Visible-light-induced aerobic C3-H fluoroalkoxylation of quinoxalin-2(1*H*)-ones with fluoroalkyl alcohols

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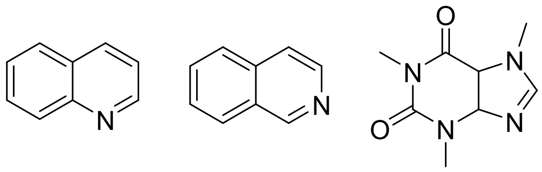
Supporting Information

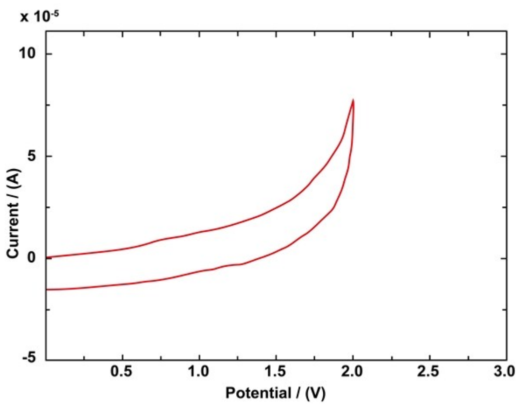


Scheme S1 Unreactive substrates for C-H fluoroalkoxylation

1. Mechanism investigation

(1) Cyclic voltammetry (CV) measurements

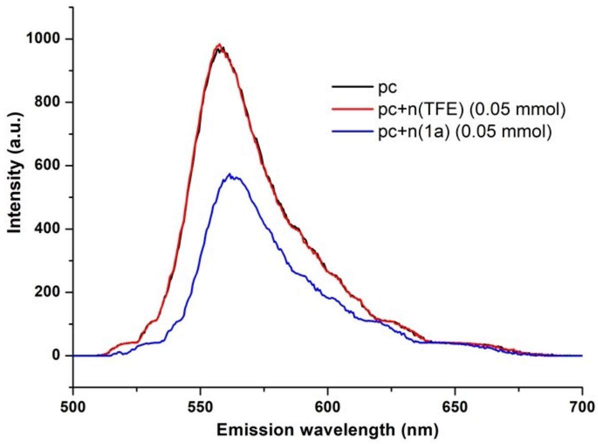
The cyclic voltammetry (CV) measurement (Ag/AgCl as a reference electrode) was determined by using *tetra*-*N*-bultylammonium hexafluorophosphate (0.1 M in dry and degassed MeCN) as electrolyte to show if the trifluoroethoxy radical could easily be generated from trifluoroethanol. The trifluoroethanol were prepared with 0.1 mmol in 5.0 mL of 0.1 M *tetra*-*N*-butylammonium hexafluorophosphate in dry and degassed MeCN. The applied potential range is 3.0 to 0 V vs Ag/AgCl at a sweep rate of 100 mV/s. It was found that no oxidation potential peak was found when measured the trifluoroethanol potential (Scheme S2), which indicated that the generation of trifluoroethoxy radical from trifluoroethanol is very difficult (Ep/2 > 2.0 V vs SCE in MeCN).[1-4]



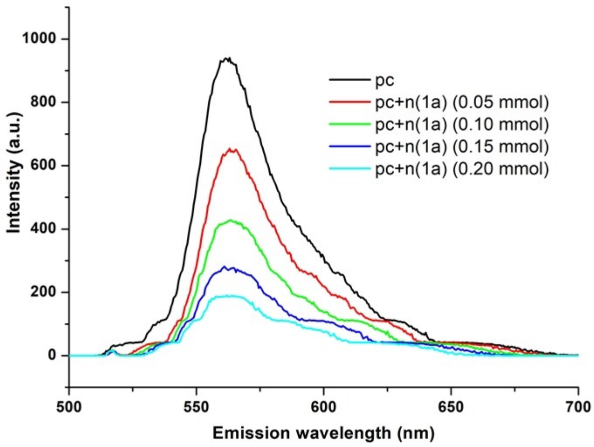
Scheme S2 Cyclic voltammetry (CV) measurement of trifluoroethanol (TFE)

(2) Fluorescence quenching experiment

The related fluorescence quenching experiments were performed, and the result was shown in scheme S3-4. In a typical experiment, to a 3.0 mL solution of Eosin Y in MeCN (1.6×10^{-5} M) was added *N*-methylquinoxalin-2(1*H*)-one (**1a**) and CF_3CH_2OH (TFE), respectively. It was found that the photocatalyst Eosin Y was obviously quenched by **1a** (*N*-methylquinoxalin-2(1*H*)-one).[3,4]



Scheme S3 Fluorescence quenching of Eosin Y (PC) emission by TFE and **1a**, respectively



Scheme S4 Fluorescence quenching of Eosin Y (PC) emission by different concentrations of **1a**

References:

1. A. Hu, Y. Chen, J.-J. Guo, N. Yu, Q. An, Z. Zuo, *J. Am. Chem. Soc.* **2018**, *140*, 13580.
2. A. Hu, J.-J. Guo, H. Pan, Z. Zuo, *Science* **2018**, *361,* 668.
3. L. Zhao, L. Wang, Y. Gao, Z. Wang, P. Li, *Adv. Synth. Catal.*, **2019**, *361*, 5363.
4. J. Zhou, P. Zhou, T. Zhao, Q. Ren, J. Li, *Adv. Synth. Catal.*, **2019**, *361*, 5371.

2. X-ray Crystal Data of Product 18

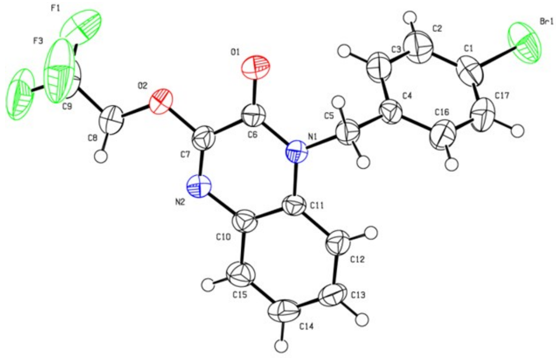


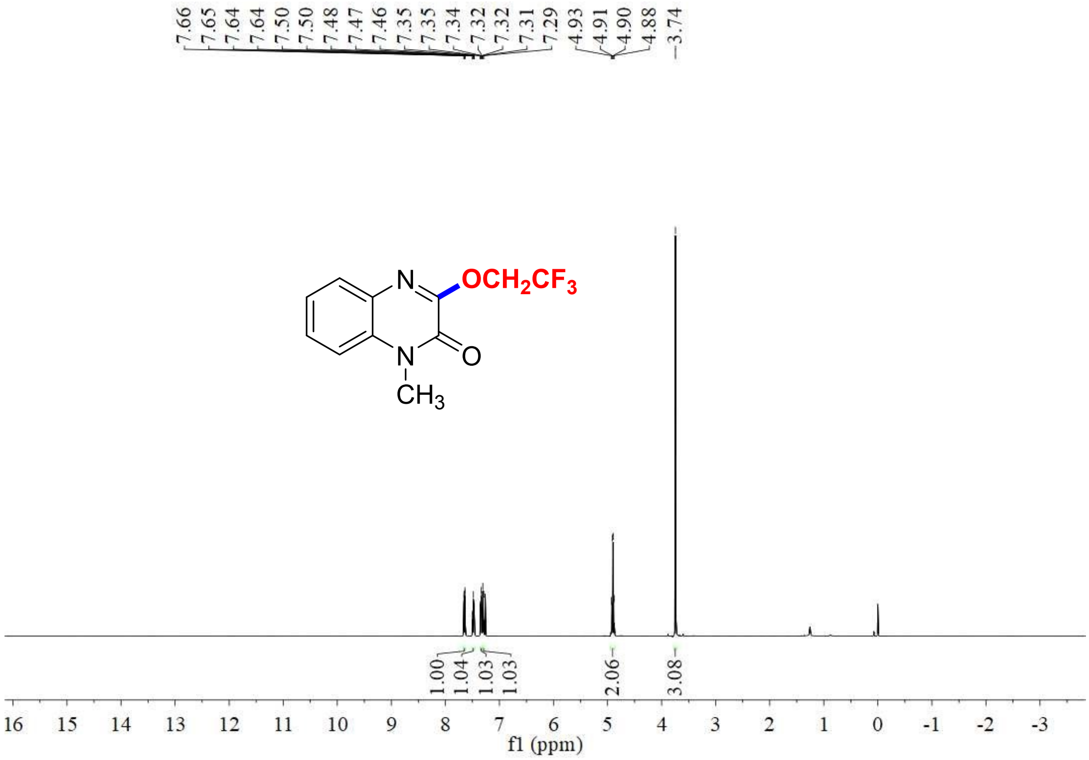
Figure 1 Single-crystal X-ray structure of **18**. Ellipsoids are represented at 30% probability.

Table S1. Crystallographic data and structure refinement for **18**.

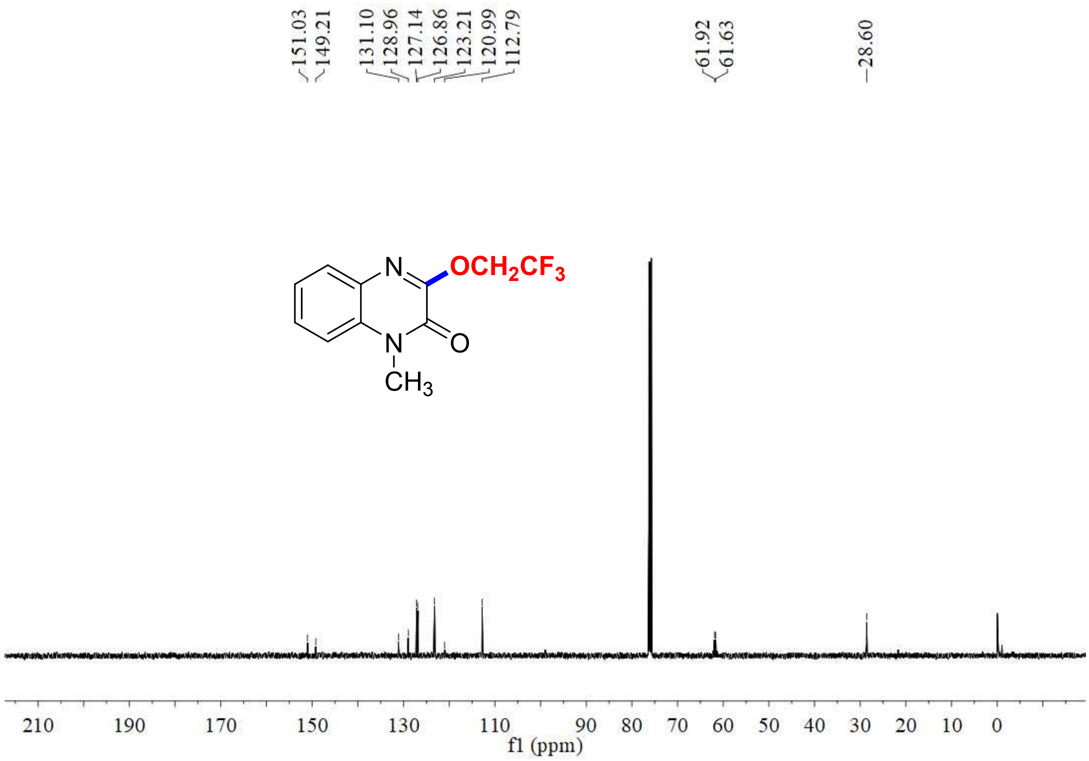
CCDC	1958968
Empirical formula	$C_{17}H_{12}BrF_3N_2O_2$
Formula weight	413.20
Temperature, K	296.15
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	C 1 2/c 1
a, *b*, *c*, Å	15.949(2), 9.0933(12), 25.010(3)
α, *β*, *γ*, °	90, 113.421(2), 90
Volume, $Å^3$	3328.3(7)
Z	8
Absorption coefficient, mm^{-1}	2.515
F (000)	1648
Theta range for data collection, °	2.600 to 27.620
Limiting indices	-20<=h<=20, -11<=k<=11, -32<=l<=25
Reflections collected / unique	9770 / 3779 [R(int) = 0.0317]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3779 / 0 / 227
Goodness of fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1044
R indices (all data)	R1 = 0.0918, wR2 = 0.1197
Largest diff. peak and hole e. A^{-3}	0.540d -0.501

3. Copies of ^1H and ^{13}C NMR Spectra

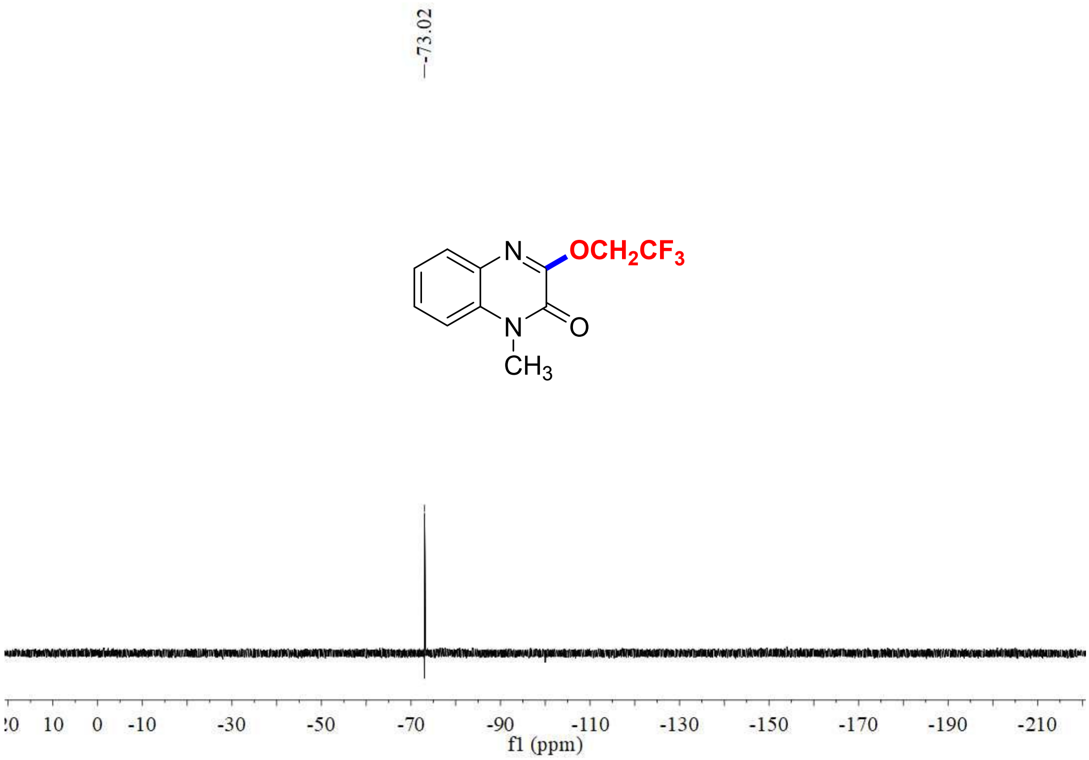
2 ^1H NMR



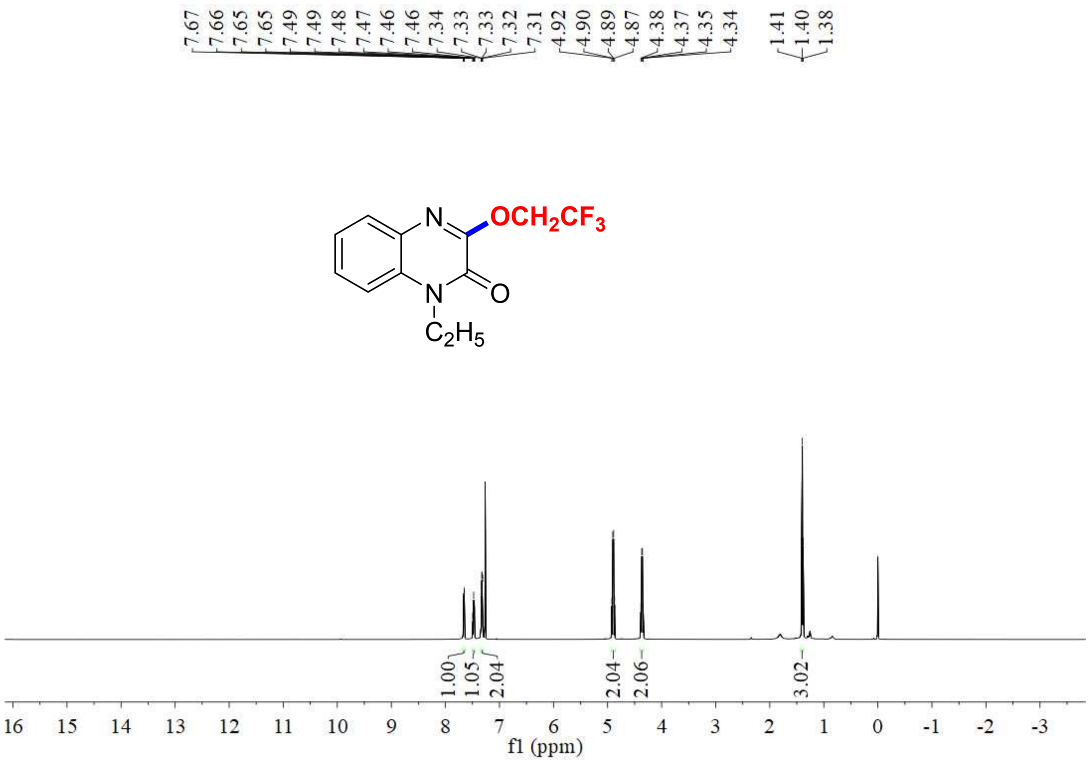
2 ^{13}C NMR



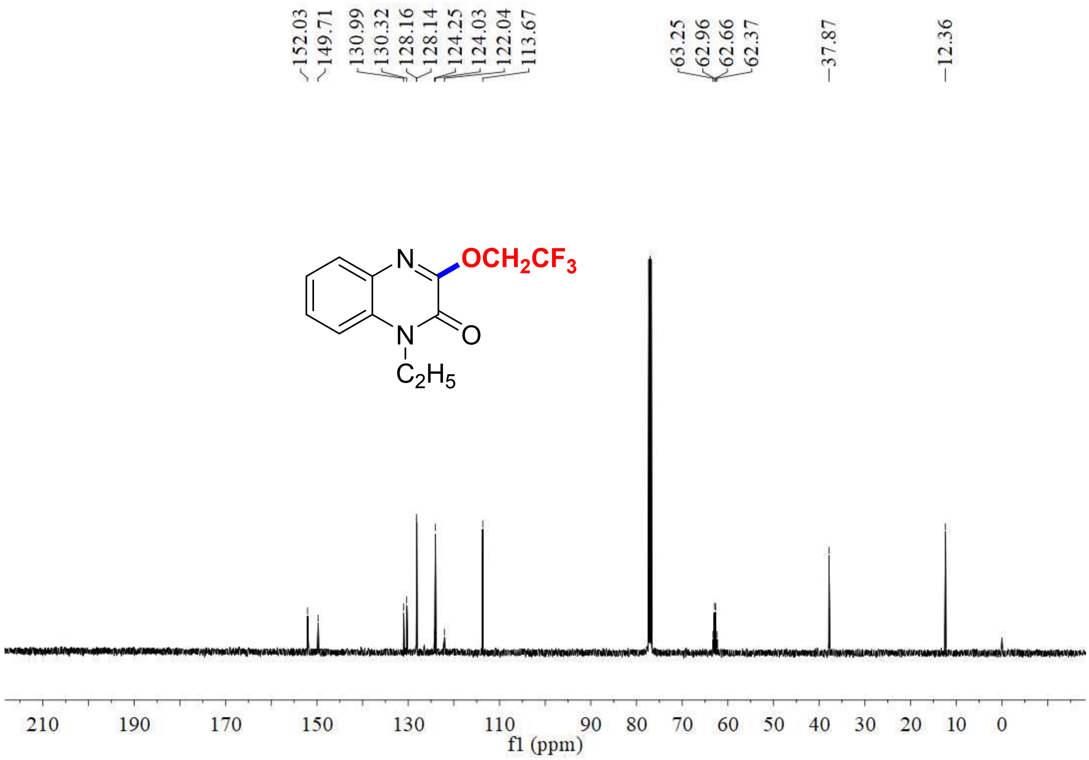
2 ^{19}F NMR



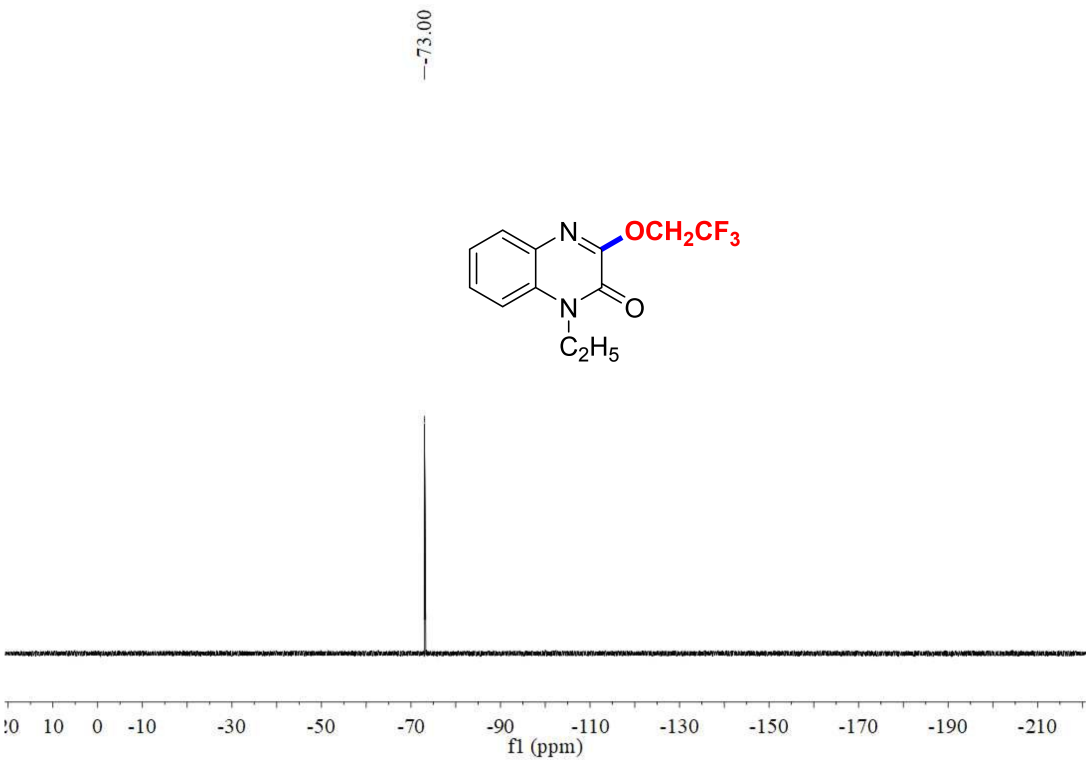
3 ^{1}H NMR



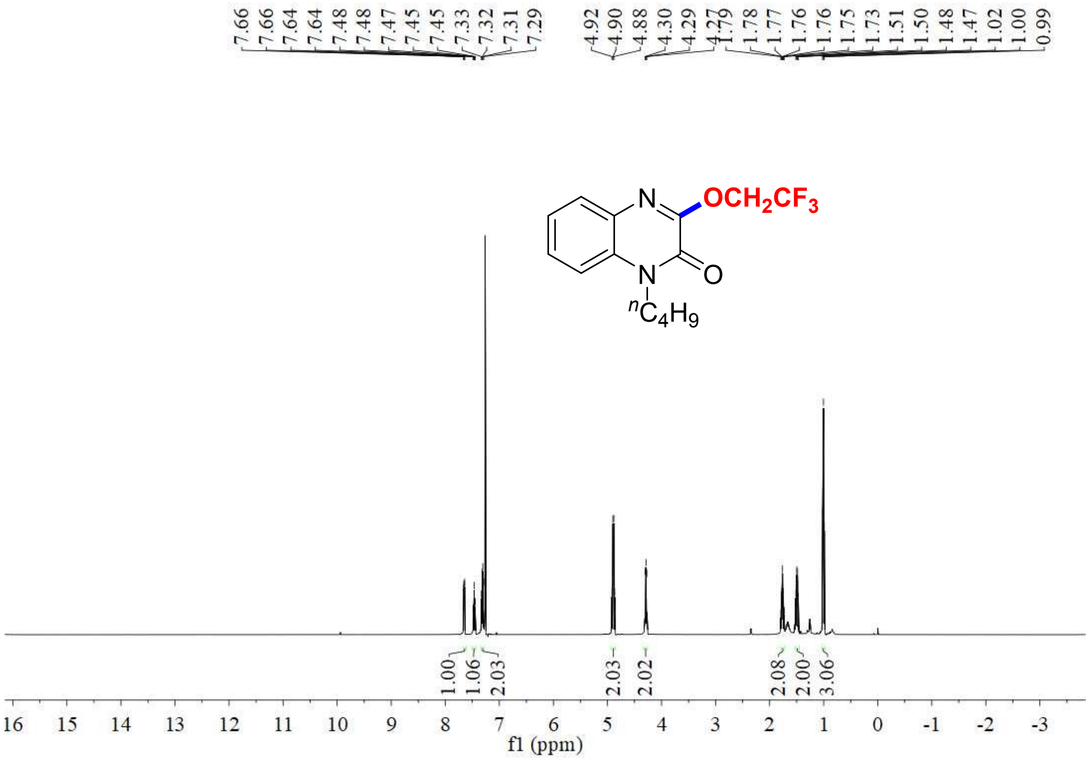
3 ^{13}C NMR



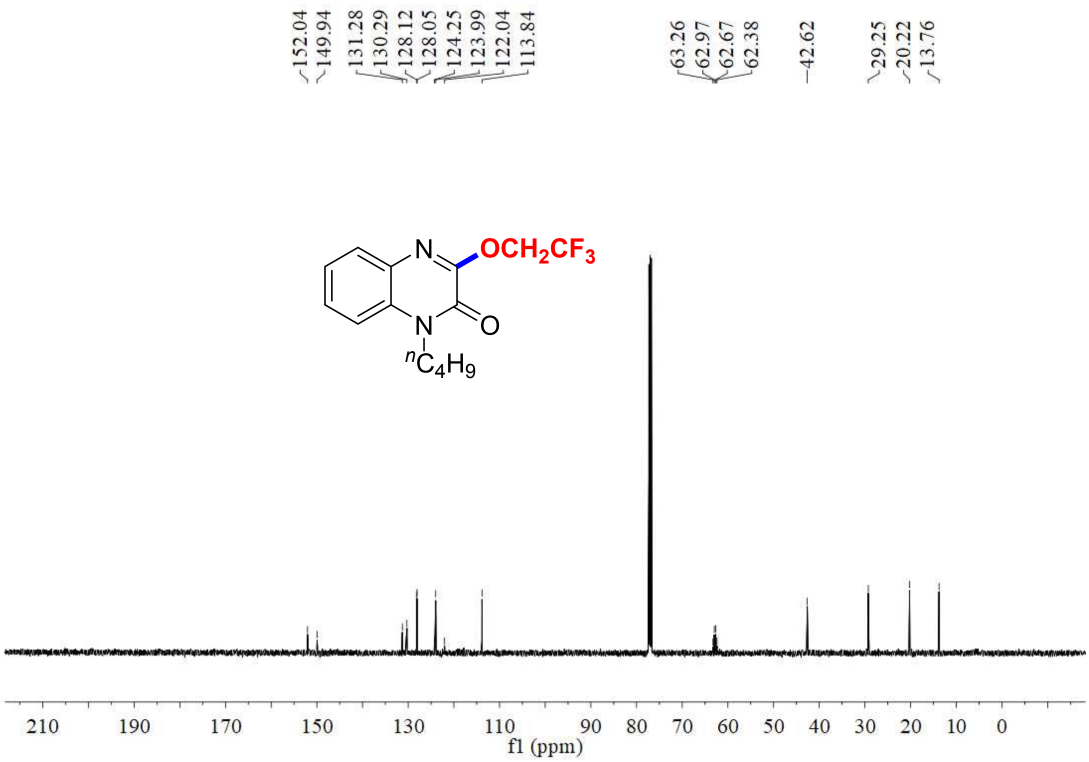
3 ^{19}F NMR



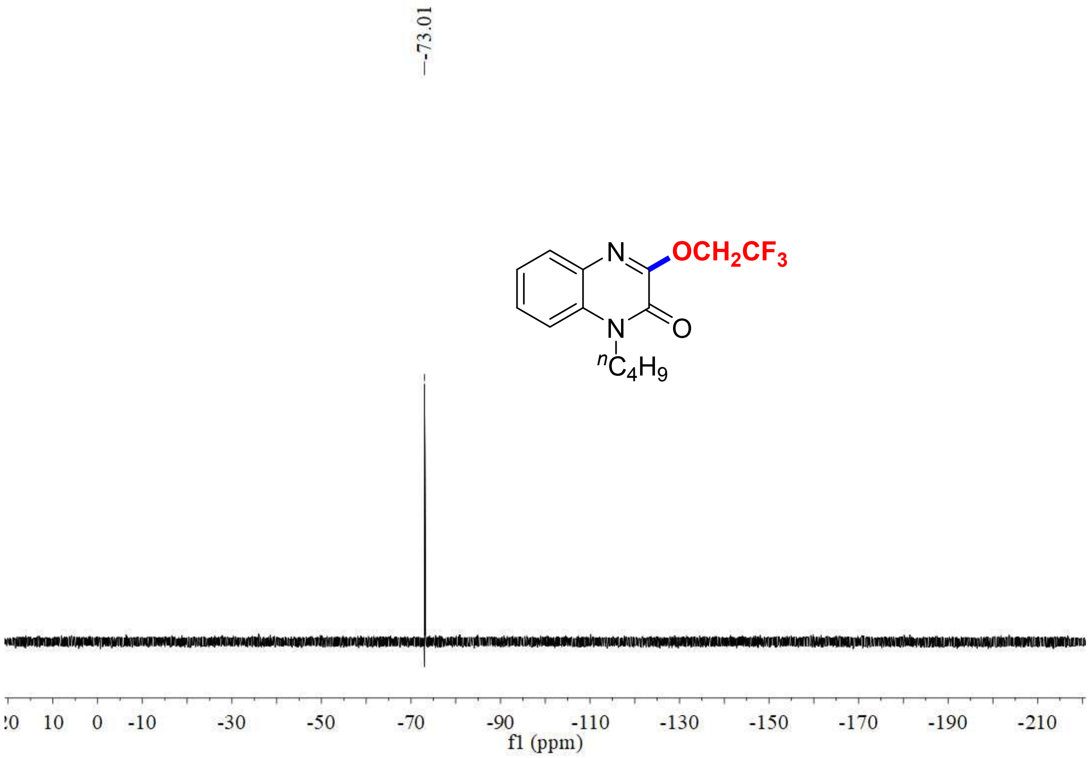
4 ^{1}H NMR



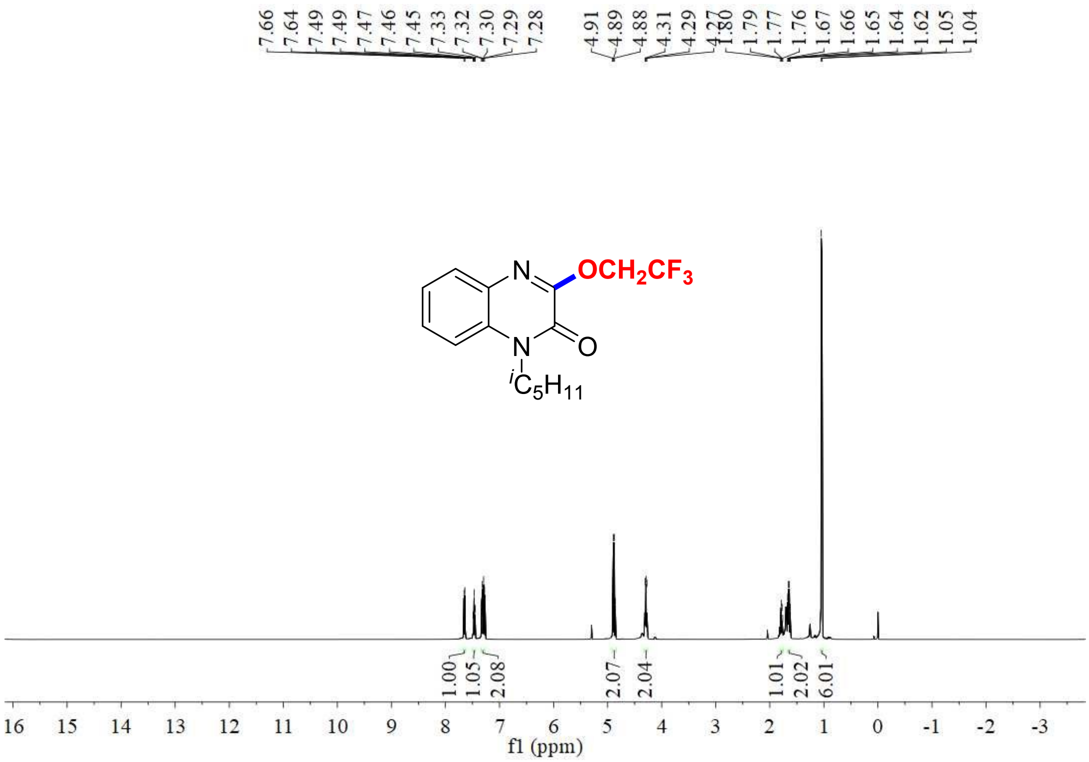
4 ^{13}C NMR



4 ^{19}F NMR



5 ^{1}H NMR



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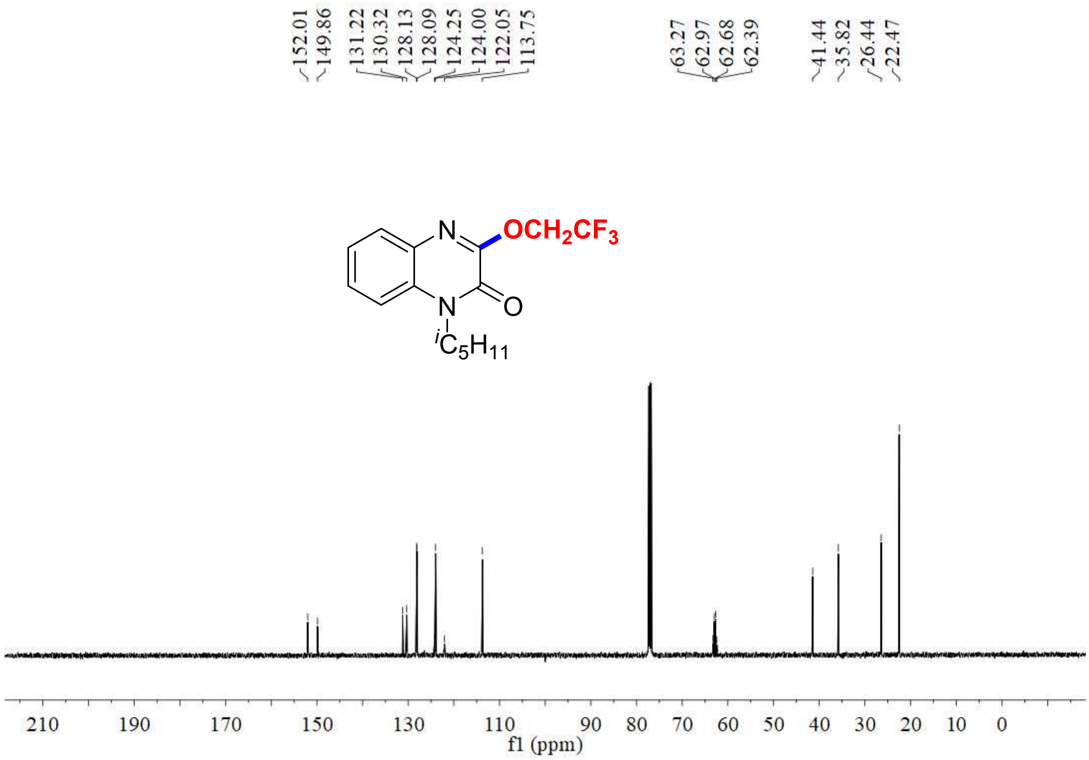

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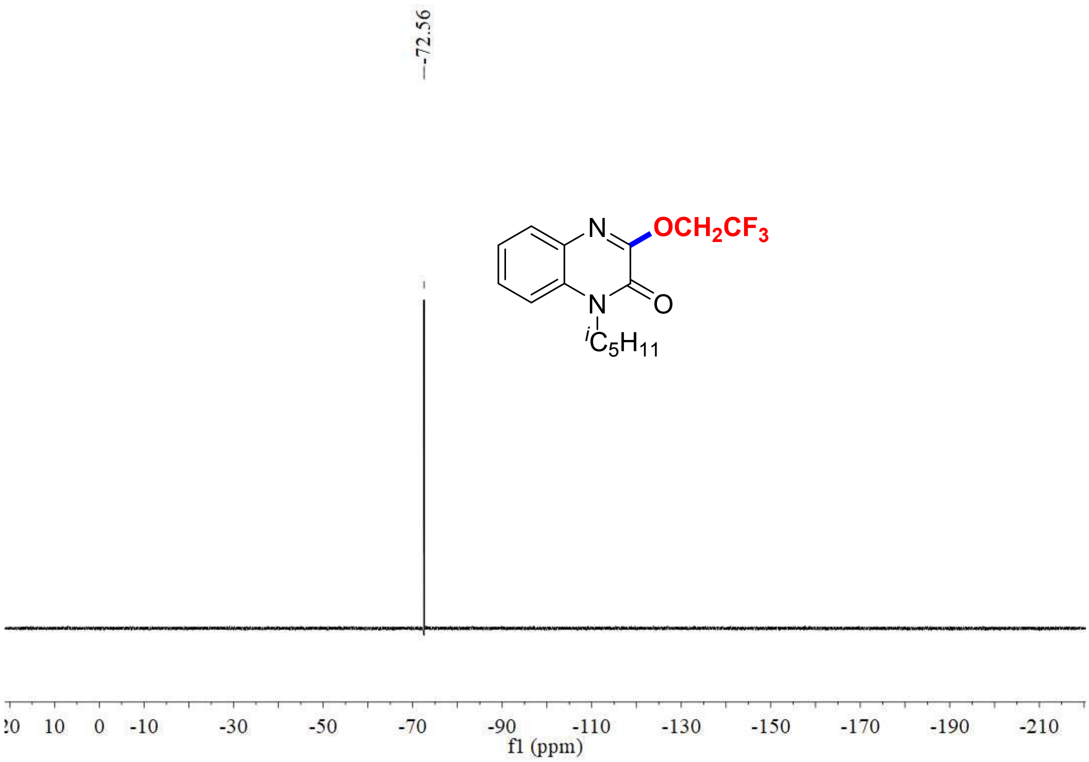
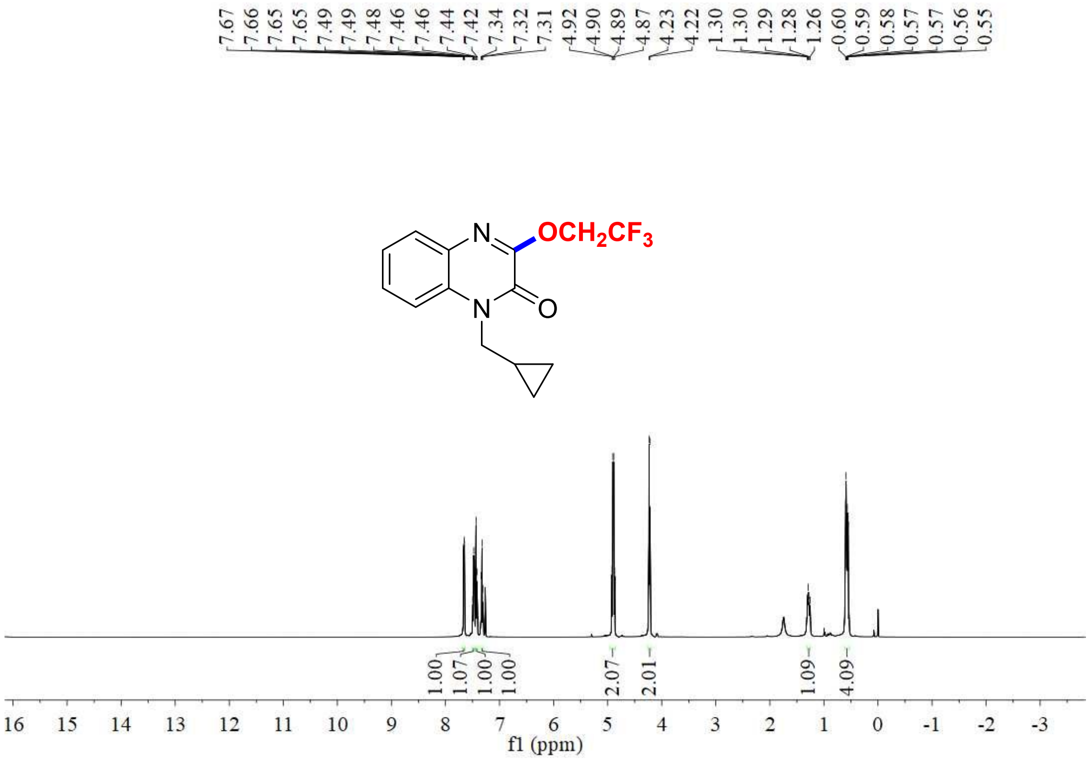


