Supporting Information

Synthesis of Di(hetero)aryl Sulfides by Defluorinative Sulfenylation of Polyfluoroalkyl Ketones with Sodium Sulfinates or Arylsulfonyl Chlorides

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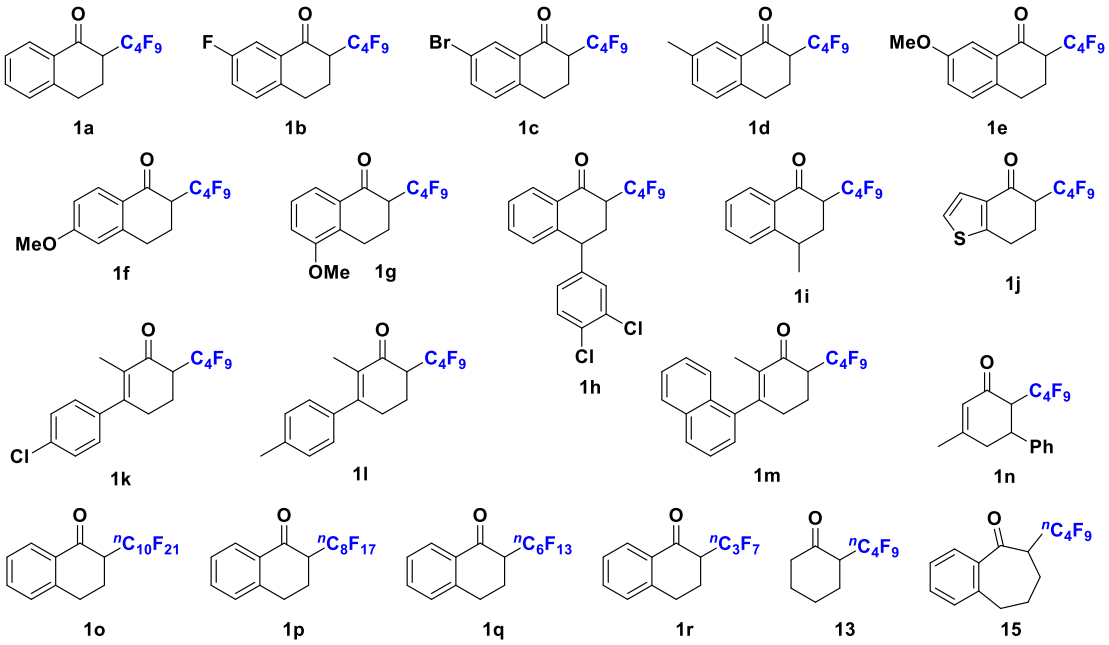
1. General information

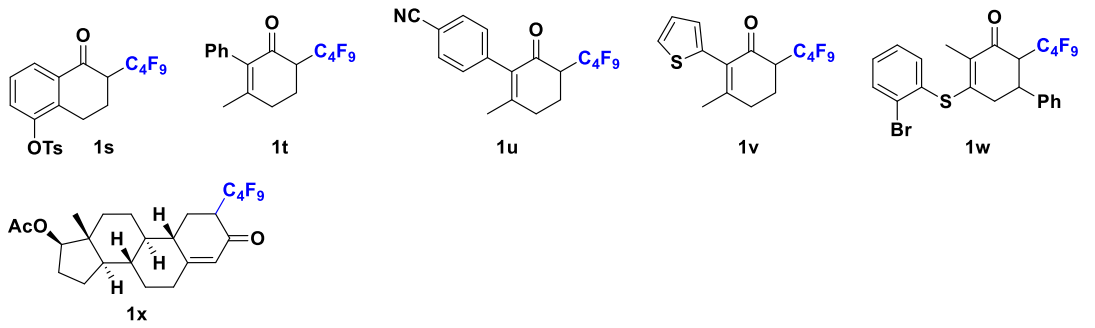
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N_2 atmosphere using undistilled solvent. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI Source). Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

2. General procedures for the synthesis of α-perfluoroalkyl ketones

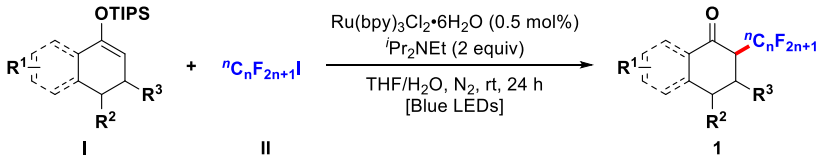
Various α-perfluoroalkyl ketones



unsuccessful substrates



General procedure A[1]



I II 1

According to MacMillan's reported method, a solution of enolsilane **I** (1.2 mmol), $Ru(bpy)_3Cl_2•6H_2O$ (4.5 mg, 0.006 mmol, 0.5 mol%), *N*-ethyl-*N*-isopropylpropan-2-amine (424.0 μL, 2.4 mmol), perfluoroalkyl iodide **II** (12 mmol), H_2O (32.0 μL, 17.8 mmol) in THF (6.0 mL) was stirred under nitrogen atmosphere (by 3 times' vacuum evacuation/N_2 backfill cycles) by irradiation with 8 W Blue LEDs at room temperature for 24 h. Upon completion of the reaction (indicated by TLC), solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (1:500) as eluent to afford the α-perfluoroalkyl ketone **1**.

Representative examples:

2-(Perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (1a)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 – 8.01 (m, 1H), 7.57 – 7.49 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 3.49 – 3.35 (m, 1H), 3.23 – 3.15 (m, 1H), 3.08 – 2.98 (m, 1H), 2.55 – 2.36 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.45 – -81.25 (m, 3F), -108.96 – -113.38 (m, 2F), -118.78 – -121.94 (m, 2F), -125.80 – -126.50 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3 (m), 142.9, 134.2, 132.3 (m), 128.7, 127.9, 127.0, 49.3 (t, J = 20.3 Hz), 27.1, 22.9 (m) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

4'-Chloro-2-methyl-4-(perfluorobutyl)-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (1k)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.35 – 3.20 (m, 1H), 2.83 – 2.71 (m, 1H), 2.70 – 2.58 (m, 1H), 2.46 – 2.29 (m, 2H), 1.79 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.80 – -80.92 (m, 3F), -110.28 – -114.09 (m, 2F), -119.53 – -121.96 (m, 2F), -125.96 – -126.14 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 154.9, 138.6, 134.2, 132.4, 128.6, 128.4, 47.6 (t, J = 20.6

Hz), 30.4, 21.8, 12.9 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

2,4'-Dimethyl-4-(perfluorobutyl)-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (1l)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.20 (m, 2H), 7.13 – 7.08 (m, 2H), 3.36 – 3.22 (m, 1H), 2.87 – 2.75 (m, 1H), 2.72 – 2.60 (m, 1H), 2.38 (s, 3H), 1.77 (t, *J* = 1.9 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.77 (t, *J* = 9.8 Hz, 3F), -109.70 – -114.25 (m, 2F), -119.29 – -122.06 (m, 2F), -125.98 (t, *J* = 15.4 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7 (t, *J* = 1.4 Hz), 156.6, 138.4, 137.3, 132.1, 129.1, 127.0, 47.6 (t, *J* = 20.2 Hz), 30.7, 22.0 (m), 21.2, 13.3 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

2-Methyl-3-(naphthalen-1-yl)-6-(perfluorobutyl)cyclohex-2-en-1-one (1m)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.86 (m, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.56 (m, 1H), 7.54 – 7.46 (m, 3H), 7.24 – 7.18 (m, 1H), 3.55 – 3.31 (m, 1H), 2.96 – 2.78 (m, 1H), 2.78 – 2.58 (m, 1H), 2.50 (d, *J* = 5.4 Hz, 2H), 1.56 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.80 (s, 3F), -109.50 – -113.97 (m, 2F), -119.36 – -122.12 (m, 2F), -125.92 (t, *J* = 12.4 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3 (m), 156.2 (d, *J* = 18.6 Hz), 138.1 (d, *J* = 5.1 Hz), 134.2 (d, *J* = 9.4 Hz), 133.6, 129.1 (d, *J* = 9.3 Hz), 128.7 (d, *J* = 9.2 Hz), 128.2 (d, *J* = 7.5 Hz), 126.8 (d, *J* = 16.2 Hz), 126.2 (d, *J* = 5.1 Hz), 125.4 (d, *J* = 11.6 Hz), 124.3 (d, *J* = 4.8 Hz), 123.6 (d, *J* = 3.6 Hz), 47.7 (q, *J* = 20.0 Hz), 31.1 (d, *J* = 23.2 Hz), 22.3 (m), 12.9 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

5-Methyl-2-(perfluorobutyl)-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (1n)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.18 (m, 3H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.12 (s, 1H), 4.00 – 3.89 (m, 1H), 3.47 – 3.26 (m, 1H), 3.03 (dd, *J* = 19.7, 5.2 Hz, 1H), 2.55 (d, *J* = 19.8 Hz, 1H), 2.03 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.81 – -81.32 (m, 3F), -110.57 – -112.97 (m, 2F), -119.91 – -

122.06 (m, 2F), -124.76 – -127.17 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.6 (m), 161.6, 142.0, 128.9, 128.9, 127.3 (t, J = 1.9 Hz), 126.8, 52.6 (t, J = 20.1 Hz), 37.4 (t, J = 1.7 Hz), 34.2, 24.1 (m) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

6-Methyl-3-(perfluorobutyl)-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one (1t)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 7.04 (d, J = 7.1 Hz, 2H), 3.40 – 3.19 (m, 1H), 2.73 – 2.59 (m, 1H), 2.56 – 2.43 (m, 1H), 2.42 – 2.30 (m, 2H), 1.81 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.91 (s, 3F), -110.17 – -113.94 (m, 2F), -119.49 – -122.08 (m, 2F), -126.06 (t, J = 14.9 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8 (m), 157.5, 137.9 (d, J = 1.1 Hz), 135.1, 129.8, 128.0, 127.3, 47.7 (t, J = 21.0 Hz), 30.1, 22.4, 21.4 (m) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

6'-Methyl-2'-oxo-3'-(perfluorobutyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (1u)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 3.43 – 3.26 (m, 1H), 2.82 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.46 – 2.37 (m, 2H), 1.85 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.83 (t, J = 9.7 Hz, 3F), -110.32 – -113.64 (m, 2F), -119.39 – -122.20 (m, 2F), -126.01 (t, J = 15.1 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2 (t, J = 2.1 Hz), 158.9, 140.1, 136.5 (d, J = 2.0 Hz), 131.9, 130.8, 118.7, 111.3, 47.5 (t, J = 21.4 Hz), 30.2, 22.4, 21.3 (m) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

3-Methyl-6-(perfluorobutyl)-2-(thiophen-2-yl)cyclohex-2-en-1-one (1v)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 4.9 Hz, 1H), 7.04 (t, J = 4.1 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 3.41 – 3.25 (m, 1H), 2.80 – 2.67 (m, 1H), 2.63 – 2.50 (m, 1H), 2.43 – 2.33 (m, 2H), 2.01 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.09 (t, J = 9.8 Hz, 3F), -109.64 – -113.10 (m, 2F), -118.74 – -

121.25 (m, 2F), -125.28 (t, *J* = 15.1 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.1 (m), 160.1, 134.6, 131.1, 128.4, 126.5, 126.4, 47.8 (t, *J* = 21.3 Hz), 30.8 (t, *J* = 1.5 Hz), 23.0, 21.3 (m) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

3-((2-Bromophenyl)thio)-5-methyl-6-(perfluorobutyl)cyclohex-2-en-1-one (1w)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.42 – 7.30 (m, 2H), 5.50 (d, *J* = 2.0 Hz, 1H), 3.12 – 2.80 (m, 3H), 2.27 (d, *J* = 18.4 Hz, 1H), 1.20 (d, *J* = 7.1 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.74 – -80.90 (m, 3F), -109.53 – -114.50 (m, 2F), -120.05 – -122.55 (m, 2F), -125.68 – -126.00 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.8 (m), 163.1, 137.7, 134.3, 132.1, 130.5, 128.8, 128.7, 120.1 (d, *J* = 1.7 Hz), 53.0 (t, *J* = 20.1 Hz), 33.6 (t, *J* = 2.6 Hz), 27.7 (m), 19.9 (d, *J* = 0.9 Hz) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-13-Methyl-3-oxo-2-(perfluorobutyl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acetate (1x)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96 (s, 1H), 4.67 – 4.57 (m, 1H), 3.18 (t, *J* = 17.9 Hz, 1H), 2.68 – 2.47 (m, 2H), 2.35 – 2.25 (m, 2H), 2.24 – 2.13 (m, 1H), 2.05 (s, 3H), 1.91 – 1.75 (m, 4H), 1.72 – 1.60 (m, 2H), 1.58 – 1.48 (m, 1H), 1.41 – 1.24 (m, 4H), 1.14 – 1.05 (m, 2H), 0.86 (s, 3H) ppm.

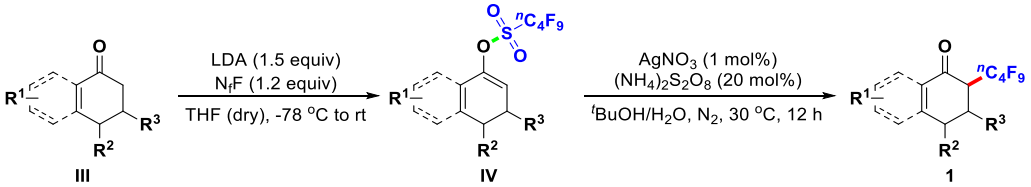
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.82 (t, *J* = 9.5 Hz, 3F), -110.30 – -113.92 (m, 2F), -120.11 – -122.69 (m, 2F), -125.83 (t, *J* = 15.1 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6 (m), 171.2, 167.9, 124.3 (d, *J* = 1.5 Hz), 82.4, 50.2, 49.4, 46.5 (t, *J* = 20.4 Hz), 42.6, 40.0, 39.9 (t, *J* = 1.4 Hz), 36.4, 35.5, 30.7, 27.4, 26.4 (m), 25.7, 23.3, 21.1, 12.0 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

5-(Perfluorobutyl)-6,7-dihydrobenzo[*b*]thiophen-4(5*H*)-one (**1j**), 5-oxo-6-(perfluorobutyl)-5,6,7,8-tetrahydronaphthalen-1-yl 4-methylbenzenesulfonate (**1s**), 2-(perfluorodecyl)-3,4-

dihydronaphthalen-1(2*H*)-one (**1o**), 2-(perfluorooctyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1p**), 2-(perfluorohexyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1q**), and 2-(perfluoropropyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1r**) were synthesized according to general procedure A.

General procedure B[2]



Step 1: The solution of ketone **III** (5 mmol) in dry THF (25 mL) was cooled to -78 °C and then lithium diisopropylamide (LDA, 3.75 mL, 7.5 mmol, 2.0 mol/L in THF/hexane) was dropwise added to the reaction mixture. Nonafluorobutanesulfonyl fluoride (**N_fF**, 1.1 mL, 6 mmol) was added slowly by a syringe over 10 min. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) on Et_3N-treated silica gel eluting with petroleum ether to afford enol nonaflate **IV**.

Step 2: A solution of enol nonaflate **IV** (0.8 mmol), $(NH_4)_2S_2O_8$ (0.16 mmol, 37 mg), and $AgNO_3$ (0.008 mmol, 1.4 mg) in ^{t}BuOH (2.0 mL) and H_2O (2.0 mL) was stirred vigorously under nitrogen atmosphere (by 3 times' vacuum evacuation/N_2 backfill cycles) at 30 °C for 12 h. Upon completion of the reaction (indicated by TLC), the reaction mixture was diluted with dichloromethane. The organic layer was separated and the aqueous layer was washed with dichloromethane (3×10 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate as eluent to afford α-perfluoroalkyl ketone **1**.

Representative examples:

6-Methoxy-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (1f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.8 Hz, 1H), 6.86 (dd, J = 8.8, 2.5 Hz, 1H), 6.70 (d,

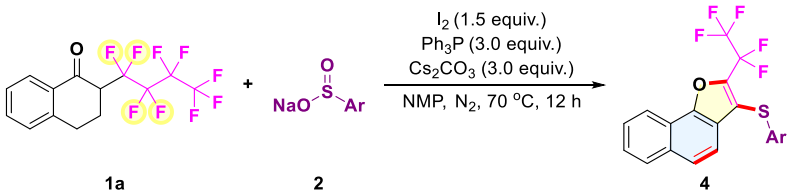
J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.44 – 3.30 (m, 1H), 3.20 – 3.10 (m, 1H), 3.00 – 2.91 (m, 1H), 2.50 – 2.34 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.45 – -81.24 (m, 3F), -108.98 – -113.48 (m, 2F), -118.81 – -121.88 (m, 2F), -125.99 – -126.55 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.8 (m), 164.1, 145.5, 130.3, 125.8, 113.7, 112.3, 55.4, 48.9 (t, J = 20.4 Hz), 27.3, 23.0 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

7-Fluoro-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1b**), 7-bromo-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1c**), 7-methyl-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1d**), 7-methoxy-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1e**), 5-methoxy-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1g**), 4-(3,4-dichlorophenyl)-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1h**), 4-methyl-2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1i**), 2-(perfluorobutyl)cyclohexan-1-one (**13**), and 6-(perfluorobutyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (**15**) were synthesized according to general procedure B.

3. General procedures for the synthesis of highly functionalized naphtho[1,2-*b*]furan derivatives by using sodium sulfinates



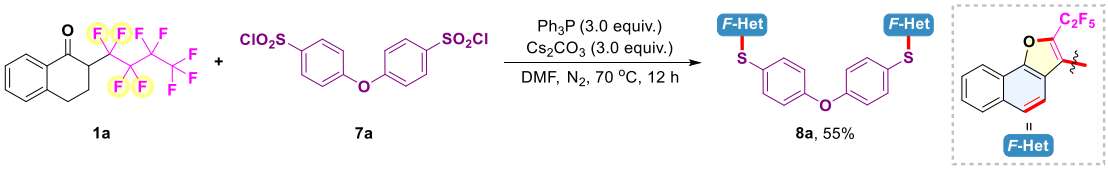
A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 73 mg, 0.2 mmol), sodium sulfinates **2** (0.24 mmol), iodine (76 mg, 0.3 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in NMP (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate or dichloromethane/methanol as eluent to afford the pure products **4**.

4. General procedures for the synthesis of highly functionalized naphtho[1,2-*b*]furan/benzofuran derivatives by using arylsulfonyl chlorides

A solution of polyfluoroalkyl ketone **1** (0.2 mmol), arylsulfonyl chloride **3** (0.24 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate or dichloromethane/methanol as eluent to afford the pure products **5** or **6**.

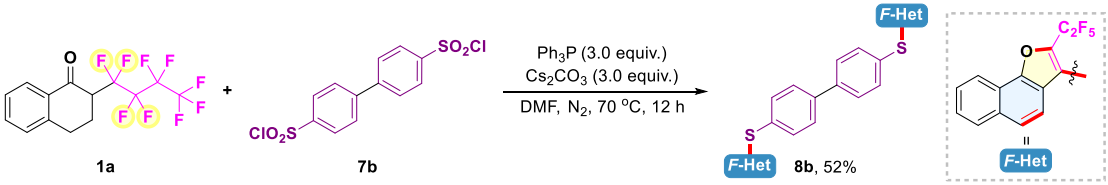
5. Further applications for the synthesis of complex molecules

1) The reaction of α-perfluoroalkyl ketone 1a with 4,4'-oxydibenzenesulfonyl chloride (7a)



A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 146 mg, 0.4 mmol), 4,4'-oxydibenzenesulfonyl chloride (**7a**, 73 mg, 0.2 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (500/1 ~ 200/1) as eluent to afford the pure product **8a** (88 mg, 55%).

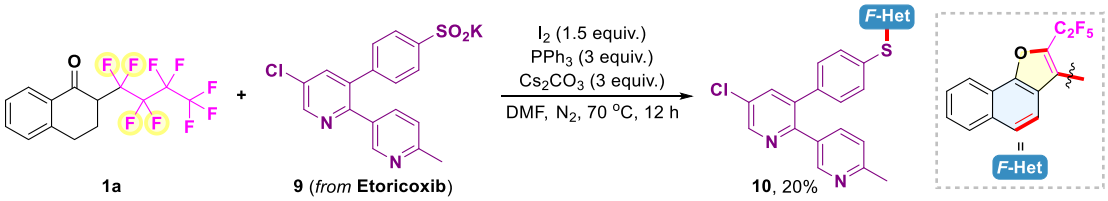
2) The reaction of α-perfluoroalkyl ketone 1a with [1,1'-biphenyl]-4,4'-disulfonyl dichloride (7b)



A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 146 mg, 0.4 mmol), [1,1'-biphenyl]-4,4'-disulfonyl dichloride (**7b**, 70 mg, 0.2 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12

h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (500/1 ~ 200/1) as eluent to afford the pure product **8b** (82 mg, 52%).

3) The reaction of α-perfluoroalkyl ketone 1a with potassium 4-(5-chloro-6'-methyl-[2,3'-bipyridin]-3-yl)benzenesulfinate (9)

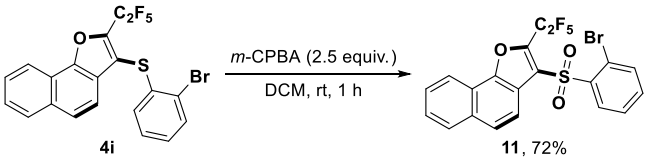


1a **9** (*from* **Etoricoxib**) **10**, 20%

A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 73 mg, 0.2 mmol), potassium 4-(5-chloro-6'-methyl-[2,3'-bipyridin]-3-yl)benzenesulfinate (**9**, 92 mg, 0.24 mmol), iodine (76 mg, 0.3 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (500/1 ~ 200/1) as eluent to afford the pure product **10** (24 mg, 20%).

6. Further transformations of product 4i

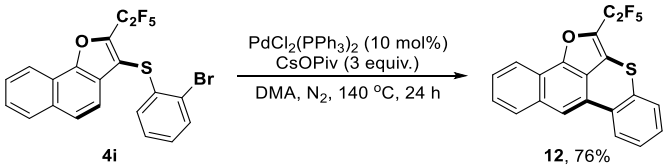
1) Synthesis of diaryl sulfone 11



4i **11**, 72%

A solution of 3-((2-bromophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (**4i**, 142 mg, 0.3 mmol) and 3-chloroperoxybenzoic acid (*m*-CPBA, 173 mg, 0.75 mmol) in DCM (2.0 mL) was stirred at room temperature for 1 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with DCM (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure product 3-((2-bromophenyl)sulfonyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (**11**, 109 mg, 72%).

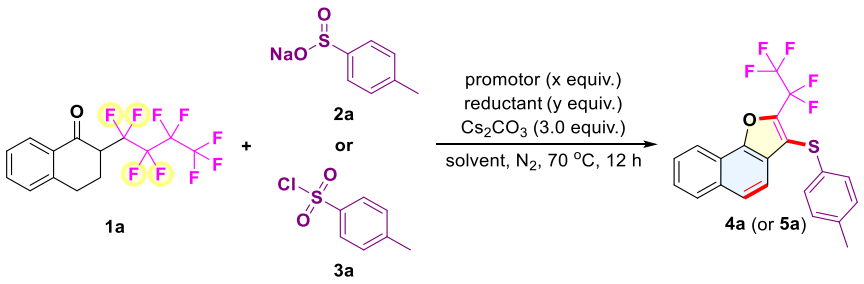
2) Synthesis of fused heterocycle 12



A solution of 3-((2-bromophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (**4i**, 142 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol), and CsOPiv (210 mg, 0.90 mmol) in DMA (2.0 mL) was stirred under nitrogen atmosphere at 140 °C for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with DCM (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure product 6-(perfluoroethyl)dibenzo[3,4:6,7]isothiochromeno[8,1-*bc*]furan (**12**, 90 mg, 76%).

7. Optimization of reaction conditions

Table S1. Optimization of reaction conditions.[a]

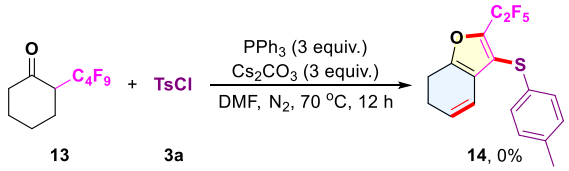


entry	with **2a** or **3a**	promoter (x equiv.)/reductant (y equiv.)	solvent	yield (%)[b]
1	**2a**	I_2 (1)/PPh_3 (2)	DMF	37
2	**2a**	I_2 (1)/PPh_3 (2)	DMSO	trace
3	**2a**	I_2 (1)/PPh_3 (2)	MeCN	<5
4	**2a**	I_2 (1)/PPh_3 (2)	$MeNO_2$	trace
5	**2a**	I_2 (1)/PPh_3 (2)	^{t}BuOH	0
6	**2a**	I_2 (1)/PPh_3 (2)	DMA	35
7	**2a**	I_2 (1)/PPh_3 (2)	NMP	56
8	**2a**	I_2 (1)/PPh_3 (2)	NMP	<10[c]
9	**2a**	I_2 (1)/P(^{n}Bu)$_3$ (2)	NMP	0
10	**2a**	I_2 (1)/$(PhO)_3P$ (2)	NMP	21
11	**2a**	I_2 (1)/$(EtO)_2P(O)H$ (2)	NMP	13
12	**2a**	I_2 (1)/--	NMP	0
13	**2a**	--/PPh_3 (2)	NMP	<10
14	**2a**	NaI (1)/PPh_3 (2)	NMP	trace
15	**2a**	NIS (1)/PPh_3 (2)	NMP	<10
16	**2a**	$PhI(OAc)_2$ (1)/PPh_3 (2)	NMP	<5
17	**2a**	TBAI (1)/PPh_3 (2)	NMP	trace
18	**2a**	I_2 (1.5)/PPh_3 (3)	NMP	70 (66)[d]
19	**3a**	--/PPh_3 (3)	NMP	68
20	**3a**	--/PPh_3 (3)	DMF	76 (71)[d]
21	**3a**	--/PPh_3 (3)	DMSO	<5
22	**3a**	--/PPh_3 (3)	DMA	39
23	**3a**	--/PPh_3 (3)	$CDCl_3$	<10
24	**3a**	--/PPh_3 (3)	THF	<10
25	**3a**	--/PPh_3 (3)	1,4-dioxane	<5

[a] Reaction conditions: **1a** (0.20 mmol), **2a** or **3a** (0.24 mmol), promoter (0-0.3 mmol), reductant (0-0.6 mmol), and Cs_2CO_3 (0.60 mmol) in solvent (2.0 mL) at 70 °C for 12 h under N_2. [b] Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard. [c] At 50 °C. [d] Isolated yield.

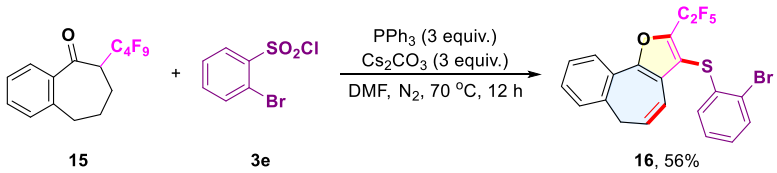
8. Mechanistic studies

1) Control experiment of 2-(perfluorobutyl)cyclohexan-1-one (13) with 4-methylbenzenesulfonyl chloride (3a)



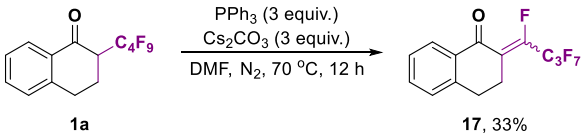
A solution of 2-(perfluorobutyl)cyclohexan-1-one (**13**, 63 mg, 0.2 mmol), 4-methylbenzenesulfonyl chloride (**3a**, 46 mg, 0.24 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. No desired product **14** was obtained. **This result suggested that the phenyl moiety or unsaturated C=C bond in the α-perfluoroalkyl ketone 1 was essential for the established cascade reaction.**

2) Control experiment of 6-(perfluorobutyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (15) with 2-bromobenzenesulfonyl chloride (3e)



A solution of 6-(perfluorobutyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (**15**, 76 mg, 0.2 mmol), 2-bromobenzenesulfonyl chloride (**3e**, 61 mg, 0.24 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with DCM (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure product **16** (55 mg, 56%). **This result suggested that the deprotonation at the β and γ positions of the perfluoroalkyl ketone 1 might be a vital course for the successive defluorination.**

3) Detection of the key intermediate 2-(perfluorobutylidene)-3,4-dihydronaphthalen-1(2*H*)-one (17)

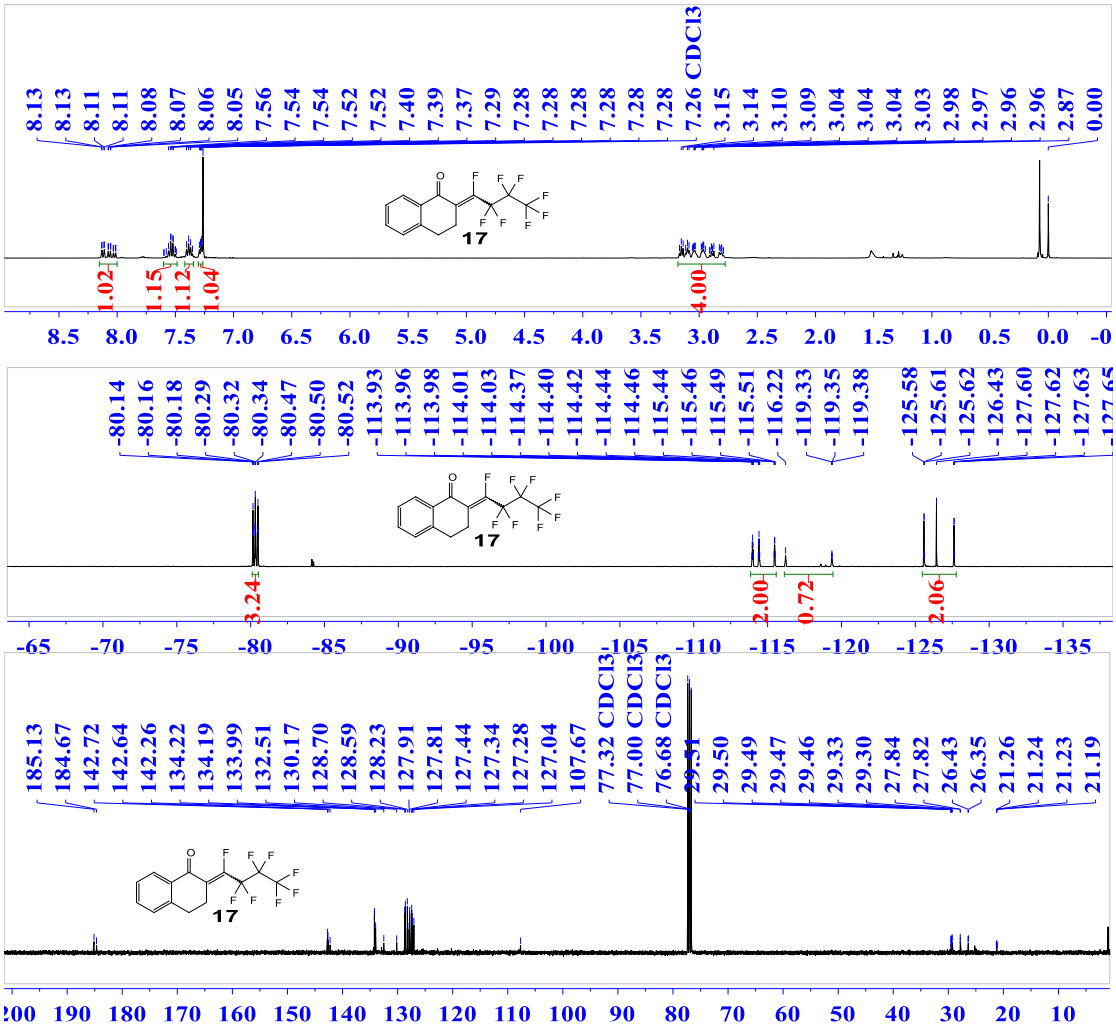


A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**1a**, 73 mg, 0.2 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl

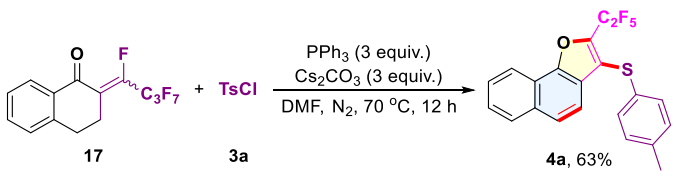
solution (20 mL) and diluted with DCM (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure 2-(perfluorobutylidene)-3,4-dihydronaphthalen-1(2*H*)-one (**17**, 23 mg, 33%). **This result suggested that compound 17 was the possible reaction intermediate.**

53% NMR yield of compound 17 was also obtained for the example of 5l in table 2.

NMR spectra of compound 17:



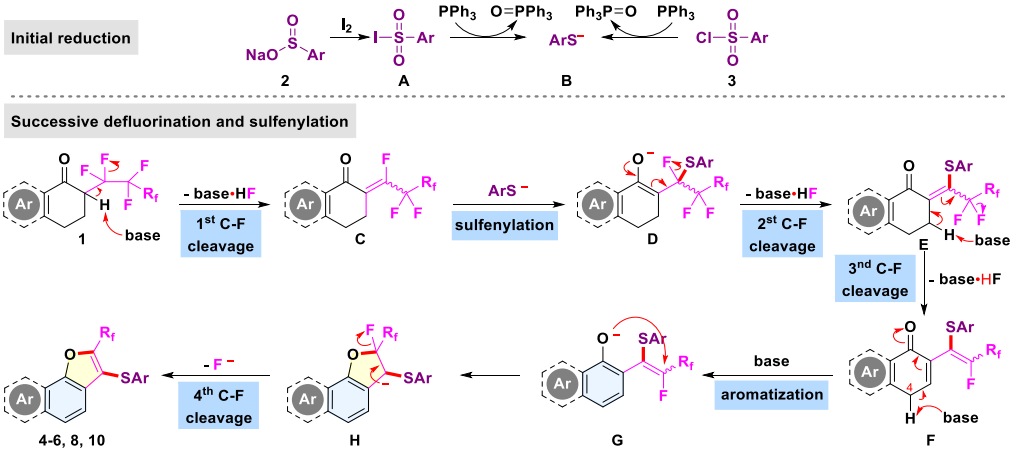
4) The reaction of 2-(perfluorobutylidene)-3,4-dihydronaphthalen-1(2*H*)-one (17) with 4-methylbenzenesulfonyl chloride (3a)



17 3a **4a**, 63%

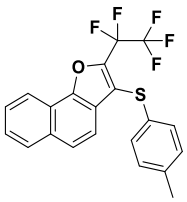
A solution of 2-(perfluorobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (**17**, 69 mg, 0.2 mmol), 4-methylbenzenesulfonyl chloride (**3a**, 46 mg, 0.24 mmol), triphenylphosphine (157 mg, 0.6 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in DMF (2.0 mL) was stirred under N_2 atmosphere at 70 °C for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and diluted with DCM (20 mL). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether as eluent to afford the product **4a** (51 mg, 63%). **This result further suggested that compound 17 was the possible reaction intermediate.**

5) Proposed reaction mechanism



Scheme S1 Proposed reaction mechanism.

9. Characterization data for products



2-(Perfluoroethyl)-3-(*p*-tolylthio)naphtho[1,2-*b*]furan (4a & 5a):

Yield = 66% (**4a**, 54 mg). Yield = 71% (**5a**, 58 mg). White solid. M.p. 102.7–103.4 °C.

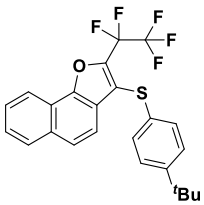
IR (KBr): ν = 3072, 1594, 1564, 808, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.64 – 7.49 (m, 3H), 7.29 (d, J = 8.7 Hz, 1H), 7.21 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.63 (t, J = 4.1 Hz, 3F), -112.18 – -113.16 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5, 141.3 (t, J = 29.6 Hz), 137.0, 132.7, 130.3, 130.0, 129.8, 129.3, 128.4, 127.1, 126.9, 125.1, 124.3, 121.0, 120.3, 118.5, 21.0 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{14}F_5OS$ $[M+H]^+$ 409.0680, found: 409.0676.



3-((4-(*tert*-Butyl)phenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4b):

Yield = 68% (61 mg). Light yellow oil.

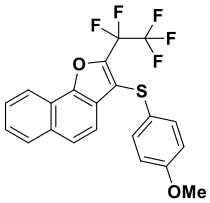
IR (KBr): ν = 2965, 1566, 1498, 810, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.65 – 7.52 (m, 3H), 7.34 (d, J = 8.7 Hz, 1H), 7.27 – 7.23 (m, 4H), 1.26 (s, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.51 – -83.68 (m, 3F), -112.53 – -112.76 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5 (d, J = 0.9 Hz), 150.2, 141.6 (t, J = 29.5 Hz), 132.8, 130.5, 128.9, 128.4, 127.1, 126.9, 126.3, 125.1, 124.4, 121.0, 120.3, 118.6, 118.1 (t, J = 36.3 Hz), 34.5, 31.2 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{20}F_5OS$ $[M+H]^+$ 451.1150, found: 451.1150.



3-((4-Methoxyphenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4c & 5b):

Yield = 62% (**4c**, 53 mg). Yield = 68% (**5b**, 58 mg). Light yellow solid. M.p. 75.5–76.9 ºC.

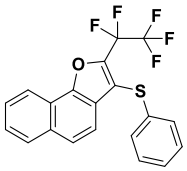
IR (KBr): ν = 3068, 1591, 1494, 809, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.67 – 7.53 (m, 3H), 7.40 – 7.33 (m, 2H), 7.30 (d, J = 8.7 Hz, 1H), 6.85 – 6.77 (m, 2H), 3.76 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.63 (t, J = 3.4 Hz, 3F), -112.43 – -112.50 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 151.4 (t, J = 1.5 Hz), 140.6 (t, J = 29.1 Hz), 132.7, 132.2, 128.3, 127.1, 126.9, 125.0, 124.2, 124.1, 121.0, 120.3, 119.3 (m), 118.5, 114.9, 55.3 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{14}F_5O_2S$ $[M+H]^+$ 425.0629, found: 425.0636.



2-(Perfluoroethyl)-3-(phenylthio)naphtho[1,2-*b*]furan (4d):

Yield = 48% (38 mg). White solid. M.p. 44.1–45.2 °C.

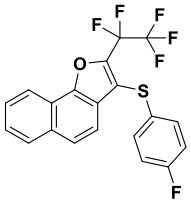
IR (KBr): ν = 3069, 1576, 1513, 809, 740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.68 – 7.56 (m, 3H), 7.35 – 7.27 (m, 3H), 7.25 – 7.15 (m, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.73 (s, 3F), -112.80 – -112.92 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5, 141.8 (t, J = 29.7 Hz), 134.2, 132.8, 129.2, 128.7, 128.4, 127.2, 127.0, 126.8, 125.2, 124.2, 121.0, 120.3, 118.5, 117.5 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{12}F_5OS$ $[M+H]^+$ 395.0524, found: 395.0522.



3-((2-Fluorophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4e):

Yield = 62% (51 mg). Light yellow solid. M.p. 84.2–85.6 °C.

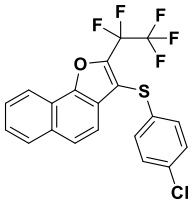
IR (KBr): ν = 3064, 1640, 1589, 810, 775 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.67 – 7.53 (m, 3H), 7.35 – 7.26 (m, 3H), 7.00 – 6.89 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.62 (t, J = 3.0 Hz, 3F), -112.54 – -112.77 (m, 2F), -114.18 – -114.25 (m, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (m), 151.6, 141.5 (t, J = 29.9 Hz), 132.8, 131.3 (m), 129.1 (m), 128.4, 127.2, 127.1, 125.3, 124.0, 121.0, 120.3, 118.2, 116.5, 116.3 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}F_6OS$ $[M+H]^+$ 413.0429, found: 413.0424.



3-((4-Chlorophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4f):

Yield = 54% (46 mg). Yellow solid. M.p. 88.8–90.0 °C.

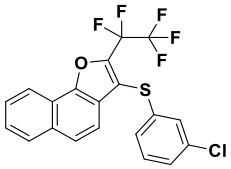
IR (KBr): ν = 3057, 1571, 1474, 812, 744 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 – 8.31 (m, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.67 – 7.54 (m, 3H), 7.31 (d, J = 8.7 Hz, 1H), 7.23 – 7.18 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.62 (t, J = 3.5 Hz, 3F), -112.74 – -112.76 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (t, J = 1.3 Hz), 142.1 (t, J = 29.7 Hz), 132.8, 132.8, 129.8, 129.4, 129.3, 128.5, 127.3, 127.1, 125.5, 124.0, 121.0, 120.3, 118.2, 116.9 (t, J = 1.0 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}ClF_5OS$ $[M+H]^+$ 429.0134, found: 429.0137.



3-((3-Chlorophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4g & 5c):

Yield = 58% (**4g**, 50 mg). Yield = 70% (**5c**, 60 mg). White solid. M.p. 84.7–86.3 °C.

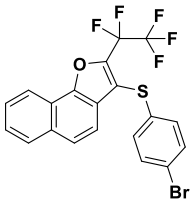
IR (KBr): ν = 3061, 1576, 1465, 812, 778 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.66 (ddd, J = 8.2, 4.6, 2.3 Hz, 2H), 7.59 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 7.26 (q, J = 1.1 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.62 (t, J = 3.5 Hz, 3F), -112.74 – -112.76 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (t, J = 1.1 Hz), 142.4 (t, J = 30.0 Hz), 136.4, 135.0, 132.9, 130.2, 128.5, 127.9, 127.3, 127.1, 126.9, 126.3, 125.6, 124.0, 121.0, 120.3, 118.1, 116.3 (d, J = 1.7 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}ClF_5OS$ $[M+H]^+$ 429.0134, found: 429.0133.



3-((4-Bromophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4h):

Yield = 58% (55 mg). Yellow solid. M.p. 90.6–92.4 °C.

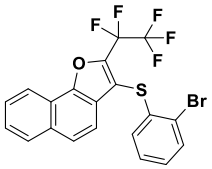
IR (KBr): ν = 3056, 1571, 1557, 810, 743 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 – 8.31 (m, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.61 –7.55 (m, 1H), 7.37 – 7.32 (m, 2H), 7.31 (d, J = 8.7 Hz, 1H), 7.14 – 7.09 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.62 (t, J = 3.8 Hz, 3F), -112.82 (q, J = 3.8 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (t, J = 1.3 Hz), 142.1 (t, J = 29.4 Hz), 133.5, 132.8, 132.2, 129.8, 128.4, 127.3, 127.1, 125.5, 123.9, 121.0, 120.6, 120.3, 118.1, 116.6 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}BrF_5OS$ $[M+H]^+$ 472.9629, found: 472.9635.



3-((2-Bromophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4i & 5e):

Yield = 55% (**4i**, 52 mg). Yield = 79% (**5e**, 75 mg). Yellow solid. M.p. 79.0–80.4 °C.

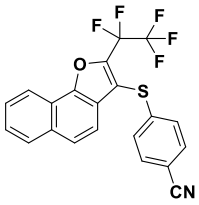
IR (KBr): ν = 3057, 1639, 1576, 811, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.66 – 7.57 (m, 2H), 7.37 (d, J = 8.7 Hz, 1H), 7.12 – 7.00 (m, 2H), 6.87 – 6.78 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.51 (t, J = 3.4 Hz, 3F), -113.03 (q, J = 3.3 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7 (t, J = 0.9 Hz), 143.0 (t, J = 29.6 Hz), 136.2, 133.0, 133.0, 128.5, 127.9, 127.9, 127.3, 127.2, 127.1, 125.6, 124.0, 121.4, 121.0, 120.3, 118.2, 116.3 (t, J = 1.6 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}BrF_5OS$ $[M+H]^+$ 472.9629, found: 472.9633.



4-((2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)thio)benzonitrile (4j & 5f):

Yield = 55% (**3j**, 46 mg). Yield = 55% (**5f**, 46 mg). Yellow solid. M.p. 110.2–110.3 °C.

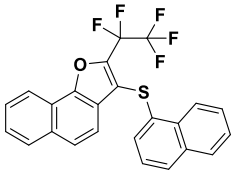
IR (KBr): ν = 3052, 2226, 1592, 1560, 808, 787 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 – 8.34 (m, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.66 – 7.60 (m, 1H), 7.51 – 7.46 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.24 – 7.20 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.62 (t, *J* = 4.2 Hz, 3F), -113.10 (q, *J* = 3.2 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 143.3 (t, *J* = 29.3 Hz), 141.8, 133.0, 132.6, 128.5, 127.5, 127.4, 127.0, 126.0, 123.7, 121.0, 120.3, 118.4, 117.7, 114.4 (t, *J* = 2.9 Hz), 109.6 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{11}F_5NOS$ $[M+H]^+$ 420.0476, found: 420.0474.



3-(Naphthalen-1-ylthio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4k & 5h):

Yield = 43% (**4k**, 38 mg). Yield = 67% (**5h**, 60 mg). Yellow solid. M.p. 88.0–89.5 °C.

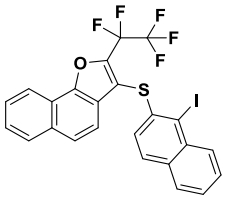
IR (KBr): ν = 3053, 1564, 1504, 810, 787 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 – 8.46 (m, 1H), 8.37 – 8.32 (m, 1H), 7.89 – 7.82 (m, 2H), 7.72 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.57 – 7.53 (m, 2H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.50 (t, *J* = 4.0 Hz, 3F), -112.45 – -113.34 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ =151.6 (m), 141.7 (t, *J* = 29.9 Hz), 133.9, 132.8, 131.9, 131.1 (t, *J* = 1.1 Hz), 128.7, 128.4, 127.6, 127.5, 127.1, 127.0, 126.8, 126.6, 125.7, 125.1, 124.3, 124.1, 121.0, 120.3, 118.4, 117.8 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{14}F_5OS$ $[M+H]^+$ 445.0680, found: 445.0681.



3-((1-Iodonaphthalen-2-yl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (4l):

Yield = 46% (52 mg). White solid. M.p. 124.2–125.7 °C.

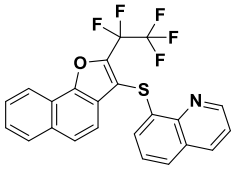
IR (KBr): ν = 3066, 1594, 1566, 808, 776 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.44 – 8.38 (m, 1H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.63 – 7.55 (m, 2H), 7.51 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.27 – 7.20 (m, 1H), 6.97 (dd, *J* = 7.5, 1.1 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.05 – -84.10 (m, 3F), -113.28 (q, *J* = 3.8 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8 (t, *J* = 1.1 Hz), 149.6, 144.8 (t, *J* = 29.3 Hz), 136.3, 136.3, 133.0, 128.5, 128.3, 127.3, 127.0, 126.7, 125.4, 124.9, 124.7, 124.5, 122.0, 121.1, 120.3, 118.6, 116.0 (t, *J* = 2.1 Hz), 110.1, 109.7 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{13}F_5IOS$ $[M+H]^+$ 570.9646, found: 570.9648.



8-((2-(Perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)thio)quinoline (4m & 5j):

Yield = 42% (**4m**, 37 mg). Yield = 71% (**5j**, 63 mg). Yellow solid. M.p. 85.1–85.5 °C.

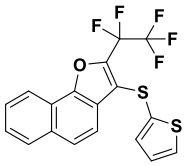
IR (KBr): ν = 3053, 1590, 1564, 810, 787 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.72 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.62 (qd, *J* = 8.2, 1.3 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.51 (t, *J* = 4.1 Hz, 3F), -112.19 – -113.65 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (t, *J* = 1.1 Hz), 144.7 (t, *J* = 30.8 Hz), 133.9, 132.8, 131.9, 131.1, 128.7, 128.4, 127.6, 127.5, 127.1, 127.0, 126.8, 126.6, 125.7, 125.1, 124.3, 124.1, 121.0, 120.3, 118.4 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{13}F_5NOS$ $[M+H]^+$ 446.0633, found: 446.0630.



2-(Perfluoroethyl)-3-(thiophen-2-ylthio)naphtho[1,2-*b*]furan (4n & 5k):

Yield = 61% (**3n**, 49 mg). Yield = 36% (**5k**, 29 mg). Yellow solid. M.p. 99.7–100.4 °C.

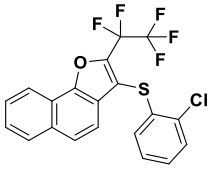
IR (KBr): ν = 3101, 1566, 1522, 758, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.61 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.33 (d, *J* = 4.8 Hz, 2H), 7.00 – 6.93 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.54 (s, 3F), -112.37 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3 (t, *J* = 1.0 Hz), 140.3 (t, *J* = 29.4 Hz), 134.3, 132.7, 131.0, 130.2, 128.3, 127.5, 127.1, 127.0, 125.2, 124.0, 120.9, 120.3, 119.5, 118.1 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{18}H_{10}F_5OS_2$ $[M+H]^+$ 401.0088, found: 401.0088.



3-((2-Chlorophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (5d):

Yield = 61% (52 mg). Yellow solid. M.p. 112.0–112.3 °C.

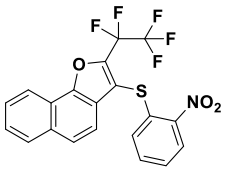
IR (KBr): ν = 3062, 1593, 1572, 805, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.60 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.10 (td, *J* = 7.7, 1.5 Hz, 1H), 7.00 (td, *J* = 7.7, 1.4 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.5 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.56 (t, *J* = 4.1 Hz, 3F), -113.12 (q, *J* = 4.0 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 151.7 (m), 143.1 (t, *J* = 29.6 Hz), 134.1, 133.0, 131.9, 129.8, 128.5, 128.1, 127.3, 127.2, 127.1, 125.6, 124.1, 121.0, 120.3, 118.2, 115.8 (t, *J* = 2.1 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}ClF_5OS$ $[M+H]^+$ 429.0134, found: 429.0137.



3-((2-Nitrophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (5g):

Yield = 84% (74 mg). Yellow solid. M.p. 136.6–137.8 °C.

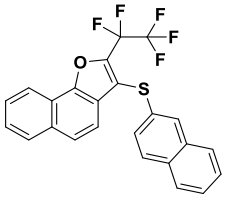
IR (KBr): ν = 3055, 1592, 1567, 818, 781 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.2 Hz, 1H), 8.36 – 8.29 (m, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 8.3, 3.9 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.38 – 7.26 (m, 3H), 6.95 (d, *J* = 7.5 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.50 (s, 3F), -113.12 – -113.25 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9 (t, *J* = 0.9 Hz), 145.2, 144.2 (t, *J* = 29.3 Hz), 135.4, 133.9, 133.1, 128.6, 128.0, 127.5, 127.4, 126.2, 126.0, 125.8, 123.8, 121.0, 120.3, 117.7, 115.4 (t, *J* = 1.6 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}F_5NO_3S$ $[M+H]^+$ 440.0374, found: 440.0378.



