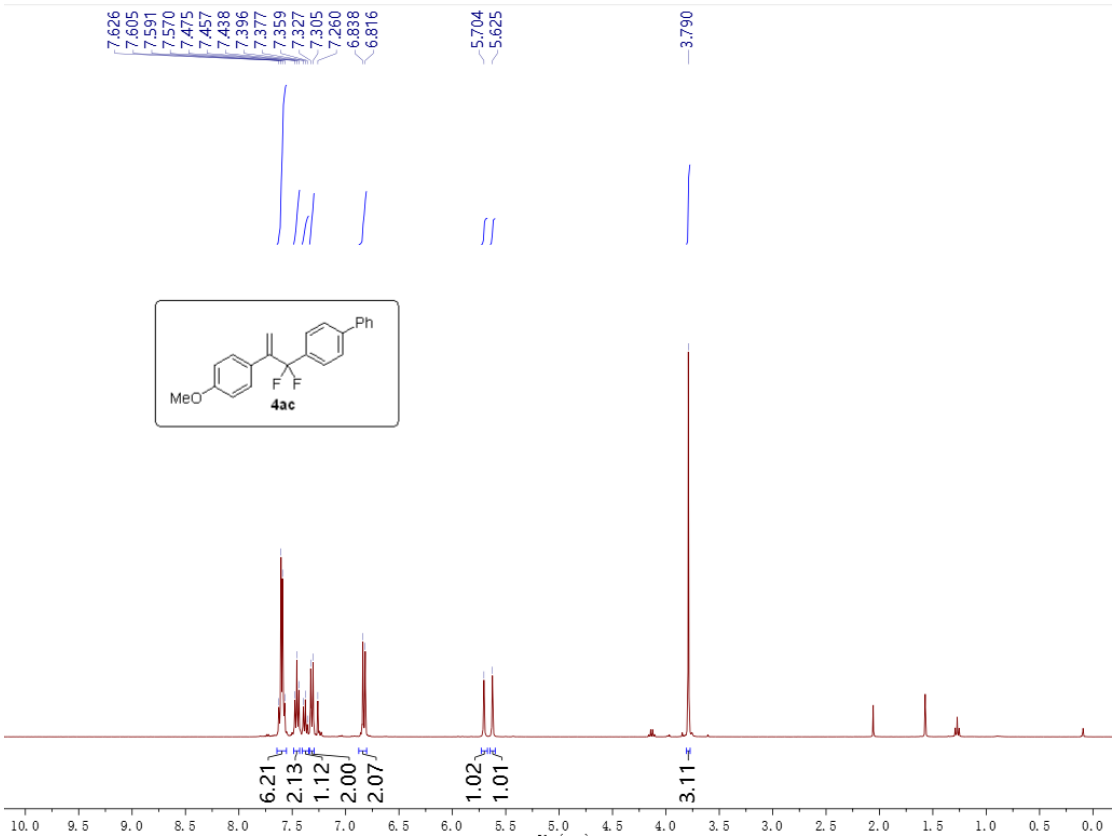
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Ph
F F
MeO
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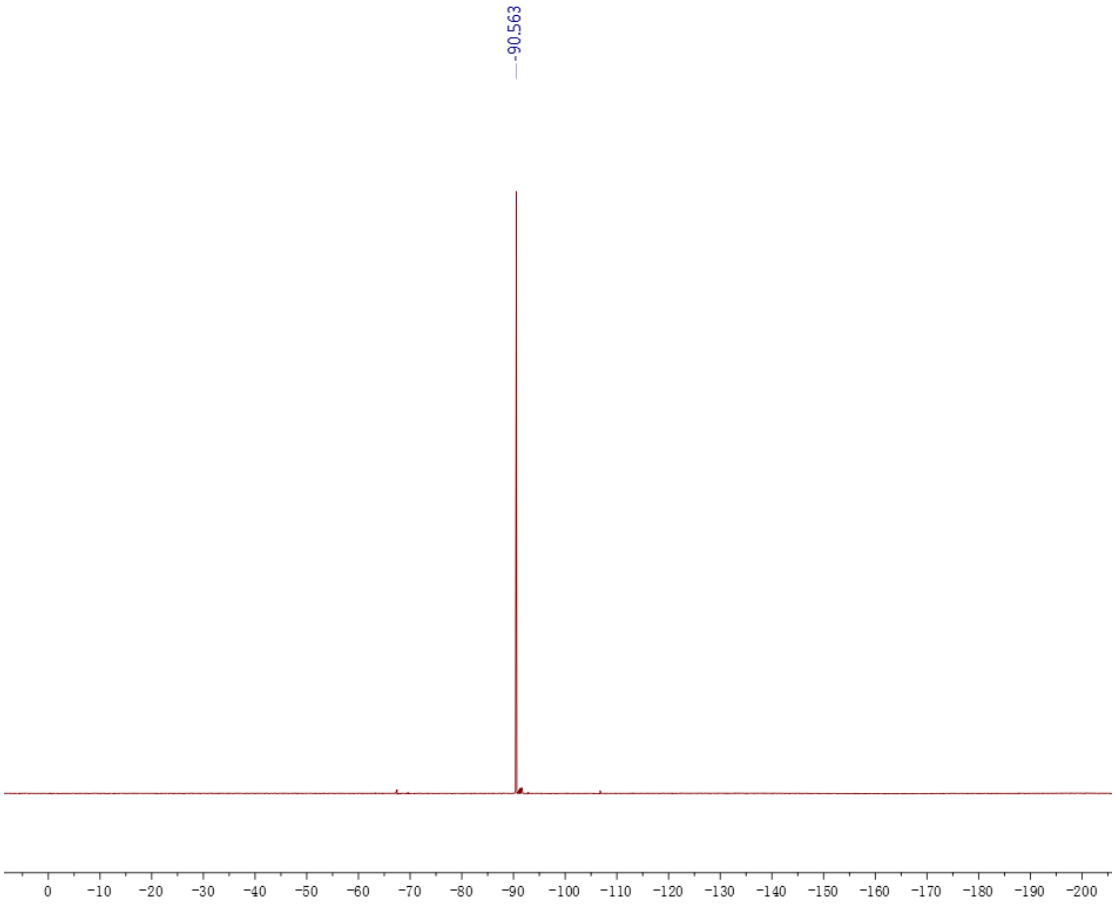
6.21
2.13
1.12
2.00
2.07
1.02
1.01
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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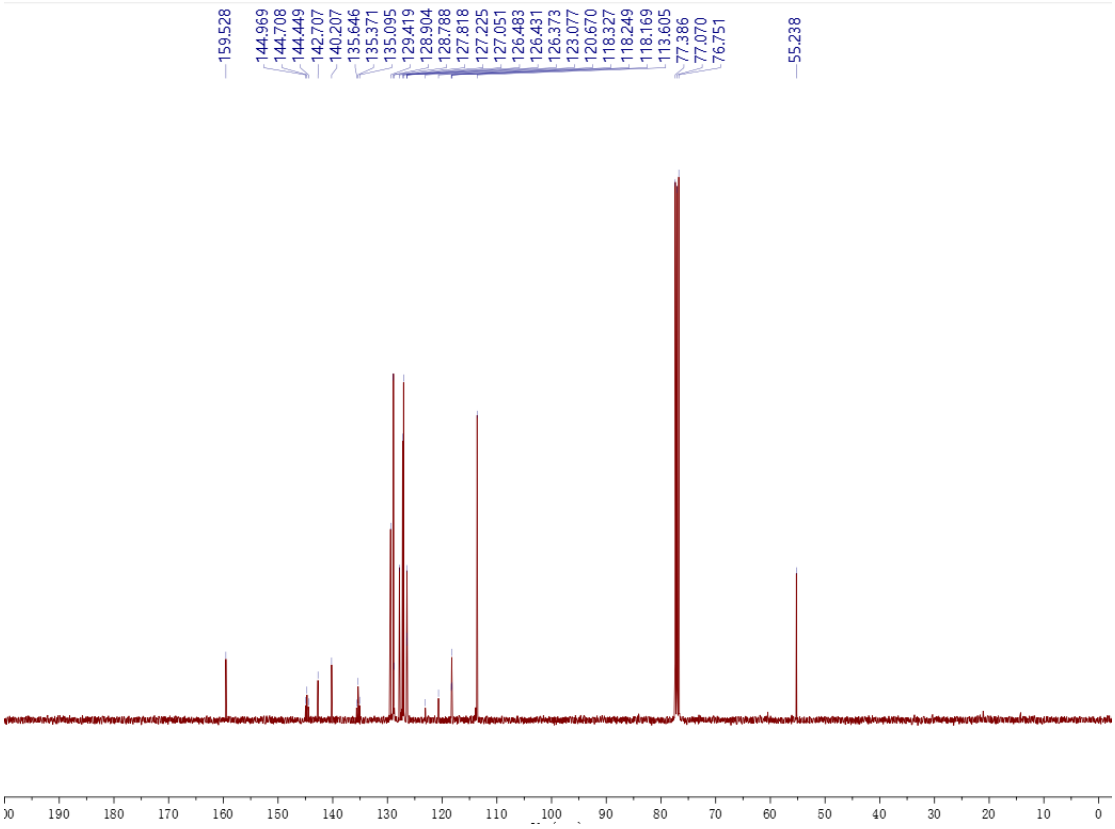
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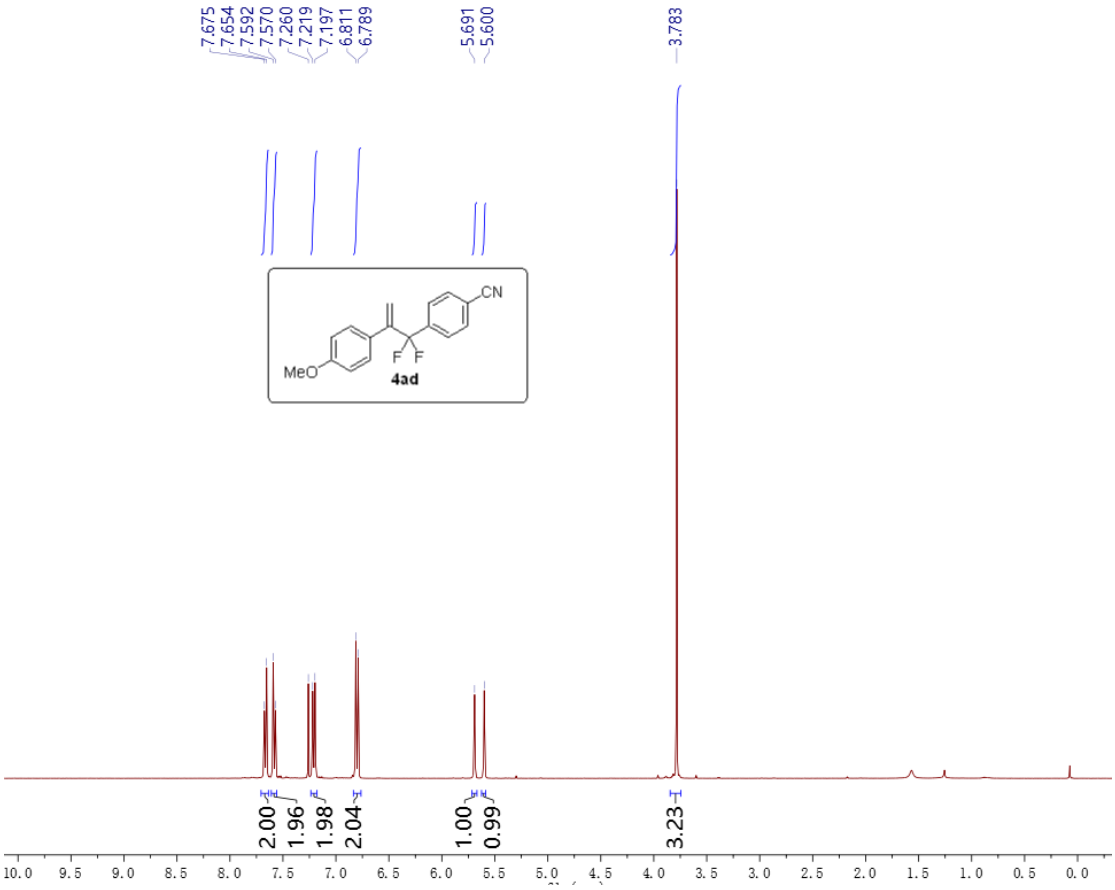
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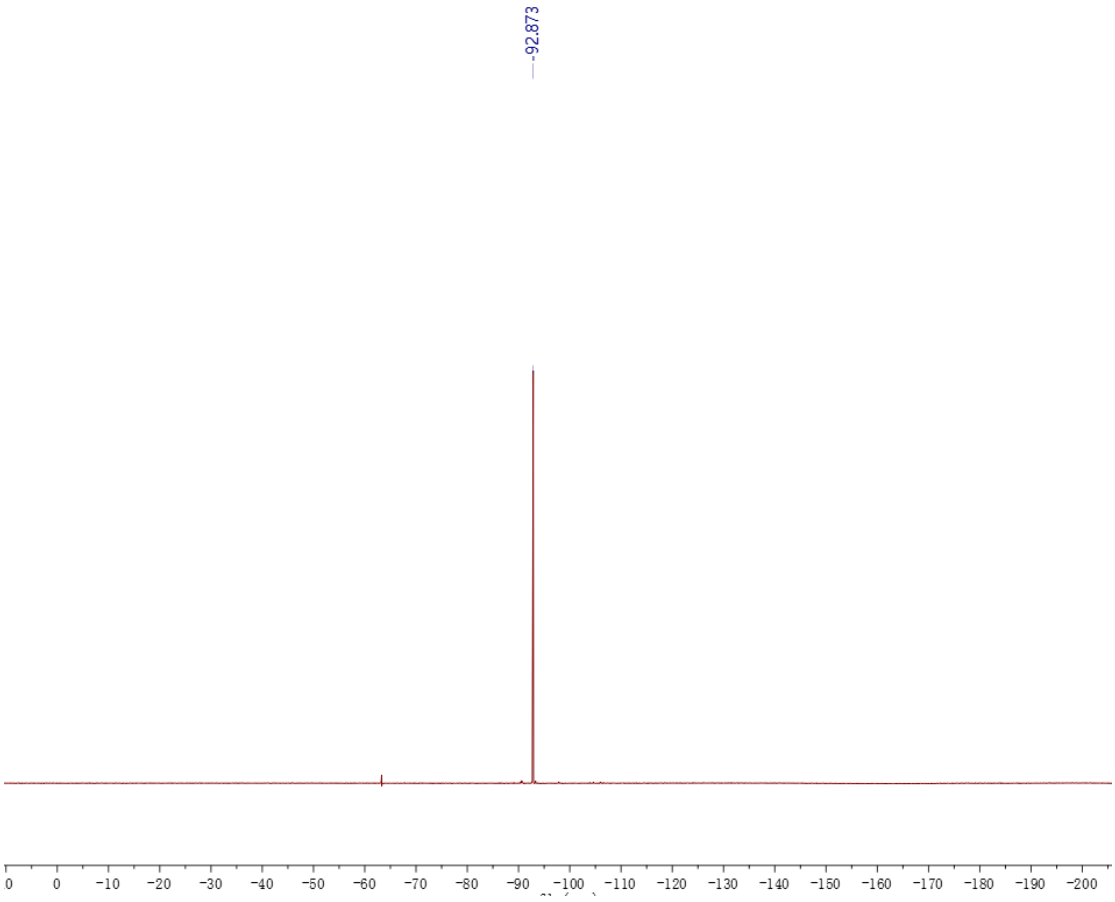
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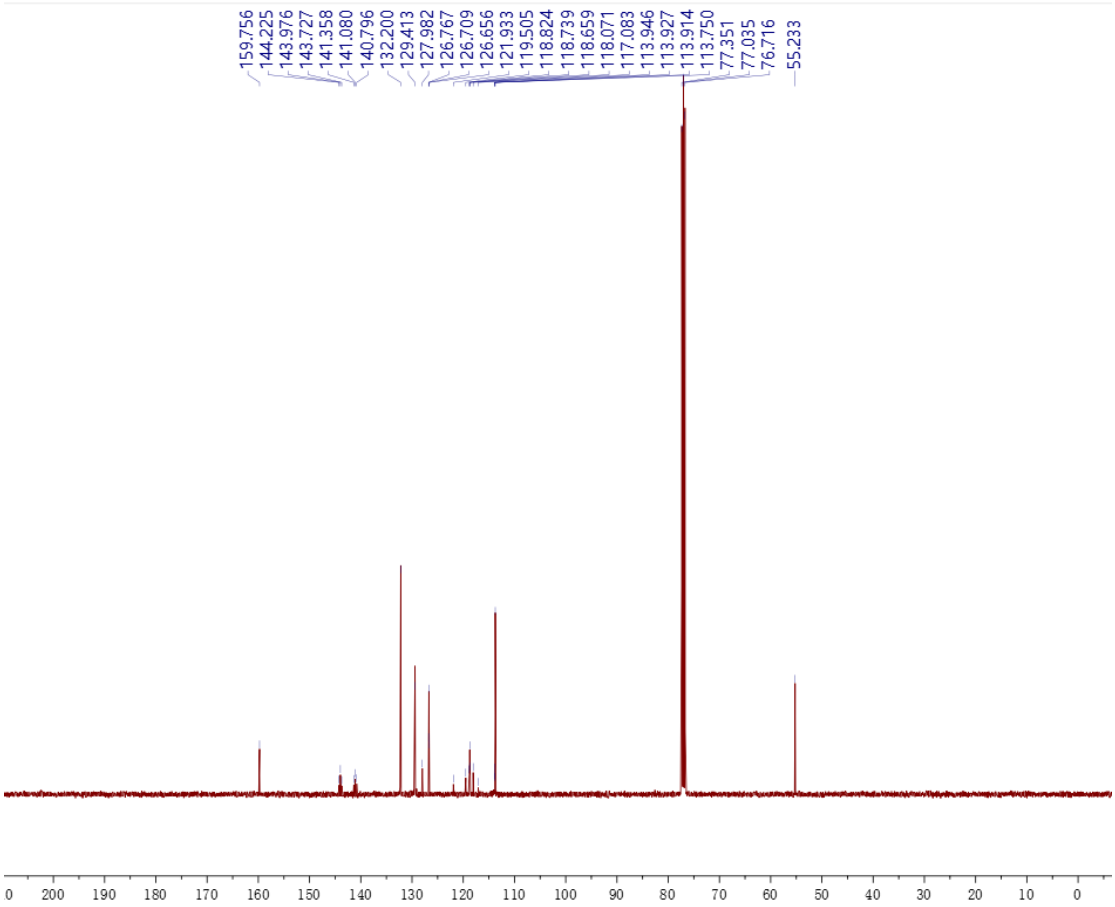
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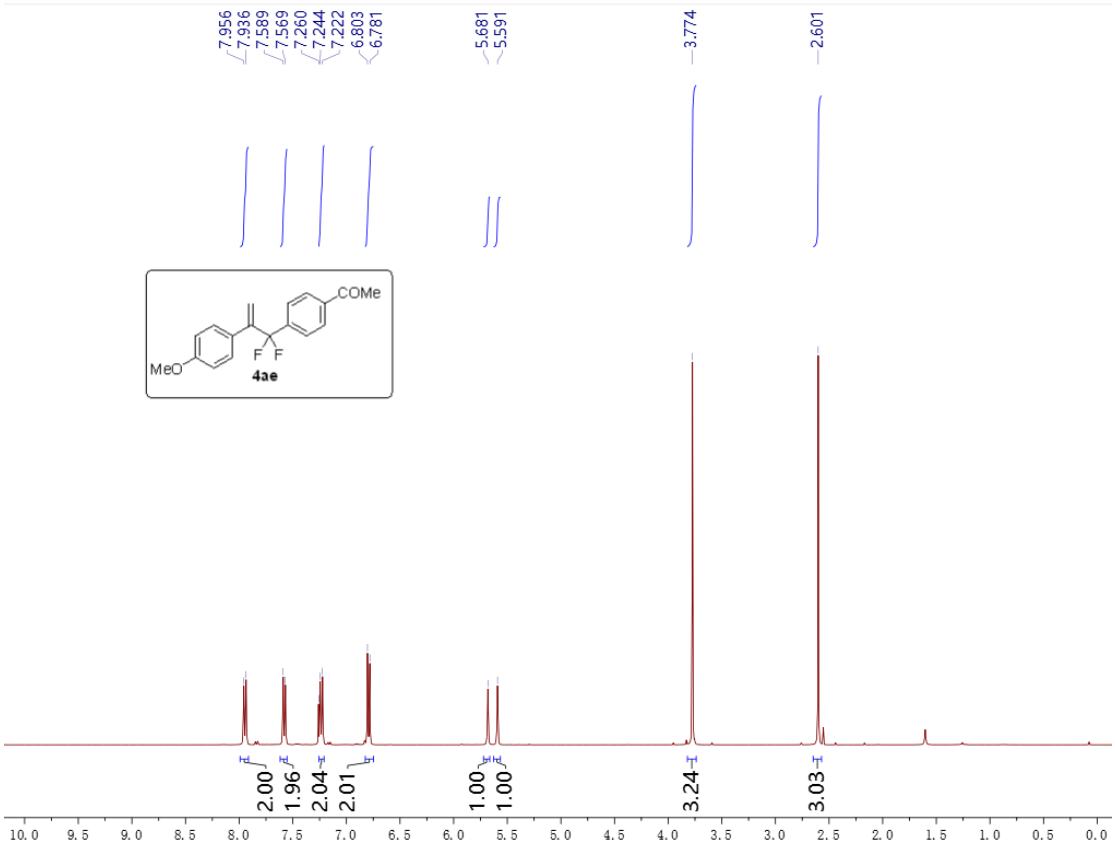
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3.03
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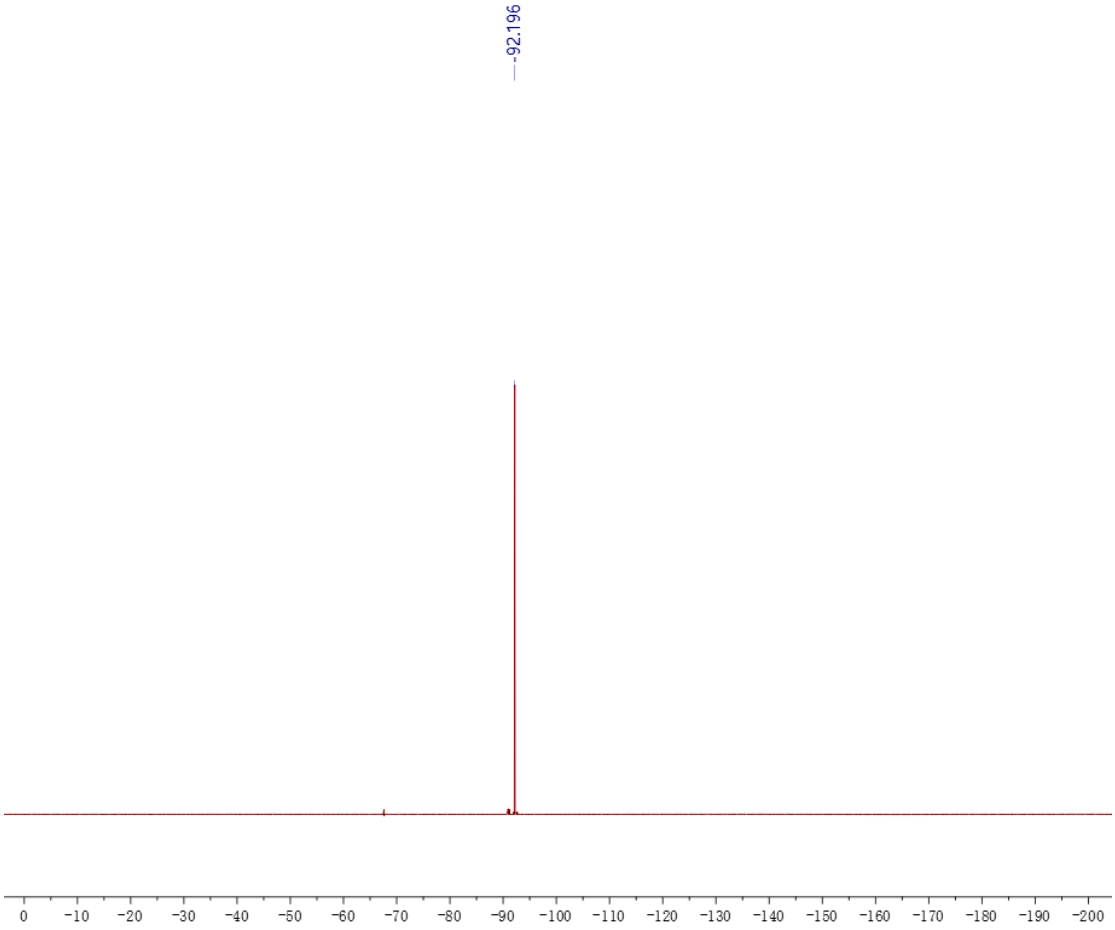
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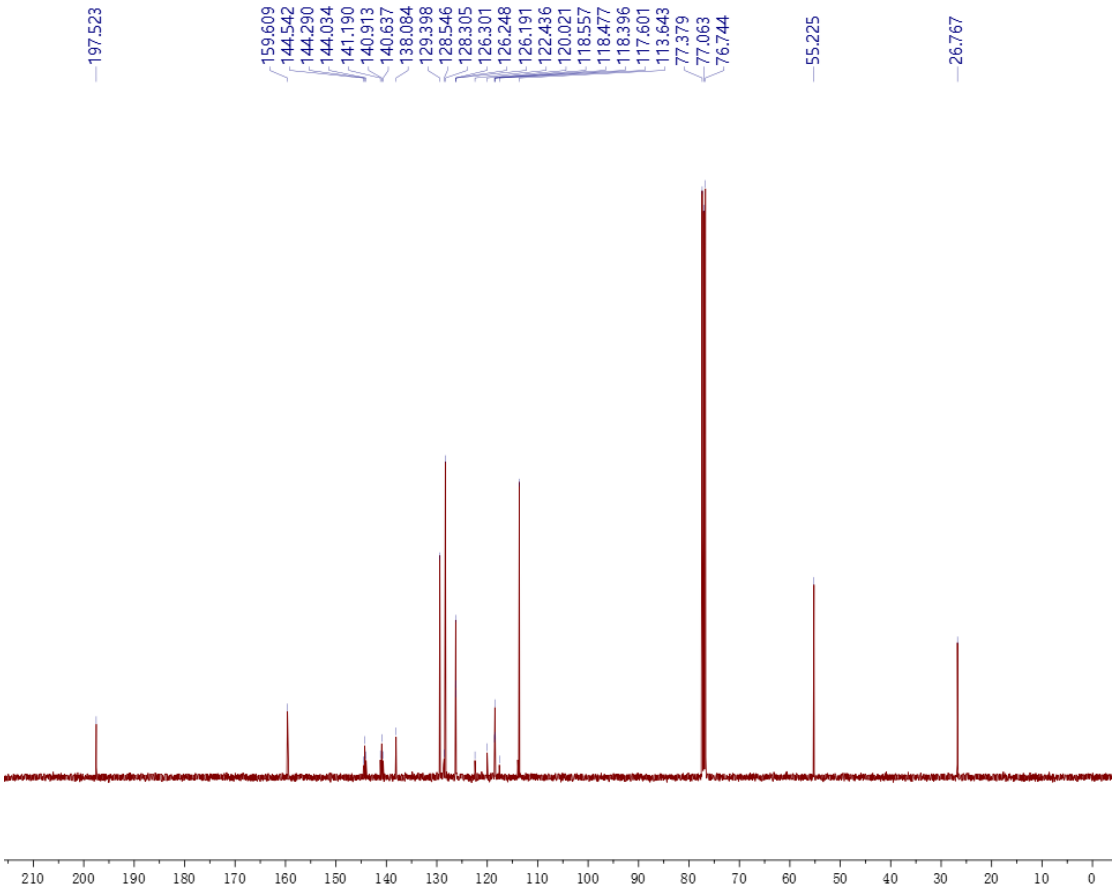
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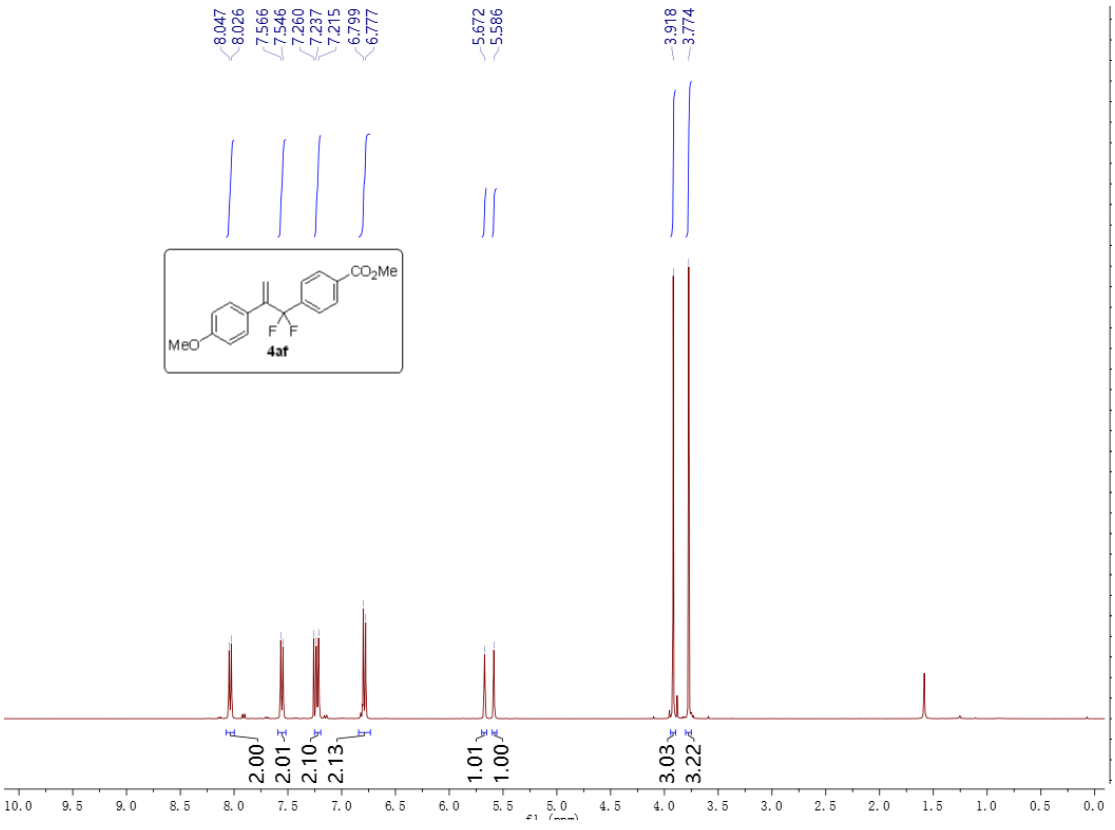
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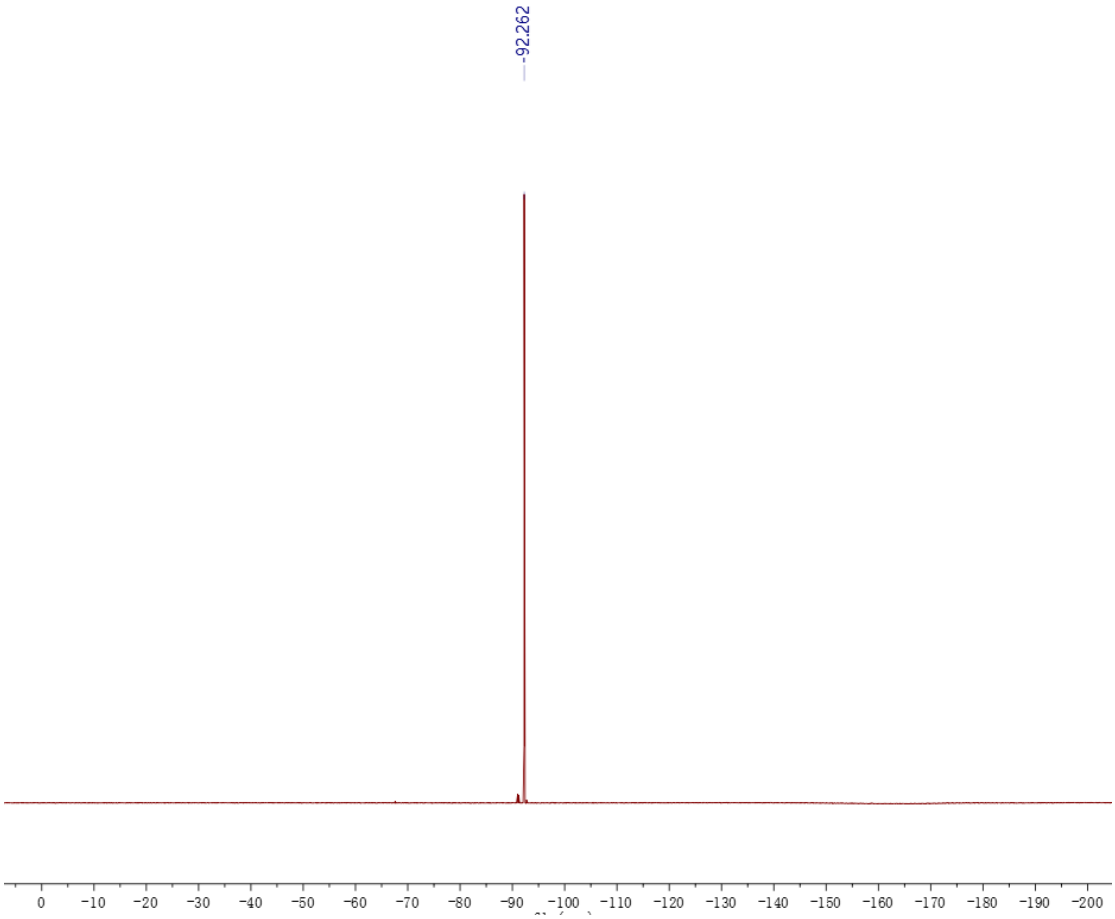
