Supporting Information for:

Silver-Catalyzed Formal [3+2]-Cycloaddition of α-Trifluoromethylated Methyl Isocyanides for the Divergent Synthesis of CF_3-Substituted Heterocycles

Table of contents

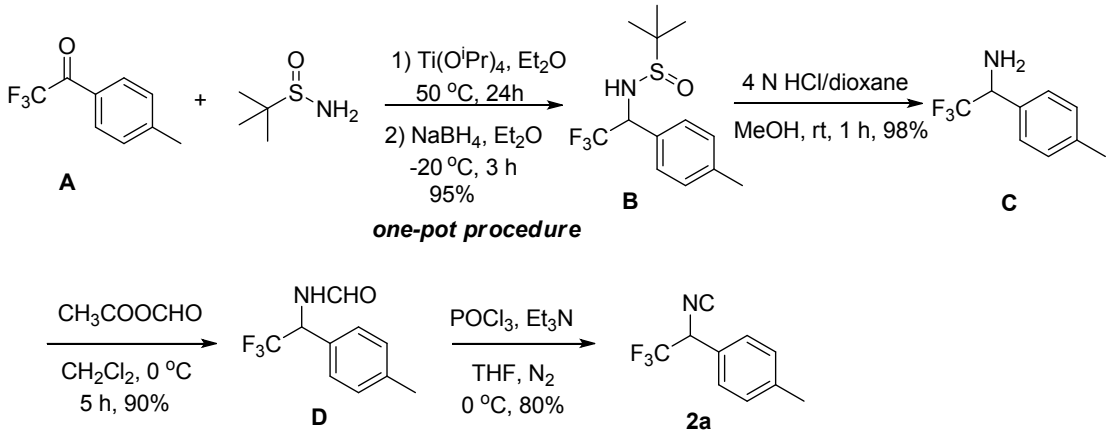
I. General Information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were uncorrected. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 25 ºC on a Varian 400 MHz, 500 MHz and 600 MHz. ^{1}H NMR and ^{13}C NMR were determined with TMS as the internal standard. ^{19}F NMR was determined with C_6H_5F as external reference. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a microTOF II focus spectrometer (ESI).

II. Synthesis and analytical data of α-trifluoromethylated isocyanide substrates 2

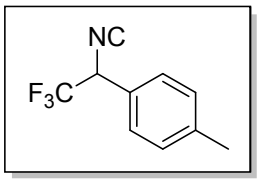
The trifluoromethylated amines were readily prepared from aryl trifluoromethyl ketones in high overall yields according to the literature procedures,[1] the trifluoromethylated isocyanides **2** were prepared by the typical procedure by formylation and dehydration.[2]

Taking 2a as an example:

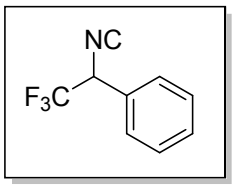


1. (a) Xu, J.; Liu, Z. J.; Yang, X. J.; Wang, L. M.; Chen, G. L.; Liu, J. T. *Tetrahedron*. **2010**, *66*, 8933−8937. (b) Evans, J. W.; Ellman, J. A. *J. Org. Chem*. **2003**, *68*, 9948−9957.
2. (a) Neochoritis, C. G.; Stotani, S.; Mishra, B.; Dömling, A. *Org. Lett.* **2015**, *17*, 2002−2005. (b) Sisko, J.; Mellinger, M.; Sheldrake, P. W.; Baine, N. H. *Tetrahedron Lett*. **1996**, *37*, 8113−8116.

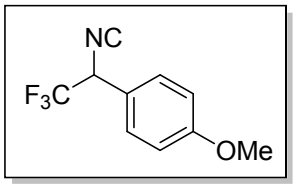
Analytical data of compounds 2



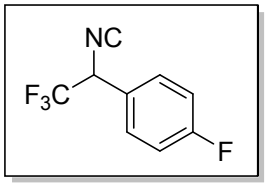
2a, 1-Methyl-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.40 (s, 3H), 5.12 (q, *J* = 6.4 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 59.5 (q, *J* = 33.0 Hz), 121.7 (q, *J* = 280.4 Hz), 124.7, 127.6, 129.8, 140.8, 163.4.



2b, (2,2,2-Trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.16 (q, *J* = 6.0 Hz, 1H), 7.48 (s, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 59.7 (q, *J* = 33.5 Hz), 121.6 (q, *J* = 280.5 Hz), 125.5, 127.8, 129.1, 130.5. 163.8.

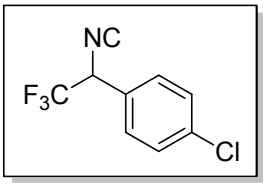


2c, 1-Methoxy-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.83 (s, 3H), 5.09 (q, *J* = 6.6 Hz, 1H), 6.96-6.98 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 55.3, 59.2 (q, *J* = 35.1 Hz), 114.5, 119.6, 121.7 (q, *J* = 279.9 Hz), 129.1, 161.2, 163.5.

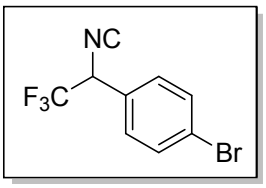


2d, 1-Fluoro-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.17 (q, *J* = 6.0 Hz, 1H), 7.15-7.19 (m, 2H), 7.46-7.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 59.0 (q, *J* = 34.6 Hz), 116.4 (d, *J* = 22.3 Hz), 121.5 (q, *J* = 280.4 Hz), 123.6 (d, *J* = 3.1 Hz), 129.8

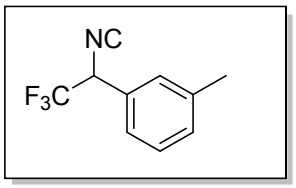
(d, J = 8.6 Hz), 163.9 (d, J = 249.6 Hz), 164.2.



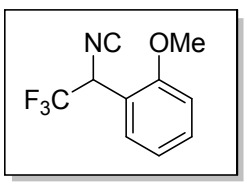
2e, 1-Chloro-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.15 (q, J = 6.0 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 59.1 (q, J = 34.4 Hz), 121.4 (q, J = 280.6 Hz), 126.1, 129.1, 129.5, 136.9. 164.4. HRMS (ESI-TOF) Calcd for $C_9H_4ClF_3N$ $(M-H)^-$ 217.9990. Found 217.9978.



2f, 1-Bromo-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.14 (q, J = 6.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.2 (q, J = 30.8 Hz), 121.3 (q, J = 280.4 Hz), 125.1, 126.6, 129.3, 132.4, 164.5.

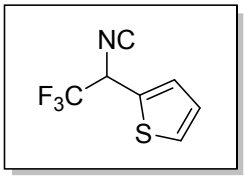


2g, 1-Methyl-3-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.40 (s, 3H), 5.11 (q, J = 6.0 Hz, 1H), 7.25-7.30 (m, 3H), 7.33-7.36 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 59.7 (q, J = 36.9 Hz), 121.7 (q, J = 280.4 Hz), 124.9, 127.5, 128.3, 129.0, 131.3, 139.2, 163.5.

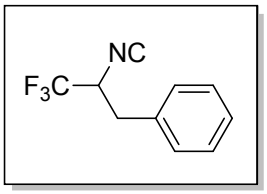


2h, 1-Methoxy-2-(2,2,2-trifluoro-1-isocyanoethyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.87 (s, 3H), 5.82 (q, J = 5.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.8 (q, J = 34.9

Hz), 55.8, 110.9, 116.6, 121.2, 122.0 (q, J = 280.6 Hz), 128.5, 131.8, 156.5, 162.0.

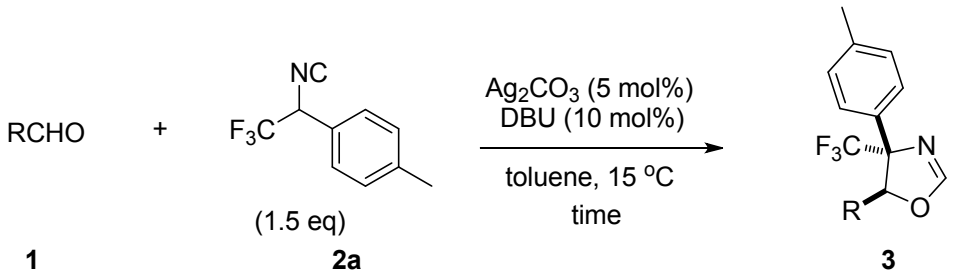


2i, 2-(2,2,2-Trifluoro-1-isocyanoethyl)thiophene. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.42 (d, J = 5.2 Hz, 1H), 7.08 (s, 1H), 7.29 (s, 1H), 7.47 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 55.6 (q, J = 40.7 Hz), 121.2 (q, J = 280.4 Hz), 127.3, 128.4, 128.8, 129.4, 164.5.



2j, (3,3,3-Trifluoro-2-isocyanopropyl)benzene. Yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.98-3.03 (m, 1H), 3.19 (d, J = 12.5 Hz, 1H), 4.18-4.22 (m, 1H), 7.28 (d, J = 7.0 Hz, 2H), 7.34-7.40 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 35.0, 58.1 (q, J = 32.0 Hz), 122.1 (q, J = 279.9 Hz), 128.1, 129.0, 129.2, 133.3, 163.7.

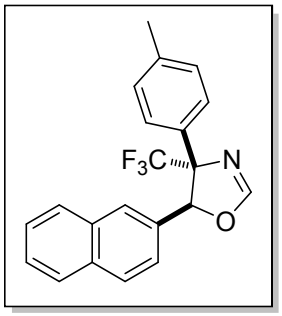
III. Synthetic procedures and analytical data of compounds 3, 5, 7, 9



1 **2a** **3**

General procedure for the synthesis of 3 (taking 3aa as an example): To a solution of 2-naphthaldehyde (**1**) (31.2 mg, 0.2 mmol) and 1-methyl-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene (**2a**) (59.7 mg, 0.3 mmol) in toluene (2 ml) at 15 ºC was added Ag_2CO_3 (2.8 mg, 5.0 mol %) and DBU (3.0 μL, 10.0 mol %). After the reaction was finished as indicated by TLC (reaction time, 2.5 h), the resulting mixture was poured into water (10 mL) and extracted with DCM (CH_2Cl_2, 10 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification of the crude product with flash column chromatography (petroleum ether /EtOAc = 15:1) to give **3aa** (67.5 mg, 95%).

3aa, the isomers could not readily be separated by silica gel chromatography. The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 3.7:1 mixture of **3aa** based on the methyne peak at δ 6.08 and at δ 5.83.

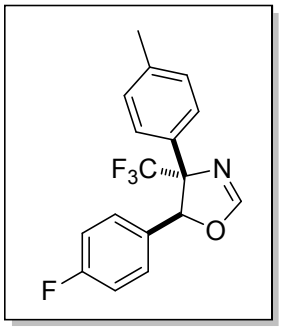


3aa, 5-(Naphthalen-2-yl)-4-(*p*-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

Mixture of two diasteroisomers, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.11 and 2.41 (s, 3H, two isomers), 5.83 and 6.08 (s, 1H, two isomers), 6.74-6.76 (m, 2H, one isomer), 7.06 (d, J = 8.0 Hz, 1H, one isomer), 7.30 (d, J = 8.0 Hz, 1H, one isomer), 7.44-7.50 (m, 3H, one isomer), 7.53-7.57 (m, 1H, one isomer), 7.62-7.63 (m, 1H, two isomers), 7.69-7.77 (m, 2H, one isomer), 7.88-7.95 (m, 1H, one isomer). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.2, -72.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}F_3NO$ ($[M + H]^+$) 356.1257, found 356.1255.

For the major isomer **3aa1**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.11 (s,

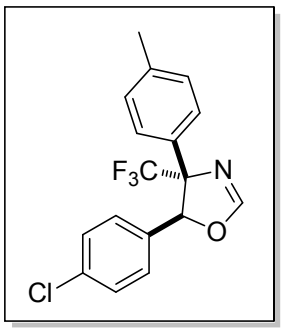
3H), 6.08 (s, 1H), 6.75-6.80 (m, 3H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.44-7.50 (m, 4H), 7.62 (s, 1H), 7.69-7.71 (m, 1H), 7.76-7.77 (m, 1H).



3ba, 5-(4-Fluorophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.9:1 mixture of **3ba** based on the methyne peak at δ 5.89 and at δ 5.64.

For **3ba**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 and 2.39 (s, 3H, two isomers), 5.64 and 5.89 (s, 1H, two isomers), 6.79-6.90 (m, 5H, two isomers), 6.99 (d, *J* = 8.0 Hz, 1H, one isomer), 7.10-7.27 (m, 1H, one isomer), 7.38 (d, *J* = 2.8 Hz, 1H, one isomer), 7.43-7.55 (m, 1H, one isomer). ^{19}F NMR (564 MHz, $CDCl_3$, the major isomer) δ -112.3 – -112.2 (m), -75.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}F_4NO$ ($[M + H]^+$) 324.1006, found 324.0998.

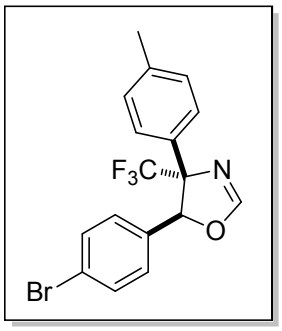


3ca, 5-(4-Chlorophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.7:1 mixture of **3ca** based on the methyne peak at δ 5.87 and at δ 5.62.

For **3ca**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.21 and 2.39 (s, 3H, two isomers), 5.62 and 5.87 (s, 1H, two isomers), 6.83-6.91 (m, 3H, two isomers), 7.00 (d, *J* = 8.0 Hz, 2H, one isomers), 7.08-7.27 (m, 2H, two isomers), 7.38-7.54 (m, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 81.6 (q, *J* = 26.4 Hz), 84.4, 125.4 (q, *J* = 281.6 Hz), 127.8, 128.3, 128.5, 129.0, 129.6, 133.4, 134.6, 138.1, 157.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.8,

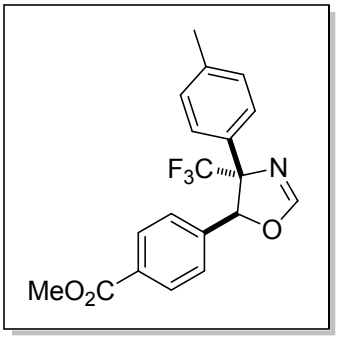
-67.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}ClF_3NO$ ($[M + H]^+$) 340.0711, found 340.0706.



3da, 5-(4-Bromophenyl)-4-(*p*-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.7:1 mixture of **3da** based on the methyne peak at δ 5.85 and at δ 5.60.

For **3da**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.22 and 2.39 (s, 3H, two isomers), 5.60 and 5.85 (s, 1H, two isomers), 6.78 (d, J = 8.4 Hz, 2H, one isomer), 6.90 (d, J = 8.4 Hz, 1H, one isomer), 7.00 (d, J = 8.4 Hz, 1H, one isomer), 7.24-7.27 (m, 2H, two isomers), 7.33-7.38 (m, 2H, two isomers), 7.52-7.57 (m, 1H, one isomer). ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.7, -67.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}BrF_3NO$ ($[M + H]^+$) 384.0205, found 384.0205.

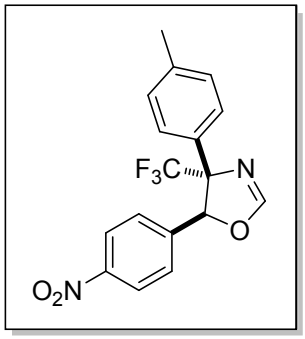


3ea, Methyl 4-(4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazol-5-yl)benzoate.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.6:1 mixture of **3ea** based on the methyne peak at δ 5.94 and at δ 5.70.

For **3ea**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 and 2.39 (s, 3H, two isomers), 3.86 and 3.94 (s, 3H, two isomers), 5.70 and 5.94 (s, 1H, two isomers), 6.86 and 7.00 (d, J = 8.4 Hz and 8.4 Hz, 5H, one isomer), 7.26-7.41 (m, 1H, two isomers), 7.56 (d, J = 8.0 Hz, 1H, one isomer), 7.79 and 8.11 (d, J = 8.4 Hz and 8.4 Hz, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 52.2, 81.9 (q, J = 26.3 Hz), 84.5, 125.3 (q, J = 281.6 Hz), 127.6,

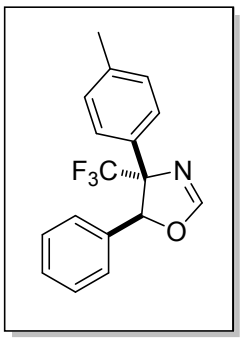
127.7, 128.5, 129.2, 129.5, 129.6, 138.1, 139.8, 157.2, 166.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.6, -67.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{17}F_3NO_3$ ($[M + H]^+$) 364.1155, found 364.1156.



3fa, 5-(4-Nitrophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3:1 mixture of **3fa** based on the methyne peak at δ 5.97 and at δ 5.74.

For **3fa**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.19 and 2.40 (s, 3H, two isomers), 5.74 and 5.97 (s, 1H, two isomers), 6.89 and 6.98 (d, J = 8.0 Hz and 8.4 Hz, 3H, one isomer), 7.11 (d, J = 8.8 Hz, 2H, one isomer), 7.28-7.44 (m, 1H, two isomers), 7.54 and 7.66 (d, J = 8.4 Hz and 8.8 Hz, 1H, one isomer), 7.98 and 8.30 (d, J = 8.8 Hz and 8.8 Hz, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 82.3 (q, J = 26.5 Hz), 83.8, 123.2, 125.2 (q, J = 281.5 Hz), 127.5, 128.4, 128.7, 129.7, 138.5, 142.0, 147.7, 157.1. ^{19}F NMR (564 MHz, $CDCl_3$, the major isomer) δ -75.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}F_3N_2O_3$ ($[M + H]^+$) 351.0951, found 351.0958.

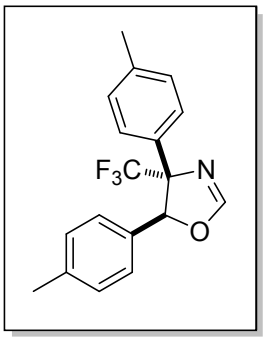


3ga, 5-(4-Nitrophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.6:1 mixture of **3ga** based on the methyne peak at δ 5.90 and at δ 5.66.

For **3ga**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 and 2.39 (s, 3H, two isomers), 5.66 and 5.90 (s, 1H, two isomers), 6.85-6.91 (m, 2H, two isomers), 7.01 (d, J = 8.0 Hz,

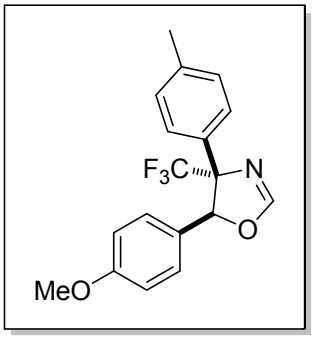
1H, one isomer), 7.12 (q, J = 7.6 Hz, 2H, one isomer), 7.26 (d, J = 8.0 Hz, 1H, one isomer), 7.39-7.47 (m, 3H, two isomers), 7.57 (d, J = 8.0 Hz, 1H, one isomer). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 81.5 (q, J = 26.4 Hz), 85.2, 125.5 (q, J = 281.8 Hz), 127.7, 127.9, 127.9, 128.0, 128.2, 128.7, 134.8, 137.8, 157.3. ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.9, -67.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{15}F_3NO$ ($[M + H]^+$) 306.1100, found 306.1108.



3ha, 4,5-Di-*p*-tolyl-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.7:1 mixture of **3ha** based on the methyne peak at δ 5.88 and at δ 5.63.

For **3ha**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 and 2.22 (s, 5H, one isomer), 2.38 and 2.39 (s, 1H, one isomer), 5.63 and 5.88 (s, 1H, two isomers), 6.77-7.04 (m, 7H, one isomer), 7.22-7.57 (m, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 21.1, 81.3 (q, J = 26.3 Hz), 85.2, 125.5 (q, J = 281.8 Hz), 127.7, 128.0, 128.2, 128.7, 129.0, 129.5, 137.7, 138.6, 157.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.2, -67.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{17}F_3NO$ ($[M + H]^+$) 320.1257, found 320.1244.

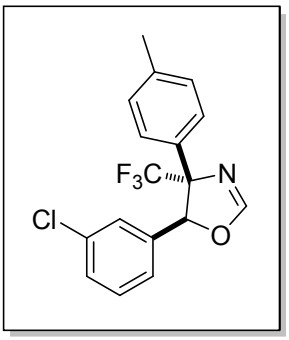


3ia, 5-(4-Methoxyphenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.7:1 mixture of **3ia** based on the methyne peak at δ 5.87 and at δ 5.62.

For **3ia**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 and 2.38 (s, 3H, two

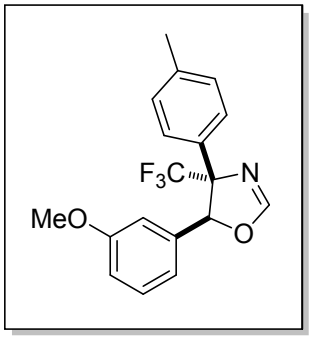
isomers), 3.71 and 3.84 (s, 3H, two isomers), 5.62 and 5.87 (s, 1H, two isomers), 6.62-6.83 (m, 3H, one isomer), 6.88-7.04 (m, 4H, two isomers), 7.24-7.56 (m, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 55.2, 81.1 (q, J = 26.0 Hz), 85.1, 113.4, 125.5 (q, J = 281.8 Hz), 126.7, 128.0, 128.3, 129.2, 129.5, 137.7, 157.3, 159.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.3, -67.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{17}F_3NO_2$ ($[M + H]^+$) 336.1206, found 336.1190.



3ja, 5-(3-Chlorophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^1H NMR Spectroscopy. The ^1H NMR spectrum of the crude product showed a 3.3:1 mixture of **3ja** based on the methyne peak at δ 5.85 and at δ 5.62.

For **3ja**, yellow oil. NMR Spectroscopy: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.20 and 2.39 (s, 3H, two isomers), 5.62 and 5.85 (s, 1H, two isomers), 6.78-6.91 (m, 4H, two isomers), 7.00-7.13 (m, 4H, two isomers), 7.26-7.55 (m, 1H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 81.8 (q, J = 26.4 Hz), 84.3, 125.3 (q, J = 281.6 Hz), 125.7, 127.7, 128.4, 128.8, 129.3, 129.5, 129.6, 134.0, 136.8, 138.1, 157.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.6, -67.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}ClF_3NO$ ($[M + H]^+$) 340.0711, found 340.0717.

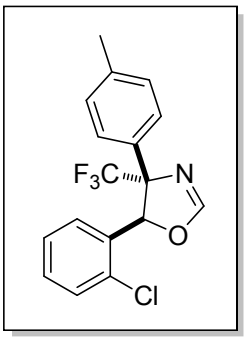


3ka, 5-(3-Methoxyphenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^1H NMR Spectroscopy. The ^1H NMR spectrum of the crude product showed a 3.9:1 mixture of **3ka** based on the methyne peak at δ 5.86 and at δ 5.61.

For **3ka**, yellow oil. NMR Spectroscopy: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.20 and 2.38 (s, 3H, two

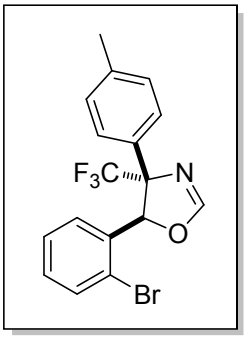
isomers), 3.58 and 3.84 (s, 3H, two isomers), 5.61 and 5.86 (s, 1H, two isomers), 6.34-6.70 (m, 2H, one isomer), 6.87-7.07 (m, 5H, two isomers), 7.25-7.58 (m, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 55.1, 81.5 (q, J = 26.5 Hz), 85.0, 112.9, 114.7, 120.3, 125.4 (q, J = 281.6 Hz), 127.8, 128.2, 129.0, 129.5, 136.2, 137.8, 157.3, 159.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.8, -67.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{17}F_3NO_2$ ([M + H]$^+$) 336.1206, found 336.1219.



3la, 5-(2-Chlorophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.7:1 mixture of **3la** based on the methyne peak at δ 6.51 and at δ 6.12.

For **3la**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 and 2.38 (s, 3H, two isomers), 6.16 and 6.51 (s, 1H, two isomers), 6.60-6.91 (m, 3H, two isomers), 7.03-7.25 (m, 4H, two isomers), 7.31-7.65 (m, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 80.7, 82.3 (q, J = 26.8 Hz), 125.3 (q, J = 282.4 Hz), 126.6, 127.6, 128.4, 129.1, 129.1, 129.2, 129.8, 133.0, 133.3, 138.0, 157.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.3, -68.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}ClF_3NO$ ([M + H]$^+$) 340.0711, found 340.0721.

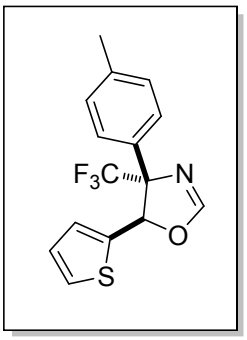


3ma, 5-(2-Bromophenyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.5:1 mixture of **3ma** based on the methyne peak at δ 6.51 and at δ 6.12.

For **3ma**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 and 2.38 (s, 3H, two

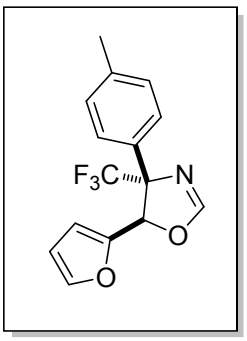
isomers), 6.12 and 6.51 (s, 1H, two isomers), 6.56 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H, one isomer), 6.88-6.99 (m, 3H, two isomers), 7.17-7.25 (m, 2H, two isomers), 7.34-7.66 (m, 3H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 82.3 (q, J = 26.8 Hz), 83.0, 123.3, 125.2 (q, J = 282.6 Hz), 127.2, 127.7, 128.4, 129.1, 129.4, 130.0, 132.4, 134.9, 138.0, 157.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.3, -68.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}BrF_3NO$ ($[M + H]^+$) 384.0205, found 384.0217.



3na, 5-(Thiophen-2-yl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 5:1 mixture of **3na** based on the methyne peak at δ 6.23 and at δ 5.92.

For **3na**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 and 2.38 (s, 3H, two isomers), 5.92 and 6.23 (s, 1H, two isomers), 6.79-6.90 (m, 2H, one isomer), 6.96 (d, J = 8.0 Hz, 2H, one isomer), 7.08-7.17 (m, 3H, two isomers), 7.25-7.33 (m, 1H, two isomers). ^{19}F NMR (470 MHz, $CDCl_3$, the major isomer) δ -78.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_{13}F_3NOS$ ($[M + H]^+$) 312.0664, found 312.0667.

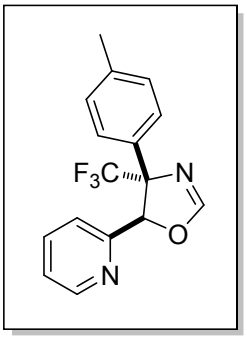


3oa, 5-(Furan-2-yl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydro oxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.5:1 mixture of **3oa** based on the methyne peak at δ 5.97 and at δ 5.71.

For **3oa**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.26 and 2.38 (s, 3H, two isomers), 5.71 and 5.97 (s, 1H, two isomers), 6.15-6.24 (m, 1H, one isomer), 6.47-6.56 (m, 1H,

one isomer), 6.98-7.06 (m, 1H, one isomer), 7.20-7.30 (m, 4H, two isomers), 7.54-7.63 (m, 1H, one isomer). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 21.0, 80.3 (q, J = 26.1 Hz), 82.7, 110.1, 110.9, 125.1 (q, J = 282.4 Hz), 127.2, 128.4, 130.2, 138.9, 143.5, 147.3, 157.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.5, -76.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_{13}F_3NO_2$ ($[M + H]^+$) 296.0893, found 296.0903.



3pa, 5-(Pyridin-2-yl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.7:1 mixture of **3pa** based on the methyne peak at δ 6.06 for **3pa1** and at δ 5.91 for **3pa2**.

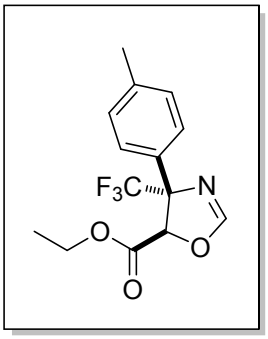
For **3pa**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 and 2.37 (s, 3H, two isomers), 5.91 and 6.06 (s, 1H, two isomers), 6.77 and 6.85 (d, J = 8.0 Hz and 8.0 Hz, 2H, one isomer), 7.00-7.09 (m, 2H, one isomer), 7.26-7.53 (m, 3H, two isomers), 7.72-7.99 (m, 1H, one isomer), 8.41 and 8.67 (d, J = 4.8 Hz and 4.4 Hz, 1H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.8, 82.0 (q, J = 26.8 Hz), 85.1, 122.3, 123.2, 125.2 (q, J = 281.8 Hz), 127.8, 128.2, 129.2, 136.0, 137.8, 148.7, 154.8, 157.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.5, -74.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}F_3N_2O$ ($[M + H]^+$) 307.1053, found 307.1053.

The major isomer **3pa1** and the minor one **3pa2** could be separated by flash column.

For **3pa1**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17 (s, 3H), 6.06 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 7.03-7.05 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.36-7.39 (m, 1H), 7.42 (s, 1H). 8.42 (d, J = 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 82.0 (q, J = 26.8 Hz), 85.2, 122.3, 123.3, 125.2 (q, J = 281.8 Hz), 127.8, 128.3, 129.9, 136.1, 137.8, 148.7, 154.8, 157.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}F_3N_2O$ ($[M + H]^+$) 307.1053, found 307.1064.

For **3pa2**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.39 (s, 3H), 5.91 (s, 1H), 7.26-7.32 (m, 3H), 7.36 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.75-7.79 (m, 1H), 7.97 (d, J = 8.0 Hz, 2H), 8.69 (d, J = 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 81.9 (q, J = 26.4 Hz), 88.8,

121.5, 123.5, 123.9 (q, J = 283.4 Hz), 128.1, 129.2, 135.1, 136.5, 138.7, 148.8, 154.4, 156.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}F_3N_2NaO$ ($[M + Na]^+$) 329.0872, found 329.0867.

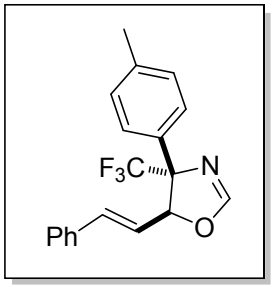


3qa, Ethyl 4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole-5-carboxylate.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 1.8:1 mixture of **3qa** based on the methyne peak at δ 5.29 and at δ 5.13.

For **3qa**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 and 1.39 (t, J = 7.5 Hz and 7.0 Hz, 3H, two isomers), 2.33 and 2.37 (s, 3H, two isomers), 3.62-4.43 (m, 2H, two isomers), 5.13 and 5.29 (s, 1H, two isomers), 7.15 (d, J = 8.5 Hz, 1H, one isomer), 7.21-7.29 (m, 2H, two isomers), 7.39 and 7.63 (d, J = 8.0 Hz and 8.0 Hz, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 13.4, 21.0, 61.8, 80.2, 81.8 (q, J = 27.4 Hz), 124.7 (q, J = 282.3 Hz), 127.4, 128.8, 129.4, 139.2, 157.4, 165.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.3, -75.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{14}H_{15}F_3NO_3$ ($[M + H]^+$) 302.0999, found 302.1011.

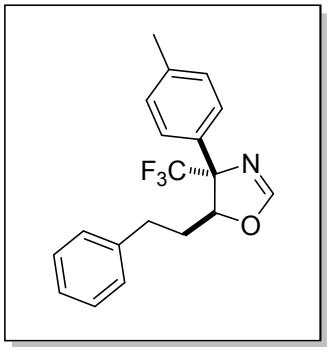
For the major isomer **3qa1**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.94 (t, J = 7.0 Hz, 3H), 2.33 (s, 3H), 3.62-3.68 (m, 1H), 3.79-3.85 (m, 1H), 5.29 (s, 1H), 7.15 (d, J = 8.5 Hz, 2H), 7.29 (s, 1H), 7.39 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.4, 21.0, 61.8, 80.3, 81.9 (q, J = 27.3 Hz), 124.7 (q, J = 282.3 Hz), 127.5 (d, J = 1.4 Hz), 128.9, 129.0, 139.2, 157.4, 166.0.



3ra, (E)-5-styryl-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 1.4:1 mixture of **3ra** based on the peak at δ 6.68 and at δ 6.89.

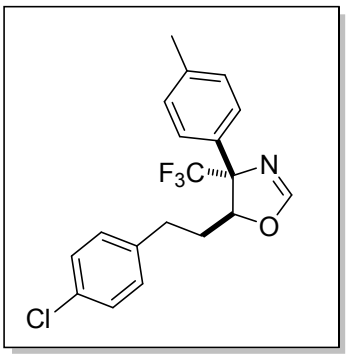
For **3ra**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 and 2.36 (s, 3H, two isomers), 5.17-5.50 (m, 2H, two isomers), 6.47-6.91 (m, 1H, two isomers), 7.11-7.15 (m, 3H, two isomers), 7.21-7.28 (m, 4H, two isomers), 7.33-7.41 (m, 2H, two isomers), 7.49-7.51 (m, 1H, one isomer). ^{13}C NMR ($CDCl_3$, 100 MHz, the major isomer) δ 21.0, 80.0 (q, J = 27.0 Hz), 88.9, 123.2, 125.3 (q, J = 282.0 Hz), 126.9, 127.1, 128.3, 128.6, 128.8, 129.4, 135.5, 135.6, 138.5, 157.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4, -72.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{17}F_3NO$ ($[M + H]^+$) 332.1257, found 332.1258.



3sa, 5-Phenethyl-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.6:1 mixture of **3sa** based on the methyne peak at δ 4.88 and at δ 4.55.

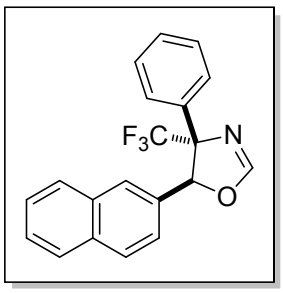
For **3sa**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18-1.61 (m, 2H, two isomers), 2.33 and 2.34 (s, 3H, two isomers), 2.55-3.08 (m, 2H, two isomers), 4.54-4.90 (m, 1H, two isomers), 7.03 (d, J = 7.2 Hz, 2H, one isomer), 7.14-7.37 (m, 8H, two isomers). ^{13}C NMR ($CDCl_3$, 100 MHz, the major isomer) δ 21.0, 31.9, 34.2, 79.8 (q, J = 26.3 Hz), 82.0, 125.5 (q, J = 281.8 Hz), 126.1, 127.7, 128.3, 128.5, 129.0, 129.6, 138.6, 140.4, 157.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.8, -75.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{19}F_3NO$ ($[M + H]^+$) 334.1413, found 334.1427.



3ta, 5-(4-Chlorophenethyl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.4:1 mixture of **3ta** based on the methyne peak at δ 4.85 and at δ 4.52.

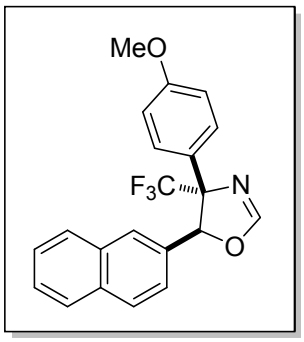
For **3ta**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.15-1.57 (m, 2H, two isomers), 2.33 and 2.34 (s, 3H, two isomers), 2.50-3.04 (m, 2H, two isomers), 4.50-4.87 (m, 1H, two isomers), 6.94 (d, J = 8.4 Hz, 1H, one isomer), 7.15-7.36 (m, 8H, two isomers). ^{13}C NMR ($CDCl_3$, 100 MHz, the major isomer) δ 21.0, 31.1, 34.1, 79.8 (q, J = 26.0 Hz), 81.7, 125.5 (q, J = 282.0 Hz), 126.5, 127.6, 128.6, 129.1, 129.7, 131.9, 138.6, 138.8, 157.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.8, -72.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{18}ClF_3NO$ ($[M + H]^+$) 368.1024, found 368.1035.



3ab, 5-(Naphthalen-2-yl)-4-phenyl-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 4:1 mixture of **3ab** based on the methyne peak at δ 6.10 and at δ 5.85.

For **3ab**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 and 6.10 (s, 1H, two isomers), 6.72-7.20 (m, 5H, two isomers), 7.43-7.95 (m, 8H, two isomers). ^{19}F NMR (564 MHz, $CDCl_3$) δ -75.9, -67.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{15}F_3NO$ ($[M + H]^+$) 342.1100, found 342.1112.

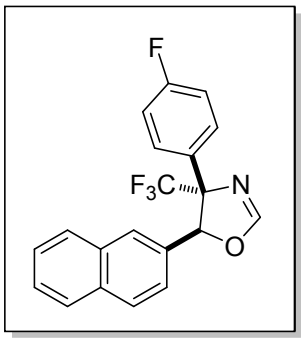


3ac, 4-(4-Methoxyphenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.1:1 mixture of **3ac** based on the methyne peak at δ 6.08 and at δ 5.83.

For **3ac**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.10 and 2.41 (s, 3H, two isomers), 5.83 and 6.08 (s, 1H, two isomers), 6.75-7.07 (m, 4H, two isomers), 7.25-7.94 (m, 8H, two isomers). ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4, -67.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{16}F_3NNaO_2$ ($[M + Na]^+$) 394.1025, found 394.1018.

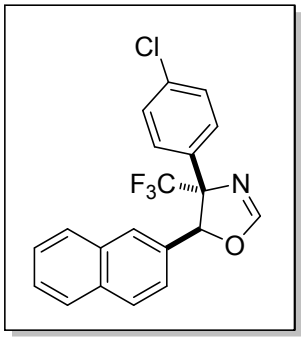
For the major isomer **3ac1**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.59 (s, 3H), 6.07 (s, 1H), 6.50 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.43-7.50 (m, 4H), 7.63 (s, 1H), 7.68-7.70 (m, 1H), 7.75-7.76 (m, 1H).



3ad, 4-(4-Fluorophenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 4.4:1 mixture of **3ad** based on the methyne peak at δ 6.08 and at δ 5.78.

For **3ad**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.78 and 6.08 (s, 1H, two isomers), 6.64-6.73 (m, 2H, one isomer), 7.14-7.22 (m, 2H, two isomers), 7.43-7.59 (m, 5H, two isomers), 7.68-7.92 (m, 3H, two isomers). ^{19}F NMR (564 MHz, $CDCl_3$) δ -113.5 – -113.5 (m), -112.7 – -112.6 (m), -77.1, -76.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{14}F_4NO$ ($[M + H]^+$) 360.1006, found 360.1019.

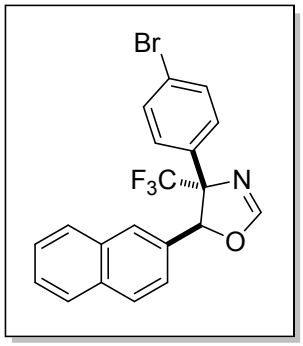


3ae, 4-(4-Chlorophenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.6:1 mixture of **3ae** based on the methyne peak at δ 6.08 and at δ 5.76.

For **3ae**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.76 and 6.08 (s, 1H, two

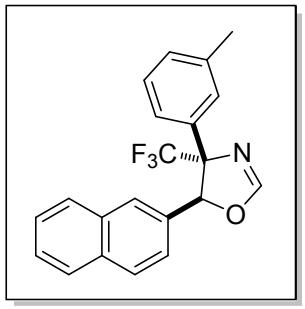
isomers), 6.71-7.14 (m, 4H, one isomer), 7.44-7.54 (m, 4H, two isomers), 7.61-7.91 (m, 4H, two isomers). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.2, -72.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{14}ClF_3NO$ ($[M + H]^+$) 376.0711, found 376.0719.



3af, 4-(4-Bromophenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 4.2:1 mixture of **3af** based on the methyne peak at δ 6.08 and at δ 5.75.

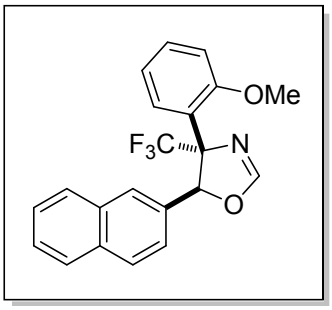
For **3af**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.75 and 6.08 (s, 1H, two isomers), 6.70-6.72 (m, 1H, one isomer), 7.07 and 7.12 (d, J = 8.0 Hz and 8.5 Hz, 3H, one isomer), 7.44-7.54 (m, 4H, two isomers), 7.61-7.91 (m, 4H, two isomers). ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.3, -68.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{14}BrF_3NO$ ($[M + H]^+$) 420.0205, found 420.0225.



3ag, 5-(Naphthalen-2-yl)-4-(m-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 4.4:1 mixture of **3ag** based on the methyne peak at δ 6.08 and at δ 5.83.