3-(Naphthalen-2-ylthio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (5i):

Yield = 70% (62 mg). White solid. M.p. 135.1–135.8 °C.

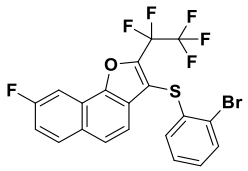
IR (KBr): ν = 3366, 1771, 1579, 1501, 810, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.74 (m, 2H), 7.70 – 7.62 (m, 3H), 7.58 – 7.53 (m, 2H), 7.45 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.55 (t, *J* = 3.8 Hz, 3F), -117.70 (q, *J* = 3.8 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (t, *J* = 1.2 Hz), 141.8 (t, *J* = 29.4 Hz), 133.6, 132.8, 132.0, 131.5, 129.0, 128.4, 127.8, 127.2, 127.2, 127.1, 127.0, 126.8, 126.3, 126.1, 125.3, 124.3, 121.0, 120.3, 118.5, 117.4 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{14}F_5OS$ $[M+H]^+$ 445.0680, found: 445.0685.



3-((2-Bromophenyl)thio)-8-fluoro-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6a):

Yield = 74% (73 mg). White solid. M.p. 102.1–102.5 °C.

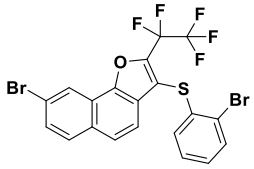
IR (KBr): ν = 2973, 1647, 1600, 828, 749 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 – 7.88 (m, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.38 – 7.31 (m, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.11 – 6.98 (m, 2H), 6.83 – 6.74 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.54 (s, 1.5F), -86.81 (s, 1.0F), -89.26 (s, 0.5F), -110.74 (s, 0.5F), -113.19 (s, 1.0F), -116.46 (s, 1.5F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 47.9 Hz), 151.2 (m), 143.5 (t, *J* = 29.4 Hz), 135.9, 133.1, 131.1 (d, *J* = 9.2 Hz), 129.8 (d, *J* = 1.4 Hz), 128.1, 128.0, 127.3, 125.3 (d, *J* = 1.0 Hz), 124.9, 121.8 (d, *J* = 9.9 Hz), 121.5, 117.5 (d, *J* = 2.6 Hz), 117.2, 117.0, 104.9 (d, *J* = 23.2 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{10}BrF_6OS$ $[M+H]^+$ 490.9534, found: 490.9540.



8-Bromo-3-((2-bromophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6b):

Yield = 83% (92 mg). White solid. M.p. 85.6–87.3 °C.

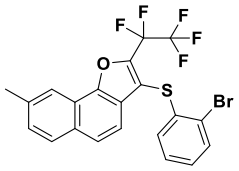
IR (KBr): ν = 3063, 1738, 1585, 794, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.10 – 6.98 (m, 2H), 6.82 – 6.75 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.51 (t, *J* = 4.1 Hz, 3F), -113.20 (q, *J* = 3.7 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4 (t, *J* = 0.9 Hz), 143.5 (t, *J* = 29.7 Hz), 135.9, 133.1, 131.3, 130.5, 130.1, 128.1, 128.0, 127.4, 125.3, 124.9, 122.8, 122.0, 121.6, 121.6, 118.7, 106.5 (d, *J* = 1.5 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{10}Br_2F_5OS$ $[M+H]^+$ 550.8734, found: 550.8740.



3-((2-Bromophenyl)thio)-8-methyl-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6c):

Yield = 72% (70 mg). Yellow solid. M.p. 98.5–99.8 °C.

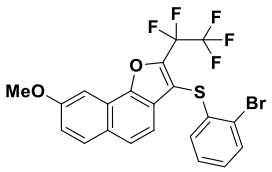
IR (KBr): ν = 3057, 1601, 1566, 828, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.06 – 6.96 (m, 2H), 6.80 – 6.73 (m, 1H), 2.60 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.48 – -83.63 (m, 3F), -113.04 – -113.23 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4 (t, *J* = 1.0 Hz), 142.9 (t, *J* = 29.9 Hz), 137.5, 136.3, 133.0, 131.2, 129.3, 128.3, 127.9, 127.9, 127.1, 125.4, 124.1, 121.3, 121.1, 119.4, 117.2, 116.1 (t, *J* = 1.8 Hz), 21.9 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{13}BrF_5OS$ $[M+H]^+$ 486.9785, found: 486.9787.



3-((2-Bromophenyl)thio)-8-methoxy-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6d):

Yield = 74% (74 mg). White solid. M.p. 133.2–134.4 °C.

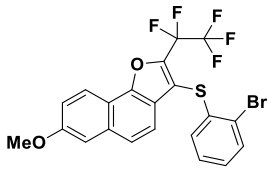
IR (KBr): ν = 2974, 1642, 1603, 834, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 9.0 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.25 – 7.18 (m, 2H), 7.07 – 6.98 (m, 2H), 6.81 – 7.75 (m, 1H), 4.02 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.55 (t, *J* = 4.0 Hz, 3F), -113.18 (q, *J* = 3.7 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 151.2 (t, *J* = 1.4 Hz), 143.0 (t, *J* = 29.4 Hz), 142.7, 136.2, 133.0, 130.1, 128.2, 127.9, 127.9, 127.1, 125.3, 124.5, 122.1, 121.3, 119.4, 115.6, 99.0, 55.7 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{13}BrF_5O_2S$ $[M+H]^+$ 502.9734, found: 502.9734.



3-((2-Bromophenyl)thio)-7-methoxy-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6e):

Yield = 74% (74 mg). Yellow solid. M.p. 82.0–83.4 °C.

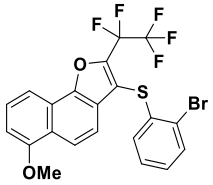
IR (KBr): ν = 3057, 1643, 1601, 820, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 9.0 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 7.07 – 6.96 (m, 2H), 6.82 – 6.75 (m, 1H), 3.93 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.56 (t, J = 4.1 Hz, 3F), -112.99 (q, J = 3.3 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 152.0 (t, J = 0.9 Hz), 142.3 (t, J = 29.6 Hz), 136.3, 134.7, 133.0, 127.9, 127.9, 127.1, 124.6, 122.2, 121.9, 121.3, 119.4, 118.8, 116.2 (t, J = 1.9 Hz), 116.0, 107.3, 55.4 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{13}BrF_5O_2S$ $[M+H]^+$ 502.9734, found: 502.9731.



3-((2-Bromophenyl)thio)-6-methoxy-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6f):

Yield = 77% (78 mg). White solid. M.p. 107.5–109.0 °C.

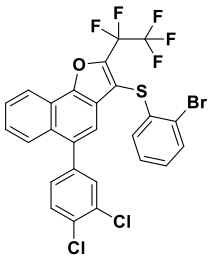
IR (KBr): ν = 2965, 1591, 1574, 800, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.9 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.64 – 7.51 (m, 2H), 7.31 (d, J = 8.9 Hz, 1H), 7.06 – 6.97 (m, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.82 – 6.72 (m, 1H), 4.00 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.44 – -83.62 (m, 3F), -113.10 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 151.6 (t, J = 0.9 Hz), 143.1 (t, J = 29.6 Hz), 136.2, 133.0, 127.9, 127.9, 127.8, 127.1, 124.6, 124.5, 122.0, 121.3, 119.6, 117.2, 116.1 (t, J = 1.5 Hz), 112.4, 105.6, 55.6 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{13}BrF_5O_2S$ $[M+H]^+$ 502.9734, found: 502.9735.



3-((2-Bromophenyl)thio)-5-(3,4-dichlorophenyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6g):

Yield = 56% (69 mg). White solid. M.p. 136.2–137.4 °C.

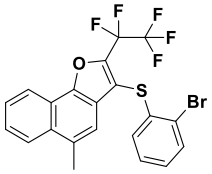
IR (KBr): ν = 3078, 2566, 1577, 821, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.62 – 7.54 (m, 2H), 7.52 (d, J = 8.2 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.26 (s, 1H), 7.22 – 7.17 (m, 1H), 7.12 – 6.99 (m, 2H), 6.86 – 6.79 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.49 (t, J = 3.7 Hz, 3F), -113.21 (q, J = 3.6 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (t, J = 0.9 Hz), 143.5 (t, J = 29.5 Hz), 139.8, 135.9, 135.7, 133.2, 132.5, 132.0, 131.9, 131.1, 130.3, 129.5, 127.9, 127.9, 127.6, 127.5, 127.3, 126.6, 123.4, 121.5, 121.3, 120.8, 119.0, 116.3 (t, J = 1.4 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{13}BrCl_2F_5OS$ $[M+H]^+$ 616.9162, found: 616.9163.



3-((2-Bromophenyl)thio)-5-methyl-2-(perfluoroethyl)naphtho[1,2-*b*]furan (6h):

Yield = 84% (82 mg). Light yellow solid. M.p. 102.7–103.9 °C.

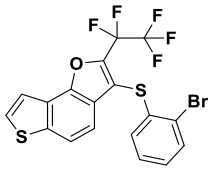
IR (KBr): ν = 2940, 1559, 1450, 863, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 – 8.34 (m, 1H), 8.07 – 7.99 (m, 1H), 7.72 – 7.60 (m, 2H), 7.59 – 7.53 (m, 1H), 7.22 – 7.17 (m, 1H), 7.07 – 6.96 (m, 2H), 6.78 – 6.71 (m, 1H), 2.63 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.53 (t, J = 3.7 Hz, 3F), -113.04 (q, J = 3.7 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9 (t, J = 0.9 Hz), 143.1 (t, J = 28.6 Hz), 136.4, 133.0, 132.3, 132.2, 127.9, 127.5, 127.0, 127.0, 126.9, 125.1, 123.6, 121.0, 121.0, 120.7, 117.8, 115.5 (t, J = 1.5 Hz), 19.8 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{13}BrF_5OS$ $[M+H]^+$ 486.9785, found: 486.9789.



3-((2-Bromophenyl)thio)-2-(perfluoroethyl)thieno[2,3-*g*]benzofuran (6i):

Yield = 68% (65 mg). Yellow solid. M.p. 73.8–75.4 °C.

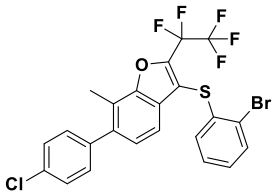
IR (KBr): ν = 3060, 1629, 1575, 791, 720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.69 (m, 2H), 7.62 (d, J = 5.5 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.79 – 6.74 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.56 (s, 3F), -113.22 (d, J = 3.1 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1 (t, J = 0.8 Hz), 142.4 (t, J = 29.7 Hz), 140.8, 136.0, 133.0, 128.4, 128.0, 127.9, 127.2, 125.5, 123.9, 121.4, 119.4, 118.8, 117.0, 116.1 (t, J = 1.7 Hz) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{18}H_9BrF_5OS_2$ $[M+H]^+$ 478.9193, found: 478.9192.



3-((2-Bromophenyl)thio)-6-(4-chlorophenyl)-7-methyl-2-(perfluoroethyl)benzofurans (6j):

Yield = 49% (54 mg). Light yellow solid. M.p. 97.0–97.3 °C.

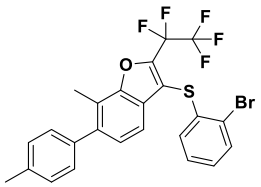
IR (KBr): ν = 3066, 1574, 1477, 816, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, J = 7.8, 1.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 (d, J = 7.4 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 7.12 – 7.07 (m, 1H), 7.06 – 7.00 (m, 1H), 6.86 – 6.81 (m, 1H), 2.48 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.54 (t, J = 3.9 Hz, 3F), -113.69 (q, J = 3.9 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (t, J = 0.9 Hz), 144.2 (t, J = 29.2 Hz), 140.3, 138.6, 135.9, 133.5, 133.0, 130.7, 128.5, 128.1, 127.9, 127.2, 126.7, 126.5, 121.5, 120.6, 118.6, 115.4 (t, J = 1.5 Hz), 12.6 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{14}BrClF_5OS$ $[M+H]^+$ 546.9552, found: 546.9556.



3-((2-Bromophenyl)thio)-7-methyl-2-(perfluoroethyl)-6-(*p*-tolyl)benzofuran (6k):

Yield = 63% (66 mg). Yellow solid. M.p. 66.3–67.2 °C.

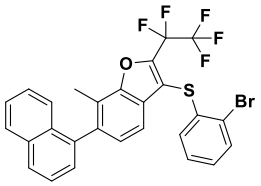
IR (KBr): ν = 2968, 1625, 1574, 811, 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 – 7.54 (m, 1H), 7.25 – 7.16 (m, 6H), 7.12 – 7.06 (m, 1H), 7.05 – 6.99 (m, 1H), 6.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.55 (t, *J* = 4.0 Hz, 3F), -113.66 (q, *J* = 3.3 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8 (t, *J* = 0.7 Hz), 144.0 (t, *J* = 29.3 Hz), 141.7, 137.3, 137.1, 136.1, 133.0, 129.3, 129.0, 128.0, 127.9, 127.1, 127.0, 126.1, 121.3, 120.6, 118.3, 115.3 (t, *J* = 1.8 Hz), 21.2, 12.7 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{17}BrF_5OS$ $[M+H]^+$ 527.0098, found: 527.0096.



3-((2-Bromophenyl)thio)-7-methyl-6-(naphthalen-1-yl)-2-(perfluoroethyl)benzofuran (6l):

Yield = 59% (66 mg). Yellow oil.

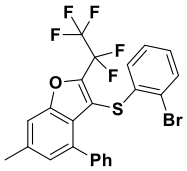
IR (KBr): ν = 3058, 1574, 1508, 801, 746 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (t, *J* = 7.9 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.46 (m, 1H), 7.45 – 7.35 (m, 2H), 7.34 – 7.31 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.11 (m, 1H), 7.07 – 7.01 (m, 1H), 6.94 – 6.90 (m, 1H), 2.25 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.46 (t, *J* = 3.0 Hz, 3F), -113.53 – -113.57 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 144.1 (t, *J* = 29.3 Hz), 140.1, 137.8, 136.0, 133.5, 133.0, 131.9, 128.4, 128.1, 128.0, 127.9, 127.6, 127.2, 127.1, 126.6, 126.3, 125.9, 125.8, 125.3, 122.1, 121.4, 118.2, 115.5 (t, *J* = 1.6 Hz), 12.5 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{17}BrF_5OS$ $[M+H]^+$ 563.0098, found: 563.0104.



3-((2-Bromophenyl)thio)-6-methyl-2-(perfluoroethyl)-4-phenylbenzofuran (6m):

Yield = 25% (26 mg). Light yellow solid. M.p. 144.7–145.3 °C.

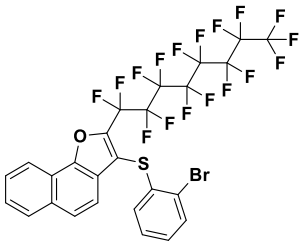
IR (KBr): ν = 3026, 1618, 1576, 838, 772 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 7.19 – 7.12 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 2H), 7.03 – 6.96 (m, 3H), 6.91 (td, *J* = 7.6, 1.3 Hz, 1H), 6.82 (td, *J* = 7.6, 1.5 Hz, 1H), 6.33 (dd, *J* = 7.9, 1.5 Hz, 1H), 2.51 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -82.95 – -84.36 (m, 3F), -113.06 (q, *J* = 4.0 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (m), 144.7 (t, *J* = 32.2 Hz), 138.4, 138.2, 137.0, 136.6, 132.3, 128.8, 128.3, 127.3, 127.2, 126.9, 126.2, 125.9, 121.1, 120.0, 114.2 (t, *J* = 2.9 Hz), 111.4, 21.7 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{15}BrF_5OS$ $[M+H]^+$ 512.9942, found: 512.9944.



3-((2-Bromophenyl)thio)-2-(perfluorooctyl)naphtho[1,2-*b*]furan (6n):

Yield = 74% (114 mg). Light yellow solid. M.p. 106.7–108.2 °C.

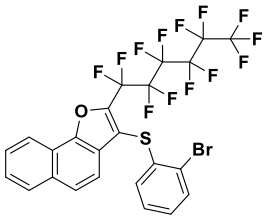
IR (KBr): ν = 3072, 1566, 1523, 804, 744 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 – 8.33 (m, 1H), 7.95 – 7.89 (m, 1H), 7.69 – 7.62 (m, 2H), 7.61 – 7.55 (m, 2H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.82 – 6.76 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.69 – -80.81 (m, 3F), -109.74 (t, *J* = 12.7 Hz, 2F), -121.44 (s, 2F), -121.56 – -122.04 (m, 6F), -122.65 (s, 2F), -126.08 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 143.1 (t, *J* = 29.7 Hz), 136.2, 133.1, 133.0, 128.5, 128.0, 127.9, 127.3, 127.2, 127.2, 125.6, 124.0, 121.4, 121.1, 120.3, 118.3, 116.8 (t, *J* = 1.7 Hz) ppm; carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{11}BrF_{17}OS$ $[M+H]^+$ 772.9437, found: 772.9441.



3-((2-Bromophenyl)thio)-2-(perfluorohexyl)naphtho[1,2-*b*]furan (6o):

Yield = 86% (116 mg). Yellow solid. M.p. 110.9–112.0 °C.

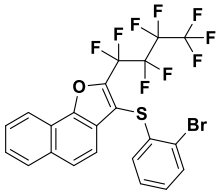
IR (KBr): ν = 3061, 1558, 1449, 806, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.62 – 7.55 (m, 2H), 7.32 (d, J = 8.7 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.83 – 6.77 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.51 – -81.01 (m, 3F), -109.58 – -109.98 (m, 2F), -121.46 – -121.95 (m, 4F), -122.44 – -122.75 (m, 2F), -125.89 – -126.14 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 143.0 (t, J = 29.7 Hz), 136.2, 133.1, 133.0, 128.5, 128.1, 127.9, 127.3, 127.2, 127.2, 125.6, 124.0, 121.4, 121.1, 120.3, 118.3, 116.8 (t, J = 1.6 Hz) ppm; carbons corresponding to the C_6F_{13} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{11}BrF_{13}OS$ $[M+H]^+$ 672.9501, found: 672.9504.



3-((2-Bromophenyl)thio)-2-(perfluorobutyl)naphtho[1,2-*b*]furan (6p):

Yield = 71% (81 mg). White solid. M.p. 109.6–110.1 °C.

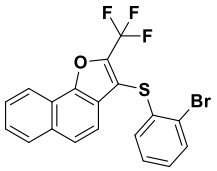
IR (KBr): ν = 3058, 1593, 1573, 805, 746 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 – 8.32 (m, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.62 – 7.54 (m, 2H), 7.31 (d, J = 8.7 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.82 – 6.76 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.33 – -81.34 (m, 3F), -109.20 – -110.96 (m, 2F), -121.82 – -123.63 (m, 2F), -125.07 – -126.71 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8 (t, J = 0.7 Hz), 142.9 (t, J = 29.9 Hz), 136.2, 133.0, 133.0, 128.5, 128.0, 127.9, 127.3, 127.2, 127.2, 125.6, 124.0, 121.4, 121.0, 120.3, 118.3, 116.8 (t, J = 2.0 Hz) ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{11}BrF_9OS$ $[M+H]^+$ 572.9565, found: 572.9570.



3-((2-Bromophenyl)thio)-2-(trifluoromethyl)naphtho[1,2-*b*]furan (6q):

Yield = 79% (67 mg). Yellow solid. M.p. 110.2–111.9 °C.

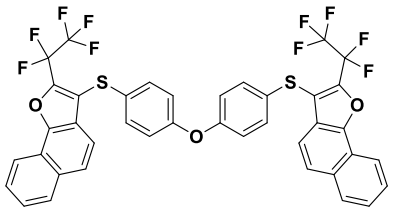
IR (KBr): ν = 3055, 1571, 1520, 809, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.62 – 7.53 (m, 2H), 7.38 (d, J = 8.7 Hz, 1H), 7.07 – 6.96 (m, 2H), 6.83 – 6.77 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.03 (s, 3F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8 (m), 144.4 (q, J = 39.5 Hz), 136.1, 133.1, 133.0, 128.5, 127.9, 127.3, 127.2, 127.0, 125.6, 123.8, 121.5, 121.1, 120.7, 120.2, 118.2, 118.0, 113.5 (q, J = 2.7 Hz) ppm.

HRMS (m/z): calcd for $C_{19}H_{11}BrF_3OS$ $[M+H]^+$ 422.9661, found: 422.9667.



3,3'-((Oxybis(4,1-phenylene))bis(sulfanediyl))bis(2-(perfluoroethyl)naphtho[1,2-*b*]furan) (8a):

Yield = 55% (88 mg). White solid. M.p. 187.1–187.9 °C.

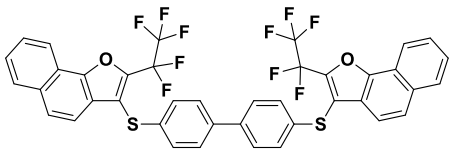
IR (KBr): ν = 3052, 1583, 1563, 809, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 7.9 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 7.69 – 7.53 (m, 6H), 7.41 – 7.25 (m, 6H), 6.86 (d, J = 8.3 Hz, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -82.43 – -84.39 (m, 6F), -111.63 – -113.49 (m, 4F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 151.5 (m), 141.4 (t, J = 30.1 Hz), 132.8, 131.3, 128.4, 128.2, 127.2, 127.0, 125.2, 124.1, 121.0, 120.3, 119.7, 118.3, 118.1 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{40}H_{21}F_{10}O_3S_2$ $[M+H]^+$ 803.0767, found: 803.0765.



4,4'-Bis((2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)thio)-1,1'-biphenyl (8b):

Yield = 52% (82 mg). White solid. M.p. 203.1–204.3 °C.

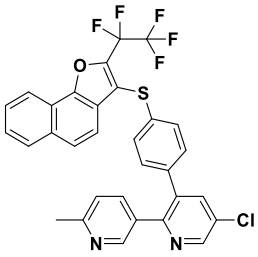
IR (KBr): ν = 3026, 1592, 1562, 810, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 – 8.33 (m, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.71 – 7.56 (m, 6H), 7.44 – 7.39 (m, 4H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.28 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.63 (t, *J* = 4.2 Hz, 6F), -112.81 (q, *J* = 4.0 Hz, 4F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 142.0 (t, *J* = 29.4 Hz), 138.4, 133.7, 132.8, 128.9, 128.4, 127.5, 127.2, 127.0, 125.3, 124.2, 121.0, 120.3, 118.4, 117.2 (m) ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{40}H_{21}F_{10}O_2S_2$ $[M+H]^+$ 787.0818, found: 787.0815.



5-Chloro-6'-methyl-3-(4-((2-(perfluoroethyl)naphtho[1,2-*b*]furan-3-yl)thio)phenyl)-2,3'-bipyridine (10):

Yield = 20% (24 mg). White solid. M.p. 143.4–144.0 °C.

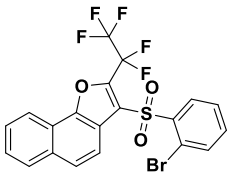
IR (KBr): ν = 3031, 1596, 1567, 811, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 2.4 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.60 (m, 4H), 7.48 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.08 – 6.98 (m, 3H), 2.51 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.61 (t, *J* = 4.0 Hz, 3F), -112.31 – -113.40 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 152.3, 151.6 (d, *J* = 1.4 Hz), 149.8, 147.5, 142.1, 137.8, 137.2, 136.4, 136.3, 134.9, 132.8, 131.7, 130.9, 130.1, 128.6, 128.4, 127.3, 127.2, 125.4, 124.0, 122.4, 121.0, 120.3, 118.3, 116.7 (m), 24.2 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{31}H_{19}ClF_5N_2OS$ $[M+H]^+$ 597.0821, found: 597.0821.



3-((2-Bromophenyl)sulfonyl)-2-(perfluoroethyl)naphtho[1,2-*b*]furan (11):

Yield = 72% (109 mg). Yellow solid. M.p. 129.3–129.7 °C.

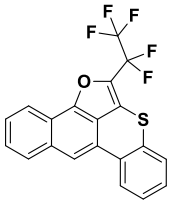
IR (KBr): ν = 3081, 1565, 1519, 805, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (dd, J = 7.9, 1.6 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.65 – 7.59 (m, 1H), 7.58 – 7.50 (m, 3H), 7.46 – 7.41 (m, 1H), 7.21 (d, J = 8.9 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -82.64 (t, J = 3.5 Hz, 3F), -110.87 – -114.02 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8 (t, J = 1.0 Hz), 142.8 (m), 140.8 (t, J = 2.2 Hz), 133.9, 133.0, 132.5, 128.2, 128.1, 128.0, 127.5, 127.4, 126.6, 125.9, 120.6, 120.2, 119.5, 119.0, 117.7 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{11}BrF_5O_3S$ $[M+H]^+$ 504.9527, found: 504.9533.



6-(Perfluoroethyl)dibenzo[3,4:6,7]isothiochromeno[8,1-*bc*]furan 7,7-dioxide (12):

Yield = 76% (97 mg). Yellow solid. M.p. 172.7–173.0 °C.

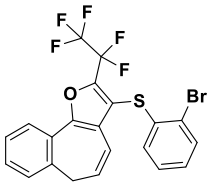
IR (KBr): ν = 3060, 1641, 1560, 805, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 – 8.05 (m, 1H), 8.04 – 8.00 (m, 1H), 7.89 – 7.83 (m, 2H), 7.53 – 7.47 (m, 2H), 7.26 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.18 – 7.14 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.75 (t, J = 4.4 Hz, 3F), -113.95 (q, J = 4.1 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8 (t, J = 0.9 Hz), 134.2, 129.7 (t, J = 1.3 Hz), 129.0, 128.9, 127.2, 127.1, 126.8, 126.7, 124.8, 124.6, 123.0, 121.8, 120.6, 120.4, 118.1, 117.8 (t, J = 2.0 Hz), 115.1 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{10}F_5OS$ $[M+H]^+$ 393.0367, found: 393.0368.



3-((2-Bromophenyl)thio)-2-(perfluoroethyl)-6*H*-benzo[6,7]cyclohepta[1,2-*b*]furan (16):

Yield = 56% (55 mg). Yellow solid. M.p. 79.0–80.4 °C.

IR (KBr): ν = 3062, 1570, 1551, 803, 772 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.50 – 7.36 (m, 2H), 7.30 – 7.23 (m, 1H), 7.16 – 7.09 (m, 1H), 7.01 (td, *J* = 7.7, 1.6 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.26 (d, *J* = 9.9 Hz, 1H), 5.78 (dt, *J* = 9.9, 6.7 Hz, 1H), 3.21 – 3.14 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.67 (t, *J* = 4.0 Hz, 3F), -113.43 (q, *J* = 4.0 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0 (t, *J* = 1.5 Hz), 141.4 (t, *J* = 30.0 Hz), 136.6, 135.1, 132.9, 130.8, 128.7, 127.9, 127.7, 127.0, 126.9, 126.7, 126.3, 125.0, 124.8, 120.8, 119.4, 118.5 (m), 34.0 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

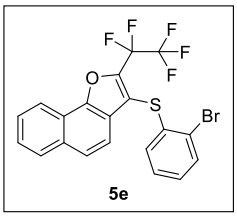
HRMS (m/z): calcd for $C_{21}H_{13}BrF_5OS$ $[M+H]^+$ 486.9785, found: 486.9788.

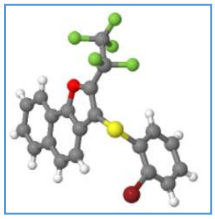
10. References

[1] P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem. Int. Ed.* **2011**, *50*, 6119–6122.

[2] (a) X. Su, H. Huang, Y. Yuan, Y. Li, *Angew. Chem., Int. Ed.* **2017**, *56*, 1338–1341. (b) T. Xie, Y.-W. Zhang, L.-L. Liu, Z.-L. Shen, T.-P. Loh, X.-Q. Chu, *Chem. Commun.* **2018**, *54*, 12722–12725.

11. The X-ray crystal structures of product 5e





Compound: 3-((2-bromophenyl)thio)-2-(perfluoroethyl)naphtho[1,2-*b*]furan

Crystal Number: CCDC 2008323

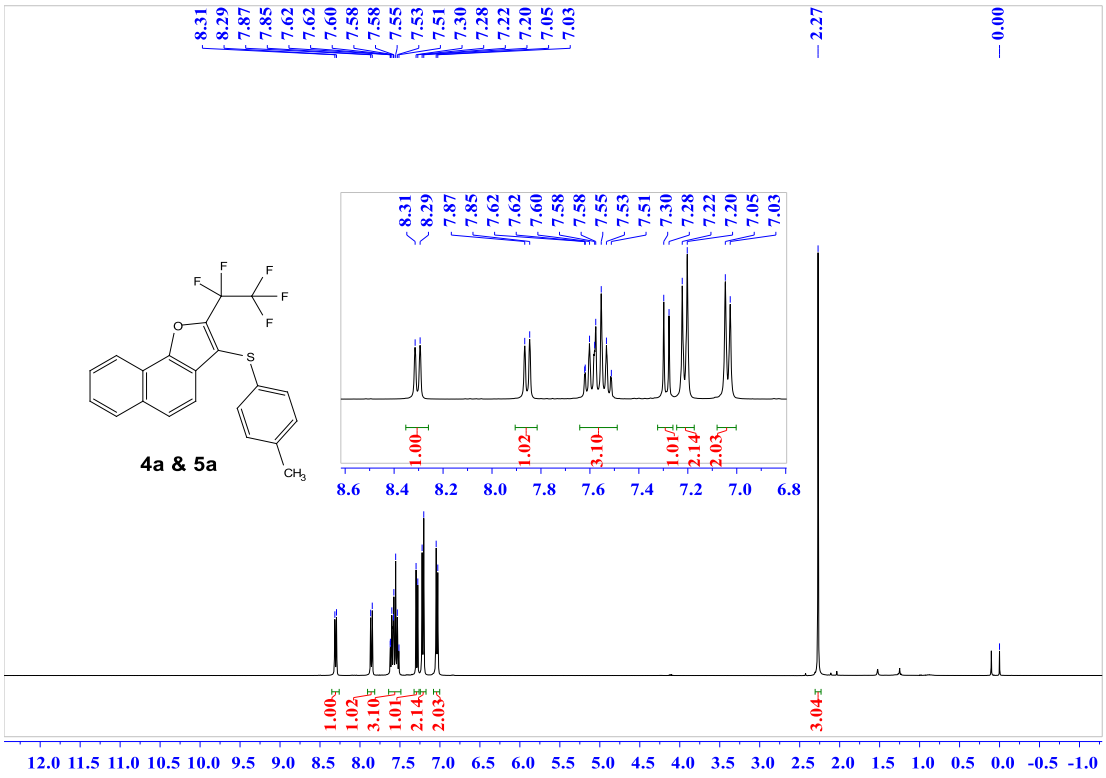
Chemical Formula: $C_{20}H_{10}BrF_5OS$

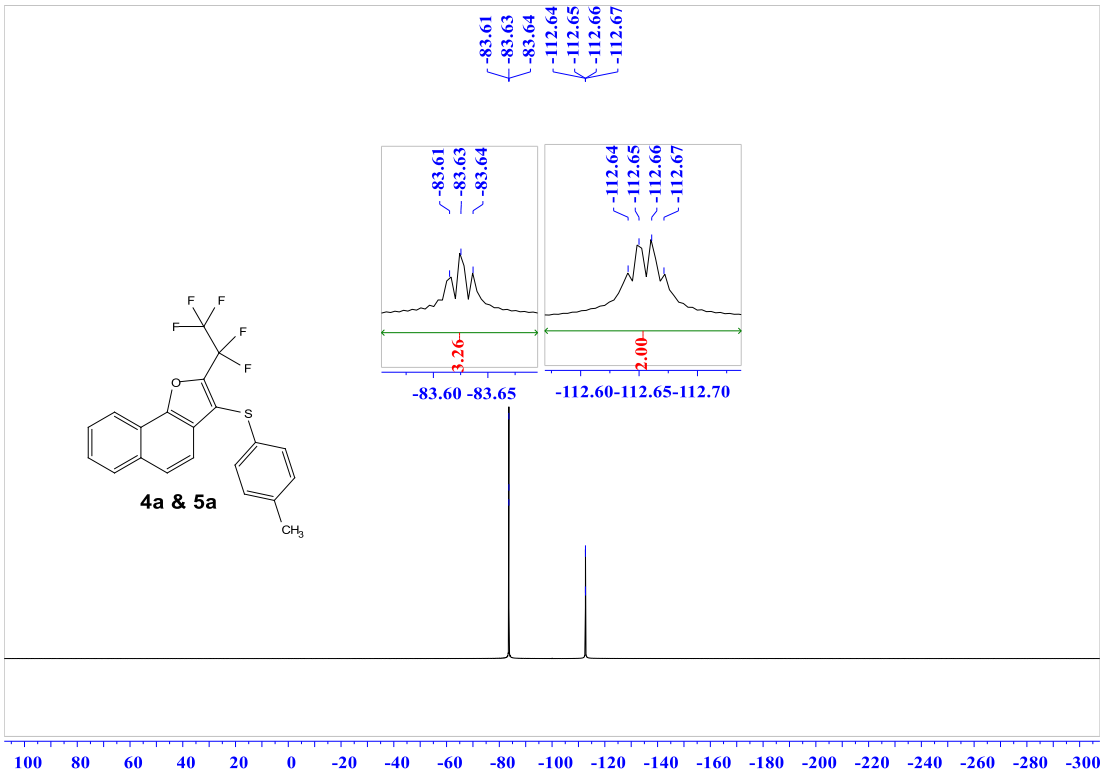
Formula weight: 473.2550

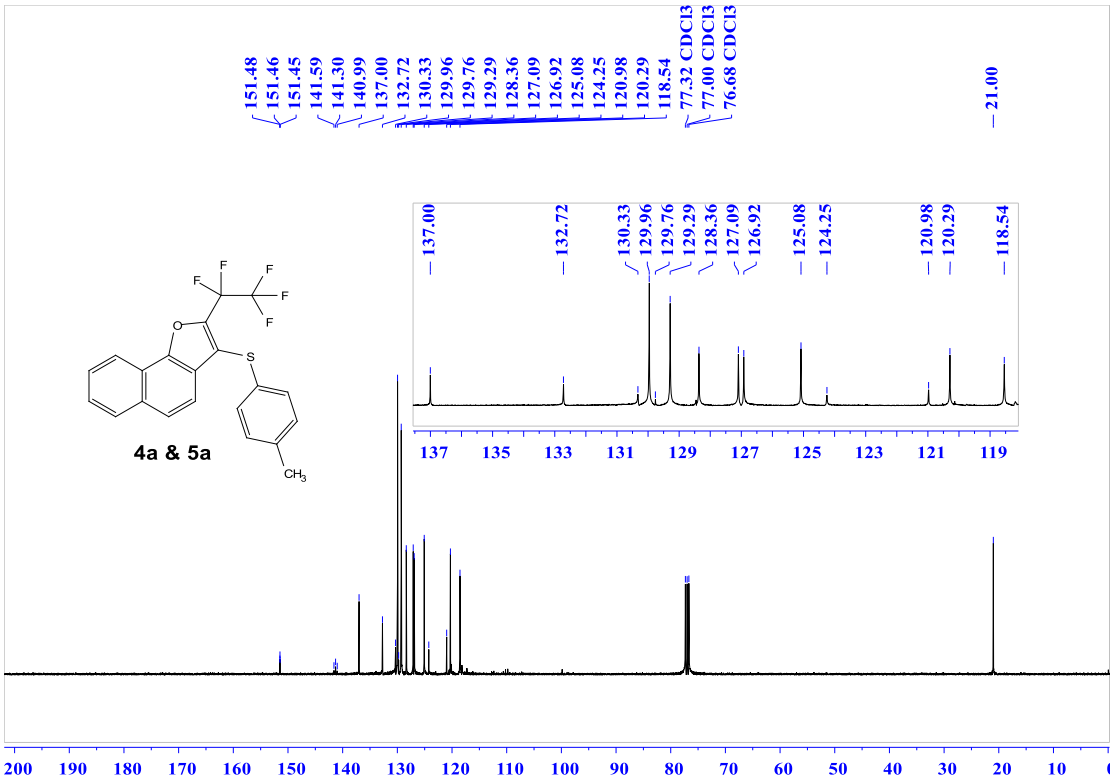
Space Group: I 41/a

Cell: a=31.0847(14) b=31.0847(14) c=7.6891(5)
alpha=90 beta=90 gamma=90

12. ^{1}H , ^{19}F, and ^{13}C spectra of products



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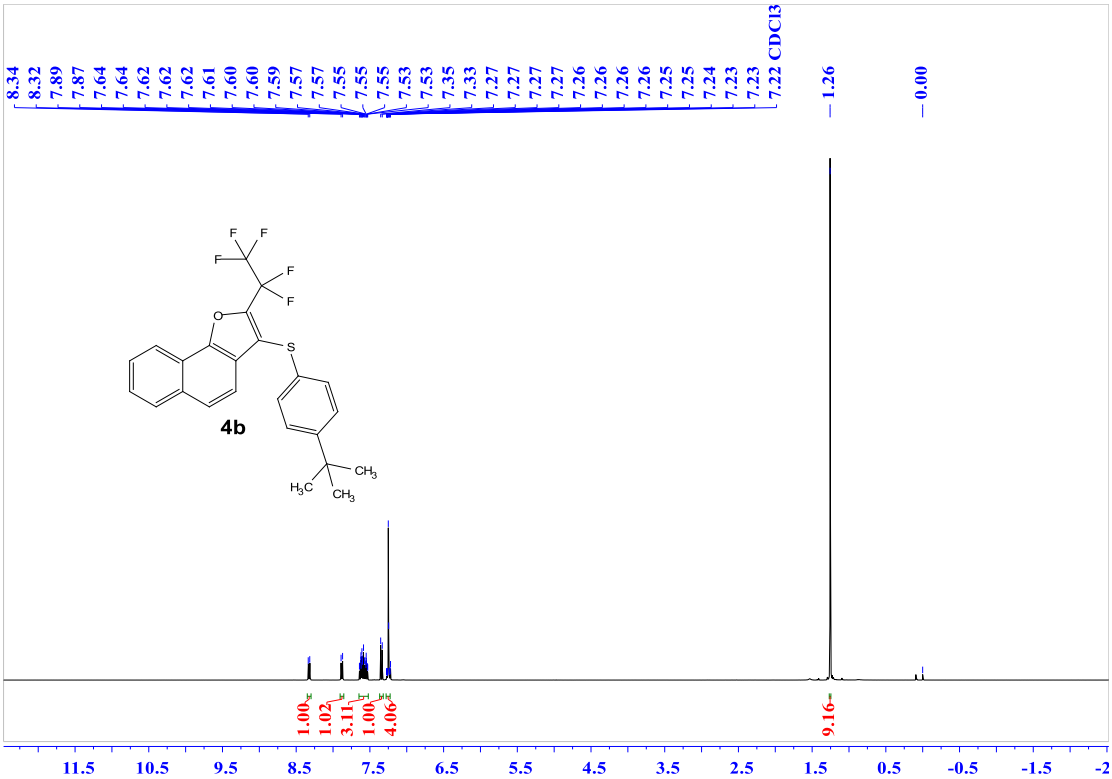
151.46
151.45
141.59
141.30
140.99
137.00
132.72
130.33
129.96
129.76
129.29
128.36
127.09
126.92
125.08
124.25
120.98
120.29
118.54
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
21.00
4a & 5a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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8.32
7.89
7.87
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7.64
7.62
7.62
7.62
7.61
7.60
7.60
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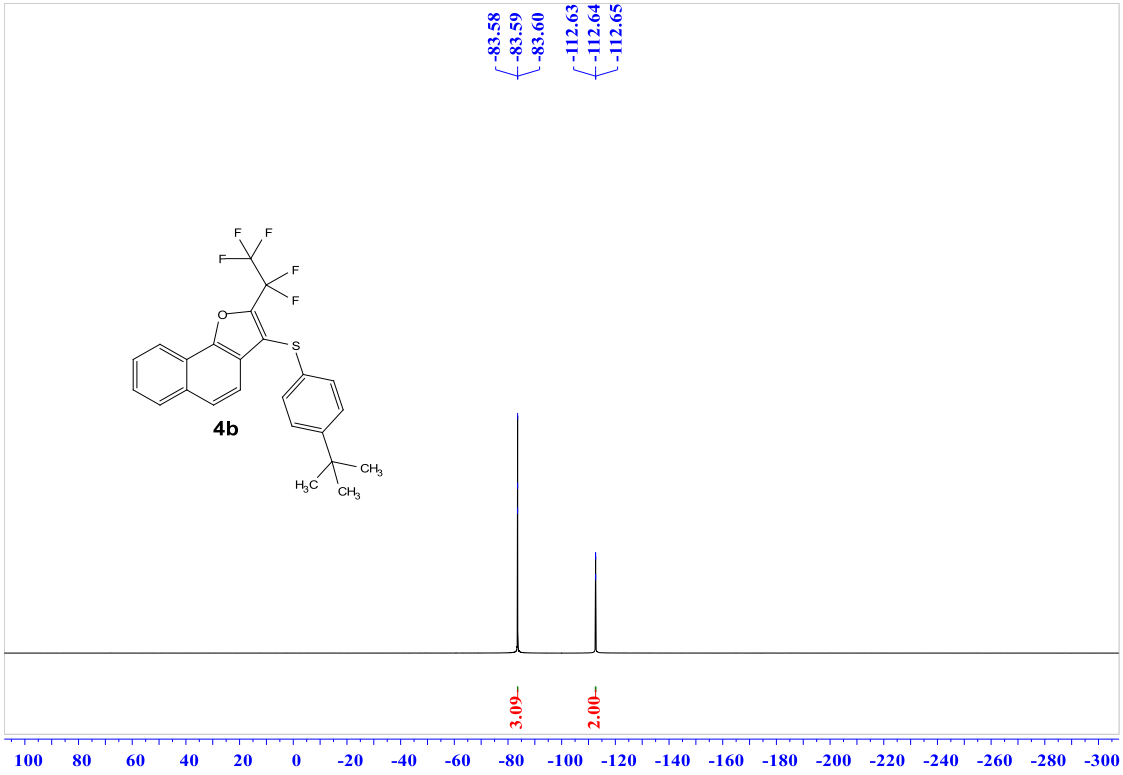
7.33
7.27
7.27
7.27
7.27
7.26
7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.22 CDCl3
1.26
0.00
4b
1.00
1.02
3.11
1.00
4.06
9.16
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5 -2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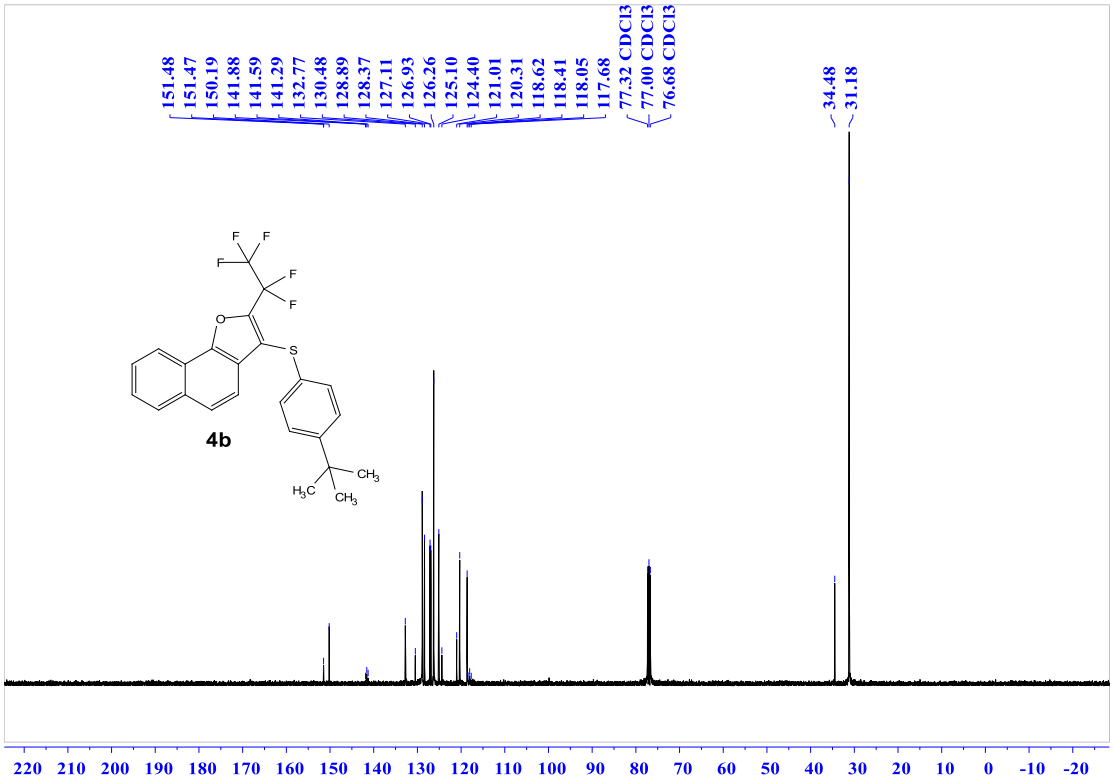
-83.60
-112.63
-112.64
-112.65
4b
3.09
2.00
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300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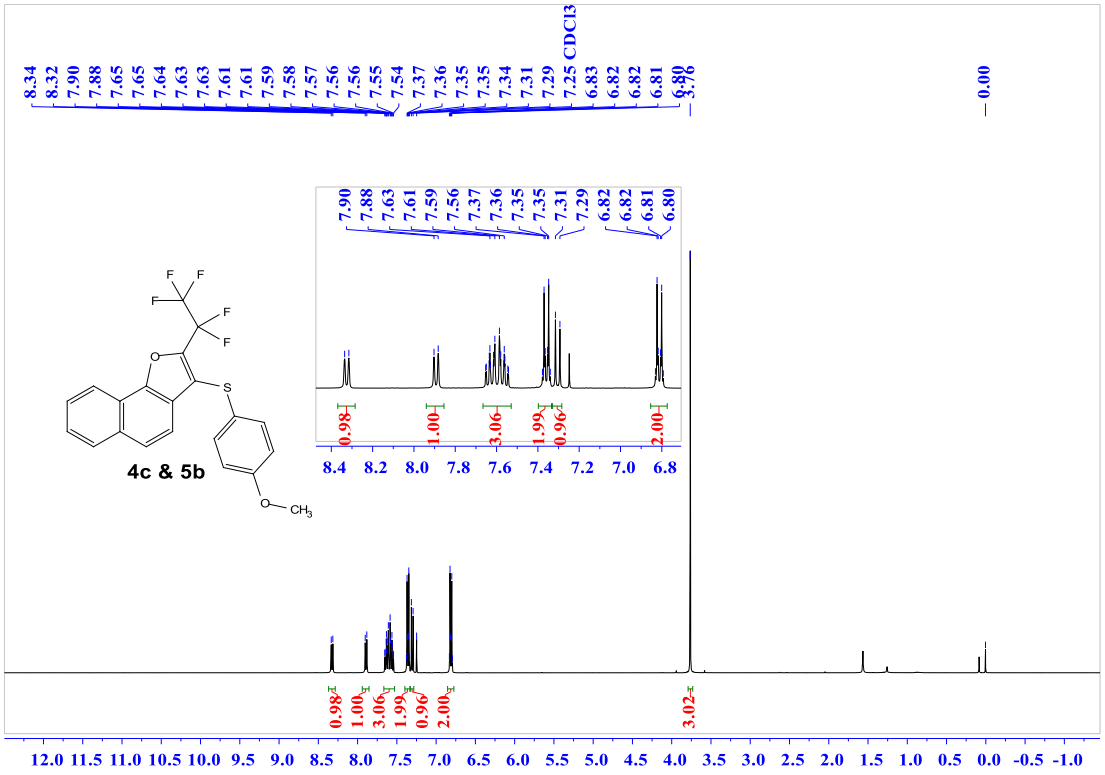
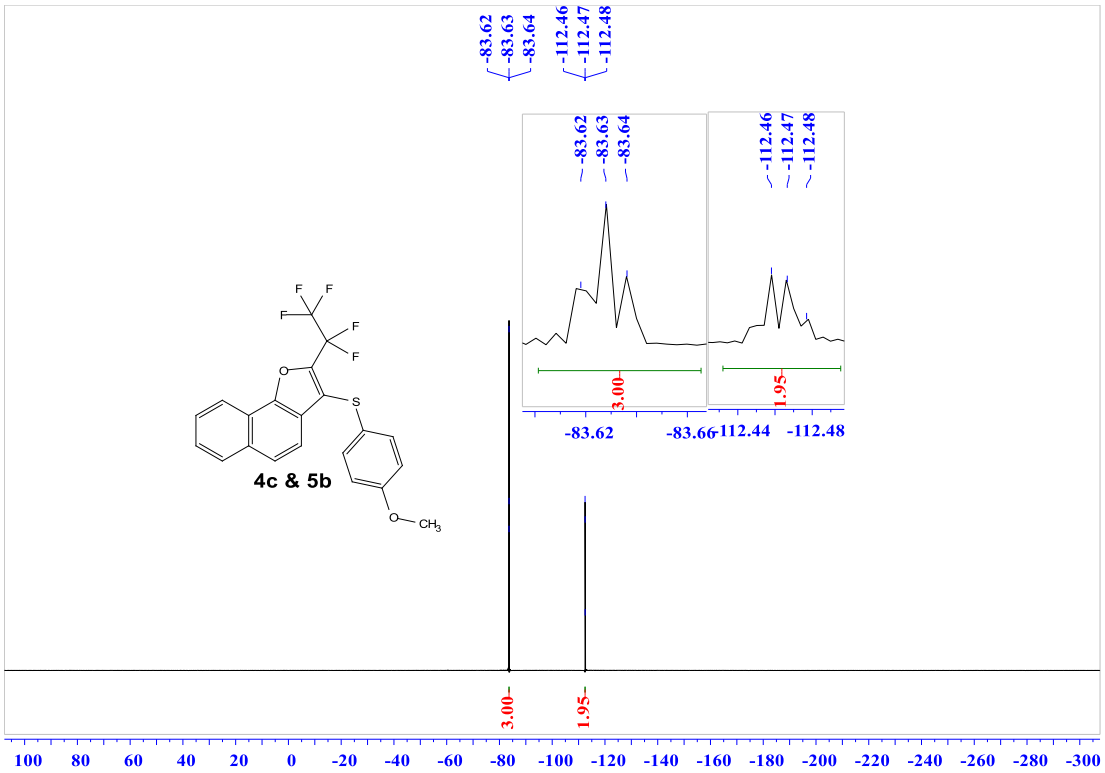
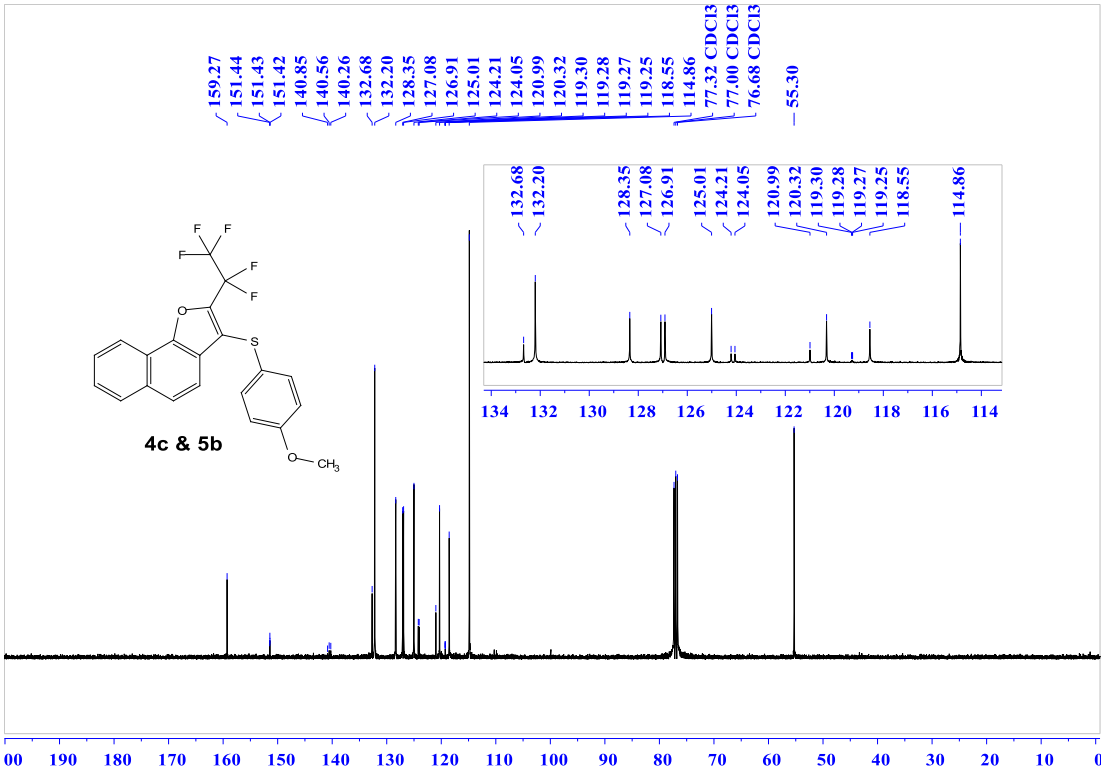
126.26
125.10
124.40
121.01
120.31
118.62
118.41
118.05
117.68
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
34.48
31.18
4b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


