Supporting Information

Pd-Catalyzed regioselective synthesis of 2,6−disubstituted pyridines through denitrogenation of pyridotriazoles and 3,8−diarylation of imidazo[1,2-a]pyridines

Table of Contents

EXPERIMENTAL SECTION

General. All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded at 600, 200, 150 and 125 MHz, respectively. The spectra were recorded in $CDCl_3$ as solvent. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and so forth, and coupling constants (J) are given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ^{1}H NMR (7.26) and ^{13}C NMR (77.0) correspond to the deuterated solvent chloroform (water peak at 1.5 ppm) respectively. Mass spectra were obtained using the electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel with 100−200 mesh size using ethyl acetate/hexane as eluent unless otherwise stated.

General procedure

(A) Synthesis of triazolopyridine derivatives (1)[1]: Hydrazine monohydrate (0.30 mmol) and acetic acid (0.02 mmol) were added to a solution of 2-acylpyridine (0.20 mmol) in ethanol (1.0 mL) at room temperature. The reaction mixture was heated at reflux for 6 h, and then EtOAc (5.0 mL) and $Cu(OAc)_2$ (0.01 mmol) were added. After stirring at the indicated temperature for the indicated time, the resulting mixture was cooled to room temperature and then diluted with EtOAc (20 mL). The organic phase was washed with water (10 mL) and then dried over anhydrous Na_2SO_4. Concentration under reduced pressure and successive purification by column chromatography gave the desired triazolopyridine derivatives.

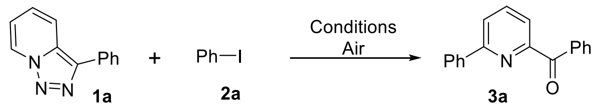
(B) Synthesis of phenyl(6-phenylpyridin-2-yl)methanone (3a) : To a reaction tube equipped with a magnetic stir bar, added 3-phenyl-[1,2,3]triazolo[1,5-a]pyridine (**1a**) (48.8 mg, 0.25 mmol), iodobenzene **2a** (102.0 mg, 0.5 mmol), palladium acetate $Pd(OAc)_2$ (5.6 mg, 10 mol%), silver carbonate Ag_2CO_3 (138.0 mg, 0.5 mmol), and 1.0 mL of dry toluene. The mixture was heated in an oil bath at 120 °C in a closed tube for 12h. Reaction was monitored by TLC, after completion of the reaction it was allowed to attain room temperature. Then the mixture was poured into 30 mL of sodium chloride solution. The product was extracted with EtOAc (15 mL X 3) and dried with anhydrous Na_2SO_4. Removal of the solvent under reduced pressure the left-out residue was purified by column chromatography using silica gel (10% EtOAc/hexane) to afford **3a** (55.0 mg; 85% yield).

Optimization of Reaction Conditions

To test our initial hypothesis, we first examined the denitrogenative[2] transannulation of pyridotriazole **1a** with iodobenzene **2a** in the presence of 10 mol % of $Pd(OAc)_2$ in dimethyl formamide at 120°C temperature in a sealed tube, and no reaction was observed up to 12 h (Table 1, entry 1). When the same reaction was performed with Ag_2CO_3 as additive, the desired product **3a** was isolated in 39% yield (Table 1, entry 2). Significant improvement in the yield (77%) of the product **3a** was observed, while conducting the reaction in toluene as solvent (entry 3). The yield was further improved to 85% the reaction in dry toluene (entry 4). When the reaction was performed under O_2 and N_2 atmosphere very low yield and no reaction was observed (Table 1, entries 5 and 6). Further enhancement in yield was not observed upon the increasing the amount of additive (entry 7), while the yield was reduced by decreasing the additive or catalyst or temperature of the reaction (Table 1, entries 8−10).

Similar yield was obtained by increasing the reaction temperature to 130°C (entry 11). The effect of other additives ($NaHCO_3$, K_2CO_3, t-BuOK, and t-BuONa) catalysts ($PdCl_2$ and CuI) were also checked for the present reaction; no product formation was observed (Table 1, entries 12−17). Upon further screening of different solvents such as p-xylene, benzene and hexane,

Table S1. Optimization of conditions[a]



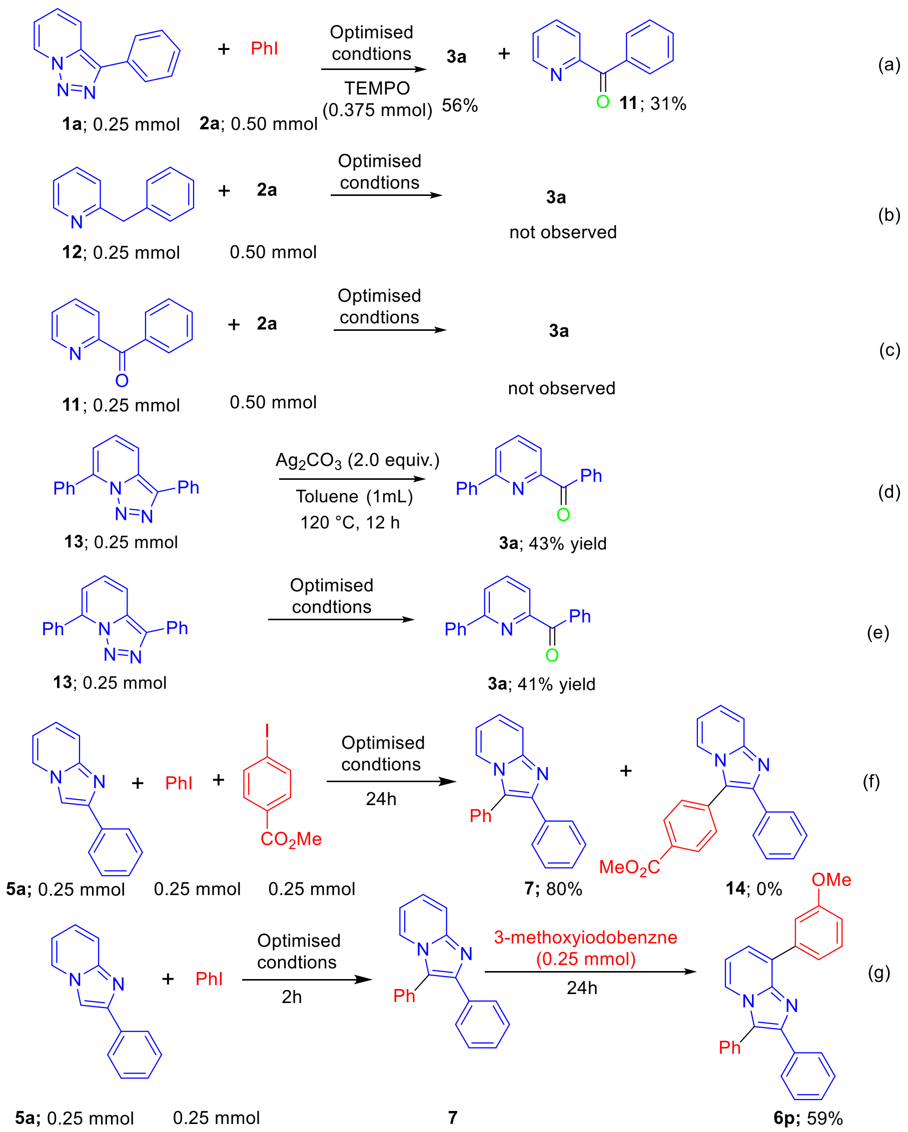
Entry	Catalyst (mol%)	Additive (equiv.)	Solvent (1 mL)	Temp (°C)	Yield(%)[b]
1	$Pd(OAc)_2$(10%)		DMF	120	nr
2	$Pd(OAc)_2$(10%)	Ag_2CO_3(2)	DMF	120	39
3	$Pd(OAc)_2$(10%)	Ag_2CO_3(2)	Toluene	120	77
4[c]	**$Pd(OAc)_2$(10%)**	**Ag_2CO_3(2)**	**Toluene**	**120**	**85**
5[d]	$Pd(OAc)_2$(10%)	Ag_2CO_3(2)	Toluene	120	18
6[e]	$Pd(OAc)_2$(10%)	Ag_2CO_3(2)	Toluene	120	nr
7	$Pd(OAc)_2$(10%)	Ag_2CO_3(3)	Toluene	120	83
8	$Pd(OAc)_2$(10%)	Ag_2CO_3(1)	Toluene	120	52
9	$Pd(OAc)_2$(5%)	Ag_2CO_3(2)	Toluene	120	67
10	$Pd(OAc)_2$(10%)	Ag_2CO_3(2)	Toluene	110	73
11	$Pd(OAc)_2$(10%)	Ag_2CO_3(2)	Toluene	130	85
12	$Pd(OAc)_2$ (10%)	$NaHCO_3$ (2)	Toluene	120	nr
13	$Pd(OAc)_2$ (10%)	K_2CO_3 (2)	Toluene	120	nr
14	$Pd(OAc)_2$ (10%)	t-BuOK (2)	Toluene	120	0
15	$Pd(OAc)_2$ (10%)	t-BuONa (2)	Toluene	120	0
16	CuI (10%)	Ag_2CO_3(2)	Toluene	120	nr
17	$PdCl_2$ (10%)	Ag_2CO_3(2)	Toluene	120	nr
18	$Pd(OAc)_2$ (10%)	Ag_2CO_3(2)	p-xylene	120	60
19	$Pd(OAc)_2$ (10%)	Ag_2CO_3(2)	Benzene	120	82
20	$Pd(OAc)_2$ (10%)	Ag_2CO_3(2)	Hexane	120	0
21[f]	$Pd(OAc)_2$ (10%)	Ag_2CO_3(2)	Toluene	120	63
22[g]	$Pd(OAc)_2$ (10%)	Ag_2CO_3(2)	Toluene	120	71

[a]Reaction condition: **1a** (0.25 mmol), **2a** (0.5 mmol), 12 h. [b]Isolated yield. [c]Dry toluene was used; [d,e]Reaction was performed under O_2 and N_2 atmosphere respectively. [f,g] Reaction time 6h and 10 h respectively.

either low yields or no reaction was observed (Table 1, entries 18−20). The reactions performed with lowering the reaction time, the yield of **3a** was reduced (Table 1, entries 21 and 22). On the basis of the results obtained, the optimized conditions were set as 0.25 mmol of **1a**, 0.5 mmol of **2a**, 10 mol% $Pd(OAc)_2$, 2.0 equivalent Ag_2CO_3, and 1.0 mL of toluene as a solvent in a sealed tube at 120°C, 12 h.

Control experiments for investigation of reaction mechanism

In order to obtain some mechanistic insights of the denitrogenative arylation of pyridotriazoles, we conducted some additional experiments (Scheme S1). Initially, the reaction of **1a** and **2a** was subjected to the optimized conditions in presence of radical scavenger TEMPO, under these conditions the desired product **3a** was isolated in 56% yield along with 31% yield of



Scheme S1. Control experiments

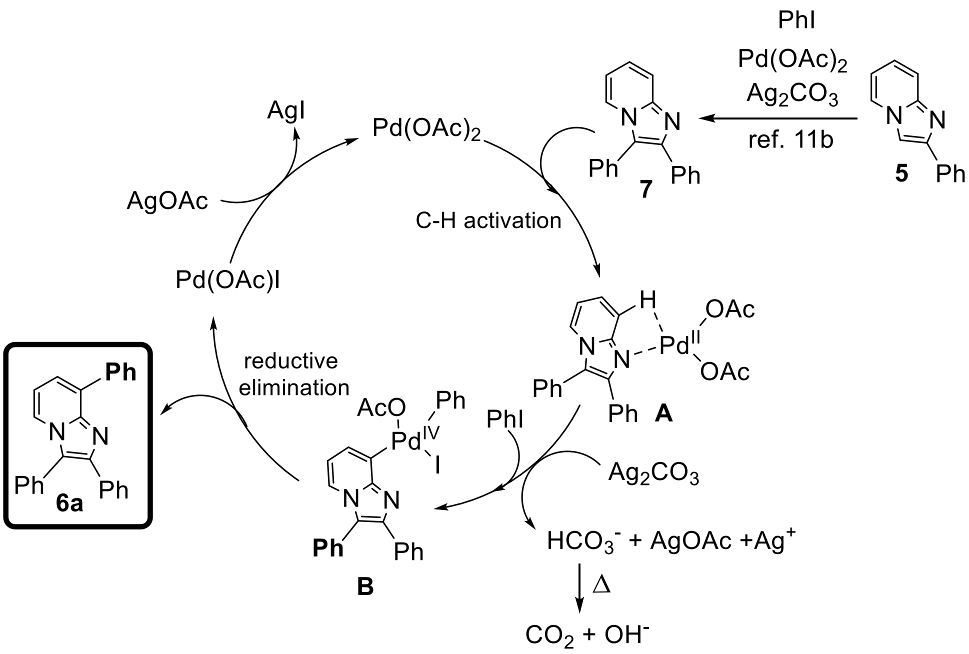
oxidized product 2-benzoylpyridine **11** (Scheme S1a). This reaction indicates that, the conversion of **1a** to **3a** is not going through radical path. To know the possible intermediates, 2-benzylpyridine **12** was reacted with **2a** under the standard conditions, the expected product

3a was not observed (Scheme S1b). Further, **11** was subjected with **2a** under the same conditions, it does not yield the arylated product **3a** (Scheme S1c). These two reactions (Scheme S1a-b) suggest that, both **11** and **12** are not the intermediates in the reaction. To confirm the intermediate, the di-phenyl pyridotriazole **13** was subjected to the optimized conditions without $Pd(OAc)_2$ catalyst, under these conditions the desired product **3a** was obtained in 43% yield (Scheme S1d). This reaction suggests that, oxidative denitrogenation of **13** under the standard conditions give the desired product **3a**. Further from the reactions of scheme S1(c-e), it confirm that, initially palladium catalyzed arylation may provide the product **13**, followed by its denitrogenative oxidation give the product **3a**.

To check the sequential C-H arylation with different aryliodides, we performed a reaction of 3-phenylimidazo[1,2-a]pyridine **5a** with 1.0 equiv. of iodobenzene and 1 equiv. of methyl 4-iodobenzoate under optimized conditions, unfortunately we got only 2,3-diphenylimidazo[1,2-a]pyridine **7** but not methyl 4-(2-phenylimidazo[1,2-a]pyridin-3-yl)benzoate **14** due to less reactivity of electron withdrawing group in present protocol (Scheme S1f). Also we performed the reaction by the sequential addition of two different iodoarenes with 3-phenylimidazo[1,2-a]pyridine **5a**, initially substitution take place at C-3 first iodoarene and subsequently at C-8 position of **5a** [see supporting information, Scheme S1(g)]. Initially reaction of **5a** with iodobenzene gives 2,3-diphenylimidazo[1,2-a]pyridine **7** in 2h under optimized conditions, further addition of 3-methoxyiodobenzene to the same reaction mixture (one pot) yield the desired diarylated product 8-(3-methoxyphenyl)-2,3-diphenylimidazo[1,2-a]pyridine **6p** in 59% isolated yield after 24h. Based on these control experiments and our observation, a plausible reaction mechanism has been proposed for **3a** (see Scheme 3 in manuscript) and for **6a** (Scheme S2).

Plausible reaction mechanism for the synthesis of 2,3,8-triphenylimidazo[1,2-a]pyridine (6a)

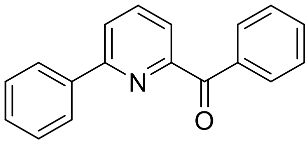
Monoarylation (C−3) of **5** to get **7** may be same as that of literature method.[3] For the selective C−8 arylation (diarylation), initially reaction of **7** with palladium generates a metalated intermediate **A** through C−H activation. Subsequently oxidative addition of aryliodide (PhI) generates palladium (IV) complex **B**, followed by its reductive elimination furnish the diarylated product **6a**.



Scheme S2. Plausible reaction mechanism for **6a**

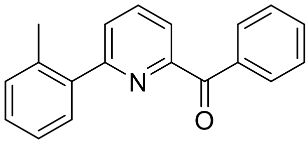
Charecterisation data:

phenyl(6-phenylpyridin-2-yl)methanone (3a)[4]



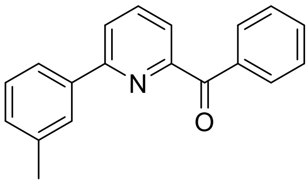
Yield (55.0 mg, 85% yield, yellow liquid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 2H), 8.05 (d, J = 7.4 Hz, 2H), 8.03 – 7.98 (m, 1H), 7.97 – 7.94 (m, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.3 Hz, 2H), 7.43 (t, J = 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 155.8, 154.7, 138.3, 137.8, 136.3, 132.7, 131.3, 129.4, 128.8, 127.9, 126.9, 122.8, 122.4.

phenyl(6-(o-tolyl)pyridin-2-yl)methanone (3b)



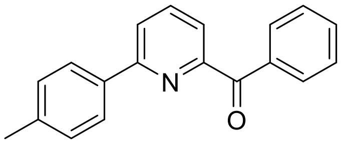
Yield (25.0 mg, 37% yield, yellow liquid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.4 Hz, 2H), 7.99 – 7.93 (m, 2H), 7.59 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (dd, J = 15.1, 7.7 Hz, 3H), 7.29 (dd, J = 14.3, 6.3 Hz, 2H), 7.24 (d, J = 7.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 158.9, 154.7, 139.5, 137.2, 136.3, 136.0, 132.7, 131.1, 130.9, 129.8, 128.6, 127.9, 126.4, 125.9, 122.3, 20.6; HRMS-ESI (m/z) [M+K]+calcd. For $C_{19}H_{15}NOK$, 312.0791; found 312.0779.

phenyl(6-(m-tolyl)pyridin-2-yl)methanone (3c)



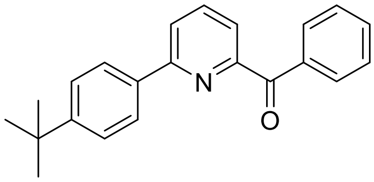
Yield (50.0 mg, 75% yield, yellow liquid), eluent: 5% ethylacetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 7.7 Hz, 2H), 7.99 – 7.96 (m, 1H), 7.94 – 7.92 (m, 2H), 7.85 (s, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.61 (s, 1H), 7.50 (t, J = 7.9 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.24 (d, J = 8.3 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 156.1, 154.7, 138.4, 137.7, 136.3, 132.8, 131.3, 130.1, 128.7, 127.9, 127.6, 124.0, 122.7, 122.5, 21.5; HRMS-ESI (m/z) [M+H]+calcd. For $C_{19}H_{16}NO$, 274.1232; found 274.1231.

phenyl(6-(p-tolyl)pyridin-2-yl)methanone (3d)



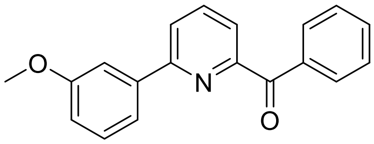
Yield (52.5 mg, 77% yield, yellow liquid), eluent: 5% ethylacetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 2H), 7.99 – 7.91 (m, 5H), 7.61 (t, J = 7.5 Hz, 1H), 7.51 (dd, J = 9.4, 5.5 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 155.8, 154.7, 139.5, 137.7, 136.4, 135.6, 132.7, 131.3, 129.5, 127.9, 126.8, 122.5, 122.1, 21.2; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{19}H_{15}NONa$, 296.1051; found 296.1041.

(6-(4-(tert-butyl)phenyl)pyridin-2-yl)(phenyl)methanone (3e)



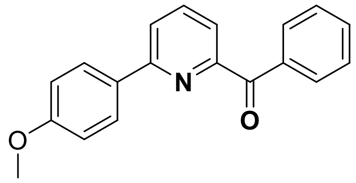
Yield (31.3 mg, 40% yield, yellow semi-solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, J = 7.9, 6.3 Hz, 5H), 7.59 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.8 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.07 (d, J = 6.8 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 155.8, 154.6, 152.6, 137.7, 136.4, 135.5, 132.6, 131.3, 127.9, 126.6, 125.7, 122.4, 122.1, 34.6, 31.2; HRMS-ESI (m/z) [M+K]+calcd. For $C_{22}H_{21}NOK$, 354.1260; found 354.1135.

(6-(3-methoxyphenyl)pyridin-2-yl)(phenyl)methanone (3f)



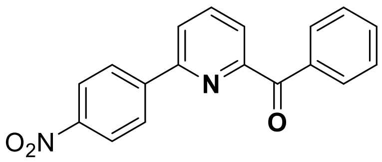
Yield (39.7 mg, 55% yield, white solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 8.02 (dd, J = 6.8, 2.0 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.65 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.9 Hz, 1H), 6.98 (dd, J = 8.1, 2.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 160.1, 155.5, 154.5, 139.7, 137.8, 136.4, 132.7, 131.3, 129.8, 127.9, 122.9, 122.5, 119.1, 115.4, 112.0, 55.2; HRMS-ESI (m/z) [M+H]+calcd. For $C_{19}H_{16}NO_2$, 290.1181; found 290.1188.

(6-(4-methoxyphenyl)pyridin-2-yl)(phenyl)methanone (3g)



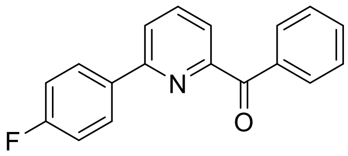
Yield (50.0 mg, 69% yield, white solid, mp= 86-88 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 8.05 – 7.98 (m, 2H), 7.91 (qd, J = 8.0, 3.8 Hz, 3H), 7.61 (t, J = 7.4 Hz, 1H), 7.55 – 7.49 (m, 2H), 6.99 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 160.7, 155.5, 154.6, 138.2, 137.6, 136.4, 132.7, 131.3, 131.0, 128.2, 127.9, 122.0, 121.6, 114.1, 55.3; HRMS-ESI (m/z) [M+H]+calcd. For $C_{19}H_{16}NO_2$, 290.1181; found 290.1210.

(6-(4-nitrophenyl)pyridin-2-yl)(phenyl)methanone (3h)



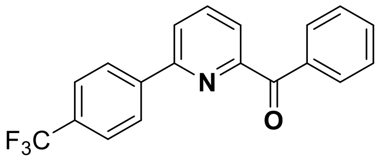
Yield (42.4 mg, 56% yield, yellow solid, mp=176-178 ℃), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, J = 8.5 Hz, 2H), 8.20 (d, J = 8.5 Hz, 2H), 8.16 (d, J = 7.6 Hz, 2H), 8.08 (dd, J = 8.8, 7.2 Hz, 1H), 8.04 (t, J = 6.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.1, 155.1, 153.2, 148.3, 144.0, 138.3, 136.0, 133.0, 131.1, 128.0, 127.6, 124.1, 124.0, 123.1; HRMS-ESI (m/z) [M+H]+calcd. For $C_{18}H_{13}N_2O_3$, 305.0926; found 305.0918.

(6-(4-fluorophenyl)pyridin-2-yl)(phenyl)methanone (3i)



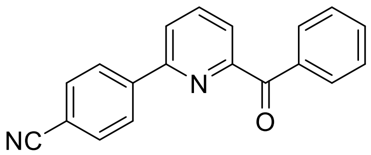
Yield (43.4 mg, 63% yield, yellow liquid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 2H), 8.05 – 8.00 (m, 2H), 7.97 (dt, J = 15.0, 7.6 Hz, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.17 – 7.13 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 164.5, 162.9, 154.83 (d, J = 12.8 Hz), 137.9, 136.3, 134.5, 132.8, 131.2, 128.78 (d, J = 8.0 Hz), 128.0, 122.7, 122.1, 115.8, 115.7; HRMS-ESI (m/z) [M+H]+calcd. For $C_{18}H_{13}FNO$, 278.0981; found 278.0985.

phenyl(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)methanone (3j)



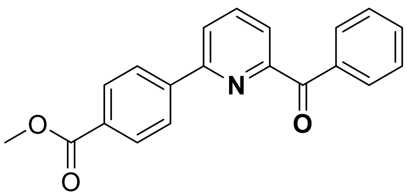
Yield (55.6 mg, 68% yield, yellow liquid), eluent: 5% ethylacetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 7.4 Hz, 2H), 8.15 (d, J = 8.1 Hz, 2H), 8.08 – 8.04 (m, 1H), 8.03 – 7.96 (m, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 154.9 (d, J= 124.9 Hz), 141.6, 138.1, 136.1, 132.9, 131.27, 131.12 (d, J = 22.2 Hz), 128.0, 127.2, 125.7, 124.9, 123.6, 123.1, 122.7; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{19}H_{12}F_3NONa$, 350.0769; found 350.0813.

