Supporting Information

Cu-catalyzed radical-triggered spirotricyclization of enediynes and enyne-nitriles for the synthesis of pentacyclic spiroindenes

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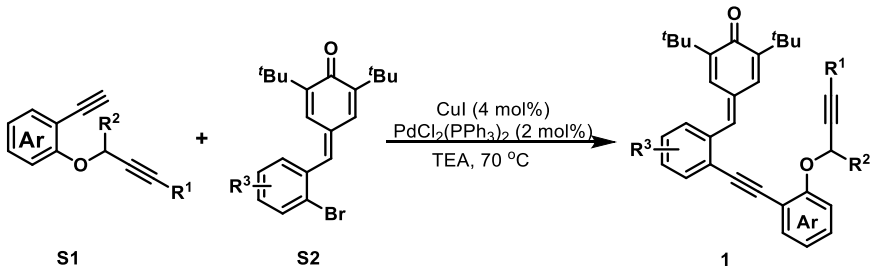
Context

General Information

PE refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, as well as DCM refers to dichloromethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated. ^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, m = multiplet), coupling constant (Hz)]. HRMS (APCI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. The melting points were measured with digital melting point detector.

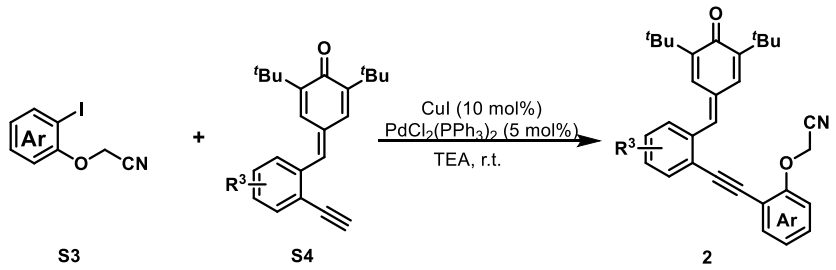
General procedure for synthesis of the substrates 1



S1 S2 1

Terminal diyne[1] **S1** (1.0 mmol, 1.0 equiv.) was added to a solution of $PdCl_2(PPh_3)_2$ (0.02 mmol, 2 mol%), CuI (0.04 mmol, 4 mol%), and 2-bromo-*para*-quinone methide[2] **S2** (1.1 mmol, 1.1 equiv.) in triethylamine (5 mL) at room temperature, and the reaction mixture was heated to 70 °C in oil bath and stirred vigorously under an argon atmosphere for 12 h. After completing reaction (by TLC), triethylamine was removed under reduced pressure and the residue was purified by column chromatography on silica gel to get pure diyne-containing *para*-quinone methide derivatives **1**.

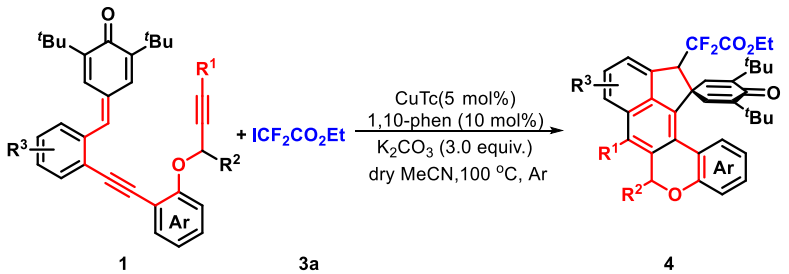
Genaral procedure for synthesis of the substrates 2



S3 S4 2

2-(2-iodoaryloxy)acetonitrile[3] **S3** (1.0 mmol, 1.0 equiv.), 2-alkynyl-*para*-quinone methide[4] **S4** (1.1 mmol, 1.1 equiv.), $PdCl_2(PPh_3)_2$ (0.05 mmol, 5 mol%) and CuI (0.10 mmol, 10 mol%) were placed in a dry Schlenk-tube (10 ml). The reaction vessel was evacuated and filled up with Ar three times, then triethylamine (5 mL) was added. The reaction mixture was stirred at room temperature until the reaction was complete (TLC monitoring). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the corresponding products **2**.

General procedure for the synthesis of compounds 4aa-4wa



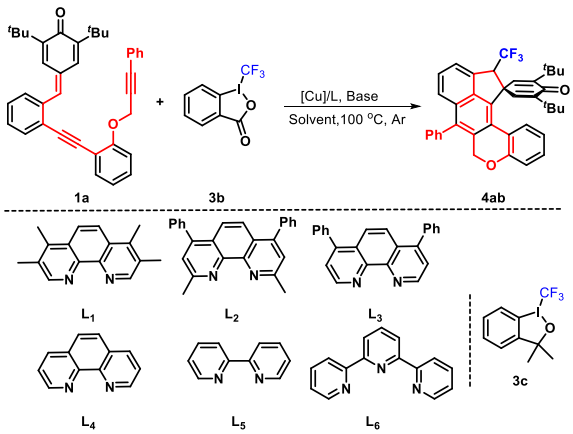
1 3a 4

To a Schlenk tube (10 ml) were added **1** (0.20 mmol, 1.0 equiv.), ethyl difluoroiodoacetate **3a** (0.40 mmol, 2.0 equiv.),

CuTc (5 mol%), 1,10-phen (10 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv.) and anhydrous MeCN (2 mL) under the protection with Argon. The resulting mixture was stirring at 100 °C in oil bath. After the reaction was complete (by TLC), the reaction mixture was cooled to room temperature and diluted with DCM (15 ml) and H_2O (20 ml). The organic layer was separated, and the aqueous layer was extracted with DCM (2 × 15 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purified product **4** was obtained after column chromatography on silica gel (PE/EA= 50/1 to 5/1 v/v).

Supplementary Table S1

Optimization of the reaction conditions for **4ab**



Entry	[Cu]	L	Solvent	Base	Yield[b]
1	CuTc	L_4	MeCN	K_2CO_3	25
2	CuTc	L_1	MeCN	K_2CO_3	34
3	CuTc	L_2	MeCN	K_2CO_3	27
4	CuTc	L_3	MeCN	K_2CO_3	32
5	CuTc	L_5	MeCN	K_2CO_3	45
6	CuTc	L_6	MeCN	K_2CO_3	40
7	CuI	L_5	MeCN	K_2CO_3	42
8	CuOAc	L_5	MeCN	K_2CO_3	38
9	CuOTf	L_5	MeCN	K_2CO_3	36
10	Cu_2O	L_5	MeCN	K_2CO_3	54
11	Cu_2O	L_5	1,4-dioxane	K_2CO_3	51
12	Cu_2O	L_5	THF	K_2CO_3	53
13	Cu_2O	L_5	DCE	K_2CO_3	46
14	Cu_2O	L_5	MeCN	---	57
15[c]	Cu_2O	L_5	MeCN	---	61
16[d]	Cu_2O	L_5	MeCN	---	42
17[e]	Cu_2O	L_5	MeCN		58
18		L_5	MeCN	---	N.D.

[a] Reaction conditions: **1a** (0.2 mmol), **3b** (0.3 mmol), [Cu] (5 mol%), L (10 mol%), solvent (2.0 mL), base (2 equiv), at 100 °C under Ar for 12h.

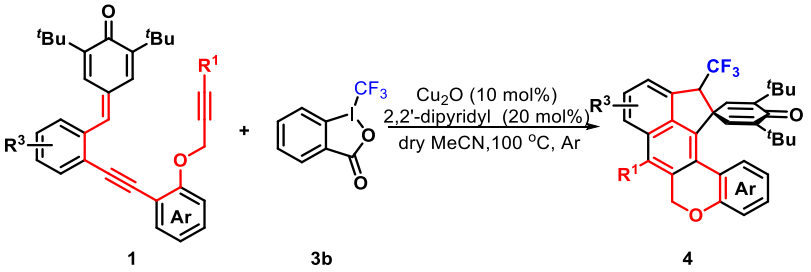
[b] Isolated yield based on **1a**.

[c] [Cu] (10 mol%), L (20 mol%).

[d] at 80 °C

[e] Togni's reagent **3c**.

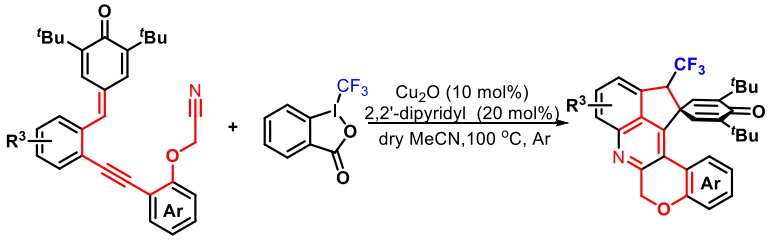
General procedure for the synthesis of compounds 4ab-4ub



1 3b 4

In a flame-dried 10 ml Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with **1** (0.20 mmol, 1.0 equiv.), Togni's reagent II **3b** (0.30 mmol, 1.5 equiv.), Cu_2O (10 mol%) and 2,2'-dipyridyl (20 mol%), followed by the addition of anhydrous MeCN (2 mL) under argon atmosphere. Then the mixture was stirred at 100 °C in oil bath until the reaction was completed, as monitored by TLC analysis. After the reaction mixture was cooled to room temperature, the reaction mixture was diluted with DCM (15 mL) and water (20 mL). Then, the phases were separated and the aqueous layer was extracted with DCM (2 × 15 mL). The combined organic layer was firstly washed with H_2O (10 ml), then washed with $NaHCO_3$ (aq.) (10 ml), and finally washed with NaCl (aq) (10 ml), dried over with an hydrous $MgSO_4$. After filtration and concentration, the residue was purified by silica gel chromatography with petroleum ether and ethyl acetate (PE/EA = 100:1 v/v) to afford **4ab-4ub**.

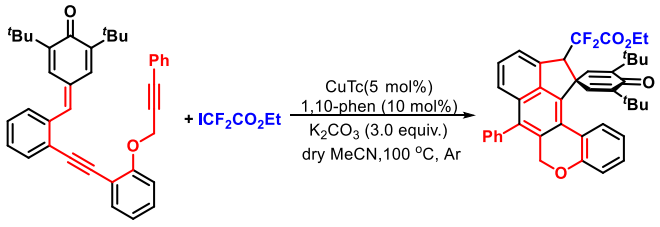
General procedure for the synthesis of compounds 5ab-5db



2 3b 5

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrates **2** (0.20 mmol, 1.0 equiv.), Togni's reagent II **3b** (0.30 mmol, 1.5 equiv.), Cu_2O (10 mol%), 2,2'-dipyridyl (20 mol%), and anhydrous MeCN (2 mL). The reaction mixture was stirred at 100 °C in oil bath for 12 h before cooled to room temperature. Upon completion (monitored by TLC), saturated $NaHCO_3$ solution (10 mL) and DCM (15 mL) were added. The phases were separated and the aqueous phase was extracted with DCM (2 × 15 mL). The combined organic solution was washed with H_2O (2 × 10 ml), dried over with anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether and ethyl acetate (PE/EA = 10:1 v/v) to afford **5ab-5db**.

Scale-up transformation of 4aa

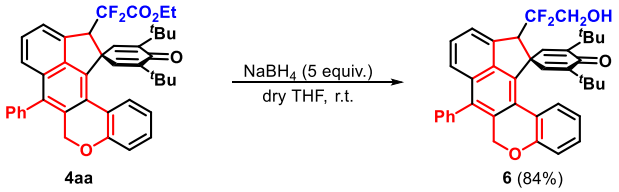


1a 3a 4aa

To a Schlenk tube (50 ml) were added **1a** (1.05 g, 2.0 mmol, 1.0 equiv.), ethyl difluoroiodoacetate **2** (1.00 g, 4.0 mmol, 2.0 equiv.), CuTc (0.02 g, 5 mol%), 1,10-phen (0.04 g, 10 mol%), K_2CO_3 (0.84 g, 6.0 mmol, 3.0 equiv.) and anhydrous MeCN (20 mL) under the protection with Argon. The resulting mixture was stirring at 100 °C in oil bath. After the reaction was complete (by TLC), the reaction mixture was cooled to room temperature and diluted with DCM (50 ml) and H_2O

(10 ml). The organic layer was separated, and the aqueous layer was extracted with DCM (2 × 50 mL). The combined organic layer was washed with brine (50 mL) and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purified product **4aa** (0.70 g, 54% yield) was obtained in 54% yield as a pale-yellow solid after column chromatography on silica gel (PE/EA= 30/1 v/v).

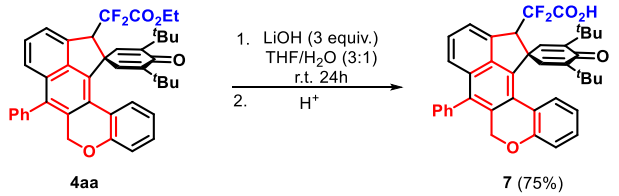
Reduction of 4aa



4aa **6** (84%)

4aa (64.7 mg, 0.1 mmol) was placed in a 10 mL tube with 2 mL of anhydrous THF in an ice bath. $NaBH_4$ (19.0 mg, 5.0 equiv.) was gradually added to the mixture. The reaction was stirred at room temperature and monitored by TLC. The reaction mixture was diluted with DCM when the raw material **4aa** was consumed, then scrubbed with saturated NH_4Cl solution (three times). The organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo, and purified by flash column chromatography (PE/EA = 20/1 v/v) to give the pure product **6** (50.8 mg, 62% yield) as a white soild, mp: 229-231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.66 (d, J = 6.8 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.53-7.45 (m, 4H), 7.36 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 6.4 Hz, 1H), 7.22-7.18 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.88-6.86 (m, 1H), 6.82-6.78 (m, 2H), 4.88 (s, 2H), 4.54-4.46 (m, 1H), 3.88-3.78 (m, 1H), 3.75-3.65 (m, 1H), 1.23 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 157.0, 147.7, 147.0, 143.6, 141.1, 138.7, 138.4, 137.4 (t, $^5J_{CF}$ = 3.0 Hz), 136.7, 134.6, 130.5, 130.2, 129.6, 129.4, 128.8(2), 128.8(9), 128.3, 128.2, 126.7, 124.1, 123.3 (t, $^1J_{CF}$ = 247.0 Hz), 123.1, 122.3(1), 122.3(7), 121.6, 117.0, 69.0, 62.7 (t, $^2J_{CF}$ = 31.0 Hz), 58.81 (t, $^3J_{CF}$ = 22.0 Hz), 55.3 (t, $^4J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.2, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -101.9 (d, J = 255.7 Hz, 1F), -104.6 (d, J =255.7 Hz, 1F). IR (KBr, ν, cm^{-1}): 3481, 2956, 1653, 1490, 1364, 1263, 1073, 882, 763. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{38}F_2O_3$ $[M + Na]^+$ 627.2687, found 627.2684.

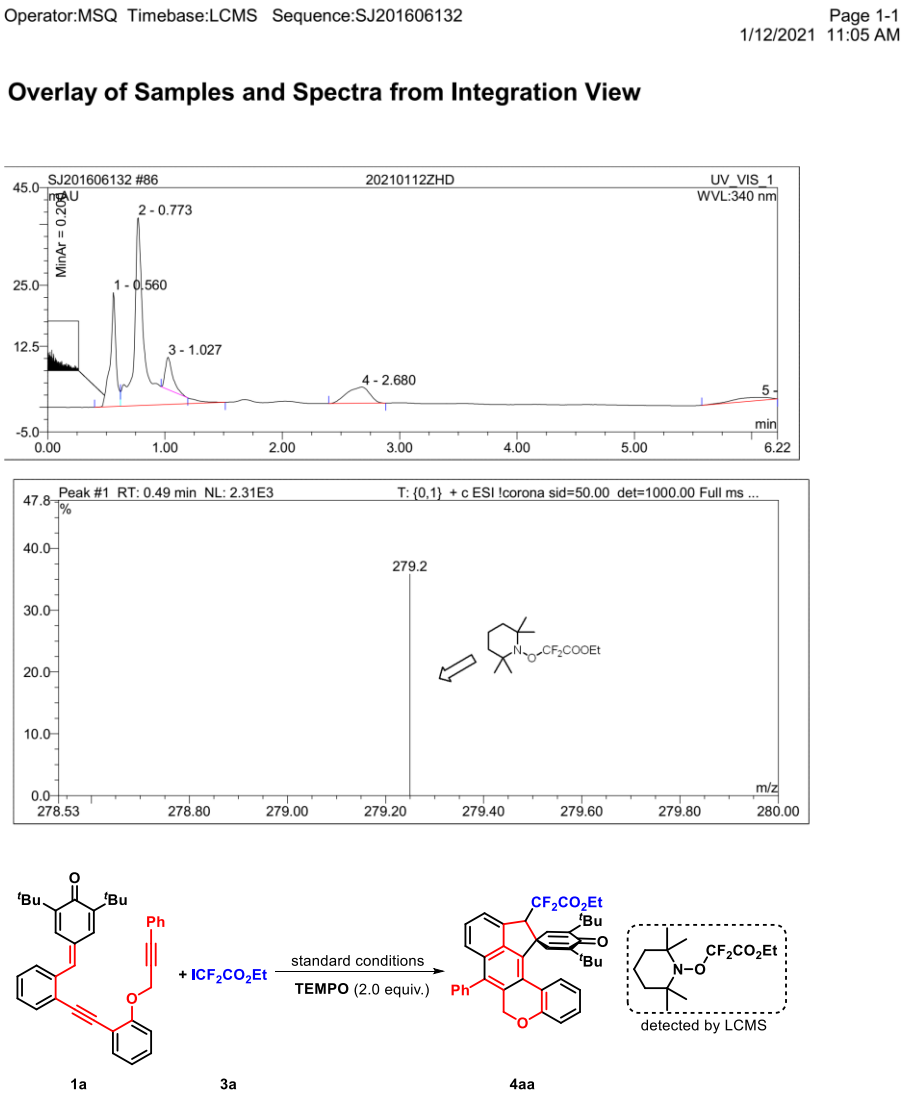
Hydrolysis of 4aa



4aa **7** (75%)

A suspension of **4aa** (64.7 mg, 0.1 mmol), LiOH (24.0 mg, 1.0 mmol) in mixed solvent THF /H_2O (v/v=3/1, 4 mL) was stirred at ambient temperature. After the reaction was complete (by TLC), the mixture was acidified with 0.2N HCl (5 mL), and extracted with DCM (2 × 10 ml). The extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA/MeOH= 5/5/1 v/v/v) to afford purified product **6** (46.4 mg, 75% yield) as the white solid, mp: 248-251 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (br, s, 1H), 7.62-7.55 (m, 3H), 7.53-7.49 (m, 4H), 7.43 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 6.8 Hz, 1H), 7.23-7.19 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 2.8 Hz, 1H), 6.82-6.77 (m, 2H), 4.96 (d, J = 13.6 Hz, 1H), 4.83 (d, J = 13.6 Hz, 1H), 4.78-4.70 (m, 1H), 1.29 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 187.9, 164.9 (t, $^2J_{CF}$ = 32.0 Hz), 156.9, 149.5, 146.3, 144.5, 139.3, 138.6, 138.5, 136.6, 135.8 (t, $^5J_{CF}$ = 3.0 Hz), 134.9, 134.5, 130.5, 130.2, 130.0, 129.6, 128.9, 128.8, 128.7, 128.3, 128.2, 126.7, 124.5, 123.1, 122.7(3), 122.7(0), 121.6, 117.15, 115.1 (t, $^1J_{CF}$ = 253.0 Hz), 68.9, 58.6 (t, $^3J_{CF}$ = 21.0 Hz), 54.7 (t, $^4J_{CF}$ = 5.0 Hz), 35.4, 35.1, 29.3, 28.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -99.9 (d, J = 282.0 Hz, 1F), -110.0 (d, J =282.0 Hz, 1F). IR (KBr, ν, cm^{-1}): 3447, 2958, 1740, 1653, 1490, 1365, 1228, 1051, 882, 759. HR-MS (ESI-TOF) *m/z* calcd for Chemical $C_{40}H_{36}F_2O_4$ $[M + Na]^+$ 641.2479, found 641.2474.

Radical-Trapping Experiment:



To a Schlenk tube (10 ml) were added **1a** (0.20 mmol, 1.0 equiv.), ethyl difluoroiodoacetate **3a** (0.40 mmol, 2.0 equiv.), CuTc (5 mol%), 1,10-phen (10 mol%), K_2CO_3 (0.6 mmol, 3.0 equiv.), TEMPO (0.4 mmol, 2.0 equiv.) anhydrous MeCN (2 mL) under the protection with Argon. The resulting mixture was stirring at 100 °C in oil bath for 2h and the solution was detected by LC-MS analysis.

Reference

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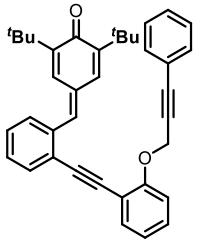
3. J. L. Portscheller and H. C. Malinakova, *Org. Lett.*, 2002, **4**, 3679.

4. A. S. Jadhav, Y. A. Pankhade and R. V. Anand, *J. Org. Chem.*, 2018, **83**, 8615.

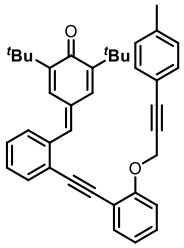
Characterization Data for Compounds 1, 2, 4aa-4wa, 4ab-4ub and 5ab-5db

2,6-di-tert-butyl-4-(2-((2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1a)



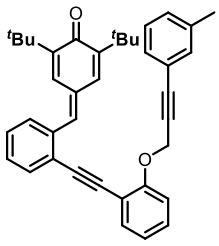
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 377 mg, 72% yield; mp: 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.74 (s, 1H), 7.69-7.66 (m, 1H), 7.52-7.47 (m, 3H), 7.43-7.34 (m, 5H), 7.32-7.27 (m, 3H), 7.20-7.18 (m, 2H), 7.01 (t, J = 7.6 Hz, 1H), 5.05 (s, 2H), 1.36 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.5, 149.3, 148.0, 141.7, 137.7, 135.2, 133.5, 132.7, 132.6, 131.8, 130.7, 130.1, 128.9(2), 128.9(6), 128.4(1), 128.4(7), 128.1, 124.7, 122.2, 121.6, 113.3, 113.2, 92.3, 92.0, 88.0, 83.6, 57.7, 35.5, 35.1, 29.6. IR (KBr, v, cm^{-1}): 2955, 2918, 2864, 1612, 1489, 1361, 1220, 819, 753. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{36}O_2$ [M + Na]$^+$ 547.2613, found 547.2610.

2,6-di-tert-butyl-4-(2-((2-((3-(p-tolyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1b)



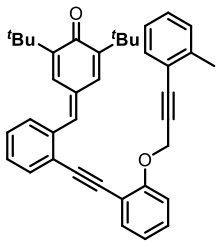
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 404 mg, 75% yield; mp: 108-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.74 (s, 1H), 7.68-7.66 (m, 1H), 7.51-7.47 (m, 3H), 7.43-7.33 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.20-7.18 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.02-7.00 (m, 1H), 5.03 (s, 2H), 2.33 (s, 3H), 1.35 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.6, 149.3, 148.0, 141.8, 139.1, 137.7, 135.2, 133.4, 132.7, 132.6, 131.8, 130.7, 130.1, 129.2, 128.9, 128.4, 128.1, 124.8, 121.5, 119.2, 113.3, 113.1, 92.3, 91.9, 88.2, 83.1, 57.7, 35.5, 35.2, 29.6(4), 29.6(2), 21.6. IR (KBr, v, cm^{-1}): 2955, 2922, 2865, 1614, 1491, 1361, 1220, 815, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_2$ [M + Na]$^+$ 561.2770, found 561.2773.

2,6-di-tert-butyl-4-(2-((2-((3-(m-tolyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1c)



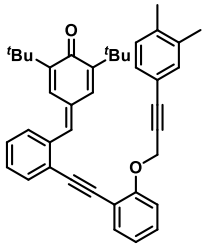
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 366 mg, 68% yield; mp: 110-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.73 (s, 1H), 7.68-7.66 (m, 1H), 7.51-7.47 (m, 3H), 7.42-7.33 (m, 3H), 7.22-7.17 (m, 5H), 7.15-7.11 (m, 1H), 7.01 (t, J = 7.6 Hz, 1H), 5.03 (s, 2H), 2.29 (s, 3H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.5, 149.3, 148.0, 141.6, 138.0, 137.7, 135.1, 133.4, 132.7, 132.5, 132.4, 130.6, 130.0, 129.6, 128.8(4), 128.8(1), 128.3, 128.2, 128.0, 124.7, 122.0, 121.5, 113.4, 113.2, 92.2, 91.9, 88.1, 83.4, 57.7, 35.5, 35.1, 29.6(7), 29.(6), 21.2. IR (KBr, v, cm^{-1}): 2955, 2920, 2864, 1613, 1491, 1361, 1220, 820, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_2$ [M + Na]$^+$ 561.2770, found 561.2775.

2,6-di-tert-butyl-4-(2-((2-((3-(o-tolyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1d)



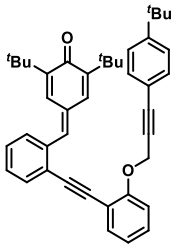
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 350 mg, 65% yield; mp: 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.68-7.66 (m, 1H), 7.52-7.47 (m, 3H), 7.43-7.33 (m, 4H), 7.23-7.19 (m, 2H), 7.17-1.15 (m, 2H), 7.13-7.09 (m, 1H), 7.03-6.99 (m, 1H), 5.09 (s, 2H), 2.35 (s, 3H), 1.36 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.5, 149.3, 148.0, 141.7, 140.6, 137.7, 135.2, 133.5, 132.7, 132.6, 132.2, 130.7, 130.0, 129.6, 128.9(3), 128.9(6), 128.4, 128.2, 125.6, 124.8, 122.0, 121.6, 113.4, 113.2, 92.3, 91.9, 87.5, 87.1, 57.7, 35.5, 35.2, 29.7, 29.6, 20.7. IR (KBr, *v*, cm^{-1}): 2956, 2920, 2865, 1613, 1492, 1454, 1361, 1220, 1018, 820, 755. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_2$ $[M + Na]^+$ 561.2770, found 561.2787.

2,6-di-tert-butyl-4-(2-((2-((3-(3,4-dimethylphenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1e)



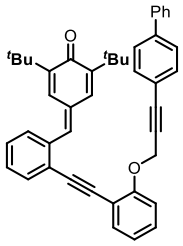
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 403 mg, 73% yield; mp: 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.74 (s, 1H), 7.68-7.66 (m, 1H), 7.51-7.46 (m, 3H), 7.41-7.33 (m, 3H), 7.20-7.18 (m, 3H), 7.16-7.13 (m, 1H), 7.05-6.98 (m, 2H), 5.03 (s, 2H), 2.24 (s, 3H), 2.20 (s, 3H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.6, 149.3, 148.0, 141.8, 137.8, 137.7, 136.7, 135.2, 133.4, 132.9, 132.7, 132.5, 130.7, 130.1, 129.7, 129.3, 128.9, 128.4, 128.1, 124.8, 121.5, 119.5, 113.3, 113.1, 92.3, 91.9, 88.3, 82.8, 57.8, 35.5, 35.2, 29.6, 19.9, 19.6. IR (KBr, *v*, cm^{-1}): 2955, 2919, 2865, 1613, 1492, 1361, 1220, 1029, 820, 752. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{40}O_2$ $[M + Na]^+$ 575.2926, found 575.2916.

2,6-di-tert-butyl-4-(2-((2-((3-(4-(tert-butyl)phenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1f)



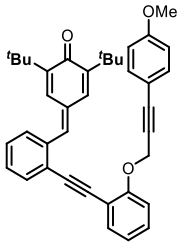
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 464 mg, 80% yield; mp: 117-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.68-7.65 (m, 1H), 7.51-7.47 (m, 3H), 7.40-7.35 (m, 3H), 7.33-7.29 (m, 4H), 7.20-7.17 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 5.03 (s, 2H), 1.35 (s, 9H), 1.29 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.6, 152.1, 149.3, 148.0, 141.6, 137.7, 135.1, 133.3, 132.7, 132.5, 131.5, 130.6, 130.0, 128.8, 128.3, 128.0, 125.3, 124.7, 121.5, 119.2, 113.4, 113.2, 92.3, 91.9, 88.1, 83.1, 57.8, 35.5, 35.1, 34.8, 31.2, 29.6(8), 29.6(6). IR (KBr, *v*, cm^{-1}): 2957, 2920, 2866, 1613, 1492, 1455, 1361, 1220, 1022, 835, 752. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{44}O_2$ $[M + Na]^+$ 603.3239, found 603.3234.

4-(2-((2-((3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1g)



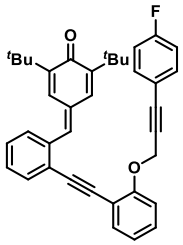
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 492 mg, 82% yield; mp: 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.74 (s, 1H), 7.69-7.67 (m, 1H), 7.58-7.55 (m, 2H), 7.54-7.52 (m, 2H), 7.51-7.46 (m, 5H), 7.44-7.41 (m, 2H), 7.40-7.34 (m, 4H), 7.22-7.18 (m, 2H), 7.04-7.00 (m, 1H), 5.07 (s, 2H), 1.36 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.6, 149.3, 148.0, 141.7, 141.6, 140.3, 137.7, 135.2, 133.5, 132.7, 132.6, 132.3, 130.7, 130.1, 129.0, 128.9, 128.4, 128.2, 127.8, 127.1(3), 127.1(0), 124.7, 121.6, 121.1, 113.3, 113.2, 92.3, 92.0, 88.0, 84.4, 57.7, 35.5, 35.2, 29.7, 29.6. IR (KBr, v, cm^{-1}): 2955, 2922, 2865, 1614, 1488, 1455, 1361, 1220, 1015, 839, 751. HR-MS (ESI-TOF) *m/z* calcd for $C_{44}H_{40}O_2$ $[M + Na]^+$ 623.2926, found 623.2928.

2,6-di-tert-butyl-4-(2-((2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1h)



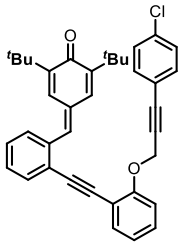
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 421 mg, 76% yield; mp: 53-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.67-7.65 (m, 1H), 7.50-7.46 (m, 3H), 7.42-7.37 (m, 2H), 7.34 (d, J = 8.8 Hz, 3H), 7.20-7.17 (m, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.82-6.80 (m, 2H), 5.02 (s, 2H), 3.79 (s, 3H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 160.1, 158.6, 149.3, 148.0, 141.8, 137.7, 135.2, 133.4(1), 133.4(7), 132.7, 132.6, 130.7, 130.1, 128.9, 128.4, 128.1, 124.8, 121.5, 114.3, 114.0, 113.3, 113.2, 92.3, 91.9, 88.0, 82.4, 57.8, 55.4, 35.5, 35.2, 29.6(4), 29.6(2). IR (KBr, v, cm^{-1}): 2956, 2922, 2865, 1611, 1508, 1456, 1361, 1250, 1033, 831, 751. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_3$ $[M + Na]^+$ 577.2719, found 577.2715.

2,6-di-tert-butyl-4-(2-((2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1i)



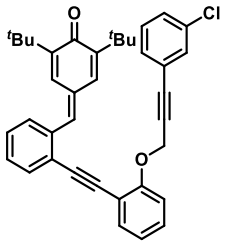
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 417 mg, 77% yield; mp: 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.67-7.65 (m, 1H), 7.52-7.46 (m, 3H), 7.41-7.34 (m, 5H), 7.18-7.16 (m, 2H), 7.03-6.96 (m, 3H), 5.02 (s, 2H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.9 (d, ^{1}J = 248.9 Hz), 158.5, 149.4, 148.0, 141.7, 137.7, 135.2, 133.8 (d, ^{3}J = 8.6 Hz), 133.5, 132.7, 132.6, 130.7, 130.1, 128.9, 128.4, 128.2, 124.7, 121.6, 118.3 (d, ^{4}J = 3.4 Hz), 115.7 (d, ^{2}J =22.0 Hz), 113.2(3), 113.2(0), 92.2, 92.0, 86.9, 83.5, 57.6, 35.5, 35.1, 29.6(3), 29.6(1). IR (KBr, v, cm^{-1}): 2956, 2922, 2865, 1613, 1507, 1455, 1361, 1220, 1020, 835, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}FO_2$ $[M + Na]^+$ 565.2519, found 565.2504.

2,6-di-tert-butyl-4-(2-((2-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1j)



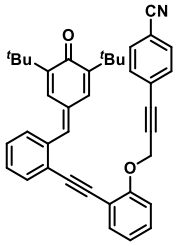
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 469 mg, 84% yield; mp: 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): δ 7.71 (s, 1H), 7.68-7.65 (m, 1H), 7.52-7.46 (m, 3H), 7.43-7.37 (m, 2H), 7.36-7.31 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.17-7.15 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 5.02 (s, 2H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.4, 149.4, 148.0, 141.5, 137.7, 135.0, 134.9, 133.4, 133.0, 132.7, 132.5, 130.6, 130.0, 128.8, 128.7, 128.2, 128.1, 124.7, 121.7, 120.7, 113.4, 113.3, 92.1, 92.0, 86.8, 84.8, 57.6, 35.5, 35.1, 29.6(8), 29.6(5). IR (KBr, v, cm^{-1}): 2955, 2920, 2865, 1613, 1489, 1361, 1219, 1090, 1015, 827, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}ClO_2$ $[M + Na]^+$ 581.2223, found 581.2213.

2,6-di-tert-butyl-4-(2-((2-((3-(3-chlorophenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1k)



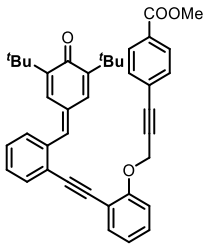
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 402 mg, 72% yield; mp: 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.68-7.66 (m, 1H), 7.52-7.46 (m, 3H), 7.41-7.34 (m, 4H), 7.31-7.28 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.16-7.14 (m, 2H), 7.04-7.00 (m, 1H), 5.03 (s, 2H), 1.34 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.3, 149.3, 147.9, 141.6, 137.6, 135.1, 134.2, 133.5, 132.7, 132.5, 131.7, 130.7, 130.1, 129.9, 129.6, 129.1, 128.9, 128.3, 128.1, 124.6, 123.8, 121.7, 113.2, 92.1, 92.0, 86.5, 85.0, 57.5, 35.5, 35.1, 29.6(8), 29.6(6). IR (KBr, v, cm^{-1}): 2955, 2922, 2865, 1613, 1455, 1361, 1219, 1022, 820, 751. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}ClO_2$ $[M + Na]^+$ 581.2223, found 581.2227.

4-(3-(2-((2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)ethynyl)phenoxy) prop-1-yn-1-yl)benzonitrile (1l)



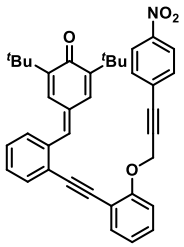
Isolation by column chromatography (PE/EA= 30/1 v/v) Yellow solid, 445 mg, 81% yield; mp: 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.70 (s, 1H), 7.67-7.65 (m, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.53-7.50 (m, 1H), 7.49-7.46 (m, 4H), 7.42-7.34 (m, 3H), 7.15-7.12 (m, 2H), 7.05-7.02 (m, 1H), 5.05 (s, 2H), 1.34 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.3, 149.4, 148.0, 141.6, 137.7, 135.1, 133.6, 132.7, 132.6, 132.3, 132.1, 130.7, 130.1, 129.0, 128.3(1), 128.3(8), 127.0, 124.6, 121.9, 118.3, 113.3(4), 113.3(5), 112.3, 92.1, 92.0, 88.2, 86.2, 57.5, 35.5, 35.1, 29.6(3), 29.6(0). IR (KBr, v, cm^{-1}): 2956, 2920, 2865, 2229, 1615, 1456, 1361, 1264, 1021, 838, 746. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{35}NO_2$ $[M + Na]^+$ 572.2565, found 572.2574.

methyl 4-(3-(2-((2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)ethynyl)phenoxy)prop-1-yn-1-yl)benzoate (1m)



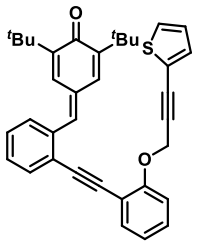
Isolation by column chromatography (PE/EA= 50/1 v/v) Yellow solid, 500 mg, 86% yield; mp: 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.97-7.95 (m, 2H), 7.71 (s, 1H), 7.68-7.66 (m, 1H), 7.52-7.50 (m, 1H), 7.49-7.43 (m, 4H), 7.41-7.34 (m, 3H), 7.17-7.15 (m, 2H), 7.04-7.01 (m, 1H), 5.05 (s, 2H), 3.91 (s, 3H), 1.34 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 166.5, 158.4, 149.4, 148.0, 141.6, 137.7, 135.1, 133.5, 132.7, 132.6, 131.8, 130.7, 130.1, 129.6, 128.9, 128.3, 128.2, 126.8, 124.7, 121.8, 113.2, 92.1, 92.0, 87.2, 86.7, 57.6, 52.4, 35.5, 35.1, 29.6(2), 29.6(0). IR (KBr, v, cm^{-1}): 2949, 2921, 2864, 1616, 1558, 1457, 1274, 1020, 829, 749. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{38}O_4$ $[M + Na]^+$ 605.2668, found 605.2667.

2,6-di-tert-butyl-4-(2-((2-((3-(4-nitrophenyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1n)



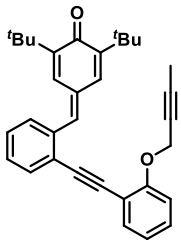
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid, 415 mg, 73% yield; mp: 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.16 (d, J = 8.8 Hz, 2H), 7.70-7.66 (m, 2H), 7.55-7.51 (m, 3H), 7.50-7.46 (m, 2H), 7.44-7.35 (m, 3H), 7.15-7.11 (m, 2H), 7.06-7.02 (m, 1H), 5.06 (s, 2H), 1.34 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.2, 149.4, 148.0, 147.5, 141.5, 137.6, 135.0, 133.6, 132.7, 132.5, 130.7, 130.1, 128.9, 128.2, 124.5, 123.6, 121.9, 113.3, 113.2, 92.1, 91.9, 89.0, 85.9, 57.4, 35.5, 35.1, 29.6, 29.5. IR (KBr, v, cm^{-1}): 2956, 2920, 2865, 1612, 1520, 1491, 1342, 1220, 1021, 858, 749. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}NO_4$ $[M + Na]^+$ 592.2464, found 592.2468.

2,6-di-tert-butyl-4-(2-((2-((3-(thiophen-2-yl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1o)



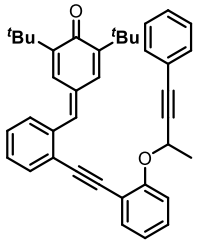
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 344 mg, 65% yield; mp: 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): δ 7.72 (s, 1H), 7.68-7.65 (m, 1H), 7.51-7.46 (m, 3H), 7.41-7.34 (m, 3H), 7.27-7.25 (m, 1H), 7.20 (d, J = 4.0 Hz, 1H), 7.17 (d, J = 2.4 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.03-6.99 (m, 1H), 6.96-6.94 (m, 1H), 5.04 (s, 2H), 1.36 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.9, 158.5, 149.4, 148.0, 141.8, 137.8, 135.3, 133.5, 133.0, 132.8, 132.6, 130.8, 130.2, 129.0, 128.4, 128.2, 128.0, 127.1, 124.8, 122.1, 121.7, 113.3, 92.2, 92.0, 87.7, 81.4, 57.8, 35.6, 35.2, 29.7(9), 29.7(6). IR (KBr, v, cm^{-1}): 2909, 2850, 1635, 1558, 1457, 1261, 820, 749. HR-MS (ESI-TOF) *m/z* calcd for $C_{36}H_{34}O_2S$ $[M + Na]^+$ 553.2177, found 553.2185.

4-(2-((2-(but-2-yn-1-yloxy)phenyl)ethynyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1p)



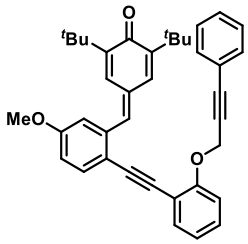
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 365 mg, 79% yield; mp: 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.66-7.64 (m, 1H), 7.49-7.47 (m, 3H), 7.42-7.37 (m, 2H), 7.36-7.31 (m, 1H), 7.17 (d, J = 2.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 7.00-6.96 (m, 1H), 4.77 (q, J = 2.4 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H), 1.37 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.6, 149.2, 147.9, 141.8, 137.7, 135.2, 133.3, 132.6, 132.5, 130.7, 130.0, 128.9, 128.3, 128.0, 124.8, 121.2, 112.9, 112.8, 92.3 91.8, 84.5, 74.0, 57.2, 35.5, 35.1, 29.6, 3.8. IR (KBr, v, cm^{-1}): 2955, 2920, 2864, 1614, 1464, 1361, 1221, 1002, 820, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{33}H_{34}O_2$ $[M + Na]^+$ 485.2457, found 485.2443.

2,6-di-tert-butyl-4-(2-((2-((4-phenylbut-3-yn-2-yl)oxy)phenyl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1q)



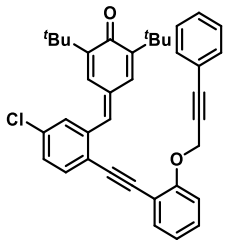
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 415 mg, 74% yield; mp: 47-48 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.68-7.65 (m, 2H), 7.51-7.49 (m, 1H), 7.48-7.46 (m, 2H), 7.41-7.36 (m, 4H), 7.34-7.32 (m, 1H), 7.30- 7.27 (m, 3H), 7.24 (d, J = 8.0Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.02-7.00 (m, 1H), 5.17 (q, J = 6.4 Hz, 1H), 1.79 (d, J = 6.8 Hz, 3H), 1.33 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 158.4, 149.4, 147.9, 141.6, 137.5, 135.2, 133.5, 133.0, 132.6, 131.8, 130.9, 130.1, 129.0, 128.7, 128.4, 128.3, 128.1, 124.9, 122.4, 121.6, 115.1, 113.7, 92.5, 91.7, 88.1, 86.4, 65.8, 35.5, 35.2, 29.6, 22.6. IR (KBr, v, cm^{-1}): 2955, 2922, 2864, 1614, 1489, 1361, 1219, 1031, 820, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_2$ $[M + Na]^+$ 561.2770, found 561.2780.

2,6-di-tert-butyl-4-(5-methoxy-2-((2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1r)



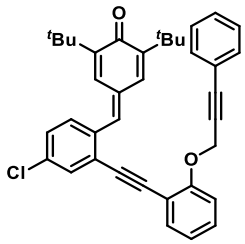
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 343 mg, 62% yield; mp: 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.69 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.52 (s, 1H), 7.49-7.46 (m, 1H), 7.41-7.39 (m, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.31-7.28 (m, 3H), 7.19-7.16 (m, 2H), 7.01-7.00 (m, 2H), 6.94- 6.91 (m, 1H), 5.03 (s, 2H), 3.87 (s, 3H), 1.35 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 159.3, 158.3, 149.4, 148.1, 141.7, 139.0, 135.2, 134.0, 133.2, 132.7, 131.9, 129.7, 128.8, 128.4, 128.3, 122.3, 121.6, 117.2, 115.7, 115.4, 113.5, 113.3, 92.0, 90.8, 88.0, 83.8, 57.7, 55.6, 35.6, 35.2, 29.7, 29.6. IR (KBr, v, cm^{-1}): 2956, 2923, 2854, 1616, 1490, 1361, 1220, 1016, 821, 751. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_3$ $[M + Na]^+$ 577.2719, found 577.2723.

2,6-di-tert-butyl-4-(5-chloro-2-((2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1s)



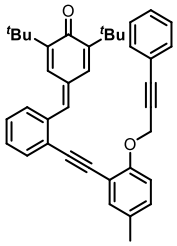
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 379 mg, 68% yield; mp: 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.65-7.63 (m, 2H), 7.54-7.52 (m, 2H), 7.47-7.44 (m, 3H), 7.42-7.39 (m, 2H), 7.38-7.34 (m, 3H), 7.23 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 5.08 (s, 2H), 1.40 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.6, 149.8, 148.5, 139.6, 139.1, 134.8, 134.0, 133.7, 133.4, 133.3, 131.8, 130.6, 130.3, 128.9(1), 128.9(7), 128.4, 127.8, 123.1, 122.2, 121.6, 113.2, 112.9, 93.1, 91.0, 88.1, 83.7, 57.7, 35.6, 35.2, 29.6(2), 29.6(8). IR (KBr, v, cm^{-1}): 2956, 2924, 2865, 1615, 1489, 1459, 1361, 1220, 1104, 886, 751. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}ClO_2$ [M + Na]$^+$ 581.2223, found 581.2230.

2,6-di-tert-butyl-4-(4-chloro-2-((2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1t)



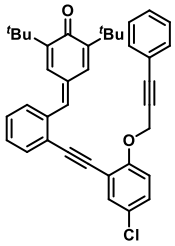
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 391 mg, 70% yield; mp: 42-44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.66 (s, 1H), 7.62 (s, 1H), 7.50-7.48 (m, 1H), 7.42-7.36 (m, 5H), 7.32-7.29 (m, 4H), 7.20-7.15 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 5.04 (s, 2H), 1.35 (m, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 158.6, 149.6, 148.2, 140.1, 136.1, 134.9, 134.8, 133.5, 132.9, 132.3, 131.8, 131.7, 130.5, 128.9, 128.4, 127.9, 126.3, 122.1, 121.6, 113.2, 112.6, 93.4, 90.7, 88.1, 83.6, 57.6, 35.5, 35.1, 29.6. IR (KBr, v, cm^{-1}): 2956, 2923, 2866, 1614, 1490, 1361, 1234, 1087, 947, 754. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}ClO_2$ [M + Na]$^+$ 581.2223, found 581.2219.

2,6-di-tert-butyl-4-(2-((5-methyl-2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1u)



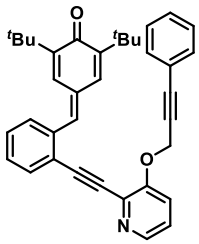
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 409 mg, 76% yield; mp: 61-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.72 (s, 1H), 7.67-7.64 (m, 1H), 7.49-7.46 (m, 2H), 7.42-7.36 (m, 4H), 7.33-7.28 (m, 4H), 7.18-7.13 (m, 2H), 7.08 (d, J = 8.4 Hz, 1H), 5.01 (s, 2H), 2.30 (s, 3H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 156.5, 149.3, 148.0, 141.8, 137.7, 135.2, 133.8, 132.7, 132.5, 131.8, 131.0, 130.7(1), 130.7(8), 128.9, 128.8, 128.4, 128.1, 124.8, 122.3, 113.6, 112.9, 92.5, 91.7, 87.8, 84.0, 57.9, 35.5, 35.1, 29.6(3), 29.6(1), 20.5. IR (KBr, v, cm^{-1}): 2956, 2923, 2865, 1615, 1489, 1361, 1223, 1021, 820, 755. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{38}O_2$ [M + Na]$^+$ 561.2770, found 561.2774.

2,6-di-tert-butyl-4-(2-((5-chloro-2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)ethynyl)benzylidene) cyclohexa-2,5-dien-1-one (1v)



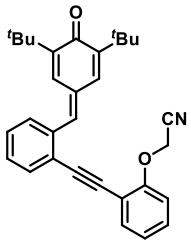
Isolation by column chromatography (PE/EA= 100/1 v/v) Yellow solid, 379 mg, 68% yield; mp: 57-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.67-7.75 (m, 2H), 7.49-7.42 (m, 4H), 7.41-7.38 (m, 3H), 7.33-7.29 (m, 4H), 7.16 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H), 5.02 (s, 2H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 157.1, 149.5, 148.2, 141.3, 137.9, 135.1, 132.8, 132.7, 131.9, 130.8, 129.8, 129.0(0), 129.0(5), 128.5(1), 128.5(5), 128.3, 126.4, 124.1, 122.0, 114.8, 114.5, 93.0, 90.8, 88.4, 83.2, 58.0, 35.5, 35.2, 29.6(3), 29.6(1). IR (KBr, v, cm^{-1}): 2956, 2924, 2865, 1615, 1489, 1361, 1222, 1015, 804, 755. HR-MS (ESI-TOF) *m/z* calcd for $C_{38}H_{35}ClO_2$ [M + Na]$^+$ 581.2223, found 581.2225.

2,6-di-tert-butyl-4-(2-((3-((3-phenylprop-2-yn-1-yl)oxy)pyridin-2-yl)ethynyl)benzylidene)cyclohexa-2,5-dien-1-one (1w)



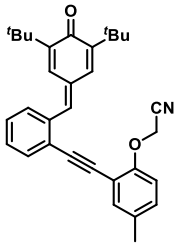
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid, 441 mg, 84% yield; mp: 59-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.30 (d, J = 4.4 Hz, 1H), 7.77-7.75 (m, 2H), 7.54-7.48 (m, 2H), 7.47-7.44 (m, 2H), 7.41-7.38 (m, 3H), 7.33-7.27 (m, 4H), 7.18 (d, J = 2.4 Hz, 1H), 5.05 (s, 2H), 1.34 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 155.5, 149.4, 148.0, 142.9, 141.2, 138.1, 135.1, 134.0, 133.3, 132.7, 131.8, 130.8, 129.1, 128.9, 128.8, 128.4, 128.2, 123.8, 123.7, 121.7, 120.3, 92.0, 91.5, 88.9, 82.7, 57.6, 35.5, 35.1, 29.6(8), 29.6(6). IR (KBr, v, cm^{-1}): 2956, 2924, 2865, 1613, 1455, 1361, 1278, 1118, 916, 757. HR-MS (ESI-TOF) *m/z* calcd for $C_{37}H_{35}NO_2$ [M + Na]$^+$ 548.2565, found 548.2566.

2-(2-((2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)ethynyl)phenoxy)acetonitrile (2a)



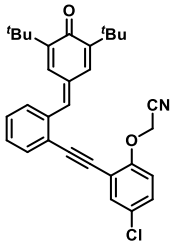
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid, 409 mg, 91% yield; mp: 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.68-7.65 (m, 1H), 7.57 (s, 1H), 7.54-7.51 (m, 1H), 7.49-7.37 (m, 5H), 7.15-7.10 (m, 2H), 7.06 (d, J = 8.3 Hz, 1H), 4.86 (s, 2H), 1.36 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 156.9, 149.4, 148.2, 140.9, 137.7, 134.8, 134.0, 132.9, 132.7, 130.7, 130.3, 128.9, 128.5, 128.2, 124.0, 123.6, 114.9, 114.0(3), 114.0(0), 92.7, 90.6, 54.7, 35.5, 35.1, 29.6, 29.5. IR (KBr, v, cm^{-1}): 2956, 2924, 2865, 2214, 1614, 1457, 1361, 1218, 820, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{31}H_{31}NO_2$ [M + Na]$^+$ 472.2252, found 472.2254.

2-(2-((2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)ethynyl)-4-methylphenoxy)acetonitrile (2b)



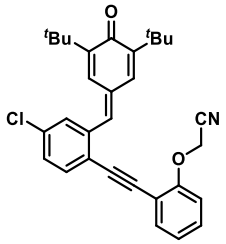
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid, 407 mg, 88% yield; mp: 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.66-7.64 (m, 1H), 7.56 (s, 1H), 7.48-7.43 (m, 3H), 7.41-7.39 (m, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.19-7.16 (m, 1H), 7.11 (d, J = 2.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 4.83 (s, 2H), 2.32 (s, 3H), 1.36 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 154.9, 149.4, 148.2, 141.0, 137.6, 134.9, 134.3, 133.4, 132.8, 132.7, 130.9, 130.7, 128.9, 128.5, 128.2, 124.0, 115.0, 114.5, 113.8, 92.4, 90.8, 55.1, 35.5, 35.1, 29.6, 29.5, 20.5. IR (KBr, v, cm^{-1}): 2956, 2924, 2866, 2214, 1615, 1457, 1361, 1221, 1042, 888, 757. HR-MS (ESI-TOF) m/z calcd for $C_{32}H_{33}NO_2$ $[M + Na]^+$ 486.2409, found 486.2400.

2-(4-chloro-2-((2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)ethynyl)phenoxy)acetonitrile (2c)



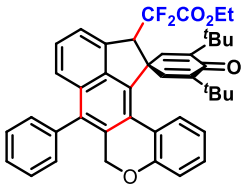
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid, 396 mg, 82% yield; mp: 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.59 (d, J = 8.0 Hz, 1H), 7.51-7.44 (m, 3H), 7.42-7.35 (m, 3H), 7.14-7.10 (m, 1H), 7.08 (d, J = 2.8 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 4.85 (s, 2H), 1.35 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.6, 156.9, 149.9, 148.7, 139.0, 138.8, 134.5, 134.0, 133.9, 133.5, 130.6, 130.5, 128.9, 127.7, 123.5, 122.3, 114.8, 113.7, 113.6, 91.7, 91.4, 54.6, 35.5, 35.2, 29.6, 29.5. IR (KBr, v, cm^{-1}): 2956, 2924, 2866, 2214, 1615, 1457, 1362, 1260, 910, 821, 750. HR-MS (ESI-TOF) m/z calcd for $C_{31}H_{30}ClNO_2$ $[M + Na]^+$ 506.1863, found 506.1872.

2-(2-((4-chloro-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)ethynyl)phenoxy)acetonitrile (2d)



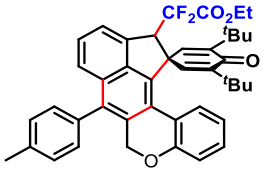
Isolation by column chromatography (PE/EA= 10/1 v/v) Yellow solid, 435 mg, 90% yield; mp: 149-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.59 (d, J = 8.4 Hz, 1H), 7.51-7.49 (m, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.44 (s, 1H), 7.40-7.35 (m, 3H), 7.14-7.10 (m, 1H), 7.08 (d, J = 2.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 4.85 (s, 2H), 1.35 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.6, 156.9, 149.9, 148.7, 139.0, 138.8, 134.5, 134.0, 133.9, 133.5, 130.6, 130.5, 128.9, 127.7, 123.5, 122.3, 114.8, 113.7, 113.6, 91.7, 91.4, 54.6, 35.5, 35.2, 29.6, 29.5. IR (KBr, v, cm^{-1}): 2957, 2924, 2866, 2214, 1614, 1521, 1457, 1361, 1220, 910, 821, 750. HR-MS (ESI-TOF) m/z calcd for $C_{31}H_{30}ClNO_2$ $[M + Na]^+$ 506.1863, found 506.1875.

ethyl 2-(3',5'-di-tert-butyl-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4aa)



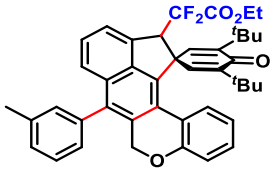
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 80 mg, 62% yield; mp: 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.59-7.55 (m, 2H), 7.53-7.48 (m, 5H), 7.41 (d, J = 7.6 Hz, 1H), 7.30-7.28 (m, 1H), 7.21-7.17 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.80-6.77 (m, 1H), 6.73-6.71 (m, 1H), 4.95 (d, J = 13.6 Hz, 1H), 4.81 (d, J = 13.6 Hz, 1H), 4.70-4.62 (m, 1H), 4.32-4.26 (m, 1H), 4.22-4.14 (m, 1H), 1.30 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm):186.8, 162.6 (t, $^2J_{CF}$ = 32.0 Hz), 157.0, 149.3, 146.0, 144.0, 138.9, 138.8, 138.6, 136.7, 136.1 (t, $^5J_{CF}$ = 3.0 Hz), 134.7, 134.6, 130.5, 130.2, 130.0, 129.5, 129.0, 128.8, 128.7, 128.2, 128.1, 126.7, 124.4, 123.1, 122.6, 122.5, 121.6, 117.1, 115.1 (t, $^1J_{CF}$ = 253.0 Hz), 68.9, 63.4, 59.0 (t, $^3J_{CF}$ = 21.0 Hz), 54.7 (d, $^4J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -99.6 (d, J = 267.0 Hz, 1F), -102.1 (d, J =267.0 Hz, 1F). IR (KBr, v, cm^{-1}): 2957, 2924, 2868, 1772, 1653, 1491, 1457, 1363, 1086, 881, 749. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{40}F_2O_4$ $[M + Na]^+$ 669.2792, found 669.2788.

ethyl 2-(3',5'-di-tert-butyl-4'-oxo-7-(p-tolyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ba)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 74 mg, 56% yield; mp: 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.56 (d, J = 8.0 Hz, 1H), 7.53-7.46 (m, 3H), 7.39-7.29 (m, 3H), 7.21-7.16 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.80-6.76 (m, 1H), 6.74-6.72 (m, 1H), 4.97 (d, J = 13.6 Hz, 1H), 4.82 (d, J = 13.6 Hz, 1H), 4.69-4.61 (m, 1H), 4.34-4.26 (m, 1H), 4.22-4.14 (m, 1H), 2.49 (s, 3H), 1.30 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^2J_{CF}$ = 32.0 Hz), 157.0, 149.3, 146.0, 144.0, 139.0, 138.7, 138.6, 137.9, 136.1 (t, $^5J_{CF}$ = 3.0 Hz), 134.7(2), 134.7(9), 133.6, 130.6, 130.1, 129.9, 129.5, 129.4, 129.0, 128.0, 126.7, 124.5, 123.2, 122.5(8), 122.5(5), 121.6, 117.1, 115.1 (t, $^1J_{CF}$ = 253.0 Hz), 69.0, 63.4, 59.0 (t, $^3J_{CF}$ = 21.0 Hz), 54.7 (d, $^4J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 21.4, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.1 (d, J = 263.2 Hz, 1F), -103.6 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2958, 2924, 2868, 1773, 1653, 1490, 1458, 1364, 1228, 1087, 881, 759. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_4$ $[M + Na]^+$ 683.2949, found 683.2955.

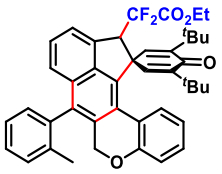
ethyl 2-(3',5'-di-tert-butyl-4'-oxo-7-(m-tolyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ca)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 85 mg, 64% yield; mp: 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.57 (d, J = 8.0 Hz, 1H), 7.50 (s, 3H), 7.47-7.39 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.23-7.17 (m, 2H), 7.09 (d, J = 10.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.88-6.86 (m, 1H), 6.81-6.77 (m, 1H), 6.75 -6.72 (m, 1H), 4.99-4.95 (m, 1H), 4.85-4.79 (m, 1H), 4.70-4.62 (m, 1H), 4.35-4.26 (m, 1H), 4.23-4.15 (m, 1H), 2.45 (d, J = 12.0 Hz, 3H), 1.30 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^2J_{CF}$ = 32.0 Hz), 157.0, 149.3, 146.0, 144.0, 139.0, 138.6, 138.5, 138.4, 136.6, 136.0 (t, $^5J_{CF}$ = 3.0 Hz), 134.9, 134.6, 130.9, 130.6,

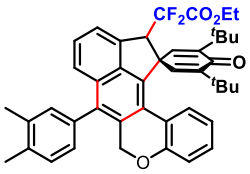
130.5, 129.5, 129.0, 128.9, 128.7, 128.6, 128.1, 127.3, 127.0, 126.7, 124.6, 124.5, 123.2, 122.5, 121.6, 117.1, 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 69.0, 63.4, 59.3 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 21.6, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.1 (d, *J* = 263.2 Hz, 1F), -102.8 (d, *J* =263.2 Hz, 1F). IR (KBr, *v*, cm^{-1}): 2957, 2921, 2867, 1772, 1654, 1490, 1457, 1261, 1087, 880, 749. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_4$ $[M + Na]^+$ 683.2949, found 683.2950.

ethyl 2-(3',5'-di-tert-butyl-4'-oxo-7-(o-tolyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4da)



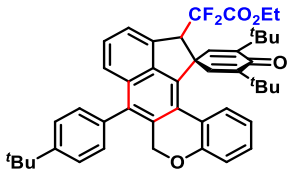
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 90 mg, 68% yield; mp: 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.61-7.56 (m, 1H), 7.53-7.45 (m, 2H), 7.43-7.27 (m, 4H), 7.24-7.14 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 9.6 Hz, 1H), 6.81-6.74 (m, 2H), 4.91-4.62 (m, 3H), 4.34-4.25 (m, 1H), 4.24-4.13 (m, 1H), 2.05 (d, *J* = 10.8 Hz, 3H), 1.31 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.9, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 157.0, 149.5, 146.2, 144.0, 139.1, 138.7 (t, $^{5}J_{CF}$ = 3.0 Hz), 137.3, 136.8, 136.4, 136.1, 134.5, 134.0, 130.6, 130.4, 130.3, 130.0, 129.6, 129.2, 128.5, 128.2, 126.8, 126.4, 124.3, 124.2, 123.2, 122.7, 122.5, 121.7, 117.2, 115.3 (t, $^{1}J_{CF}$ = 253.0 Hz), 68.9, 63.4, 59.2 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.2, 29.4, 28.8, 20.0, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -102.8 (d, *J* = 267.0 Hz, 1F), -104.0 (d, *J* =267.0 Hz, 1F). IR (KBr, *v*, cm^{-1}): 2957, 2924, 2868, 1772, 1653, 1558, 1457, 1264, 747. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_4$ $[M + Na]^+$ 683.2949, found 683.2927.

ethyl 2-(3',5'-di-tert-butyl-7-(3,4-dimethylphenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ea)



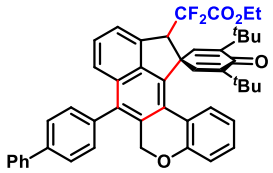
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 77 mg, 57% yield; mp: 109-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.56-7.48 (m, 4H), 7.33-7.27 (m, 1H), 7.21-7.13 (m, 2H), 7.05-6.97 (m, 2H), 6.87-6.85 (m, 1H), 6.80-6.76 (m, 1H), 6.74-6.70 (m, 1H), 5.00-4.96 (m, 1H), 4.85-4.79 (m, 1H), 4.69-4.60 (m, 1H), 4.34-4.25 (m, 1H), 4.22-4.14 (m, 1H), 2.39 (s, 3H), 2.34 (d, *J* = 12.8 Hz, 3H), 1.29 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.9, 162.7 (t, $^{2}J_{CF}$ = 32.0 Hz), 157.1, 149.4, 146.0, 144.2, 139.1, 138.7, 138.5, 137.0, 136.6, 136.1 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.9, 134.7, 134.1, 131.4, 131.1, 130.7, 130.0(4), 130.0(5), 129.5, 129.1, 128.0, 127.7, 127.4, 126.8, 124.7(1), 124.7(7), 123.3, 122.5, 121.6, 117.2, 115.2 (t, $^{1}J_{CF}$ = 252.0 Hz), 69.1, 63.4, 59.1 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.2, 29.4, 28.8, 20.0, 19.8, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.1 (d, *J* = 267.0 Hz, 1F), -101.7 (d, *J* =267.0 Hz, 1F). IR (KBr, *v*, cm^{-1}): 2957, 2921, 2867, 1775, 1655, 1463, 1365, 1262, 1087, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{44}H_{44}F_2O_4$ $[M + Na]^+$ 697.3105, found 697.3105.

ethyl 2-(3',5'-di-tert-butyl-7-(4-(tert-butyl)phenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4fa)



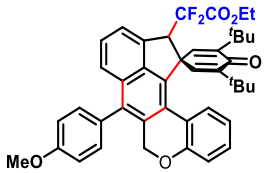
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 79 mg, 56% yield; mp: 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.58-7.54 (m, 3H), 7.52-7.47 (m, 3H), 7.35-7.33 (m, 1H), 7.22-7.17 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.80-6.76 (m, 1H), 6.74-6.72 (m, 1H), 4.97 (d, J = 13.6 Hz, 1H), 4.82 (d, J = 13.6 Hz, 1H), 4.69-4.61 (m, 1H), 4.34-4.26 (m, 1H), 4.22-4.14 (m, 1H), 1.43 (s, 9H), 1.30 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 157.0, 151.1, 149.3, 146.0, 144.0, 139.0, 138.7, 138.5, 136.0 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.8, 134.7, 133.5, 130.6, 129.9, 129.7, 129.5, 129.0, 128.0, 126.7, 125.6(4), 125.6(5), 124.6, 123.2, 122.5, 122.4, 121.6, 117.1, 115.2 (t, $^{1}J_{CF}$ = 252.0 Hz), 69.1, 63.4, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 34.8, 31.5, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 263.2 Hz, 1F), -102.9 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2958, 2923, 2867, 1776, 1655, 1491, 1365, 1263, 1087, 882, 751. HR-MS (ESI-TOF) *m/z* calcd for $C_{46}H_{48}F_2O_4$ $[M + Na]^+$ 725.3418, found 725.3419.

ethyl 2-(7-([1,1'-biphenyl]-4-yl)-3',5'-di-tert-butyl-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ga)



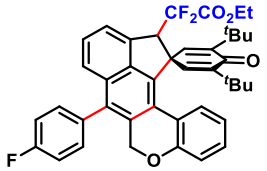
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 92 mg, 62% yield; mp: 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.82-7.75 (m, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.60-7.58 (m, 2H), 7.54-7.49 (m, 5H), 7.44-7.40 (m, 1H), 7.38-7.36 (m, 1H), 7.23-7.19 (m, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 2.8 Hz, 1H), 6.83-6.79 (m, 1H), 6.76-6.74 (m, 1H), 5.04 (d, J = 13.6 Hz, 1H), 4.88 (d, J = 13.6 Hz, 1H), 4.72-4.64 (m, 1H), 4.36-4.28 (m, 1H), 4.24-4.16 (m, 1H), 1.31 (s, 9H), 1.28 (t, J = 7.2 Hz, 3H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.9, 162.7 (t, $^{2}J_{CF}$ = 32.0 Hz), 157.1, 149.4, 146.1, 144.1, 141.1, 140.6, 139.0, 138.9, 138.8, 136.2 (t, $^{5}J_{CF}$ = 3.0 Hz), 135.6, 134.8, 134.4, 130.8, 130.6, 130.5, 129.6, 129.1, 128.2, 127.8, 127.5(4), 127.5(6), 127.3, 126.8, 124.6, 123.2, 122.7, 121.7, 117.2, 115.2 (t, $^{1}J_{CF}$ = 252.0 Hz), 69.1, 63.5, 59.1 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.2, 29.4, 28.8, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 263.2 Hz, 1F), -102.8 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2958, 2924, 2867, 1774, 1654, 1489, 1365, 1228, 1087, 882, 764. HR-MS (ESI-TOF) *m/z* calcd for $C_{48}H_{44}F_2O_4$ $[M + Na]^+$ 745.3105, found 745.3112.

ethyl 2-(3',5'-di-tert-butyl-7-(4-methoxyphenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ha)



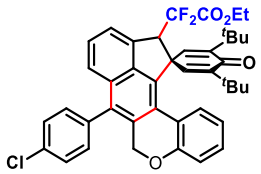
Isolation by column chromatography (PE/EA= 30/1 v/v) White solid, 87 mg, 64% yield; mp: 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.57-7.49 (m, 4H), 7.35-7.32 (m, 1H), 7.21-7.17 (m, 2H), 7.11-7.04 (m, 2H), 7.00-6.98 (m, 1H), 6.86 (d, J = 2.8 Hz, 1H), 6.80-6.76 (m, 1H), 6.73-6.71 (m, 1H), 4.98 (d, J = 13.6 Hz, 1H), 4.83 (d, J = 13.6 Hz, 1H), 4.69-4.61 (m, 1H), 4.34-4.26 (m, 1H), 4.22-4.14 (m, 1H), 3.92 (s, 3H), 1.29 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 159.5, 157.0, 149.3, 146.0, 144.0, 139.0, 138.7, 138.5, 136.1 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.9, 134.4, 131.4, 131.2, 130.7, 129.5, 129.0, 128.7, 128.0, 126.7, 124.5, 123.2, 122.5(8), 122.5(5), 121.6, 117.1, 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 114.2, 69.0, 63.4, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 55.4, 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.1 (d, J = 263.2 Hz, 1F), -102.2 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2958, 2925, 2868, 1774, 1654, 1491, 1365, 1248, 1087, 881, 760. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_5$ $[M + Na]^+$ 699.2898, found 699.2884.

ethyl 2-(3',5'-di-tert-butyl-7-(4-fluorophenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ia)



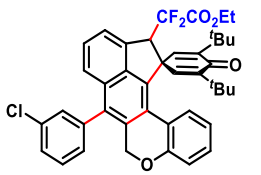
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 85 mg, 64% yield; mp: 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.56 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 5.2 Hz, 2H), 7.47-7.44 (m, 1H), 7.41-7.37 (m, 1H), 7.31-7.27 (m, 1H), 7.25-7.18 (m, 3H), 6.99 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 2.8 Hz, 1H), 6.81-6.77 (m, 1H), 6.72-6.70 (m, 1H), 4.93 (d, J = 13.6 Hz, 1H), 4.80 (d, J = 13.6 Hz, 1H), 4.69-4.61 (m, 1H), 4.34-4.26 (m, 1H), 4.22-4.16 (m, 1H), 1.29 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.7 (d, $^{2}J_{CF}$ = 246.0 Hz), 162.6 (t, $^{3}J_{CF}$ = 32.0 Hz), 156.9, 149.4, 146.1, 143.8, 139.0, 138.8, 138.6, 136.2 (t, $^{8}J_{CF}$ = 3.0 Hz), 134.7, 133.5, 132.5 (d, $^{9}J_{CF}$ = 3.0 Hz), 131.9 (d, $^{2}J_{CF}$ = 8.0 Hz), 131.7 (d, $^{2}J_{CF}$ = 8.0 Hz), 130.5, 129.6, 129.0, 128.2, 126.7, 124.2, 123.0, 122.7, 121.7, 117.1, 115.9 (d, $^{4}J_{CF}$ = 21.0 Hz), 115.8 (d, $^{5}J_{CF}$ = 21.0 Hz), 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 68.8, 63.4, 59.0 (t, $^{6}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{7}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.1 (d, J = 278.2 Hz, 1F), -108.3 (d, J =278.2 Hz, 1F), -113.6 (s, 1F). IR (KBr, v, cm^{-1}): 2957, 2922, 2851, 1775, 1655, 1491, 1365, 1225, 1087, 882, 761. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}F_3O_4$ $[M + Na]^+$ 687.2698, found 687.2697.

ethyl 2-(3',5'-di-tert-butyl-7-(4-chlorophenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ja)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 98 mg, 72% yield; mp: 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.57-7.51 (m, 5H), 7.46-7.44 (m, 1H), 7.37-7.35 (m, 1H), 7.25-7.18 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 2.8 Hz, 1H), 6.81-6.77 (m, 1H), 6.71-6.69 (m, 1H), 4.93 (d, J = 13.6 Hz, 1H), 4.80 (d, J = 13.6 Hz, 1H), 4.69-4.61 (m, 1H), 4.34-4.26 (m, 1H), 4.22-4.14 (m, 1H), 1.29 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 156.9, 149.4, 146.1, 143.8, 139.2, 138.7, 138.6, 136.2 (t, $^{5}J_{CF}$ = 3.0 Hz), 135.1, 134.8, 134.3, 133.3, 131.6, 131.4, 130.3, 129.7, 129.1(4), 129.1(5), 129.0, 128.3, 126.7, 124.1, 123.0, 122.7(4), 122.7(0), 121.7, 117.1, 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 68.8, 63.4, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.1 (d, J = 263.2 Hz, 1F), -101.9 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2957, 2923, 2867, 1776, 1653, 1489, 1365, 1228, 1088, 882, 763. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}ClF_2O_4$ $[M + Na]^+$ 703.2403, found 703.2404.

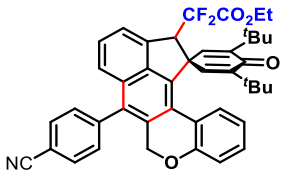
ethyl 2-(3',5'-di-tert-butyl-7-(3-chlorophenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ka)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 86 mg, 63% yield; mp: 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.56 (d, J = 8.0 Hz, 1H), 7.54-7.49 (m, 3H), 7.47-7.43 (m, 2H), 7.33-7.31 (m, 1H), 7.22-7.18 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 2.8 Hz, 1H), 6.81-6.77 (m, 1H), 6.72-6.70 (m, 1H), 4.94 (d, J = 13.6 Hz, 1H),

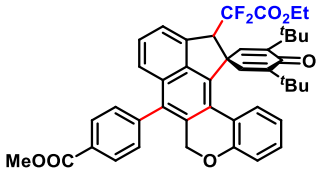
4.84-4.78 (m, 1H), 4.70-4.62 (m, 1H), 4.35-4.26 (m, 1H), 4.23-4.15 (m, 1H), 1.30 (s, 9H), 1.27 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H). ^{3}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 156.9, 149.4, 146.1, 143.8, 139.3, 138.7, 138.6, 138.5, 136.2 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.8(4), 134.8(7), 134.7, 133.1, 130.3, 130.2, 130.1, 129.7, 129.0, 128.5, 128.4(2), 128.4(9), 128.3, 128.2, 126.7, 124.1, 122.9, 122.8, 121.7(2), 121.7(0), 117.1, 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 68.8, 63.4, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 263.2 Hz, 1F), -101.1 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2957, 2923, 2868, 1775, 1655, 1488, 1365, 1229, 1087, 881, 764. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}ClF_2O_4$ $[M + Na]^+$ 703.2403, found 703.2415.

ethyl 2-(3',5'-di-tert-butyl-7-(4-cyanophenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4la)



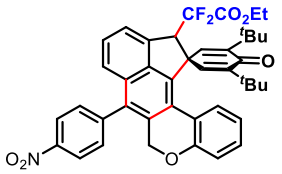
Isolation by column chromatography (PE/EA= 20/1 v/v) White solid, 67 mg, 50% yield; mp: 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.90-7.84 (m, 2H), 7.59-7.51 (m, 4H), 7.45-7.43 (m, 1H), 7.37-7.34 (m, 1H), 7.23-7.19 (m, 1H), 7.01-6.99 (m, 1H), 6.84 (d, J = 2.8 Hz, 1H), 6.82-6.78 (m, 1H), 6.69-6.67 (m, 1H), 4.87 (d, J = 13.6 Hz, 1H), 4.77 (d, J = 13.6 Hz, 1H), 4.70-4.62 (m, 1H), 4.35-4.27 (m, 1H), 4.23-4.15 (m, 1H), 1.29 (s, 9H), 1.27 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 156.8, 149.7, 146.3, 143.7, 141.9, 139.9, 138.7, 138.5, 136.5 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.7, 132.7(3), 132.7(8), 132.5, 131.2, 131.0, 129.9, 129.7, 129.1, 128.7, 126.8, 123.7, 123.1, 122.8, 121.9, 118.6, 117.3, 115.1 (t, $^{1}J_{CF}$ = 253.0 Hz), 112.4, 68.7, 63.5, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.2, 29.3, 28.8, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 267.0 Hz, 1F), -101.3 (d, J =267.0 Hz, 1F). IR (KBr, v, cm^{-1}): 2959, 2925, 2868, 2230, 1774, 1655, 1522, 1490, 1348, 1228, 1088, 1051, 856, 764. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{39}F_2NO_4$ $[M + Na]^+$ 694.2745, found 694.2754.

methyl 4-(3',5'-di-tert-butyl-11-(2-ethoxy-1,1-difluoro-2-oxoethyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-7-yl)benzoate (4ma)



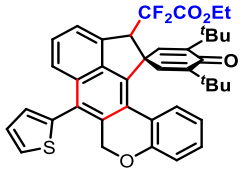
Isolation by column chromatography (PE/EA= 20/1 v/v) White solid, 75 mg, 53% yield; mp: 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.26-8.20 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.52-7.49 (m, 3H), 7.42-7.38 (m, 2H), 7.22-7.18 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 6.81-6.77 (m, 1H), 6.72-6.70 (m, 1H), 4.91 (d, J = 13.6 Hz, 1H), 4.80 (d, J = 13.6 Hz, 1H), 4.70-4.62 (m, 1H), 4.33-4.26 (m, 1H), 4.23-4.15 (m, 1H), 4.00 (s, 3H), 1.30 (s, 9H), 1.27 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.7, 166.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 156.9, 149.5, 146.1, 143.8, 141.6, 139.4, 138.7, 138.6, 136.3 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.6, 133.5, 130.4, 130.2, 130.1, 130.0(3), 130.0(9), 129.7, 129.0, 128.4, 126.7, 124.0, 122.9, 122.8(0), 122.8(6), 121.7, 117.1, 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 68.7, 63.4, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 52.4, 35.3, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 267.0 Hz, 1F), -101.4 (d, J =267.0 Hz, 1F). IR (KBr, v, cm^{-1}): 2956, 2922, 2852, 1775, 1727, 1655, 1464, 1365, 1274, 1087, 882, 764. HR-MS (ESI-TOF) *m/z* calcd for $C_{44}H_{42}ClF_2O_6$ $[M + Na]^+$ 727.2847, found 727.2845.

ethyl 2-(3',5'-di-tert-butyl-7-(4-nitrophenyl)-4'-oxo-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4na)



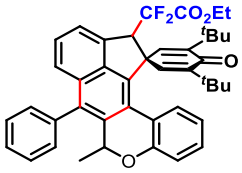
Isolation by column chromatography (PE/EA= 30/1 v/v) White solid, 94 mg, 68% yield; mp: 211-213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.47-8.41 (m, 2H), 7.66-7.63 (m, 1H), 7.59-7.54 (m, 3H), 7.52-7.50 (m, 1H), 7.38-7.35 (m, 1H), 7.24-7.20 (m, 1H), 7.01-6.99 (m, 1H), 6.85 (d, J = 2.8 Hz, 1H), 6.83-6.78 (m, 1H), 6.70-6.68 (m, 1H), 4.88 (d, J = 13.6 Hz, 1H), 4.79 (d, J = 13.6 Hz, 1H), 4.71-4.63 (m, 1H), 4.36-4.28 (m, 1H), 4.23-4.15 (m, 1H), 1.30 (s, 9H), 1.28 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 156.8, 149.5, 147.9, 146.3, 143.9, 143.6, 140.1, 138.7, 138.5, 136.5 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.8, 132.2, 131.5, 131.3, 129.9, 129.7, 129.1, 128.8, 126.8, 124.2, 124.1, 123.7, 123.2, 123.1, 122.8, 121.9, 117.3, 115.1 (t, $^{1}J_{CF}$ = 252.0 Hz), 68.6, 63.6, 59.0 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.2, 29.3, 28.8, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 263.2 Hz, 1F), -102.8 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2957, 2924, 2868, 1773, 1654, 1522, 1490, 1348, 1228, 1088, 856, 764. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}F_2NO_6$ $[M + Na]^+$ 714.2643, found 714.2675.

ethyl 2-(3',5'-di-tert-butyl-4'-oxo-7-(thiophen-2-yl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4oa)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 63 mg, 48% yield; mp: 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.70 (d, J = 8.0 Hz, 1H), 7.57-7.51 (m, 4H), 7.26-7.24 (m, 1H), 7.22-7.18 (m, 1H), 7.10 (d, J = 3.6 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 2.8 Hz, 1H), 6.80-6.76 (m, 1H), 6.71-6.69 (m, 1H), 5.09 (d, J = 13.6 Hz, 1H), 4.89 (d, J = 13.6 Hz, 1H), 4.68-4.60 (m, 1H), 4.33-4.25 (m, 1H), 4.22-4.14 (m, 1H), 1.29 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.8, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 157.0, 149.5, 146.2, 143.8, 139.9, 138.8, 138.6, 137.1, 136.5, 136.1 (t, $^{5}J_{CF}$ = 3.0 Hz), 131.4, 129.7, 129.0, 128.5, 127.6, 127.3, 127.0, 126.8, 124.4, 123.0, 122.9, 121.7, 117.2, 115.1 (t, $^{1}J_{CF}$ = 253.0 Hz), 69.0, 63.5, 59.1 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.2, 29.3, 28.8, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.2 (d, J = 263.2 Hz, 1F), -102.4 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2957, 2923, 2868, 1774, 1654, 1490, 1364, 1260, 1086, 881, 768. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{38}F_2O_4S$ $[M + Na]^+$ 675.2357, found 675.2363.

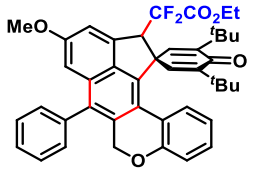
ethyl 2-(3',5'-di-tert-butyl-6-methyl-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4qa)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 74 mg, 56% yield; mp: 259-261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.59-7.48 (m, 5H), 7.47-7.43 (m, 1H), 7.37 (d, J = 6.8 Hz, 2H), 7.28 (s, 1H), 7.20-7.16 (m, 1H), 7.01 (d, J = 2.8 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.77-6.73 (m, 1H), 6.62-6.60 (m, 1H), 5.36 (q, J = 6.8 Hz, 1H), 4.66-4.58 (m, 1H), 4.35-4.27 (m, 1H), 4.14-4.06 (m, 1H), 1.38 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 187.0, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 153.7, 150.1, 145.1, 139.2, 138.7, 138.4, 138.3, 137.1, 135.8 (t, $^{4}J_{CF}$ = 3.0 Hz), 134.3, 131.0, 130.5, 129.7, 129.1, 128.6, 128.0(4), 128.0(6), 125.5, 124.7, 122.9,

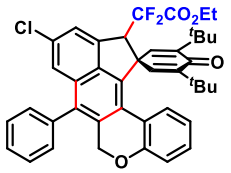
122.8, 121.4, 118.7, 114.9 (t, $^{1}J_{CF}$ = 254.0 Hz), 73.3, 63.4, 59.3 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.6 (d, $^{5}J_{CF}$ = 5.0 Hz), 35.3(0), 35.3(9), 29.5, 28.7, 19.6, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.4 (d, *J* = 263.2 Hz, 1F), -103.2 (d, *J* =263.2 Hz, 1F). IR (KBr, *v*, cm^{-1}): 2958, 2926, 2868, 1776, 1655, 1490, 1365, 1225, 1085, 881, 763. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_4$ $[M + Na]^+$ 683.2949, found 683.2944.

ethyl 2-(3',5'-di-tert-butyl-9-methoxy-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ra)



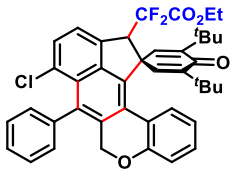
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 74 mg, 55% yield; mp: 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.59-7.49 (m, 4H), 7.42-7.40 (m, 1H), 7.30-7.27 (m, 1H), 7.18-7.14 (m, 2H), 6.98-6.95 (m, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.78-6.74 (m, 2H), 6.71-6.69 (m, 1H), 4.90 (d, *J* = 13.6 Hz, 1H), 4.78 (d, *J* = 13.6 Hz, 1H), 4.64-4.56 (m, 1H), 4.33-4.26 (m, 1H), 4.23-4.15 (m, 1H), 3.77 (s, 3H), 1.29 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.8, 162.5 (t, $^{2}J_{CF}$ = 32.0 Hz), 160.2, 156.6, 149.2, 146.1, 143.9, 138.9, 138.5, 138.0 (t, $^{5}J_{CF}$ = 3.0 Hz), 136.9, 135.2, 134.2, 133.6, 131.2, 130.2, 129.9, 129.1, 128.9, 128.8, 128.7, 128.1, 124.5, 123.3, 121.6, 117.0, 115.0 (t, $^{1}J_{CF}$ = 253.0 Hz), 103.5, 69.0, 63.4, 58.5 (t, $^{3}J_{CF}$ = 21.0 Hz), 55.7, 54.9 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.8, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, *J* = 263.2 Hz, 1F), -102.3 (d, *J* =263.2 Hz, 1F). IR (KBr, *v*, cm^{-1}): 2957, 2922, 2852, 1774, 1654, 1420, 1365, 1225, 1153, 1091, 883, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_5$ $[M + Na]^+$ 699.2898, found 699.2879.

ethyl 2-(3',5'-di-tert-butyl-9-chloro-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4sa)



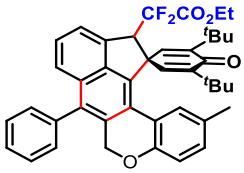
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 66 mg, 49% yield; mp: 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.61-7.50 (m, 5H), 7.46 (d, *J* = 9.2 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.22-7.18 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 2.8 Hz, 1H), 6.80-6.76 (m, 1H), 6.67-6.66 (m, 1H), 4.92 (d, *J* = 13.6 Hz, 1H), 4.79 (d, *J* = 13.6 Hz, 1H), 4.66-4.58 (m, 1H), 4.32-4.26 (m, 1H), 4.23-4.17 (m, 1H), 1.29 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 162.3(t, $^{2}J_{CF}$ = 32.0 Hz), 156.9, 149.6, 146.3, 143.4, 138.6, 138.3, 138.1 (t, $^{5}J_{CF}$ = 3.0 Hz), 137.0, 136.0, 135.7, 134.2, 134.0, 130.7, 130.1, 129.9, 129.8, 129.0(3), 129.0(6), 128.9, 128.5, 127.1, 123.7(1), 123.7(7), 123.5, 122.8, 121.7, 117.2, 114.9 (t, $^{1}J_{CF}$ = 253.0 Hz), 68.8, 63.6, 58.6 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.7 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.1, 29.3, 28.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -99.6 (d, *J* = 263.2 Hz, 1F), -101.6 (d, *J* =263.2 Hz, 1F). IR (KBr, *v*, cm^{-1}): 2958, 2923, 2852, 1776, 1654, 1489, 1365, 1265, 1091, 881, 768. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}ClF_2O_4$ $[M + Na]^+$ 703.2403, found 703.2416.

ethyl 2-(3',5'-di-tert-butyl-8-chloro-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ta)



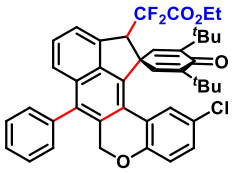
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 79 mg, 58% yield; mp: 108-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.55-7.50 (m, 2H), 7.47-7.44 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.35-7.27 (m, 2H), 7.22-7.18 (m, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 2.8 Hz, 1H), 6.79-6.76 (m, 1H), 6.71-6.69 (m, 1H), 4.81 (d, J = 14.0 Hz, 1H), 4.67 (d, J = 14.0 Hz, 1H), 4.57-4.50 (m, 1H), 4.32-4.24 (m, 1H), 4.22-4.14 (m, 1H), 1.30 (s, 9H), 1.26 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.6, 162.4 (t, $^{2}J_{CF}$ = 32.0 Hz), 157.0, 149.6, 146.3, 143.7, 140.3, 139.3, 138.5(9), 138.5(7), 138.3, 137.7, 135.3 (t, $^{5}J_{CF}$ = 3.0 Hz), 133.7, 130.7, 130.3, 130.2, 129.9(4), 129.9(1), 129.0, 128.3, 128.0(4), 128.0(7), 127.3, 126.7, 122.8(1), 122.8(7), 122.6, 121.6, 117.1, 114.8 (t, $^{1}J_{CF}$ = 253.0 Hz), 69.0, 63.4, 58.3 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.5 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.3, 35.1, 29.3, 28.7, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -99.5 (d, J = 263.2 Hz, 1F), -101.6 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2959, 2926, 2869, 1776, 1655, 1490, 1366, 1227, 1051, 881, 765. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}ClF_2O_4$ [M + Na]$^{+}$ 703.2403, found 703.2427.

ethyl 2-(3',5'-di-tert-butyl-2-methyl-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4ua)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 74 mg, 56% yield; mp: 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.58-7.54 (m, 1H), 7.52-7.44 (m, 5H), 7.40 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.24 (s, 1H), 7.00-6.98 (m, 1H), 6.92-6.89 (m, 2H), 6.83-6.81 (m, 1H), 4.90 (d, J = 13.6 Hz, 1H), 4.75 (d, J = 13.6 Hz, 1H), 4.65-4.57 (m, 1H), 4.35-4.27 (m, 1H), 4.23-4.15 (m, 1H), 2.15 (s, 3H), 1.32 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.1, 162.8 (t, $^{2}J_{CF}$ = 32.0 Hz), 155.1, 149.1, 145.7, 144.8, 139.8, 138.7, 138.4, 136.7, 135.8 (t, $^{4}J_{CF}$ = 3.0 Hz), 135.2, 134.6, 130.9, 130.7, 130.4, 130.3, 130.1, 129.0, 128.8(4), 128.8(0), 128.2, 128.0, 127.1, 124.5, 123.2, 122.5, 117.0, 115.2 (t, $^{1}J_{CF}$ = 254.0 Hz), 69.2, 63.4, 59.8 (t, $^{3}J_{CF}$ = 21.0 Hz), 55.2, 35.4, 35.3, 29.6, 29.0, 21.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -101.9 (d, J = 263.2 Hz, 1F), -105.1 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2958, 2924, 2868, 1774, 1654, 1496, 1365, 1233, 1087, 881, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{43}H_{42}F_2O_4$ [M + Na]$^{+}$ 683.2949, found 683.2939.