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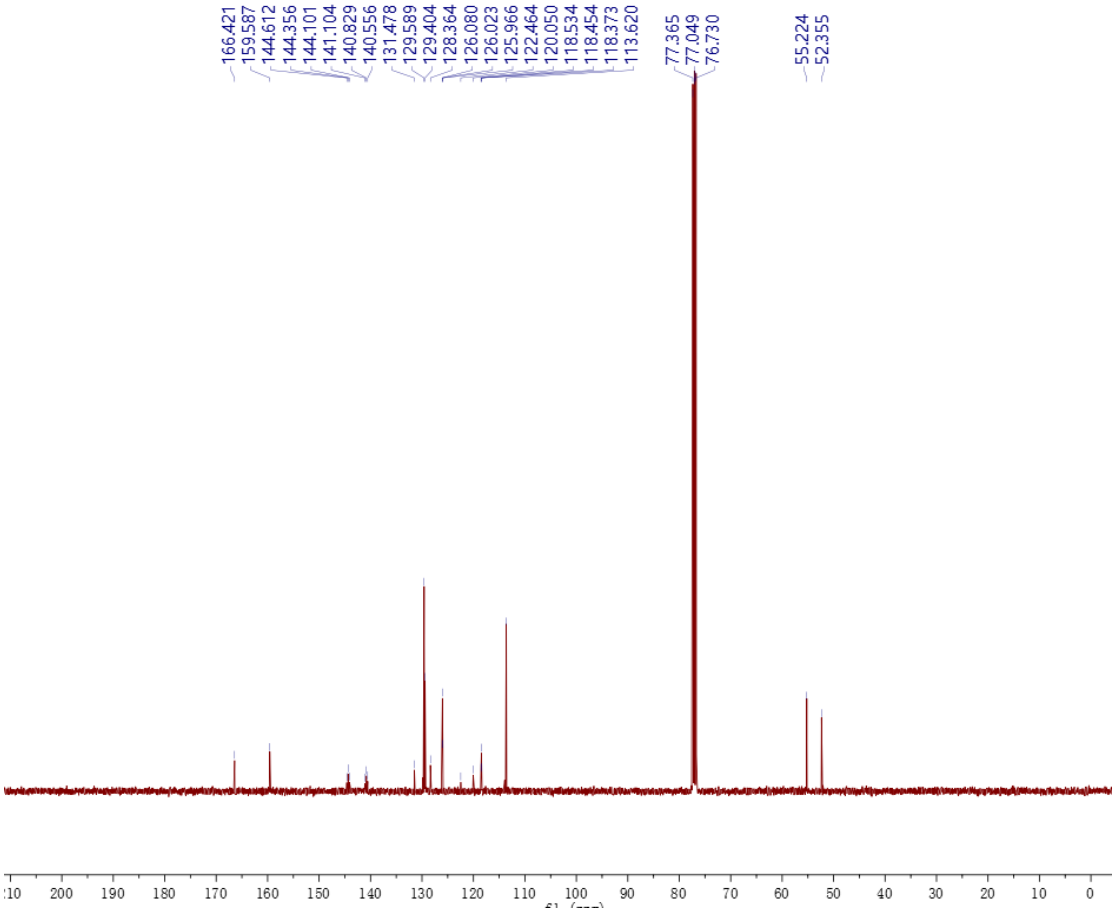
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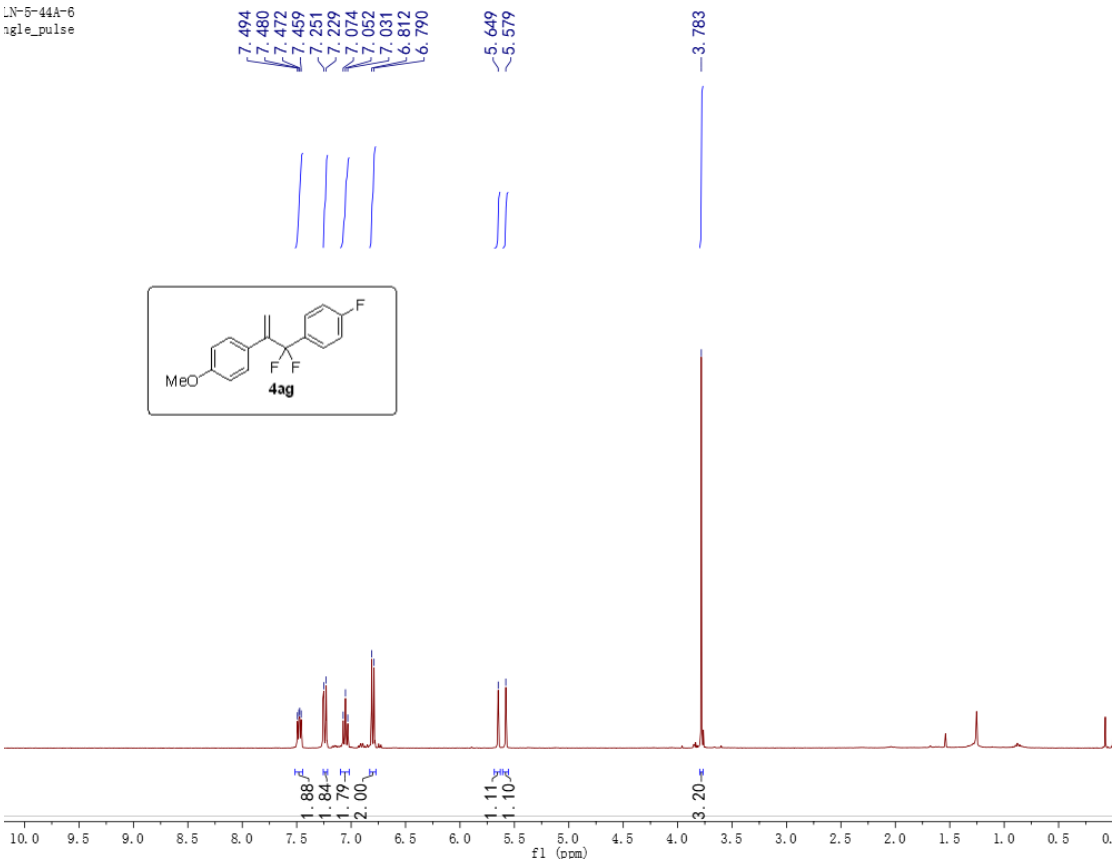
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MeO
F
F F
4ag
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1.11
1.10
3.20
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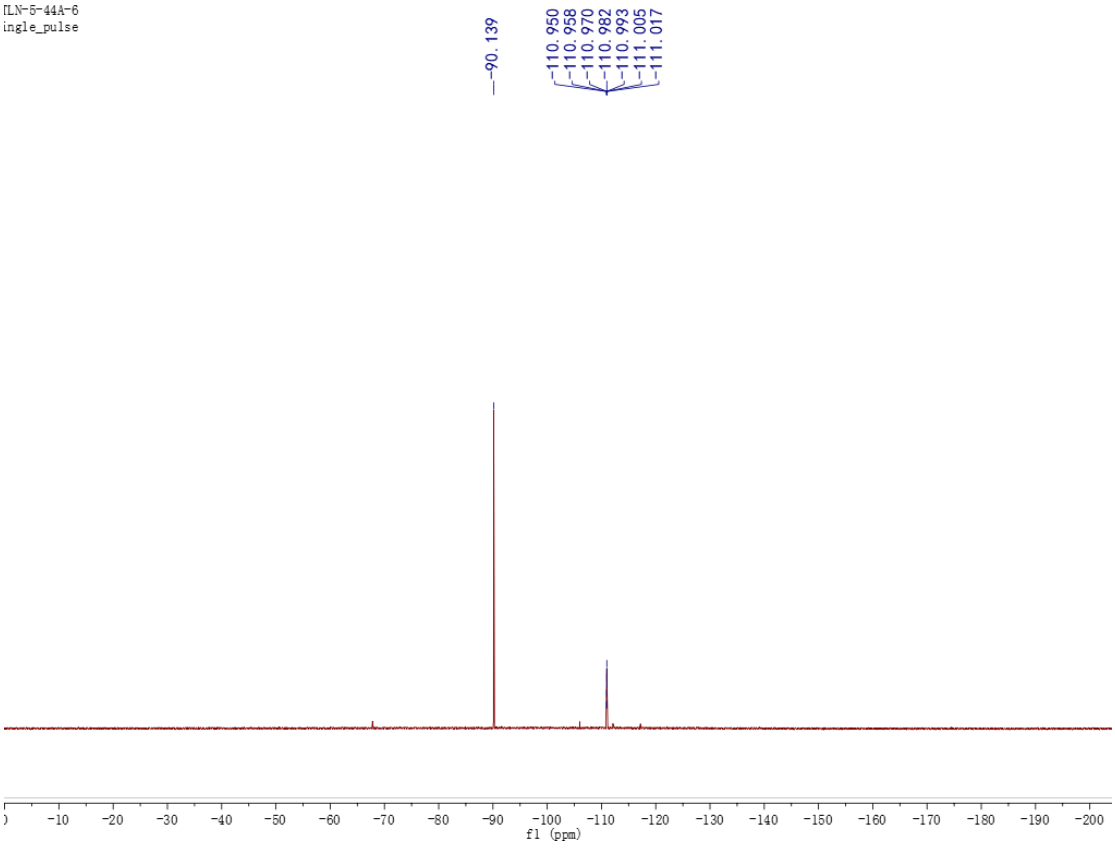
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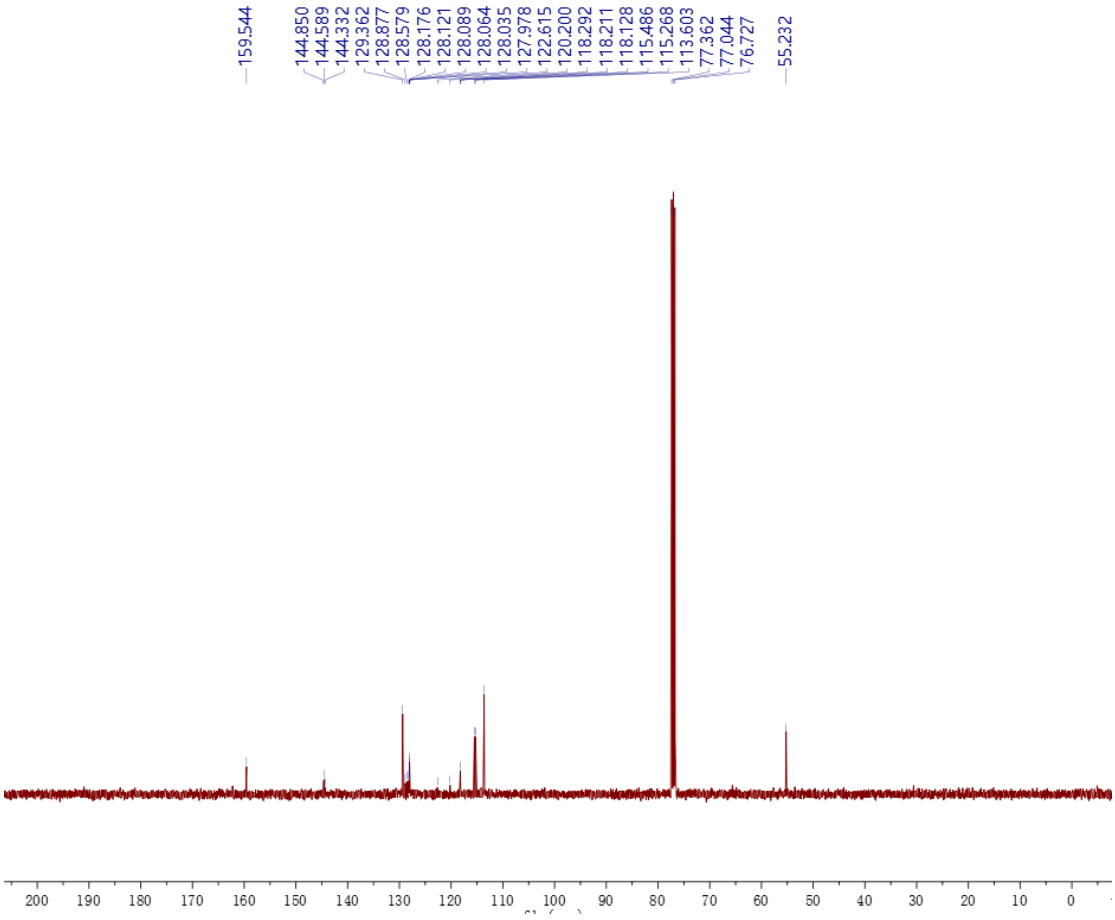
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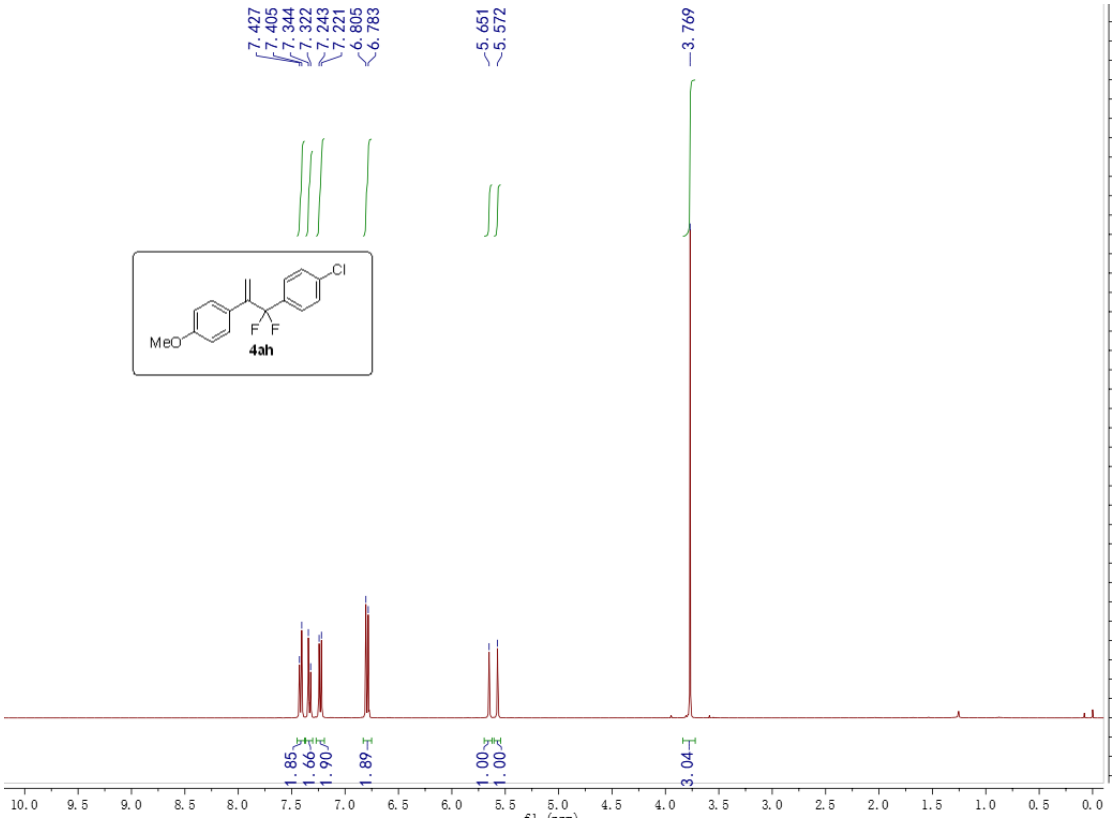
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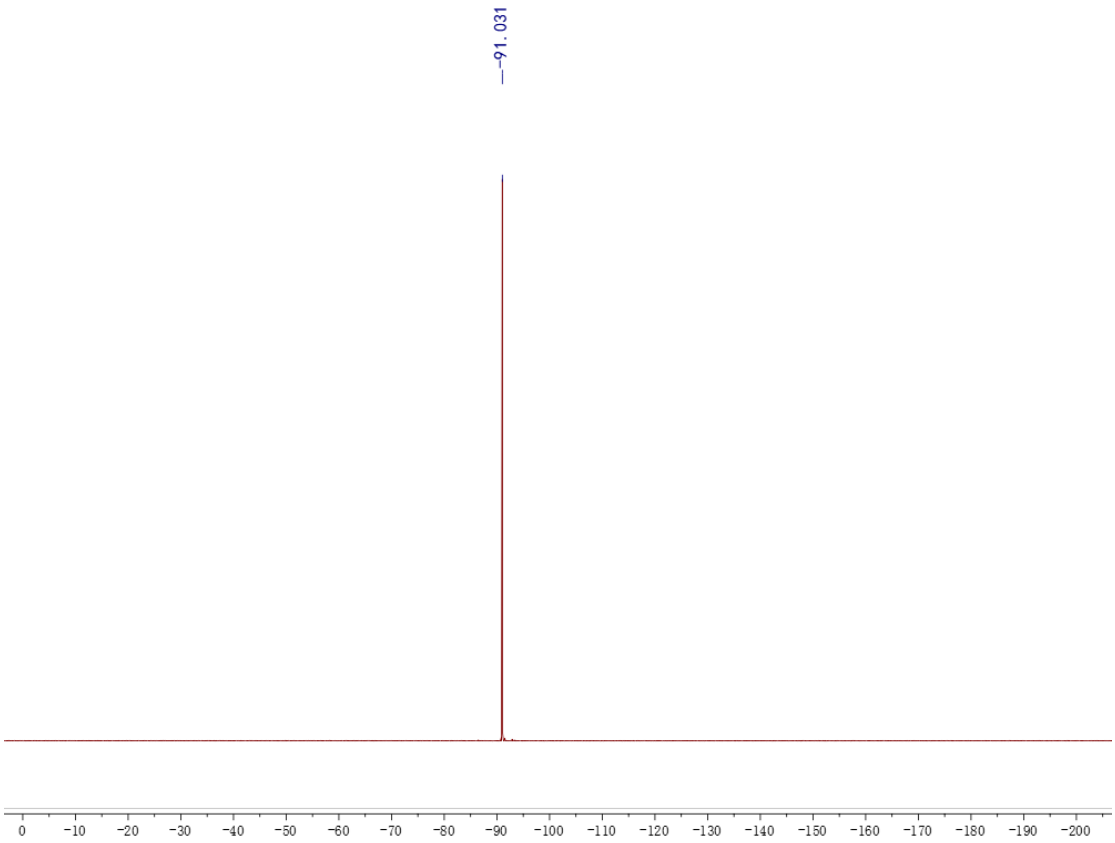
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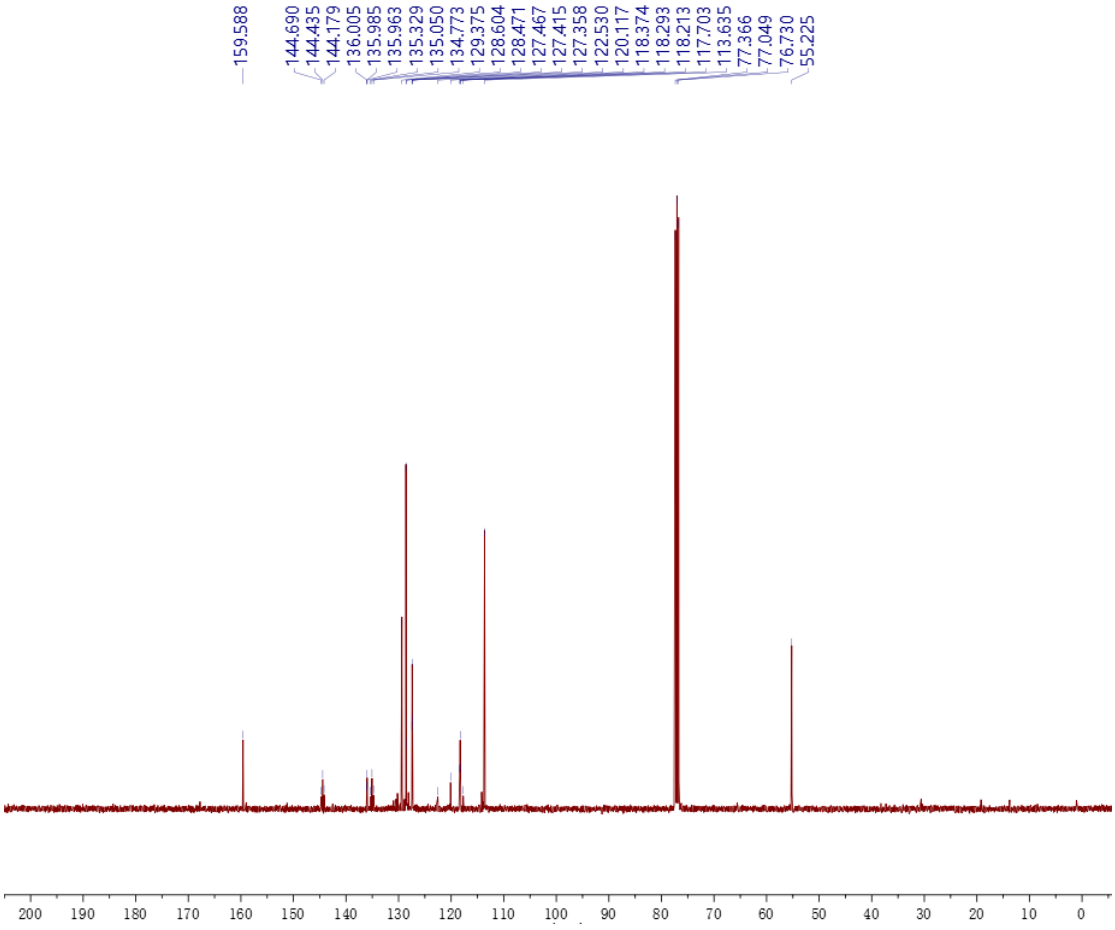
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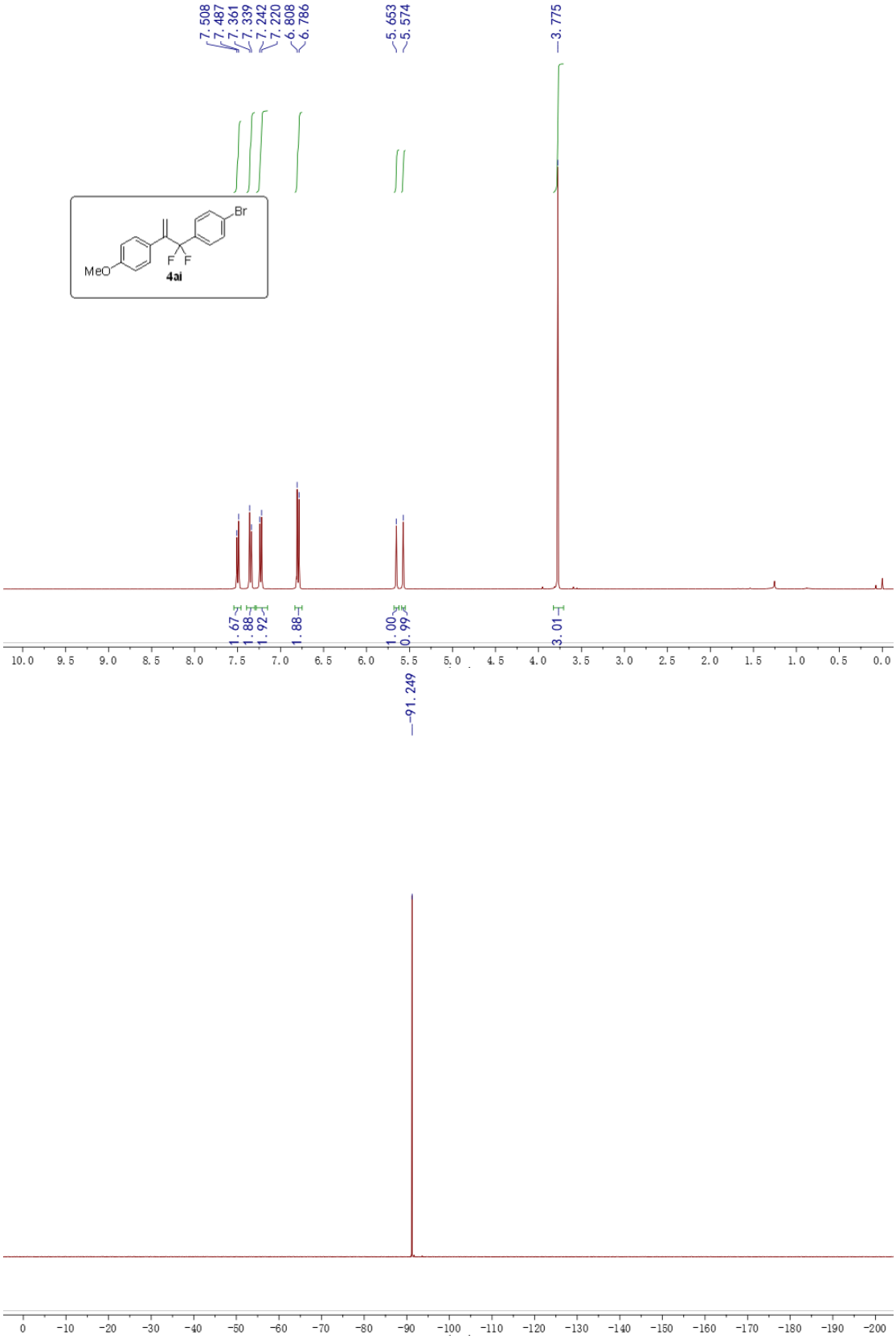
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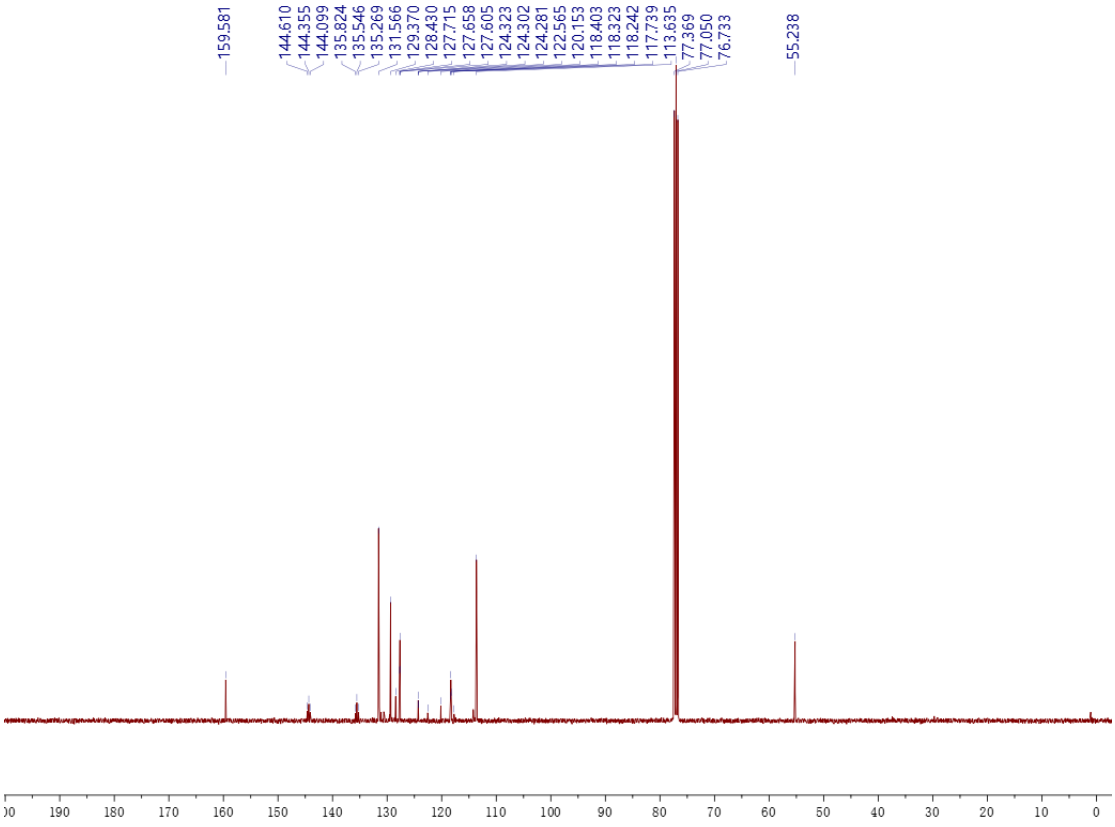
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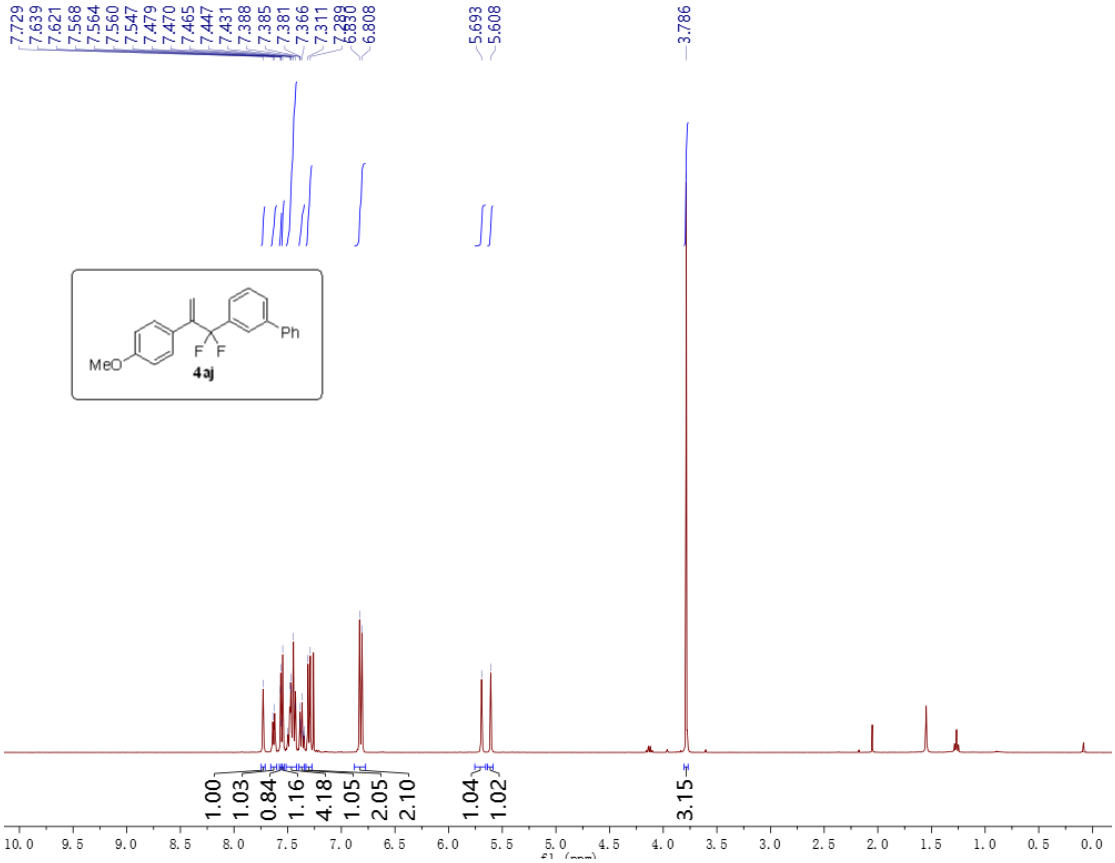
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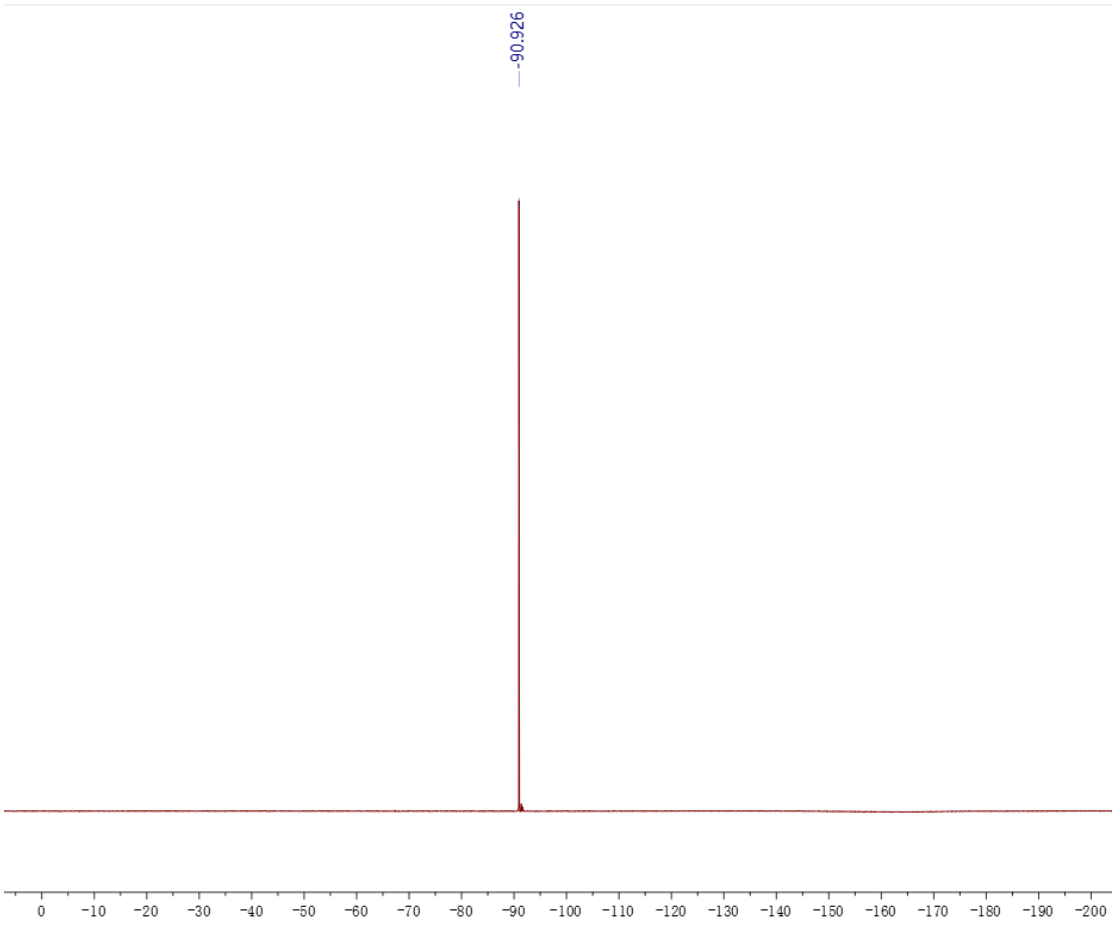