4-(6-benzoylpyridin-2-yl)benzonitrile (3k)



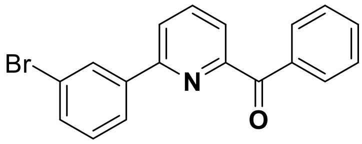
Yield (50.8 mg, 72% yield, white solid, mp= 230-232 ℃), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.6, 5.4 Hz, 4H), 8.06 (d, J = 6.5 Hz, 1H), 8.04 – 8.01 (m, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 155.1, 153.6, 142.3, 138.2, 136.0, 133.0, 132.6, 131.1, 128.0, 127.4, 123.9, 122.8, 118.6, 112.8; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{19}H_{12}N_2ONa$, 307.0847; found 307.0835.

methyl 4-(6-benzoylpyridin-2-yl)benzoate (3l)



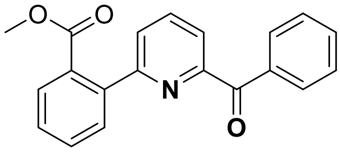
Yield (51.7 mg, 65% yield, white solid, mp=156-158 ℃), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, CDCl3) δ 8.20 (d, J = 7.9 Hz, 2H), 8.12 (q, J = 8.5 Hz, 4H), 8.06 – 8.03 (m, 1H), 8.02 – 7.99 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.9 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 166.7, 154.9, 154.6, 142.4, 138.0, 136.2, 132.9, 131.2, 130.7, 130.1, 128.0, 126.8, 123.5, 122.9, 52.2; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{20}H_{15}NO_3Na$, 340.0950; found 340.0957.

(6-(3-bromophenyl)pyridin-2-yl)(phenyl)methanone (3m)



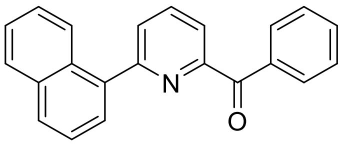
Yield (50.5 mg, 60% yield, white solid, mp= 136-138 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (dd, J = 5.1, 2.4 Hz, 3H), 8.02 (d, J = 7.7 Hz, 1H), 7.98 (dd, J = 15.9, 8.1 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.54 (dt, J = 15.8, 8.0 Hz, 3H), 7.34 (t, J = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 154.9, 154.3, 140.4, 138.0, 136.21, 132.9, 132.3, 131.2, 130.38, 130.0, 128.0, 125.4, 123.3, 122.5; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{18}H_{12}BrNONa$, 360.0000; found 359.9985.

methyl 2-(6-benzoylpyridin-2-yl)benzoate (3n)



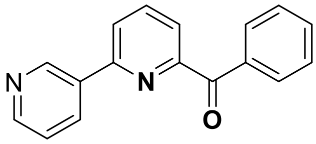
Yield (37.9 mg, 48% yield, white semi-solid), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 7.9 Hz, 2H), 8.12 (q, J = 8.5 Hz, 4H), 8.06 – 8.03 (m, 1H), 8.02 – 7.99 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.9 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 166.7, 154.9, 154.6, 142.4, 138.0, 136.2, 132.9, 131.2, 130.7, 130.1, 128.0, 126.8, 123.5, 122.9, 52.2; HRMS-ESI (m/z) [M+H]+calcd. For $C_{20}H_{17}NO_3$, 318.1130; found 318.1106

(6-(naphthalen-1-yl)pyridin-2-yl)(phenyl)methanone (3o)



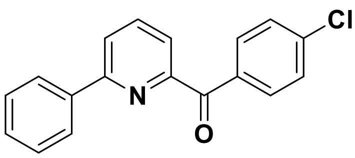
Yield (40.2 mg, 52% yield, yellow semi-solid), eluent: 2% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 7.4 Hz, 2H), 8.14 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.04 (t, J = 7.9 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 6.7 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.53 – 7.48 (m, 2H), 7.45 (t, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 158.0, 155.2, 137.7, 137.3, 136.2, 133.9, 132.8, 131.2, 131.0, 129.2, 128.4, 128.0, 127.9, 127.47, 126.4, 125.9, 125.4. 125.3, 122.8; HRMS-ESI (m/z) [M+K]+calcd. For $C_{22}H_{15}NOK$, 348.1791; found 348.1729.

[2,3'-bipyridin]-6-yl(phenyl)methanone (3p)



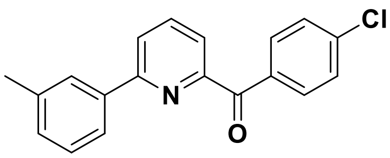
Yield (47.8 mg, 74% yield, green semi-solid), eluent: 30% ethylacetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.65 (d, J = 4.5 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.8 Hz, 1H), 8.00 (td, J = 8.0, 2.3 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.39 (dd, J = 7.5, 5.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 155.0, 153.3, 150.28, 150.20, 148.2, 138.1, 136.1, 134.3, 133.8, 132.9, 131.1, 128.0, 123.6, 123.5, 122.4; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{17}H_{12}N_2ONa$, 283.0847; found 283.0825.

(4-chlorophenyl)(6-phenylpyridin-2-yl)methanone (4a)



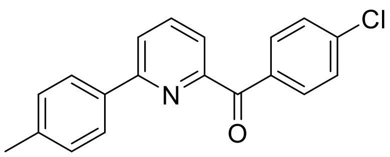
Yield (57.5 mg, 78% yield, brown solid, mp= 116-118 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 8.02 (t, J = 5.1 Hz, 3H), 8.00 – 7.95 (m, 2H), 7.52 – 7.46 (m, 4H), 7.45 (dd, J = 7.8, 5.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 155.9, 154.3, 139.2, 138.2, 137.9, 134.7, 132.7, 129.5, 128.9, 128.3, 126.8, 122.9, 122.7; HRMS-ESI (m/z) [M+H]+calcd. For $C_{18}H_{13}ClNO$, 294.0686; found 294.0677.

(4-chlorophenyl)(6-(m-tolyl)pyridin-2-yl)methanone (4b)



Yield (53.2 mg, 69% yield, white solid, mp= 100-102 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.20 (d, J = 2.1 Hz, 1H), 8.00 (dd, J = 5.7, 3.4 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.84 – 7.79 (m, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 6.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 156.0, 154.2, 139.2, 138.5, 138.2, 137.8, 134.6, 132.8, 130.3, 128.8, 128.2, 127.5, 124.0, 122.7, 21.6; HRMS-ESI (m/z) [M+H]+calcd. For $C_{19}H_{15}ClNO$, 308.0842; found 308.0825.

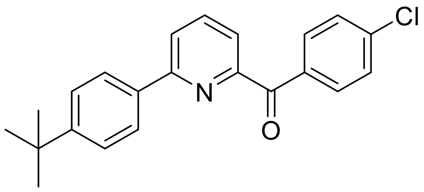
(4-chlorophenyl)(6-(p-tolyl)pyridin-2-yl)methanone (4c)



Yield (56.1 mg, 73% yield, yellow semi-solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 –

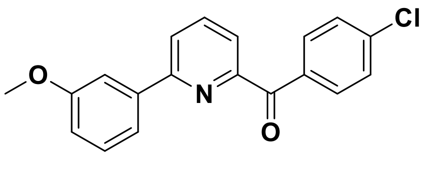
8.19 (m, 2H), 7.99 (dd, J = 6.8, 2.2 Hz, 1H), 7.96 – 7.91 (m, 4H), 7.50 – 7.47 (m, 2H), 7.29 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 155.9, 154.2, 139.6, 139.1, 137.8, 135.4, 134.7, 132.8, 129.6, 128.2, 126.7, 122.7, 122.5, 122.3, 21.2; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{19}H_{14}ClNONa$, 330.0662; found 330.0657.

(6-(4-(tert-butyl)phenyl)pyridin-2-yl)(4-chlorophenyl)methanone (4d)



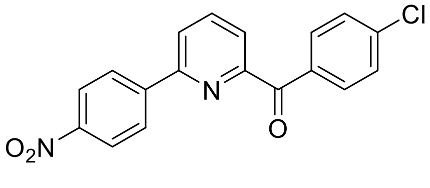
Yield (43.8 mg, 50% yield, white semi-solid), eluent: 2% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 – 8.19 (m, 2H), 8.01 – 7.99 (m, 1H), 7.96 (dd, J = 15.0, 6.6 Hz, 4H), 7.54 – 7.47 (m, 4H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 155.8, 154.2, 152.8, 139.1, 137.8, 135.4, 134.7, 132.8, 128.2, 126.5, 125.8, 122.7, 122.5, 122.4, 34.7, 31.2; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{22}H_{20}ClNONa$, 372.1131; found 372.1137.

(4-chlorophenyl)(6-(3-methoxyphenyl)pyridin-2-yl)methanone (4e)



Yield (58.9 mg, 73% yield, white solid, mp= 124-126 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 – 8.19 (m, 2H), 8.03 (dd, J = 6.9, 2.2 Hz, 1H), 7.97 (q, J = 7.8 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.47 (dd, J = 6.5, 4.6 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 6.99 (dd, J = 8.1, 2.4 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 160.1, 155.6, 154.2, 139.6, 139.2, 138.0, 134.7, 132.8, 129.9, 128.2, 123.0, 122.8, 119.1, 115.3, 112.2, 55.3; HRMS-ESI (m/z) [M+H]+calcd. For $C_{19}H_{15}ClNO_2$, 324.0719; found 324.0787.

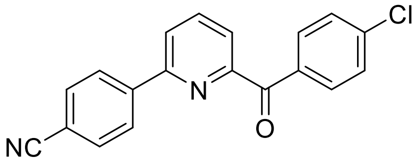
(4-chlorophenyl)(6-(4-nitrophenyl)pyridin-2-yl)methanone (4f)



Yield (47.4 mg, 56% yield, yellow solid, mp= 228-230 ℃), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, J = 8.6 Hz, 2H), 8.19 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 6.7 Hz, 1H), 8.09 – 8.03 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H).

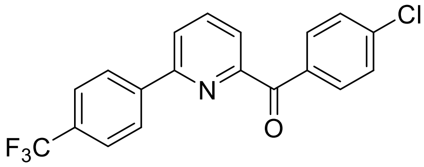
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 153.3, 143.9, 139.6, 138.5, 134.3, 132.6, 128.4, 127.7, 124.2, 124.1, 123.4; HRMS-ESI (m/z) [M+H]+calcd. For $C_{18}H_{12}ClN_2O_3$, 339.0536; found 339.0538.

4-(6-(4-chlorobenzoyl)pyridin-2-yl)benzonitrile (4g)



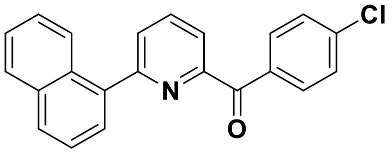
Yield (50.2 mg, 63% yield, white solid, mp= 204-206 ℃), eluent: 10% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 2.3 Hz, 2H), 8.13 (d, J = 2.2 Hz, 2H), 8.08 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.01 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 153.8, 142.3, 139.6, 138.5, 134.5, 132.8, 132.6, 128.5, 127.5, 124.1, 123.2, 118.6, 113.1; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{19}H_{11}ClN_2ONa$, 341.0458; found 341.0443.

(4-chlorophenyl)(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)methanone (4h)



Yield (64.0 mg, 71% yield, yellow solid, mp= 120-122 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (dd, J = 6.4, 4.3 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.09 – 8.07 (m, 1H), 8.05 – 7.99 (m, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.49 (dd, J = 6.0, 4.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 154.5 (d, J= 37.5 Hz), 141.4, 139.4, 138.3, 134.5, 132.6, 131.4 (d, J= 38.1 Hz), 128.3, 127.1, 125.8, 123.7, 123.0; HRMS-ESI (m/z) [M+H]+calcd. For $C_{19}H_{12}ClF_3NO$, 362.0560; found 362.0552.

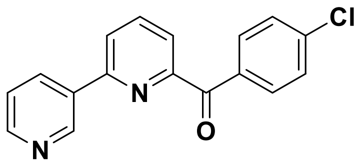
(4-chlorophenyl)(6-(naphthalen-1-yl)pyridin-2-yl)methanone (4i)



Yield (46.4 mg, 54% yield, yellow solid, mp= 136-138 ℃), eluent: 2% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 – 8.21 (m, 2H), 8.11 (dd, J = 17.0, 8.1 Hz, 2H), 8.04 (t, J = 7.6 Hz, 1H), 7.94 (t, J = 7.2 Hz, 2H), 7.81 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 7.4 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.49 (dd, J = 8.5, 6.2 Hz, 1H), 7.40 (t, J = 5.0 Hz, 2H).

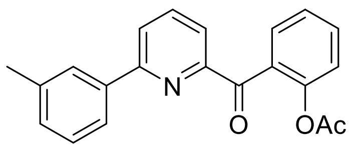
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.0, 158.0, 154.7, 139.3, 137.6, 137.5, 134.5, 133.9, 132.7, 130.9, 129.3, 128.5, 128.3, 127.8, 127.7, 126.5, 126.0, 125.3, 125.2, 122.9; HRMS-ESI (m/z) [M+H]+calcd. For $C_{22}H_{15}ClNO$, 344.0842; found 344.0824.

[2,3'-bipyridin]-6-yl(4-chlorophenyl)methanone (4j)



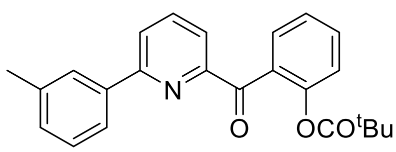
Yield (48.1 mg, 65% yield, yellow solid, mp= 130-132 ℃), eluent: 30% ethylacetate/hexane; ^1H NMR (600 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.68 (d, J = 4.2 Hz, 1H), 8.31 (dt, J = 8.0, 1.8 Hz, 1H), 8.16 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 7.4 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.42 (dd, J = 7.9, 4.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 154.7, 153.4, 150.3, 148.2, 139.4, 138.3, 134.5, 133.7, 132.6, 128.4, 123.6, 122.7; HRMS-ESI (m/z) [M+H]+calcd. For $C_{17}H_{12}ClN_2O$, 295.0638; found 295.0631.

2-(6-(m-tolyl)picolinoyl)phenyl acetate (4k)



Yield (31.8 mg, 39% yield, colourless liquid), eluent: 10% ethylacetate/hexane; ^1H NMR (600 MHz, $CDCl_3$) δ 7.96 (dt, J = 14.3, 5.5 Hz, 3H), 7.86 (d, J = 6.1 Hz, 1H), 7.79 (s, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.61 (dd, J = 11.3, 5.1 Hz, 1H), 7.38 (dd, J = 9.0, 6.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 2.2 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 2.41 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 169.0, 156.7, 154.4, 149.6, 137.7, 132.7, 132.0, 130.3, 128.8, 127.7, 125.3, 124.2, 123.0, 122.9, 122.0, 29.7, 20.7; HRMS-ESI (m/z) [M+H]+calcd. For $C_{21}H_{18}NO_3$, 332.1287; found 332.1262.

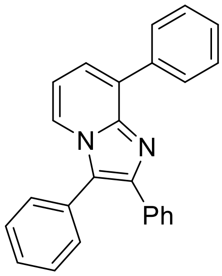
2-(6-(m-tolyl)picolinoyl)phenyl pivalate (4l)



Yield (71.8 mg, 77% yield, colourless liquid), eluent: 5% ethylacetate/hexane; ^1H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, J = 5.8, 2.3 Hz, 1H), 7.92 (d, J = 2.4 Hz, 1H), 7.91 (s, 1H), 7.78 – 7.72 (m, 3H), 7.60 – 7.55 (m, 1H), 7.33 (dt, J = 19.0, 7.5 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H), 1.03 (s, 9H). ^{13}C

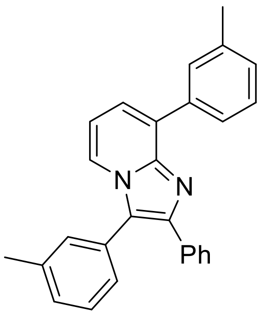
NMR (150 MHz, $CDCl_3$) δ 193.9, 176.1, 138.1, 137.6, 132.1, 131.3, 130.1, 128.6, 127.7, 125.1, 124.1, 123.1, 122.4, 121.8, 38.9, 26.7, 21.5; HRMS-ESI (m/z) [M-H]+calcd. For $C_{24}H_{22}NO_3$, 372.1304; found 372.1349.

2,3,8-triphenylimidazo[1,2-a]pyridine (6a)



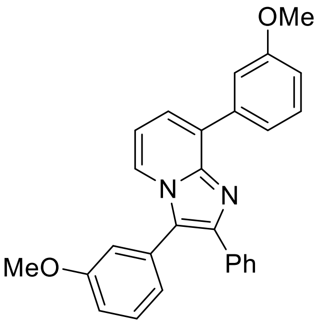
Yield (52.5 mg, 61% yield, brown solid, mp= 190-192 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 2H), 7.93 (d, J = 6.8 Hz, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.53 (ddd, J = 18.9, 10.2, 5.8 Hz, 7H), 7.46 – 7.42 (m, 1H), 7.35 (d, J = 7.0 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 6.8 Hz, 1H), 6.82 (t, J = 6.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 142.47, 136.5, 134.3, 130.8, 130.2, 130.0, 129.5, 129.0, 128.8, 128.4, 128.2, 128.1, 127.2, 122.91 (d, J = 9.9 Hz), 122.2, 121.3, 112.37 (d, J = 4.5 Hz); HRMS-ESI (m/z) [M+Na]+calcd. For $C_{25}H_{18}N_2Na$, 369.1368; found 369.1363.

2-phenyl-3,8-di-m-tolylimidazo[1,2-a]pyridine (6b)



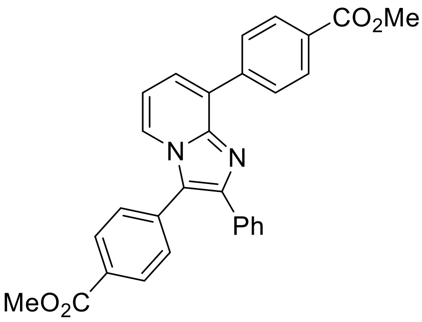
Yield (58.4 mg, 62% yield, yellow liquid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 6.6 Hz, 2H), 7.88 (d, J = 6.8 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.42 (q, J = 8.0 Hz, 2H), 7.30 (d, J = 6.9 Hz, 3H), 7.25 (dt, J = 15.1, 7.5 Hz, 5H), 6.78 (t, J = 6.9 Hz, 1H), 2.48 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 142.1, 139.2, 137.8, 136.5, 134.4, 131.3, 130.19, 130.14, 129.7, 129.6, 129.4, 128.9, 128.3, 128.08, 128.05, 127.9, 127.2, 126.2, 122.8, 122.2, 121.4, 112.2, 21.6, 21.4; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{27}H_{22}N_2Na$, 397.1681; found 397.1698.

3,8-bis(3-methoxyphenyl)-2-phenylimidazo[1,2-a]pyridine (6c)



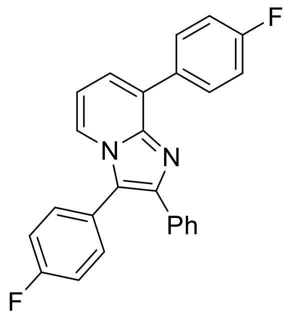
Yield (82.2 mg, 81% yield, green semi-solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 6.8 Hz, 1H), 7.91 (s, 1H), 7.76 (d, J = 7.7 Hz, 2H), 7.70 (d, J = 7.7 Hz, 1H), 7.44 (dt, J = 20.5, 7.9 Hz, 2H), 7.35 (d, J = 6.9 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.23 (dd, J = 14.3, 7.3 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.04 (dd, J = 8.2, 2.1 Hz, 1H), 7.01 (s, 1H), 6.99 (dd, J = 8.4, 2.3 Hz, 1H), 6.80 (t, J = 6.9 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 159.5, 143.3, 142.2, 137.8, 134.3, 131.4, 130.6, 129.7, 129.3, 128.1, 128.0, 127.3, 123.1, 122.9, 122.4, 121.3, 121.1, 116.0, 114.67, 114.63, 114.2, 112.3, 55.3; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{27}H_{22}N_2O_2Na$, 429.1579; found 429.1581.

dimethyl 4,4'-(2-phenylimidazo[1,2-a]pyridine-3,8-diyl)dibenzoate (6d)



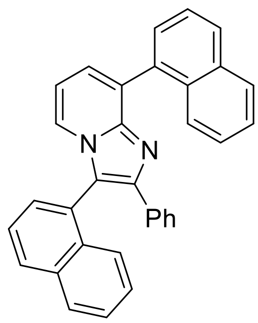
Yield (63.8 mg, 55% yield, brown solid, mp= 202-204 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, J = 8.1 Hz, 2H), 8.20 (t, J = 7.9 Hz, 4H), 8.02 (d, J = 6.8 Hz, 1H), 7.66 (dd, J = 7.9, 1.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.0 Hz, 1H), 7.27 (t, J = 7.7 Hz, 3H), 6.88 (t, J = 6.9 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 166.5, 143.55 (d, J = 11.1 Hz), 140.8, 134.7, 133.7, 130.7, 130.6, 130.3, 129.7, 129.1, 129.0, 128.3, 127.8, 123.8, 122.7, 120.3, 112.7, 52.3, 52.1; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{19}H_{22}N_2O_4Na$, 485.1477; found 485.1470.

3,8-bis(4-fluorophenyl)-2-phenylimidazo[1,2-a]pyridine (6e)



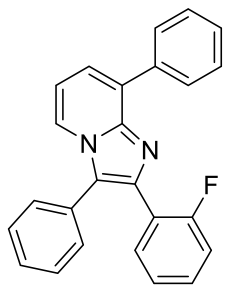
Yield (52.5 mg, 55% yield, yellow liquid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.26 – 8.10 (m, 2H), 7.86 (dd, J = 6.9, 1.1 Hz, 1H), 7.76 – 7.63 (m, 2H), 7.55 – 7.39 (m, 2H), 7.37 – 7.13 (m, 8H), 6.82 (t, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (d, J = 15.8 Hz), 161.9 (d, J = 13.7 Hz), 143.3, 142.7, 134.0, 132.83 (d, J = 8.0 Hz), 132.4, 130.78 (d, J = 7.8 Hz), 129.0, 128.3, 128.16 (d, J = 25.1 Hz), 127.5, 126.1, 122.7, 122.1, 120.2, 116.9, 116.7, 115.5, 115.3 (d, J = 21.3 Hz), 112.5; HRMS-ESI (m/z) [M+K]+calcd. For $C_{25}H_{16}F_2N_2K$, 421.0919; found 421.0915.

3,8-di(naphthalen-1-yl)-2-phenylimidazo[1,2-a]pyridine (6f)



Yield (54.4 mg, 49% yield, brown solid, 112-114 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 1H), 8.03 (d, J = 8.2 Hz, 1H), 8.01 – 7.95 (m, 3H), 7.90 (d, J = 6.9 Hz, 1H), 7.65 (dd, J = 8.8, 5.1 Hz, 3H), 7.58 (t, J = 7.5 Hz, 1H), 7.55 – 7.50 (m, 5H), 7.46 (dd, J = 15.4, 8.0 Hz, 2H), 7.29 (d, J = 6.8 Hz, 1H), 7.11 – 7.05 (m, 3H), 6.78 (t, J = 6.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.2, 132.0, 130.4, 129.9, 128.7, 128.6, 128.3, 128.0, 127.7, 127.2, 126.6, 126.2, 126.1, 125.9, 125.8, 125.7 , 125.4, 125.3, 123.2, 119.3; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{33}H_{22}N_2Na$, 469.1681; found 469.1691.

