Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Rh-Catalyzed Intramolecular sp(2) C-H Bond Difluoromethylenation

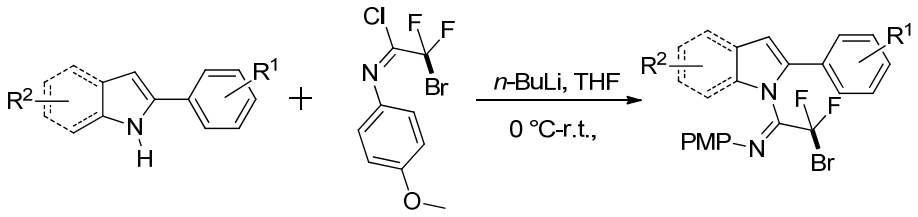
Yajun Li, [ab] Jiangtao Zhu, [a] Haibo Xie, [a] Shan Li, [a] Dongjie Peng, [a] Zhengke Li, [a] Yongming Wu*[a] and Yuefa Gong* [b]

General Information

Melting points were measured on a Melt-Temp apparatus and were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-300 spectrometer (300 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM-300(282 MHz) spectrometer using $PhCF_3$ as external standard. ^{13}C NMR spectra were taken a Bruker AM-400(100 MHz) spectrometer. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra and elemental analyses were recorded in this institute. Solvents were purchased form commercial sources and purified before used by standard procedures. Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in a flame-dried Schlenk tube and magnetic stirring. TLC analysis was performed on silica gel plates, column chromatography over silica gel (mesh 300-400) and petroleum ethyl acetate combination was used as the eluent.

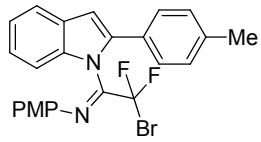
2-aryl indoles were prepared by fischer indole synthesis. 2-aryl pyrroles[1] were prepared according to literature. Substrate **3f**[2] was prepared according to literature.

Synthesis of N-(2-bromo-2, 2-difluoro-1-(2-phenyl-1H-indol-1-yl) ethylidene)-4-methoxyaniline 1a and Analogues

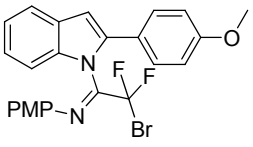


General procedure: A solution of 2-Phenyl indole (3.6 mmol) in THF (3 ml) was stirred at 0 °C for 10 min, and then n-BuLi (3.6 mmol) was added dropwise in 20 min. The mixture was stirred at 0 °C for another 1h before 2-bromo-2, 2-difluoro-N-(4-methoxyphenyl)acetimidoyl chloride (3 mmol) in THF (3 ml) was added dropwise. Then the mixture was stirred overnight at room temperature. To the mixture saturated ammonium chloride solution was added, then extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. After filtration the resulting solution was evaporated *in vacuo* and the crude residue was purified by column chromatography (ethyl acetate and petrol ether) to give **1a** as a yellow solid (91%).

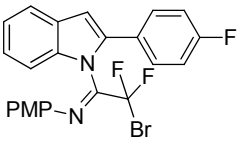
Scheme S1. Structures and Yields of 1



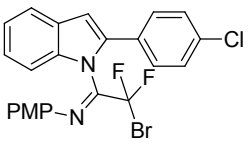
1b, 72%



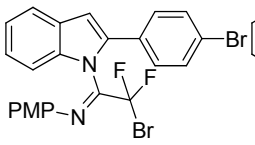
1c, 89%



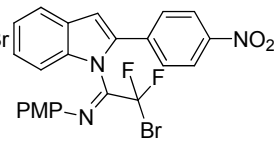
1d, 85%



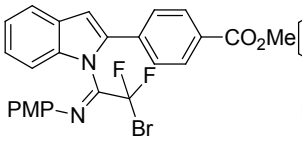
1e, 85%



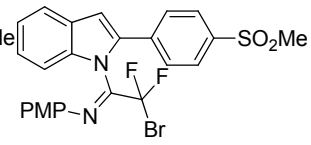
1f, 83%



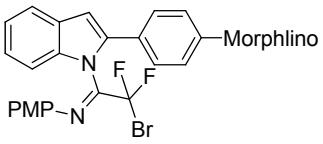
1g, 50%



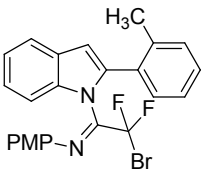
1h,46%



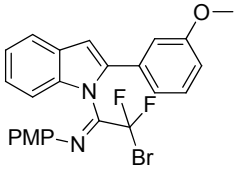
1i, 57%



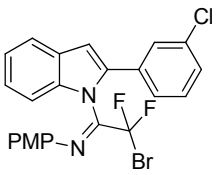
1j, 77%



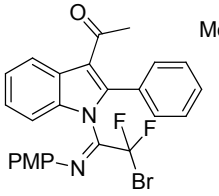
1k, 95%



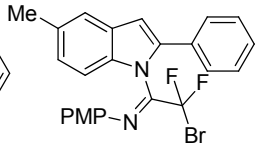
1l, 72%



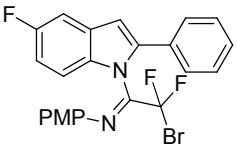
1m, 90%



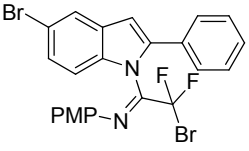
1n, 61%



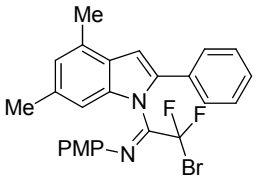
1o, 75%



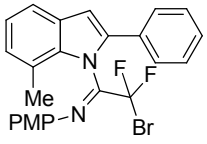
1p, 81%



1q, 77%

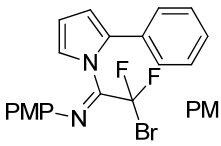


1r, 85%

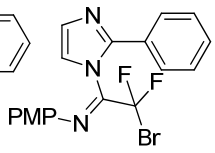


1s, 68%

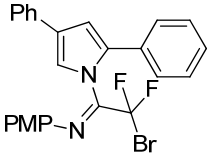
Scheme S2. Structures and Yields of 3



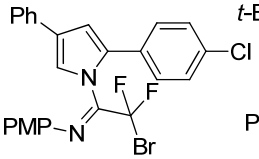
3a, 86%



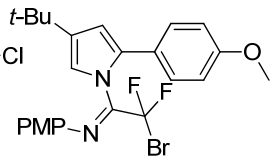
3b, 69%



3c, 78%



3d, 92%

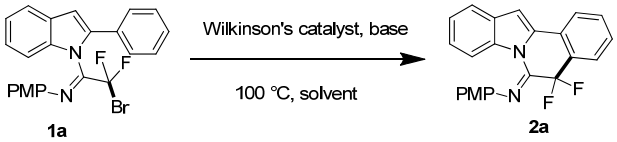


3e, 91%

General Procedure for Optimization of Intramolecular C-H Bond Difluoromethylenation of 1a

$Rh(PPh_3)_3Cl$ (5 mol% , 9.2mg), base (1 equiv.), and **1a** (0.2 mmol) were suspended in solvent (2 ml) in a Schlenk tube under nitrogen. The resulting mixture was stirred at 100 °C, and then detected directly by ^{19}FNMR without purification.

Table 1. Optimization of Intramolecular C-H Bond Difluoromethylenation of **1a**[a]



Entry	Solvent	Base	Yield(%)[b]
1	toluene	Cs_2CO_3	58
2	toluene	K_2CO_3	33
3	toluene	K_3PO_4	10
4	toluene	Et_3N	29
5	toluene	DBU	5
6	toluene	KOH	54
7	toluene	Ag_2CO_3	62
8	**1, 4-dioxane**	**Ag_2CO_3**	**99(94)[c]**
9	DMF	Ag_2CO_3	33
10	DMSO	Ag_2CO_3	12
11	CH_3CN	Ag_2CO_3	5
12	THF	Ag_2CO_3	74
13	1, 4-dioxane	Ag_2CO_3	15[d]
14	1, 4-dioxane	---	13[e]
15	1, 4-dioxane	Ag_2CO_3	0[f]

[a] General conditions: **1a** (0.2mmol), base(1 equiv.), $RhCl(PPh_3)_3$ (5 mol %) in solvent at 100 °C. [b] Yields were based on **1a** determined by ^{19}F NMR. [c] Isolated yield in parenthesis. [d] Reaction temperature is 90 °C. [e] Without base. [f] In the absence of $RhCl(PPh_3)_3$.

The reaction was optimized with respect to solvent, base and temperature. As show in table 1, compared to K_2CO_3 and K_3PO_4, Cs_2CO_3 provided the most encouraging result in toluene (entries 1 vs. 2 and 3, Table 1), obtaining the product **2a** in up to 58% yield, which was confirmed by X-ray crystal diffraction studies. This effect may be due to the higher solubility of Cs_2CO_3 in organic solvents. However, the organic bases, such as Et_3N and DBU, were found not suitable for the reaction (entries 4 and 5, Table 1). When KOH was chosen as a base, it performed less efficiency than Cs_2CO_3 (entry 6, Table 1). Interestingly, when Ag_2CO_3 took place of Cs_2CO_3, 62% yield of **2a** was detected (entry 7, Table 1). The solvent was also screened. While the polar solvents such as DMF (entry 9, Table 1), DMSO (entry 10, Table 1) and CH_3CN (entry 11, Table 1) couldn't improve the product yield, 1, 4-dioxane offered the highest yield (entry 8, Table 1). Neither the catalyst nor the base alone could give satisfied performance (entries 14, 15 vs. 1, Table 1). Surprisingly, decreasing the reaction temperature to 90 °C would significantly affect the product yield (entry 13, Table 1), that might be due to the energy barrier of this reaction. In the end, the final optimized conditions (5 mol % of $RhCl(PPh_3)_3$, 1 equiv. Ag_2CO_3, at 100 °C in 1, 4-dioxane for 2h) provided intramolecular C-H bond difluoromethylenated product **2a** in 94% isolated yield.

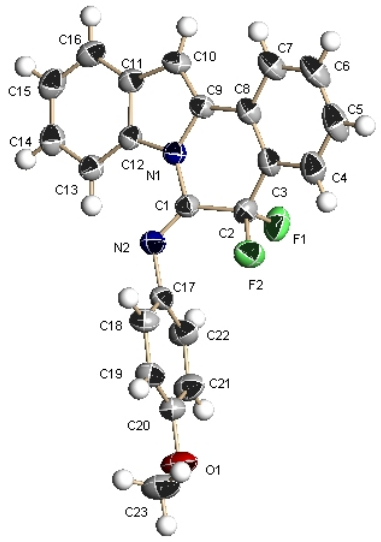
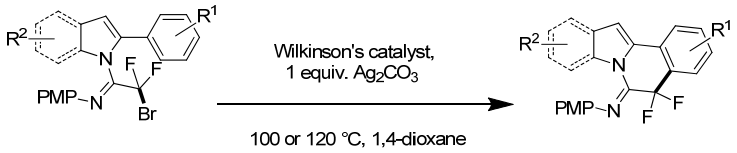


Figure 1. X-ray Crystal Structure of 2a

General procedure for the intramolecular difluoromethylenation of 2-arylindole



Representative experimental procedure for the synthesis of 2a

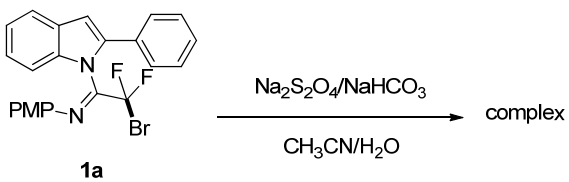
$RhCl(PPh_3)_3$ (5 mol% , 9.2mg), Ag_2CO_3 (1 equiv. 55.2mg), and **1a** (0.2 mmol) were suspended in 1, 4-dioxane (2 ml) in a Schlenk tube under nitrogen. The resulting mixture was stirred at 100 °C for 2h. After cooling to room temperature, the solution was filtered through a short path of silica gel, eluting with ethyl acetate. The volatile compounds were removed *in vacuo* and the crude residue was purified by column chromatography (ethyl acetate and petrol ether) to give **2a** as a yellow solid (94%).

Hydrolysis of products 2a and 4e[3]

To a stirring solution of iminoethanones **2a** or **4e** (0.2 mmol) in THF (3 ml), 10% HCl (1 ml) was added. The reaction mixture was then stirred at room temperature for 10min and poured into water. The products were extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to obtain the products.

Control Experiments and Mechanism Studies

Reaction under sulfinatodehalogenation reagent

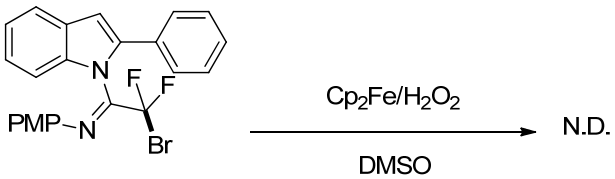


1a

To a mixed solution of CH_3CN and water (5:1, 2.4 ml) was added **1a** (0.5 mmol) under nitrogen,

$Na_2S_2O_4$-$NaHCO_3$ mixture (1:1, 1.5 equiv.) was added partially. The resulting solution was stirred at room temperature for 5h. No corresponding product was detected.

Reaction under Fenton reagent



1a

Substrate **1a** (0.2 mmol), Cp_2Fe (9 mg, 0.05 mmol), and DMSO (2.0 mL) were charged in a two-neck flask in Ar atmosphere. Then, a 30% aqueous solution of H_2O_2 (40 uL) was added continuously over 5 min. The reaction solution was stirred at room temperature for 12 h, and then detected directly by ^{19}F NMR without purification.

Reaction using Hu's strategy

Under N_2 atmosphere, into a 10-mL Schlenk flask was added **1a** (92 mg, 0.2 mmol), Cu powder (25 mg, 0.4mmol), and DMSO (2 mL). The reaction mixture was vigorously stirred at 65 ^oC for 3h, and then detected directly by $^{19}FNMR$ without purification.

General procedure for the controlling experiments and mechanism studies

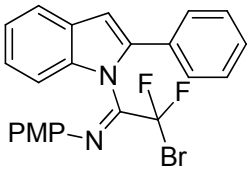
$Rh(PPh_3)_3Cl$ (5 mol% , 9.2mg), Ag_2CO_3 (1 equiv. 55.2mg), additive (20 mol%) and **1a** (0.2 mmol) were suspended in 1, 4-dioxane (2 ml) in a Schlenk tube under nitrogen. The resulting mixture was stirred at 100 °C for 2h. The product yield was determined by ^{19}F NMR using $PhCF_3$ as external standard.

References:

1. M. J. Hall, S. O. McDonnell, J. Killoran, and D. F. O'Shea, *J. Org. Chem.* 2005, **70**, 5571-5578.
2. S. K. Guchhait, M. Kashyap, and H. Kamble, *J. Org. Chem.* 2011, **76**, 4753–4758.
3. Y. Suzuki, A. B. Md., T. Tanoi, N. Nomura, and M. Sato, *Tetrahedron* 2011, **67**, 4710-4715.

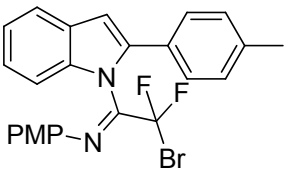
Characterization data for the substrates and Products

N-(2-bromo-2,2-difluoro-1-(2-phenyl-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1a)



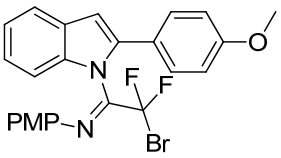
yellow solid; **mp**: 84-85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.57 (m, 1H), 7.31 (m, 5H), 7.22-7.08 (m, 3H), 6.80 (s, 1H), 6.84-6.82 (m, 2H), 6.72-6.70 (m, 2H), 3.71 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.49 (dd, *J* = 428.5, 156.8 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.28, 140.79 (t, *J*=29.4Hz), 139.35, 135.97, 135.73, 131.97, 129.12, 128.78, 128.39, 127.32, 126.81, 123.55, 122.03, 120.97, 114.41, 114.85 (t, *J*=309.6Hz), 111.78, 105.89, 55.40; **IR** (KBr, cm^{-1}): ν 3052, 2957, 2835, 1647, 1591, 1504, 1452, 1338, 1255, 744; **MS (EI)** m/z (relative intensity) 545 (34, ^{79}Br) [M^+], 546 (34, ^{81}Br) [M^+], 264 (100), 262 (98); **Anal. Calcd.** For $C_{23}H_{17}BrF_2N_2O$: C, 60.67; H, 3.76; N, 6.15. Found: C, 60.80; H, 3.80; N, 6.04.

N-(2-bromo-2,2-difluoro-1-(2-(p-tolyl)-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1b)



yellow solid; **mp**: 136-137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 1H), 7.28-7.03 (m, 7H), 6.81 (s, 1H), 6.81-6.76 (m, 2H), 6.67-6.64 (m, 2H), 3.71 (s, 3H), 2.35 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.58 (dd, *J* = 499.1, 155.9 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.28, 140.86 (t, *J*=29.3Hz), 129.20, 129.14, 127.17, 126.88, 123.32, 121.93, 120.82, 114.82 (t, *J*=308.9 Hz), 114.40, 111.70, 105.39, 55.39, 21.26; **IR** (KBr, cm^{-1}): ν 3074, 2995, 2830, 1641, 1590, 1317, 1452, 745, 540, 512; **MS (EI)** m/z (relative intensity) 468 (39, ^{79}Br) [M^+], 470 (39, ^{81}Br) [M^+], 262 (100), 264 (98); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O$: C, 61.42; H, 4.08; N, 5.97. Found: C, 61.61; H, 4.18; N, 5.86.

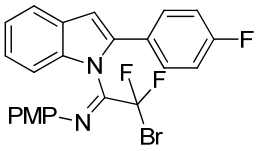
N-(2-bromo-2,2-difluoro-1-(2-(4-methoxyphenyl)-1H-indol-1-yl)ethylidene)-4-methoxyanilin e (1c)



yellow solid; **mp**: 150-152 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 1H), 7.30 – 7.06 (m, 5H), 6.86-6.84 (m, 2H), 6.79 – 6.75 (m, 2H), 6.71 (s, 1H), 6.67-6.64 (m, 2H), 3.80 (s, 3H), 3.71 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.47 (dd, *J* = 445.6, 156.6 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.27, 141.58 (t, *J*=30.8Hz), 159.85, 129.25, 128.70, 126.84, 124.50, 123.20, 121.93, 120.72, 114.89 (t, *J*=311.8Hz), 114.39, 114.23, 111.65, 105.03, 55.40, 55.32; **IR** (KBr, cm^{-1}): ν 2963, 2830, 1253, 1501, 1451, 1253, 1031, 969, 799, 539; **MS (EI)** m/z (relative intensity) 486 (25, ^{79}Br) [M^+], 484 (23, ^{81}Br) [M^+], 43 (100); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O_2$: C, 59.40; H, 3.95; N, 5.77. Found: C, 59.19; H, 4.10; N, 5.56.

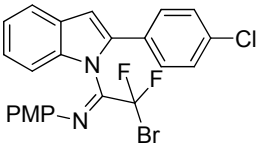
N-(2-bromo-2,2-difluoro-1-(2-(4-fluorophenyl)-1H-indol-1-yl)ethylidene)-4-methoxyaniline

(1d)



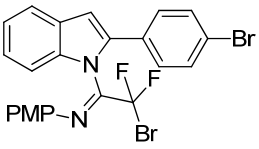
yellow solid; **mp**: 140-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.27 – 7.13 (m, 5H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.74 (s, 1H), 6.72-6.70 (m, 2H), 6.66-6.64 (m, 2H), 3.72 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.23 (q, *J* = 158.3 Hz, 2F), -101.15 – -125.05 (m, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.07, 161.60, 160.35, 140.58 (t, *J* = 34.3 Hz), 138.27, 136.03, 135.62, 129.33, 129.24, 129.00, 128.04, 126.74, 123.68, 122.14, 120.97, 115.89, 115.67, 114.41, 111.78, 55.42; **IR** (KBr, cm^{-1}): ν 3000, 2825, 1588, 1503, 1135, 970, 800, 520; **MS (EI)** m/z (relative intensity) 472 (5, ^{79}Br) [M^+], 474 (5, ^{81}Br) [M^+], 160 (100); **Anal. Calcd.** For $C_{23}H_{16}BrF_3N_2O$: C, 58.37; H, 3.41; N, 5.92. Found: C, 58.55; H, 3.63; N, 5.80.

N-(2-bromo-1-(2-(4-chlorophenyl)-1H-indol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline (1e)



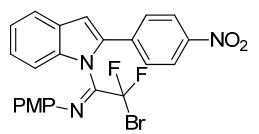
yellow solid; **mp**: 169-172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 1H), 7.30-7.28 (m, 2H), 7.22 – 7.14 (m, 5H), 6.78 (s, 1H), 6.74-6.71 (m, 2H), 6.67-6.65 (m, 2H), 3.73 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.40 (q, *J* = 158.1 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.50, 140.08 (t, *J* = 26.8 Hz), 136.12, 134.45, 128.69, 125.27, 123.48, 121.71, 121.10, 114.49 (t, *J* = 309.6 Hz), 114.20, 112.01, 106.79, 55.30; **IR** (KBr, cm^{-1}): ν 2931, 2840, 1589, 1503, 1113, 1027, 866, 543; **MS (EI)** m/z (relative intensity) 490 (22) [M^+], 262 (100); **Anal. Calcd.** For $C_{23}H_{16}BrClF_2N_2O$: C, 56.41; H, 3.29; N, 5.72. Found: C, 56.41; H, 3.42; N, 5.68.

N-(2-bromo-1-(2-(4-bromophenyl)-1H-indol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline (1f)



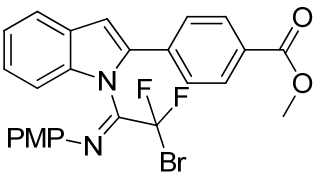
yellow solid; **mp**: 171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.11 (m, 5H), 6.78 (s, 1H), 6.74-6.71 (m, 2H), 6.67-6.65 (m, 2H), 3.72 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.36 (q, *J* = 158.0 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.39, 140.41 (t, *J* = 28.6 Hz), 138.07, 136.17, 135.55, 131.92, 130.83, 128.94, 128.80, 126.77, 123.89, 122.62, 122.21, 121.07, 114.84 (t, *J* = 28.6 Hz), 114.44, 111.83, 106.34, 55.43; **IR** (KBr, cm^{-1}): ν 3005, 2840, 1589, 1503, 1338, 1135, 970, 800, 746, 520; **MS (ESI)** m/z 535 [$M+H^+$]; **Anal. Calcd.** For $C_{23}H_{16}Br_2F_2N_2O$: C, 51.71; H, 3.02; N, 5.24. Found: C, 51.97; H, 3.19; N, 5.19.

N-(2-bromo-2,2-difluoro-1-(2-(4-nitrophenyl)-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1g)



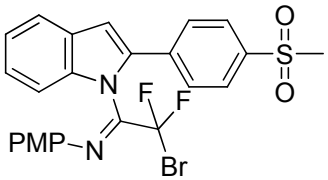
yellow solid; **mp**: 169-171 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.74 – 7.66 (m, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.28-7.19 (m, 3H), 6.96 (s, 1H), 6.70 (dd, *J* = 18.5, 9.0 Hz, 4H), 3.75 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.34 (q, *J* = 159.5 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.62, 147.30, 138.11, 136.79, 136.68, 135.26, 128.65, 127.67, 126.81, 124.89, 124.07, 122.62, 121.54, 114.55, 112.03, 108.47, 55.47; **IR** (KBr, cm^{-1}): ν 3085, 2926, 2835, 1598, 1351, 1125, 967, 750, 522; **MS (ESI)** m/z 500 [$M+H^+$], 522 [$M+Na^+$]; **HRMS (ESI)** *m/e* calcd. for $C_{23}H_{16}F_2N_3NaO_3^+$ [$M+Na^+$] 522.0235, Found: 522.02422.

methyl 4-(1-(2-bromo-2,2-difluoro-1-((4-methoxyphenyl)imino)ethyl)-1H-indol-2-yl)benzoate (1h)



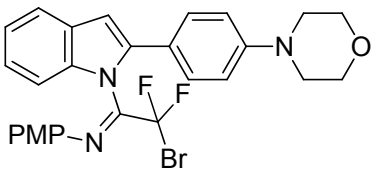
yellow solid; **mp**: 118-120°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.80 – 7.59 (m, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.13 (m, 3H), 6.88 (s, 1H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.69 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -50.12 (q, *J* = 158.3 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.56, 160.35, 140.28 (t, *J* = 29.2 Hz), 138.05, 136.34, 136.18, 135.46, 130.04, 129.63, 128.83, 126.95, 126.73, 124.21, 122.29, 121.26, 114.70 (t, *J* = 308.3 Hz), 114.43, 111.87, 107.25, 55.39, 52.21; **IR** (KBr, cm^{-1}): ν 2952, 1717, 1592, 1449, 1282, 1132, 964, 865, 510; **MS (EI)** m/z (relative intensity) 512 (12, ^{79}Br) [M^+], 514 (11, ^{81}Br) [M^+], 262 (100), 264 (99); **Anal. Calcd.** For $C_{25}H_{19}BrF_2N_2O_3$: C, 58.49; H, 3.73; N, 5.46. Found: C, 58.55; H, 3.86; N, 5.18.

N-(2-bromo-2,2-difluoro-1-(2-(4-(methylsulfonyl)phenyl)-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1i)



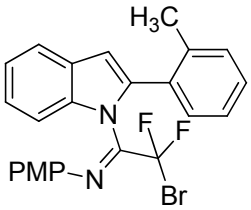
yellow solid; **mp**: 120-122°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.63 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.12 (m, 3H), 6.93 (s, 1H), 6.65-6.74 (m, 4H), 3.74 (s, 3H), 3.06 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.19 (q, *J* = 159.4 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.60, 139.87 (t, *J* = 29.1 Hz), 137.19, 136.97, 136.63, 135.29, 128.70, 127.88, 127.81, 126.81, 124.72, 122.58, 121.53, 114.79 (t, *J* = 307.1 Hz), 114.56, 112.00, 108.16, 55.49, 44.51; **IR** (KBr, cm^{-1}): ν 2920, 1645, 1590, 1505, 1448, 1310, 1148, 967, 537; **MS (EI)** m/z (relative intensity) 532 (6, ^{79}Br) [M^+], 534 (6, ^{81}Br) [M^+], 262 (100), 264 (98); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O_3S$: C, 54.04; H, 3.59; N, 5.25. Found: C, 54.27; H, 3.67; N, 5.43.

N-(2-bromo-2,2-difluoro-1-(2-(4-morpholinophenyl)-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1j)



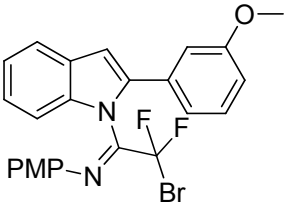
yellow solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.5 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.19 – 7.07 (m, 3H), 6.85 (d, *J* = 8.9 Hz, 4H), 6.74 (s, 1H), 6.67 (d, *J* = 9.0 Hz, 2H), 3.92 – 3.75 (m, 4H), 3.71 (s, 3H), 3.31 – 3.07 (m, 4H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -50.33 (dd, *J* = 560.5, 155.5 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.28, 151.13, 141.06 (t, *J* = 29.0 Hz), 139.50, 135.79, 135.71, 129.36, 128.22, 126.94, 123.18, 123.07, 121.91, 120.65, 115.29, 114.83 (t, *J* = 309.0 Hz), 114.42, 111.60, 104.62, 66.78, 55.39, 48.69; **IR** (KBr, cm^{-1}): ν 2963, 2850, 1609, 1505, 1452, 1260, 1094, 1024, 800; **MS (EI)** m/z (relative intensity) 539 (38, ^{79}Br) [M^+], 541 (35, ^{81}Br) [M^+], 277 (100); **HRMS (EI)** calcd. For $C_{27}H_{24}BrF_2N_3O_2$: 539.1020, Found: 539.1017.

N-(2-bromo-2,2-difluoro-1-(2-(o-tolyl)-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1k)



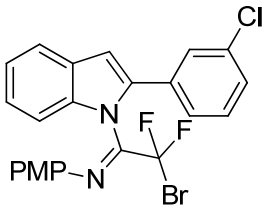
yellow solid; **mp**: 79-80°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70-7.61 (m, 1H), 7.35 – 7.12 (m, 5H), 7.08 (s, 1H), 6.96-6.89 (m, 1H), 6.69 (s, 5H), 3.74 (s, 3H), 2.23 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.76 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.32, 140.63 (t, *J* = 29.3 Hz), 137.67, 137.23, 135.80, 135.37, 130.89, 130.79, 129.14, 128.94, 128.73, 126.91, 125.65, 123.48, 121.97, 120.98, 114.90(t, *J* = 310.3 Hz), 114.45, 111.75, 107.56, 55.45, 20.43; **IR** (KBr, cm^{-1}): ν 3053, 2824, 1645, 1589, 1504, 1453, 1338, 969, 762, 529; **MS (EI)** m/z (relative intensity) 468 (22, ^{79}Br) [M^+], 470 (26, ^{81}Br) [M^+], 262 (97), 264 (100); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O$: C, 61.42; H, 4.08; N, 5.97. Found: C, 61.37; H, 4.15; N, 5.89.

N-(2-bromo-2,2-difluoro-1-(2-(3-methoxyphenyl)-1H-indol-1-yl)ethylidene)-4-methoxyanilin e (1l)



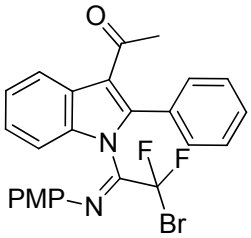
yellow solid; **mp**: 78-79°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 1H), 7.26-7.13 (m, 4H), 6.96 – 6.72 (m, 6H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.72 (s, 3H), 3.72 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.51 (dd, *J* = 514.3, 157.0 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.36, 140.80 (t, *J* = 27.1 Hz), 159.89, 139.30, 136.00, 135.74, 133.24, 129.93, 129.10, 126.91, 123.69, 122.15, 121.08, 119.70, 114.64, 114.92 (t, *J* = 312.6 Hz), 114.47, 112.42, 111.82, 106.00, 55.40, 55.22; **IR** (KBr, cm^{-1}): ν 2963, 2840, 1500, 1340, 1178, 743, 538; **MS (EI)** m/z (relative intensity) 484 (31, ^{79}Br) [M^+], 486 (34, ^{81}Br) [M^+], 262 (100), 264 (96); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O_2$: C, 59.40; H, 3.95; N, 5.77. Found: C, 59.52; H, 4.02; N, 5.66.

N-(2-bromo-1-(2-(3-chlorophenyl)-1H-indol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline (1m)



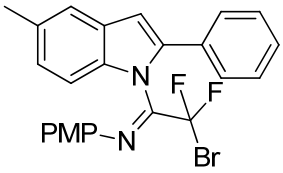
yellow solid; **mp**: 88-92 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.66-7.64 (m, 1H), 7.28 – 7.19 (m, 6H), 7.14-7.12 (m, 1H), 6.79 (s, 1H), 6.64 (s, 4H), 3.74 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -42.12 – -51.39 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.26, 140.74 (t, *J* = 29.4 Hz), 137.85, 136.39, 135.68, 134.63, 133.53, 129.87, 128.85, 128.39, 127.70, 126.32, 125.29, 124.06, 122.28, 121.19, 115.00 (t, *J* = 308.9 Hz), 114.41, 111.89, 55.43; **IR** (KBr, cm^{-1}): ν 3078, 2846, 1648, 1590, 1500, 970, 800, 531; **MS (ESI)** m/z 491 [M+H$^+$]; **Anal. Calcd.** For $C_{23}H_{16}BrClF_2N_2O$: C, 56.41; H, 3.29; N, 5.72. Found: C, 56.70; H, 3.28; N, 5.63.

1-(1-(2-bromo-2,2-difluoro-1-((4-methoxyphenyl)imino)ethyl)-2-phenyl-1H-indol-3-yl)ethanone(1n)



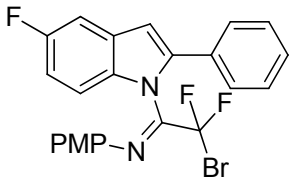
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.0 Hz, 1H), 7.45-7.37 (m, 2H), 7.35-7.30 (m, 4H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.72 (d, *J* = 9.2 Hz,2H), 6.64 (d, *J* = 9.2 Hz, 2H), 3.77 (s, 3H), 1.98 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -50.56 (q, *J* = 161.4 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.36, 160.83, 143.70, 138.76(t, *J* = 30.9 Hz), 135.16, 135.07, 130.28, 130.11, 130.07, 128.40, 127.18, 126.90, 125.04, 124.05, 123.31, 122.34, 118.84, 114.60(t, *J* = 308.5 Hz), 114.43, 111.13, 67.10, 55.49, 30.41; **IR** (KBr, cm^{-1}): ν 2840, 1720, 1654, 1591, 1505, 1387, 1256, 1166, 1029, 747; **MS (EI)** m/z (relative intensity) 496 (3, ^{79}Br) [M$^+$], 498 (3, ^{81}Br) [M$^+$], 122 (100); **HRMS (EI)** calcd. For $C_{25}H_{19}BrF_2N_2O_2$: 496.0598, Found: 496.0596.

N-(2-bromo-2,2-difluoro-1-(5-methyl-2-phenyl-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1o)



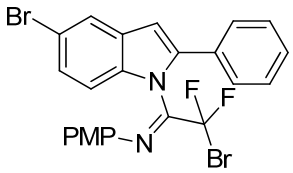
yellow solid; **mp**: 114-115°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.30 (s, 5H), 7.01 (s, 2H), 6.81 – 6.63 (m, 5H), 3.73 (s, 3H), 2.43 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.49 (dd, *J* = 409.7, 156.8 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.23, 141.05 (t, *J* = 27.2 Hz)，139.41, 135.85, 134.39, 132.12, 131.47, 129.42, 128.78, 128.3, 127.26, 126.83, 125.15, 120.78, 114.90 (t, *J* = 309.6 Hz), 114.42, 111.48, 55.41, 21.44; **IR** (KBr, cm^{-1}): ν 3053, 2904, 2835, 1595, 1500, 1462, 1256, 1027, 800, 520; **MS (EI)** m/z (relative intensity) 468 (42, ^{79}Br) [M$^+$], 470 (42, ^{81}Br) [M$^+$], 262 (100), 264 (98); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O$: C, 61.42; H, 4.08; N, 5.97. Found: C, 61.66; H, 4.28; N, 5.85.

N-(2-bromo-2,2-difluoro-1-(5-fluoro-2-phenyl-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1p)



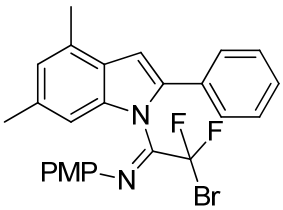
yellow solid; **mp**: 121-122 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33-7.30 (m, 6H), 7.04-7.00(m,1H), 6.93-6.87 (m, 1H), 6.77-6.66 (m, 5H), 3.74 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.76 (dd, *J* = 441.5, 156.6 Hz, 2F), -81.25 – -133.35 (m, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.45, 158.95 (d, *J* = 237.8 Hz), 140.98, 140.27 (t, *J* = 26.8 Hz), 135.52, 132.23, 131.68, 129.69 (d, *J* = 10.4 Hz), 128.87, 128.68, 127.27, 126.84, 114.64 (t, *J* = 305.7 Hz), 114.49, 112.58 (d, *J* = 9.6 Hz), 111.93, 111.67, 106.21, 105.97, 105.71 (d, *J* = 4.3 Hz), 55.43; **IR** (KBr, cm^{-1}): ν 3021, 2960, 2830, 1590, 1504, 1467, 967, 521; **MS (EI)** m/z (relative intensity) 472 (3) [M^+], 160 (100); **Anal. Calcd.** For $C_{23}H_{16}BrF_3N_2O$: C, 58.37; H, 3.41; N, 5.92. Found: C, 58.60; H, 3.61; N, 5.89.

N-(2-bromo-1-(5-bromo-2-phenyl-1H-indol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline (1q)



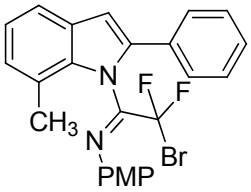
yellow solid; **mp**: 145-146 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.39-7.25 (m, 6H), 6.98-6.95 (m, 1H), 6.79-6.67 (m, 5H), 3.75 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.84 (dd, *J* = 451.3, 156.8 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.54, 140.60, 139.83 (t, *J* = 27.5 Hz), 135.40, 134.53, 131.48, 130.77, 128.93, 128.80, 127.31, 126.89, 126.41, 123.55, 115.28, 114.55 (t, *J* = 310.3 Hz), 114.58, 113.20, 105.07, 55.45; **IR** (KBr, cm^{-1}): ν 3074, 2835, 1650, 1591, 1353, 840, 518; **MS (EI)** m/z (relative intensity) 534 (6) [M^+], 218 (100); **Anal. Calcd.** For $C_{23}H_{16}Br_2F_2N_2O$: C, 51.71; H, 3.02; N, 5.24. Found: C, 51.90; H, 3.21; N, 5.26.

N-(2-bromo-1-(4,6-dimethyl-2-phenyl-1H-indol-1-yl)-2,2-difluoroethylidene)-4-methoxyanili ne (1r)



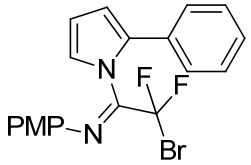
yellow solid; **mp**: 132-133 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33–7.21 (m, 5H), 6.83-6.76 (m, 5H), 6.69-6.66 (m, 2H), 3.74 (s, 3H), 2.54 (s, 3H), 2.35 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.09 (q, *J* = 157.6 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.18, 141.17 (t, *J* = 27.2 Hz), 138.14, 136.35, 135.88, 133.66, 132.20, 130.08, 128.66, 128.06, 127.23, 126.86, 126.75, 124.18, 115.02 (t, *J* = 308.1 Hz), 114.37, 109.28, 104.40, 55.40, 21.87, 18.58; **IR** (KBr, cm^{-1}): ν 3021, 2915, 2840, 1587, 1503, 1255, 1026, 831, 532; **MS (EI)** m/z (relative intensity) 482 (41, ^{79}Br) [M^+], 484 (39, ^{81}Br) [M^+], 262 (100), 264 (93); **Anal. Calcd.** For $C_{25}H_{21}BrF_2N_2O$: C, 62.12; H, 4.38; N, 5.80. Found: 61.94; H, 4.48; N, 5.66.