6 ^{1}H NMR



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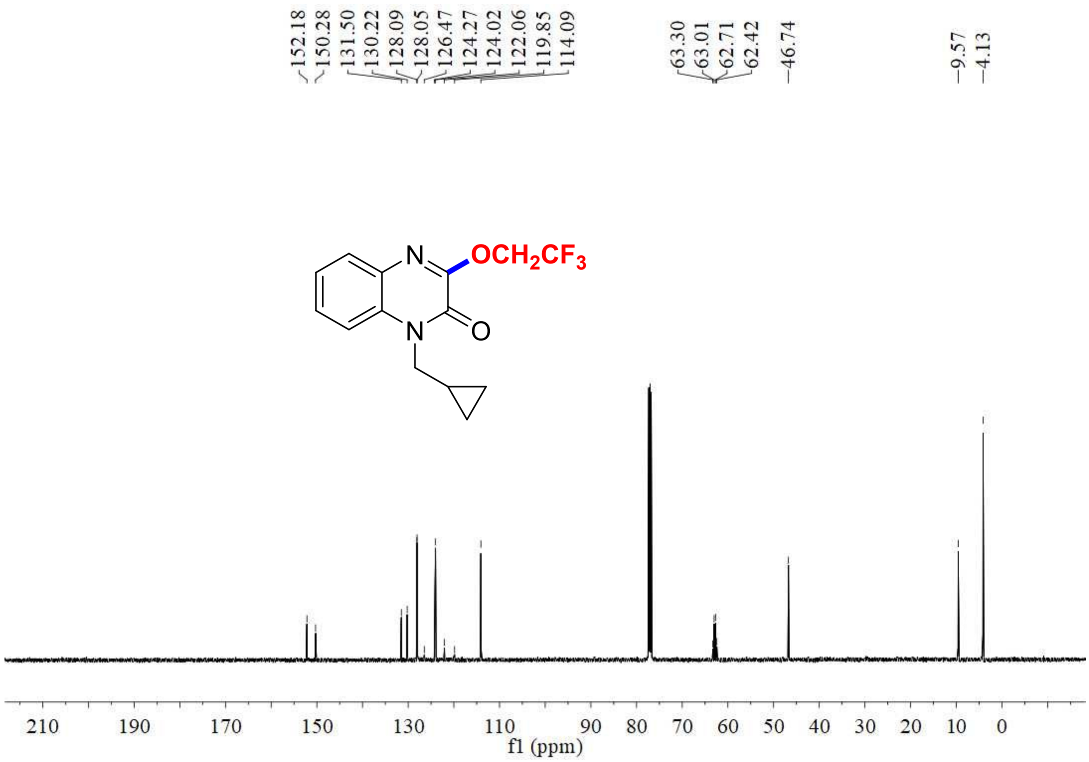
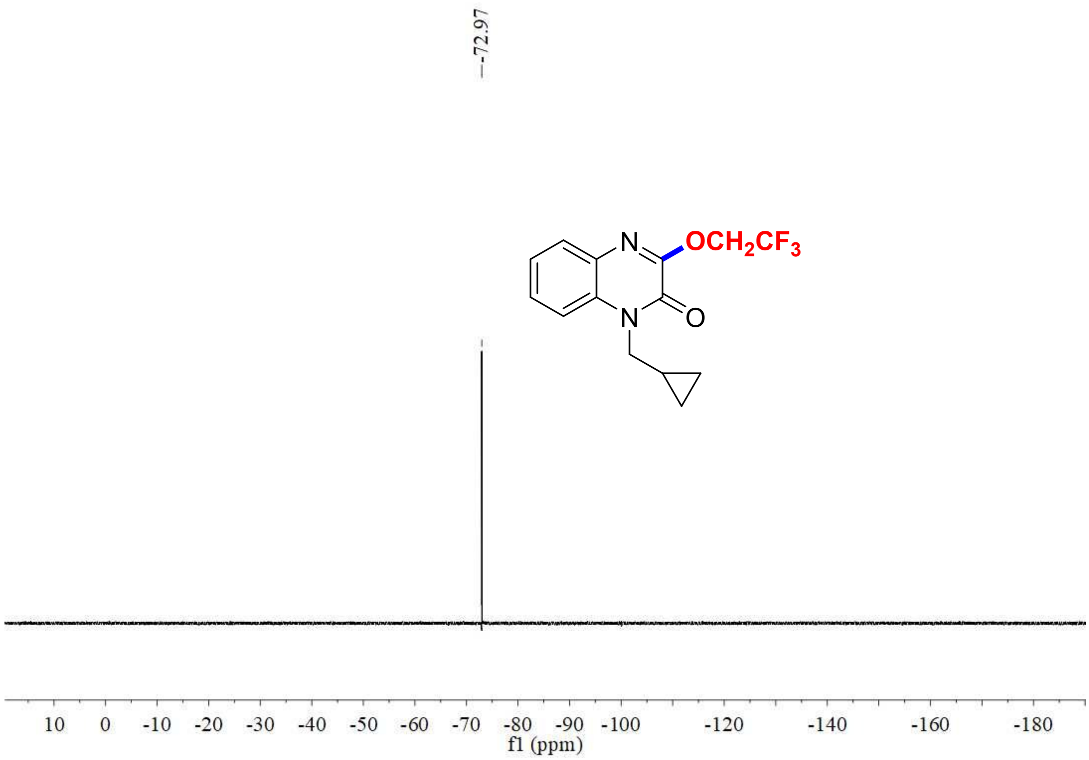
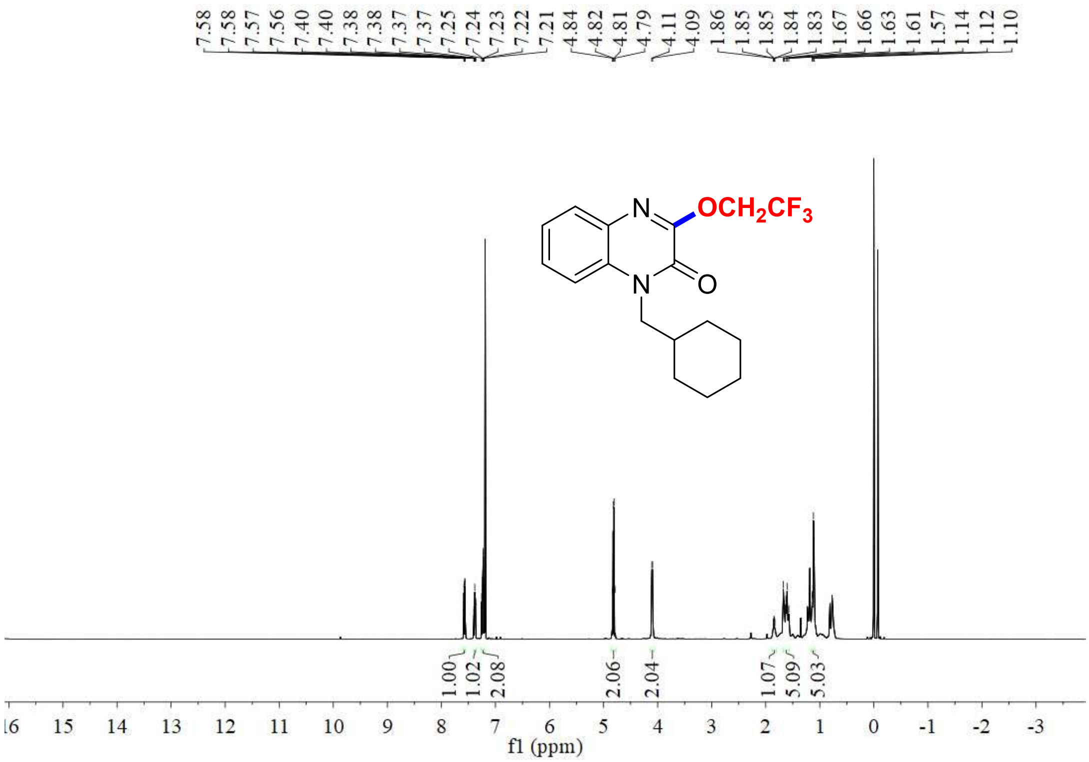


6 ^{19}F NMR



7 ^{1}H NMR



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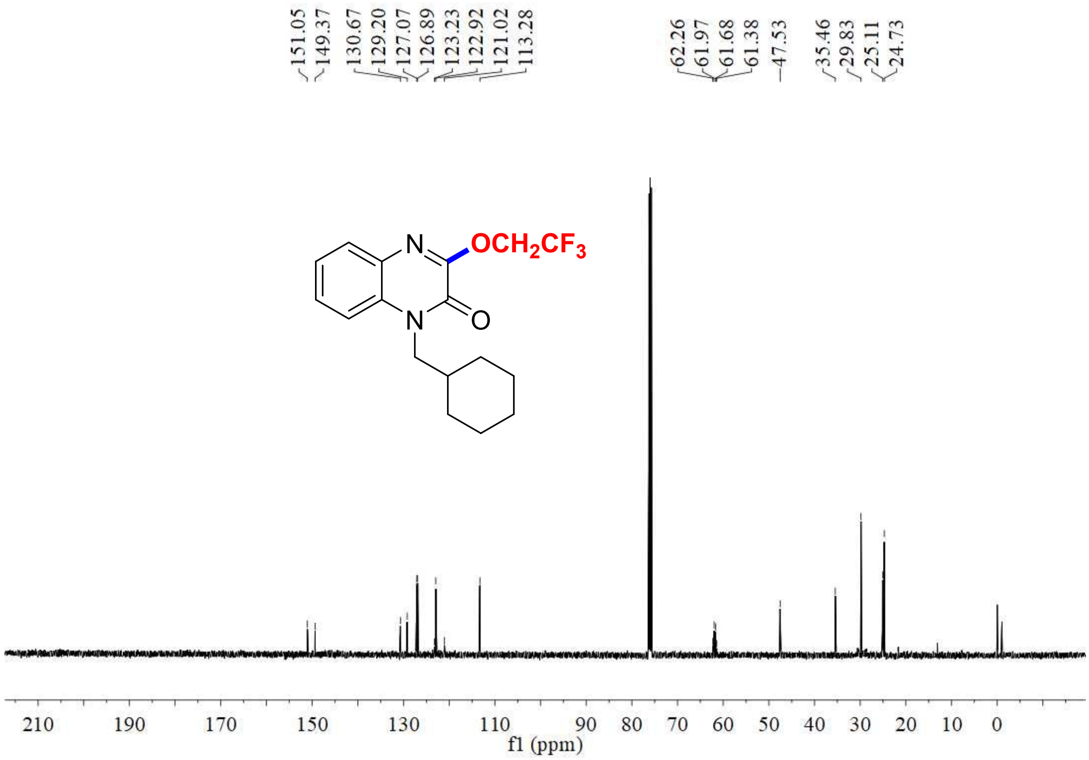

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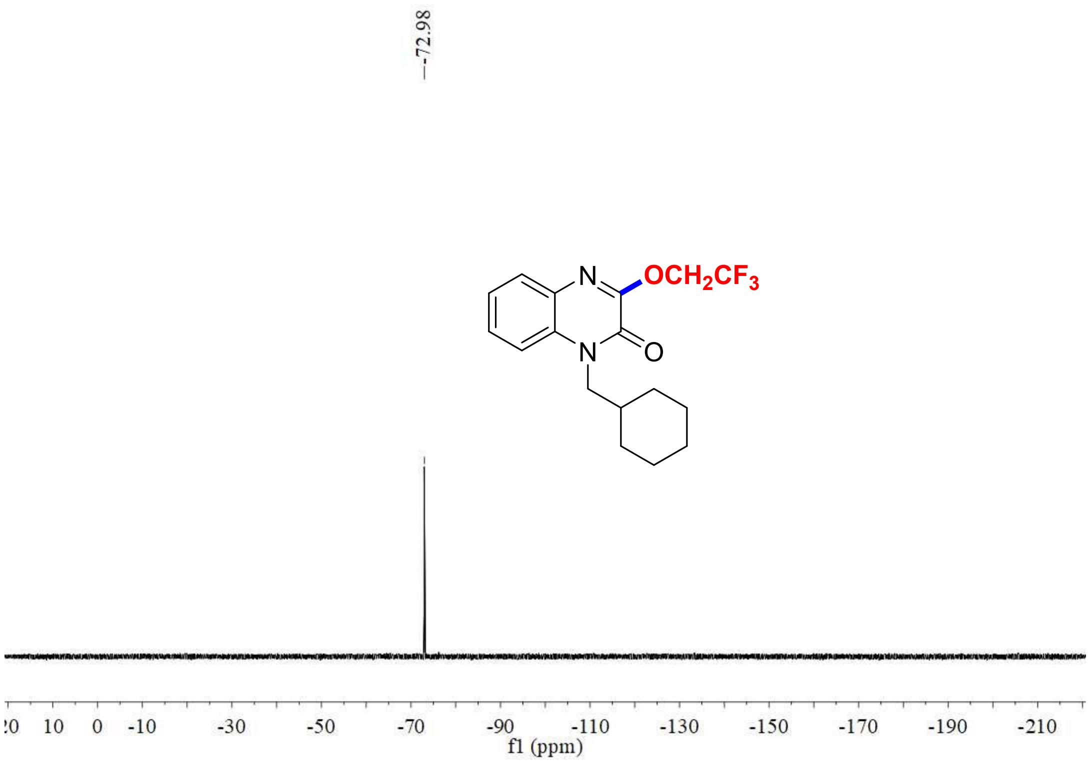

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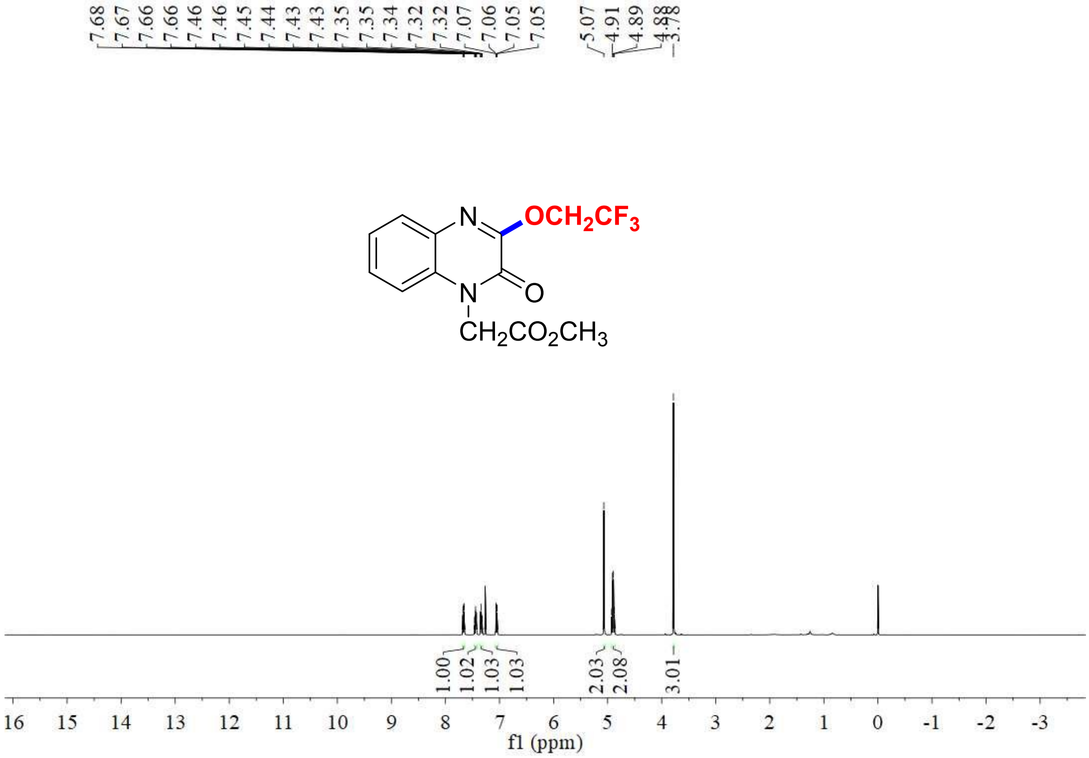

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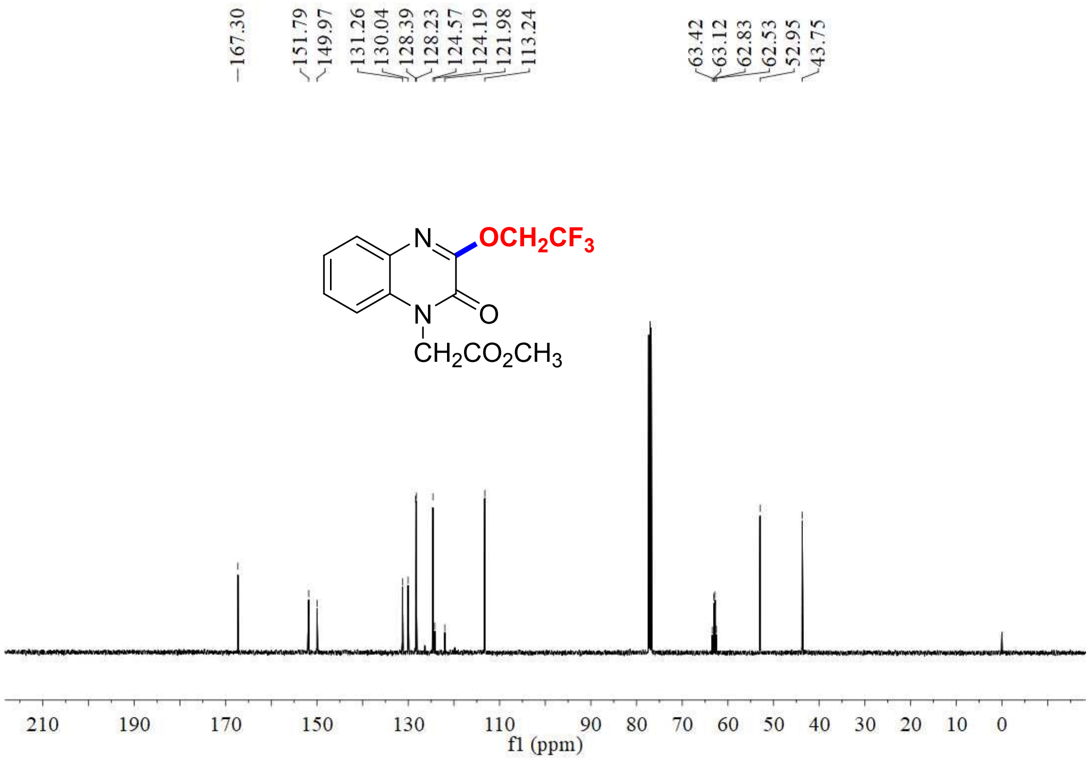
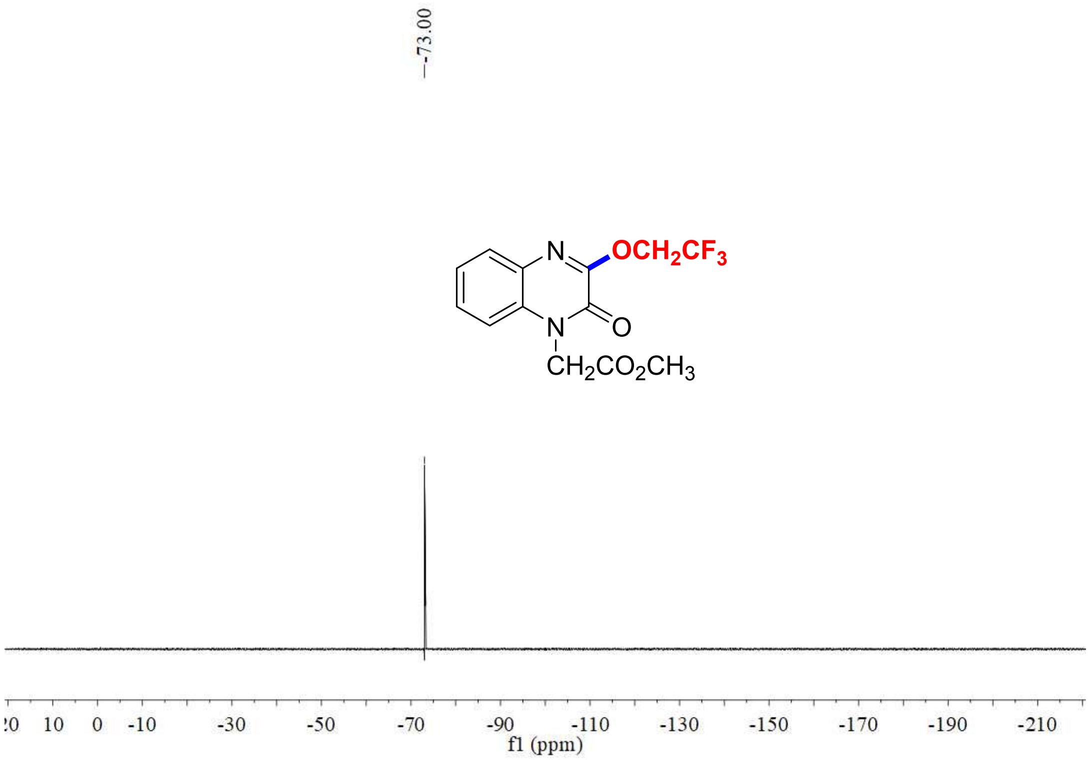
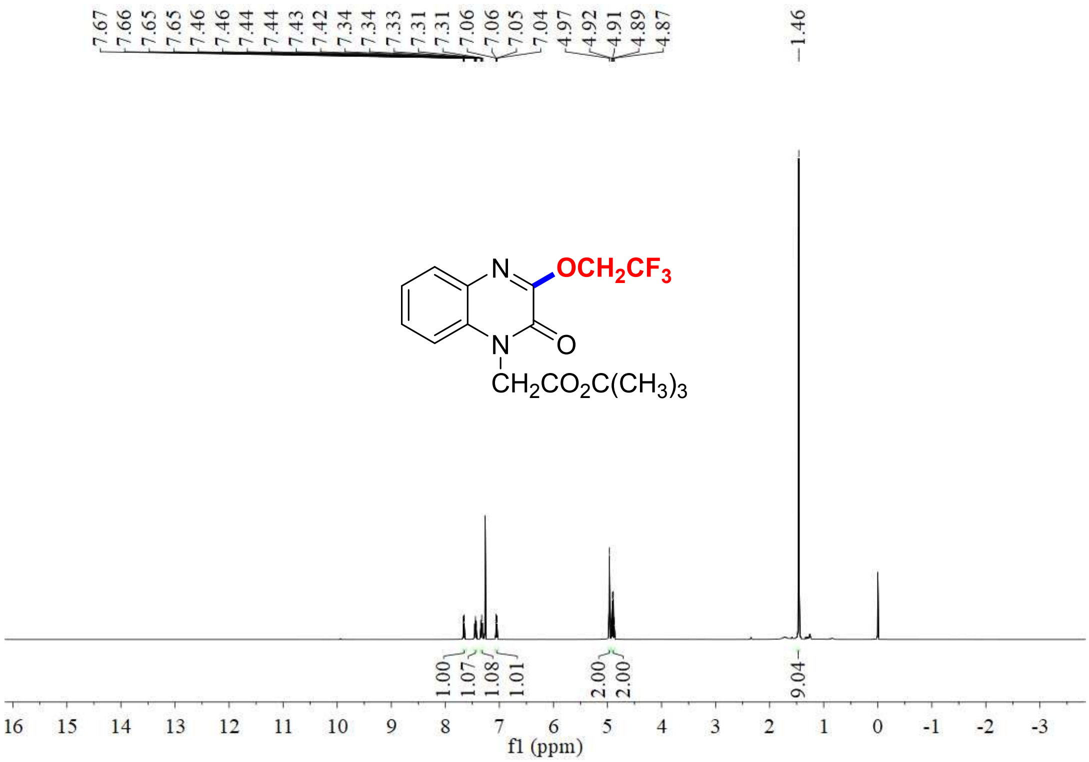


8 [19]F NMR



9 [1]H NMR



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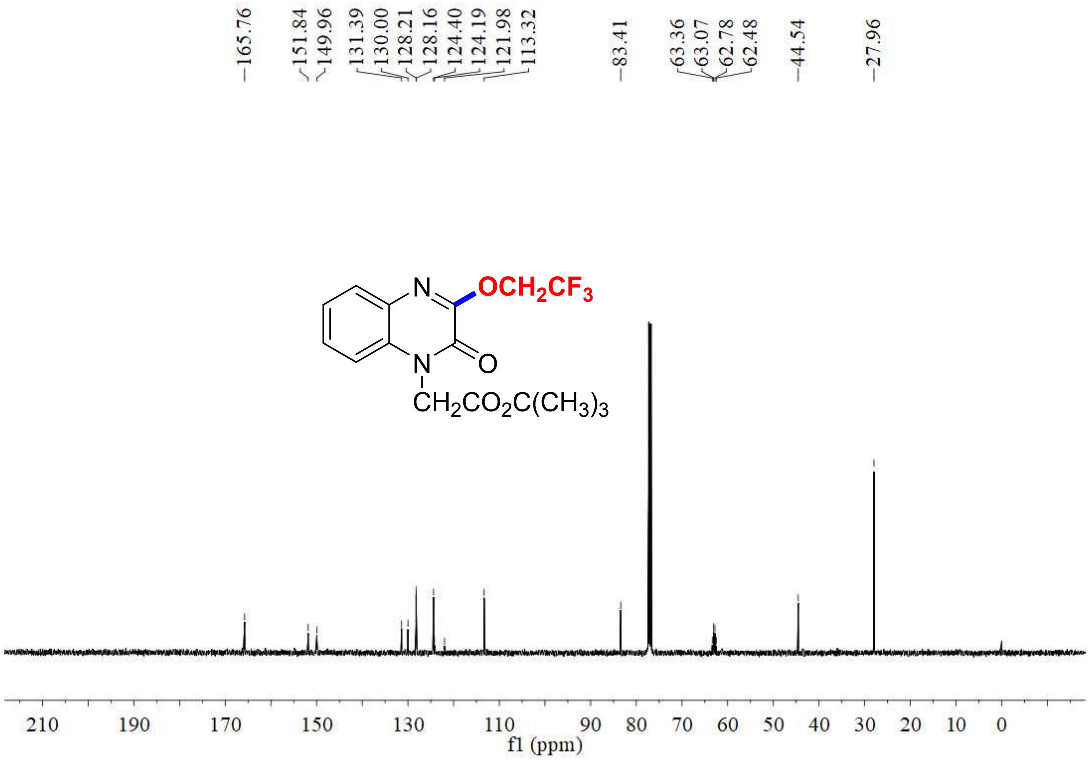

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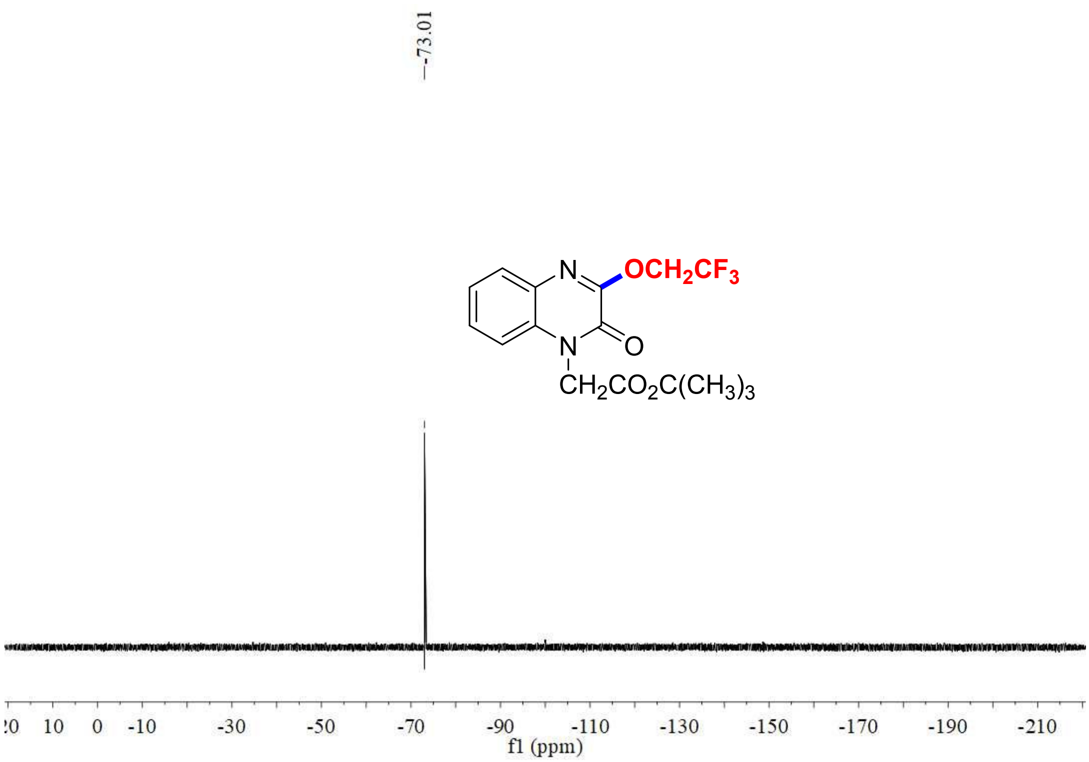

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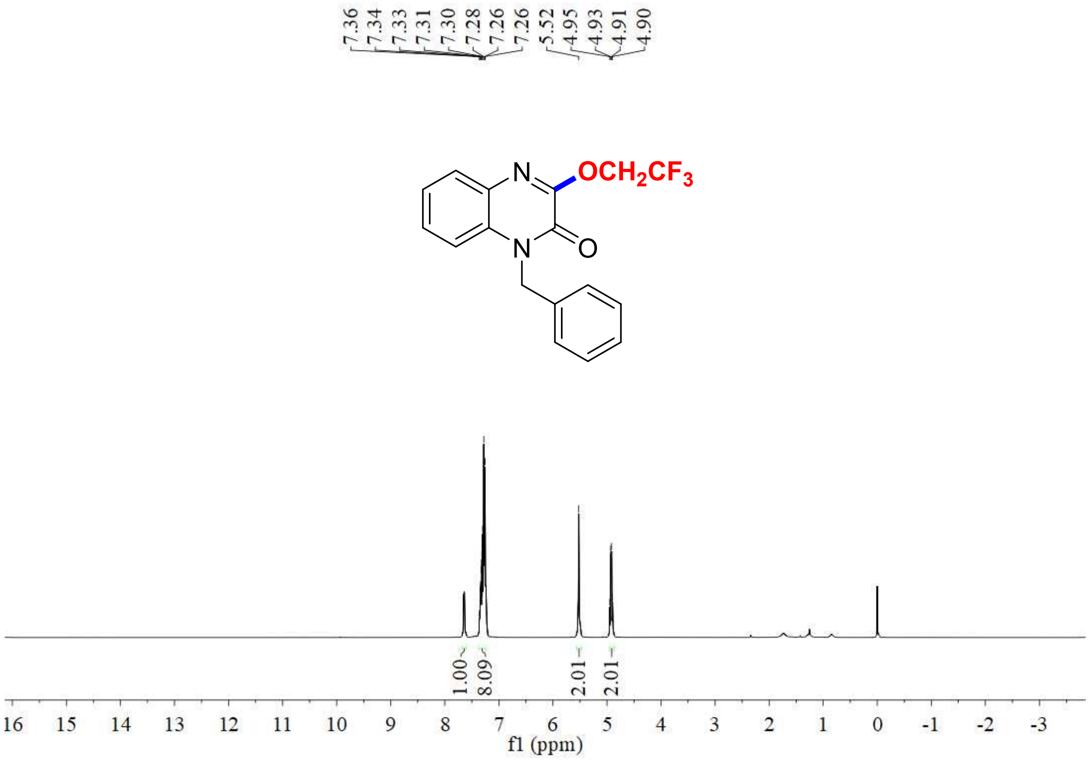

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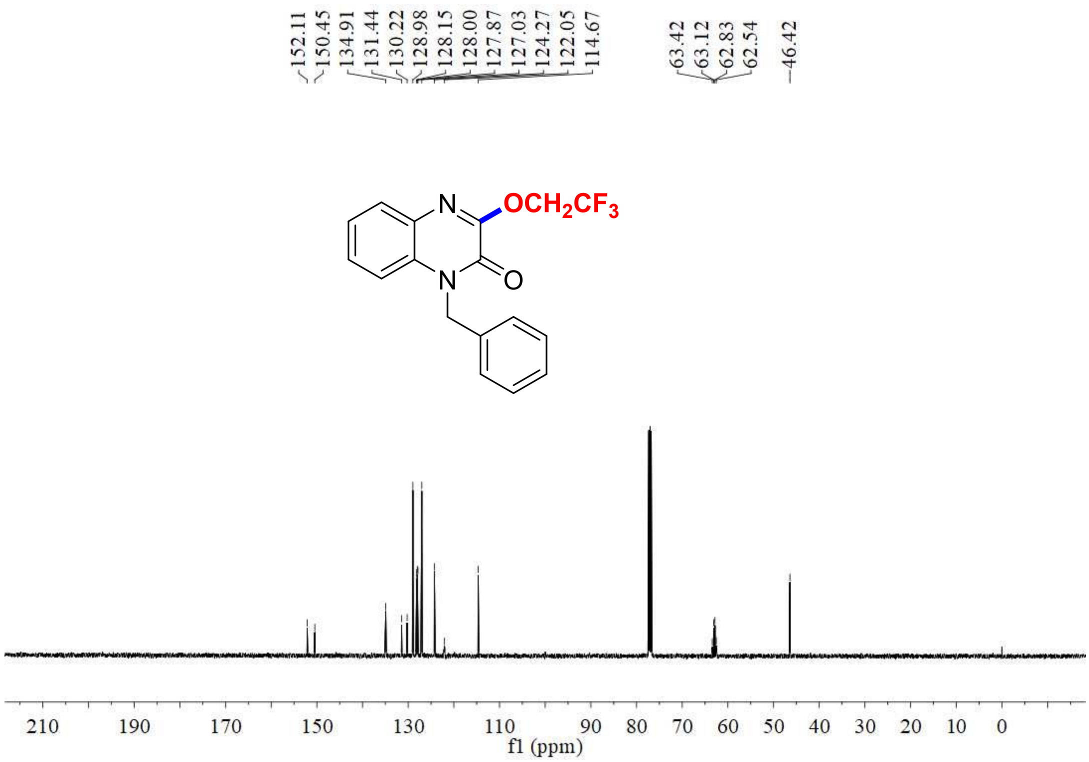

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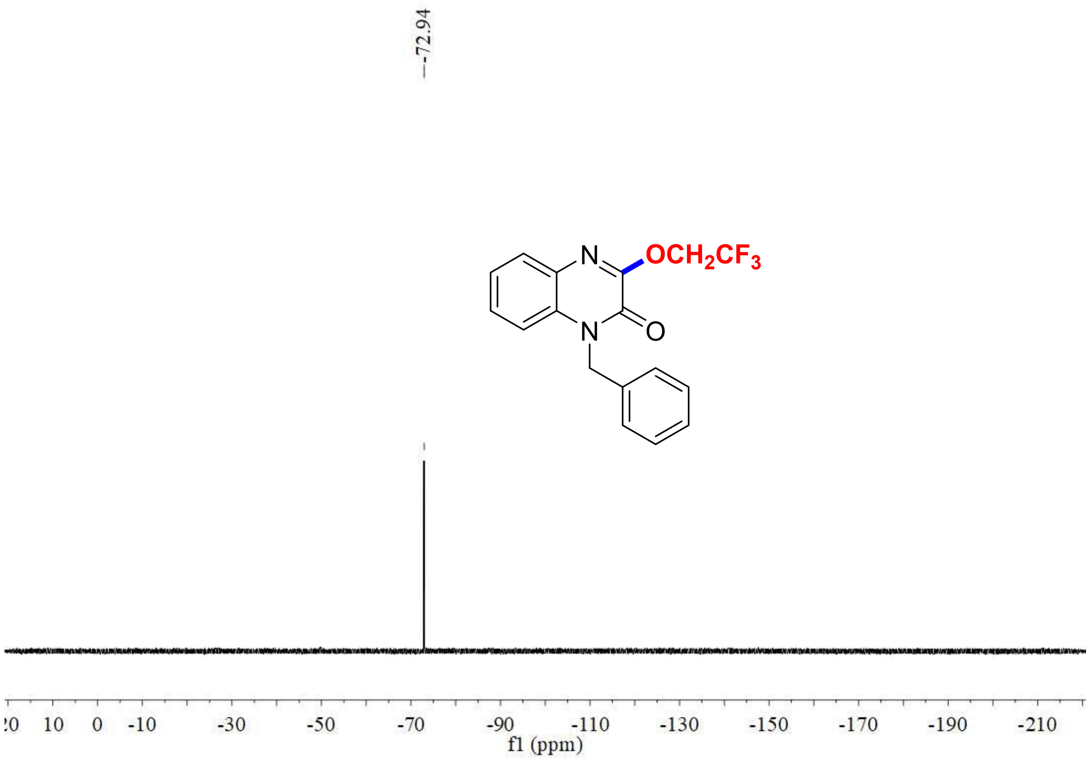

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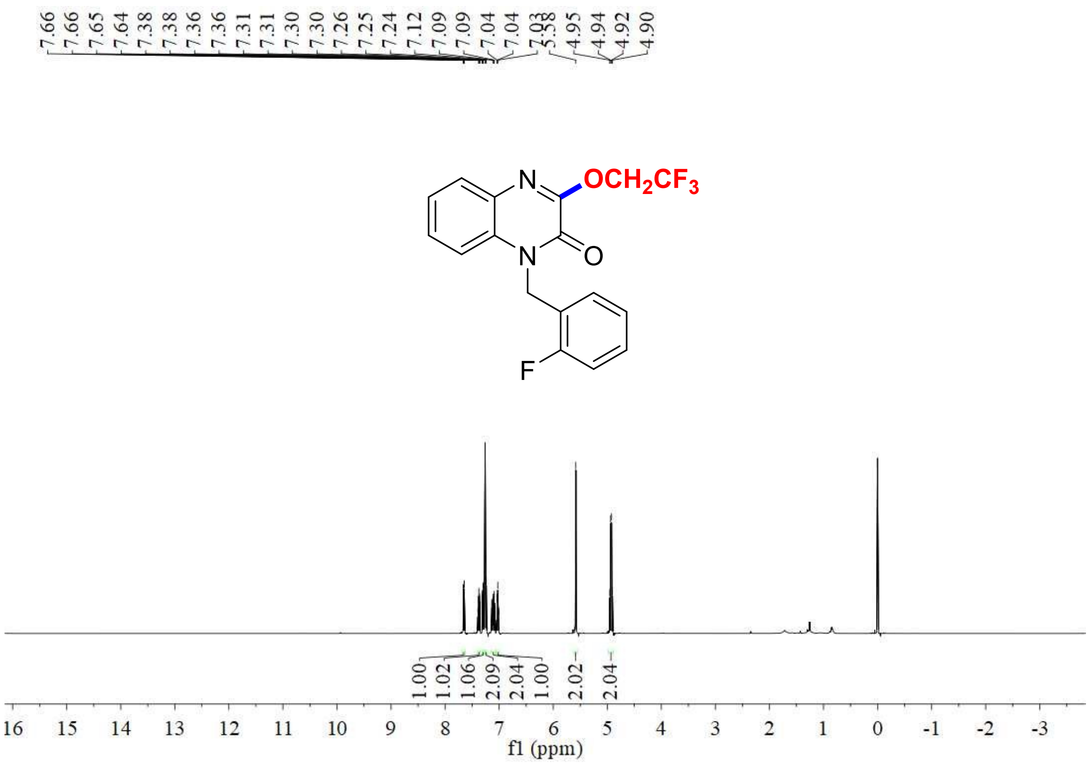

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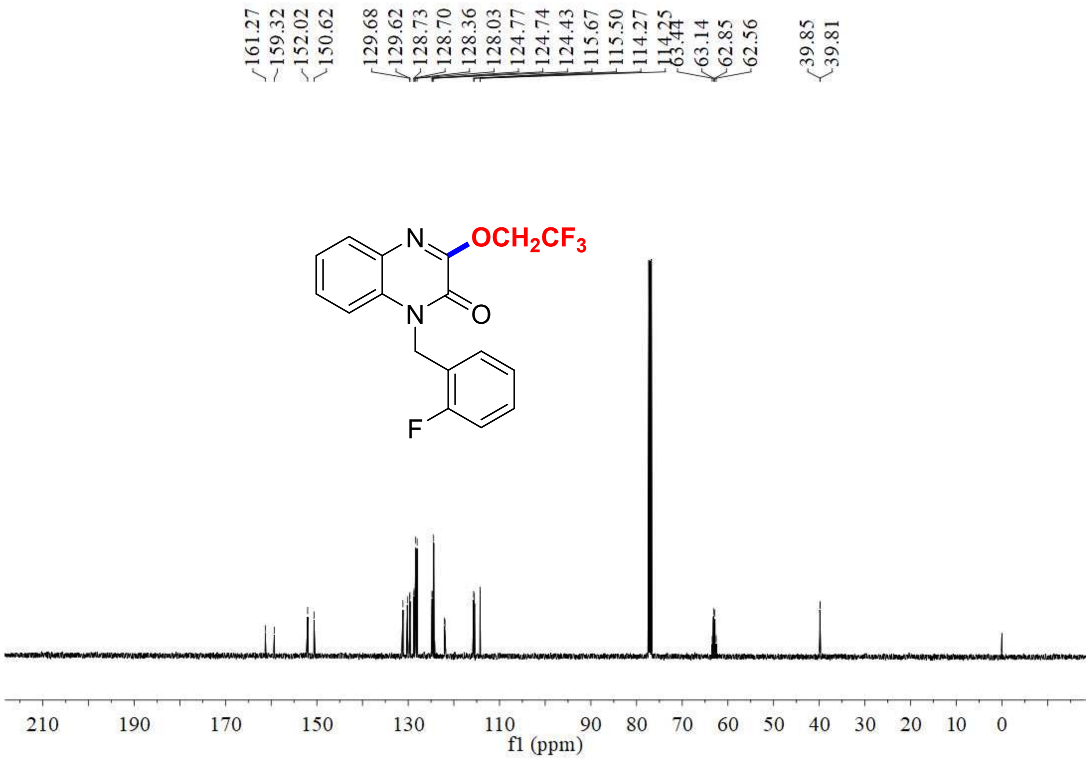
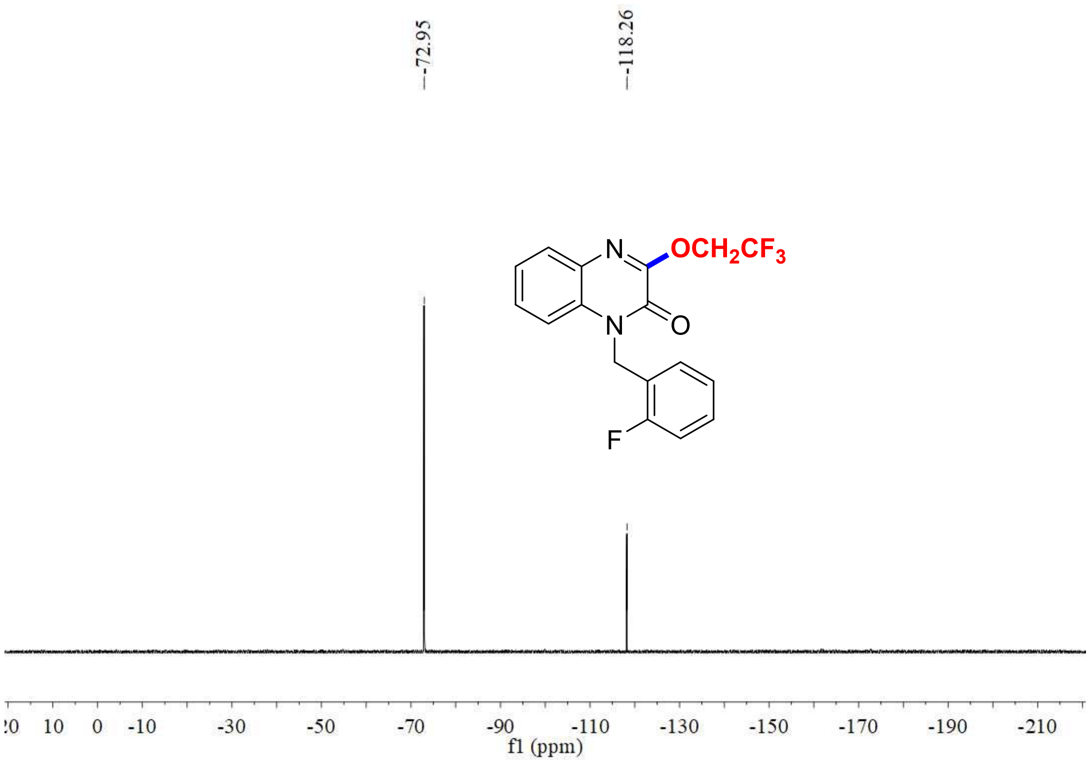


