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Two-in-One Strategy for Fluorene-Based Spirocycles *via* Pd(0)-Catalyzed Spiroannulation of *o*-Iodobiaryls with Bromonaphthols

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Supporting Information

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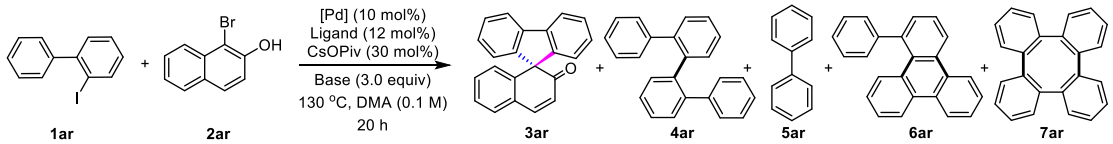
A. General information:

All reactions were carried out under an argon atmosphere using Standard Schlenk-Lines or a glovebox (Innovative Technology). All reagents were used as received unless otherwise noted. DMF, DMA and DCM were dried over CaH_2. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}), visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; dd, quartet; t, triplet; m, multiplet. Coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d*. Fluorine nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 spectrometer, and chemical shifts are reported relative to inter standard $CFCl_3$ at 0.0 ppm. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a Bruker Daltonics MicroTof-Q II or Agilent 7890B-5977A mass spectrometer. Substrates **1aa,**[1] **1ab**,[2] **1ae,**[3] **1ag-1ai,**[4] **1al,**[4] **1am,**[4] **1ap,**[5] **1aq-1as,**[4] **1au,**[2] **1ax,**[6] **1ay,**[7] **1az,**[8] **1ba-1bb,**[8] **1bc,**[9] **1bd,**[10] **1be,**[11] **1bf,**[12] **1bh,**[13] and 1-bromo-2-naphthols **2bi-2bu,**[14-15] **2by,**[14] **2bz-2ca**[16] were prepared according to the literature methods.

B. Optimization of reaction conditions:

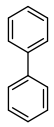


1ar **2ar** **3ar** **4ar** **5ar** **6ar** **7ar**

Entry[a]	[Pd]	Ligand	Additive	Base	Yield (%)[b] 3ar	4ar	5ar	6ar	7ar
1	$Pd(OAc)_2$	PPh_3	CsOPiv	Li_2CO_3	0	0	11	0	36
2	$Pd(OAc)_2$	PPh_3	CsOPiv	Na_2CO_3	0	trace	18	0	38
3	$Pd(OAc)_2$	PPh_3	CsOPiv	K_2CO_3	38	trace	24	8	0
4	$Pd(OAc)_2$	PPh_3	CsOPiv	Cs_2CO_3	56	trace	11	trace	6
5	$Pd(OAc)_2$	PPh_3	CsOPiv	K_3PO_4	31	trace	16	trace	13
6[c]	$Pd(OAc)_2$	PPh_3	CsOPiv	^{t}BuOK	10	6	20	trace	0
7[c]	$Pd(OAc)_2$	PPh_3	CsOPiv	CsOAc	0	0	13	trace	0
8[c]	$Pd(OAc)_2$	P(*o*-Tol)$_3$	CsOPiv	Cs_2CO_3	33	trace	14	0	0
9[c]	$Pd(OAc)_2$	P(*p*-Anisyl)$_3$	CsOPiv	Cs_2CO_3	37	trace	0	9	0
10[c]	$Pd(OAc)_2$	TFP	CsOPiv	Cs_2CO_3	29	0	10	0	13
11	$Pd(OAc)_2$	PCy_3	CsOPiv	Cs_2CO_3	43	0	31	0	11
12	$Pd(OAc)_2$	P(*p*-Cl-C_6H_4)$_3$	CsOPiv	Cs_2CO_3	61	0	11	0	0
13	**$Pd(OAc)_2$**	**P(*p*-F-C_6H_4)$_3$**	**CsOPiv**	**Cs_2CO_3**	**83**	**0**	**trace**	**0**	**0**
14	$Pd(OAc)_2$	DPPM	CsOPiv	Cs_2CO_3	28	trace	56	0	trace
15	$Pd(OAc)_2$	DPPF	CsOPiv	Cs_2CO_3	24	trace	46	trace	15
16	$Pd(OAc)_2$	BINAP	CsOPiv	Cs_2CO_3	38	0	0	0	17
17[c]	$Pd(OAc)_2$	DIBPY	CsOPiv	Cs_2CO_3	17	trace	0	0	0
18	$PdCl_2$	P(*p*-F-C_6H_4)$_3$	CsOPiv	Cs_2CO_3	60	trace	15	0	11
19[c]	$Pd(TFA)_2$	P(*p*-F-C_6H_4)$_3$	CsOPiv	Cs_2CO_3	27	0	trace	0	13
20	$Pd_2(dba)_3$	P(*p*-F-C_6H_4)$_3$	CsOPiv	Cs_2CO_3	29	trace	21	0	23
21[d]	$Pd(OAc)_2$	P(*p*-F-C_6H_4)$_3$	BINA-PO_2H	Cs_2CO_3	40	0	15	0	11
22	$Pd(OAc)_2$	P(*p*-F-C_6H_4)$_3$	$(BnO)_2PO_2H$	Cs_2CO_3	37	18	trace	trace	trace

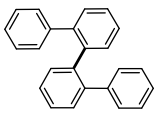
[a] Reaction conditions: 2-iodo-1,1'-biphenyl (0.24 mmol), 1-bromonaphthalen-2-ol (0.2 mmol), [Pd] (10 mol%), ligand (12 mol%), additive (30 mol%) and base (3.0 equiv) in 2.0 mL DMA at 130 °C for 20 h. [b] Yields were determined by ^{1}H NMR analysis. [c] A large amount of 2-iodo-1,1'-biphenyl **1ar** was remaining. [d] BINA-PO_2H: 1,1'-dinaphthyl-2,2'-diyl hydrogenphosphate.

Byproducts of the above reaction: 4ar-7ar



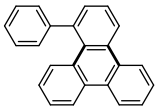
1,1'-Biphenyl (4ar)

White solid. Mp = 68.5-70.0 °C. Eluent: PE, R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.57 (m, 4H), 7.47 (dd, *J* = 8.0, 7.5 Hz, 4H), 7.40-7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.8, 127.3, 127.2 ppm. Analytical data are in accordance with the literature values.[17]



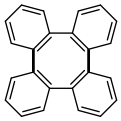
1,1':2',1'':2'',1'''-Quaterphenyl (5ar)

White solid. Mp = 108.3-109.4 °C. Eluent: PE, R_f = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 2H), 7.39-7.29 (m, 4H), 7.21-7.15 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 4H), 6.63 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.9, 140.0, 131.7, 130.0, 129.3, 127.4, 127.4, 127.0, 125.9 ppm. Analytical data are in accordance with the literature values.[18]



1-Phenyltriphenylene (6ar)

White solid. Mp = 155.1-156.0 °C. Eluent: PE, R_f = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67-8.61 (m, 3H), 8.55 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.70-7.61 (m, 3H), 7.54 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.50-7.37 (m, 6H), 7.10-7.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 140.8, 131.6, 131.5, 131.1, 130.3, 130.1, 130.0, 129.8, 129.2, 129.0, 128.7, 127.4, 127.3, 126.9, 126.6, 126.4, 125.0, 123.7, 123.2, 123.1, 122.3 ppm. Analytical data are in accordance with the literature values.[7]

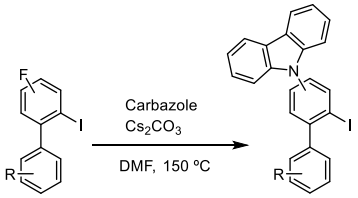


Tetraphenylene (7ar)

White solid. Mp = 186.6-187.5 °C. Eluent: PE, R_f = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 8H), 7.17-7.15 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 129.0, 127.2 ppm. Analytical data are in accordance with the literature values.[19]

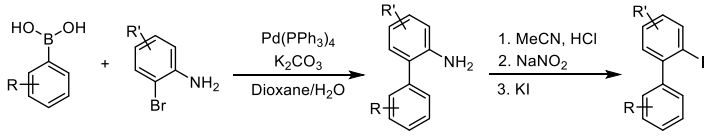
C. Preparation of substrates:

General procedure A for the preparation of *o*-iodobiaryls:



A mixture of fluorinated aryl iodide (3.0 mmol), carbazole (125 mg, 0.75 mmol) and Cs_2CO_3 (0.98 g, 3.0 mmol) in solvent (3.0 mL) was allowed to react under air atmosphere. The reaction mixture was heated to the 150 °C for 24 h. After reaction completion, the mixture was added to brine (15 mL) and extracted with CH_2Cl_2. The organic layers were combined and dried over $MgSO_4$. After filtration and evaporation, The crude product was purified by silica gel flash chromatography to afford the corresponding substrates.

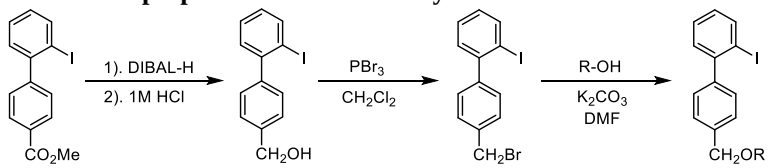
General procedure B for the preparation of *o*-iodobiaryls:



A 50 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), K_2CO_3 (1.0 g, 7.5 mmol), substituted boronic acid (3.0 mmol), *ortho*-bromoaniline derivatives (2.5 mmol), 10.0 mL deoxygenated dioxane and 2.0 mL deoxygenated water. The reaction mixture was stirred at 90 ºC for 20 h. After the reaction was cooled down to room temperature, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude products were purified by flash chromatography on silica gel to afford the desired compound.

To a solution of the above product dissolved in MeCN (8.0 mL) was added aq. HCl (1.5 mL conc. HCl in 5.0 mL water), then the mixture was cooled to 0 °C, and a solution of $NaNO_2$ (0.24 g in 5.0 mL water) was added to the reaction. After addition, the reaction was kept at the temperature lower than 5 ºC for 1.0 h and it was added a solution of KI (0.73 g in 5.0 mL water). The reaction was kept at room temperature overnight. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

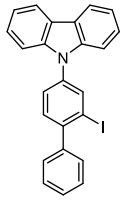
General procedure C for the preparation of *o*-iodobiaryls:



To a -78 °C solution of methyl 2'-iodo-[1,1'-biphenyl]-4-carboxylate (2.0 g, 5.9 mmol) in CH_2Cl_2 (10 mL) was slowly added diisobutylaluminum hydride (11.8 mL, 1.0 M solution in hexane) over 15 minutes. After stirring at -78 °C for 1.0 hours, TLC analysis revealed that no more starting material was remained and the reaction was quenched by cannulation of the mixture into an ice cold 1N HCl solution and extracted with CH_2Cl_2. The organic layers were combined and dried over $MgSO_4$. After filtration and evaporation, The crude product was purified by silica gel flash chromatography to afford the corresponding substrates (2'-iodo-[1,1'-biphenyl]-4-yl)methanol). (Colorless oil, 1.55 g, 85% yield). Eluent: PE:EA = 20:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 1H), 7.47-7.28 (m, 6H), 7.11-6.99 (m, 1H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.5, 140.4, 139.6, 130.2, 129.5, 128.9, 128.3, 126.7, 126.6, 98.8, 64.9 ppm. IR (KBr): 3437, 2855, 1243, 1102, 1056, 851, 847, 755, 688 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{12}IO$ $[M+H]^+$ 310.9933, found 310.9935.

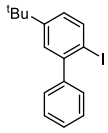
To a solution of phenylmethanols (1.55 g, 5 mmol) dissolved in methylene chloride (50 mL) in an ice-water bath was added phosphorus tribromide (1.48 g, 5.5 mmol), and the mixture was stirred at the same temperature for 30 min. The mixture was washed with cool water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with PE/EA (PE:EA = 50:1, R_f = 0.41) to afford 4'-(bromomethyl)-2-iodo-1,1'-biphenyl as a colorless oil (1.51 g, 81% yield).[20]

4'-(bromomethyl)-2-iodo-1,1'-biphenyl (0.3 g, 0.8 mmol), phenols (0.96 mmol), and anhydrous K_2CO_3 (0.33 g, 2.4 mmol) were added to a 10 mL glass vial equipped with a stir bar. The vial was sealed with a Teflon-lined septum cap, connected to a vacuum manifold *via* a needle in the septum, evacuated and back-filled with nitrogen for three cycles. Anhydrous DMF (4 mL) was then added to the vial with a syringe. The reaction mixture was stirred at 60 °C for 8 hours and cooled to room temperature. The mixture was transferred to a separatory funnel containing water and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate to afford the corresponding ether compounds.



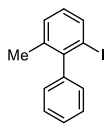
9-(2-Iodo-[1,1'-biphenyl]-4-yl)-9*H*-carbazole (1ac)

Compound **1ac** was synthesized by general procedure A. White solid, 0.44 g, 33% yield. Mp = 59.7-61.3 °C. Eluent: PE:EA = 20:1, R_f = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 21.0, 4.7 Hz, 3H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.54-7.45 (m, 10H), 7.17 (dd, *J* = 19.6, 12.9 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7, 143.5, 140.7, 137.7, 130.8, 129.3, 128.2, 128.0, 126.7, 126.2, 123.6, 120.4, 120.3, 109.8, 98.9 ppm. IR (KBr): 3061, 1602, 1444, 1336, 1230, 998, 786, 753, 674 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{11}IONa$ $[M+Na]^+$ 468.0225, found 468.0227.



5-(*Tert*-butyl)-2-iodo-1,1'-biphenyl (1ad)

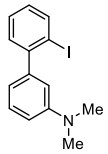
Compound **1ad** was synthesized by general procedure B. Colorless oil, 0.48 g, 57% yield. Eluent: PE, R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.48-7.39 (m, 3H), 7.38-7.35 (m, 2H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.5 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ151.5, 146.1, 144.6, 139.0, 129.4, 128.0, 127.6, 127.5, 126.3, 94.8, 34.7, 31.2 ppm. IR (KBr): 3055, 2961, 2867, 1589, 1467, 1380, 1252, 1117, 1012, 820, 758, 698, 634, 571 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{17}INa$ $[M+Na]^+$ 359.0273, found 359.0273.



2-Iodo-6-methyl-1,1'-biphenyl (1af)

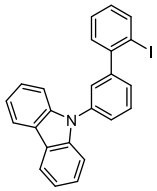
Compound **1af** was synthesized by general procedure B. Colorless oil, 0.46 g, 63% yield. Eluent: PE, R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.51-7.37 (m, 3H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.19-7.10 (m, 2H), 6.97 (t, *J* = 7.7 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3 144.5,

137.7, 136.5, 129.8, 129.0, 128.4, 127.5, 100.9, 22.3 ppm. IR (KBr): 3440, 2990, 1764, 1447, 1377, 1243, 1055 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}INa$ $[M+Na]^+$ 316.9803, found 316.9804.



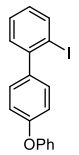
2'-Iodo-*N*, *N*-dimethyl-[1,1'-biphenyl]-3-amine (1aj)

Compound **1aj** was synthesized by general procedure B. Colorless oil, 0.28 g, 37% yield. Eluent: PE, R_f = 0.53. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.42-7.27 (m, 3H), 7.05-7.01 (m, 1H), 6.78 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.70-6.65 (m, 2H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 147.5, 145.0, 139.4, 130.1, 128.7, 128.6, 128.0, 117.5, 113.7, 111.7, 98.8, 40.7 ppm. IR (KBr): 3055, 2887, 1483, 1352, 1228, 1063, 953, 852, 757 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{15}IN$ $[M+H]^+$ 324.0249, found 324.0247.



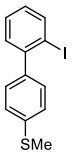
9-(2'-Iodo-[1,1'-biphenyl]-3-yl)-9*H*-carbazole(1ak)

Compound **1ak** was synthesized by general procedure B. Pale yellow solid, 0.58 g, 52% yield. Mp = 61.3-62.6 °C. Eluent: PE:EA = 20:1, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.74-7.55 (m, 5H), 7.51-7.38 (m, 5H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.08 (dd, *J* = 10.4, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 145.7, 140.9, 139.6, 137.4, 130.1, 129.6, 129.3, 128.3, 128.1, 126.3, 126.0, 123.5, 120.4, 120.1, 110.0, 98.5 ppm. IR (KBr): 3053, 1592, 1457, 1321, 1229, 1011, 798, 748, 647 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{11}IONa$ $[M+Na]^+$ 468.0225, found 468.0226.



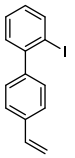
2-Iodo-4'-phenoxy-1,1'-biphenyl (1an)

Compound **1an** was synthesized by general procedure B. Pale yellow solid, 0.54 g, 58% yield. Mp = 53.9-54.6 °C. Eluent: PE, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.44-7.35 (m, 3H), 7.36-7.29 (m, 3H), 7.20-7.09 (m, 3H), 7.09-7.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.8, 146.0, 139.6, 139.0, 130.8, 130.2, 129.9, 128.8, 128.2, 123.6, 119.4, 117.9, 99.0 ppm. IR (KBr): 3064, 2923, 1450, 1416, 1376, 1033, 864, 814, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{13}IONa$ $[M+Na]^+$ 394.9909, found 394.9906.



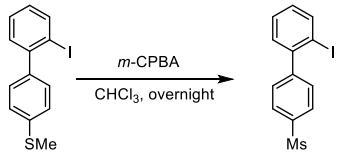
(2'-Iodo-[1,1'-biphenyl]-4-yl)(methyl)sulfane (1ao)

Compound **1ao** was synthesized by general procedure B. Yellow solid, 0.55 g, 67% yield. Mp = 43.7-44.3 °C. Eluent: PE, R_f = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.44-7.39 (m, 1H), 7.37-7.28 (m, 5H), 7.08-7.04 (m, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 140.8, 139.6, 138.1, 130.2, 129.7, 128.8, 128.2, 125.7, 98.7, 15.6 ppm. IR (KBr): 3052, 2918, 1495, 1455, 1313, 1249, 960, 821, 757 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}ISNa$ $[M+Na]^+$ 348.9524, found 348.9526.



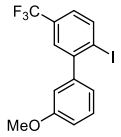
2-Iodo-4'-vinyl-1,1'-biphenyl (1at)

Compound **1at** was synthesized by general procedure B. Colorless oil, 0.28 g, 37% yield. Eluent: PE, R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.94 (m, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.42-7.38 (m, 1H), 7.32 (dd, *J* = 12.2, 4.9 Hz, 3H), 7.06-7.02 (m, 1H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.6, 139.6, 136.9, 136.5, 130.1, 129.5, 128.9, 128.2, 125.9, 114.3, 98.5 ppm. IR (KBr): 3050, 1626, 1511, 1460, 1264, 1112, 999, 839, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{11}INa$ $[M+Na]^+$ 328.9803, found 328.9803.



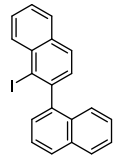
2-Iodo-4'-(methylsulfonyl)-1,1'-biphenyl (1av)

(2'-Iodo-[1,1'-biphenyl]-4-yl)(methyl)sulfane (0.56 g, 2.0 mmol) in chloroform (18 mL) was treated with *m*-chloroperbenzoic acid (1.15 g, 4.0 mmol), stirred at 0 °C for 3 hours and then at the room temperature for overnight. The mixture was partitioned between dilute sodium bicarbonate aqueous solution and chloroform, dried over anhydrous $MgSO_4$, filtered and concentrated to provide crude product as a white solid. Recrystallized in dichloromethane and ether to afford **1av** as a white solid (0.46 g, 64% yield). Mp = 161.1-162.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 9.2 Hz, 3H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.08-6.91 (m, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 144.6, 139.8, 139.7, 130.4, 129.9, 129.8, 128.4, 127.2, 97.5, 44.6 ppm. IR (KBr): 3150, 2906, 1503, 1459, 1301, 1269, 951, 757, 698 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}IO_2SNa$ $[M+Na]^+$ 380.9422, found 380.9424.



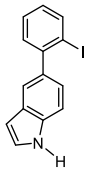
2-Iodo-3'-methoxy-5-(trifluoromethyl)-1,1'-biphenyl (1aw)

Compound **1aw** was synthesized by general procedure B. Yellow solid, 0.64 g, 68% yield. Mp = 46.3-47.7 °C. Eluent: PE, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.29-7.20 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 140.1, 138.2, 130.8 (q, *J* = 32.8 Hz), 129.0, 126.5 (q, *J* = 3.7 Hz), 125.1 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 272.4 Hz), 103.2 (d, *J* = 1.5 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.80 (s, 3F) ppm. IR (KBr): 3434, 2928, 1596, 1332, 1268, 1170, 755, 709 cm^{-1}. MS (EI) m/z calculated for $C_{14}H_{10}F_3IO$ $[M]^+$ 378.0, found 378.0.



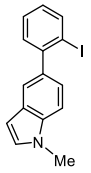
1'-Iodo-1,2'-binaphthalene (1bg)

Compound **1bg** was synthesized by general procedure B. Yellow solid, 0.57 g, 60% yield. Mp = 133.2-134.0 °C. Eluent: PE, R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.02-7.82 (m, 4H), 7.68-7.58 (m, 3H), 7.55-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.9, 135.0, 133.6, 133.2, 131.5, 128.4, 128.3, 128.2, 128.1, 127.1, 126.8, 126.2, 126.1, 126.0, 125.3, 105.9 ppm. IR (KBr): 3453, 3051, 1634, 1546, 1497, 1250, 1129, 741, 672 cm^{-1}. MS (EI) m/z calculated for $C_{20}H_{13}I$ $[M]^+$ 380.0, found 380.0.



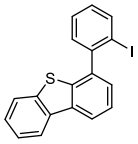
5-(2-Iodophenyl)-1*H*-indole (1bi)

Compound **1bi** was synthesized by general procedure B. Yellow solid, 0.39 g, 49% yield. Mp = 192.0-192.5 °C. Eluent: PE:EA = 20:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.48-7.34 (m, 3H), 7.24 (s, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.08-6.91 (m, 1H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 139.4, 136.4, 135.2, 130.7, 128.3, 128.1, 127.5, 124.9, 123.8, 121.4, 110.4, 103.1, 99.9 ppm. IR (KBr): 3425, 2924, 1453, 1416, 1265, 1010, 888, 808, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{10}NINa$ $[M+Na]^+$ 341.9756, found 341.9756.



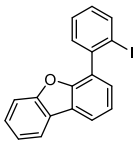
5-(2-Iodophenyl)-1-methyl-1*H*-indole (1bj)

Compound **1bj** was synthesized by general procedure B. Yellow solid, 0.38 g, 46% yield. Mp = 94.5-95.4 °C. Eluent: PE:EA = 200:1, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 1.1 Hz, 1H), 7.42-7.36 (m, 3H), 7.23 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.12 (d, *J* = 3.1 Hz, 1H), 7.06-6.99 (m, 1H), 6.55 (d, *J* = 3.1 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 139.3, 136.1, 135.8, 130.7, 129.5, 128.3, 128.0, 123.3, 121.6, 108.5, 101.4, 100.0, 33.0 ppm. IR (KBr): 3441, 3001, 1628, 1455, 1330, 1268, 801, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{12}NINa$ $[M+Na]^+$ 355.9912, found 355.9916.



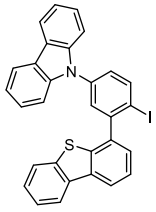
4-(2-Iodophenyl)dibenzo[b,d]thiophene (1bk)

Compound **1bk** was synthesized by general procedure B. White solid, 0.40 g, 42% yield. Mp = 88.3-89.1 °C. Eluent: PE:EA = 100:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 6.9, 2.9 Hz, 2H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.81 (dd, *J* = 6.5, 2.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.53-7.43 (m, 4H), 7.36 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.19-7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.8, 139.7, 139.3, 135.9, 135.8, 130.0, 129.8, 128.4, 127.5, 126.9, 124.6, 124.5, 122.8, 121.9, 121.0, 99.0 ppm. IR (KBr): 3453, 1639, 1448, 1409, 1267, 1188, 747, 652, 612 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{11}ISNa$ $[M+Na]^+$ 408.9524, found 408.9526.



4-(2-Iodophenyl)dibenzo[b,d]furan (1bl)

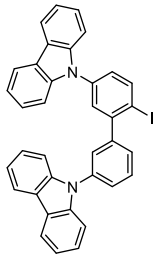
Compound **1bl** was synthesized by general procedure B. White solid, 0.45 g, 49% yield. Mp = 120.2-121.0 °C. Eluent: PE:EA = 100:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-7.97 (m, 3H), 7.57-7.36 (m, 7H), 7.18-7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 153.1, 141.8, 139.5, 130.9, 129.6, 128.6, 128.4, 128.2, 127.3, 124.5, 124.3, 122.8, 122.6, 120.8, 120.5, 112.0, 99.7 ppm. IR (KBr): 3467, 1630, 1453, 1402, 1269, 1180, 757, 663, 626 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{11}IONa$ $[M+Na]^+$ 392.9752, found 392.9750.



9-(3-(Dibenzo[b,d]thiophen-4-yl)-4-iodophenyl)-9*H*-carbazole (1bm)

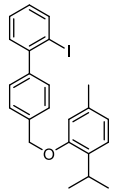
Compound **1bm** was synthesized by general procedure A. Pale yellow solid, 0.96 g, 58% yield. Mp = 123.2-124.9 °C. Eluent: PE:EA = 20:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.09 (m, 5H), 7.87 (dd, *J* = 6.0, 2.7 Hz, 1H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.64-7.54 (m, 3H), 7.54-7.40 (m, 6H), 7.32 (dd, *J* = 13.1,

6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 141.1, 140.4, 139.7, 139.4, 138.3, 136.0, 135.8, 128.3, 128.1, 127.5, 127.0, 126.2, 124.7, 124.6, 123.7, 122.9, 122.0, 121.4, 120.4, 120.3, 109.8, 96.6 ppm. IR (KBr): 3434, 1637, 1455, 1406, 1320, 1186, 743, 657, 618 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{19}INS$ $[M+H]^+$ 552.0283, found 552.0288.



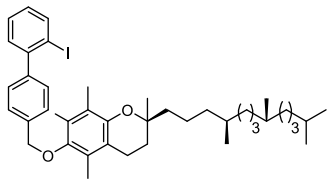
9,9'-(6-Iodo-[1,1'-biphenyl]-3,3'-diyl)bis(9*H*-carbazole) (1bn)

Compound **1bn** was synthesized by general procedure A. Pale white solid, 0.93 g, 51% yield. Mp = 145.2-146.2 °C. Eluent: PE:EA = 20:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 18.6, 8.8 Hz, 5H), 7.74-7.64 (m, 4H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.54-7.40 (m, 7H), 7.33 (dd, *J* = 10.5, 4.2 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 145.3, 141.0, 140.9, 140.5, 138.2, 137.7, 129.9, 128.4, 128.1, 127.9, 127.7, 126.8, 126.2, 126.1, 123.7, 123.5, 120.5, 120.4, 120.3, 120.1, 110.0, 109.7, 96.2 ppm. IR (KBr): 3431, 2853, 1590, 1455, 1321, 924, 798, 741, 643 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{18}INS$ $[M+H]^+$ 611.0984, found 611.0982.



2-Iodo-4'-((2-isopropyl-5-methylphenoxy)methyl)-1,1'-biphenyl (1bo)

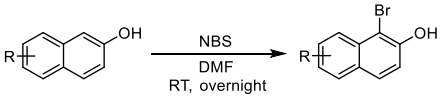
Compound **1bo** was synthesized by general procedure C. Colorless oil, 0.24 g, 67% yield. Eluent: PE:EA = 20:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.53 (dd, *J* = 4.9, 3.4 Hz, 2H), 7.44-7.33 (m, 4H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.08-7.04 (m, 1H), 6.82 (d, *J* = 7.0 Hz, 2H), 5.16 (s, 2H), 3.48-3.41 (m, 1H), 2.36 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 146.4, 143.5, 139.6, 137.1, 136.4, 134.5, 130.2, 129.5, 128.9, 128.2, 126.6, 126.0, 121.6, 112.9, 98.6, 69.8, 26.6, 22.9, 21.4 ppm. IR (KBr): 3452, 2924, 1454, 1162, 1129, 928, 814, 750, 719 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{23}IONa$ $[M+Na]^+$ 465.0691, found 465.0691.



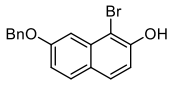
6-((2'-Iodo-[1,1'-biphenyl]-4-yl)methoxy)-2,5,7,8-tetramethyl-2-((4S,6R)-4,6,8- trimethylnonyl) chromane (1bp)

Compound **1bp** was synthesized by general procedure C. Pale yellow oil, 0.33 g, 62% yield. Eluent: PE:EA = 20:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.62-7.33 (m, 6H), 7.14-6.99 (m, 1H), 4.79 (s, 2H), 2.64 (t, *J* = 6.6 Hz, 2H), 2.23 (dd, *J* = 31.8, 21.5 Hz, 9H), 1.89-1.79 (m, 2H), 1.64-1.51 (m, 3H), 1.30 (d, *J* = 12.2 Hz, 15H), 1.15 (dd, *J* = 16.8, 9.1 Hz, 6H), 0.89 (t, *J* = 7.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 148.0, 146.4, 143.7, 139.6, 137.5, 130.2, 129.6, 129.4, 128.8, 128.2, 128.0, 127.4, 126.0, 123.0, 117.6, 98.5, 74.7, 74.5, 40.1, 39.4, 37.6, 37.5, 37.4, 32.8, 31.4, 31.3, 29.7, 28.0, 24.8, 24.5, 23.9, 22.7, 22.6, 21.1, 20.7, 19.8, 19.7, 12.9, 12.1, 11.9 ppm. IR (KBr): 3441, 2925, 1374, 1016, 917, 808, 752, 691 cm^{-1}. HRMS (ESI) m/z calculated for $C_{38}H_{52}IO_2$ $[M+H]^+$ 667.3012, found 667.3021.

General procedure for the preparation of bromonaphthols:

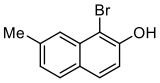


To solution of the corresponding naphthalene-2-ol (5 mmol) in DMF (30 mL) at 0 °C was added *N*-bromosuccinimid (5.5 mmol, 1.1 equiv.) over 0.5 h. It was stirred at room temperature for overnight. The mixture was extracted with ethyl acetate and washed with brine. The combined organic layer was dried over anhydrous $MgSO_4$. The concentrated residue was purified by column chromatography on silica gel to afford the desired product.



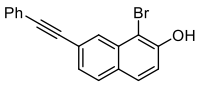
7-(Benzyloxy)-1-bromonaphthalen-2-ol (2cd)

2cd (Yellow solid, 1.28 g, 78% yield). Mp = 103.3-104.8 °C. Eluent: PE:EA = 20:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 12.9, 8.8 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.45-7.33 (m, 4H), 7.12 (dd, *J* = 8.8, 2.3 Hz, 2H), 5.87 (s, 1H), 5.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 151.1, 136.6, 133.7, 129.9, 129.0, 128.6, 128.1, 127.7, 125.0, 116.8, 114.6, 105.9, 105.3, 70.2 ppm. IR (KBr): 3489, 2920, 1623, 1510, 1441, 1379, 1187, 829, 752 cm^{-1}. MS (EI) m/z calculated for $C_{17}H_{13}BrO_2$ $[M]^+$ 328.0, found 328.0.



1-Bromo-7-methylnaphthalen-2-ol (2ce)

2ce (White solid, 0.83 g, 70% yield). Mp = 87.7-88.3 °C. Eluent: PE:EA = 20:1, R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.68 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.22 (dd, *J* = 20.0, 9.1 Hz, 2H), 5.89 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 137.9, 132.4, 129.0, 128.1, 127.9, 126.3, 124.4, 116.1, 105.6, 22.0 ppm. IR (KBr): 3501, 2921, 1626, 1510, 1267, 1182 cm^{-1}. MS (EI) m/z calculated for $C_{11}H_9BrO$ $[M]^+$ 236.0, found 236.0.

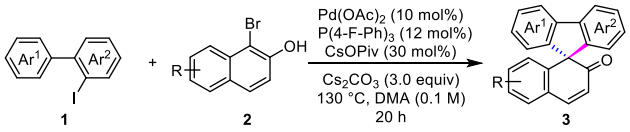


1-Bromo-7-(phenylethynyl)naphthalen-2-ol (2cf)

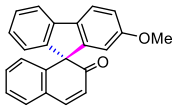
2cf (Gray solid, 1.16 g, 72% yield). Mp = 78.2-79.5 °C. Eluent: PE:EA = 20:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.75 (dd, *J* = 12.7, 8.6 Hz, 2H), 7.65-7.63 (m, 2H), 7.53 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.45-7.38 (m, 3H), 7.29 (d, *J* = 8.7 Hz, 1H), 5.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 131.9, 131.6, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2, 126.7, 123.0, 122.6, 117.7, 105.7, 90.6, 89.7 ppm. IR (KBr): 3490, 3060, 2925, 1617, 1505, 1374, 1180, 836, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{12}BrO$ $[M+H]^+$ 323.0072, found 323.0070.

D. Catalytic results:

General procedure for palladium-catalyzed [4+1] spiroannulation

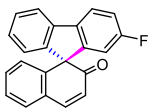


In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(*p*-F-C_6H_4)$_3$ (7.6 mg, 0.024 mmol), CsOPiv (14.0 mg, 0.06 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), **1** (0.24 mmol), **2** (0.20 mmol) followed by sequential addition of DMA (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography to afford the desired product **3**.



2-Methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3aa)

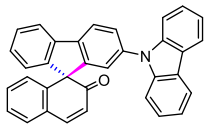
3aa (Yellow solid, 49.3 mg, 76% yield). Mp = 201.5-202.3 °C. Eluent: PE:EA = 10:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.65 (m, 3H), 7.45-7.40 (m, 1H), 7.37-7.31 (m, 1H), 7.28-7.23 (m, 1H), 7.16-7.04 (m, 3H), 6.94 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 159.9, 149.1, 147.0, 146.2, 142.7, 141.7, 134.8, 130.4, 129.8, 129.6, 128.3, 128.0, 127.7, 126.8, 125.9, 123.9, 121.4, 119.9, 114.2, 110.0, 68.4, 55.5 ppm. IR (KBr): 3010, 2926, 2844, 1664, 1611, 1455, 1270, 1036, 817, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}O_2Na$ $[M+Na]^+$ 347.1048, found 347.1050.



2-Fluoro-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ab)

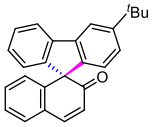
3ab (Yellow solid, 31.2 mg, 50% yield). Mp = 54.1-55.7 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.68 (m, 3H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.42-7.36 (m, 1H), 7.32-7.28 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.15-7.06 (m, 3H), 6.83 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H),

6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 162.7 (d, *J* = 246.8 Hz), 149.3, 149.2 (d, *J* = 8.2 Hz, 1H), 147.3 (d, *J* = 1.8 Hz), 146.3, 141.9, 140.9, 138.0 (d, *J* = 2.5 Hz), 130.5, 129.8, 129.7, 128.5, 127.9, 127.8, 127.7, 125.8, 124.1, 121.7 (d, *J* = 8.8 Hz), 120.4, 115.6 (d, *J* = 23.0 Hz), 111.8 (d, *J* = 23.7 Hz), 68.4 (d, *J* = 2.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.85 (s, 1F) ppm. IR (KBr): 3060, 2923, 1666, 1537, 1482, 1263, 1199, 903, 819, 752 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{13}FONa$ $[M+Na]^+$ 335.0848, found 335.0845.



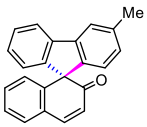
2-(9*H*-Carbazol-9-yl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ac)

3ac (Pale yellow solid, 66.2 mg, 72% yield). Mp = 224.3-225.6 °C. Eluent: PE:EA = 5:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 10.0 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46-7.29 (m, 9H), 7.25-7.14 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.41 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 149.1, 147.7, 146.4, 142.0, 141.1, 141.0, 140.7, 137.1, 130.5, 129.9, 129.8, 128.6, 128.4, 128.0, 127.8, 127.0, 126.0, 125.7, 124.3, 123.4, 122.9, 121.8, 120.9, 120.3, 120.0, 109.8, 68.6 ppm. IR (KBr): 3449, 2931, 1726, 1655, 1609, 1033, 916, 823, 747, 649 cm^{-1}. HRMS (ESI) m/z calculated for $C_{34}H_{21}NO$ $[M]^+$ 460.1701, found 460.1699.



3-(*Tert*-butyl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ad)

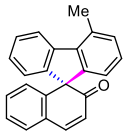
3ad (Yellow solid, 57.5 mg, 82% yield). Mp = 79.3-80.6 °C. Eluent: PE:EA = 10:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.81 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 9.9 Hz, 1H), 7.45-7.34 (m, 2H), 7.28-7.15 (m, 3H), 7.12-7.00 (m, 3H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 9.9 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 151.4, 147.9, 146.1, 144.6, 142.9, 142.4, 141.5, 130.3, 129.9, 129.5, 128.3, 127.9, 127.8, 127.6, 125.9, 125.5, 124.2, 123.4, 120.5, 117.6, 68.2, 34.9, 31.6 ppm. IR (KBr): 3057, 2961, 2869, 1667, 1612, 1480, 1118, 823, 749, 641 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{22}ONa$ $[M+Na]^+$ 373.1568, found 373.1564.



3-Methyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ae)

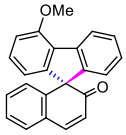
3ae (Pale yellow solid, 49.3 mg, 80% yield). Mp = 200.1-201.2 °C. Eluent: PE:EA = 10:1, R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 9.9 Hz, 1H), 7.66 (s, 1H), 7.45-7.41 (m, 2H), 7.33-7.26 (m, 1H), 7.25-7.21 (m, 1H), 7.17-7.01 (m, 4H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 147.8, 146.0, 144.8, 142.9, 142.1, 141.9, 138.2,

130.3, 129.9, 129.5, 129.0, 128.3, 127.9, 127.6, 126.0, 124.1, 123.8, 121.3, 120.6, 68.2, 21.6 ppm. IR (KBr): 3446, 1662, 1618, 1446, 1390, 1236, 871, 813, 747, 636 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{26}ONa$ $[M+Na]^+$ 331.1109, found 331.1110.



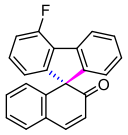
4-Methyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3af)

3af (Yellow oil, 45.0 mg, 73% yield). Eluent: PE:EA = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 9.9 Hz, 1H), 7.45-7.37 (m, 2H), 7.28-7.05 (m, 6H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 147.9, 146.2, 143.1, 143.0, 139.9, 133.8, 130.7, 130.4, 129.8, 129.5, 128.3, 128.0, 127.7, 127.6, 127.4, 125.9, 124.1, 123.8, 121.6, 68.2, 21.1 ppm. IR (KBr): 3056, 2964, 2860, 1665, 1483, 1268, 1235, 1199, 751 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}ONa$ $[M+Na]^+$ 331.1099, found 331.1097.



4-Methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ag)

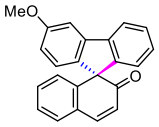
3ag (Yellow solid, 49.3 mg, 76% yield). Mp = 162.6-163.3 °C. Eluent: PE:EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 9.9 Hz, 1H), 7.35-7.24 (m, 2H), 7.15 (dd, *J* = 9.3, 5.7 Hz, 1H), 7.08 (dd, *J* = 16.4, 8.1 Hz, 2H), 7.02-6.94 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 156.0, 149.2, 146.9, 146.1, 142.8, 141.2, 130.3, 130.0, 129.8, 129.5, 129.1, 128.2, 128.0, 127.6, 127.0, 126.0, 124.6, 123.4, 116.4, 110.5, 68.6, 55.4 ppm. IR (KBr): 3057, 2942, 2837, 1664, 1592, 1485, 1266, 1066, 802, 752 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}O_2Na$ $[M+Na]^+$ 347.1048, found 347.1048.



4-Fluoro-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ah)

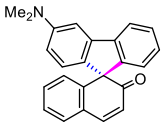
3ah (Yellow solid, 31.2 mg, 50% yield). Mp = 153.2-154.0 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 9.9 Hz, 1H), 7.49-7.37 (m, 2H), 7.32-7.05 (m, 6H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 158.2 (d, *J* = 251.6 Hz), 149.9 (d, *J* = 5.5 Hz), 146.9, 146.3, 142.0, 138.9 (d, *J* = 3.1 Hz), 130.5, 129.7, 129.6, 129.3 (d, *J* = 7.2 Hz), 129.2 (d, *J* = 15.3 Hz), 128.7, 128.2, 127.9, 127.8, 125.7, 124.2 (d, *J* = 5.7 Hz), 123.2, 120.0 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 19.8 Hz), 68.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -

118.73 (s, 1F) ppm. IR (KBr): 3061, 2925, 1667, 1601, 1447, 1234, 1199, 875, 755, 689 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{13}FONa$ $[M+Na]^+$ 335.0848, found 335.0844.



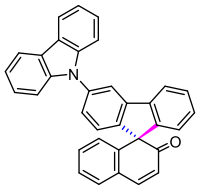
3-Methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ai)

3ai (Yellow solid, 55.8 mg, 86% yield). Mp = 170.2-171.8 °C. Eluent: PE:EA = 10:1, R_f = 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 9.9 Hz, 1H), 7.44-7.34 (m, 2H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.28-7.24 (m, 1H), 7.21-7.17 (m, 1H), 7.12-7.05 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 9.9 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 160.2, 148.3, 146.1, 143.4, 142.9, 141.7, 139.6, 130.3, 129.9, 129.6, 128.3, 128.1, 127.8, 127.6, 125.9, 124.9, 124.1, 120.7, 114.3, 105.8, 67.8, 55.6 ppm. IR (KBr): 3057, 2948, 2837, 1666, 1611, 1485, 1213, 1030, 816, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}O_2Na$ $[M+Na]^+$ 347.1048, found 347.1048.



(Dimethylamino)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3aj)

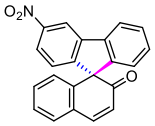
3aj (Yellow solid, 41.8 mg, 62% yield). Mp = 240.1-241.1 °C. Eluent: PE : EA = 10:1, R_f = 0.37. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 9.9 Hz, 1H), 7.33-7.26 (m, 2H), 7.17-7.15 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 7.01-6.97 (m, 2H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, 1H), 2.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 151.1, 148.3, 145.8, 143.6, 142.8, 142.5, 135.5, 130.2, 129.9, 129.4, 128.1, 127.9, 127.7, 127.3, 126.0, 124.4, 124.1, 120.4, 112.8, 104.3, 67.8, 40.9 ppm. IR (KBr): 3067, 2924, 2802, 1653, 1498, 1442, 1277, 951, 808, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{19}NONa$ $[M+Na]^+$ 360.1364, found 360.1363.



3-(9*H*-Carbazol-9-yl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ak)

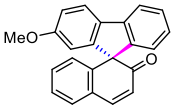
3ak (Pale yellow solid, 46.9 mg, 51% yield). Mp = 131.6-132.8 °C. Eluent: PE:EA = 5:1, R_f = 0.31. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.7 Hz, 2H), 8.00 (s, 1H), 7.79 (t, *J* = 7.9 Hz, 2H), 7.58-7.40 (m, 7H), 7.40-7.28 (m, 5H), 7.22 (dd, *J* = 7.0, 4.9 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 148.0, 146.4, 146.3, 143.8, 142.2, 141.2, 140.9, 138.0, 130.6, 130.0, 129.8, 128.8, 128.6, 128.0, 126.7, 126.0, 125.9, 125.4, 124.5, 123.5, 121.0, 120.4, 120.1, 119.3, 110.0, 68.4

ppm. IR (KBr): 3437, 2923, 1723, 1665, 1608, 1028, 917, 820, 748, 655 cm^{-1}. HRMS (ESI) m/z calculated for $C_{34}H_{21}NO$ $[M+H]^+$ 460.1701, found 460.1699.



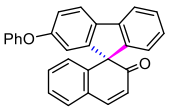
3-Nitro-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3al)

3al (Yellow solid, 19.7 mg, 29% yield). Mp = 254.4-255.1 °C. Eluent: PE:EA = 5:1, R_f = 0.27. ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 9.9 Hz, 1H), 7.47-7.36 (m, 2H), 7.28-7.22 (m, 2H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.11-7.02 (m, 2H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 153.9, 148.6, 147.9, 146.7, 143.9, 140.8, 139.5, 130.7, 130.1, 129.8, 129.6, 129.0, 128.4, 127.8, 125.6, 125.0, 124.3, 123.3, 121.5, 115.7, 68.4 ppm. IR (KBr): 3421, 2920, 2361, 1620, 1522, 1345, 1283, 876, 816, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{13}NO_3Na$ $[M+Na]^+$ 362.0793, found 362.0793.



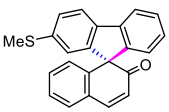
2-Methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3am)

3am (Yellow solid, 52.5 mg, 81% yield). Mp = 201.5-202.3 °C. Eluent: PE:EA = 10:1, R_f = 0.34. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75-7.65 (m, 3H), 7.45-7.40 (m, 1H), 7.37-7.31 (m, 1H), 7.28-7.23 (m, 1H), 7.16-7.04 (m, 3H), 6.94 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 159.9, 149.1, 147.0, 146.2, 142.7, 141.7, 134.8, 130.4, 129.8, 129.6, 128.3, 128.0, 127.7, 126.8, 125.9, 123.9, 121.4, 119.9, 114.2, 110.0, 68.4, 55.5 ppm. IR (KBr): 3010, 2926, 2844, 1664, 1611, 1455, 1270, 1036, 817, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}O_2Na$ $[M+Na]^+$ 347.1048, found 347.1050.



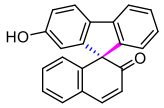
2-Phenoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3an)

3an (Pale yellow solid, 61.1 mg, 79% yield). Mp = 167.9-169.0 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 9.9 Hz, 1H), 7.45-7.35 (m, 2H), 7.29 (dd, *J* = 15.8, 8.2 Hz, 3H), 7.22-7.00 (m, 5H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 157.2, 157.1, 149.3, 147.3, 146.3, 142.3, 141.3, 137.3, 130.5, 129.8, 129.7, 128.4, 127.9, 127.8, 127.5, 125.8, 124.1, 123.3, 121.6, 120.3, 118.9, 118.6, 115.4, 68.4 ppm. IR (KBr): 3447, 1662, 1482, 1453, 1257, 1218, 822, 750, 698 cm^{-1}. HRMS (ESI) m/z calculated for $C_{28}H_{18}O_2Na$ $[M+Na]^+$ 409.1204, found 409.1202.



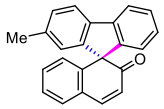
2-(Methylthio)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ao)

3ao (Pale yellow solid, 33.4 mg, 49% yield). Mp = 152.9-154.3 °C. Eluent: PE:EA = 10:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 13.4, 8.5 Hz, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22-7.13 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 2H), 6.90 (s, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 148.3, 147.3, 146.3, 142.4, 141.4, 139.3, 138.5, 130.5, 129.8, 129.7, 128.4, 128.0, 127.8, 126.8, 125.8, 124.1, 122.5, 121.0, 120.5, 68.3, 16.2 ppm. IR (KBr): 3450, 1663, 1400, 1305, 1139, 961, 833, 788, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}OS$ $[M+H]^+$ 341.1000, found 341.1003.



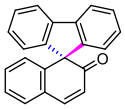
2-Hydroxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ap)

3ap (Pale yellow solid, 37.9 mg, 61% yield). Mp = 208.4-210.0 °C. Eluent: PE:EA = 10:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 16.1, 8.8 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.36-7.32 (m, 1H), 7.29-7.22 (m, 1H), 7.15-7.00 (m, 3H), 6.78 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.52 (t, *J* = 4.5 Hz, 2H), 6.32 (d, *J* = 9.9 Hz, 1H), 4.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 156.2, 149.0, 146.8, 146.6, 142.7, 141.8, 134.6, 130.5, 129.7, 129.6, 128.4, 128.0, 127.7, 126.8, 125.7, 123.9, 121.6, 119.8, 115.9, 111.6, 68.3 ppm. IR (KBr): 3445, 2925, 1646, 1458, 1379, 1094, 1028, 806, 725 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{15}O_2$ $[M+H]^+$ 311.1072, found 311.1073.



2-Methyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3aq)

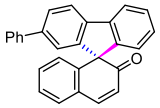
3aq (Yellow solid, 48.7 mg, 79% yield). Mp = 140.7-141.6 °C. Eluent: PE:EA = 10:1, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.62 (m, 3H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30-7.22 (m, 1H), 7.21-7.12 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.91 (s, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 147.8, 147.5, 146.2, 142.9, 142.0, 139.3, 138.2, 130.4, 129.9, 129.6, 129.3, 128.3, 128.0, 127.6, 126.0, 124.8, 124.1, 120.4, 68.3, 21.7 ppm. IR (KBr): 3056, 2921, 2861, 1665, 1612, 1455, 1236, 1202, 820, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}ONa$ $[M+Na]^+$ 331.1099, found 331.1095.



2'*H*-Spiro[fluorene-9,1'-naphthalen]-2'-one (3ar)

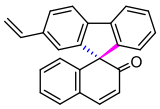
3ar (Yellow solid, 47.7 mg, 81% yield). Mp = 148.7-149.5 °C. Eluent: PE:EA = 10:1, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 9.9 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.31-7.24 (m, 1H), 7.24-7.20 (m, 2H), 7.14-7.05 (m, 3H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.4, 147.5, 146.2, 142.6, 141.9, 130.4, 129.9, 129.6,

128.4, 128.1, 127.9, 127.7, 125.9, 124.1, 120.7, 68.5 ppm. IR (KBr): 3057, 1664, 1444, 1269, 1200, 1115, 819, 796, 754, 714 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{14}ONa$ $[M+Na]^+$ 317.0942, found 317.0941.



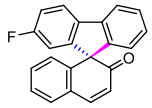
2-Phenyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3as)

3as (Yellow solid, 51.9 mg, 70% yield). Mp = 208.4-209.2 °C. Eluent: PE:EA = 10:1, R_f = 0.35. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 10.0 Hz, 1H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.53-7.47 (m, 2H), 7.47-7.34 (m, 4H), 7.33-7.18 (m, 4H), 7.15-7.06 (m, 2H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.38 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 148.2, 147.8, 146.3, 142.5, 141.6, 141.2, 141.1, 141.0, 130.5, 129.9, 129.7, 128.7, 128.4, 128.1, 128.0, 127.7, 127.5, 127.3, 127.2, 125.9, 124.2, 122.9, 121.0, 120.8, 68.5 ppm. IR (KBr): 3058, 2924, 2856, 1665, 1610, 1456, 1267, 831, 751, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{28}H_{18}ONa$ $[M+Na]^+$ 393.1255, found 393.1255.



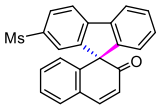
2-Vinyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3at)

3at (Yellow oil, 32.7 mg, 51% yield). Eluent: PE:EA = 10:1, R_f = 0.39. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.69 (m, 3H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11 (dd, *J* = 14.0, 6.1 Hz, 3H), 6.65 (dd, *J* = 17.5, 10.9 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 6.37 (d, *J* = 9.9 Hz, 1H), 5.66 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 148.0, 147.8, 146.1, 142.5, 141.7, 141.5, 137.6, 136.7, 130.4, 129.9, 129.6, 128.4, 128.0, 127.7, 126.7, 125.9, 124.1, 121.9, 120.7, 113.9, 68.3 ppm. IR (KBr): 3450, 3069, 2924, 1661, 1456, 1267, 1200, 828, 751, 578 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{16}ONa$ $[M+Na]^+$ 343.1099, found 343.1096.



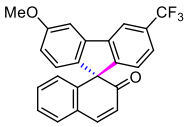
2-Fluoro-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3au)

3au (Yellow solid, 31.9 mg, 51% yield). Mp = 54.1-55.7 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.68 (m, 3H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.42-7.36 (m, 1H), 7.32-7.28 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.15-7.06 (m, 3H), 6.83 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 162.7 (d, *J* = 246.8 Hz), 149.3, 149.2 (d, *J* = 8.2 Hz, 1H), 147.3 (d, *J* = 1.8 Hz), 146.3, 141.9, 140.9, 138.0 (d, *J* = 2.5 Hz), 130.5, 129.8, 129.7, 128.5, 127.9, 127.8, 127.7, 125.8, 124.1, 121.7 (d, *J* = 8.8 Hz), 120.4, 115.6 (d, *J* = 23.0 Hz), 111.8 (d, *J* = 23.7 Hz), 68.4 (d, *J* = 2.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.85 (s, 1F) ppm. IR (KBr): 3060, 2923, 1666, 1537, 1482, 1263, 1199, 903, 819, 752 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{13}FONa$ $[M+Na]^+$ 335.0848, found 335.0845.



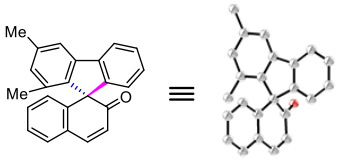
2-(Methylsulfonyl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3av)

3av (Yellow solid, 38.0 mg, 51% yield). Mp = 275.1-275.6 °C. Eluent: PE:EA = 3:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.91 (m, 2H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 9.9 Hz, 1H), 7.67 (s, 1H), 7.46 (dd, *J* = 14.3, 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.13 (dd, *J* = 14.3, 7.0 Hz, 2H), 6.43 (d, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 148.8, 148.7, 147.7, 146.9, 140.8, 139.6, 130.8, 130.1, 130.0, 129.8, 128.8, 128.3, 128.1, 127.8, 125.5, 124.3, 123.4, 121.9, 121.2, 68.3, 44.8 ppm. IR (KBr): 3431, 3017, 1634, 1597, 1456, 1009, 962, 875, 788, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}O_3SNa$ $[M+Na]^+$ 395.0718, found 395.0720.



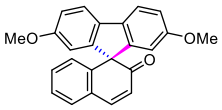
3-Methoxy-6-(trifluoromethyl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3aw)

3aw (Yellow solid, 41.6 mg, 53% yield). Mp = 158.2-160.0 °C. Eluent: PE:EA = 10:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.50-7.43 (m, 2H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.32-7.28 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.15-7.09 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 160.4, 151.7, 146.4, 142.7, 141.8, 141.7, 139.8, 130.7 (q, *J* = 32.2 Hz), 130.5, 129.8, 128.0, 127.7, 125.7, 125.0 (q, *J* = 4.0 Hz), 124.9, 124.6, 124.2 (q, *J* = 272.5 Hz), 117.5 (q, *J* = 3.8 Hz), 115.6, 105.9, 67.7, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22 (s, 3F) ppm. IR (KBr): 3001, 1666, 1613, 1331, 1271, 1166, 1123, 819, 753, 688 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{15}F_3O_2Na$ $[M+Na]^+$ 415.0922, found 415.0921.



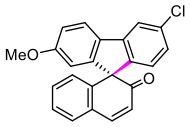
1,3-Dimethyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ax)

3ax (Light yellow solid, 36.1 mg, 56% yield). Mp = 147.1-148.7 °C. Eluent: PE:EA = 10:1, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 2H), 7.48 (s, 1H), 7.46-7.40 (m, 1H), 7.32-7.22 (m, 2H), 7.11-7.03 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 9.9 Hz, 1H), 2.44 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 148.1, 146.2, 144.1, 143.3, 142.3, 141.2, 138.6, 134.0, 131.0, 130.5, 129.6, 128.1, 127.5, 127.4, 127.0, 126.5, 122.8, 121.1, 118.4, 67.3, 21.6, 18.7 ppm. IR (KBr): 2964, 2922, 2858, 1662, 1388, 1267, 1093, 1025, 753,731 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}ONa$ $[M+Na]^+$ 345.1255, found 345.1253.



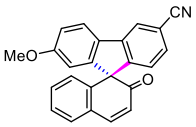
2,7-Dimethoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ay)

3ay (Yellow solid, 58.8 mg, 83% yield). Mp = 109.6-119.6 °C. Eluent: PE:EA = 5:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.9 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.29-7.22 (m, 1H), 7.12-7.08 (m, 1H), 6.90 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.62 (d, *J* = 2.3 Hz, 2H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 9.9 Hz, 1H), 3.71 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 159.1, 148.6, 146.2, 142.8, 134.7, 130.5, 129.7, 129.6, 128.1, 127.7, 125.8, 120.6, 114.0, 110.1, 68.3, 55.5 ppm. IR (KBr): 3055, 2837, 1666, 1609, 1469, 1274, 1230, 1040, 878, 739 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}O_3Na$ $[M+Na]^+$ 377.1154, found 377.1154.



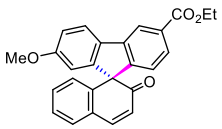
6-Chloro-2-methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3az)

3az (Yellow solid, 45.9 mg, 64% yield). Mp = 154.1-155.3 °C. Eluent: PE:EA = 10:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.53 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.21-7.17 (m, 1H), 7.07-6.98 (m, 2H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 160.5, 149.6, 146.3, 145.3, 143.8, 142.1, 134.5, 133.4, 130.5, 129.8, 129.7, 127.9, 127.8, 126.7, 125.7, 125.0, 121.8, 120.1, 114.4, 110.0, 67.9, 55.5 ppm. IR (KBr): 3441, 2838, 1666, 1606, 1460, 1339, 1038, 865, 819, 747 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{15}ClO_2Na$ $[M+Na]^+$ 381.0658, found 381.0660.



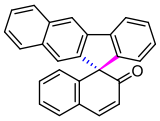
2-Methoxy-2'-oxo-2'*H*-spiro[fluorene-9,1'-naphthalene]-6-carbonitrile (3ba)

3ba (Pale yellow solid, 30.0 mg, 43% yield). Mp = 95.8-96.2 °C. Eluent: PE:EA = 5:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.72 (dd, *J* = 14.1, 9.2 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.36-7.30 (m, 1H), 7.15 (dd, *J* = 9.4, 7.9 Hz, 2H), 6.97 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.65 (d, *J* = 2.2 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 161.0, 151.6, 149.3, 146.6, 143.1, 141.1, 132.4, 130.7, 130.5, 130.0, 129.7, 128.3, 127.9, 125.6, 124.8, 123.2, 122.1, 119.0, 114.7, 112.3, 110.0, 68.5, 55.6 ppm. IR (KBr): 3429, 2927, 1665, 1609, 1486, 1344, 1270, 877, 826, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{15}NO_2Na$ $[M+Na]^+$ 372.1000, found 372.1001.



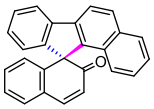
Ethyl-2-methoxy-2'-oxo-2'*H*-spiro[fluorene-9,1'-naphthalene]-6-carboxylate (3bb)

3bb (Pale yellow solid, 40.4 mg, 51% yield). Mp = 55.3-56.1 °C. Eluent: PE:EA = 5:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.1 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71-7.61 (m, 2H), 7.40-7.34 (m, 1H), 7.25-7.15 (m, 1H), 7.05-7.00 (m, 2H), 6.90-6.86 (m, 1H), 6.57 (d, *J* = 2.3 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.28 (d, *J* = 9.9 Hz, 1H), 4.37-4.27 (m, 2H), 3.66 (s, 3H), 1.32 (t, *J* = 4.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 166.5, 160.4, 151.7, 149.3, 146.3, 142.3, 141.9, 133.7, 130.8, 130.5, 129.7, 128.4, 127.9, 125.7, 123.8, 121.9, 120.9, 114.4, 110.0, 68.4, 61.1, 55.5, 29.7, 14.4 ppm. IR (KBr): 3417, 2931, 1665, 1615, 1502, 1458, 1281, 956, 817, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{20}O_4Na$ $[M+Na]^+$ 419.1259, found 419.1259.



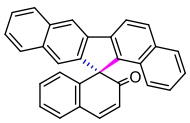
2'*H*-Spiro[benzo[b]fluorene-11,1'-naphthalen]-2'-one (3bc or 3bd)

3bc or 3bd (Yellow solid, 44.8 mg, 65% yield for **3bc**; 43.4mg, 63% yield for **3bd**). Mp = 173.1-174.1 °C. Eluent: PE:EA = 10:1, R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.93 (dd, *J* = 15.9, 7.9 Hz, 2H), 7.76 (d, *J* = 9.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.54 (s, 1H), 7.50-7.35 (m, 4H), 7.31-7.22 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.09-7.07 (m, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 147.9, 146.3, 145.6, 143.6, 141.4, 139.9, 133.8, 133.6, 130.4, 129.7, 129.6, 128.8, 128.6, 128.4, 128.3, 128.2, 127.7, 126.2, 125.9, 125.6, 124.5, 123.1, 121.3, 119.1, 67.9 ppm. IR (KBr): 3055, 2961, 1664, 1601, 1265, 1200, 1118, 877, 801, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{16}ONa$ $[M+Na]^+$ 367.1099, found 367.1096.



2'*H*-Spiro[benzo[a]fluorene-11,1'-naphthalen]-2'-one (3be)

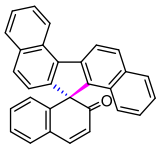
3be (Yellow solid, 42.0 mg, 61% yield). Mp = 179.2-180.3 °C. Eluent: PE : EA = 10:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.97 (m, 2H), 7.91-7.83 (m, 3H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.38-7.34 (m, 2H), 7.27-7.24 (m, 2H), 7.12 (d, *J* = 4.0 Hz, 2H), 7.03-6.95 (m, 2H), 6.50 (d, *J* = 9.9 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 148.6, 146.4, 143.5, 142.5, 141.5, 141.3, 134.3, 130.7, 129.9, 129.8, 129.4, 129.2, 129.1, 128.2, 127.7, 127.4, 127.2, 127.1, 126.4, 125.5, 124.6, 122.7, 121.0, 118.5, 67.8 ppm. IR (KBr): 3054, 1662, 1621, 1461, 1390, 1232, 1118, 867, 821, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{16}ONa$ $[M+Na]^+$ 367.1099, found 367.1097.