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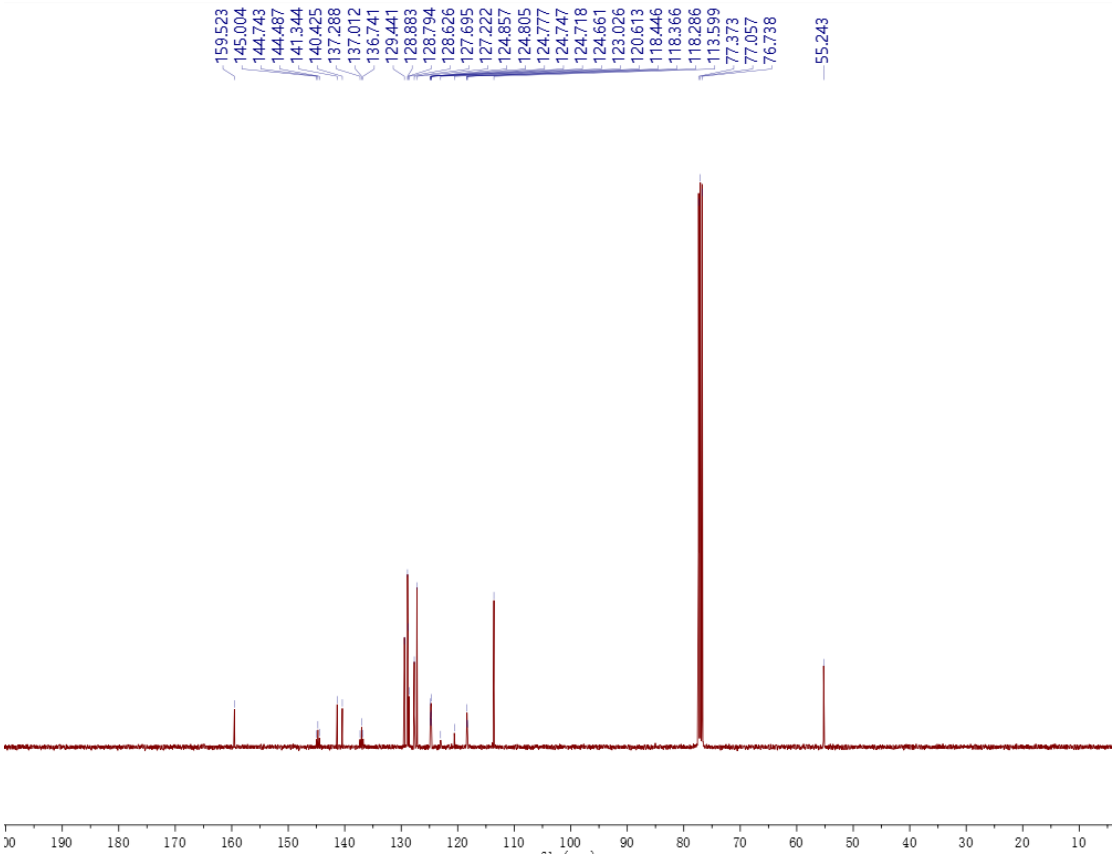
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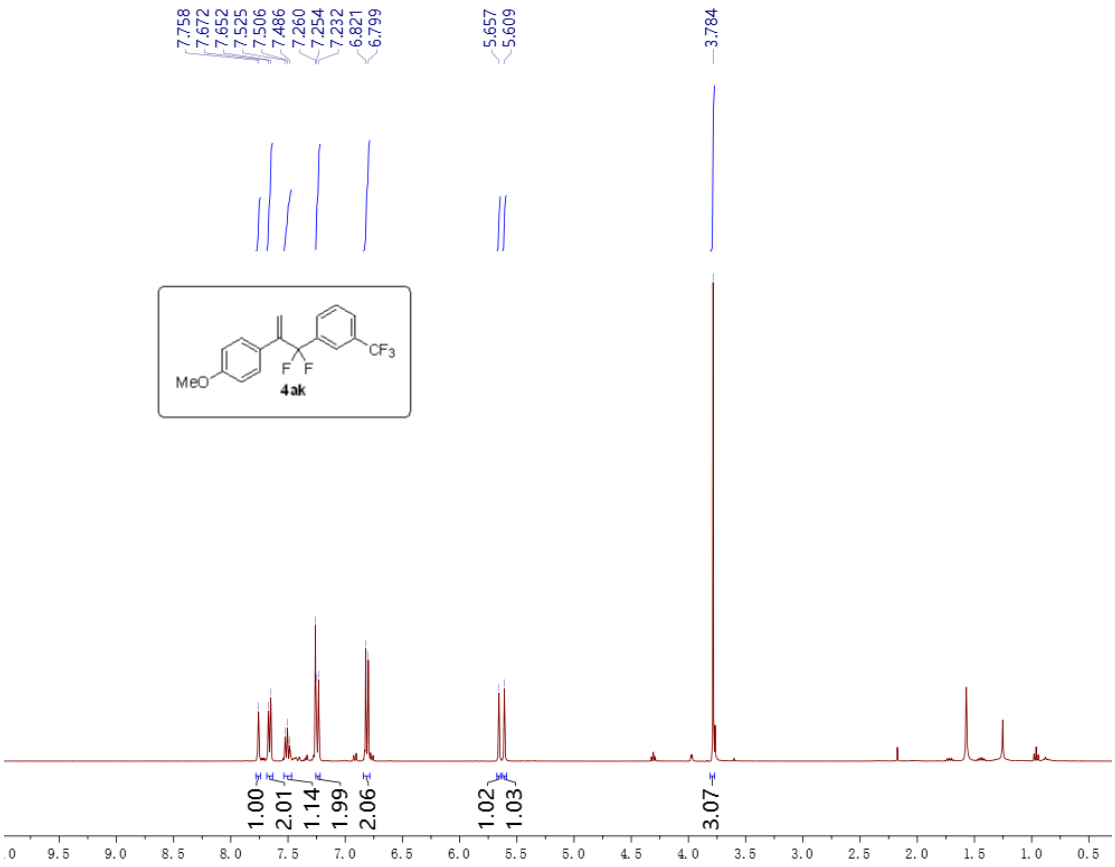
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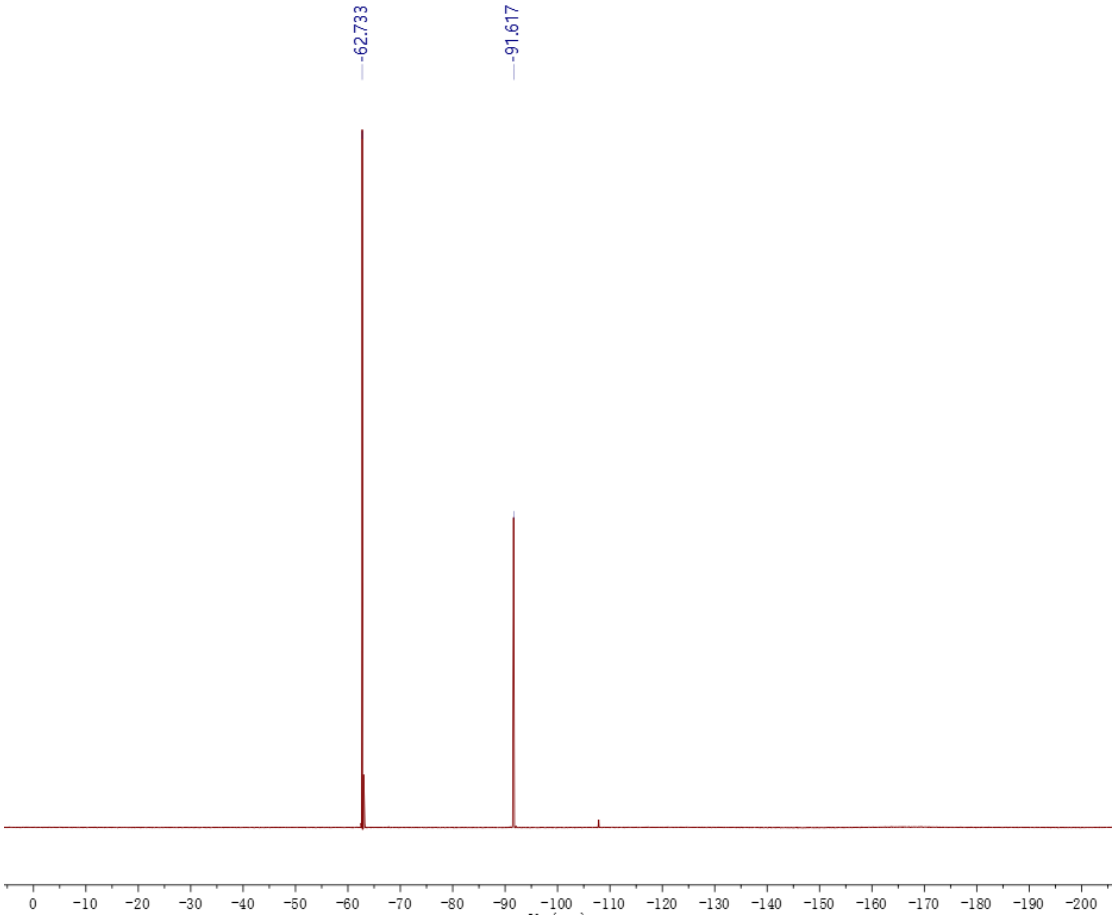
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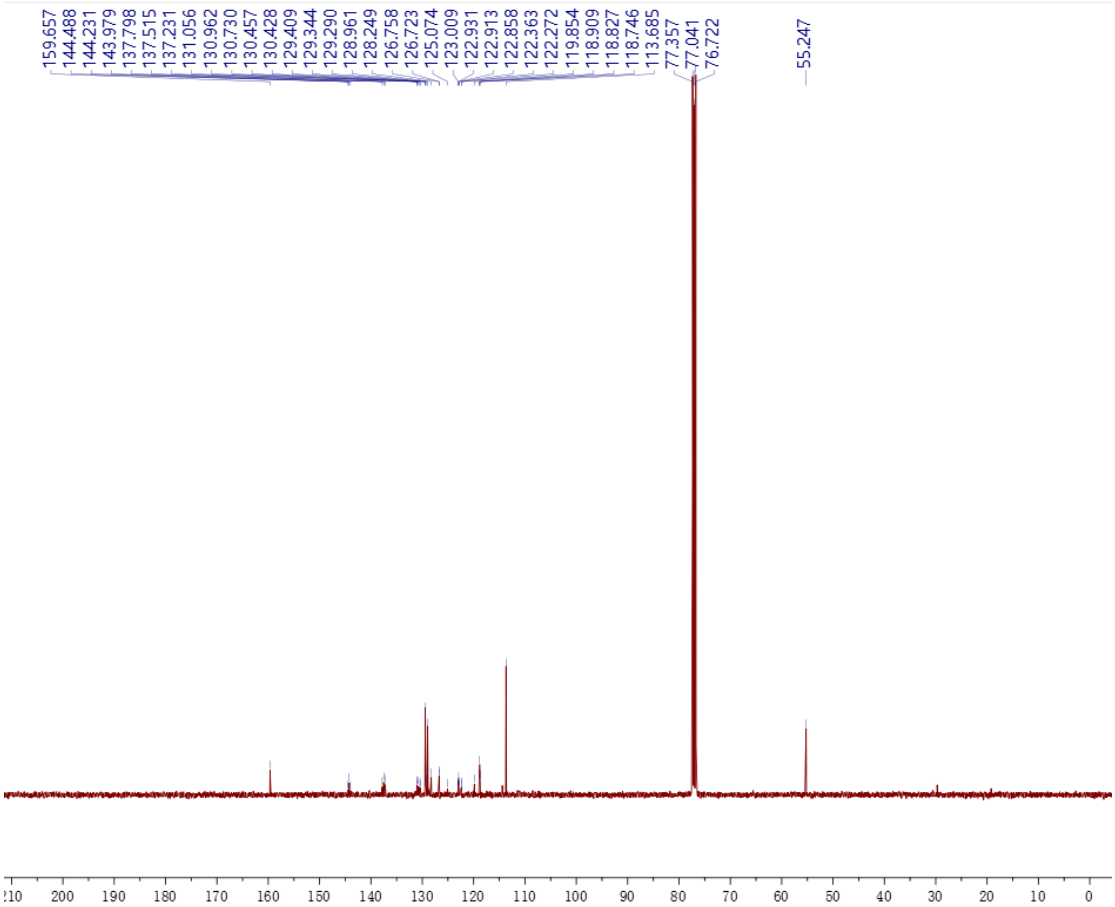
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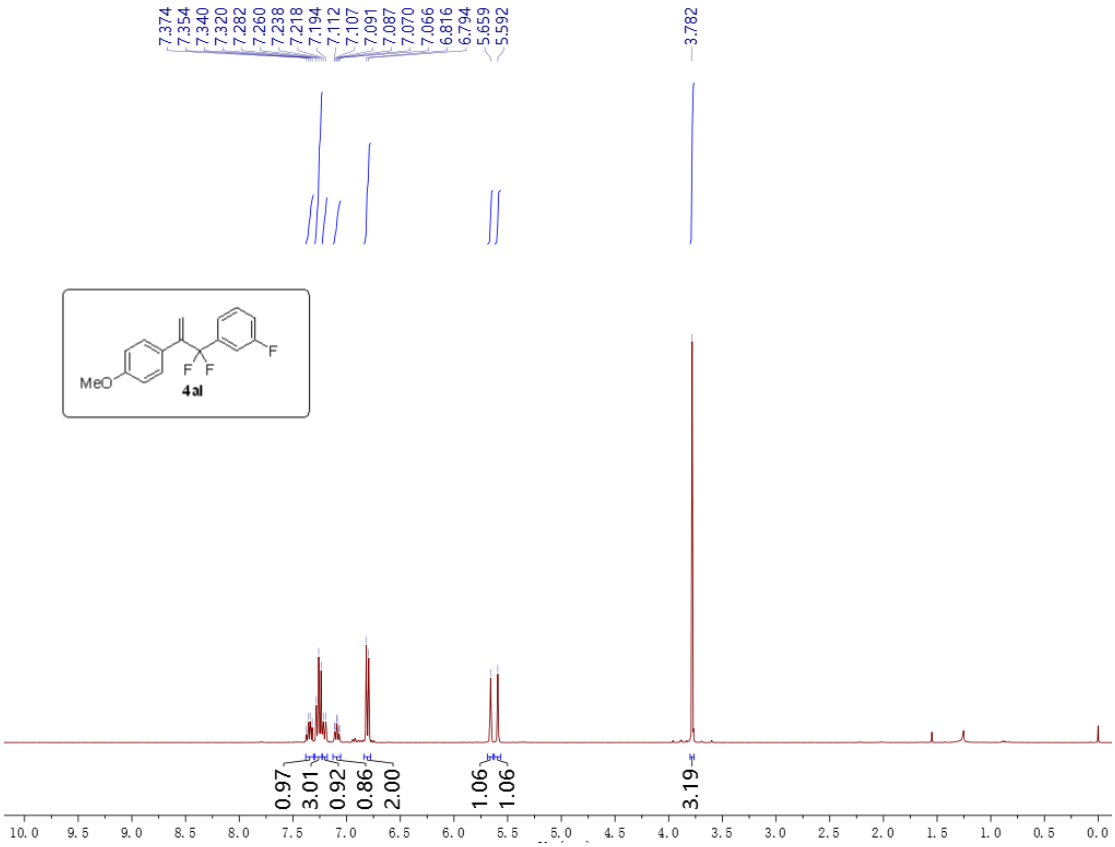
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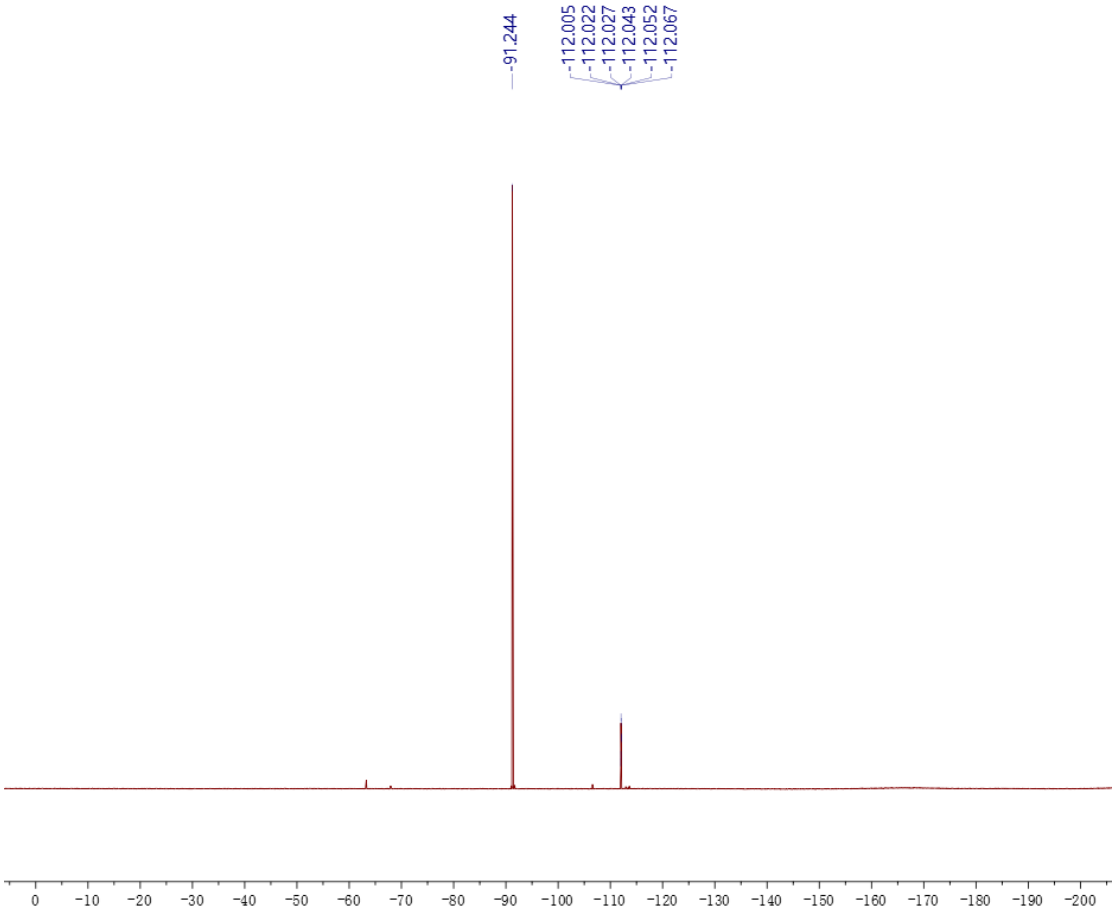
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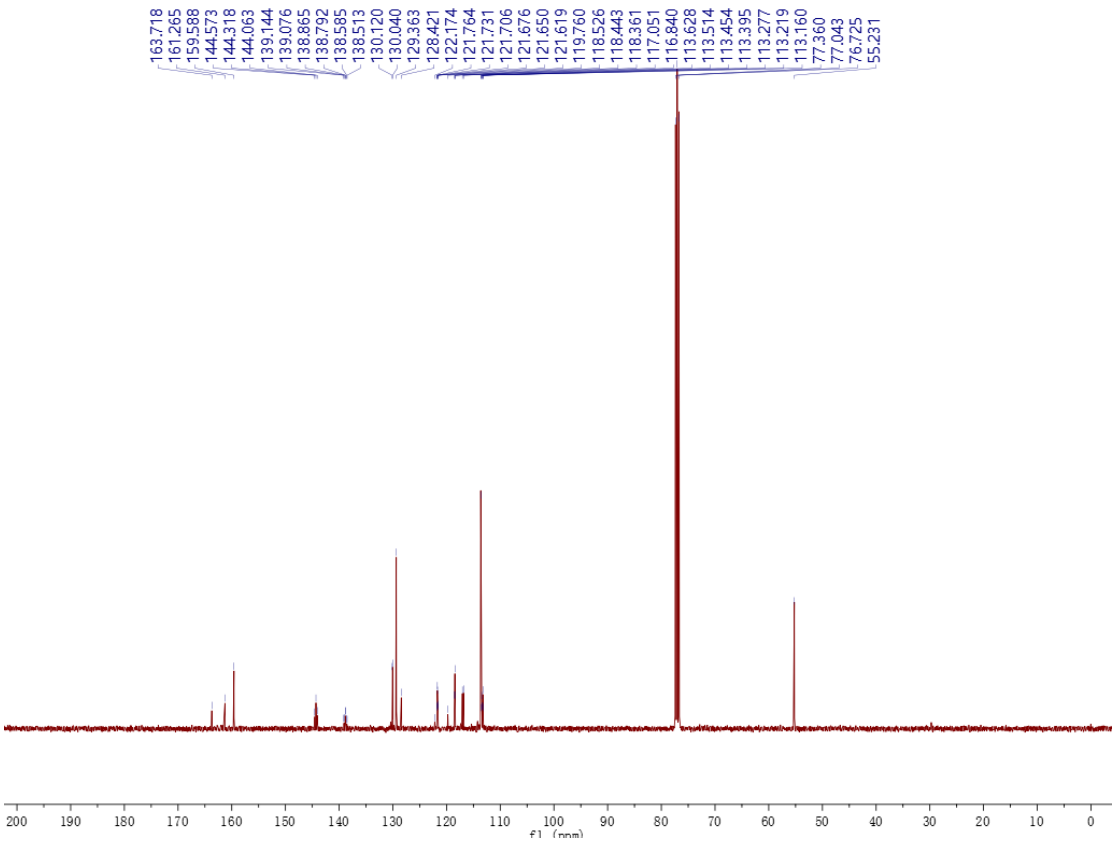
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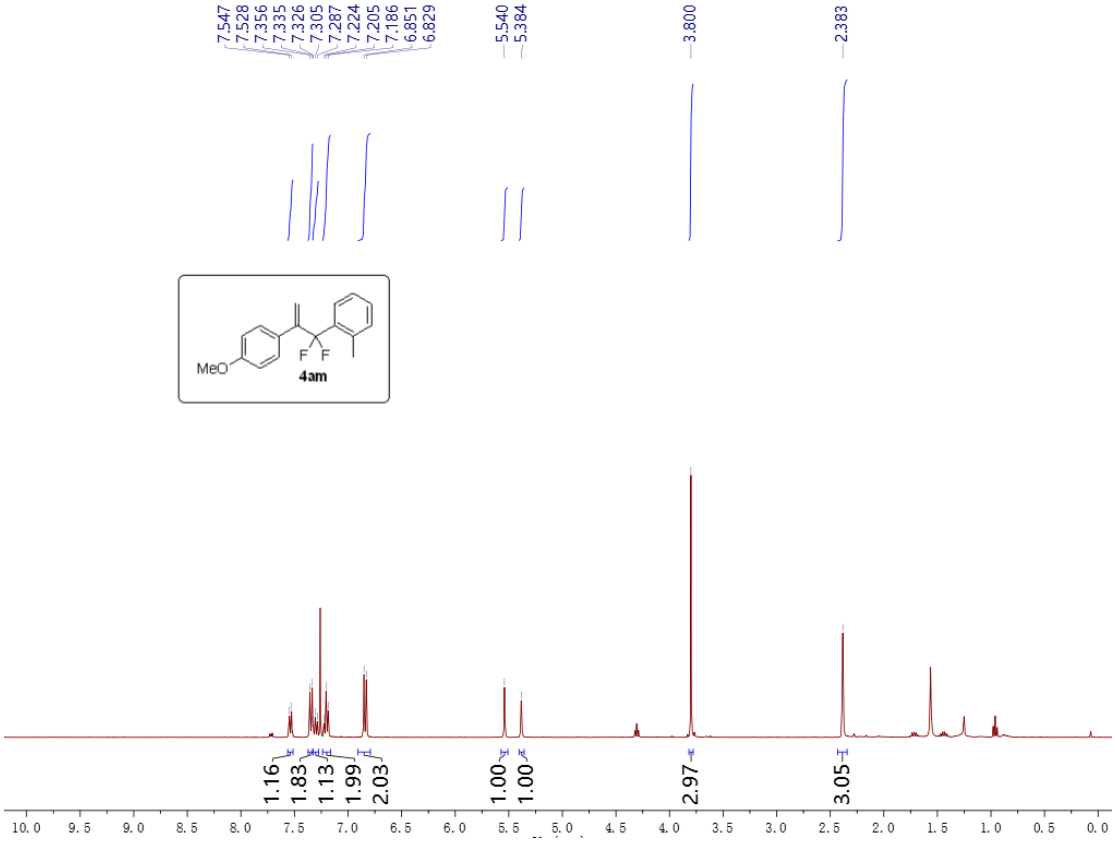
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3.800
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F F
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1.13
1.99
2.03
1.00
1.00
2.97
3.05
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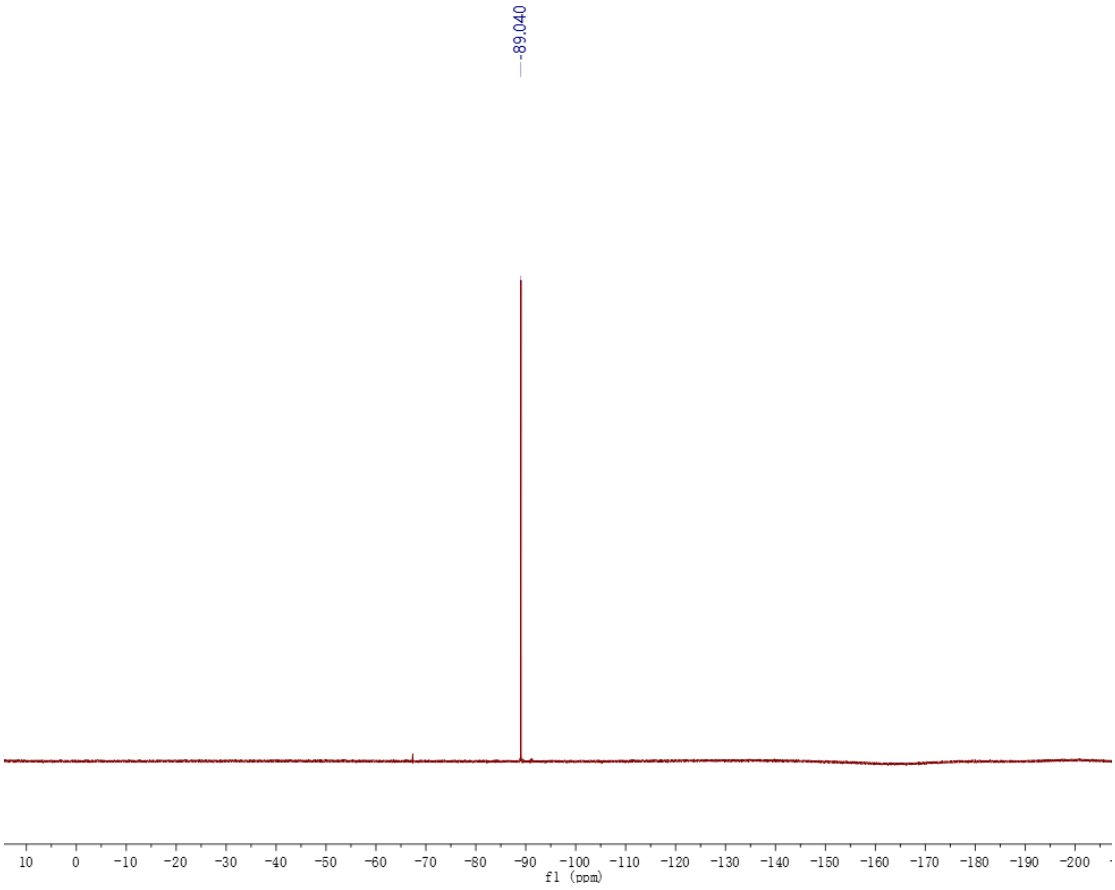
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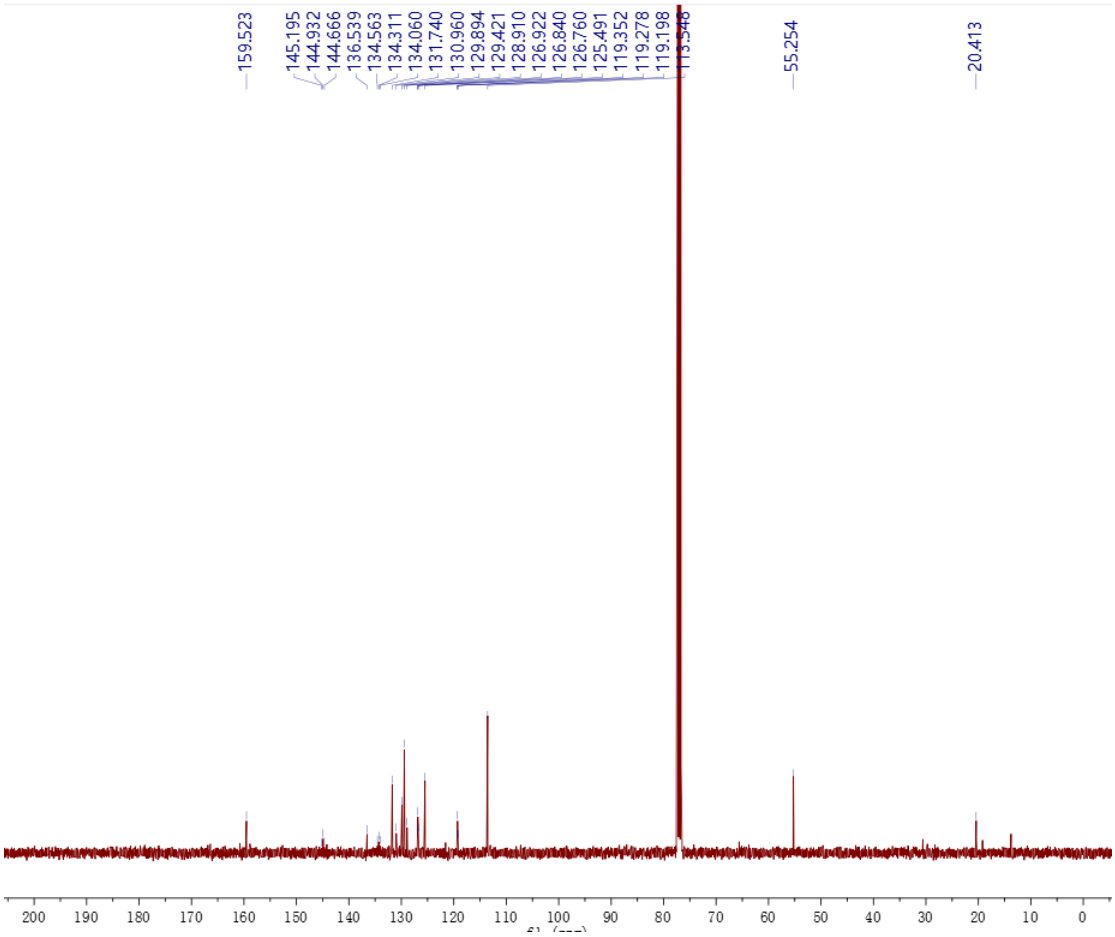