N-(2-bromo-2,2-difluoro-1-(7-methyl-2-phenyl-1H-indol-1-yl)ethylidene)-4-methoxyaniline (1s)



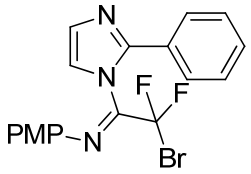
yellow solid; **mp**: 85-86 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.25-7.30 (m, 5H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.77-6.65 (m, 5H), 3.74 (s, 3H), 2.39 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.10 (q, *J* = 157.9 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.23, 141.09 (t, *J* = 28.6 Hz), 138.78, 136.56, 135.86, 133.65, 132.09, 128.72, 128.20, 127.29, 126.95, 126.81, 123.82, 120.60, 115.01 (t, *J* = 310.8 Hz), 114.39, 111.72, 105.85, 55.41, 21.98; **IR** (KBr, cm^{-1}): ν 3050, 2910, 2835, 1590, 1503, 1259, 1027, 837, 522; **MS (EI)** m/z (relative intensity) 468 (36, ^{79}Br) [M^+], 470 (36, ^{81}Br) [M^+], 262 (100), 264 (95); **Anal. Calcd.** For $C_{24}H_{19}BrF_2N_2O$: C, 61.42; H, 4.08; N, 5.97. Found: C, 61.70; H, 4.21; N, 5.92.

N-(2-bromo-2,2-difluoro-1-(2-phenyl-1H-pyrrol-1-yl)ethylidene)-4-methoxyaniline (3a)



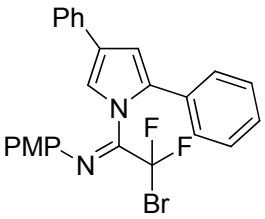
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14-7.16 (m, 3H), 6.97-7.00 (m, 3H), 6.57 (d, *J* = 7.0 Hz, 2H), 6.43 (m, 1H), 6.32 (m, 1H), 6.20 (d, *J* = 7.0 Hz, 2H), 3.74 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -50.13 (dd, *J* = 516.8, 162.3 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.23, 140.98 (t, *J* = 27.3 Hz), 136.19, 134.93, 131.59, 128.23, 127.15, 126.75, 124.94, 120.75, 114.92 (t, *J* = 306.2 Hz), 113.92, 112.06, 111.64, 55.44; **IR** (KBr, cm^{-1}): ν 2920, 1663, 1605, 1509, 1446, 1134, 750, 537; **MS (EI)** m/z (relative intensity) 404 (24, ^{79}Br) [M^+], 406 (24, ^{81}Br) [M^+], 133 (100); **HRMS (EI)** calcd. For $C_{19}H_{15}BrF_2N_2O$: 404.0336, Found: 404.0335.

N-(2-bromo-2,2-difluoro-1-(2-phenyl-1H-imidazol-1-yl)ethylidene)-4-methoxyaniline (3b)



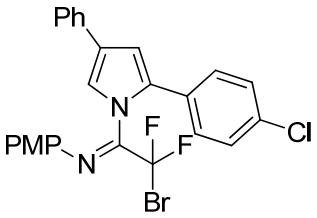
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.06 (m, 7H), 6.62 (d, *J* = 7.0 Hz, 2H), 6.35 (d, *J* = 7.0 Hz, 2H), 3.74 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -51.31 (dd, *J* = 653.9, 163.2 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.85, 147.40, 138.66 (t, *J* = 28.3 Hz), 135.27, 130.84, 129.27, 128.41, 127.03, 124.94, 119.38, 114.39 (t, *J* = 306.8 Hz), 114.03, 55.36; **IR** (KBr, cm^{-1}): ν 3061, 2840, 1592, 1504, 1388, 1254, 971, 816; **MS (EI)** m/z (relative intensity) 405 (22, ^{79}Br) [M^+], 407 (21, ^{81}Br) [M^+], 264 (100), 262(97); **HRMS (EI)** calcd. For $C_{18}H_{14}BrF_2N_3O$: 405.0288, Found: 405.0292.

N-(2-bromo-1-(2,4-diphenyl-1H-pyrrol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline(3c)



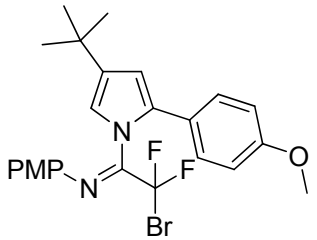
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.43 (m, 2H), 7.31 (m, 2H), 7.19 (m, 3H), 7.06 (m, 2H), 6.68 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -50.69 (dd, *J* = 549.3, 162.8 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.34, 140.49 (t, *J* = 27.5 Hz), 136.14, 135.99, 133.98, 131.41, 128.91, 128.33, 128.08, 127.45, 126.84, 126.79, 125.53, 125.01, 116.69, 114.93 (t, *J* = 308.2 Hz), 114.06, 109.87, 55.47; **IR** (KBr, cm^{-1}): ν 2963, 2830, 1654, 1479, 1504, 1249, 964, 758; **MS (ESI)** m/z 481 [$M+H^+$], 503 [$M+Na^+$]; **HRMS (ESI)** *m/e* calcd. for $C_{25}H_{20}BrF_2N_2O^+$ [$M+Na^+$] 481.07216, Found: 481.07036.

N-(2-bromo-1-(2-(4-chlorophenyl)-4-phenyl-1H-pyrrol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline(3d)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.1 Hz, 2H), 7.41 (m, 2H), 7.30 (d, *J* = 14.0 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.66 – 6.52 (m, 3H), 6.29 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.89 (dd, *J* = 505.1, 163.8 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.46, 140.03 (t, *J* = 27.4 Hz), 135.95, 134.71, 133.72, 133.44, 129.85, 128.91, 128.47, 128.18, 128.01, 126.95, 125.51, 125.00, 116.91, 114.87 (t, *J* = 307.8 Hz), 114.09, 110.25, 67.12, 55.46; **IR** (KBr, cm^{-1}): ν 2958, 2835, 1652, 1598, 1504, 1468, 1357, 1249, 965, 815; **MS (EI)** m/z (relative intensity) 514 (3) [M^+], 88 (100); **HRMS (EI)** calcd. For $C_{25}H_{18}BrClF_2N_2O$: 514.0259, Found: 514.0255.

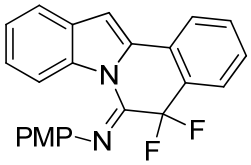
N-(2-bromo-1-(4-(tert-butyl)-2-(4-methoxyphenyl)-1H-pyrrol-1-yl)-2,2-difluoroethylidene)-4-methoxyaniline(3e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.7 Hz, 2H), 6.69 (s, 1H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.60 – 6.49 (m, 2H), 6.16 (m, 3H), 3.73 (s, 3H), 3.72 (s, 3H), 1.29 (s, 9H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -49.30 (dd, *J* = 527.1, 164.3 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.04, 158.84, 141.75 (t, *J* = 27.3 Hz), 139.15, 136.52, 134.81, 127.96, 124.98, 124.64, 115.16, 114.86 (t, *J* = 306.0 Hz), 113.72, 113.59, 110.01, 55.43, 55.25, 31.37, 30.74; **IR** (KBr, cm^{-1}): ν 2960, 2835, 1650, 1613, 1525, 1505, 1250, 963, 815; **MS (EI)** m/z (relative intensity) 490 (26, ^{79}Br) [M^+], 492 (25, ^{81}Br) [M^+], 262 (99), 264 (100); **HRMS (EI)** calcd. For $C_{24}H_{25}F_2N_2O_2Br$: 490.1067, Found:

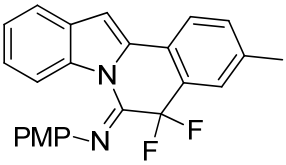
490.1069.

N-(5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2a)



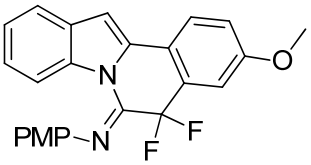
yellow solid; **mp**: 193-195°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.30-7.24 (m, 2H), 7.05 (s, 1H), 7.02-7.00 (m,2H), 6.94-6.92 (m, 2H), 3.83 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.61 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.18, 141.41 (t, *J* = 28.6 Hz), 140.36, 136.65, 132.88, 131.90, 130.40, 128.73, 127.21 (t, *J* = 28.5 Hz), 125.94, 125.73, 123.92, 123.63, 121.15, 120.79, 116.82, 113.87, 104.00, 55.52; **IR** (KBr, cm^{-1}): ν 3101, 2835, 1668, 1504, 1449, 1240, 1028, 749, 488; **MS (EI)** m/z (relative intensity) 374 (100) [M^+]; **Anal. Calcd.** For $C_{23}H_{16}F_2N_2O$: C, 73.79; H, 4.31; N, 7.48. Found: C, 73.77; H, 4.54; N, 7.30.

N-(5,5-difluoro-3-methylindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2b)



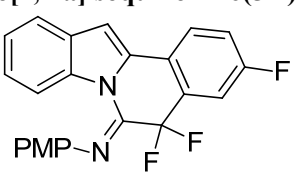
yellow solid; **mp**: 223-224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.43 (s, 1H), 7.34-7.21 (m, 3H), 7.07 – 6.88 (m, 5H), 3.83 (s, 3H), 2.37 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.65 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.13, 140.45, 139.11, 136.53, 133.13, 132.92, 130.52, 127.07 (t, *J* = 29.1 Hz), 126.07, 125.46, 123.85, 123.65, 116.74, 113.84, 103.24, 55.53, 21.41; **IR** (KBr, cm^{-1}): ν 3058, 2835, 1669, 1504, 1450, 1242, 1013, 806, 747, 488; **MS (EI)** m/z (relative intensity) 388 (100) [M^+]; **HRMS (EI)** calcd. For $C_{24}H_{18}F_2N_2O$: 388.1387, Found: 388.1391.

N-(5,5-difluoro-3-methoxyindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2c)



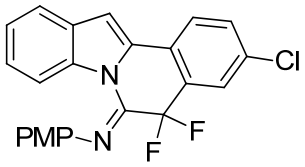
yellow solid; **mp**: 206-207 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.27-7.20 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.97 – 6.86 (m, 3H), 3.83 (s, 3H), 3.80 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.65 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.06, 156.13, 140.46, 136.40, 133.06, 130.67, 128.40 (t, *J* = 23.5 Hz), 125.41, 125.23, 123.85, 120.82, 119.85, 119.65, 116.67, 113.84, 109.04, 102.46, 55.57, 55.52; **IR** (KBr, cm^{-1}): ν 3064, 2830, 1662, 1503, 1450, 1348, 1233, 1040, 805, 542; **MS (EI)** m/z (relative intensity) 404 (100) [M^+]; **Anal. Calcd.** For $C_{24}H_{18}F_2N_2O_2$: C, 71.28; H, 4.49; N, 6.93. Found: C, 71.25; H, 4.56; N, 6.86.

4-methoxy-N-(3,5,5-trifluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)aniline (2d)



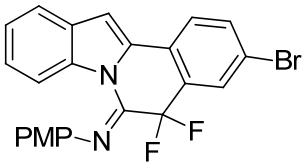
yellow solid; **mp**: 199-200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.80-7.87 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.18 (m, 4H), 7.07 – 6.90 (m, 5H), 3.84 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.93 (s, 2F), -109.63 (s, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.70, 161.21, 156.28, 140.11, 136.54, 132.07, 130.31, 126.00 (d, *J* = 8.1 Hz), 125.80, 124.03, 123.27, 121.14, 120.77, 119.98 (d, *J* = 22.6 Hz), 116.78, 113.90, 112.77 (d, *J* = 24.2 Hz), 103.82, 100.00, 55.52; **IR** (KBr, cm^{-1}): ν 3069, 2835, 1658, 1498, 1449, 1241, 1036, 858, 750, 530; **MS (EI)** m/z (relative intensity) 392 (100) [M^+]; **HRMS (EI)** calcd. For $C_{23}H_{15}F_3N_2O$: 392.1136, Found: 392.1135.

N-(3-chloro-5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2e)



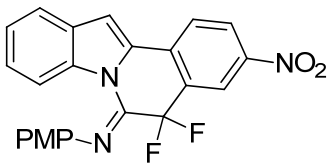
yellow solid; **mp**: 220-222 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 6.8 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.58-7.57 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.20 (m, 2H), 7.02-6.92 (m, 5H), 3.84 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.20 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.33, 140.72 (t, *J* = 26.0 Hz), 140.07, 136.65, 134.53, 132.34, 131.91, 130.23, 128.50 (t, *J* = 24.7 Hz), 126.09, 126.05, 125.10, 124.07, 121.26, 120.78, 116.81, 113.91, 110.29 (t, *J* = 246.2 Hz), 104.47, 55.54; **IR** (KBr, cm^{-1}): ν 3080, 2835, 1668, 1505, 1398, 1242, 1034, 748, 490; **MS (EI)** m/z (relative intensity) 408 (100) [M^+]; **Anal. Calcd.** For $C_{23}H_{15}ClF_2N_2O$: C, 67.57; H, 3.70; N, 6.85. Found: C, 67.54; H, 3.86; N, 6.83.

N-(3-bromo-5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2f)



yellow solid; **mp**: 222-224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.76 (s, 1H), 7.65 (s, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.19 (m, 2H), 7.05 (s, 1H), 6.96 (dd, *J* = 29.4, 8.1 Hz, 4H), 3.84 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.16 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.34, 140.42 (t, *J* = 27.8 Hz), 140.05, 136.69, 135.18, 131.96, 130.22, 129.08, 128.66 126.06, (t, *J* = 25.4 Hz), 125.69, 125.19, 124.08, 122.24, 121.27, 120.77, 116.80, 113.90, 110.19 (t, *J* = 246.9 Hz), 104.54, 55.54; **IR** (KBr, cm^{-1}): ν 3075, 2830, 1669, 1504, 1448, 1242, 1033, 748, 485; **MS (EI)** m/z (relative intensity) 454 (100, ^{79}Br) [M^+], 542 (92, ^{81}Br) [M^+]; **Anal. Calcd.** For $C_{23}H_{15}BrF_2N_2O$: C, 60.94; H, 3.34; N, 6.18. Found: C, 61.15; H, 3.57; N, 6.13.

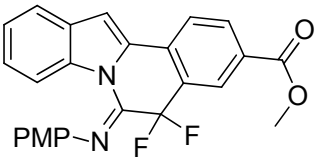
N-(5,5-difluoro-3-nitroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2g)



yellow solid; **mp**: 259-260 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.63 – 8.50 (m, 2H), 8.38 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.20 (m, 3H), 6.99 (dd, *J* = 23.4, 8.3 Hz, 4H), 3.86 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.47 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.60, 147.17, 140.02 139.63, 137.20, 132.18, 130.75, 129.94, 128.01 (t, *J* = 26.3 Hz), 127.29, 126.71, (t, *J* = 28.2 Hz), 124.68, 124.46, 122.36, 121.88, 120.79, 117.01, 113.98, 109.82 (t, *J* = 247.5 Hz), 107.67, 55.54; **IR** (KBr, cm^{-1}): ν 3069, 2920, 2835, 1656, 1603, 1341,

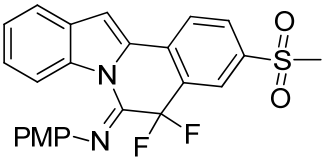
1038, 826, 742, 538; **MS (ESI)** m/z 420 [M+H$^+$]; **HRMS (ESI)** *m/e* calcd for $C_{23}H_{16}F_2N_3O_3^+$ [M+H$^+$] 420.1154, Found: 420.11551.

methyl-5,5-difluoro-6-((4-methoxyphenyl)imino)-5,6-dihydroindolo[2,1-a]isoquinoline-3-carboxylate (2h)



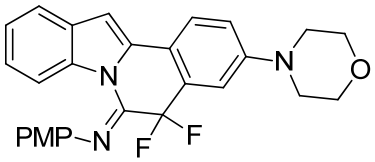
yellow solid; **mp**: 217-219°C;**^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.58-8.55 (m, 1H), 8.32 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.20 (m, 2H), 7.15 (s, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.65 ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.48, 156.35, 140.08, 136.92, 132.65, 131.87, 130.15, 127.87, 127.19 (t, *J* = 24.7 Hz), 126.51, 124.15, 123.68, 121.54, 120.78, 116.93, 113.89, 106.04, 55.54, 52.43; **IR** (KBr, cm^{-1}): ν 2954, 1716, 1668, 1505, 1450, 1239, 1042, 751; **MS (EI)** m/z (relative intensity) 432 (100) [M$^+$]; **Anal. Calcd.** For $C_{25}H_{18}F_2N_2O_3$: C, 69.44; H, 4.20; N, 6.48. Found: C, 69.29; H, 4.22; N, 6.40.

N-(5,5-difluoro-3-(methylsulfonyl)indolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2i)



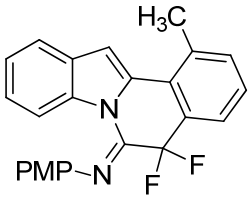
yellow solid; **mp**: 259-261°C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.23 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.20 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 3.85 (s, 3H), 3.07 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.56; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.56, 140.38, 139.74, 137.08, 131.51, 130.97, 130.45, 129.95, 127.04, 126.13, 124.72, 124.38, 121.80, 120.77, 116.96, 113.96, 107.09, 55.55, 44.44; **IR** (KBr, cm^{-1}): ν 2926, 1666, 1605, 1505, 1446, 1305, 1134, 750, 540; **MS (EI)** m/z (relative intensity) 452 (100) [M$^+$]; **Anal. Calcd.** For $C_{25}H_{19}F_2NO_3S$: C, 63.71; H, 4.01; N, 6.19. Found: C, 63.43; H, 3.98; N, 6.13.

N-(5,5-difluoro-3-morpholinoindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2j)



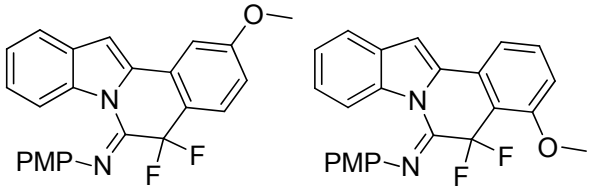
yellow solid; **mp**: 245-247°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.53 (m, 1H), 7.24 (m, 2H), 6.96 (m, 7H), 3.83 (m, 7H), 3.18 (m, 4H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.35 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.07, 151.31, 140.58, 136.34, 133.37, 130.82, 128.16 (t, *J* = 22.4 Hz), 125.03, 123.81, 120.72, 120.66, 119.12, 117.88(t, *J* = 5.3 Hz), 116.61, 113.81, 110.59(t, *J* = 4.3 Hz), 101.83, 66.58, 55.52, 48.35; **IR** (KBr, cm^{-1}): ν 2830, 1659, 1504, 1449, 1239, 917, 749; **MS (EI)** m/z (relative intensity) 459 (100); **HRMS (EI)** calcd. For $C_{27}H_{23}F_2N_3O_2$: 459.1758, Found: 459.1760.

N-(5,5-difluoro-1-methylindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2k)



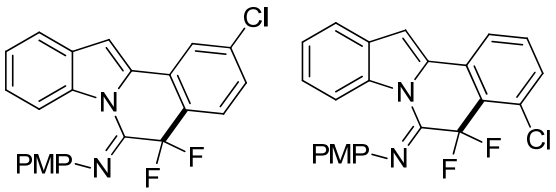
yellow solid; **mp**: 209-212 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.26 (m, 3H), 7.13 (s, 1H), 6.98 (dd, *J* = 25.5, 8.2 Hz, 4H), 3.84 (s, 3H), 2.72 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.77 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ156.21, 140.40, 136.00, 135.35, 135.14, 132.34, 130.33, 128.03, 125.92, 123.90, 123.71, 121.25, 120.74, 116.15, 113.92, 109.64, 55.51, 23.80; **IR** (KBr, cm^{-1}): ν 2915, 2840, 1662, 1504, 1458, 1245, 1016, 748, 552; **MS (EI)** m/z (relative intensity) 389 (100) [M^+]; **HRMS (EI)** calcd. For $C_{24}H_{18}F_2N_2O$: 388.1387, Found: 388.1386.

mixture of N-(5,5-difluoro-2-methoxyindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2l) and N-(5,5-difluoro-4-methoxyindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2l')



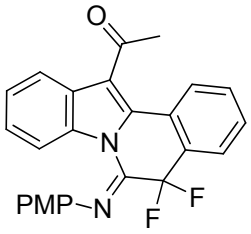
yellow solids; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.60 (m, 1.1H), 7.60 (m, 1.2H), 7.50-7.46 (m, 2.2H), 7.37 – 7.19 (m, 3.5H), 7.08 (s, 1.2H), 7.05 – 6.84 (m, 4.4H), 3.85 (s, 3H), 3.84 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.92, -81.70; **IR** (KBr, cm^{-1}): ν 3042, 2963, 2835, 1587, 1454, 1340, 1258, 1130, 810, 538; **MS (EI)** m/z (relative intensity) 404 (100) [M^+]; **Anal. Calcd.** For $C_{24}H_{18}F_2N_2O_2$: C, 71.28; H, 4.49; N, 6.93. Found: C, 71.30; H, 4.55; N, 6.89.

Mixture of N-(2-chloro-5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2m) and N-(4-chloro-5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2m')



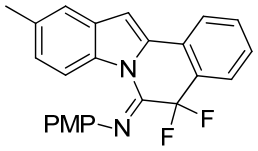
yellow solids; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.63-7.59 (m, 1H), 7.52 – 7.20 (m, 4H), 7.11-6.92 (m, 5H), 3.85 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.75 (s), -81.29 (s); **IR** (KBr, cm^{-1}): ν 3080, 2915, 2835, 1664, 1505, 1454, 1239, 1047, 826, 544; **MS (EI)** m/z (relative intensity) 408 (100) [M^+]; **HRMS (EI)** calcd. For $C_{23}H_{15}ClF_2N_2O$: 408.0841, Found: 408.0845.

1-(5,5-difluoro-6-((4-methoxyphenyl)imino)-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)ethanone(2n)



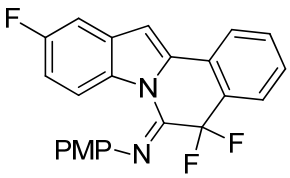
yellow solid; **mp**: 198-200°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.88 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 6.4 Hz, 1H), 7.34 (m, 2H), 7.02- 6.94 (m, 4H), 3.83 (s, 3H), 2.71 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -85.46 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.96, 156.71, 140.67, 139.75, 135.69, 132.18, 131.94, 129.89, 128.33, 127.81, 126.15, 125.67, 124.68, 120.73, 119.96, 116.17, 114.01, 55.51, 31.95; **IR** (KBr, cm^{-1}): ν 2915, 1659, 1504, 1449, 1241, 1139, 1035, 747; **MS (EI)** m/z (relative intensity) 416 (100) [M^+]; **Anal. Calcd.** For $C_{25}H_{18}F_2N_2O_2$: C, 72.11; H, 4.36; N, 6.73. Found: C, 72.38; H, 4.46; N, 6.78.

N-(5,5-difluoro-10-methylindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2o)



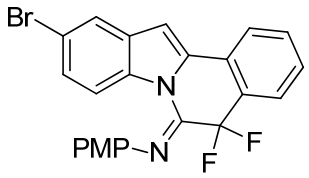
yellow solid; **mp**: 187-189 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.62 (s, 1H), 7.58 – 7.49 (m, 1H), 7.38 (s, 2H), 7.12 (s, 1H), 7.00-6.93 (m, 5H), 3.84 (s, 3H), 2.44 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.63 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.11, 141.35 (t, *J* = 28.9 Hz), 140.51, 134.90, 133.52, 132.85, 131.84, 130.65, 128.58, 127.11, 126.78, 110.95, 125.92, 123.55, 121.07, 120.83, 116.52, 113.86, 103.82, 55.53, 21.40; **IR** (KBr, cm^{-1}): ν 3000, 2839, 1656, 1505, 1463, 1399, 1238, 1017, 761, 490; **MS (EI)** m/z (relative intensity) 389 (100) [M^+]; **Anal. Calcd.** For $C_{24}H_{18}F_2N_2O$: C, 74.21; H, 4.67; N, 7.21. Found: C, 74.21; H, 4.76; N, 7.01.

4-methoxy-N-(5,5,10-trifluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)aniline (2p)



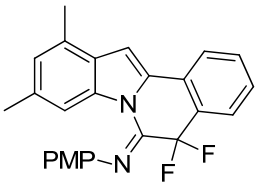
yellow solid; **mp**: 192-193 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.3 Hz, 1H), 7.03-6.92 (m, 6H), 3.85 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.70 (s, 2F), -118.72 - -118.63(m, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.04, 158.65, 156.29, 141.23 (t, *J* = 27.2 Hz), 140.10, 134.32, 133.00, 131.99, 131.37 (d, *J* = 9.3 Hz), 129.08, 127.35 (t, *J* = 24.9 Hz), 126.31, 126.01, 123.72, 120.82, 118.03, 113.88, 113.30 (d, *J* = 24.0 Hz), 106.52 (d, *J* = 24.0 Hz), 103.41 (d, *J* = 4.0 Hz), 55.52; **IR** (KBr, cm^{-1}): ν 3048, 2835, 1659, 1505, 1461, 1146, 1034, 770, 515; **MS (EI)** m/z (relative intensity) 393 (100) [M^+]; **Anal. Calcd.** For $C_{23}H_{15}F_3N_2O$: C, 70.40; H, 3.85; N, 7.14. Found: C, 70.41; H, 4.06; N, 7.03.

N-(10-bromo-5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2q)



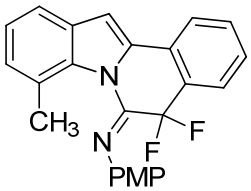
yellow solid; **mp**: 205-206 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.73 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45-7.37 (m, 2H), 7.03-9.92 (m, 5H), 3.85 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.98 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.38, 139.96, 135.25, 133.98, 132.11, 132.02, 129.18, 128.38, 127.38 (t, *J* = 24.9 Hz), 126.01, 123.80, 123.65, 120.80, 118.25, 117.14, 113.89, 102.81, 55.52; **IR** (KBr, cm^{-1}): ν 3021, 2825, 1654, 1505, 1448, 1248, 1031, 902, 768, 546; **MS (ESI)** m/z 453 [M+H$^+$]; **HRMS (ESI)** *m/e* calcd for $C_{23}H_{16}F_2N_2O^+$ [M+H$^+$] 453.0409, Found: 453.04105.

N-(5,5-difluoro-9,11-dimethylindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2r)



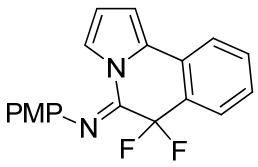
yellow solid; **mp**: 254-255 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 – 6.83 (m, 6H), 3.85 (s, 3H), 2.53 (s, 3H), 2.42 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.61 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.05, 140.60, 136.24, 131.80, 130.14, 128.27, 127.92, 126.02, 125.89, 123.38, 120.75, 114.37, 113.82, 102.60, 55.53, 22.01, 18.44; **IR** (KBr, cm^{-1}): ν 3005, 2830, 1666, 1506, 1412, 1242, 1039, 763, 556; **MS (EI)** m/z (relative intensity) 403 (100) [M$^+$]; **Anal. Calcd.** For $C_{25}H_{20}F_2N_2O$: C, 74.61; H, 5.01; N, 6.96. Found: C, 74.73; H, 5.12; N, 6.72.

N-(5,5-difluoro-8-methylindolo[2,1-a]isoquinolin-6(5H)-ylidene)-4-methoxyaniline (2s)



yellow solid; **mp**: 230-321 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.43 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.15 – 6.89 (m, 6H), 3.85 (s, 3H), 2.46 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.59 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.11, 141.57 (t, *J* = 20.2 Hz), 140.55, 137.07, 136.12, 132.31, 131.84, 128.44, 128.15, 126.95 (t, *J* = 24.7 Hz), 125.89, 125.44, 123.45, 120.76, 116.86, 113.85, 104.07, 55.54, 22.10; **IR** (KBr, cm^{-1}): ν 3003, 2830, 1660, 1506, 1400, 1242, 1023, 764, 482; **MS (EI)** m/z (relative intensity) 389 (100) [M$^+$]; **HRMS (EI)** calcd. For $C_{24}H_{18}F_2N_2O$: 388.1387, Found: 388.1384.

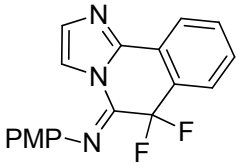
N-(6,6-difluoropyrrolo[2,1-a]isoquinolin-5(6H)-ylidene)-4-methoxyaniline(4a)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.40 (m, 4H), 7.40 – 7.16 (m, 1H), 6.99-6.89 (m, 4H), 6.68

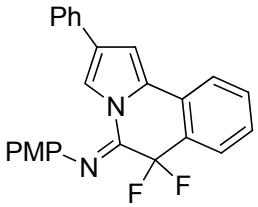
(s, 1H), 6.36 (s, 1H), 3.81 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.29 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.47, 140.65 (t, *J* = 26.1 Hz), 139.88, 131.95, 128.26, 127.21, 126.12, 126.01, 122.31, 120.92, 119.85, 115.06, 113.81, 108.98, 55.46; **IR** (KBr, cm^{-1}): ν 3140, 2835, 1661, 1609, 1505, 1452, 1421, 1275, 1040, 839, 757; **MS (ESI)** m/z 347 [M+Na^+]; **HRMS (ESI)** *m/e* calcd for $C_{23}H_{16}F_2N_2O^+$ [M+Na^+] 347.09664, Found: 347.09556.

N-(6,6-difluoroimidazo[2,1-a]isoquinolin-5(6H)-ylidene)-4-methoxyaniline(4b)



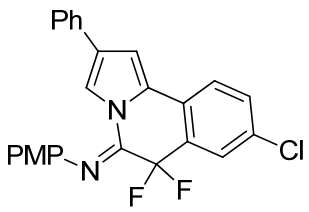
yellow solid; **mp**: 157-160°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.62 (m, 2H), 7.49 (d, *J* = 6.5 Hz, 1H), 7.00 (s, 1H), 6.93 (d, *J* = 7.3 Hz, 2H), 3.84 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.76 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.08, 157.13, 142.70, 138.66, 132.41, 131.85, 130.08, 128.65, 126.00, 124.12, 121.05, 116.26, 113.90, 55.45; **IR** (KBr, cm^{-1}): ν 3144, 2907, 1687, 1505, 1414, 1266, 834, 778, 575; **MS (EI)** m/z (relative intensity) 325 (100) [M^+]; **Anal. Calcd.** For $C_{18}H_{13}F_2N_3O$: C, 66.46; H, 4.03; N, 12.92. Found: C, 66.71; H, 4.11; N, 13.03.

N-(6,6-difluoro-2-phenylpyrrolo[2,1-a]isoquinolin-5(6H)-ylidene)-4-methoxyaniline(4c)



yellow solid; **mp**: 179-181°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.79 – 7.58 (m, 3H), 7.54 (s, 1H), 7.49 – 7.29 (m, 5H), 7.16 – 6.79 (m, 5H), 3.88 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.54, 139.81, 133.58, 132.00, 129.53, 129.11, 128.84, 127.50, 127.13, 126.83, 126.67, 126.43, 126.19, 126.10, 125.54, 122.38, 121.00, 115.60, 113.85, 107.09, 55.48; **IR** (KBr, cm^{-1}): ν 2825, 1665, 1504, 1418, 1410, 1275, 1241, 1034, 764, 750; **MS (EI)** m/z (relative intensity) 400 (100); **Anal. Calcd.** For $C_{25}H_{18}F_2N_2O$: C, 74.99; H, 4.53; N, 7.00. Found: C, 75.28; H, 4.76; N, 7.08.

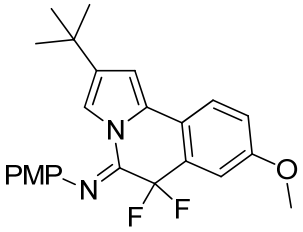
N-(8-chloro-6,6-difluoro-2-phenylpyrrolo[2,1-a]isoquinolin-5(6H)-ylidene)-4-methoxyaniline (4d)



yellow solid; **mp**: 195-197°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.56 (m, 3H), 7.49 – 7.35 (m, 3H), 7.35 – 7.19 (m, 2H), 6.96 (m, 5H), 3.83 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.39 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.73, 139.51, 133.36, 133.10, 132.36, 129.69, 128.86, 127.76, 127.52, 127.24, 126.23, 125.52, 123.81, 120.99, 115.90, 113.89, 107.51, 55.49; **IR** (KBr, cm^{-1}): ν 2920, 2846, 1734, 1665, 1504, 1407, 1240, 885, 833, 543; **MS (EI)** m/z (relative

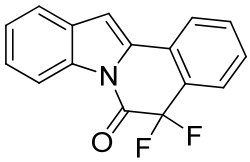
intensity) 434 (100) [M^+]; **Anal. Calcd.** For $C_{25}H_{17}ClF_2N_2O$: C, 69.05; H, 3.94; N, 6.44. Found: C, 69.20; H, 4.12; N, 6.43.

N-(2-(tert-butyl)-6,6-difluoro-8-methoxypyrrolo[2,1-a]isoquinolin-5(6H)-ylidene)-4-methoxy aniline(4e)



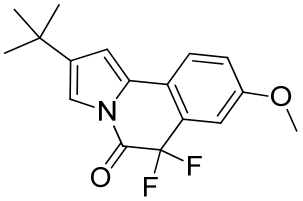
yellow solid; **mp**: 140-141°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 9.0 Hz, 1H), 7.33 (s, 1H), 7.01 (m, 2H), 6.93 (m, 4H), 6.52 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 1.29 (s, 9H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.75 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.80, 156.26, 140.89 (t, *J* = 27.9 Hz), 140.80, 140.22, 128.42, 127.41 (t, *J* = 24.1 Hz), 123.89, 120.88, 120.34, 119.45, 114.98, 113.78, 113.62, 110.94, 109.48, 106.40, 55.44, 30.96, 30.87; **IR** (KBr, cm^{-1}): ν 2975, 1671, 1506, 1045, 841, 586; **MS (EI)** m/z (relative intensity) 410 (27) [M^+], 218 (100); **Anal. Calcd.** For $C_{24}H_{24}F_2N_2O_2$: C, 70.23; H, 5.89; N, 6.82. Found: C, 70.24; H, 6.07; N, 6.77.

5,5-difluoroindolo[2,1-a]isoquinolin-6(5H)-one (2aa)



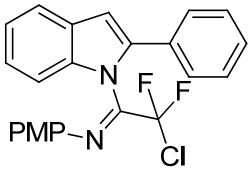
white solid; **mp**: 157-158°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.69 (m, 2H), 7.57-7.50 (m, 2H), 7.47 – 7.22 (m, 3H), 7.01 (s, 1H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -91.91 (2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.53 (t, *J* = 31.6 Hz), 135.82, 132.89, 132.14, 130.48, 129.34, 126.93, 126.67 (t, *J* = 3.1 Hz), 125.73, 123.74, 121.50, 116.58, 107.91 (t, *J* = 240.5 Hz), 107 .50; **IR** (KBr, cm^{-1}): ν 3117, 1717, 1610, 1455, 1402, 1155, 1024, 750, 491; **MS (EI)** m/z (relative intensity) 269 (100) [M^+]; **Anal. Calcd.** For $C_{16}H_9F_2NO$: C, 71.37; H, 3.37; N, 5.20. Found: C, 71.34; H, 3.37; N, 5.28.

2-(tert-butyl)-6,6-difluoro-8-methoxypyrrolo[2,1-a]isoquinolin-5(6H)-one(4ea)



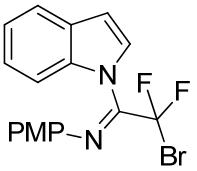
white solid; **mp**: 132-133°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.54 (s, 1H), 3.87 (s, 3H), 1.26 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -95.04 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.43, 158.14 (t, *J* = 31.4 Hz), 143.29, 129.97, 127.32 (t, *J* = 23.3 Hz), 124.36, 119.61, 119.33 (t, *J* = 6.1 Hz), 112.73, 110.12, 109.15, 107.92 (t, *J* = 241.7 Hz), 55.60, 30.83, 30.38; **IR** (KBr, cm^{-1}): ν 3108, 2966, 1728, 1620, 1604, 1538, 1491, 1343, 1023, 754, 630; **MS (EI)** m/z (relative intensity) 305 (61) [M^+], 290 (100); **Anal. Calcd.** For $C_{17}H_{17}F_2NO_2$: C, 66.87; H, 5.61; N, 4.59. Found: C, 66.90; H, 5.62; N, 4.58.

N-(2-chloro-2,2-difluoro-1-(2-phenyl-1H-indol-1-yl)ethylidene)-4-methoxyaniline (5a)



yellow solid; **mp**: 78-79 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 3.7 Hz, 1H), 7.37 – 7.24 (m, 5H), 7.21- (m, 3H), 6.79 (s, 1H), 6.67 (q, *J* = 9.0 Hz, 4H), 3.73 (s, 3H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -48.07 – -60.67 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.19, 140.27 (t, *J* = 27.3 Hz), 139.51, 136.14, 135.78, 131.79, 129.08, 128.69, 128.35, 127.38, 126.60, 123.63, 122.37 (t, *J* = 296.6 Hz), 122.04, 121.01, 114.32, 111.50, 105.90, 55.40; **IR** (KBr, cm^{-1}): ν 3059, 2835, 1650, 1588, 1504, 1453, 1338, 979, 748, 523; **MS (ESI)** m/z 411 [M+H^+]; **Anal. Calcd.** For $C_{23}H_{17}ClF_2N_2O$: C, 67.24; H, 4.17; N, 6.82. Found: C, 67.34; H, 4.22; N, 6.77.