For **3ag**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.99 and 2.43 (s, 3H, two isomers), 5.83 and 6.08 (s, 1H, two isomers), 6.74-6.83 (m, 3H, two isomers), 6.91-7.01 (m, 2H, one isomer), 7.23-7.47 (m, 4H, two isomers), 7.51-7.59 (m, 1H, two isomers), 7.66-7.94 (m, 2H, two isomers). ^{19}F NMR (470 MHz, $CDCl_3$) δ -77.8, -72.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}F_3NO$ ($[M + H]^+$) 356.1257, found 356.1265.

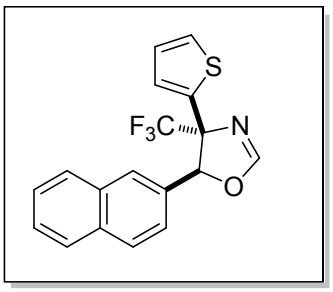


3ah, 4-(2-Methoxyphenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The products could readily be separated by silica gel chromatography. The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.2:1 mixture of **3ah**.

For **3ah1**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.15 (s, 3H), 6.17 (s, 1H), 6.29 (d, J = 8.4 Hz, 1H), 6.93-6.99 (m, 2H), 7.10-7.15 (m, 1H), 7.34 (s, 1H), 7.39-7.42 (m, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.67-7.68 (m, 2H), 8.11 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 54.2, 80.3 (q, J = 27.5 Hz), 85.4, 110.6, 120.4, 121.7, 124.7, 125.3 (q, J = 285.2 Hz), 126.1, 126.4, 127.0, 127.5, 127.7, 127.9, 130.5, 130.6, 132.3, 133.0, 134.0, 155.5, 157.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{16}F_3NNaO_2$ ($[M + Na]^+$) 394.1025, found 394.1022.

For **3ah2**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.04 (s, 3H), 6.34 (s, 1H), 7.03-7.08 (m, 2H), 7.40-7.45 (m, 2H), 7.50-7.54 (m, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.82-7.88 (m, 4H), 7.97 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}F_3NO_2$ ($[M + H]^+$) 372.1206, found 372.1189.

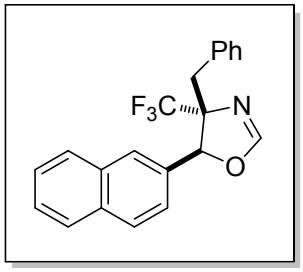


3ai, 5-(Naphthalen-2-yl)-4-(thiophen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 3.1:1 mixture of **3ai** based on the methyne peak at δ 6.07 and at δ 5.88.

For **3ai**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.88 and 6.07 (s, 1H, two isomers), 6.39-6.56 (m, 1H, one isomer), 6.89-7.03 (m, 1H, one isomer), 7.11-7.40 (m, 1H, one isomer), 7.44-7.62 (m, 5H, two isomers), 7.71-7.93 (m, 3H, two isomers). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.0, -73.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{13}F_3NOS$ ([M

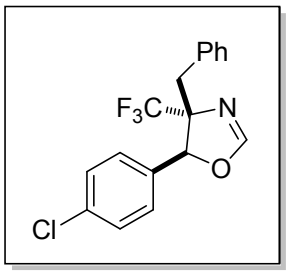
+ H]$^+$) 348.0664, found 348.0670.



3aj, 4-Benzyl-5-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.5:1 mixture of **3aj** based on the methyne peak at δ 5.93 and at δ 5.59.

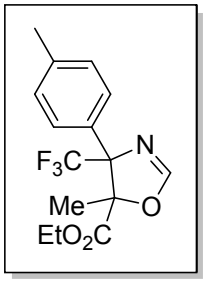
For **3aj**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.52-3.63 (m, 2H, two isomers), 5.59 and 5.93 (s, 1H, two isomers), 6.83 (d, J = 7.6 Hz, 1H, one isomer), 6.97-7.12 (m, 3H, two isomers), 7.20-7.40 (m, 3H, two isomers), 7.47-7.62 (m, 3H, two isomers), 7.75-7.85 (m, 3H, two isomers). ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.1, -72.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{17}F_3NO$ ([M + H]$^+$) 356.1257, found 356.1264.



3cj, 4-Benzyl-5-(4-chlorophenyl)-4-(trifluoromethyl)-4,5-dihydrooxazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 1.7:1 mixture of **3cj** based on the methyne peak at δ 5.73 and at δ 5.38.

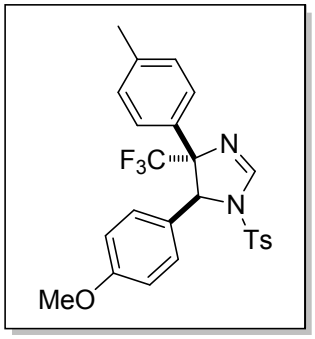
For **3cj**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.47-3.59 (m, 2H, two isomers), 5.38 and 5.73 (s, 1H, two isomers), 6.86-6.88 (m, 1H, one isomer), 7.07-7.14 (m, 4H, two isomers), 7.19-7.25 (m, 1H, two isomers), 7.30-7.37 (m, 4H, two isomers). ^{13}C NMR ($CDCl_3$, 100 MHz, the major isomer) δ 37.3, 78.9 (q, J = 25.0 Hz), 82.0, 125.7 (q, J = 282.0 Hz), 126.6, 127.6, 128.7, 130.4, 131.5, 132.8, 134.0, 134.6, 156.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4, -72.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}ClF_3NO$ ([M + H]$^+$) 340.0711, found 340.0717.



5, Ethyl 5-methyl-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole-5-carboxylate.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 0.9:1 mixture of **5**.

For **5**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.81-1.16 (m, 3H, two isomers), 1.38-1.99 (m, 3H, two isomers), 2.32 and 2.37 (s, 3H, two isomers), 3.49-3.60 (m, 1H, one isomer), 4.30-4.45 (m, 1H, one isomer), 7.14 (d, J = 8.5 Hz, 1H, one isomer), 7.21-7.28 (m, 2H, two isomers), 7.44-7.66 (m, 2H, two isomers). ^{13}C NMR ($CDCl_3$, 100 MHz, the major isomer) δ 13.2, 18.5, 21.1, 61.9, 83.2 (q, J = 26.3 Hz), 88.7, 124.4 (q, J = 284.6 Hz), 128.6, 128.9, 130.2, 139.0, 157.6, 168.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.5, -73.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_{17}F_3NO_3$ ($[M + H]^+$) 316.1155, found 316.1167.



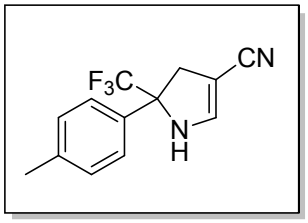
7, 5-(4-Methoxyphenyl)-4-(p-tolyl)-1-tosyl-4-(trifluoromethyl)-4,5-dihydro-1H-imidazole.

The ratio of the isomers was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 4.2:1 mixture of **7** based on the methyne peak at δ 5.26 and at δ 5.08.

For **7**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.16-2.35 (m, 6H, two isomers), 3.66 and 3.78 (s, 3H, two isomers), 5.08 and 5.26 (s, 1H, two isomers), 5.94-6.09 (m, 1H, two isomers), 6.70-7.13 (m, 8H, two isomers), 7.31-7.40 (m, 3H, two isomers), 7.97 and 7.97 (s, 1H, two isomers). ^{13}C NMR ($CDCl_3$, 125 MHz, the major isomer) δ 20.9, 21.5, 55.0, 65.9, 84.3 (q, J = 26.0 Hz), 112.2, 114.0, 123.8, 123.9 (q, J = 279.4 Hz), 125.8, 127.2, 128.2, 129.6, 130.5, 134.4, 137.8, 144.6, 151.2, 159.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{23}F_3N_2NaO_3S$ ($[M + Na]^+$) 511.1274, found 511.1271.

For the major isomer, white solid. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (s, 3H), 2.38 (s, 3H), 3.68 (s, 3H), 5.23 (s, 1H), 5.97 (s, 1H), 6.12 (s, 1H), 6.70 (s, 1H), 6.84 (d, J = 8.5 Hz,

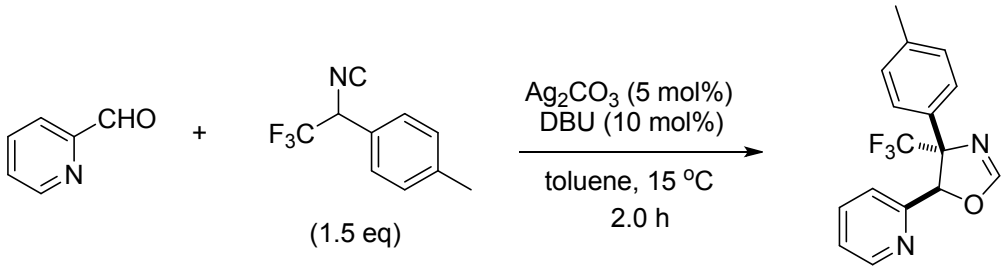
2H), 6.93 (s, 2H), 7.14 (d, J = 8.5 Hz, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.95 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.9, 21.6, 55.1, 65.9, 84.4 (q, J = 26.3 Hz), 112.3, 114.1, 125.0 (q, J = 282.4 Hz), 126.0, 127.3, 128.2, 129.6, 130.6, 134.5, 137.9, 144.7, 151.3, 159.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}F_3N_2O_3S$ ([M + H]$^+$) 489.1454, found 489.1473.



9, 5-(P-tolyl)-5-(trifluoromethyl)-4,5-dihydro-1H-pyrrole-3-carbonitrile.

For **9**, yellow oil. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.37 (s, 3H), 3.14 (d, J = 15.5 Hz, 1H), 3.51 (dd, J_1 = 1.0 Hz, J_2 = 15.5 Hz, 1H), 5.07 (s, 1H), 7.03-7.04 (m, 1H), 7.22 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 39.4, 70.9 (q, J = 28.4 Hz), 79.3, 117.3, 125.4 (q, J = 282.6 Hz), 125.9, 129.5, 134.5, 139.1, 148.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}F_3N_2$ ([M + H]$^+$) 253.0947, found 253.0943.

IV. General procedures for a gram scale synthesis of 3pa



1p **2a** **3pa**

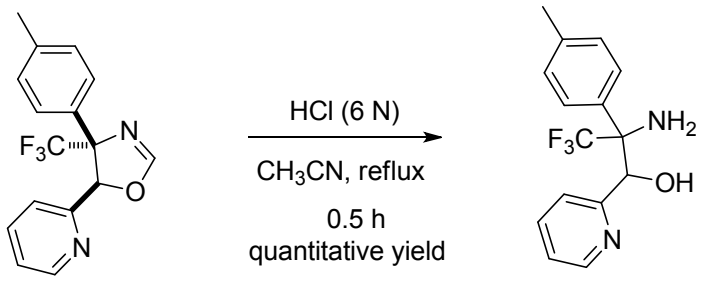
To a solution of picolinaldehyde (**1p**) (0.5 g, 5.0 mmol) and 1-methyl-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene (**2a**) (1.5 g, 7.5 mmol) in toluene (50 ml) at 15 ºC was added Ag_2CO_3 (68.9 mg, 5.0 mol %) and DBU (75.0 μL, 10.0 mol %). After the reaction was finished as indicated by TLC (reaction time, 2.0 h), the resulting mixture was poured into water (100 mL) and extracted with DCM (CH_2Cl_2, 100 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification of the crude product with flash column chromatography (petroleum ether /EtOAc = 15:1) to give **3pa** (1.5 g, 98%).

3pa, 5-(Pyridin-2-yl)-4-(p-tolyl)-4-(trifluoromethyl)-4,5-dihydrooxazole. The ratio of the isomor

was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the crude product showed a 2.8:1 mixture of **3pa**.

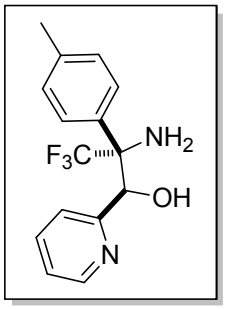
V. General procedures for synthesis application of products.

2-Amino-3,3,3-trifluoro-1-(pyridin-2-yl)-2-(p-tolyl)propan-1-ol (10a)

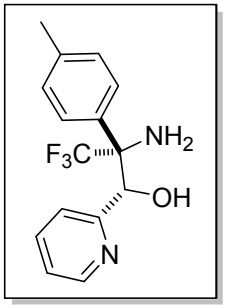


3pa1 **10a**

Oxazoline **3pa1** (61.2 mg, 0.2 mmol) was dissolved in 2 mL of CH_3CN and 5 pipette drops of HCl (6N) were added. The reaction mixture was refluxed for 0.5 h. After the reaction mixture was cooled to room temperature, the mixture was quenched with saturated $NaHCO_3$ solution (10 ml). The aqueous layer was extracted with CH_2Cl_2 (10 ml × 3), and combined organic layers were dried over Na_2SO_4 and concentrated to give **10a** in quantitative yield as a white solid.

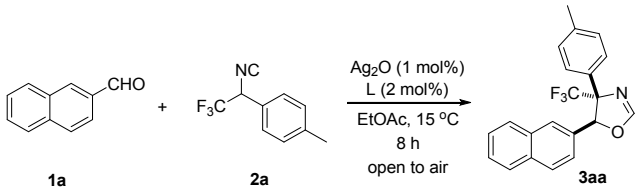


10a, 2-Amino-3,3,3-trifluoro-1-(pyridin-2-yl)-2-(p-tolyl)propan-1-ol. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.85 (s, 2H), 2.36 (s, 3H), 5.39 (s, 1H), 5.56 (s, 1H), 6.06 (d, J = 8.0 Hz, 1H), 7.11-7.14 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.25-7.30 (m, 1H), 7.38 (d, J = 8.4 Hz, 2H), 8.50 (d, J = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 65.6 (q, J = 24.6 Hz), 74.4, 122.8, 123.0, 126.5, 126.8 (q, J = 286.0 Hz), 129.2, 133.1, 135.7, 138.3, 147.4, 155.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_{15}F_3N_2NaO$ ($[M + Na]^+$) 319.1029, found 319.1020.



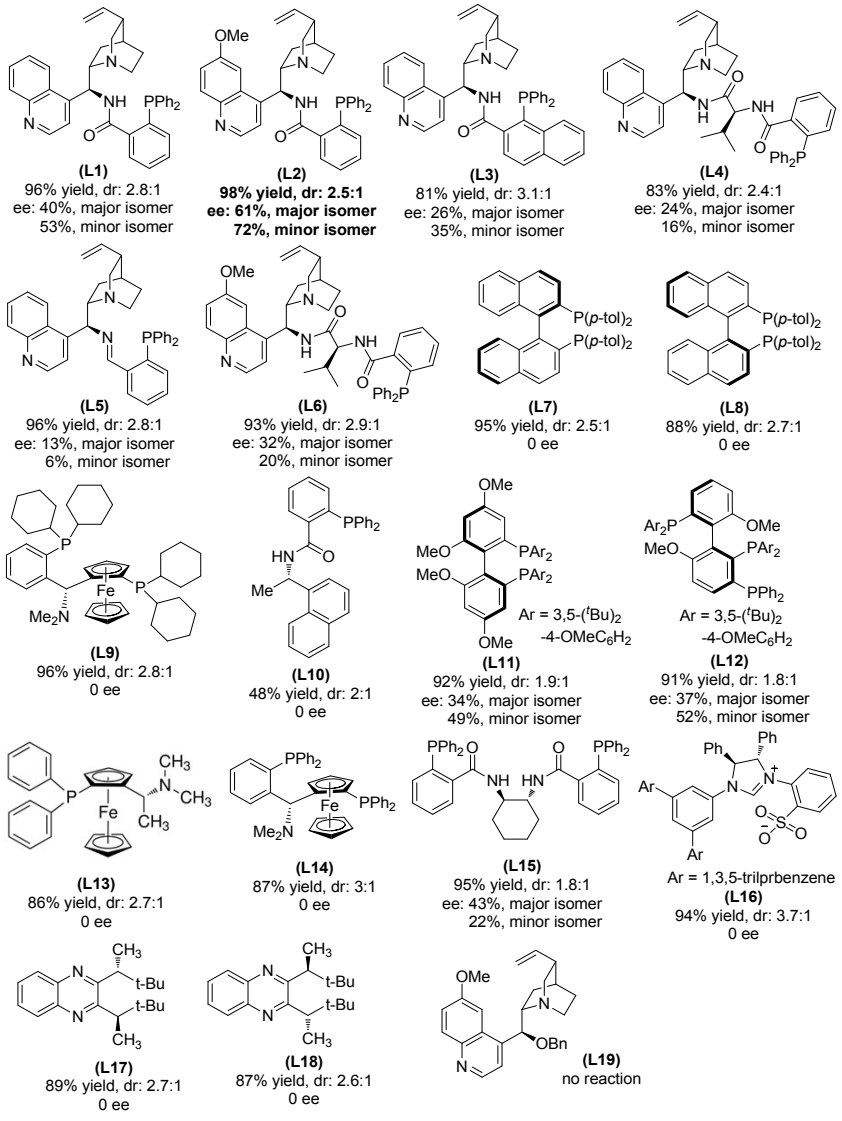
10b, 2-Amino-3,3,3-trifluoro-1-(pyridin-2-yl)-2-(p-tolyl)propan-1-ol. NMR Spectroscopy: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (s, 2H), 2.36 (s, 3H), 4.45 (d, J = 8.0 Hz, 1H), 5.22 (d, J = 6.8 Hz, 1H), 7.18-7.24 (m, 4H), 7.58 (d, J = 8.4 Hz, 2H), 7.62-7.66 (m, 1H), 8.54 (d, J = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 65.9 (q, J = 24.0 Hz), 74.7, 123.3, 123.5, 126.4 (q, J = 284.6 Hz), 126.8, 129.1, 133.5, 136.3, 138.1, 148.3, 157.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_{15}F_3N_2NaO$ ($[M + Na]^+$) 319.1029, found 319.1019.

VI. Preliminary asymmetric studies

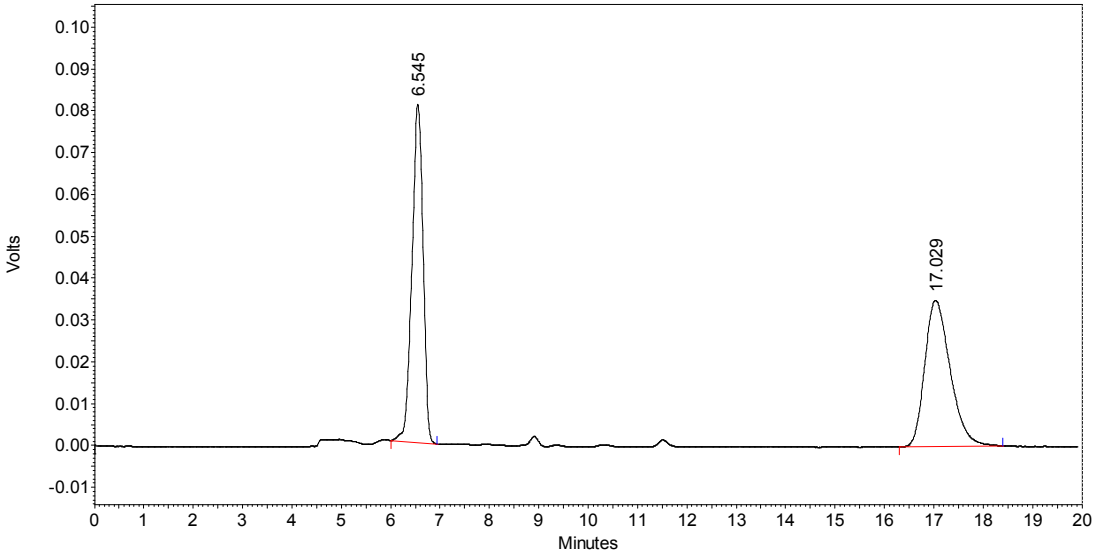


1a 2a 3aa

To a 10 mL vial charged with L (1.2 mg, 2.0 mol%) and Ag_2O (0.2 mg, 1.0 mol%) was added EtOAc (1.0 mL). The mixture was allowed to stir at ambient temperature for 10 min, then 2-naphthaldehyde **1a** (16 mg, 0.1 mmol), 1-methyl-4-(2,2,2-trifluoro-1-isocyanoethyl)benzene **2a** (30 mg, 0.15 mmol) were added in one portion. The mixture was stirred for 8 h. The crude reaction mixture was then subjected to a silica gel column to afford the desired product **3aa**.

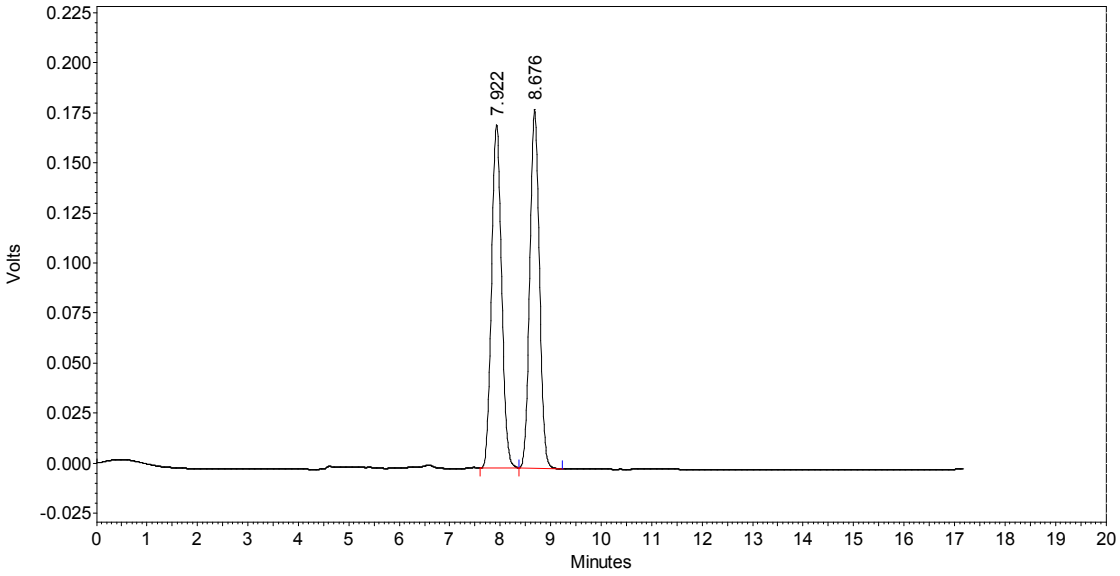


The ee of **3aa** was determined by HPLC using an AD column (*n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{major} = 6.6 min and 16.4 min, t_{minor} = 8.1min and 8.6 min). Product **3aa**: 98% yield, 61% ee (major), 72% ee (minor), Ligand **L2**, $[\alpha]_D^{17}$ = -4.5 (major, c = 0.2, $CHCl_3$).



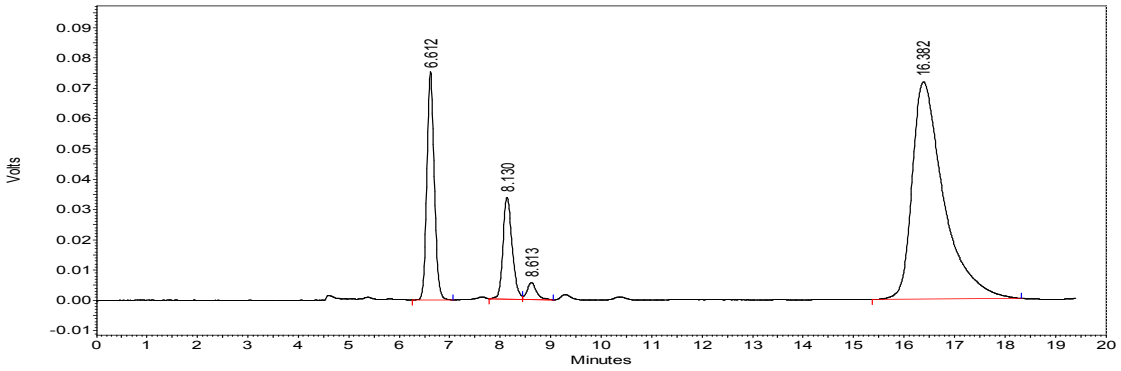
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	6.545	1266551	50.264	80943	69.867
2	17.029	1253226	49.736	34910	30.133
Totals		2519776	100.000	115853	100.000



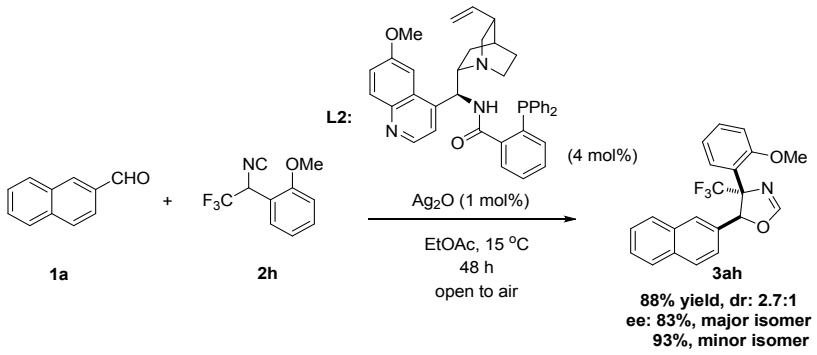
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	7.922	2372280	50.027	171688	48.886
2	8.676	2369677	49.973	179513	51.114
Totals		4741957	100.000	351201	100.000



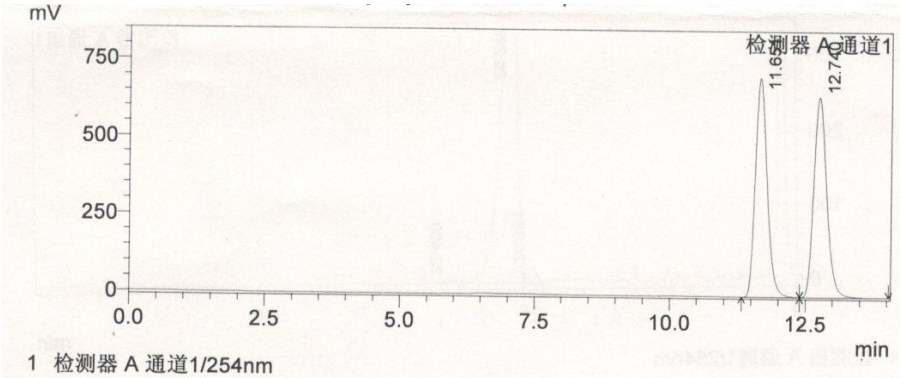
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	6.612	768039	17.578	75402	40.487
2	8.130	424187	9.708	33530	18.004
3	8.613	69964	1.601	5524	2.966
4	16.382	3107229	71.113	71779	38.542
Totals		4369419	100.000	186234	100.000



To a 10 mL vial charged with L2 (2.4 mg, 4.0 mol%) and Ag_2O (0.2 mg, 1.0 mol%) was added EtOAc (1.0 mL). The mixture was allowed to stir at ambient temperature for 10 min, then 2-naphthaldehyde **1a** (16 mg, 0.1 mmol), 1-methoxy-2-(2,2,2-trifluoro-1-isocyanoethyl)benzene **2h** (35 mg, 0.15 mmol) were added in one portion. The mixture was stirred for 48 h. The crude reaction mixture was then subjected to a silica gel column to afford the desired product **3ah**.

The ee of **3ah** was determined by HPLC using an ID column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, t_{major} = 12.3 min and 13.4 min, t_{minor} = 16.1 min and 17.2 min). Product **3ah**: 88% yield, 83% ee (major), 93% ee (minor), Ligand **L2**, $[\alpha]_D^{17}$ = -19.8 (major, c = 0.2, $CHCl_3$).



峰表

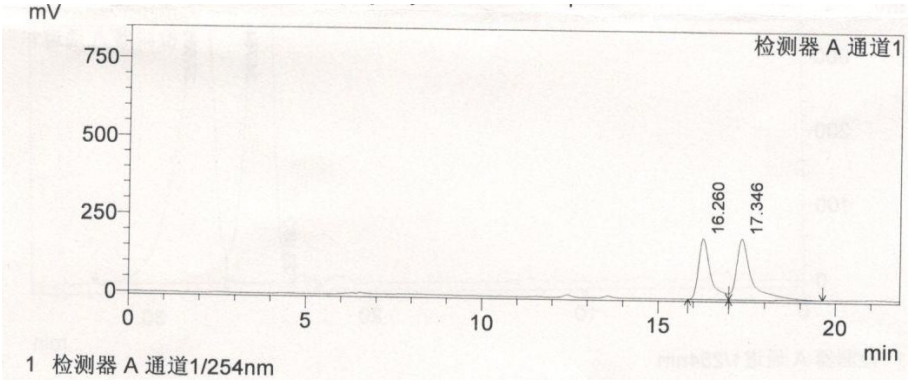
检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	11.651	10655521	704506	49.949	52.255
2	12.740	10677238	643691	50.051	47.745
总计		21332759	1348197	100.000	100.000

Translation

Detector A (254nm)

Pk #	Retention Time	Area	Height	Area%	Height %
1	11.651	10655521	704506	49.949	52.255
2	12.740	10677238	643691	50.051	47.745
Totals		21332759	1348197	100.000	100.000



峰表

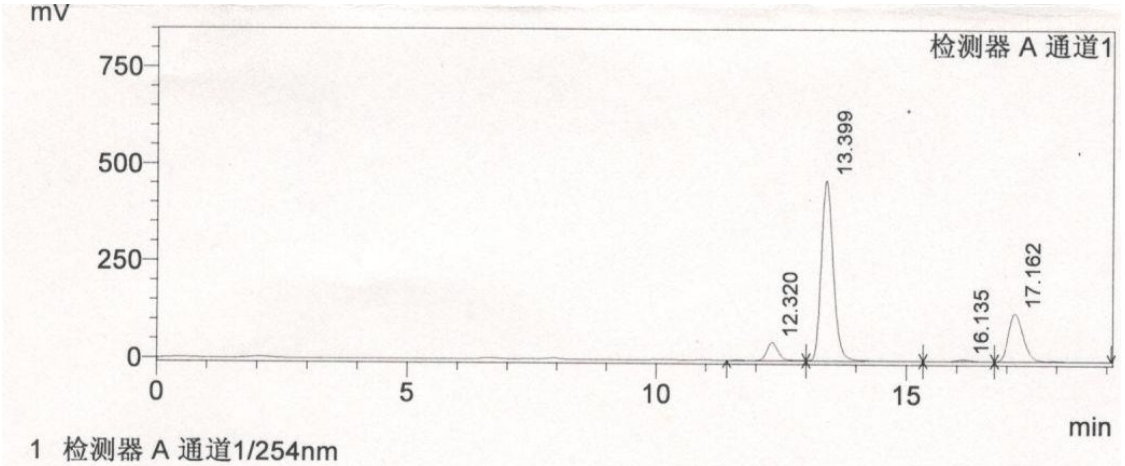
检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.260	4596902	193124	44.193	49.981
2	17.346	5804946	193267	55.807	50.019
总计		10401848	386391	100.000	100.000

Translation

Detector A (254nm)

Pk #	Retention Time	Area	Height	Area%	Height %
1	16.260	4596902	193124	44.193	49.981
2	17.346	5804946	193267	55.807	50.019
Totals		10401848	386391	100.000	100.000



1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

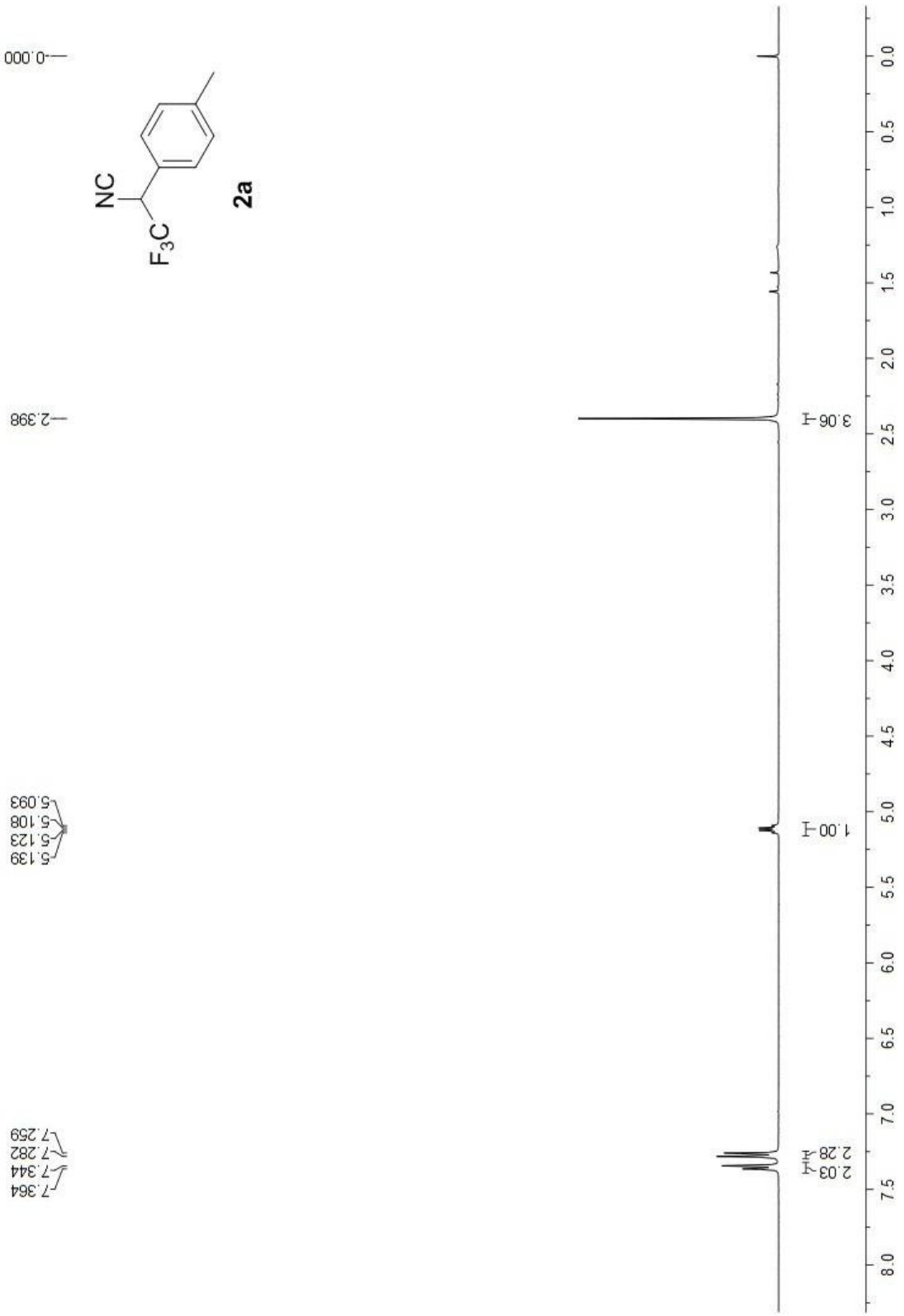
峰#	保留时间	面积	高度	面积 %	高度 %
1	12.320	721532	43457	6.497	7.175
2	13.399	7700674	440792	69.344	72.778
3	16.135	88032	4021	0.793	0.664
4	17.162	2594835	117400	23.366	19.384
总计		11105073	605670	100.000	100.000

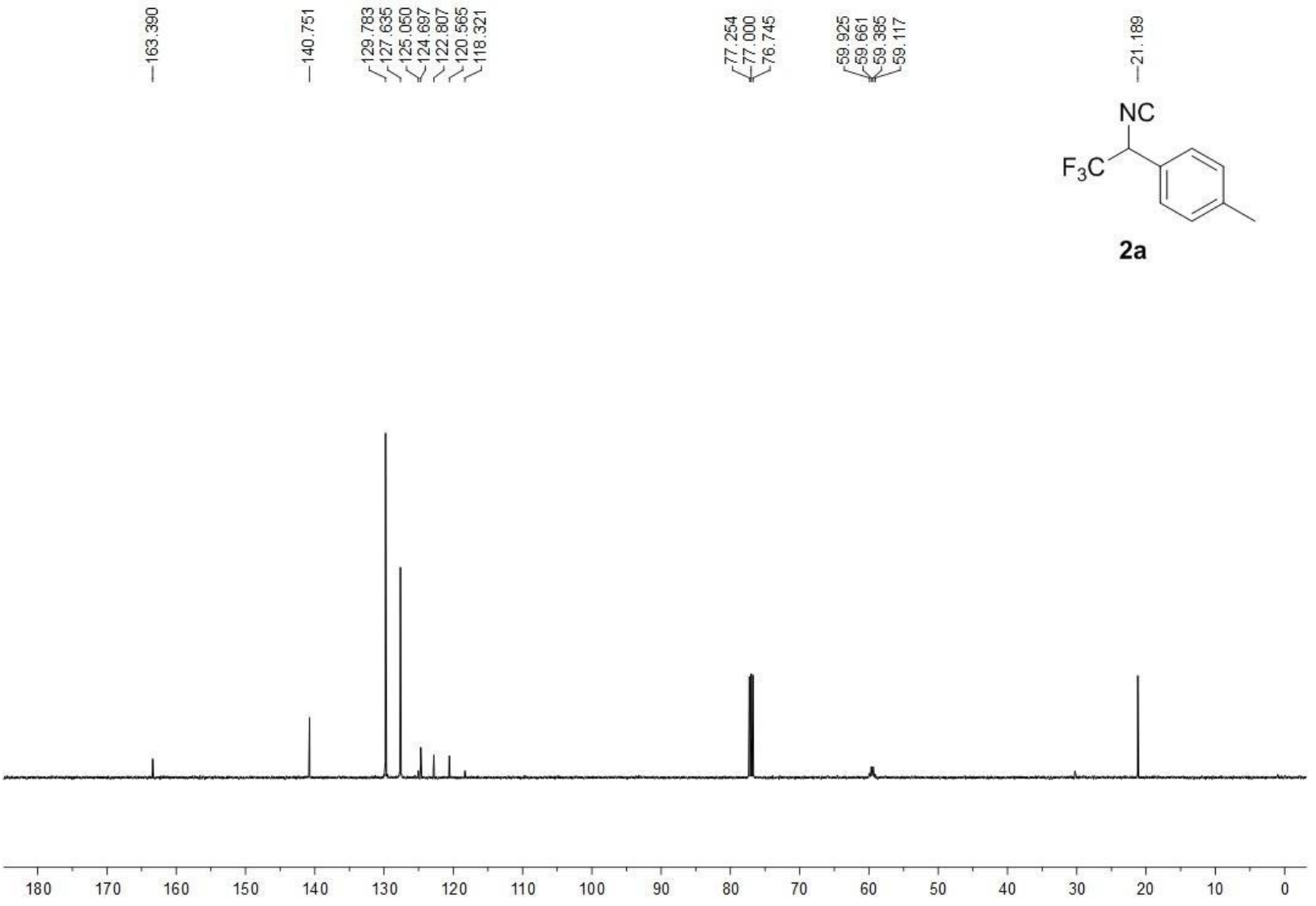
Translation

Detector A (254nm)

Pk #	Retention Time	Area	Height	Area%	Height %
1	12.320	721532	43457	6.497	7.175
2	13.399	7700674	440792	69.344	72.778
3	16.135	88032	4021	0.793	0.664
4	17.162	2594835	117400	23.366	19.384
Totals		11105073	605670	100.000	100.000

Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 2

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59.117
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150
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110
100
90
80
70
60
50
40
30
20
10
0