f1 (ppm)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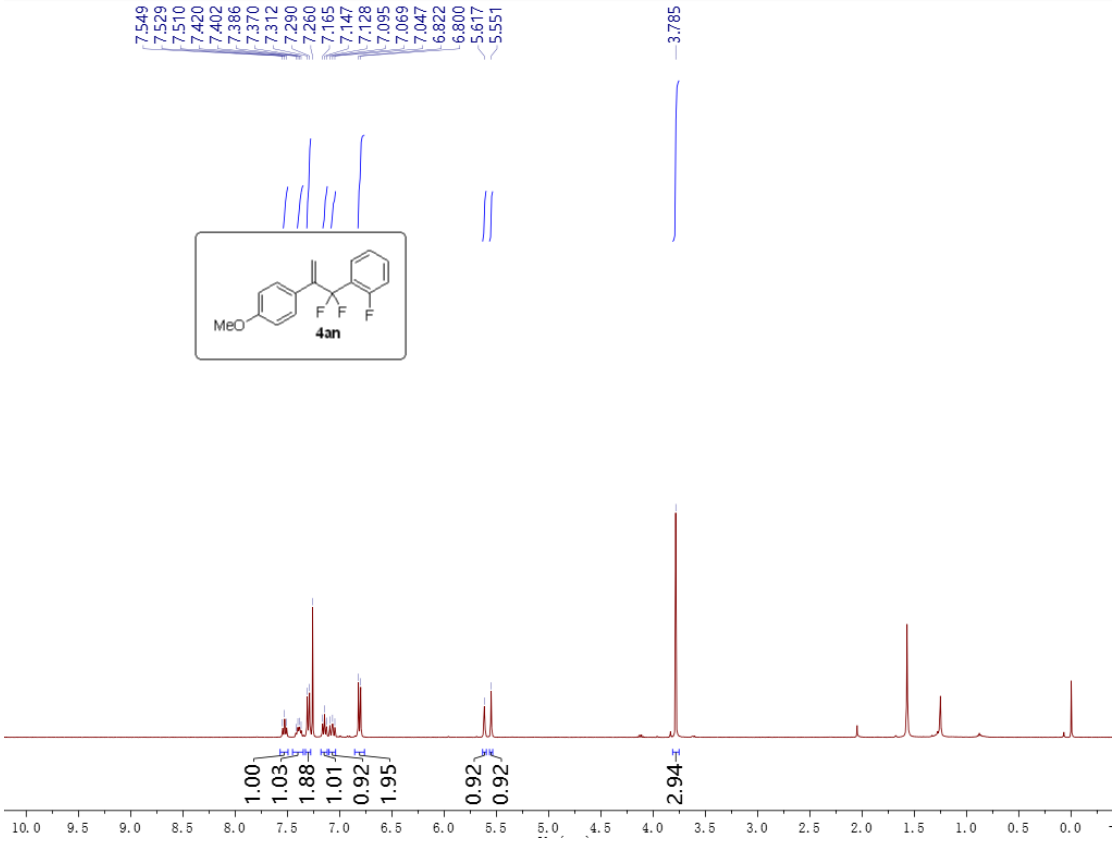
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5.551
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MeO
F F F
4an
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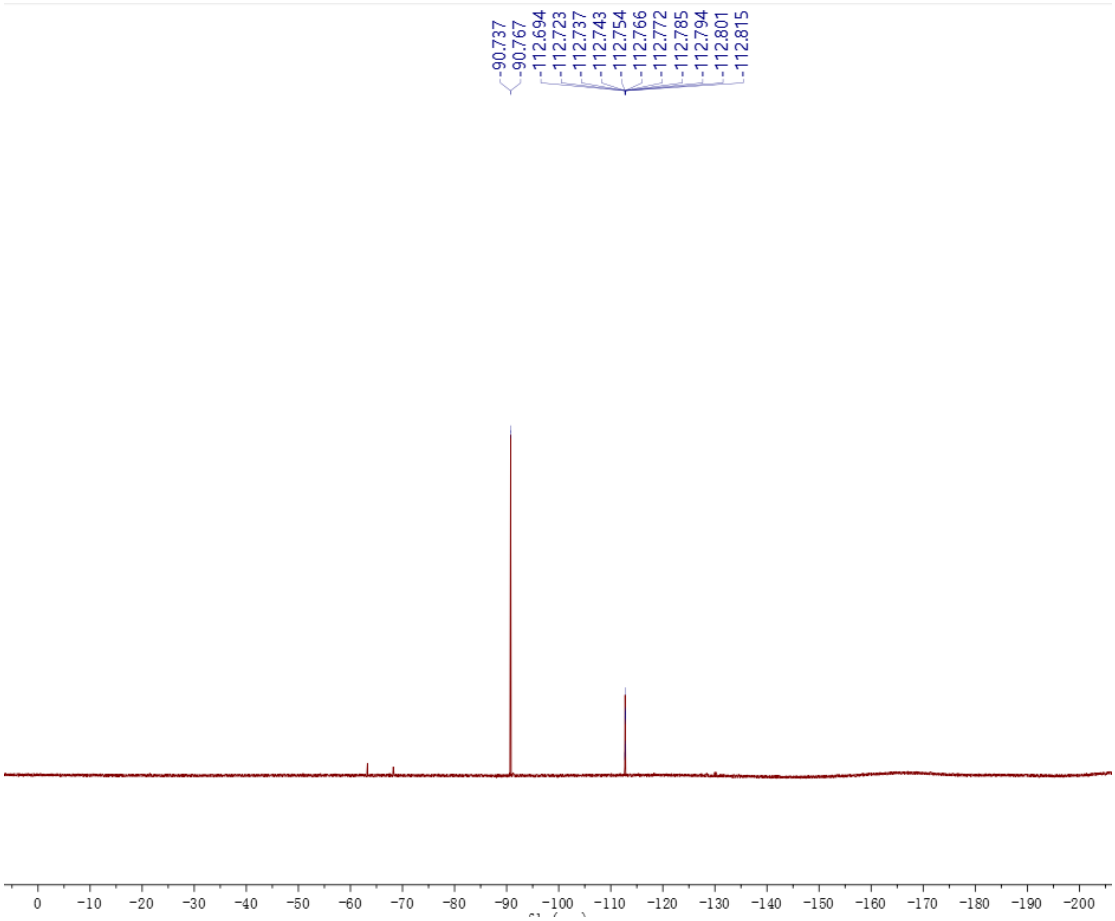
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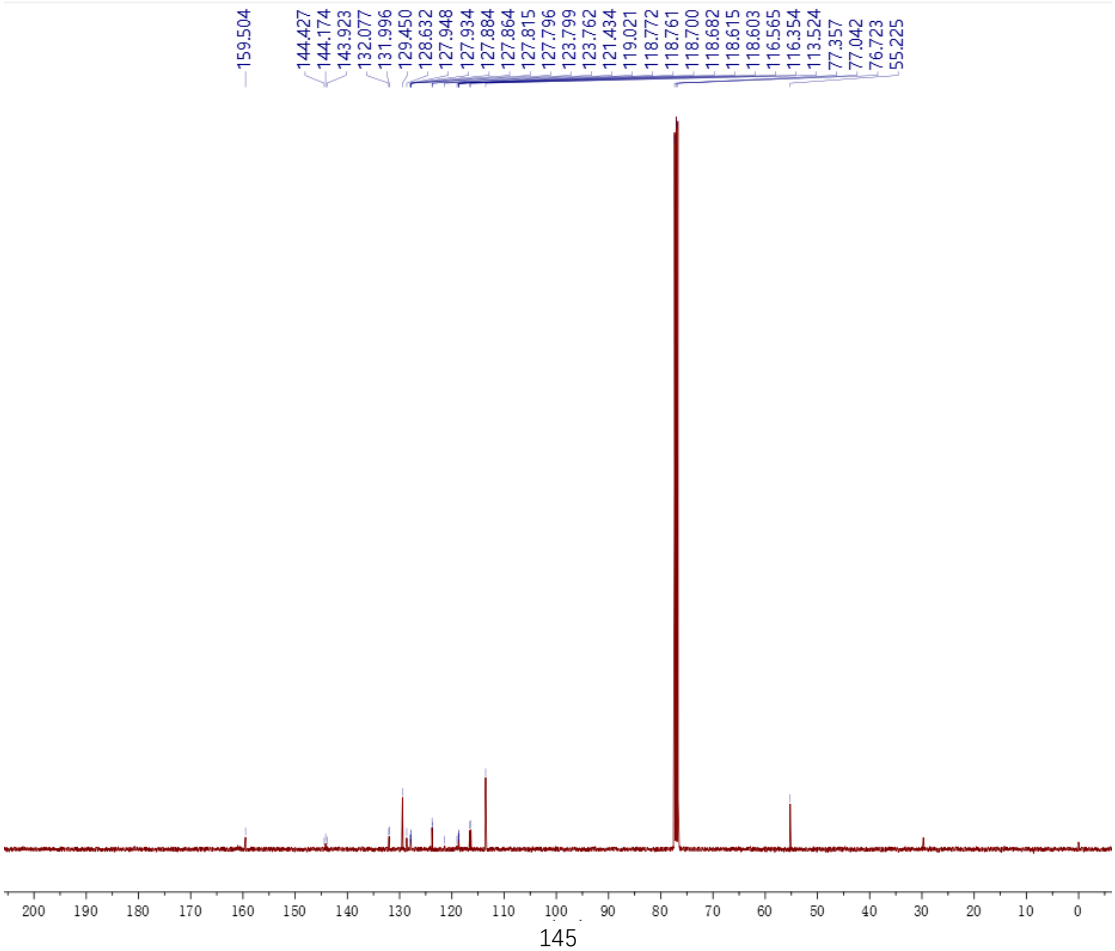
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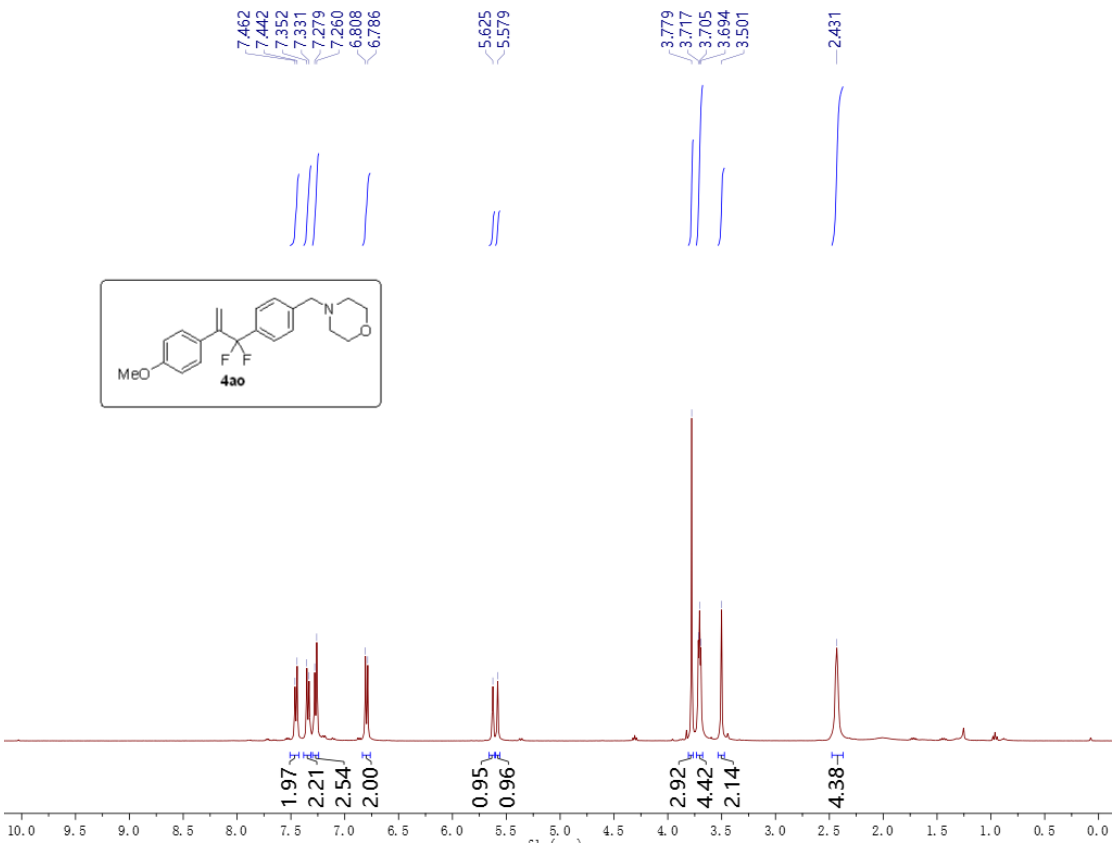
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N
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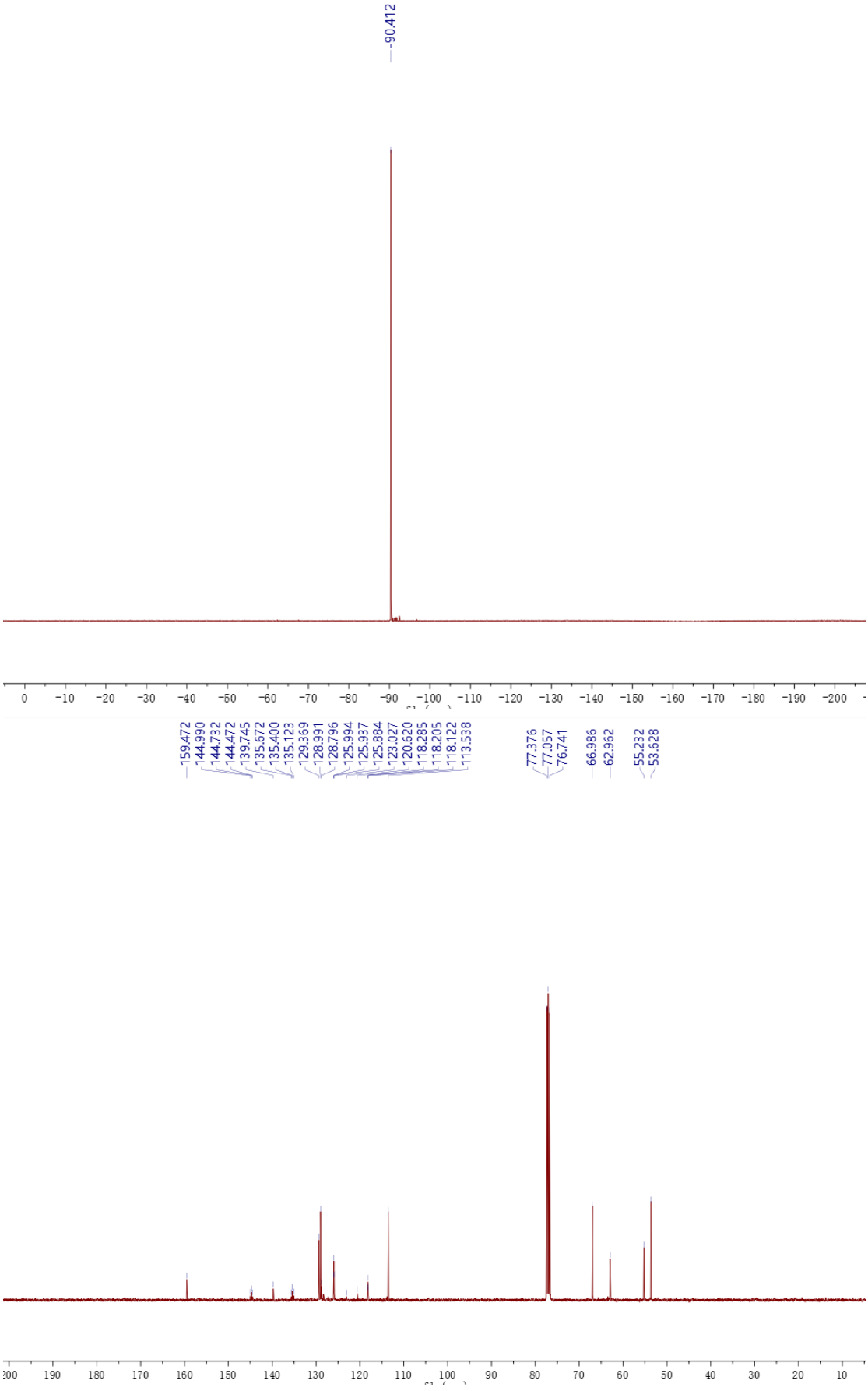
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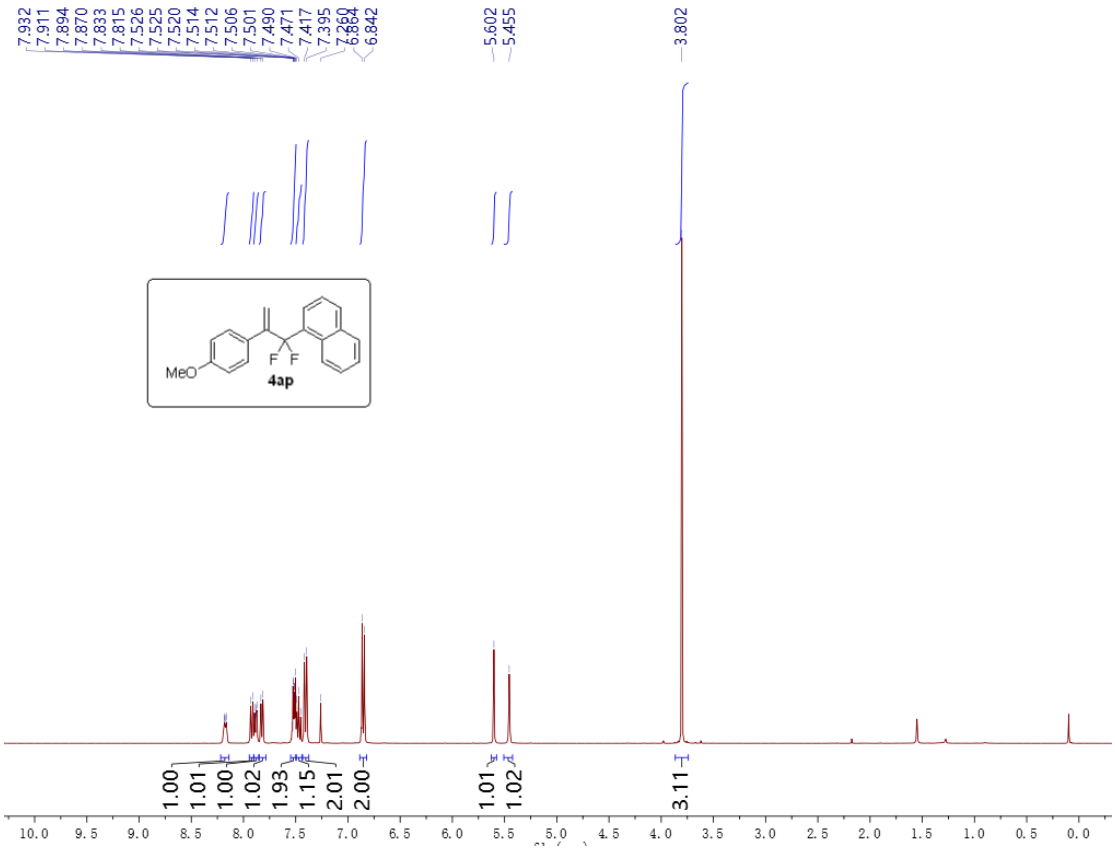
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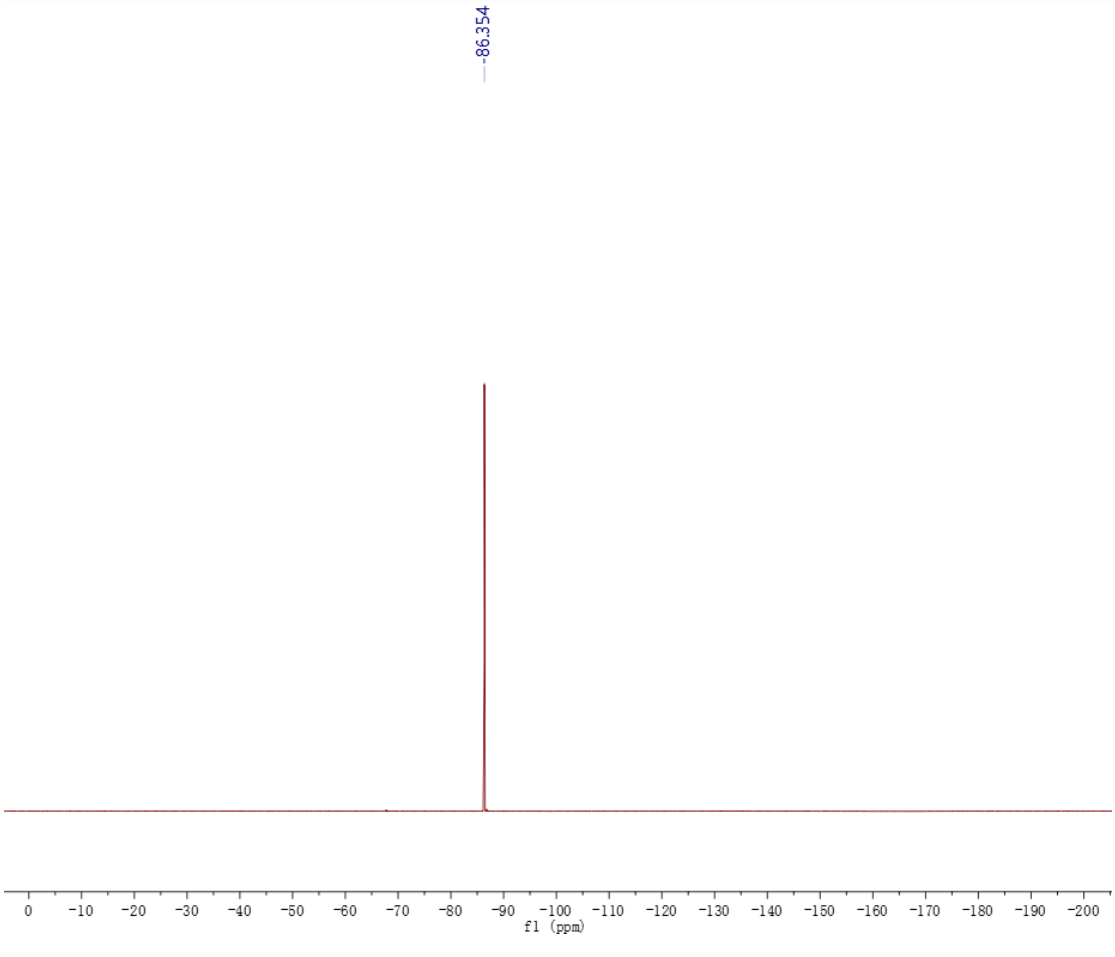
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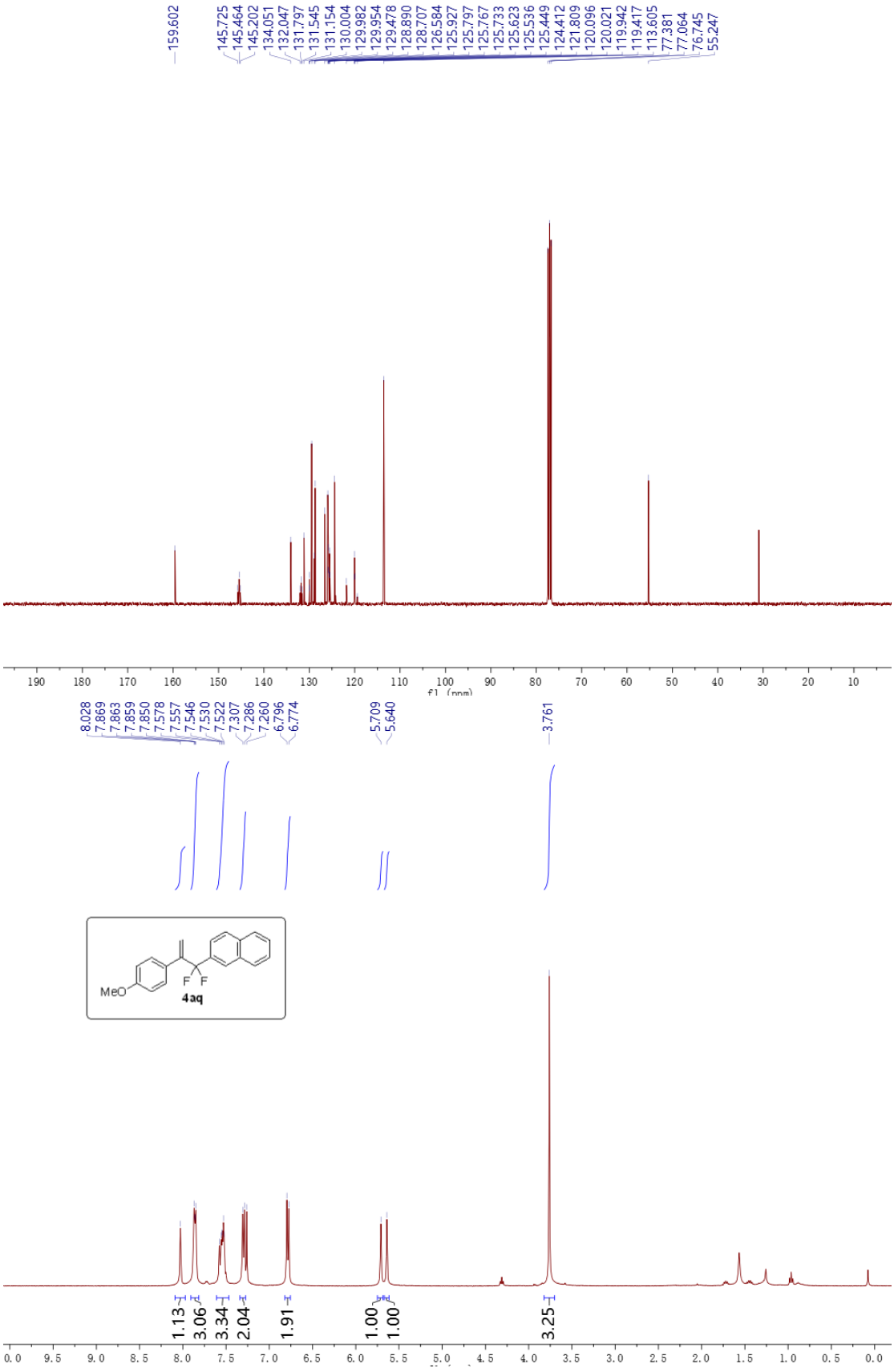
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f1 (ppm)
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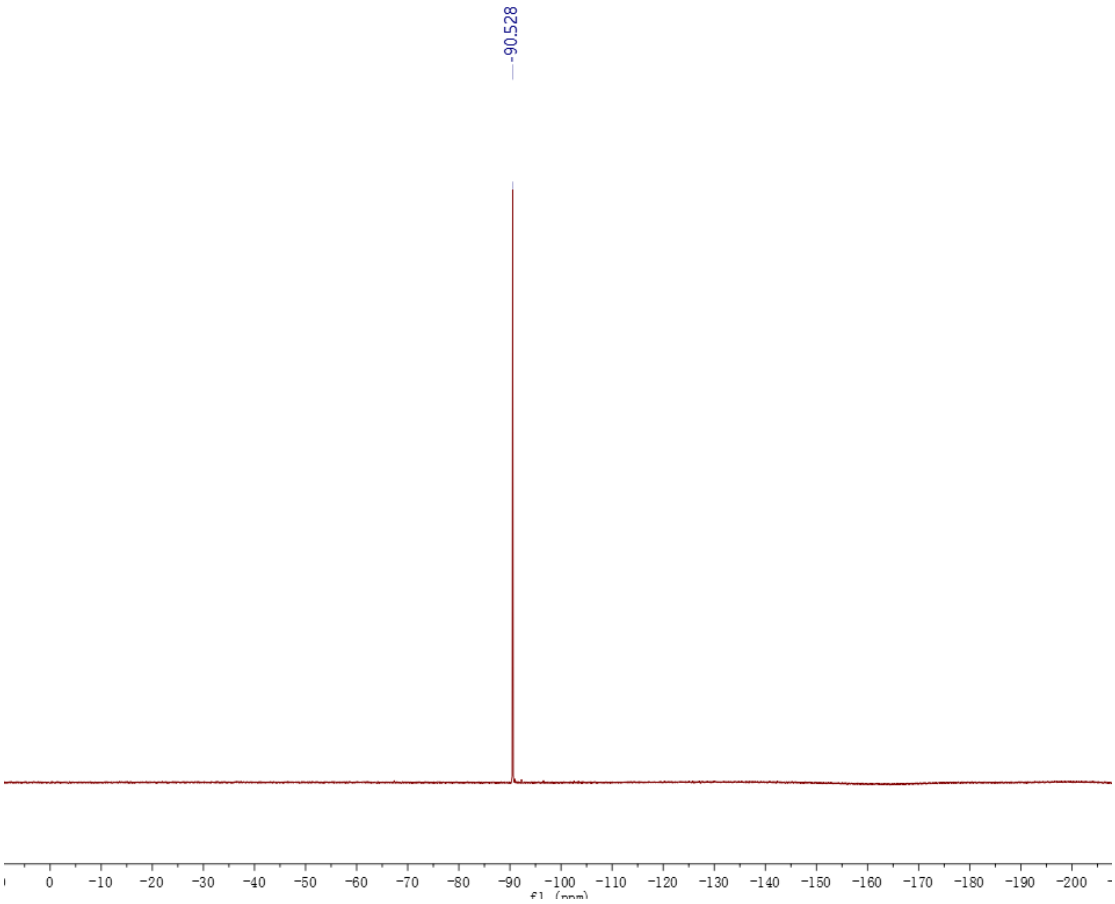
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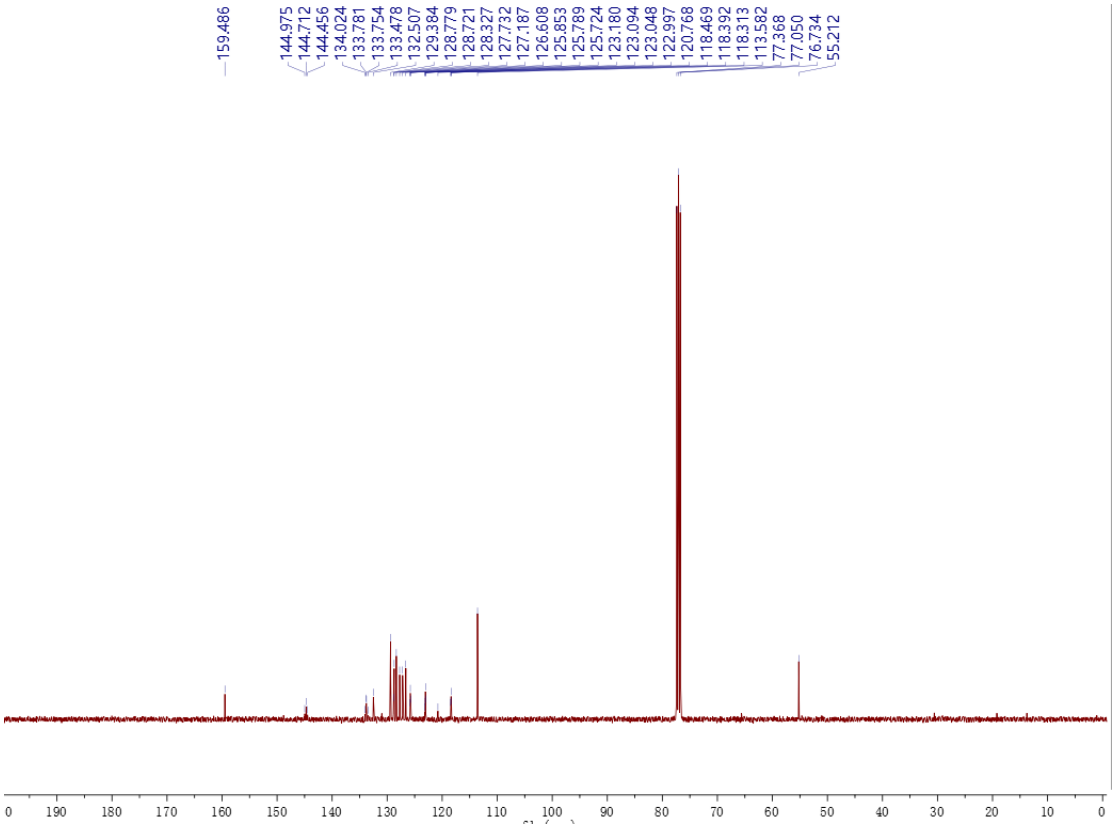