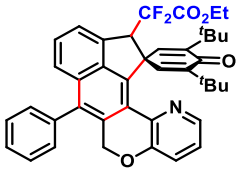
ethyl 2-(3',5'-di-tert-butyl-2-chloro-4'-oxo-7-phenyl-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-11-yl)-2,2-difluoroacetate (4va)



Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 69 mg, 51% yield; mp: 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.59-7.55 (m, 1H), 7.53-7.49 (m, 4H), 7.48-7.46 (m, 2H), 7.40 (d, J = 7.2 Hz, 1H), 7.28-7.27 (m, 1H), 7.16-7.13 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.76-6.74 (m, 1H), 4.94 (d, J = 13.6 Hz, 1H), 4.77 (d, J = 13.6 Hz, 1H), 4.64-4.56 (m, 1H), 4.35-4.27 (m, 1H), 4.22-4.14 (m, 1H), 1.34 (s, 9H), 1.24 (t, J = 7.2 Hz, 3H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.9, 162.6 (t, $^{2}J_{CF}$ = 32.0 Hz), 155.6, 150.1, 146.6, 143.6, 139.4, 138.6, 136.4, 136.0 (t, $^{5}J_{CF}$ = 3.0 Hz), 134.8, 134.4, 130.6, 130.2, 129.9, 129.5, 128.8(4), 128.8(9), 128.4, 128.3(0), 128.3(5), 126.7, 125.6, 124.7, 124.5, 122.6, 118.6, 115.1 (t, $^{1}J_{CF}$ = 253.0 Hz), 69.1, 63.4, 59.9 (t, $^{3}J_{CF}$ = 21.0 Hz), 54.9 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.4, 35.2, 29.6, 29.1, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -100.0 (d, J = 263.2 Hz, 1F), -102.8 (d, J =263.2 Hz, 1F). IR (KBr, v, cm^{-1}): 2959, 2924, 2868, 1774, 1654, 1487, 1366, 1260, 1087, 882, 765. HR-MS (ESI-TOF) *m/z* calcd for $C_{42}H_{39}ClF_2O_4$ [M + Na]$^{+}$ 703.2403, found 703.2415.

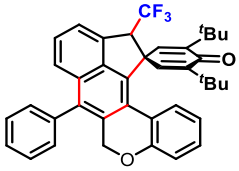
ethyl 2-(3,5-di-tert-butyl-4-oxo-7'-phenyl-6'H,11'H-spiro[cyclohexane-1,12'-indeno[1',7':5,6,7]isochromeno[4,3-

b]pyridine]-2,5-dien-11'-yl)-2,2-difluoroacetate (4wa)



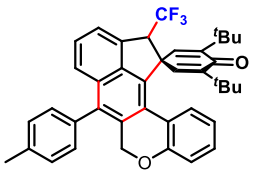
Isolation by column chromatography (PE/EA= 50/1 v/v) White solid, 89 mg, 69% yield; mp: 215-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.99 (d, J = 4.4 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.59-7.49 (m, 4H), 7.44 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.02-6.99 (m, 1H), 6.72 (d, J = 2.8 Hz, 1H), 6.65-6.63 (m, 1H), 5.03 (d, J = 13.6 Hz, 1H), 4.98 (d, J = 13.6 Hz, 1H), 4.82-4.74 (m, 1H), 4.39-4.30 (m, 1H), 4.23-4.15 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.27 (s, 9H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 187.6, 162.7 (t, $^{2}J_{CF}$ = 32.0 Hz), 152.3, 147.7, 144.4, 143.9, 142.7, 142.6, 140.8, 138.9, 138.3, 137.8 (t, $^{5}J_{CF}$ = 3.0 Hz), 136.7, 134.6, 133.0, 131.4, 130.1, 130.0, 128.9(4), 128.9(6), 128.8, 128.3, 126.4, 124.3, 123.8, 123.4, 122.7, 122.6, 115.7 (t, $^{1}J_{CF}$ = 251.0 Hz), 68.3, 63.2, 58.2 (t, $^{3}J_{CF}$ = 21.0 Hz), 55.4 (d, $^{4}J_{CF}$ = 5.0 Hz), 35.2, 34.8, 29.5, 29.0, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -96.6 (d, J = 267.0 Hz, 1F), -97.9 (d, J =267.0 Hz, 1F). IR (KBr, v, cm^{-1}): 2957, 2924, 2870, 1774, 1636, 1466, 1364, 1267, 1088, 882, 768. HR-MS (ESI-TOF) *m/z* calcd for $C_{41}H_{39}F_2NO_4$ $[M + Na]^+$ 670.2745, found 670.2758.

3',5'-di-tert-butyl-7-phenyl-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4ab)



Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 72 mg, 61% yield; mp: 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.67-7.65 (m, 1H), 7.57-7.50 (m, 6H), 7.36-7.33 (m, 2H), 7.23-7.19 (m, 1H), 6.99-6.97 (m, 1H), 6.82-6.76 (m, 3H), 4.92 (d, J = 13.6 Hz, 1H), 4.87 (d, J = 13.6 Hz, 1H), 4.48 (q, J = 9.6 Hz, 1H), 1.23 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.3, 157.0, 148.7, 147.8, 142.1, 139.1, 138.2, 138.1, 136.6, 135.0(3), 135.0(6), 134.4, 130.6, 130.2, 130.0, 129.9, 129.2, 128.9, 128.8, 128.3, 127.0, 125.7 (q, $^{1}J_{CF}$ = 279.0 Hz), 124.7, 122.7, 121.6, 121.4, 117.1, 68.8, 59.6 (q, $^{2}J_{CF}$ = 26.0 Hz), 54.7, 35.4, 35.1, 29.2, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.75. IR (KBr, v, cm^{-1}): 2958, 2924, 2867, 1655, 1490, 1365, 1263, 1098, 883, 760. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{35}F_3O_2$ $[M + Na]^+$ 615.2487, found 615.2466.

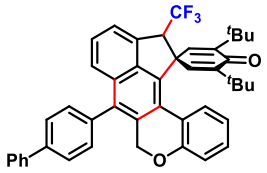
3',5'-di-tert-butyl-7-(p-tolyl)-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4bb)



Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 69 mg, 57% yield; mp: 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.66 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 6.8 Hz, 1H), 7.53-7.48 (m, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.25-7.19 (m, 3H), 6.98 (d, J = 8.0 Hz, 1H), 6.92-6.76 (m, 3H), 4.94 (d, J = 13.6 Hz, 1H), 4.88 (d, J = 13.6 Hz, 1H), 4.48 (q, J = 9.6 Hz, 1H), 2.50 (s, 3H), 1.23 (s, 9H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.2, 157.0, 148.7, 147.7, 142.1, 139.1, 138.0(3), 138.0(6), 135.1, 134.9, 134.4, 133.5, 130.8, 130.1, 129.9, 129.8, 129.5(3), 129.5(8), 129.2, 128.2, 127.0, 125.7 (q, $^{1}J_{CF}$ = 279.0 Hz), 124.7, 122.8, 121.5, 121.4, 117.0, 68.8, 59.6 (q, $^{2}J_{CF}$ = 26.0 Hz), 54.6,

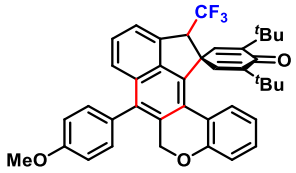
35.4, 35.0, 29.1, 28.9, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.75. IR (KBr, *v*, cm^{-1}): 2958, 2925, 2867, 1655, 1491, 1365, 1248, 1098, 882, 743. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{37}F_3O_2$ $[M + Na]^+$ 629.2643, found 629.2652.

7-([1,1'-biphenyl]-4-yl)-3',5'-di-tert-butyl-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4gb)



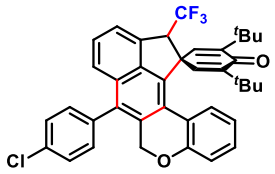
Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 61 mg, 46% yield; mp: 75-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.81-7.77 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.61-7.58 (m, 2H), 7.56-7.50 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 3H), 7.24-7.20 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.83-6.77 (m, 3H), 5.00 (d, *J* = 13.6 Hz, 1H), 4.93 (d, *J* = 13.6 Hz, 1H), 4.50 (q, *J* = 9.6 Hz, 1H), 1.24 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.2, 157.0, 148.7, 147.8, 142.0, 141.1, 140.6, 139.0, 138.2, 138.1, 135.5, 135.0, 134.7, 134.5, 130.7, 130.6, 130.5, 129.9, 129.2, 129.0, 128.3, 127.7, 127.5(2), 127.5(7), 127.2, 127.0, 125.7 (q, $^1J_{CF}$ = 279.0 Hz), 124.5, 122.7, 121.6, 121.4, 117.1, 68.8, 59.6 (q, $^2J_{CF}$ = 26.0 Hz), 54.7, 35.4, 35.1, 29.1, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.74. IR (KBr, *v*, cm^{-1}): 2958, 2925, 2867, 1659, 1490, 1365, 1264, 1097, 835, 761. HR-MS (ESI-TOF) *m/z* calcd for $C_{45}H_{39}F_3O_2$ $[M + Na]^+$ 691.2800, found 691.2805.

3',5'-di-tert-butyl-7-(4-methoxyphenyl)-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4hb)



Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 87 mg, 70% yield; mp: 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.65 (d, *J* = 7.6 Hz, 1H), 7.57-7.49 (m, 3H), 7.29-7.27 (m, 1H), 7.25-7.19 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.82-6.75 (m, 3H), 4.95 (d, *J* = 13.2 Hz, 1H), 4.89 (d, *J* = 13.2 Hz, 1H), 4.48 (q, *J* = 9.6 Hz, 1H), 3.93 (s, 3H), 1.23 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.3, 159.6, 157.0, 148.7, 147.8, 142.1, 139.1, 138.1, 138.0, 135.0, 134.8, 134.7, 131.4, 131.2, 131.0, 129.8, 129.2, 128.6, 128.2, 127.0, 125.7 (q, $^1J_{CF}$ = 279.0 Hz), 124.7, 122.8, 121.6, 121.4, 117.1, 114.3, 114.2, 68.8, 59.6 (q, $^2J_{CF}$ = 26.0 Hz), 55.5, 54.7, 35.4, 35.1, 29.2, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.76. IR (KBr, *v*, cm^{-1}): 2957, 2924, 2854, 1654, 1489, 1364, 1263, 1098, 882, 764. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{37}F_3O_3$ $[M + Na]^+$ 645.2592, found 645.2579.

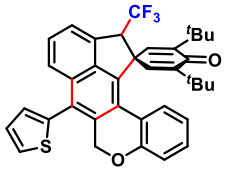
3',5'-di-tert-butyl-7-(4-chlorophenyl)-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4jb)



Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 81 mg, 65% yield; mp: 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.66 (d, *J* = 8.0 Hz, 1H), 7.59-7.51 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24-7.20 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.83-6.75 (m, 3H), 4.91 (d, *J* = 13.6 Hz, 1H), 4.86 (d, *J* = 13.6 Hz, 1H), 4.49 (q, *J* = 9.6 Hz, 1H), 1.23 (s, 9H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.2, 156.9, 148.8, 147.8, 141.9, 138.9, 138.6, 138.1, 135.1, 135.0, 134.5(3), 134.5(6), 133.6, 131.6, 131.4, 130.4, 130.0, 129.2(0), 129.2(5), 128.5,

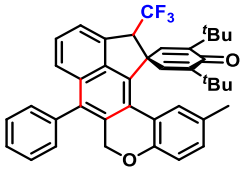
127.0, 125.6 (q, $^{1}J_{CF}$ = 279.0 Hz), 124.3, 122.6, 121.8, 121.5, 117.1, 68.6, 59.6 (q, $^{2}J_{CF}$ = 26.0 Hz), 54.67, 35.4, 35.1, 29.1, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.76. IR (KBr, *v*, cm^{-1}): 2957, 2925, 2867, 1658, 1464, 1365, 1262, 1147, 1098, 882, 757. HR-MS (ESI-TOF) *m/z* calcd for $C_{39}H_{34}ClF_3O_2$ $[M + Na]^+$ 649.2097, found 649.2116.

3',5'-di-tert-butyl-7-(thiophen-2-yl)-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4ob)



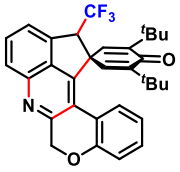
Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 50 mg, 42% yield; mp: 79-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.72-7.70 (m, 1H), 7.65-7.63 (m, 1H), 7.60-7.54 (m, 3H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.24-7.20 (m, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.82-6.76 (m, 2H), 6.73 (d, *J* = 2.8 Hz, 1H), 5.04 (d, *J* = 13.6 Hz, 1H), 4.97 (d, *J* = 13.6 Hz, 1H), 4.47 (q, *J* = 9.6 Hz, 1H), 1.22 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 186.2, 156.9, 148.9, 147.9, 141.8, 139.3, 138.8, 138.0, 136.8, 136.4, 134.9, 131.6, 130.0, 129.2, 129.0, 128.7, 127.6, 127.3(1), 127.3(8), 127.0, 125.6 (q, $^{1}J_{CF}$ = 279.0 Hz), 124.5, 122.5, 121.9, 121.5, 117.1, 68.8, 59.6 (q, $^{2}J_{CF}$ = 26.0 Hz), 54.7, 35.4, 35.1, 29.1, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.80. IR (KBr, *v*, cm^{-1}): 2956, 2923, 2852, 1654, 1457, 1363, 1265, 1097, 881, 750. HR-MS (ESI-TOF) *m/z* calcd for $C_{37}H_{33}F_3O_2S$ $[M + Na]^+$ 621.2051, found 621.2048.

3',5'-di-tert-butyl-2-methyl-7-phenyl-11-(trifluoromethyl)-6H,11H-spiro[acenaphtho[4,3-c]chromene-12,1'-cyclohexane]-2',5'-dien-4'-one (4ub)



Isolation by column chromatography (PE/EA= 100/1 v/v) Pale yellow solid, 80 mg, 66% yield; mp: 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 7.58-7.52 (m, 4H), 7.51-7.49 (m, 2H), 7.37-7.31 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.91-6.86 (m, 2H), 6.80 (d, *J* = 2.8 Hz, 1H), 4.89 (d, *J* = 13.6 Hz, 1H), 4.80 (d, *J* = 13.6 Hz, 1H), 4.47 (q, *J* = 9.6 Hz, 1H), 2.16 (s, 3H), 1.27 (s, 9H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 185.7, 155.0, 148.3, 147.7, 142.6, 139.9, 138.0, 137.8, 136.6, 135.0, 134.9, 134.7, 130.8(0), 130.8(5), 130.5, 130.3, 130.0, 129.0, 128.9, 128.8, 128.3, 128.2, 127.3, 125.7 (q, $^{1}J_{CF}$ = 279.0 Hz), 124.6, 122.7, 121.4, 116.9, 68.9, 60.0 (q, $^{2}J_{CF}$ = 26.0 Hz), 55.2, 35.5, 35.1, 29.4, 29.2, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.52. IR (KBr, *v*, cm^{-1}): 2955, 2923, 2866, 1661, 1458, 1366, 1266, 1161, 1097, 883, 763. HR-MS (ESI-TOF) *m/z* calcd for $C_{40}H_{37}F_3O_2$ $[M + Na]^+$ 629.2643, found 629.2666.

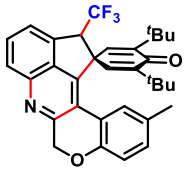
3',5'-di-tert-butyl-11-(trifluoromethyl)-6H,11H-spiro[chromeno[3,4-b]cyclopenta[de]quinoline-12,1'-cyclohexane]-2',5'-dien-4'-one (5ab)



Isolation by column chromatography (PE/EA= 10/1 v/v) White solid, 73 mg, 71% yield; mp: 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 8.03 (d, *J* = 8.4 Hz, 1H), 7.85-7.81 (m, 1H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.55-7.53 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.84-6.80 (m, 1H), 6.68 (d, *J* = 2.8 Hz, 1H), 6.66-6.62 (m, 1H), 5.33 (d, *J* = 14.0 Hz, 1H), 5.28 (d, *J* = 14.0 Hz, 1H), 4.50 (q, *J* = 9.6 Hz, 1H), 1.23 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 185.8, 158.6, 156.4, 149.9, 148.7, 147.3, 145.1, 139.7, 136.5, 135.6(2), 135.6(0), 133.2, 131.9, 131.0, 130.6,

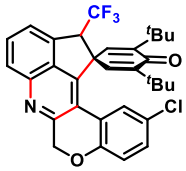
129.5, 126.5, 125.3 (q, $^{1}J_{CF}$ = 279.0 Hz), 122.6, 122.3, 121.8, 120.5, 117.7, 72.1, 59.4 (q, $^{2}J_{CF}$ = 26.0 Hz), 55.2, 35.5, 35.2, 29.1, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.87. IR (KBr, *v*, cm^{-1}): 2956, 2923, 2864, 1654, 1458, 1365, 1265, 1096, 883, 763. HR-MS (ESI-TOF) *m/z* calcd for $C_{32}H_{30}F_3NO_2$ [M + Na]$^+$ 540.2126, found 540.2131.

3',5'-di-tert-butyl-2-methyl-11-(trifluoromethyl)-6H,11H-spiro[chromeno[3,4-b]cyclopenta[de]quinoline-12,1'-cyclohexane]-2',5'-dien-4'-one (5bb)



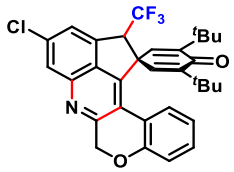
Isolation by column chromatography (PE/EA= 10/1 v/v) White solid, 66 mg, 62% yield; mp: 222-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 8.01 (d, *J* = 8.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.24 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.73-6.70 (m, 2H), 5.30 (d, *J* = 14.0 Hz, 1H), 5.21 (d, *J* = 14.0 Hz, 1H), 4.48 (q, *J* = 9.6 Hz, 1H), 2.14 (s, 3H), 1.24 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 185.3, 159.2, 154.6, 149.5, 148.6, 147.0, 145.0, 140.3, 137.4, 135.4, 133.3, 131.9, 131.7, 131.4, 129.2, 126.5, 125.4 (q, $^{1}J_{CF}$ = 279.0 Hz), 123.0, 122.2, 120.6, 117.6, 72.3, 59.9 (q, $^{2}J_{CF}$ = 26.0 Hz), 55.7, 35.7, 35.3, 29.4, 29.1, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.66. IR (KBr, *v*, cm^{-1}): 2957, 2924, 2854, 1654, 1458, 1364, 1266, 1099, 881, 749. HR-MS (ESI-TOF) *m/z* calcd for $C_{33}H_{32}F_3NO_2$ [M + Na]$^+$ 554.2283, found 554.2291.

3',5'-di-tert-butyl-2-chloro-11-(trifluoromethyl)-6H,11H-spiro[chromeno[3,4-b]cyclopenta[de]quinoline-12,1'-cyclohexane]-2',5'-dien-4'-one (5cb)



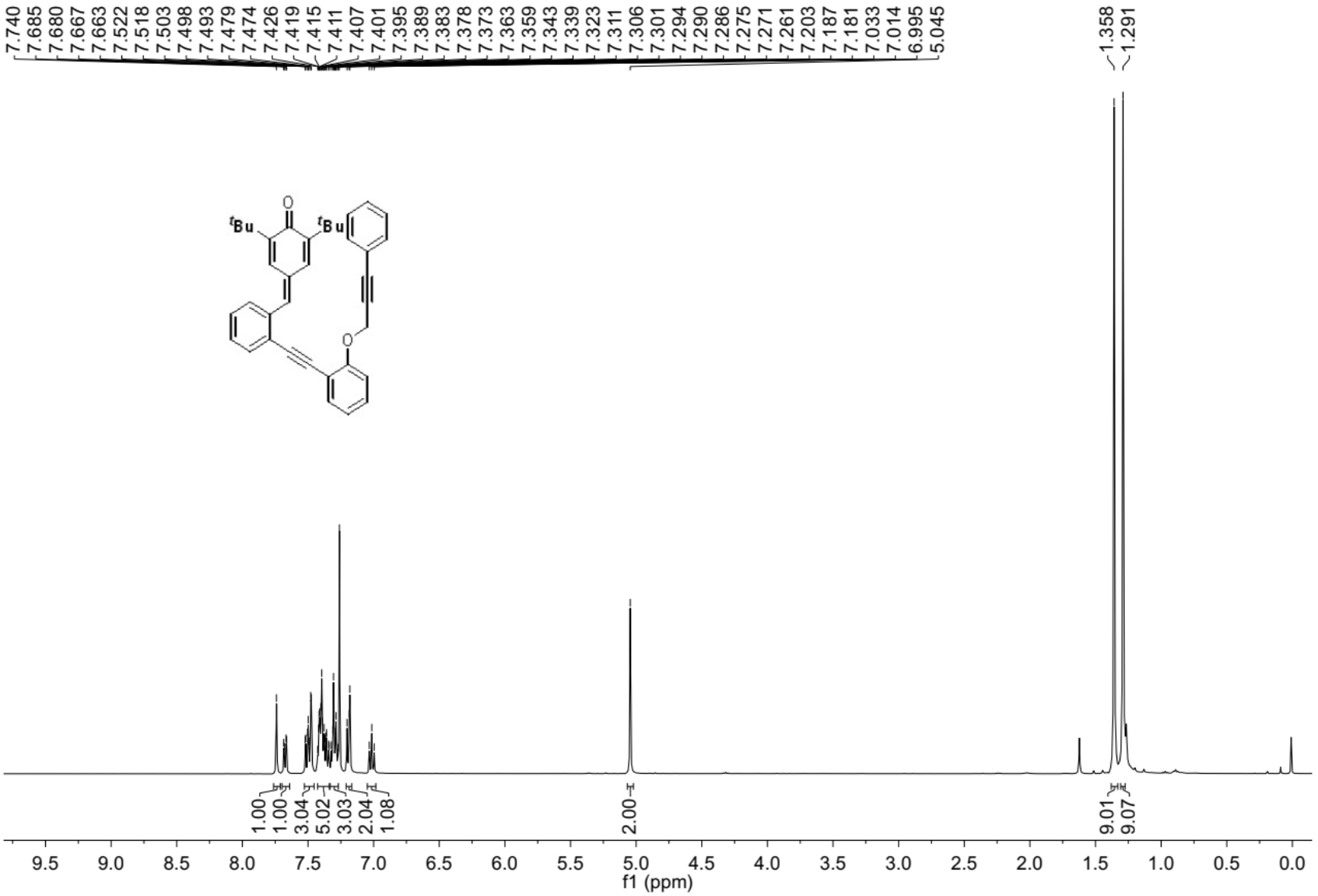
Isolation by column chromatography (PE/EA= 10/1 v/v) White solid, 73 mg, 66% yield; mp: 224-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 8.02 (s, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.28-7.26 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.84-6.80 (m, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.62-6.60 (m, 1H), 5.31 (d, *J* = 14.0 Hz, 1H), 5.26 (d, *J* = 14.0 Hz, 1H), 4.46 (q, *J* = 9.6 Hz, 1H), 1.22 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 185.7, 159.8, 156.5, 150.2, 149.1, 147.1, 145.1, 139.1, 137.9, 137.1, 136.1, 131.8, 131.0, 129.5, 126.1, 125.1 (q, $^{1}J_{CF}$ = 278.0 Hz), 123.6, 122.9, 121.9, 120.3, 117.8, 72.0, 59.1 (q, $^{2}J_{CF}$ = 26.0 Hz), 55.4, 35.6, 35.3, 29.1, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.78. IR (KBr, *v*, cm^{-1}): 2958, 2924, 2867, 1655, 1490, 1365, 1263, 1098, 883, 760. IR (KBr, *v*, cm^{-1}): 2958, 2924, 2854, 1662, 1457, 1366, 1266, 1163, 882, 762. HR-MS (ESI-TOF) *m/z* calcd for $C_{32}H_{29}ClF_3NO_2$ [M + Na]$^+$ 574.1737, found 574.1730.

3',5'-di-tert-butyl-9-chloro-11-(trifluoromethyl)-6H,11H-spiro[chromeno[3,4-b]cyclopenta[de]quinoline-12,1'-cyclohexane]-2',5'-dien-4'-one (5db)

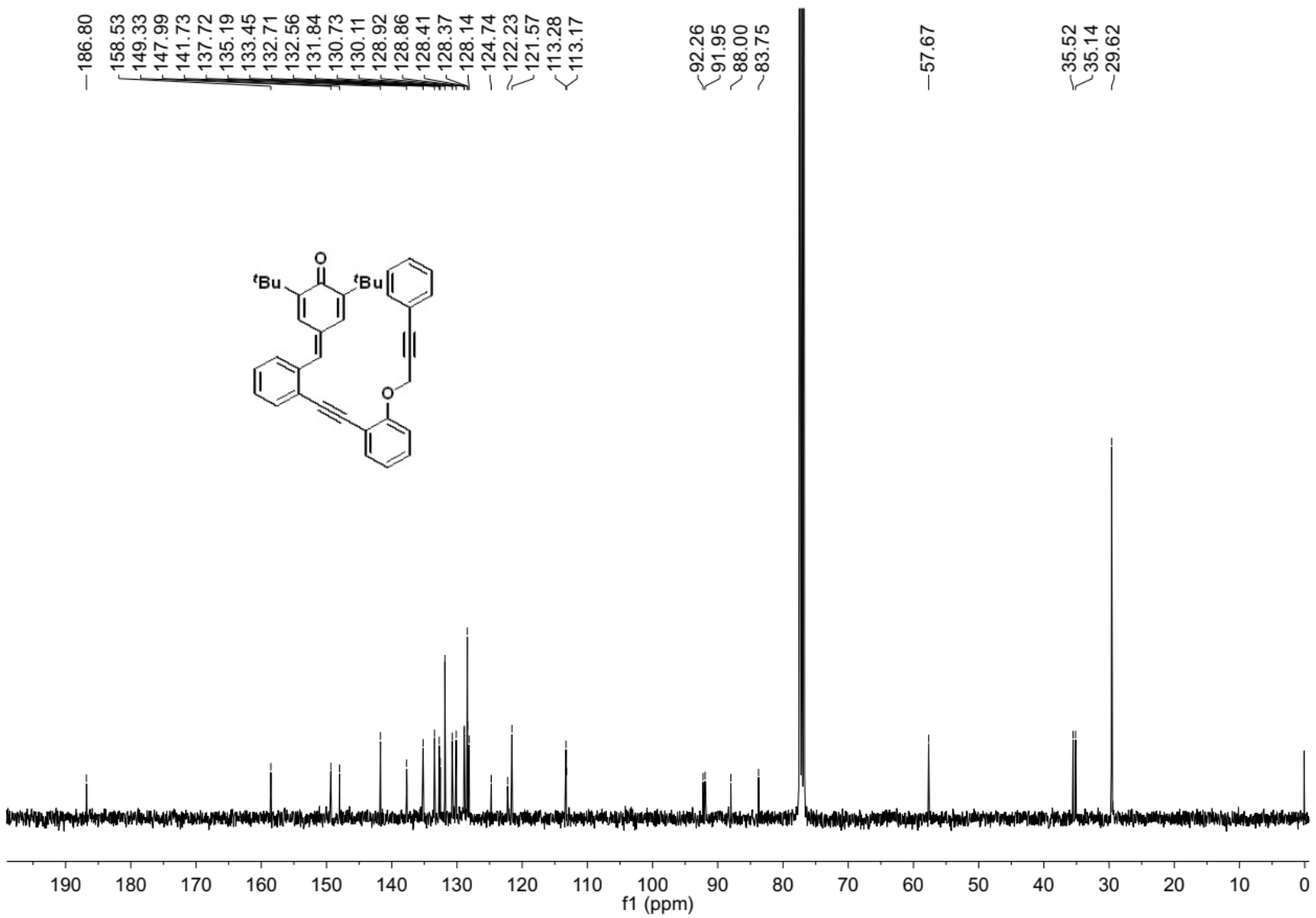


Isolation by column chromatography (PE/EA= 10/1 v/v) White solid, 57 mg, 52% yield; mp: 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm): 8.02 (s, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.26-7.24 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.84-6.80(m, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.62-6.59 (m, 1H), 5.31 (d, *J* = 14.0 Hz, 1H), 5.26 (d, *J* = 14.0 Hz, 1H), 4.46 (q, *J* = 9.6 Hz, 1H), 1.22 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (*δ*, ppm): 185.7, 159.8, 156.5, 150.2, 149.1, 147.1, 145.1, 139.1, 137.9, 137.1, 136.1, 131.8, 131.0, 129.5, 126.1, 125.1 (q, $^{1}J_{CF}$ = 279.0 Hz), 123.6, 122.9, 121.9, 120.3,

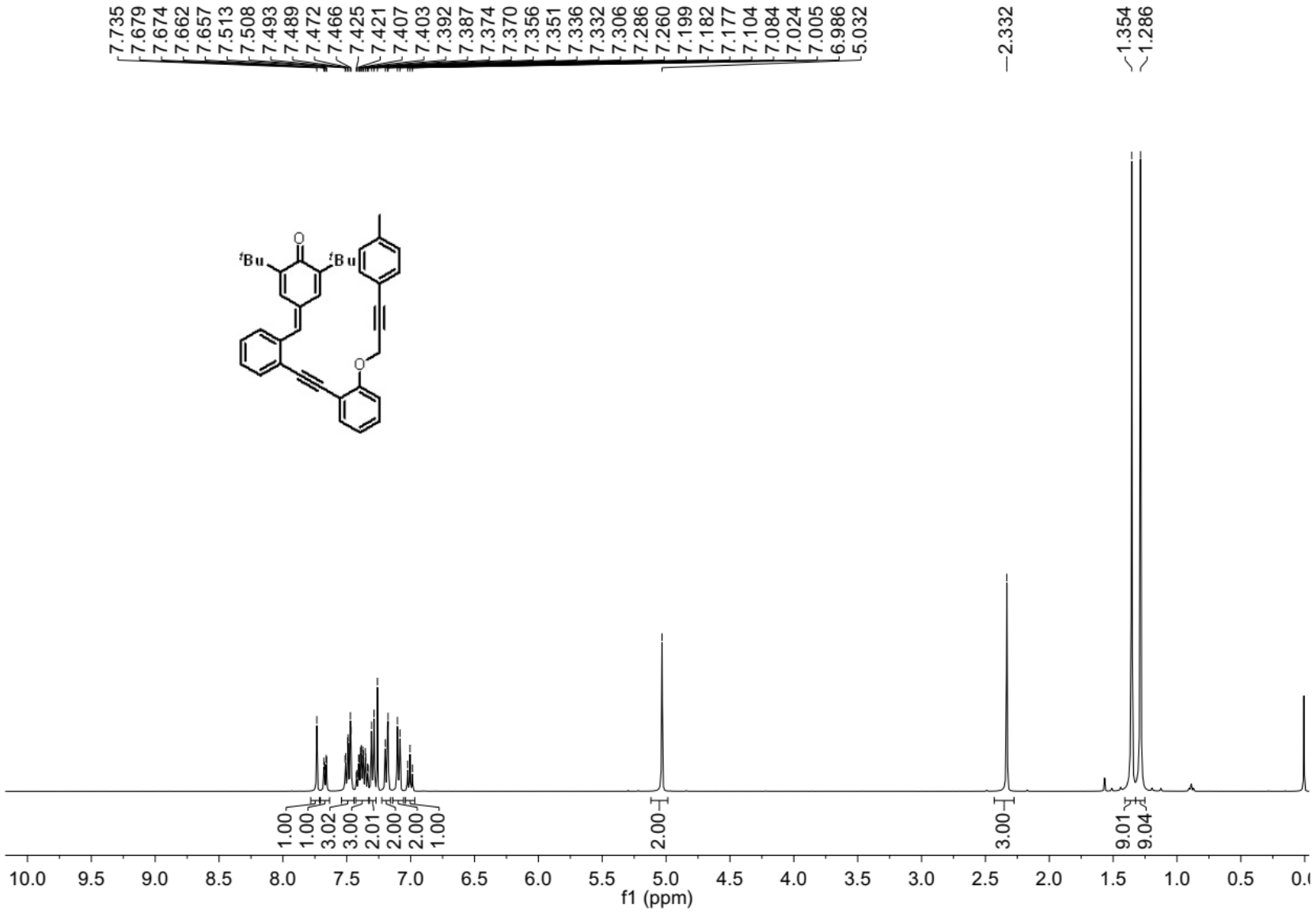
117.8, 72.0, 59.1 (q, $^{2}J_{CF}$ = 26.0 Hz), 55.4, 35.6, 35.3, 29.1, 28.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -63.78. IR (KBr, *v*, cm^{-1}): 2954, 2922, 2852, 1654, 1457, 1357, 1262, 1100, 884, 761. HR-MS (ESI-TOF) *m/z* calcd for $C_{32}H_{29}ClF_3NO_2$ $[M + Na]^+$ 574.1737, found 574.1724.