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Ph
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5.153
5.140
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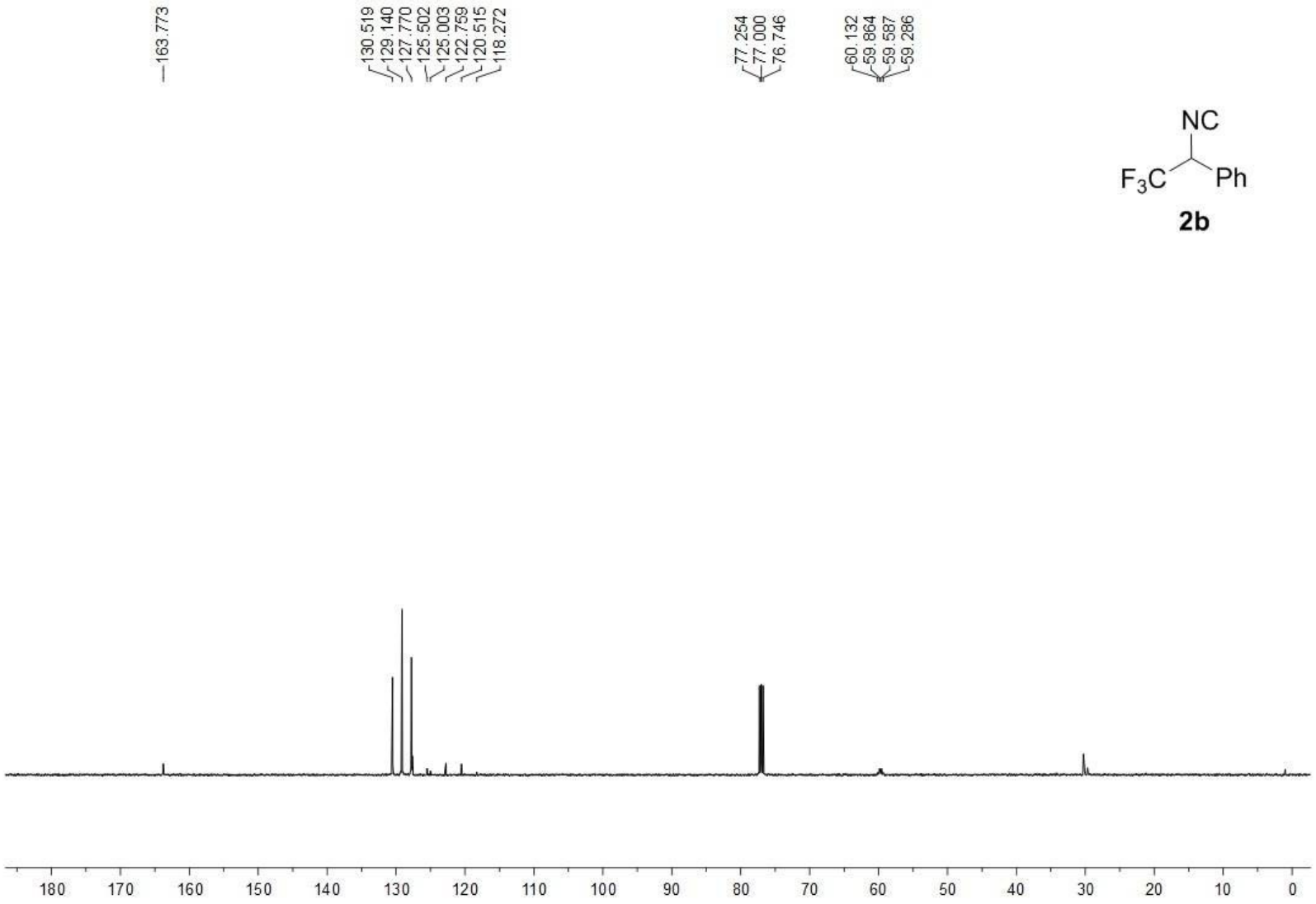
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120.515
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59.587
59.286
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F3C
Ph
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150
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130
120
110
100
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80
70
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50
40
30
20
10
0

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OMe
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5.089
5.100
5.110
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6.958
6.966
6.970
6.975
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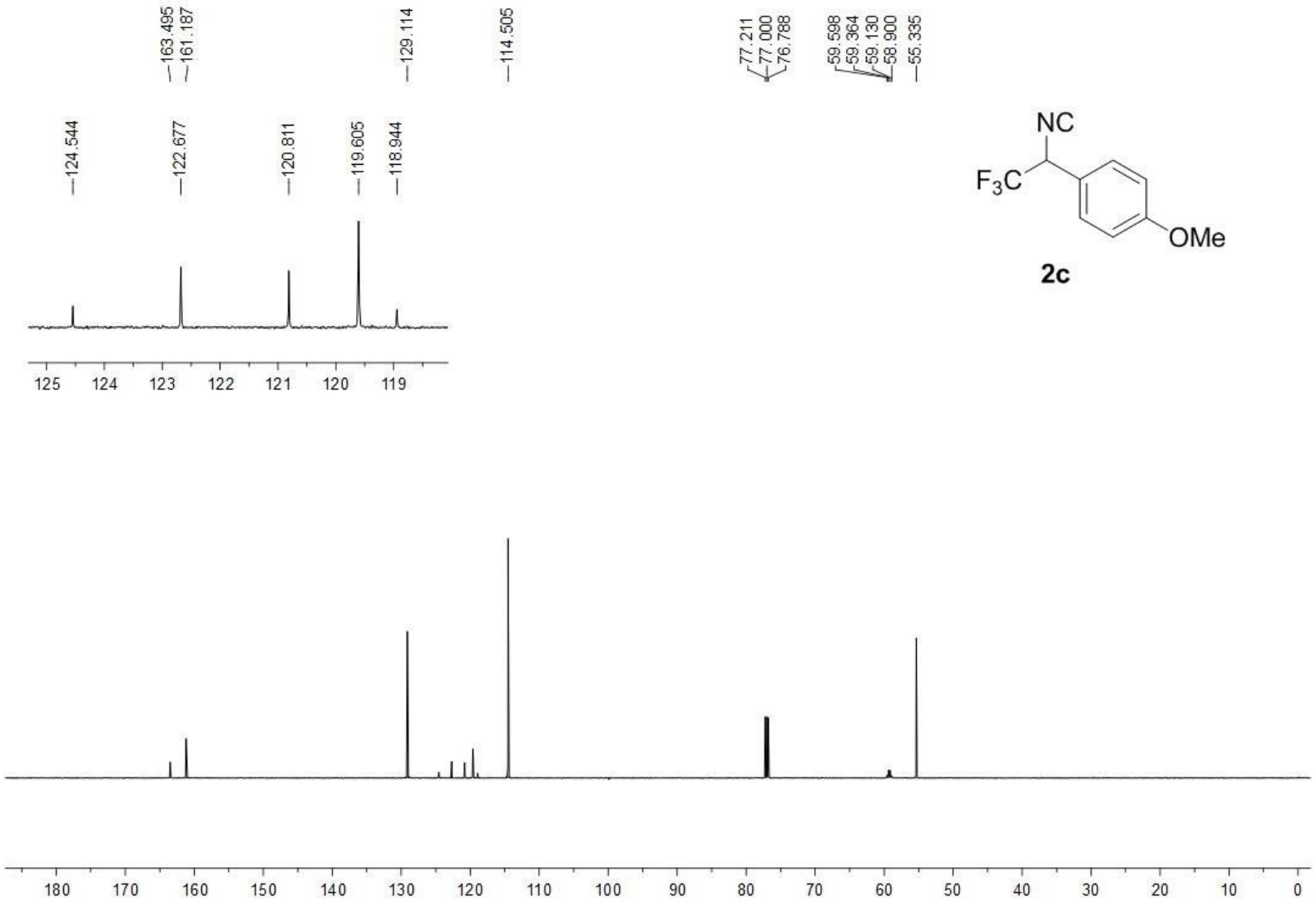
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120
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150
140
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60
50
40
30
20
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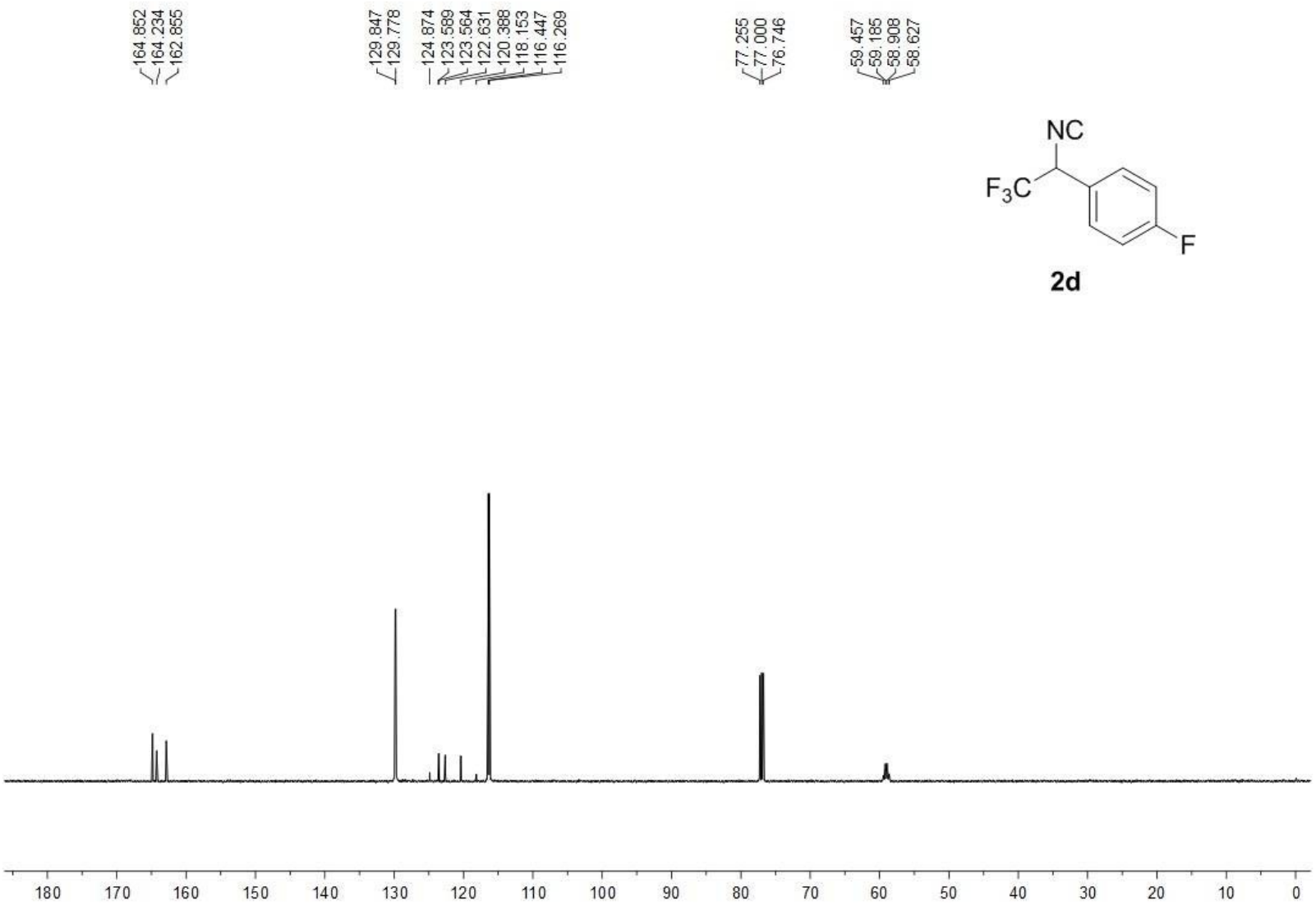
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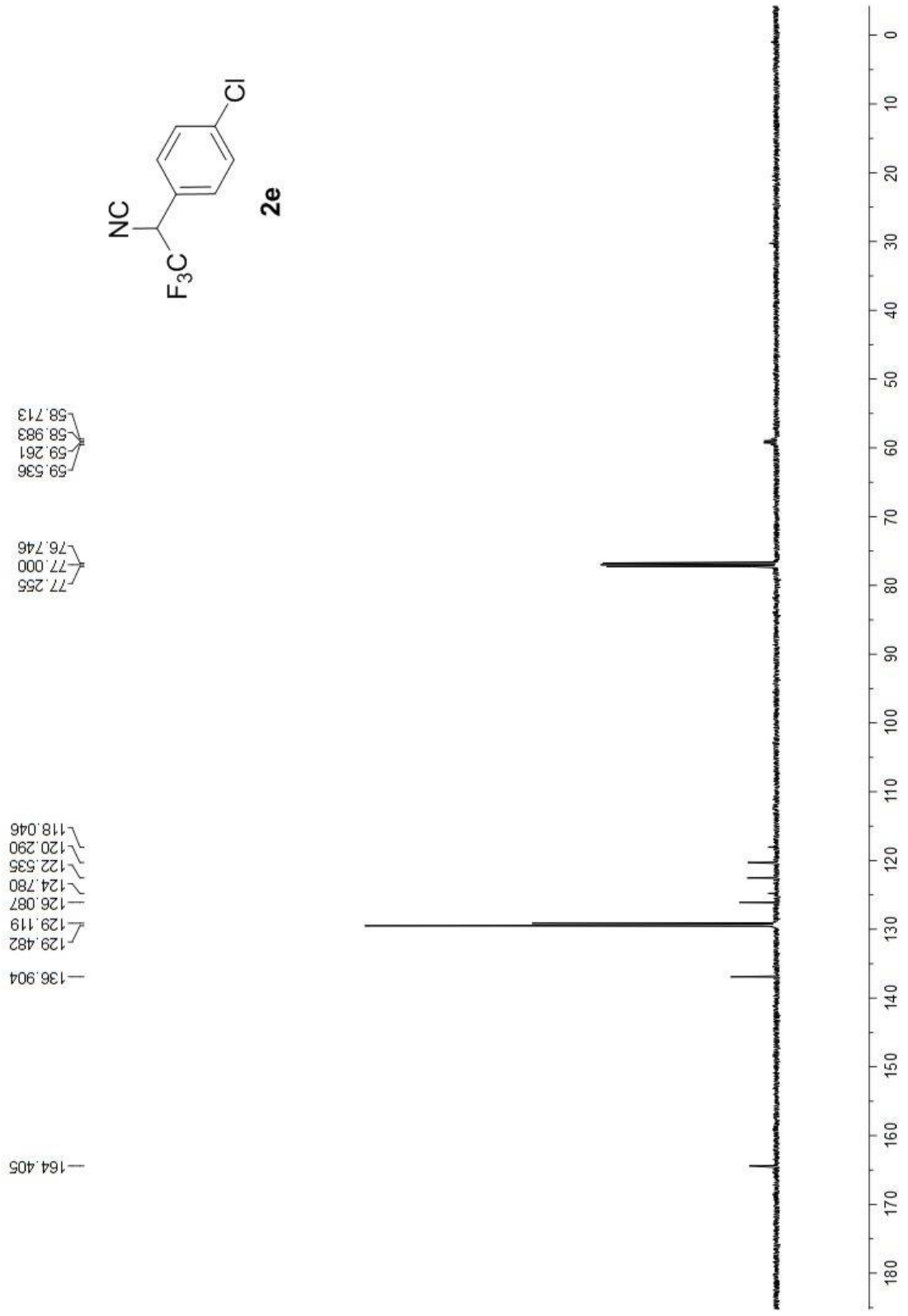
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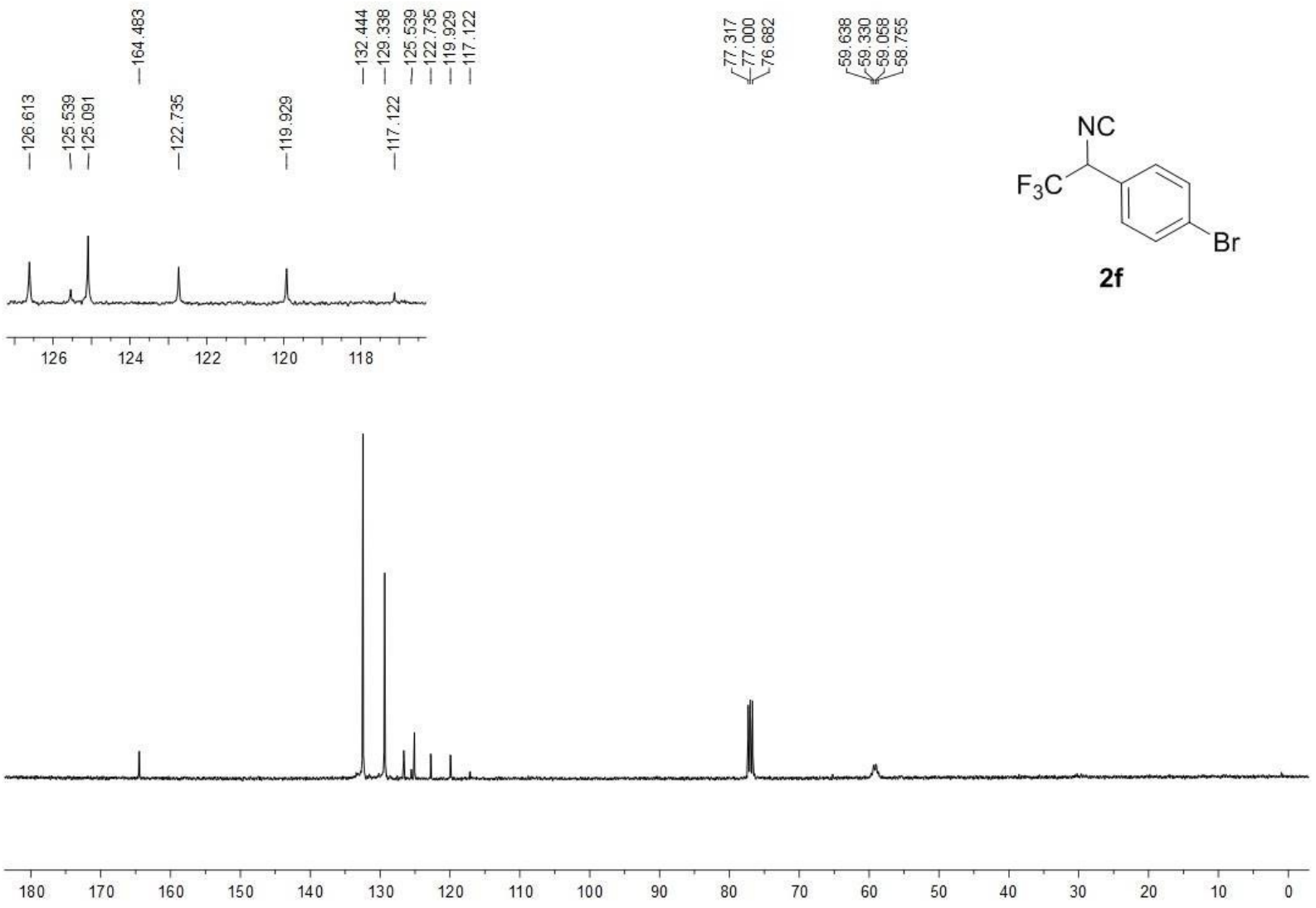
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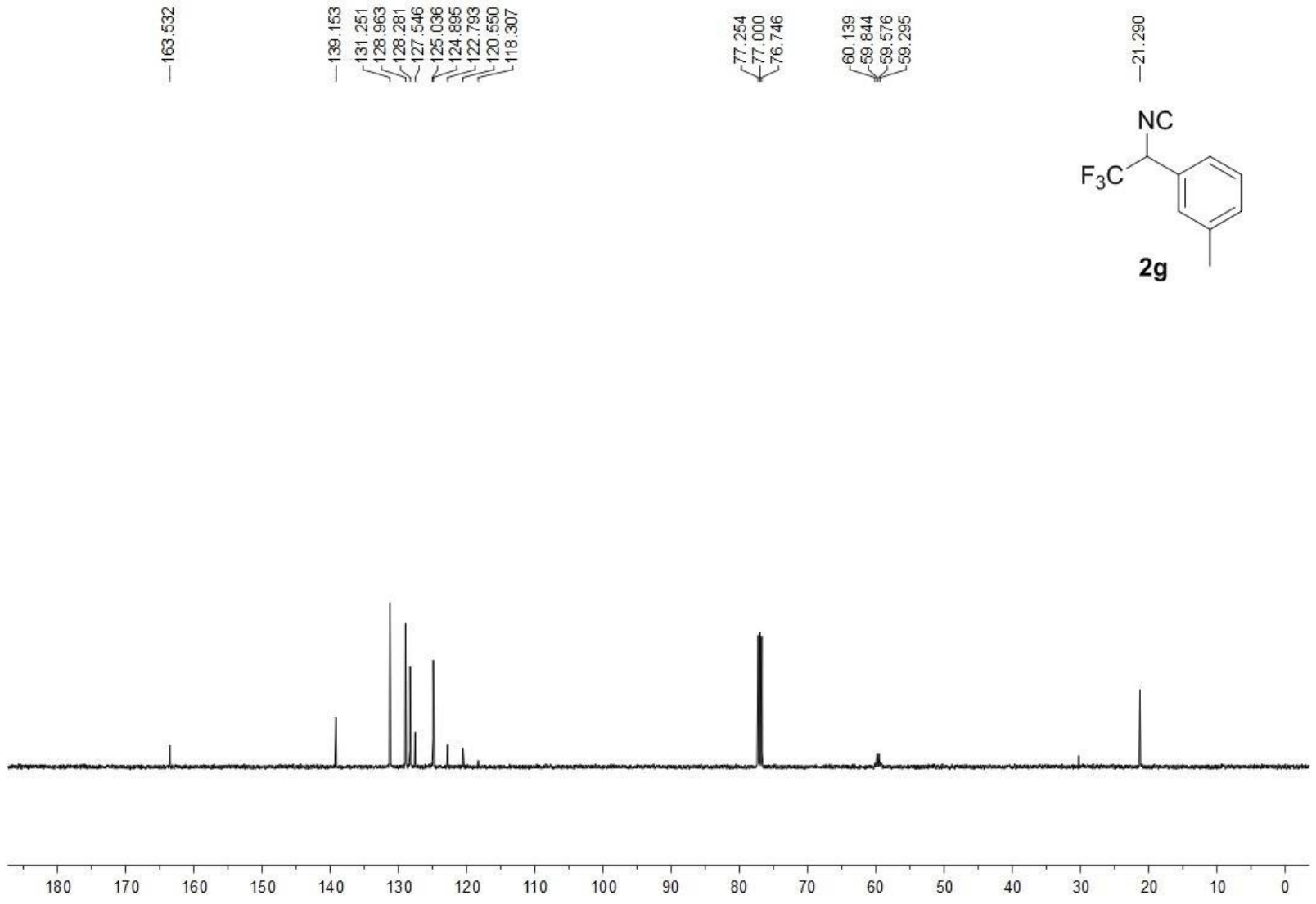
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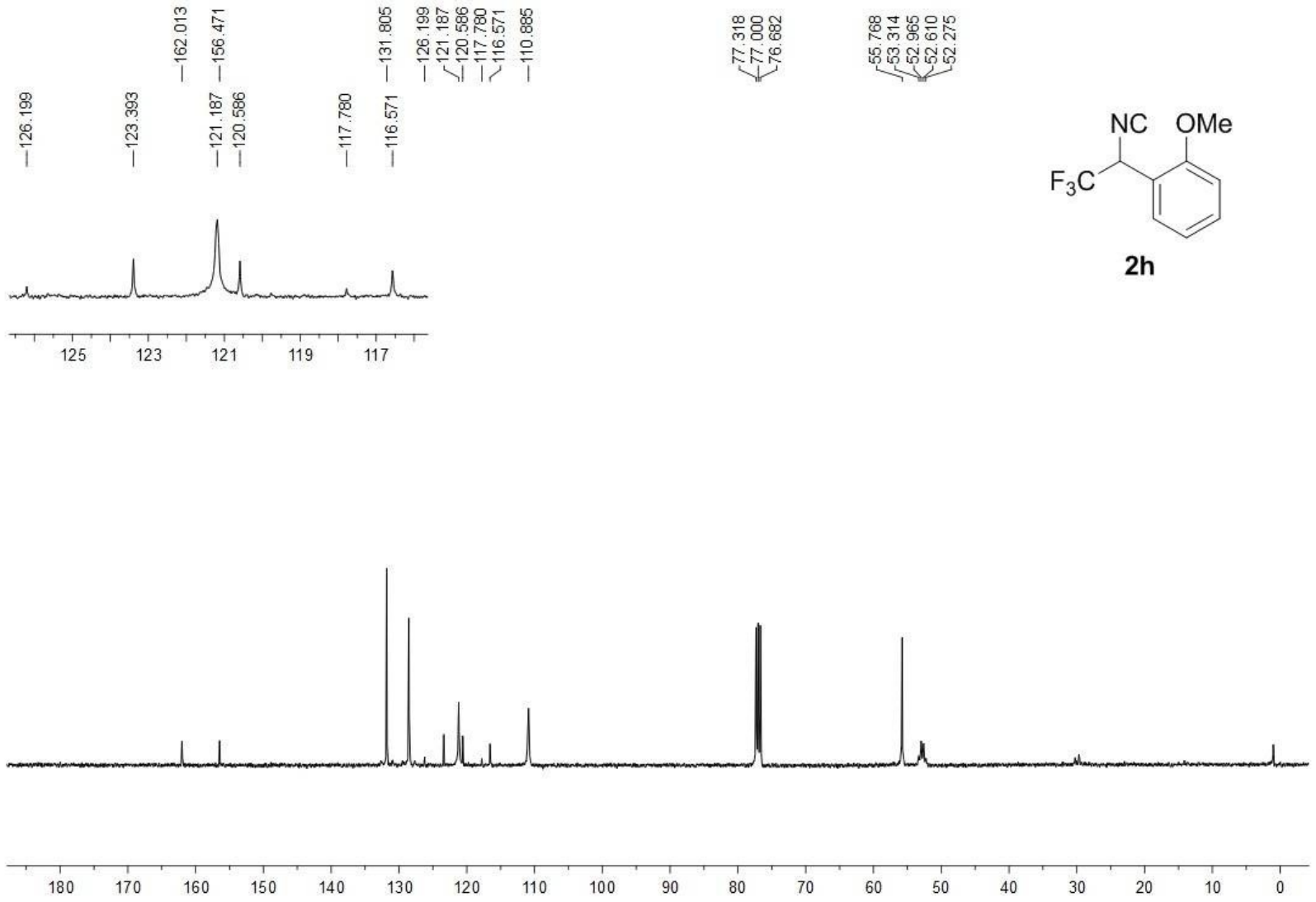
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117
180
170
160
150
140
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120
110
100
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50
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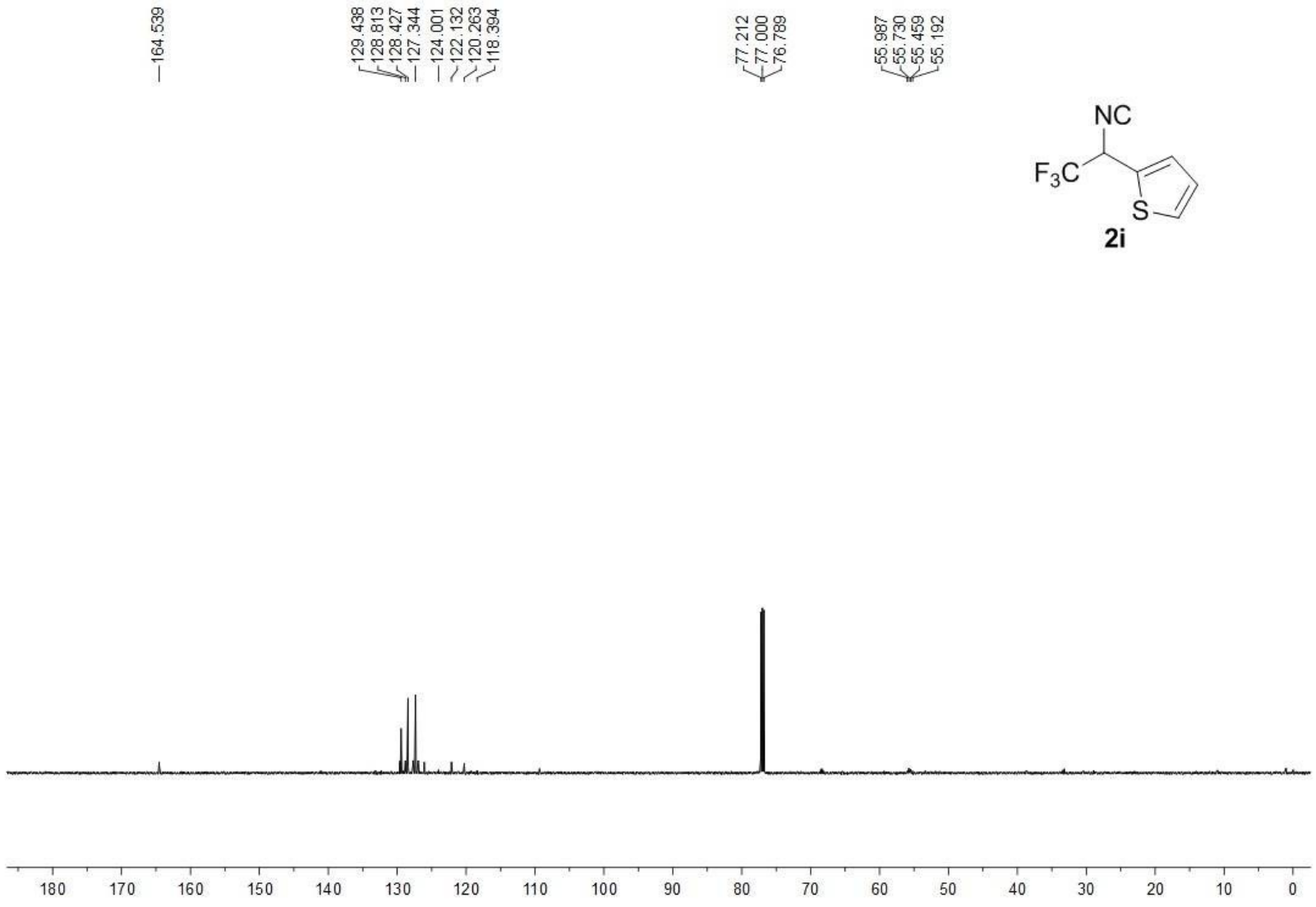
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CN
F3C
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4.175
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7.371
7.385
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1.00
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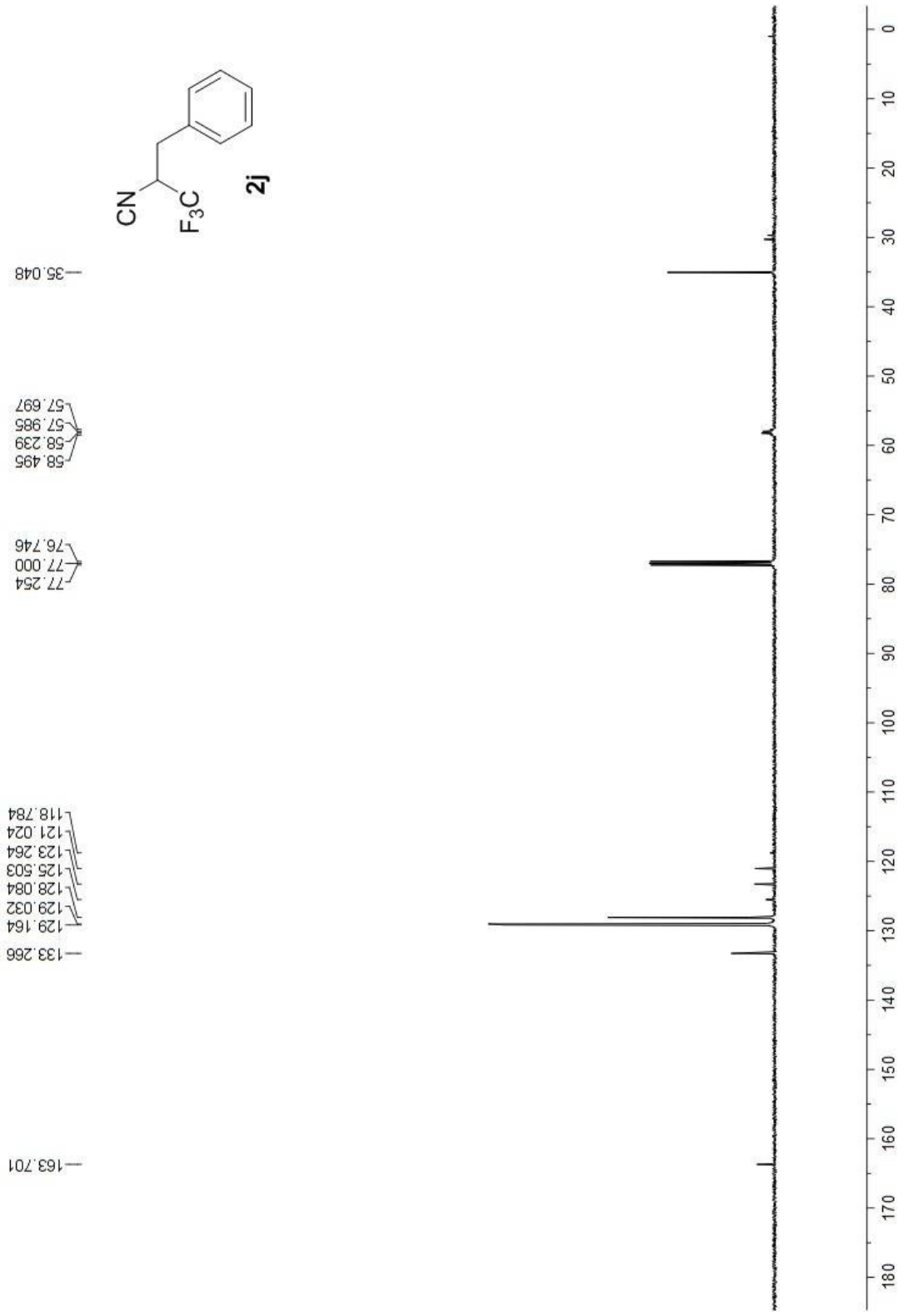
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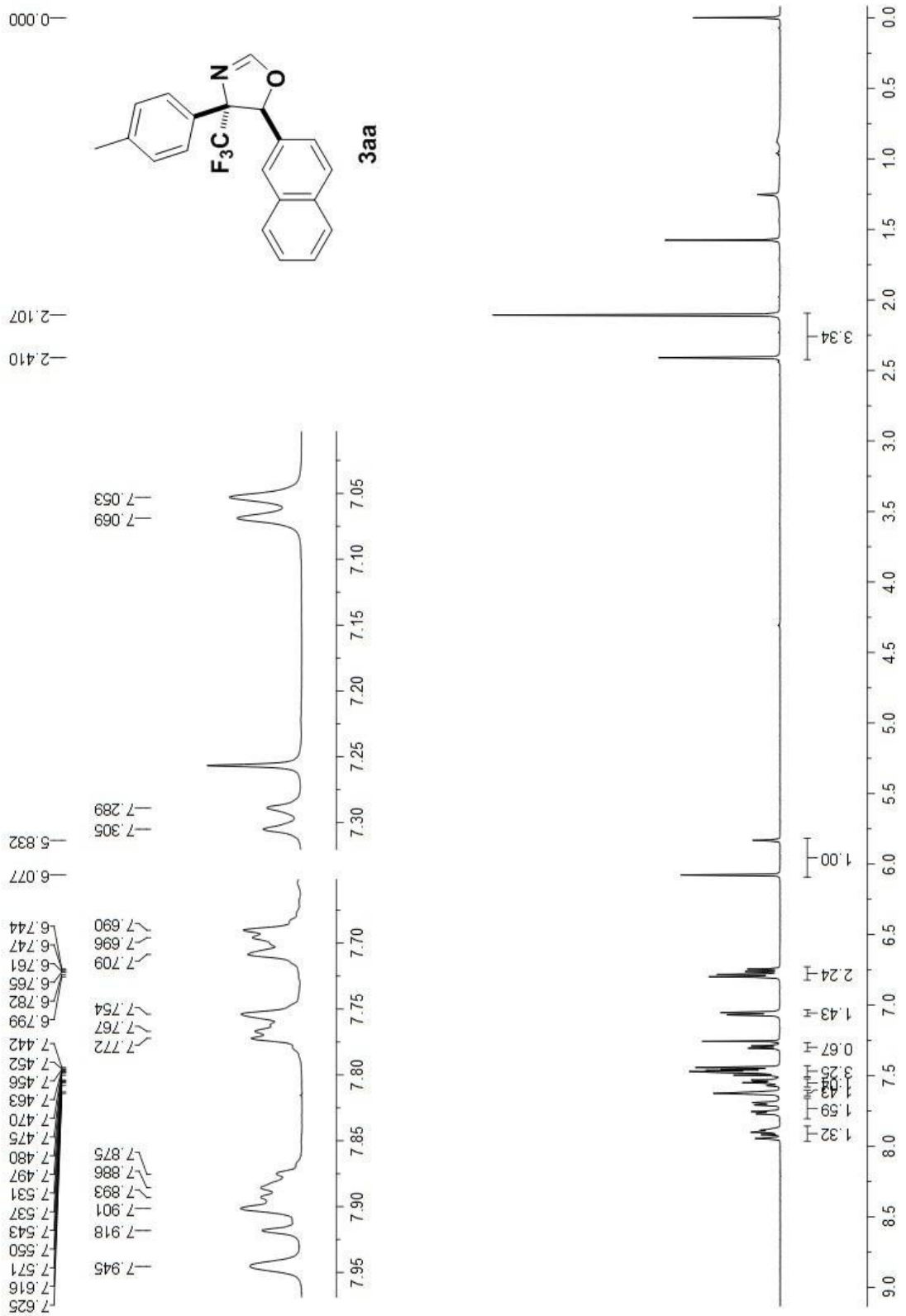
Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 3

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O

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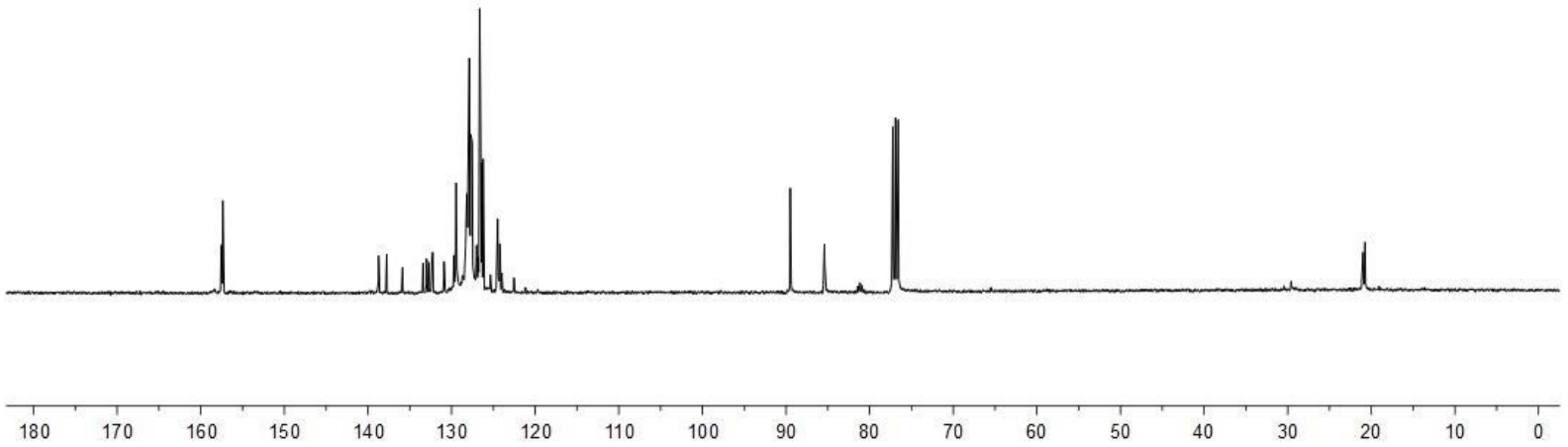
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N
O
F3C
3aa