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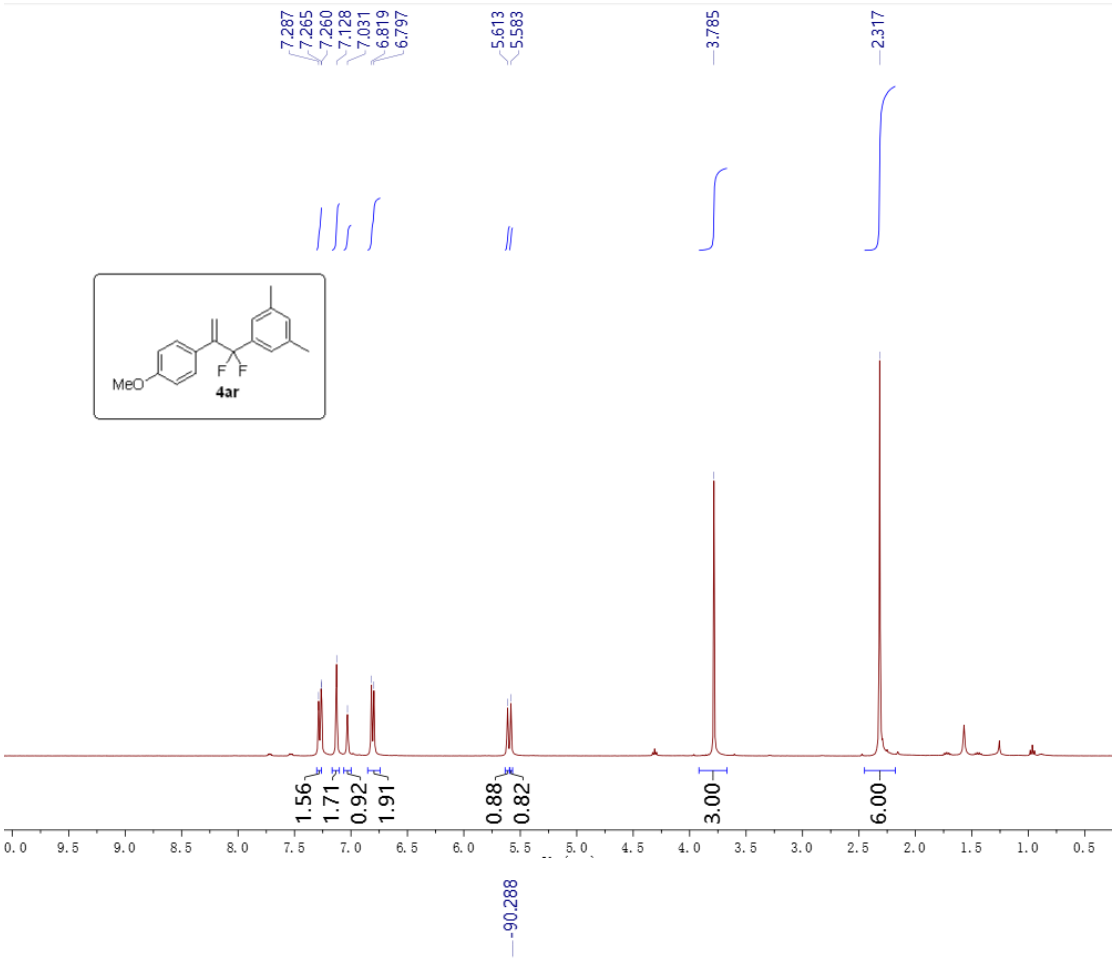
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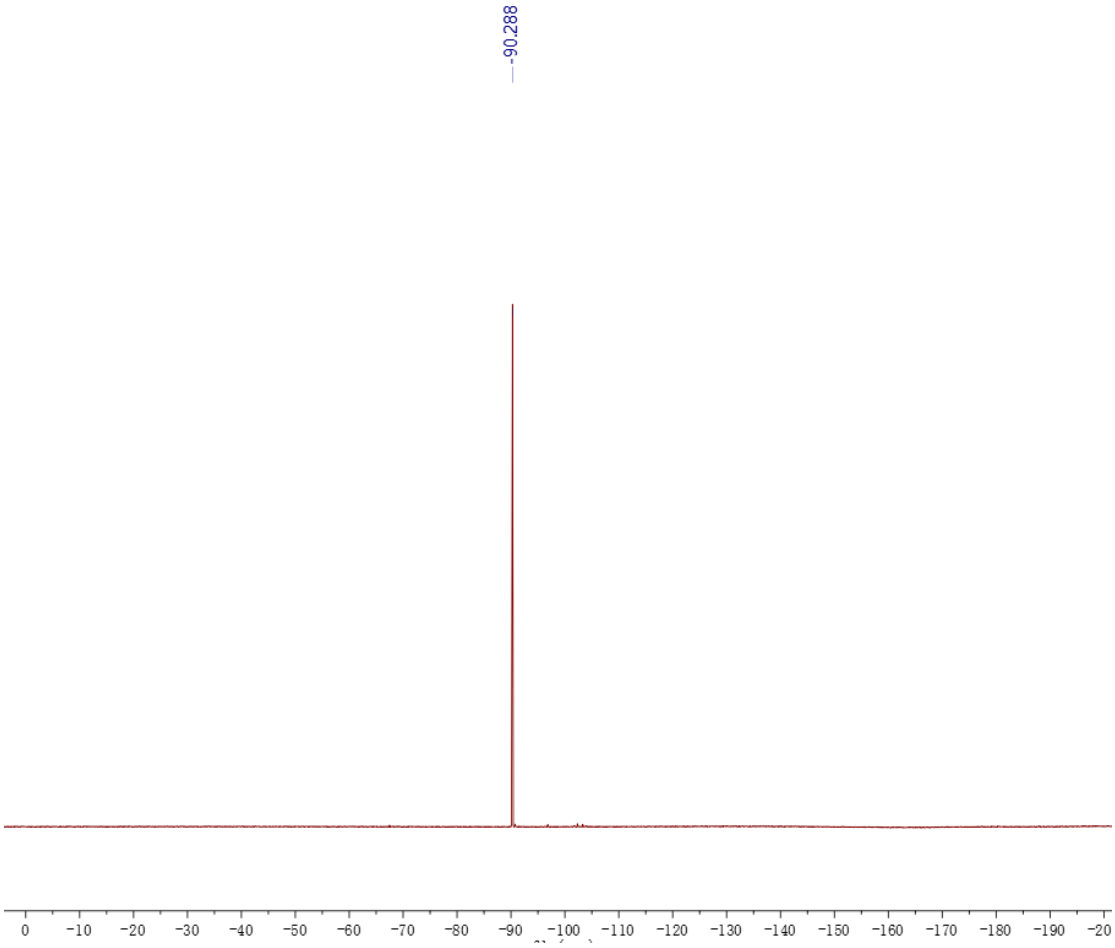
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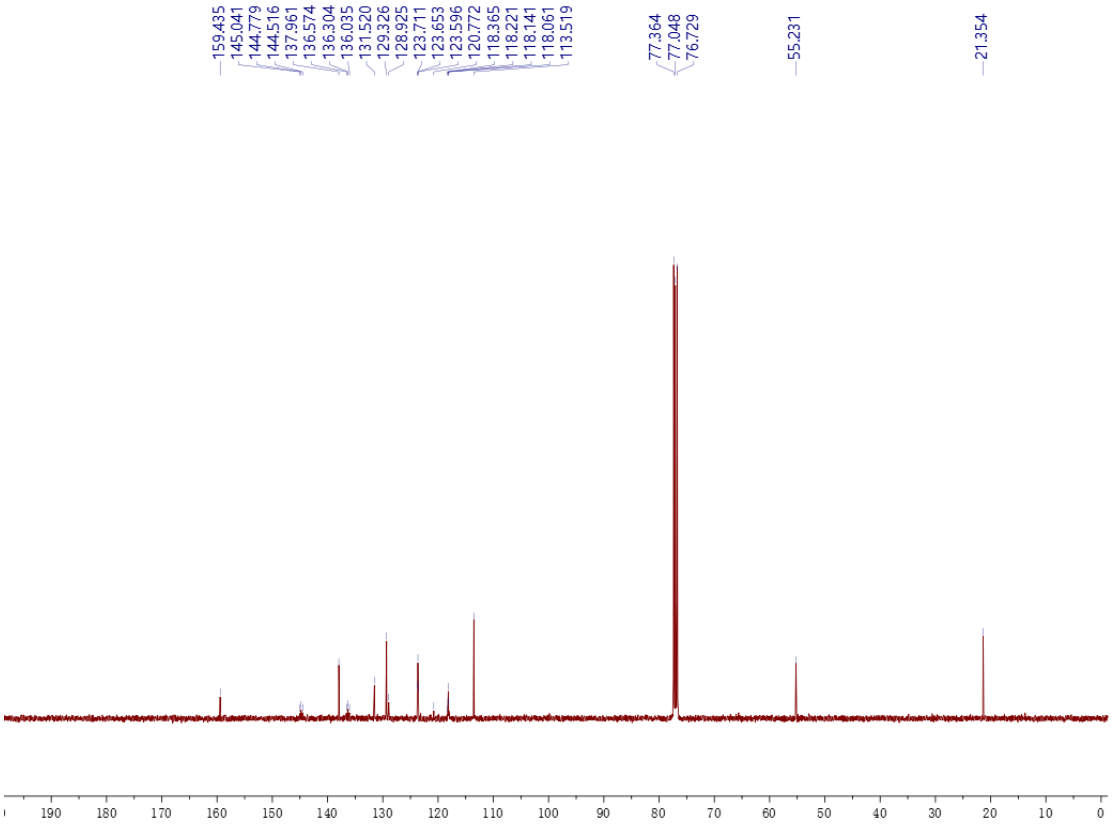
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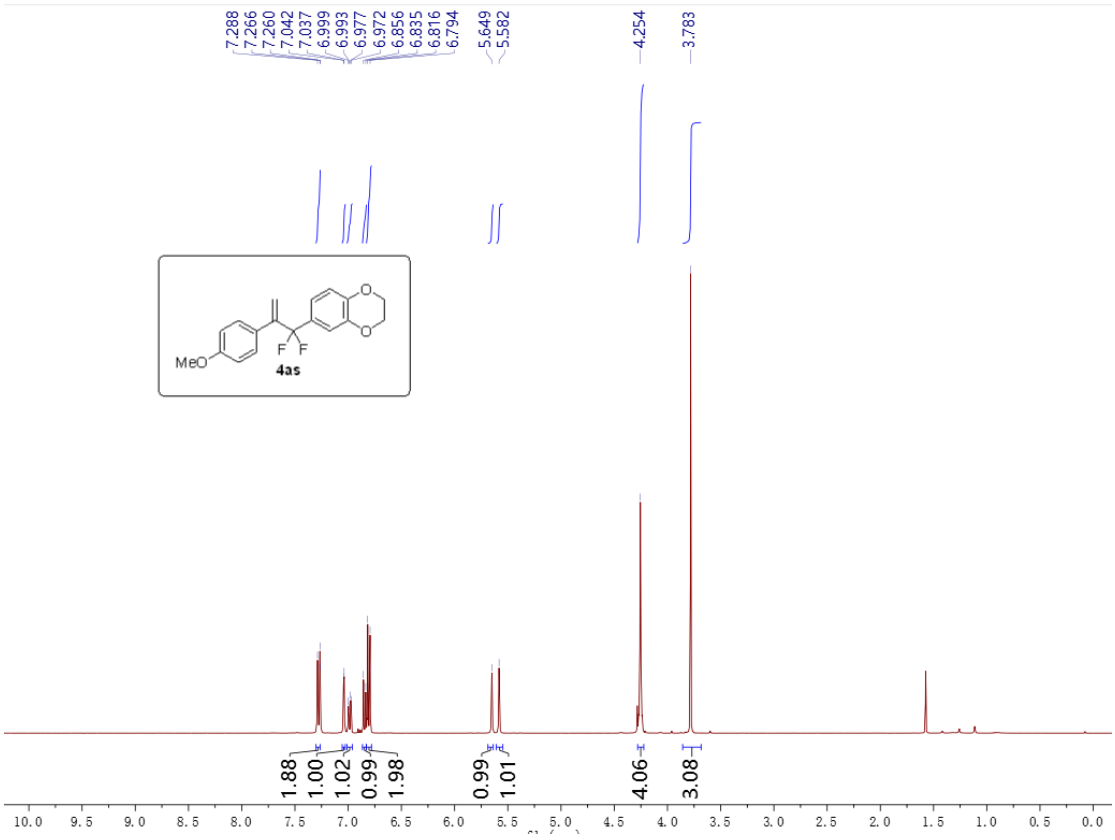
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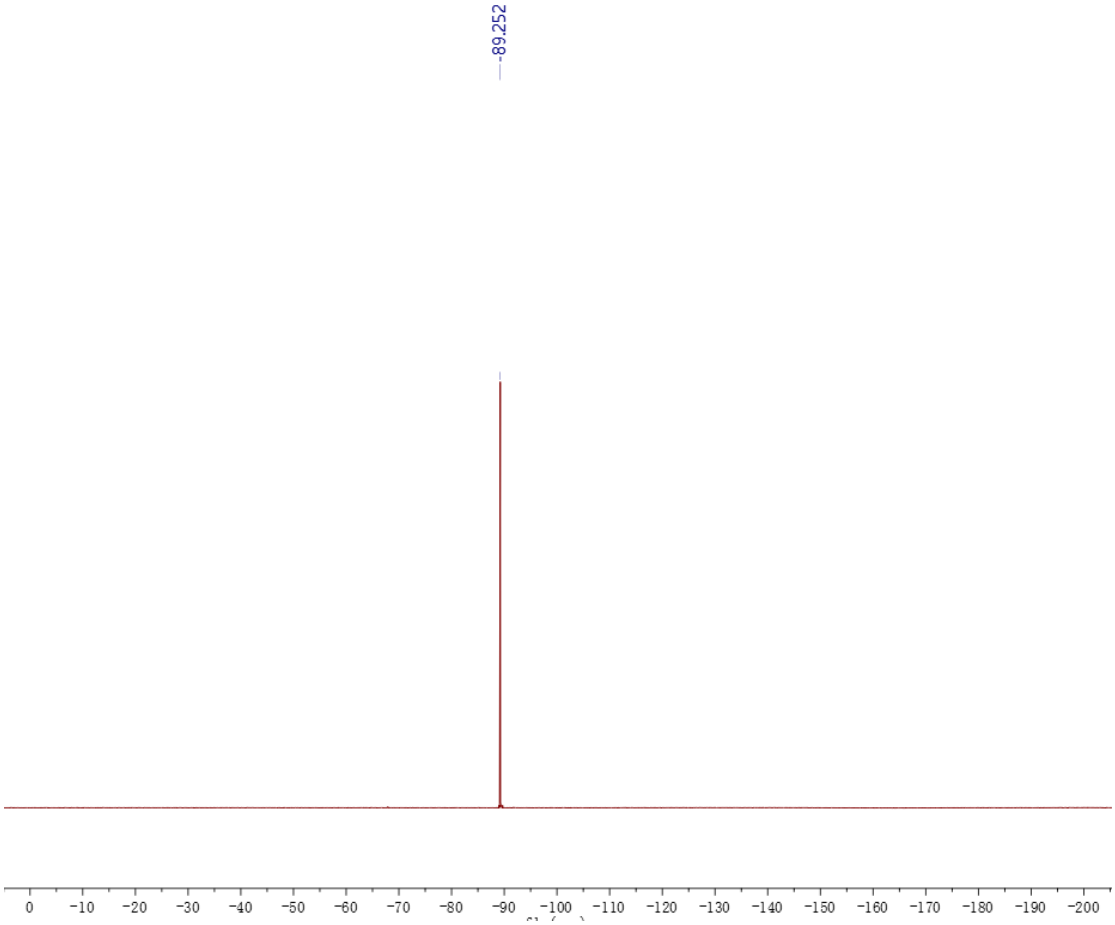
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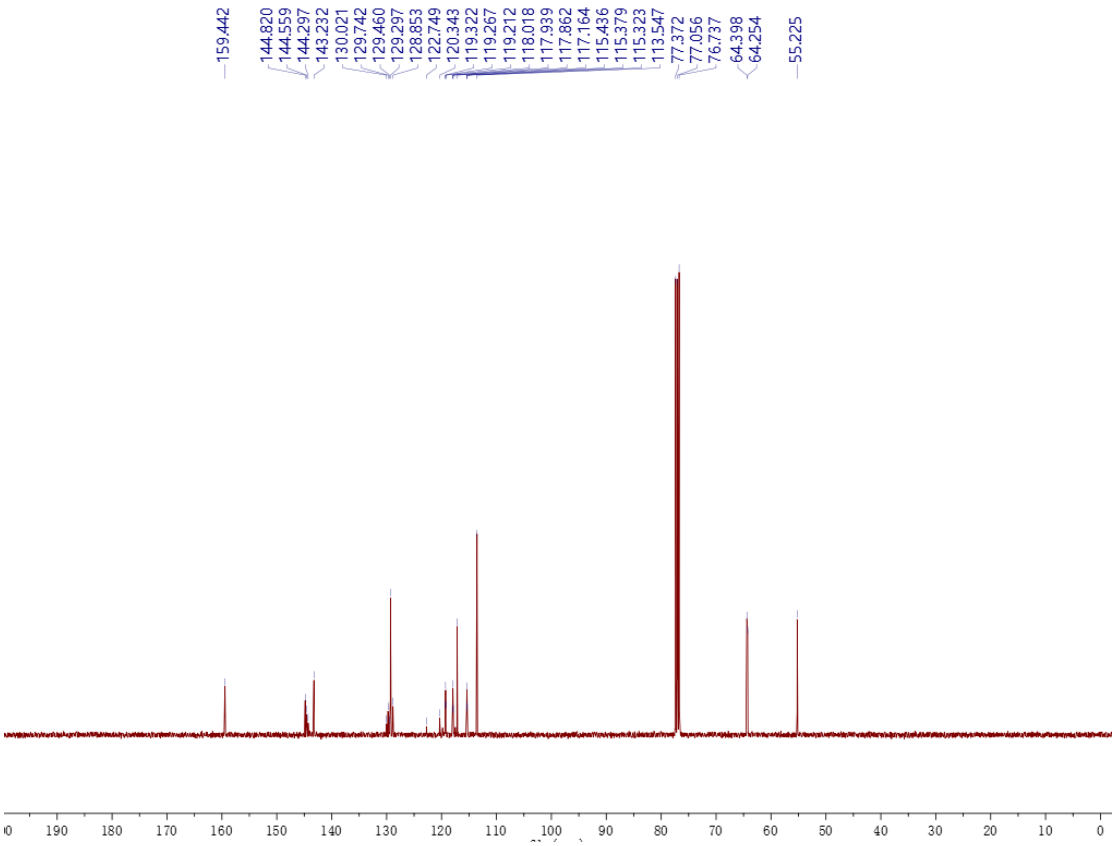
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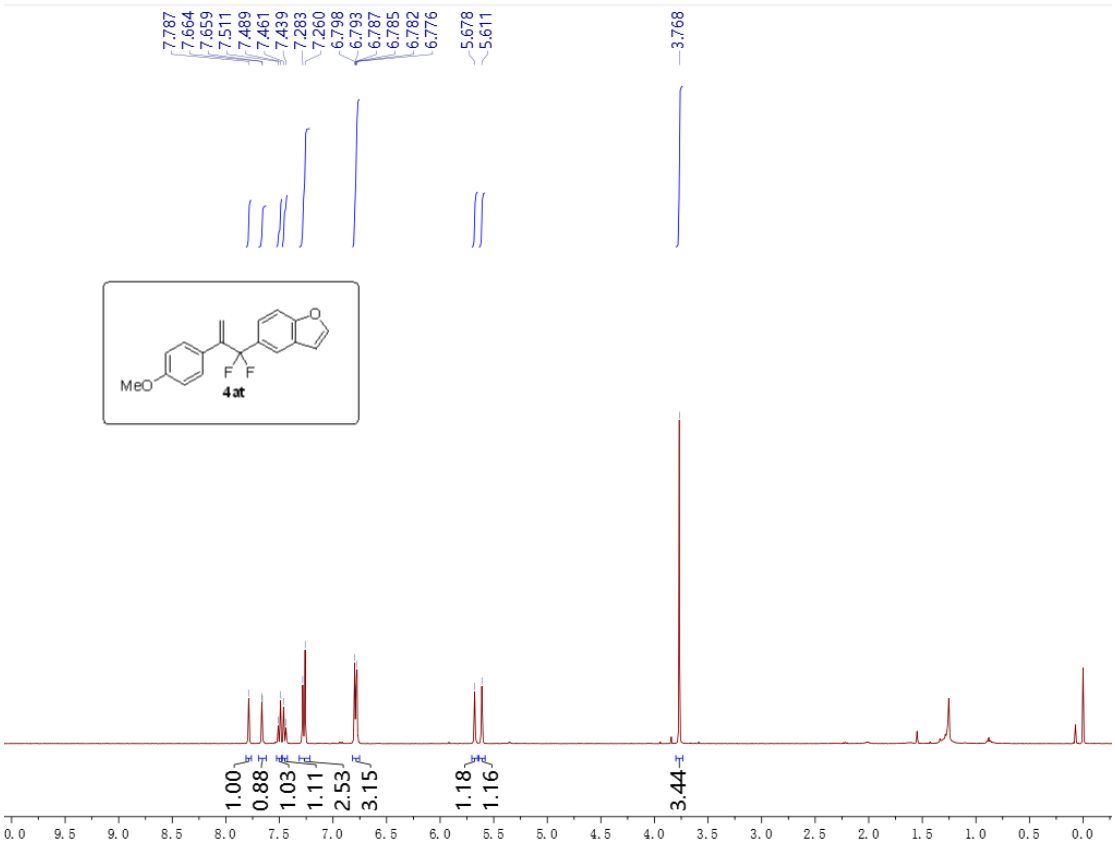
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MeO
F F
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2.53
3.15
1.18
1.16
3.44
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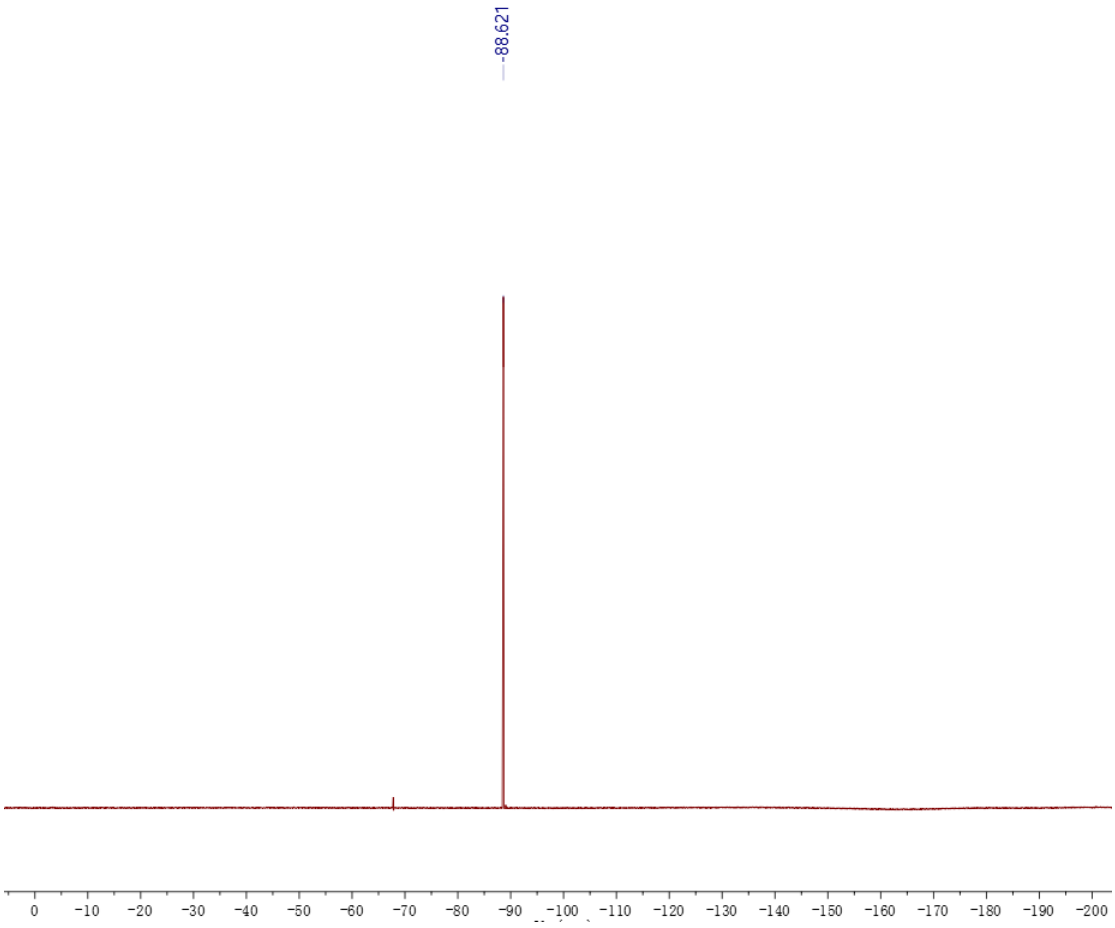
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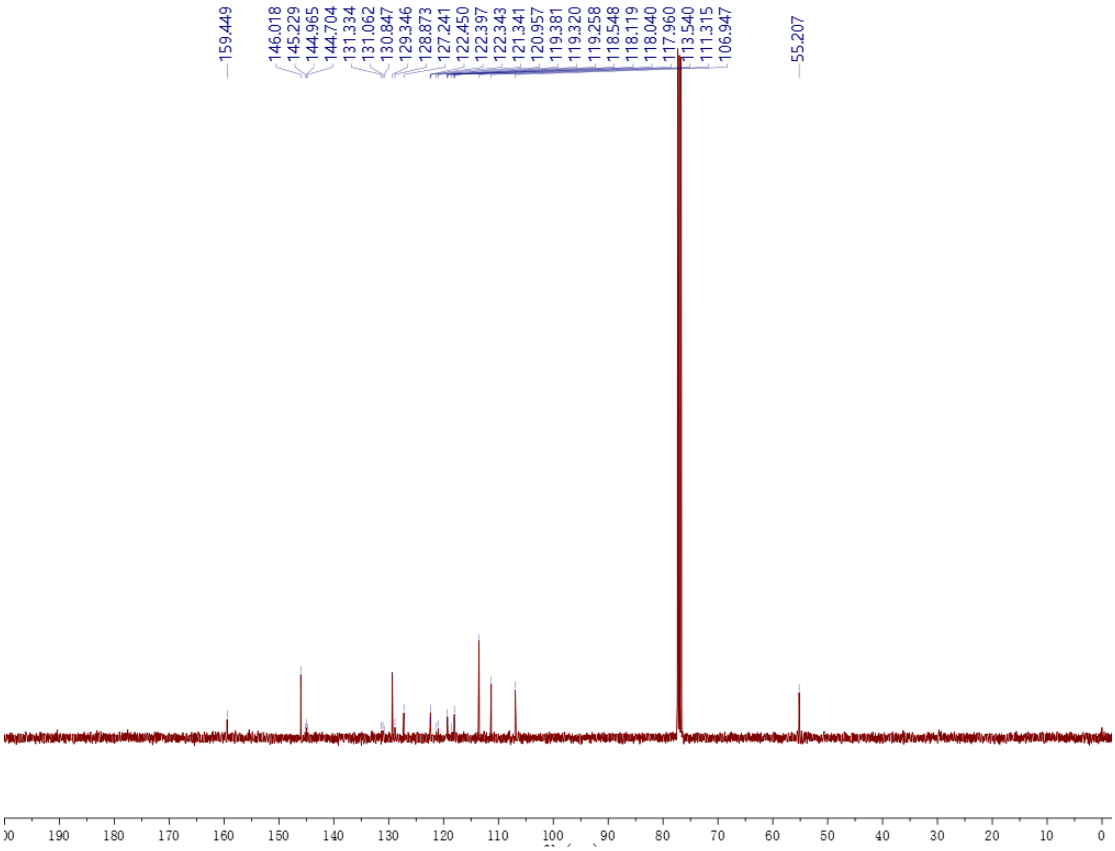
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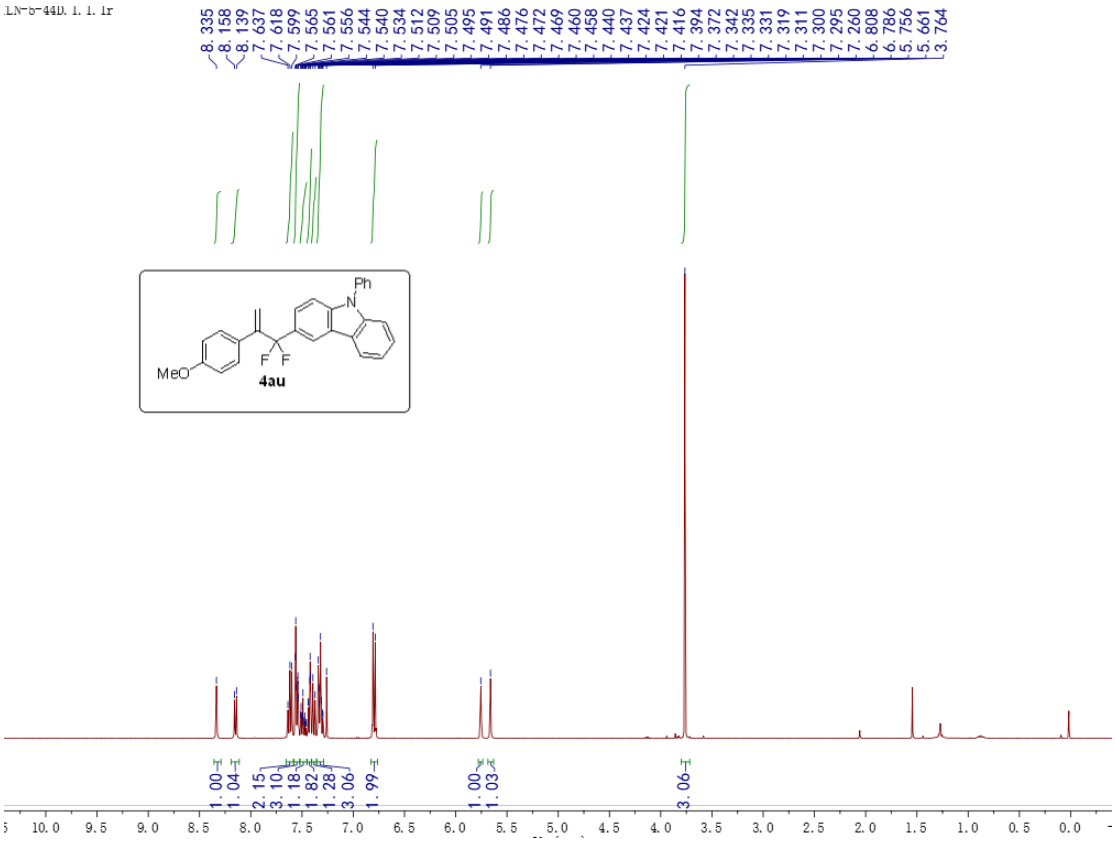
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Ph
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MeO