11 ^{19}F NMR



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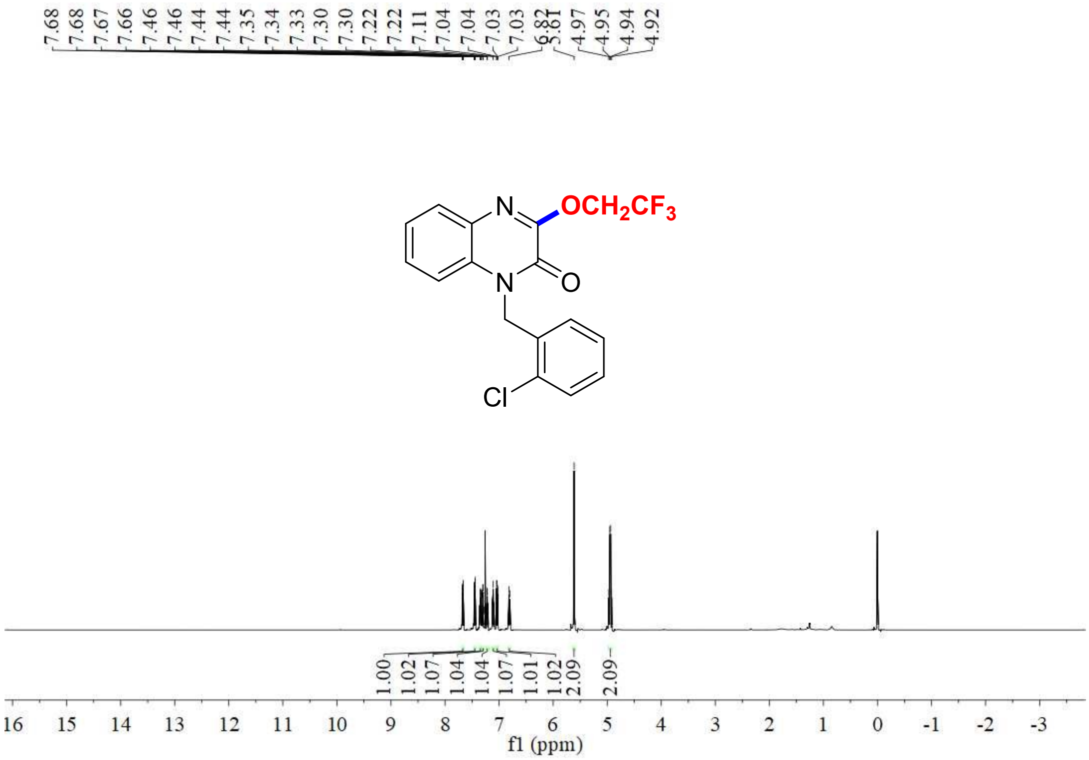

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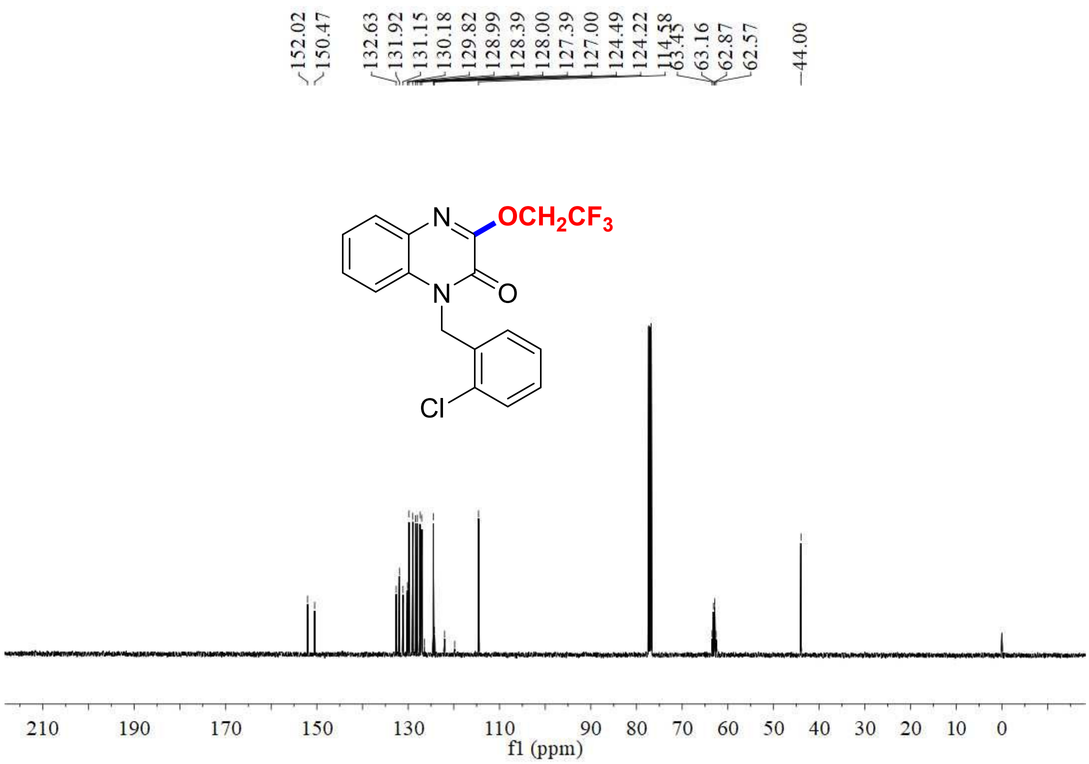

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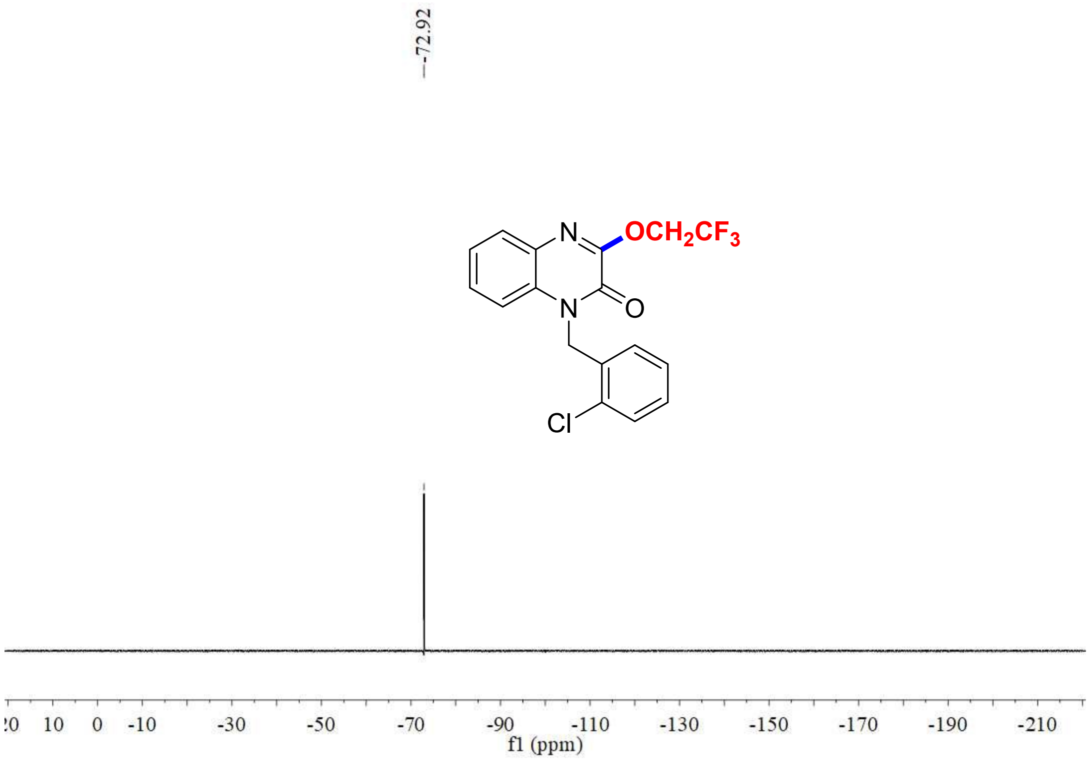

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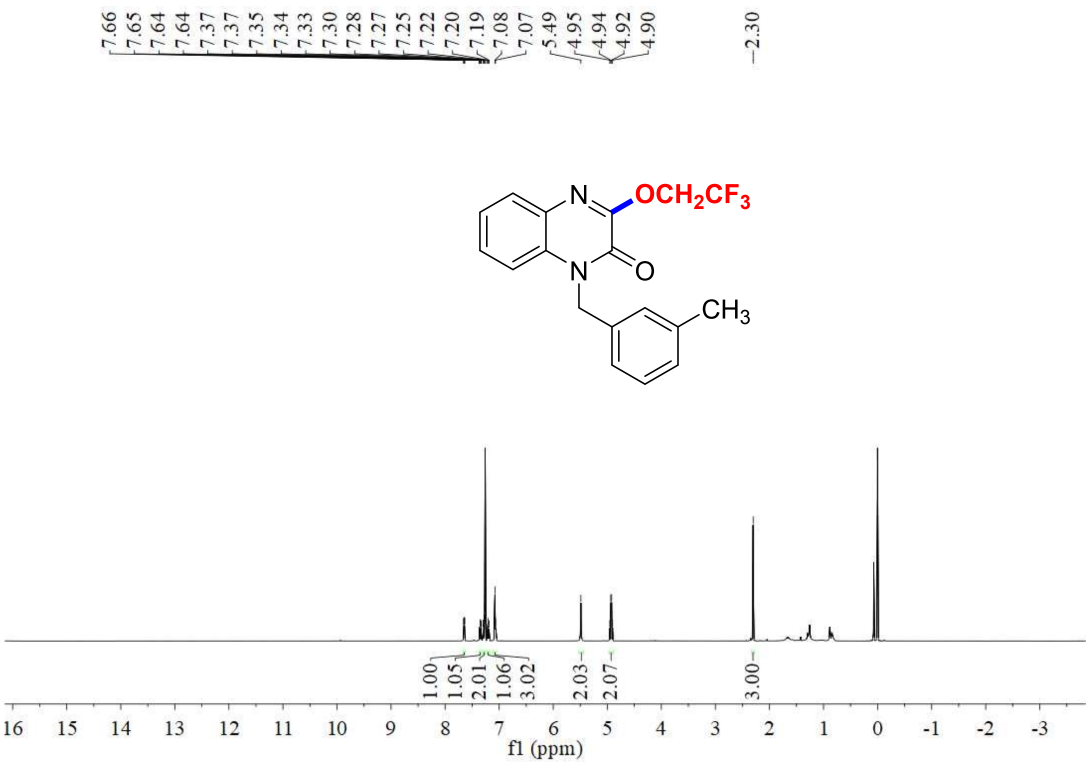

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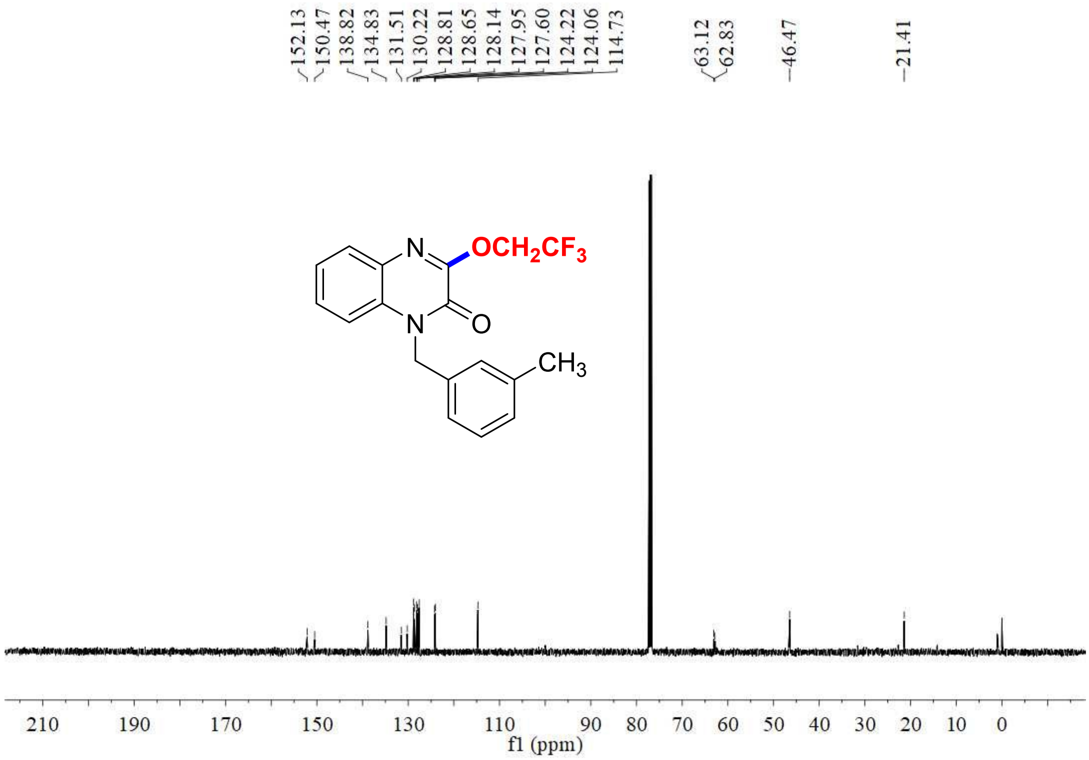

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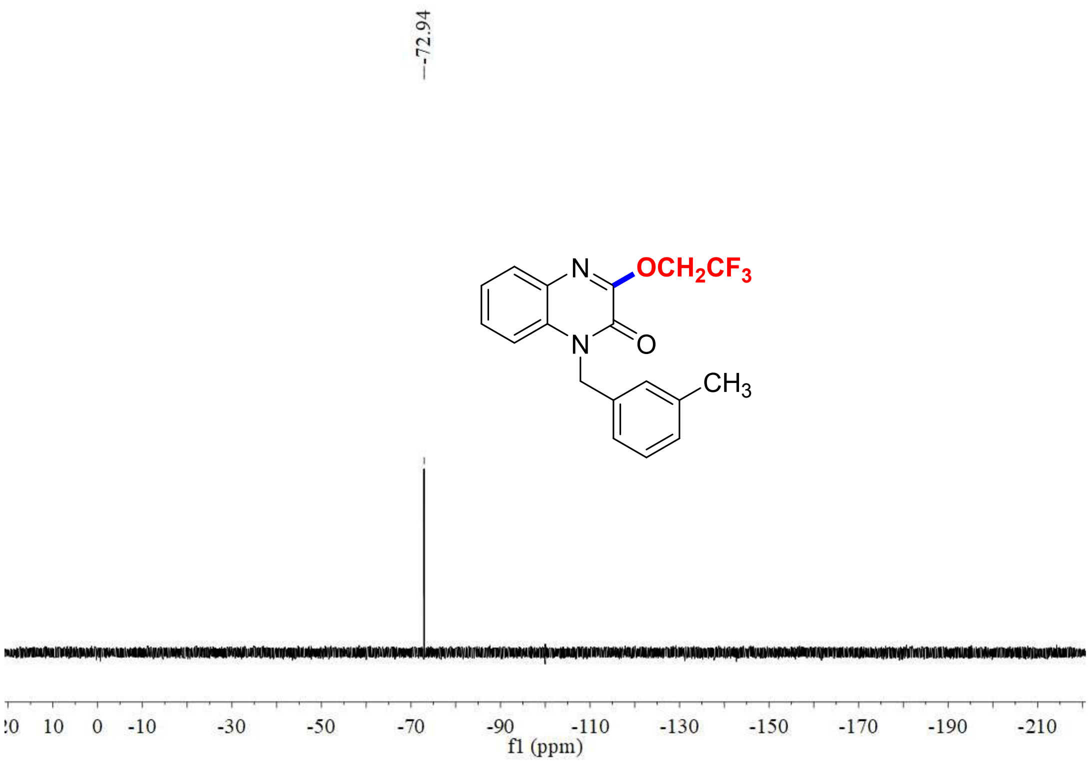

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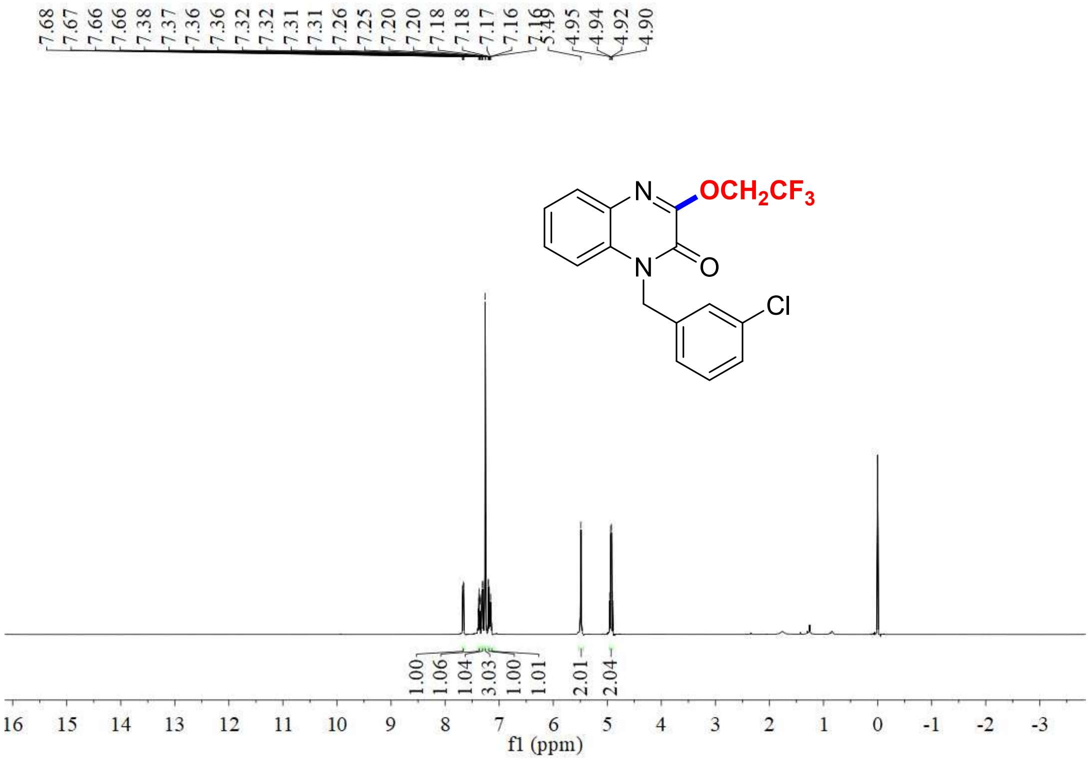

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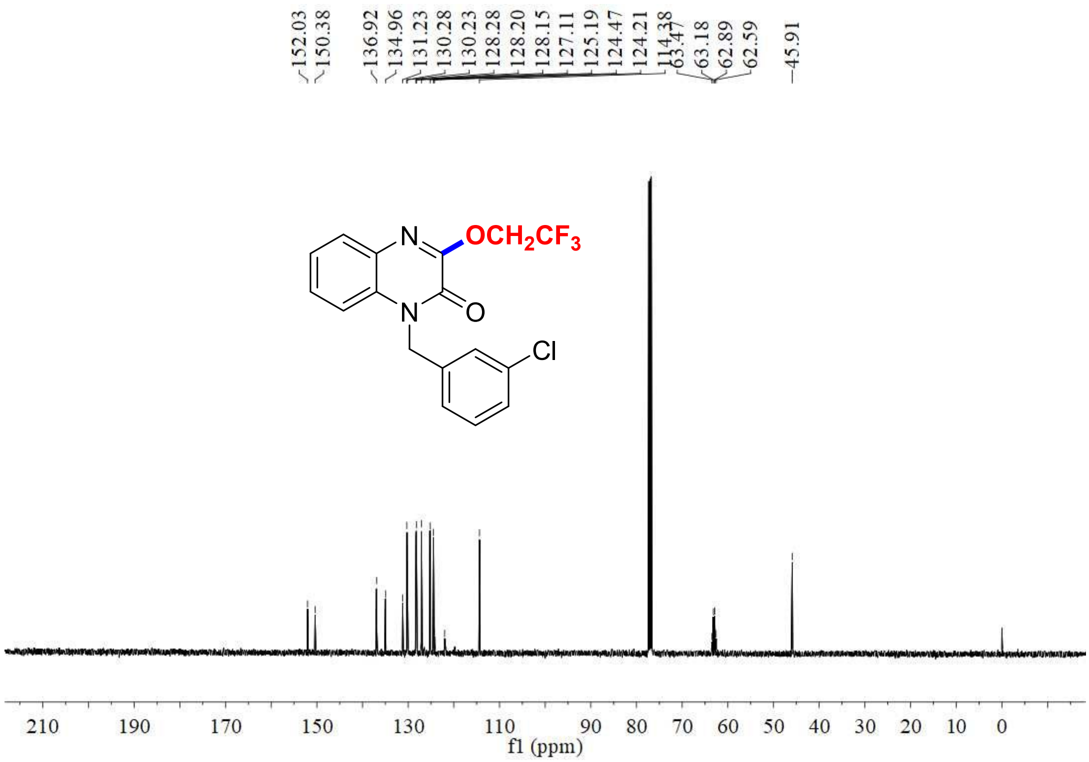

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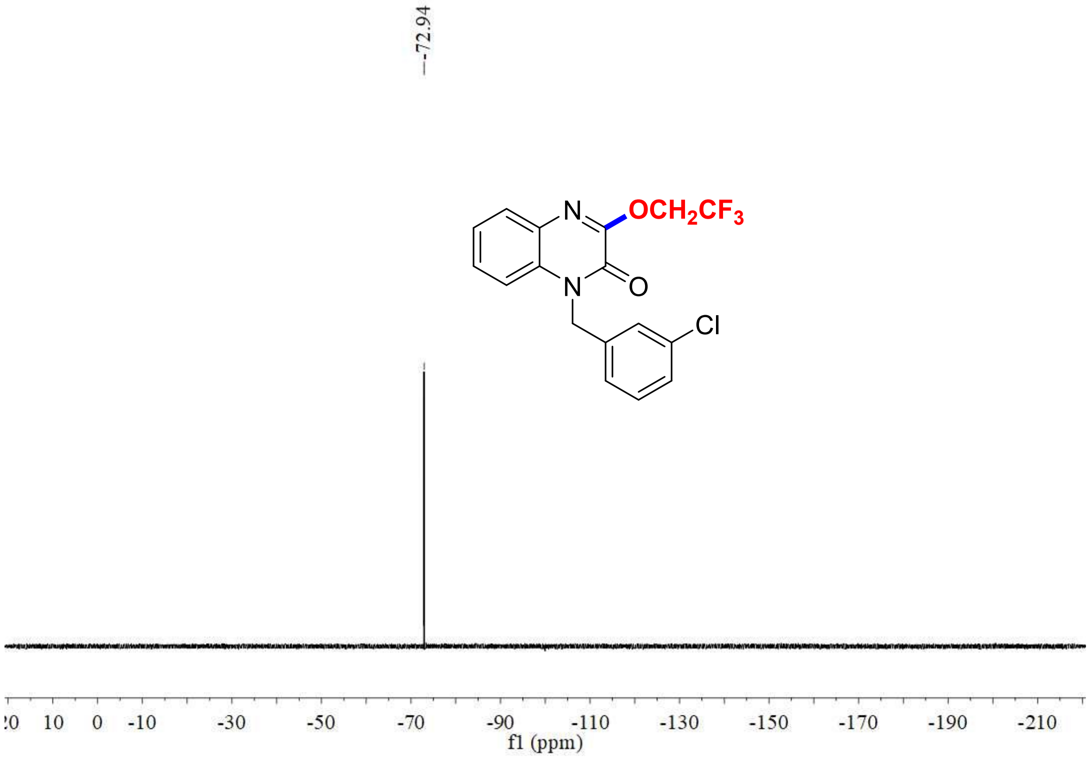

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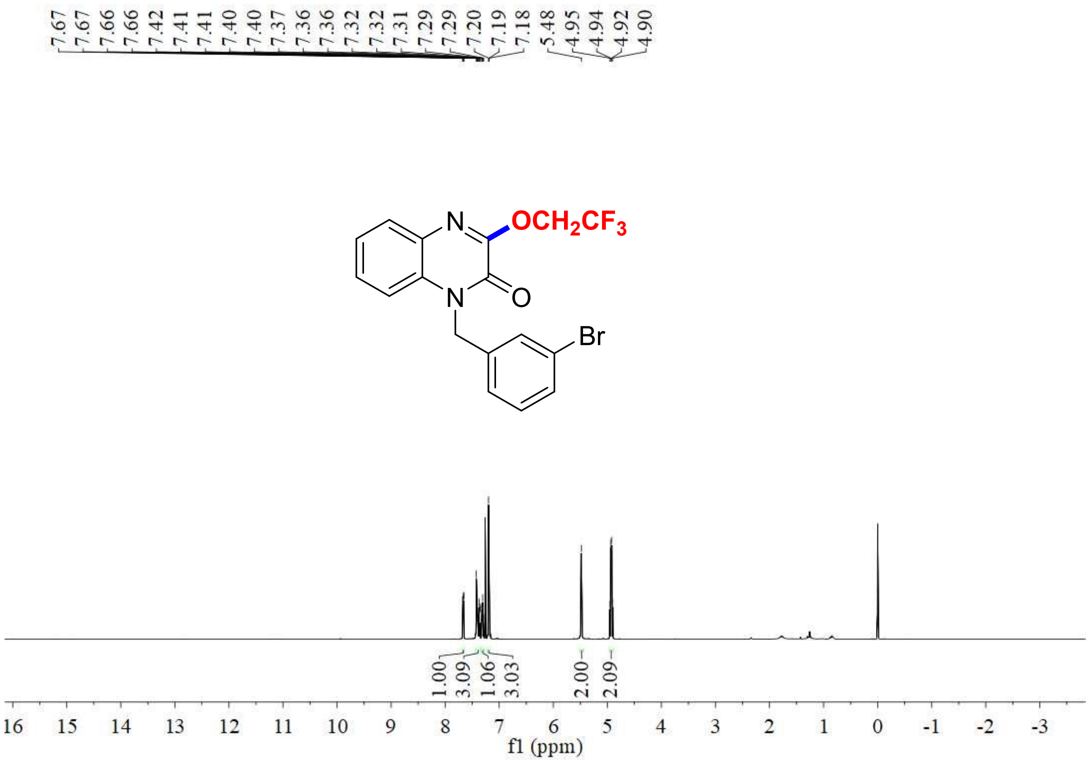

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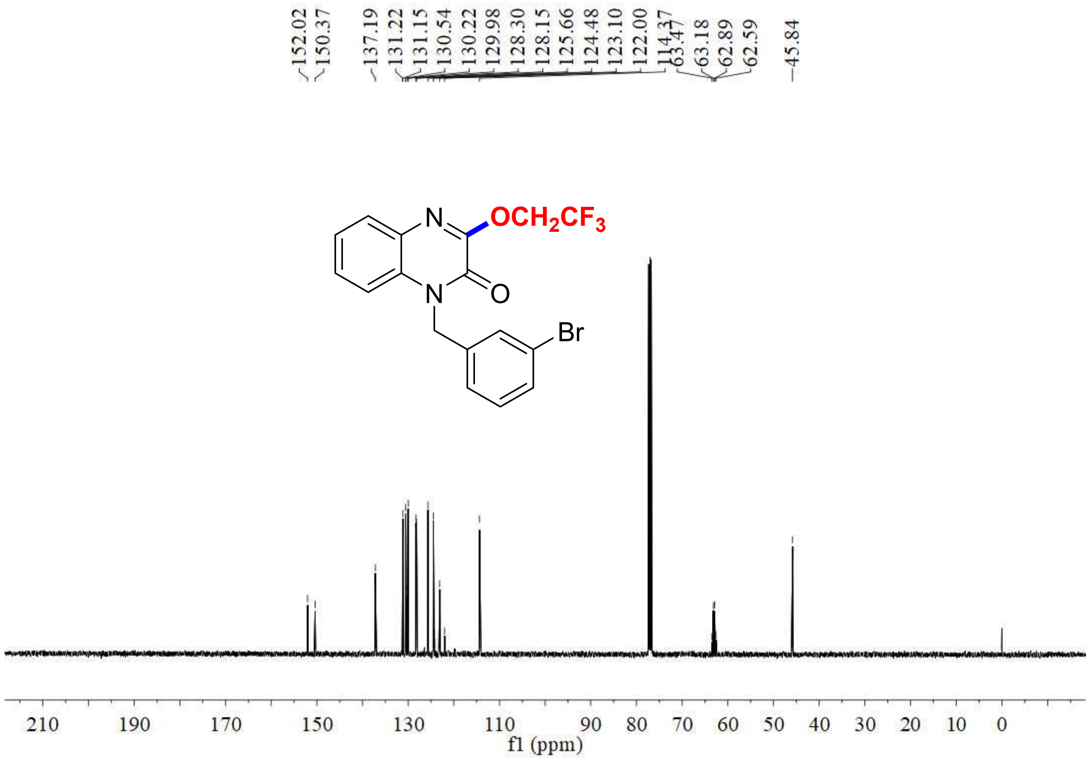

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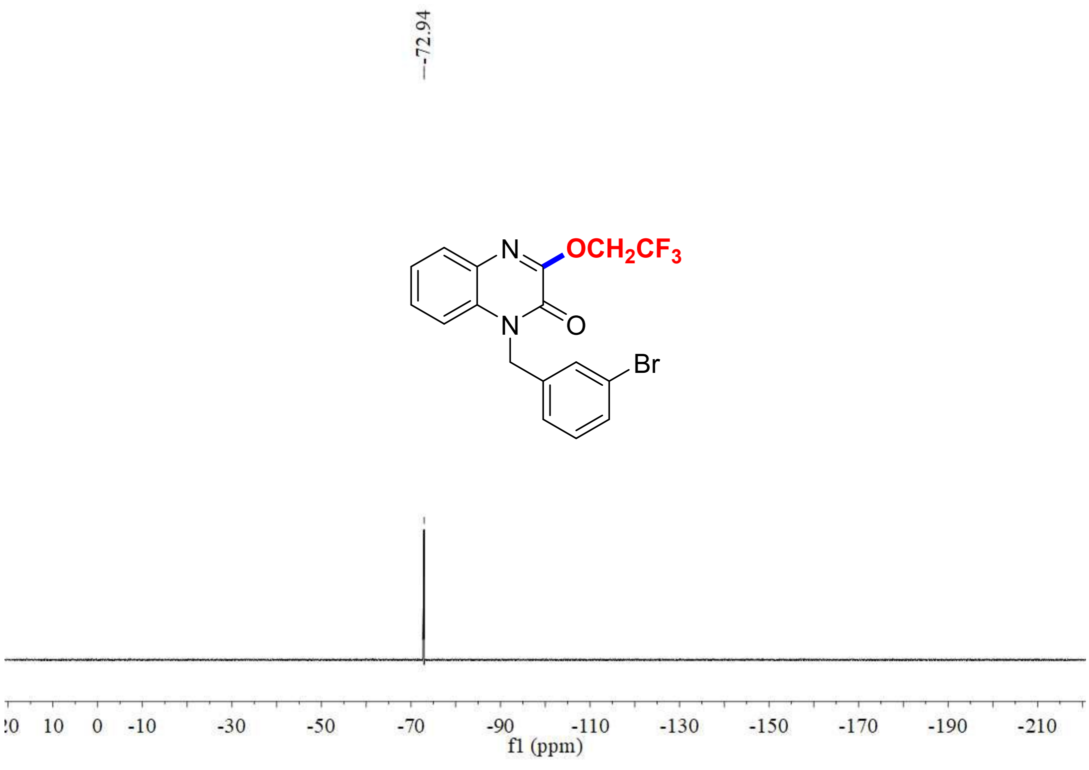

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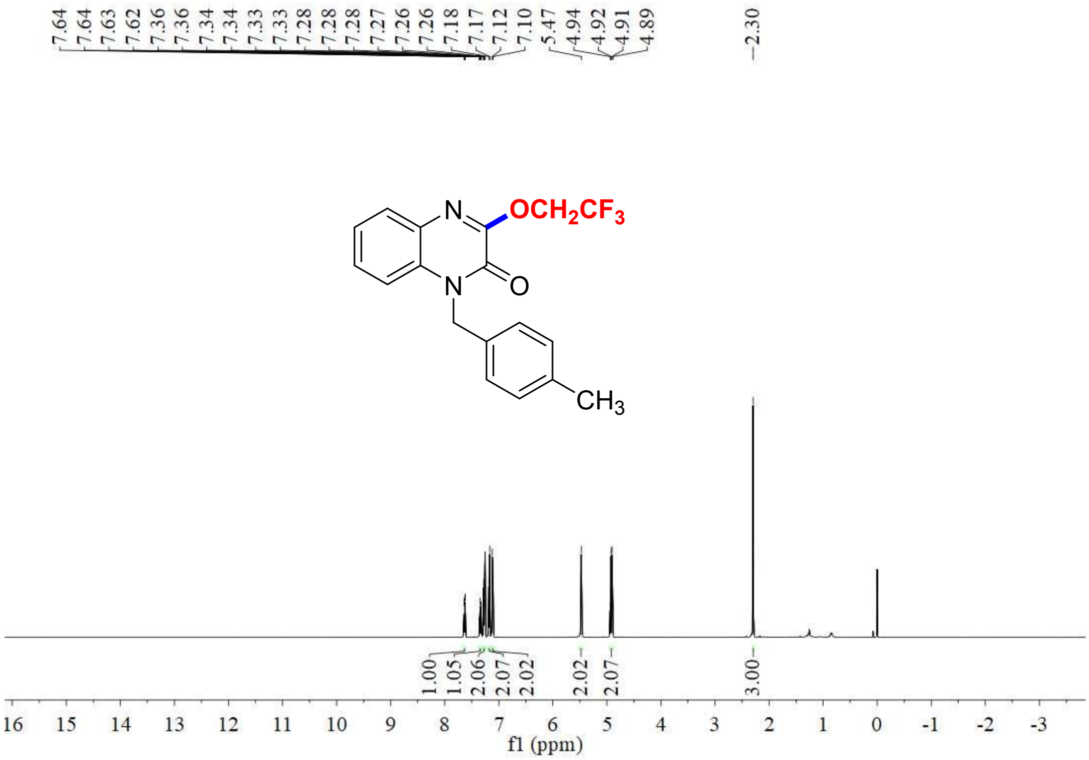

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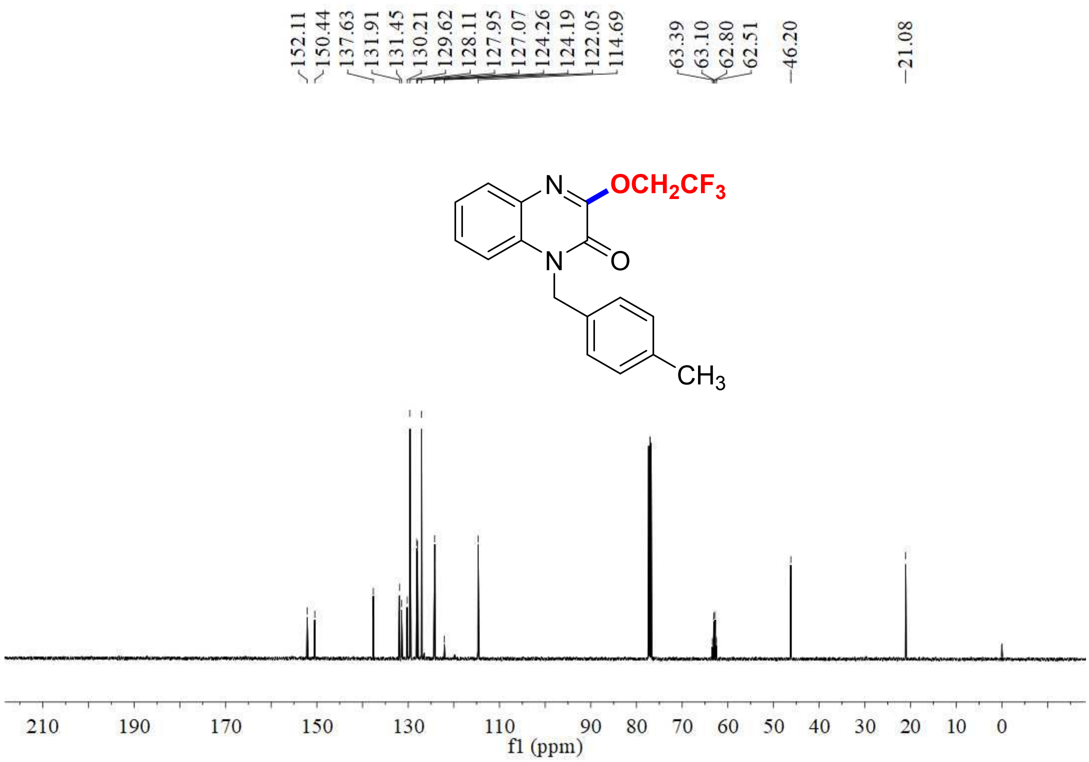

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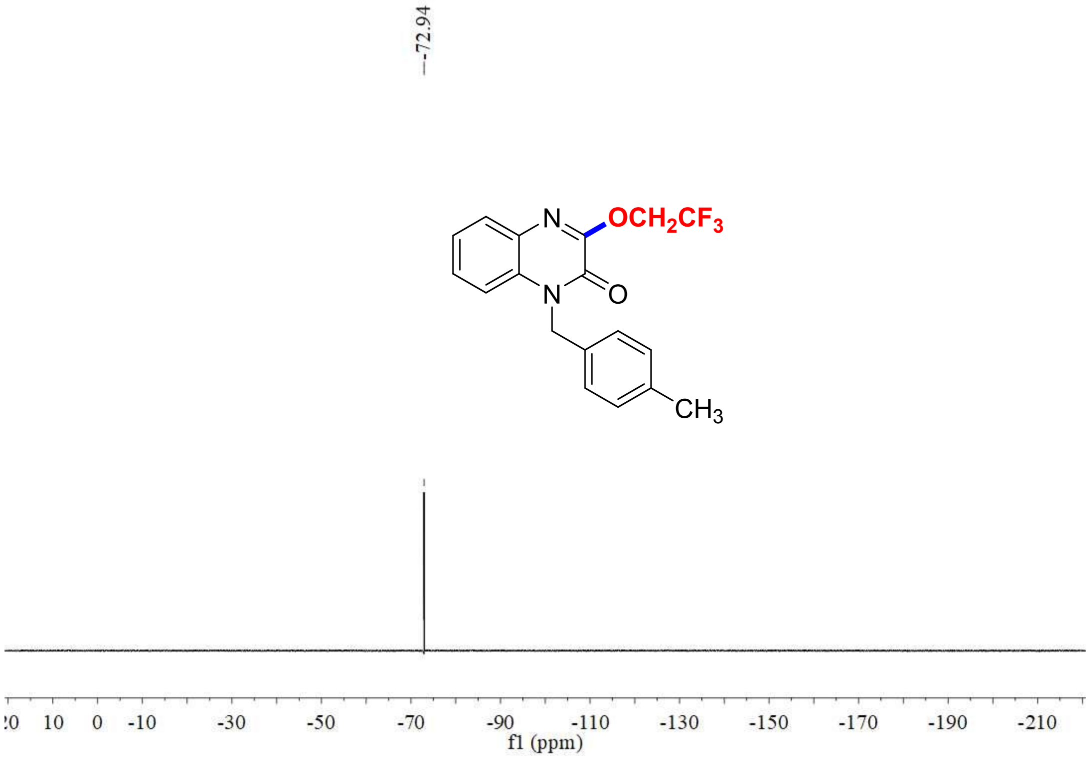

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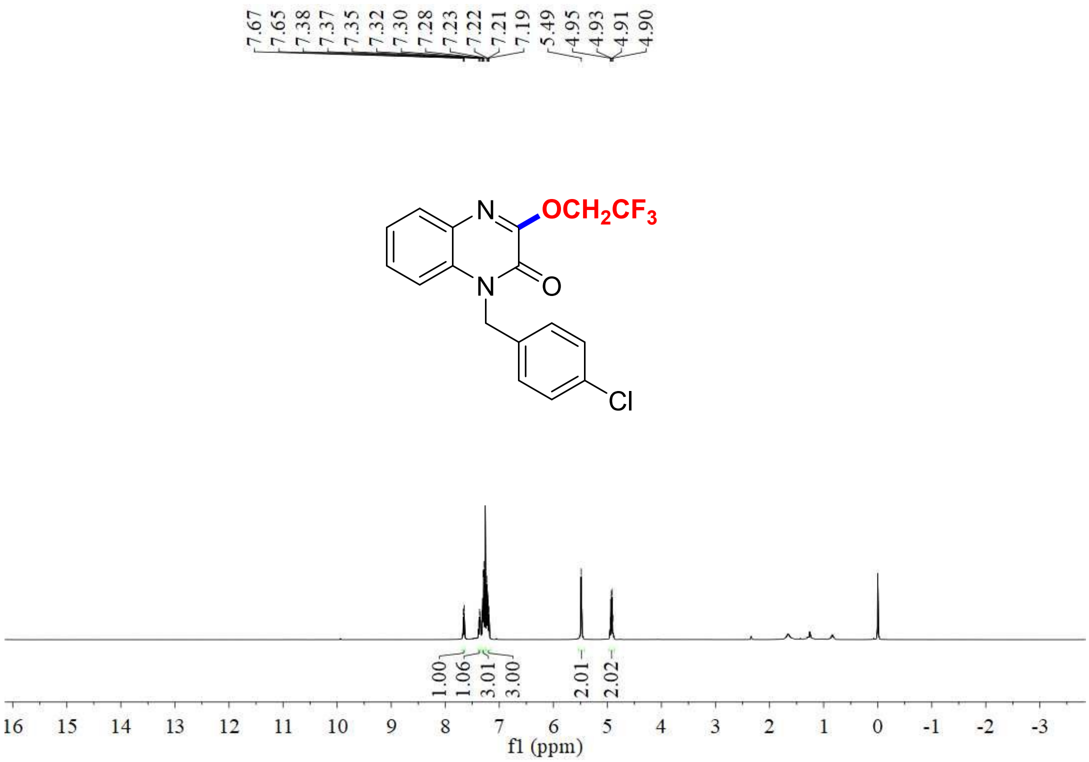