72.246
78.199
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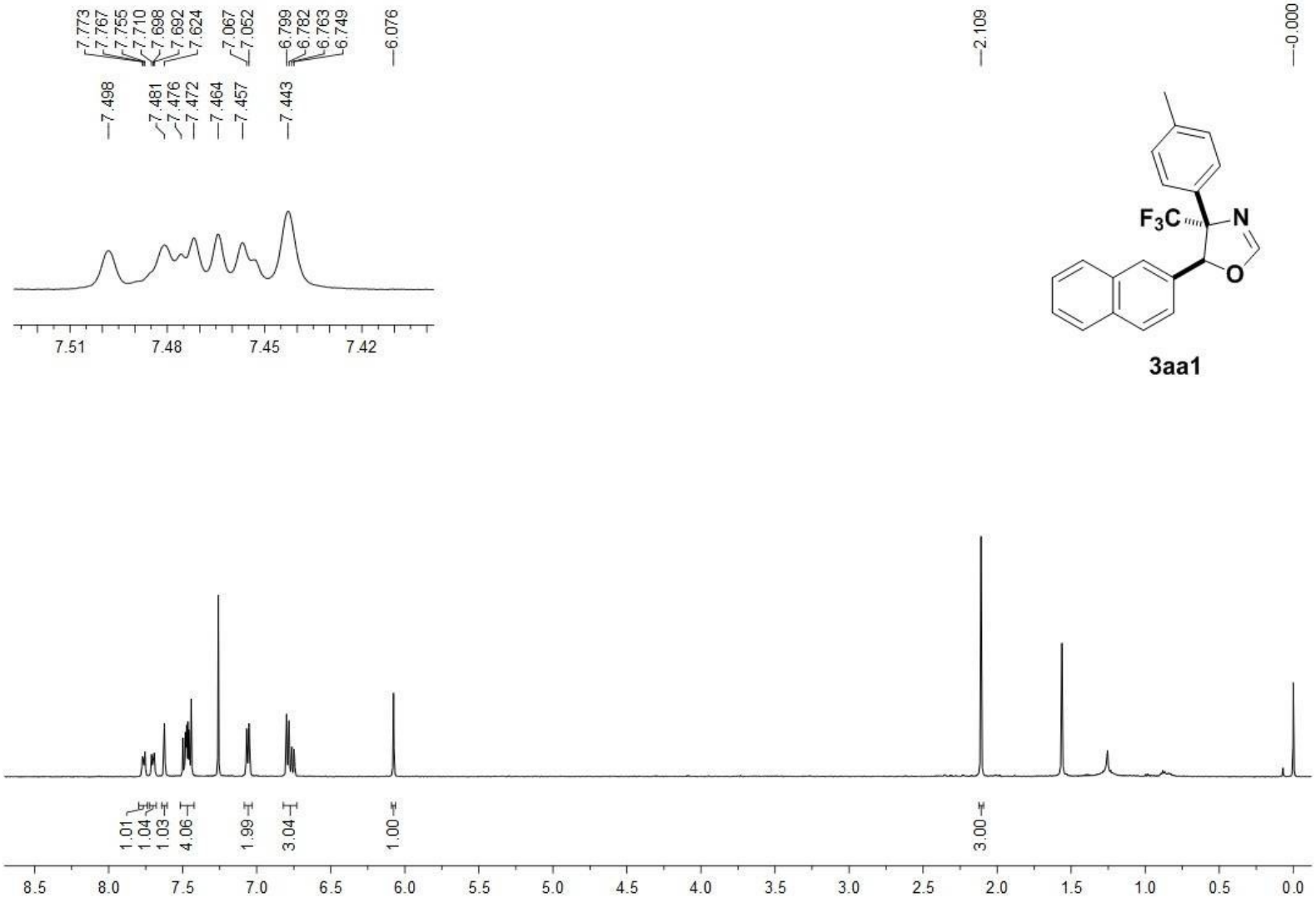
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1.03
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3.04
1.00
3.00
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6.882
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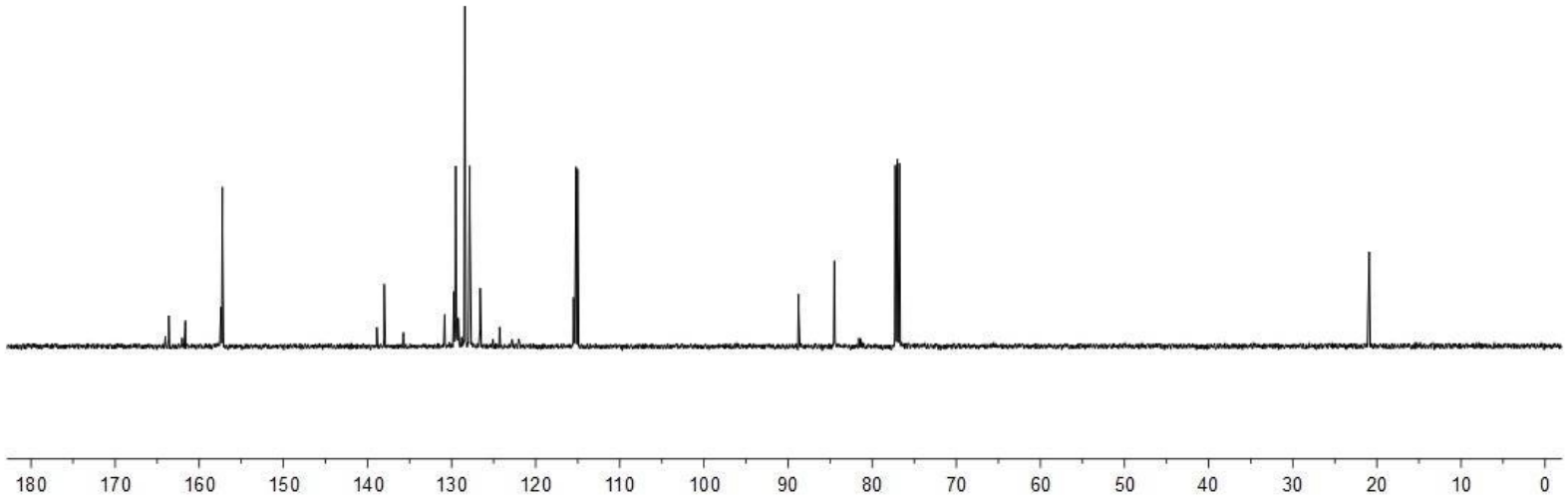
F

3ba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O
F
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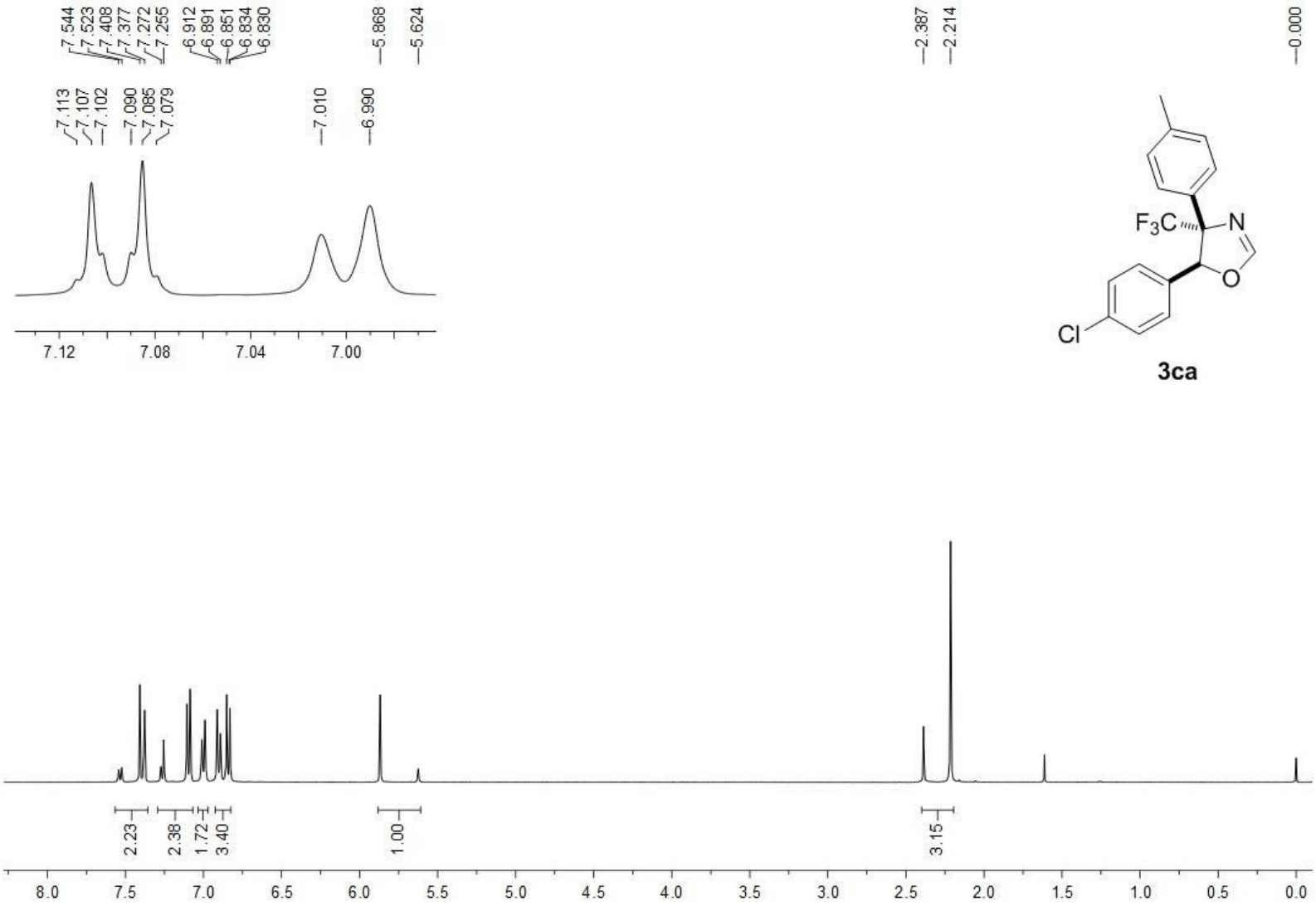
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6.990
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O
Cl
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3.40
1.00
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7.0
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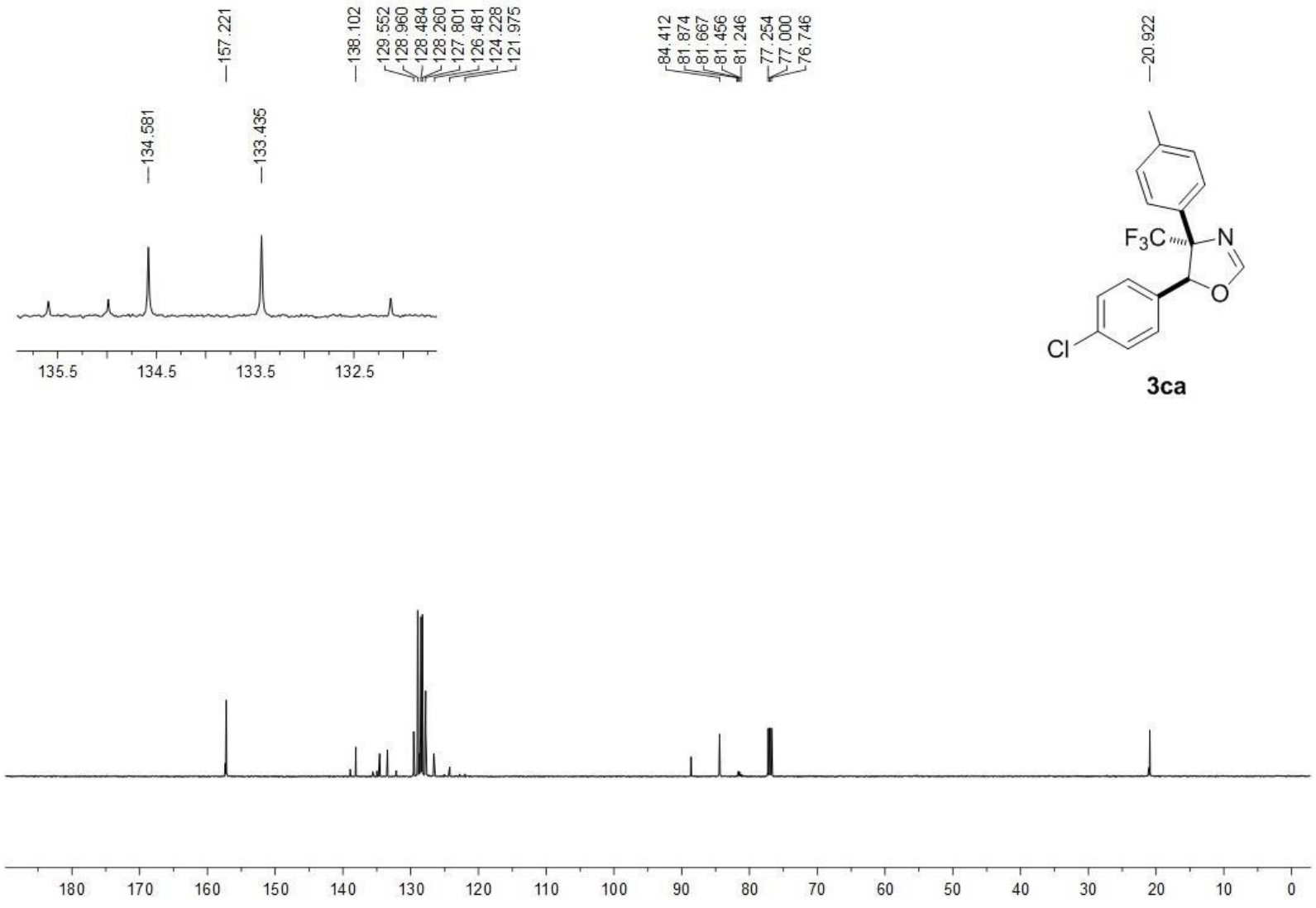
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81.246
77.254
77.000
76.746
20.922
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133.435
135.5
134.5
133.5
132.5
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O
Cl
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150
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60
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20
10
0

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-220

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7.542
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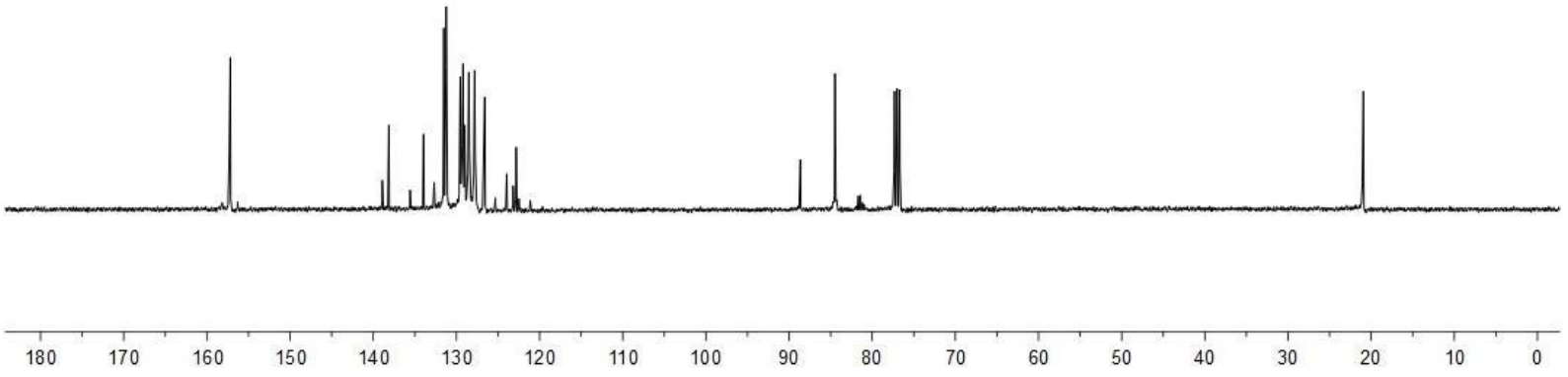
O
Br

3da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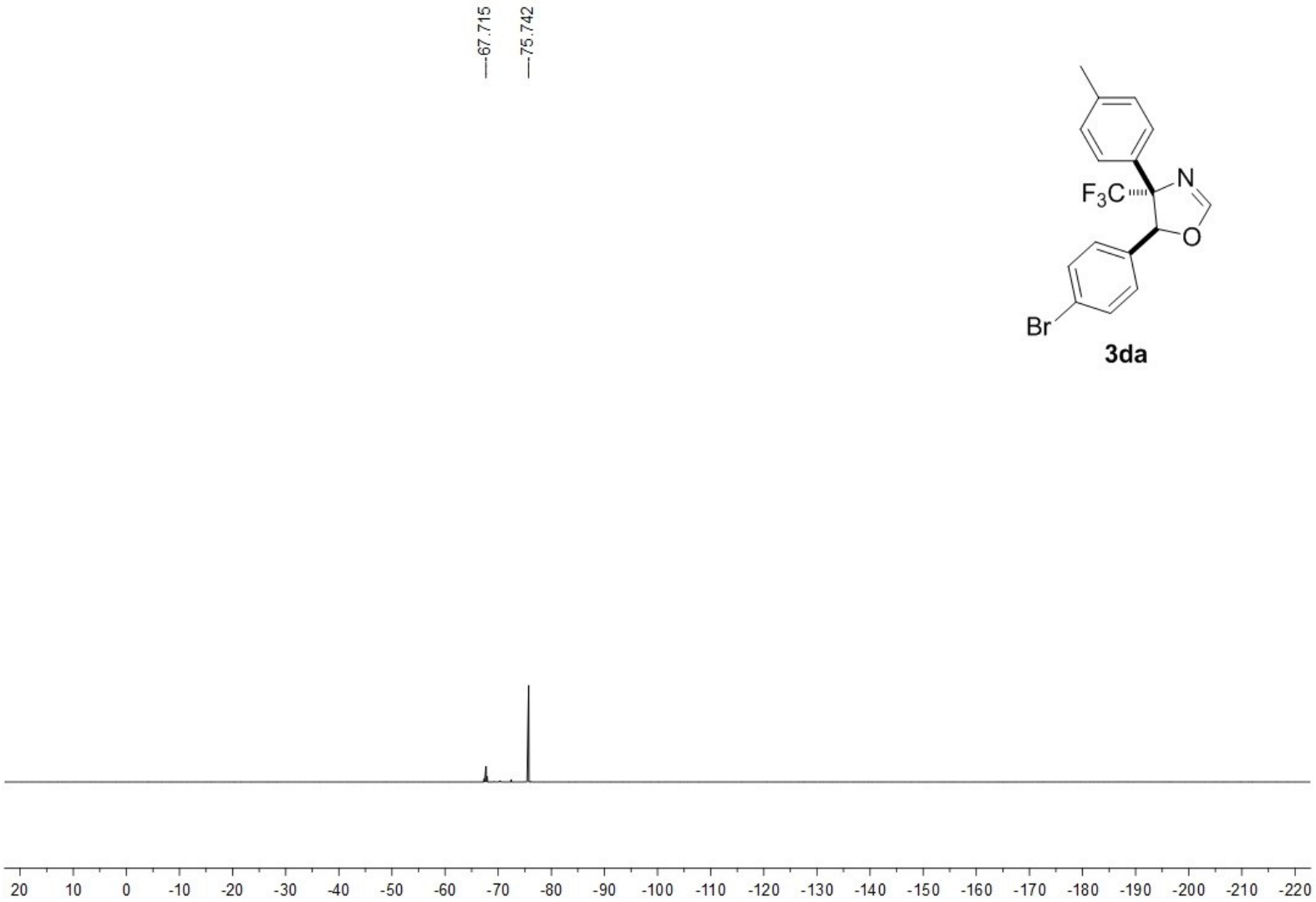
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-150
-160
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-190
-200
-210
-220

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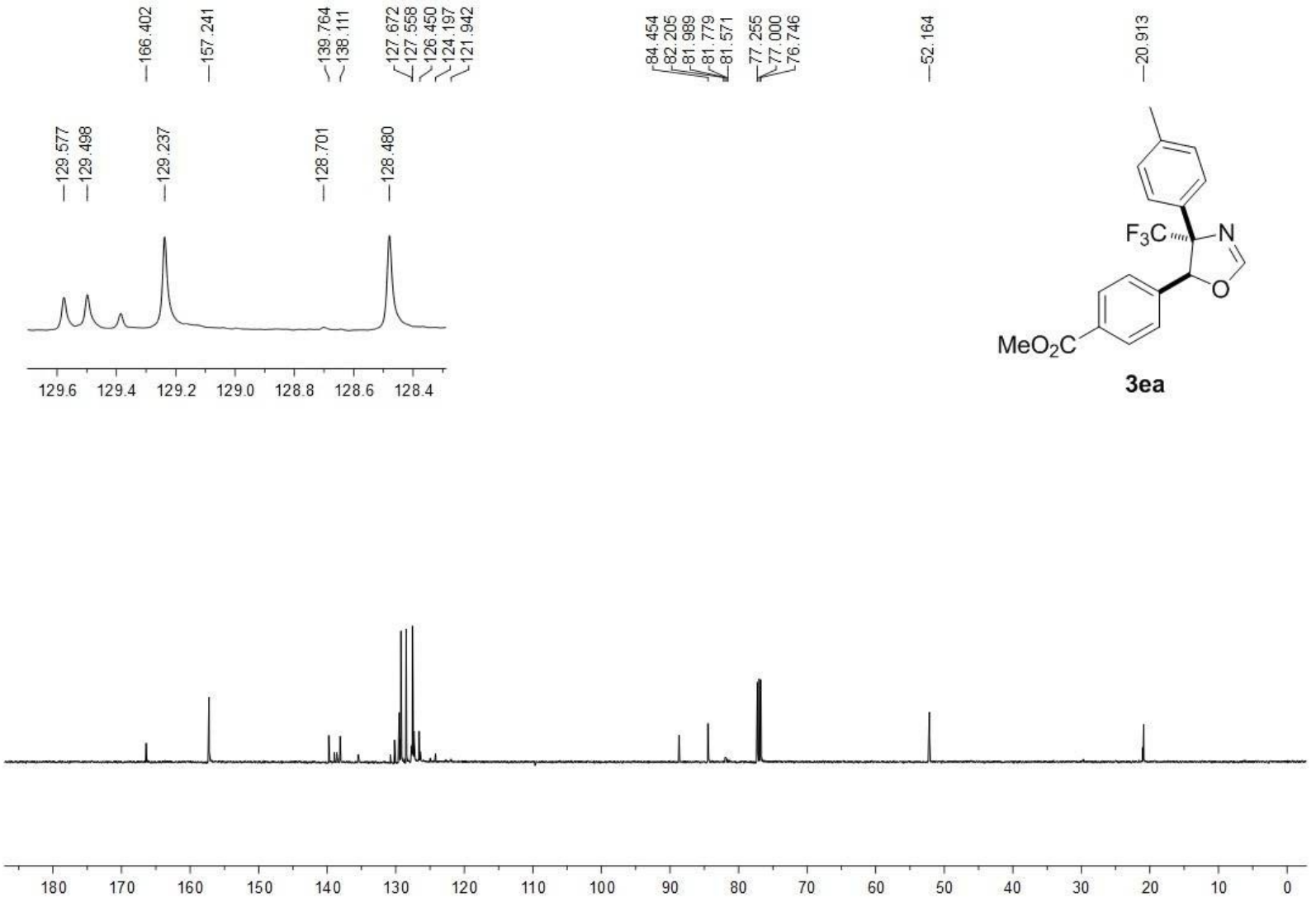
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129.498
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128.4
F3C
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MeO2C
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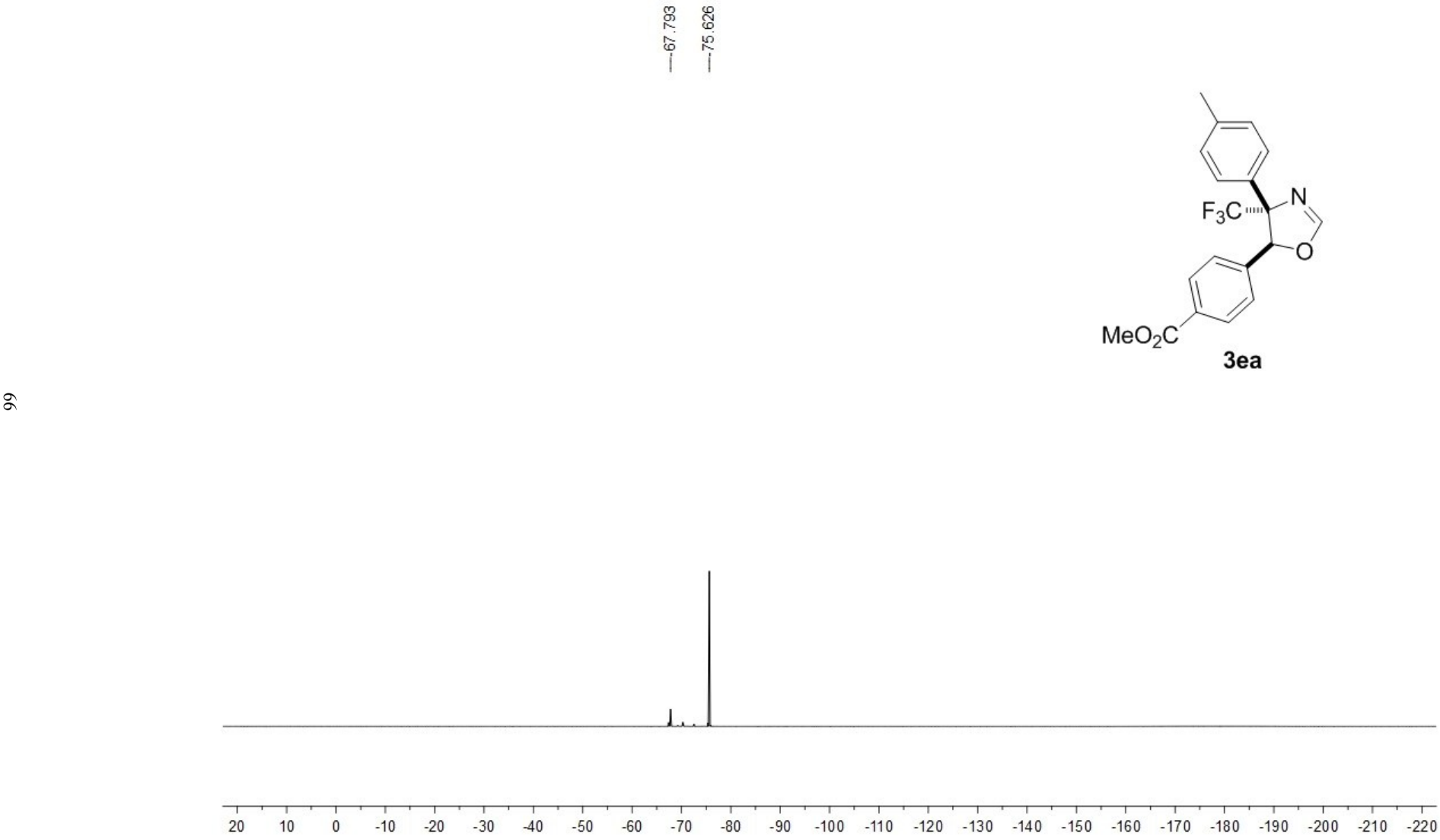
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-160
-170
-180
-190
-200
-210
-220

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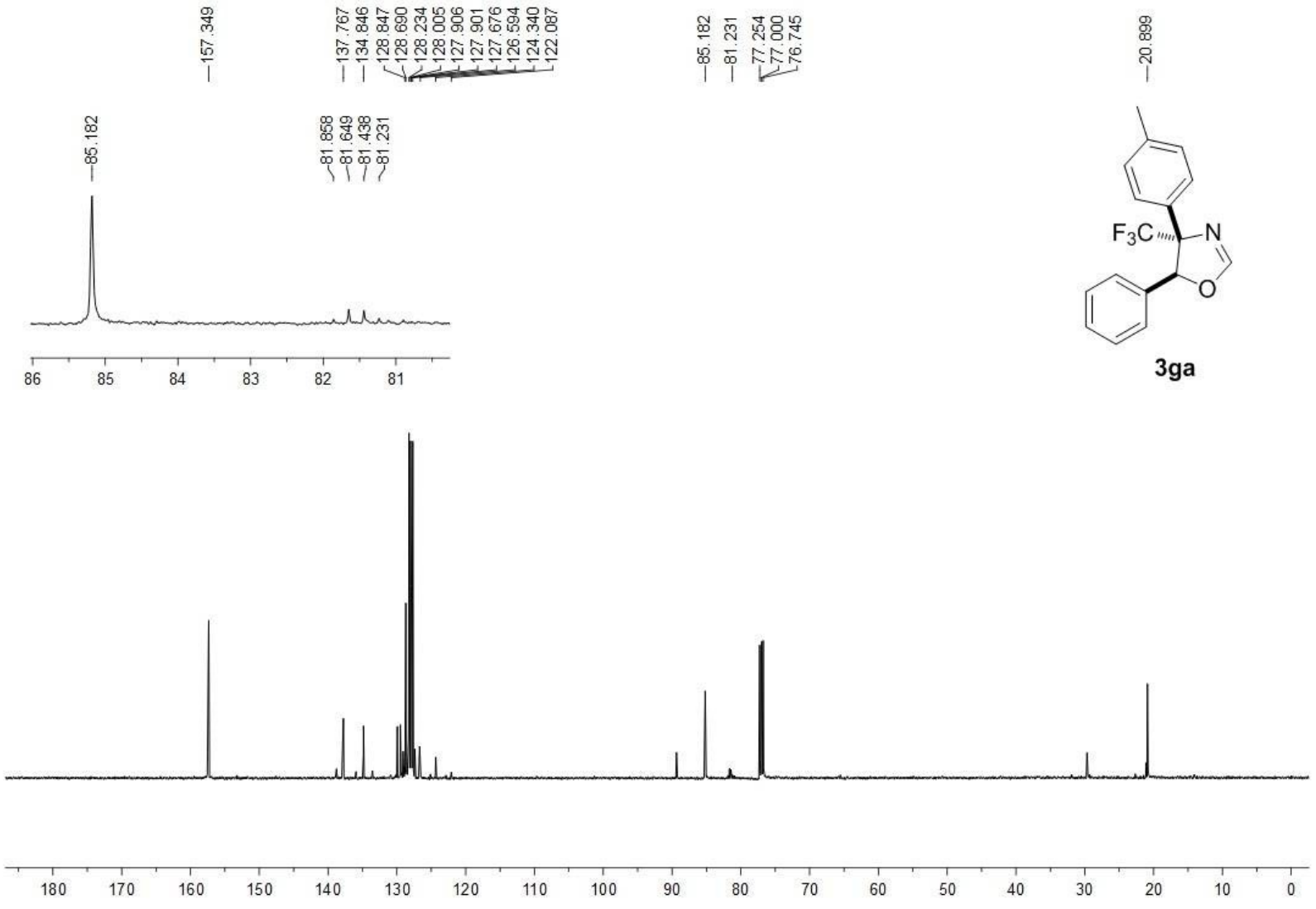
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F3C
3ga

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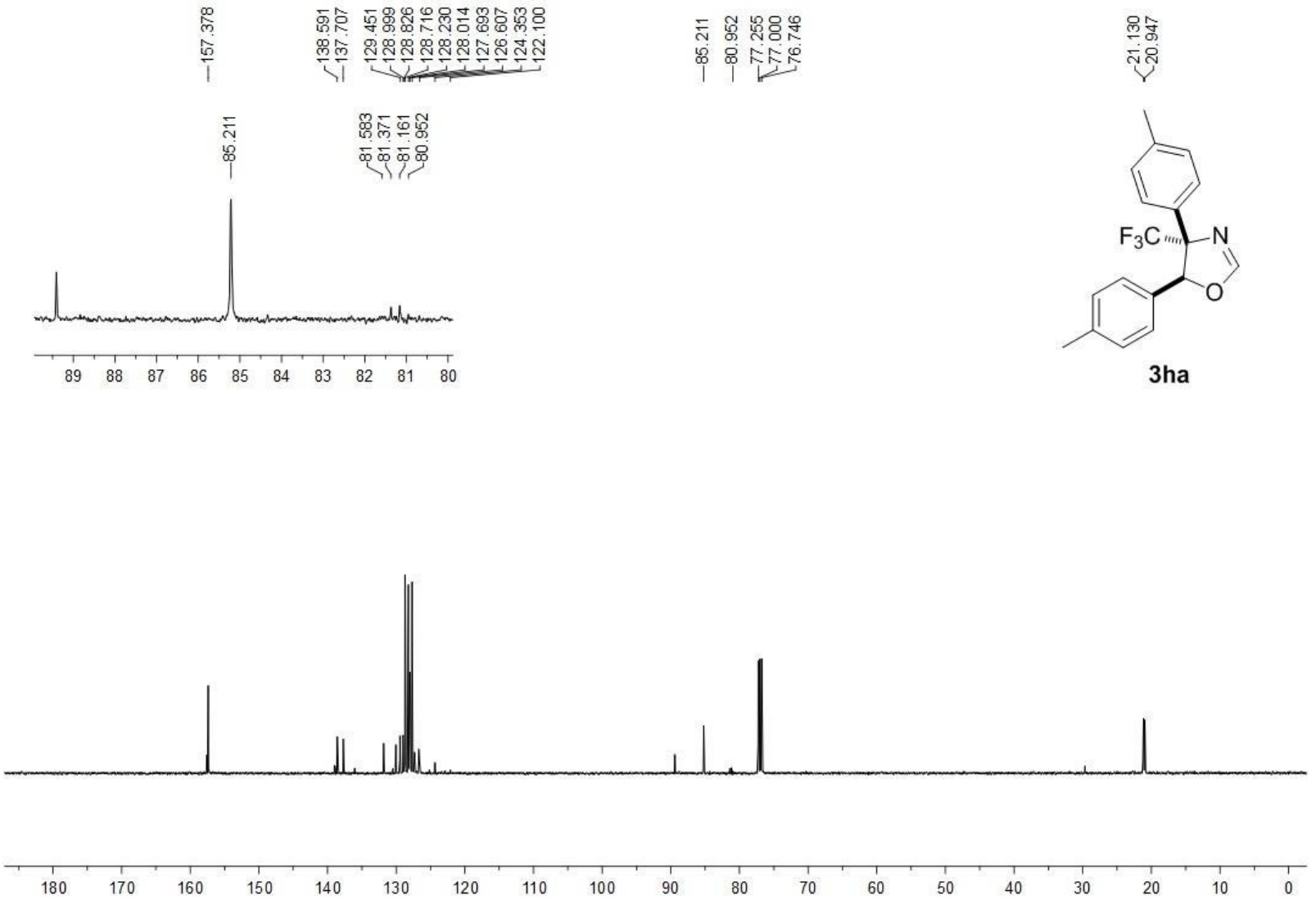
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N
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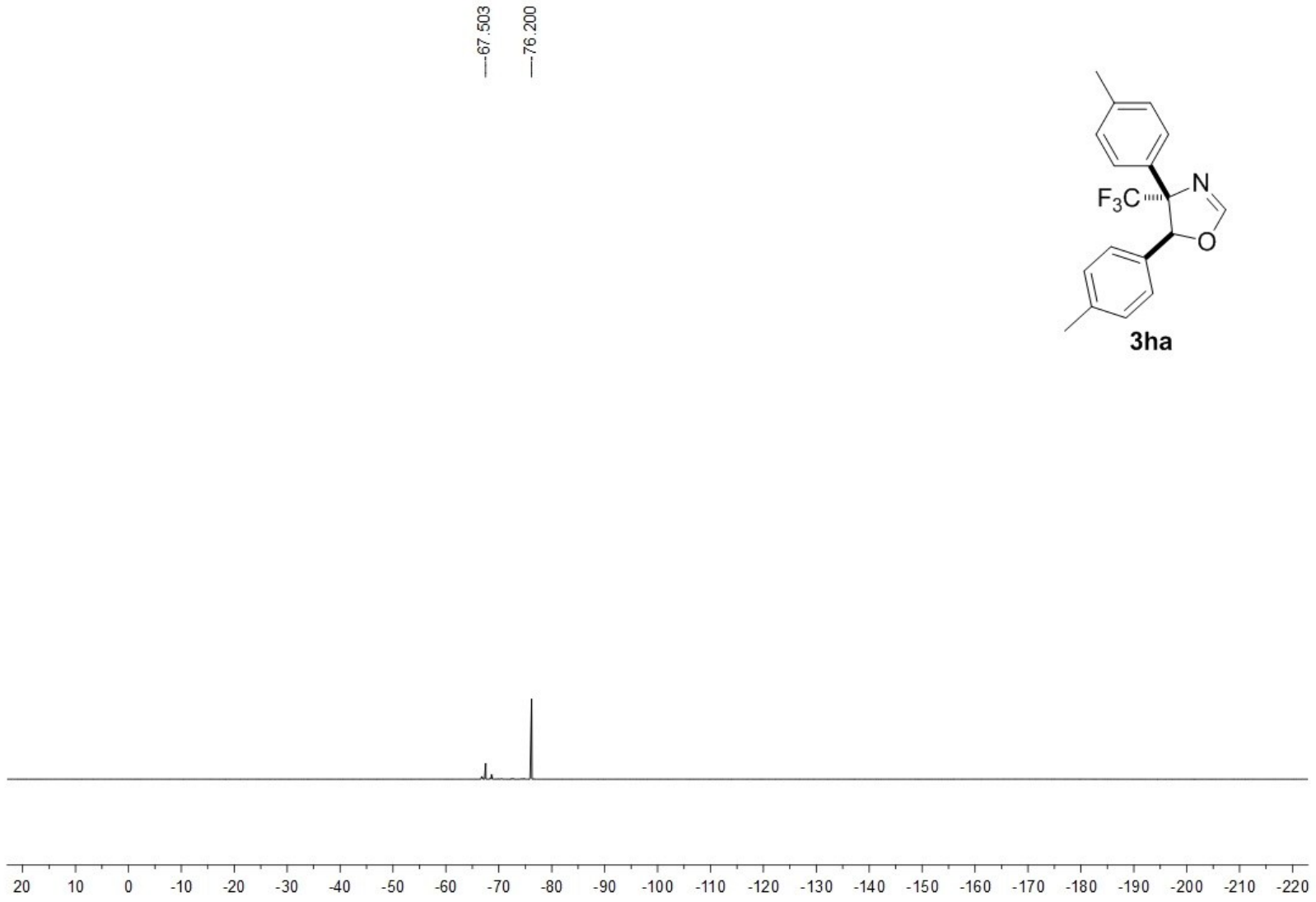
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3ia
MeO
F3C
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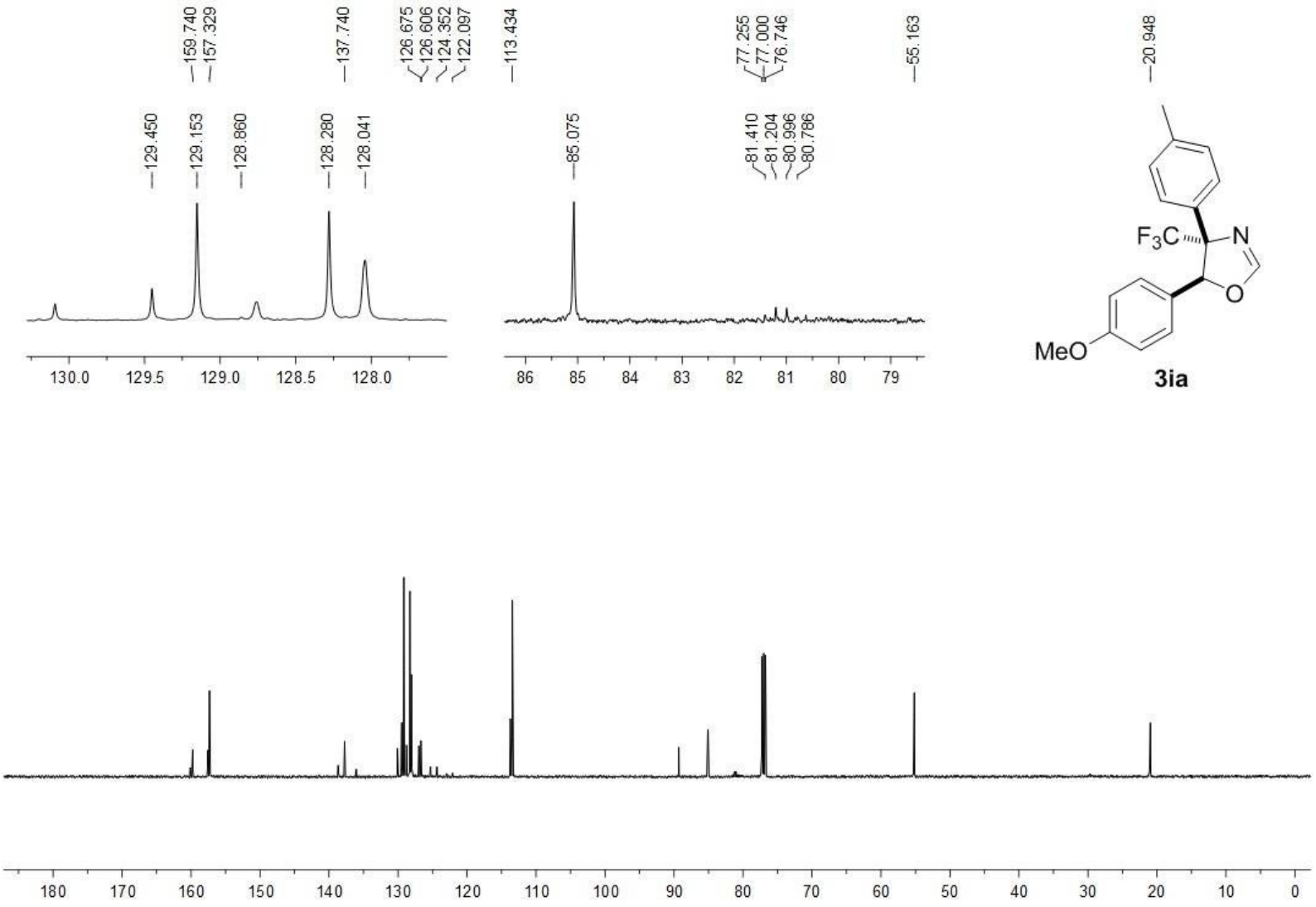
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MeO
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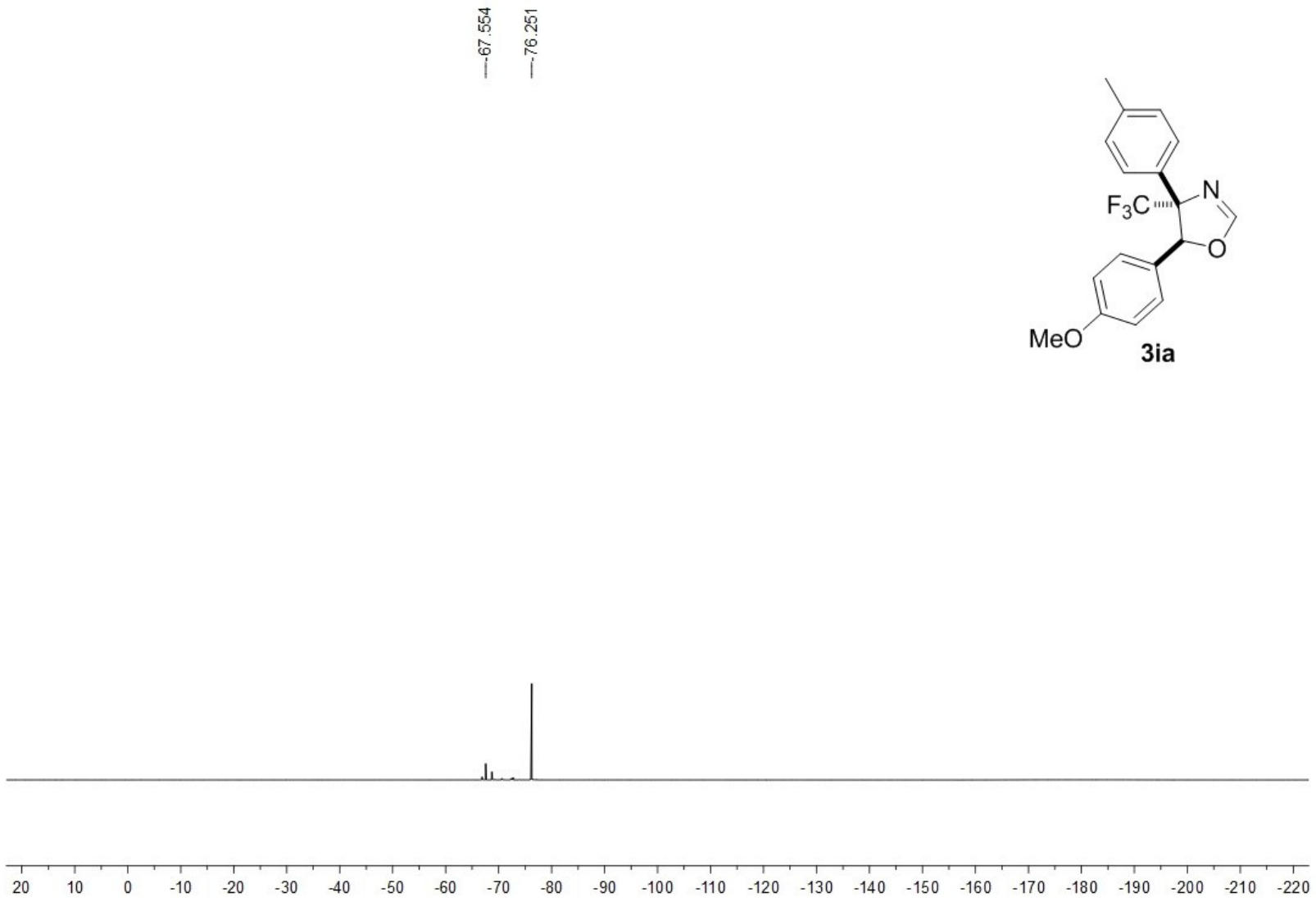
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7.127
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7.12
7.08
7.04
7.00
F3C
N
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Cl
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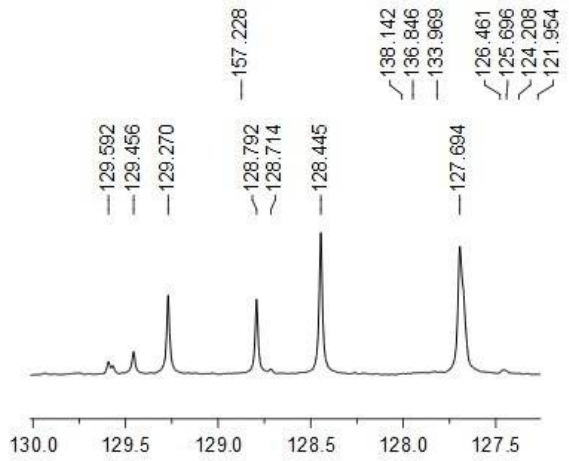
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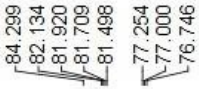
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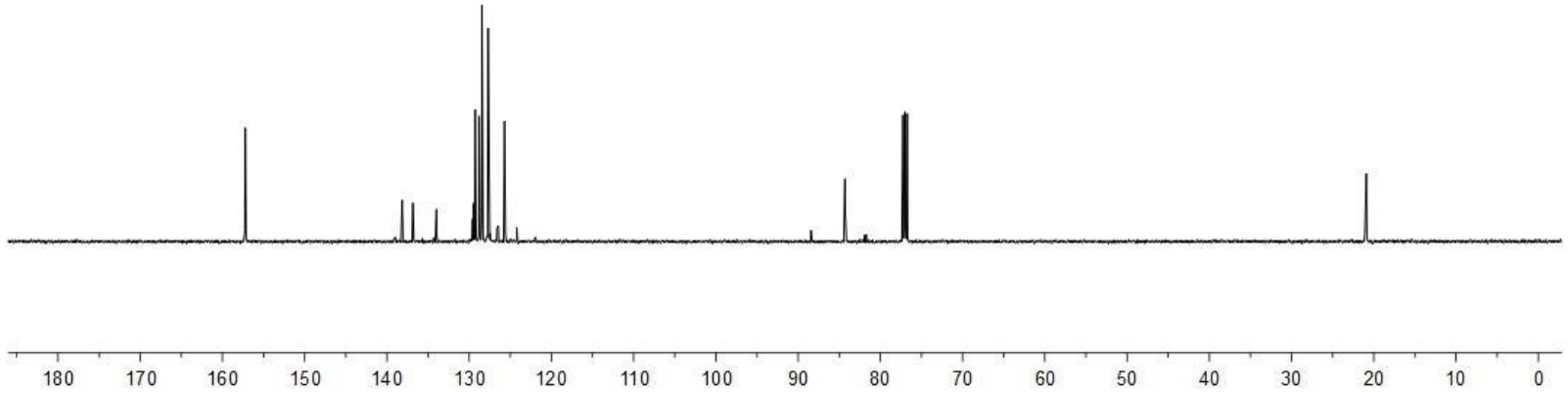
O