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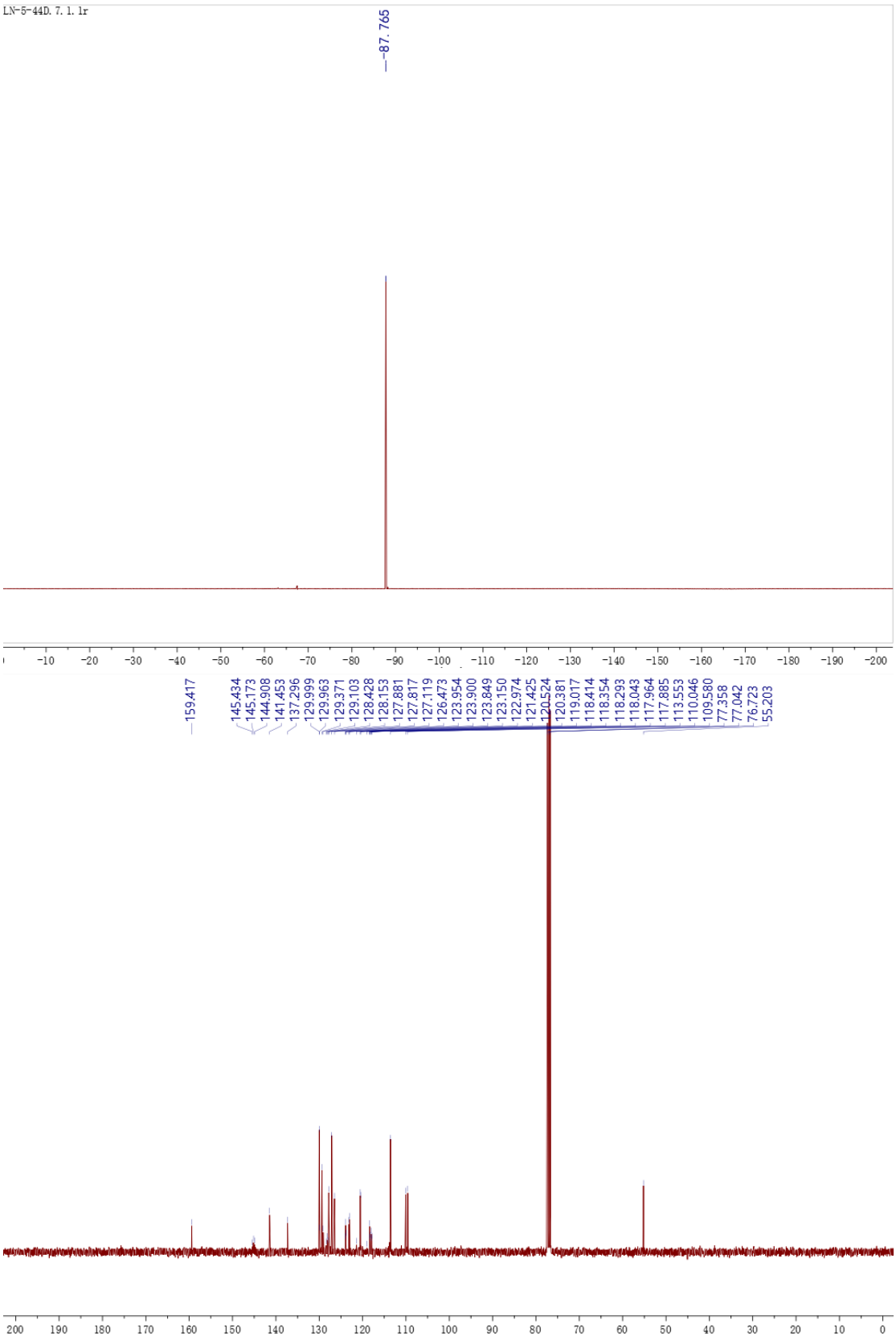
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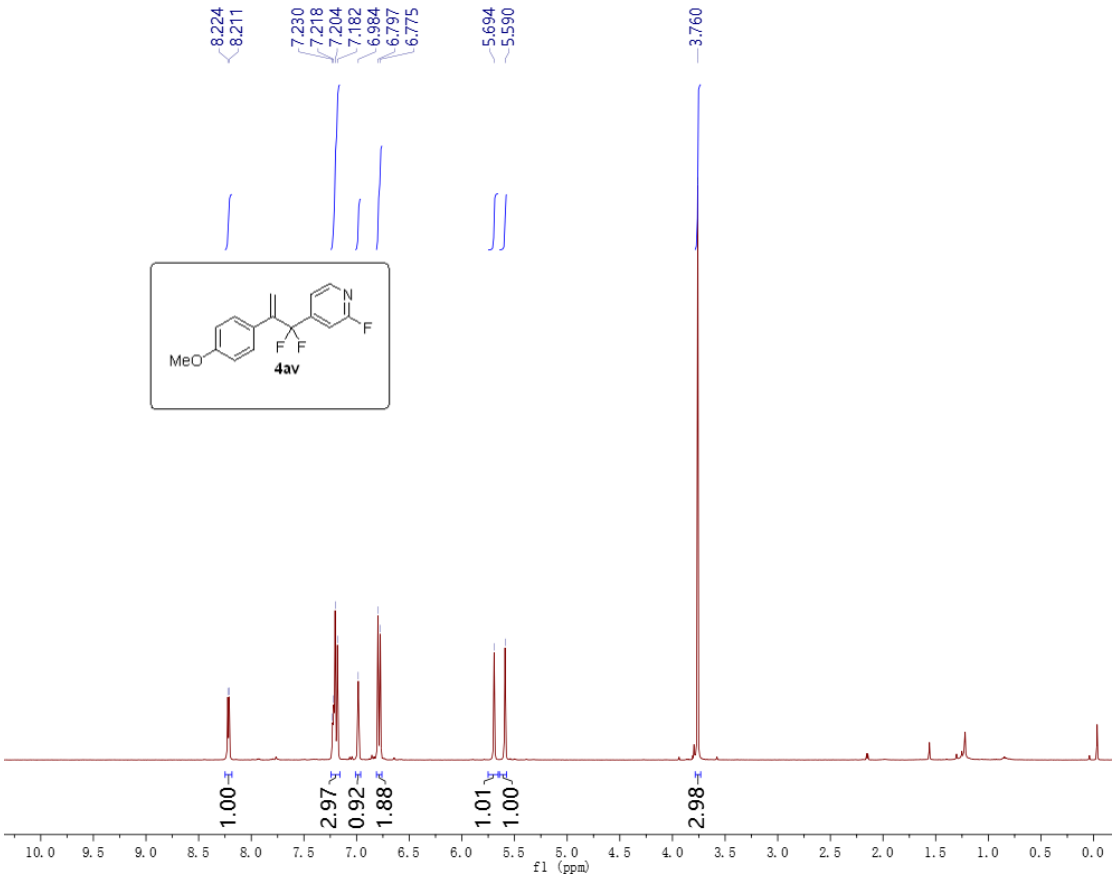
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MeO
F
F F
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2.97
0.92
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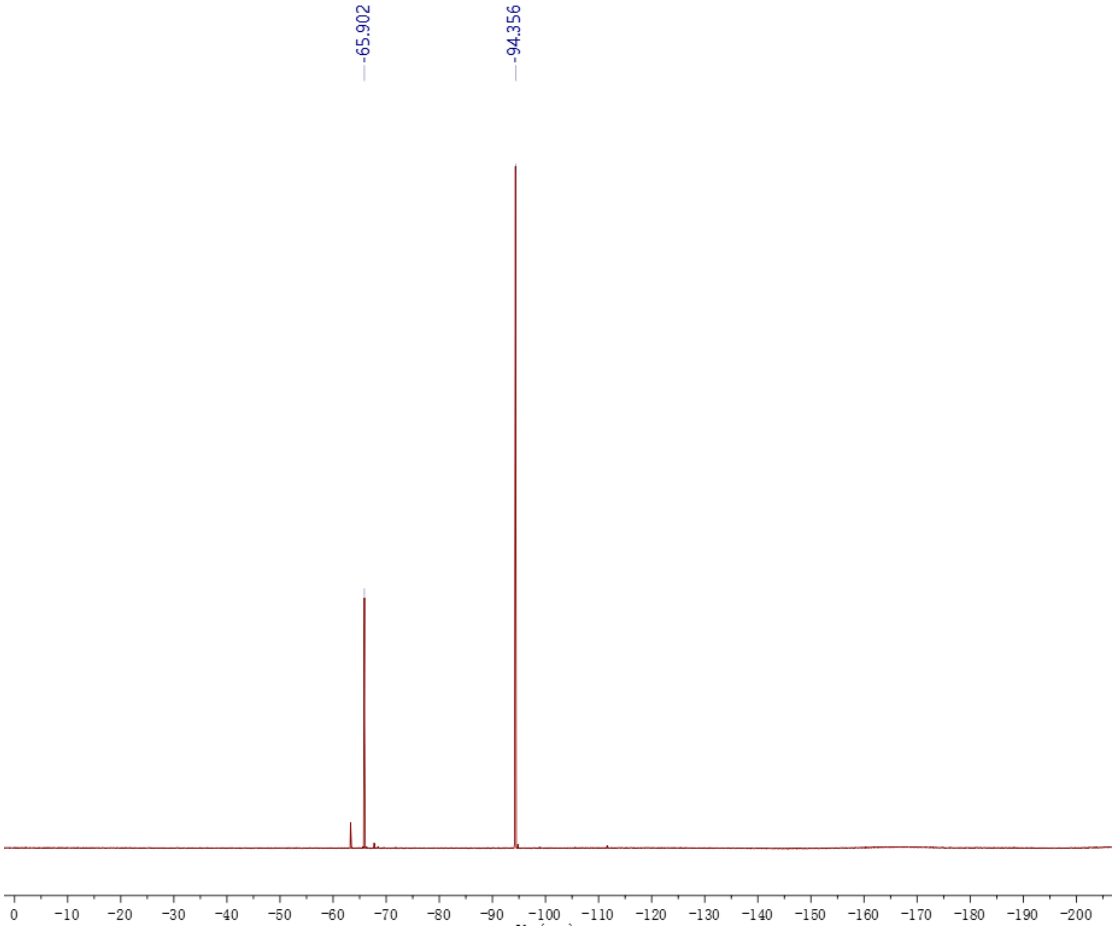
1.01
1.00
2.98
f1 (ppm)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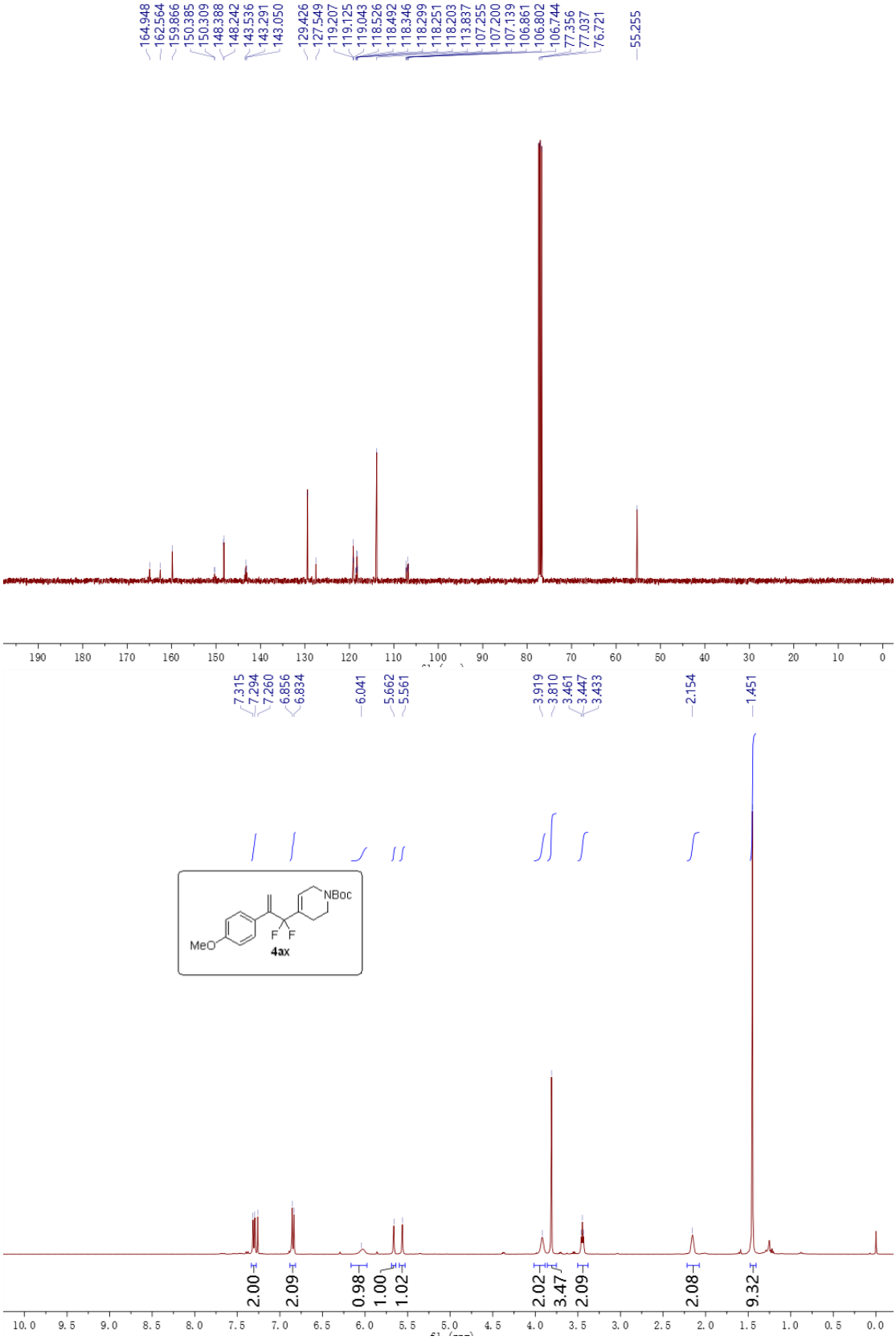
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118.251
118.203
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107.139
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106.744
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77.037
76.721
55.255
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7.294
7.260
6.856
6.834
6.041
5.662
5.561
3.919
3.810
3.461
3.447
3.433
2.154
1.451
NBoc
F F
MeO
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0.98
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1.02
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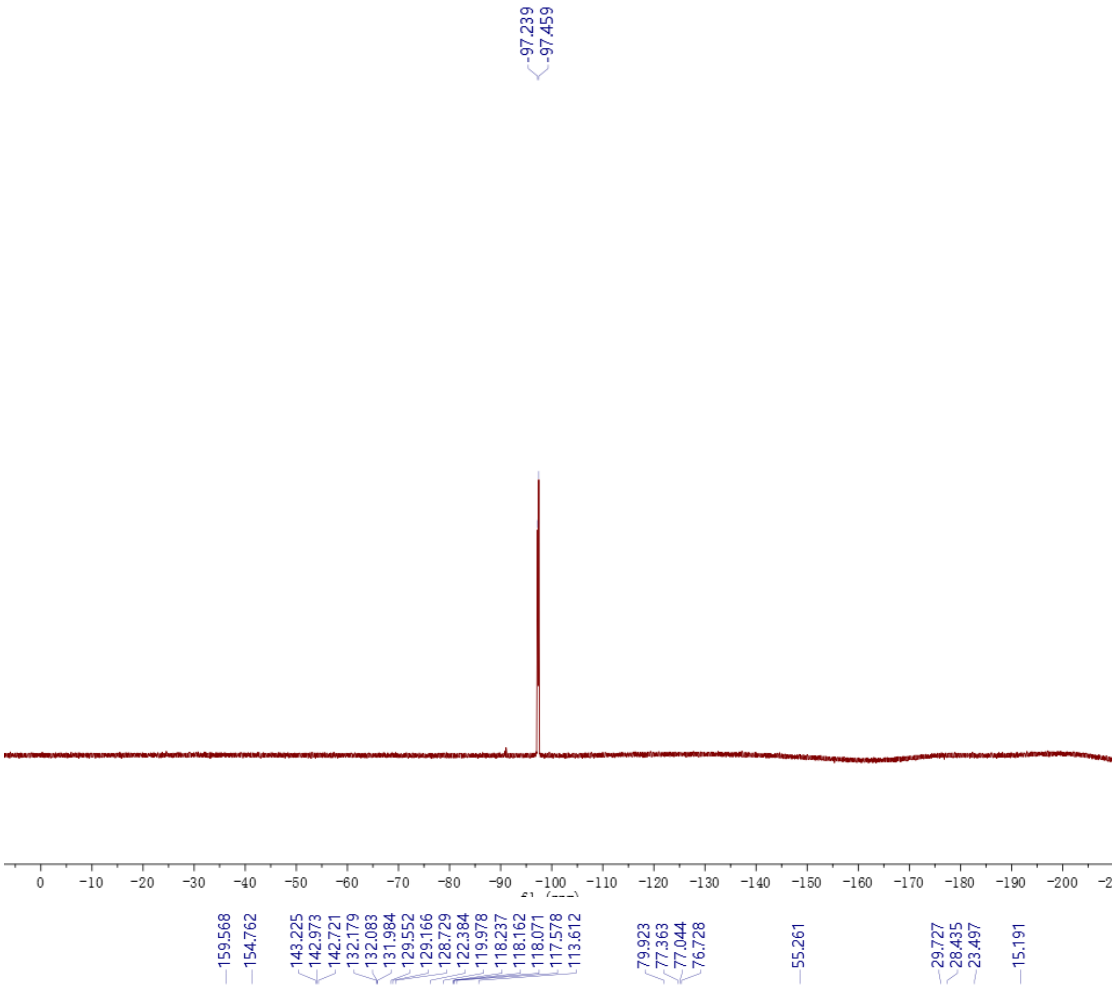
3.47
2.09
2.08