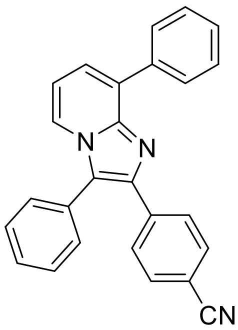
2-(2-fluorophenyl)-3,8-diphenylimidazo[1,2-a]pyridine (6g)



Yield (62.8 mg, 69% yield, green solid, mp= 150-152 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (t, J = 7.1 Hz, 3H), 7.76 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.50 – 7.45 (m, 3H), 7.43 (d, J = 6.7 Hz, 4H), 7.36 (d, J = 6.8 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.18 (t, J = 7.4 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.87 (t, J = 6.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 159.1, 143.7, 138.3, 136.5, 132.3 (d, J = 2.5 Hz), 130.4, 130.1, 129.8, 129.6, 129.3 (t, J

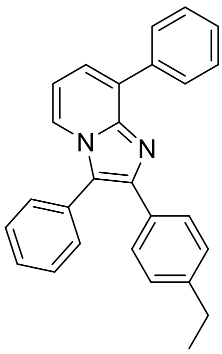
= 15.7 Hz), 129.2, 129.0, 128.4, 128.3, 128.2, 127.1 (d, J = 44.4 Hz), 123.9, 123.4, 123.1, 122.6 (d, J = 14.5 Hz), 122.2, 115.7 (d, J = 21.9 Hz), 112.5; HRMS-ESI (m/z) [M+K]+calcd. For $C_{25}H_{17}FN_2K$, 403.1013; found 403.1074.

4-(3,8-diphenylimidazo[1,2-a]pyridin-2-yl)benzonitrile (6h)



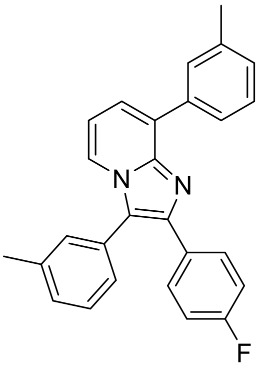
Yield (41.8 mg, 45% yield, yellow solid, mp= 176-178 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$ δ 8.15 (d, J = 7.7 Hz, 2H), 7.89 (d, J = 6.8 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.59 (dd, J = 14.1, 6.6 Hz, 3H), 7.55 – 7.51 (m, 4H), 7.47 (dd, J = 8.8, 4.0 Hz, 3H), 7.38 (d, J = 6.8 Hz, 1H), 6.86 (t, J = 6.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.7, 140.2, 139.0, 136.2, 131.9, 130.7, 130.4, 129.9, 129.8, 129.5, 129.4, 129.2, 129.0, 128.4, 128.2, 123.5, 122.7, 122.4, 119.1, 112.9, 110.4; HRMS-ESI (m/z) [M+K]+calcd. For $C_{26}H_{17}N_3K$, 410.1060; found 410.1081.

2-(4-ethylphenyl)-3,8-diphenylimidazo[1,2-a]pyridine (6i)



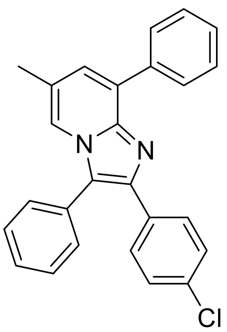
Yield (74.6 mg, 80% yield, yellow solid, mp= 150-152 ℃), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 6.8 Hz, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.54 (dd, J = 13.7, 7.3 Hz, 4H), 7.51 (t, J = 5.9 Hz, 3H), 7.43 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 6.8 Hz, 1H), 7.10 (d, J = 7.9 Hz, 2H), 6.81 (t, J = 6.9 Hz, 1H), 2.62 (q, J = 7.5 Hz, 2H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 142.6, 136.6, 131.7, 130.9, 130.4, 129.9, 129.5, 129.1, 128.7, 128.3, 128.1, 128.0, 127.6, 122.7, 122.2, 120.9, 112.2, 28.5, 15.4; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{27}H_{22}N_2Na$, 397.1681; found 397.1683.

2-(4-fluorophenyl)-3,8-di-m-tolylimidazo[1,2-a]pyridine (6j)



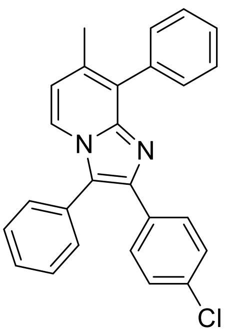
Yield (73.5 mg, 75% yield, yellow semi-solid), eluent: 5% ethylacetate/hexane; [1]H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 10.1 Hz, 2H), 7.88 (d, J = 7.3 Hz, 1H), 7.70 (t, J = 6.2 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.31 (d, J = 7.7 Hz, 2H), 7.28 (s, 1H), 7.25 (s, 2H), 6.95 (t, J = 8.6 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 2.48 (s, 3H), 2.42 (s, 3H); [13]C NMR (150 MHz, $CDCl_3$) δ 163.0 (d, J= 244.5 Hz), 143.4, 141.3, 139.4, 137.8, 136.5, 131.2, 130.6, 130.1, 129.77, 129.71 (d, J= 7.4 Hz) , 129.5, 129.0, 128.3, 127.9, 126.2, 122.9, 122.2, 121.1, 115.0, 114.9, 112.3, 21.6, 21.4; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{27}H_{21}FN_2Na$, 415.1586; found 415.1601.

2-(4-chlorophenyl)-6-methyl-3,8-diphenylimidazo[1,2-a]pyridine (6k)



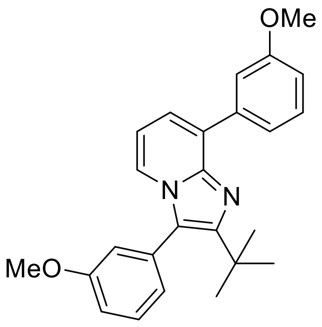
Yield (71.1 mg, 72% yield, yellow solid, mp= 238-240 ℃), eluent: 5% ethylacetate/hexane; [1]H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 7.7 Hz, 2H), 7.68 (s, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.57 (t, J = 7.1 Hz, 2H), 7.55 – 7.51 (m, 3H), 7.47 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 7.7 Hz, 3H), 2.32 (s, 3H); [13]C NMR (150 MHz, $CDCl_3$) δ 142.5, 141.1, 136.4, 133.0, 132.9, 130.8, 130.1, 129.6, 129.3, 129.2, 129.0, 128.4, 128.3, 128.2, 126.39, 126.32, 122.0, 121.1, 119.9, 18.4; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{26}H_{19}ClN_2Na$, 417.1134; found 417.1111.

2-(4-chlorophenyl)-7-methyl-3,8-diphenylimidazo[1,2-a]pyridine (6l)



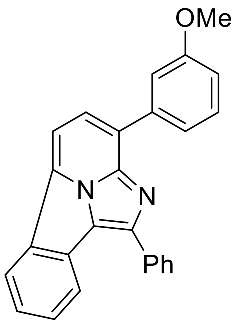
Yield (73.0 mg, 74% yield, yellow semi-solid), eluent: 5% ethylacetate/hexane; [1]H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 6.8 Hz, 2H), 8.11 (d, J = 8.5 Hz, 4H), 7.58 – 7.48 (m, 9H), 7.45 (d, J = 6.8 Hz, 3H), 7.31 (d, J = 8.0 Hz, 5H), 7.23 (dd, J = 14.5, 7.2 Hz, 5H), 7.17 – 7.12 (m, 3H), 7.02 (d, J = 7.5 Hz, 4H), 6.81 (d, J = 6.8 Hz, 2H), 2.30 (s, 7H).; [13]C NMR (150 MHz, $CDCl_3$) δ 150.2, 147.1, 137.4, 135.3, 135.0, 134.3, 134.1, 132.1, 130.04, 129.6, 129.4, 129.1, 128.3, 128.2, 127.8, 125.4, 122.3, 116.7, 105.7, 19.75; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{26}H_{19}ClN_2Na$, 417.1134; found 417.1111.

2-(tert-butyl)-3,8-bis(3-methoxyphenyl)imidazo[1,2-a]pyridine (6m)



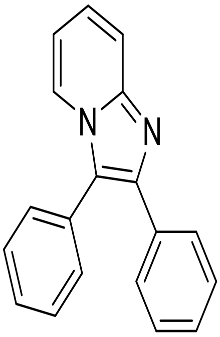
Yield (75.9 mg, 79% yield, greenish liquid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 1H), 7.55 – 7.48 (m, 1H), 7.32 (t, J = 3.9 Hz, 2H), 7.22 (s, 1H), 7.12 – 7.00 (m, 2H), 6.92 – 6.75 (m, 3H), 6.58 (d, J = 7.3 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 159.3, 156.9, 143.9, 138.0, 136.7, 136.2, 130.1, 129.0, 127.5, 122.3, 120.8, 120.4, 114.8, 114.4, 114.3, 113.8, 112.0, 105.3, 55.3, 55.1, 32.4, 30.2; HRMS-ESI (m/z) [M+Na]+calcd. For $C_{25}H_{26}N_2O_2Na$, 409.1892; found 409.1866.

3-(3-methoxyphenyl)-1-phenylbenzo[a]imidazo[5,1,2-cd]indolizine (6n)



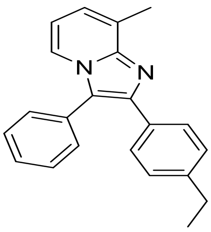
Yield (52.6 mg, 56% yield, green solid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, J = 7.8 Hz, 3H), 8.40 (d, J = 7.9 Hz, 1H), 8.21 – 8.16 (m, 2H), 8.10 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.63 (dd, J = 14.4, 7.3 Hz, 3H), 7.53 – 7.48 (m, 2H), 7.03 (dd, J = 8.1, 2.3 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 134.8, 131.2, 129.8, 128.9, 128.4, 126.4, 124.8, 124.1, 122.9, 121.6, 120.9, 115.0, 114.3, 109.2, 55.4; HRMS-ESI (m/z) [M+H]+calcd. For $C_{26}H_{19}N_2O$, 375.1497; found 375.1485.

8-(3-methoxyphenyl)-2,3-diphenylimidazo[1,2-a]pyridine (6p)



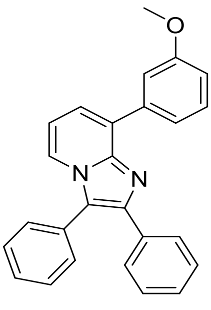
Yield (55.5 mg, 59 % yield, yellow semi solid), 5% ethylacetate/hexane; ^{1}H NMR (500 MHz, $CDCl_3$) 1H NMR (500 MHz, CDCl3) δ 7.84 (dd, J = 12.8, 4.3 Hz, 2H), 7.63 (dd, J = 13.1, 6.0 Hz, 3H), 7.49 – 7.43 (m, 2H), 7.41 (dd, J = 10.6, 4.4 Hz, 3H), 7.34 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 7.0 Hz, 1H), 7.16 (dd, J = 14.3, 7.1 Hz, 3H), 6.91 (dd, J = 8.2, 2.0 Hz, 1H), 6.72 (t, J = 6.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 143.3, 142.3, 137.8, 134.3, 130.8, 130.1, 129.7, 129.5, 129.3, 128.8, 128.1, 128.0, 127.3, 122.9, 122.3, 121.37, 121.30, 114.6, 114.2, 112.3, 55.3.

2,3-diphenylimidazo[1,2-a]pyridine (7)[5]



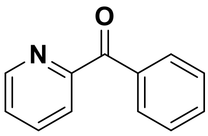
Yield (75.9 mg, 79% yield, brown liquid), eluent: 20% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 6.9 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.54 (t, J = 7.0 Hz, 2H), 7.52 – 7.49 (m, 1H), 7.48 (t, J = 5.6 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.19 (m, 1H), 6.75 (t, J = 6.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 142.3, 134.0, 130.7, 129.8, 129.5, 128.8, 128.2, 128.0, 127.4, 124.6, 123.2, 117.5, 112.2.

2-(4-ethylphenyl)-8-methyl-3-phenylimidazo[1,2-a]pyridine (9)



Yield (74.4 mg, 95% yield, brown liquid), eluent: 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 6.9 Hz, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.49 (q, J = 8.0 Hz, 2H), 7.44 (t, J = 7.0 Hz, 3H), 7.11 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 6.8 Hz, 1H), 6.62 (t, J = 6.8 Hz, 1H), 2.69 (s, 3H), 2.65 – 2.59 (m, 2H), 1.21 (t, J= 7.5Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.1, 143.3, 142.1, 131.8, 130.7, 130.3, 129.3, 128.5, 128.1, 127.7, 127.3, 123.1, 121.0, 112.0, 28.5, 17.1, 15.3.

phenyl(pyridin-2-yl)methanone (11)[6]



Yield (14.0 mg, 31 % yield, white solid, mp= 42-44 ℃), 5% ethylacetate/hexane; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 4.3 Hz, 1H), 8.07 (d, J = 7.7 Hz, 2H), 8.03 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 7.58 (t, J = 7.3 Hz, 1H), 7.47 (dd, J = 14.2, 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 154.9, 148.4, 136.9, 136.1, 132.7, 130.8, 128.0, 126.0, 124.4.

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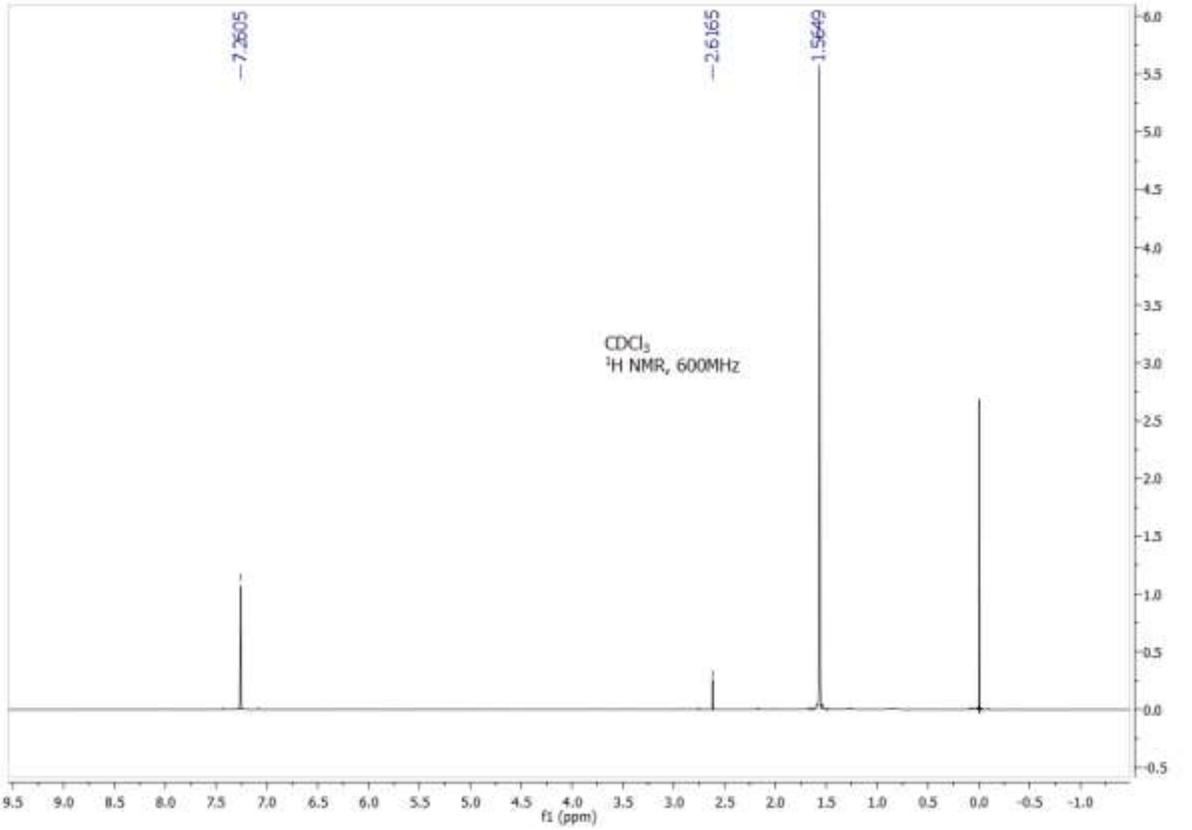
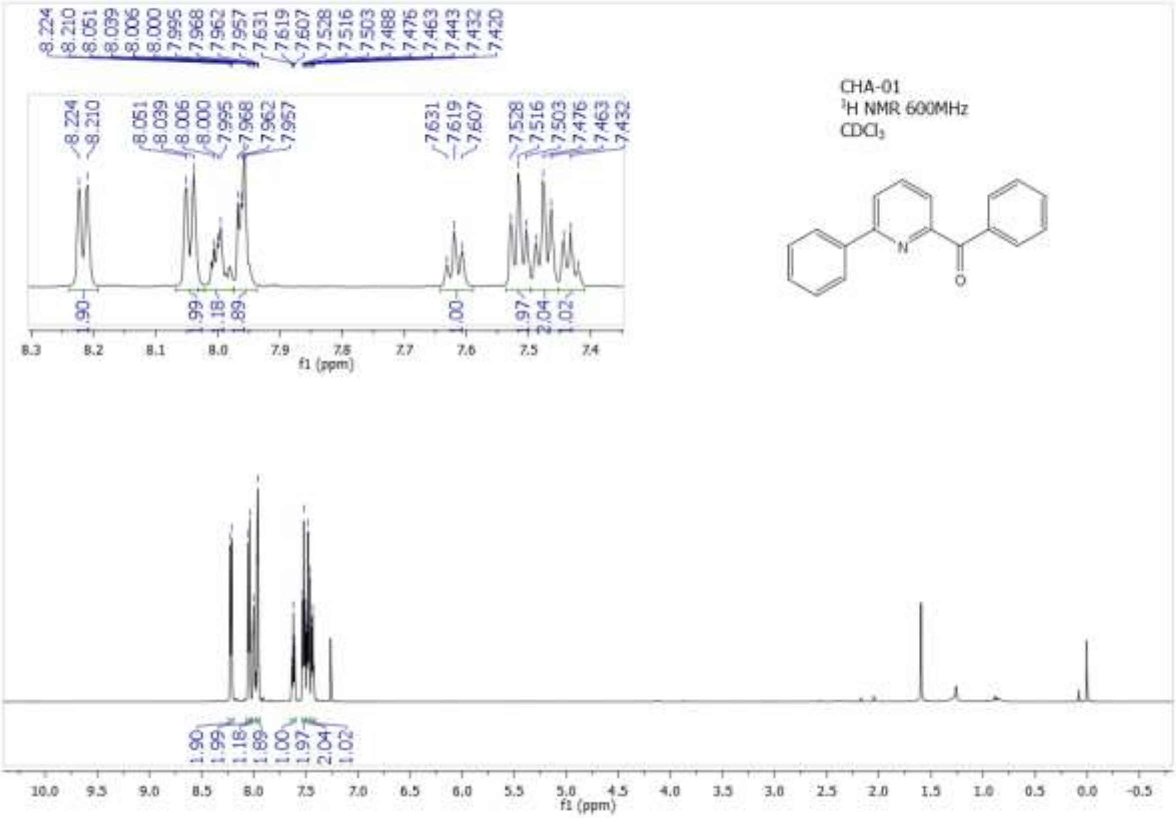
6. A. Joshi, R. Kumar, R. Semwal, D. Rawat, S. Adimurthy. *Green Chem.* 2019, **21**, 962.

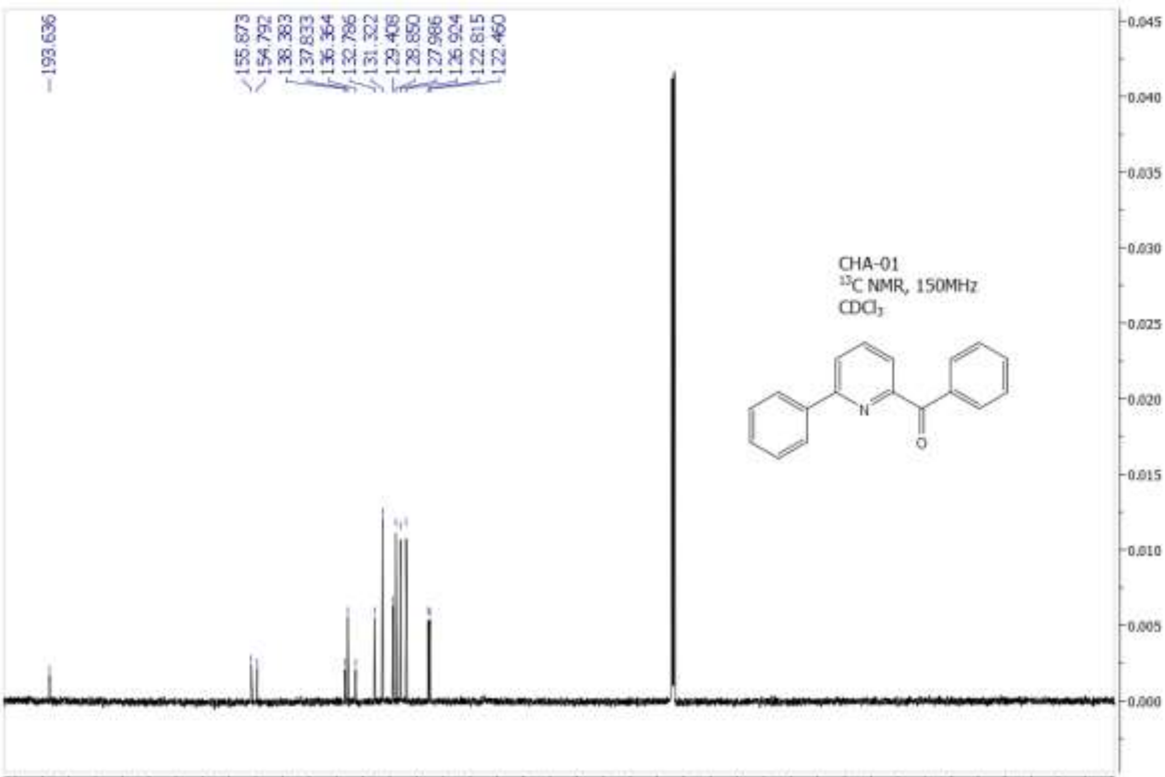
Copies of ^{1}H & ^{13}C NMR



^{1}H NMR of **$CDCl_3$**



[1]H NMR of **3a**



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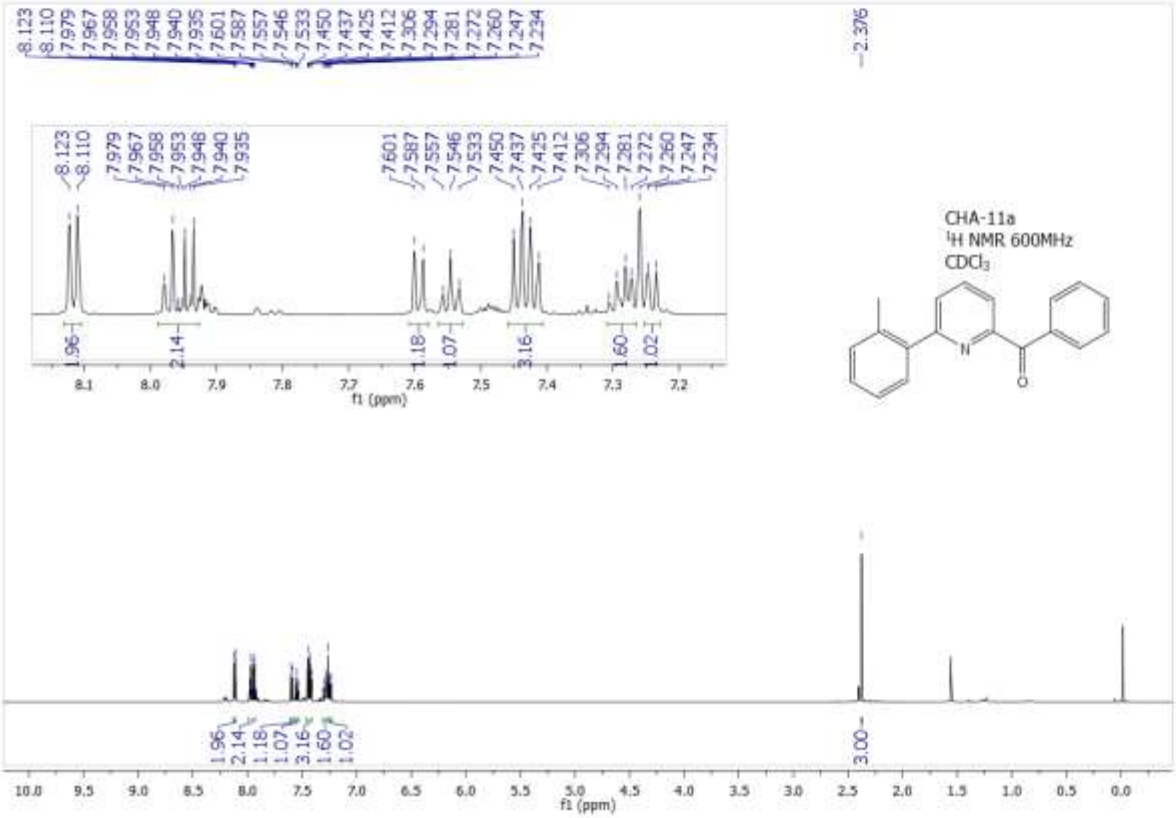