3ja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N
O
F3C
Cl

3ja

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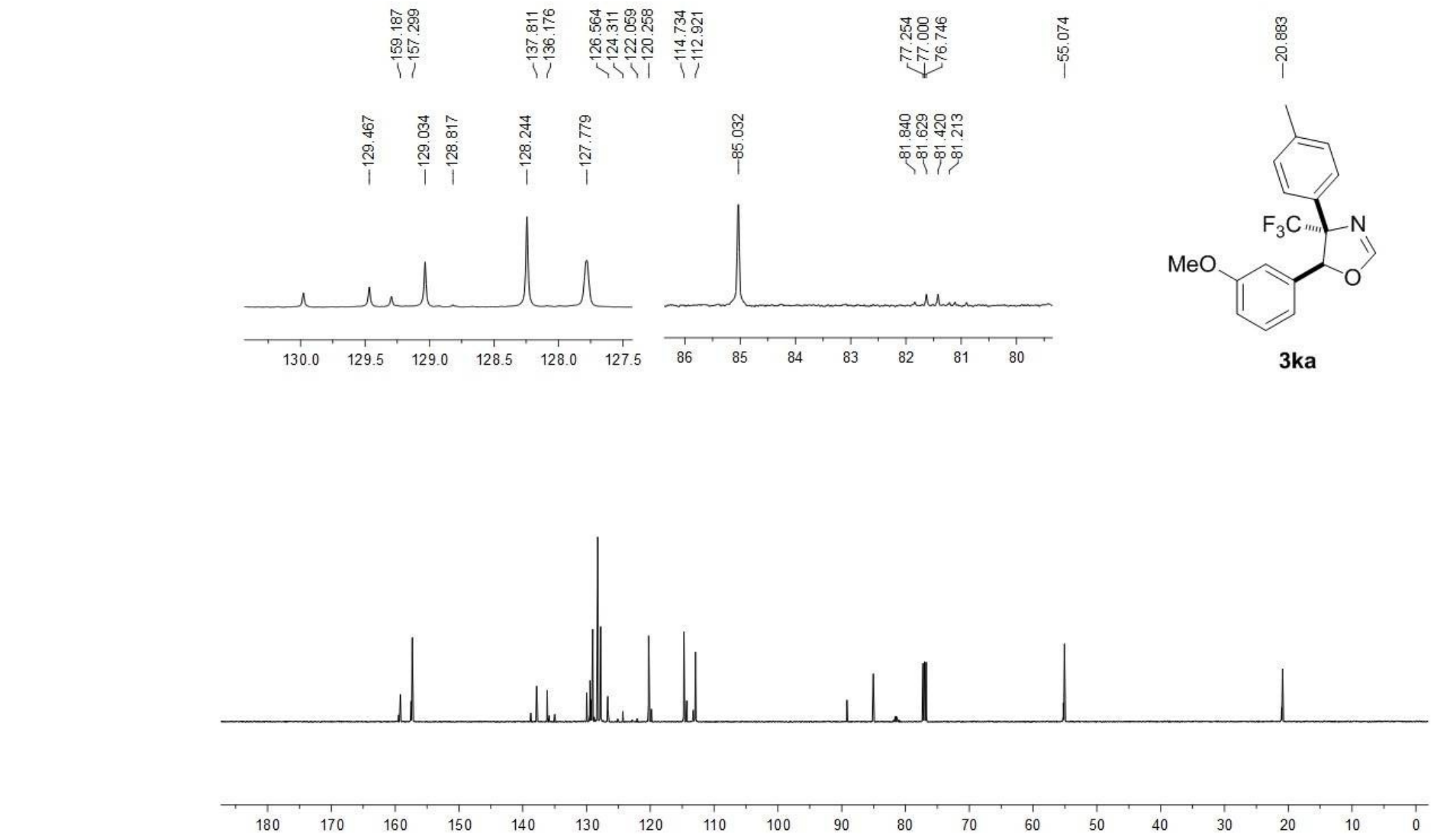
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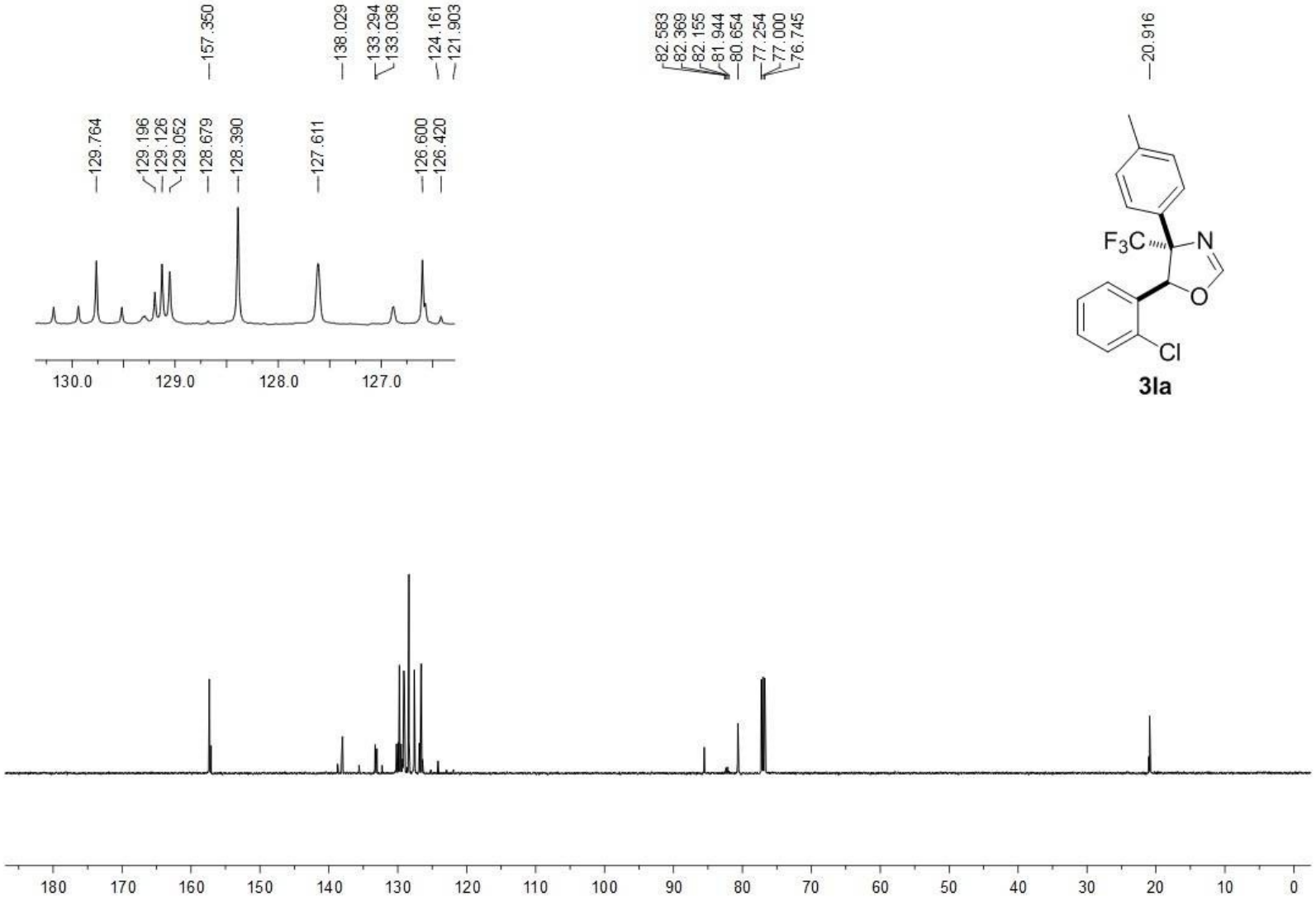
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O
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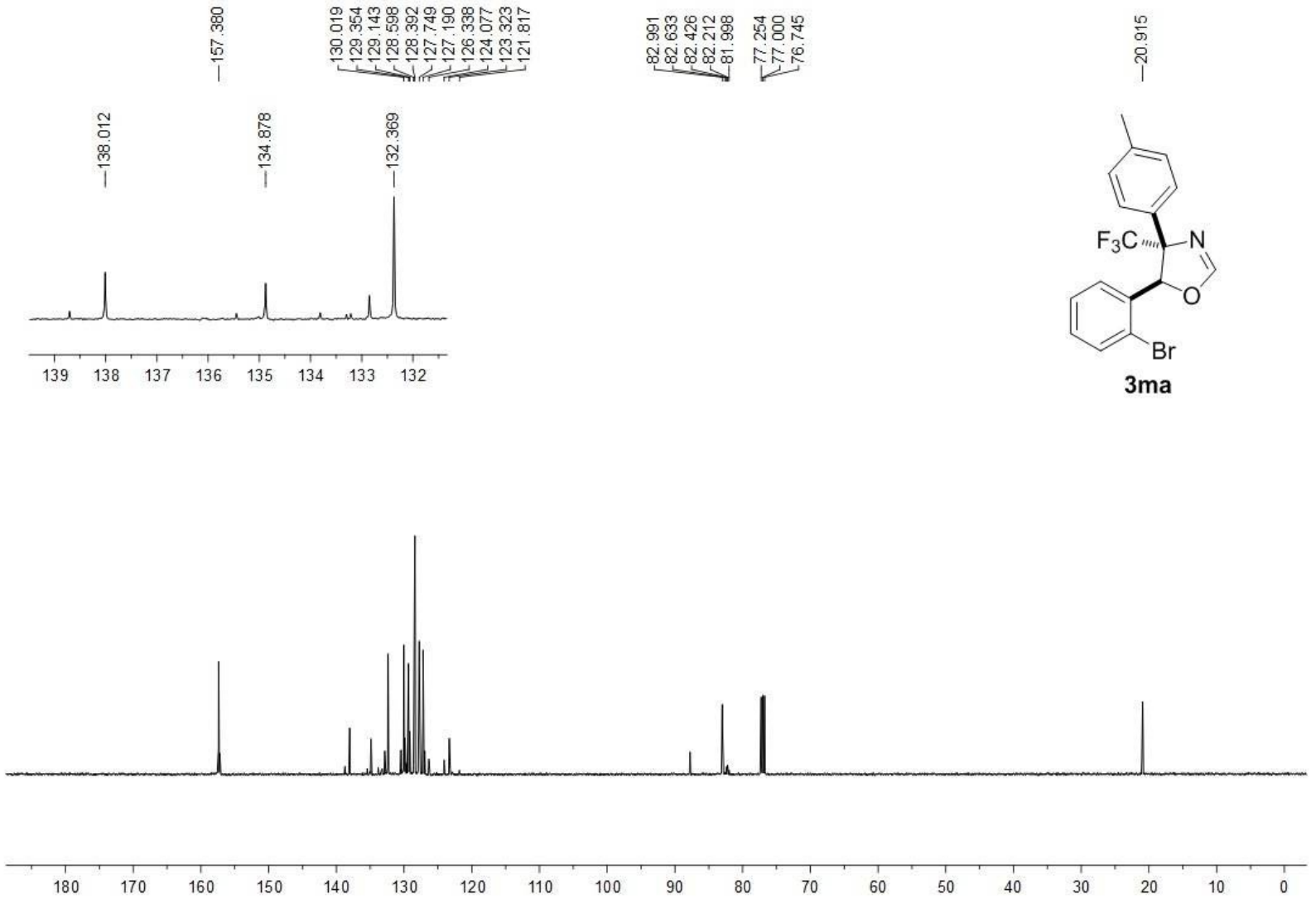
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Br
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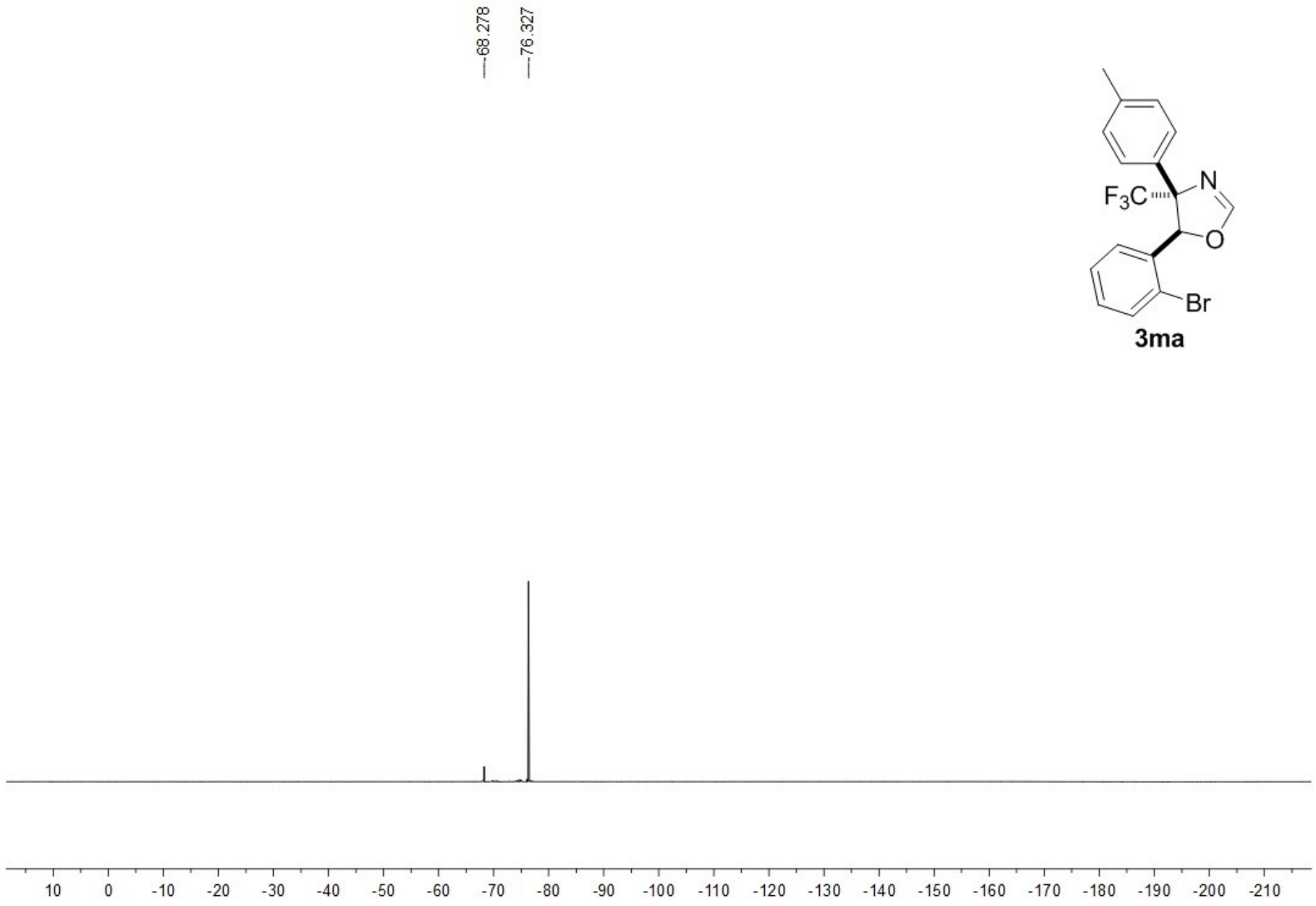
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3na

N
O
F3C
S

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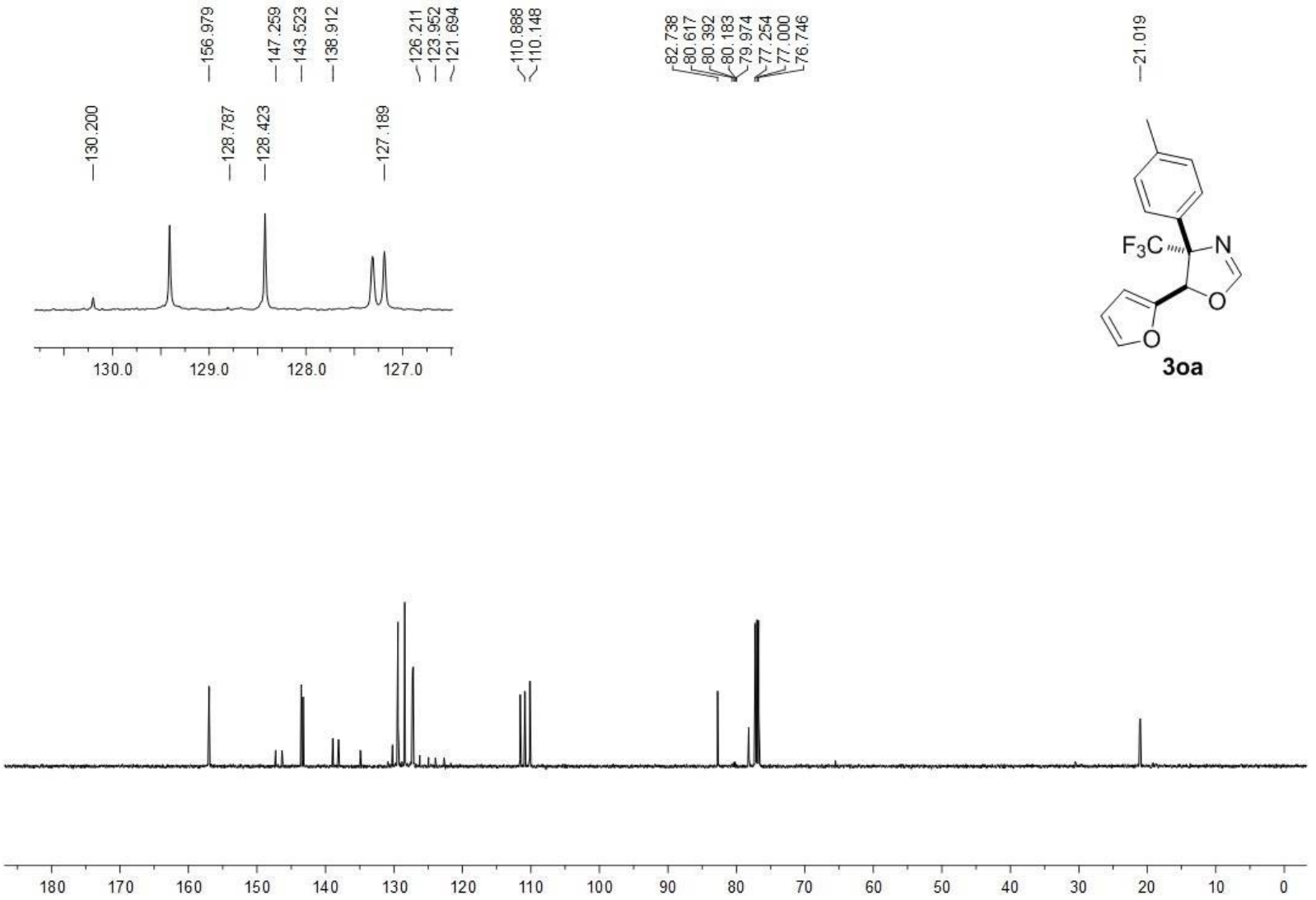
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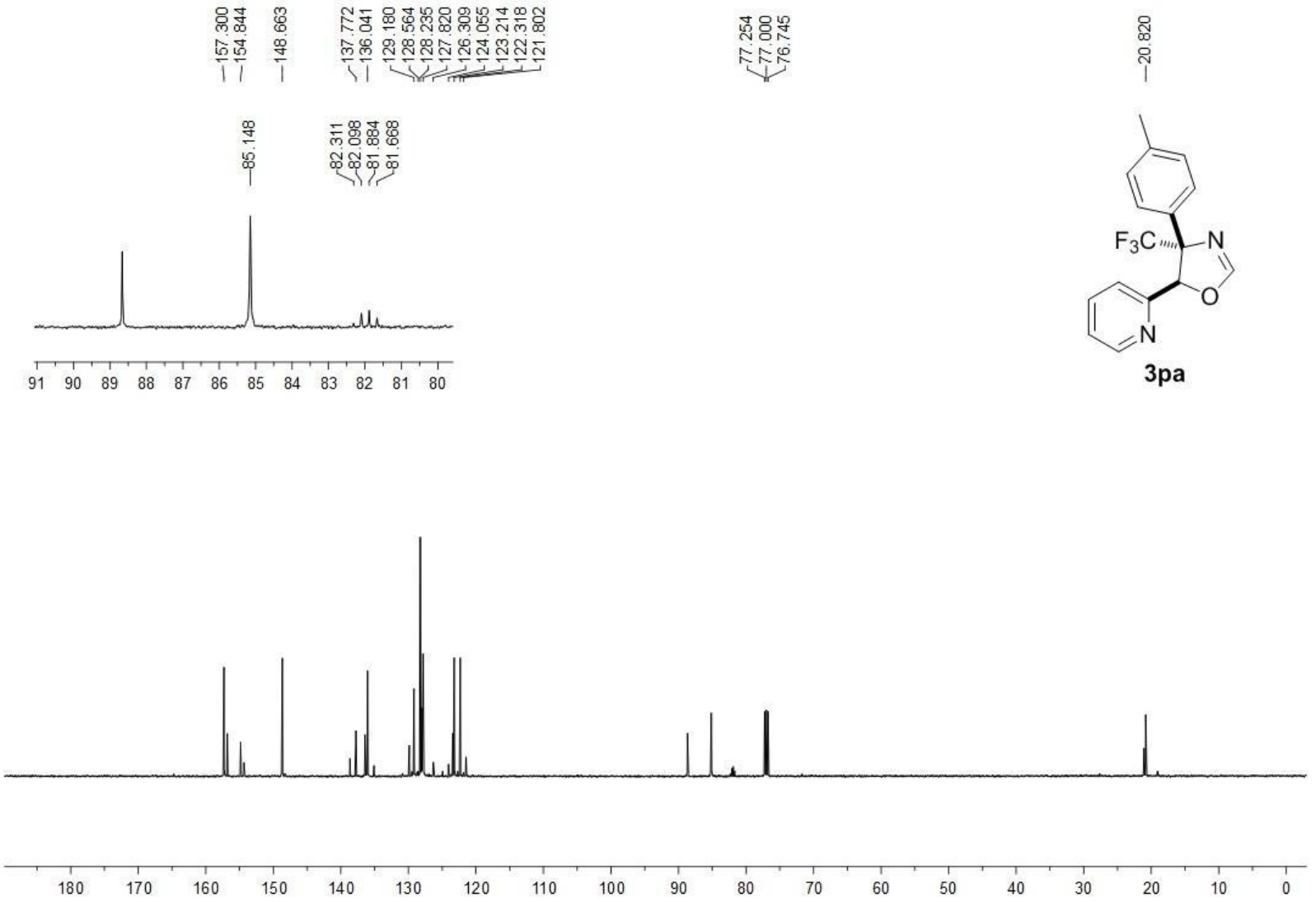
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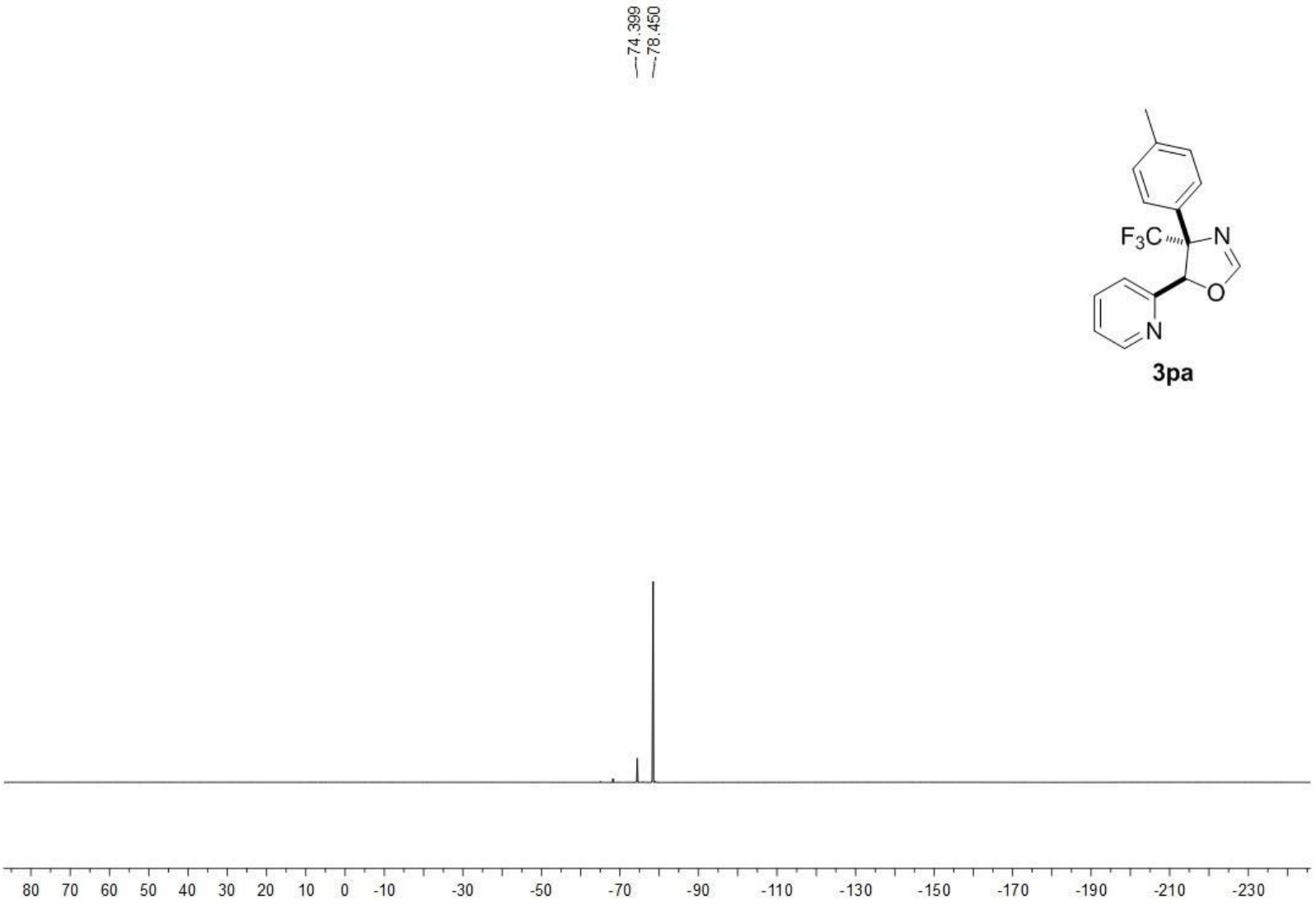
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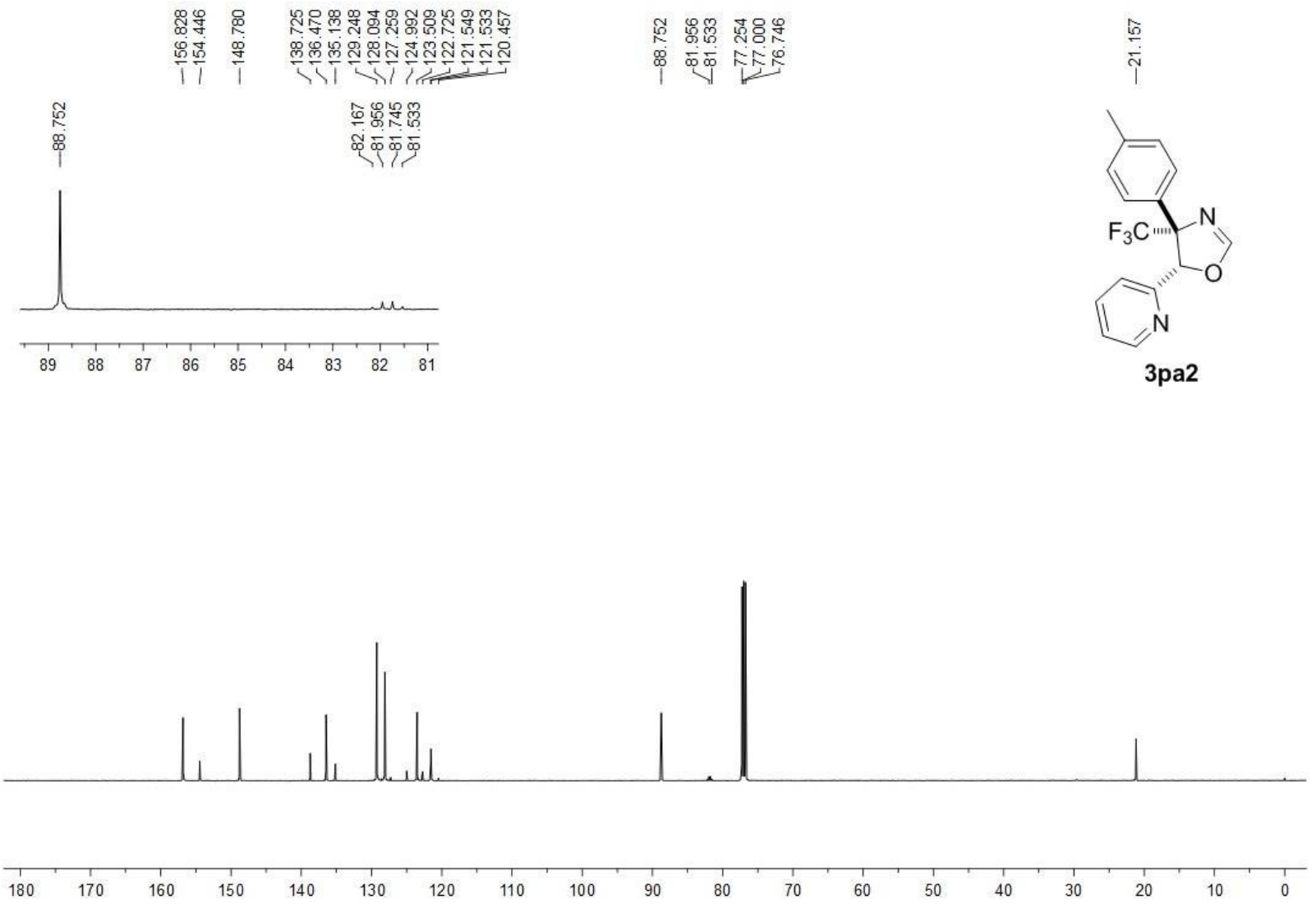
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3qa