2'*H*-Spiro[dibenzo[a,h]fluorene-13,1'-naphthalen]-2'-one (3bf)

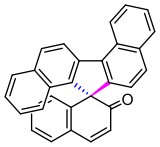
3bf (Yellow oil, 32.3 mg, 41% yield). Eluent: PE:EA = 5:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.58 (s, 2H),

7.55-7.38 (m, 5H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.41 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 146.3, 146.0, 144.5, 139.3, 134.0, 133.9, 130.2, 129.6, 129.5, 128.8, 128.4, 128.3, 127.6, 126.3, 126.0, 125.4, 123.3, 119.7, 67.4 ppm. IR (KBr): 3427, 2853, 1651, 1500, 1453, 1379, 1265, 843, 819, 741 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}ONa$ $[M+Na]^+$ 417.1255, found 417.1255.



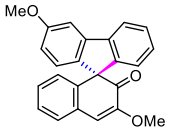
2'*H*-Spiro[dibenzo[a,g]fluorene-13,1'-naphthalen]-2'-one (3bg)

3bg (Pale yellow oil, 32.3 mg, 41% yield). Eluent: PE:EA = 5:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.5 Hz, 1H), 8.72 (s, 1H), 7.91 (dd, *J* = 26.9, 8.1 Hz, 2H), 7.78-7.66 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56-7.47 (m, 2H), 7.40-7.36 (m, 3H), 7.27-7.08 (m, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 147.0, 146.4, 143.1, 140.8, 136.6, 134.3, 133.9, 132.6, 130.5, 130.1, 129.9, 129.8, 129.7, 129.5, 128.7, 128.4, 127.9, 127.8, 127.3, 126.2, 126.0, 124.2, 122.6, 122.5, 122.2, 67.8 ppm. IR (KBr): 3424, 2858, 1645, 1508, 1450, 1385, 1265, 844, 810, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}ONa$ $[M+Na]^+$ 417.1255, found 417.1257.



2'*H*-Spiro[dibenzo[a,g]fluorene-13,1'-naphthalen]-2'-one (3bh)

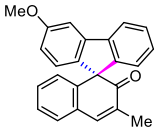
3bh (Yellow oil, 41.8 mg, 53% yield). Eluent: PE:EA = 5:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.5 Hz, 1H), 8.72 (s, 1H), 7.91 (dd, *J* = 26.9, 8.1 Hz, 2H), 7.78-7.66 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56-7.47 (m, 2H), 7.40-7.36 (m, 3H), 7.27-7.08 (m, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 147.0, 146.4, 143.1, 140.8, 136.6, 134.3, 133.9, 132.6, 130.5, 130.1, 129.9, 129.8, 129.7, 129.5, 128.7, 128.4, 127.9, 127.8, 127.3, 126.2, 126.0, 124.2, 122.6, 122.5, 122.2, 67.8 ppm. IR (KBr): 3424, 2858, 1645, 1508, 1450, 1385, 1265, 844, 810, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}ONa$ $[M+Na]^+$ 417.1255, found 417.1257.



3,7'-Dimethoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bi)

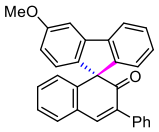
3bi (Yellow solid, 33.3 mg, 47% yield). Mp = 147.2-148.2 °C. Eluent: PE:EA = 5:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.38-7.35 (m, 1H), 7.33-7.28 (m, 2H), 7.23-7.15 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.96-6.92 (m, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.44 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 160.3, 150.4, 148.0, 143.4, 141.7, 139.4, 138.8, 130.7, 128.4, 128.2, 127.9, 127.7, 127.6, 127.3, 124.9, 124.1, 120.7, 116.2, 114.3,

105.8, 68.8, 55.7, 55.6 ppm. IR (KBr): 3058, 2847, 1677, 1617, 1482, 1452, 1279, 1209, 1103, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}O_3Na$ $[M+Na]^+$ 377.1154, found 377.1155.



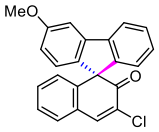
3-Methoxy-3'-methyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bj)

3bj (Yellow solid, 51.4 mg, 76% yield). Mp = 202.7-203.4 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.49 (s, 1H), 7.40-7.32 (m, 2H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.25-7.15 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.05-6.97 (m, 2H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 160.1, 148.5, 143.4, 142.4, 142.2, 141.7, 139.9, 133.6, 130.6, 129.1, 128.6, 128.2, 128.1, 127.5, 127.4, 124.8, 124.0, 120.6, 114.2, 105.8, 67.6, 55.6, 16.4 ppm. IR (KBr): 3058, 2927, 1661, 1615, 1485, 1278, 861, 816, 753, 626 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}O_2Na$ $[M+Na]^+$ 361.1204, found 361.1207.



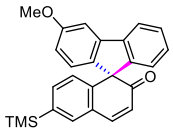
3-Methoxy-3'-phenyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bk)

3bk (Yellow solid, 58.5 mg, 73% yield). Mp = 206.2-207.3 °C. Eluent: PE:EA = 5:1, R_f = 0.26. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.72 (m, 2H), 7.52-7.43 (m, 3H), 7.41-7.18 (m, 8H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 160.3, 147.4, 143.3, 142.5, 142.4, 141.7, 138.7, 136.4, 135.7, 130.8, 129.9, 129.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.3, 125.1, 124.3, 120.7, 114.3, 105.9, 69.1, 55.6 ppm. IR (KBr): 3057, 2937, 2838, 1668, 1610, 1484, 1215, 1029, 754, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{29}H_{20}O_2Na$ $[M+Na]^+$ 423.1361, found 423.1358.



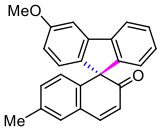
3'-Chloro-3-methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bl)

3bl (Yellow solid, 32.3 mg, 45% yield). Mp = 202.6-203.2 °C. Eluent: PE:EA = 10:1, R_f = 0.32. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.45-7.37 (m, 2H), 7.33-7.18 (m, 3H), 7.14-7.07 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 160.4, 147.6, 143.3, 143.2, 141.9, 141.6, 138.9, 130.5, 130.1, 129.6, 129.1, 128.6, 128.3, 127.9, 127.8, 124.8, 124.0, 120.8, 114.4, 106.0, 68.8, 55.6 ppm. IR (KBr): 3057, 2932, 2841, 1680, 1609, 1486, 1161, 1030, 750, 642 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{15}O_2ClNa$ $[M+Na]^+$ 381.0658, found 381.0661.



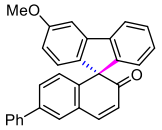
3,7'-Dimethoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bm)

3bm (Yellow solid, 55.5 mg, 70% yield). Mp = 61.7-62.6 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 17.5, 8.8 Hz, 2H), 7.53 (s, 1H), 7.39-7.35 (m, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.26-7.15 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 9.9 Hz, 1H), 3.86 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 161.4, 149.4, 147.7, 144.6, 144.5, 142.9, 141.9, 140.8, 136.6, 135.8, 130.4, 129.5, 129.3, 128.2, 127.0, 126.1, 125.3, 121.8, 115.5, 107.0, 69.0, 56.8, 0.00 ppm. IR (KBr): 3052, 2840, 1666, 1613, 1486, 1450, 1247, 1211, 834, 748 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{24}O_2SiNa$ $[M+Na]^+$ 419.1443, found 419.1446.



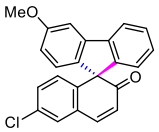
3-Methoxy-6'-methyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bn)

3bn (Yellow solid, 48.1 mg, 71% yield). Mp = 56.7-58.3 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 9.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.24 (d, *J* = 5.1 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 6.32 (d, *J* = 9.9 Hz, 1H), 3.86 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 160.2, 148.5, 146.2, 143.4, 141.6, 139.8, 137.3, 131.2, 130.1, 129.8, 128.2, 128.1, 127.7, 125.9, 124.8, 124.0, 120.6, 114.3, 105.8, 67.5, 55.6, 20.9 ppm. IR (KBr): 3054, 2931, 1665, 1612, 1571, 1486, 1170, 861, 817, 743 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}O_2Na$ $[M+Na]^+$ 361.1204, found 361.1206.



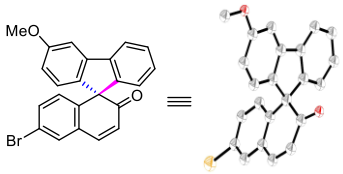
3-Methoxy-6'-phenyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bo)

3bo (Yellow oil, 58.5 mg, 73% yield). Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.71 (m, 2H), 7.62 (d, *J* = 1.7 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.46-7.26 (m, 6H), 7.24-7.18 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 160.3, 148.3, 146.1, 143.5, 141.7, 140.7, 139.9, 139.6, 130.3, 129.0, 128.4, 128.3, 128.2, 128.1, 127.8, 127.0, 126.3, 124.9, 124.1, 120.7, 114.4, 105.9, 67.6, 55.6 ppm. IR (KBr): 3055, 2929, 1665, 1611, 1485, 1280, 1030, 816, 749, 698 cm^{-1}. HRMS (ESI) m/z calculated for $C_{29}H_{20}O_2Na$ $[M+Na]^+$ 423.1361, found 423.1366.



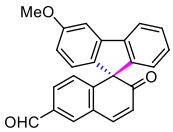
6'-Chloro-3-methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bp)

3bp (Yellow oil, 48.8 mg, 68% yield). Eluent: PE:EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 10.0 Hz, 1H), 7.43-7.35 (m, 2H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11-7.02 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.1, 160.4, 147.8, 144.5, 143.4, 141.6, 141.2, 139.1, 133.4, 131.4, 130.1, 129.3, 129.0, 128.5, 128.3, 127.1, 124.8, 124.0, 120.8, 114.4, 105.9, 67.3, 55.6 ppm. IR (KBr): 3056, 2951, 1667, 1611, 1485, 1450, 1273, 1030, 813, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{15}ClO_2Na$ $[M+Na]^+$ 381.0658, found 381.0660.



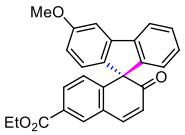
6'-Bromo-3-methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bq)

3bq (Yellow solid, 20.2 mg, 25% yield). Mp = 94.1-95.3 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 10.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.44-7.35 (m, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.24-7.16 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.39 (dd, *J* = 9.1, 5.3 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 159.3, 146.6, 143.3, 142.3, 140.7, 140.6, 138.0, 132.0, 130.9, 130.7, 128.5, 127.5, 127.2, 126.0, 123.7, 122.9, 120.2, 119.7, 113.3, 104.9, 66.3, 54.6 ppm. IR (KBr): 3057, 2961, 1664, 1615, 1485, 1450, 1265, 1094, 805, 753 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{15}BrO_2Na$ $[M+Na]^+$ 425.0153, found 425.0157.



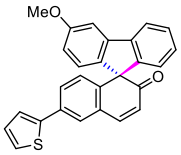
3-Methoxy-2'-oxo-2'*H*-spiro[fluorene-9,1'-naphthalene]-6'-carbaldehyde (3br)

3br (Yellow solid, 20.4 mg, 29% yield). Mp = 67.5-68.8 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.95 (d, *J* = 1.6 Hz, 1H), 7.82-7.74 (m, 2H), 7.59 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.44-7.40 (m, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.24-7.20 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 10.0 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 191.1, 160.5, 149.6, 147.4, 144.7, 143.6, 141.7, 138.7, 135.7, 131.3, 130.6, 130.1, 128.7, 128.6, 128.4, 127.3, 124.8, 124.0, 120.9, 114.5, 106.0, 68.0, 55.6 ppm. IR (KBr): 3435, 2923, 2875, 1614, 1451, 1269, 1213, 1163, 814, 753 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{16}O_3Na$ $[M+Na]^+$ 375.0997, found 375.0999.



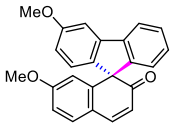
Ethyl-3-methoxy-2'-oxo-2'*H*-spiro[fluorene-9,1'-naphthalene]-6'-carboxylate (3bs)

3bs (Yellow solid, 53.9 mg, 68% yield). Mp = 46.8-47.7 °C. Eluent: PE:EA = 5:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.6 Hz, 1H), 7.80-7.72 (m, 3H), 7.40 (m, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.22-7.18 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 6.42 (d, *J* = 9.9 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 165.7, 160.4, 147.8, 147.6, 145.2, 143.4, 141.7, 138.9, 131.0, 130.6, 130.0, 128.6, 128.3, 128.0, 126.7, 124.8, 124.0, 120.8, 114.4, 106.0, 67.8, 61.3, 55.6, 14.3 ppm. IR (KBr): 3057, 2838, 1716, 1669, 1615, 1484, 1449, 1026, 817, 751 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{20}O_4Na$ $[M+Na]^+$ 419.1259, found 419.1266.



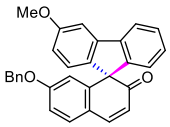
3-Methoxy-6'-(thiophen-2-yl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bt)

3bt (Yellow solid, 63.8 mg, 78% yield). Mp = 86.4-87.9 °C. Eluent: PE:EA = 5:1, R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 17.4, 8.8 Hz, 2H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.40 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.34-7.27 (m, 4H), 7.20 (dd, *J* = 7.5, 6.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.07-7.02 (m, 2H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 160.3, 148.1, 145.7, 143.4, 143.0, 141.8, 141.7, 139.5, 133.9, 130.4, 128.4, 128.2, 127.6, 126.8, 126.5, 125.3, 124.9, 124.1, 123.6, 120.7, 114.3, 105.9, 67.6, 55.6 ppm. IR (KBr): 3327, 2961, 2365, 1662, 1457, 1401, 1105, 766, 692, 640 cm^{-1}. HRMS (ESI) m/z calculated for $C_{27}H_{28}SO_2Na$ $[M+Na]^+$ 429.0925, found 429.0923.



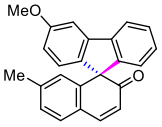
3,7'-Dimethoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bu)

3bu (Yellow solid, 63.1 mg, 89% yield). Mp = 176.2-176.9 °C. Eluent: PE:EA = 5:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 9.9 Hz, 1H), 7.39-7.32 (m, 2H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.21-7.17 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.78-6.74 (m, 2H), 6.21 (d, *J* = 9.9 Hz, 1H), 6.06 (d, *J* = 2.5 Hz, 1H), 3.86 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 161.3, 160.2, 148.2, 146.1, 145.3, 143.4, 141.6, 139.6, 131.2, 128.3, 128.1, 124.9, 124.1, 123.3, 123.2, 120.7, 114.3, 114.1, 112.4, 105.8, 68.1, 55.6, 55.2 ppm. IR (KBr): 3054, 2842, 1662, 1605, 1489, 1453, 1282, 1033, 836, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}O_3Na$ $[M+Na]^+$ 377.1154, found 377.1155.



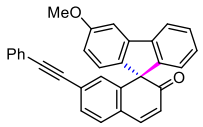
7'-(Benzyloxy)-3-methoxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bv)

3bv (Yellow oil, 72.3 mg, 84% yield). Eluent: PE:EA = 5:1, R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 9.9 Hz, 1H), 7.31-7.26 (m, 2H), 7.22-7.18 (m, 4H), 7.15-7.06 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.14 (d, *J* = 9.9 Hz, 1H), 6.07 (d, *J* = 2.5 Hz, 1H), 4.71 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 160.4, 160.2, 148.2, 145.8, 145.3, 143.4, 141.6, 139.6, 136.0, 131.1, 128.6, 128.2, 128.1, 128.0, 127.7, 124.9, 124.1, 123.5, 123.4, 120.6, 114.8, 114.4, 113.4, 105.8, 70.0, 68.0, 55.6 ppm. IR (KBr): 3434, 2854, 1665, 1605, 1492, 1453, 1271, 911, 826, 744 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{22}O_3Na$ $[M+Na]^+$ 453.1467, found 453.1470.



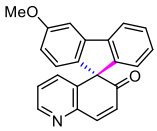
3-Methoxy-7'-methyl-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bw)

3bw (Yellow solid, 45.3 mg, 67% yield). Mp = 172.1-173.2 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 9.9 Hz, 1H), 7.41-7.37 (m, 1H), 7.35-7.30 (m, 2H), 7.23-7.19 (m, 1H), 7.13-7.05 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.33 (s, 1H), 6.29 (d, *J* = 9.9 Hz, 1H), 3.89 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 160.2, 148.4, 146.0, 143.4, 142.9, 141.7, 140.8, 139.8, 129.5, 128.4, 128.3, 128.2, 128.1, 127.4, 124.9, 124.8, 124.1, 120.6, 114.3, 105.7, 68.0, 55.6, 21.5 ppm. IR (KBr): 3427, 2853, 1662, 1609, 1483, 1449, 1286, 912, 836, 744 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{18}O_2Na$ $[M+Na]^+$ 361.1204, found 361.1206.



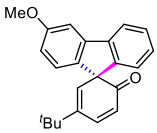
3-Methoxy-7'-(phenylethynyl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3bx)

3bx (Yellow solid, 50.9 mg, 60% yield). Mp = 106.5-107.3 °C. Eluent: PE:EA = 5:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 11.1 Hz, 1H), 7.35-7.30 (m, 5H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.23-7.17 (m, 3H), 7.15-7.10 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 14.6, 7.0 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.60 (s, 1H), 6.28 (d, *J* = 9.9 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 160.3, 147.9, 145.1, 143.5, 143.1, 141.7, 139.2, 131.6, 130.8, 130.7, 129.8, 129.5, 128.6, 128.4, 128.3, 128.2, 126.2, 125.3, 124.9, 124.1, 122.6, 120.8, 114.4, 105.9, 91.8, 88.8, 67.6, 55.6 ppm. IR (KBr): 3447, 2924, 1662, 1482, 1453, 1257, 1218, 822, 750, 698 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{20}O_2Na$ $[M+Na]^+$ 447.1361, found 447.1365.



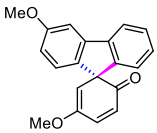
3-Methoxy-6'*H*-spiro[fluorene-9,5'-quinolin]-6'-one (3by)

3by (Yellow solid, 39.7 mg, 61% yield). Mp = 114.3-115.7 °C. Eluent: PE:EA = 5:1, R_f = 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.89 (d, *J* = 10.2 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.43-7.39 (m, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.24-7.20 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.05-6.98 (m, 2H), 6.85-6.76 (m, 2H), 6.58 (d, *J* = 10.1 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 160.5, 149.0, 148.8, 147.2, 147.0, 143.5, 141.7, 139.1, 138.5, 135.2, 129.8, 128.7, 128.4, 124.8, 124.1, 124.0, 120.9, 114.4, 106.0, 66.9, 55.6 ppm. IR (KBr): 3053, 3004, 2930, 2841, 1671, 1611, 1485, 1447, 1224, 1029, 808, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{15}O_2NNa$ $[M+Na]^+$ 348.1000, found 348.0995.



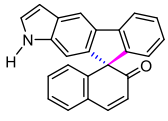
3-(*Tert*-butyl)-3'-methoxyspiro[cyclohexane-1,9'-fluorene]-2,4-dien-6-one (3bz)

3bz (Yellow solid, 41.6 mg, 63% yield). Mp = 123.1-124.3 °C. Eluent: PE:EA = 20:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 10.2, 2.6 Hz, 1H), 7.41-7.37 (m, 1H), 7.32-7.21 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.22 (d, *J* = 10.2 Hz, 1H), 5.86 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 160.3, 145.9, 144.2, 143.6, 142.0, 141.6, 137.2, 133.4, 128.4, 128.0, 126.1, 124.5, 123.8, 120.7, 114.2, 105.9, 65.7, 55.6, 34.4, 29.0 ppm. IR (KBr): 2960, 1666, 1479, 1269, 1218, 1030, 755 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{22}O_2Na$ $[M+Na]^+$ 352.1517, found 352.1513.



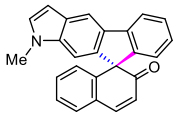
3,3'-Dimethoxyspiro[cyclohexane-1,9'-fluorene]-2,4-dien-6-one (3ca)

3ca (Yellow solid, 21.3 mg, 35% yield). Mp = 147.1-148.1 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.34-7.30 (m, 1H), 7.23-7.12 (m, 3H), 7.05 (dd, *J* = 9.4, 3.5 Hz, 2H), 6.74 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 1H), 4.98 (d, *J* = 3.1 Hz, 1H), 3.81 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 160.3, 151.0, 147.1, 143.2, 143.0, 141.6, 138.4, 128.4, 128.0, 127.2, 124.6, 123.9, 120.6, 114.1, 107.2, 105.8, 64.3, 55.6, 55.2 ppm. IR (KBr): 3003, 1638, 1482, 1450, 1404, 1269, 1172, 1027, 822, 755 cm^{-1}. HRMS (ESI) m/z calculated for $C_{20}H_{16}O_3Na$ $[M+Na]^+$ 327.0997, found 327.0994.



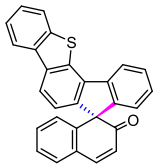
1*H*,2'*H*-Spiro[indeno[1,2-f]indole-9,1'-naphthalen]-2'-one (3cb)

3cb (Yellow solid, 36.7 mg, 55% yield). Mp = 191.3-192.1 °C. Eluent: PE:EA = 5:1, R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.00 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 9.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 6.6 Hz, 1H), 7.30-7.21 (m, 1H), 7.16-7.01 (m, 5H), 6.60-6.50 (m, 2H), 6.36 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 146.9, 146.1, 144.3, 142.7, 142.3, 136.2, 134.4, 130.3, 129.7, 129.4, 128.4, 128.3, 127.4, 126.8, 125.7, 125.1, 125.0, 124.0, 120.0, 112.4, 107.1, 103.0, 67.9 ppm. IR (KBr): 3409, 3009, 1657, 1595, 1562, 1452, 1359, 1288, 1262, 1204, 876, 764, 597, 507 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{15}NONa$ $[M+Na]^+$ 356.1501, found 356.1501.



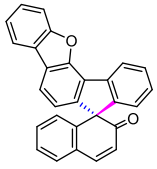
1-Methyl-1*H*,2'*H*-spiro[indeno[1,2-f]indole-9,1'-naphthalen]-2'-one (3cc)

3cc (Yellow solid, 49.3 mg, 71% yield). Mp = 199.6-200.2 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) 8.02 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 9.9 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40-7.32 (m, 1H), 7.31-7.27 (m, 1H), 7.15-7.05 (m, 3H), 7.04-6.99 (m, 2H), 6.55 (dd, *J* = 9.6, 5.4 Hz, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 147.1, 146.0, 144.4, 142.6, 142.2, 137.2, 134.1, 130.3, 129.7, 129.6, 129.4, 129.1, 128.4, 128.3, 127.4, 126.7, 125.9, 123.8, 120.0, 112.5, 105.3, 101.6, 67.9, 33.0 ppm. IR (KBr): 3421, 3060, 2922, 2360, 2340, 1662, 1618, 1562, 1508, 1458, 1387, 1367, 1274 ,1201, 1112, 876, 827, 750, 594 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{17}NONa$ $[M+Na]^+$ 370.1208, found 370.1208



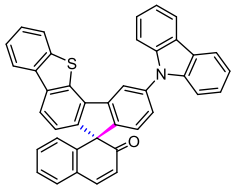
2'*H*-Spiro[benzo[b]fluoreno[3,4-d]thiophene-7,1'-naphthalen]-2'-one (3cd)

3cd (Yellow solid, 52.1 mg, 65% yield). Mp = 233.9-234.6 °C. Eluent: PE:EA = 10:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 6.1, 2.7 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 8.00 (dd, *J* = 6.1, 2.5 Hz, 1H), 7.79 (d, *J* = 9.9 Hz, 1H), 7.62-7.46 (m, 4H), 7.34-7.23 (m, 4H), 7.12 (dd, *J* = 11.0, 4.2 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 148.1, 146.5, 146.4, 142.3, 141.1, 139.7, 136.7, 136.4, 135.0, 132.6, 130.5, 129.9, 129.7, 128.7, 128.0, 127.9, 127.0, 126.0, 124.8, 124.0, 123.1, 122.9, 121.8, 121.2, 120.5, 68.9 ppm. IR (KBr): 3057, 1664, 1565, 1432, 1393, 1345, 1202, 822, 744, 647 cm^{-1}. HRMS (ESI) m/z calculated for $C_{28}H_{16}OS$ $[M+H]^+$ 401.1000, found 401.1000.



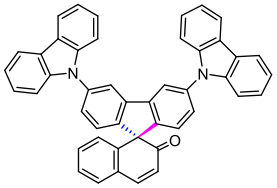
2'*H*-Spiro[fluoreno[4,3-b]benzofuran-7,1'-naphthalen]-2'-one (3cf)

3cf (Yellow solid, 53.8 mg, 70% yield). Mp = 212.3-213.4 °C. Eluent: PE:EA = 10:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 4.7, 2.9 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 15.5, 9.1 Hz, 2H), 7.62-7.47 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 13.7, 6.3 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16-7.10 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 156.9, 150.7, 147.6, 147.1, 146.2, 142.5, 139.5, 130.4, 129.9, 129.7, 128.7, 128.0, 127.9, 127.8, 127.3, 126.5, 126.0, 125.0, 124.0, 123.9, 123.8, 123.1, 120.7, 120.1, 118.7, 112.0, 69.1 ppm. IR (KBr): 3448, 3056, 1665, 1570, 1446, 1240, 1115, 877, 745, 649 cm^{-1}. HRMS (ESI) m/z calculated for $C_{28}H_{16}O_2$ $[M+H]^+$ 385.1229, found 385.1229.



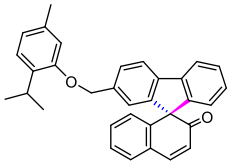
10-(9*H*-Carbazol-9-yl)-2'*H*-spiro[fluoreno[4,3-b]benzofuran-7,1'-naphthalen]-2'-one (3cg)

3cg (Pale yellow solid, 57.2 mg, 52% yield). Mp = 163.9-165.7 °C. Eluent: PE:EA = 3:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 9.9 Hz, 1H), 7.45 (dd, *J* = 16.1, 8.1 Hz, 3H), 7.40-7.30 (m, 5H), 7.29-7.17 (m, 5H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.33 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 156.9, 150.7, 147.5, 146.6, 142.0, 141.4, 141.1, 138.2, 130.7, 129.9, 128.1, 128.0, 127.5, 126.7, 126.1, 125.9, 125.8, 125.3, 125.0, 123.8, 123.5, 123.2, 122.6, 120.9, 120.7, 120.4, 120.1, 118.9, 112.1, 110.1, 69.0 ppm. IR (KBr): 3054, 2925, 1666, 1605, 1485, 1453, 1231, 883, 745, 655 cm^{-1}. HRMS (ESI) m/z calculated for $C_{40}H_{23}NO_2Na$ $[M+Na]^+$ 572.1626, found 572.1631.



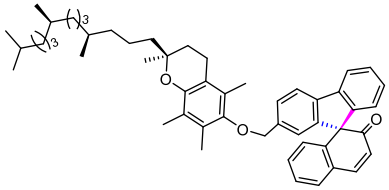
3,6-Di(9*H*-carbazol-9-yl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ch)

3ch (Pale yellow solid, 76.2 mg, 61% yield). Mp = 260.3-261.7 °C. Eluent: PE:EA = 3:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 4H), 7.89 (d, *J* = 1.3 Hz, 2H), 7.73 (d, *J* = 9.9 Hz, 1H), 7.47-7.37 (m, 7H), 7.38-7.24 (m, 7H), 7.25-7.12 (m, 5H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.40 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 146.8, 146.6, 143.1, 141.7, 140.8, 138.3, 130.8, 130.0, 128.3, 128.0, 127.4, 126.0, 125.9, 125.7, 123.5, 120.4, 120.1, 119.5, 109.9, 68.3 ppm. IR (KBr): 3438, 3053, 2852, 1665, 1454, 1331, 1228, 821, 745, 644 cm^{-1}. HRMS (ESI) m/z calculated for $C_{46}H_{28}N_2ONa$ $[M+Na]^+$ 647.2099, found 647.2094.



2-((2-Isopropyl-5-methylphenoxy)methyl)-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3ci)

3ci (Pale yellow oil, 63.9 mg, 70% yield). Eluent: PE:EA = 10:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 9.9 Hz, 1H), 7.39-7.30 (m, 3H), 7.21-7.17 (m, 1H), 7.15-7.11 (m, 2H). 7.07-6.96 (m, 3H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.58 (s, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 6.27 (d, *J* = 9.9 Hz, 1H), 4.90 (s, 2H), 3.17-3.13 (m, 1H), 2.18 (d, *J* = 5.9 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 155.7, 147.7, 147.6, 146.1, 142.5, 141.9, 141.3, 137.6, 136.3, 134.3, 130.4, 129.9, 129.6, 128.4, 128.1, 127.9, 127.7, 127.3, 126.0, 125.9, 124.4, 122.9, 121.5, 120.8, 120.7, 112.8, 69.9, 68.6, 26.7, 22.8, 21.3 ppm. IR (KBr): 3447, 2959, 2862, 1660, 1455, 1348, 1201, 1029, 814, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{33}H_{28}O_2Na$ $[M+Na]^+$ 479.1987, found 479.1985.

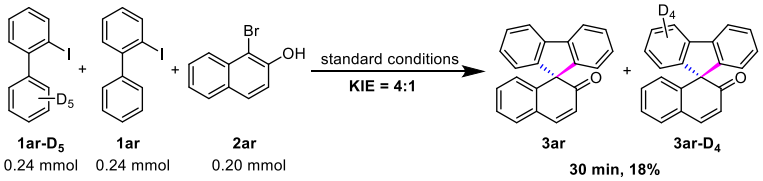


2-(((2,5,7,8-Tetramethyl-2-((4R,6R)-4,6,8-trimethylnonyl)chroman-6-yl)oxy)methyl)-2'*H*-spiro [fluorene-9,1'-naphthalen]-2'-one (3cj)

3cj (Pale yellow oil, 54.5 mg, 40% yield). Eluent: PE:EA = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 9.9 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.47-7.37 (m, 2H), 7.31-7.26 (m, 1H), 7.24-7.16 (m, 2H), 7.13-7.09 (m, 2H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H), 4.66 (s, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.13-2.01 (m, 9H), 1.86-1.71 (m, 2H), 1.57-1.03 (m, 24H), 0.91-0.81 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 148.1, 147.9, 147.8, 147.7, 146.1, 142.5, 141.7, 141.5, 138.2, 130.4, 129.9, 129.5, 128.3, 128.0, 127.9, 127.6, 126.0, 125.9, 124.1, 123.5, 122.9, 120.7, 120.5, 117.6, 74.8, 74.7, 68.5, 40.1, 39.4, 37.6, 37.5, 37.4, 32.8, 32.7, 31.4, 28.0, 24.8, 24.5, 23.9, 23.8, 22.7, 21.1, 20.7, 19.8, 19.7, 19.6, 13.0, 12.1, 11.8 ppm. IR (KBr): 3452, 2929, 2861, 1634, 1459, 1377, 1256, 813, 753, 616 cm^{-1}. HRMS (ESI) m/z calculated for $C_{48}H_{57}O_3$ $[M+H]^+$ 681.4308, found 681.4316.

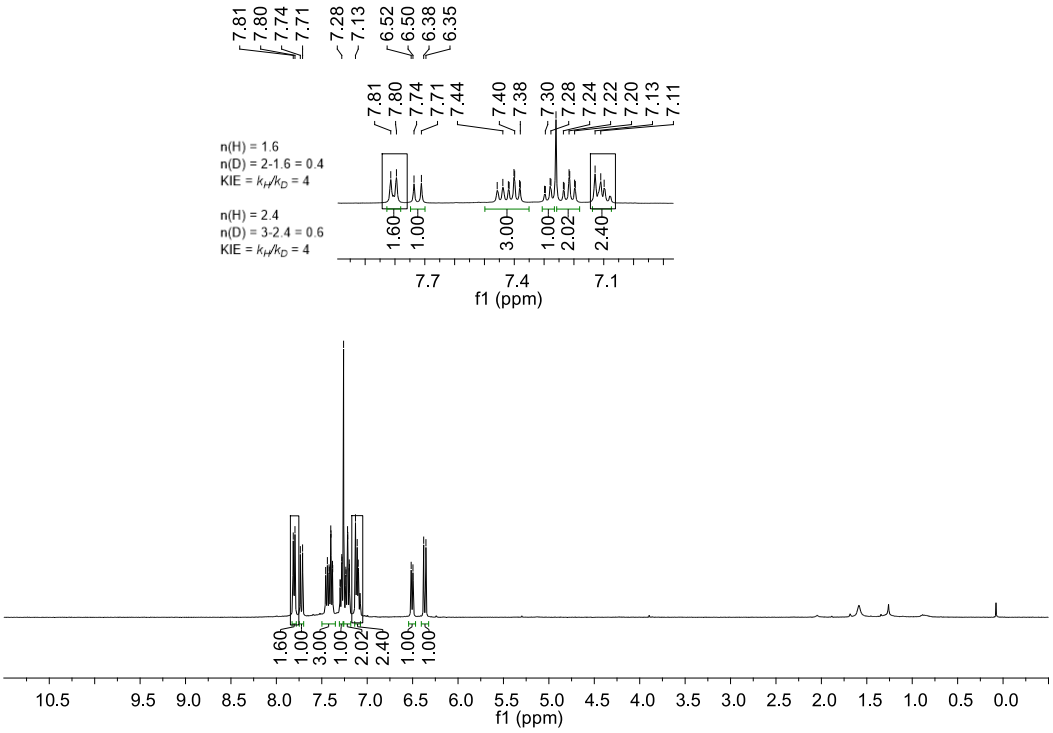
E. Preliminary mechanistic studies:

A). Kinetic isotope effect experiment:

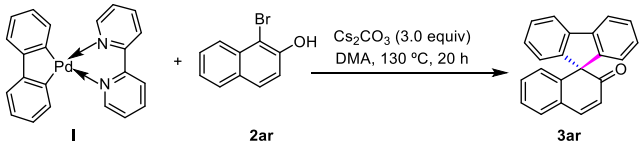


In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(*p*-F-C_6H_4)$_3$ (7.6 mg, 0.024 mmol), CsOPiv (14 mg, 0.06 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), **1ar-D$_5$**[3] (68.4 mg, 0.24 mmol), **1ar** (67.2 mg, 0.24 mmol), **2ar** (22.4 mg, 0.20 mmol) followed by sequential addition of DMA (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 30 min. The crude reaction mixture was quenched with a saturated

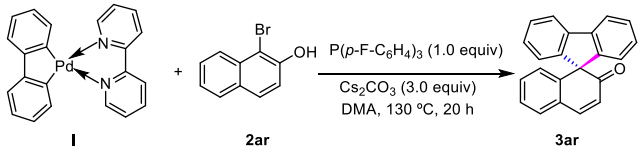
solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography with petroleum ether/ethyl acetate (PE:EA = 10:1, R_f = 0.40) to afford desired product **3ar** and **3ar-D₄** as a pale yellow solid (10.6 mg, 18% total yield). The D/H incorporation in **3ar** and **3ar-D₄** was determined by ^{1}H-NMR spectroscopy. The intermolecular kinetic isotopic effect of this reaction was determined to be **3ar:3ar-D₄** = k_H/k_D = 4:1.



B). Study on Pd complexes in this reaction:

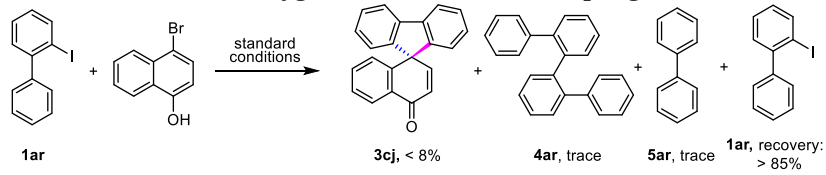


In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with Pd complexes **I** [22] (83.0 mg, 0.20 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), **2ar** (44.6 mg, 0.20 mmol) and 2.0 mL DMA were added. The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (PE:EA = 10:1, R_f = 0.40) to afford **3ar** as a yellow solid (10.6 mg, 18% yield).

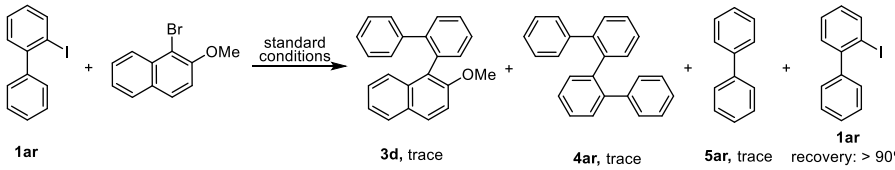


In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with Pd complexes **I** [22] (83.0 mg, 0.20 mmol), P(*p*-F-C_6H_4)$_3$ (63.2 mg, 0.20 mmol) and 2.0 mL DMA were stirred 30 min at room temperature, next Cs_2CO_3 (195 mg, 0.60 mmol), **2ar** (44.6 mg, 0.20 mmol) were added. The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (PE:EA = 10:1, R_f = 0.40) to afford **3ar** as a yellow solid (35.3 mg, 60% yield).

C). Study on the chelation of vicinal oxygen atom in the cross-coupling:

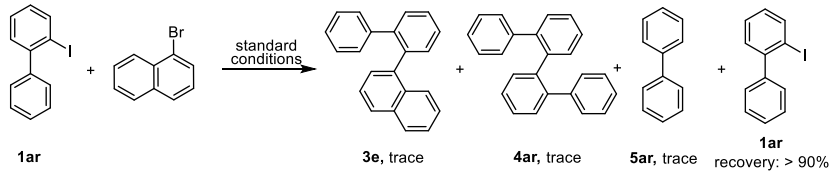


In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(*p*-F-C_6H_4)$_3$ (7.6 mg, 0.024 mmol), CsOPiv (14.0 mg, 0.06 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), **1ar** (67.2 mg, 0.24 mmol), 4-bromonaphthalen-1-ol (44.6 mg, 0.20 mmol) followed by sequential addition of DMA (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography to afford the desired product **3cj** (< 8% yield). A large amount of 2-iodo-1,1'-biphenyl **1ar** was remaining (> 85% yield).



In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(*p*-F-C_6H_4)$_3$ (7.6 mg, 0.024 mmol), CsOPiv (14.0 mg, 0.06 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), **1ar** (67.2 mg, 0.24 mmol), 1-bromo-2-methoxynaphthalene (47.4 mg, 0.20 mmol) followed by sequential addition of DMA (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product

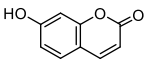
was purified by silica gel flash chromatography to afford trace amount of the desired product **3d** and undesired product **4ar**, **5ar**. A large amount of 2-iodo-1,1'-biphenyl **1ar** was remaining (> 90% yield).



In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(*p*-F-C_6H_4)$_3$ (7.6 mg, 0.024 mmol), CsOPiv (14.0 mg, 0.06 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), **1** (67.2 mg, 0.24 mmol), 1-bromonaphthalene (41.4 mg, 0.20 mmol) followed by sequential addition of DMA (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography to afford trace amount of the desired product **3e** and undesired product **4ar**, **5ar**. A large amount of 2-iodo-1,1'-biphenyl **1ar** was remaining (> 90% yield).

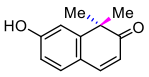
F. Spectroscopical and pK$_a$ studies of O-/C-coumarins:

A). Synthesis of 7-hydroxy-2*H*-chromen-2-one (4), 7-hydroxy-1,1-dimethylnaphnaphthalen-2(1*H*)-one (5) and 7'-hydroxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3cl)



7-Hydroxy-2*H*-chromen-2-one (4)

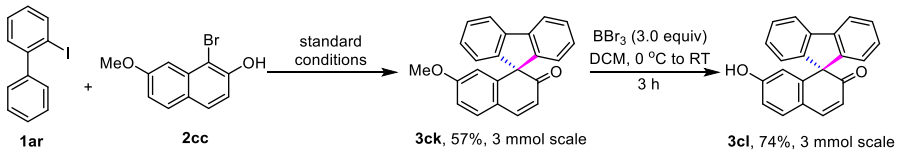
4 (White solid). Mp = 225.5-226.7 °C. Eluent: PE:EA = 5:1, R_f = 0.30. ^{1}H NMR (400 MHz, DMSO) δ 10.57 (s, 1H), 7.93 (d, J = 9.5 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 6.79 (dd, J = 8.5, 2.3 Hz, 1H), 6.72 (d, J = 2.2 Hz, 1H), 6.20 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 161.8, 160.9, 156.0, 145.0, 130.2, 113.6, 111.9, 111.8, 102.6 ppm. Analytical data are in accordance with the literature values. [23]



7-Hydroxy-1,1-dimethylnaphnaphthalen-2(1*H*)-one (5)

5 (White solid). Mp = 157.8-158.7 °C. Eluent: PE:EA = 5:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 9.7 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.42 (s, 1H), 6.06 (d, *J* = 9.8 Hz, 1H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 158.3, 150.4, 145.6, 131.4, 121.8, 121.5, 113.9, 47.6, 28.1 ppm. Analytical data are in accordance with the literature values.[24]

7'-Hydroxy-2'*H*-spiro[fluorene-9,1'-naphthalen]-2'-one (3cl)



1ar **2cc** **3ck**, 57%, 3 mmol scale **3cl**, 74%, 3 mmol scale

3.0 mmol scale: In a glovebox, a 50 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (67.5 mg, 0.3 mmol), P(*p*-F-$C_6H_4)_3$ (114 mg, 0.36 mmol), CsOPiv (210.6 mg, 0.9 mmol), Cs_2CO_3 (2.9 g, 9.0 mmol), **1ar** (3.6 mmol), **2cc** (3.0 mmol) followed by sequential addition of DMA (30 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 20 h. The crude reaction mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine. The extracts were then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography to afford the desired product **3ck** (Yellow solid, 554.7 mg, 57%). Mp = 146.6-147.5 °C. Eluent: PE:EA = 10:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 9.9 Hz, 1H), 7.39 (dd, *J* = 11.0, 4.7 Hz, 3H), 7.24-7.20 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.79 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.23 (d, *J* = 9.9 Hz, 1H), 6.05 (d, *J* = 2.5 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 161.3, 147.5, 146.0, 145.0, 141.8, 131.1, 128.3, 128.0, 124.1, 123.4, 123.3, 120.7, 114.2, 112.4, 68.7, 55.2 ppm. IR (KBr): 3061, 2939, 1665, 1610, 1582, 1486, 1163, 868, 817, 745 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{16}O_2Na$ $[M+Na]^+$ 347.1048, found 347.1046.

Under an argon atmosphere, a solution of BBr_3 (5.1 mmol) in dry DCM (3.6 mL) was slowly added to a solution of the above product **3ck** (1.7 mmol) in dry DCM (18.2 mL) at 0 ºC and the mixture was stirred at room temperature for 3 h. After cooling to 0 ºC, the reaction was quenched with cold water and extracted with DCM. The organic phase was dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the obtained residue was purified by column chromatography to give **3cl** (White solid, 390.4 mg, 74%). Mp = 238.2-239.4 °C. Eluent: PE:EA = 5:1, R_f = 0.20. ^{1}H NMR (400 MHz, DMSO) δ 9.82 (s, 1H), 7.93 (dd, *J* = 17.8, 8.7 Hz, 3H), 7.50-7.41 (m, 3H), 7.27-7.23 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.71 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.11 (d, *J* = 9.8 Hz, 1H), 5.80 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 197.8, 160.0, 148.3, 147.7, 145.0, 141.8, 132.5, 128.7, 128.6, 124.4, 122.0, 121.2, 115.3, 114.5, 68.5 ppm. IR (KBr): 3428, 3058, 1598, 1453, 1392, 1227, 1119, 908, 835, 740 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{14}O_2Na$ $[M+Na]^+$ 333.0891, found 333.0890.

B). Spectroscopical and pK$_a$ studies of 4, 5 and 3cl

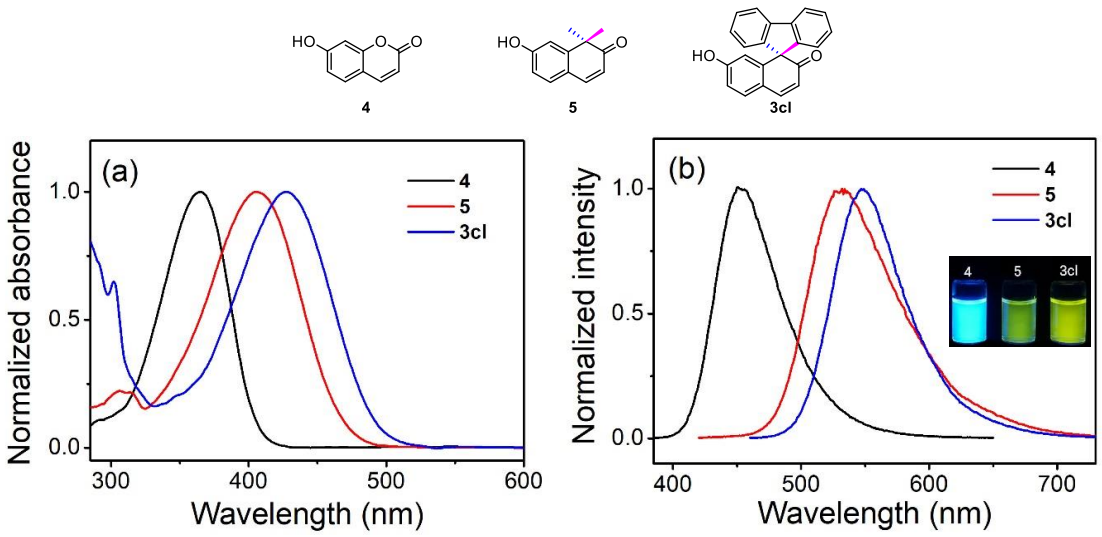


Figure 1. Normalized absorption **(a)** and fluorescence spectra **(b)** of **4**, **5** and **3cl** in $NaHCO_3$-NaOH buffer (10 mM, pH 10.0, containing 1% EtOH); Photographs of **4**, **5** and **3cl** in $NaHCO_3$-NaOH buffer (10 mM, pH 10.0, containing 1% EtOH) under UV light at 365 nm.

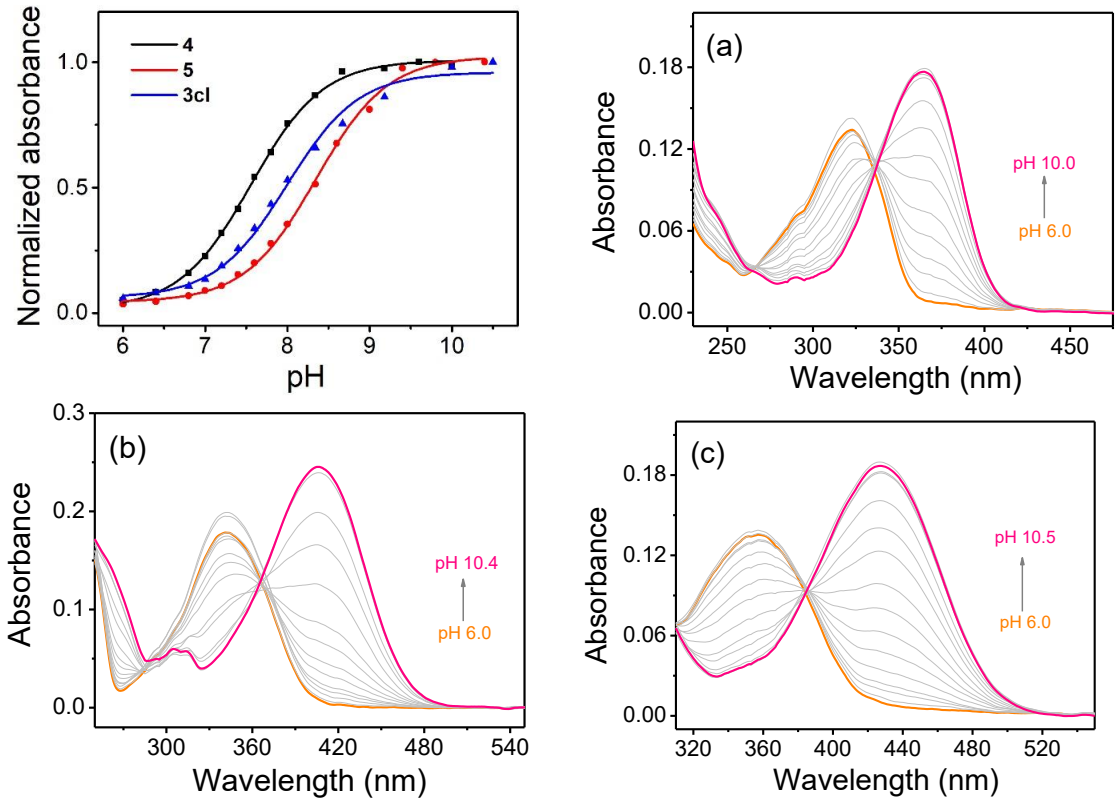


Figure 2. pH-dependent absorbance changes of **4** (λ_{abs} = 365 nm), **5** (λ_{abs} = 406 nm) **3cl** (λ_{abs} = 429 nm); Absorption spectra of **4** (a), **5** (b) and **3cl** (c) (20 μM for each) in various pH values.

Table 1. Photophysical characterization of **4**, **5** and **3cl** in $NaHCO_3$-NaOH buffer (10 mM, pH 10.0, containing 1% EtOH).

Compounds	λ_{abs}/nm [a]	$\varepsilon_{max}/\times10^4$ $M^{-1}cm^{-1}$	λ_{em}/nm [b]	Φ_F [c]	pK_a
4	365	1.72	452	0.76 [25]	7.56
5	406	1.19	532	0.14	8.35
3cl	429	0.92	547	0.40	7.99

[a] The maximal absorption of the dye. [b] The maximal emission of the dye. [c] Φ_F is the relative fluorescence quantum yield, which was measured by using fluorescein (Φ_F = 0.92 in 0.1M NaOH solution) as standard.[26]

G. References:

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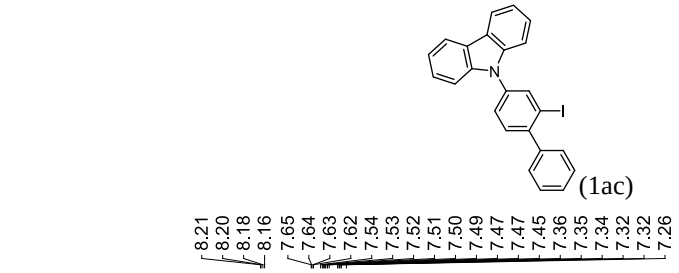