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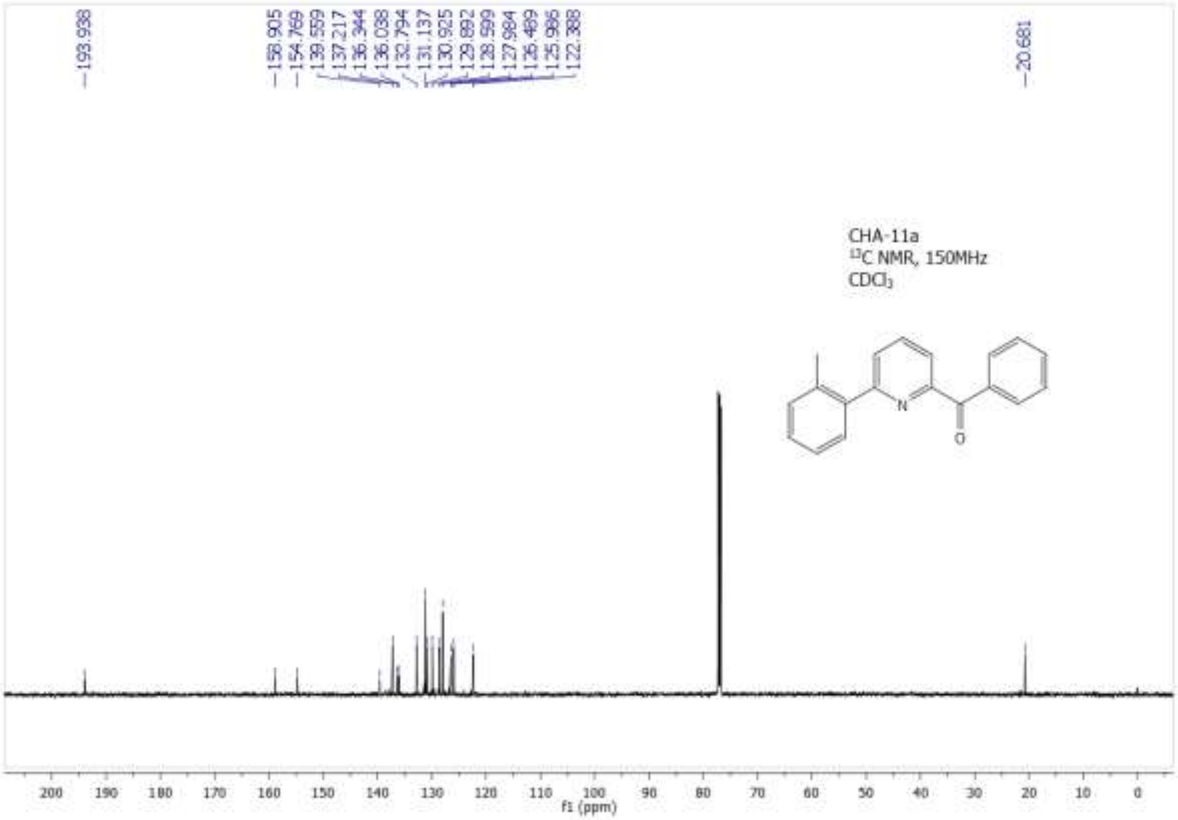

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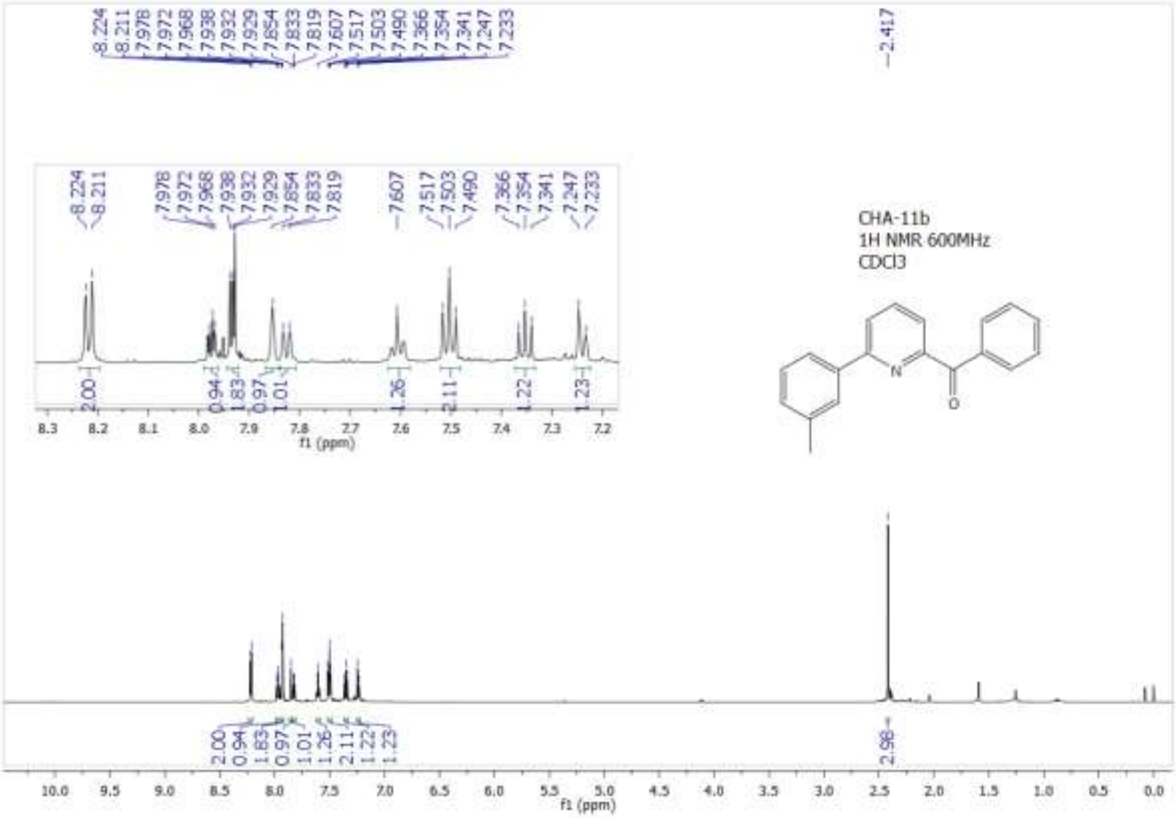

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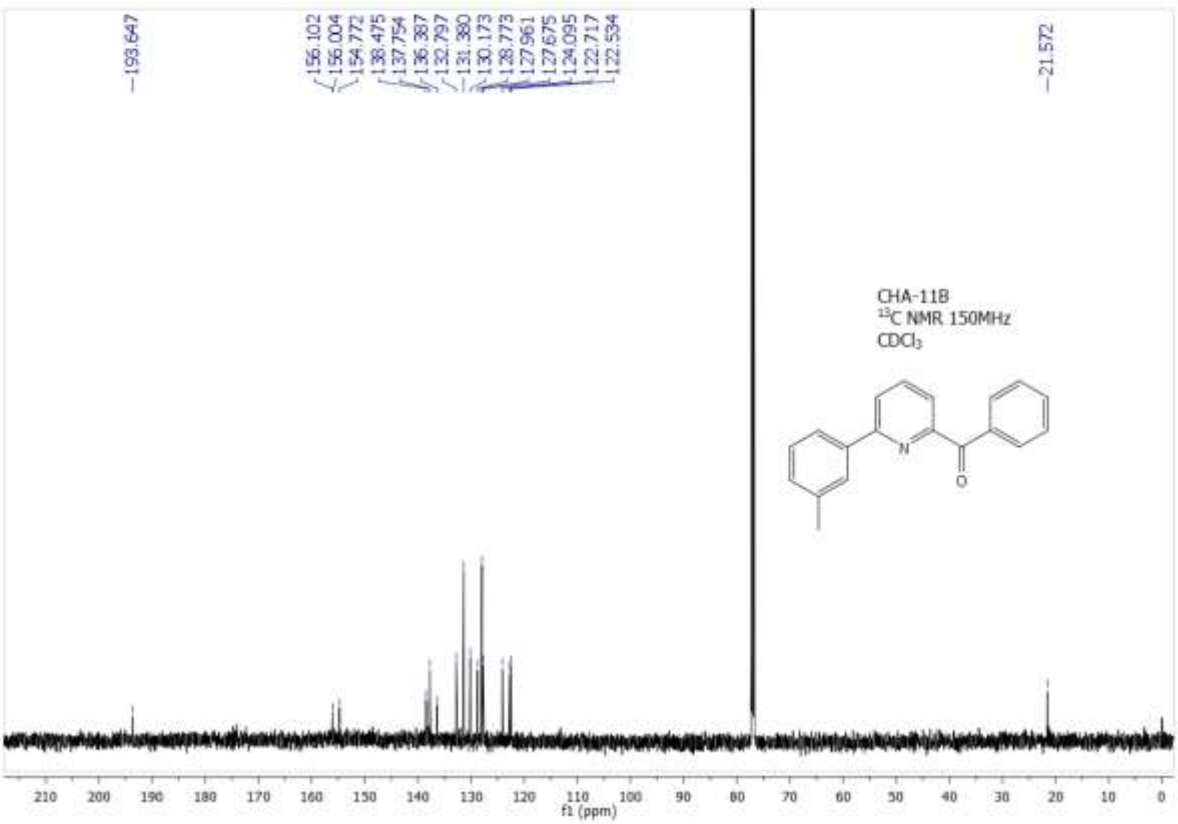

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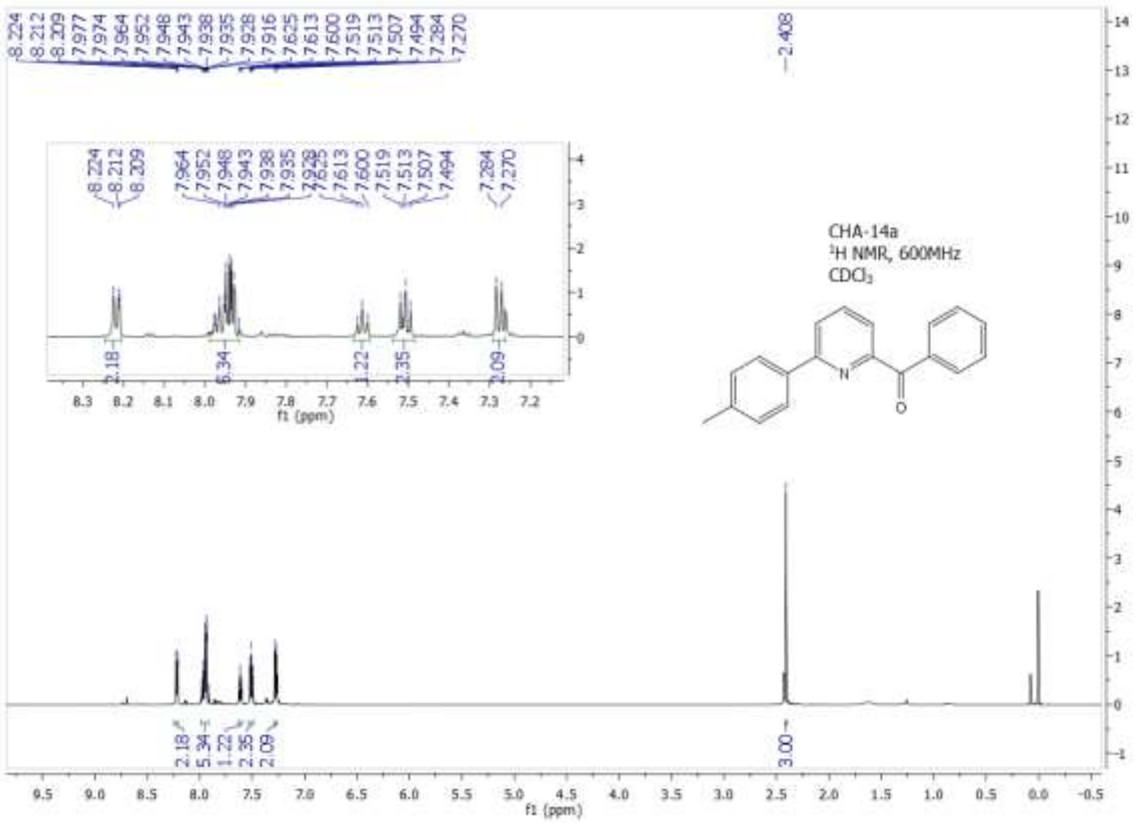

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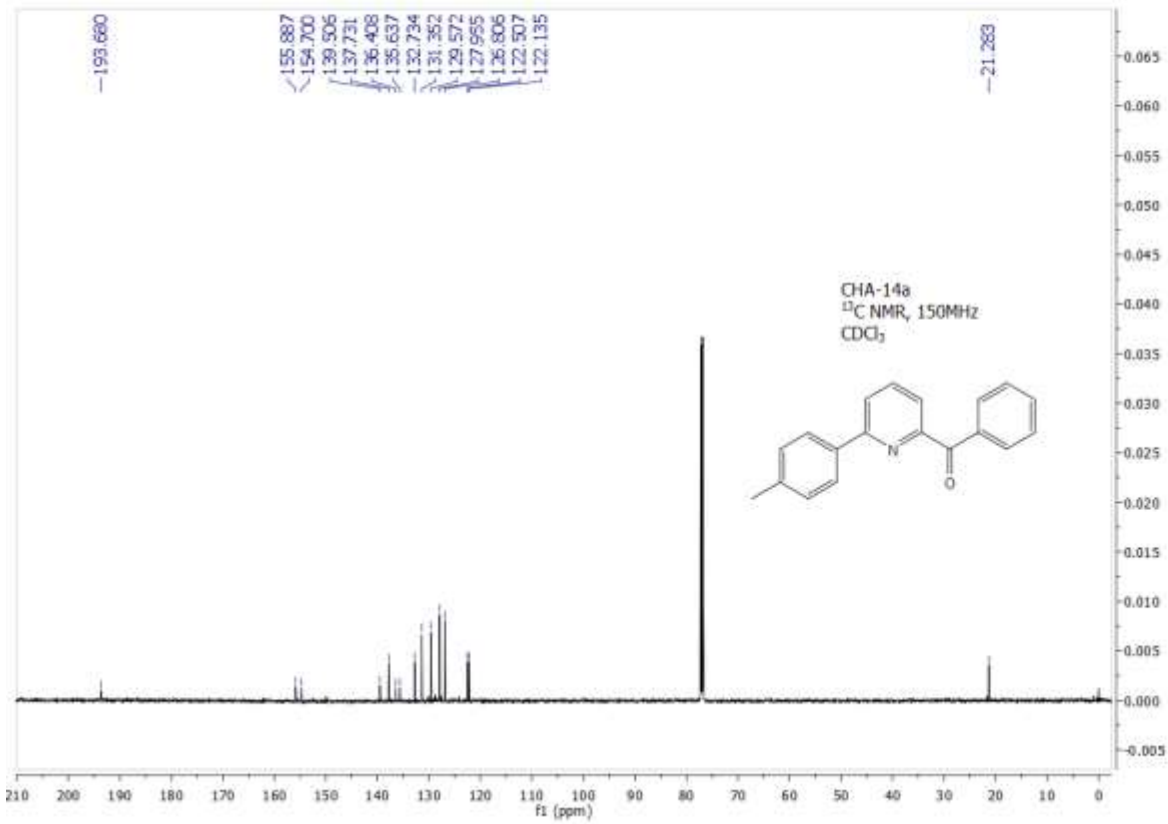

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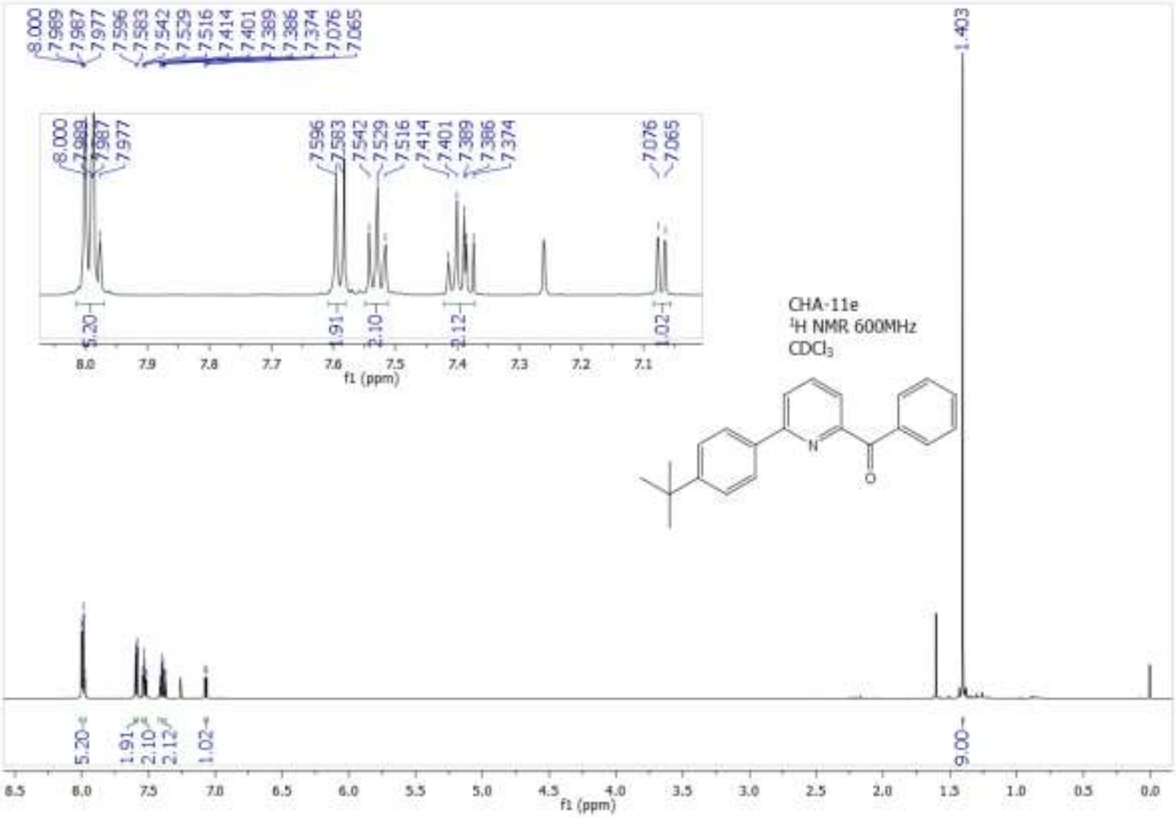

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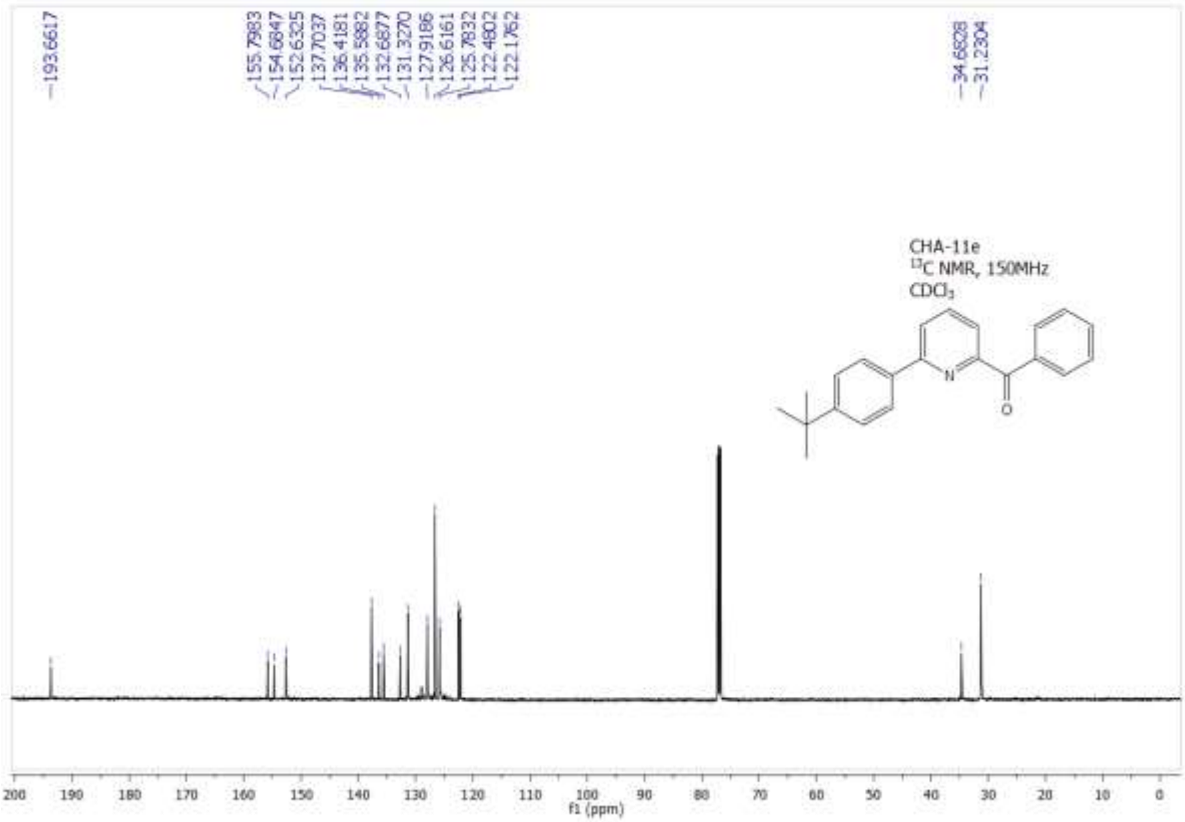