8.34 8.32 7.90 7.88 7.65 7.65 7.64 7.63 7.63 7.61 7.61 7.59 7.58 7.57 7.56 7.56 7.55 7.54 7.37 7.36 7.35 7.35 7.34 7.31 7.29 CDCl3 6.83 6.82 6.82 6.81 6.80 3.76
0.00
7.90 7.88 7.63 7.61 7.59 7.56 7.37 7.36 7.35 7.35 7.31 7.29 6.82 6.82 6.81 6.80
0.98 1.00 3.06 1.99 0.96 2.00
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
4c & 5b
0.98 1.00 3.06 1.99 0.96 2.00 3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


-83.62 -83.63 -83.64 -112.46 -112.47 -112.48
-83.62 -83.63 -83.64
-112.46 -112.47 -112.48
3.00
1.95
-83.62 -83.66 -112.44 -112.48
4c & 5b
3.00 1.95
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300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151.42
140.85
140.56
140.26
132.68
132.20
128.35
127.08
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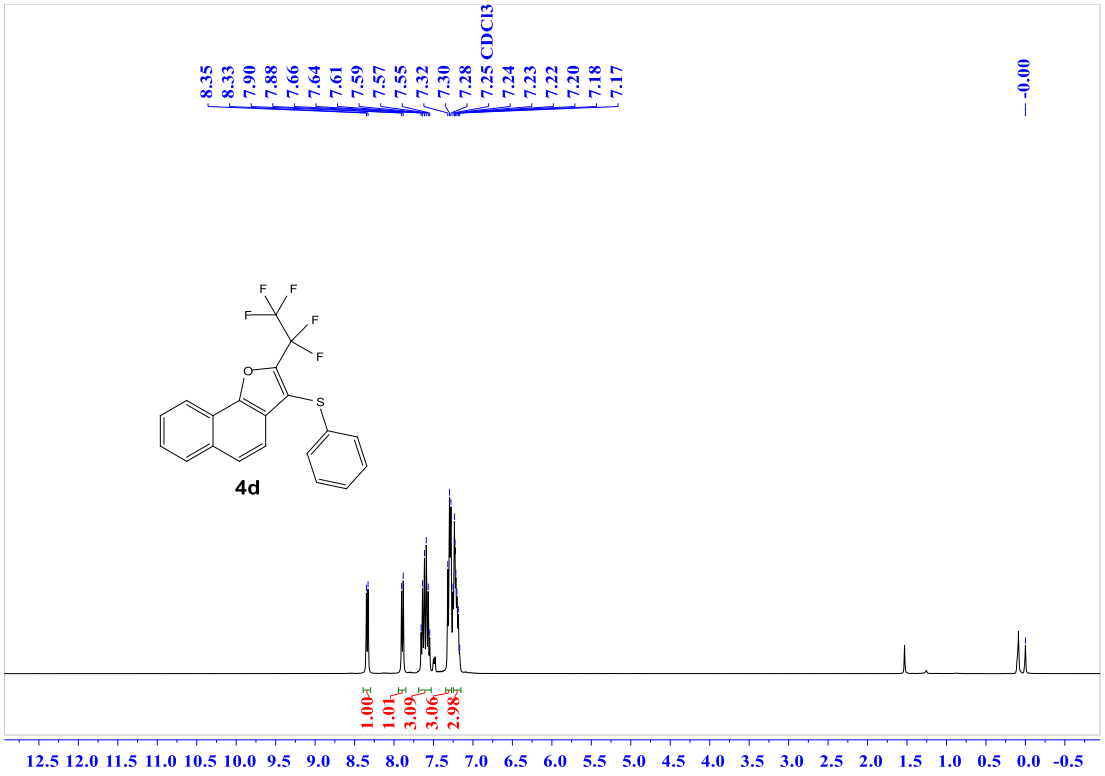
125.01
124.21
124.05
120.99
120.32
119.30
119.28
119.27
119.25
118.55
114.86
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.30
4c & 5b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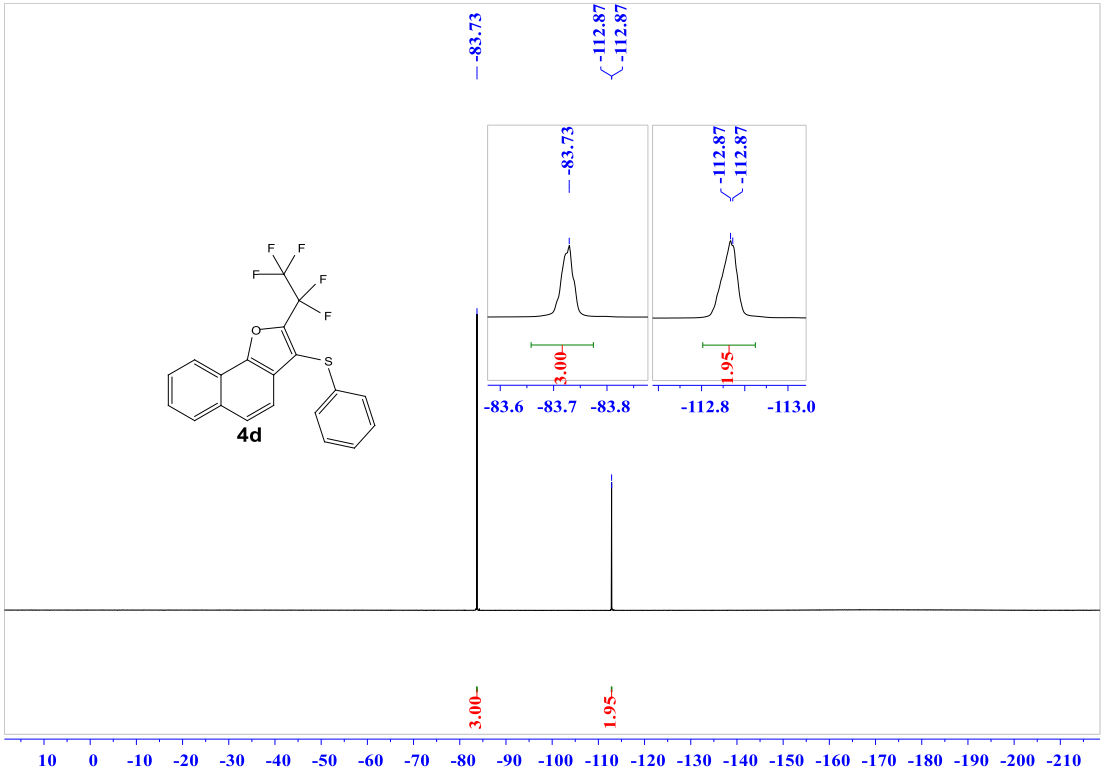
8.33
7.90
7.88
7.66
7.64
7.61
7.59
7.57
7.55
7.32
7.30
7.28
7.25 CDCl3
7.24
7.23
7.22
7.20
7.18
7.17
0.00
4d
1.00
1.01
3.09
3.06
2.98