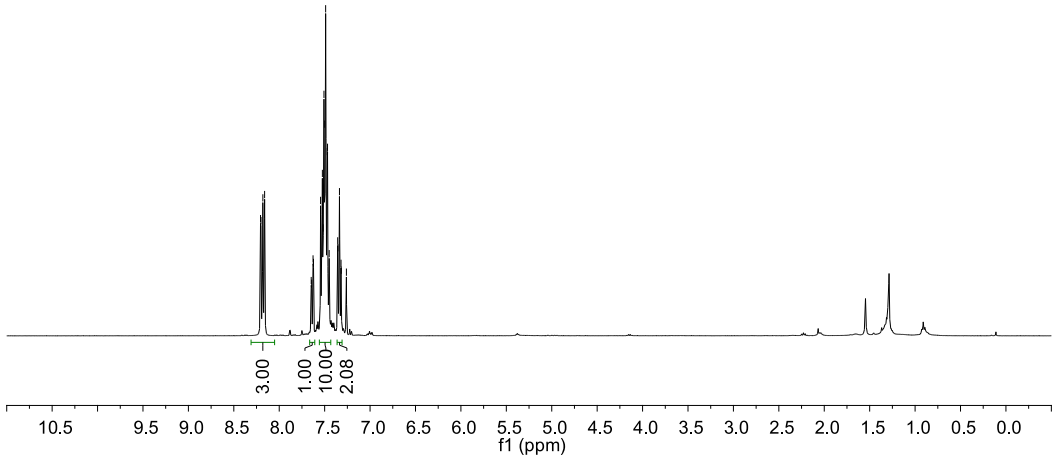

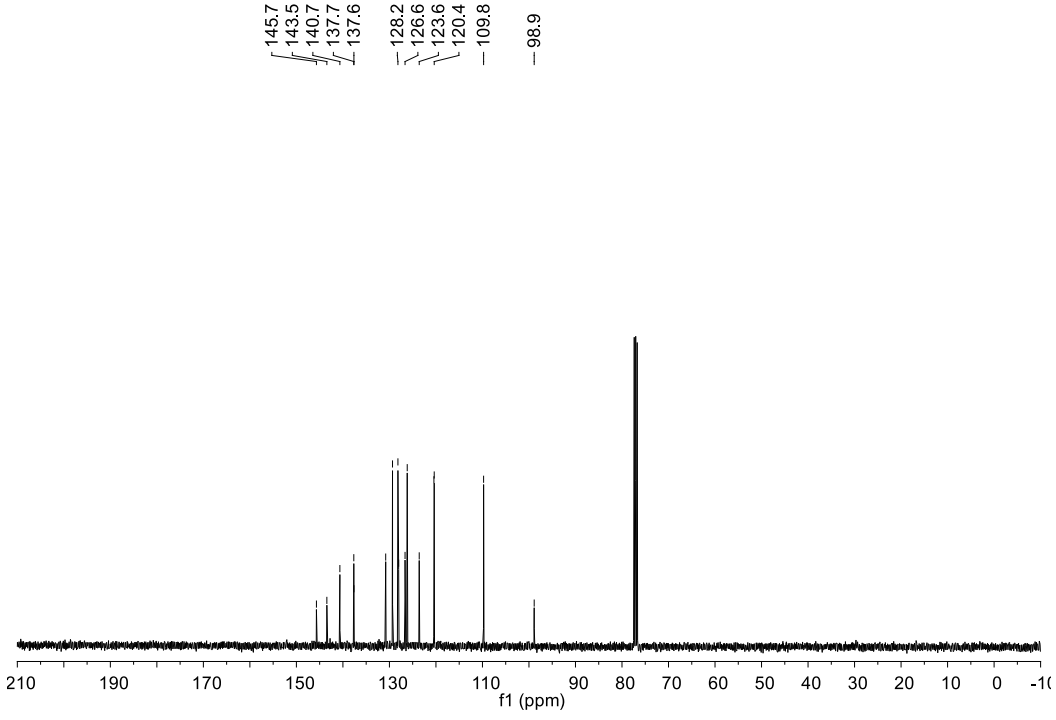

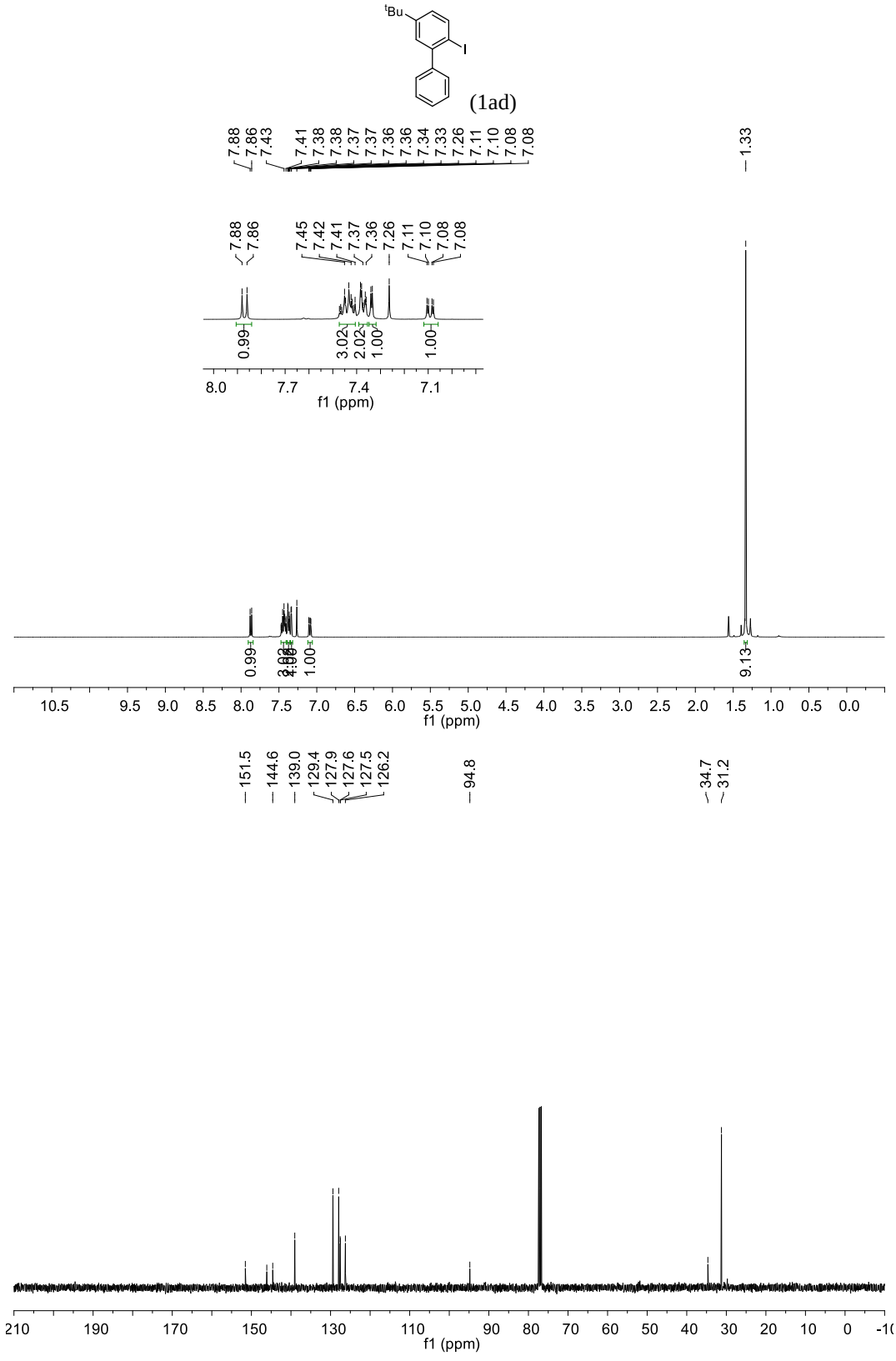
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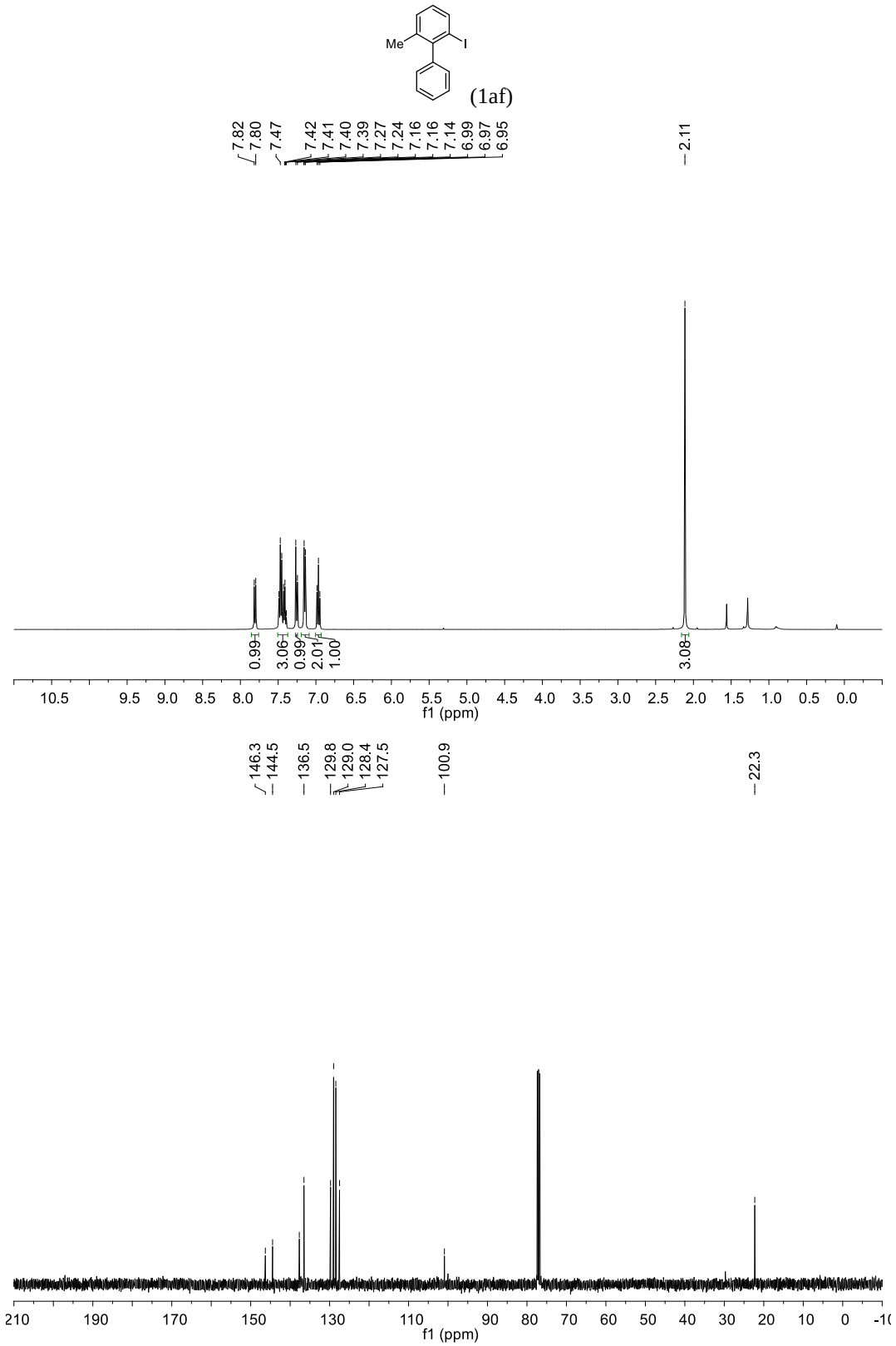
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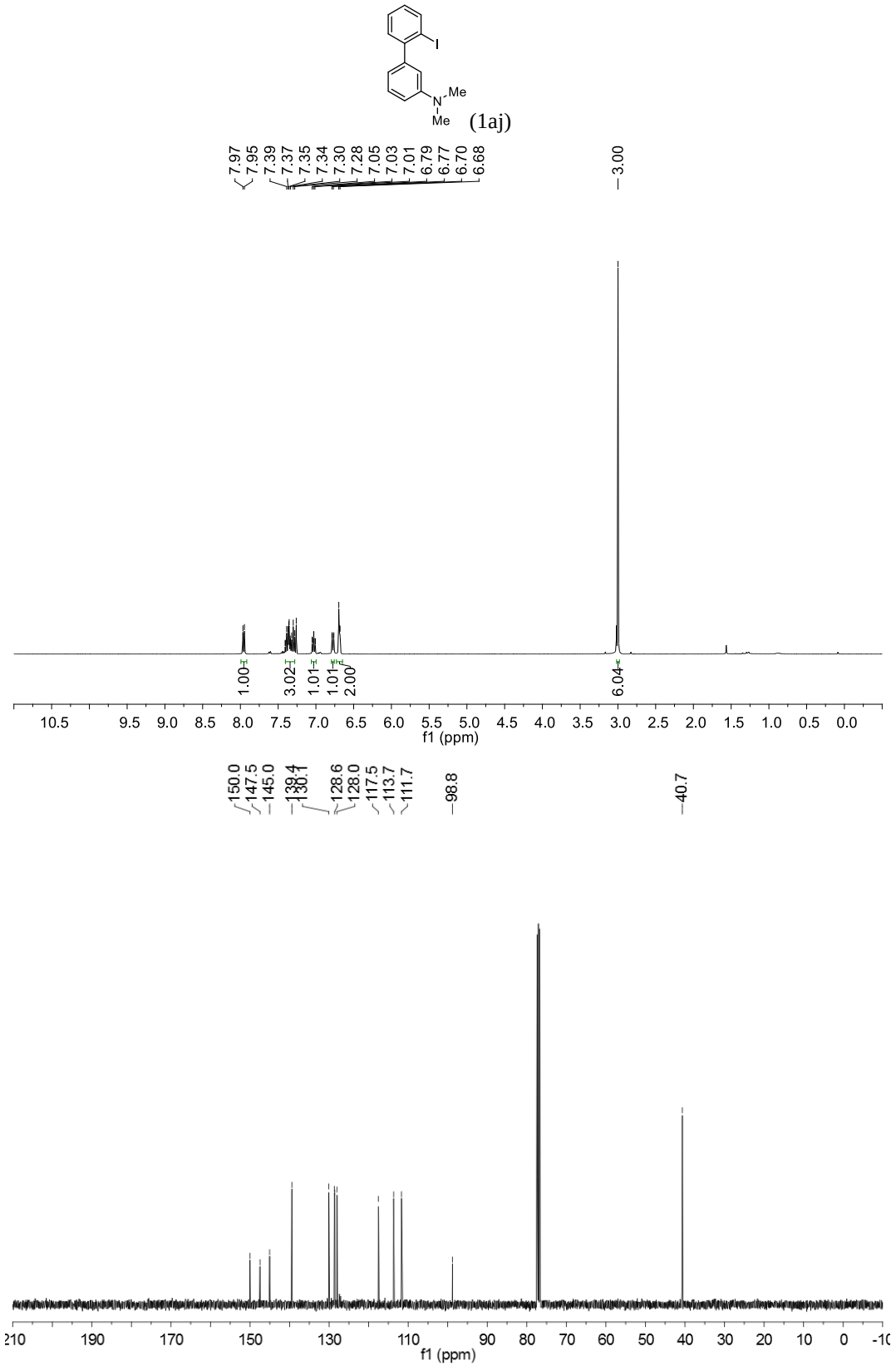
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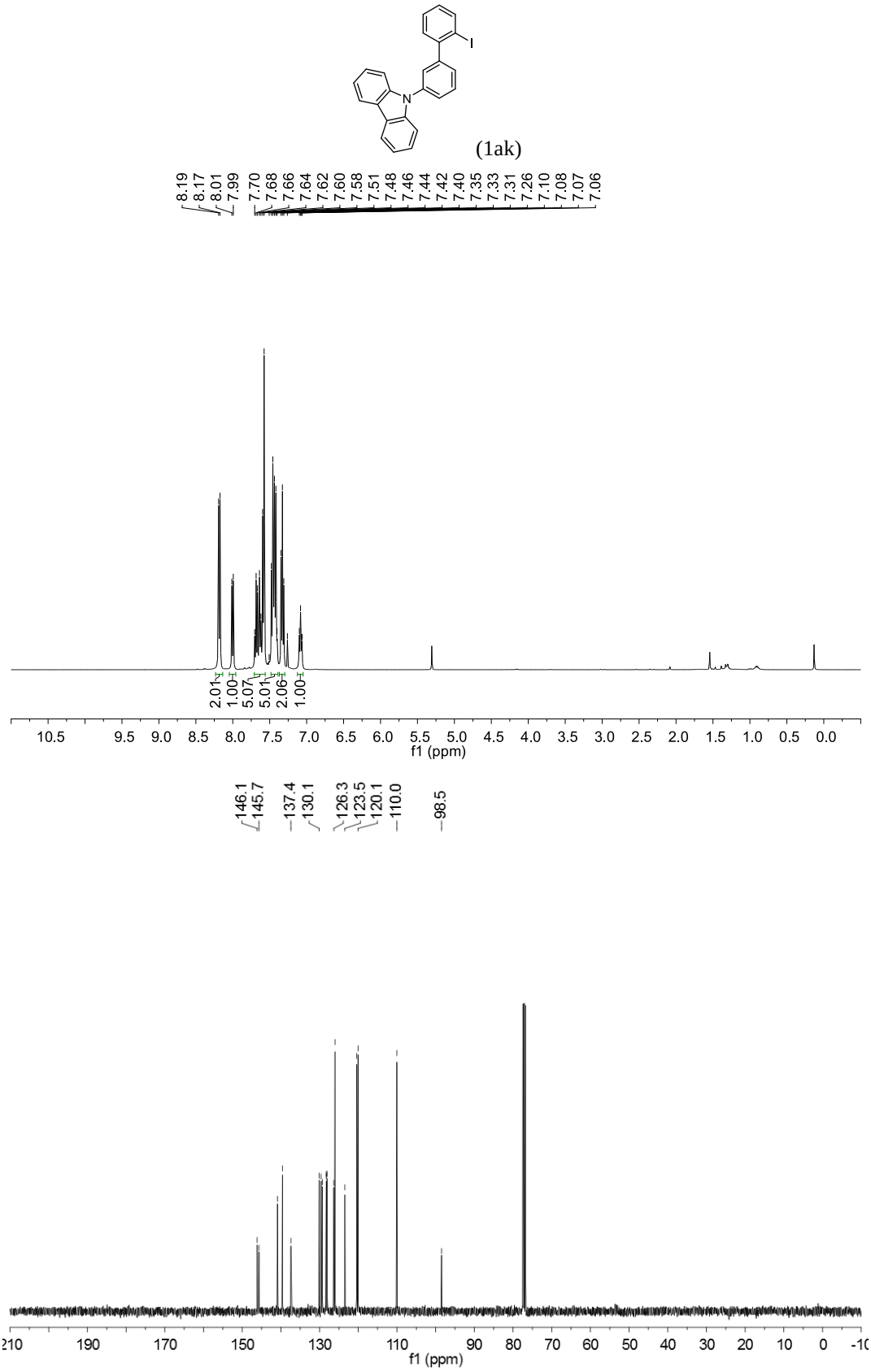
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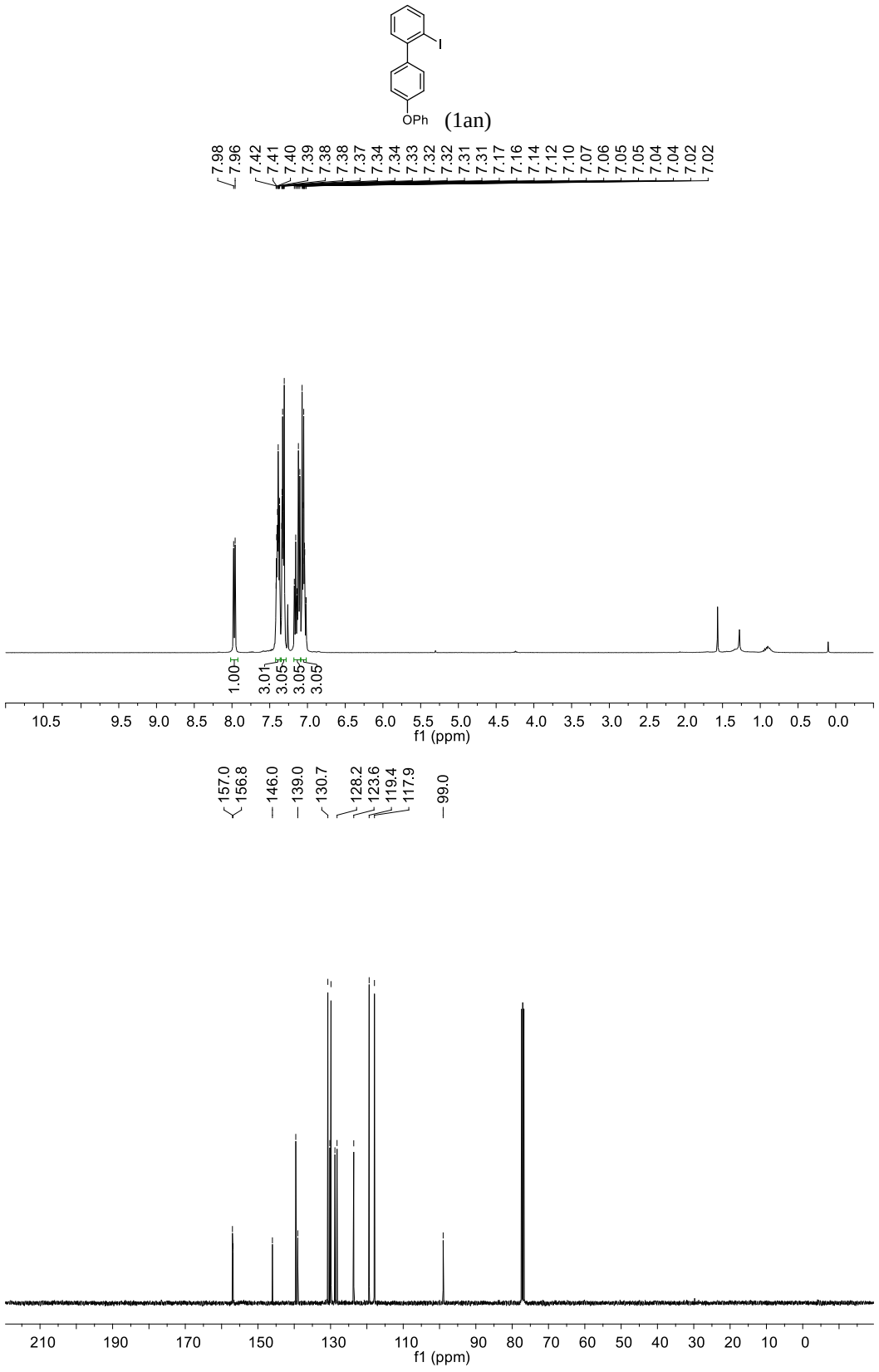
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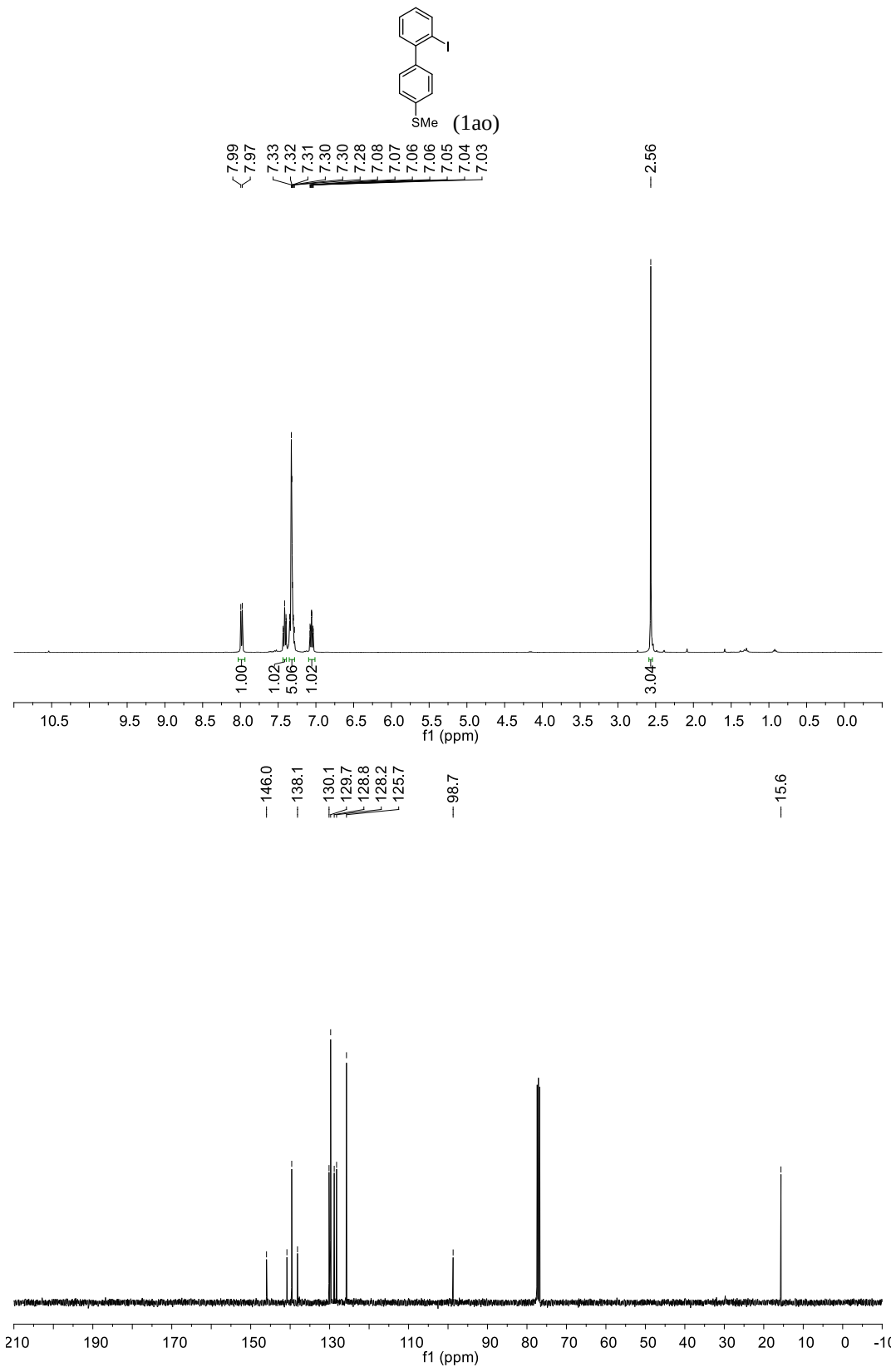
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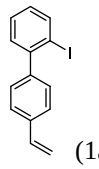
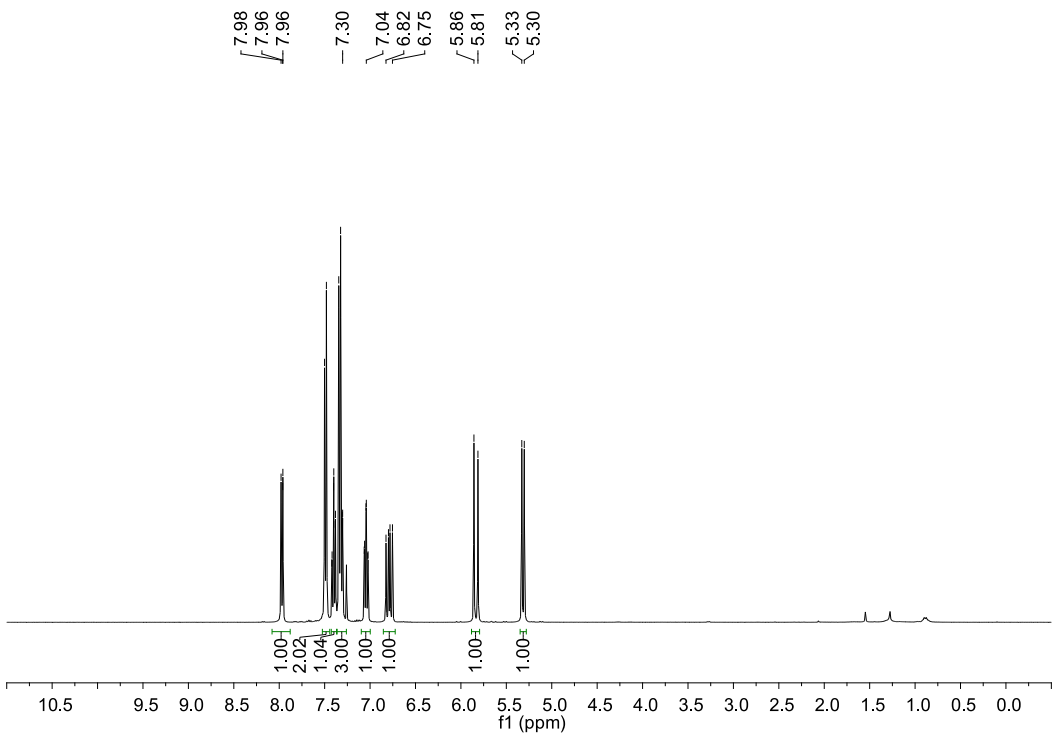
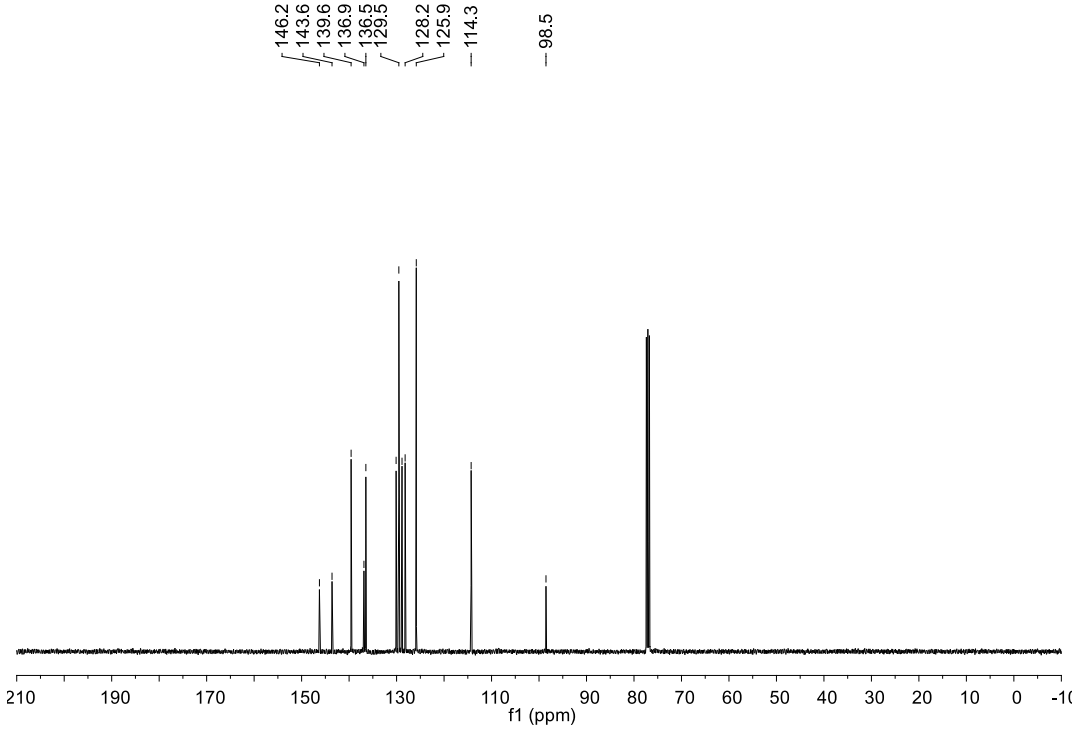
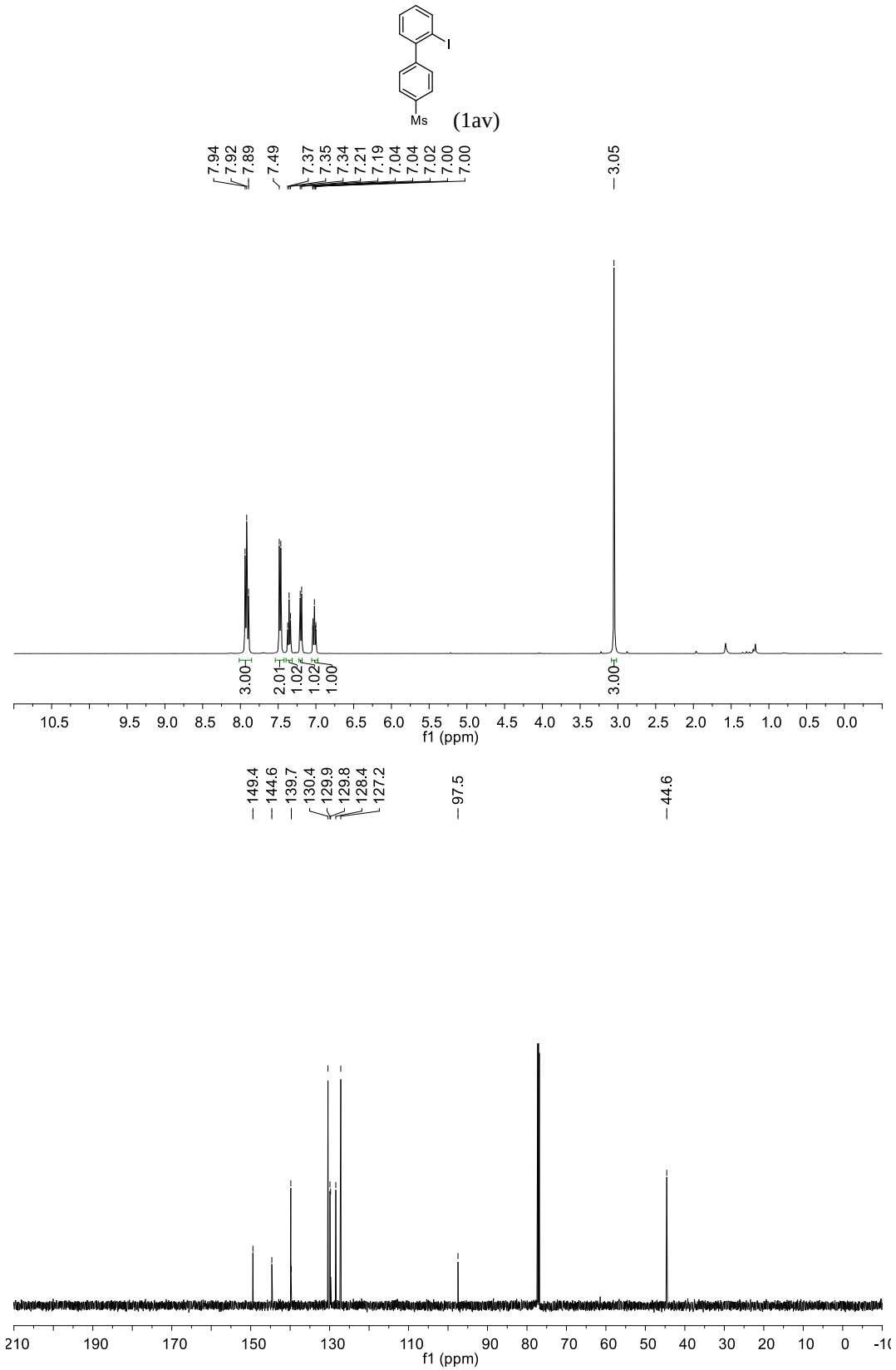
f1 (ppm)

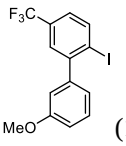


(1at)

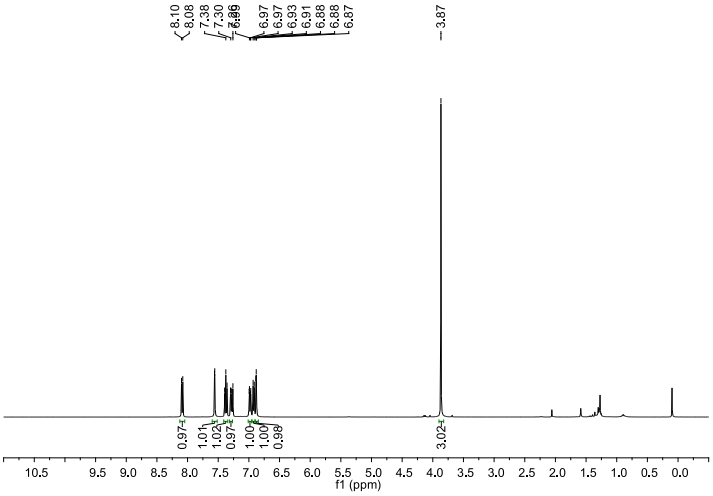

7.98
7.96
7.96
7.30
7.04
6.82
6.75
5.86
5.81
5.33
5.30
1.00
2.02
1.04
3.00
1.00
1.00
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

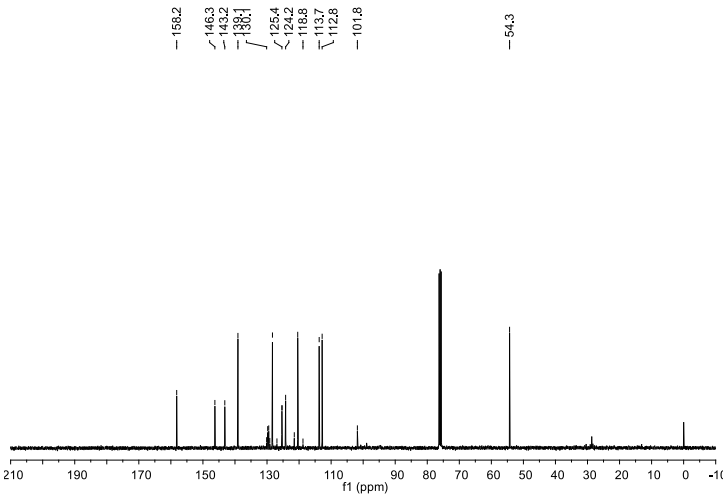

146.2
143.6
139.6
136.9
136.5
129.5
128.2
125.9
114.3
98.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

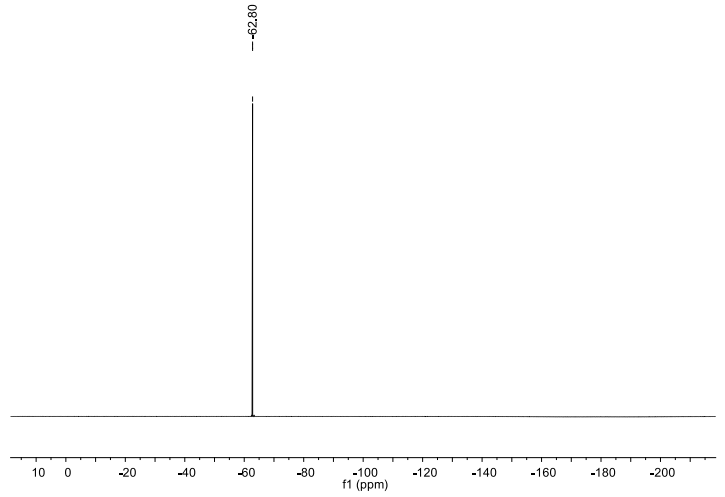

I
Ms
(1av)
7.94
7.92
7.89
7.49
7.37
7.35
7.34
7.21
7.19
7.04
7.04
7.02
7.00
7.00
3.05
3.00
2.01
1.02
1.02
1.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
149.4
144.6
139.7
130.4
129.9
129.8
128.4
127.2
97.5
44.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

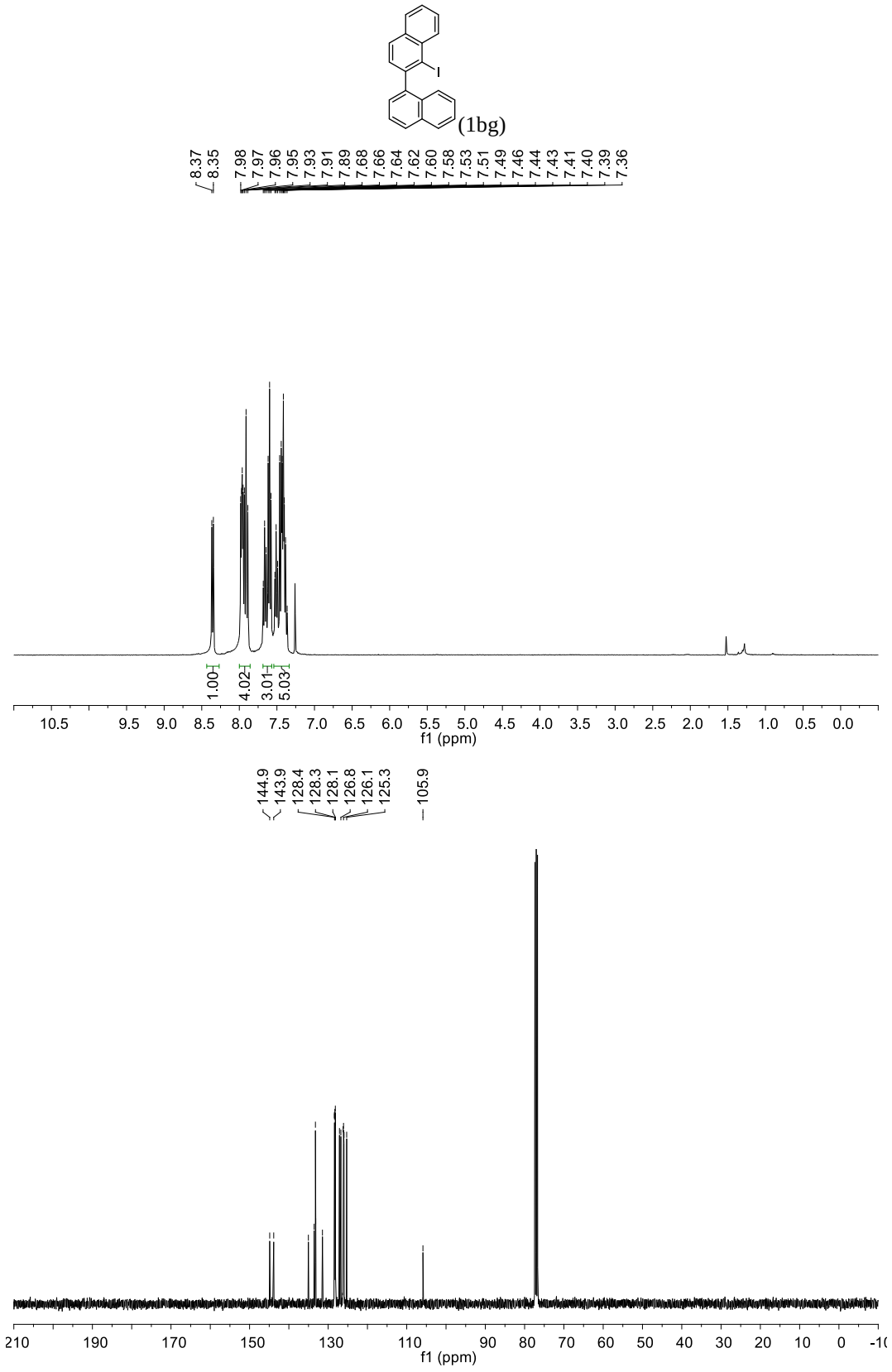

F3C
I
MeO

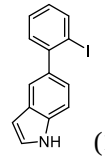
(1aw)


8.10
8.08
7.38
7.30
6.97
6.97
6.93
6.91
6.88
6.88
6.87
3.87
0.97
1.01
1.02
0.97
1.00
1.00
0.99
3.02
f1 (ppm)

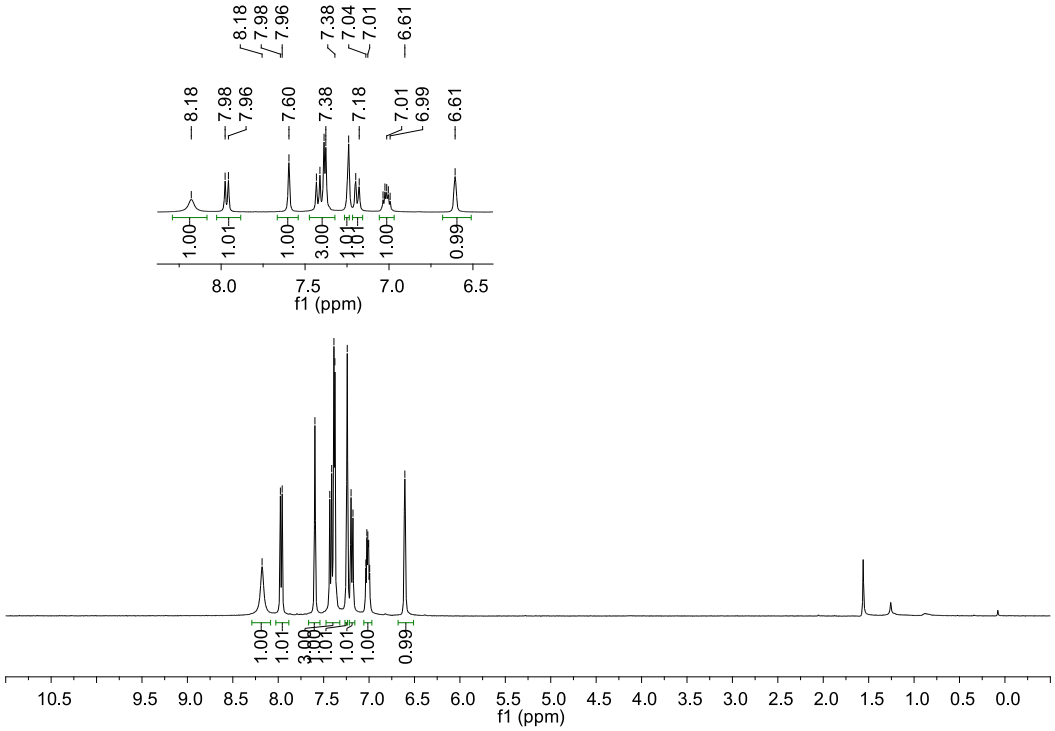

158.2
146.3
143.2
138.1
130.1
125.4
124.2
118.8
113.7
112.8
101.8
54.3
f1 (ppm)

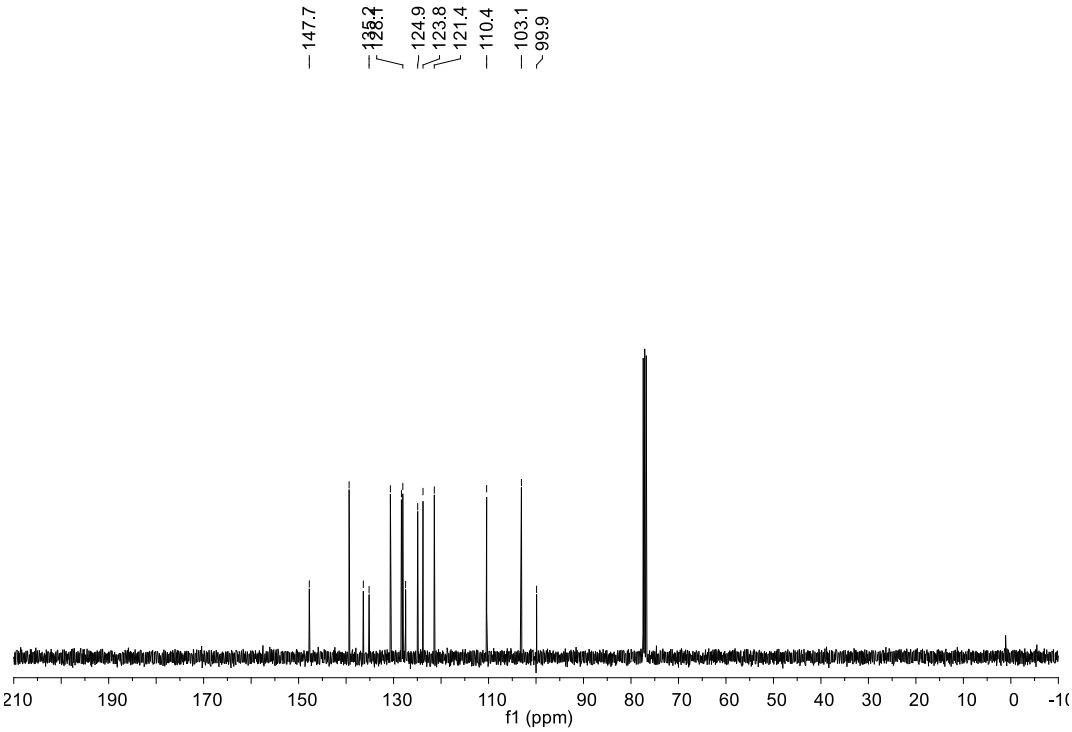

-62.80
f1 (ppm)

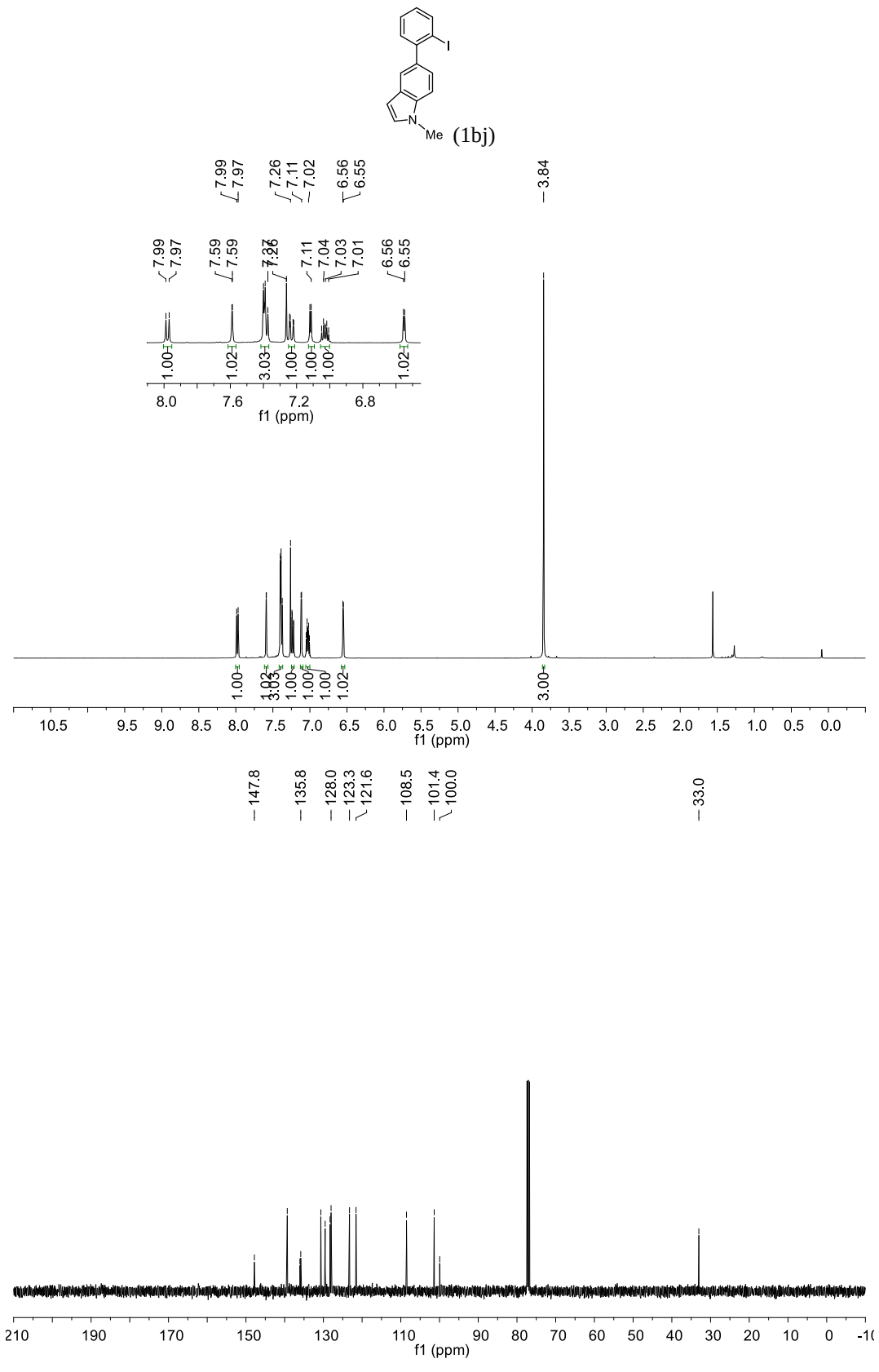

(1bg)
8.37
8.35
7.98
7.97
7.96
7.95
7.93
7.91
7.89
7.68
7.66
7.64
7.62
7.60
7.58
7.53
7.51
7.49
7.46
7.44
7.43
7.41
7.40
7.39
7.36
1.00
4.02
3.01
5.03
f1 (ppm)
144.9
143.9
128.4
128.3
128.1
126.8
126.1
125.3
105.9
f1 (ppm)

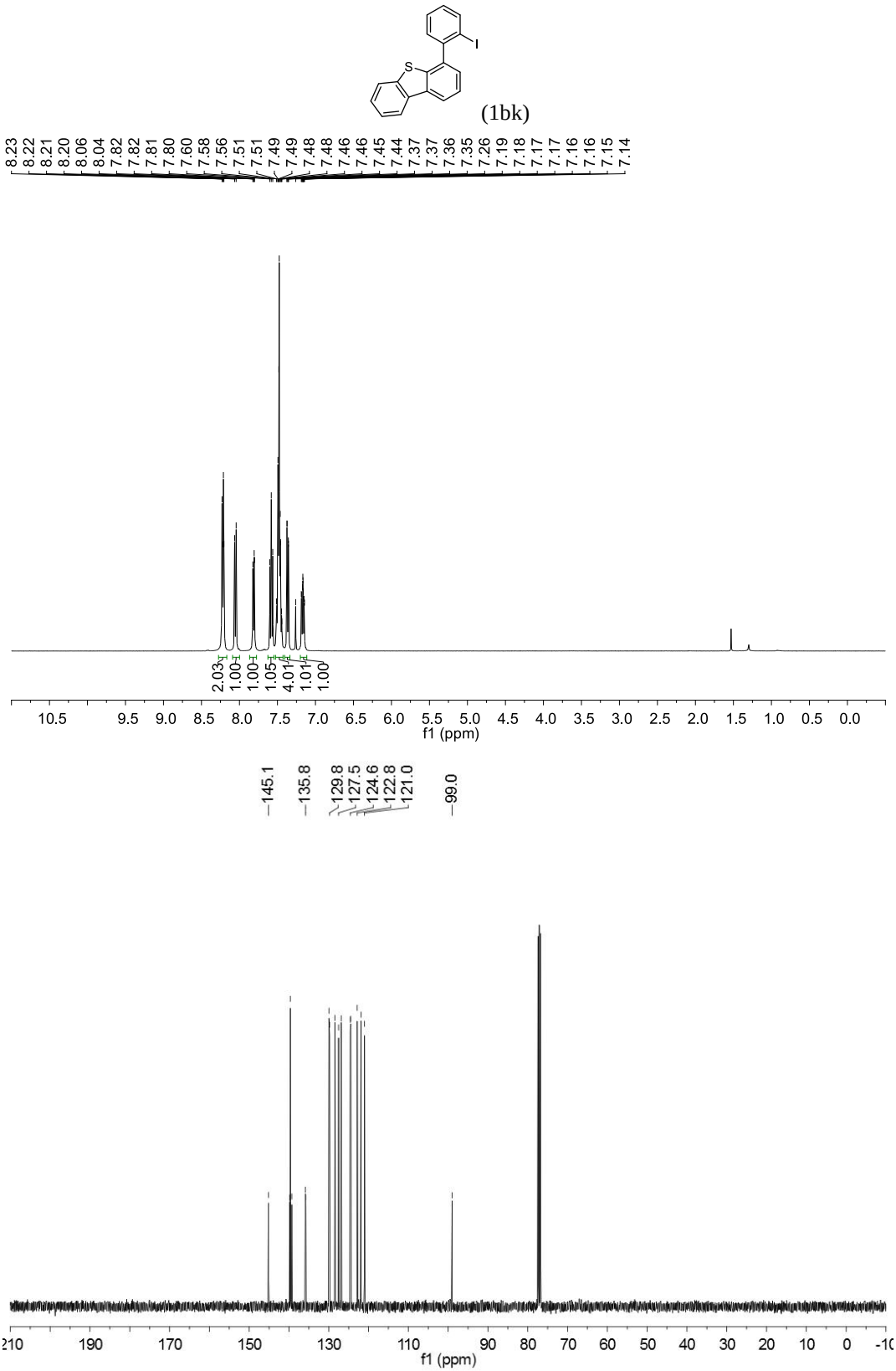

I
NH

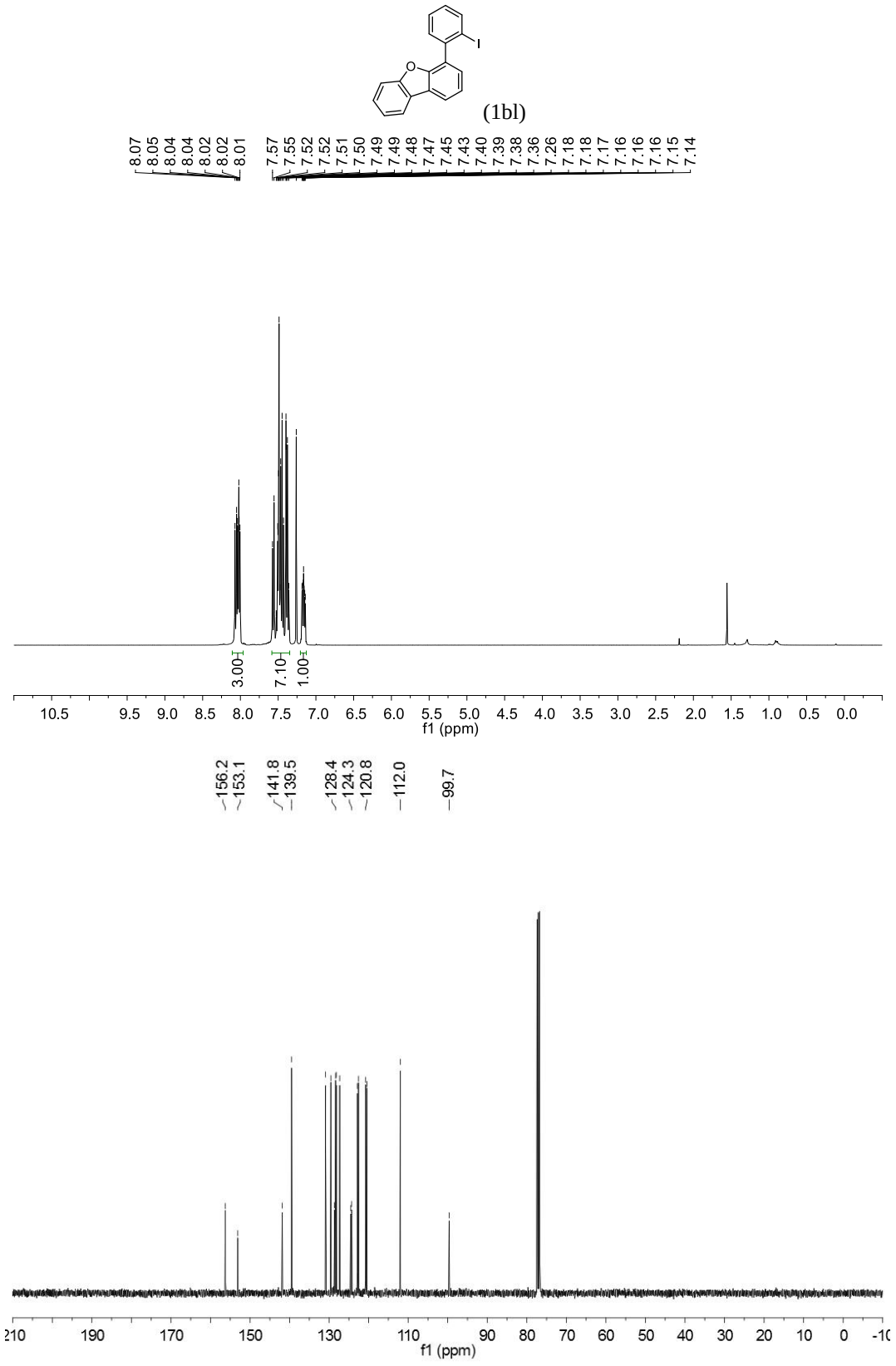
(1bi)


8.18
7.98
7.96
7.38
7.04
7.01
6.61
8.18
7.98
7.96
7.60
7.38
7.18
7.01
6.99
6.61
1.00
1.01
1.00
3.00
1.01
1.00
0.99
8.0
7.5
7.0
6.5
f1 (ppm)
1.00
1.01
1.00
0.99
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.7
124.9
123.8
121.4
110.4
103.1
99.9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

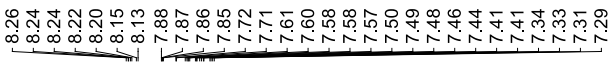

I
N
Me
(1bj)
7.99
7.97
7.26
7.11
7.02
6.56
6.55
3.84
7.59
7.59
7.37
7.26
7.04
7.03
7.01
1.00
1.02
3.03
1.00
1.00
1.00
1.02
8.0
7.6
7.2
6.8
f1 (ppm)
1.00
1.03
3.05
1.00
1.00
1.00
1.02
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
147.8
135.8
128.0
123.3
121.6
108.5
101.4
100.0
33.0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

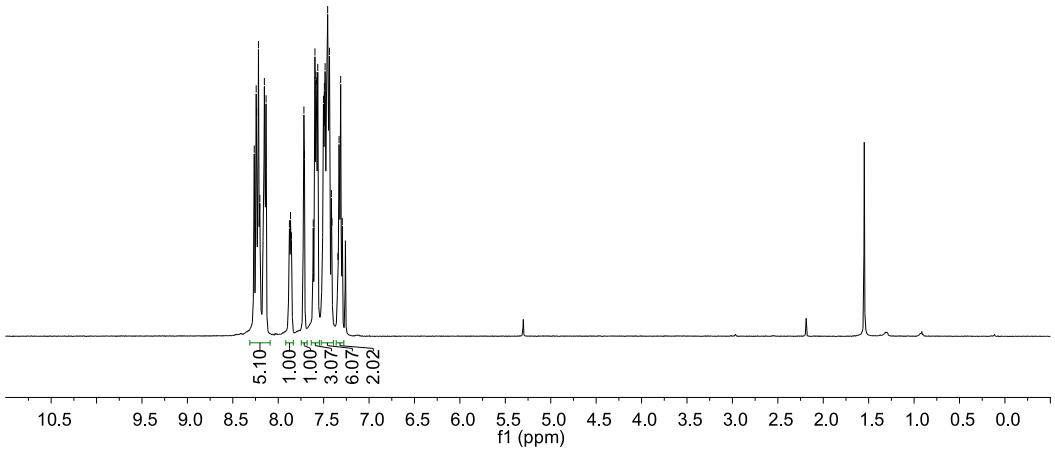

I
S
(1bk)
8.23
8.22
8.21
8.20
8.06
8.04
7.82
7.82
7.81
7.80
7.60
7.58
7.56
7.51
7.51
7.49
7.49
7.48
7.48
7.46
7.46
7.45
7.44
7.37
7.37
7.36
7.35
7.26
7.19
7.18
7.17
7.17
7.16
7.15
7.14
2.03
1.00
1.00
1.05
4.01
1.01
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
145.1
135.8
129.8
127.5
124.6
122.8
121.0
99.0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

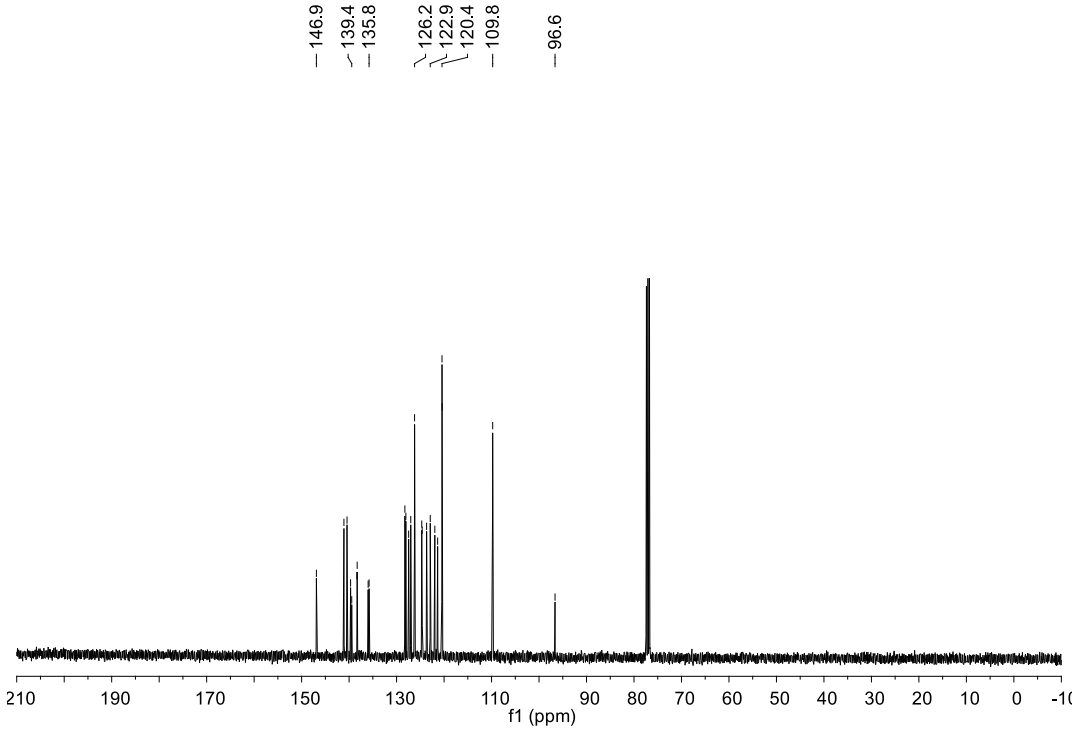

(1bl)
8.07
8.05
8.04
8.04
8.02
8.02
8.01
7.57
7.55
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.45
7.43
7.40
7.39
7.38
7.36
7.26
7.18
7.18
7.17
7.16
7.16
7.16
7.15
7.14
3.00
7.10
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
156.2
153.1
141.8
139.5
128.4
124.3
120.8
112.0
99.7
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
I
S

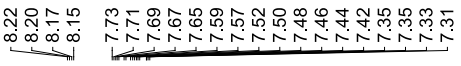
(1bm)

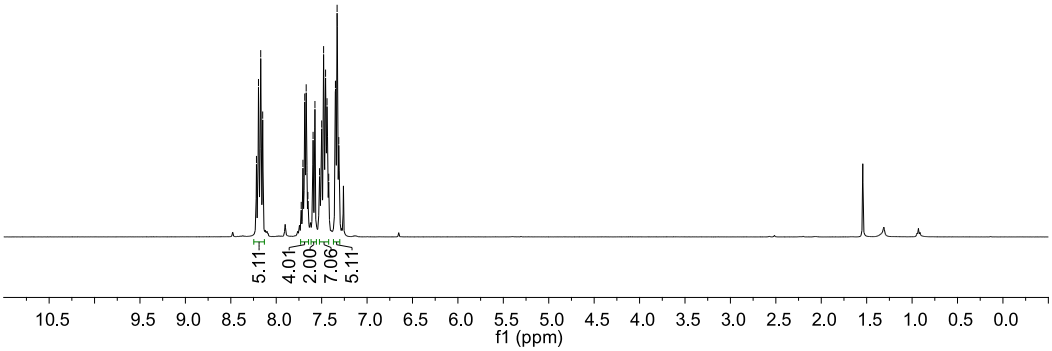

8.26
8.24
8.24
8.22
8.20
8.15
8.13
7.88
7.87
7.86
7.85
7.72
7.71
7.61
7.60
7.58
7.58
7.57
7.50
7.49
7.48
7.46
7.44
7.41
7.41
7.34
7.33
7.31
7.29

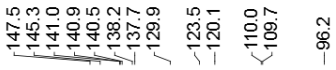

5.10
1.00
1.00
3.07
6.07
2.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

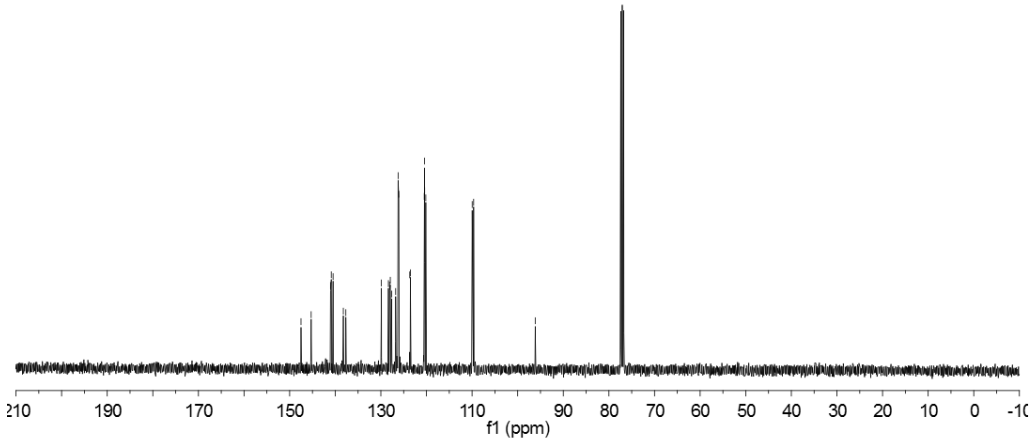

146.9
139.4
135.8
126.2
122.9
120.4
109.8
96.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