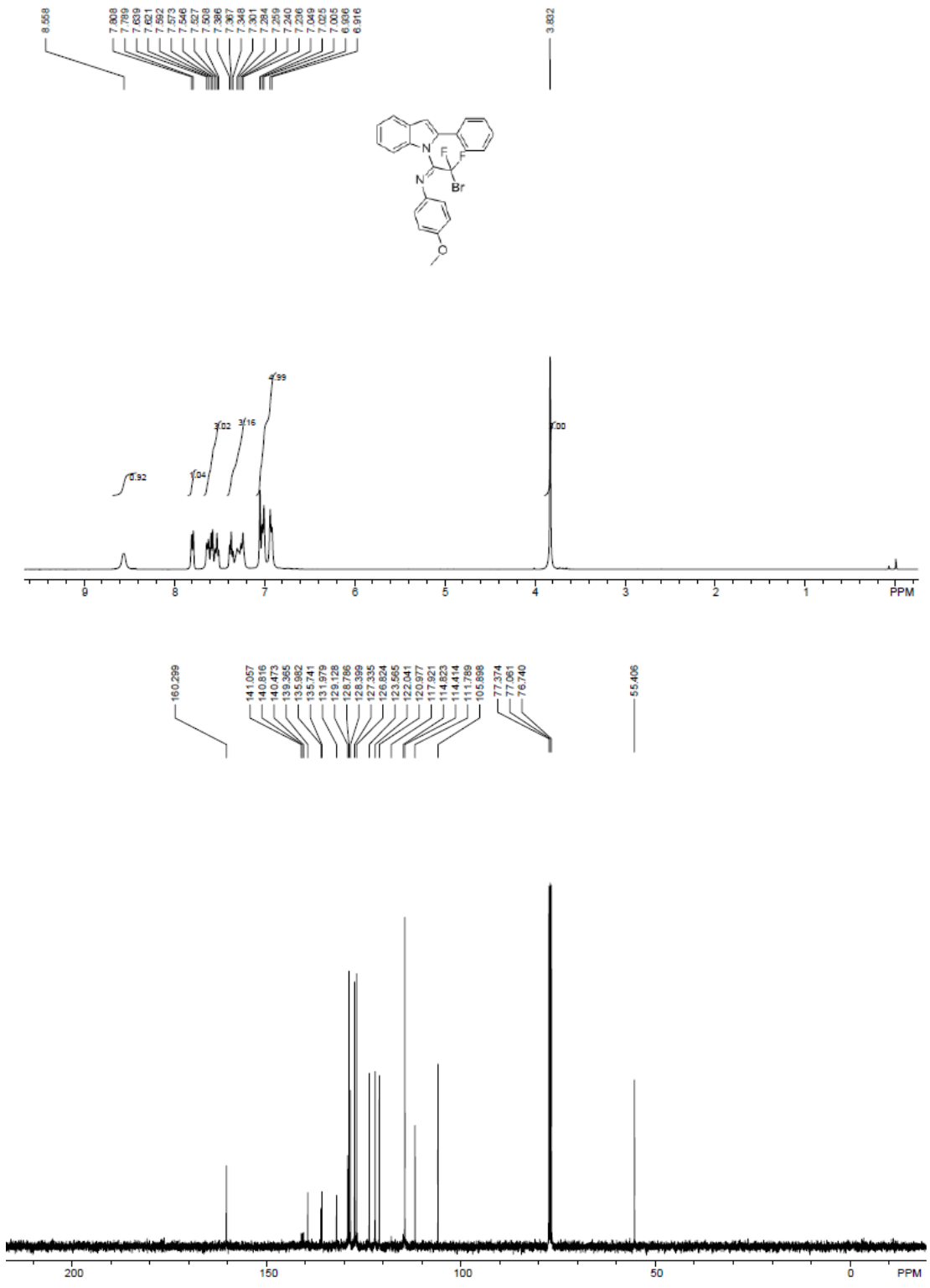
N-(2-bromo-2,2-difluoro-1-(1H-indol-1-yl)ethylidene)-4-methoxyaniline (6a)



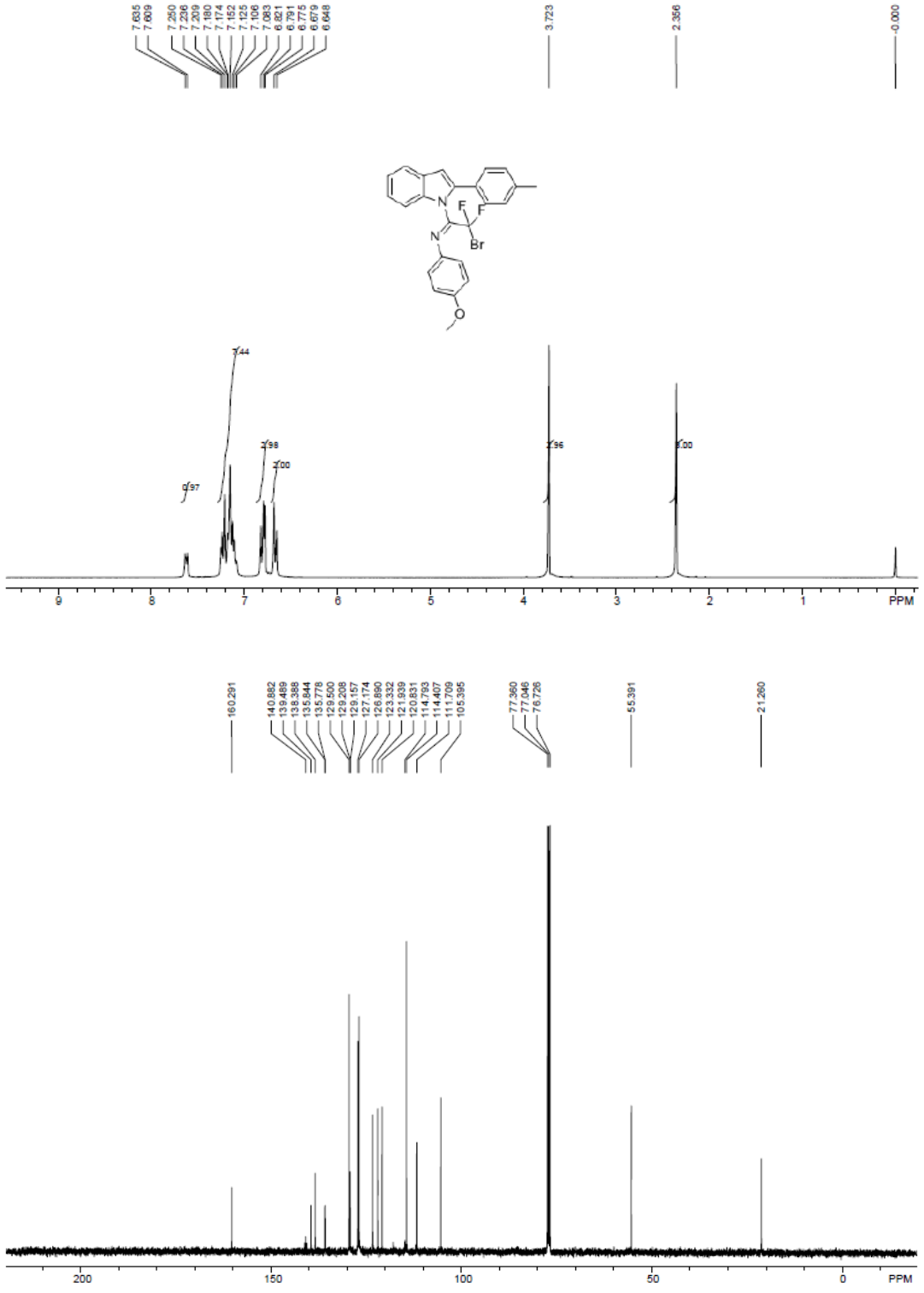
white solid; **mp**: 57-59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.23 (s, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.63-6.57 (m, 4H), 3.65 (s, 3H).; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -53.04 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.50, 140.08 (t, *J* = 26.8 Hz), 136.12, 134.45, 128.69, 125.27, 123.48, 121.71, 121.10, 114.20, 112.01, 106.79, 55.30; **IR** (KBr, cm^{-1}): ν 3016, 2846, 1650, 1591, 1503, 1452, 1325, 959, 812, 532; **MS (EI)** m/z (relative intensity) 378 (50, ^{79}Br) [M^+], 380 (47, ^{81}Br) [M^+], 262 (100), 264 (98); **Anal. Calcd.** For $C_{17}H_{13}BrF_2N_2O$: C, 53.85; H, 3.46; N, 7.39. Found: C, 54.09; H, 3.58; N, 7.39.

NMR Spectra for the Substrates and Products

1a



1b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6.791
6.775
6.679
6.648
3.723
2.356
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F
F
Br
N
O
7.44
2.98
2.00
0.97
2.96
3.00
PPM
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139.489
138.388
135.844
135.778
129.500
129.208
128.157
127.174
126.890
123.332
121.939
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76.726
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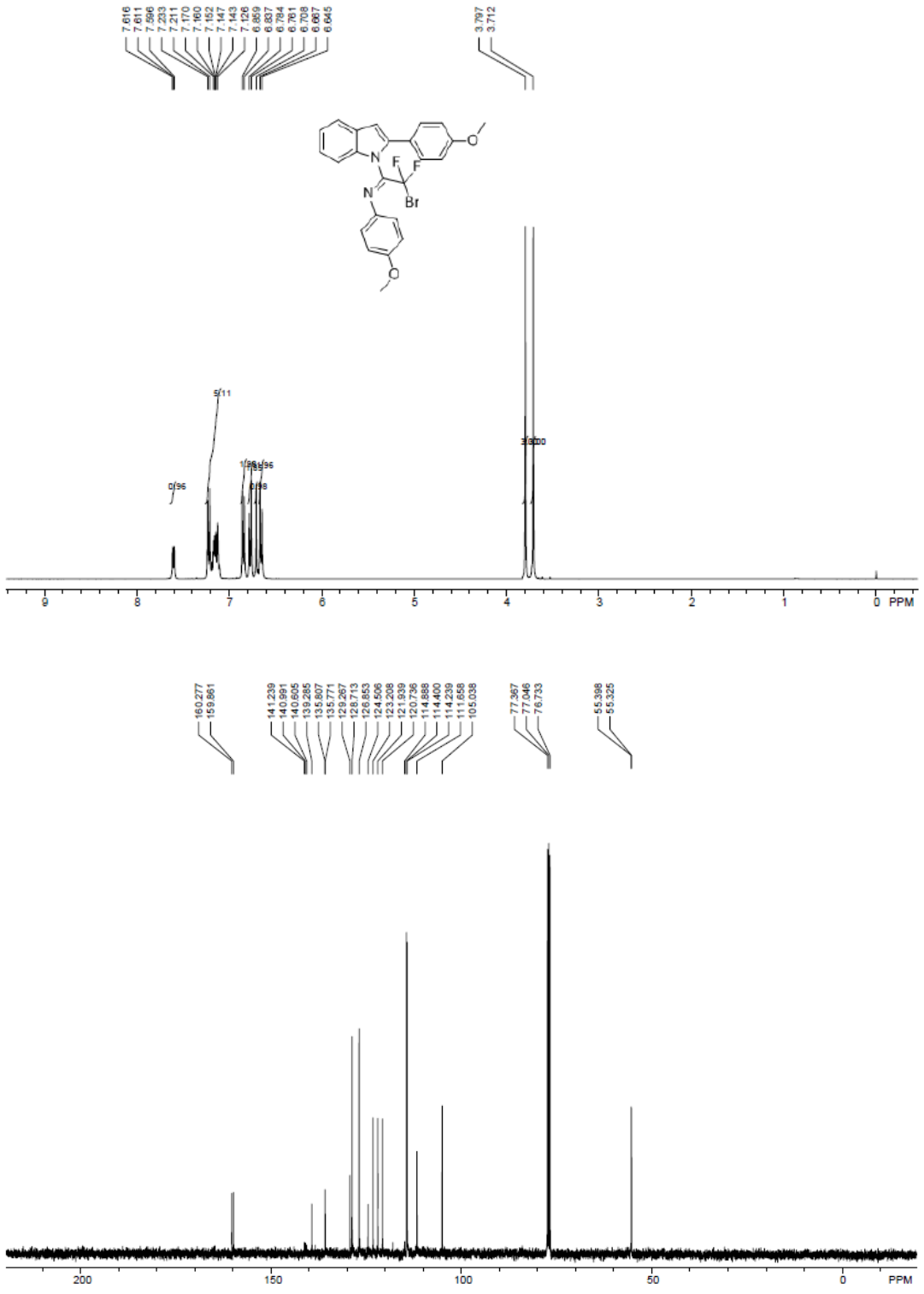
PPM

1c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6.784
6.761
6.708
6.667
6.645
3.797
3.712
F
F
Br
N
O
5.11
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0.96
0.98
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9
8
7
6
5
4
3
2
1
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135.771
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124.506
123.208
121.939
120.736
114.888
114.400
114.239
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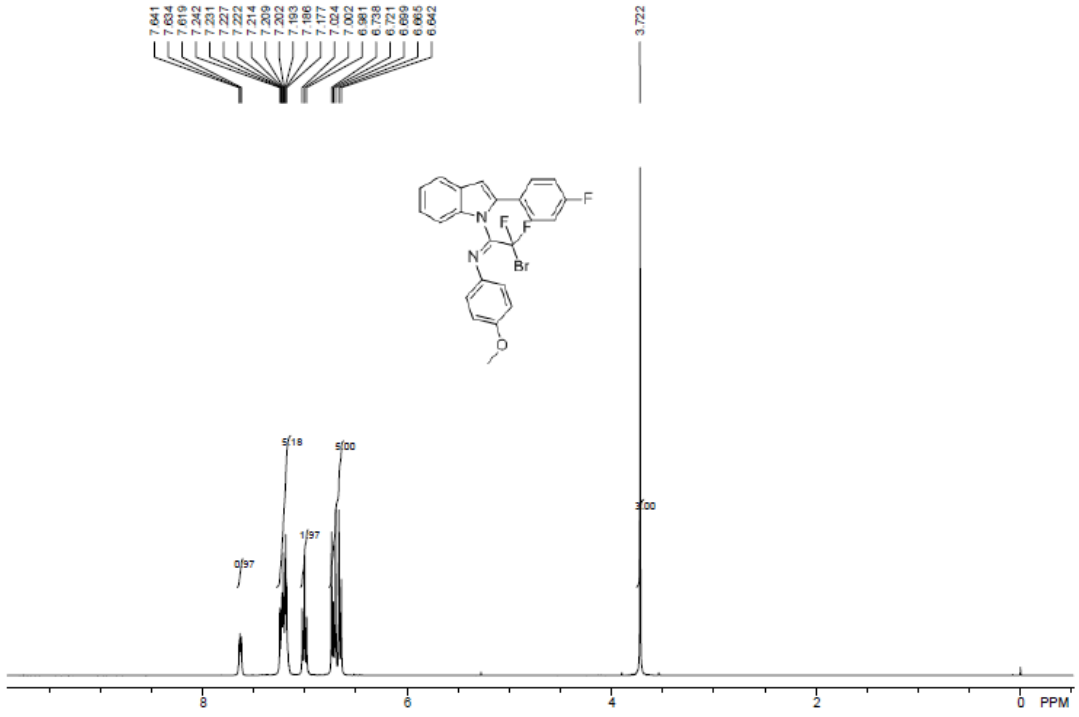
PPM

1d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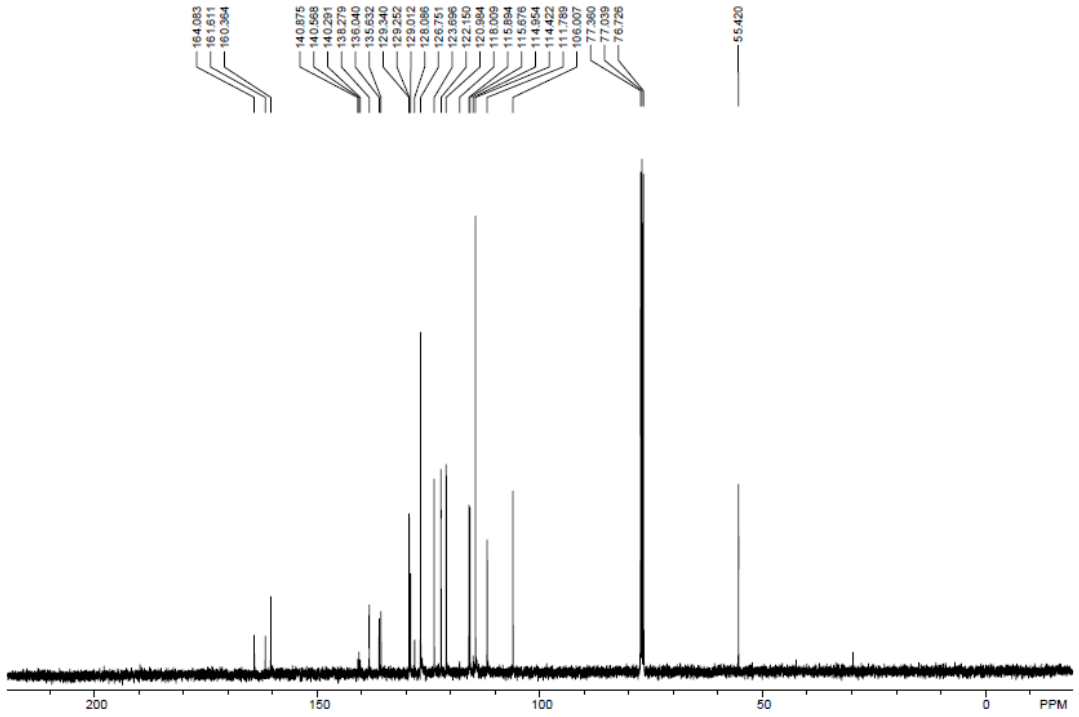
PPM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126.751
123.696
122.150
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118.009
115.884
115.676
114.954
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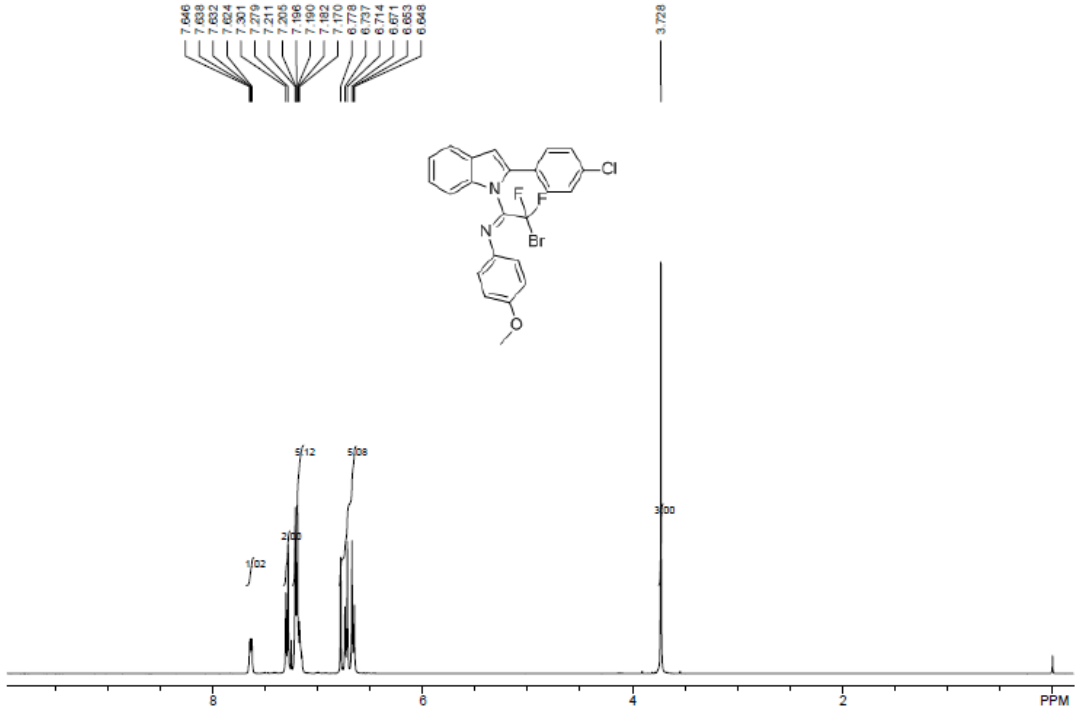
PPM

1e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6.737
6.714
6.671
6.663
6.648
3.728
Cl
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Br
N
O
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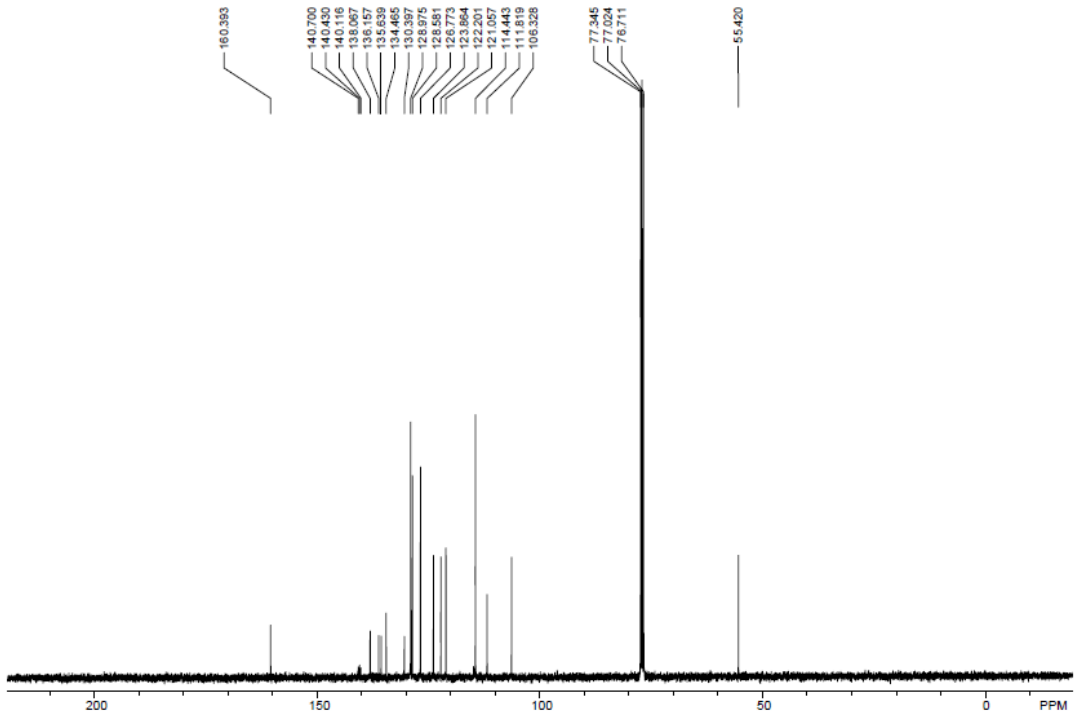
3.00
8
6
4
2
PPM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123.864
122.201
121.057
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106.328
77.345
77.024
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200
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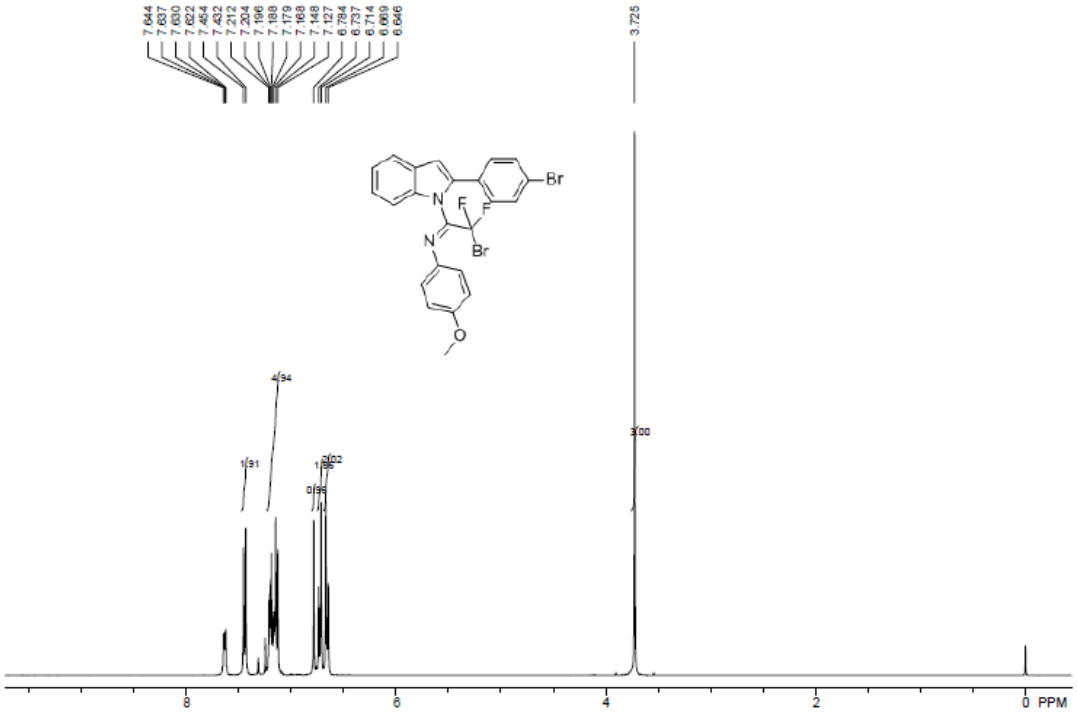
PPM

1f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6.737
6.714
6.669
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3.725
Br
N
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Br
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O
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3.00
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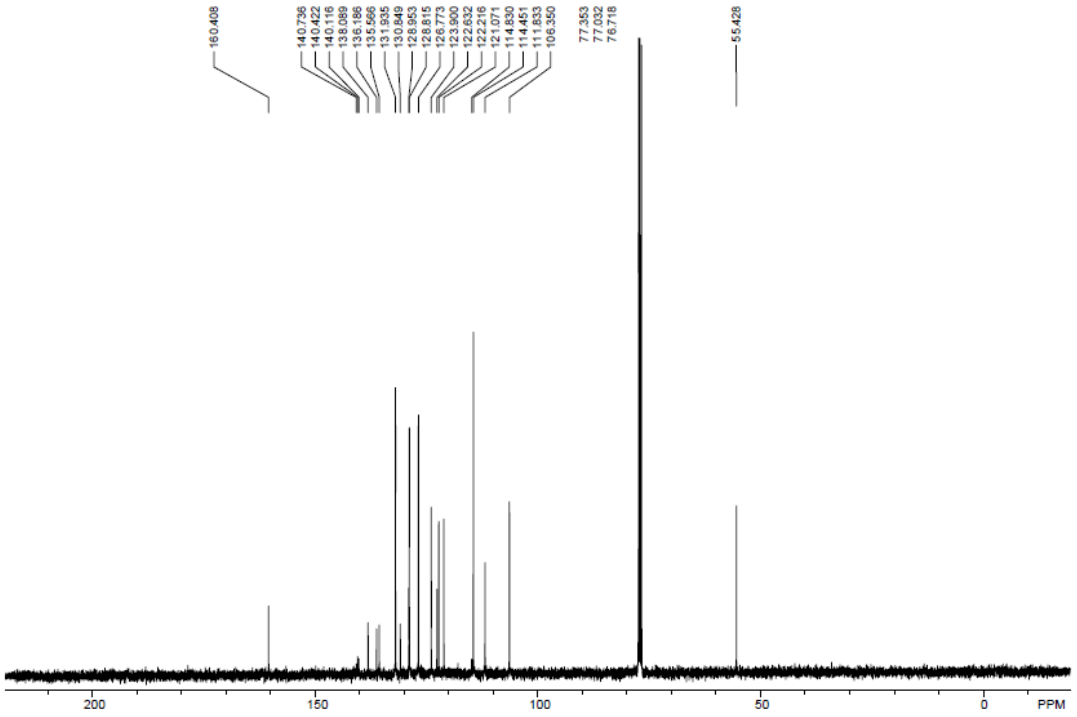
4
2
0 PPM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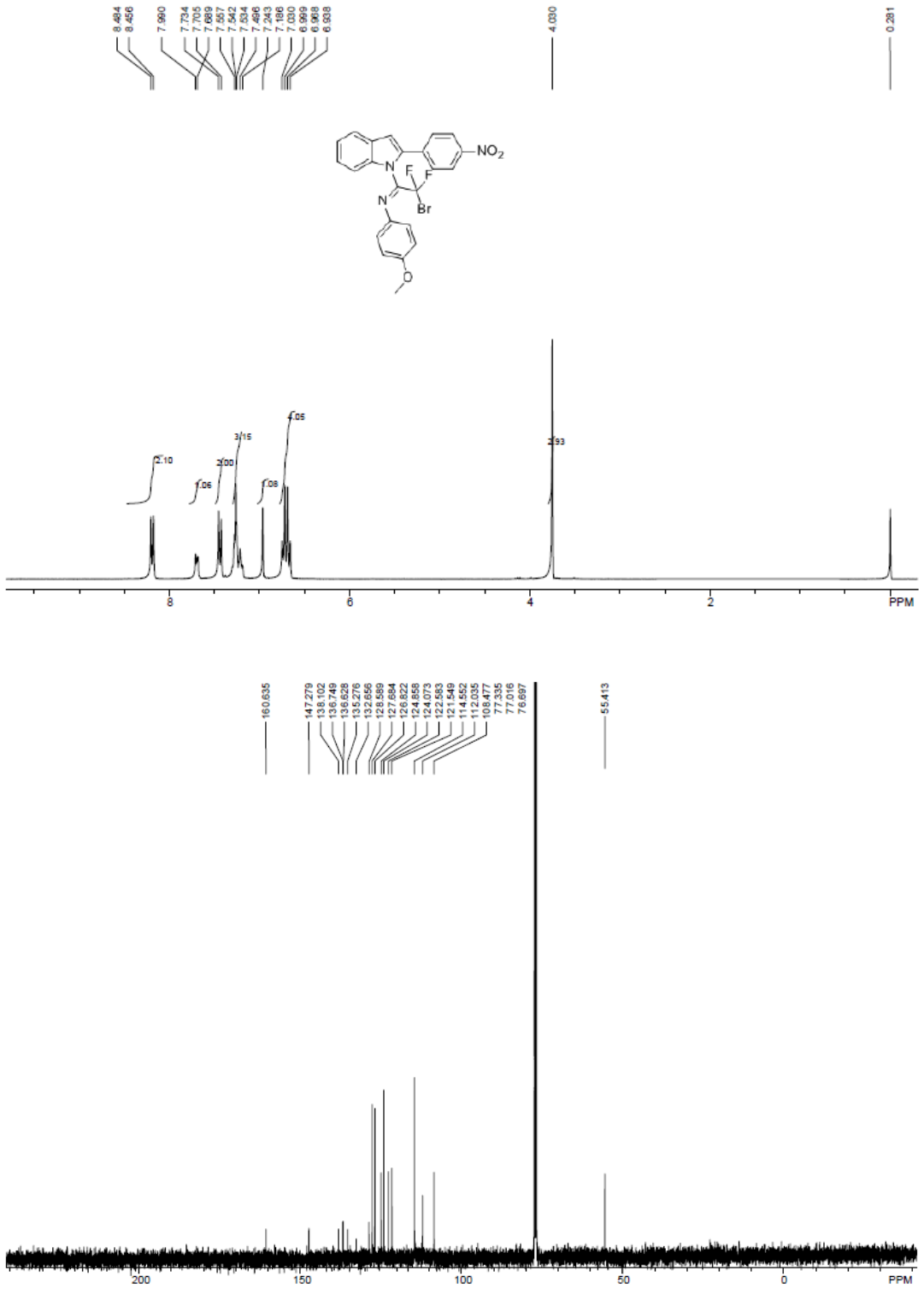
PPM

1g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7.030
6.999
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6.938
4.030
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F
F
N
Br
O
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1.06
2.00
3.15
1.05
1.08
2.93
8
6
4
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150
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50
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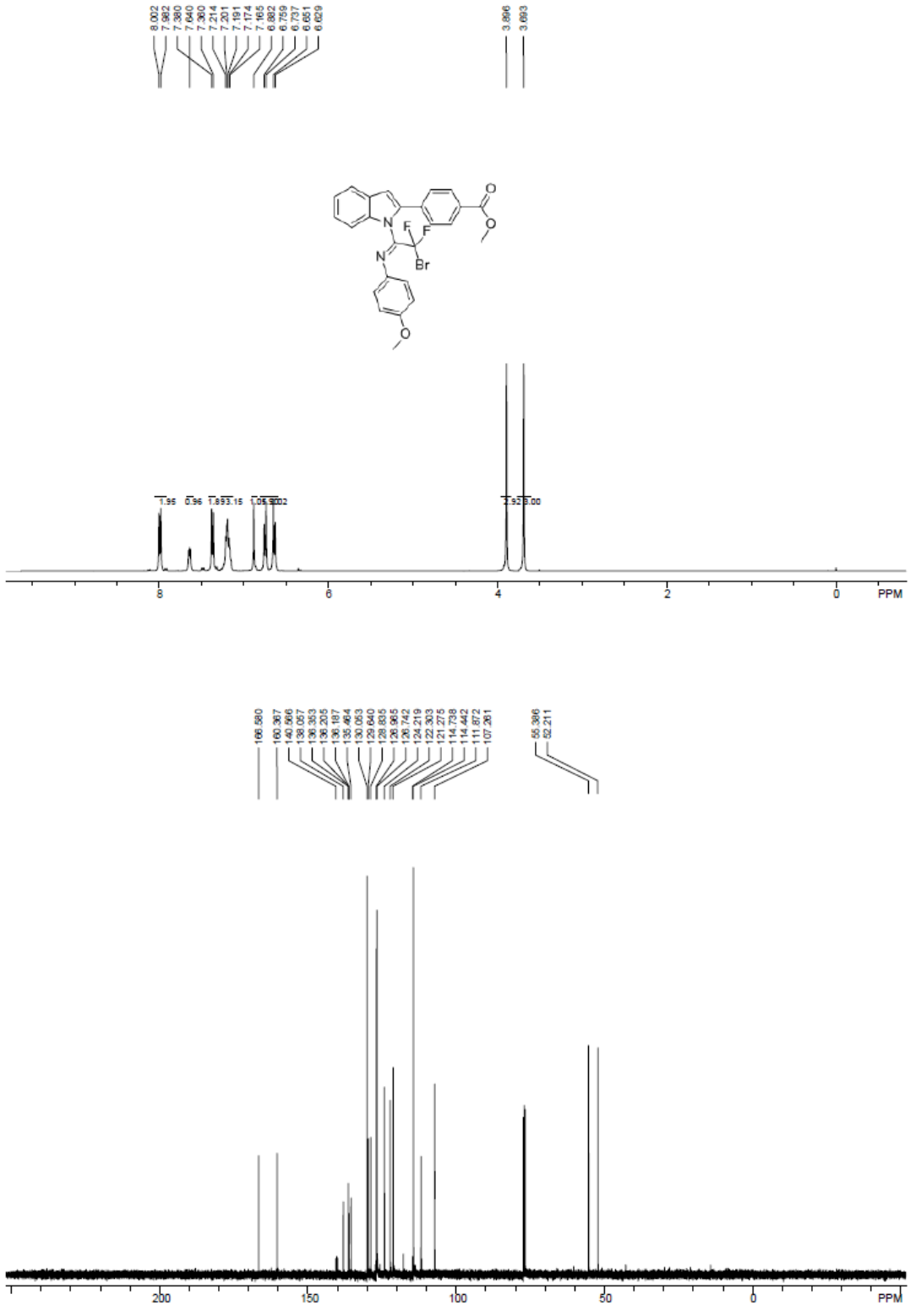
PPM

