

Supporting Information

Organocatalytic enantio- and diastereoselective synthesis of trifluoro-ethylamine allenoate derivatives containing axial and central chiralities

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1. General Information

Reactions were monitored by thin layer chromatography (TLC), and compounds were visualized with a UV light at 254 nm and 365 nm. Column chromatography purifications were carried out using silica gel. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker (400 MHz) spectrometer in CDCl_3 using tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant in Hertz (Hz). Mass peaks are identified by the corresponding m/z values. The infrared data is measured by thermo scientific NICOLET (is50 FT-IR). The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiralpak (IA-3, IC) column. Optical rotations were measured on a digital polarimeter and are reported as follows: $[\alpha]_{\text{D}}^{\text{T}}$ (1 g/100 mL, CHCl_3).

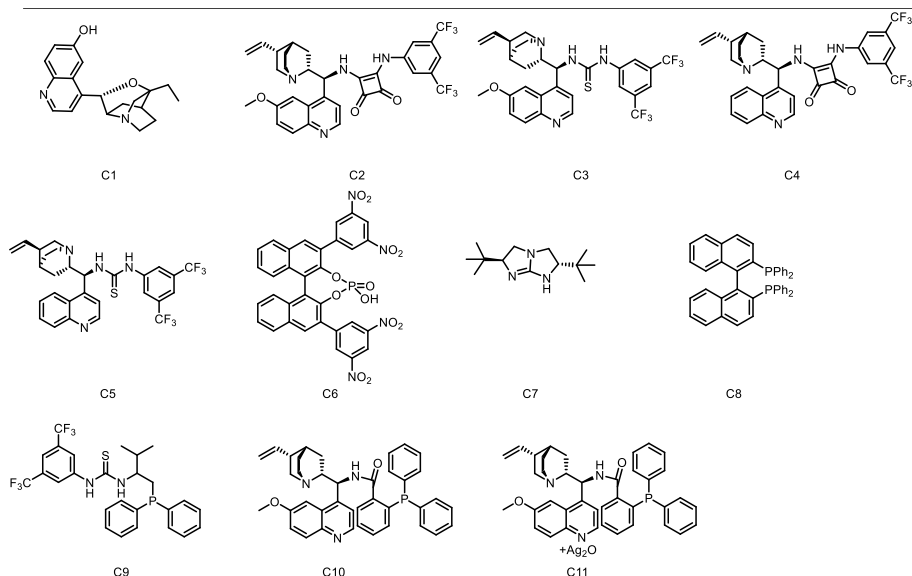
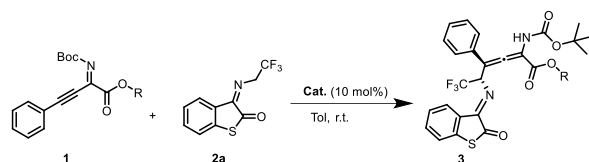
All solvents were obtained from commercial sources and were purified according to standard procedures. The starting materials, 1-alkynyl ketimines, and trifluoromethyl ketimines, were synthesized using the literature method.^[1-2]

2. References

- [1] (a) X. Zhang, X. -X. Song and J. -Q. Ni, *Chem. Commun.*, 2024, **60**, 831-834; (b) J. Yang, Z. Wang, Z. He, G. Li, L. Hong, W. Sun and R. Wang, *Angew. Chem., Int. Ed.* 2020, **59**, 642.
- [2] D. Chen, Y. Deng, S. Sun, P. Jia, J. Huang, W. Yan, *Adv. Synth. Catal.*, 2023, **365**, 178–193.

3. Experimental Section

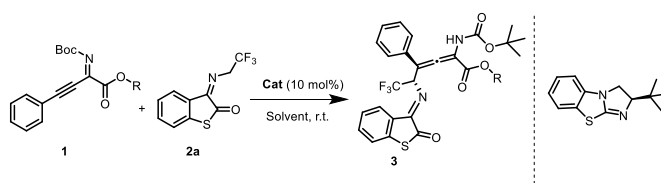
Table S1 Evaluation of different types of catalysts.^a



Entry	solvent	catalyst	time (h)	yield (%) ^b	ee (%) ^c
1	Tol	C1	2.5	40	18
2	Tol	C2	5	50	racemic
3	Tol	C3	3	mixture	--
4	Tol	C4	5	35	16
5	Tol	C5	4	40	8
6	Tol	C6	6	mixture	--
7	Tol	C7	8	60	--
8	Tol	C8	1.5	65	--
9	Tol	C9	1.5	73	--
10	Tol	C10	3	70	racemic
11	Tol	C11	3.5	72	racemic

^a All reactions were performed with catalyst (0.01 mmol, 10 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol) in toluene (1 mL) at rt, and the product *dr* values were determined by chiral phase HPLC or ¹H NMR and ¹⁹F NMR (> 20:1 *dr*, in all cases). ^b Isolated yield. ^c Determined by chiral phase HPLC.

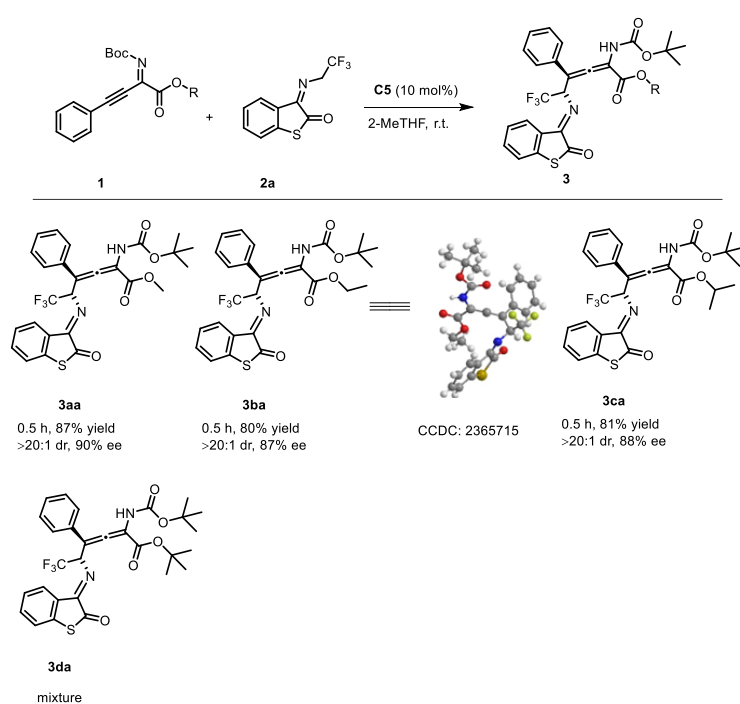
Table S2 Optimization of the Reaction Conditions^a



Entry	solvent	time (min)	yield (%) ^b	ee (%) ^c
1	DCM	60	75	85

2	DCE	60	79	86
3	PhCl	40	75	87
4	TFT	30	86	82
5	THF	30	78	87
6 ^d	2-MeTHF	25	87	90
7 ^e	MTBE	20	75	89
8	EA	28	75	88
9 ^d	2-MeTHF	40n	73	90
10 ^e	2-MeTHF	80	65	88
11 ^f	2-MeTHF	95	62	86

^a Unless otherwise noted, all reactions were performed with catalyst (0.01 mmol, 10 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol) in solvent (1 mL) at rt, and the product *dr* values were determined by chiral phase HPLC or ¹H NMR and ¹⁹F NMR (> 20:1 *dr*, in all cases). ^b Isolated yield. ^c Determined by chiral phase HPLC. ^d Performed at 0 °C. ^e Performed at -10 °C. ^f Performed at -20 °C.



Scheme S1 The limitation of PGs on 1-alkynyl ketimines.

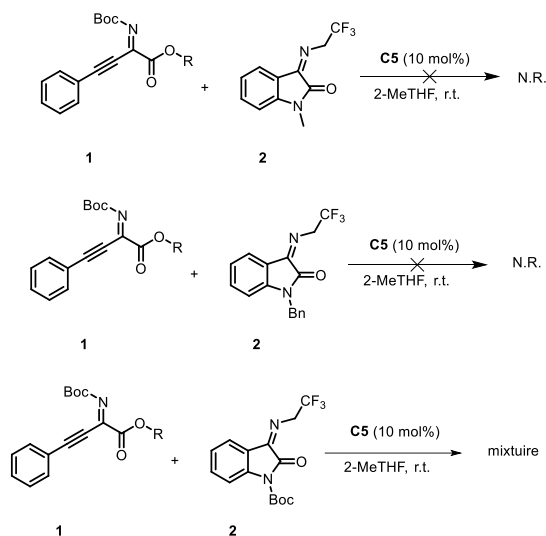
Reaction conditions: **1** (0.10 mmol), **2a** (0.12 mmol), and catalyst **C5** (10 mol%) in 2-MeTHF (1 ml) at room temperature, the reaction time required for each substrate is given. The yields of the isolated products are reported. The ee and *dr* values were determined by HPLC or ¹H NMR and ¹⁹F NMR. ^a Furnished at room temperature.

Table S3 Optimization of the reaction conditions of trifluoromethyl-ketimine derived from *N*-Ac isatin^a

Entry	solvent	catalyst	time (min)	yield (%) ^b	ee (%) ^c
1	Tol	C1	50	75	83
2	Tol	C2	80	72	80

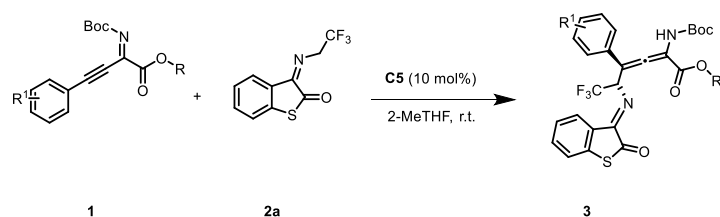
3	Tol	C3	50	65	63
4	Tol	C4	30	70	82
5	Tol	C5	30	80	86
6	Tol	C6	30	50	83
7	Tol	C7	40	79	80
8	Tol	C8	50	80	81
9	DCM	C5	60	75	85
10	DCE	C5	60	79	86
11	PhCl	C5	40	75	87
12	TFT	C5	30	86	82
13	THF	C5	30	78	87
14 ^d	2-MeTHF	C5	60	82	88
15 ^e	MTBE	C5	20	60	85
16	EA	C5	28	70	83
17 ^d	2-MeTHF	C5	40	75	86
18 ^e	2-MeTHF	C5	80	66	85
19 ^f	2-MeTHF	C5	95	60	86

^a Unless otherwise noted, all reactions were performed with catalyst (0.01 mmol, 10 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol) in solvent (1 mL) at rt, and the product *dr* values were determined by chiral phase HPLC or ¹H NMR and ¹⁹F NMR (> 20:1 *dr*, in all cases). ^b Isolated yield. ^c Determined by chiral phase HPLC. ^d Performed at 0 °C. ^e Performed at -10 °C. ^f Performed at -20 °C.



Scheme S2 The failed reaction of trifluoromethyl-ketimines with isatin 1-alkynyl ketimines.

4. General Procedure for the Synthesis of Compounds 3aa–3pa

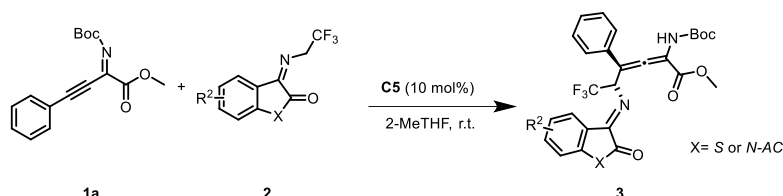


1-Alkynyl ketimines **1** (0.1 mmol) was added to a solution of catalyst **C5** (0.01 mmol,

10 mol%) and trifluoromethyl ketimine **2a** (0.12 mmol) in anhydrous 2-MeTHF (1.0 mL) at r.t, after completion (monitored by TLC), the reaction mixture was directly purified by flash column chromatography on silica gel (EA:PE = 1:50(v/v)) to obtain the title compounds **3aa-3pa**.

Racemates were prepared following the general procedure with 10 mol% 2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole.

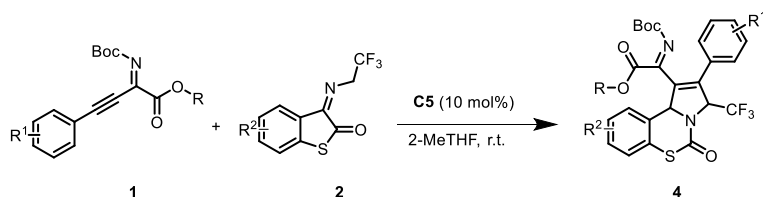
5. General Procedure for the Synthesis of Compounds **3ab-3ap**



1-Alkynyl ketimines **1a** (0.1 mmol) was added to a solution of catalyst **C5** (0.01 mmol, 10 mol%) and trifluoromethyl ketimine **2** (0.12 mmol) in anhydrous 2-MeTHF (1.0 mL) at r.t, after completion (monitored by TLC), the reaction mixture was directly purified by flash column chromatography on silica gel (EA:PE = 1:50(v/v)) to obtain the title compounds **3ab-3ap**.

Racemates were prepared following the general procedure with 10 mol% 2,3-dihydrobenzo[*d*]imidazo[2,1-*b*]thiazole.

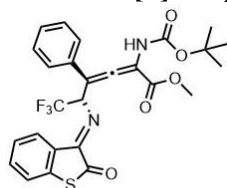
6. General Procedure for the Synthesis of Compounds **4**



1-Alkynyl ketimines **1** (0.1 mmol) was added to a solution of catalyst **C5** (0.01 mmol, 10 mol%) and trifluoromethyl ketimine **2** (0.12 mmol) in anhydrous 2-MeTHF (1.0 mL) at r.t, after completion (monitored by TLC), the reaction mixture was directly purified by flash column chromatography on silica gel (EA:PE = 1:20(v/v)) to obtain the title compounds **4aa-4ea**, **4ka**, **4ma**, **4oa**, **4ab**.

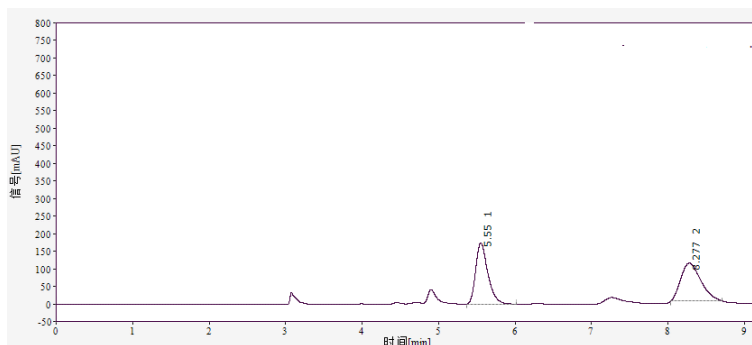
7. Analytical Data and HPLC Chromatogram of the Products

Methy (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-phenylhexa-2,3-dienoate

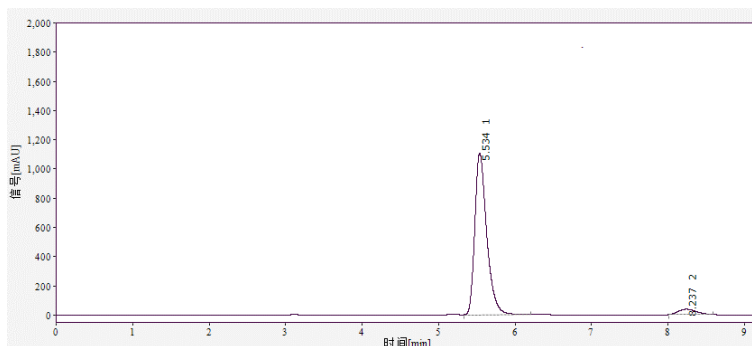


3aa

From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 46.3 mg (87% yield) of compound **3aa** was obtained as a yellow solid, $[\alpha]_D^{25} = -100$ ($c = 1.0$, CHCl_3), Mp. = 124 - 125 °C. Dr (> 20:1) was determined by HPLC analysis. 90% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.5$ min, $t_{\text{minor}} = 8.2$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 6.5$ Hz, 1H), 7.72 (d, $J = 7.7$ Hz, 2H), 7.50 (t, $J = 6.9$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.37 – 7.27 (m, 3H), 6.48 (q, $J = 6.5$ Hz, 1H), 6.11 (s, 1H), 3.35 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 185.5, 164.2, 156.5, 151.4, 137.1, 134.2, 133.7, 129.0, 128.6, 128.5, 127.6, 127.3, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.8$ Hz), 123.8, 113.5, 105.8, 81.2, 61.5 (q, $J_{\text{C-F}} = 32.4$ Hz), 53.0, 28.1. ^{19}F NMR (376 MHz, CDCl_3) δ -73.36. IR (cm^{-1}) ν 3345.6, 3059.7-2930.6, 1955.8, 1725.3-1694.9, 1506.6, 1297.1-1129.5, 931.8, 768.9. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 555.1172, found 555.1166.

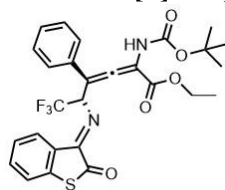


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1	5.550	1930.115	49.4	BB
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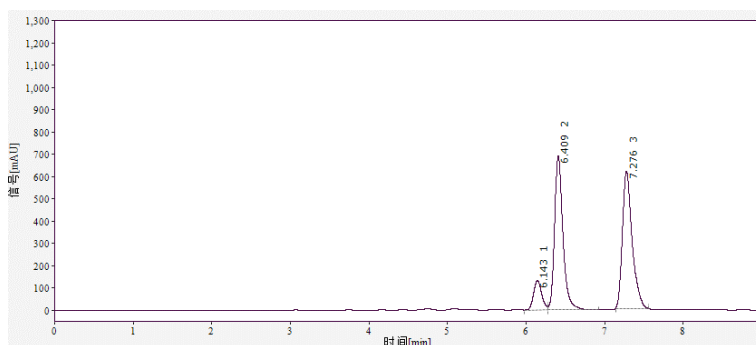
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1	5.534	11971.412	95.2	BB
2	8.237	599.803	4.8	BB

Ethyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-phenylhexa-2,3-dienoate

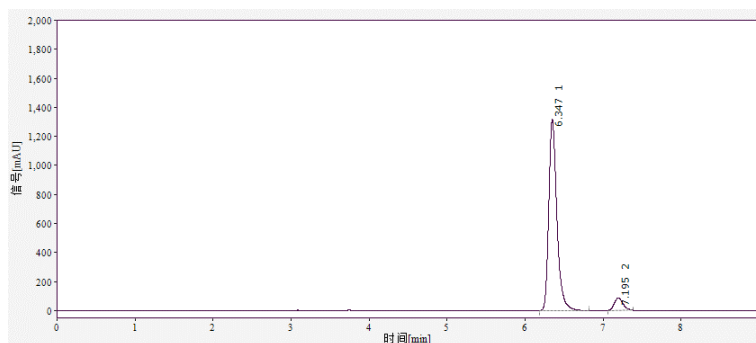


3ba

From 30.1 mg (0.1 mmol, 1.0 equiv) of **1b** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 43.7 mg (80% yield) of compound **3ba** was obtained as a yellow solid, $[\alpha]_D^{25} = -81$ ($c = 1.0$, CHCl_3), Mp. = 117 - 118 °C. Dr (> 20:1) was determined by HPLC analysis. 87% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.3$ min, $t_{\text{minor}} = 7.2$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.0$ Hz, 1H), 7.69 (d, $J = 7.7$ Hz, 2H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.31 (q, $J = 9.0$ Hz, 3H), 6.55 (q, $J = 6.6$ Hz, 1H), 6.13 (s, 1H), 4.10 – 3.91 (m, 1H), 3.85 – 3.71 (m, 1H), 1.43 (s, 9H), 0.93 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.4, 185.7, 163.8, 156.5, 151.4, 137.2, 134.2, 133.8, 129.1, 128.5, 128.3, 127.7, 127.2, 124.5 (q, $J_{\text{C-F}} = 282.8$ Hz), 123.8, 113.1, 105.9, 81.1, 62.4, 61.7 (q, $J_{\text{C-F}} = 32.8$ Hz), 28.1, 13.8. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.08. IR (cm^{-1}) ν 3432.5, 3064.6-2873.0, 1958.0, 1732.5-1709.1, 1491.0-1455.0, 1287.8-1130.9, 933.0, 777.4. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1331.

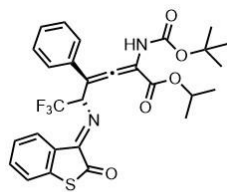


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3	7.276	5304.820	46.5	BB



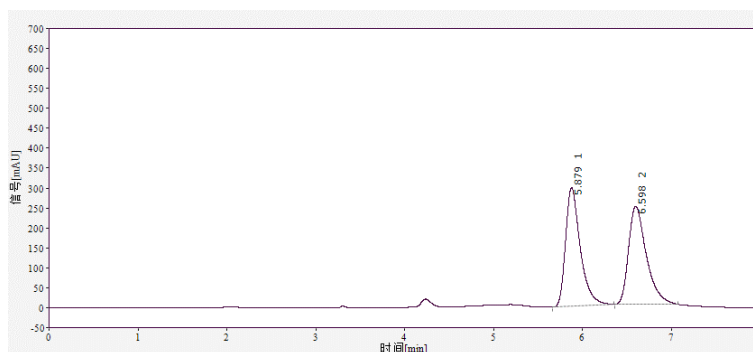
No	Retention Time	Area	% Area	Int Type
1	6.347	19517.738	93.5	BB
2	7.190	657.309	6.5	BB

Isopropyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-phenylhexa-2,3-dienoate

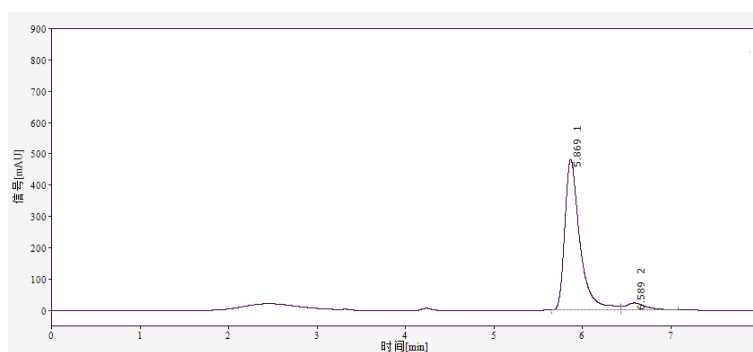


3ca

From 31.5 mg (0.1 mmol, 1.0 equiv) of **1c** and 45.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 45.4 mg (81% yield) of compound **3ca** was obtained as a yellow solid, $[\alpha]_D^{25} = -121$ ($c = 1.0$, CHCl_3), Mp. = 62 - 63 °C. Dr (> 20:1) was determined by HPLC analysis. 88% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 98:2, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.9$ min, $t_{\text{minor}} = 6.6$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 2H), 7.40 (td, $J = 7.6, 1.4$ Hz, 1H), 7.25 - 7.17 (m, 2H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.40 (q, $J = 6.4$ Hz, 1H), 6.03 (s, 1H), 3.24 (s, 3H), 2.58 (q, $J = 7.6$ Hz, 2H), 1.36 (s, 9H), 1.16 (t, $J = 7.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.9, 185.5, 164.2, 156.5, 151.4, 144.8, 137.1, 134.2, 130.9, 129.0, 128.1, 127.5, 127.3, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.4$ Hz), 123.8, 113.5, 105.7, 81.2, 61.4 (q, $J_{\text{C-F}} = 29.3$ Hz), 52.9, 28.6, 28.1, 15.4. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.36. IR (cm^{-1}) ν 3424.1, 3064.0-2933.1, 1948.6, 1708.6, 1492.3, 1264.2-1131.4, 933.5. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 583.1485, found 583.1483.

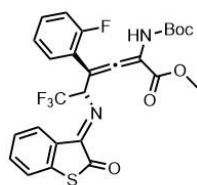


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1	5.879	3425.107	49.9	BB
2	6.598	3439.217	50.1	BB



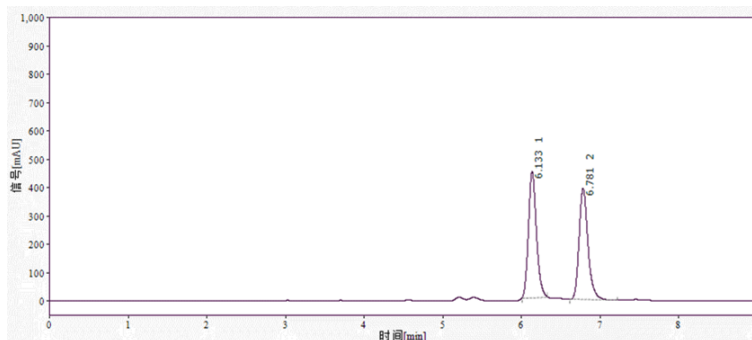
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1	5.869	5706.137	94.2	BB
2	6.589	349.135	5.8	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-(2-fluorophenyl)-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate

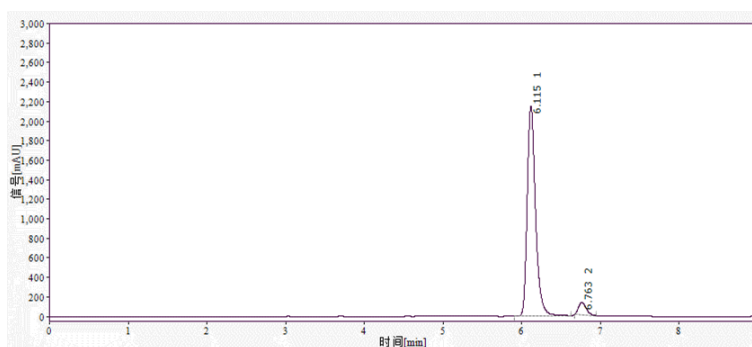


3ea

From 30.5 mg (0.1 mmol, 1.0 equiv) of **1e** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 46.8 mg (85% yield) of compound **3ea** was obtained as a yellow solid, $[\alpha]_D^{25} = -134$ ($c = 1.0$, CHCl_3), Mp. = 86 - 87 °C. Dr ($> 20:1$) was determined by HPLC analysis. 90% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.1$ min, $t_{\text{minor}} = 6.8$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.76 (m, 1H), 7.67 (t, $J = 7.8$ Hz, 1H), 7.50 (td, $J = 7.7, 1.5$ Hz, 1H), 7.29 (dd, $J = 7.8, 4.1$ Hz, 3H), 7.19 – 7.05 (m, 2H), 6.66 (q, $J = 6.7$ Hz, 1H), 6.08 (s, 1H), 3.45 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 206.6, 185.3, 164.3, 161.5, 159.0, 156.8, 151.3, 137.2, 134.2, 130.7, 130.2, 130.1, 129.1, 127.2, 125.8, 124.5 (q, $J_{\text{C-F}} = 282.7$ Hz), 124.2, 123.8, 121.7, 121.6, 116.3, 116.1, 108.3, 105.2, 81.2, 61.7 (q, $J_{\text{C-F}} = 31.3$ Hz), 53.0, 29.7, 28.1. ^{19}F NMR (376 MHz, CDCl_3) δ -73.13, -111.59. IR (cm^{-1}) ν 33711.9, 3067.0-2932.9, 1747.8-1724.7, 1272.3-1135.6, 762.5. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{F}_4\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 573.1078, found 572.1070.

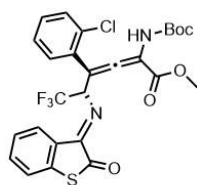


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1	6.133	3129.399	50.3	BB
2	6.781	3091.611	49.7	BB



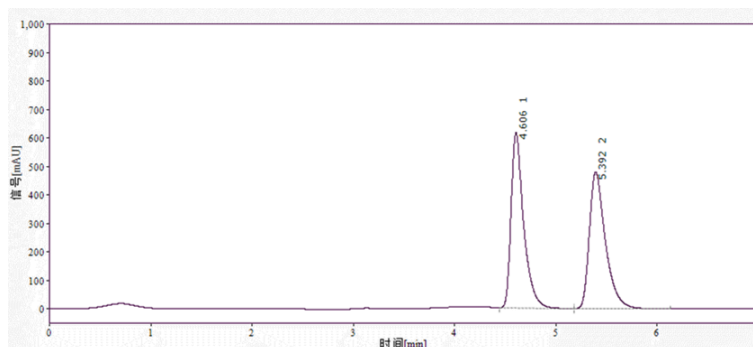
No	Retention Time	Area	% Area	Int Type
1	6.115	15804.089	94.9	BB
2	6.763	845.778	5.1	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-4-(2-chlorophenyl)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(*2H*)-ylidene)amino)hexa-2,3-dienoate

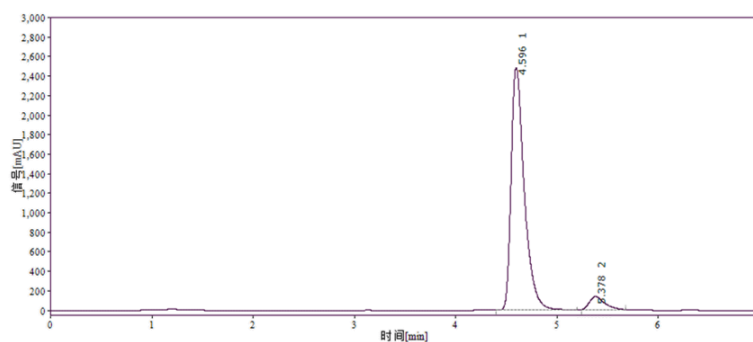


3fa

From 32.1 mg (0.1 mmol, 1.0 equiv) of **1f** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 44.7 mg (79% yield) of compound **3fa** was obtained as a yellow solid, $[\alpha]_D^{25} = -99$ ($c = 1.0$, CHCl_3), Mp. = 73 - 74 °C. Dr (> 20:1) was determined by HPLC analysis. 88% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 4.6$ min, $t_{\text{minor}} = 5.4$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.1$ Hz, 1H), 7.69 (s, 1H), 7.50 (t, $J = 6.9$ Hz, 1H), 7.41 – 7.35 (m, 1H), 7.35 – 7.22 (m, 5H), 6.78 (q, $J = 6.7$ Hz, 1H), 6.07 (s, 1H), 3.59 (s, 3H), 1.45 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.4, 185.8, 164.6, 156.9, 151.1, 137.1, 134.2, 133.3, 133.1, 131.6, 129.9, 129.5, 129.3, 127.1, 126.8, 125.8, 124.1 (q, $J_{\text{C-F}} = 282.5$ Hz), 123.8, 109.4, 105.0, 80.8, 62.4 (q, $J_{\text{C-F}} = 29.8$ Hz), 52.9, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -71.92. IR (cm^{-1}) ν 3366.5, 3067.3-2873.0, 1721.5, 1491.1-1436.6, 1254.6-1136.9, 759.3. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{ClF}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 589.0782, found 589.0782.

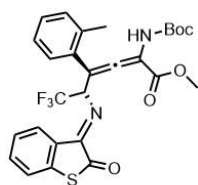


No	Retention Time	Area	% Area	Int Type
1	4.606	5292.374	50.0	BB
2	5.302	5288.669	50.0	BB



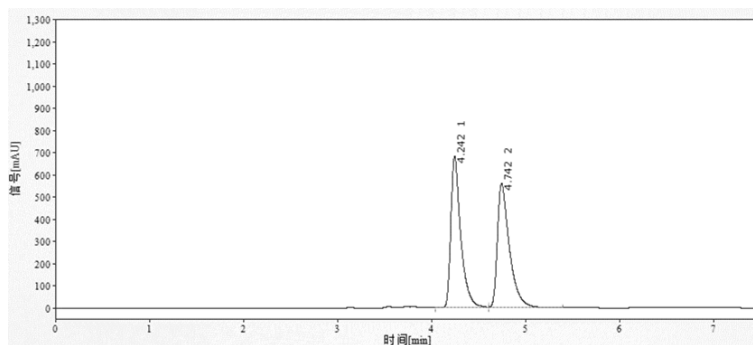
No	Retention Time	Area	% Area	Int Type
1	4.596	22474.674	94.2	BB
2	5.378	1384.494	5.8	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-(*o*-tolyl)hexa-2,3-dienoate

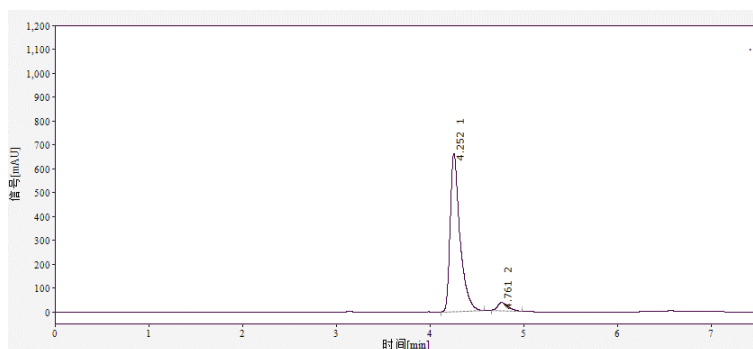


3ga

From 30.1 mg (0.1 mmol, 1.0 equiv) of **1g** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 47.5 mg (87% yield) of compound **3ga** was obtained as a yellow solid, $[\alpha]_D^{25} = -57$ ($c = 1.0$, CHCl_3), Mp. = 56 - 57 °C. Dr ($> 20:1$) was determined by HPLC analysis. 90% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 4.3$ min, $t_{\text{minor}} = 4.8$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.0$ Hz, 1H), 7.50 – 7.37 (m, 2H), 7.32 – 7.14 (m, 2H), 7.16 – 7.05 (m, 3H), 6.58 (q, $J = 6.8$ Hz, 1H), 5.94 (s, 1H), 3.55 (s, 3H), 2.32 (s, 3H), 1.35 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 203.5, 186.0, 164.8, 156.8, 151.0, 137.2, 137.0, 134.2, 133.2, 130.5, 129.4, 129.2, 128.4, 128.3, 127.2, 125.9, 125.6, 125.6, 123.8, 122.8, 120.0, 110.8, 103.9, 80.7, 63.8, 63.5, 63.2, 62.9, 52.9, 28.1, 20.0. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -71.61. IR (cm^{-1}) ν 3363.9, 3065.8-2872.3, 1719.8, 1258.6-1134.1, 928.4, 760.5-728. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1327.

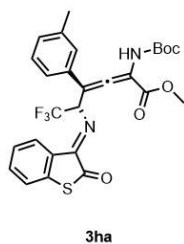


No	Retention Time	Area	% Area	Int Type
1	4.242	5019.486	50.1	BB
2	4.742	4992.605	49.9	BB

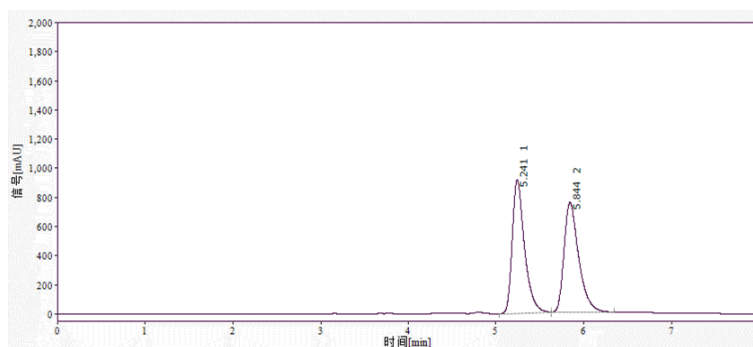


No	Retention Time	Area	% Area	Int Type
1	4.252	4798.851	95.0	BB
2	4.761	250.859	5.0	BB

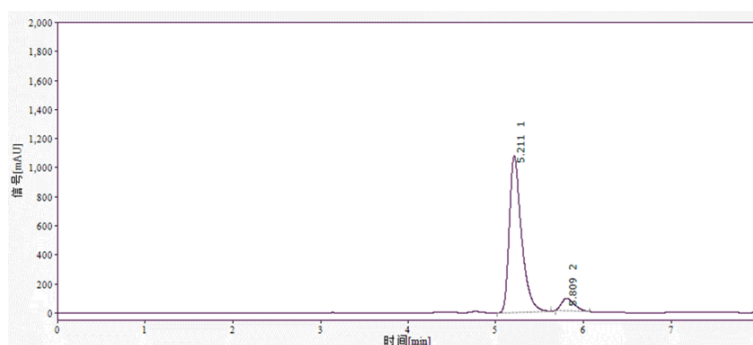
Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-(*m*-tolyl)hexa-2,3-dienoate



From 30.1 mg (0.1 mmol, 1.0 equiv) of **1h** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 48.0 mg (88% yield) of compound **3ha** was obtained as a yellow solid, $[\alpha]_D^{25} = -109$ ($c = 1.0$, CHCl_3), Mp. = 85 - 86 °C. Dr (> 20:1) was determined by HPLC analysis. 84% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.2$ min, $t_{\text{minor}} = 5.8$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.5$ Hz, 1H), 7.49 – 7.34 (m, 3H), 7.22 (td, $J = 7.3, 2.7$ Hz, 3H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.40 (q, $J = 6.4$ Hz, 1H), 6.04 (s, 1H), 3.26 (s, 3H), 2.30 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.1, 185.5, 164.3, 156.5, 151.5, 138.1, 137.1, 134.2, 133.6, 129.4, 129.0, 128.4, 128.3, 127.3, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.2$ Hz), 123.8, 113.6, 105.8, 81.2, 61.5 (q, $J_{\text{C-F}} = 28.0$ Hz), 53.0, 29.7, 28.1, 21.6. ^{19}F NMR (376 MHz, CDCl_3) δ -73.30. IR (cm^{-1}) ν 3339.9, 3065.2-2870.9, 1955.1, 1727.5-1714.2, 1631.9-1435.4, 1293.3-1130.0, 930.6, 769.9. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1333.

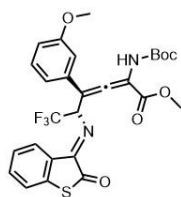


No	Retention Time	Area	% Area	Int Type
1	5.241	8865.704	50.4	BB
2	5.844	8725.868	49.6	BB



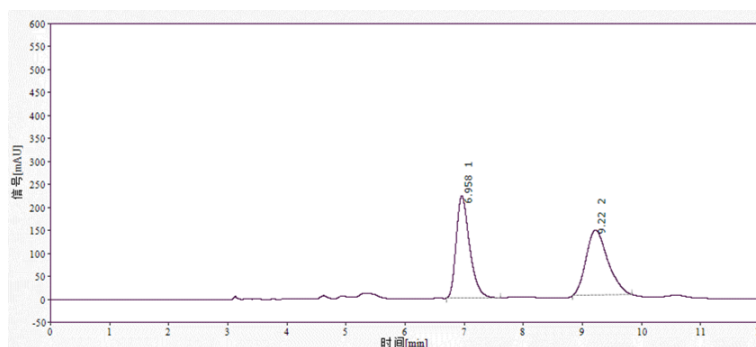
No	Retention Time	Area	% Area	Int Type
1	5.211	10351.396	92.1	BB
2	5.809	882.552	7.9	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-(3-methoxyphenyl)-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(*2H*)-ylidene)amino)hexa-2,3-dienoate

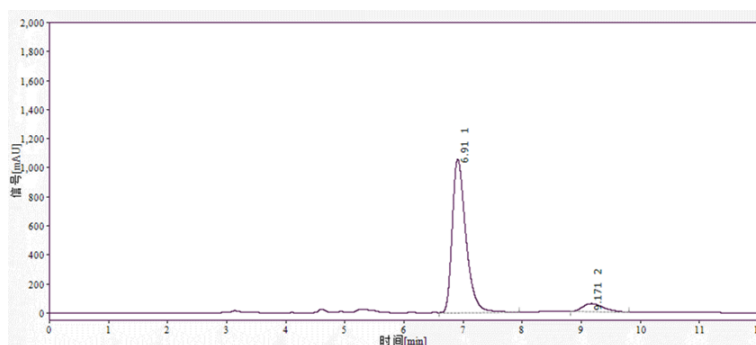


3ia

From 31.7 mg (0.1 mmol, 1.0 equiv) of **1i** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 46.1 mg (82% yield) of compound **3ia** was obtained as a yellow solid, $[\alpha]_D^{25} = -110$ ($c = 1.0$, CHCl_3), Mp. = 129 - 130 °C. Dr (> 20:1) was determined by HPLC analysis. 85% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.9$ min, $t_{\text{minor}} = 9.2$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.49 – 7.37 (m, 1H), 7.31 – 7.18 (m, 5H), 6.90 – 6.77 (m, 1H), 6.38 (q, $J = 6.5$ Hz, 1H), 6.03 (s, 1H), 3.75 (s, 3H), 3.27 (s, 3H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.3, 185.5, 164.2, 159.7, 156.5, 151.4, 137.2, 135.1, 134.2, 129.5, 129.0, 127.3, 124.5 (q, $J_{\text{C-F}} = 282.8$ Hz), 123.8, 119.9, 114.4, 113.5, 113.4, 105.7, 81.2, 61.7 (q, $J_{\text{C-F}} = 32.3$ Hz), 55.2, 53.0, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.40. IR (cm^{-1}) ν 3340.3, 3068.4-2834.5, 1954.8, 1725.4-1712.8, 1291.5-1129.6, 933.2, 755.0. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 585.1278, found 585.1263.

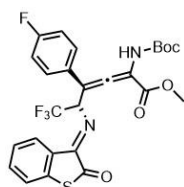


No	Retention Time	Area	% Area	Int Type
1	6.958	3518.513	49.4	BB
2	9.220	3606.859	50.6	BB



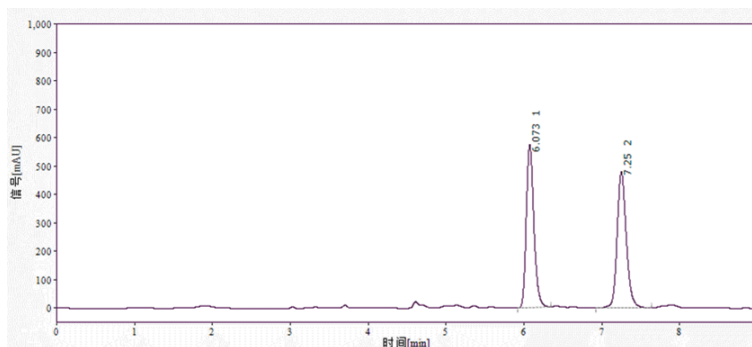
No	Retention Time	Area	% Area	Int Type
1	6.910	16927.451	92.3	BB
2	9.171	1405.873	7.7	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-(4-fluorophenyl)-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(*2H*)-ylidene)amino)hexa-2,3-dienoate

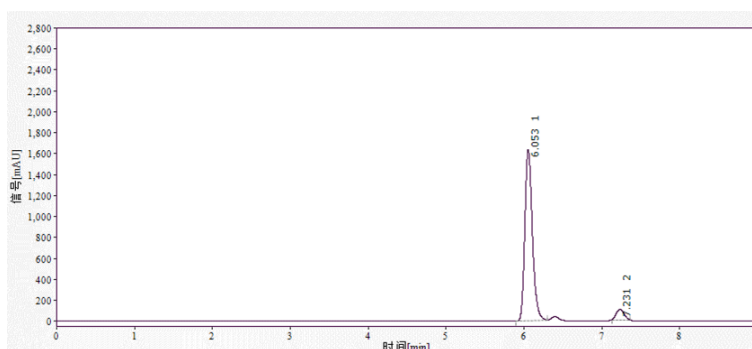


3ja

From 30.5 mg (0.1 mmol, 1.0 equiv) of **1j** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 46.2 mg (84% yield) of compound **3ja** was obtained as a yellow solid, $[\alpha]_D^{25} = -95$ ($c = 1.0$, CHCl_3), Mp. = 66 - 67 °C. Dr (> 20:1) was determined by HPLC analysis. 88% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.1$ min, $t_{\text{minor}} = 7.2$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 6.8$ Hz, 1H), 7.73 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.51 (t, $J = 7.0$ Hz, 1H), 7.38 – 7.27 (m, 2H), 7.09 (t, $J = 8.7$ Hz, 2H), 6.40 (q, $J = 6.5$ Hz, 1H), 6.11 (s, 1H), 3.37 (s, 3H), 1.45 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.8, 185.7, 164.1, 161.6, 156.6, 151.3, 137.1, 134.3, 129.8, 129.5, 129.5, 128.9, 127.4, 125.8, 124.5 (q, $J_{\text{C-F}} = 282.7$ Hz), 123.8, 115.7, 115.5, 112.6, 105.8, 81.2, 61.8 (q, $J_{\text{C-F}} = 31.4$ Hz), 53.0, 29.7, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.39, -113.23. IR (cm^{-1}) ν 3424.2, 3340.9, 3070.7-2873.2, 1956.5, 1717.3, 1509.2, 1281.2-1131.0, 930.4. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{F}_4\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 573.1078, found 573.1061.

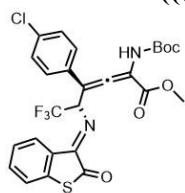


No	Retention Time	Area	% Area	Int Type
1	6.073	3864.781	49.8	BB
2	7.250	39.228	50.2	BB



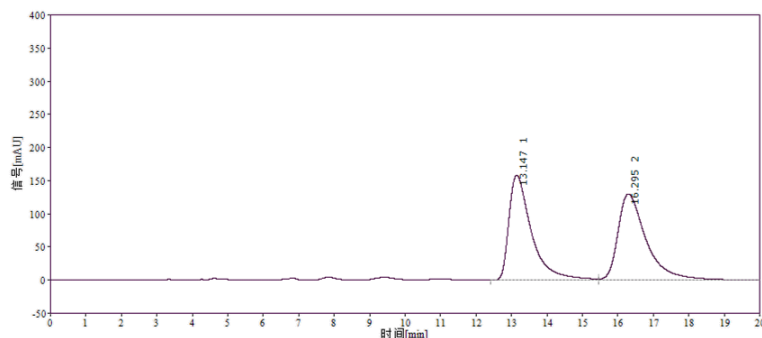
No	Retention Time	Area	% Area	Int Type
1	6.053	10943.225	94	BB
2	7.231	702.761	6	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-4-(4-chlorophenyl)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate

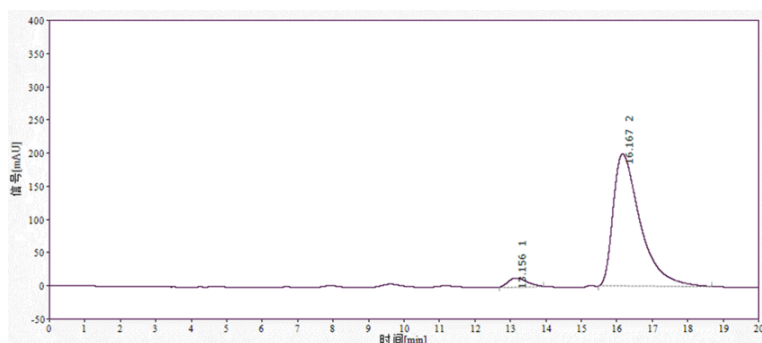


3ka

From 32.1 mg (0.1 mmol, 1.0 equiv) of **1k** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 45.8 mg (81% yield) of compound **3ka** was obtained as a yellow solid [α] $D^{25} = -109$ ($c = 1.0$, CHCl_3), Mp. = 58 - 59 °C. Dr (> 20:1) was determined by HPLC analysis. 91% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 99:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 16.2$ min, $t_{\text{minor}} = 13.2$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 2H), 7.58 - 7.47 (m, 1H), 7.37 (d, $J = 8.7$ Hz, 2H), 7.32 (dt, $J = 7.3, 3.4$ Hz, 2H), 6.39 (q, $J = 6.5$ Hz, 1H), 6.11 (s, 1H), 3.36 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 204.3, 184.6, 162.9, 155.6, 150.2, 136.1, 133.4, 133.3, 131.3, 130.1, 127.9, 127.9, 127.7, 126.3, 124.8, 123.5 (q, $J_{\text{C-F}} = 282.7$ Hz), 122.8, 111.6, 105.0, 80.3, 60.5 (q, $J_{\text{C-F}} = 29.9$ Hz), 52.0, 27.0. ^{19}F NMR (376 MHz, CDCl_3) δ -73.44. IR (cm^{-1}) ν 3420.8, 3068.4-2872.3, 1947.9, 1719.6, 1491.1-1454.4, 1289.5-1130.6, 929.7. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{ClF}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 589.0782, found 589.0783.

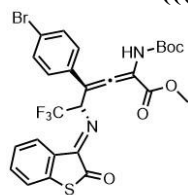


No	Retention Time	Area	% Area	Int Type
1	13.147	7023.659	49.3	BB
2	16.295	7227.811	50.7	BB



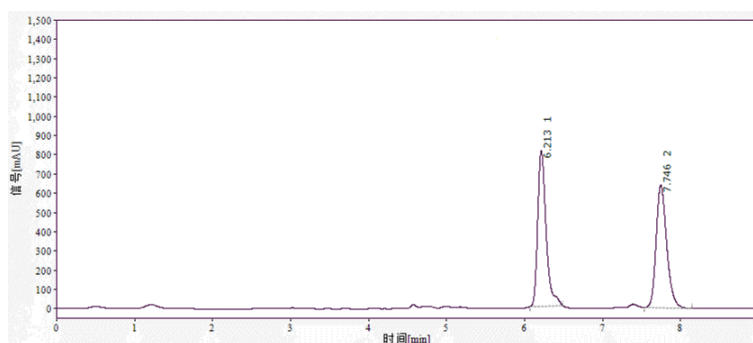
No	Retention Time	Area	% Area	Int Type
1	13.156	475.664	4.3	BB
2	16.167	10600.140	95.7	BB

Methyl (3*S*,5*S*)-4-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate

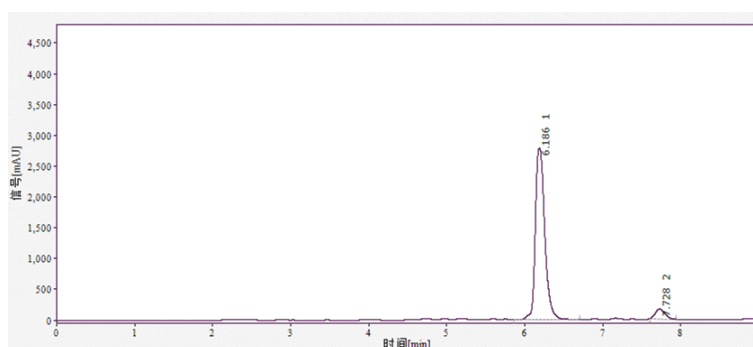


31a

From 36.5 mg (0.1 mmol, 1.0 equiv) of **11** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 52.5 mg (86% yield) of compound **31a** was obtained as a yellow solid, $[\alpha]_D^{25} = -105$ ($c = 1.0$, CHCl_3), Mp. = 85 - 86 °C. Dr (> 20:1) was determined by HPLC analysis. 89% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.2$ min, $t_{\text{minor}} = 7.7$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 – 7.78 (m, 1H), 7.61 (d, $J = 8.3$ Hz, 2H), 7.58 – 7.41 (m, 3H), 7.31 (dt, $J = 7.6, 3.6$ Hz, 2H), 6.39 (q, $J = 6.5$ Hz, 1H), 6.11 (s, 1H), 3.36 (s, 3H), 1.45 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.3, 185.7, 163.9, 156.7, 151.3, 137.2, 134.3, 132.8, 131.7, 129.2, 128.9, 127.4, 125.8, 124.5 (q, $J_{\text{C-F}} = 282.4$ Hz), 122.7, 112.7, 106.1, 81.4, 61.5 (q, $J_{\text{C-F}} = 27.2$ Hz), 53.1, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.42. IR (cm^{-1}) ν 3421.6, 3067.6-2930.3, 1946.9, 1718.9, 1489.4, 1289.2-1131.2, 929.9. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{BrF}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 633.0277, found 633.0262.

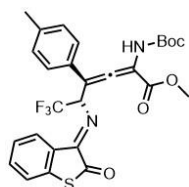


No	Retention Time	Area	% Area	Int Type
1	6.213	6026.924	50.1	BB
2	7.746	6005.234	49.9	BB



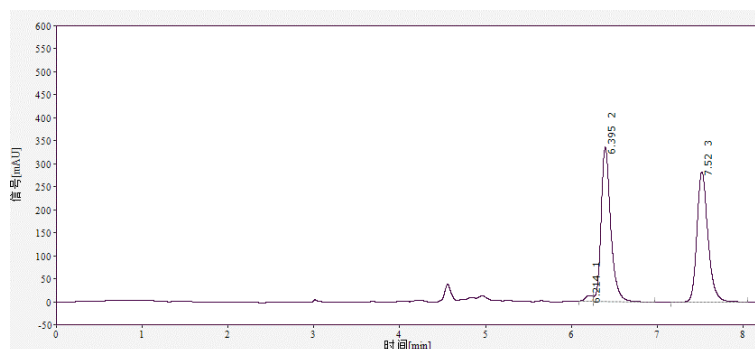
No	Retention Time	Area	% Area	Int Type
1	6.186	23307.593	94.4	BB
2	7.728	1394.429	5.6	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-(*p*-tolyl)hexa-2,3-dienoate

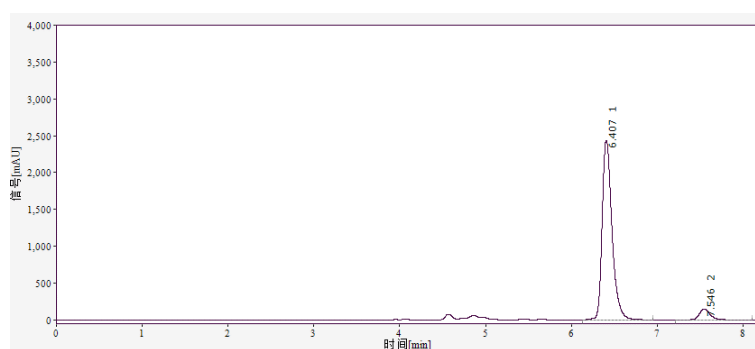


3ma

From 30.1 mg (0.1 mmol, 1.0 equiv) of **1m** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 48.0 mg (88% yield) of compound **3ma** was obtained as a yellow solid, $[\alpha]_D^{25} = -103$ ($c = 1.0$, CHCl_3), Mp. = 86 - 87 °C. Dr (> 20:1) was determined by HPLC analysis. 87% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.4$ min, $t_{\text{minor}} = 7.5$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 6.6$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 2H), 7.54 – 7.45 (m, 1H), 7.36 – 7.26 (m, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.46 (q, $J = 6.5$ Hz, 1H), 6.10 (s, 1H), 3.33 (s, 3H), 2.36 (s, 3H), 1.44 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.9, 185.4, 164.2, 156.5, 151.4, 138.5, 137.1, 134.2, 130.7, 129.3, 129.0, 127.4, 127.3, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.6$ Hz), 123.8, 113.5, 105.7, 81.2, 61.4 (q, $J_{\text{C-F}} = 29.8$ Hz), 52.9, 28.1, 21.3. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.38. IR (cm^{-1}) ν 3423.5, 2963.4-2850.4, 1946.4, 1717.2, 1491.5, 1262.5, 1167.9-1021.9, 928.9, 800.8. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1338.

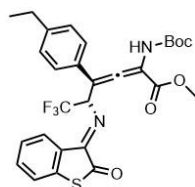


No	Retention Time	Area	% Area	Int Type
1	6.214	71.309	1.4	BB
2	6.395	2604.943	49.6	BB
3	7.520	2570.974	49.0	BB



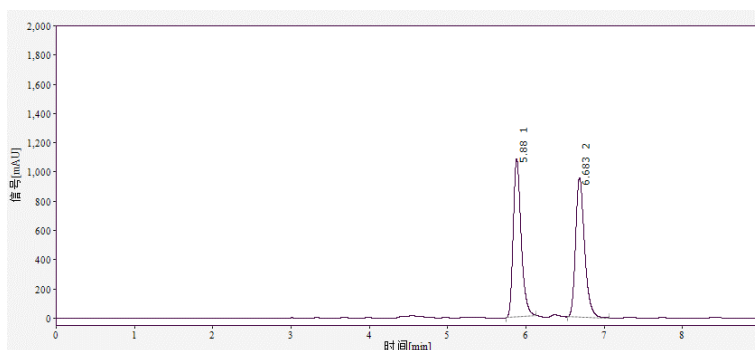
No	Retention Time	Area	% Area	Int Type
1	6.407	19455.734	93.5	BB
2	7.546	1342.336	6.5	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-4-(4-ethylphenyl)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate

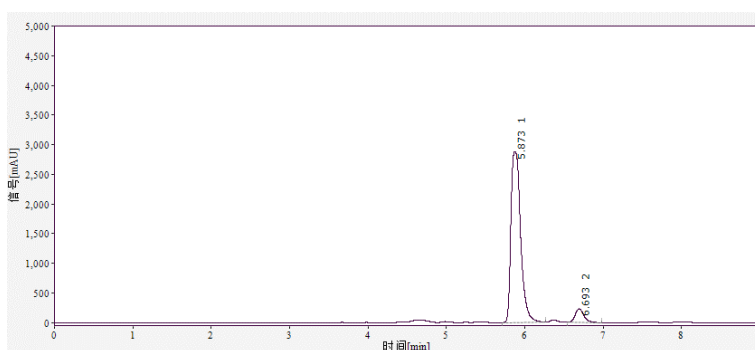


3na

From 31.5 mg (0.1 mmol, 1.0 equiv) of **1n** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 42.6 mg (76% yield) of compound **3na** was obtained as a yellow solid, $[\alpha]_D^{25} = -232$ ($c = 1.0$, CHCl_3), Mp. = 63 - 64 °C. Dr (> 20:1) was determined by HPLC analysis. 87% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.9$ min, $t_{\text{minor}} = 6.7$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 6.7$ Hz, 1H), 7.63 (d, $J = 7.9$ Hz, 2H), 7.50 (d, $J = 7.0$ Hz, 1H), 7.36 – 7.20 (m, 5H), 6.48 (q, $J = 6.5$ Hz, 1H), 6.11 (s, 1H), 3.33 (s, 3H), 2.66 (q, $J = 7.6$ Hz, 2H), 1.44 (s, 9H), 1.24 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 204.9, 185.5, 164.2, 156.5, 151.4, 144.8, 137.1, 134.2, 130.9, 129.0, 128.1, 127.9, 127.5, 127.3, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.3$ Hz), 113.5, 105.7, 81.2, 61.4 (q, $J_{\text{C-F}} = 32.4$ Hz), 52.9, 28.6, 28.1, 15.4. ^{19}F NMR (376 MHz, CDCl_3) δ -73.36. IR (cm^{-1}) ν 3422.2, 3067.9-2841.9, 1946.1, 1715.7, 1512.7-1492.2, 1292.3-1129.3, 929.0. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 583.1485, found 583.1485.

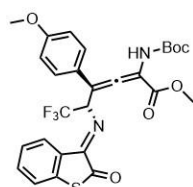


No	Retention Time	Area	% Area	Int Type
1	5.880	7571.076	50.0	BB
2	6.683	7581.970	50.0	BB



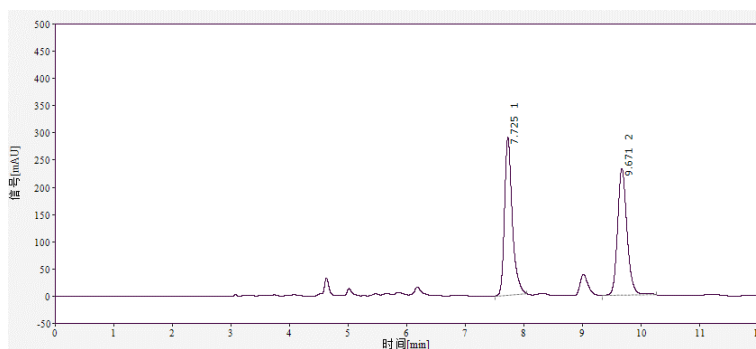
No	Retention Time	Area	% Area	Int Type
1	5.873	24691.892	93.4	BB
2	6.693	1756.627	6.6	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-(4-methoxyphenyl)-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate

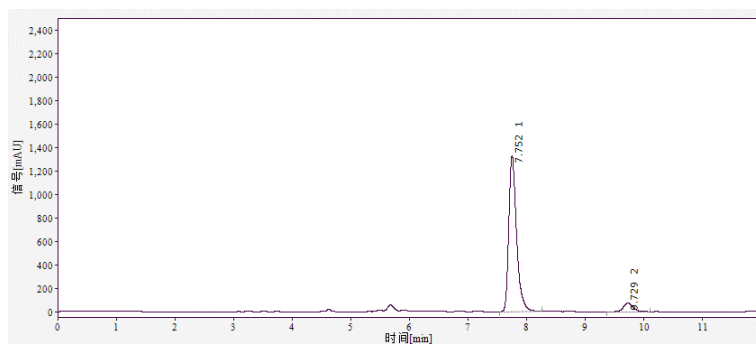


3oa

From 31.7 mg (0.1 mmol, 1.0 equiv) of **1o** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 50.1 mg (90% yield) of compound **3oa** was obtained as a yellow solid, $[\alpha]_D^{25} = -125$ ($c = 1.0$, CHCl_3), Mp. = 67 - 68 °C. Dr (> 20:1) was determined by HPLC analysis. 87% ee was determined by HPLC analysis (Daicel Chiralpak IA column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 7.8$ min, $t_{\text{minor}} = 9.7$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 6.5$ Hz, 1H), 7.72 (d, $J = 7.7$ Hz, 2H), 7.50 (t, $J = 6.9$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.37 - 7.27 (m, 3H), 6.48 (q, $J = 6.5$ Hz, 1H), 6.11 (s, 1H), 3.35 (s, 3H), 1.44 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.5, 185.5, 164.2, 159.9, 156.5, 151.5, 137.1, 134.2, 129.0, 128.9, 127.3, 125.9, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.2$ Hz), 123.8, 114.1, 113.2, 105.6, 81.1, 61.5 (q, $J_{\text{C-F}} = 32.8$ Hz), 55.3, 52.9, 29.7, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.38. IR (cm^{-1}) ν 3423.8, 2962.7-2851.3, 1947.1, 1718.3, 1491.5, 1263.0-1129.7, 1021.8, 929.1, 801.5. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 585.1278, found 585.1260.

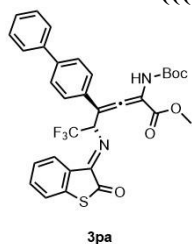


No	Retention Time	Area	% Area	Int Type
1	7.725	2670.838	50.4	BB
2	9.671	2629.996	49.6	BB

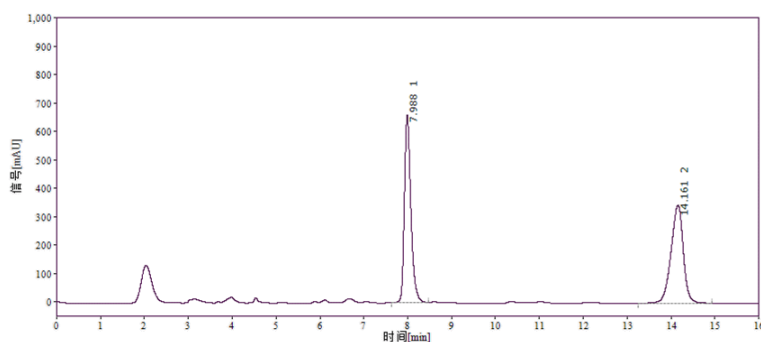


No	Retention Time	Area	% Area	Int Type
1	7.752	12252.845	93.5	BB
2	9.729	845.110	6.5	BB

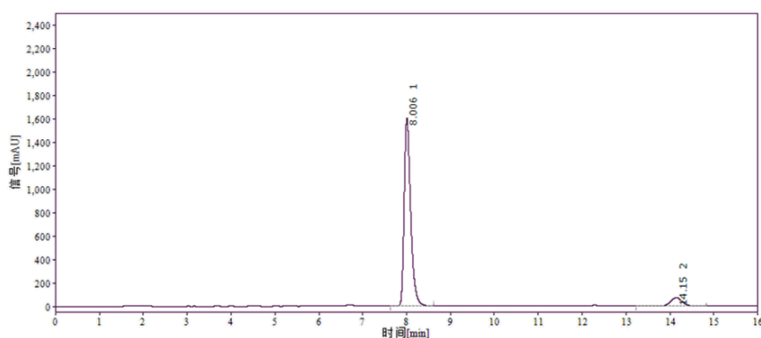
Methyl (3*S*,5*S*)-4-([1,1'-biphenyl]-4-yl)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate



From 36.3 mg (0.1 mmol, 1.0 equiv) of **1p** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 51.7 mg (85% yield) of compound **3pa** was obtained as a yellow solid, $[\alpha]_D^{25} = -125$ ($c = 1.0$, CHCl_3), Mp. = 90 - 91 °C. Dr ($> 20:1$) was determined by HPLC analysis. 84% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 8.0$ min, $t_{\text{minor}} = 14.2$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.92 – 7.74 (m, 3H), 7.62 (dd, $J = 10.3, 7.8$ Hz, 4H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.40 – 7.27 (m, 3H), 6.52 (q, $J = 6.5$ Hz, 1H), 6.13 (s, 1H), 3.35 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 185.6, 164.2, 156.6, 151.4, 141.3, 140.6, 137.2, 134.2, 132.5, 129.0, 128.8, 128.0, 127.5, 127.4, 127.3, 127.1, 125.8, 124.6 (q, $J_{\text{C-F}} = 282.0$ Hz), 123.8, 113.3, 106.0, 81.3, 61.4 (q, $J_{\text{C-F}} = 25.9$ Hz), 53.0, 29.7, 28.1. ^{19}F NMR (376 MHz, CDCl_3) δ -73.37. IR (cm^{-1}) ν 3421.1, 3061.2-2929.8, 1946.3, 1716.0, 1488.6, 1289.5-1130.0, 929.6, 767.1. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{27}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 631.1485, found 631.1471.