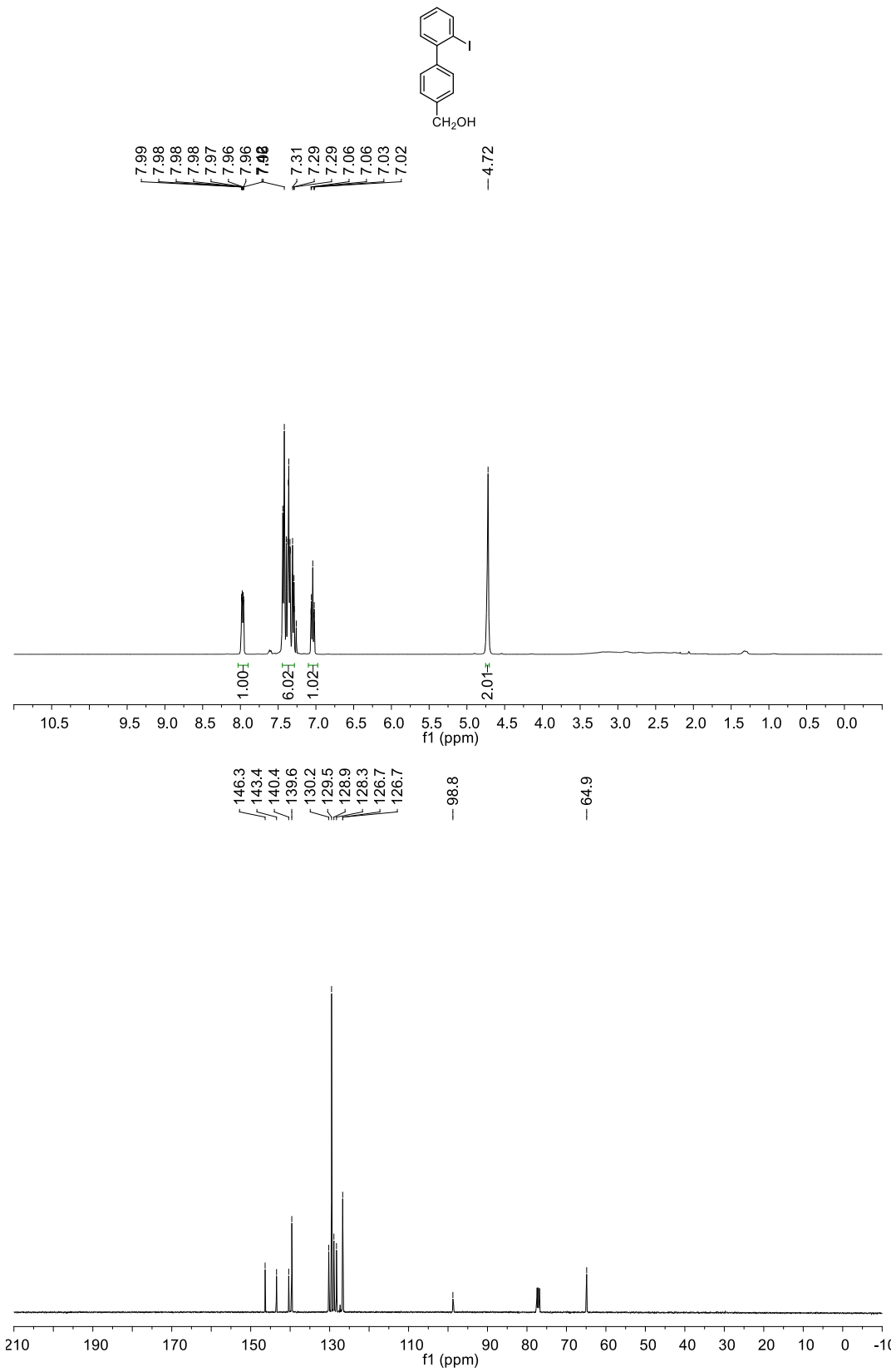
(1bn)

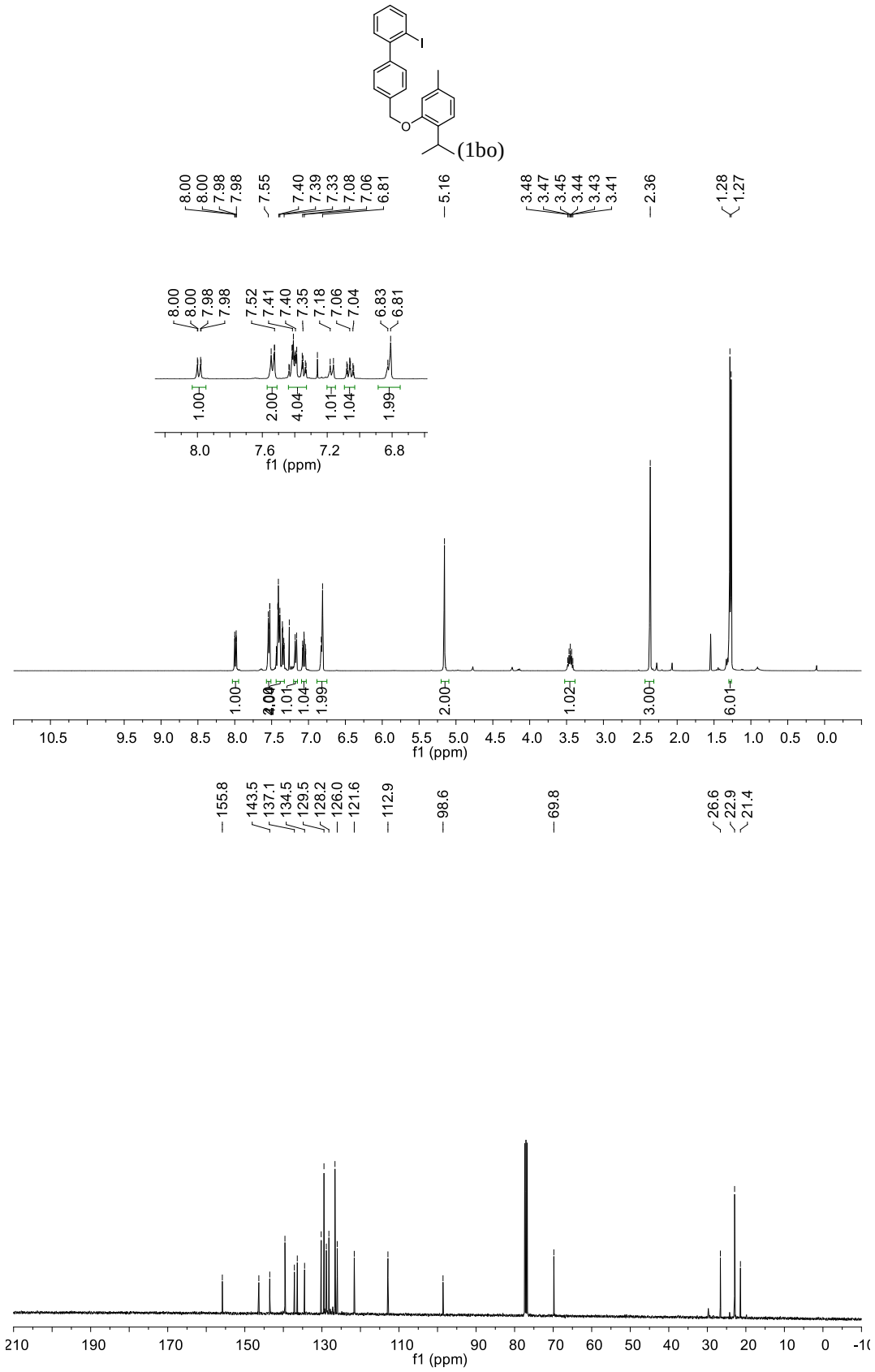

8.22
8.20
8.17
8.15
7.73
7.71
7.69
7.67
7.65
7.59
7.57
7.52
7.50
7.48
7.46
7.44
7.42
7.35
7.35
7.33
7.31

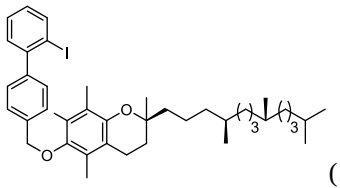

5.11
4.01
2.00
7.06
5.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.5
145.3
141.0
140.9
140.5
138.2
137.7
129.9
123.5
120.1
110.0
109.7
96.2

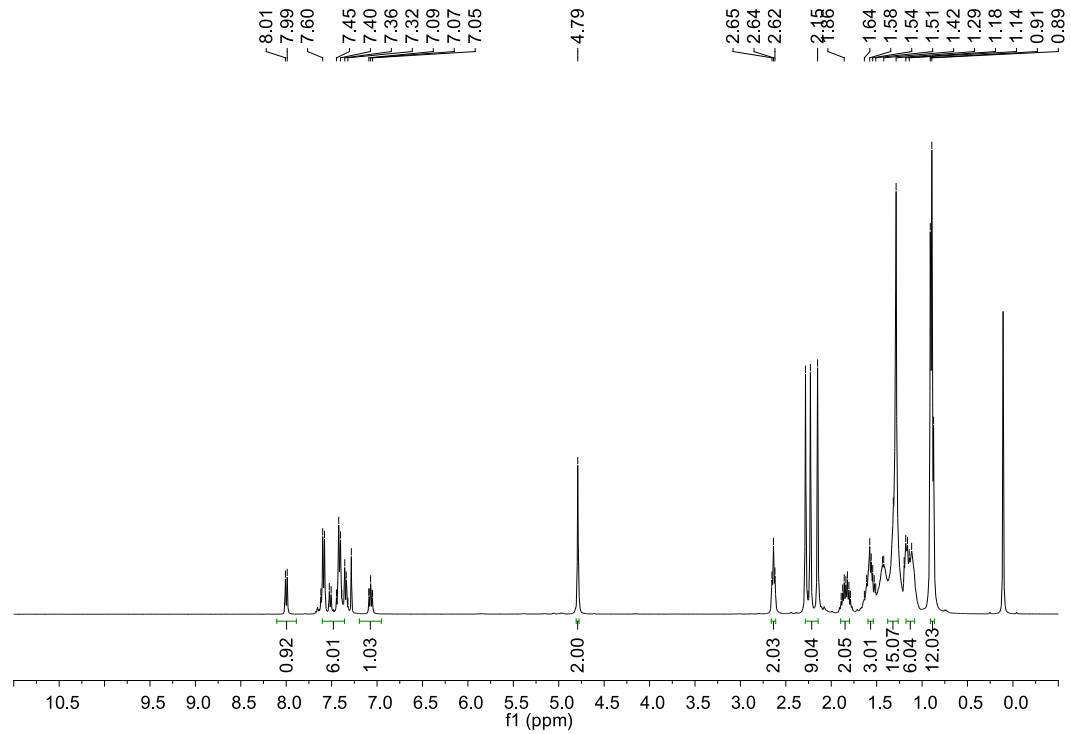

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

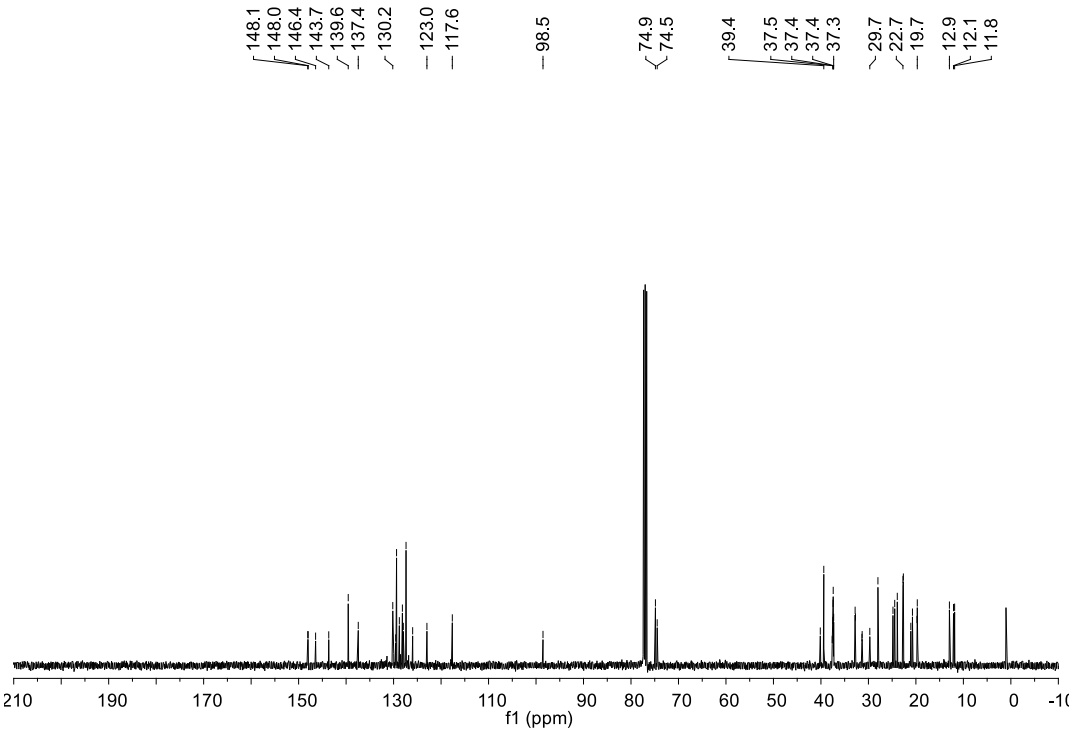

I
CH2OH
7.99
7.98
7.98
7.98
7.97
7.96
7.96
7.31
7.29
7.29
7.06
7.06
7.03
7.02
4.72
1.00
6.02
1.02
2.01
f1 (ppm)
146.3
143.4
140.4
139.6
130.2
129.5
128.9
128.3
126.7
126.7
98.8
64.9
f1 (ppm)

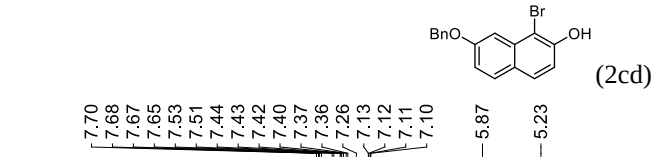

(1bo)
8.00
8.00
7.98
7.98
7.55
7.40
7.39
7.33
7.08
7.06
6.81
5.16
3.48
3.47
3.45
3.44
3.43
3.41
2.36
1.28
1.27
7.52
7.41
7.40
7.35
7.18
7.06
7.04
6.83
6.81
1.00
2.00
4.04
1.01
1.04
1.99
f1 (ppm)
2.00
1.02
3.00
6.01
155.8
143.5
137.1
134.5
129.5
128.2
126.0
121.6
112.9
98.6
69.8
26.6
22.9
21.4



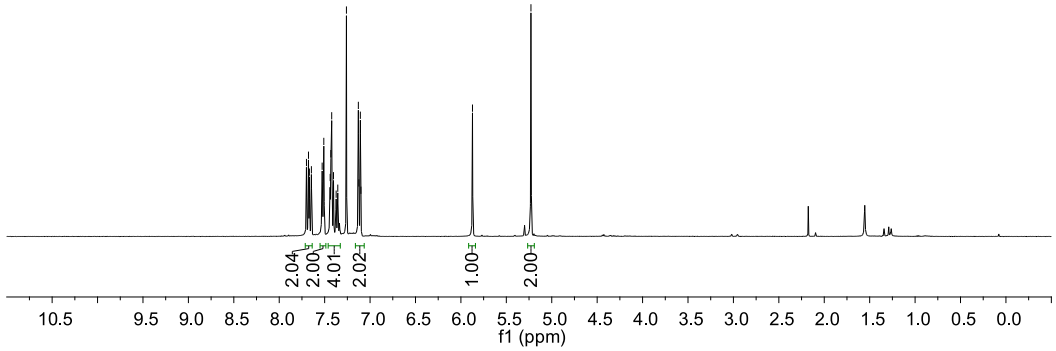
(1bp)

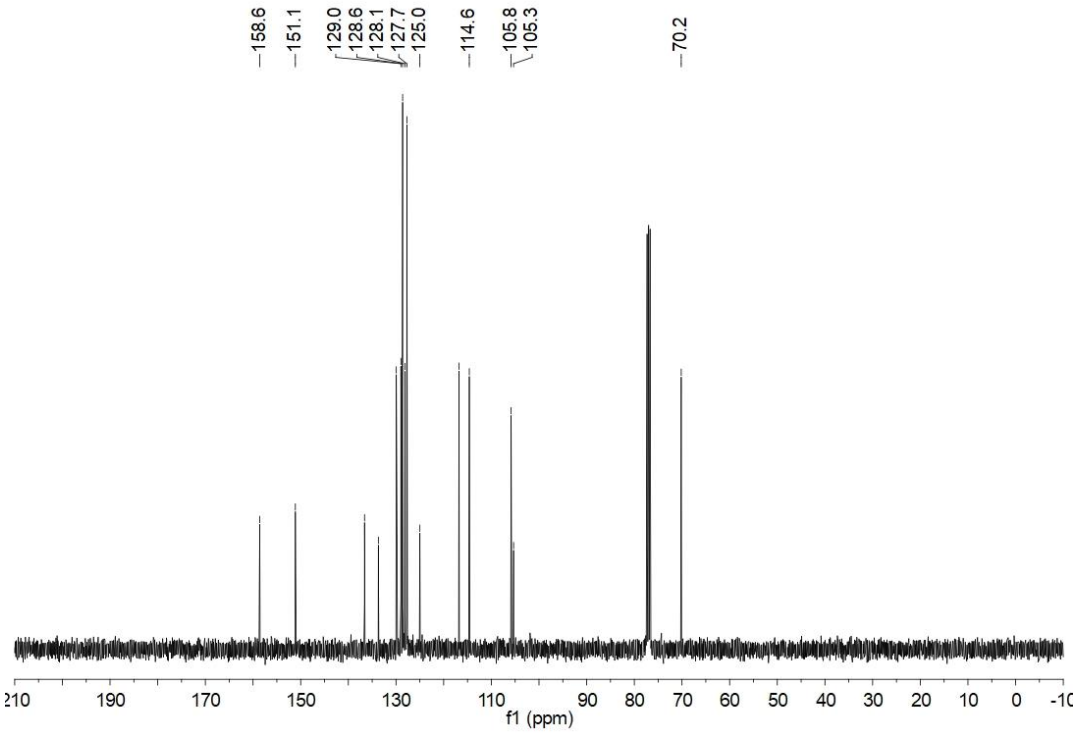

8.01
7.99
7.60
7.45
7.40
7.36
7.32
7.09
7.07
7.05
4.79
2.65
2.64
2.62
1.64
1.58
1.54
1.51
1.42
1.29
1.18
1.14
0.91
0.89
0.92
6.01
1.03
2.00
2.03
9.04
2.05
3.01
15.07
6.04
12.03
f1 (ppm)

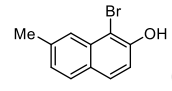

148.1
148.0
146.4
143.7
139.6
137.4
130.2
123.0
117.6
98.5
74.9
74.5
39.4
37.5
37.4
37.4
37.3
29.7
22.7
19.7
12.9
12.1
11.8
f1 (ppm)


Br
BnO
OH
7.70
7.68
7.67
7.65
7.53
7.51
7.44
7.43
7.42
7.40
7.37
7.36
7.26
7.13
7.12
7.11
7.10
5.87
5.23

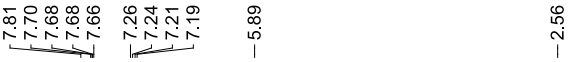
(2cd)

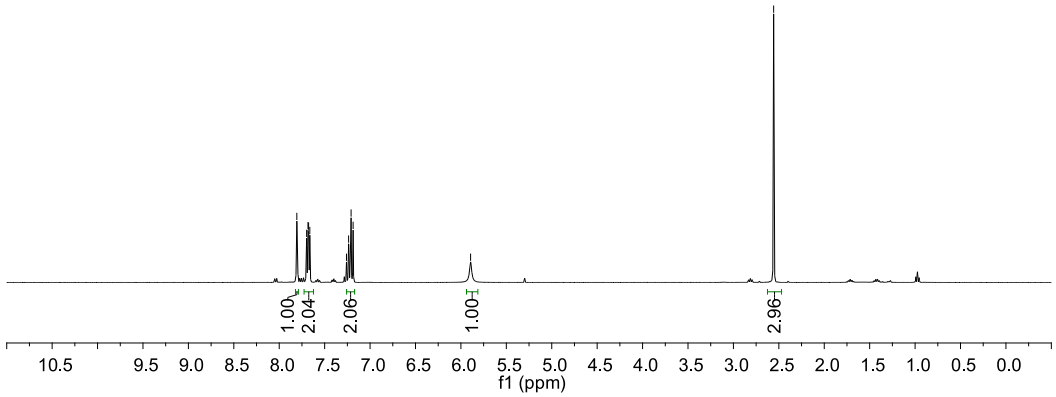

2.04
2.00
4.01
2.02
1.00
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.6
151.1
129.0
128.6
128.1
127.7
125.0
114.6
105.8
105.3
70.2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

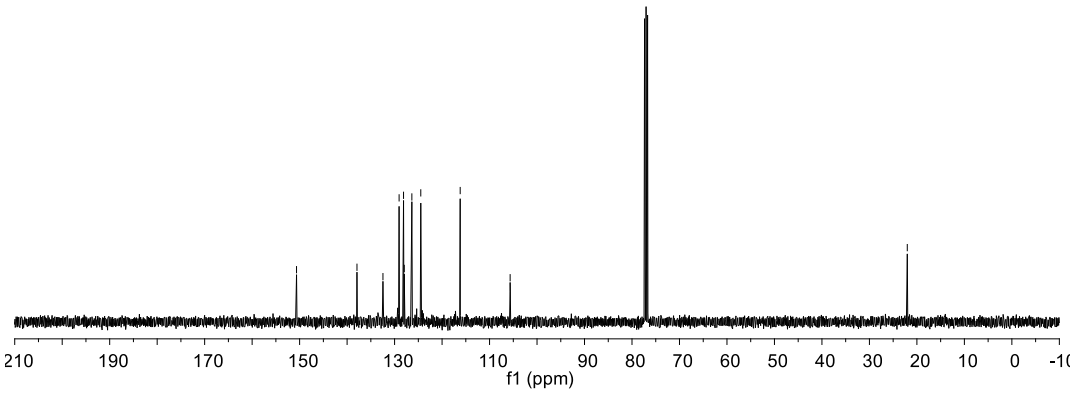

Br
Me
OH

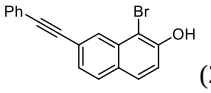
(2ce)


7.81
7.70
7.68
7.68
7.66
7.26
7.24
7.21
7.19
5.89
2.56

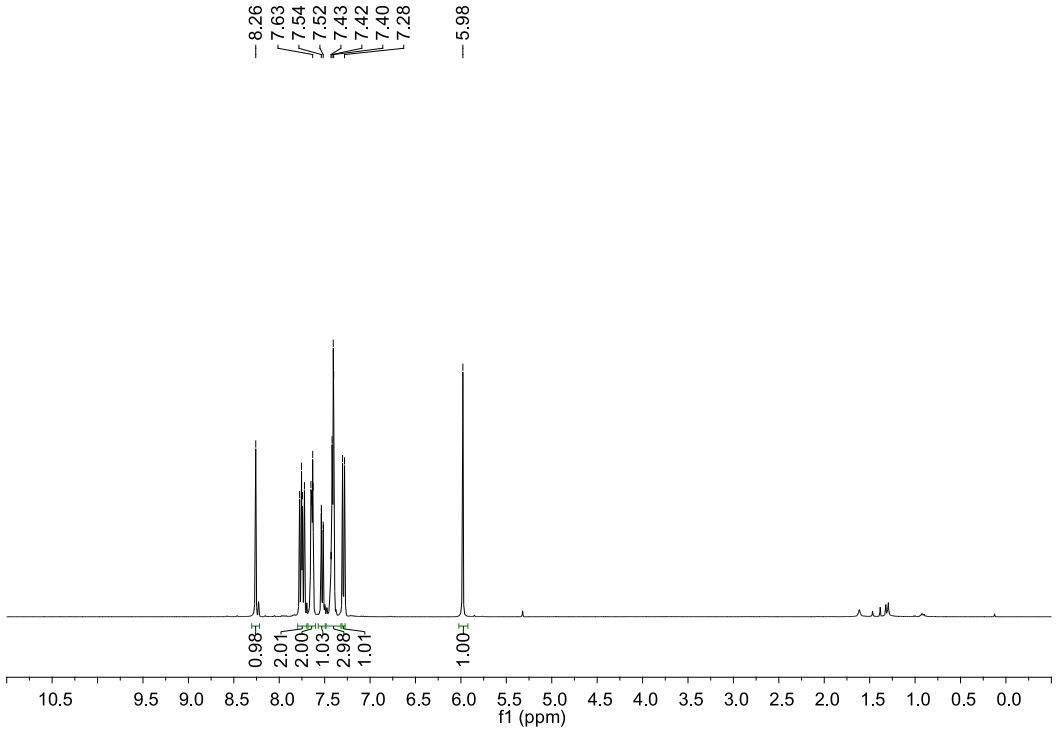

1.00
2.04
2.06
1.00
2.96
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

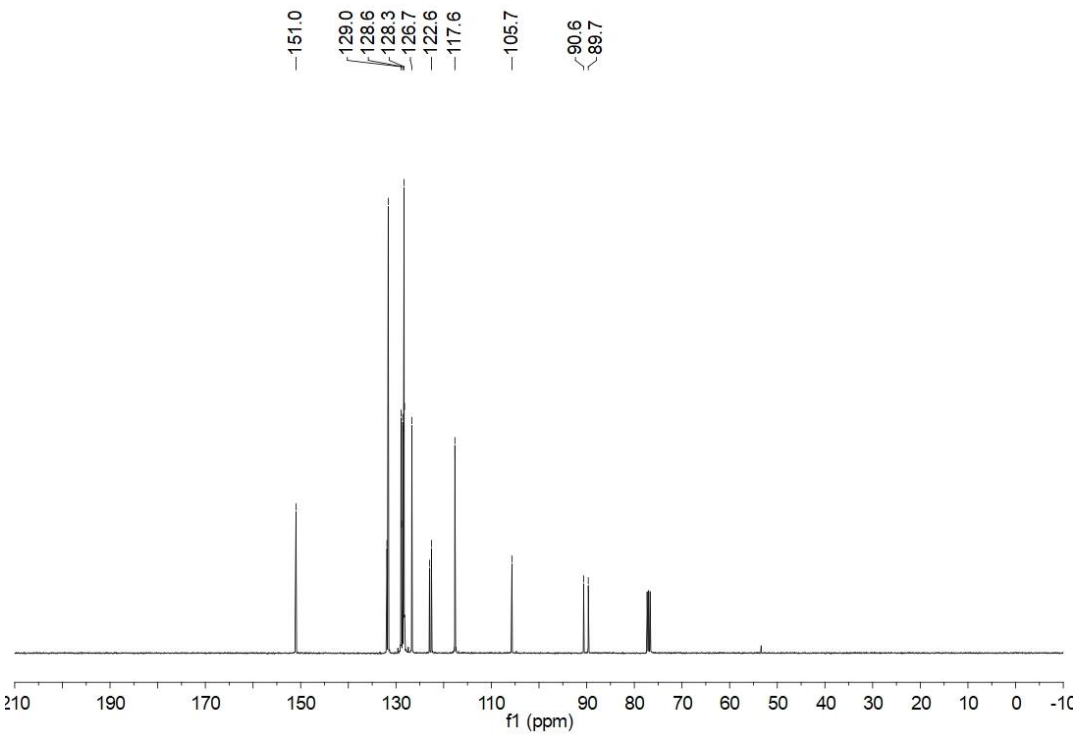

150.6
137.9
128.1
124.5
116.2
105.7
22.0

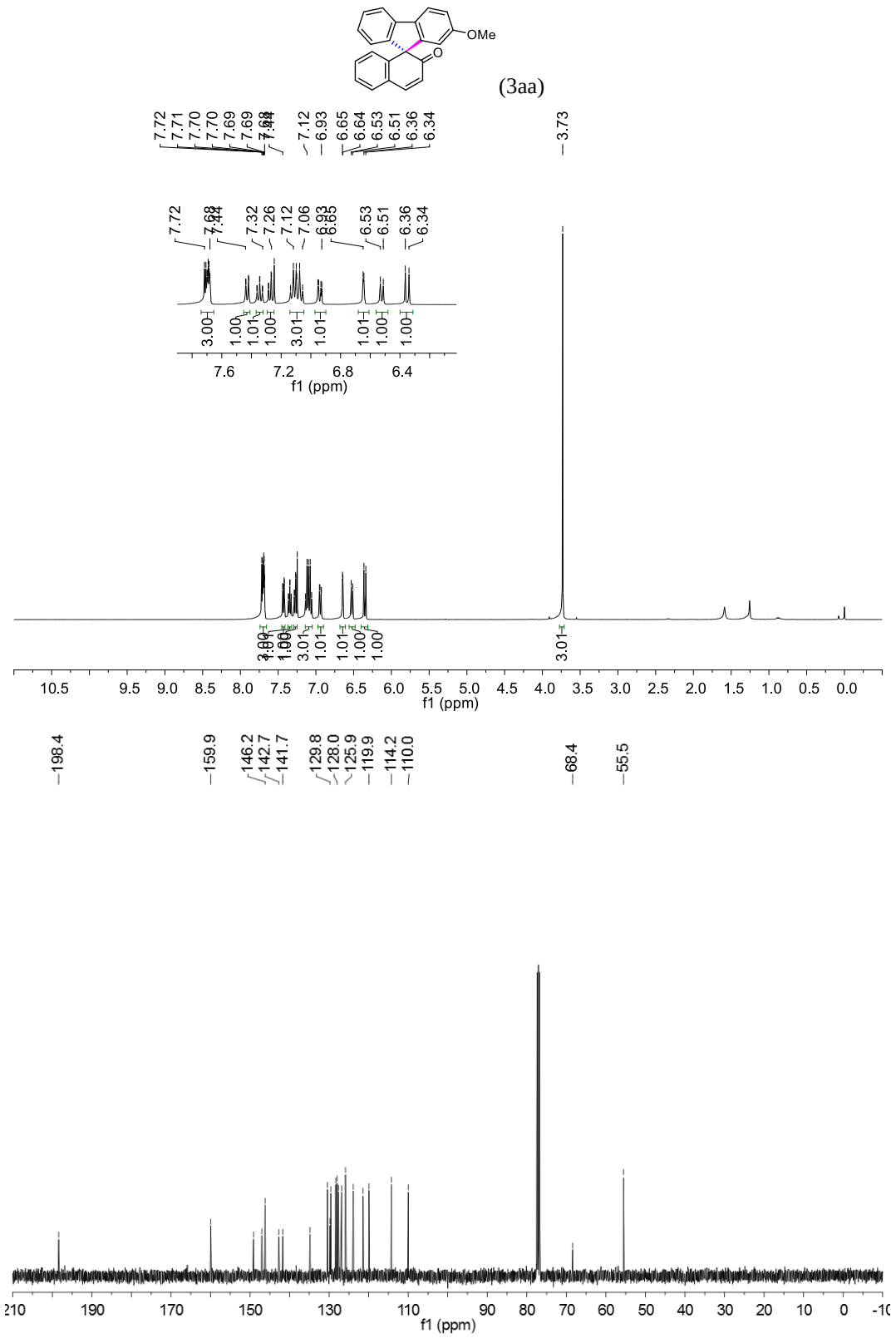

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

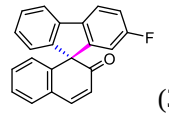

Ph
Br
OH

(2cf)

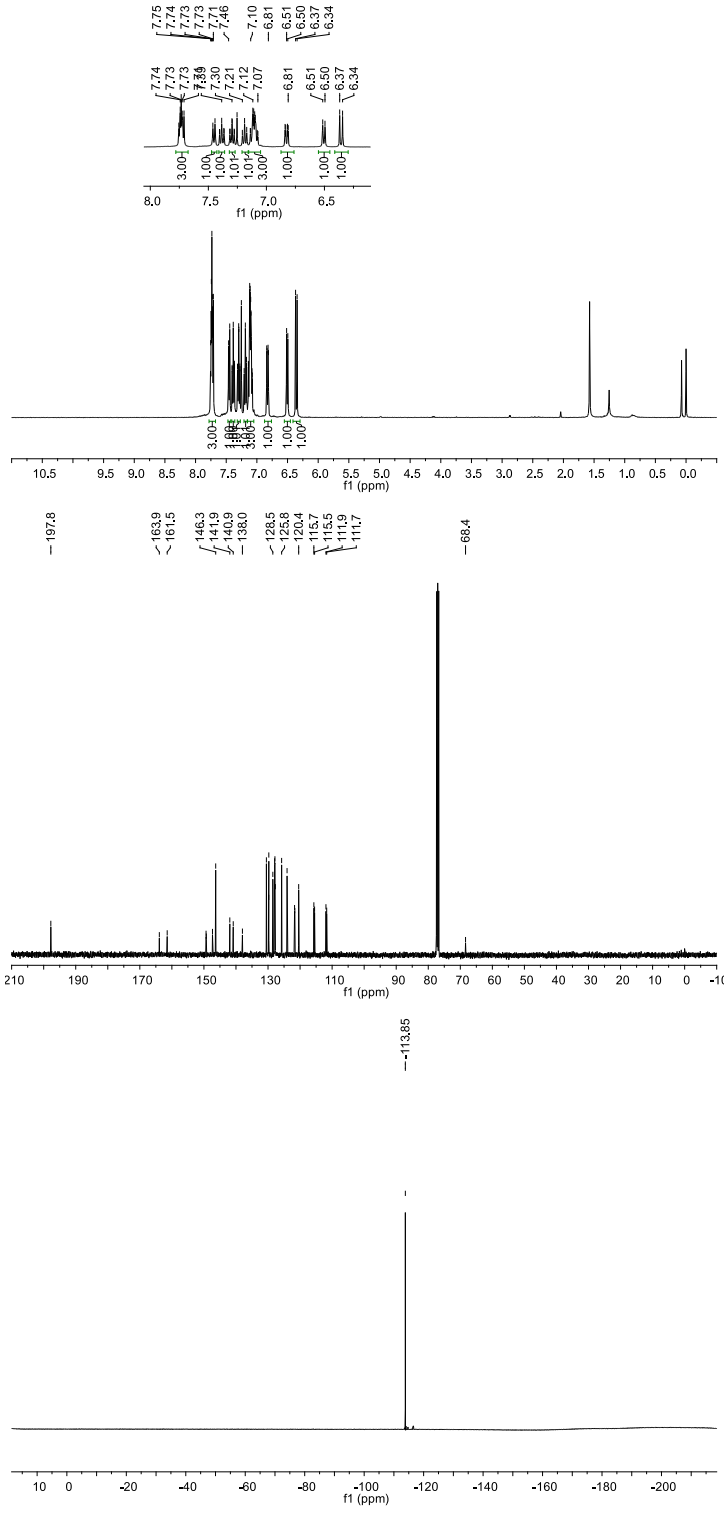

8.26
7.63
7.54
7.52
7.43
7.42
7.40
7.28
5.98
0.98
2.01
2.00
1.03
2.98
1.01
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.0
129.0
128.6
128.3
126.7
122.6
117.6
105.7
90.6
89.7
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

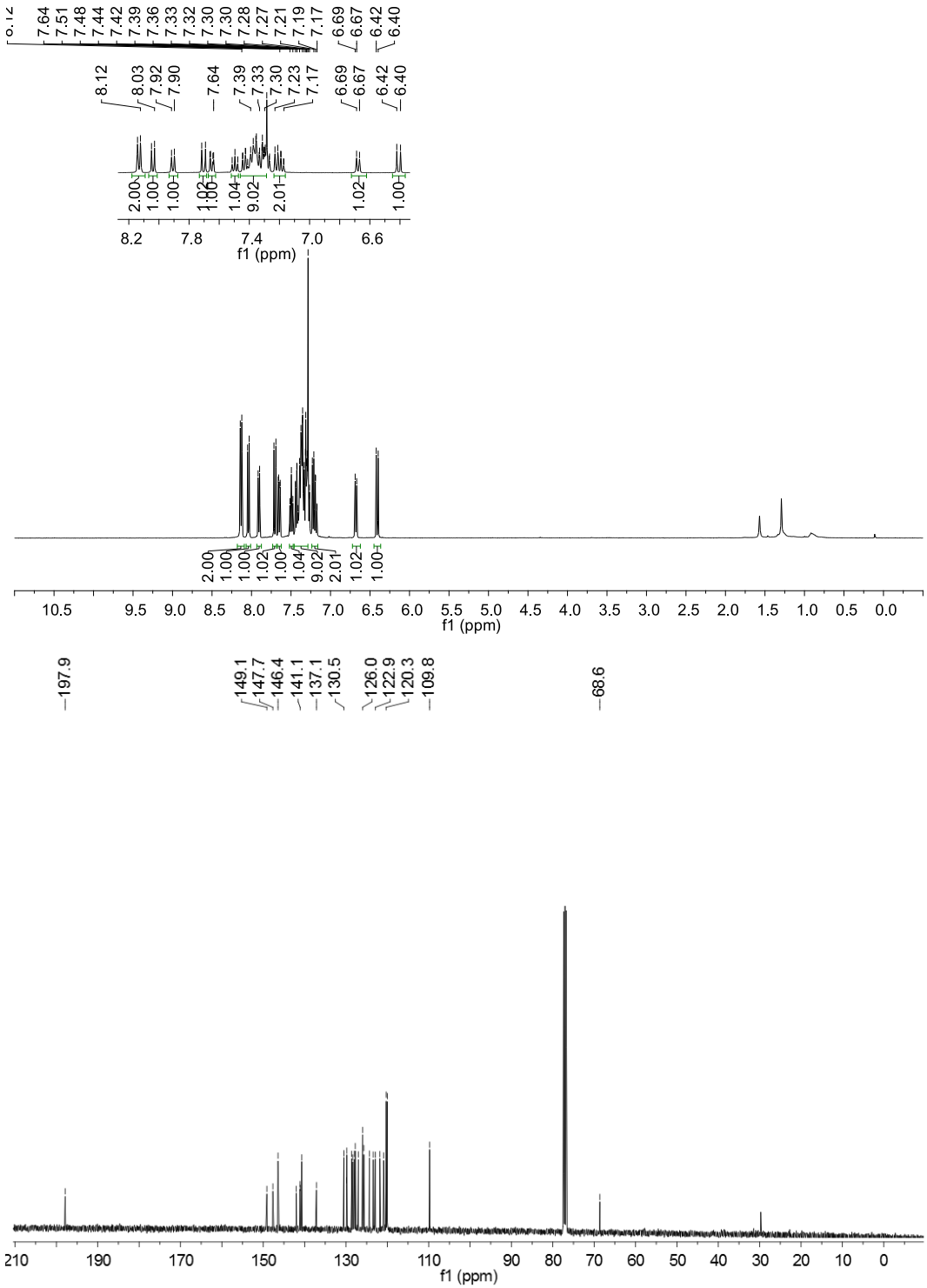

OMe
O
(3aa)
7.72
7.71
7.70
7.69
7.12
6.93
6.65
6.64
6.53
6.51
6.36
6.34
3.73
7.32
7.26
7.06
3.00
1.00
1.01
1.00
3.01
1.01
1.01
1.00
1.00
7.6
7.2
6.8
6.4
f1 (ppm)
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.4
159.9
146.2
142.7
141.7
129.8
128.0
125.9
119.9
114.2
110.0
68.4
55.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

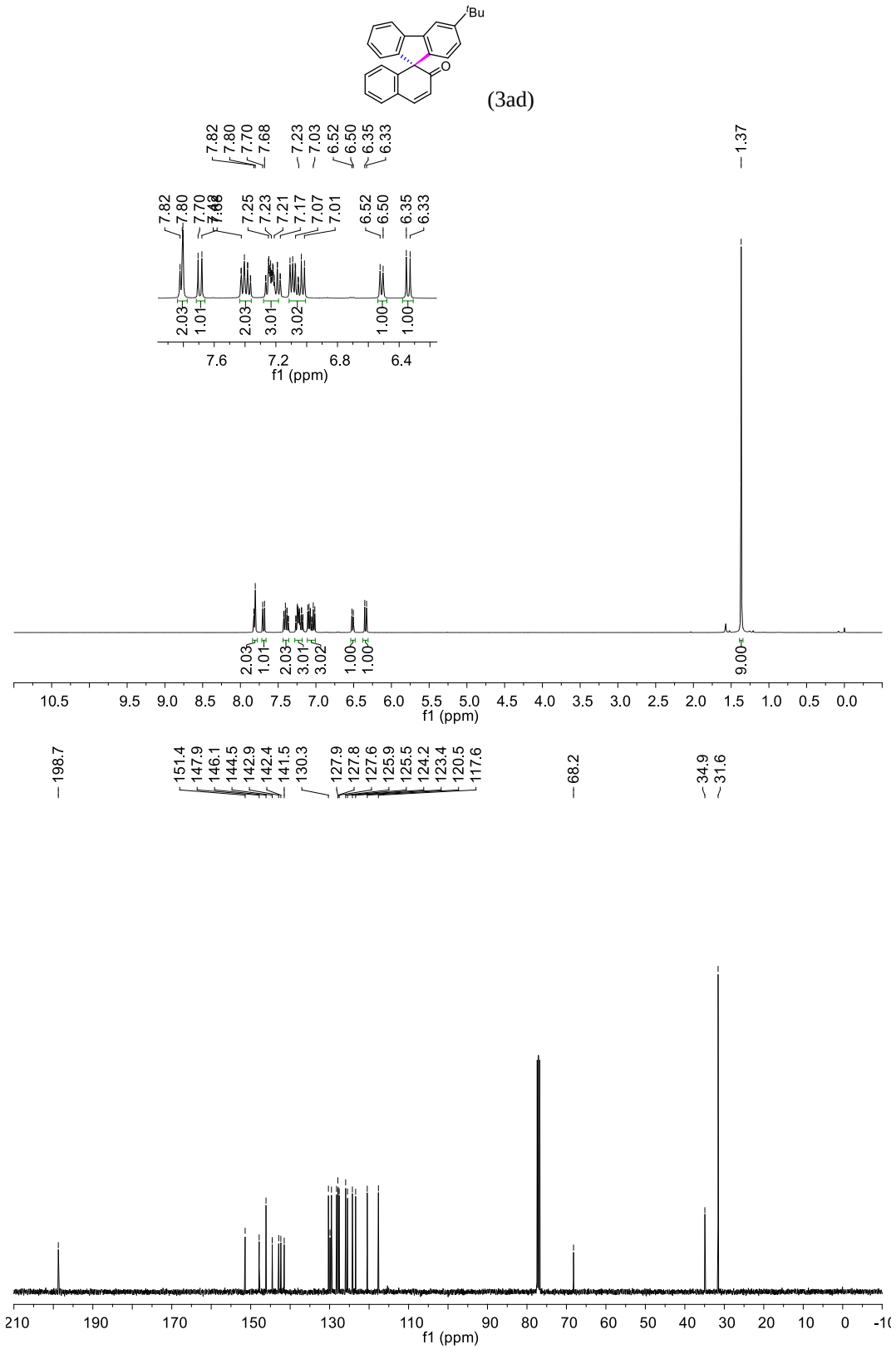

F
O

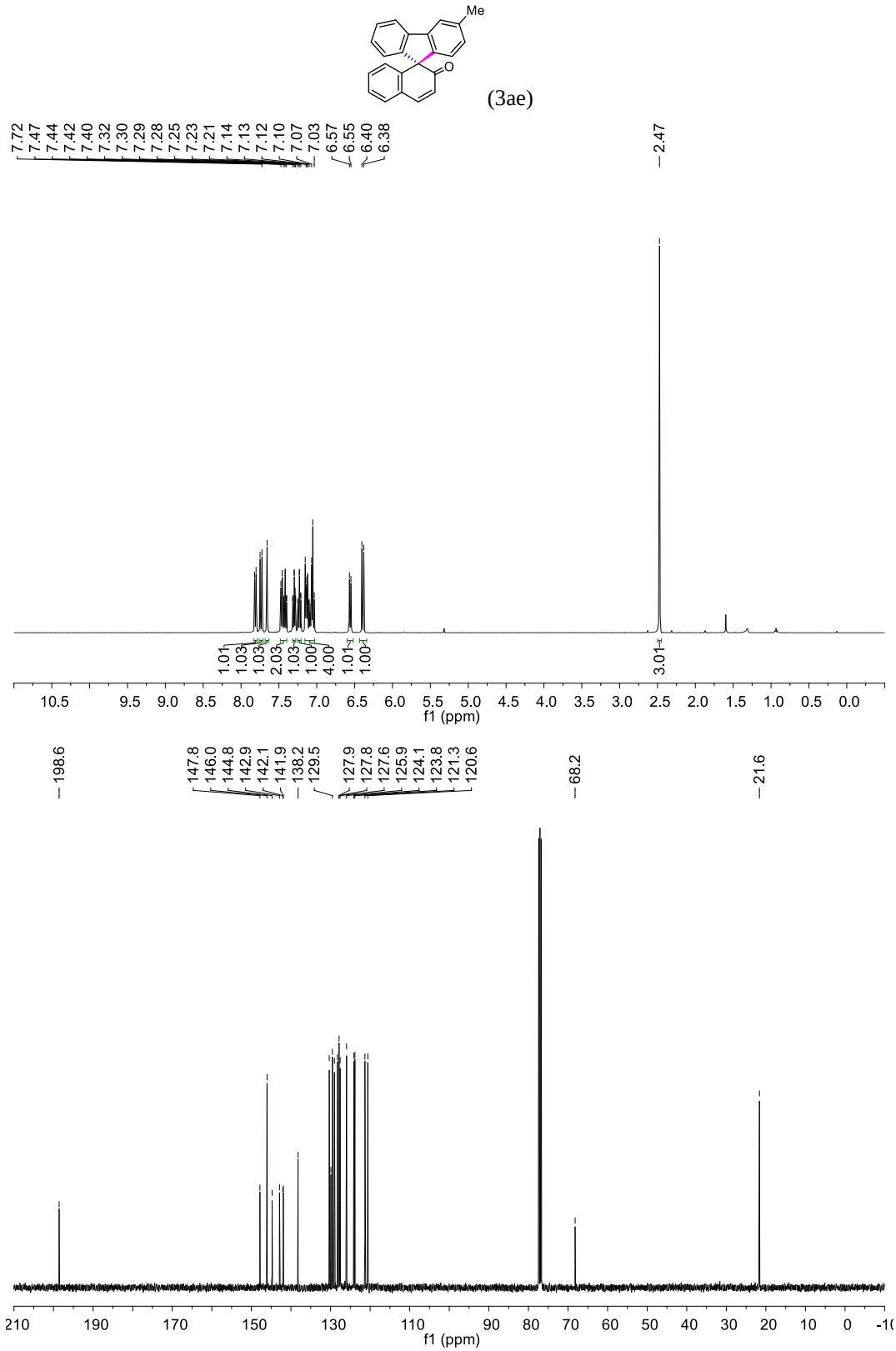
(3ab)

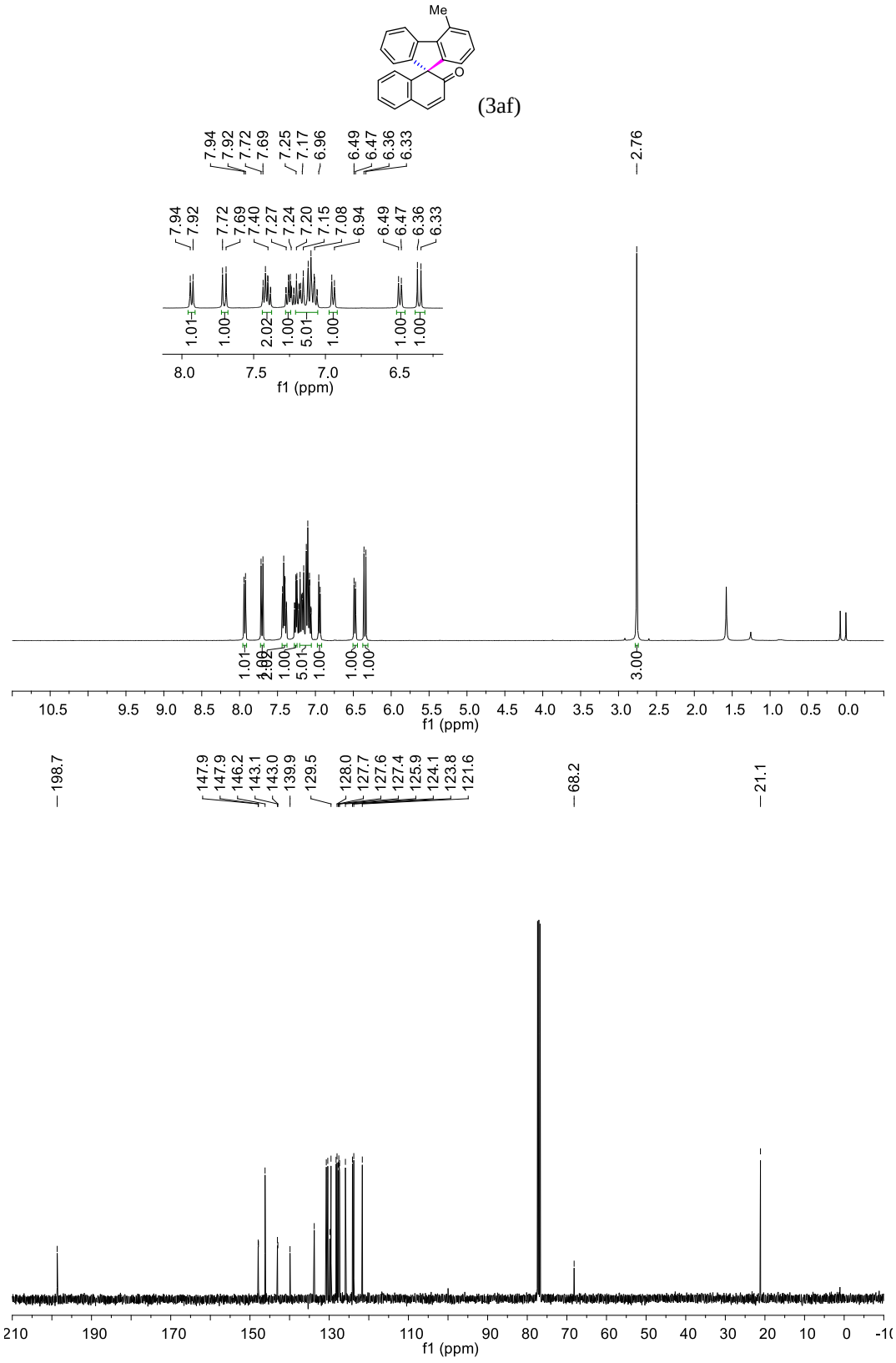

7.75
7.74
7.73
7.73
7.71
7.46
7.10
6.81
6.51
6.50
6.37
6.34
f1 (ppm)
197.8
163.9
161.5
146.3
141.9
140.9
138.0
128.5
125.8
120.4
115.7
115.5
111.9
111.7
68.4
-113.85

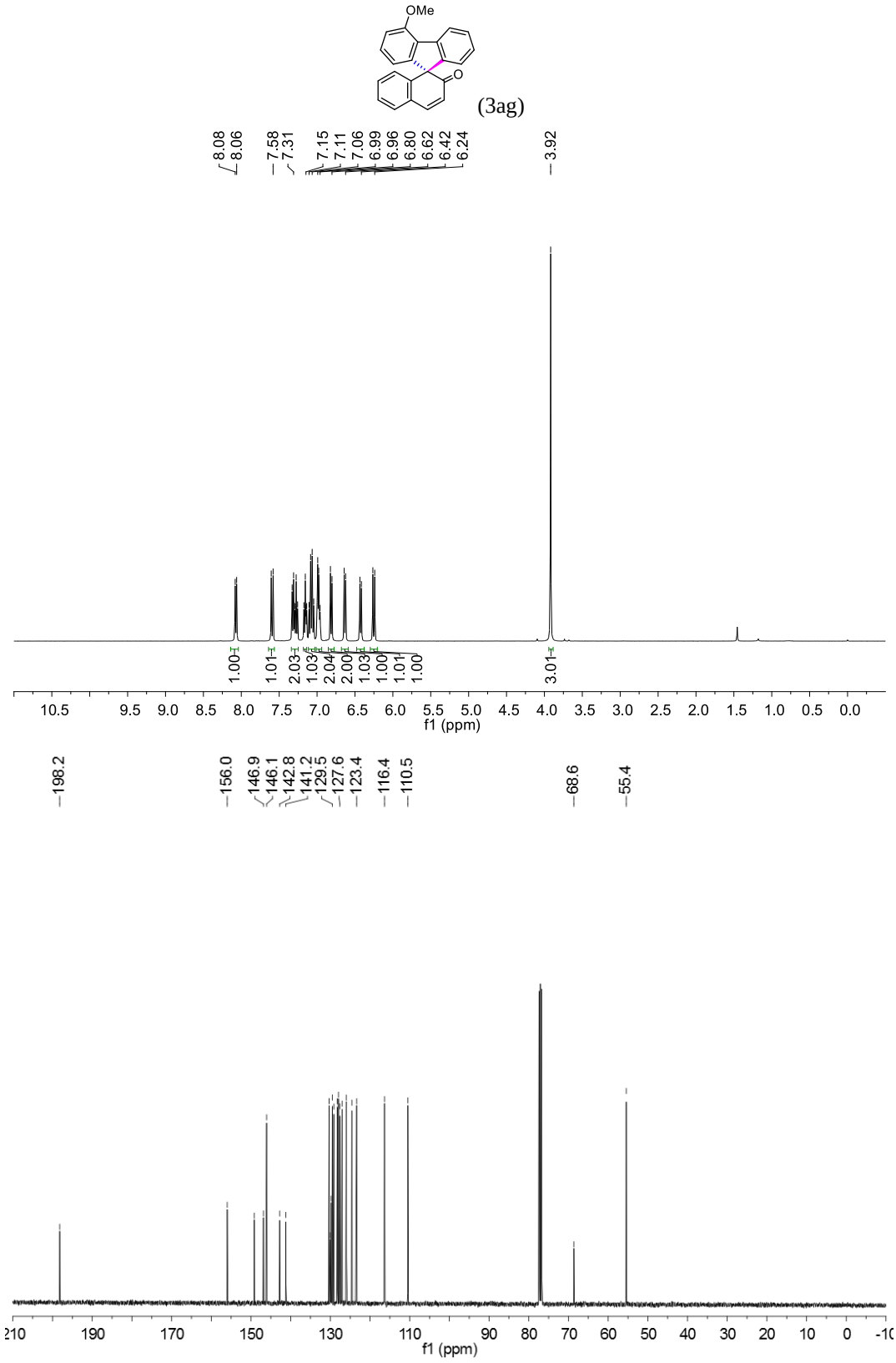
(3ac)

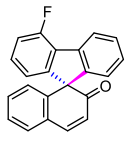

7.64
7.51
7.48
7.44
7.42
7.39
7.36
7.33
7.32
7.30
7.30
7.28
7.27
7.21
7.19
7.17
6.69
6.67
6.42
6.40
8.12
8.03
7.92
7.90
7.64
7.39
7.33
7.30
7.23
7.17
6.69
6.67
6.42
6.40
2.00
1.00
1.00
1.00
1.04
9.02
2.01
1.02
1.00
f1 (ppm)
2.00
1.00
1.00
1.02
1.00
1.04
9.02
2.01
1.02
1.00
f1 (ppm)
197.9
149.1
147.7
146.4
141.1
137.1
130.5
126.0
122.9
120.3
109.8
68.6
f1 (ppm)


tBu
O
(3ad)
7.82
7.80
7.70
7.68
7.23
7.03
6.52
6.50
6.35
6.33
1.37
7.25
7.23
7.21
7.17
7.07
7.01
2.03
1.01
2.03
3.01
3.02
1.00
1.00
9.00
f1 (ppm)
198.7
151.4
147.9
146.1
144.5
142.9
142.4
141.5
130.3
127.9
127.8
127.6
125.9
125.5
124.2
123.4
120.5
117.6
68.2
34.9
31.6

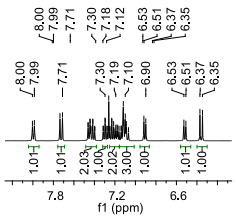

Me
O
(3ae)
7.72
7.47
7.44
7.42
7.40
7.32
7.30
7.29
7.28
7.25
7.23
7.21
7.14
7.13
7.12
7.10
7.07
7.03
6.57
6.55
6.40
6.38
2.47
1.01
1.03
1.03
2.03
1.03
1.00
4.00
1.01
1.00
3.01
f1 (ppm)
198.6
147.8
146.0
144.8
142.9
142.1
141.9
138.2
129.5
127.9
127.8
127.6
125.9
124.1
123.8
121.3
120.6
68.2
21.6
f1 (ppm)

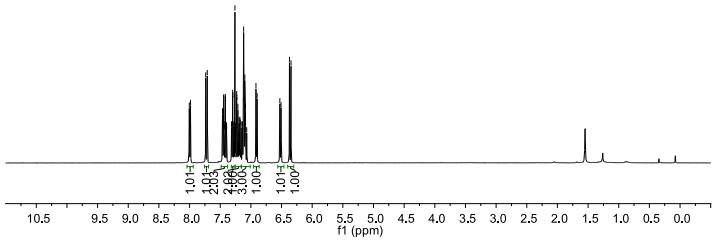

Me
O
(3af)
7.94
7.92
7.72
7.69
7.25
7.17
6.96
6.49
6.47
6.36
6.33
2.76
1.01
1.00
2.02
1.00
5.01
1.00
1.00
1.00
3.00
f1 (ppm)
198.7
147.9
147.9
146.2
143.1
143.0
139.9
129.5
128.0
127.7
127.6
127.4
125.9
124.1
123.8
121.6
68.2
21.1
f1 (ppm)

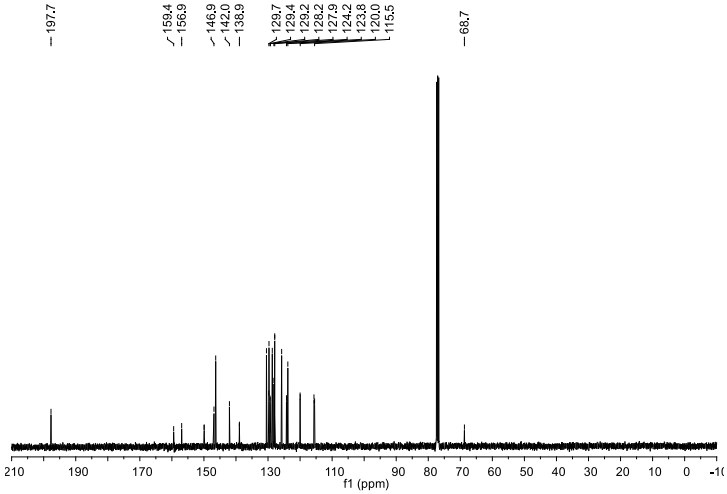

OMe
O
(3ag)
8.08
8.06
7.58
7.31
7.15
7.11
7.06
6.99
6.96
6.80
6.62
6.42
6.24
3.92
1.00
1.01
2.03
1.03
2.04
2.00
1.03
1.00
1.01
1.00
3.01
f1 (ppm)
198.2
156.0
146.9
146.1
142.8
141.2
129.5
127.6
123.4
116.4
110.5
68.6
55.4
f1 (ppm)

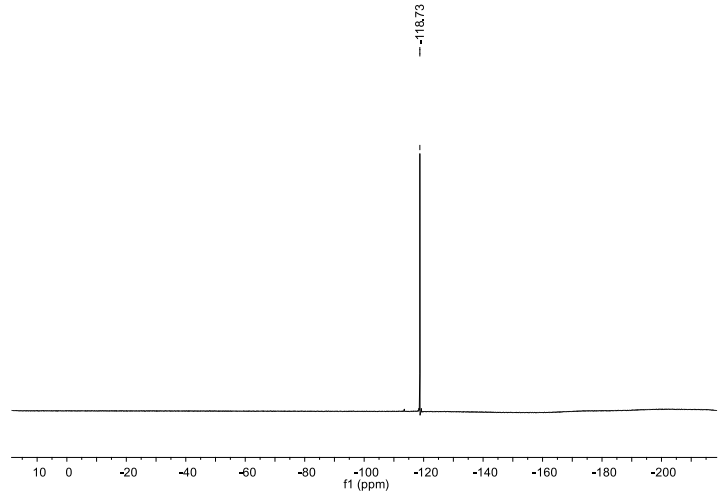

F
O

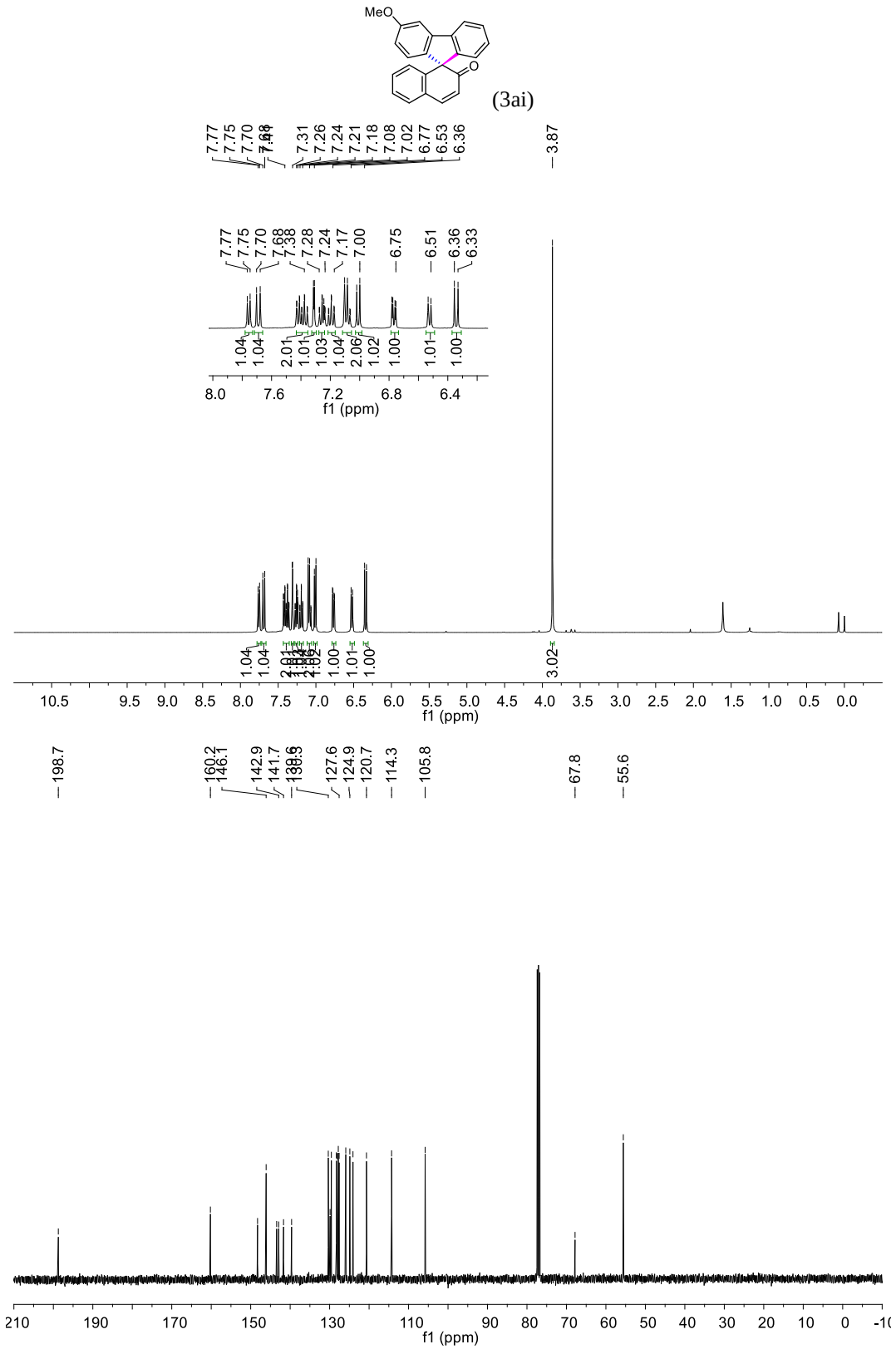
(3ah)