1h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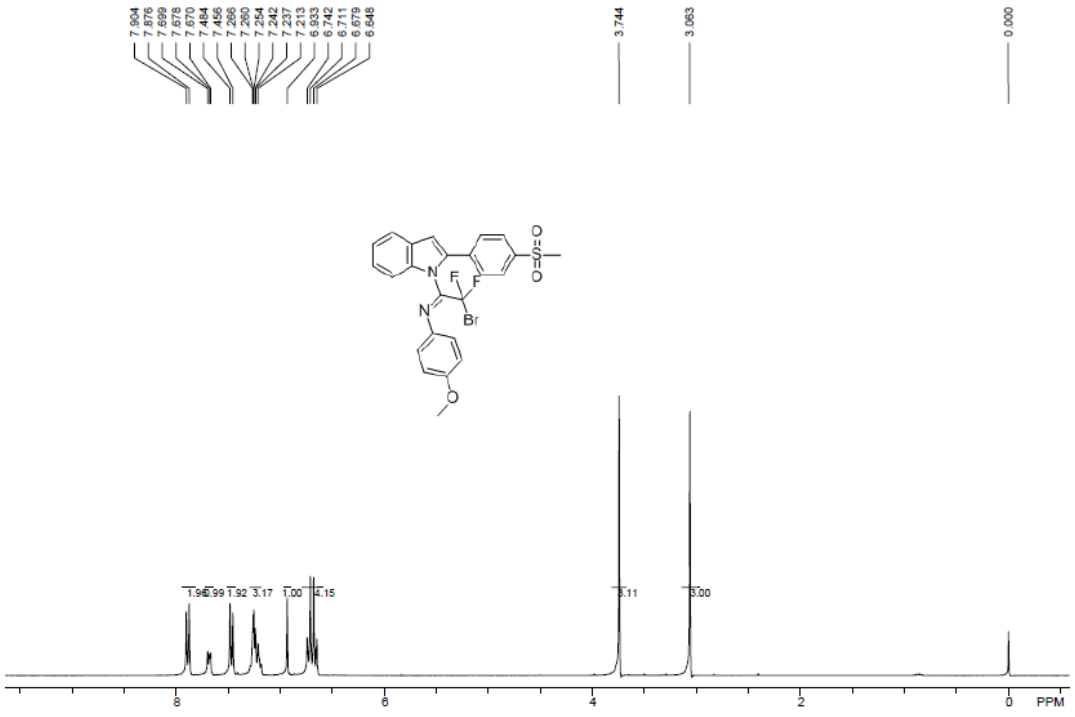
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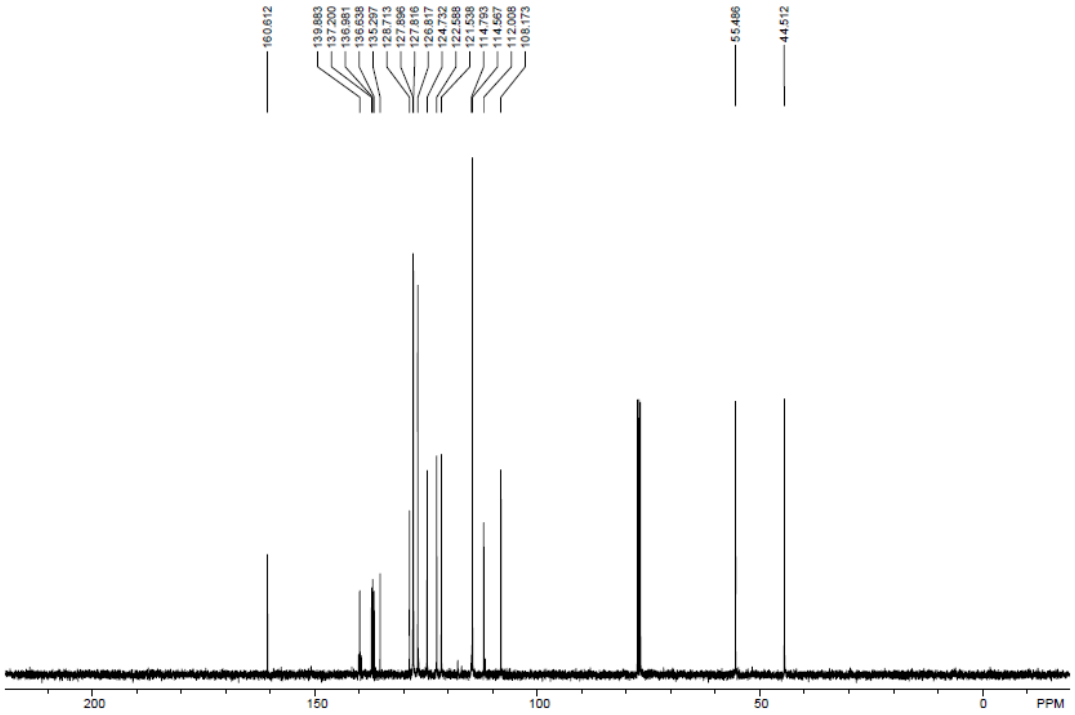
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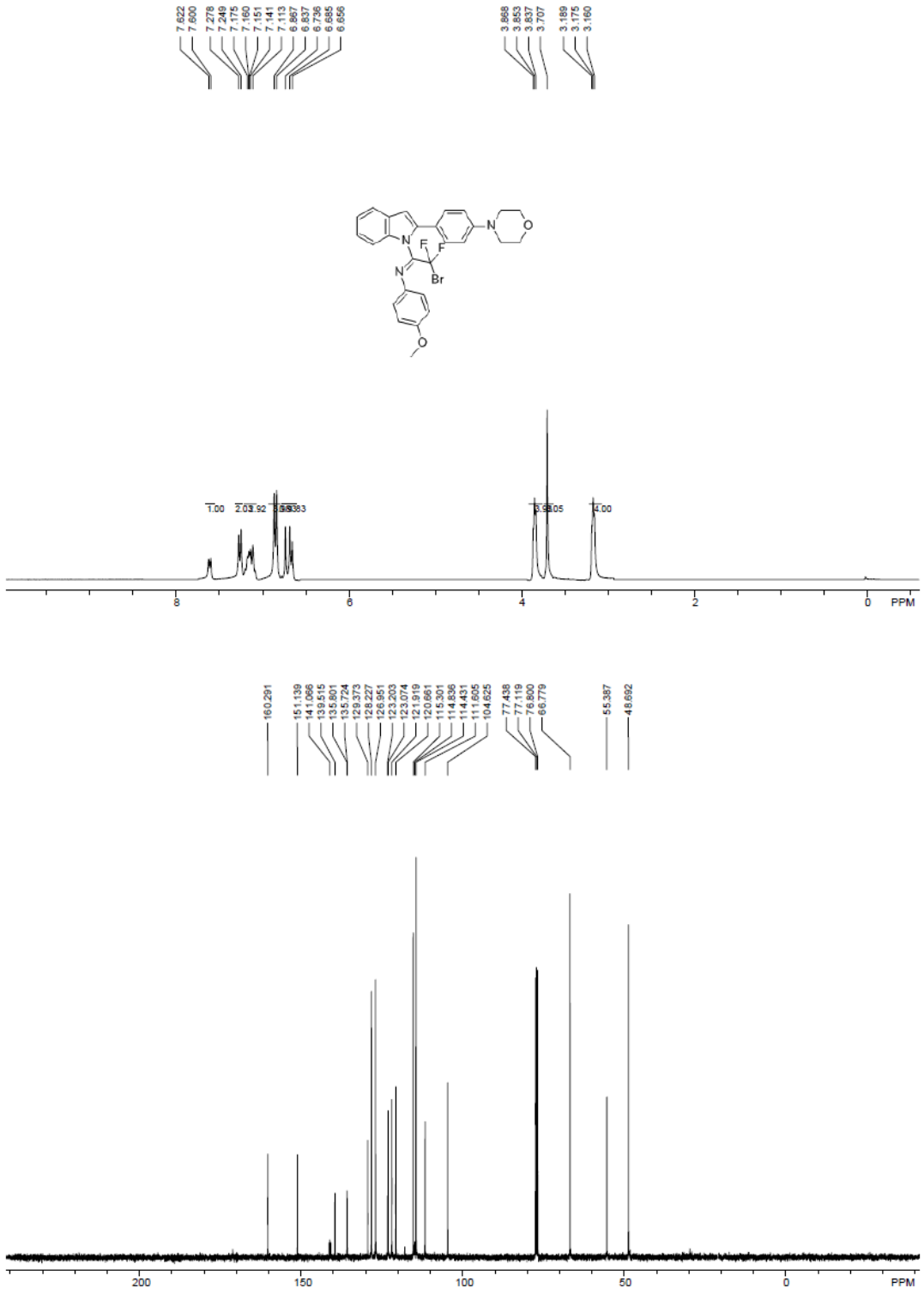
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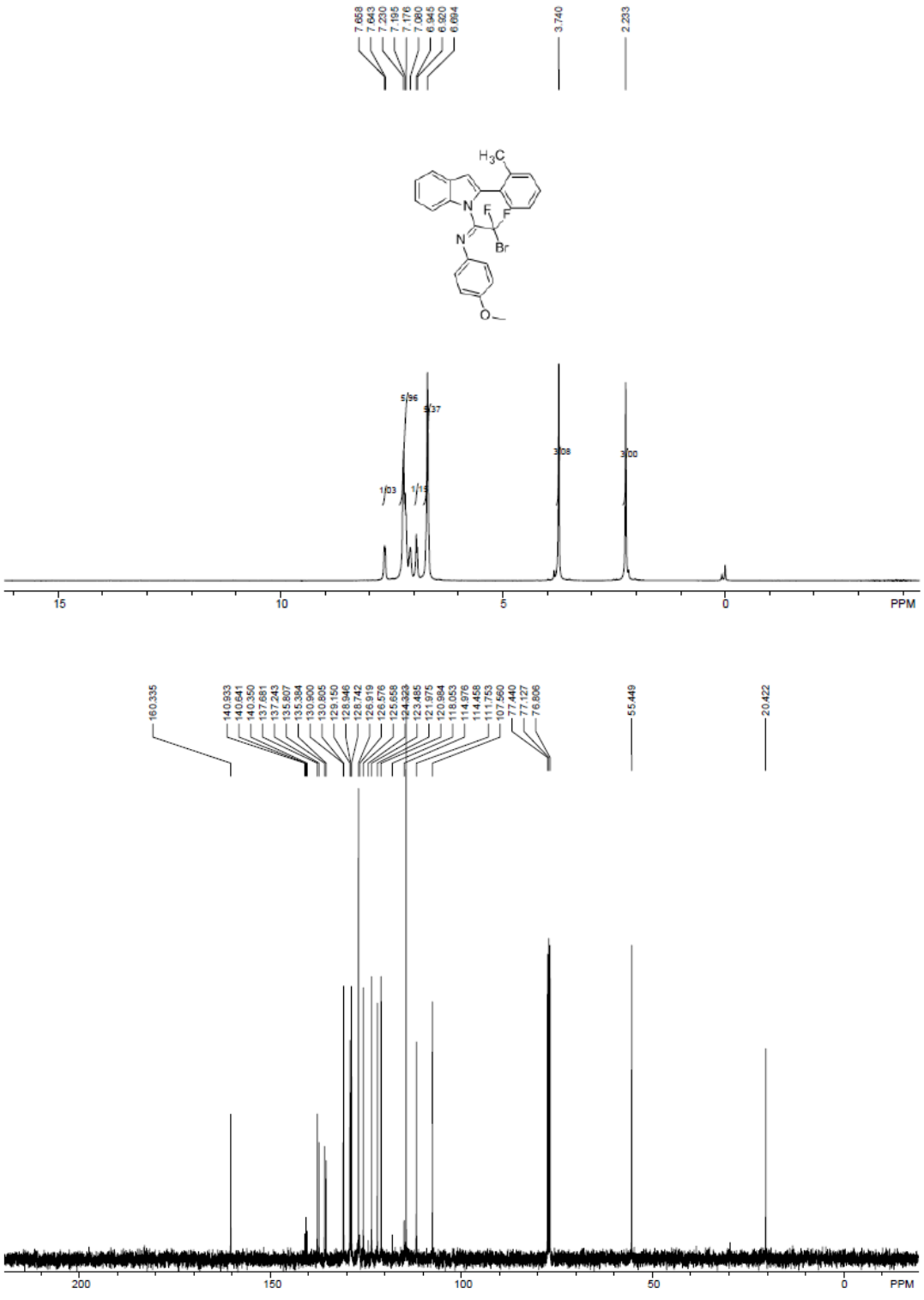
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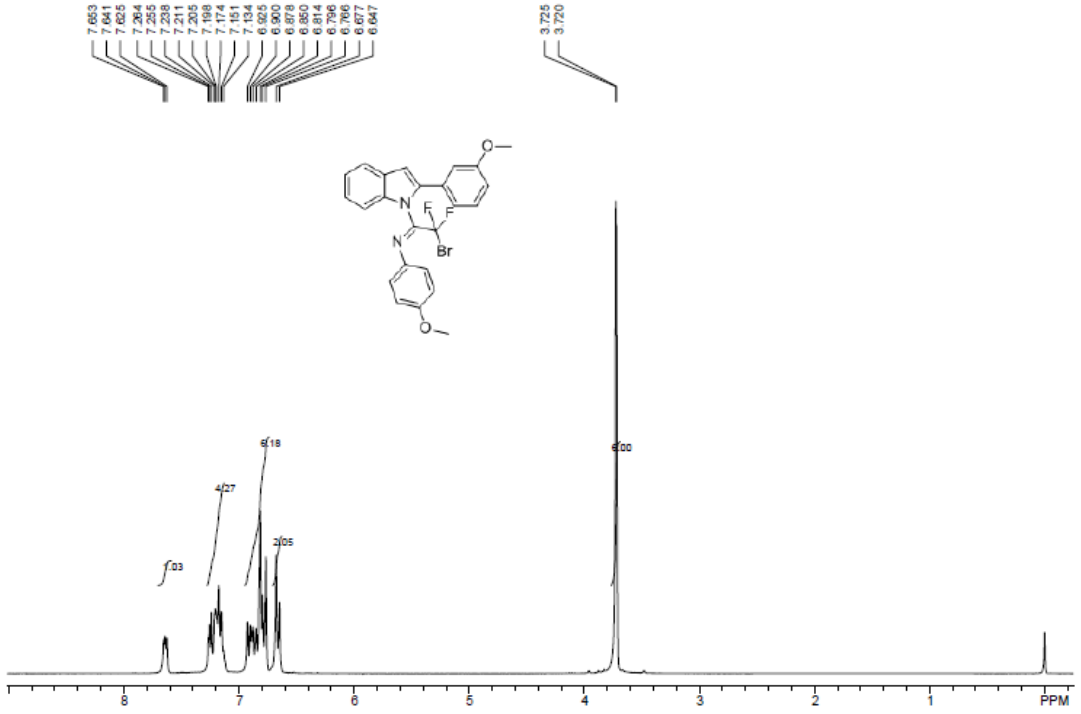
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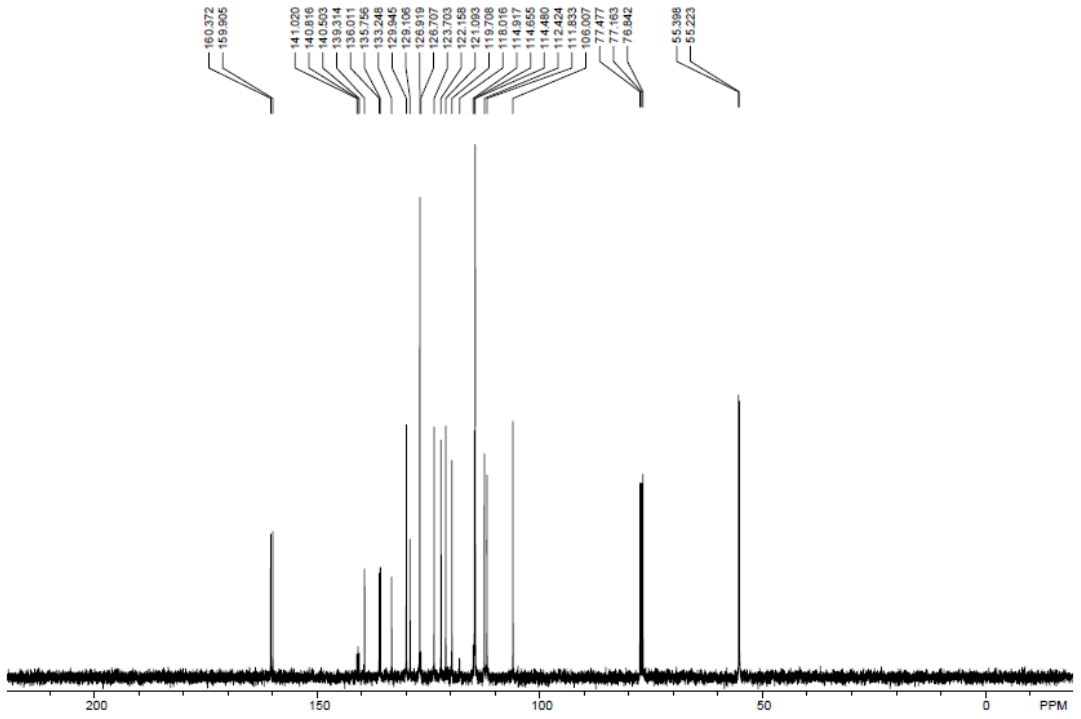
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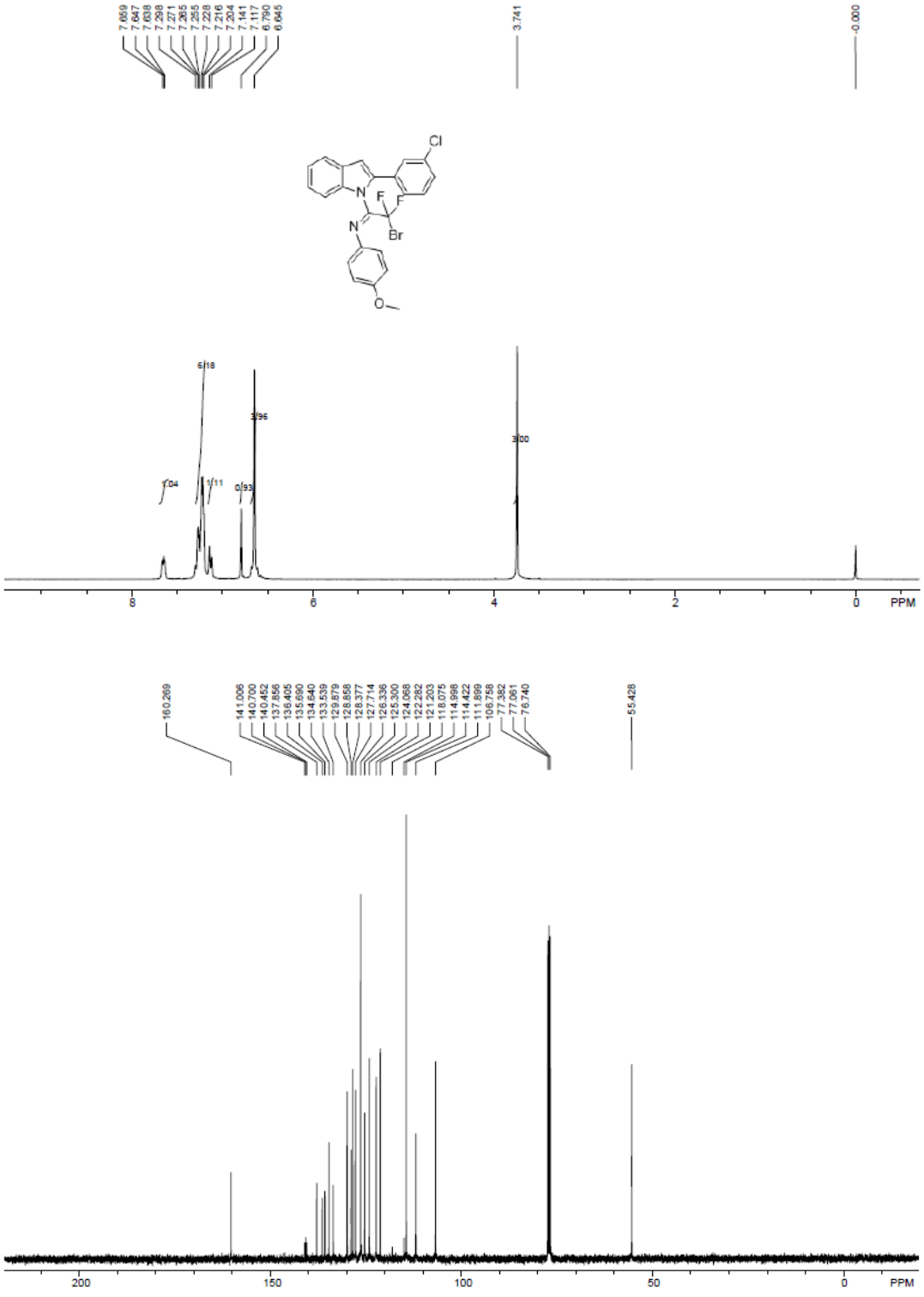
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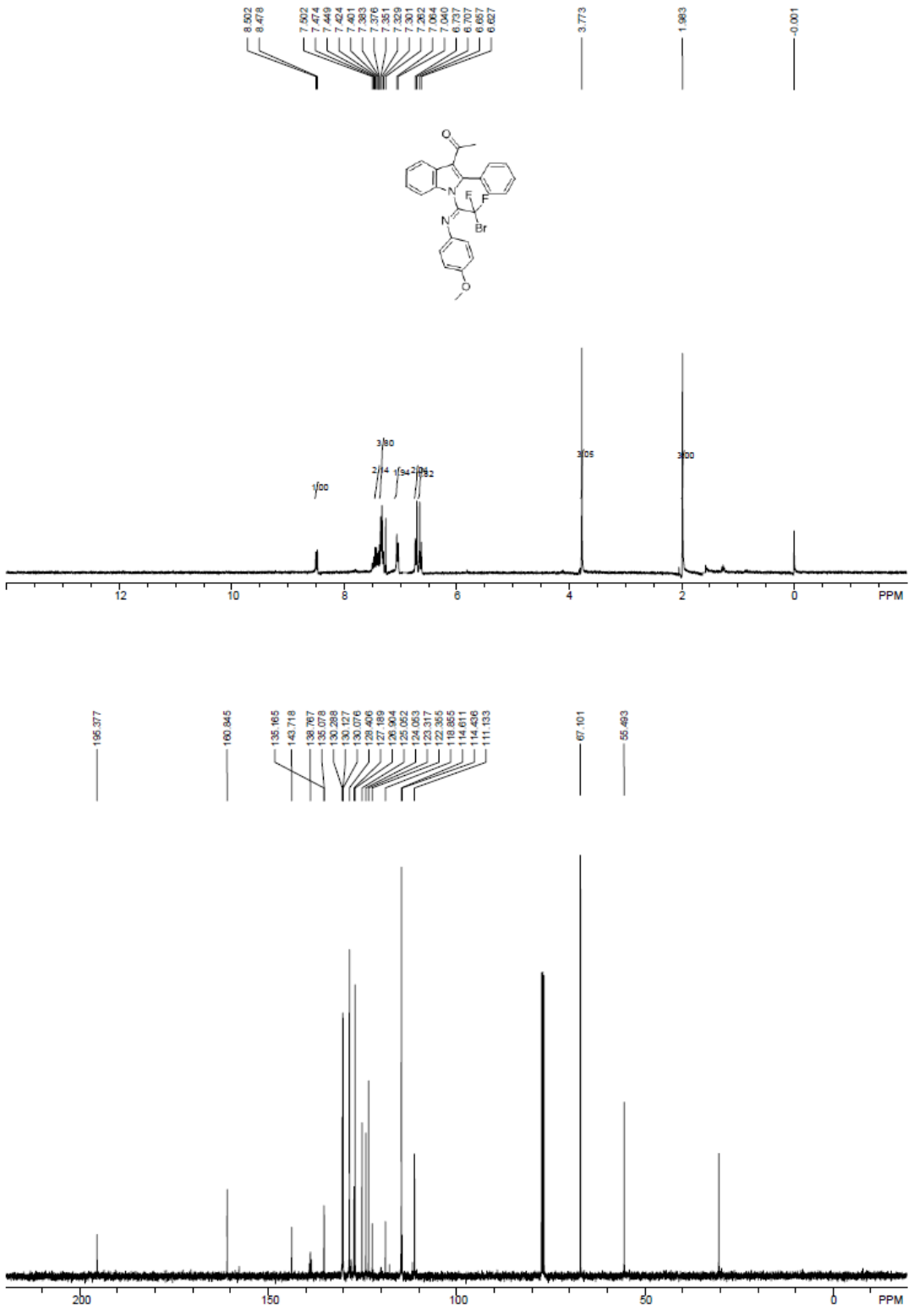
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6.707
6.657
6.627
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2.04
2.02
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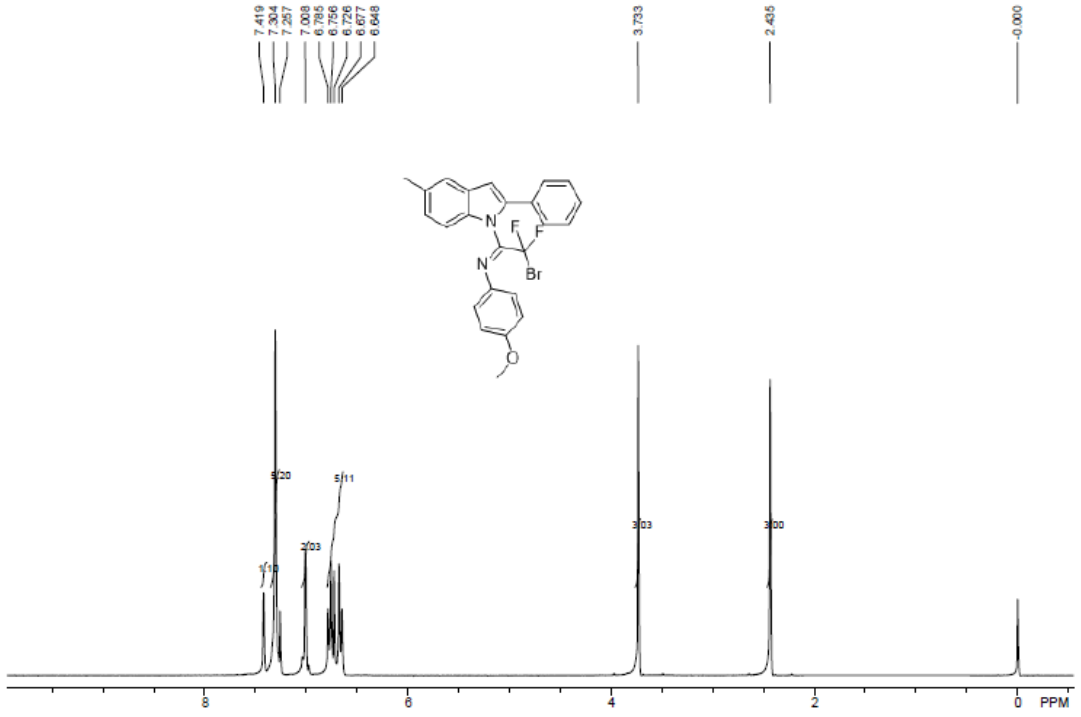
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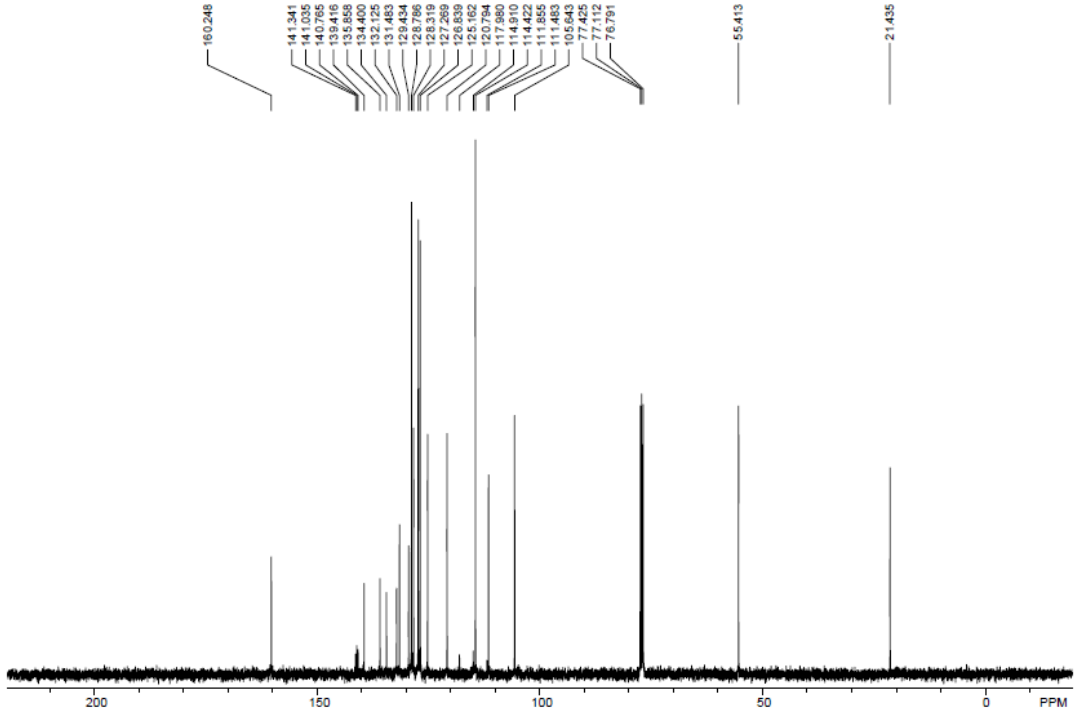
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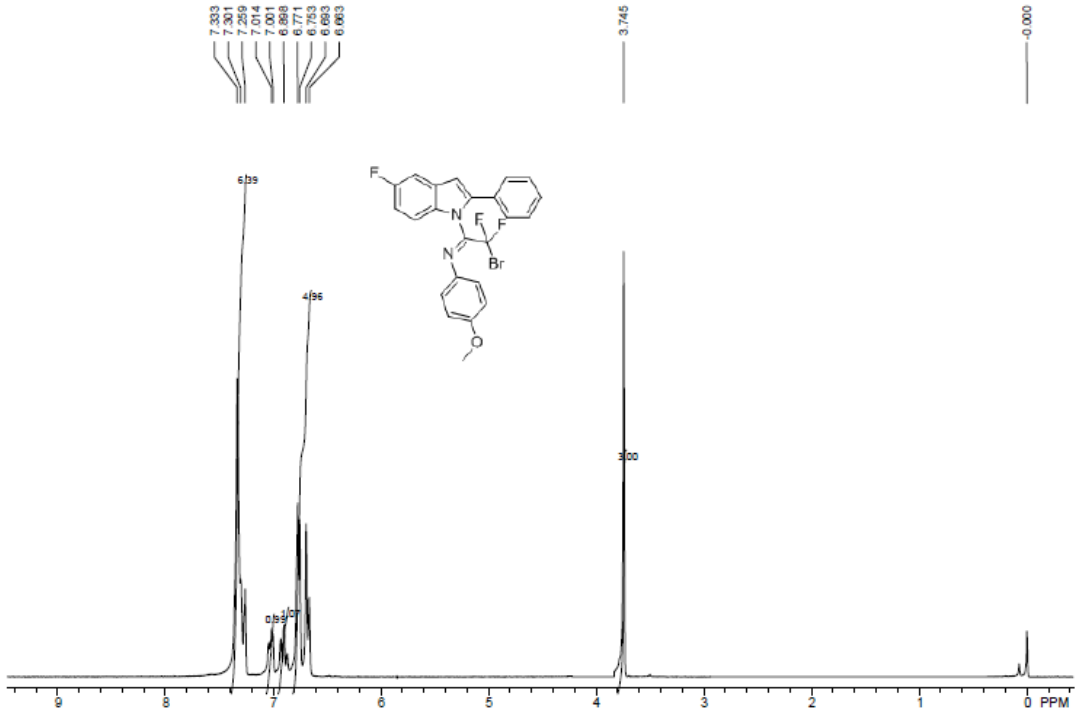
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3.00
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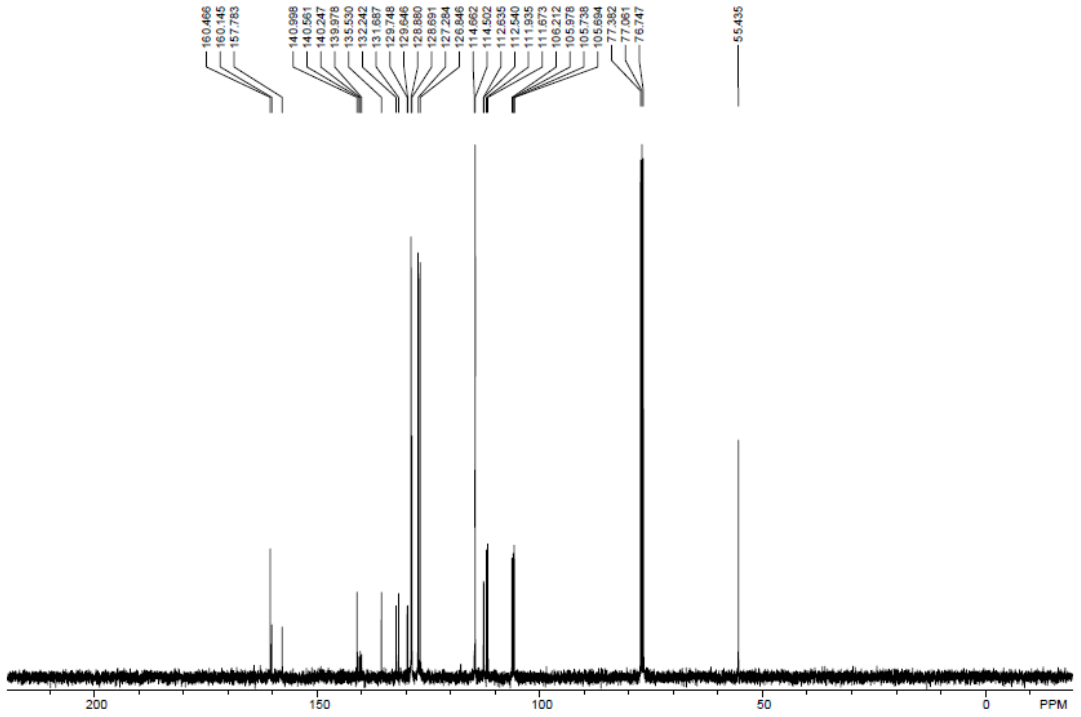
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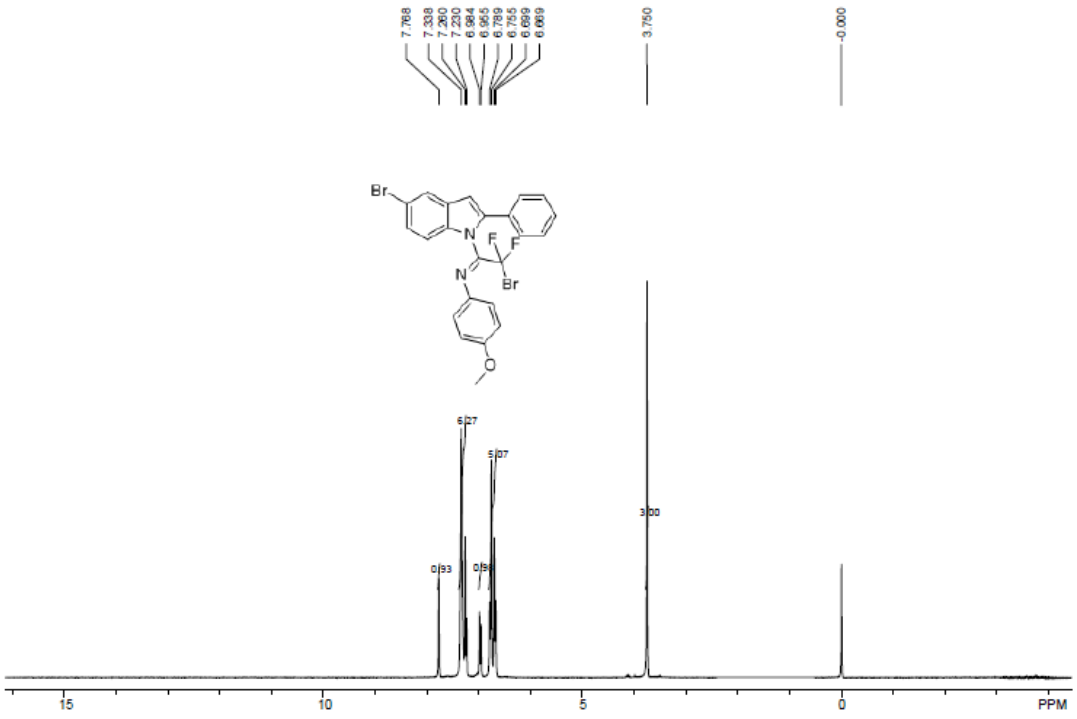
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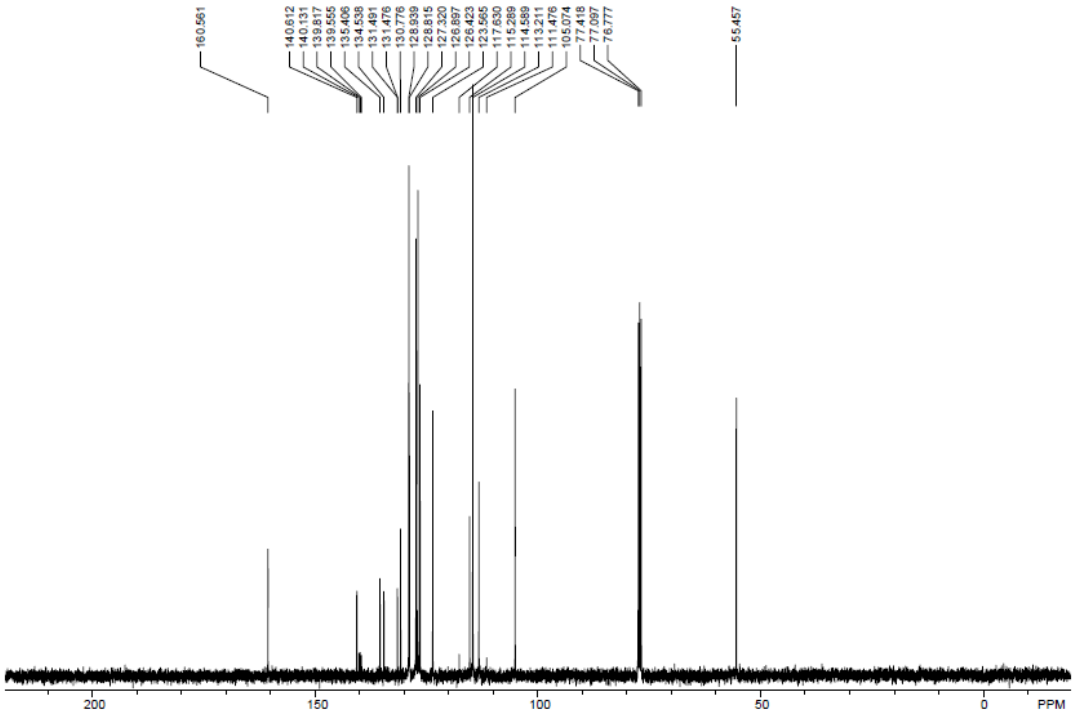
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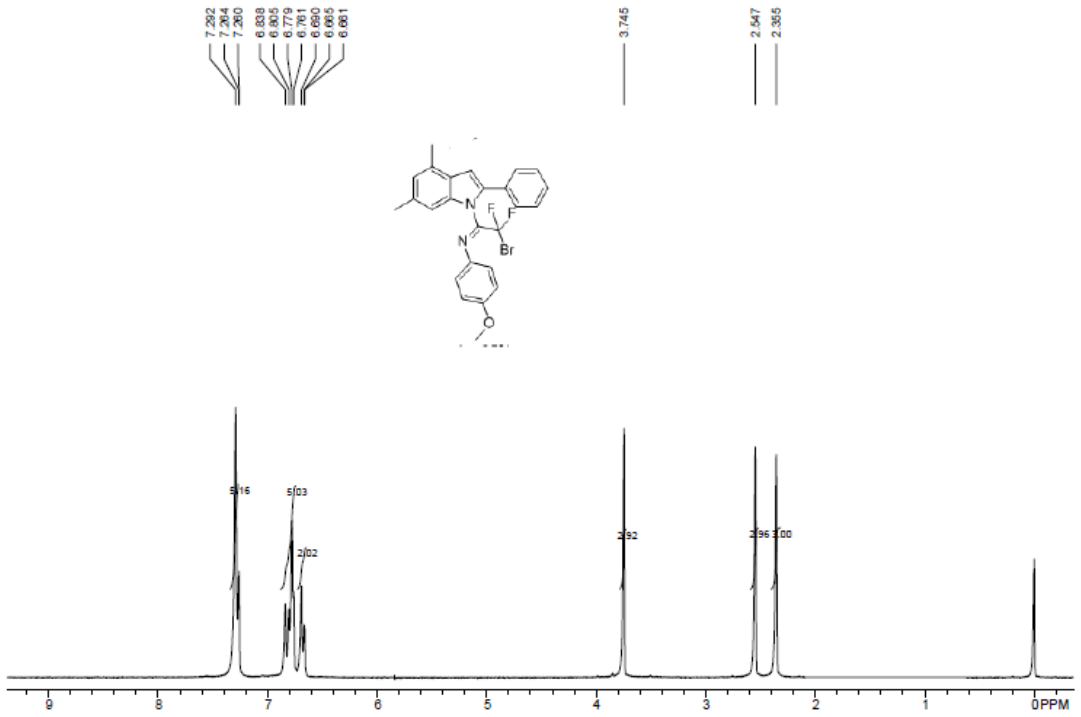
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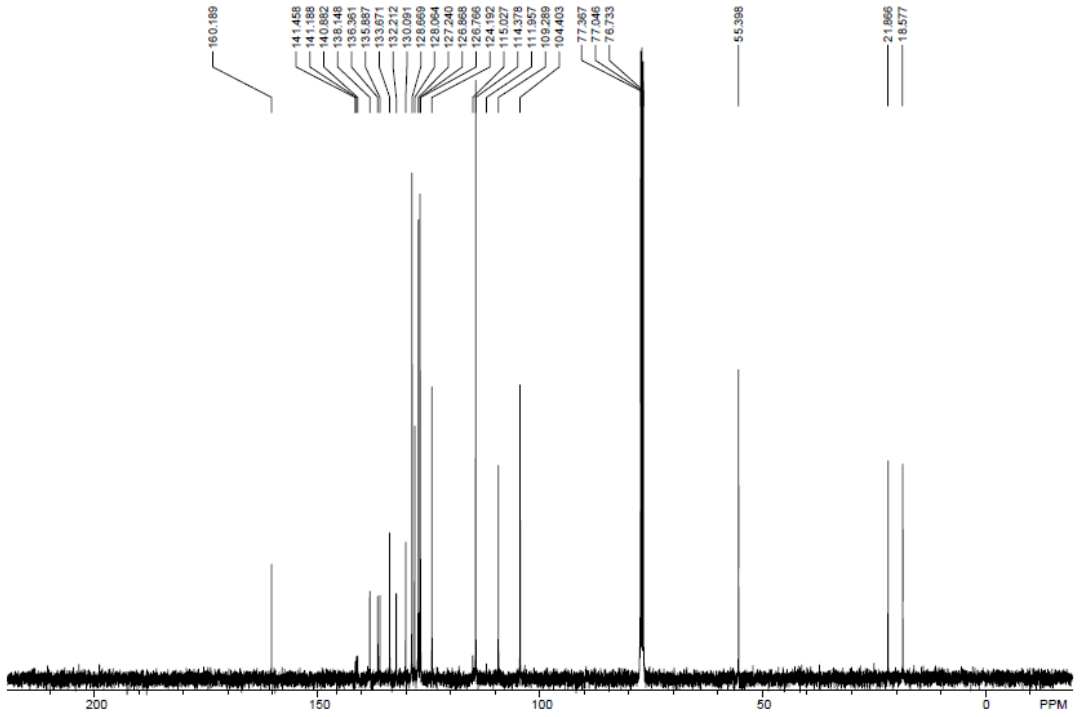
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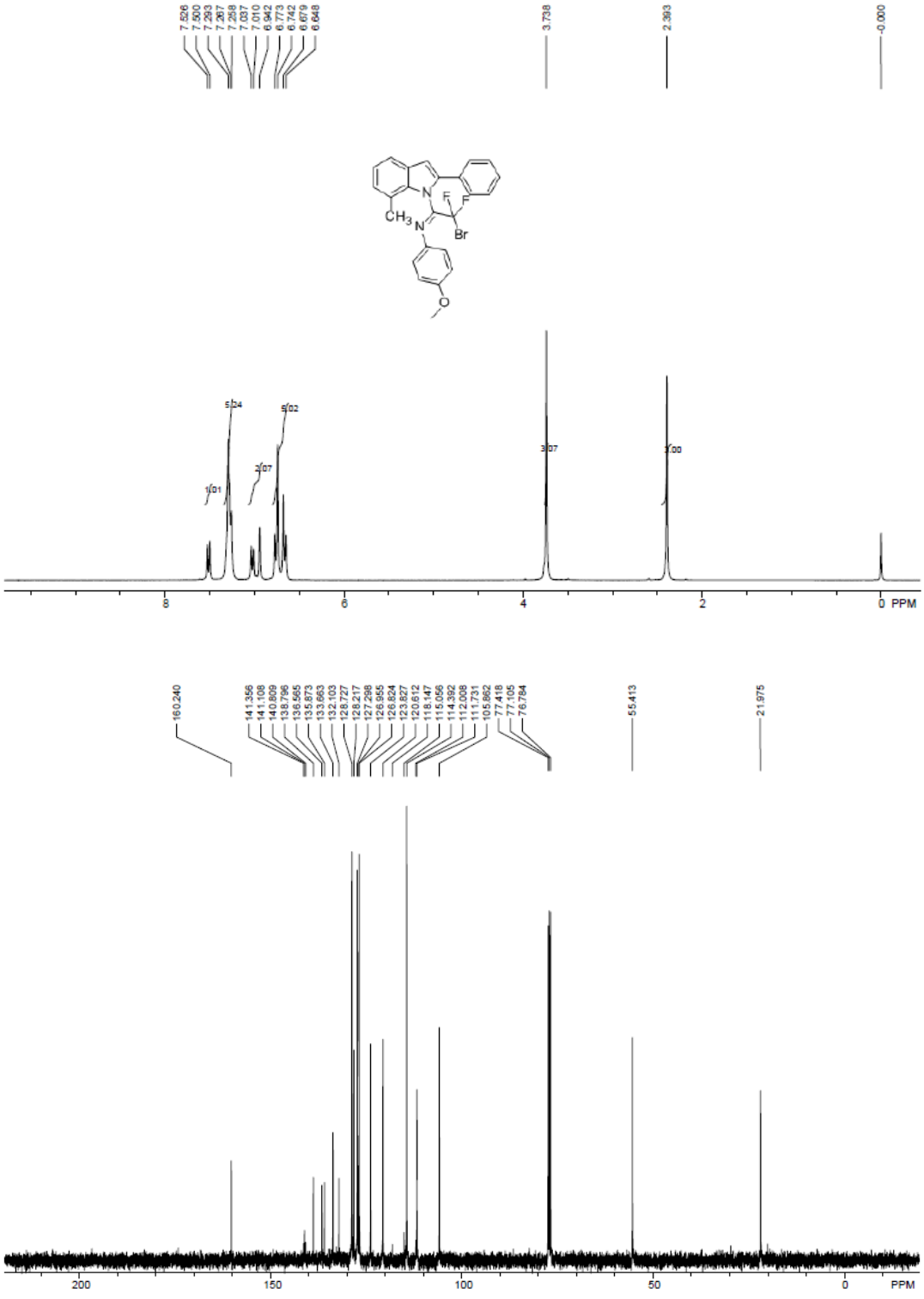
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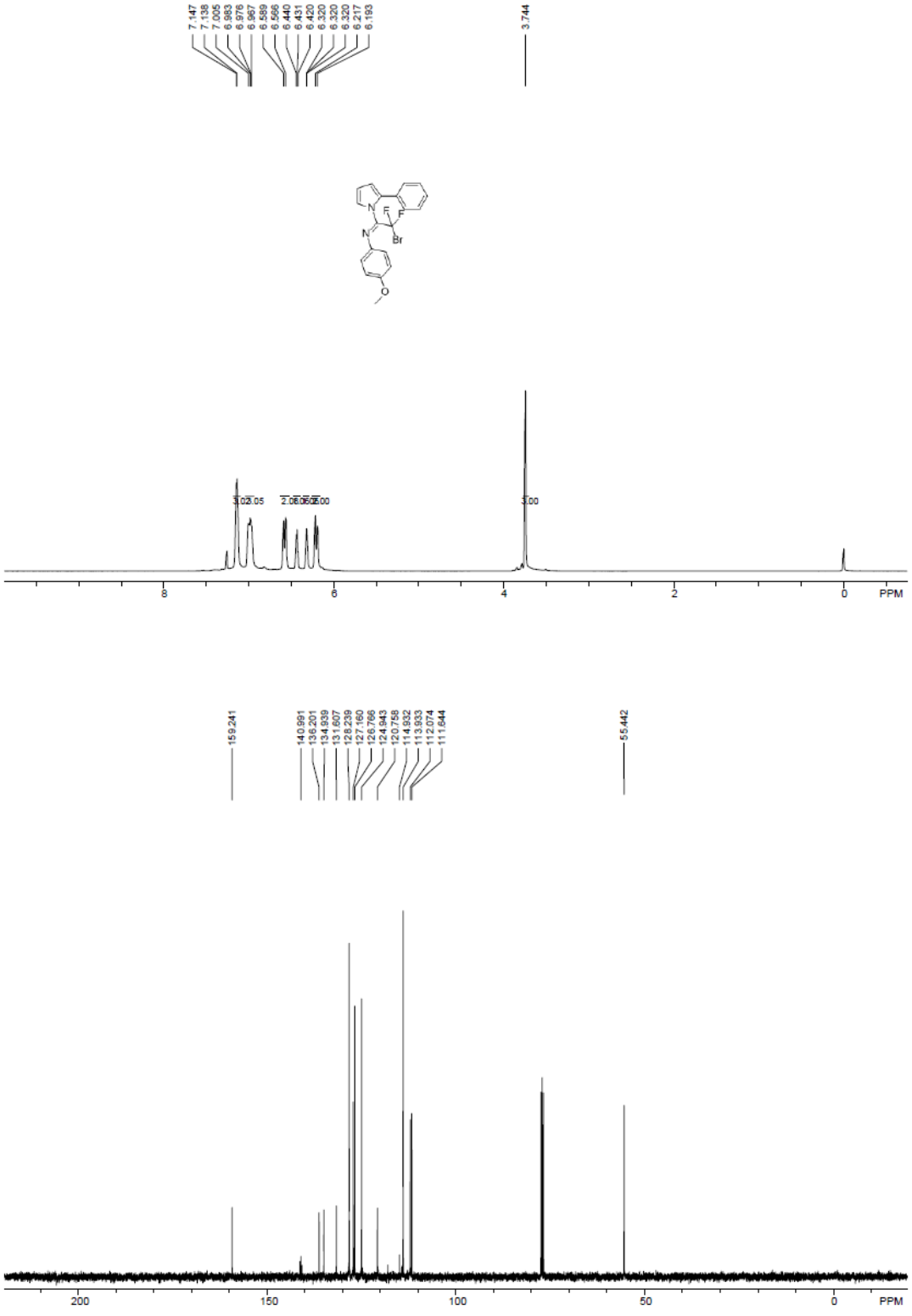
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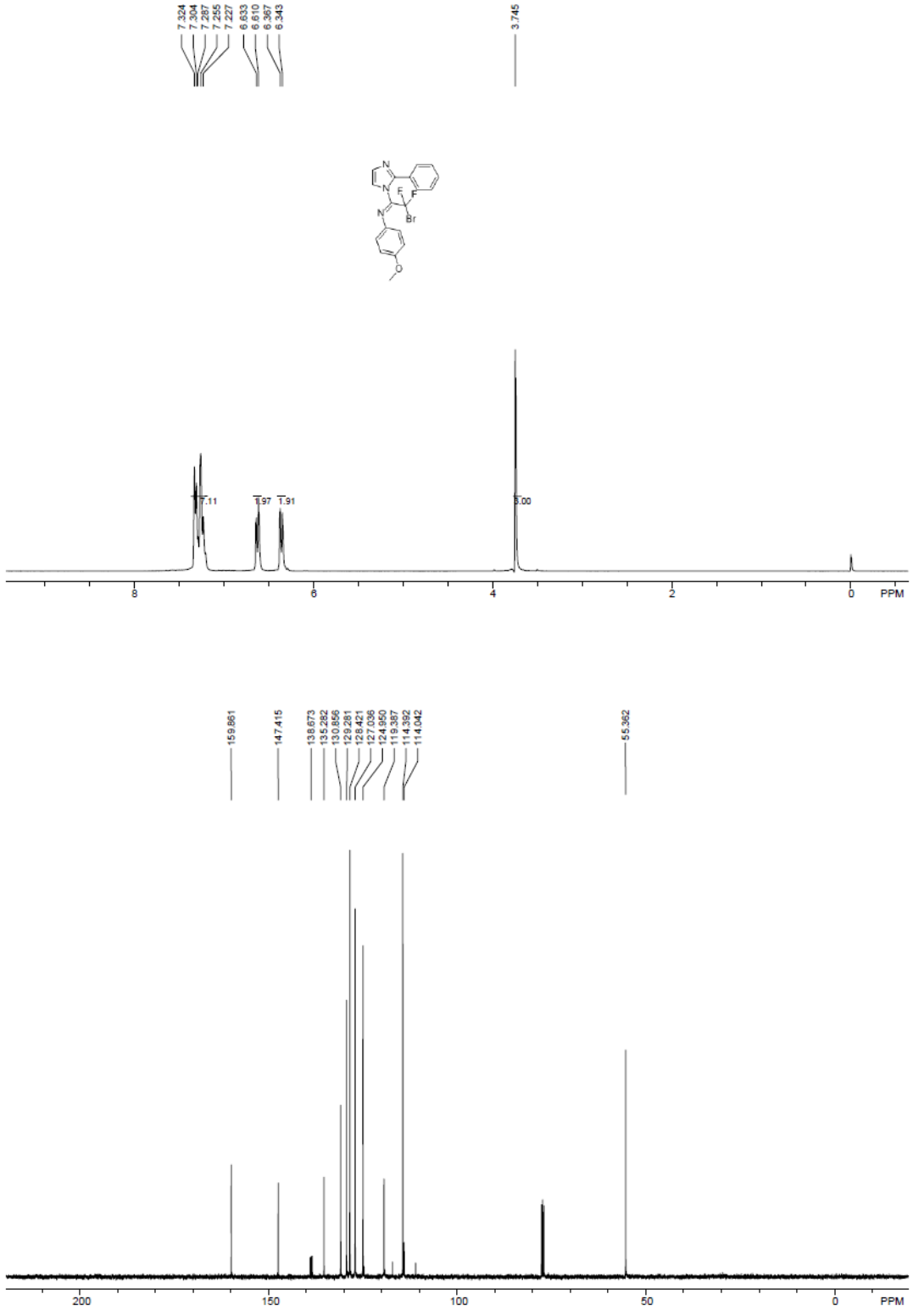
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Br
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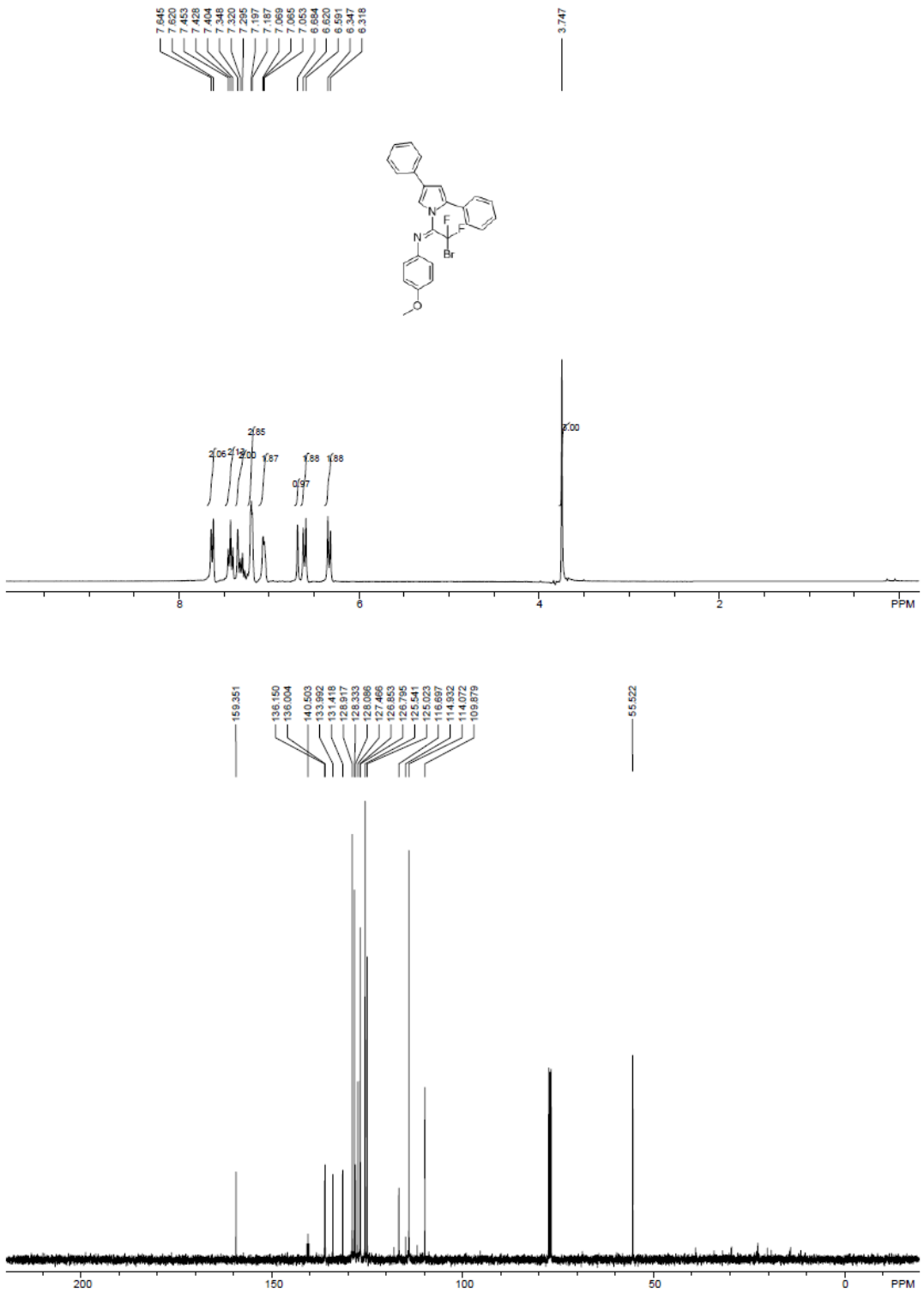
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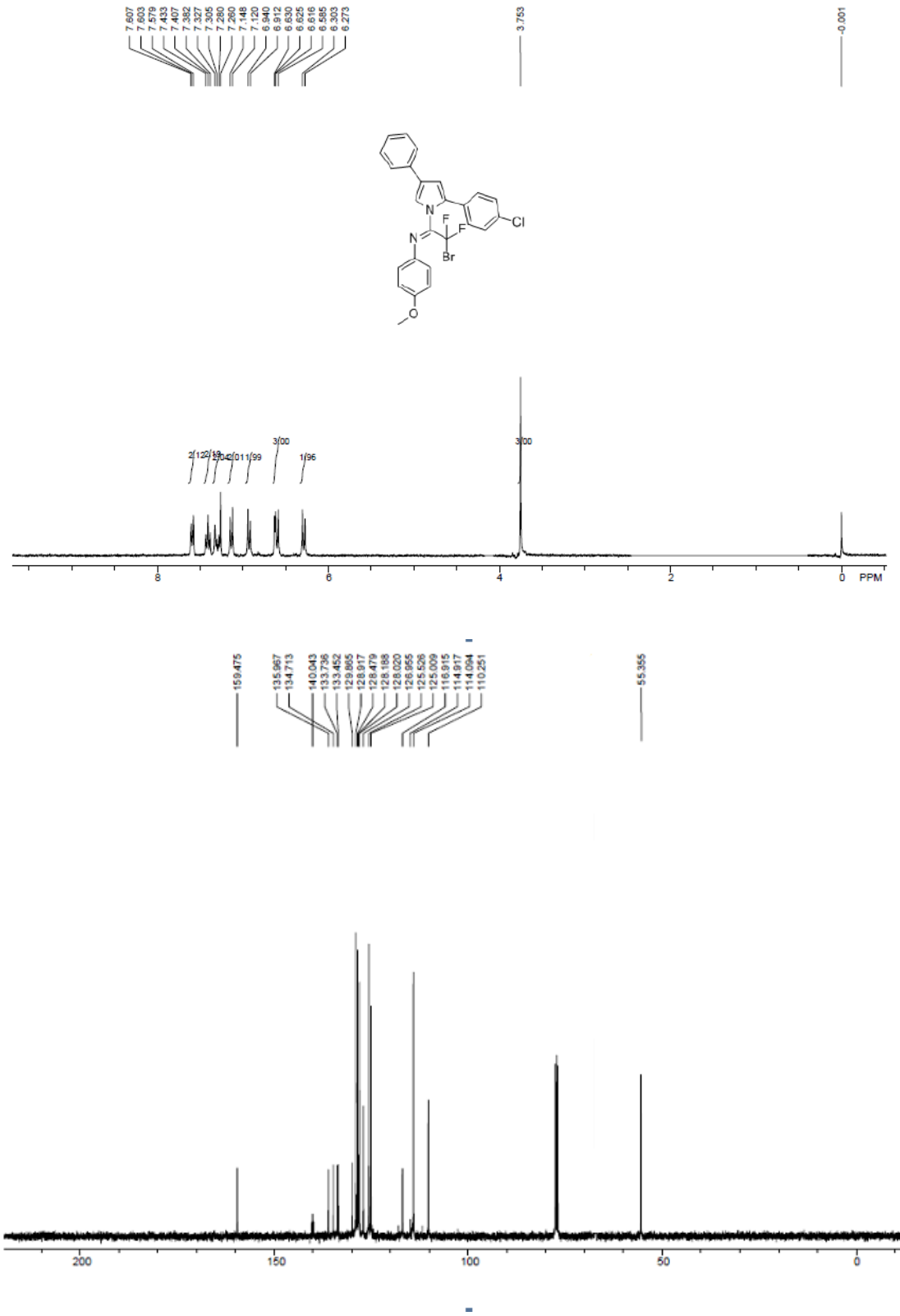
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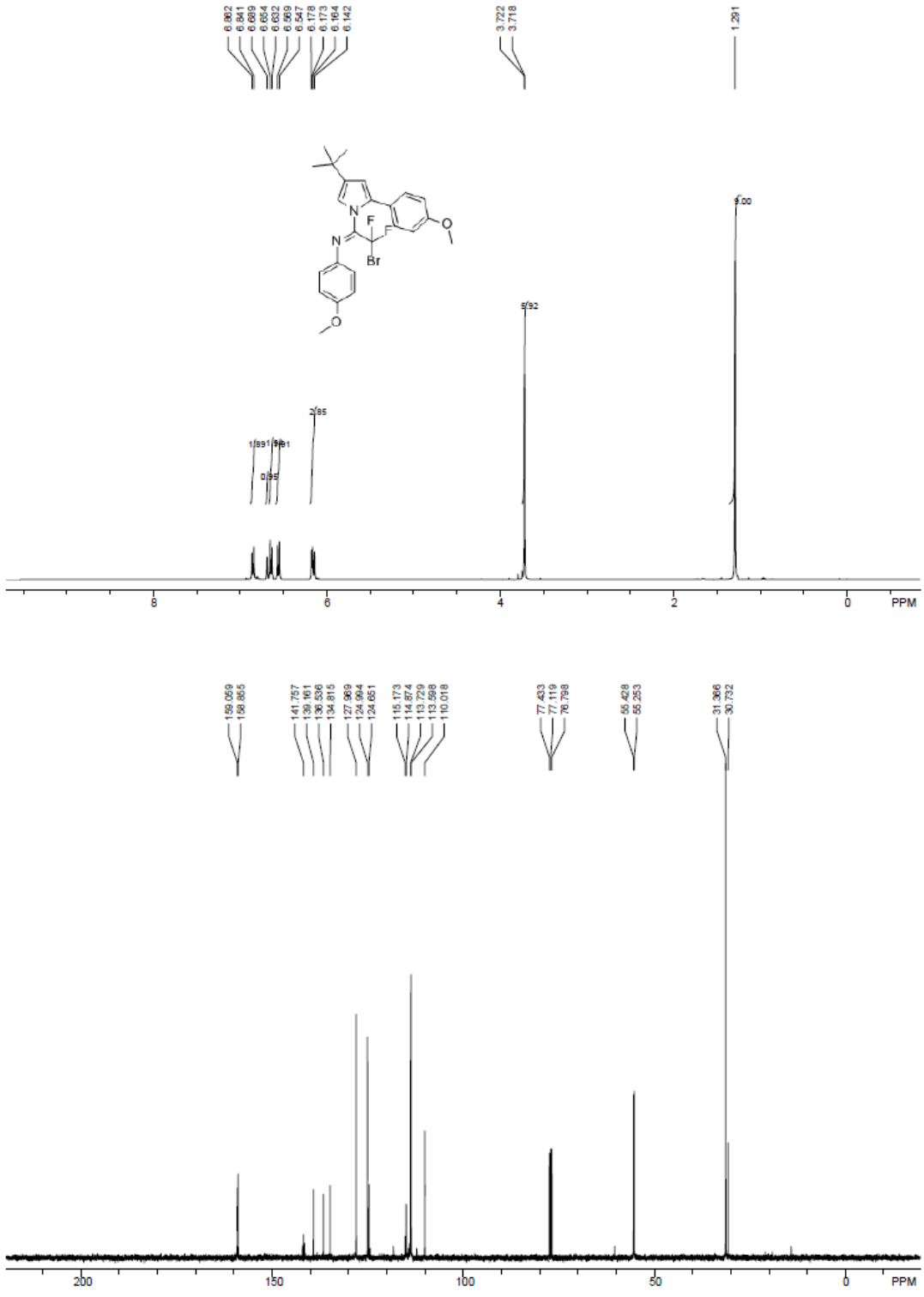
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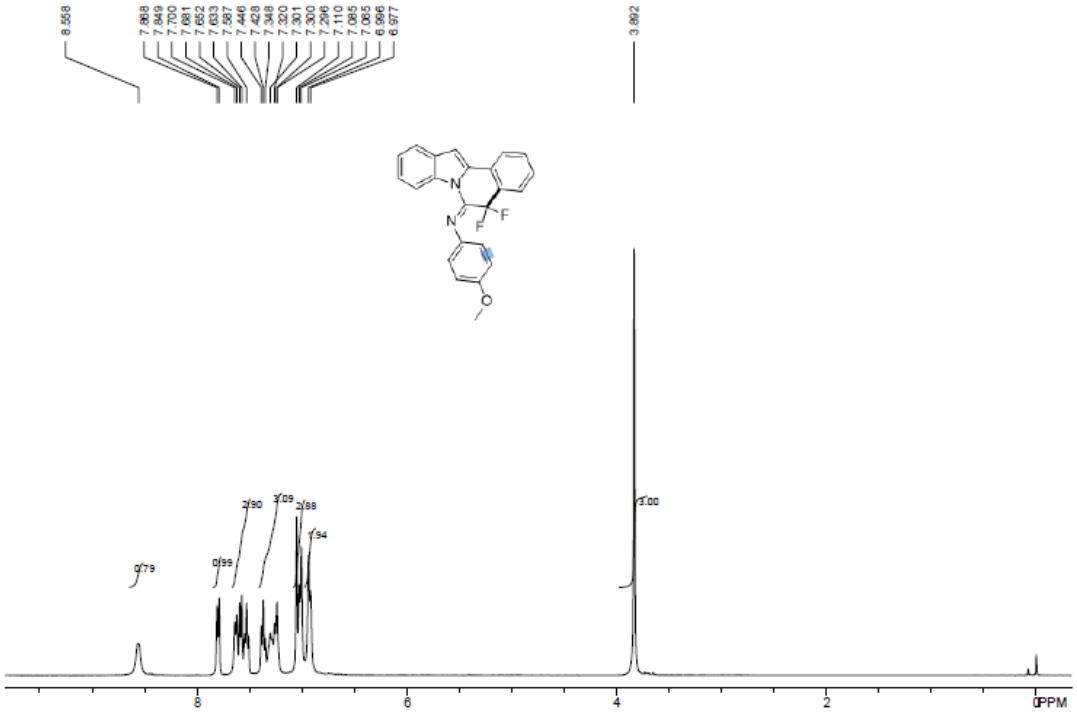
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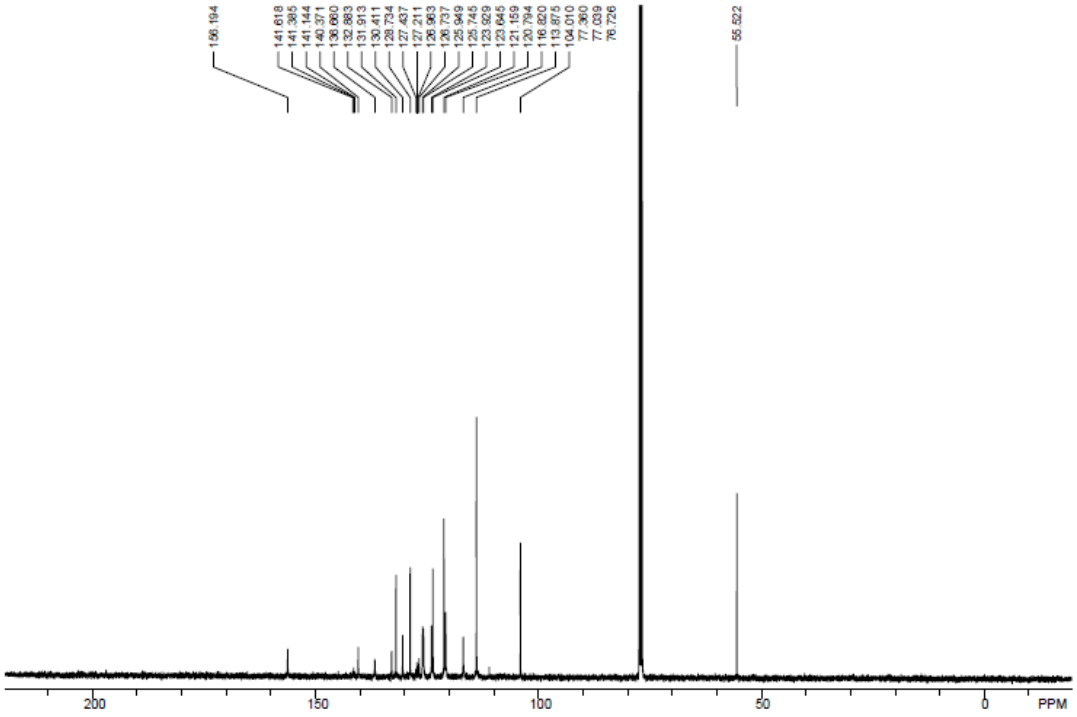
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141.144
140.371
136.660
132.883
131.913
130.411
128.734
127.437
127.211
126.963
126.737
125.949
125.745
123.929
123.645
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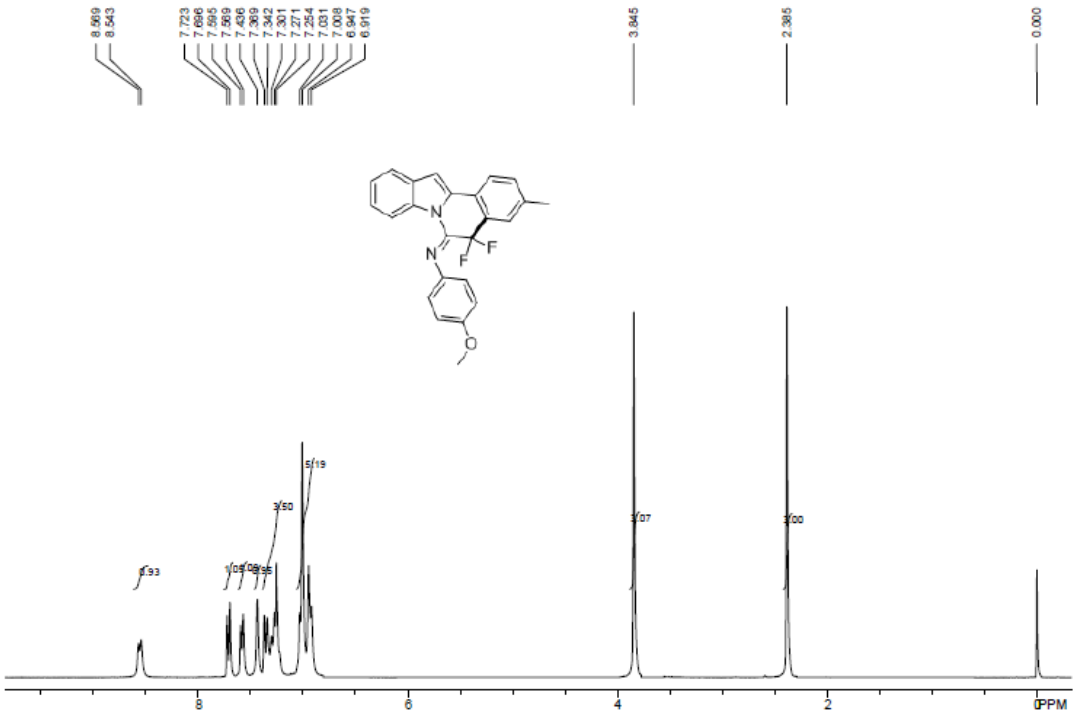
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7.342
7.301
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7.008
6.947
6.919
3.845
2.385
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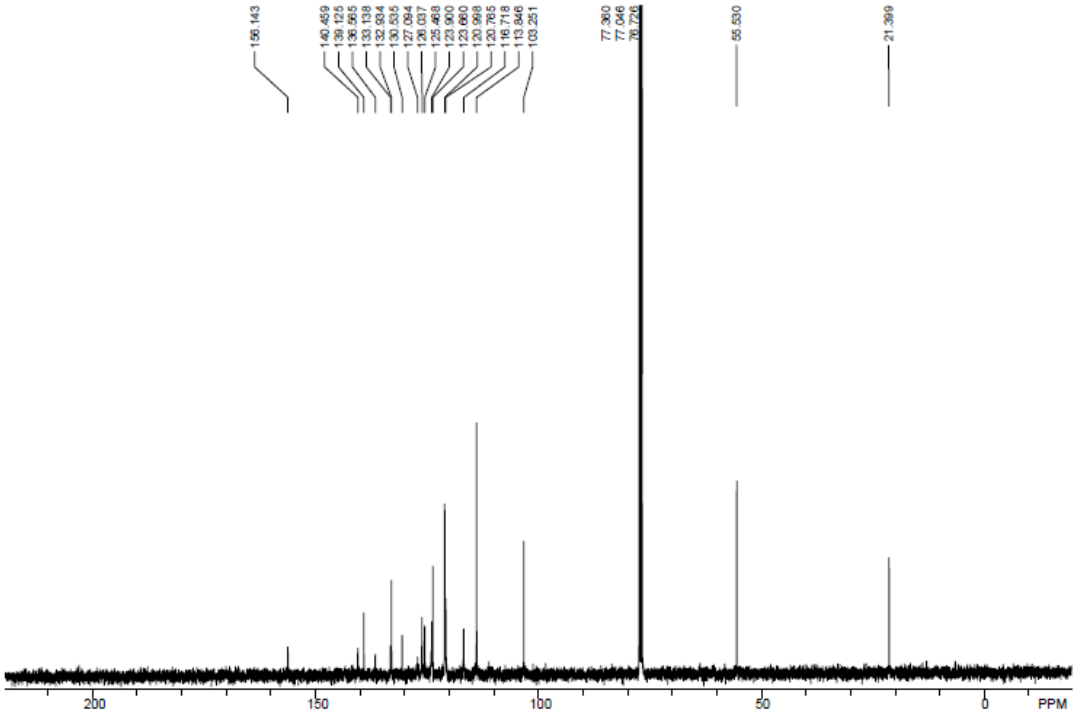
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127.094
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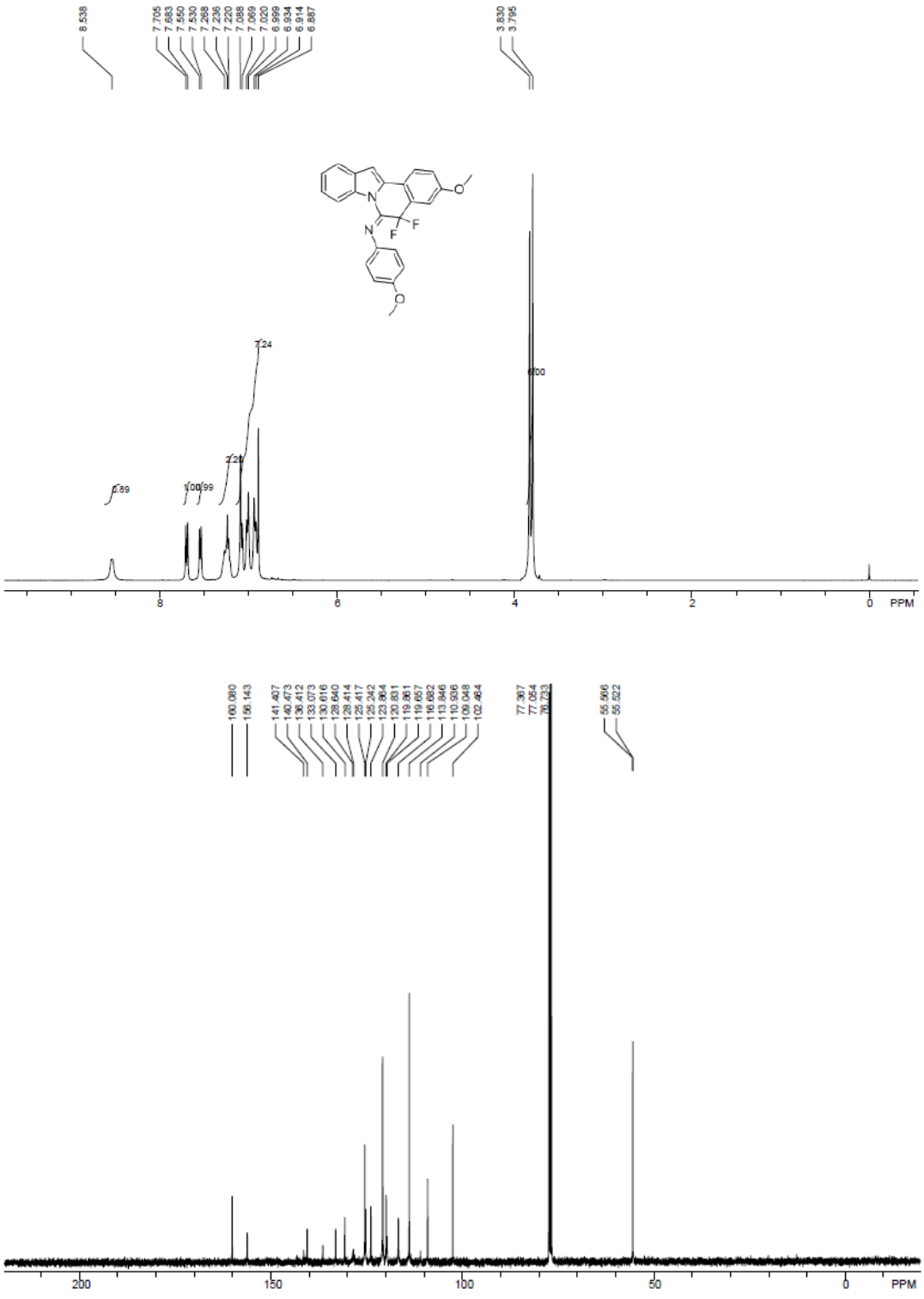
2c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7.069
7.020
6.999
6.934
6.914
6.887
3.830
3.795
7.24
6.00
2.21
1.89
1.00
0.99
PPM
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141.407
140.473
136.412
133.073
130.616
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125.417
125.242
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119.657
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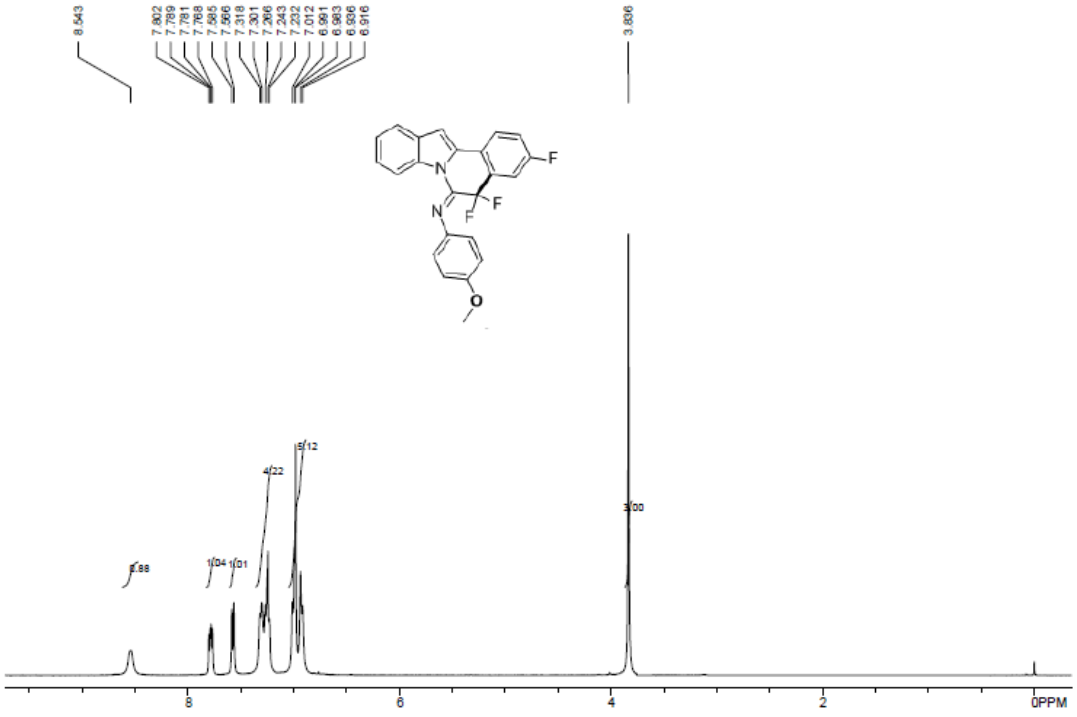
2d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7.012
6.991
6.983
6.936
6.916
3.836
F
N
F
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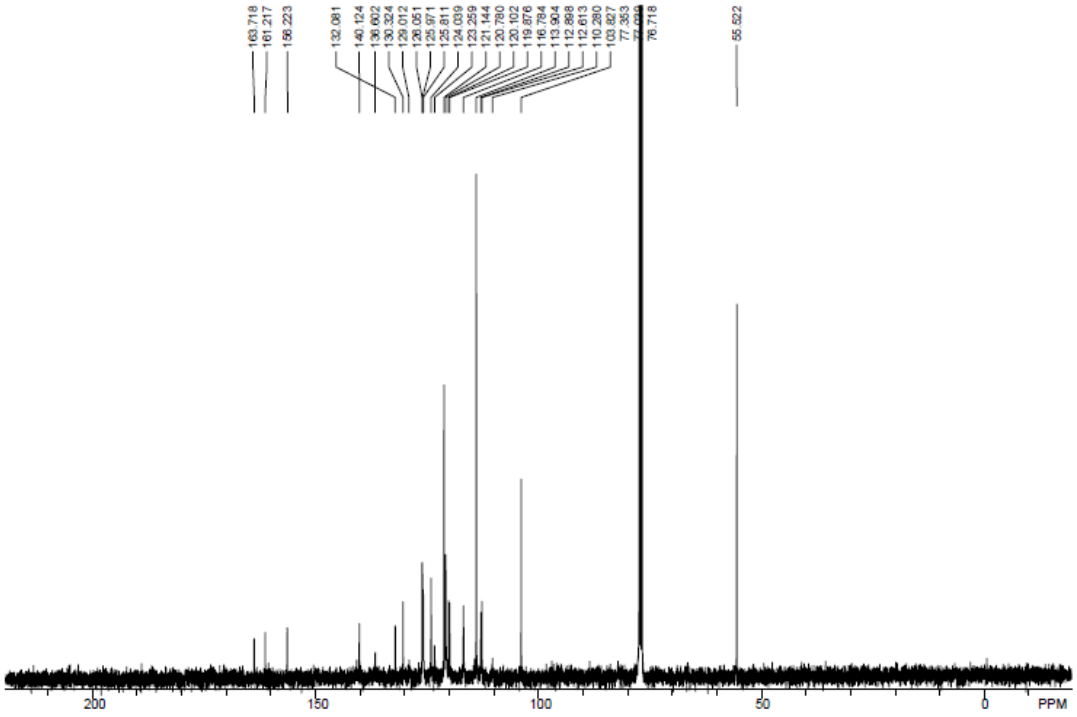
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123.259
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120.780
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116.784
113.964
112.868
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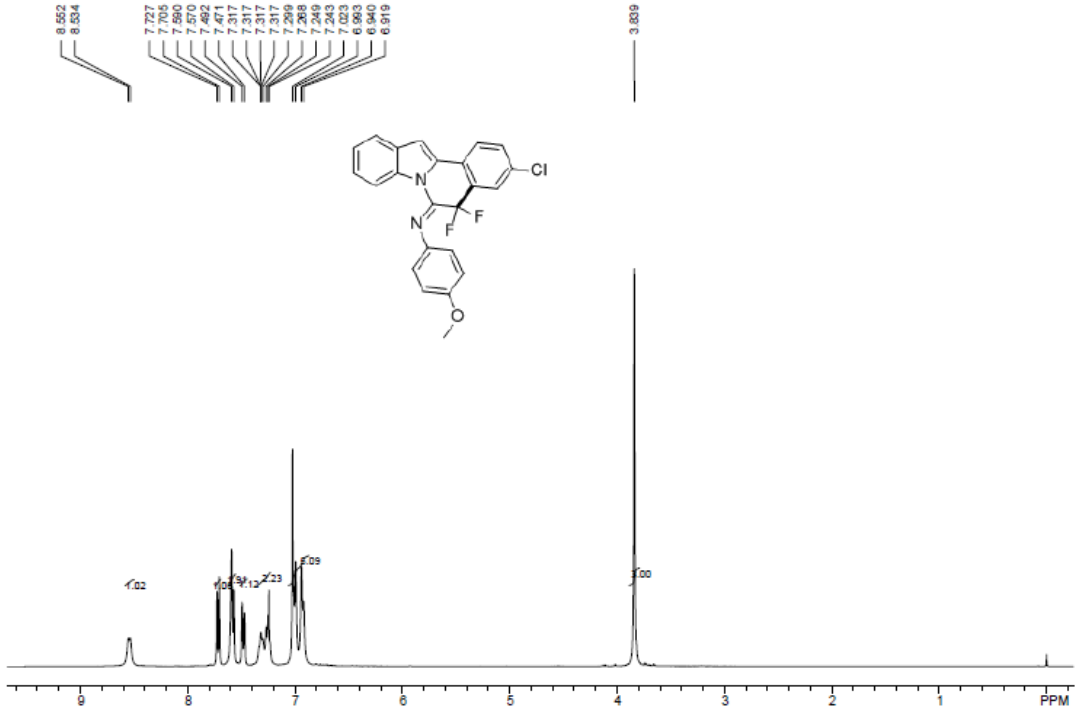
2e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7.268
7.249
7.243
7.023
6.963
6.940
6.919
3.839
Cl
N
N
F
F
O
1.02
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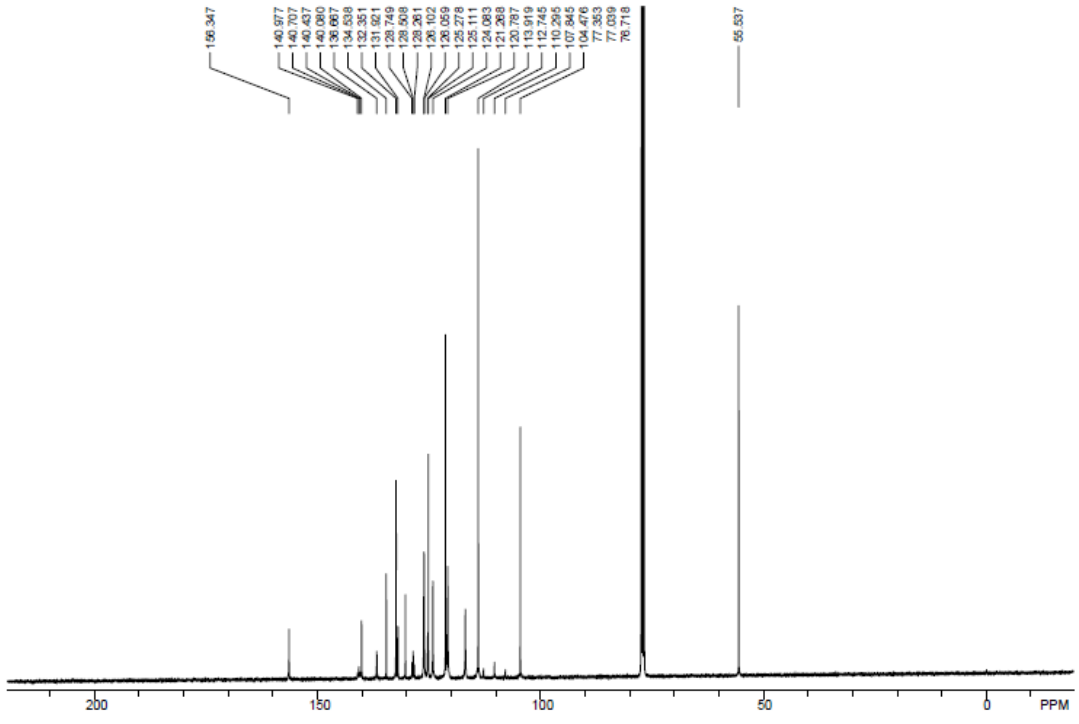
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128.261
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126.059
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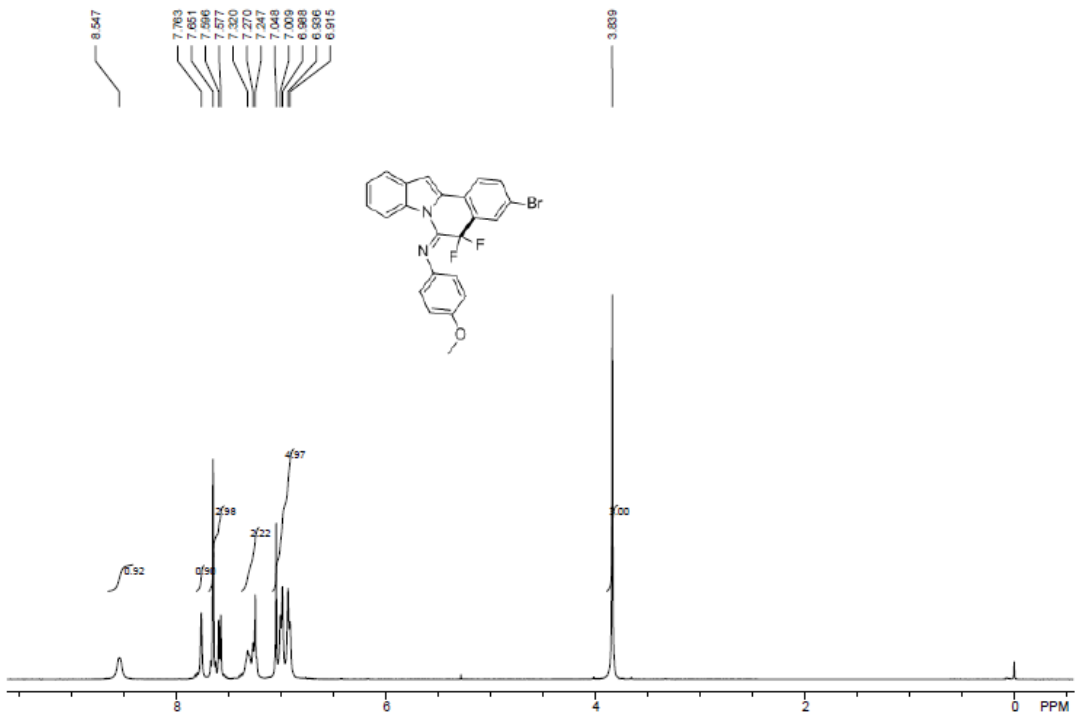
2f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7.247
7.048
7.009
6.988
6.936
6.915
3.839
Br
N
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2.98
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3.00
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6
4
2
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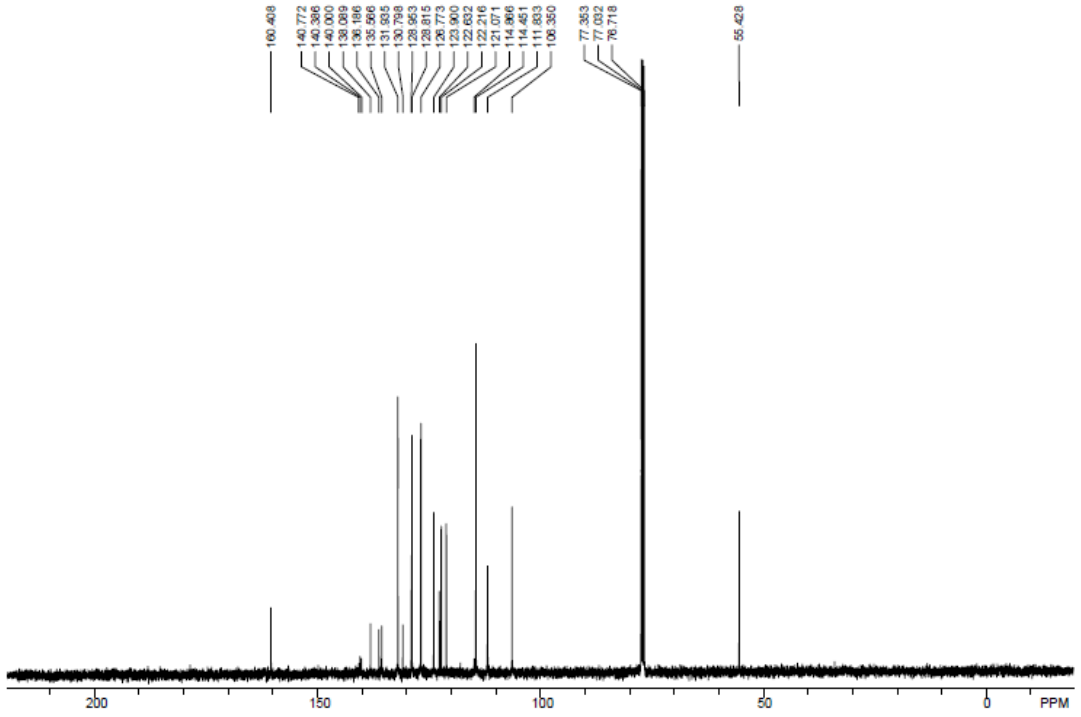
PPM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126.773
123.900
122.632
122.216
121.071
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77.092
76.718
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200
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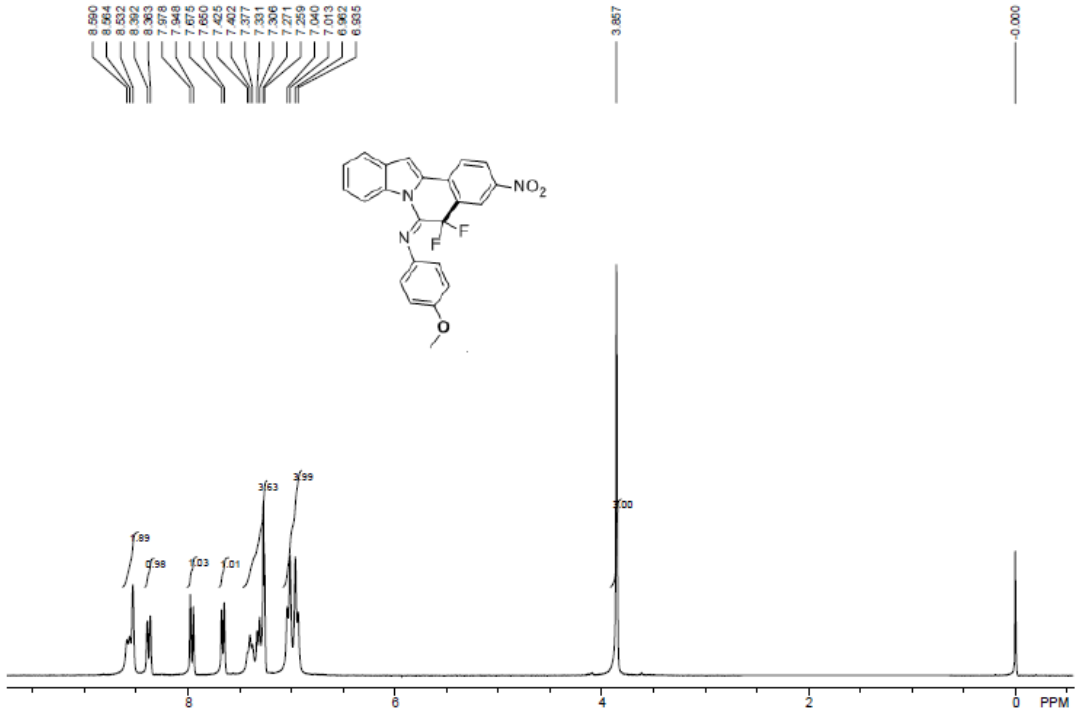
100
50
0
PPM