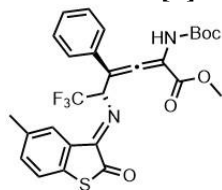


No	Retention Time	Area	% Area	Int Type
1	7.988	6784.480	50.3	BB
2	14.161	6693.881	49.7	BB



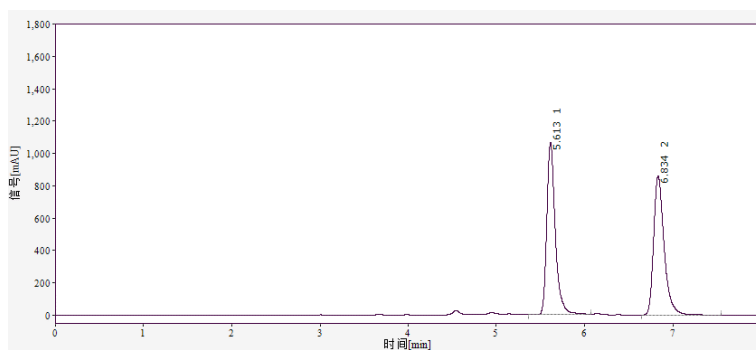
No	Retention Time	Area	% Area	Int Type
1	8.006	1606.918	92.2	BB
2	14.150	1396.581	7.8	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-5-methyl-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-phenylhexa-2,3-dienoate

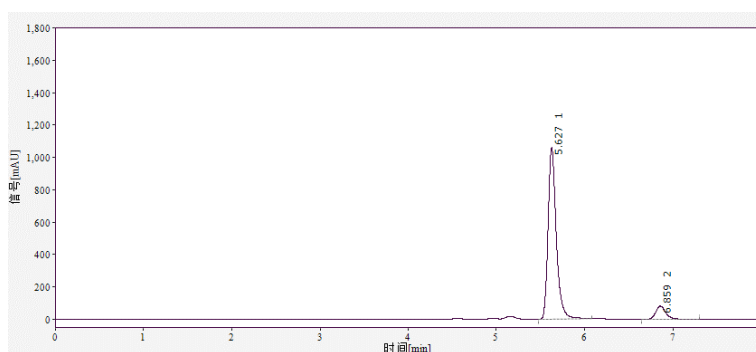


3ab

From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 31.1 mg (0.12 mmol, 1.2 equiv) of **2b**, 47.5 mg (87% yield) of compound **3ab** was obtained as a yellow solid, $[\alpha]_D^{25} = -120$ ($c = 1.0$, CHCl_3), Mp. = 94 - 95 °C. Dr (> 20:1) was determined by HPLC analysis. 83% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.6$ min, $t_{\text{minor}} = 6.9$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 1.8$ Hz, 1H), 7.34 (d, $J = 7.4$ Hz, 2H), 7.24 (d, $J = 7.3$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.38 (q, $J = 6.5$ Hz, 1H), 6.04 (s, 1H), 3.29 (s, 3H), 2.31 (s, 3H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.1, 186.0, 164.3, 156.7, 151.4, 137.5, 135.2, 133.8, 128.8, 128.6, 128.5, 127.6, 126.2, 124.6 (q, $J_{\text{C-F}} = 281.4$ Hz), 123.5, 113.6, 105.8, 81.3, 61.4 (q, $J_{\text{C-F}} = 28.2$ Hz), 53.0, 29.7, 28.1, 21.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.40. IR (cm^{-1}) ν 3354.2, 3058.2-2931.4, 1954.7, 1726.9-1697.4, 1503.6, 1294.7-1128.1, 952.7, 768.2. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1335.

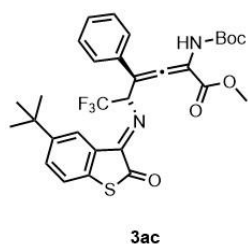


No	Retention Time	Area	% Area	Int Type
1	5.613	7118.399	49.9	BB
2	6.834	7141.862	50.1	BB



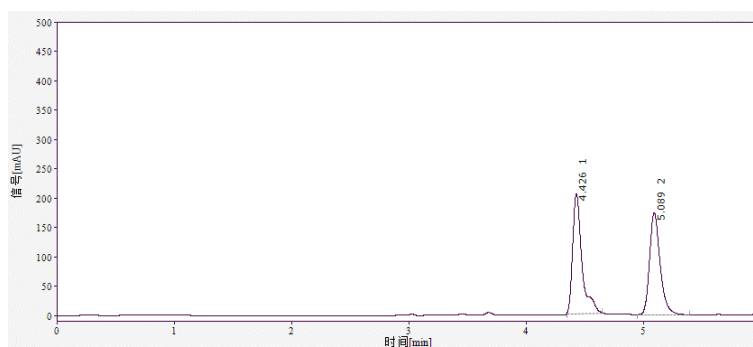
No	Retention Time	Area	% Area	Int Type
1	5.627	6850.227	91.3	BB
2	6.859	653.473	8.7	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-5-(((*E*)-5-(*tert*-butyl)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-

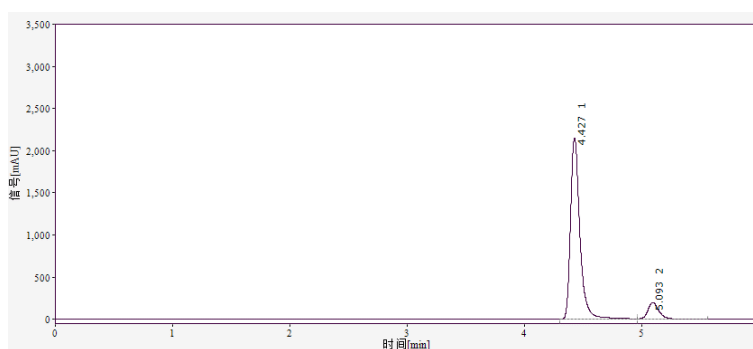


dienoate

From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 36.1 mg (0.12 mmol, 1.2 equiv) of **2c**, 52.9 mg (90% yield) of compound **3ac** was obtained as a yellow solid, $[\alpha]_D^{25} = -144$ ($c = 1.0$, CHCl_3), Mp. = 126 - 127 °C. Dr ($> 20:1$) was determined by HPLC analysis. 80% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 4.4$ min, $t_{\text{minor}} = 5.1$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.72 (d, $J = 7.7$ Hz, 2H), 7.55 (dd, $J = 8.3, 2.2$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.36 - 7.27 (m, 1H), 7.22 (d, $J = 5.2$ Hz, 1H), 6.55 (q, $J = 6.5$ Hz, 1H), 6.13 (s, 1H), 3.29 (s, 3H), 1.44 (s, 9H), 1.35 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.5, 186.3, 164.2, 156.7, 151.5, 151.1, 133.9, 133.7, 131.6, 128.7, 128.6, 128.5, 127.6, 124.6 (q, $J_{\text{C-F}} = 282.4$ Hz), 123.5, 122.6, 113.6, 105.9, 81.2, 61.1 (q, $J_{\text{C-F}} = 28.3$ Hz), 52.9, 34.9, 31.2, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.20. IR (cm^{-1}) ν 3428.8, 3084.3-2870.7, 1952.5, 1736.0-1697.9, 1488.6, 1292.3-1128.9, 1021.2, 946.1, 768.0. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{31}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 611.1798, found 611.1797.

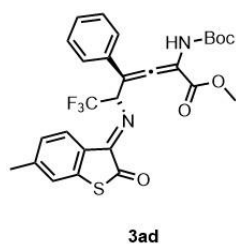


No	Retention Time	Area	% Area	Int Type
1	4.426	1119.025	50.7	BB
2	5.089	1088.623	49.3	BB

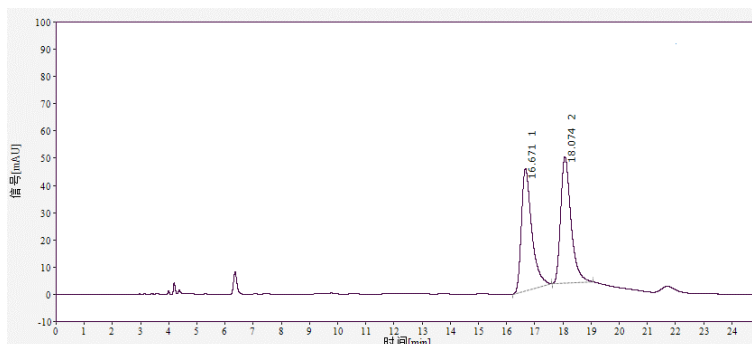


No	Retention Time	Area	% Area	Int Type
1	4.427	12047.976	90.0	BB
2	5.093	1338.974	10.0	BB

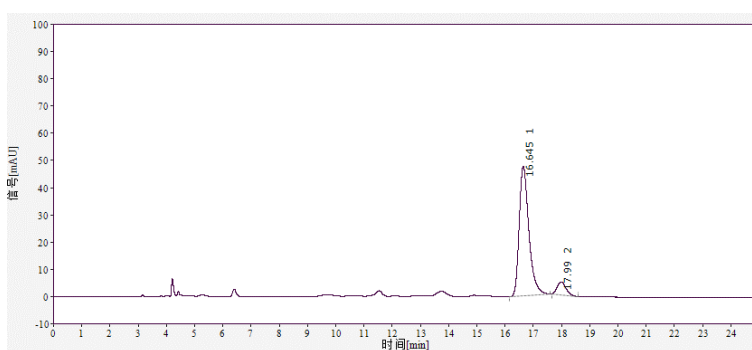
Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-5-(((*E*)-5-(*tert*-butyl)-2-oxobenzo[*b*]thiophen-3(*2*H*)-ylidene)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate*



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 31.1 mg (0.12 mmol, 1.2 equiv) of **2d**, 49.1 mg (90% yield) of compound **3ad** was obtained as a yellow solid, $[\alpha]_D^{25} = -97$ ($c = 1.0$, CHCl_3), Mp. = 172 - 173 °C. Dr (> 20:1) was determined by HPLC analysis. 83% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 99:1, 1.0 mL/min). Retention time: $t_{\text{major}} = 16.6$ min, $t_{\text{minor}} = 18.0$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 7.9, 4.3$ Hz, 3H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 1H), 7.02 (d, $J = 8.2$ Hz, 2H), 6.39 (q, $J = 6.5$ Hz, 1H), 6.03 (s, 1H), 3.28 (s, 3H), 2.32 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 186.0, 164.3, 156.3, 151.4, 145.5, 133.8, 128.6, 128.5, 128.3, 127.6, 126.7, 125.7, 124.6 (q, $J_{\text{C-F}} = 282.9$ Hz), 124.2, 113.7, 105.8, 81.2, 61.4 (q, $J_{\text{C-F}} = 31.9$ Hz), 53.0, 29.7, 28.1, 22.1. ^{19}F NMR (376 MHz, CDCl_3) δ -73.36. IR (cm^{-1}) ν 3427.1, 3345.8, 3059.0-2930.9, 1954.6, 1727.0-1697.5, 1503.1, 1295.1-1123.4, 1022.2, 939.7-932.2, 769.1. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1314.

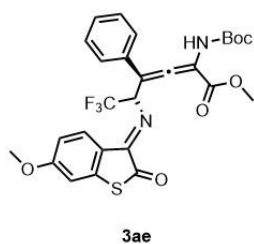


No	Retention Time	Area	% Area	Int Type
1	16.671	1151.558	49.3	BB
2	18.074	1182.098	50.7	BB

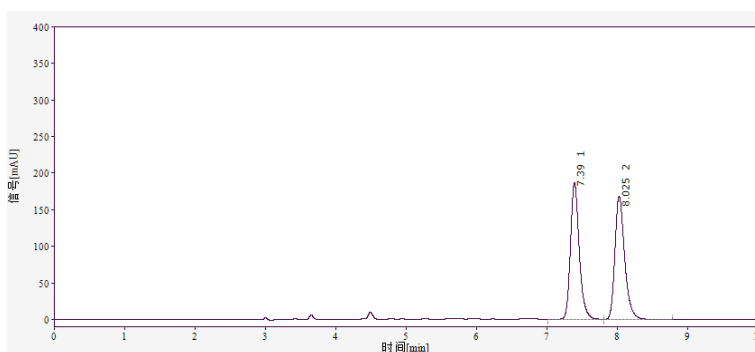


No	Retention Time	Area	% Area	Int Type
1	16.645	1137.300	91.7	BB
2	17.990	103.555	8.3	BB

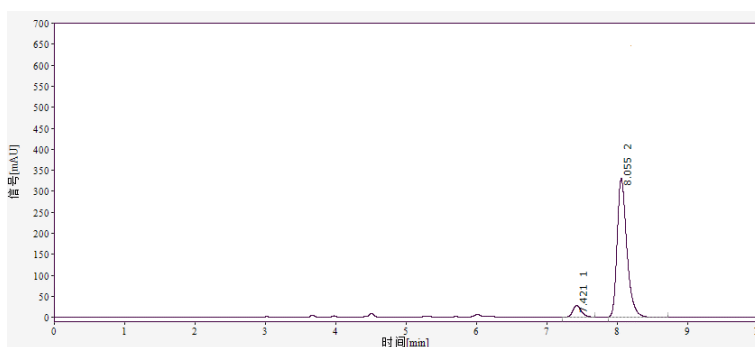
Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-6-methoxy-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 33.0 mg (0.12 mmol, 1.2 equiv) of **2e**, 51.1 mg (91% yield) of compound **3ae** was obtained as a yellow solid, $[\alpha]_D^{25} = -80$ ($c = 1.0$, CHCl_3), Mp. = 132 -133 °C. Dr ($> 20:1$) was determined by HPLC analysis. 86% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2 -propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 8.1$ min, $t_{\text{minor}} = 7.4$ min. ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.61 (m, 3H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.28 – 7.19 (m, 1H), 6.79 – 6.64 (m, 2H), 6.36 (q, $J = 6.5$ Hz, 1H), 6.04 (s, 1H), 3.78 (s, 3H), 3.30 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 185.9, 164.3, 164.3, 155.5, 151.4, 139.2, 133.8, 128.5, 128.4, 127.6, 124.7 (q, $J_{\text{C-F}} = 282.4$ Hz), 122.3, 113.8, 113.3, 109.1, 105.8, 81.2, 61.2 (q, $J_{\text{C-F}} = 27.1$ Hz), 55.8, 53.0, 29.7, 28.1. ^{19}F NMR (376 MHz, CDCl_3) δ -73.37. IR (cm^{-1}) ν 3426.2, 3346.1, 3061.4-2844.4, 1955.1, 1727.4-1713.1, 1596.7, 1489.8, 1294.0-1122.4, 940.0-931.9, 768.2, 696.3. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 585.1278, found 585.1269.

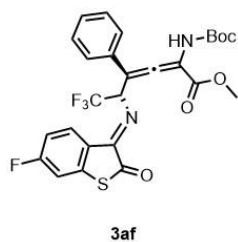


No	Retention Time	Area	% Area	Int Type
1	7.390	1630.636	50.0	BB
2	8.025	1628.279	50.0	BB



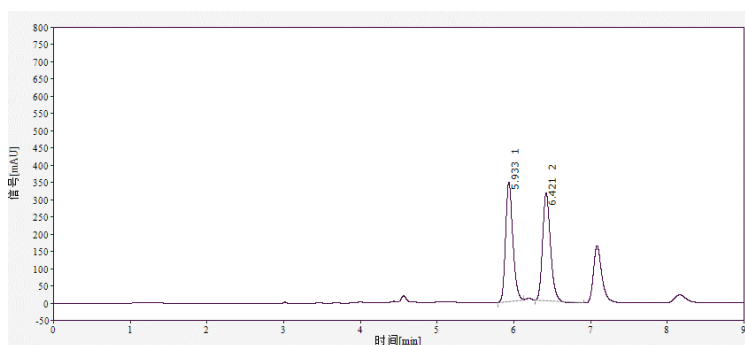
No	Retention Time	Area	% Area	Int Type
1	7.421	241.632	7.1	BB
2	8.055	3168.765	92.9	BB

Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-5-(((*E*)-6-fluoro-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-4-phenylhexa-2,3-dienoate

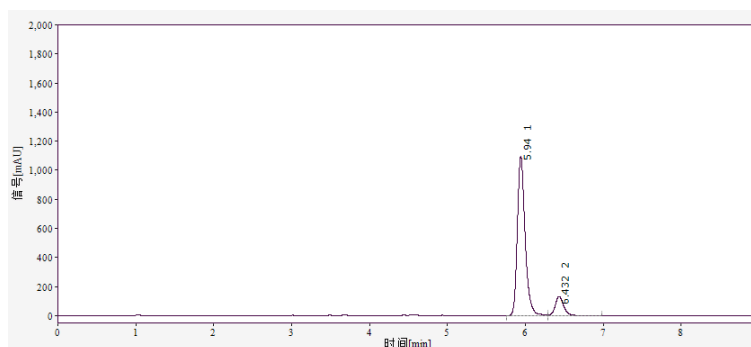


From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 31.6 mg (0.12 mmol, 1.2 equiv) of **2f**, 45.1 mg (82% yield) of compound **3af** was obtained as a yellow solid, $[\alpha]_D^{25} = -68$ ($c = 1.0$, CHCl_3), Mp. = 121 - 122 °C. Dr (> 20:1) was determined by HPLC analysis. 77% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min).

Retention time: $t_{\text{major}} = 5.9$ min, $t_{\text{minor}} = 6.4$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.74 (m, 1H), 7.63 (d, $J = 7.7$ Hz, 2H), 7.37 – 7.28 (m, 2H), 7.25 (t, $J = 7.3$ Hz, 1H), 7.06 – 6.88 (m, 2H), 6.37 (q, $J = 6.5$ Hz, 1H), 6.03 (s, 1H), 3.32 (s, 3H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.1, 184.5, 167.2, 164.7, 164.2, 155.1, 151.4, 139.5, 139.4, 133.6, 128.6, 128.5, 128.1, 128.0, 127.6, 125.3, 125.3, 124.5 (q, $J_{\text{C-F}} = 282.0$ Hz), 115.1, 114.9, 113.5, 111.6, 111.3, 105.8, 81.3, 61.5 (q, $J_{\text{C-F}} = 28.8$ Hz), 53.0, 28.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.30, -101.22. IR (cm^{-1}) ν 3423.7, 3343.6, 3066.3-2931.0, 1955.6, 1725.7-1713.2, 1505.6, 1296.0-1123.0, 943.3-935.7, 768.4. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{F}_4\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 573.1078, found 573.1078.

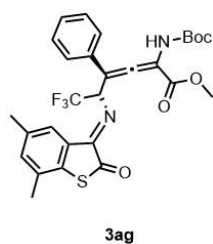


No	Retention Time	Area	% Area	Int Type
1	5.933	2264.715	50.3	BB
2	6.421	2238.192	49.7	BB

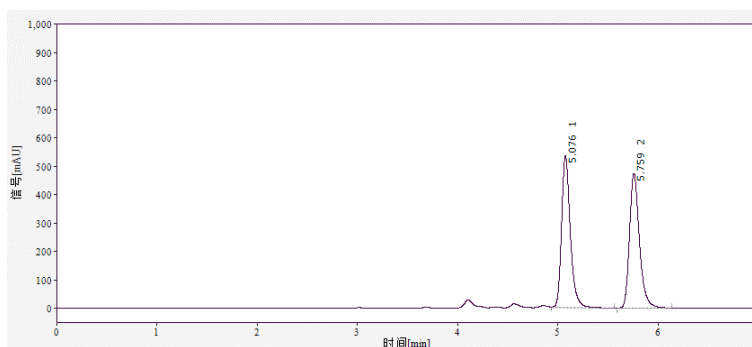


No	Retention Time	Area	% Area	Int Type
1	5.940	7593.366	88.4	BB
2	6.432	995.711	11.6	BB

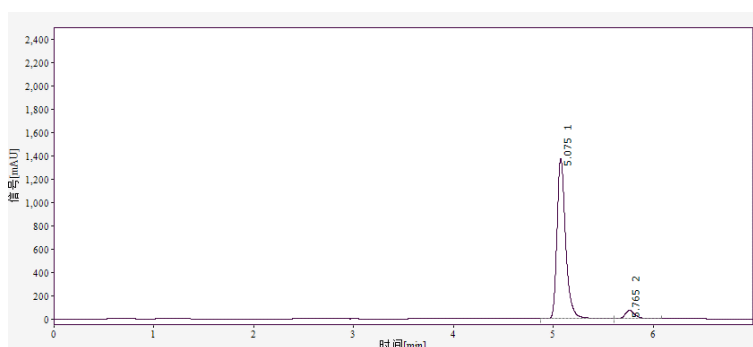
Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-5-(((*E*)-5,7-dimethyl-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 32.8 mg (0.12 mmol, 1.2 equiv) of **2g**, 50.4 mg (90% yield) of compound **3ag** was obtained as a yellow solid, $[\alpha]_D^{25} = -110$ ($c = 1.0$, CHCl_3), Mp. = 89 - 90 °C. Dr (> 20:1) was determined by HPLC analysis. 88% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.1$ min, $t_{\text{minor}} = 5.8$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.7$ Hz, 2H), 7.40 (s, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.28 – 7.20 (m, 1H), 7.07 (s, 1H), 6.38 (q, $J = 6.5$ Hz, 1H), 6.04 (s, 1H), 3.27 (s, 3H), 2.27 (s, 3H), 2.15 (s, 3H), 1.36 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.1, 186.2, 164.3, 157.3, 151.4, 137.3, 136.0, 133.8, 133.4, 132.5, 128.9, 128.6, 128.5, 127.6, 124.6 (q, $J_{\text{C-F}} = 282.4$ Hz), 123.5, 113.6, 105.8, 81.3, 61.5 (q, $J_{\text{C-F}} = 28.2$ Hz), 52.9, 29.7, 28.1, 20.9, 19.2. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -73.37. IR (cm^{-1}) ν 3406.1, 3057.0-2930.7, 1954.8, 1719.9, 1292.2-1131.7, 879.6, 767.2. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 583.1485, found 583.1484.

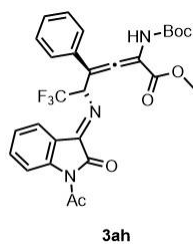


No	Retention Time	Area	% Area	Int Type
1	5.076	3218.064	49.7	BB
2	5.759	3253.889	50.3	BB

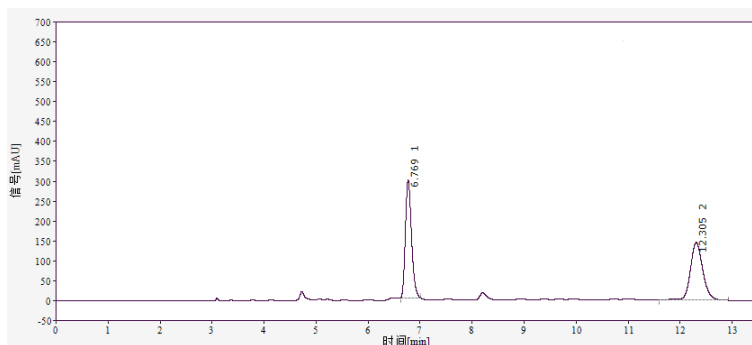


No	Retention Time	Area	% Area	Int Type
1	5.075	8299.005	94.2	BB
2	5.765	510.566	5.8	BB

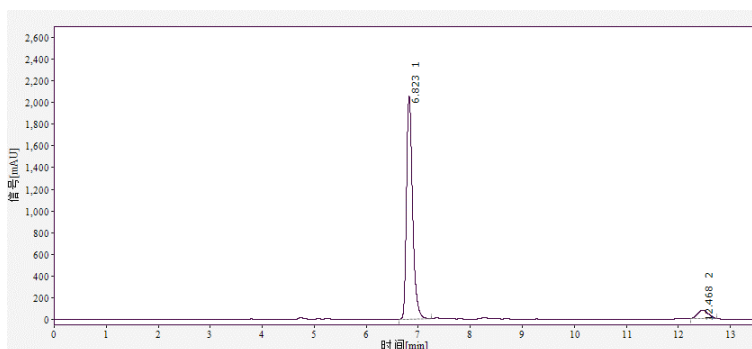
Methyl (3S,5S)-5-(((E)-1-acetyl-2-oxoindolin-3-ylidene)amino)-2-((tert-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 32.4 mg (0.12 mmol, 1.2 equiv) of **2h**, 45.7 mg (82% yield) of compound **3ah** was obtained as a yellow solid, $[\alpha]_D^{25} = -40$ ($c = 1.0$, CHCl_3), Mp. = 77 – 78 °C. Dr (> 20:1) was determined by HPLC analysis. 88% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.8$ min, $t_{\text{minor}} = 12.5$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.2$ Hz, 1H), 7.82 – 7.64 (m, 3H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.14 (m, 3H), 6.68 (q, $J = 6.6$ Hz, 1H), 6.02 (s, 1H), 3.17 (s, 3H), 2.62 (s, 3H), 1.36 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.3, 170.2, 163.9, 157.9, 153.8, 151.3, 143.0, 134.4, 133.8, 128.6, 127.9, 127.2 (q, $J_{\text{C-F}} = 254.7$ Hz), 122.9, 121.9, 116.9, 114.0, 105.8, 81.2, 61.5 (q, $J_{\text{C-F}} = 32.1$ Hz), 52.8, 29.7, 28.1, 26.7. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.91. IR (cm^{-1}) ν 3443.0, 3129.9-2935.0, 1948.0, 1754.1-1723.2, 1409.4, 1274.4-1128.8, 764.7. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{F}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 580.1666, found 580.1665.

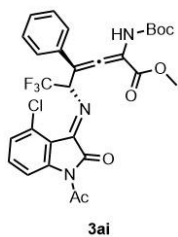


No	Retention Time	Area	% Area	Int Type
1	6.769	2440.985	50.5	BB
2	12.305	2393.897	49.5	BB



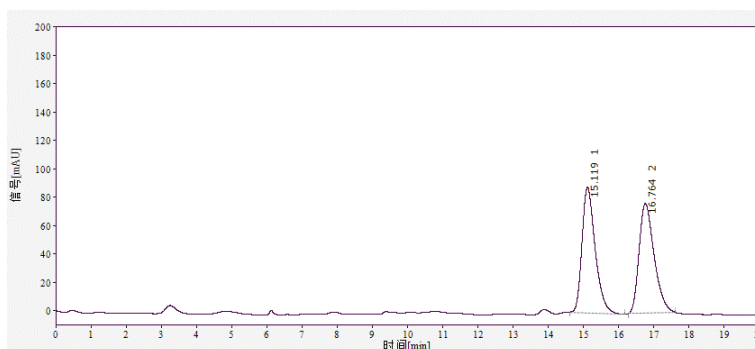
No	Retention Time	Area	% Area	Int Type
1	6.823	16748.179	93.8	BB
2	12.468	1110.501	6.2	BB

Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-4-chloro-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate

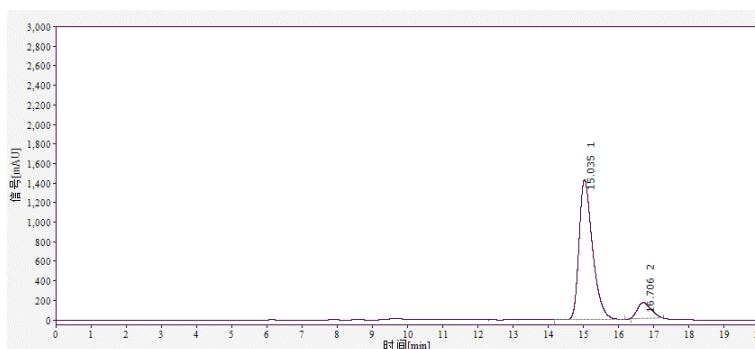


3ai

From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 36.5 mg (0.12 mmol, 1.2 equiv) of **2i**, 51.4 mg (87% yield) of compound **3ai** was obtained as a yellow solid, $[\alpha]_D^{25} = -120$ ($c = 1.0$, CHCl_3), Mp. = 69 - 70 °C. Dr (> 20:1) was determined by HPLC analysis. 80% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2 - propanol 90:10, 0.5 mL/min). Retention time: $t_{\text{major}} = 15.0$ min, $t_{\text{minor}} = 16.7$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.2$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.52 – 7.10 (m, 6H), 6.85 (q, $J = 6.6$ Hz, 1H), 6.06 (s, 1H), 3.22 (s, 3H), 2.60 (s, 3H), 1.33 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 206.2, 170.1, 164.0, 156.8, 152.2, 151.5, 144.1, 134.1, 133.5, 131.9, 128.5, 128.5, 128.0, 124.5 (q, $J_{\text{C-F}} = 282.8$ Hz), 118.3, 115.0, 113.5, 105.7, 81.1, 62.0 (q, $J_{\text{C-F}} = 32.7$ Hz), 52.7, 29.7, 28.1, 26.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.89. IR (cm^{-1}) ν 3424.1, 3128.9-2872.8, 1949.3, 1755.8-1719.8, 1594.5, 1494.7, 1269.9-1128.0, 1045.1-1022.8, 786.8-765.4. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{ClF}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 614.1276, found 614.1284.

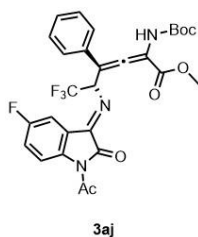


No	Retention Time	Area	% Area	Int Type
1	15.119	2302.116	50	BB
2	16.764	2305.343	50	BB

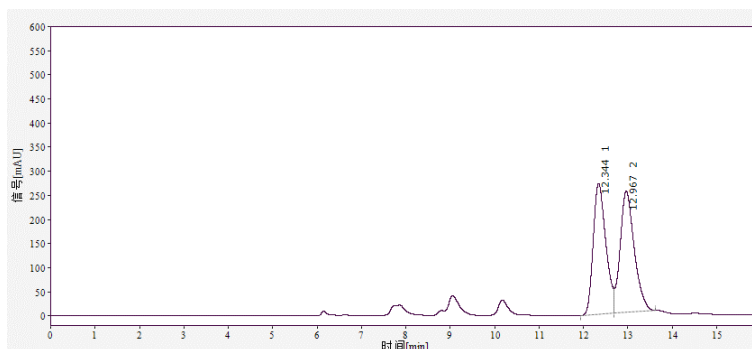


No	Retention Time	Area	% Area	Int Type
1	15.035	38091.044	89.8	BB
2	16.706	4307.423	10.2	BB

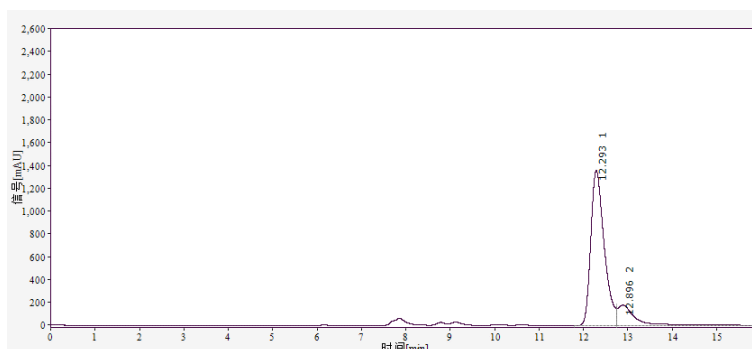
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-5-fluoro-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 34.6 mg (0.12 mmol, 1.2 equiv) of **2j**, 47.7 mg (83% yield) of compound **3aj** was obtained as a yellow solid, $[\alpha]_D^{25} = -16$ ($c = 1.0$, CHCl_3), Mp. = 64 - 65 °C. Dr (> 20:1) was determined by HPLC analysis. 70% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 0.5 mL/min). Retention time: $t_{\text{major}} = 12.3$ min, $t_{\text{minor}} = 12.9$ min. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (dd, $J = 8.9, 4.2$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.53 (dd, $J = 7.0, 2.9$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.38 - 7.29 (m, 1H), 7.28 - 7.18 (m, 1H), 6.73 (q, $J = 6.6$ Hz, 1H), 6.11 (s, 1H), 3.31 (s, 3H), 2.68 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 170.0, 163.8, 161.7, 159.2, 157.5, 153.3, 153.3, 151.3, 139.2, 139.2, 133.7, 128.6, 128.5, 127.9, 124.4 (q, $J_{\text{C-F}} = 282.4$ Hz), 123.5, 123.4, 121.1, 120.9, 118.7, 118.6, 113.8, 109.8, 109.5, 105.7, 81.2, 61.9 (q, $J_{\text{C-F}} = 27.5$ Hz), 52.8, 29.7, 28.1, 26.6. ^{19}F NMR (376 MHz, CDCl_3) δ -72.80, -114.60. IR (cm^{-1}) ν 3425.3, 3132.8-2873.3, 1949.6, 1758.4-1719.5, 1483.9, 1293.5-1127.7, 878.2, 765.9. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{F}_4\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 598.1572, found 598.1566.

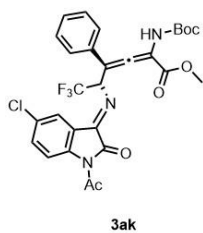


No	Retention Time	Area	% Area	Int Type
1	12.344	5398.054	49.2	BB
2	12.967	5574.220	50.8	BB

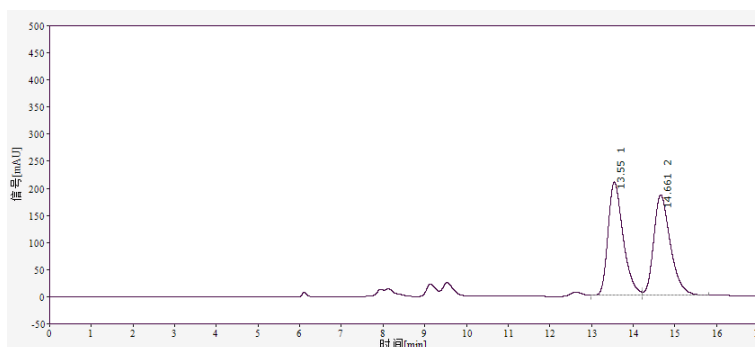


No	Retention Time	Area	% Area	Int Type
1	12.293	28579.826	85.1	BB
2	12.896	5019.568	14.9	BB

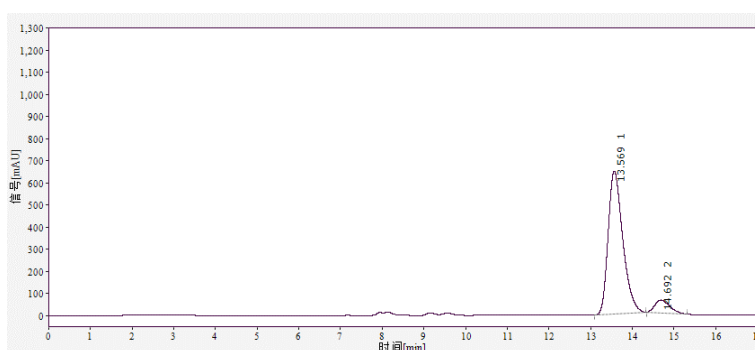
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-5-chloro-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 36.5 mg (0.12 mmol, 1.2 equiv) of **2k**, 50.8 mg (86% yield) of compound **3ak** was obtained as a yellow solid, $[\alpha]_D^{25} = -55$ ($c = 1.0$, CHCl_3), Mp. = 72 - 73 °C. Dr (> 20:1) was determined by HPLC analysis. 83% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 0.5 mL/min). Retention time: $t_{\text{major}} = 13.6$ min, $t_{\text{minor}} = 14.7$ min. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.7$ Hz, 1H), 7.78 (dd, $J = 26.1, 5.0$ Hz, 3H), 7.49 (d, $J = 6.4$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.38 – 7.29 (m, 1H), 6.71 (q, $J = 6.6$ Hz, 1H), 6.11 (s, 1H), 3.33 (s, 3H), 2.68 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 170.0, 163.8, 157.3, 153.0, 151.3, 141.4, 134.1, 133.7, 131.9, 128.6, 128.5, 127.9, 124.4 (q, $J_{\text{C-F}} = 282.7$ Hz), 123.2, 122.7, 118.3, 113.8, 105.7, 81.2, 61.9 (q, $J_{\text{C-F}} = 25.2$ Hz), 52.9, 29.7, 28.1, 26.6. ^{19}F NMR (376 MHz, CDCl_3) δ -72.75. IR (cm^{-1}) ν 3424.1, 3059.8-2873.0, 1948.8, 1757.9-1720.2, 1493.7-1467.3, 1289.6-1129.7, 766.2. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{ClF}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 614.1276, found 614.1267.

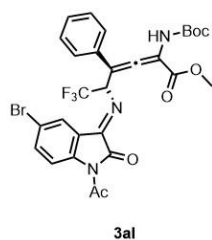


No	Retention Time	Area	% Area	Int Type
1	13.550	5289.472	50.5	BB
2	14.661	5182.987	49.5	BB



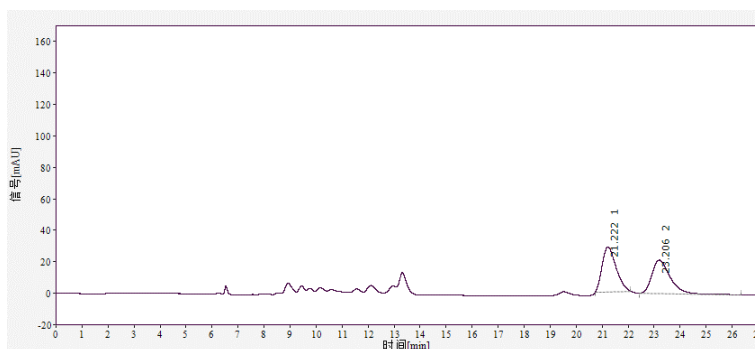
No	Retention Time	Area	% Area	Int Type
1	13.569	15745.032	91.7	BB
2	14.692	1429.660	8.3	BB

Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-5-bromo-2-oxindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate

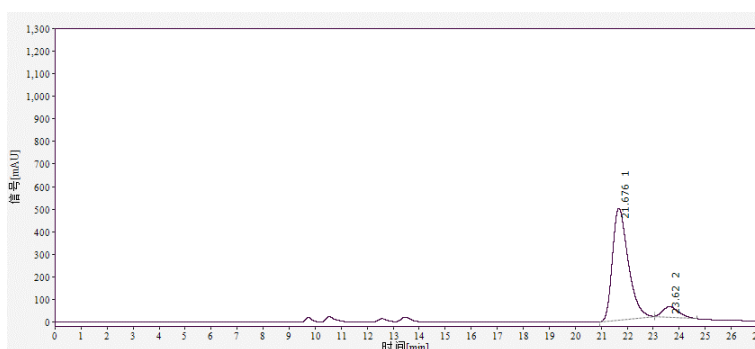


3al

From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 41.8 mg (0.12 mmol, 1.2 equiv) of **2l**, 59.7 mg (94% yield) of compound **3al** was obtained as a yellow solid, $[\alpha]_D^{25} = -61$ ($c = 1.0$, CHCl_3), Mp. = 83 - 84 °C. Dr (> 20:1) was determined by HPLC analysis. 83% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 98:2, 0.5 mL/min). Retention time: $t_{\text{major}} = 21.7$ min, $t_{\text{minor}} = 23.6$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.6$ Hz, 1H), 7.87 (d, $J = 2.2$ Hz, 1H), 7.67 (d, $J = 7.7$ Hz, 2H), 7.59 – 7.52 (m, 1H), 7.28 (dt, $J = 31.0$, 7.4 Hz, 3H), 6.63 (q, $J = 6.6$ Hz, 1H), 6.04 (s, 1H), 3.25 (s, 3H), 2.59 (s, 3H), 1.35 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.2, 170.0, 163.8, 157.1, 152.9, 151.3, 141.9, 137.0, 133.7, 128.6, 127.9, 125.6, 124.4 (q, $J_{\text{C-F}} = 282.8$ Hz), 123.5, 119.3, 118.6, 113.8, 105.8, 81.3, 62.0 (q, $J_{\text{C-F}} = 29.2$ Hz), 52.9, 28.1, 26.6. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.75. IR (cm^{-1}) ν 3423.8, 2958.5-2858.0, 1757.5-1719.9, 1494.1-1464.4, 1288.9-1129.6. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{BrF}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 658.0771, found 658.0760.

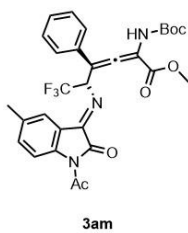


No	Retention Time	Area	% Area	Int Type
1	21.222	1047.624	50.4	BB
2	23.206	1031.613	49.6	BB

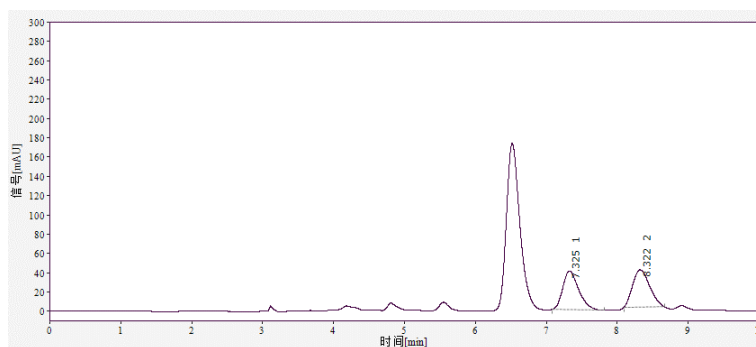


No	Retention Time	Area	% Area	Int Type
1	21.676	20777.769	91.5	BB
2	23.620	1936.248	8.5	BB

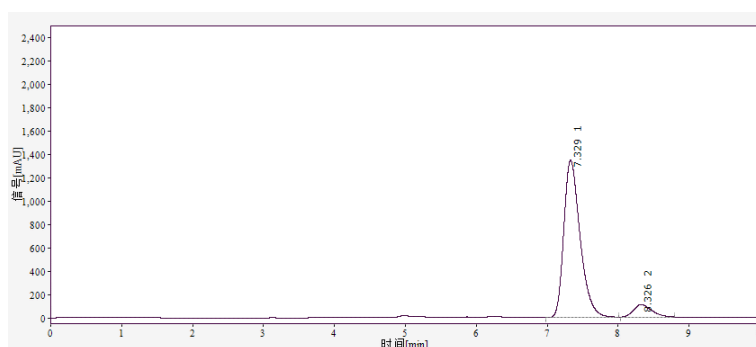
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-5-methyl-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 34.1 mg (0.12 mmol, 1.2 equiv) of **2m**, 43.4 mg (76% yield) of compound **3am** was obtained as a yellow solid, $[\alpha]_D^{25} = -41$ ($c = 1.0$, CHCl_3), Mp. = 85 - 86 °C. Dr (> 20:1) was determined by HPLC analysis. 84% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 7.3$ min, $t_{\text{minor}} = 8.3$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.3$ Hz, 1H), 7.70 (d, $J = 7.5$ Hz, 2H), 7.58 (s, 1H), 7.30 (dt, $J = 31.2, 7.6$ Hz, 4H), 6.65 (q, $J = 6.6$ Hz, 1H), 6.03 (s, 1H), 3.18 (s, 3H), 2.60 (s, 3H), 2.31 (s, 3H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.2, 170.0, 164.0, 158.1, 153.9, 140.9, 136.0, 135.1, 133.8, 128.5, 128.5, 127.9, 124.6 (q, $J_{\text{C-F}} = 283.1$ Hz), 123.0, 121.8, 116.7, 114.0, 105.7, 81.2, 61.5 (q, $J_{\text{C-F}} = 27.0$ Hz), 52.8, 29.7, 28.1, 26.6, 20.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.96. IR (cm^{-1}) ν 3425.7, 2959.7-2930.5, 1949.0, 1756.5-1719.4, 1488.0, 1302.9-1127.3. HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{28}\text{F}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 594.1822, found 594.1814.

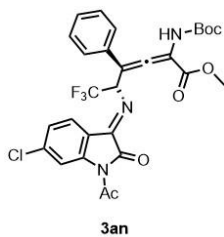


No	Retention Time	Area	% Area	Int Type
1	7.325	626.813	49.4	BB
2	8.322	642.796	50.6	BB

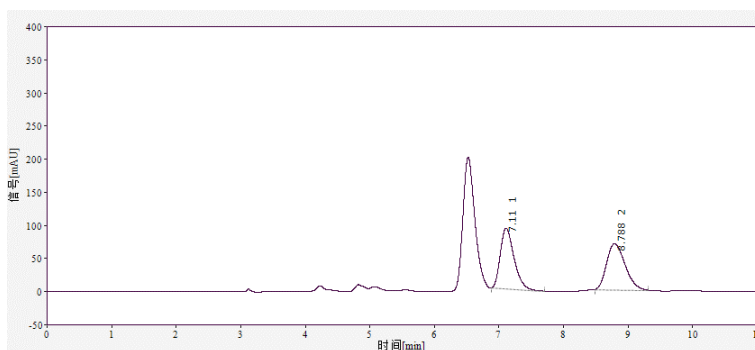


No	Retention Time	Area	% Area	Int Type
1	7.329	21474.496	91.9	BB
2	8.326	1892.464	8.1	BB

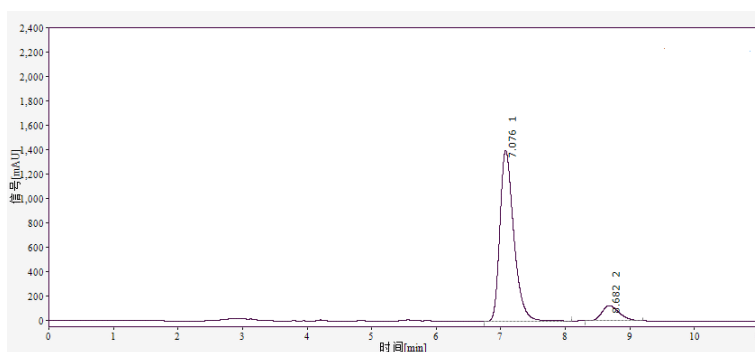
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-6-chloro-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 36.5 mg (0.12 mmol, 1.2 equiv) of **2n**, 49.6 mg (84% yield) of compound **3an** was obtained as a yellow solid, $[\alpha]_D^{25} = -25$ ($c = 1.0$, CHCl_3), Mp. = 75 - 76 °C. Dr (> 20:1) was determined by HPLC analysis. 80% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 7.1$ min, $t_{\text{minor}} = 8.7$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 (d, $J = 1.8$ Hz, 1H), 7.76 (dd, $J = 10.5, 7.8$ Hz, 3H), 7.46 – 7.36 (m, 2H), 7.37 – 7.29 (m, 1H), 7.27 (dd, $J = 8.2, 1.8$ Hz, 1H), 6.71 (q, $J = 6.6$ Hz, 1H), 6.10 (s, 1H), 3.31 (s, 3H), 2.69 (s, 3H), 1.43 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.2, 170.0, 163.8, 157.4, 153.0, 151.3, 143.5, 133.7, 129.3, 128.9, 128.6, 128.5, 127.9, 124.4 (q, $J_{\text{C-F}} = 283.4$ Hz), 123.9, 120.7, 120.3, 113.8, 105.7, 81.3, 61.8 (q, $J_{\text{C-F}} = 25.0$ Hz), 52.9, 28.1, 26.6. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.81. IR (cm^{-1}) ν 3424.6, 3129.9-2872.4, 1948.9, 1757.1-1720.0, 1494.6, 1275.4-1129.8. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{ClF}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 614.1276, found 614.1256.

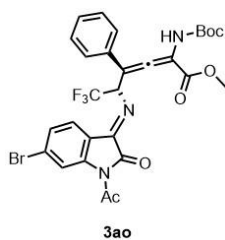


No	Retention Time	Area	% Area	Int Type
1	7.110	1361.739	49.5	BB
2	6.788	1387.869	50.5	BB

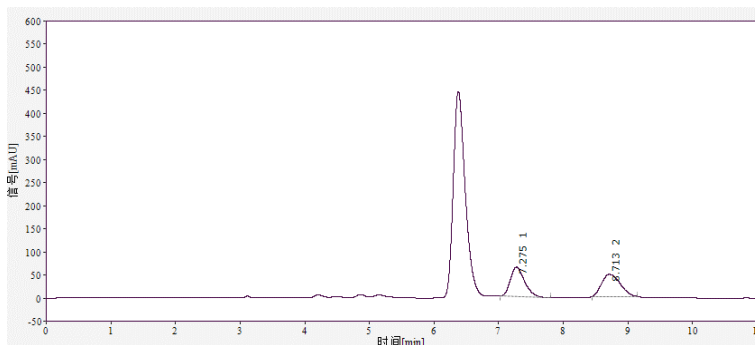


No	Retention Time	Area	% Area	Int Type
1	7.076	20942.787	90.1	BB
2	8.682	2297.349	9.9	BB

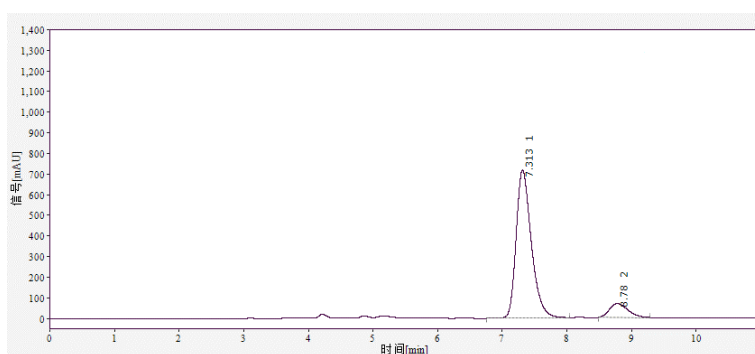
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-6-bromo-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 41.8 mg (0.12 mmol, 1.2 equiv) of **2o**, 52.7 mg (83% yield) of compound **3ao** was obtained as a yellow solid, $[\alpha]_D^{25} = -23$ ($c = 1.0$, CHCl_3), Mp. = 87 - 88 °C. Dr (> 20:1) was determined by HPLC analysis. 80% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 7.3$ min, $t_{\text{minor}} = 8.8$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.50 (s, 1H), 7.73 (dd, $J = 16.1, 7.9$ Hz, 3H), 7.52 – 7.36 (m, 3H), 7.33 (t, $J = 7.3$ Hz, 1H), 6.70 (q, $J = 6.6$ Hz, 1H), 6.09 (s, 1H), 3.31 (s, 3H), 2.69 (s, 3H), 1.43 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.2, 170.1, 170.0, 163.8, 157.5, 152.9, 151.3, 143.6, 140.4, 133.7, 128.6, 128.5, 127.9, 126.3, 124.5 (q, $J_{\text{C-F}} = 281.6$ Hz), 123.8, 120.3, 117.5, 113.9, 105.7, 81.3, 61.7 (q, $J_{\text{C-F}} = 30.3$ Hz), 52.9, 29.7, 28.1, 26.6. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.81. IR (cm^{-1}) ν 3423.6, 3128.1-2872.6, 1948.0, 1755.4-1720.2, 1493.7, 1274.8-1129.3, 923.5, 766.1, 606.8. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{BrF}_3\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 658.0771, found 658.0759.

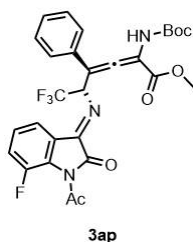


No	Retention Time	Area	% Area	Int Type
1	7.275	974.413	50.6	BB
2	8.713	950.180	49.4	BB

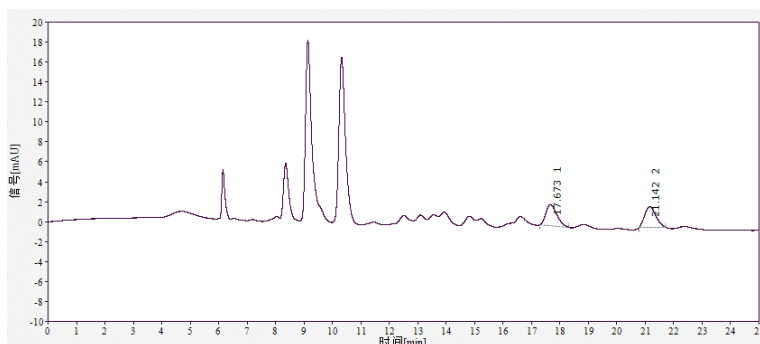


No	Retention Time	Area	% Area	Int Type
1	7.313	11700.736	89.8	BB
2	8.780	1335.122	10.2	BB

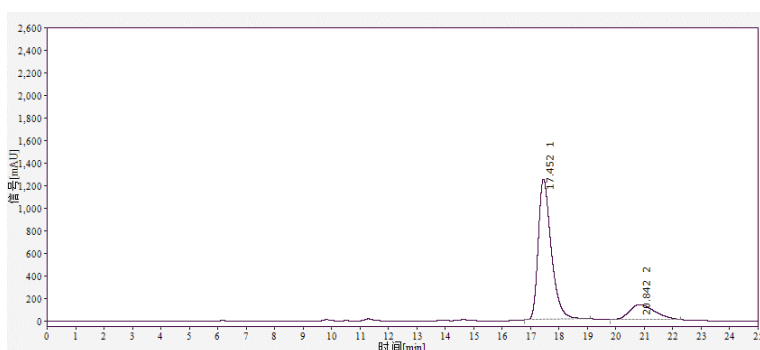
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-7-fluoro-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 34.6 mg (0.12 mmol, 1.2 equiv) of **2p**, 46.0 mg (80% yield) of compound **3ap** was obtained as a yellow solid, $[\alpha]_D^{25} = -51$ ($c = 1.0$, CHCl_3), Mp. = 65 - 66 °C. Dr (> 20:1) was determined by HPLC analysis. 66% ee was determined by HPLC analysis (Daicel Chiralpak IC column, 245 nm, hexane/2-propanol 90:10, 0.5 mL/min). Retention time: $t_{\text{major}} = 17.5$ min, $t_{\text{minor}} = 20.8$ min. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 6.7$ Hz, 1H), 7.40 (d, $J = 7.9$ Hz, 2H), 7.38 – 7.21 (m, 4H), 6.72 (q, $J = 6.6$ Hz, 1H), 6.09 (s, 1H), 3.30 (s, 3H), 2.71 (s, 3H), 1.44 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 205.3, 167.7, 163.8, 157.1, 153.7, 153.7, 151.3, 150.9, 148.4, 133.7, 129.1, 129.0, 128.6, 127.9, 127.4, 127.3, 125.2, 124.4 (q, $J_{\text{C-F}} = 282.4$ Hz), 122.9, 122.7, 118.9, 118.9, 113.8, 105.8, 81.3, 61.7 (q, $J_{\text{C-F}} = 28.4$ Hz), 52.9, 29.7, 28.1, 26.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.89, -110.16. IR (cm^{-1}) ν 3424.6, 3058.7-2873.2, 1948.5, 1719.4, 1494.1, 1294.5-1128.7, 1046.9-1020.9, 802.5, 765.6, 698.1. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{F}_4\text{N}_3\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 598.1572, found 598.1567.



No	Retention Time	Area	% Area	Int Type
1	17.673	57.358	50.3	BB
2	21.142	56.664	49.7	BB

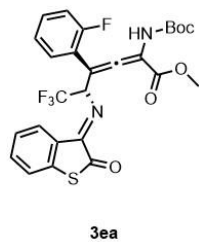


No	Retention Time	Area	% Area	Int Type
1	17.452	39498.113	82.9	BB
2	20.842	8156.178	17.1	BB

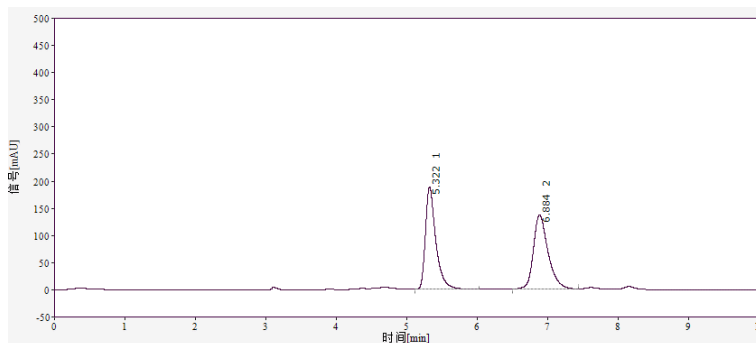
8. Gram-scale asymmetric cycloaddition for the synthesis of **3ea** and

3ah

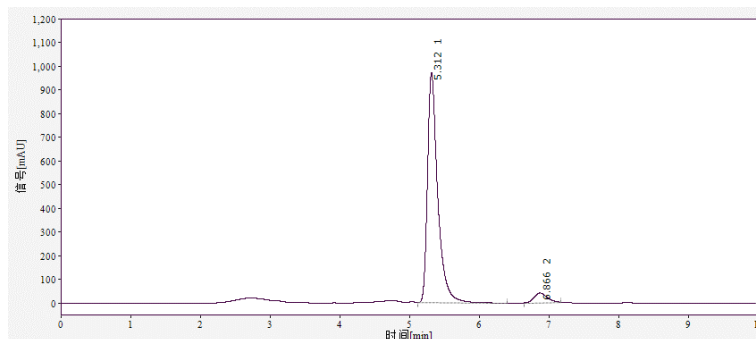
Methyl (3*S*,5*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-(2-fluorophenyl)-5-(((*E*)-2-oxobenzo[*b*]thiophen-3(2*H*)-ylidene)amino)hexa-2,3-dienoate



From 0.61 g (2 mmol, 1.0 equiv) of **1e** and 0.59 g (2.4 mmol, 1.2 equiv) of **2a**, 0.66 g (60% yield) of compound **3ea** was obtained as a yellow solid. Dr (> 20:1) was determined by HPLC analysis. 90% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 5.3$ min, $t_{\text{minor}} = 6.9$ min.

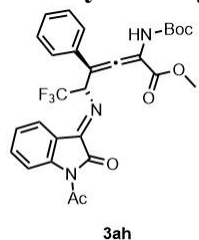


No	Retention Time	Area	% Area	Int Type
1	5.322	1932.564	49.5	BB
2	6.884	1968.281	50.5	BB

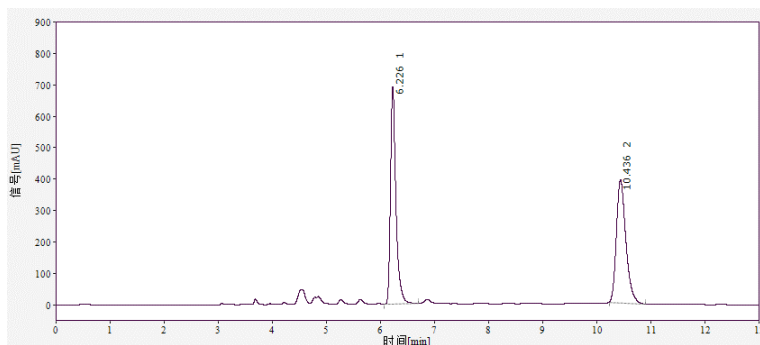


No	Retention Time	Area	% Area	Int Type
1	5.312	9863.283	94.9	BB
2	6.866	527.449	5.1	BB

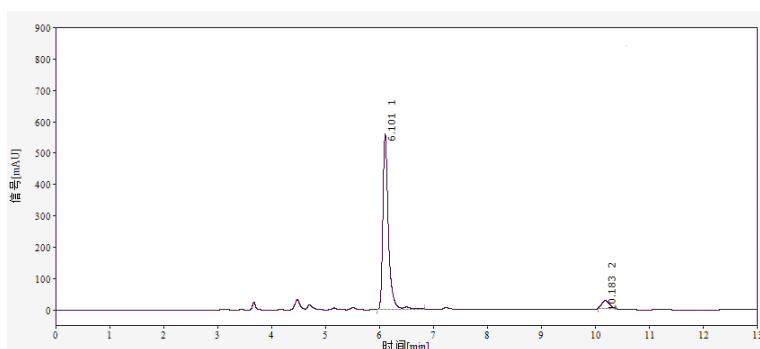
Methyl (3*S*,5*S*)-5-(((*E*)-1-acetyl-2-oxoindolin-3-ylidene)amino)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluoro-4-phenylhexa-2,3-dienoate



From 0.57 g (2 mmol, 1.0 equiv) of **1a** and 0.65 g (0.12 mmol, 1.2 equiv) of **2h**, 0.78 g (70% yield) of compound **3ah** was obtained as a yellow solid. Dr (> 20:1) was determined by HPLC analysis. 88% ee was determined by HPLC analysis (Daicel Chiralpak IA-3 column, 245 nm, hexane/2-propanol 90:10, 1.0 mL/min). Retention time: $t_{\text{major}} = 6.2$ min, $t_{\text{minor}} = 10.4$ min.

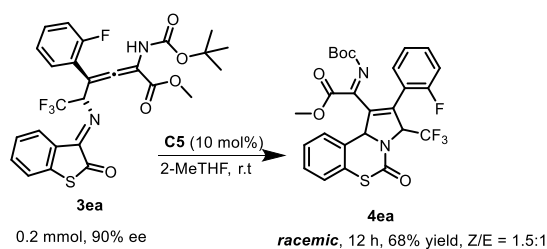


No	Retention Time	Area	% Area	Int Type
1	6.226	4878.169	50.4	BB
2	10.436	4792.972	49.6	BB

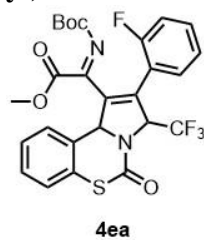


No	Retention Time	Area	% Area	Int Type
1	6.101	3968.968	94.2	BB
2	10.183	243.820	5.8	BB

9. Synthetic transformation of 3ea



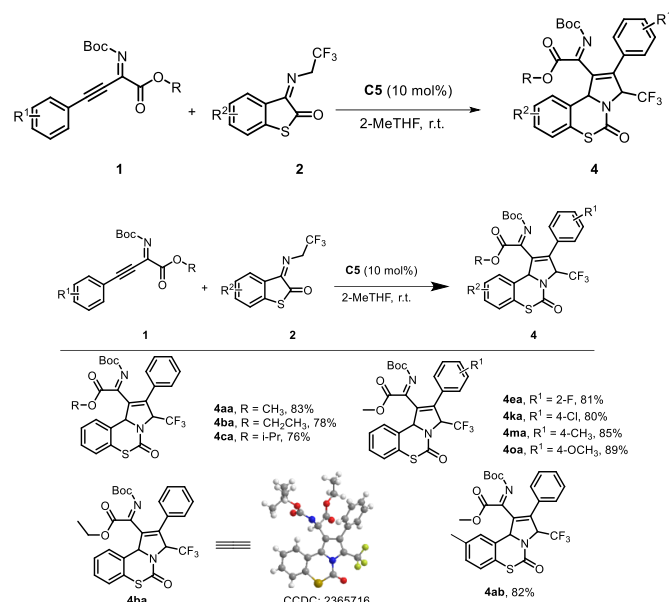
Methyl (Z)-2-((tert-butoxycarbonyl)imino)-2-(2-(2-fluorophenyl)-5-oxo-3-(trifluoromethyl)-3,10b-dihydro-5H-benzo[e]pyrrolo[1,2-c][1,3]thiazin-1-yl)acetate



From 30.5 mg (0.1 mmol, 1.0 equiv) of **1e** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 44.6 mg (81% yield) of compound **4ea** was obtained as a white solid, Mp. = 188 - 189 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 6.4, 3.0 Hz, 1H), 7.50 – 7.41 (m, 5H), 7.15 (t, *J* = 9.0 Hz, 2H), 5.83 (d, *J* = 9.0 Hz, 1H), 5.41 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.41 (s, 3H), 1.47 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.7, 161.2, 159.6, 158.8, 155.1, 134.0, 132.2, 131.4, 129.1, 127.6, 125.2, 124.8 (q, *J*_{C-F} = 348.0 Hz), 124.1, 121.5, 120.2, 119.1, 115.8, 80.6, 53.0, 52.7, 28.2, 25.9. ¹⁹F NMR (376 MHz,

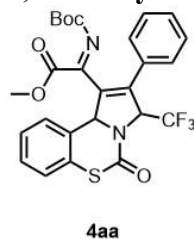
CDCl₃) δ -52.97, -112.42. IR (cm⁻¹) ν 3439.5, 3140.52.8-2931.8, 1727.6-1710.4, 1489.3, 1368.0-1222.3, 1168.5-1143.7, 934.7, 761.9. HRMS (ESI) m/z calcd for C₂₆H₂₃F₃N₂NaO₅S [M+Na]⁺: 467.0848, found 467.084

10 One-pot synthesis of derivatized products 4



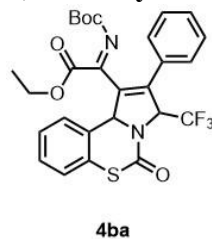
Scheme S3 The scope of derivatized products and the single crystal structure of 4ba.

Methyl (*Z*)-2-((*tert*-butoxycarbonyl)imino)-2-(5-oxo-2-phenyl-3-(trifluoromethyl)-3,10b-dihydro-5*H*-benzo[*e*]pyrrolo[1,2-*c*][1,3]thiazin-1-yl)acetate



From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 44.2 mg (83% yield) of compound **4aa** was obtained as a white solid, Mp. = 164 - 165 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 7.2 Hz, 1H), 7.4 (ddd, J = 16.3, 7.0, 3.7 Hz, 5H), 7.33 (d, J = 7.0 Hz, 1H), 7.17 - 7.10 (m, 1H), 5.91 (d, J = 8.8 Hz, 1H), 4.99 (d, J = 8.9 Hz, 1H), 3.59 (s, 3H), 1.41 (s, 9H), 0.98 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 170.2, 159.7, 154.8, 135.1, 135.1, 133.4, 131.5, 129.5, 129.0, 129.0, 128.5, 128.3, 127.9, 127.7, 127.5, 126.5, 125.2, 123.0, 121.7, 121.2, 120.6 (q, J_{C-F} = 270.5 Hz), 118.3, 118.0, 108.2, 80.6, 52.9, 50.6, 45.5, 34.4, 28.2, 25.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -52.14. IR (cm⁻¹) ν 3440.7, 3140.5-2932.0, 1724.5-1711.7, 1489.2, 1313.2-1168.5, 1172.1-1135.3, 935.7. HRMS (ESI) m/z calcd for C₂₆H₂₃F₃N₂NaO₅S [M+Na]⁺: 555.1172, found 555.1191.