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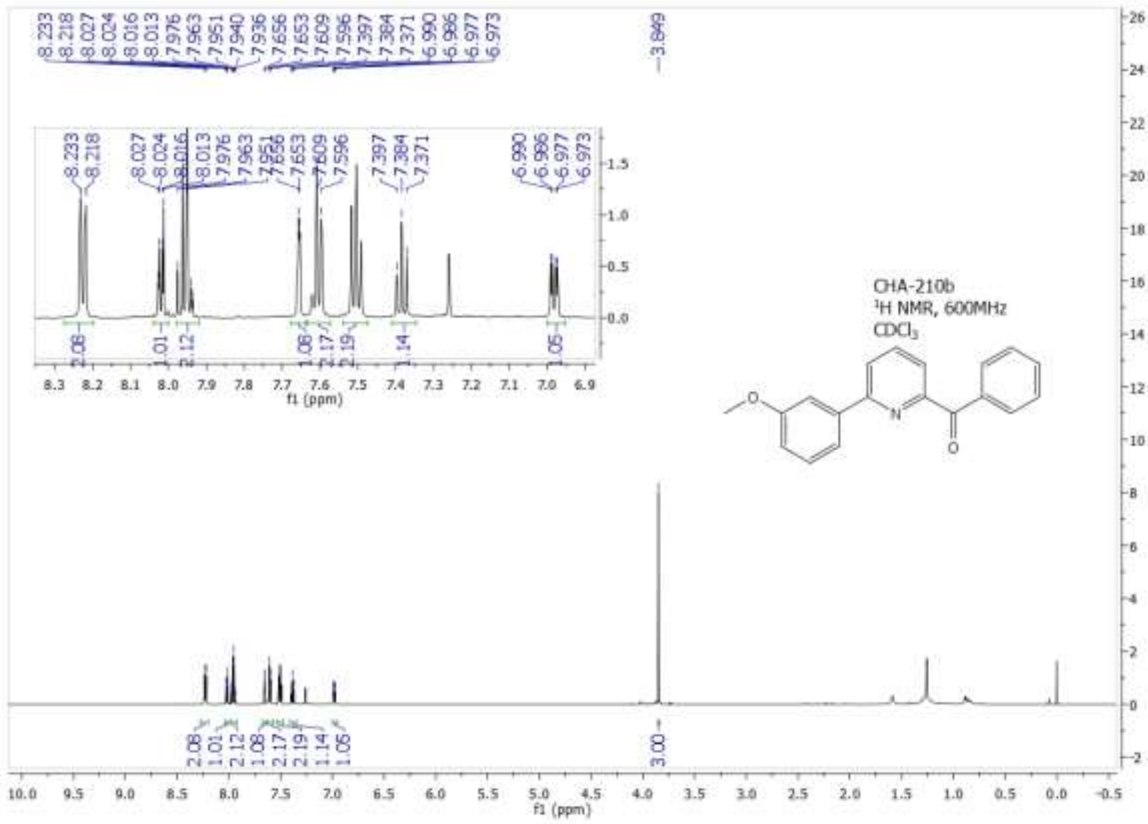

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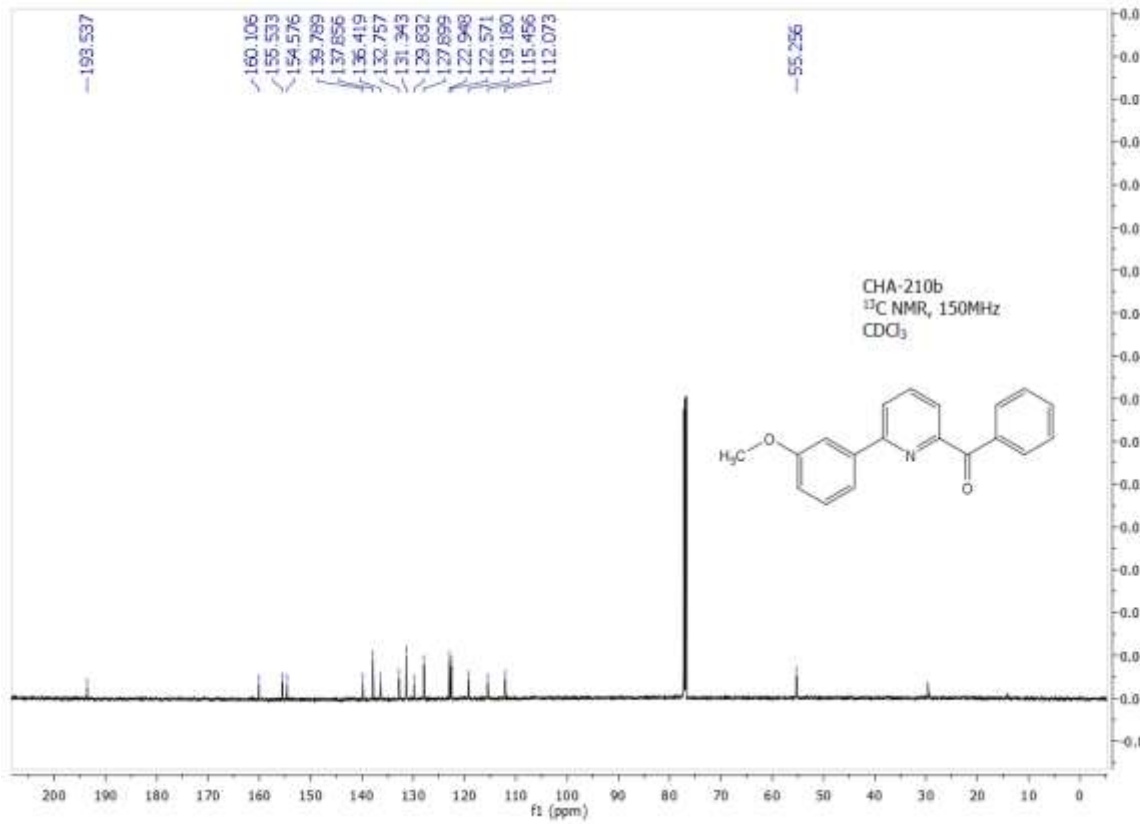

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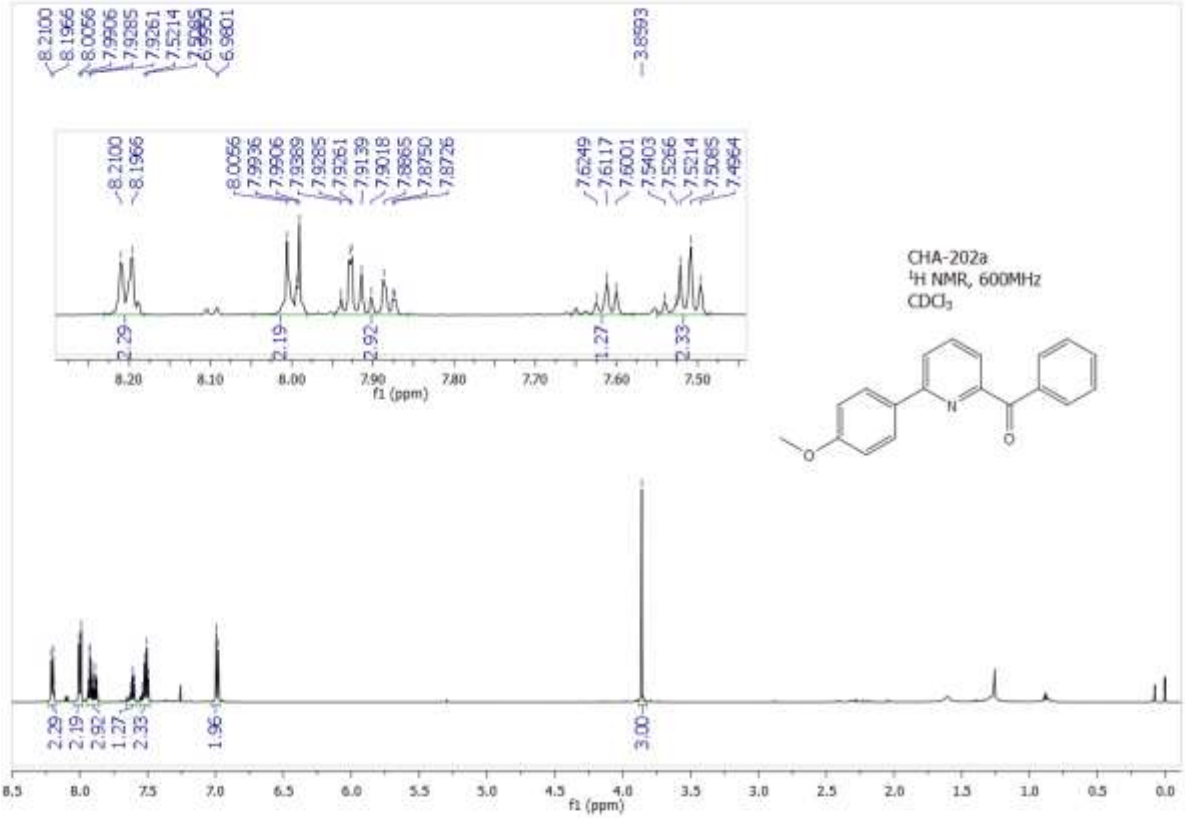

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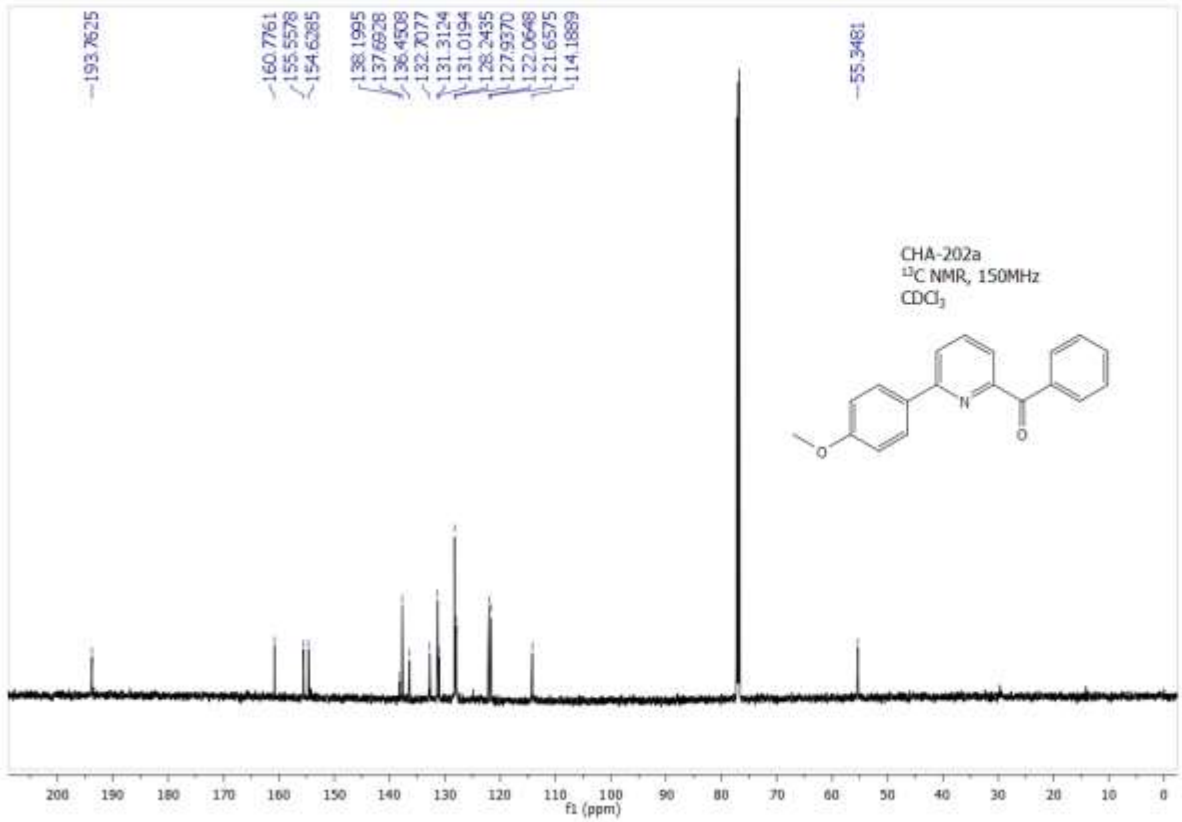

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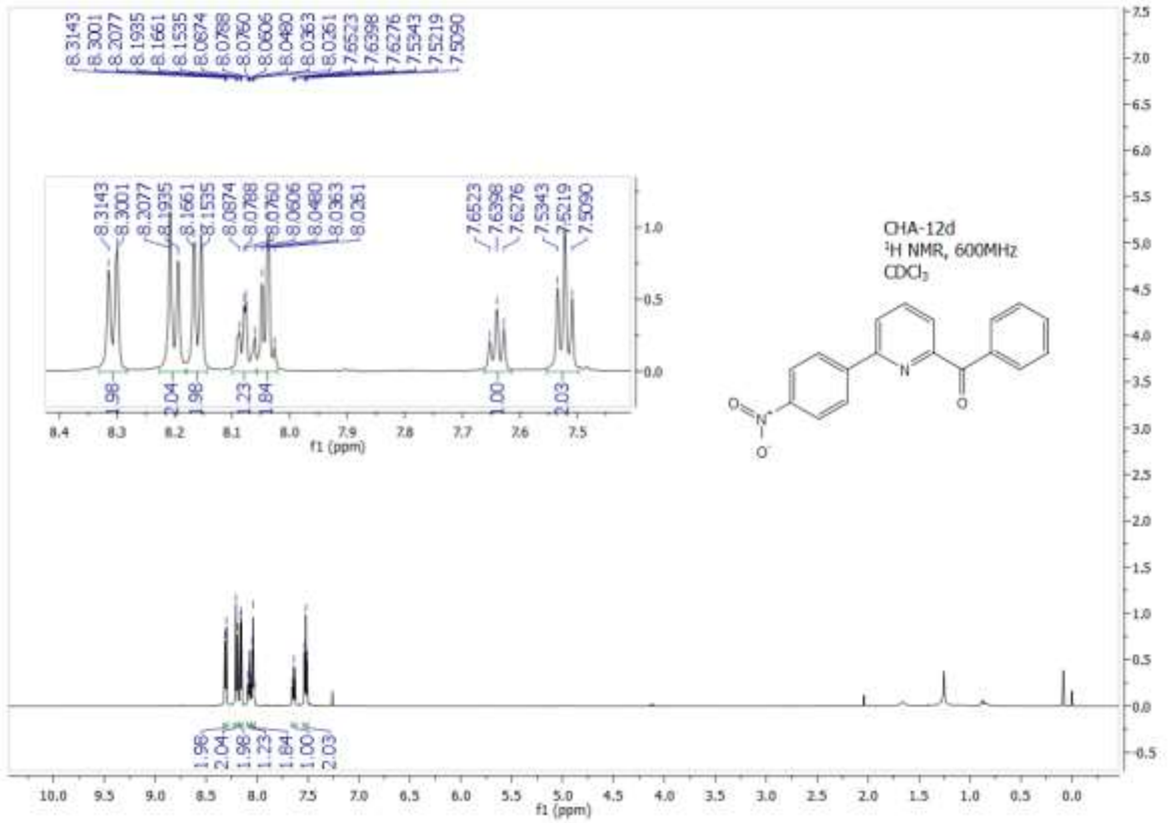

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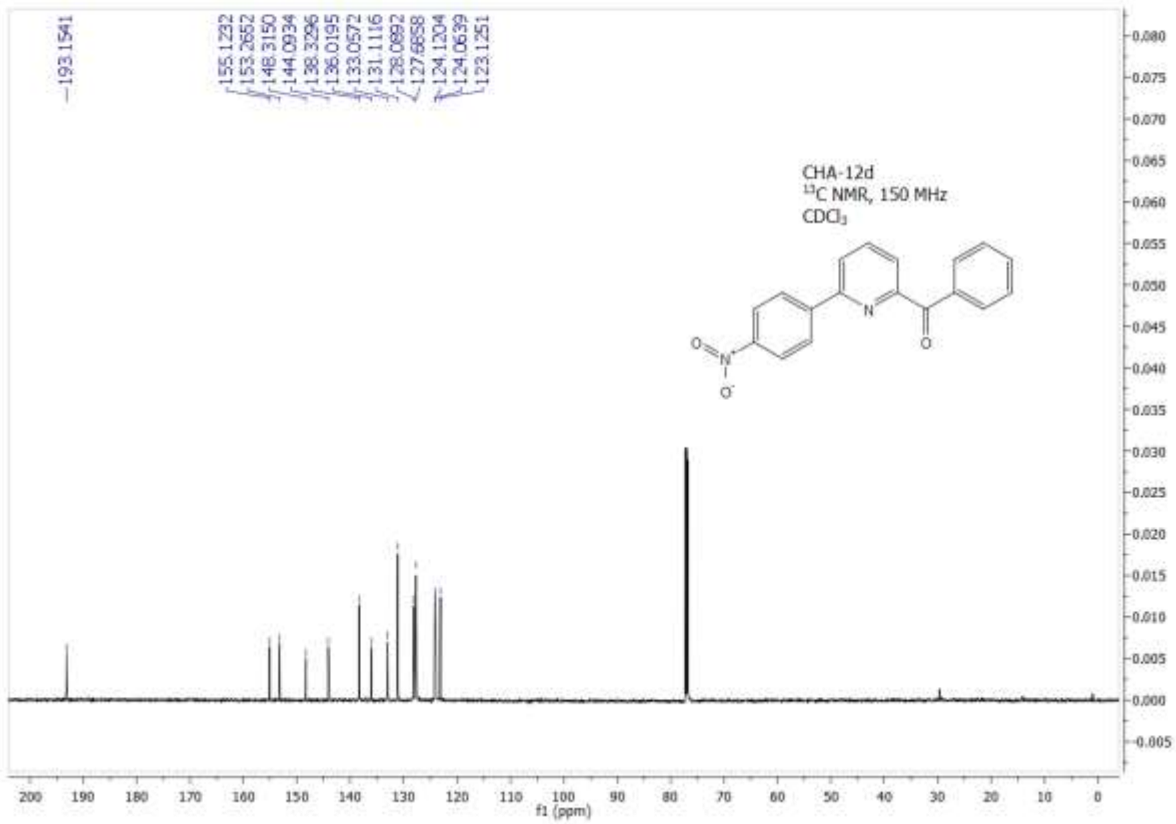

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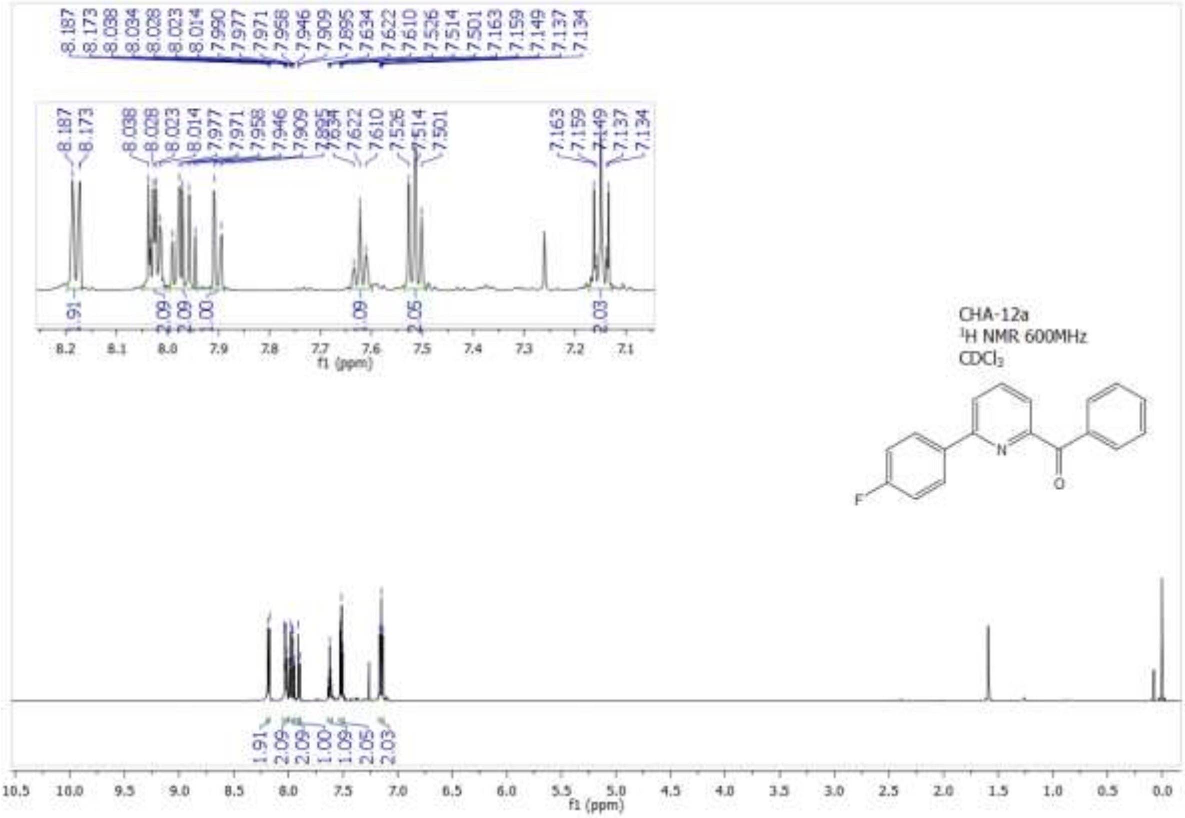

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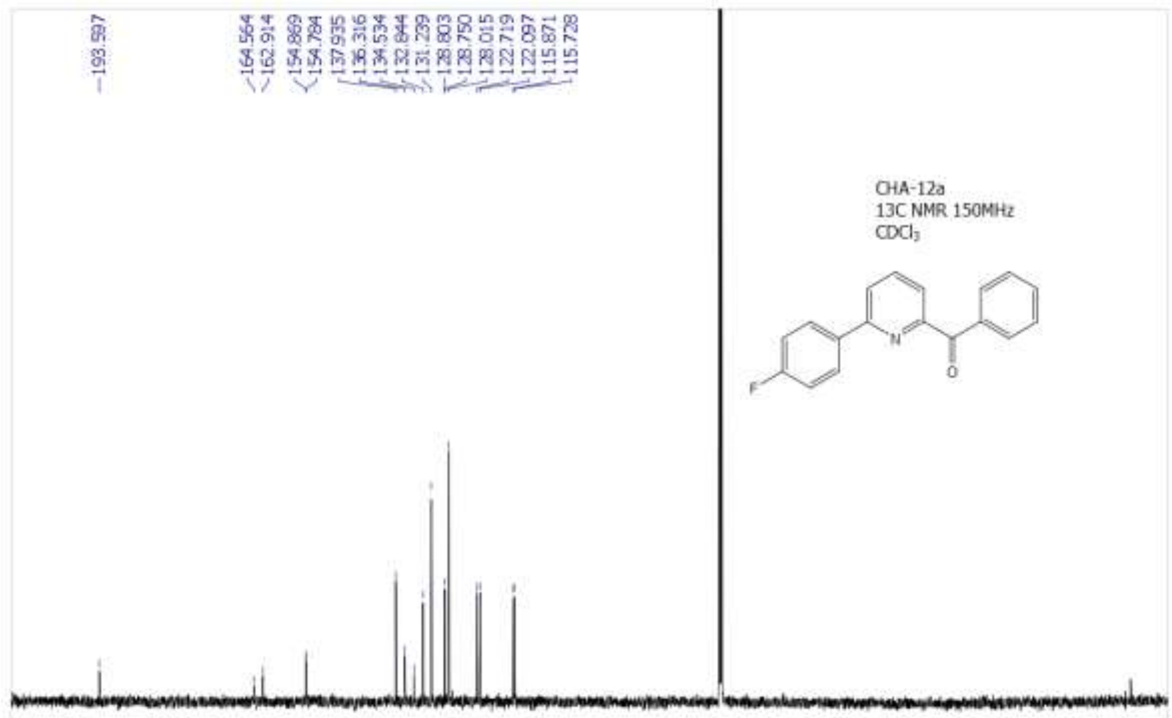