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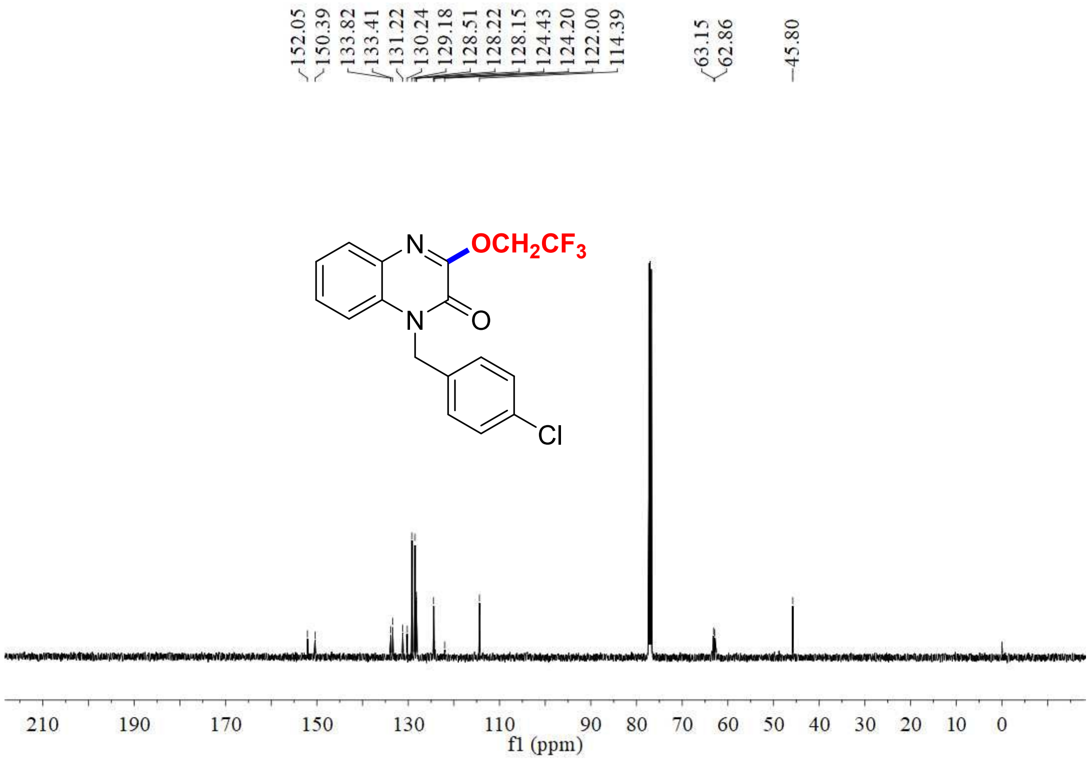

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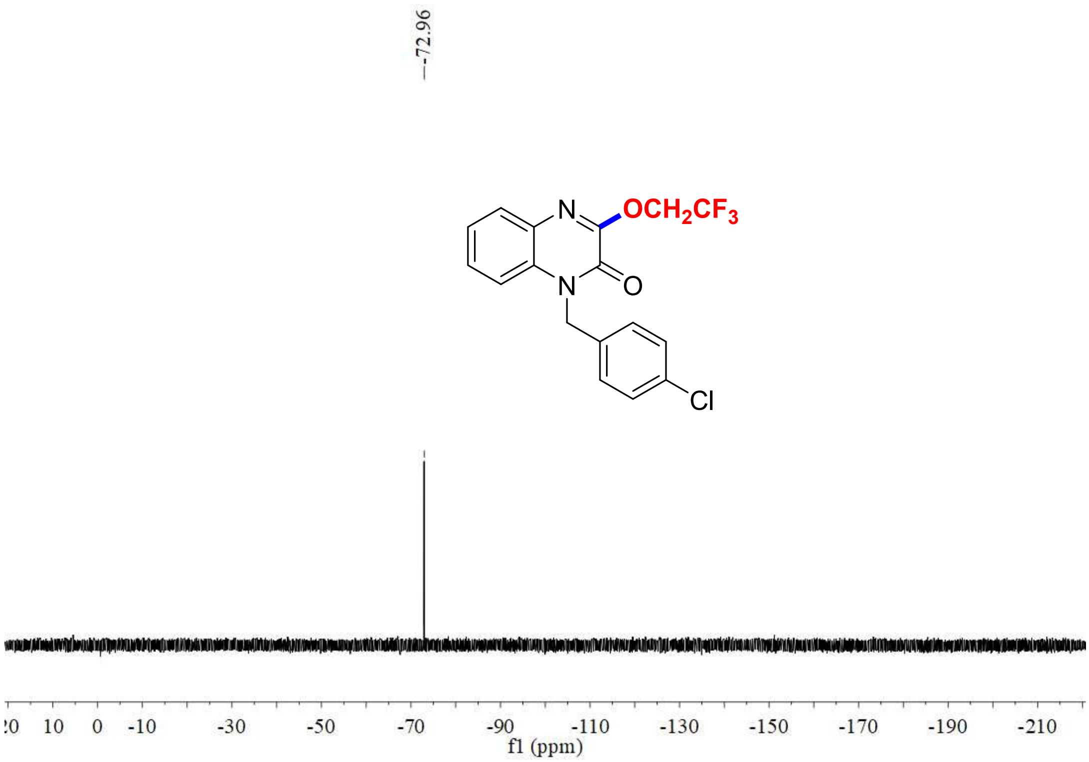
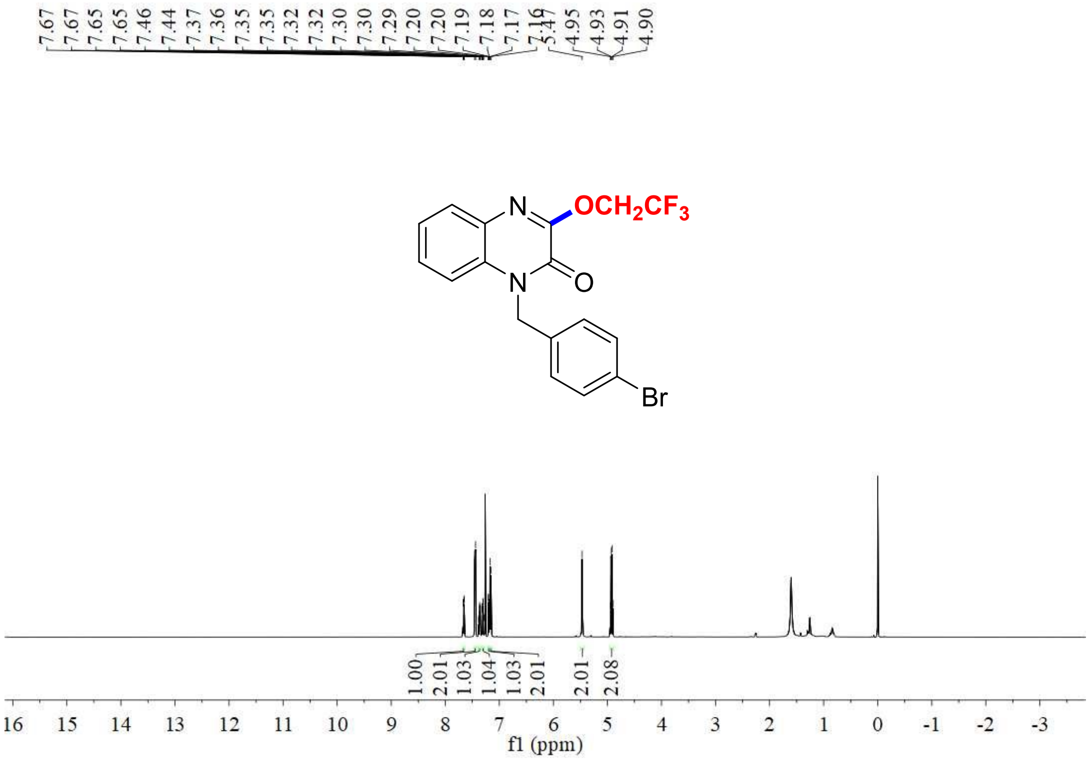


18 ^{1}H NMR



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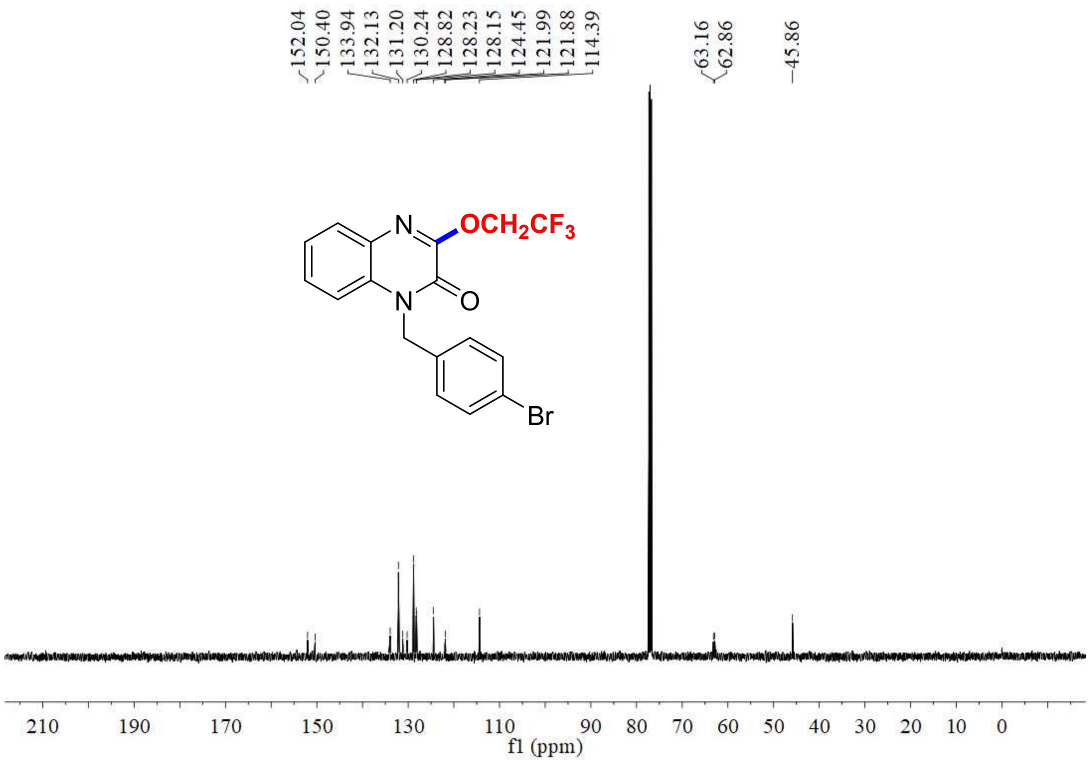

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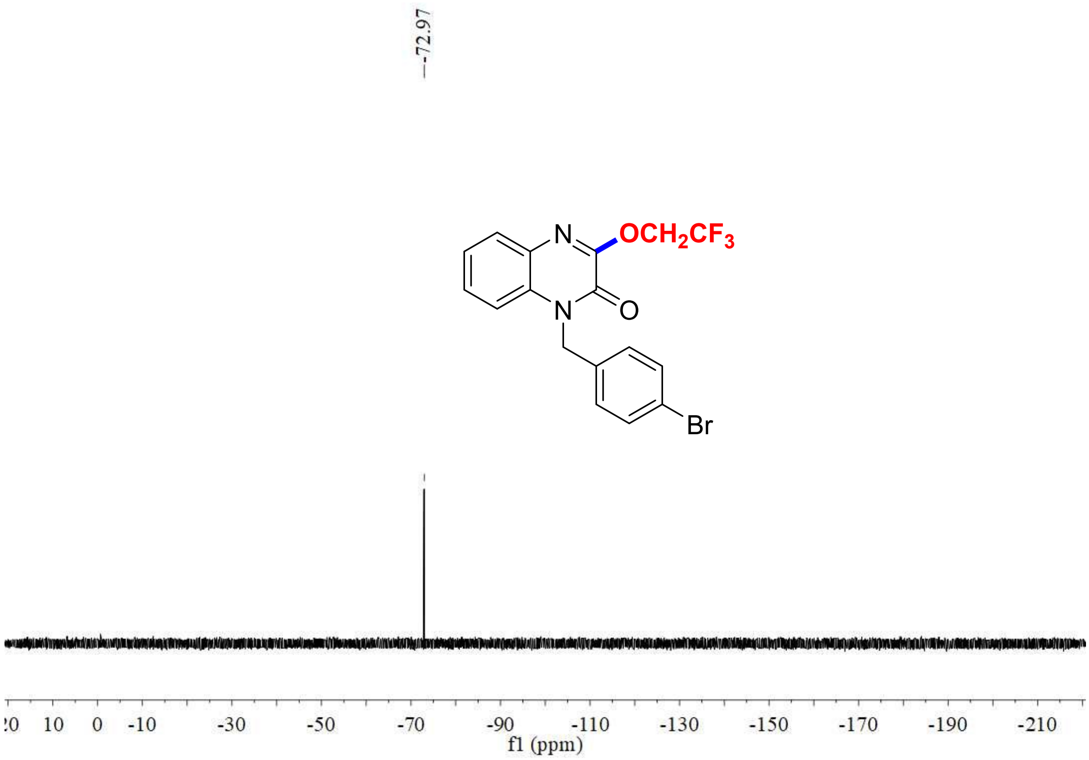
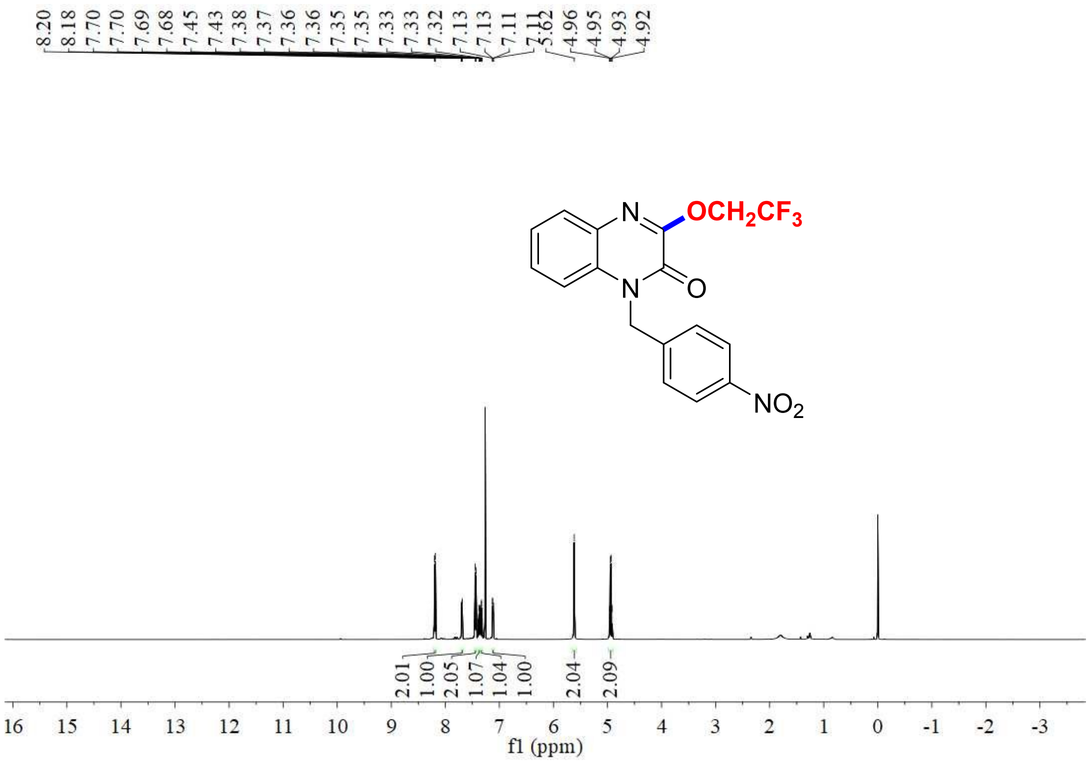


19 [1]H NMR



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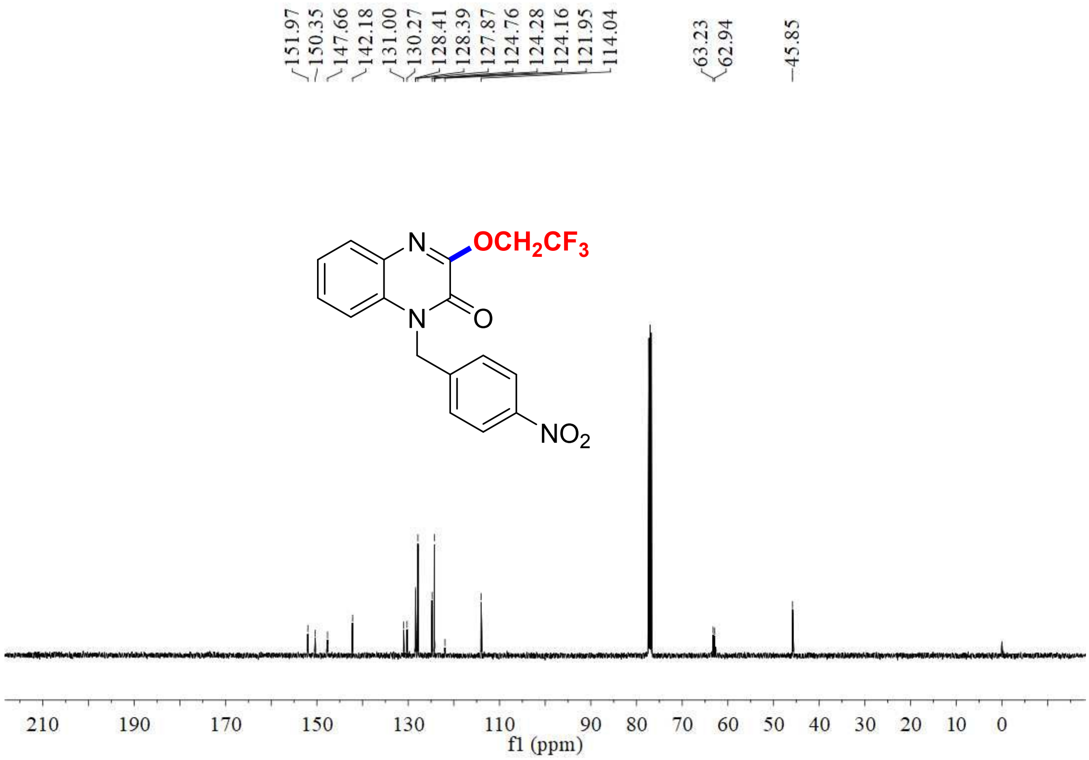

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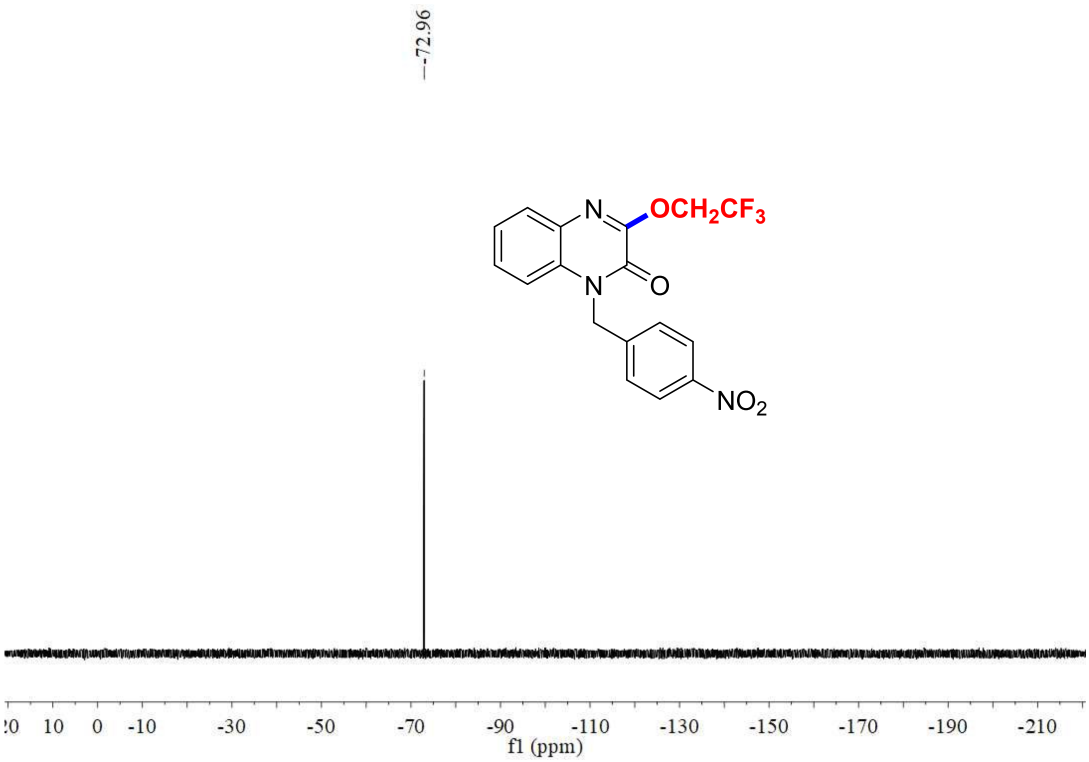
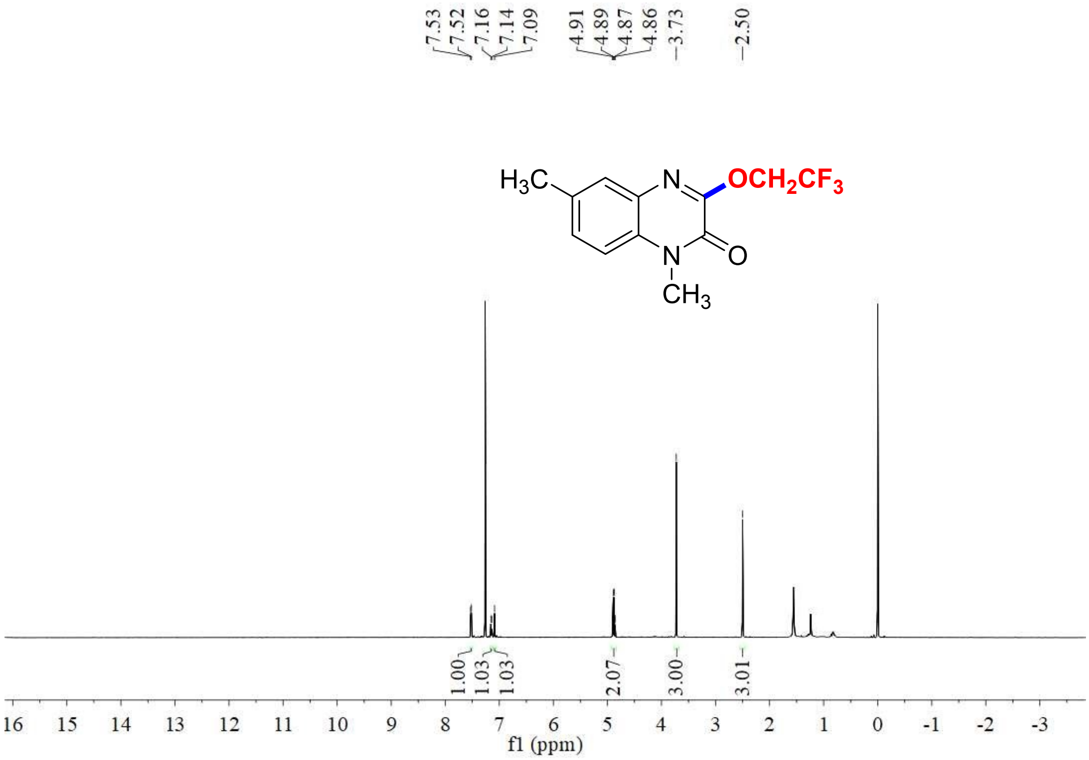
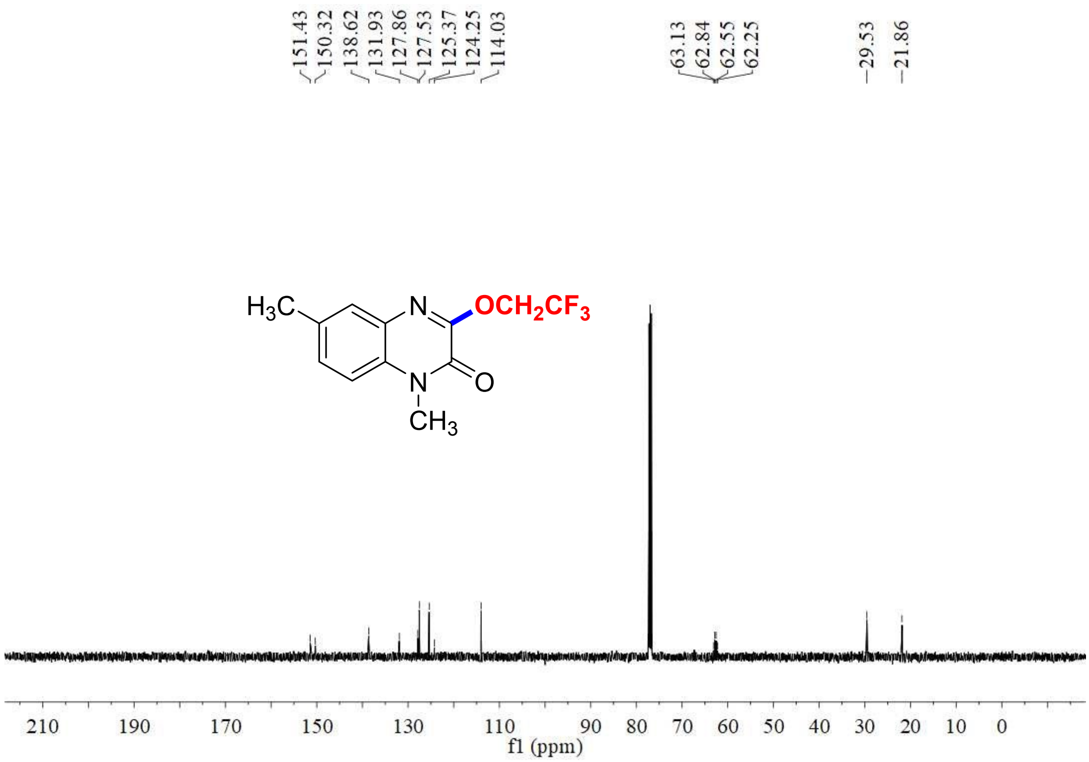


20 ^{1}H NMR



20 ^{13}C NMR



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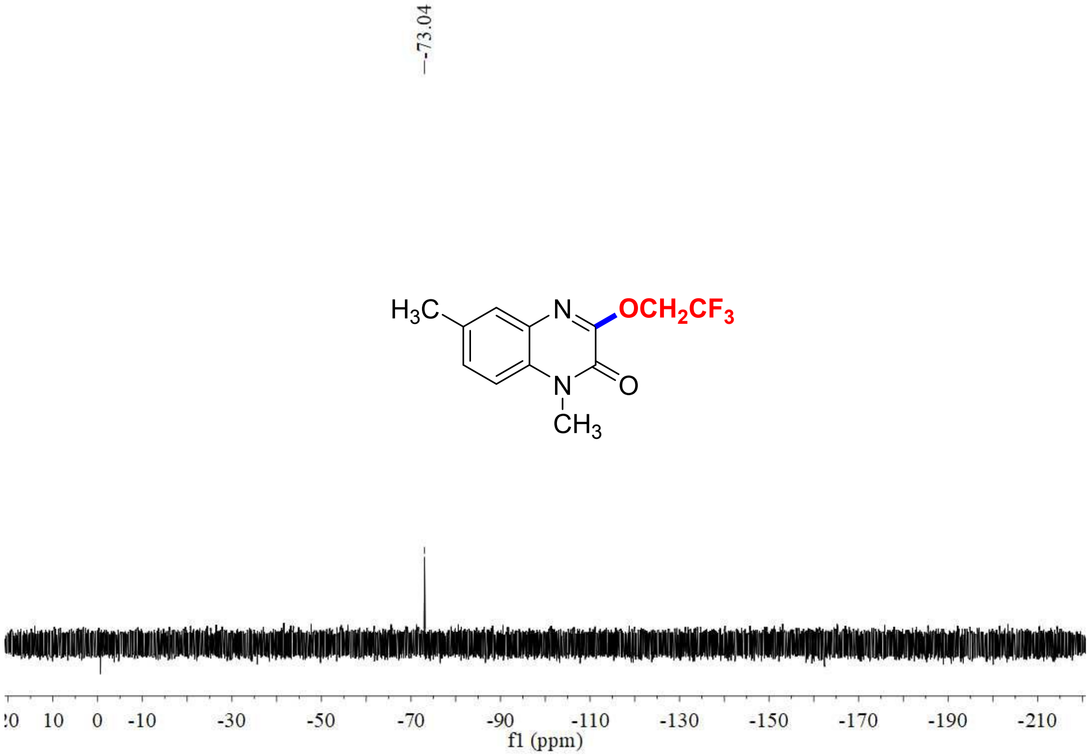
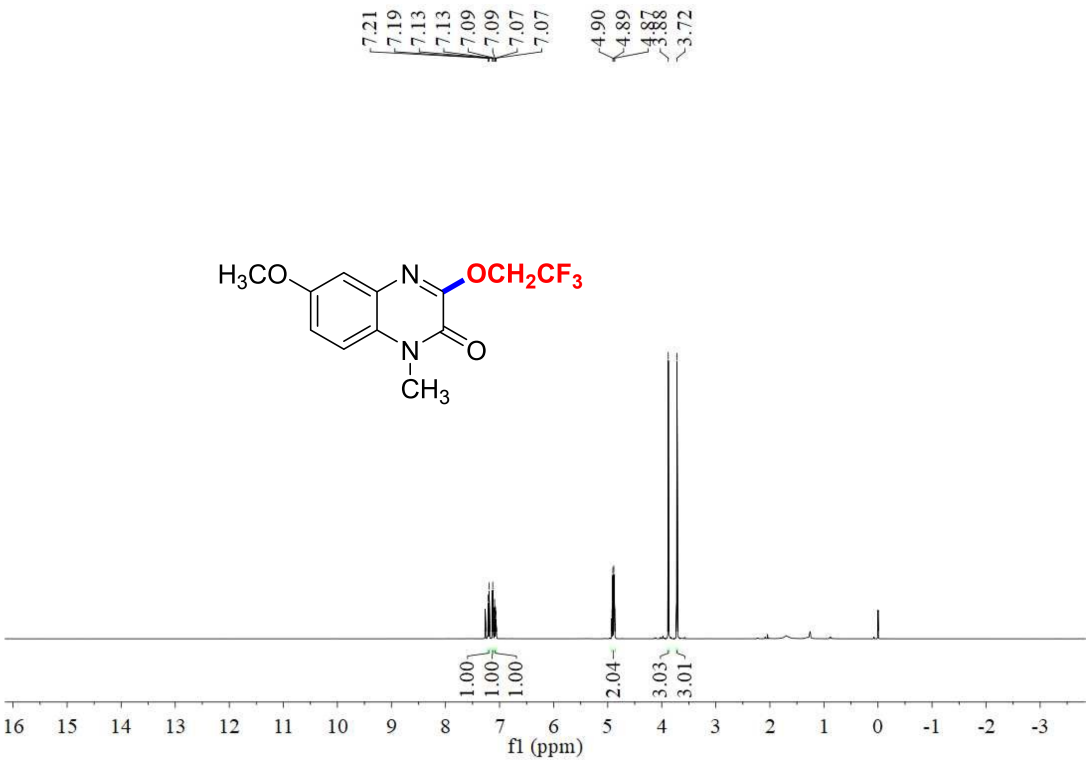
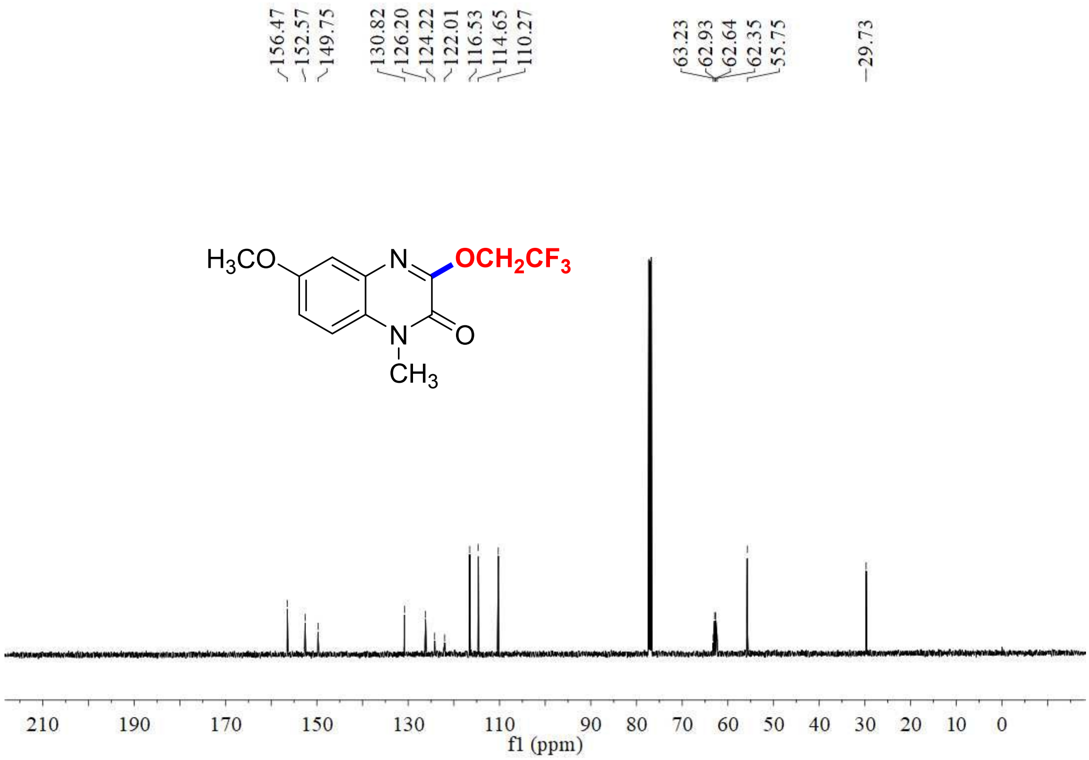


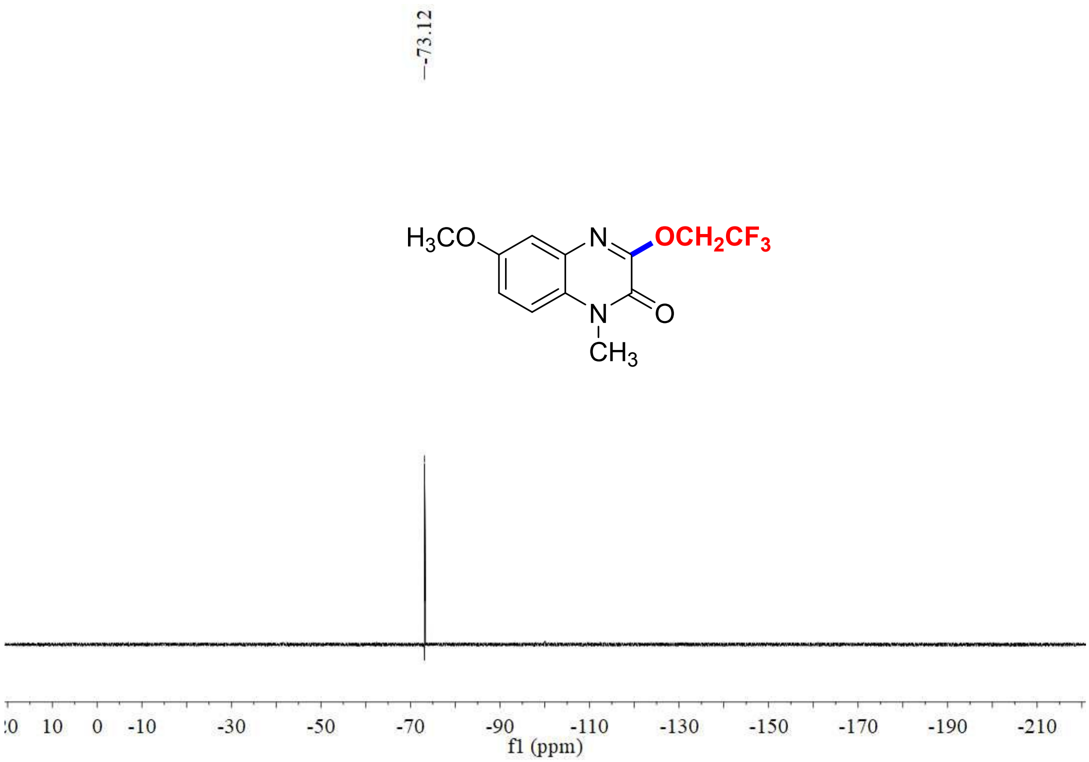
21 ^{1}H NMR



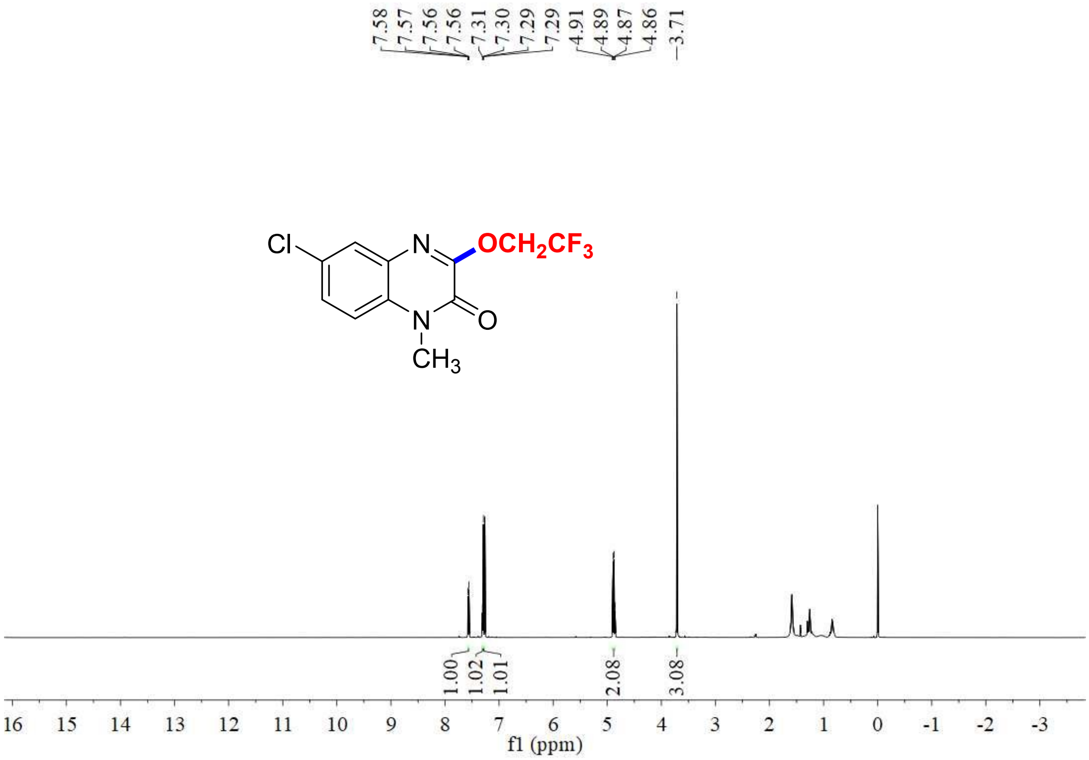
21 ^{13}C NMR



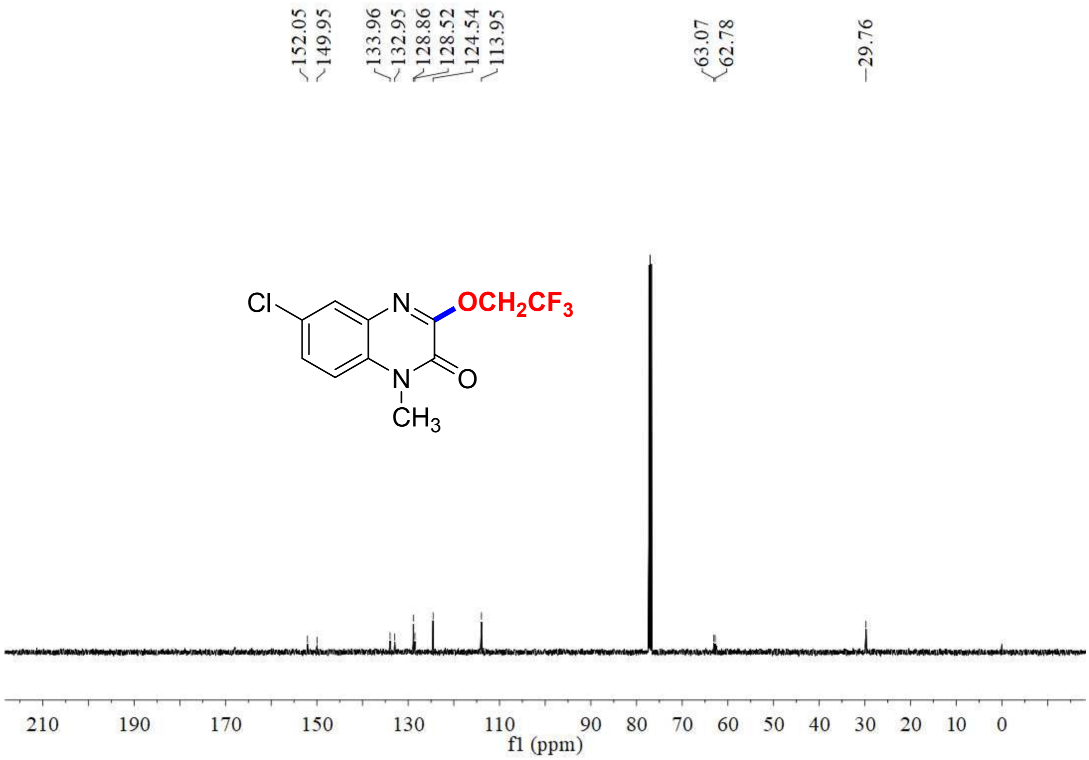
21 ^{19}F NMR



22 ^{1}H NMR



22 ^{13}C NMR



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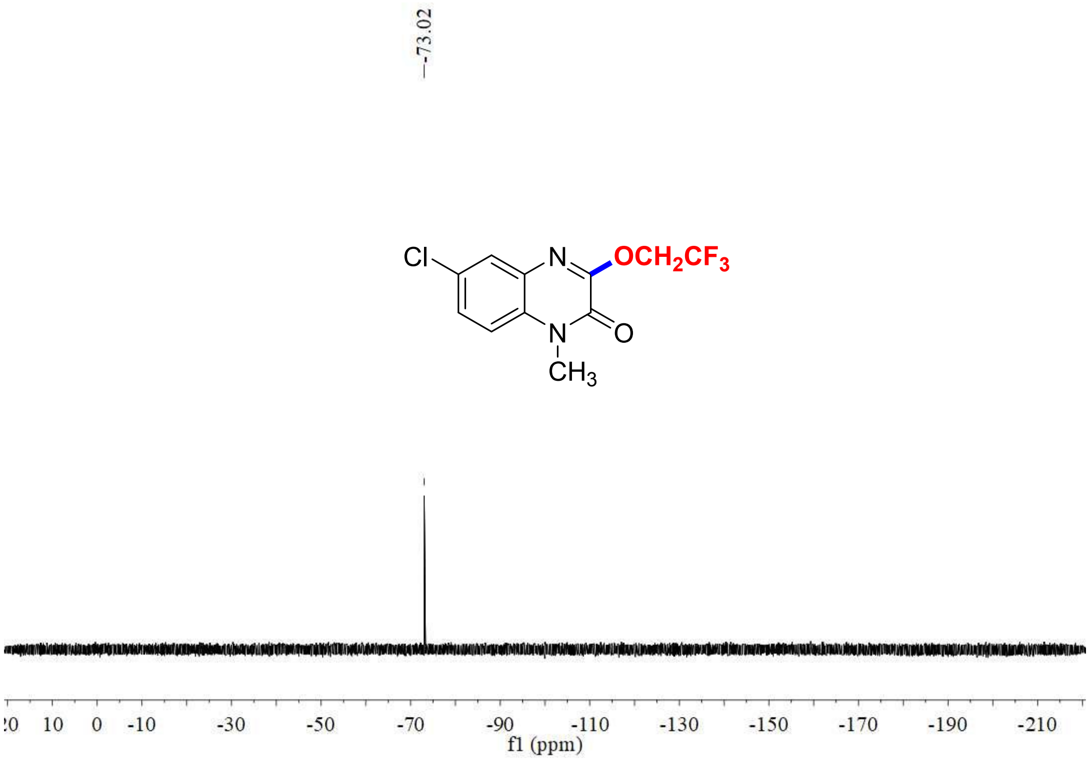