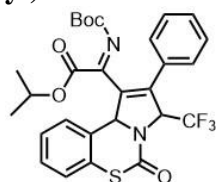
Ethyl (*Z*)-2-((*tert*-butoxycarbonyl)imino)-2-(5-oxo-2-phenyl-3-(trifluoromethyl)-3,10b-dihydro-5*H*-benzo[*e*]pyrrolo[1,2-*c*][1,3]thiazin-1-yl)acetate



From 30.1 mg (0.1 mmol, 1.0 equiv) of **1b** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 42.6 mg (78% yield) of compound **4ba** was obtained as a white solid, Mp. = 159 - 160 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.21 - 8.11 (m, 1H), 7.52 - 7.38 (m, 5H), 7.34 (d, J = 6.2 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 5.87 (d, J = 8.6 Hz, 1H), 4.96 (d, J = 8.7 Hz, 1H), 4.06 (p, J = 6.9 Hz, 2H), 1.39 (s, 9H), 1.17 (t, J =

7.1 Hz, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.8, 159.7, 154.7, 135.2, 133.3, 131.6, 129.7, 129.5, 129.0, 128.9, 128.4, 128.3, 127.8, 127.5, 125.2, 121.8, 121.4, 120.6 (q, $J_{\text{C-F}} = 271.1$ Hz), 118.3, 117.9, 80.4, 62.4, 50.7, 28.2, 14.0. ^{19}F NMR (376 MHz, CDCl_3) δ -52.11. IR (cm^{-1}) ν 3431.2, 3078.2-2931.5, 1714.4, 1487.9, 1174.3-1133.3. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1312.

Isopropyl (Z)-2-((tert-butoxycarbonyl)imino)-2-(5-oxo-2-phenyl-3-(trifluoromethyl)-3,10b-dihydro-5H-benzo[e]pyrrolo[1,2-c][1,3]thiazin-1-yl)acetate



4ca

From 31.5 mg (0.1 mmol, 1.0 equiv) of **1c** and 45.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 42.6 mg (76% yield) of compound **4ca** was obtained as a white solid, Mp. = 200 - 201 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.22 – 8.08 (m, 1H), 7.60 – 7.38 (m, 5H), 7.38 – 7.31 (m, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 5.82 (d, $J = 8.4$ Hz, 1H), 4.94 (dq, $J = 12.4, 6.1$ Hz, 2H), 1.37 (s, 9H), 1.18 (t, $J = 5.6$ Hz, 7H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 159.7, 154.6, 135.3, 133.2, 131.7, 129.8, 128.9, 128.8, 128.6 (q, $J_{\text{C-F}} = 167.3$ Hz), 128.3, 127.5, 125.2, 121.8, 121.6, 119.3, 118.2, 117.8, 80.3, 70.6, 50.9, 28.2, 25.9, 21.6, 21.6. ^{19}F NMR (376 MHz, CDCl_3) δ -52.07. IR (cm^{-1}) ν 3371.3, 3307.4, 3006.2-2930.5, 1755.1-1694.2, 1153.0, 928.9. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{27}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 583.1485, found 583.1492.

Methyl (Z)-2-((tert-butoxycarbonyl)imino)-2-(2-(4-chlorophenyl)-5-oxo-3-(trifluoromethyl)-3,10b-dihydro-5H-benzo[e]pyrrolo[1,2-c][1,3]thiazin-1-yl)acetate



4ka

From 32.1 mg (0.1 mmol, 1.0 equiv) of **1k** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 45.3 mg (80% yield) of compound **4ka** was obtained as a white solid, Mp. = 143 - 144 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.51 – 7.29 (m, 5H), 7.20 (d, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.2$ Hz, 1H), 5.85 – 5.70 (m, 1H), 4.95 (d, $J = 8.2$ Hz, 1H), 3.54 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.2, 159.6, 154.6, 135.2, 134.0, 133.4, 131.0, 130.9, 130.0, 129.1, 128.8, 128.6, 127.9, 127.7, 127.5, 125.3, 121.6, 120.9, 120.5 (q, $J_{\text{C-F}} = 271.1$ Hz), 118.5, 118.1, 80.7, 53.1, 50.6, 28.2, 25.9. ^{19}F NMR (376 MHz, CDCl_3) δ -52.04. IR (cm^{-1}) ν 3436.2, 3138.0-2933.4, 1712.4, 1486.8, 1175.2-1133.6, 934.7. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{22}\text{ClF}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 589.0782, found 589.0775.

Methyl (Z)-2-((tert-butoxycarbonyl)imino)-2-(5-oxo-2-(p-tolyl)-3-(trifluoromethyl)-3,10b-dihydro-5H-benzo[e]pyrrolo[1,2-c][1,3]thiazin-1-yl)acetate



4ma

From 30.1 mg (0.1 mmol, 1.0 equiv) of **1m** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 46.4 mg (85% yield) of compound **4ma** was obtained as a white solid, Mp. = 178 - 179 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 7.2$ Hz, 1H), 7.41 – 7.29 (m, 3H), 7.25 – 7.10 (m, 4H), 6.93 (d, $J = 5.7$ Hz, 1H), 5.84 (d, $J = 8.8$ Hz, 1H), 4.93 (d, $J = 8.8$ Hz, 1H), 3.52 (s, 3H), 2.35 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.2, 159.7, 154.8, 138.9, 135.2, 133.3, 129.3, 129.1, 129.0, 128.4, 127.9, 127.7, 127.5, 125.2, 121.7, 121.4, 120.6 (q, $J_{\text{C-F}} = 271.0$ Hz), 118.4, 118.0, 80.5, 52.9, 50.6, 29.7,

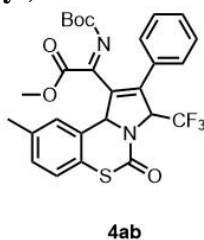
28.2, 21.4. ^{19}F NMR (376 MHz, CDCl_3) δ -52.21. IR (cm^{-1}) ν 3314.8, 3066.1-2873.2, 1759.8-1696.1, 1176.1-1131.4, 928.8. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1340.

Methyl (Z)-2-((tert-butoxycarbonyl)imino)-2-(2-(4-methoxyphenyl)-5-oxo-3-(trifluoromethyl)-3,10b-dihydro-5H-benzo[e]pyrrolo[1,2-c][1,3]thiazin-1-yl)acetate

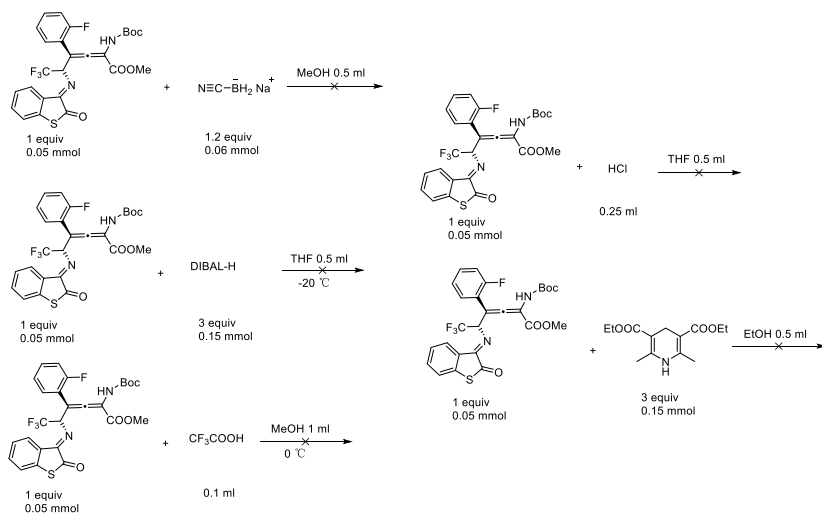


From 31.7 mg (0.1 mmol, 1.0 equiv) of **1o** and 29.4 mg (0.12 mmol, 1.2 equiv) of **2a**, 50.0 mg (89% yield) of compound **4oa** was obtained as a white solid, Mp. = 197 - 198 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.13 - 7.97 (m, 1H), 7.51 - 7.11 (m, 5H), 7.07 - 6.81 (m, 3H), 5.83 (d, J = 8.7 Hz, 1H), 4.95 (d, J = 8.8 Hz, 1H), 3.79 (s, 3H), 3.53 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3, 160.0, 159.7, 154.8, 135.1, 133.3, 130.7, 129.0, 127.9, 127.7, 127.5, 125.2, 123.4, 121.7, 121.5, 120.6 (q, $J_{\text{C-F}}$ = 270.9 Hz), 118.5, 118.1, 114.0, 113.9, 80.5, 55.3, 53.0, 50.6, 29.7, 28.2. ^{19}F NMR (376 MHz, CDCl_3) δ -52.27. IR (cm^{-1}) ν 3317.1, 3068.4-2842.0, 1757.2-1696.0, 1251.0, 1178.6-1153.7, 927.8. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 585.1278, found 585.1266.

Methyl (Z)-2-((tert-butoxycarbonyl)imino)-2-(9-methyl-5-oxo-2-phenyl-3-(trifluoromethyl)-3,10b-dihydro-5H-benzo[e]pyrrolo[1,2-c][1,3]thiazin-1-yl)acetate

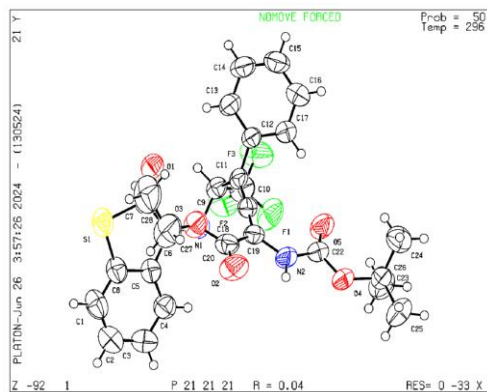


From 28.7 mg (0.1 mmol, 1.0 equiv) of **1a** and 34.1 mg (0.12 mmol, 1.2 equiv) of **2b**, 44.8 mg (82% yield) of compound **4ab** was obtained as a white solid, Mp. = 179 - 180 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.3 Hz, 1H), 7.66 - 7.37 (m, 3H), 7.33 (d, J = 7.0 Hz, 1H), 7.29 - 7.18 (m, 3H), 7.13 (d, J = 5.3 Hz, 1H), 5.89 (d, J = 8.8 Hz, 1H), 4.98 (d, J = 8.8 Hz, 1H), 3.58 (s, 3H), 2.41 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3, 159.9, 154.8, 139.7, 135.1, 133.6, 131.6, 129.5, 129.0, 128.9, 128.5, 128.3, 127.7, 127.3, 126.5, 125.3, 123.0, 120.7 (q, $J_{\text{C-F}}$ = 270.5 Hz), 120.4, 119.0, 117.9, 117.6, 108.2, 80.5, 52.9, 50.6, 45.5, 34.4, 28.2, 25.9, 21.1. ^{19}F NMR (376 MHz, CDCl_3) δ -52.08. IR (cm^{-1}) ν 3395.5, 3031.1-2871.3, 1717.4-1694.1, 1267.9-1249.0, 1153.3-1131.1, 934.5, 772.2, 699.9. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 569.1328, found 569.1321.

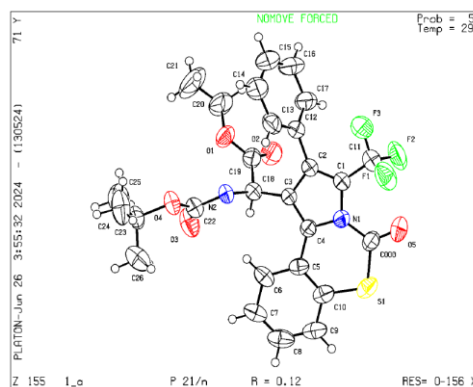


Scheme S4 Failed derivatization of **3ea**

11. X-ray Structures of Compounds **3ba** and **4ba**

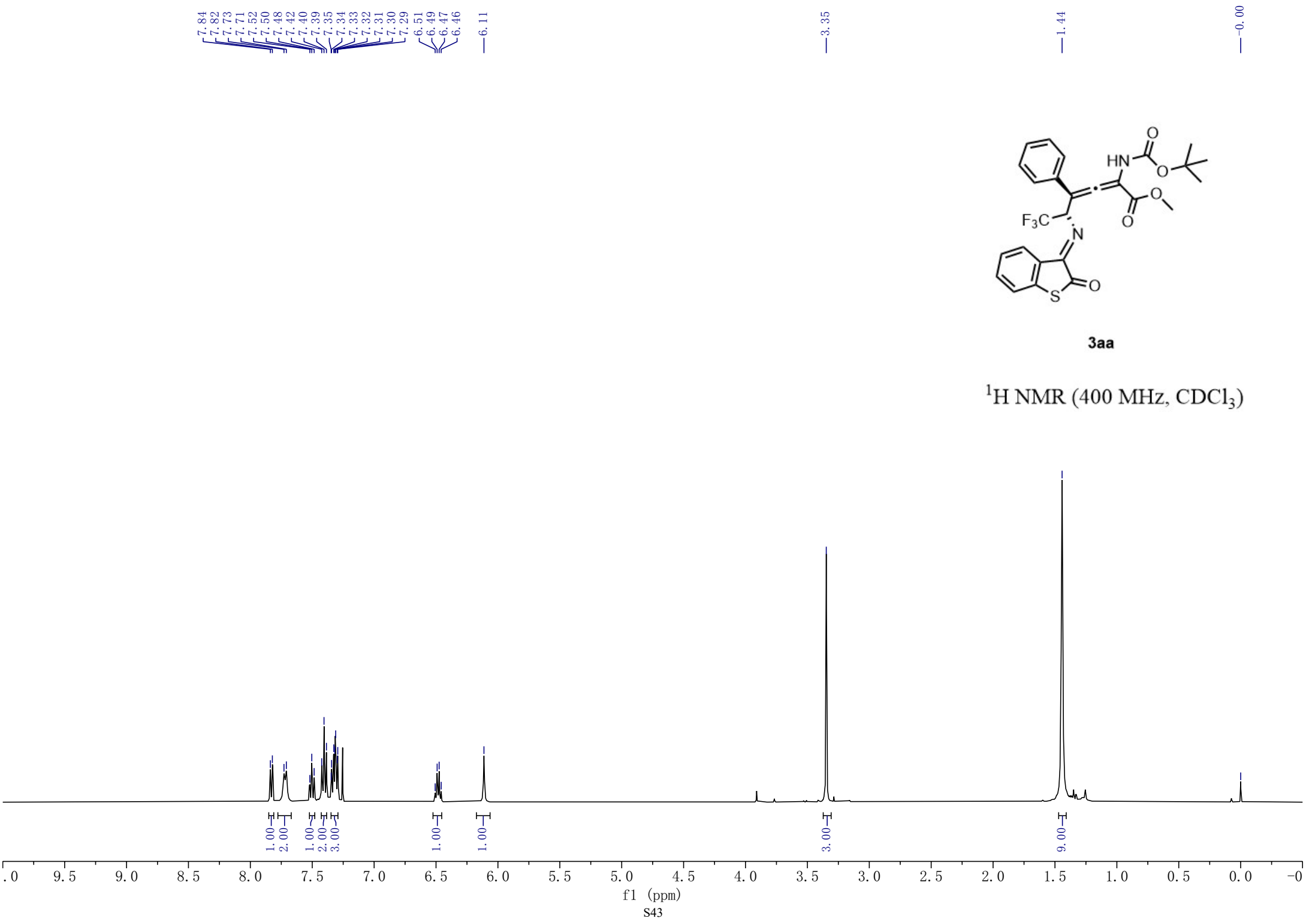


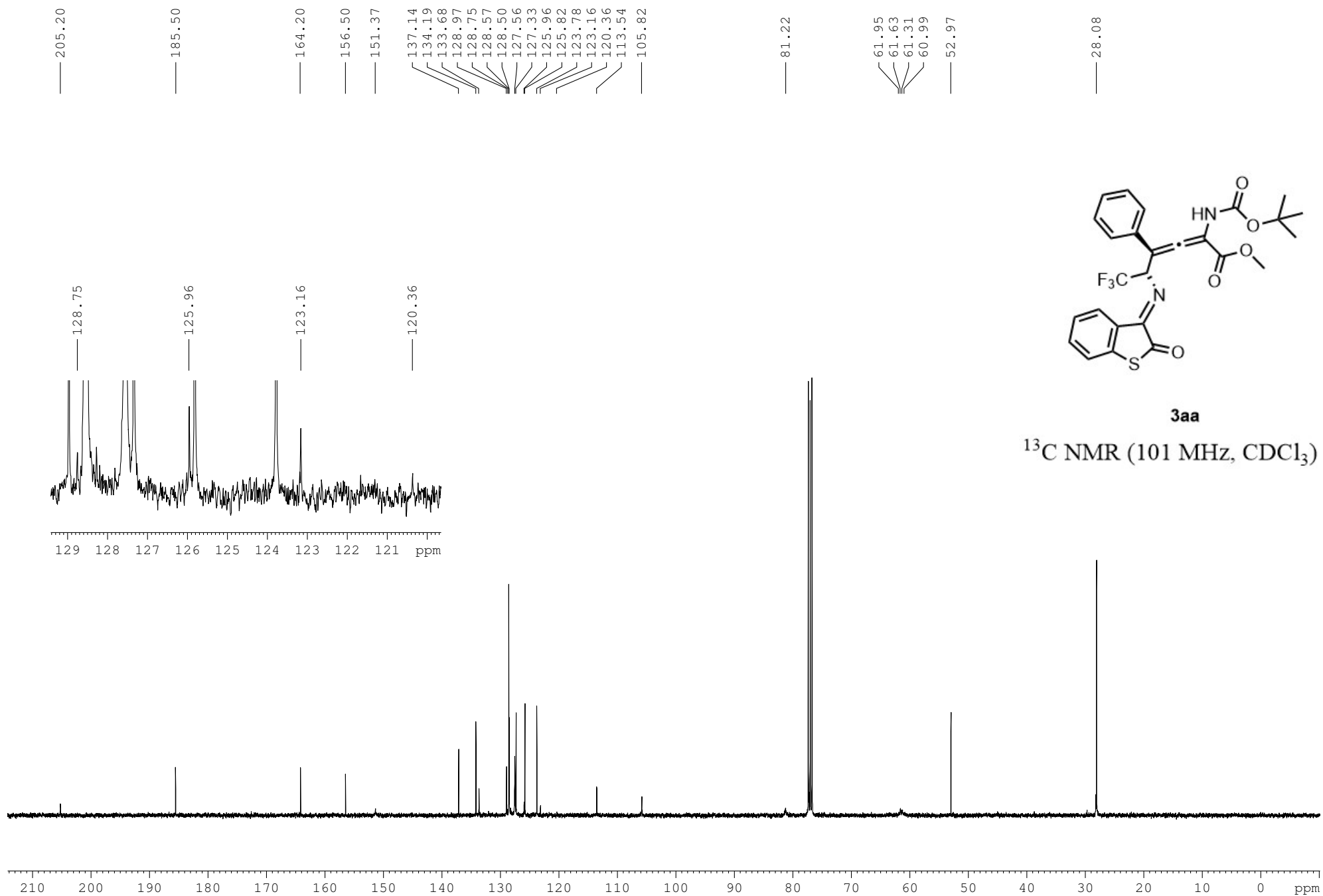
3ba
CCDC: 2365716



4ba
CCDC: 2365716

12. Copies of ¹H, ¹⁹F, ¹³C NMR and IR Spectra

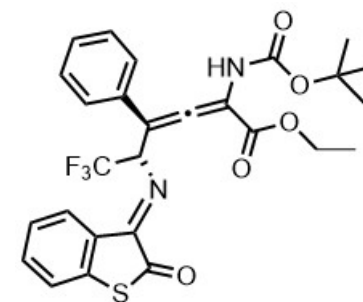




7.84
7.82
7.70
7.68
7.52
7.50
7.48
7.41
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7.37
7.33
7.32
7.31
7.29
6.57
6.56
6.54
6.52
6.13

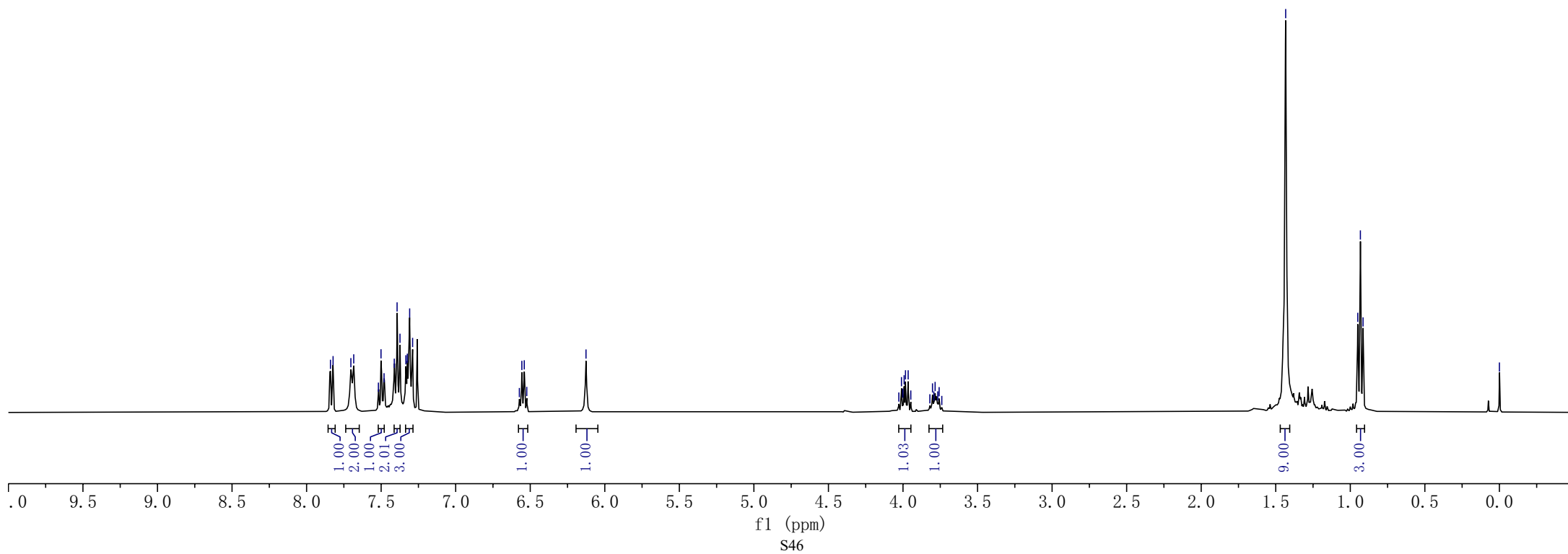
4.03
4.01
4.00
3.99
3.98
3.97
3.95
3.82
3.80
3.79
3.78
3.77
3.76
3.74

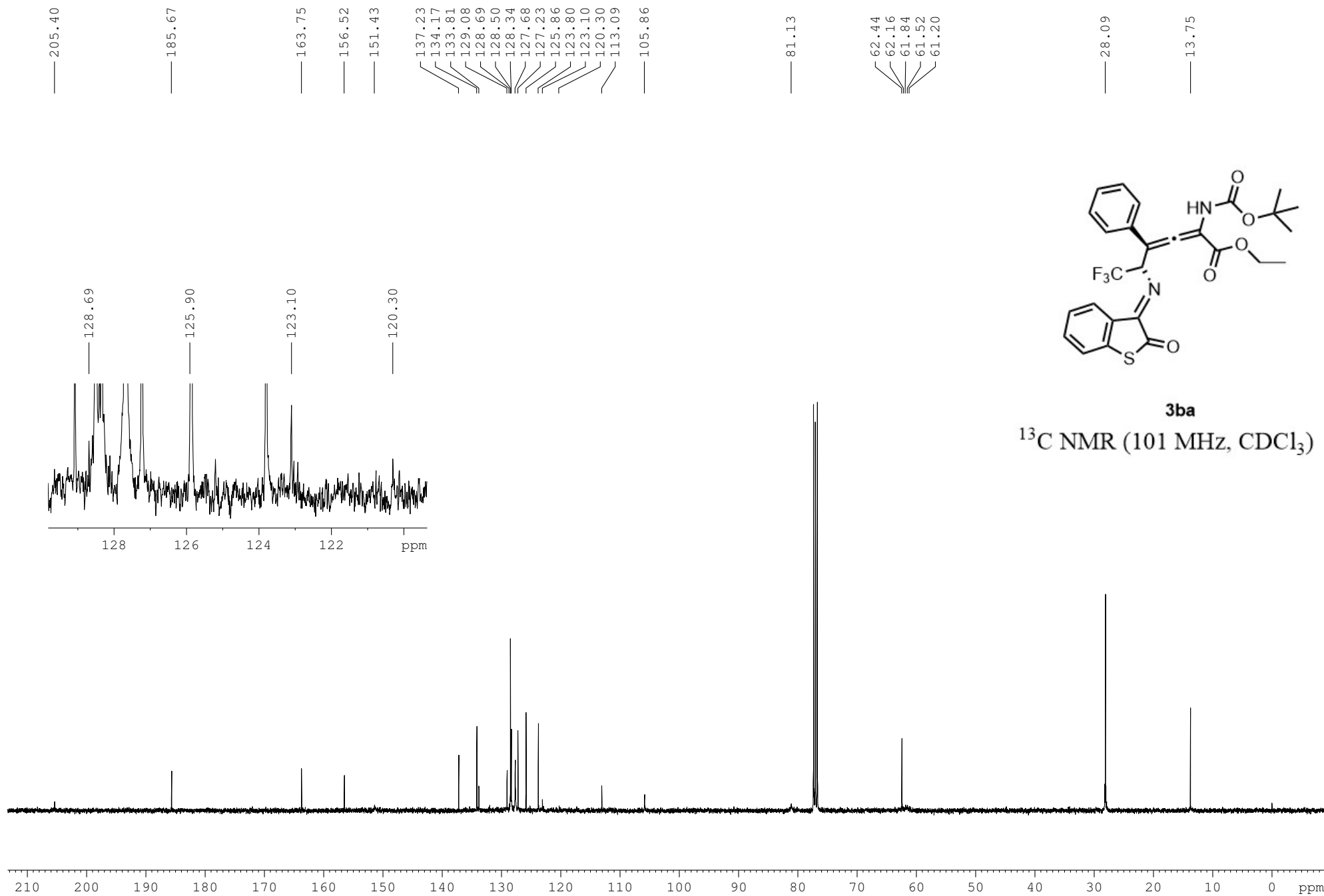
1.43
0.95
0.93
0.91
-0.00



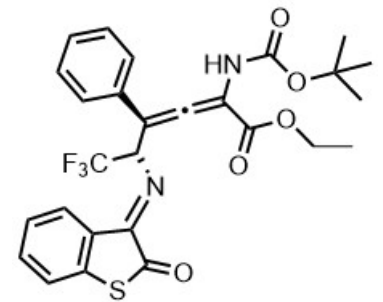
3ba

¹H NMR (400 MHz, CDCl₃)



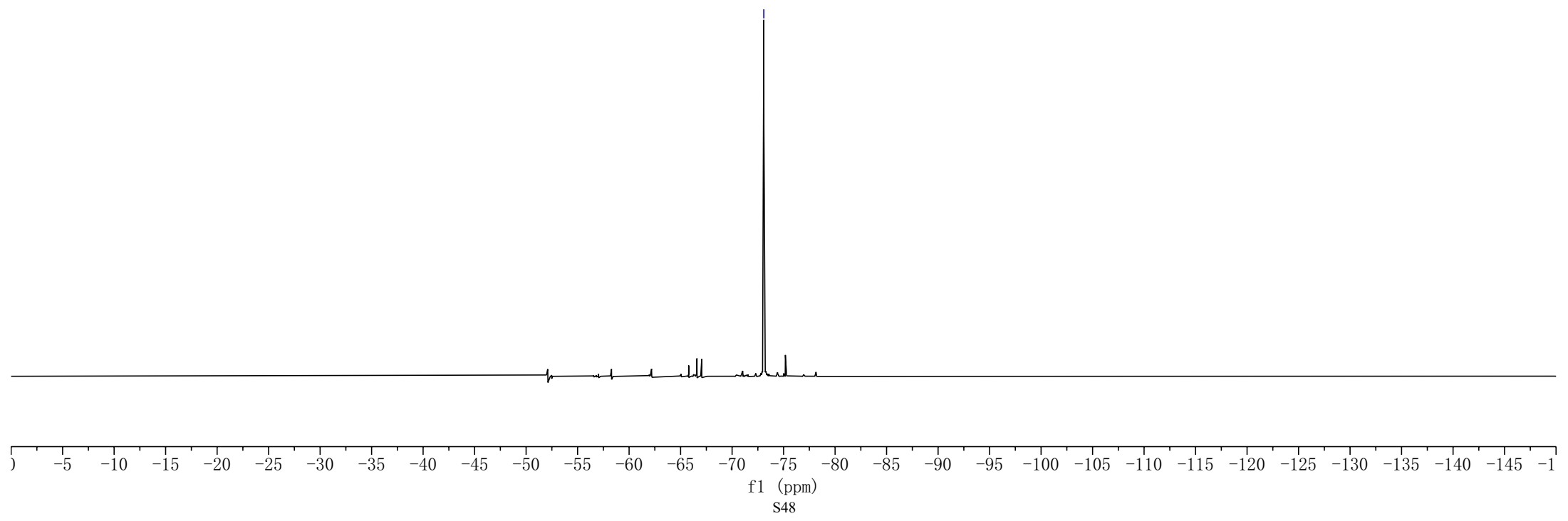


-73.08



3ba

¹⁹F NMR (376 MHz, CDCl₃)



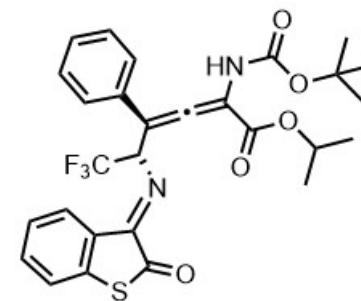
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7.72
7.56
7.54
7.43
7.42
7.41
7.40
7.39
7.38
7.23
7.22
7.21
7.20
7.19
7.16
7.14
6.42
6.41
6.39
6.37
— 6.03

— 3.24

2.61
2.59
2.57
2.55

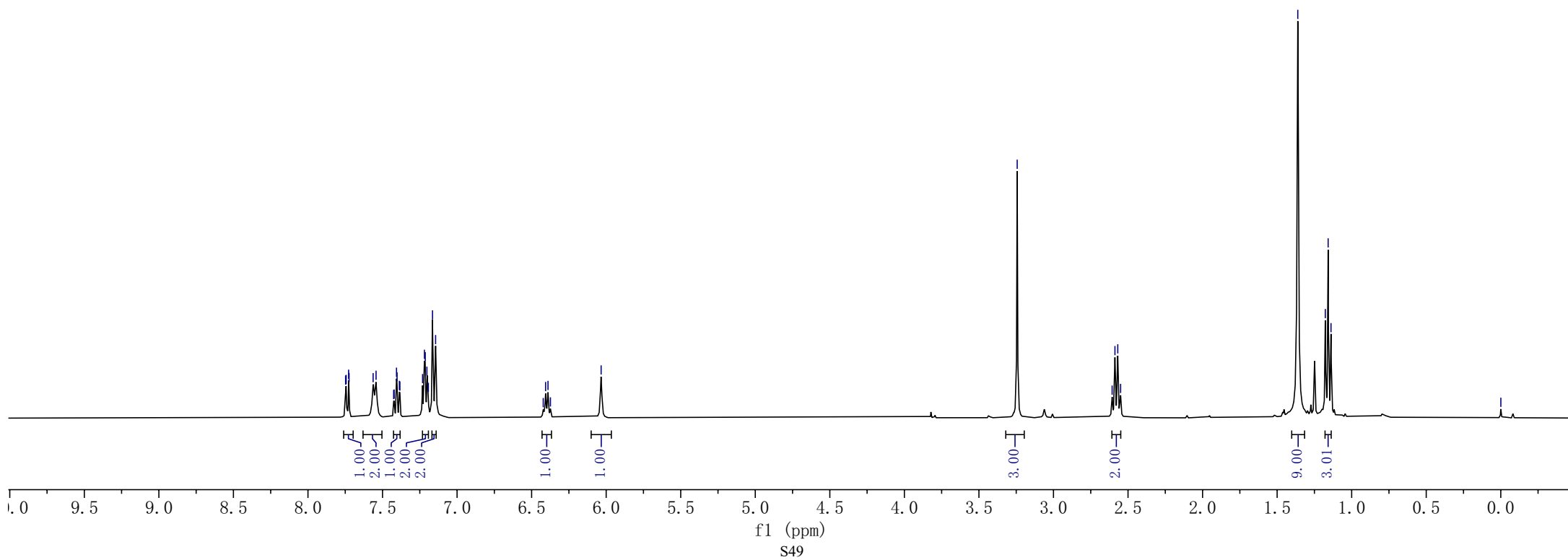
1.36
1.18
1.16
1.14

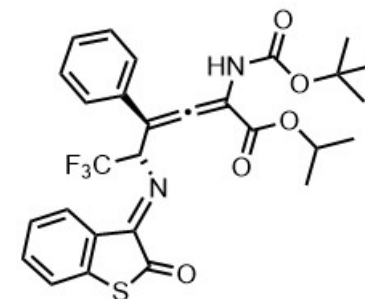
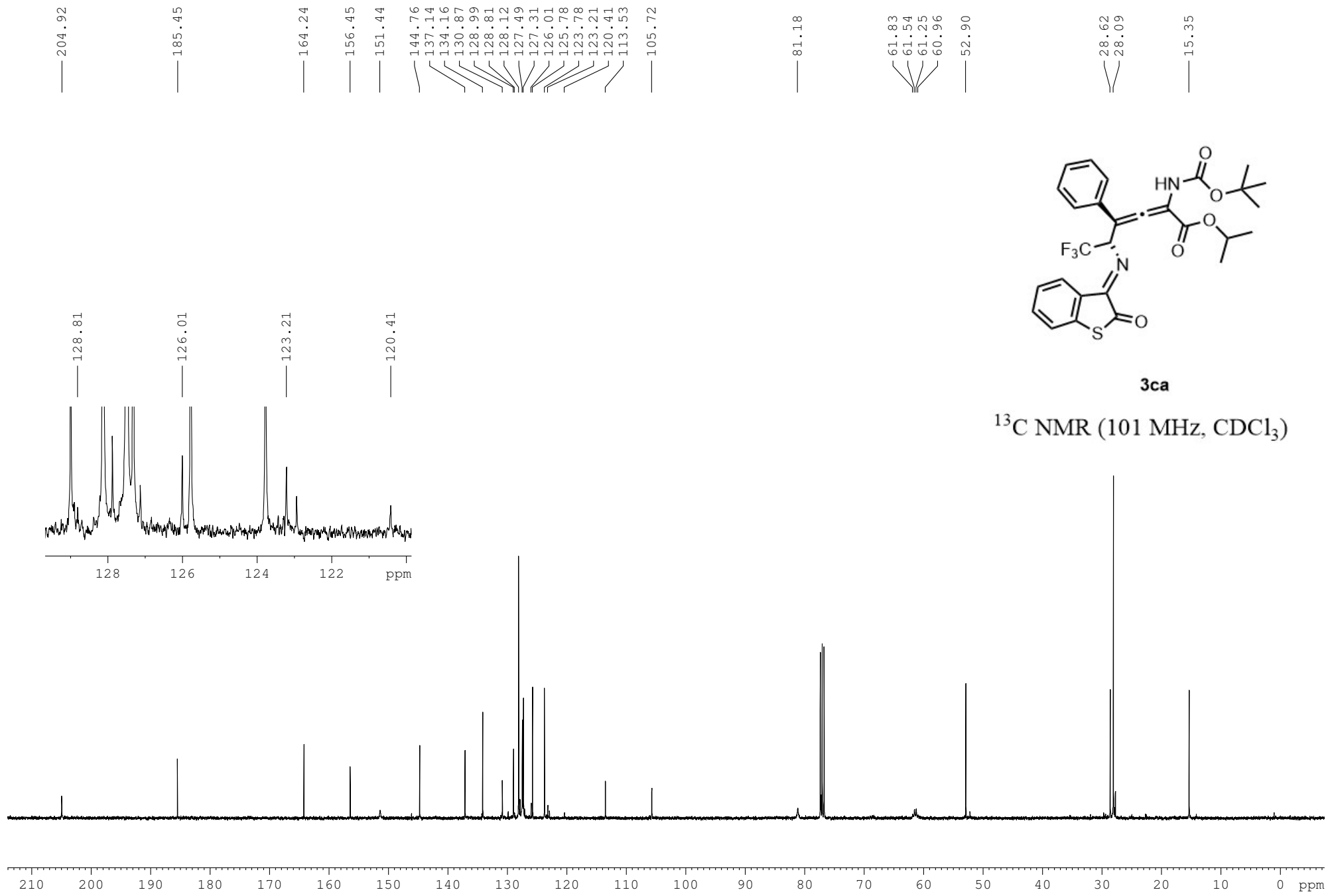
— 0.00



3ca

¹H NMR (400 MHz, CDCl₃)





3ca

¹³C NMR (101 MHz, CDCl₃)

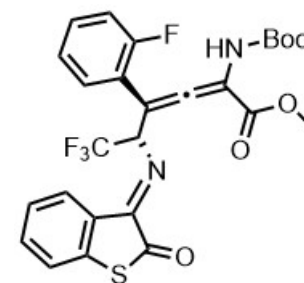
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7.33
7.31
7.30
7.29
7.28
7.18
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7.09
7.08
7.06
6.69
6.67
6.65
6.64

6.08

3.45

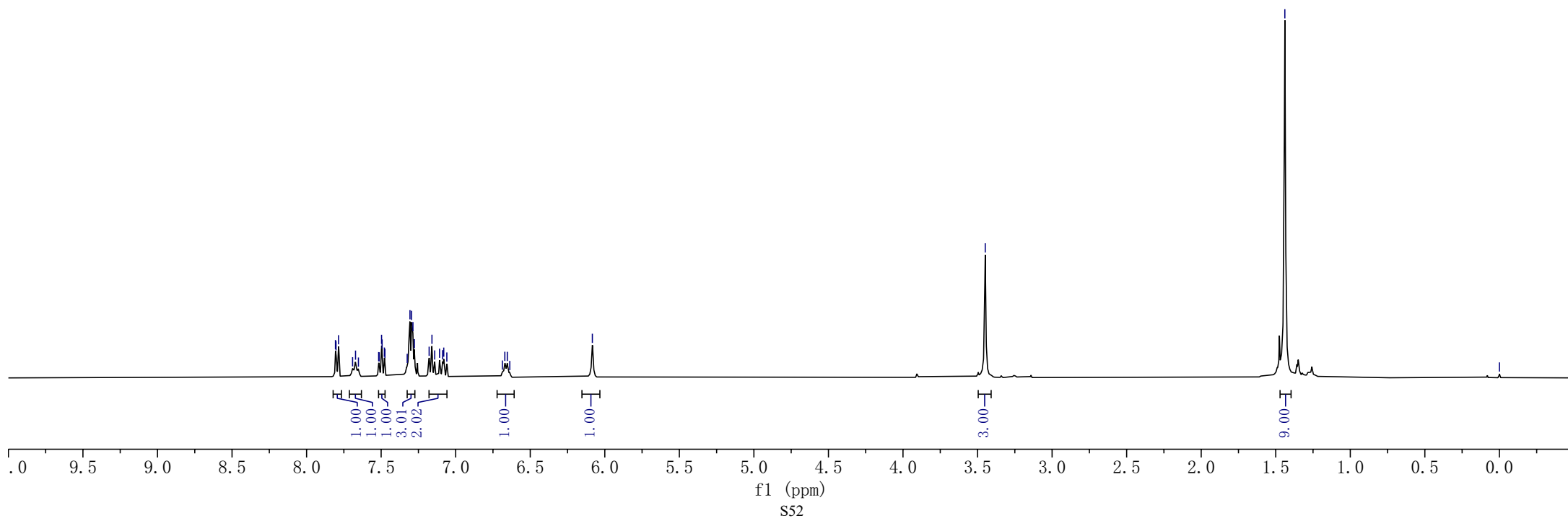
1.44

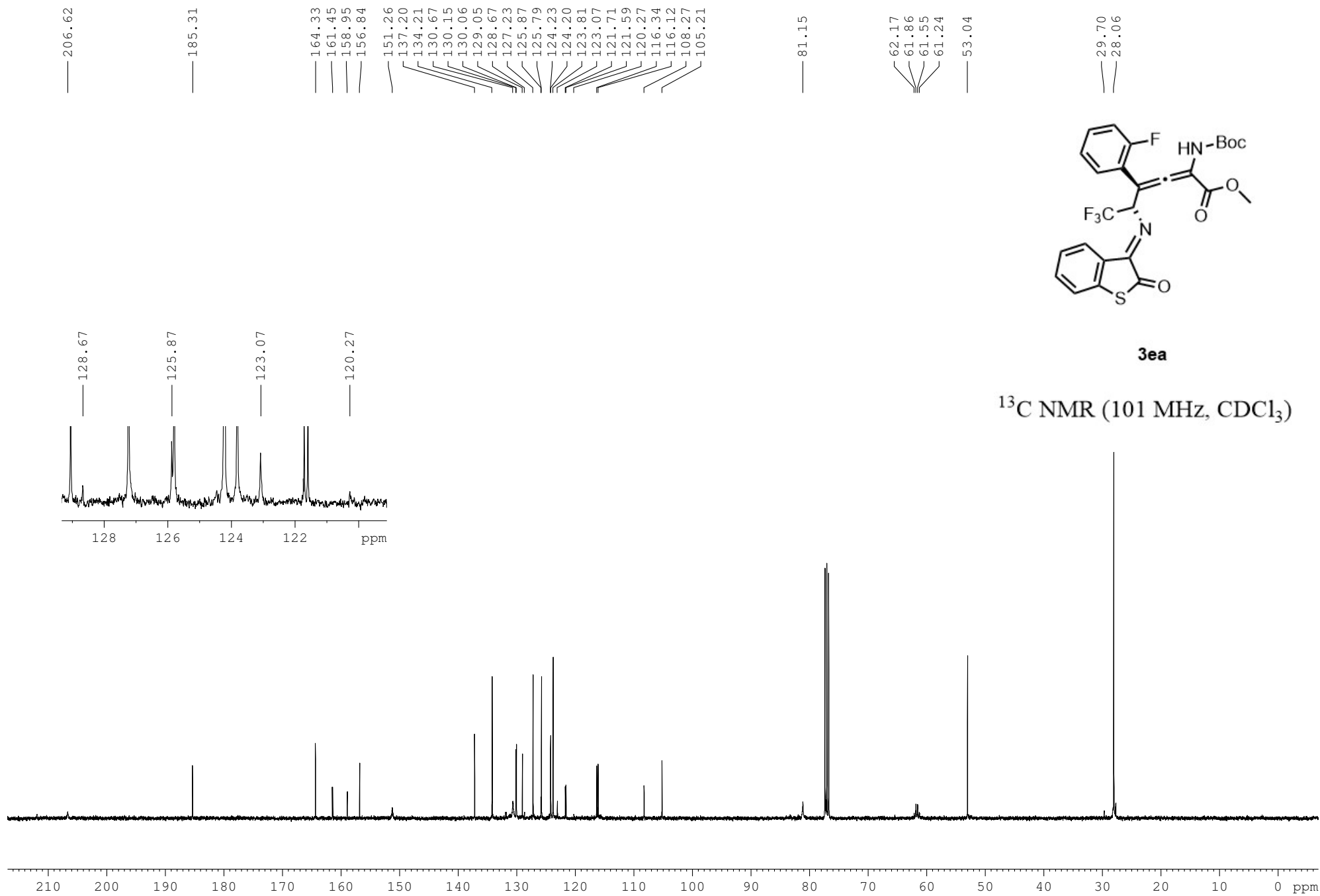
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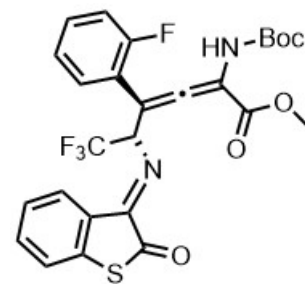


3ea

¹H NMR (400 MHz, CDCl₃)

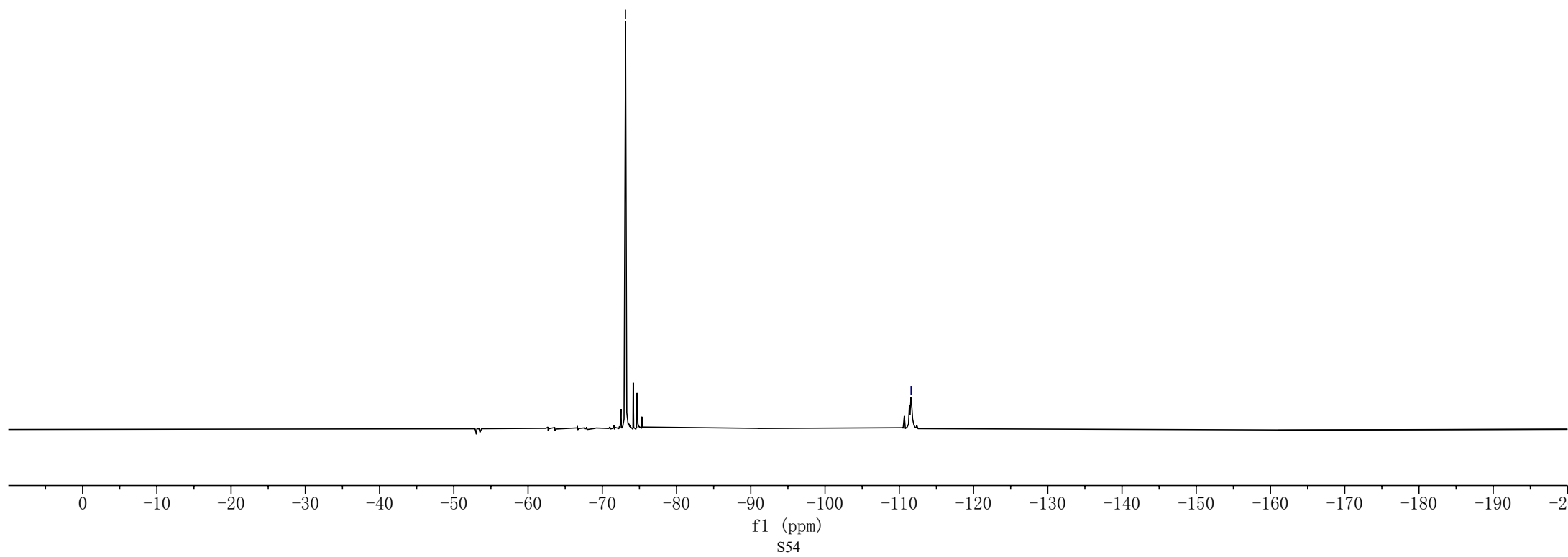


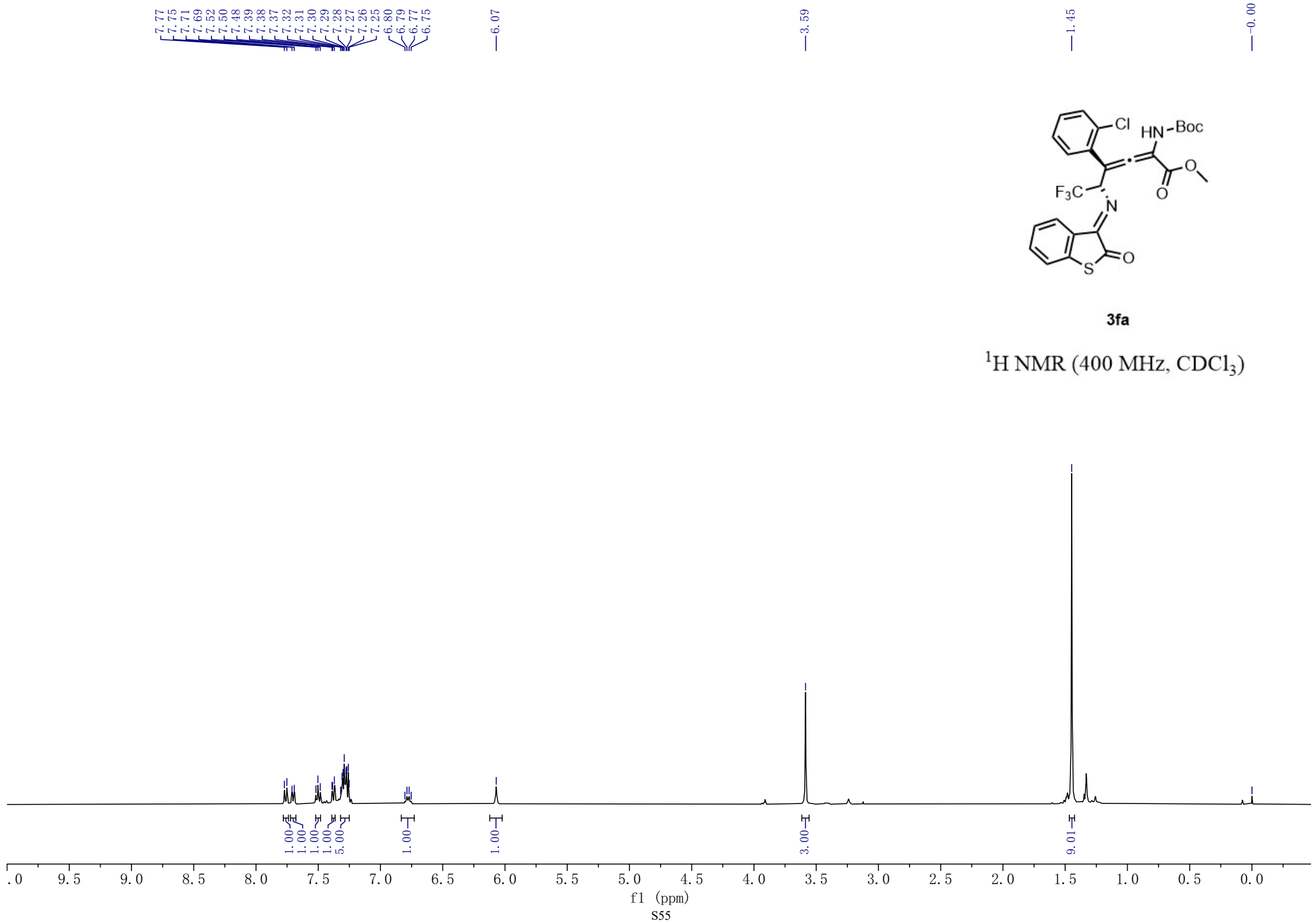


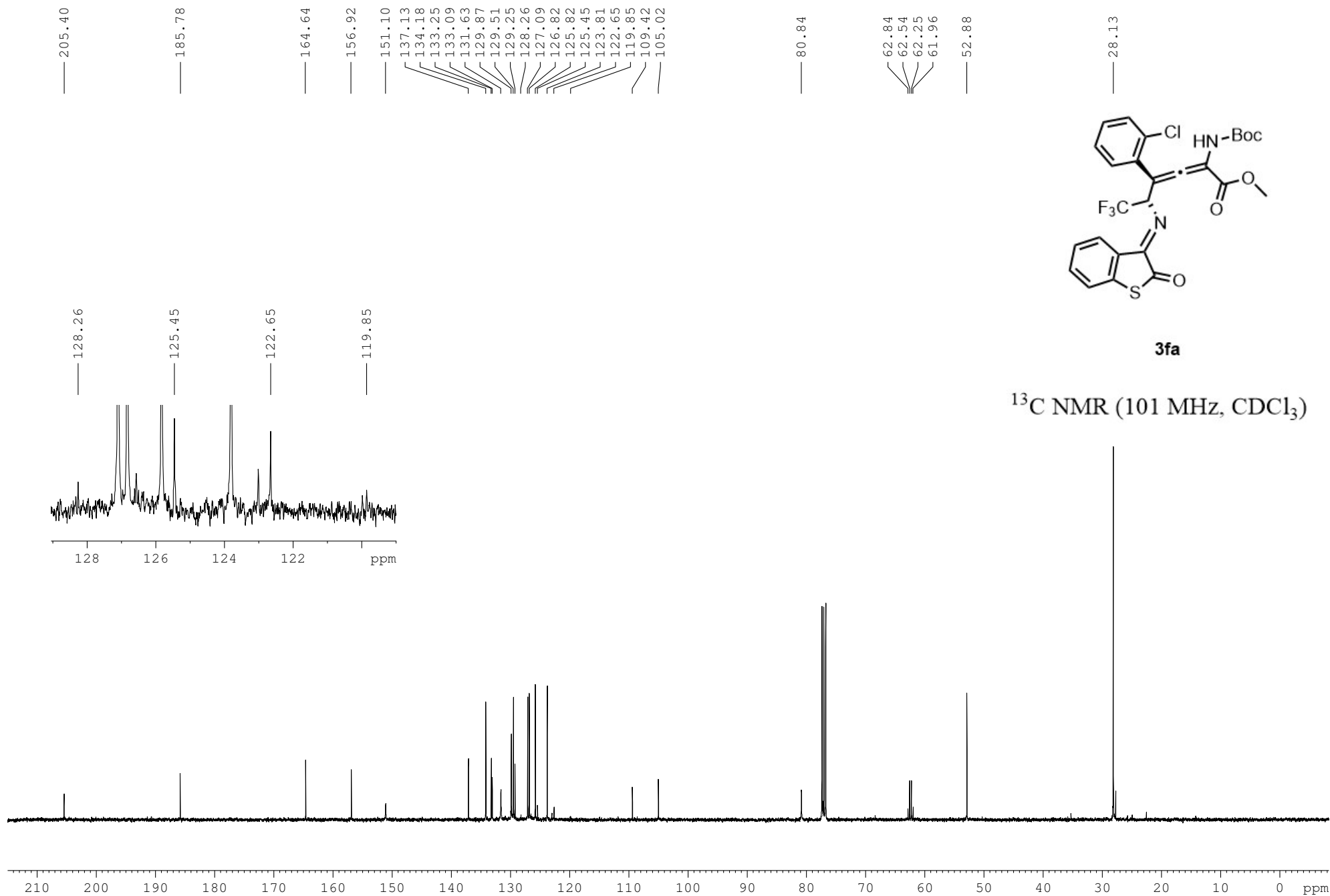


3ea

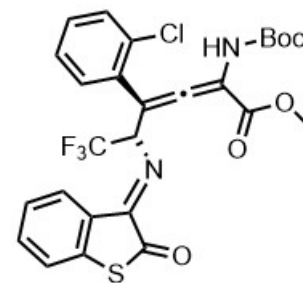
^{19}F NMR (376 MHz, CDCl_3)





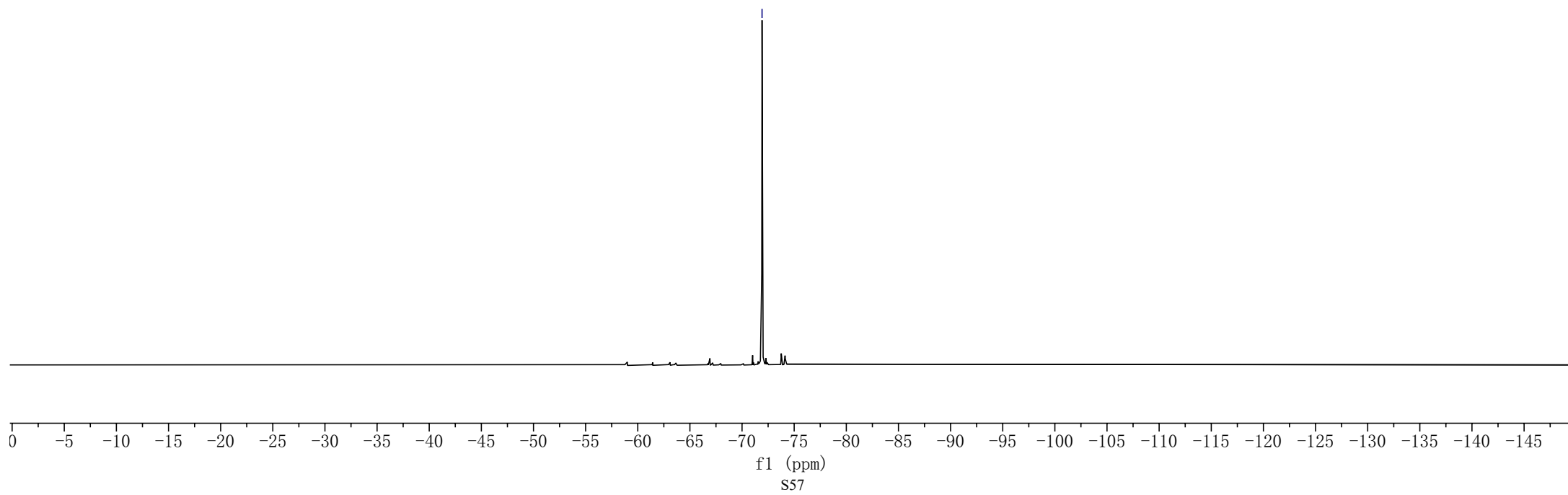


-71.92



3fa

^{19}F NMR (376 MHz, CDCl_3)



7.72
7.70
7.46
7.45
7.44
7.43
7.41
7.39
7.21
7.20
7.19
7.18
7.16
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7.13
7.12
7.11
7.10
7.09
7.08
6.61
6.59
6.57
6.55

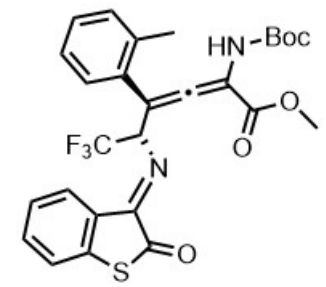
5.94

3.55

2.32

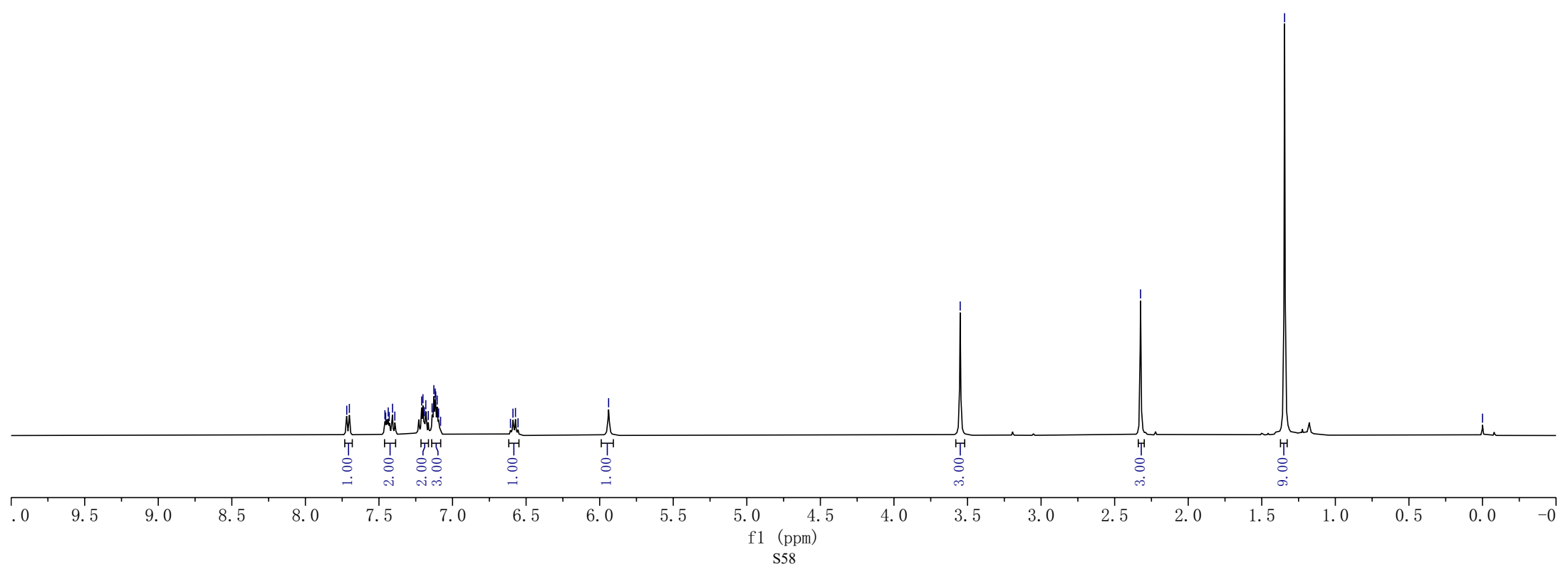
1.35

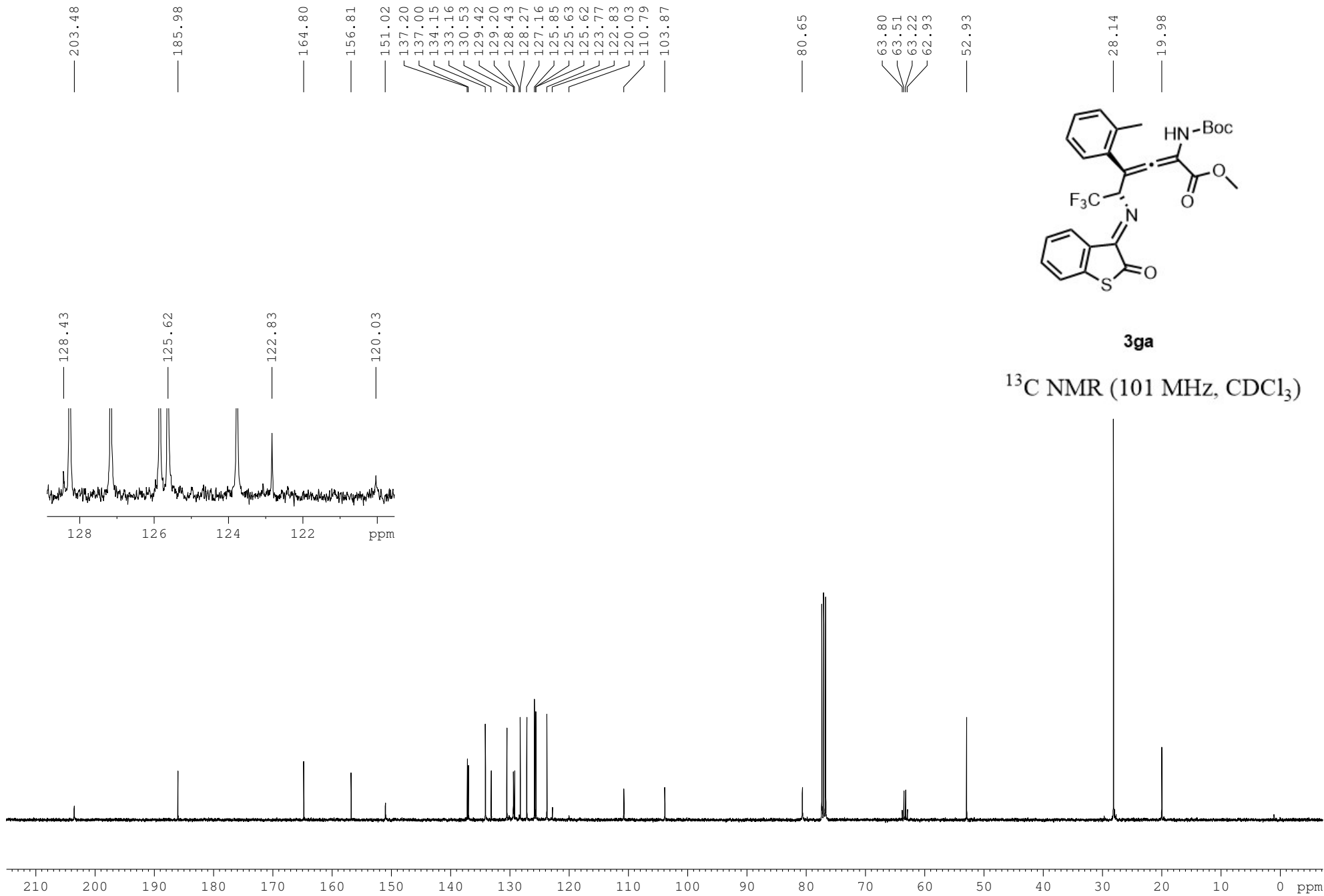
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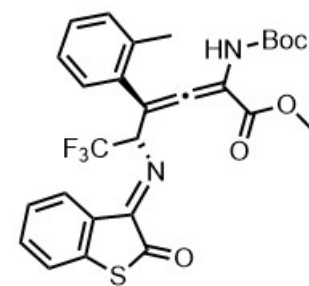


3ga

¹H NMR (400 MHz, CDCl₃)