2g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7.675
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7.425
7.402
7.377
7.331
7.306
7.271
7.259
7.040
7.013
6.962
6.935
3.867
0.000
NO2
N
F
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2.00
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4
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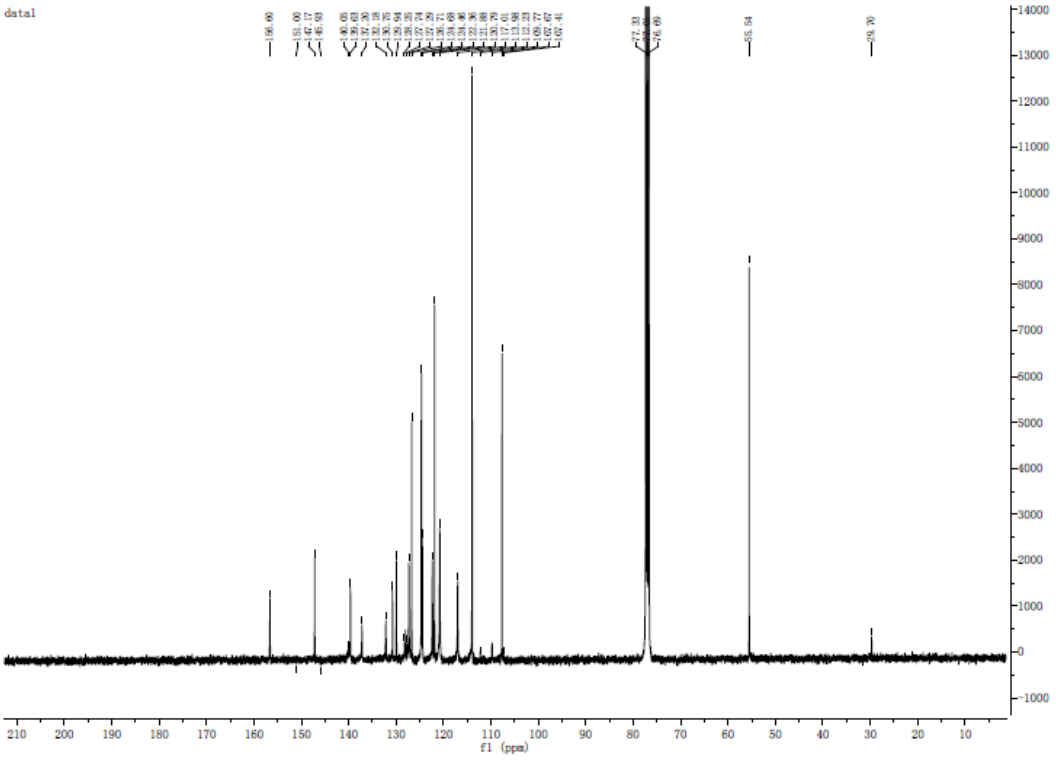
PPM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14000
13000
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11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
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120
110
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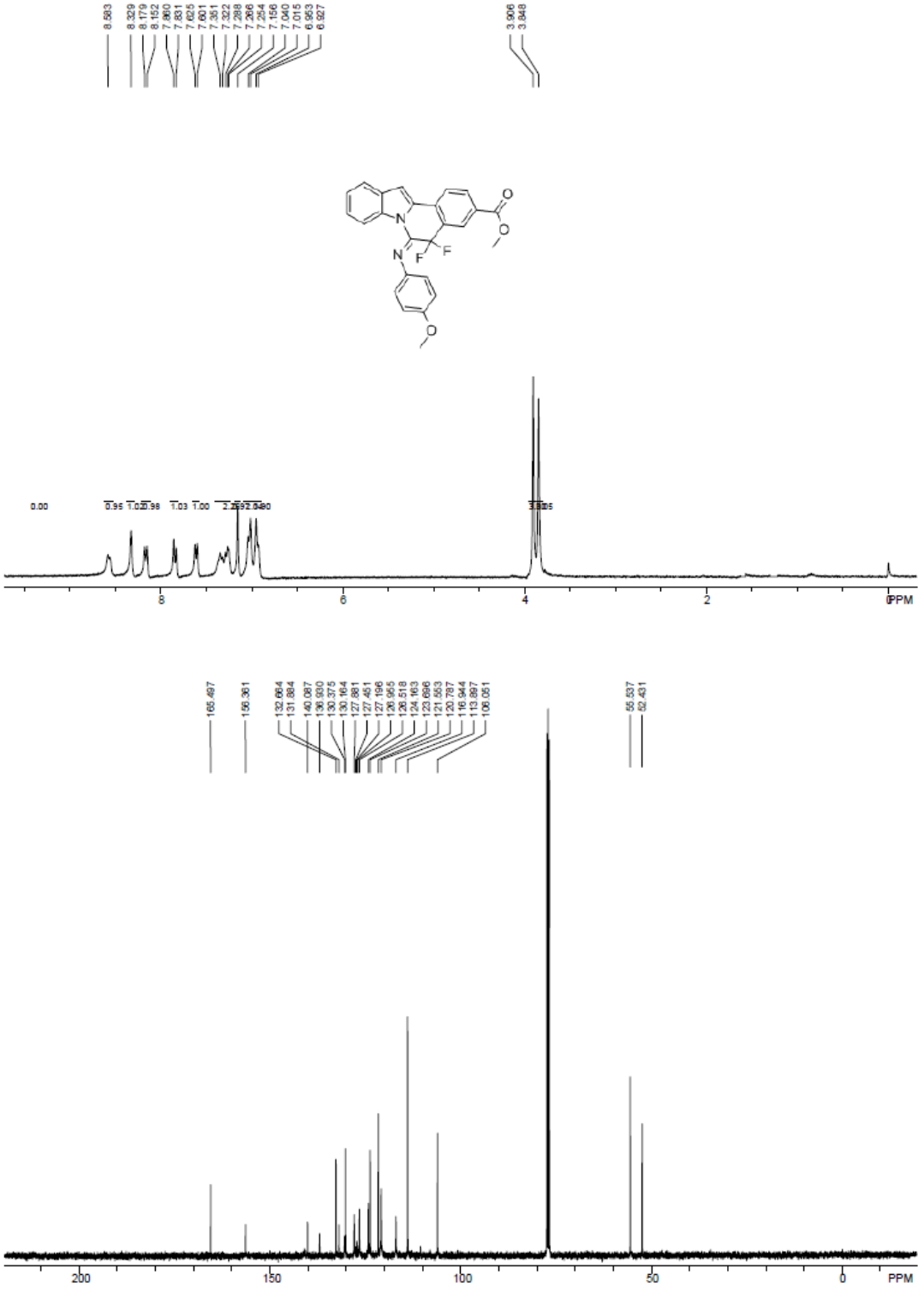
20
10
f1 (ppm)