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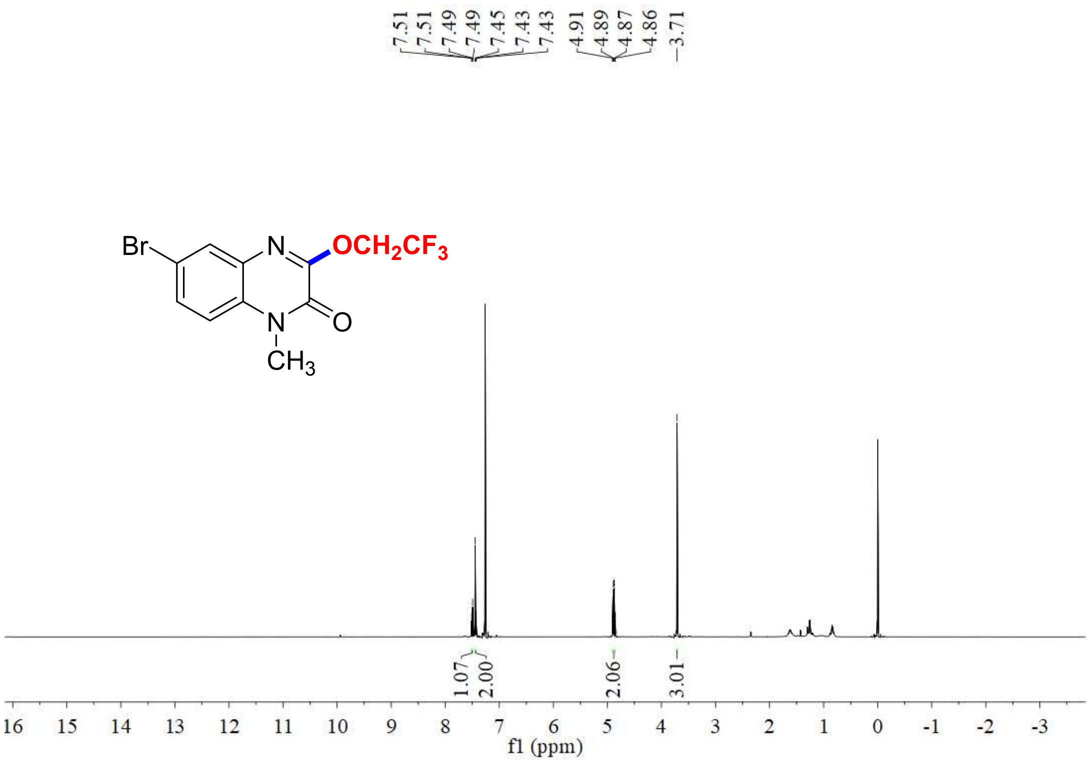

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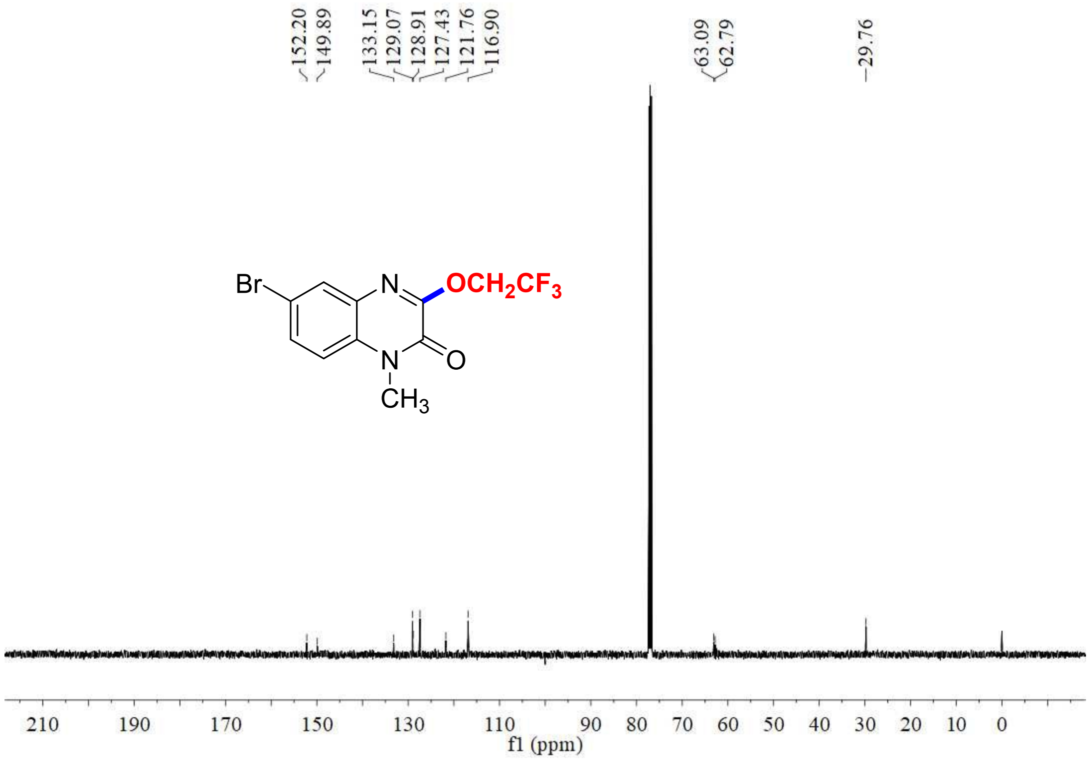

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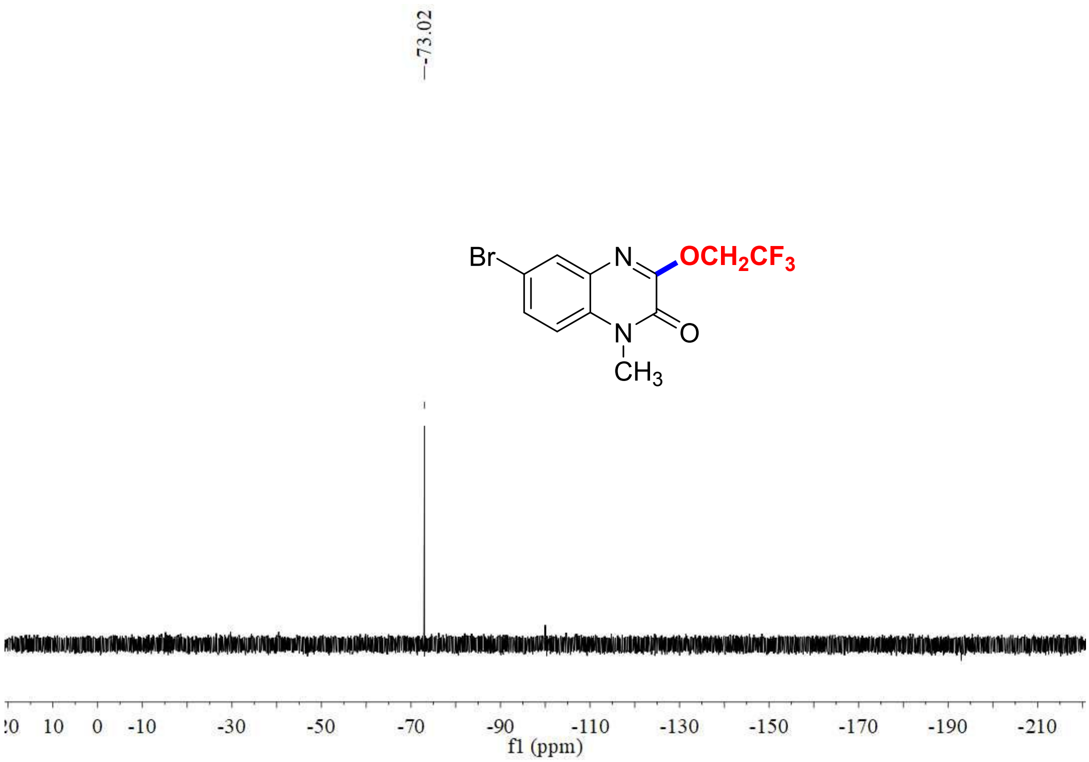

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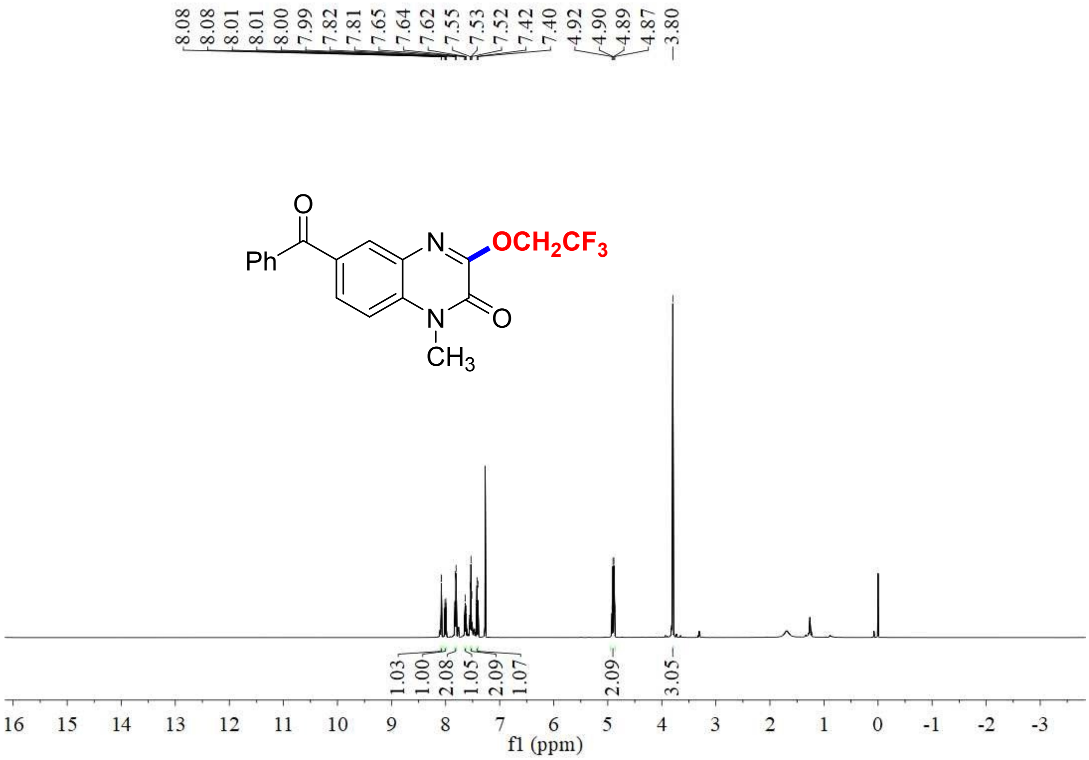

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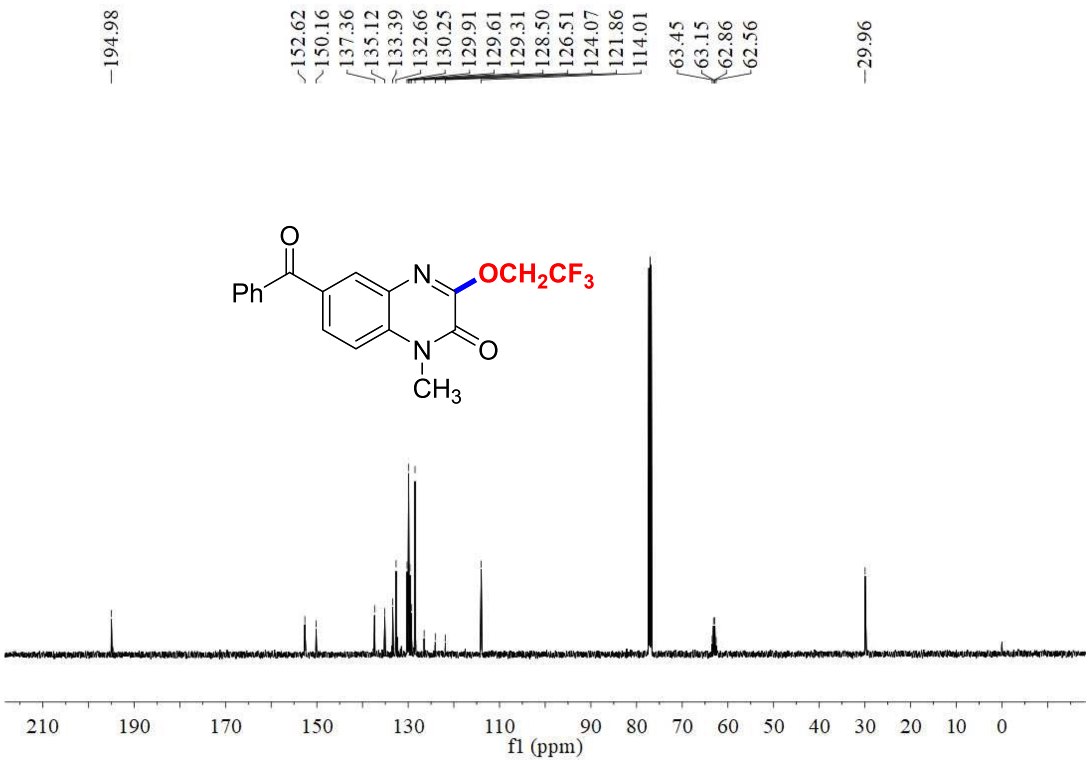

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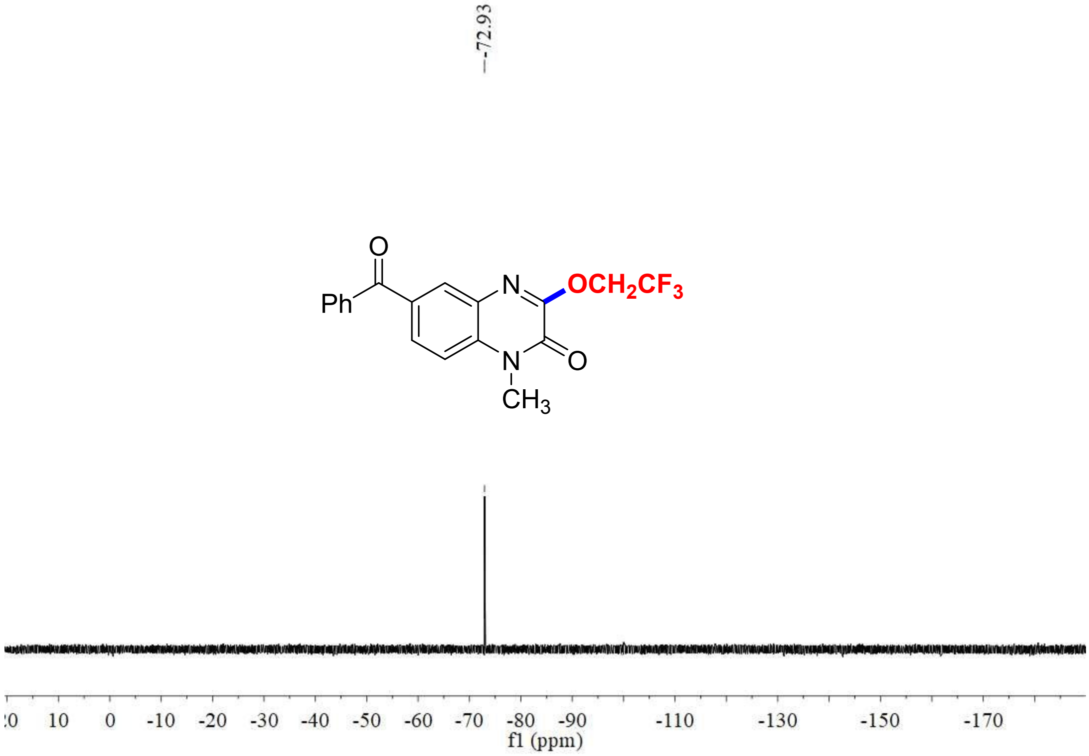

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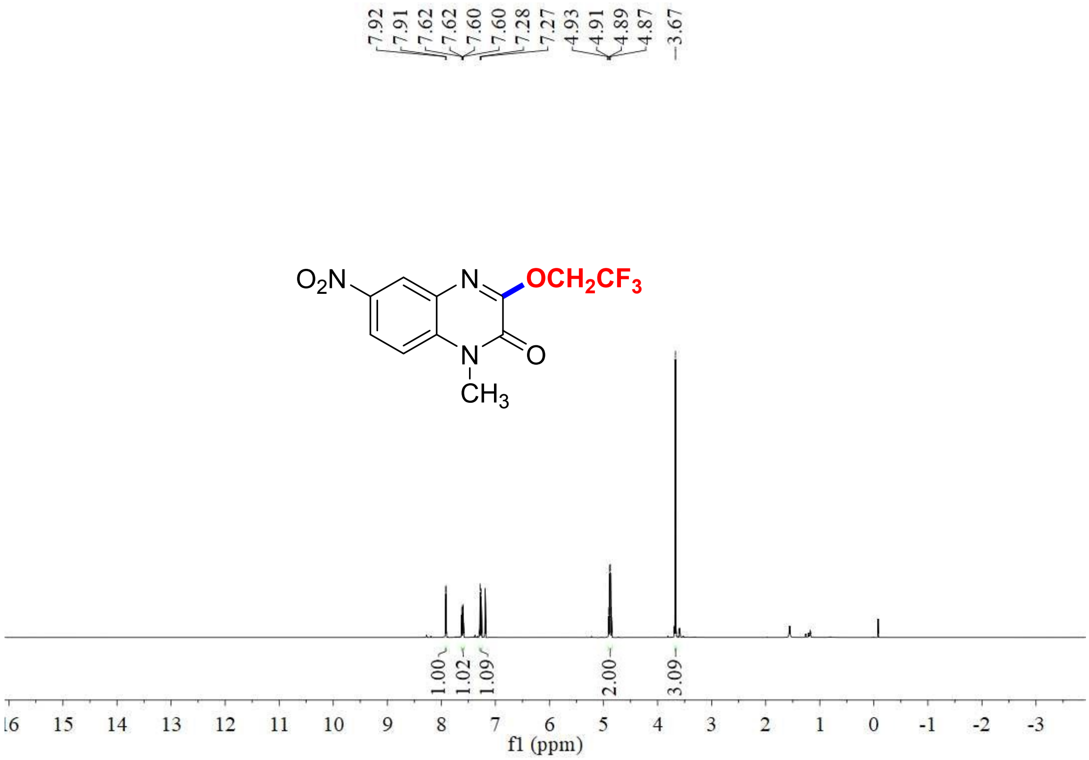

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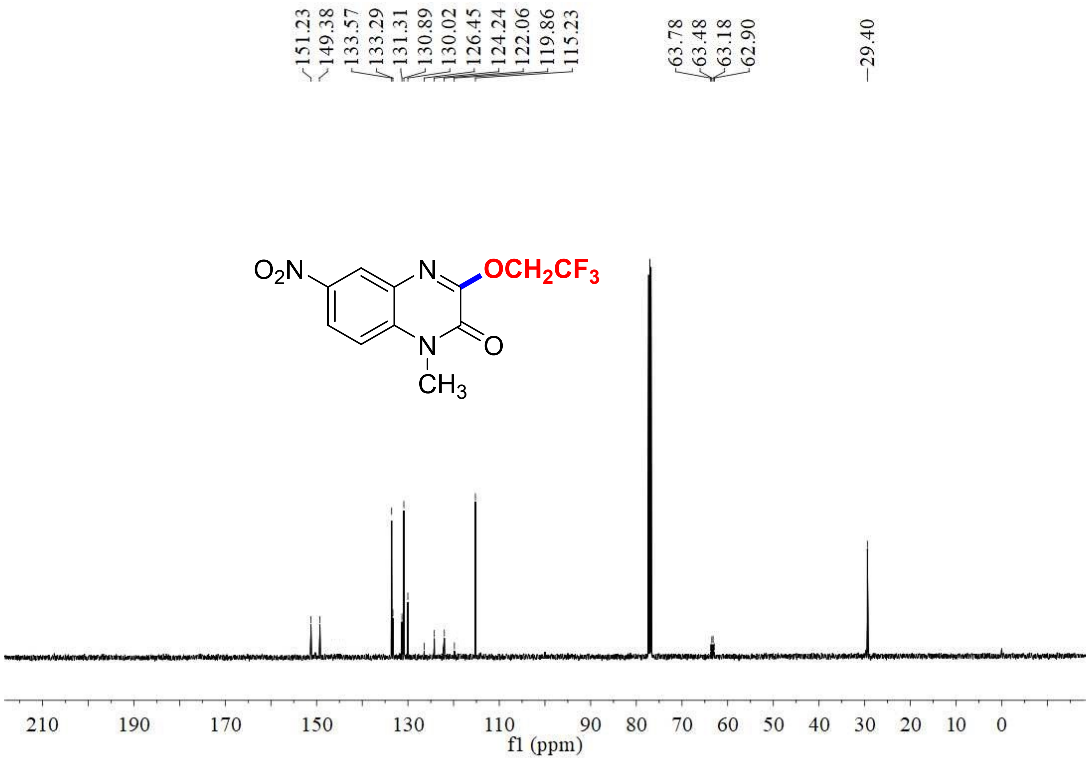

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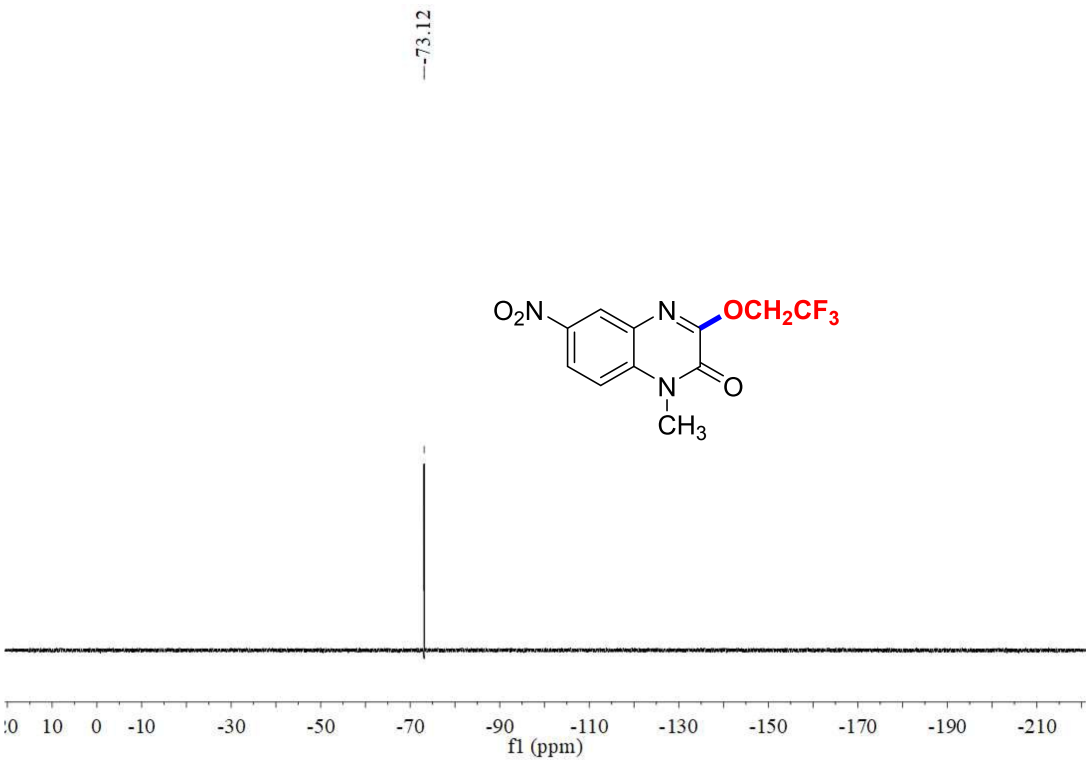
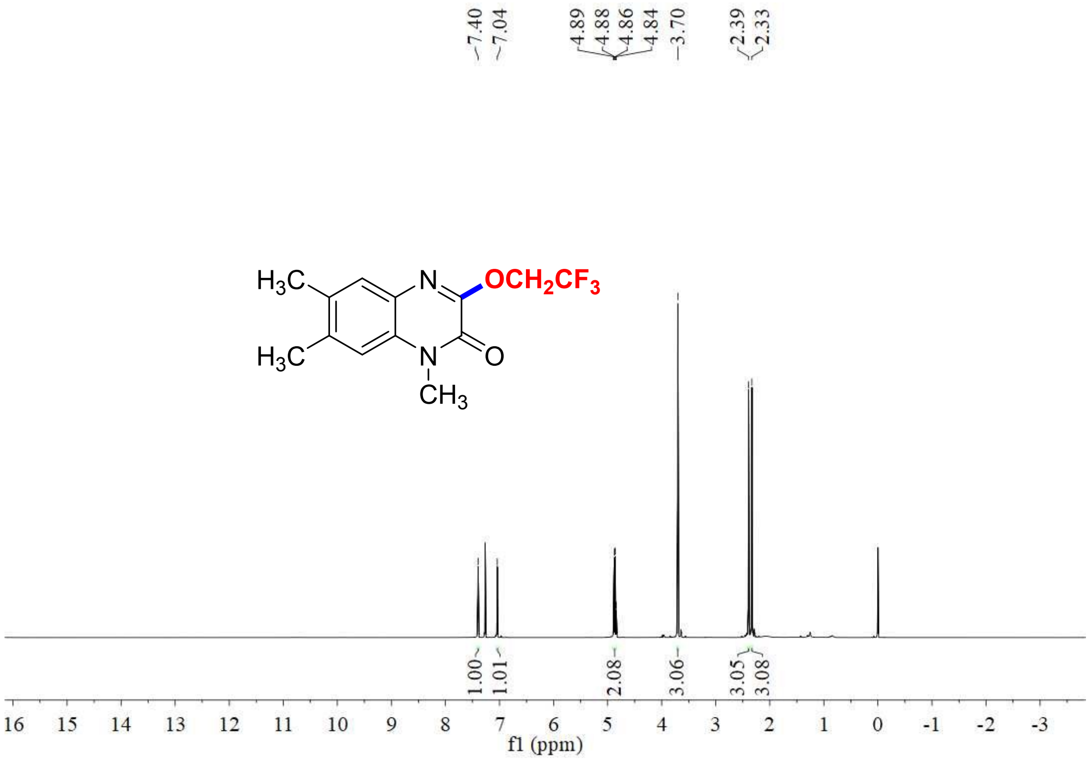


26 ^{1}H NMR



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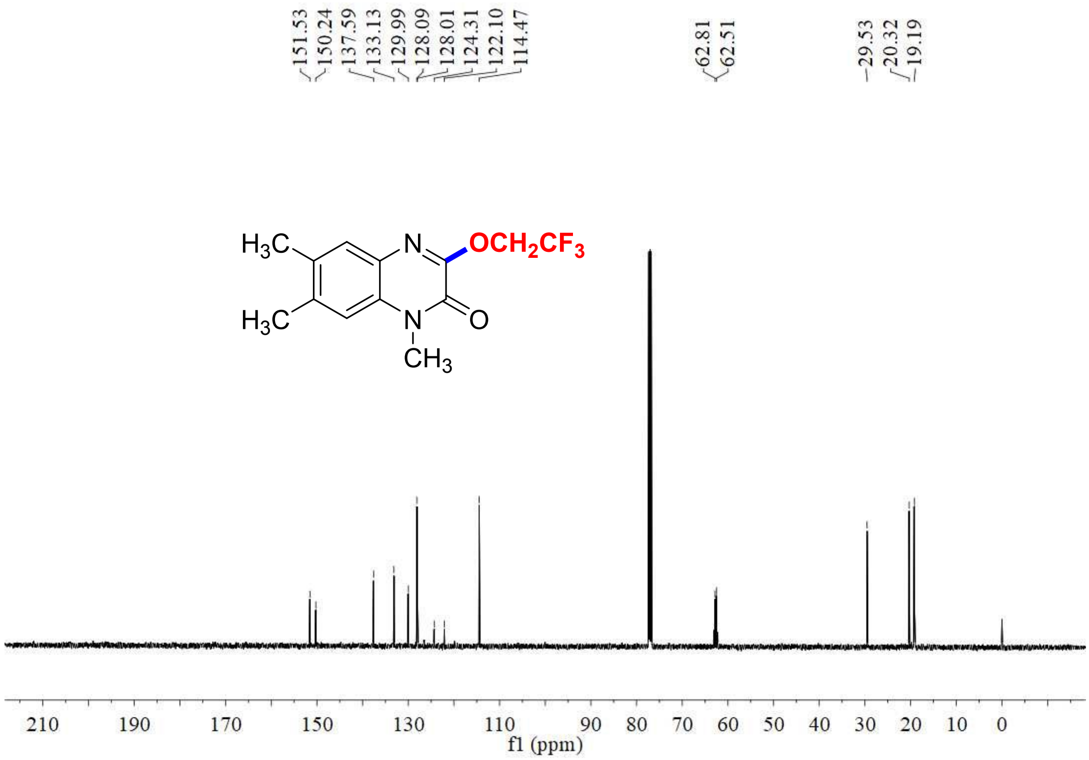

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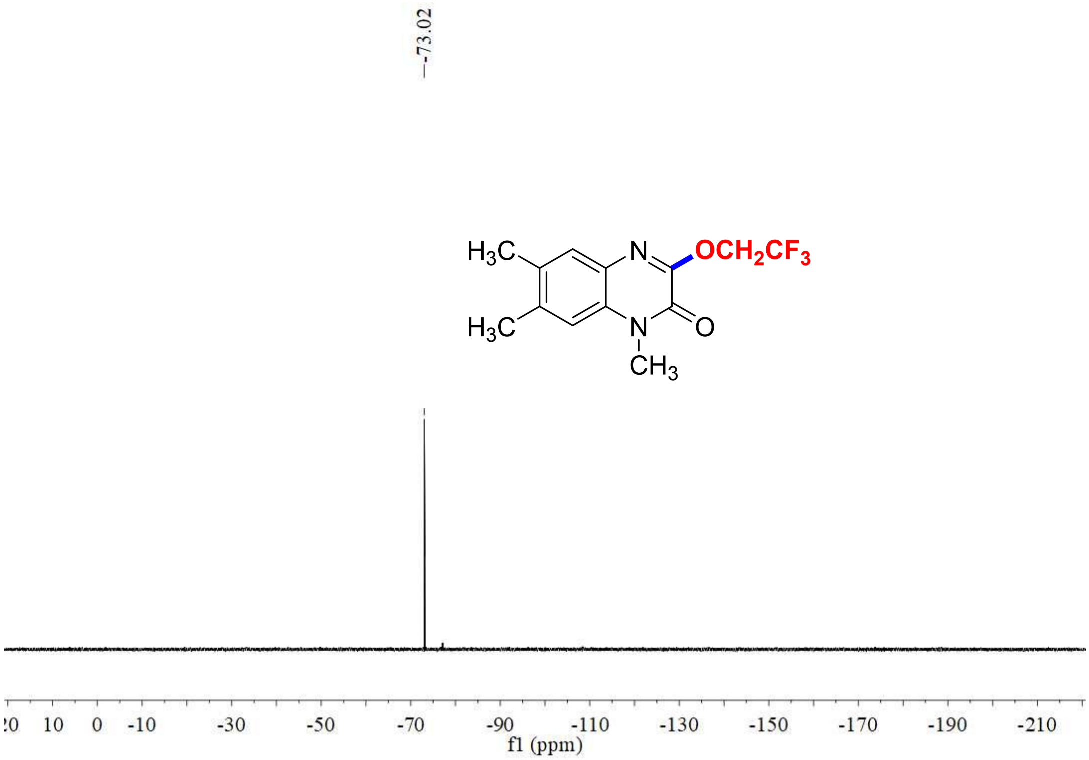

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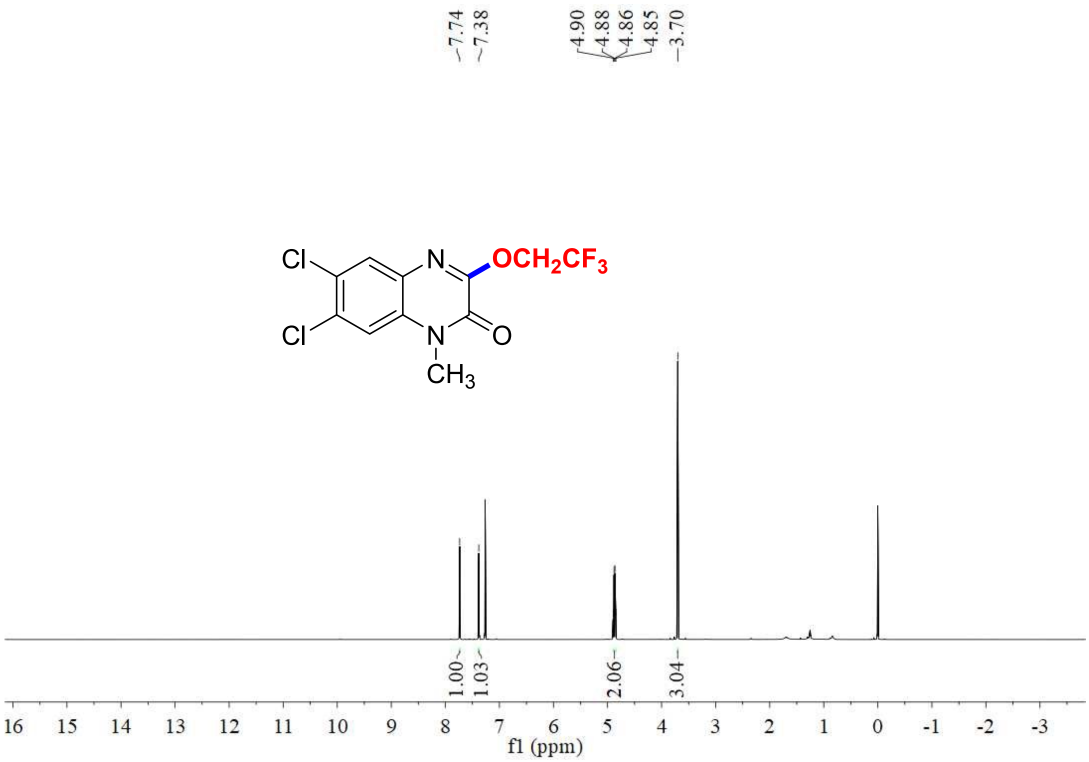

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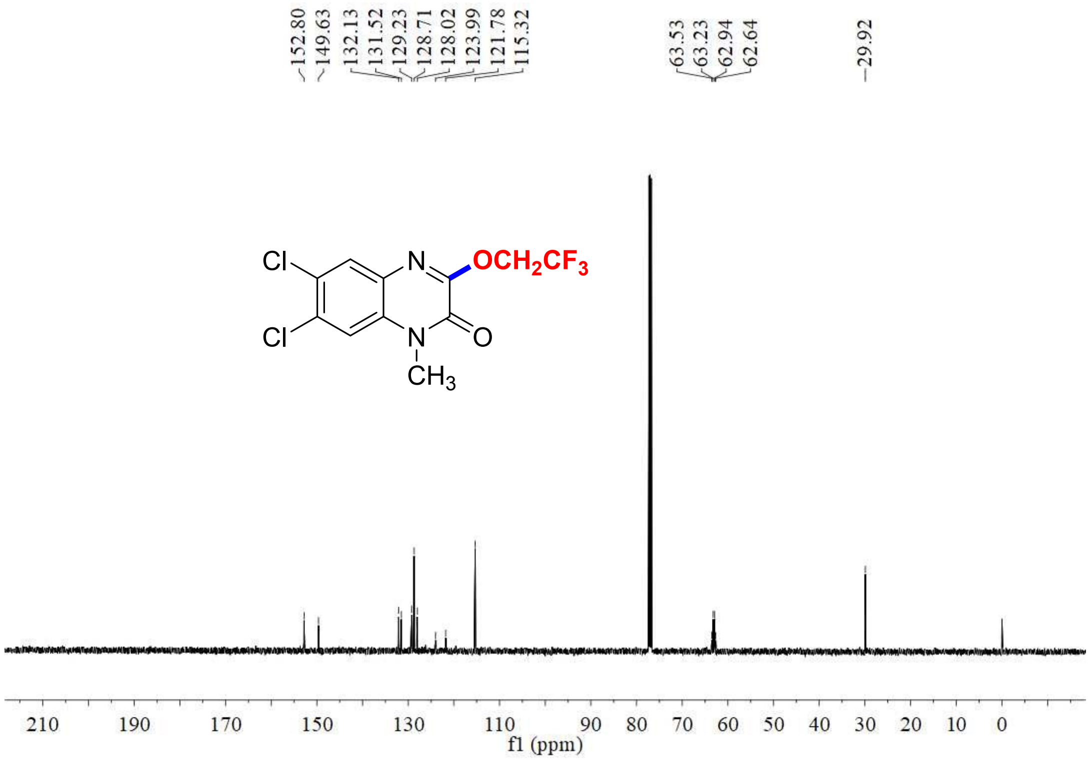

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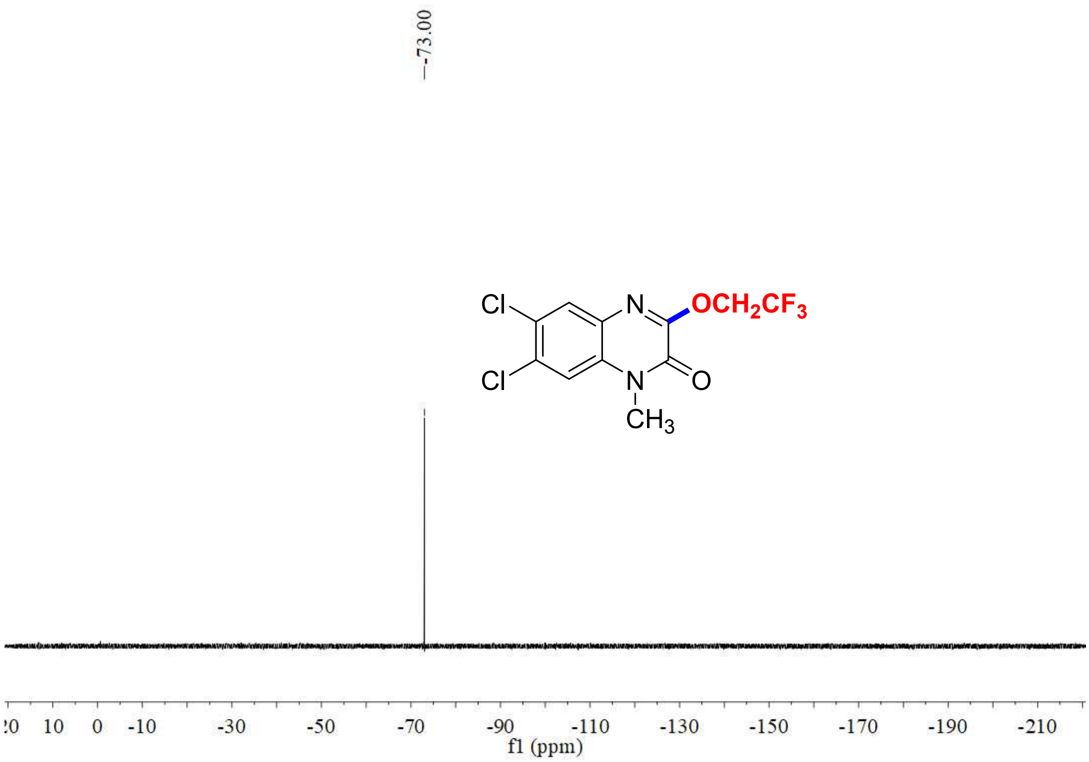