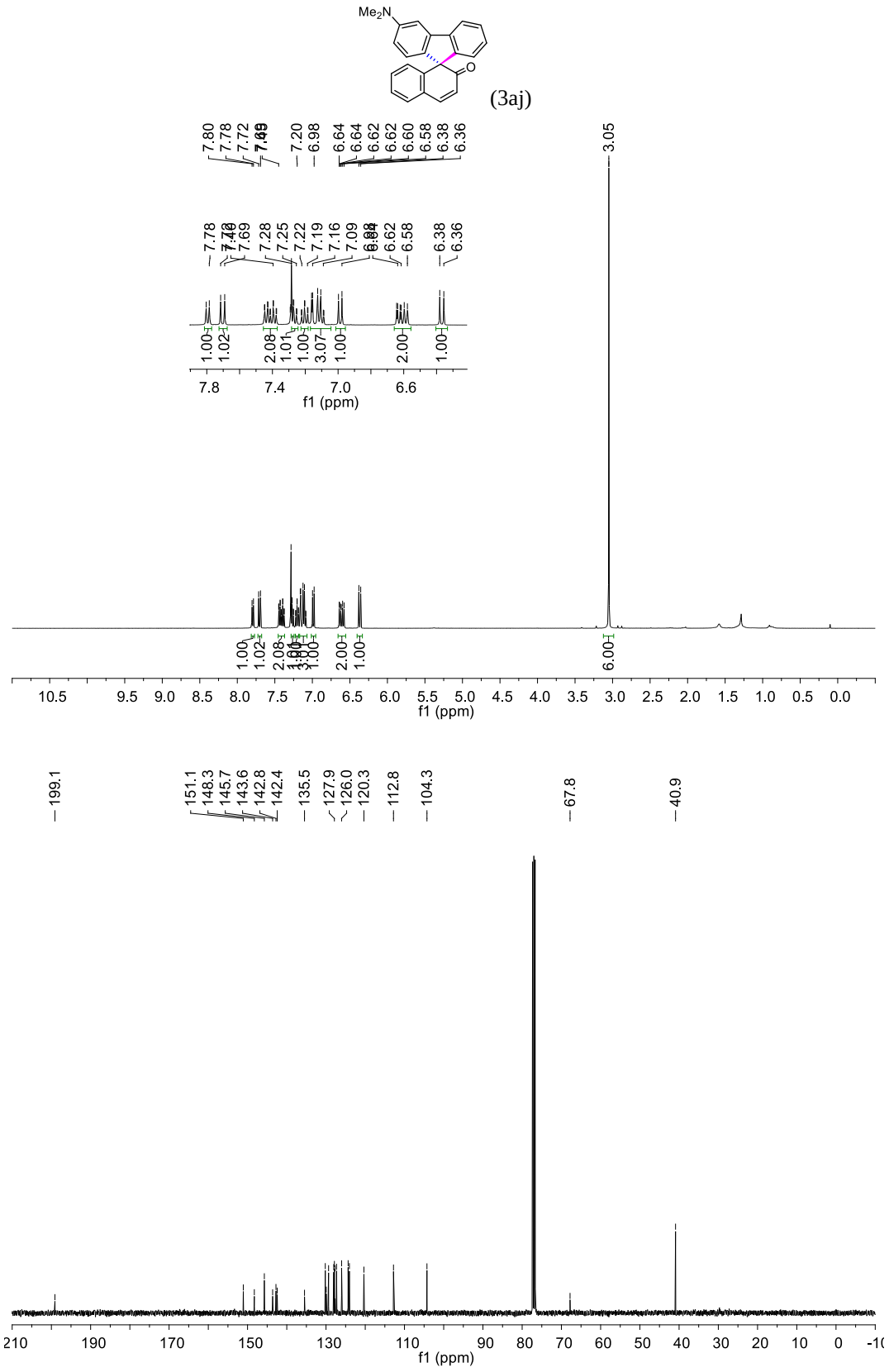

8.00
7.99
7.71
7.30
7.18
7.12
6.53
6.51
6.37
6.35
1.01
1.01
2.03
1.00
2.02
3.00
1.00
1.01
1.00
7.8
7.2
6.6
f1 (ppm)

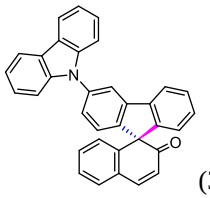

1.01
1.01
2.03
1.00
2.02
3.00
1.00
1.01
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.7
159.4
156.9
146.9
142.0
138.9
129.7
129.4
128.2
128.2
127.9
124.2
123.8
120.0
115.5
68.7
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

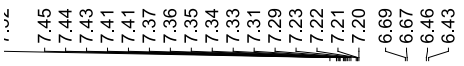

-118.73
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

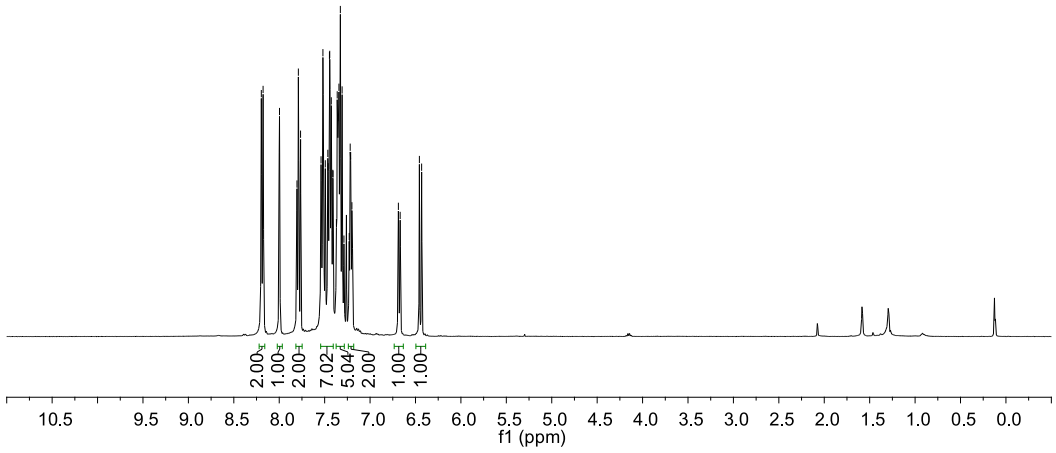

MeO
O
(3ai)
7.77
7.75
7.70
7.68
7.38
7.31
7.28
7.26
7.24
7.21
7.18
7.17
7.08
7.02
7.00
6.77
6.75
6.53
6.51
6.36
6.33
3.87
1.04
1.04
2.01
1.01
1.03
1.04
2.06
1.02
1.00
1.01
1.00
3.02
8.0
7.6
7.2
6.8
6.4
f1 (ppm)
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.7
160.2
146.1
142.9
141.7
138.6
138.3
127.6
124.9
120.7
114.3
105.8
67.8
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

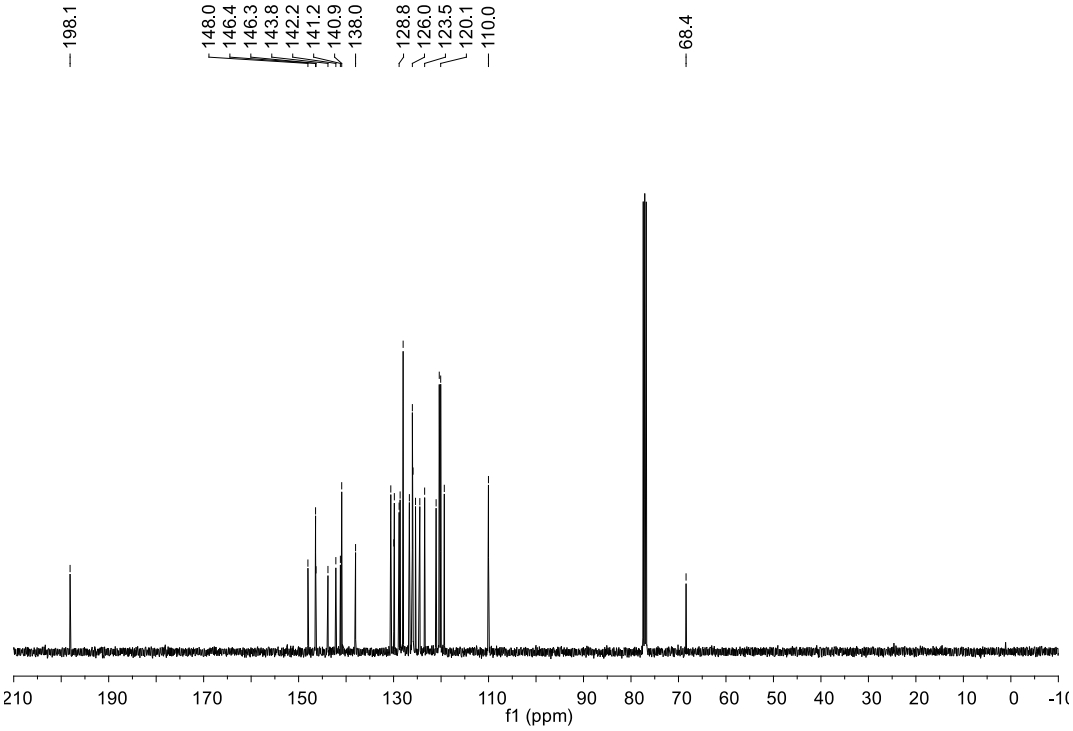

Me2N
O
(3aj)
7.80
7.78
7.72
7.20
6.98
6.64
6.62
6.60
6.58
6.38
6.36
3.05
7.69
7.28
7.25
7.22
7.19
7.16
7.09
6.62
6.58
6.38
6.36
1.00
1.02
2.08
1.01
1.00
3.07
1.00
2.00
1.00
7.8
7.4
7.0
6.6
f1 (ppm)
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
199.1
151.1
148.3
145.7
143.6
142.8
142.4
135.5
127.9
126.0
120.3
112.8
104.3
67.8
40.9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

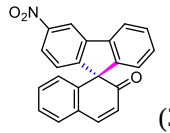


(3ak)

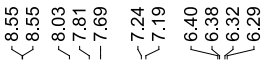

7.45
7.44
7.43
7.41
7.41
7.37
7.36
7.35
7.34
7.33
7.31
7.29
7.23
7.22
7.21
7.20
6.69
6.67
6.46
6.43


2.00
1.00
2.00
7.02
5.04
2.00
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.1
148.0
146.4
146.3
143.8
142.2
141.2
140.9
138.0
128.8
126.0
123.5
120.1
110.0
68.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O2N
O

(3al)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8.03
7.81
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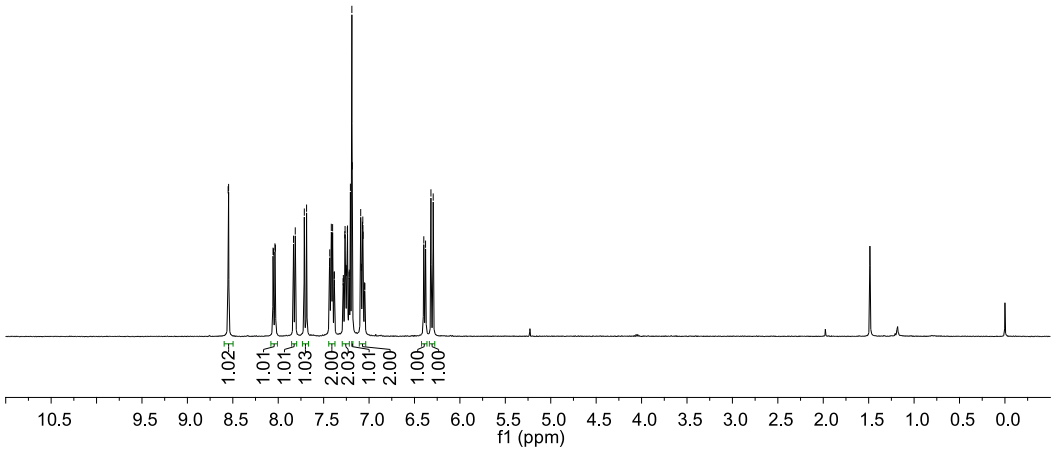
7.24
7.19
6.40
6.38
6.32
6.29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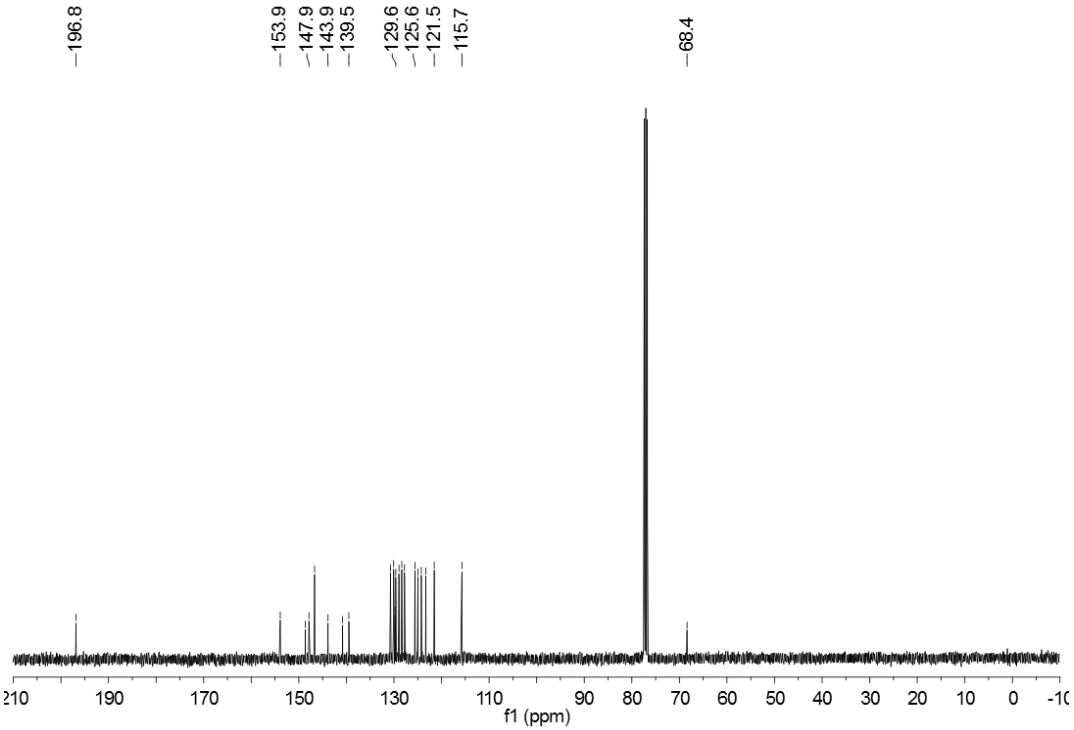
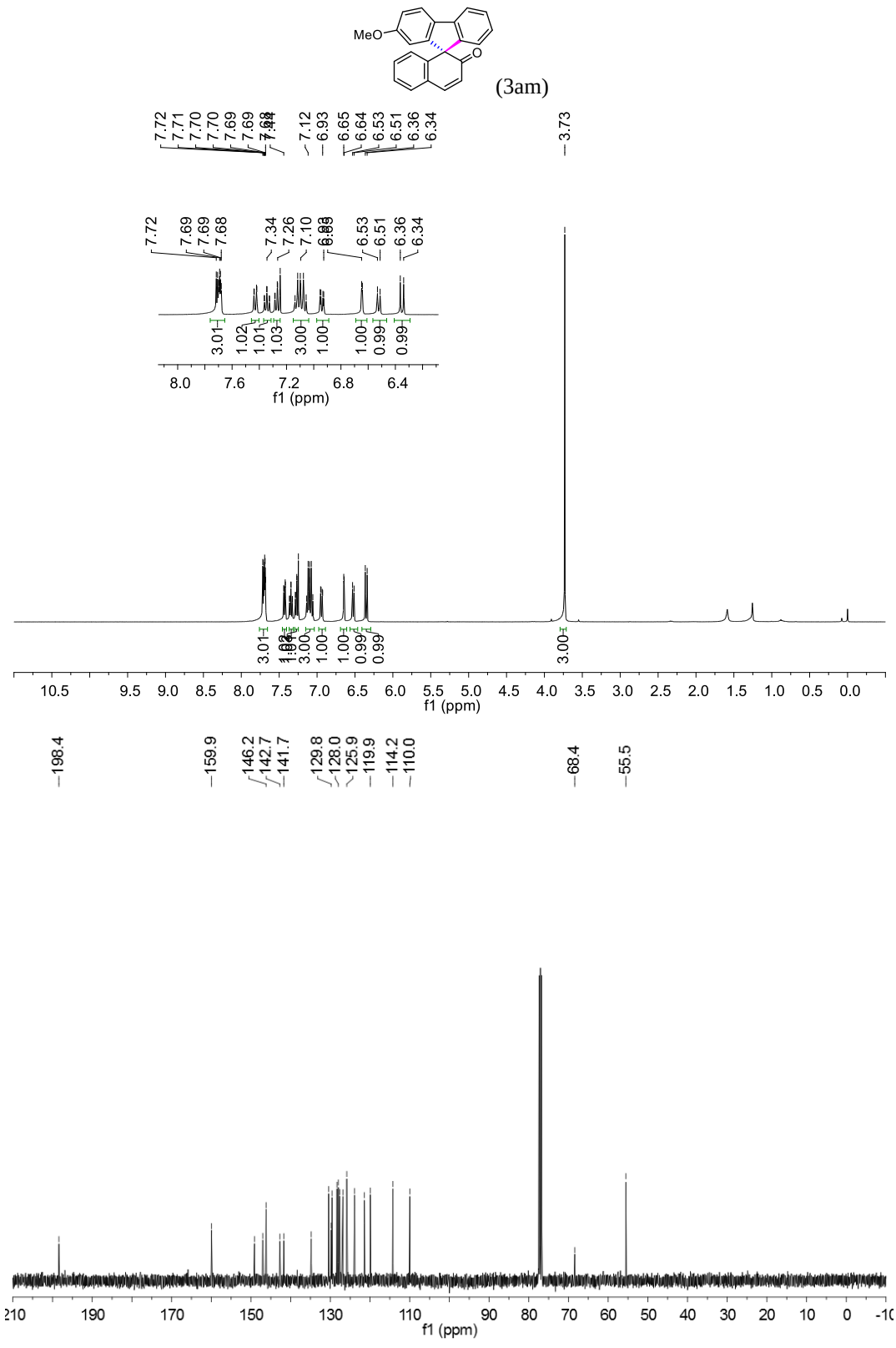
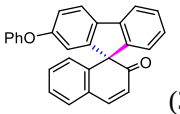
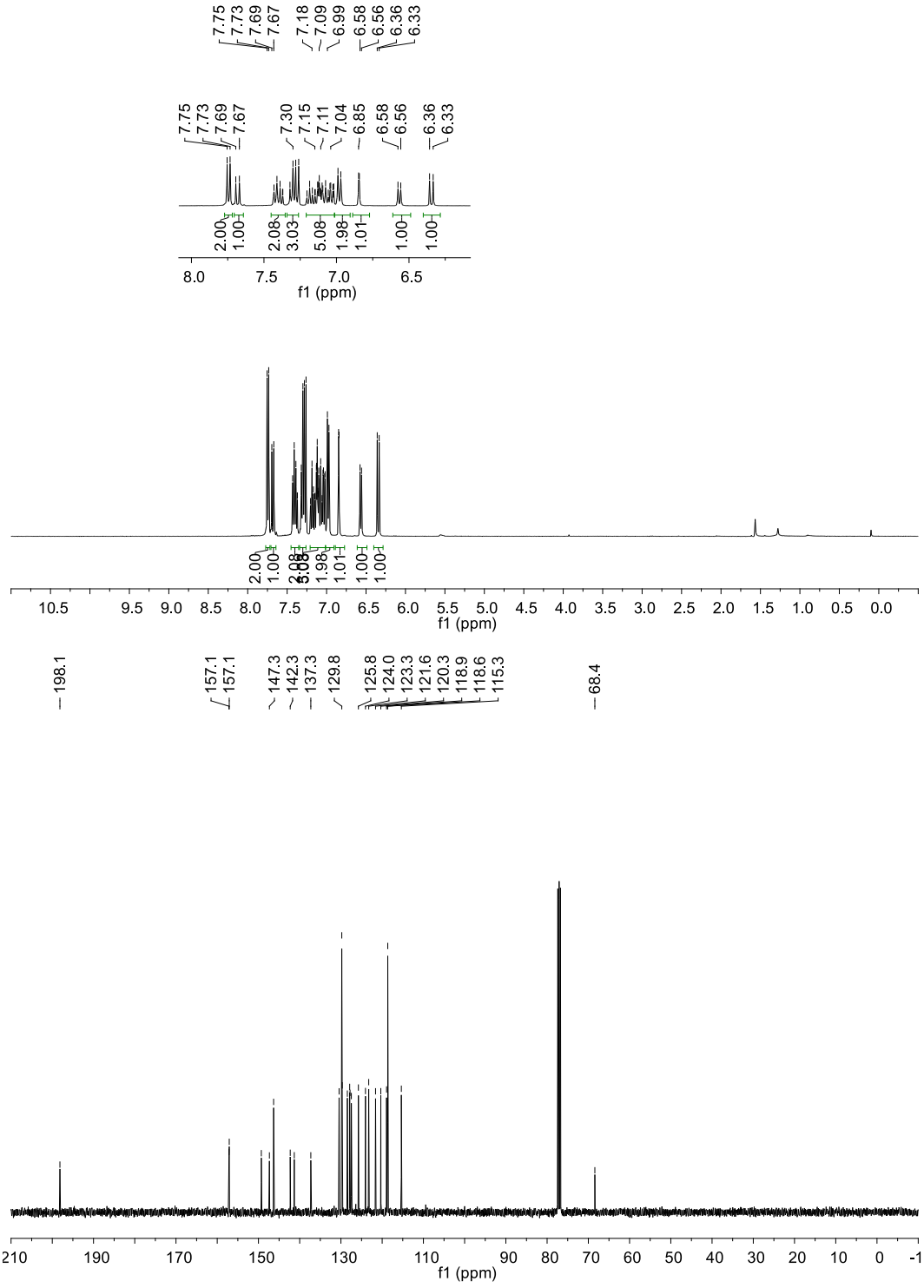
1.01
1.01
1.03
2.00
2.03
1.01
2.00
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


196.8
153.9
147.9
143.9
139.5
129.6
125.6
121.5
115.7
68.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
O
(3am)
7.72
7.71
7.70
7.69
7.69
7.12
6.93
6.65
6.64
6.53
6.51
6.36
6.34
3.73
7.72
7.69
7.69
7.68
7.34
7.26
7.10
6.53
6.51
6.36
6.34
3.01
1.02
1.01
1.03
3.00
1.00
1.00
0.99
0.99
8.0
7.6
7.2
6.8
6.4
f1 (ppm)
3.01
3.00
1.00
1.00
0.99
0.99
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.4
159.9
146.2
142.7
141.7
129.8
128.0
125.9
119.9
114.2
110.0
68.4
55.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


PhO
O

(3an)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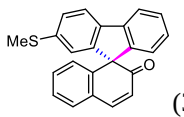
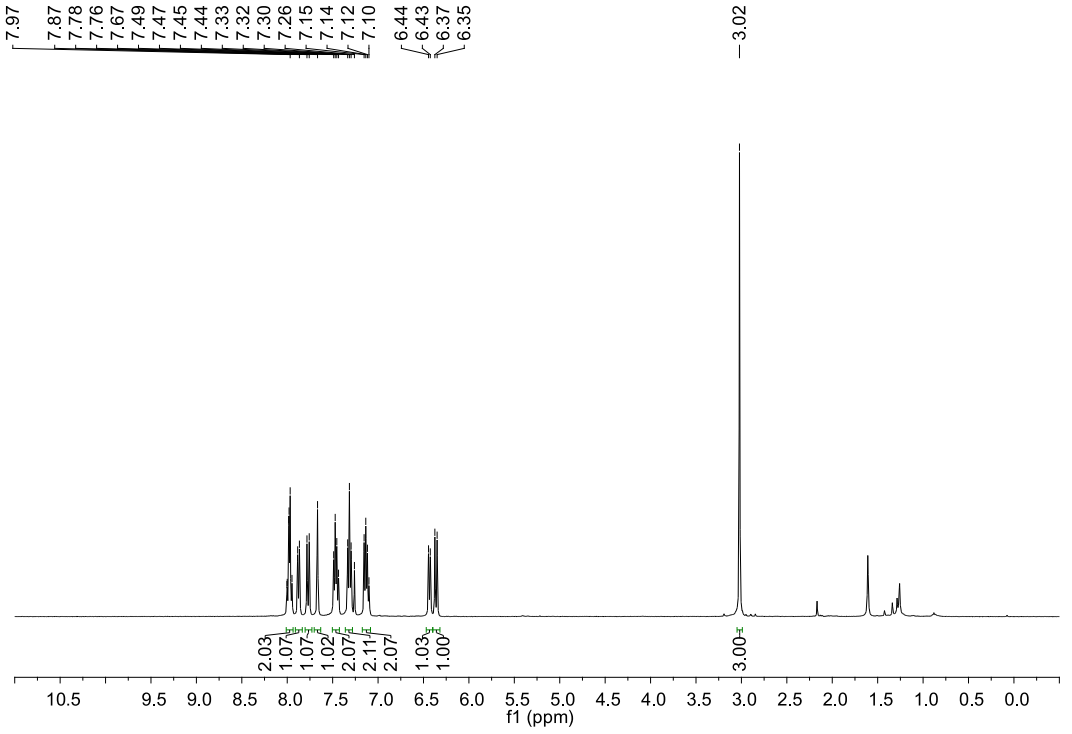
7.69
7.67
7.18
7.09
6.99
6.58
6.56
6.36
6.33
7.30
7.15
7.11
7.04
6.85
2.00
1.00
2.08
3.03
5.08
1.98
1.01
f1 (ppm)
198.1
157.1
147.3
142.3
137.3
129.8
125.8
124.0
123.3
121.6
120.3
118.9
118.6
115.3
68.4


MeS
O

(3ao)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7.87
7.78
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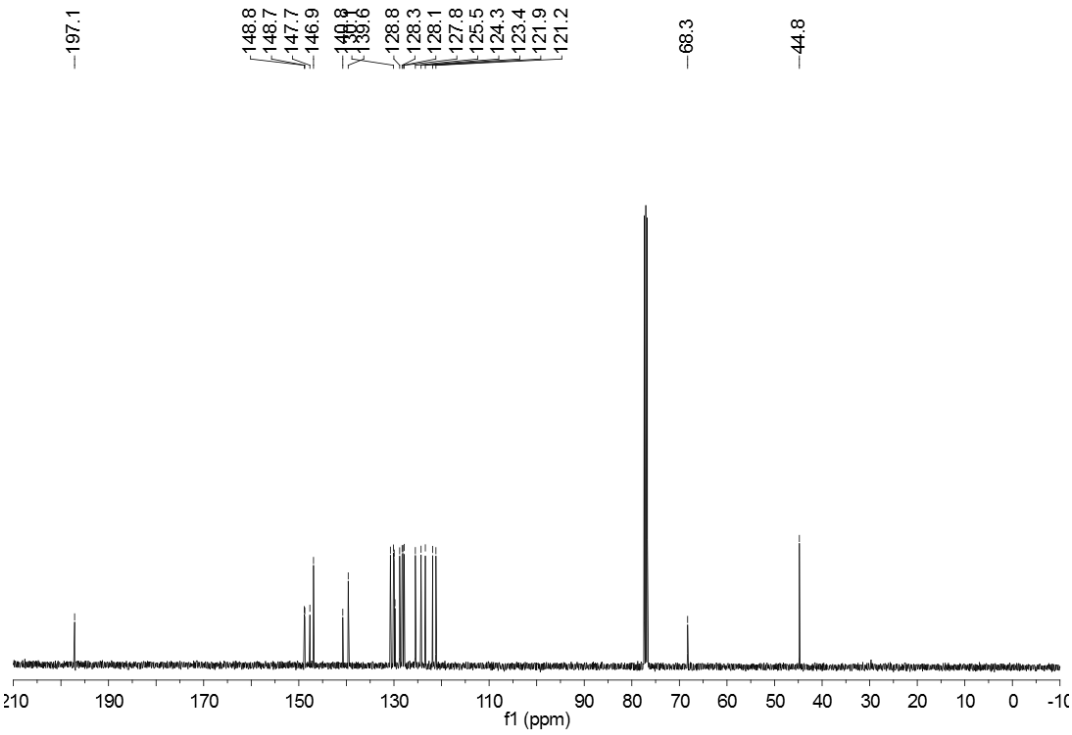
7.49
7.47
7.45
7.44
7.33
7.32
7.30
7.26
7.15
7.14
7.12
7.10
6.44
6.43
6.37
6.35
3.02
2.03
1.07
1.07
1.02
2.07
2.11
2.07
1.03
1.00
3.00
f1 (ppm)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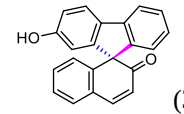
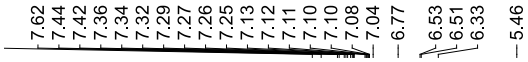
148.8
148.7
147.7
146.9
128.8
128.3
128.1
127.8
125.5
124.3
123.4
121.9
121.2
68.3
44.8
f1 (ppm)


HO
O

(3ap)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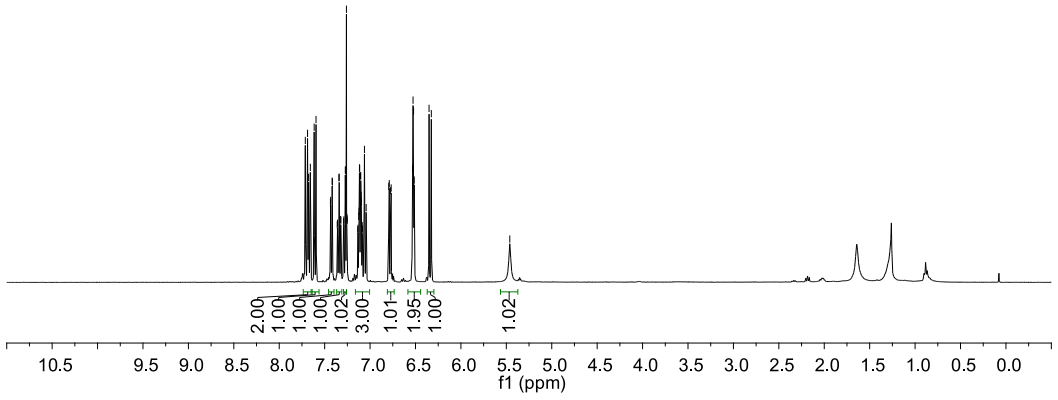
7.44
7.42
7.36
7.34
7.32
7.29
7.27
7.26
7.25
7.13
7.12
7.11
7.10
7.10
7.08
7.04
6.77
6.53
6.51
6.33
5.46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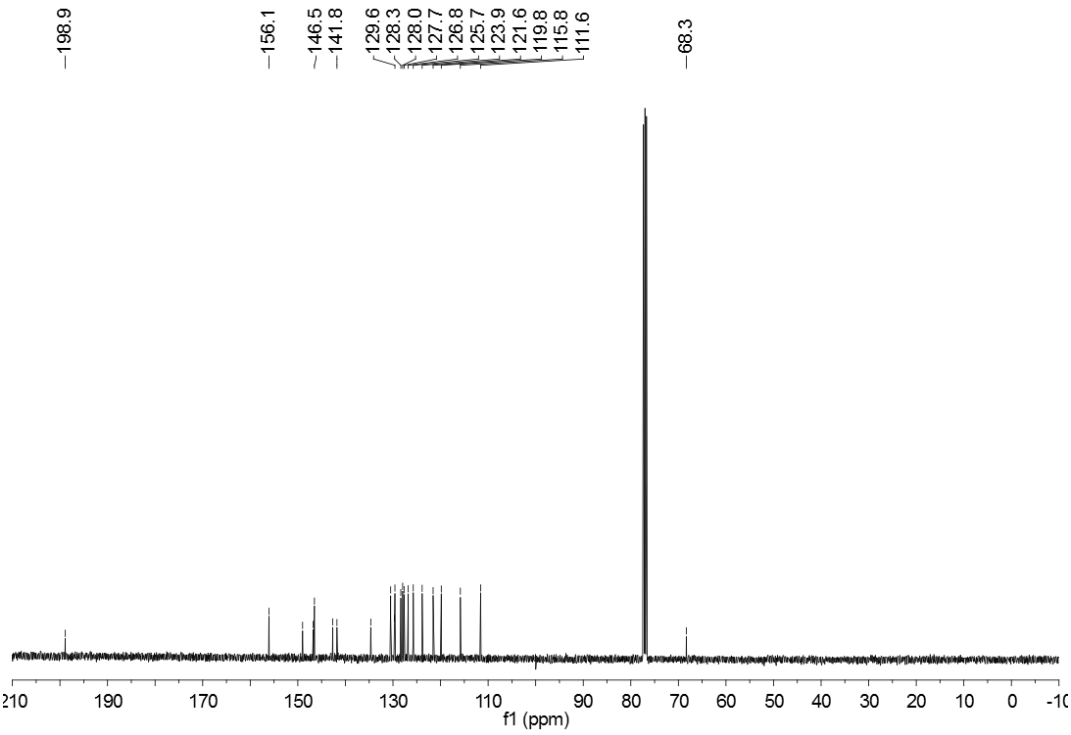
3.00
1.01
1.95
1.00
1.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.9
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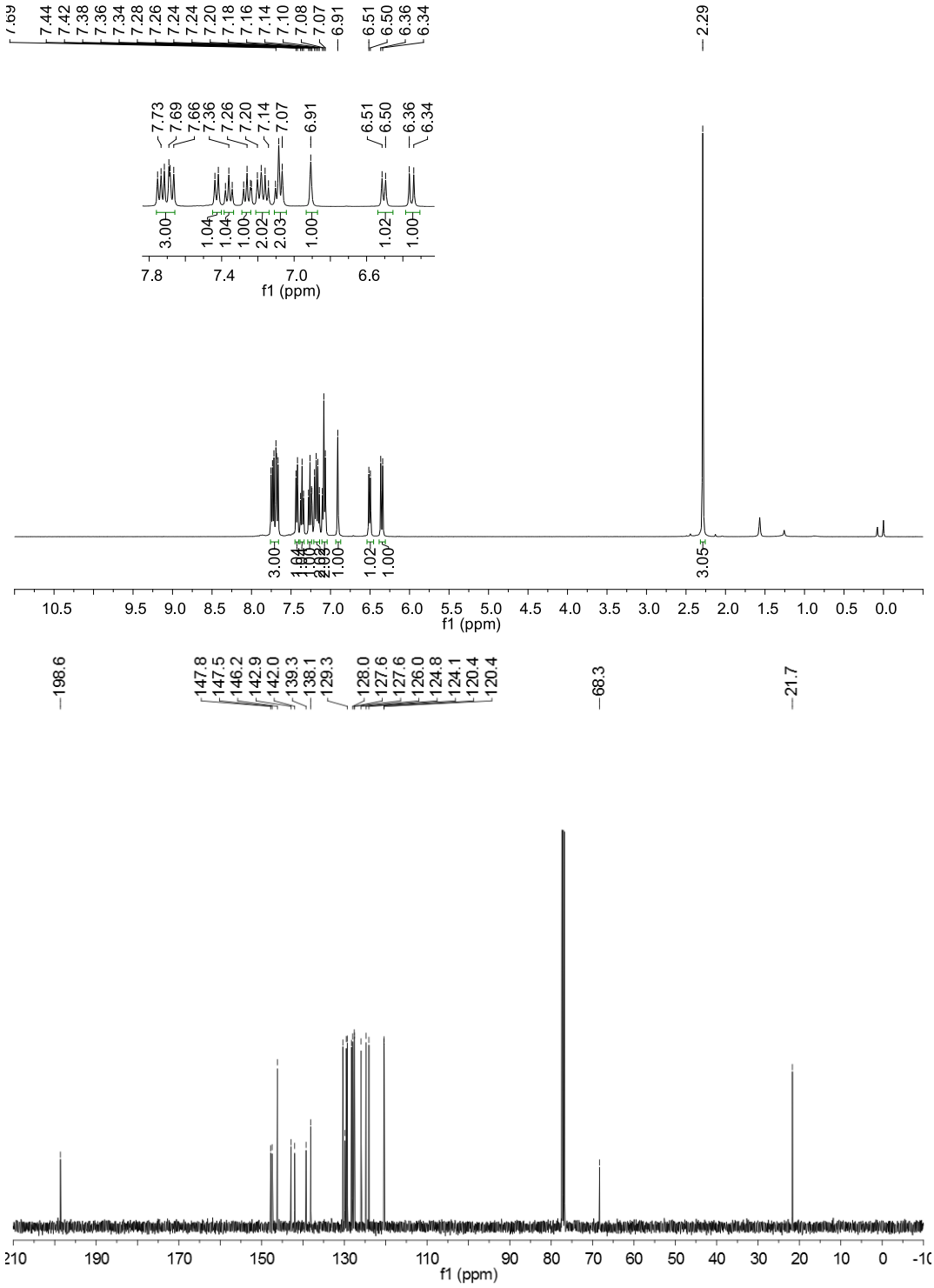
146.5
141.8
129.6
128.3
128.0
127.7
126.8
125.7
123.9
121.6
119.8
115.8
111.6
68.3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
O

(3aq)


7.69
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7.42
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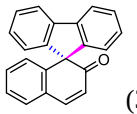
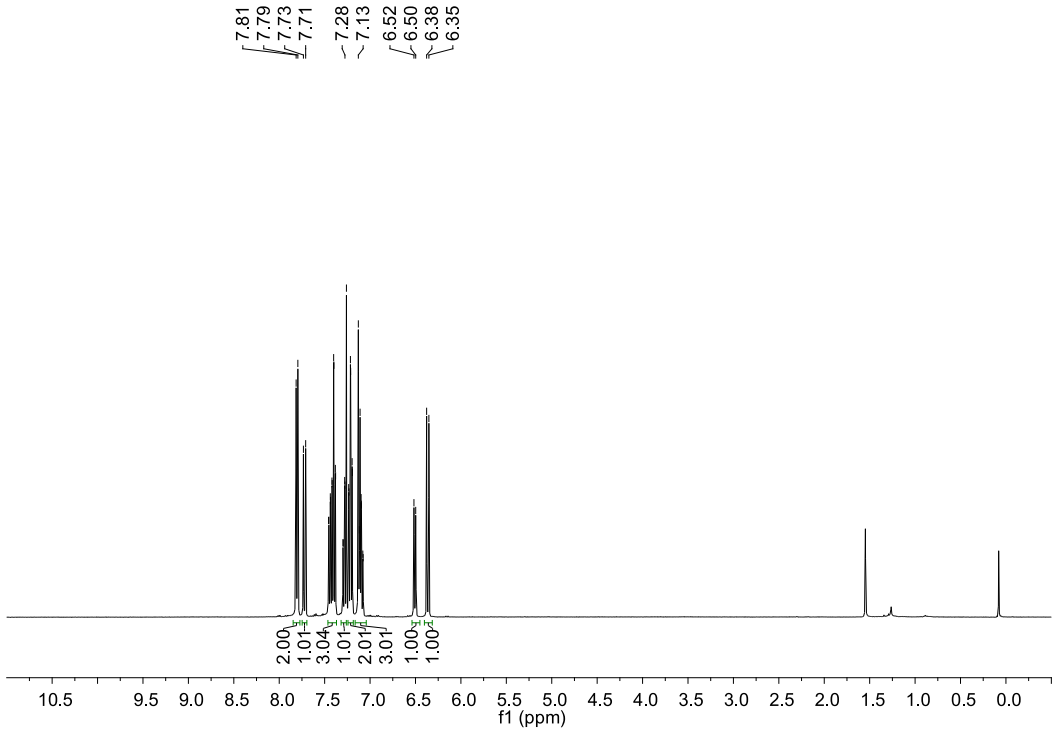
7.36
7.34
7.28
7.26
7.24
7.24
7.20
7.18
7.16
7.14
7.10
7.08
7.07
6.91
6.51
6.50
6.36
6.34
2.29
7.73
7.69
7.66
7.36
7.26
7.20
7.14
7.07
6.91
6.51
6.50
6.36
6.34
3.00
1.04
1.04
1.00
2.02
2.03
1.00
1.02
1.00
7.8
7.4
7.0
6.6
f1 (ppm)
3.00
1.02
1.00
3.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.6
147.8
147.5
146.2
142.9
142.0
139.3
138.1
129.3
128.0
127.6
127.6
126.0
124.8
124.1
120.4
120.4
68.3
21.7
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



(3ar)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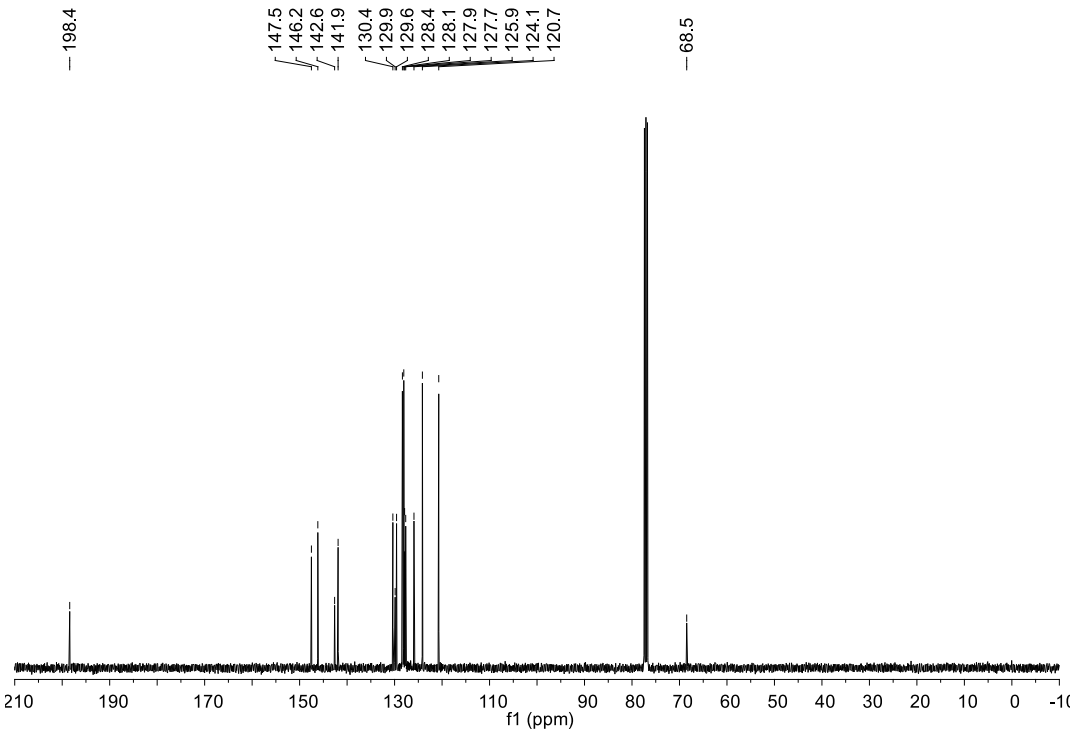
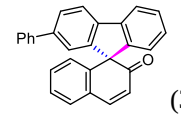
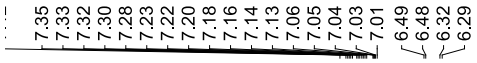
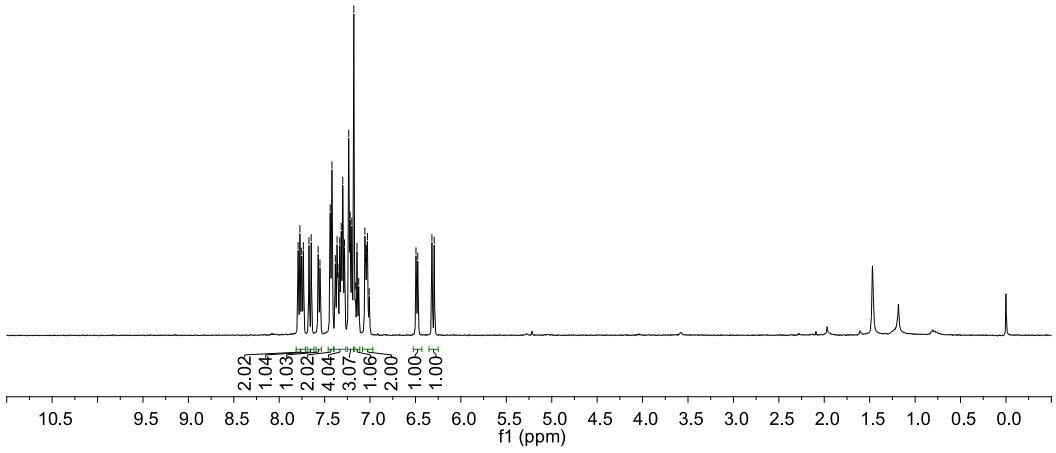
7.13
6.52
6.50
6.38
6.35
2.00
1.01
3.04
1.01
2.01
3.01
1.00
1.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

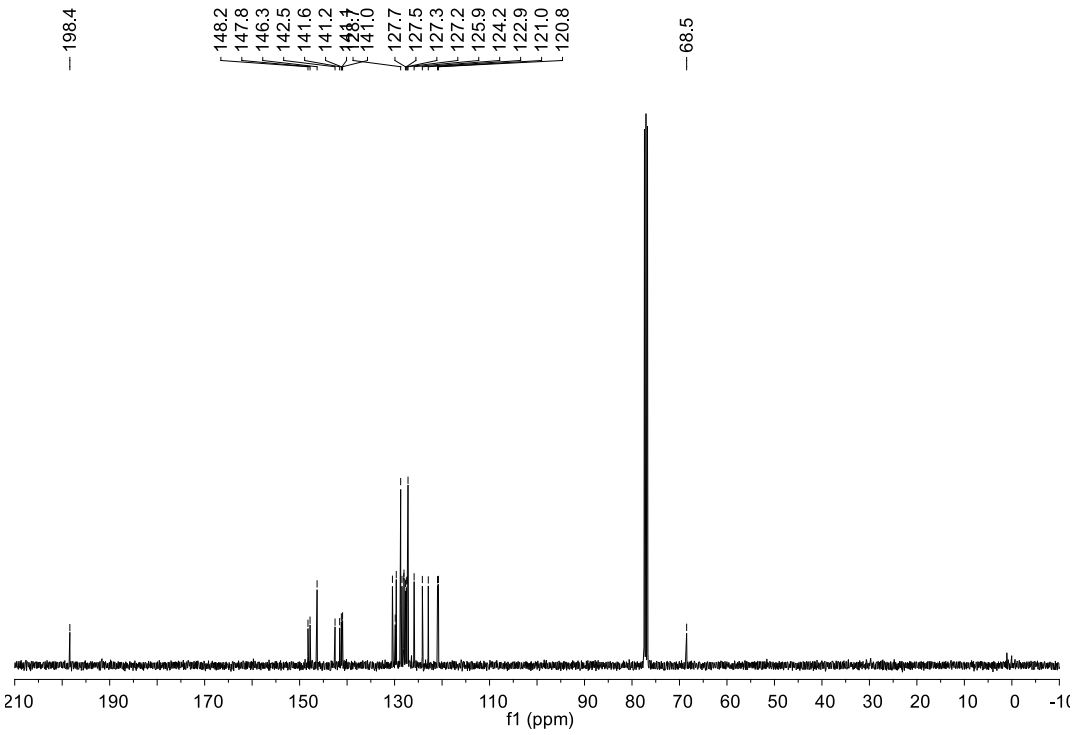

198.4
147.5
146.2
142.6
141.9
130.4
129.9
129.6
128.4
128.1
127.9
127.7
125.9
124.1
120.7
68.5
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

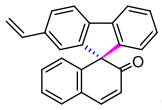

Ph
O

(3as)


7.35
7.33
7.32
7.30
7.28
7.23
7.22
7.20
7.18
7.16
7.14
7.13
7.06
7.05
7.04
7.03
7.01
6.49
6.48
6.32
6.29


2.02
1.04
1.03
2.02
4.04
3.07
1.06
2.00
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.4
148.2
147.8
146.3
142.5
141.6
141.2
141.0
127.7
127.5
127.3
127.2
125.9
124.2
122.9
121.0
120.8
68.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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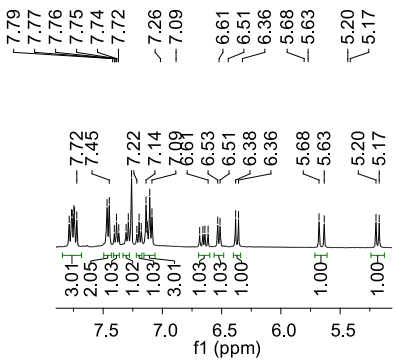
(3at)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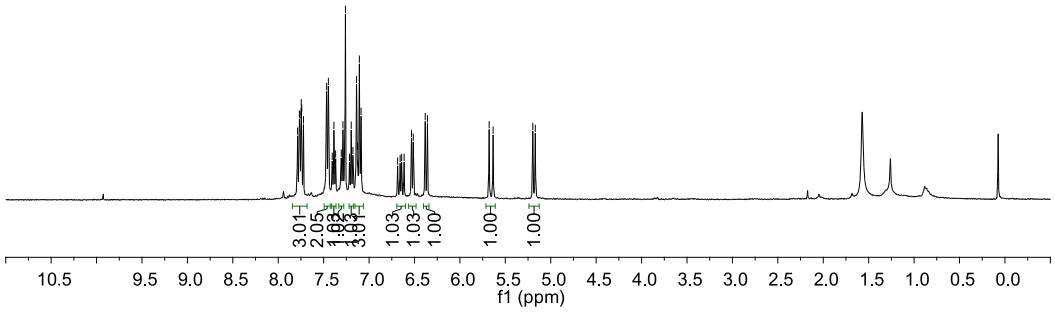
7.75
7.74
7.72
7.26
7.09
6.61
6.51
6.36
5.68
5.63
5.20
5.17
7.72
7.45
7.22
7.14
7.09
6.81
6.53
6.51
6.38
6.36
5.68
5.63
5.20
5.17
3.01
2.05
1.03
1.02
1.03
3.01
1.03
1.03
1.00
1.00
1.00
7.5
7.0
6.5
6.0
5.5
f1 (ppm)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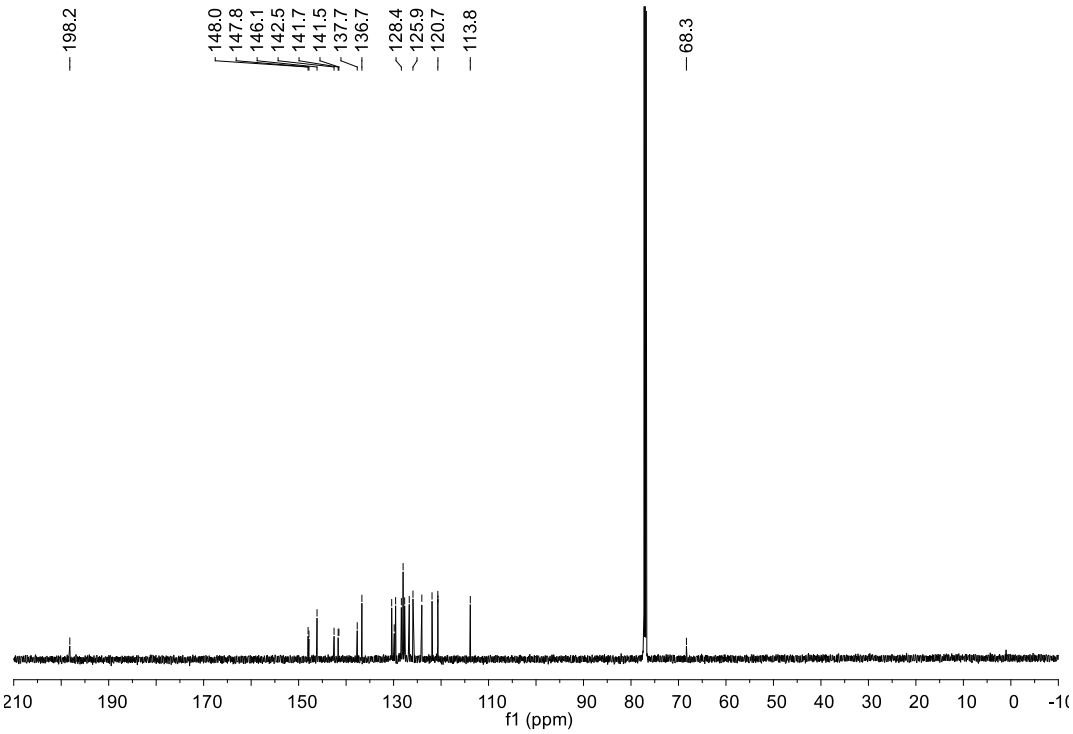
2.05
1.03
1.03
1.00
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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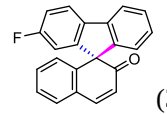
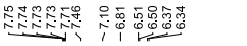
147.8
146.1
142.5
141.7
141.5
137.7
136.7
128.4
125.9
120.7
113.8
68.3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O

(3au)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6.81
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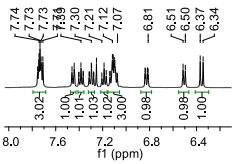
6.50
6.37
6.34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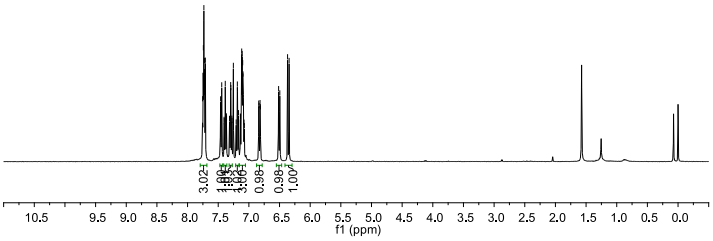
7.73
7.73
7.30
7.21
7.12
7.07
6.81
6.51
6.50
6.37
6.34
3.02
1.00
1.01
1.03
1.02
3.00
0.98
0.98
1.00
8.0
7.6
7.2
6.8
6.4
f1 (ppm)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0.98
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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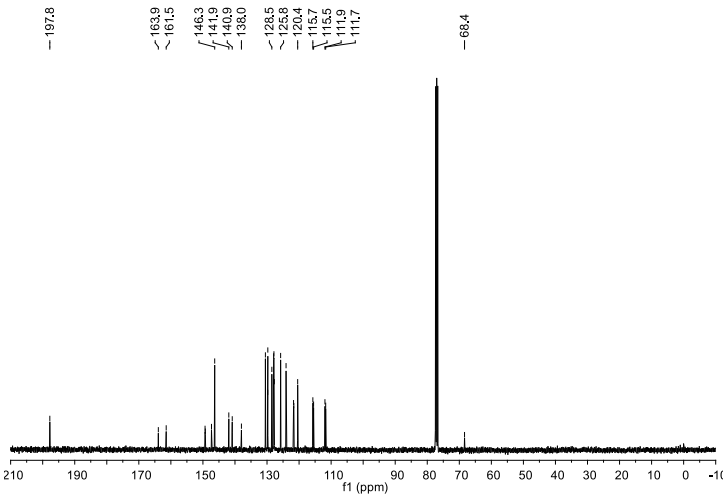
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.8
163.9
161.5
146.3
141.9
140.9
138.0
128.5
125.8
120.4
115.7
115.5
111.9
111.7
68.4
210
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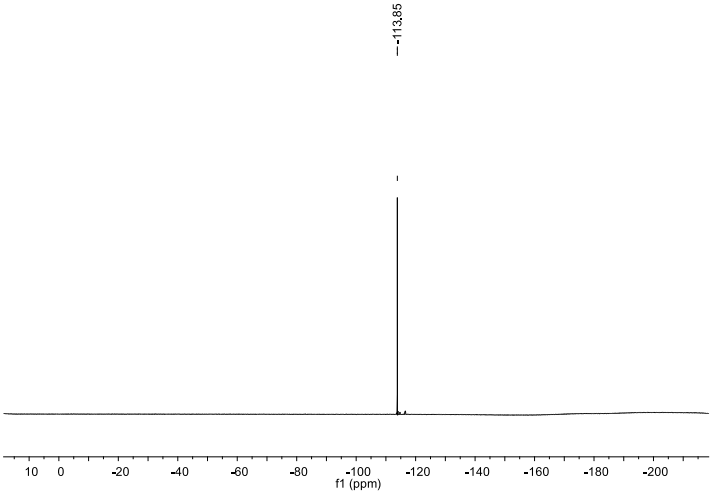
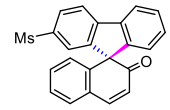
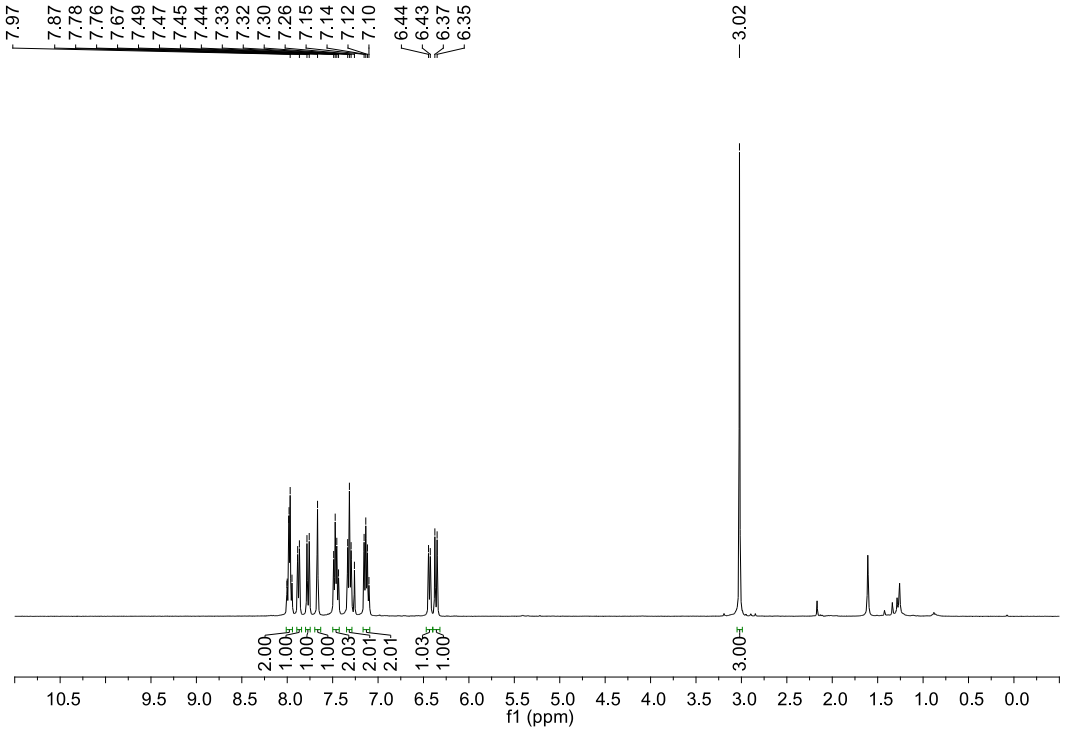
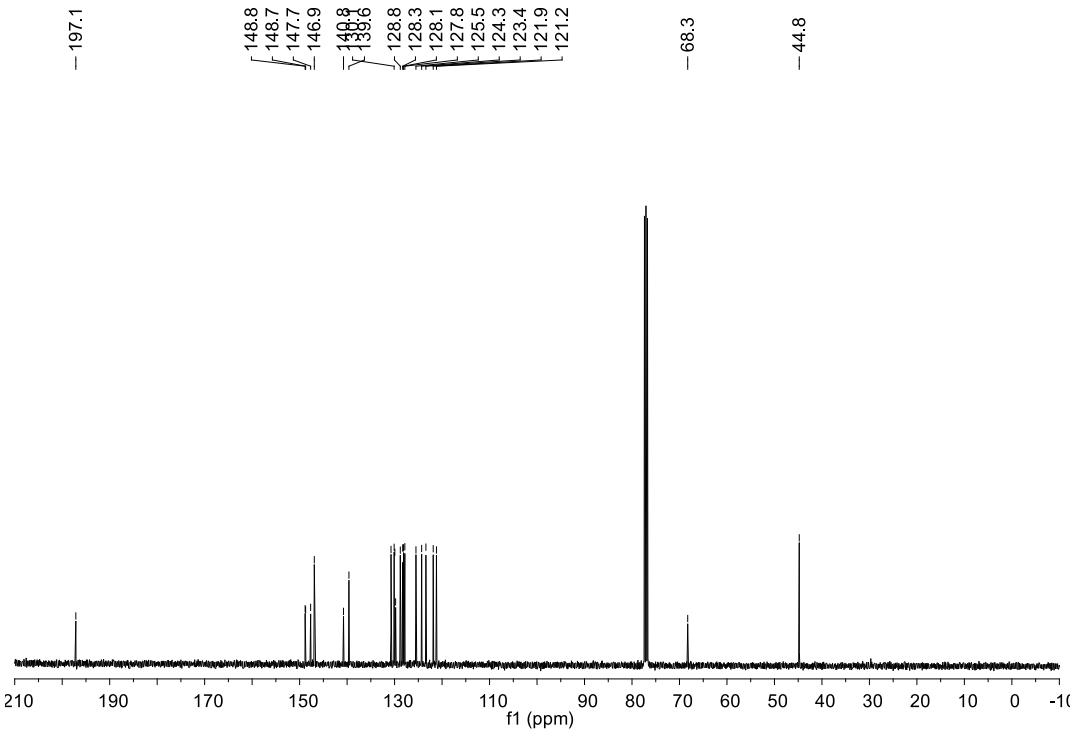
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