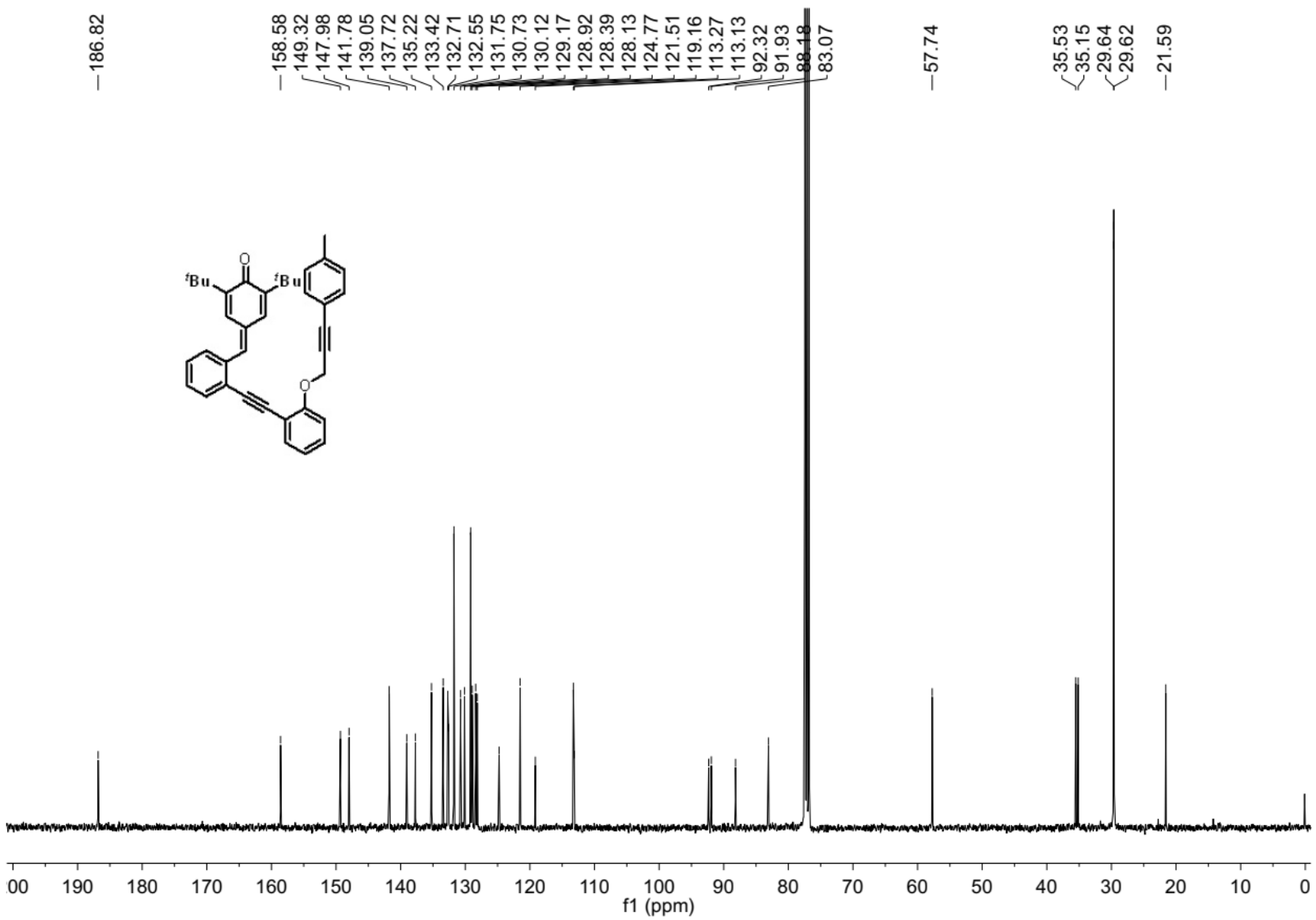
^{1}H NMR Spectrum of Compound 1a



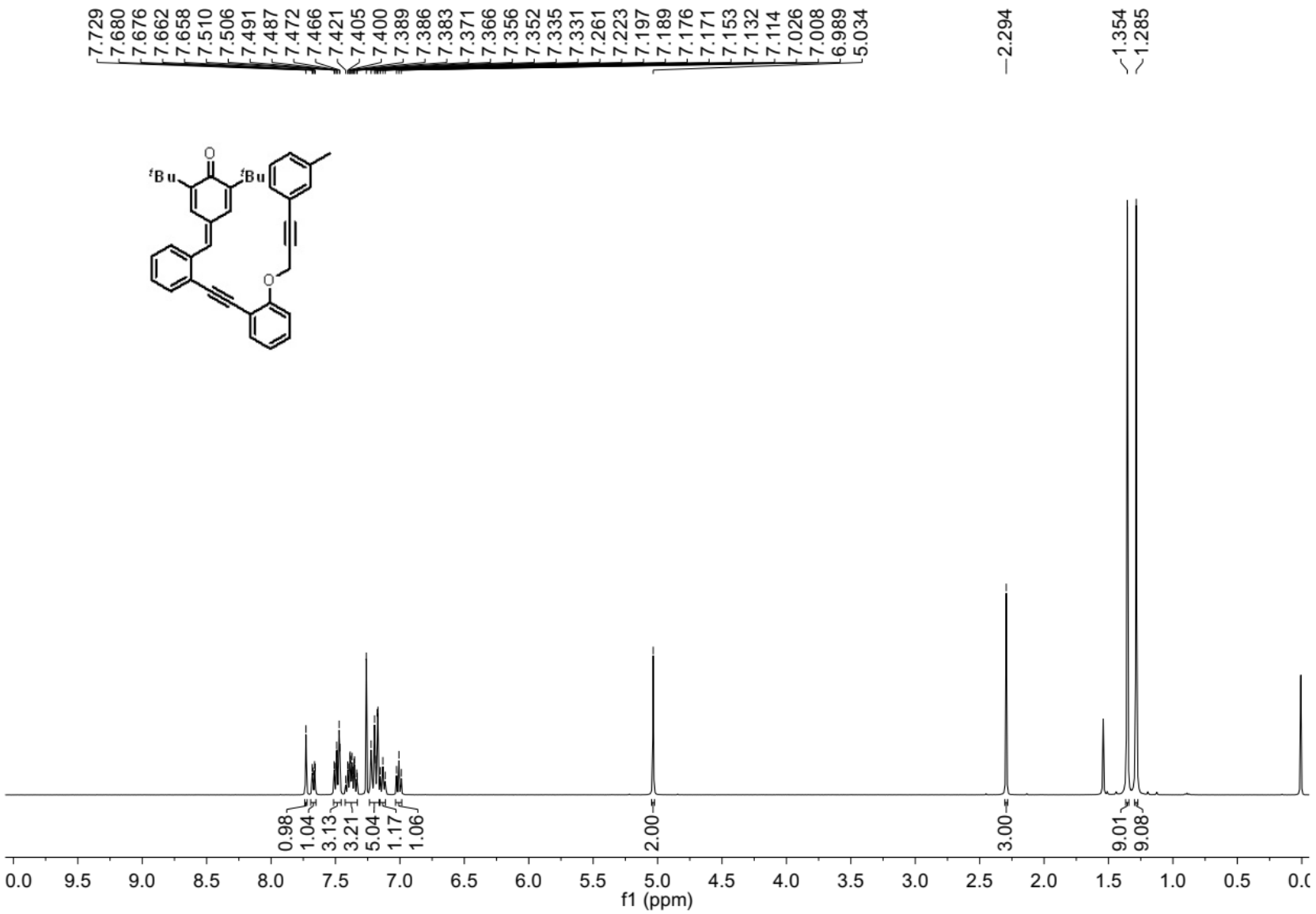
^{13}C NMR Spectrum of Compound 1a



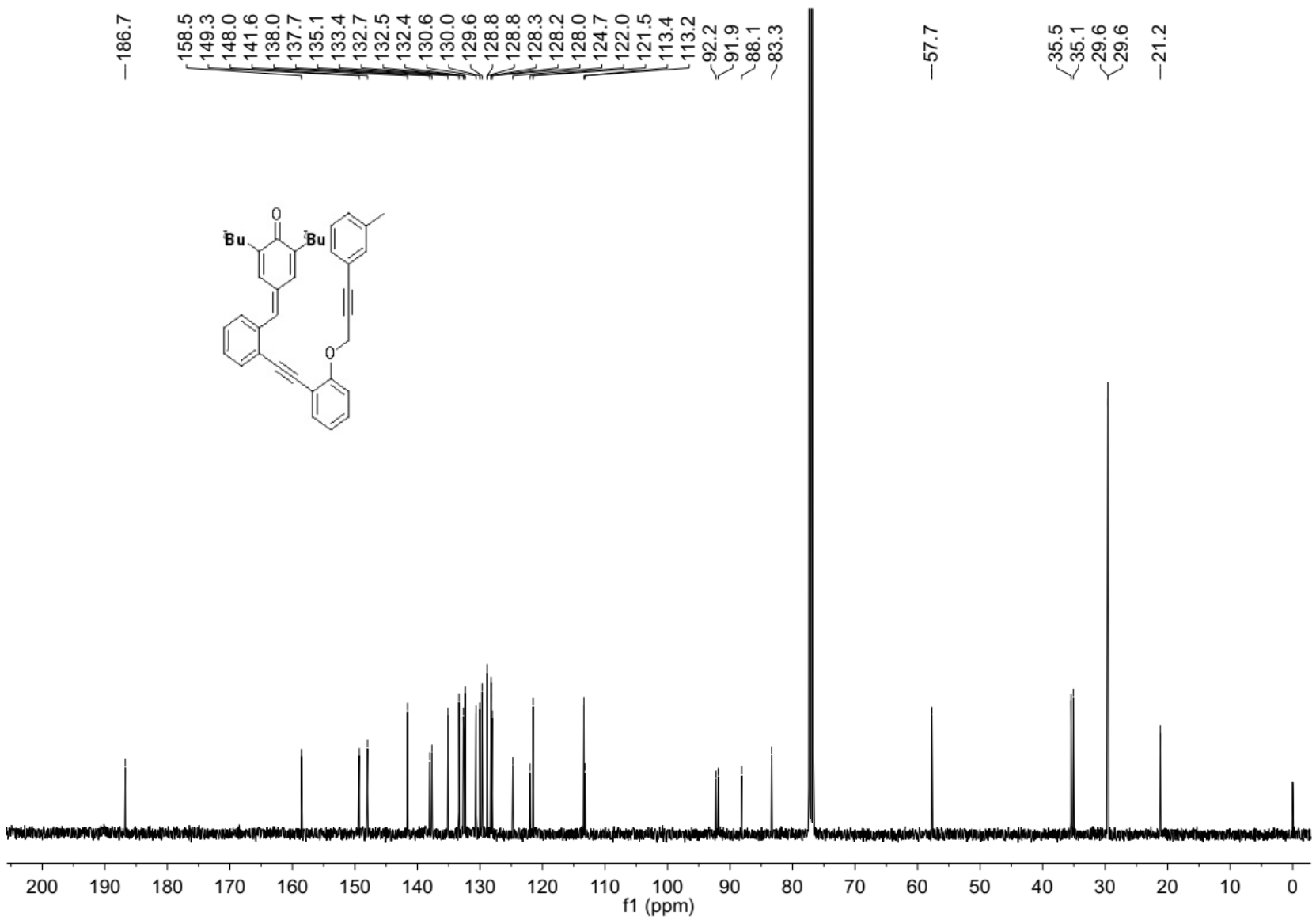
^{1}H NMR Spectrum of Compound 1b



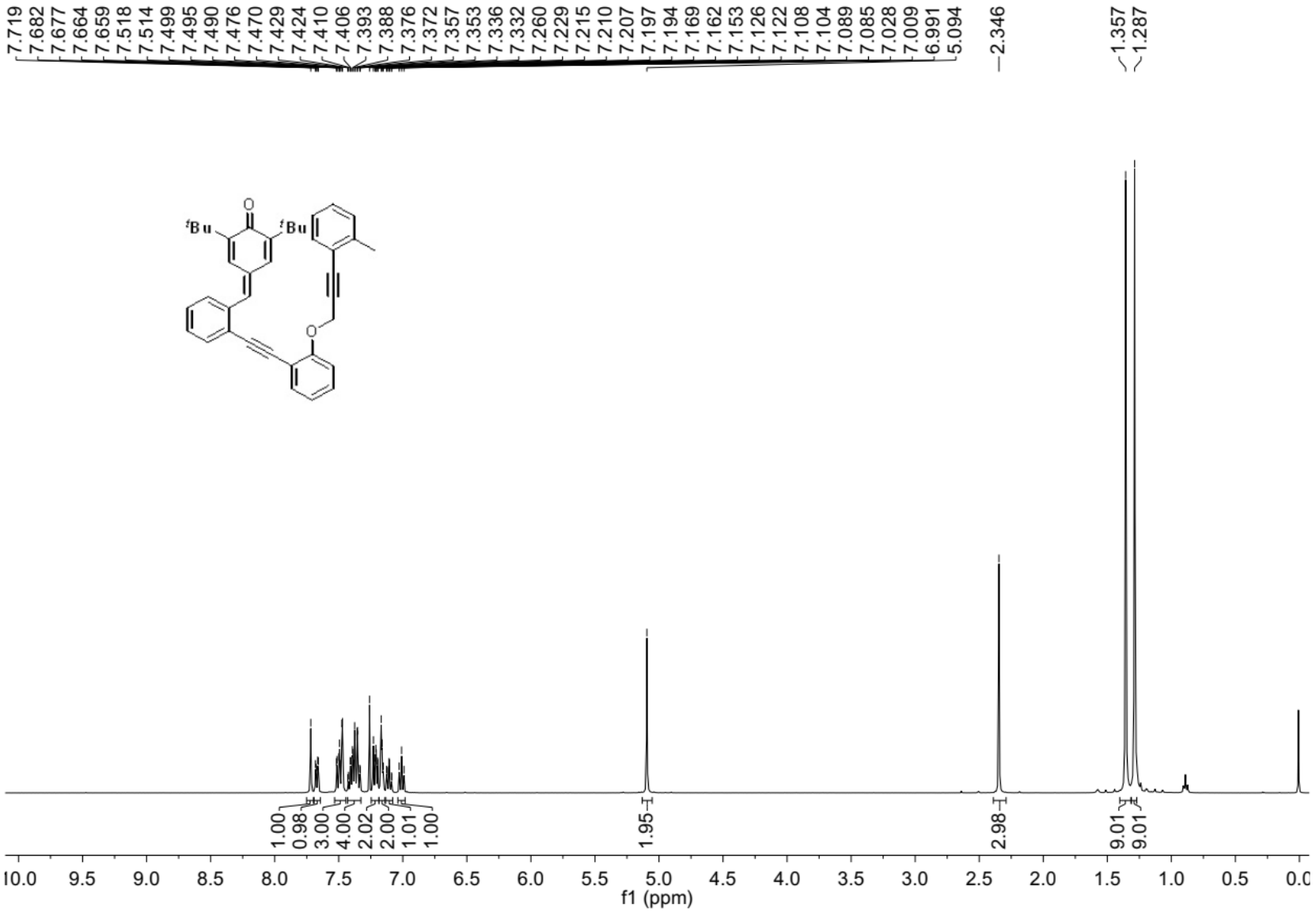
^{13}C NMR Spectrum of Compound 1b



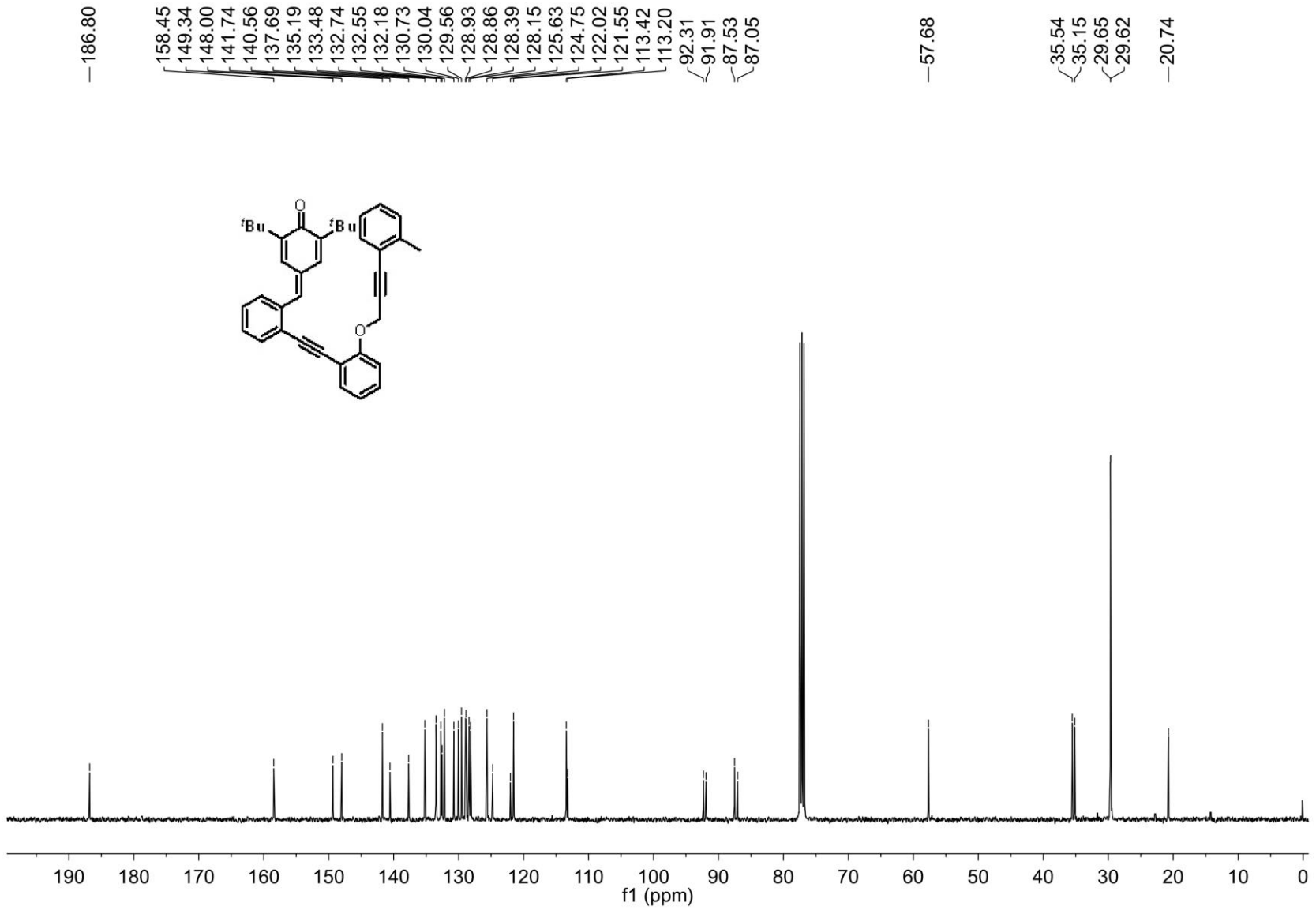
^{1}H NMR Spectrum of Compound 1c



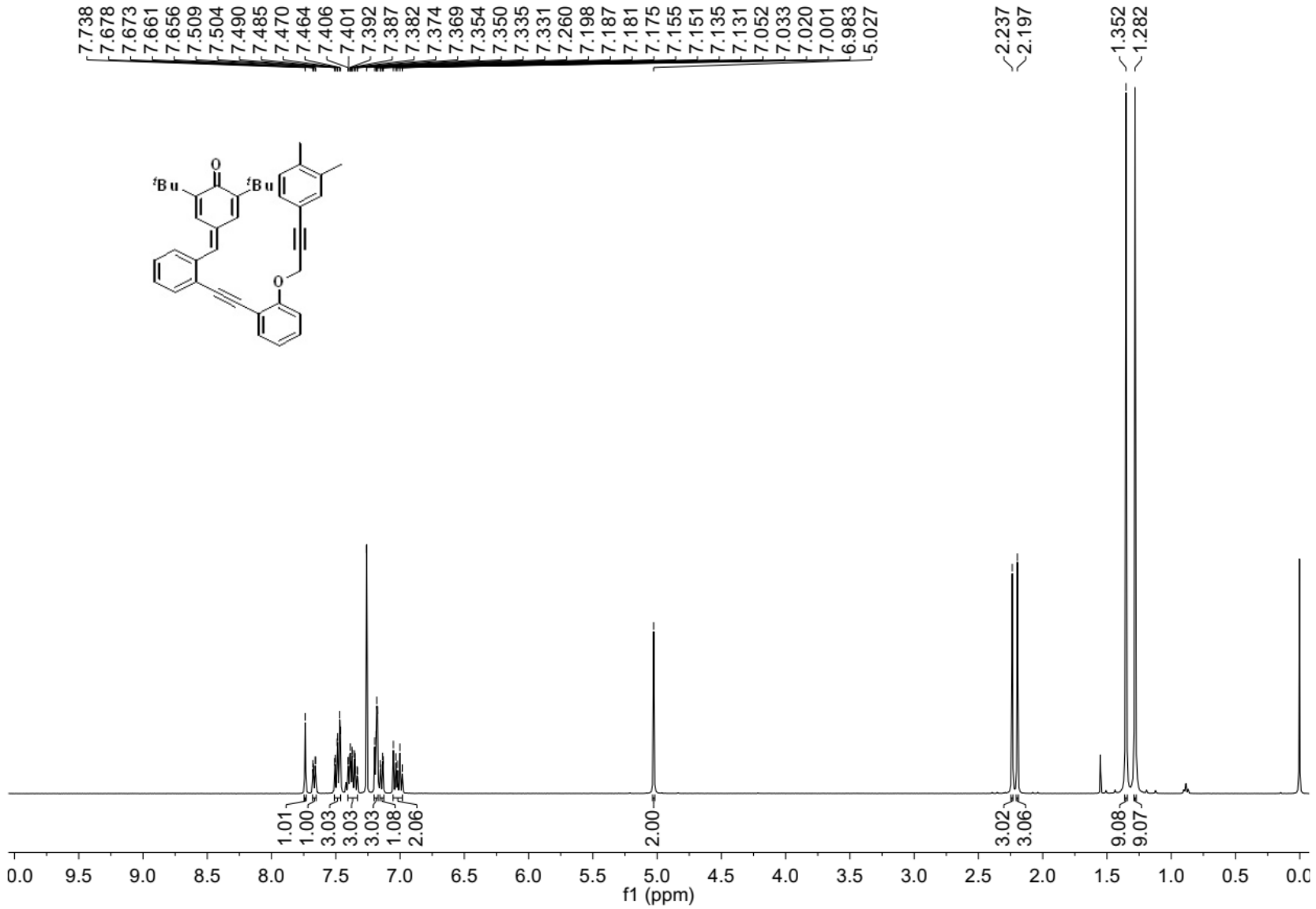
^{13}C NMR Spectrum of Compound 1c



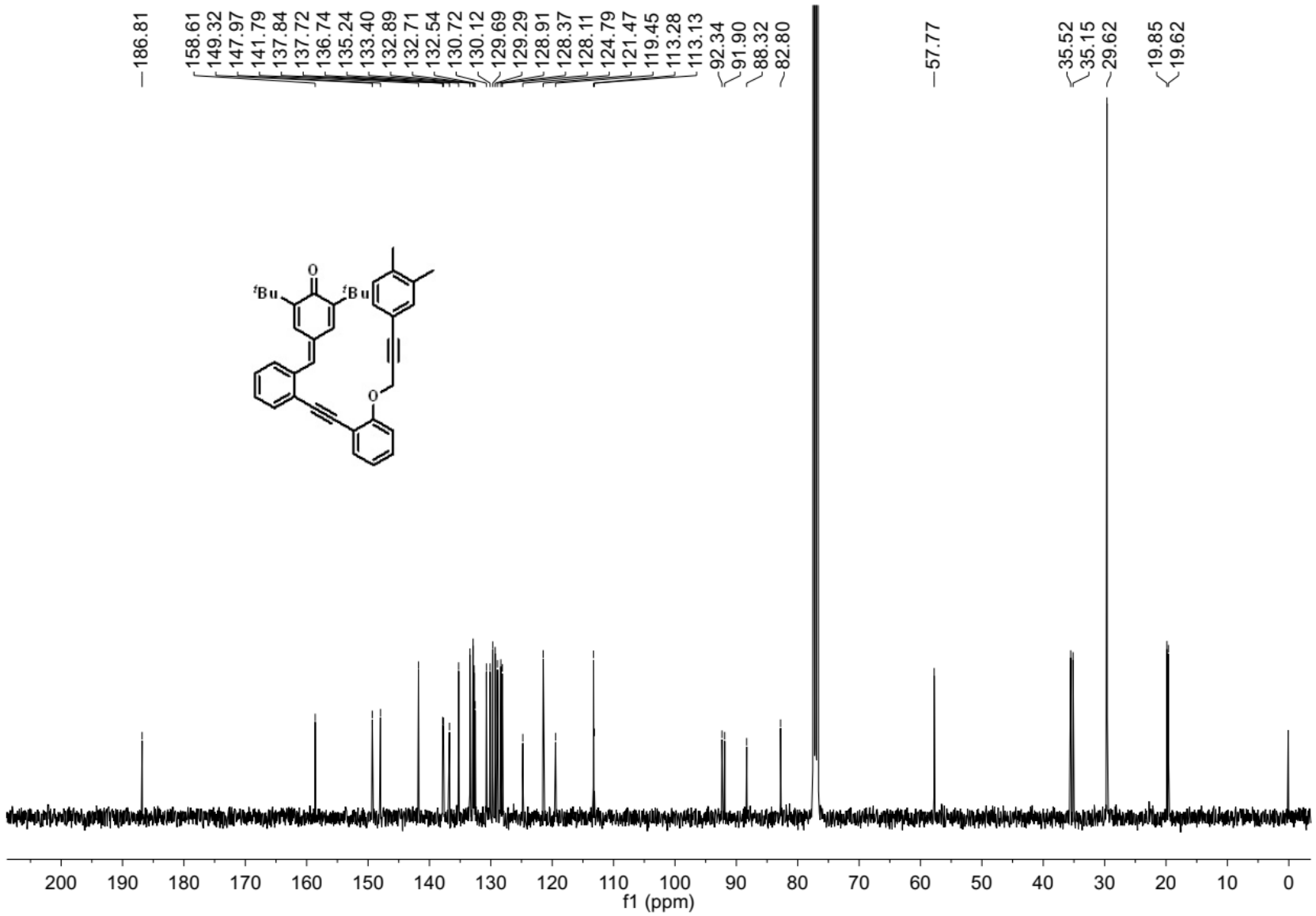
^{1}H NMR Spectrum of Compound 1d



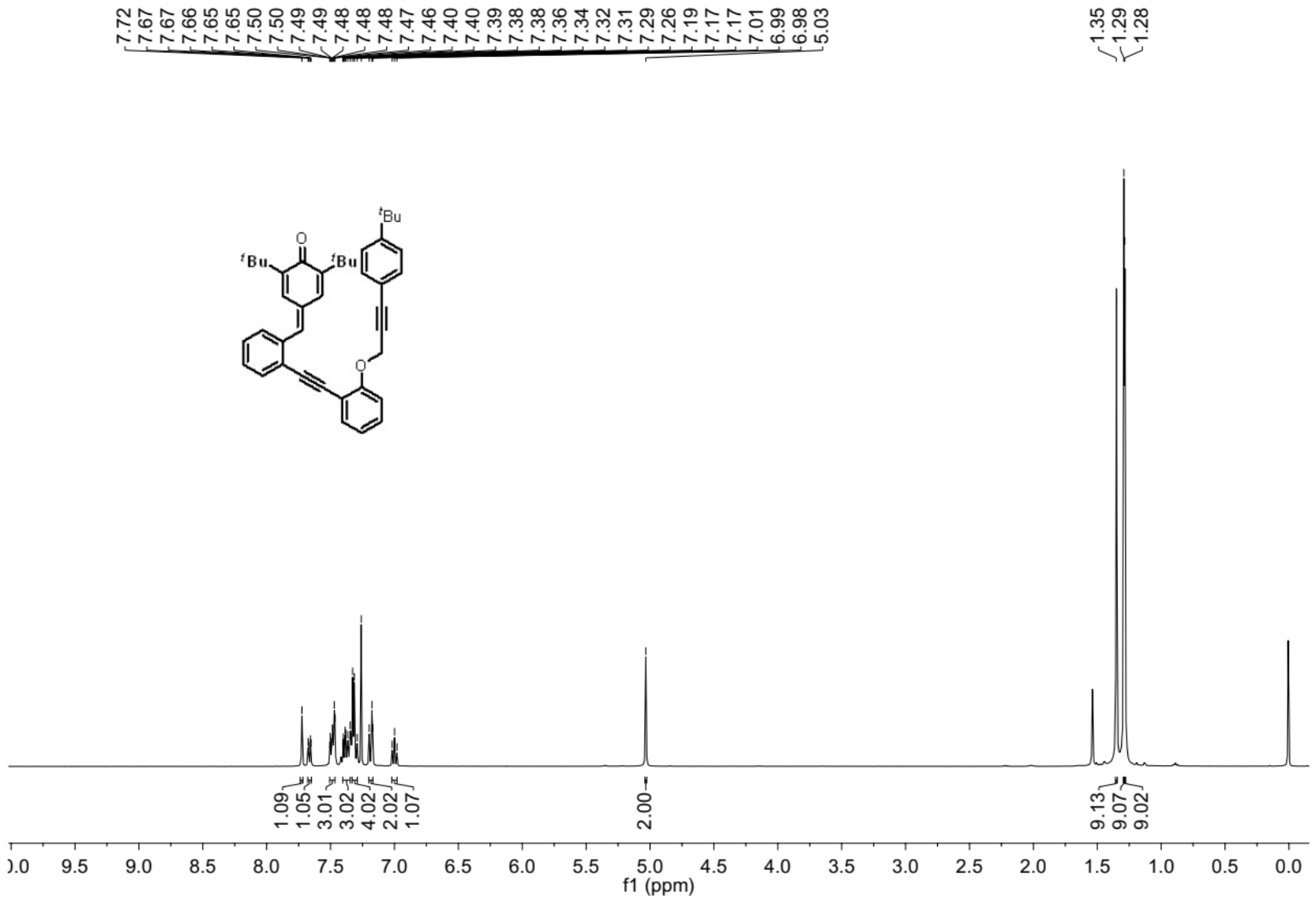
^{13}C NMR Spectrum of Compound 1d



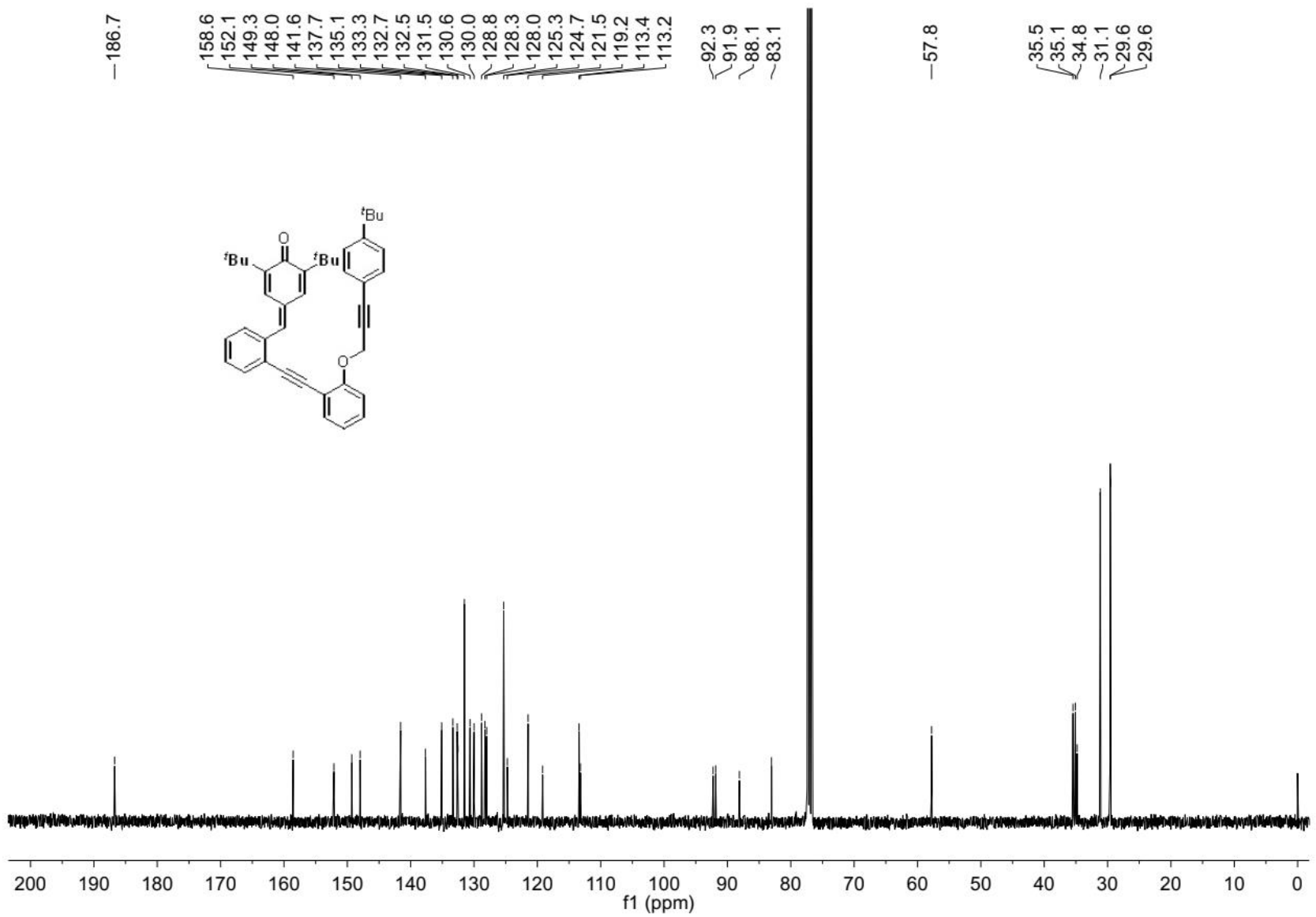
^{1}H NMR Spectrum of Compound 1e



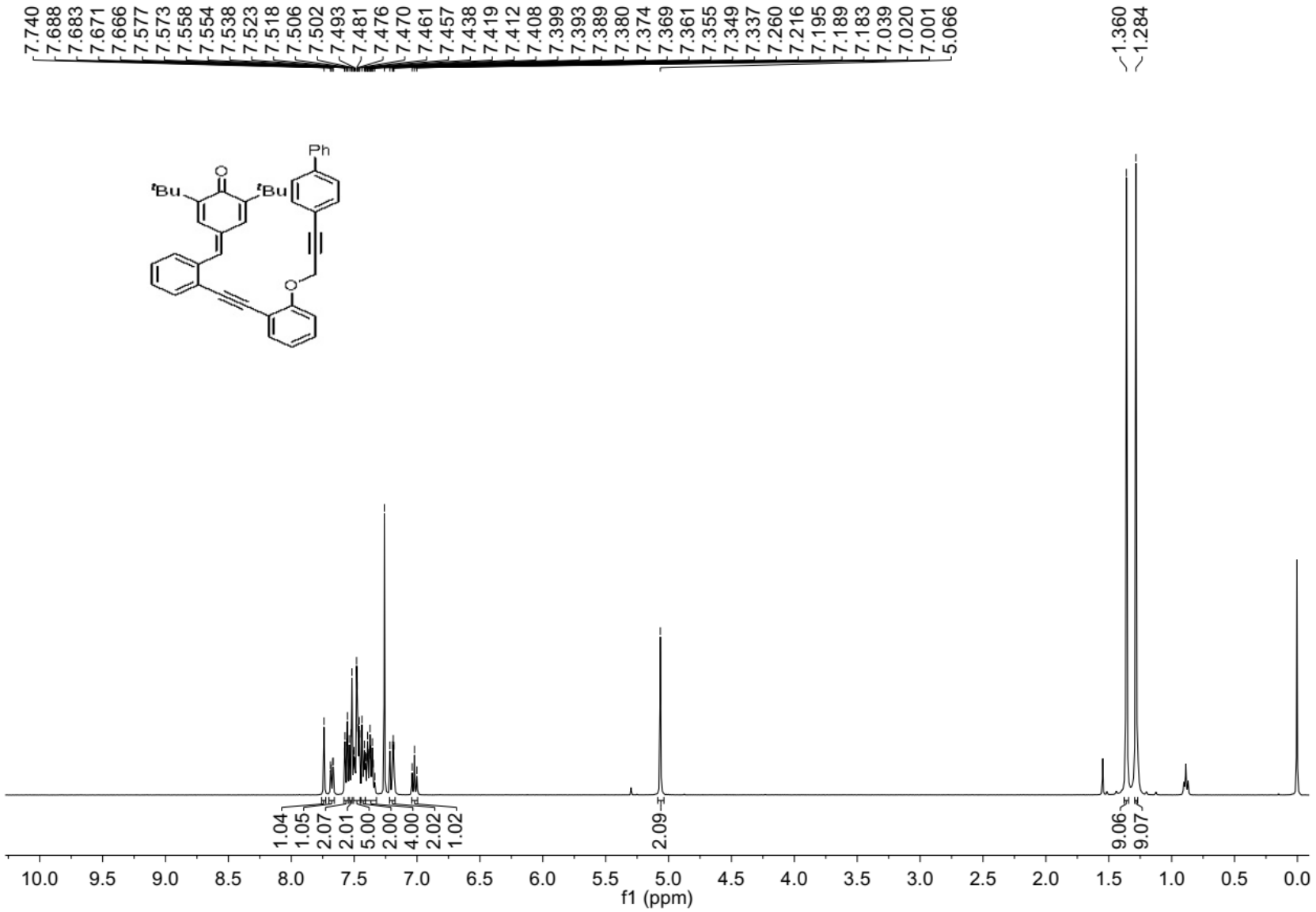
^{13}C NMR Spectrum of Compound 1e



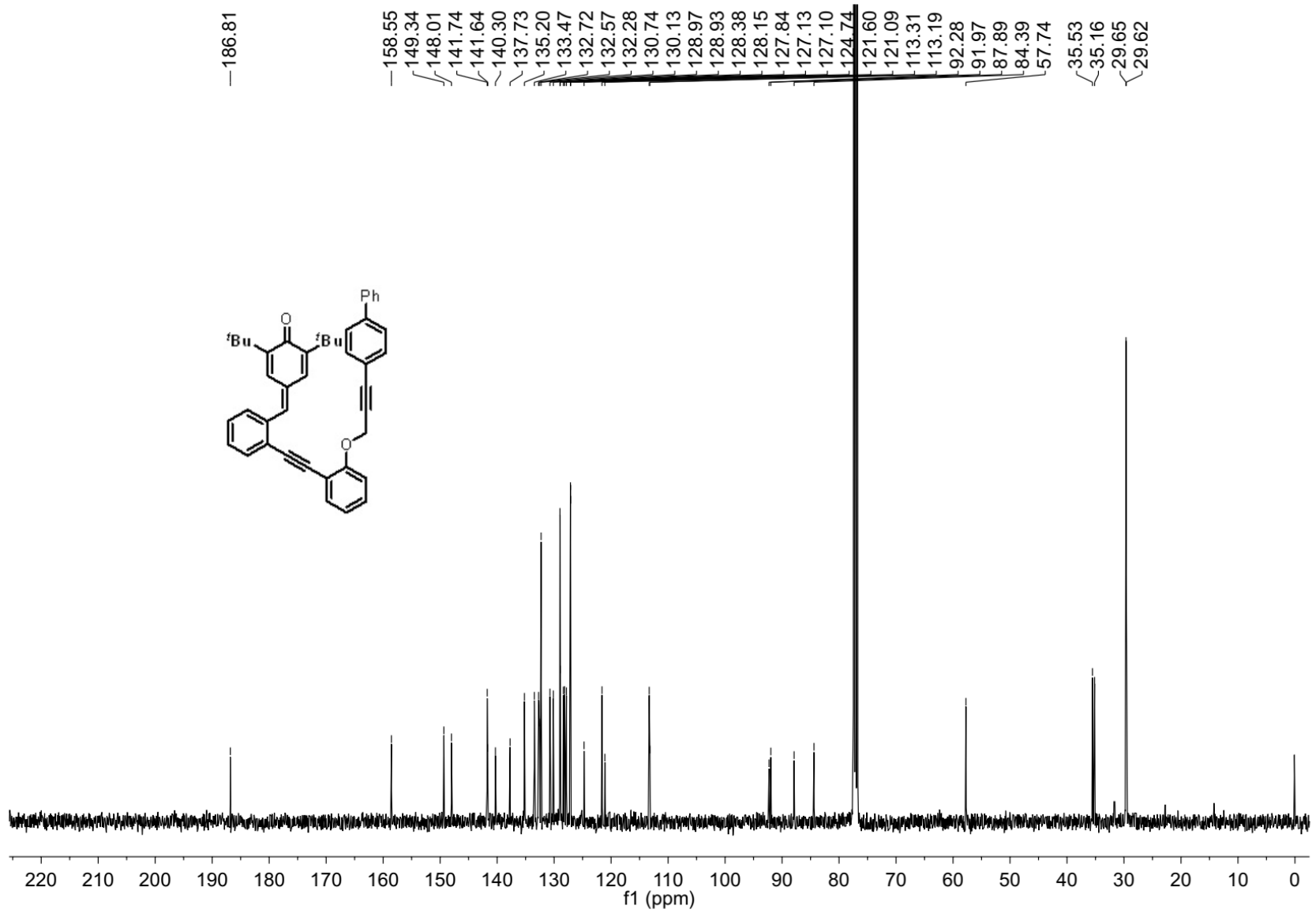
^{1}H NMR Spectrum of Compound 1f



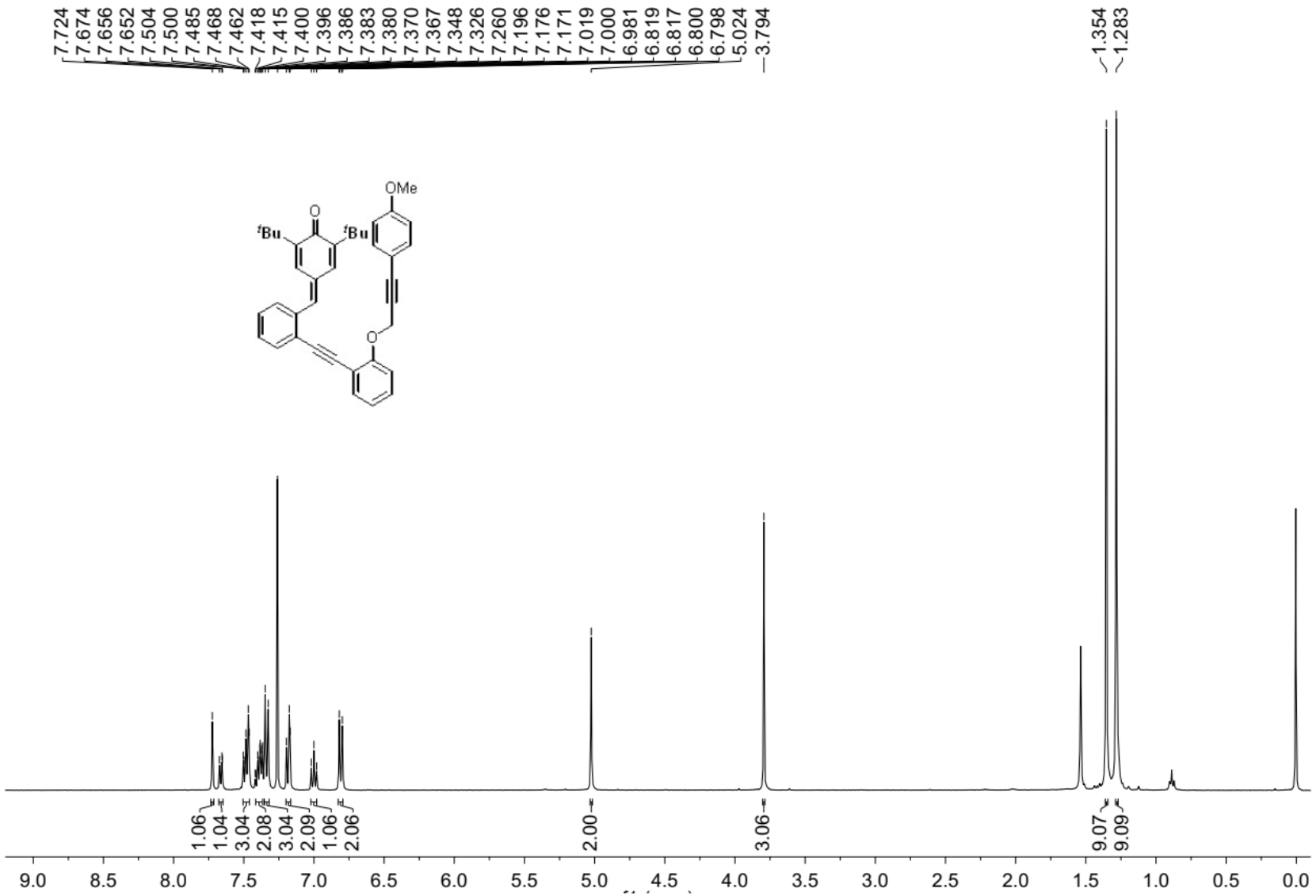
^{13}C NMR Spectrum of Compound 1f



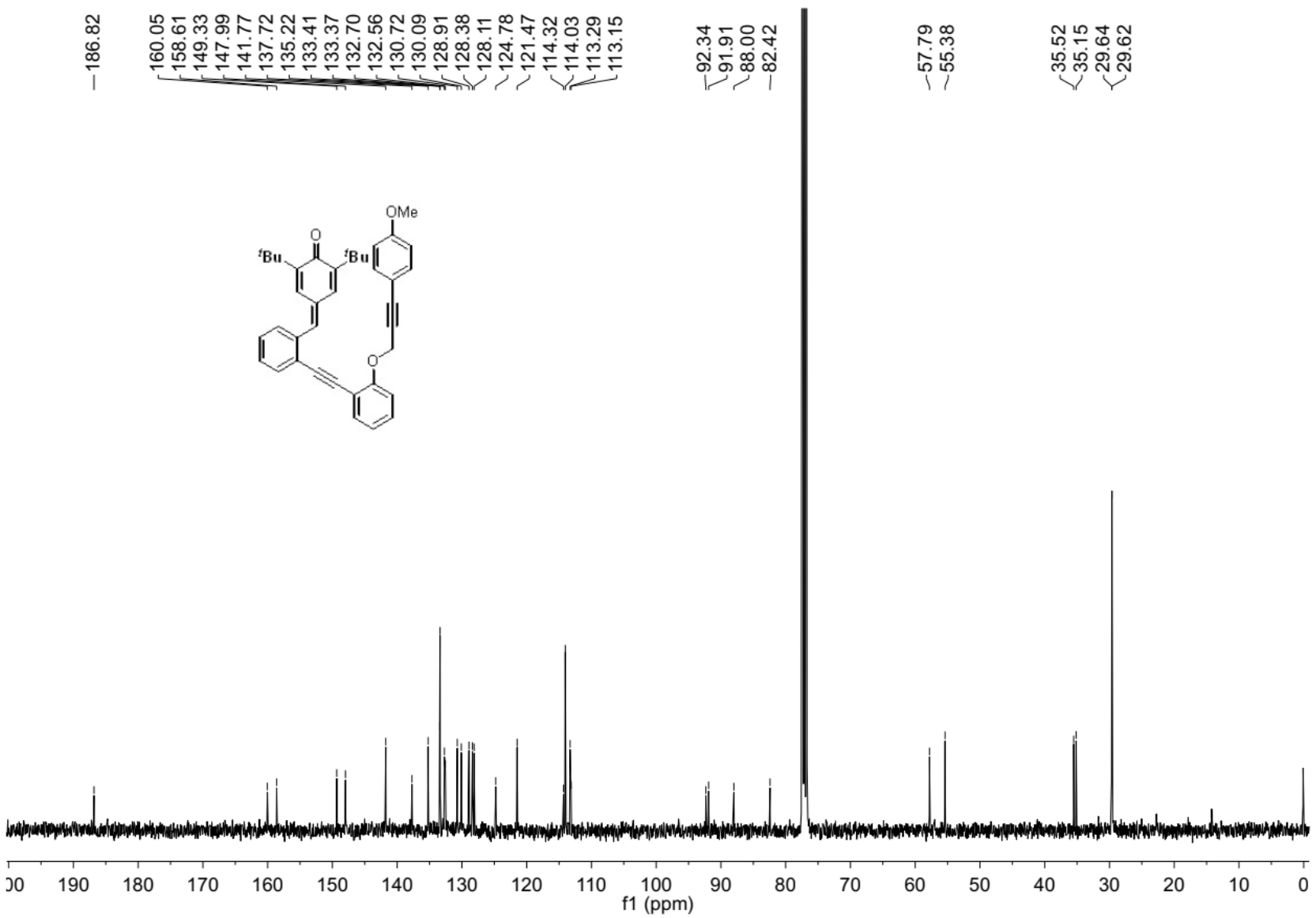
^{1}H NMR Spectrum of Compound 1g



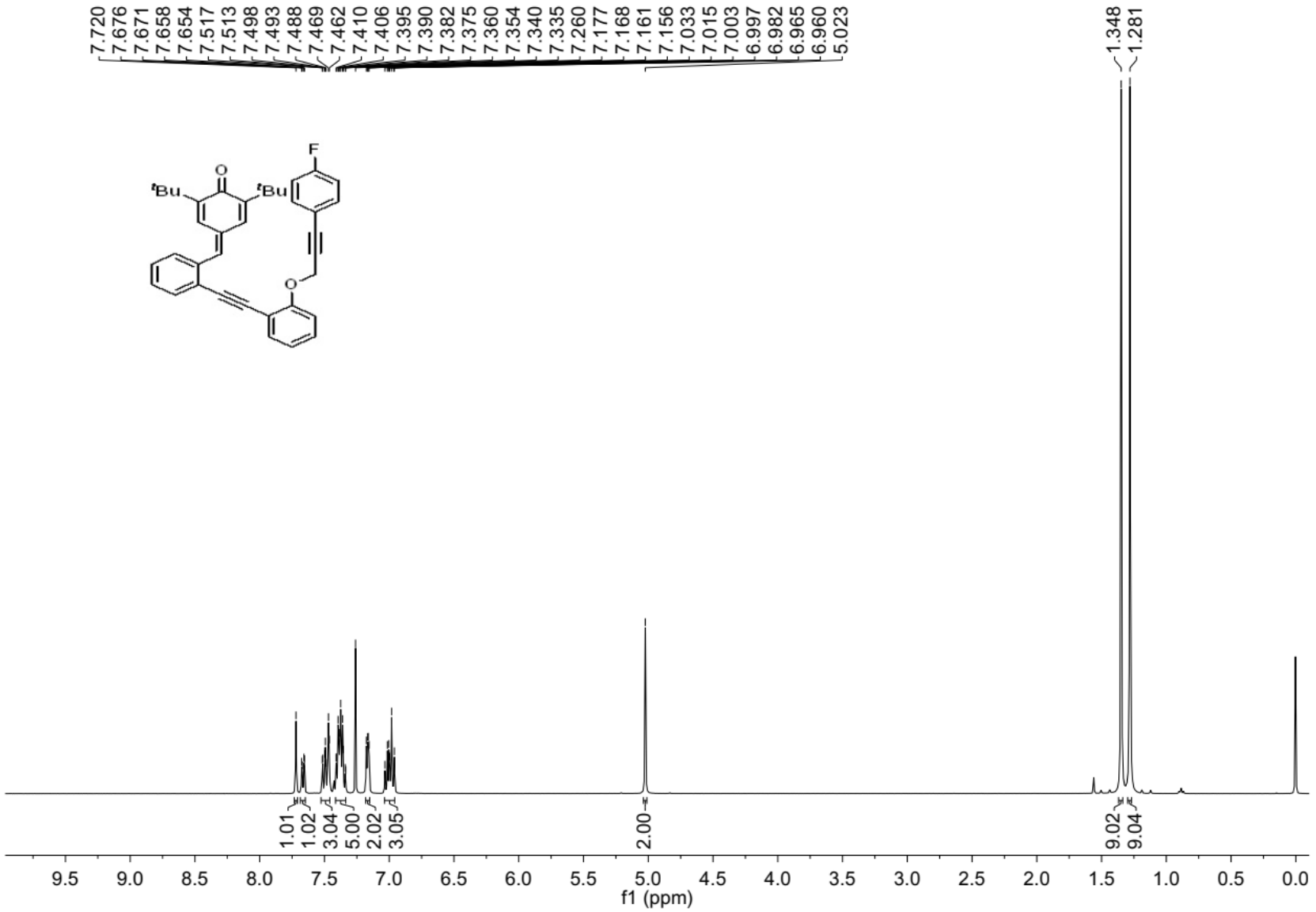
^{13}C NMR Spectrum of Compound 1g



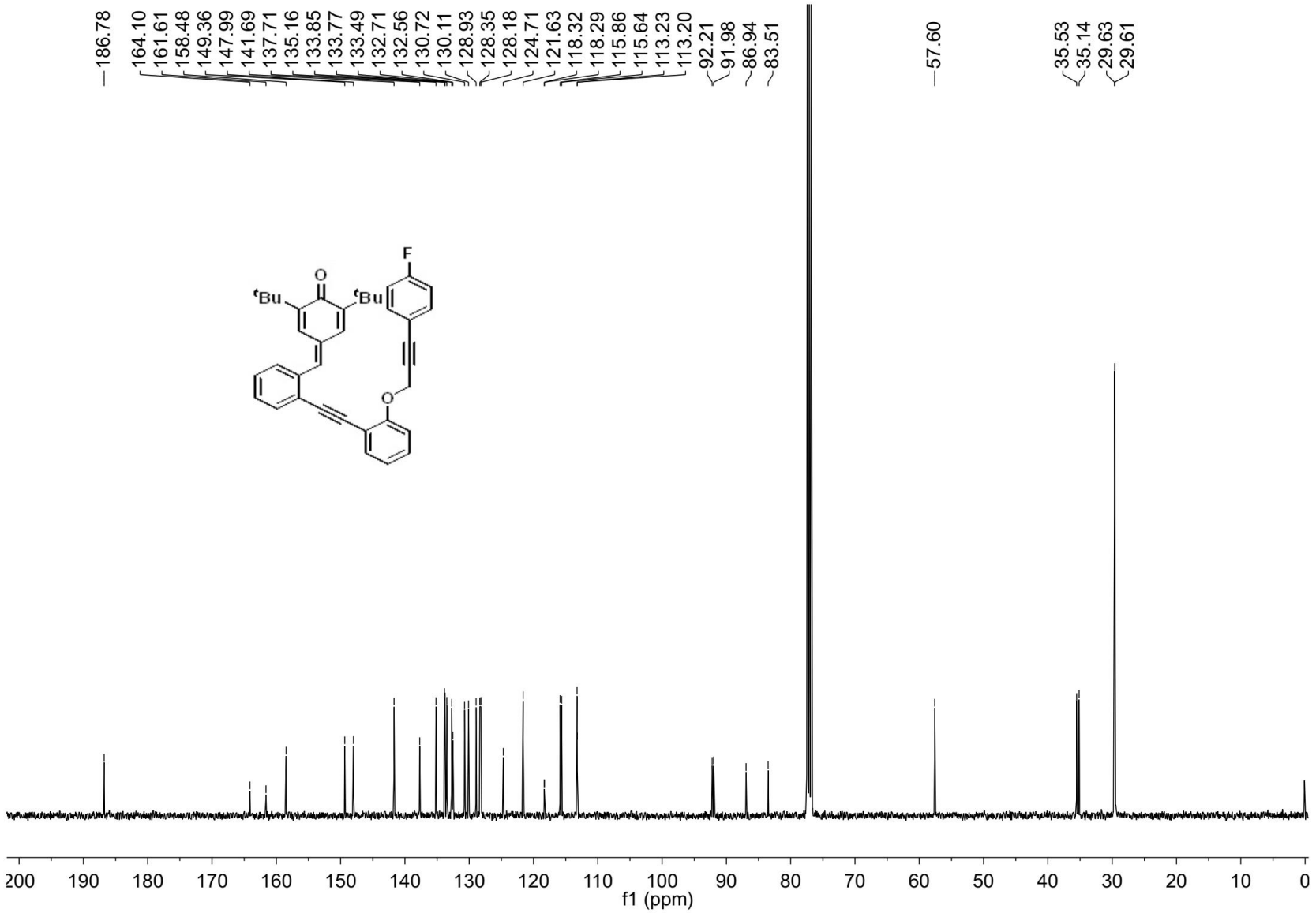
^{1}H NMR Spectrum of Compound 1h



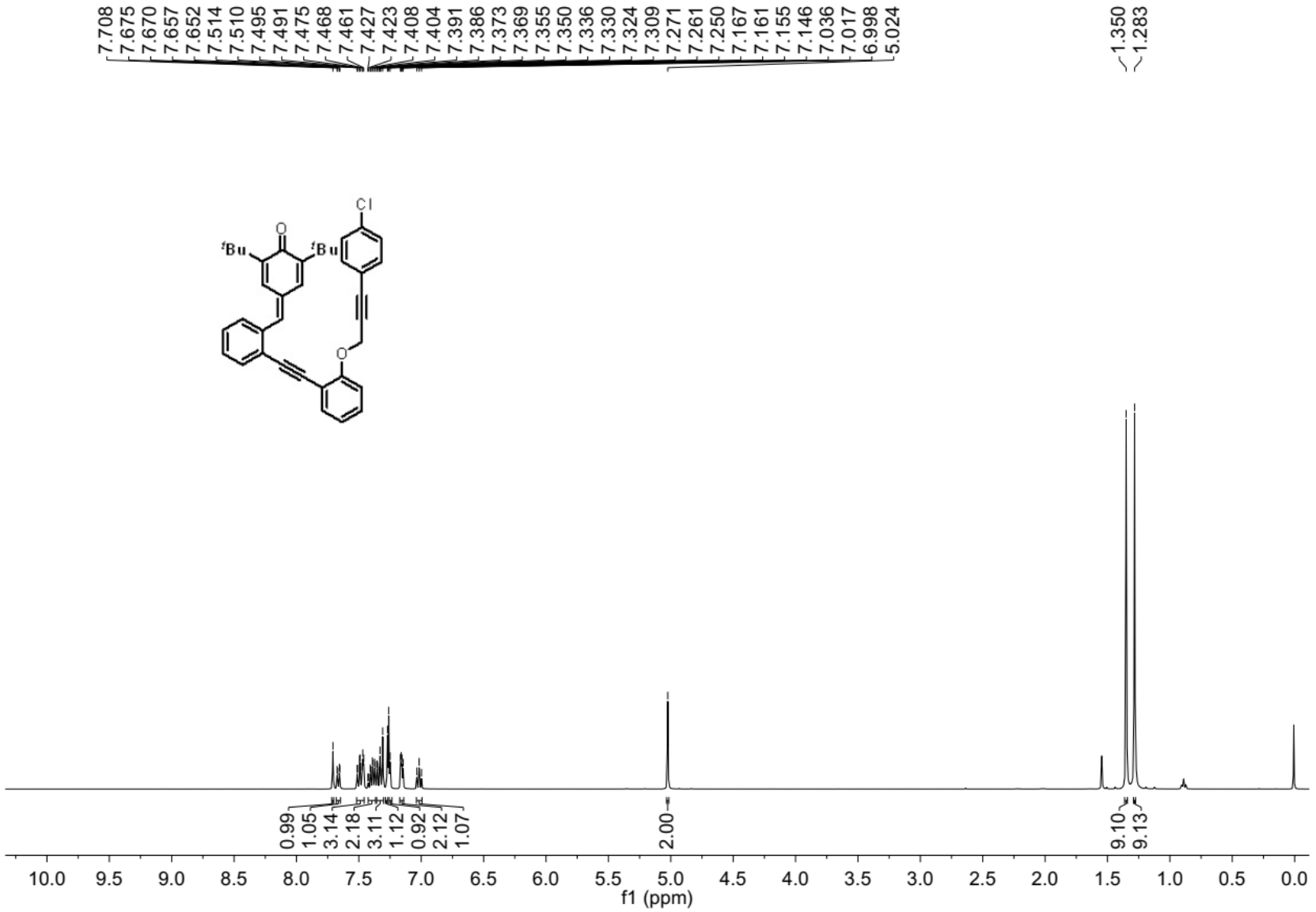
^{13}C NMR Spectrum of Compound 1h



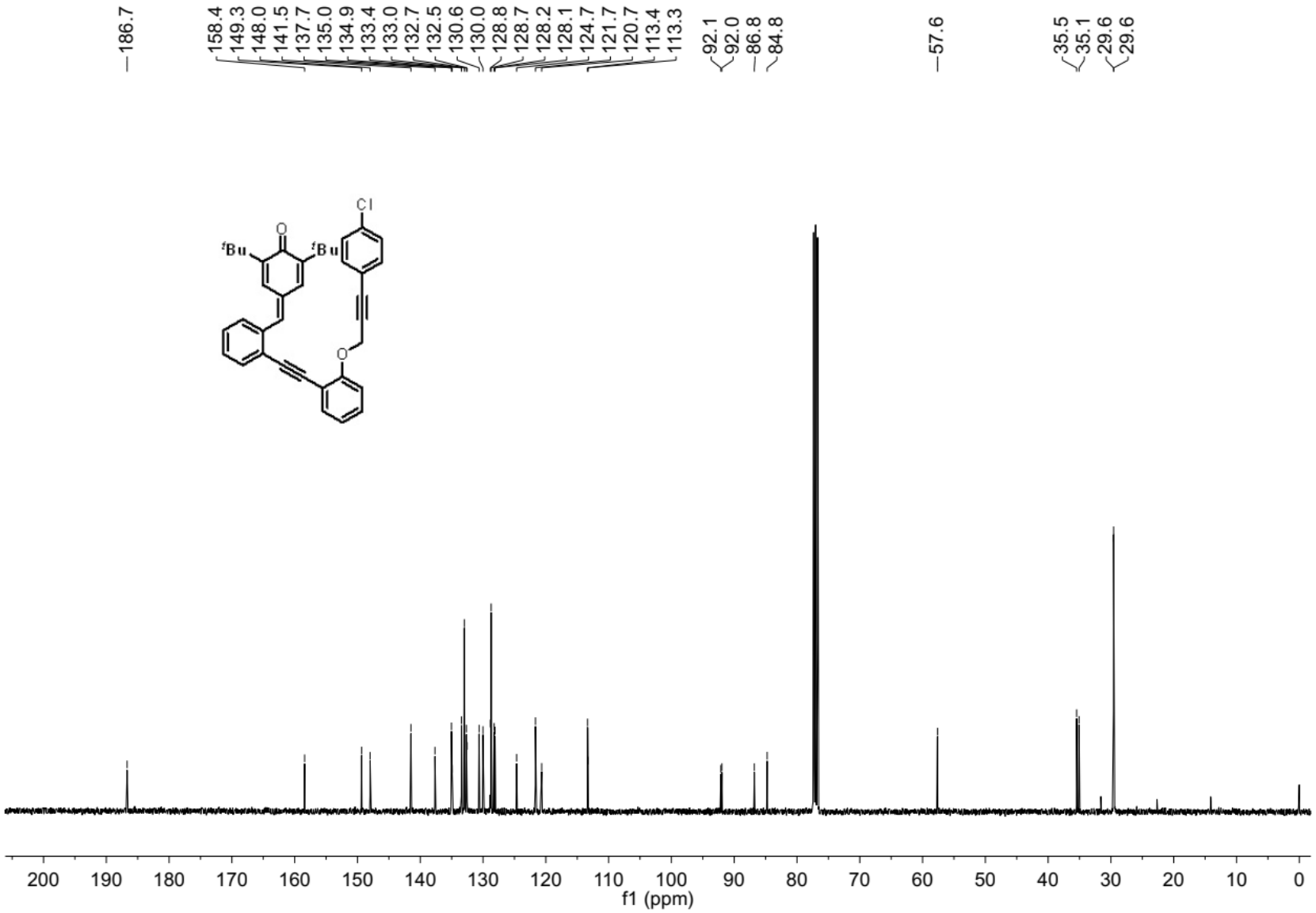
^{1}H NMR Spectrum of Compound 1i



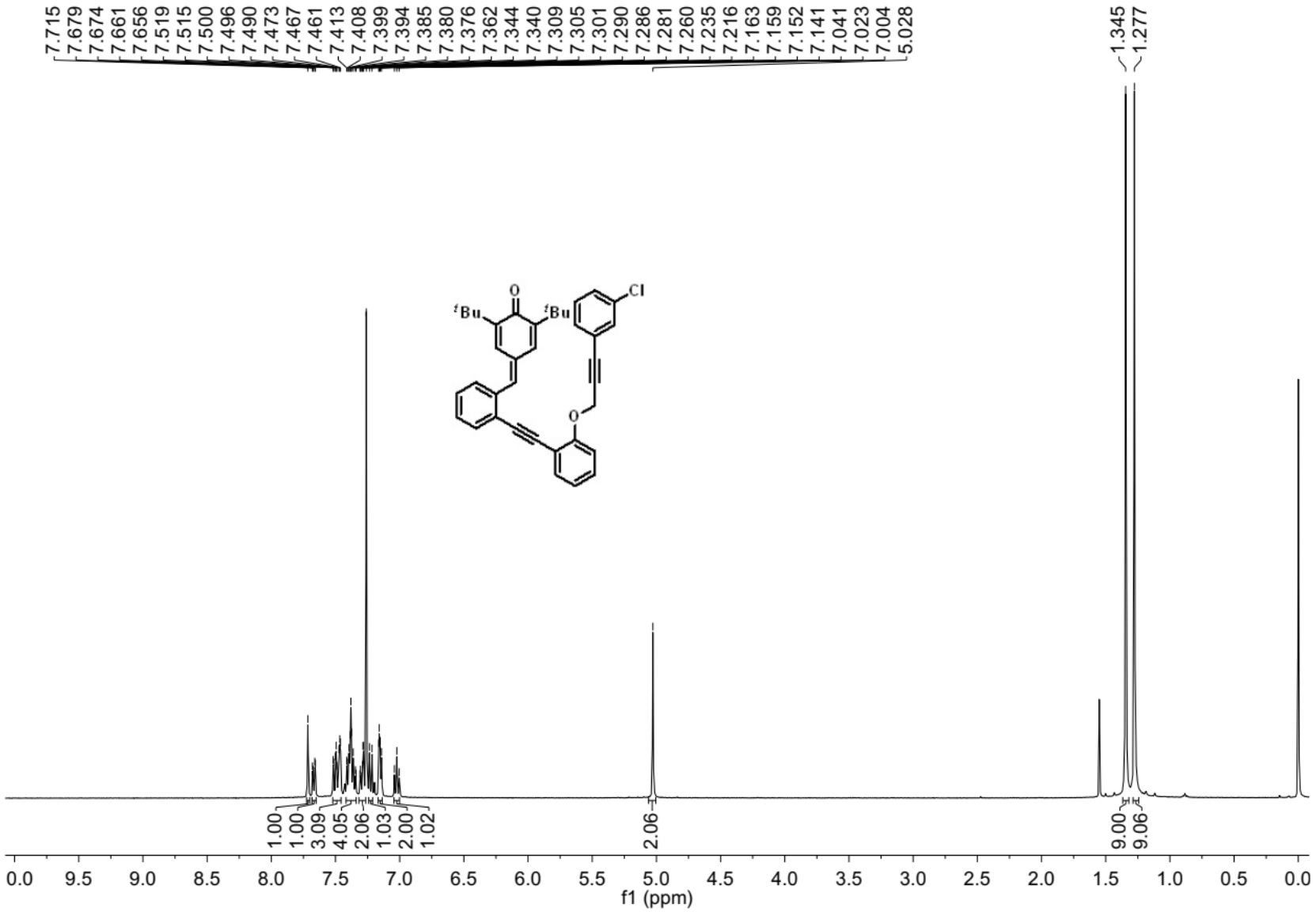
^{13}C NMR Spectrum of Compound 1i



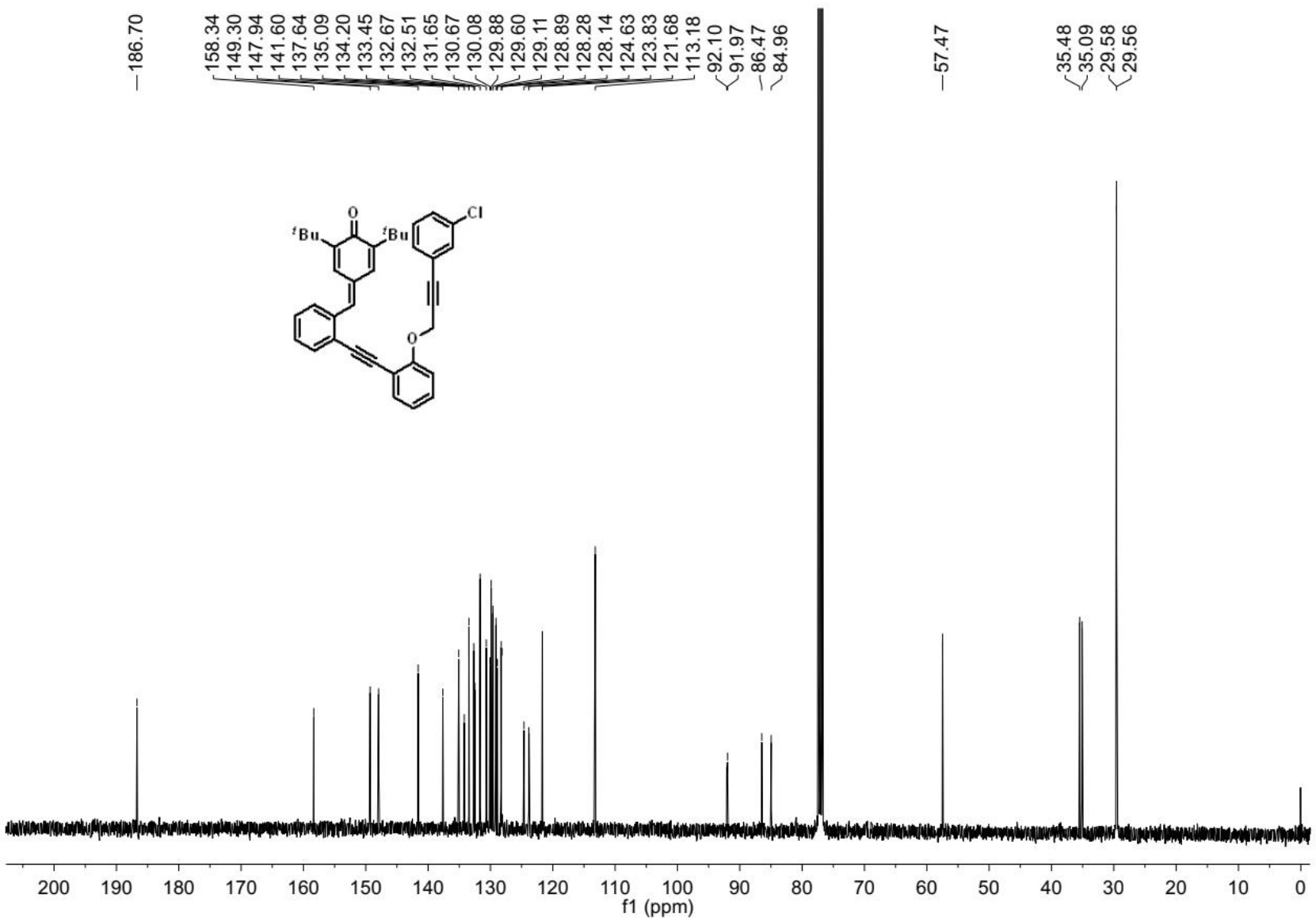
^{1}H NMR Spectrum of Compound 1j



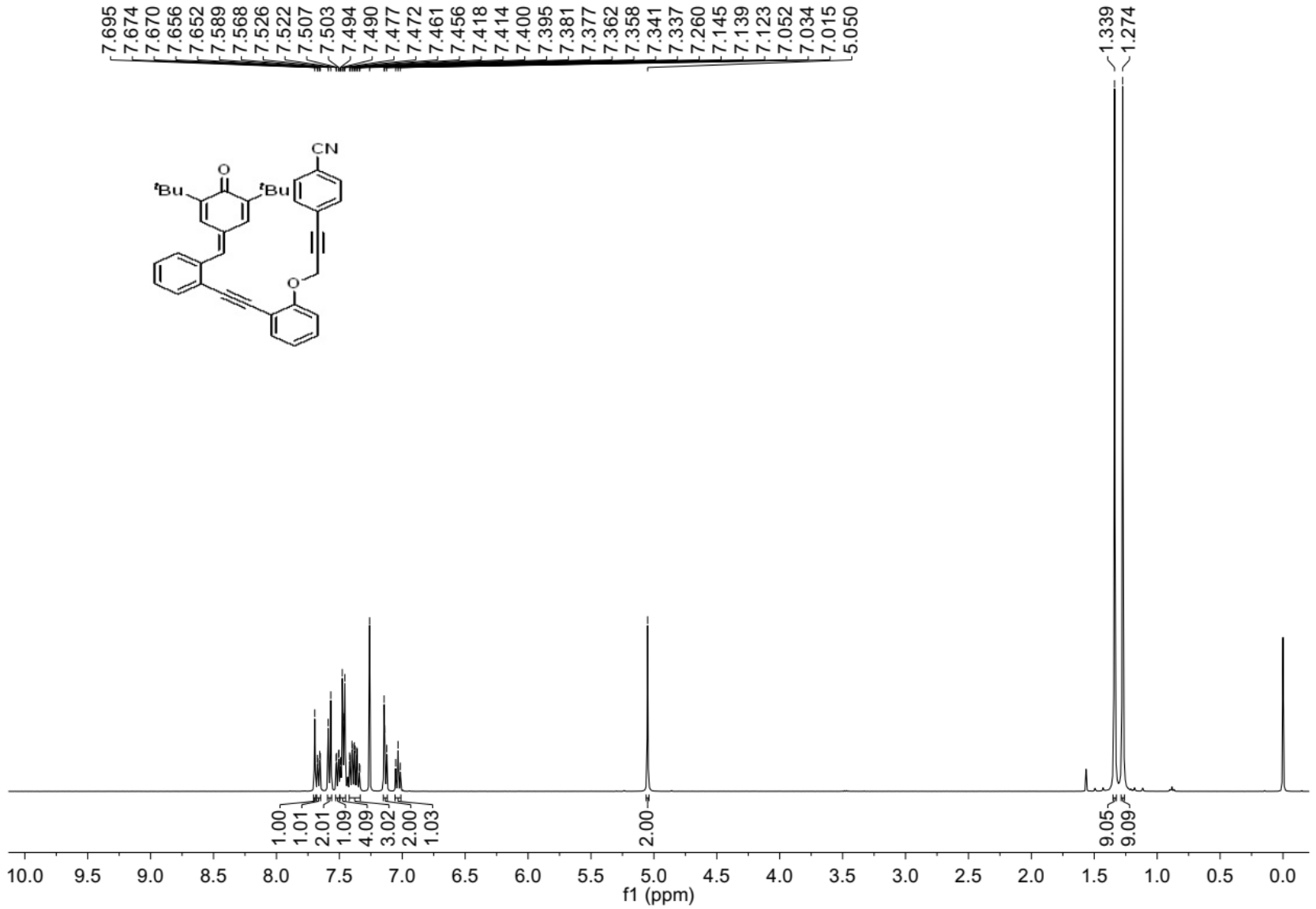
^{13}C NMR Spectrum of Compound 1j



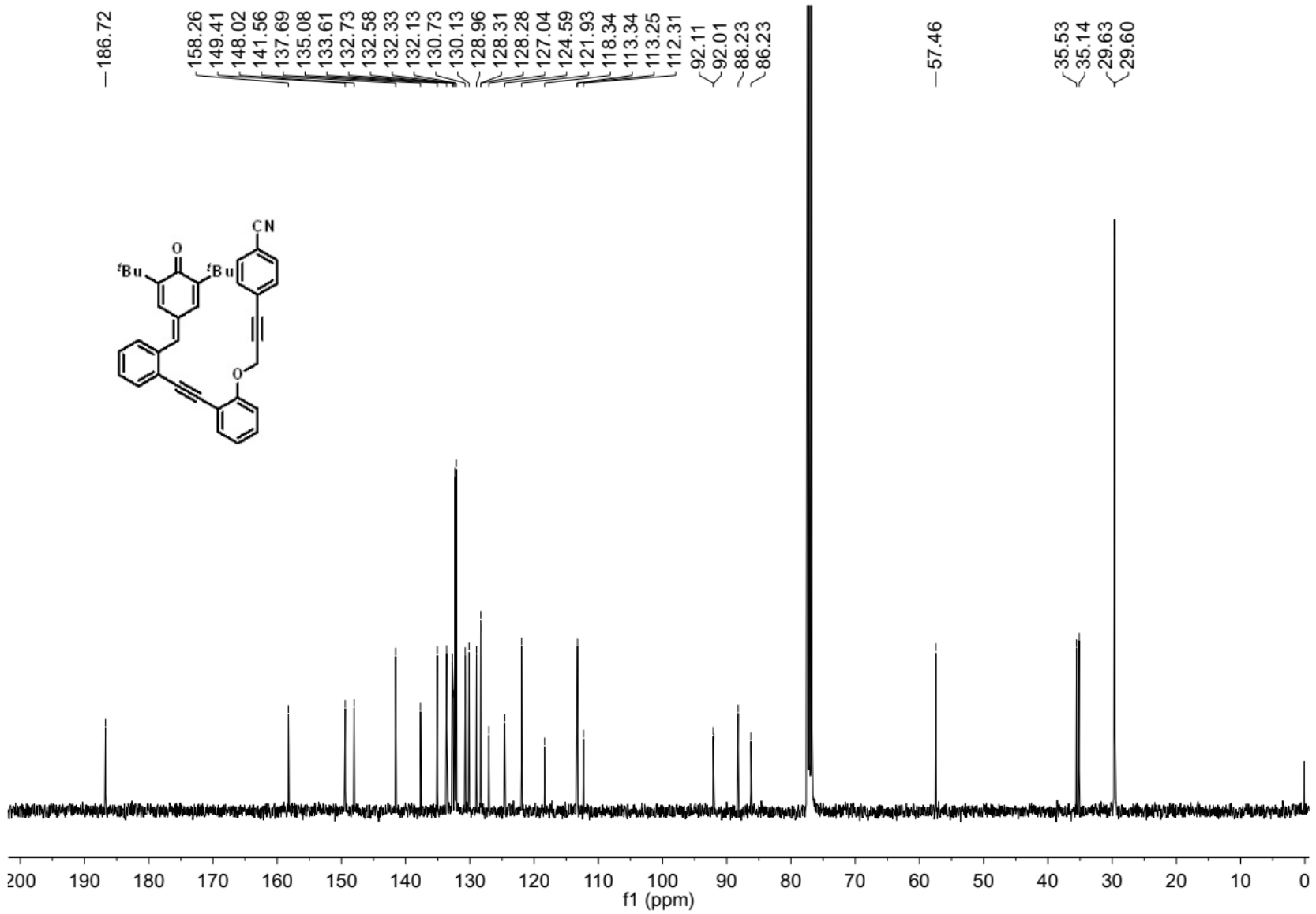
^{1}H NMR Spectrum of Compound 1k



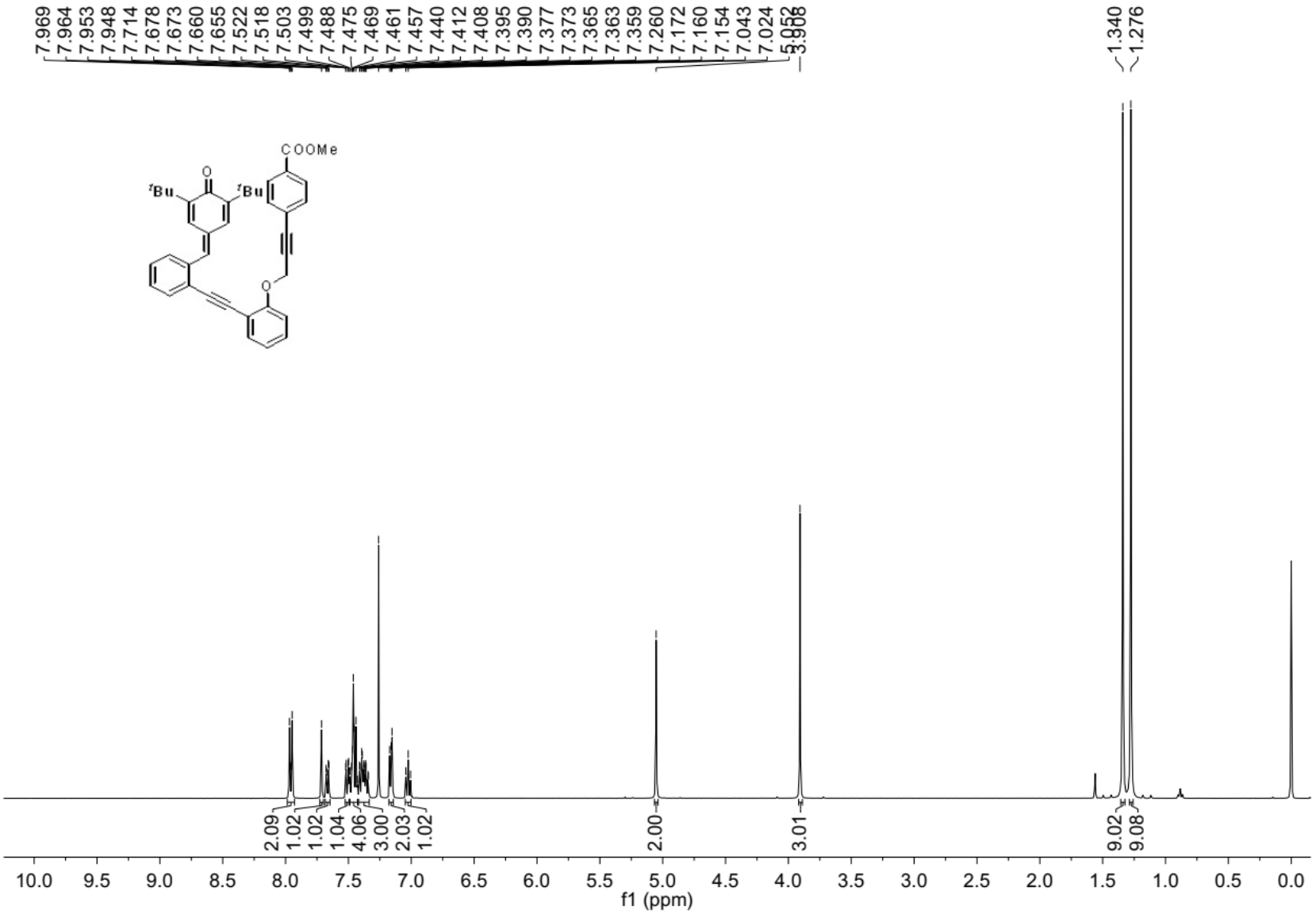
^{13}C NMR Spectrum of Compound 1k



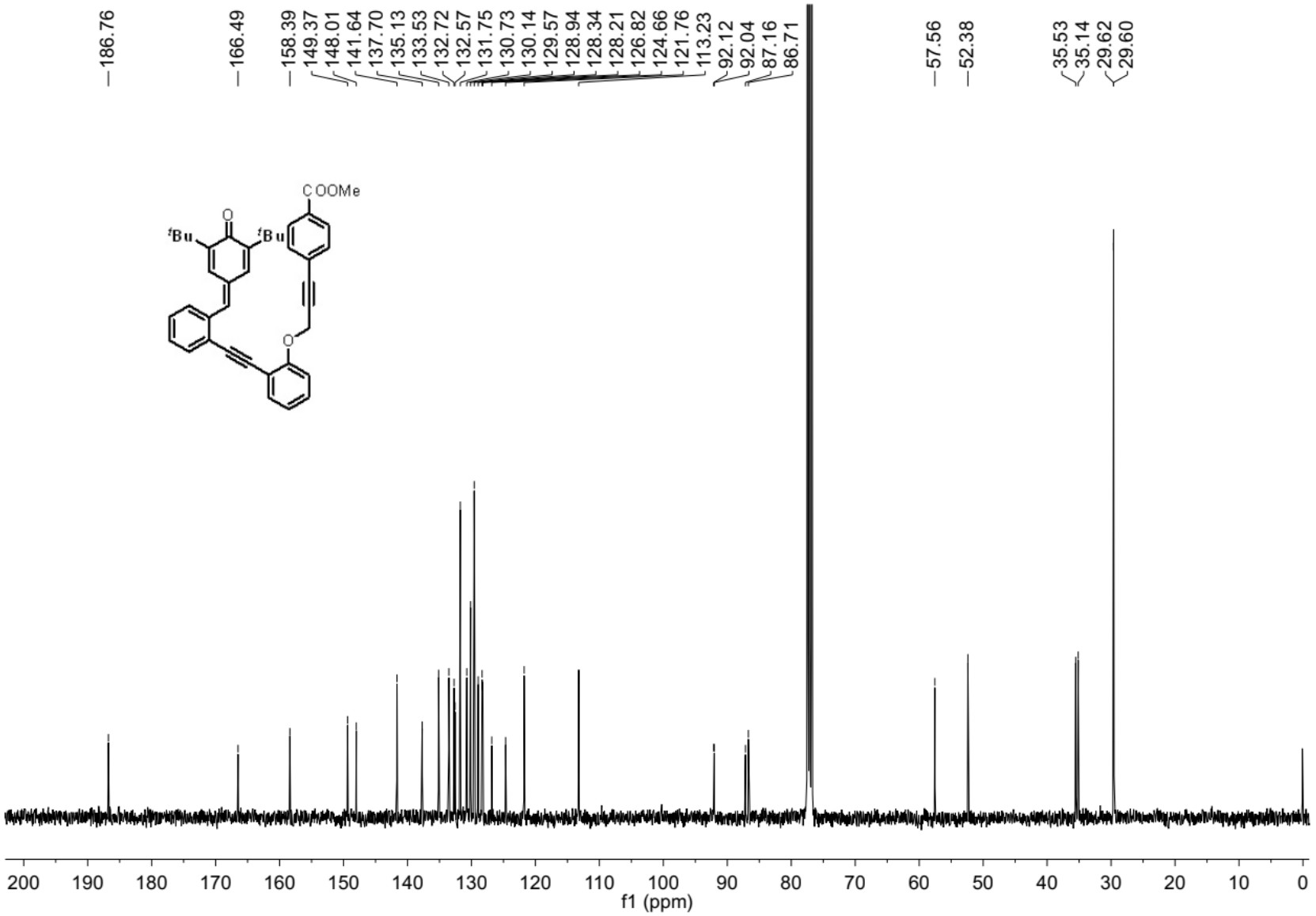
^{1}H NMR Spectrum of Compound 1l



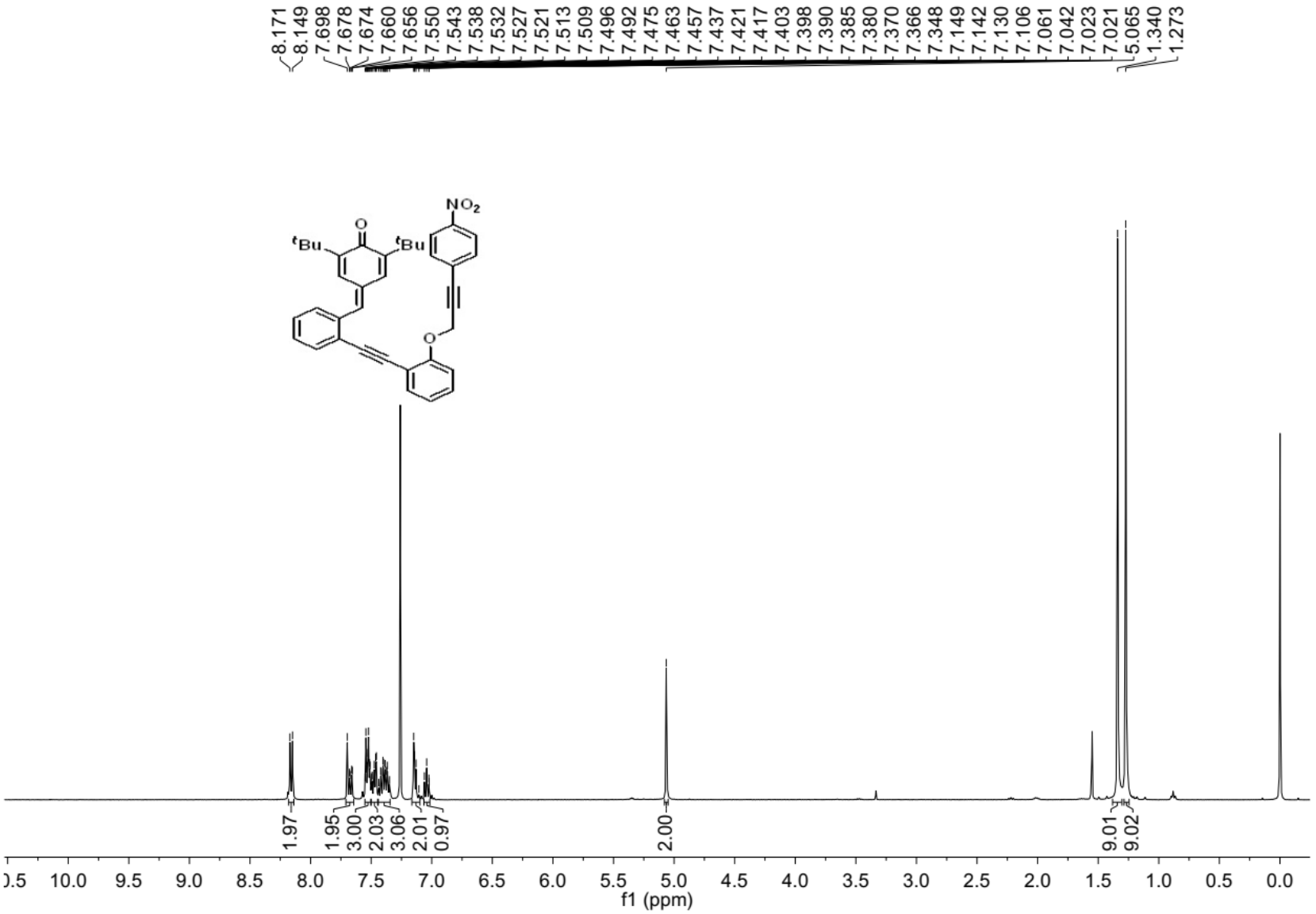
^{13}C NMR Spectrum of Compound 1l



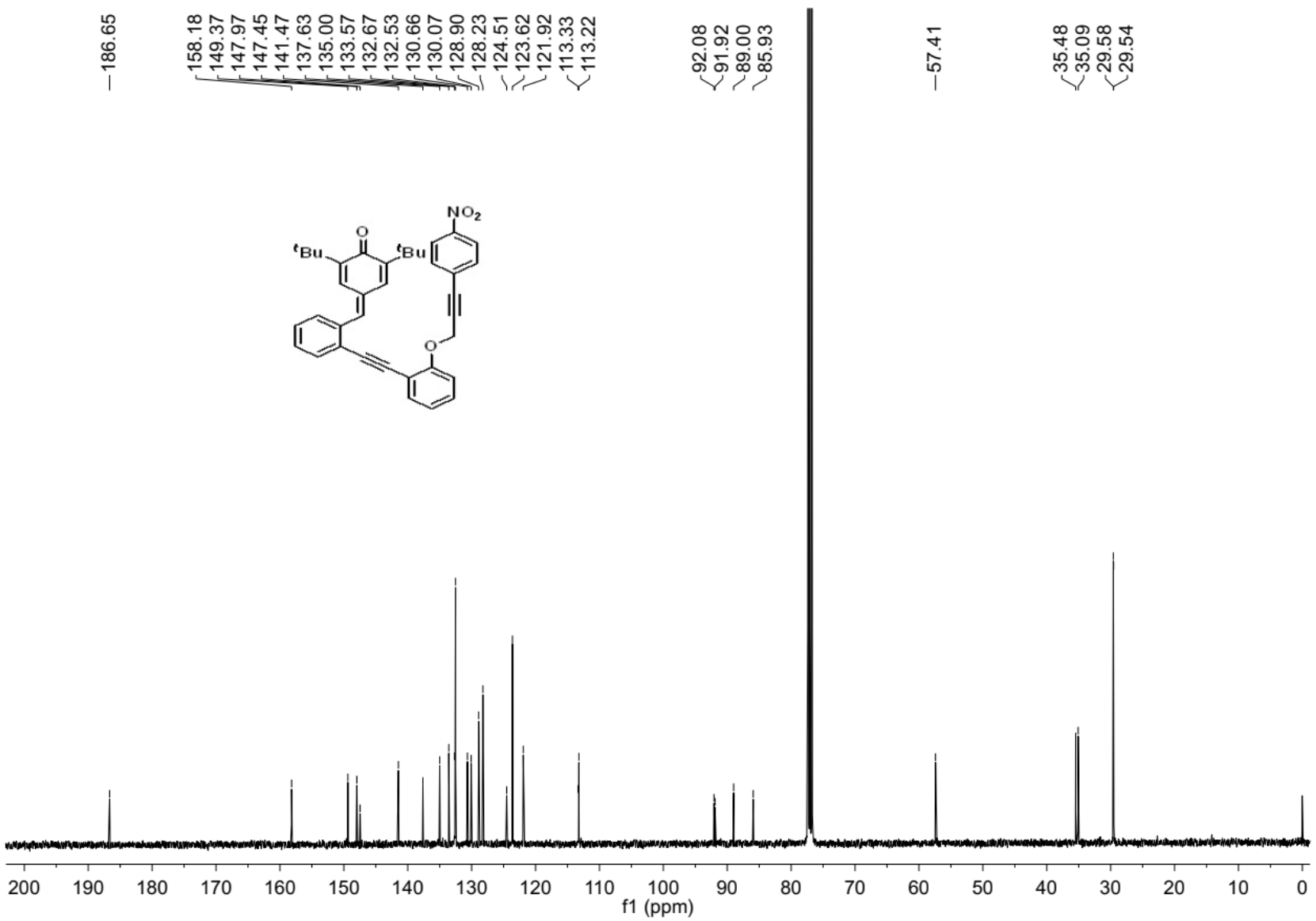
^{1}H NMR Spectrum of Compound 1m



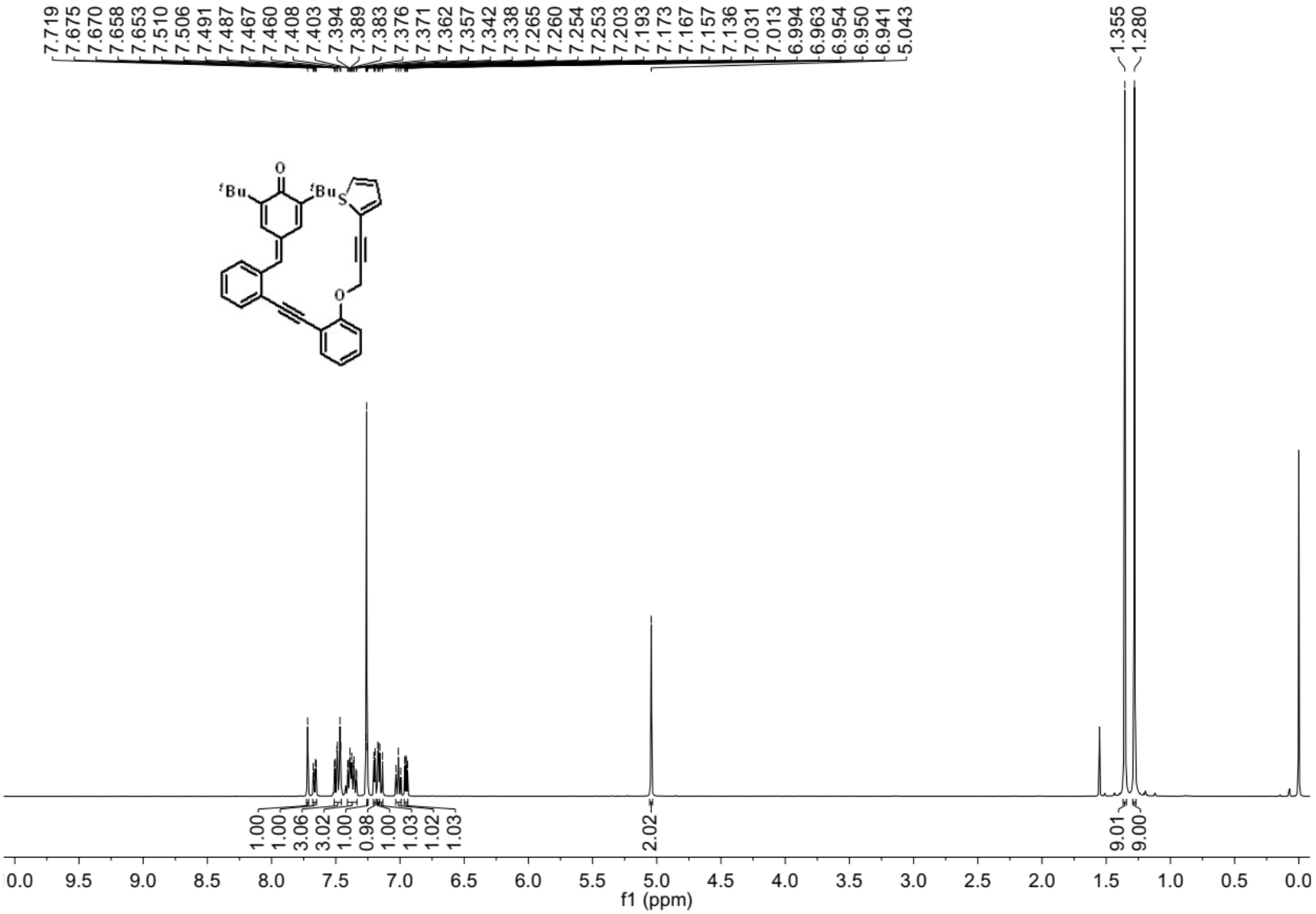
^{13}C NMR Spectrum of Compound 1m



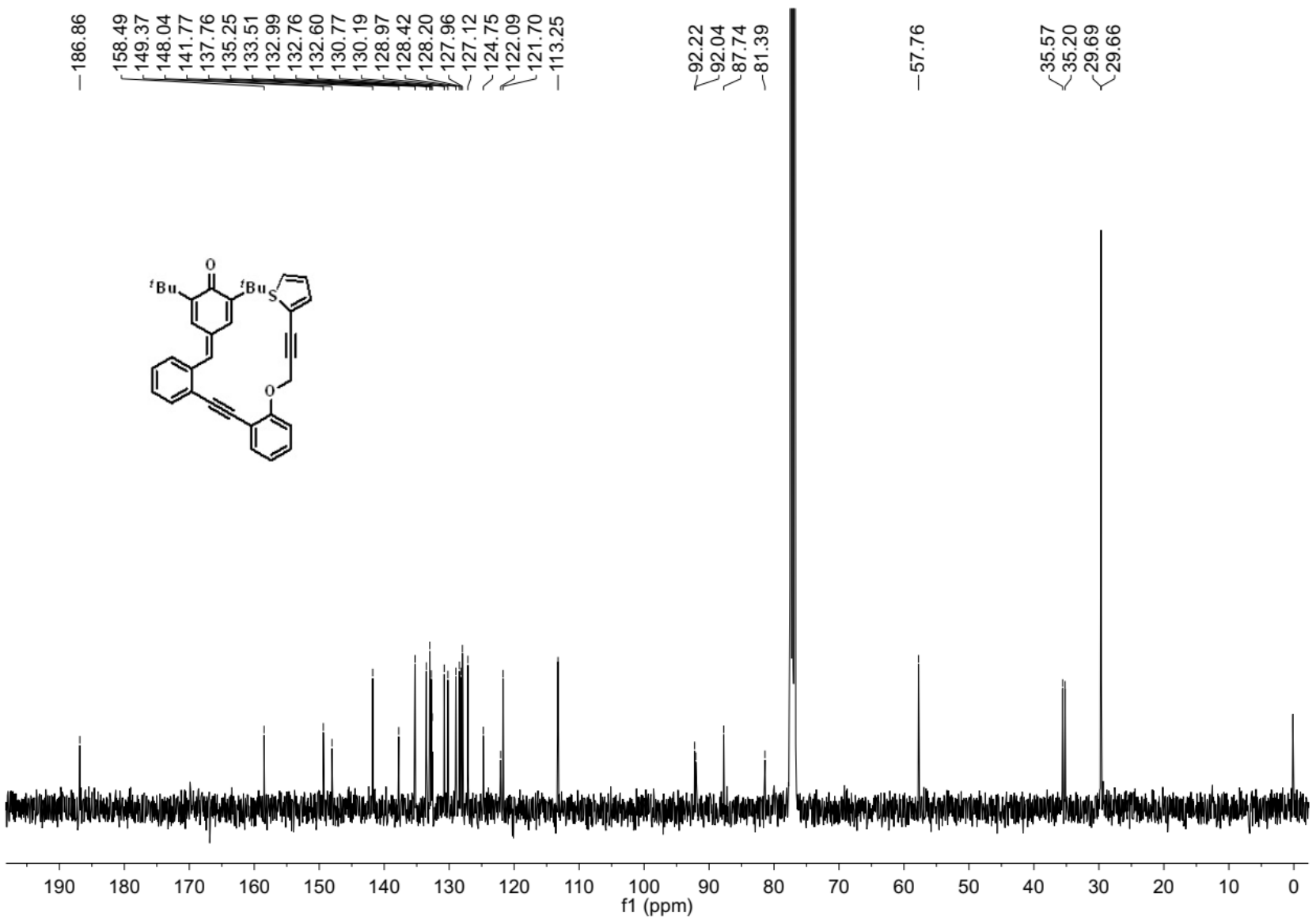