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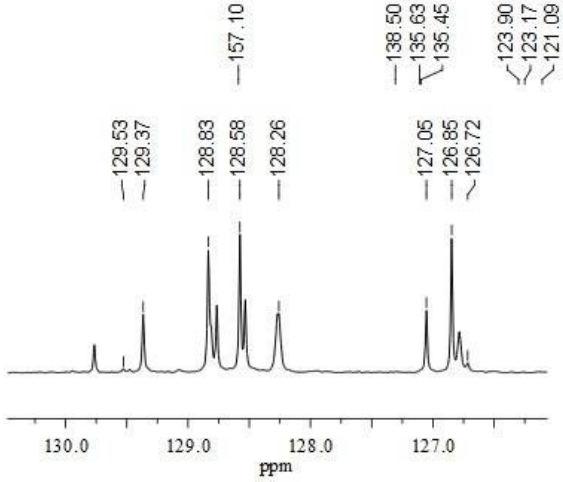
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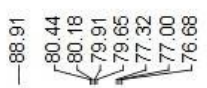
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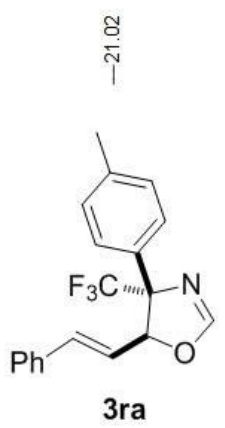
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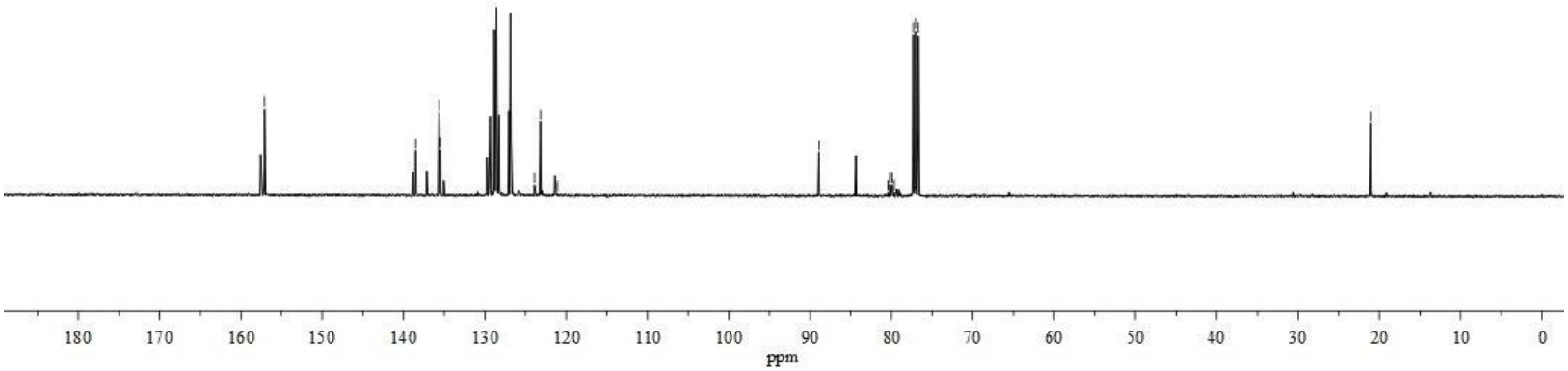
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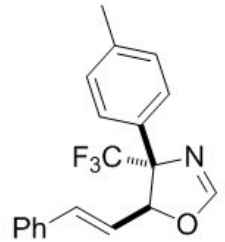
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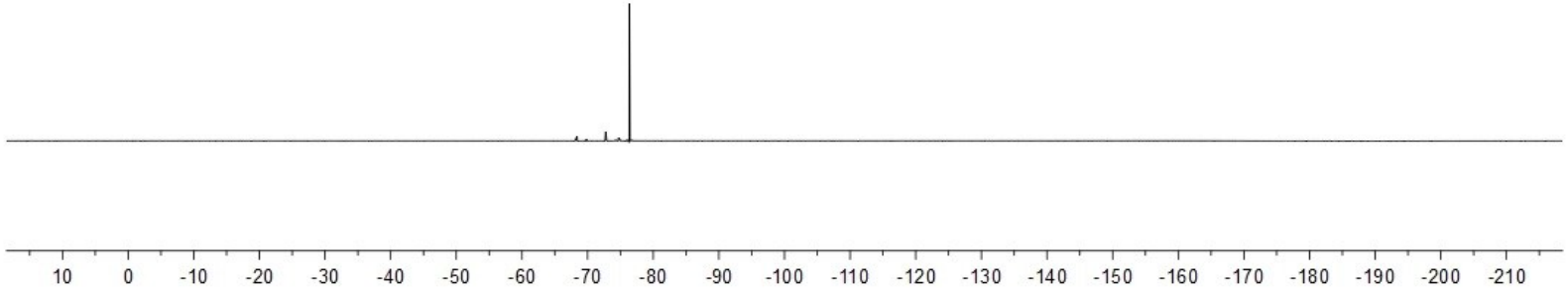
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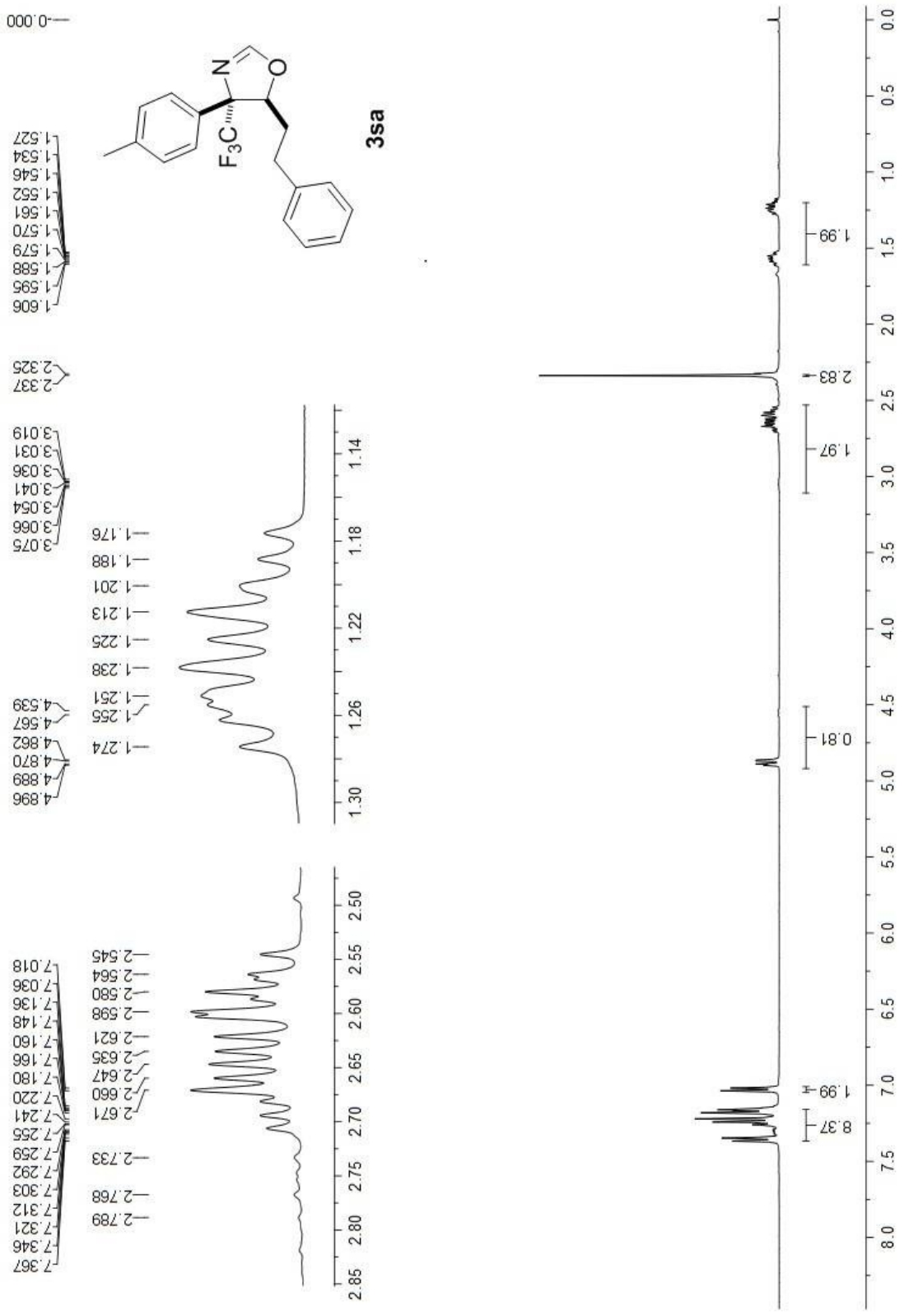
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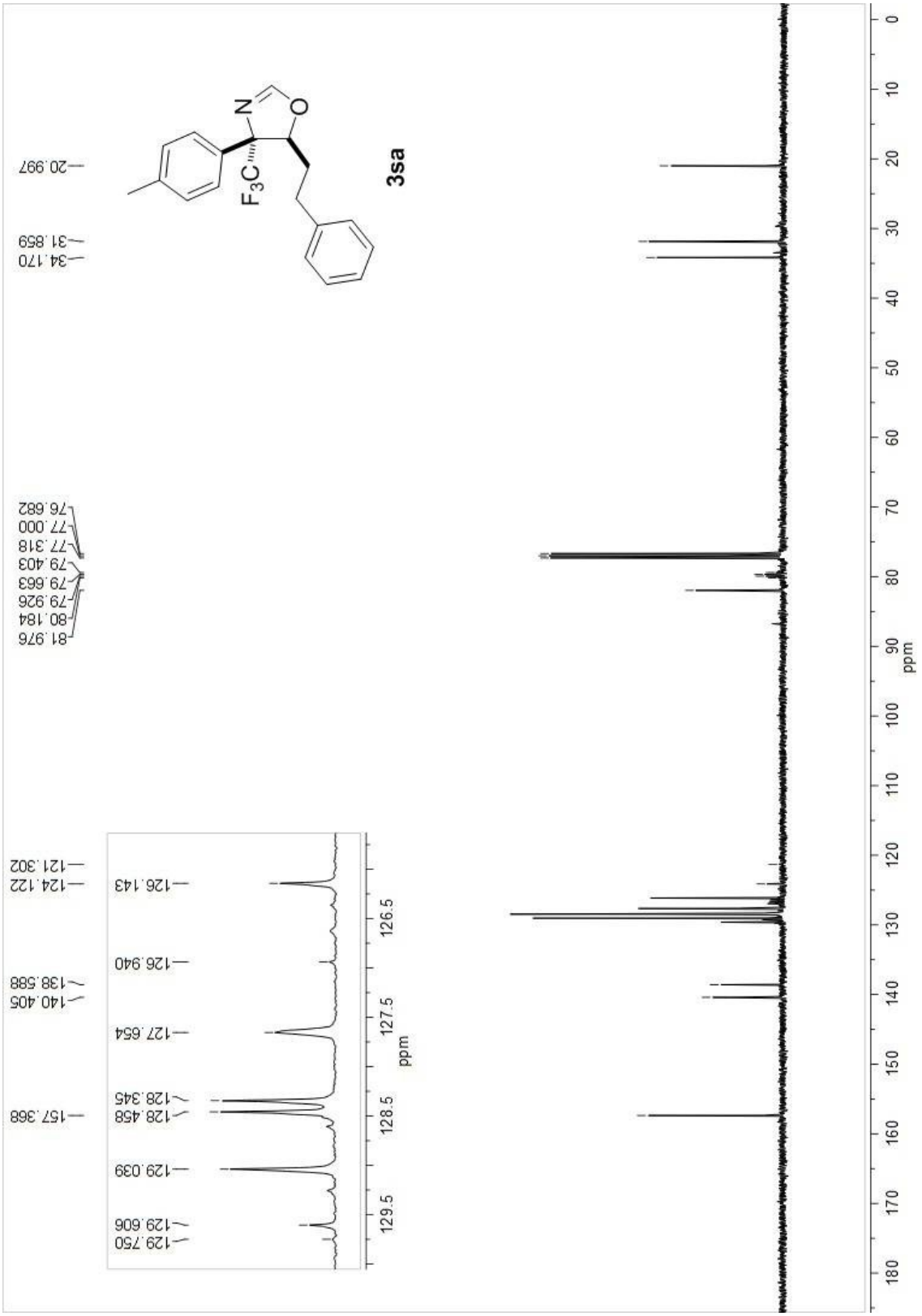
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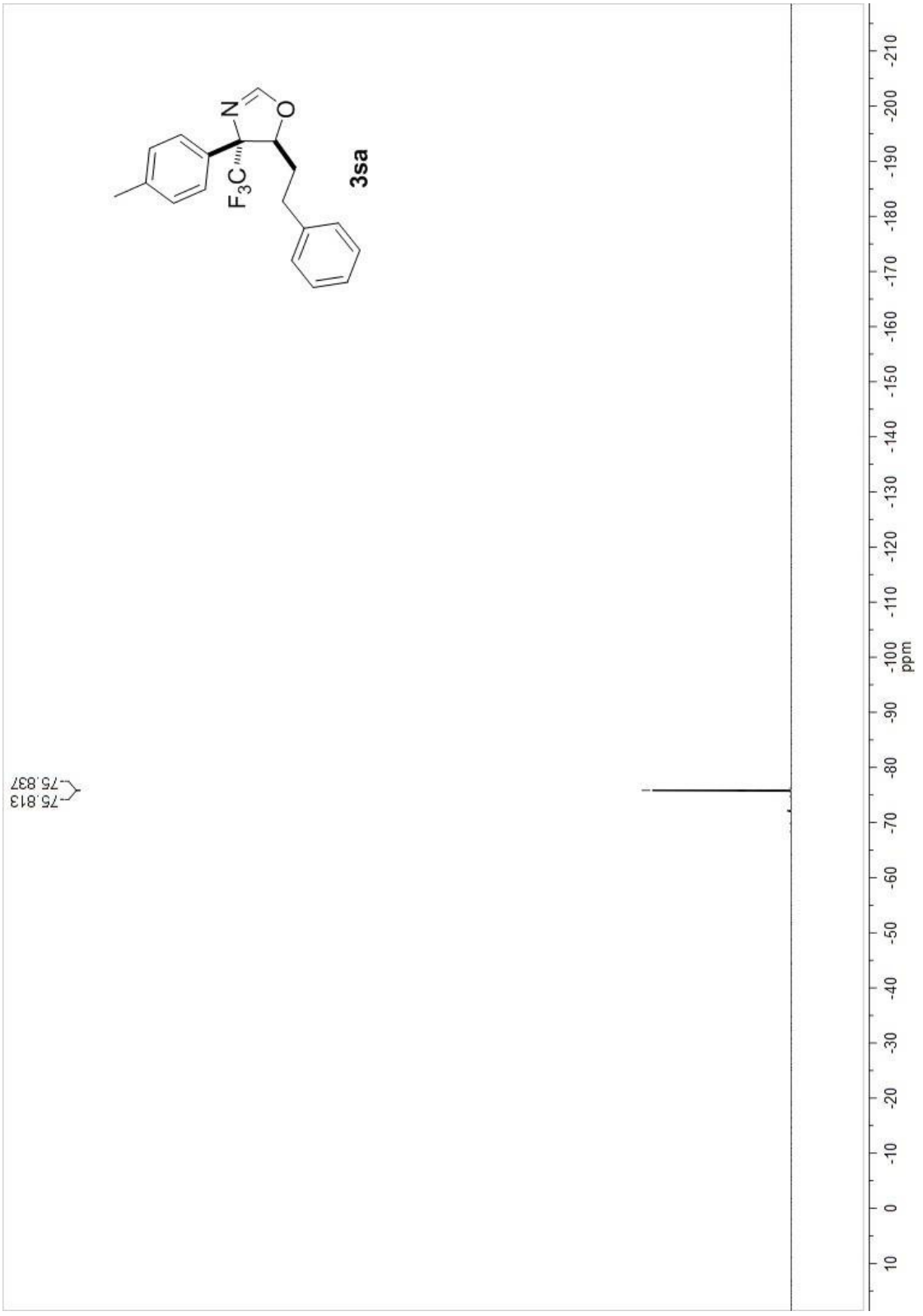
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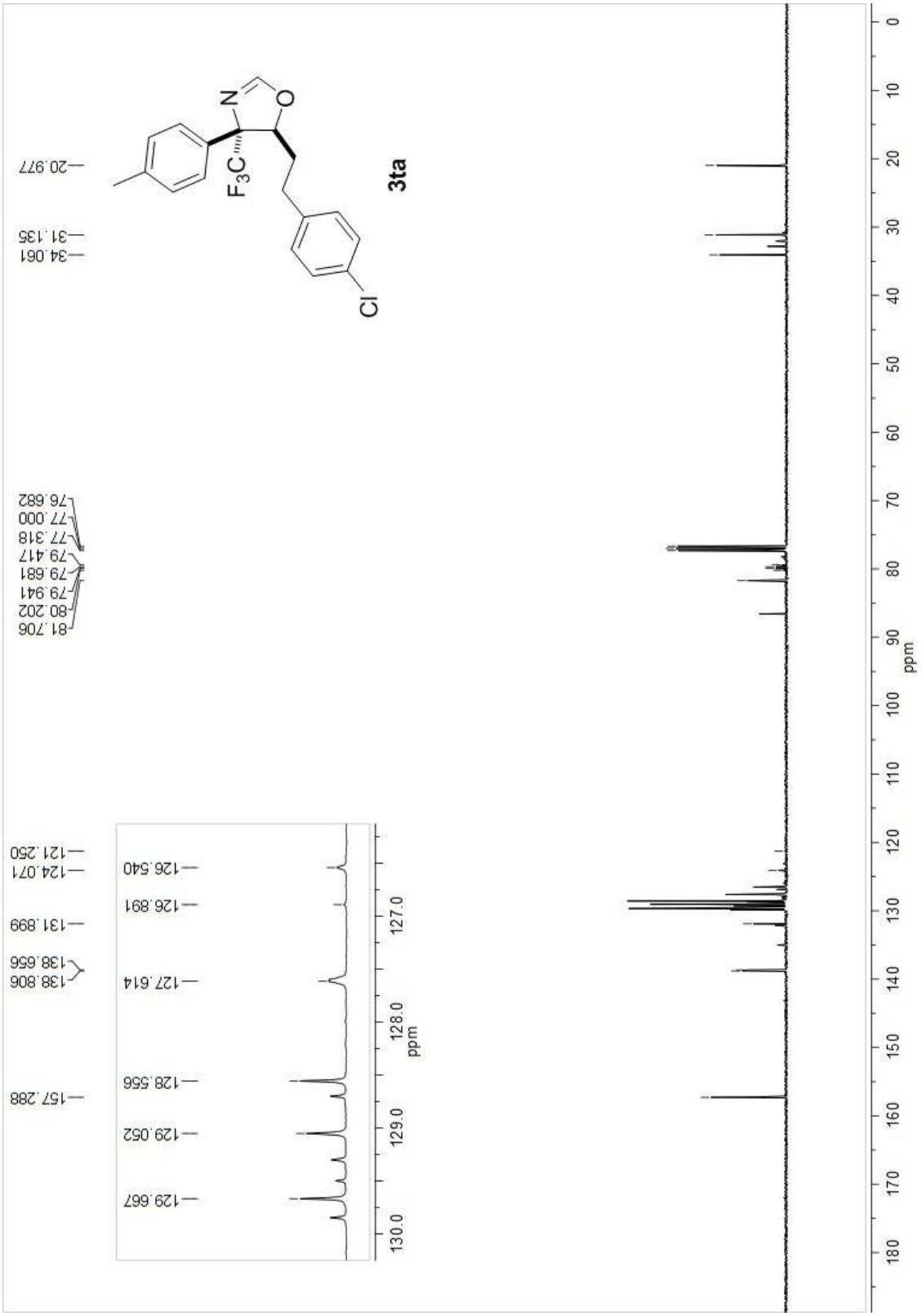
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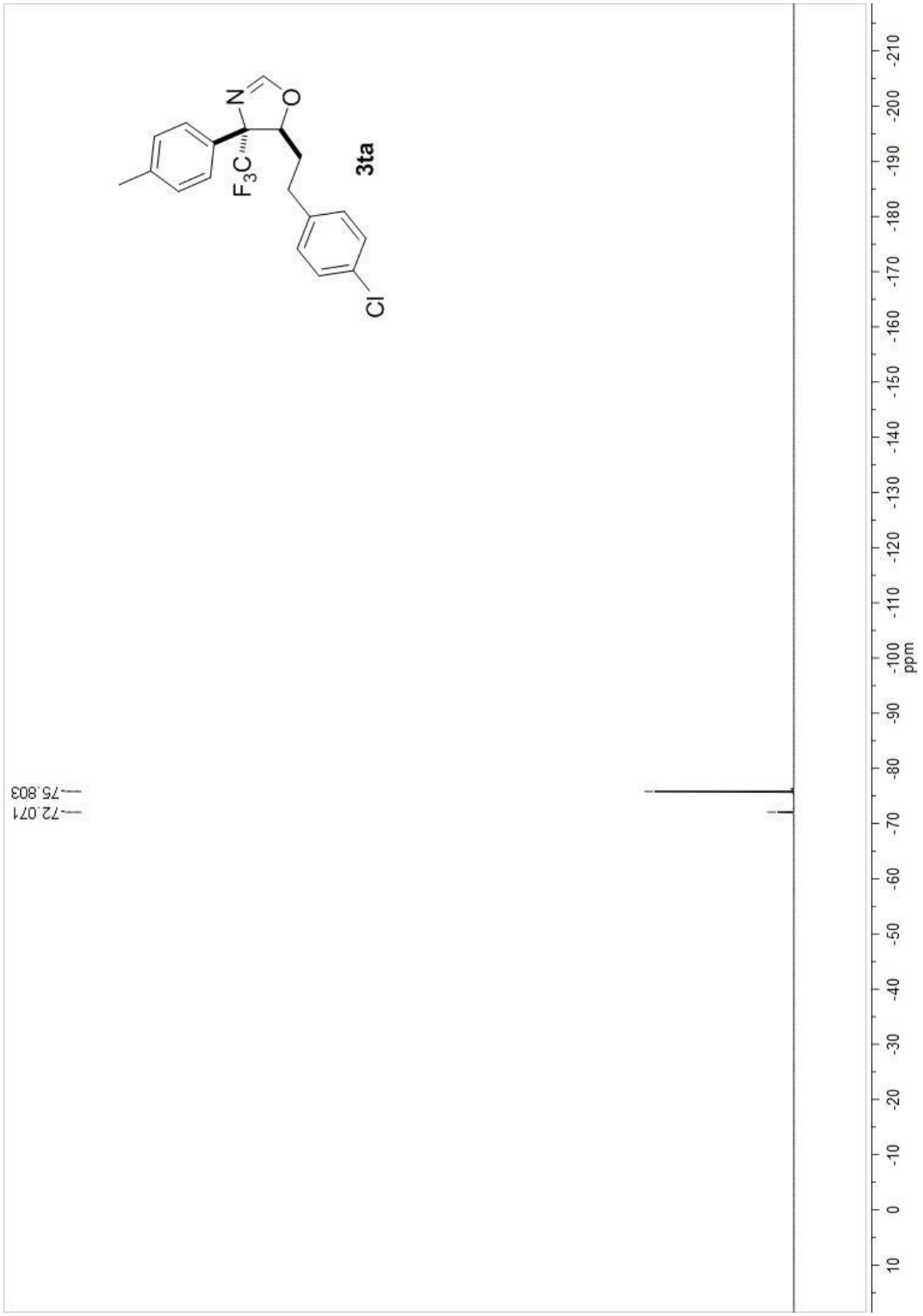
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O

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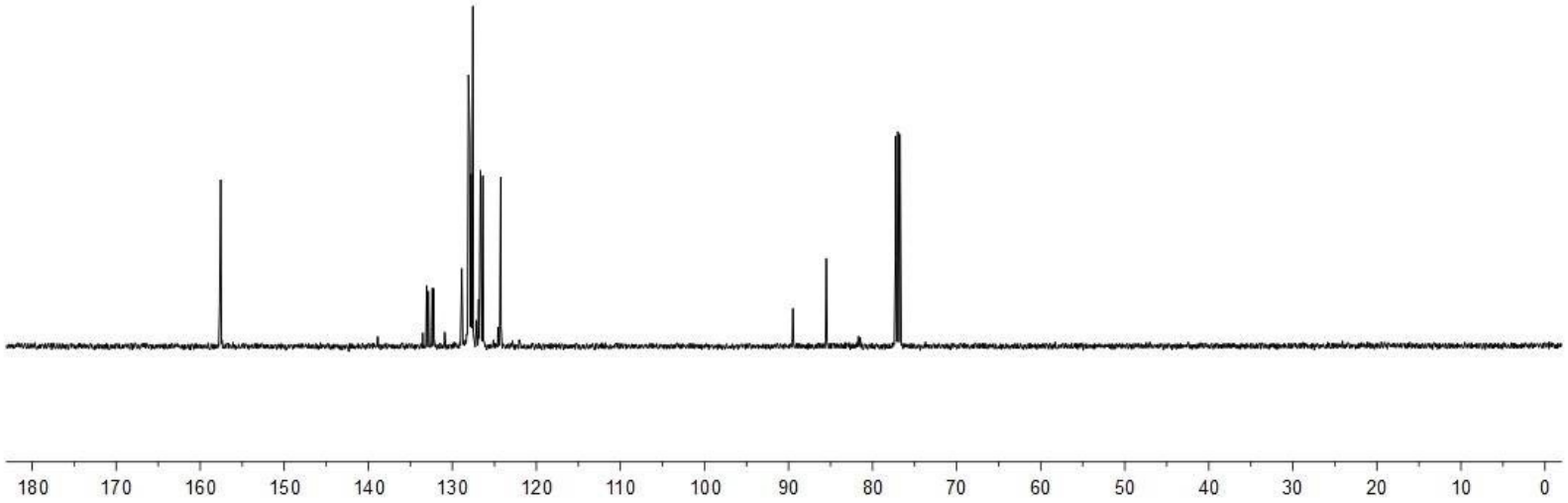
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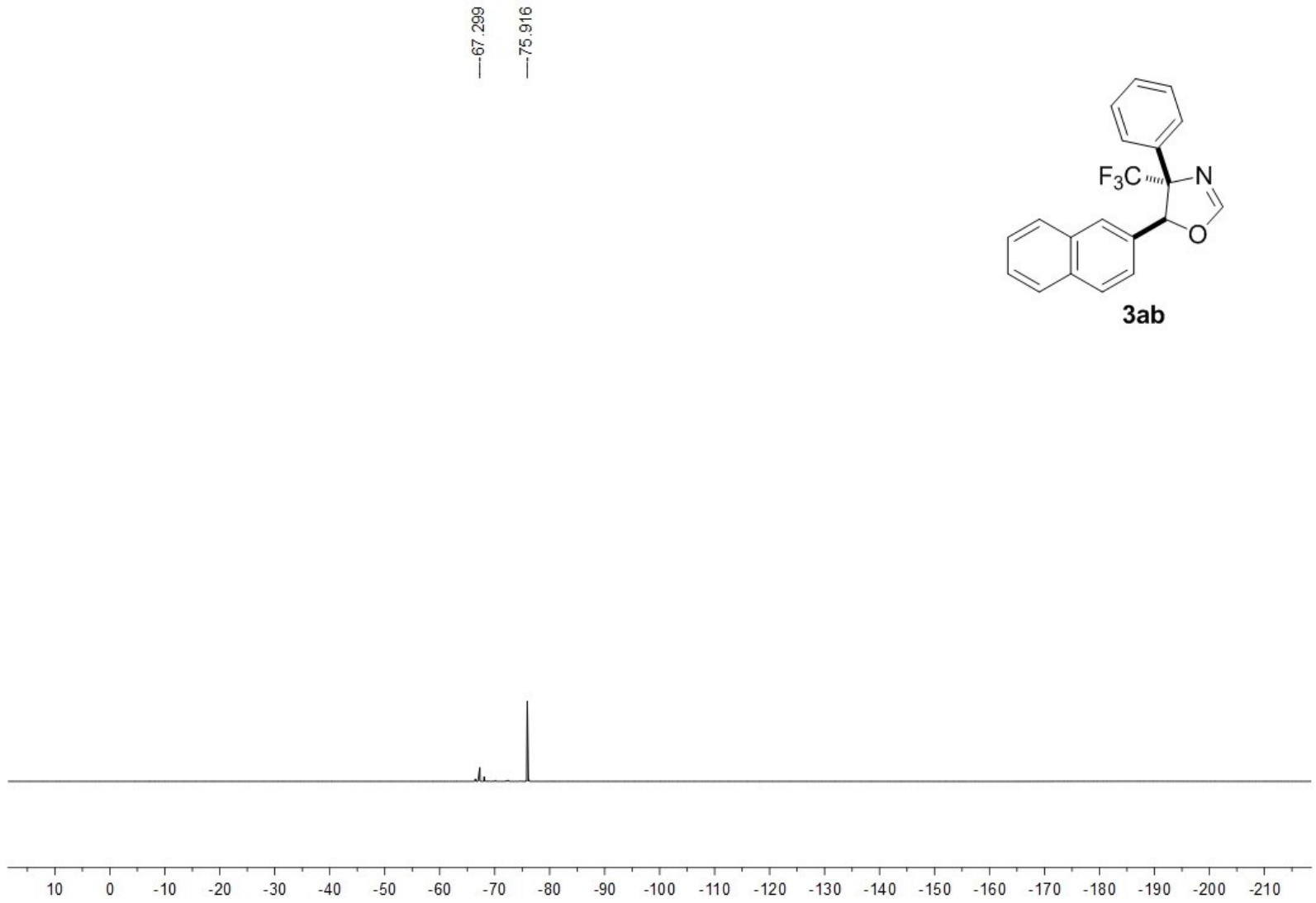
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-150
-160
-170
-180
-190
-200
-210

MeO
F3C
N
O
3ac
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6.777
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7.053
7.072
5.830
6.076
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7.471
7.495
7.531
7.546
7.571
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7.944
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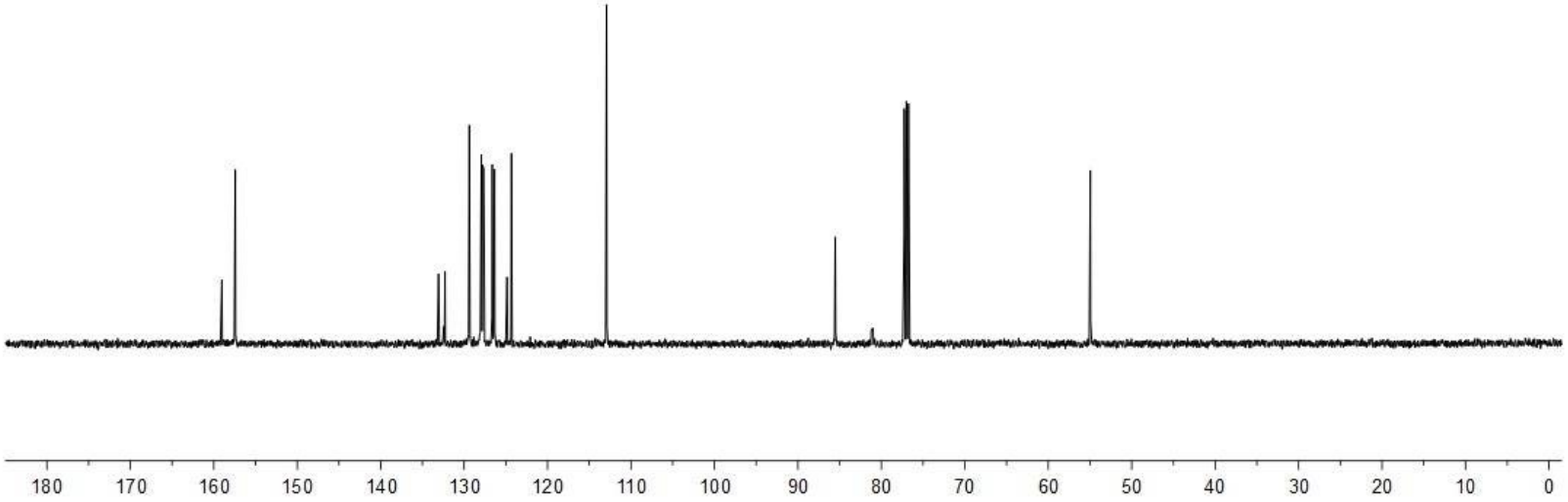
8.43


MeO
F3C
N
O

3ac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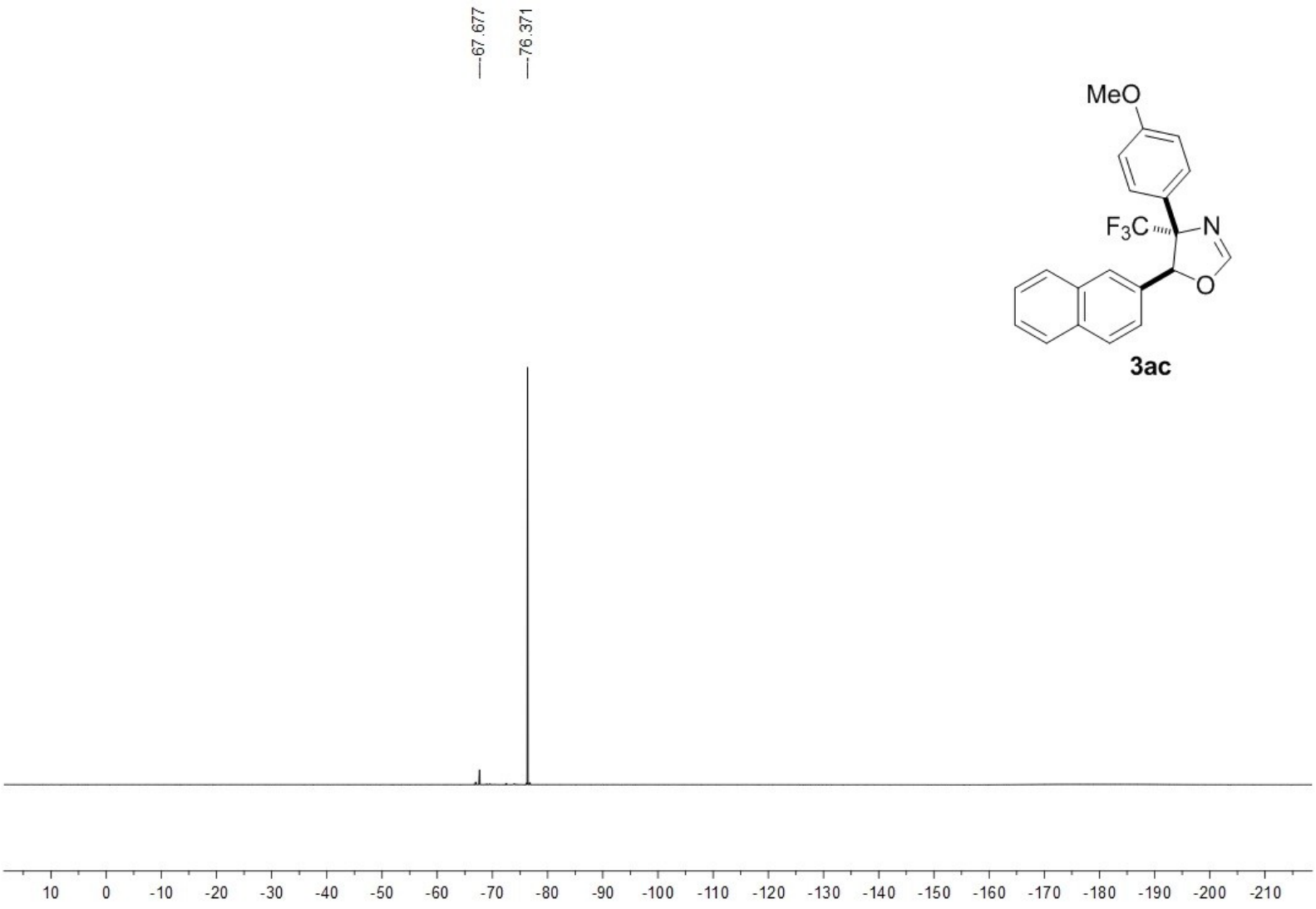
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-100
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-120
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-150
-160
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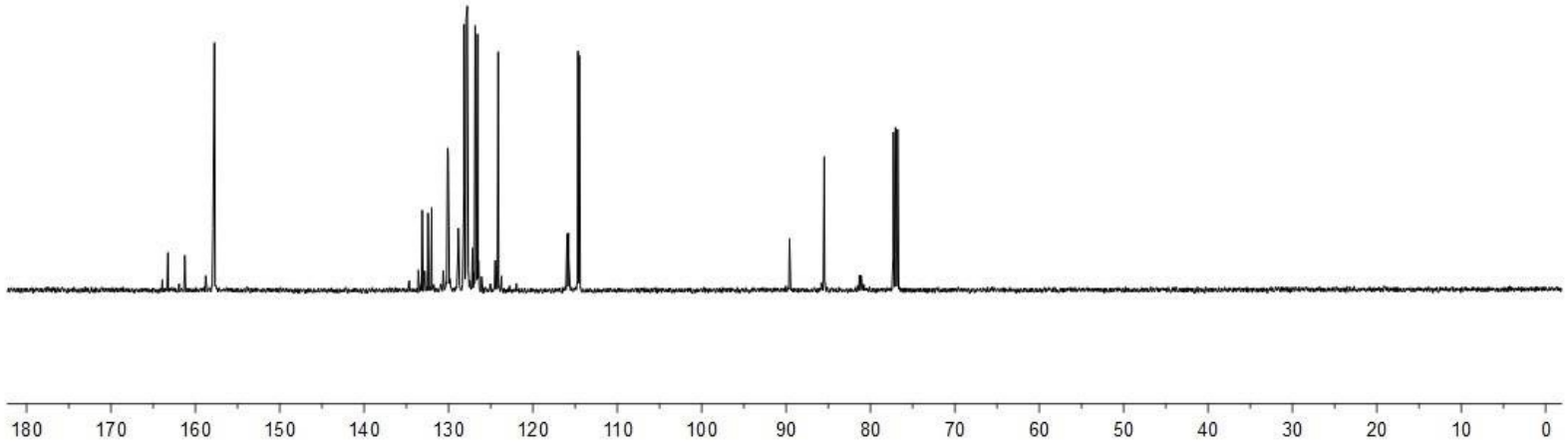
N
O
3ac1

3ad


F
F3C
N
O

3ad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20
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F
F3C
N
O
3ad

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-113.485
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-112.651
-112.642
-112.633
-112.628
-112.619
-77.139
-76.310

10
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-70
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-210

3ae
Cl
F3C
N
O
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7.666
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7.126
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6.967
6.727
6.724
6.710
6.707
5.758
6.081
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7.537
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7.525
7.514
7.497
7.474
7.466
7.459
7.446
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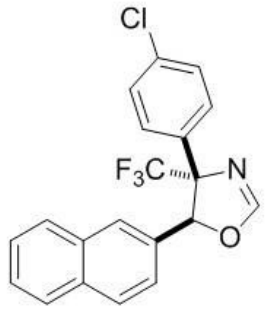
4.46
3.86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O

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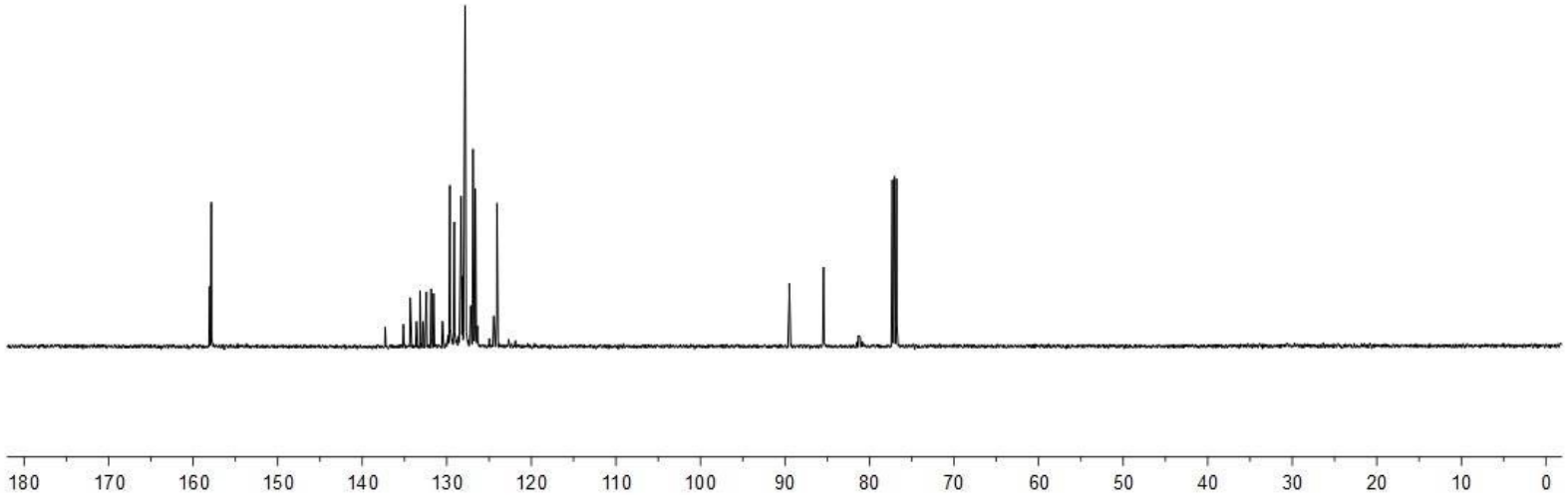
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30
20
10
0

Cl
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O
3ae
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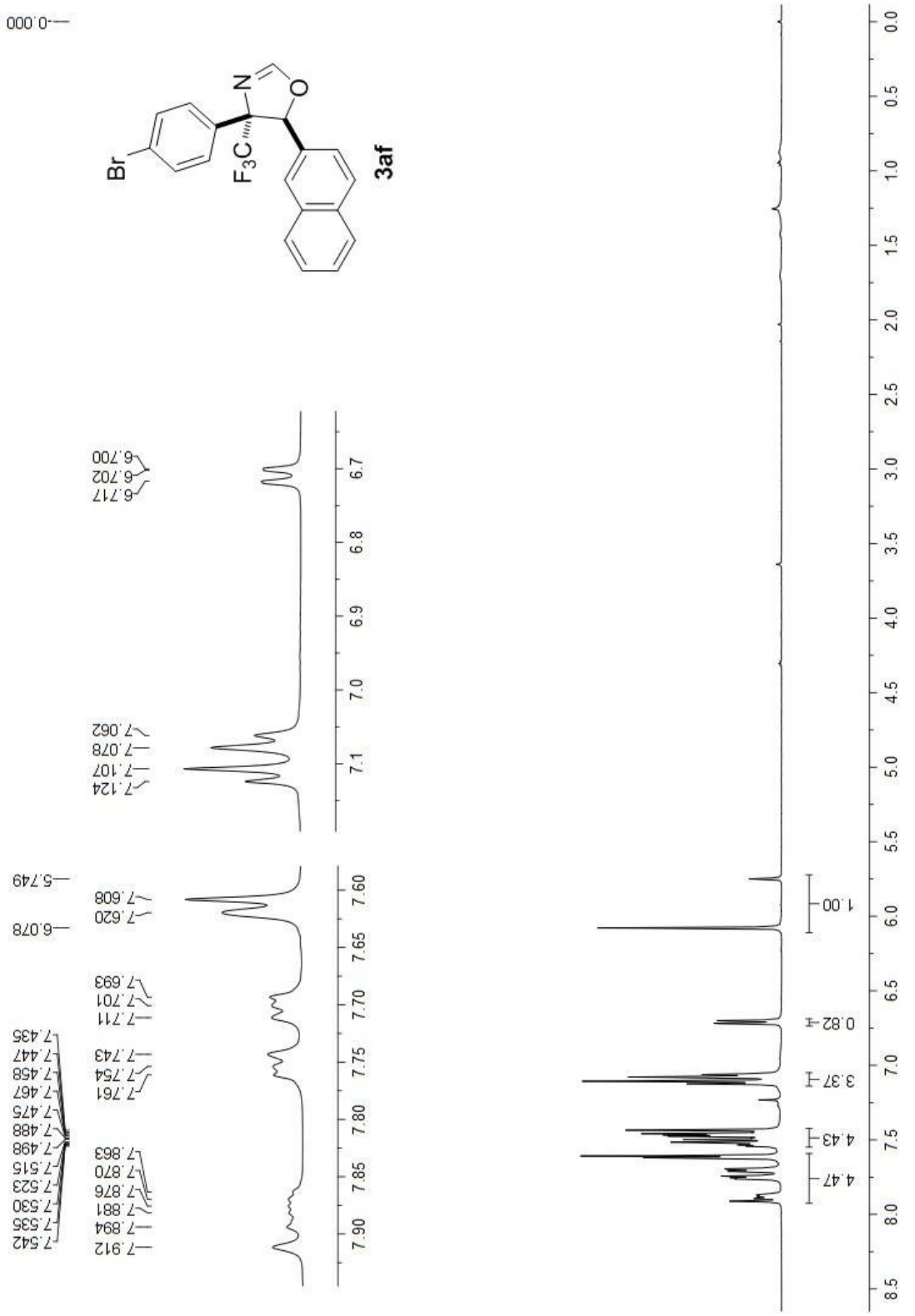
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7.711
7.701
7.693
7.620
7.608
7.542
7.535
7.530
7.523
7.515
7.498
7.488
7.475
7.467
7.458
7.447
7.435
7.124
7.107
7.078
7.062
6.717
6.702
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6.078
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0.82
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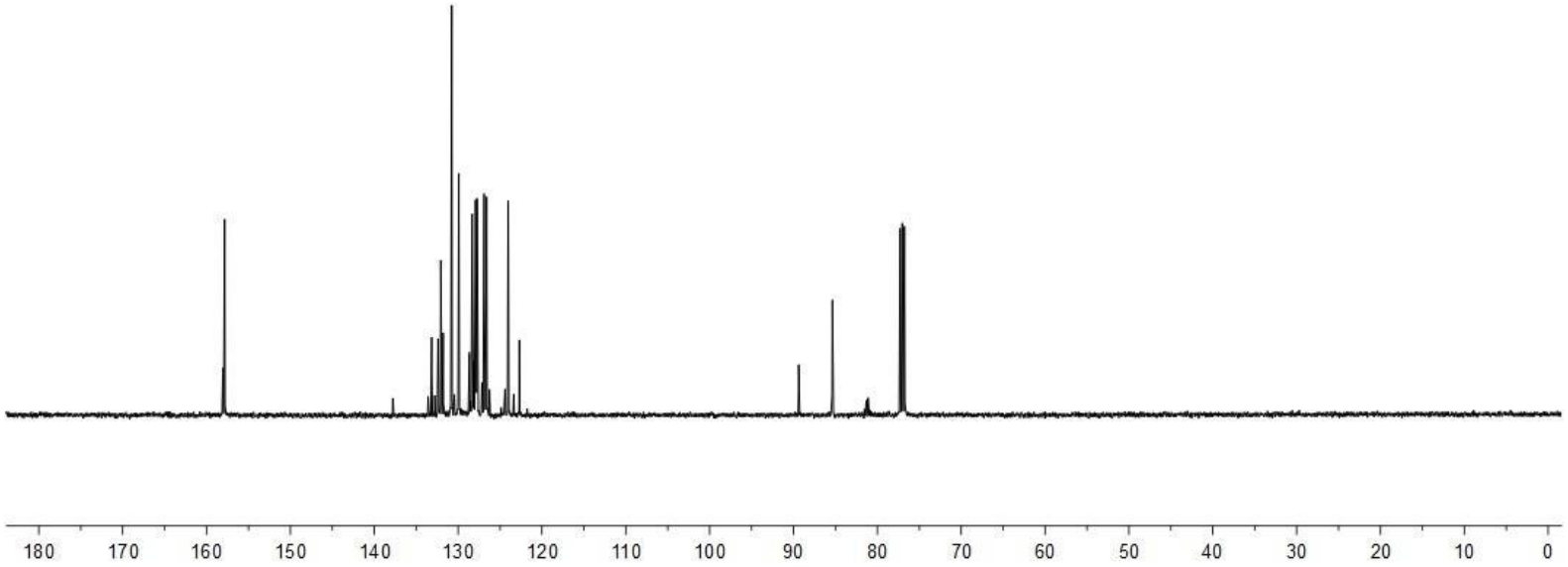
4.43
4.47