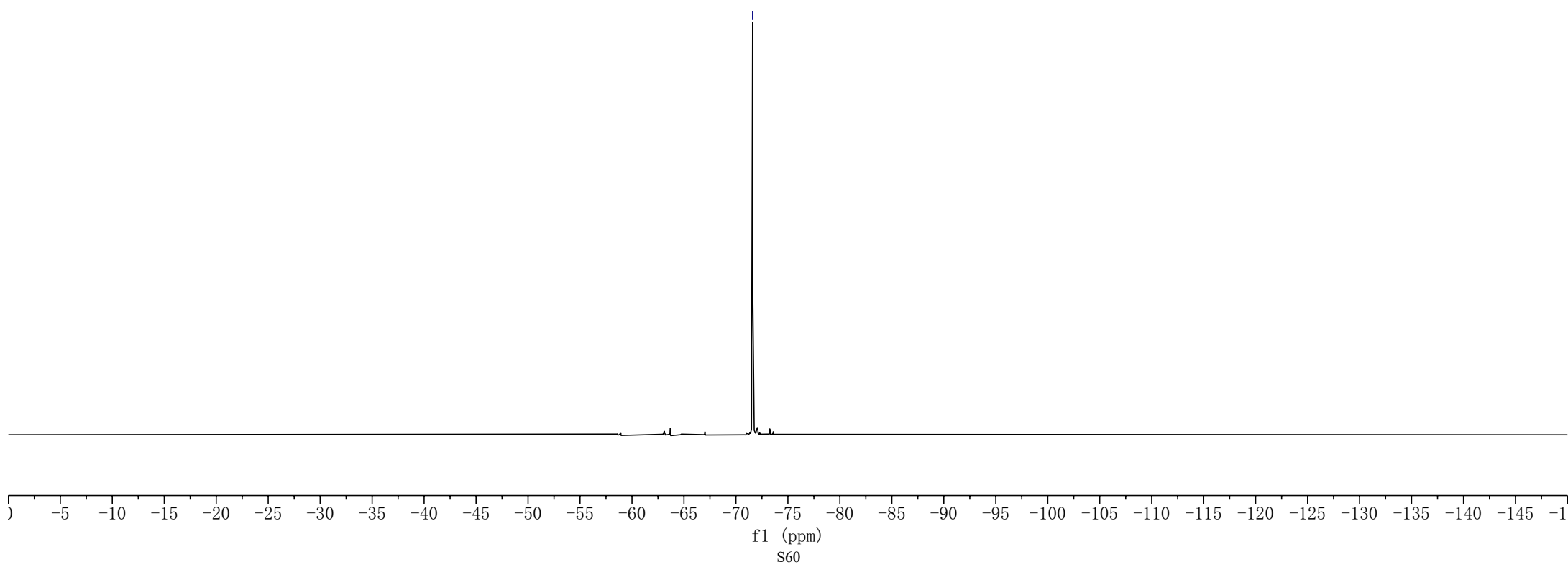




3ga

^{19}F NMR (376 MHz, CDCl_3)

—71.61



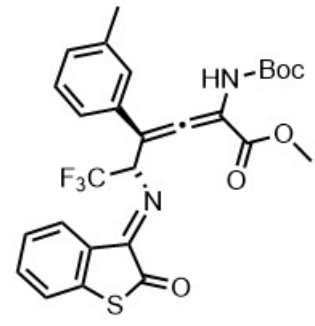
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6.39
6.38
6.04

3.26

2.30

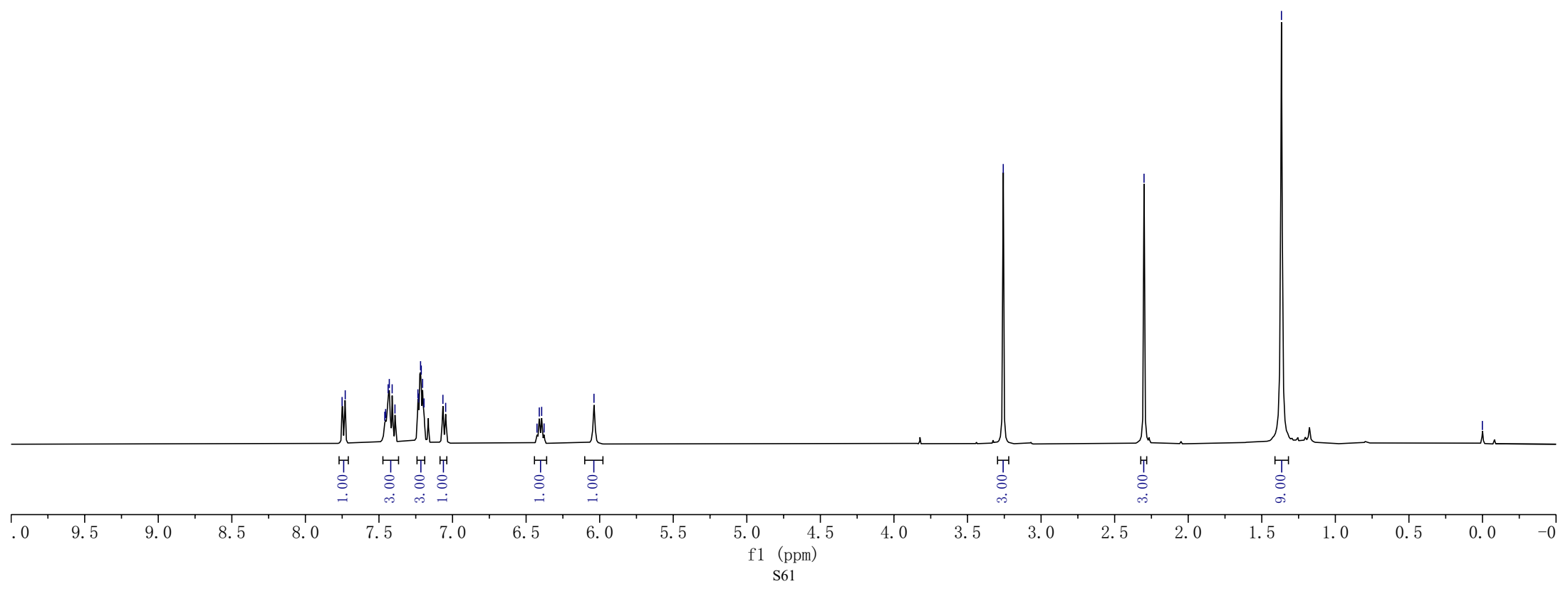
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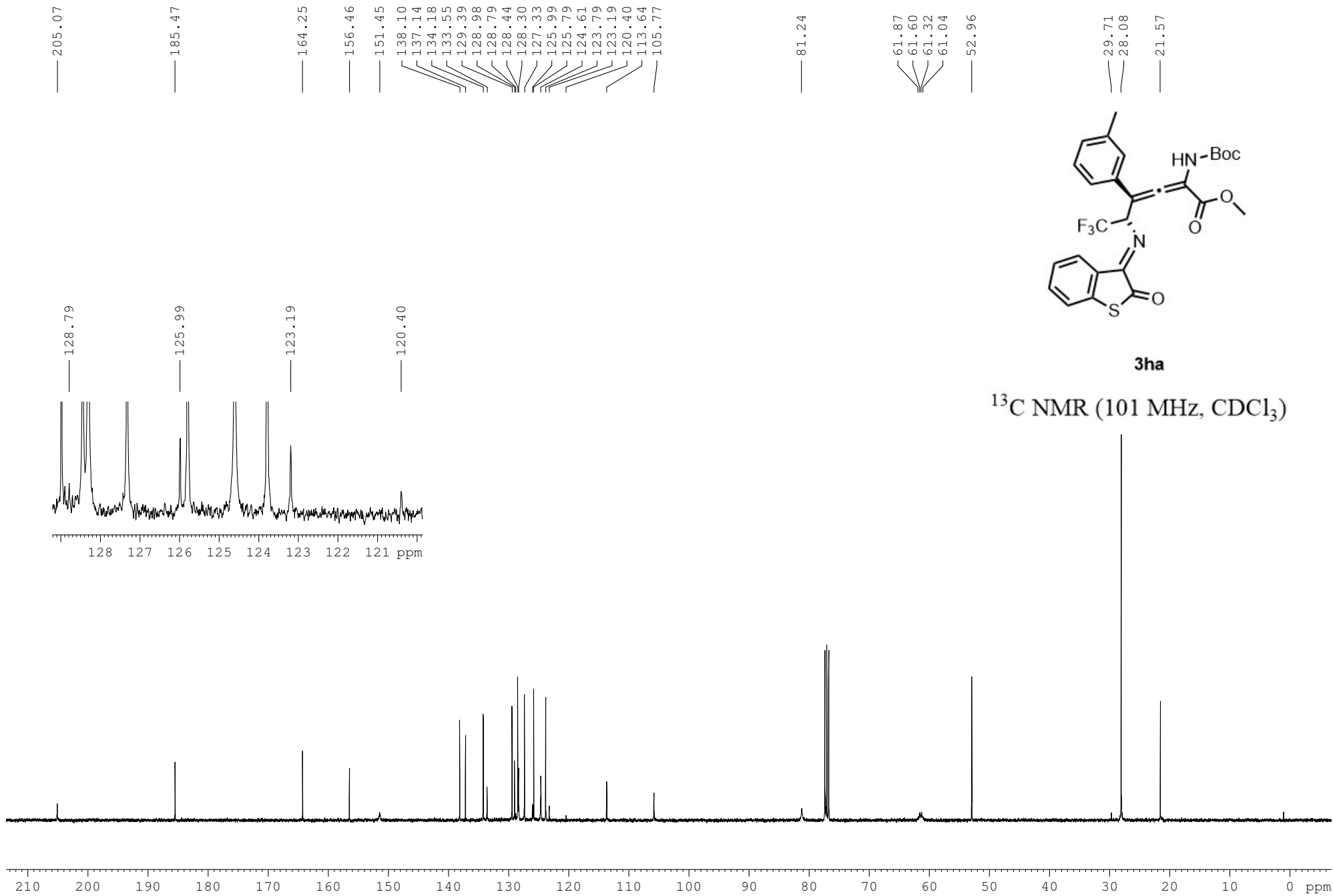
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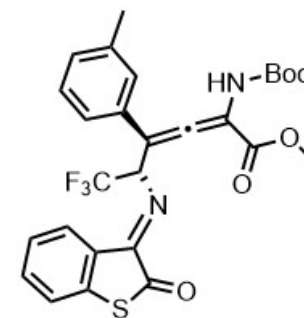


3ha

¹H NMR (400 MHz, CDCl₃)



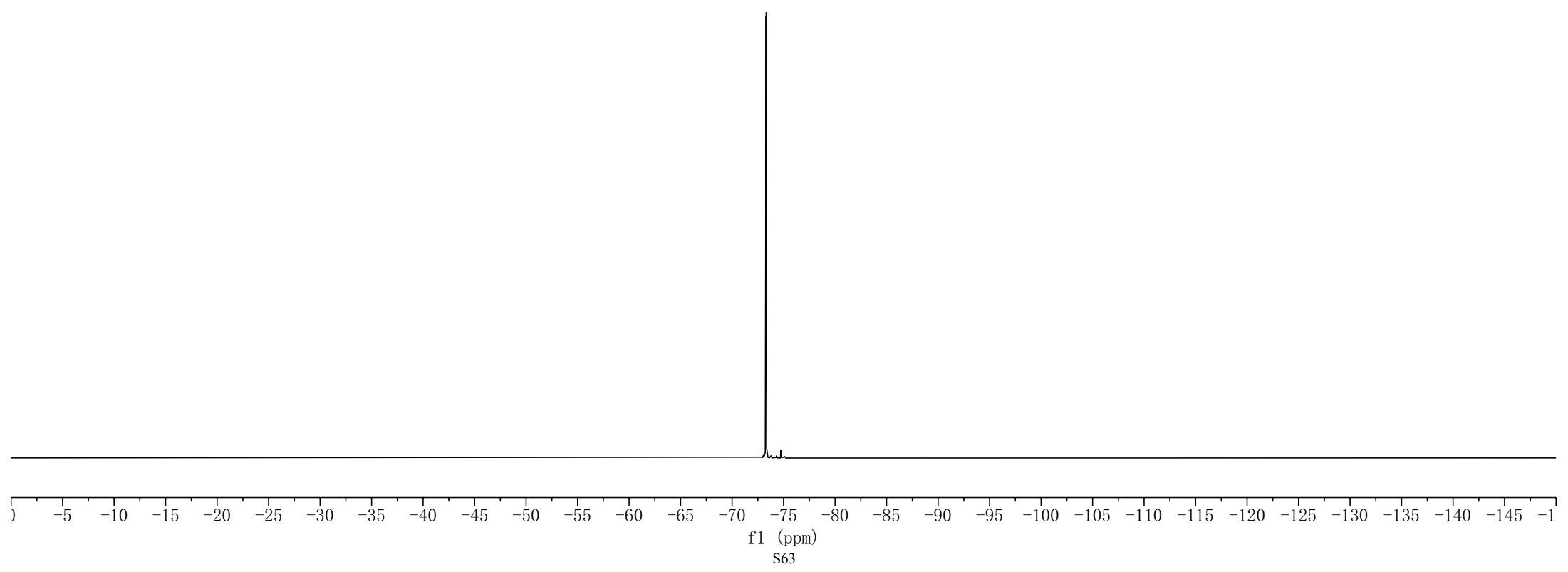




3ha

^{19}F NMR (376 MHz, CDCl_3)

— -73.30



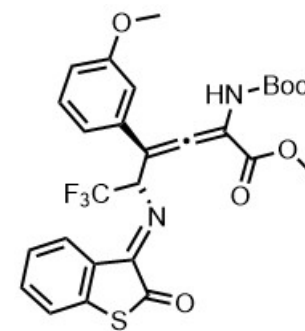
7.76
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7.27
7.26
7.25
7.24
7.23
7.22
7.21
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6.81
6.80
6.79
6.40
6.39
6.37
6.35
6.03

3.75

3.27

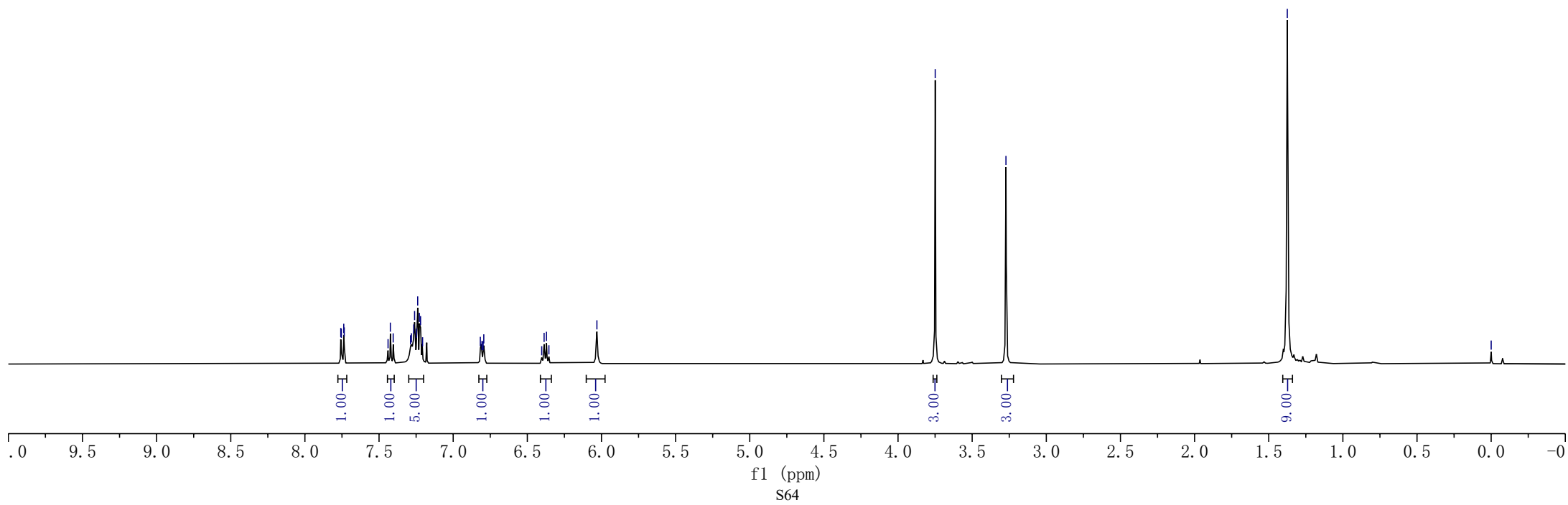
1.37

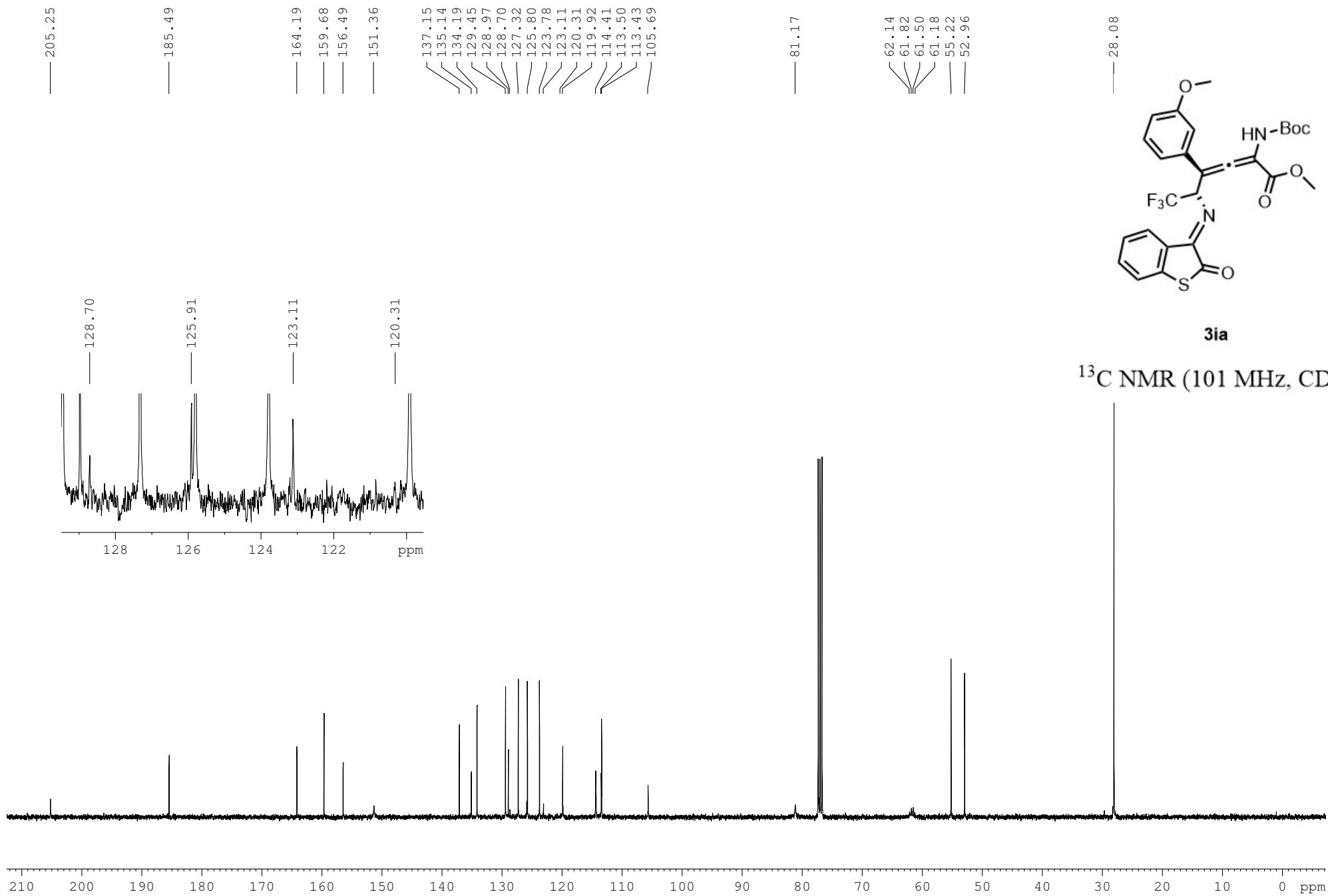
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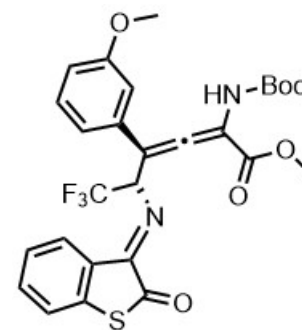


3ia

¹H NMR (400 MHz, CDCl₃)

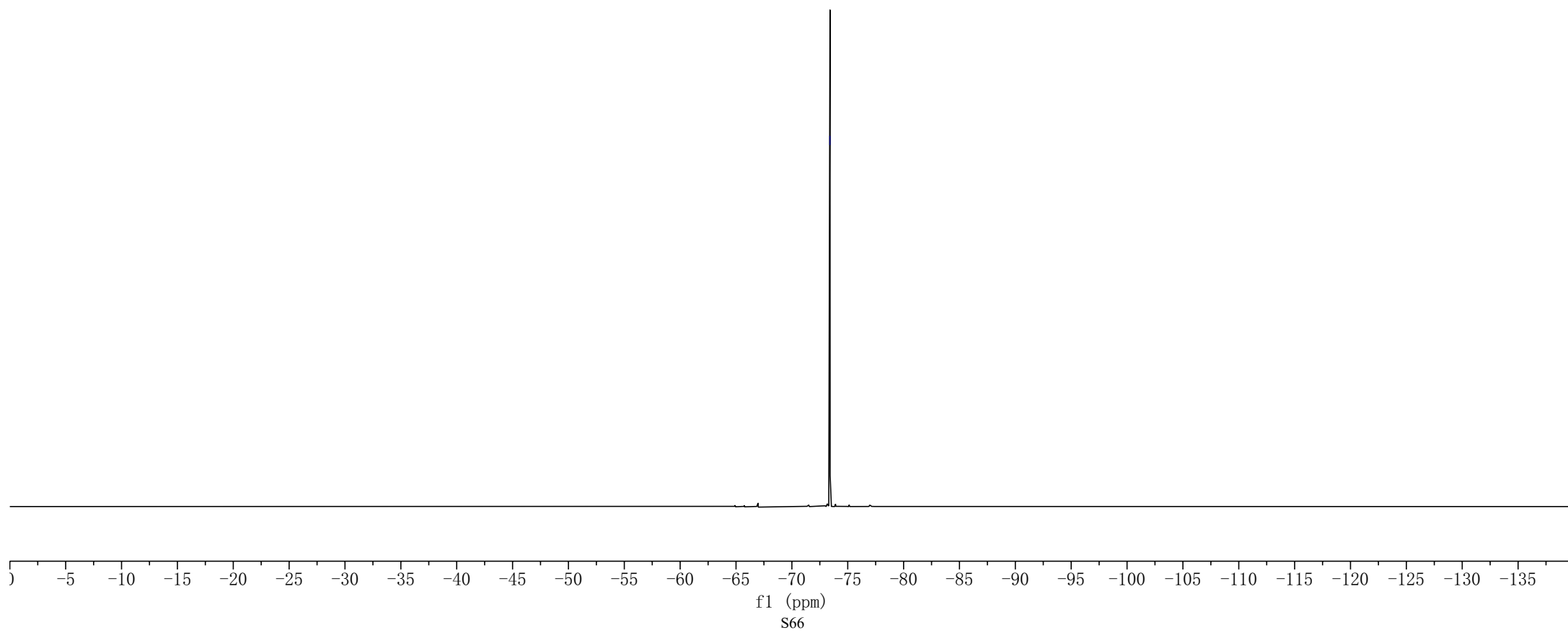






3ia

^{19}F NMR (376 MHz, CDCl_3)

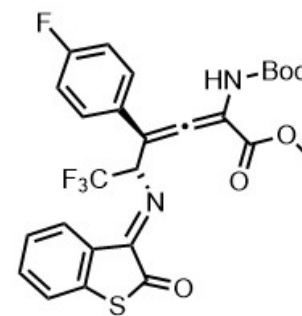


7.84
7.82
7.75
7.73
7.72
7.71
7.53
7.51
7.49
7.33
7.32
7.31
7.30
7.29
7.11
7.09
7.07
6.41
6.39
6.37
6.11

3.37

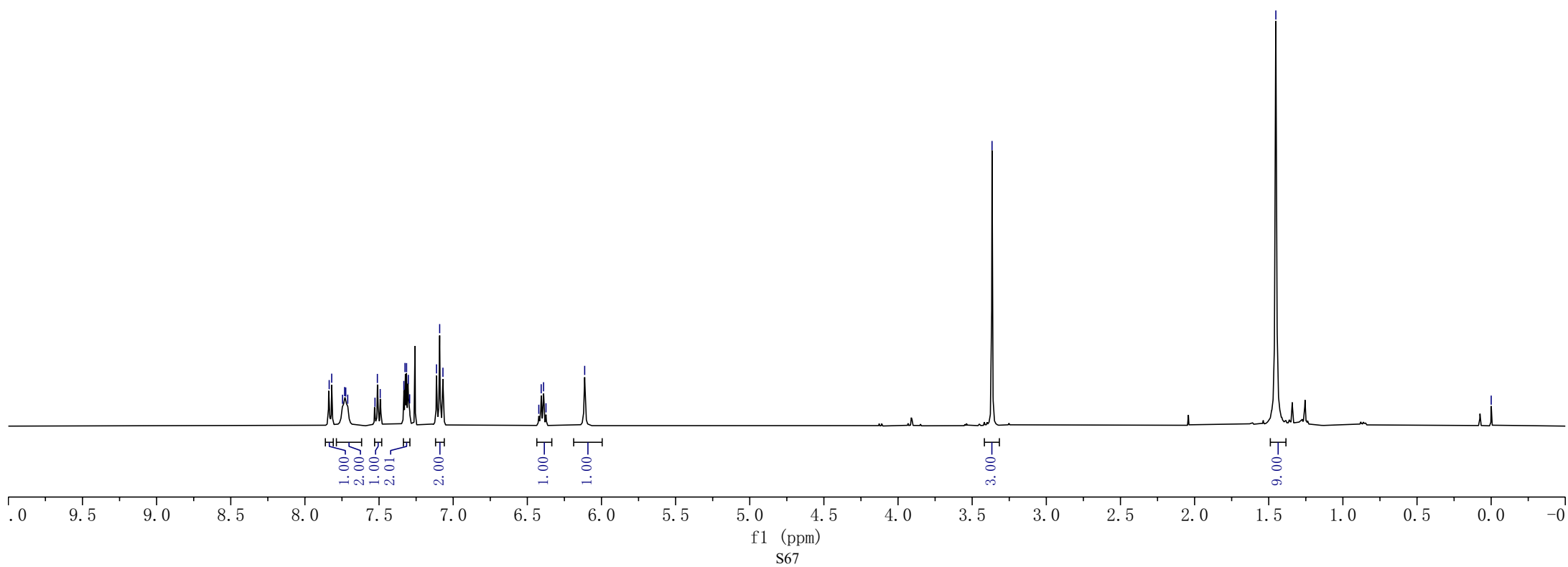
1.45

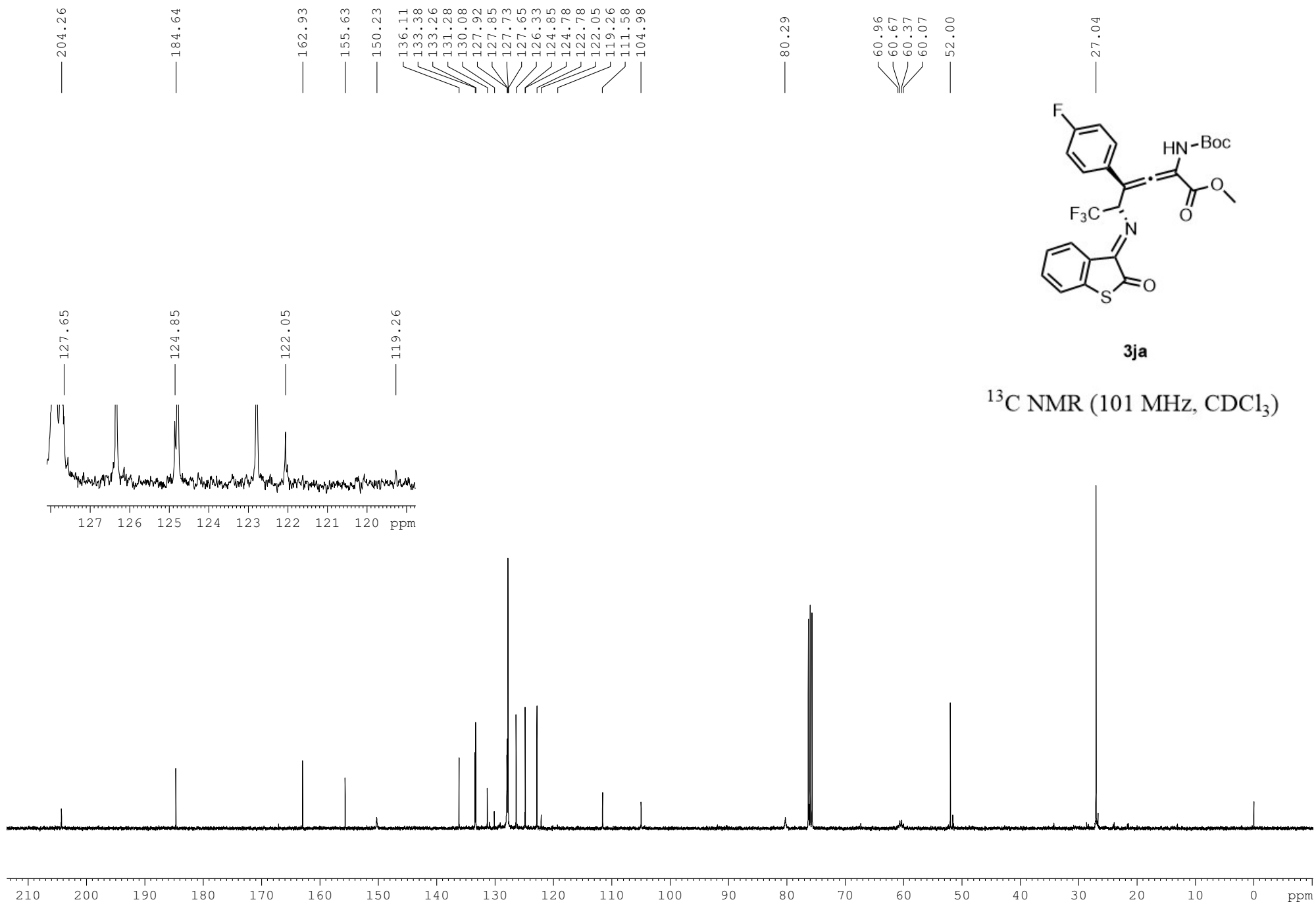
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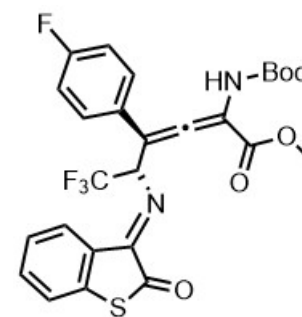


3ja

¹H NMR (400 MHz, CDCl₃)

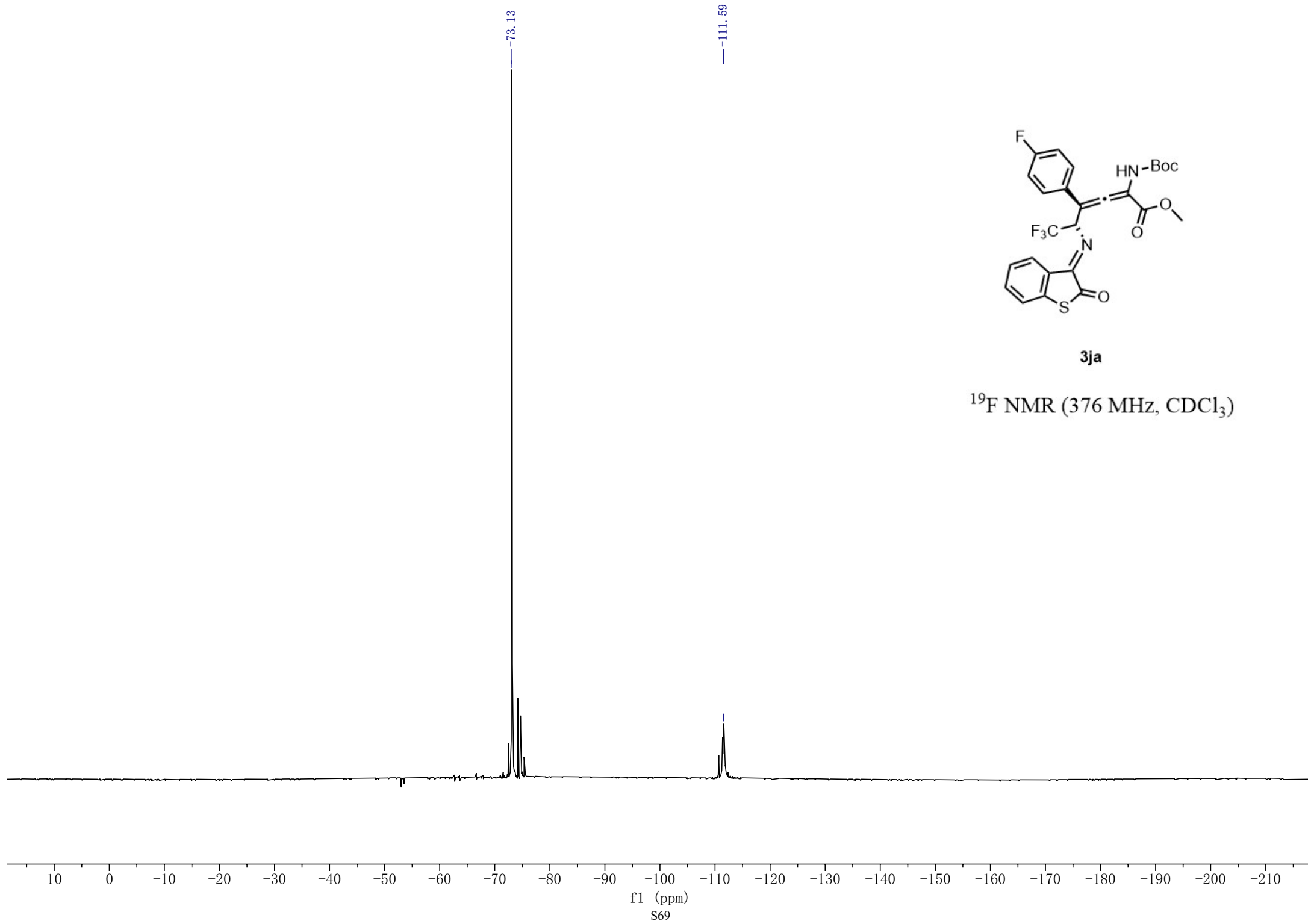






3ja

^{19}F NMR (376 MHz, CDCl_3)



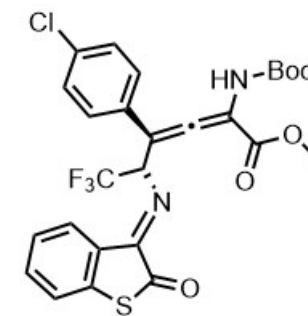
7.84
7.82
7.68
7.66
7.53
7.51
7.50
7.49
7.38
7.36
7.34
7.33
7.32
7.31
7.30

6.41
6.40
6.38
6.37
6.11

3.36

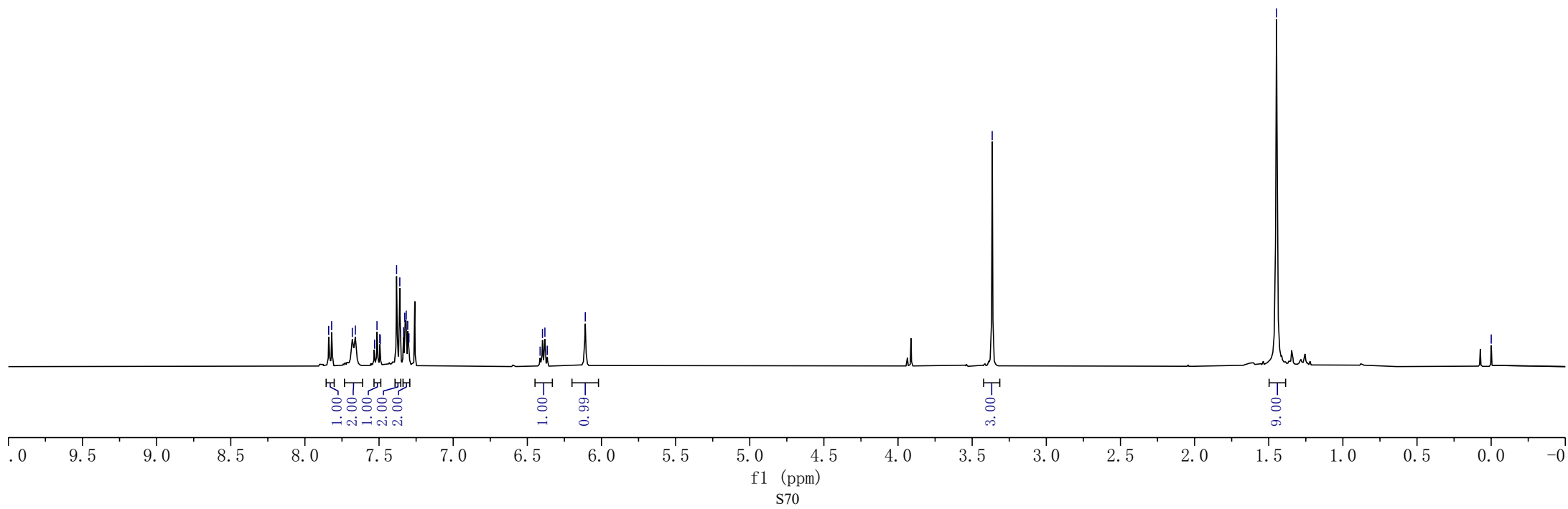
1.45

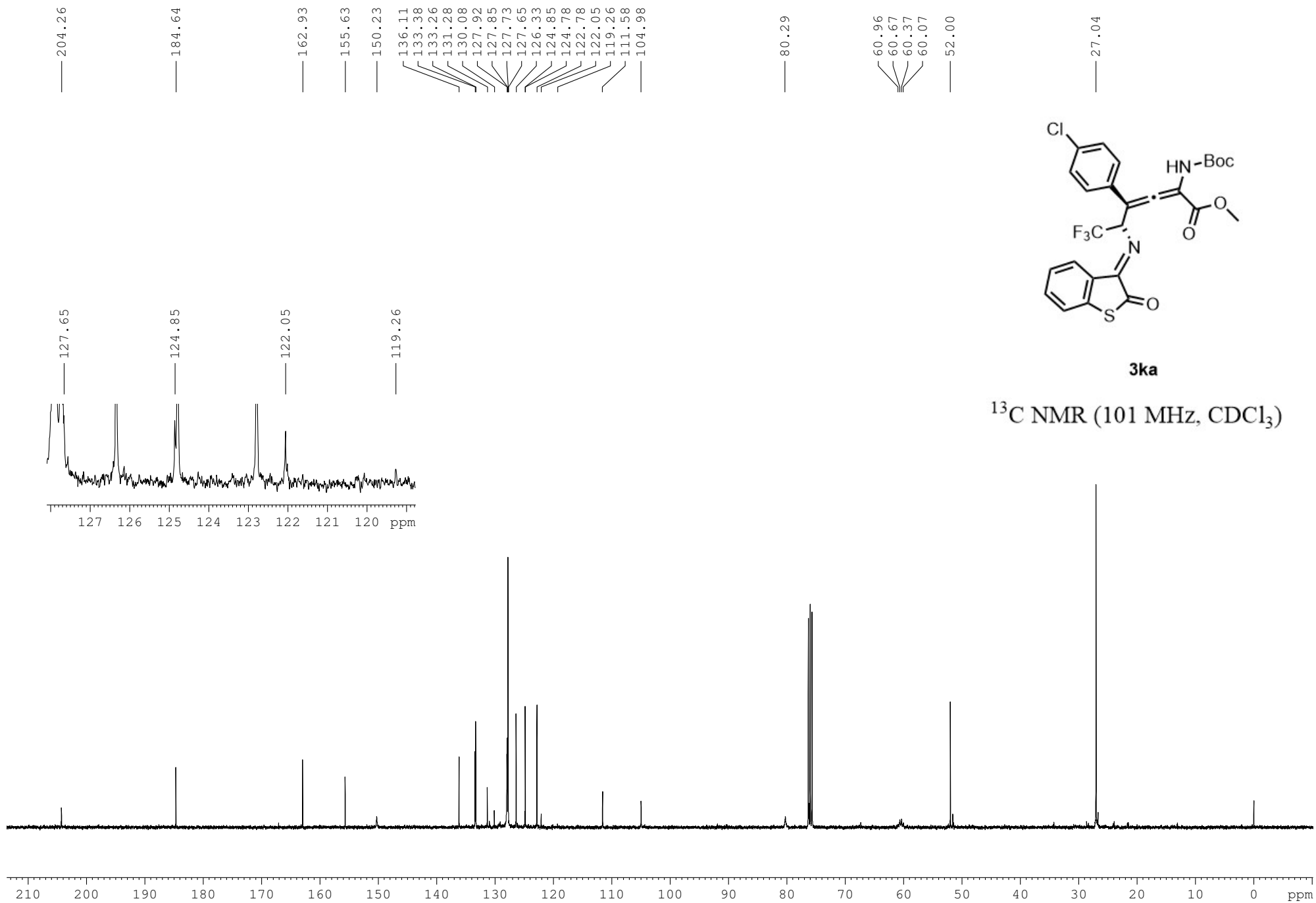
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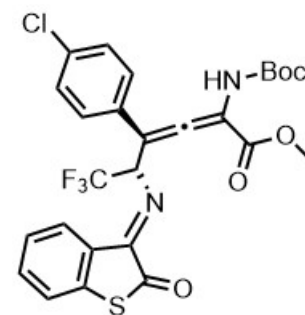


3ka

¹H NMR (400 MHz, CDCl₃)



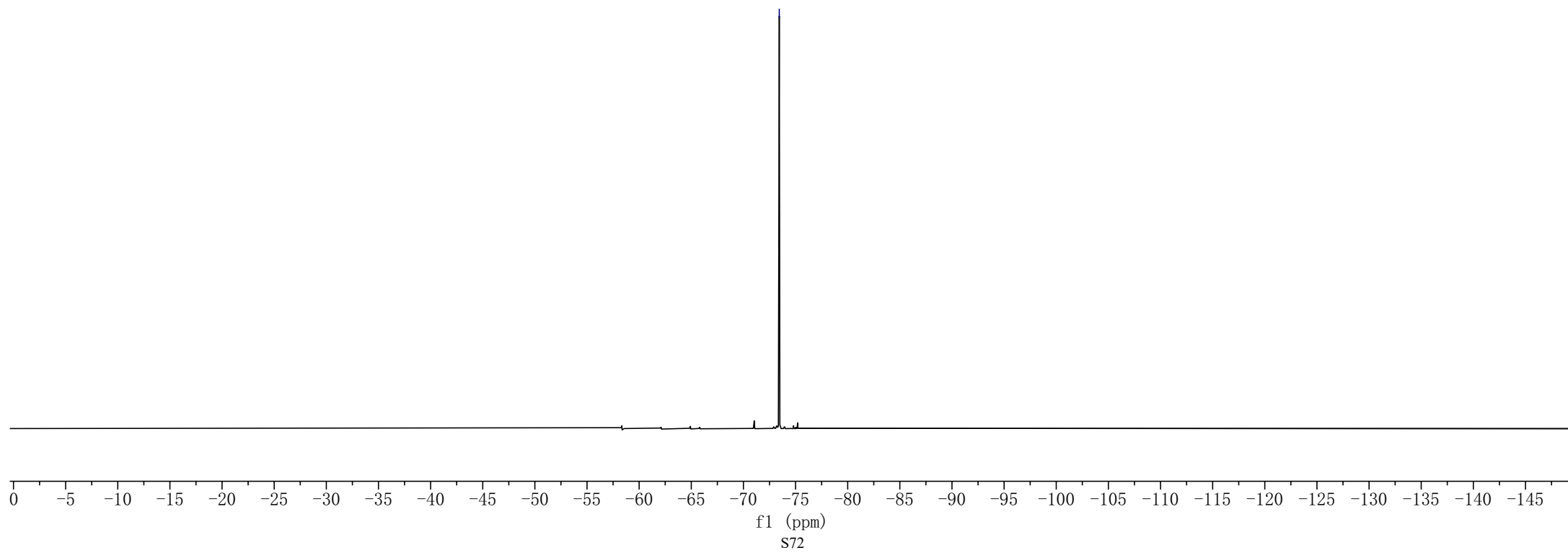




3ka

^{19}F NMR (376 MHz, CDCl_3)

—73.44



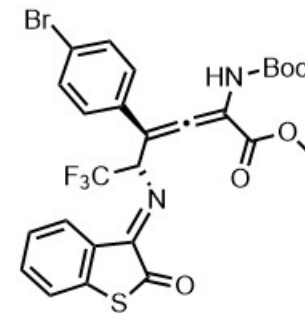
7.84
7.83
7.81
7.62
7.60
7.53
7.52
7.51
7.49
7.33
7.32
7.31
7.30
7.29

6.41
6.39
6.38
6.36
6.11

3.36

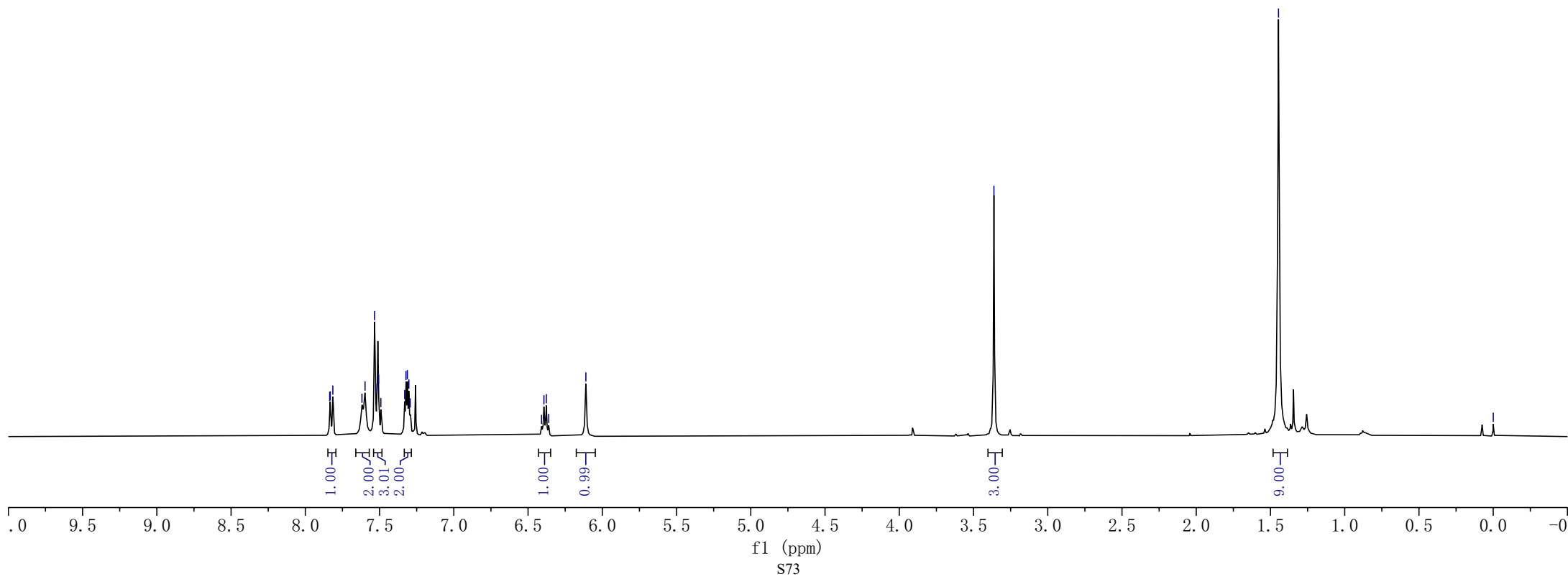
1.45

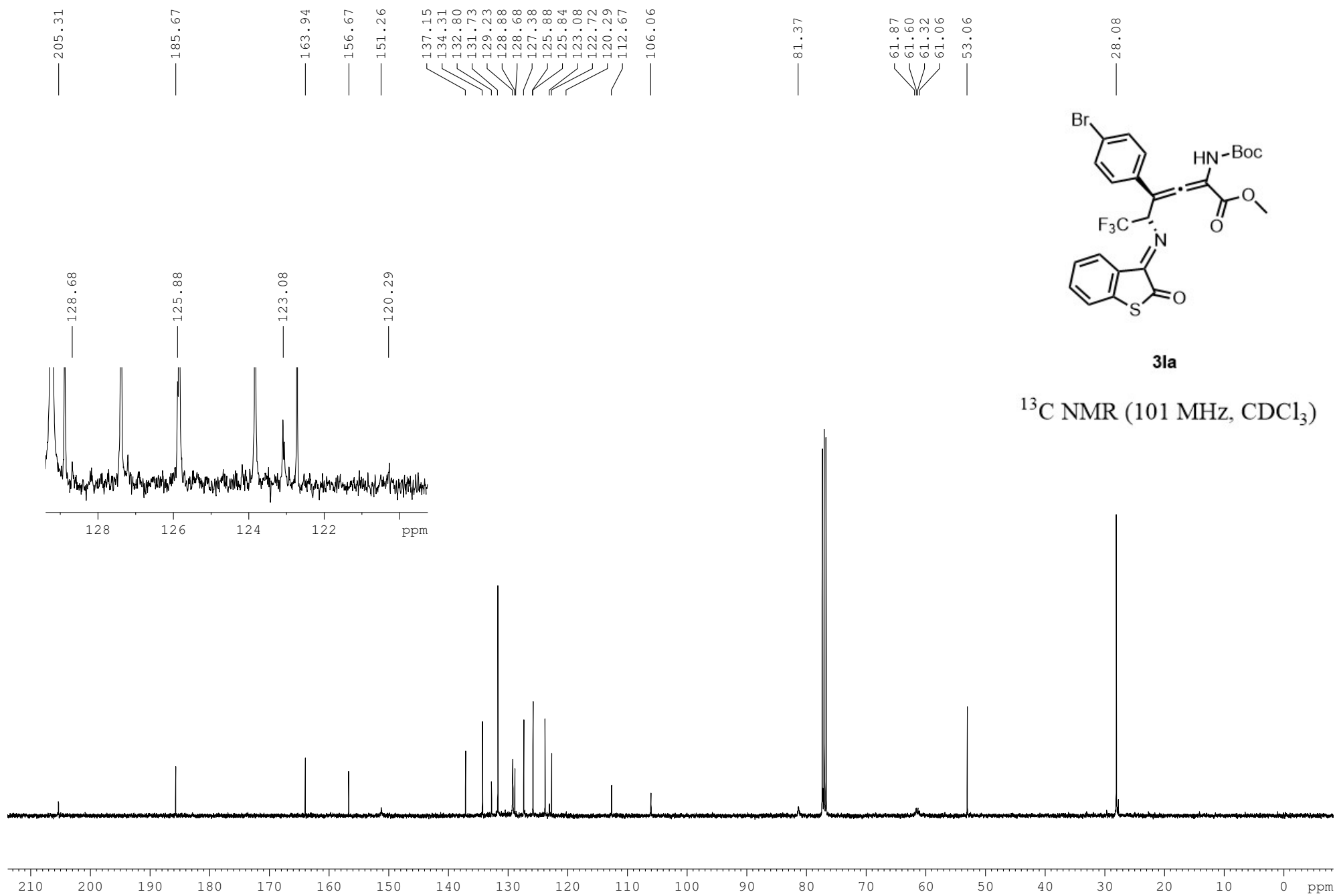
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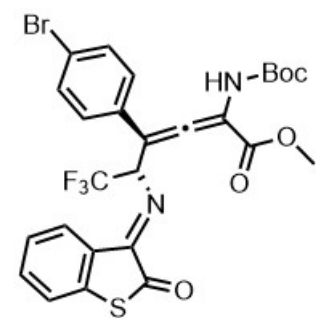


3la

^1H NMR (400 MHz, CDCl_3)

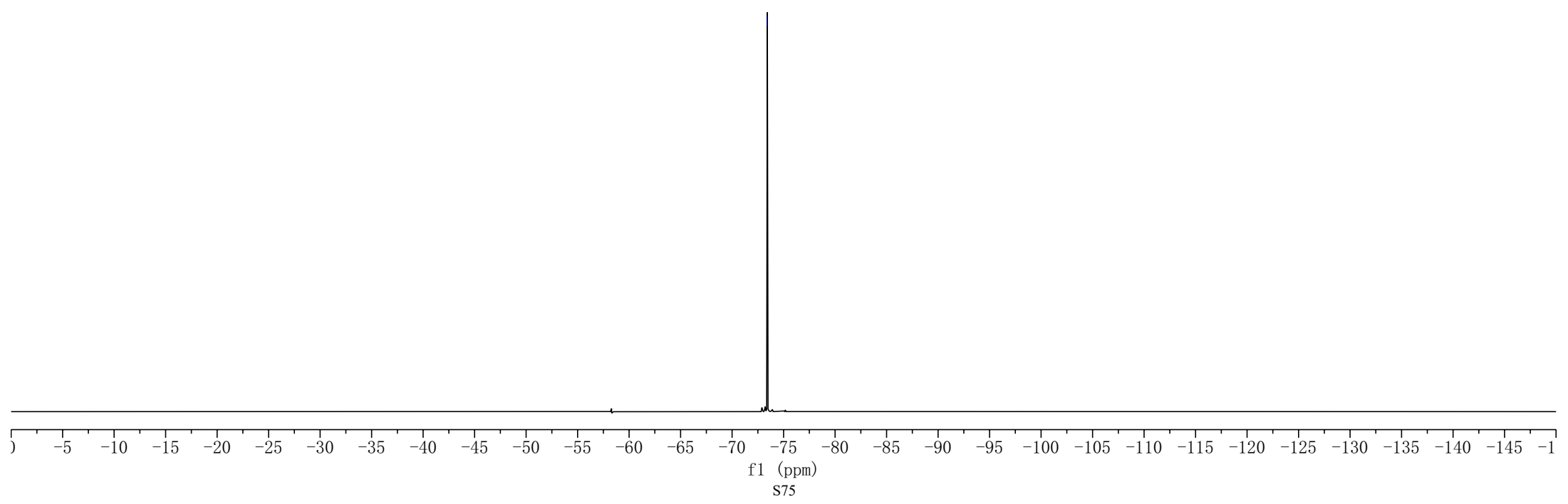




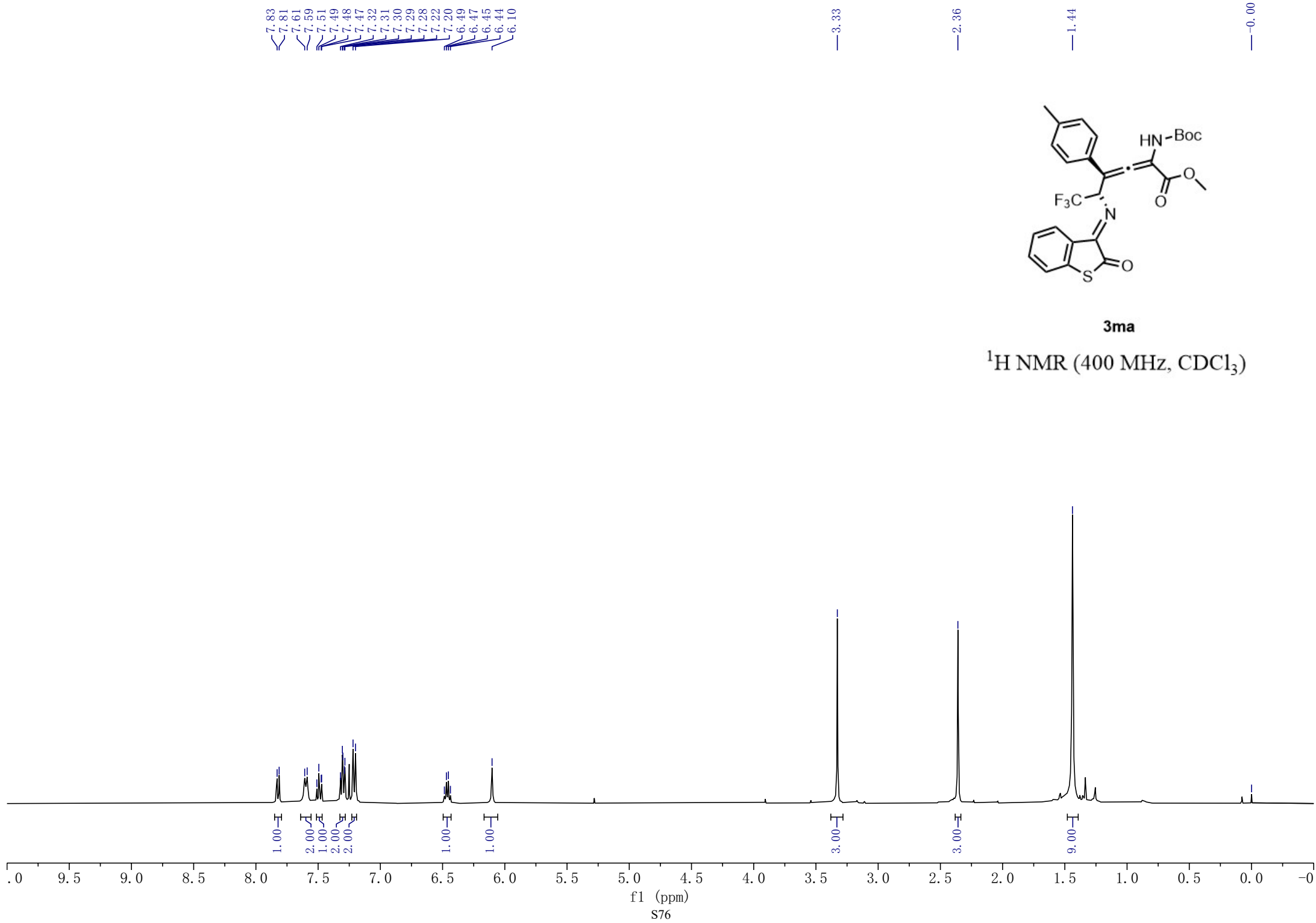


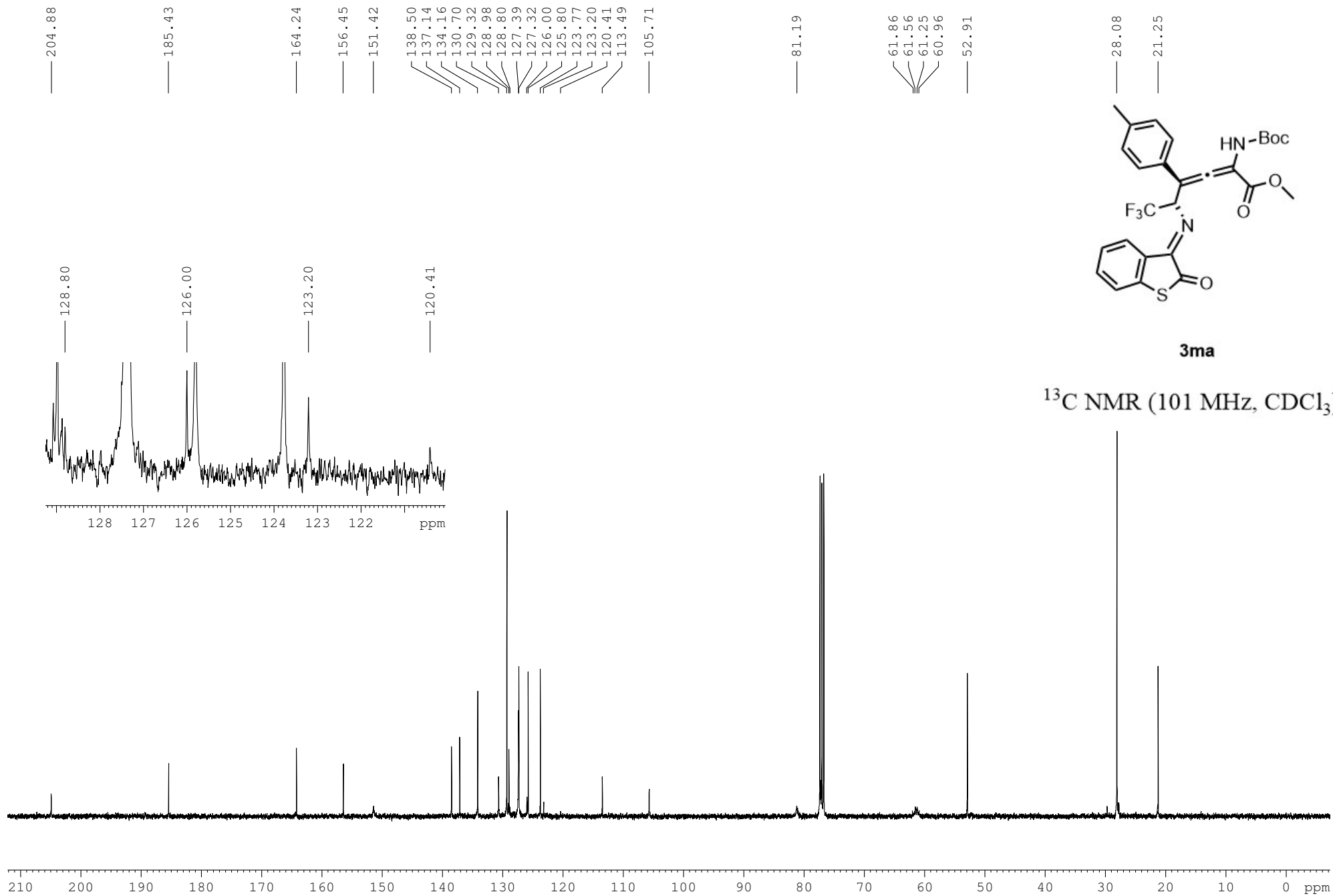
3la

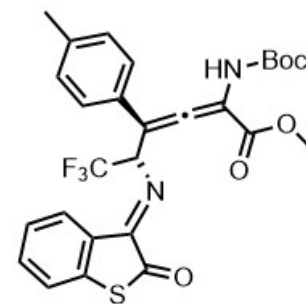
¹⁹F NMR (376 MHz, CDCl₃)



-73.42



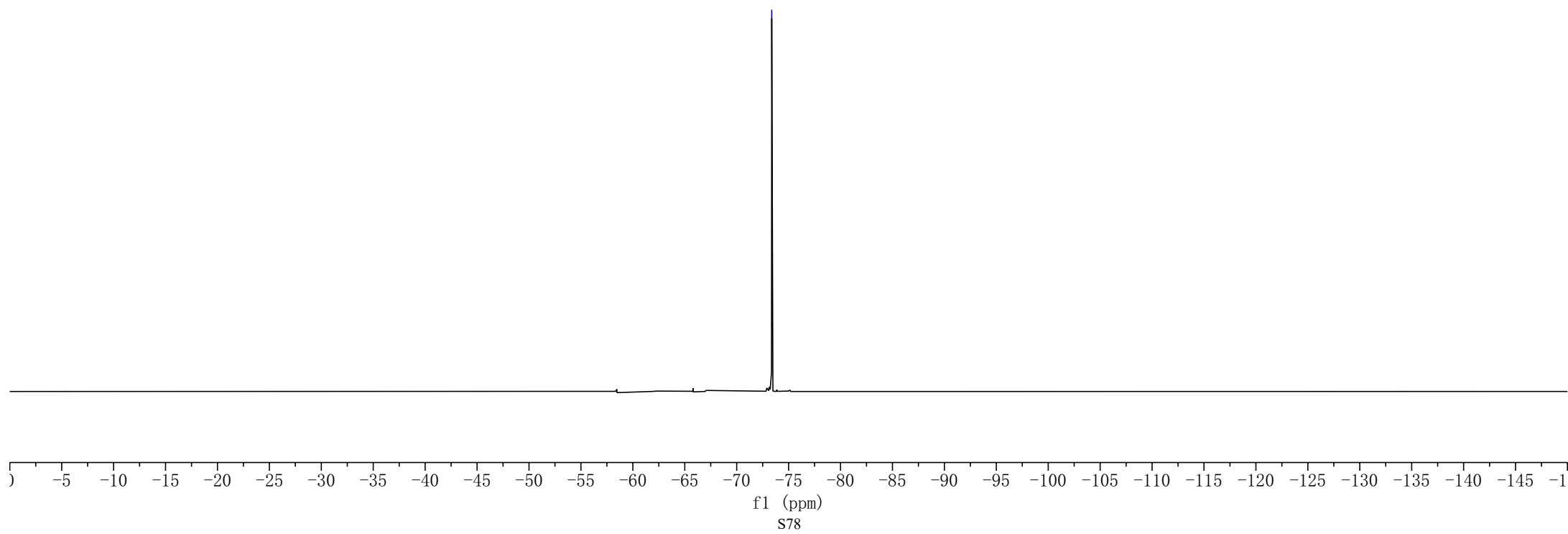




3ma

^{19}F NMR (376 MHz, CDCl_3)

—73.38



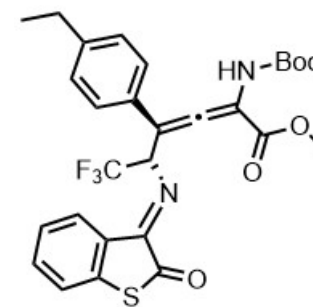
7.83
7.81
7.64
7.62
7.51
7.49
7.47
7.32
7.30
7.29
7.28
7.25
7.23
6.50
6.49
6.47
6.45
6.11