^{1}H NMR Spectrum of Compound 1n



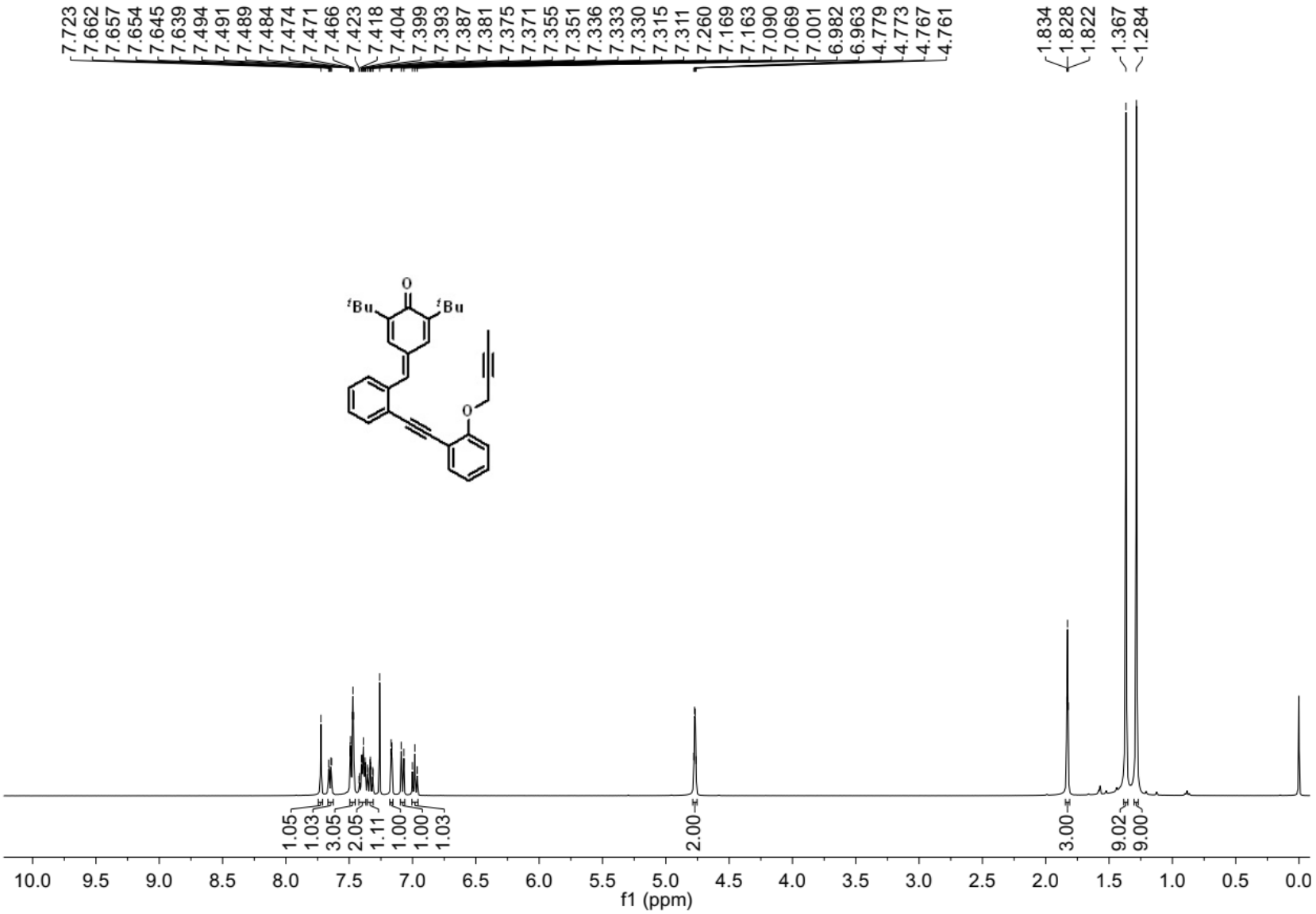
^{13}C NMR Spectrum of Compound 1n



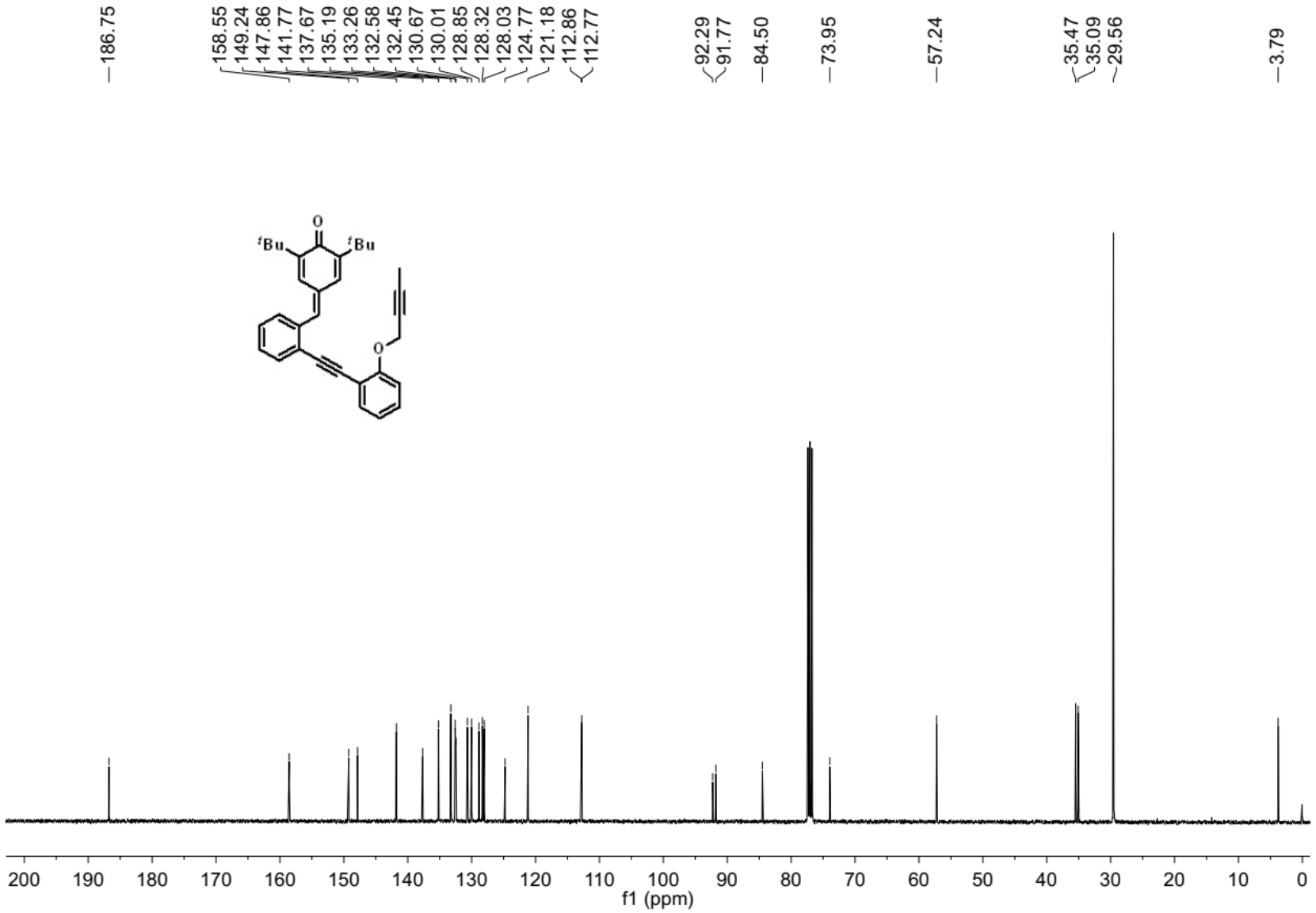
^{1}H NMR Spectrum of Compound 1o



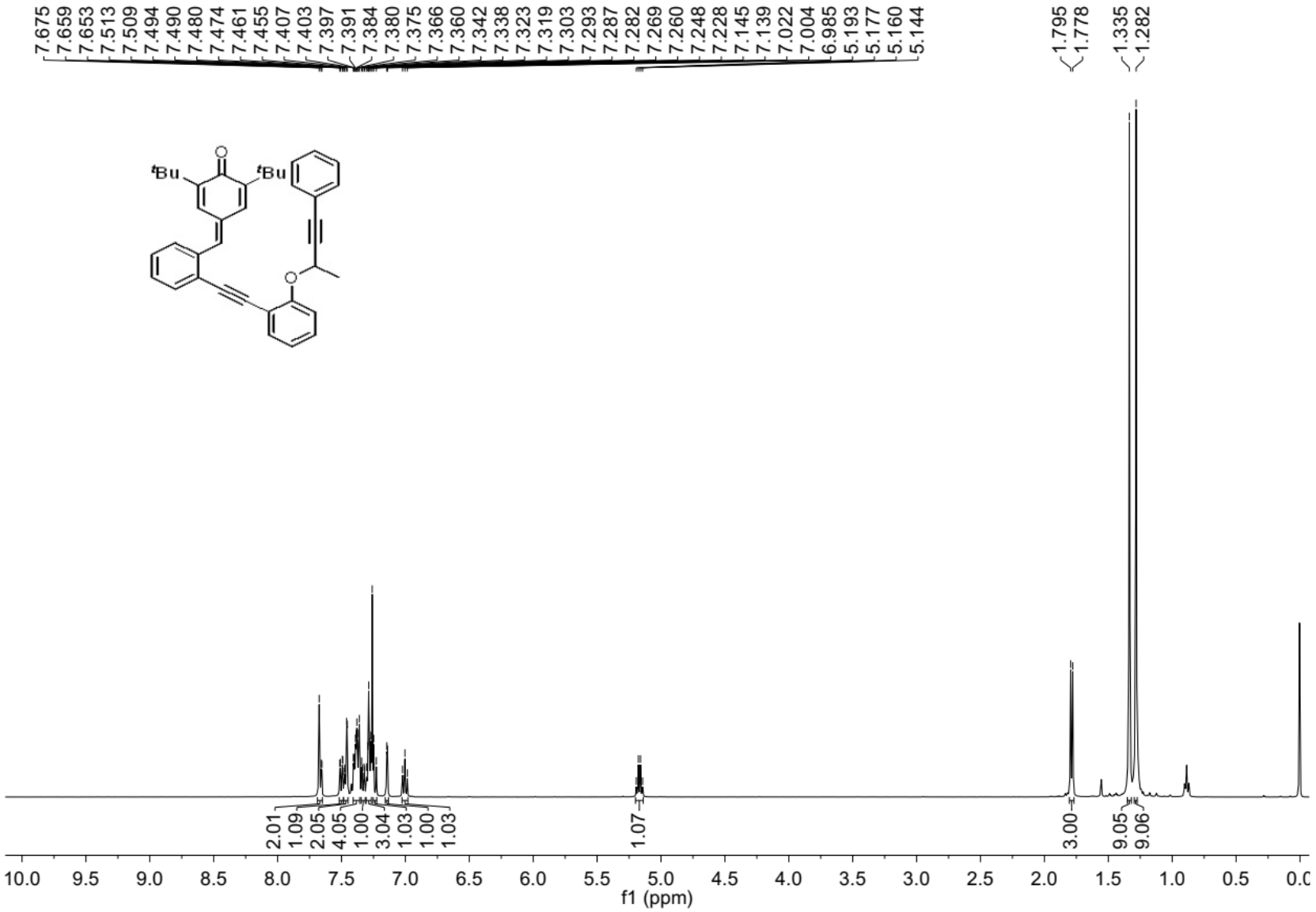
^{13}C NMR Spectrum of Compound 1o



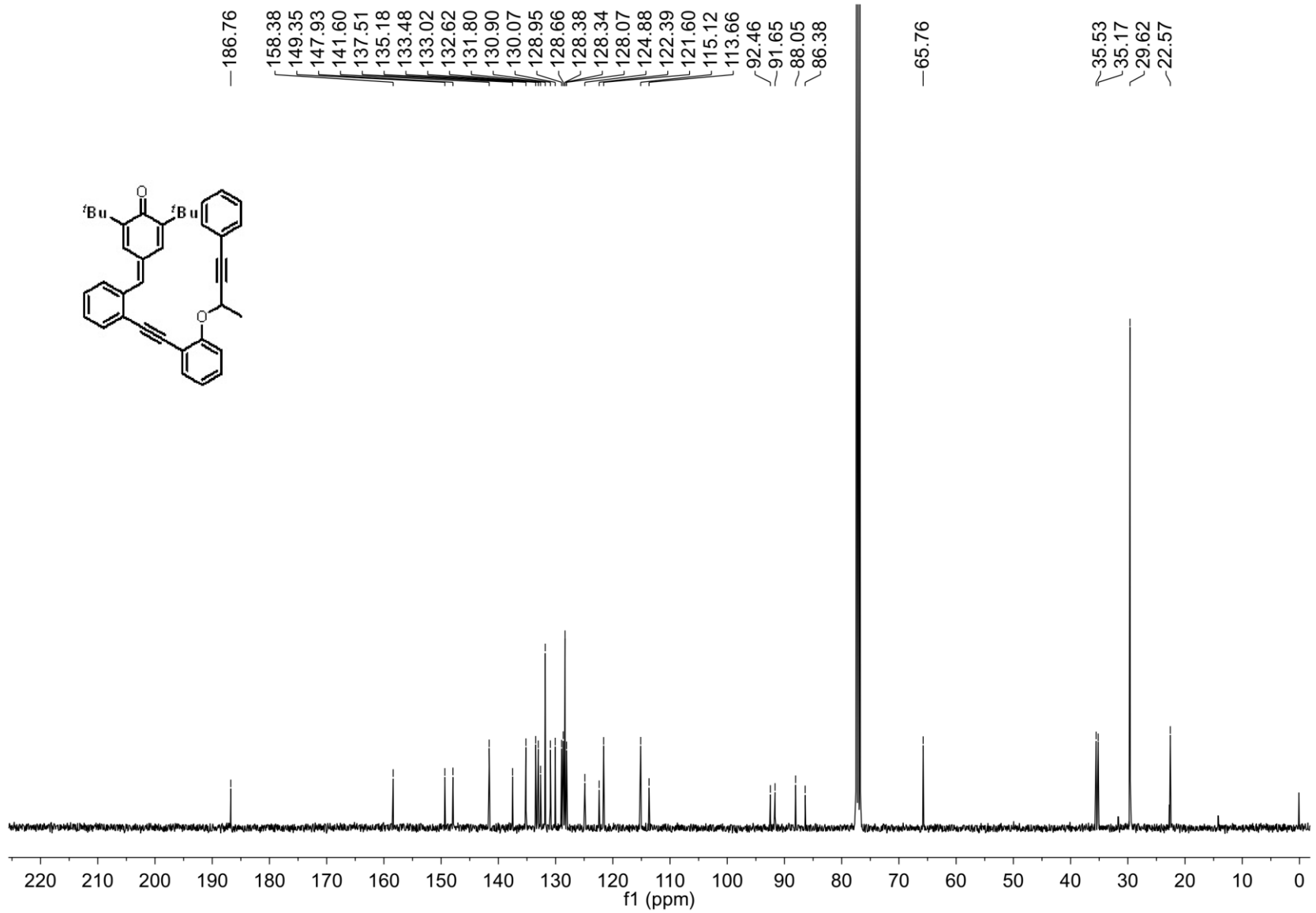
^{1}H NMR Spectrum of Compound 1p



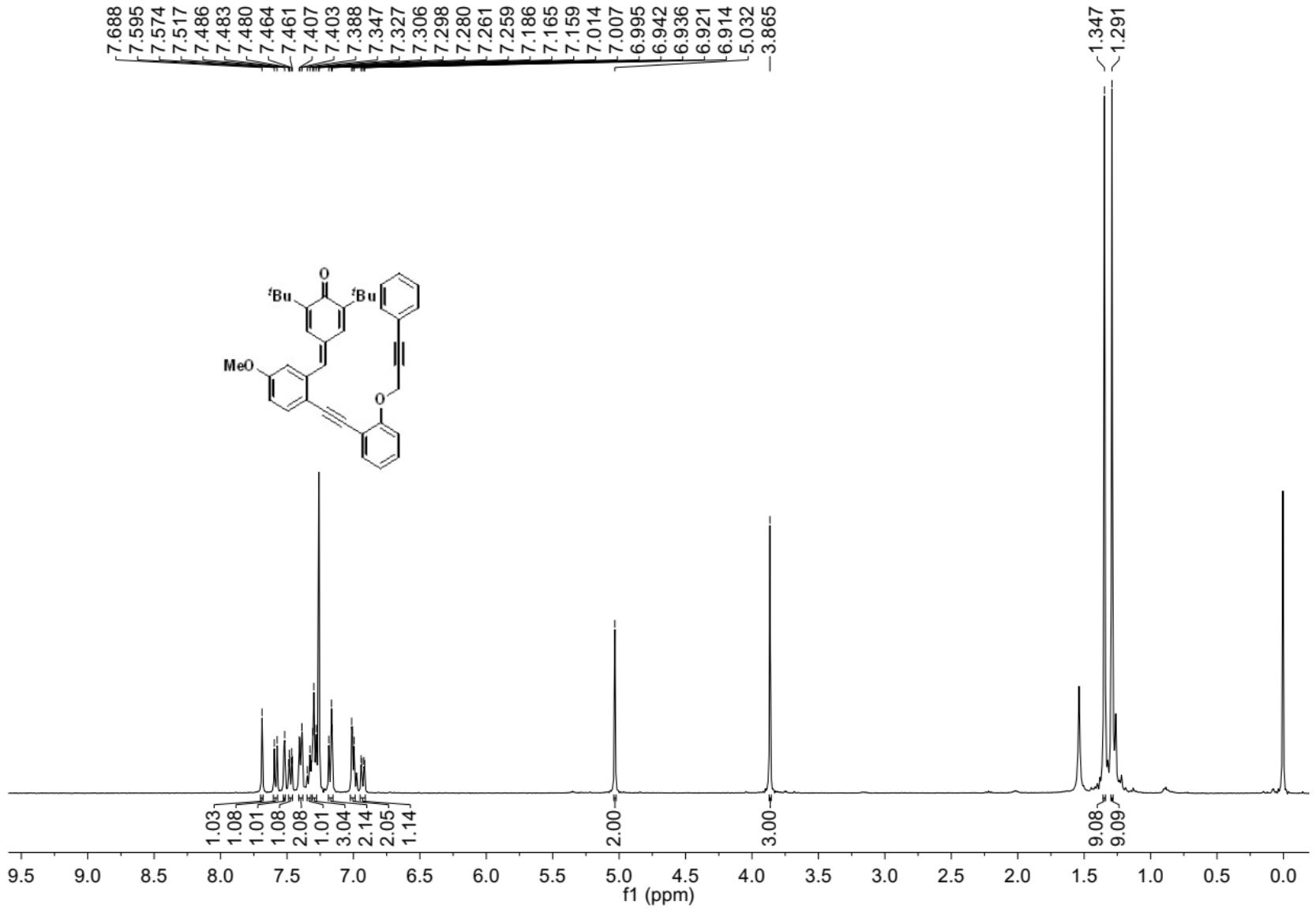
^{13}C NMR Spectrum of Compound 1p



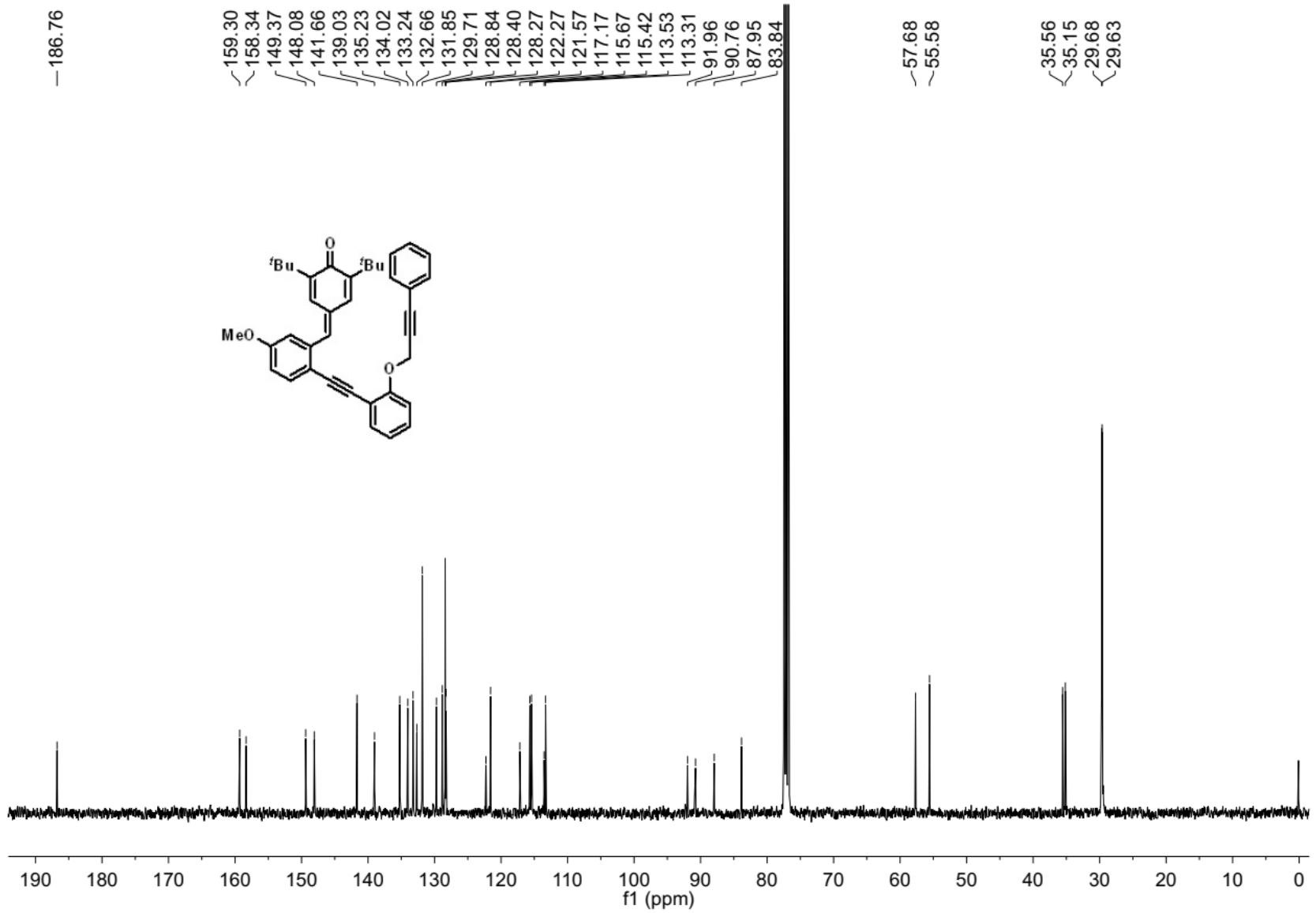
^{1}H NMR Spectrum of Compound 1q



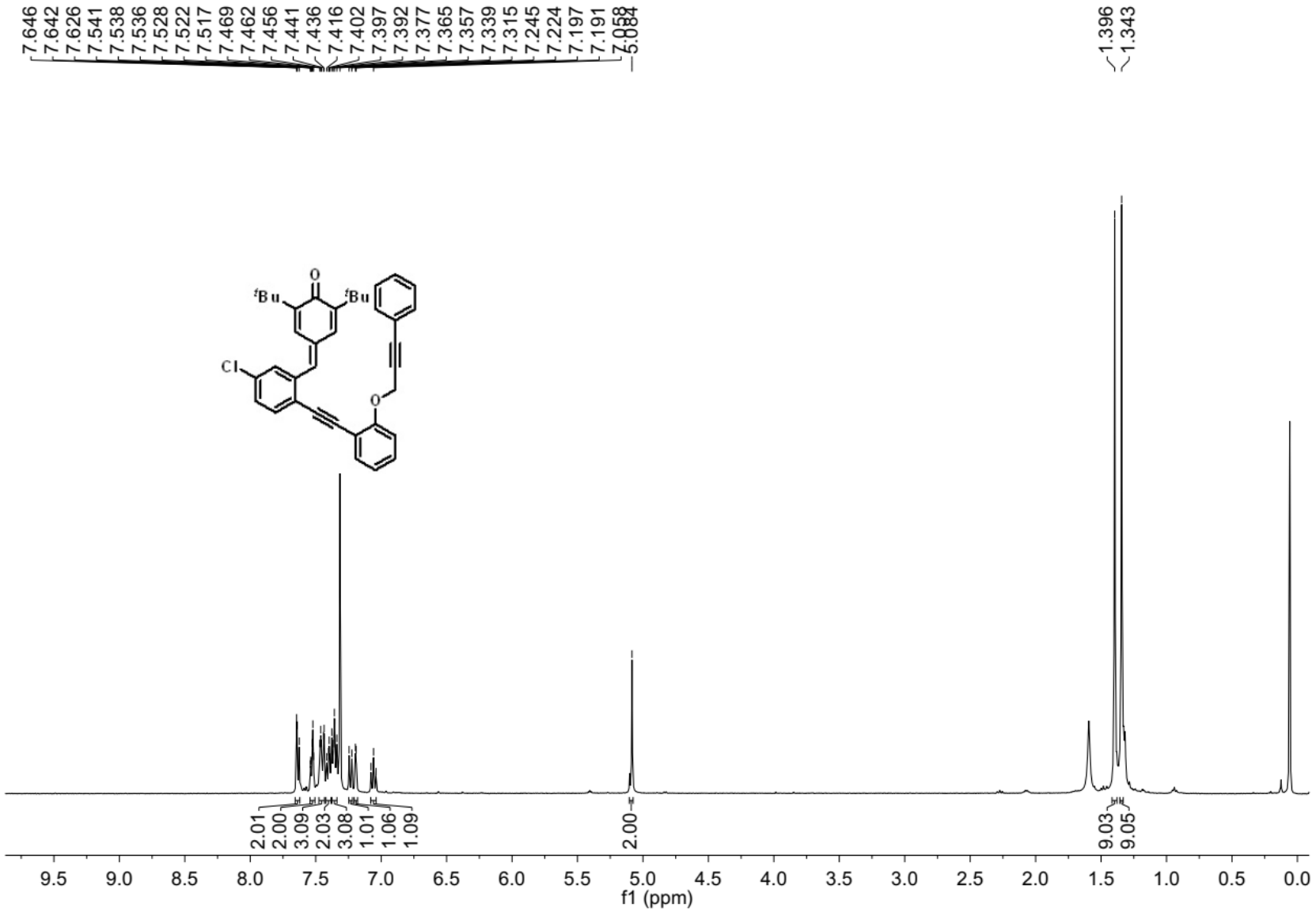
^{13}C NMR Spectrum of Compound 1q



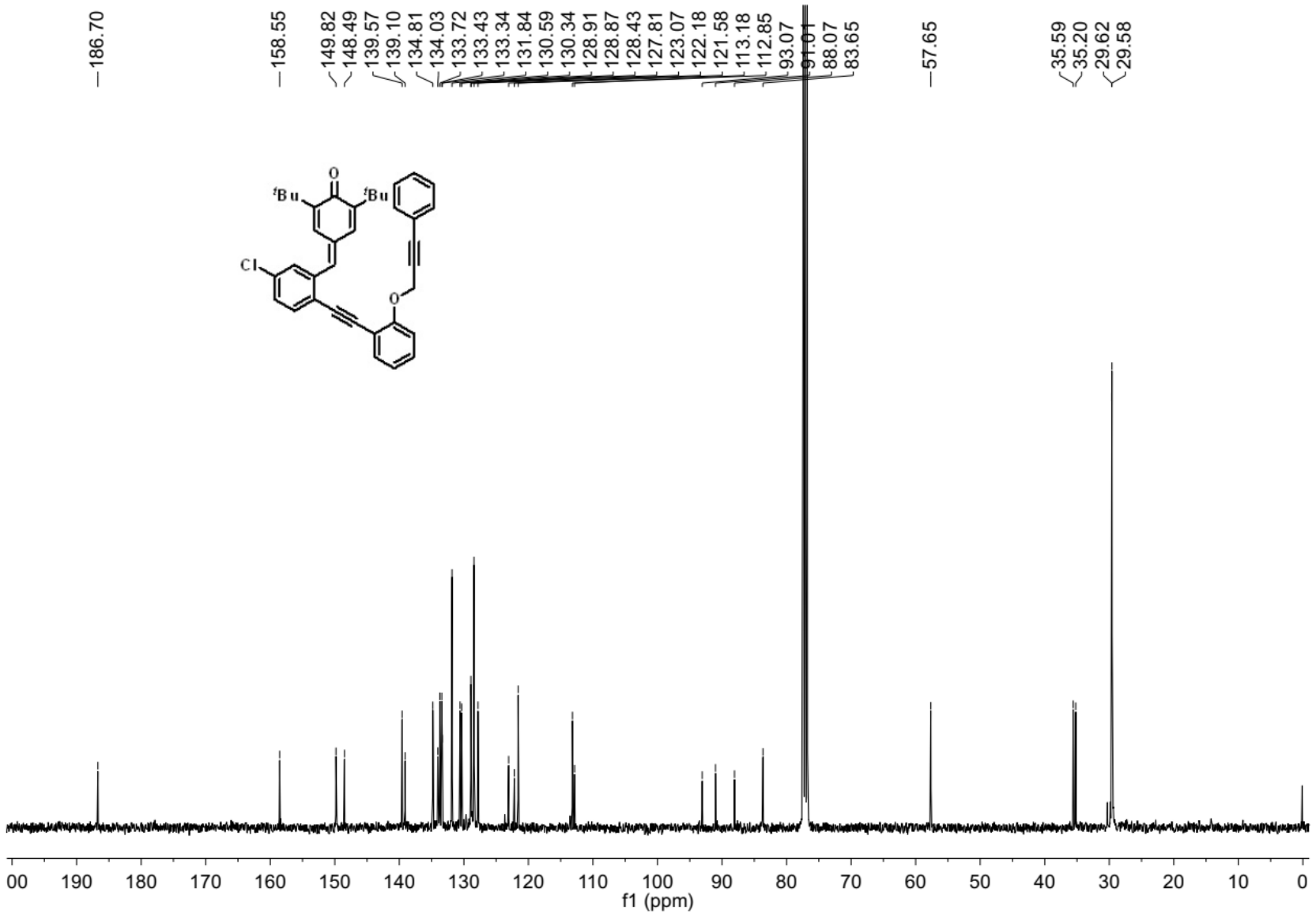
^{1}H NMR Spectrum of Compound 1r



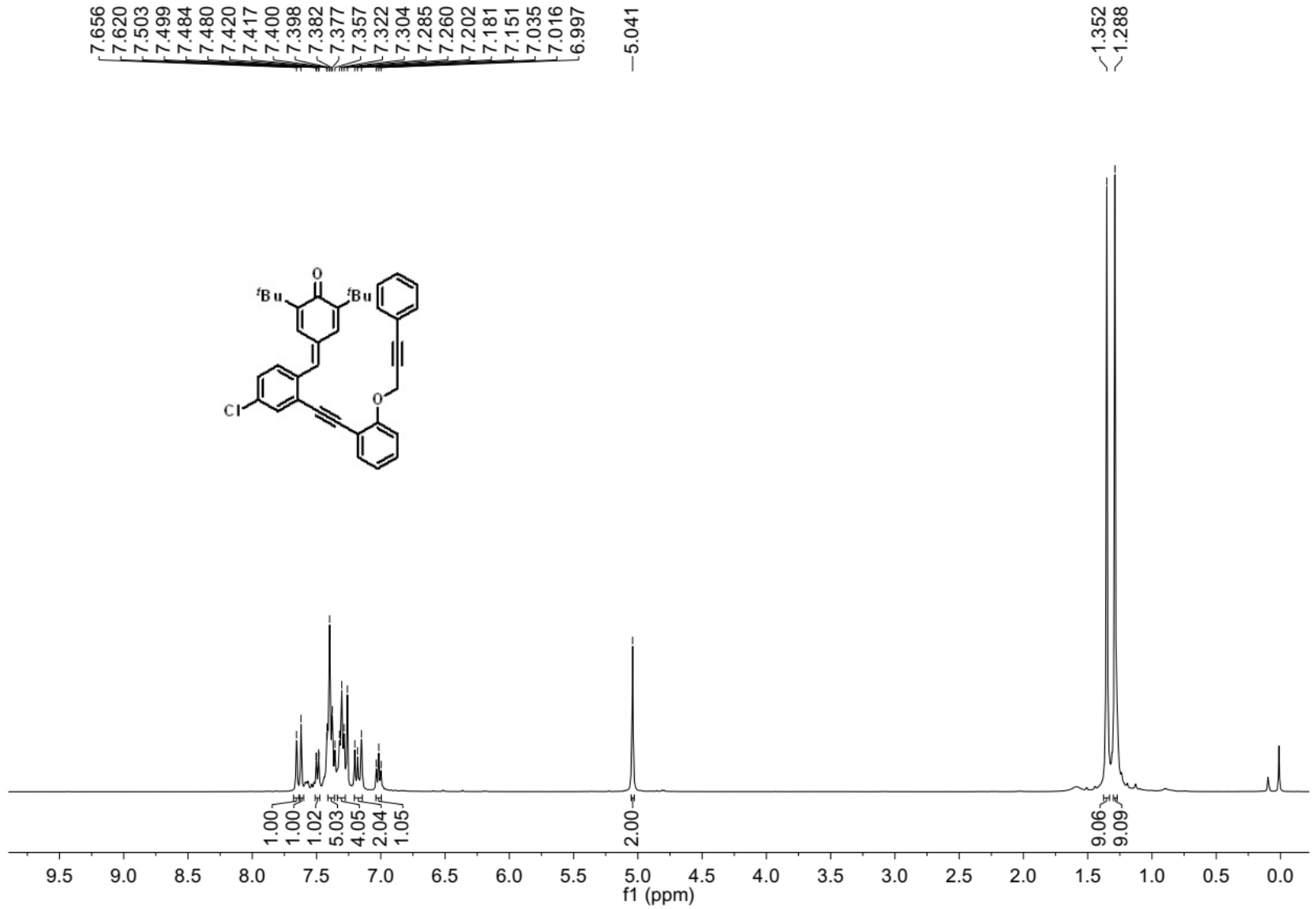
^{13}C NMR Spectrum of Compound 1r



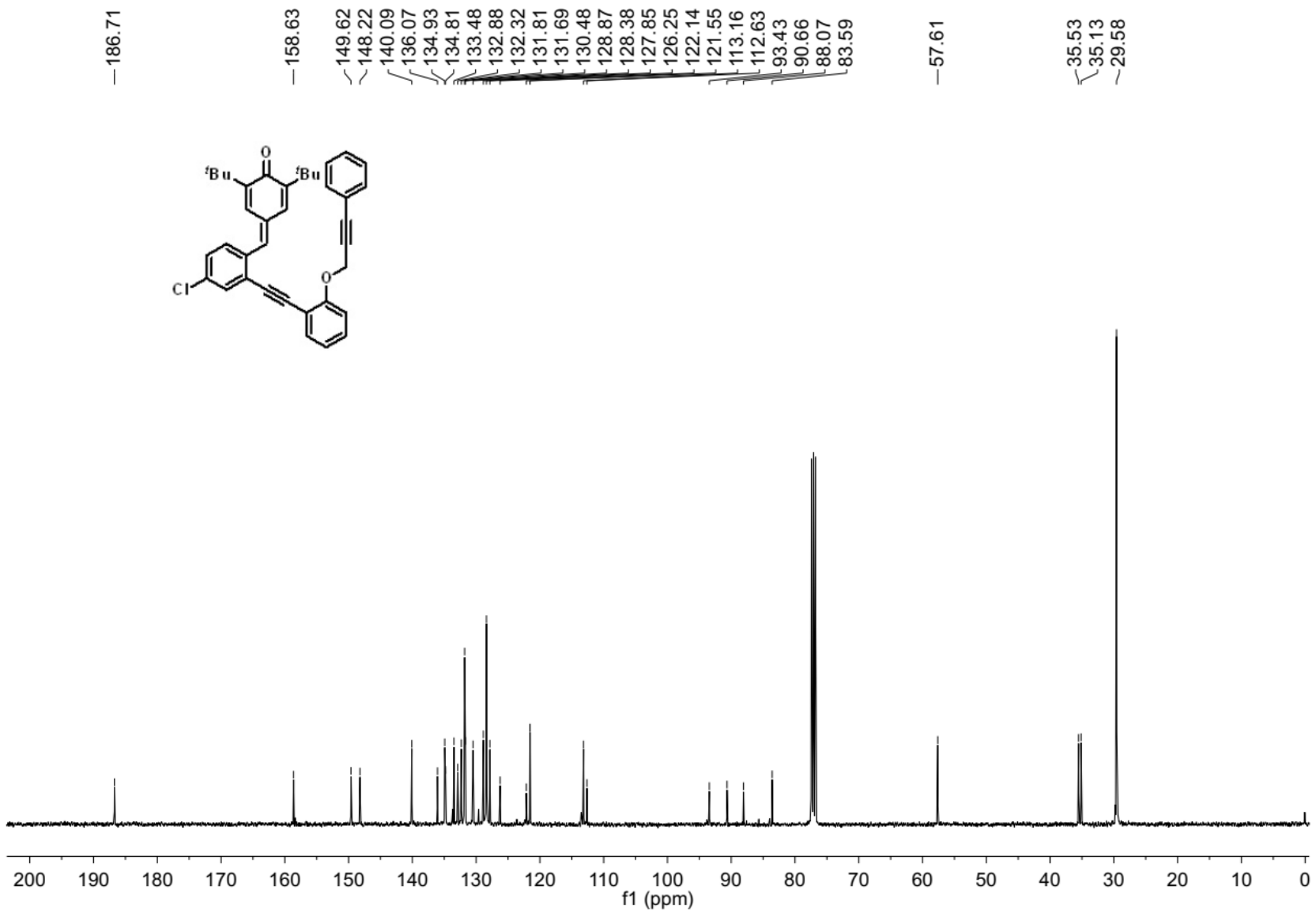
^{1}H NMR Spectrum of Compound 1s



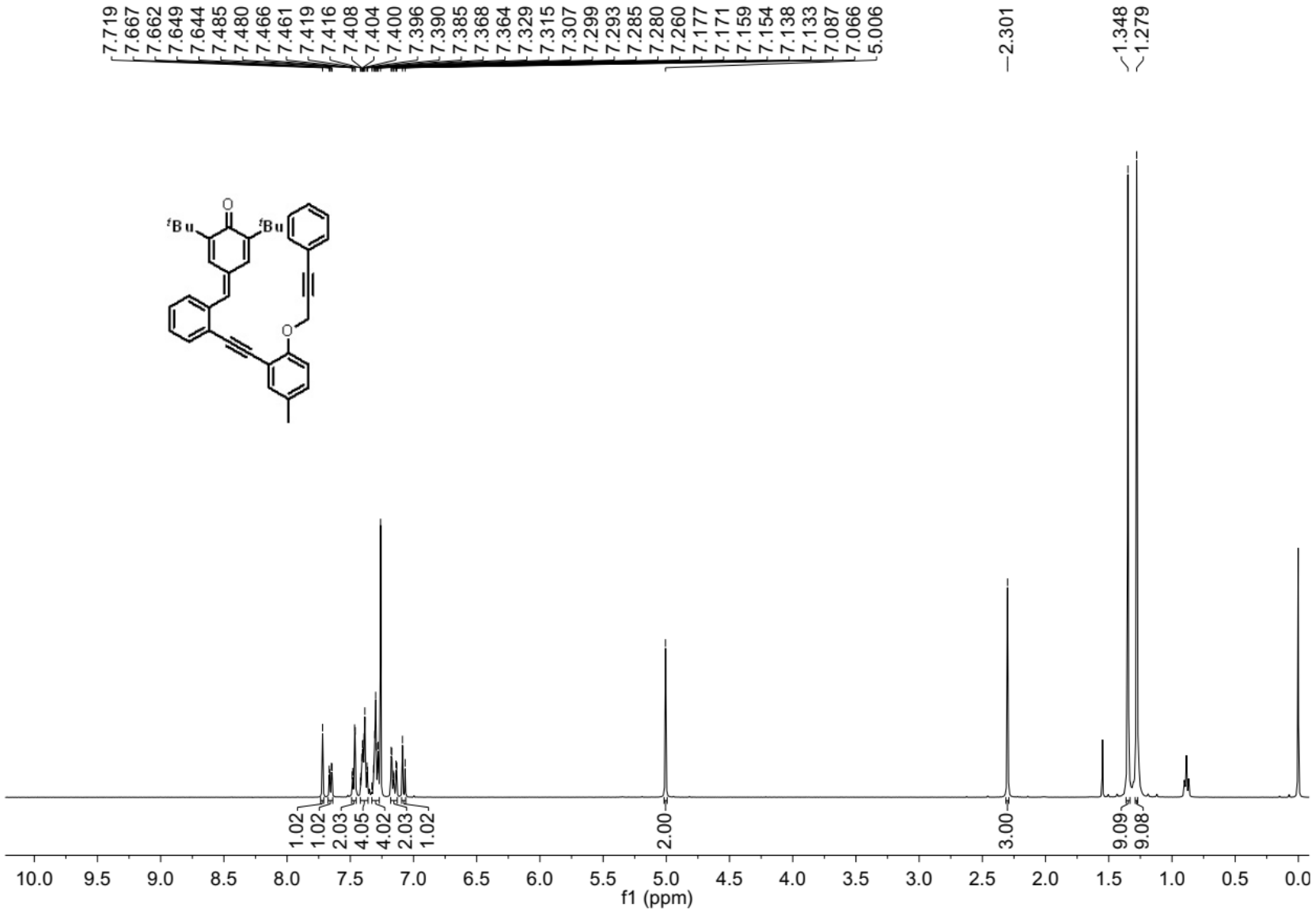
^{13}C NMR Spectrum of Compound 1s



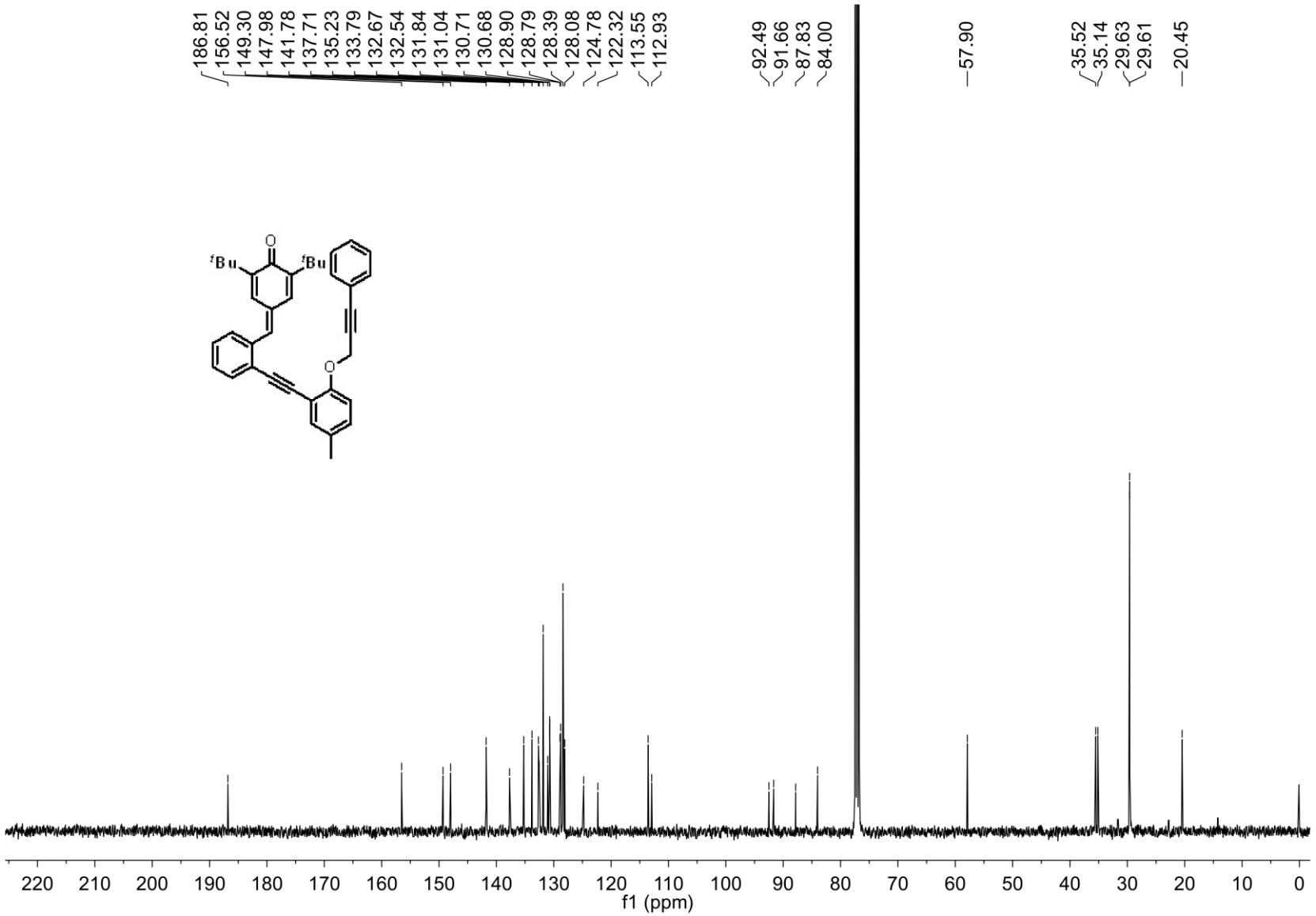
^{1}H NMR Spectrum of Compound 1t



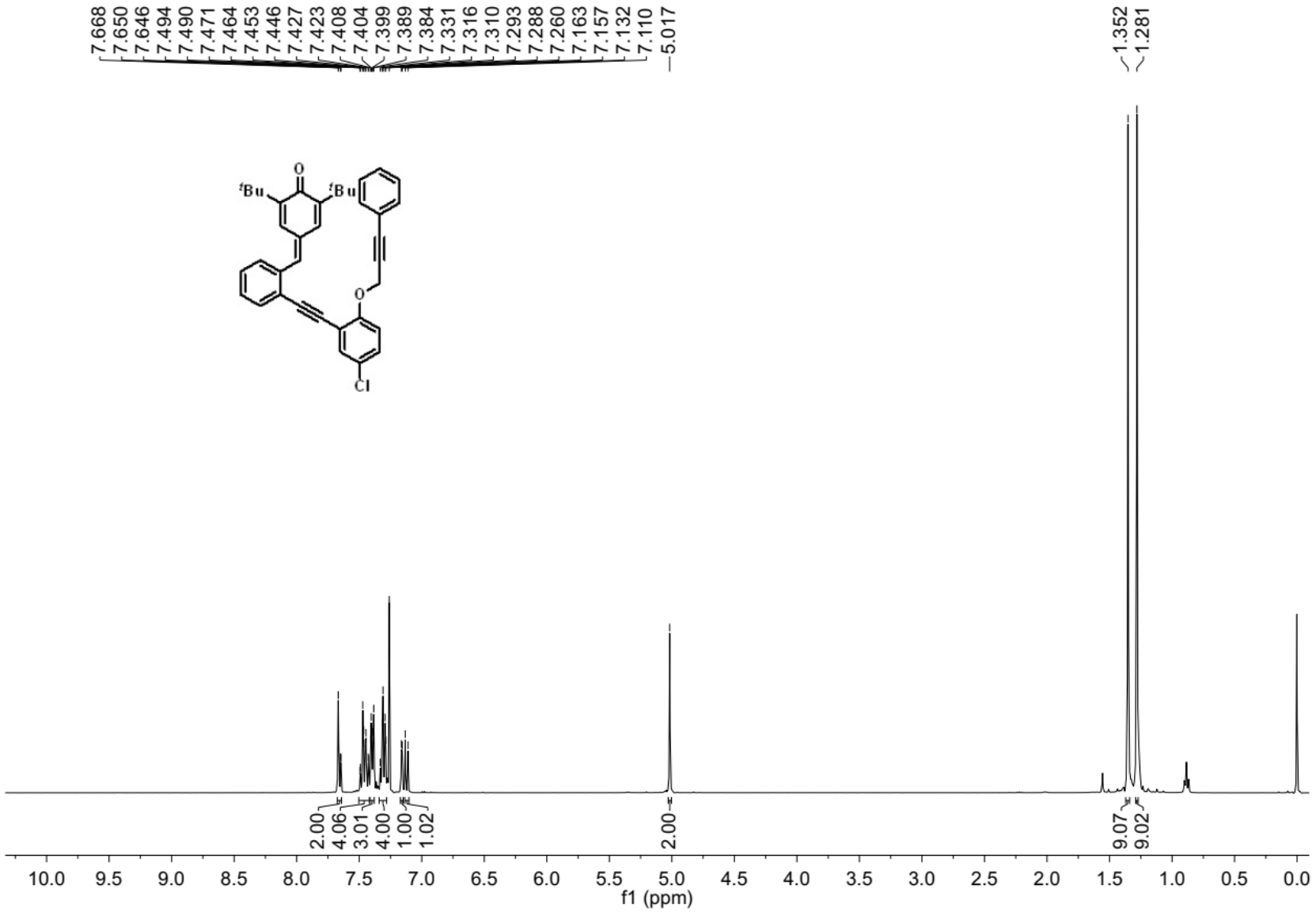
^{13}C NMR Spectrum of Compound 1t



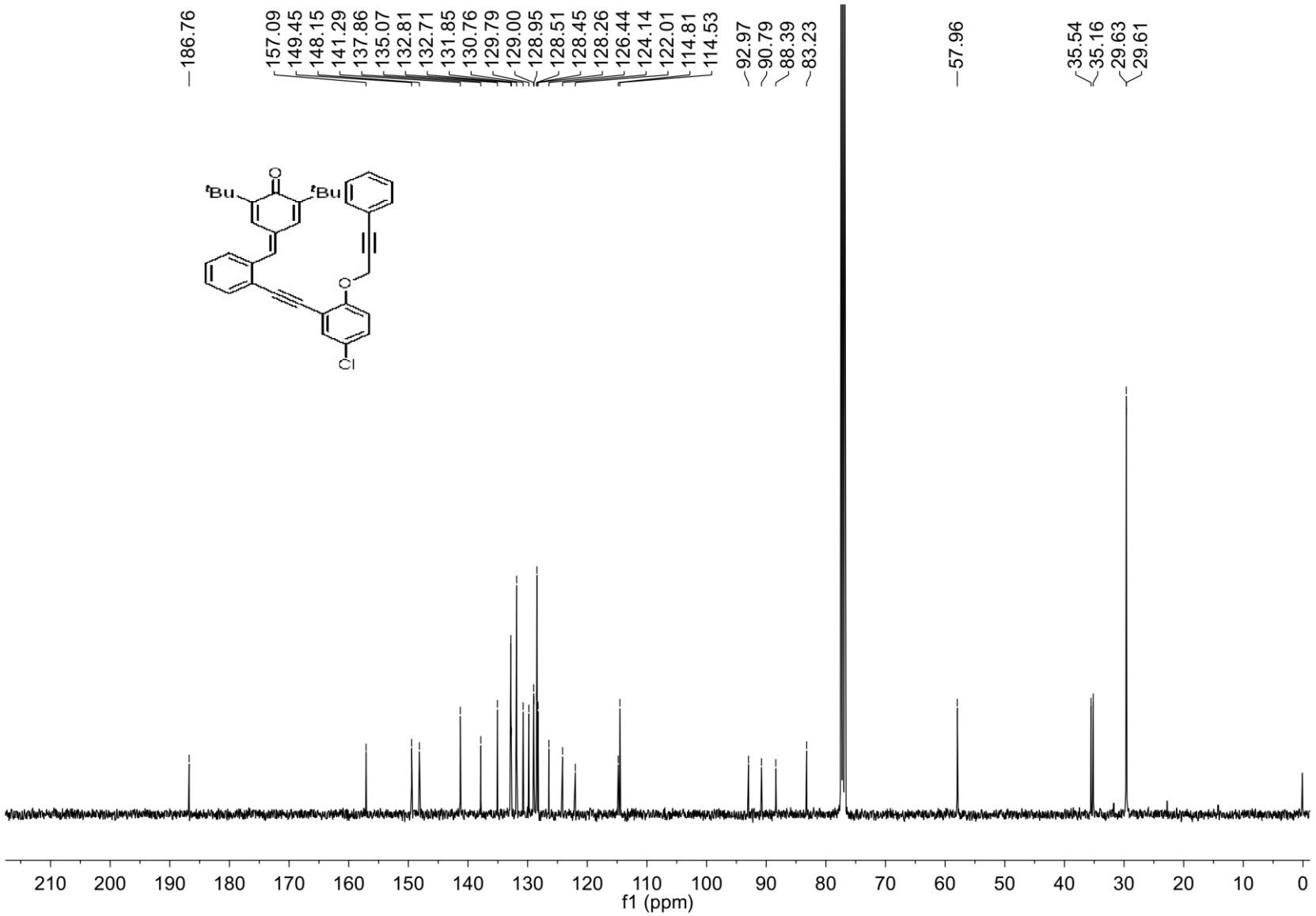
^{1}H NMR Spectrum of Compound 1u



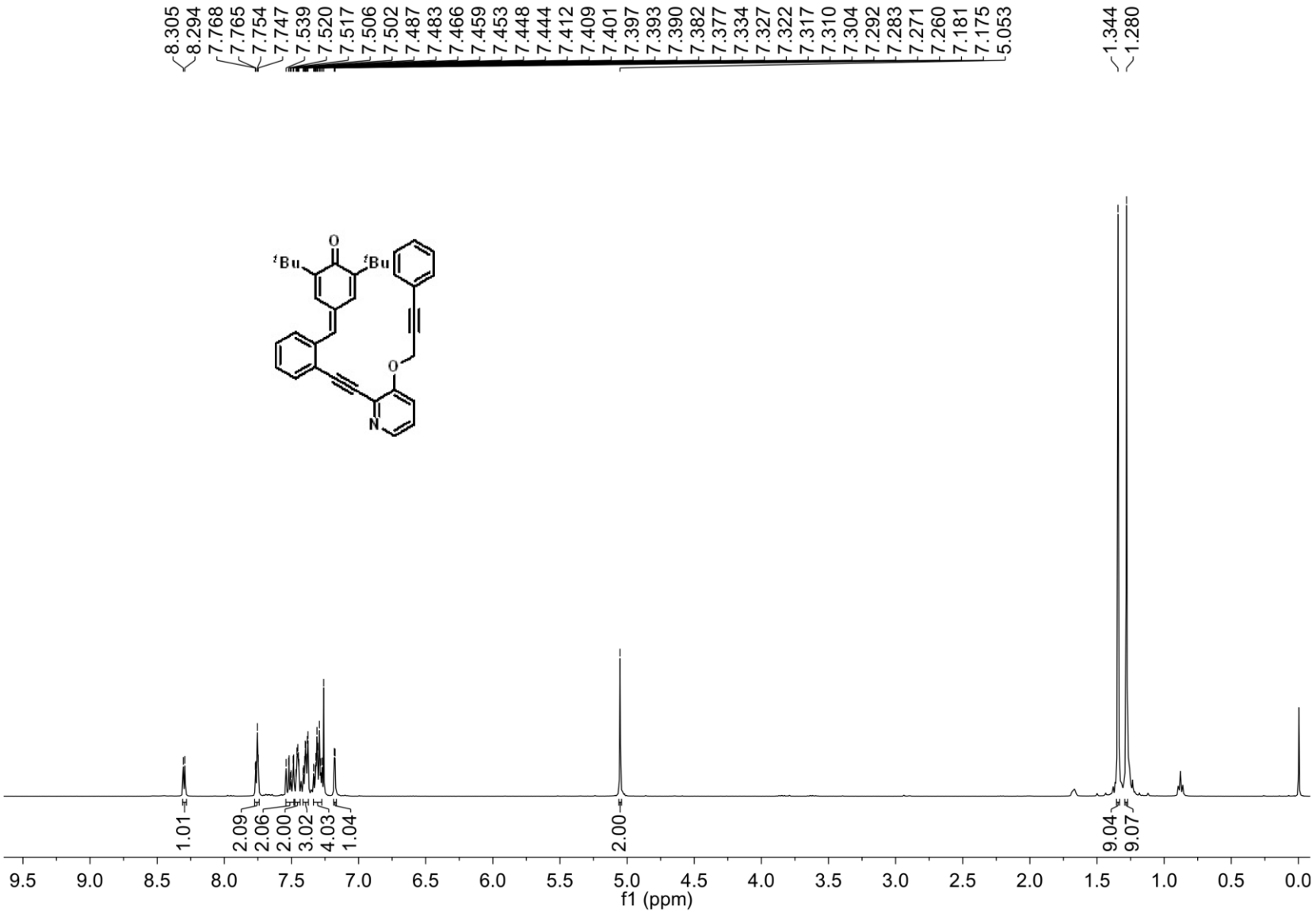
^{13}C NMR Spectrum of Compound 1u



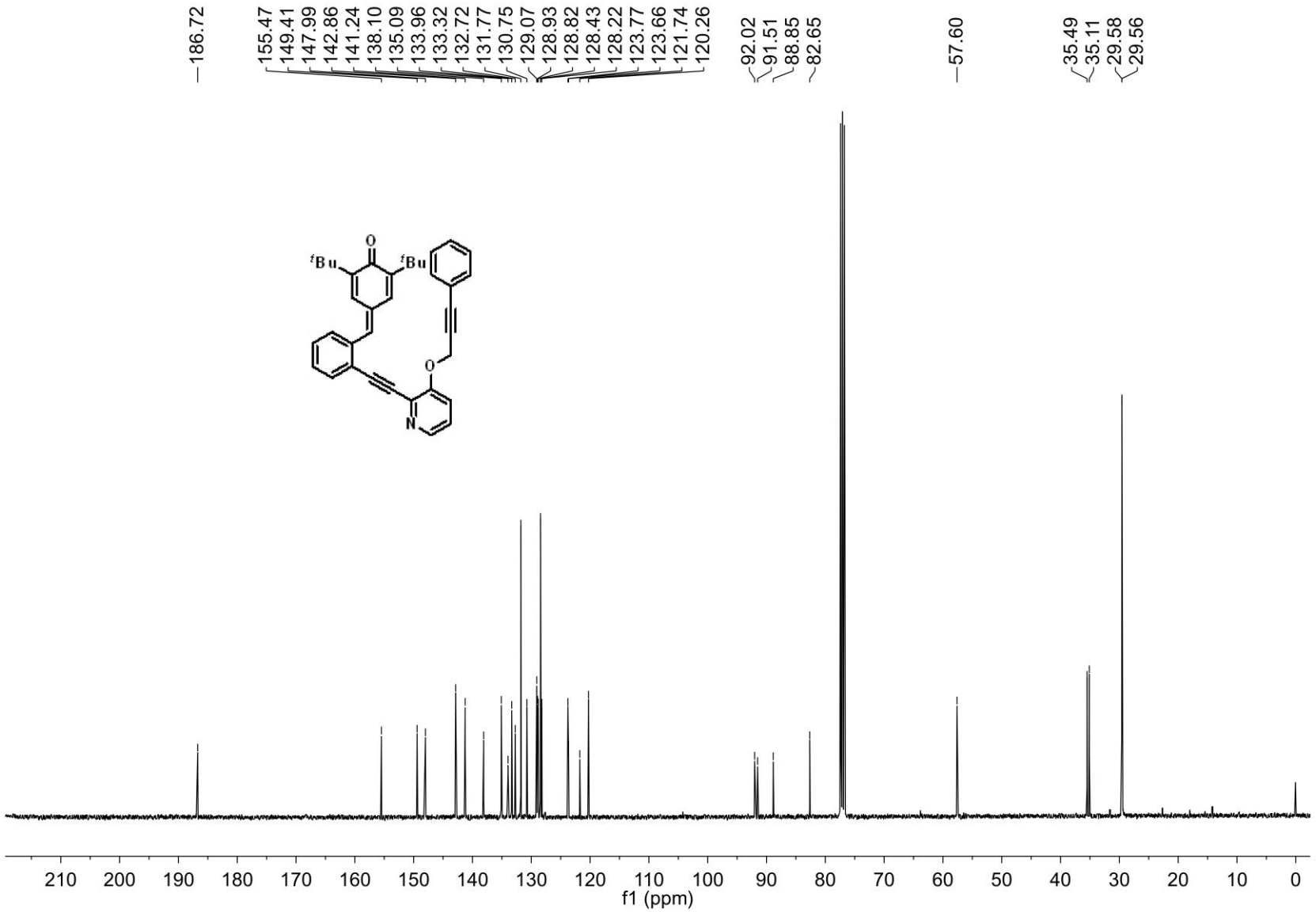
^{1}H NMR Spectrum of Compound 1v



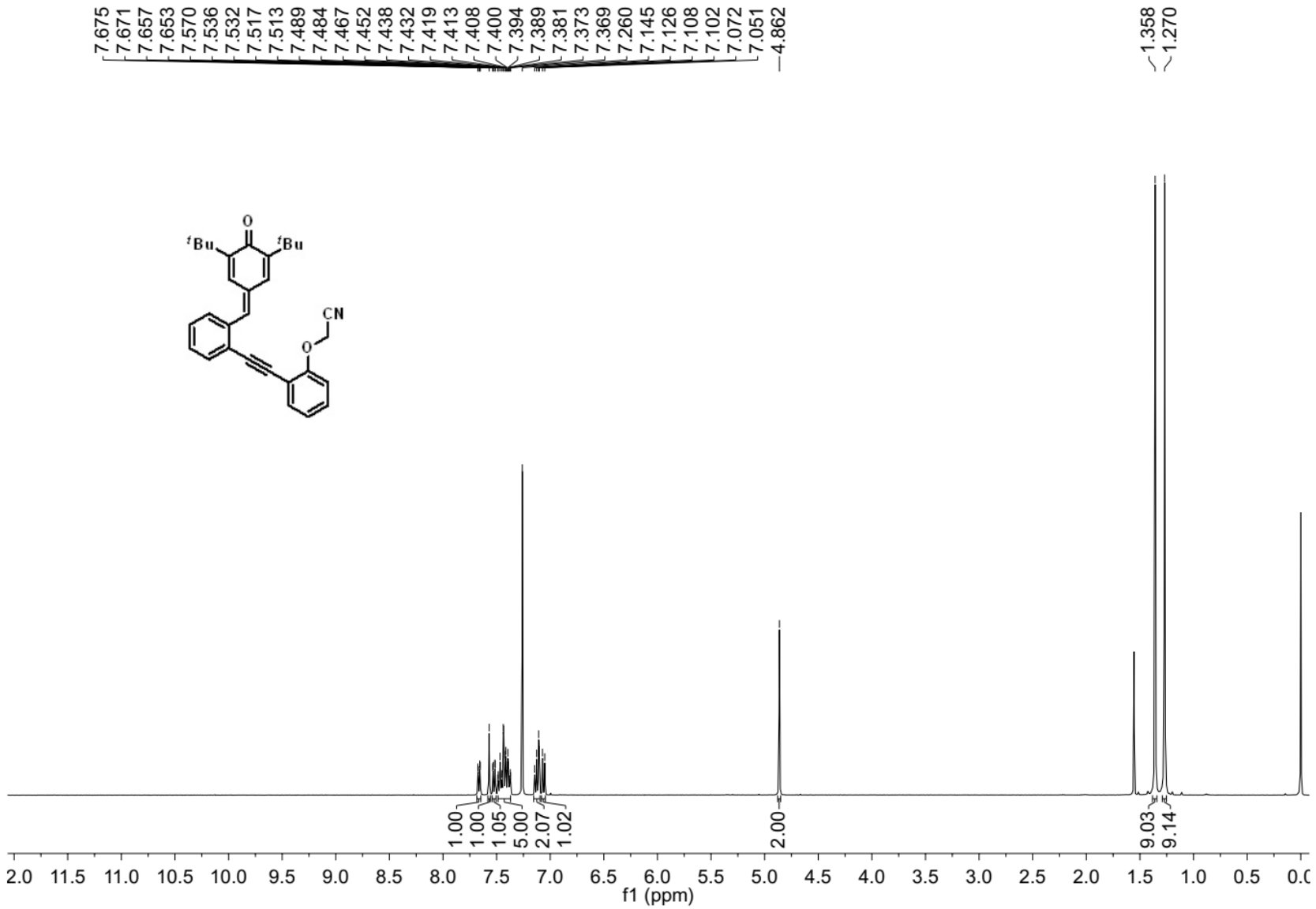
^{13}C NMR Spectrum of Compound 1v



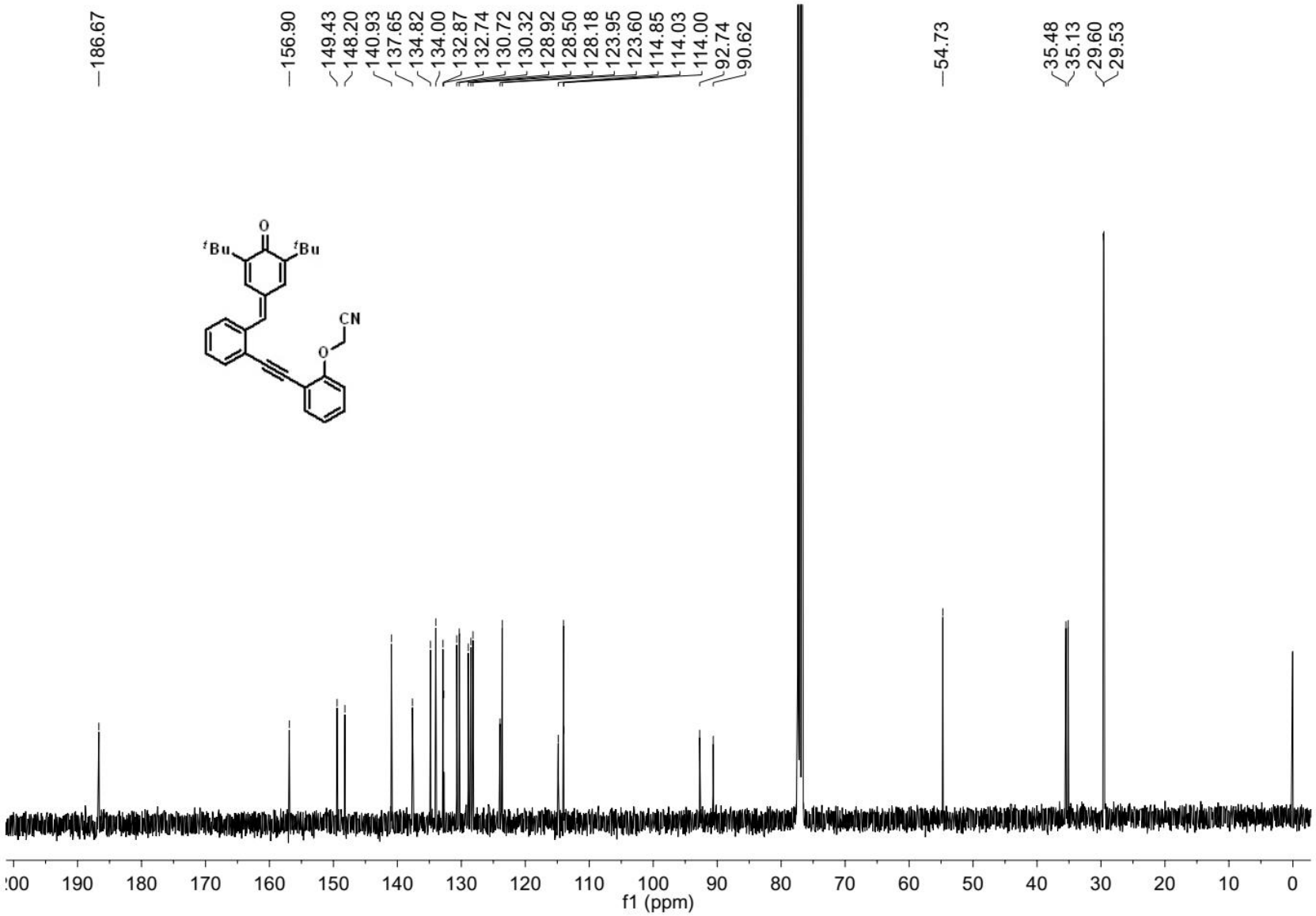
^{1}H NMR Spectrum of Compound 1w



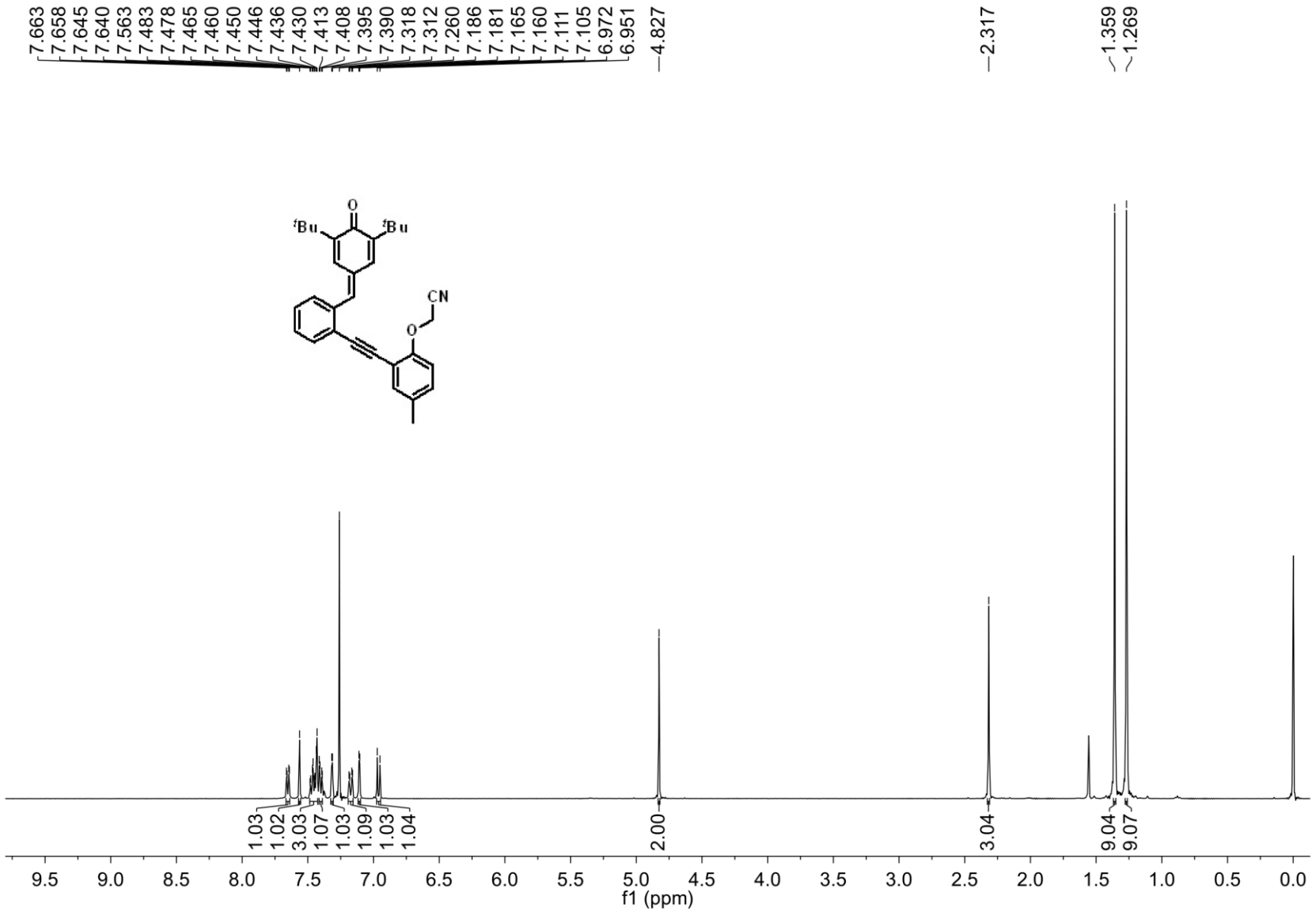
^{13}C NMR Spectrum of Compound 1w



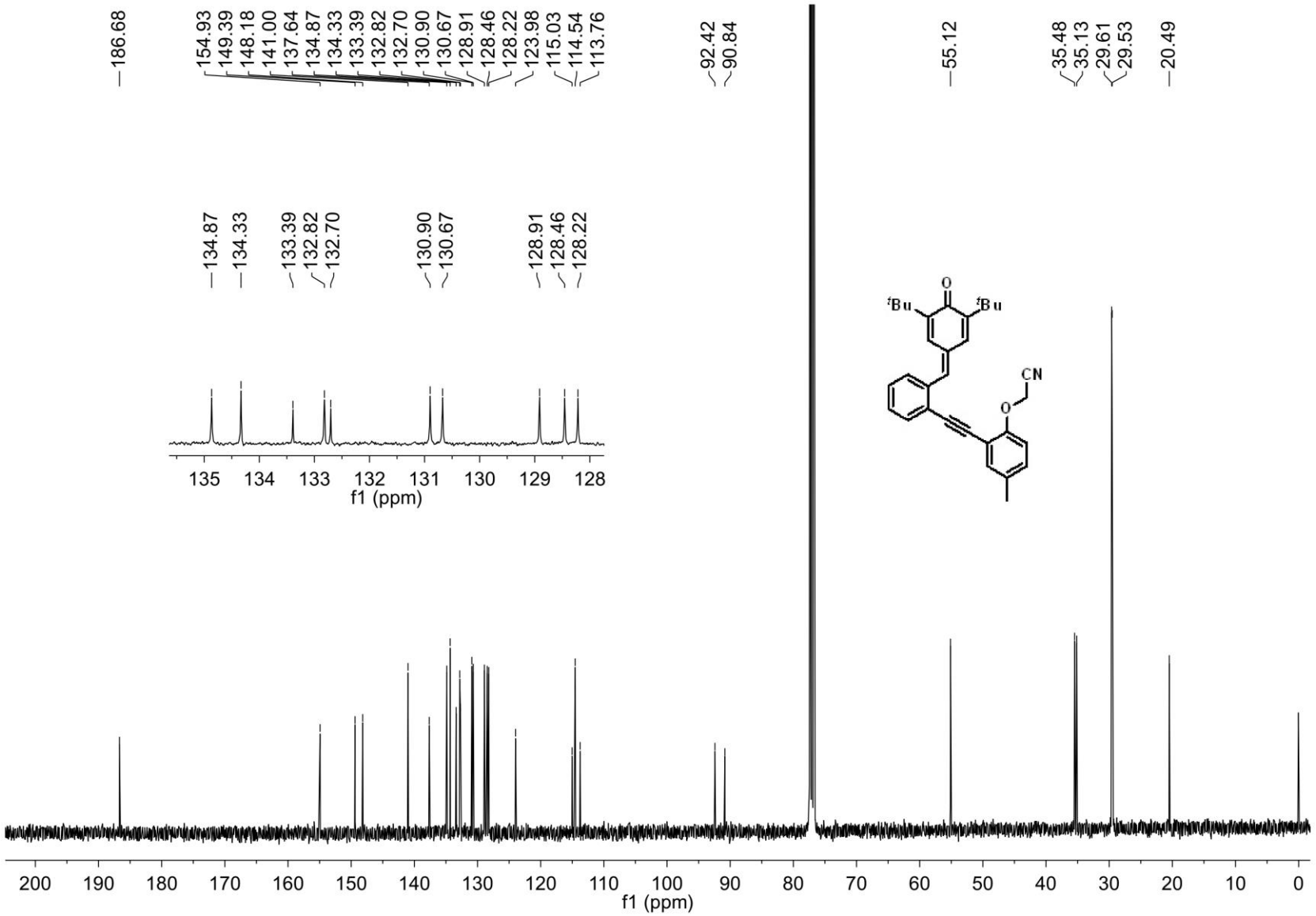
^{1}H NMR Spectrum of Compound 2a



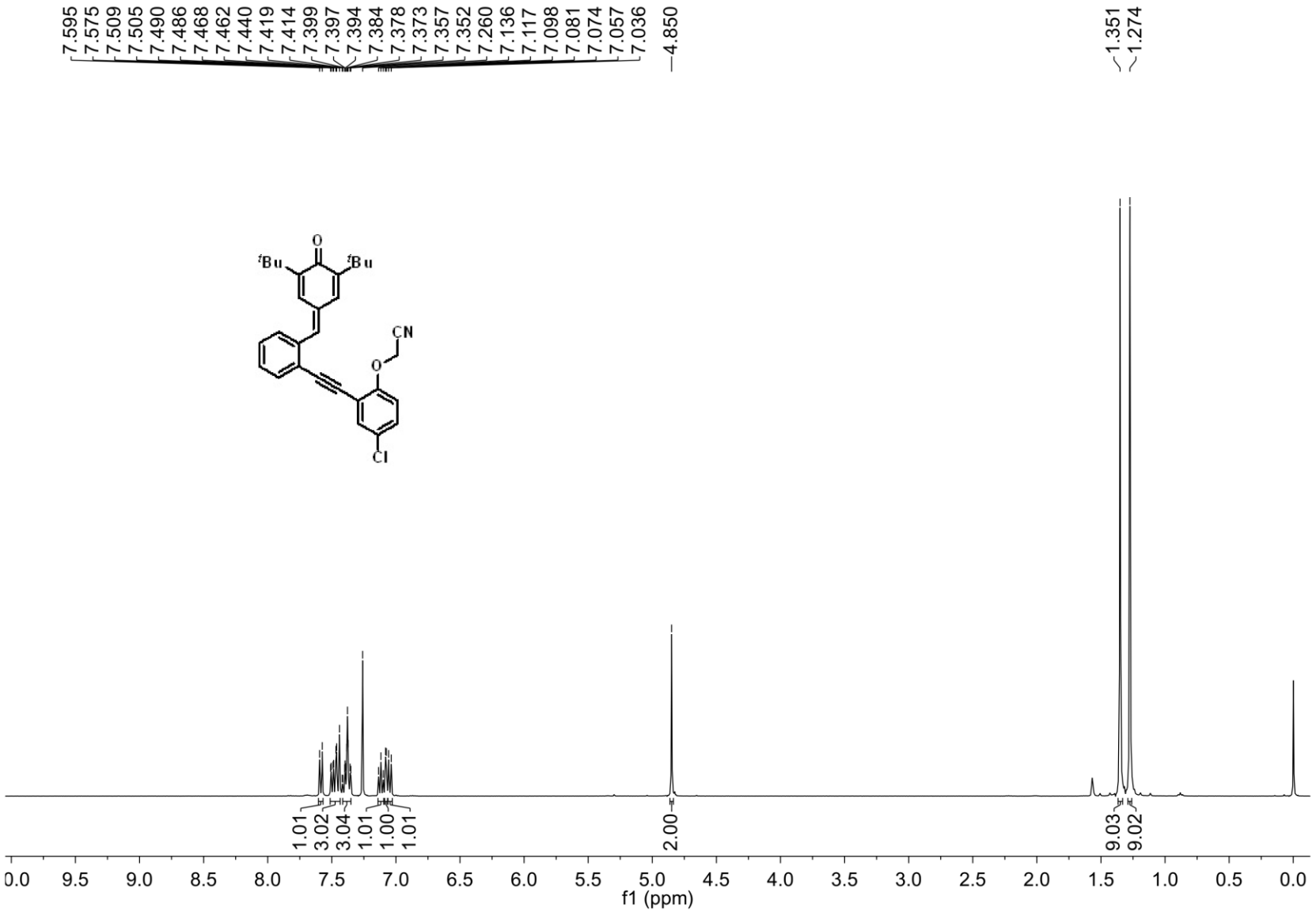
^{13}C NMR Spectrum of Compound 2a



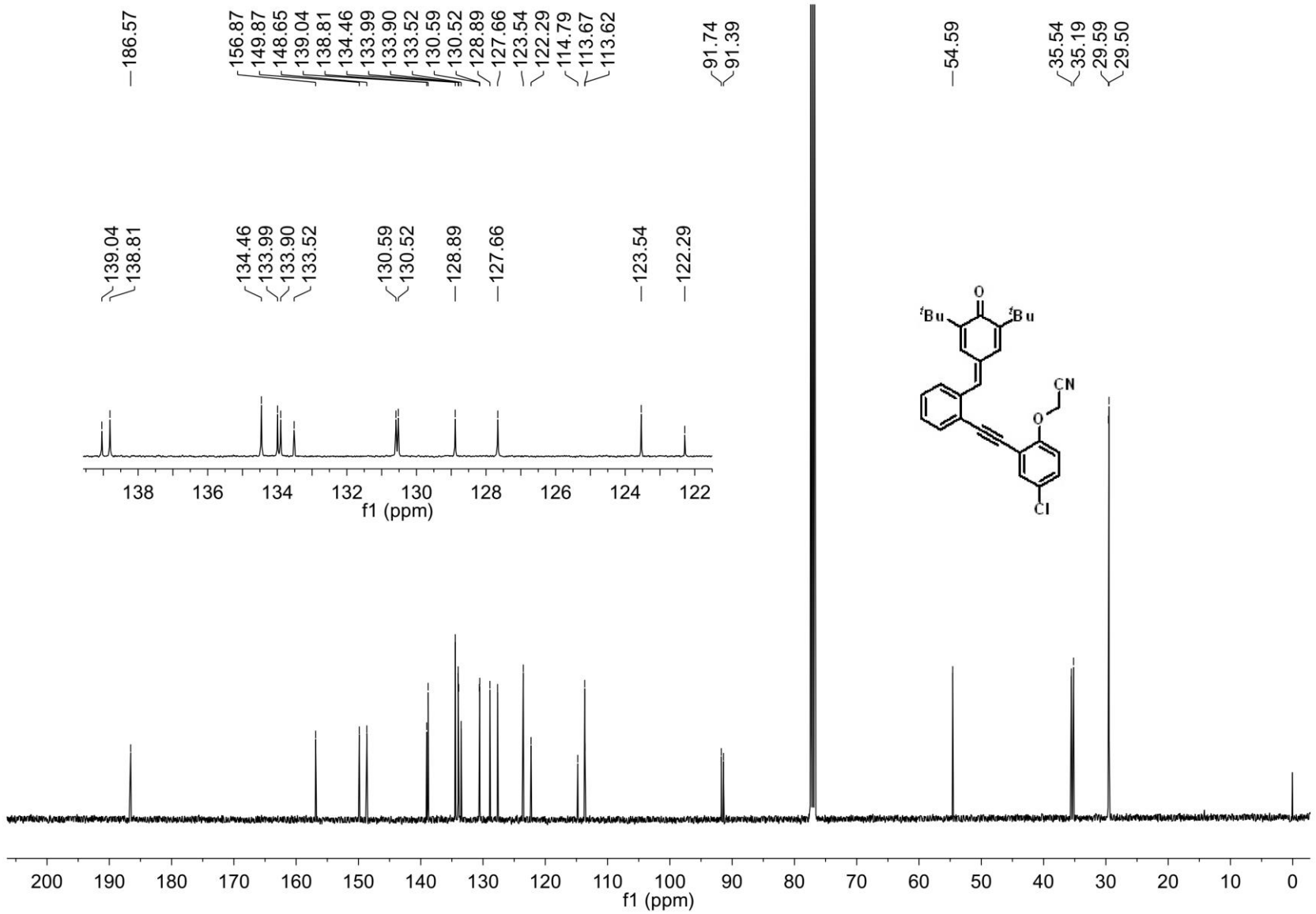
^{1}H NMR Spectrum of Compound 2b



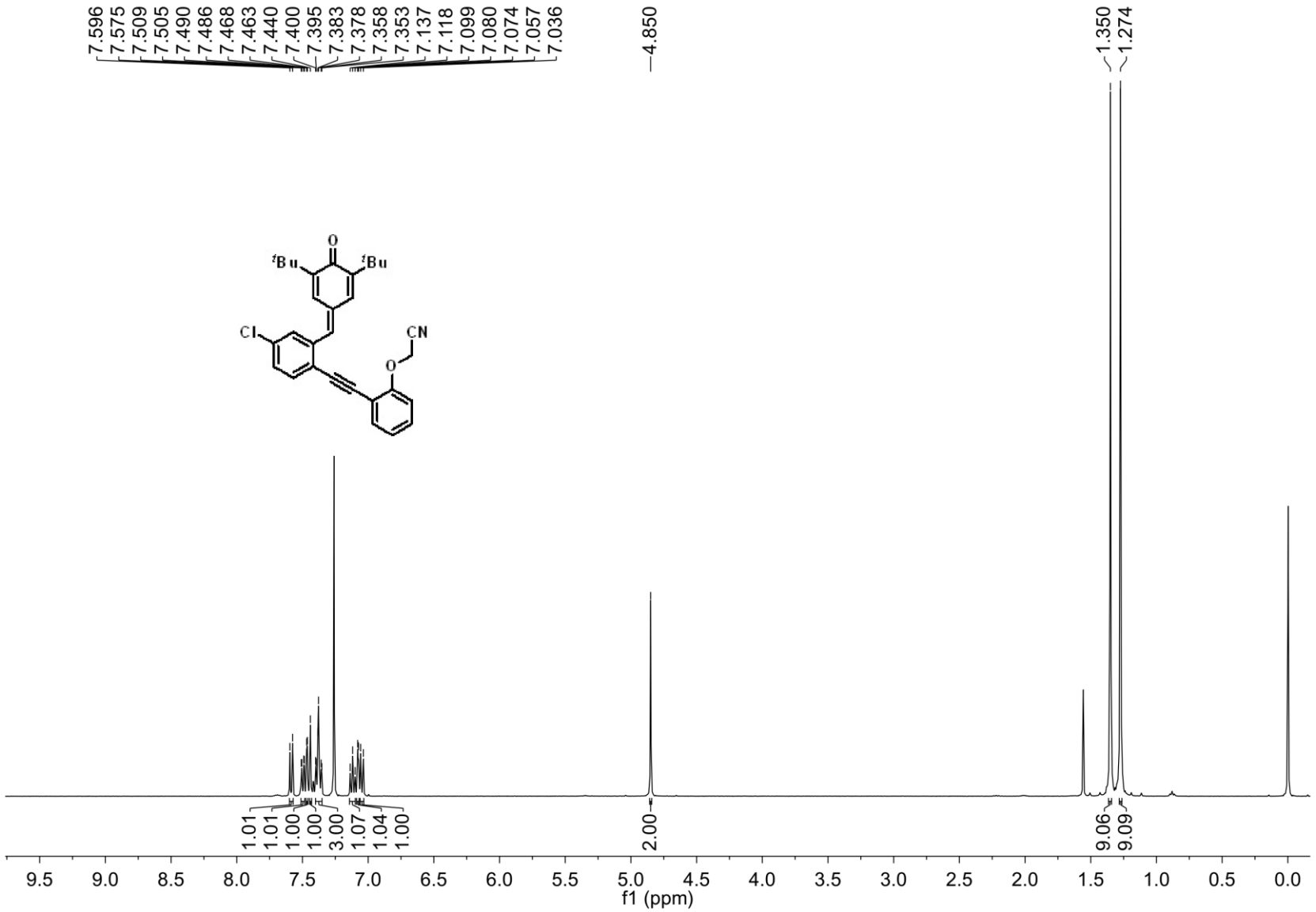
^{13}C NMR Spectrum of Compound 2b



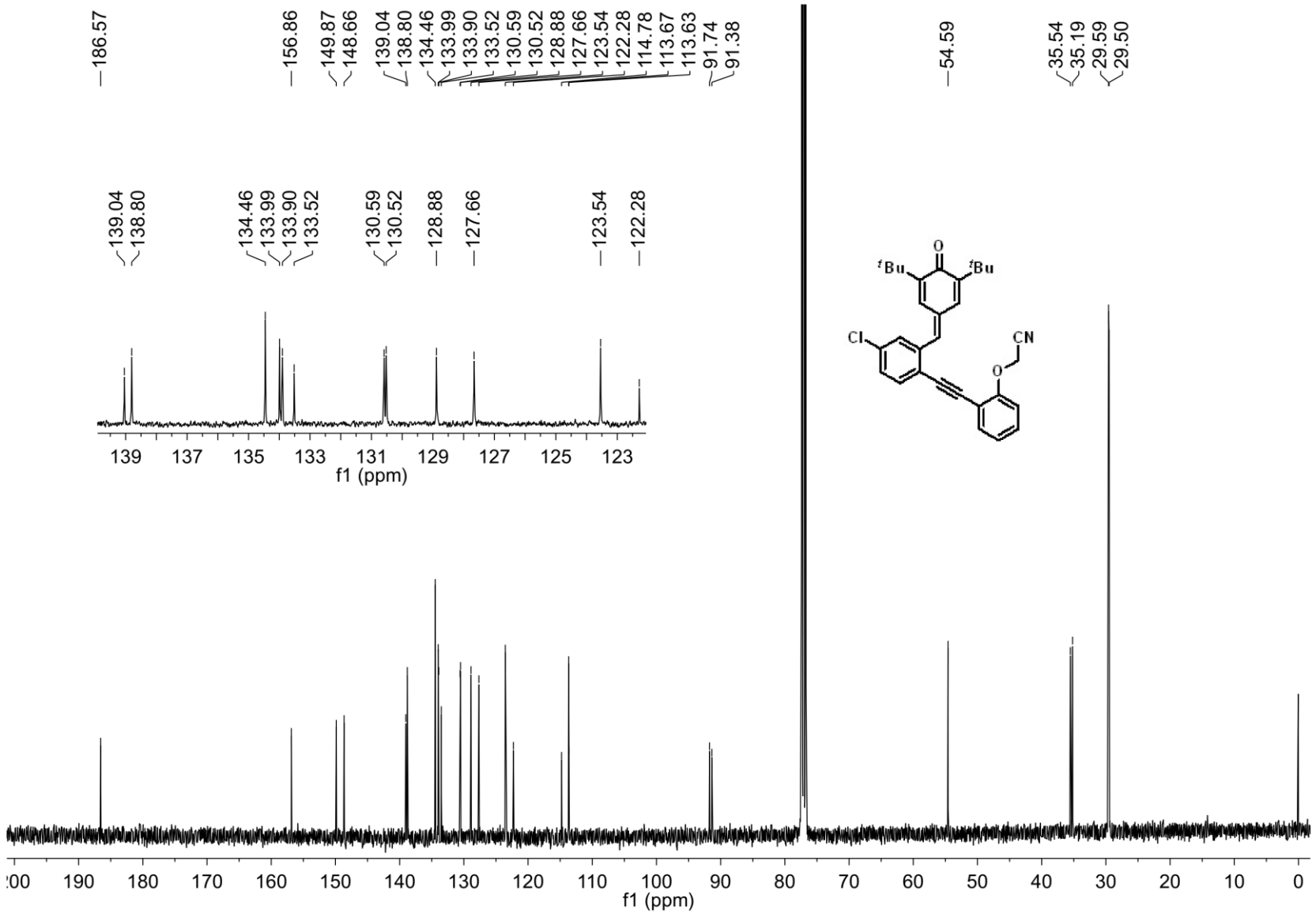
^{1}H NMR Spectrum of Compound 2c



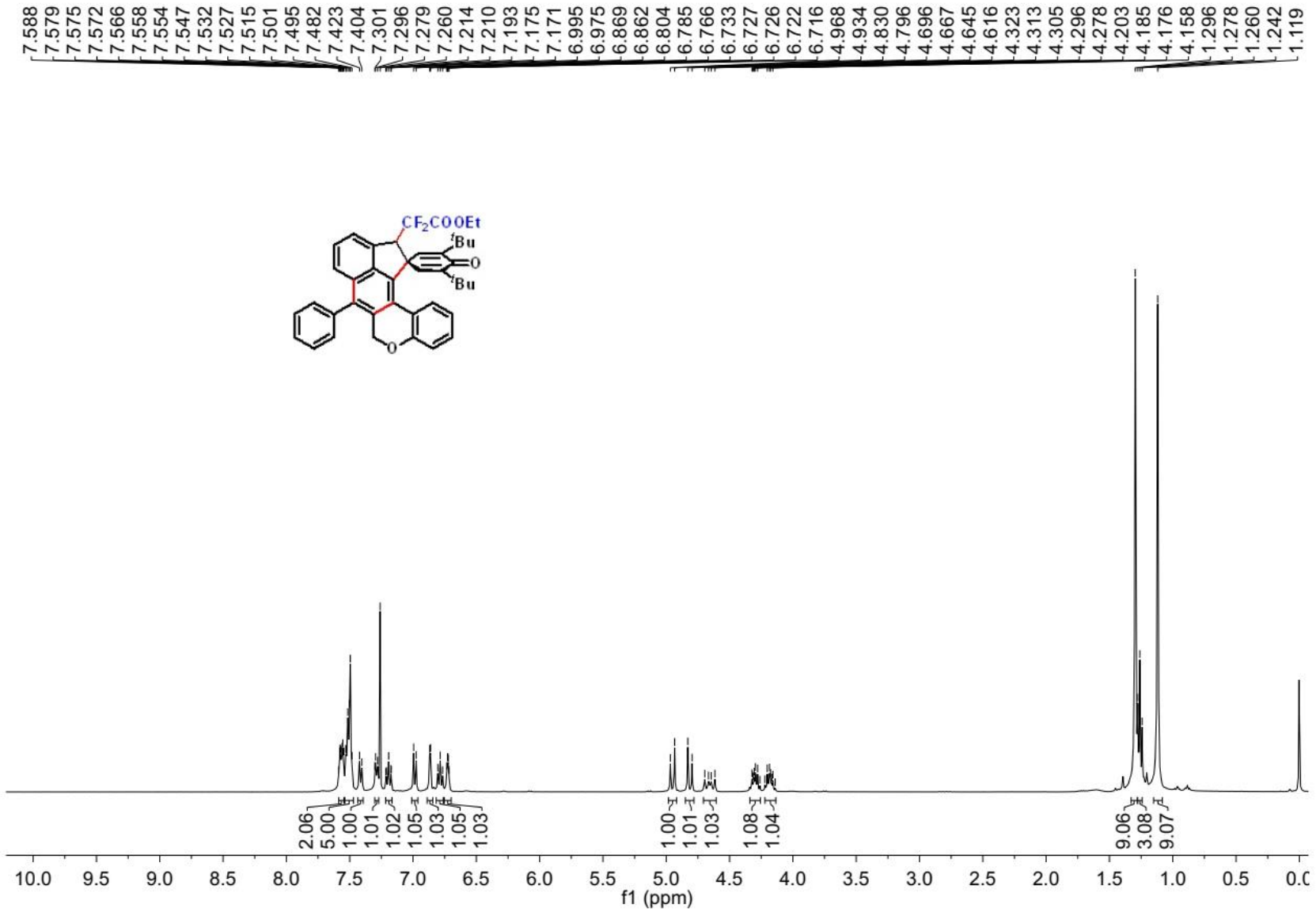
^{13}C NMR Spectrum of Compound 2c



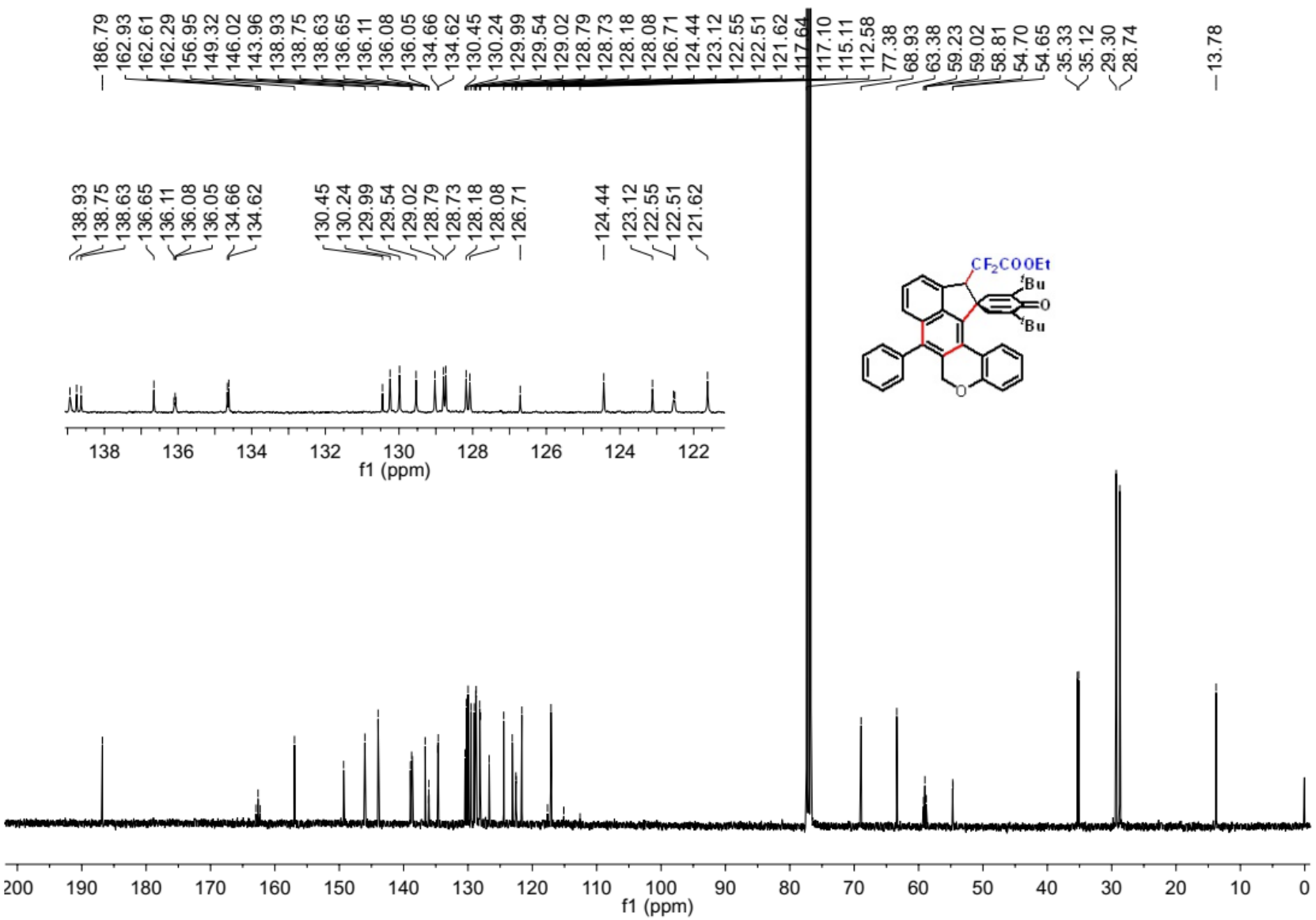
^{1}H NMR Spectrum of Compound 2d