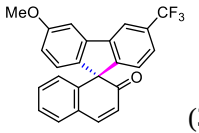

-113.85
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


Ms
O

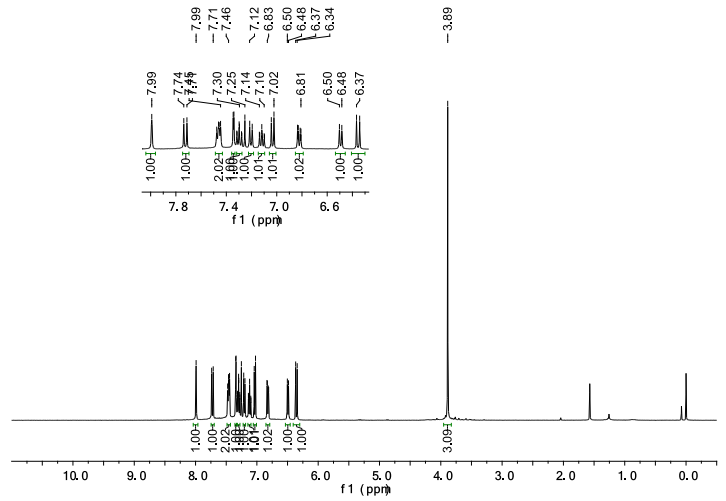
(3av)

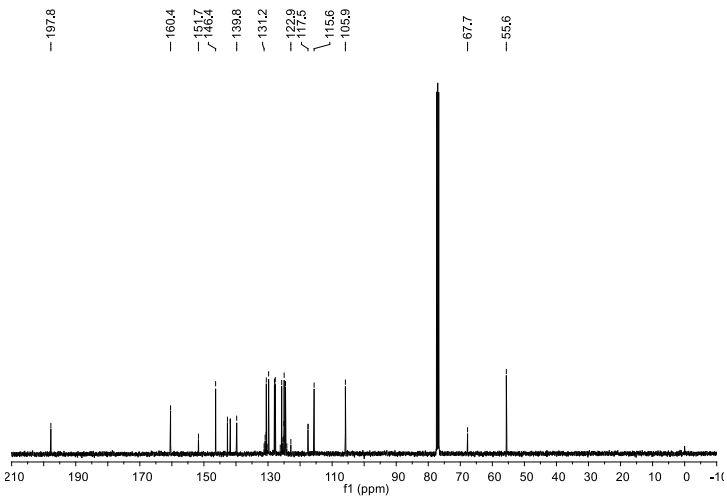

7.97
7.87
7.78
7.76
7.67
7.49
7.47
7.45
7.44
7.33
7.32
7.30
7.26
7.15
7.14
7.12
7.10
6.44
6.43
6.37
6.35
3.02
2.00
1.00
1.00
1.00
2.03
2.01
2.01
1.03
1.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

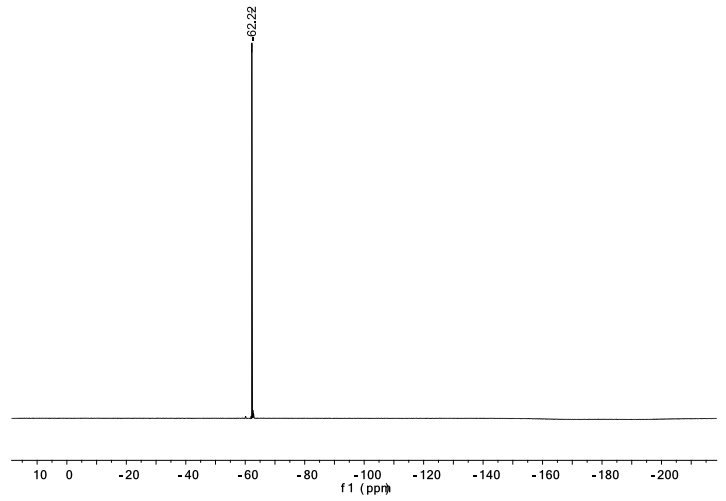

197.1
148.8
148.7
147.7
146.9
140.8
139.6
128.8
128.3
128.1
127.8
125.5
124.3
123.4
121.9
121.2
68.3
44.8
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

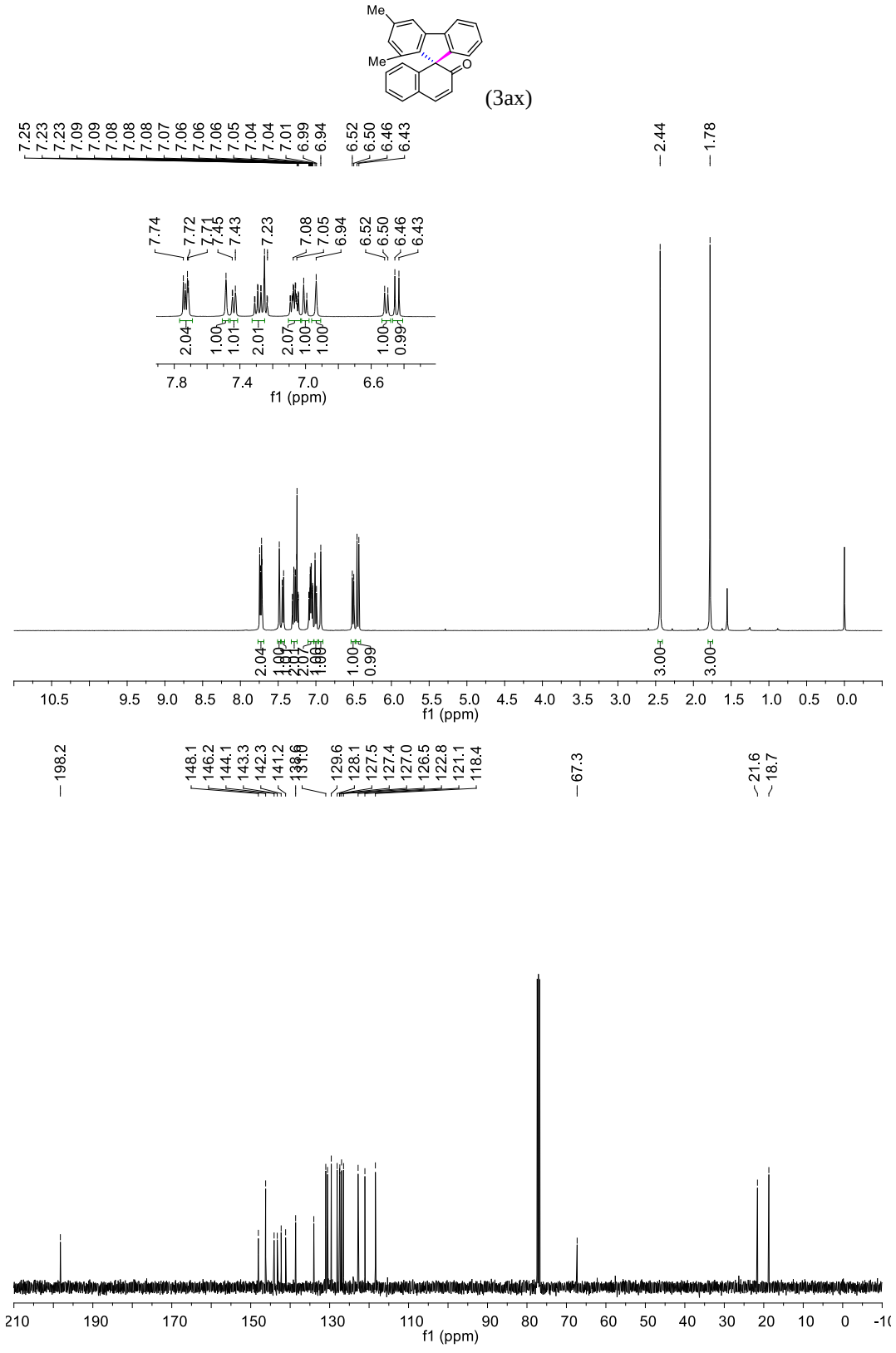

MeO
CF3
O

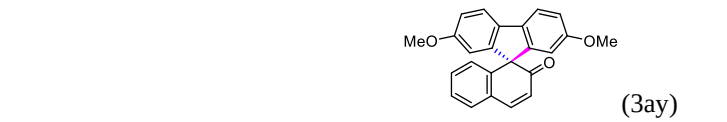
(3aw)


7.99
7.71
7.46
7.12
6.83
6.50
6.48
6.37
6.34
3.89
f1 (ppm)

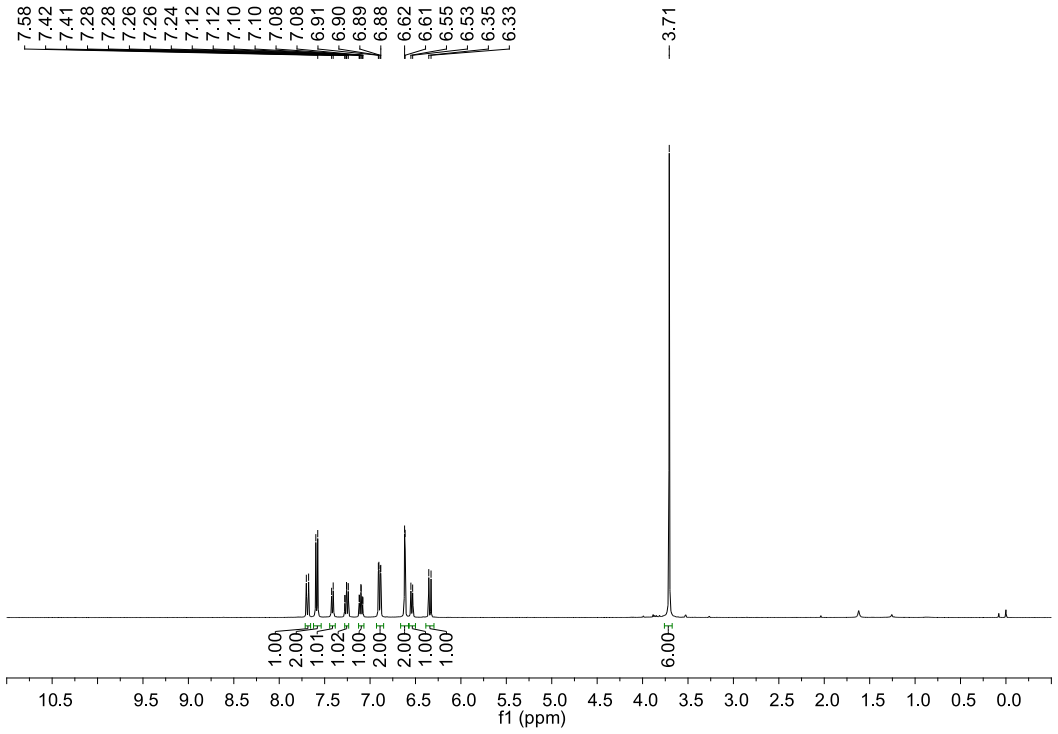

197.8
160.4
151.7
146.4
139.8
131.2
122.9
117.5
115.6
105.9
67.7
55.6
f1 (ppm)

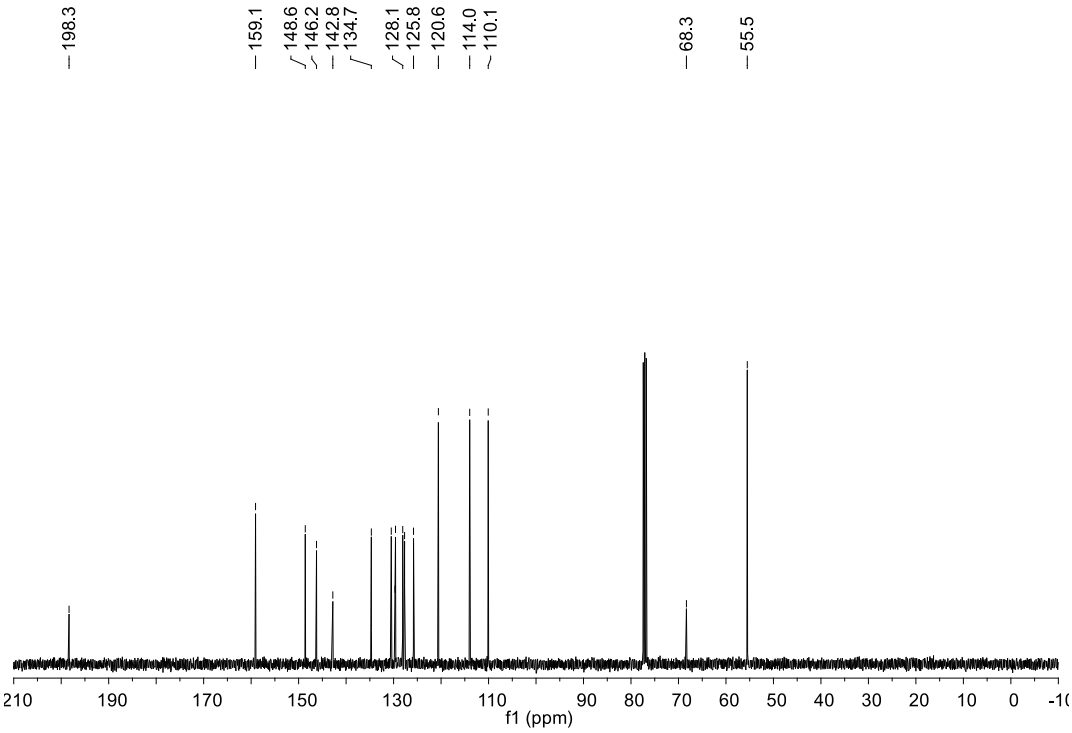

-62.22
f1 (ppm)

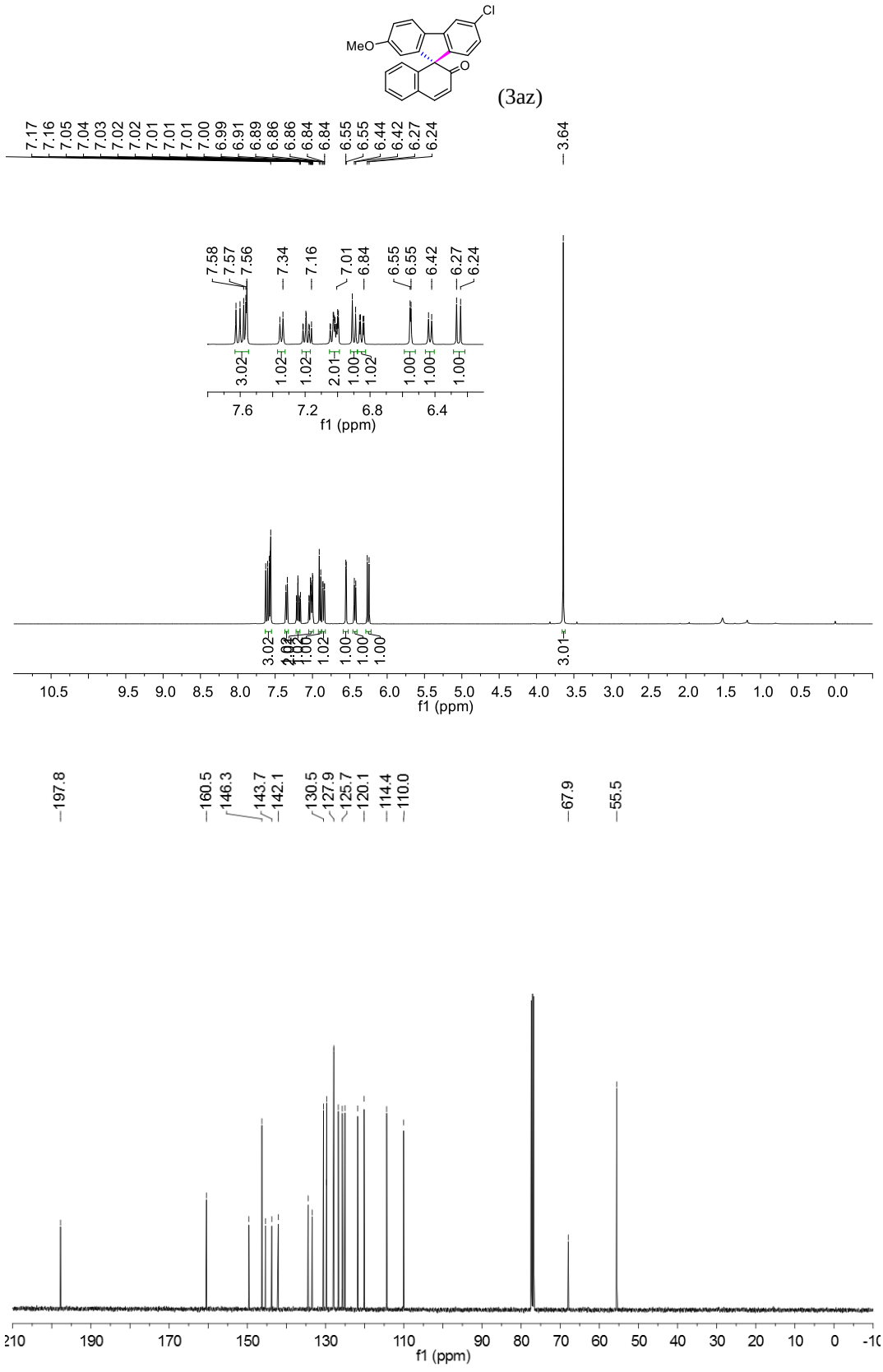

Me
Me
O
(3ax)
7.25
7.23
7.23
7.09
7.09
7.08
7.08
7.08
7.07
7.06
7.06
7.06
7.05
7.04
7.04
7.01
6.99
6.94
6.52
6.50
6.46
6.43
2.44
1.78
7.74
7.72
7.71
7.45
7.43
7.23
7.08
7.05
6.94
6.52
6.50
6.46
6.43
2.04
1.00
1.01
2.01
2.07
1.00
1.00
1.00
0.99
7.8
7.4
7.0
6.6
f1 (ppm)
2.04
1.00
1.01
2.01
2.07
1.00
1.00
1.00
0.99
3.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.2
148.1
146.2
144.1
143.3
142.3
141.2
138.6
137.0
129.6
128.1
127.5
127.4
127.0
126.5
122.8
121.1
118.4
67.3
21.6
18.7
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

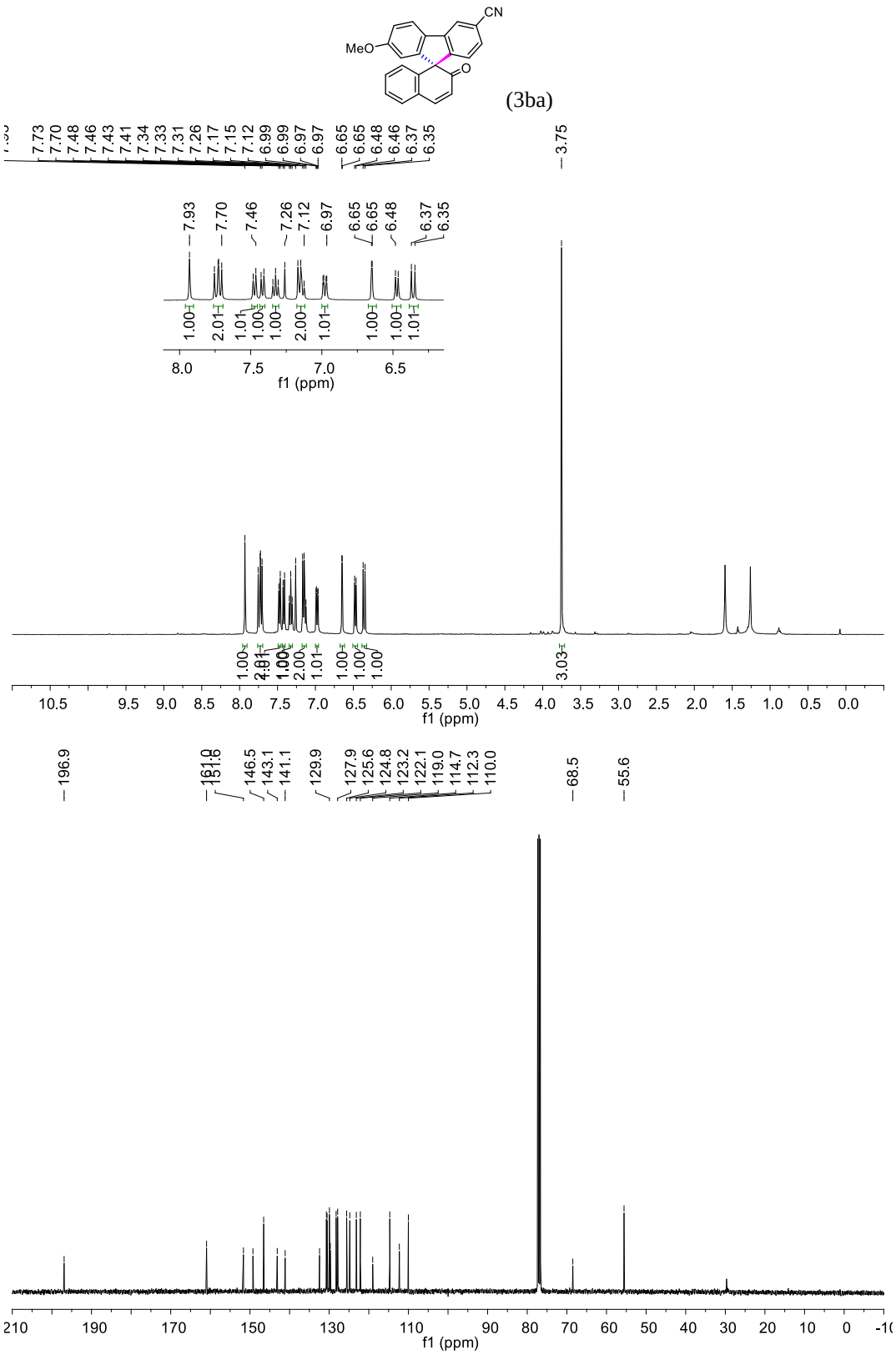

MeO
OMe
O

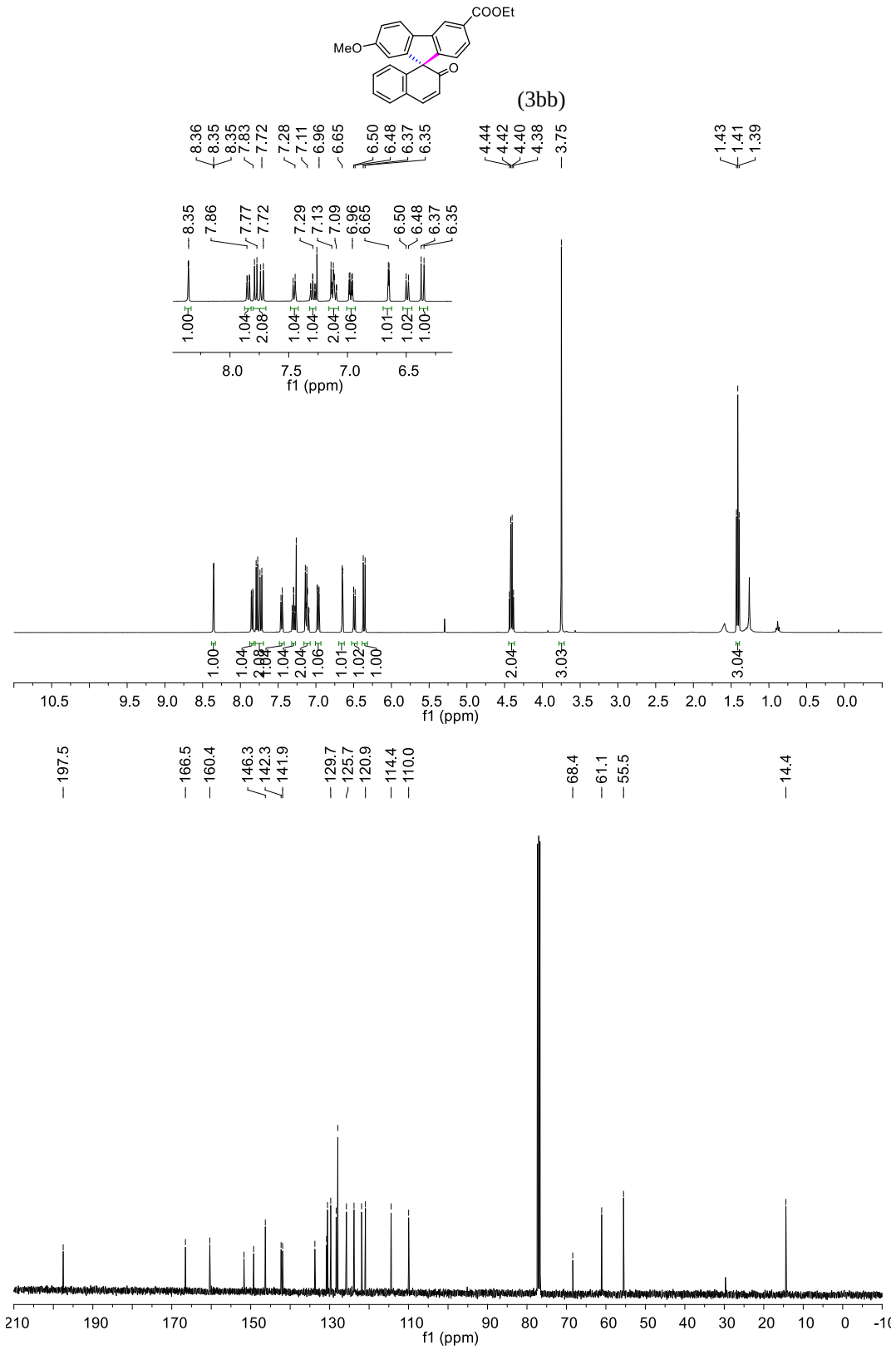
(3ay)

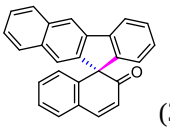

7.58
7.42
7.41
7.28
7.28
7.26
7.26
7.24
7.12
7.12
7.10
7.10
7.08
7.08
6.91
6.90
6.89
6.88
6.62
6.61
6.55
6.53
6.35
6.33
3.71
1.00
2.00
1.01
1.02
1.00
2.00
2.00
1.00
1.00
6.00
f1 (ppm)


198.3
159.1
148.6
146.2
142.8
134.7
128.1
125.8
120.6
114.0
110.1
68.3
55.5
f1 (ppm)

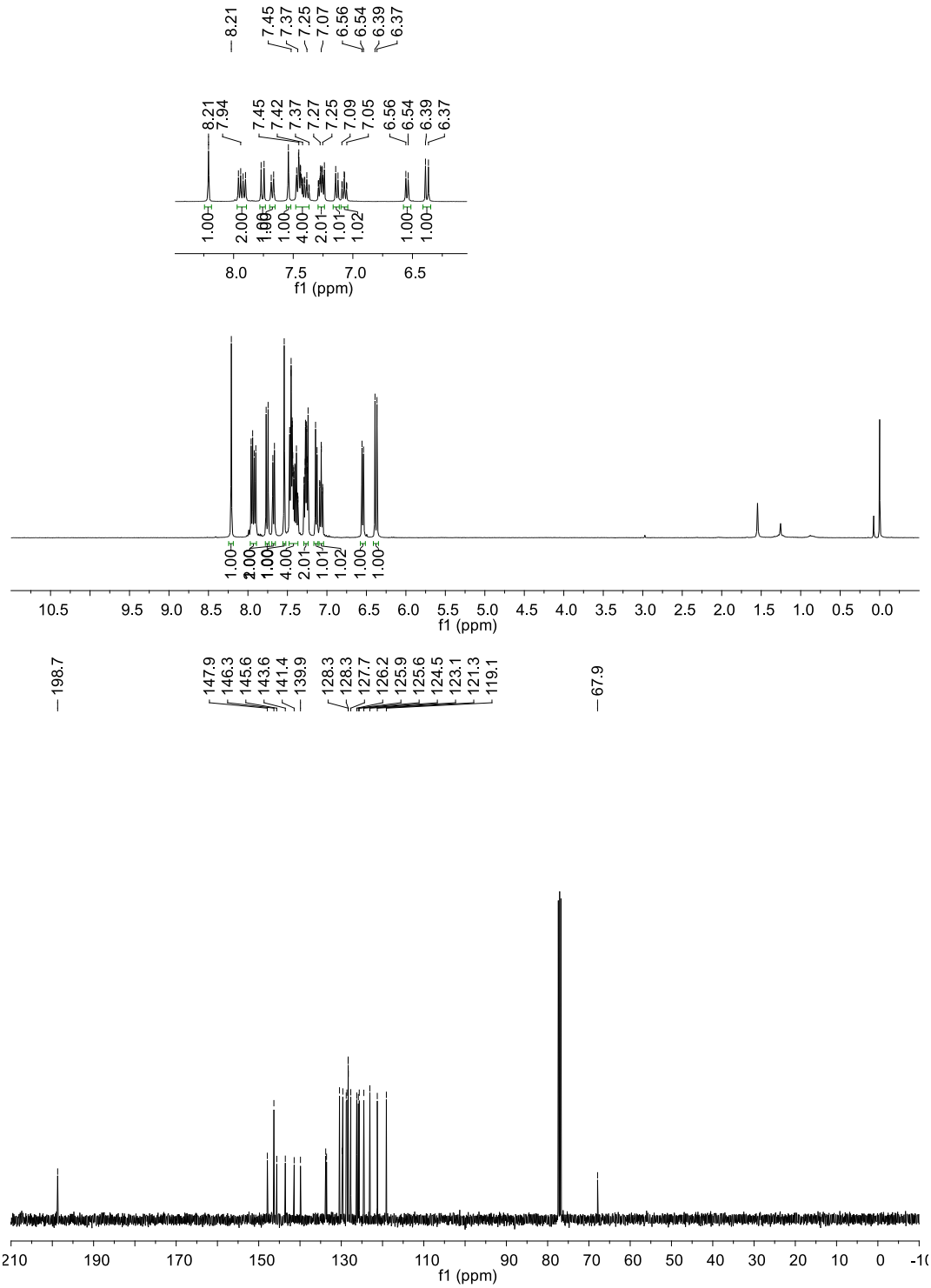

Cl
MeO
O
(3az)
7.17
7.16
7.05
7.04
7.03
7.02
7.02
7.01
7.01
7.01
7.00
6.99
6.91
6.89
6.86
6.86
6.84
6.84
6.55
6.55
6.44
6.42
6.27
6.24
3.64
7.58
7.57
7.56
7.34
7.16
7.01
6.84
6.55
6.55
6.42
6.27
6.24
3.02
1.02
1.02
2.01
1.00
1.02
1.00
1.00
1.00
7.6
7.2
6.8
6.4
f1 (ppm)
3.02
1.02
1.00
1.00
1.00
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
197.8
160.5
146.3
143.7
142.1
130.5
127.9
125.7
120.1
114.4
110.0
67.9
55.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

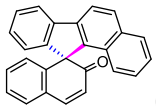

CN
MeO
O
(3ba)
f1 (ppm)


COOEt
MeO
O
(3bb)
8.36
8.35
8.35
7.83
7.72
7.28
7.11
6.96
6.65
6.50
6.48
6.37
6.35
4.44
4.42
4.40
4.38
3.75
1.43
1.41
1.39
f1 (ppm)
197.5
166.5
160.4
146.3
142.3
141.9
129.7
125.7
120.9
114.4
110.0
68.4
61.1
55.5
14.4
f1 (ppm)

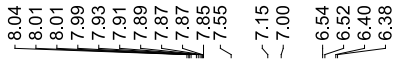


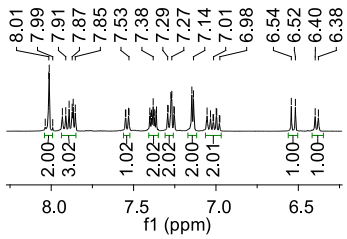
(3bc) or (3bd)

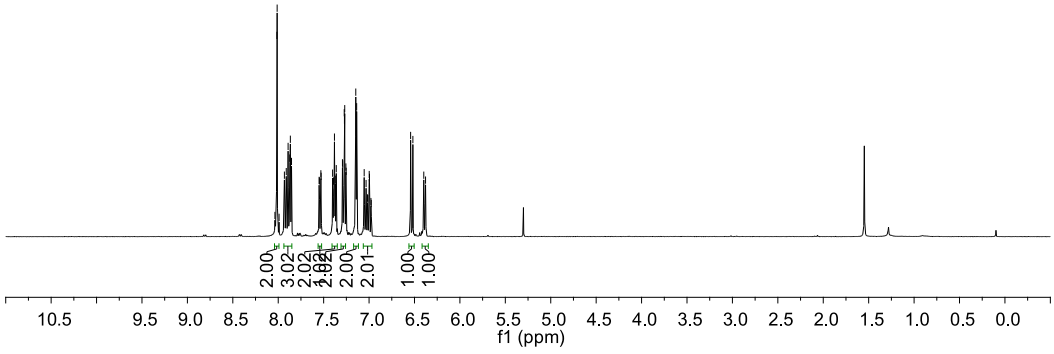

8.21
7.45
7.37
7.25
7.07
6.56
6.54
6.39
6.37
8.21
7.94
7.45
7.42
7.37
7.27
7.25
7.09
7.05
6.56
6.54
6.39
6.37
1.00
2.00
1.00
4.00
2.01
1.01
1.02
1.00
1.00
8.0
7.5
7.0
6.5
f1 (ppm)
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.7
147.9
146.3
145.6
143.6
141.4
139.9
128.3
128.3
127.7
126.2
125.9
125.6
124.5
123.1
121.3
119.1
67.9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

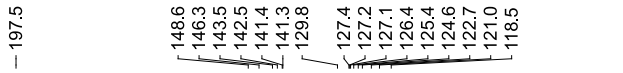


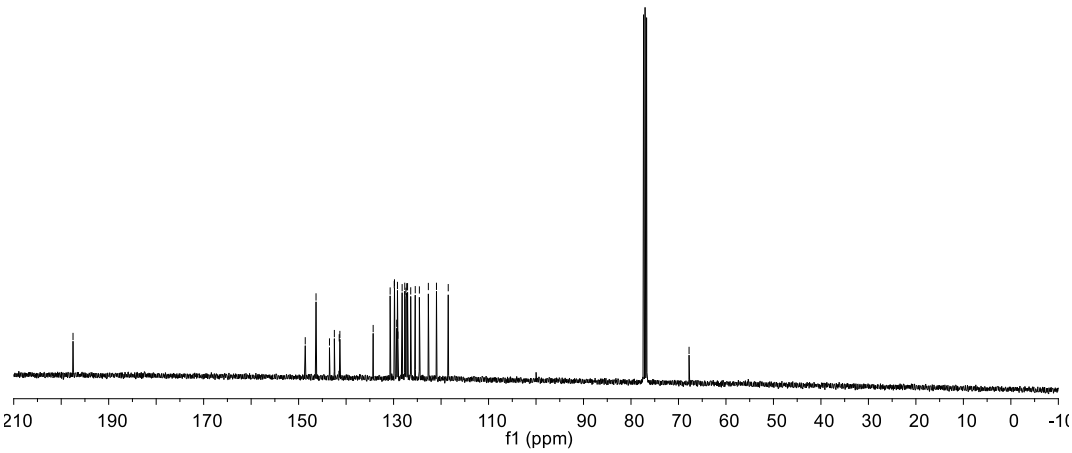
(3be)

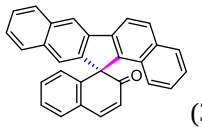

8.04
8.01
8.01
7.99
7.93
7.91
7.89
7.87
7.87
7.85
7.55
7.15
7.00
6.54
6.52
6.40
6.38


8.01
7.99
7.91
7.87
7.85
7.53
7.38
7.29
7.27
7.14
7.01
6.98
6.54
6.52
6.40
6.38
2.00
3.02
1.02
2.02
2.02
2.00
2.01
1.00
1.00
8.0
7.5
7.0
6.5
f1 (ppm)

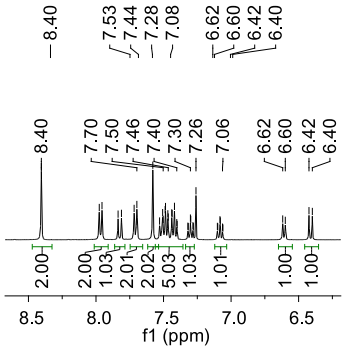

2.00
3.02
2.02
2.00
2.01
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

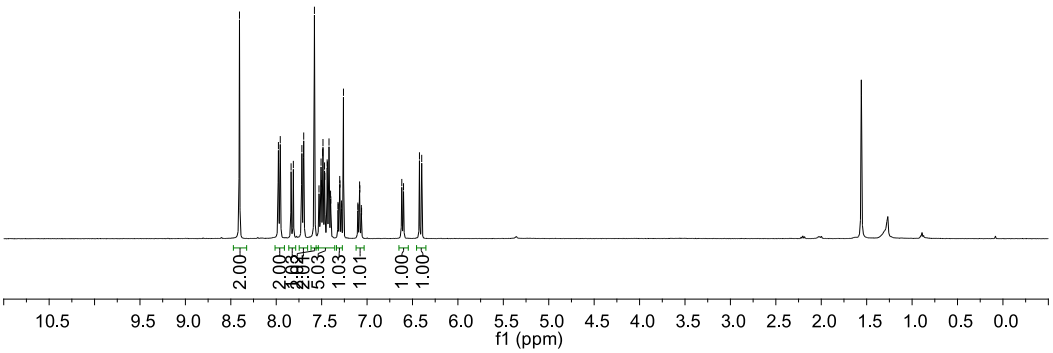

197.5
148.6
146.3
143.5
142.5
141.4
141.3
129.8
127.4
127.2
127.1
126.4
125.4
124.6
122.7
121.0
118.5
67.8

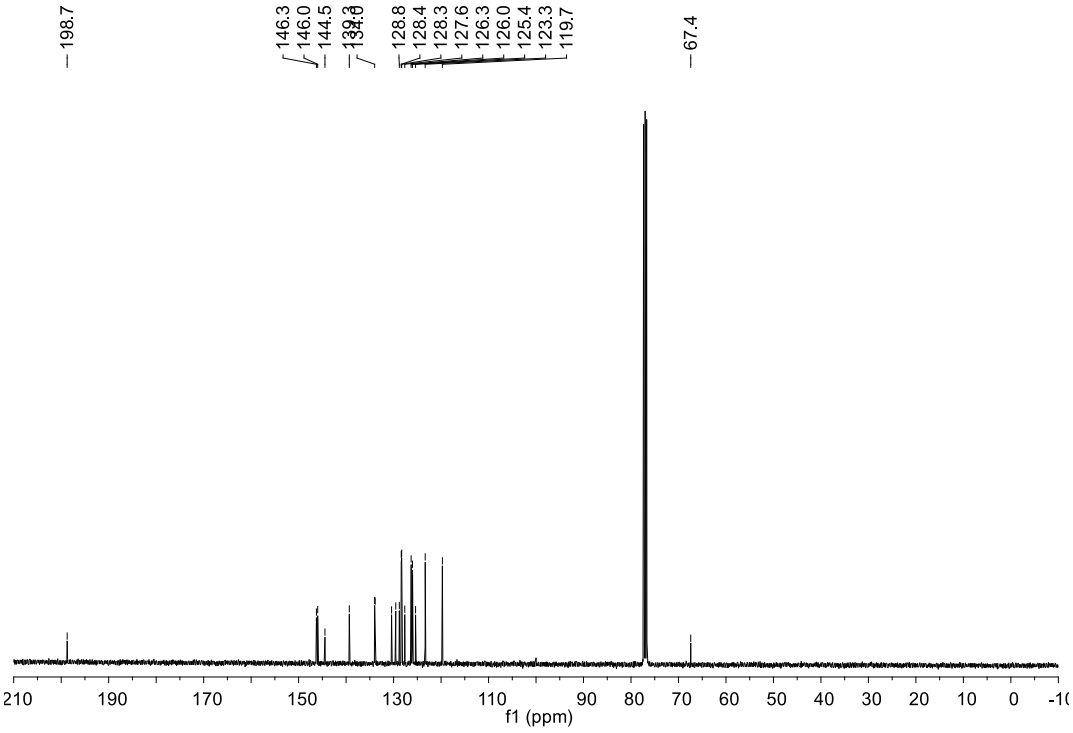

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

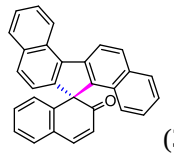


(3bf)

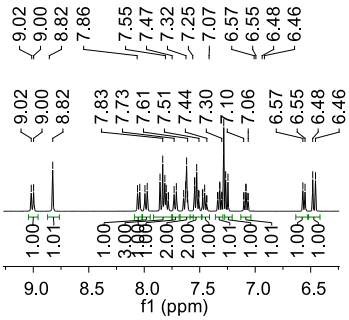

8.40
7.53
7.44
7.28
7.08
6.62
6.60
6.42
6.40
8.40
7.70
7.50
7.46
7.40
7.30
7.26
7.06
6.62
6.60
6.42
6.40
2.00
2.00
1.03
2.01
2.02
5.03
1.03
1.01
1.00
1.00
8.5
8.0
7.5
7.0
6.5
f1 (ppm)

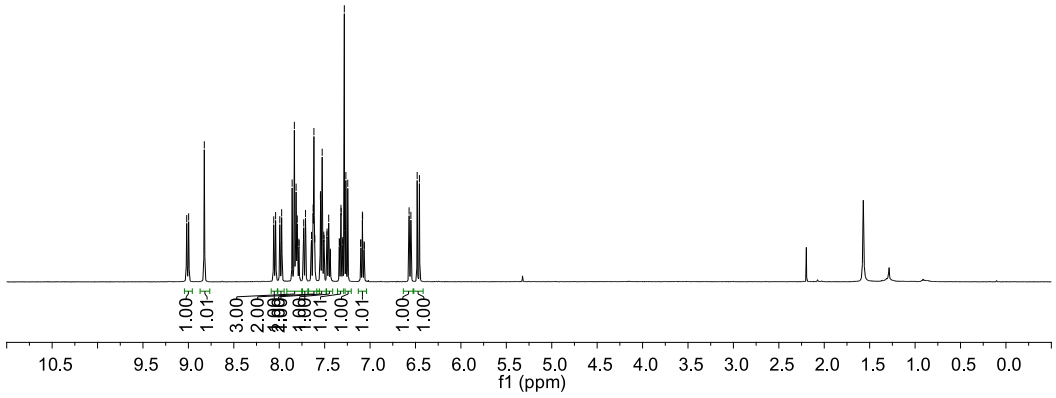

2.00
2.00
1.03
1.01
1.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

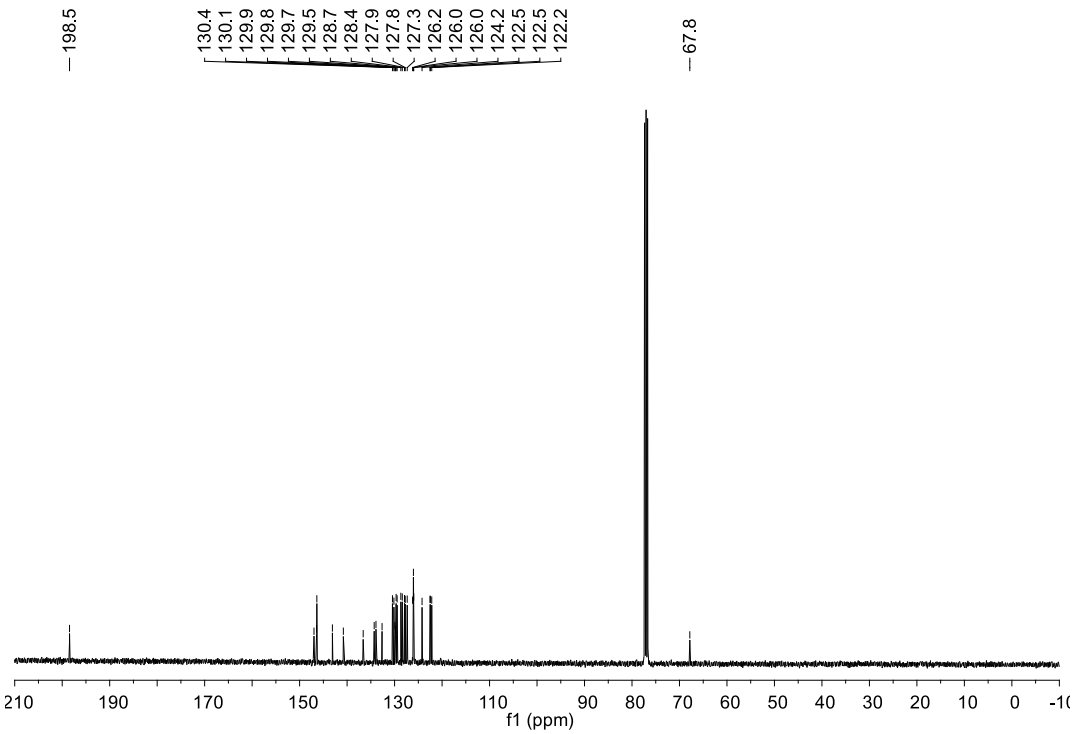

198.7
146.3
146.0
144.5
128.8
128.4
128.3
127.6
126.3
126.0
125.4
123.3
119.7
67.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

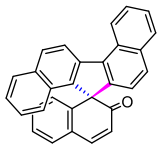


(3bg)

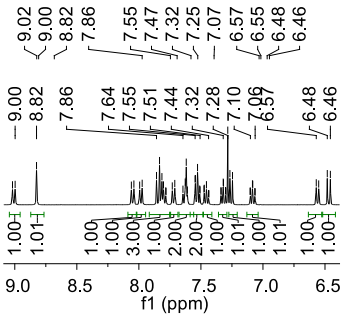

9.02
9.00
8.82
7.86
7.55
7.47
7.32
7.25
7.07
6.57
6.55
6.48
6.46
7.83
7.73
7.61
7.51
7.44
7.30
7.10
7.06
f1 (ppm)

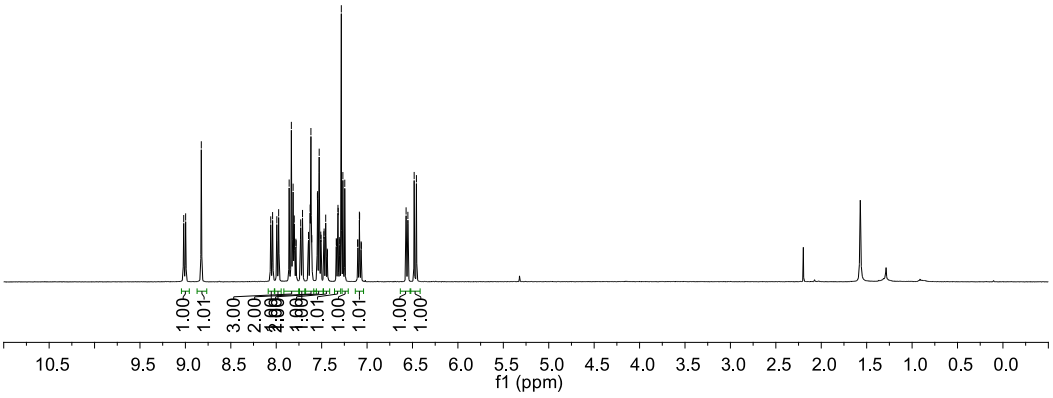

f1 (ppm)

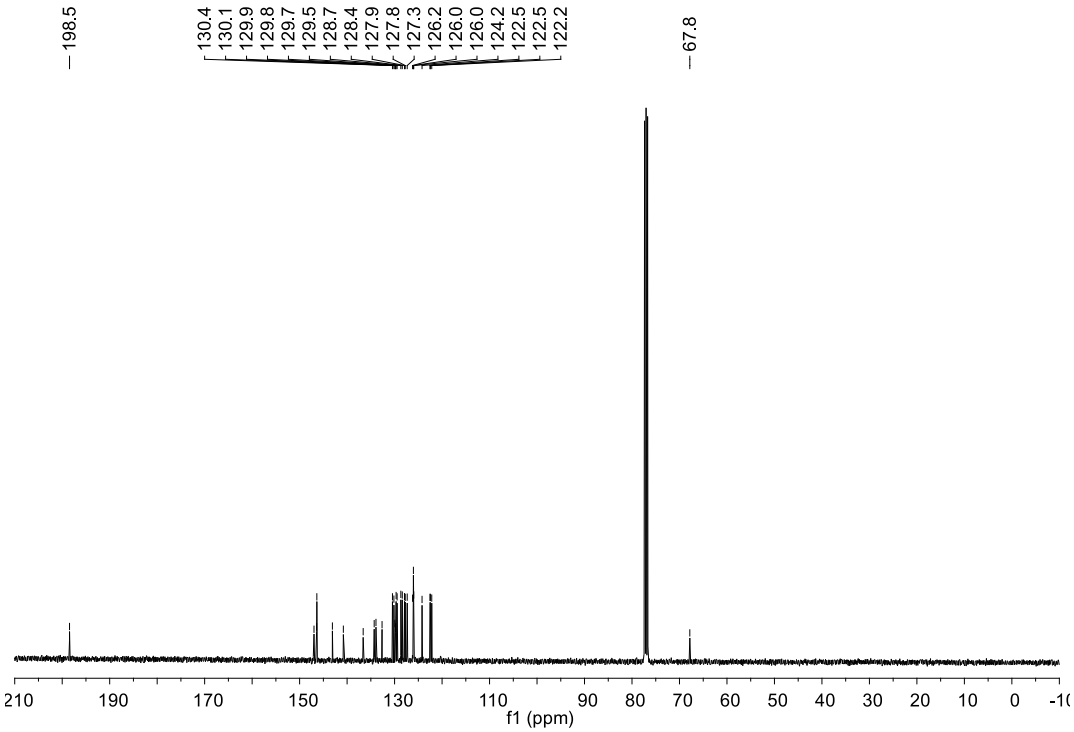

198.5
130.4
130.1
129.9
129.8
129.7
129.5
128.7
128.4
127.9
127.8
127.3
126.2
126.0
126.0
124.2
122.5
122.5
122.2
67.8
f1 (ppm)

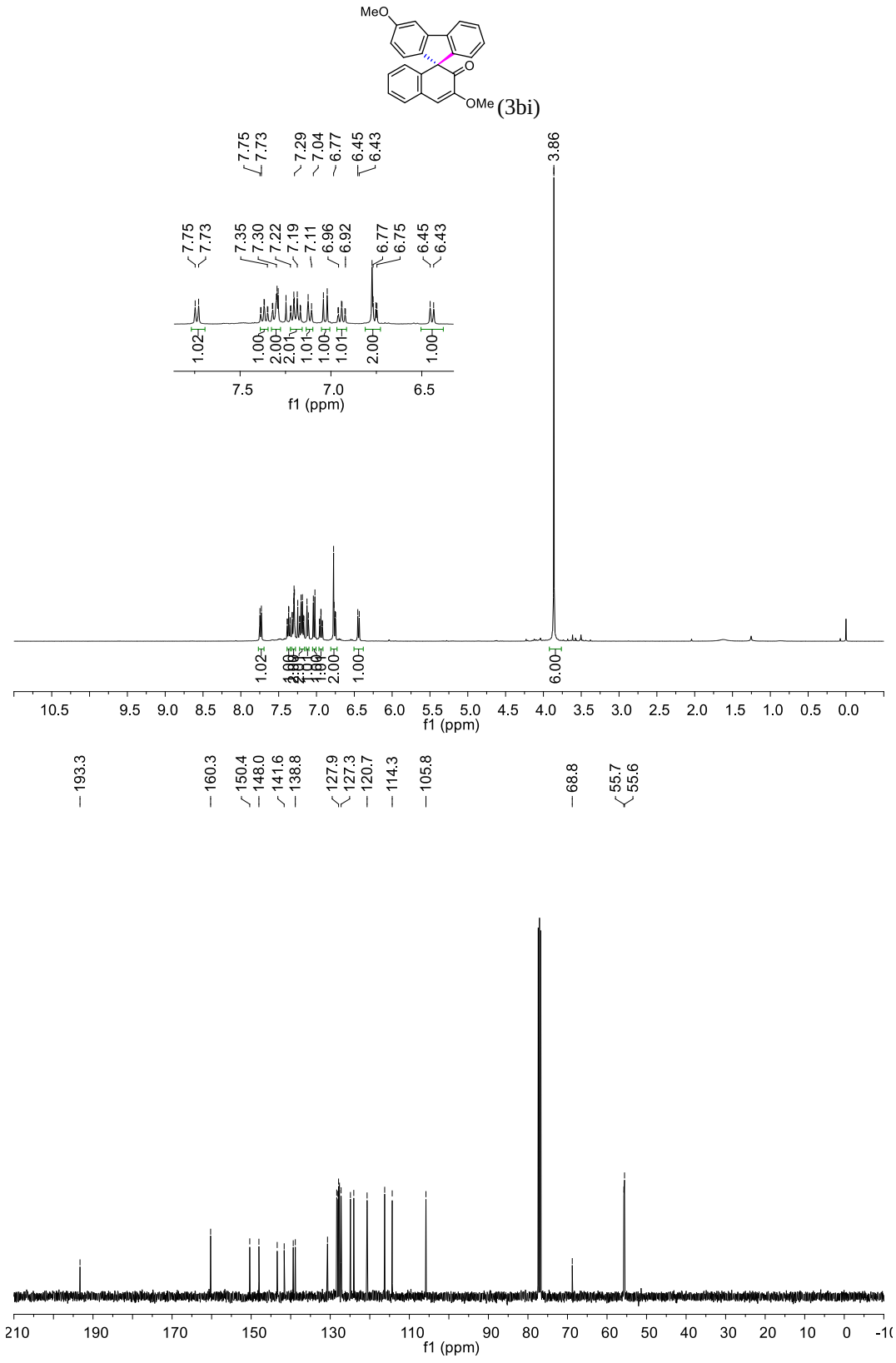


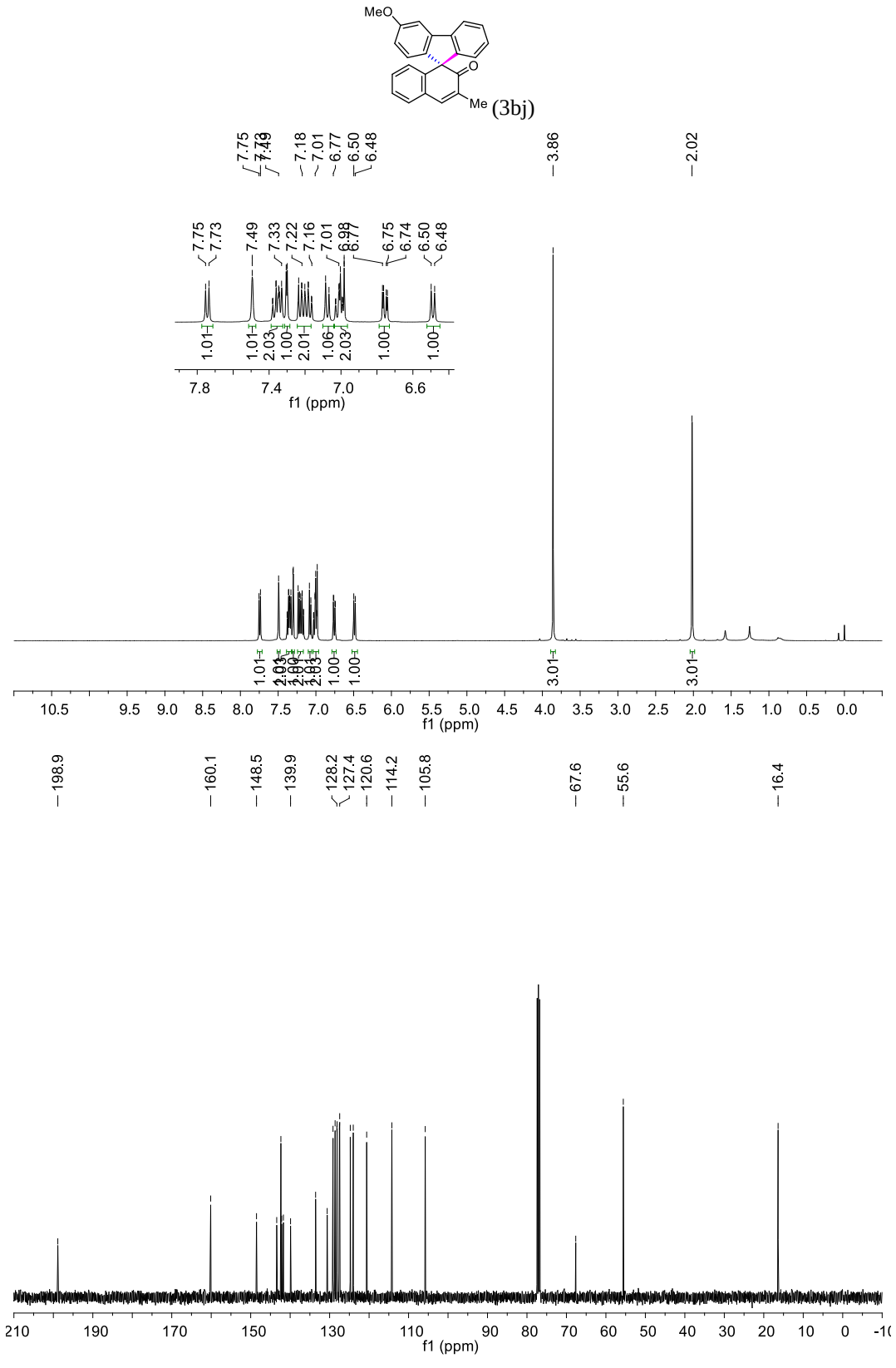
(3bh)

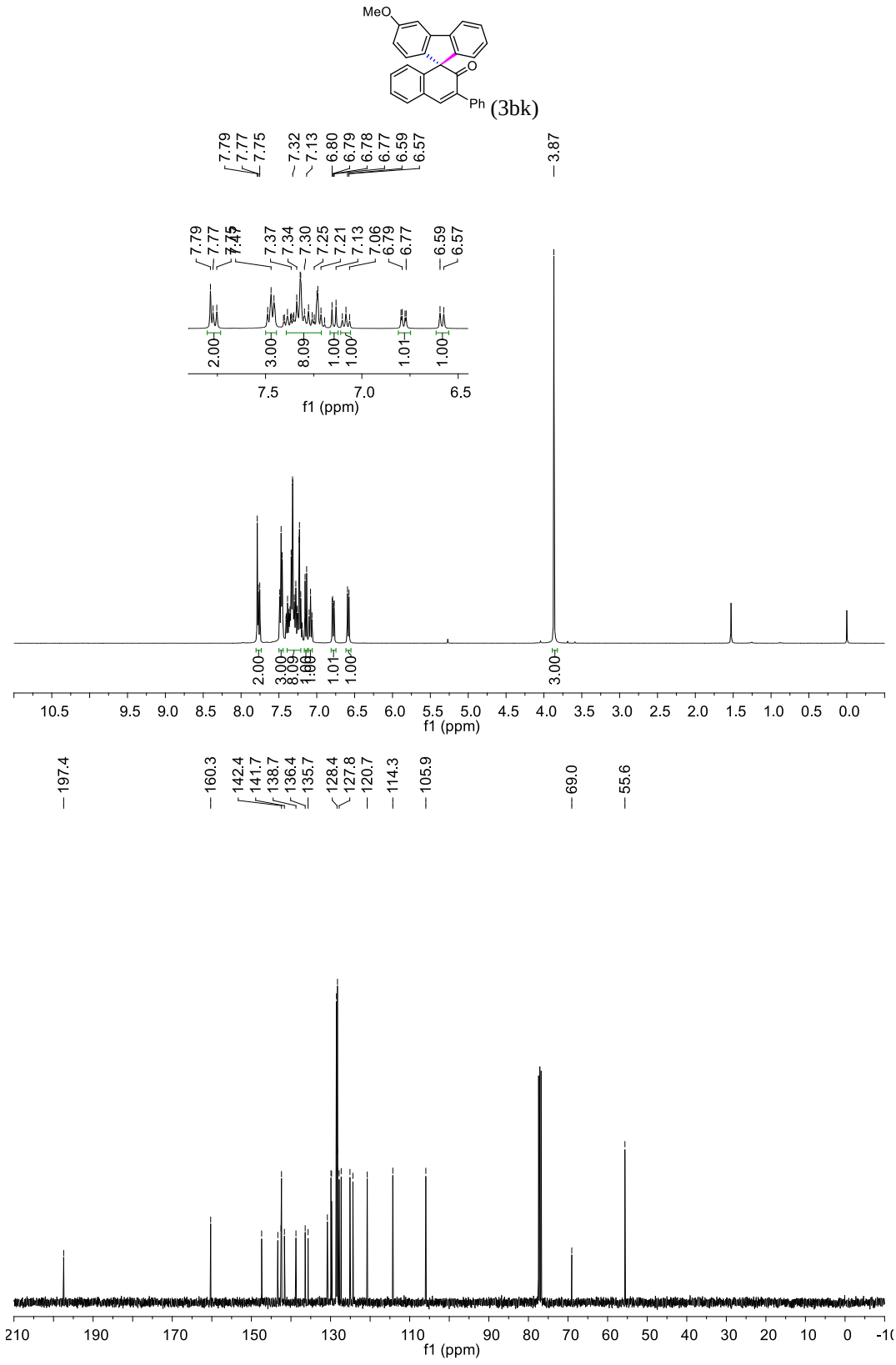

9.02
9.00
8.82
7.86
7.55
7.47
7.32
7.25
7.07
6.57
6.55
6.48
6.46
f1 (ppm)