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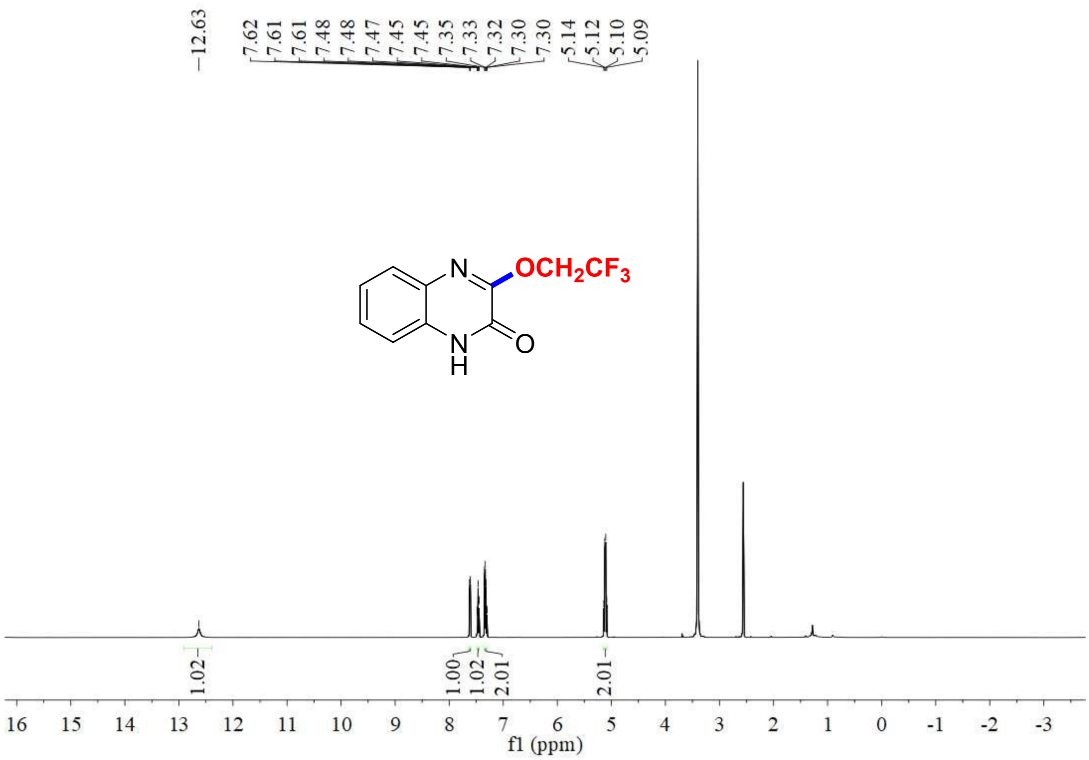

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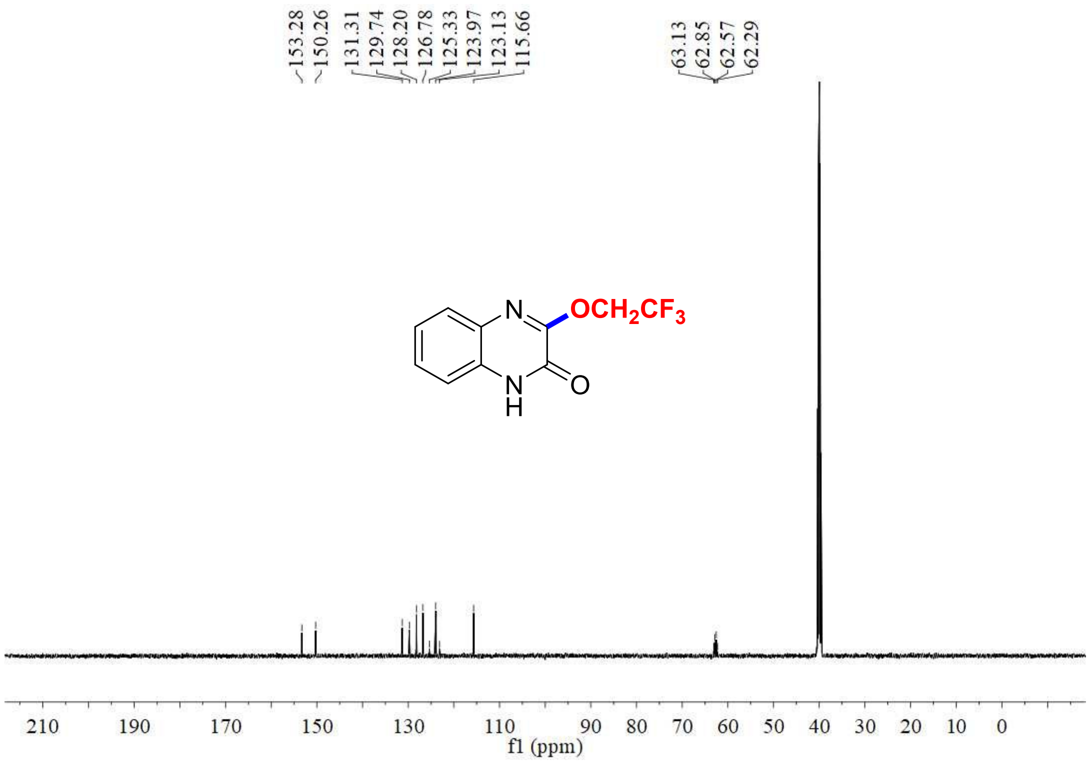

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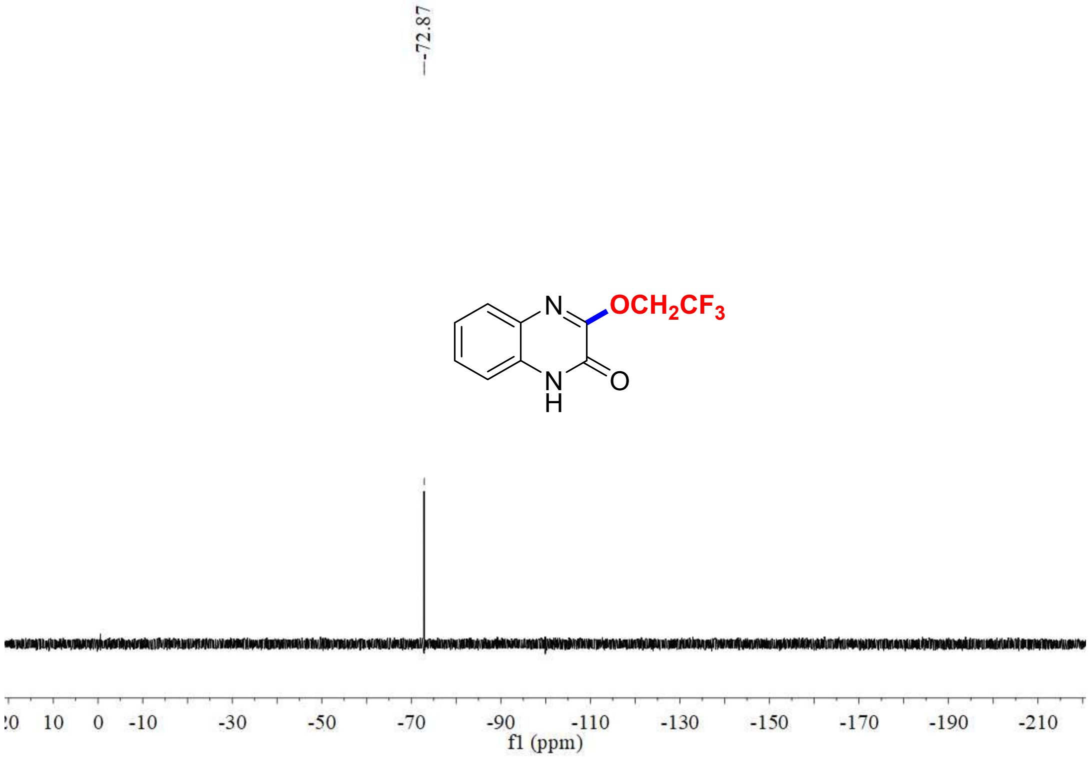

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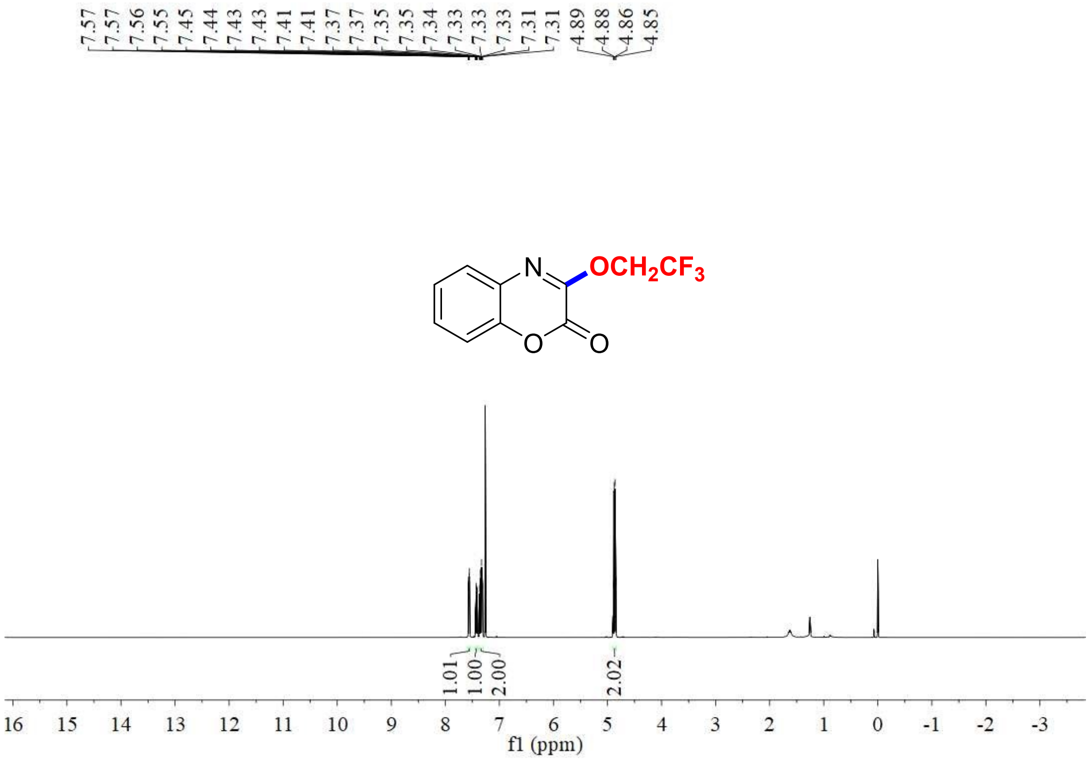

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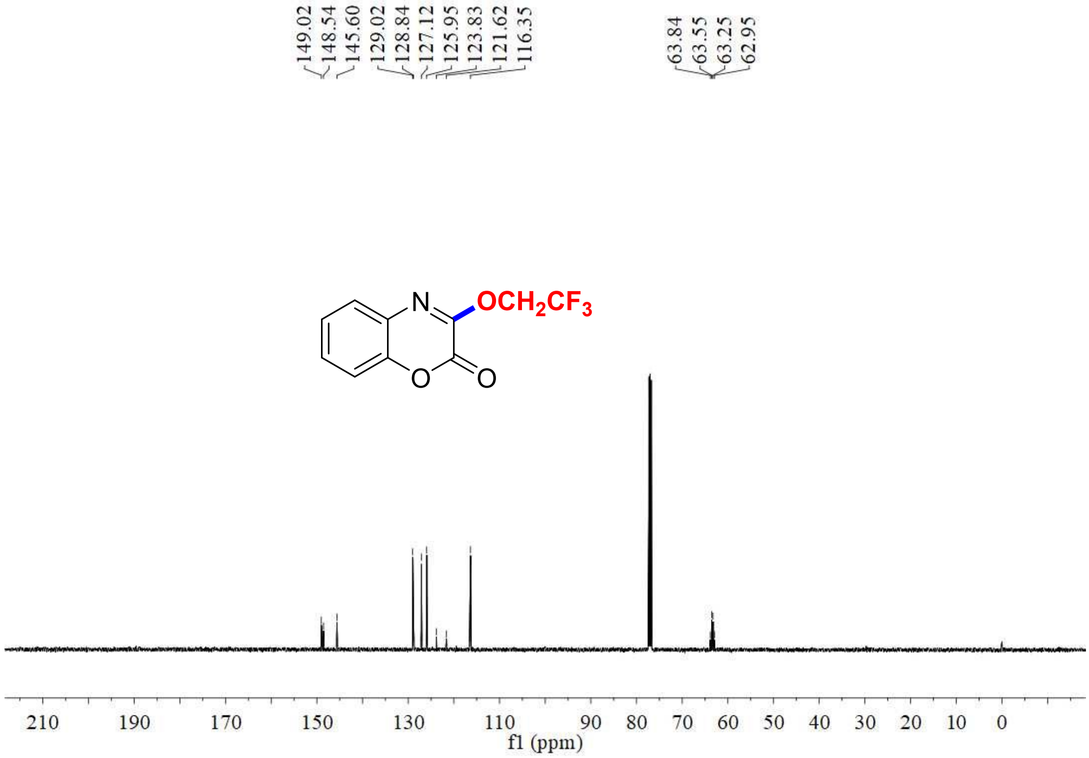

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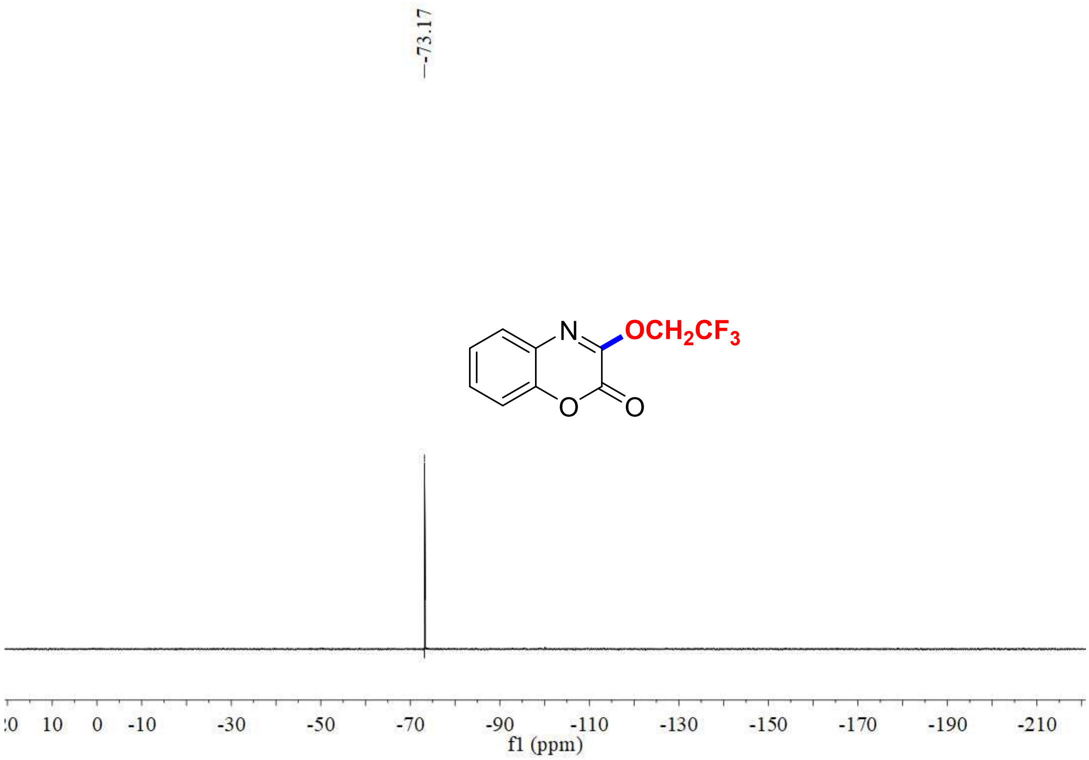

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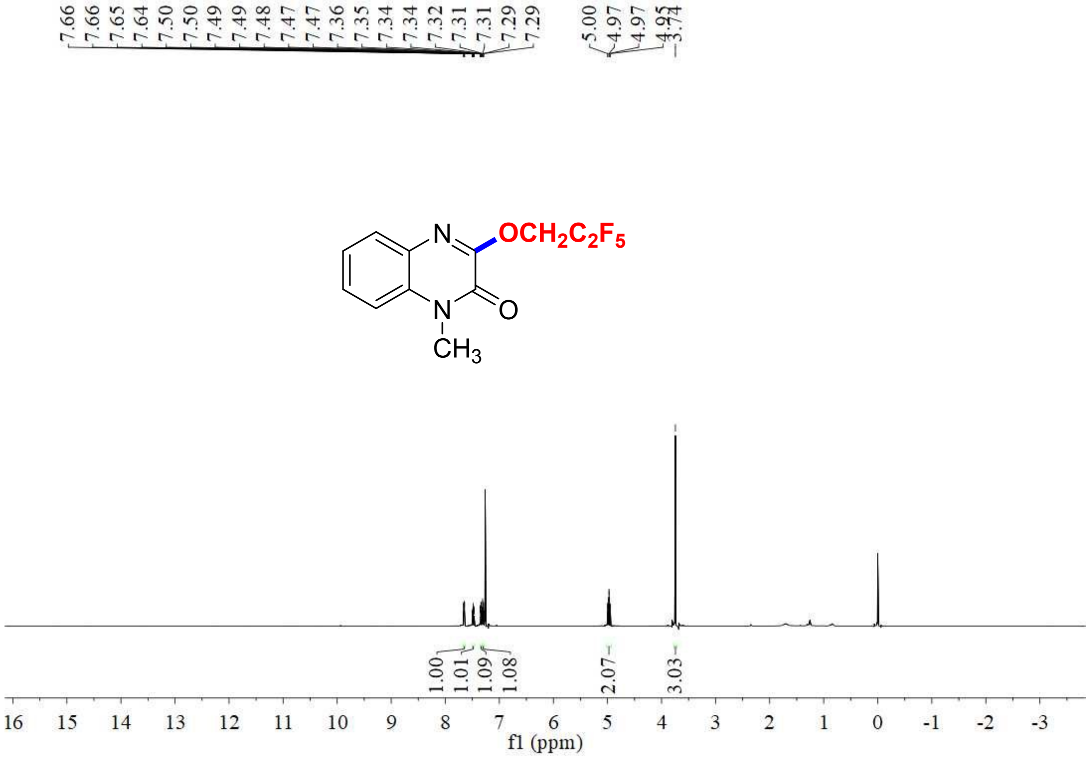

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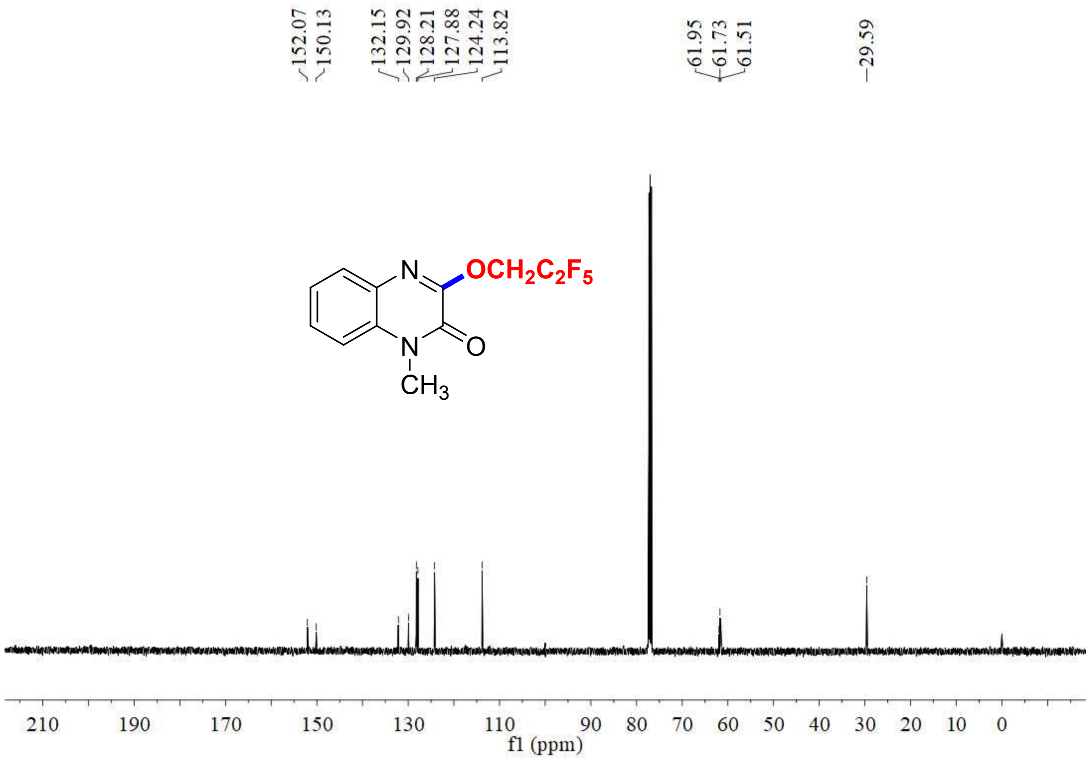

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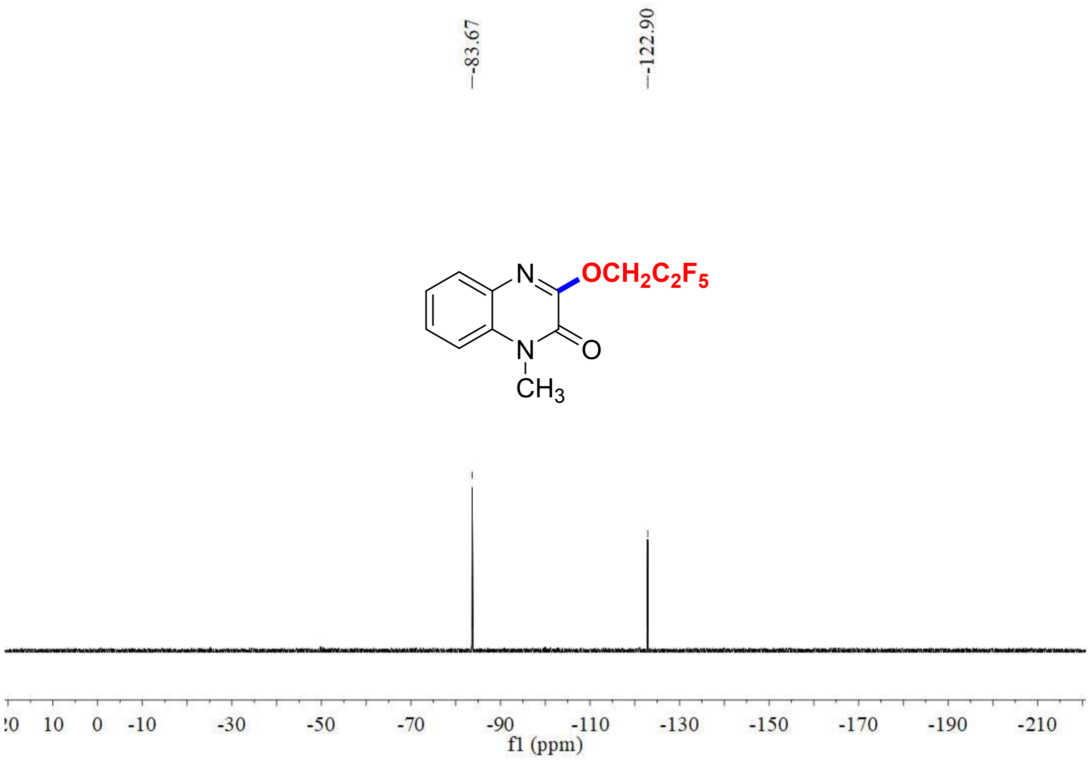

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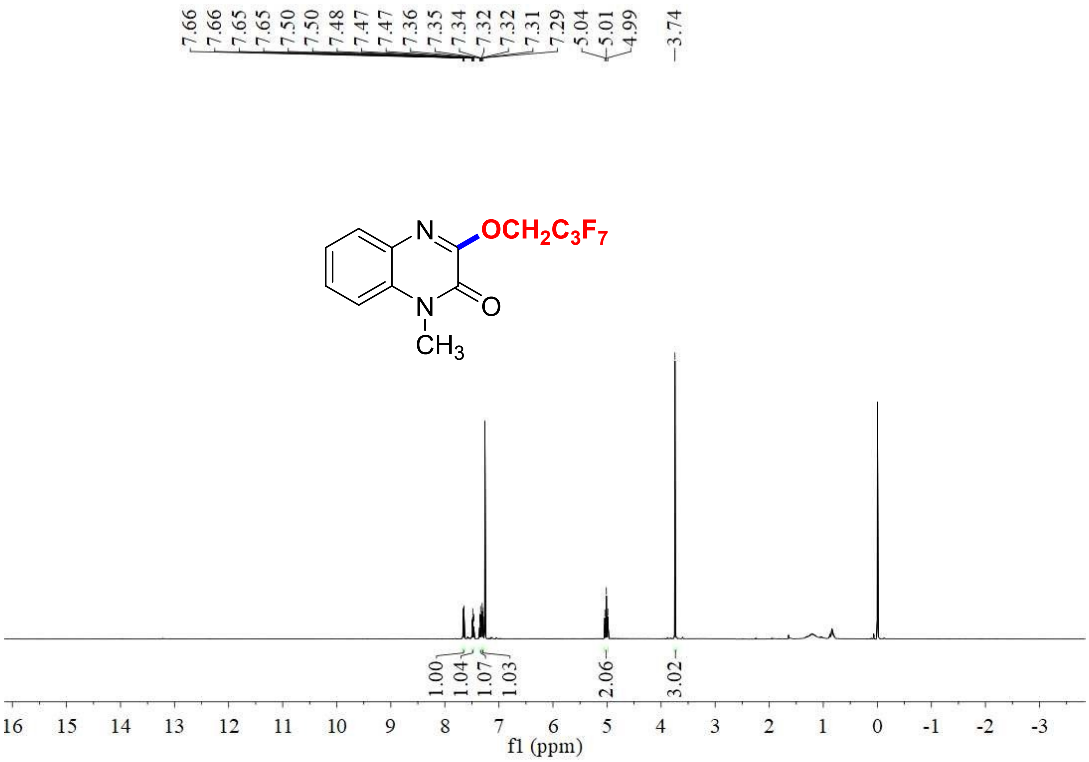

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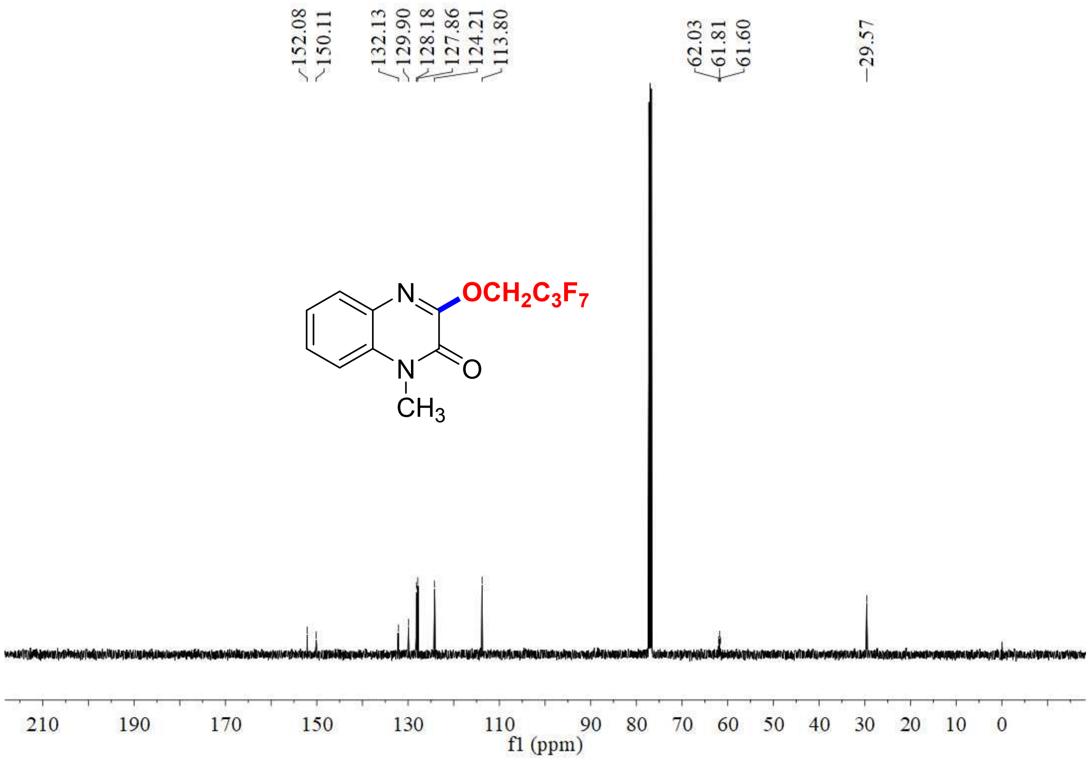

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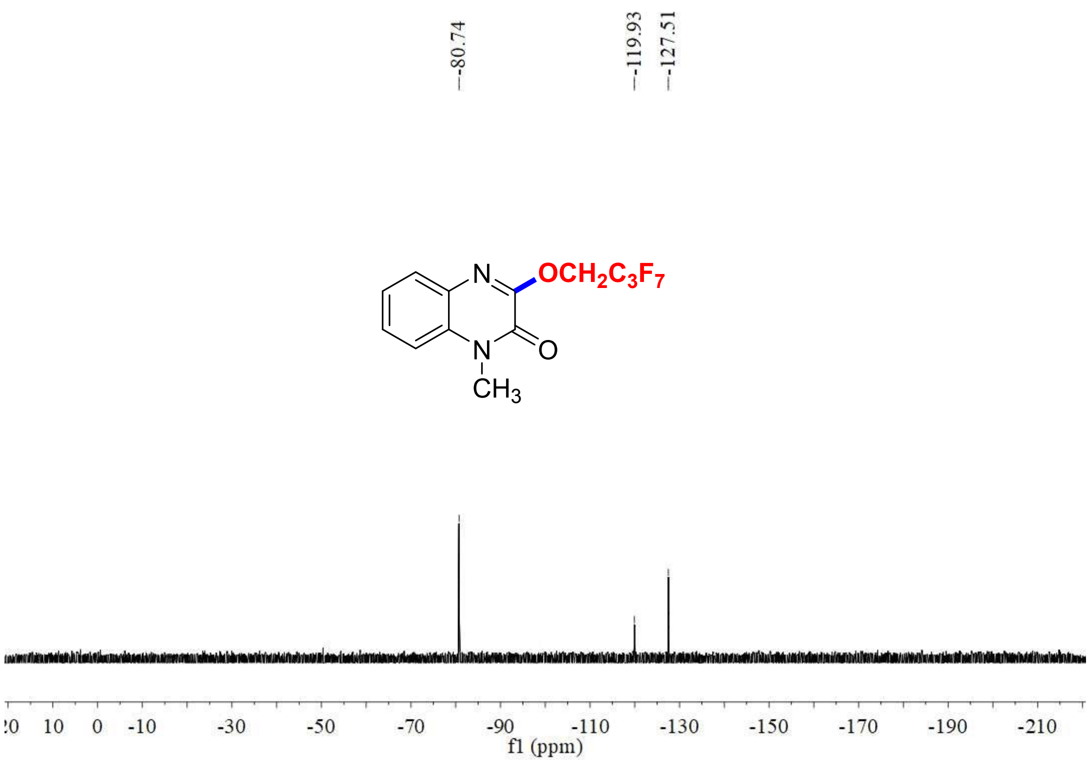

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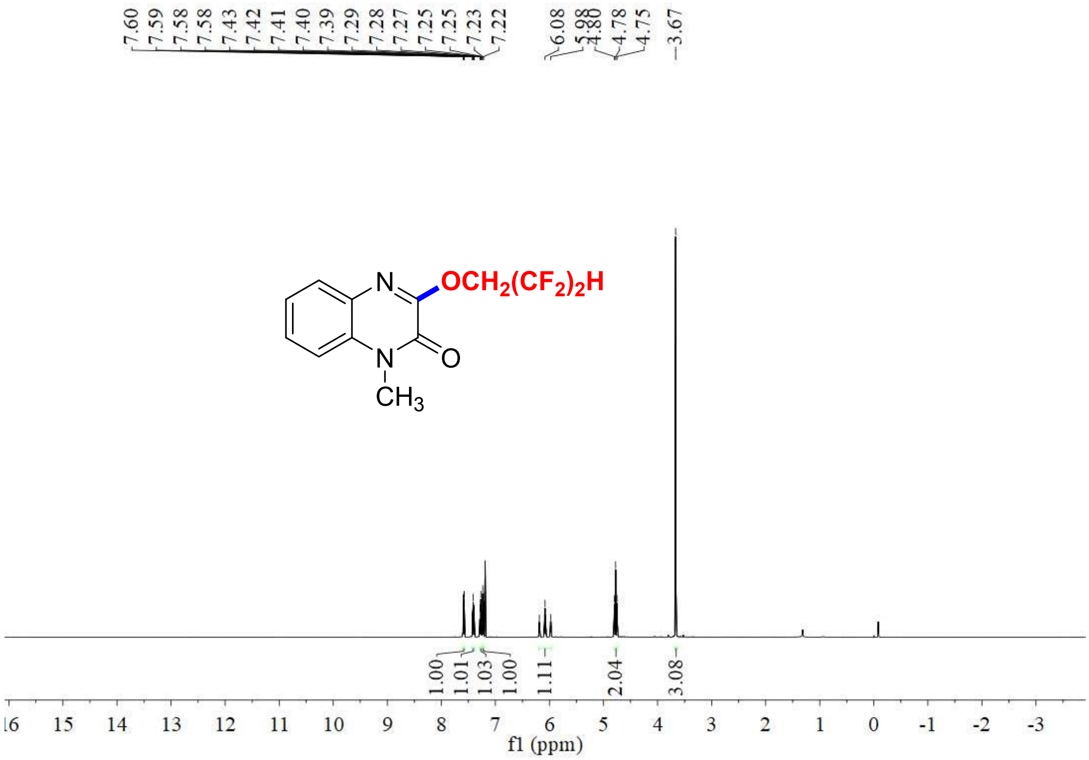

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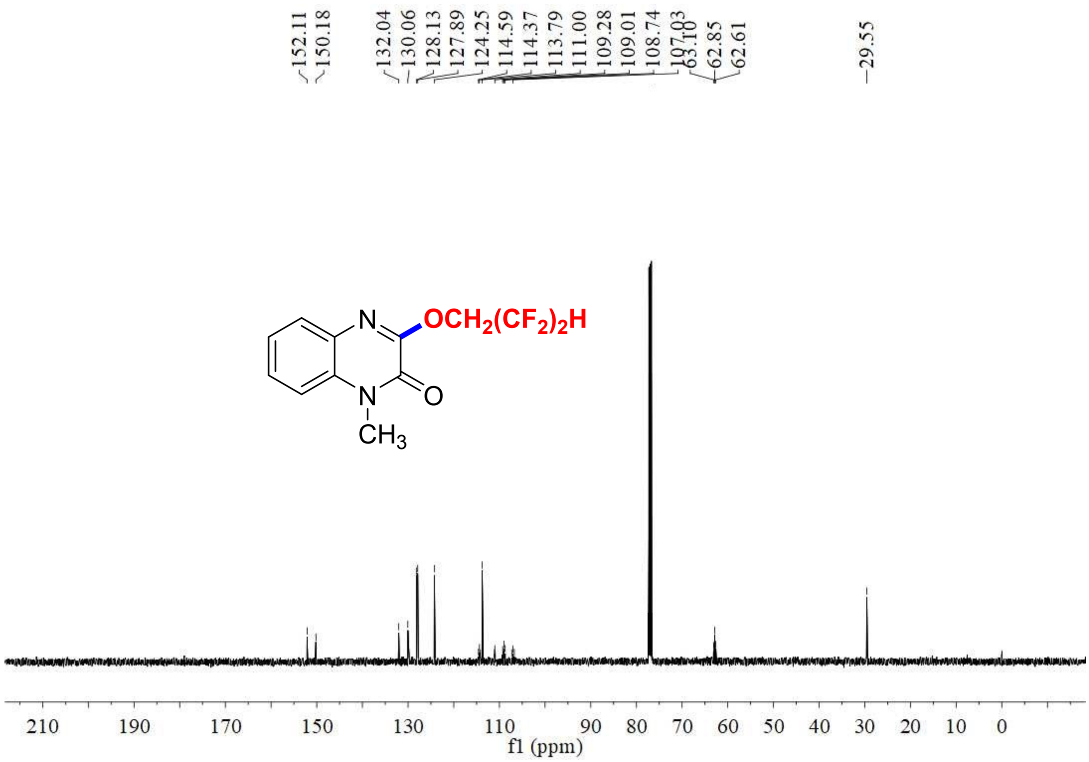

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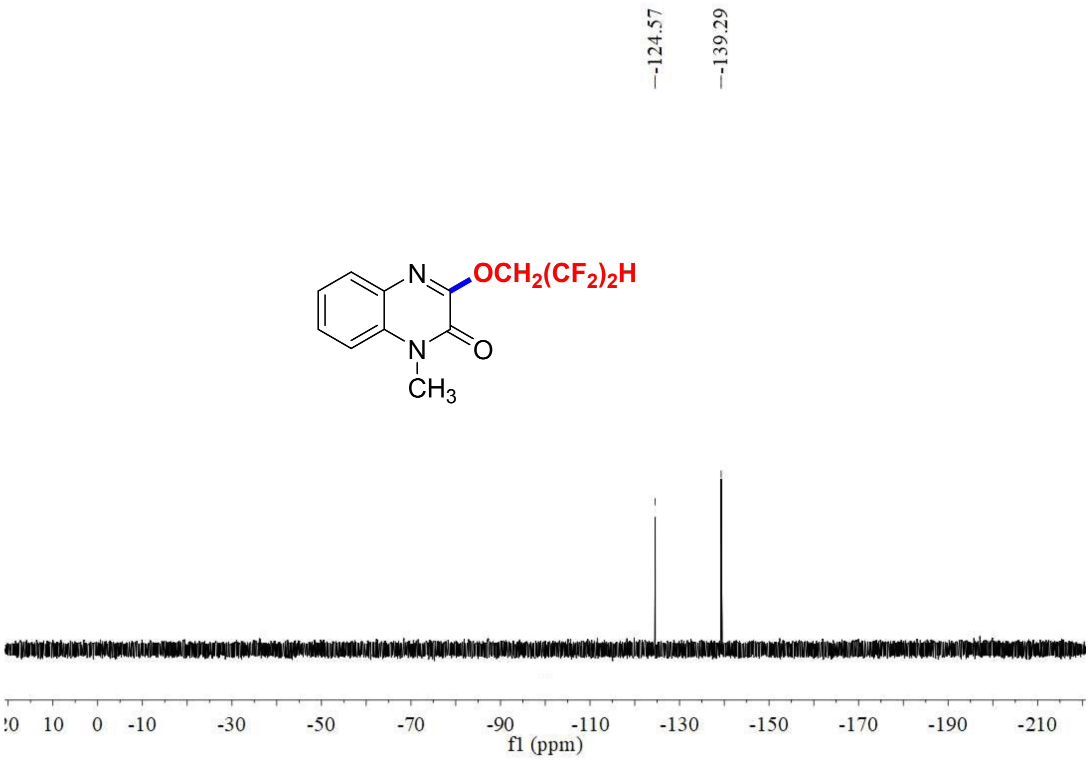

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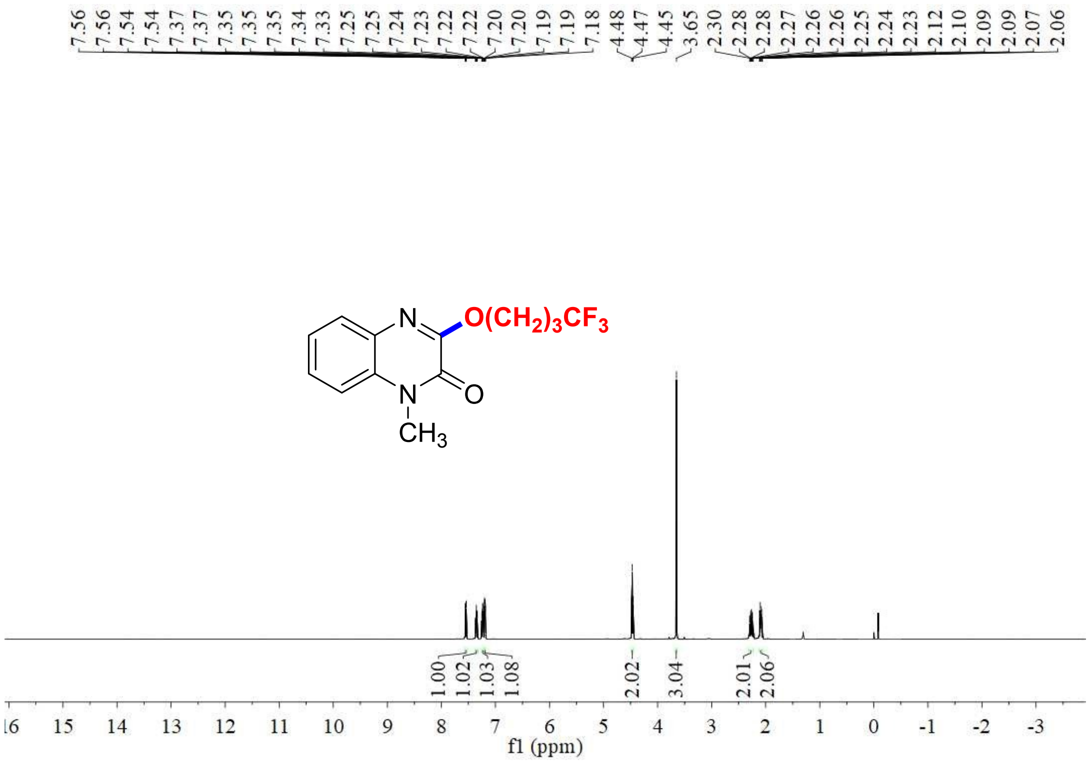

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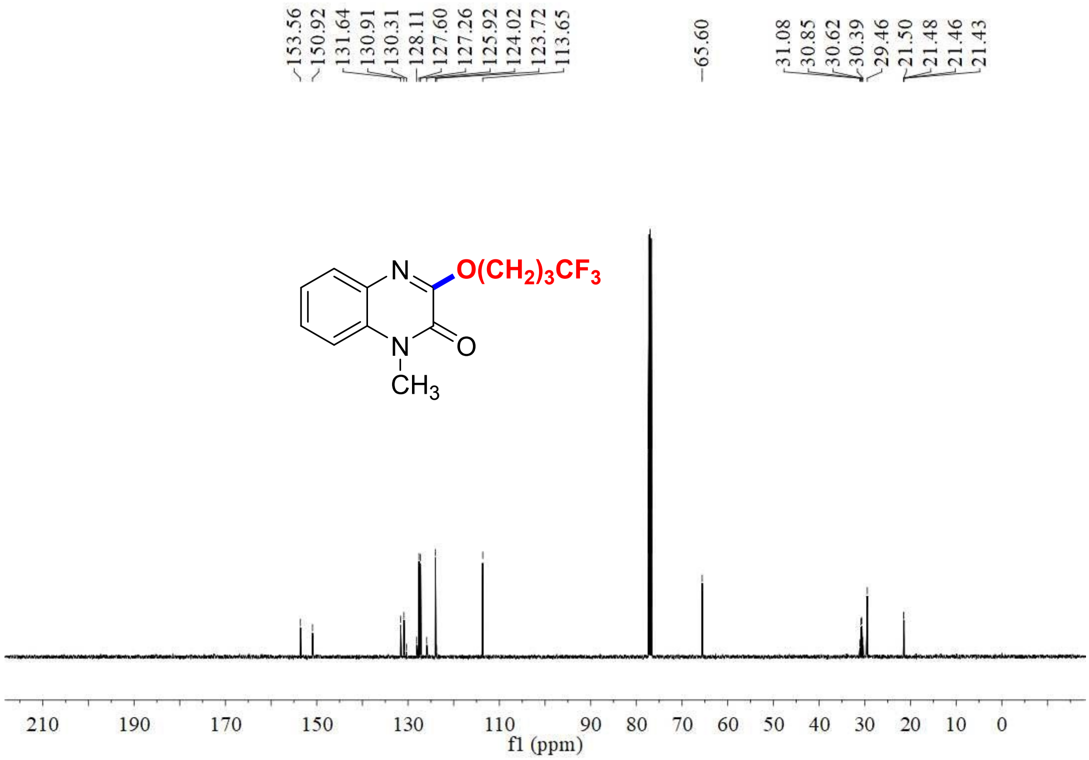