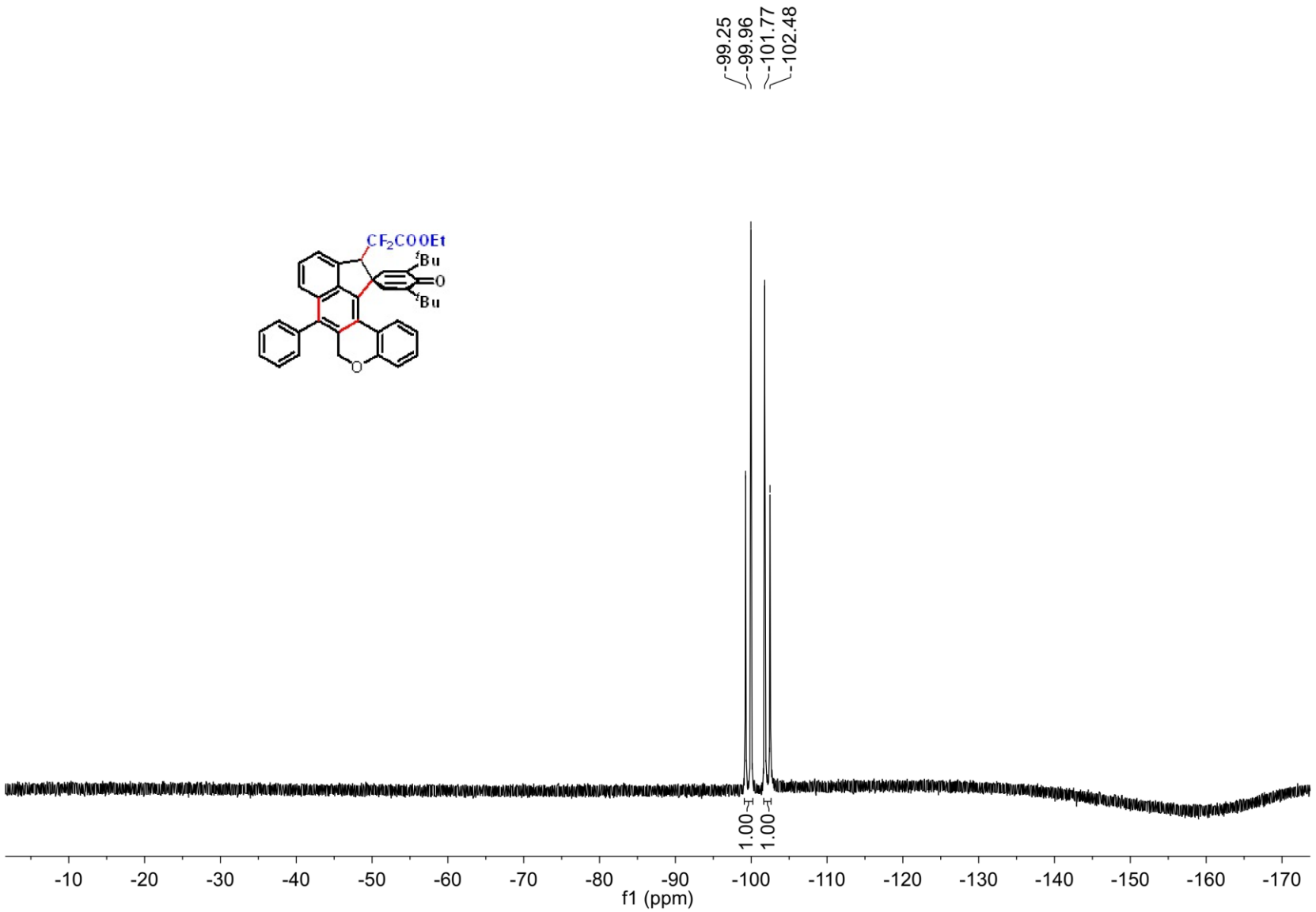
^{13}C NMR Spectrum of Compound 2d



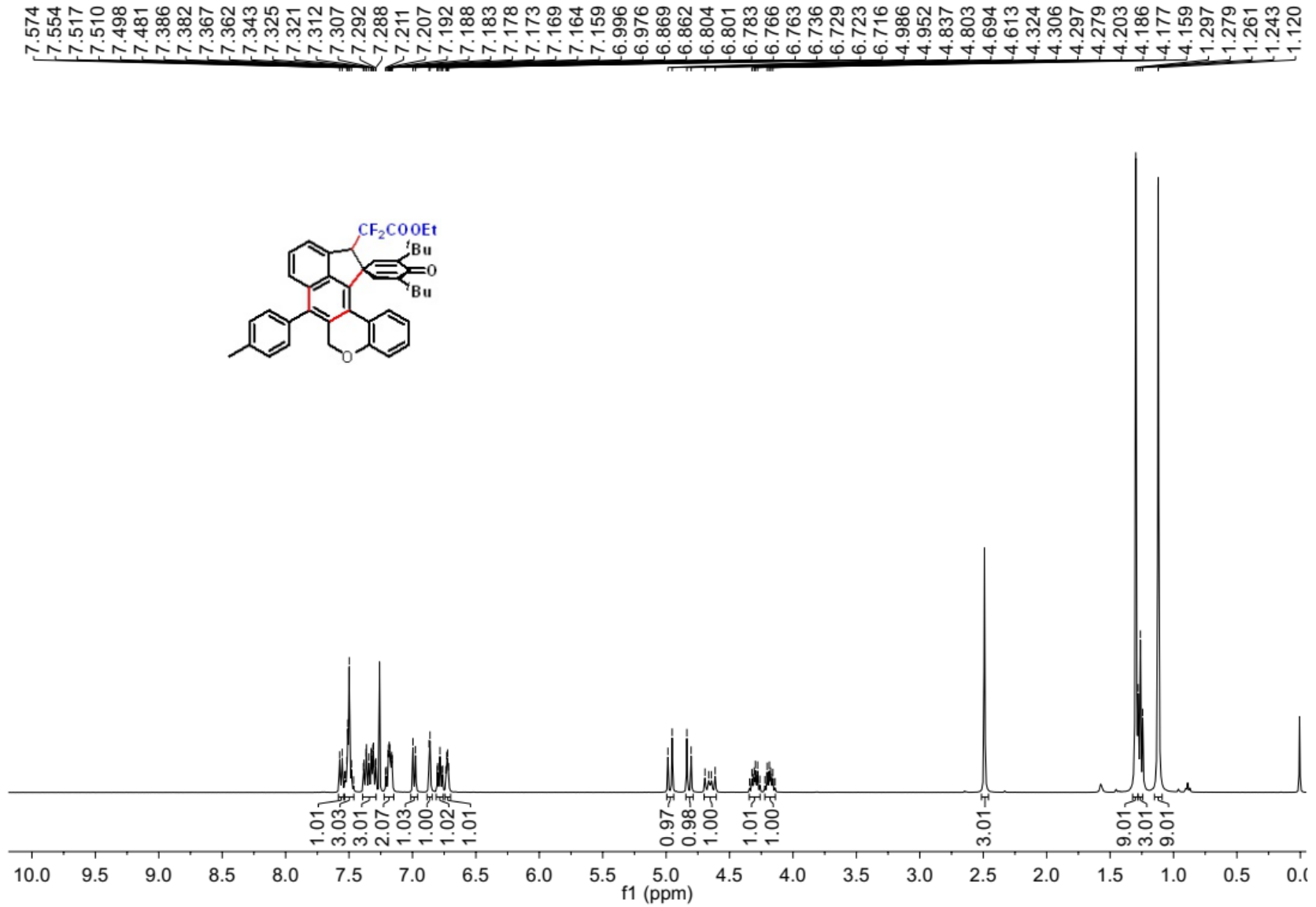
^{1}H NMR Spectrum of Compound 4aa



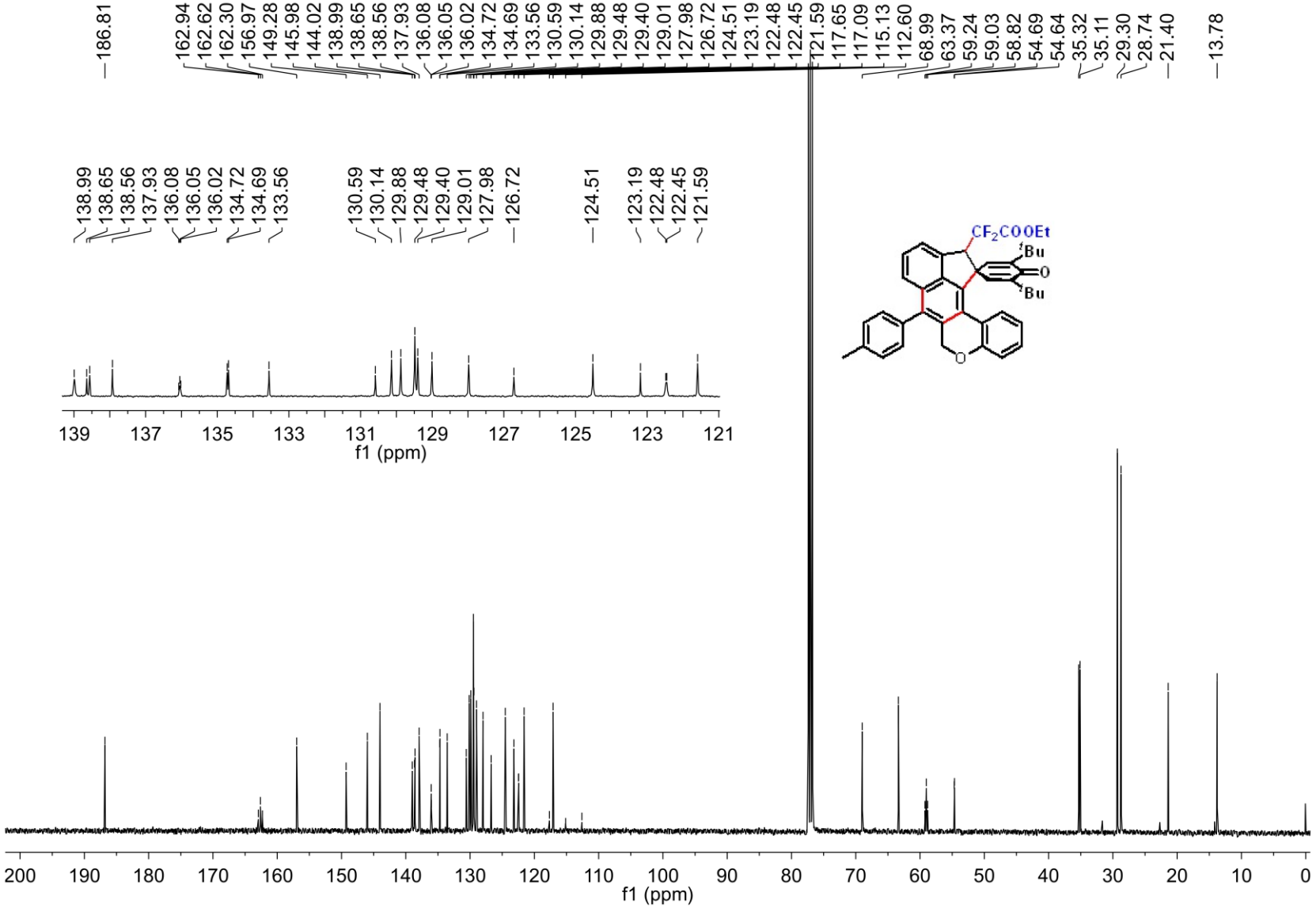
^{13}C NMR Spectrum of Compound 4aa



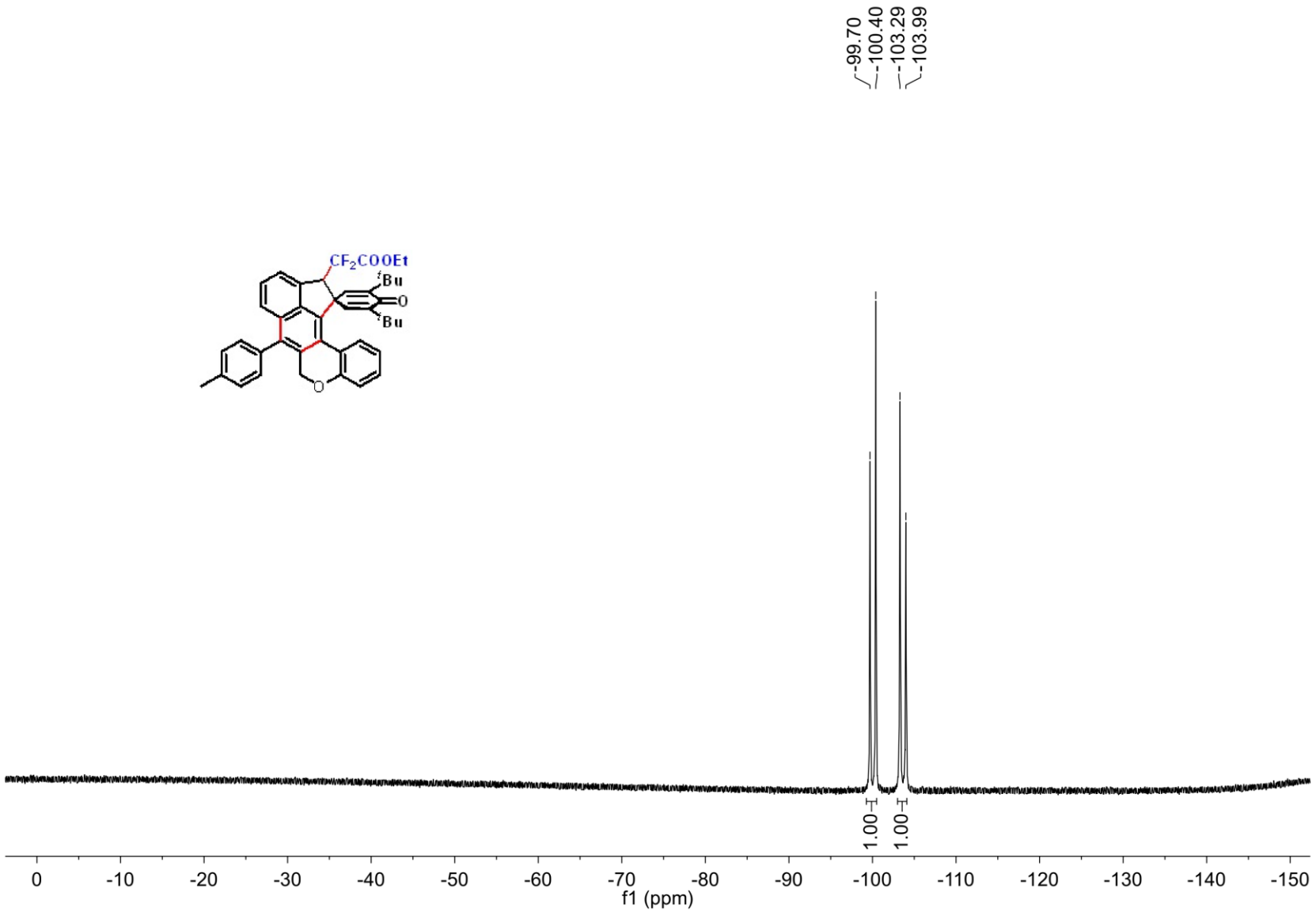
^{19}F NMR Spectrum of Compound 4aa



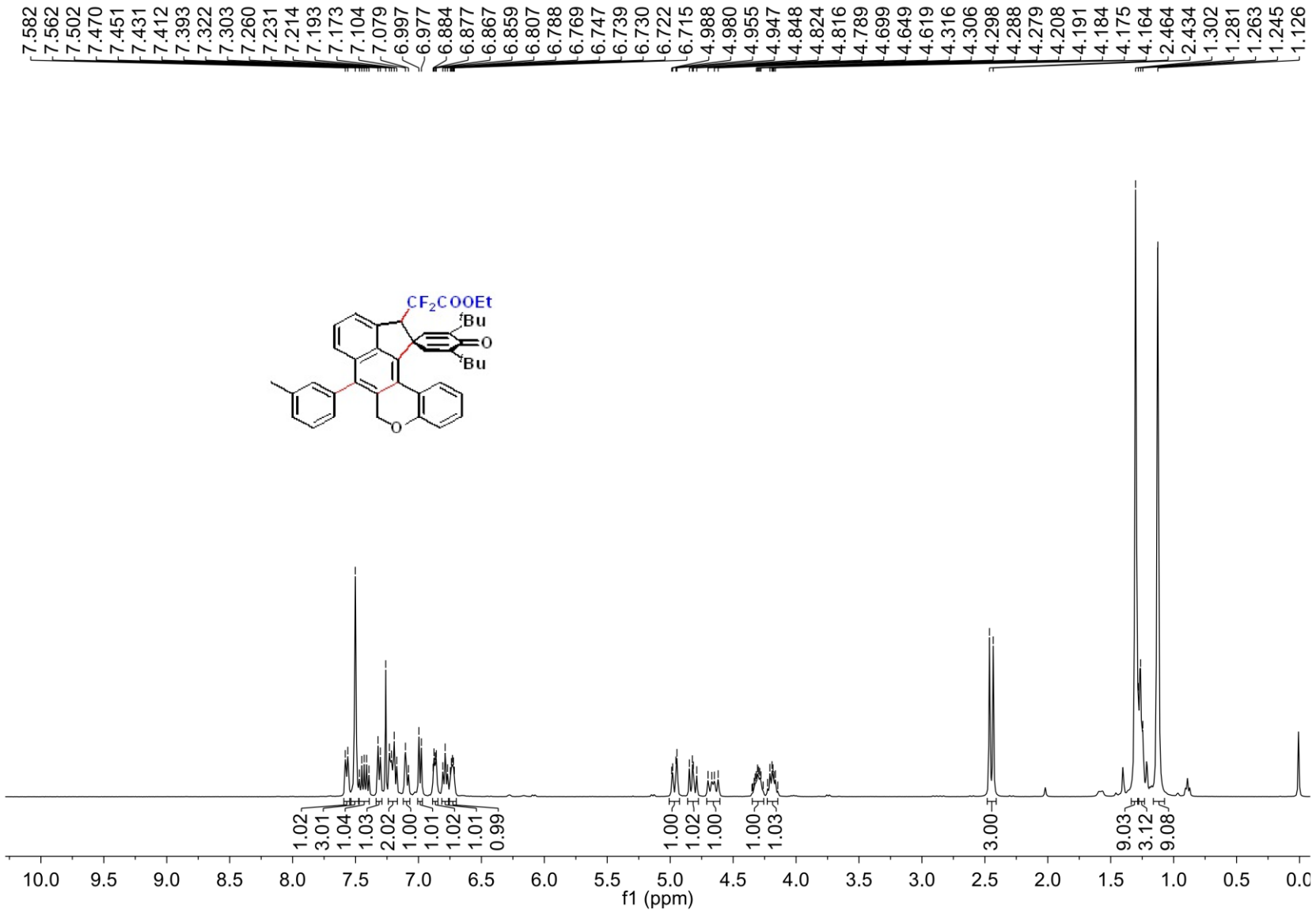
^{1}H NMR Spectrum of Compound 4ba



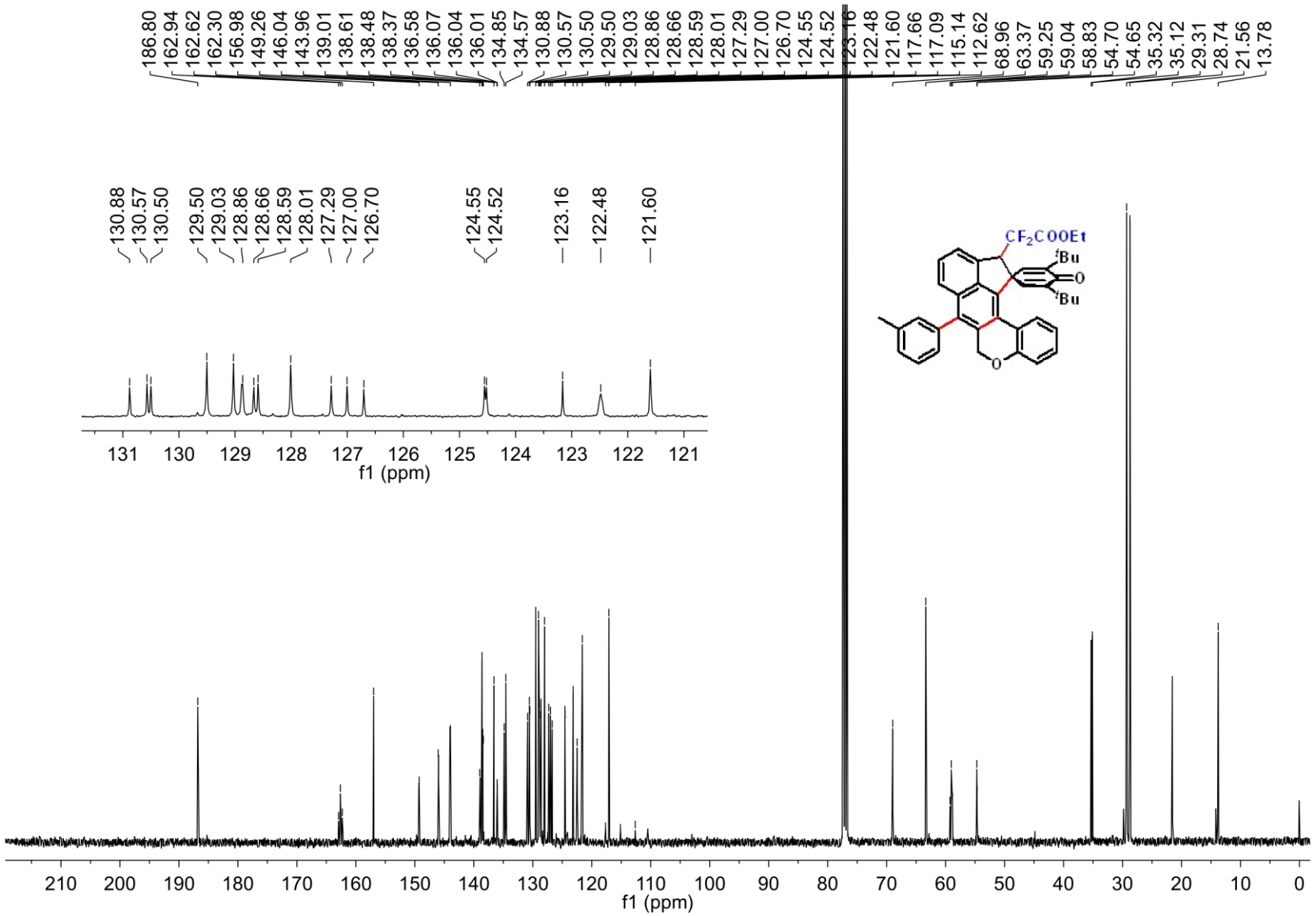
^{13}C NMR Spectrum of Compound 4ba



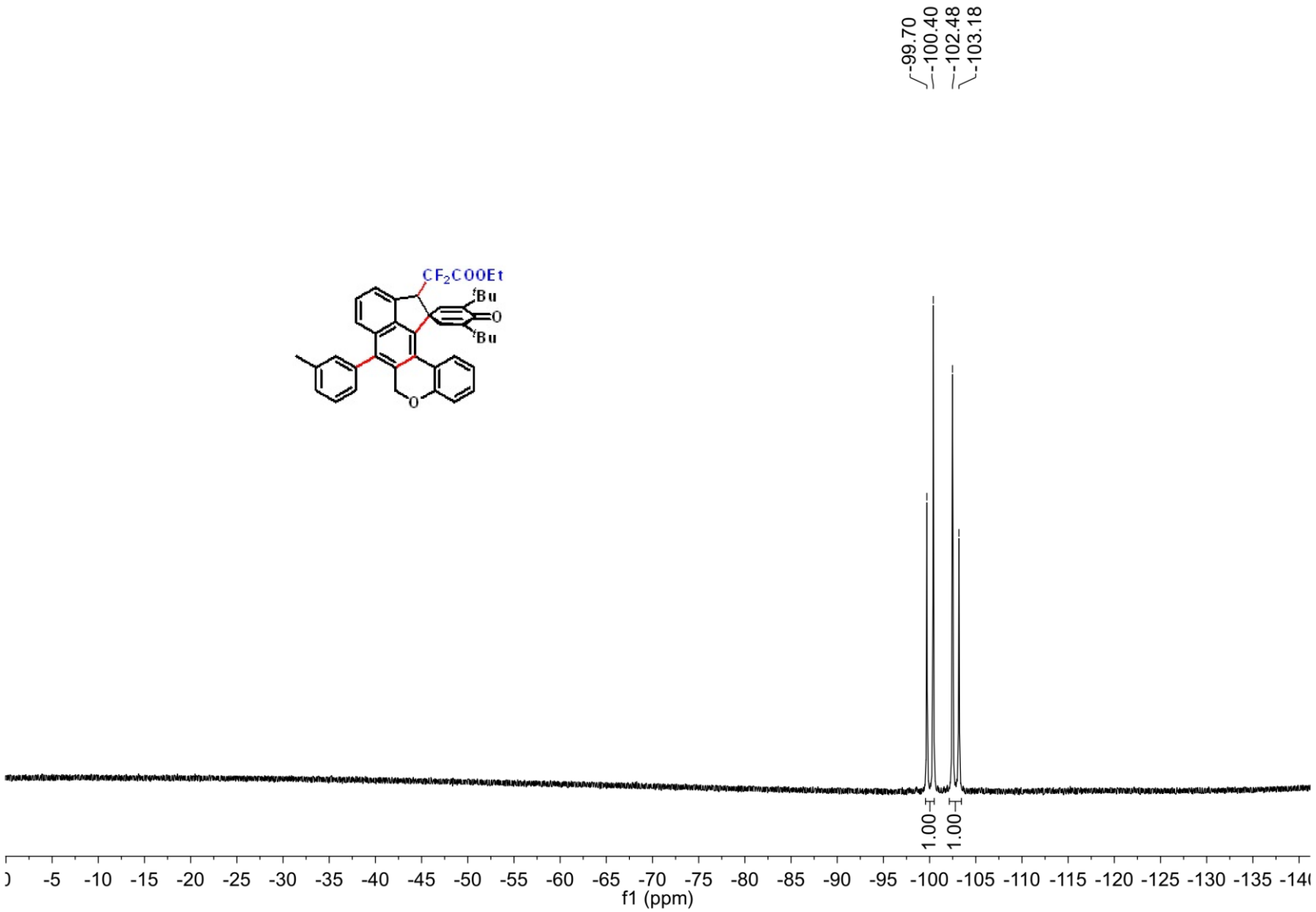
^{19}F NMR Spectrum of Compound 4ba



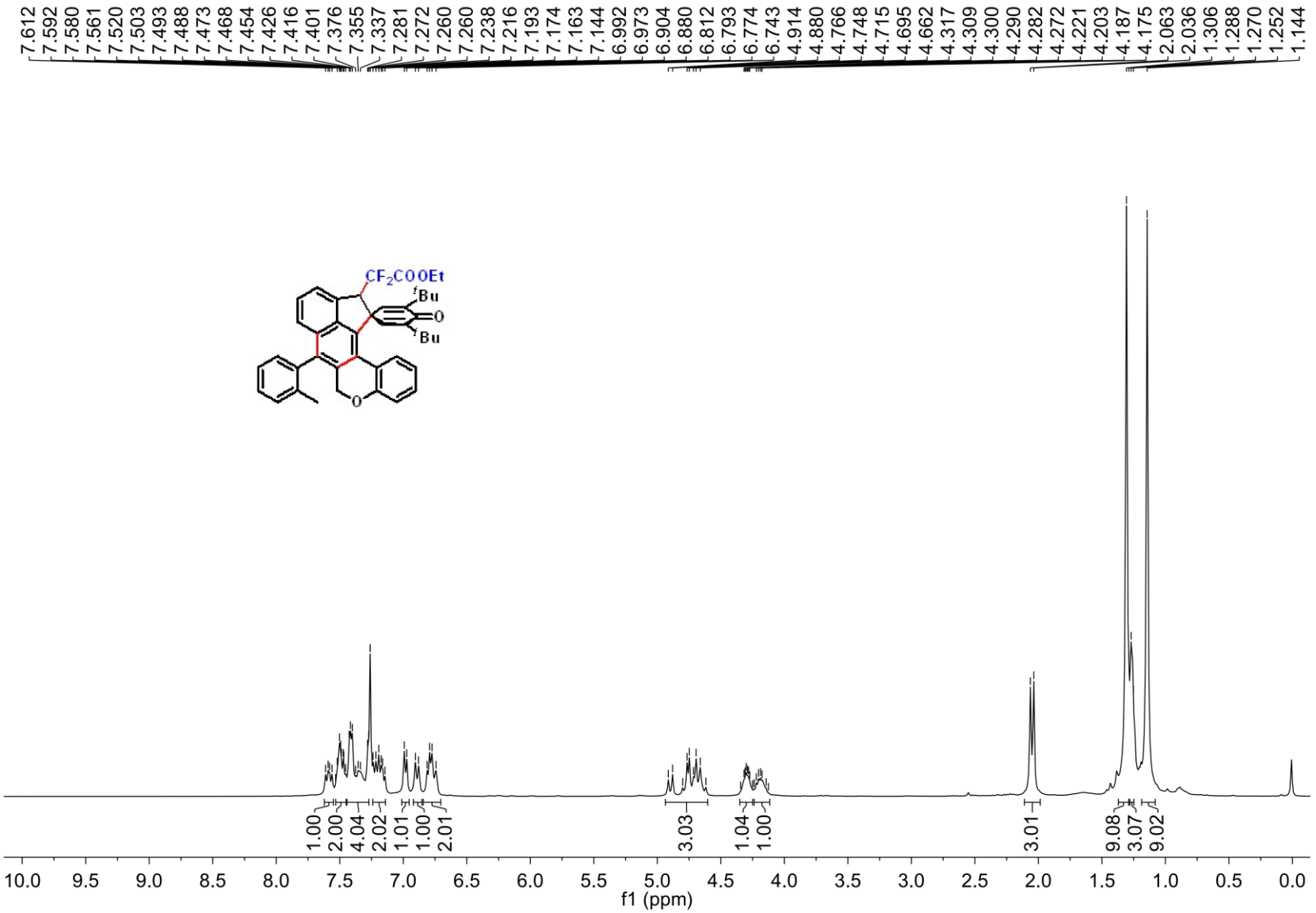
^{1}H NMR Spectrum of Compound 4ca



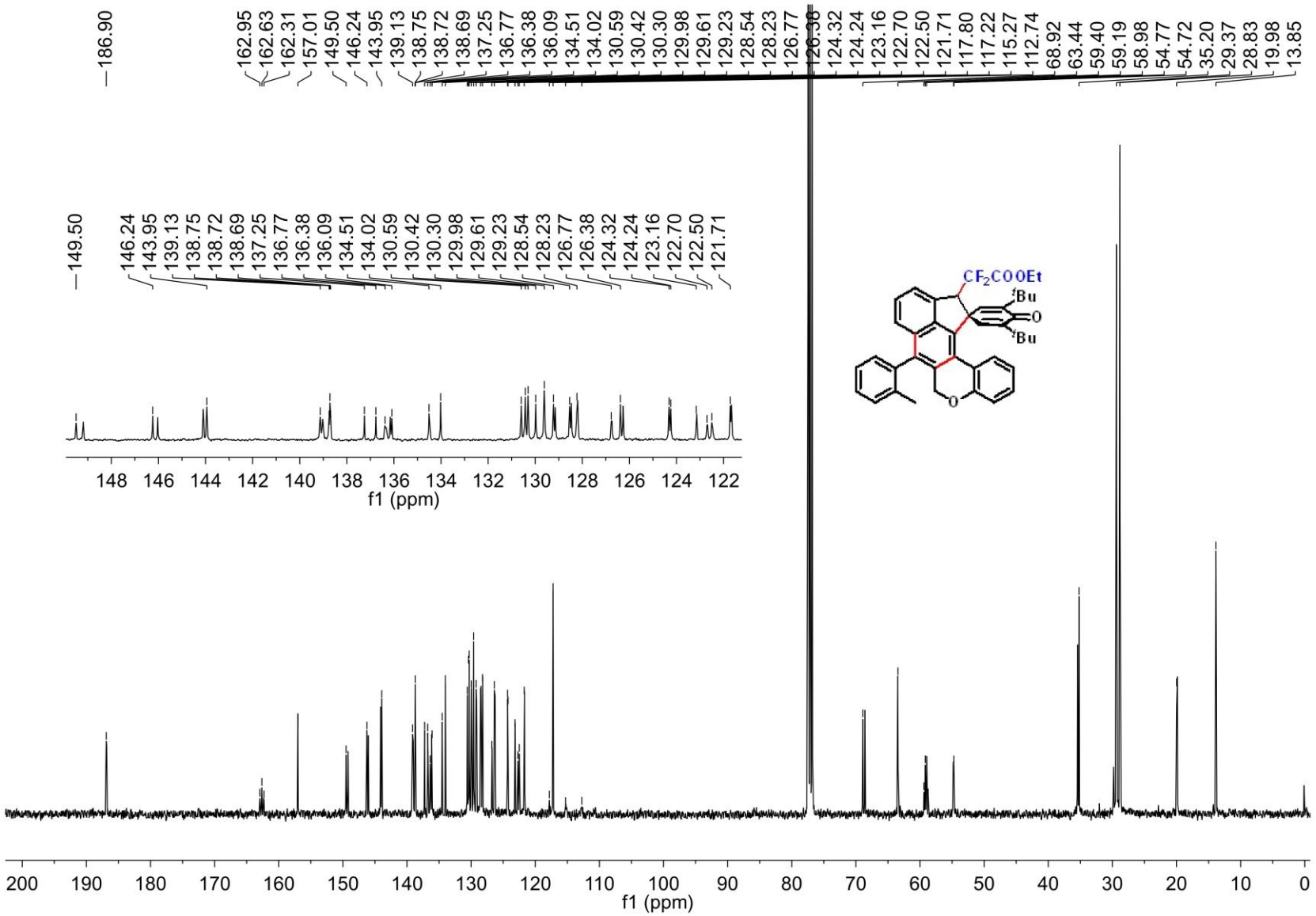
^{13}C NMR Spectrum of Compound 4ca



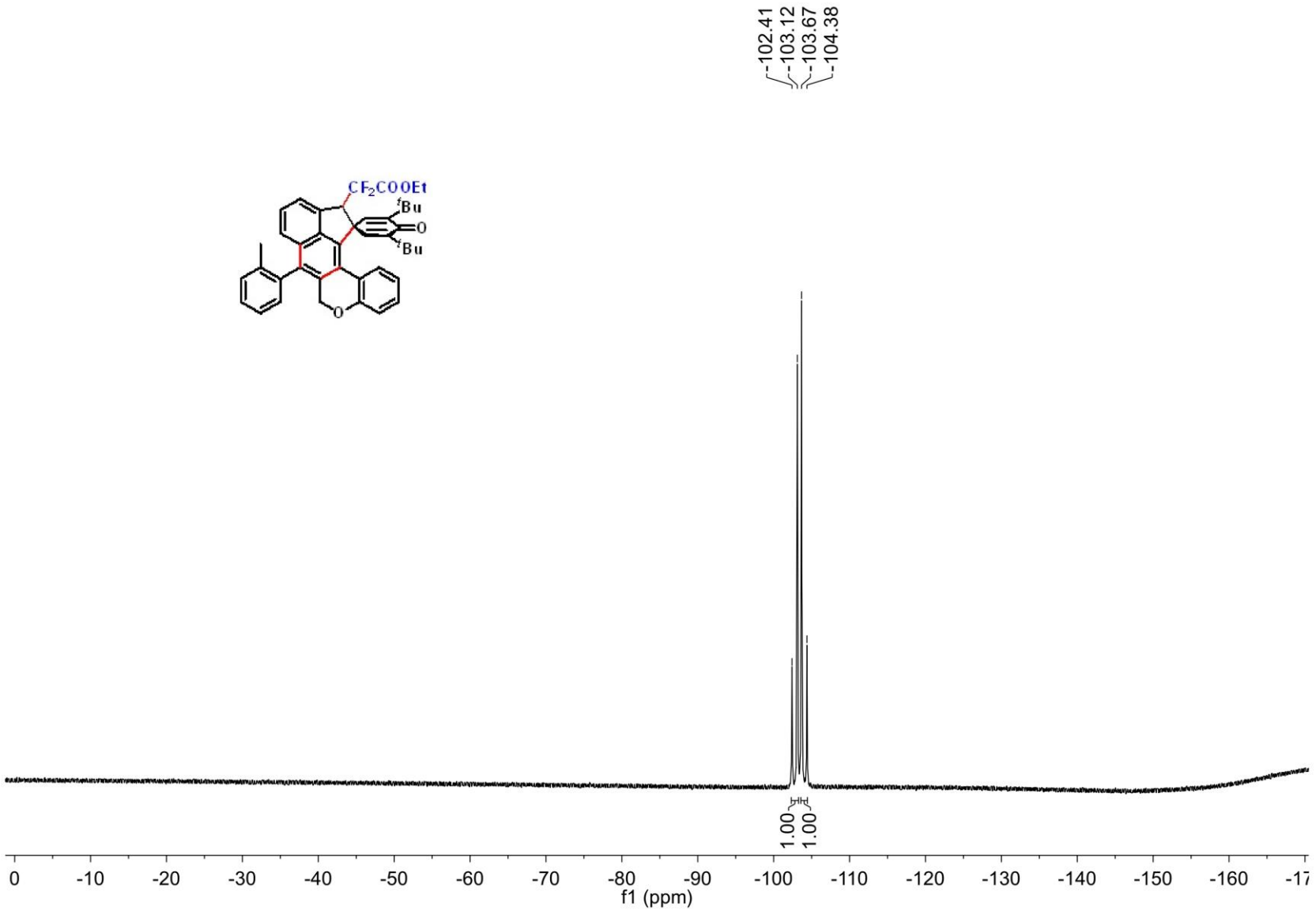
^{19}F NMR Spectrum of Compound 4ca



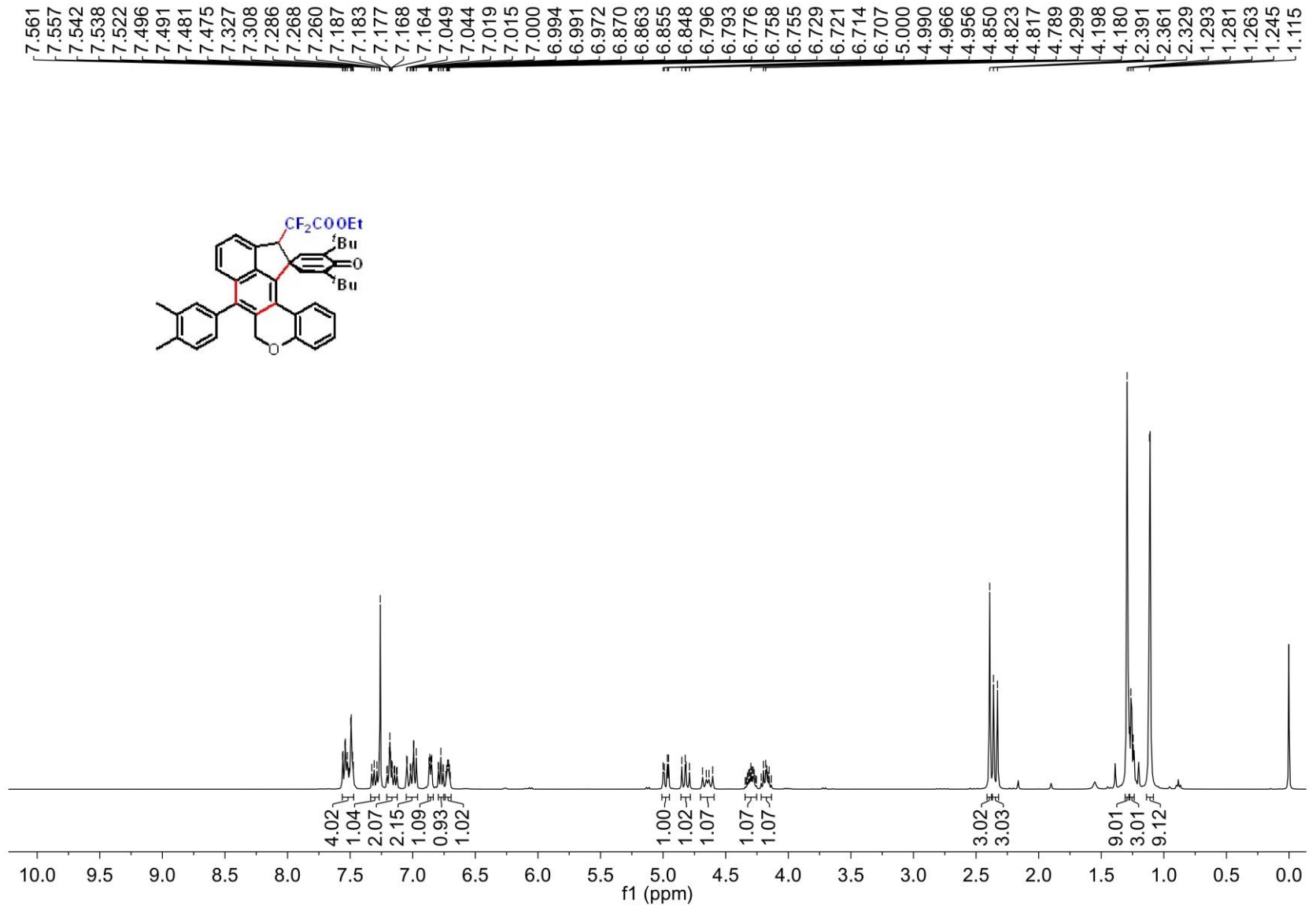
^{1}H NMR Spectrum of Compound 4da



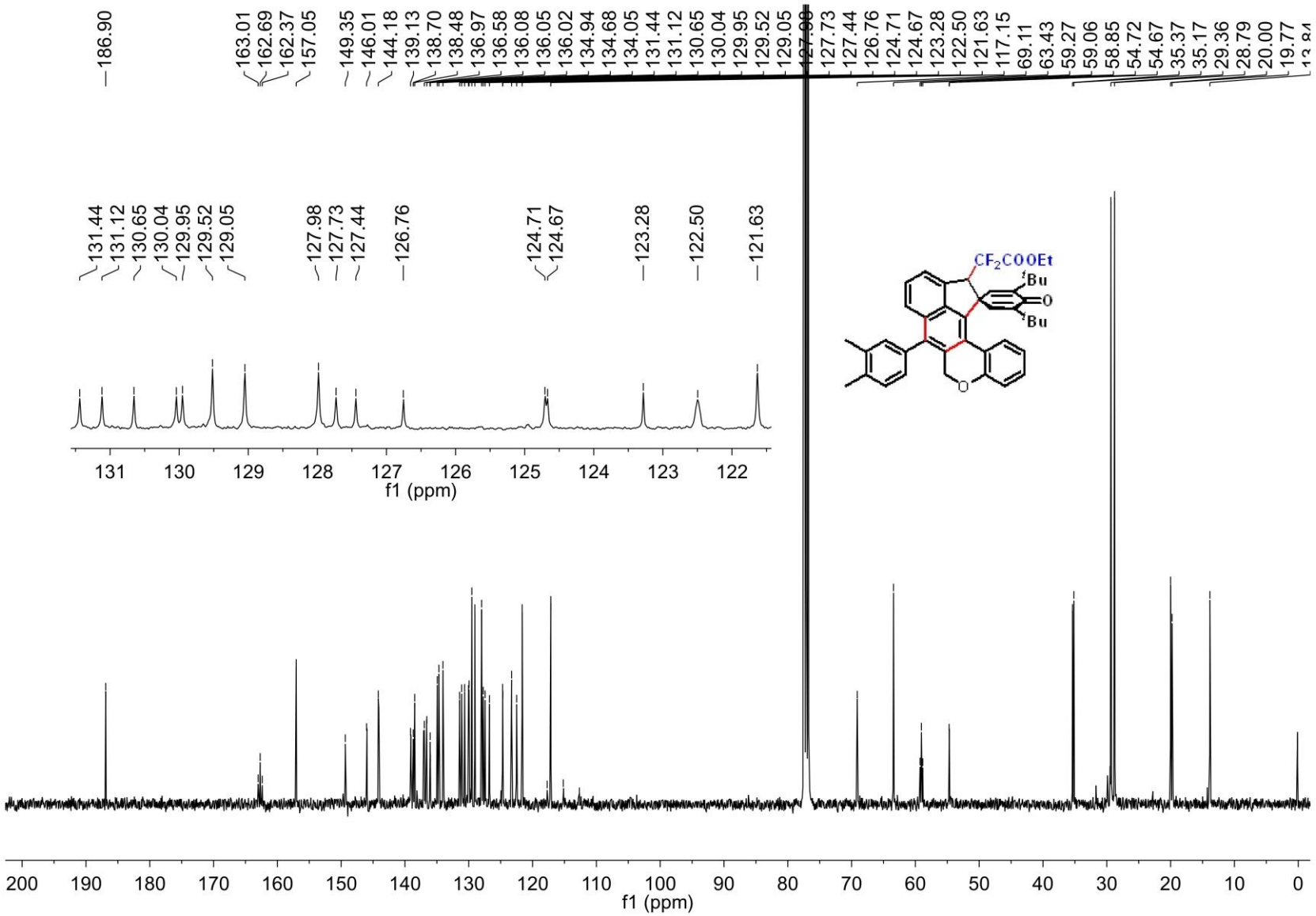
^{13}C NMR Spectrum of Compound 4da



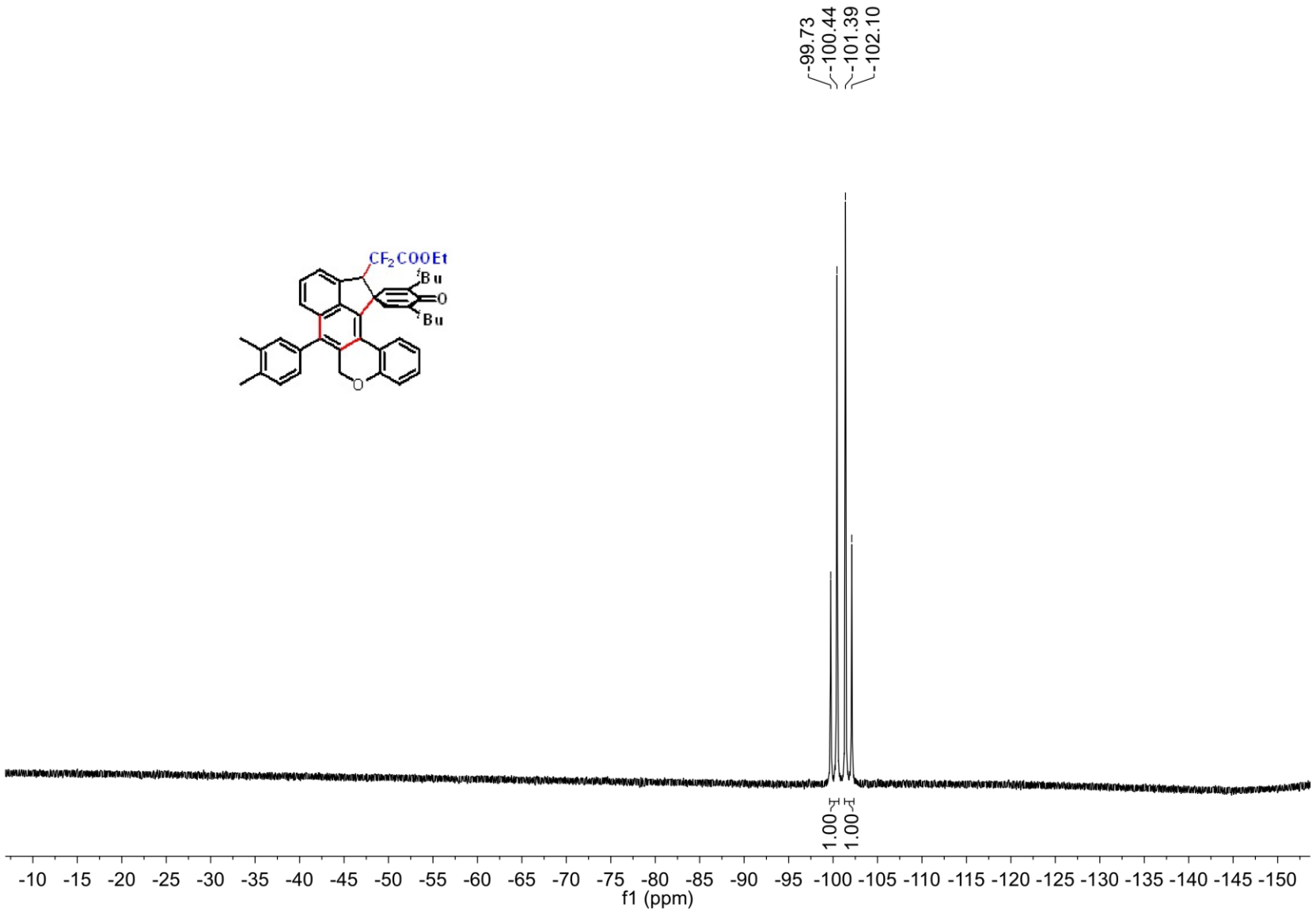
^{19}F NMR Spectrum of Compound 4da



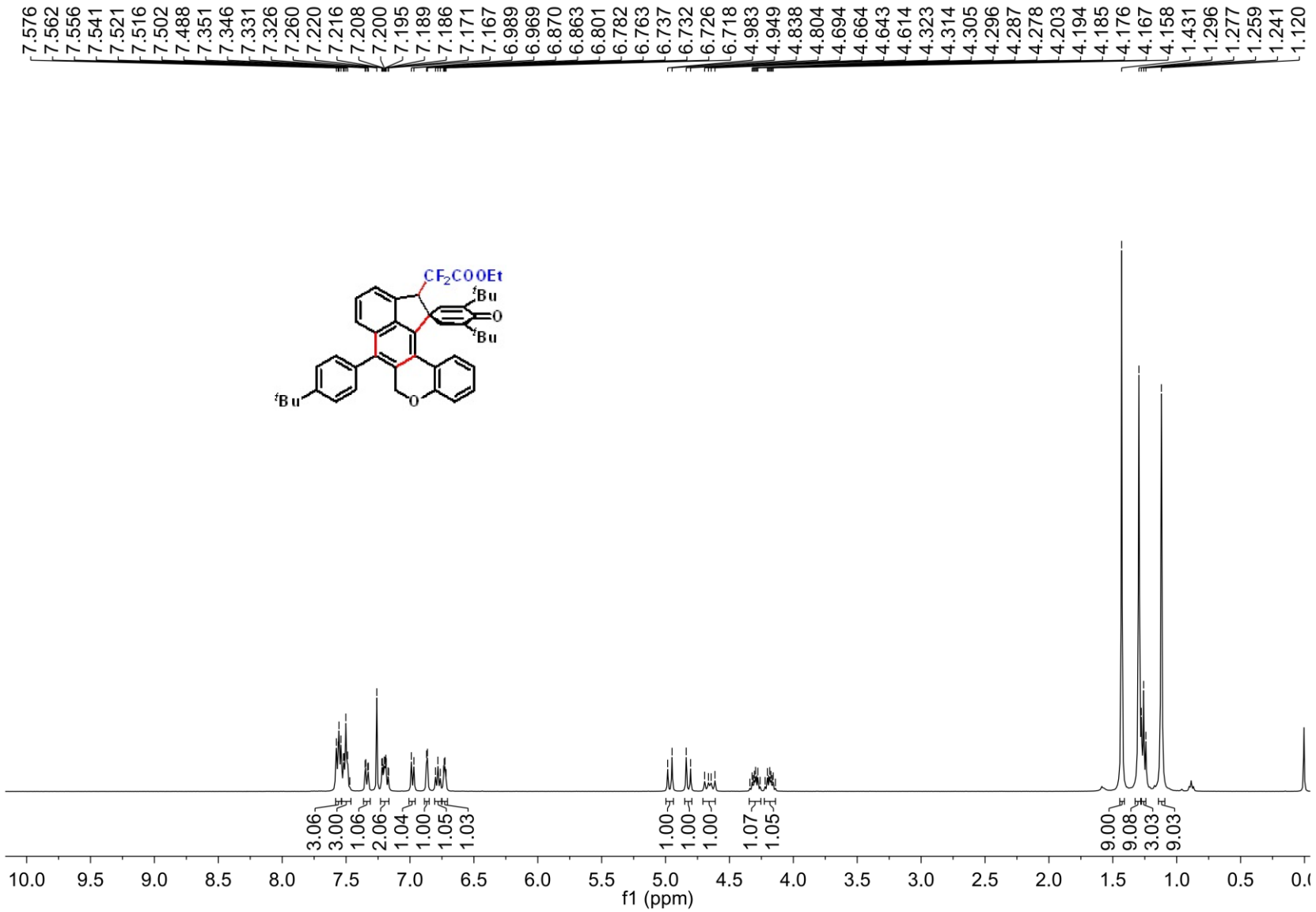
^{1}H NMR Spectrum of Compound 4ea



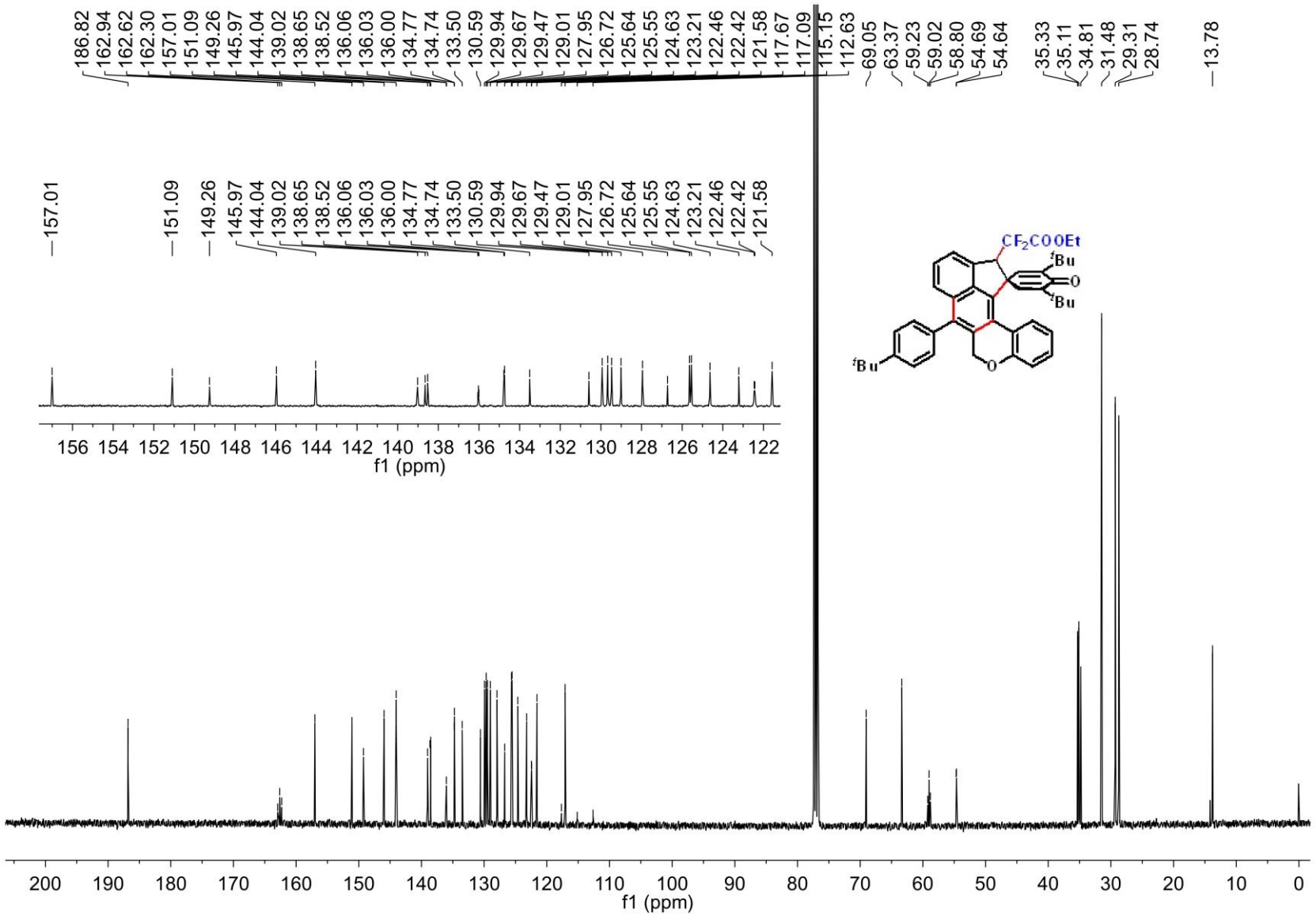
^{13}C NMR Spectrum of Compound 4ea



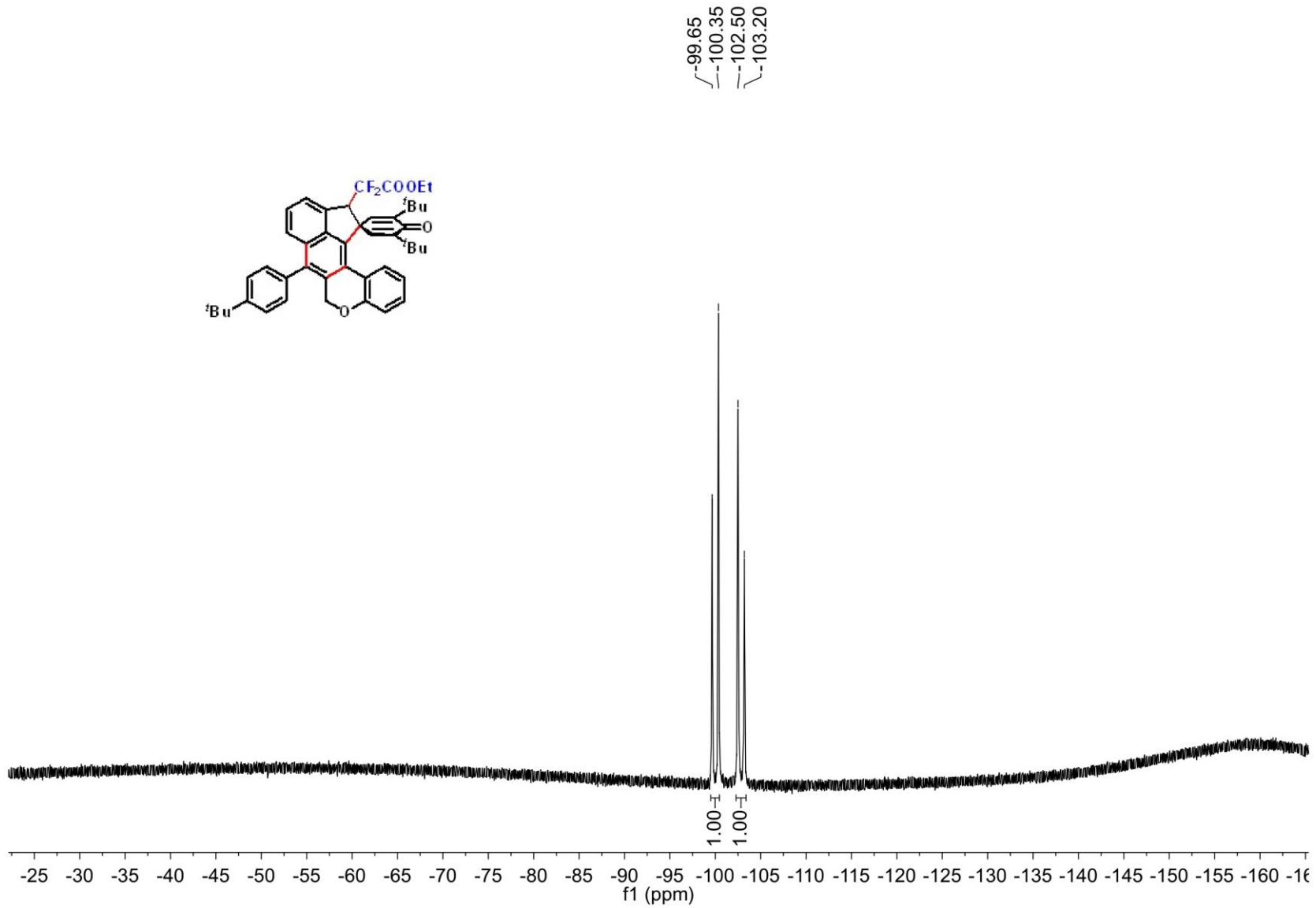
^{19}F NMR Spectrum of Compound 4ea



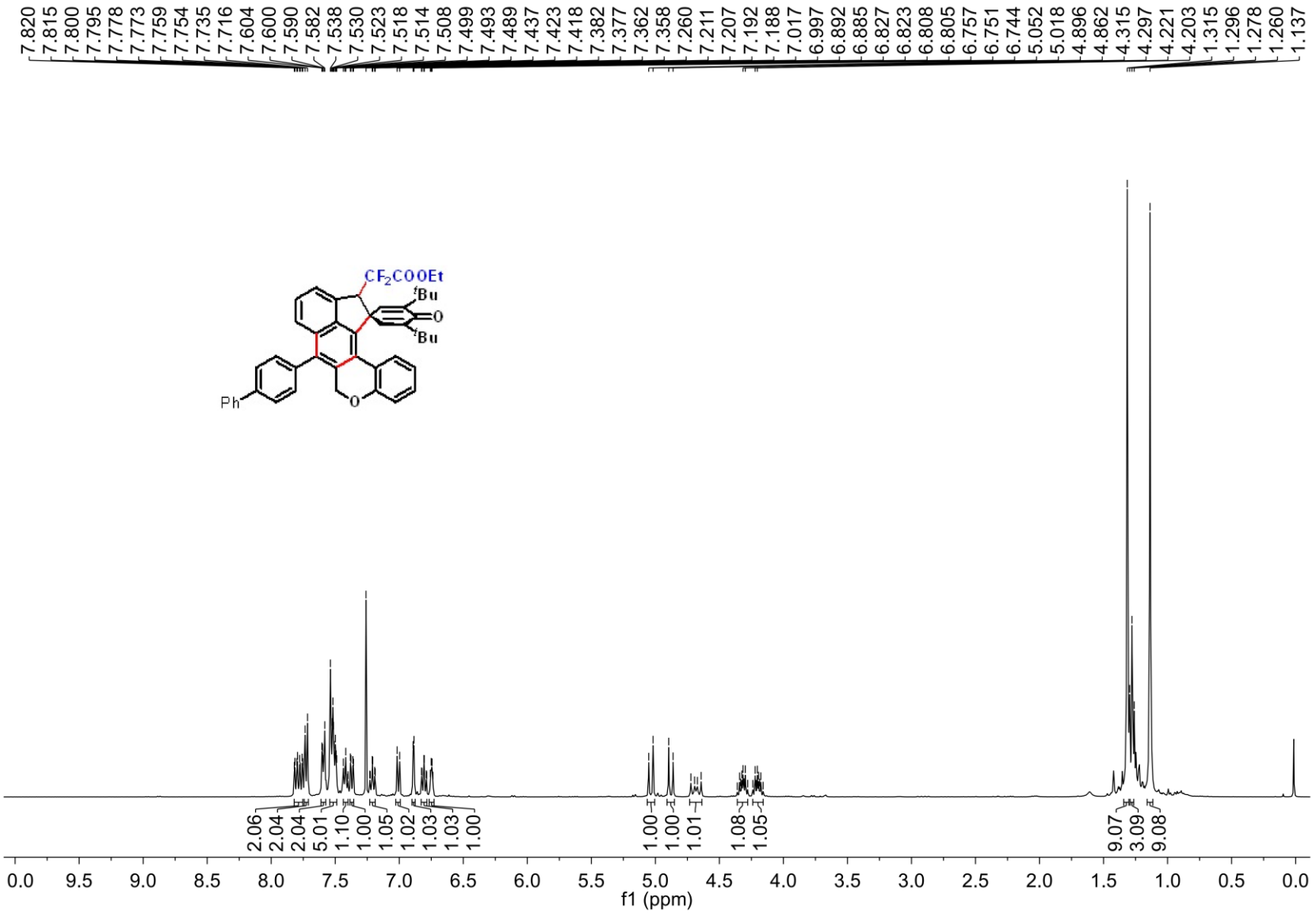
^{1}H NMR Spectrum of Compound 4fa



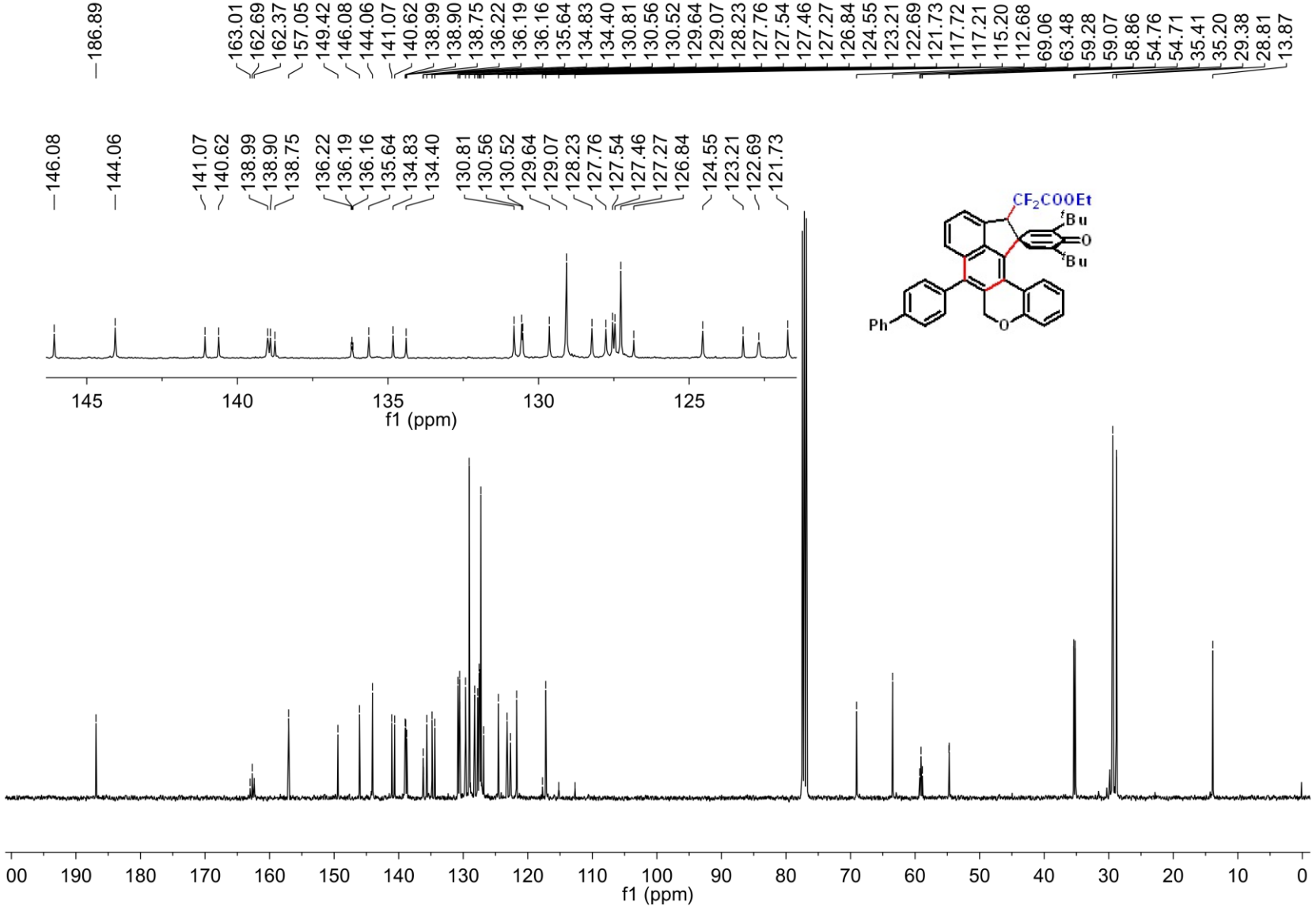
^{13}C NMR Spectrum of Compound 4fa



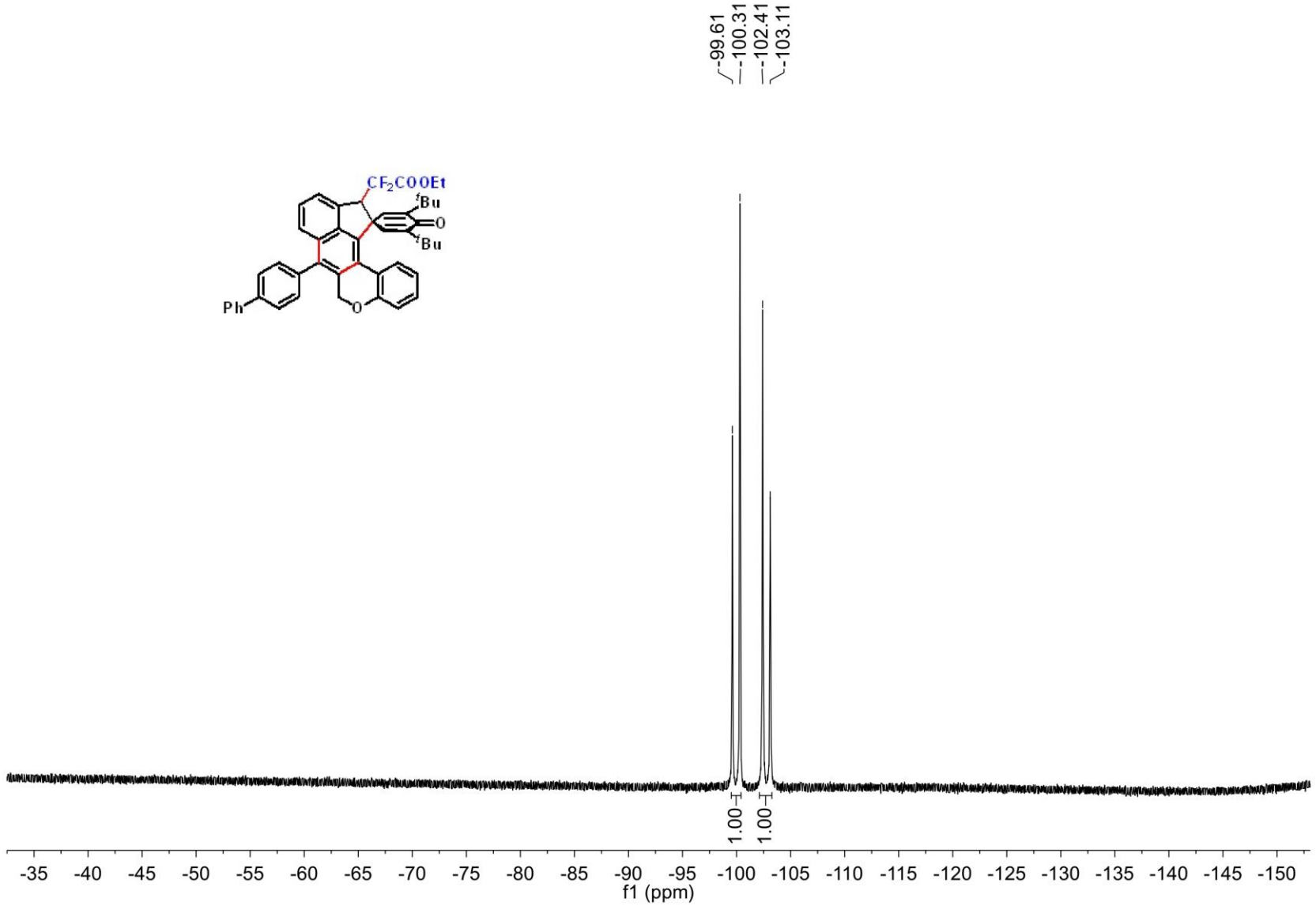
^{19}F NMR Spectrum of Compound 4fa



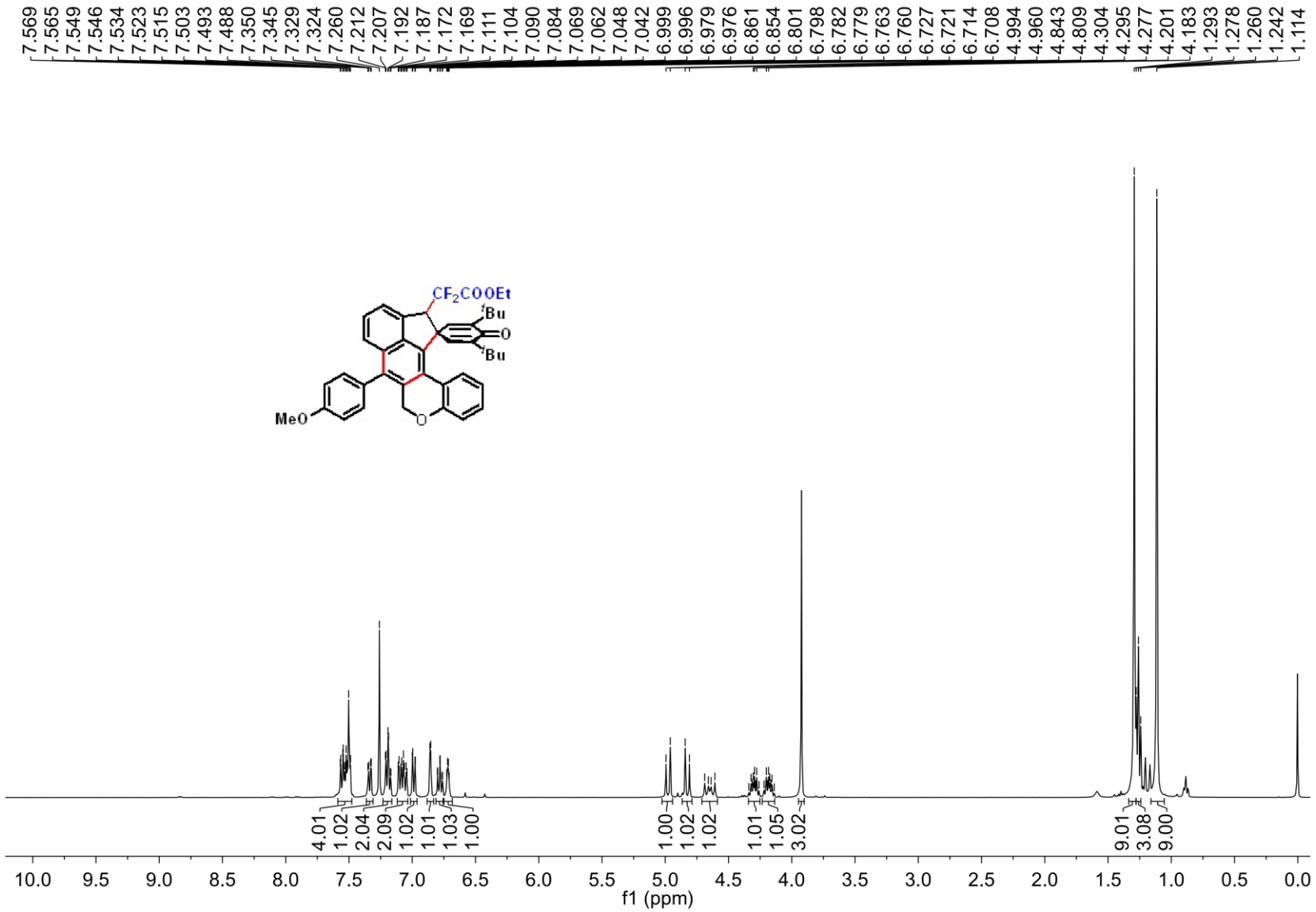
^{1}H NMR Spectrum of Compound 4ga



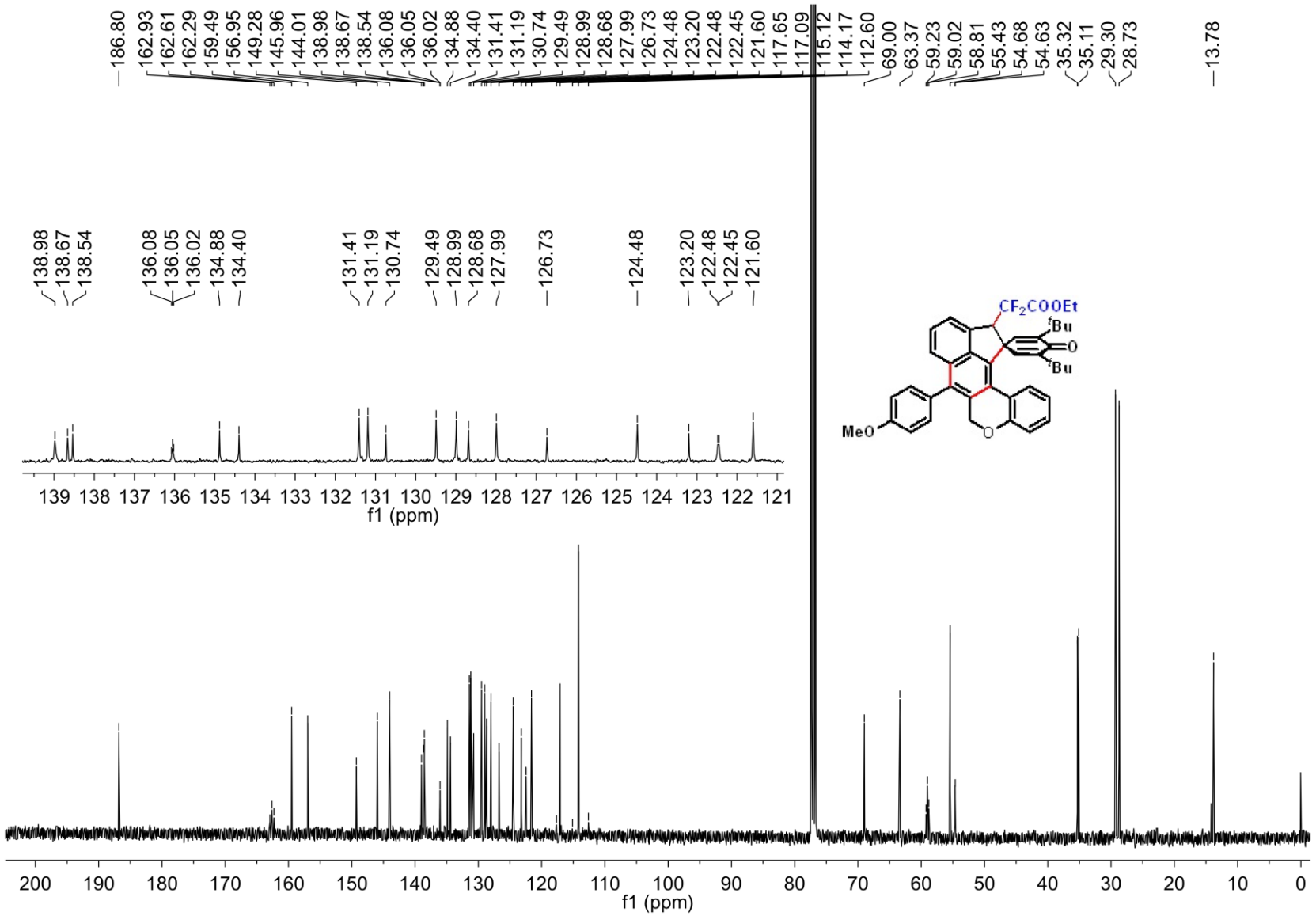
^{13}C NMR Spectrum of Compound 4ga



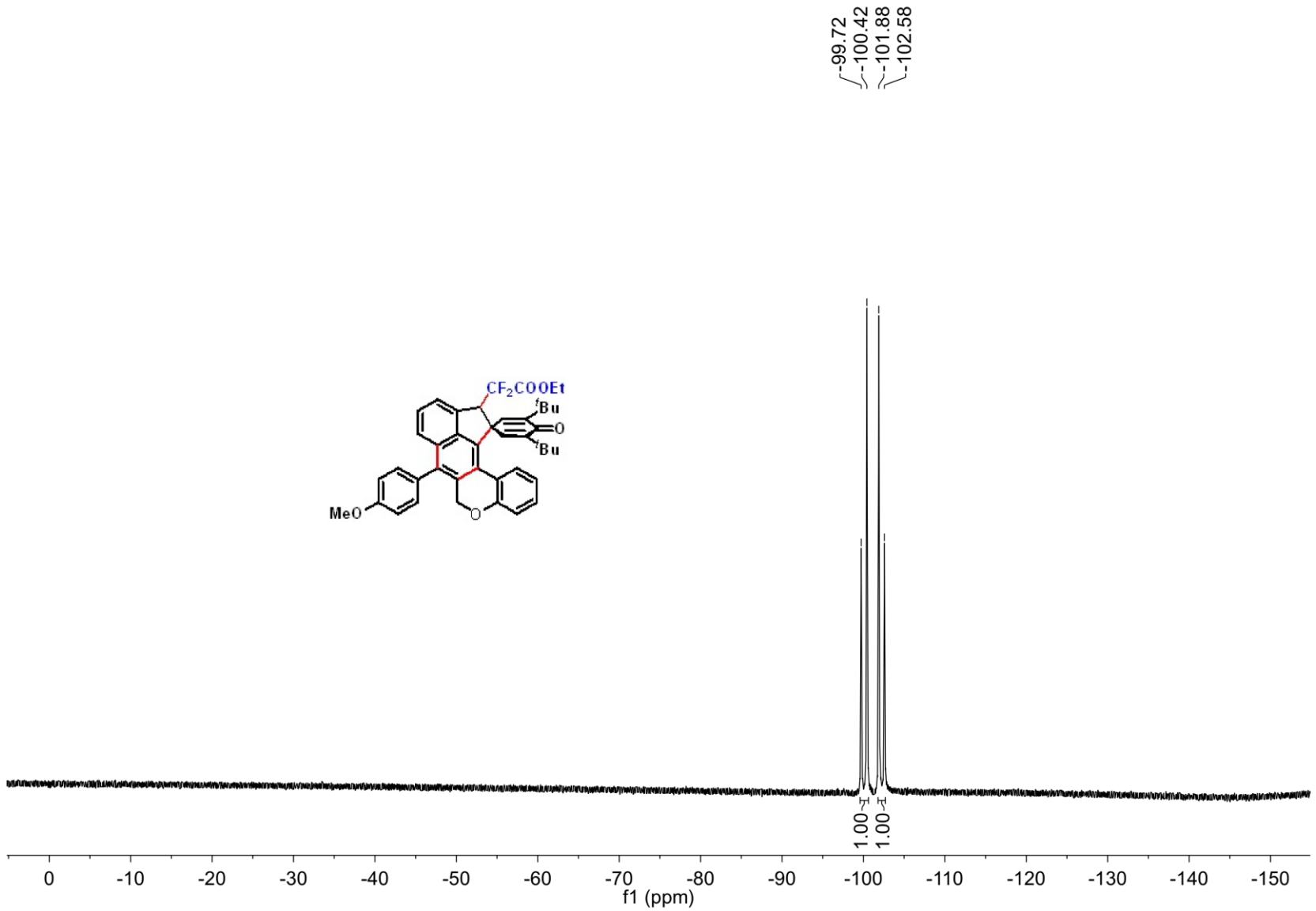
^{19}F NMR Spectrum of Compound 4ga



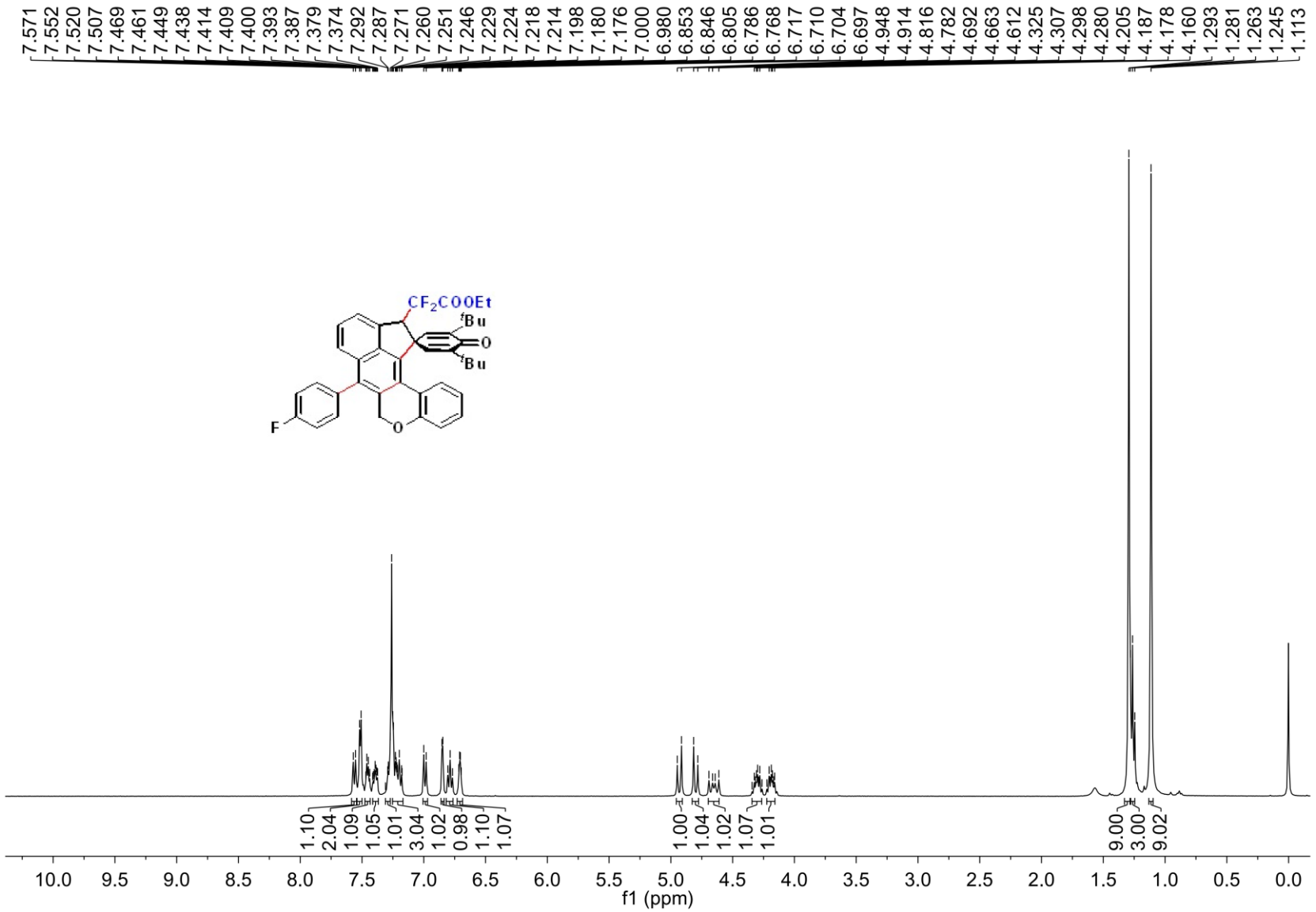
^{1}H NMR Spectrum of Compound 4ha



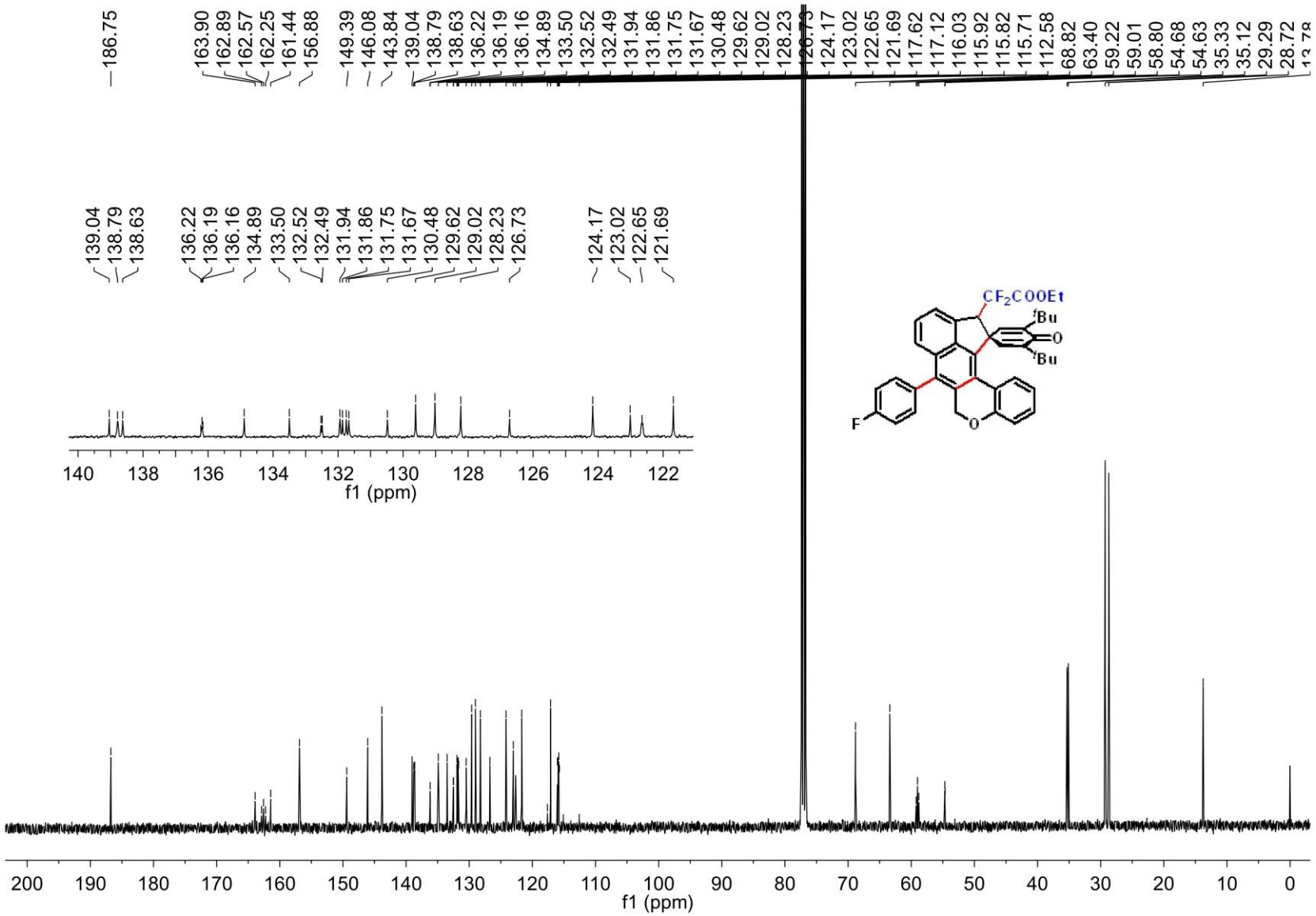
^{13}C NMR Spectrum of Compound 4ha



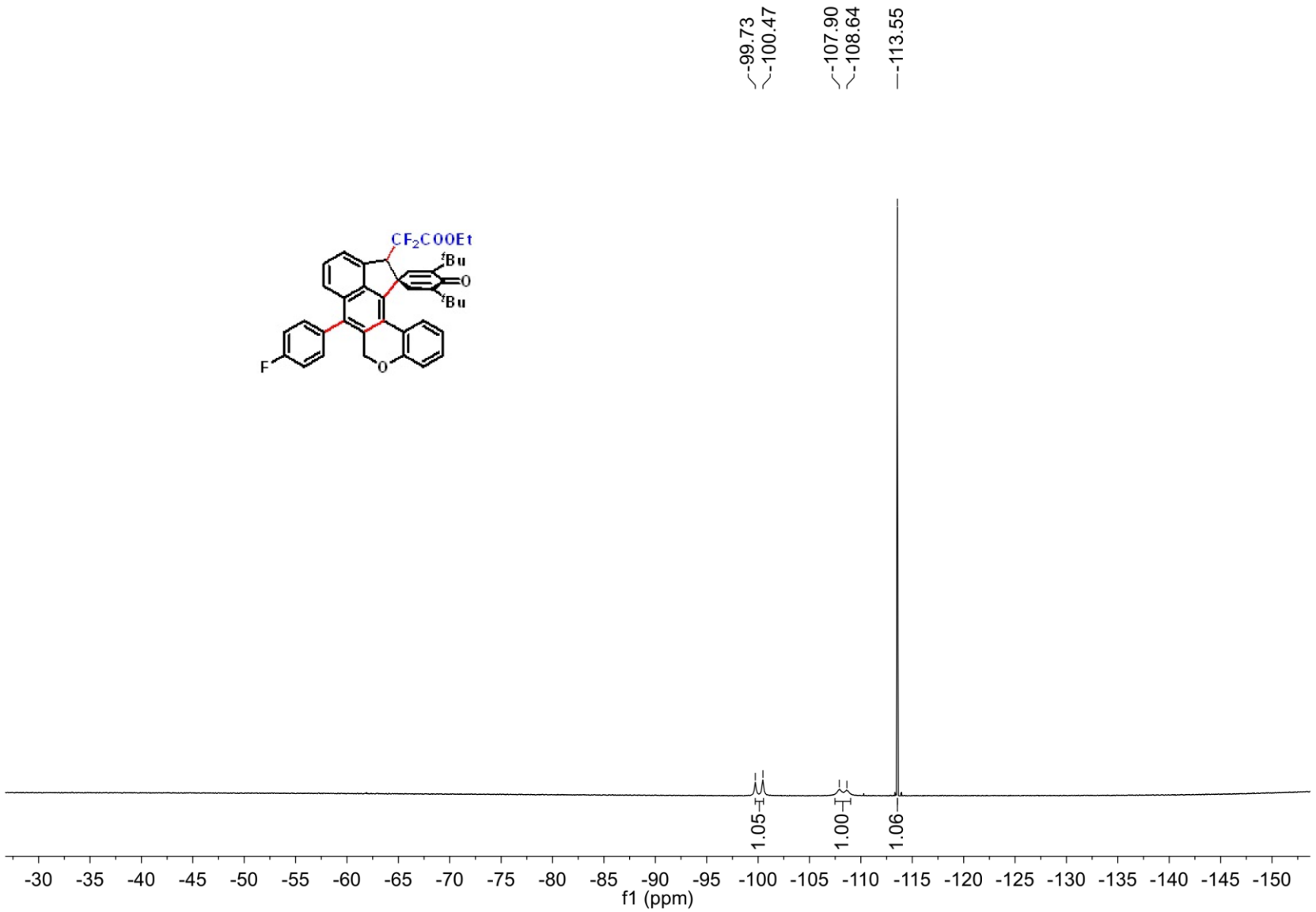
^{19}F NMR Spectrum of Compound 4ha



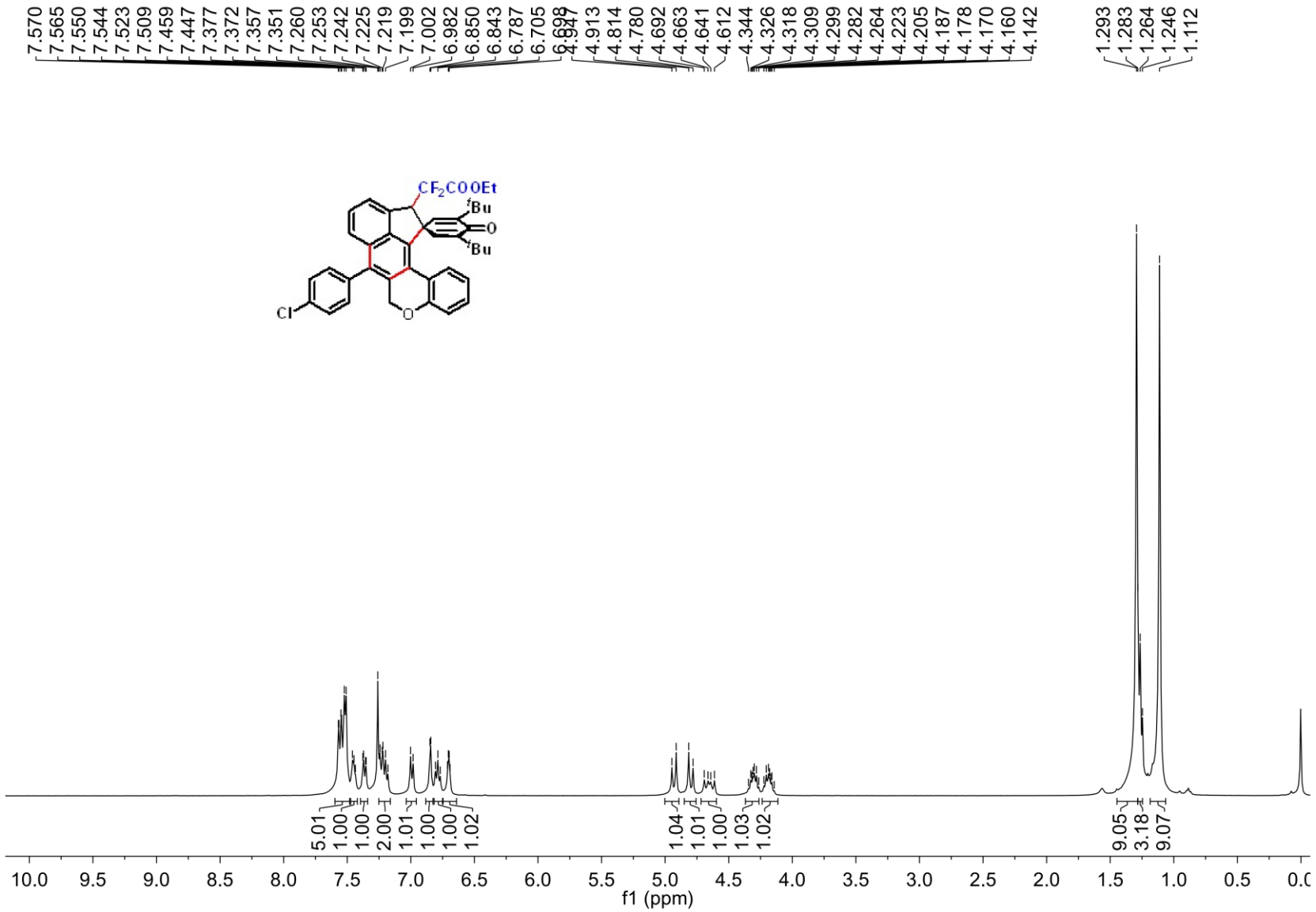
^{1}H NMR Spectrum of Compound 4ia