9.32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143.225
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142.721
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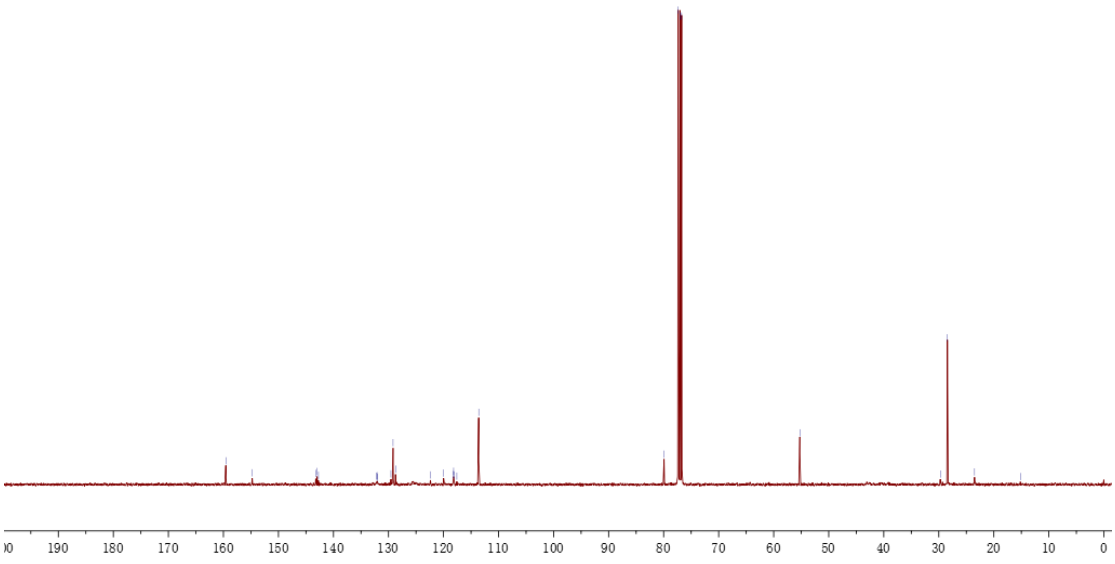
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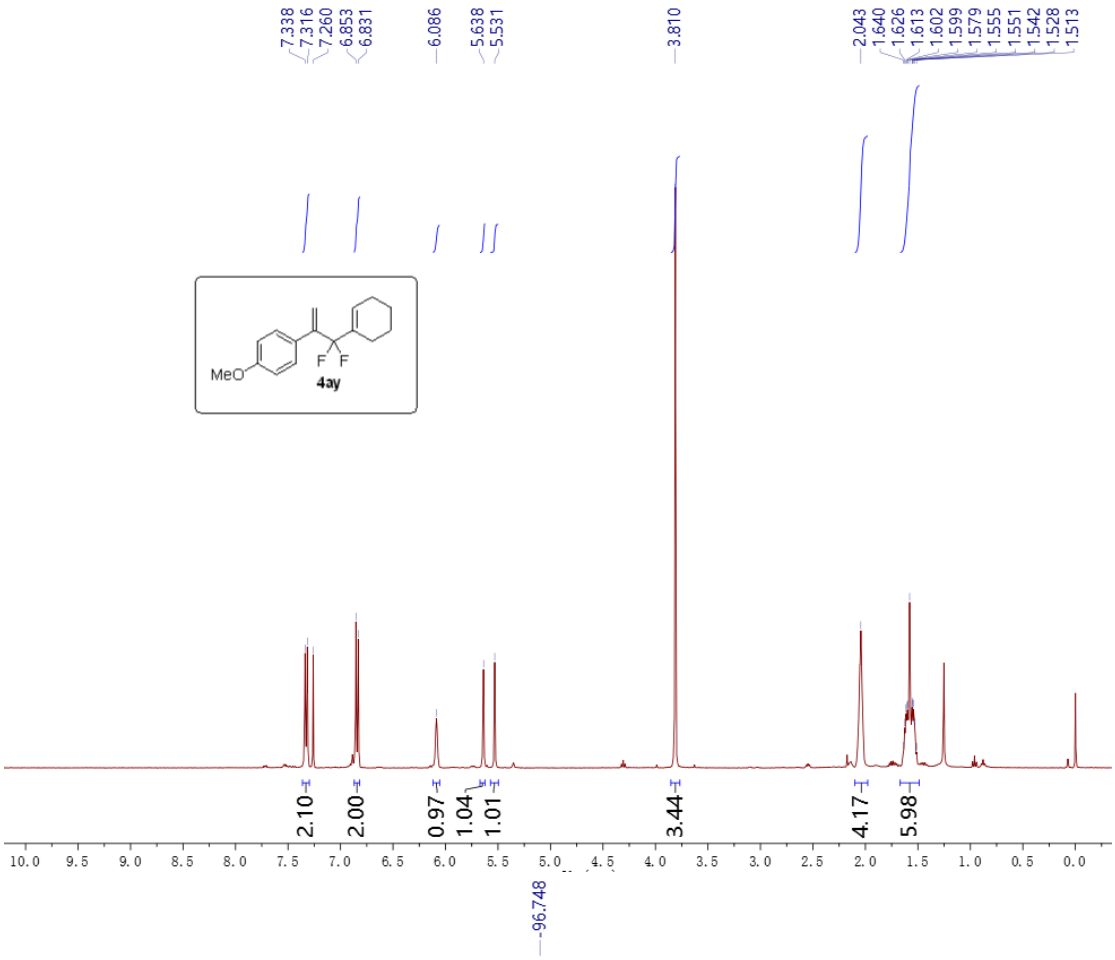
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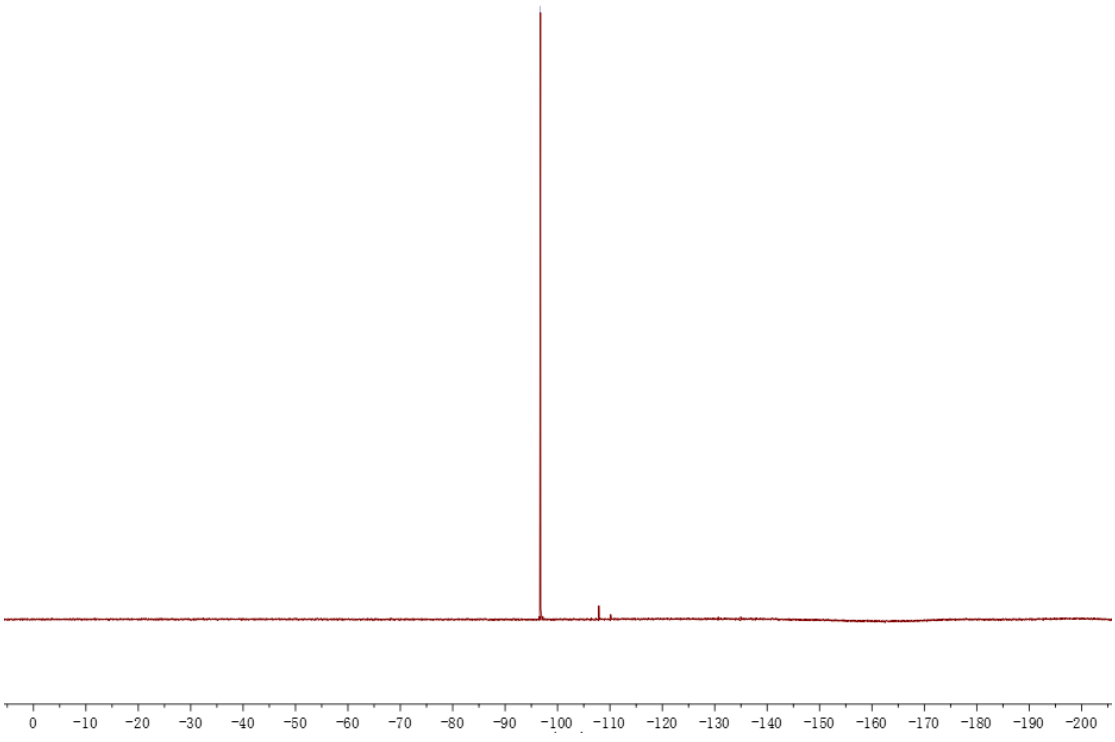
1.602
1.599
1.579
1.555
1.551
1.542
1.528
1.513
MeO
F F
4ay
2.10
2.00
0.97
1.04
1.01
3.44
4.17
5.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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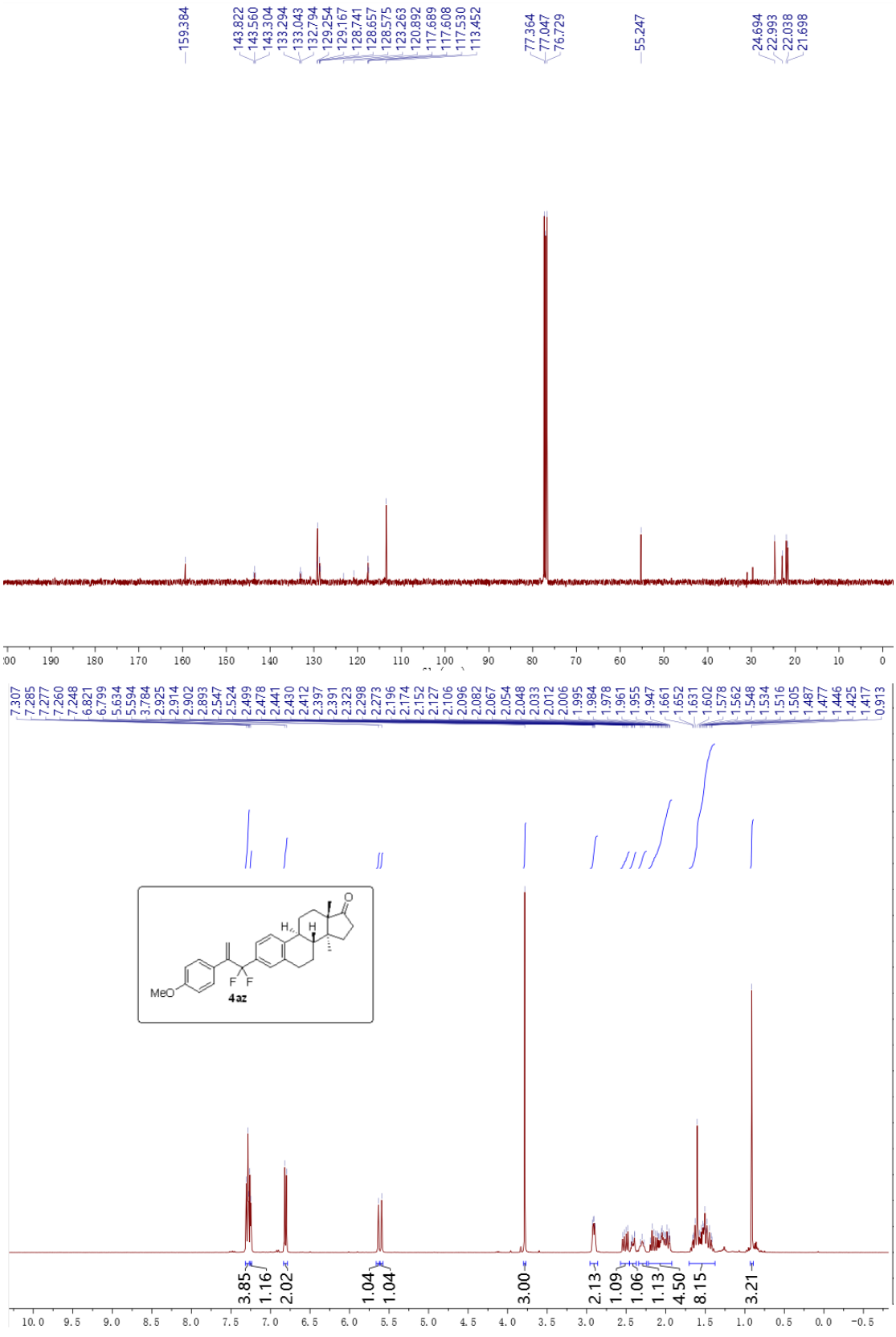
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1.487
1.477
1.446
1.425
1.417
0.913
MeO
F
F
H
H
O
4az
3.85
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1.09
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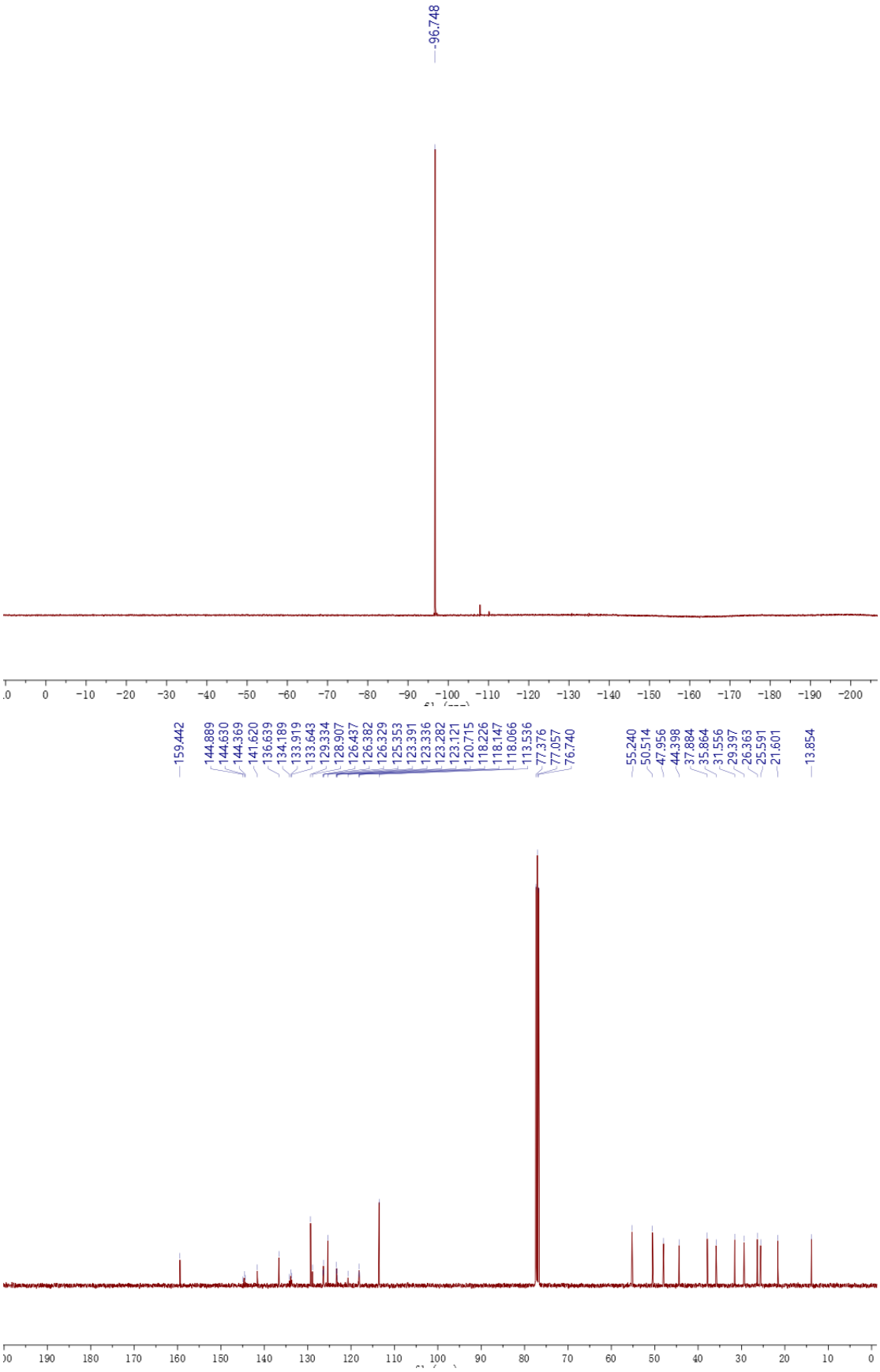
3.21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50.514
47.956
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37.884
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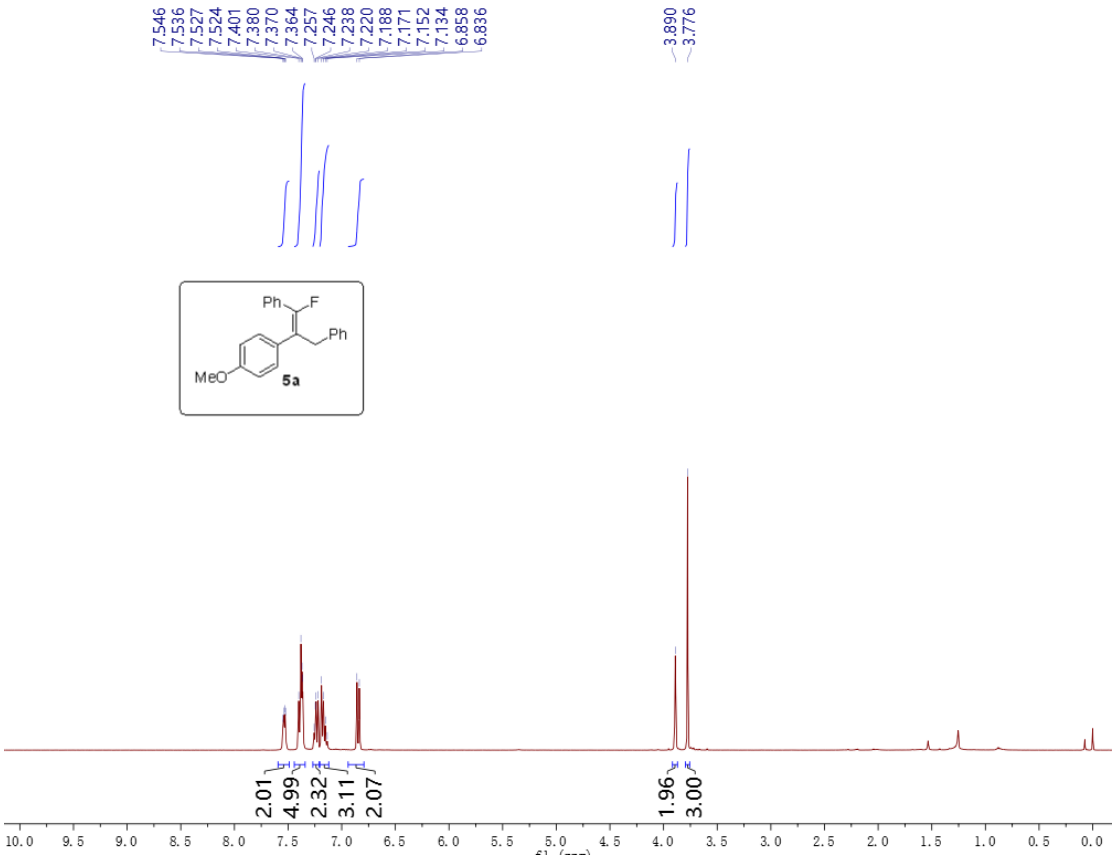
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7.171
7.152
7.134