3.33

2.69
2.67
2.65
2.63

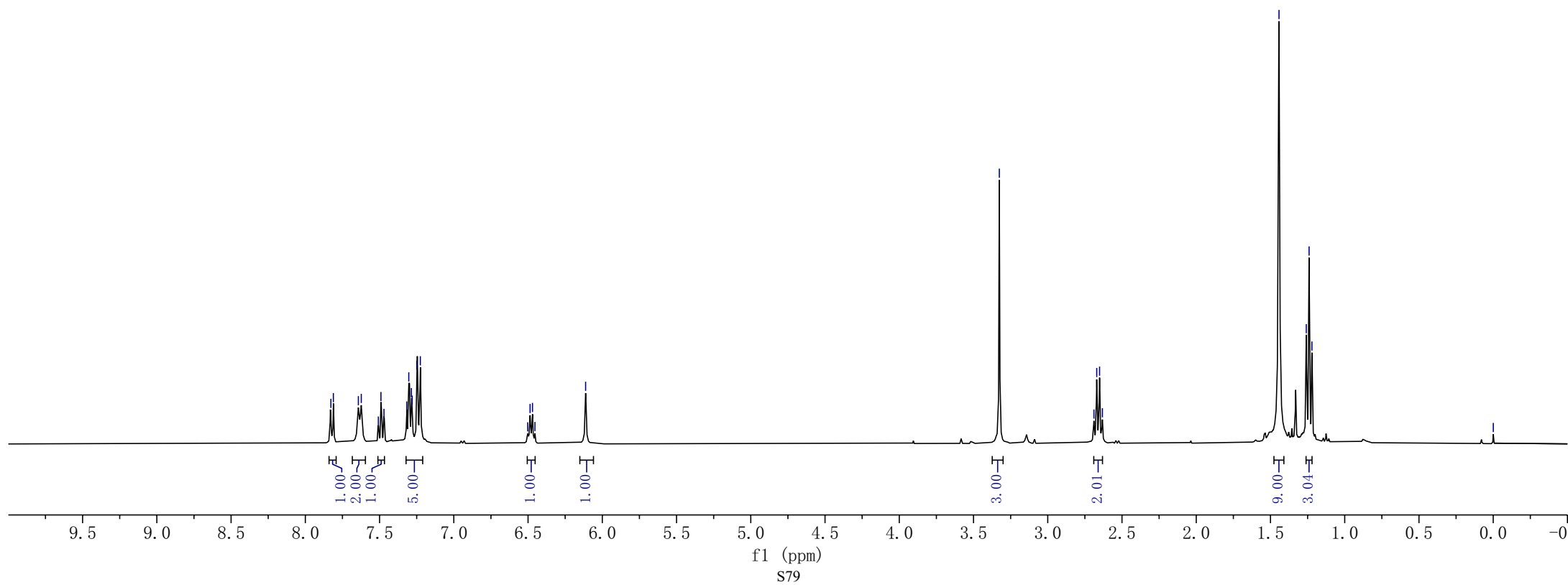
1.44
1.26
1.24
1.22

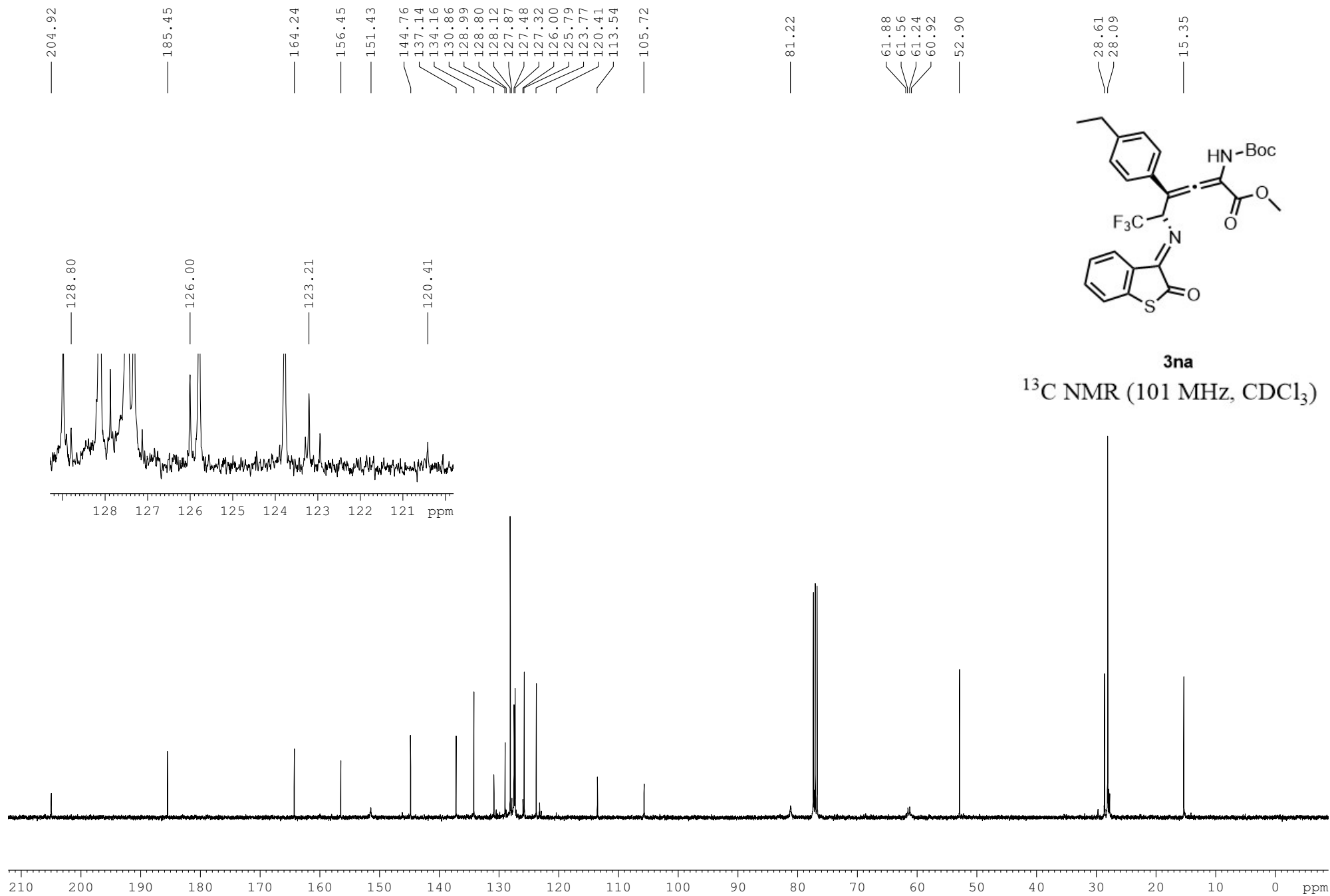
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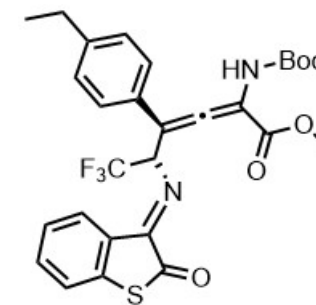


3na

¹H NMR (400 MHz, CDCl₃)

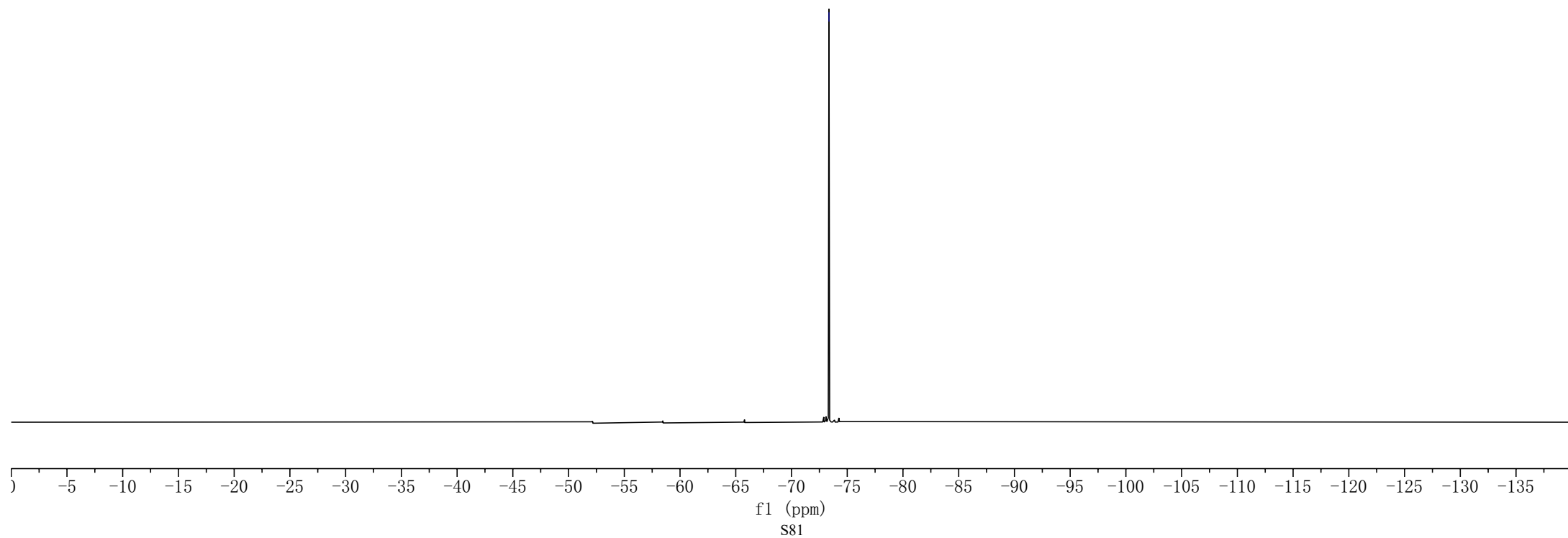






3na

^{19}F NMR (376 MHz, CDCl_3)



-73.36

f1 (ppm)
S81

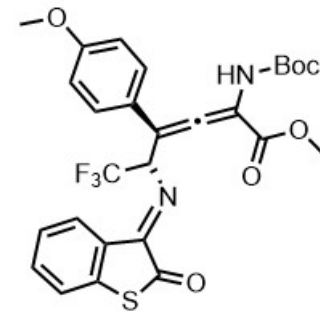
7.75
7.73
7.59
7.57
7.43
7.41
7.39
7.24
7.23
7.22
7.21
7.20
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6.85
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6.38
6.36
6.35
6.33
6.04

3.74

3.25

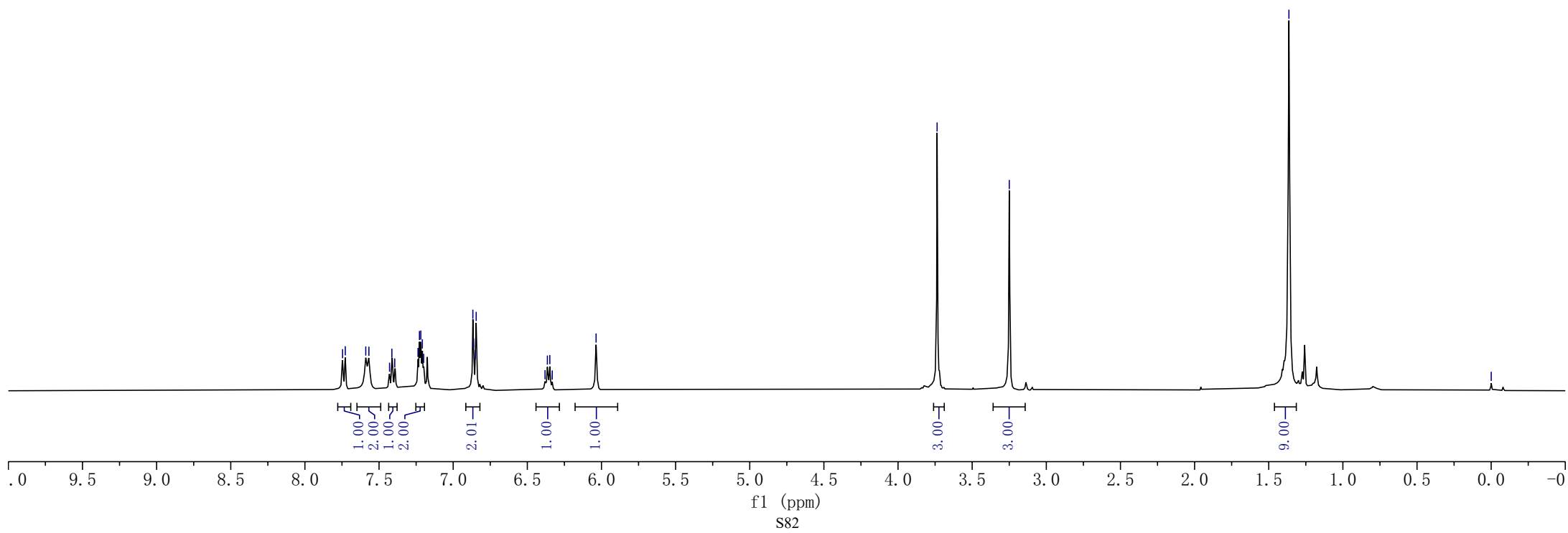
1.36

0.00



3oa

¹H NMR (400 MHz, CDCl₃)

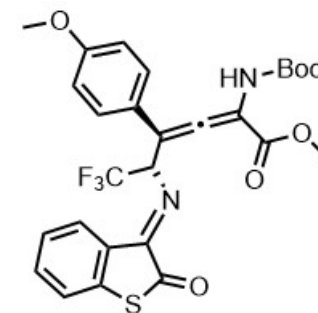
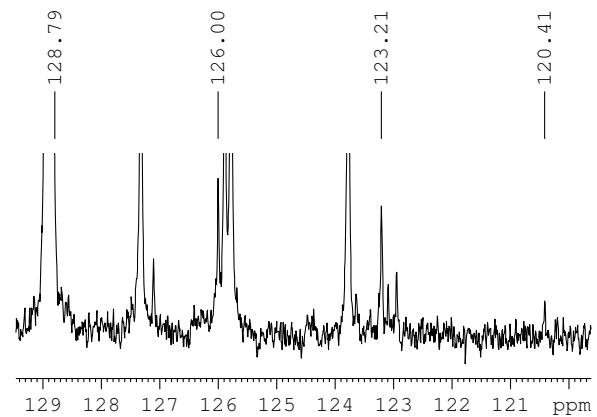


— 204.45
 — 185.53
 — 164.22
 — 159.88
 — 156.46
 — 151.45
 — 137.12
 — 134.17
 — 128.97
 — 128.88
 — 128.79
 — 127.32
 — 126.00
 — 125.89
 — 125.78
 — 123.78
 — 123.21
 — 120.41
 — 114.05
 — 113.22
 — 105.59

— 81.13

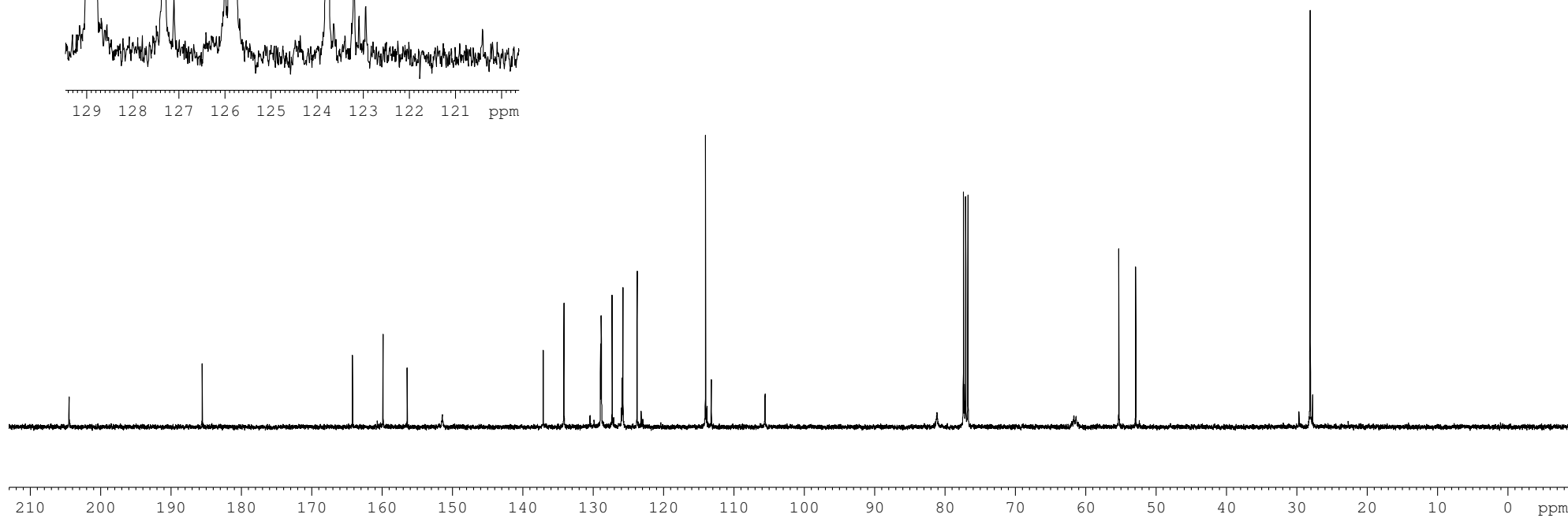
— 62.01
 — 61.69
 — 61.37
 — 61.04
 — 55.30
 — 52.90

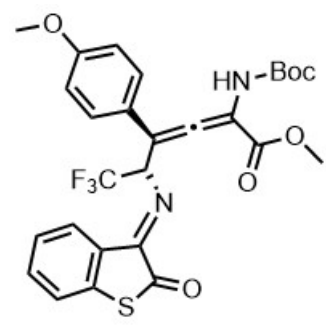
— 29.70
 — 28.09



3oa

^{13}C NMR (101 MHz, CDCl_3)

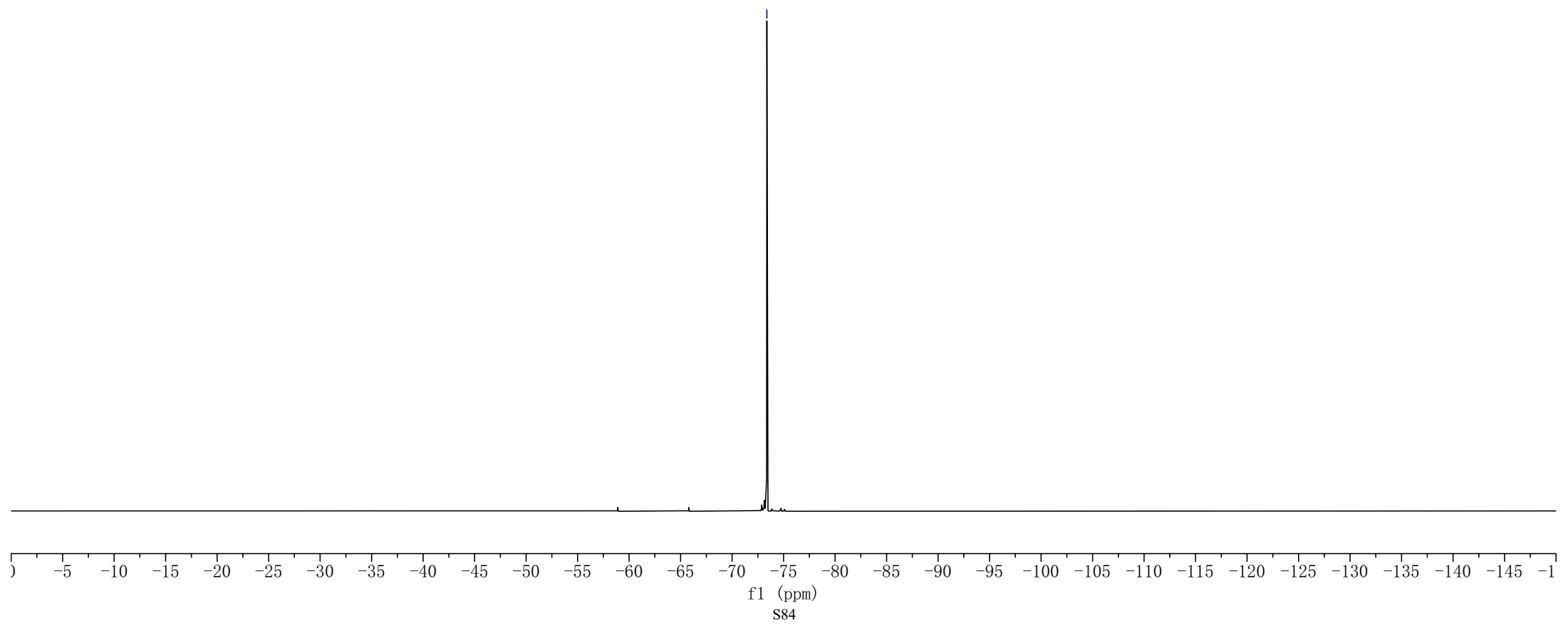


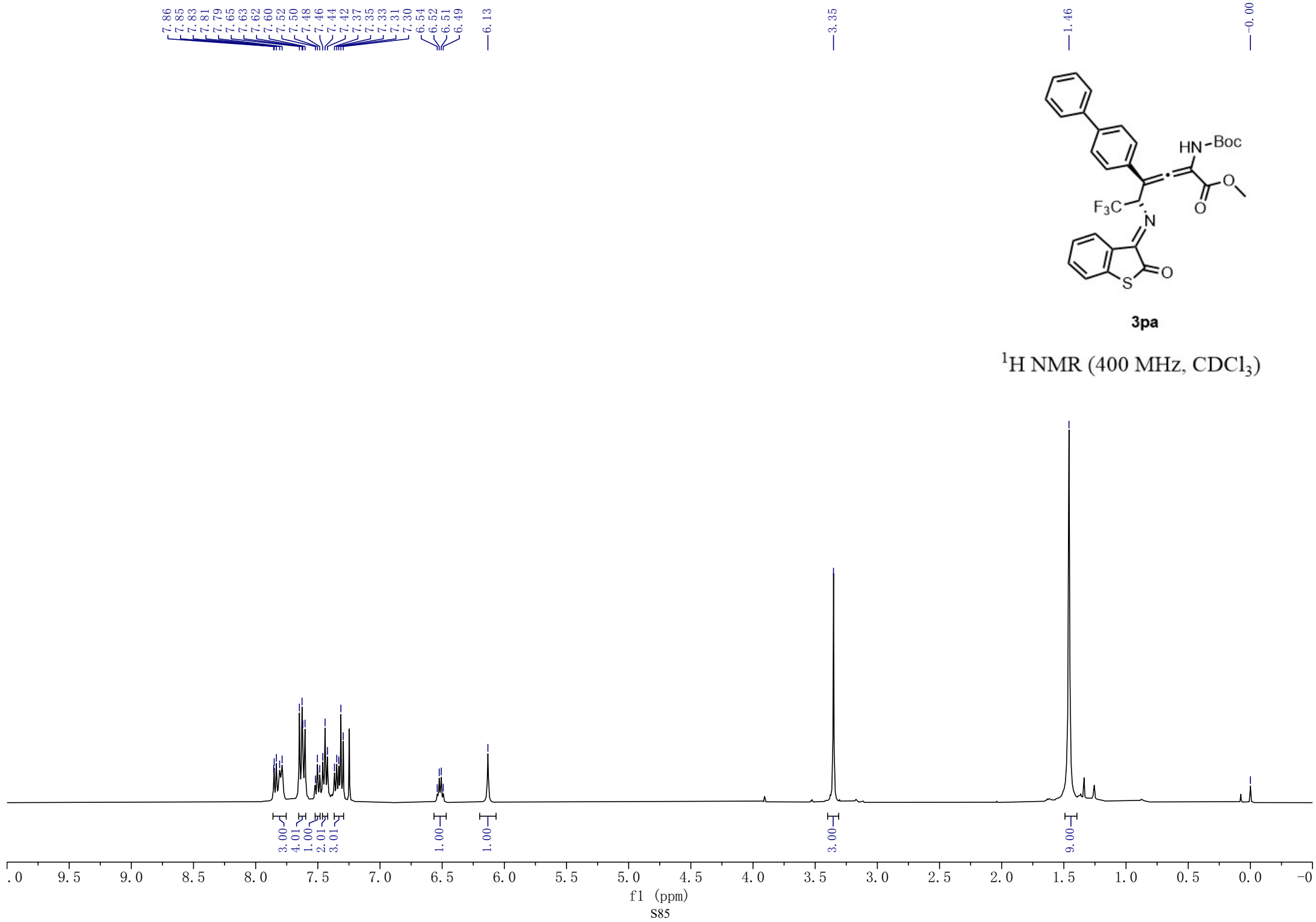


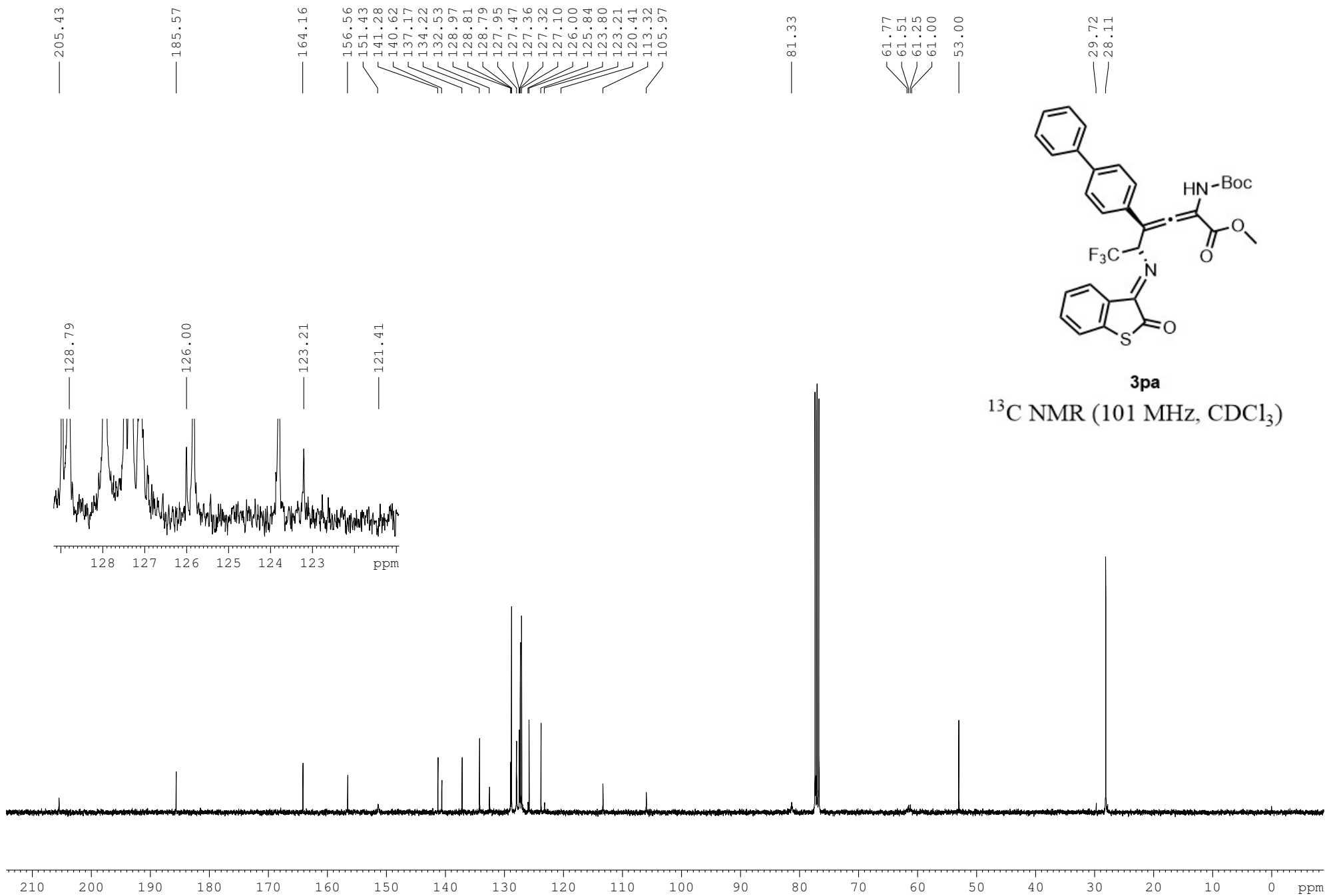
3oa

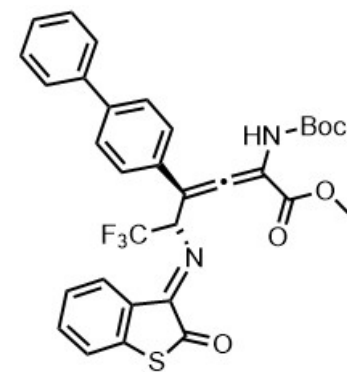
¹⁹F NMR (376 MHz, CDCl₃)

-73.38





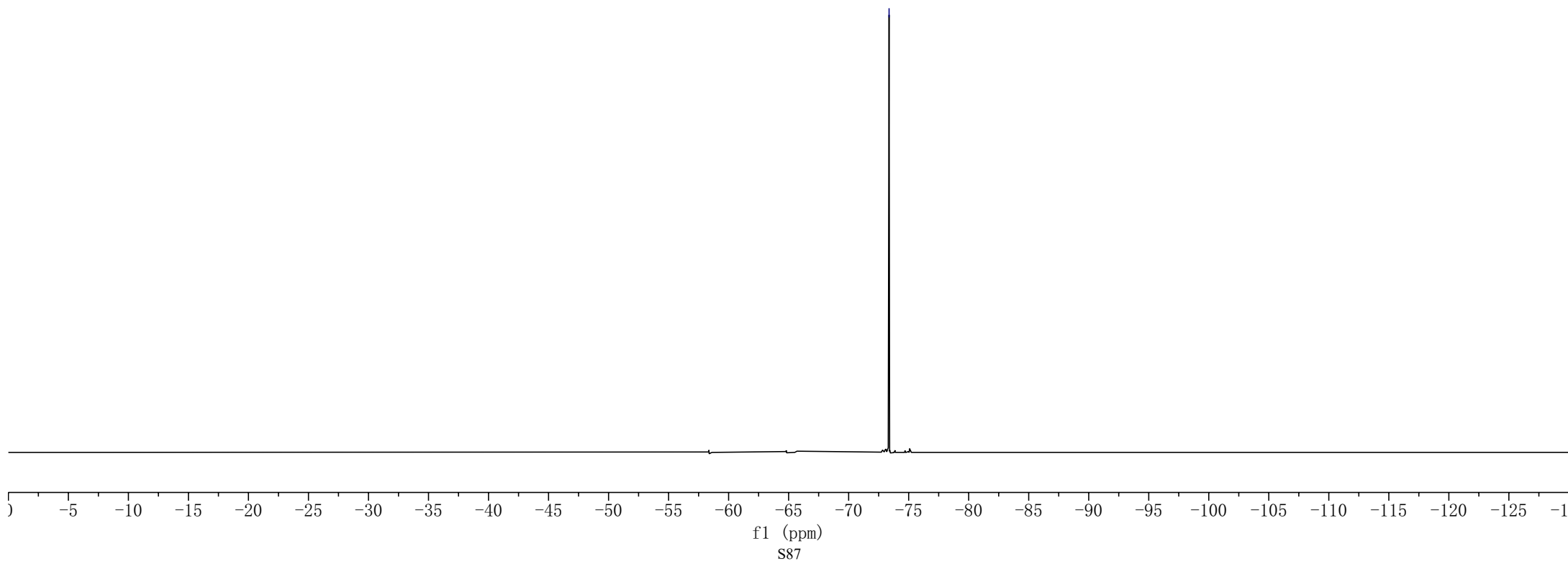




3pa

^{19}F NMR (376 MHz, CDCl_3)

-73.37



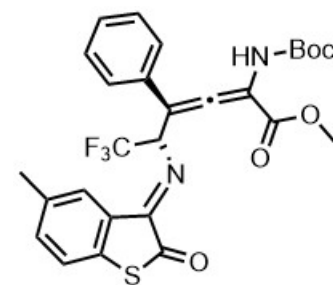
7.66
7.64
7.57
7.56
7.35
7.33
7.31
7.27
7.26
7.25
7.23
7.12
7.10
6.40
6.39
6.37
6.36
6.04

3.29

2.31

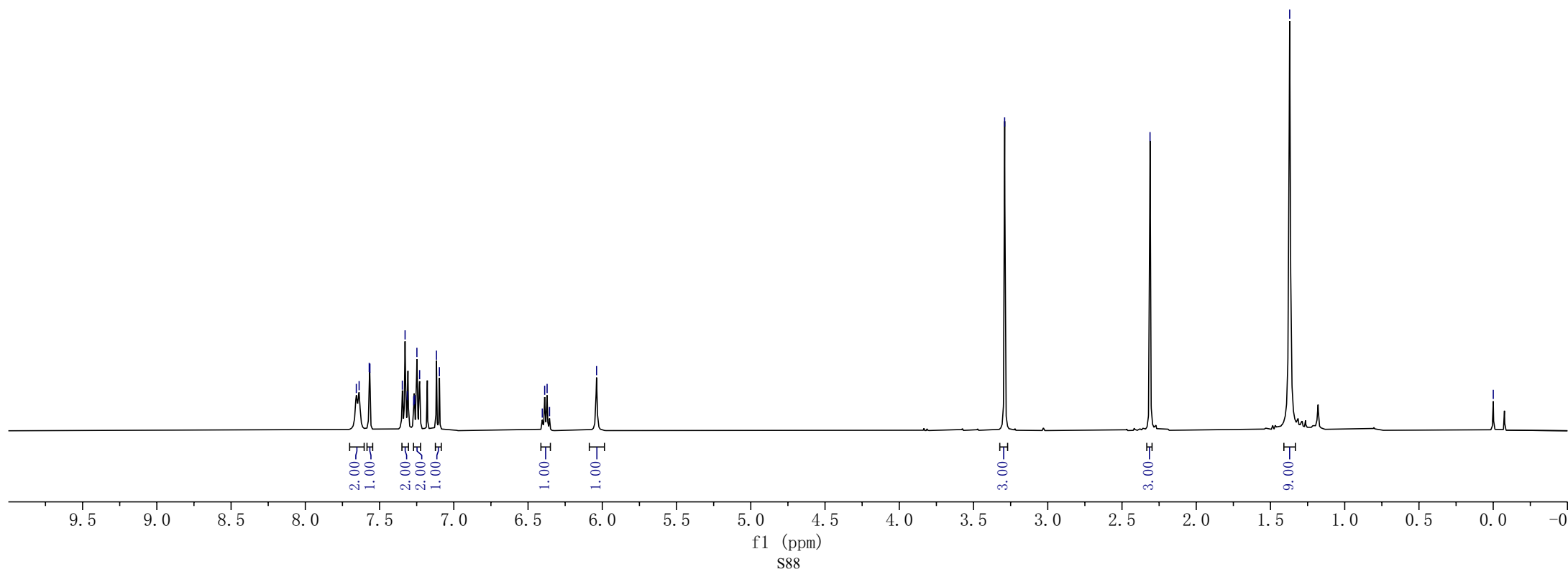
1.37

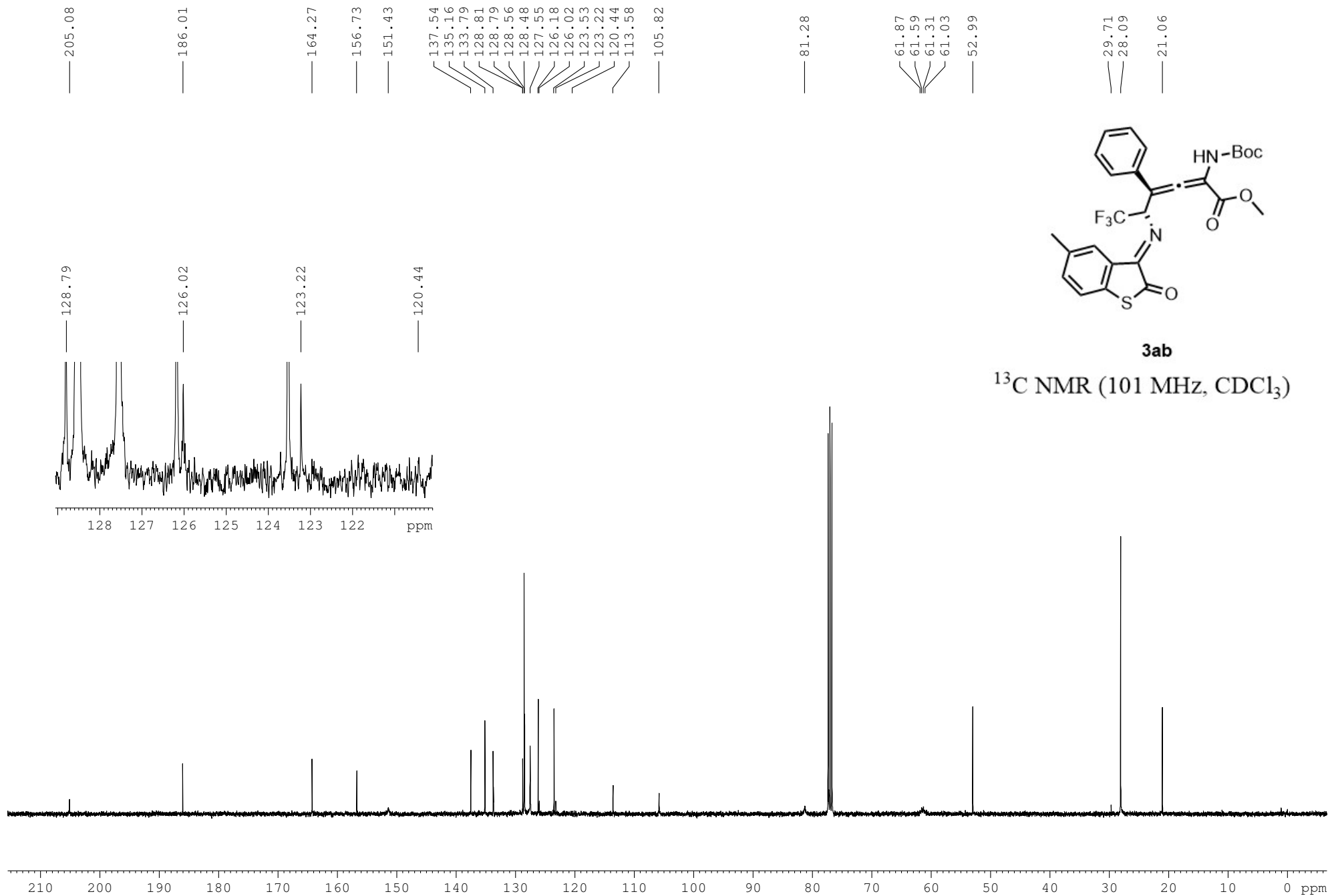
-0.00



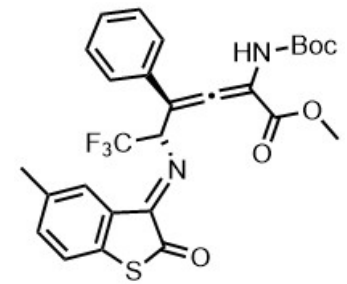
3ab

¹H NMR (400 MHz, CDCl₃)



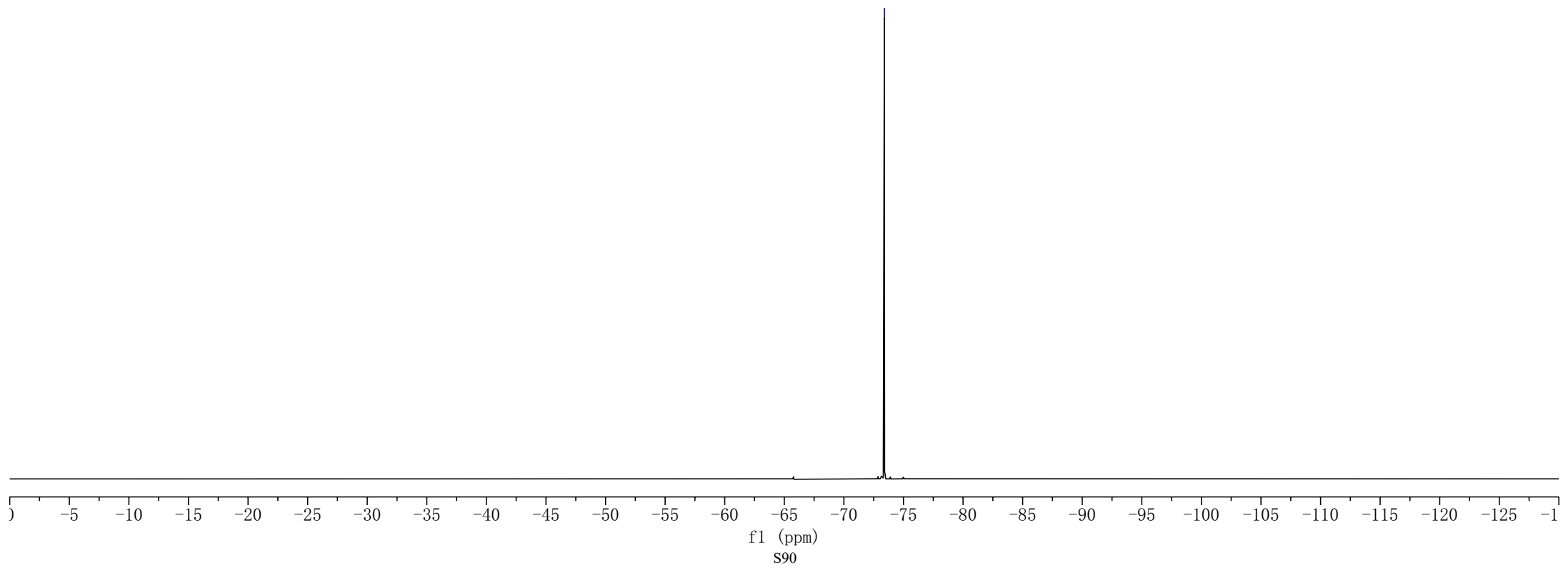


-73.40



3ab

^{19}F NMR (376 MHz, CDCl_3)

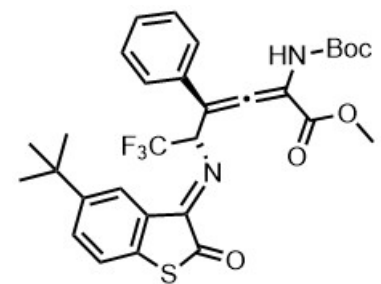


7.79
7.73
7.71
7.56
7.55
7.54
7.53
7.42
7.40
7.39
7.38
7.37
7.34
7.33
7.32
7.31
7.30
7.23
7.21
6.58
6.56
6.55
6.53
— 6.13

— 3.29

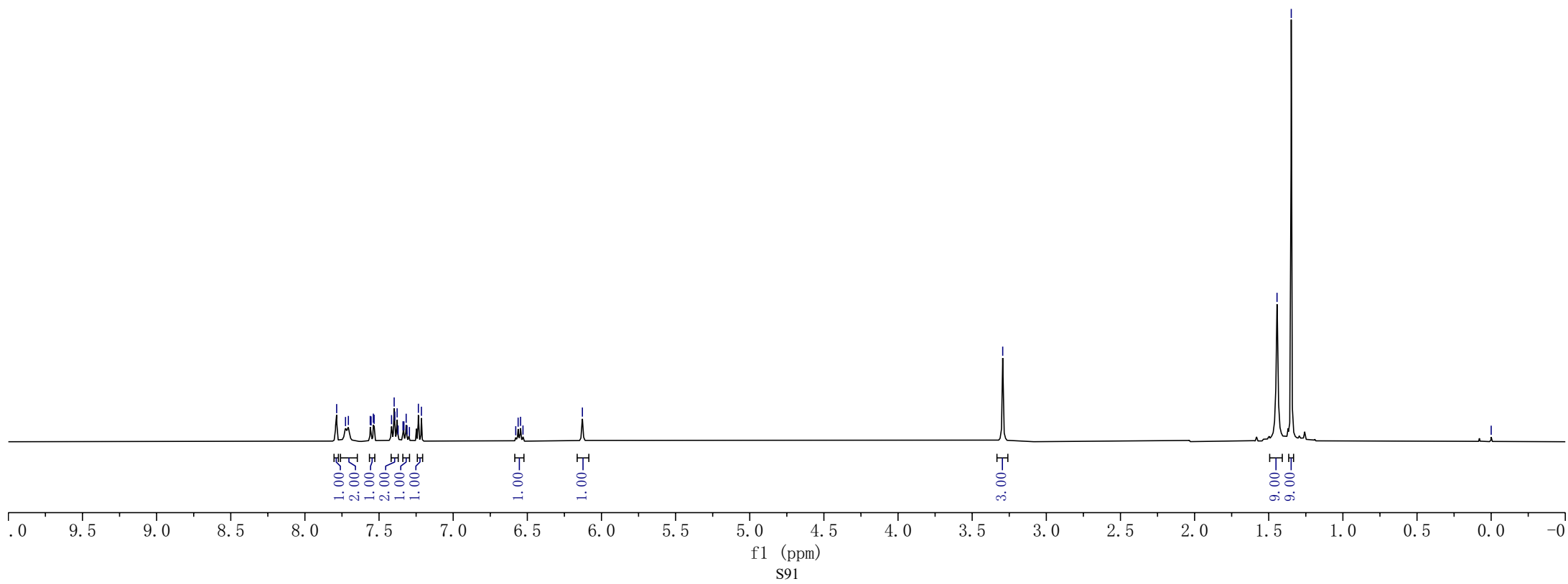
1.44
1.35

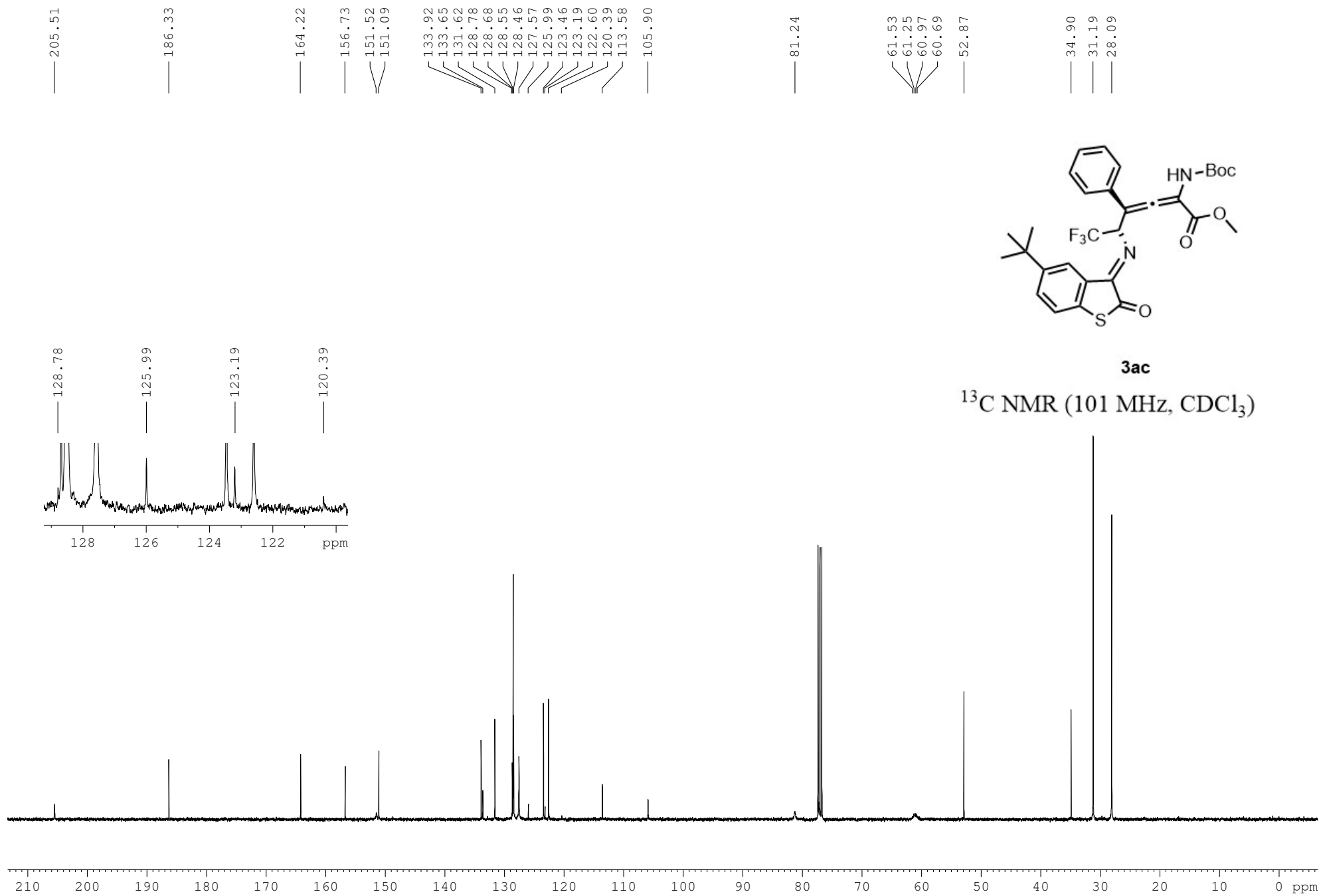
— 0.00

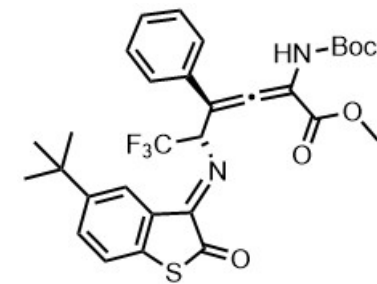


3ac

¹H NMR (400 MHz, CDCl₃)

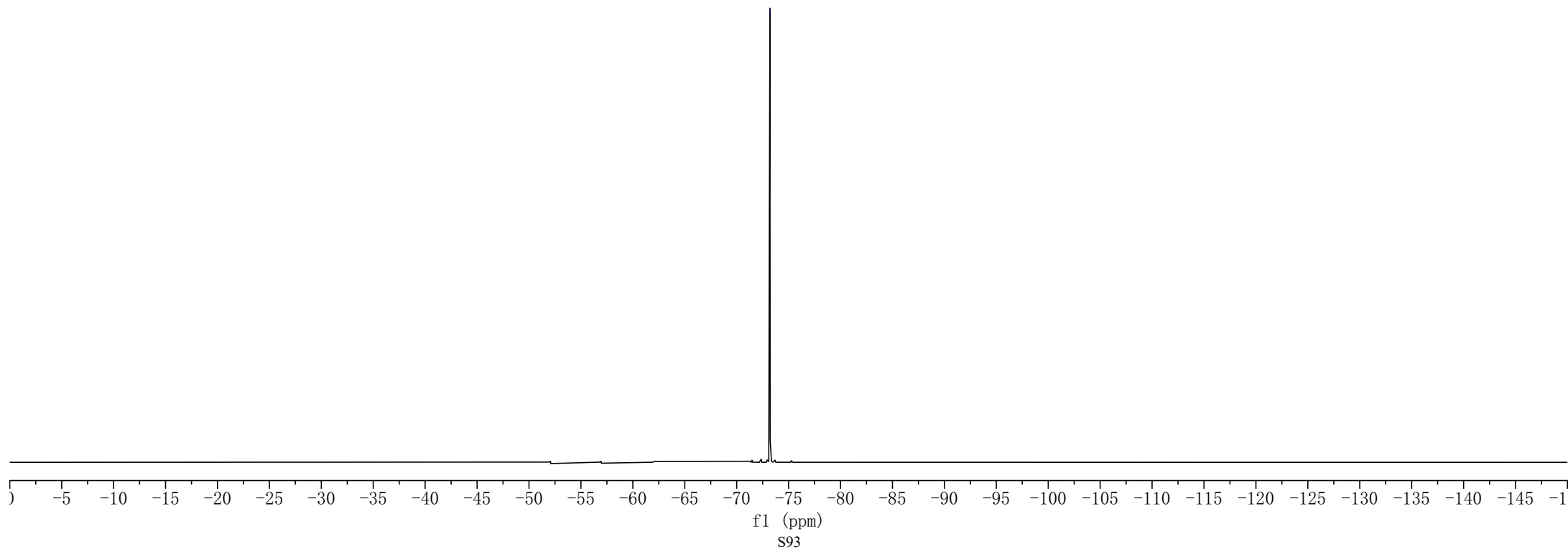






3ac

¹⁹F NMR (376 MHz, CDCl₃)



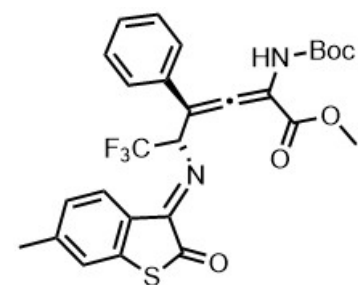
7.65
7.64
7.63
7.62
7.34
7.32
7.30
7.26
7.24
7.22
7.03
7.01
6.41
6.39
6.38
6.36
6.03

3.28

2.32

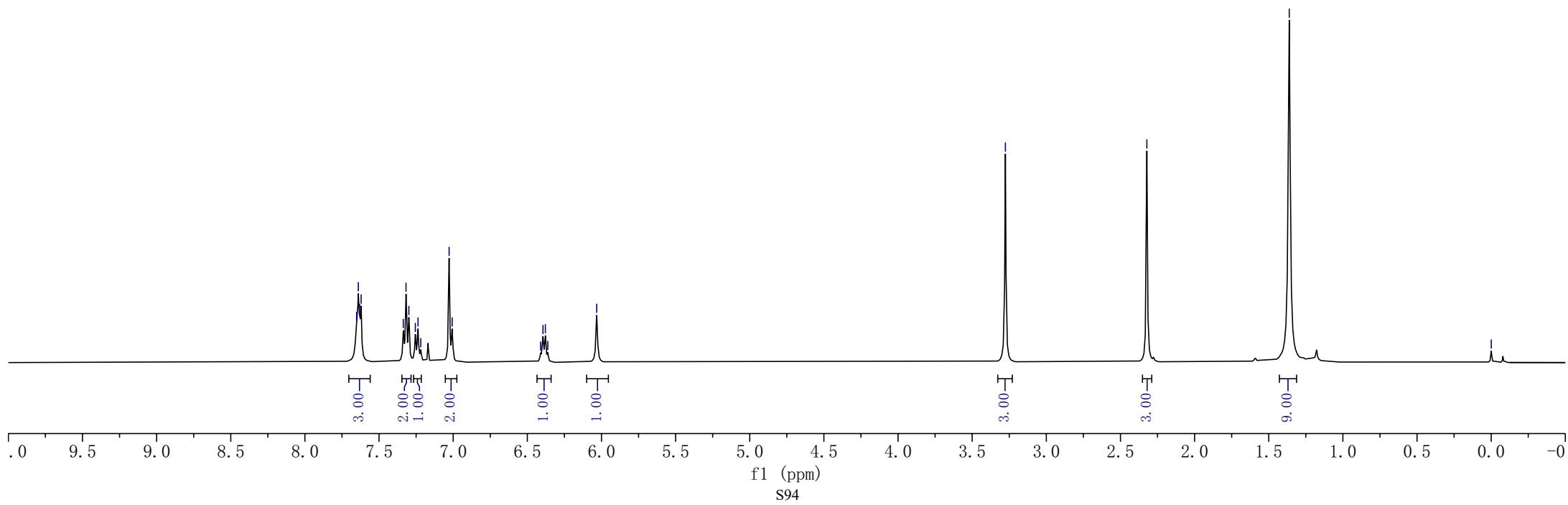
1.36

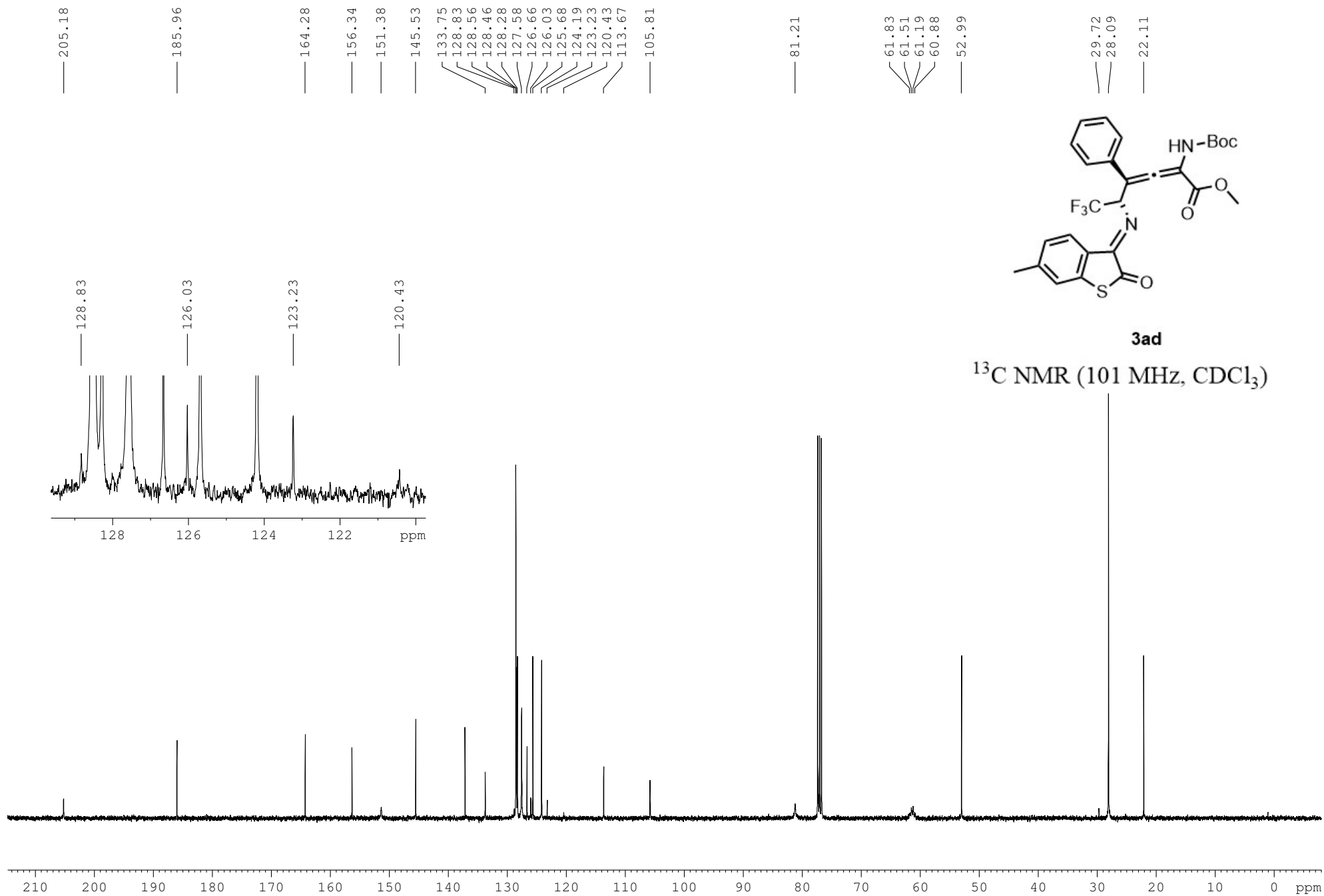
0.00

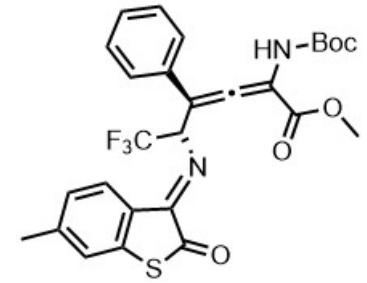


3ad

$^1\text{H NMR}$ (400 MHz, CDCl_3)

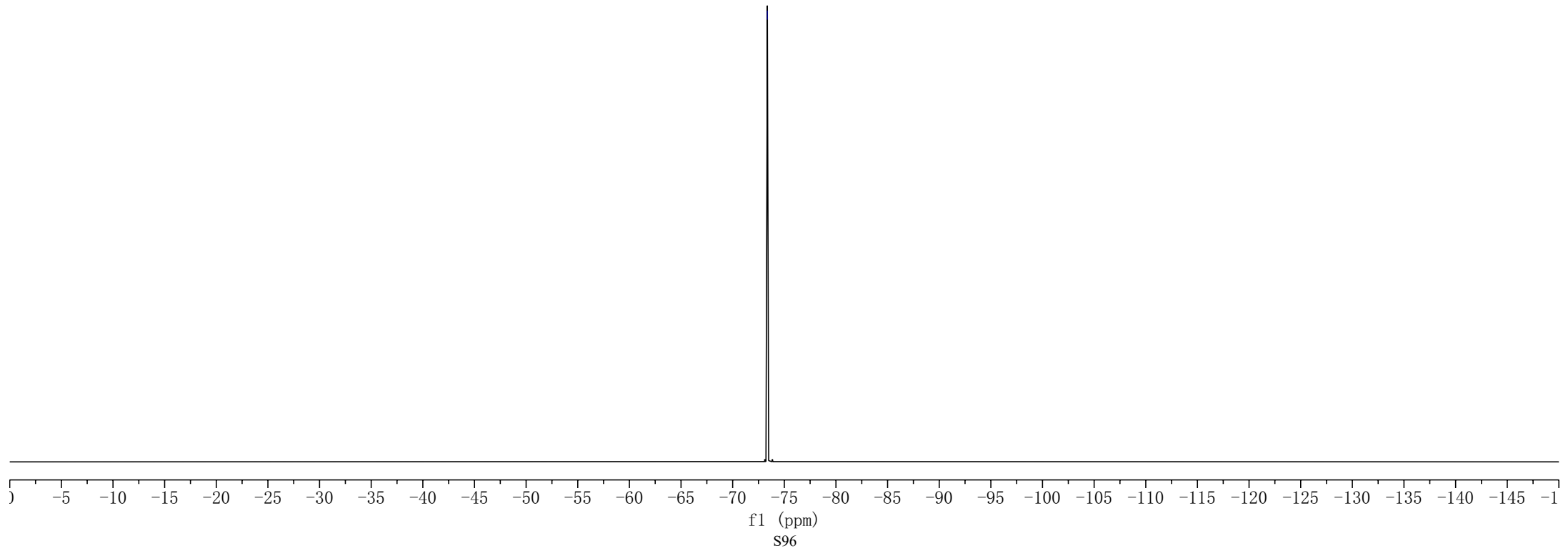






3ad

^{19}F NMR (376 MHz, CDCl_3)



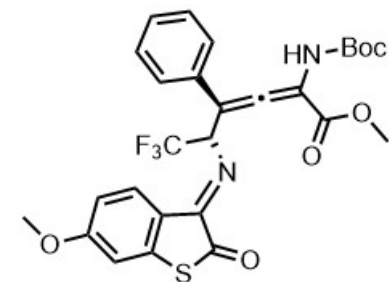
7.70
7.69
7.68
7.67
7.65
7.63
7.33
7.31
7.30
7.29
7.25
7.24
7.23
7.21
6.72
6.71
6.70
6.69
6.39
6.37
6.36
6.34
6.04