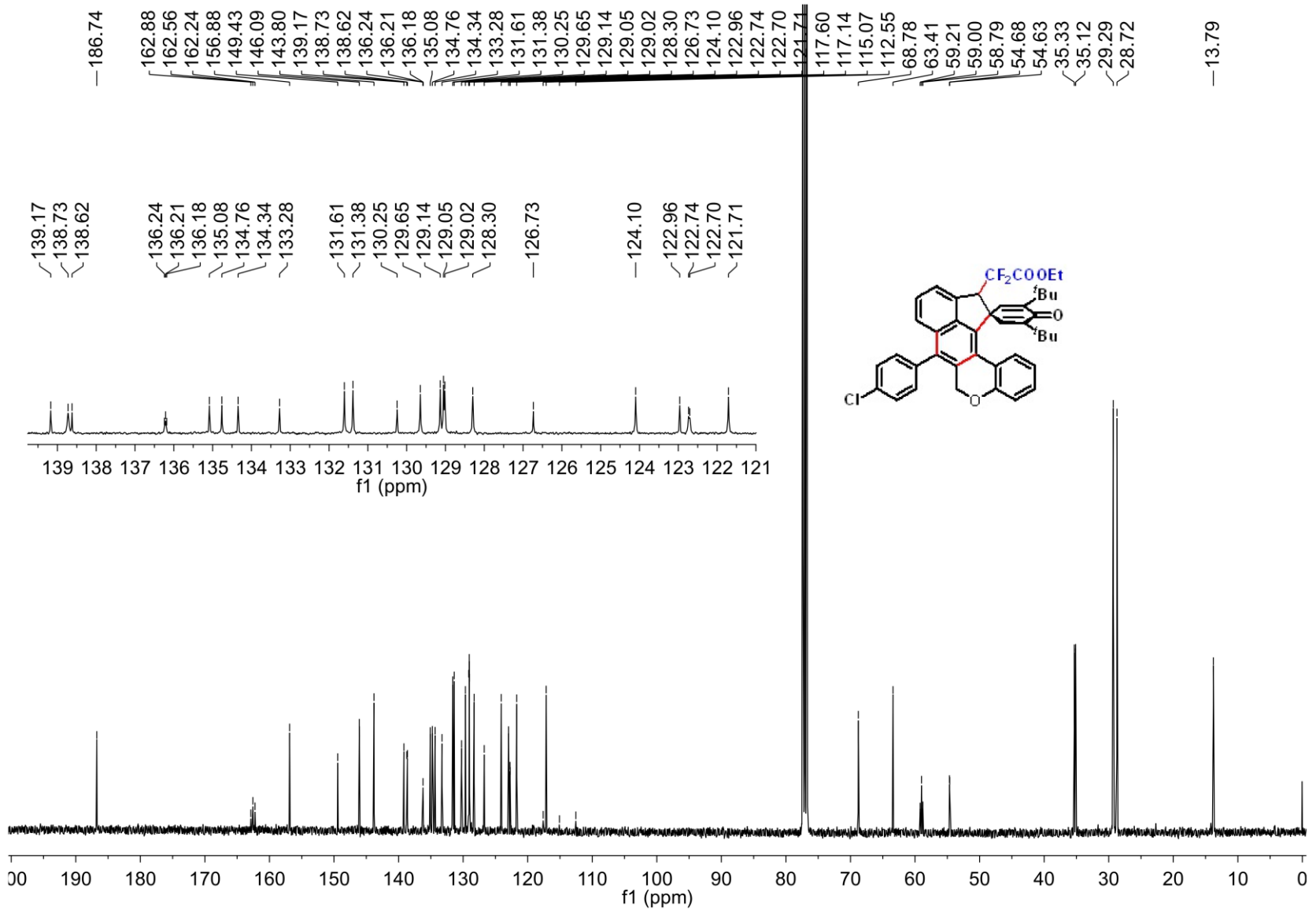
^{13}C NMR Spectrum of Compound 4ia



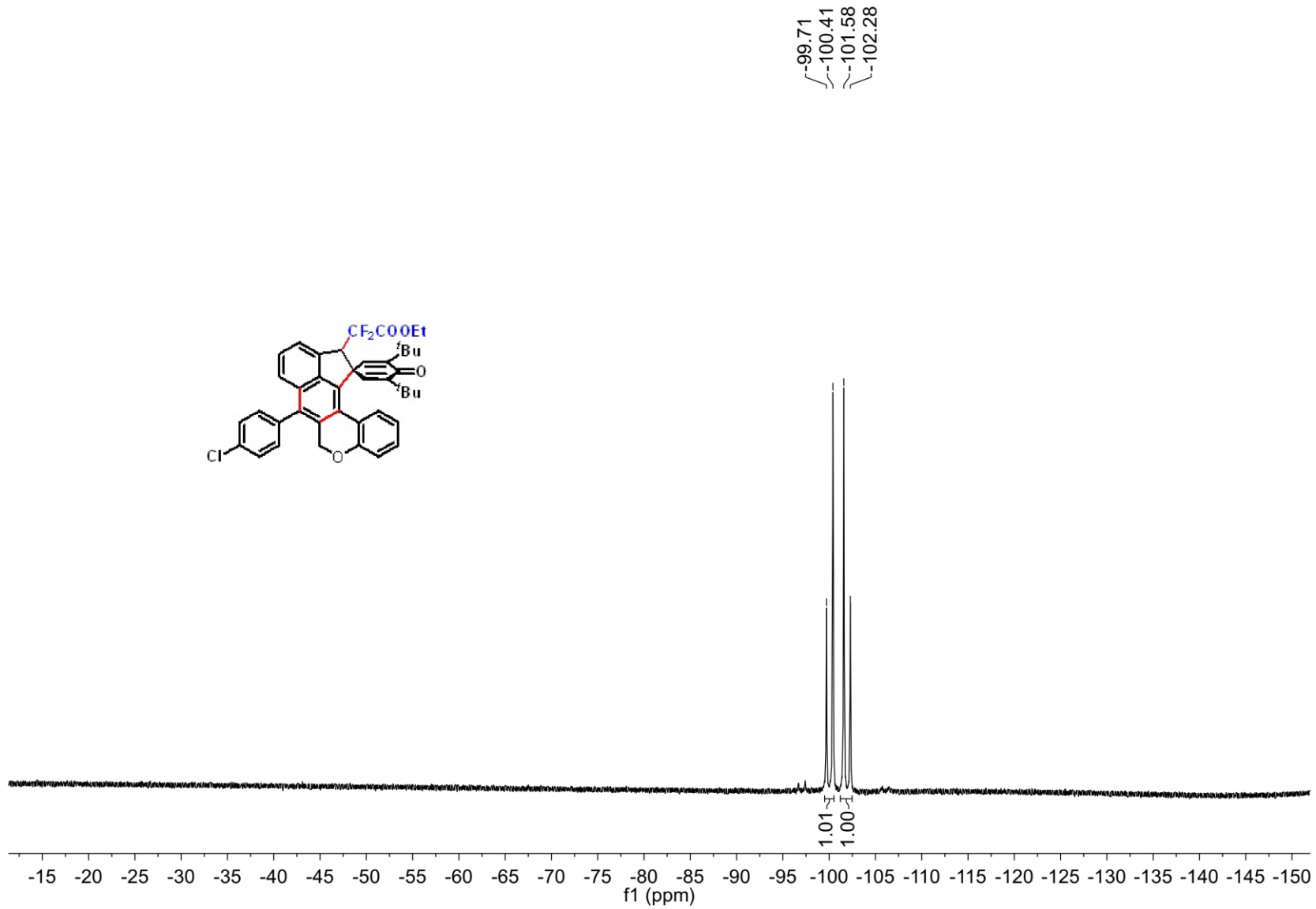
^{19}F NMR Spectrum of Compound 4ia



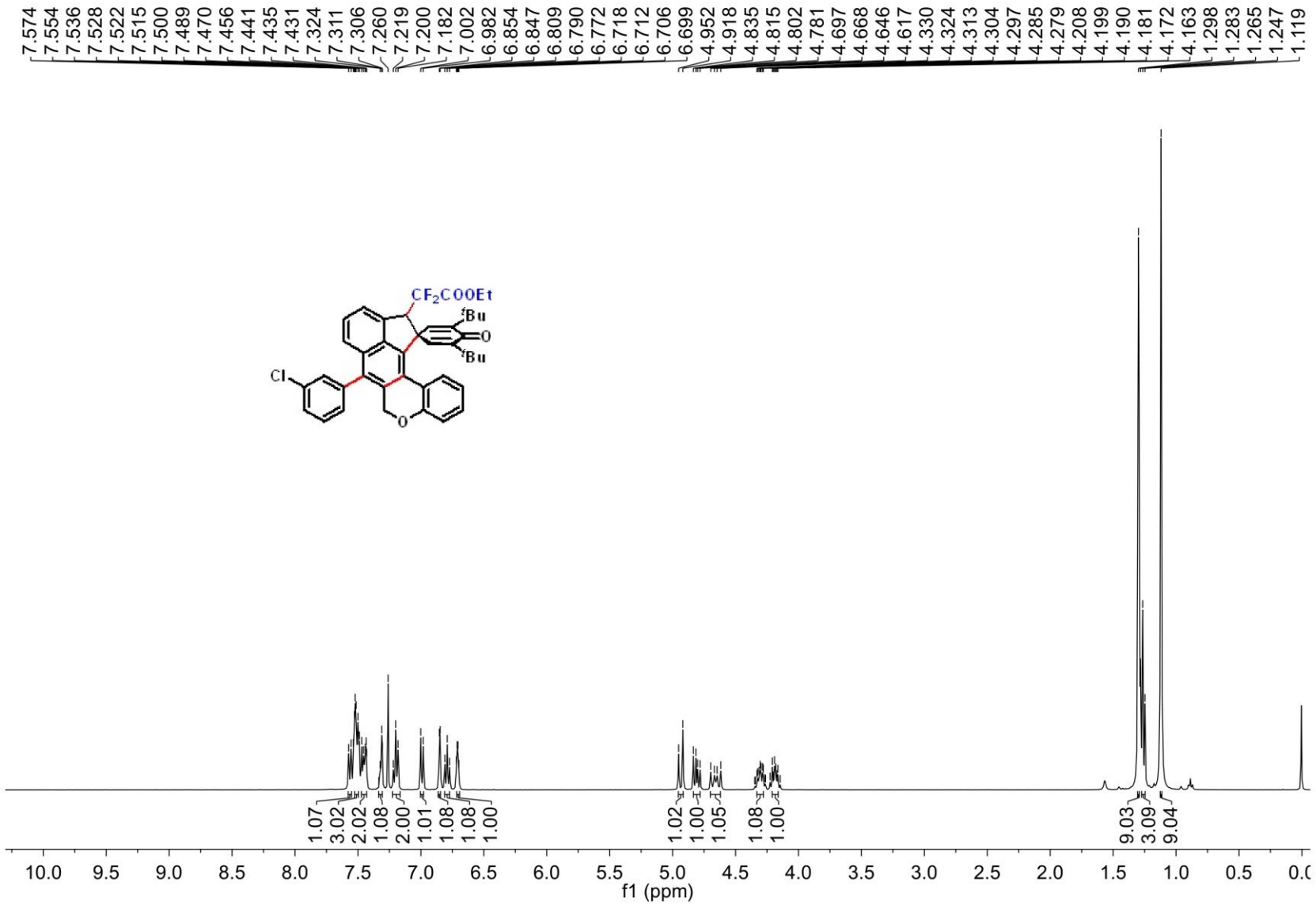
^{1}H NMR Spectrum of Compound 4ja



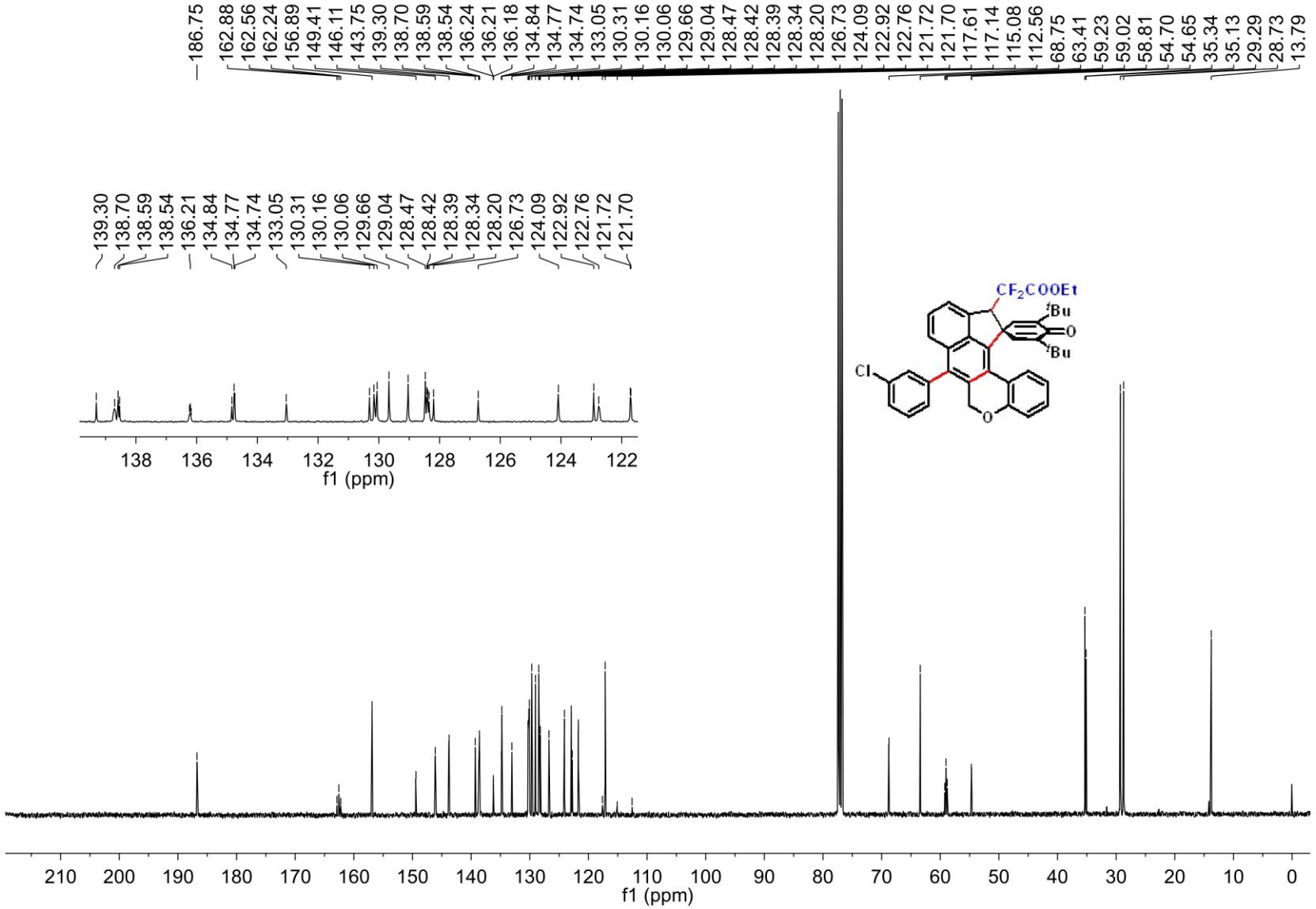
^{13}C NMR Spectrum of Compound 4ja



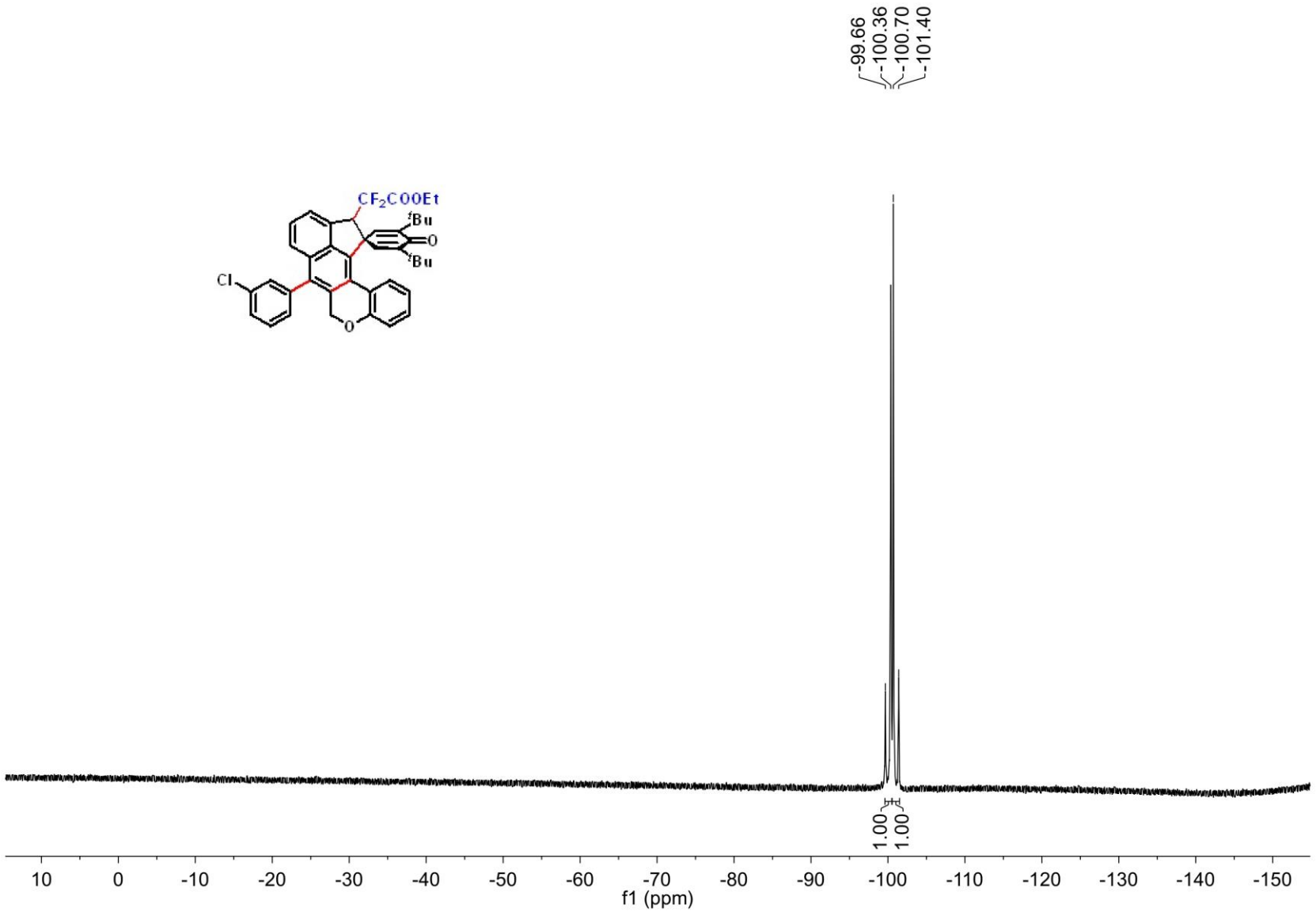
^{19}F NMR Spectrum of Compound 4ja



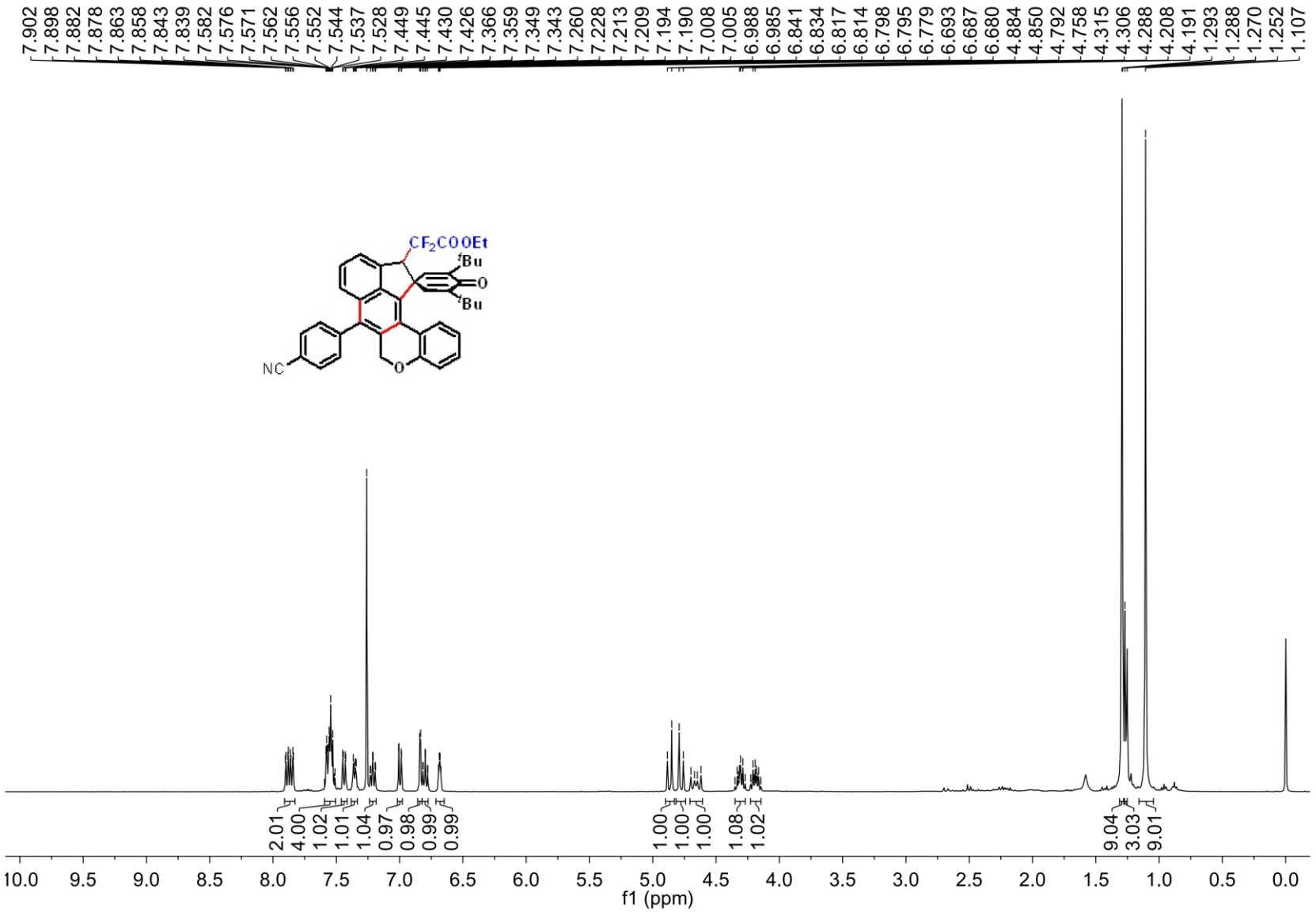
^{1}H NMR Spectrum of Compound 4ka



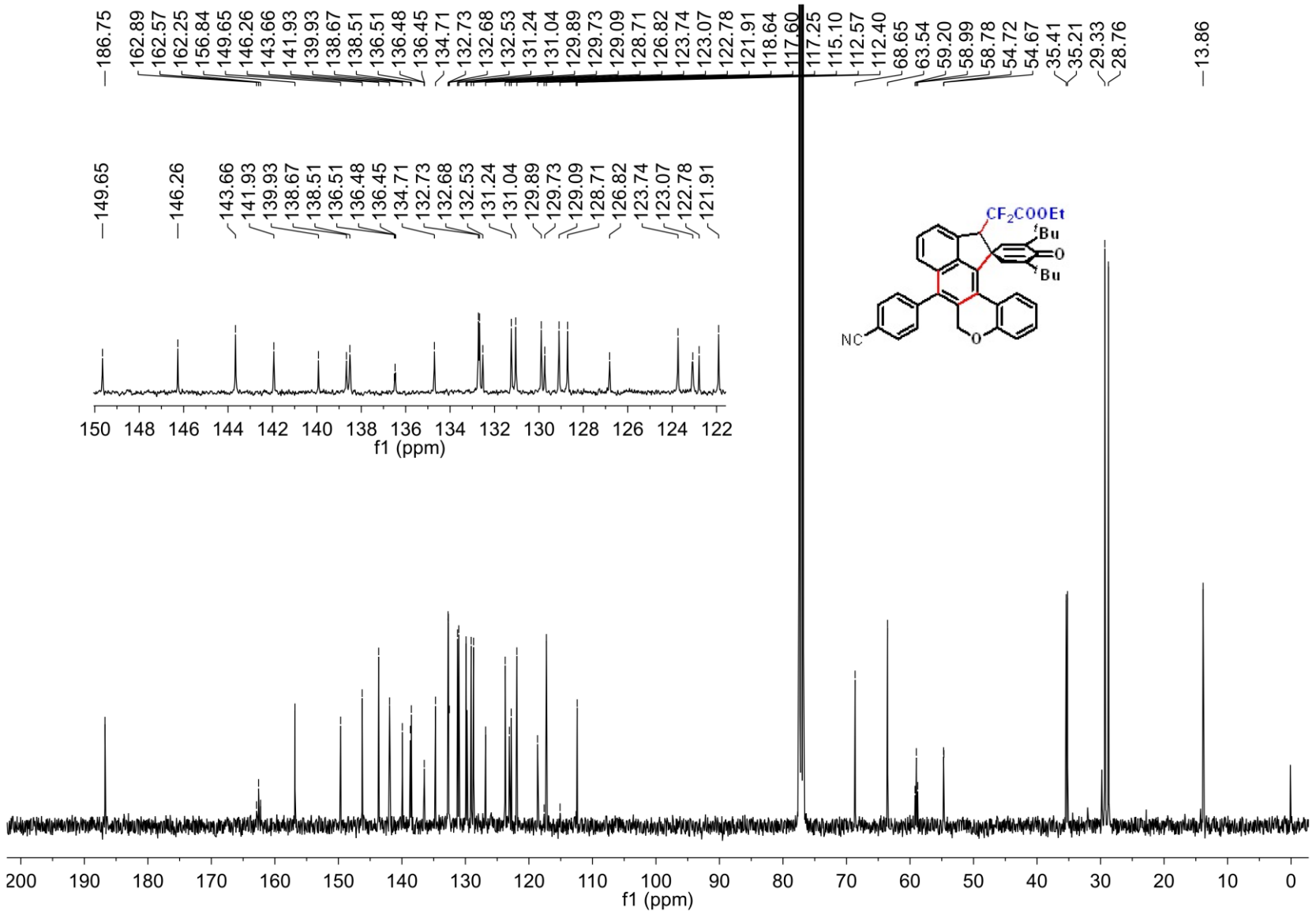
^{13}C NMR Spectrum of Compound 4ka



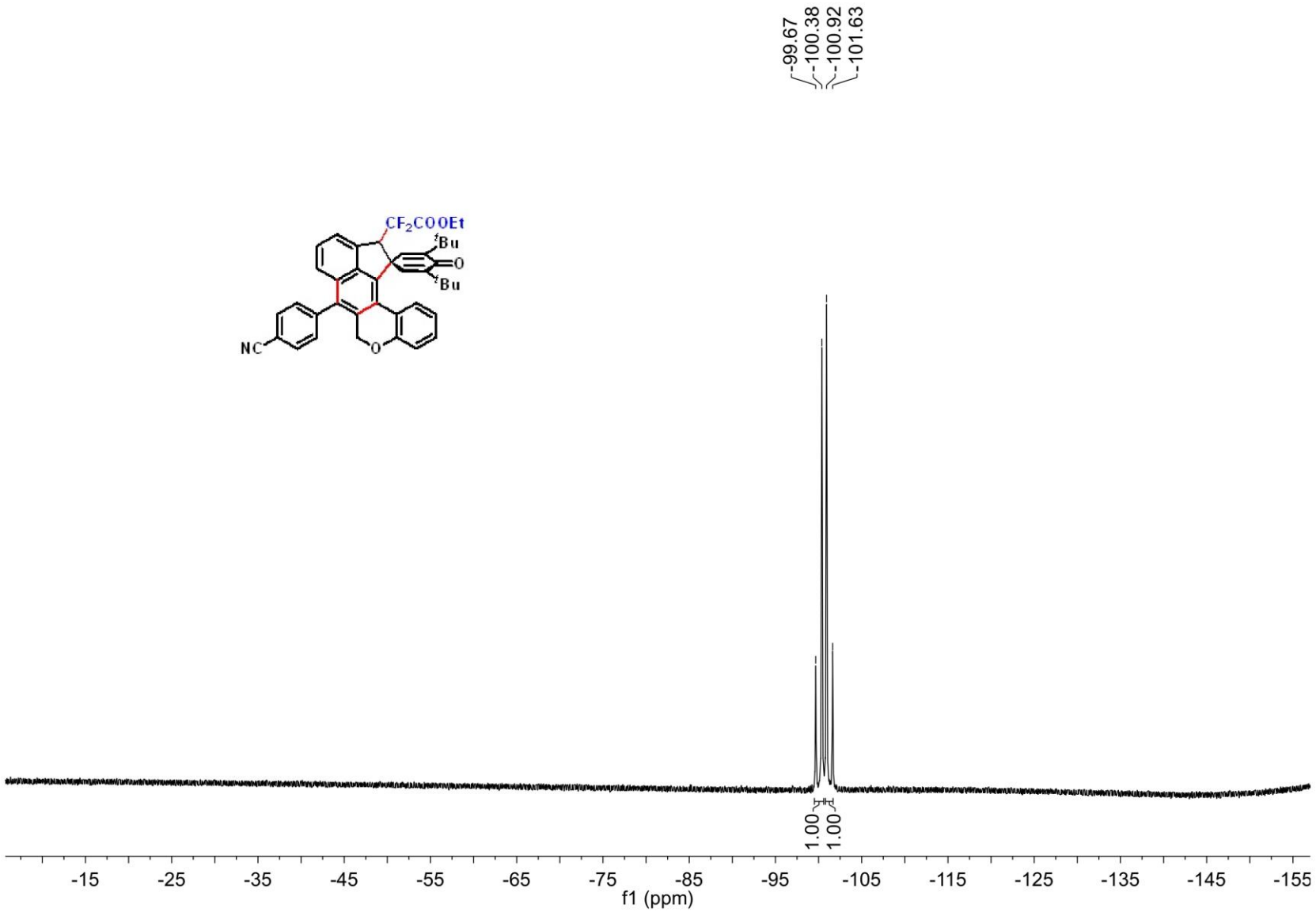
^{19}F NMR Spectrum of Compound 4ka



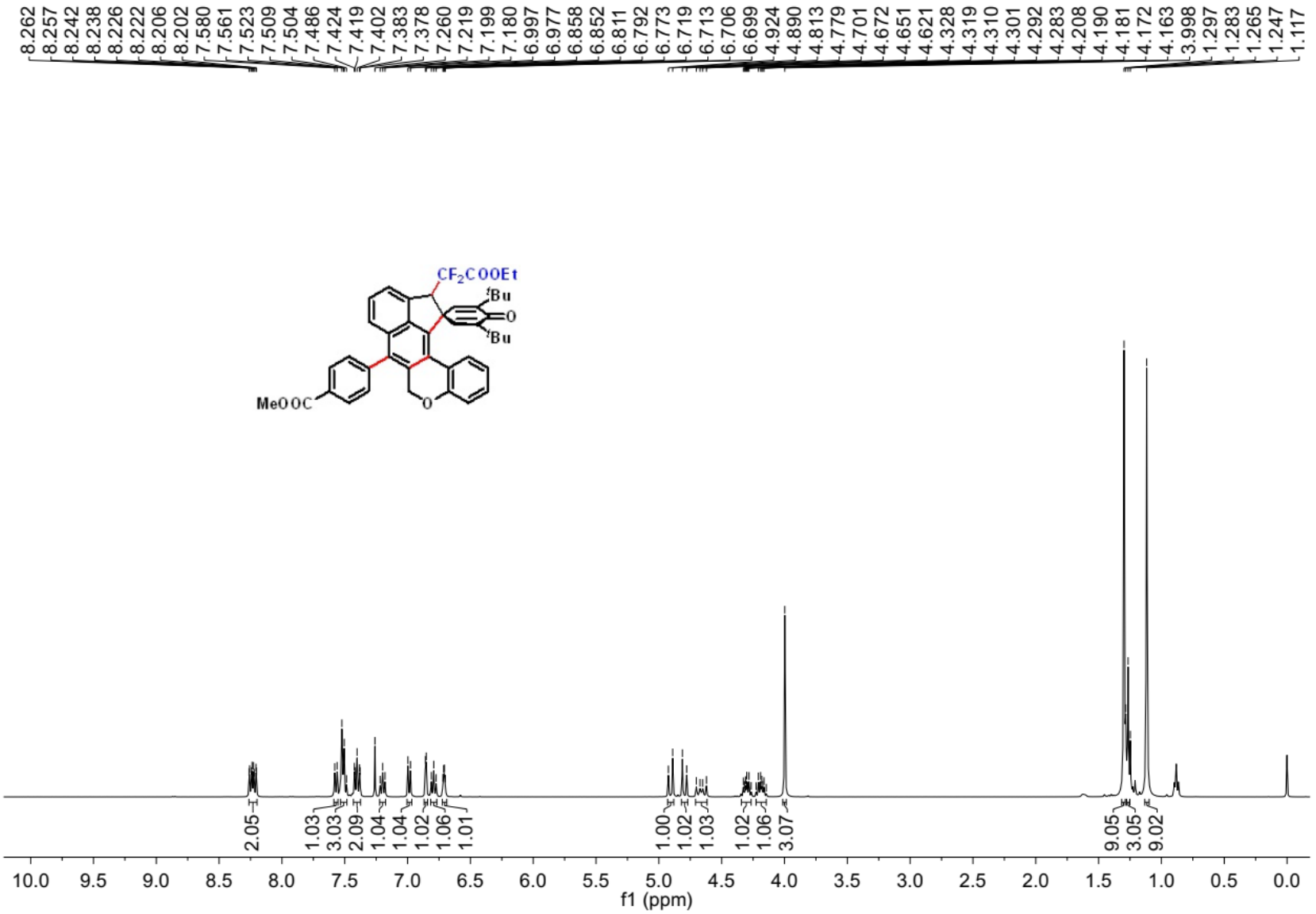
^{1}H NMR Spectrum of Compound 4la



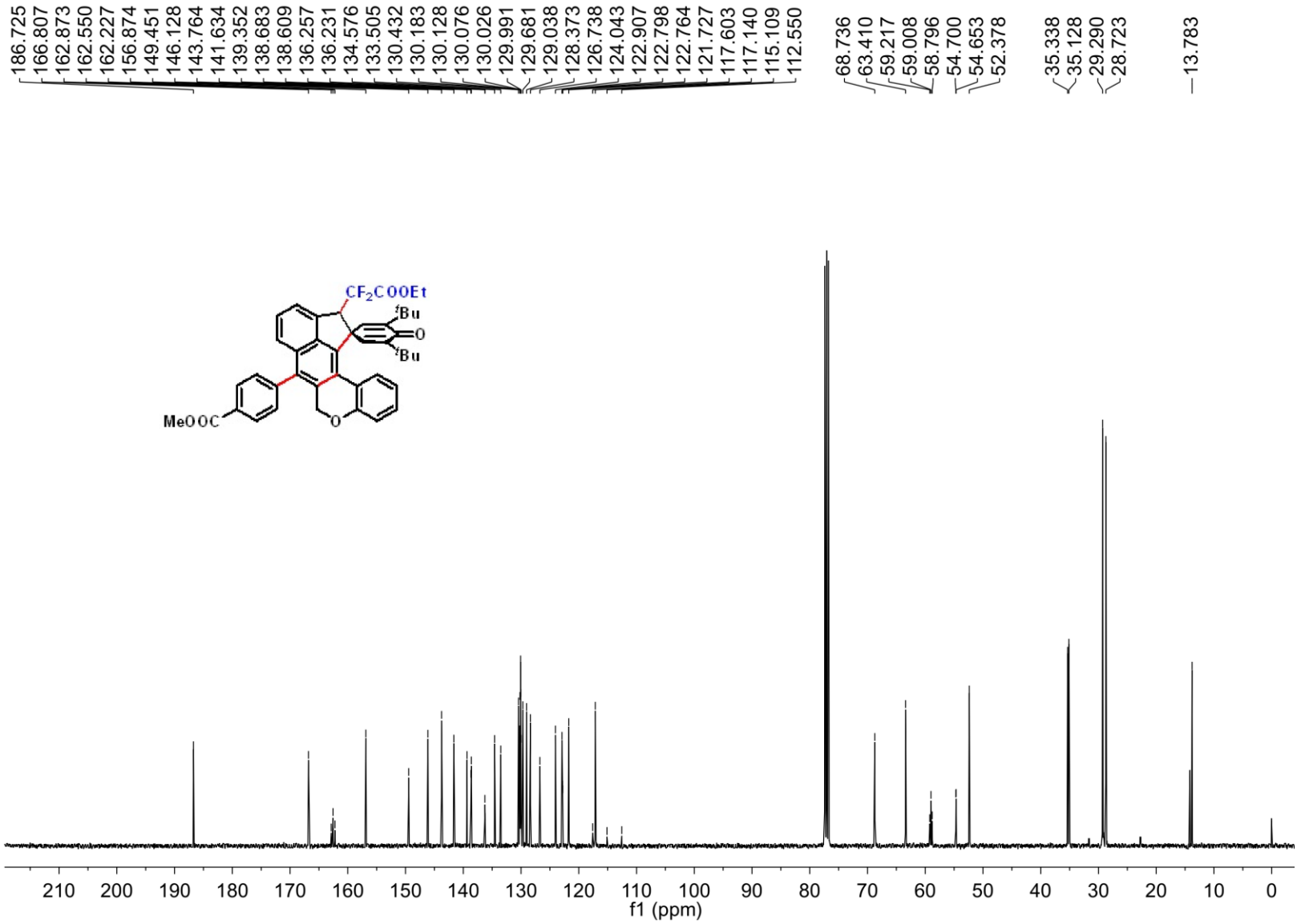
^{13}C NMR Spectrum of Compound 4la



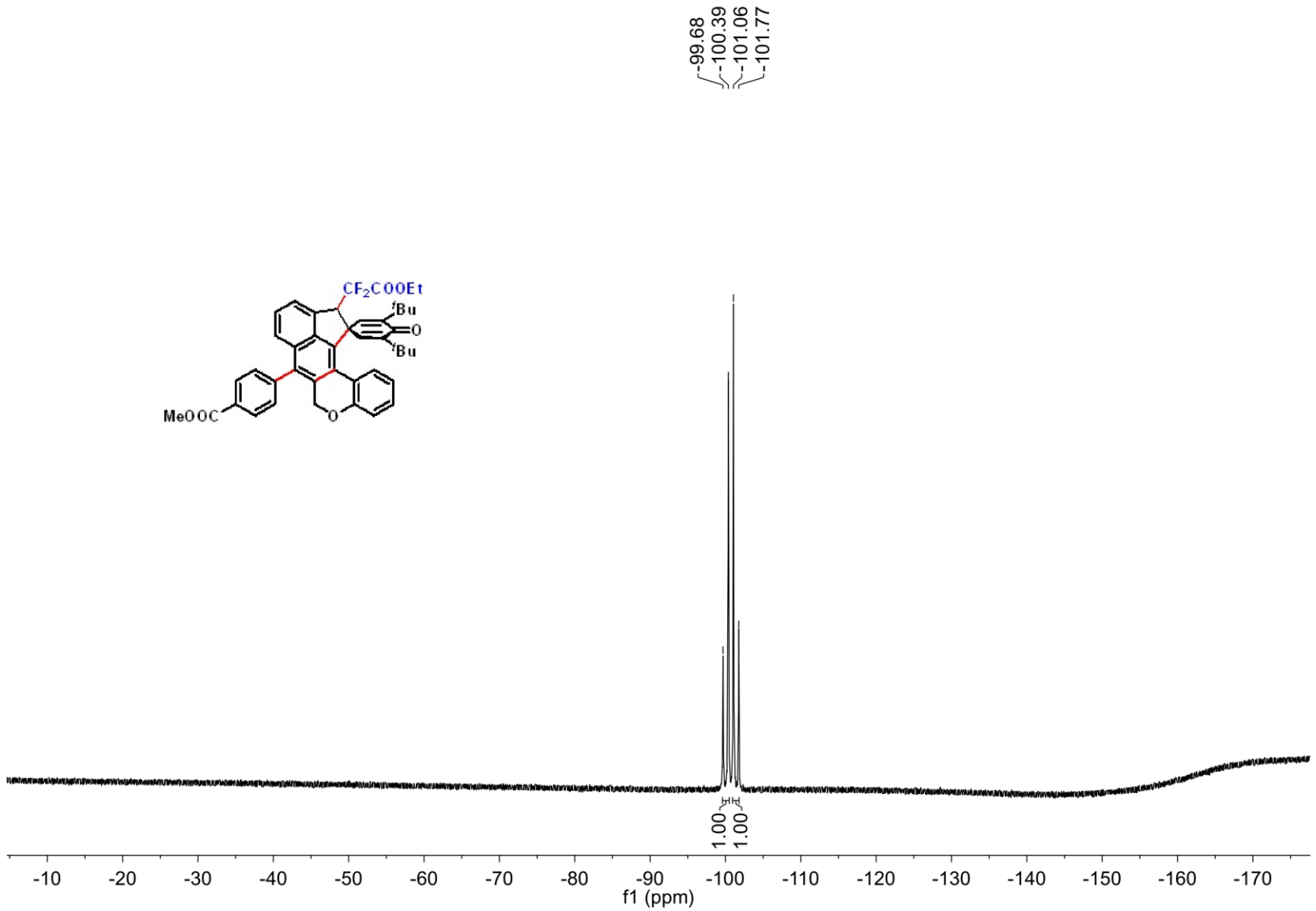
^{19}F NMR Spectrum of Compound 4la



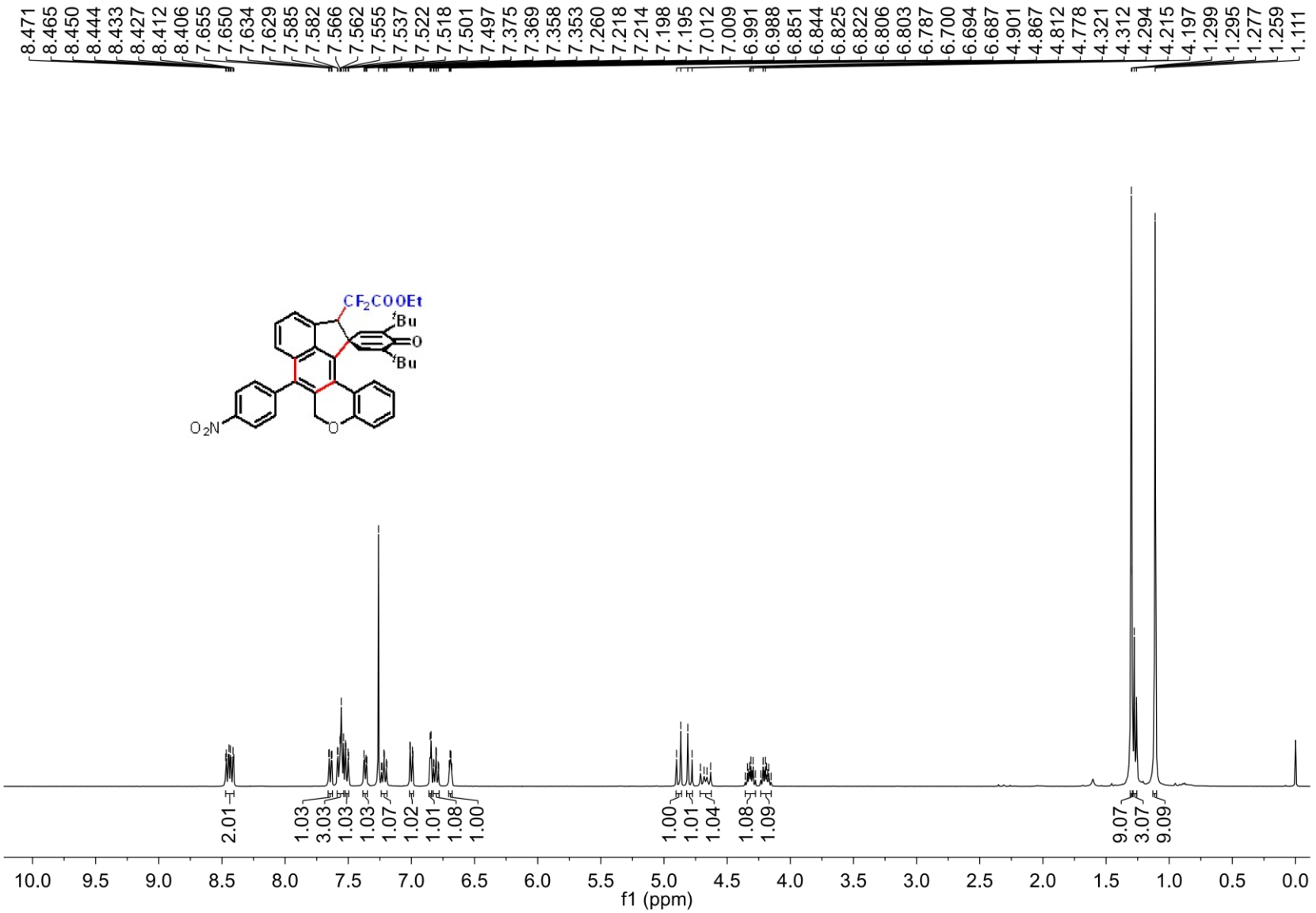
^{1}H NMR Spectrum of Compound 4ma



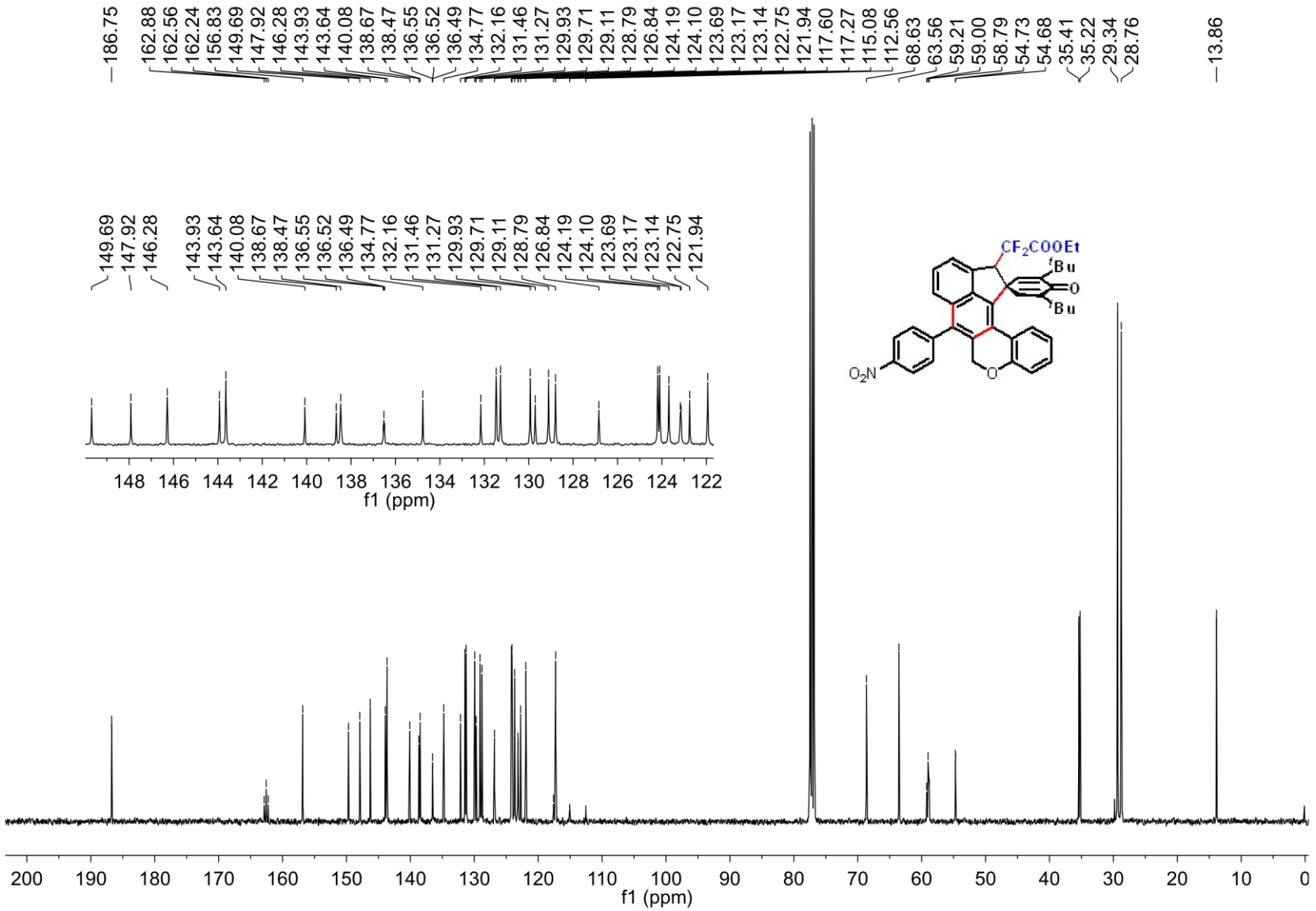
^{13}C NMR Spectrum of Compound 4ma



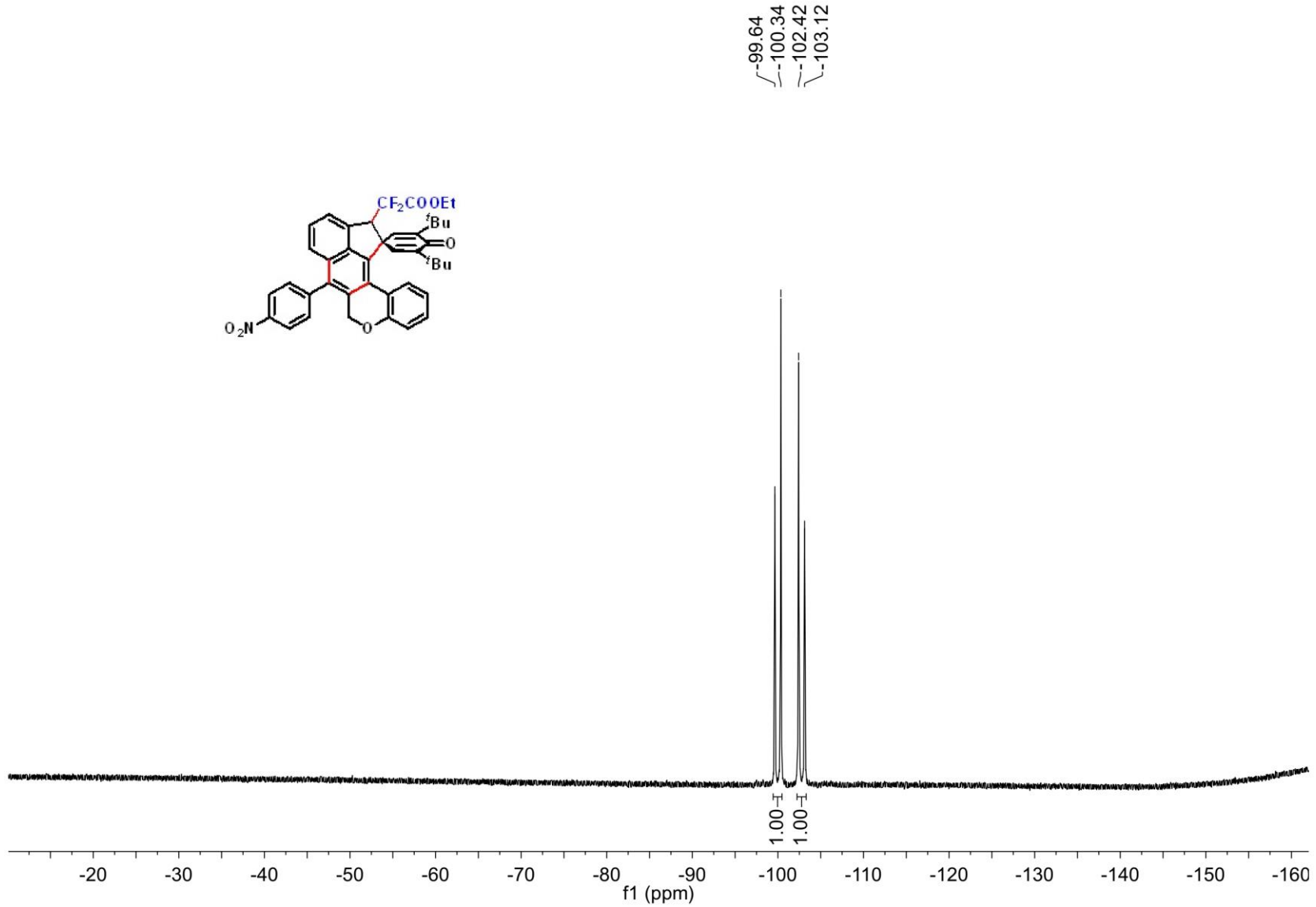
^{19}F NMR Spectrum of Compound 4ma



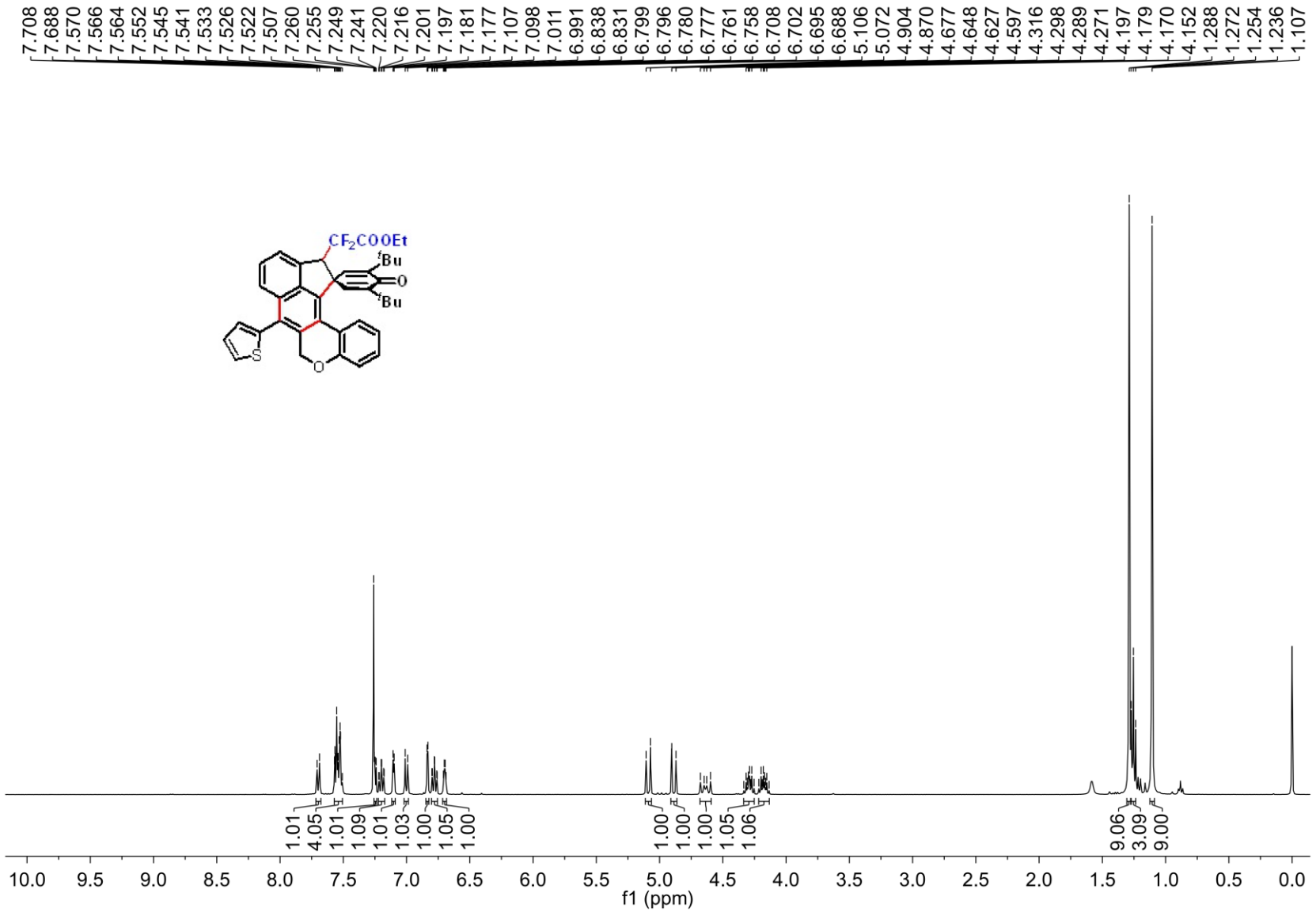
^{1}H NMR Spectrum of Compound 4na



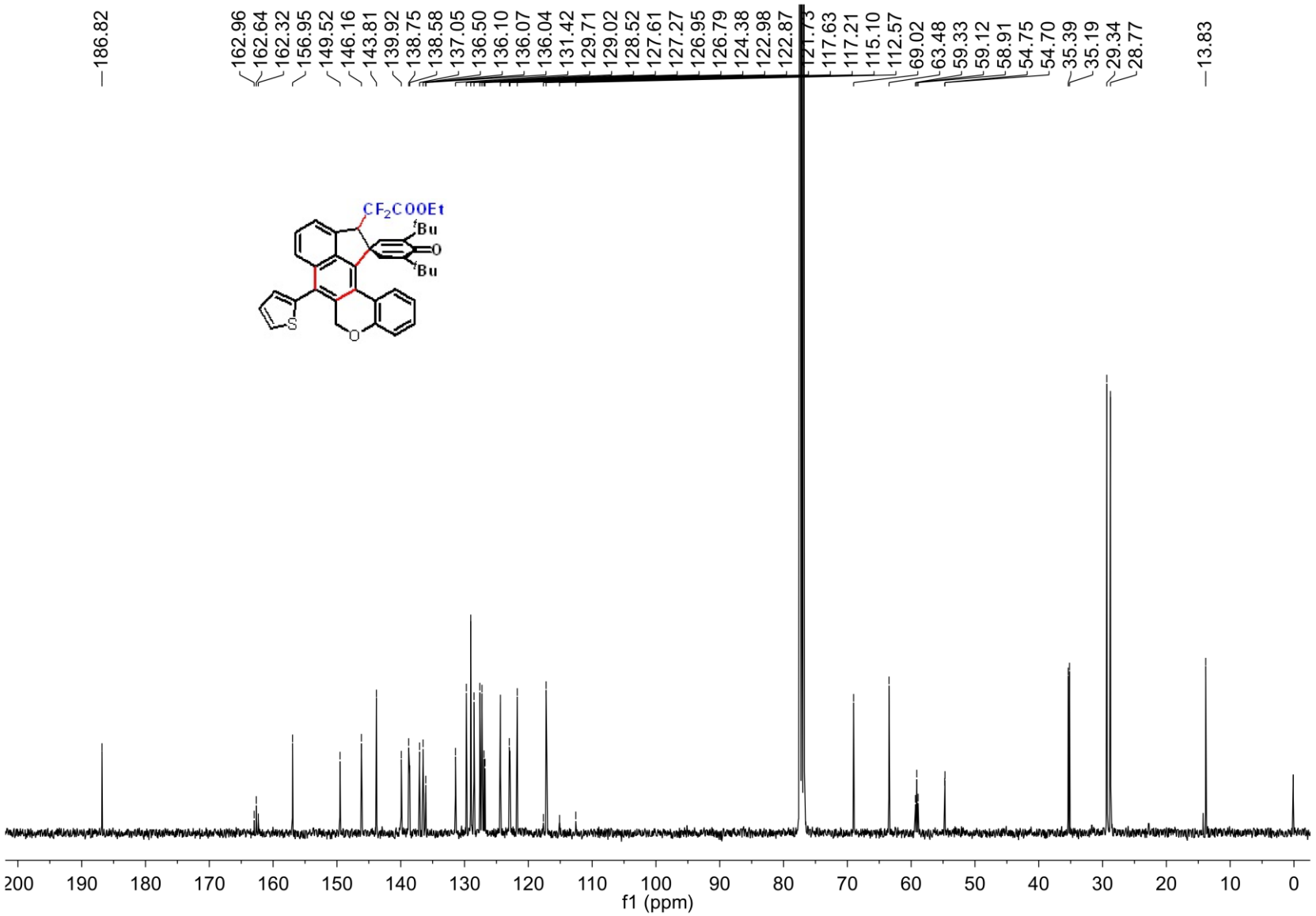
^{13}C NMR Spectrum of Compound 4na



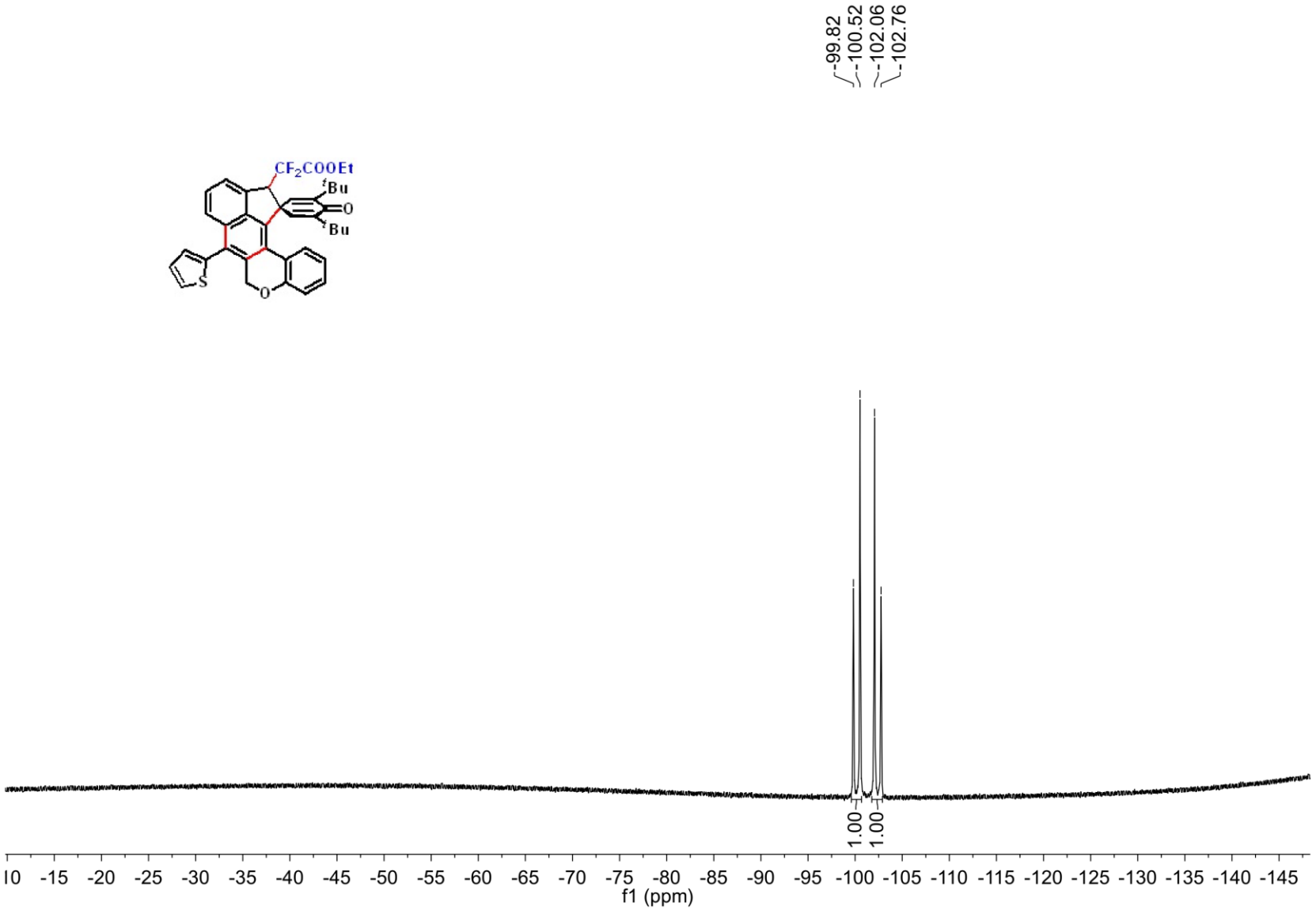
^{19}F NMR Spectrum of Compound 4na



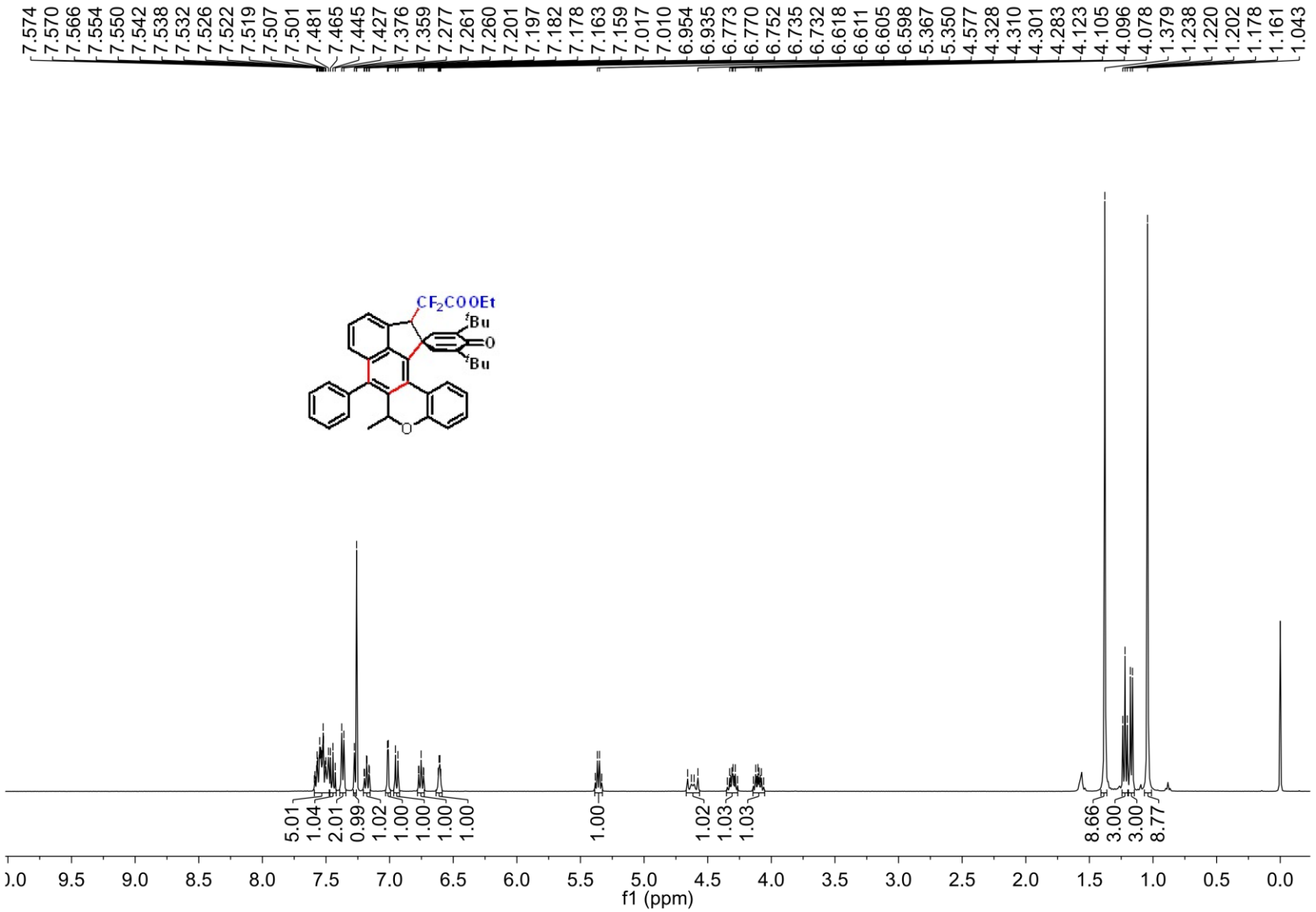
^{1}H NMR Spectrum of Compound 4oa



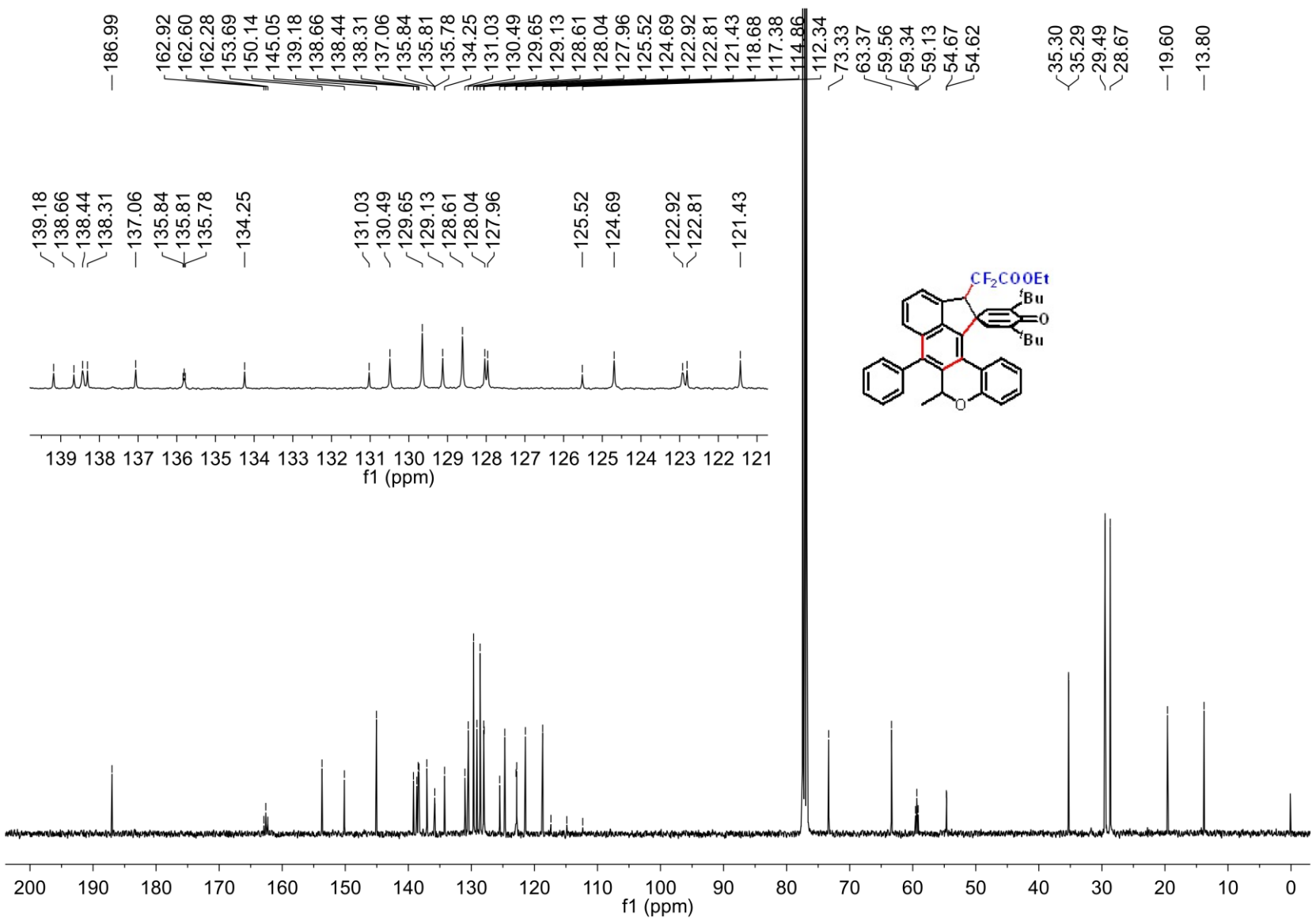
^{13}C NMR Spectrum of Compound 4oa



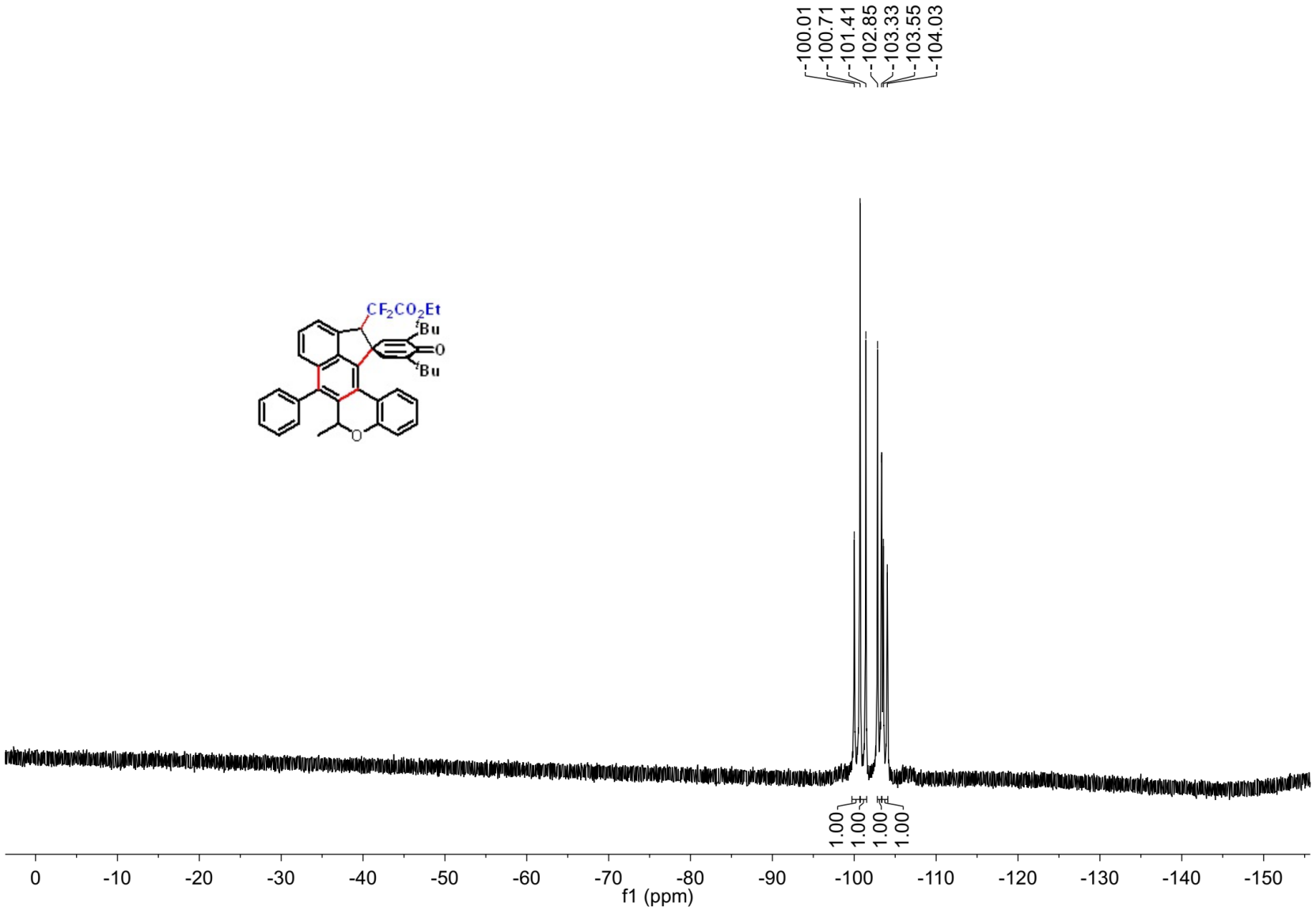
^{19}F NMR Spectrum of Compound 4oa



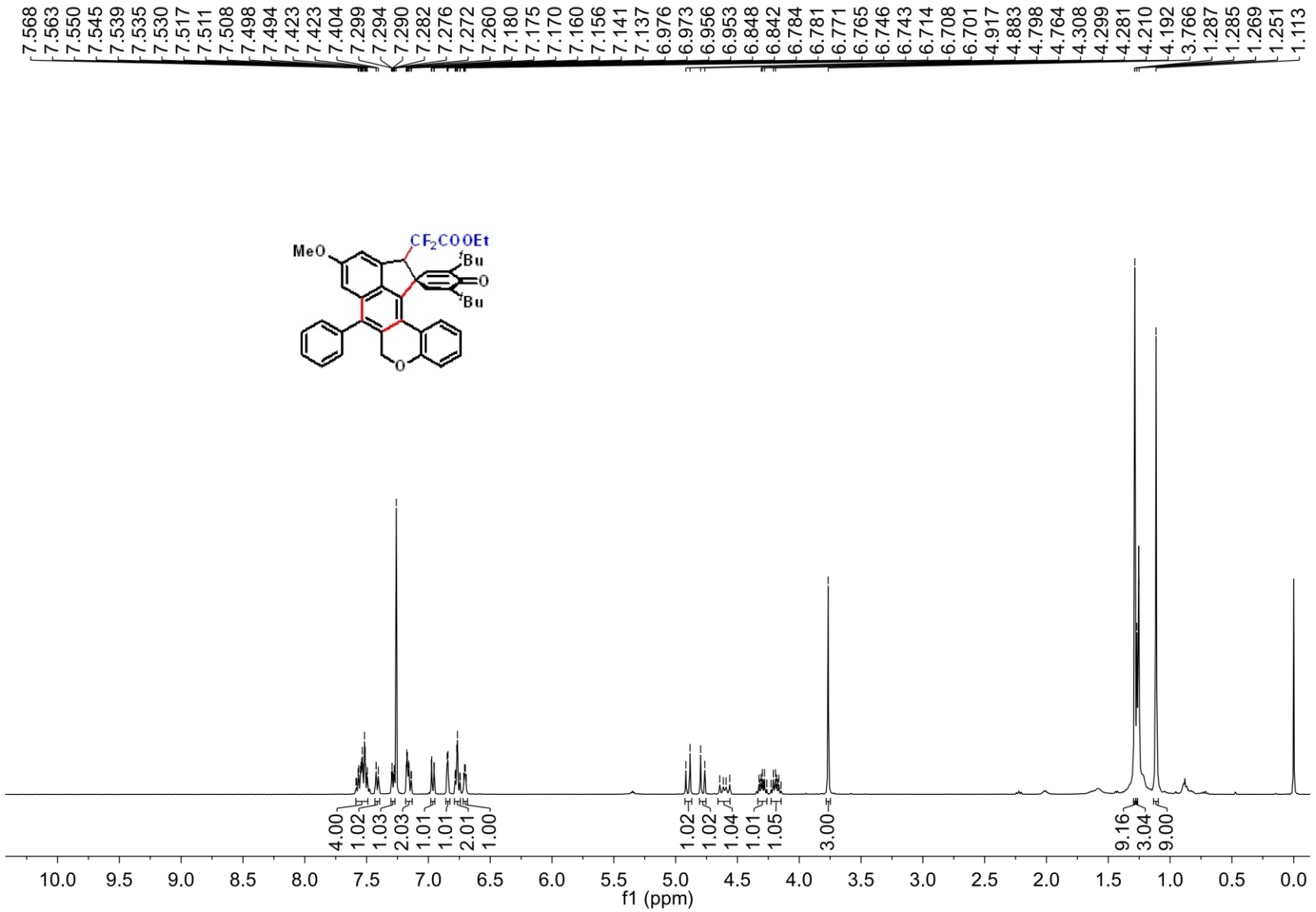
^{1}H NMR Spectrum of Compound 4qa



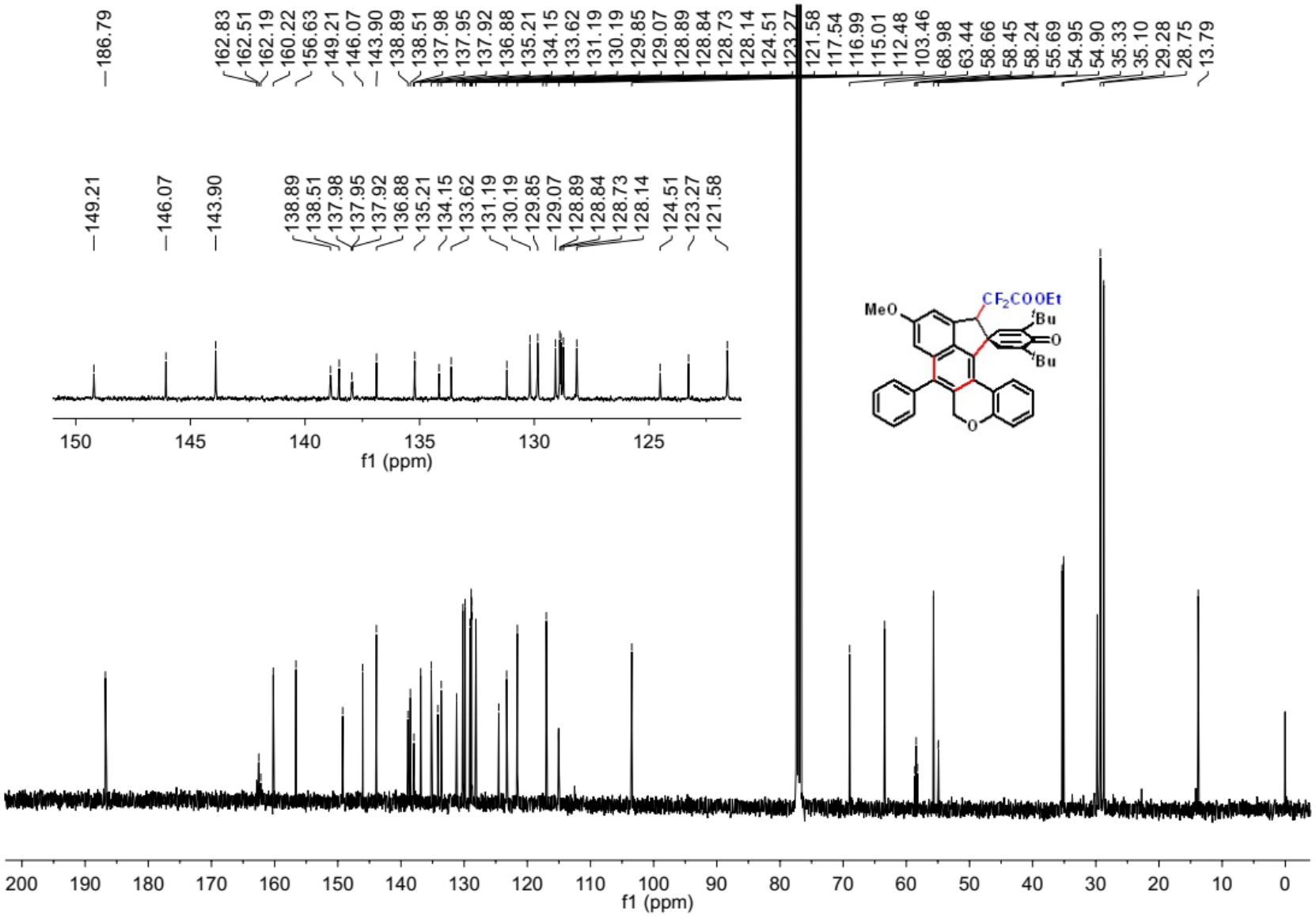
^{13}C NMR Spectrum of Compound 4qa



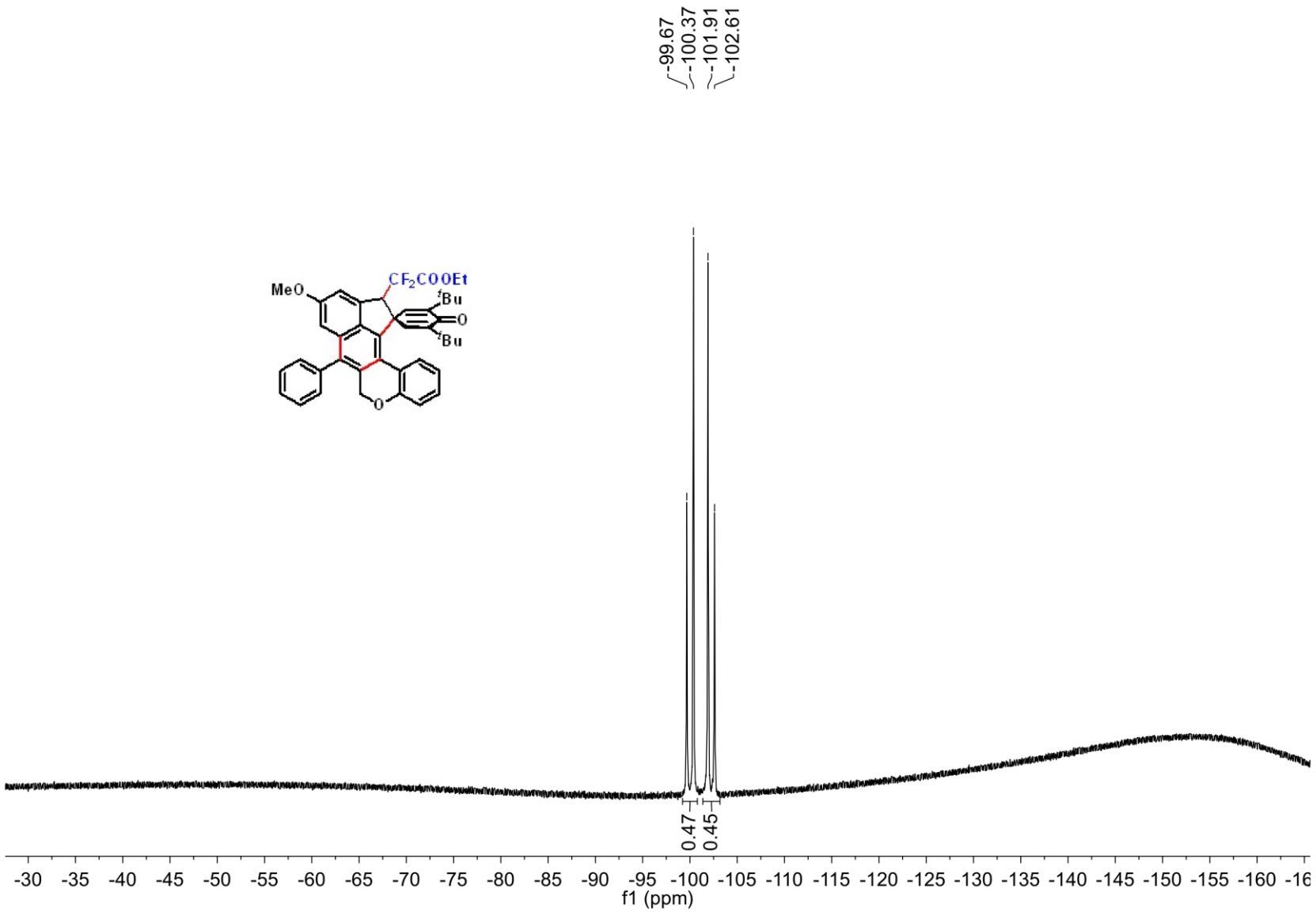
^{19}F NMR Spectrum of Compound 4qa



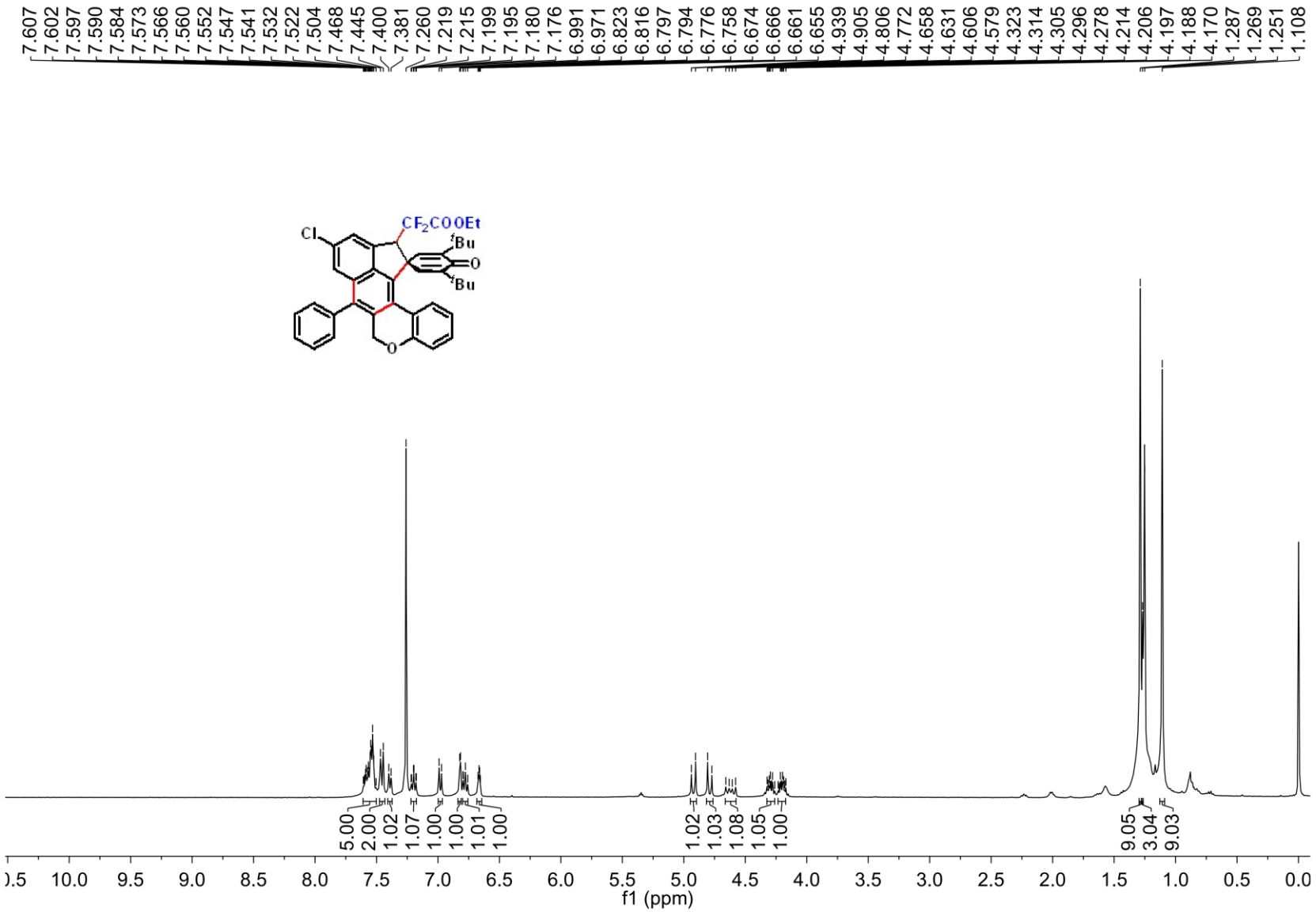
^{1}H NMR Spectrum of Compound 4ra



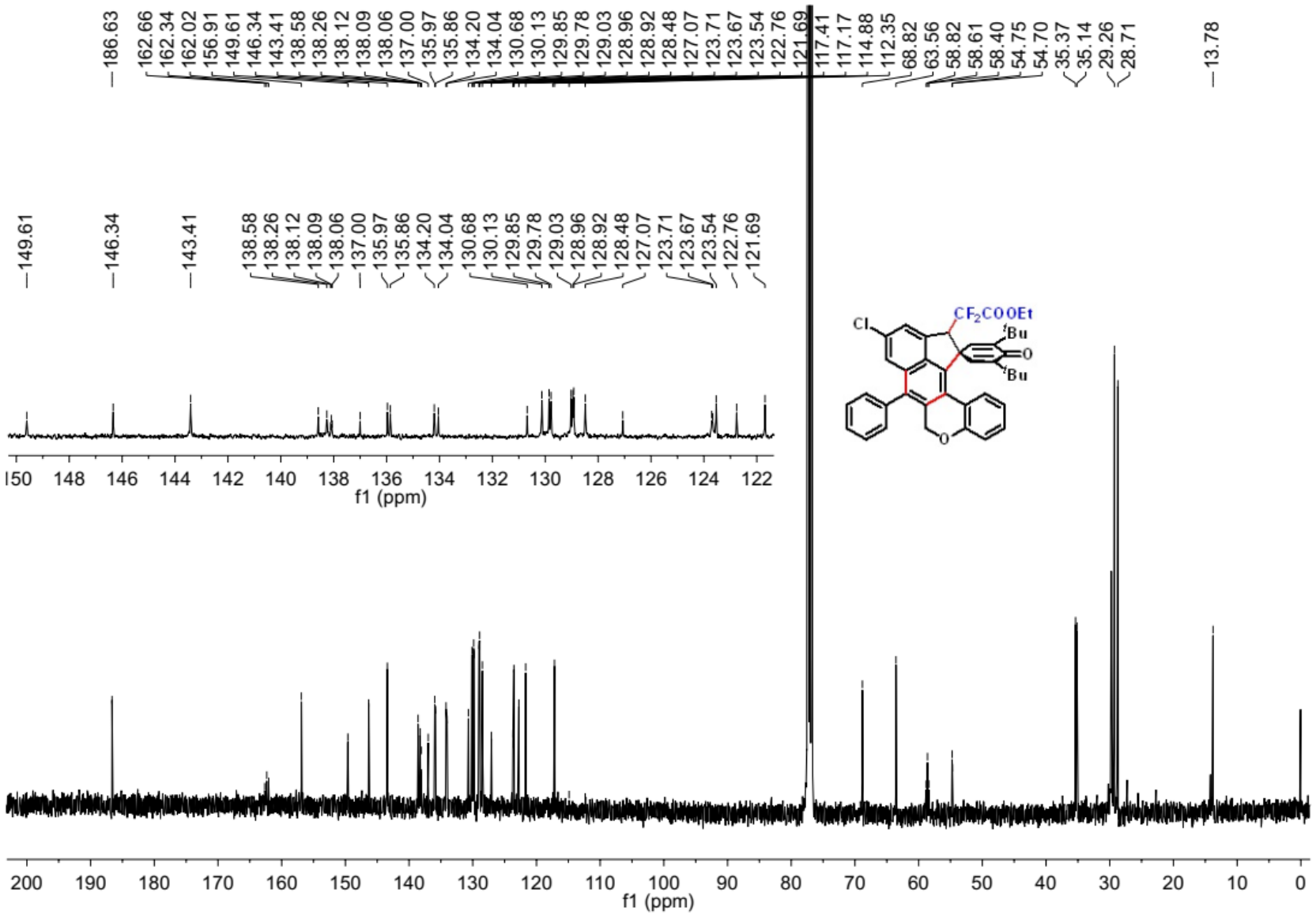
^{13}C NMR Spectrum of Compound 4ra



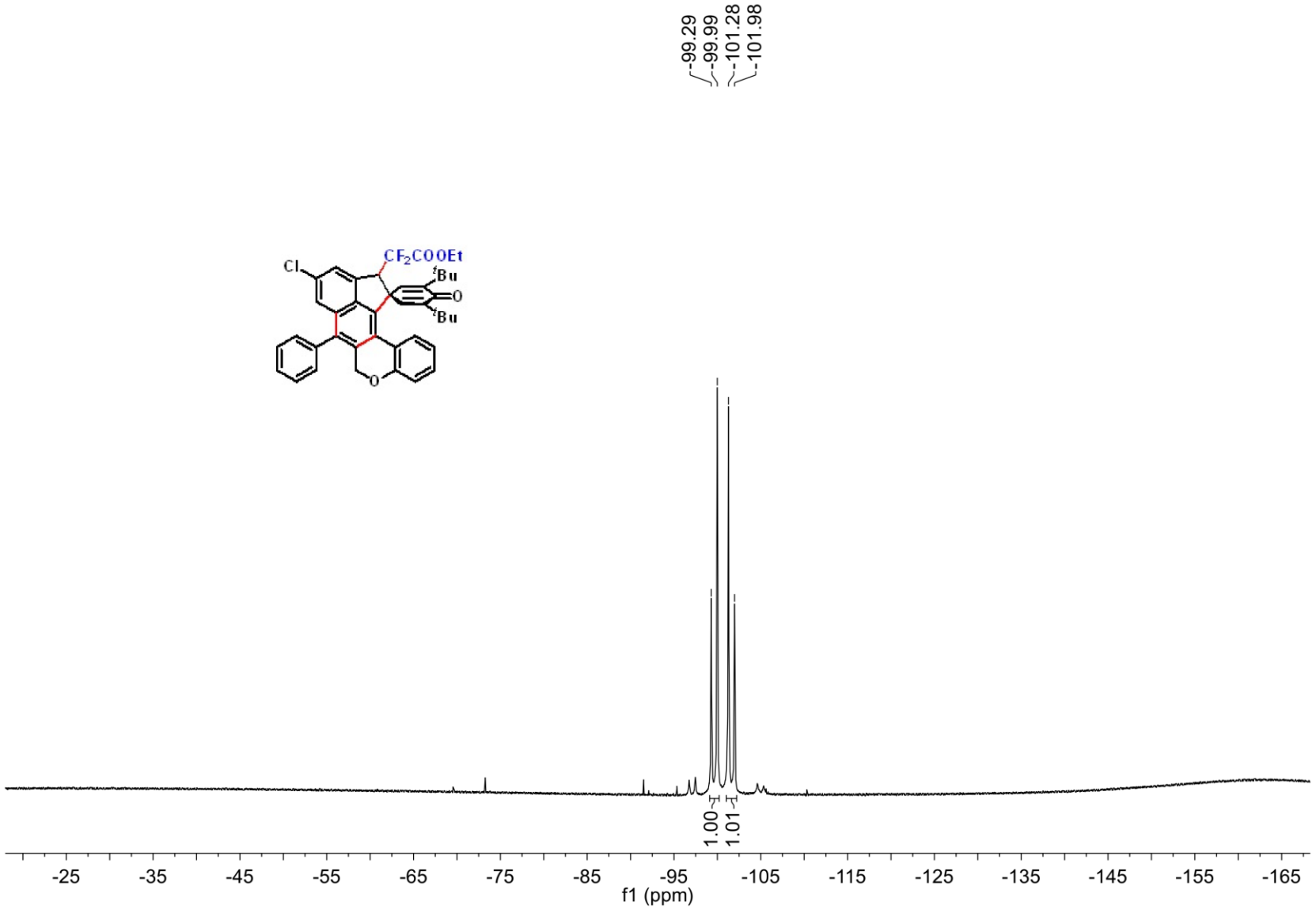
^{19}F NMR Spectrum of Compound 4ra