-83.73
-112.87
-112.87
4d
3.00
1.95
-83.6 -83.7 -83.8
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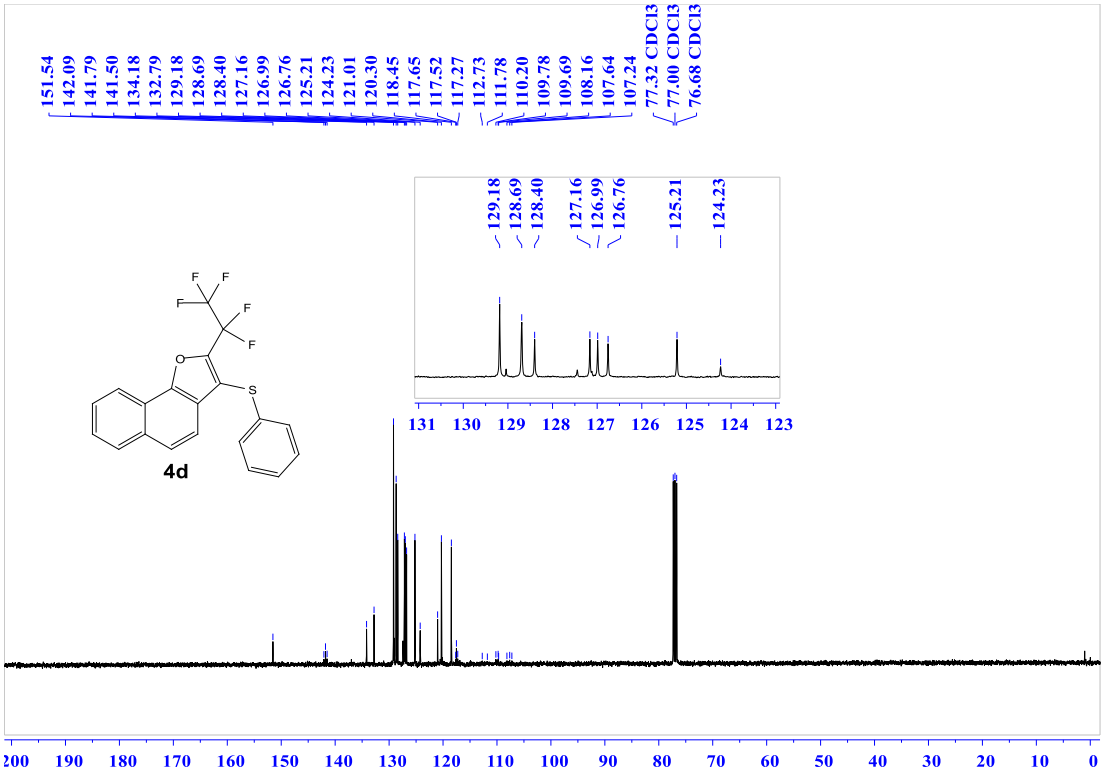
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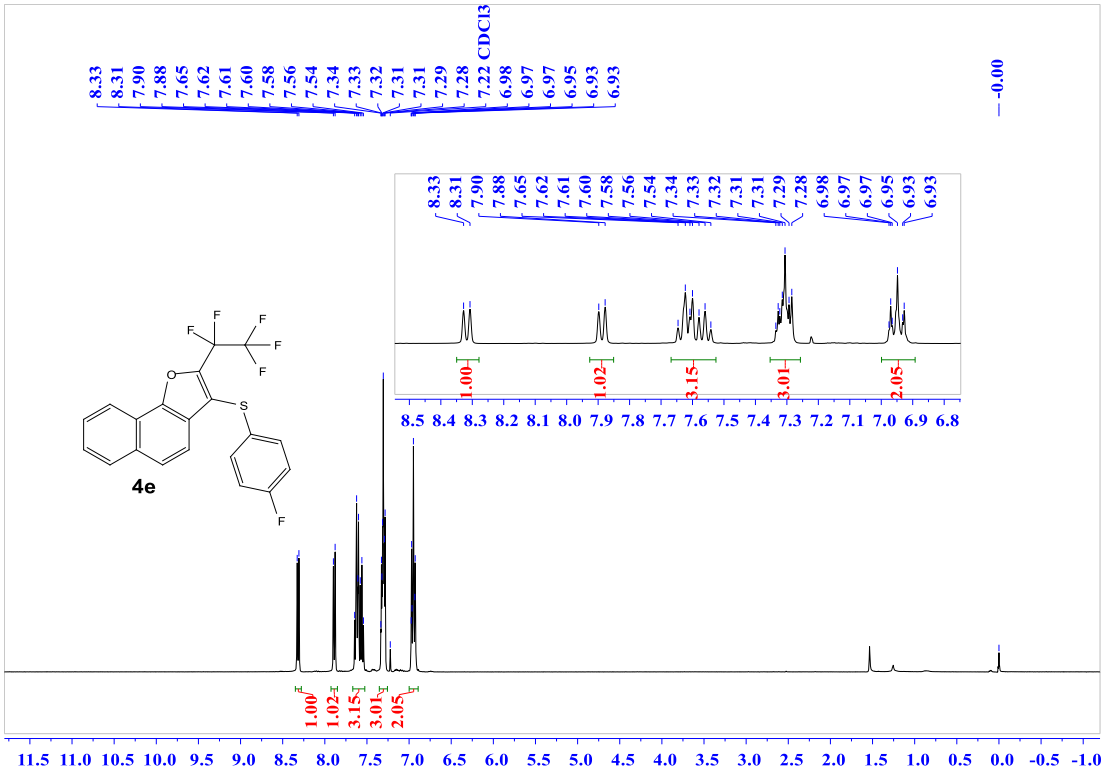
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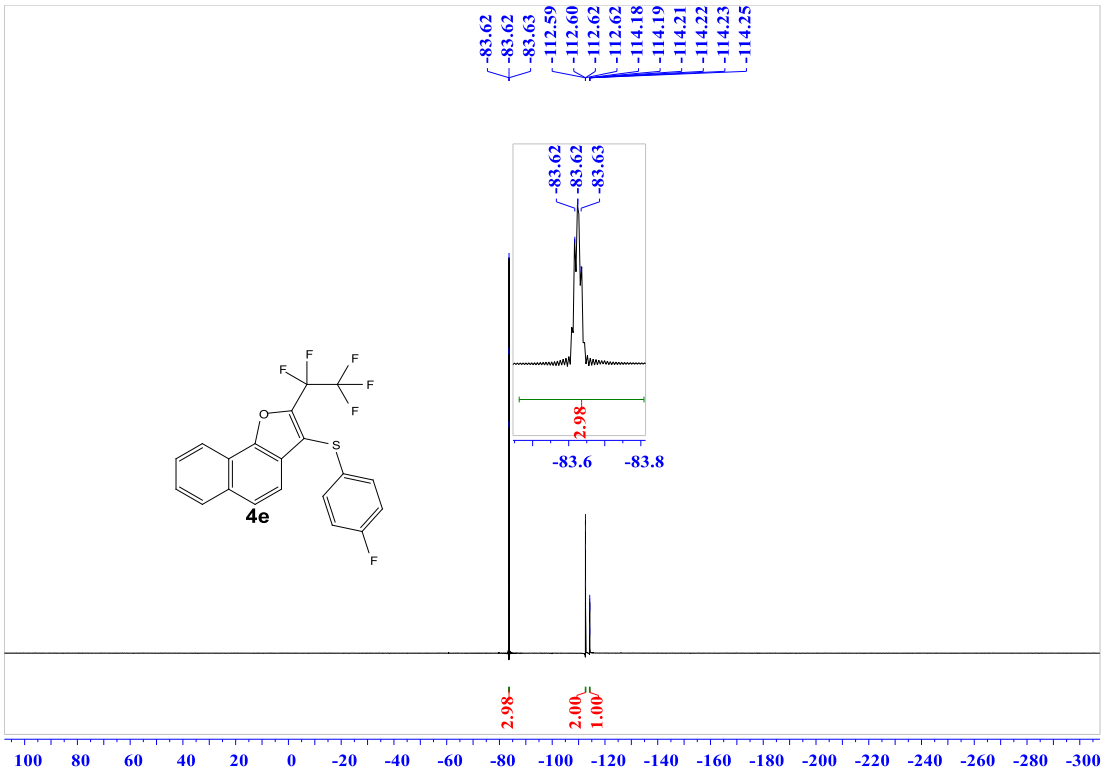
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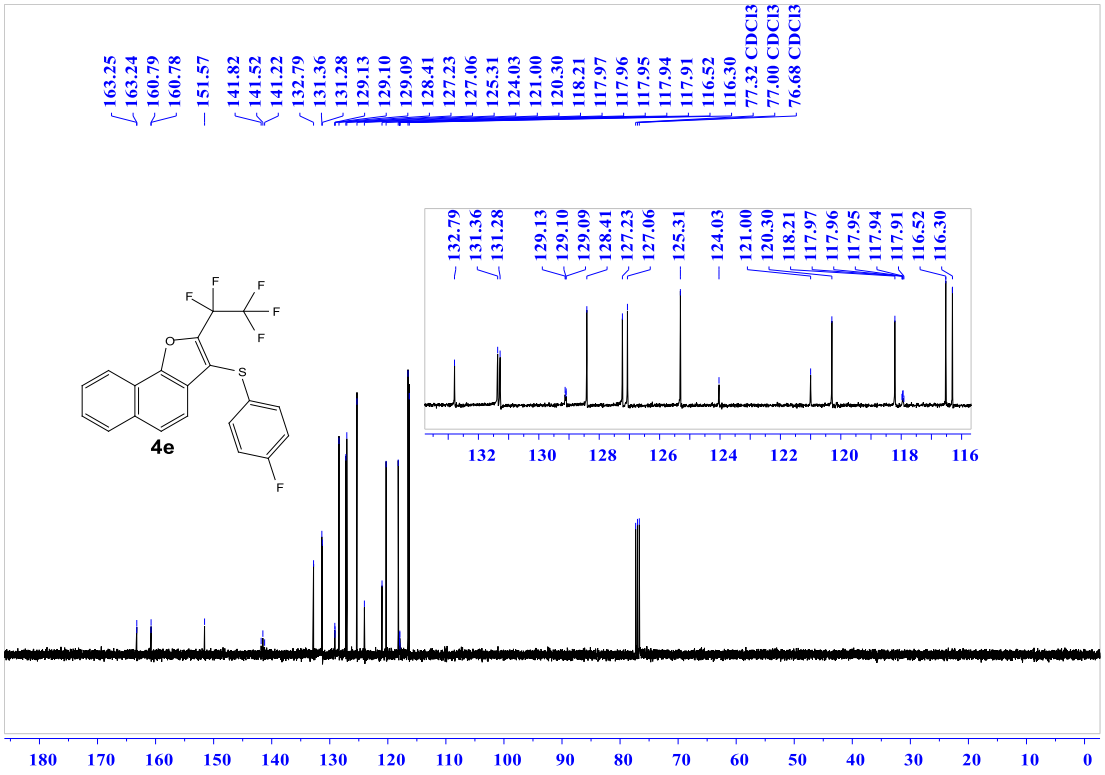
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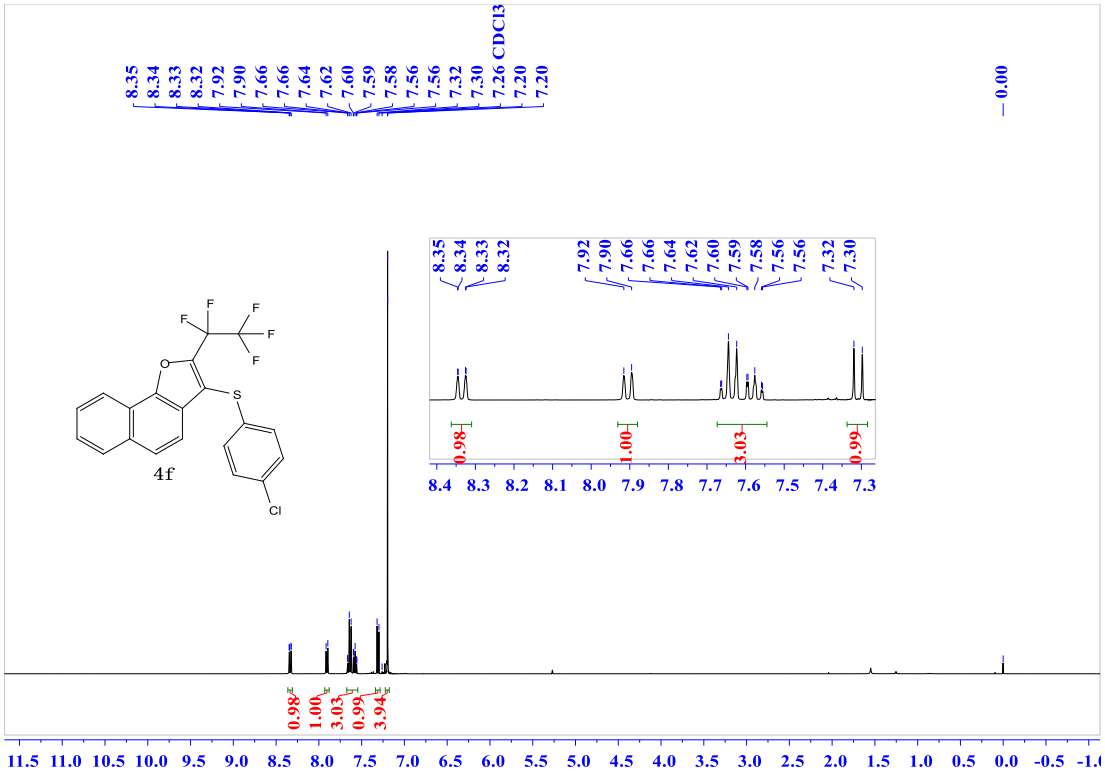
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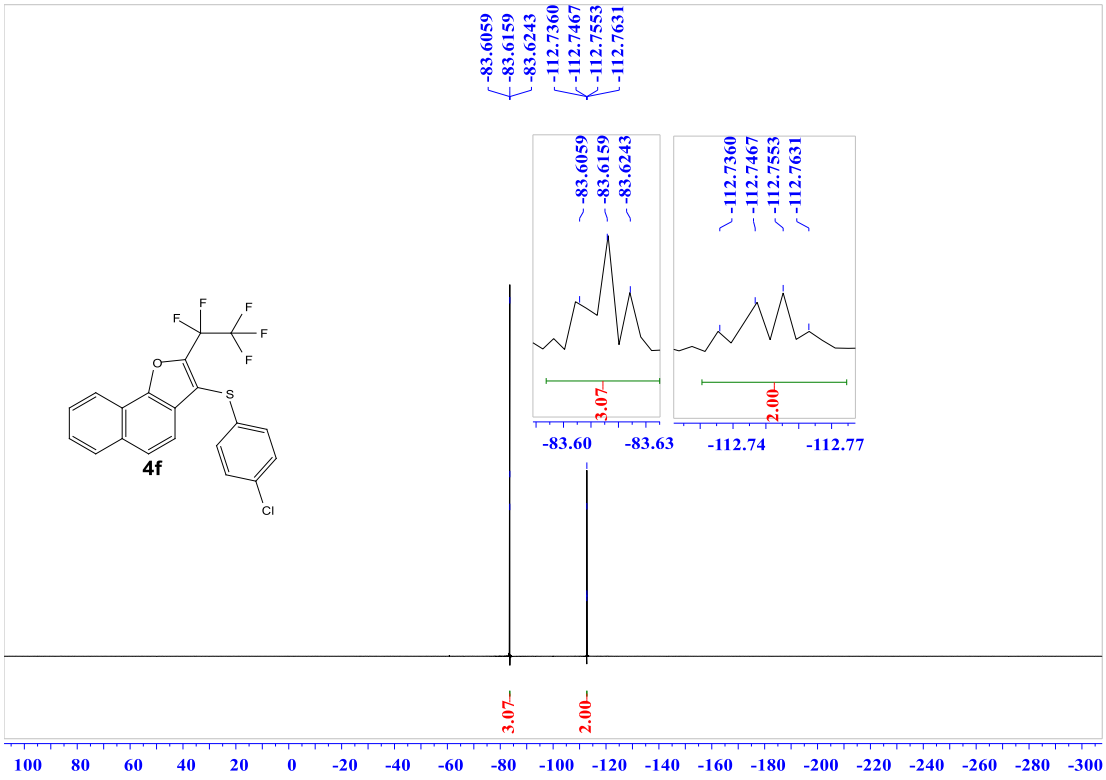
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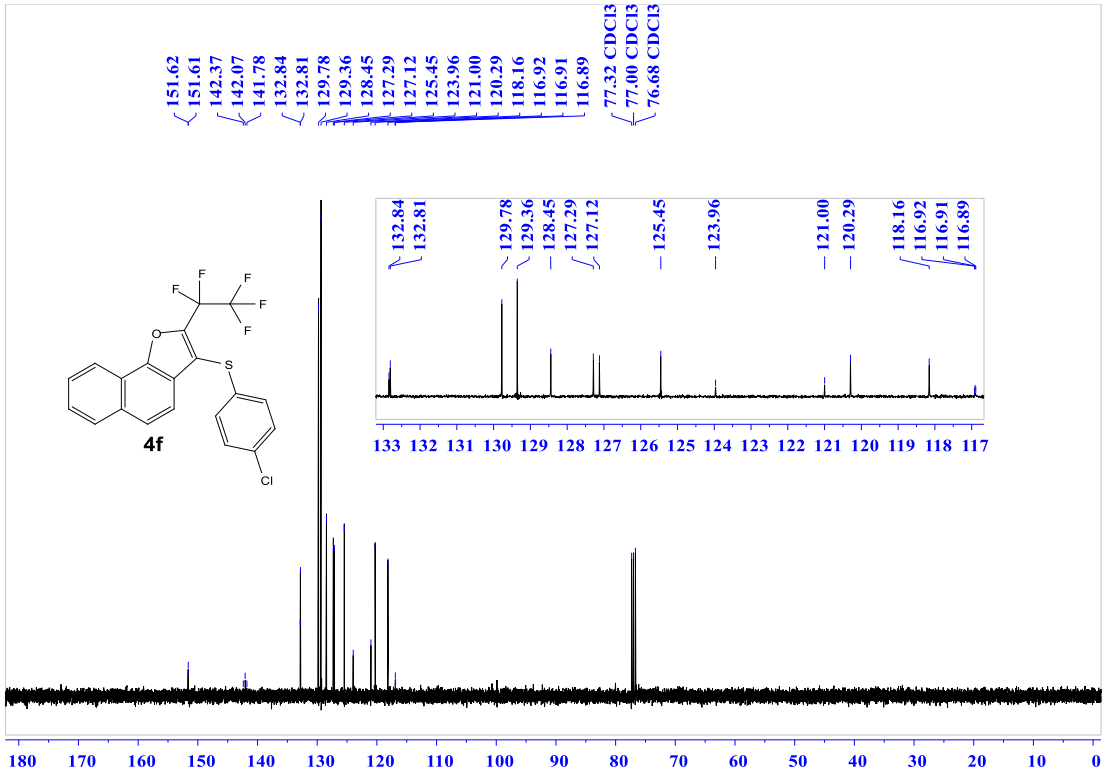
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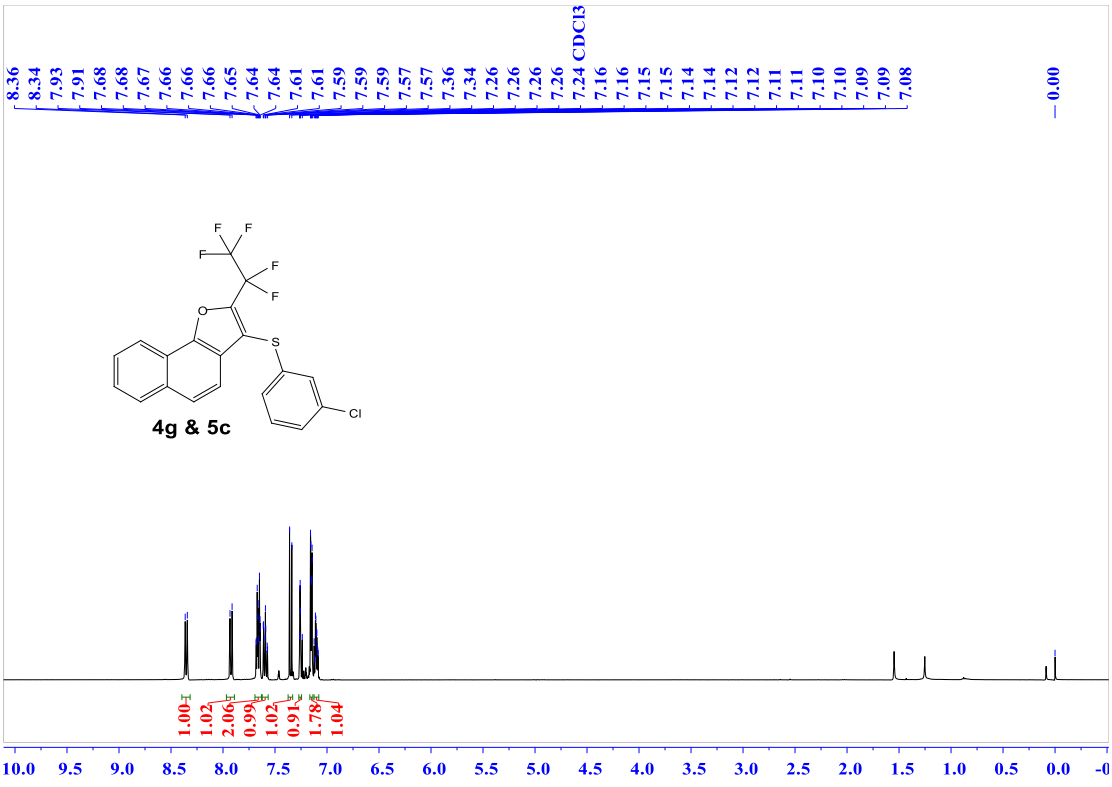
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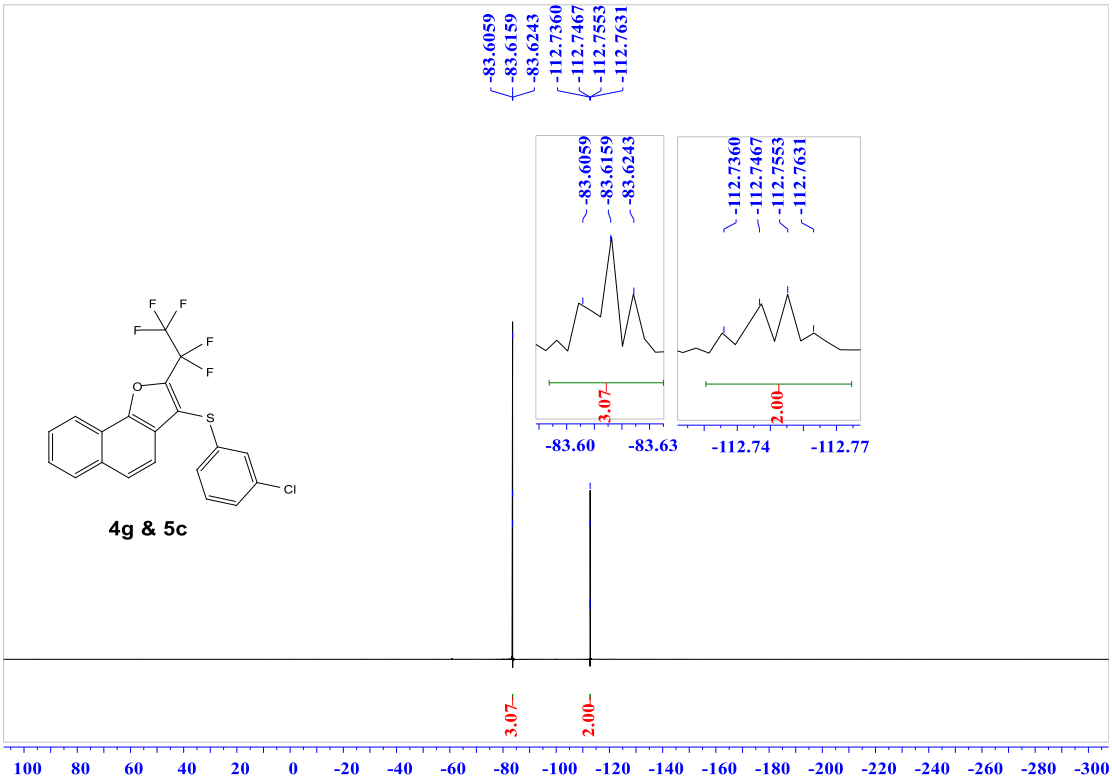
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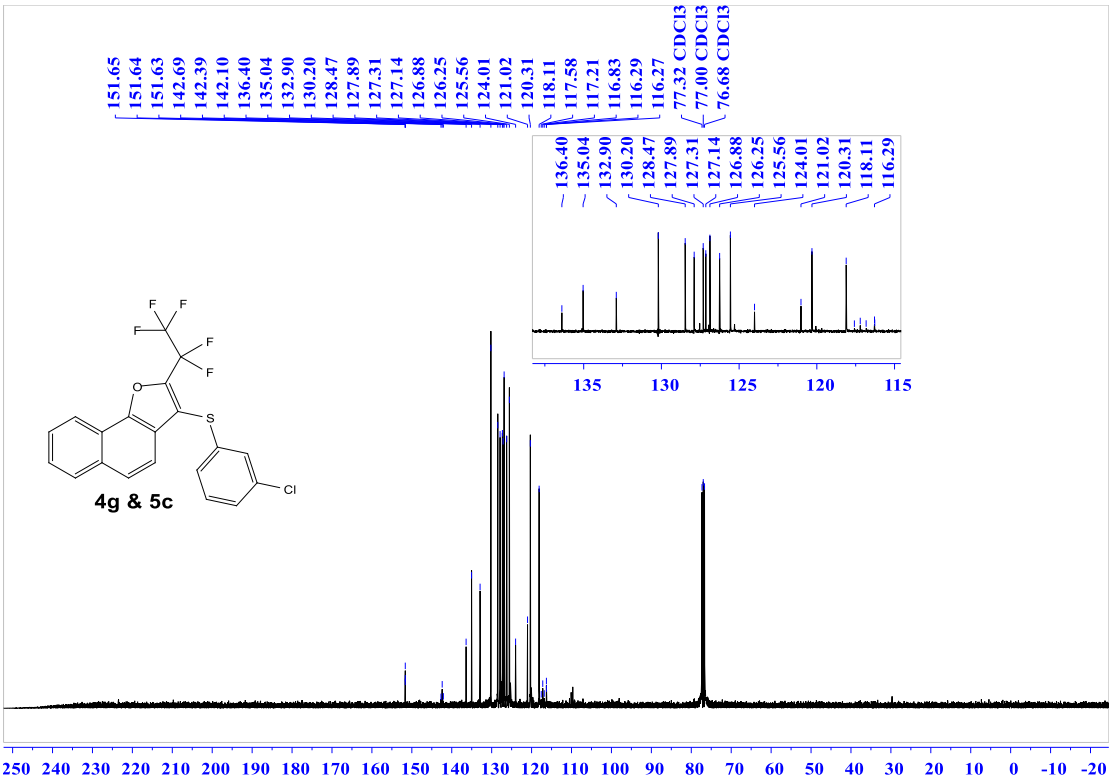
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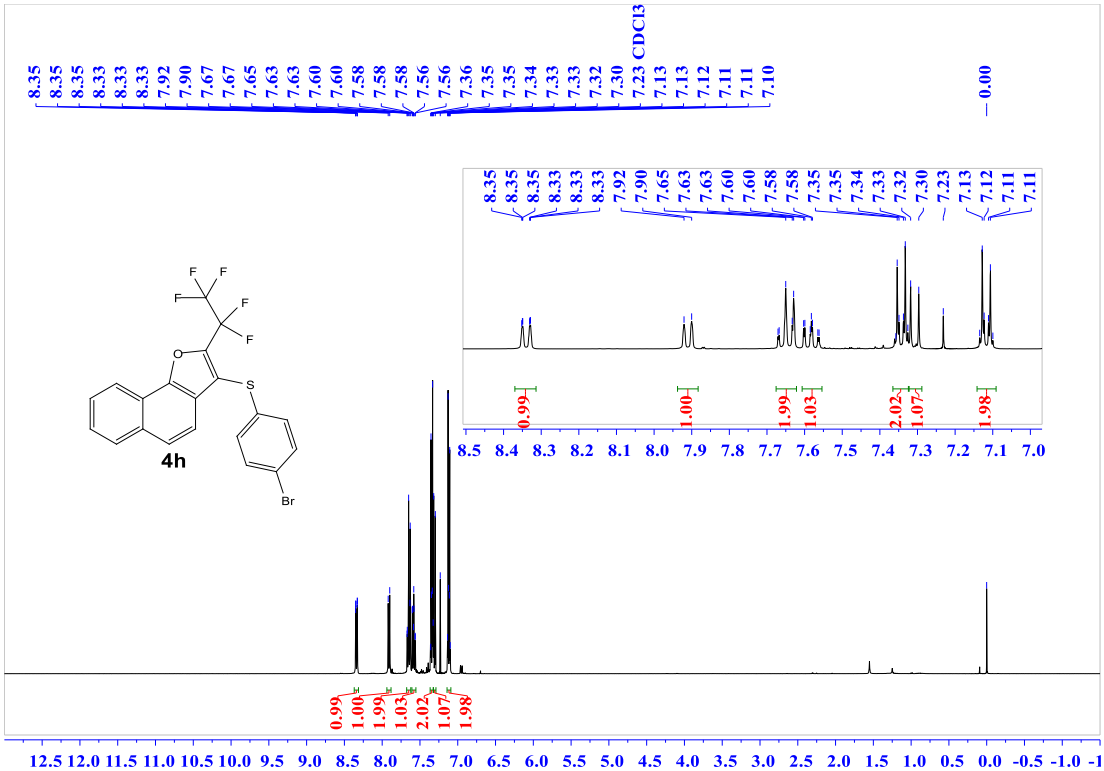
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2.02
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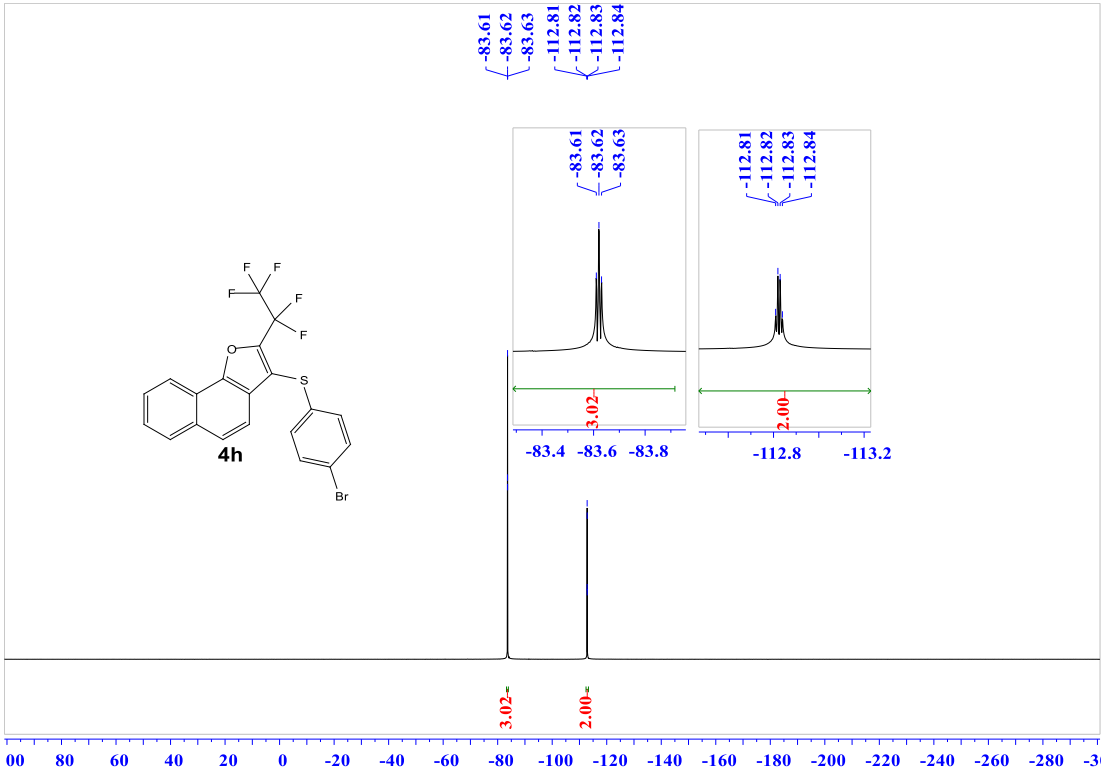
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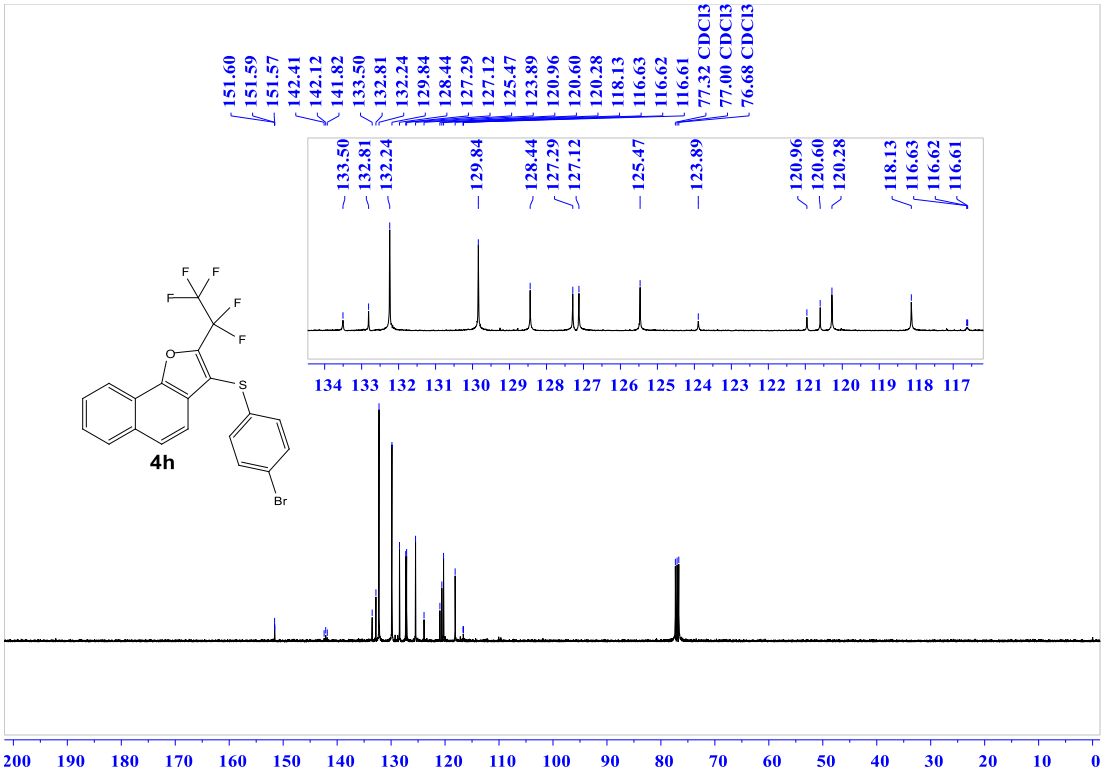
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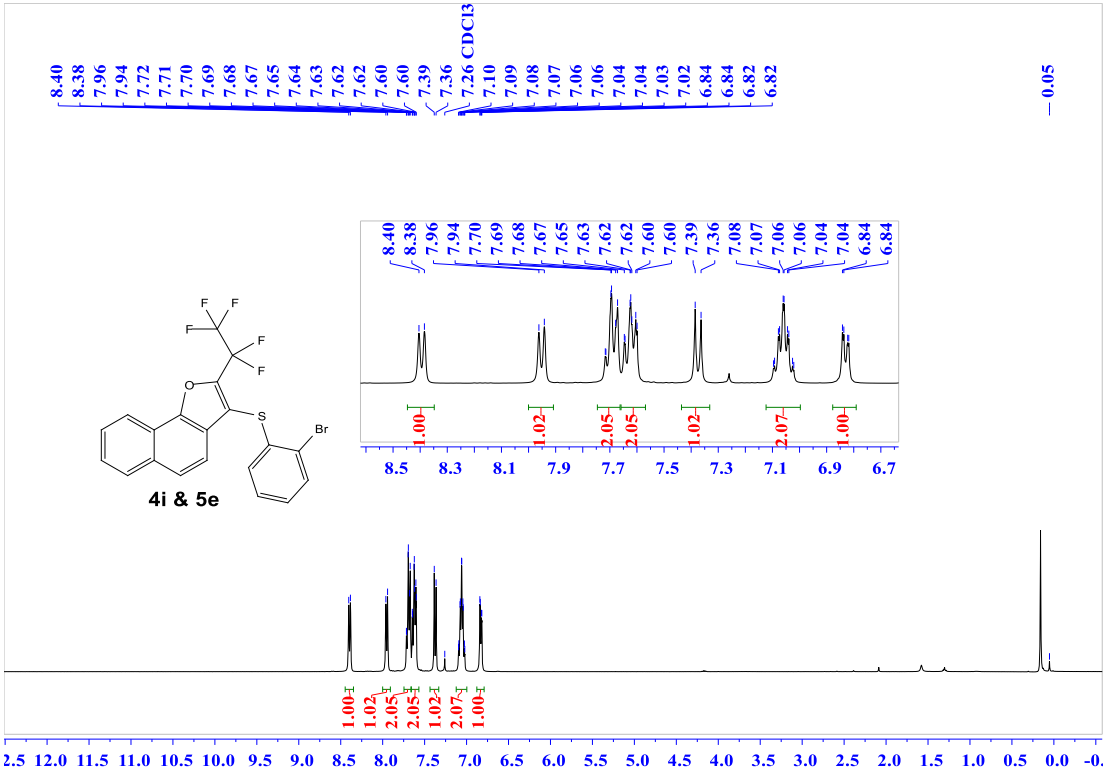
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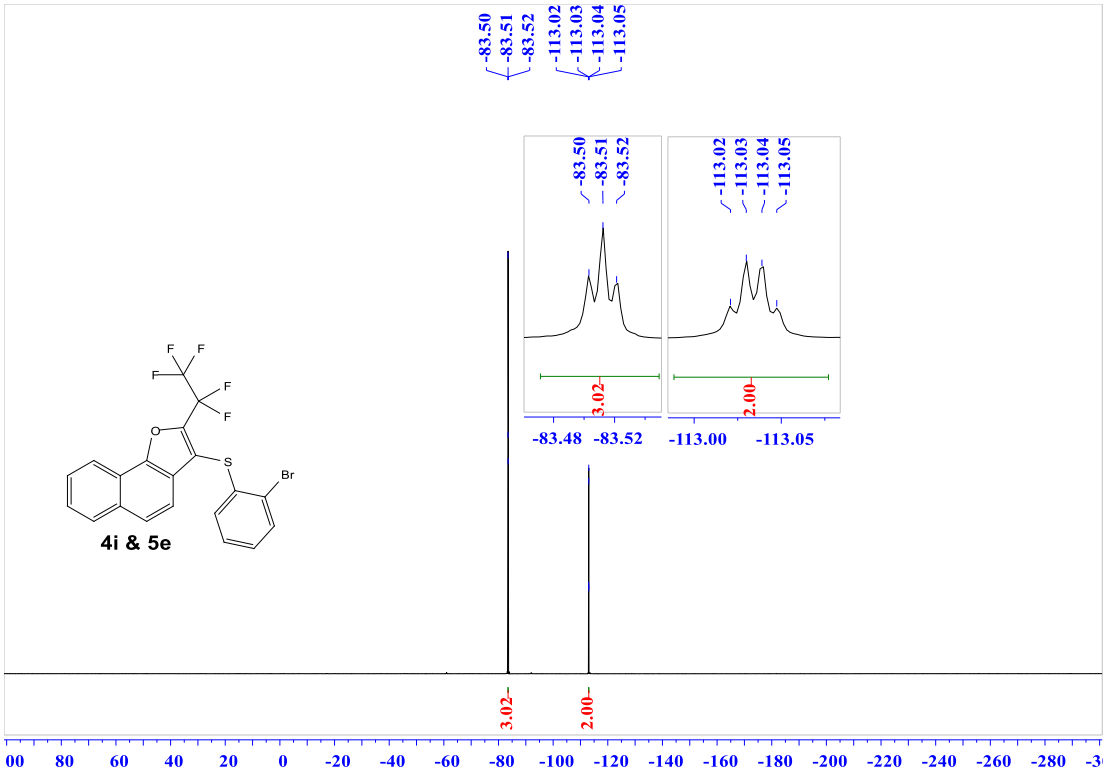
0.05
4i & 5e
1.00 1.02 2.05 2.05 1.02 2.07 1.00
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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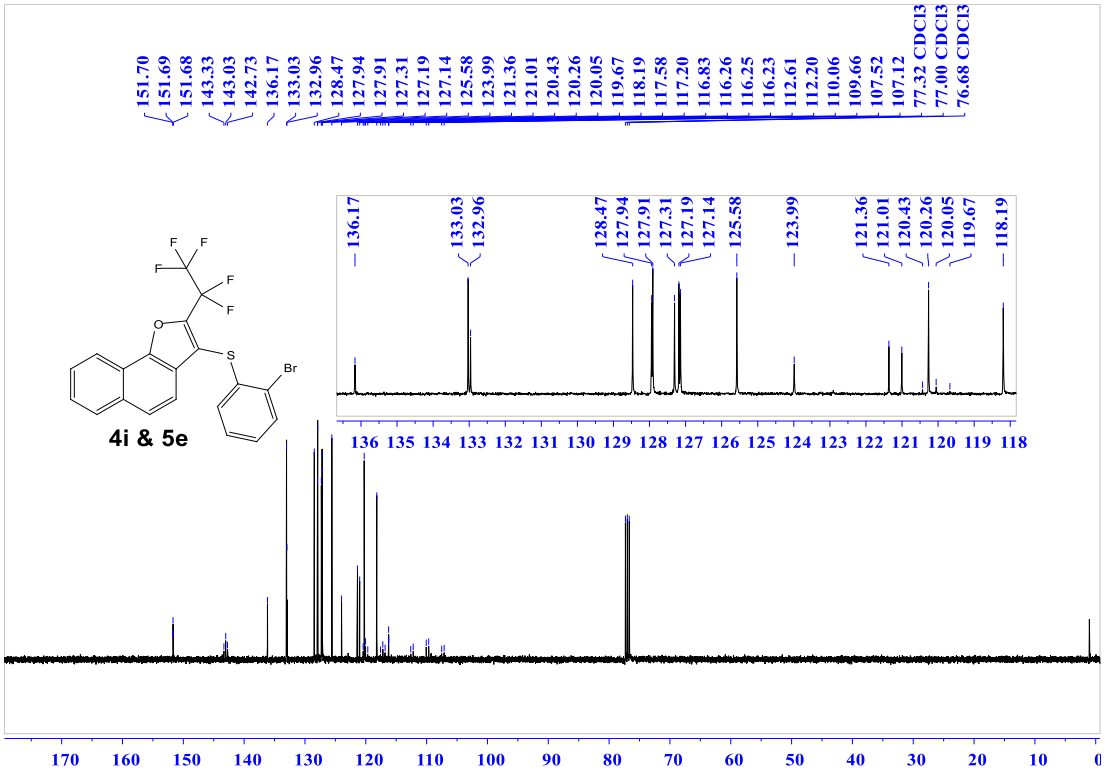
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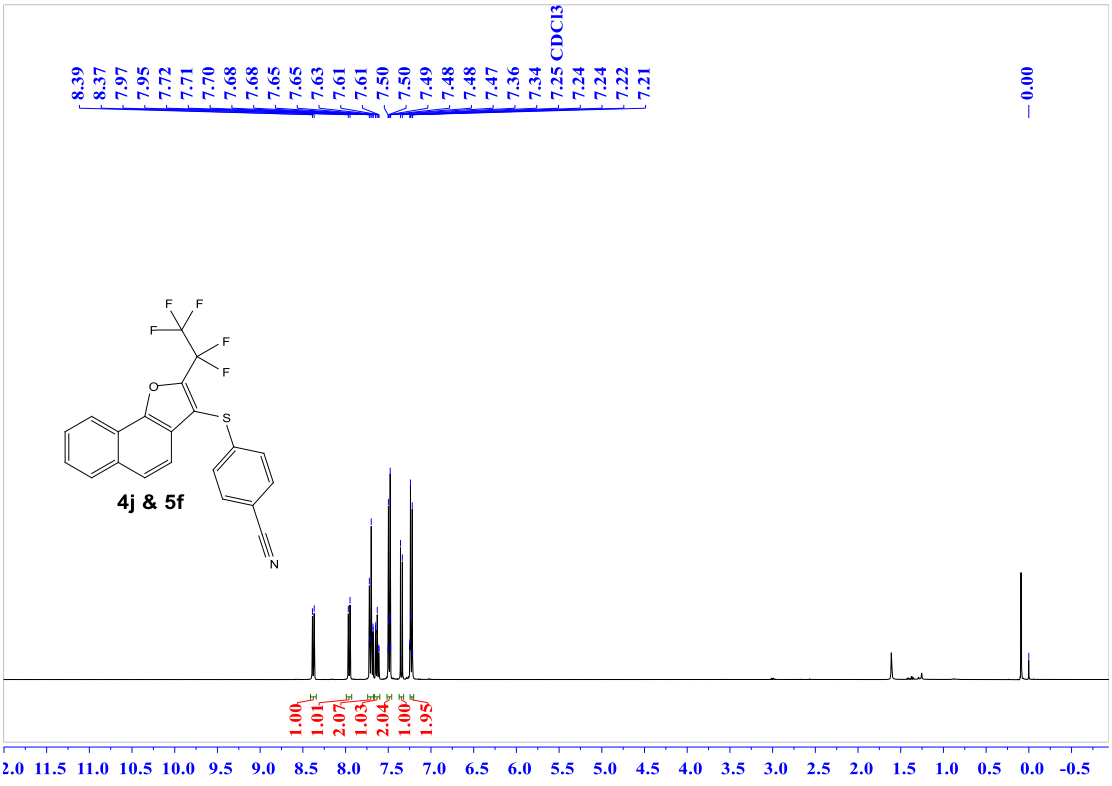
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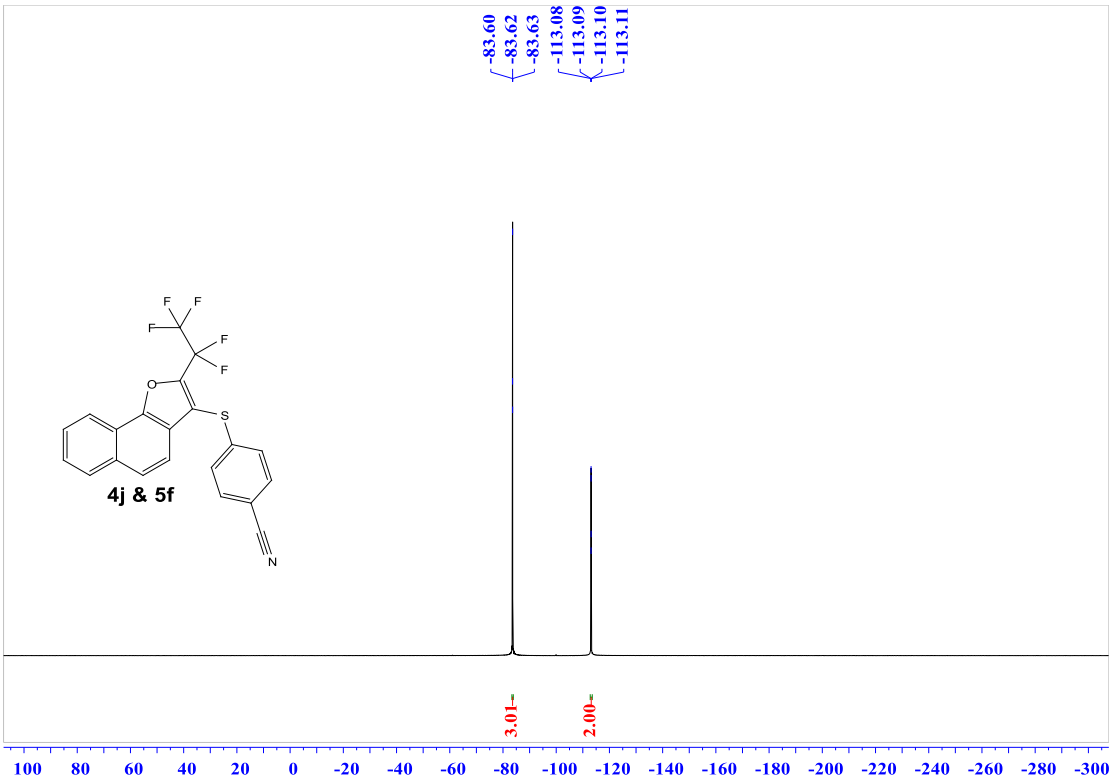
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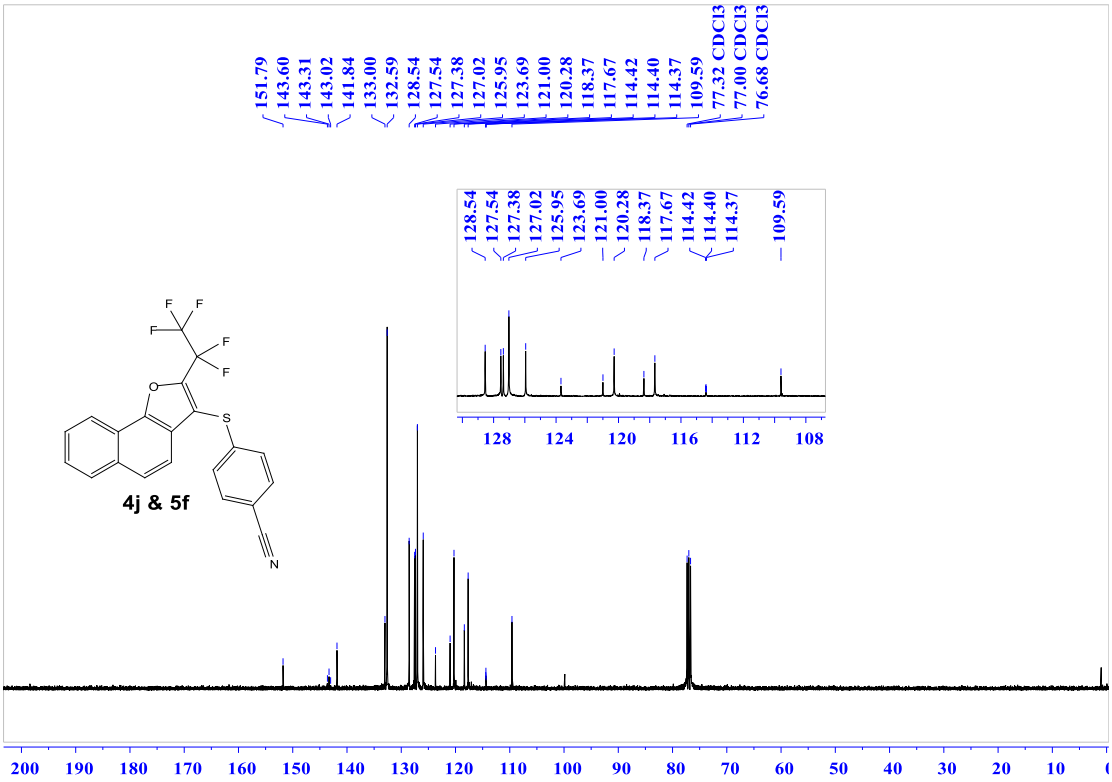
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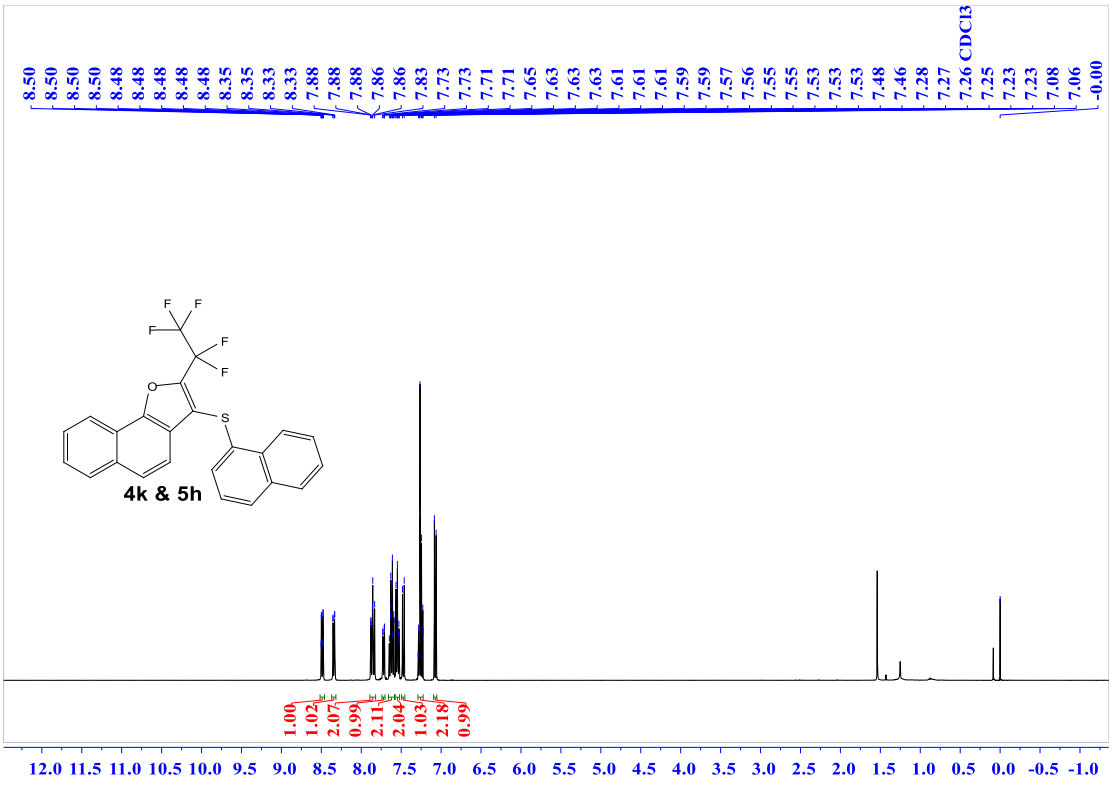