3.78

3.30

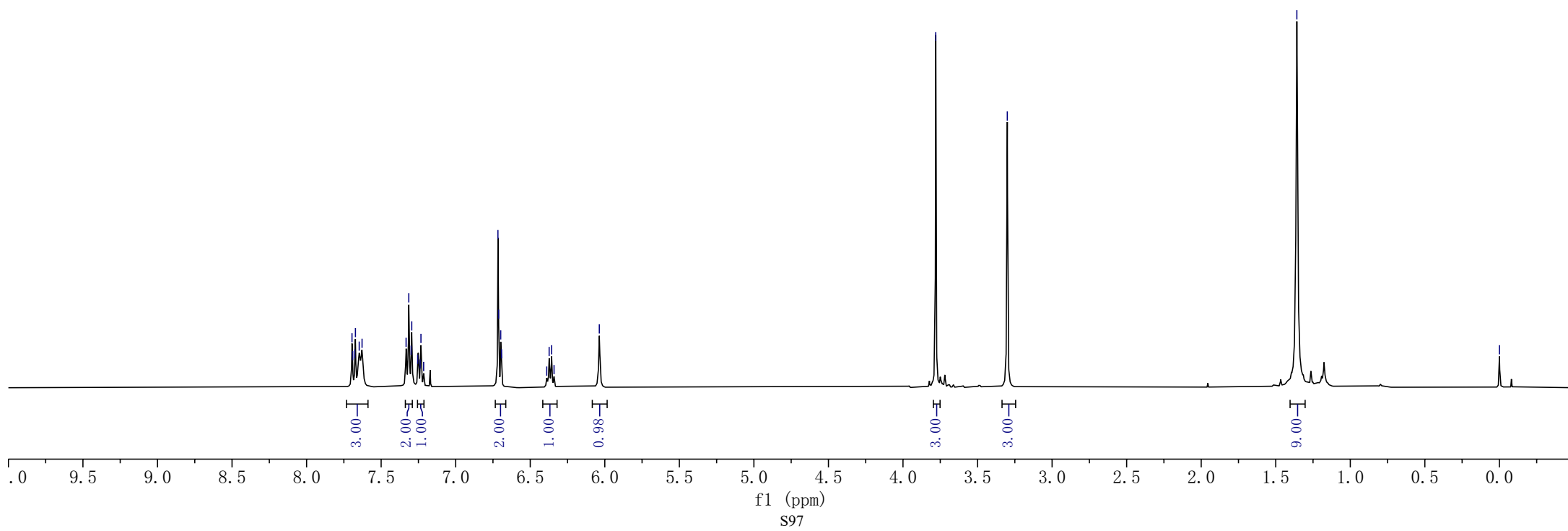
1.36

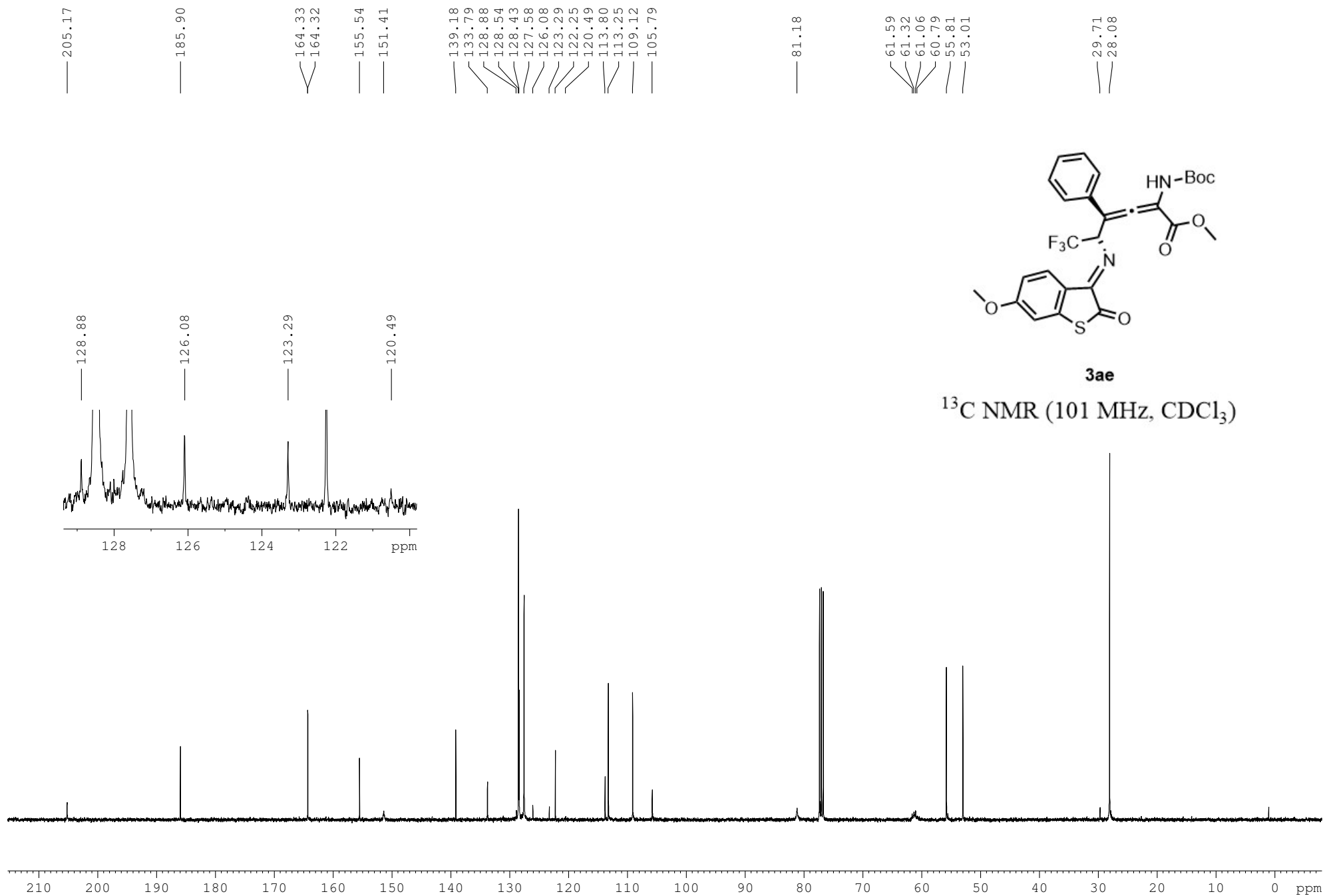
-0.00



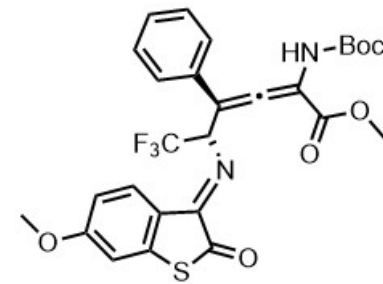
3ae

¹H NMR (400 MHz, CDCl₃)



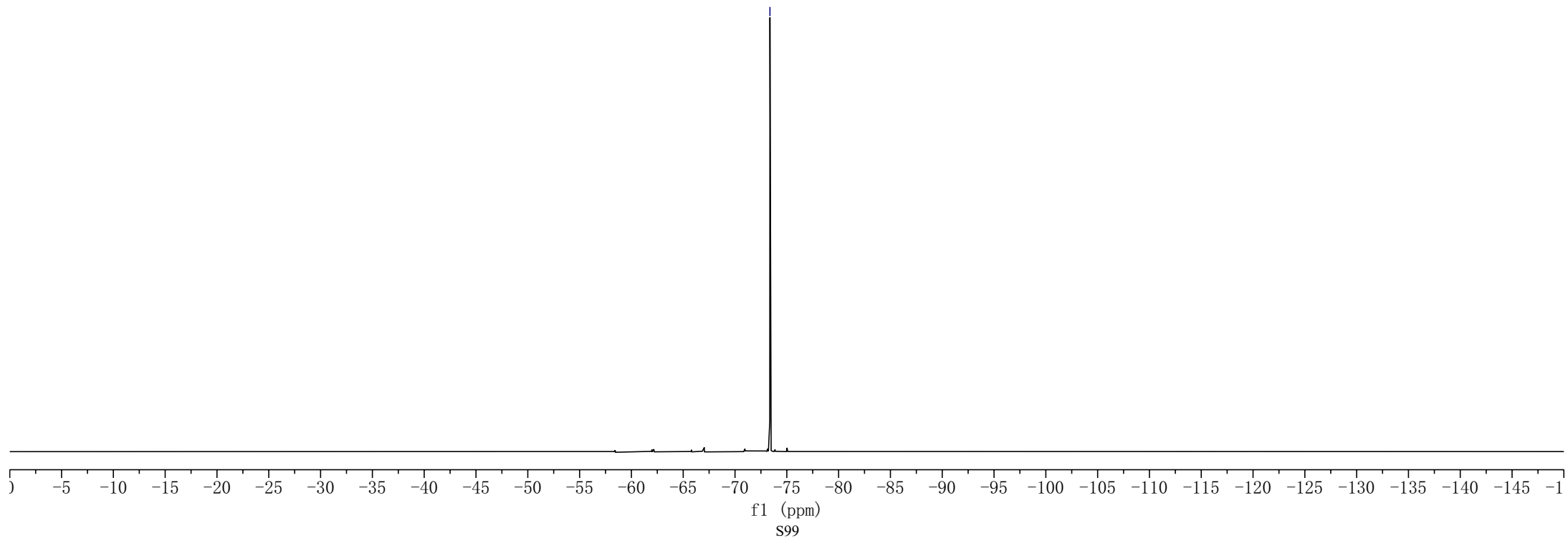


-73.37



3ae

^{19}F NMR (376 MHz, CDCl_3)

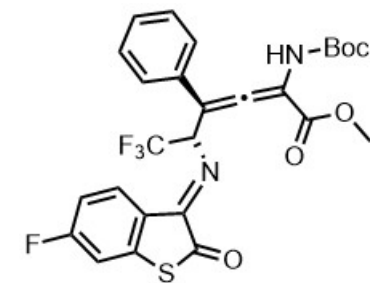


7.80
7.78
7.76
7.64
7.62
7.34
7.33
7.32
7.31
7.27
7.25
7.24
7.23
6.99
6.98
6.97
6.96
6.95
6.94
6.93
6.91
6.39
6.38
6.36
6.34
6.03

—3.32

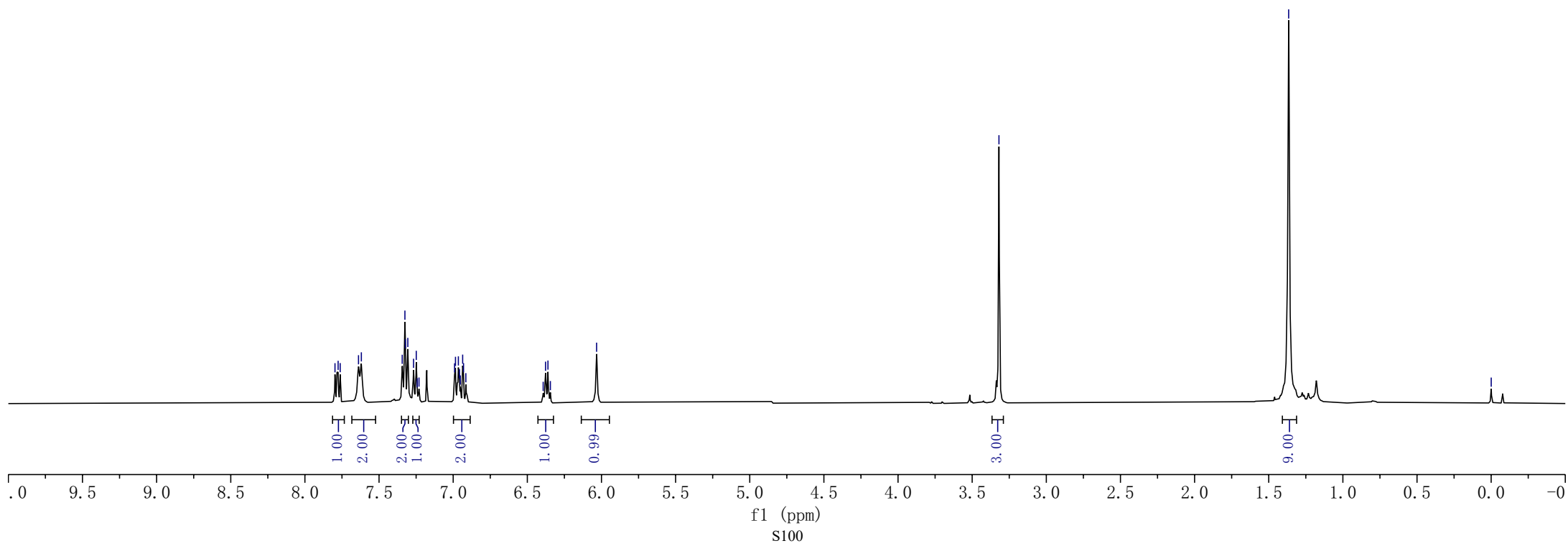
—1.37

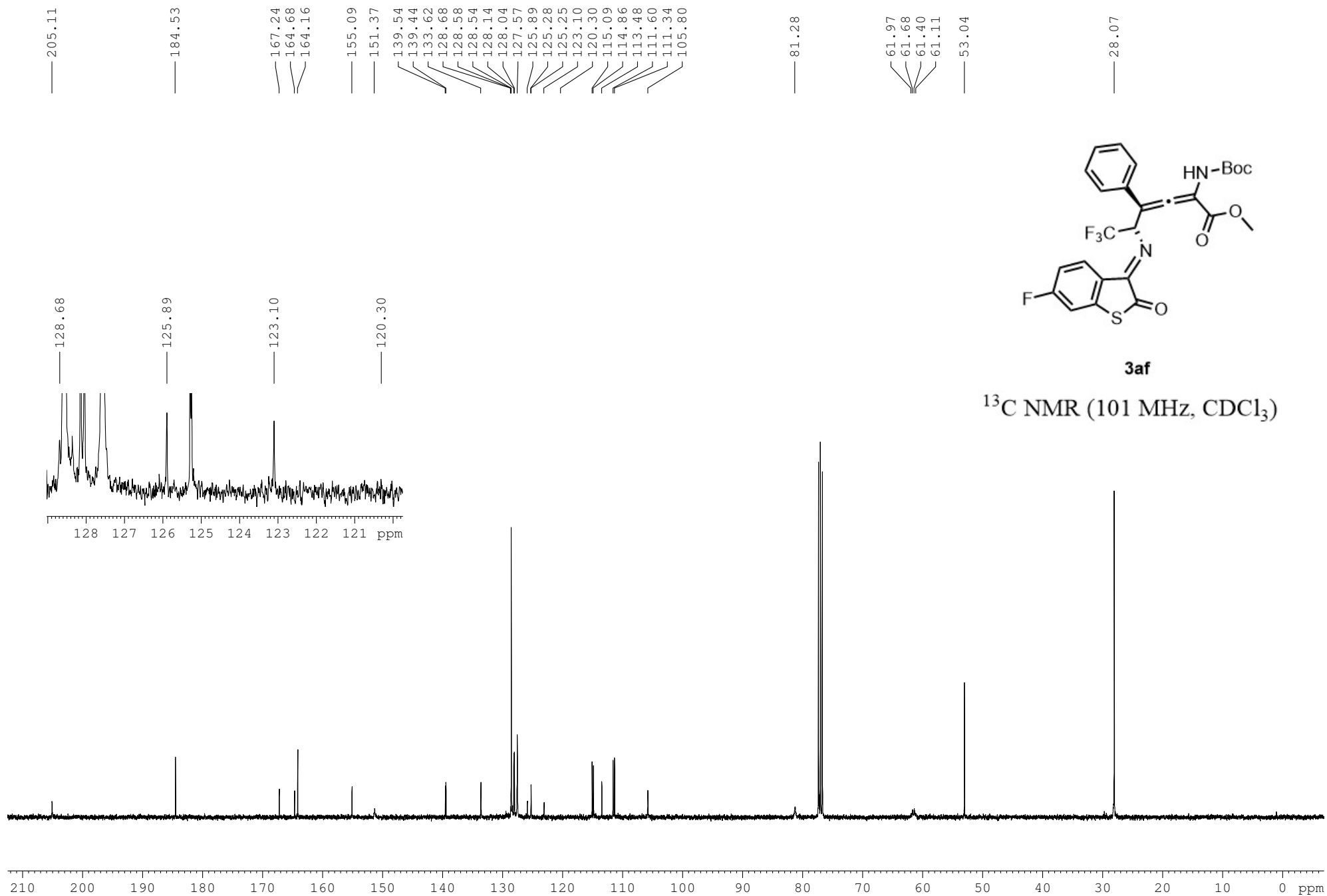
—0.00

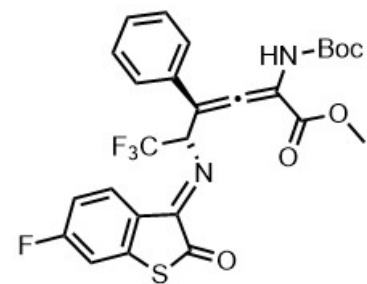


3af

¹H NMR (400 MHz, CDCl₃)

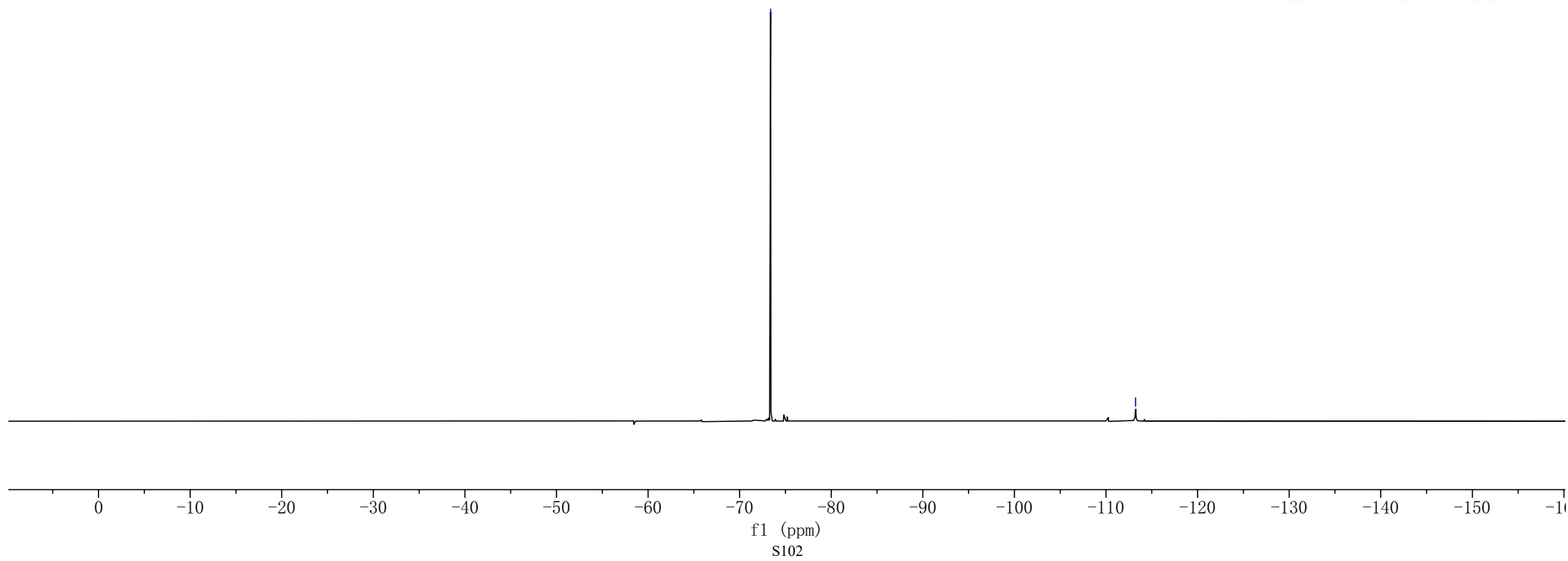






3af

^{19}F NMR (376 MHz, CDCl_3)



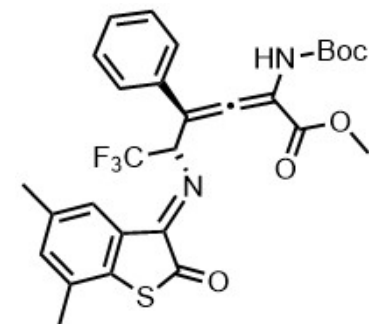
7.66
7.64
7.40
7.34
7.32
7.30
7.26
7.25
7.24
7.23
7.22
7.07
6.41
6.39
6.37
6.36
6.04

3.27

2.27
2.15

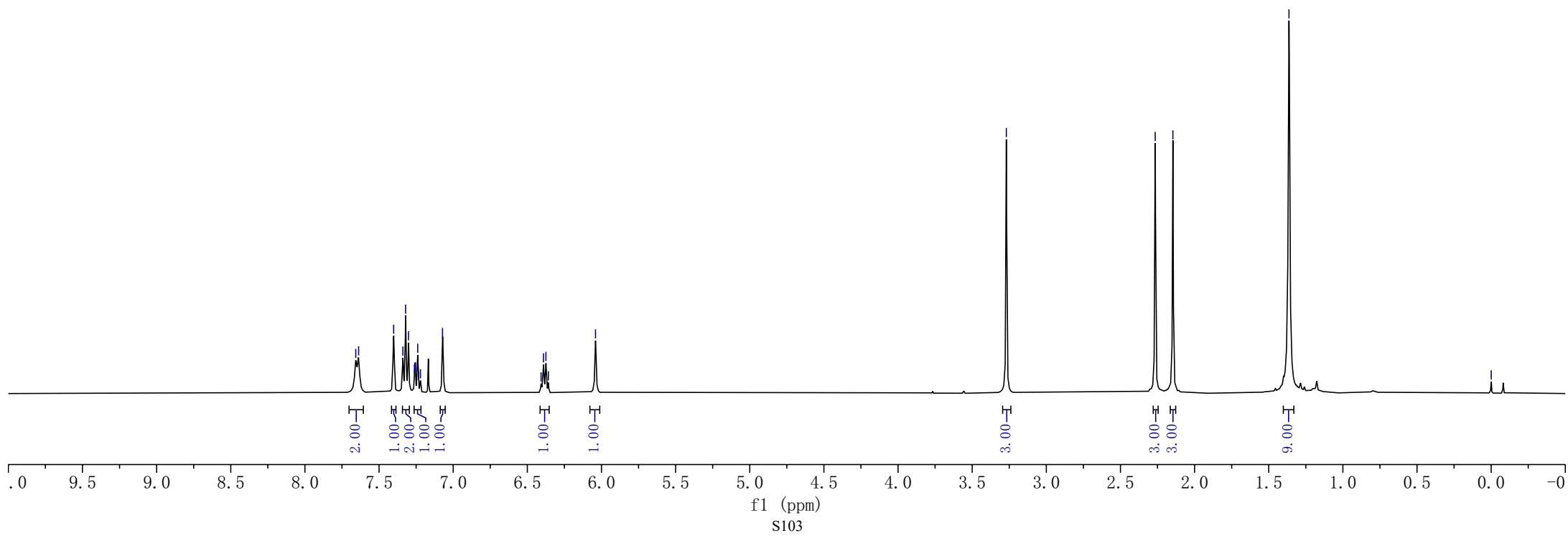
1.36

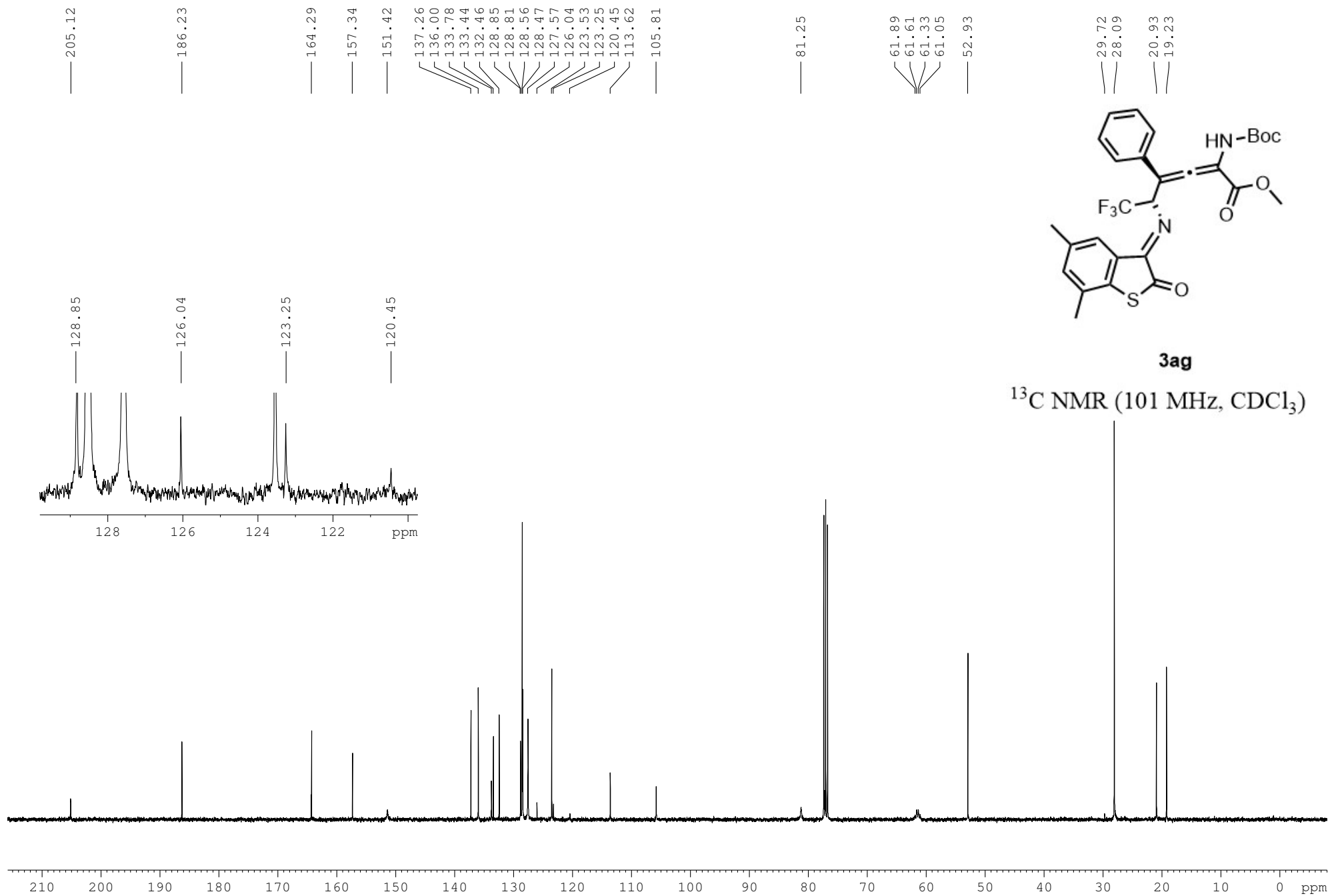
-0.00

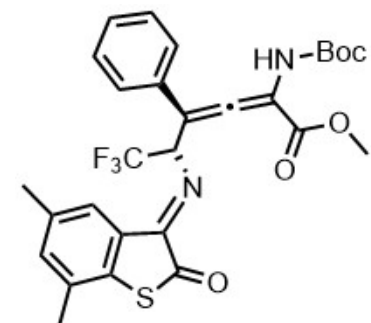


3ag

¹H NMR (400 MHz, CDCl₃)



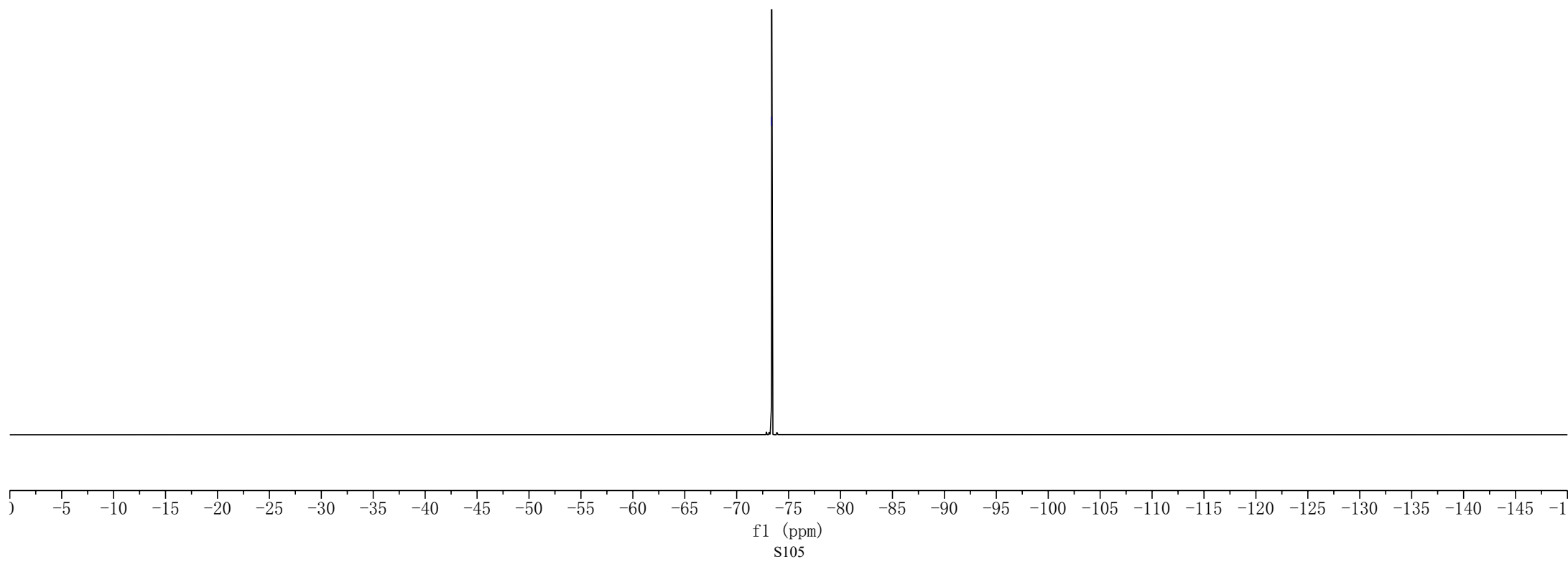




3ag

^{19}F NMR (376 MHz, CDCl_3)

—73.37



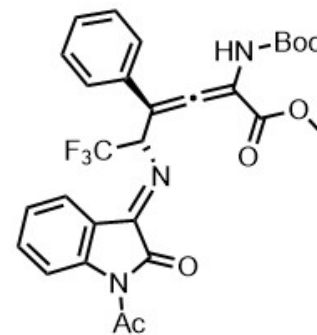
8.19
8.17
7.77
7.75
7.70
7.69
7.47
7.45
7.44
7.35
7.34
7.32
7.27
7.26
7.24
7.22
7.21
7.19
7.18
6.71
6.69
6.66
6.02

— 3.17

— 2.62

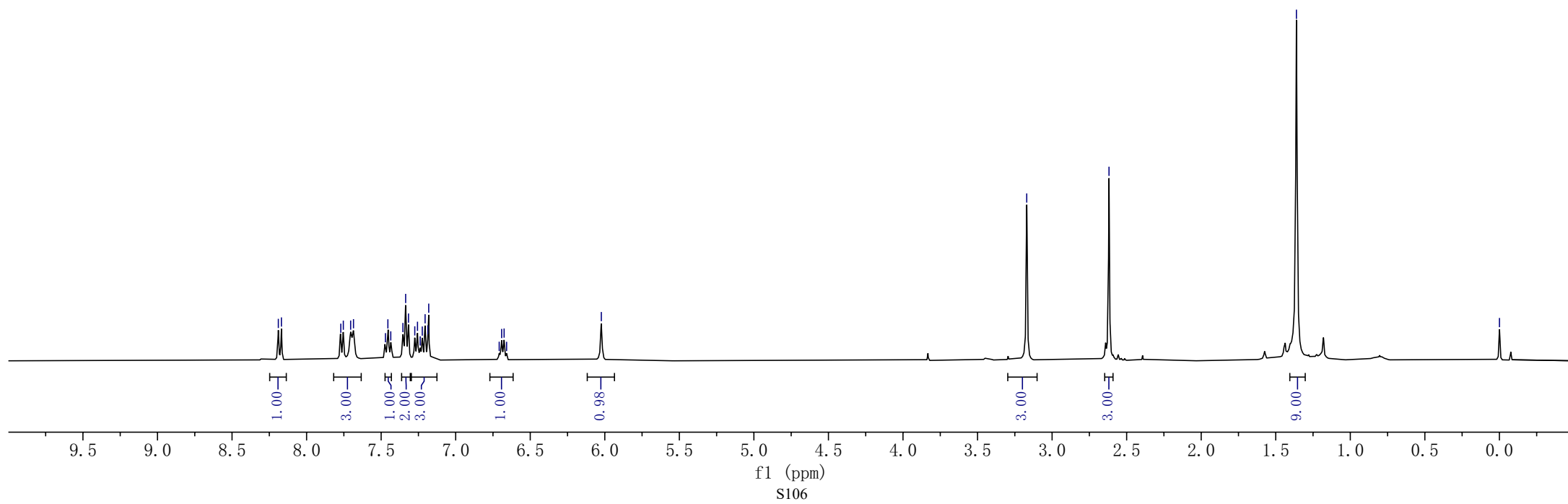
— 1.36

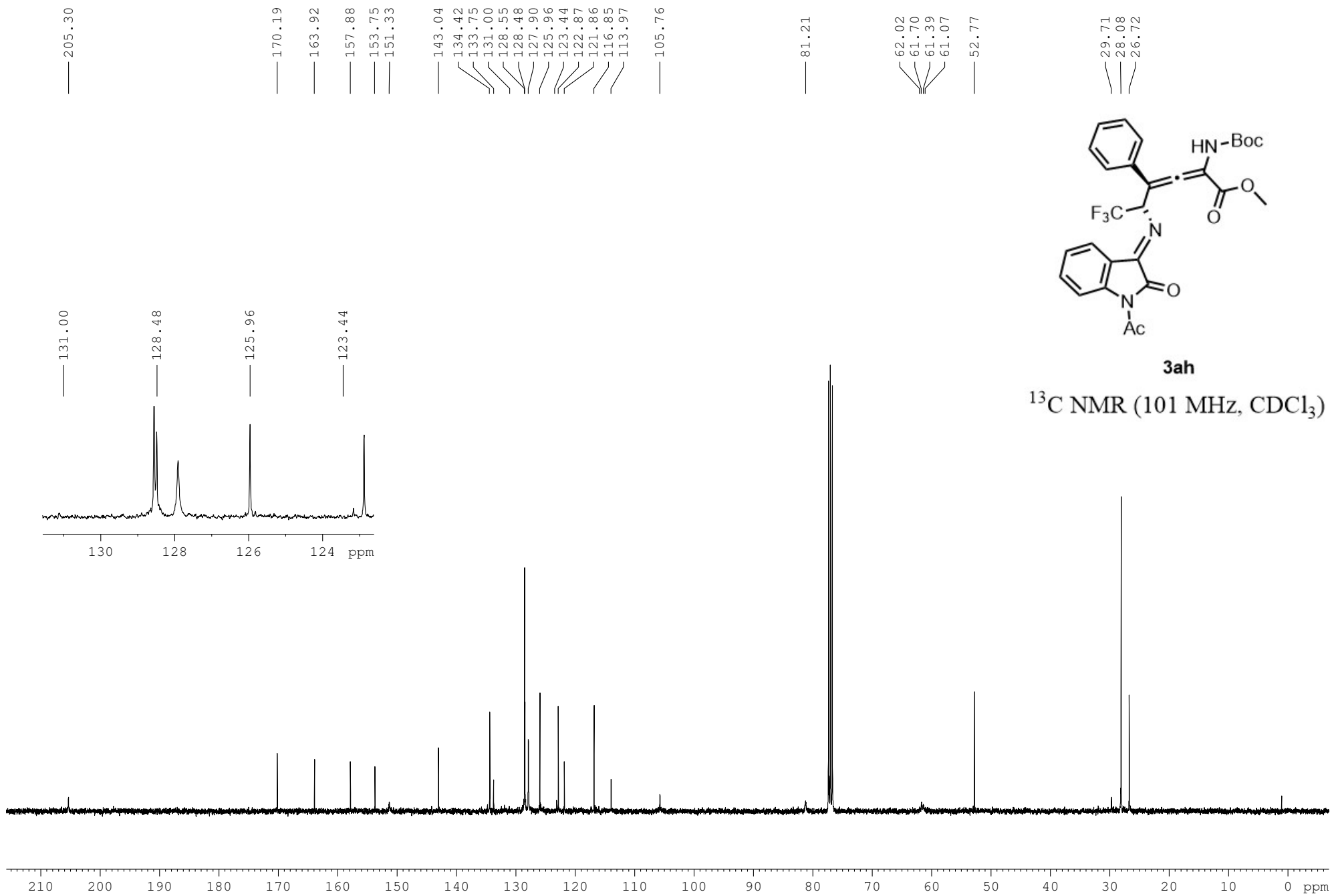
— -0.00

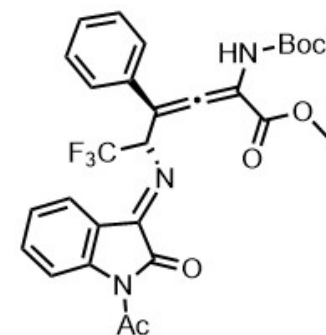


3ah

¹H NMR (400 MHz, CDCl₃)



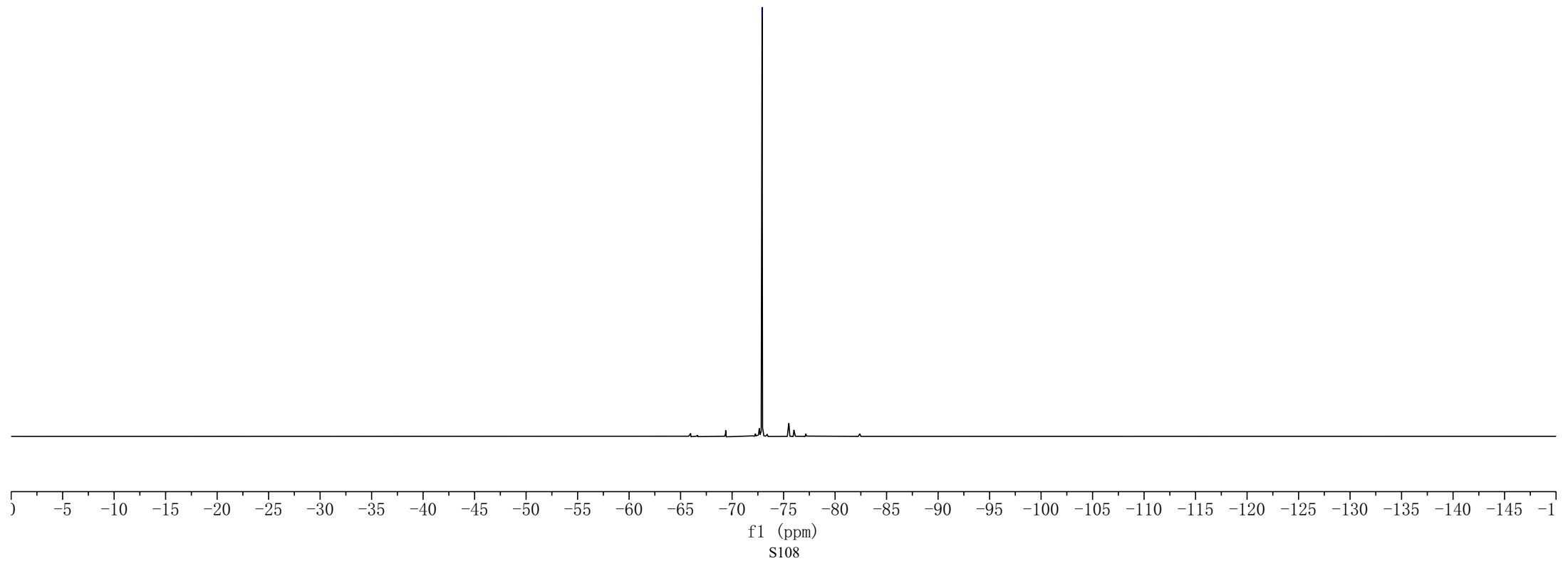




3ah

¹⁹F NMR (376 MHz, CDCl₃)

-72.91



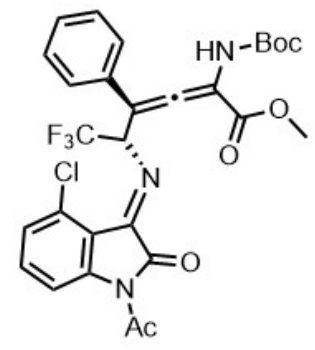
8.14
8.12
7.70
7.68
7.34
7.33
7.32
7.31
7.30
7.29
7.25
7.23
7.21
7.18
7.17
7.16
6.88
6.86
6.84
6.83
6.06

3.22

2.60

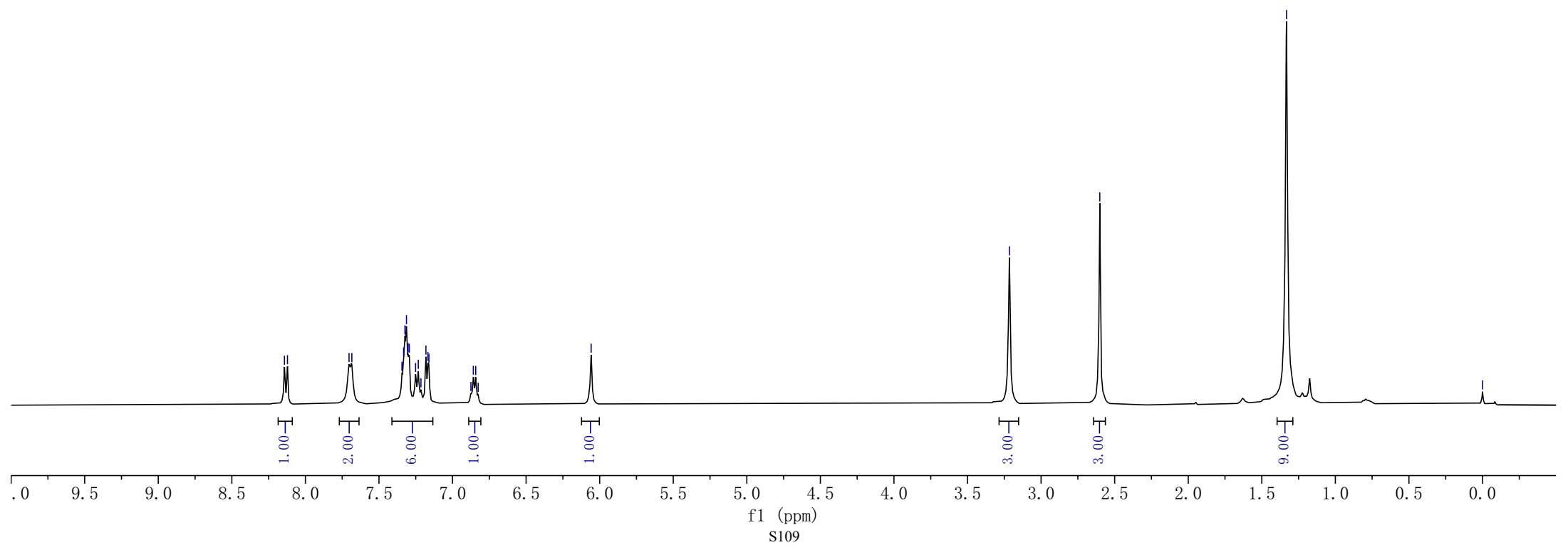
1.33

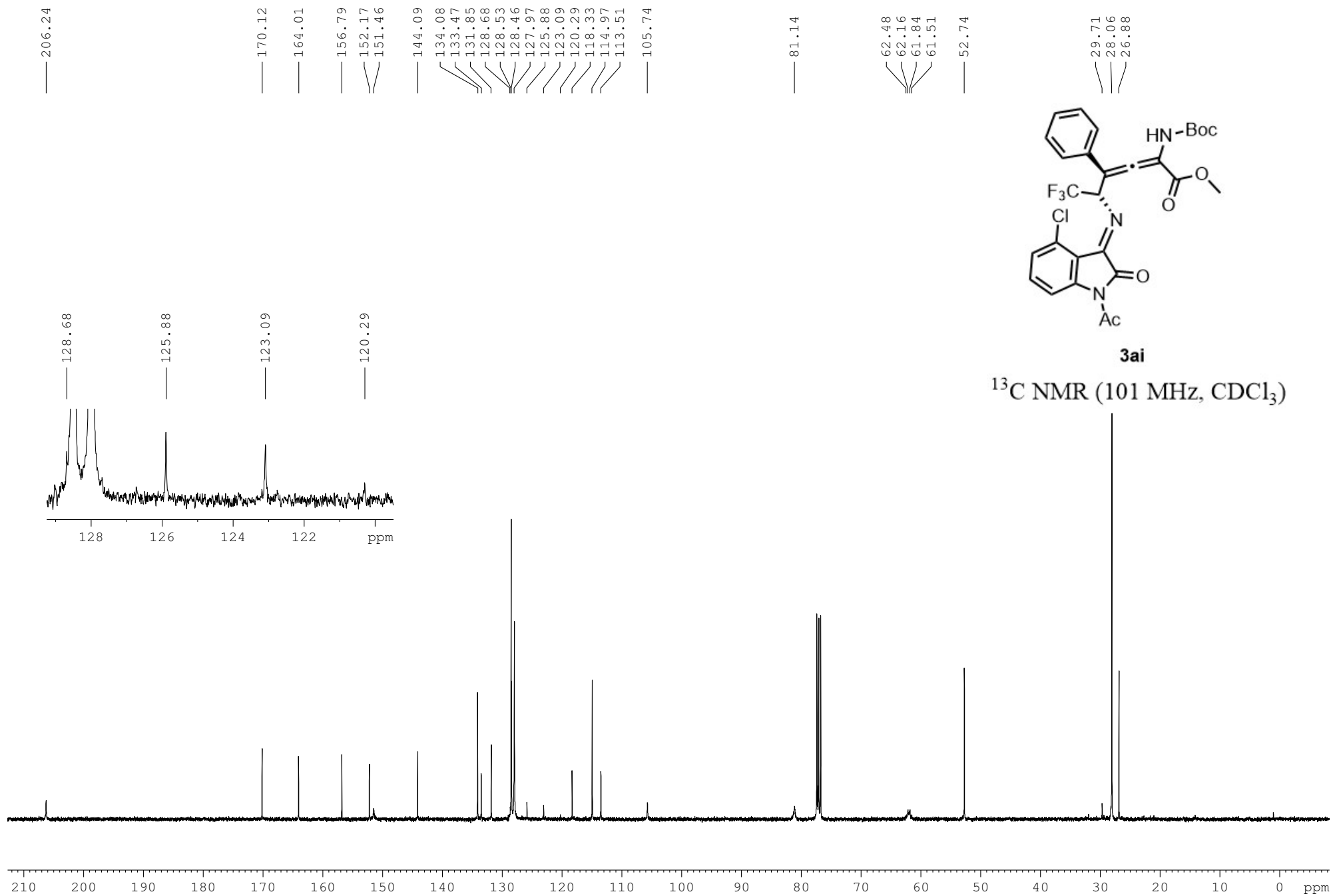
-0.00

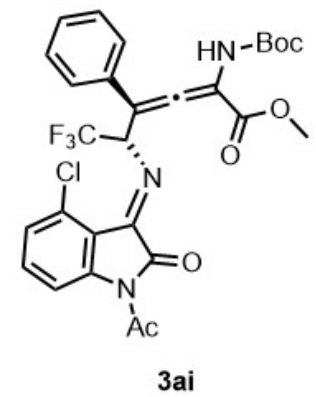


3ai

¹H NMR (400 MHz, CDCl₃)

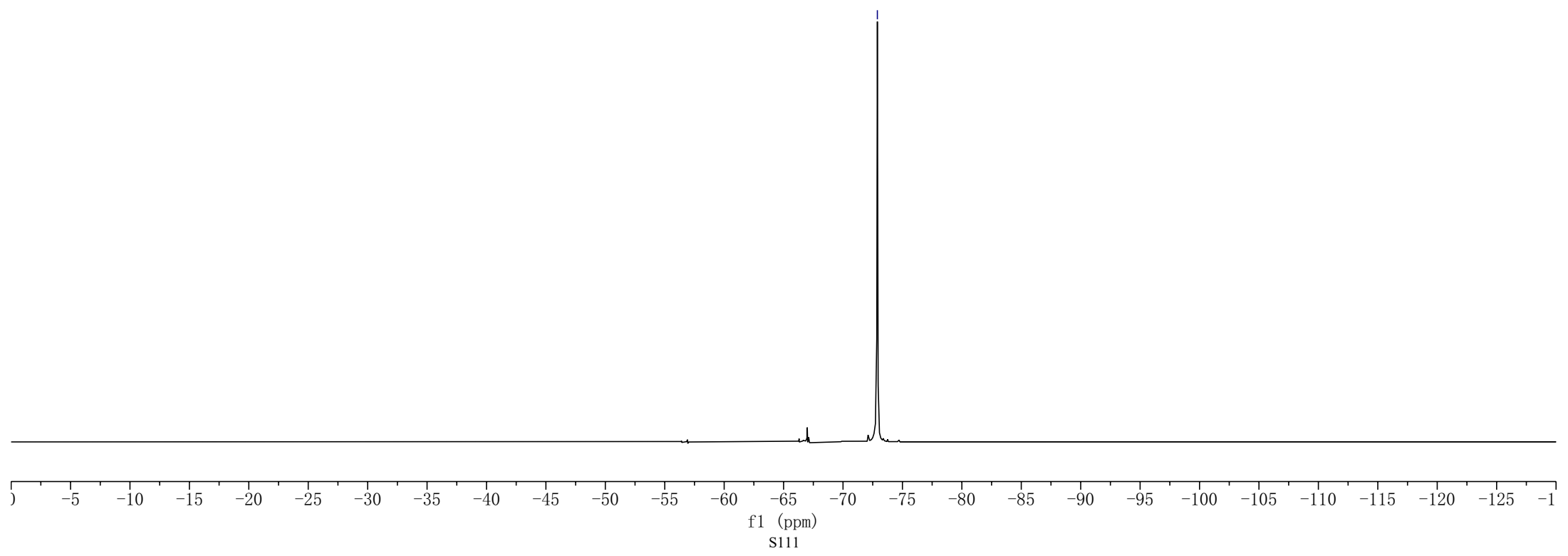






¹⁹F NMR (376 MHz, CDCl₃)

-72.89



8.29
8.28
8.27
8.26
7.77
7.75
7.55
7.54
7.53
7.52
7.43
7.41
7.39
7.35
7.34
7.33
7.32
7.31
7.25
7.23
7.21
7.20
6.76
6.74
6.72
6.71

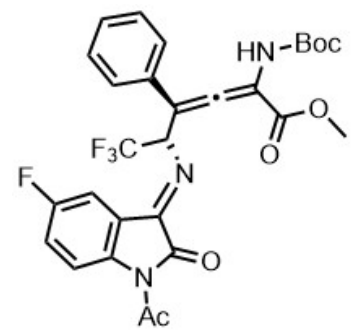
6.11

3.31

2.68

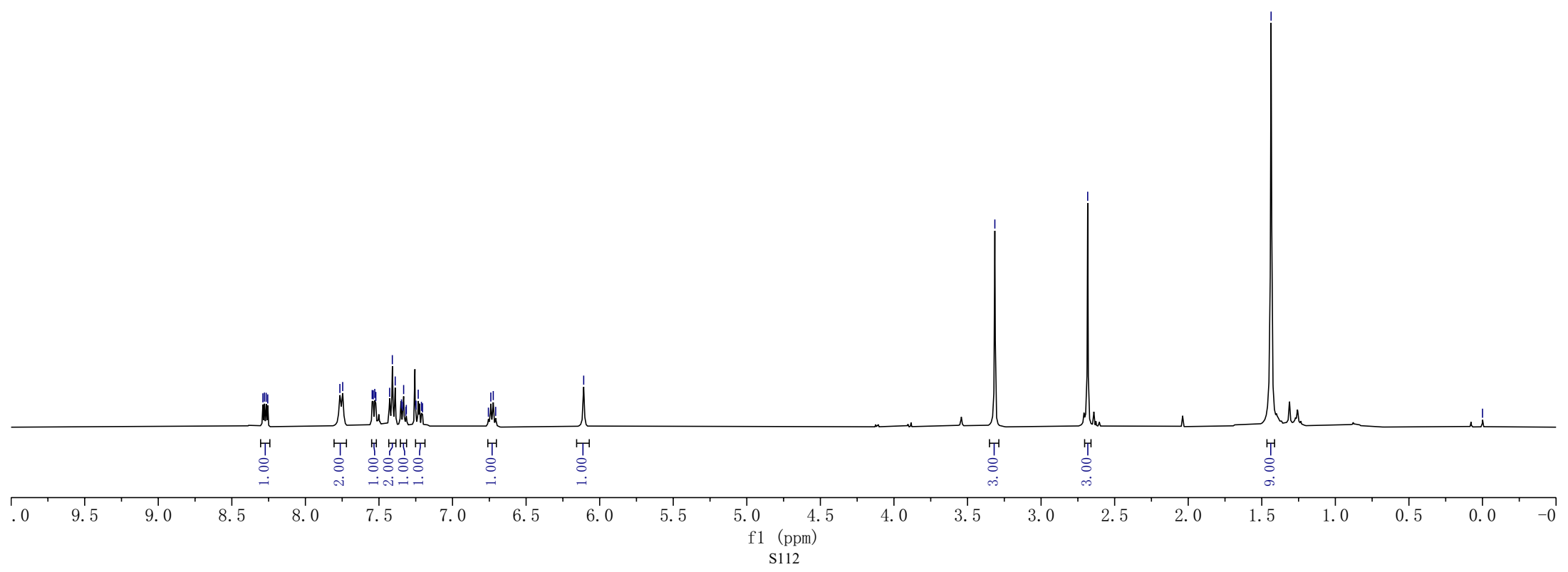
1.44

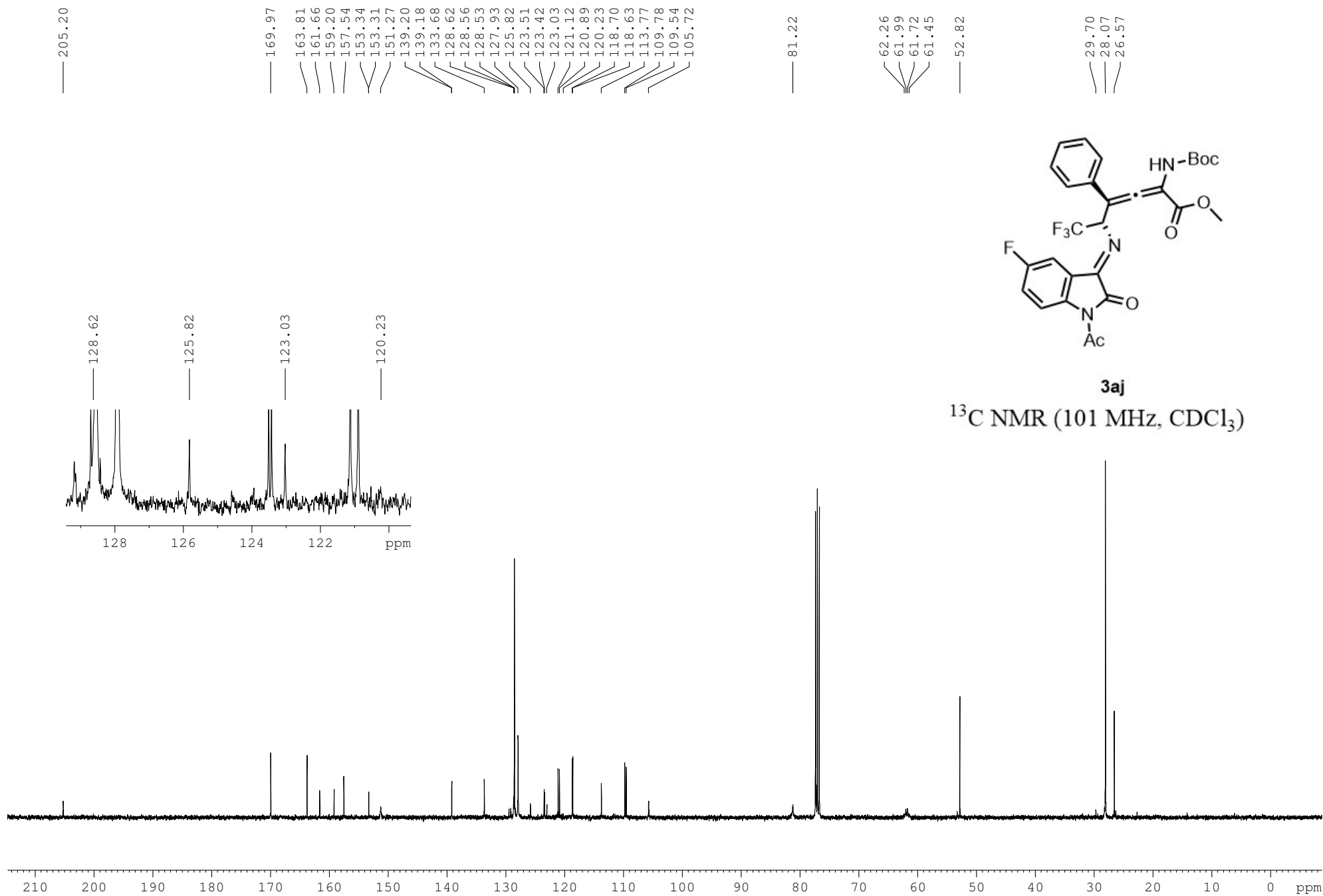
-0.00

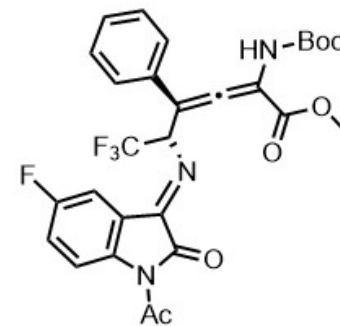


3aj

¹H NMR (400 MHz, CDCl₃)

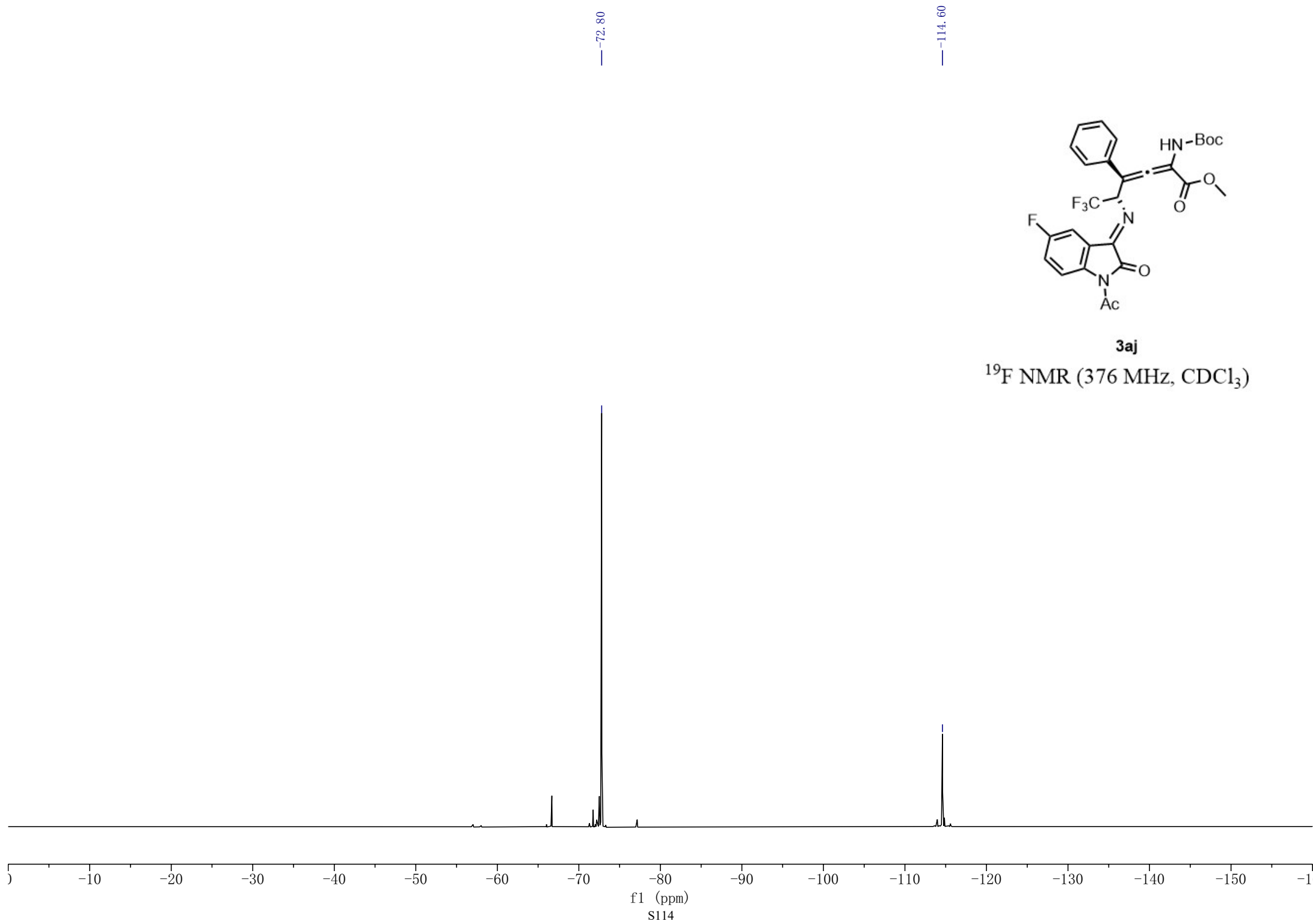






3aj

¹⁹F NMR (376 MHz, CDCl₃)



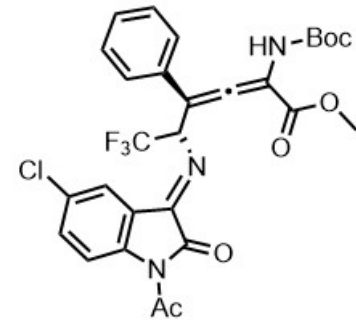
8.24
8.22
7.82
7.81
7.76
7.74
7.50
7.48
7.43
7.41
7.39
7.36
7.35
7.34
7.33
7.32
6.74
6.72
6.70
6.69
6.11

3.33

2.68

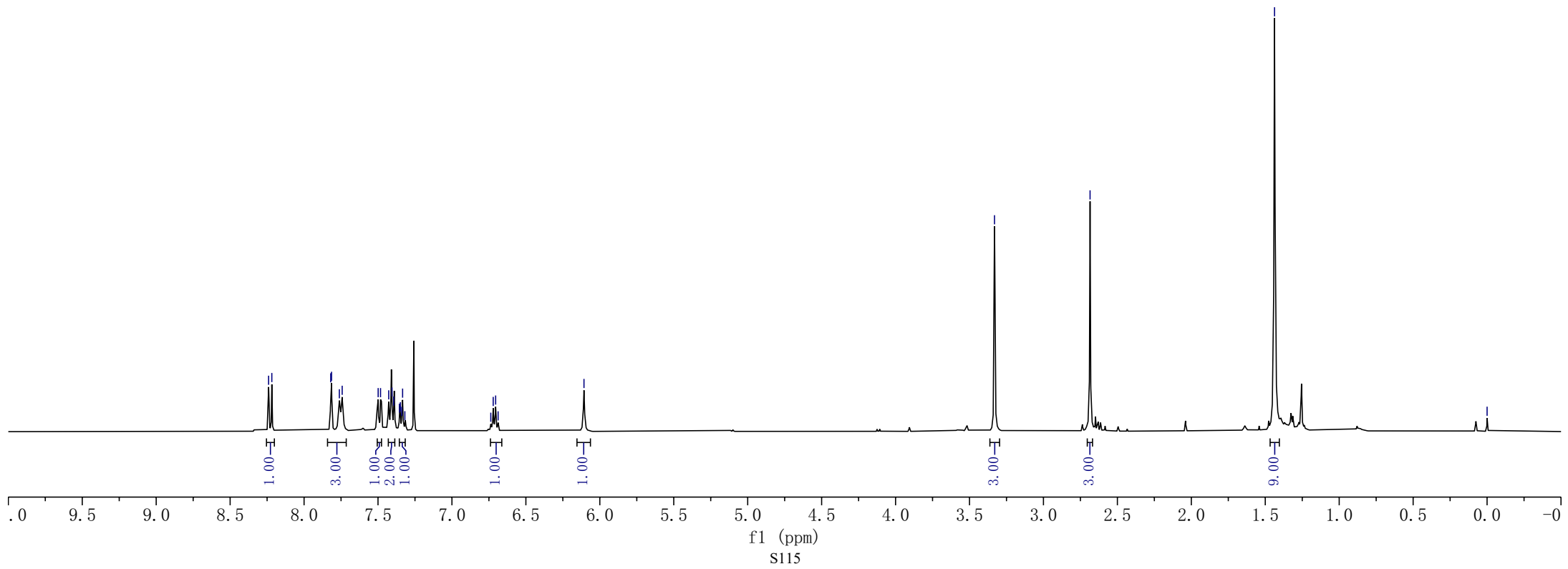
1.44

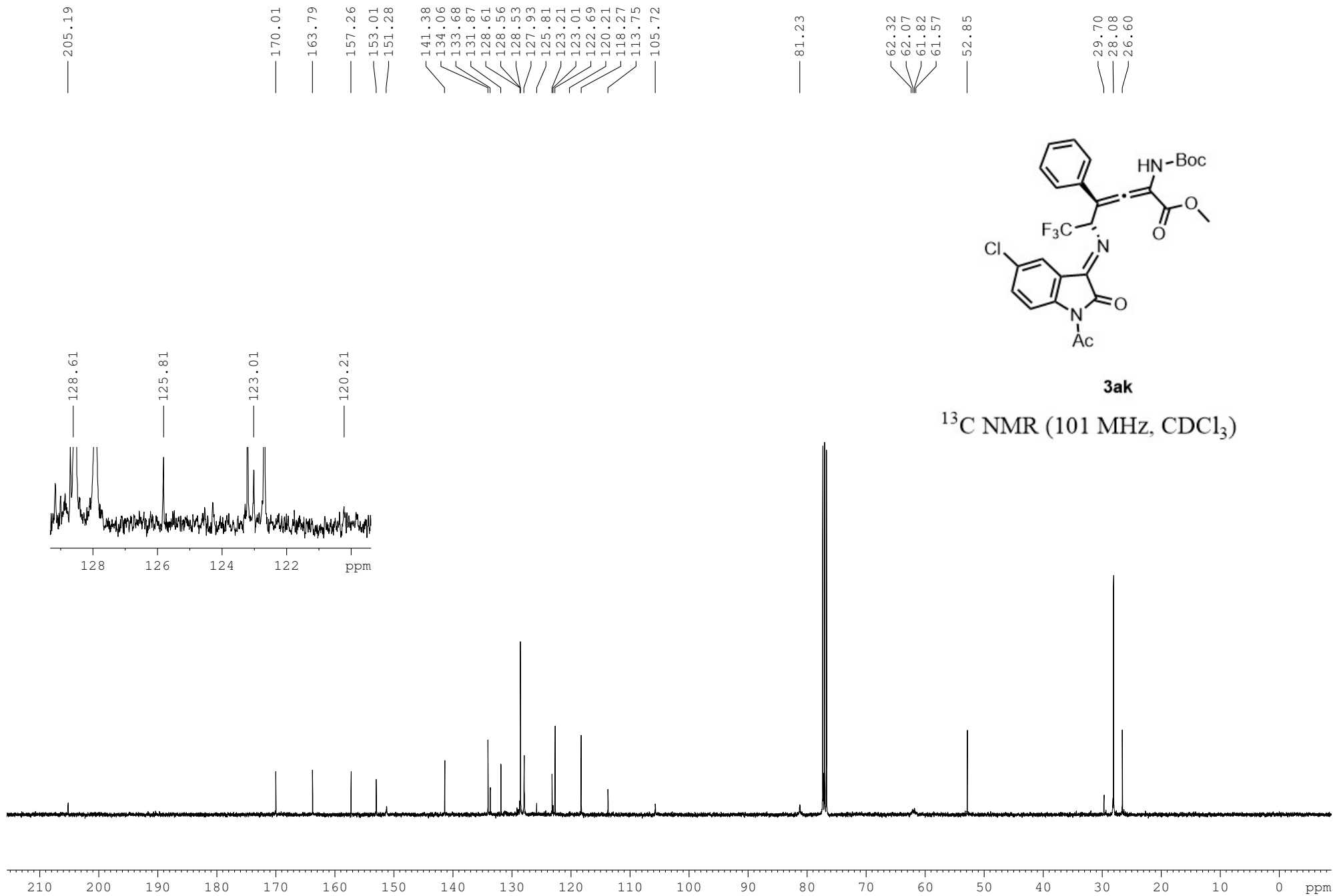
-0.00



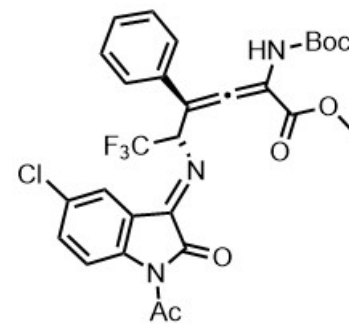
3ak

¹H NMR (400 MHz, CDCl₃)