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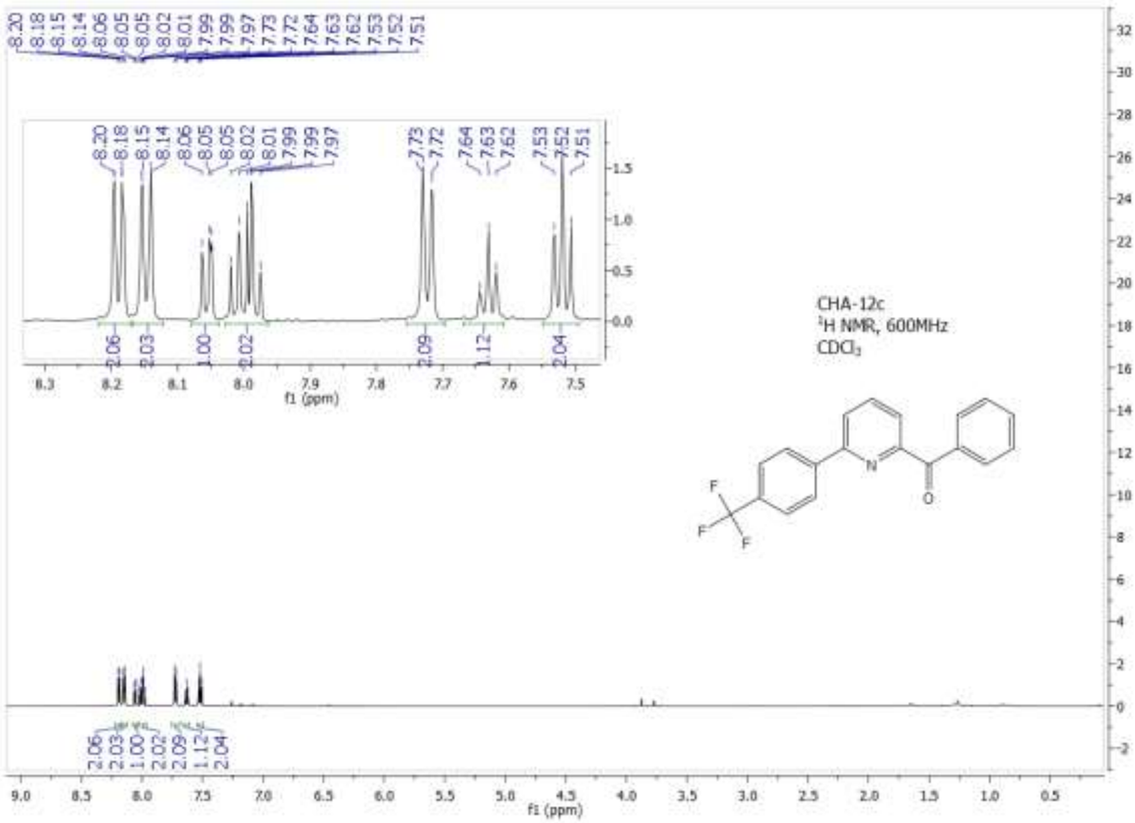

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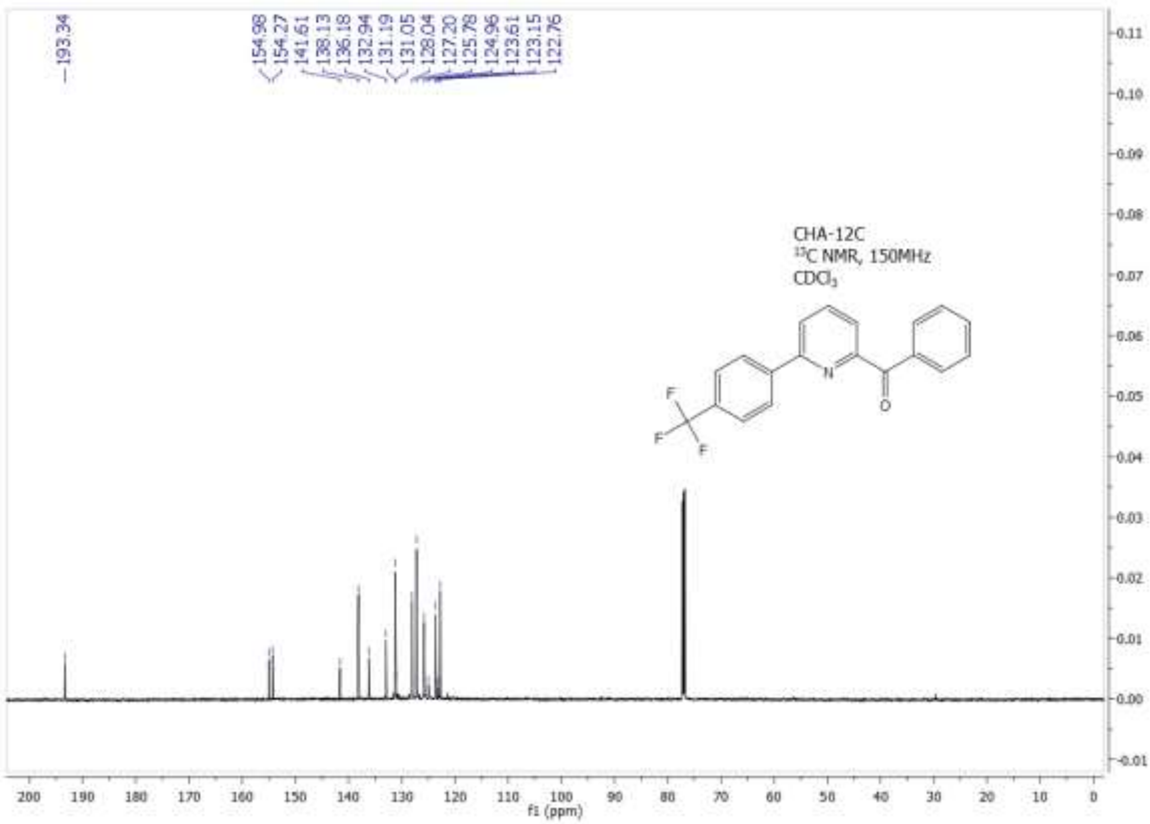

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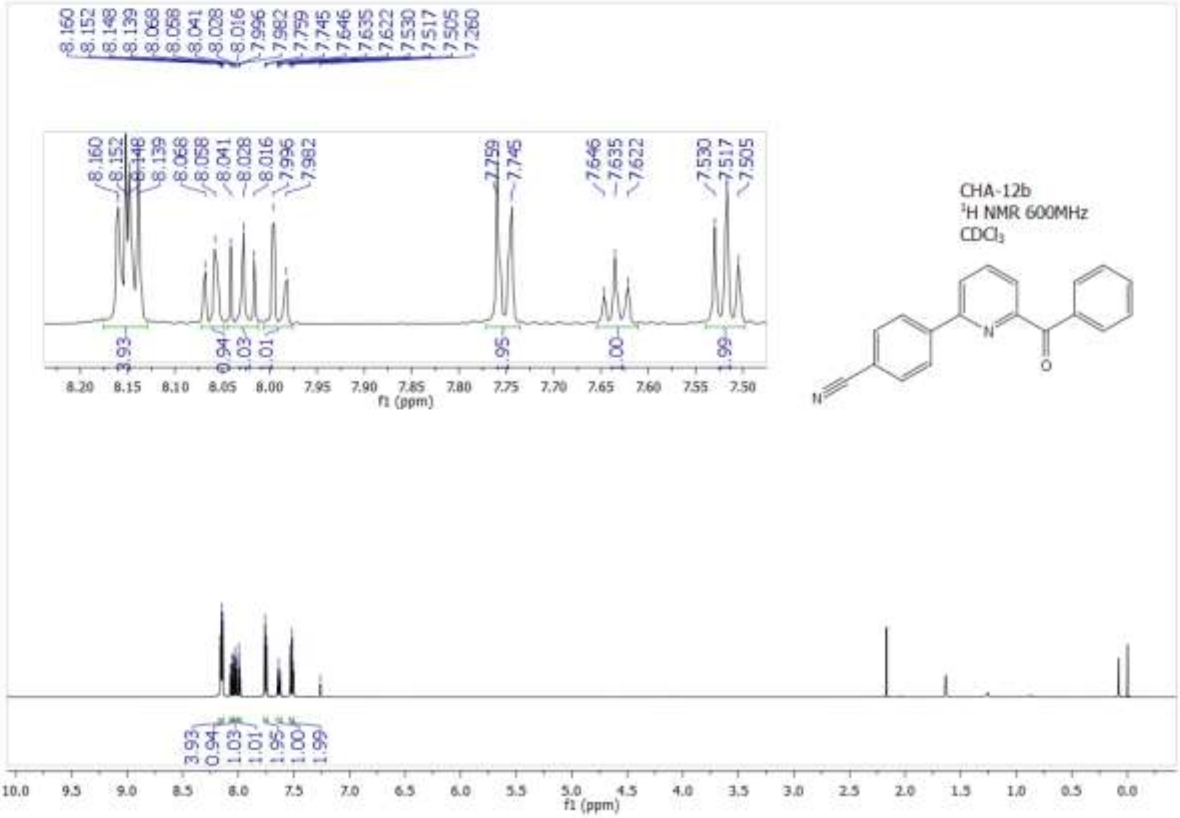

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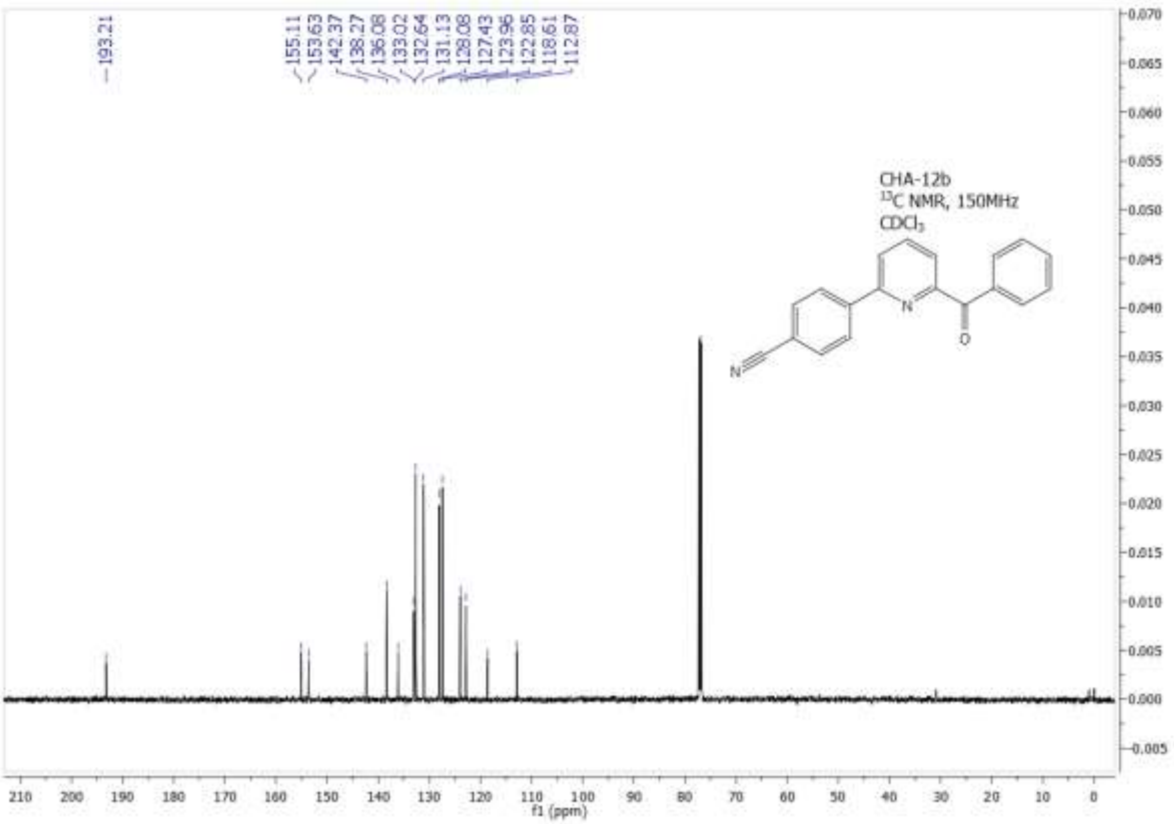

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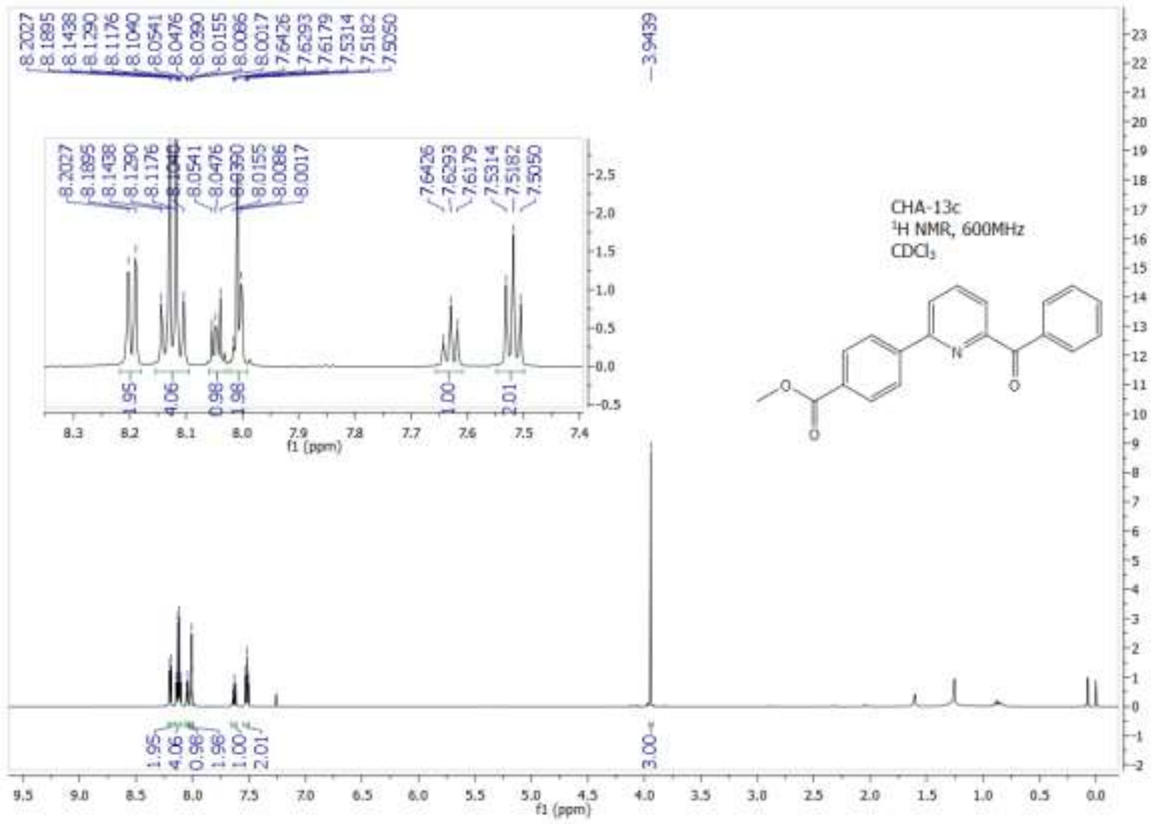

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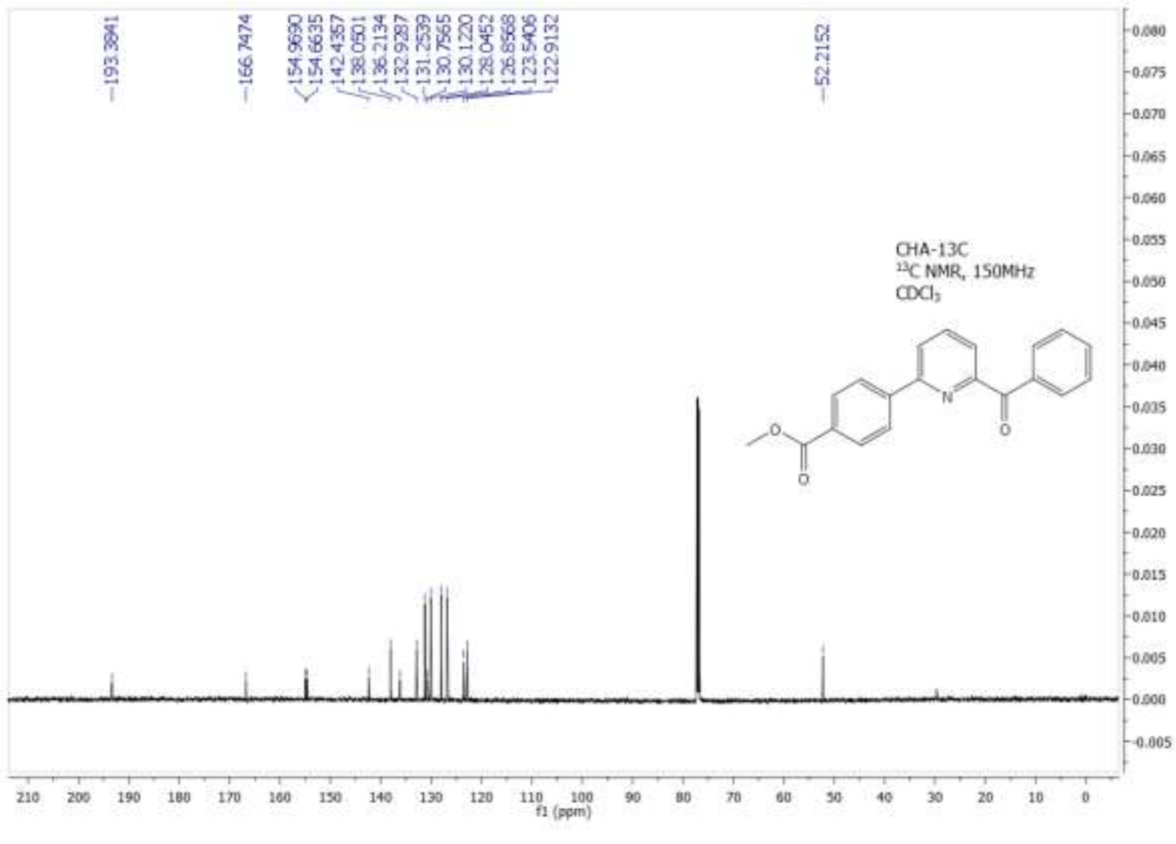

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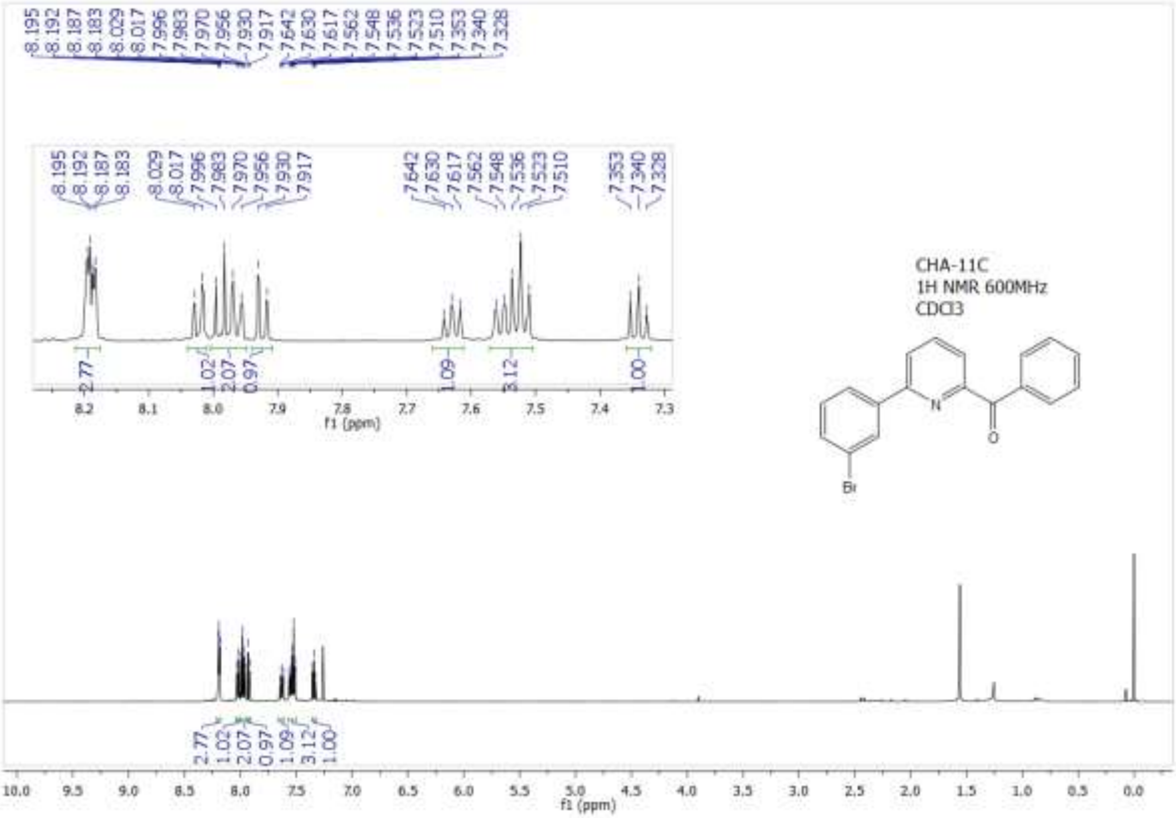

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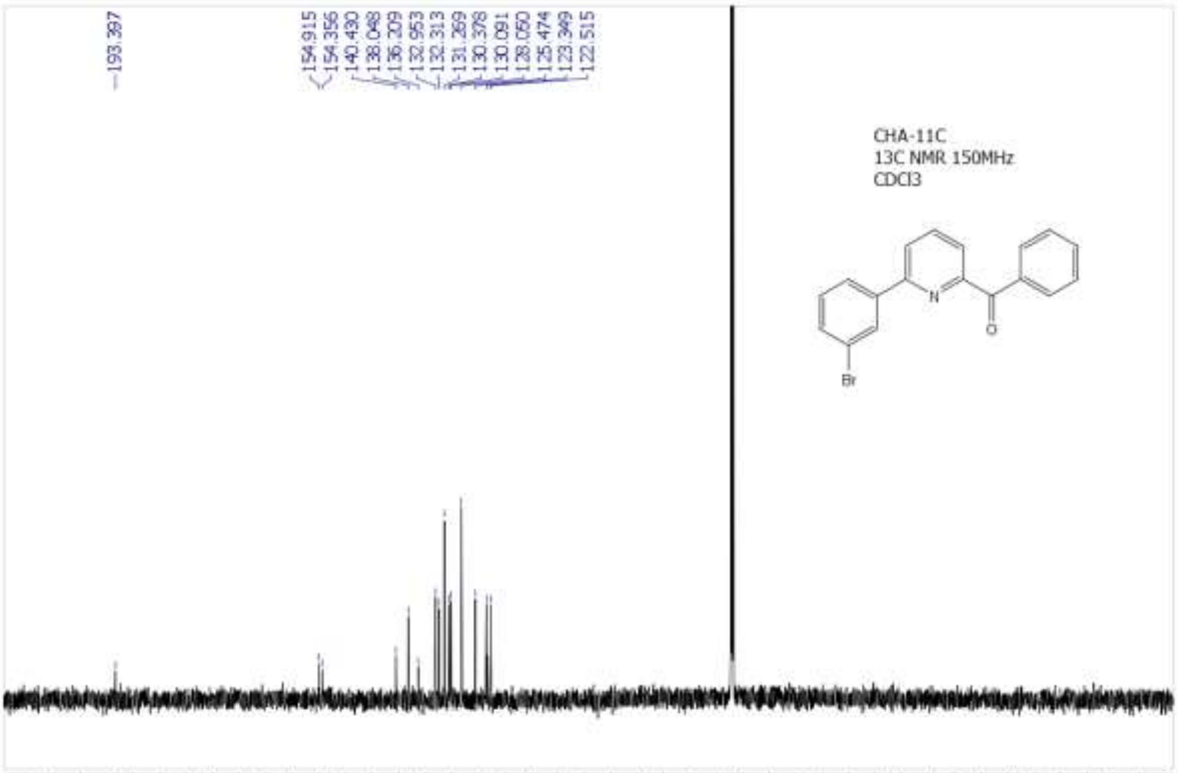