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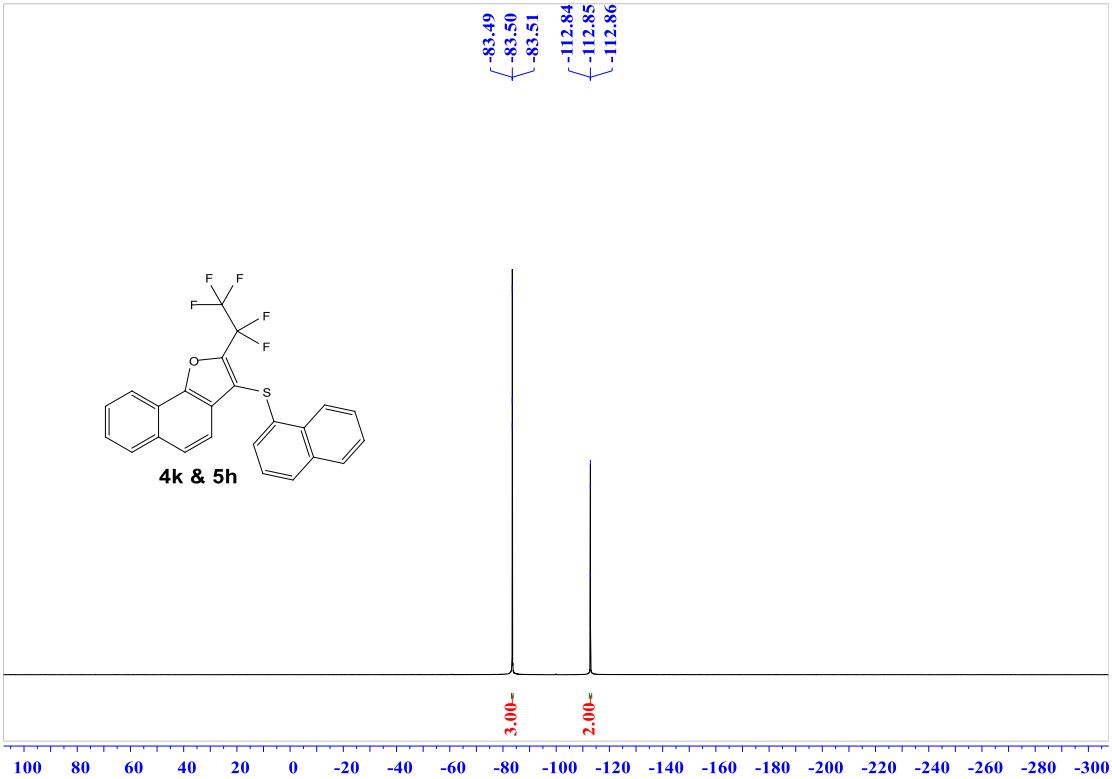
4k & 5h
1.00 1.02 2.07 0.99 2.11 2.04 1.03 2.18 0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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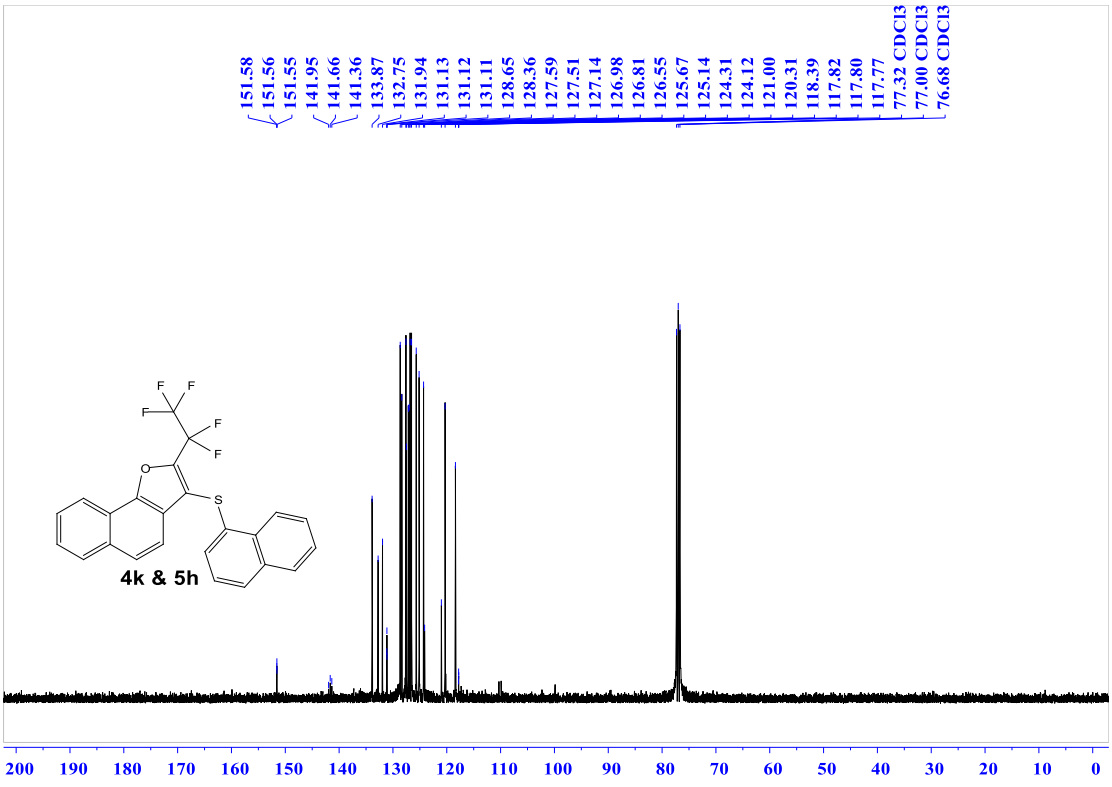
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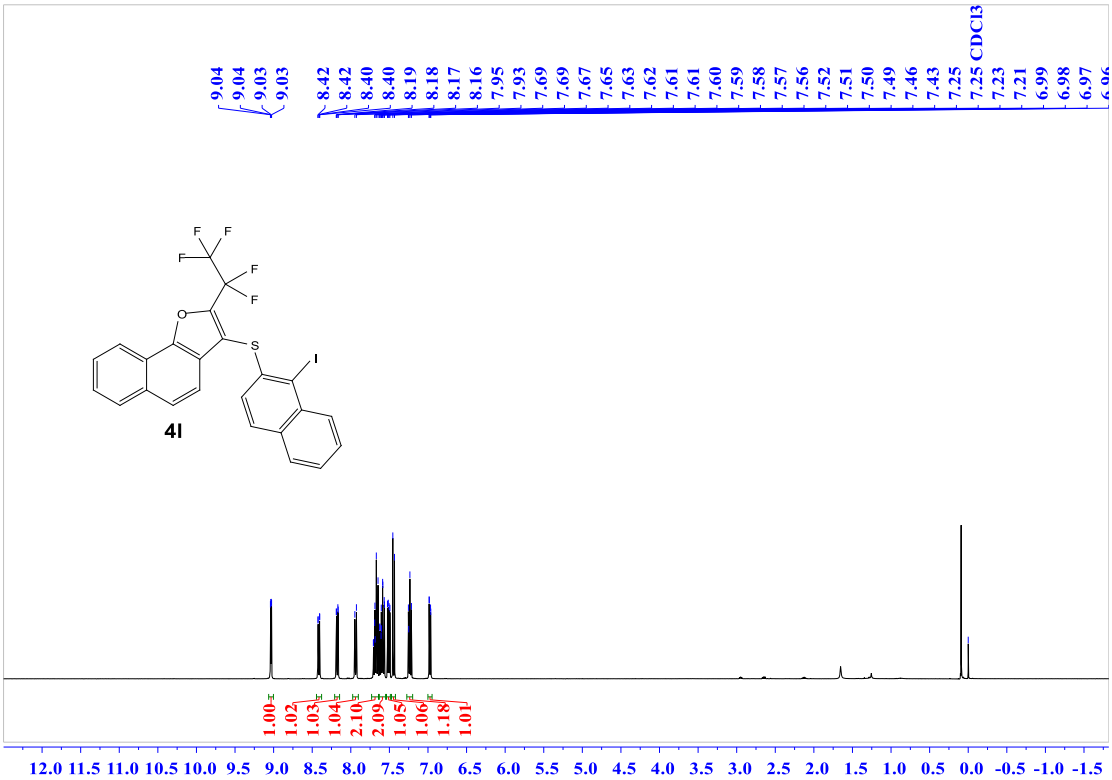
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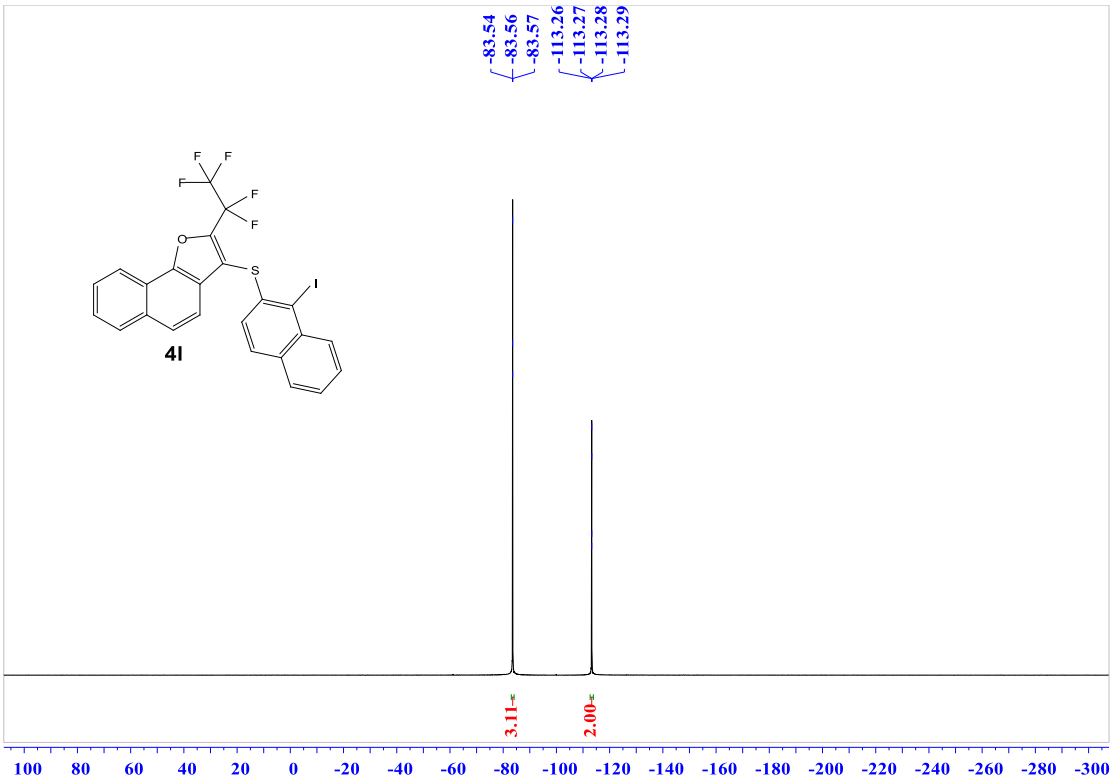
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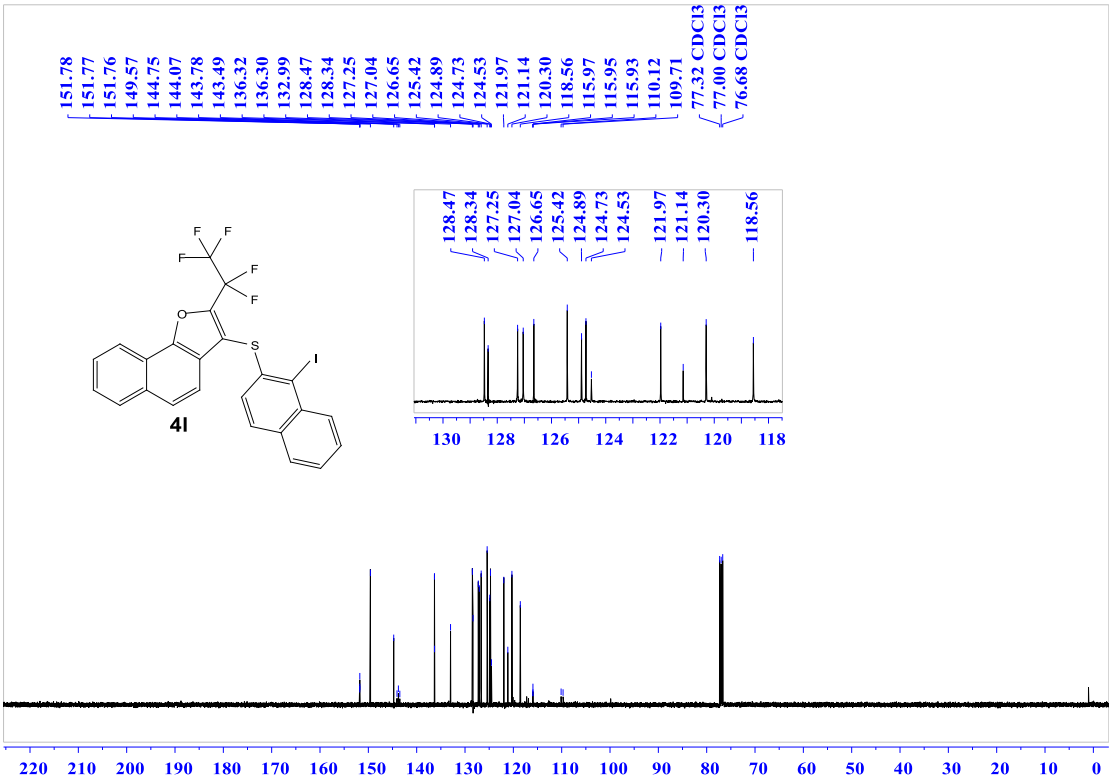
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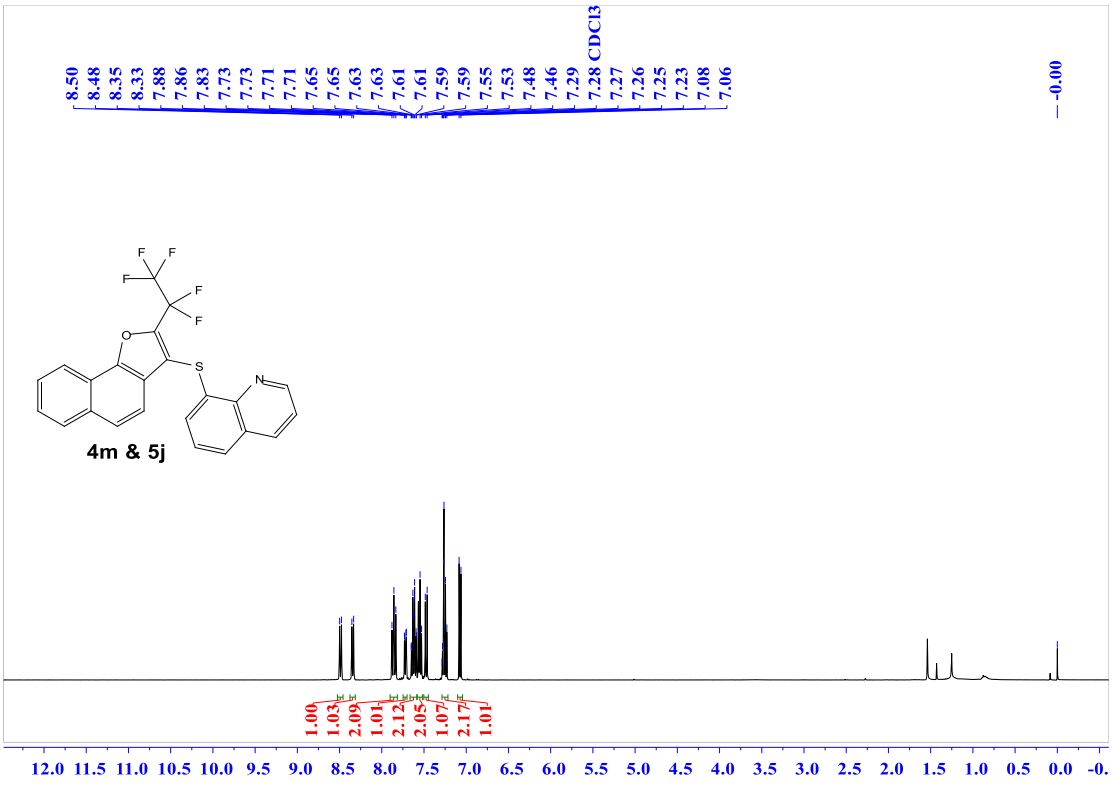
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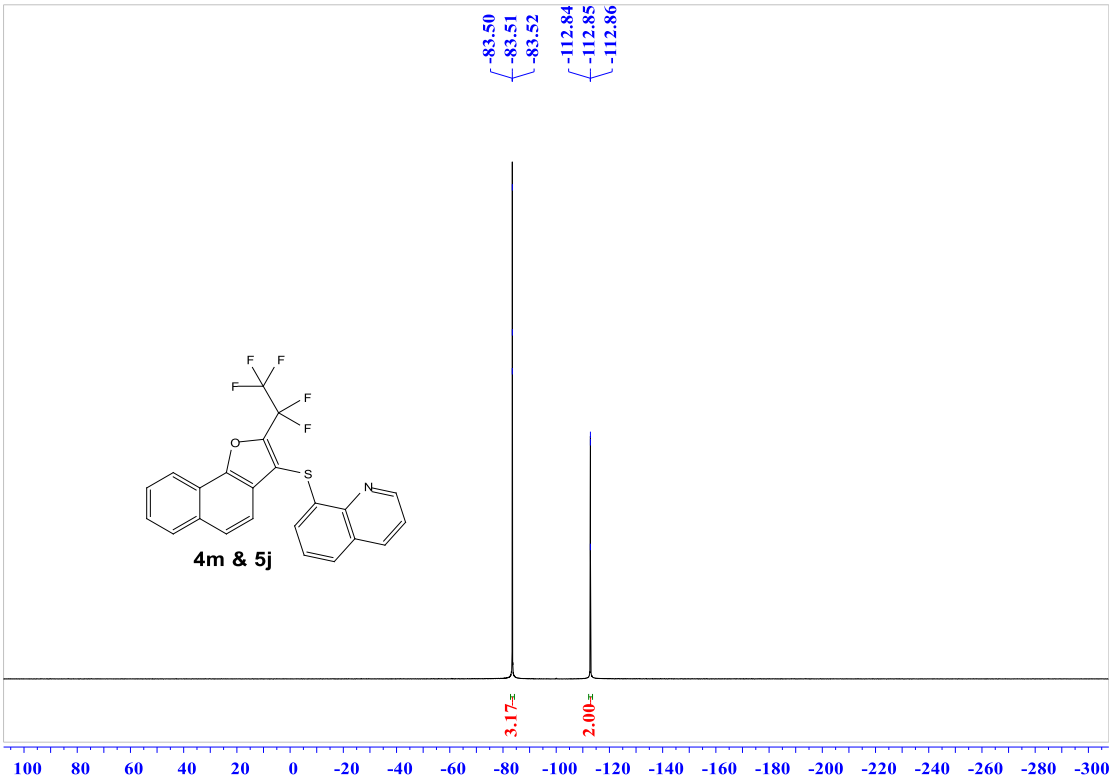
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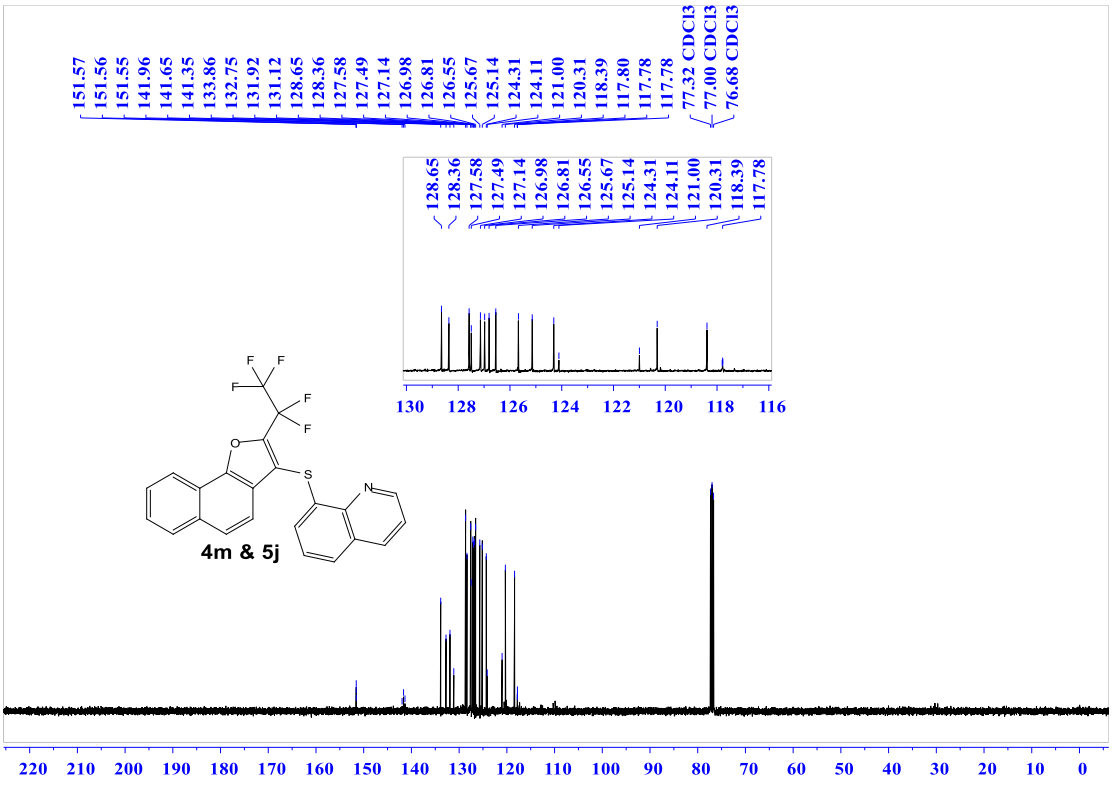
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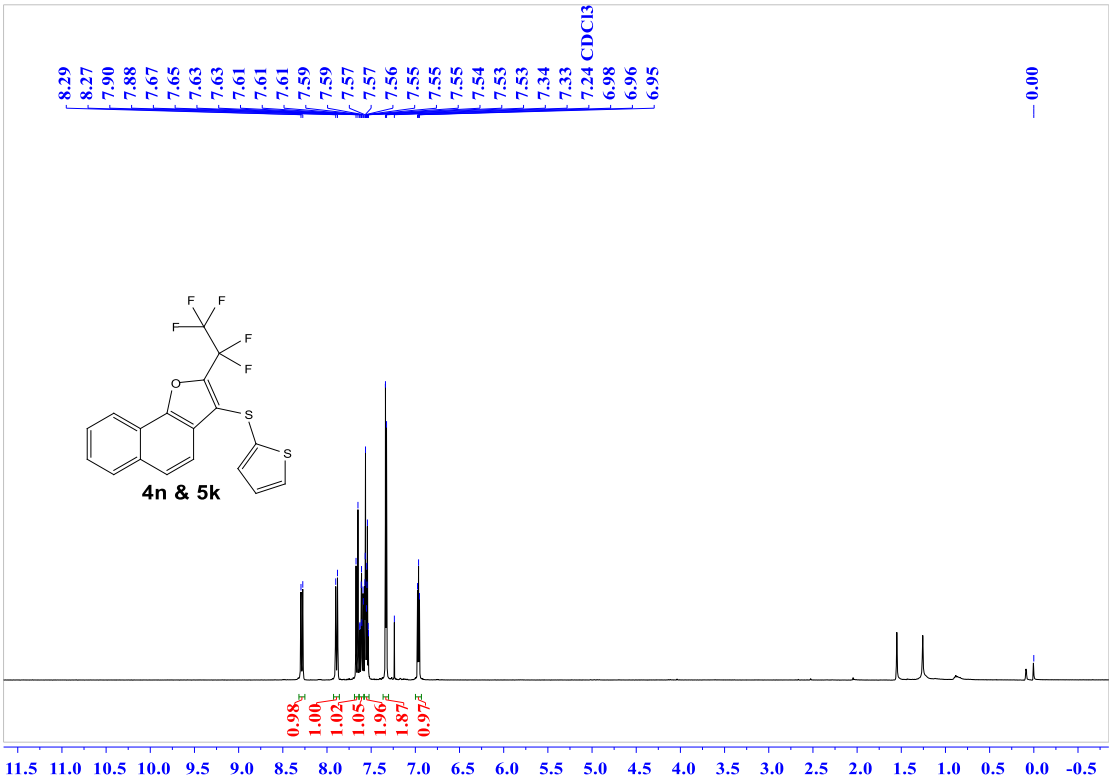
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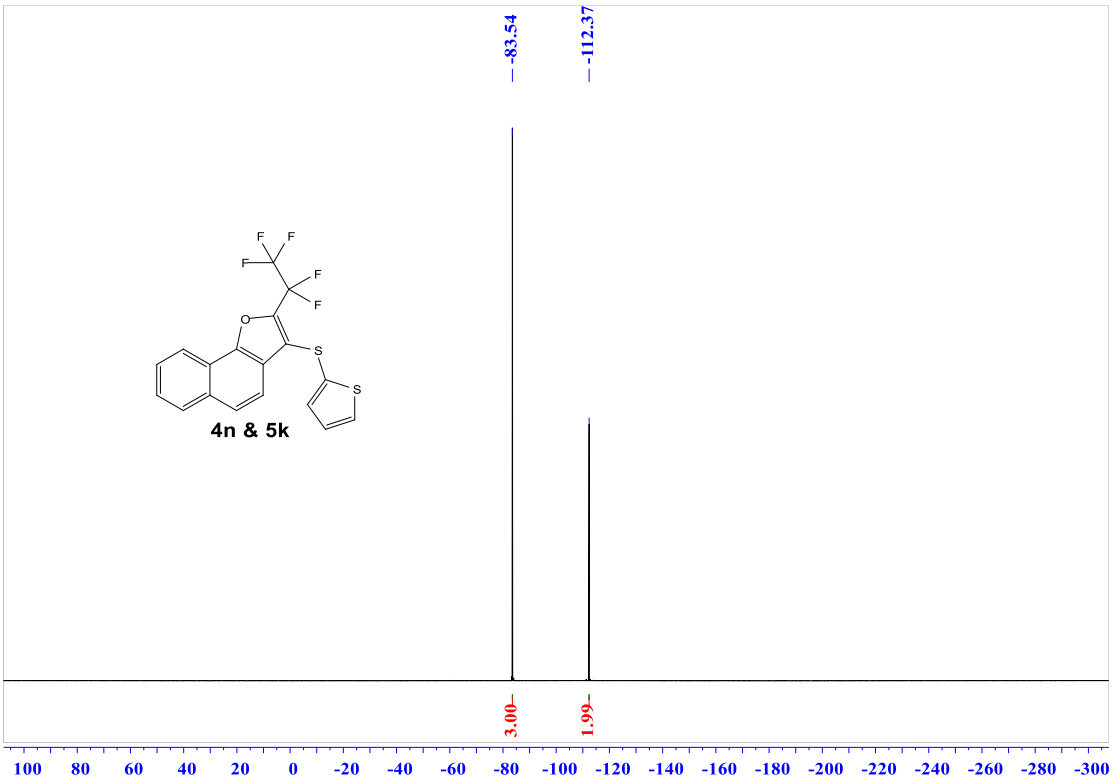
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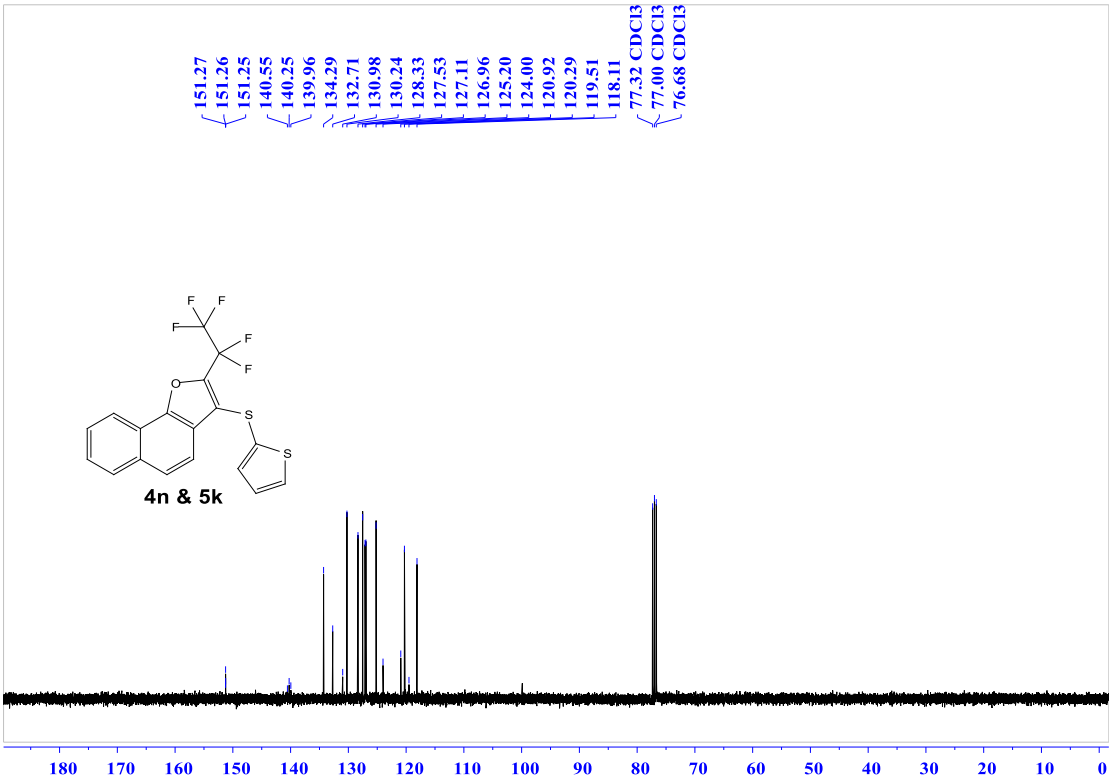
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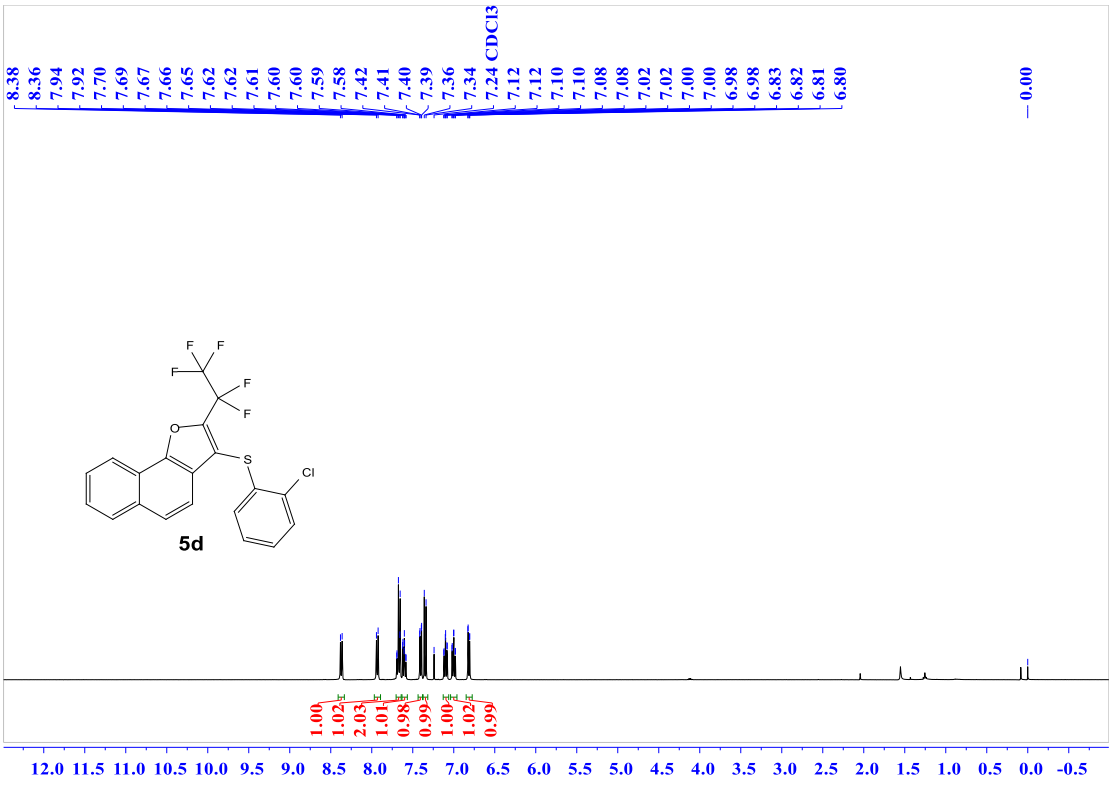
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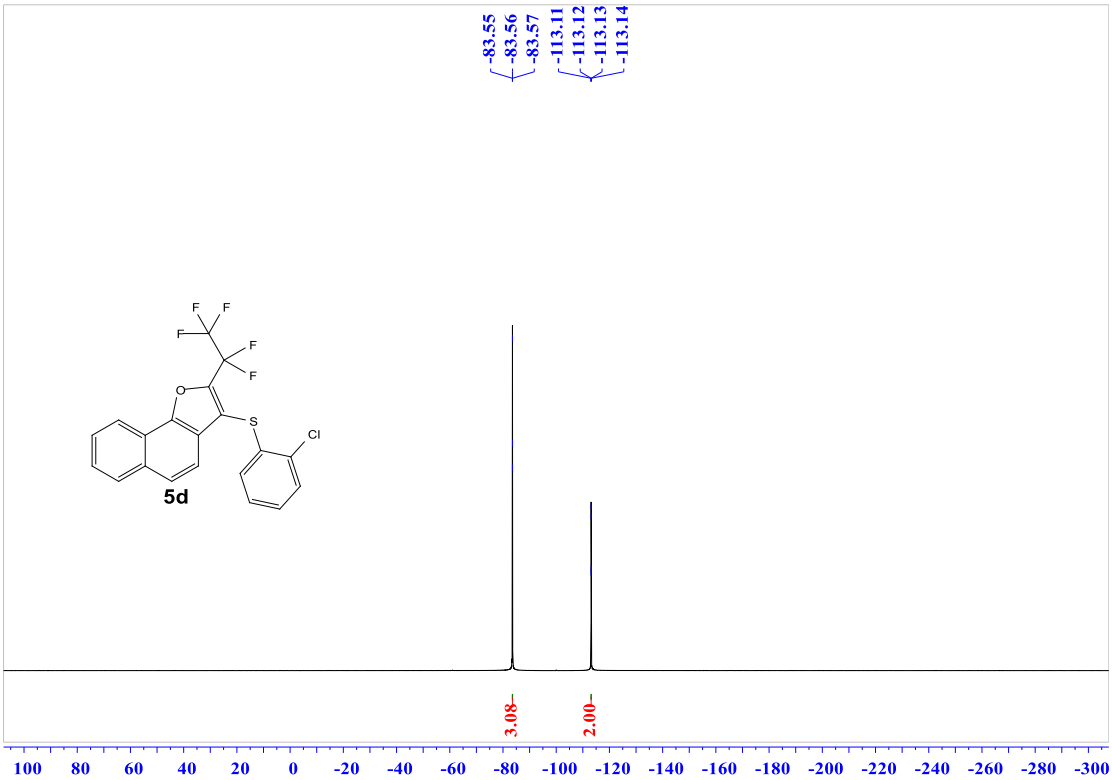
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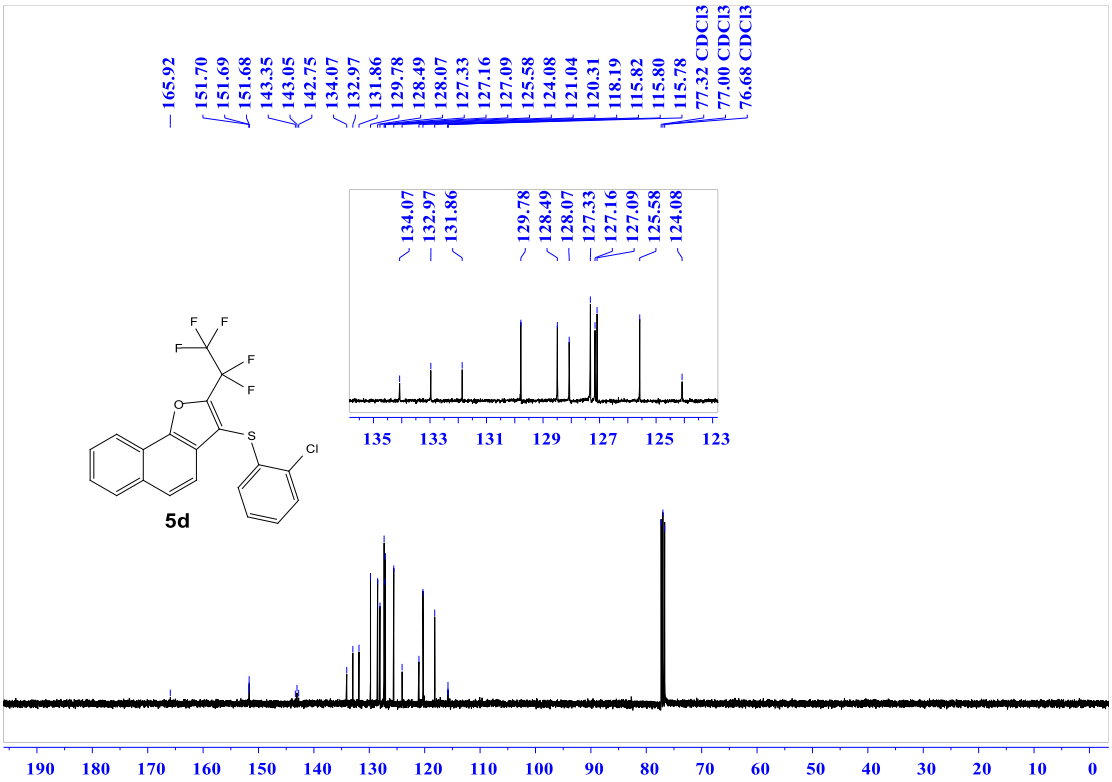
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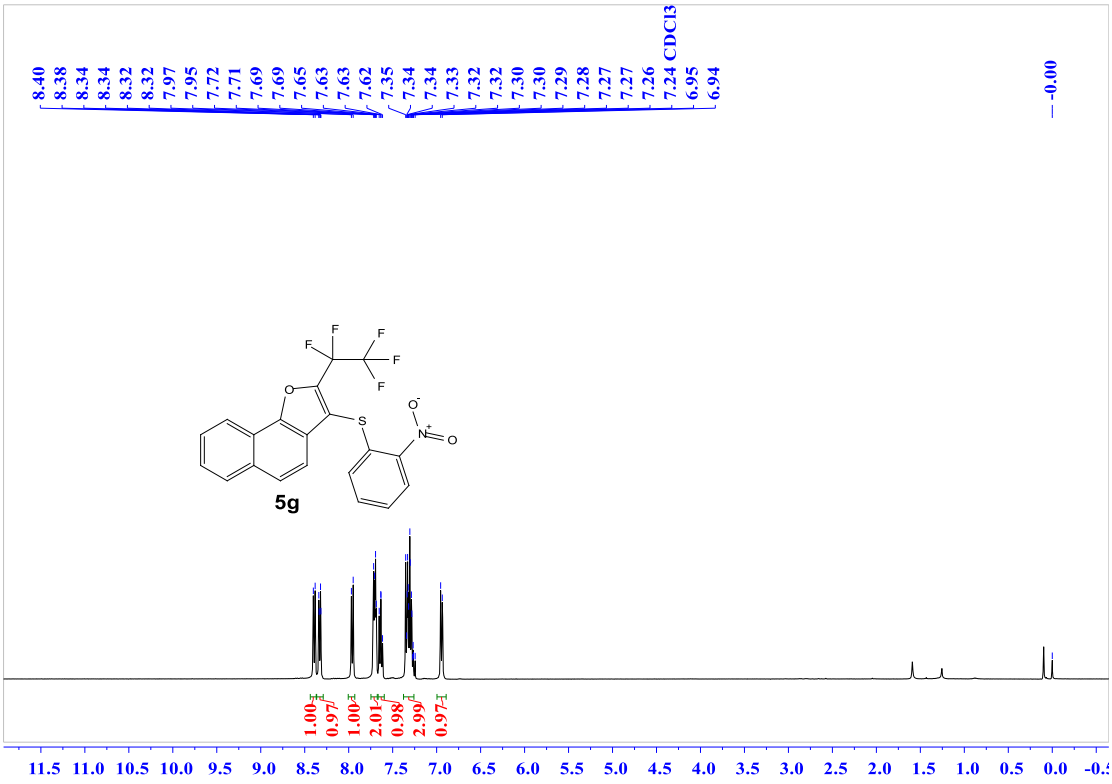
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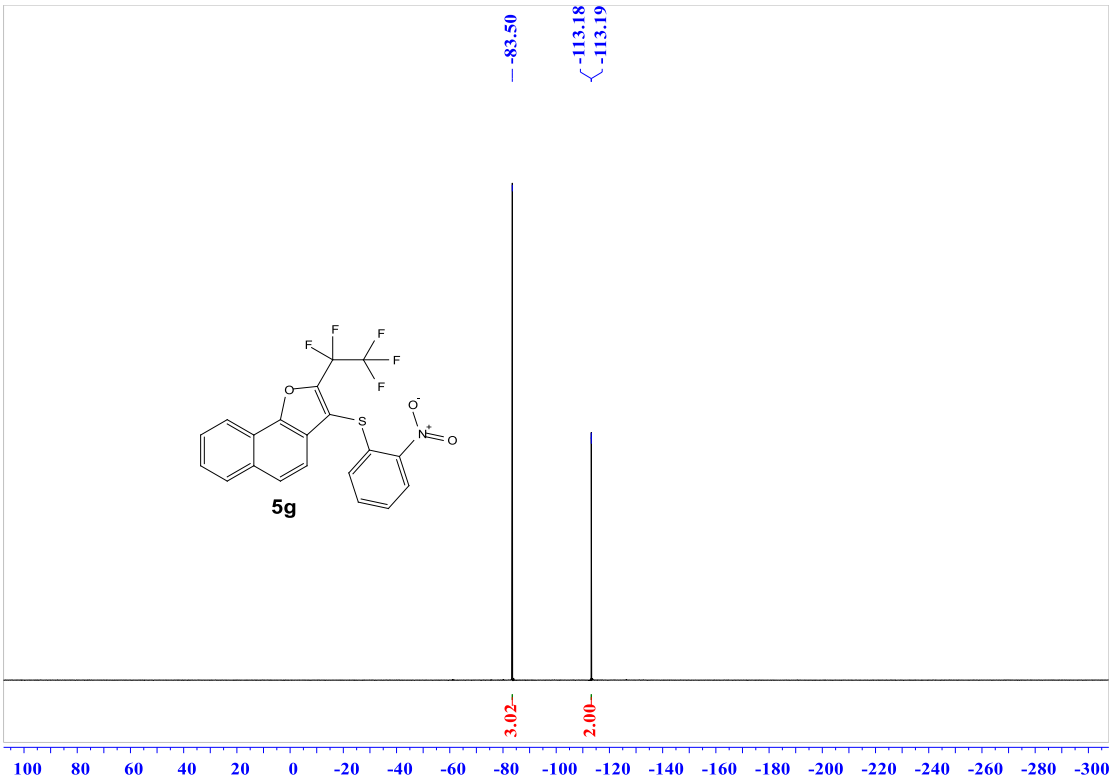
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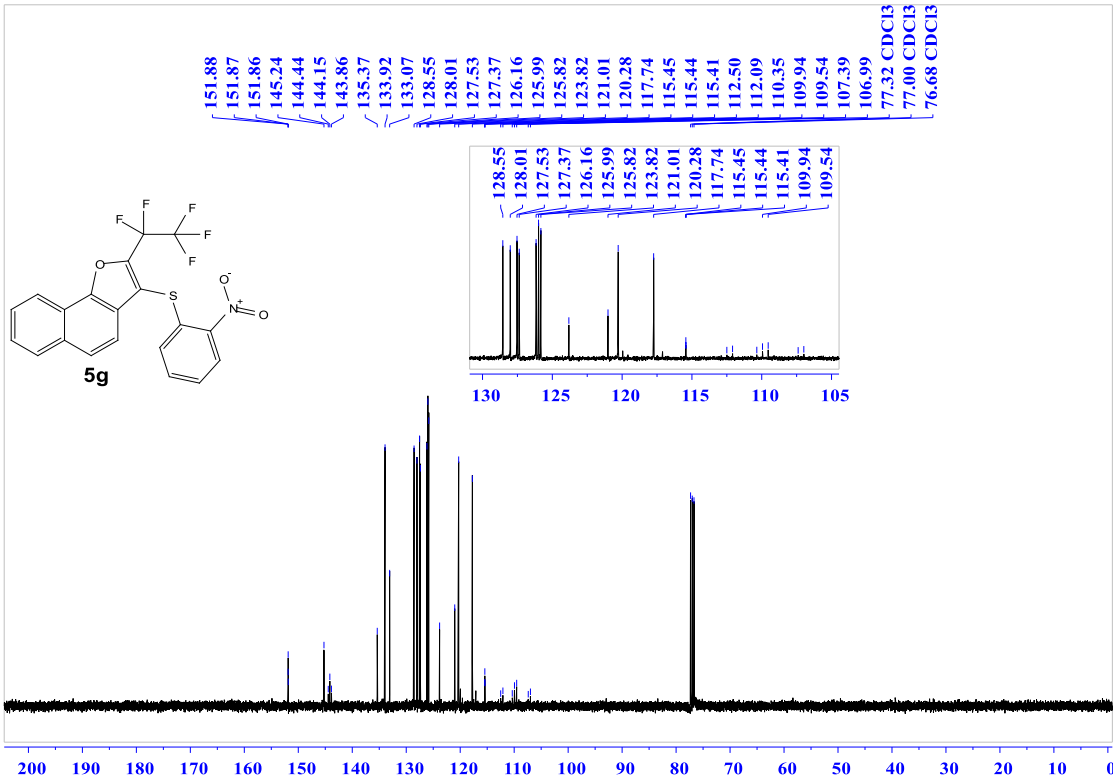
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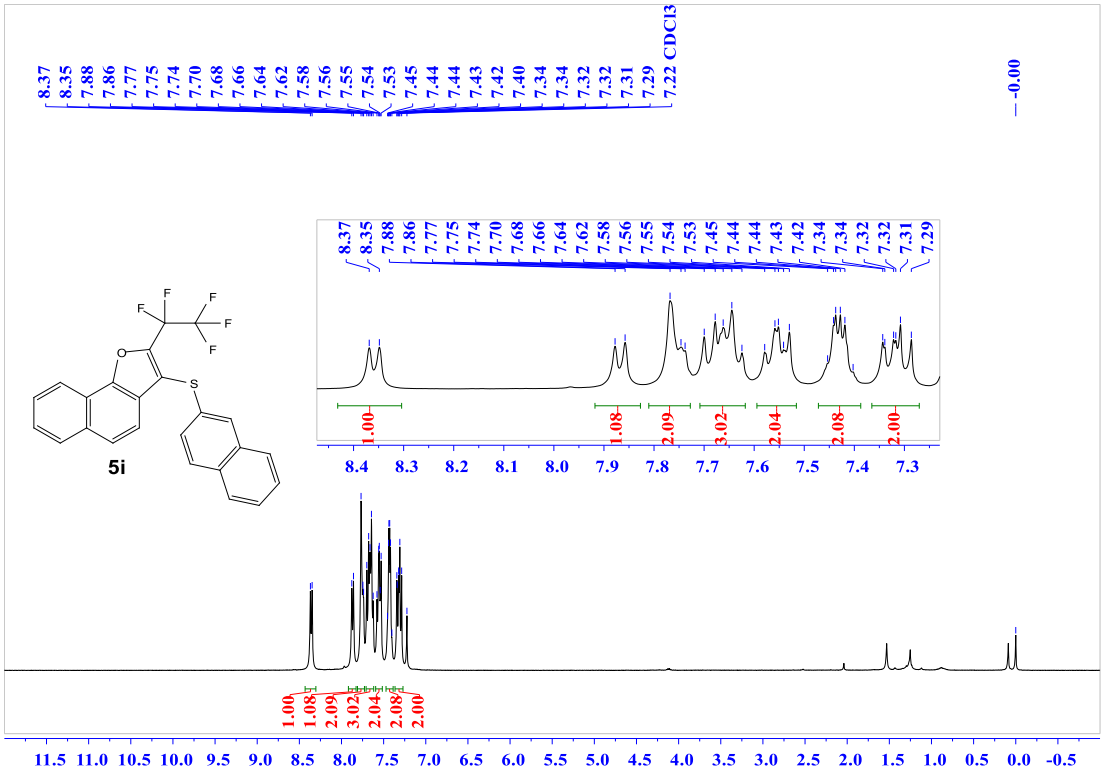
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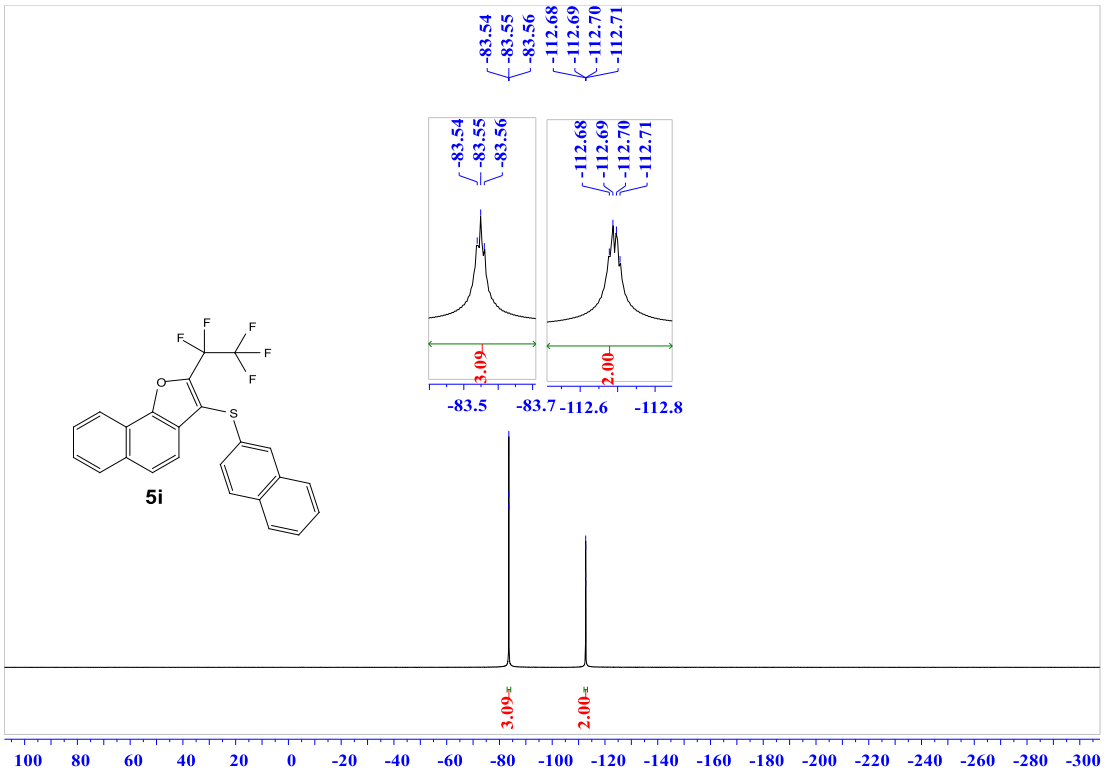
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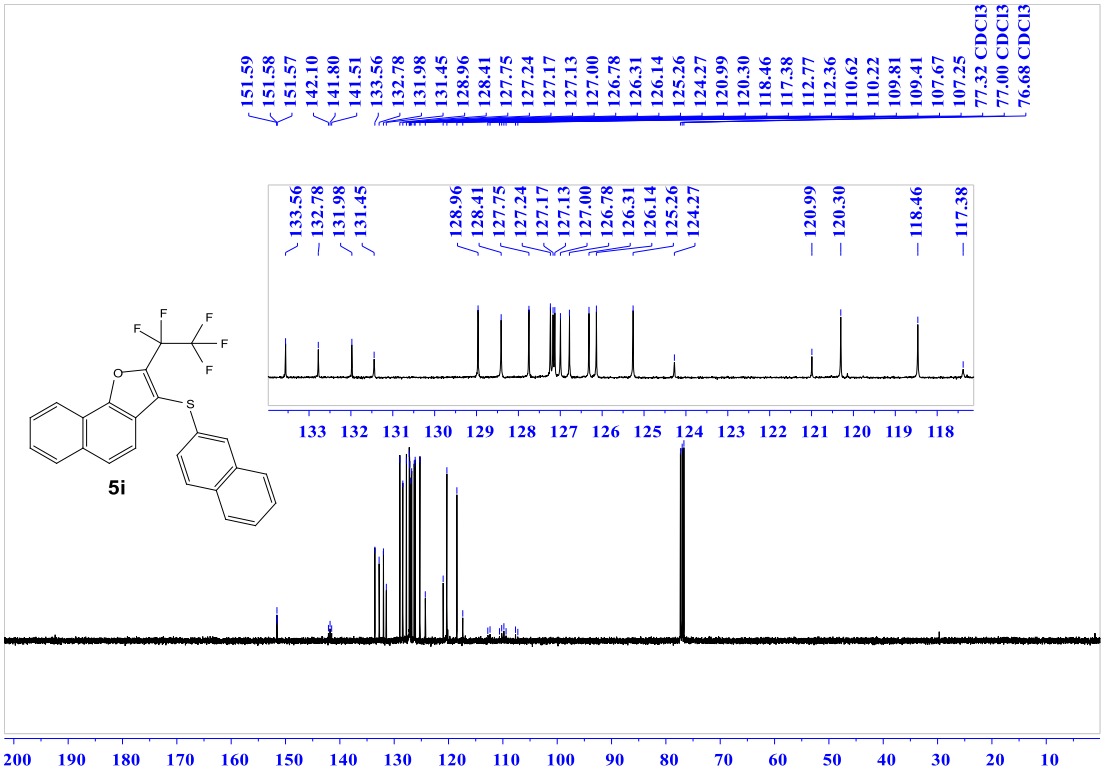
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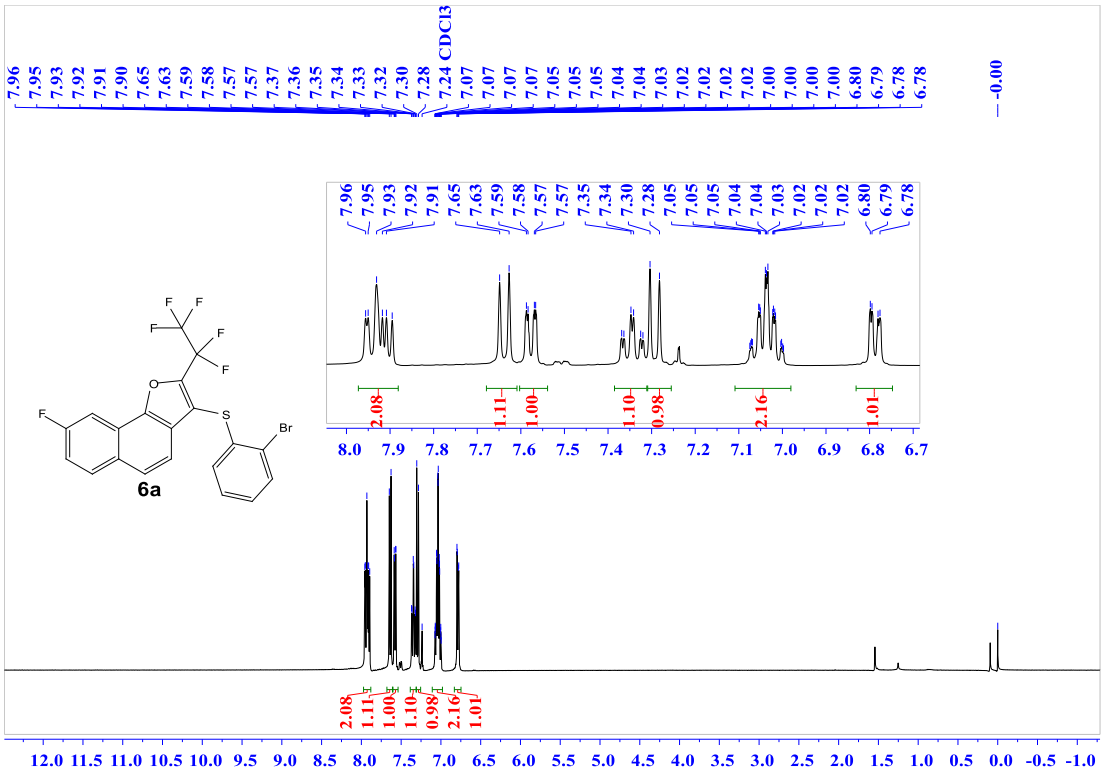
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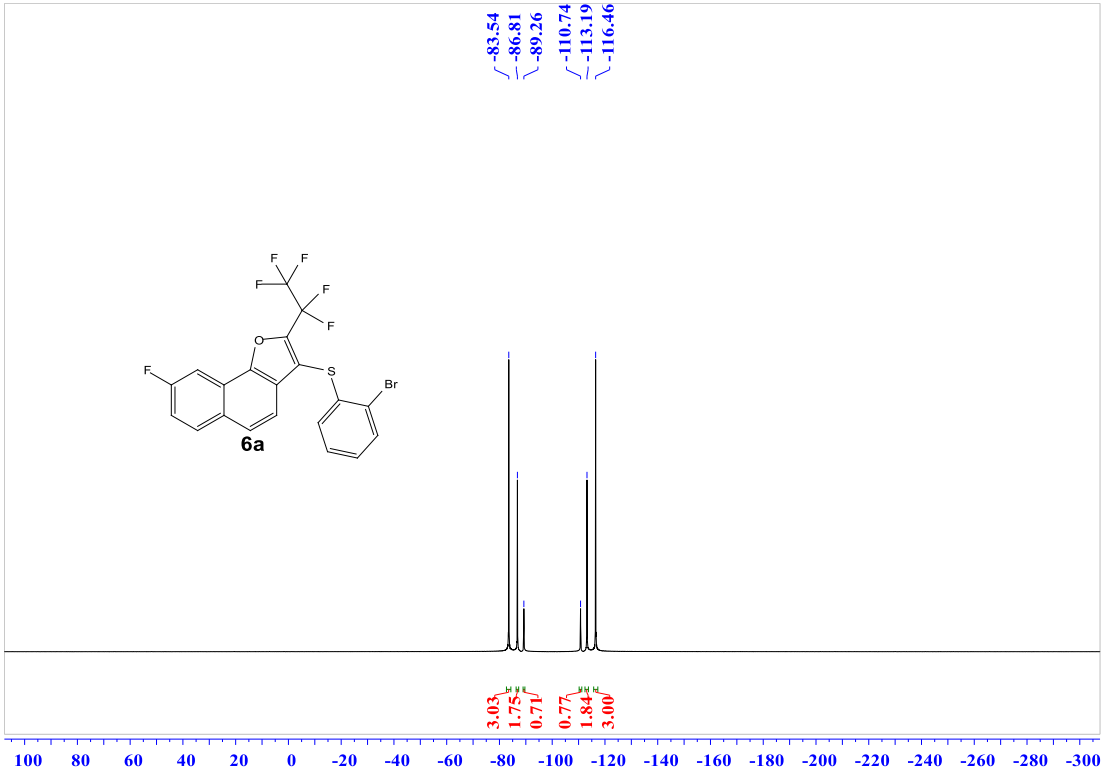