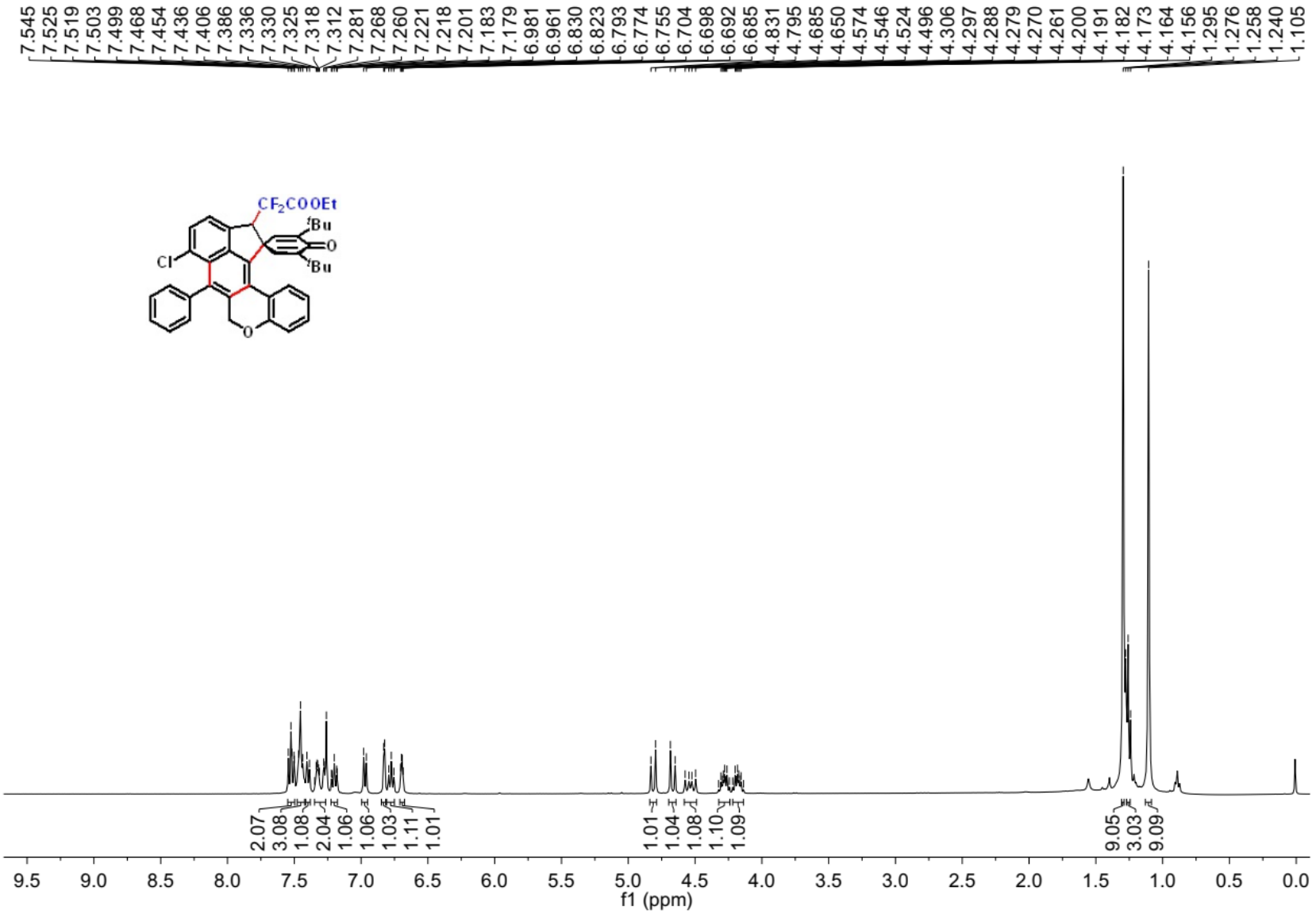
^{1}H NMR Spectrum of Compound 4sa



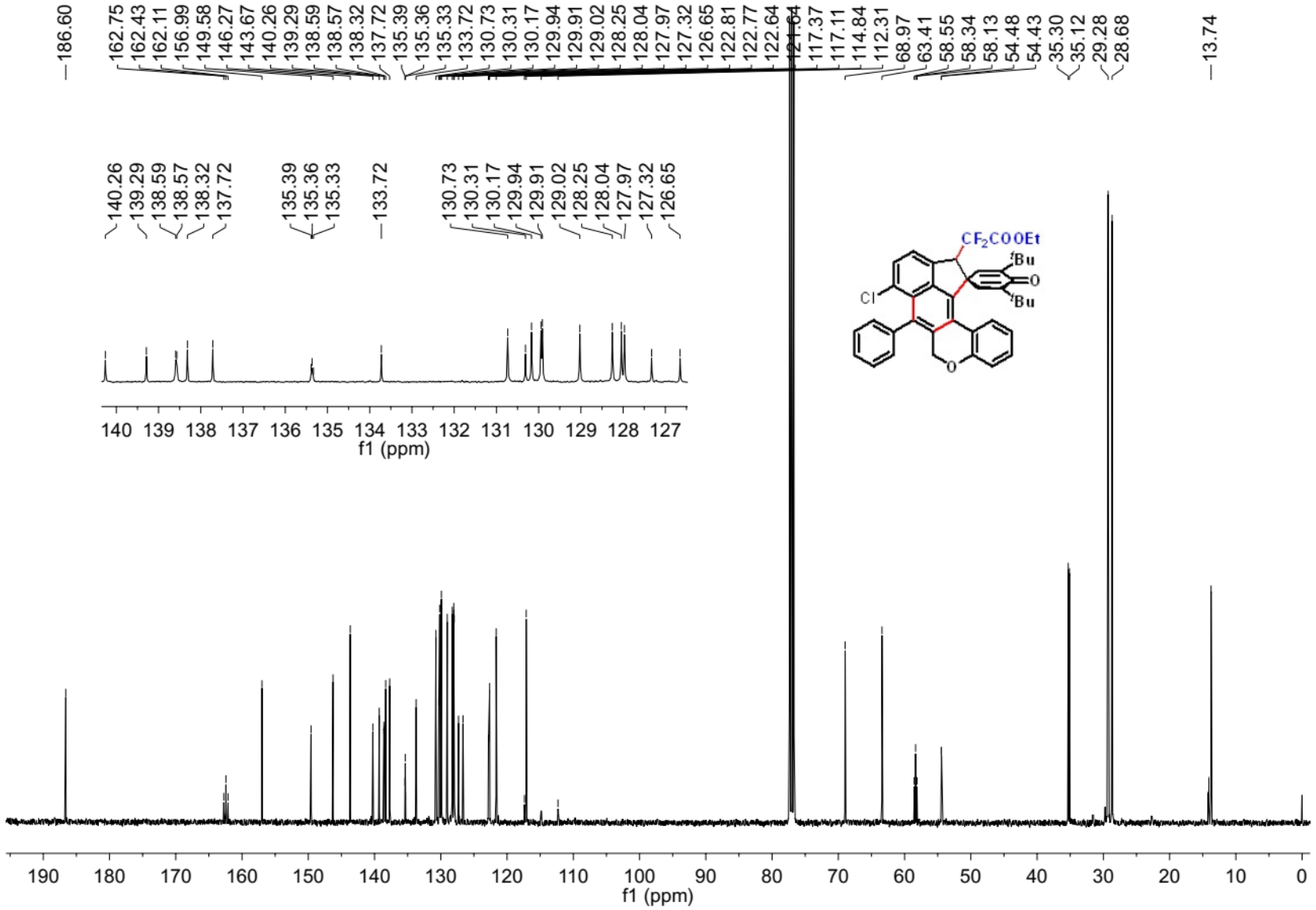
^{13}C NMR Spectrum of Compound 4sa



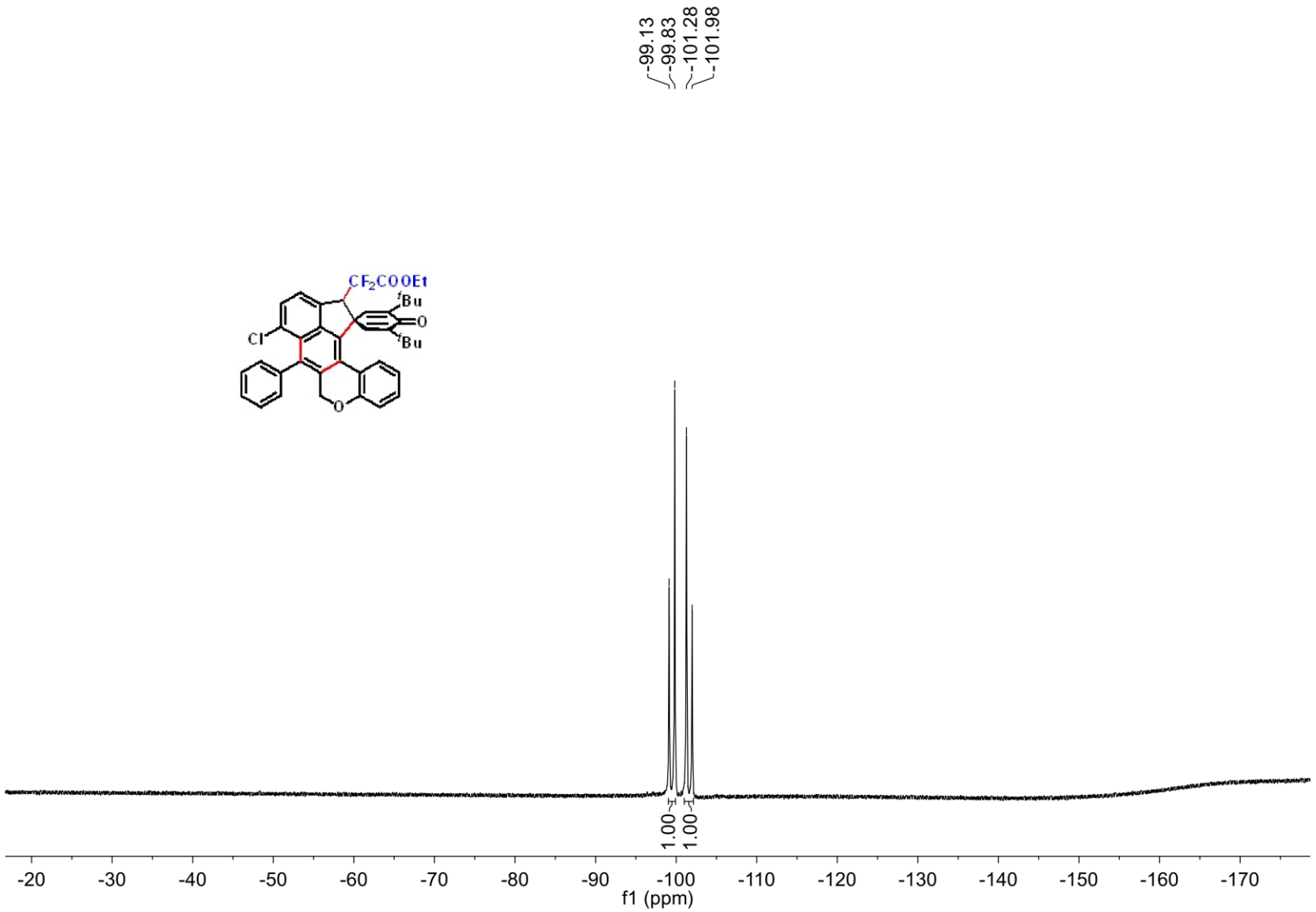
^{19}F NMR Spectrum of Compound 4sa



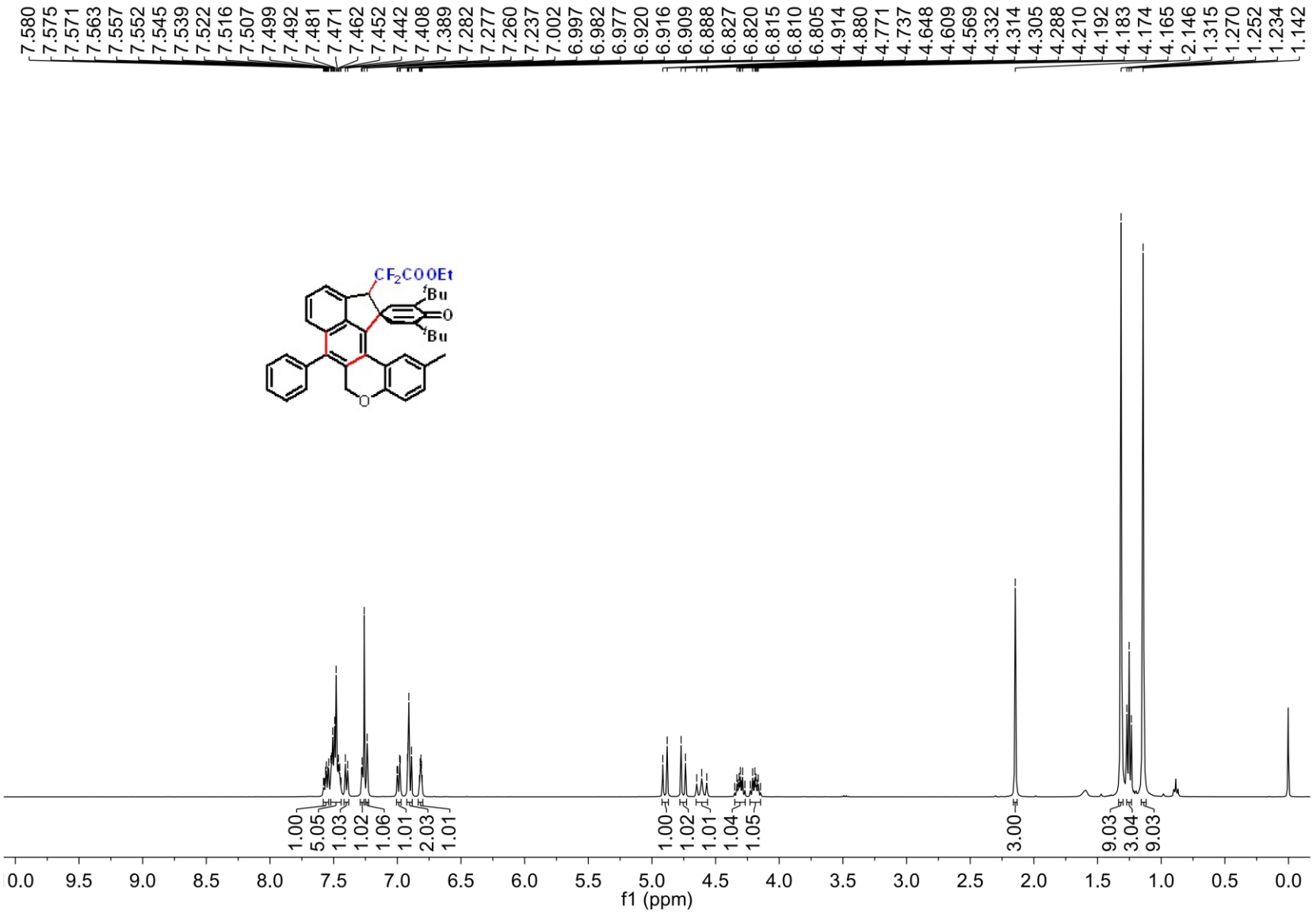
^{1}H NMR Spectrum of Compound 4ta



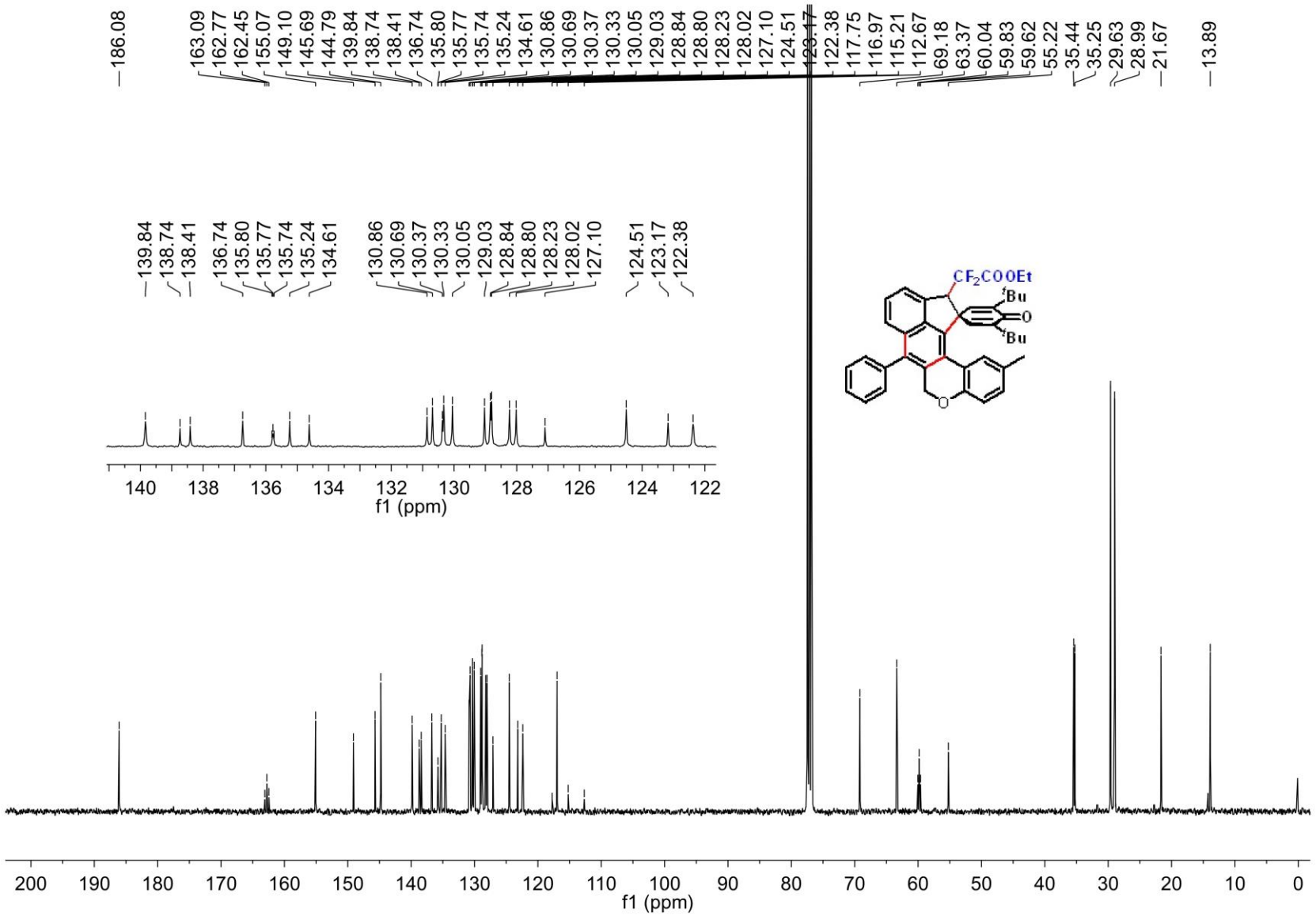
^{13}C NMR Spectrum of Compound 4ta



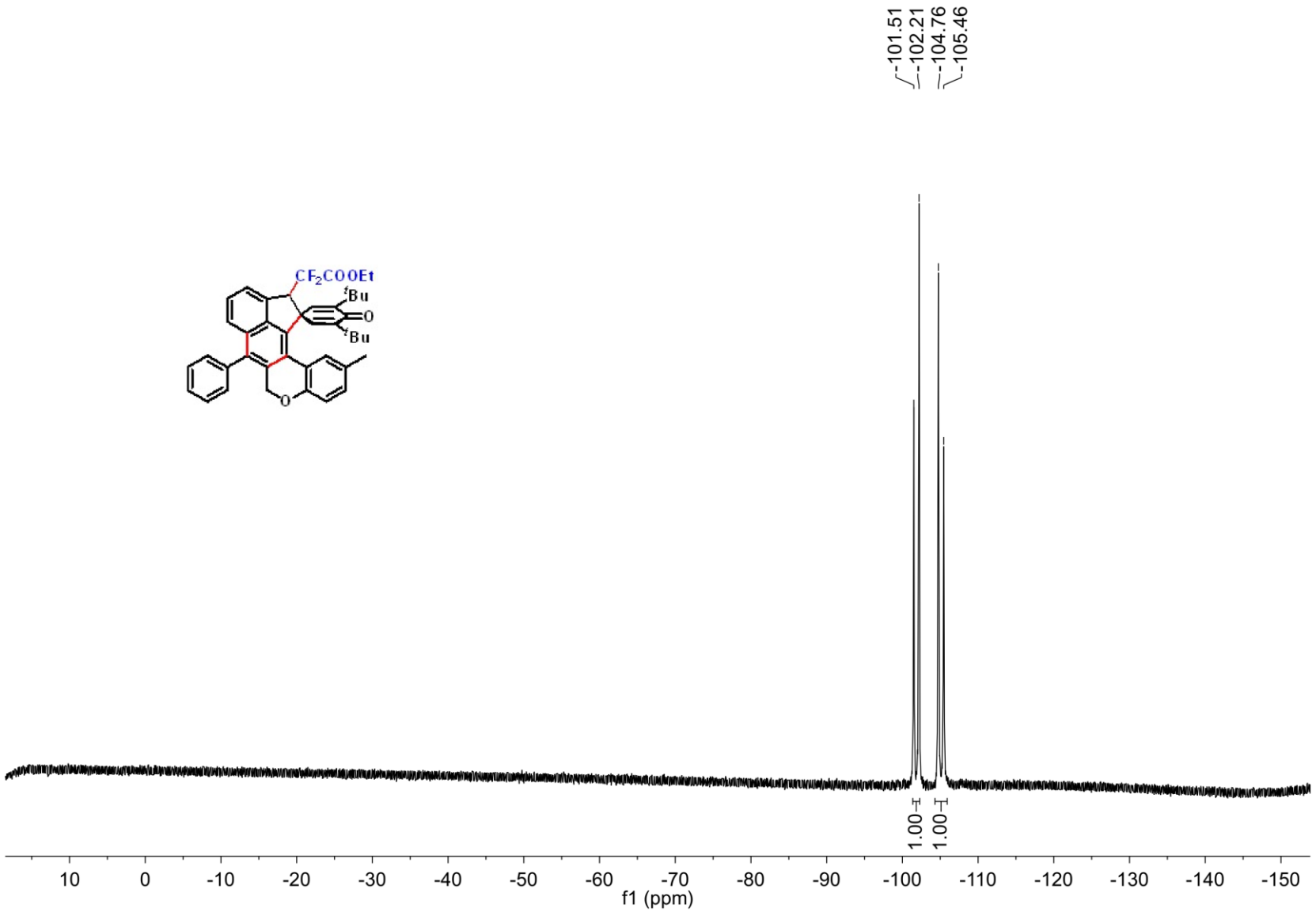
^{19}F NMR Spectrum of Compound 4ta



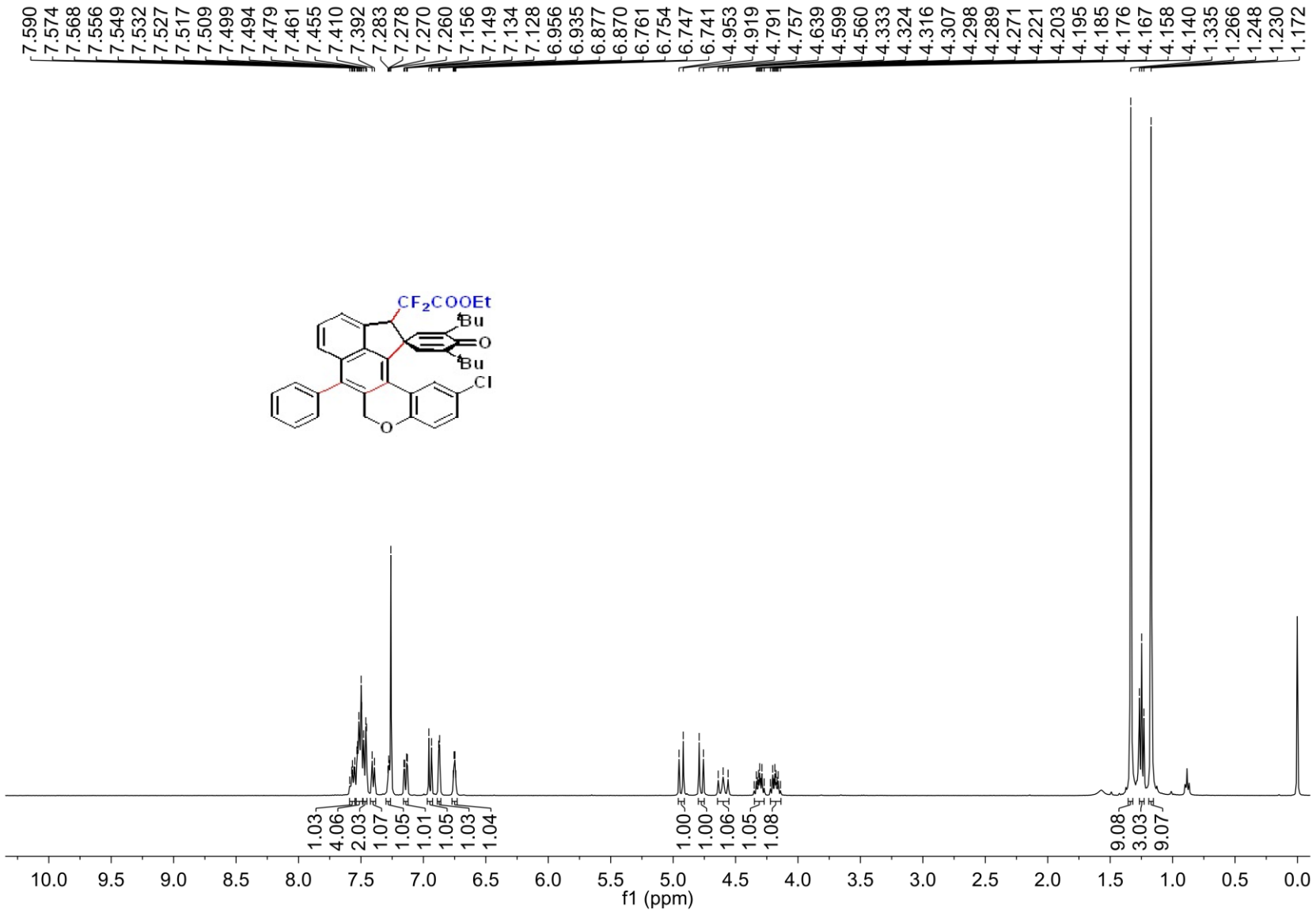
^{1}H NMR Spectrum of Compound 4ua



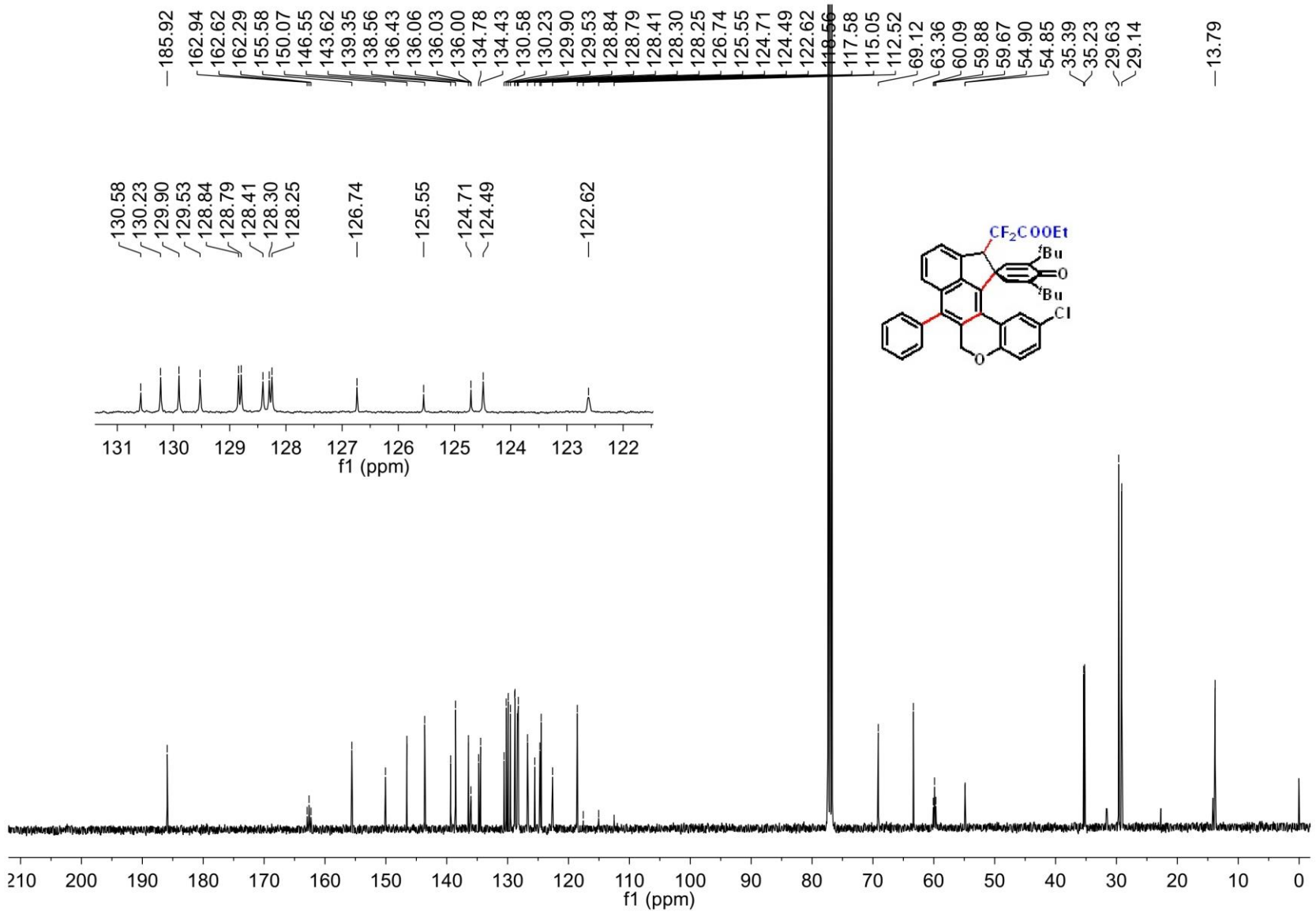
^{13}C NMR Spectrum of Compound 4ua



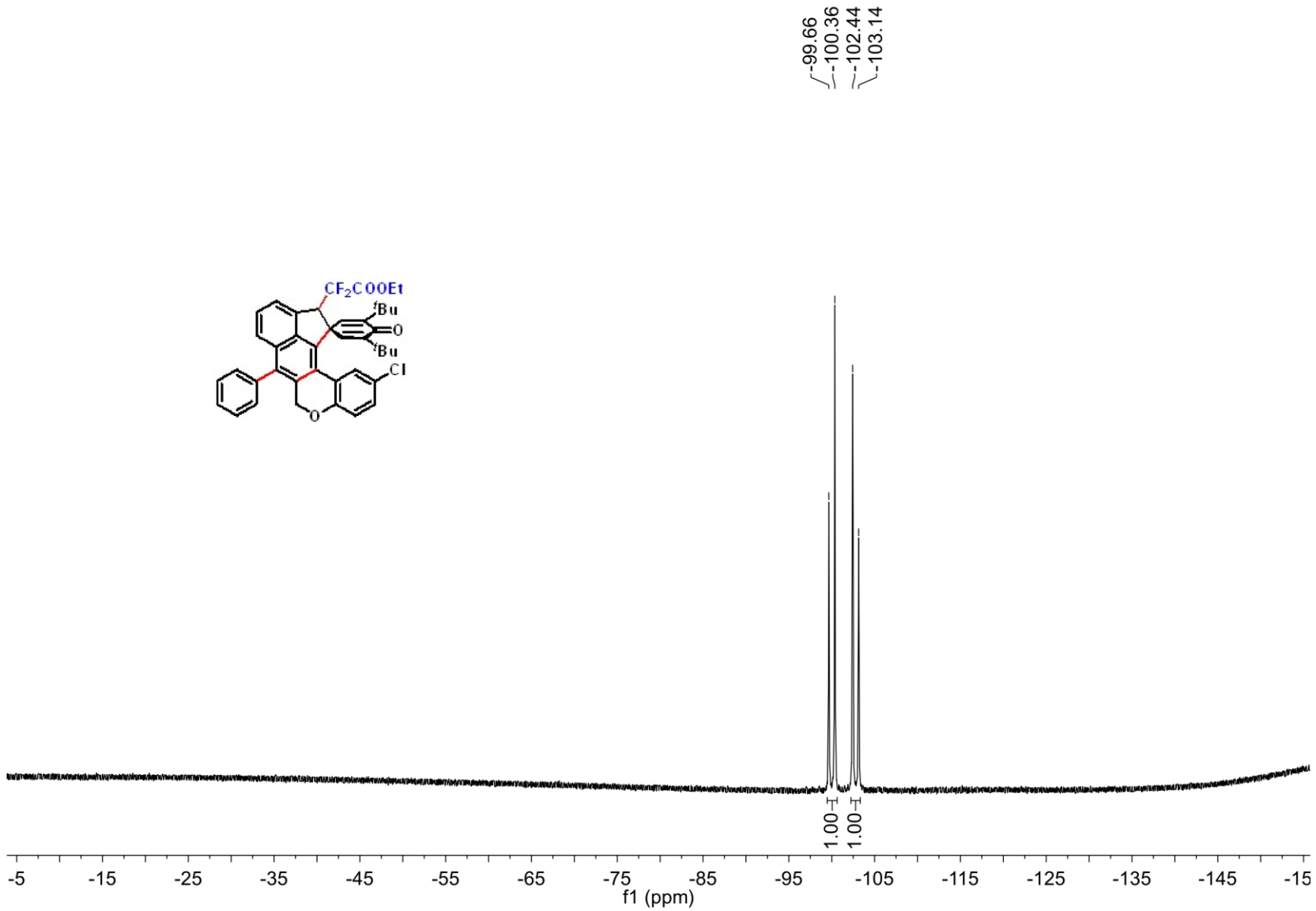
^{19}F NMR Spectrum of Compound 4ua



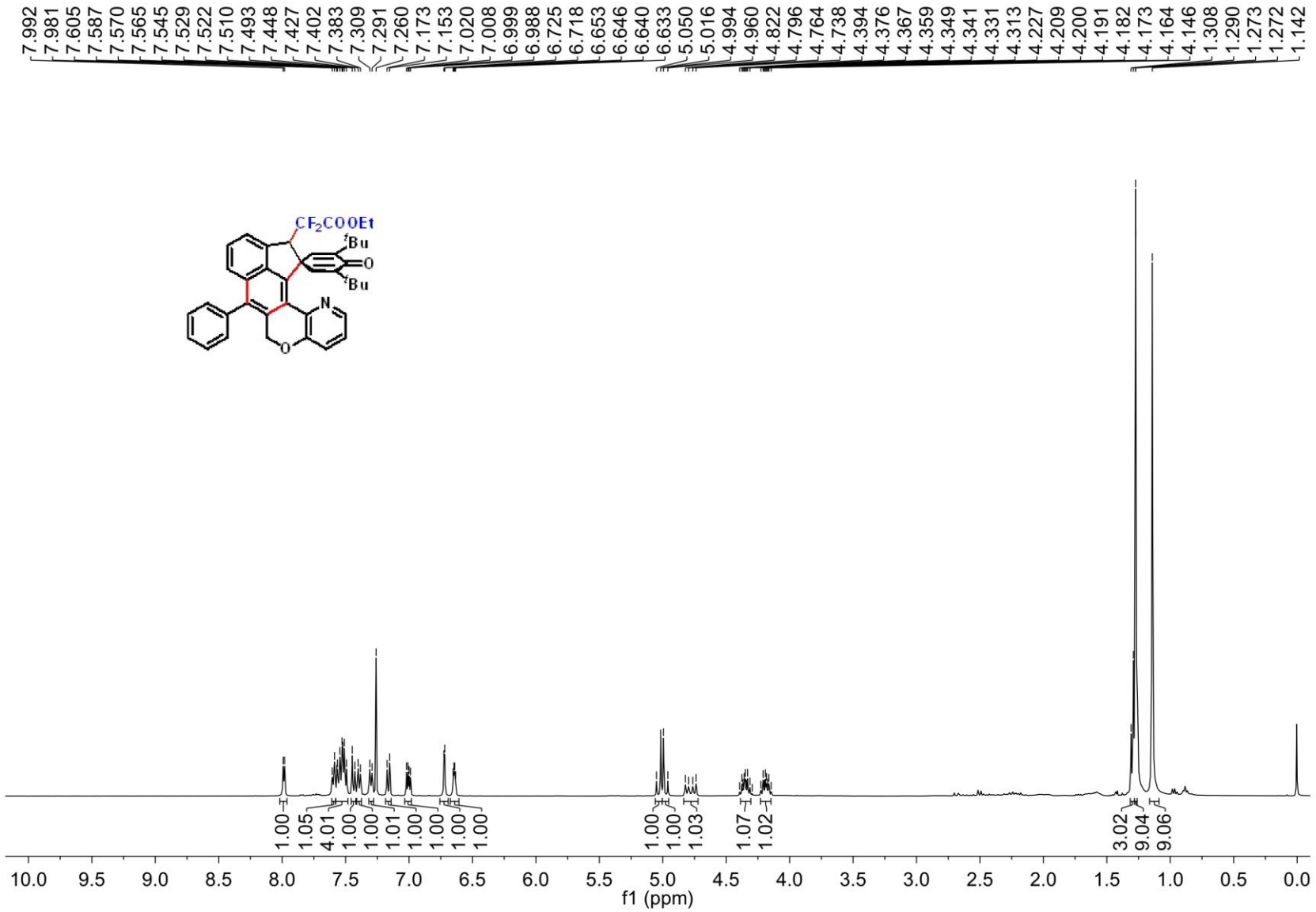
^{1}H NMR Spectrum of Compound 4va



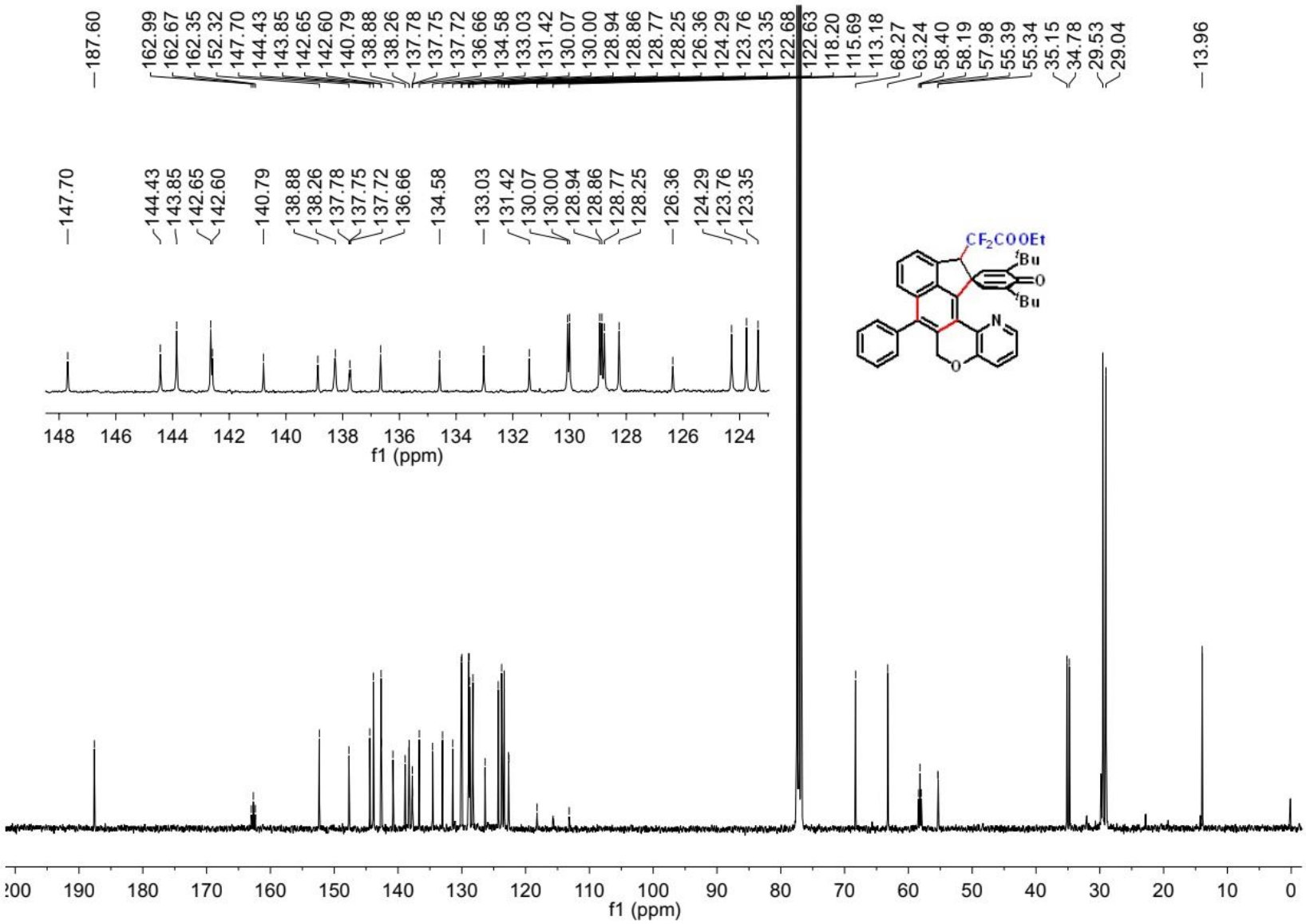
^{13}C NMR Spectrum of Compound 4va



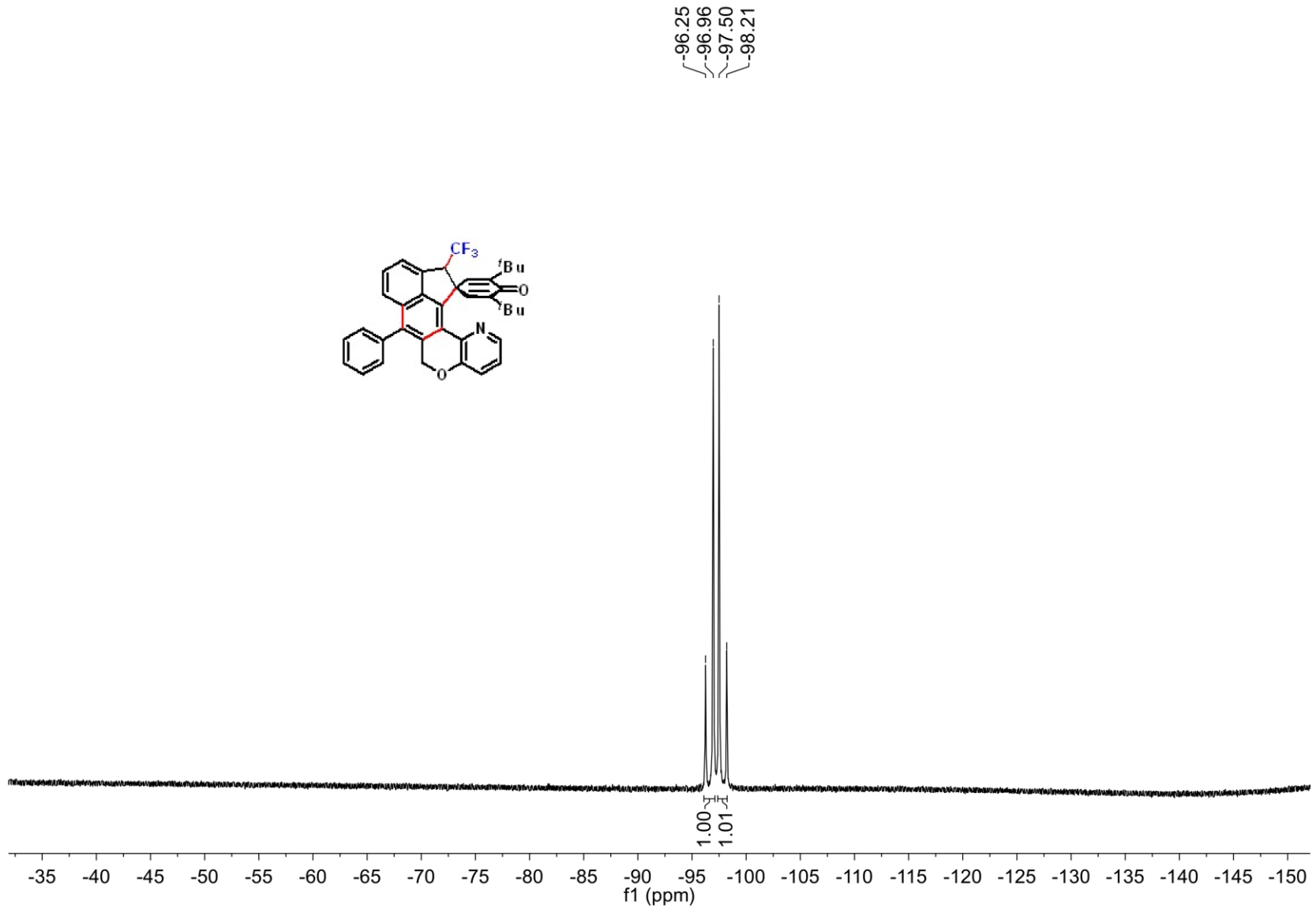
^{19}F NMR Spectrum of Compound 4va



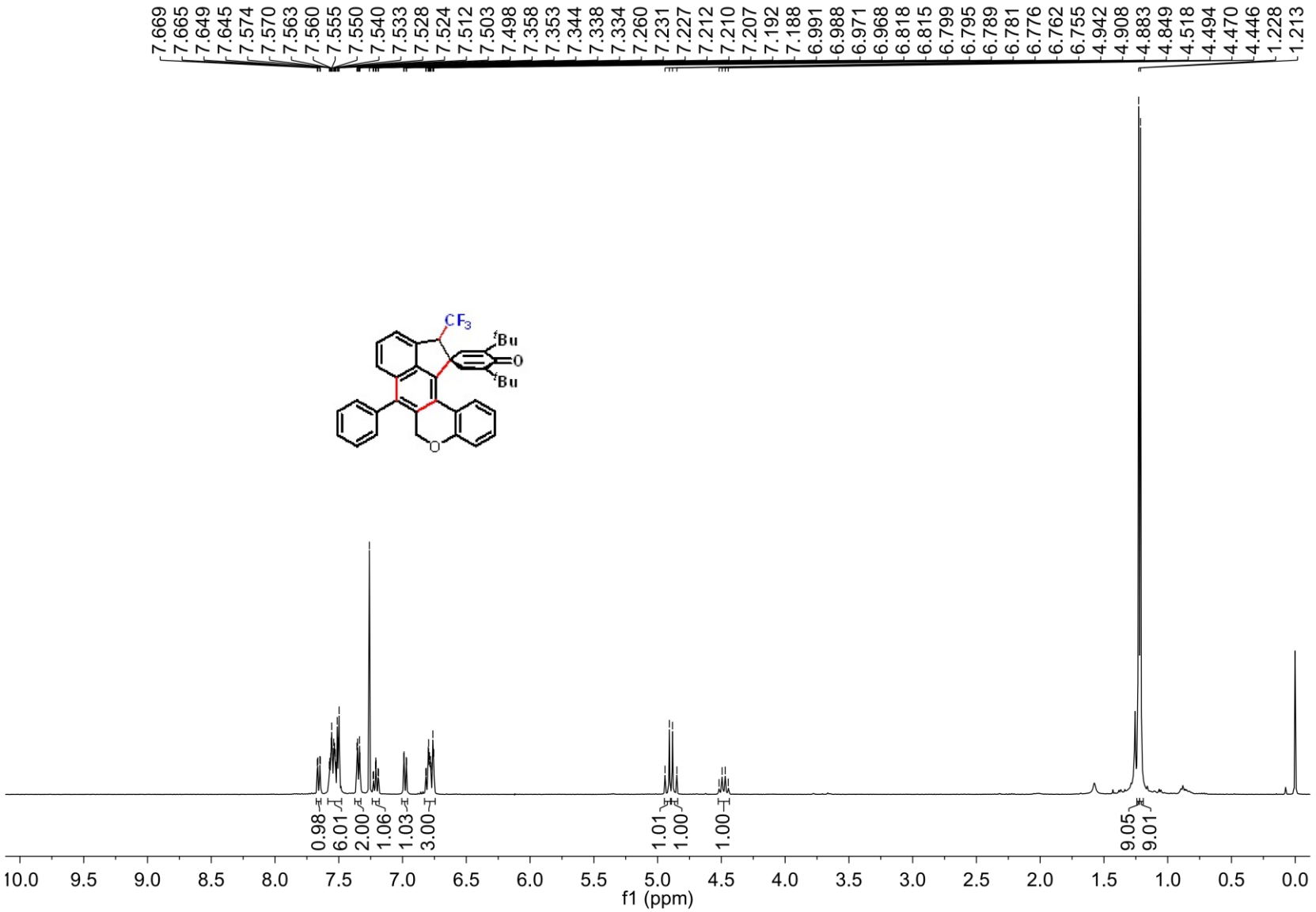
^{1}H NMR Spectrum of Compound 4wa



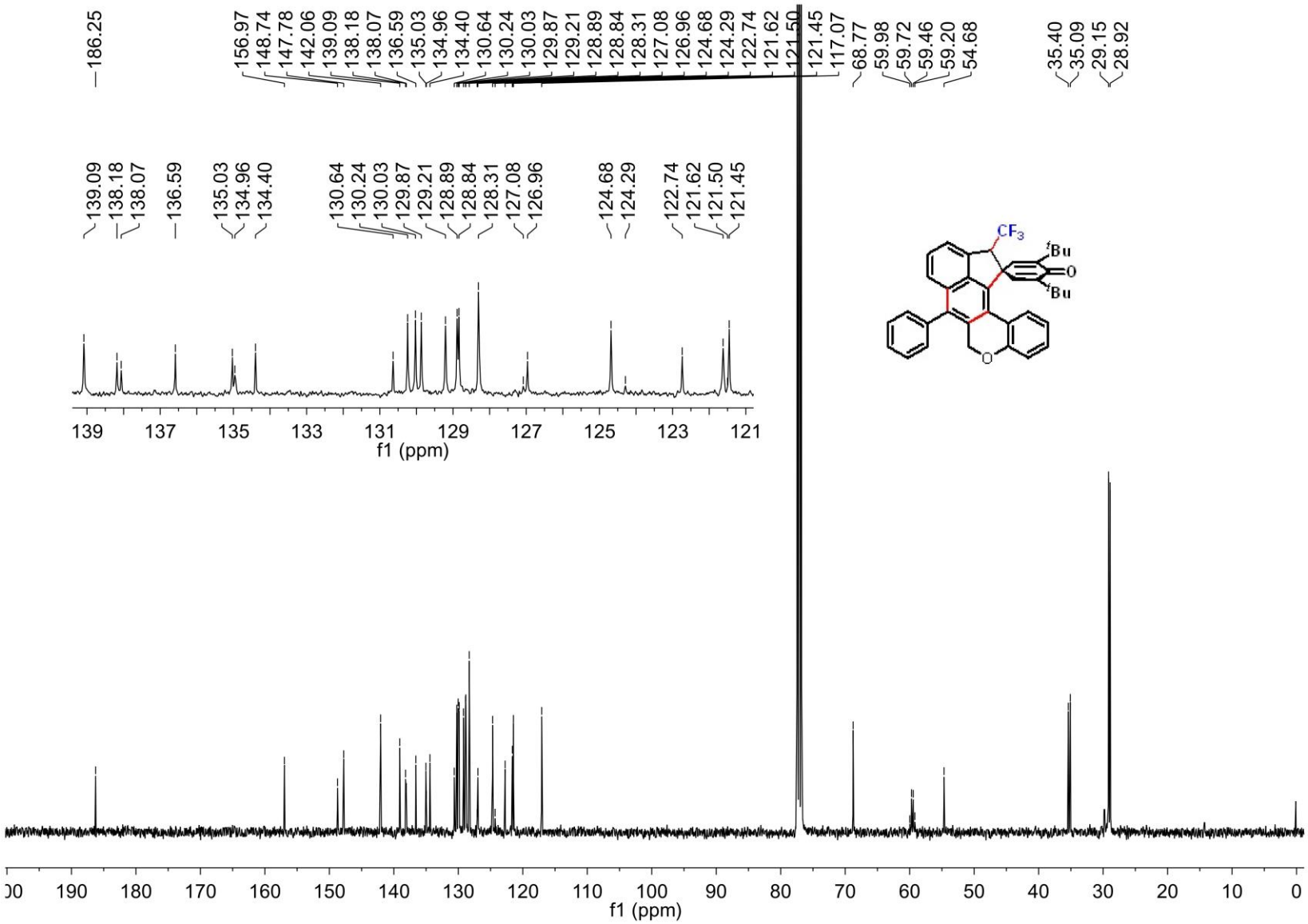
^{13}C NMR Spectrum of Compound 4wa



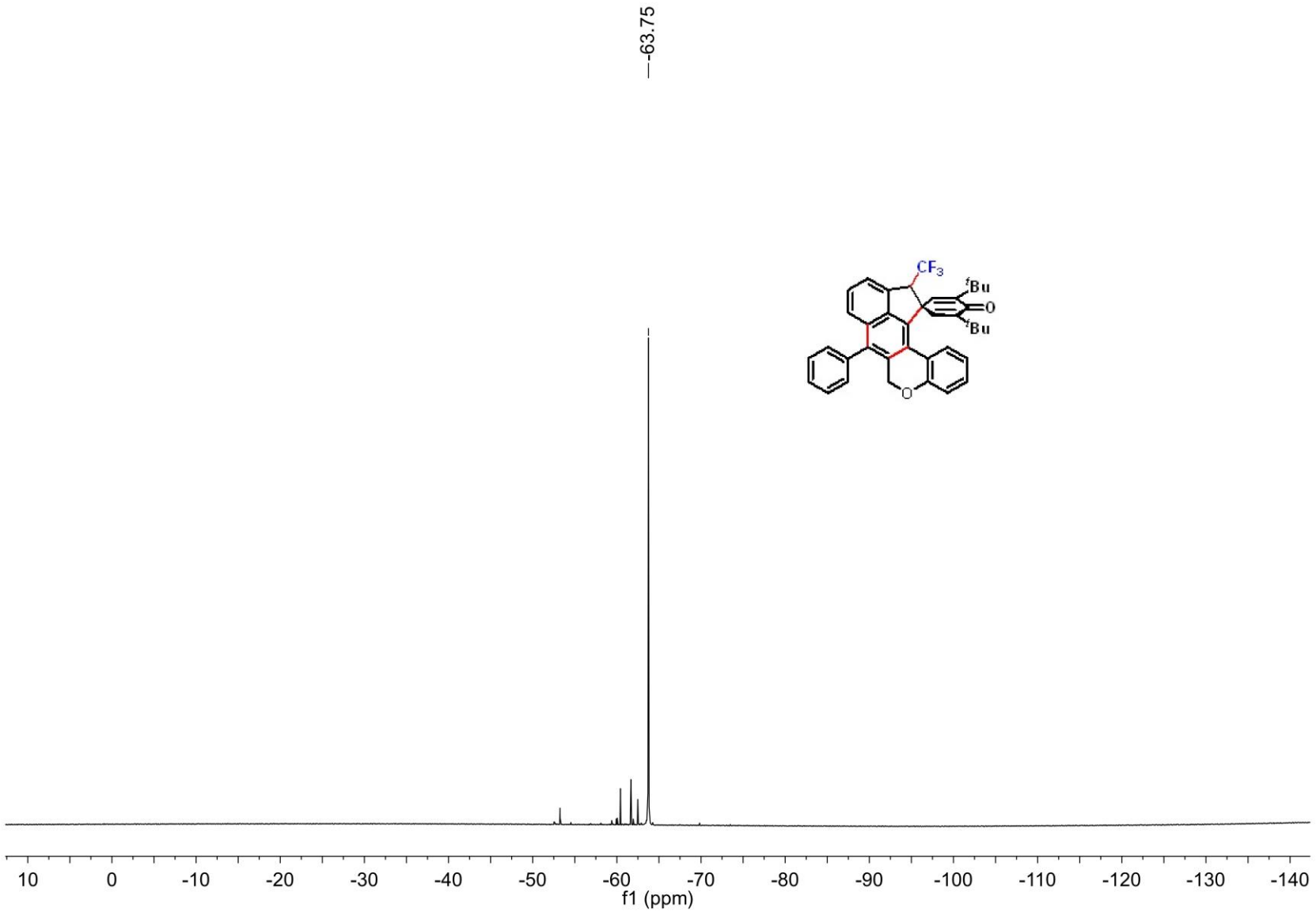
^{19}F NMR Spectrum of Compound 4wa



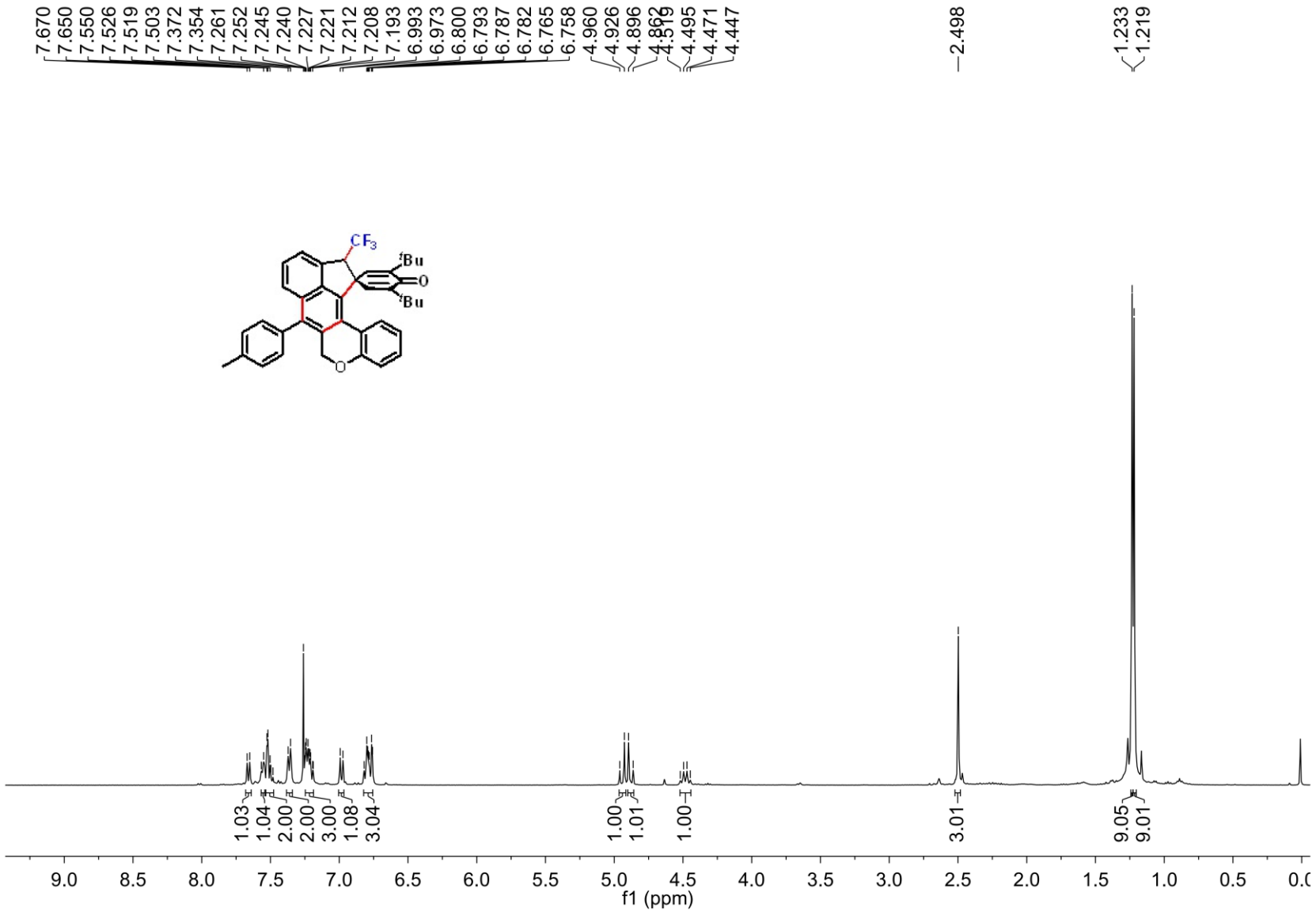
^{1}H NMR Spectrum of Compound 4ab



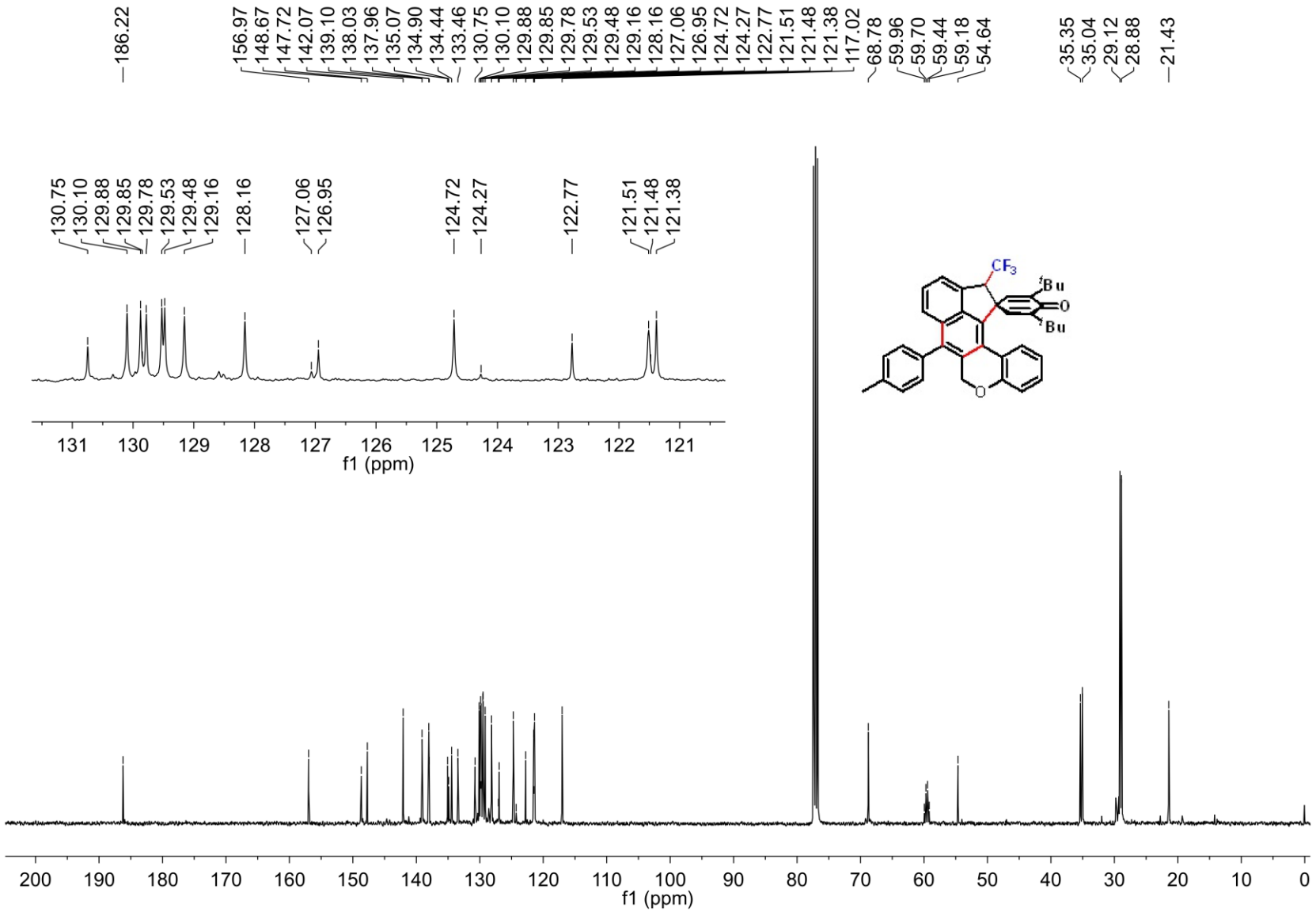
^{13}C NMR Spectrum of Compound 4ab



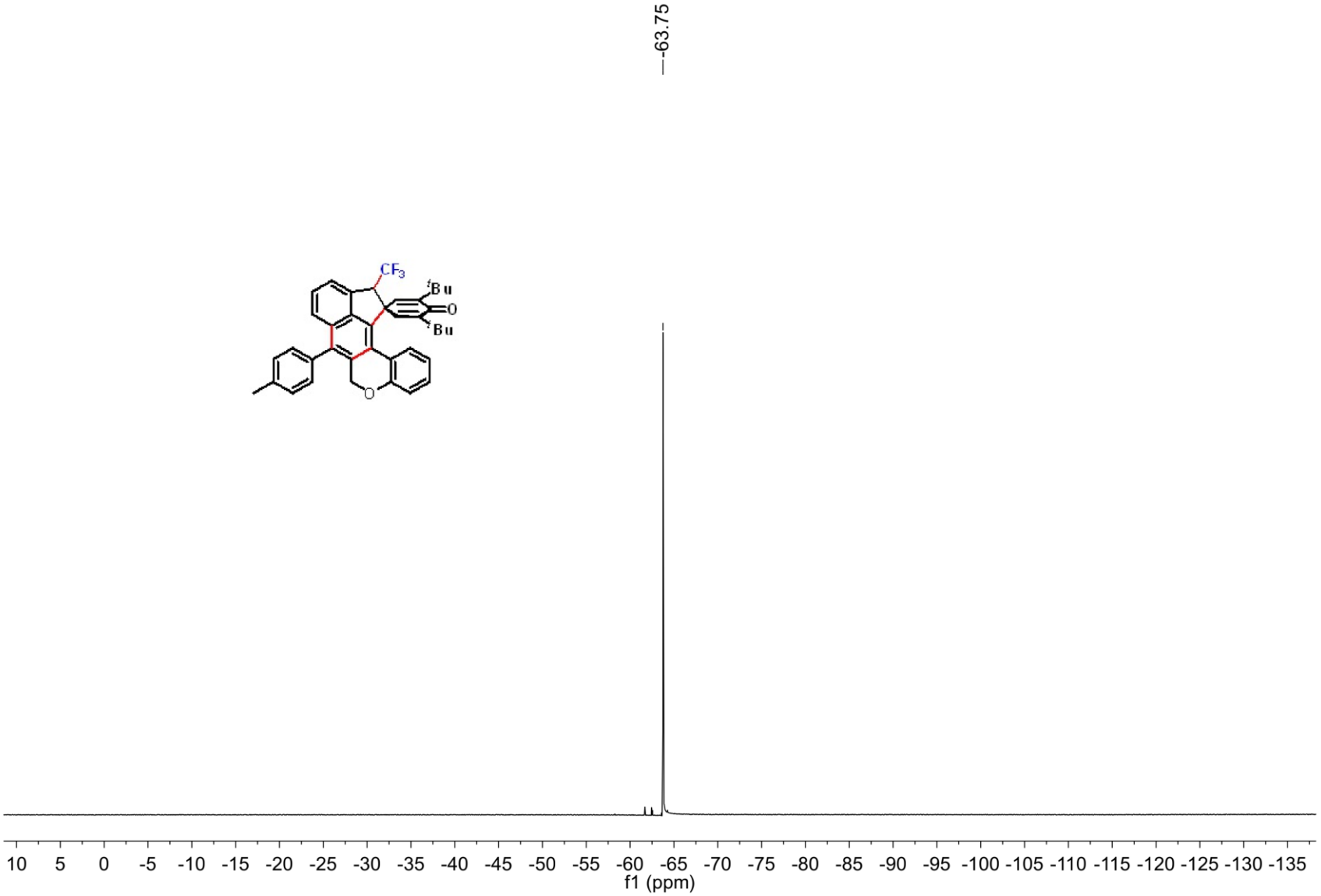
^{19}F NMR Spectrum of Compound 4ab



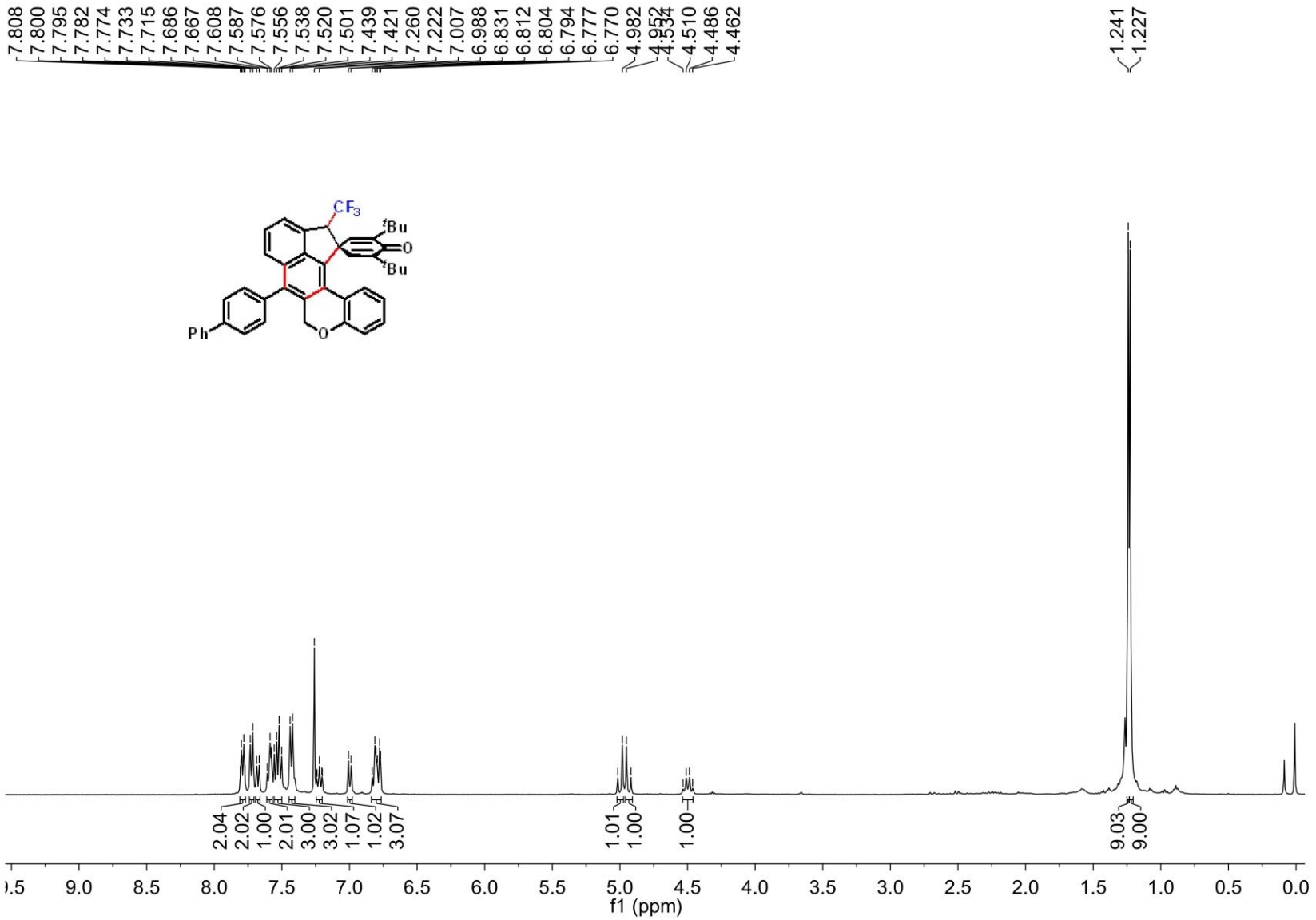
^{1}H NMR Spectrum of Compound 4bb



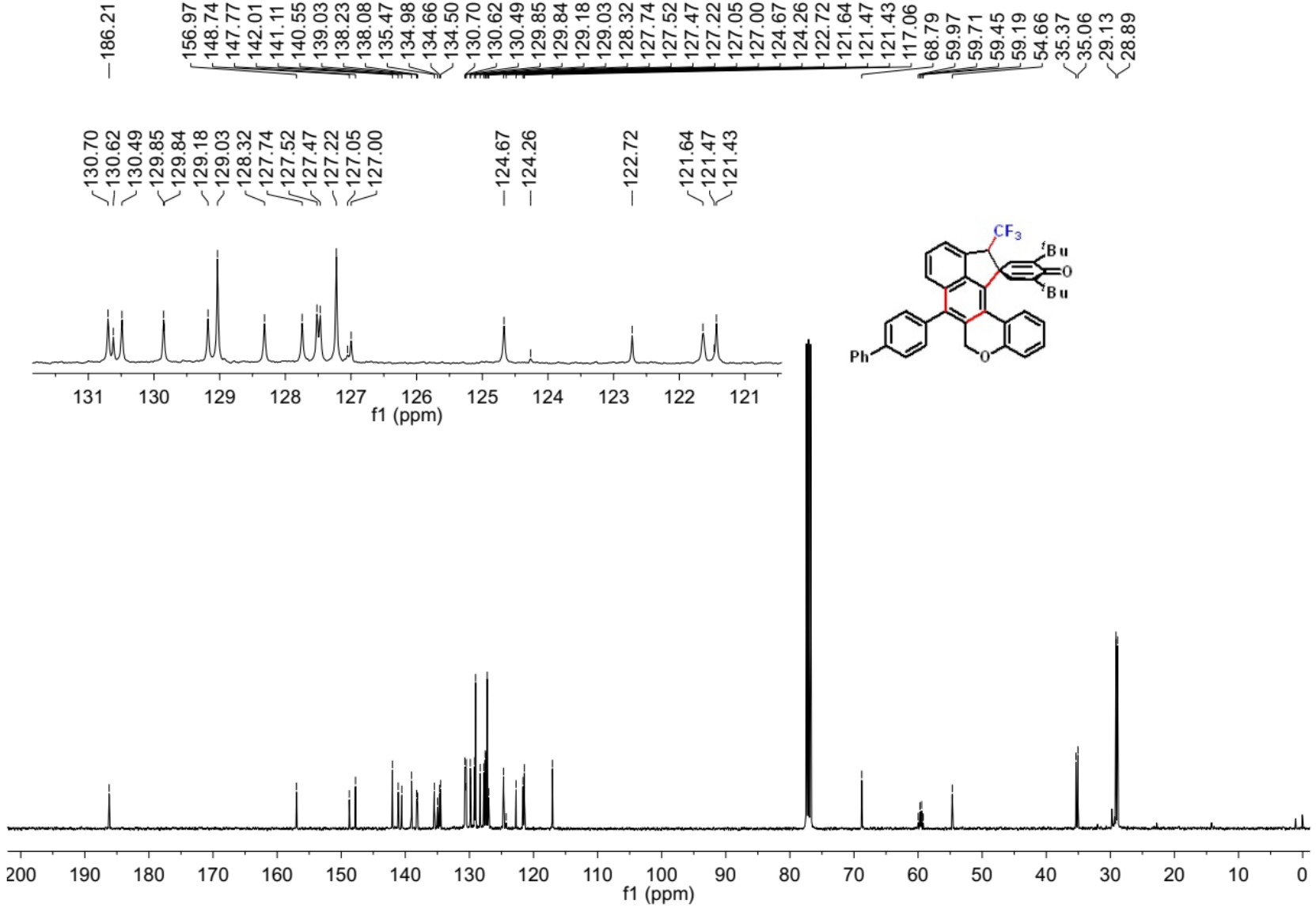
^{13}C NMR Spectrum of Compound 4bb



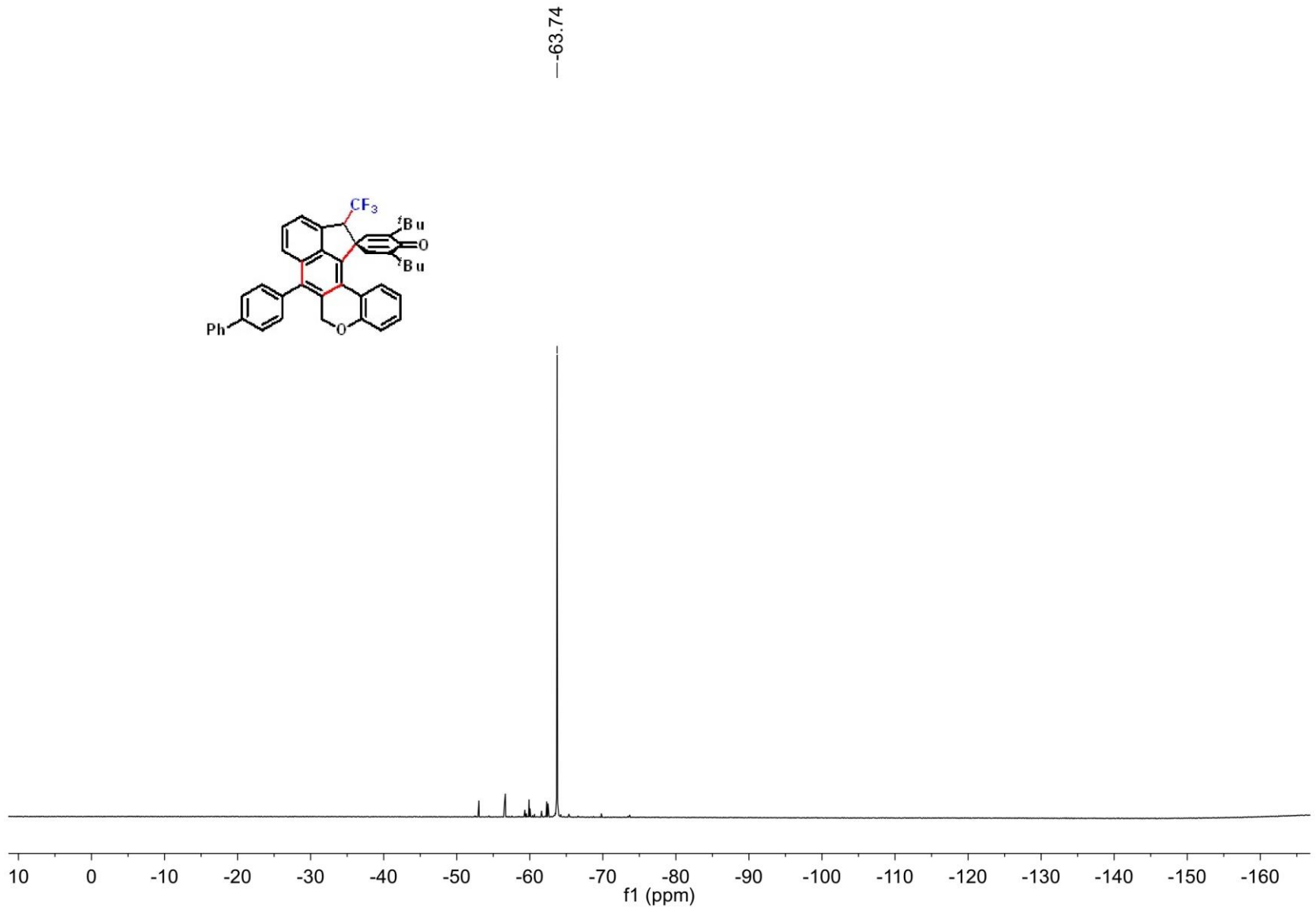
^{19}F NMR Spectrum of Compound 4bb



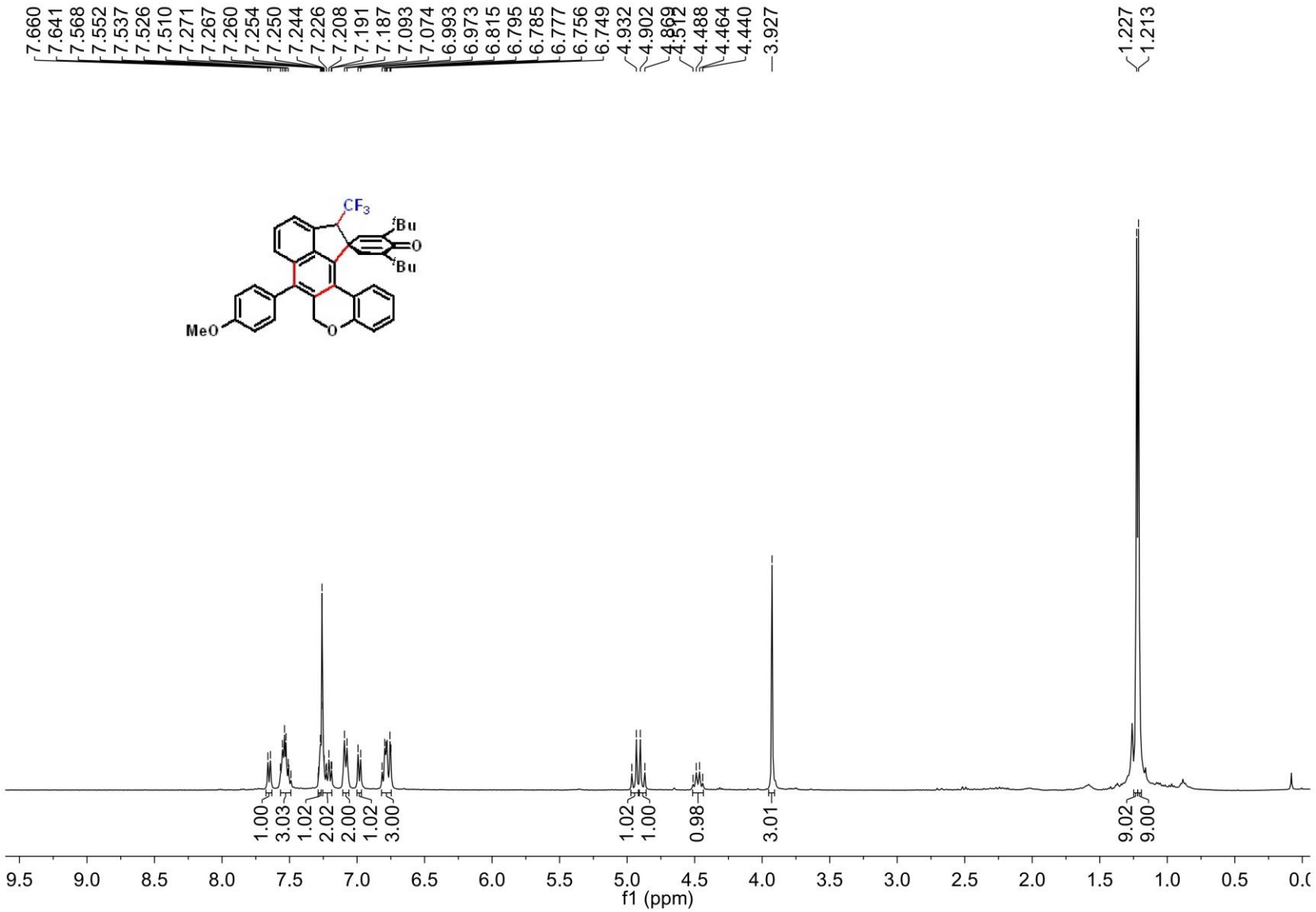
^{1}H NMR Spectrum of Compound 4gb



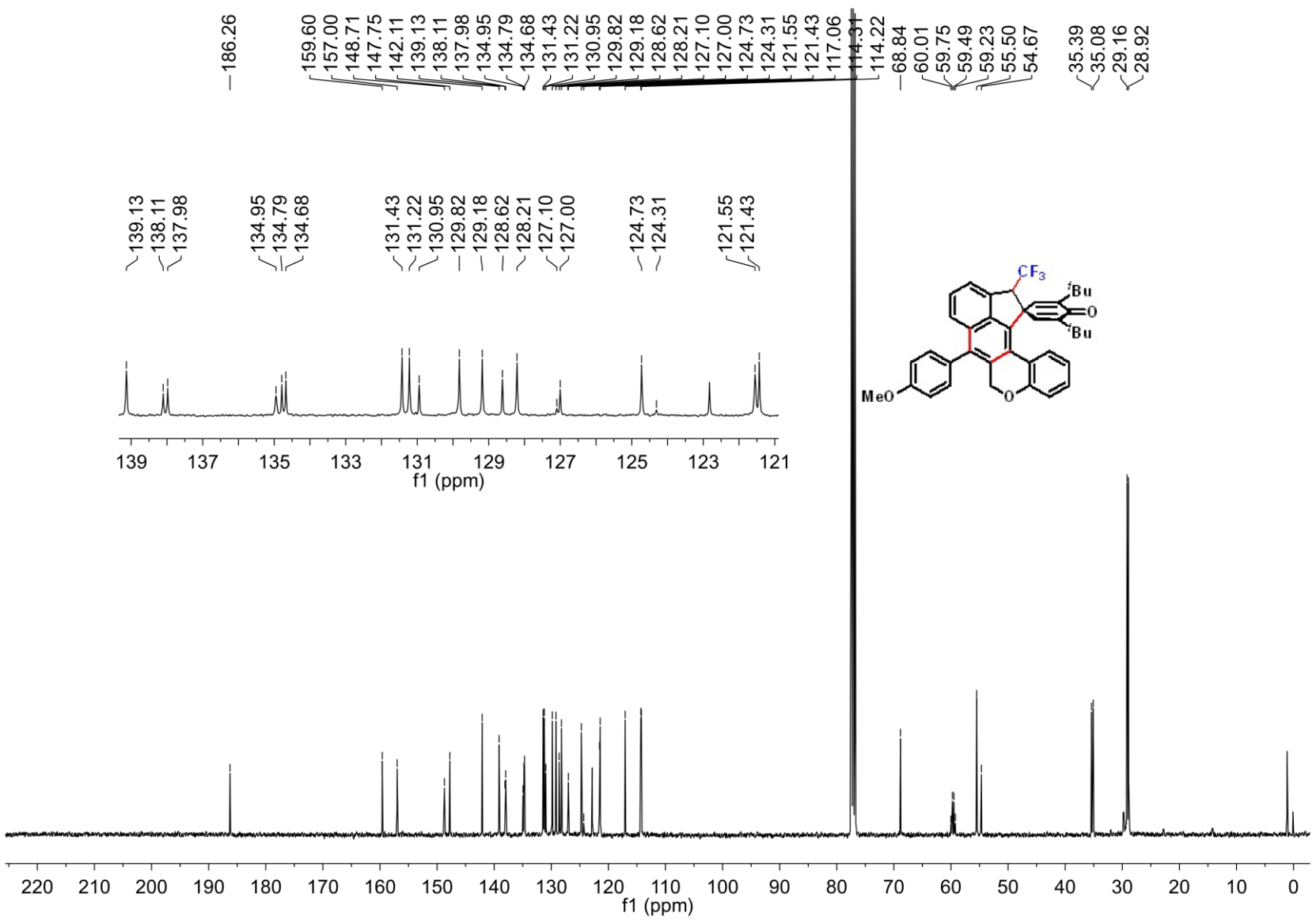
^{13}C NMR Spectrum of Compound 4gb



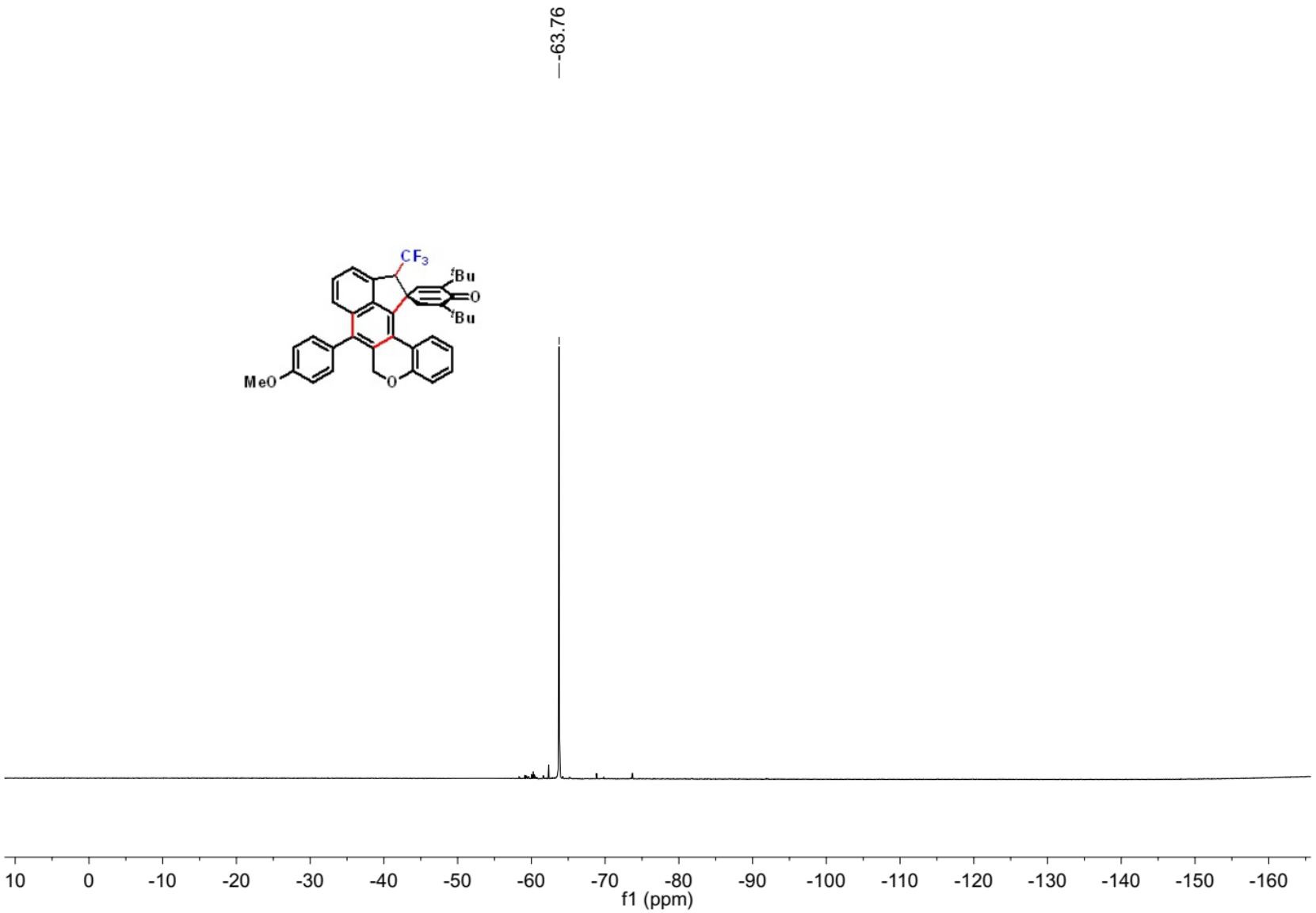
^{19}F NMR Spectrum of Compound 4gb



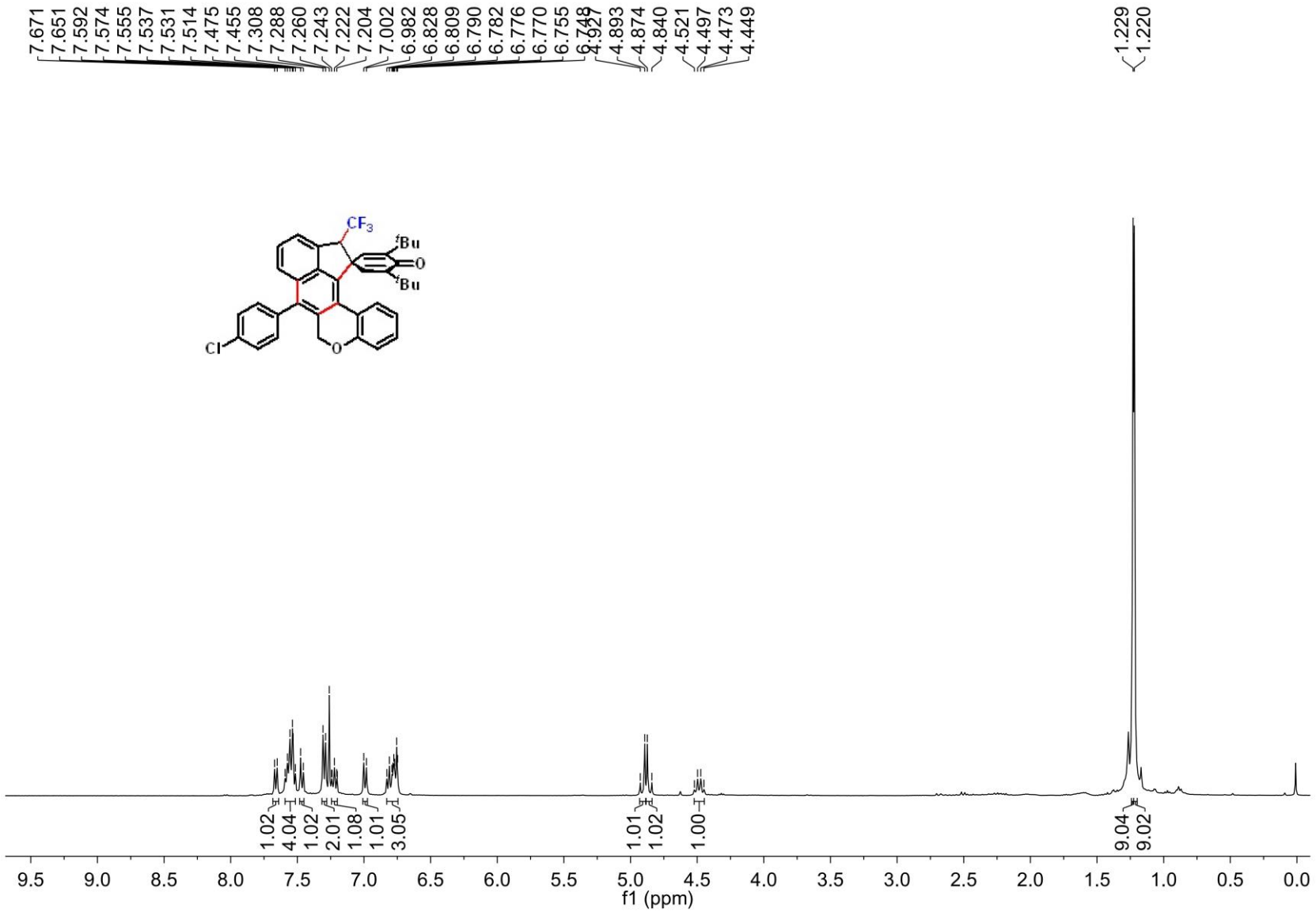
^{1}H NMR Spectrum of Compound 4hb



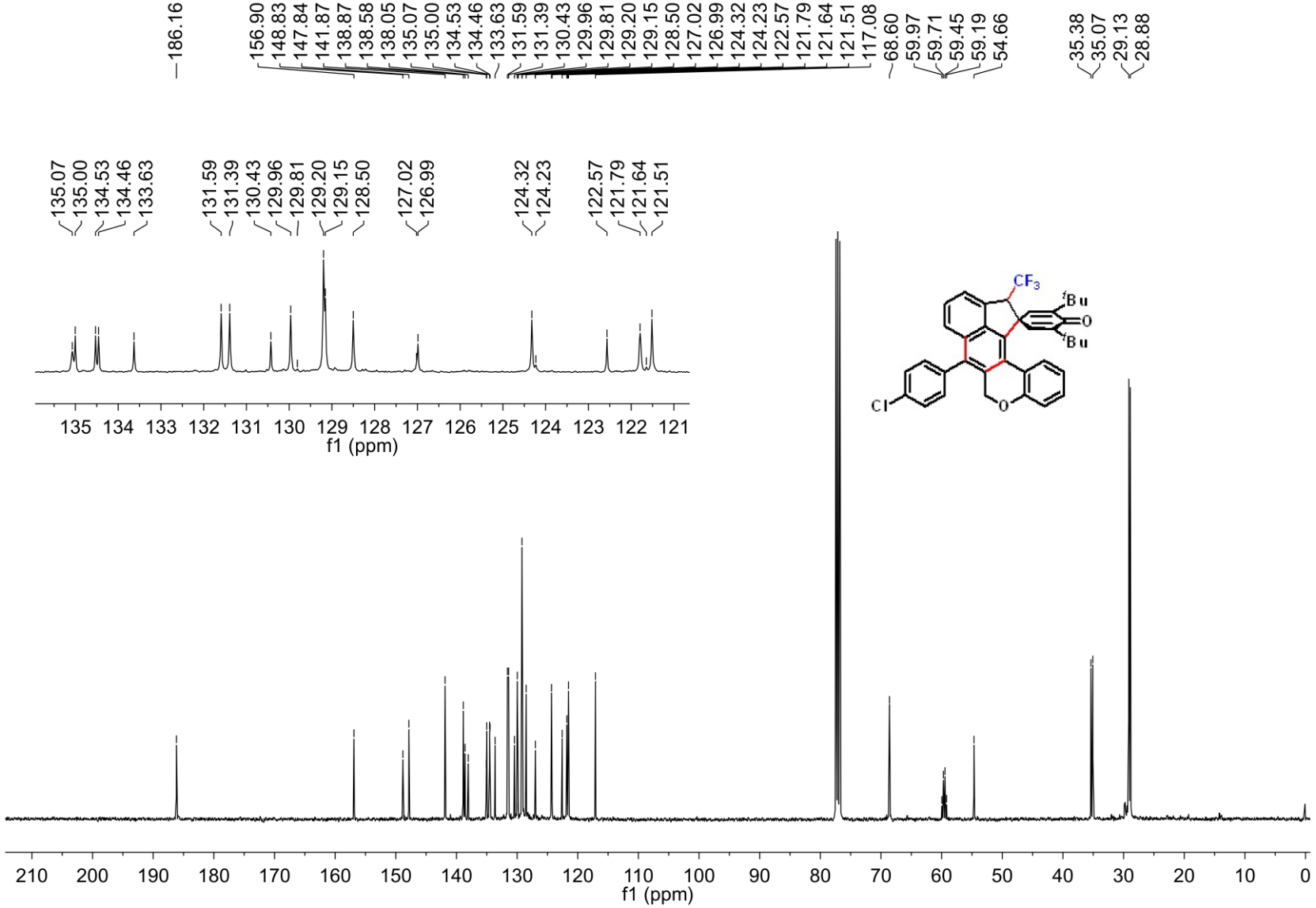
^{13}C NMR Spectrum of Compound 4hb