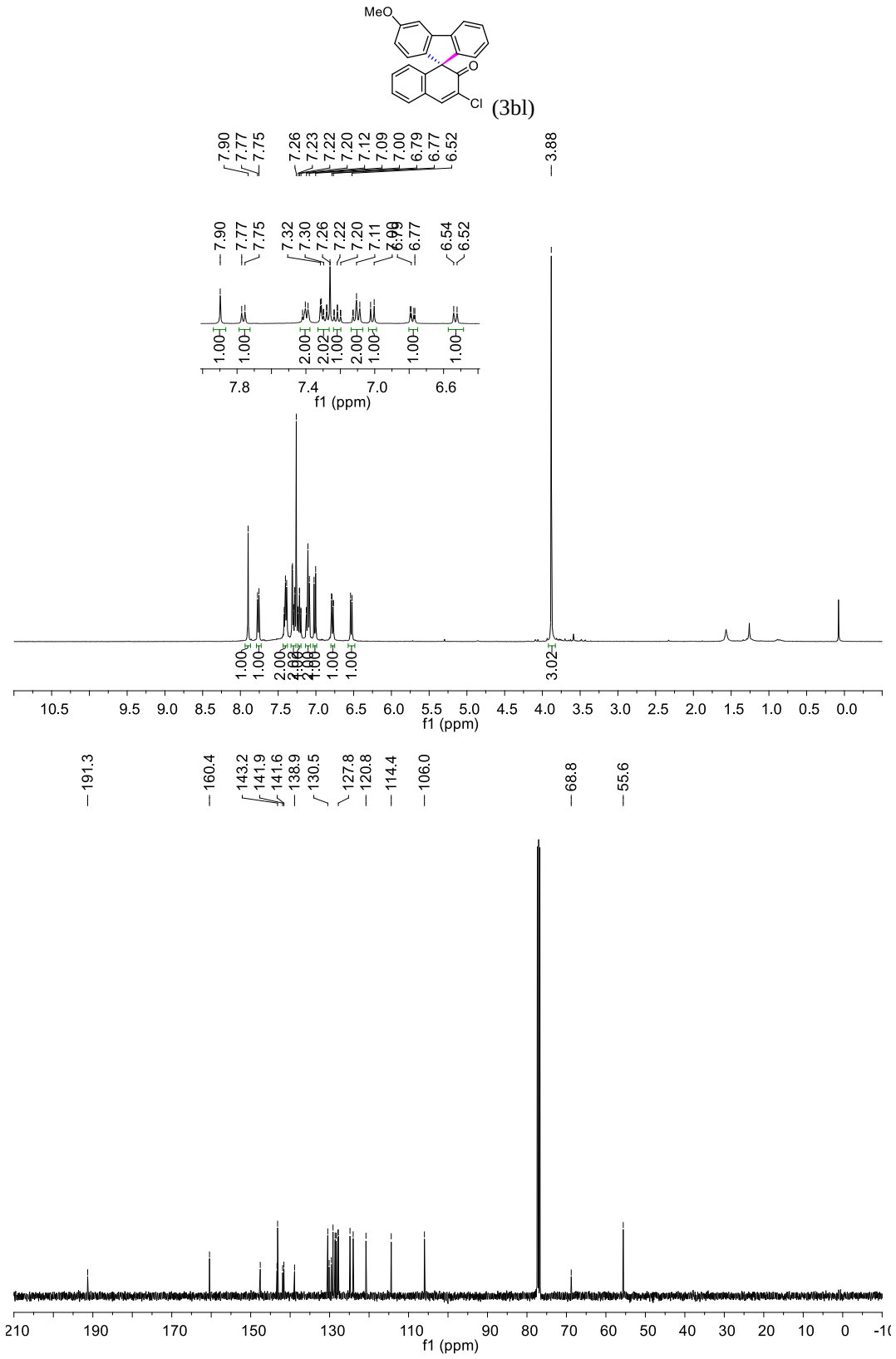

f1 (ppm)


198.5
130.4
130.1
129.9
129.8
129.7
129.5
128.7
128.4
127.9
127.8
127.3
126.2
126.0
126.0
124.2
122.5
122.5
122.2
67.8
f1 (ppm)


MeO
O
OMe
(3bi)
7.75
7.73
7.29
7.04
6.77
6.45
6.43
3.86
7.35
7.30
7.22
7.19
7.11
6.96
6.92
6.77
6.75
f1 (ppm)
193.3
160.3
150.4
148.0
141.6
138.8
127.9
127.3
120.7
114.3
105.8
68.8
55.7
55.6

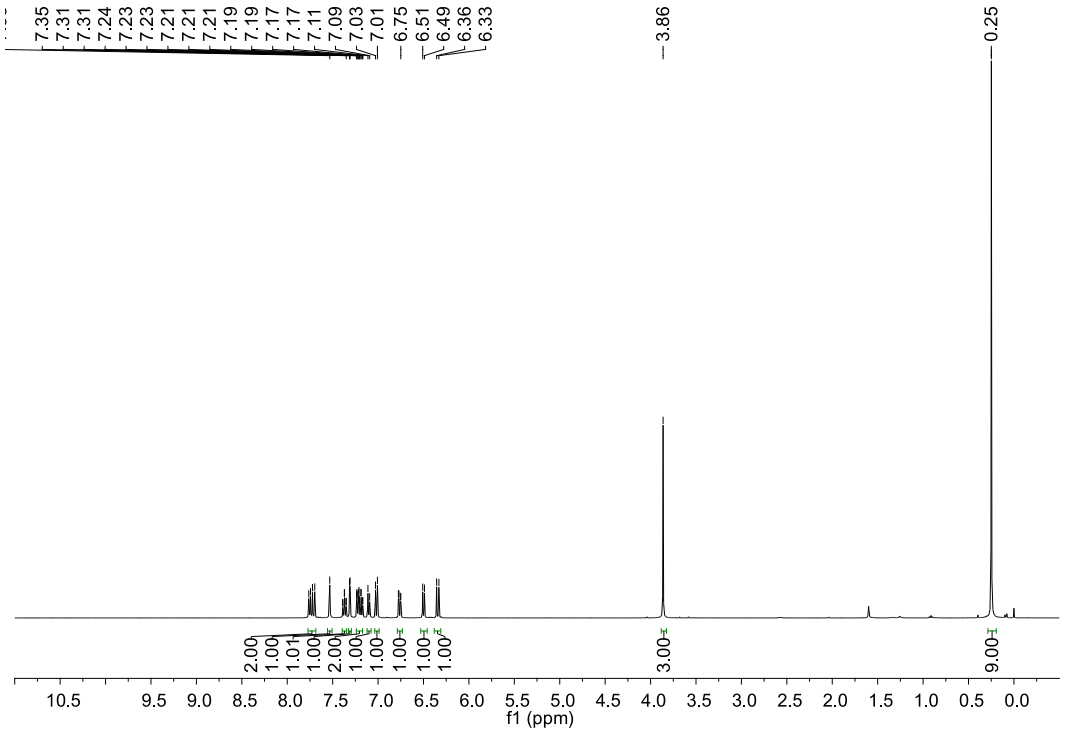

MeO
O
Me
(3bj)
7.75
7.73
7.49
7.33
7.22
7.16
7.01
6.98
6.77
6.75
6.74
6.50
6.48
3.86
2.02
1.01
1.01
2.03
1.00
2.01
1.06
2.03
1.00
1.00
7.8
7.4
7.0
6.6
f1 (ppm)
3.01
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.9
160.1
148.5
139.9
128.2
127.4
120.6
114.2
105.8
67.6
55.6
16.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

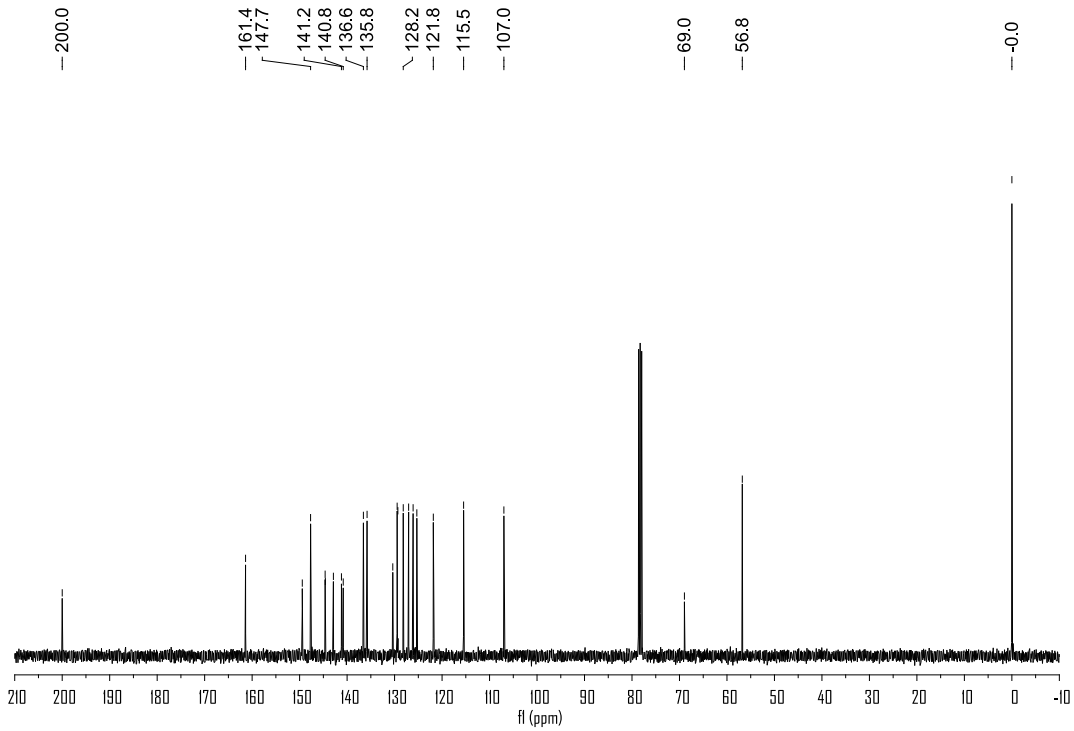

MeO
O
Ph
(3bk)
7.79
7.77
7.75
7.32
7.13
6.80
6.79
6.78
6.77
6.59
6.57
3.87
7.37
7.34
7.30
7.25
7.21
7.06
2.00
3.00
8.09
1.00
1.01
f1 (ppm)
f1 (ppm)
197.4
160.3
142.4
141.7
138.7
136.4
135.7
128.4
127.8
120.7
114.3
105.9
69.0
55.6
f1 (ppm)

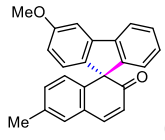

MeO
O
Cl
(3bl)
7.90
7.77
7.75
7.26
7.23
7.22
7.20
7.12
7.09
7.00
6.79
6.77
6.52
3.88
7.32
7.30
6.54
6.52
f1 (ppm)
191.3
160.4
143.2
141.9
141.6
138.9
130.5
127.8
120.8
114.4
106.0
68.8
55.6


MeO
O
TMS

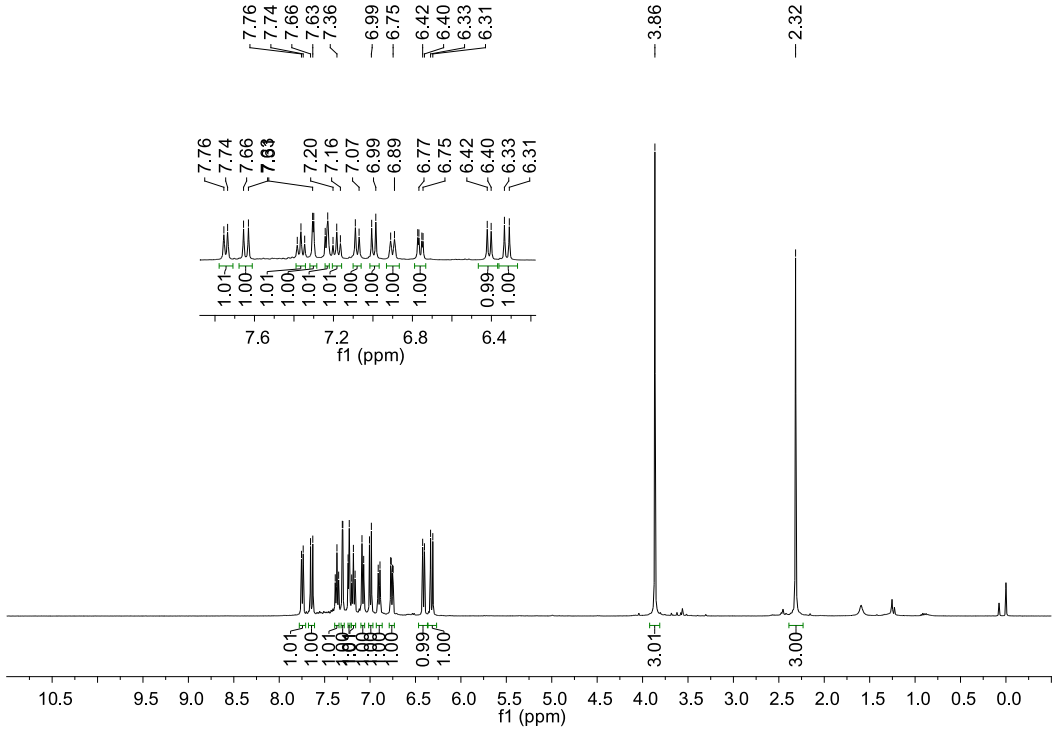
(3bm)

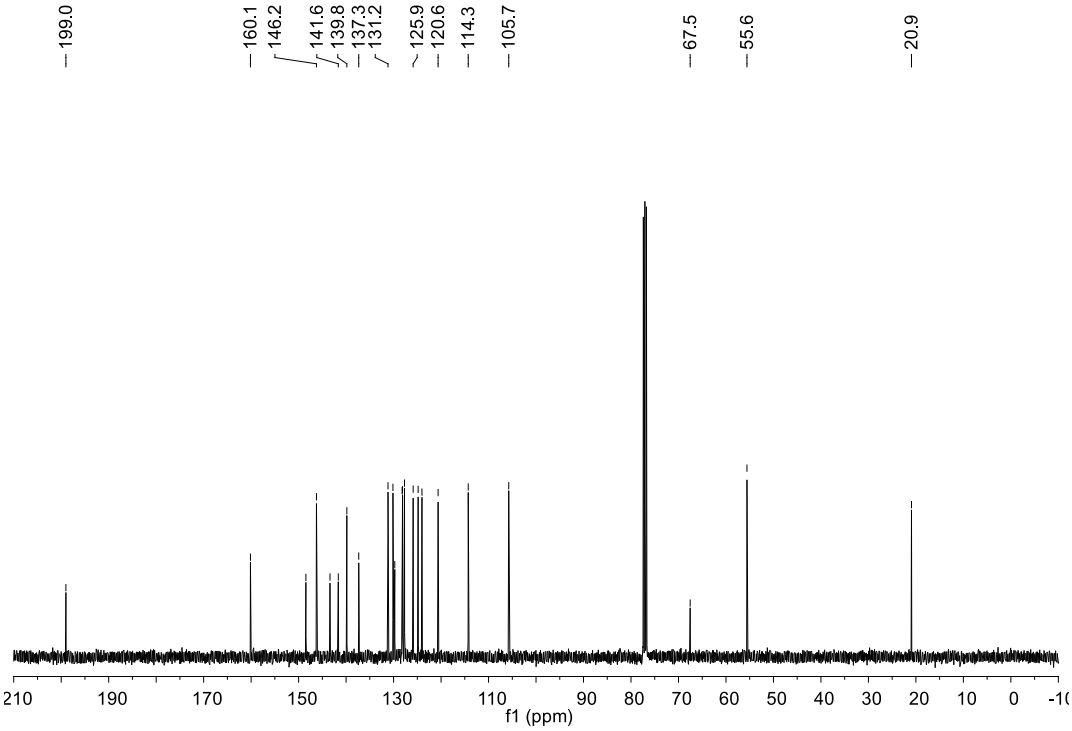

7.35
7.31
7.31
7.24
7.23
7.23
7.21
7.21
7.21
7.19
7.19
7.17
7.17
7.11
7.09
7.03
7.01
6.75
6.51
6.49
6.36
6.33
3.86
0.25
2.00
1.00
1.01
1.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
9.00
f1 (ppm)

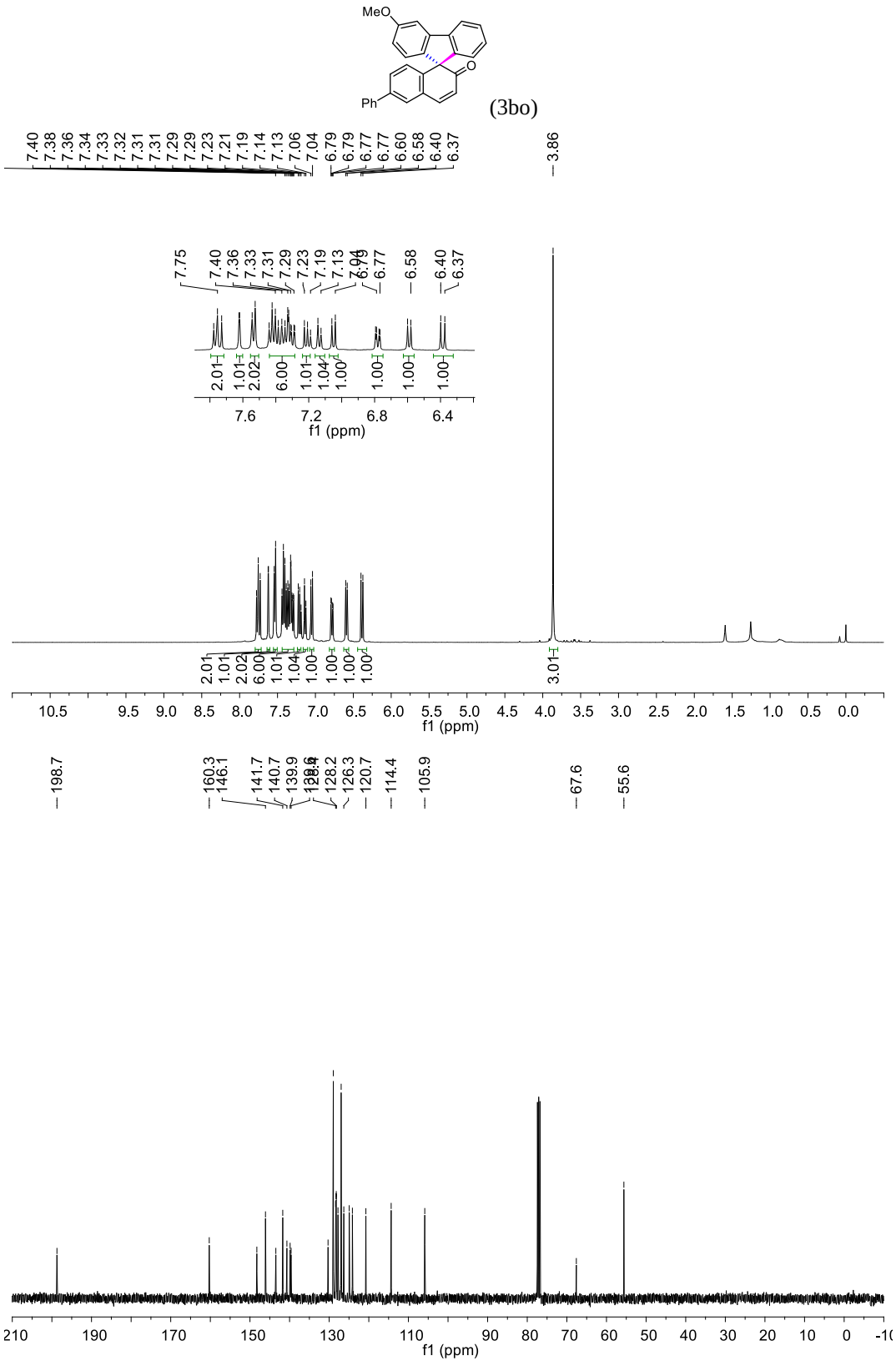

200.0
161.4
147.7
141.2
140.8
136.6
135.8
128.2
121.8
115.5
107.0
69.0
56.8
-0.0
f1 (ppm)

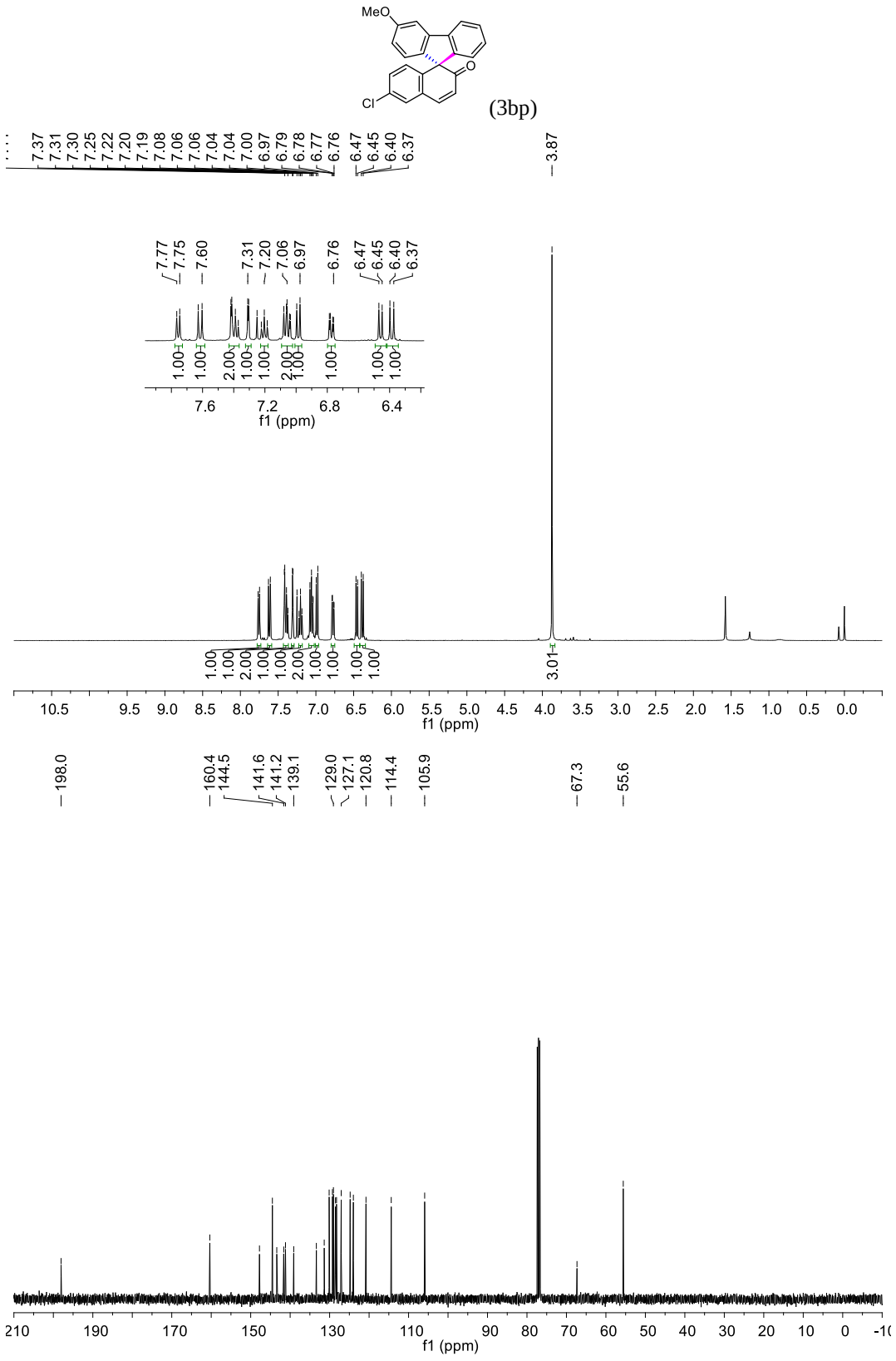

MeO
O
Me

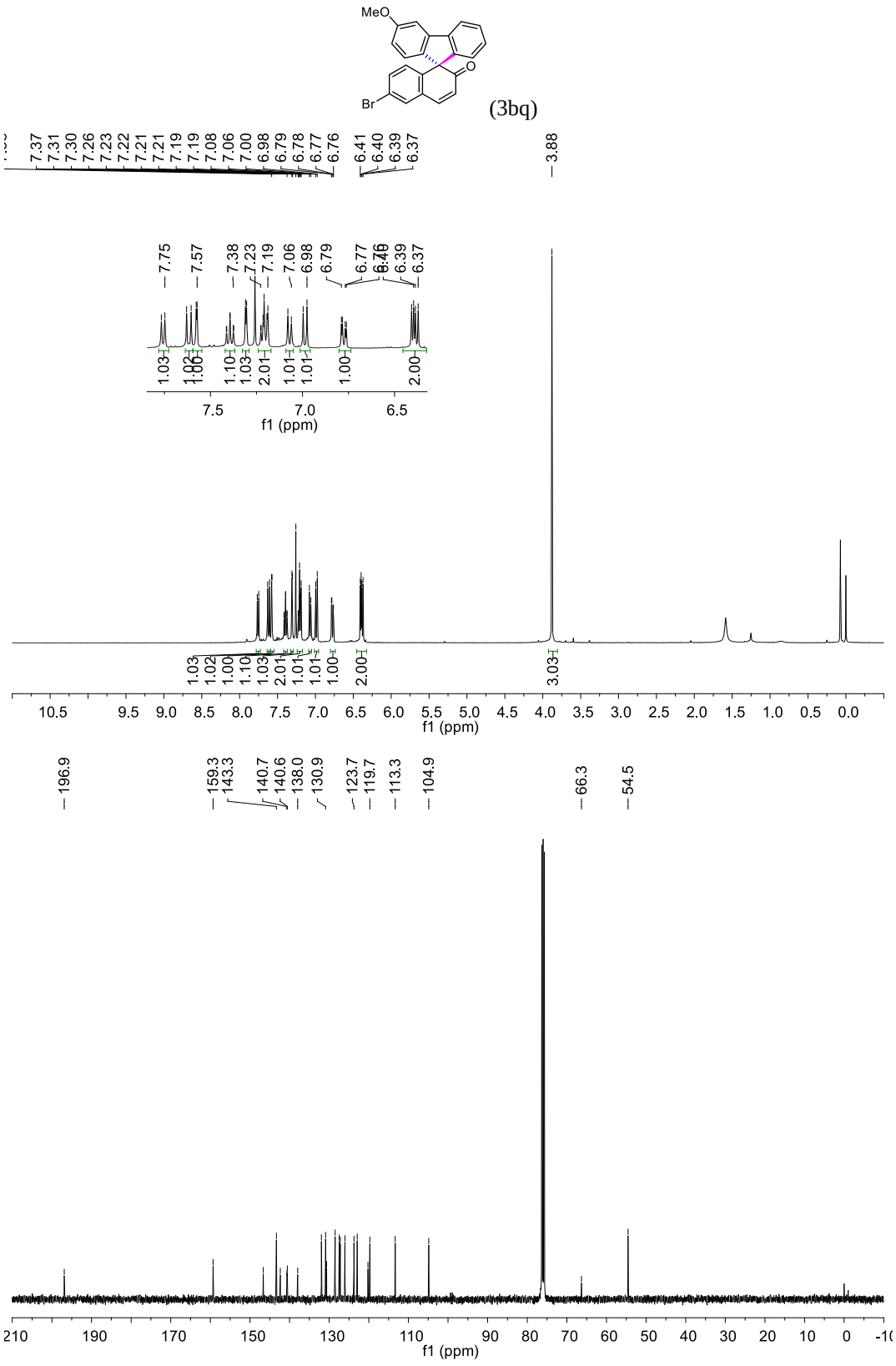
(3bn)

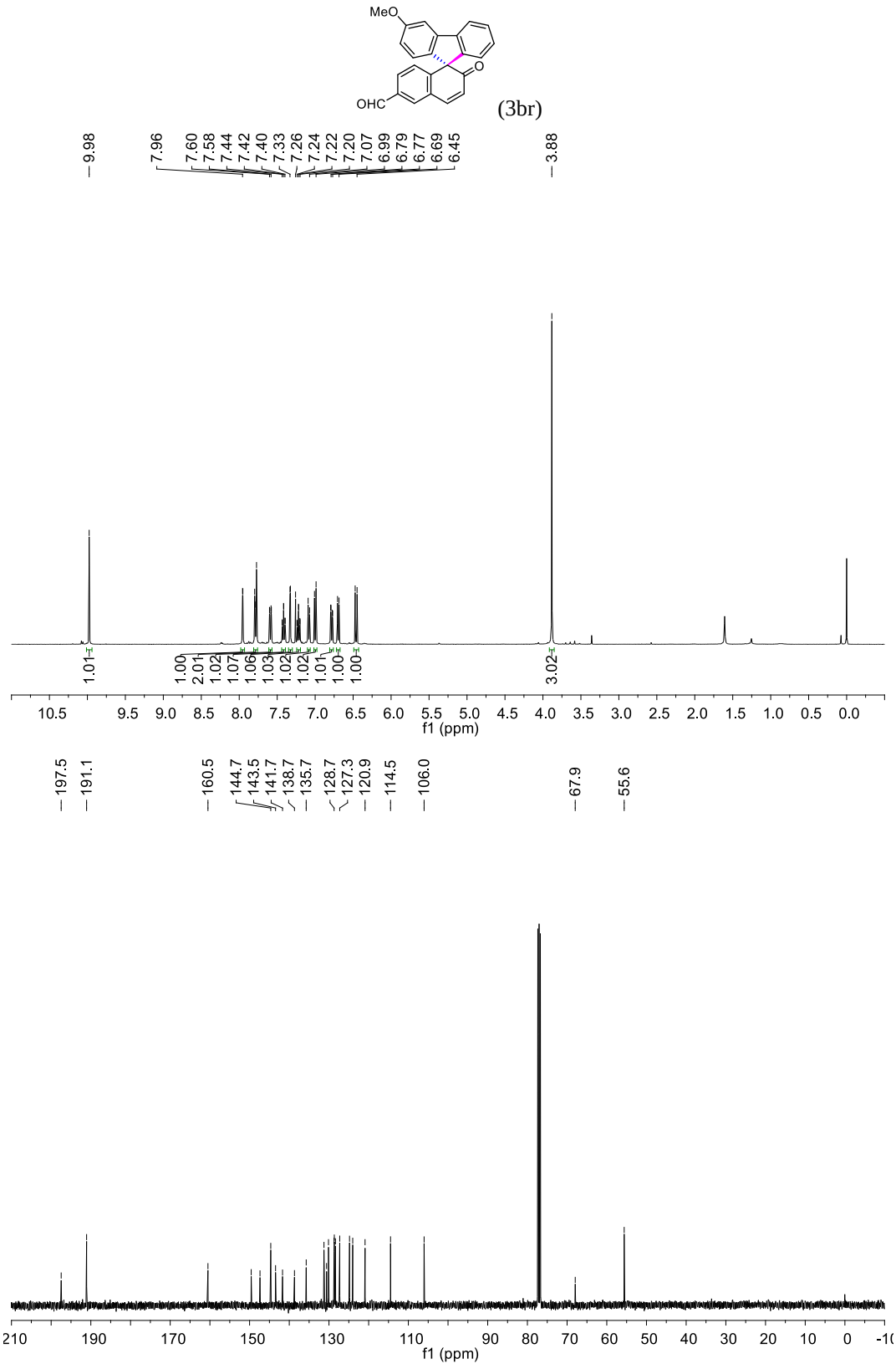

7.76
7.74
7.66
7.63
7.36
6.99
6.75
6.42
6.40
6.33
6.31
3.86
2.32
7.20
7.16
7.07
6.89
6.77
6.75
1.01
1.00
0.99
3.01
3.00
f1 (ppm)

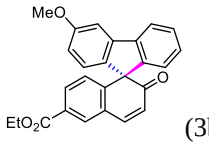

199.0
160.1
146.2
141.6
139.8
137.3
131.2
125.9
120.6
114.3
105.7
67.5
55.6
20.9
f1 (ppm)


MeO
O
Ph
(3bo)
7.40
7.38
7.36
7.34
7.33
7.32
7.31
7.31
7.29
7.29
7.23
7.21
7.19
7.14
7.13
7.06
7.04
6.79
6.79
6.77
6.77
6.60
6.58
6.40
6.37
3.86
7.75
7.40
7.36
7.33
7.31
7.29
7.23
7.19
7.13
6.77
6.58
6.40
6.37
2.01
1.01
2.02
6.00
1.01
1.04
1.00
1.00
1.00
1.00
7.6
7.2
6.8
6.4
f1 (ppm)
2.01
1.01
2.02
6.00
1.01
1.04
1.00
1.00
1.00
1.00
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.7
160.3
146.1
141.7
140.7
139.9
128.2
126.3
120.7
114.4
105.9
67.6
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

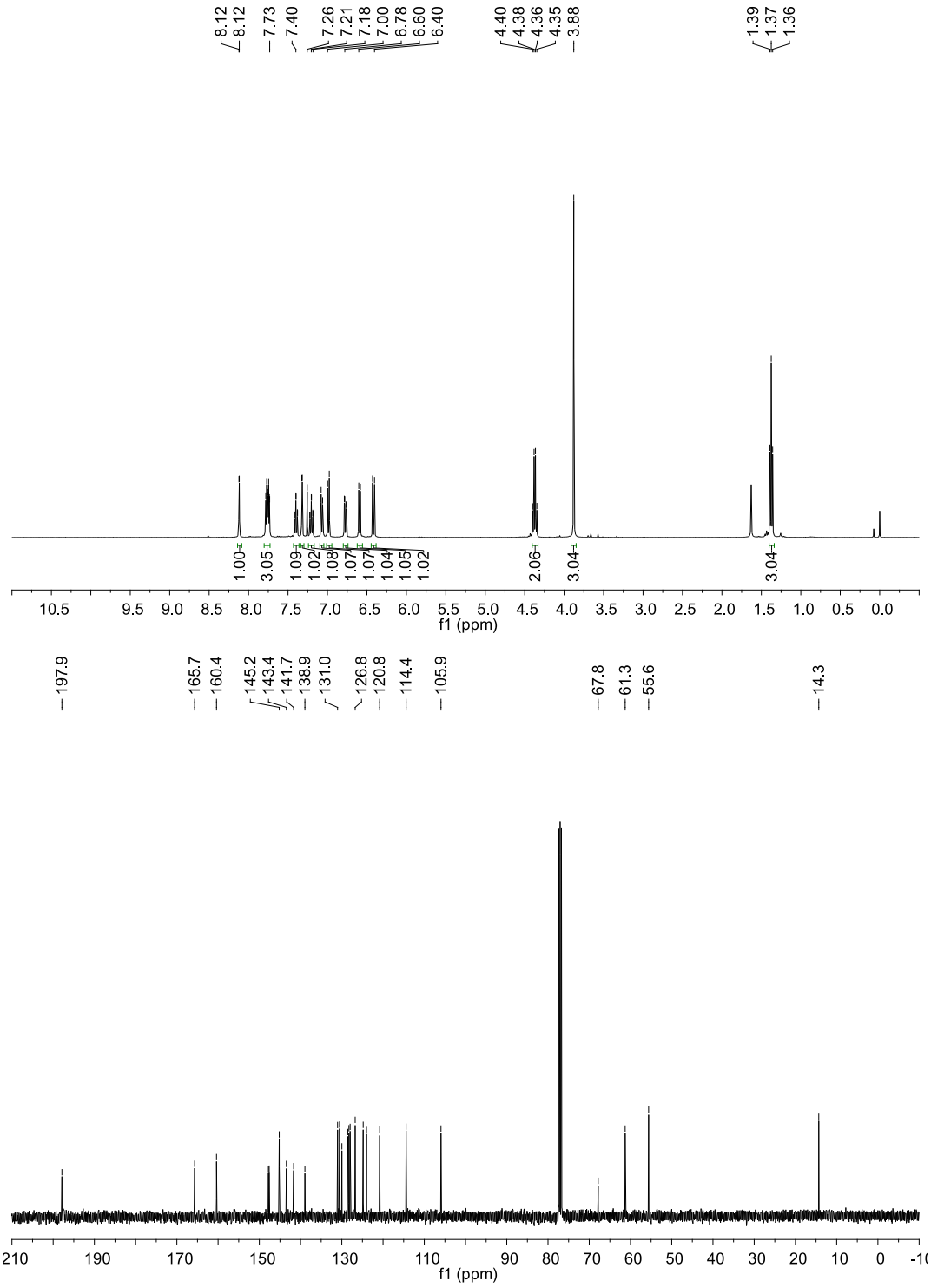

MeO
O
Cl
(3bp)
7.37
7.31
7.30
7.25
7.22
7.20
7.19
7.08
7.06
7.06
7.04
7.04
7.00
6.97
6.79
6.78
6.77
6.76
6.47
6.45
6.40
6.37
3.87
7.77
7.75
7.60
7.31
7.20
7.06
6.97
6.76
6.47
6.45
6.40
6.37
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
7.6
7.2
6.8
6.4
f1 (ppm)
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.0
160.4
144.5
141.6
141.2
139.1
129.0
127.1
120.8
114.4
105.9
67.3
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

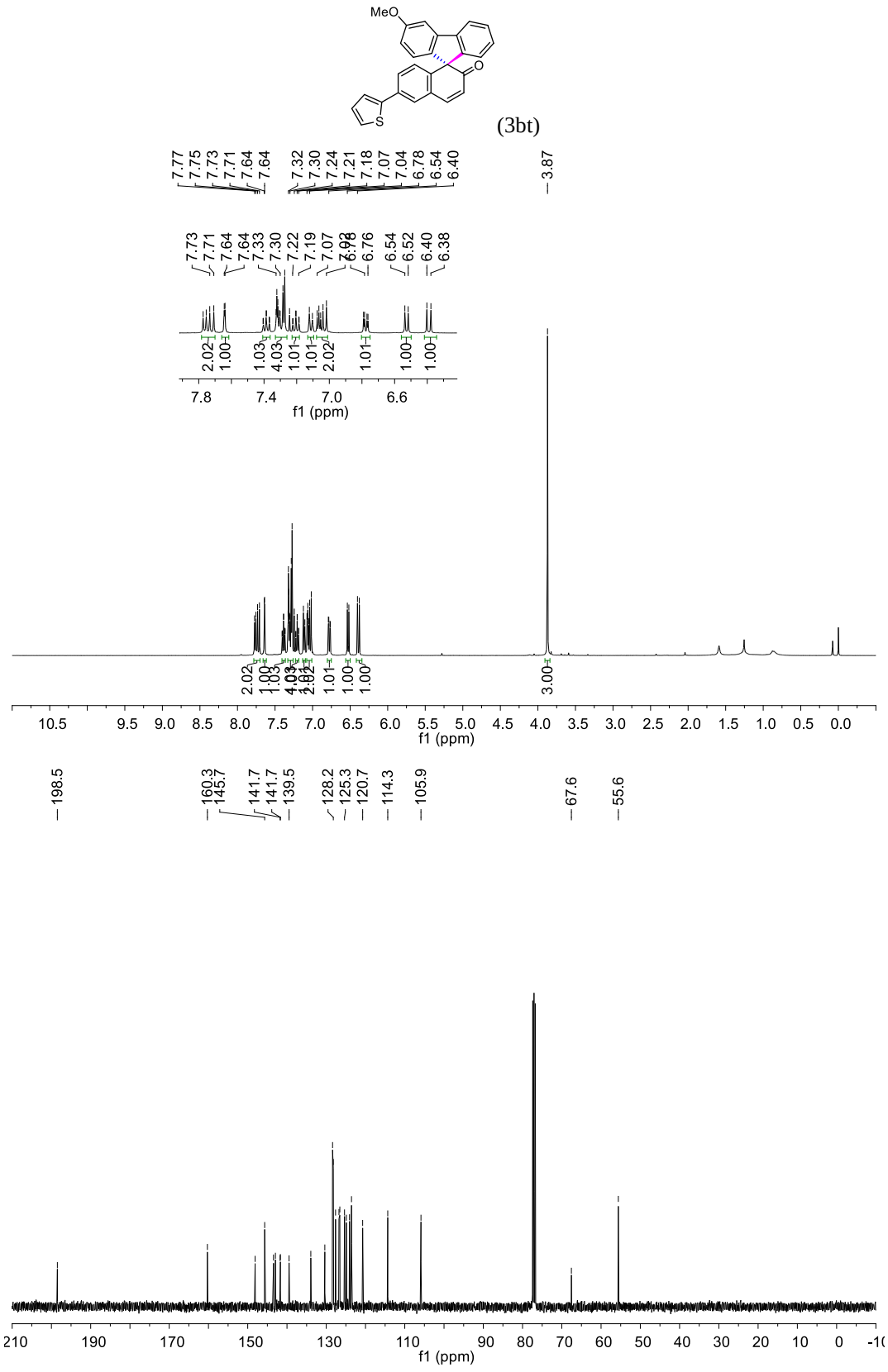

MeO
O
Br
(3bq)
7.37
7.31
7.30
7.26
7.23
7.22
7.21
7.21
7.19
7.19
7.08
7.06
7.00
6.98
6.79
6.78
6.77
6.76
6.41
6.40
6.39
6.37
3.88
7.75
7.57
7.38
7.23
7.19
7.06
6.98
6.79
6.77
6.39
6.37
1.03
1.02
1.00
1.10
1.03
2.01
1.01
1.01
1.00
2.00
7.5
7.0
6.5
f1 (ppm)
3.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
196.9
159.3
143.3
140.7
140.6
138.0
130.9
123.7
119.7
113.3
104.9
66.3
54.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

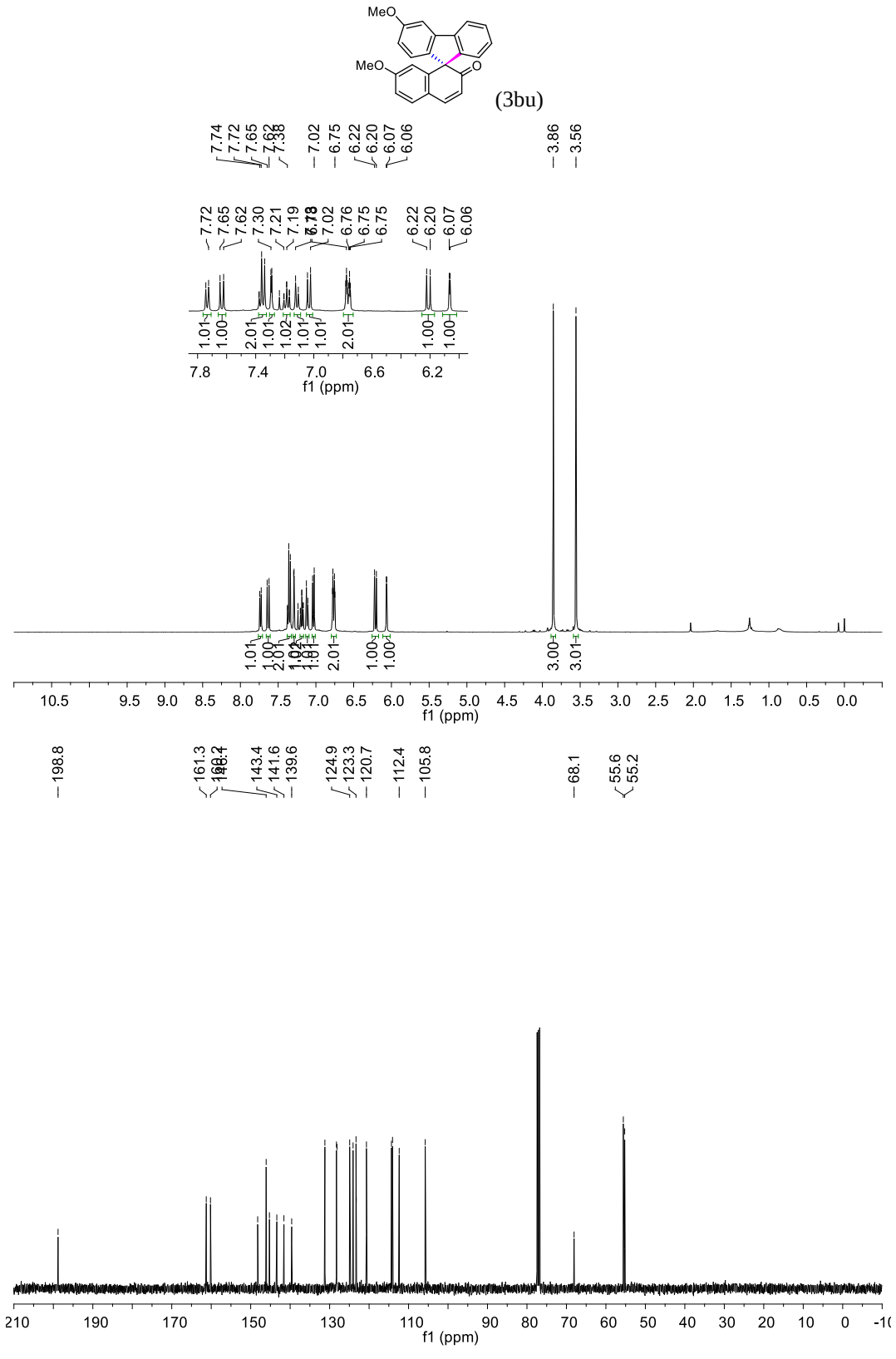

MeO
O
OHC
(3br)
9.98
7.96
7.60
7.58
7.44
7.42
7.40
7.33
7.26
7.24
7.22
7.20
7.07
6.99
6.79
6.77
6.69
6.45
3.88
1.01
1.00
2.01
1.02
1.07
1.06
1.03
1.02
1.02
1.01
1.00
1.00
3.02
f1 (ppm)
197.5
191.1
160.5
144.7
143.5
141.7
138.7
135.7
128.7
127.3
120.9
114.5
106.0
67.9
55.6
f1 (ppm)

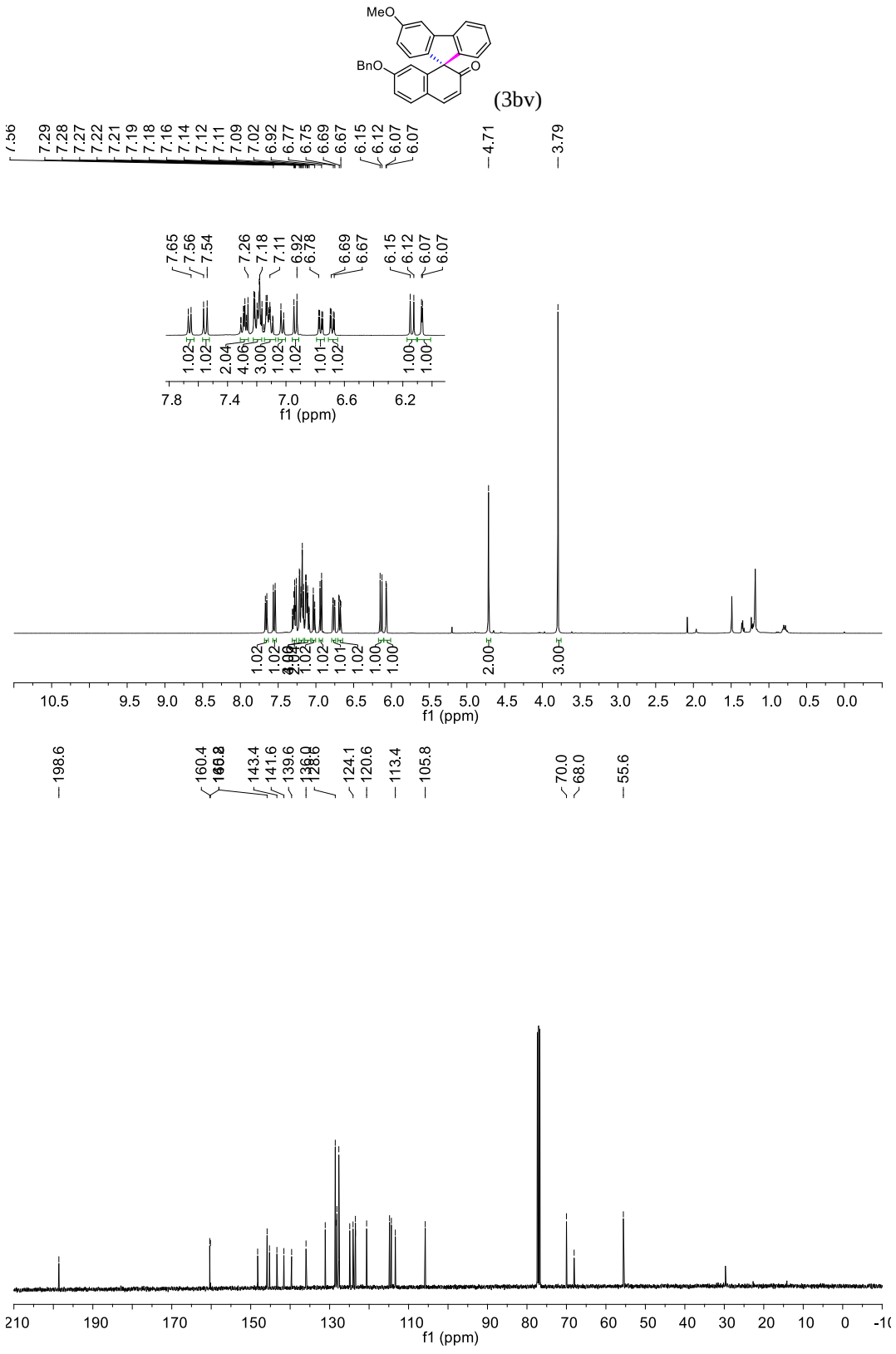

MeO
O
EtO2C

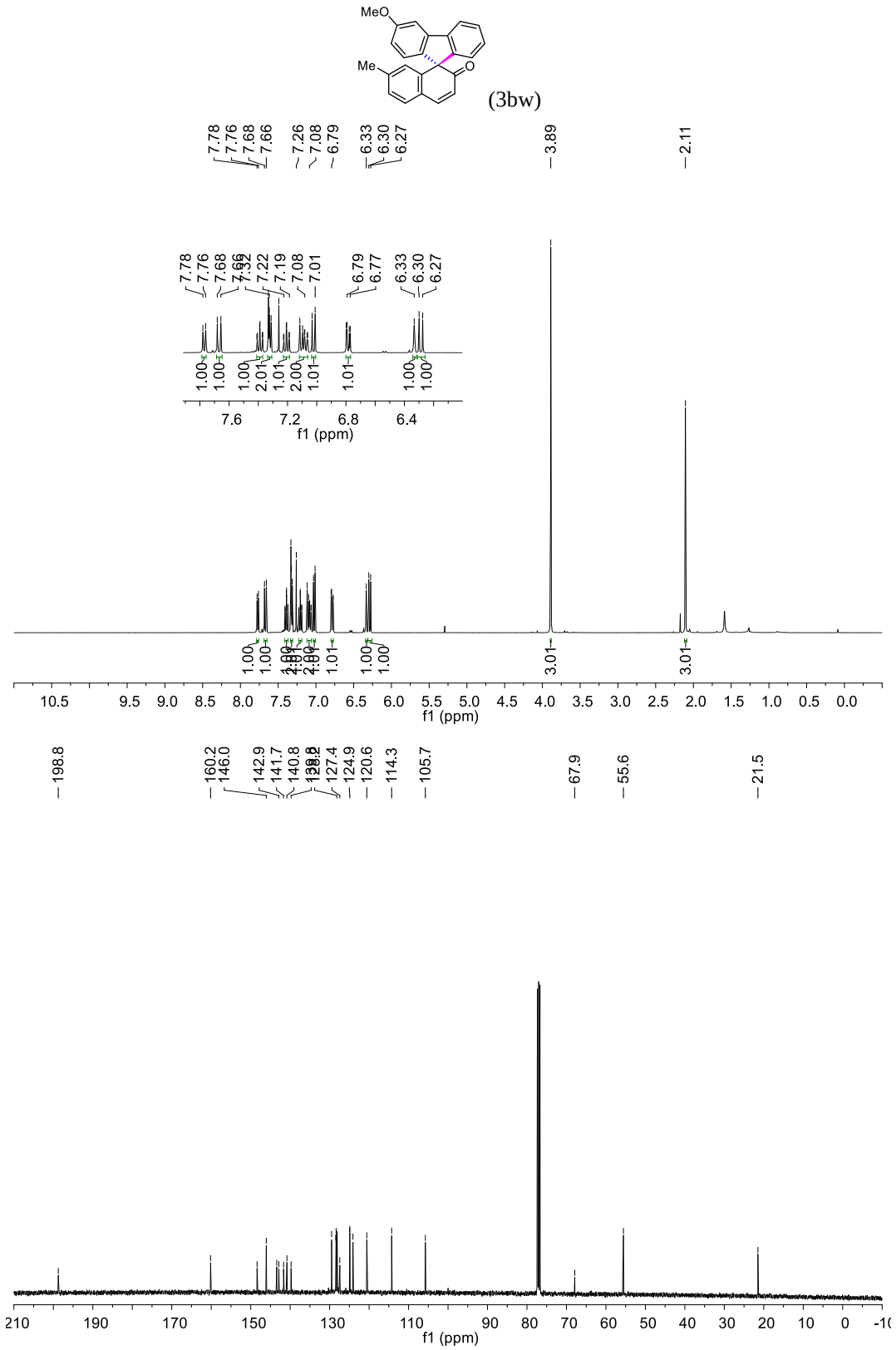
(3bs)

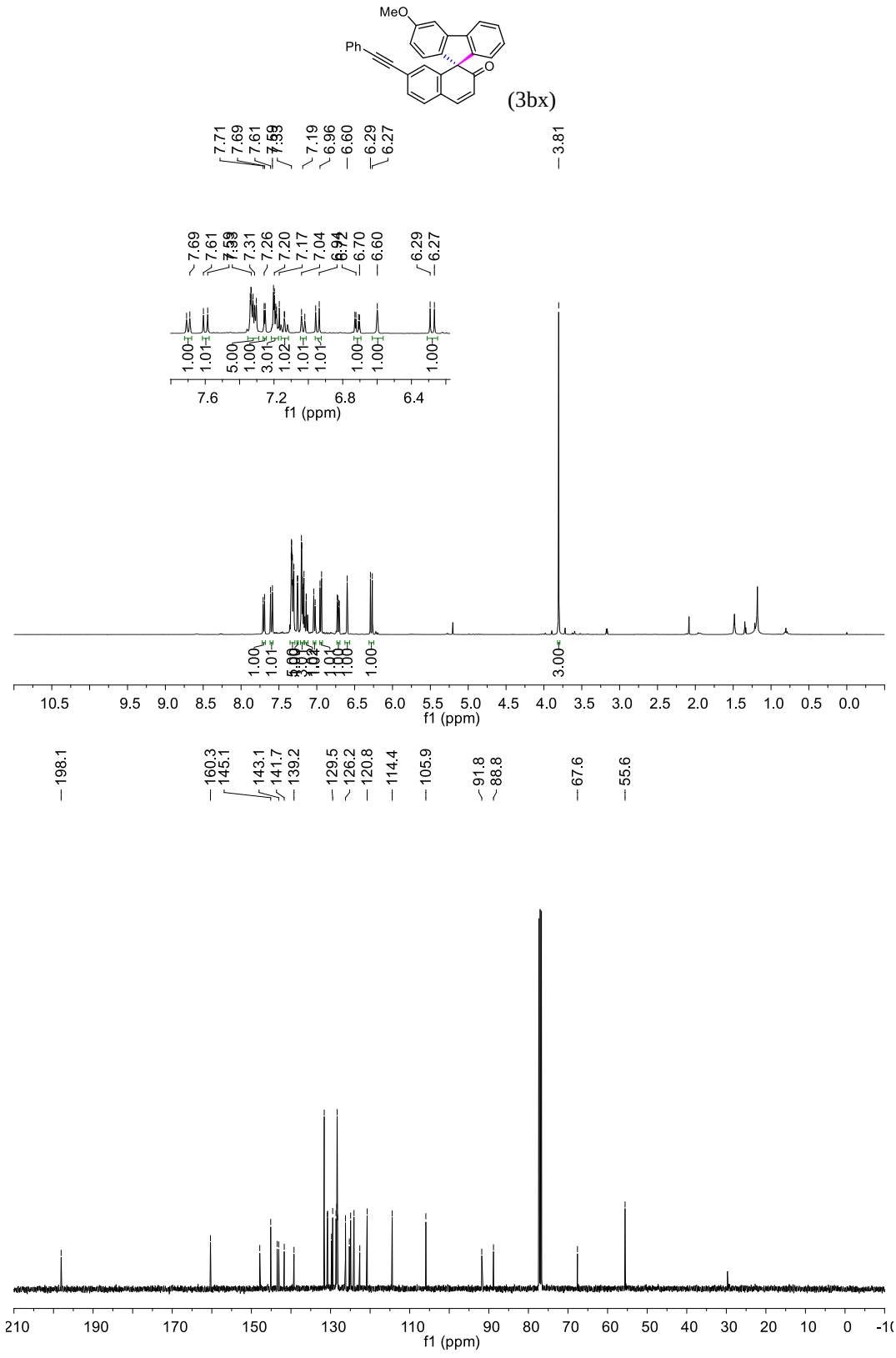

8.12
8.12
7.73
7.40
7.26
7.21
7.18
7.00
6.78
6.60
6.40
4.40
4.38
4.36
4.35
3.88
1.39
1.37
1.36
1.00
3.05
1.09
1.02
1.08
1.07
1.07
1.04
1.05
1.02
2.06
3.04
3.04
f1 (ppm)
197.9
165.7
160.4
145.2
143.4
141.7
138.9
131.0
126.8
120.8
114.4
105.9
67.8
61.3
55.6
14.3
f1 (ppm)

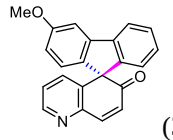

MeO
O
S
(3bt)
7.77
7.75
7.73
7.71
7.64
7.64
7.32
7.30
7.24
7.21
7.18
7.07
7.04
6.78
6.54
6.40
3.87
7.8
7.4
7.0
6.6
f1 (ppm)
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.5
160.3
145.7
141.7
141.7
139.5
128.2
125.3
120.7
114.3
105.9
67.6
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
MeO
O
(3bu)
7.74
7.72
7.65
7.62
7.38
7.02
6.75
6.22
6.20
6.07
6.06
3.86
3.56
7.72
7.65
7.62
7.30
7.21
7.19
7.02
6.76
6.75
6.75
6.22
6.20
6.07
6.06
1.01
1.00
2.01
1.01
1.02
1.01
1.01
2.01
1.00
1.00
7.8
7.4
7.0
6.6
6.2
f1 (ppm)
1.01
1.00
2.01
1.02
1.01
1.01
2.01
1.00
1.00
3.00
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.8
161.3
143.4
141.6
139.6
124.9
123.3
120.7
112.4
105.8
68.1
55.6
55.2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

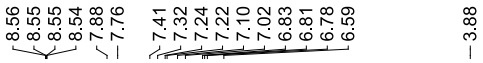

MeO
BnO
O
(3bv)
7.29
7.28
7.27
7.22
7.21
7.19
7.18
7.16
7.14
7.12
7.11
7.09
7.02
6.92
6.77
6.75
6.69
6.67
6.15
6.12
6.07
6.07
4.71
3.79
7.65
7.56
7.54
7.26
7.18
7.11
6.92
6.78
6.69
6.67
6.15
6.12
6.07
6.07
1.02
1.02
2.04
4.06
3.00
1.02
1.02
1.01
1.02
1.00
1.00
7.8
7.4
7.0
6.6
6.2
f1 (ppm)
1.02
1.02
1.02
1.02
1.01
1.02
1.00
1.00
2.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.6
160.4
143.4
141.6
139.6
124.1
120.6
113.4
105.8
70.0
68.0
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