Br
F3C
N
O

3af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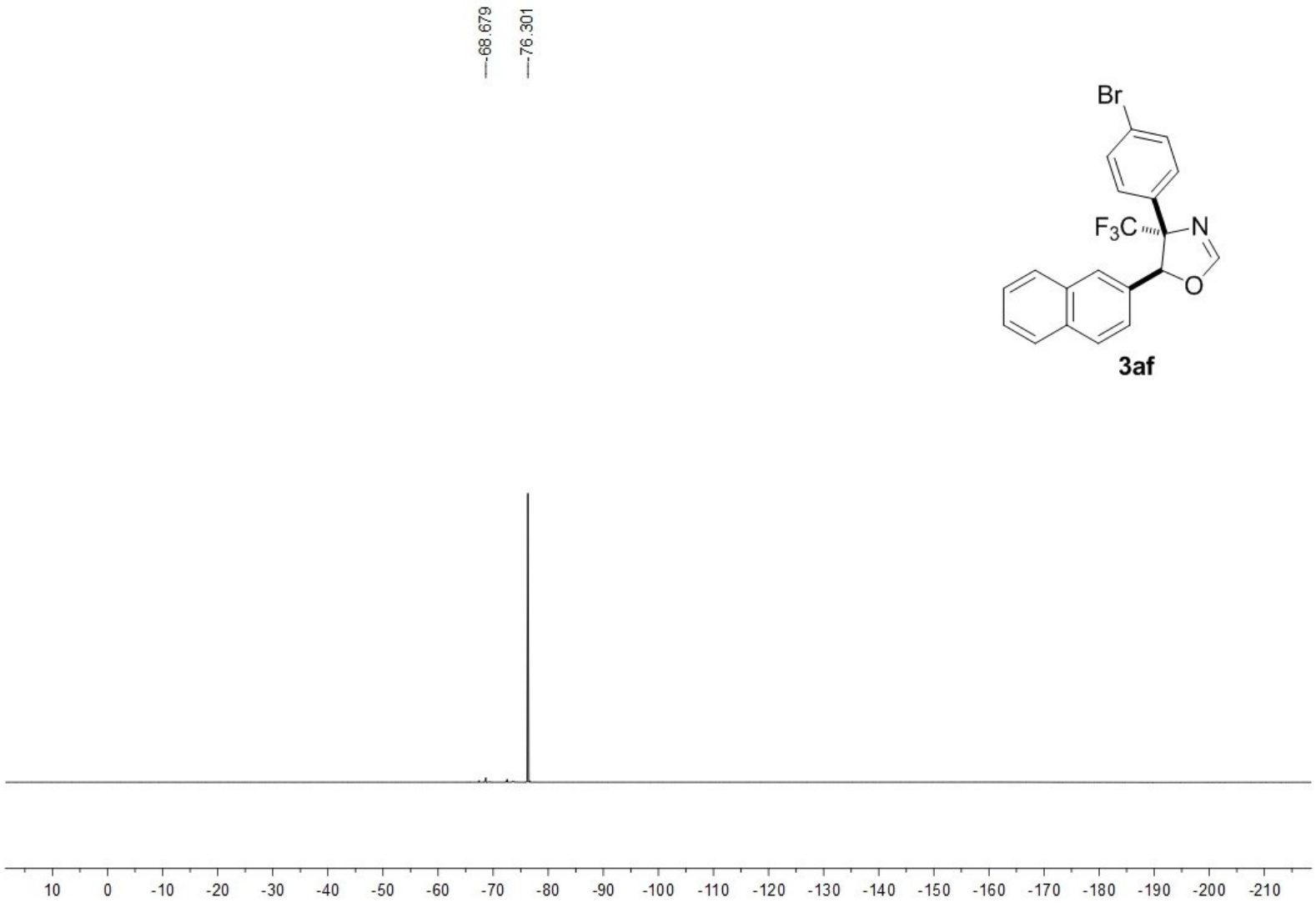
30
20
10
0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-76.301
Br
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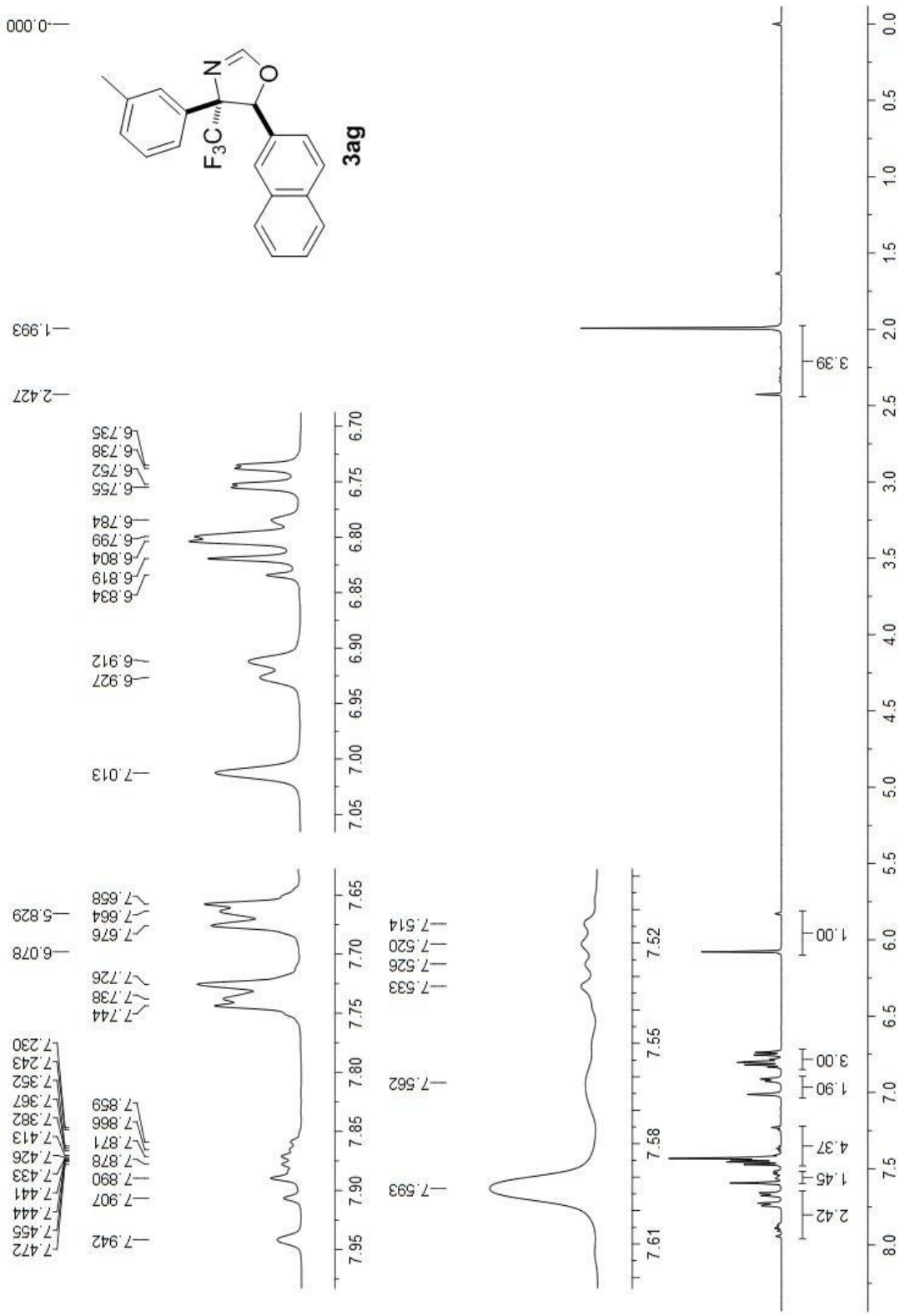
-200
-210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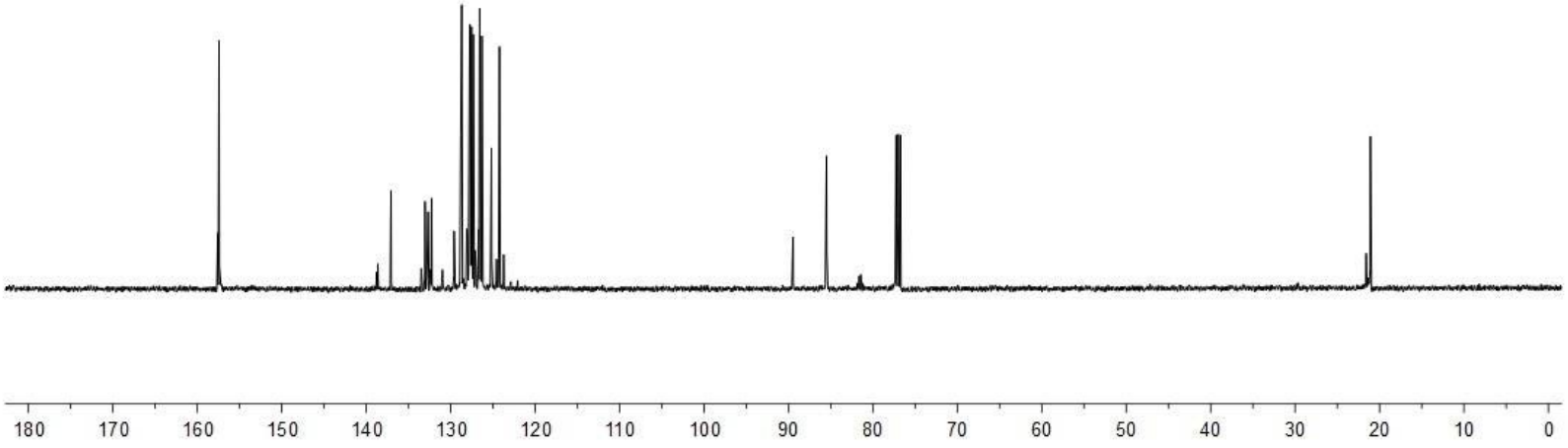
F3C
N
O


F3C
N
O

3ag


180
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160
150
140
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120
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100
90
80
70
60
50
40
30
20
10
0

N
O
F3C

3ag

-77.773
-71.967
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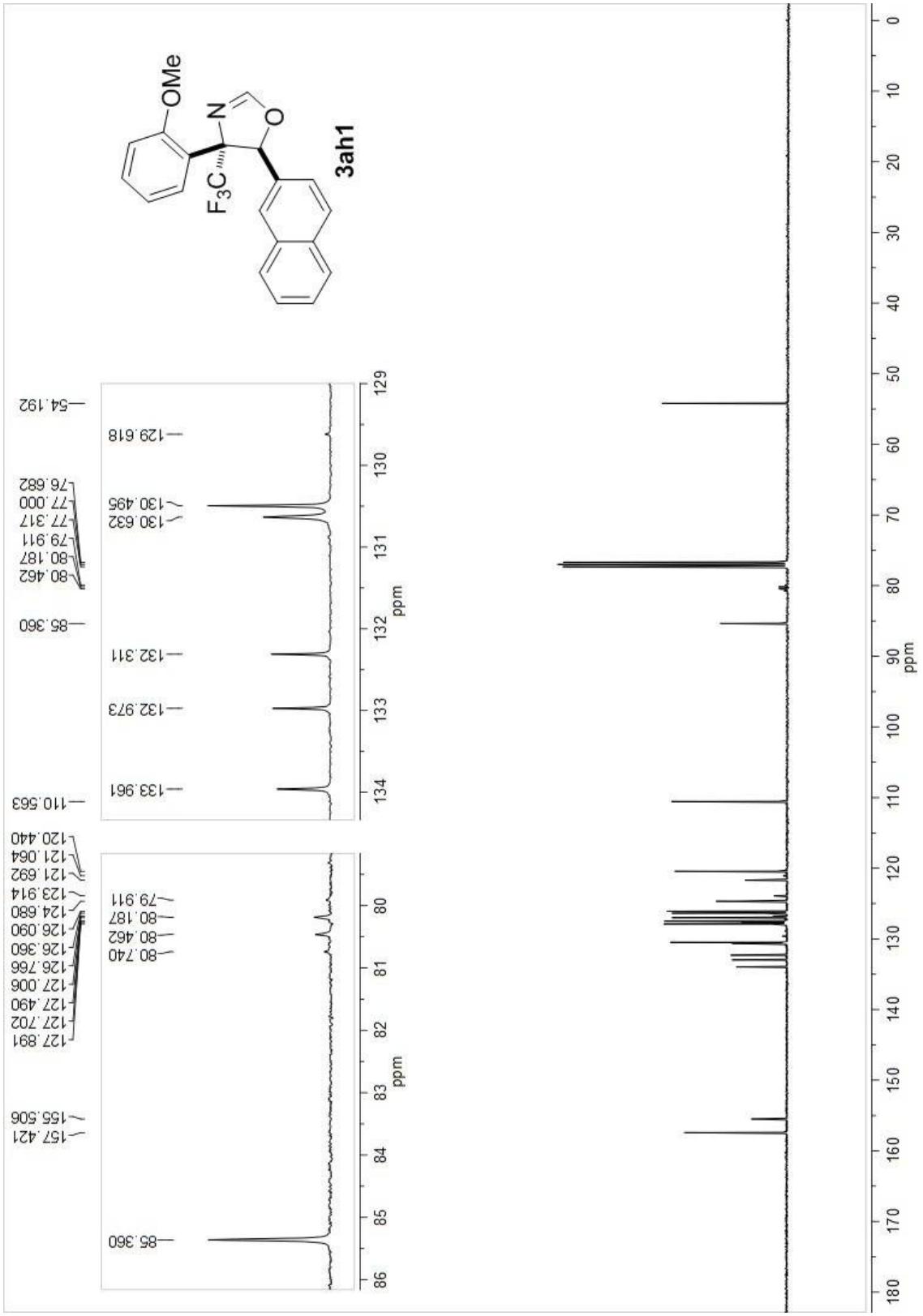
OMe
N
O
F3C
3ah1


OMe
N
O
F3C
3ah1
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130.632
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132.973
133.961
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80.462
80.187
79.911
77.317
77.000
76.682
110.563
120.440
121.064
121.692
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126.090
126.360
126.766
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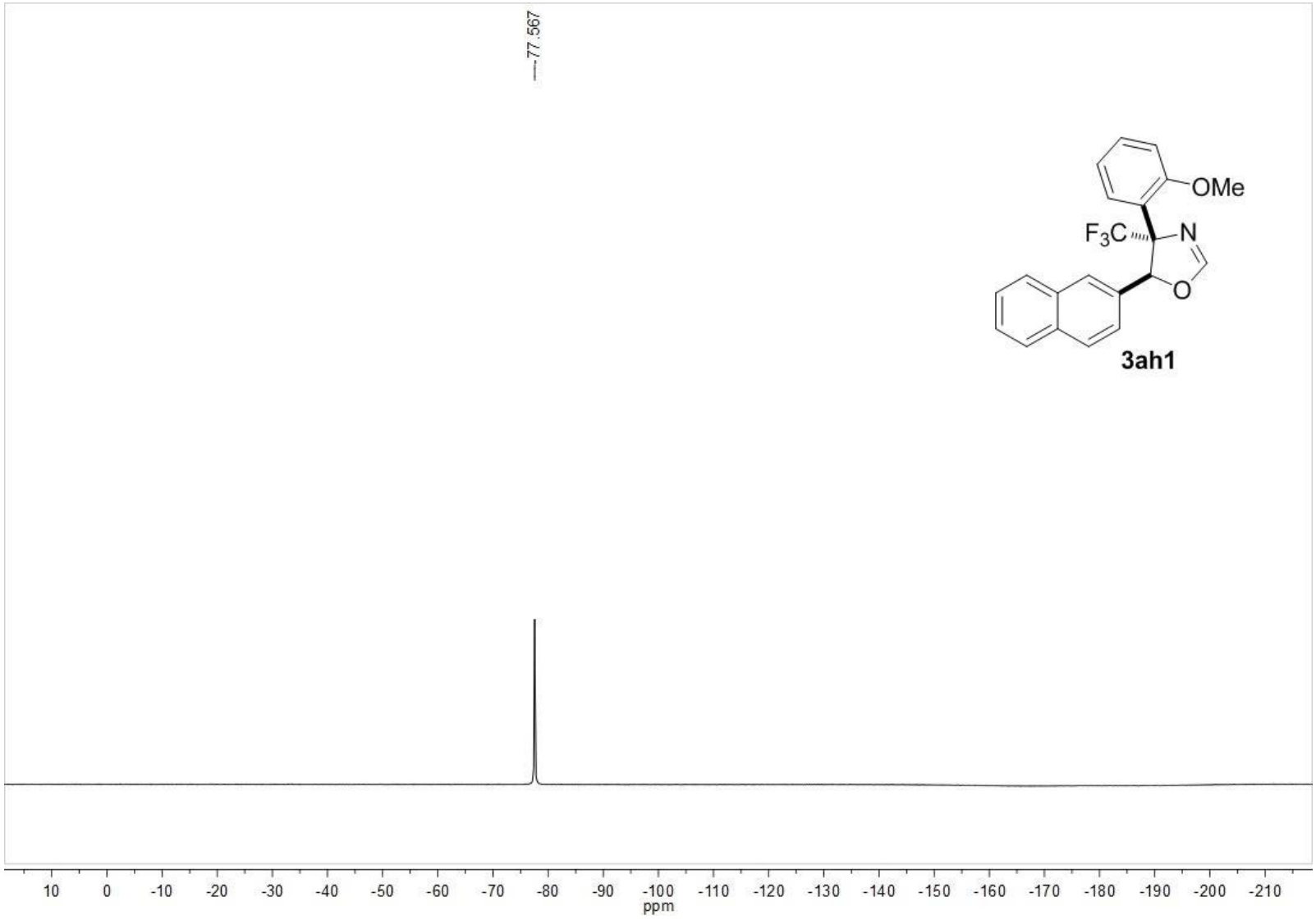
127.702
127.891
155.506
157.421
ppm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O
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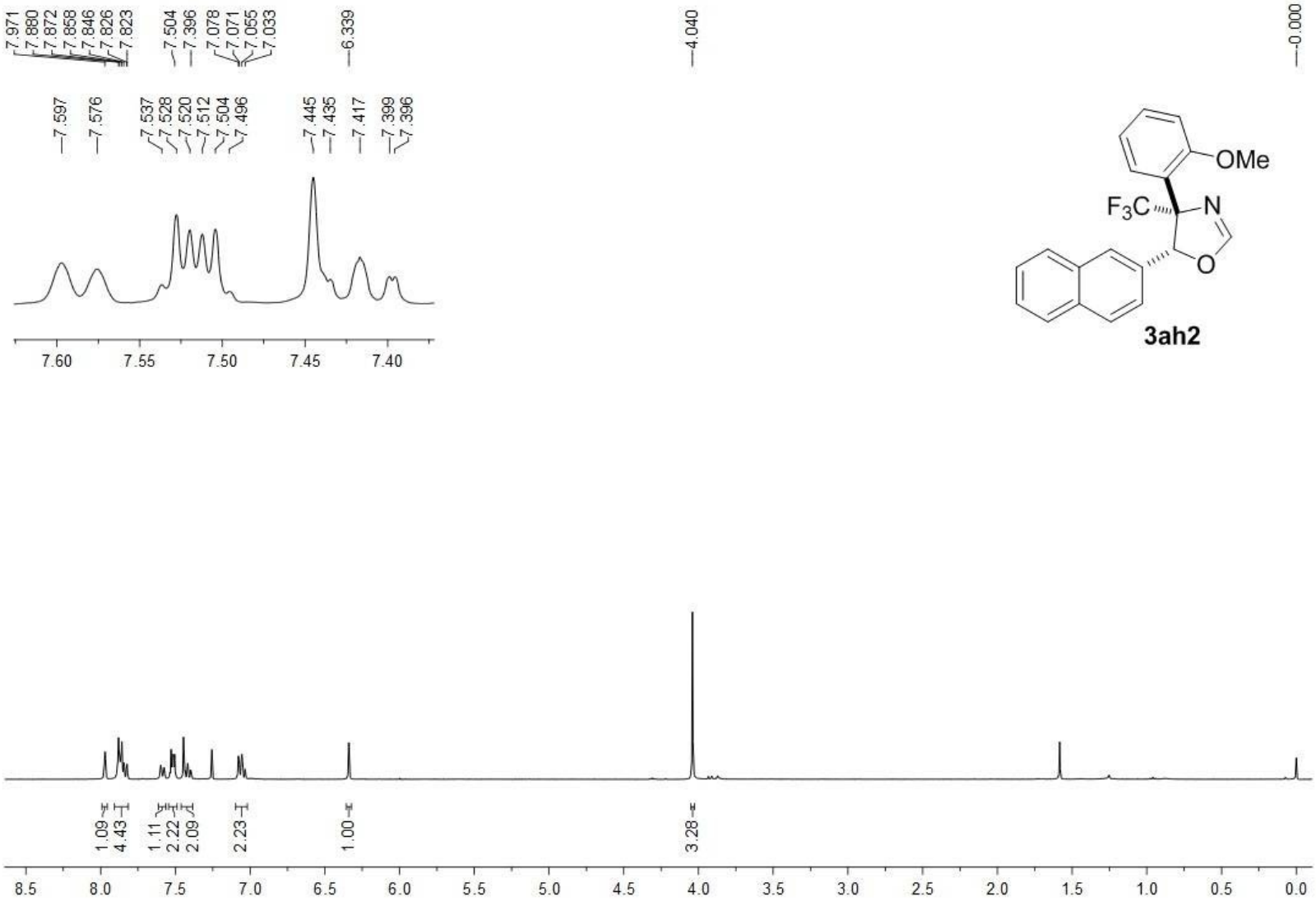
ppm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7.078
7.071
7.055
7.033
6.339
4.040
0.000
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7.576
7.537
7.528
7.520
7.512
7.504
7.496
7.445
7.435
7.417
7.399
7.396
7.60
7.55
7.50
7.45
7.40
OMe
F3C
N
O
3ah2
1.09
4.43
1.11
2.22
2.09
2.23
1.00
3.28
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

OMe
N
O
F3C
3ah2
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-160
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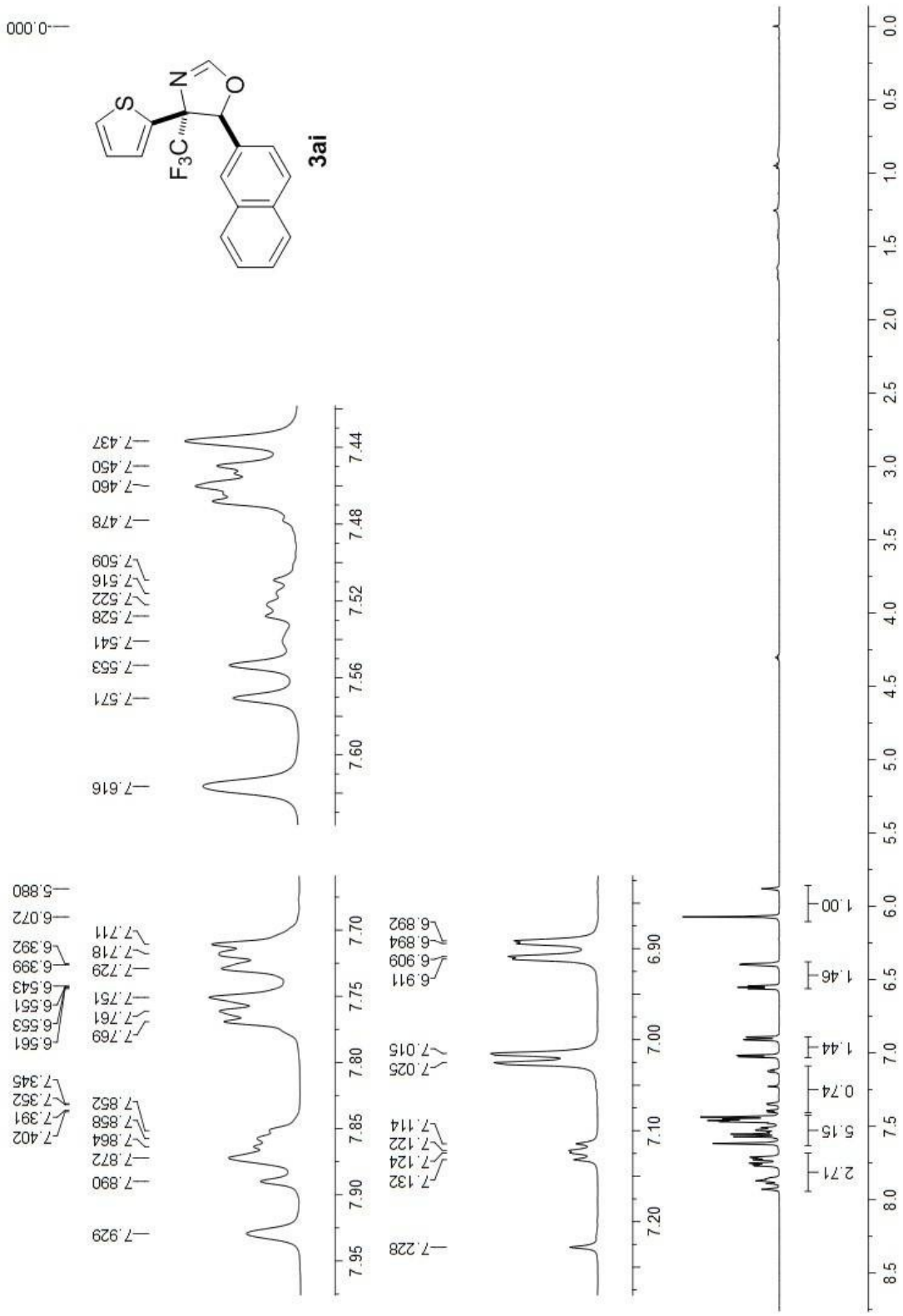
-180
-190
-200
-210
ppm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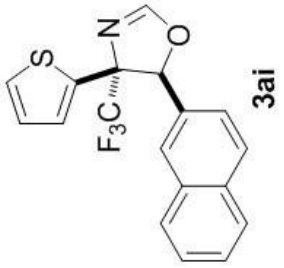
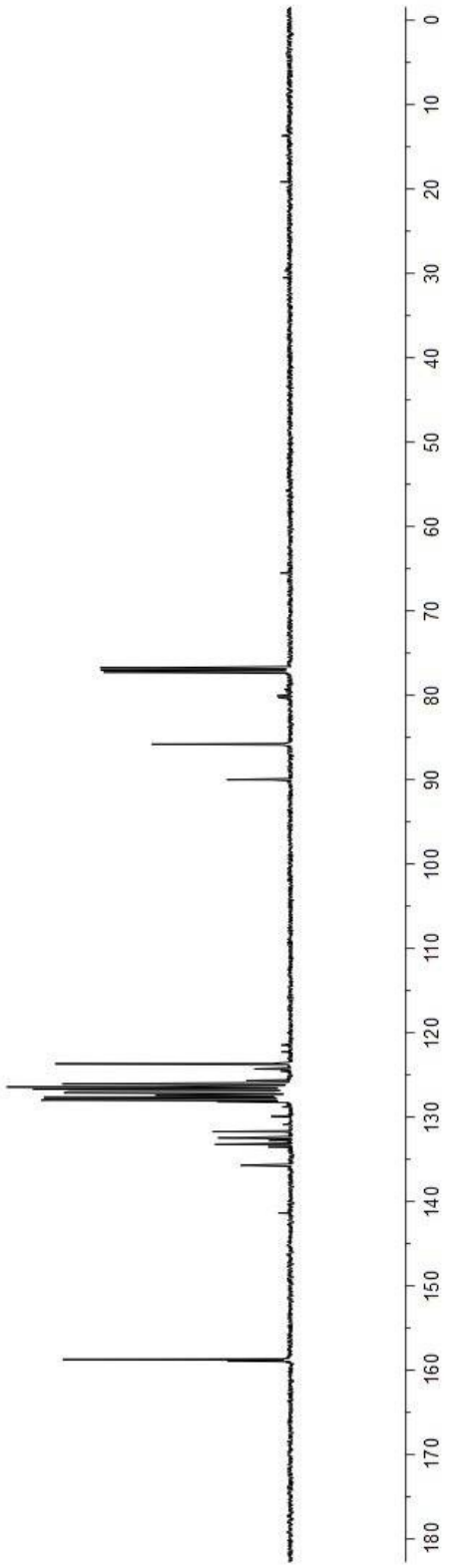

S
N
O
F3C

3ai


0
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20
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40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

S
N
O
F3C
3ai
-73.693
-79.038
80
70
60
50
40
30
20
10
0
-20
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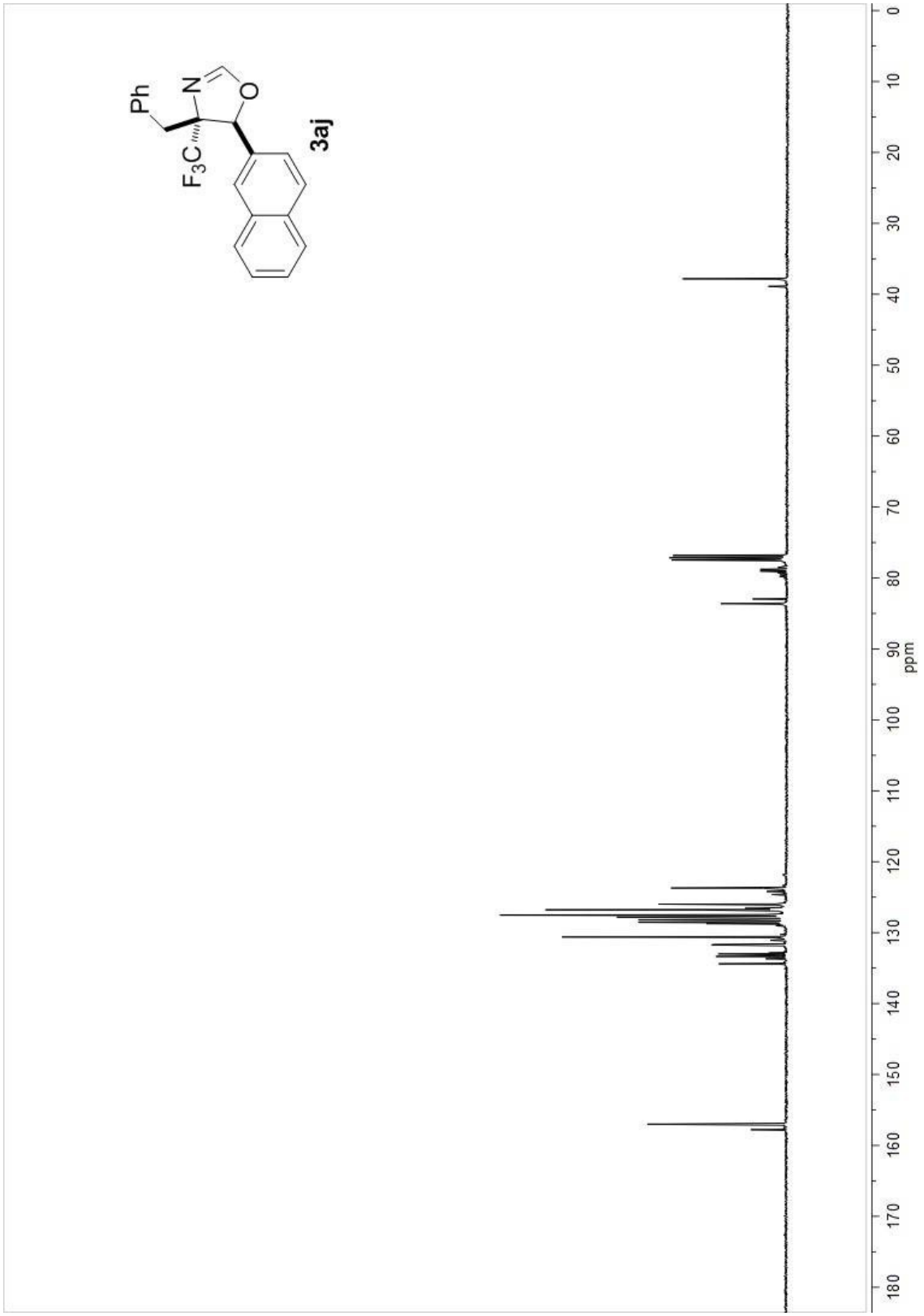
-80
-100
-120
-140
-160
-180
-200
-220

Ph
N
O
F3C
3aj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O
F3C
3aj
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20
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40
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70
80
90
100
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120
130
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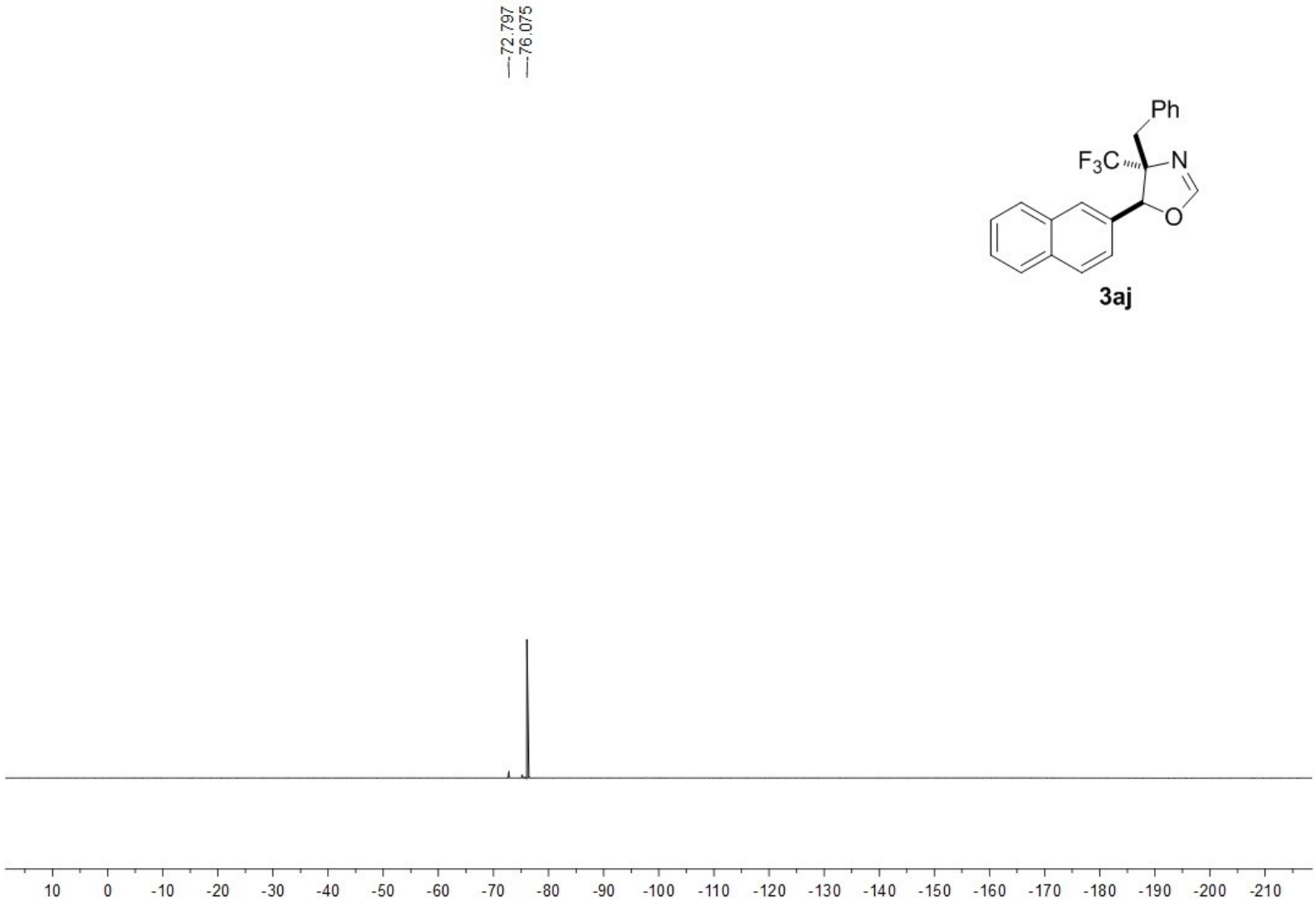
150
160
170
180
ppm


72.797
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O
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-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

0.000
Ph
N
O
F3C
Cl
3cj
2.474
2.511
2.761
2.797
3.090
3.125
3.552
3.587
5.379
5.730
6.859
6.863
6.879
6.882
7.068
7.083
7.105
7.126
7.131
7.141
7.186
7.208
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7.302
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7.10
7.15
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1.5
2.0
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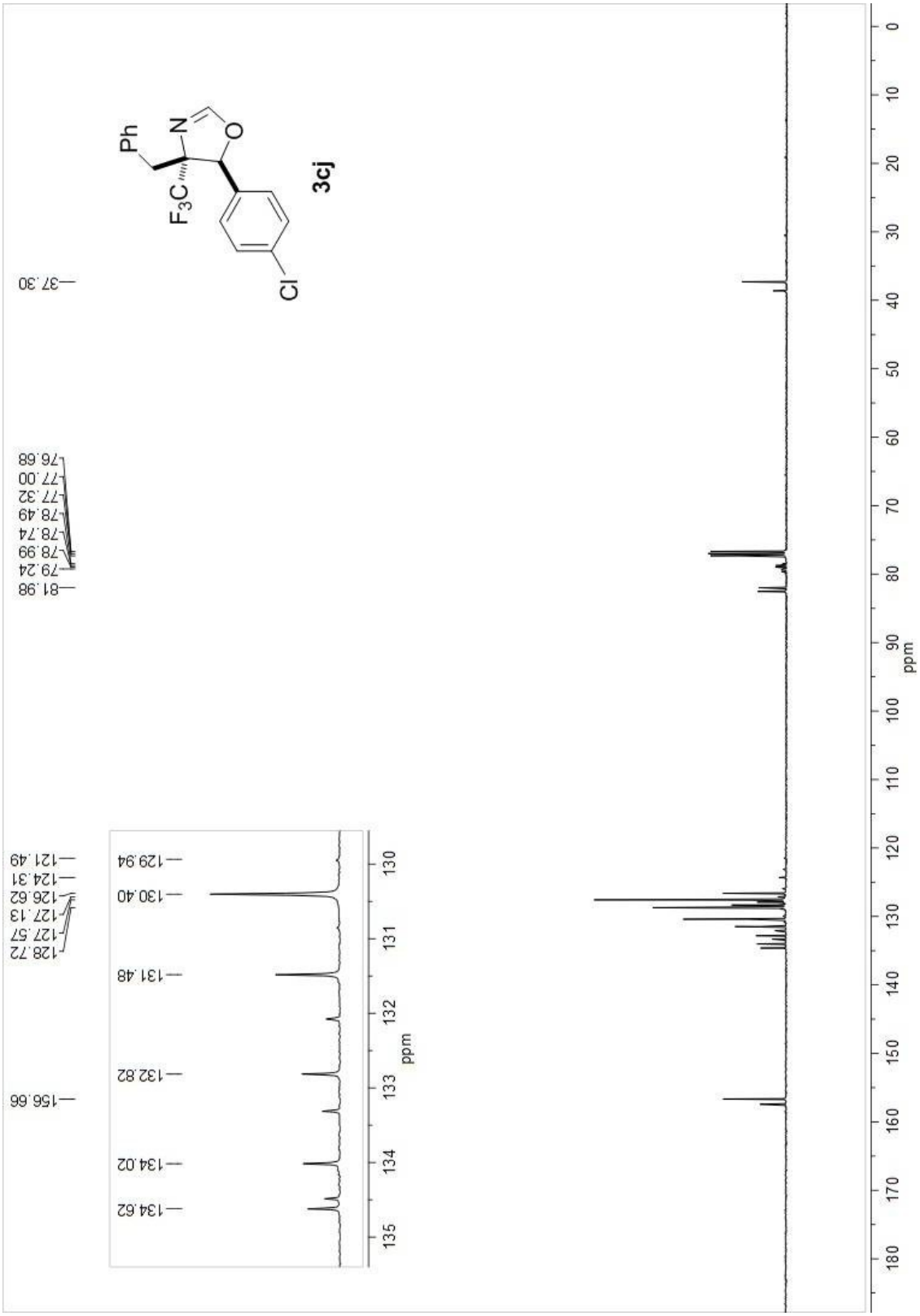
8.0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O
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Cl
3cj
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124.31
126.62
127.13
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134.02
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ppm