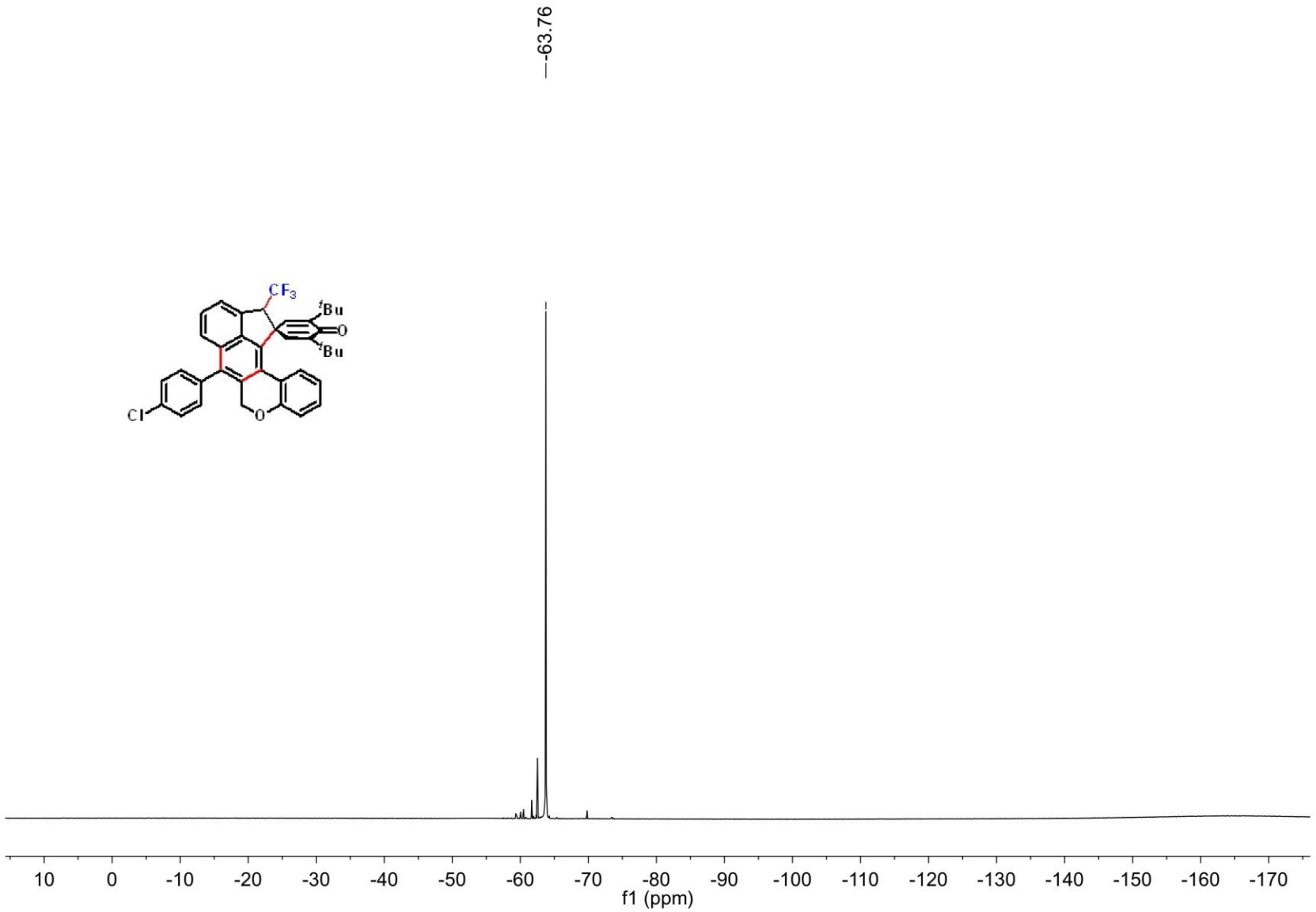
^{19}F NMR Spectrum of Compound 4hb



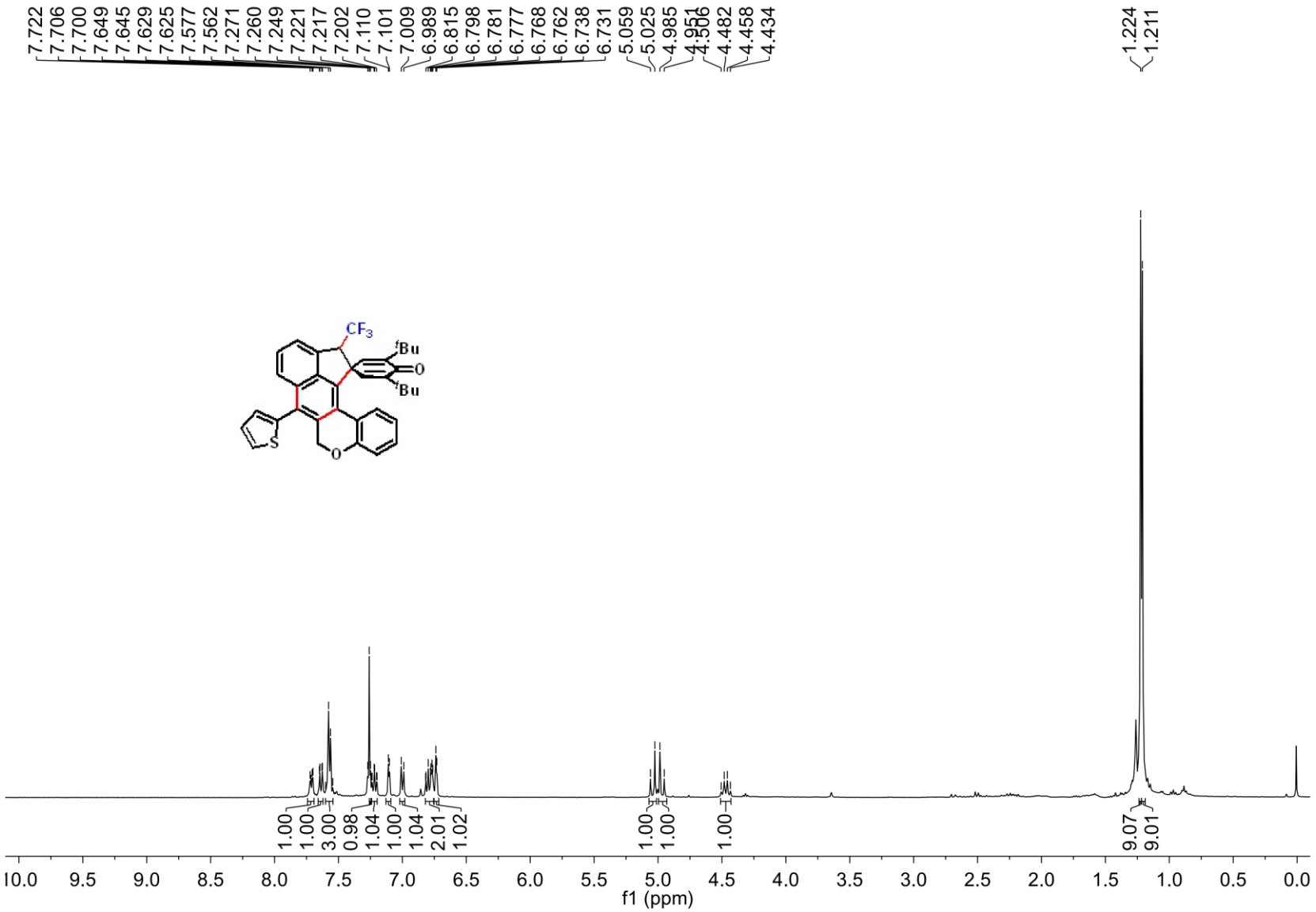
^{1}H NMR Spectrum of Compound 4jb



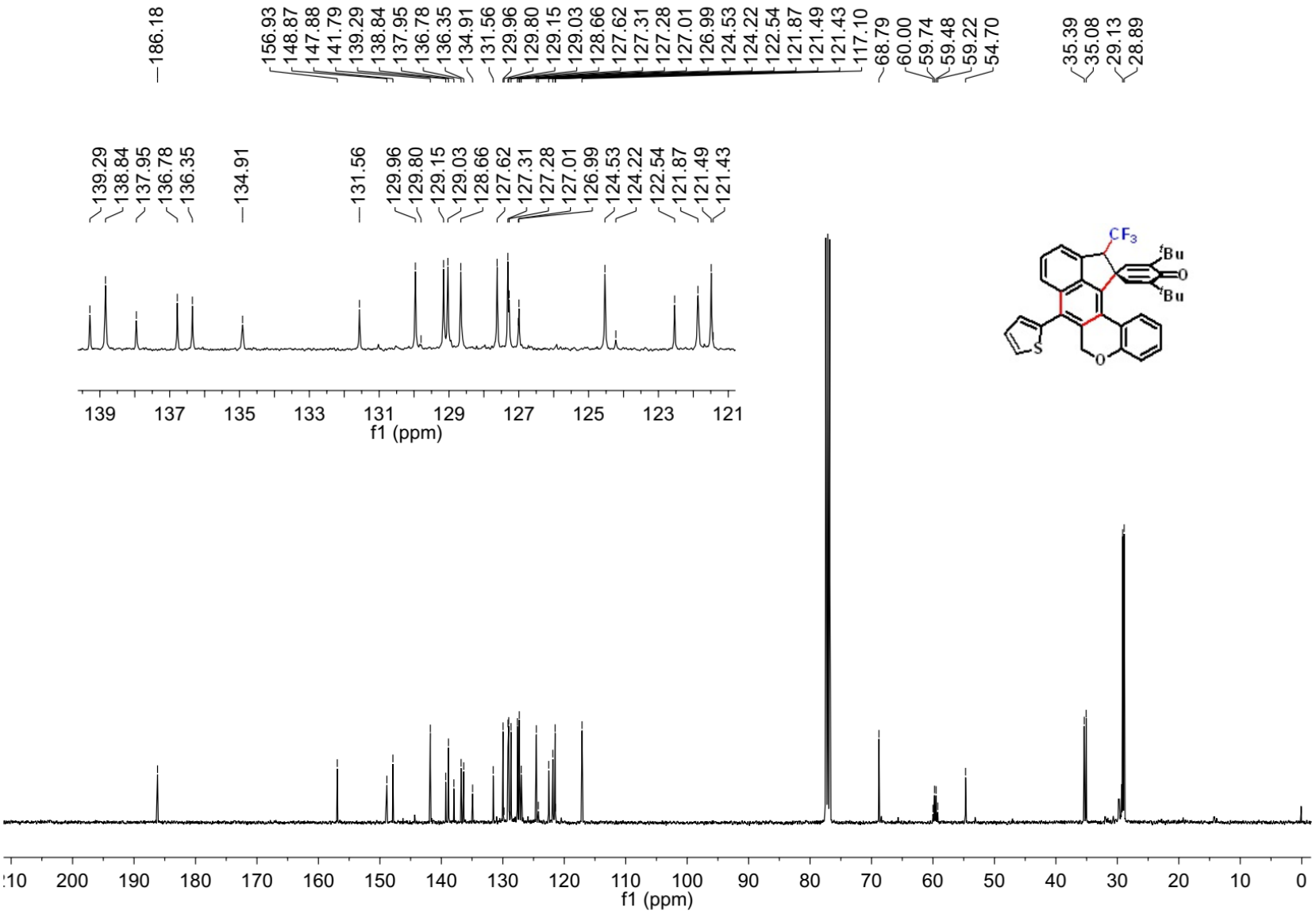
^{13}C NMR Spectrum of Compound 4jb



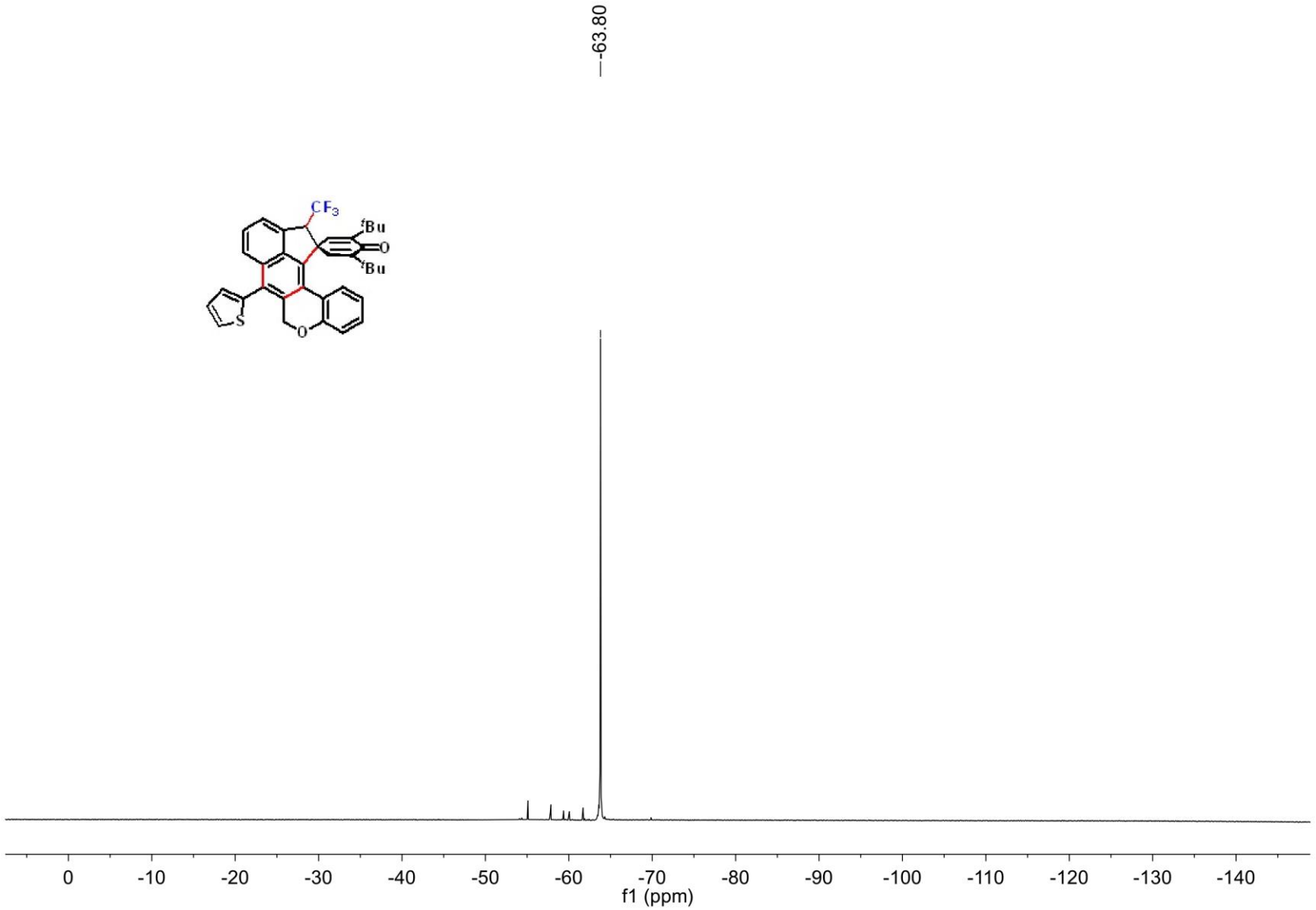
^{19}F NMR Spectrum of Compound 4jb



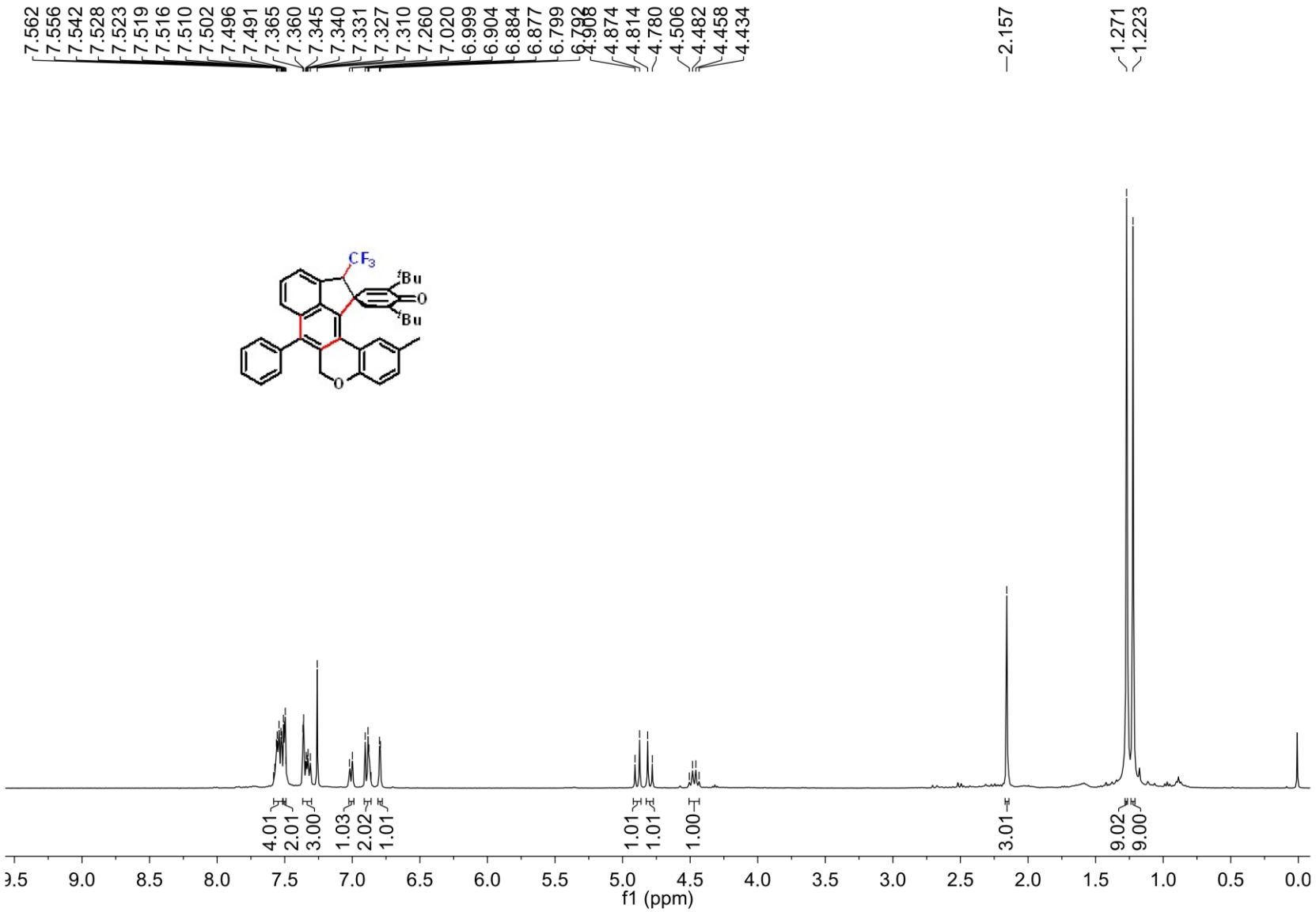
^{1}H NMR Spectrum of Compound 4ob



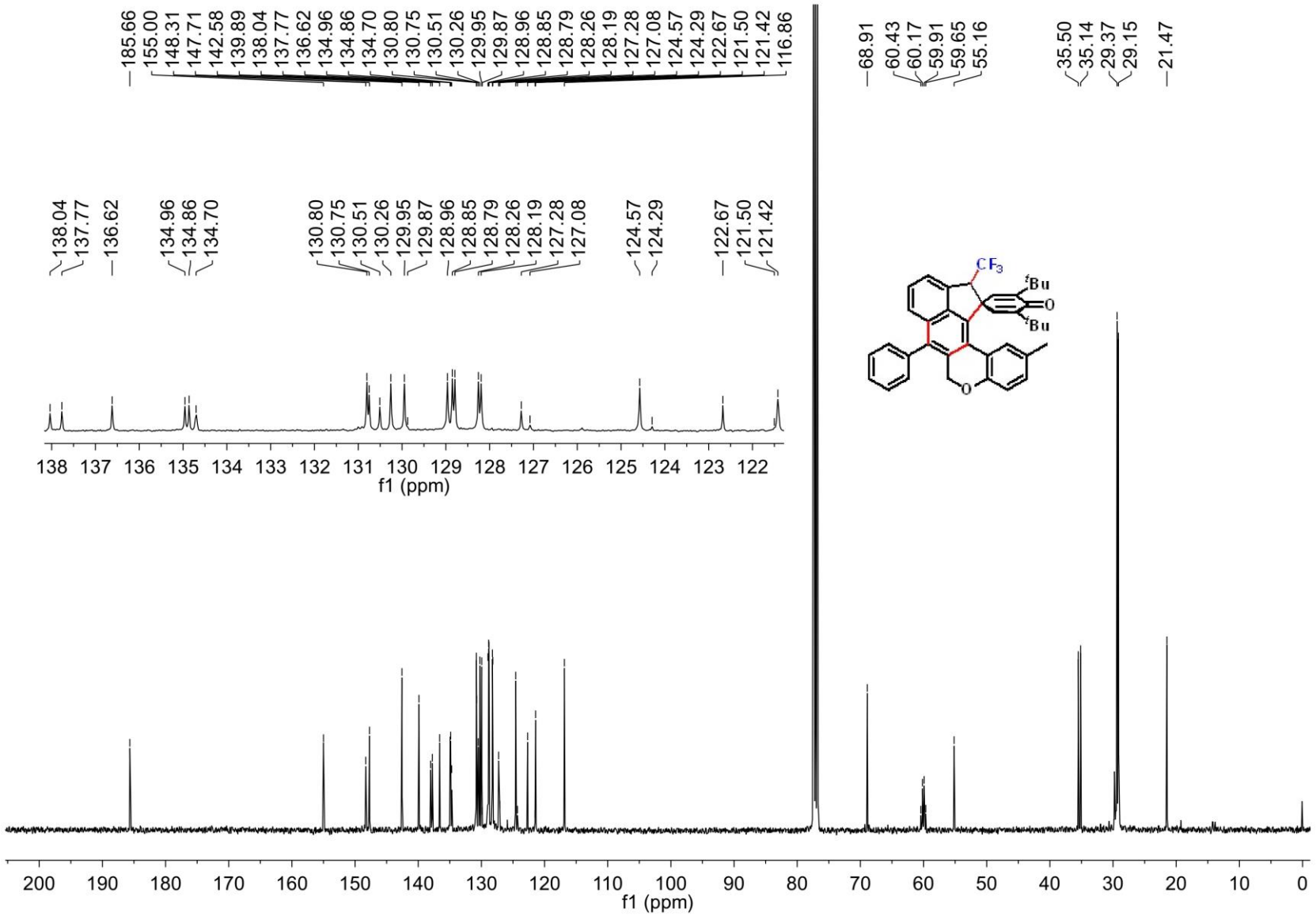
^{13}C NMR Spectrum of Compound 4ob



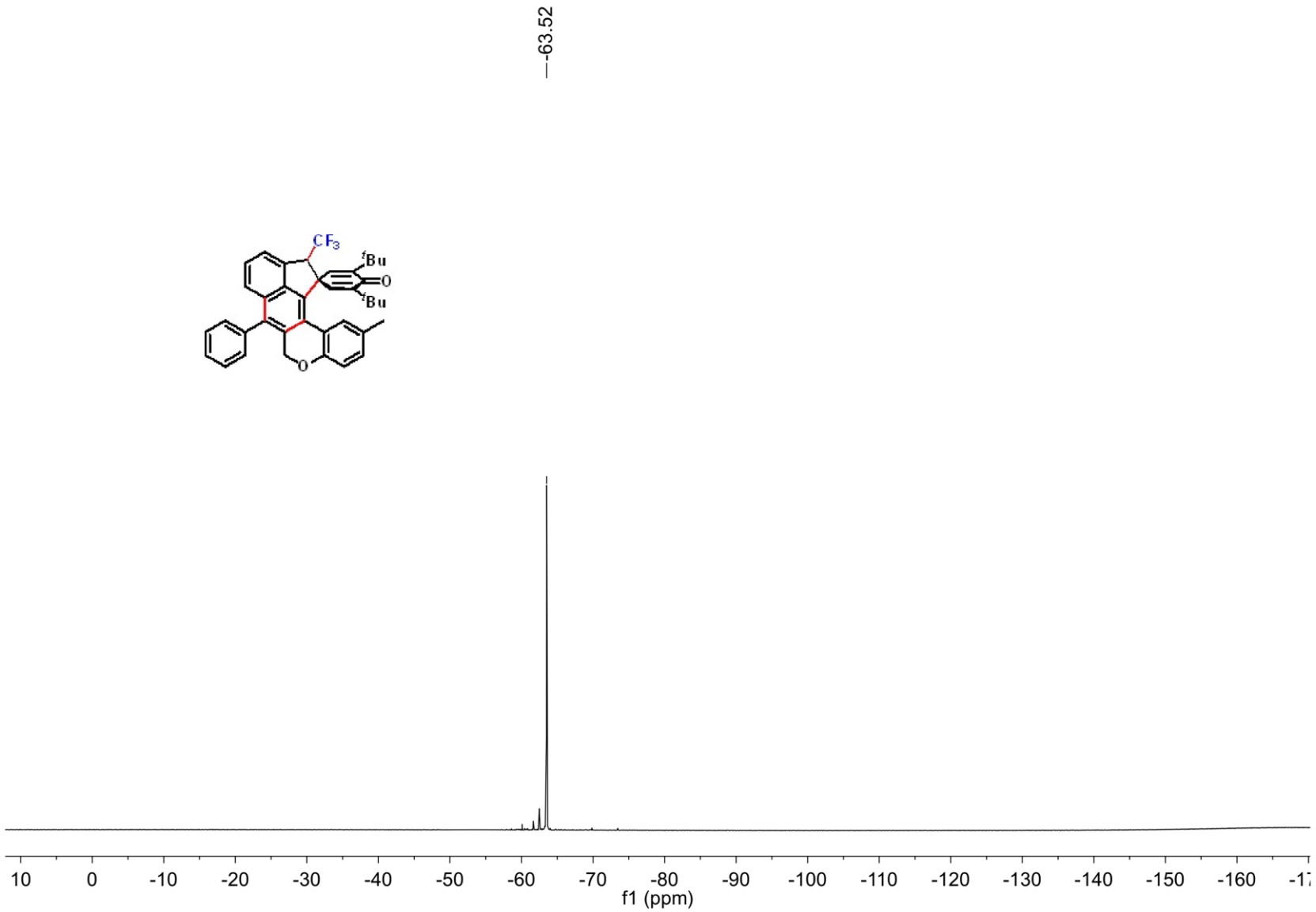
^{19}F NMR Spectrum of Compound 4ob



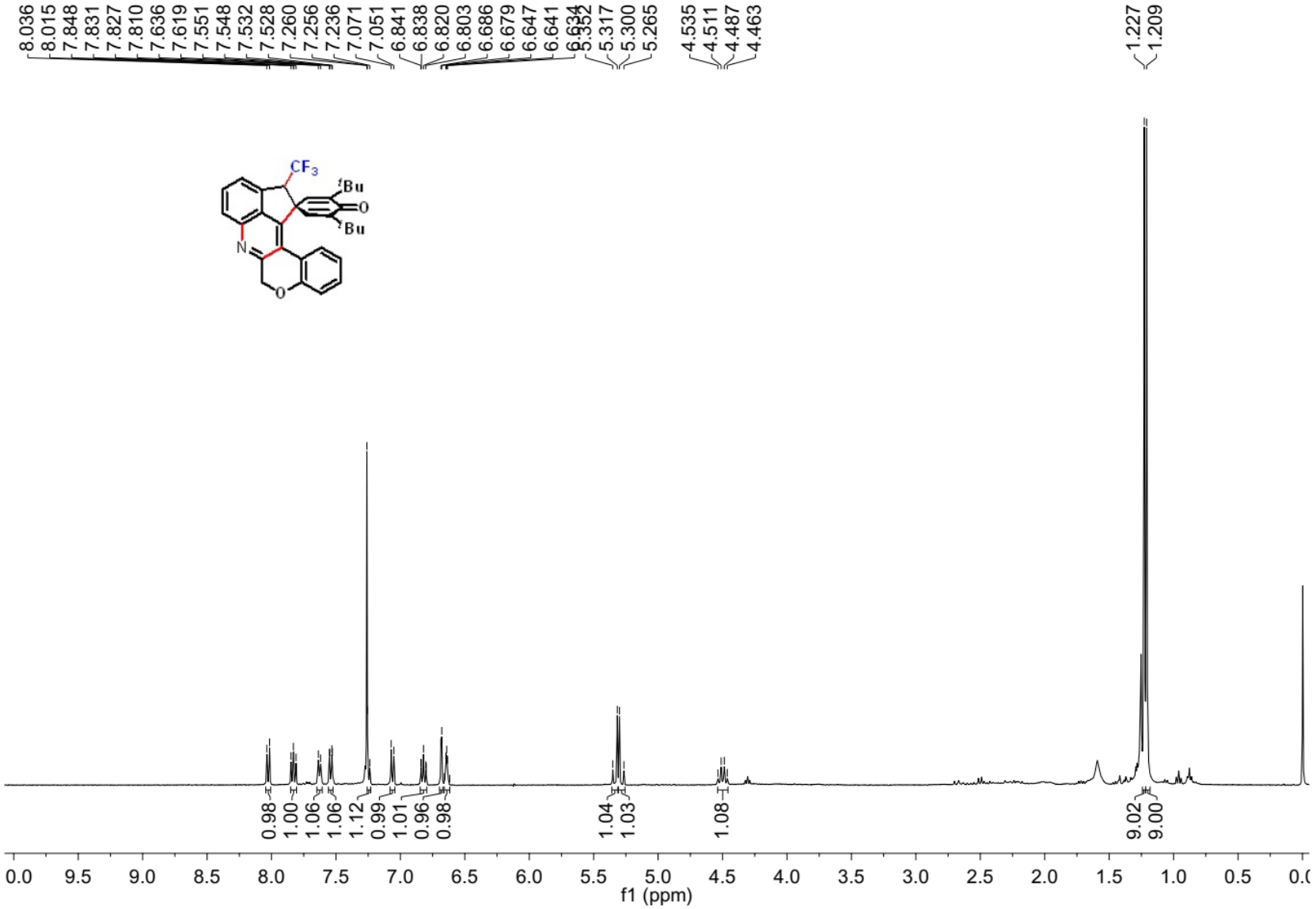
^{1}H NMR Spectrum of Compound 4ub



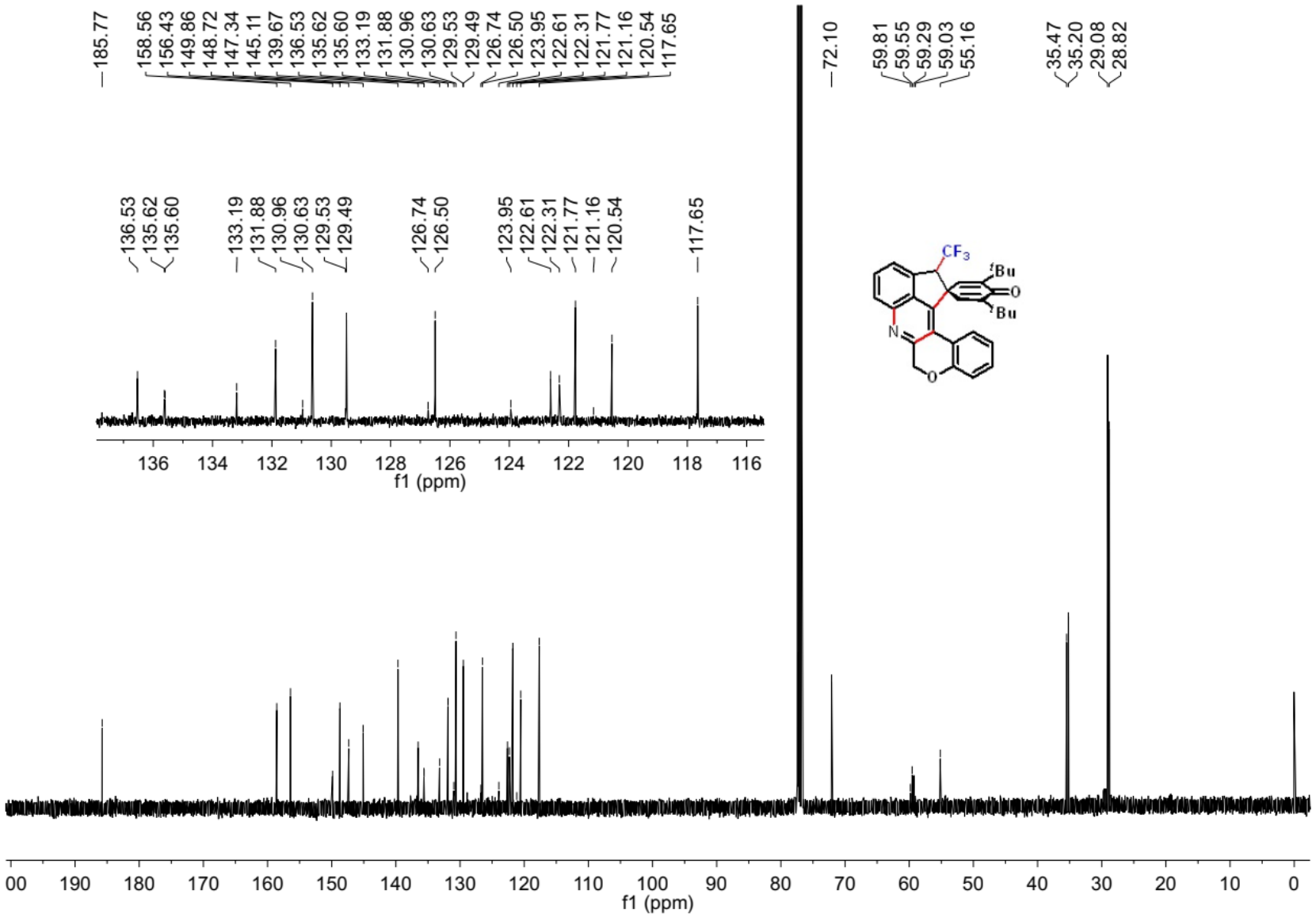
^{13}C NMR Spectrum of Compound 4ub



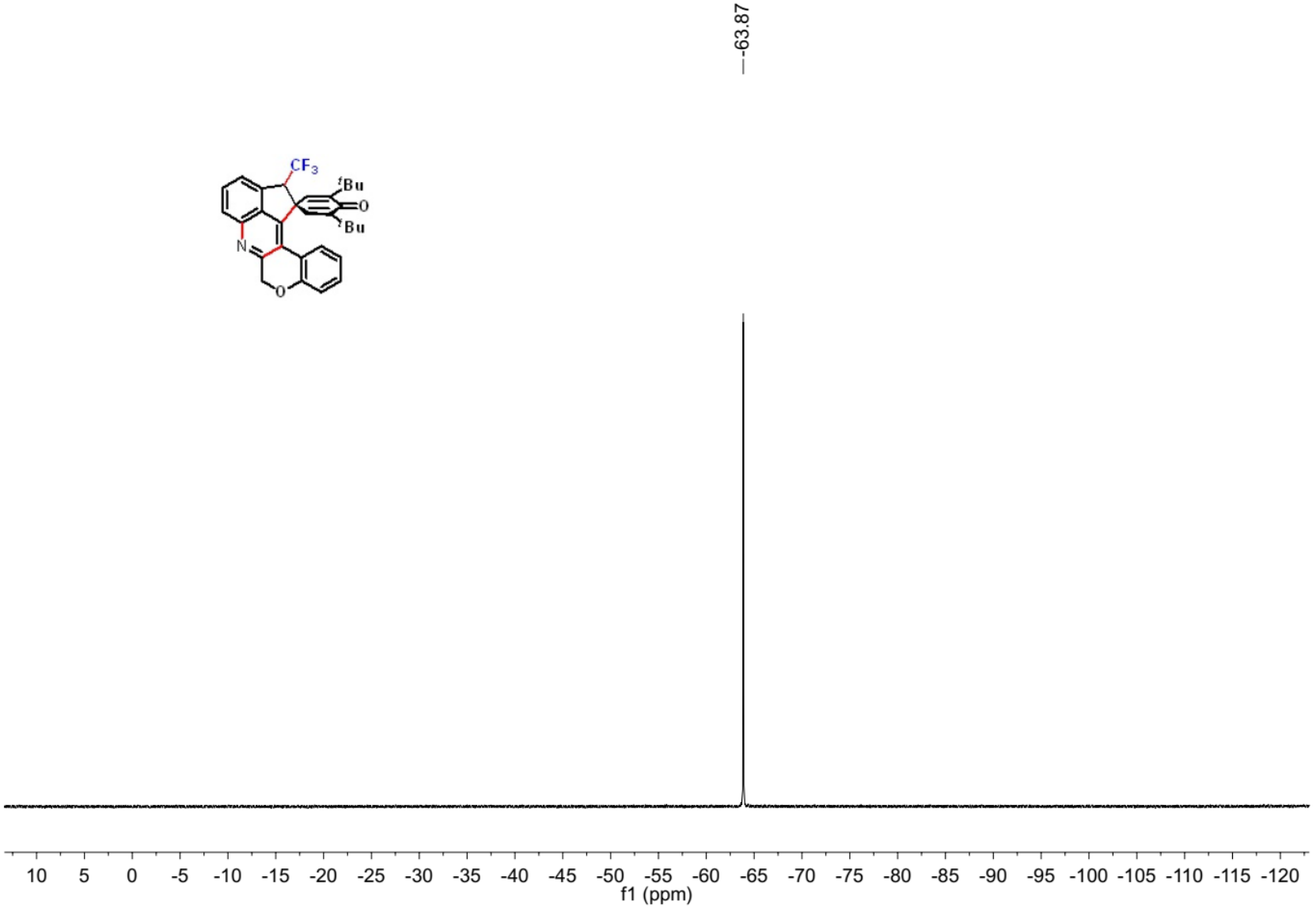
^{19}F NMR Spectrum of Compound 4ub



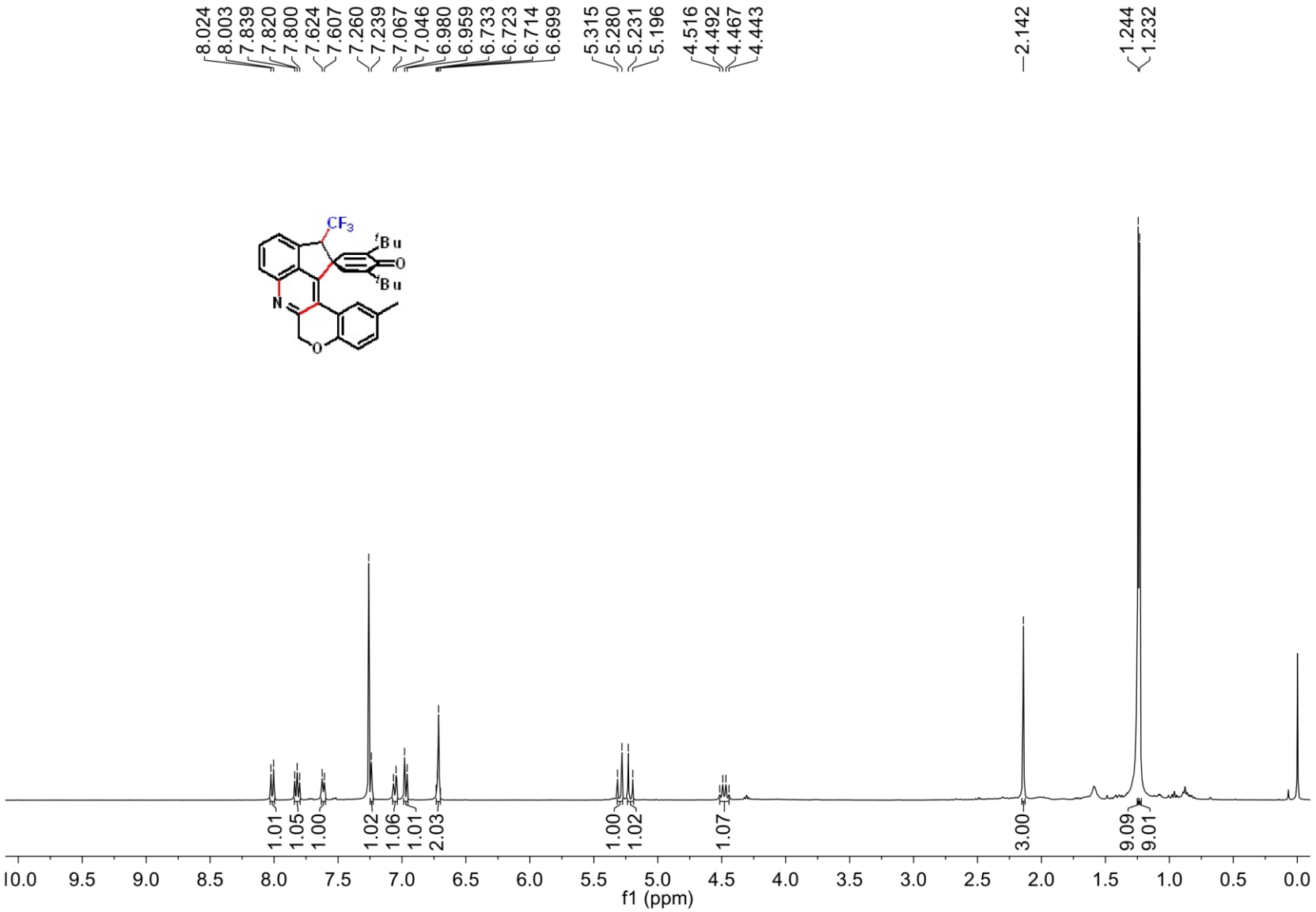
^{1}H NMR Spectrum of Compound 5ab



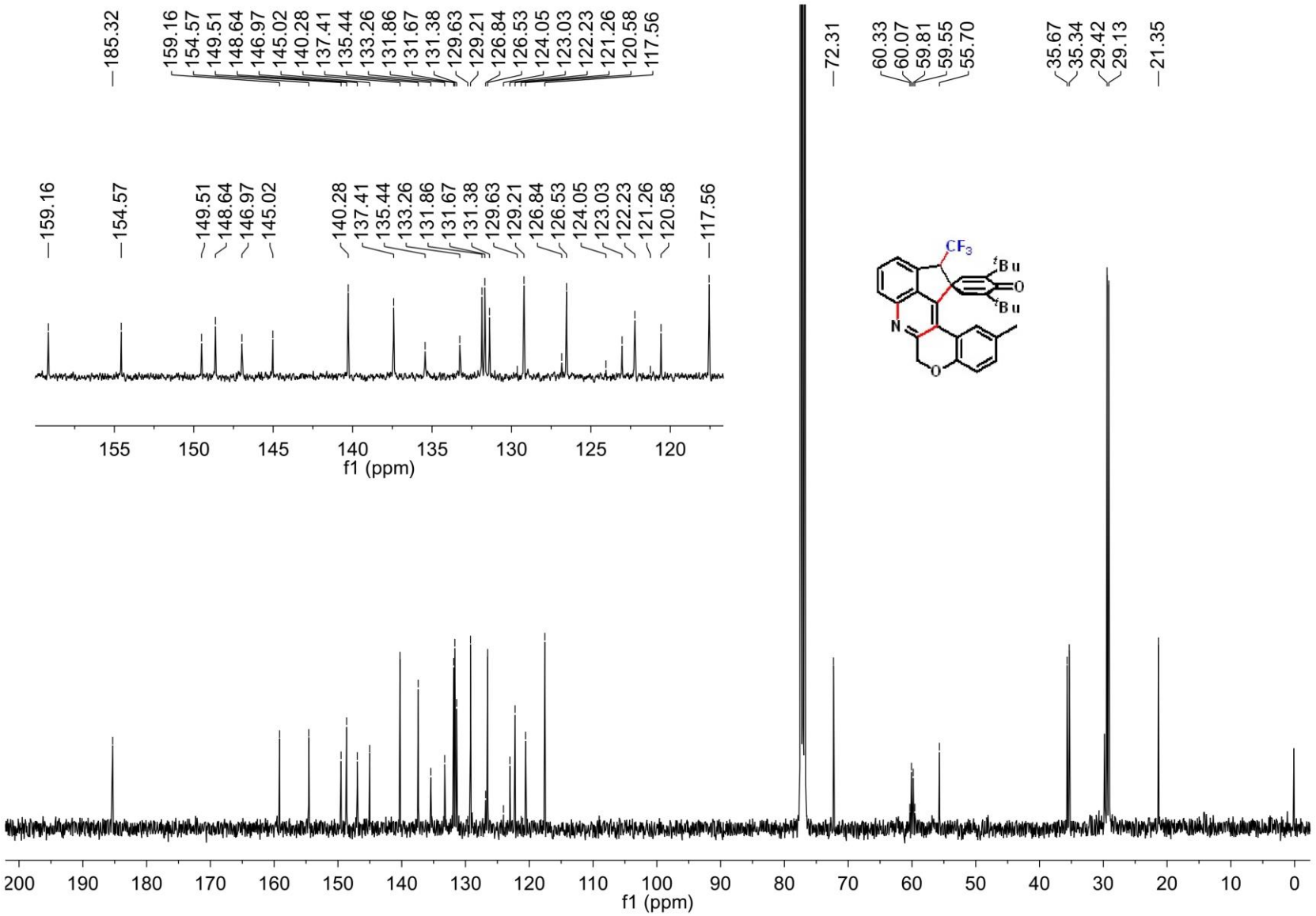
^{13}C NMR Spectrum of Compound 5ab



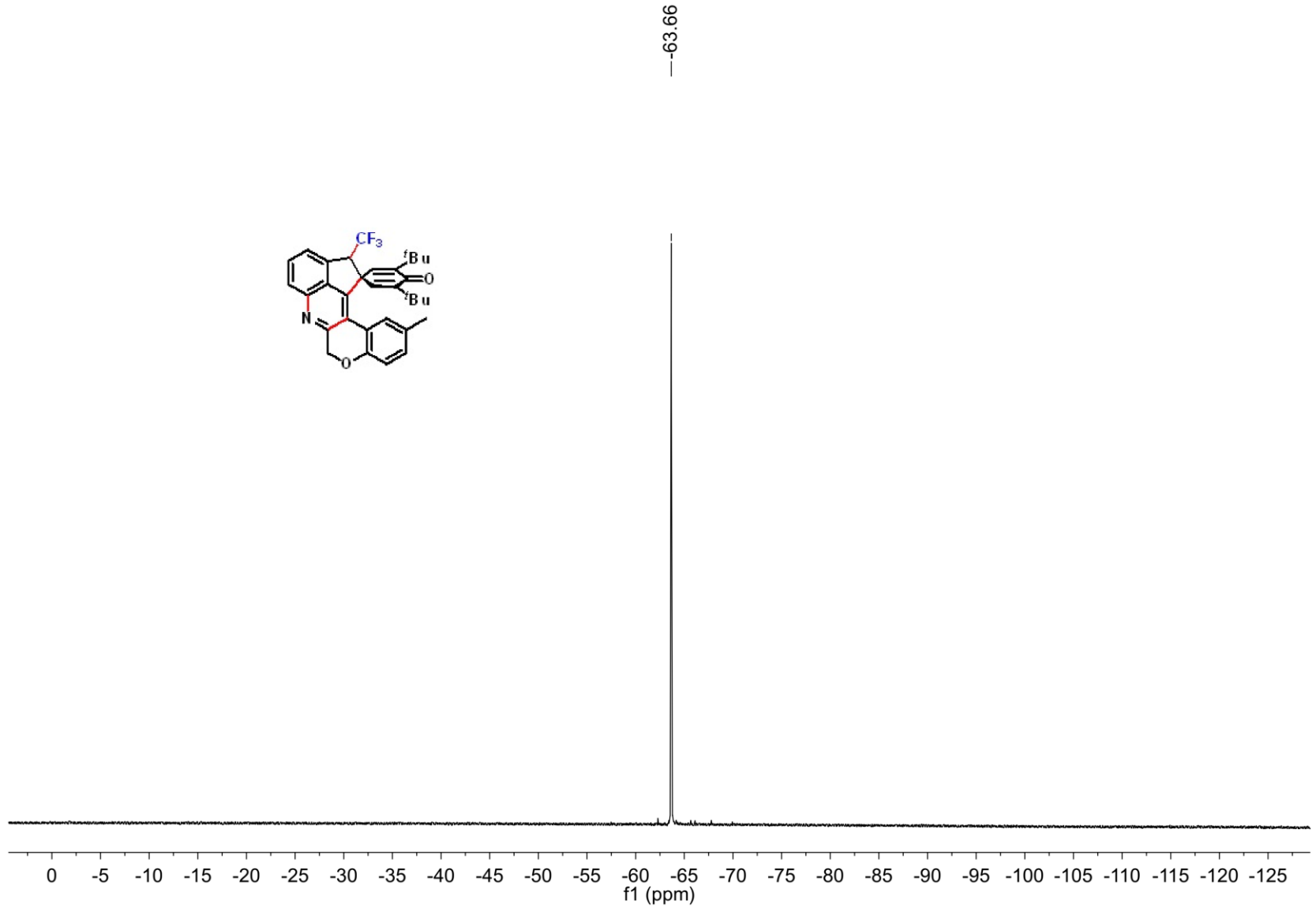
^{19}F NMR Spectrum of Compound 5ab



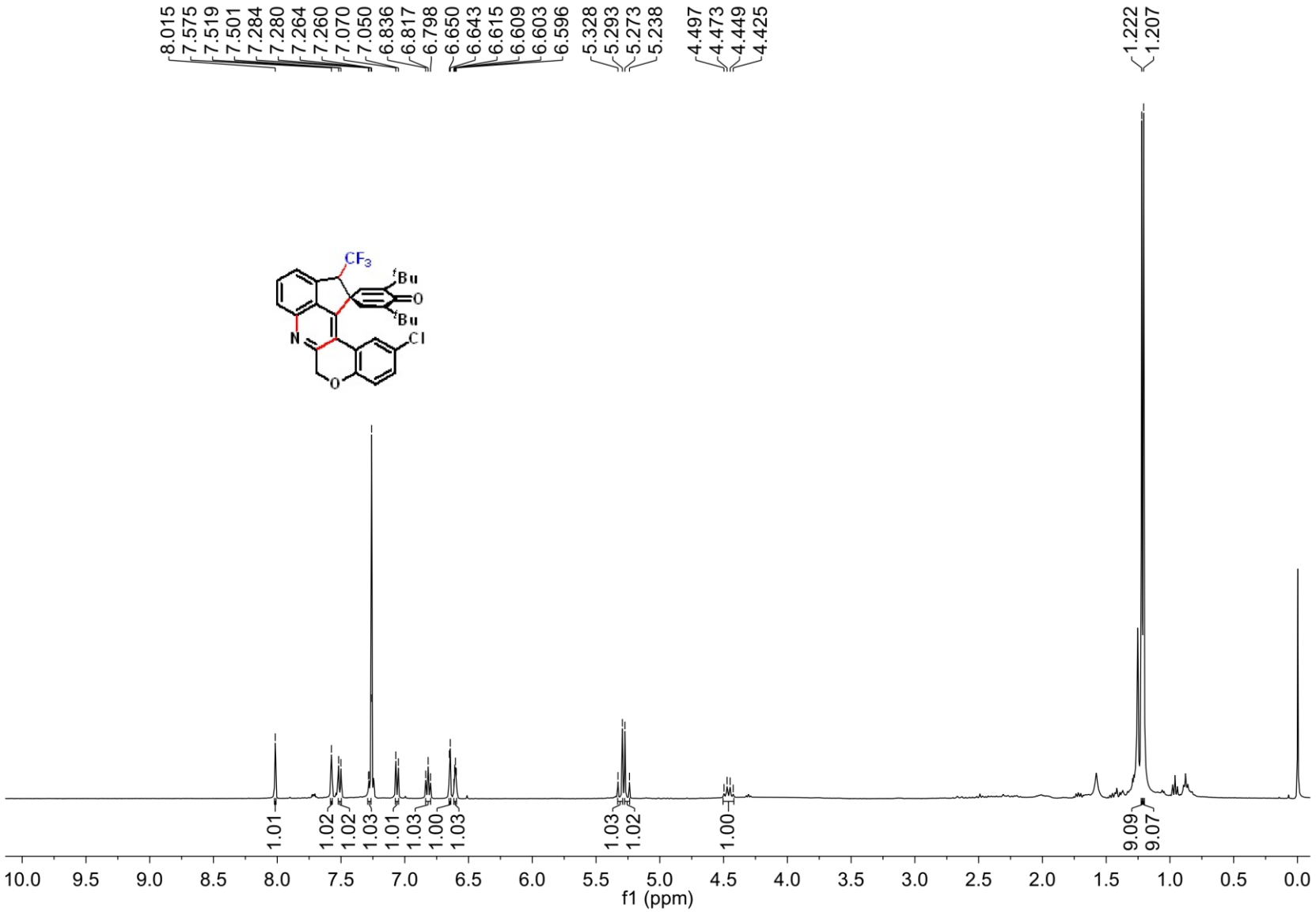
^{1}H NMR Spectrum of Compound 5bb



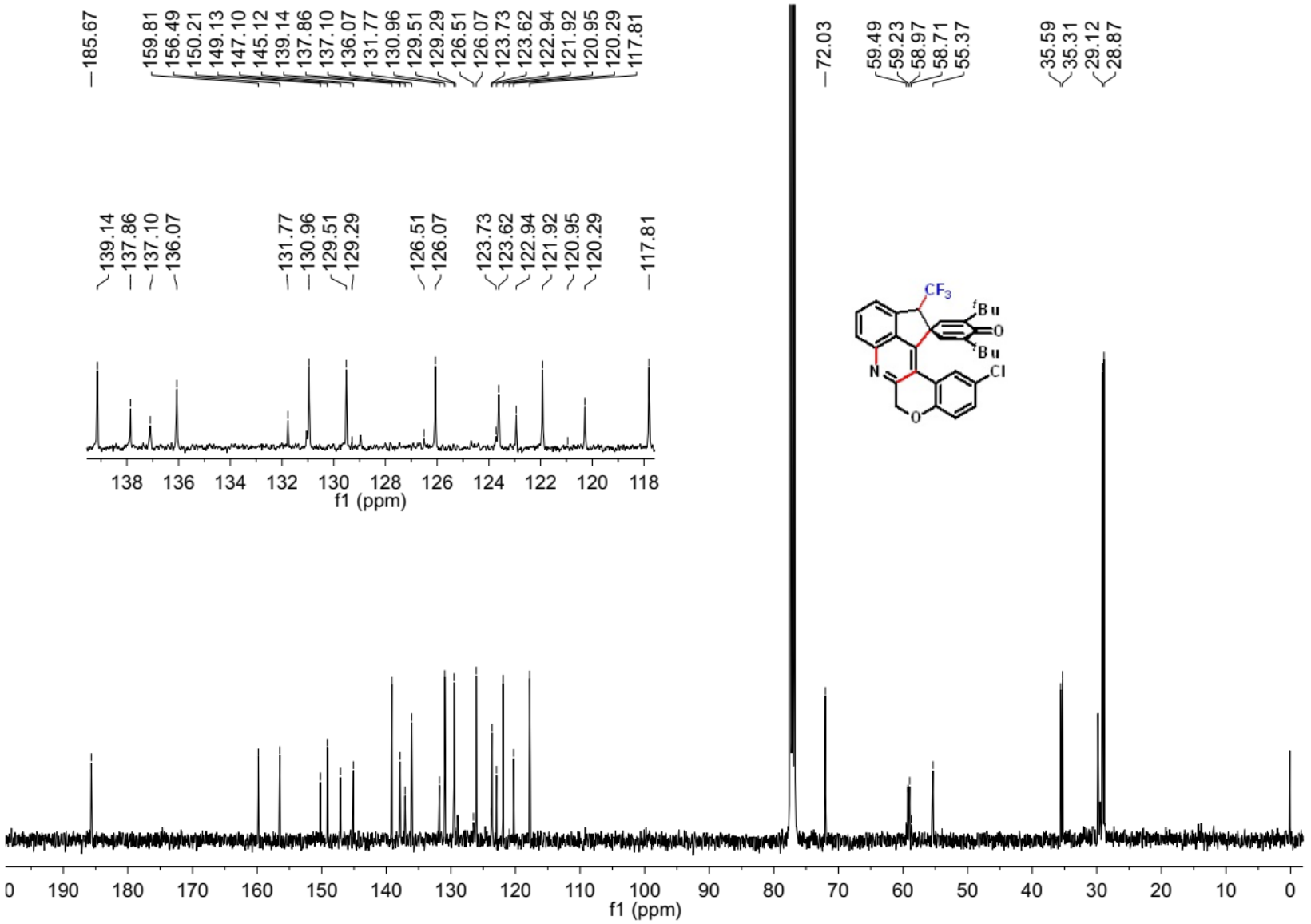
^{13}C NMR Spectrum of Compound 5bb



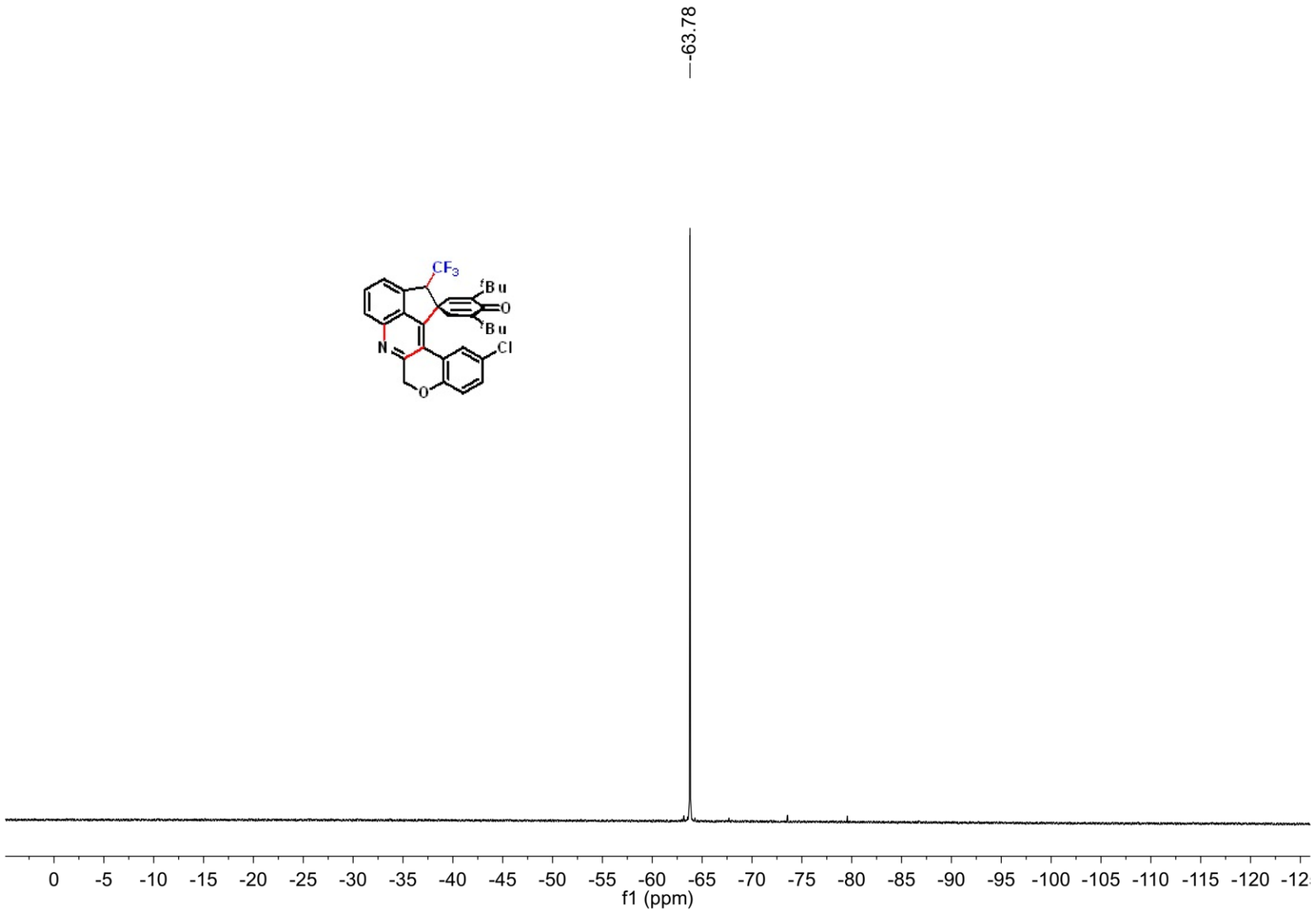
^{19}F NMR Spectrum of Compound 5bb



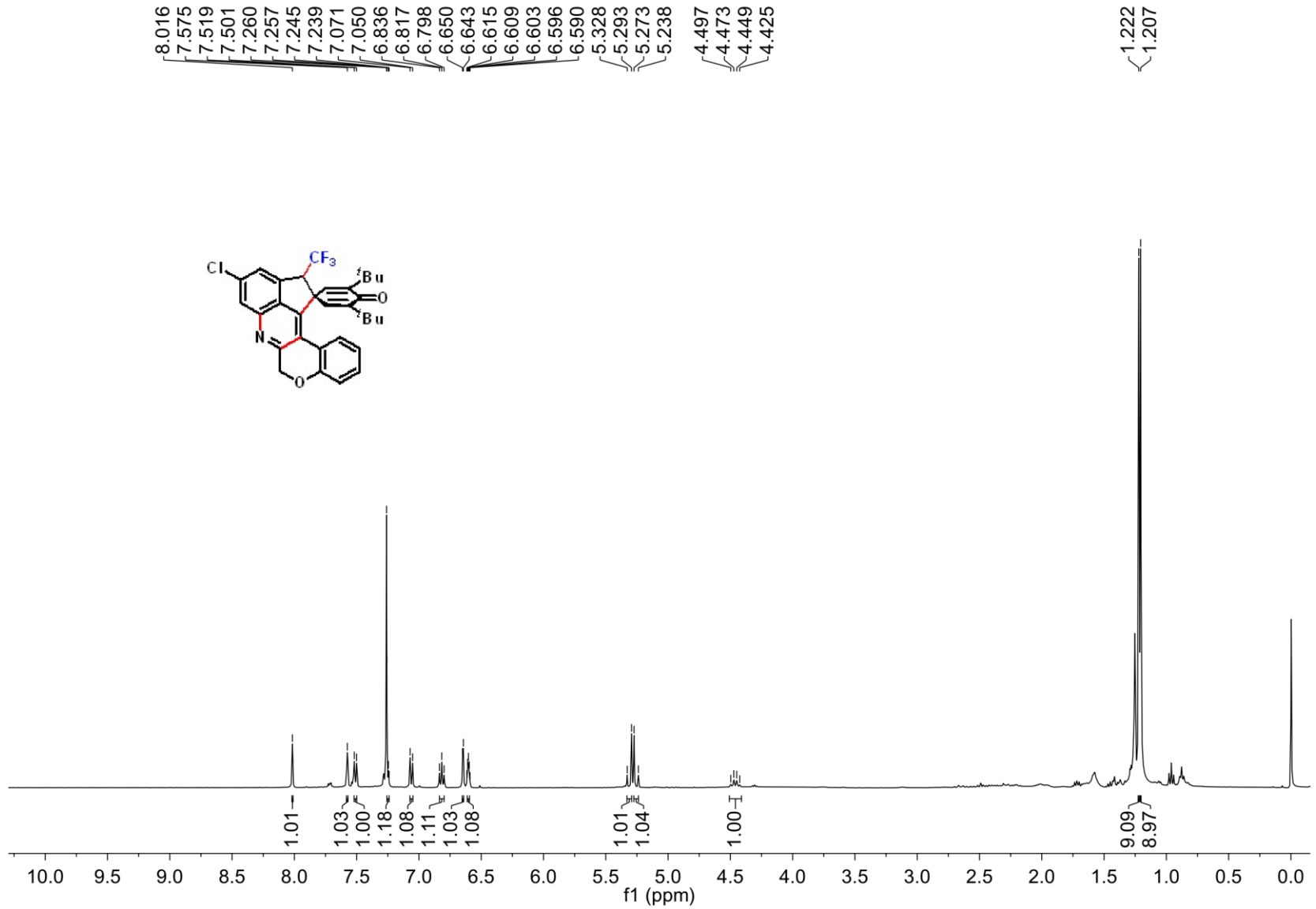
^{1}H NMR Spectrum of Compound 5cb



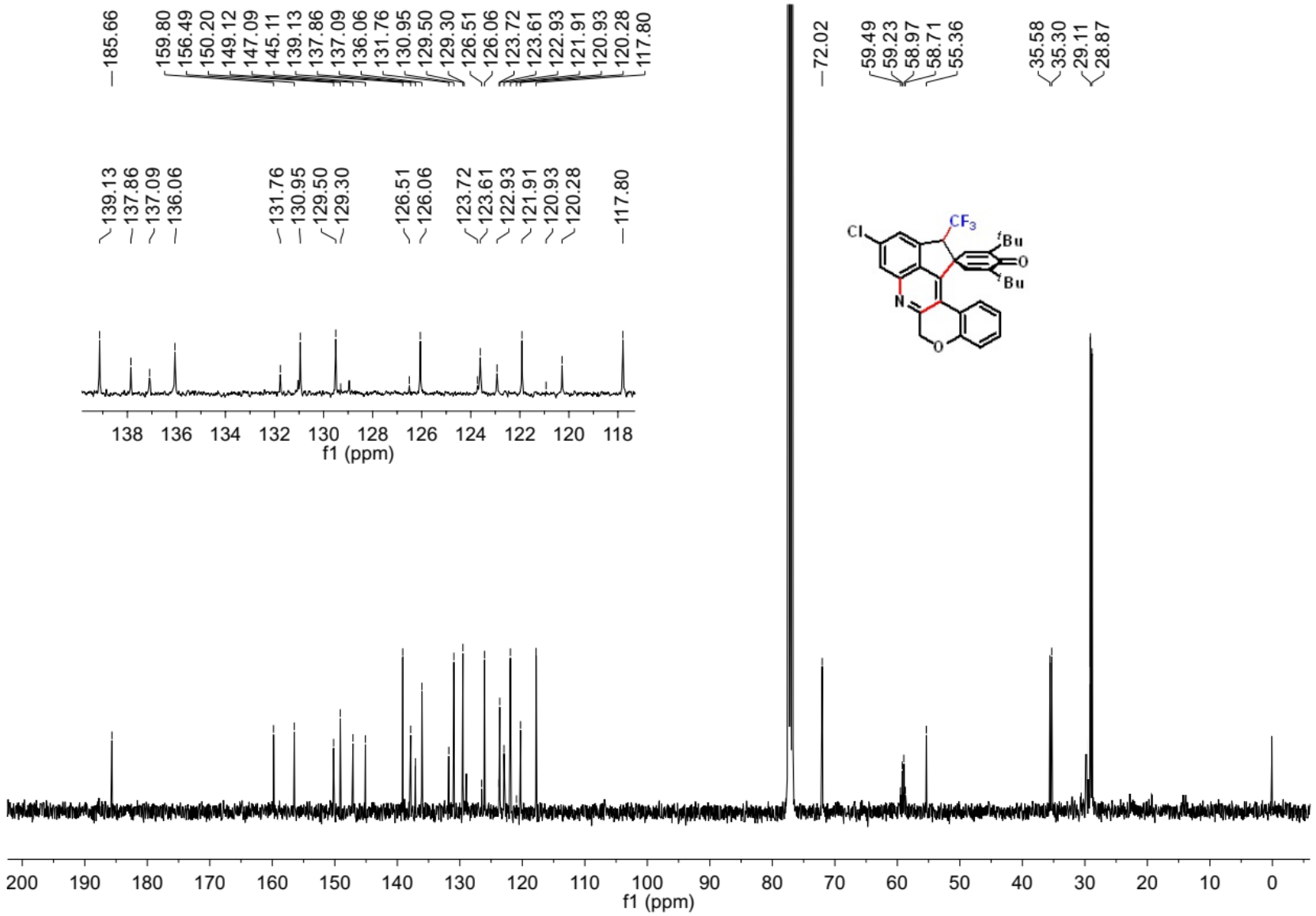
^{13}C NMR Spectrum of Compound 5cb



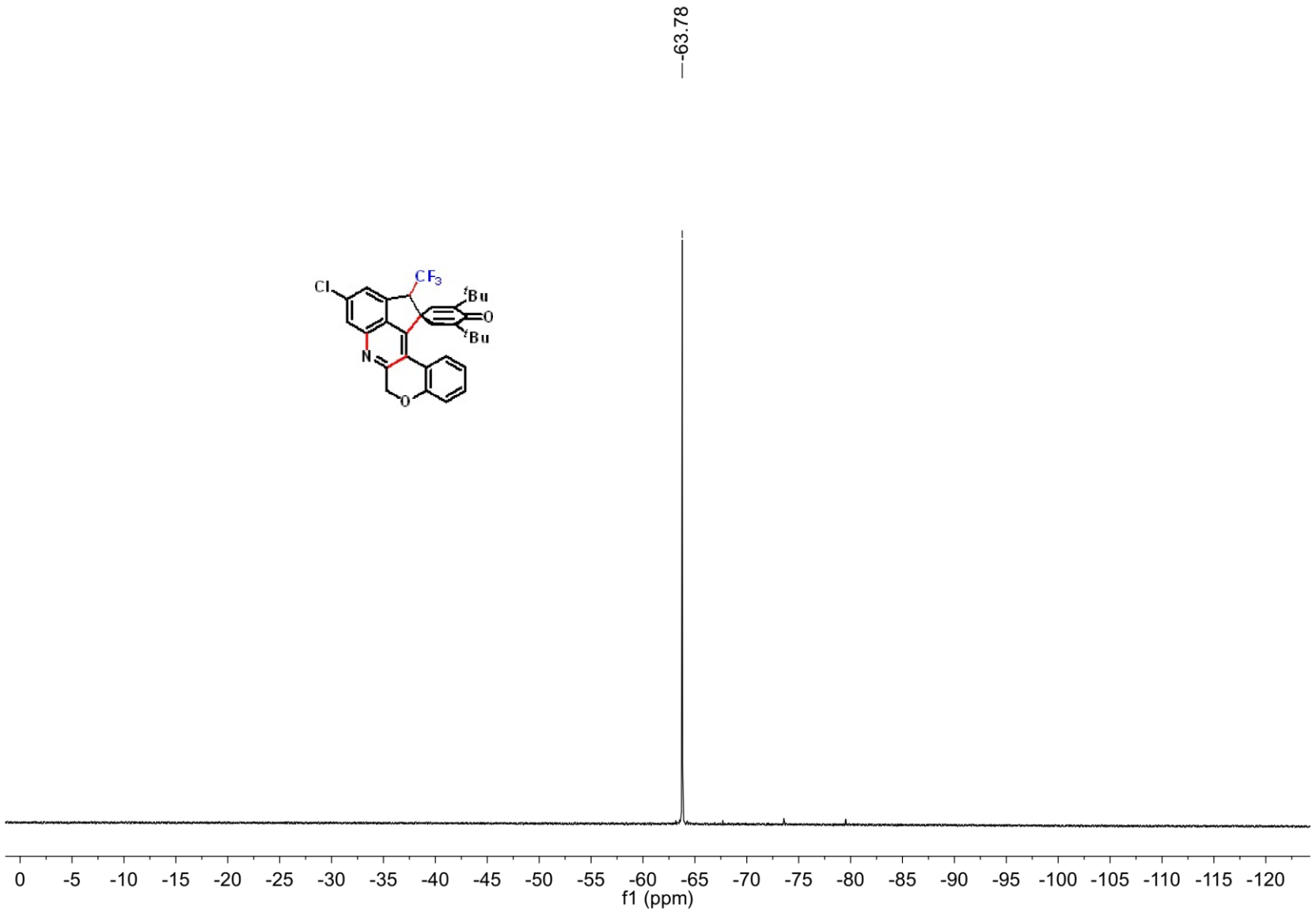
^{19}F NMR Spectrum of Compound 5cb



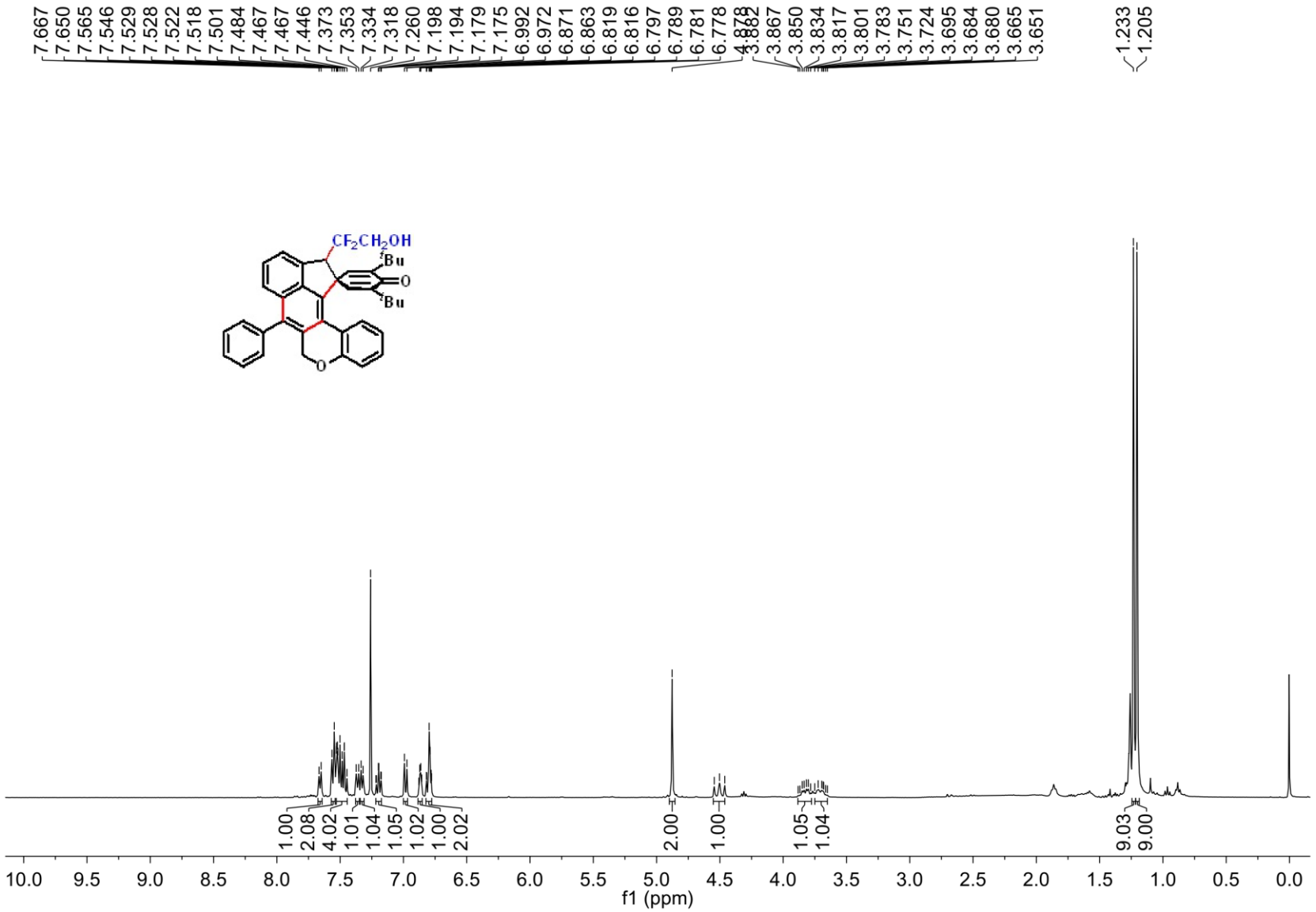
^{1}H NMR Spectrum of Compound 5db



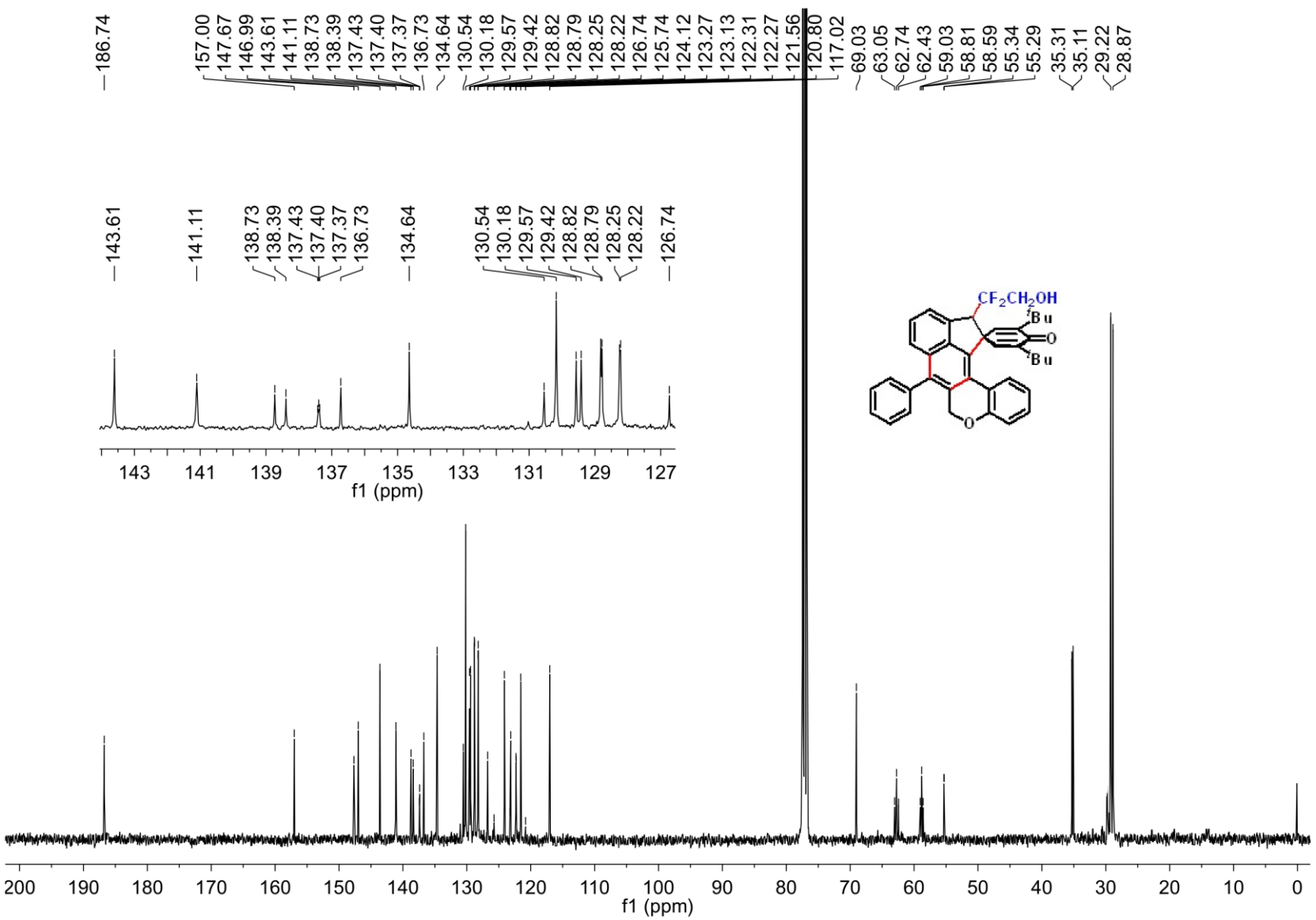
^{13}C NMR Spectrum of Compound 5db



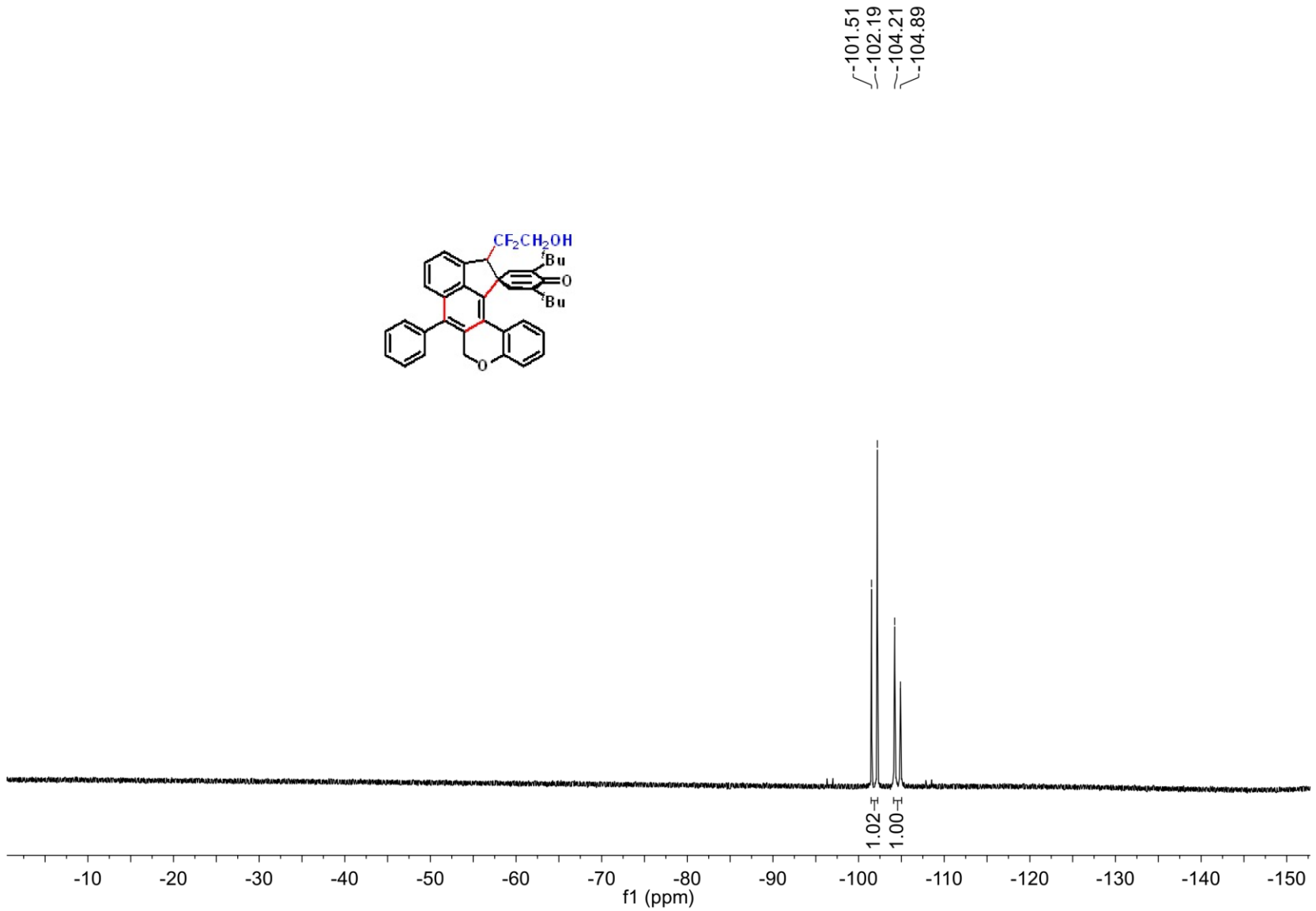
^{19}F NMR Spectrum of Compound 5db



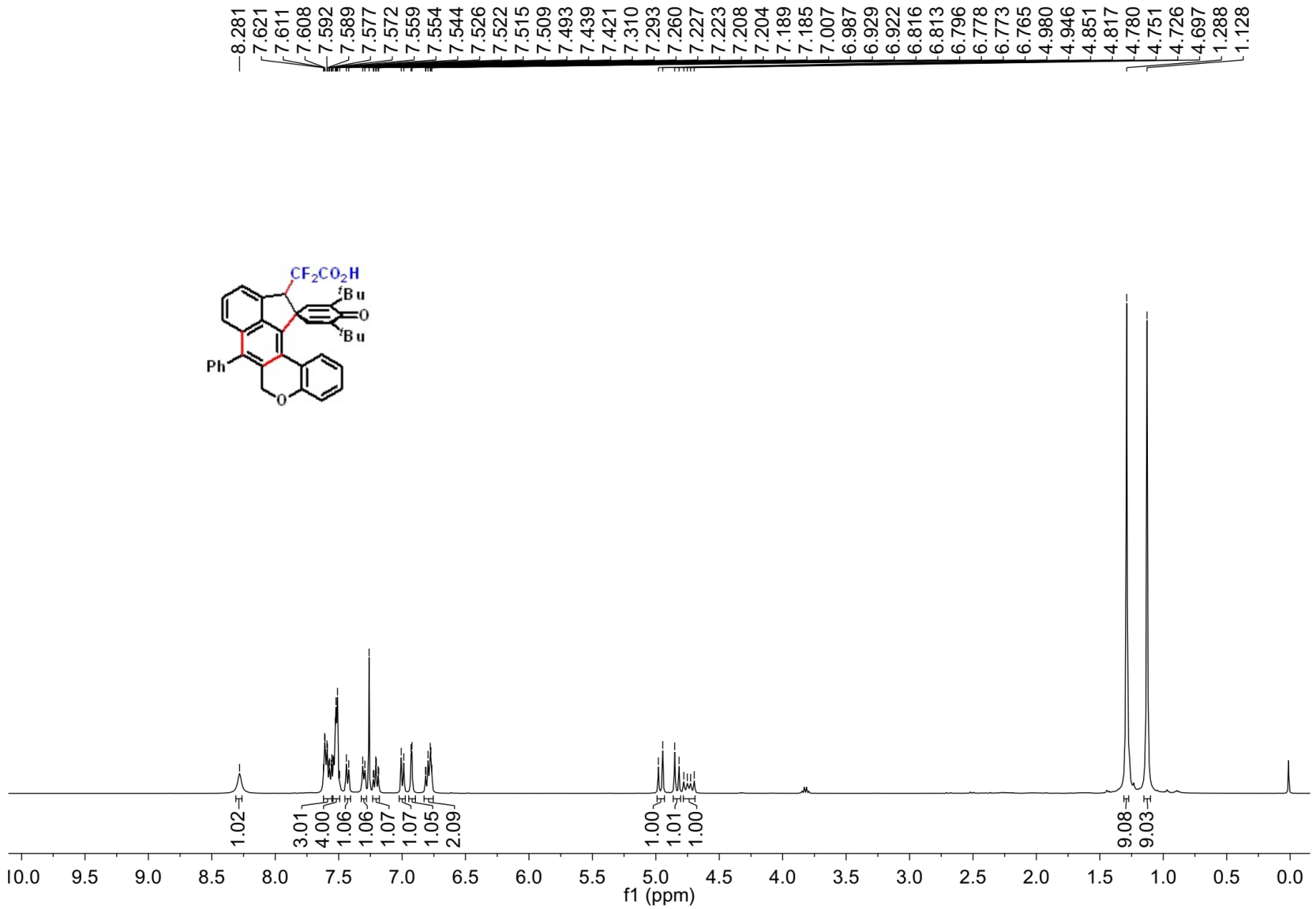
^{1}H NMR Spectrum of Compound 6



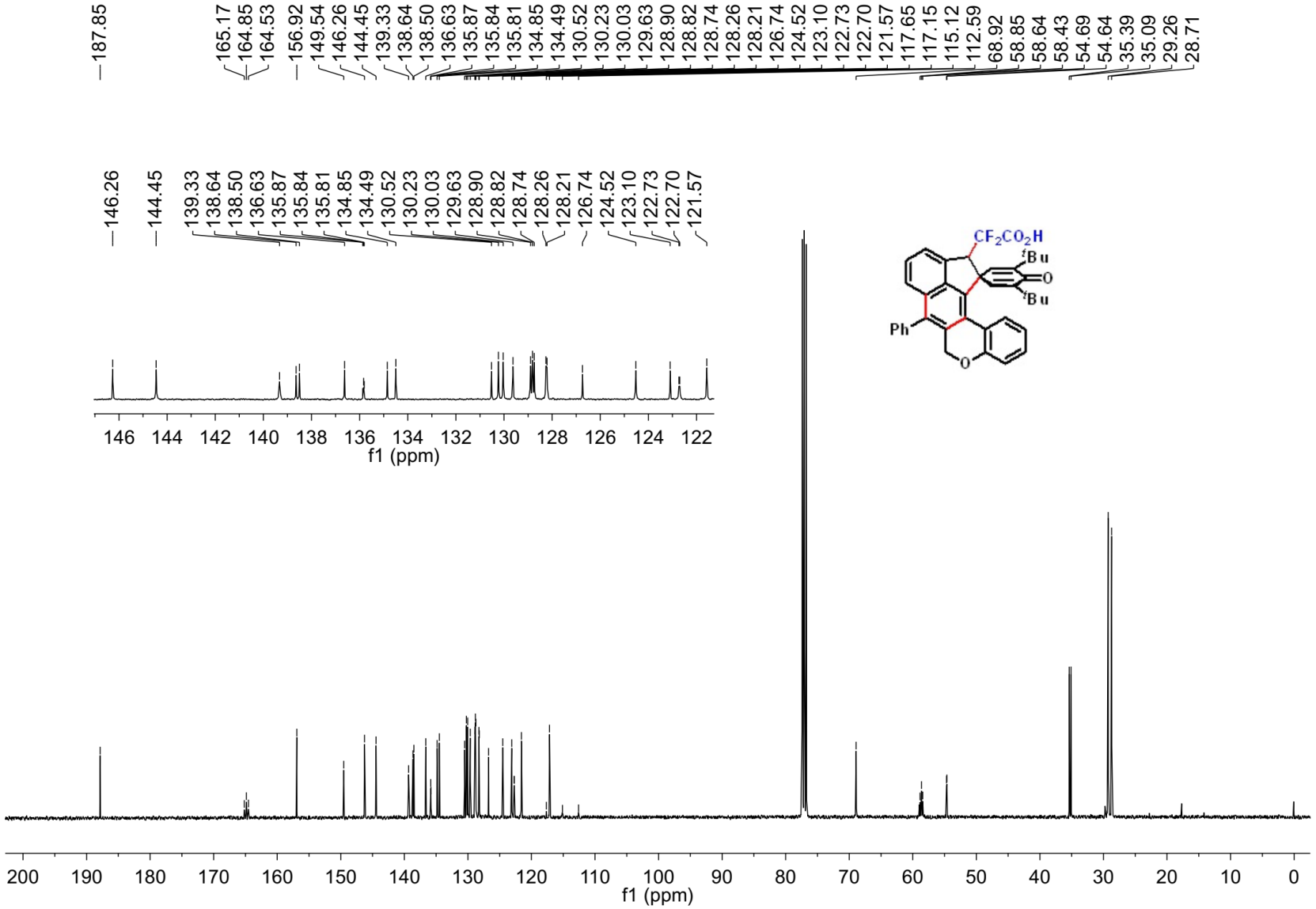
^{13}C NMR Spectrum of Compound 6



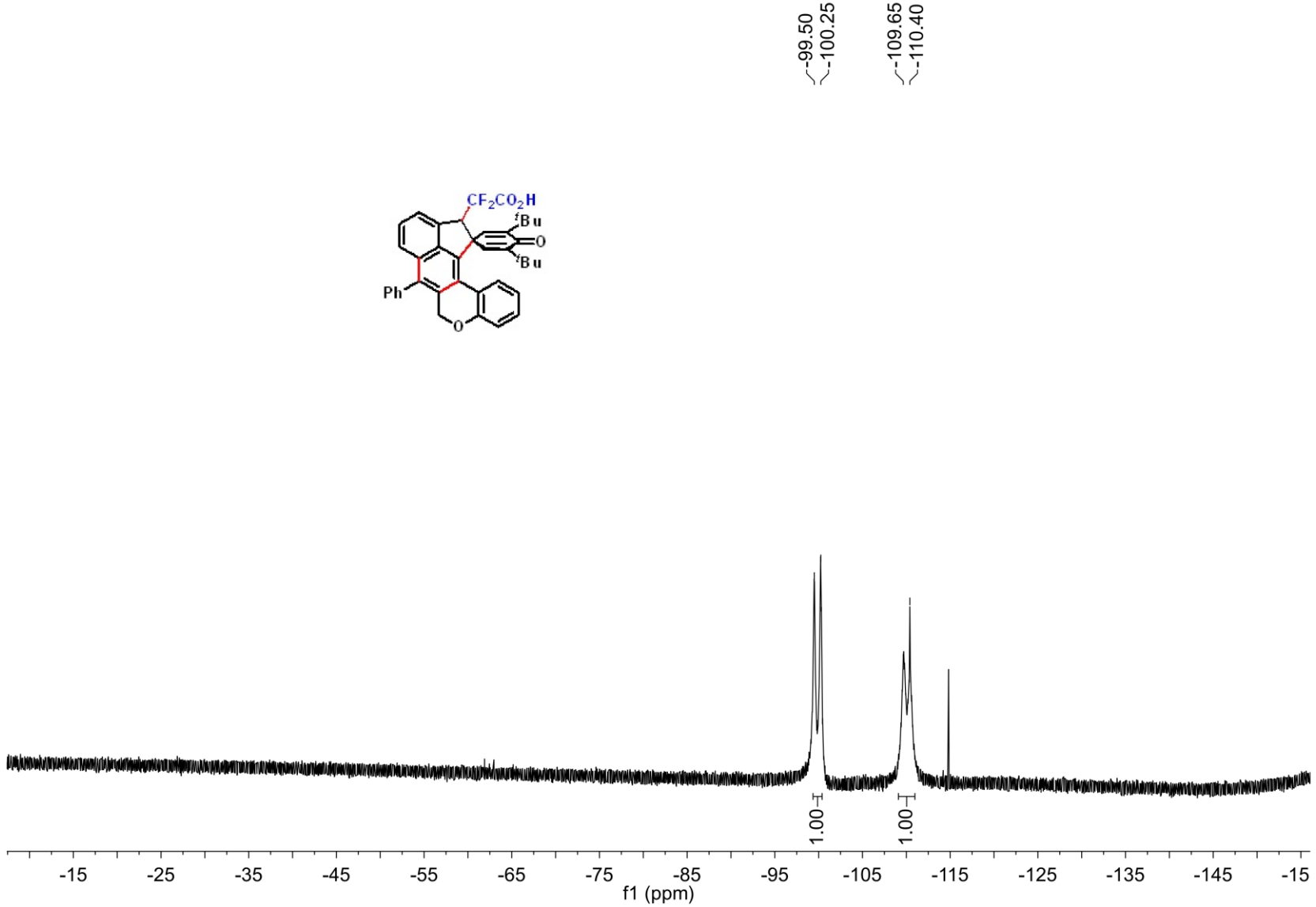
^{19}F NMR Spectrum of Compound 6



^{1}H NMR Spectrum of Compound 7



^{13}C NMR Spectrum of Compound 7



^{19}F NMR Spectrum of Compound 7