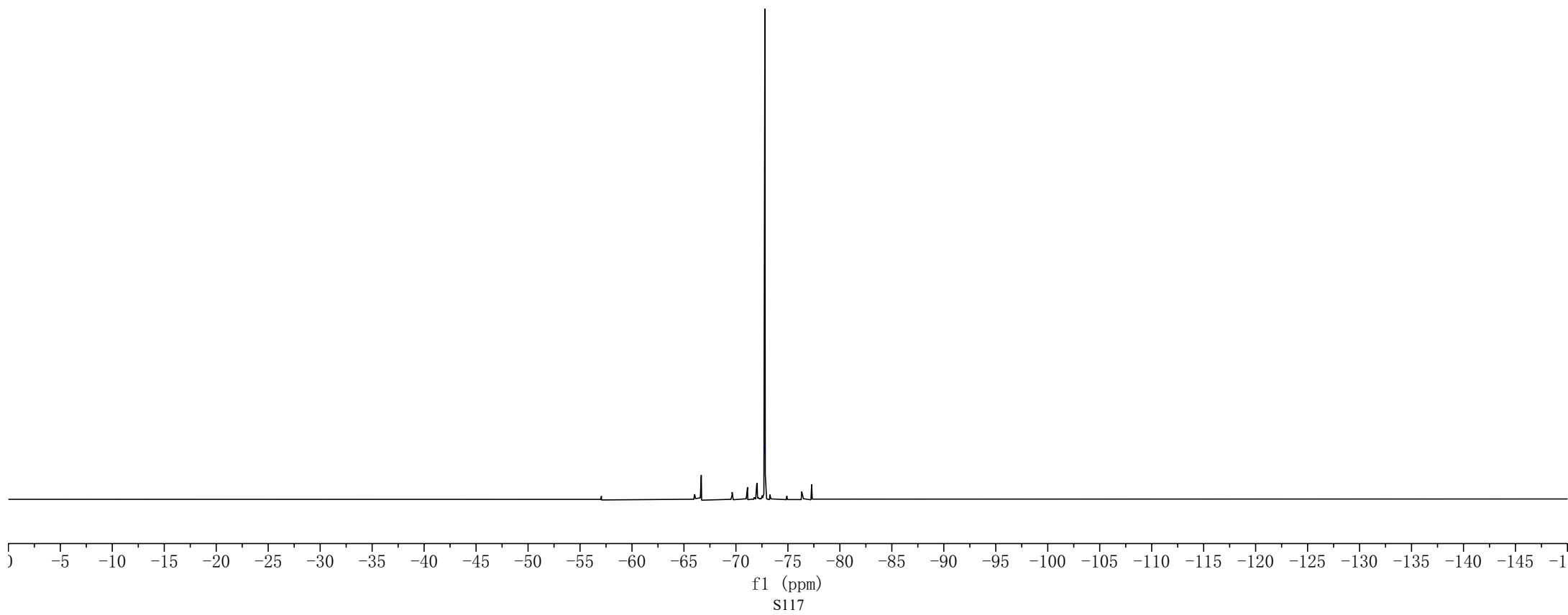


-72.75



3ak

¹⁹F NMR (376 MHz, CDCl₃)



8.09
8.07
7.88
7.87
7.68
7.66
7.57
7.56
7.54
7.34
7.32
7.30
7.26
7.24
7.23
6.65
6.63
6.62
6.60

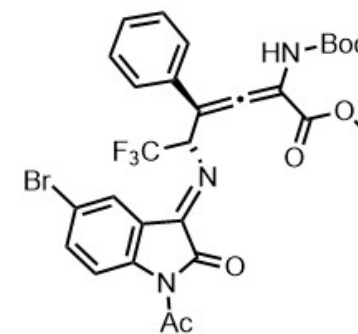
— 6.04

— 3.25

— 2.59

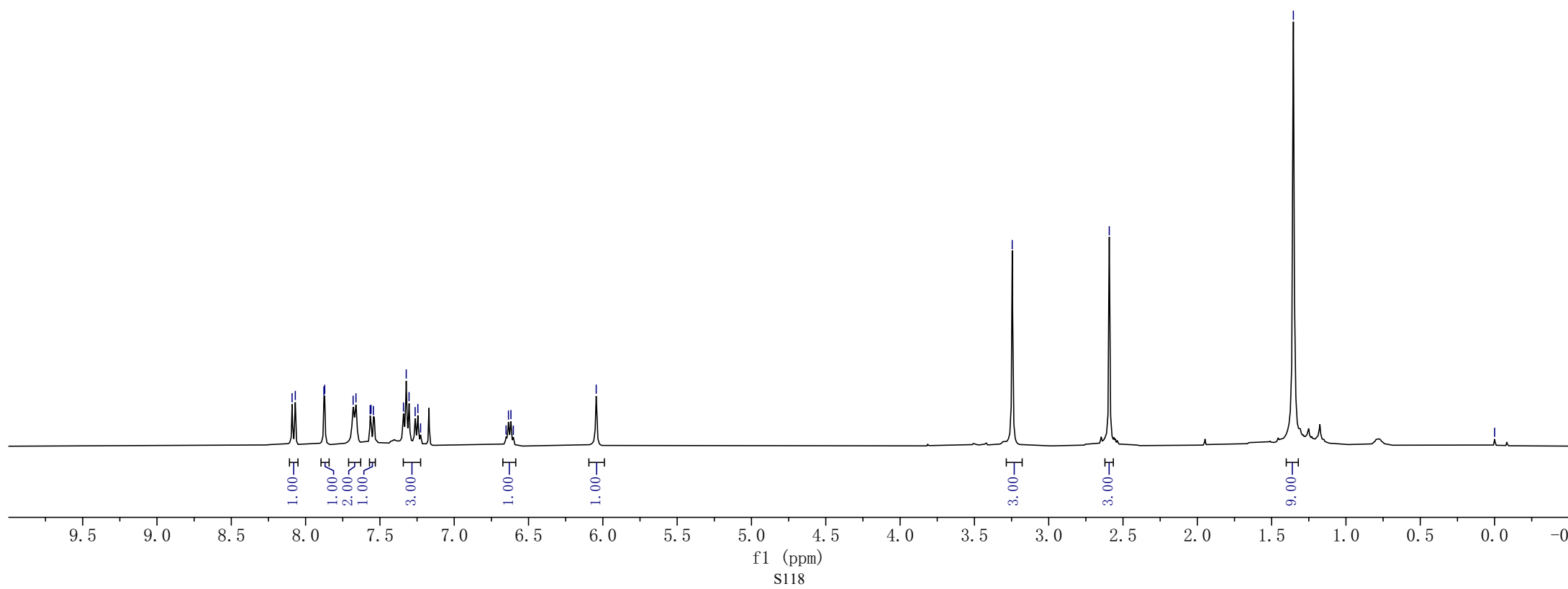
— 1.35

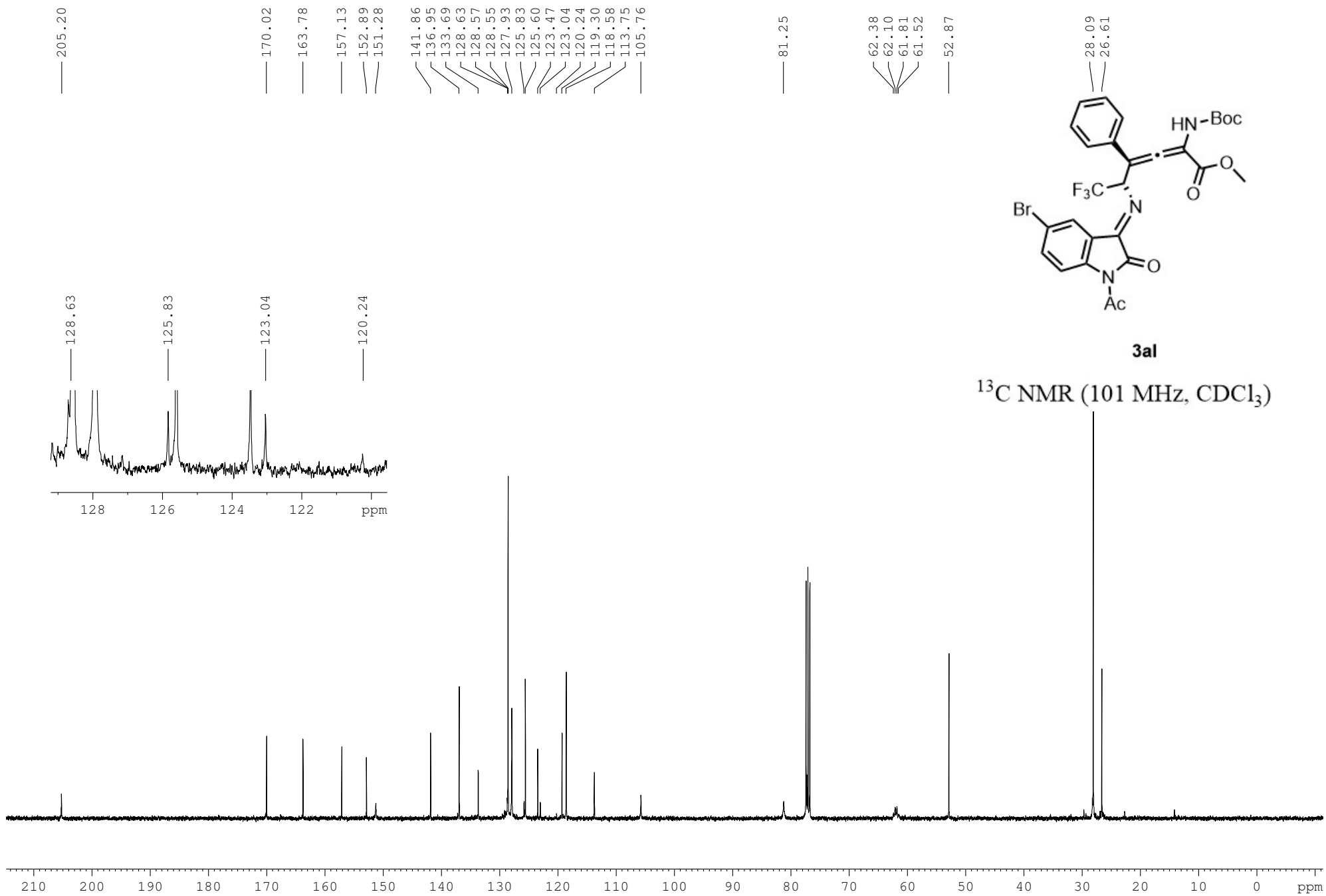
— -0.00



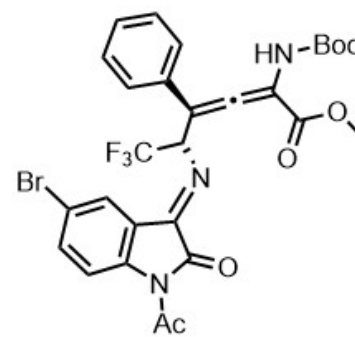
3aI

¹H NMR (400 MHz, CDCl₃)



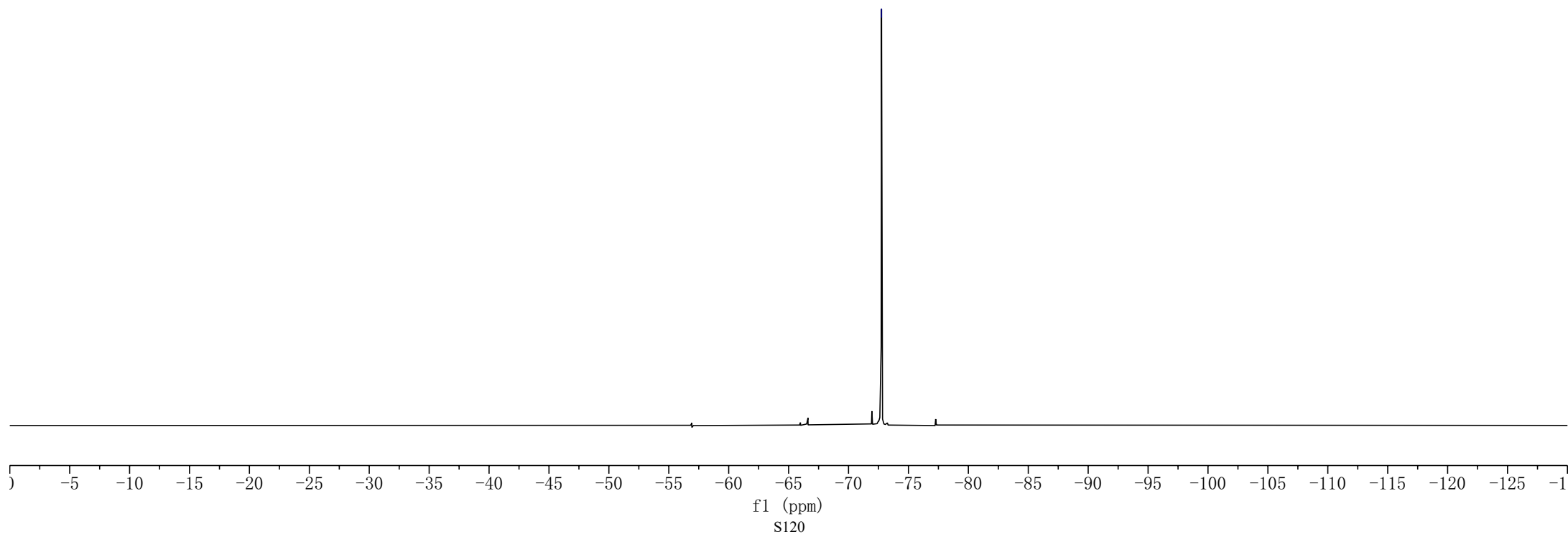


-72.75



3aI

¹⁹F NMR (376 MHz, CDCl₃)



8.06
8.04
7.71
7.69
7.58
7.36
7.34
7.32
7.28
7.26
7.24
6.67
6.66
6.64
6.63
6.03

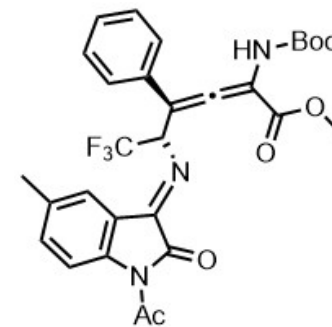
3.18

2.60

2.31

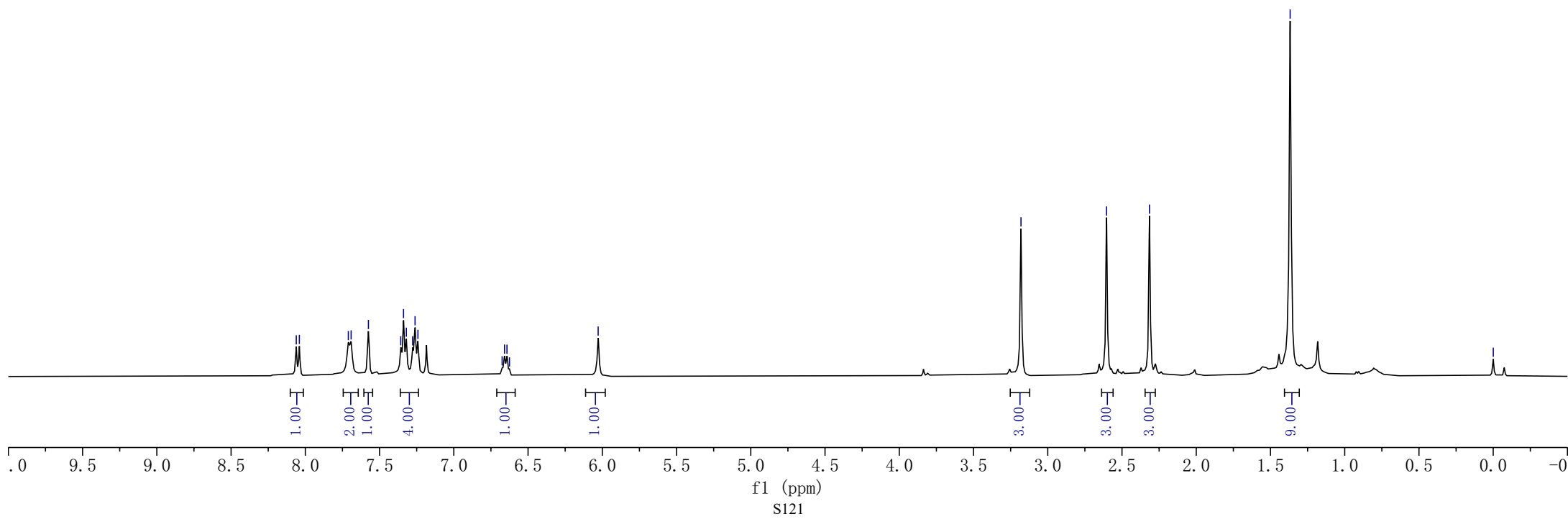
1.37

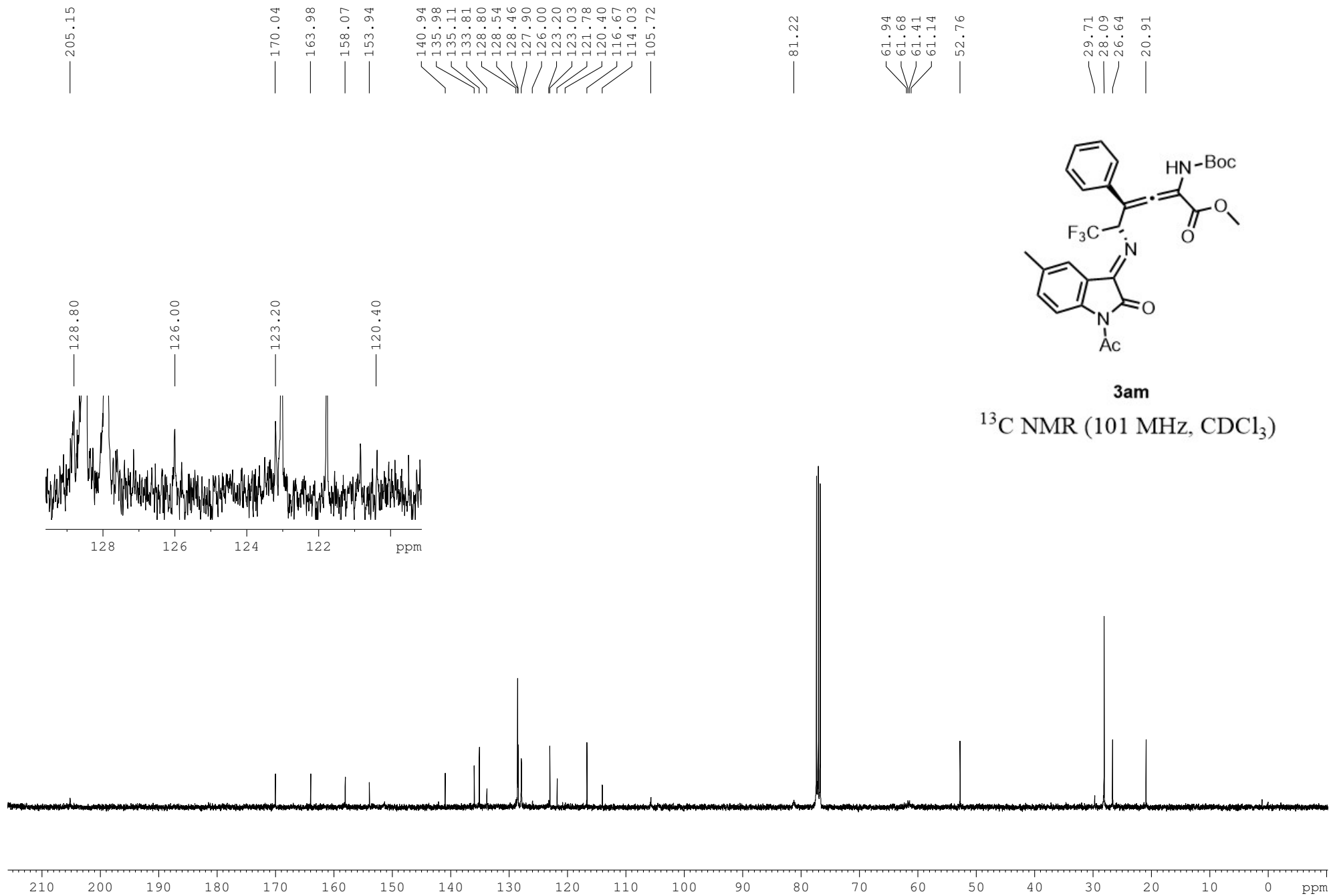
-0.00



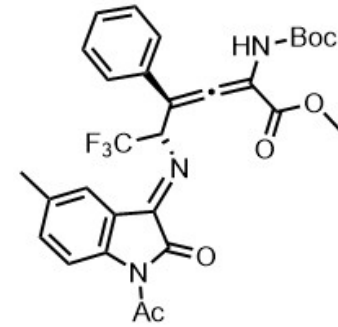
3am

¹H NMR (400 MHz, CDCl₃)



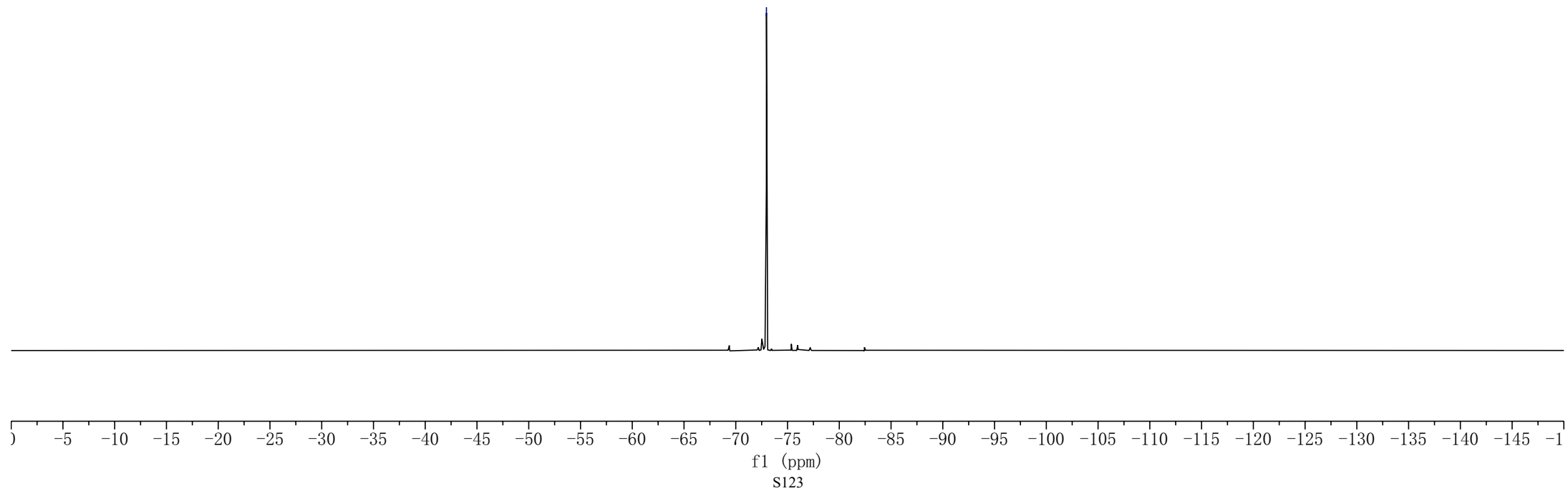


-72.96



3am

¹⁹F NMR (376 MHz, CDCl₃)



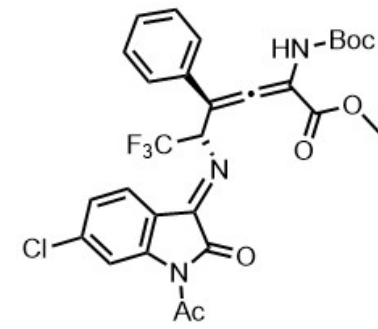
8.33
8.33
7.79
7.77
7.76
7.74
7.43
7.42
7.40
7.39
7.35
7.34
7.33
7.32
7.31
7.29
7.28
7.27
7.26
6.74
6.72
6.71
6.69
6.33
6.10

— 3.31

— 2.69

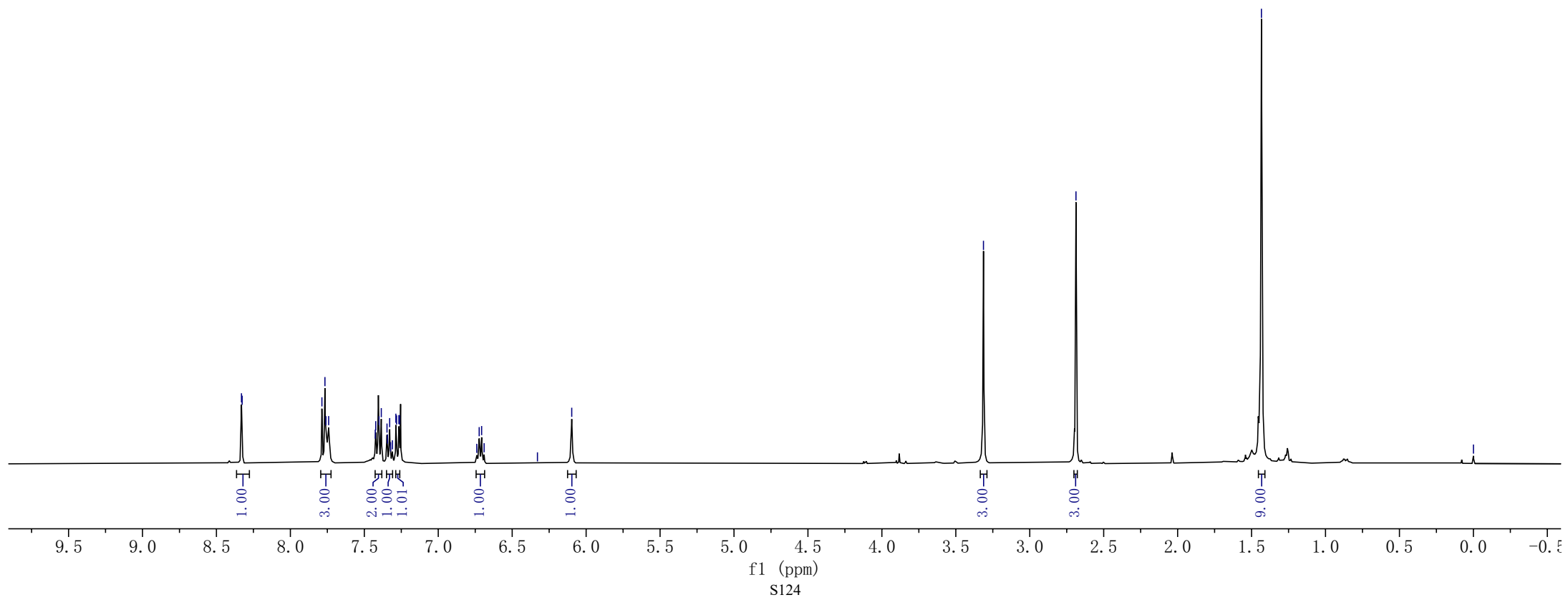
— 1.43

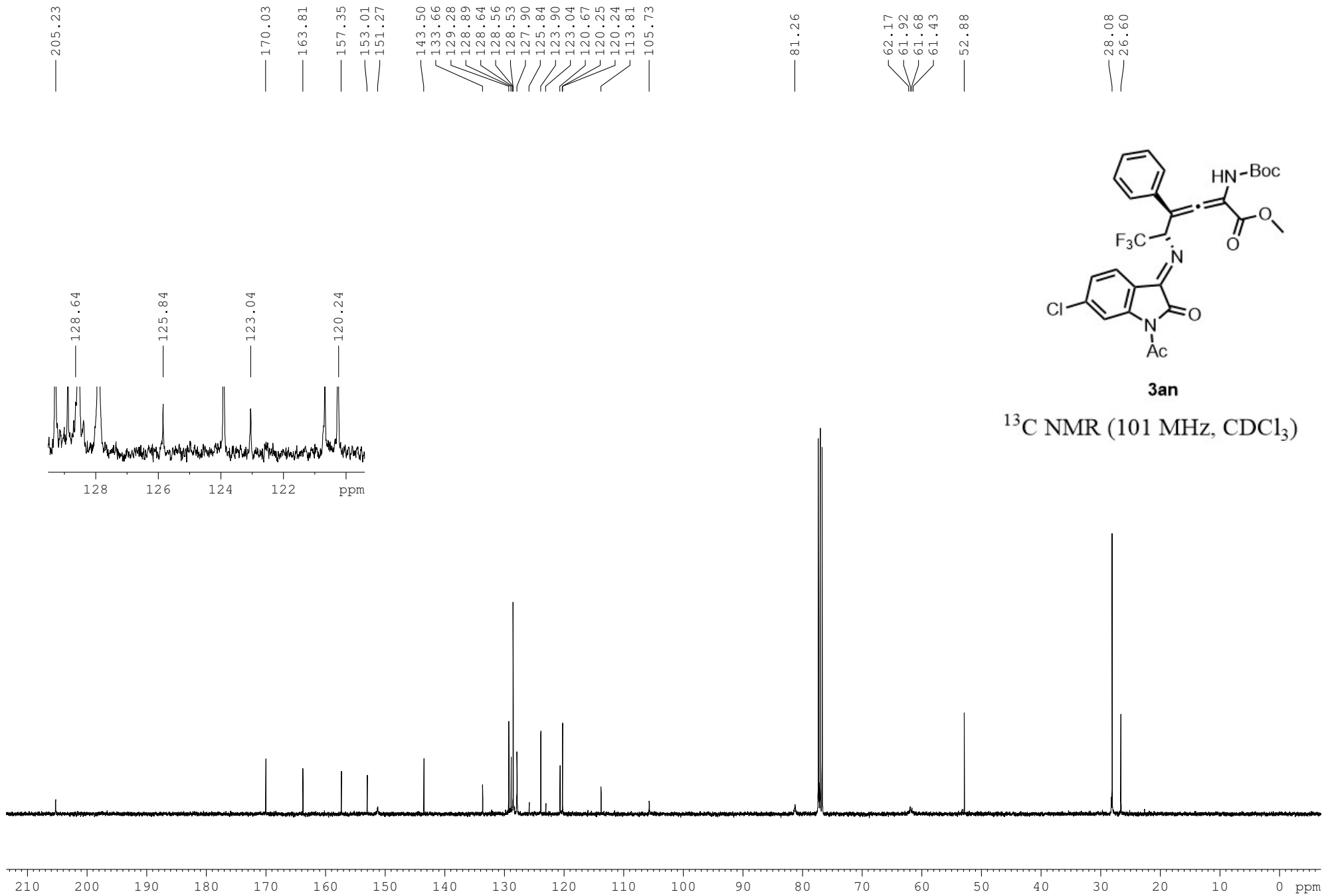
— 0.00



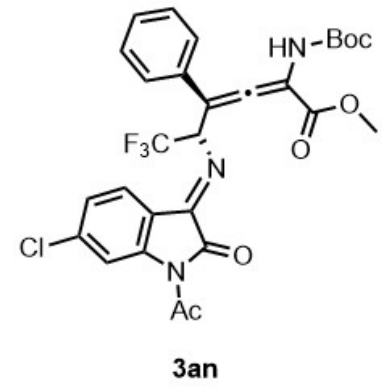
3an

¹H NMR (400 MHz, CDCl₃)

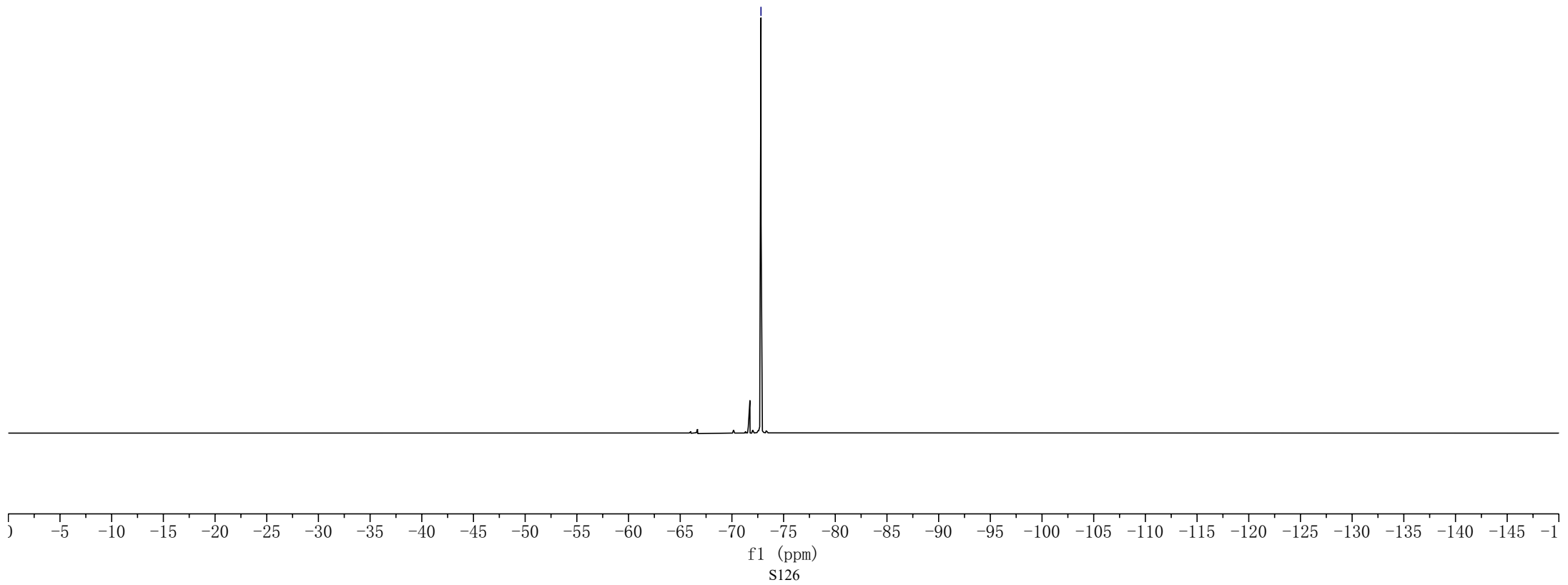


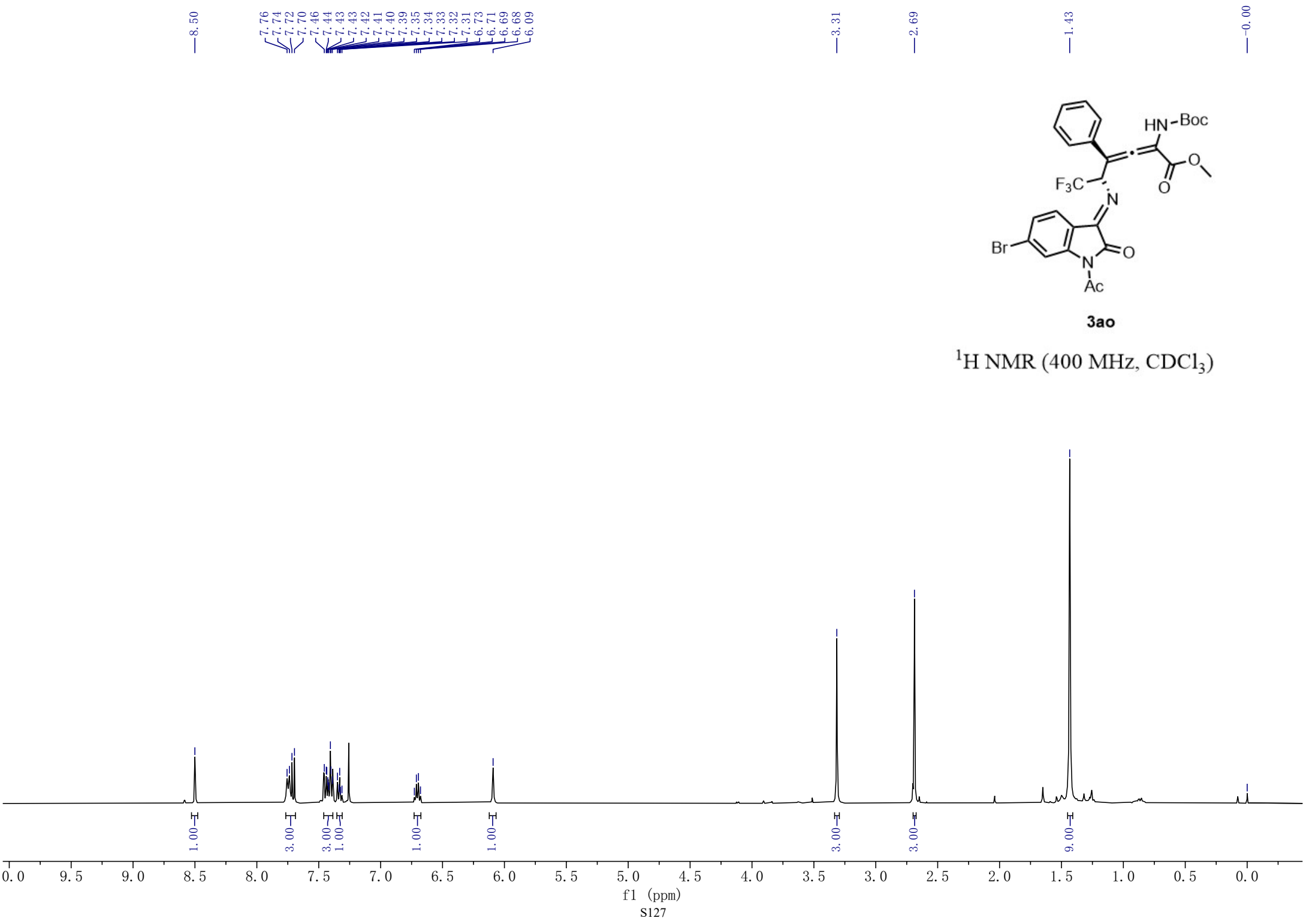


-72.81



¹⁹F NMR (376 MHz, CDCl₃)





— 205.23

170.11
170.03

— 163.82

— 157.46

152.85

151.29

143.55

140.39

133.68

128.67

128.56

128.53

127.91

126.33

125.87

123.81

123.07

120.28

120.27

117.48

113.87

— 81.28

62.19

61.89

61.59

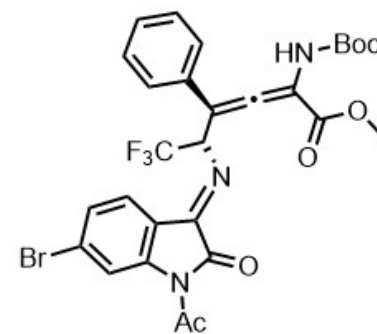
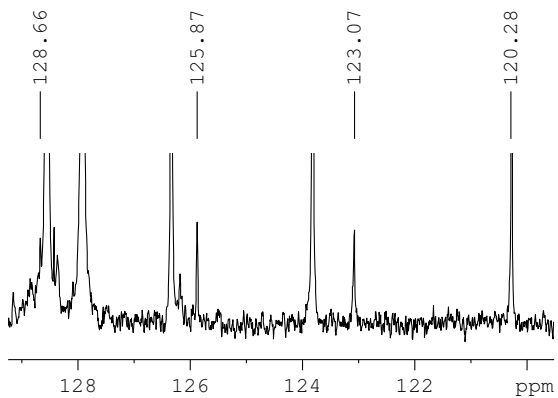
61.29

— 52.86

29.71

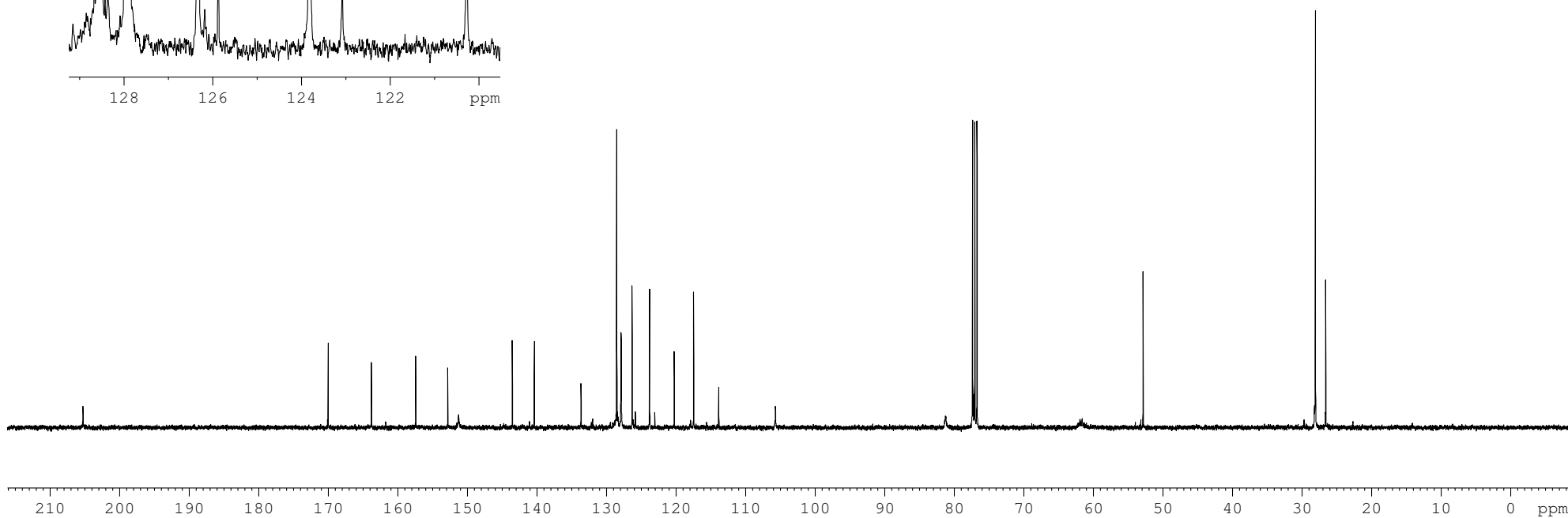
28.08

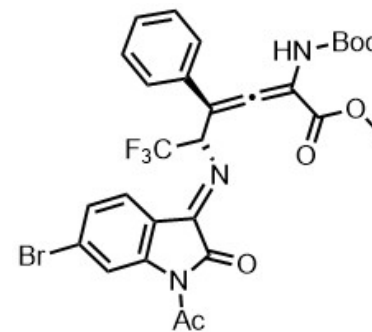
26.59



3ao

¹³C NMR (101 MHz, CDCl₃)

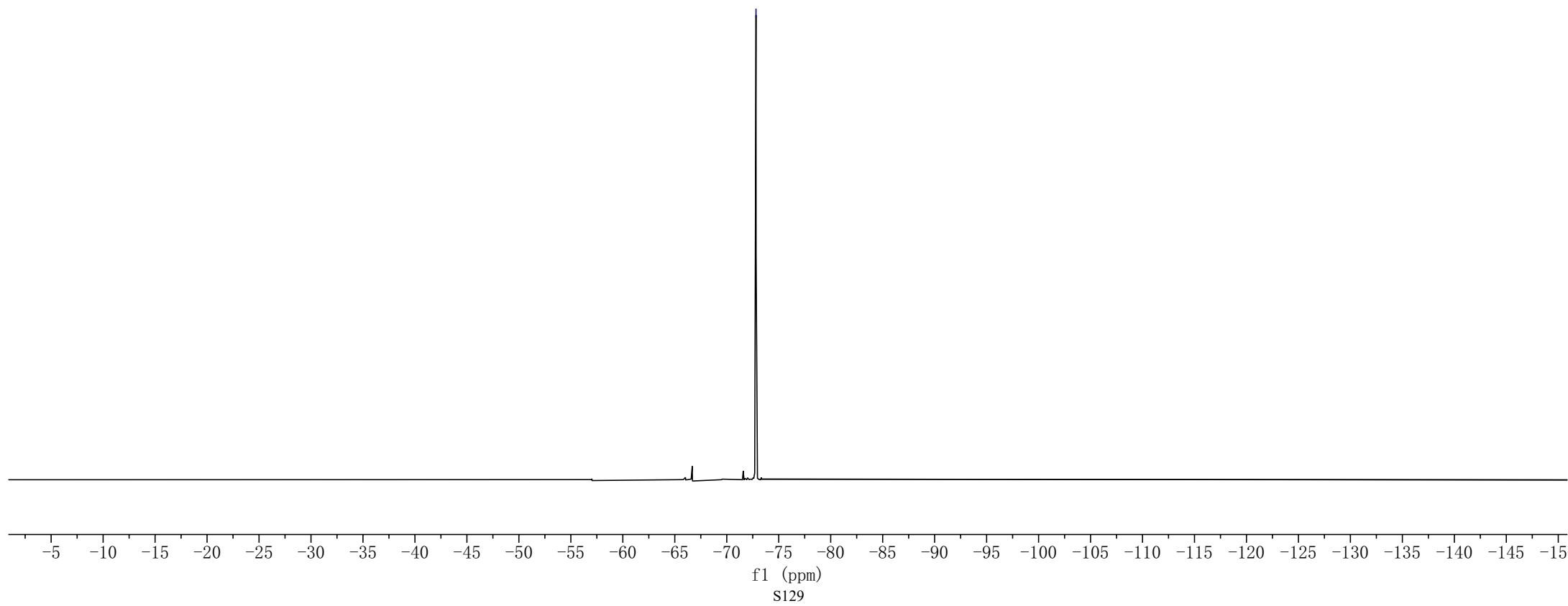




3ao

^{19}F NMR (376 MHz, CDCl_3)

-72.81



7.77
7.75
7.67
7.65
7.43
7.42
7.41
7.39
7.36
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
6.75
6.73
6.71
6.70

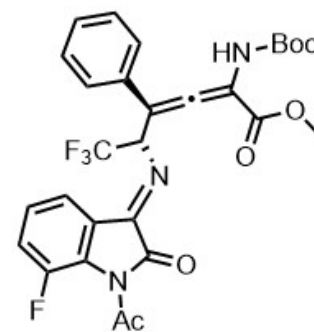
— 6.09

— 3.30

— 2.71

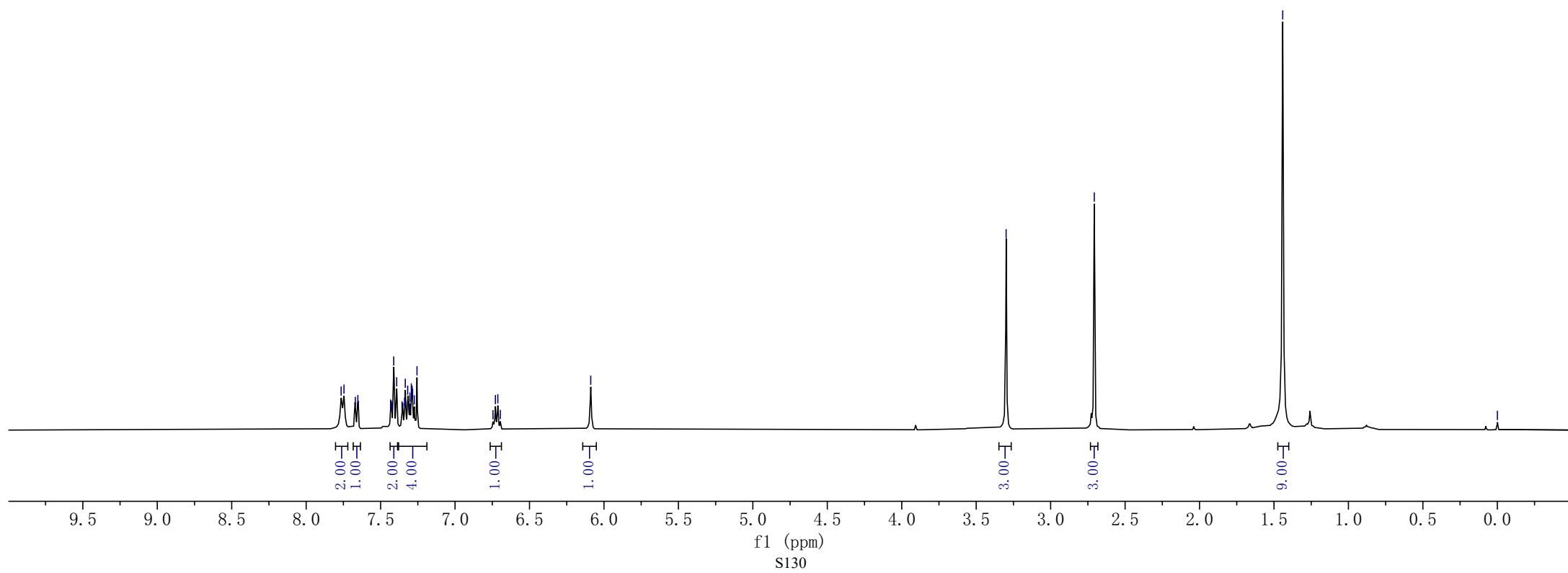
— 1.44

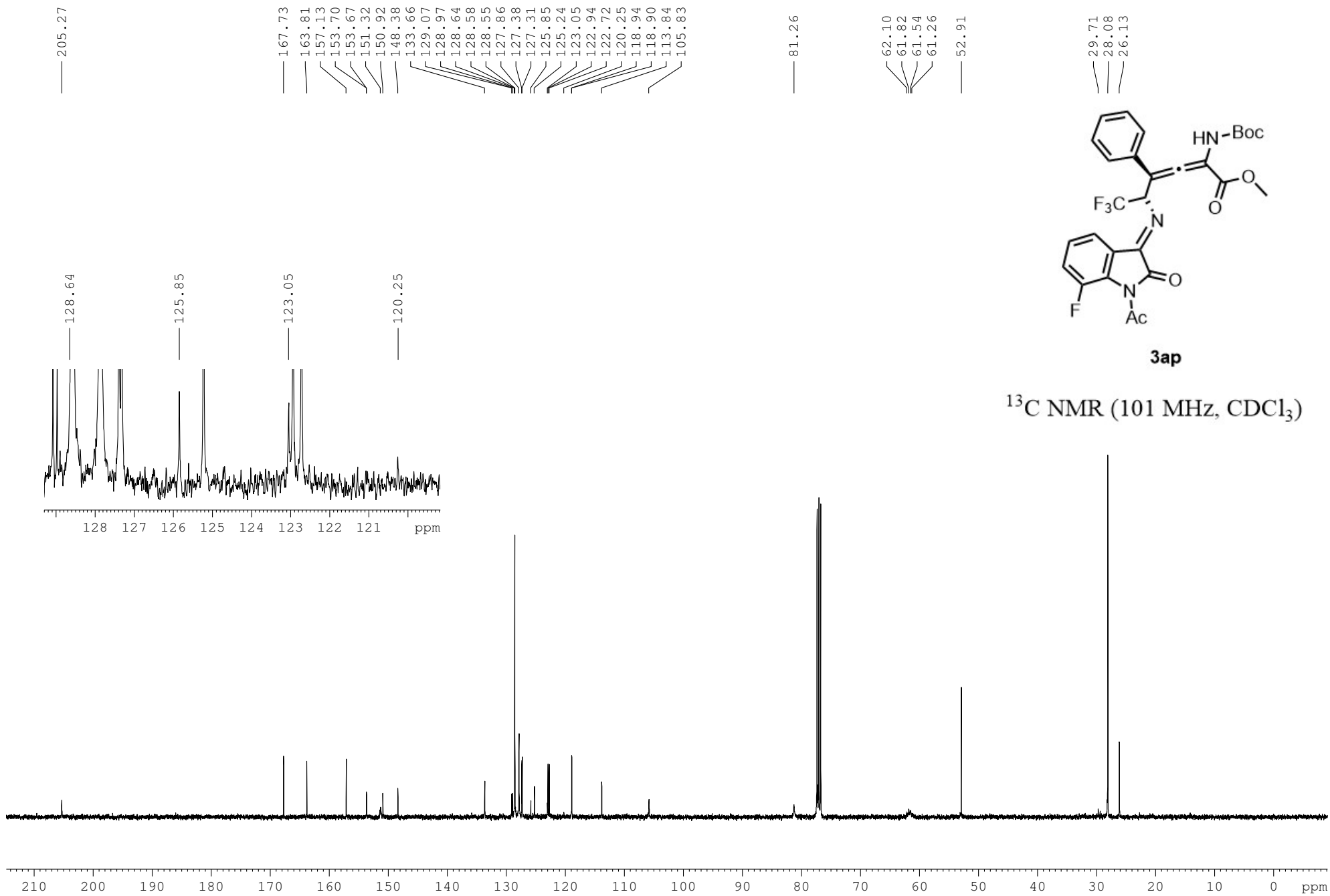
— 0.00

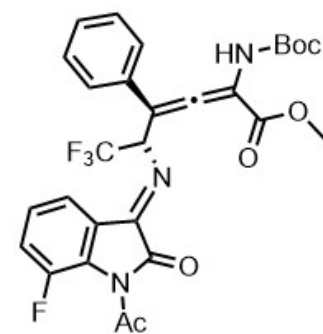


3ap

¹H NMR (400 MHz, CDCl₃)

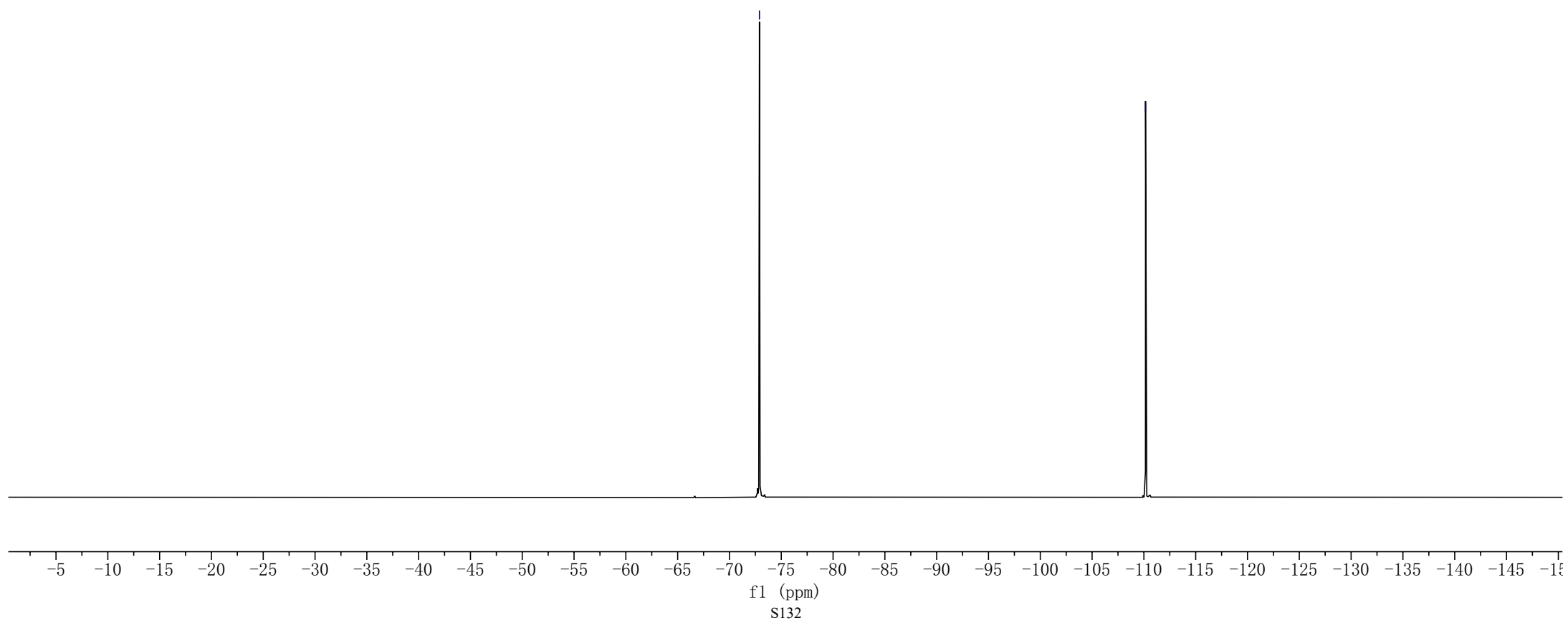






3ap

^{19}F NMR (376 MHz, CDCl_3)



8.15
8.13
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.34
7.32
7.15
7.14
7.13
7.12

5.92
5.90

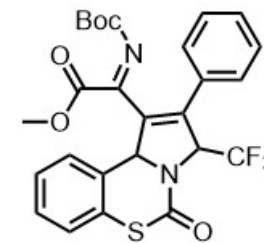
5.00
4.98

3.59

1.41

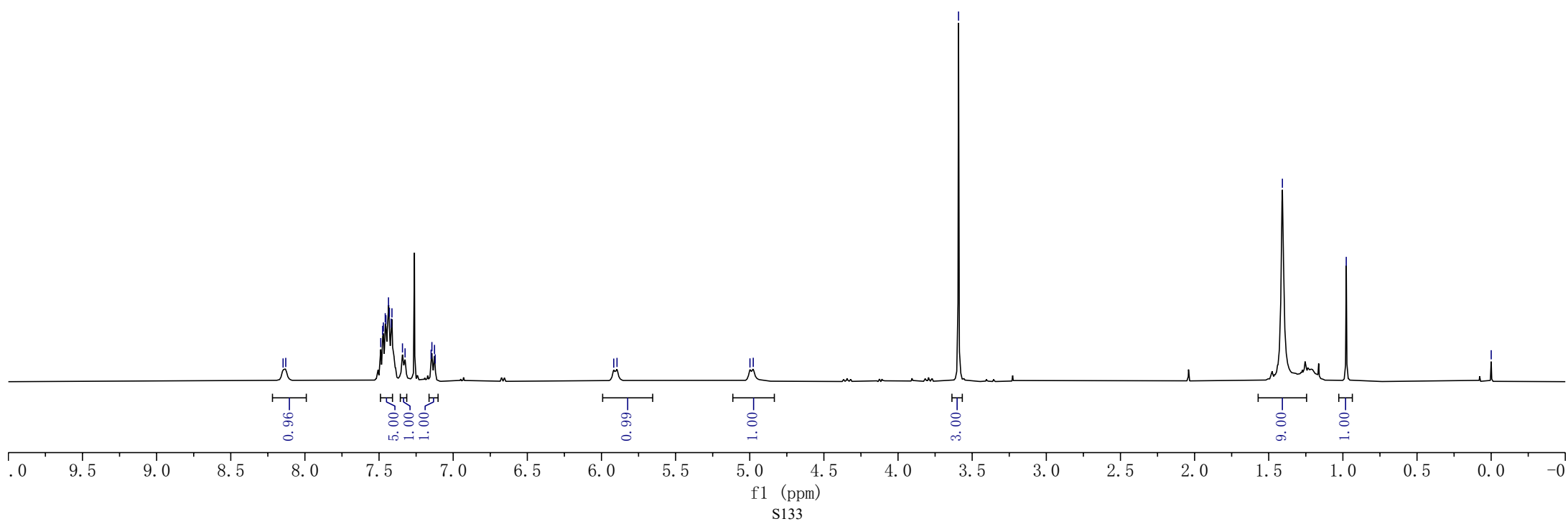
0.98

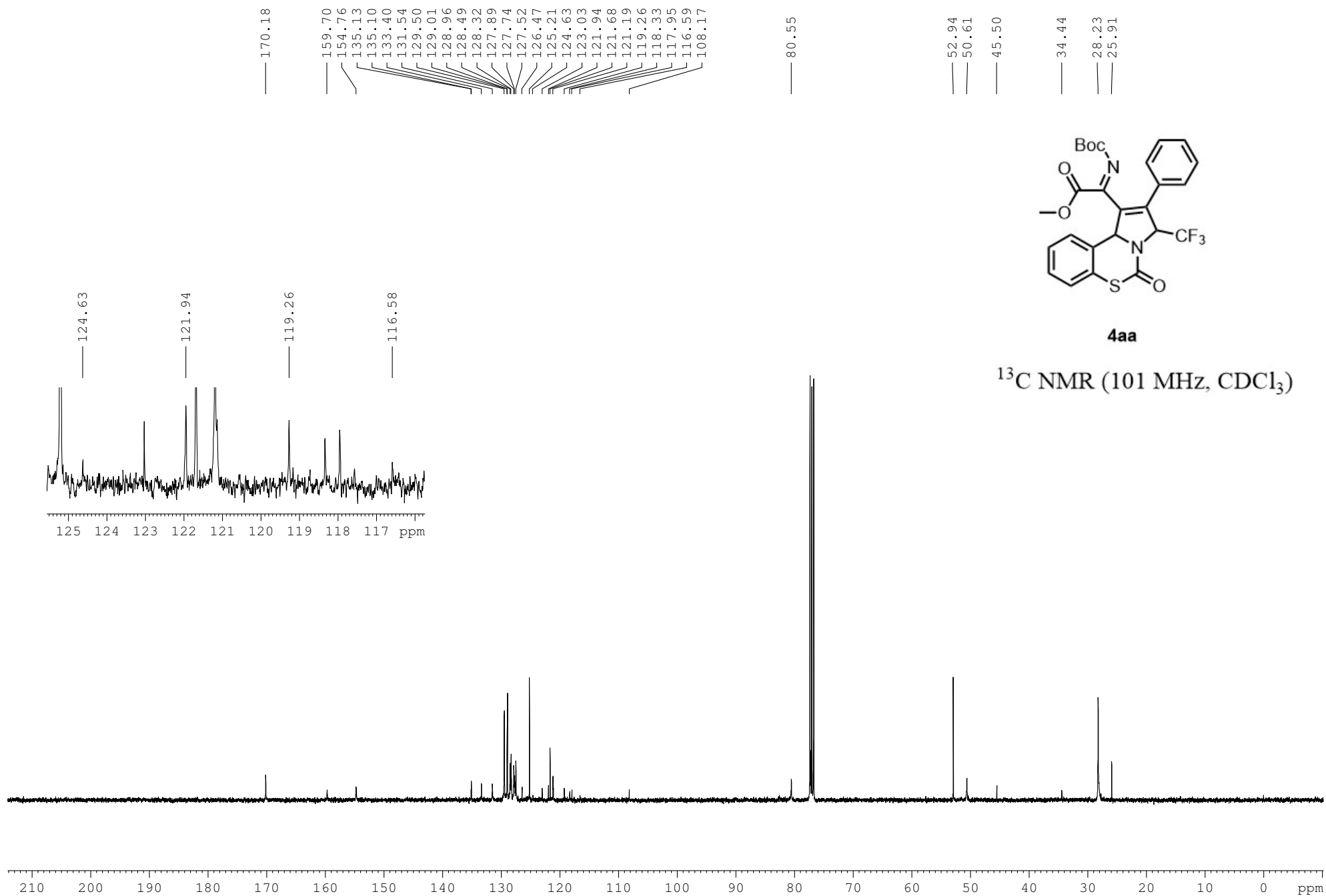
-0.00



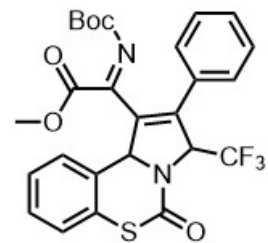
4aa

¹H NMR (400 MHz, CDCl₃)