6.858
6.836
3.890
3.776
Ph
F
Ph
MeO
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4.99
2.32
3.11
2.07
1.96
3.00
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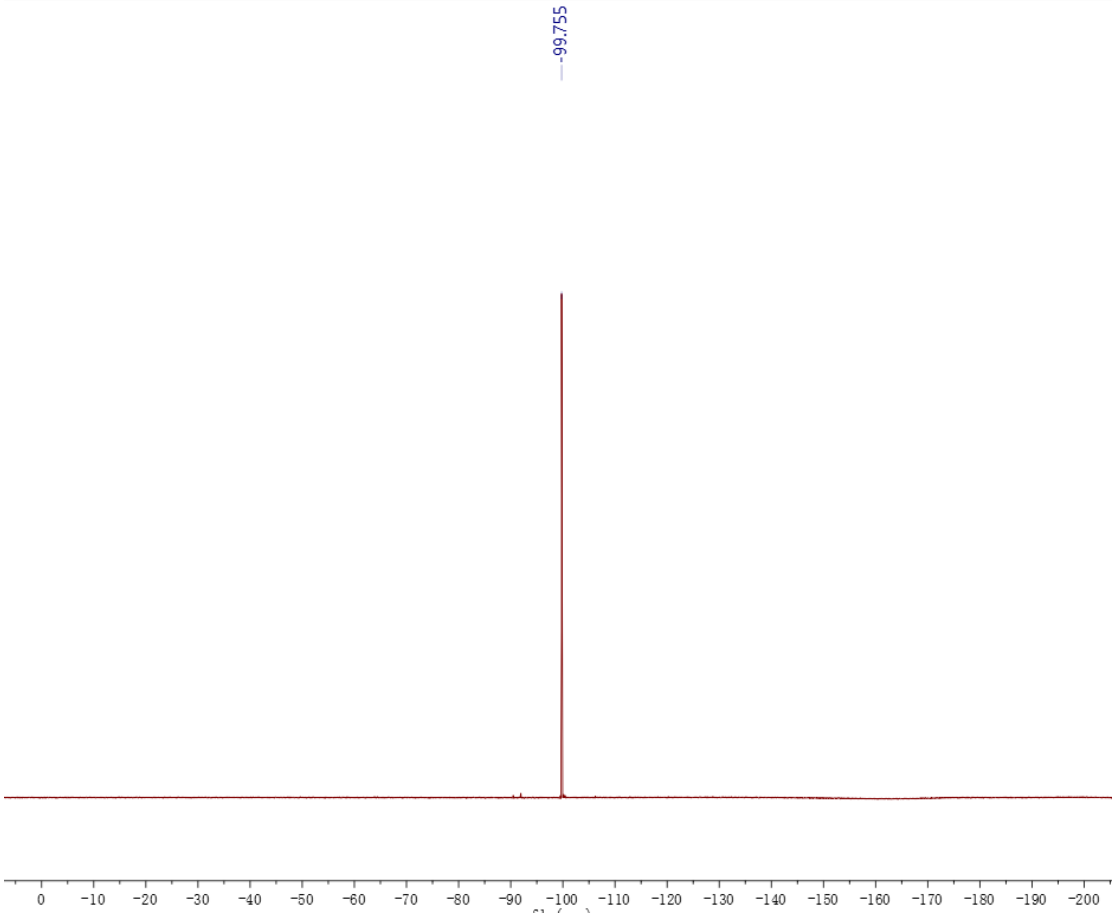
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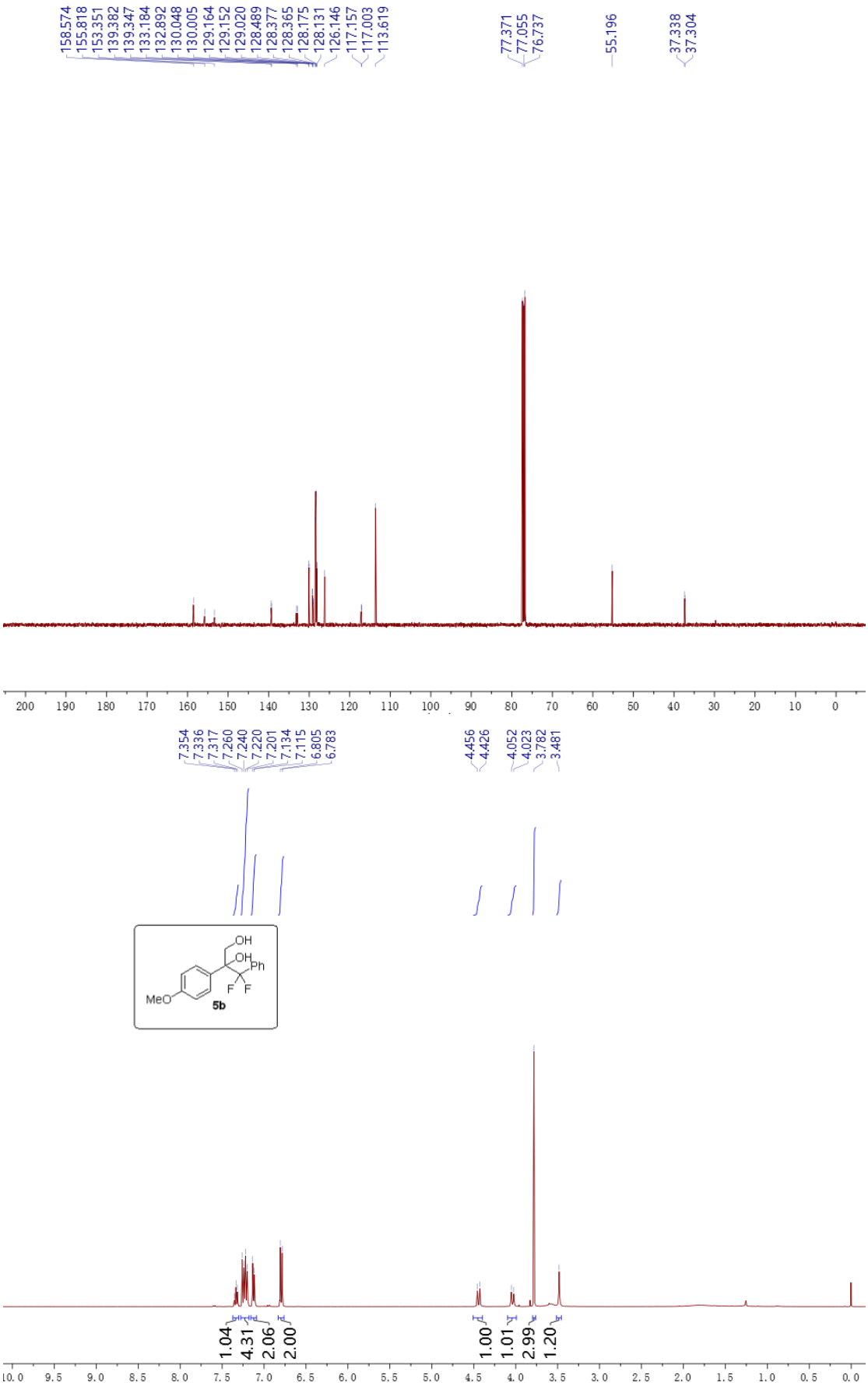
-200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37.304
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MeO
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2.00
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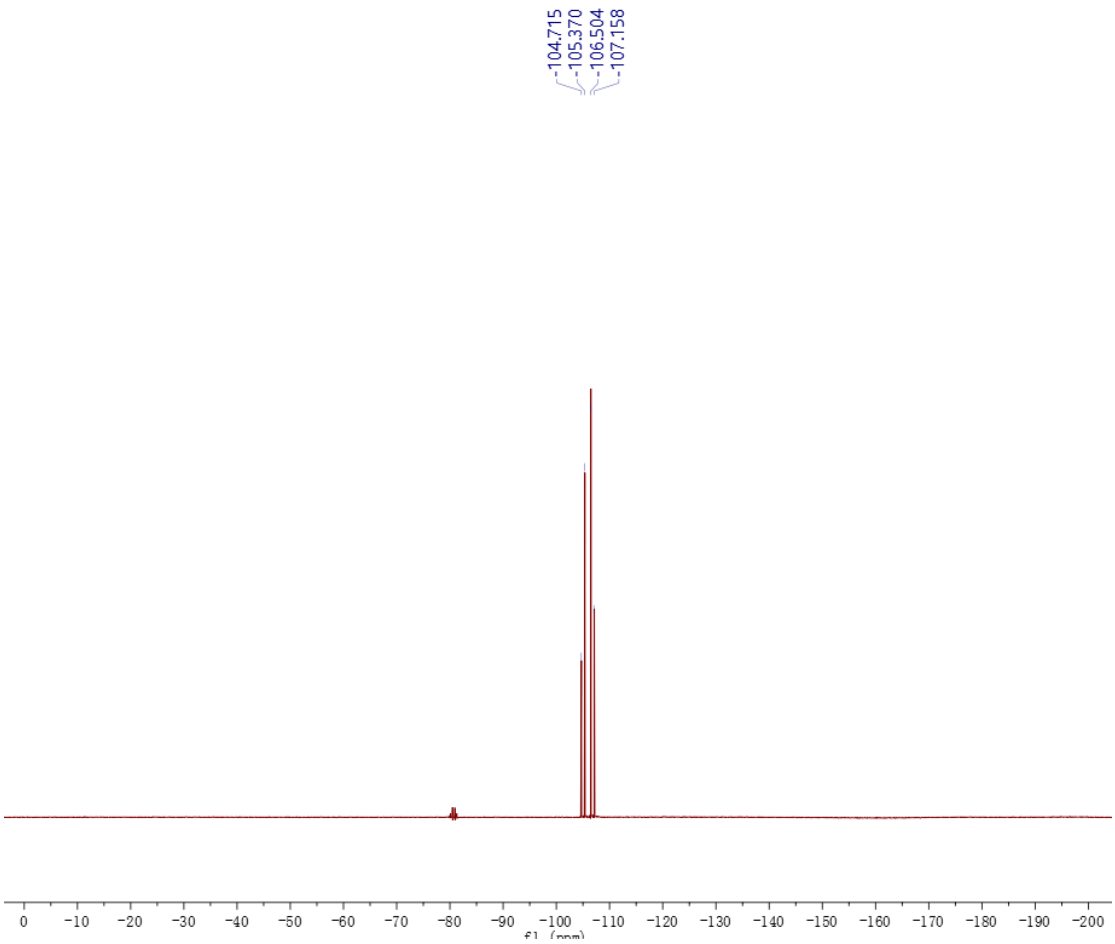
2.99
1.20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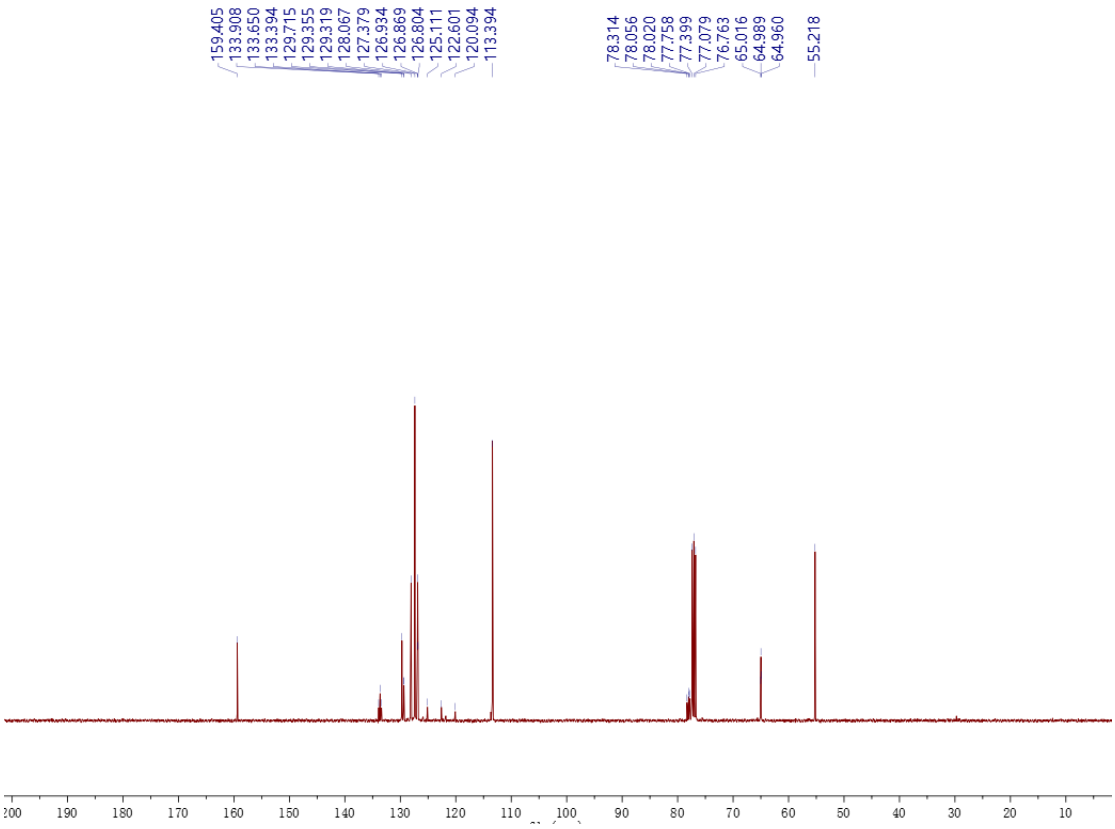
f1 (ppm)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77.399
77.079
76.763
65.016
64.989
64.960
55.218
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

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[1] a) T. Ichitsuka, T. Fujita, T. Arita, J. Ichikawa, *Angew. Chem. Int. Ed*. **2014**, 53, 7564 –7568; b) Y. Liu, Y. Zhou, Y. Zhao, J. Qu, *Org. Lett*. **2017**, 19, 946−949.

[2] T. A. Hamlin, C. B. Kelly, R. M. Cywar, N. E. Leadbeater, *J. Org. Chem*. **2014,** 79, 1145−1155.