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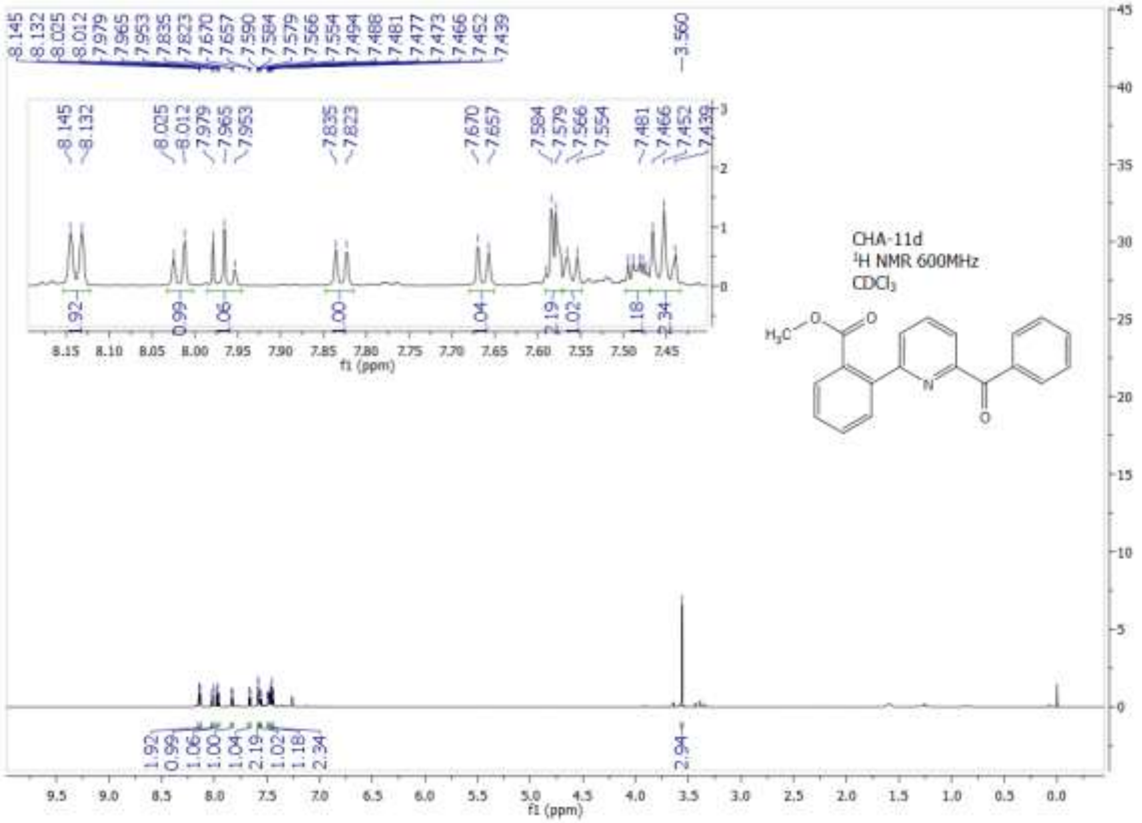

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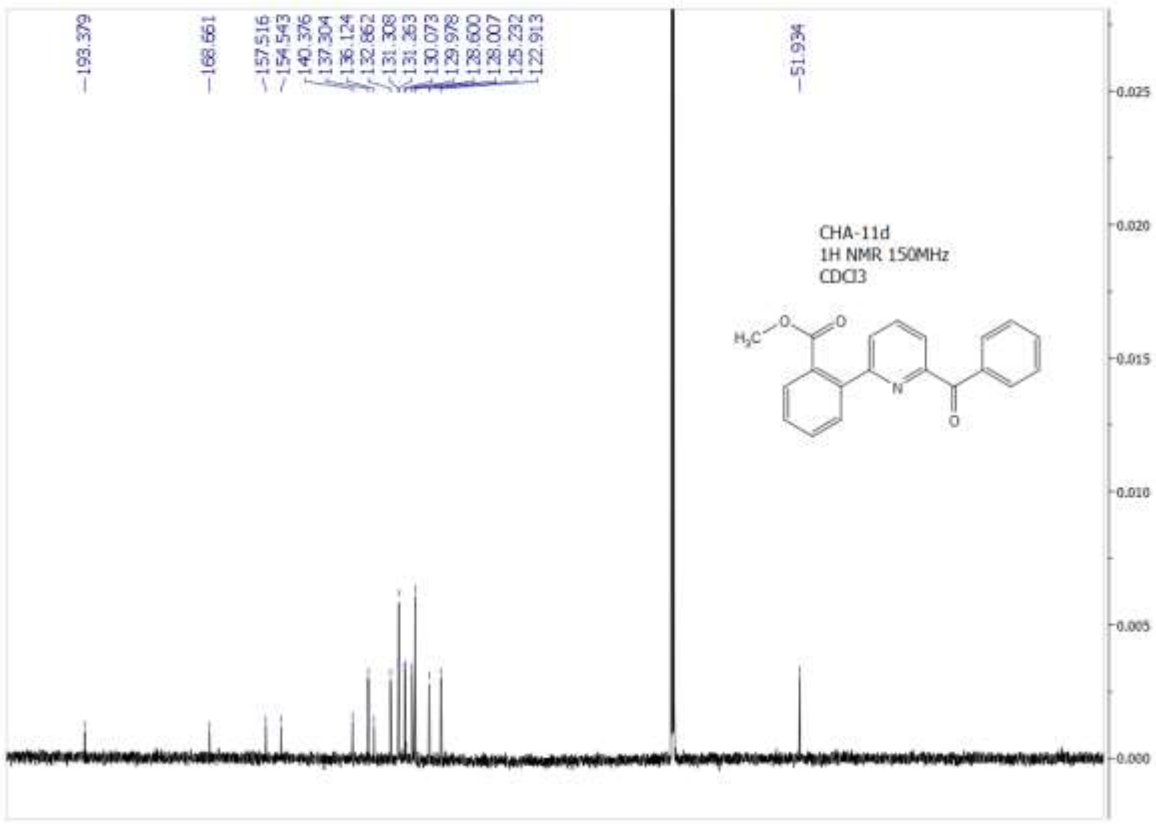

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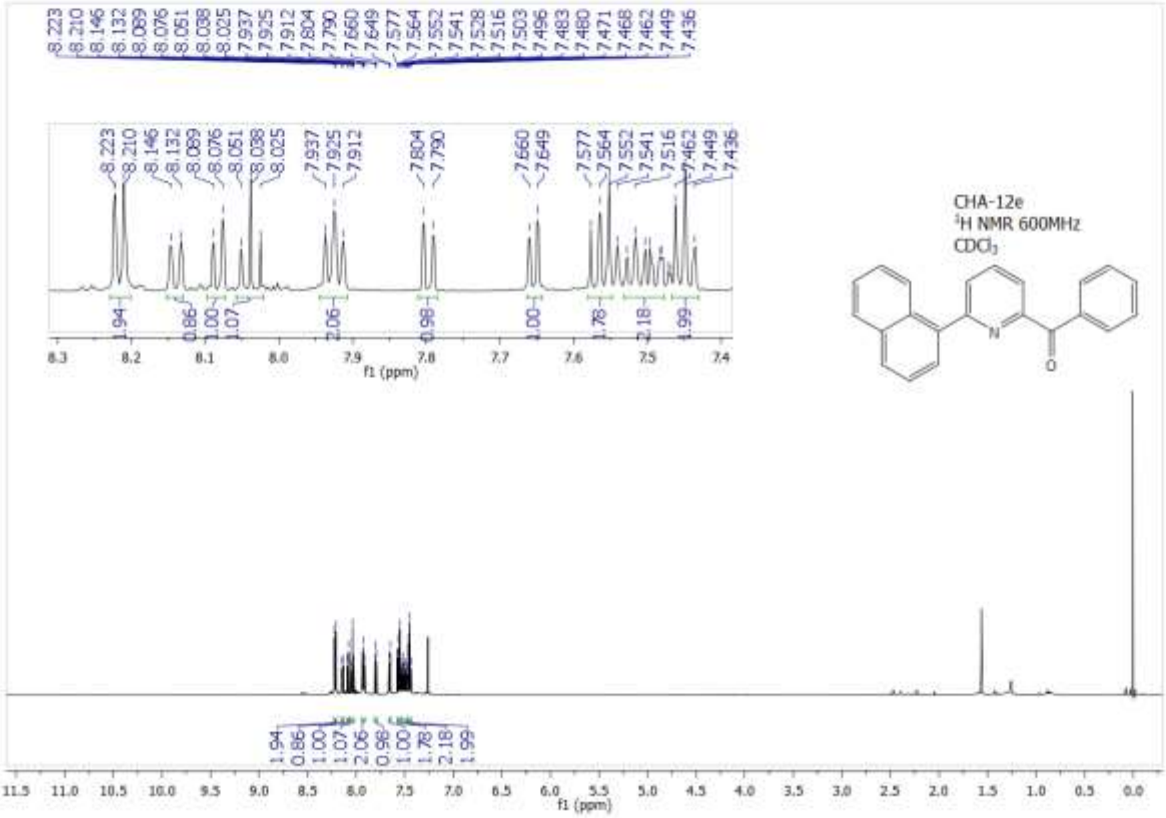

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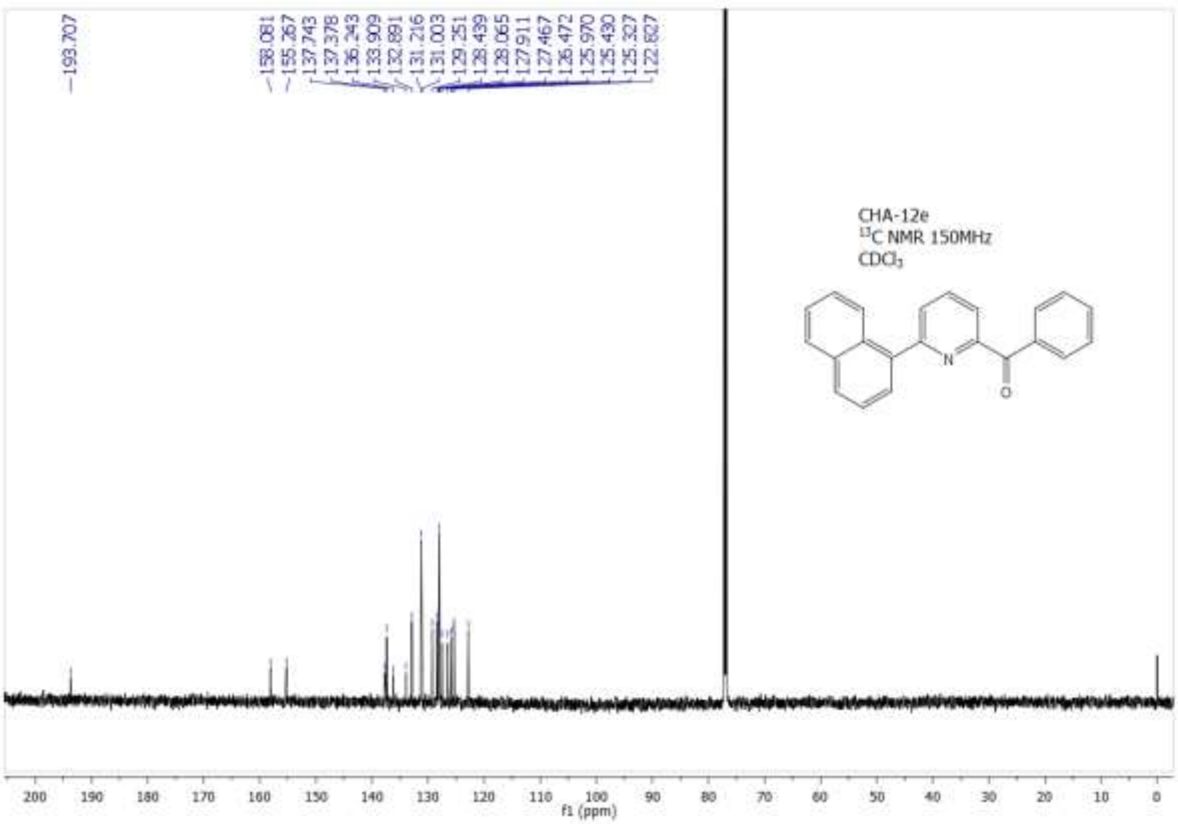

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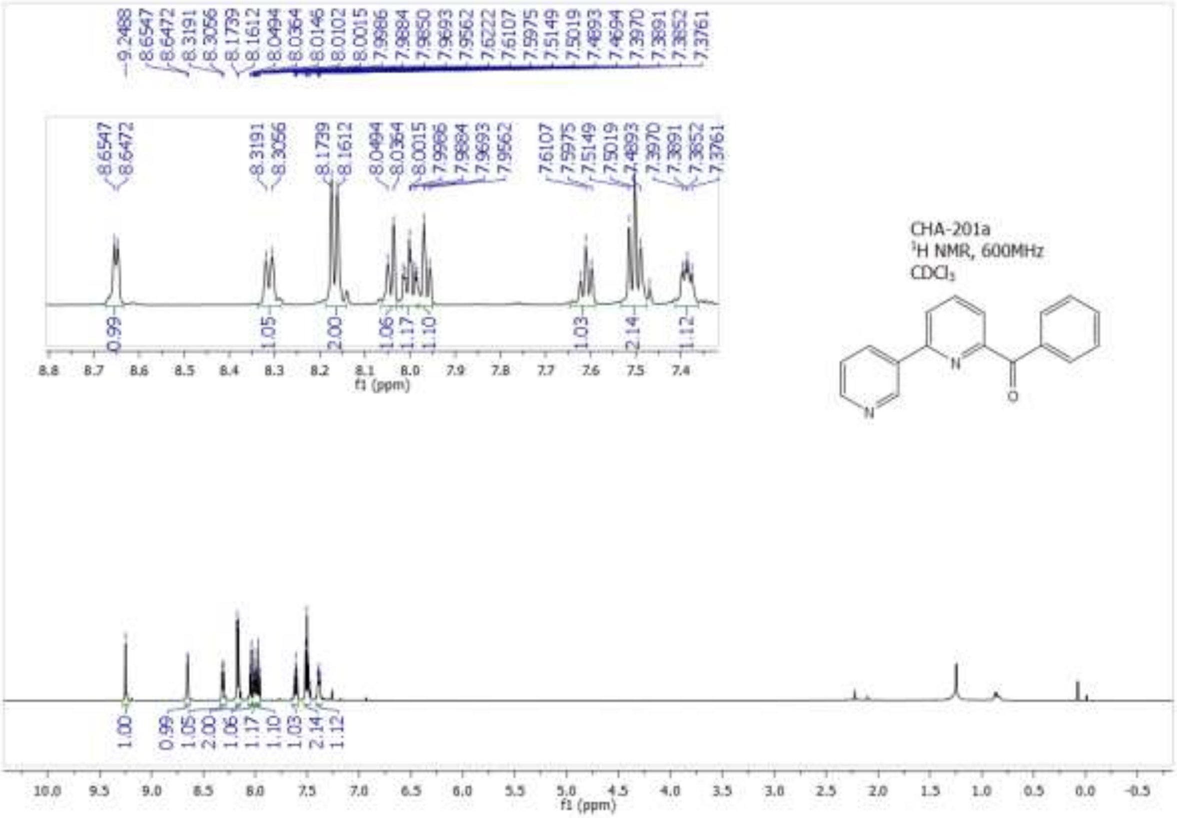

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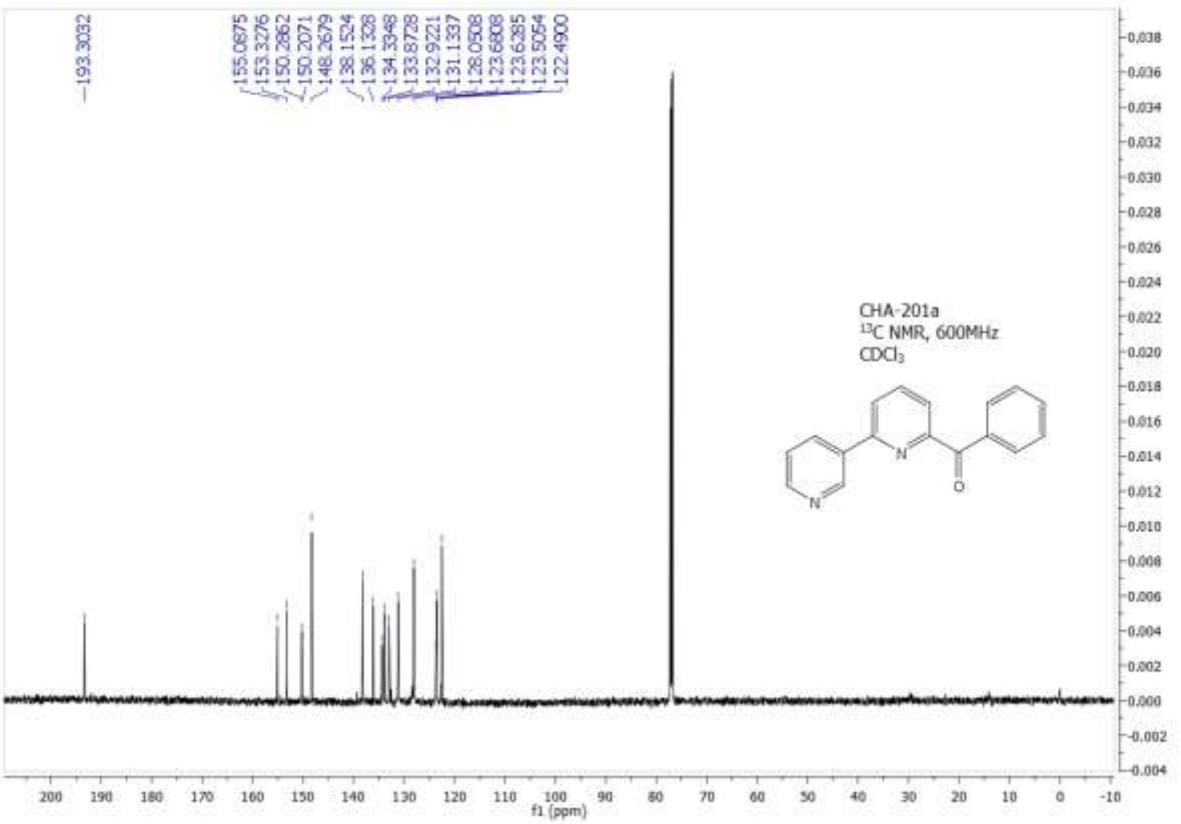

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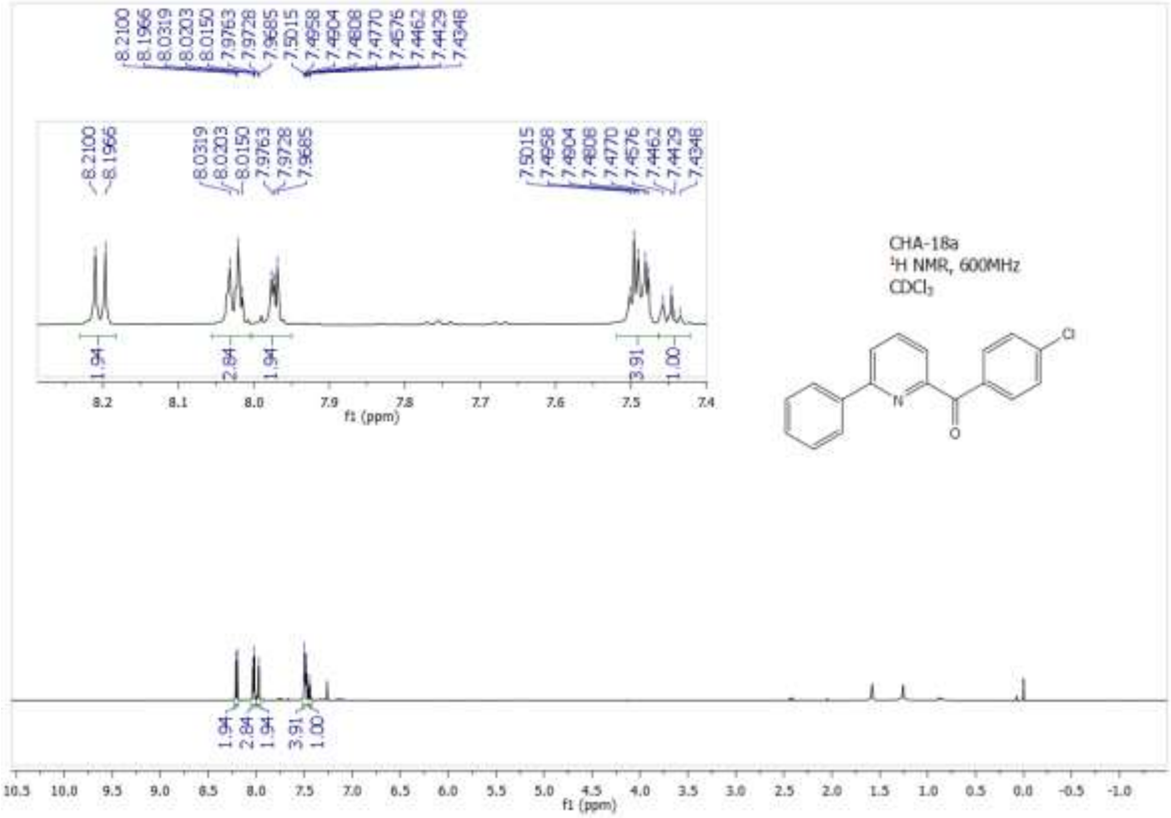

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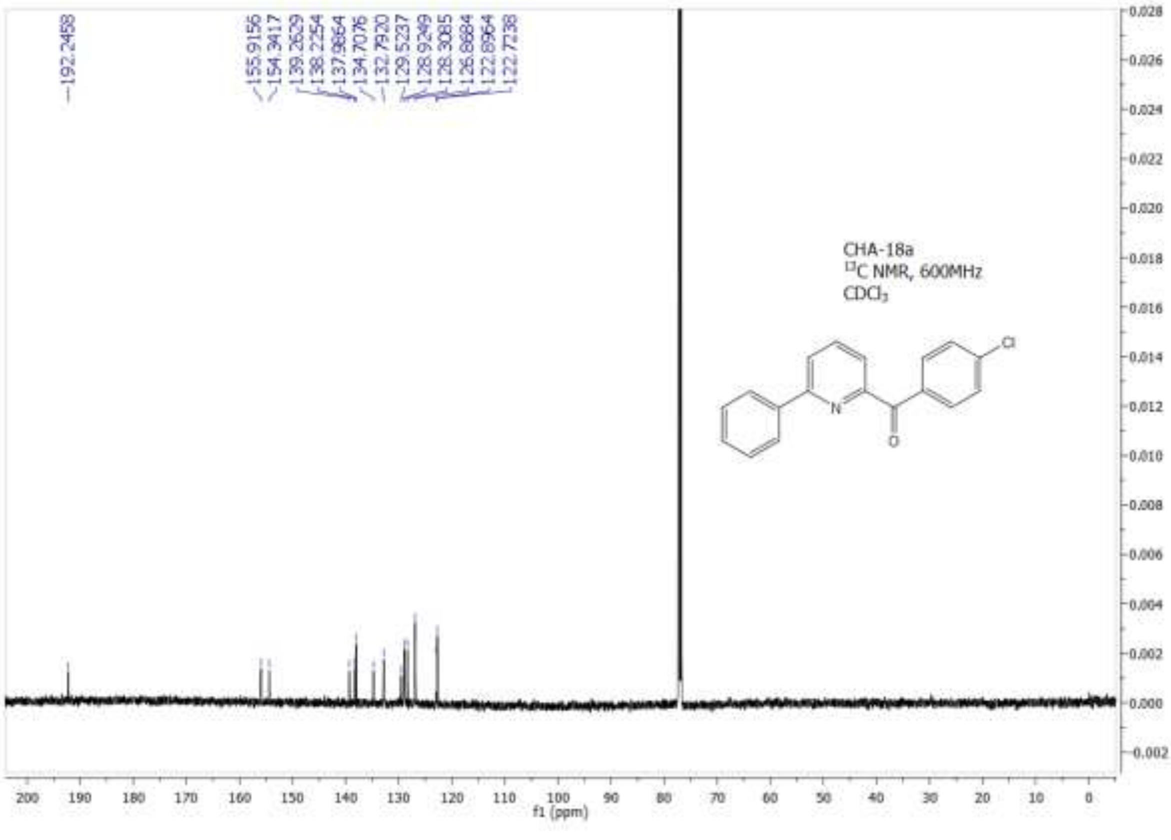