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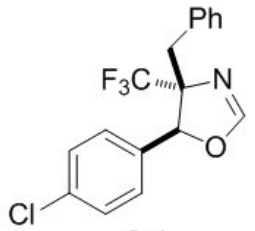
-76.420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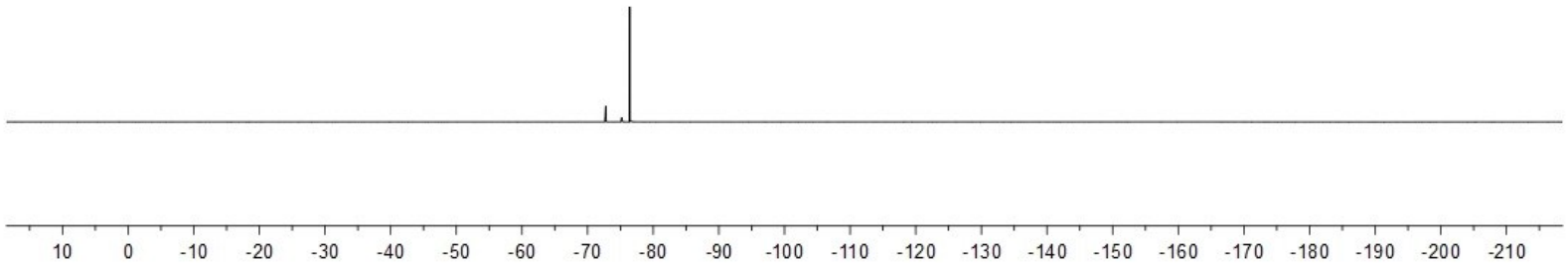
N
O
Cl

3cj


10
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-10
-20
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-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

5
F3C
Me
EtO2C
N
O
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0.810
0.824
0.839
1.162
1.382
1.396
1.410
1.987
1.989
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2.374
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4.309
4.322
4.330
4.345
4.352
4.359
4.366
4.373
4.381
4.387
4.395
4.402
4.409
4.416
4.423
4.431
4.438
4.452
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3.504
3.511
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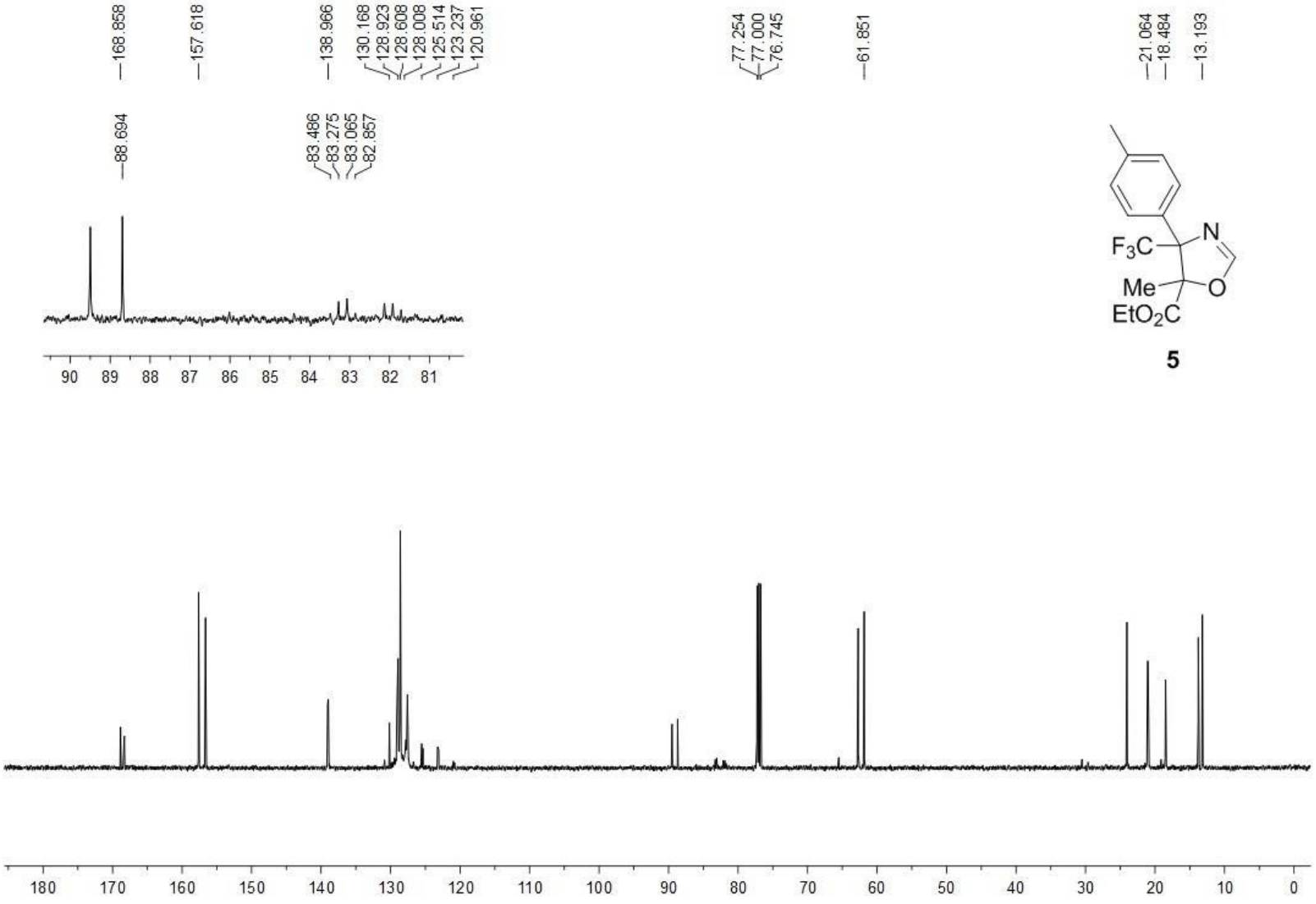
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18.484
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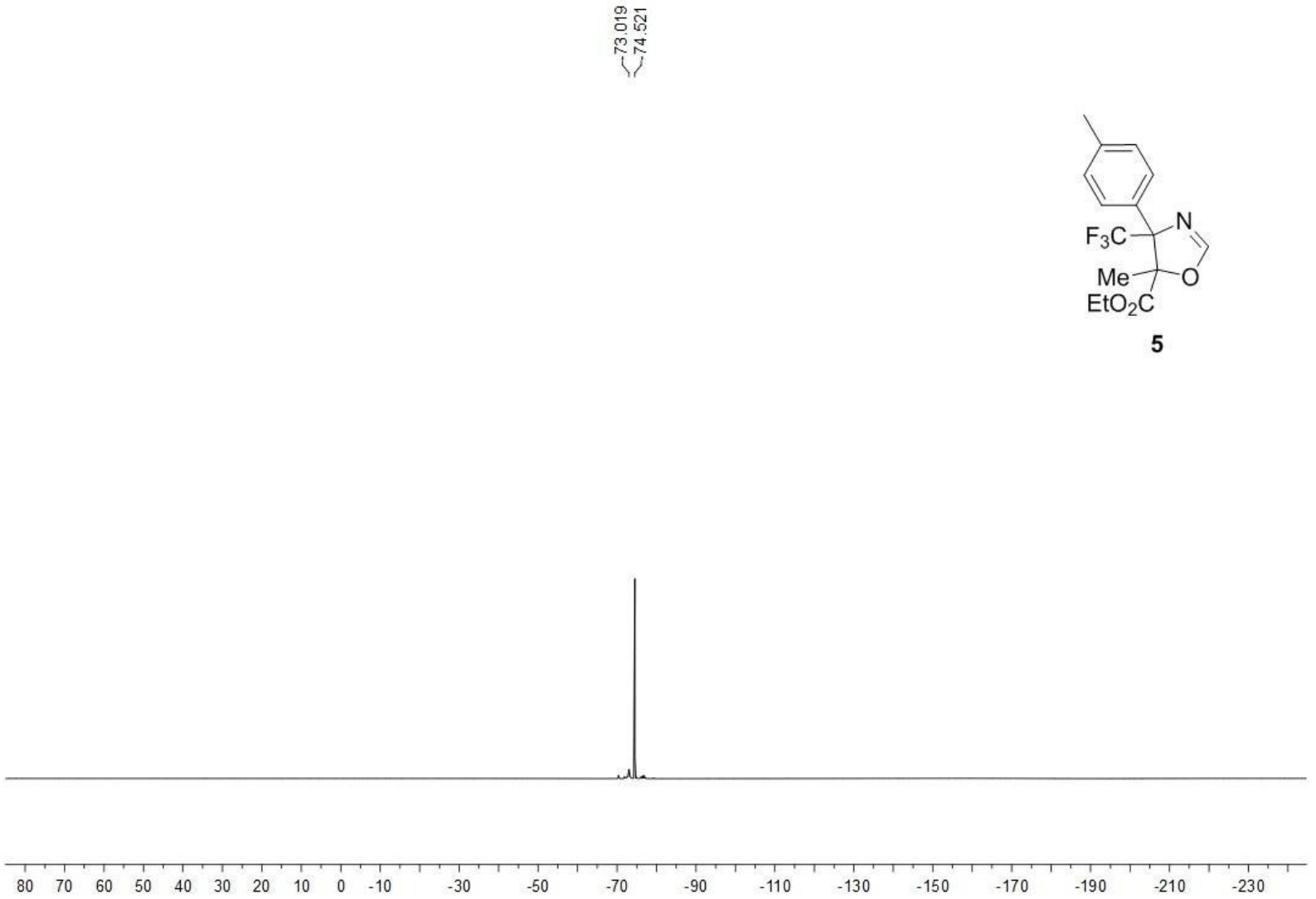
N
Me
O
EtO2C
5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Me
O
EtO2C
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3.784
5.079
5.257
5.940
6.088
6.700
6.826
6.841
6.940
7.037
7.053
7.112
7.128
7.305
7.319
7.334
7.382
7.399
7.965
7.973
7.25
7.30
7.35
7.40
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1.20
0.90
3.08
6.46
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0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
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6.0
6.5
7.0
7.5
8.0
8.5
N
N
Ts
F3C
MeO
7

21.481
20.882
N
N
Ts
F3C
MeO
7
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76.746
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128.5
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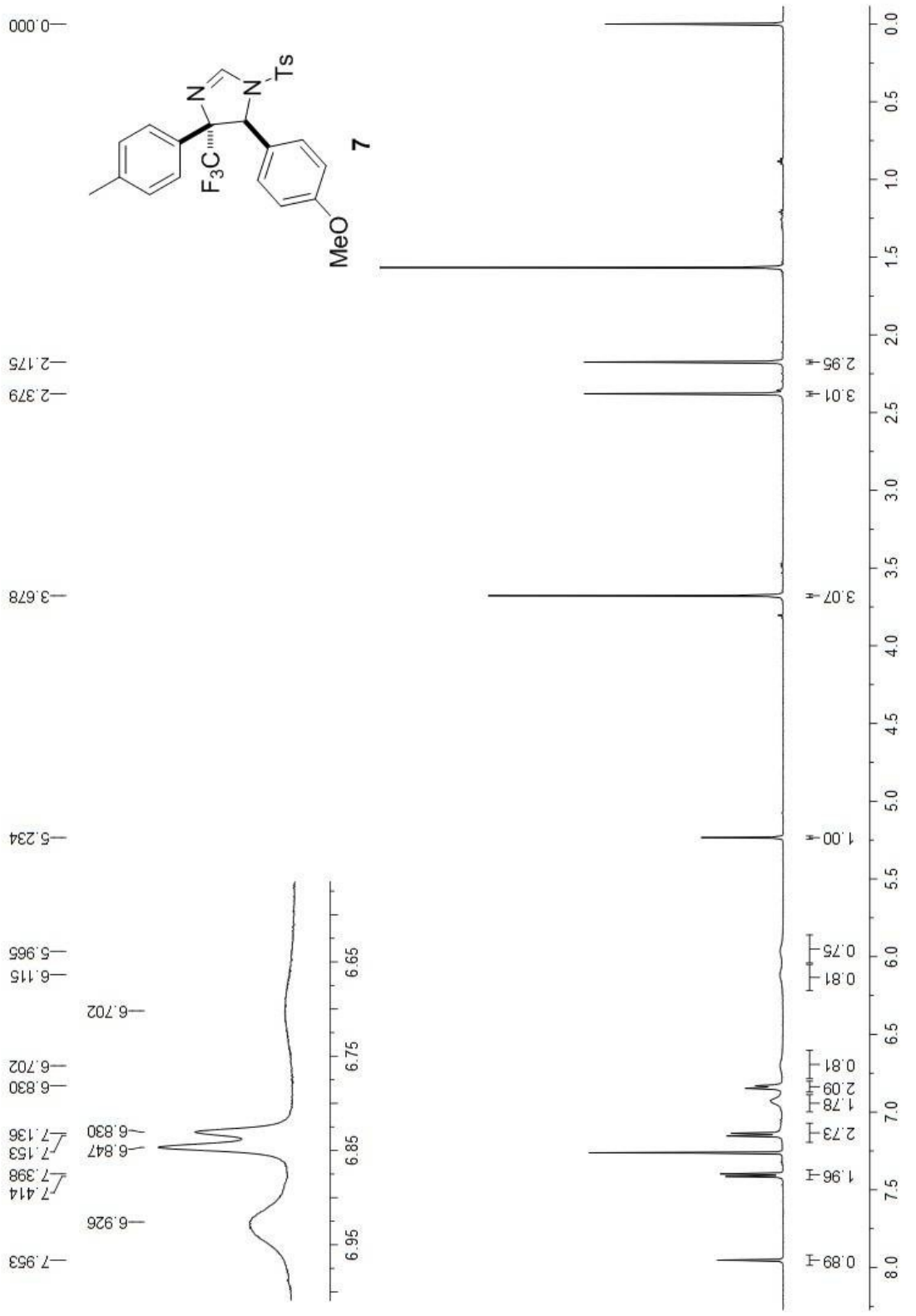
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N
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6.702
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7.398
7.414
6.926
7.953
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1.78
2.09
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0.81
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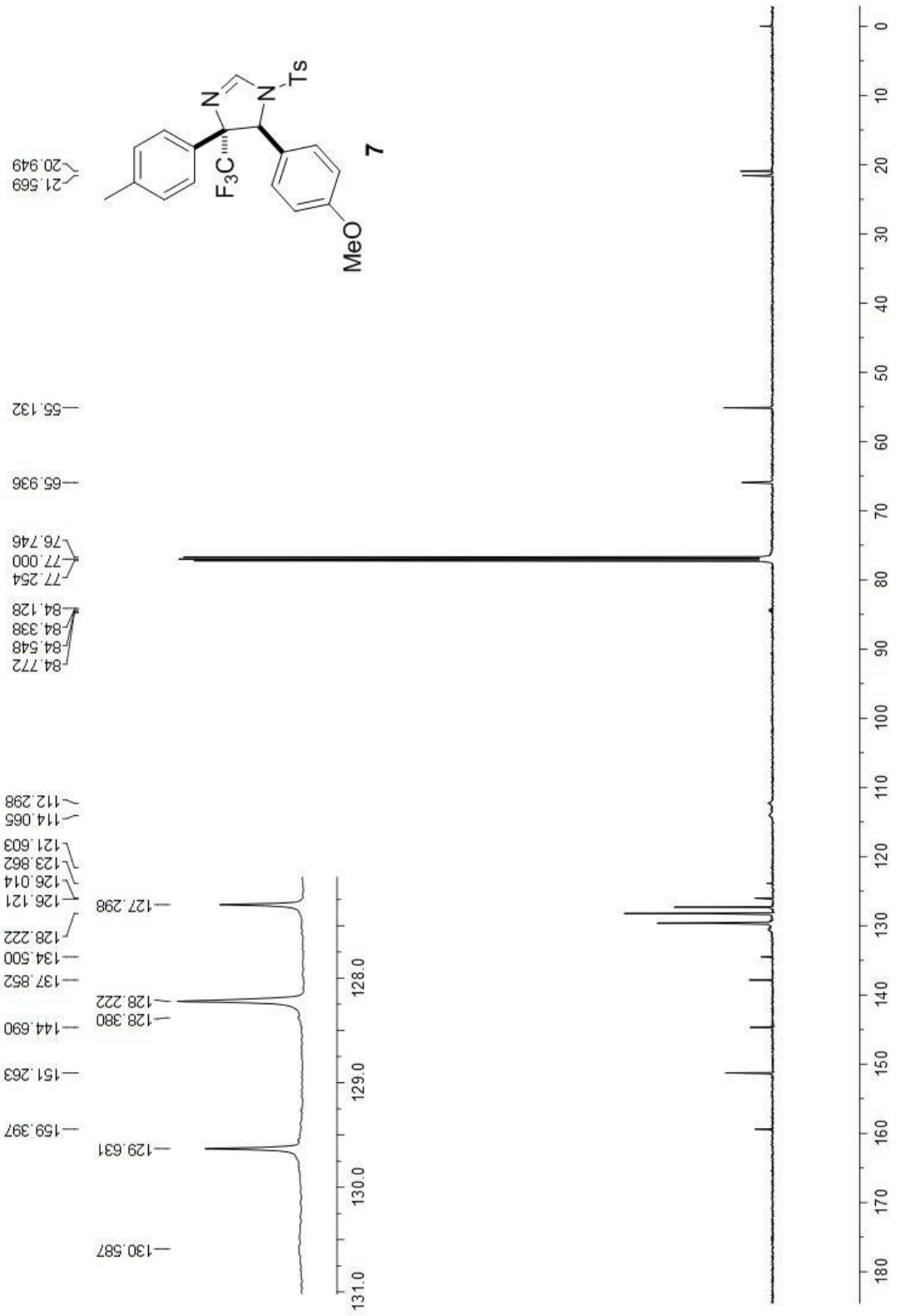
2.95


7
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129.631
130.587
128.0
129.0
130.0
131.0

N
N
Ts
F3C
MeO

7

-79.008
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

0.000
2.365
3.128
3.159
3.489
3.491
3.520
3.522
5.070
7.033
7.035
7.213
7.230
7.252
7.269
CN
NH
F3C
9
3.05
1.00
1.00
0.91
0.82
1.99
1.99
0.0
0.5
1.0
1.5
2.0
2.5
3.0
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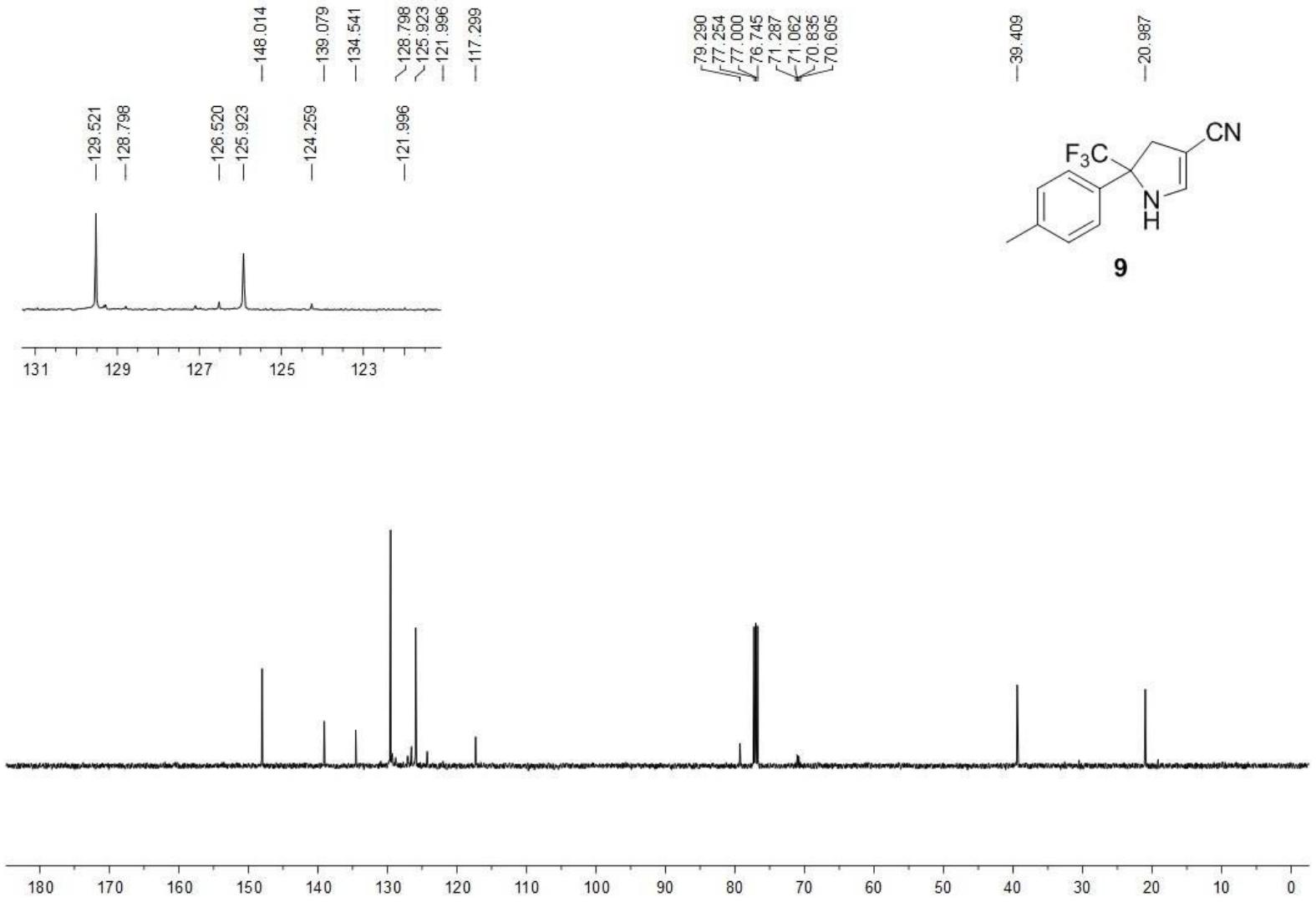
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5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139.079
134.541
128.798
125.923
121.996
117.299
79.290
77.254
77.000
76.745
71.287
71.062
70.835
70.605
39.409
20.987
129.521
128.798
126.520
125.923
124.259
121.996
131
129
127
125
123
F3C
CN
N
H
9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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0

CN
NH
F3C
9
-81.720
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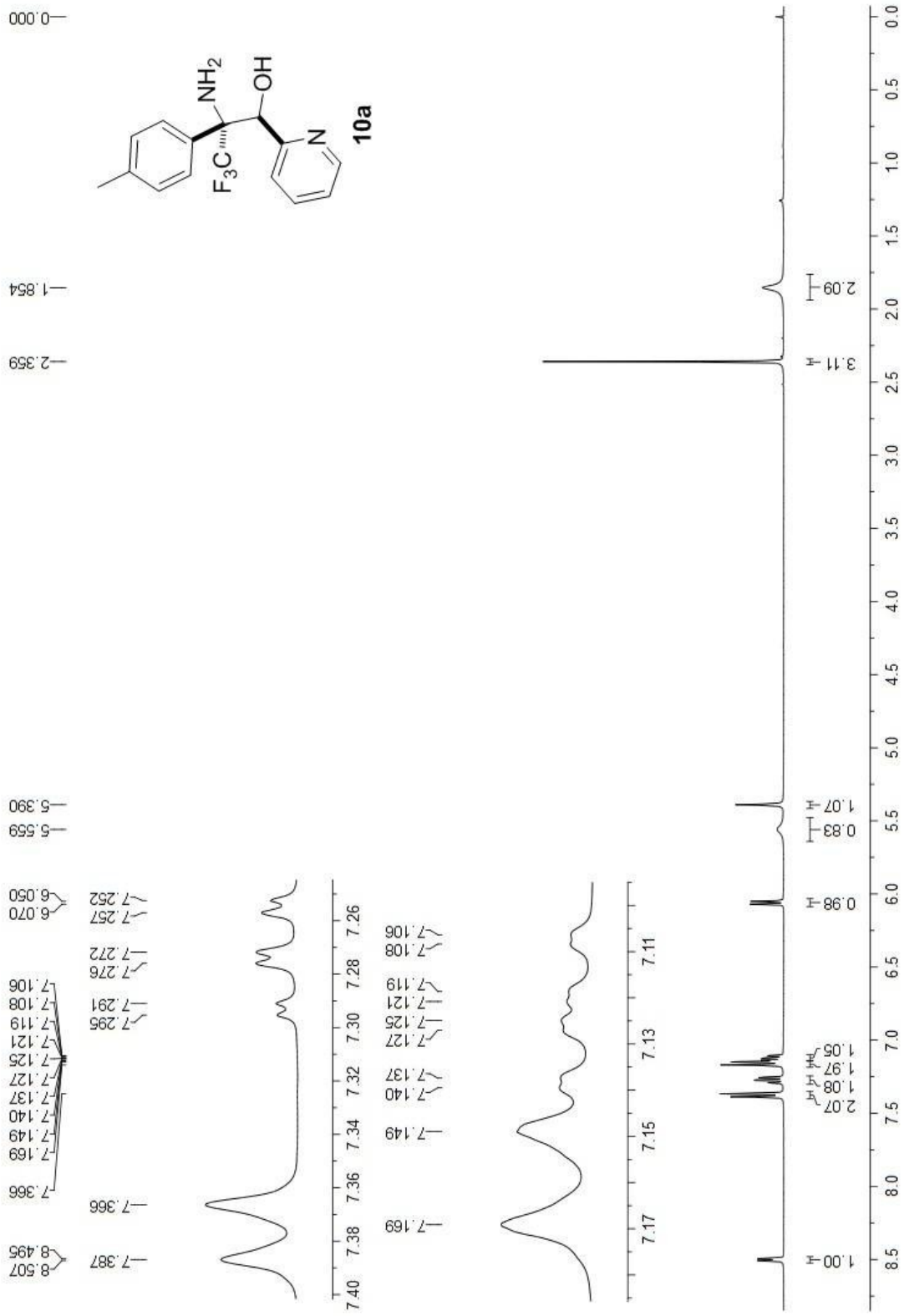
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NH2
OH
F3C
N

20.991
NH2
OH
F3C
N
10a
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65.934
74.442
76.746
77.000
77.254
122.817
122.967
123.381
125.668
126.491
127.956
129.167
130.244
133.119
138.333
147.401
155.493
135.663
138.333

NH2
OH
F3C
N
10a
-73.738
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230

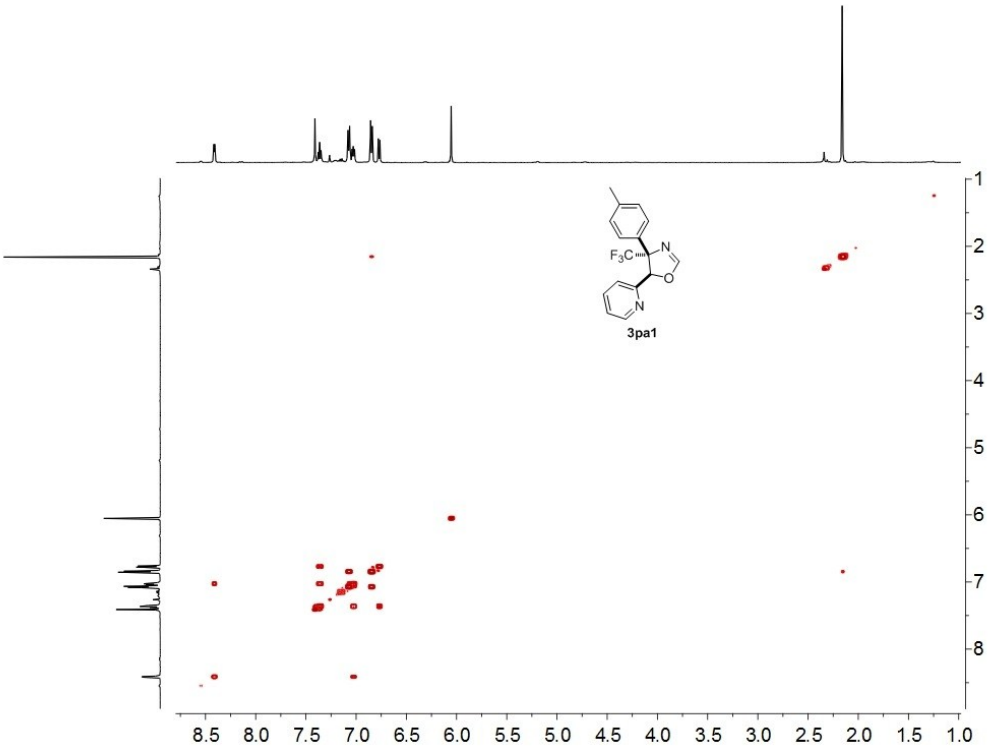
10b
NH2
OH
F3C
N
0.000
2.171
2.358
4.438
4.458
5.211
5.228
8.535
8.547
7.179
7.195
7.215
7.221
7.236
7.241
7.254
7.568
7.589
7.615
7.619
7.635
7.639
7.654
7.658
7.568
7.589
7.615
7.619
7.635
7.639
7.654
7.658
1.00
2.22
1.14
4.22
1.12
1.05
3.20
2.00

20.984
NH2
OH
F3C
N
10b
157.045
148.300
138.142
136.282
133.498
129.854
129.054
127.577
126.836
125.300
123.546
123.285
123.023
77.254
77.000
76.746
74.704
66.296
66.007
65.815
65.554

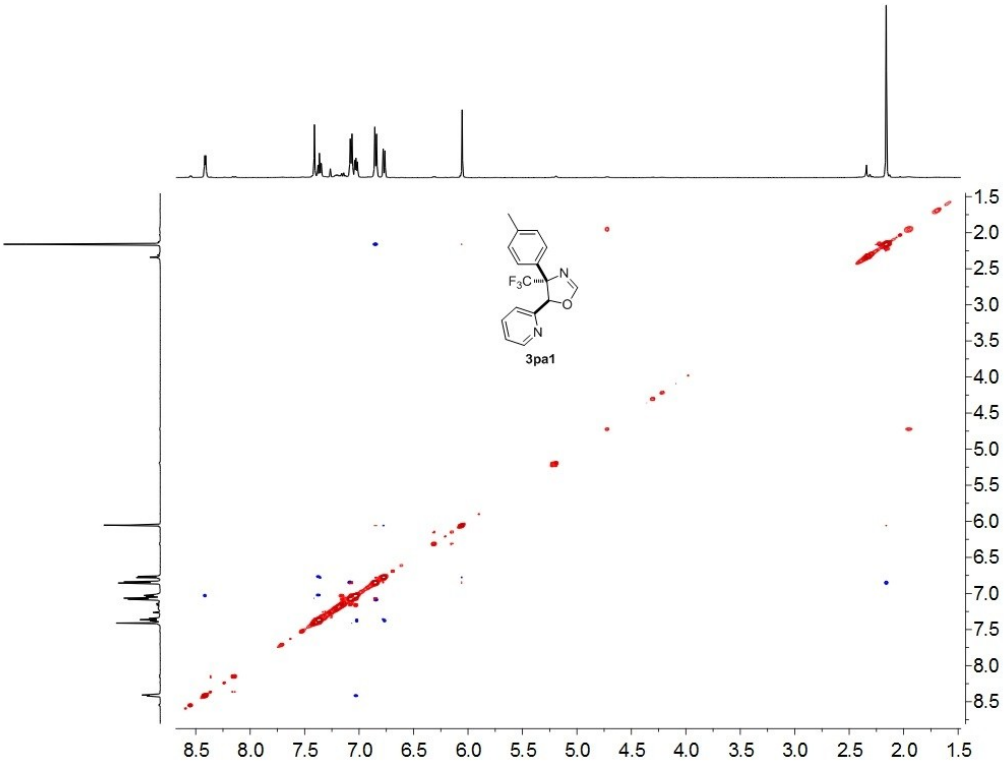
NH2
OH
F3C
N
10b

-73.783
80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220

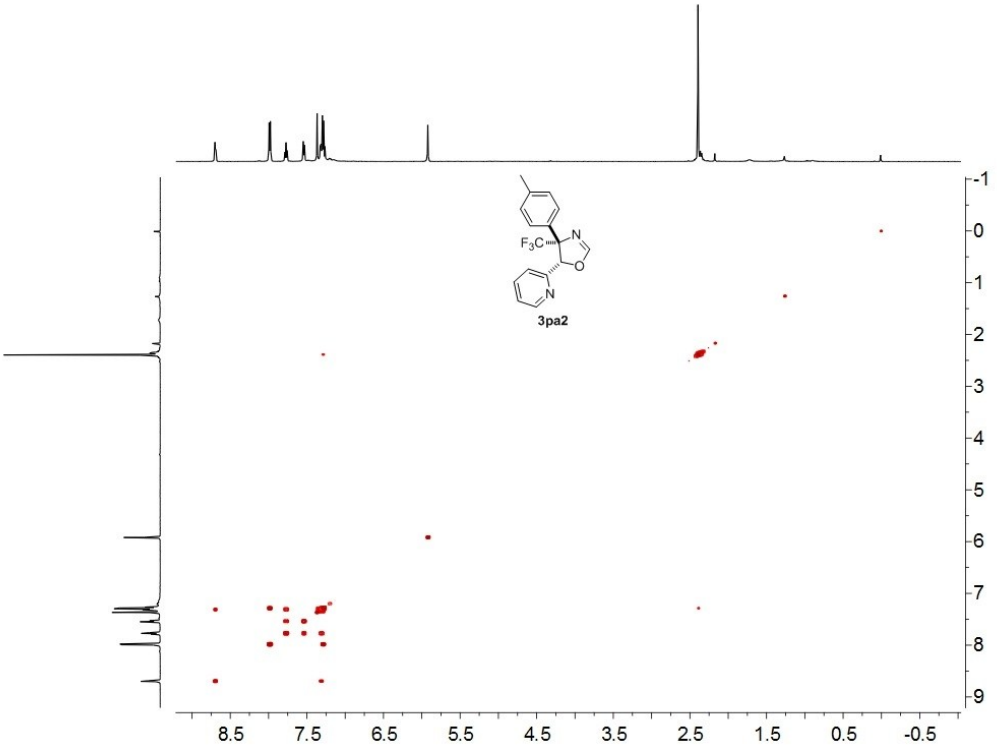
COSY spectrum of 3pa1



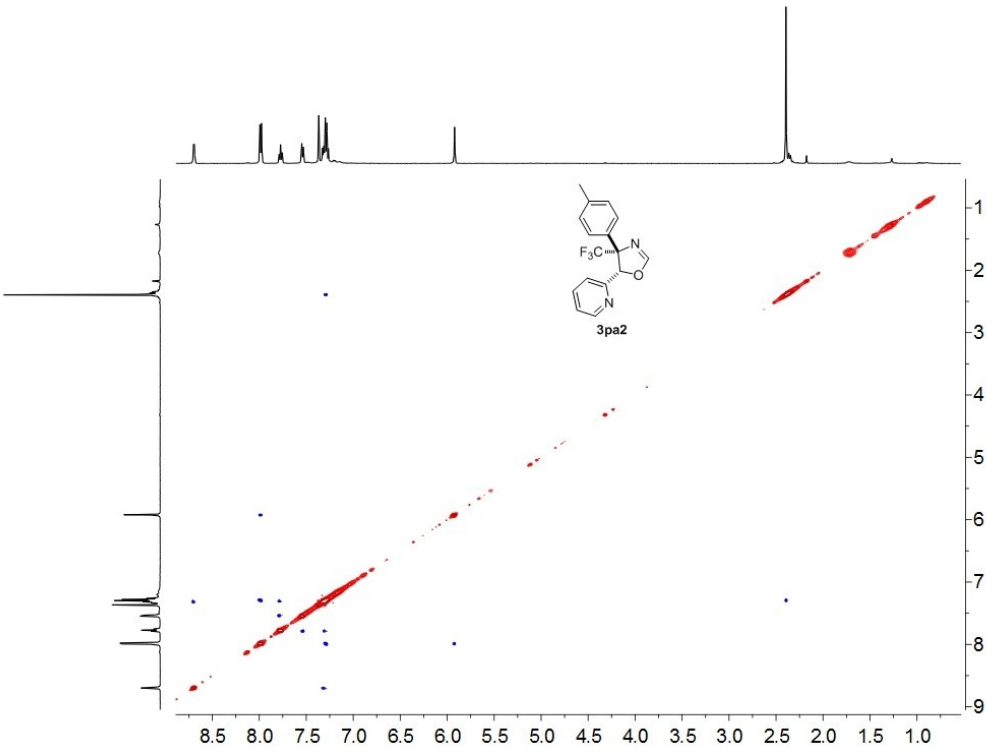
NOE spectrum of 3pa1



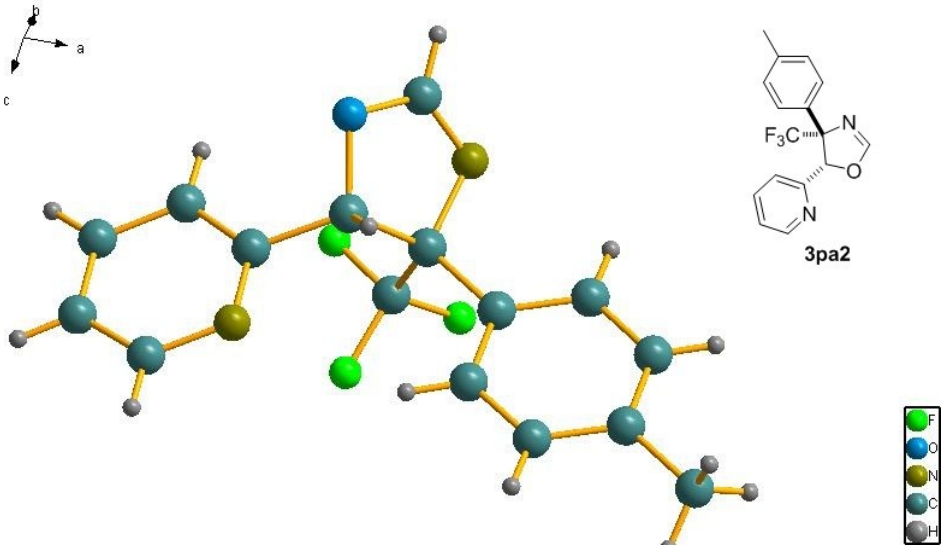
COSY spectrum of 3pa2



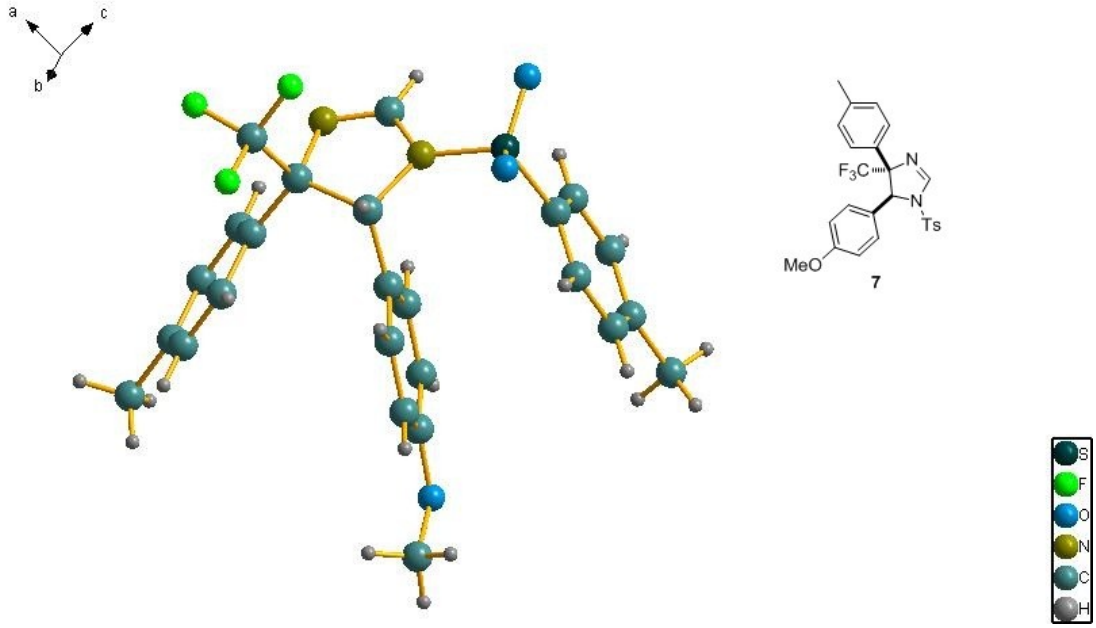
NOE spectrum of 3pa2



Crystal Data



3pa2



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