2h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7.601
7.361
7.322
7.288
7.266
7.254
7.156
7.040
7.015
6.953
6.927
3.906
3.848
O
O
N
F
F
N
O
0.00
0.95
1.02
0.98
1.03
1.00
2.69
2.92
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3.00
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4
2
PPM
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123.696
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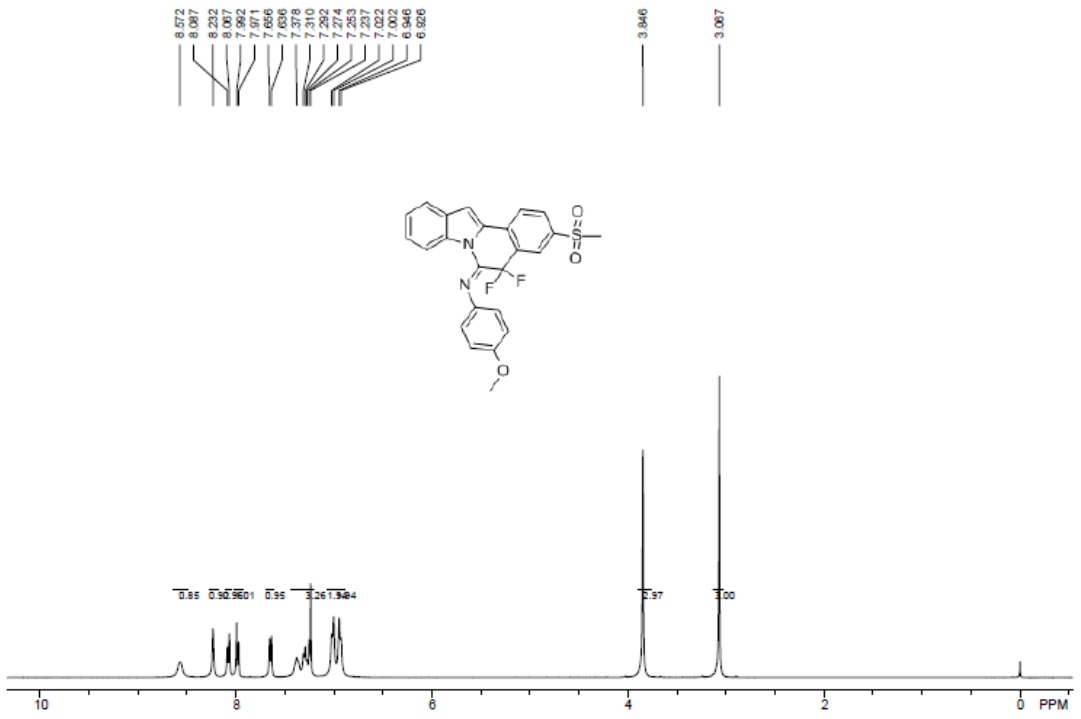
2i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7.274
7.253
7.237
7.022
7.002
6.946
6.926
3.846
3.067
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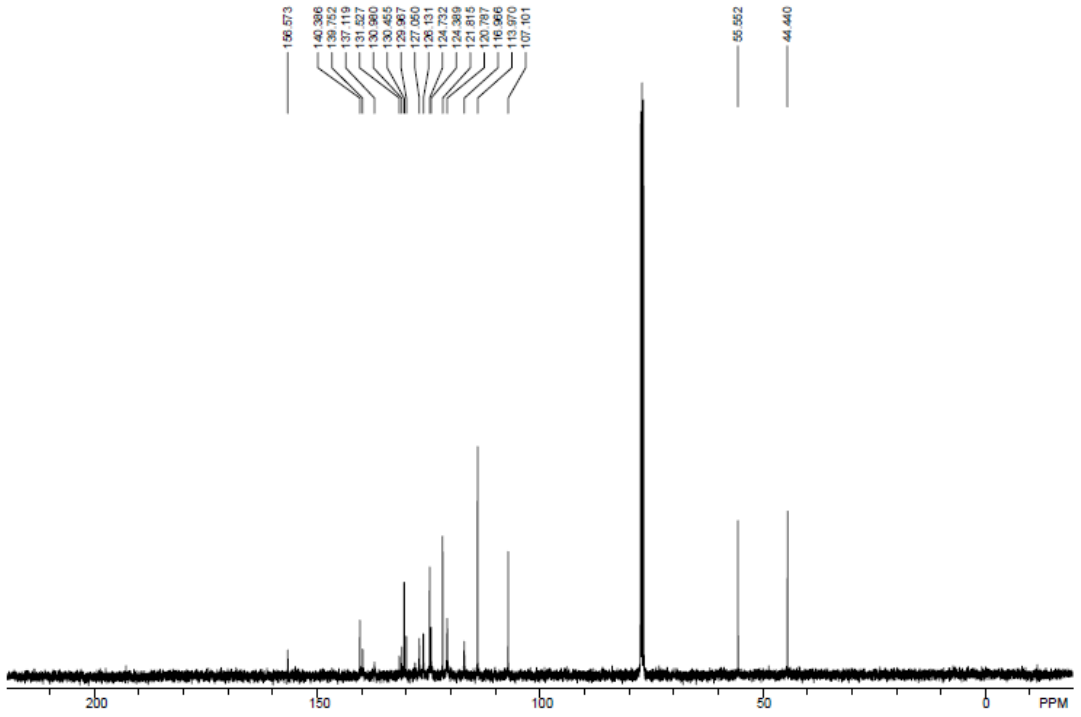
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PPM

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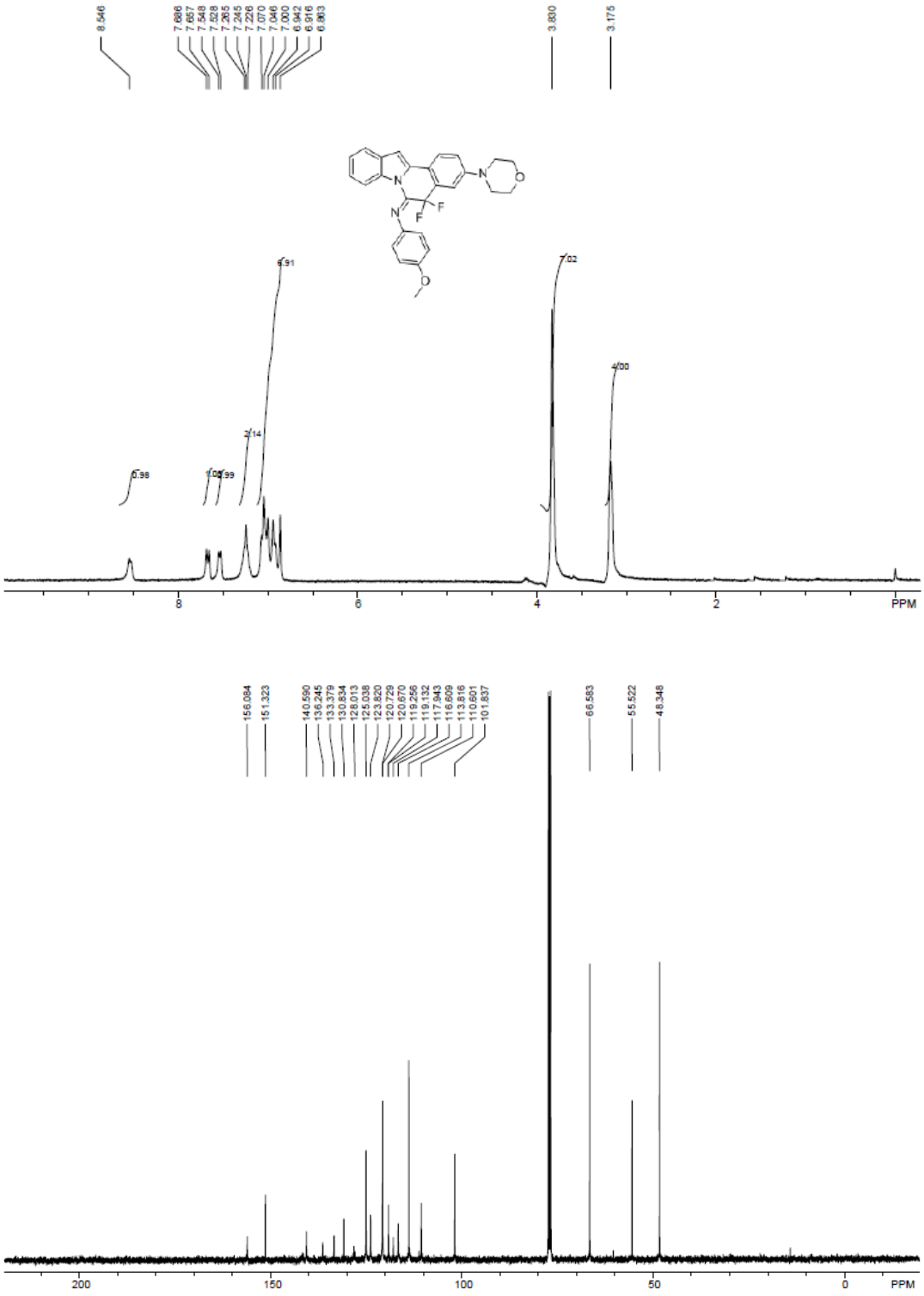
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7.046
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6.916
6.863
3.830
3.175
6.91
7.02
4.00
2.14
0.98
1.02
0.99
8
6
4
2
PPM
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136.245
133.379
130.834
128.013
125.038
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120.729
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119.256
119.132
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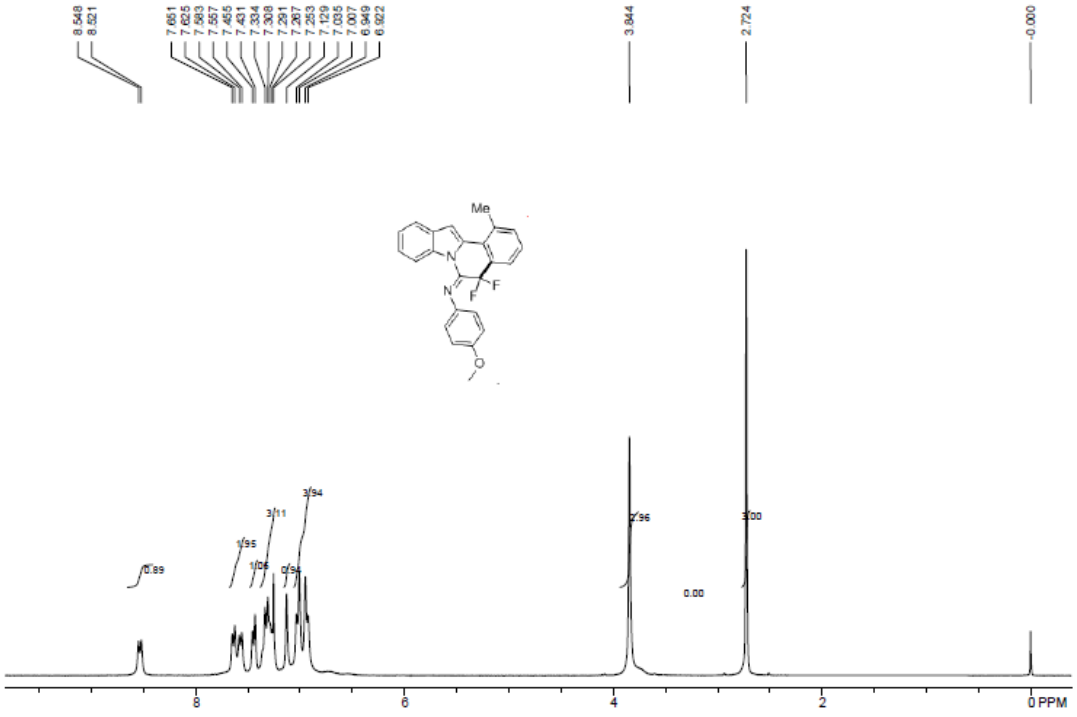
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7.308
7.291
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7.253
7.129
7.035
7.007
6.949
6.922
3.844
2.724
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F
O
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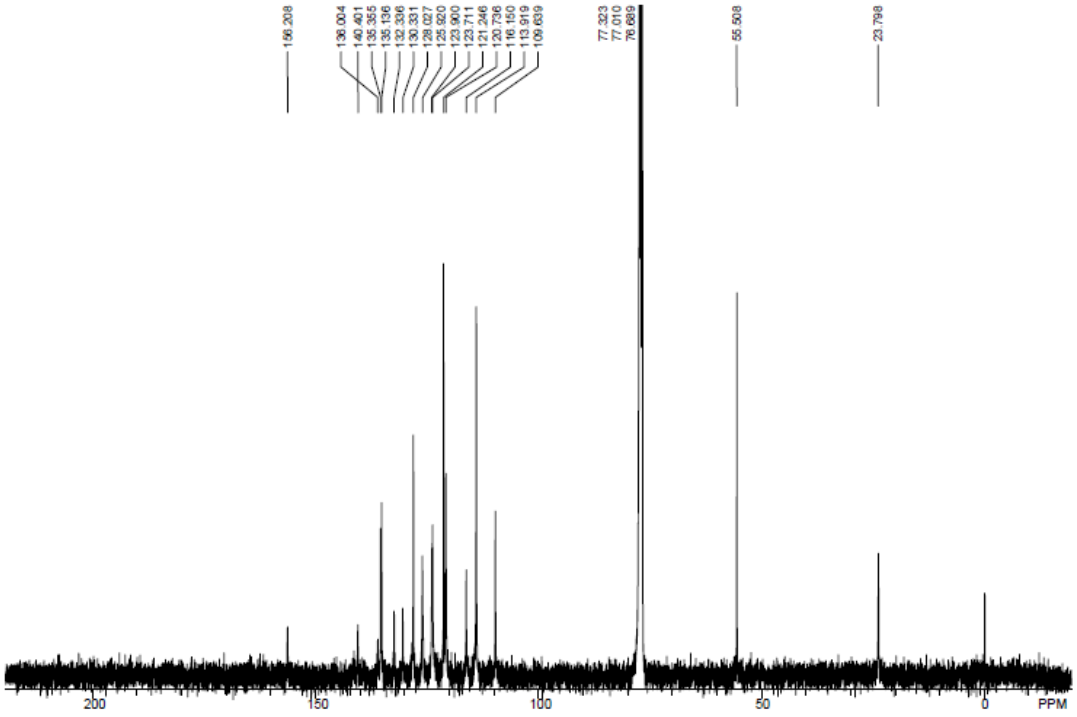
0 PPM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123.900
123.711
121.246
120.736
116.150
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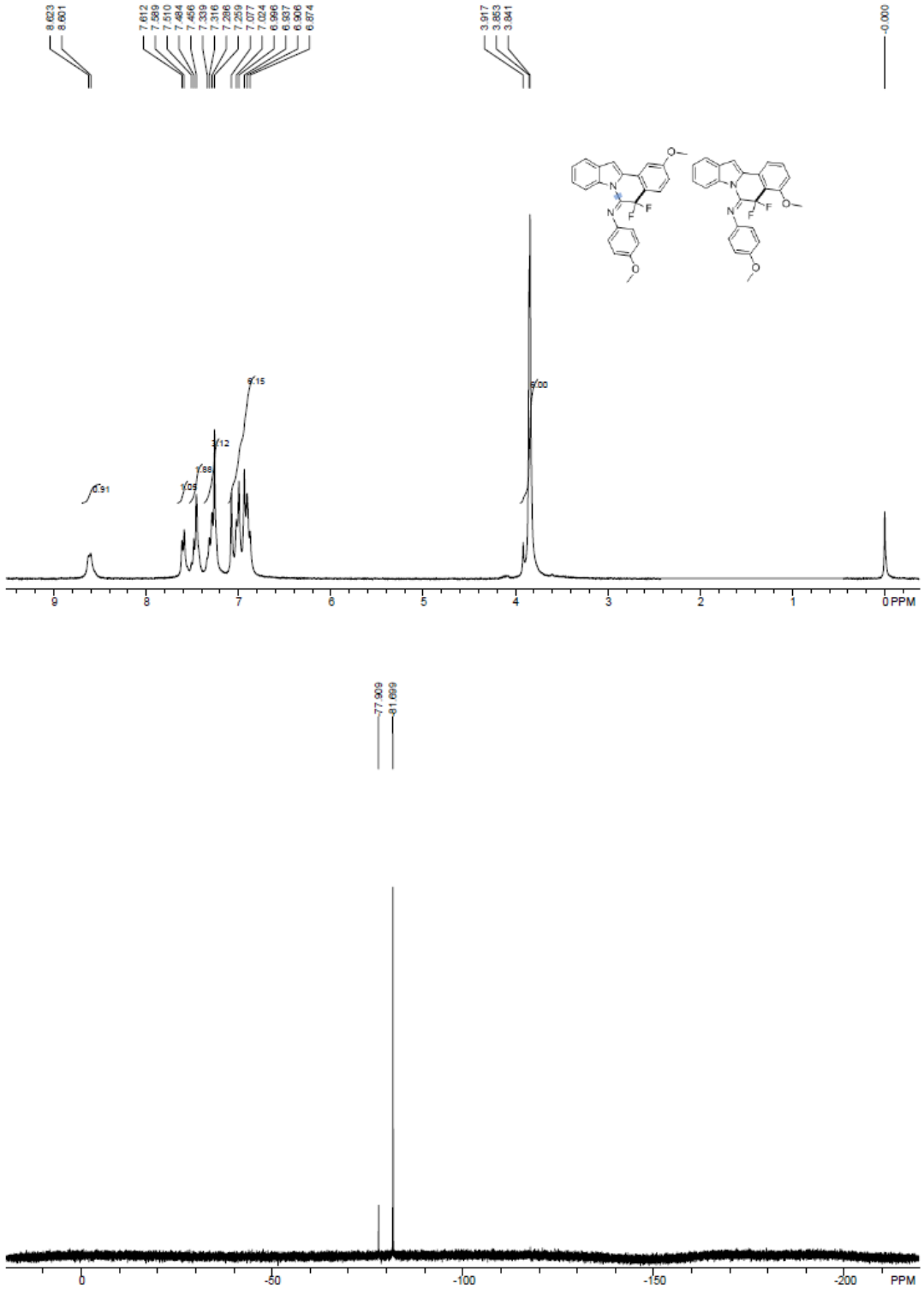
50
0
PPM