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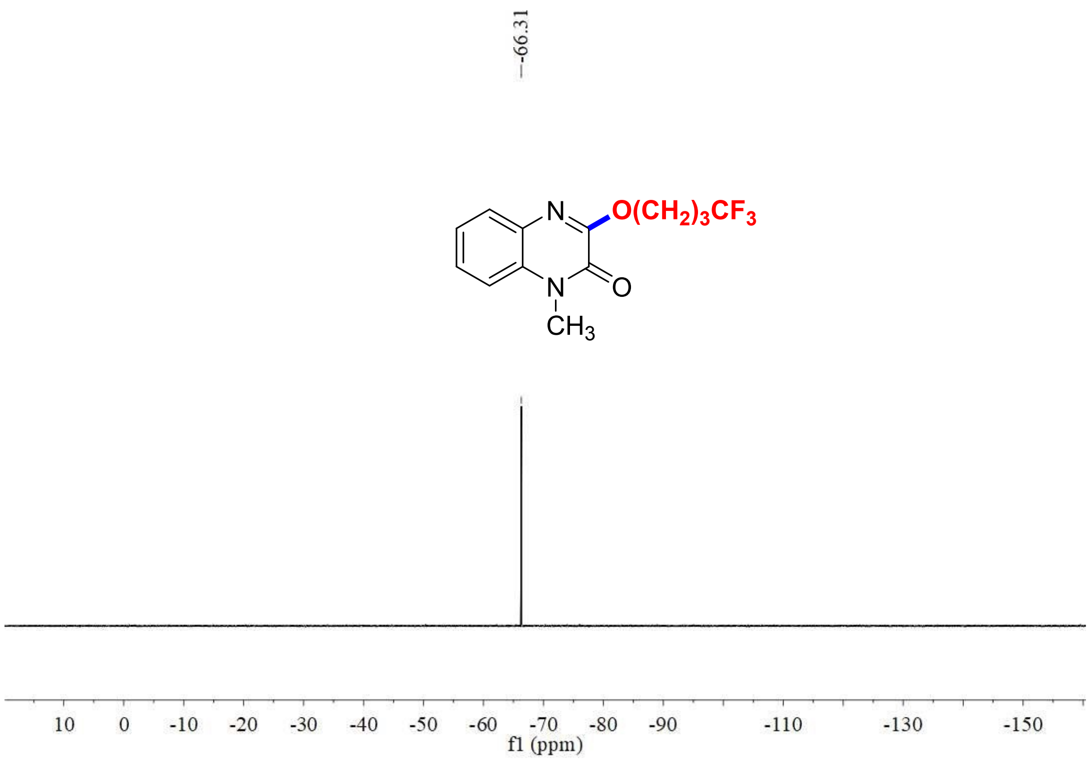

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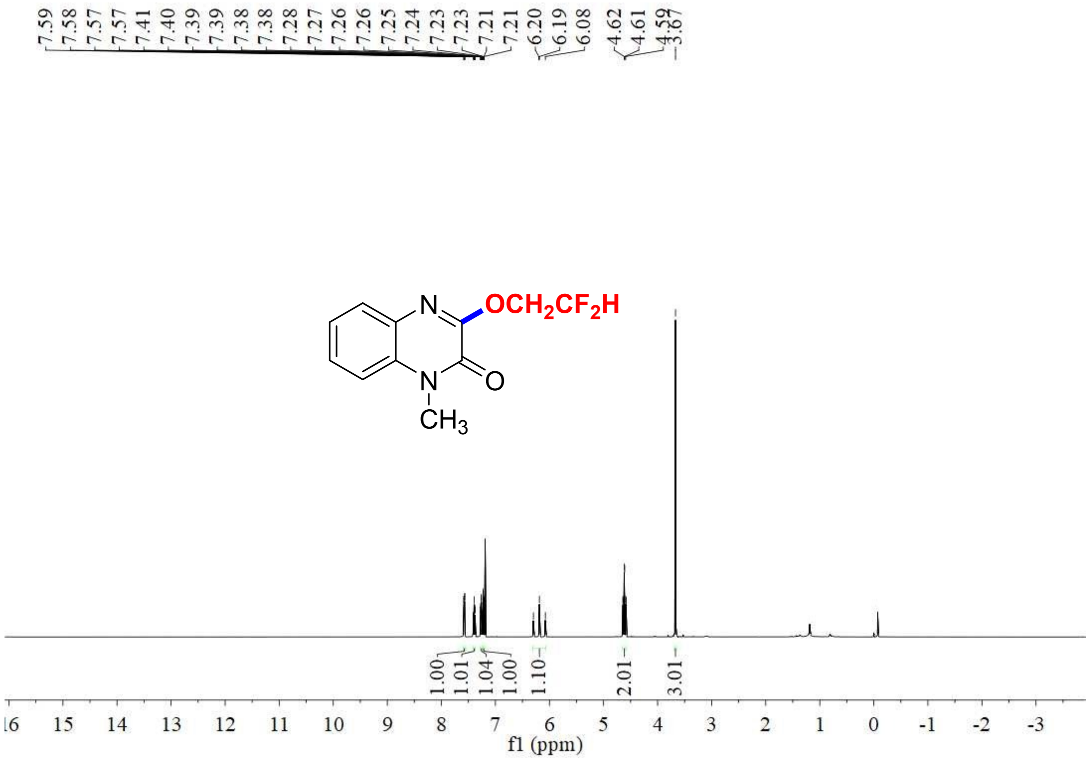

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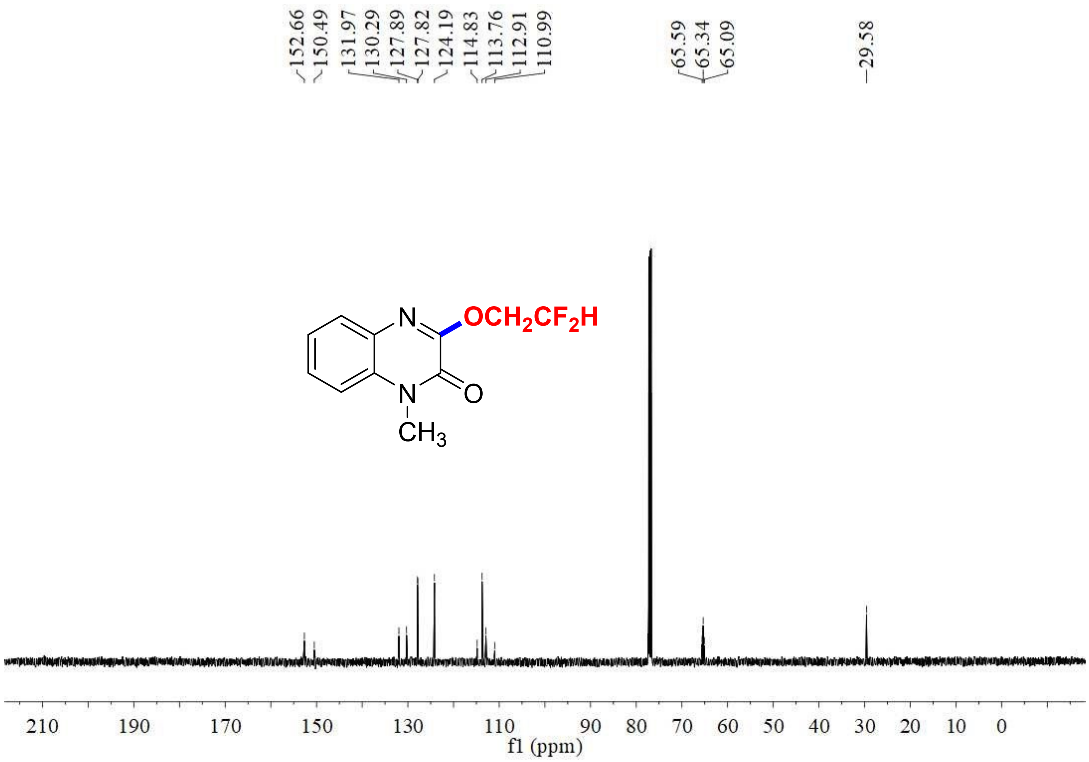

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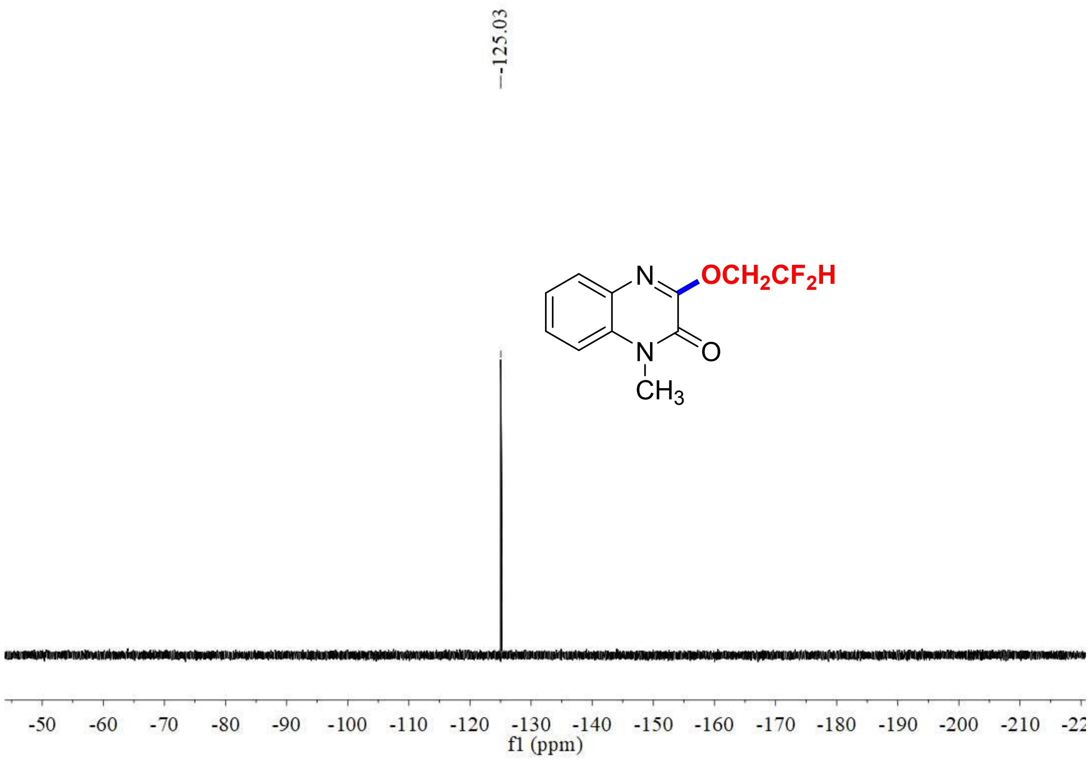

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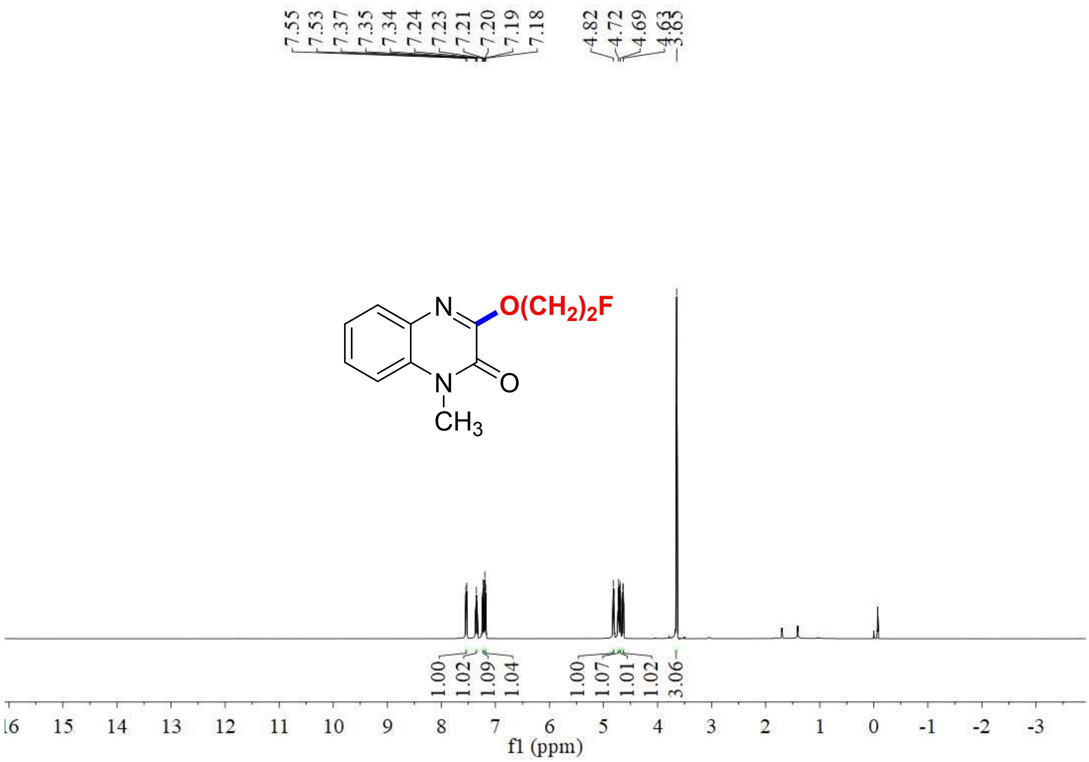

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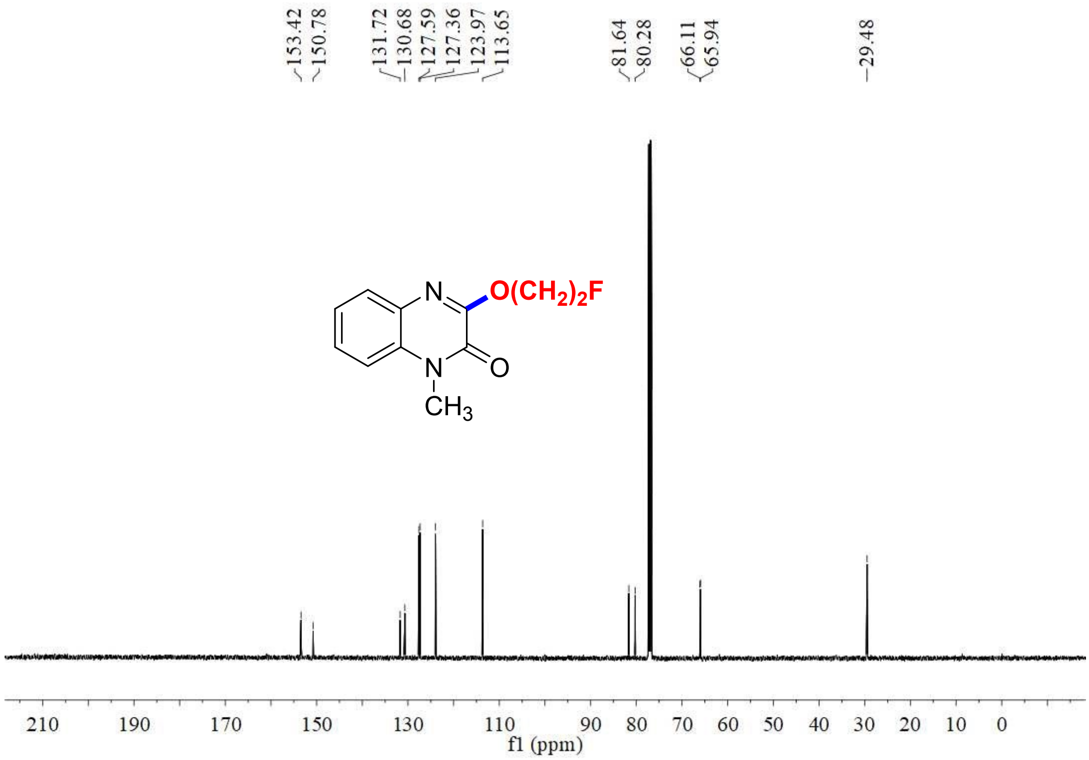

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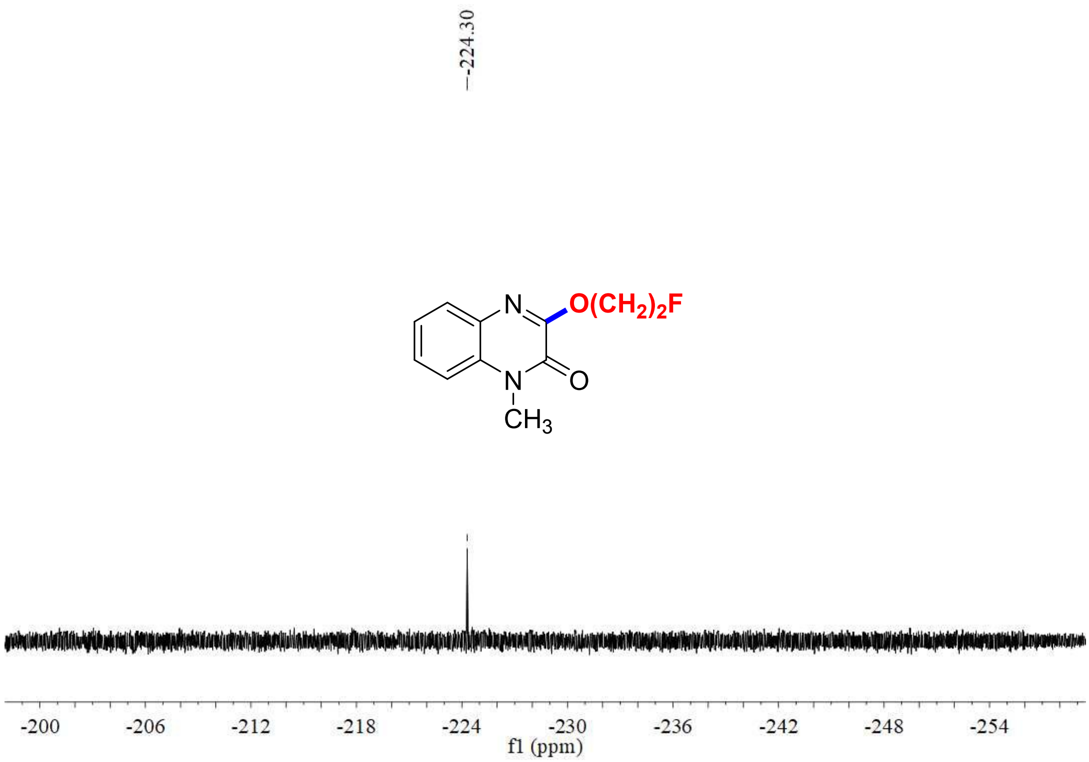

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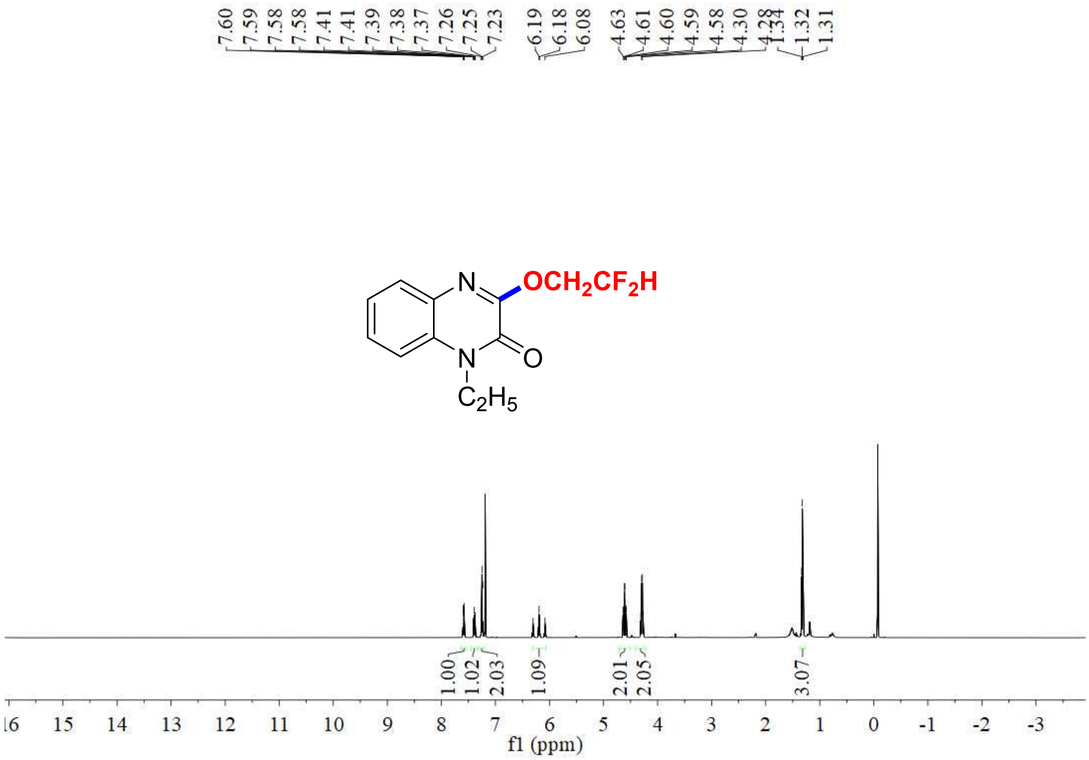

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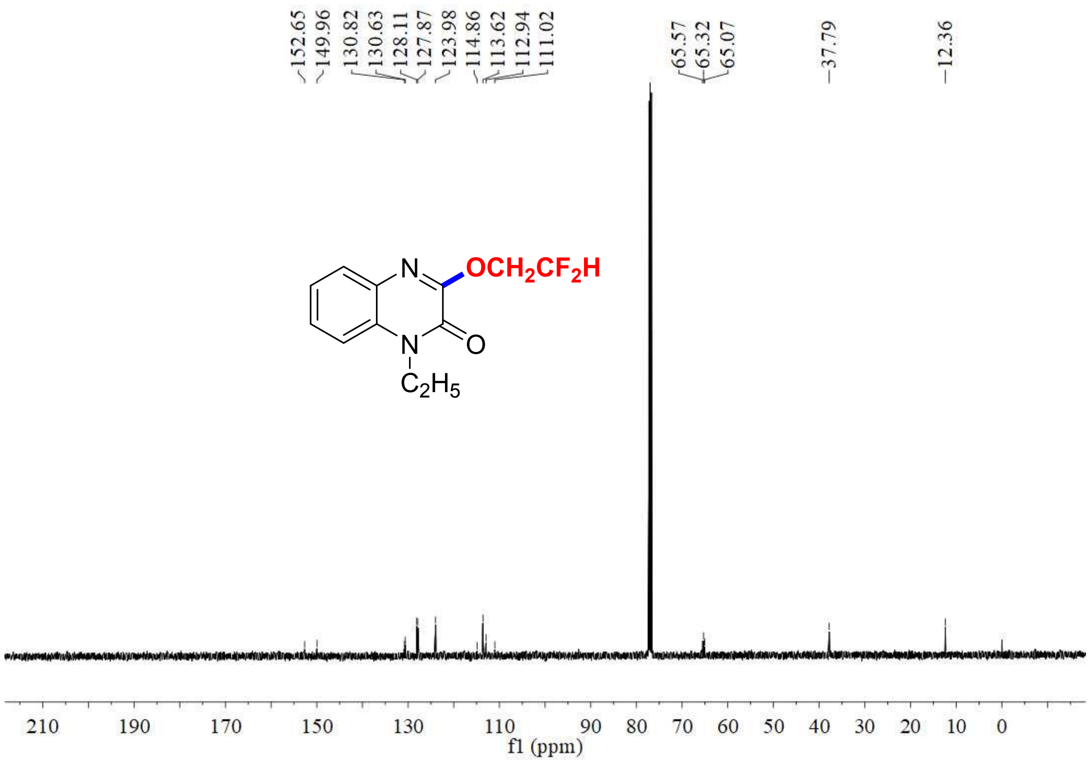

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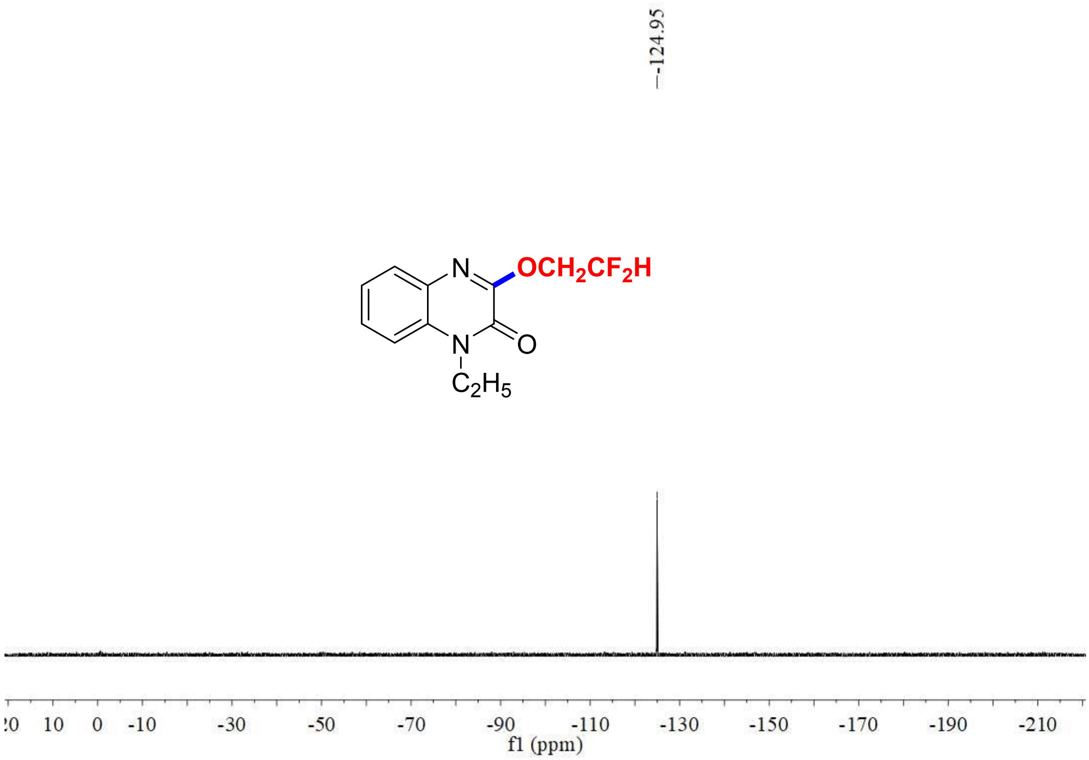

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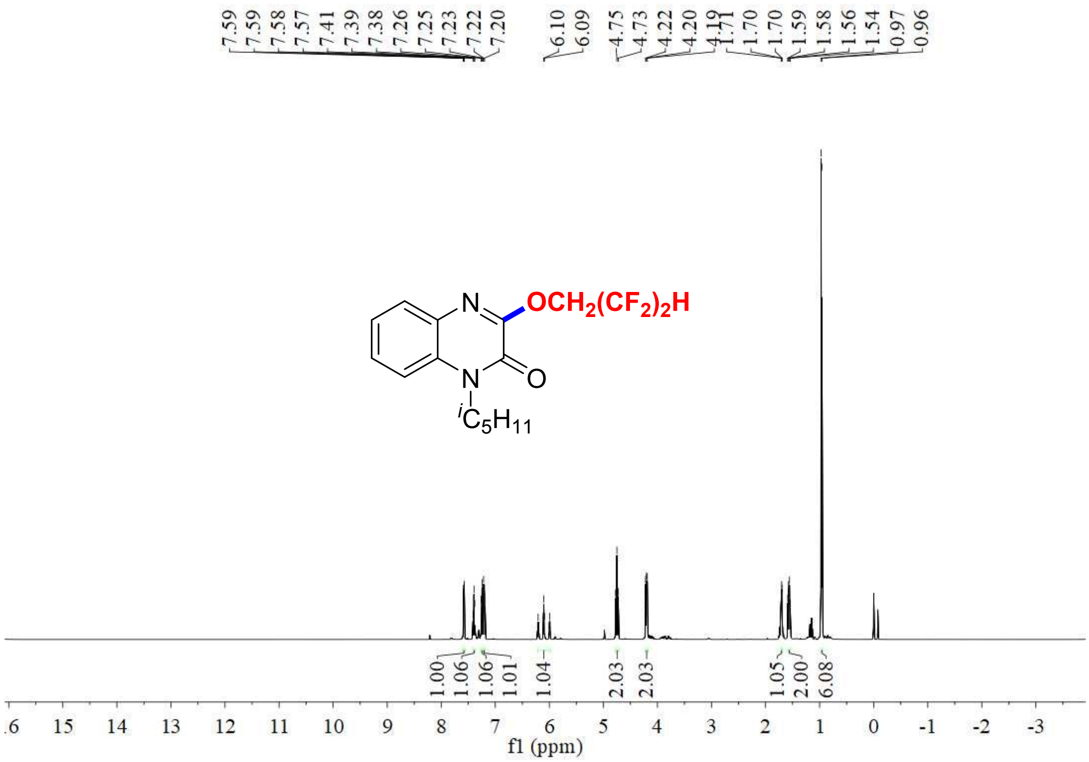

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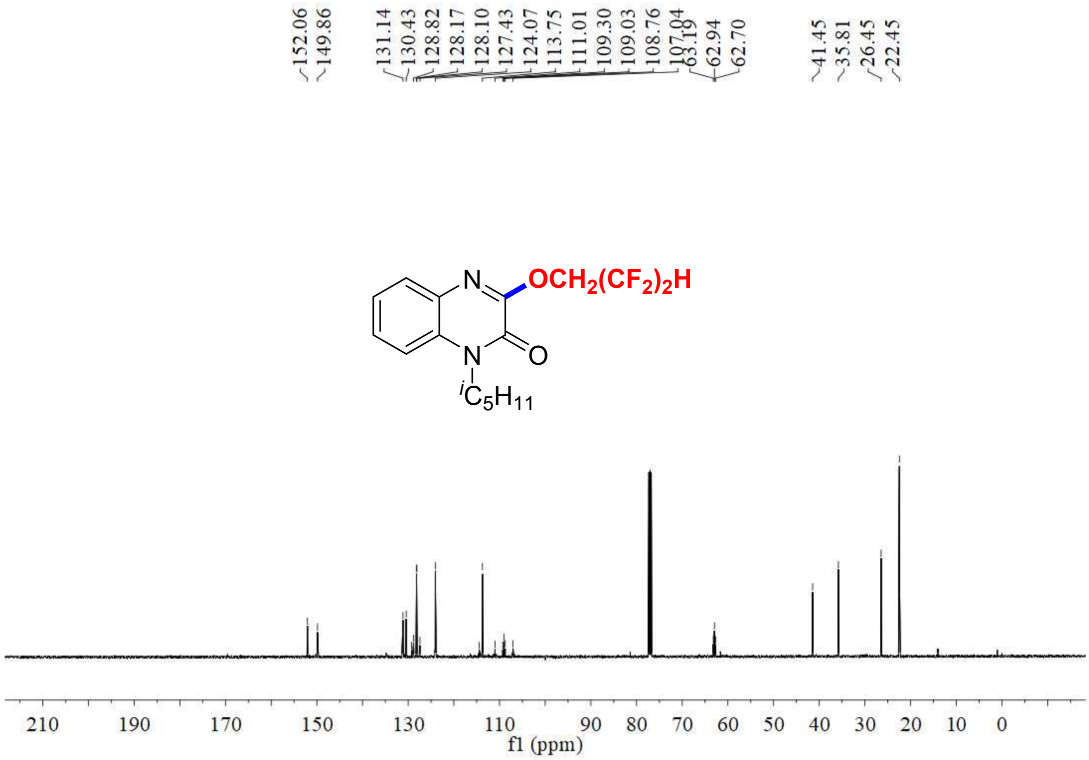

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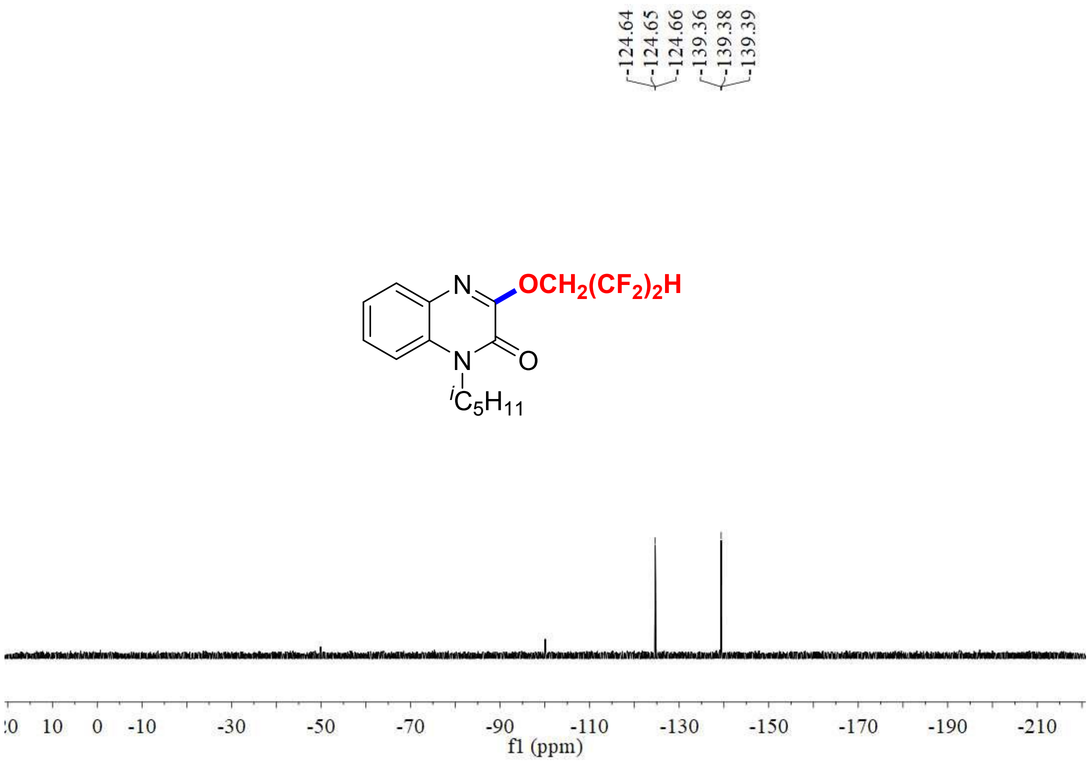

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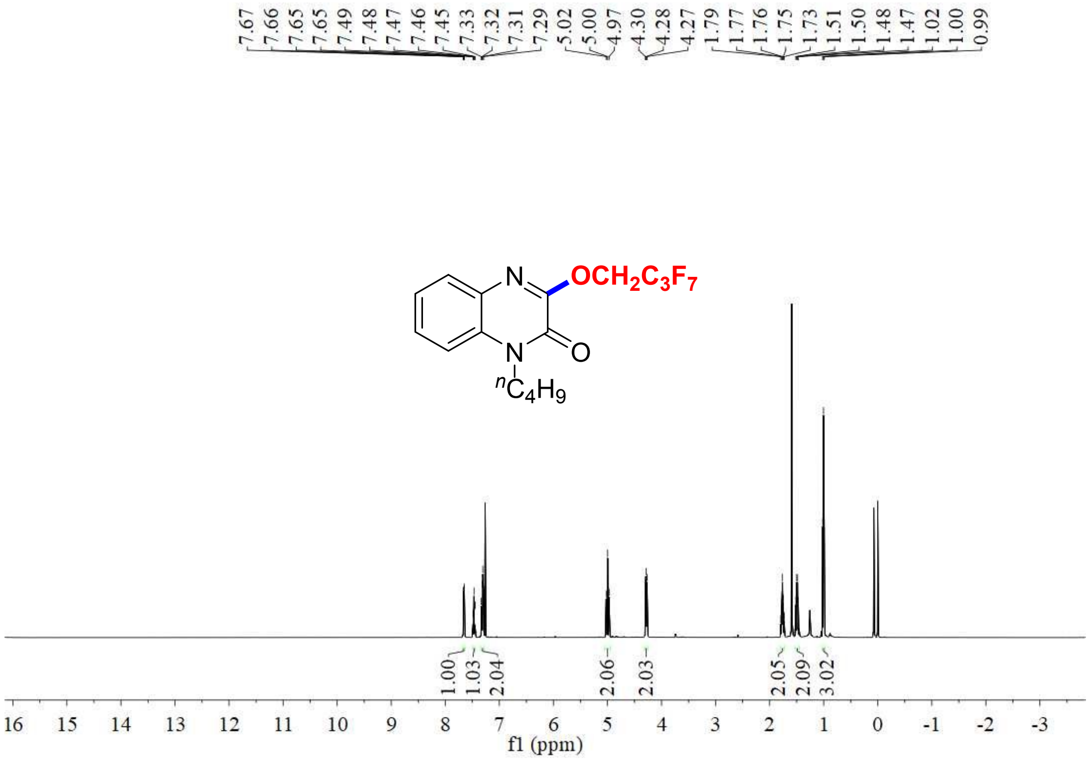

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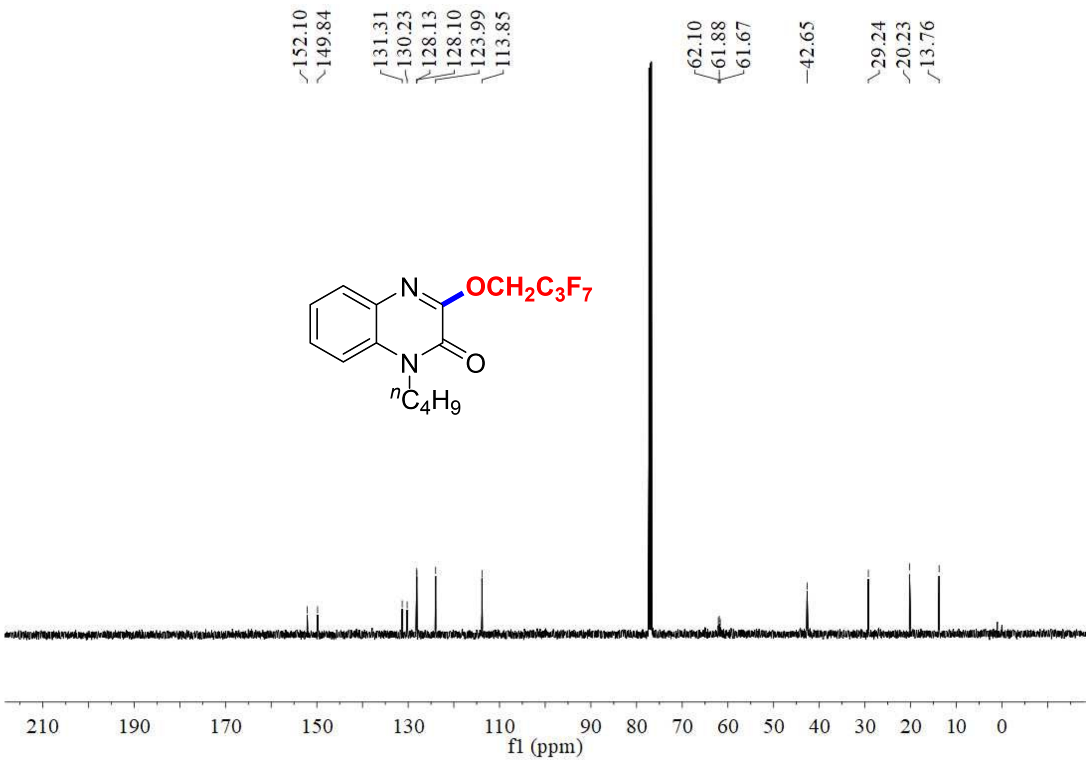

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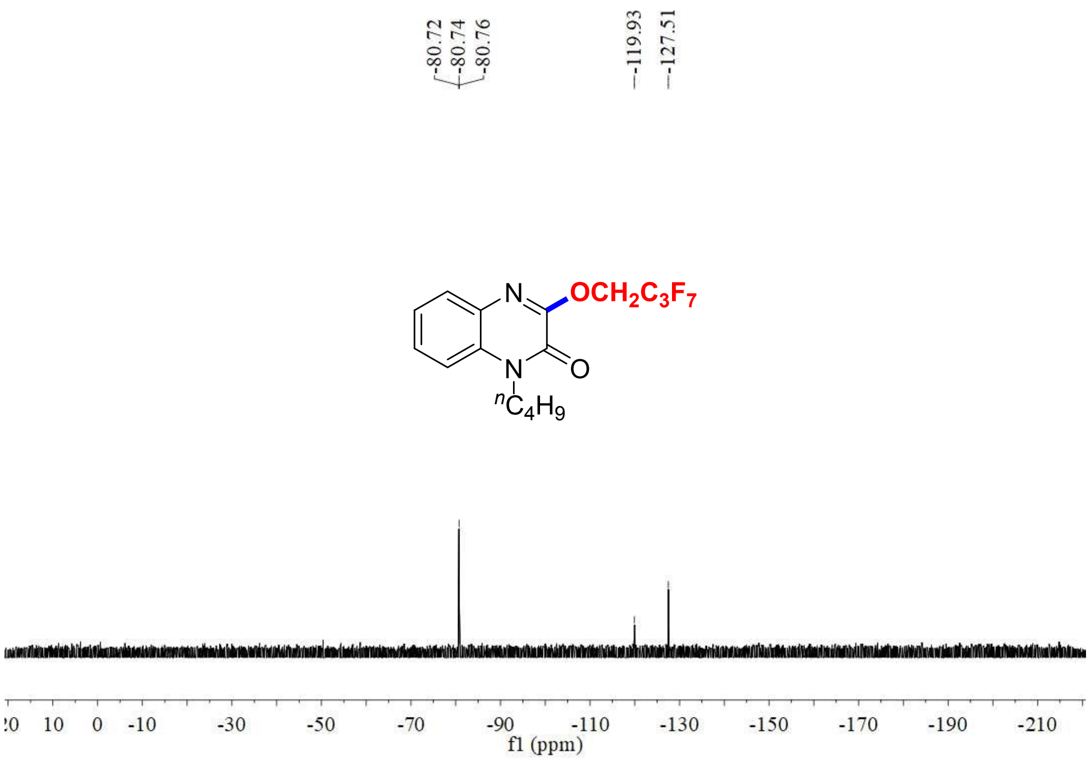