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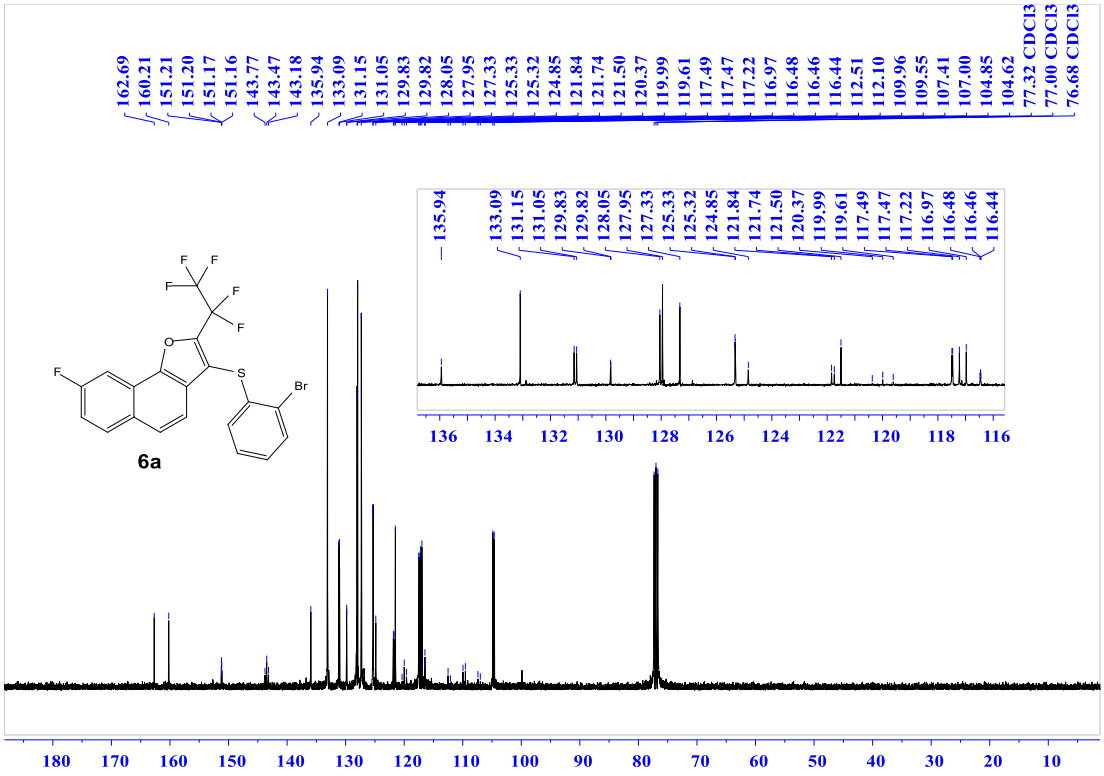
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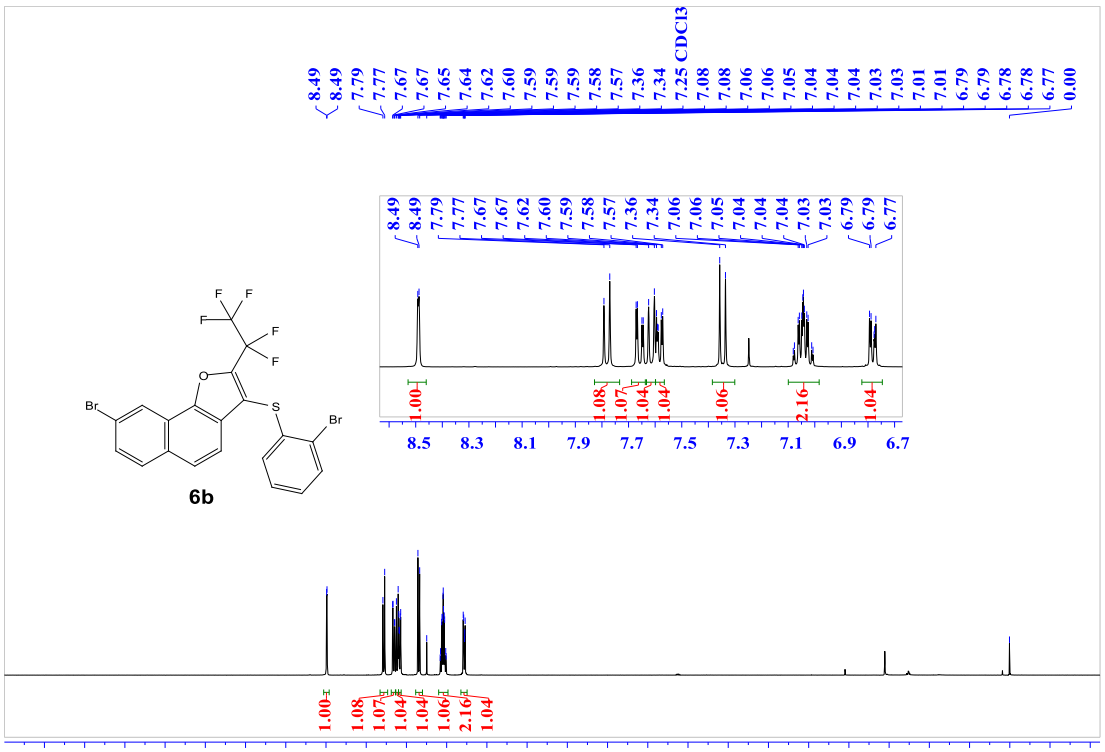
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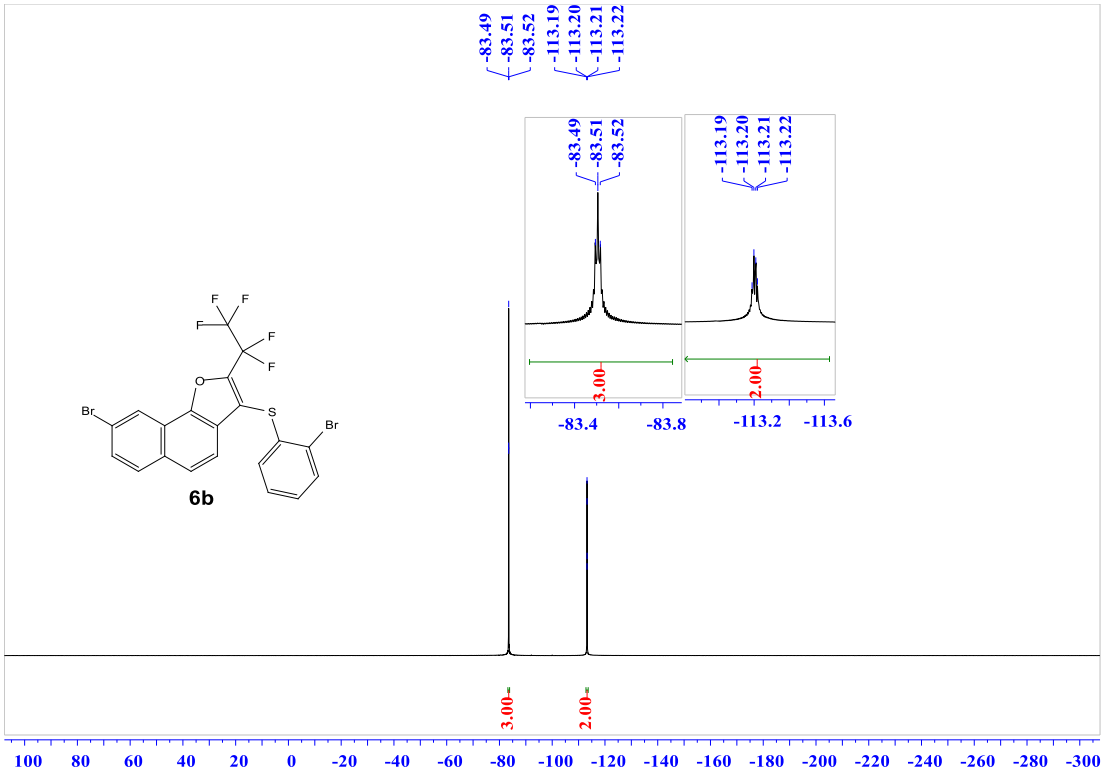
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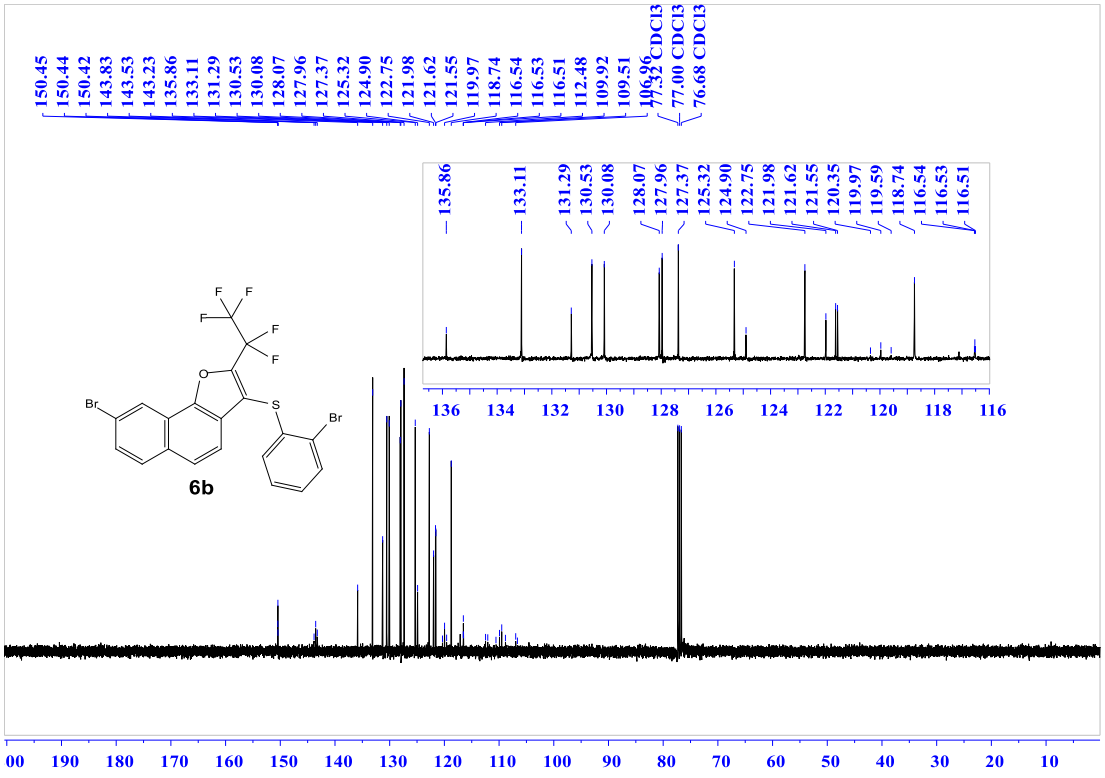
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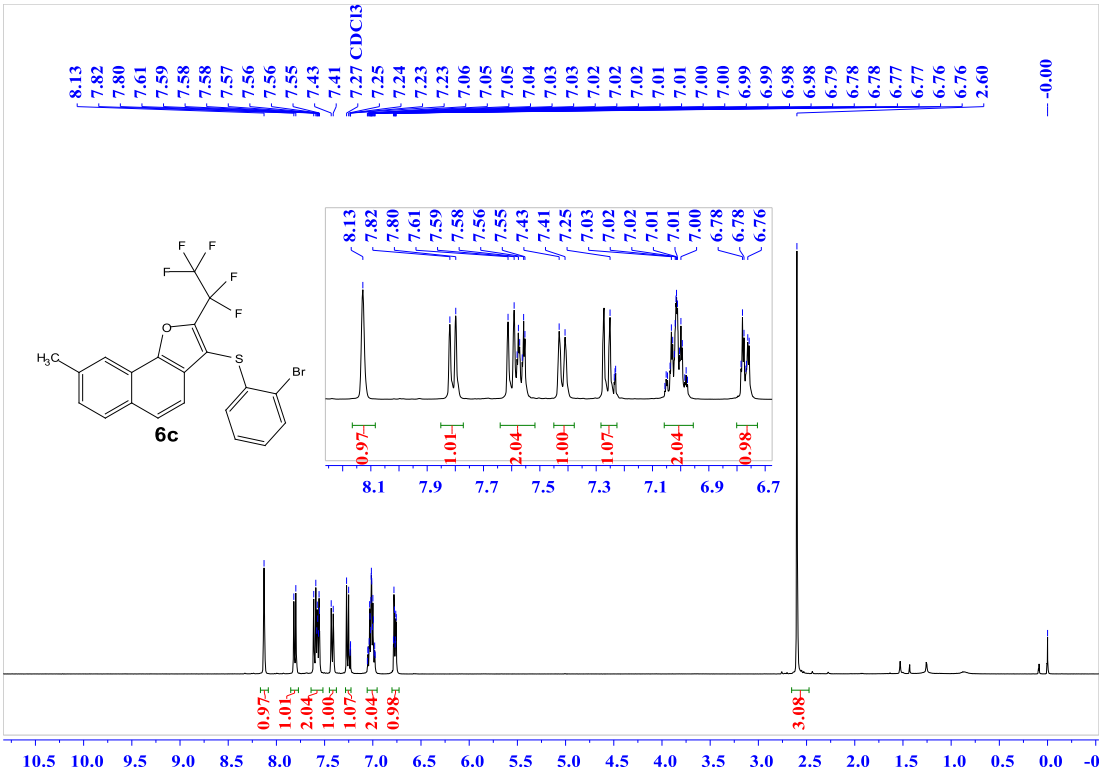
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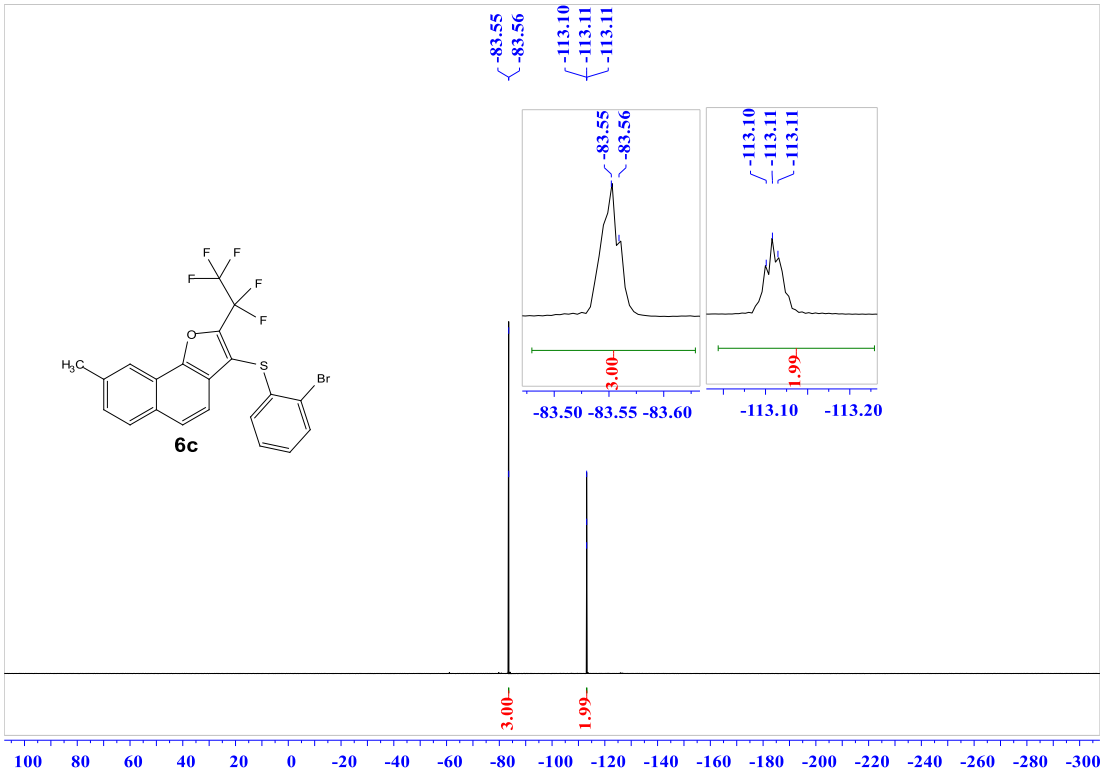
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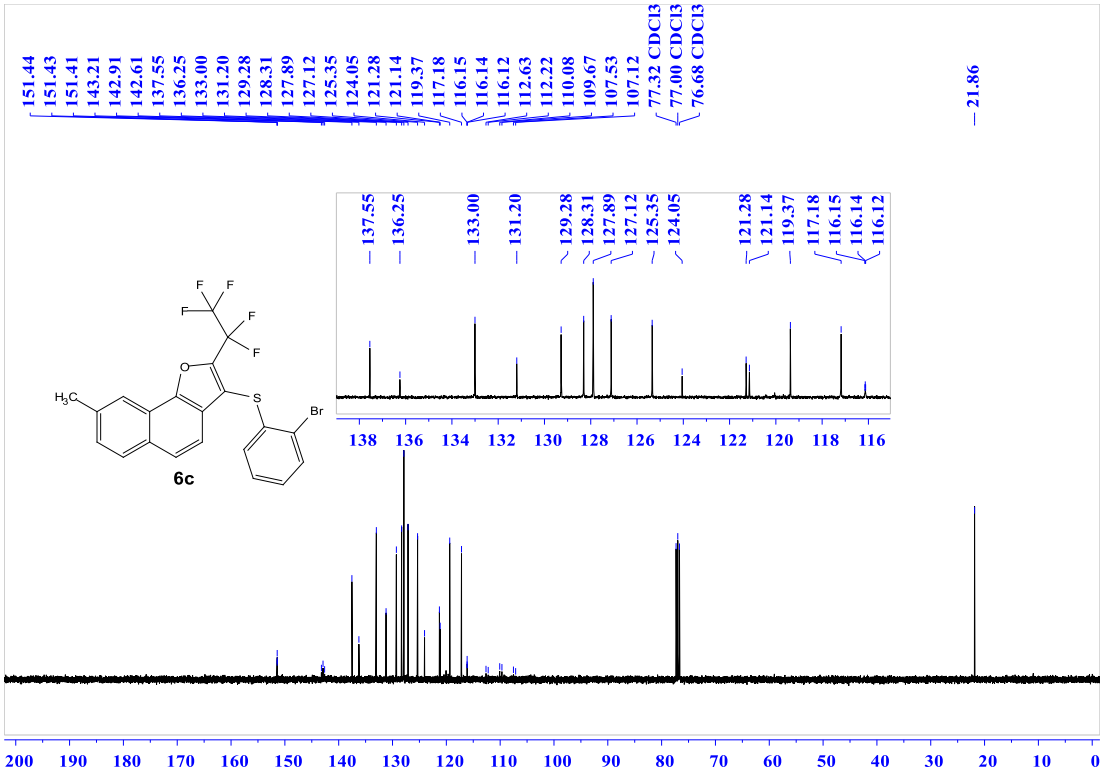
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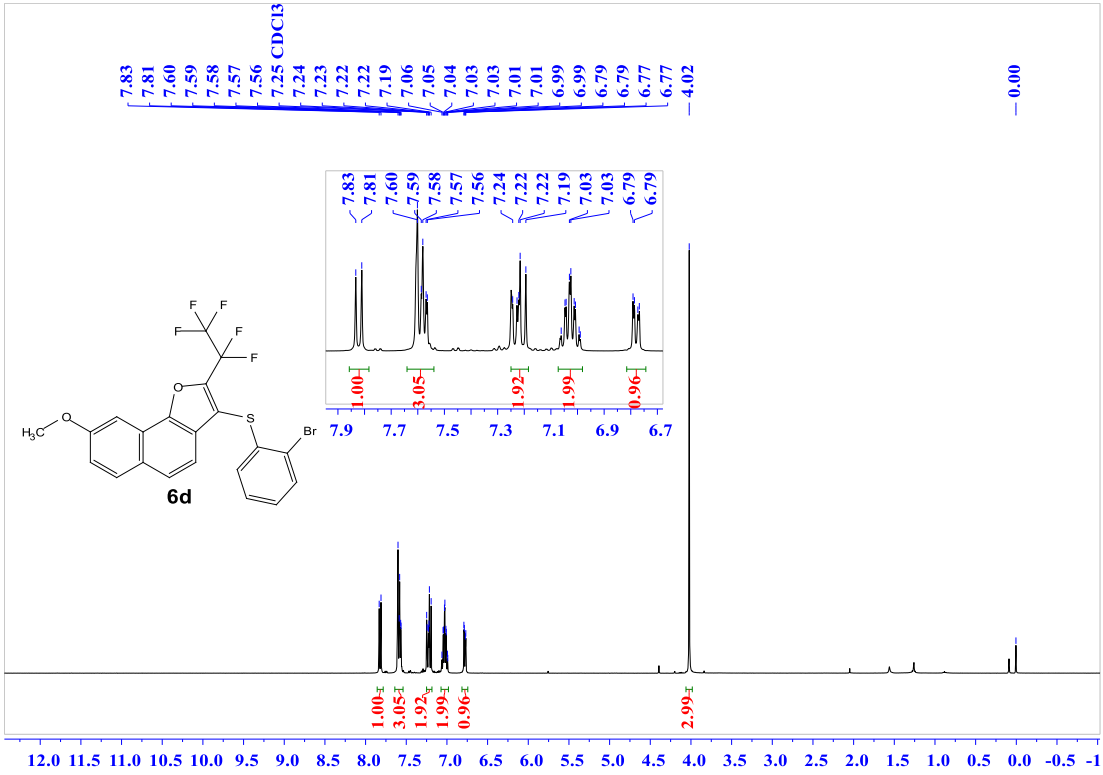
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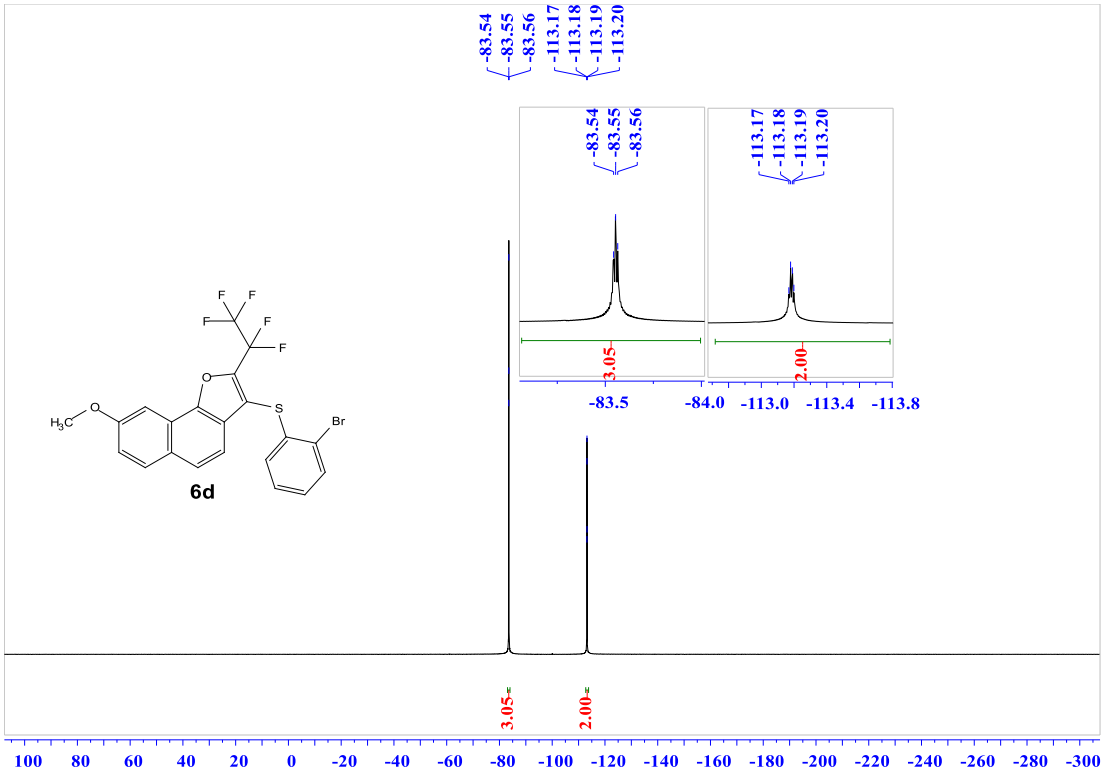
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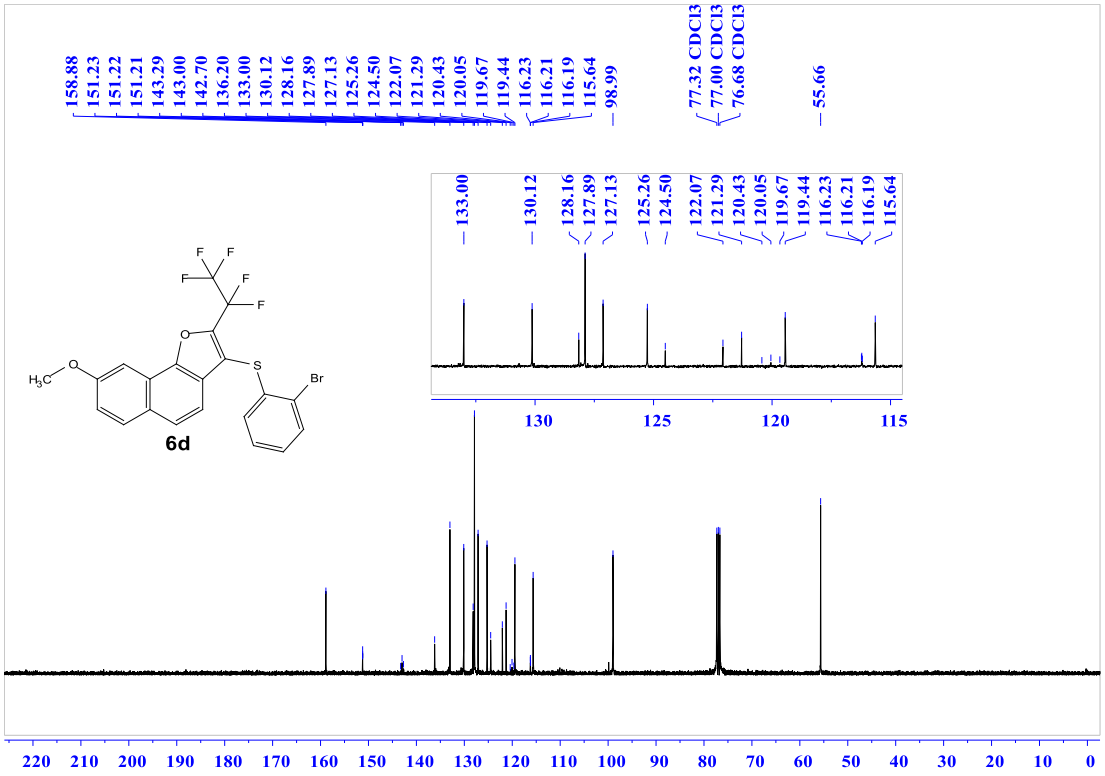
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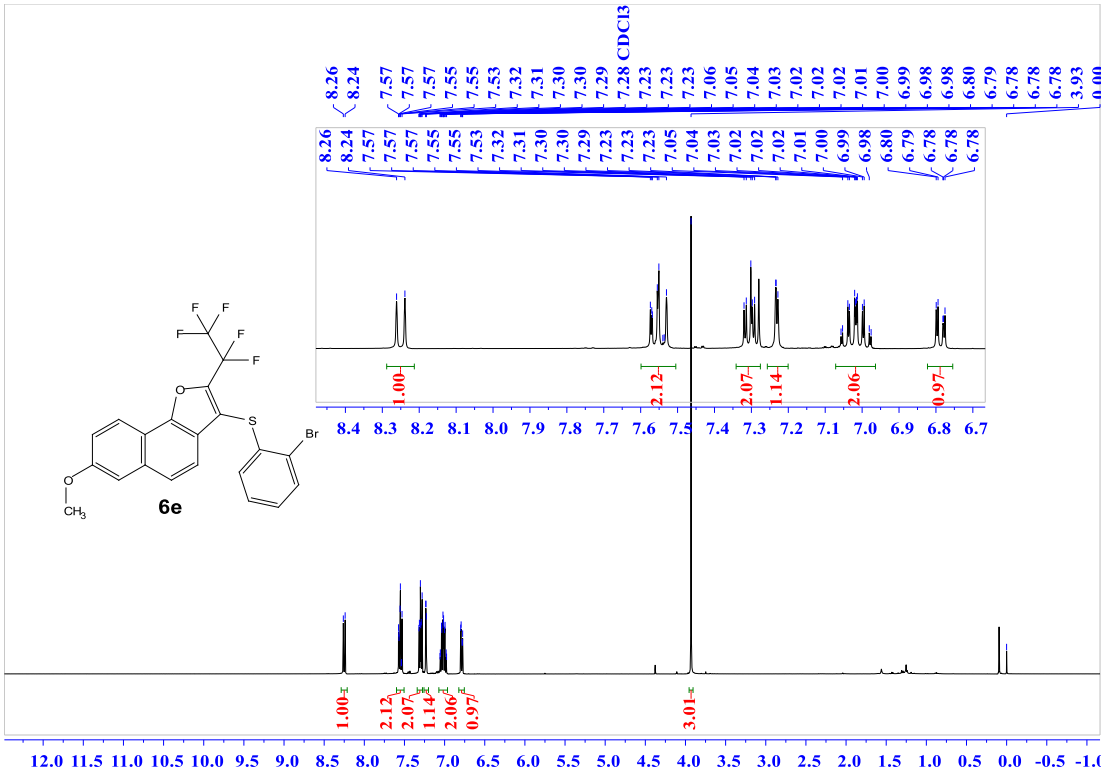
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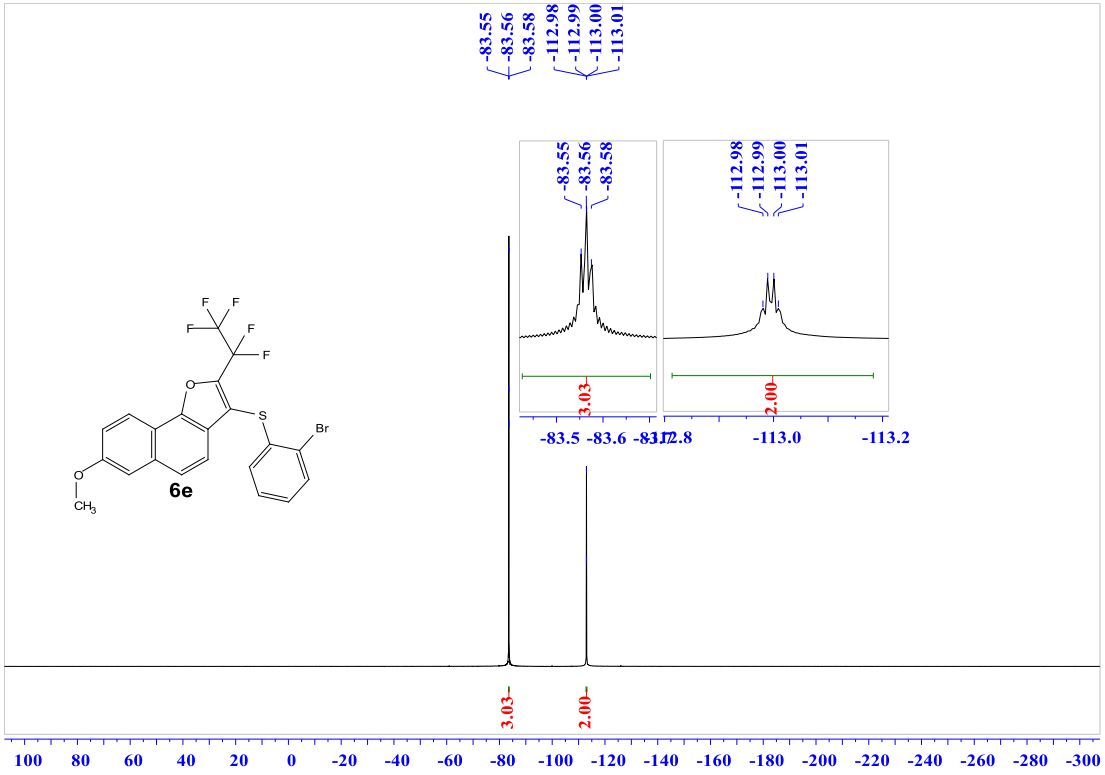
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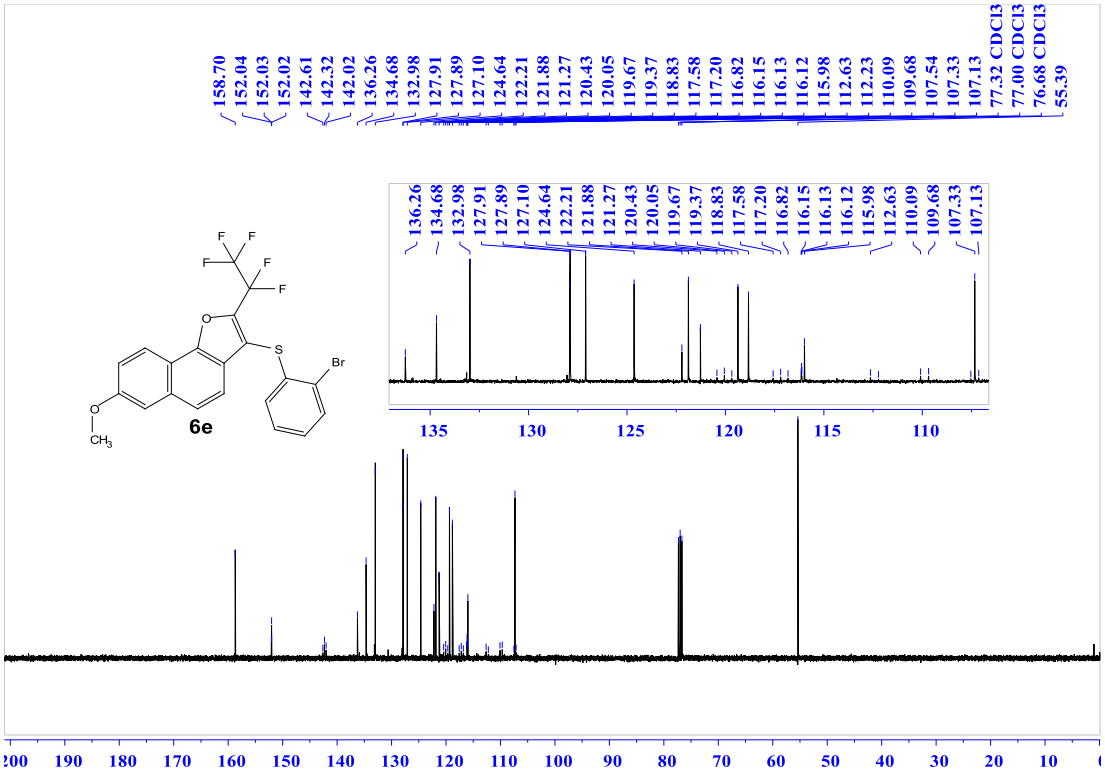
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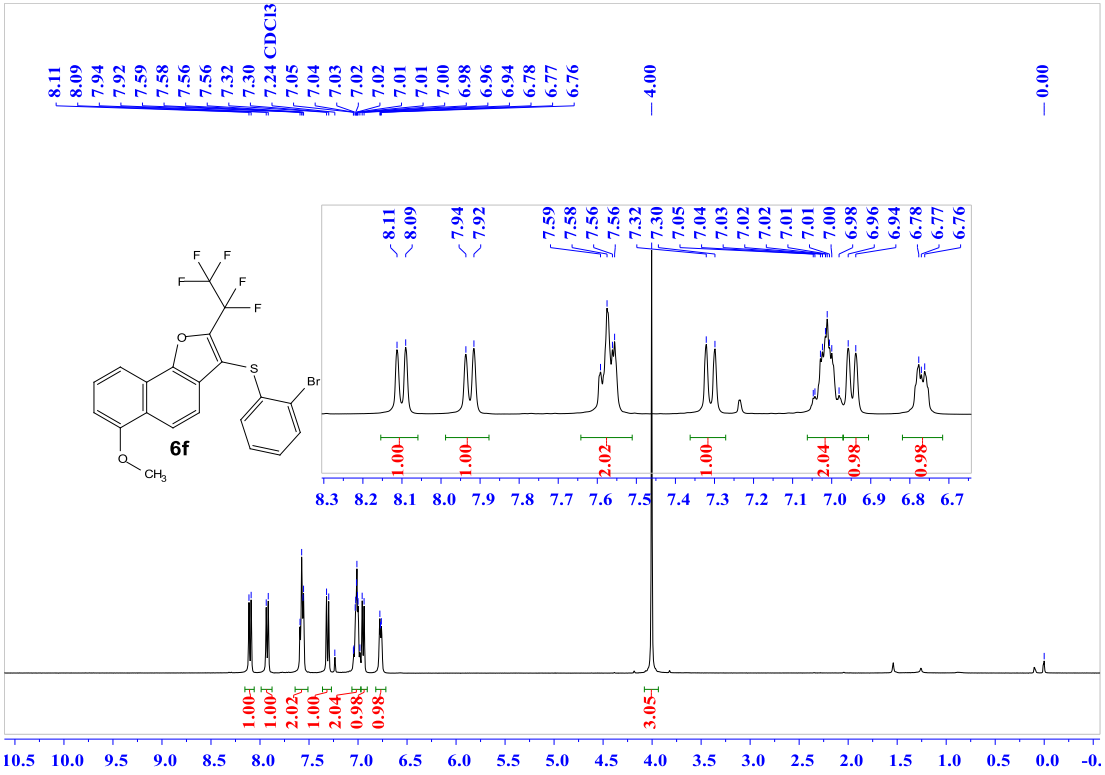
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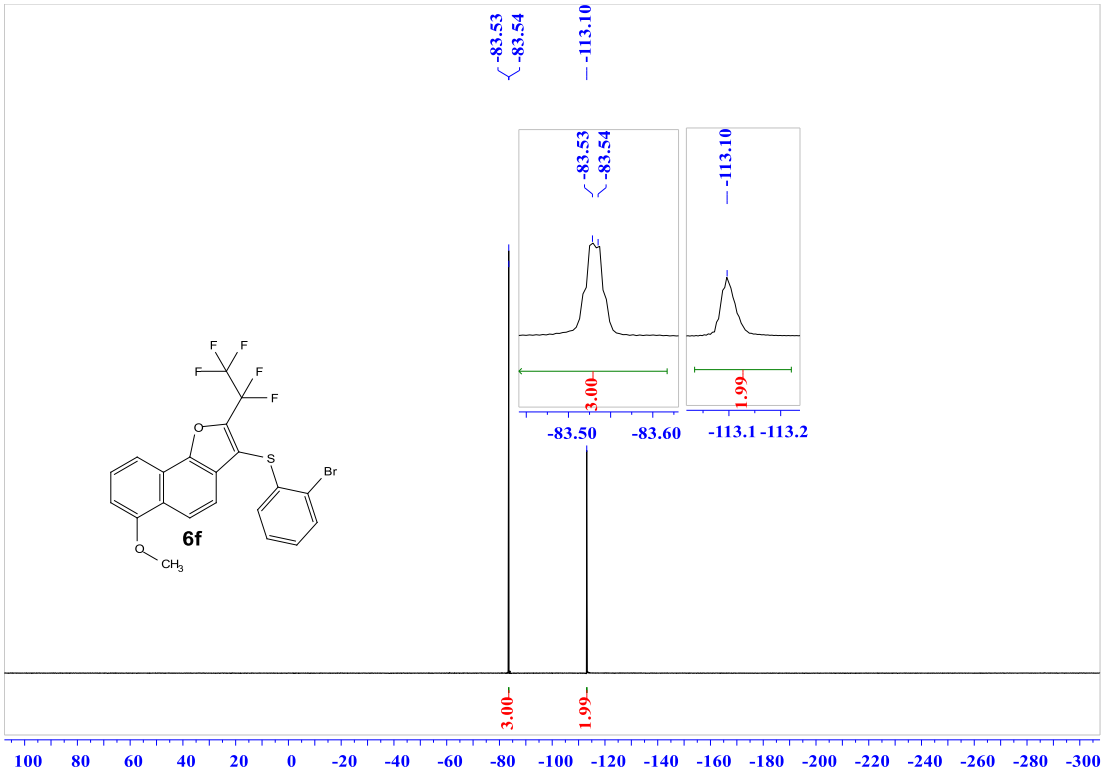
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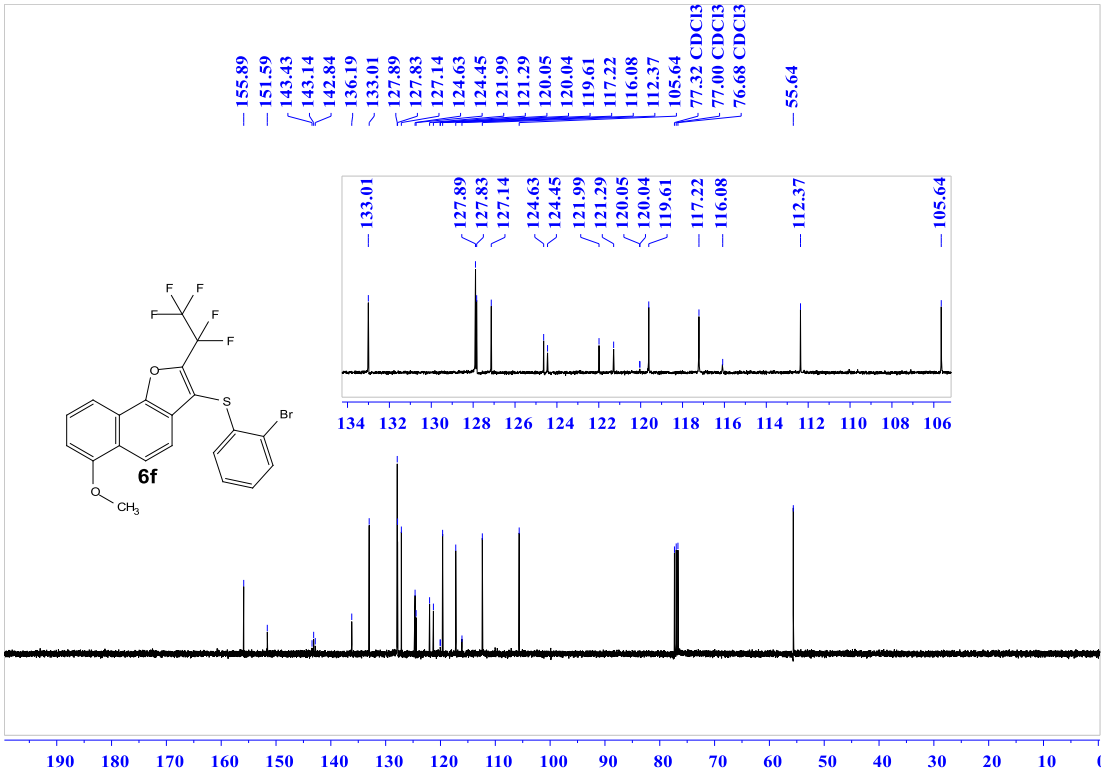
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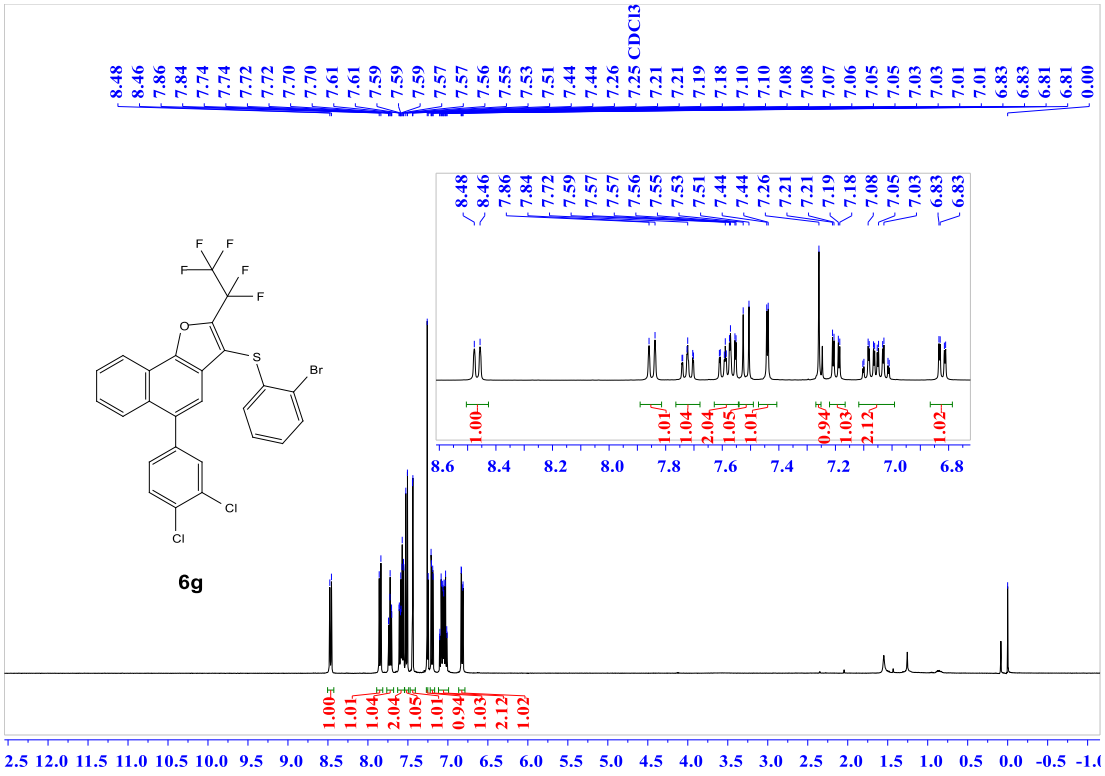
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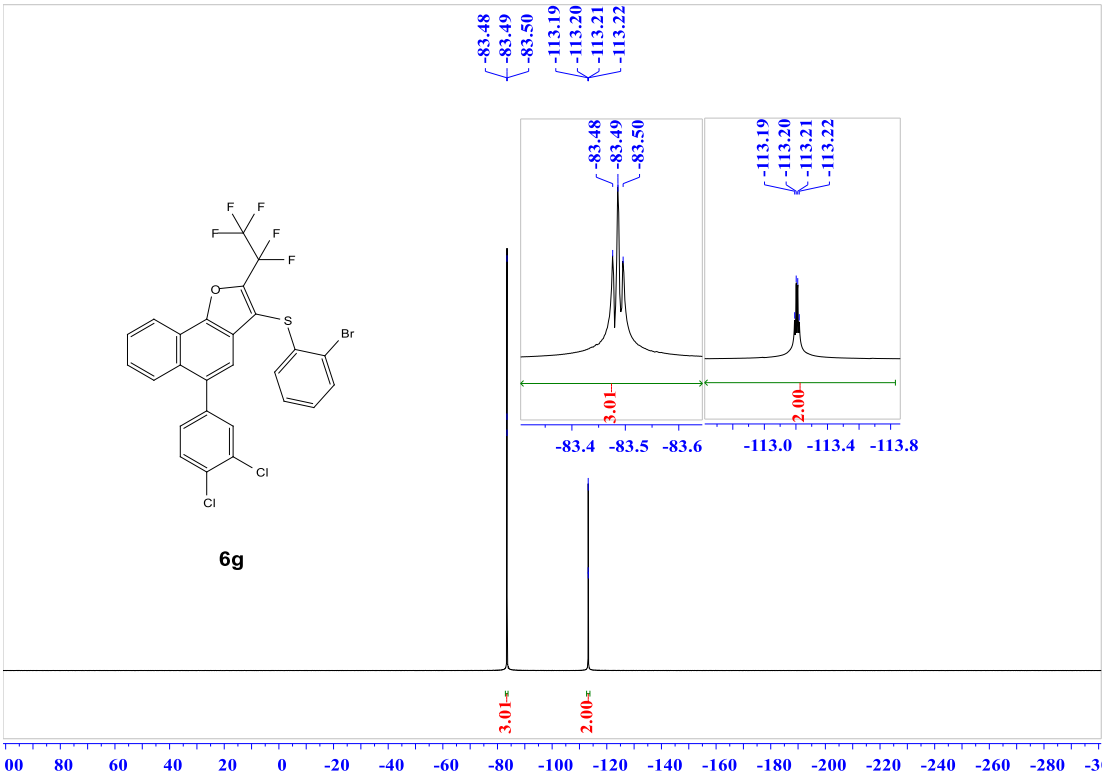
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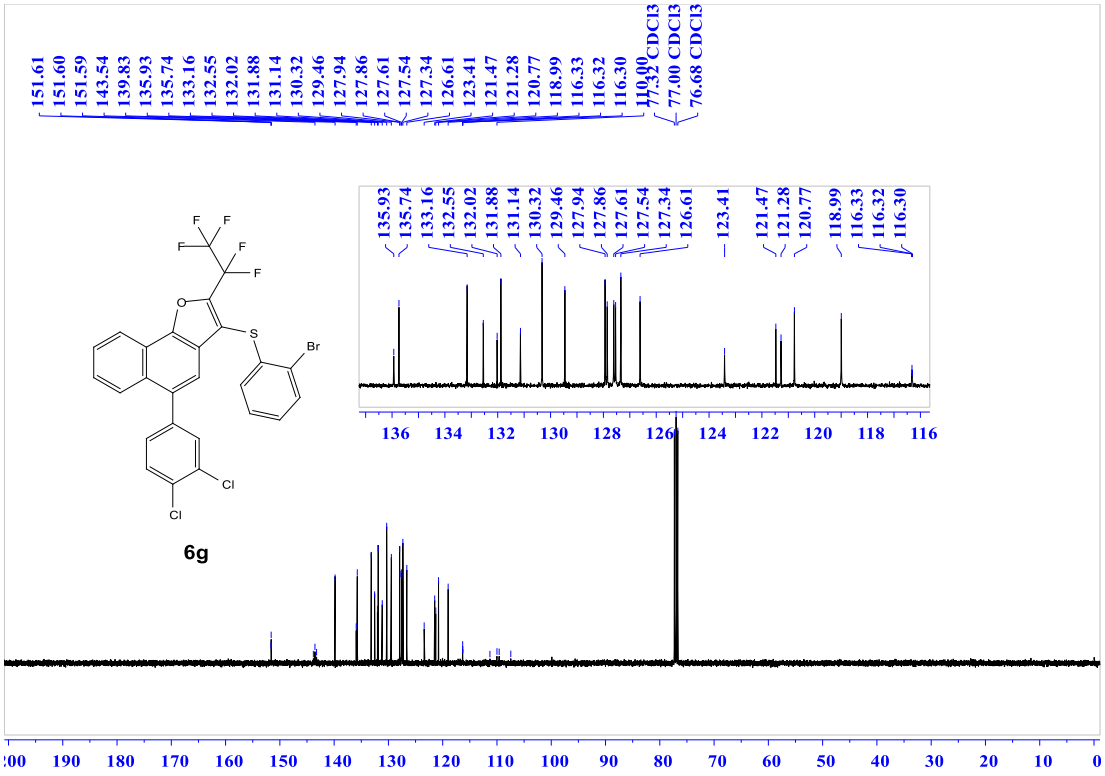
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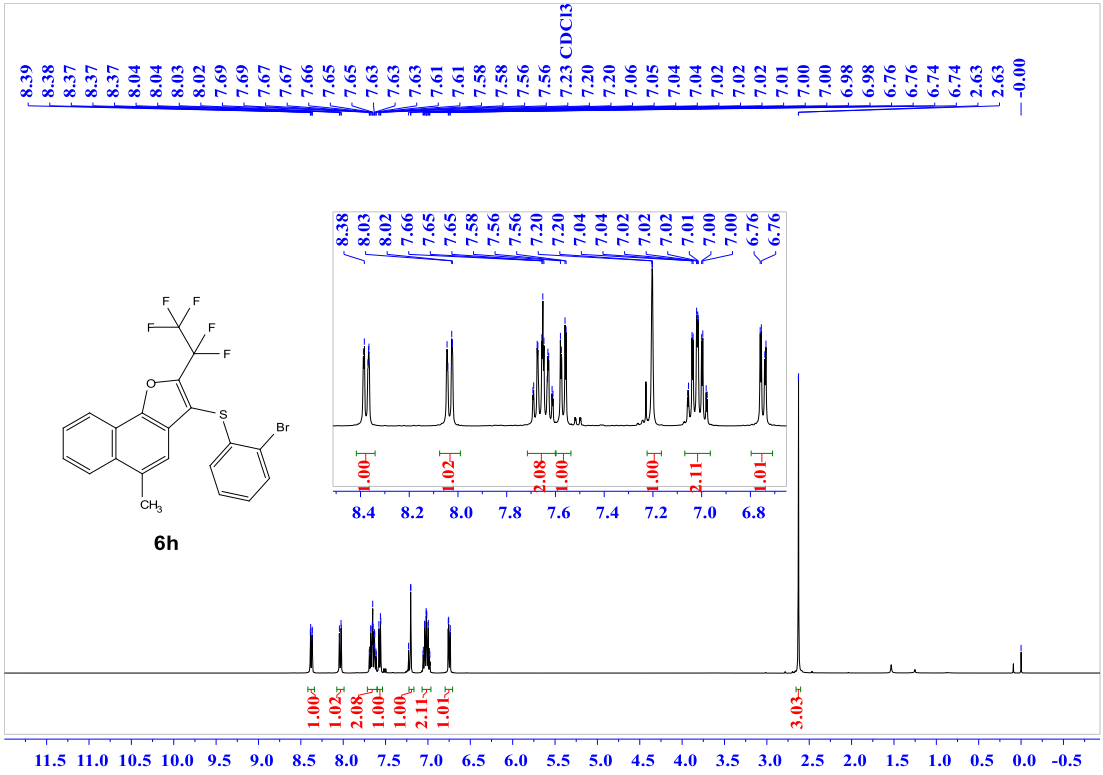
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F F F F F O S Br CH3
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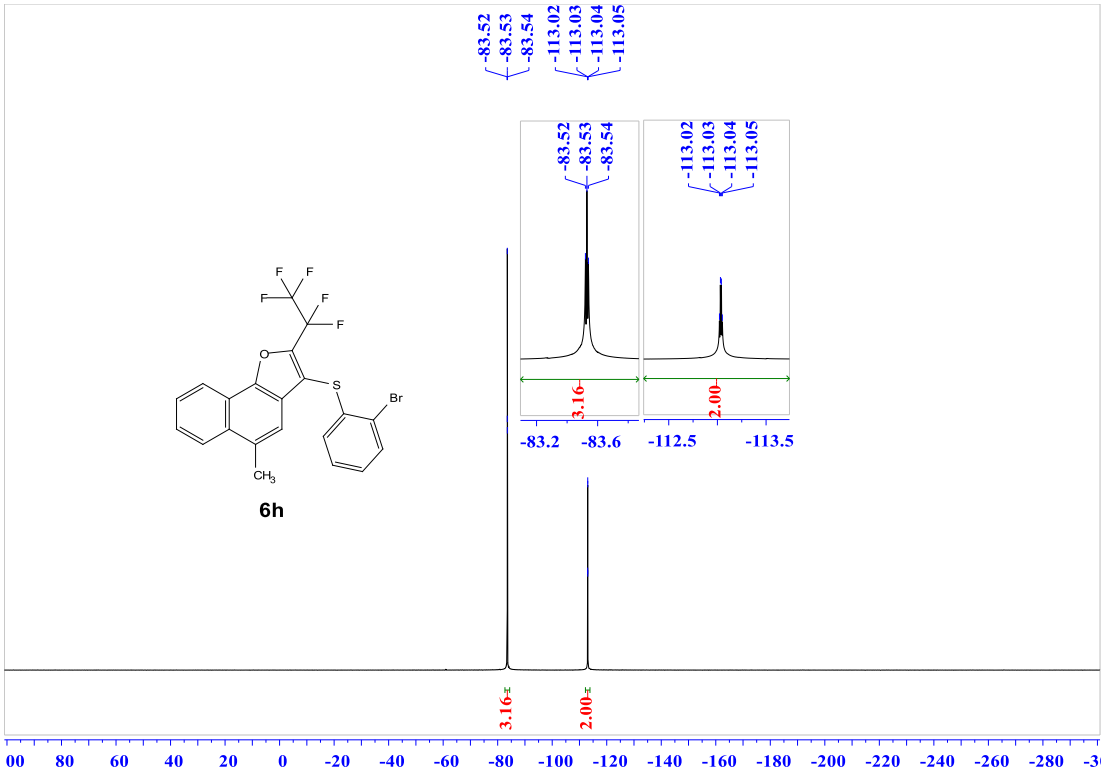