2l & 2l'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7.286
7.259
7.077
7.024
6.996
6.937
6.906
6.874
3.917
3.853
3.841
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1.05
1.88
3.12
6.15
9.00
9
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3
2
1
0 PPM
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0
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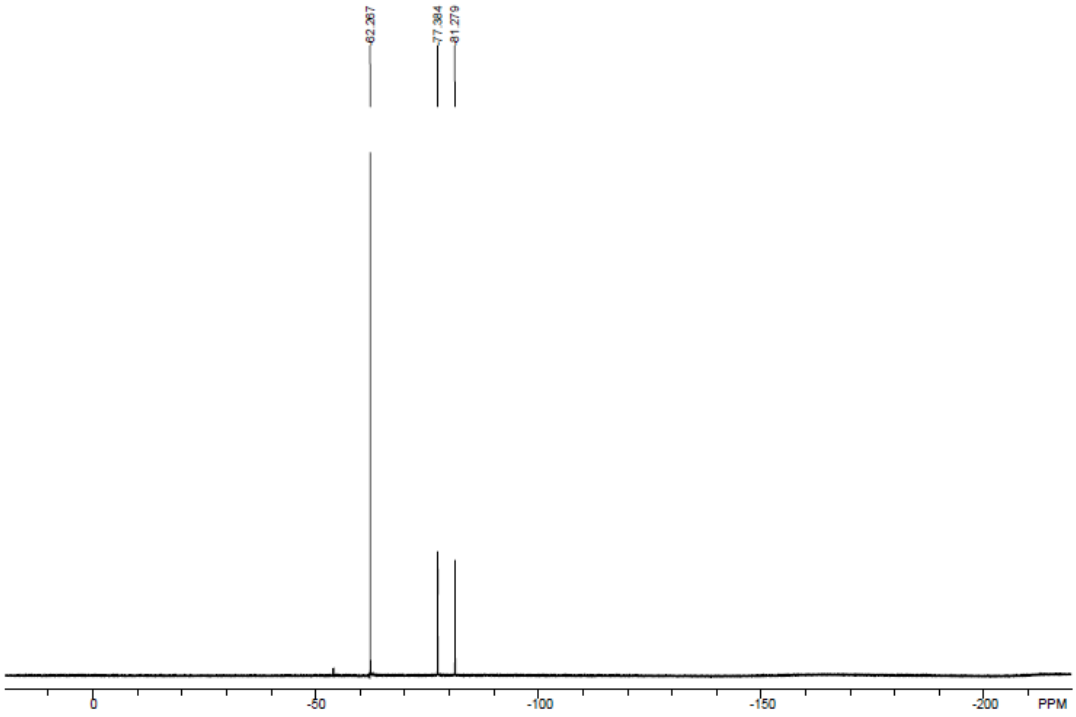
-100
-150
-200
PPM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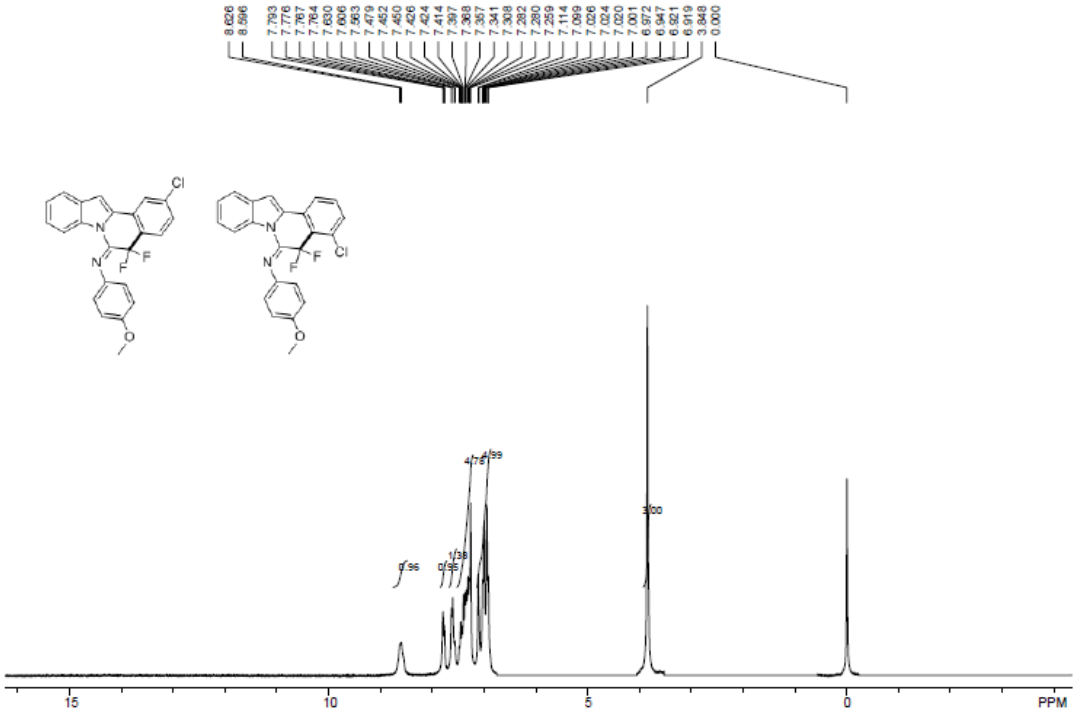
2m & 2m'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7.452
7.450
7.426
7.424
7.414
7.397
7.368
7.357
7.341
7.308
7.282
7.280
7.259
7.114
7.099
7.026
7.024
7.020
7.001
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6.947
6.921
6.919
3.848
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5
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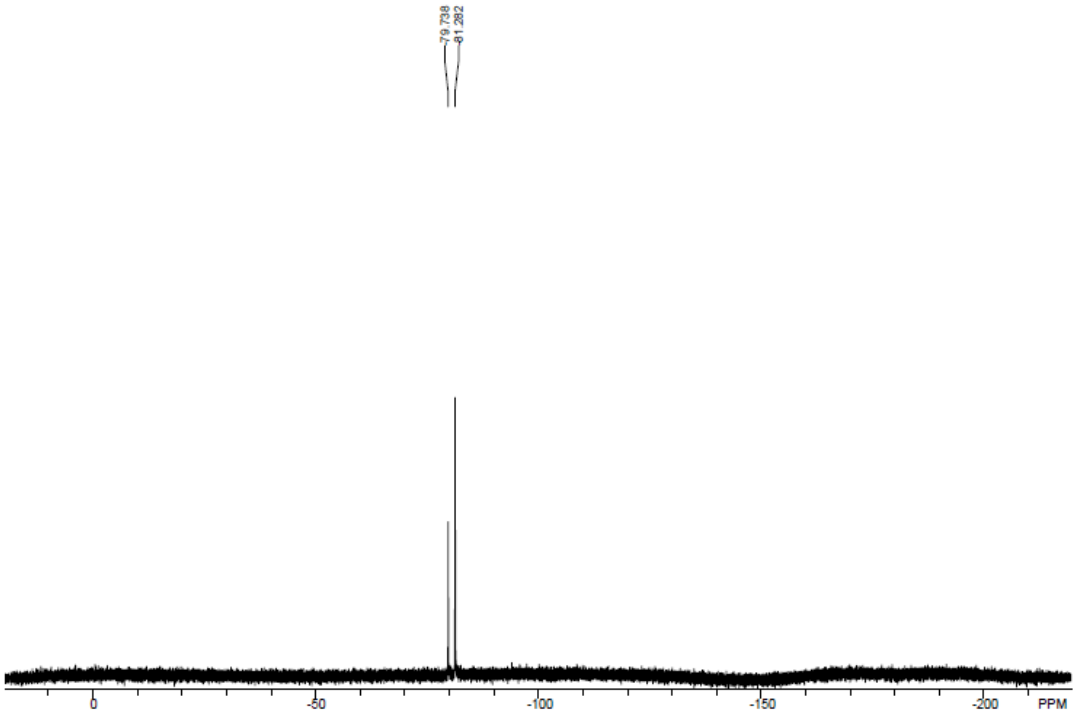
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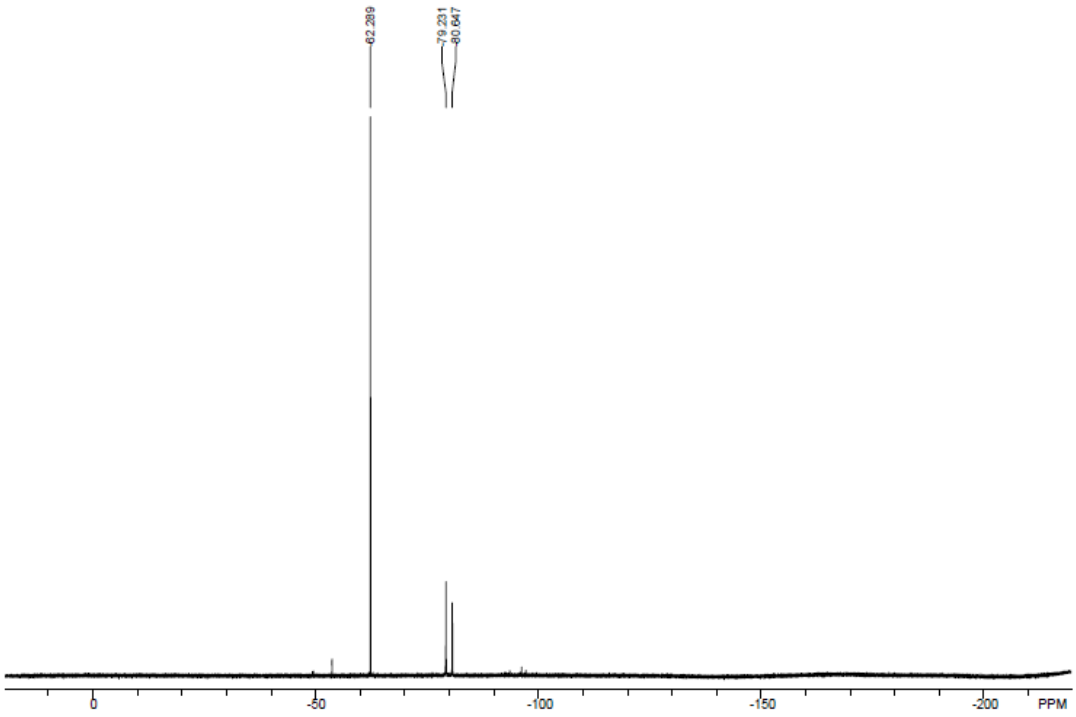
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-200
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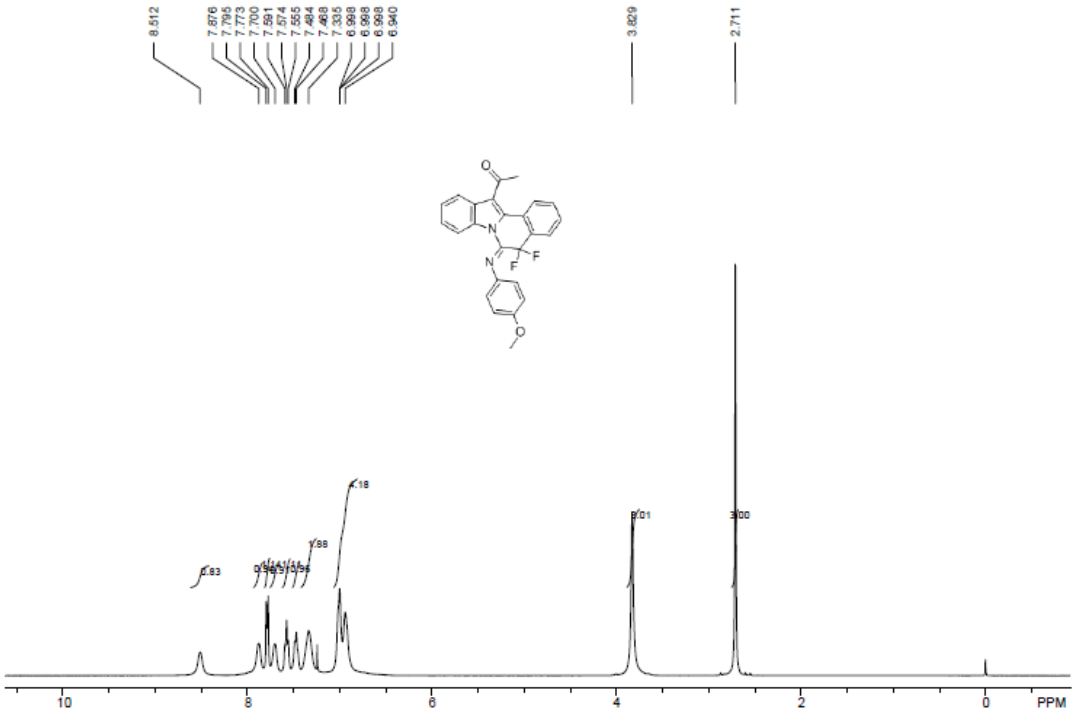
2n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7.555
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7.468
7.335
6.998
6.998
6.998
6.940
3.829
2.711
O
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10
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6
4
2
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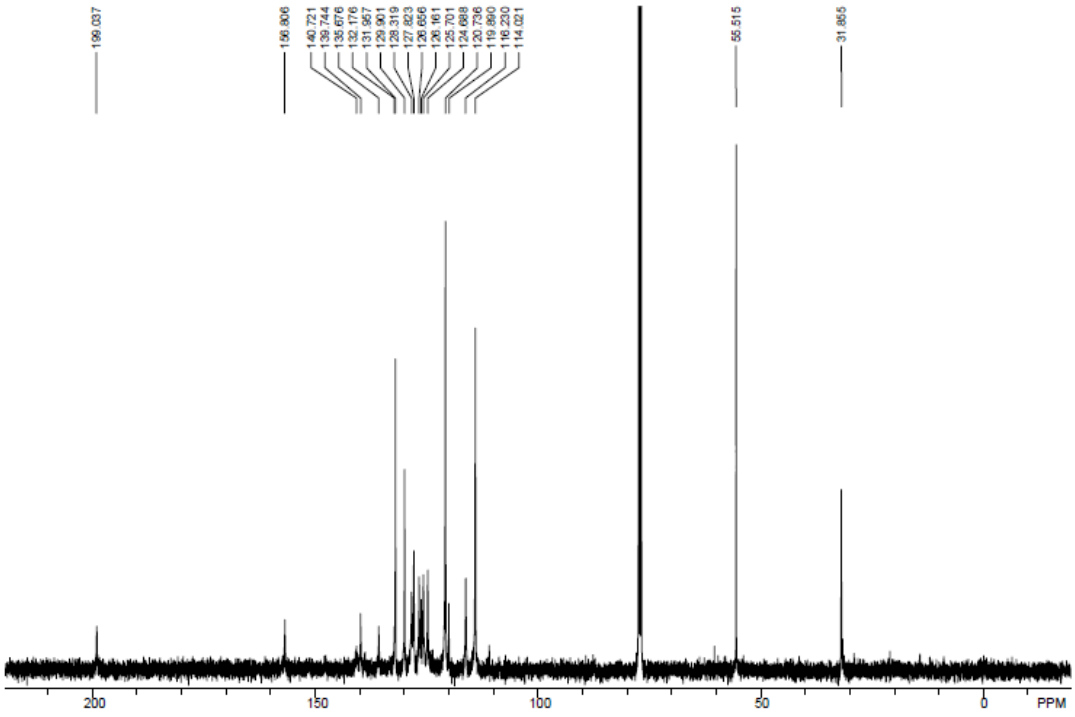
PPM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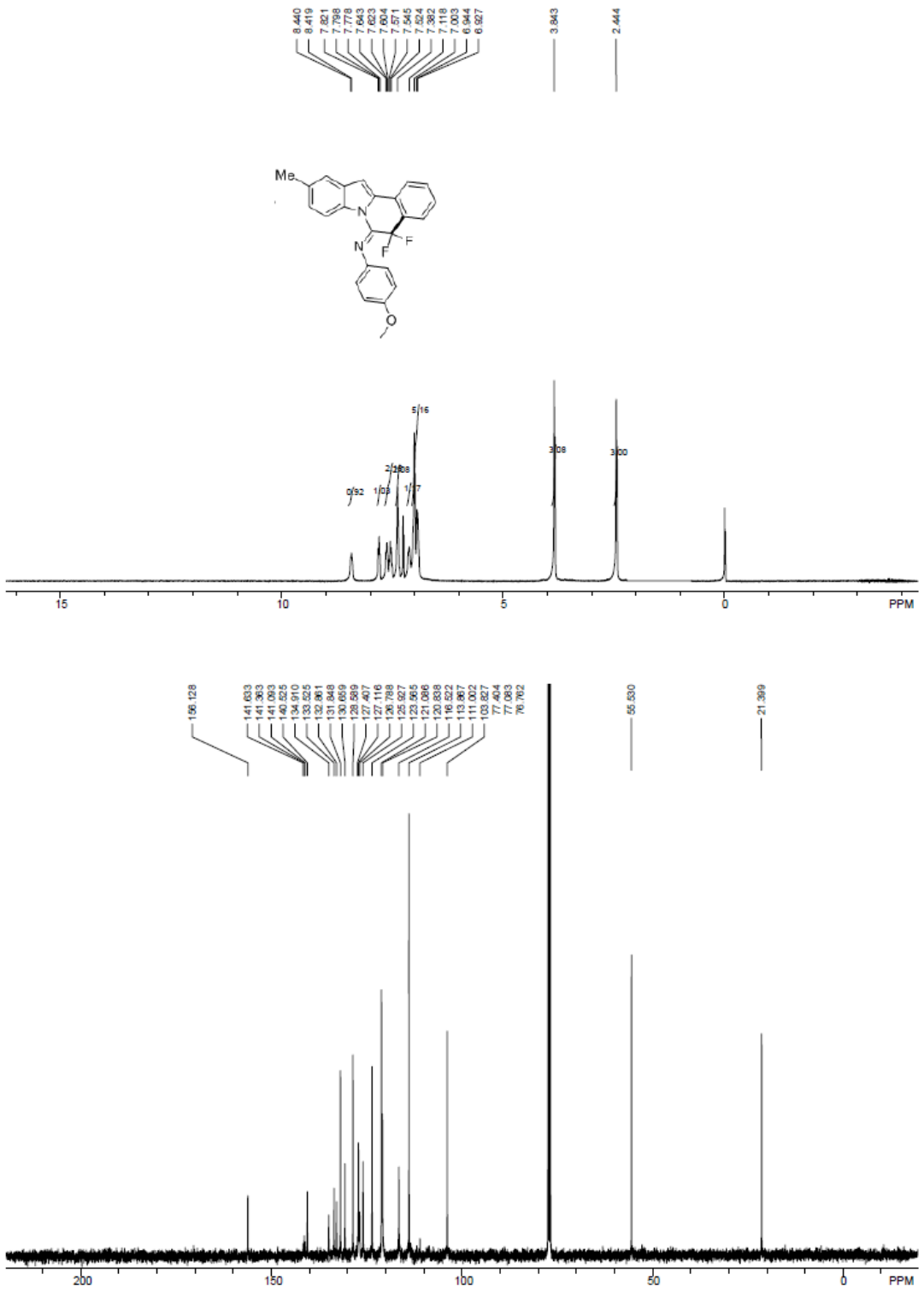
2o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7.118
7.003
6.944
6.927
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Me
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3.08
3.00
15
10
5
0
PPM
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128.589
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125.927
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121.086
120.838
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76.762
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200
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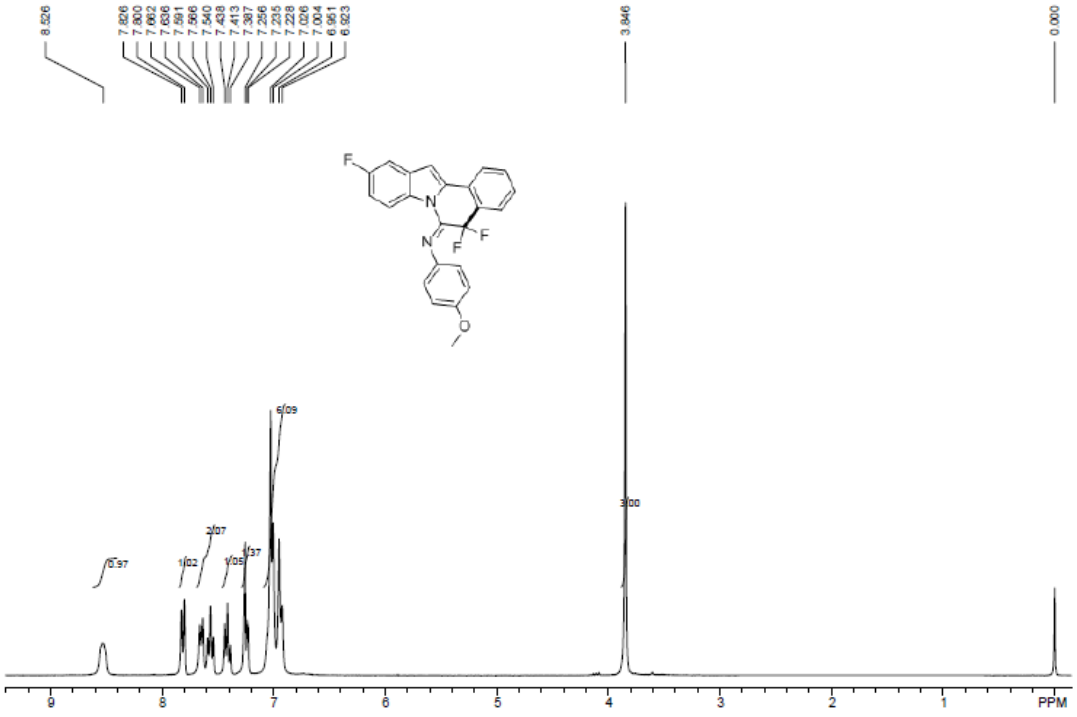
50
0
PPM