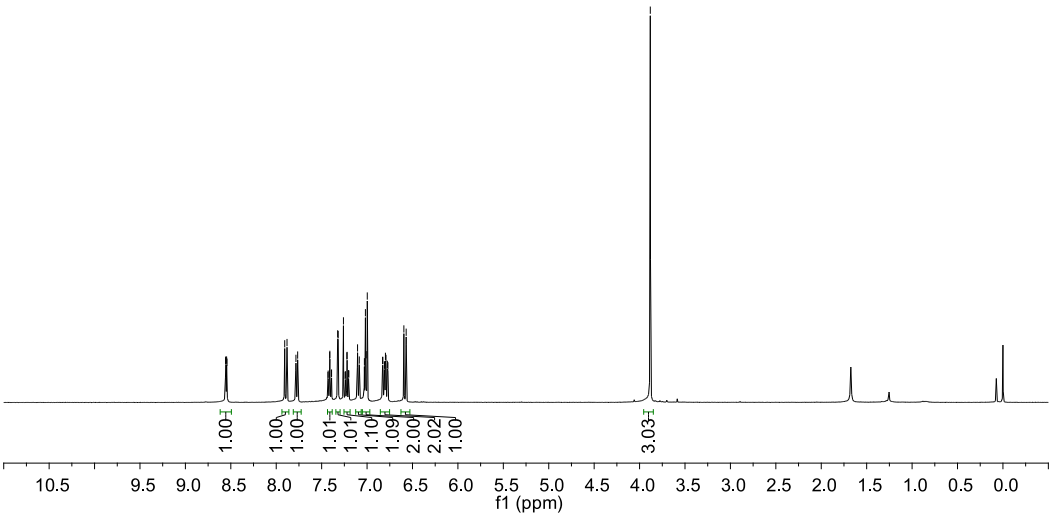

MeO
Me
O
(3bw)
7.78
7.76
7.68
7.66
7.26
7.08
6.79
6.33
6.30
6.27
3.89
2.11
7.78
7.76
7.68
7.66
7.32
7.22
7.19
7.08
7.01
6.79
6.77
6.33
6.30
6.27
1.00
1.00
1.00
2.01
1.01
2.00
1.01
1.01
1.00
1.00
7.6
7.2
6.8
6.4
f1 (ppm)
1.00
1.00
1.00
1.01
1.00
1.00
3.01
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.8
160.2
146.0
142.9
141.7
140.8
127.4
124.9
120.6
114.3
105.7
67.9
55.6
21.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

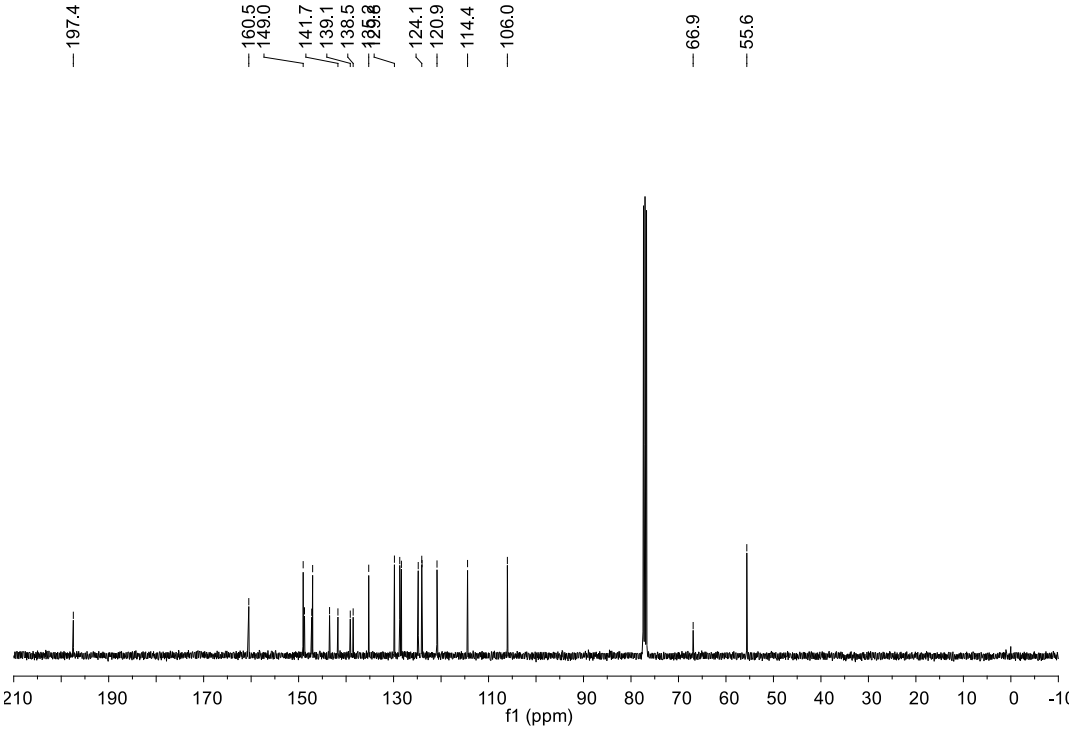

MeO
Ph
O
(3bx)
7.71
7.69
7.61
7.19
6.96
6.60
6.29
6.27
3.81
7.69
7.61
7.31
7.26
7.20
7.17
7.04
6.70
6.60
6.29
6.27
1.00
1.01
5.00
1.00
3.01
1.02
1.01
1.01
1.00
1.00
1.00
7.6
7.2
6.8
6.4
f1 (ppm)
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.1
160.3
145.1
143.1
141.7
139.2
129.5
126.2
120.8
114.4
105.9
91.8
88.8
67.6
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

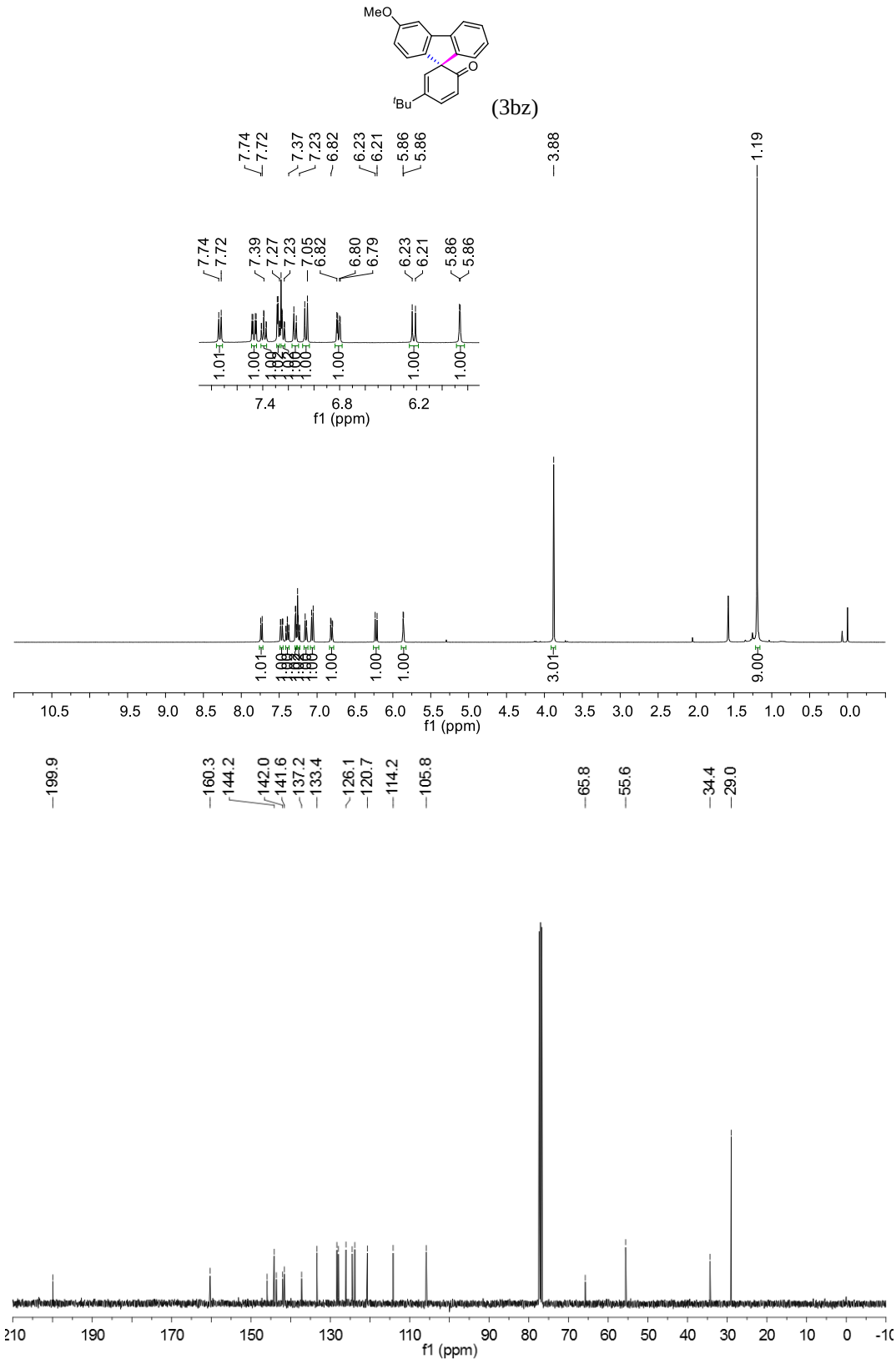

MeO
O
N

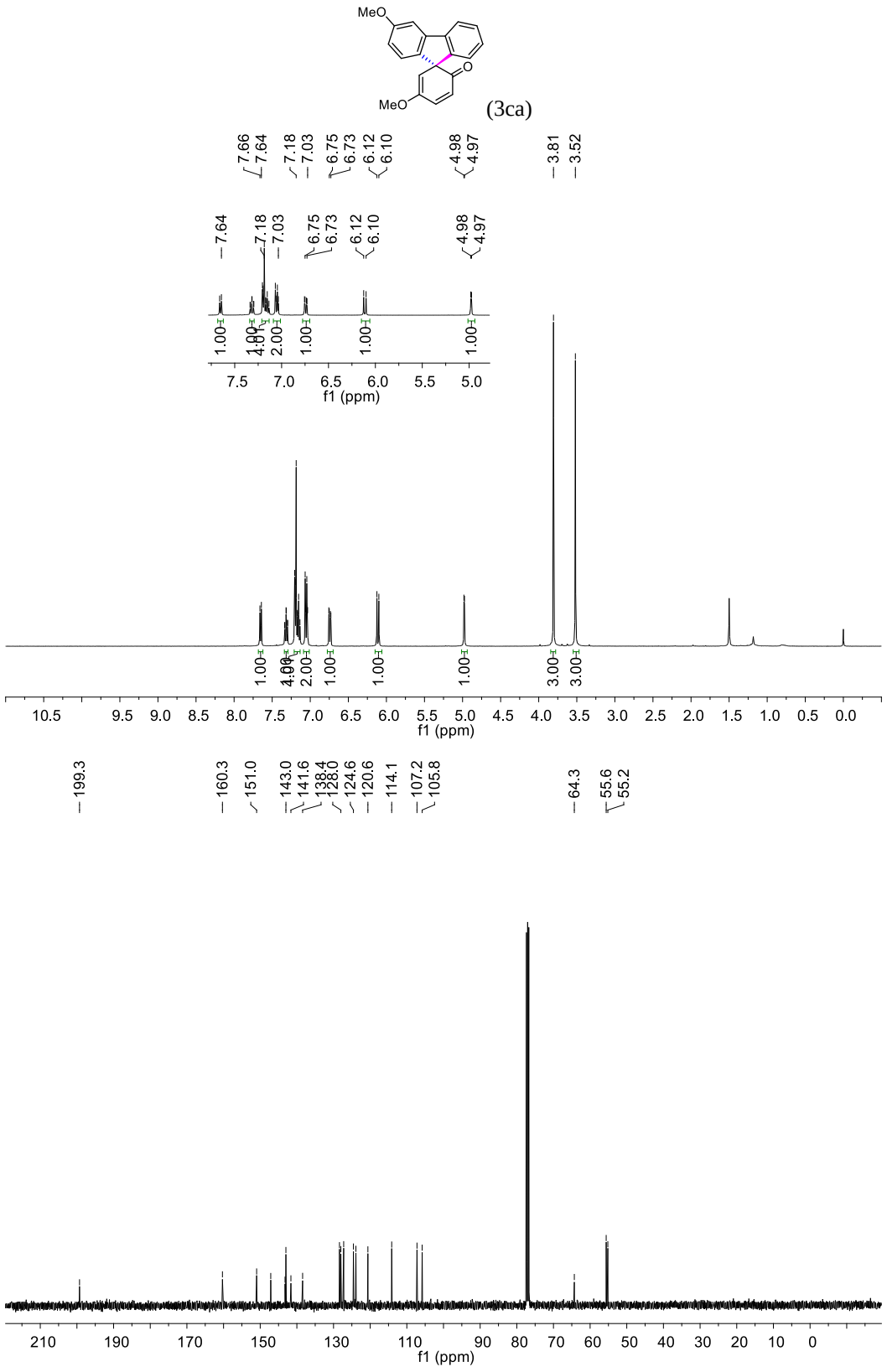
(3by)

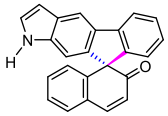

8.56
8.55
8.55
8.54
7.88
7.76
7.41
7.32
7.24
7.22
7.10
7.02
6.83
6.81
6.78
6.59
3.88


1.00
1.00
1.00
1.01
1.01
1.10
1.09
2.00
2.02
1.00
3.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

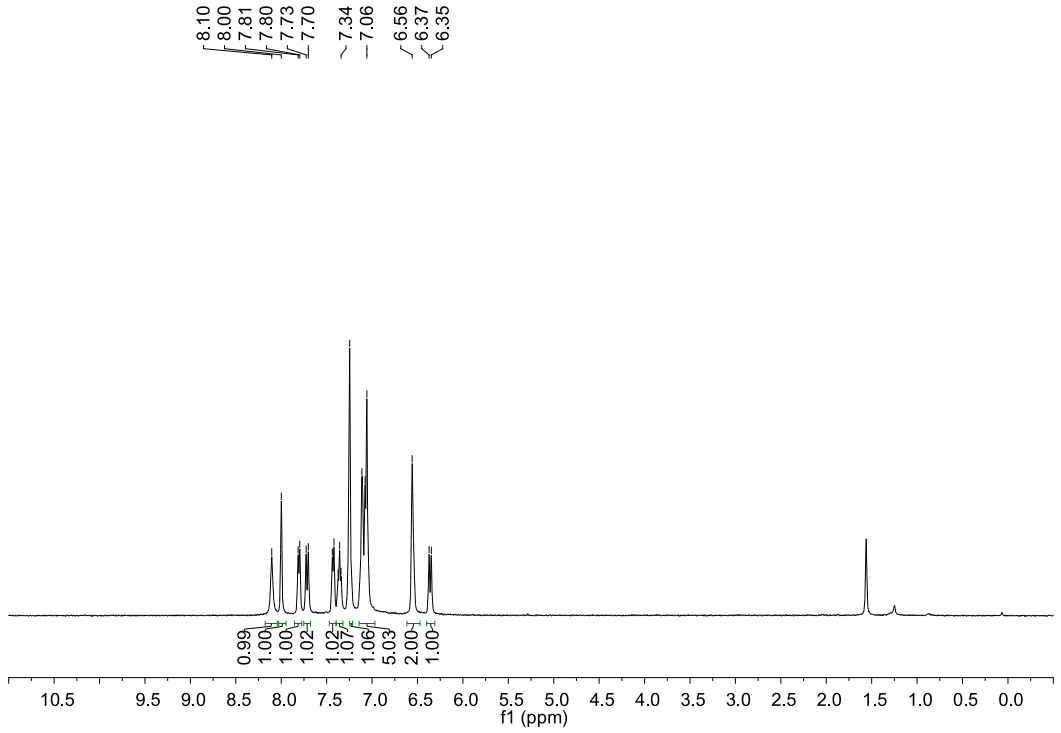

197.4
160.5
149.0
141.7
139.1
138.5
124.1
120.9
114.4
106.0
66.9
55.6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

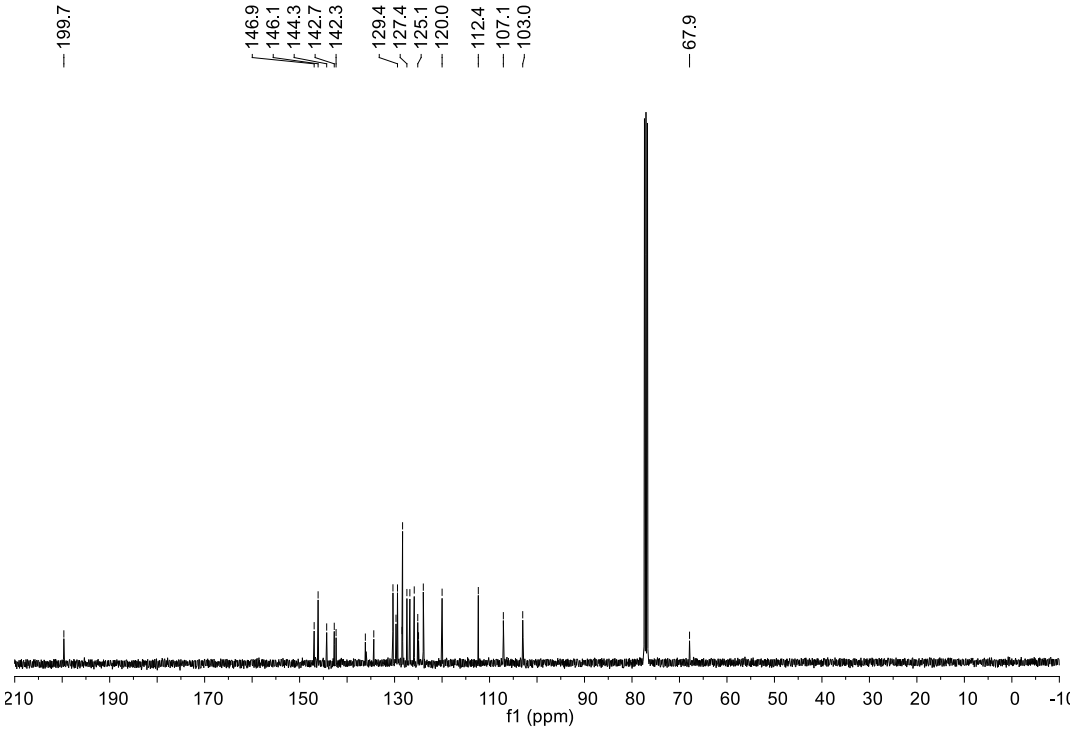

MeO
O
tBu
(3bz)
7.74
7.72
7.37
7.23
6.82
6.23
6.21
5.86
5.86
3.88
1.19
7.39
7.27
7.05
6.80
6.79
1.01
1.00
1.00
1.00
1.00
1.00
7.4
6.8
6.2
f1 (ppm)
3.01
9.00
f1 (ppm)
199.9
160.3
144.2
142.0
141.6
137.2
133.4
126.1
120.7
114.2
105.8
65.8
55.6
34.4
29.0
f1 (ppm)

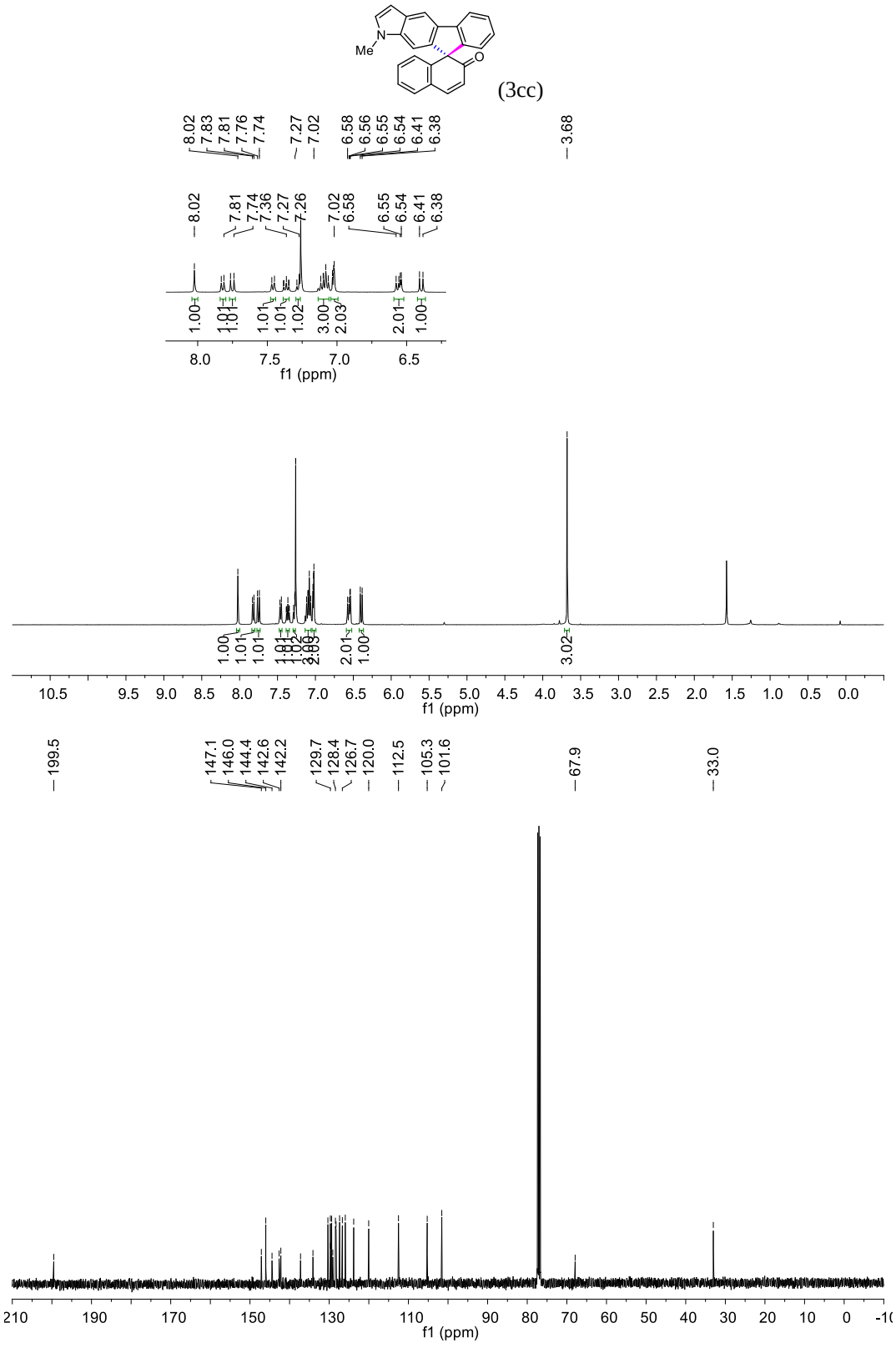

MeO
O
MeO
(3ca)
7.66
7.64
7.18
7.03
6.75
6.73
6.12
6.10
4.98
4.97
3.81
3.52
1.00
1.00
4.00
2.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)
199.3
160.3
151.0
143.0
141.6
138.4
128.0
124.6
120.6
114.1
107.2
105.8
64.3
55.6
55.2
f1 (ppm)

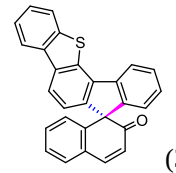

N
H
O

(3cb)

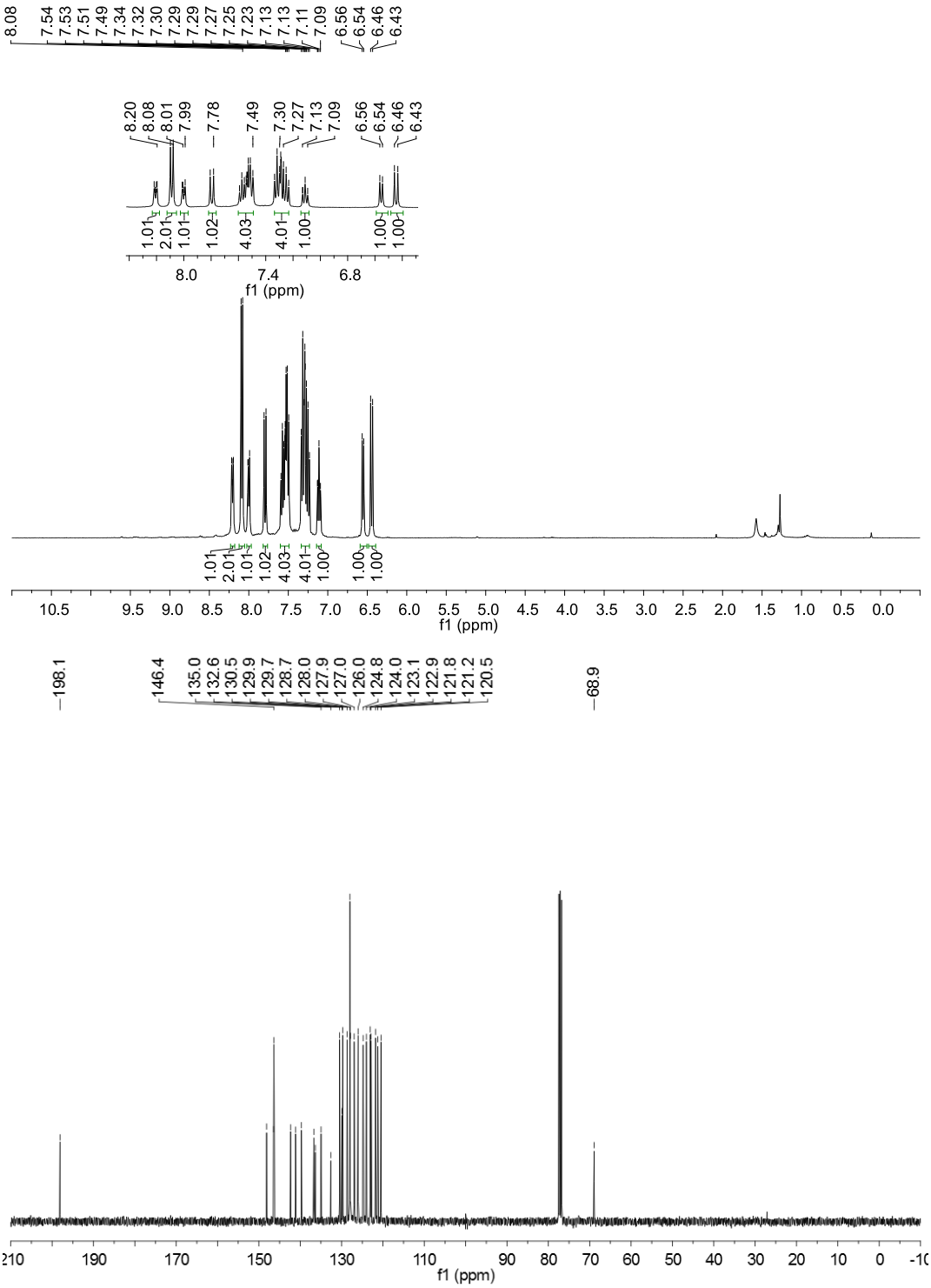

8.10
8.00
7.81
7.80
7.73
7.70
7.34
7.06
6.56
6.37
6.35
0.99
1.00
1.00
1.02
1.02
1.07
1.06
5.03
2.00
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

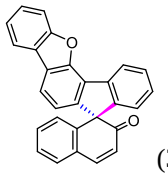

199.7
146.9
146.1
144.3
142.7
142.3
129.4
127.4
125.1
120.0
112.4
107.1
103.0
67.9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
N
O
(3cc)
8.02
7.83
7.81
7.76
7.74
7.27
7.02
6.58
6.56
6.55
6.54
6.41
6.38
3.68
f1 (ppm)
199.5
147.1
146.0
144.4
142.6
142.2
129.7
128.4
126.7
120.0
112.5
105.3
101.6
67.9
33.0

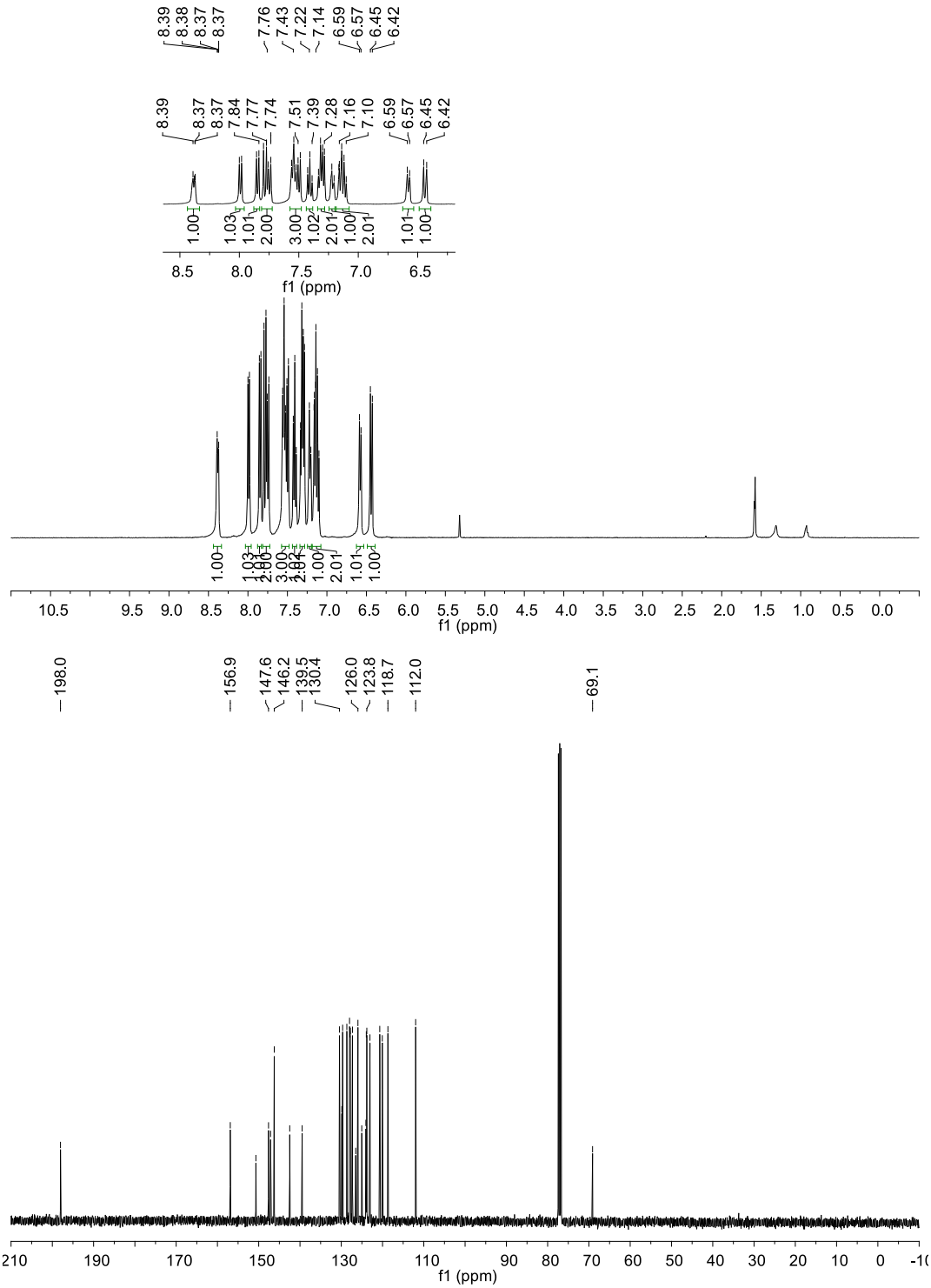

S
O

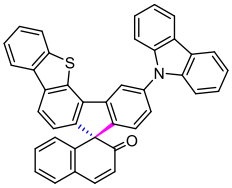
(3cd)


8.08
7.54
7.53
7.51
7.49
7.34
7.32
7.30
7.29
7.29
7.27
7.25
7.23
7.13
7.13
7.11
7.09
6.56
6.54
6.46
6.43
8.20
8.08
8.01
7.99
7.78
7.49
7.30
7.27
7.13
7.09
6.56
6.54
6.46
6.43
1.01
2.01
1.01
1.02
4.03
4.01
1.00
1.00
1.00
8.0
7.4
6.8
f1 (ppm)
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.1
146.4
135.0
132.6
130.5
129.9
129.7
128.7
128.0
127.9
127.0
126.0
124.8
124.0
123.1
122.9
121.8
121.2
120.5
68.9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

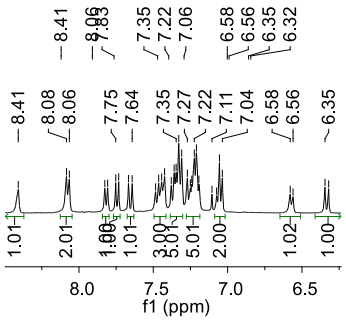


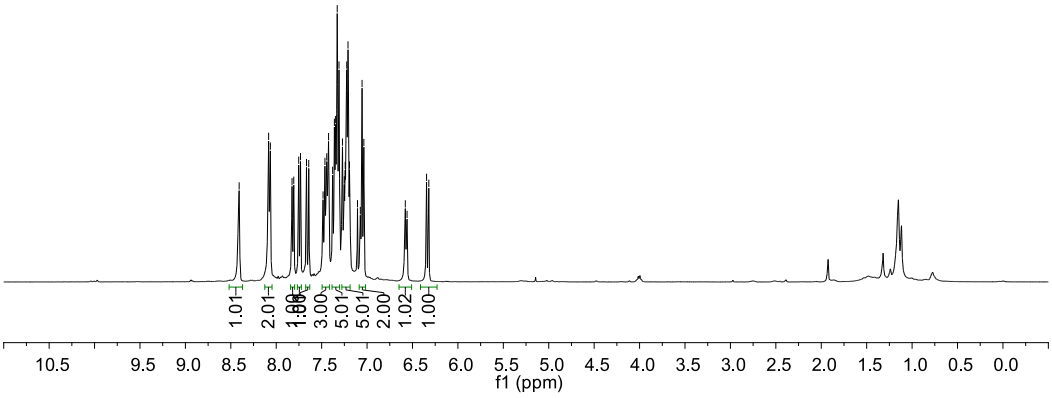
(3ce)

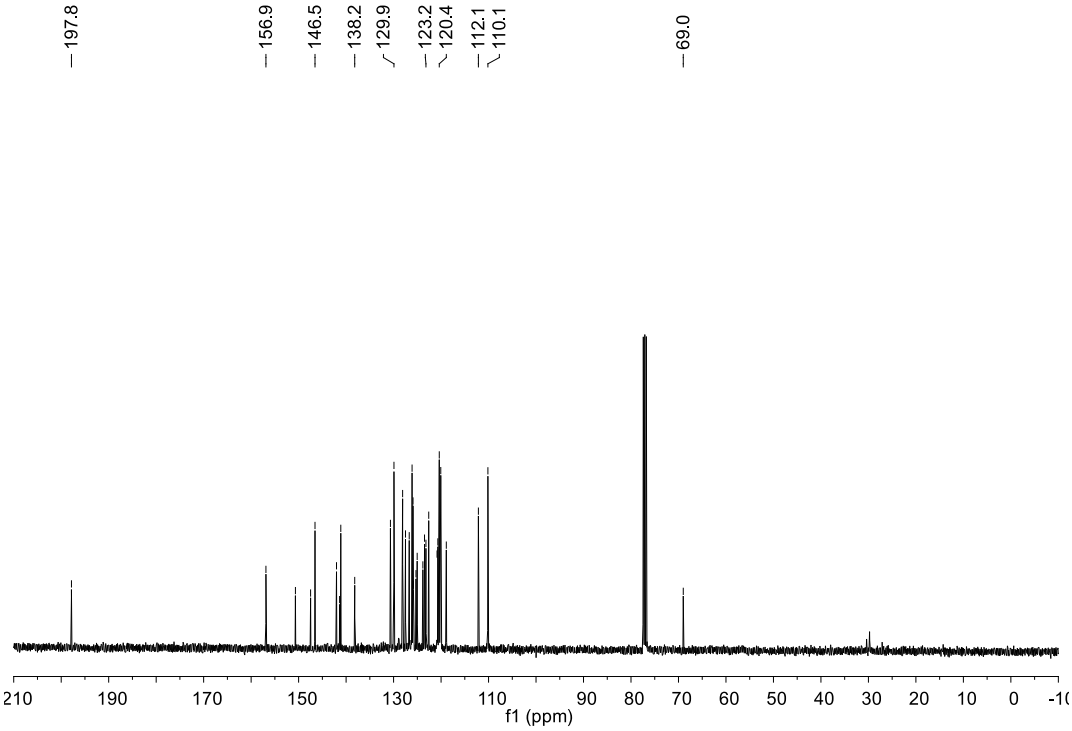

8.39
8.38
8.37
8.37
7.76
7.43
7.22
7.14
6.59
6.57
6.45
6.42
f1 (ppm)
198.0
156.9
147.6
146.2
139.5
130.4
126.0
123.8
118.7
112.0
69.1
f1 (ppm)

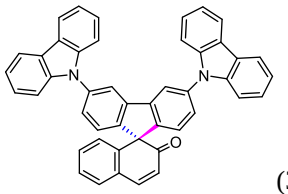

S
N
O

(3cf)

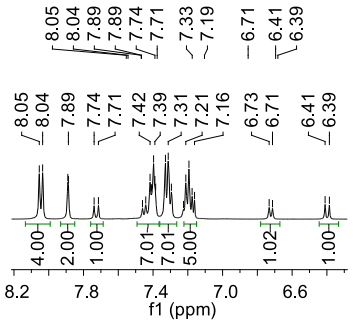

8.41
8.08
8.06
7.75
7.64
7.35
7.27
7.22
7.11
7.04
6.58
6.56
6.35
1.01
2.01
1.01
3.00
5.01
2.00
1.02
1.00
8.0
7.5
7.0
6.5
f1 (ppm)

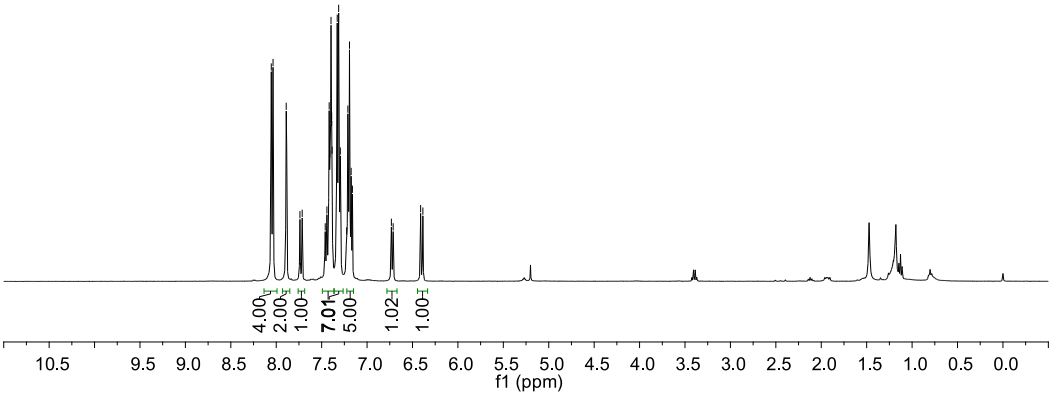

1.01
2.01
3.00
5.01
2.00
1.02
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

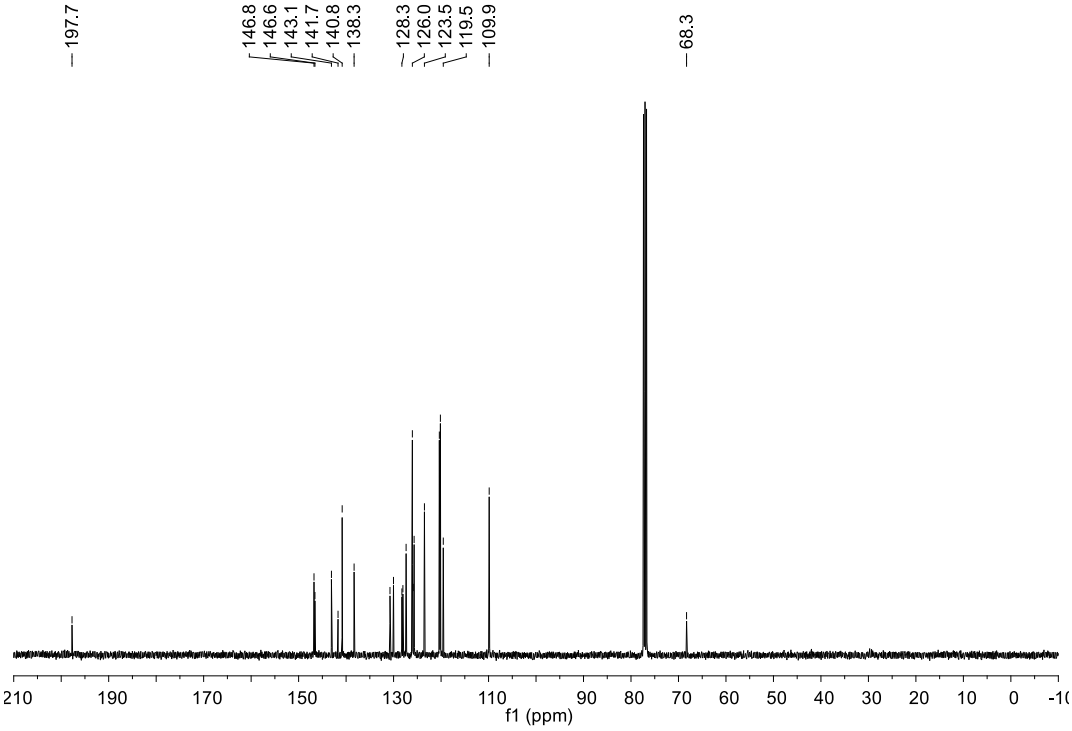

197.8
156.9
146.5
138.2
129.9
123.2
120.4
112.1
110.1
69.0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

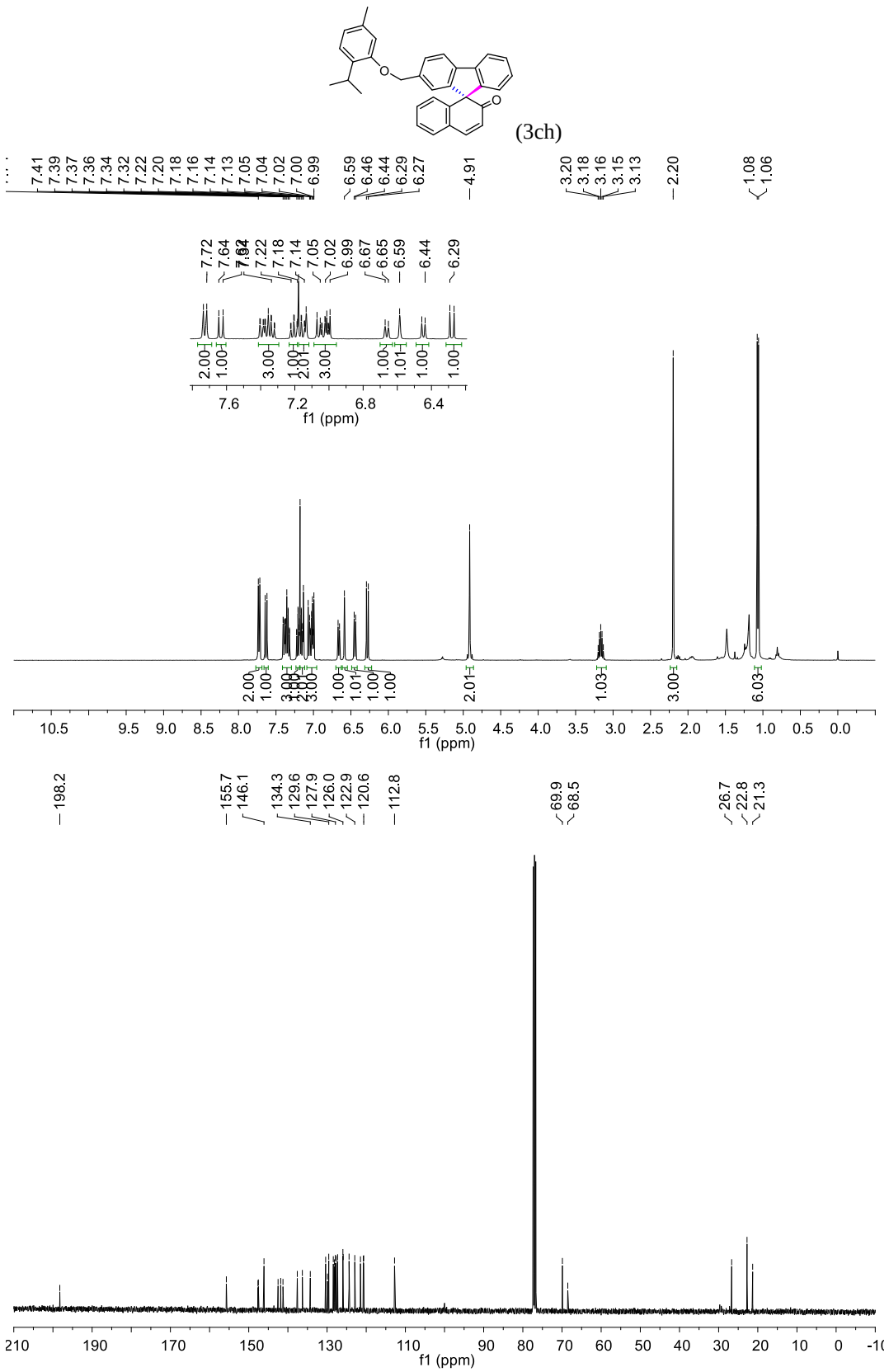


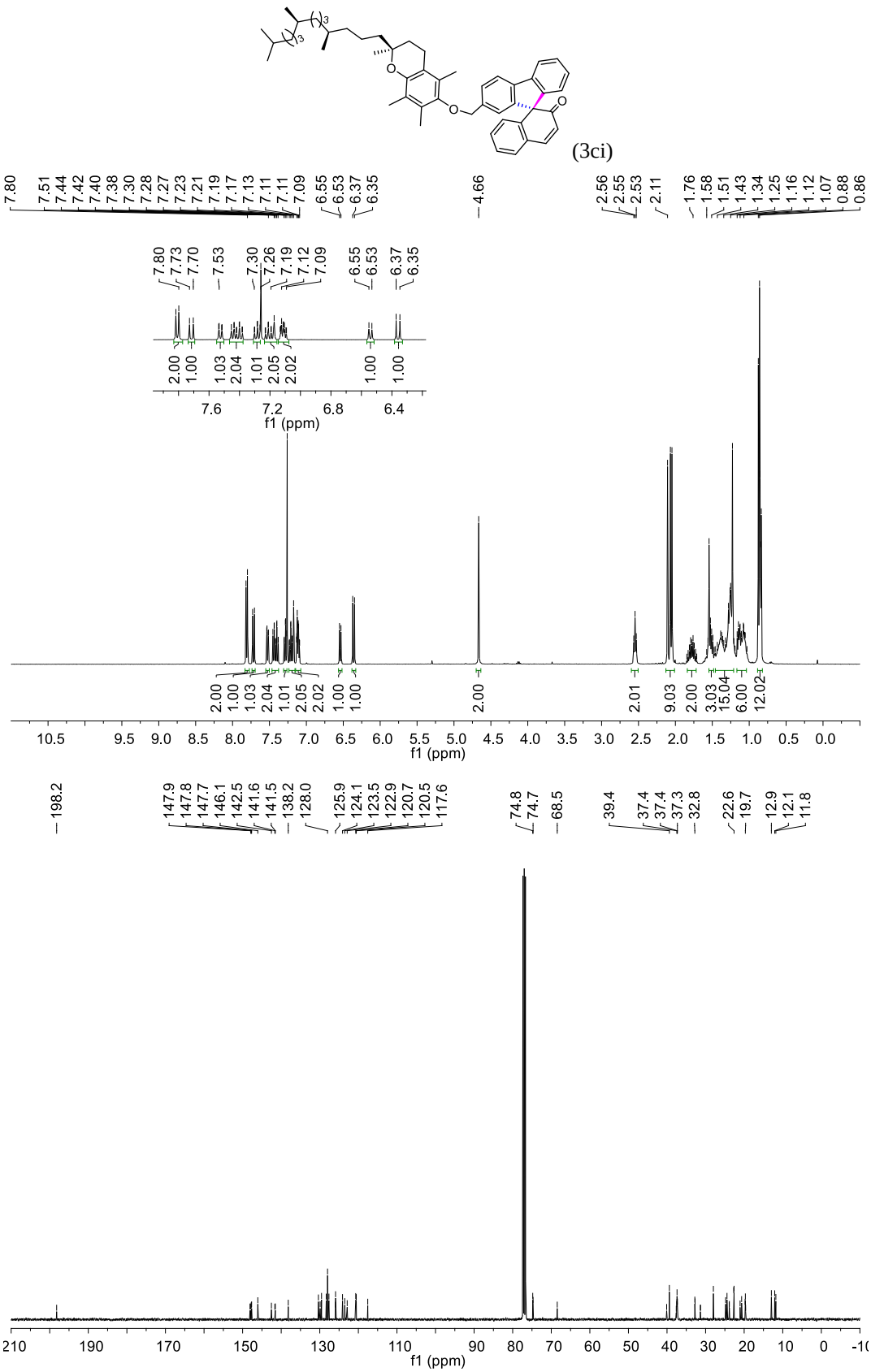
(3cg)

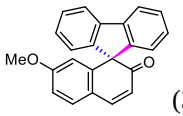

8.05
8.04
7.89
7.89
7.74
7.71
7.33
7.19
6.71
6.41
6.39
8.05
8.04
7.89
7.74
7.71
7.42
7.39
7.31
7.21
7.16
6.73
6.71
6.41
6.39
4.00
2.00
1.00
7.01
7.01
5.00
1.02
1.00
8.2
7.8
7.4
7.0
6.6
f1 (ppm)


4.00
2.00
1.00
7.01
5.00
1.02
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

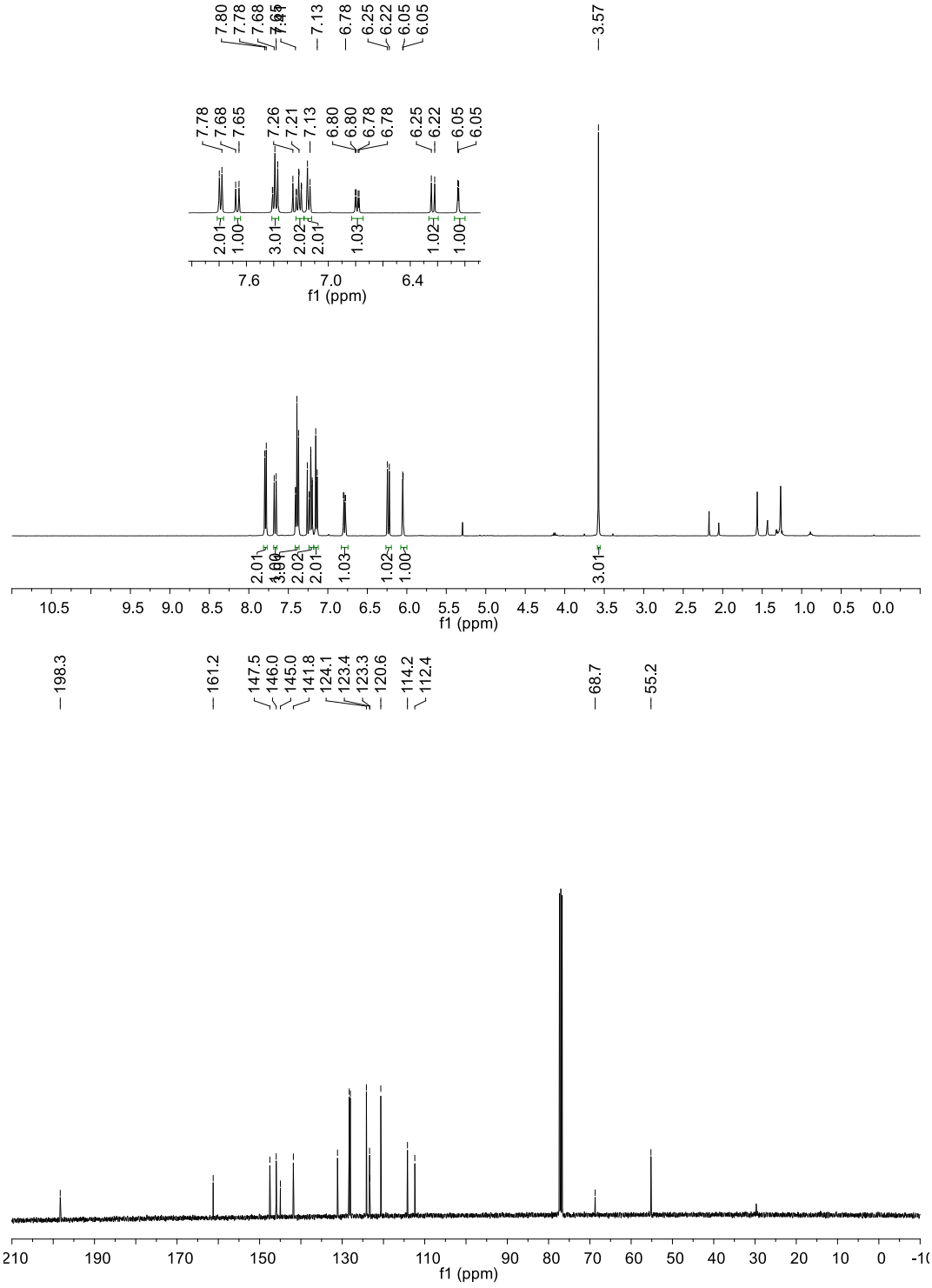

197.7
146.8
146.6
143.1
141.7
140.8
138.3
128.3
126.0
123.5
119.5
109.9
68.3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

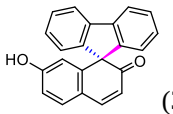

(3ch)
7.41 7.39 7.37 7.36 7.34 7.32 7.22 7.20 7.18 7.16 7.14 7.13 7.05 7.04 7.02 7.00 6.99 6.59 6.46 6.44 6.29 6.27 4.91 3.20 3.18 3.16 3.15 3.13 2.20 1.08 1.06
7.72 7.64 7.22 7.18 7.14 7.05 7.02 6.99 6.67 6.65 6.59 6.44 6.29
2.00 1.00 3.00 1.00 2.01 3.00 1.00 1.01 1.00 1.00
7.6 7.2 6.8 6.4
f1 (ppm)
2.00 1.00 1.00 1.01 1.00 1.00 2.01 1.03 3.00 6.03
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.2 155.7 146.1 134.3 129.6 127.9 126.0 122.9 120.6 112.8 69.9 68.5 26.7 22.8 21.3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(3ci)
f1 (ppm)

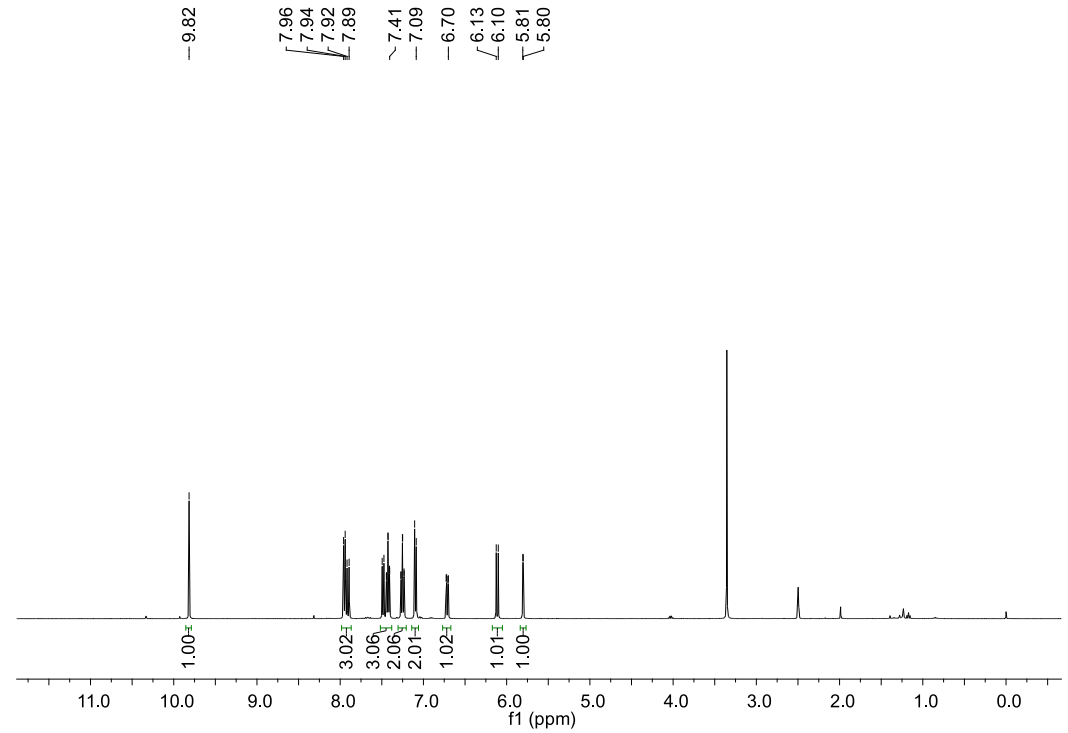

MeO
O

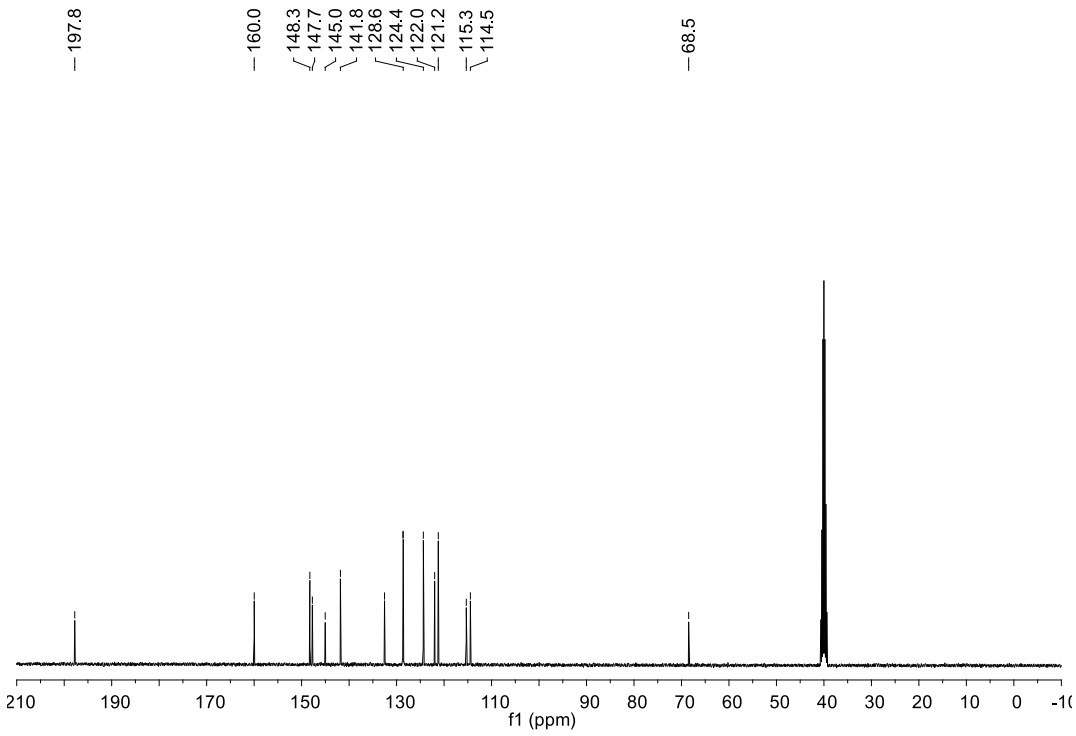
(3ck)


7.80
7.78
7.68
7.65
7.13
6.78
6.25
6.22
6.05
6.05
3.57
7.78
7.68
7.65
7.26
7.21
7.13
6.80
6.80
6.78
6.78
6.25
6.22
6.05
6.05
2.01
1.00
3.01
2.02
2.01
1.03
1.02
1.00
7.6
7.0
6.4
f1 (ppm)
2.01
3.00
2.02
2.01
1.03
1.02
1.00
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
198.3
161.2
147.5
146.0
145.0
141.8
124.1
123.4
123.3
120.6
114.2
112.4
68.7
55.2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O

(3cl)


9.82
7.96
7.94
7.92
7.89
7.41
7.09
6.70
6.13
6.10
5.81
5.80
1.00
3.02
3.06
2.06
2.01
1.02
1.01
1.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


197.8
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148.3
147.7
145.0
141.8
128.6
124.4
122.0
121.2
115.3
114.5
68.5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)