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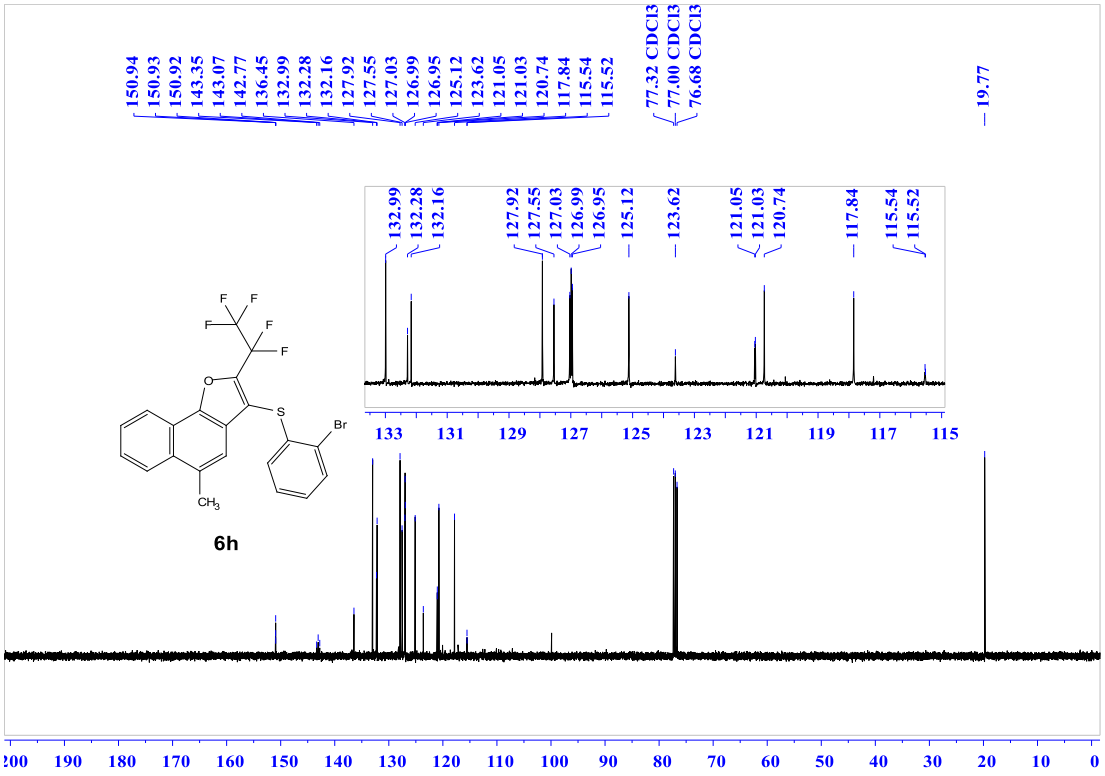
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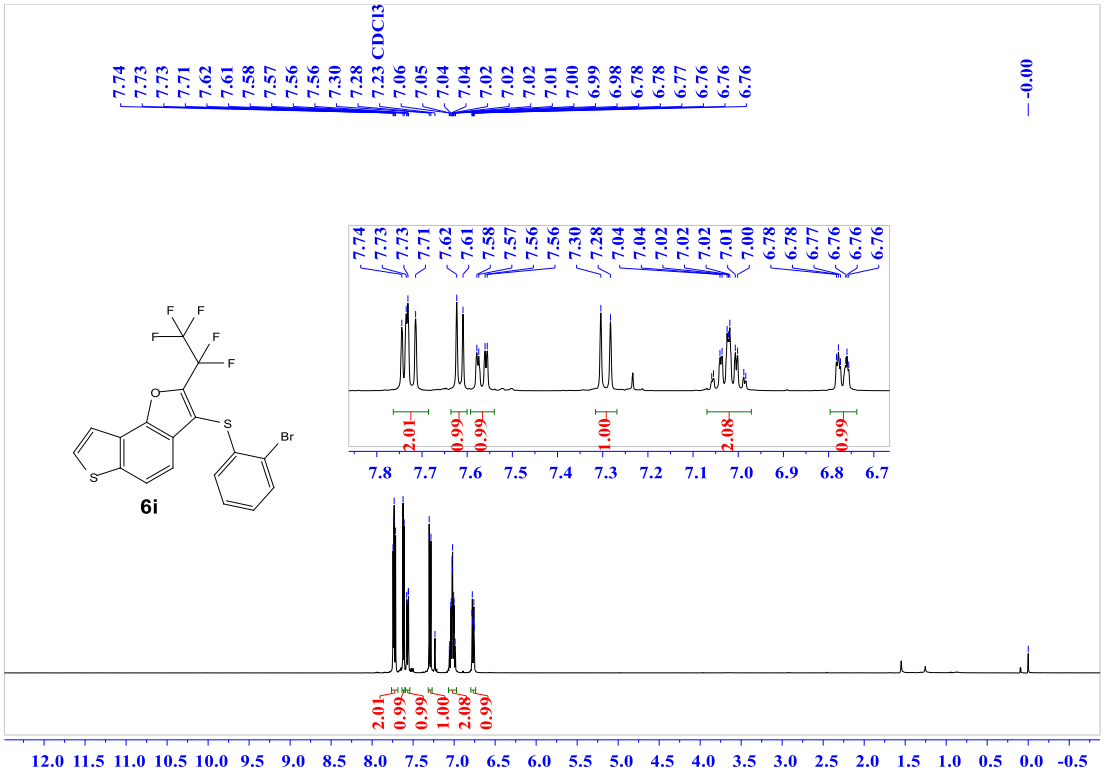
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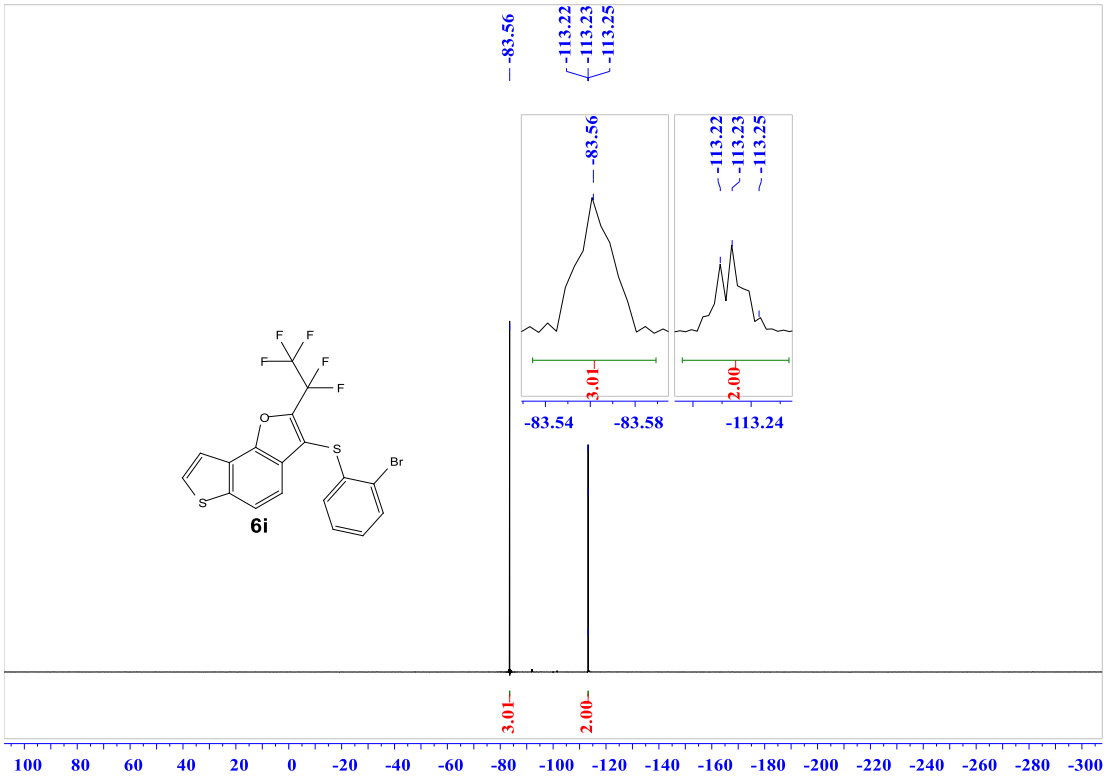
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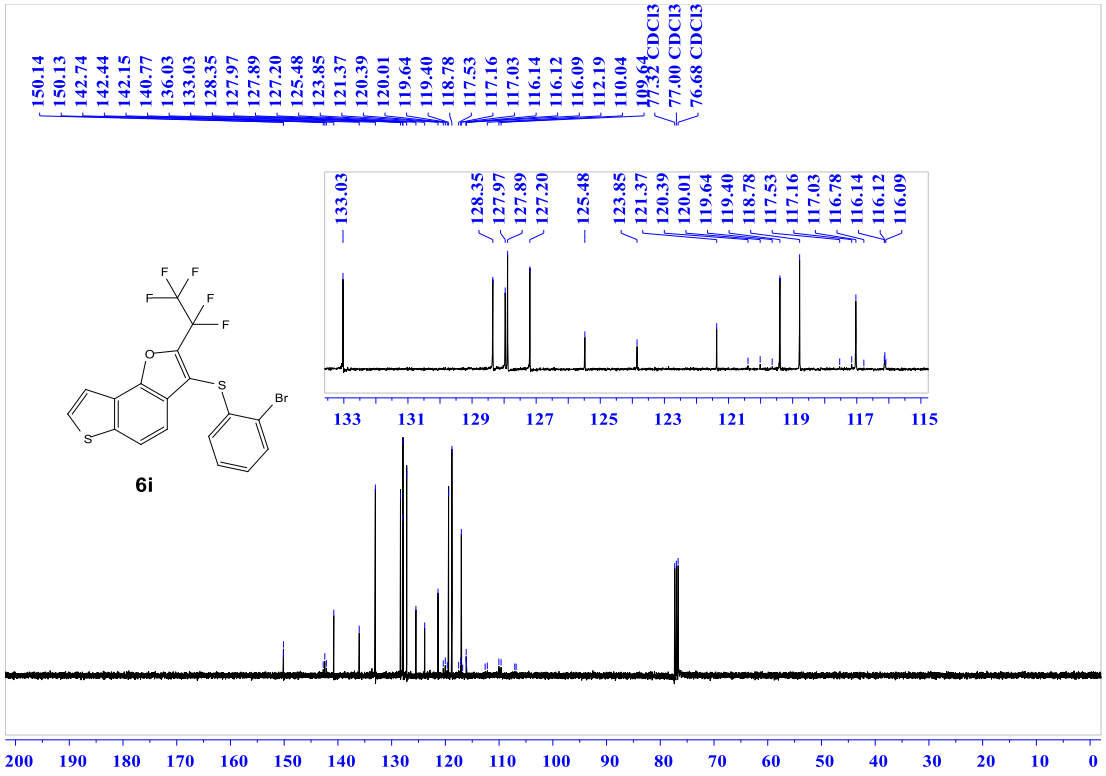
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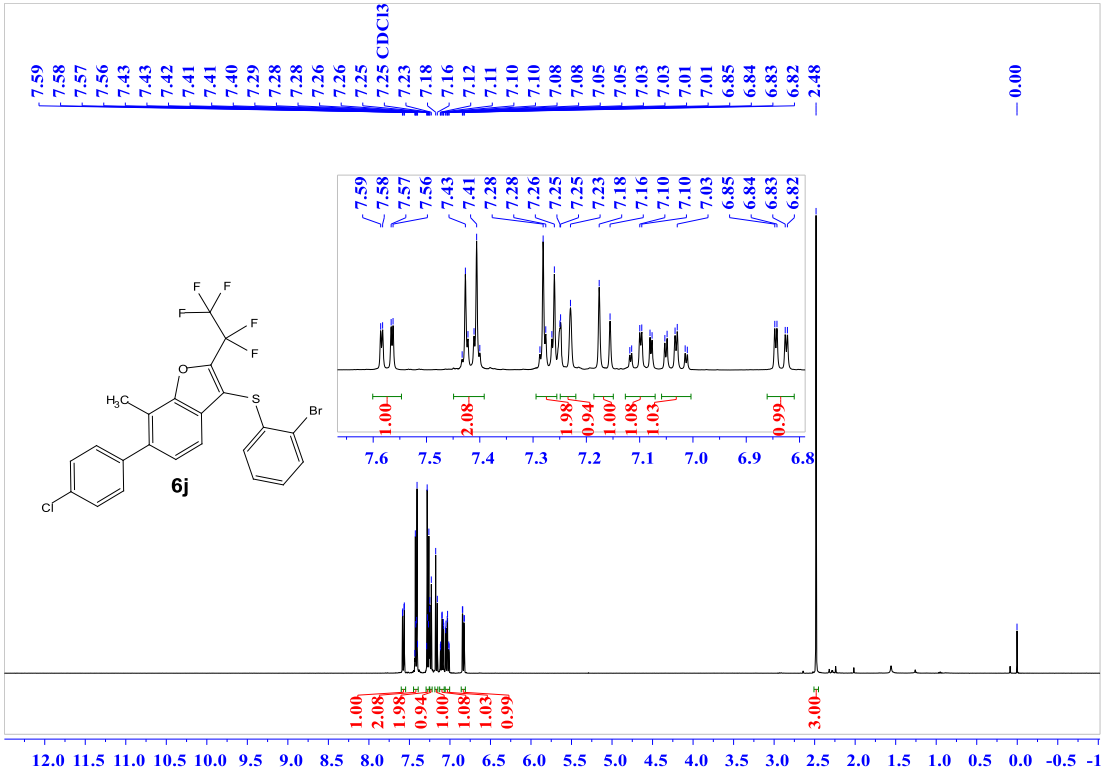
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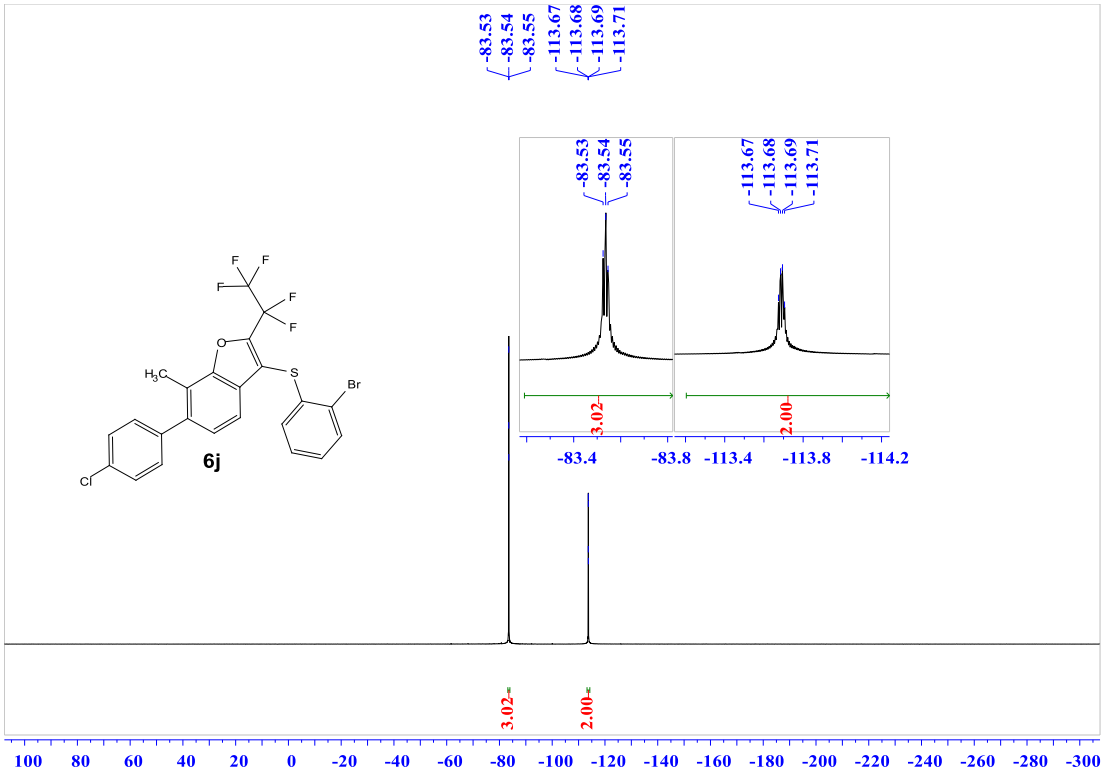
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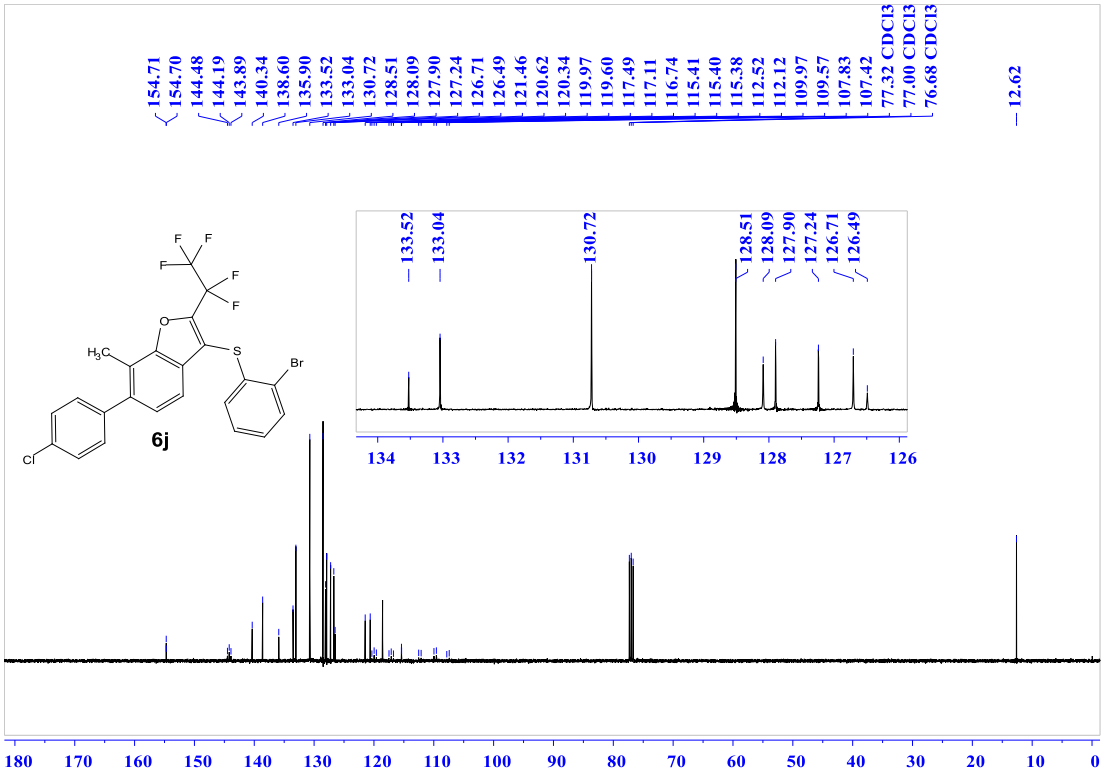
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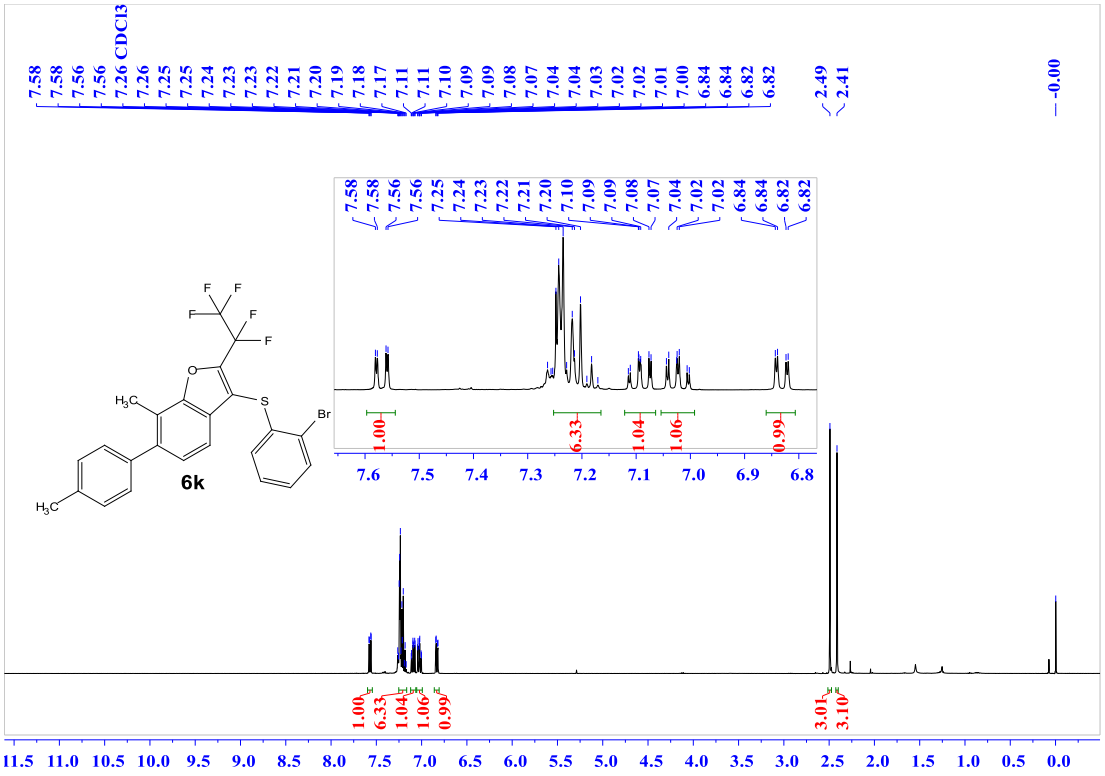
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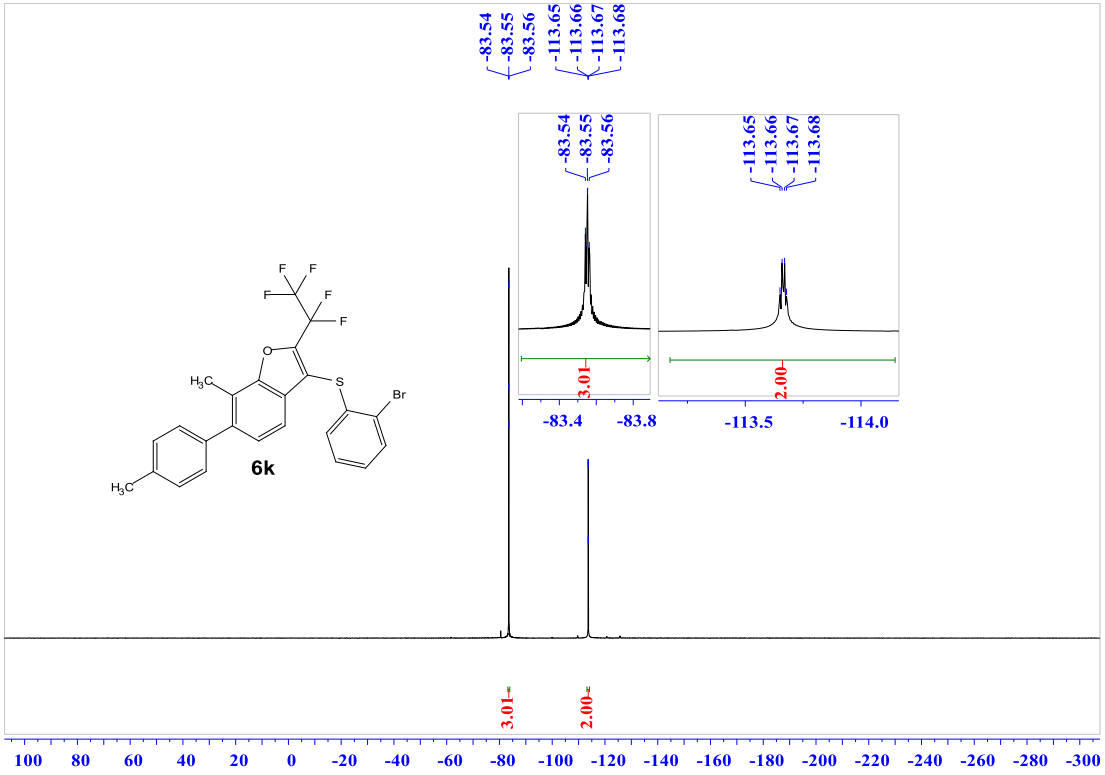
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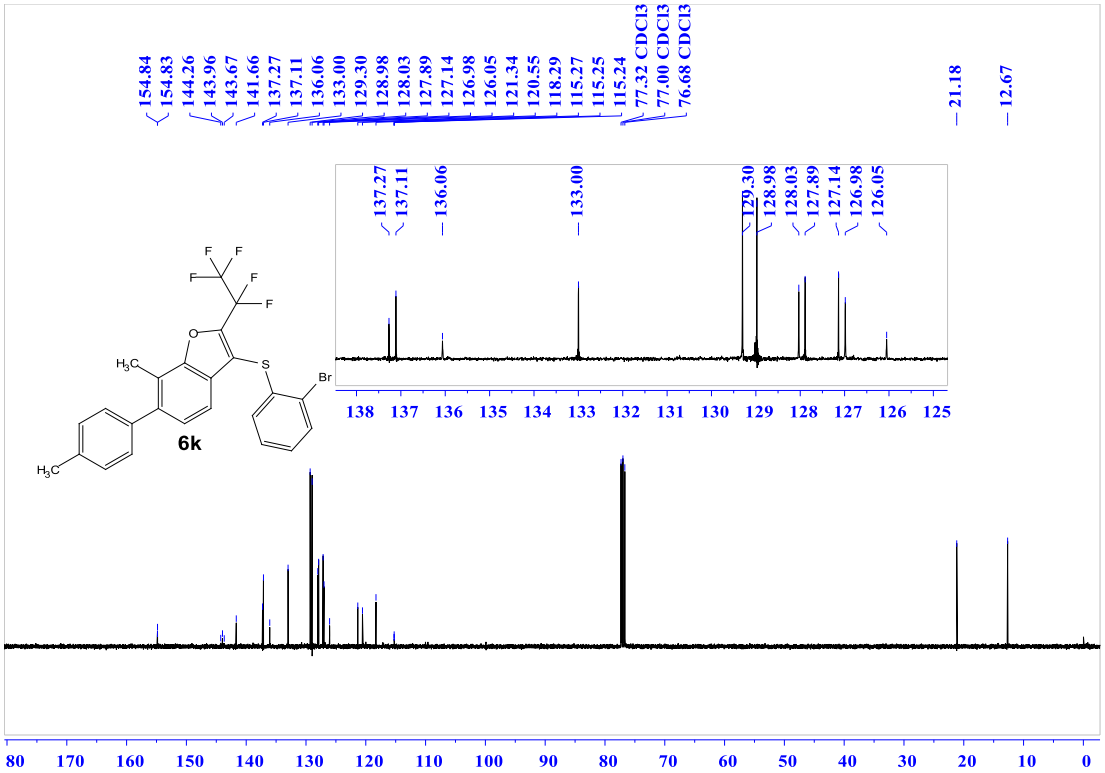
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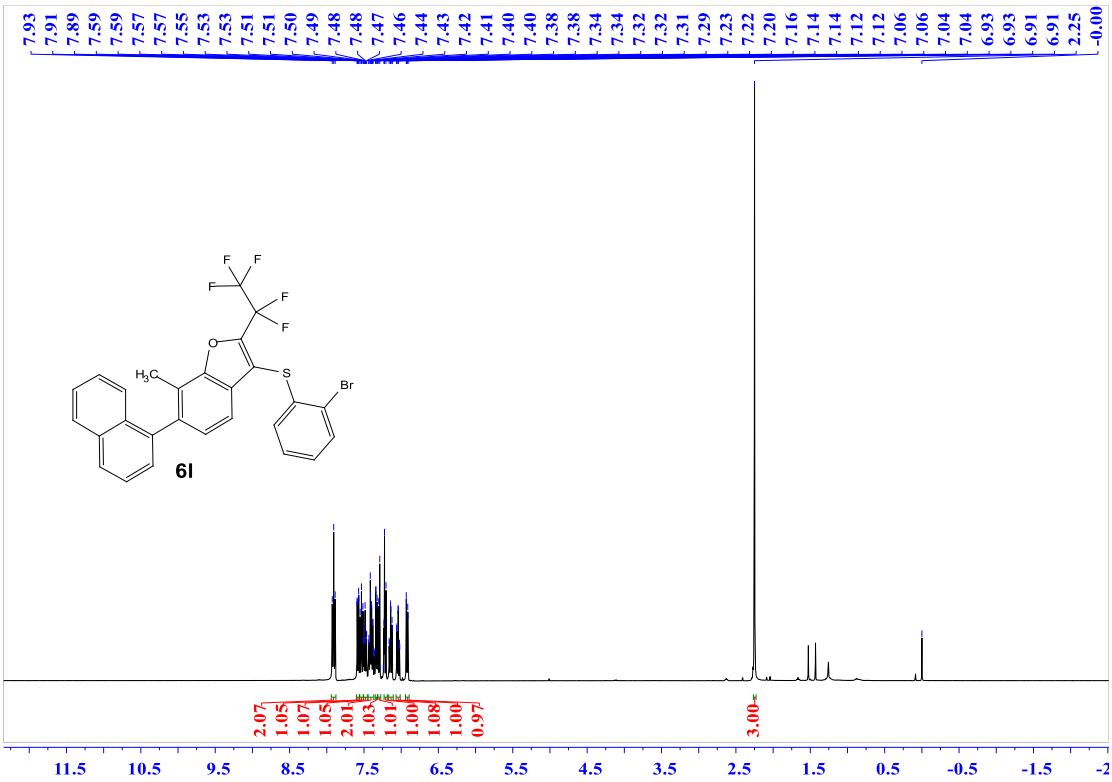
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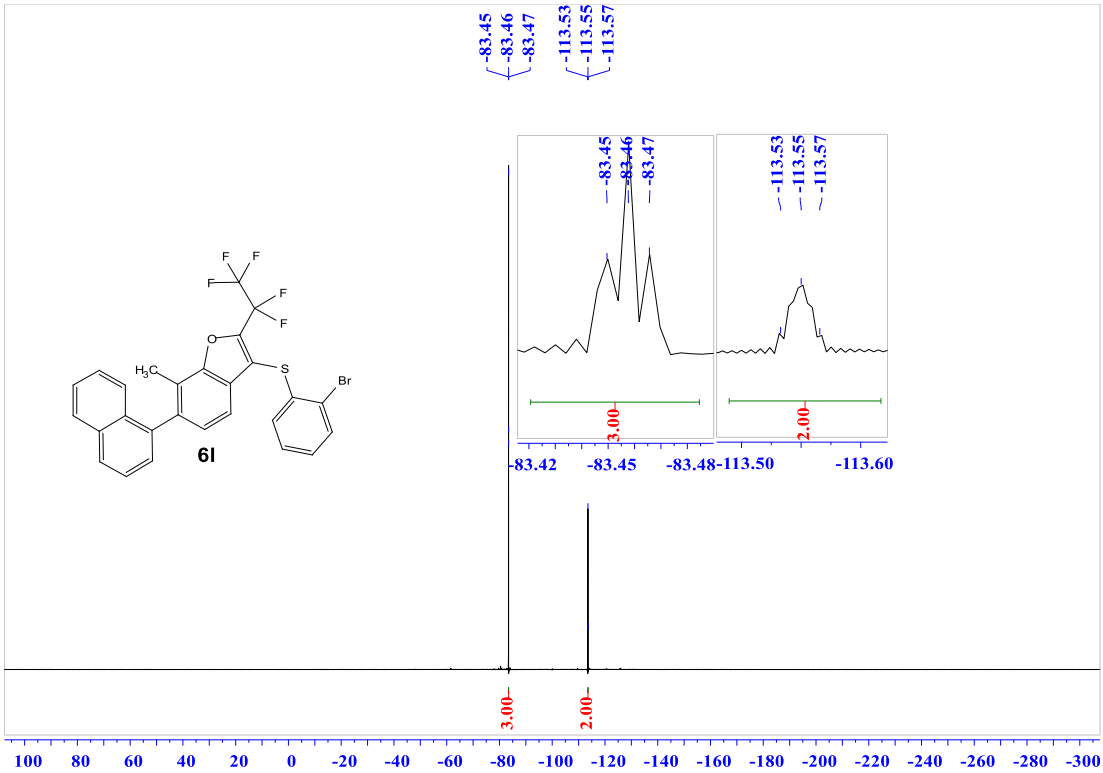
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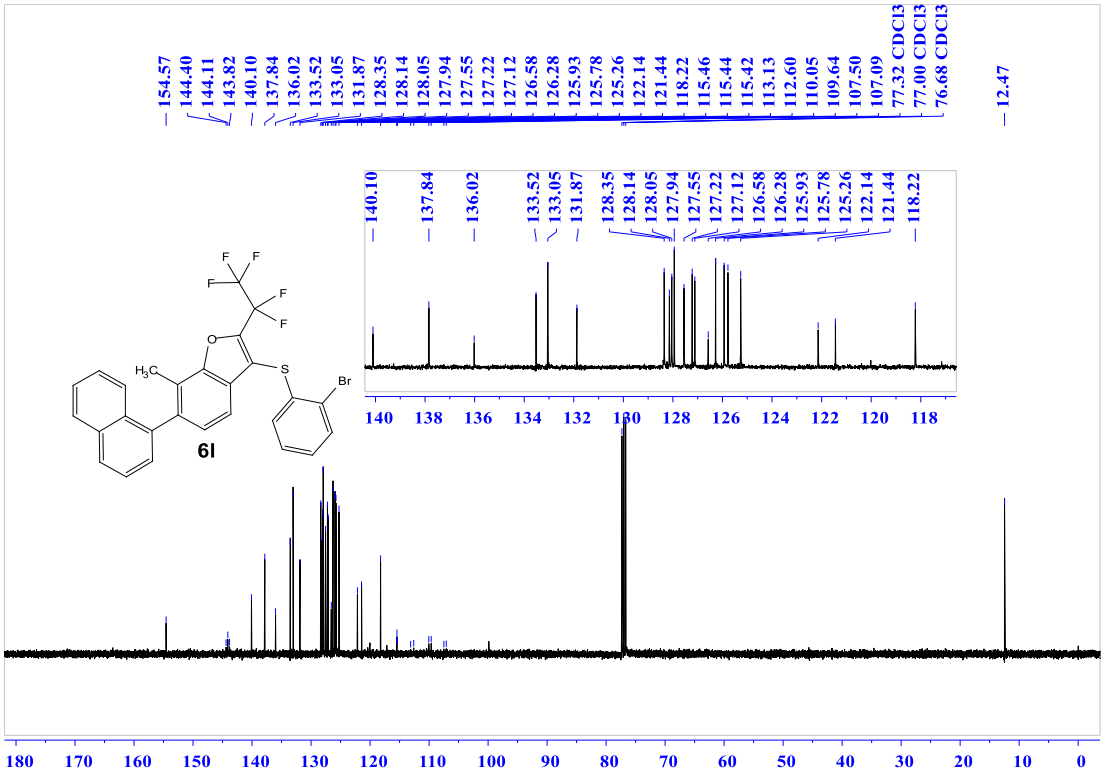
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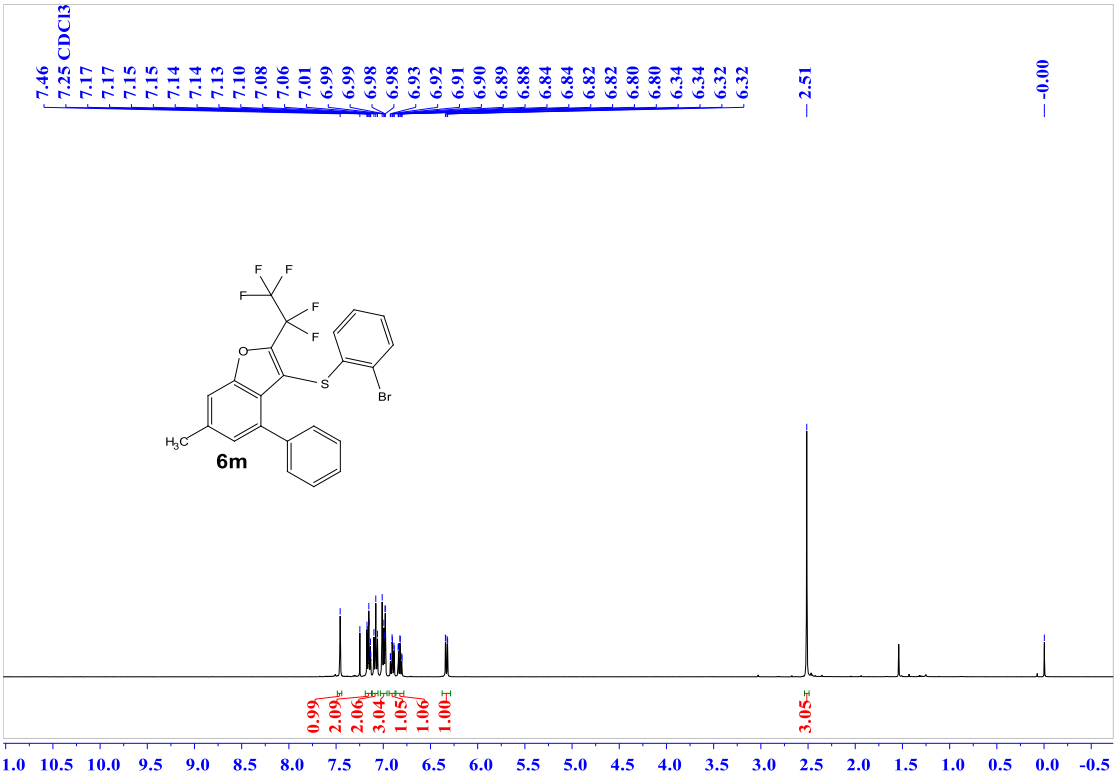
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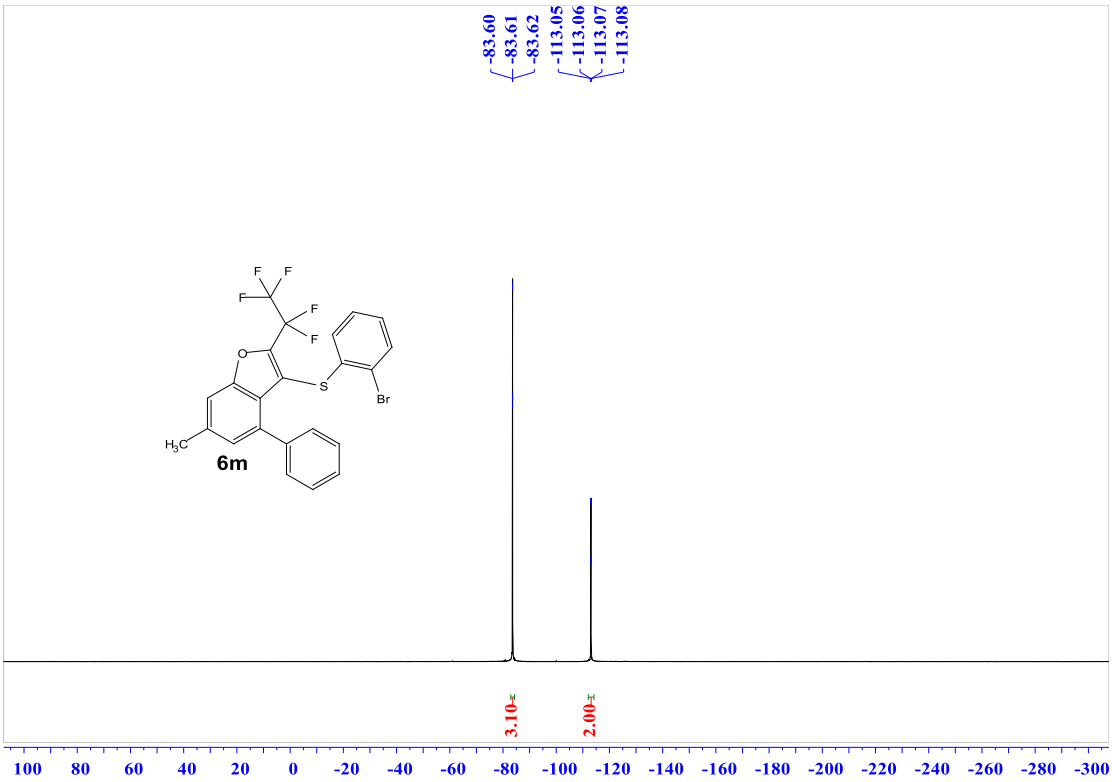
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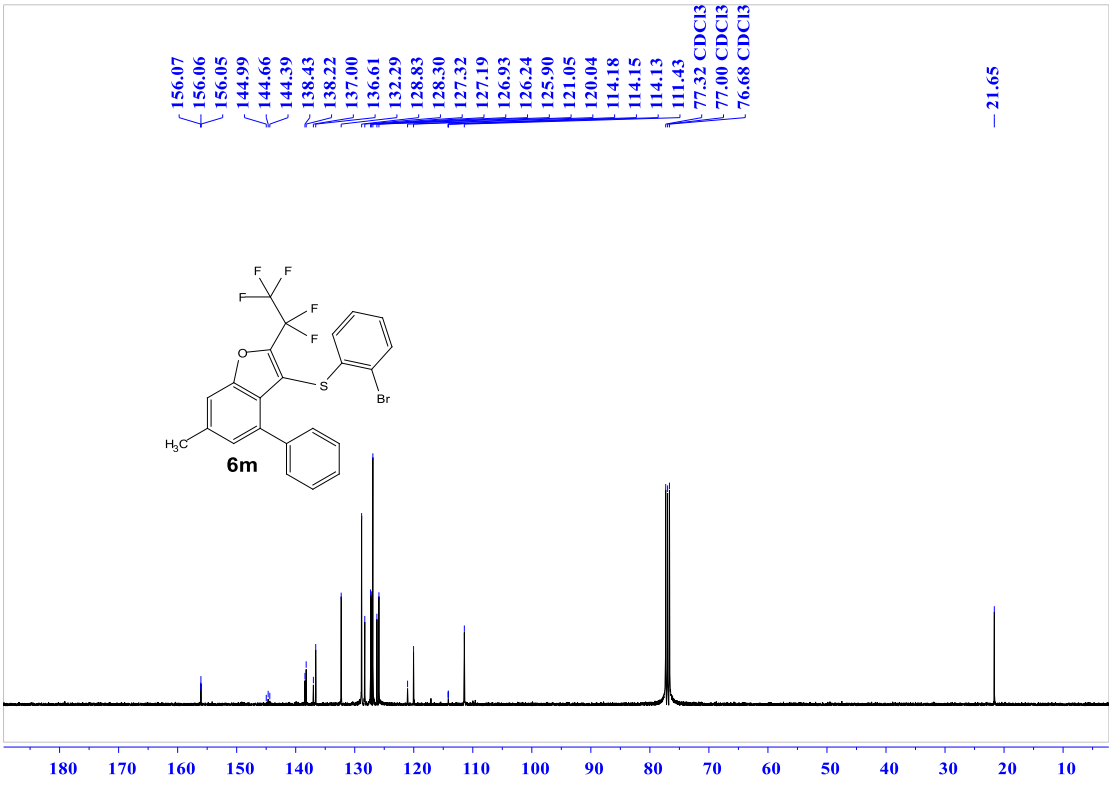
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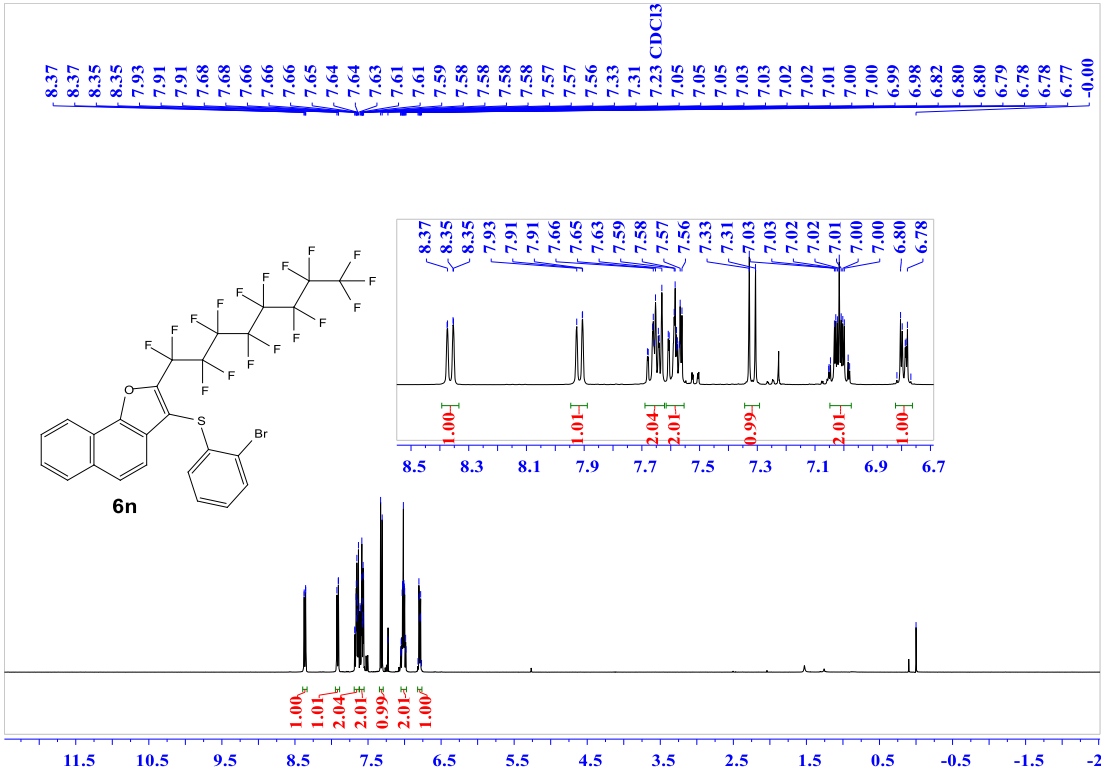
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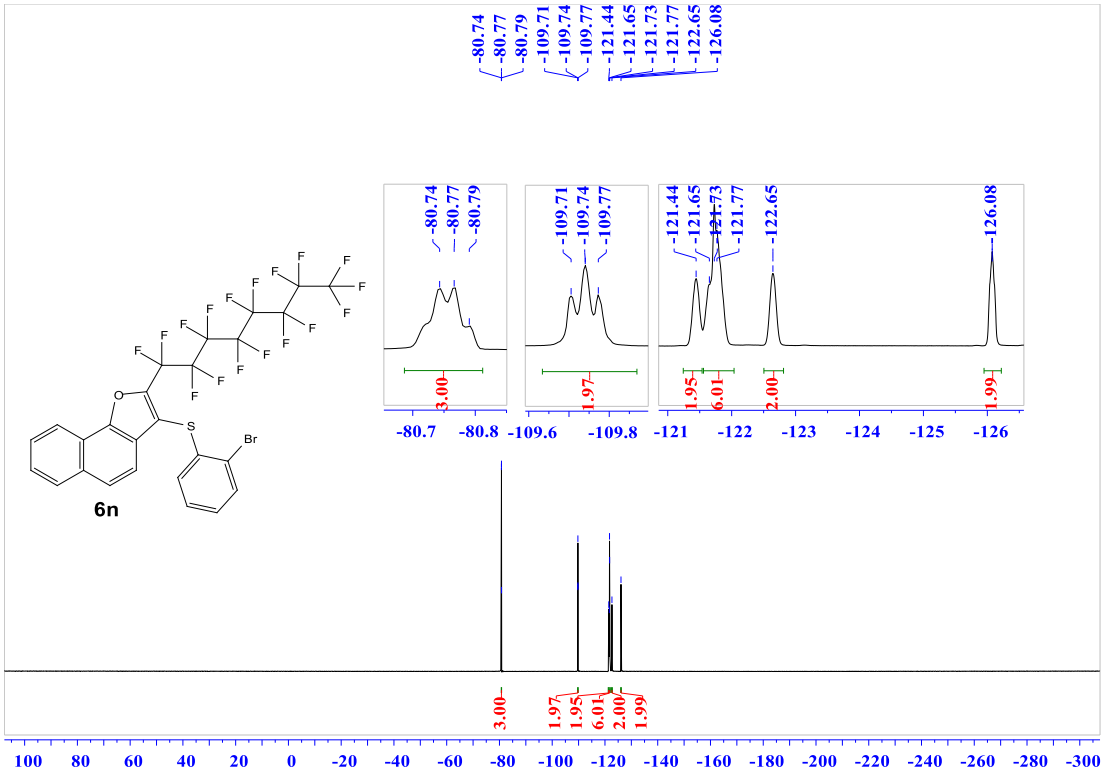
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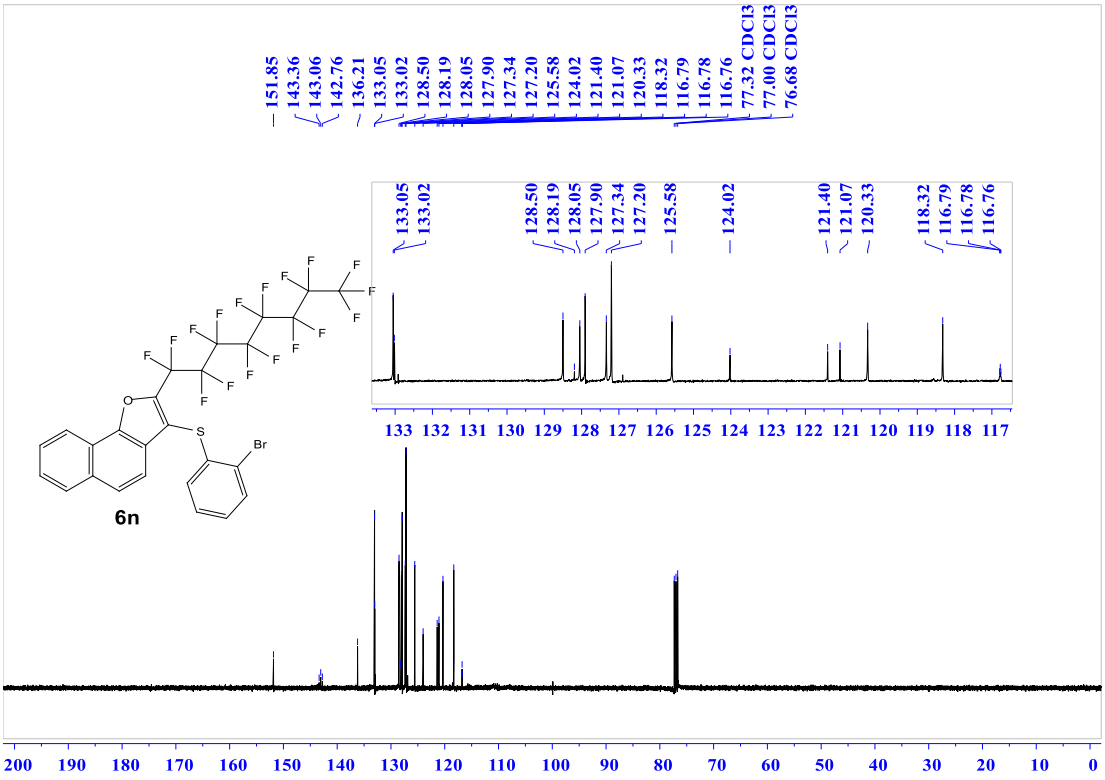
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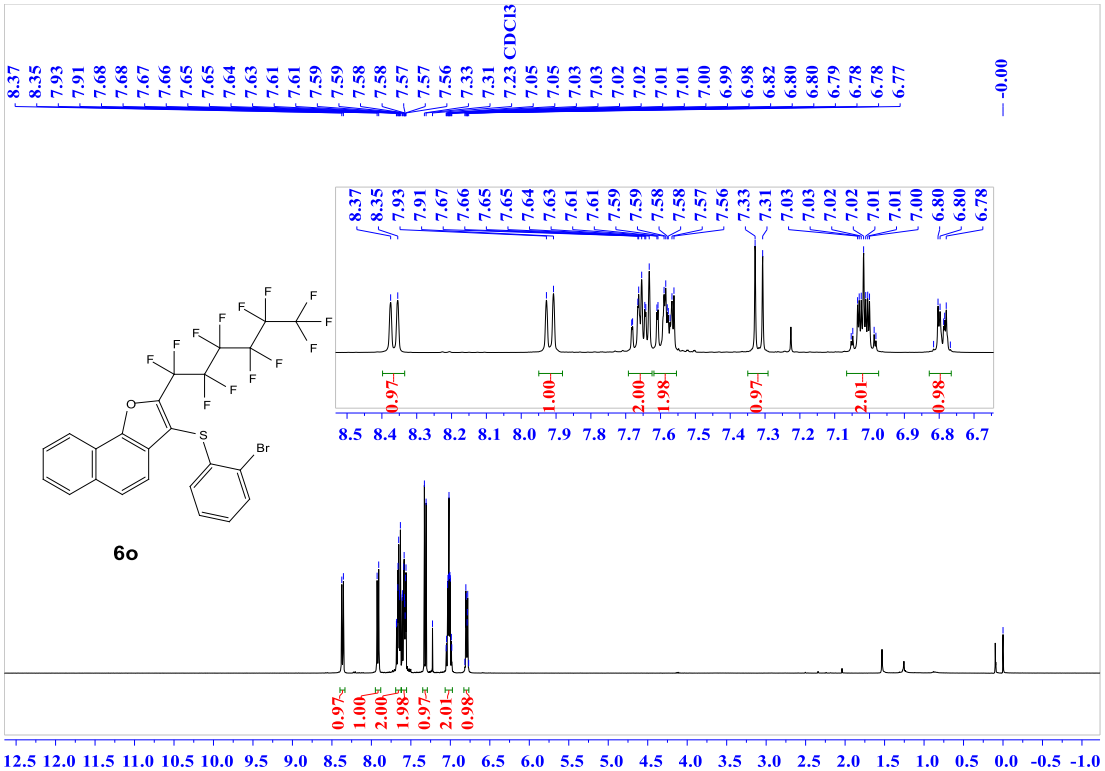
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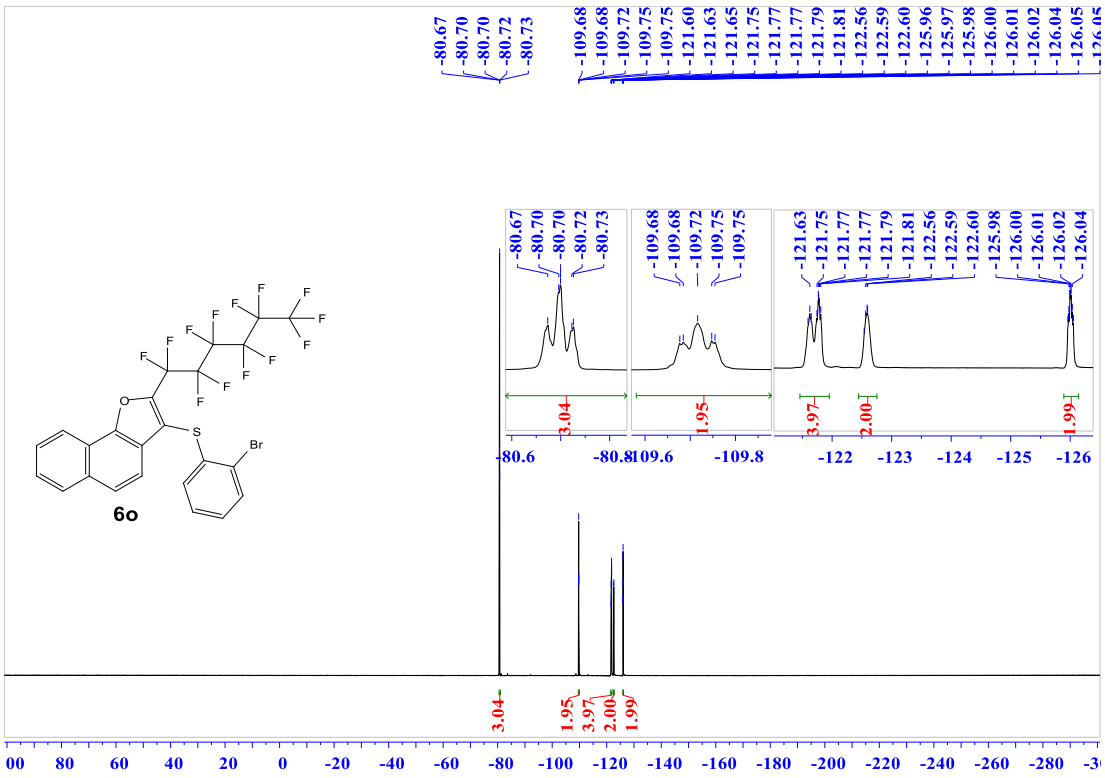
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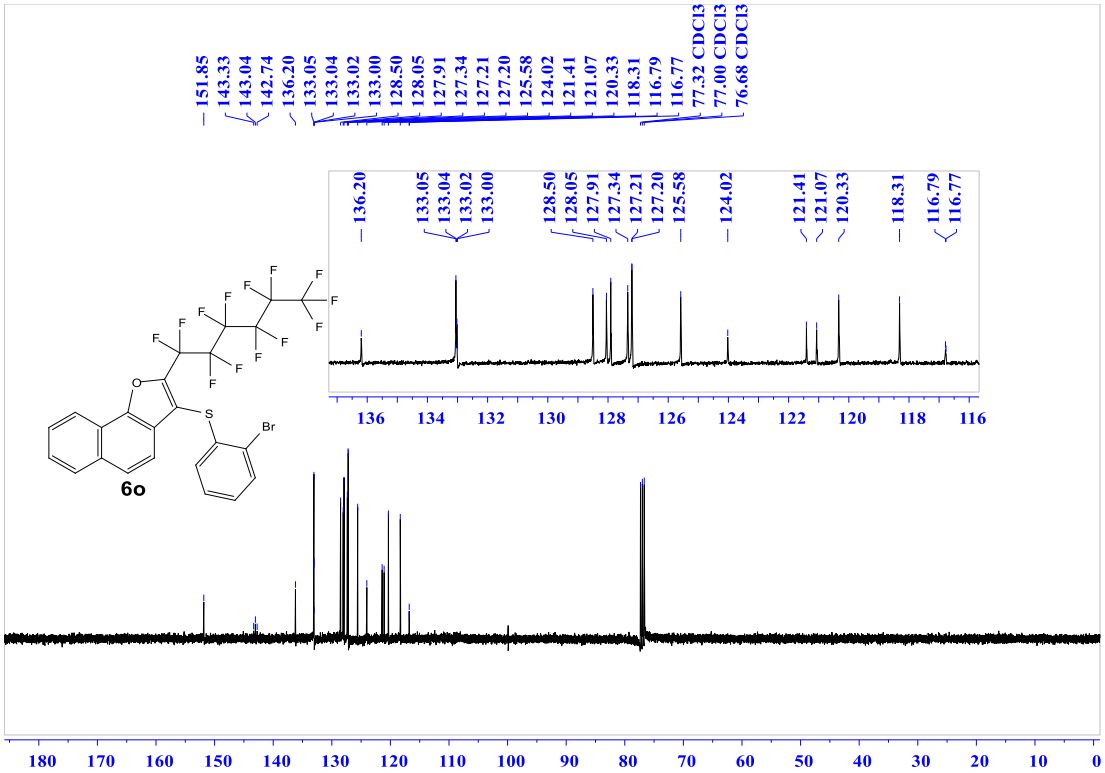
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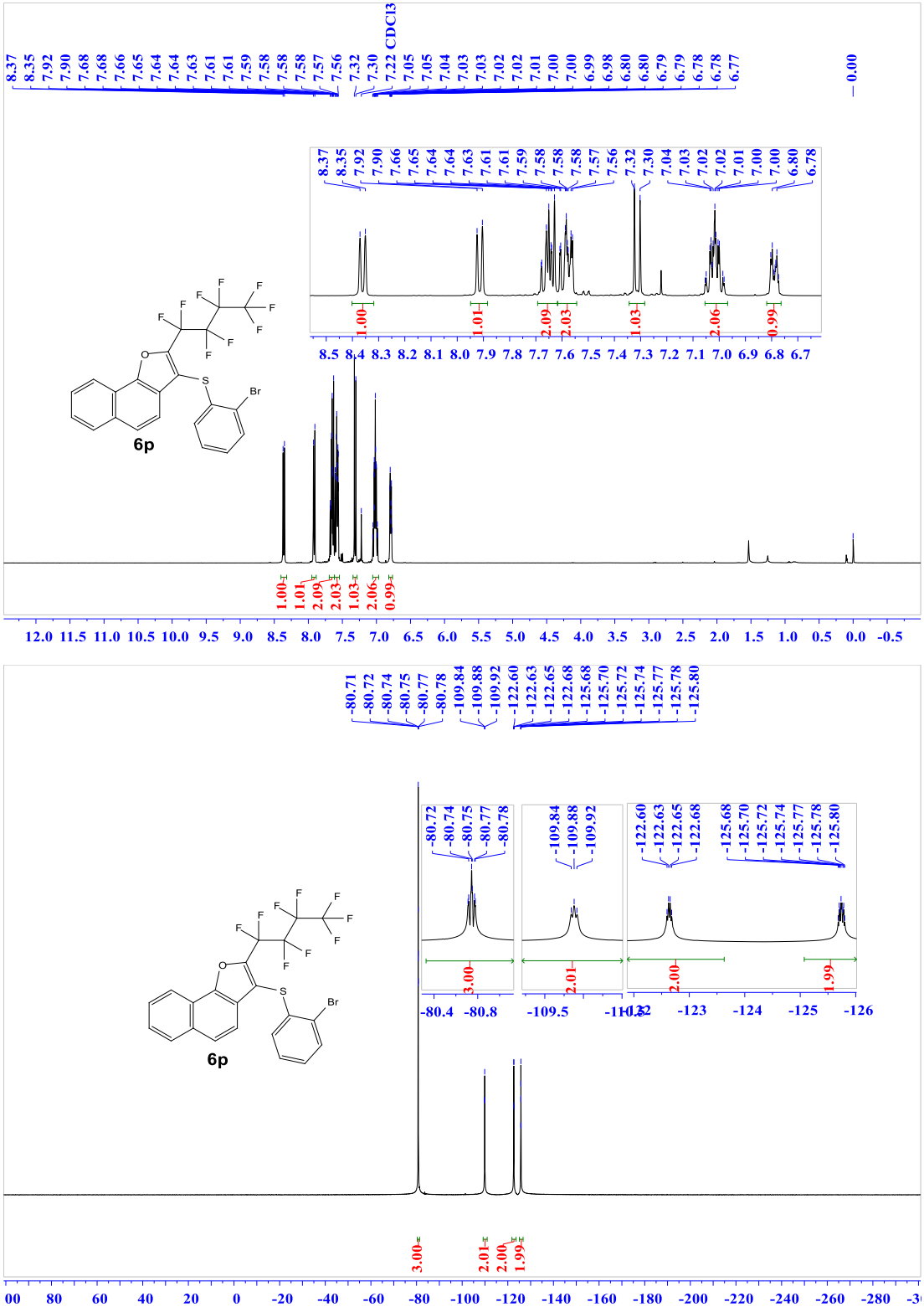