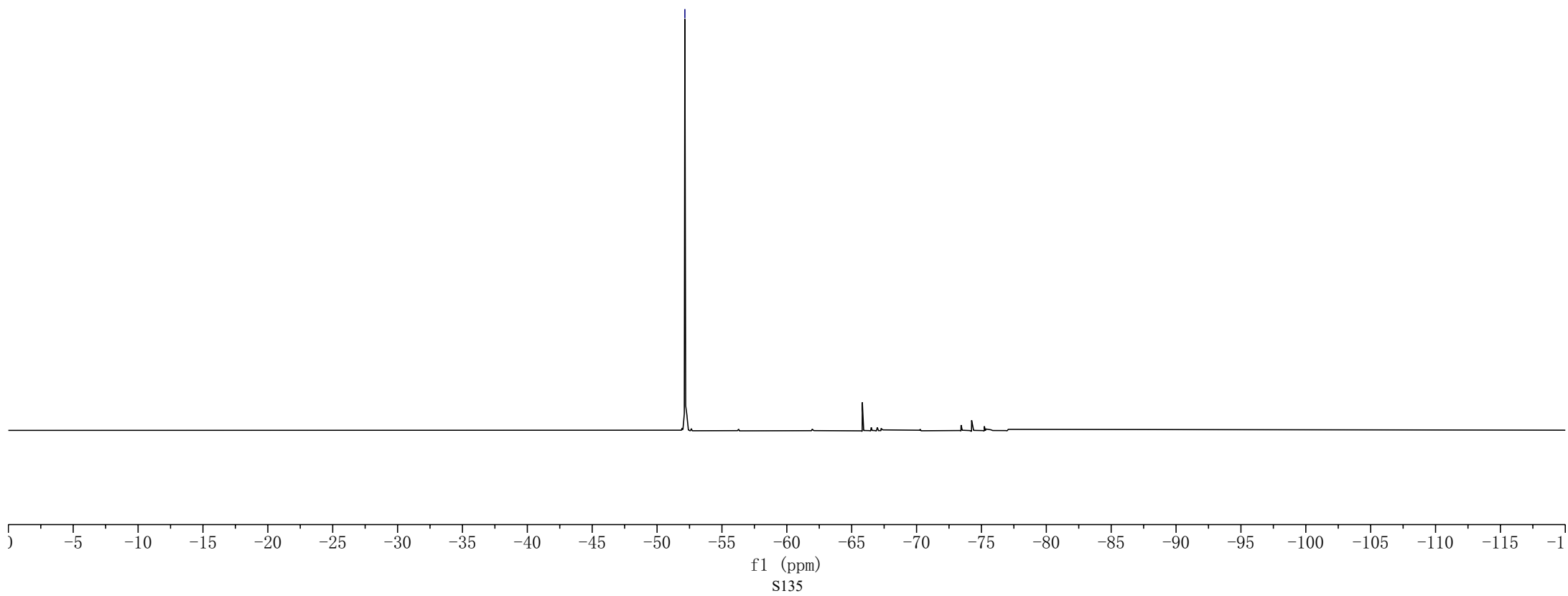


-52.14



4aa

^{19}F NMR (376 MHz, CDCl_3)



8.15
8.14
8.13
7.48
7.47
7.46
7.45
7.44
7.43
7.41
7.40
7.35
7.34
7.33
7.17
7.15

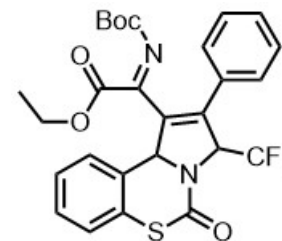
5.88
5.86

4.97
4.95

4.09
4.08
4.06
4.04
4.02

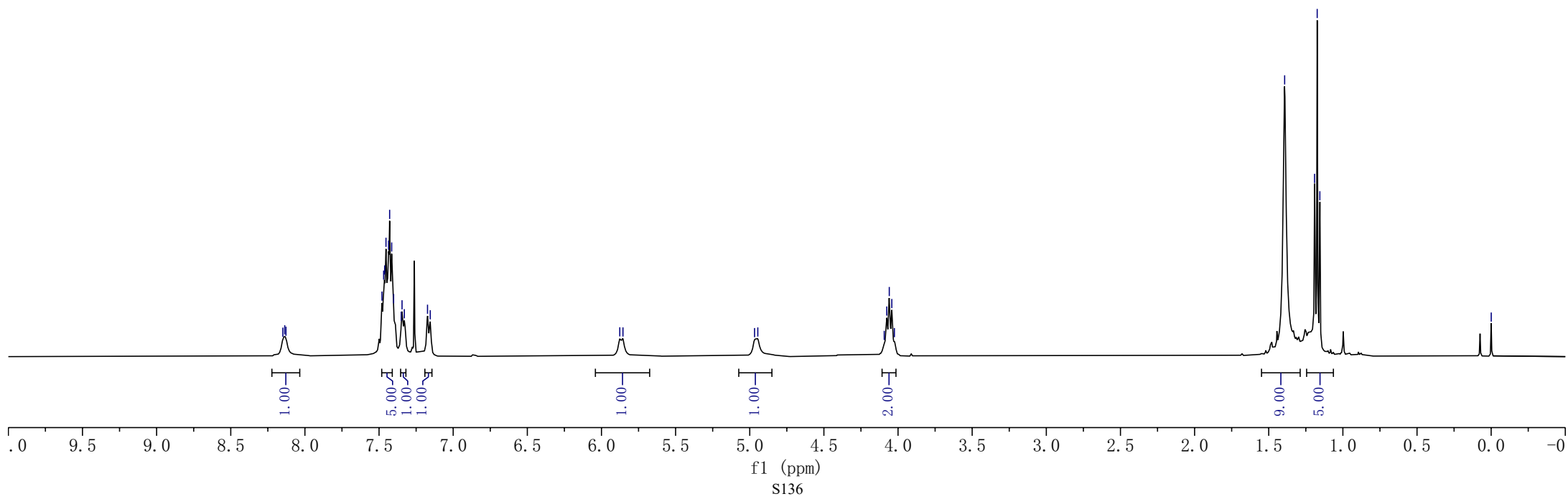
1.39
1.19
1.17
1.16

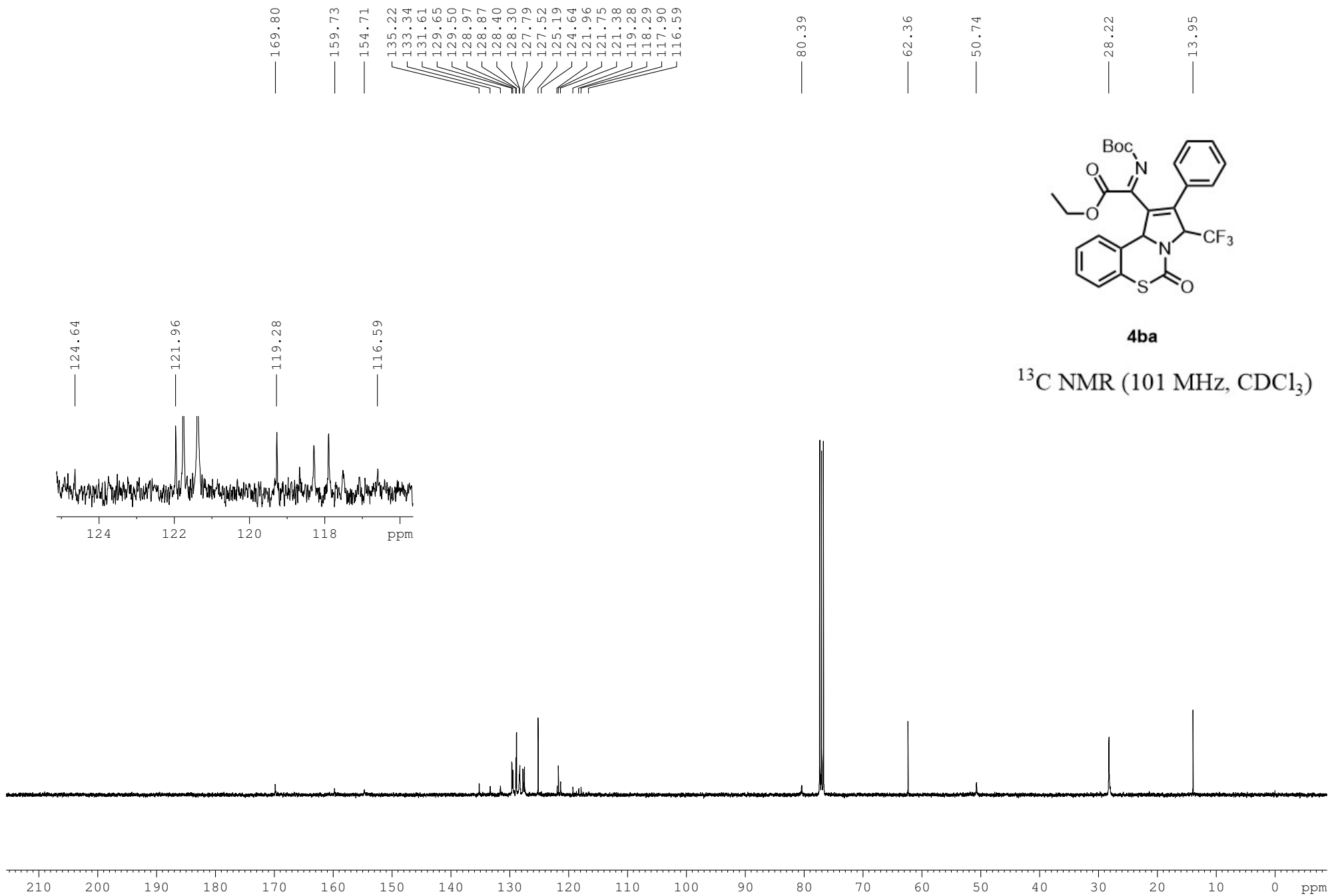
-0.00

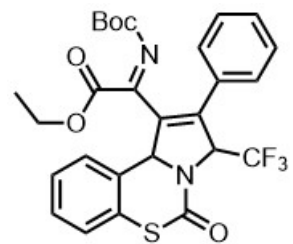


4ba

$^1\text{H NMR}$ (400 MHz, CDCl_3)



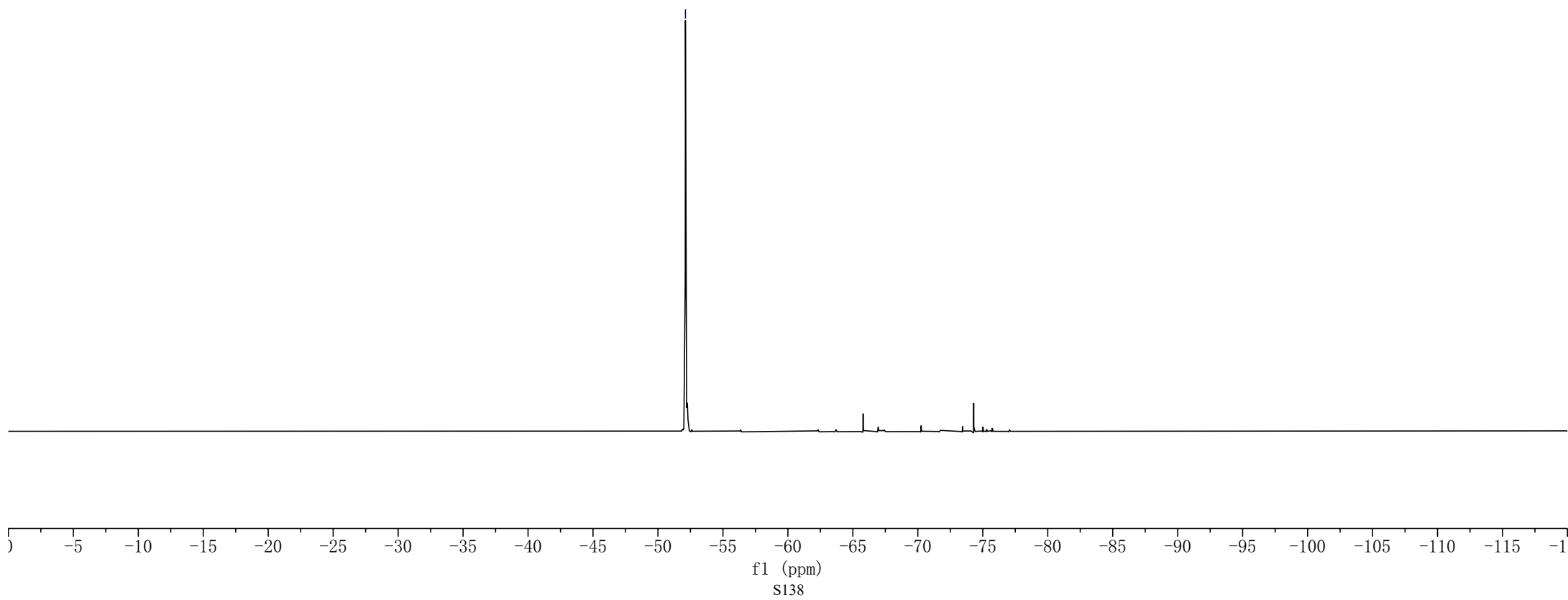




4ba

^{19}F NMR (376 MHz, CDCl_3)

—52.11



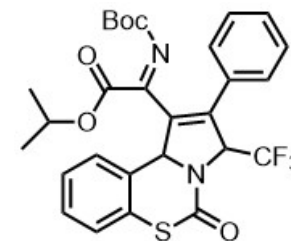
8.12
8.11
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.35
7.34
7.33
7.21
7.19

5.83
5.81

4.98
4.96
4.95
4.93
4.91
4.90

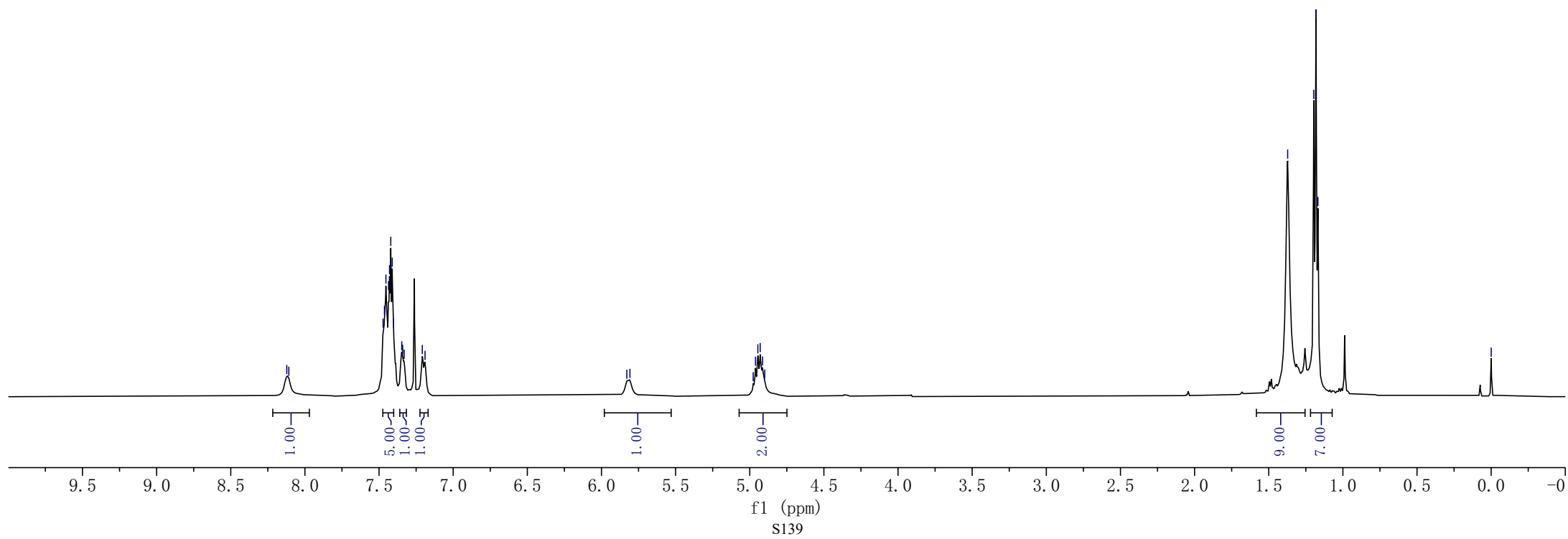
1.37
1.20
1.18
1.17

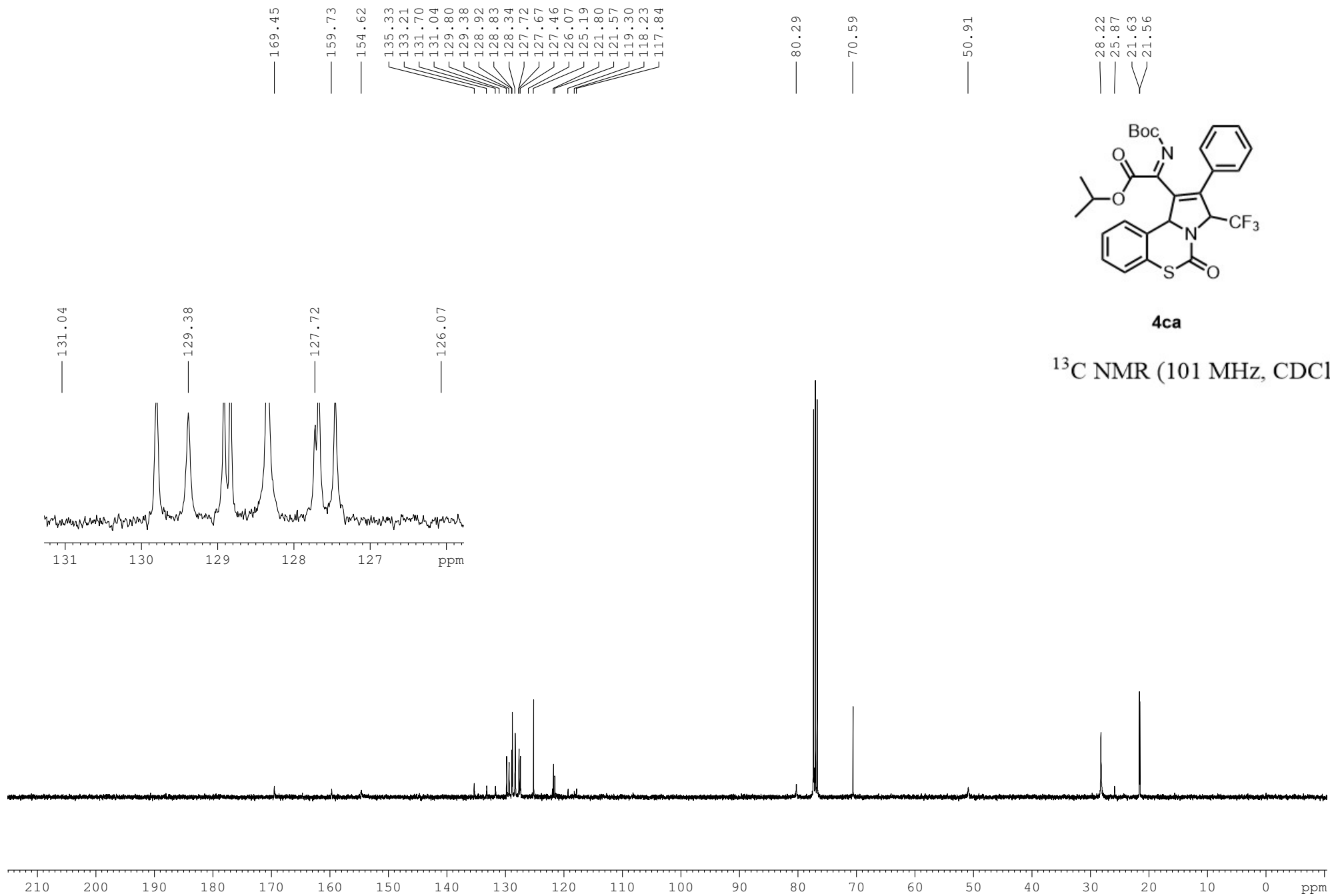
-0.00



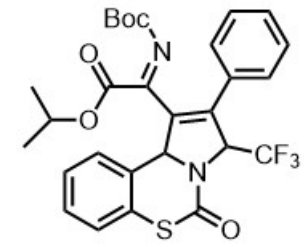
4ca

¹H NMR (400 MHz, CDCl₃)



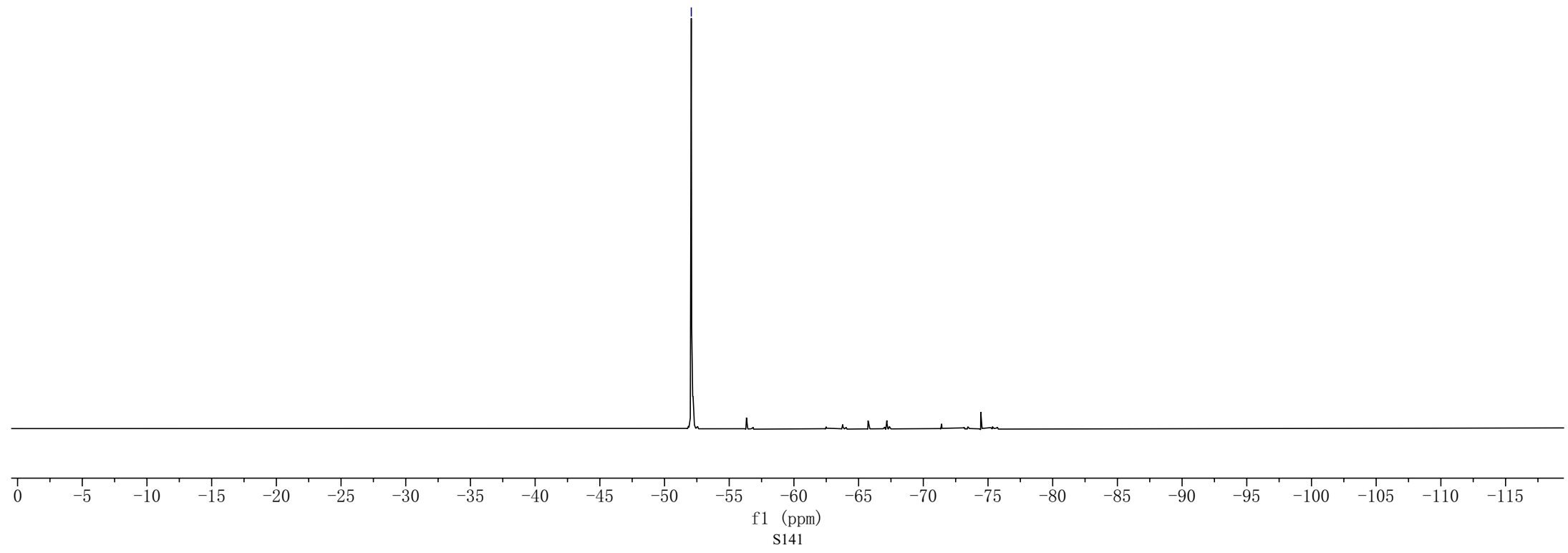


-52.07



4ca

¹⁹F NMR (376 MHz, CDCl₃)



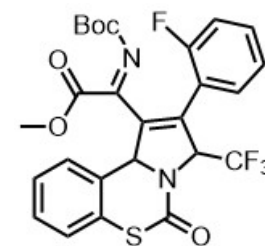
8.06
8.05
8.04
8.03
7.48
7.47
7.46
7.45
7.44
7.43
7.17
7.15
7.13
7.12

5.84
5.82
5.42
5.41
5.40
5.39

3.41

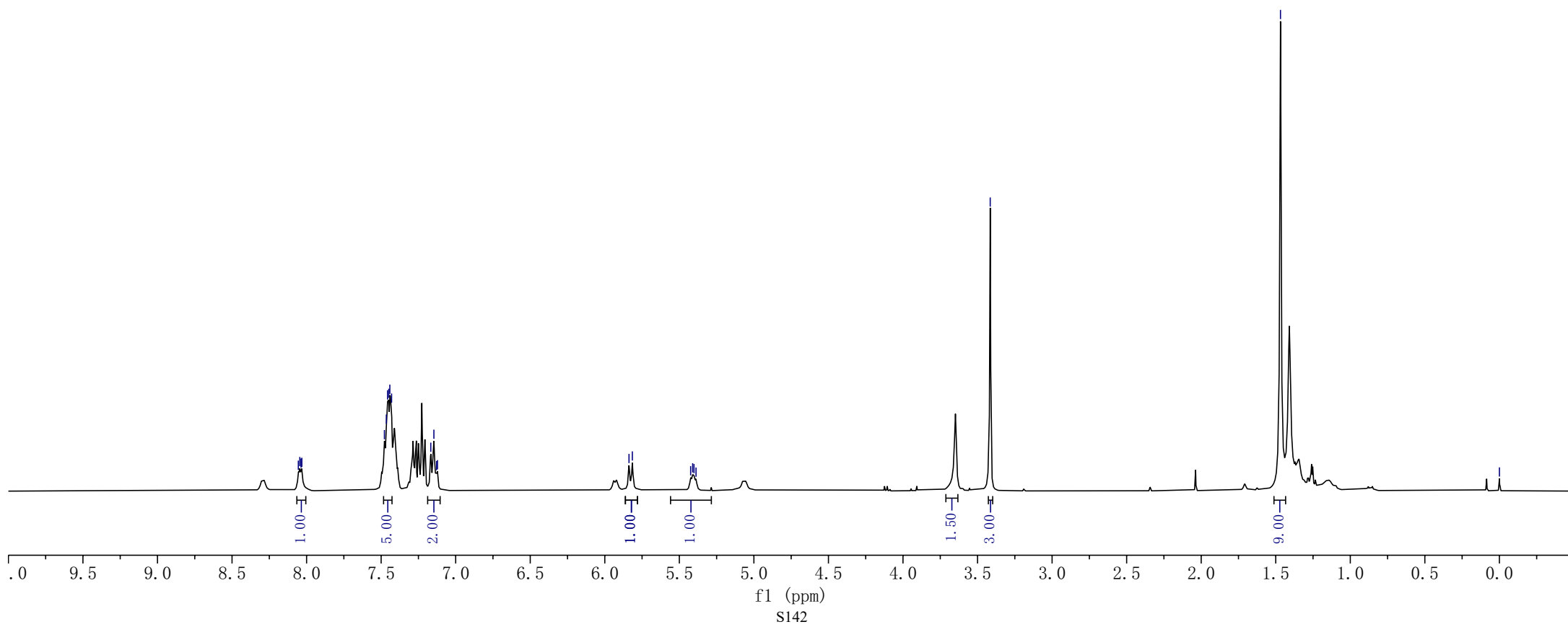
1.47

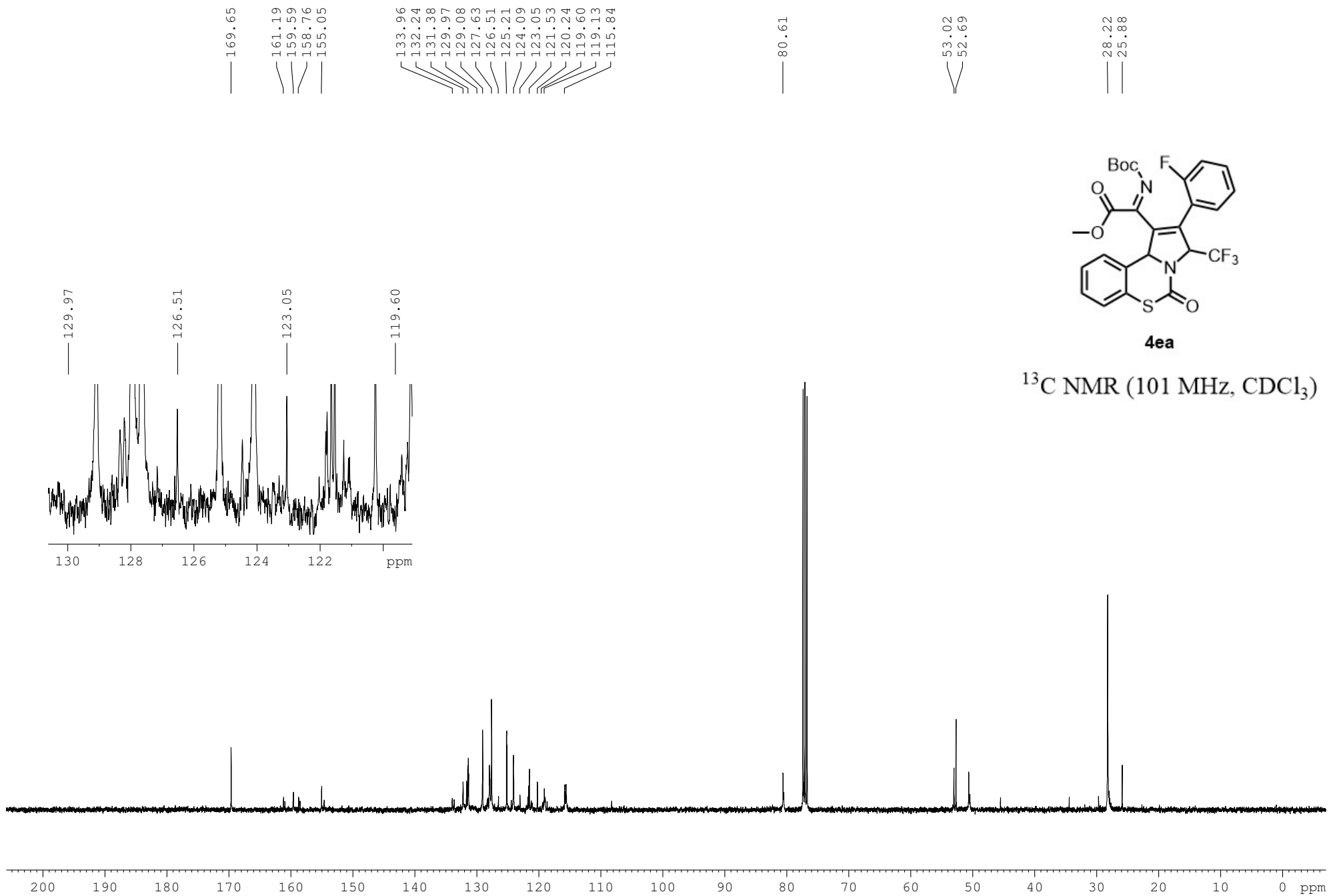
-0.00

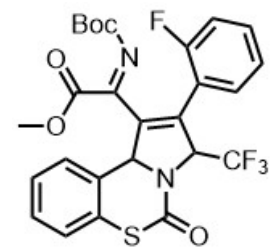


4ea

¹H NMR (400 MHz, CDCl₃)

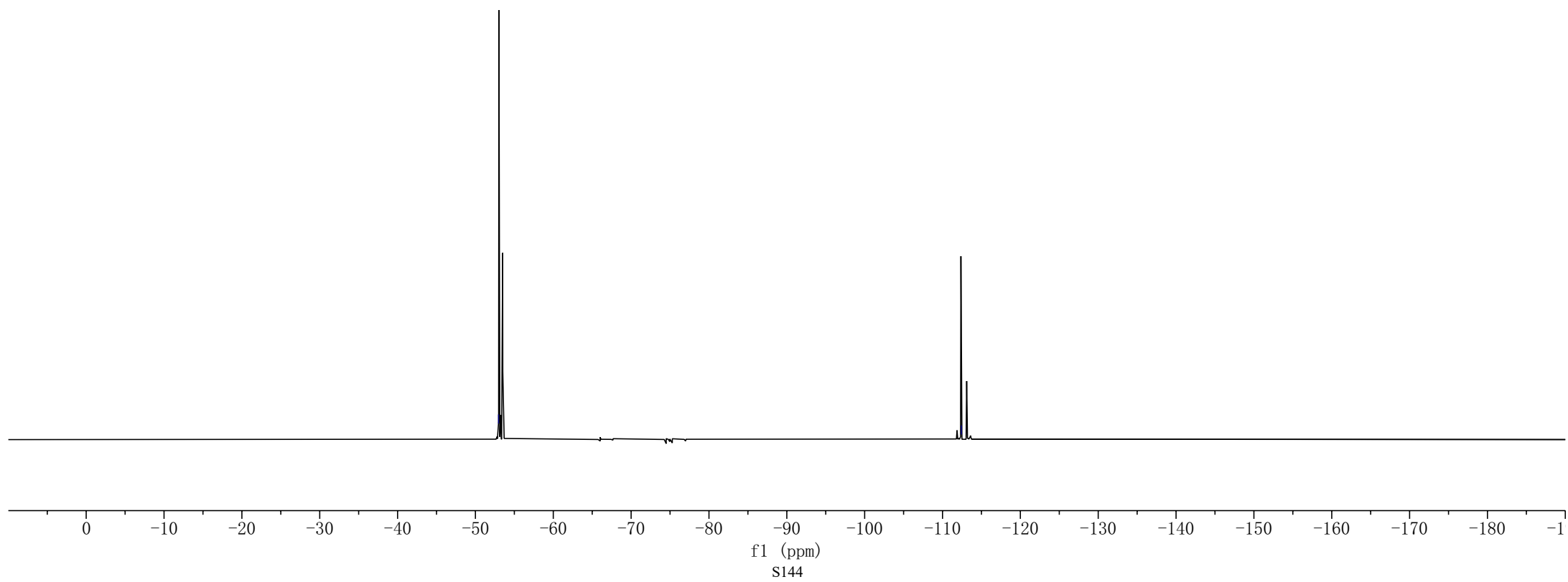






4ea

¹⁹F NMR (376 MHz, CDCl₃)



8.03
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.21
7.19
7.03
7.01

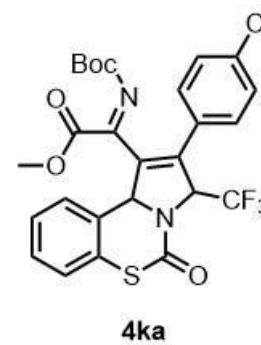
5.79
5.77

4.96
4.94

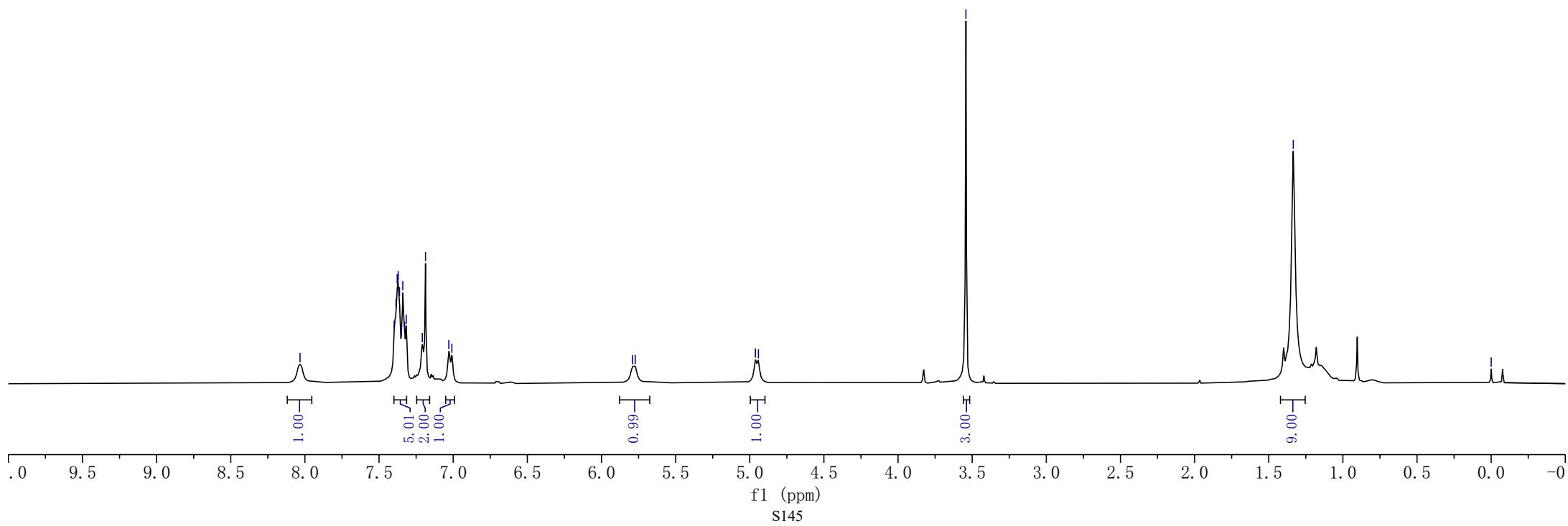
3.54

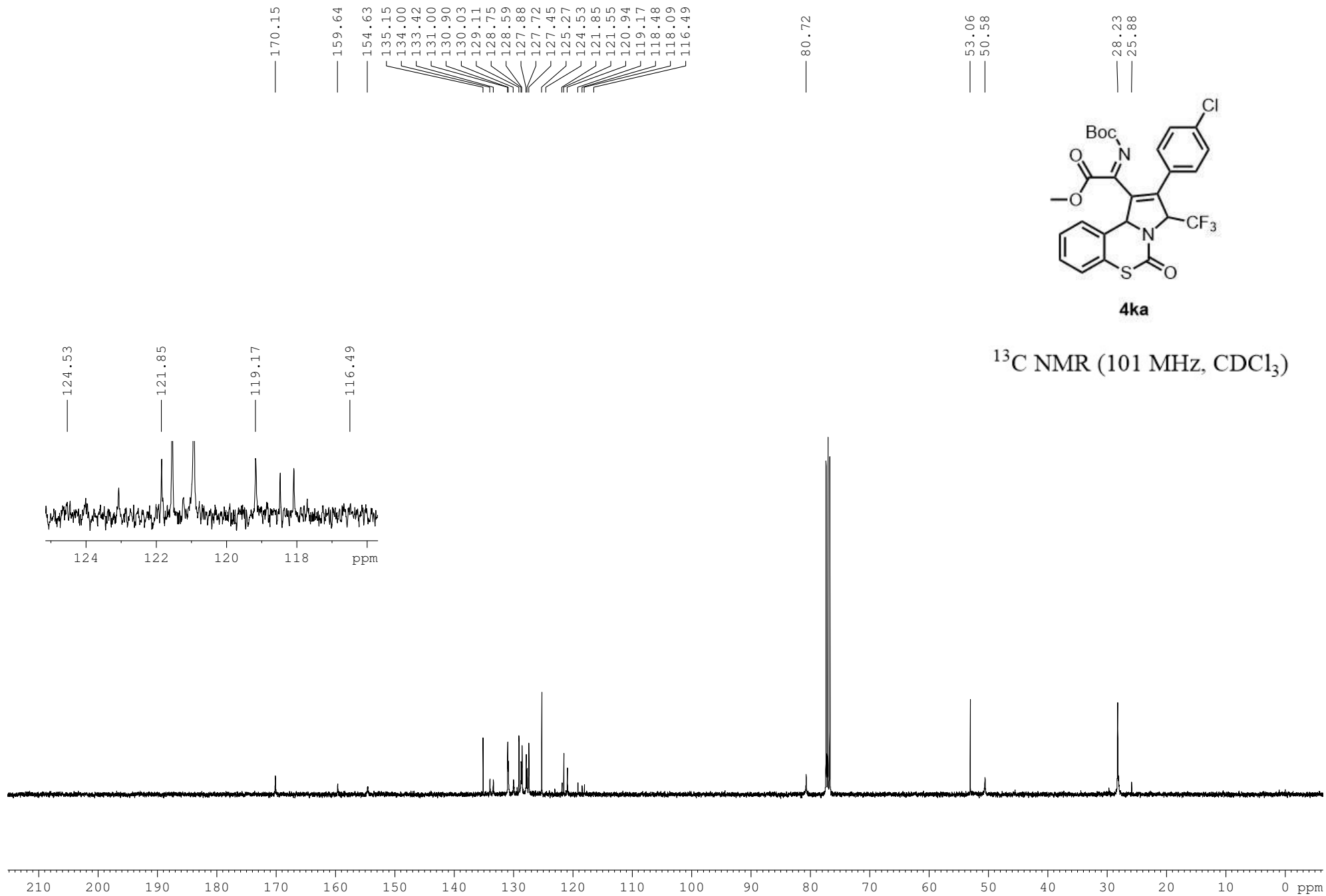
1.33

-0.00



¹H NMR (400 MHz, CDCl₃)



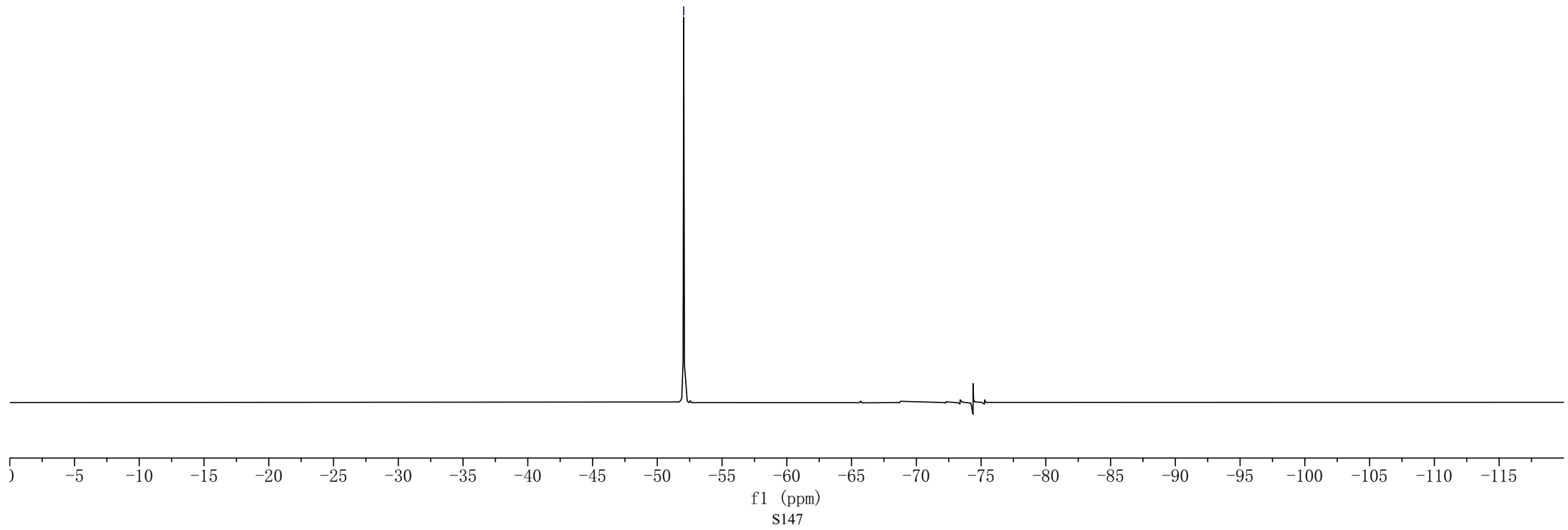


-52.04



4ka

^{19}F NMR (376 MHz, CDCl_3)



8.07
8.05
7.38
7.37
7.36
7.35
7.33
7.32
7.22
7.20
7.18
7.15
7.14
7.13
7.12
6.94
6.92

5.85
5.83

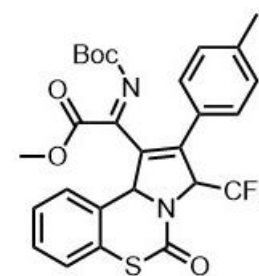
4.94
4.92

3.52

2.35

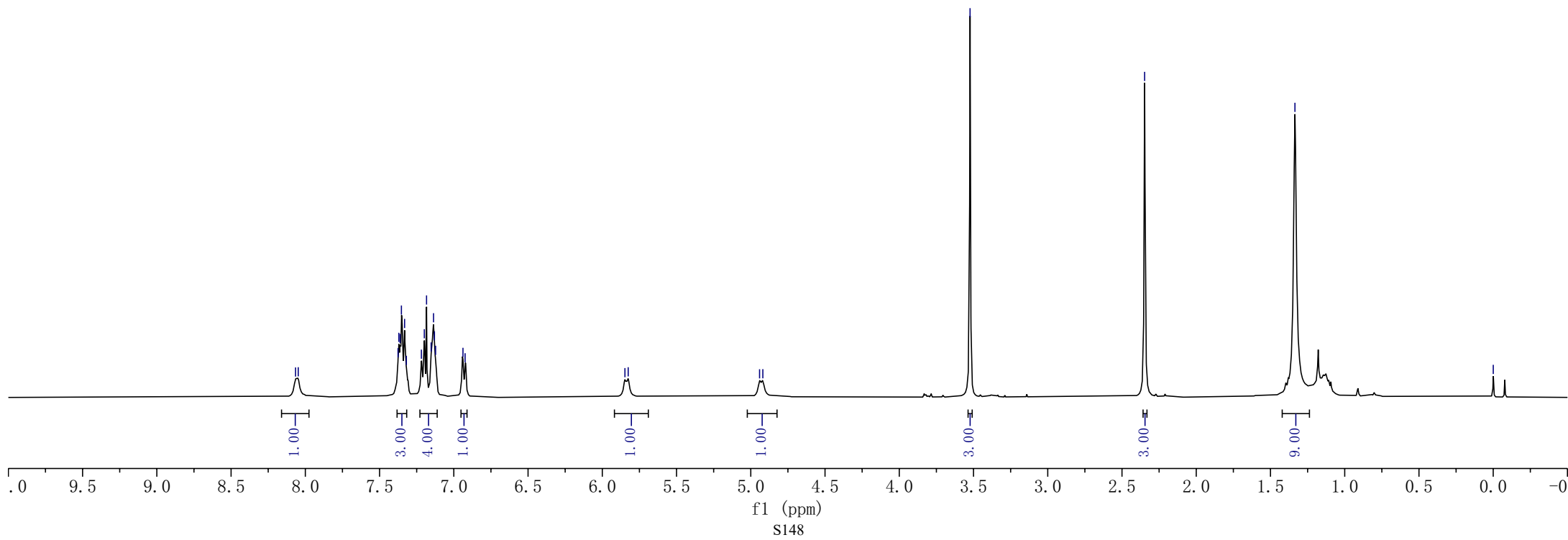
1.34

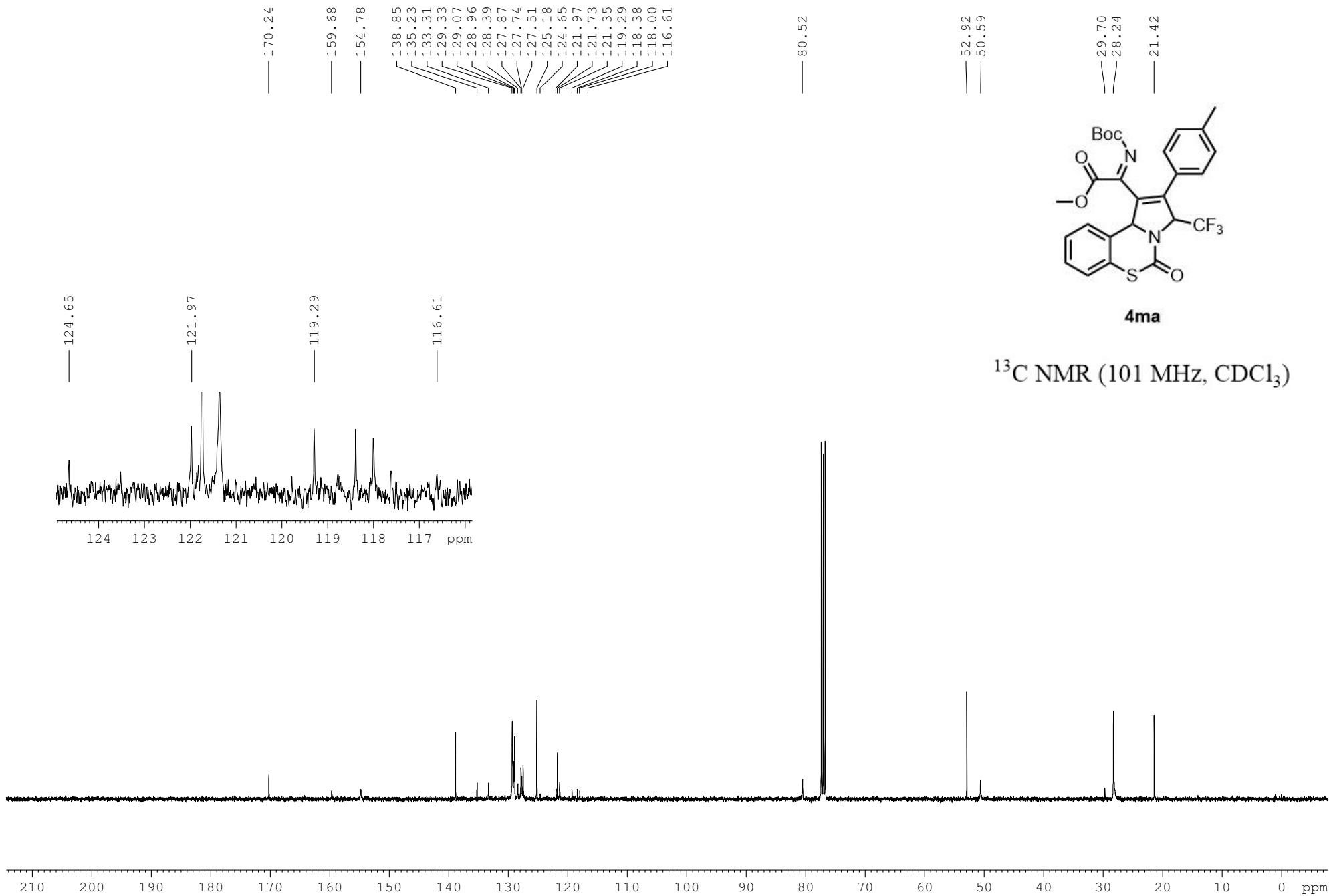
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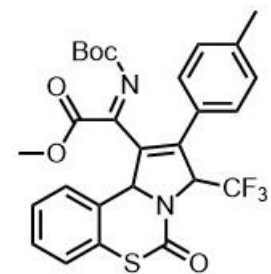


4ma

¹H NMR (400 MHz, CDCl₃)



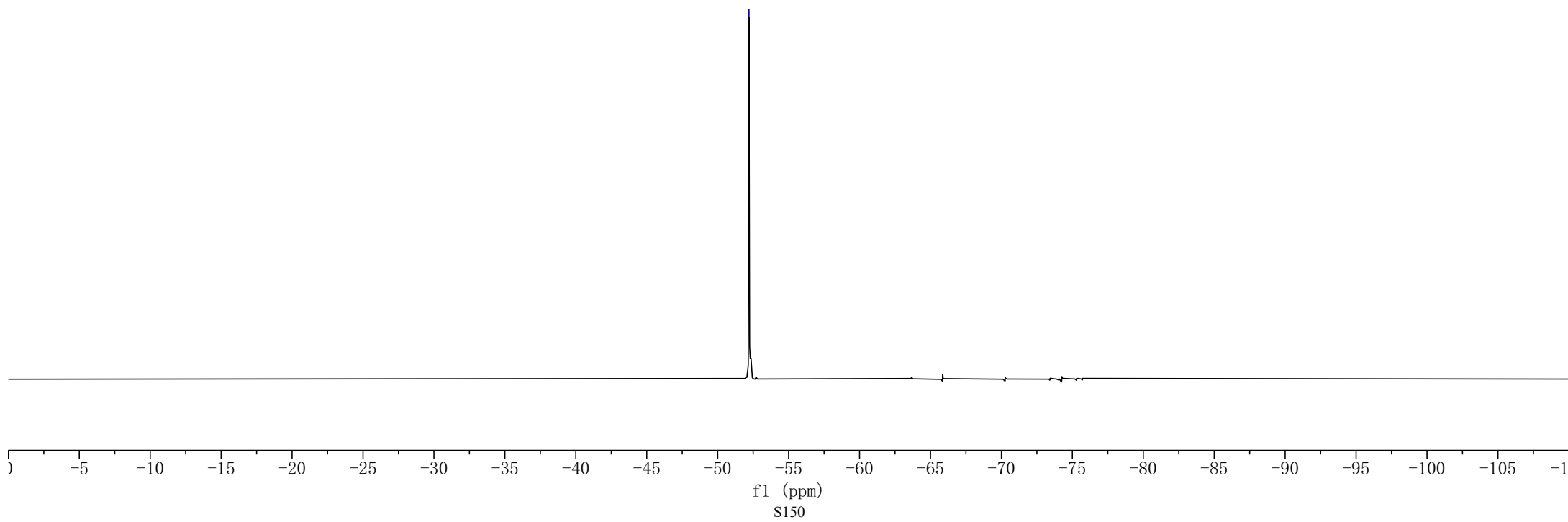




4ma

^{19}F NMR (376 MHz, CDCl_3)

—52.21



8.05
8.04
7.37
7.36
7.35
7.33
7.30
7.18
7.16
6.98
6.96
6.94
6.93
6.92
6.91
6.87
6.85
6.84

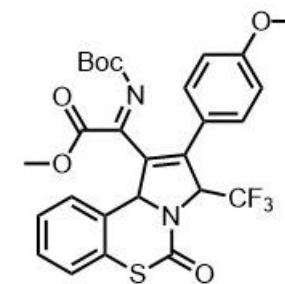
5.85
5.82

4.96
4.93

3.79
3.53

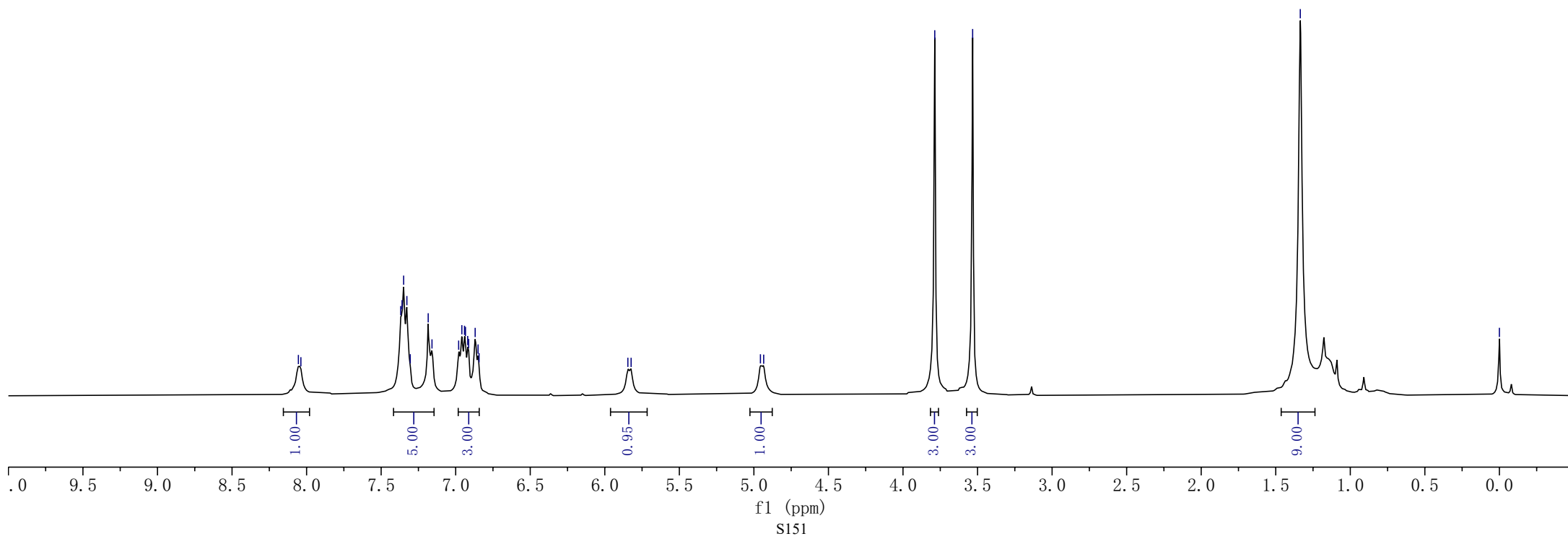
1.34

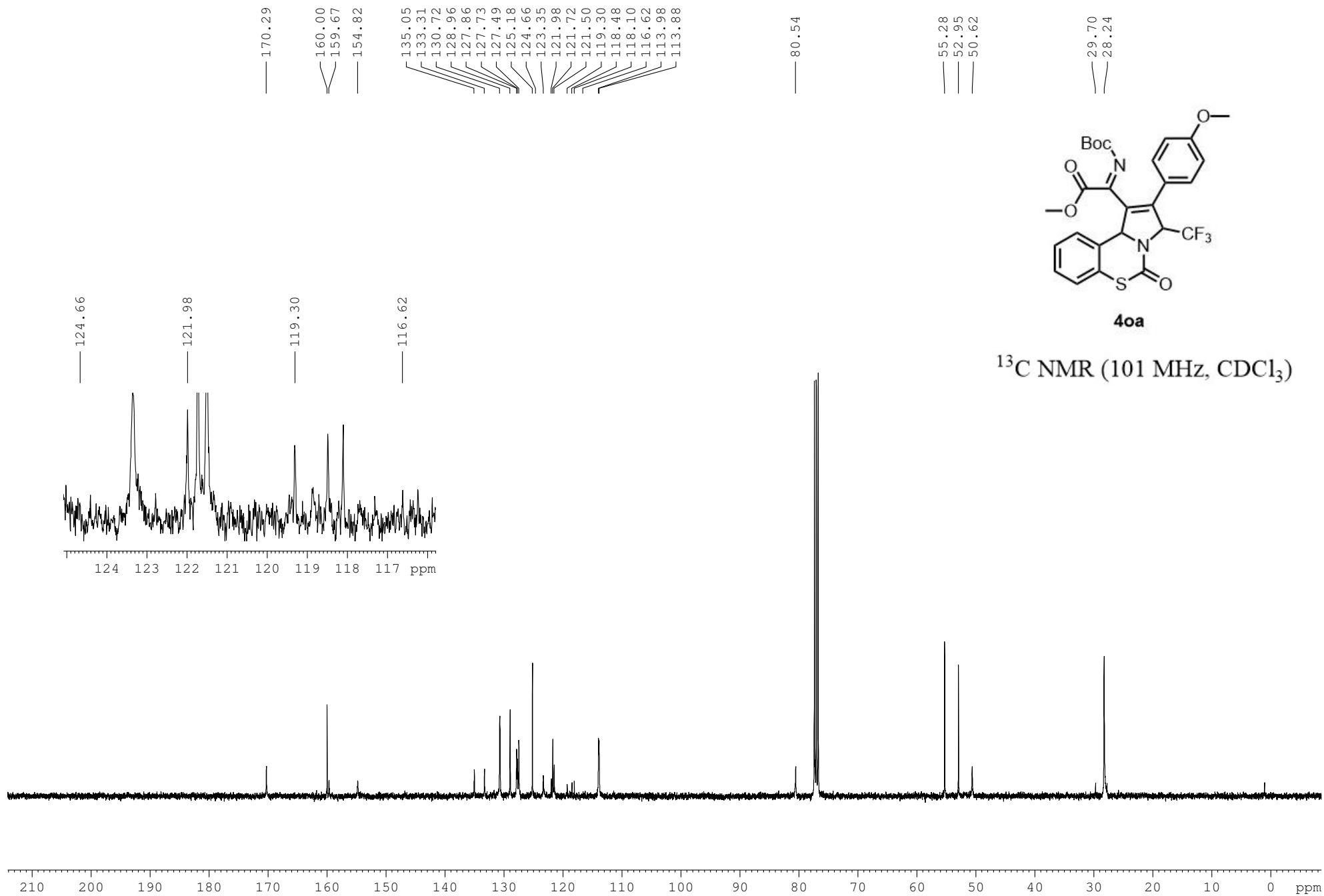
-0.00



4oa

¹H NMR (400 MHz, CDCl₃)





8.03
8.01
7.50
7.49
7.48
7.47
7.46
7.45
7.43
7.41
7.34
7.32
7.27
7.26
7.24
7.20
7.15
7.14
7.13
7.12
5.90
5.87

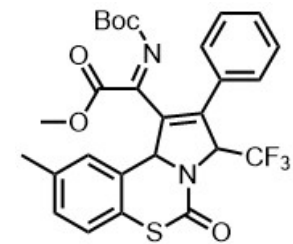
4.99
4.97

3.58

2.41

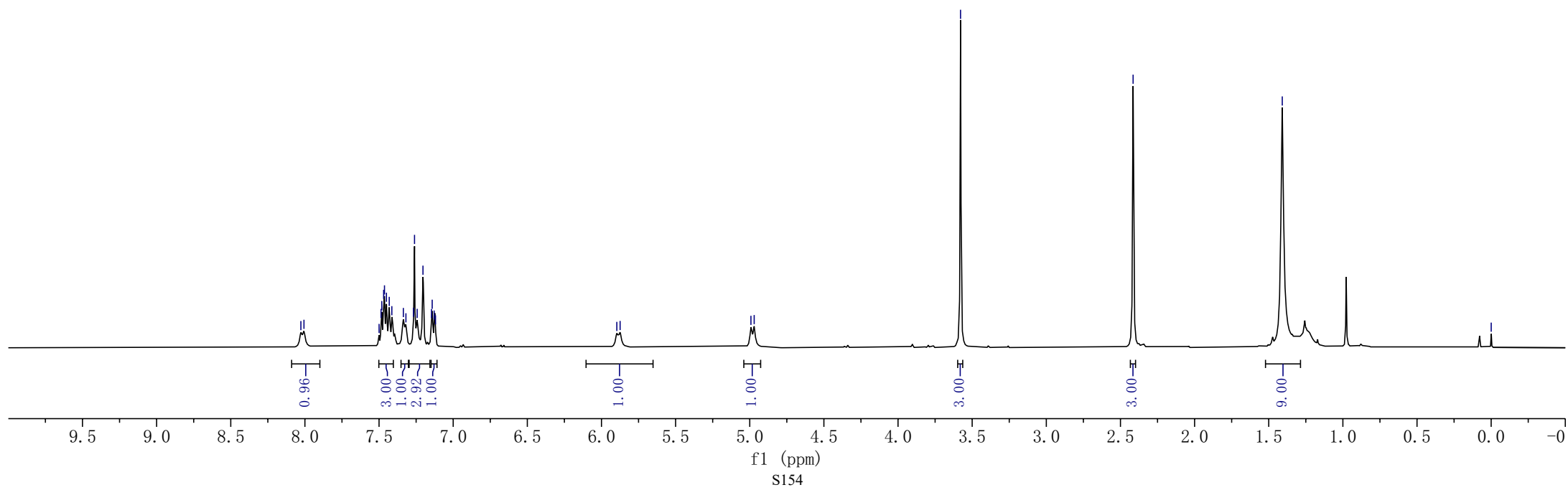
1.41

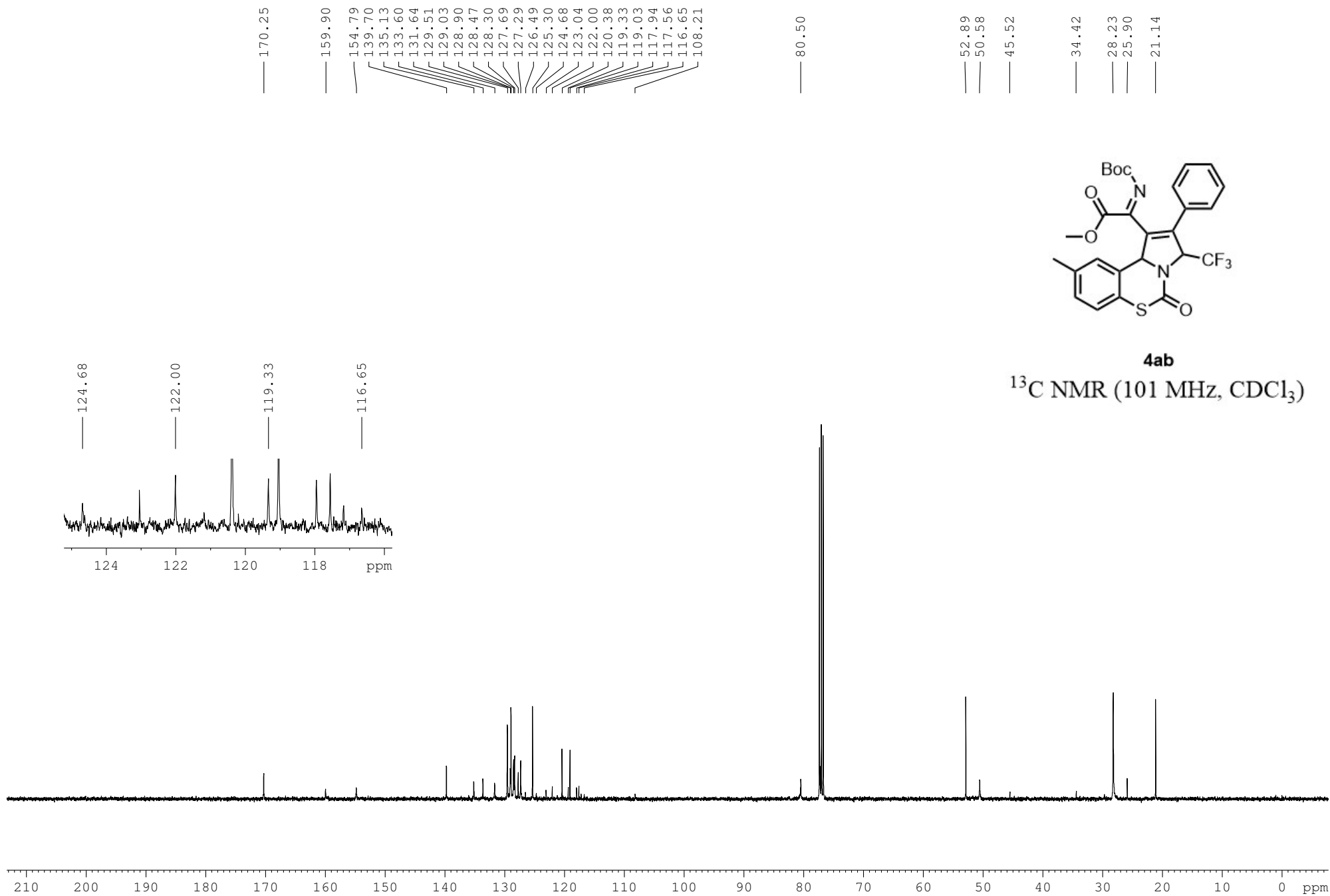
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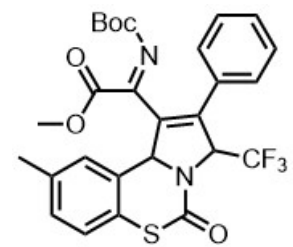


4ab

¹H NMR (400 MHz, CDCl₃)







4ab

¹⁹F NMR (376 MHz, CDCl₃)

-52.08