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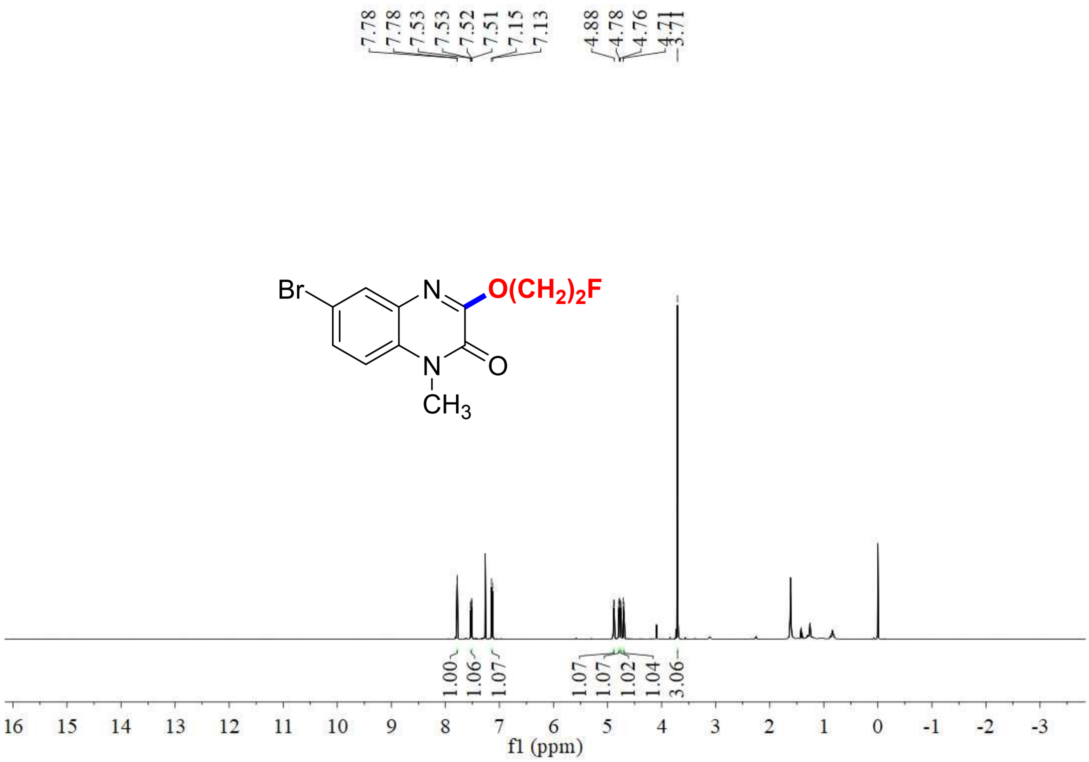

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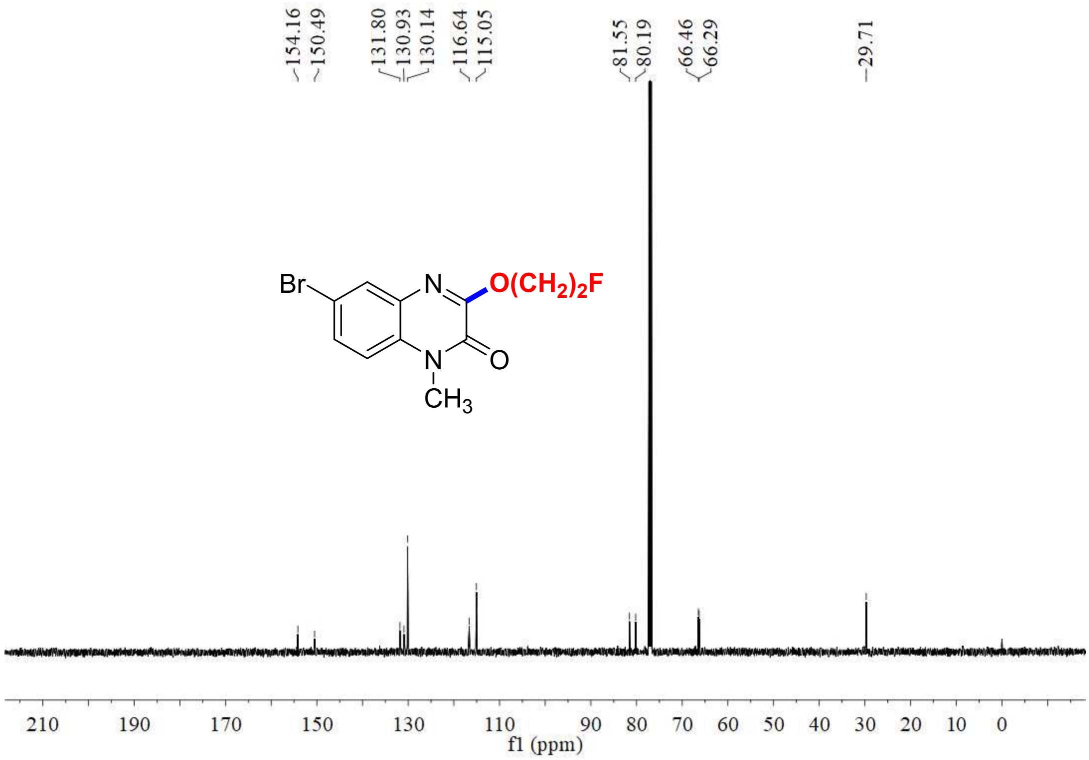

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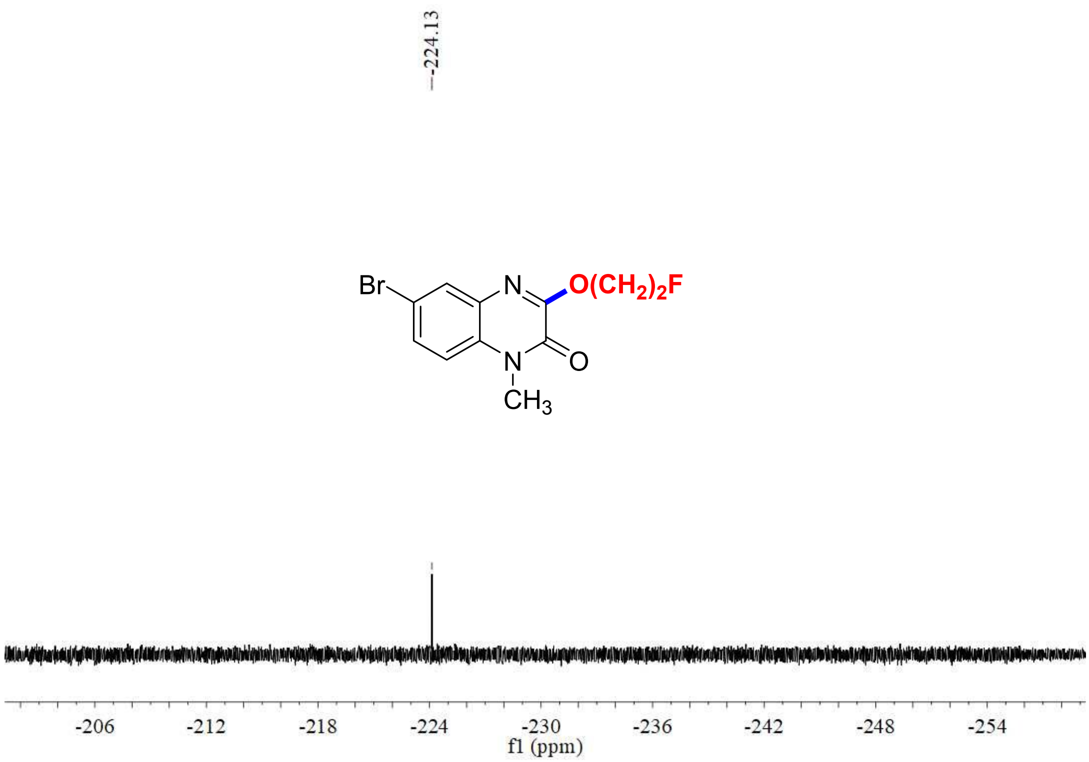

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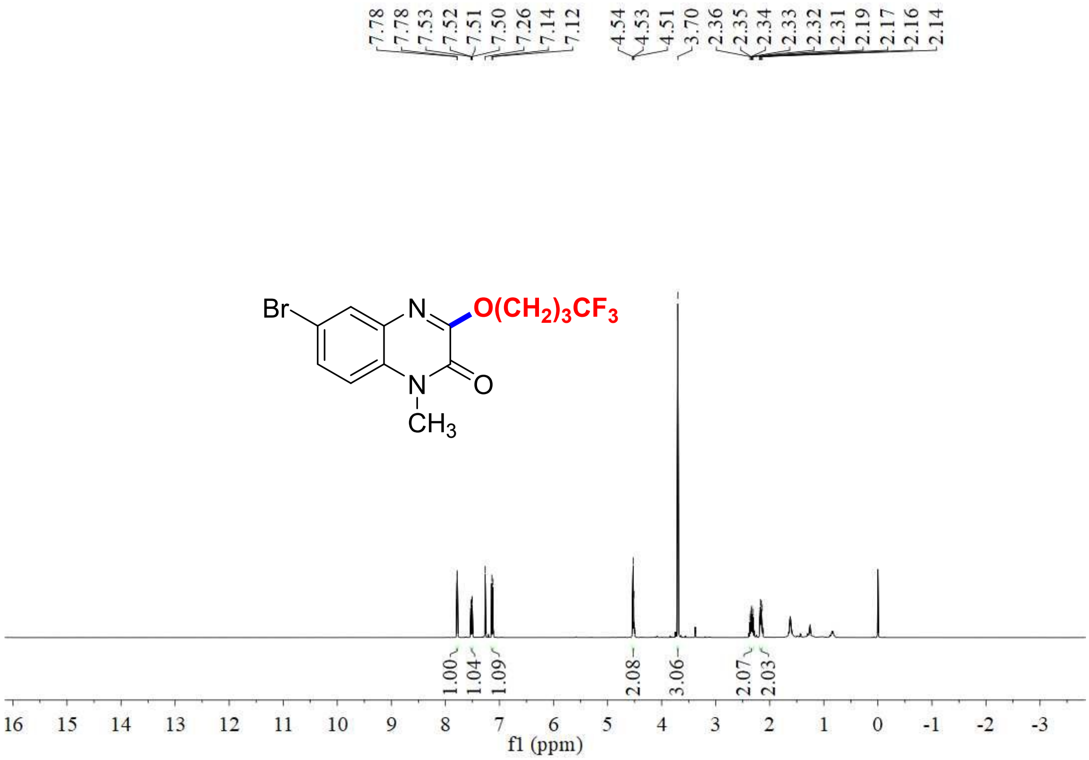

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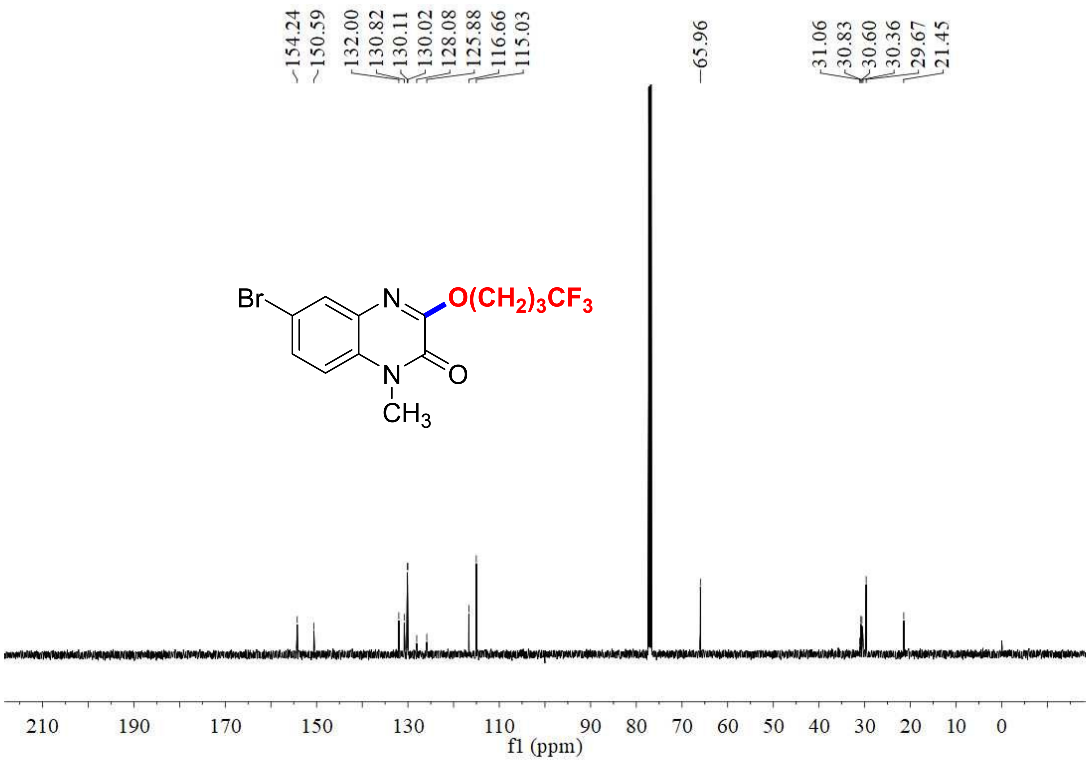

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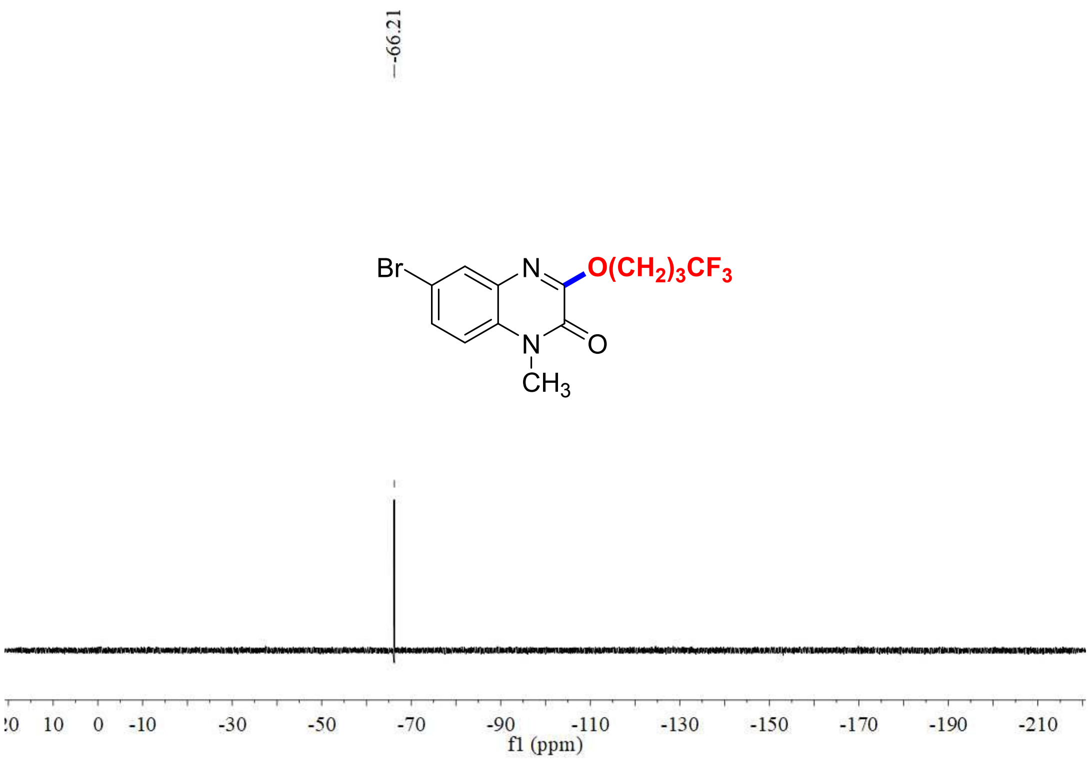

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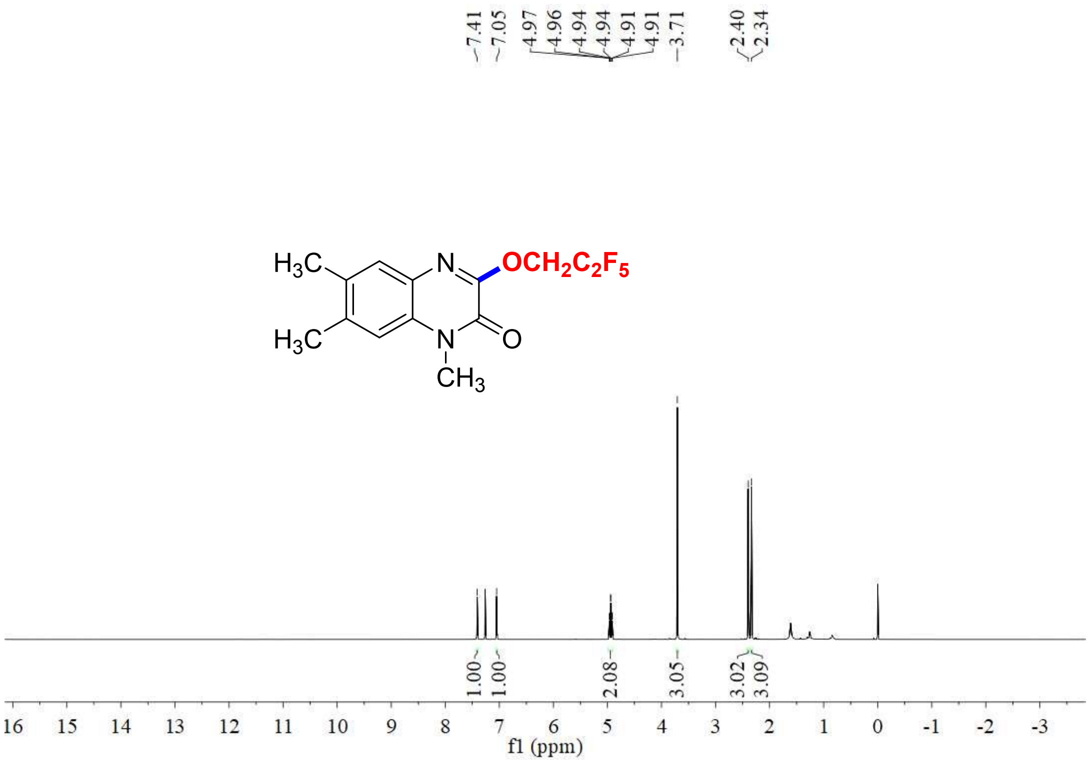

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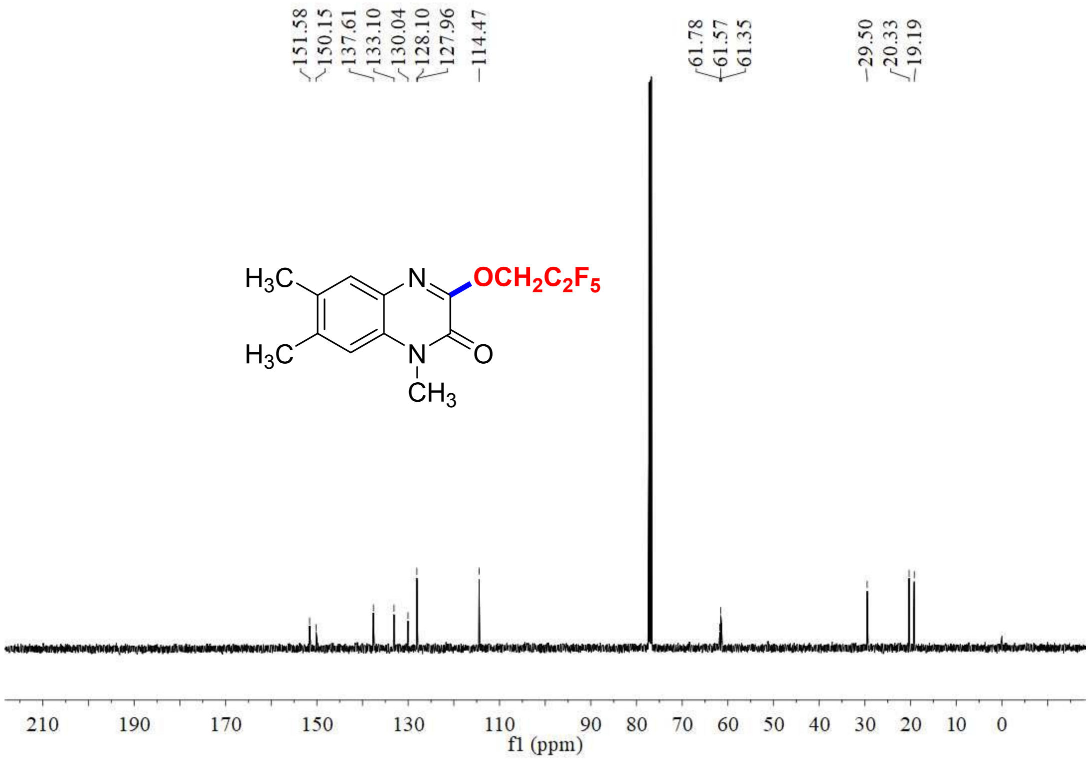

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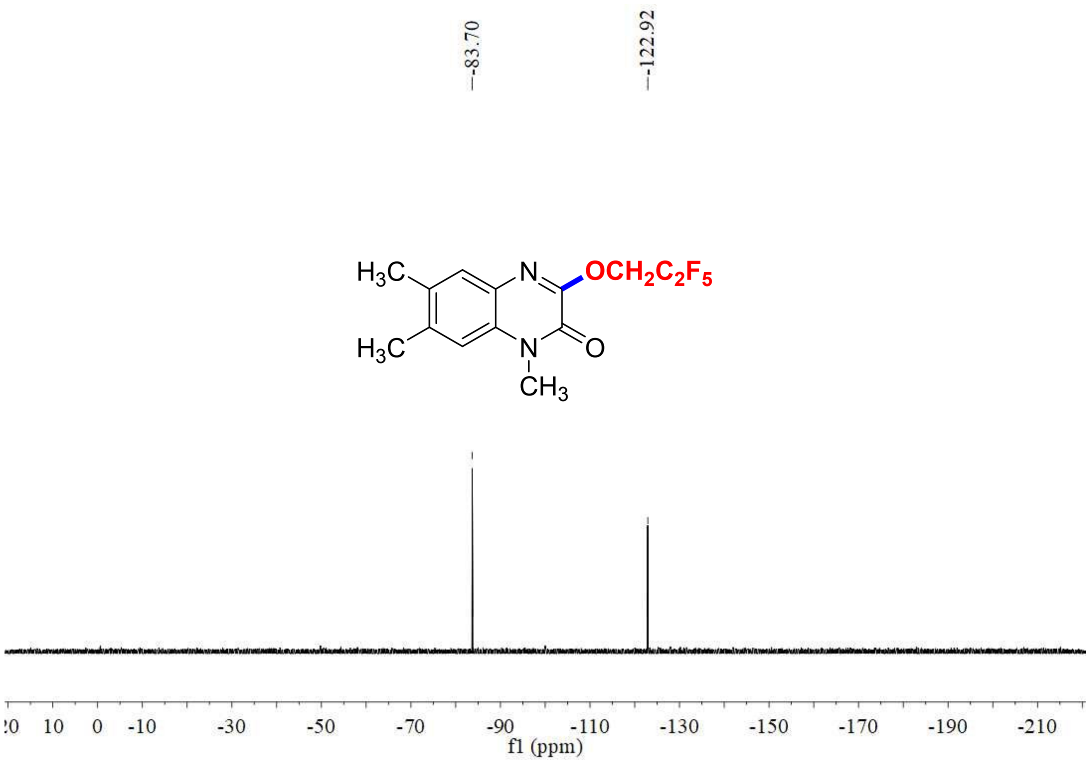

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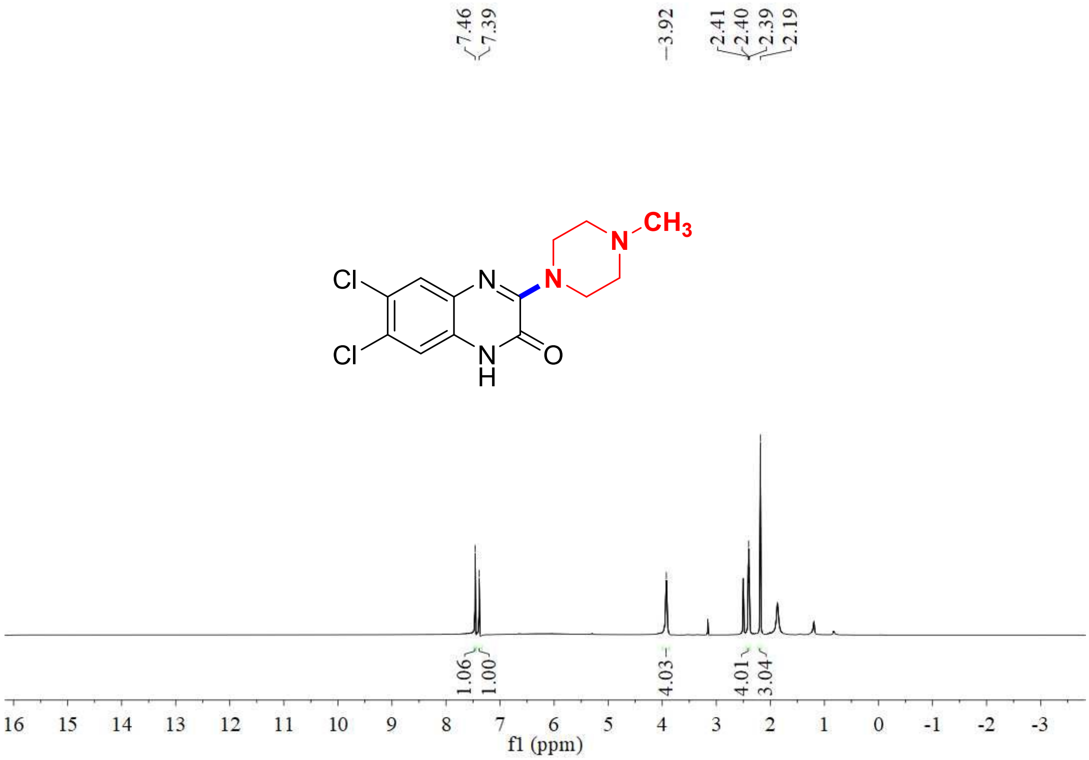

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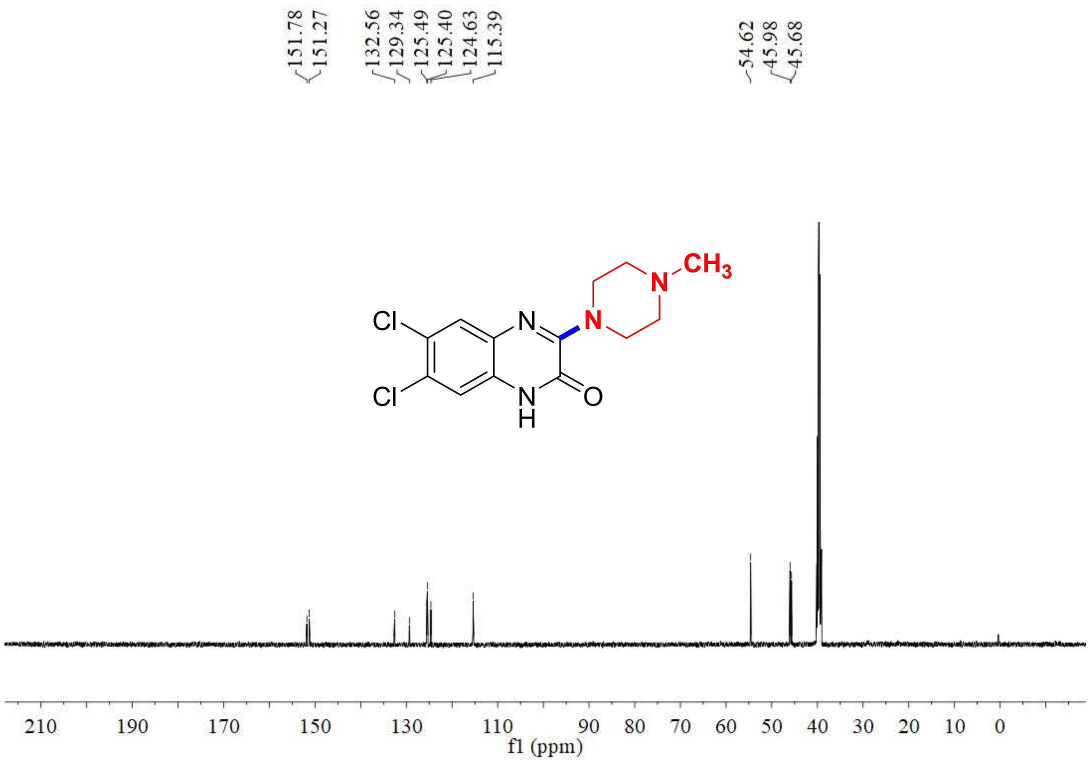

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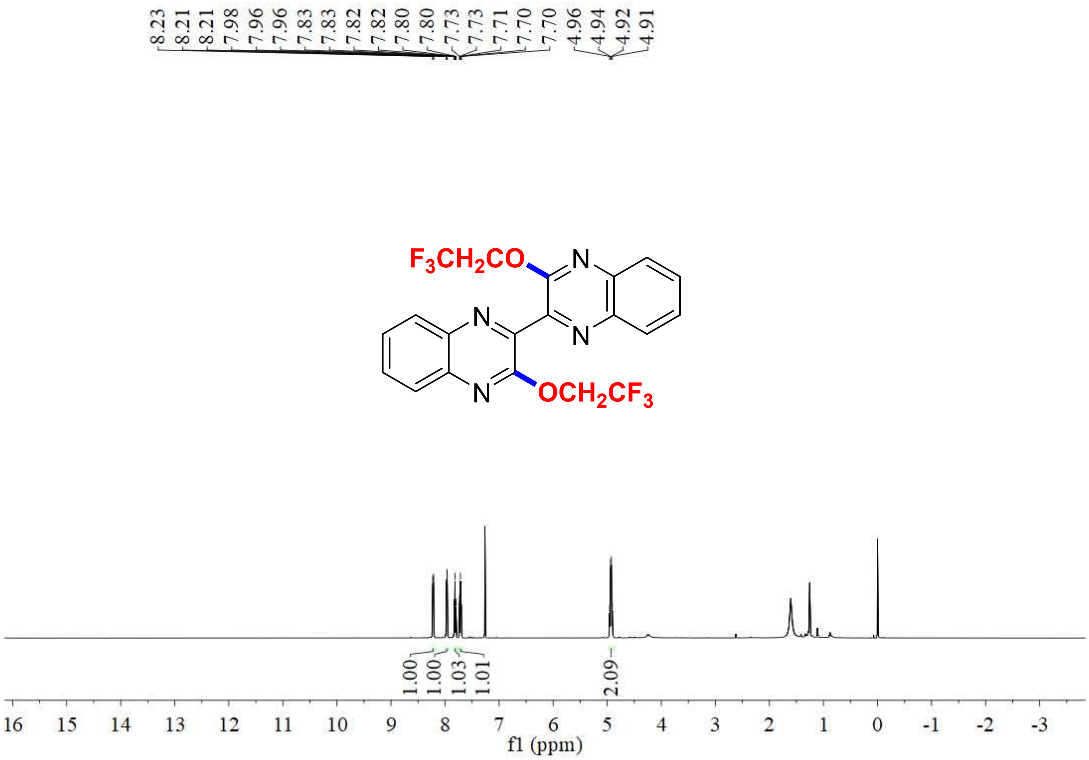

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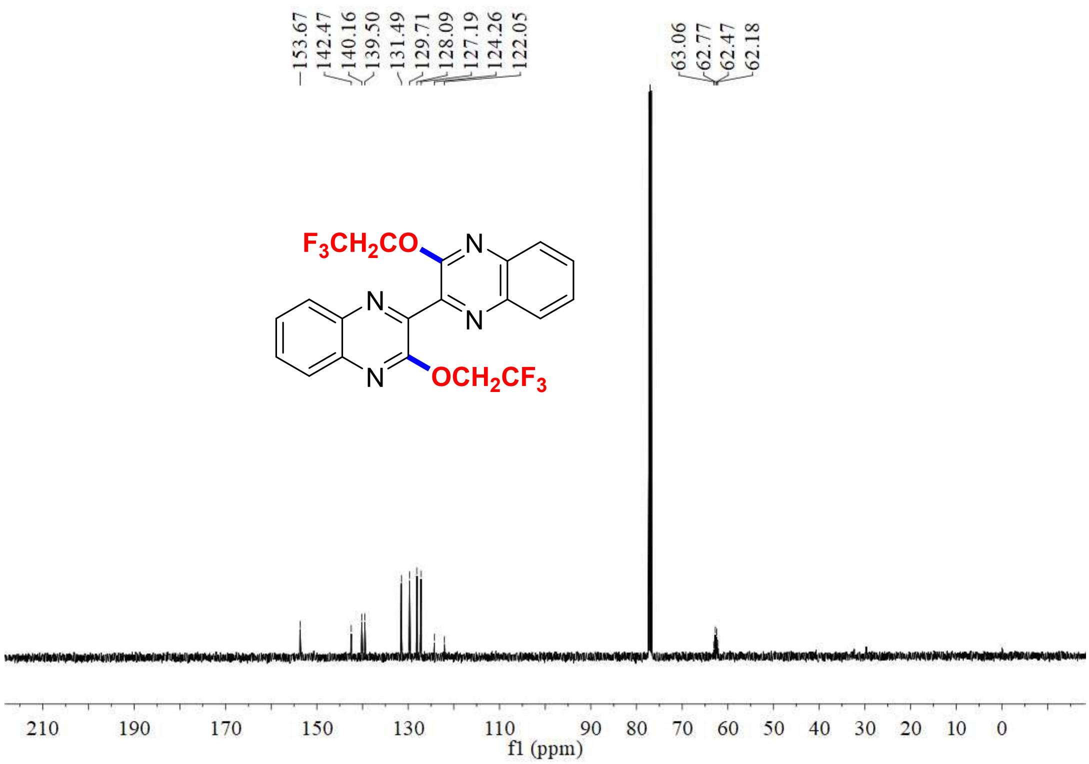

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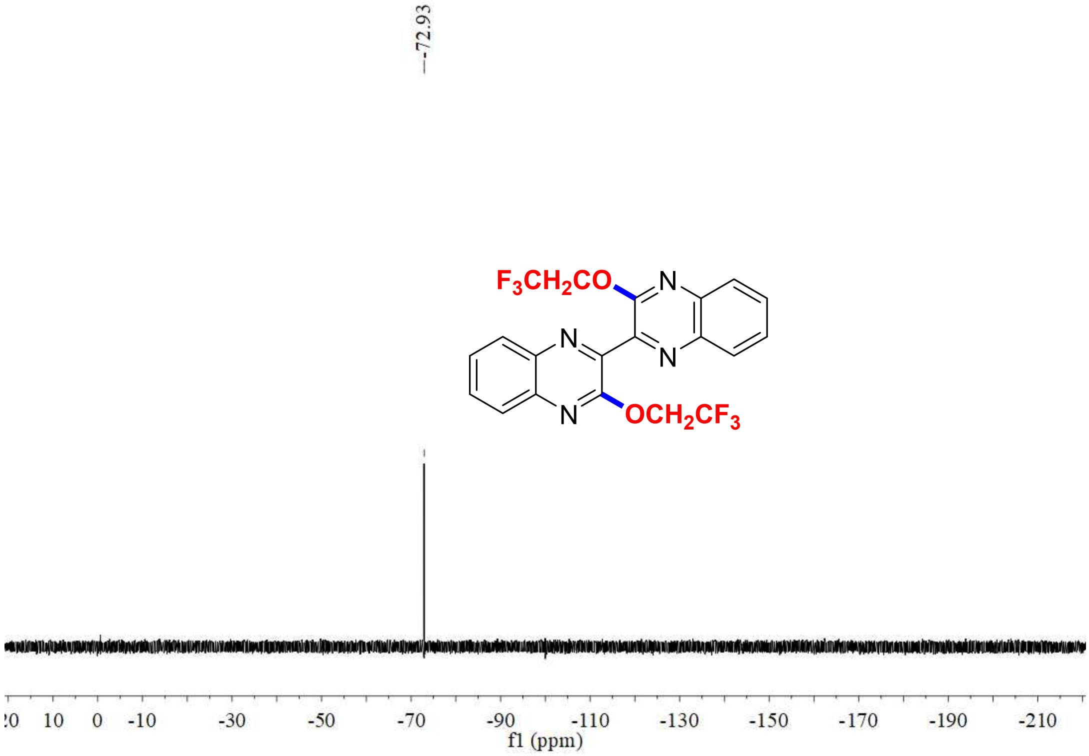

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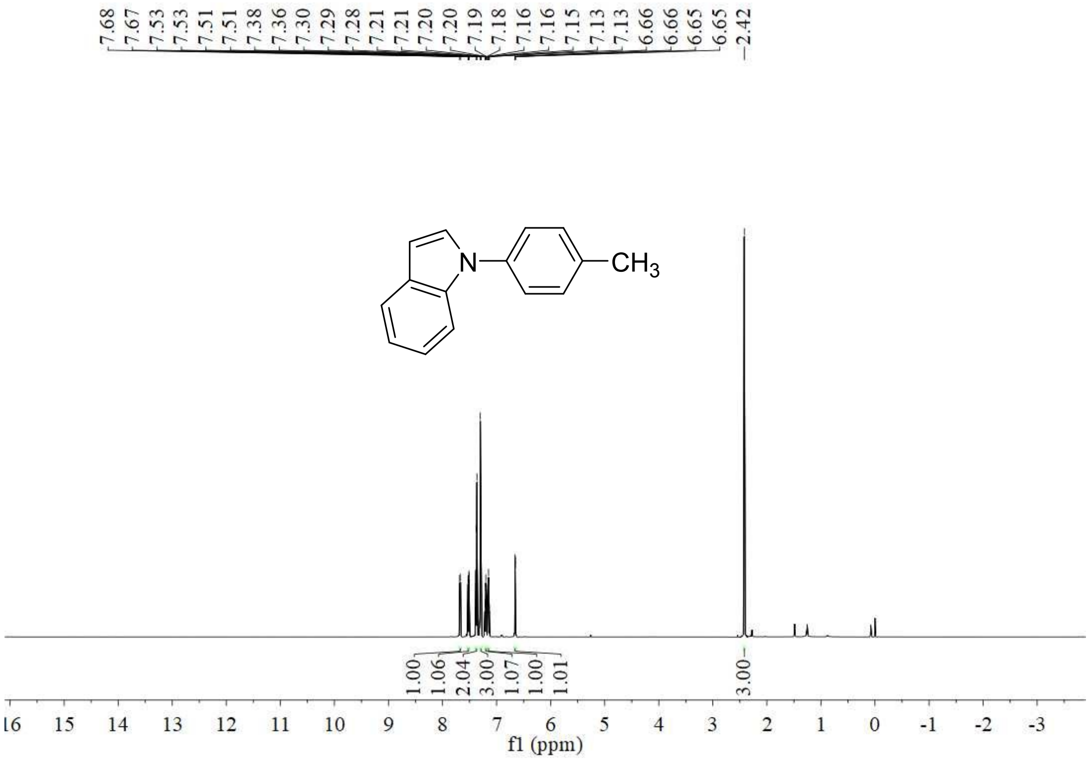

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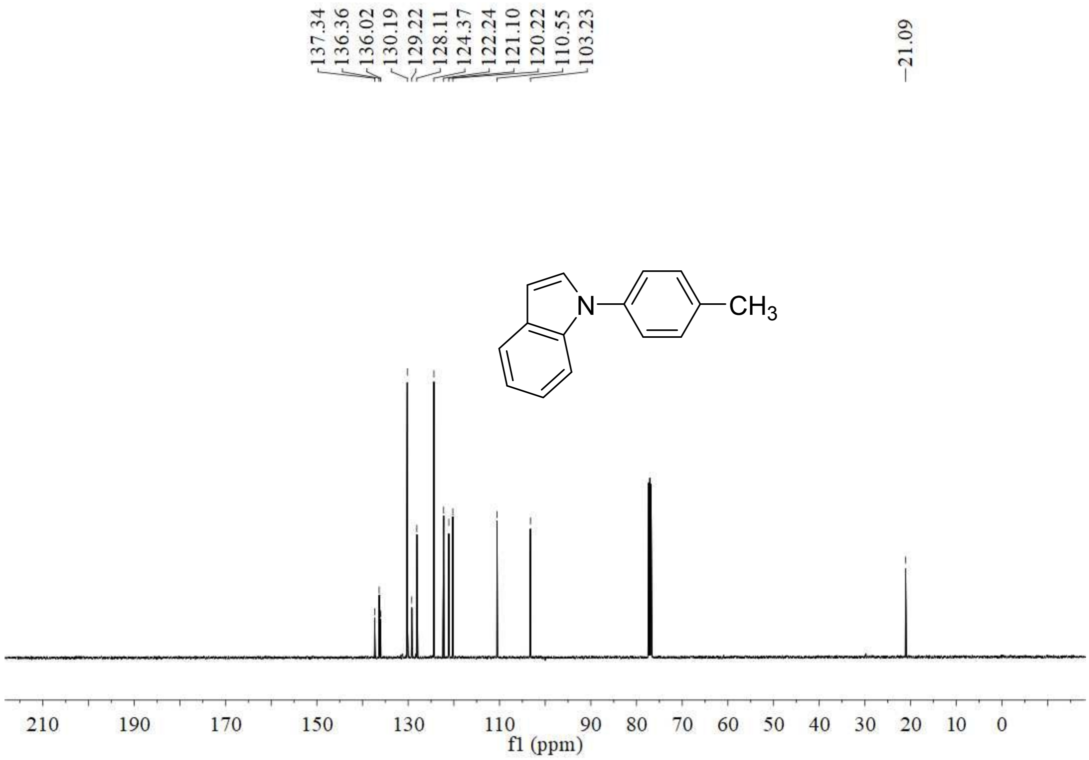

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f1 (ppm)