2p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7.235
7.228
7.026
7.004
6.951
6.923
3.846
0.000
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N
F
F
N
O
6.09
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1.02
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3
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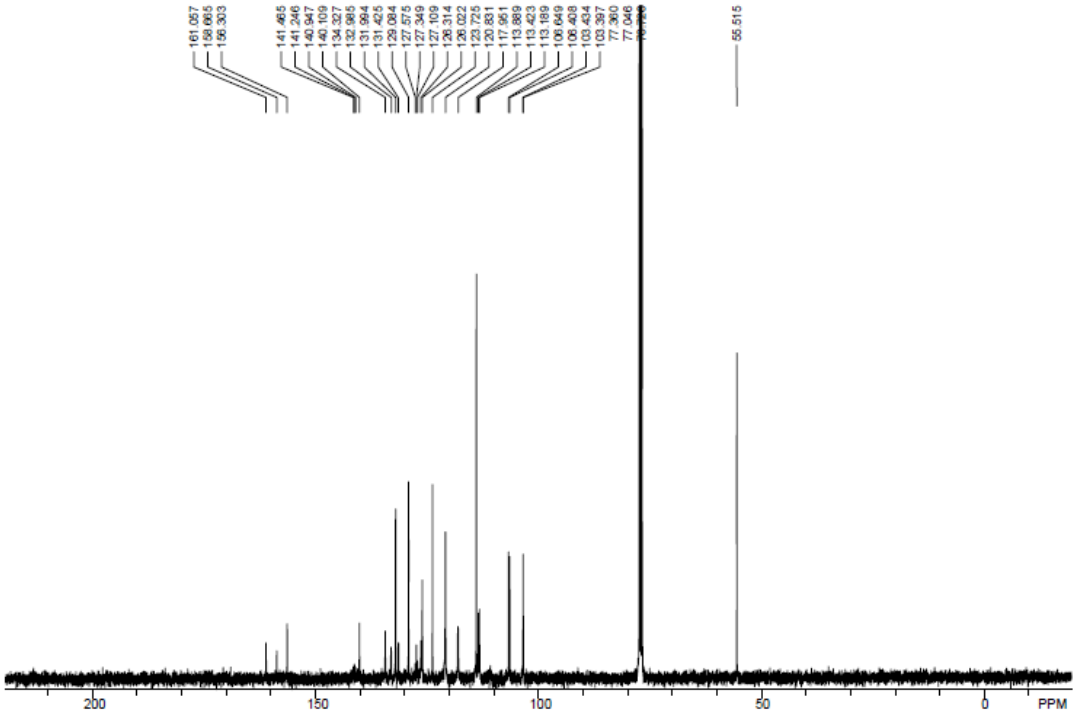
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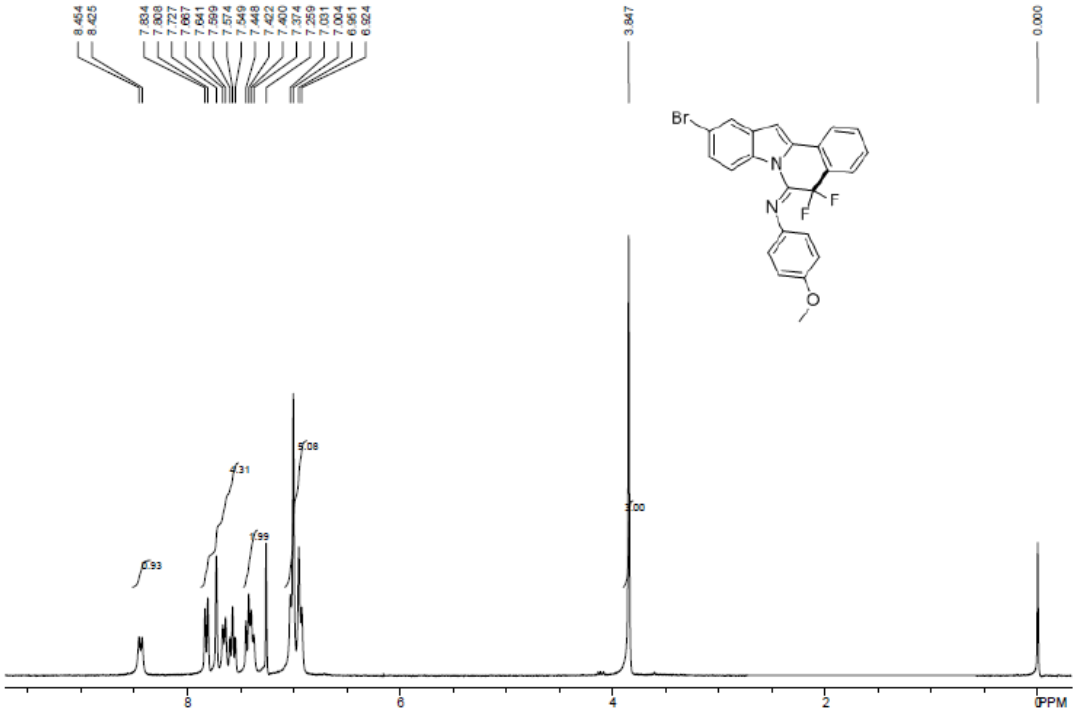
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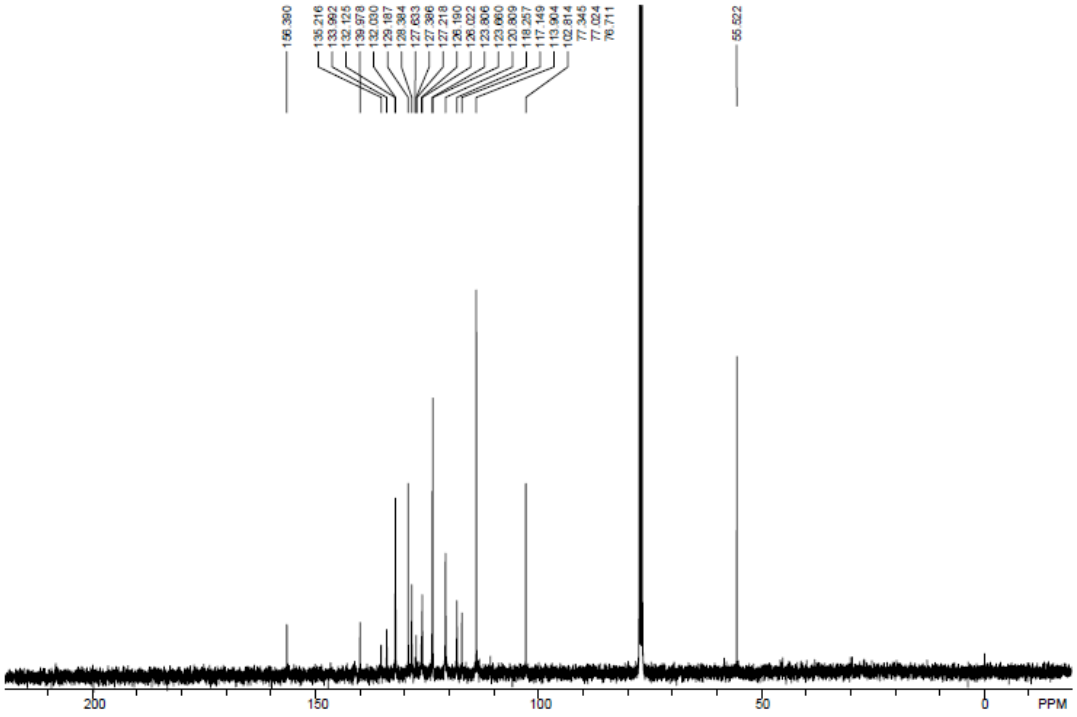
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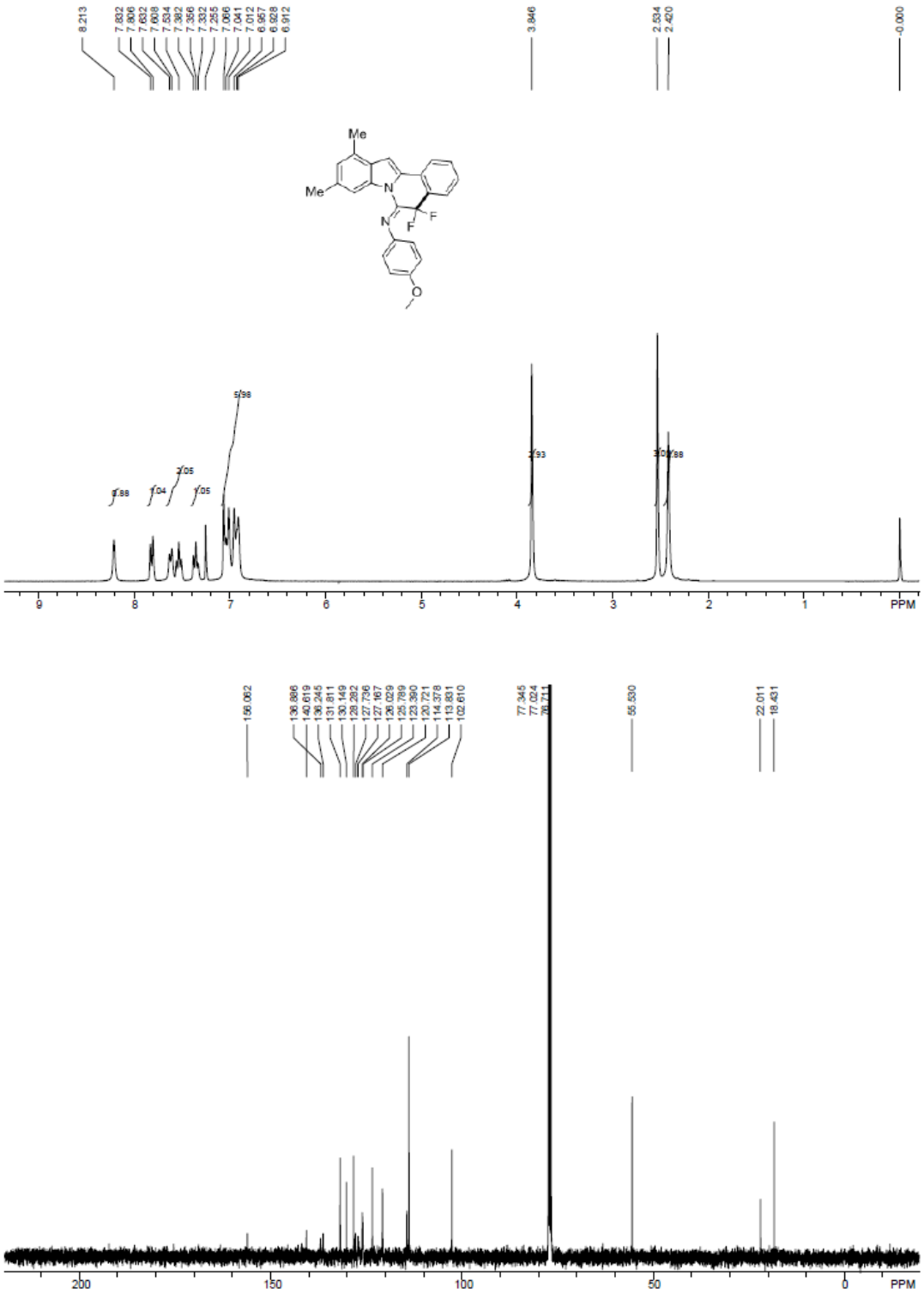
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7.012
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6.928
6.912
3.846
2.534
2.420
-0.000
Me
Me
N
N
F
F
O
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2.05
1.88
2.04
2.05
2.93
3.04
3.98
9
8
7
6
5
4
3
2
1
PPM
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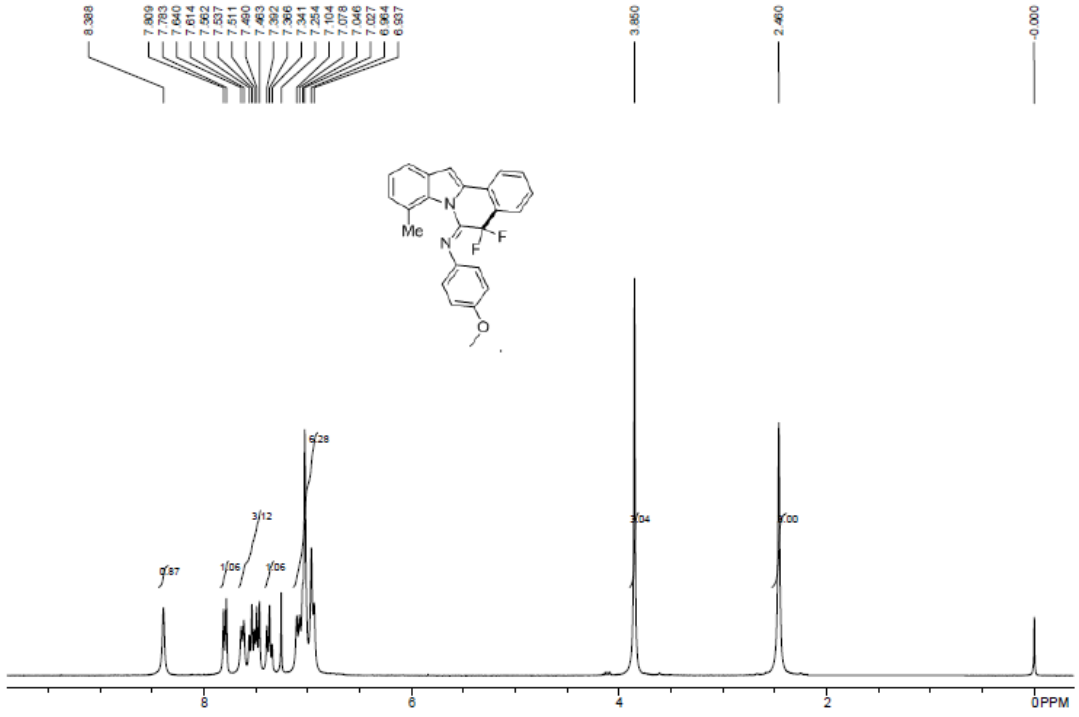
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Me
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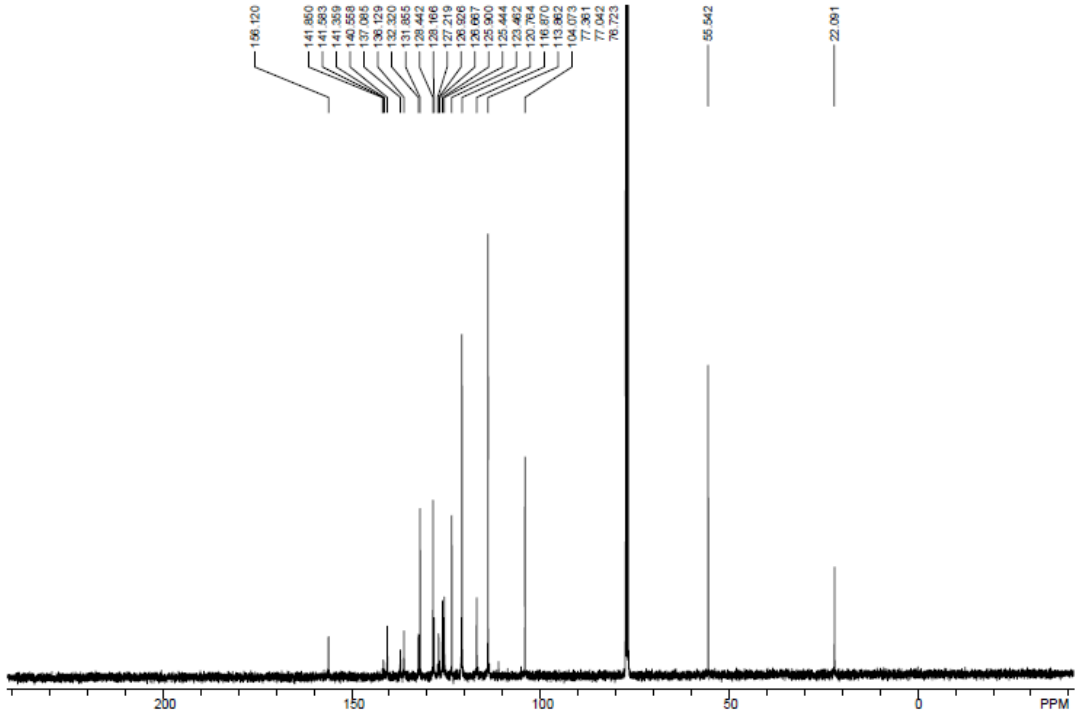
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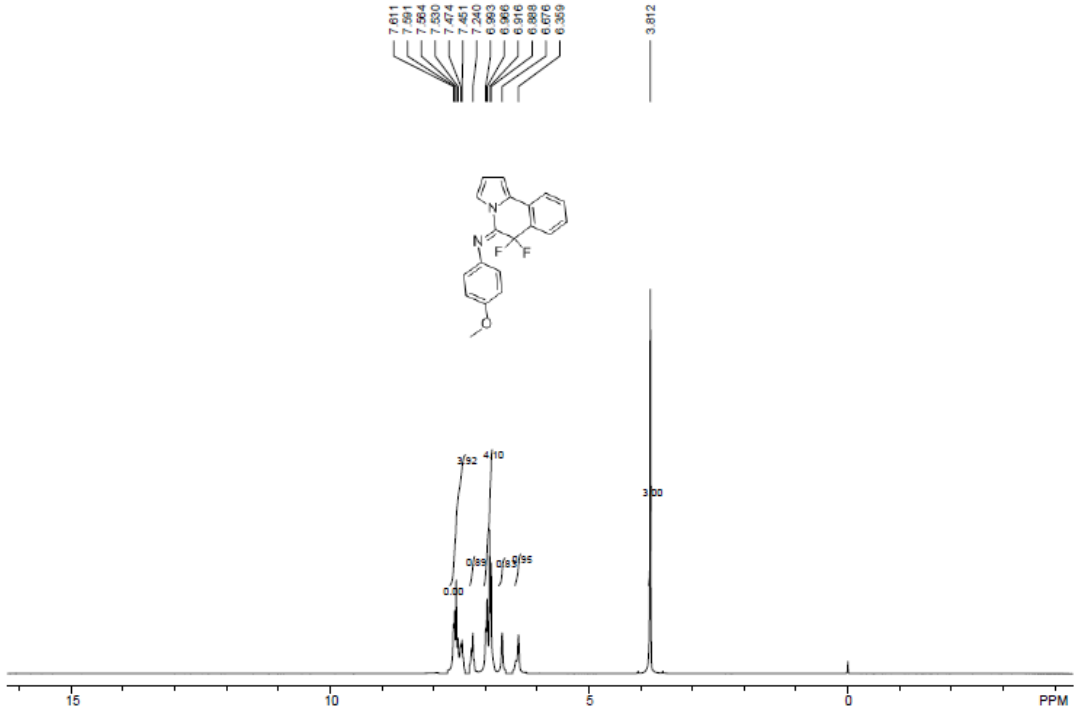
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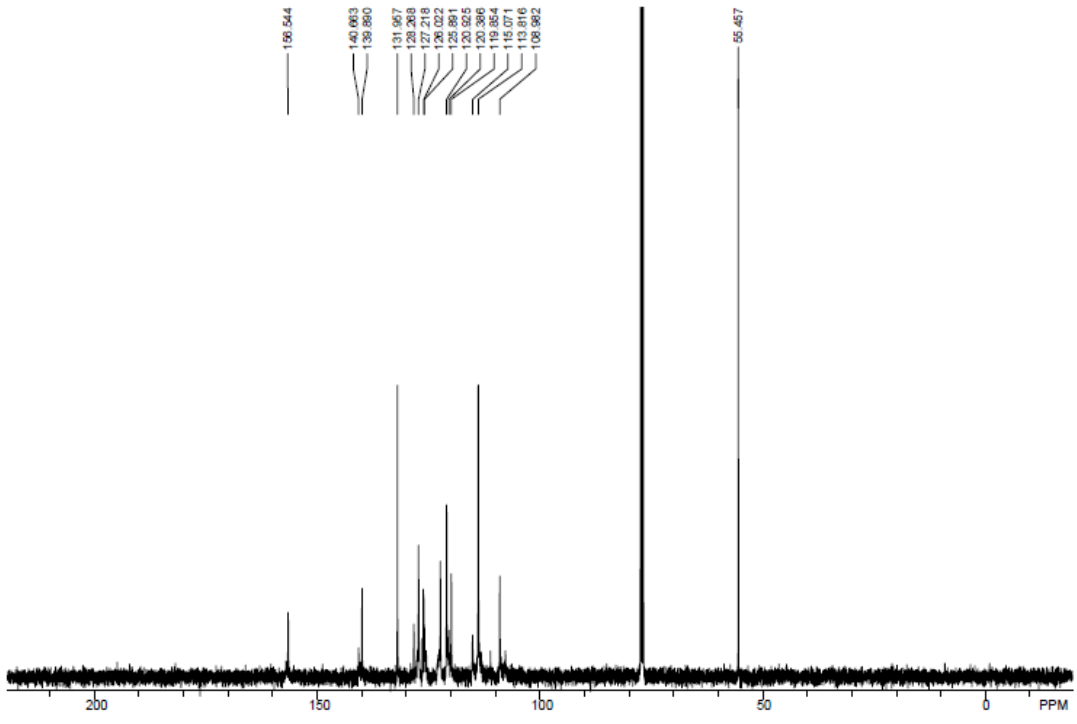
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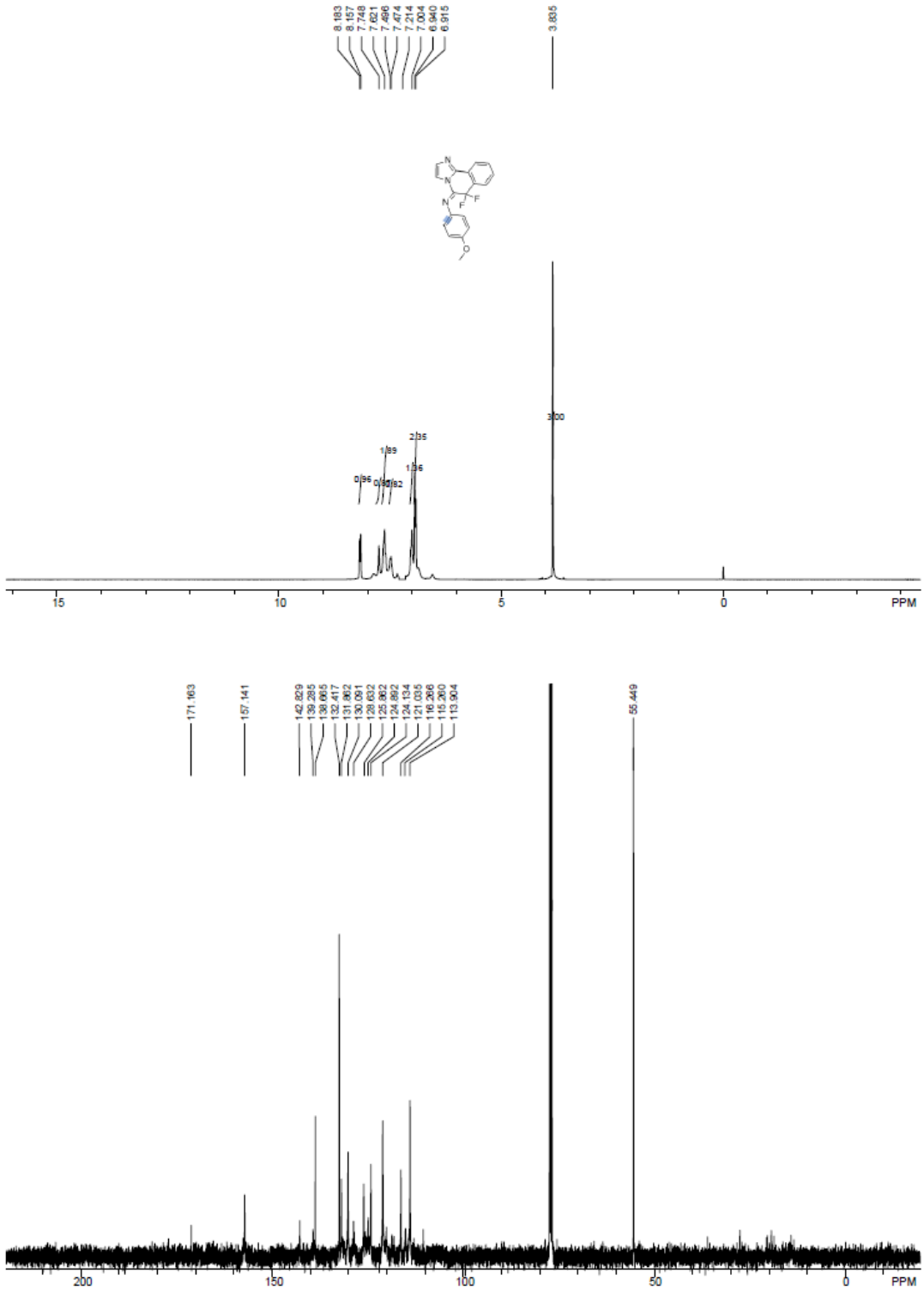
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2.35
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1.36
0.96
0.92
0.82
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10
5
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139.285
138.665
132.417
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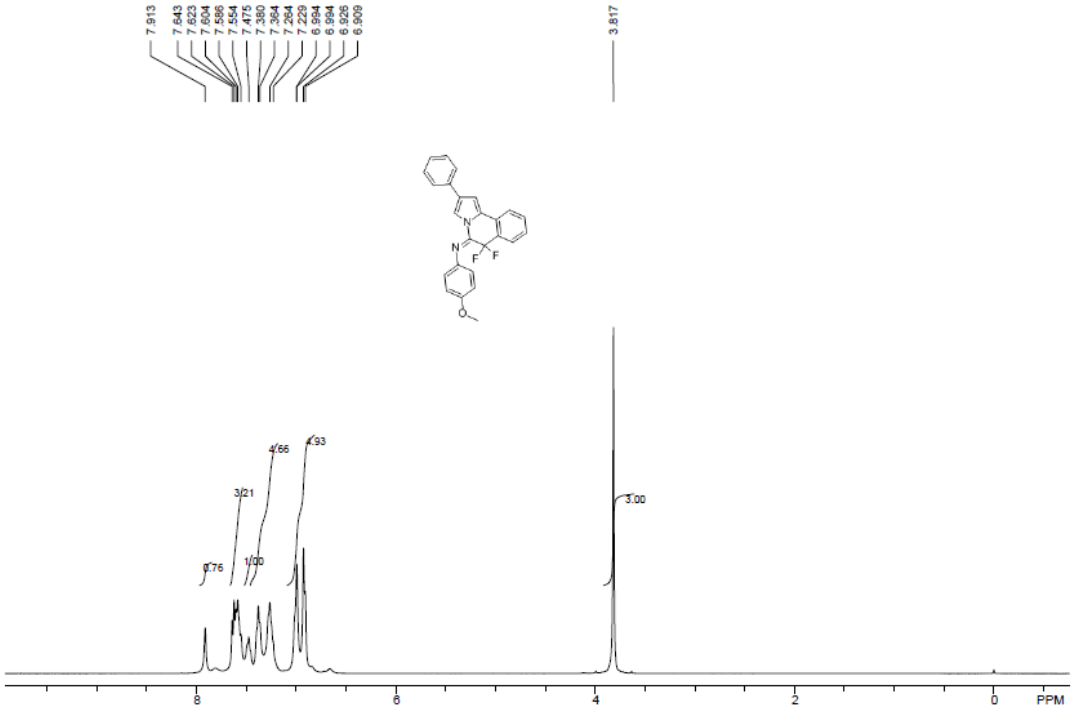
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6.994
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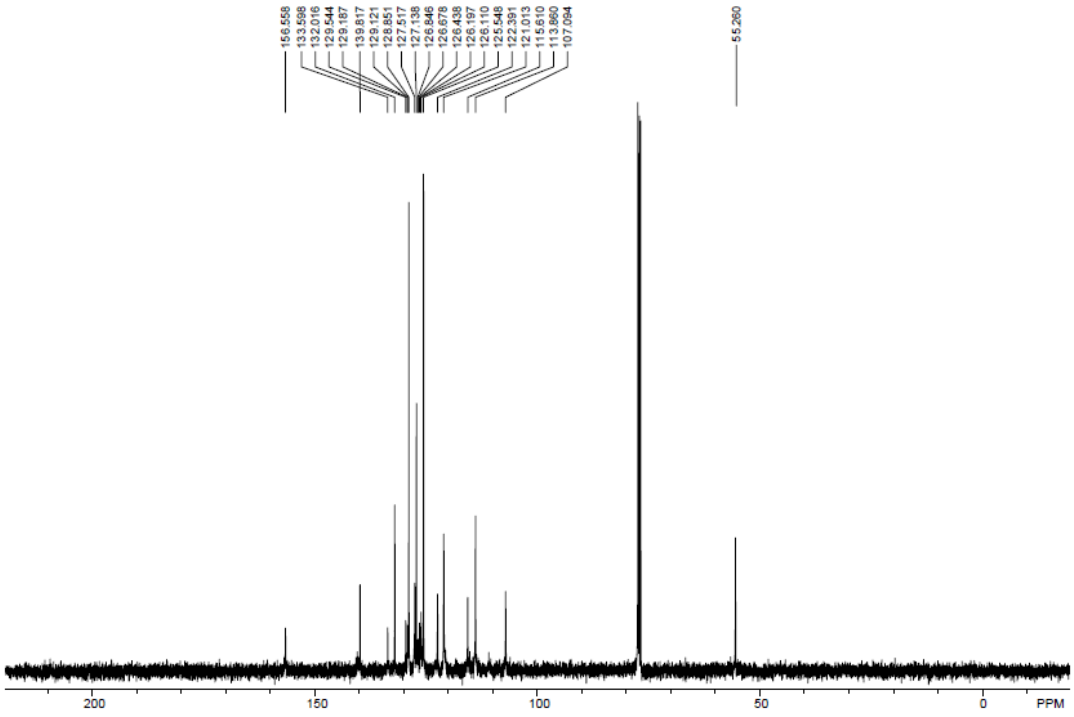
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126.197
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121.013
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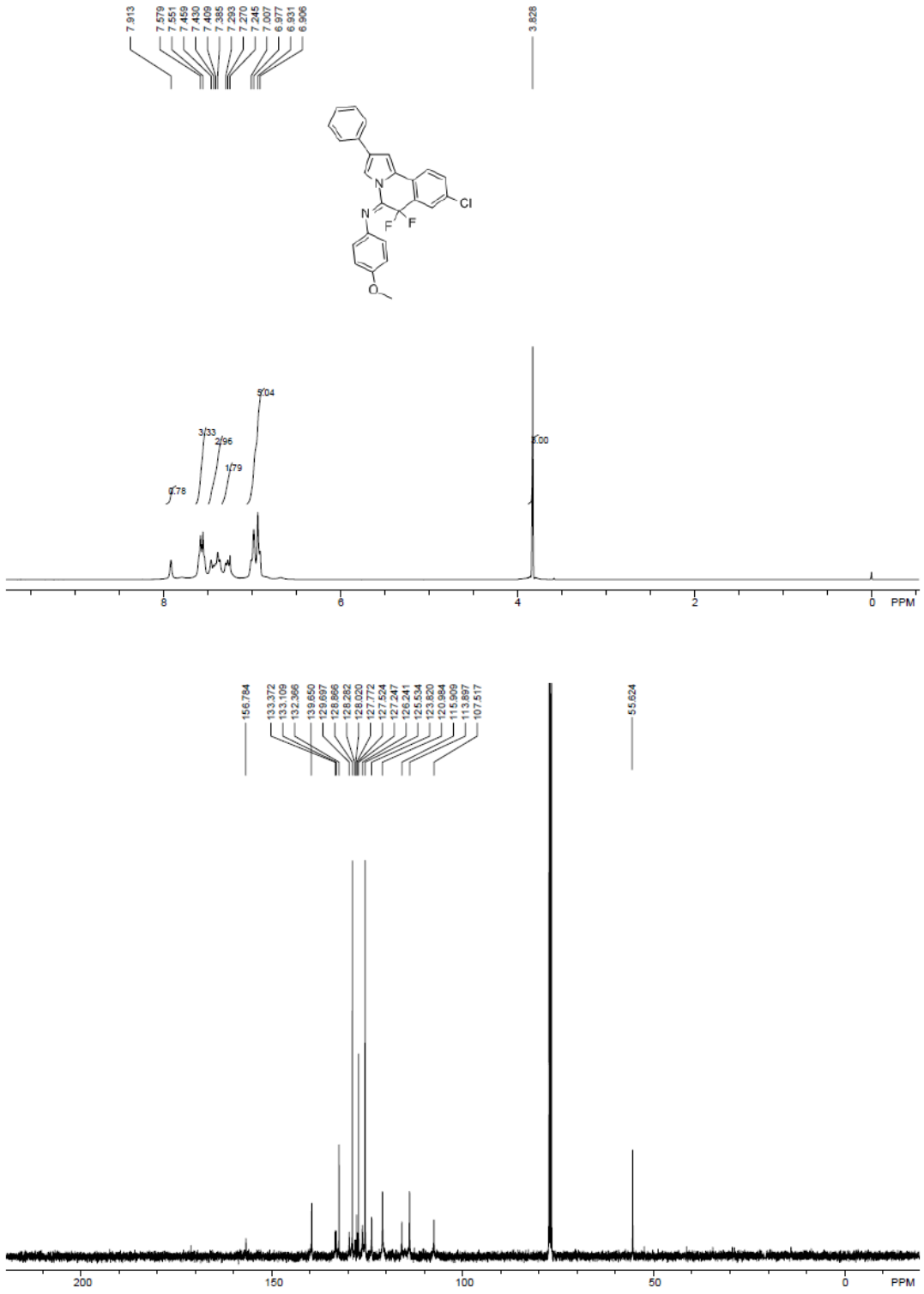
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6.906
3.828
Cl
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F
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2.96
1.79
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4.00
8
6
4
2
0
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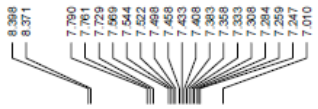
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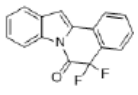
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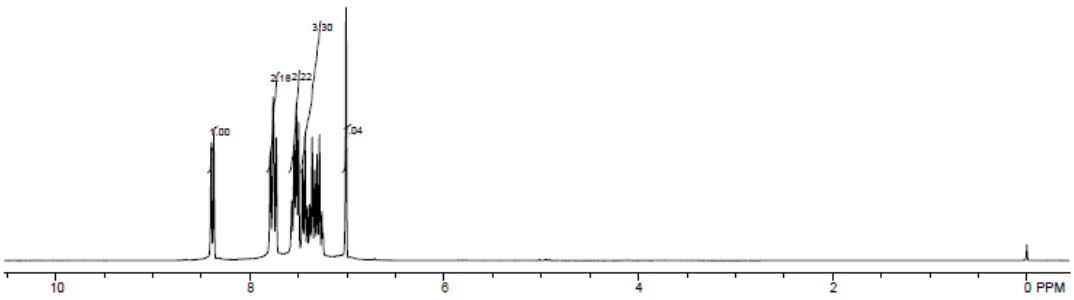
F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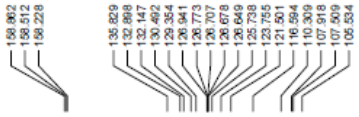
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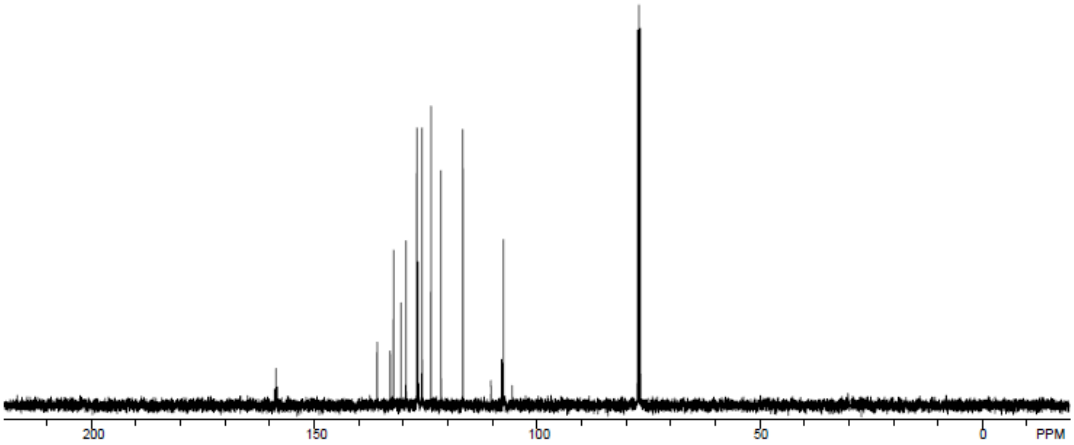
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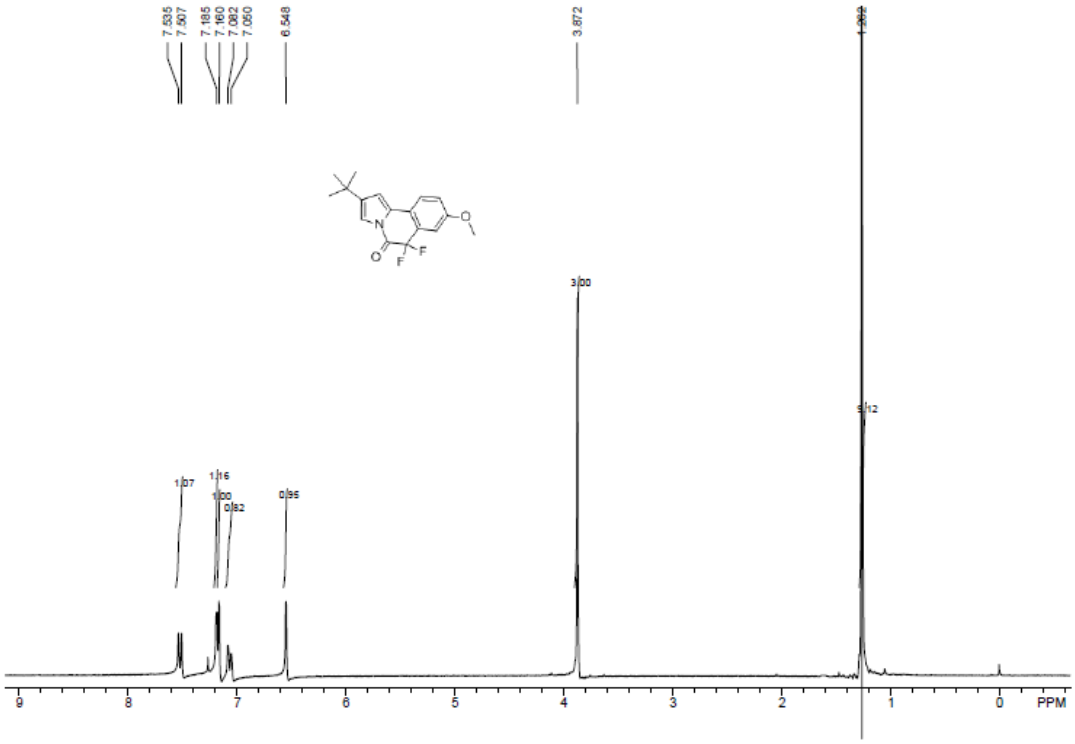
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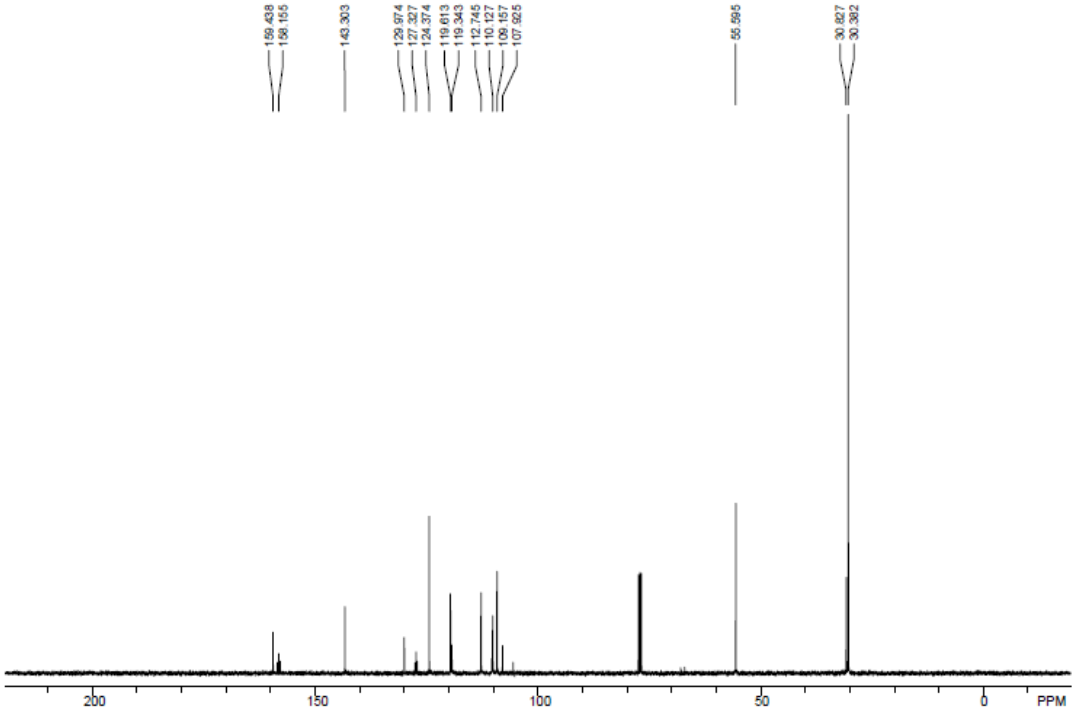
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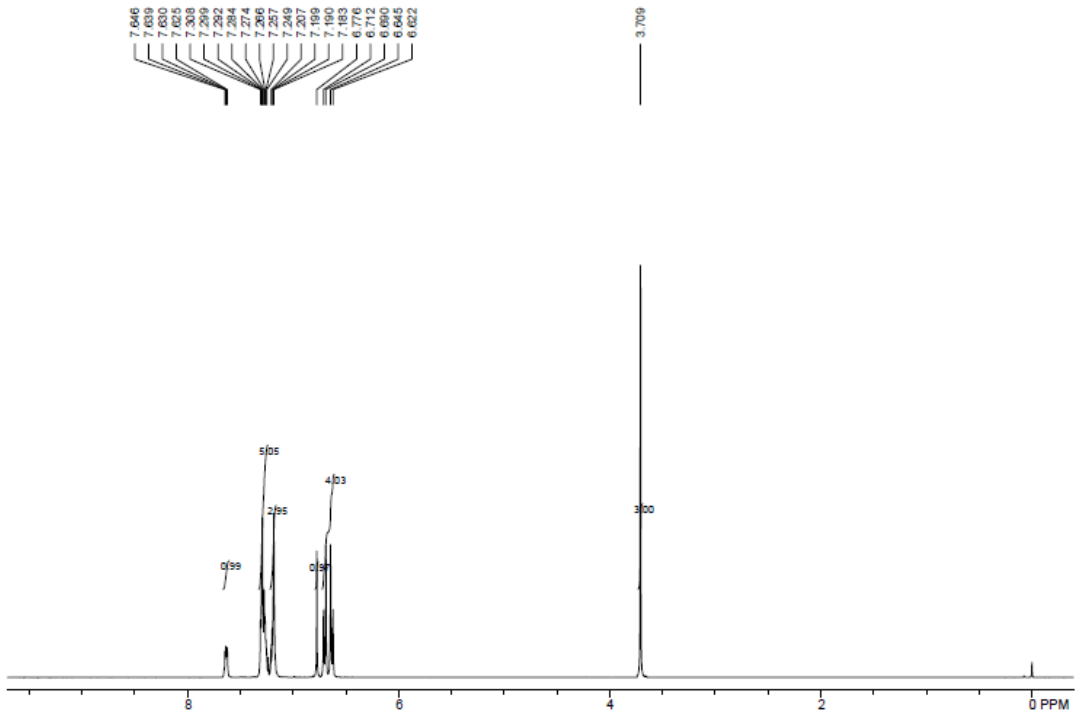
5a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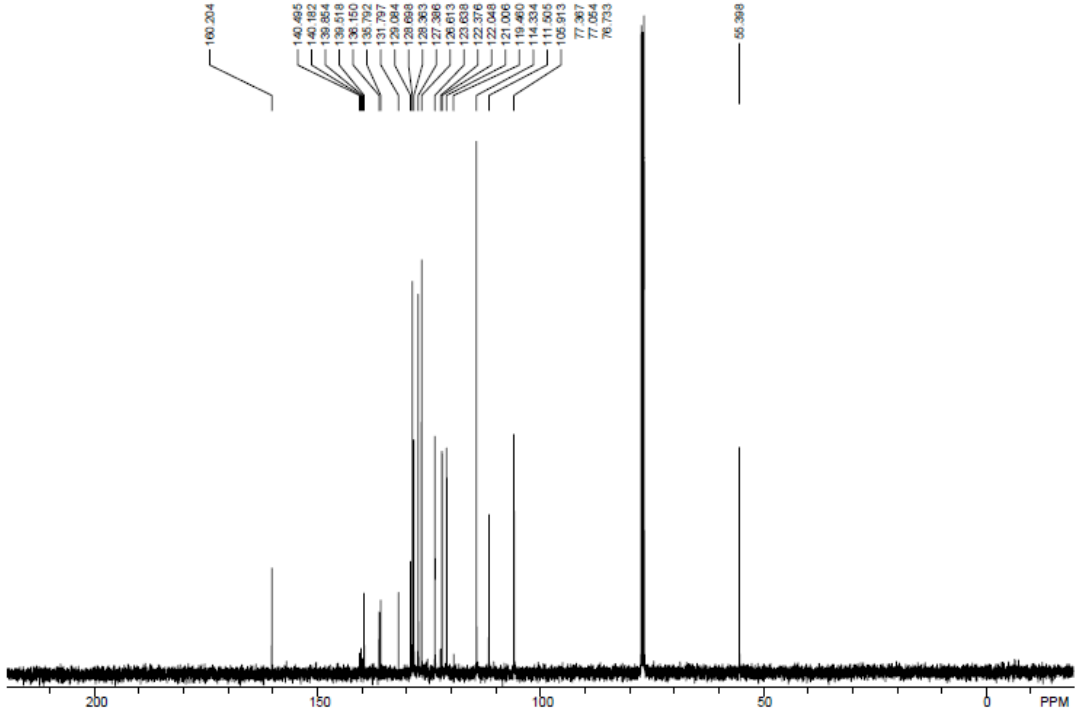
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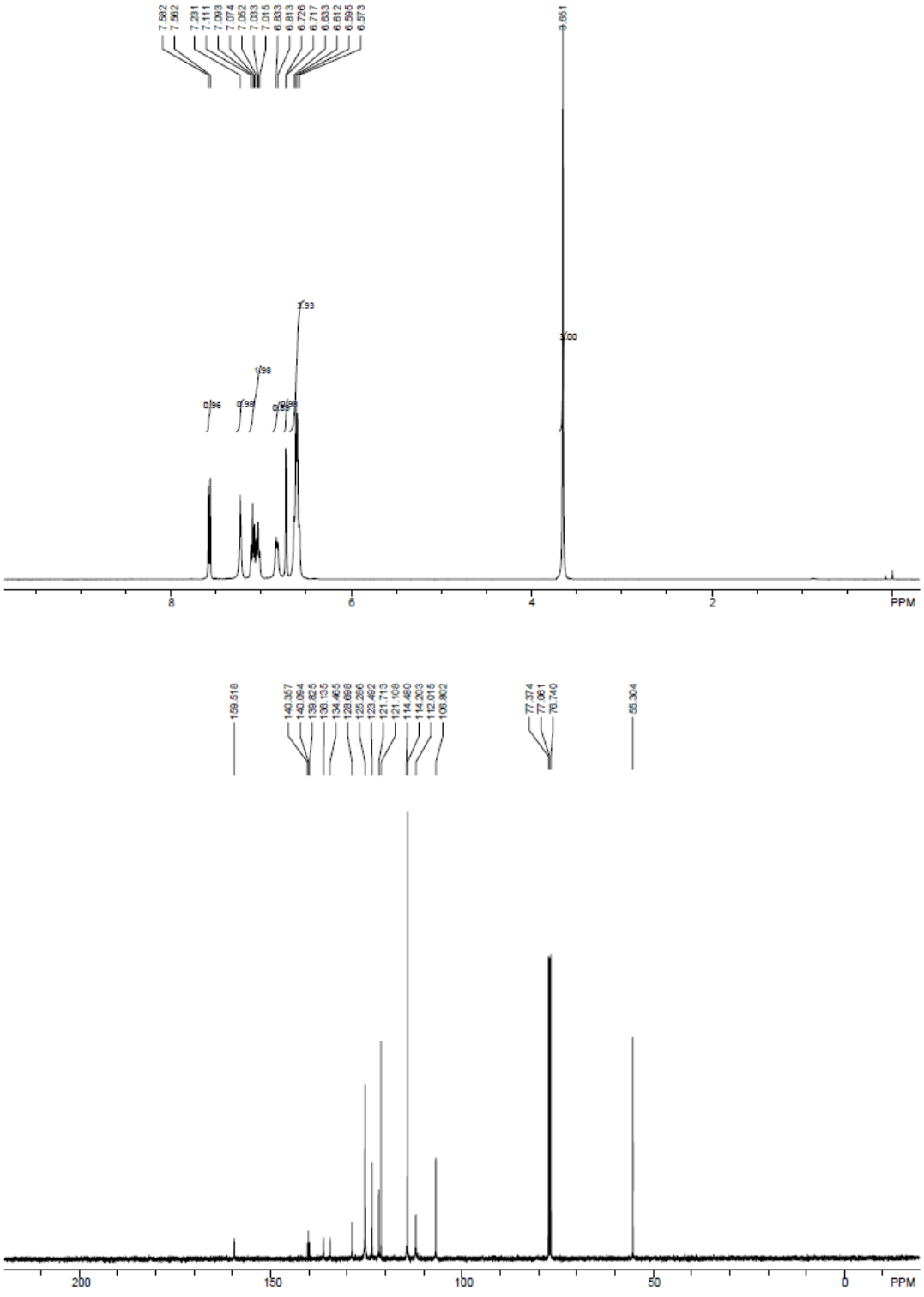
6a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4
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