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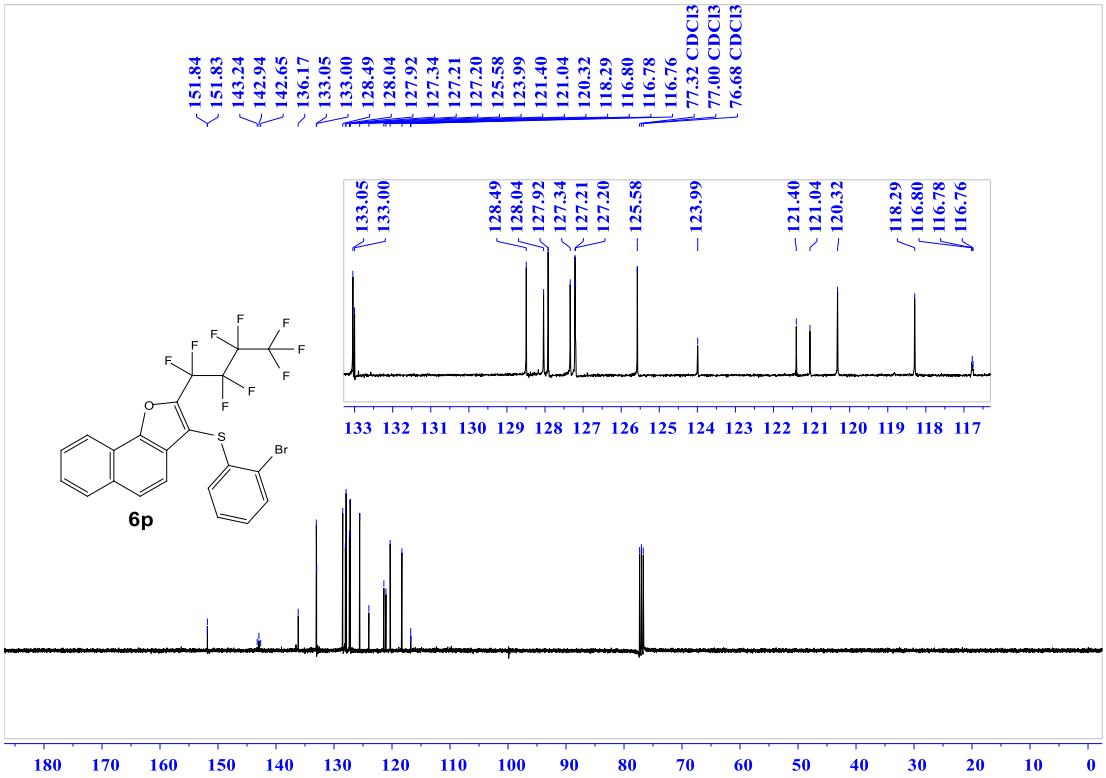
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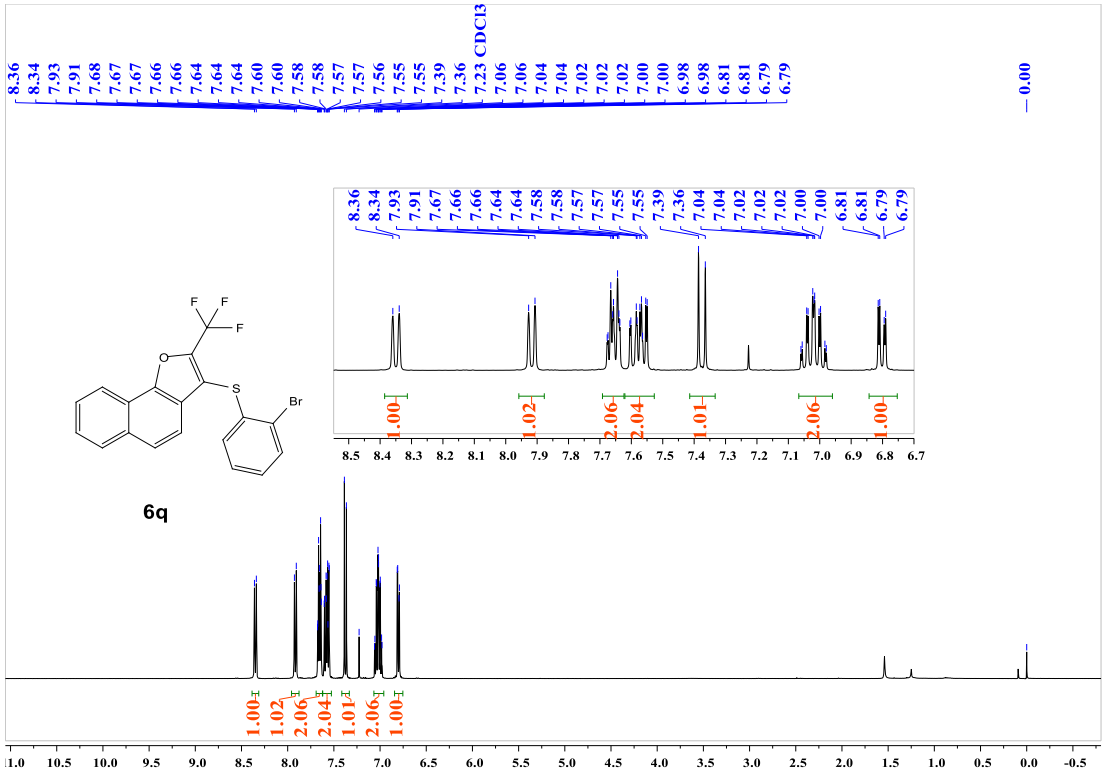
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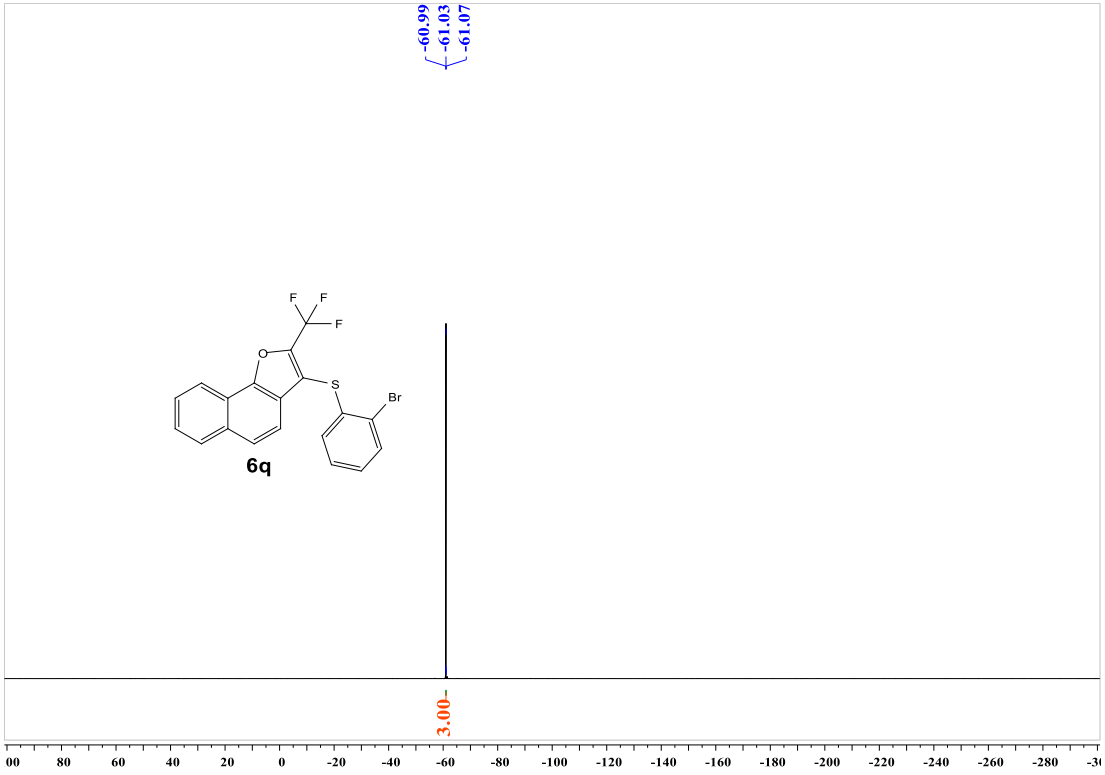
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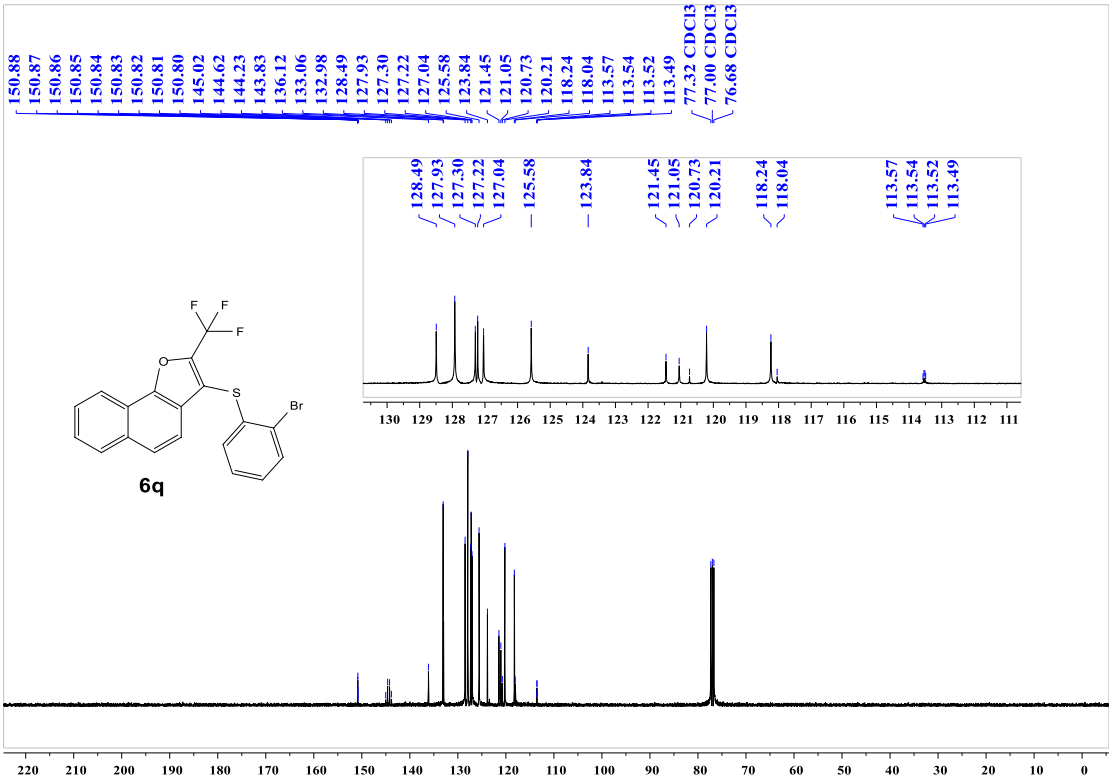
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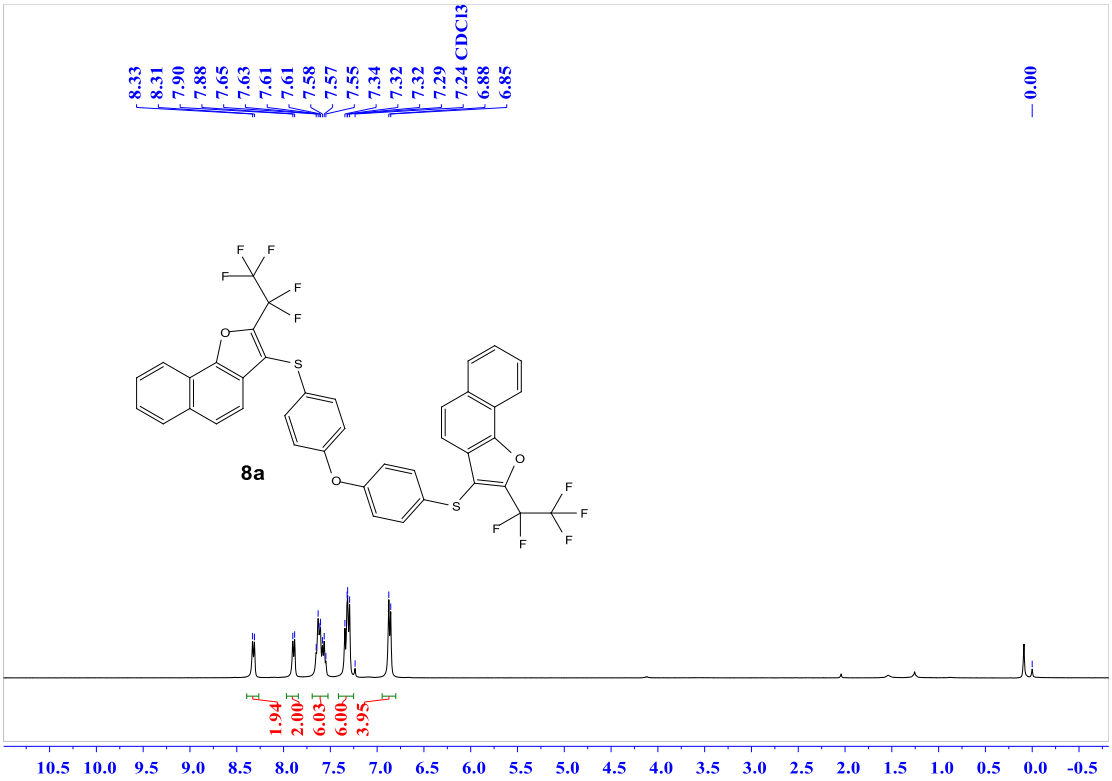
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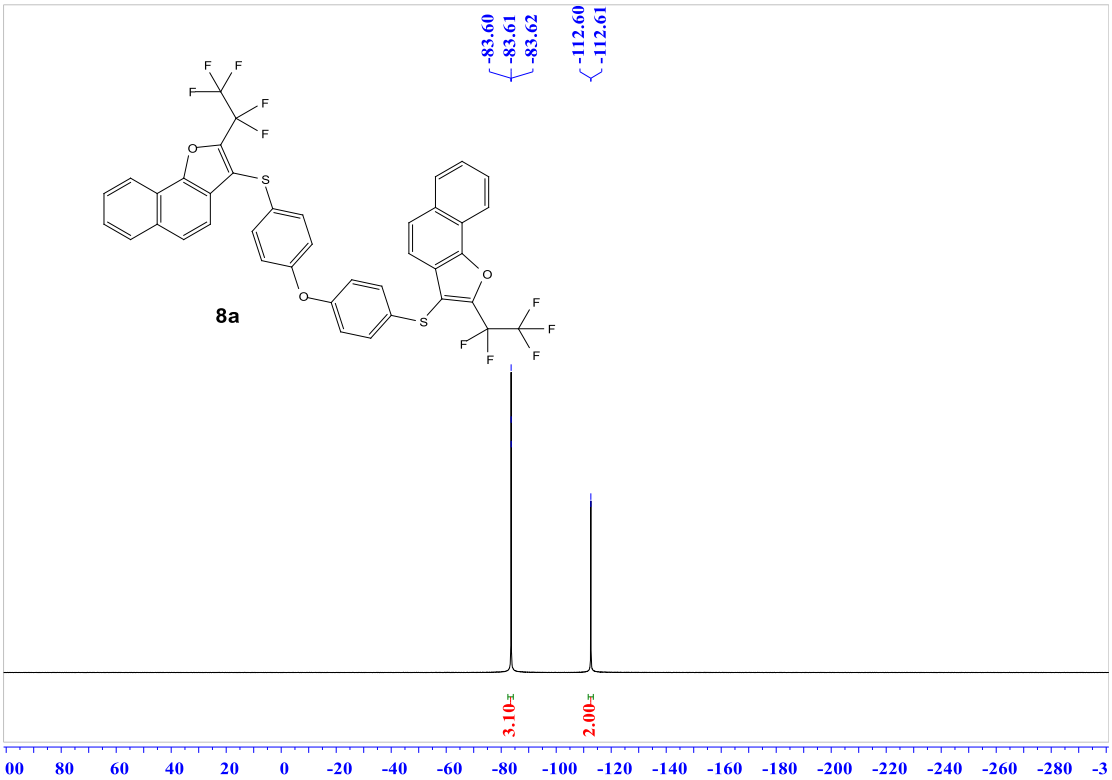
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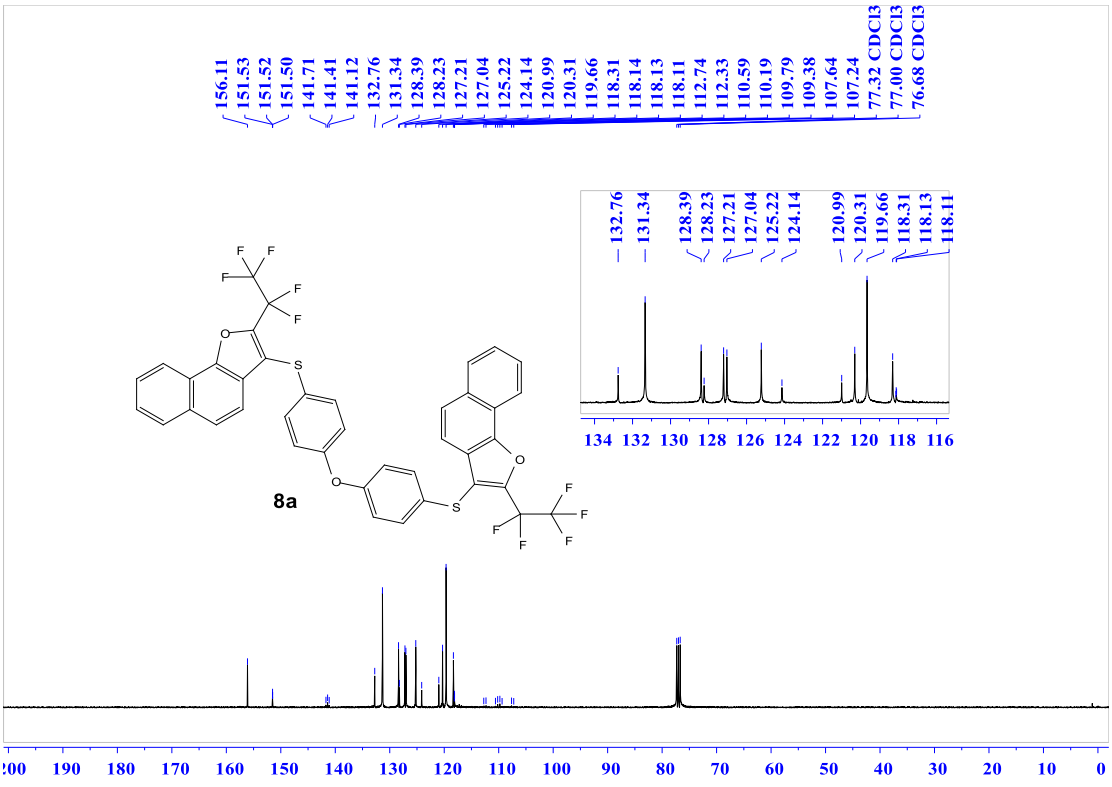
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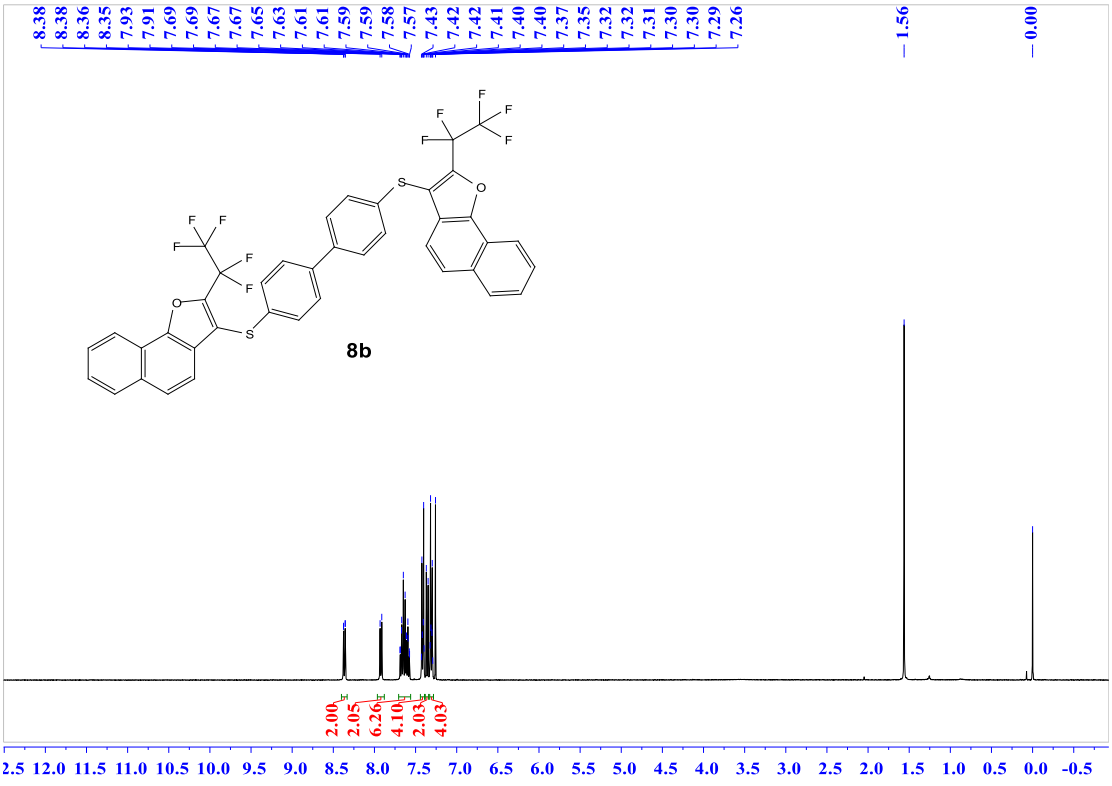
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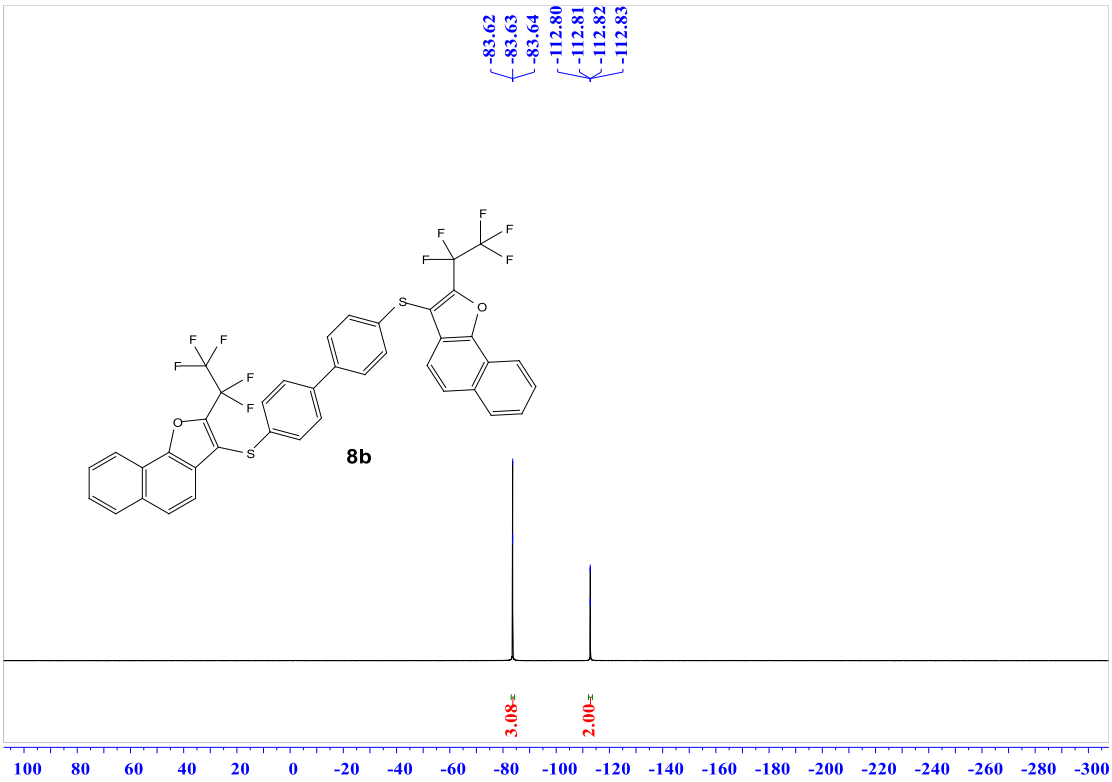
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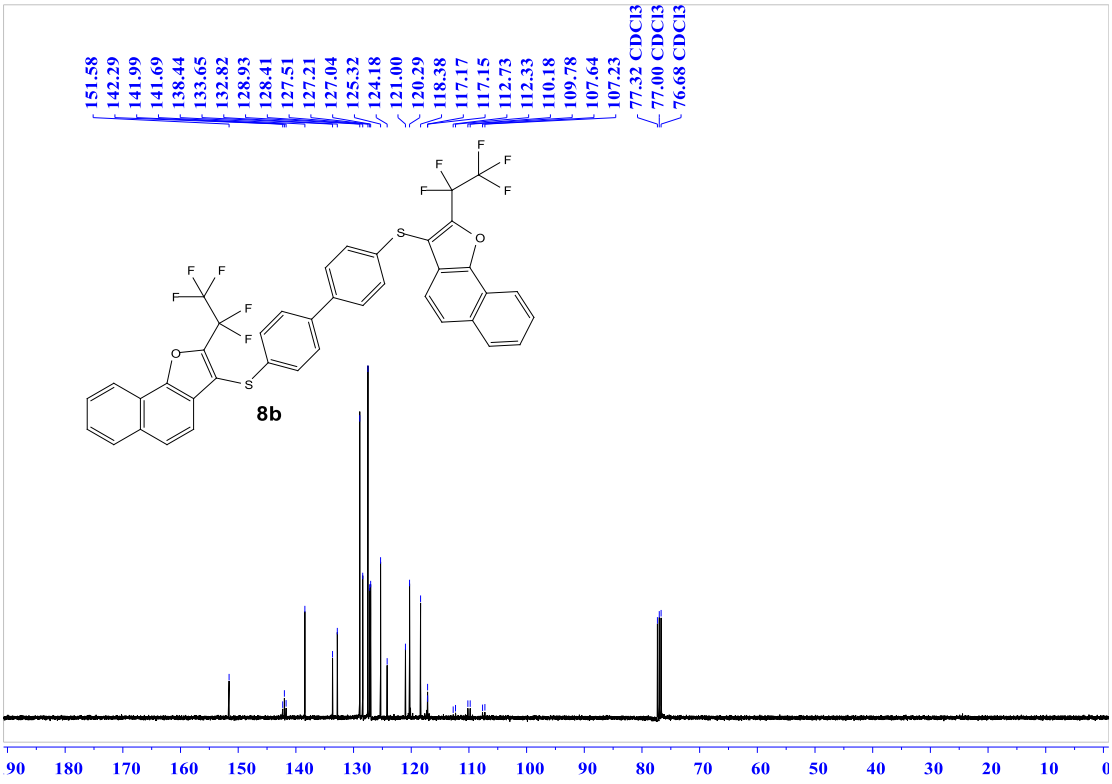
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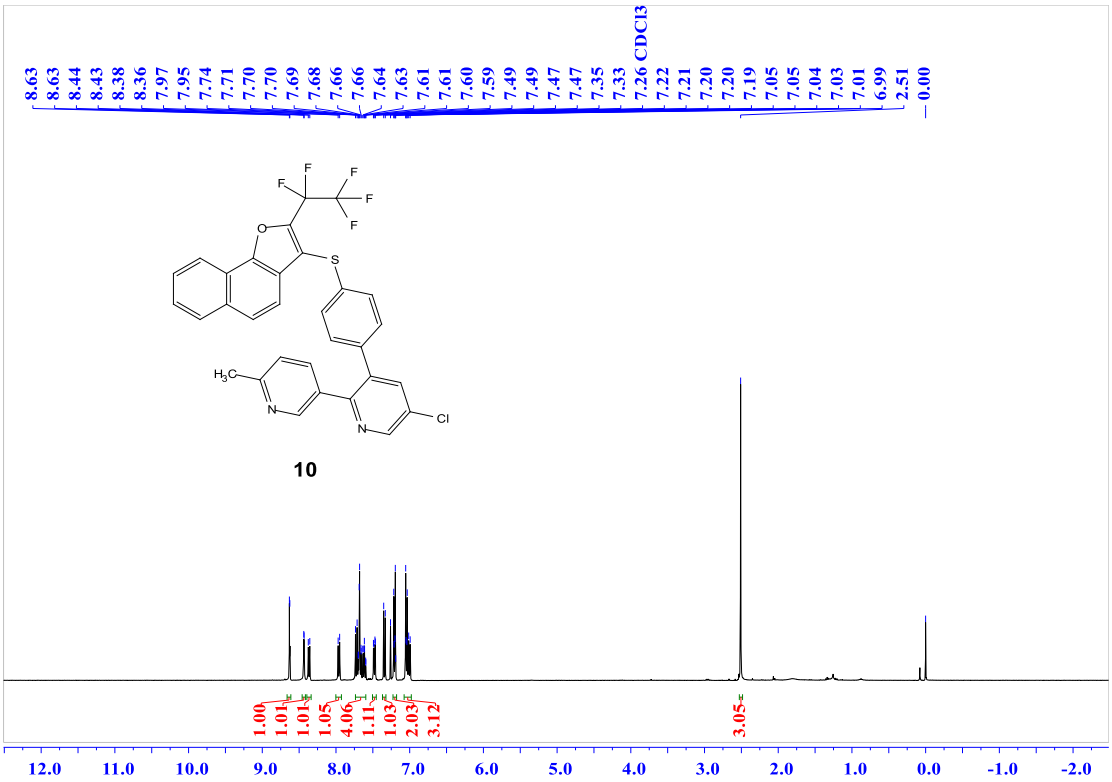
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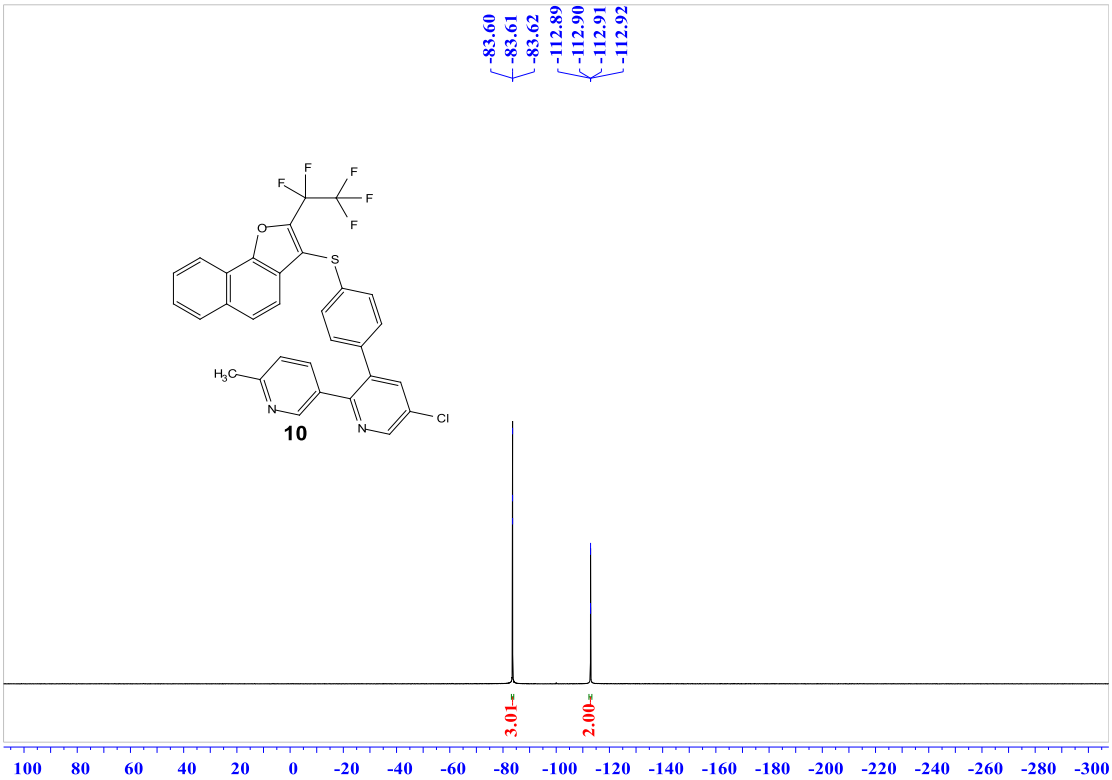
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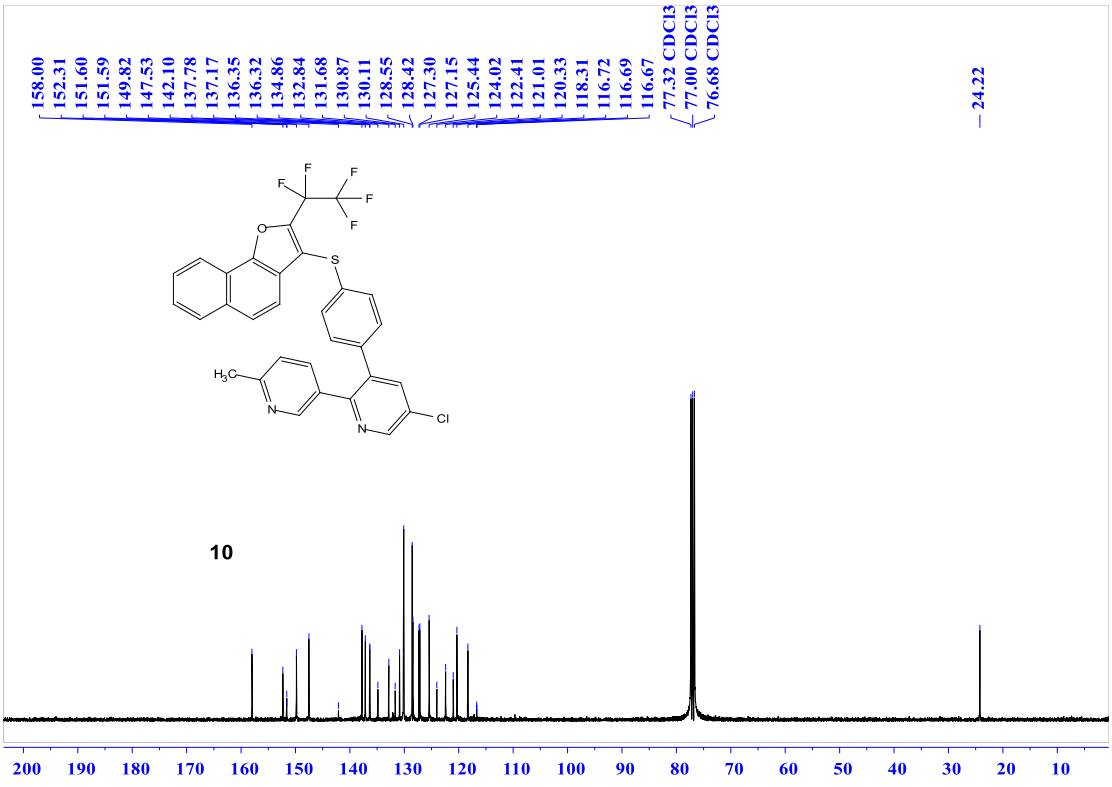
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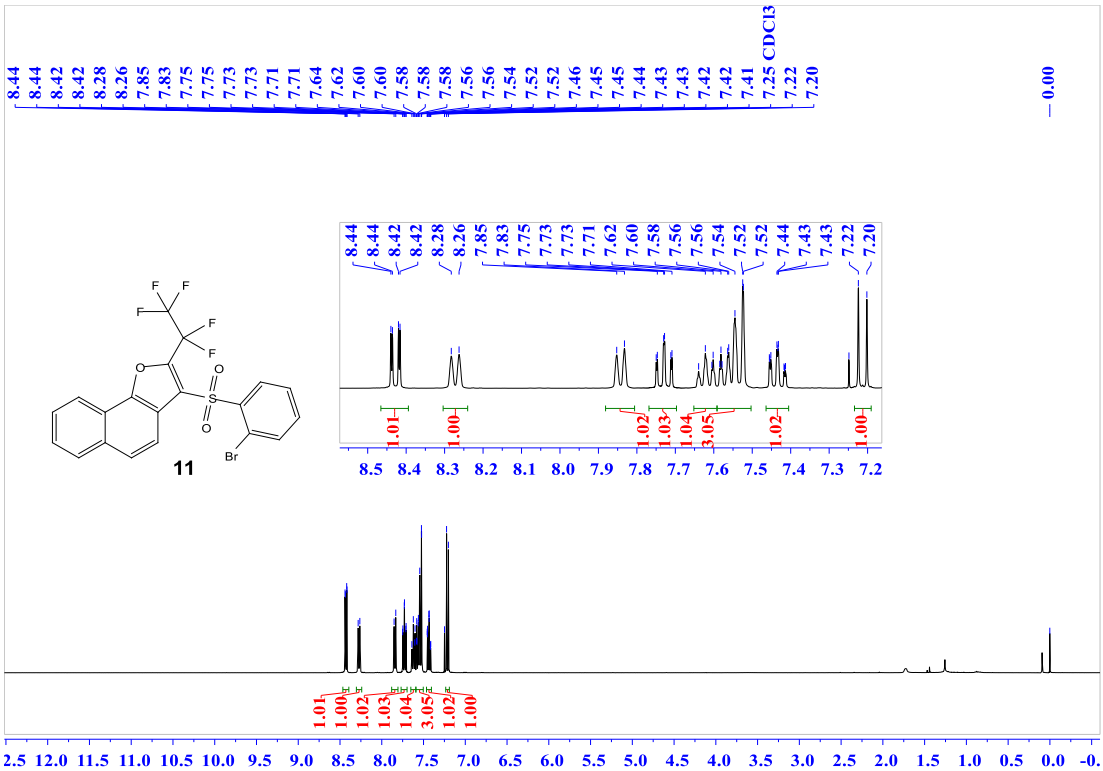
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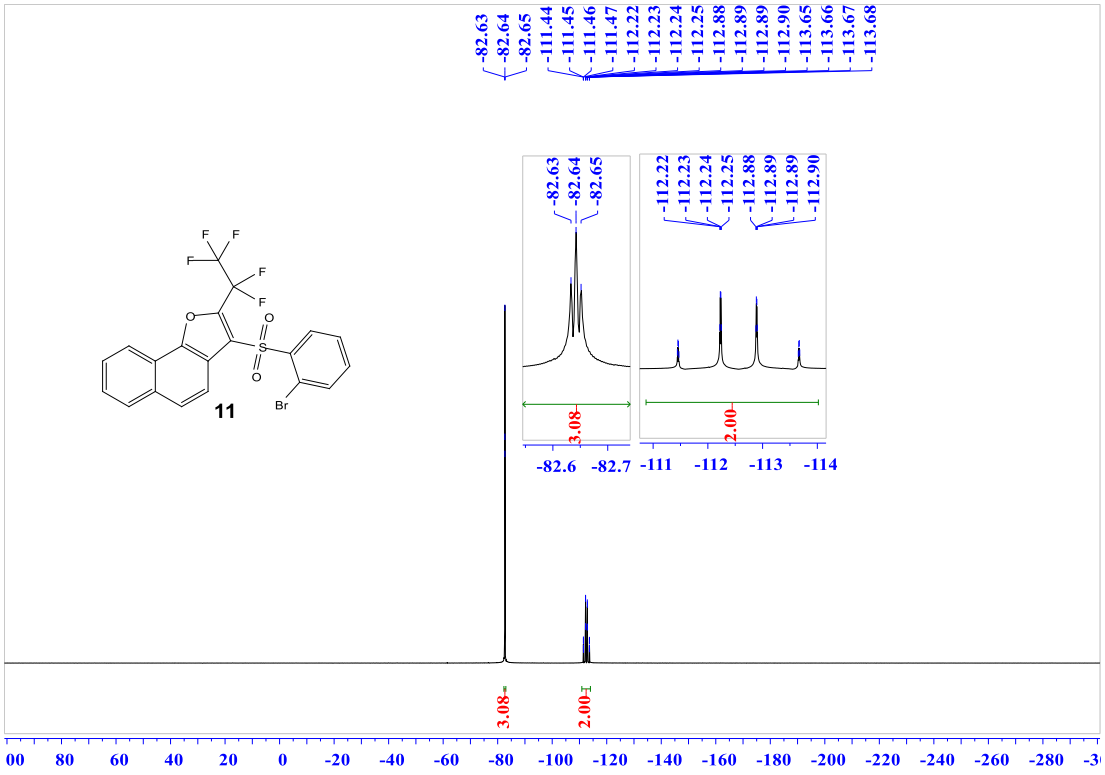
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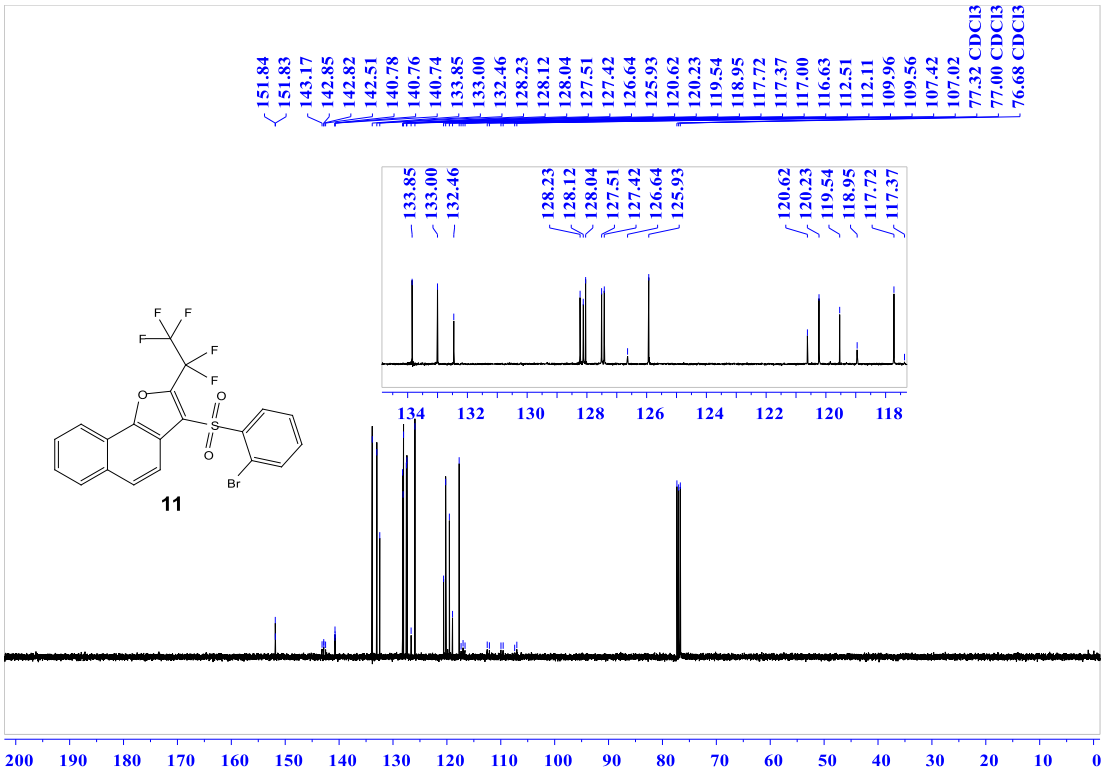
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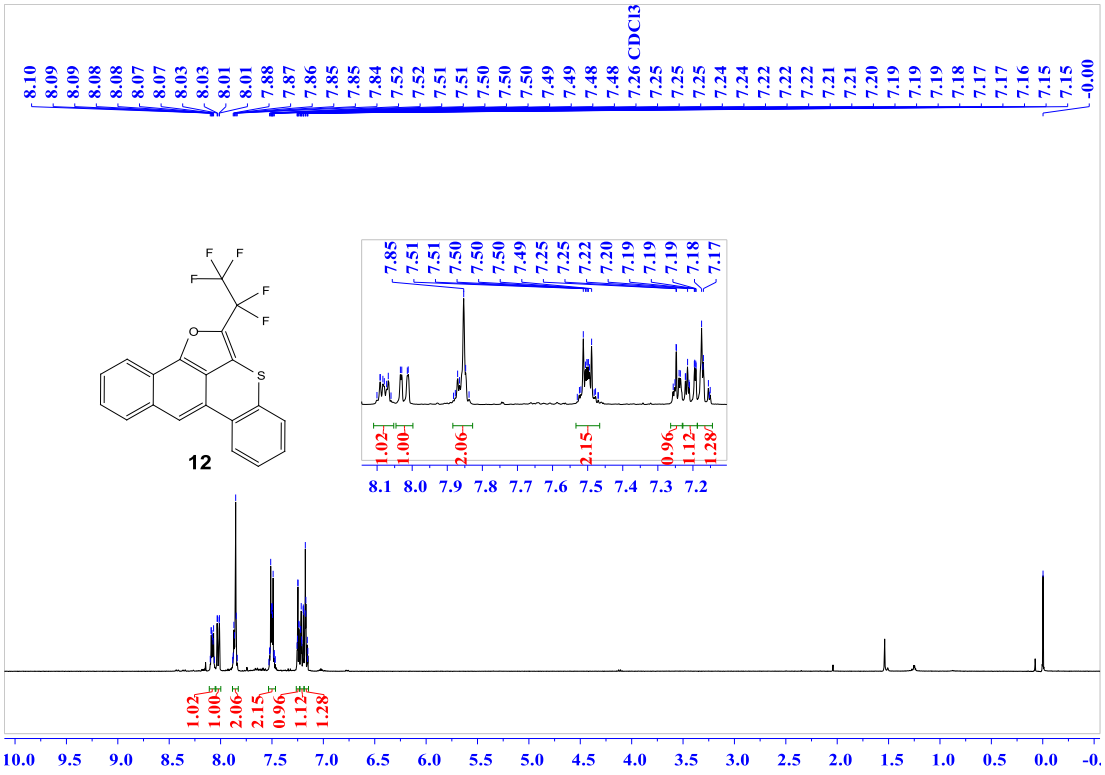
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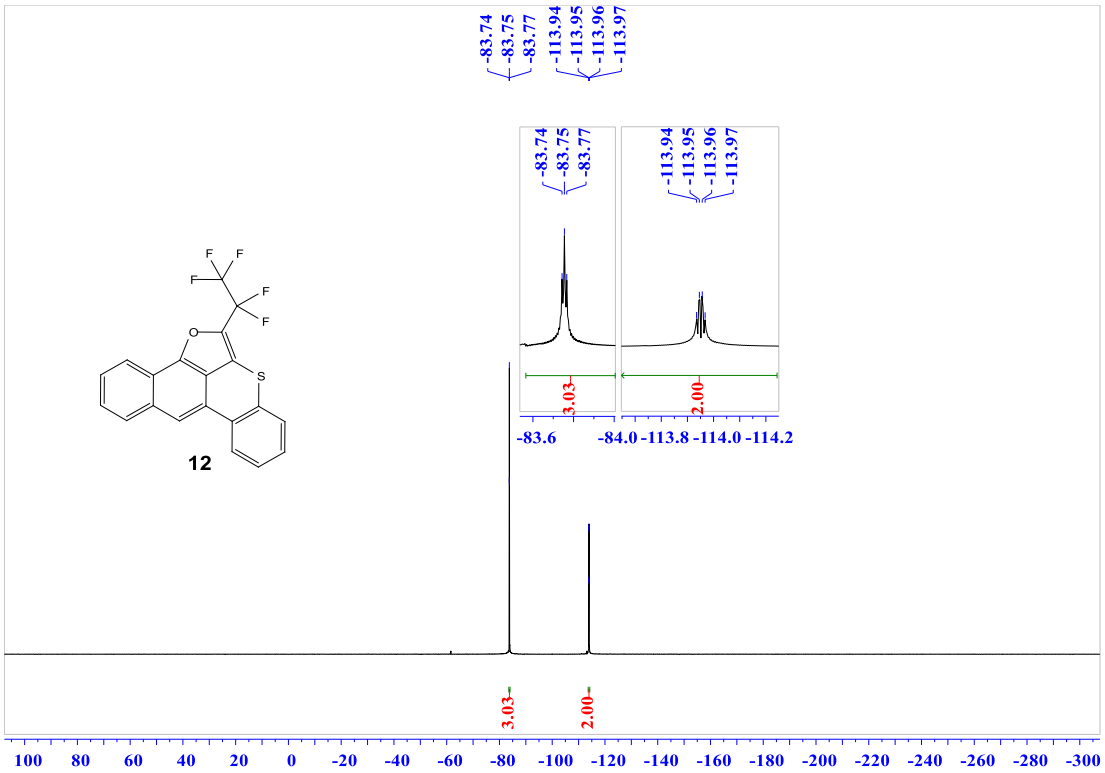
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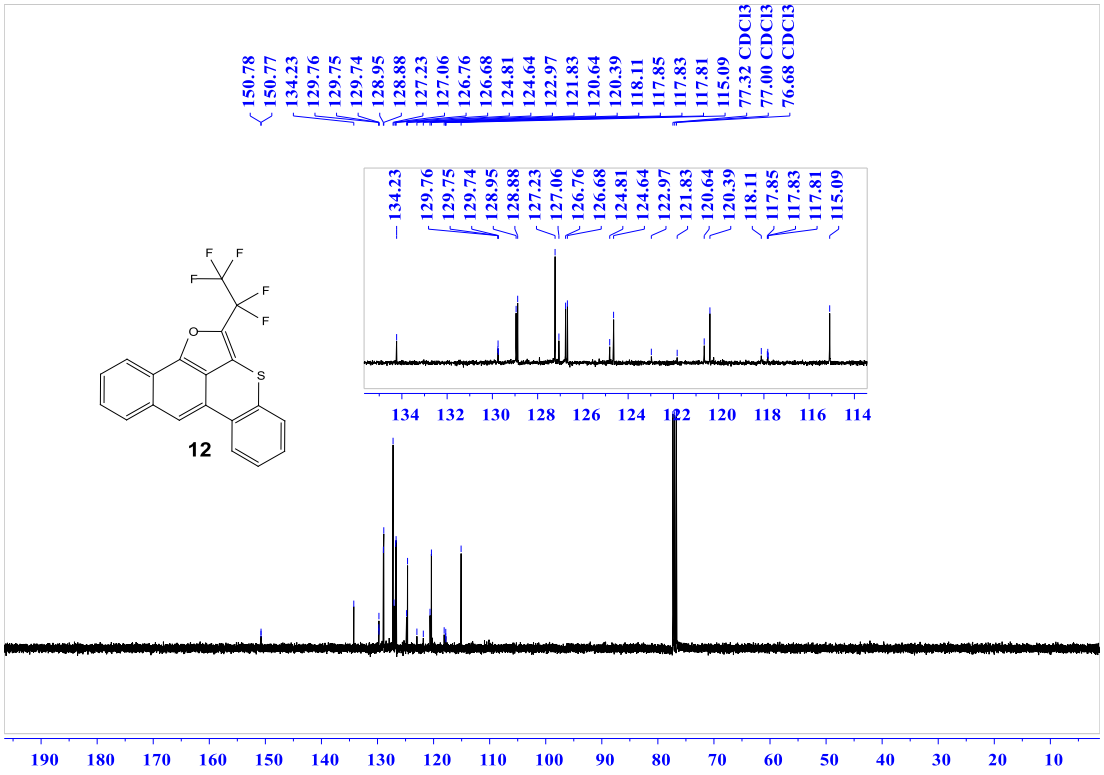
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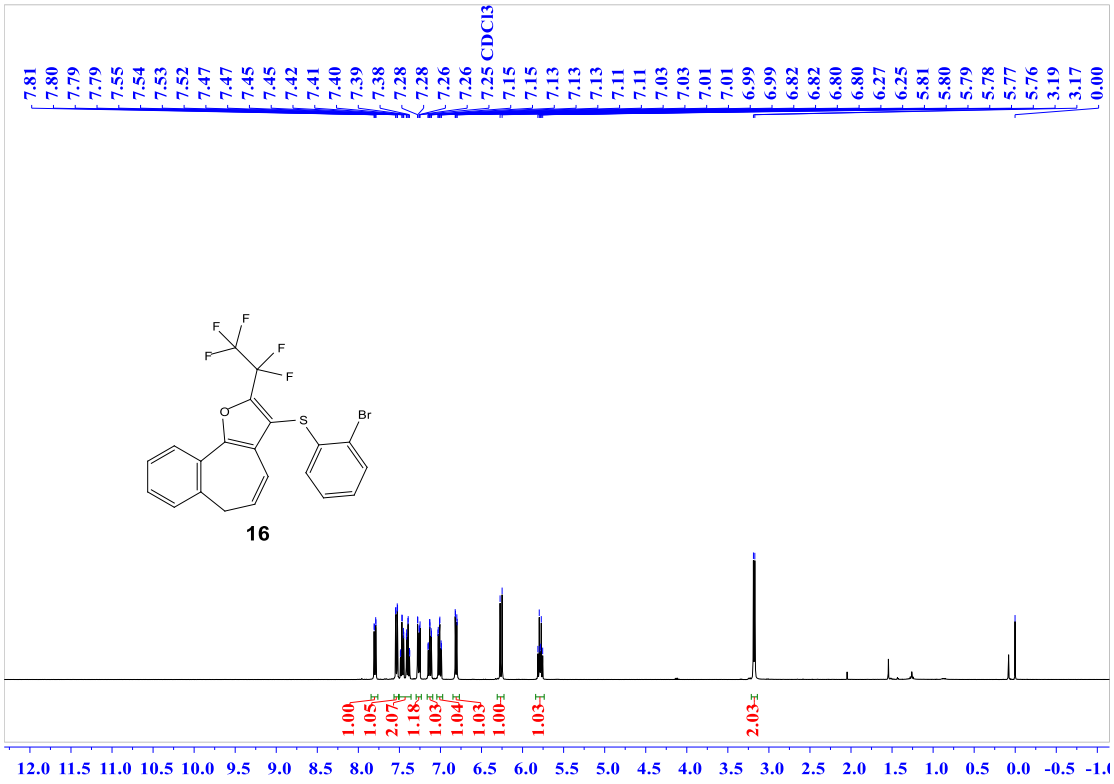
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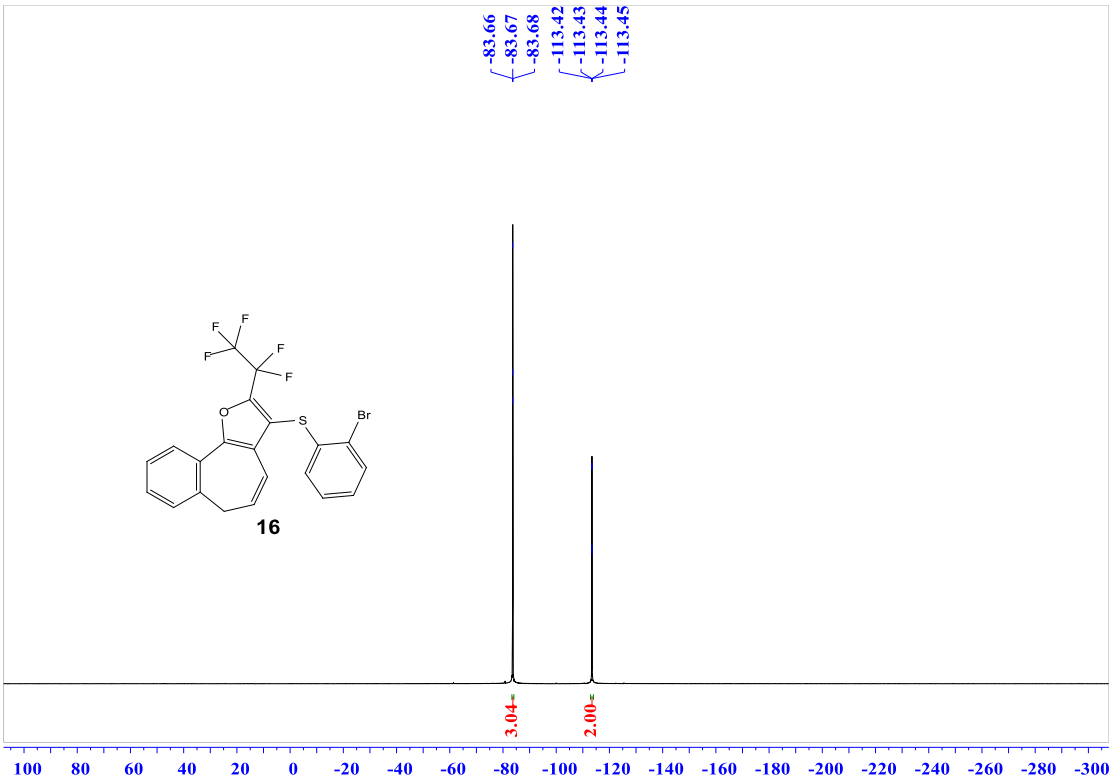
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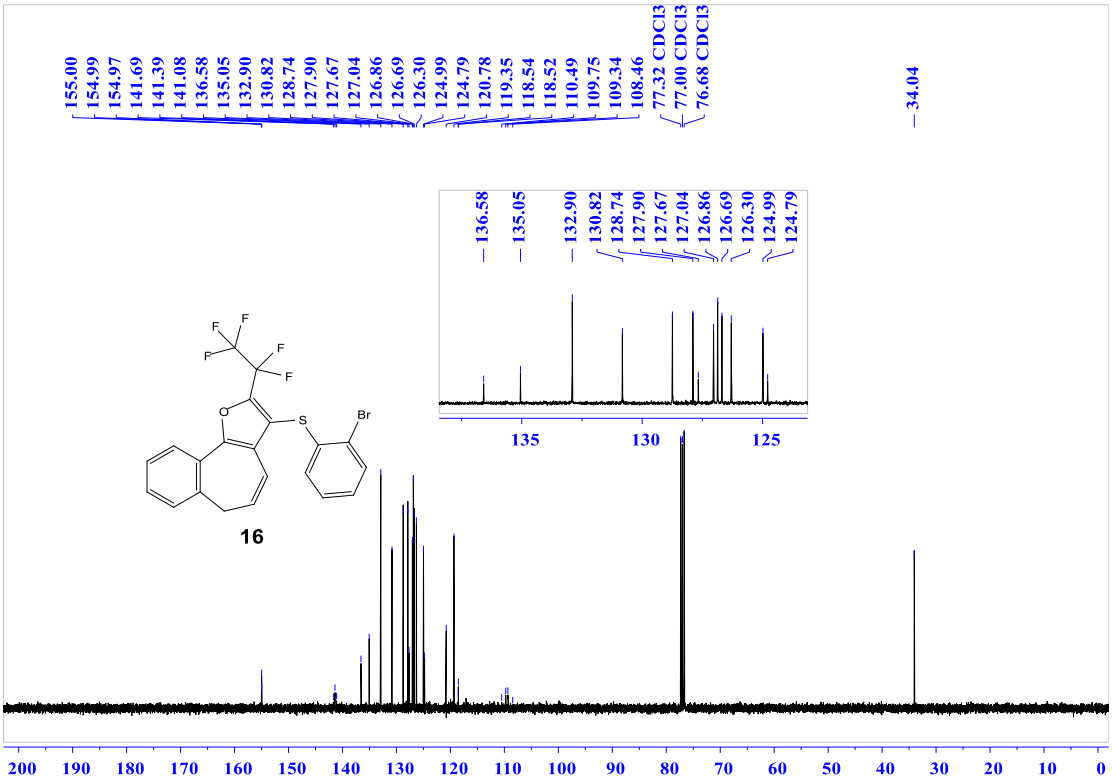
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