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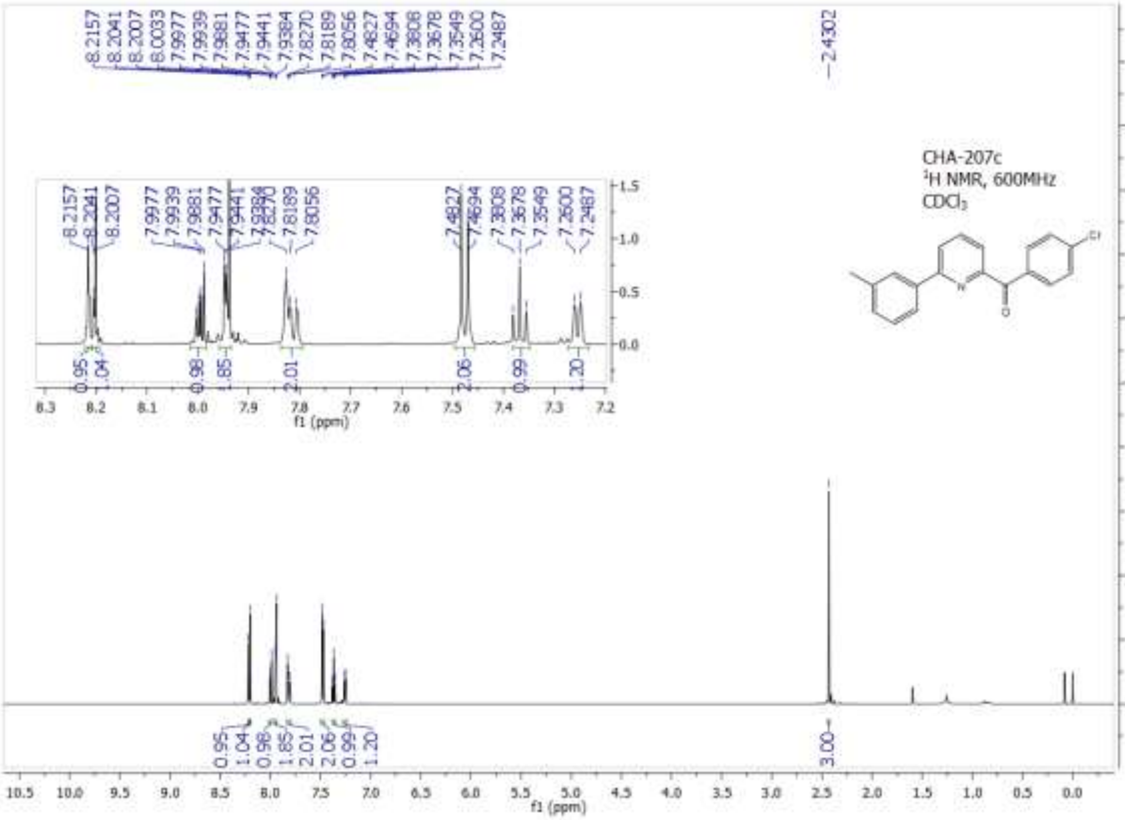

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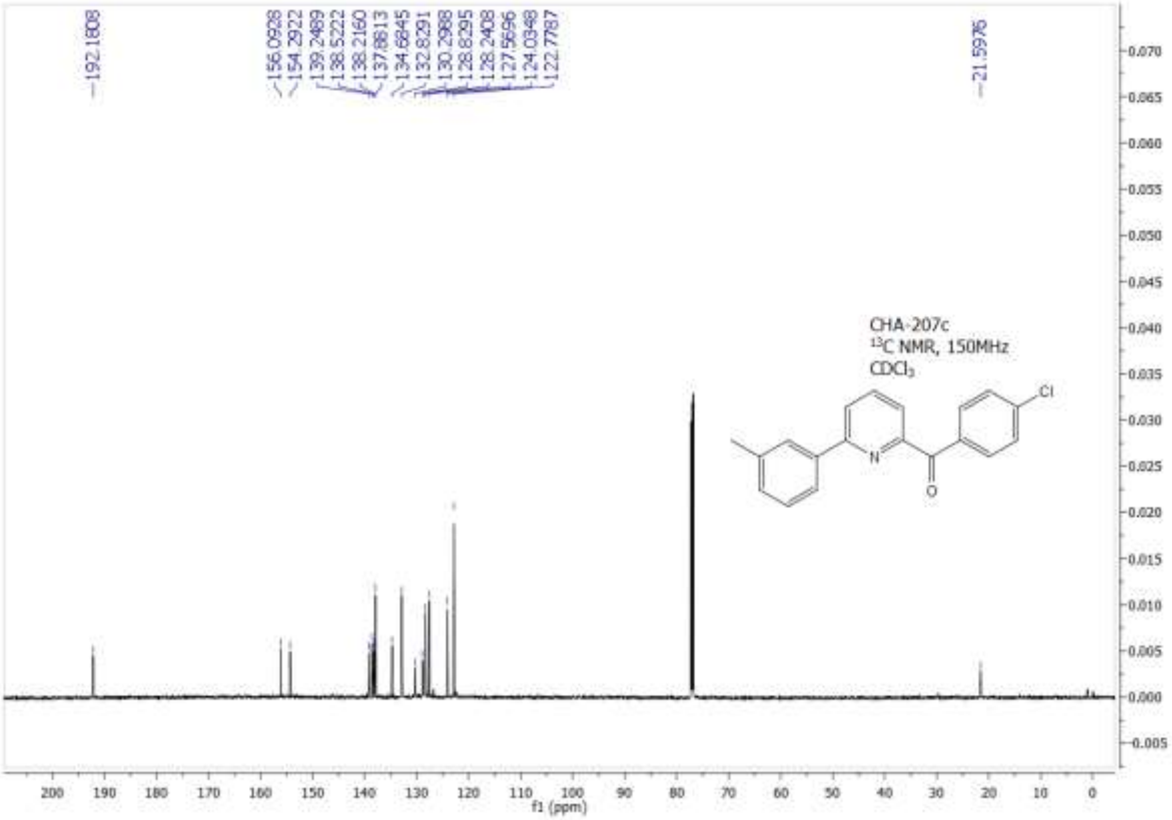

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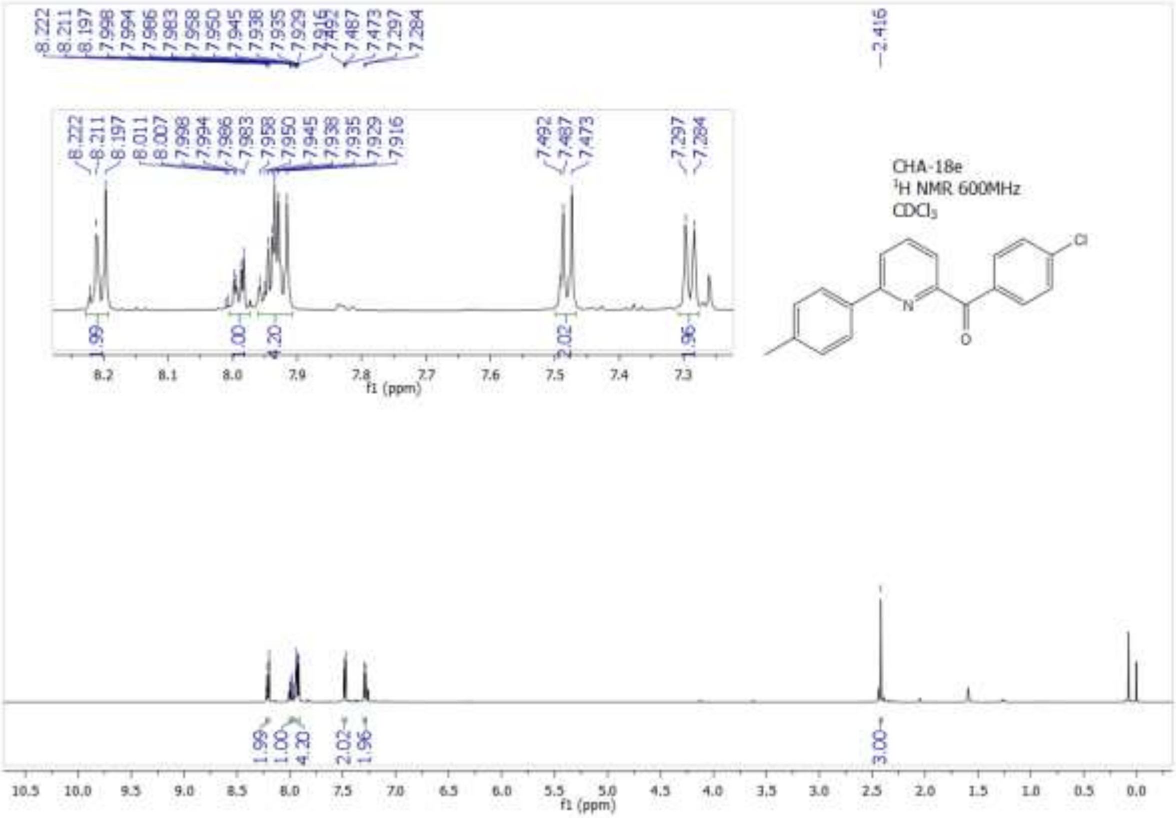

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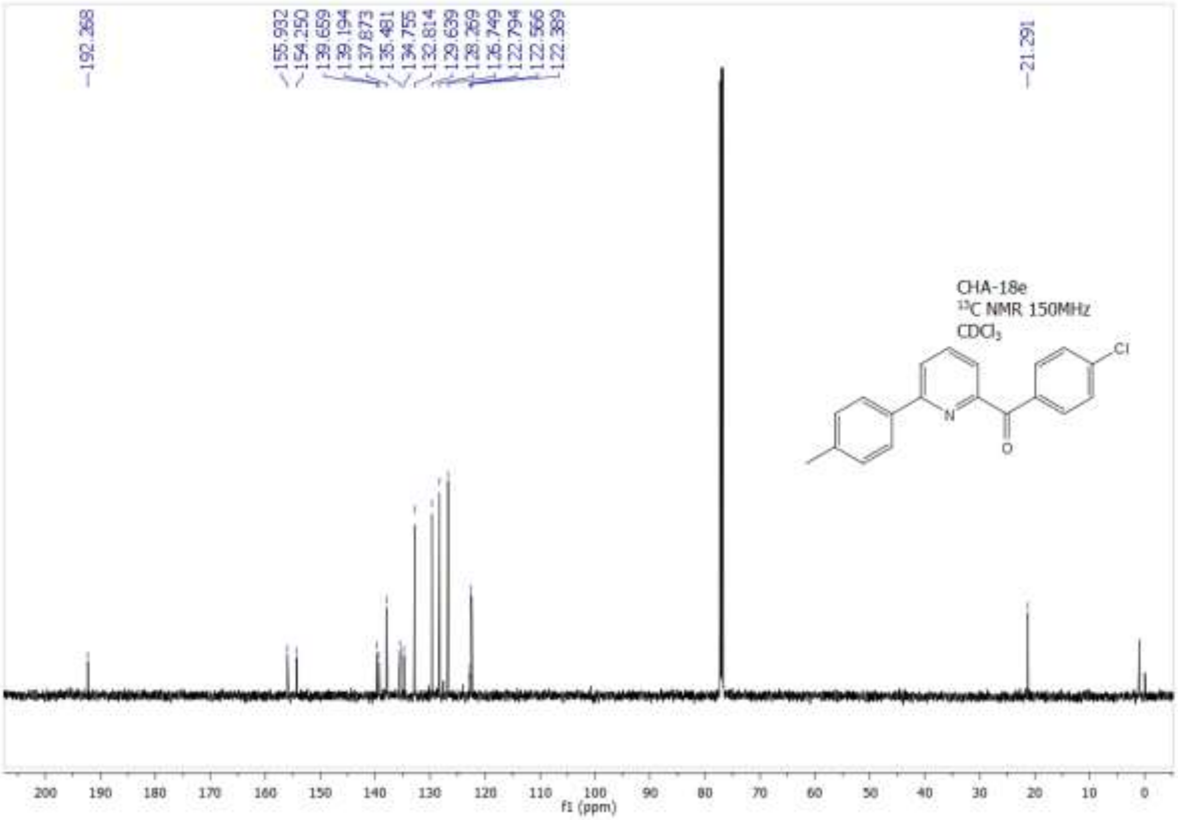

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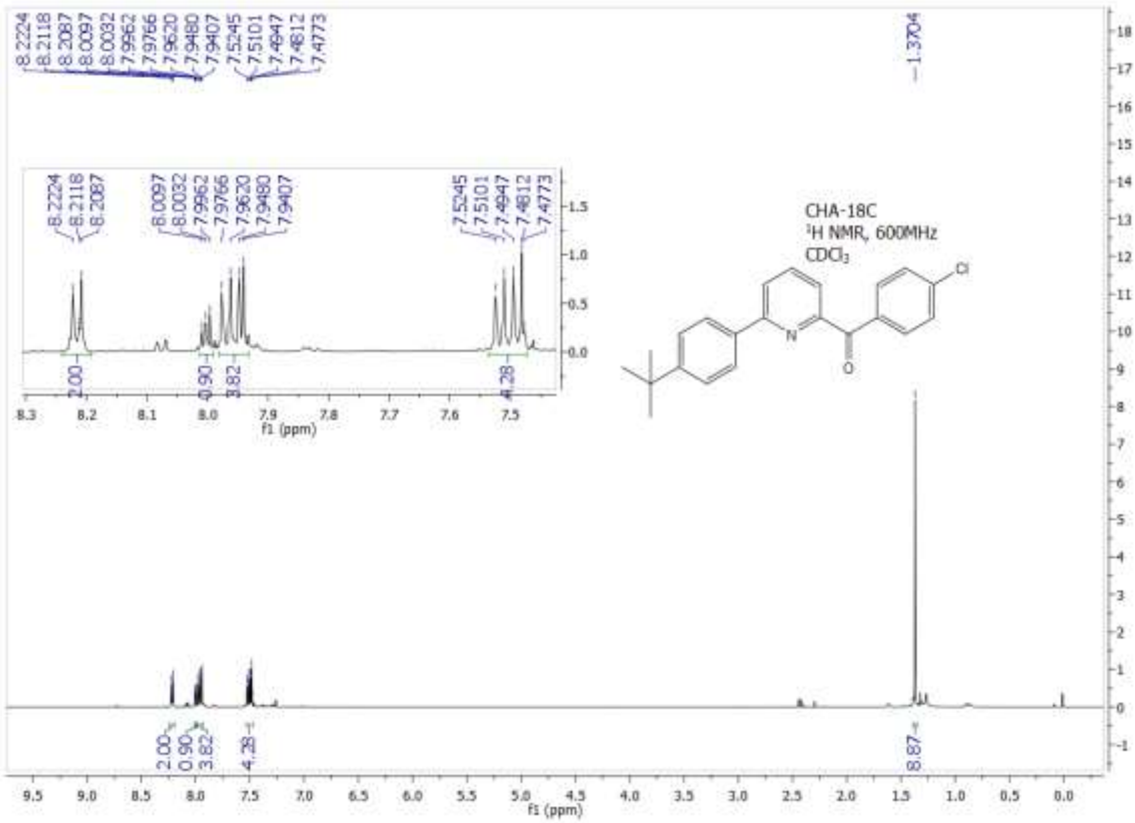

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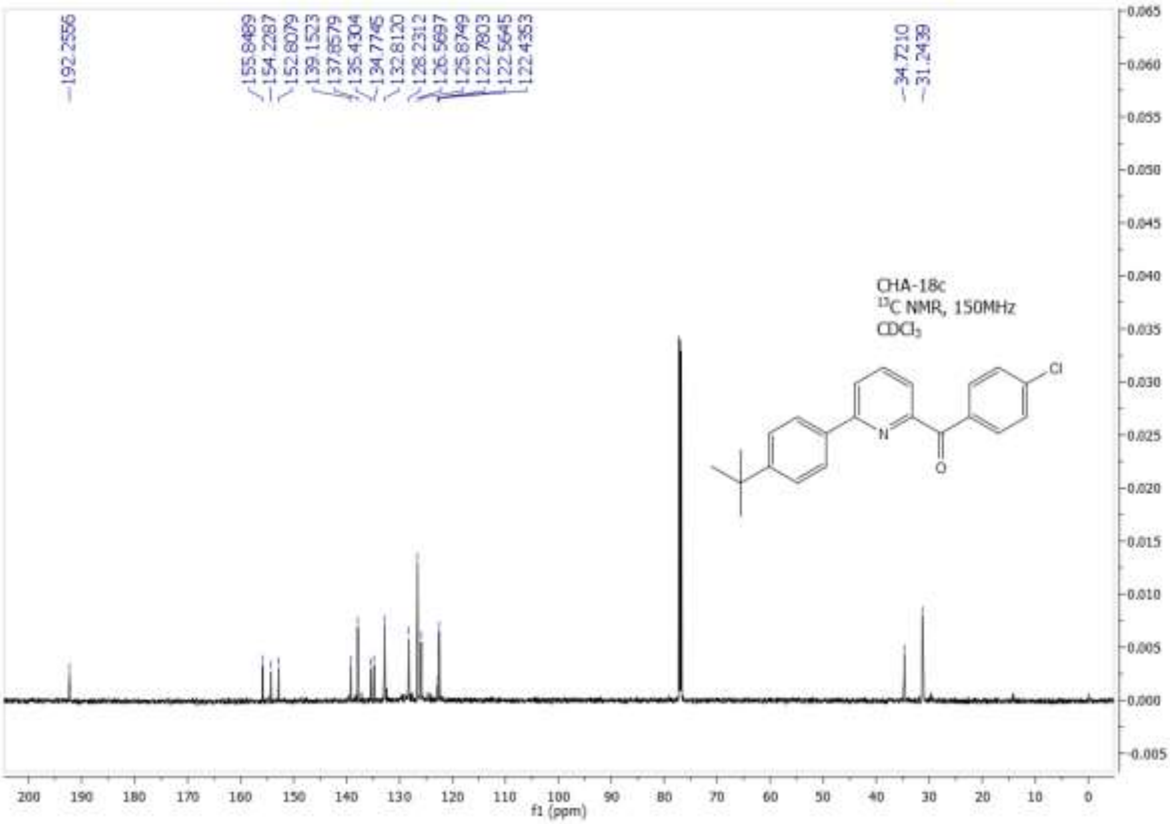

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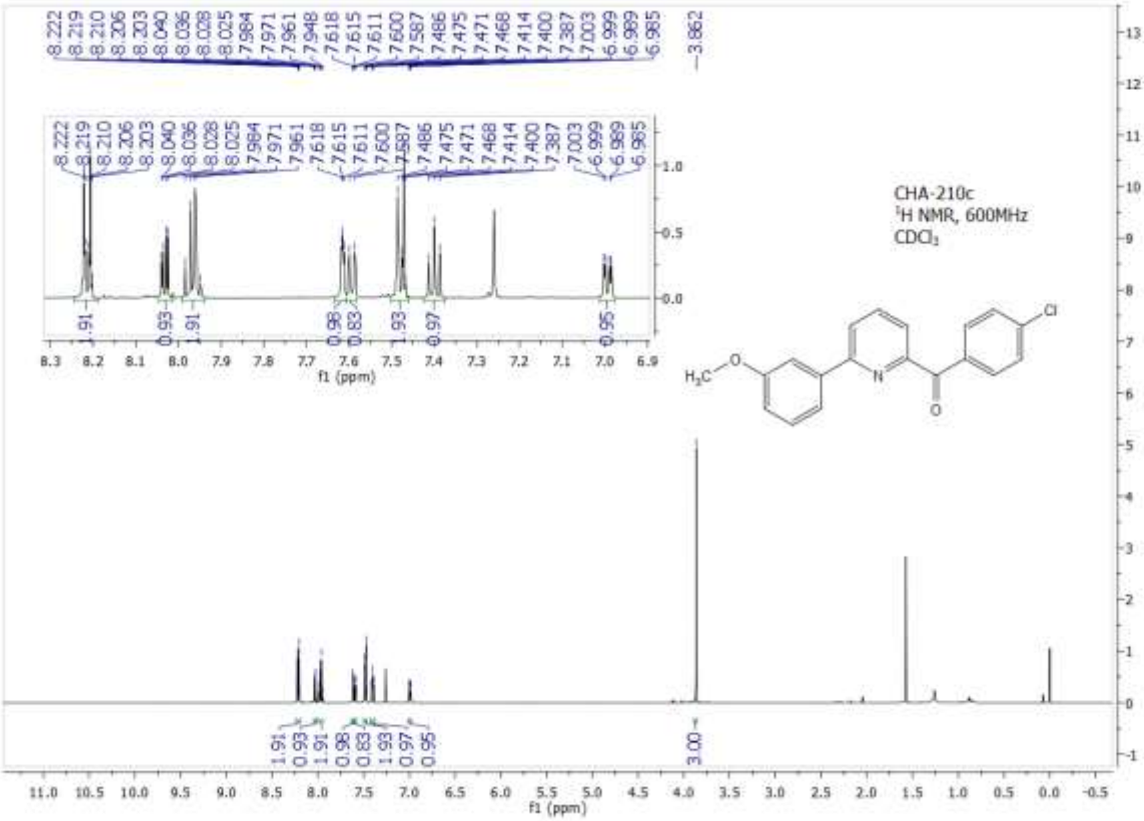

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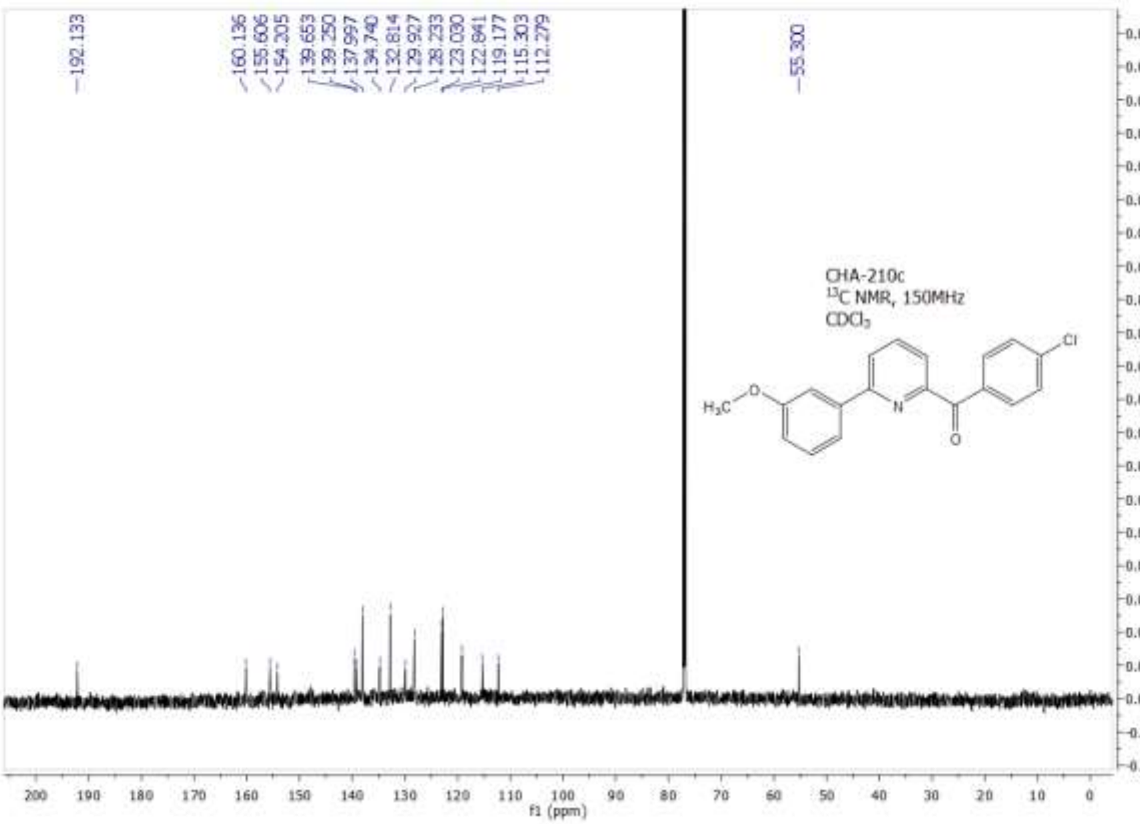

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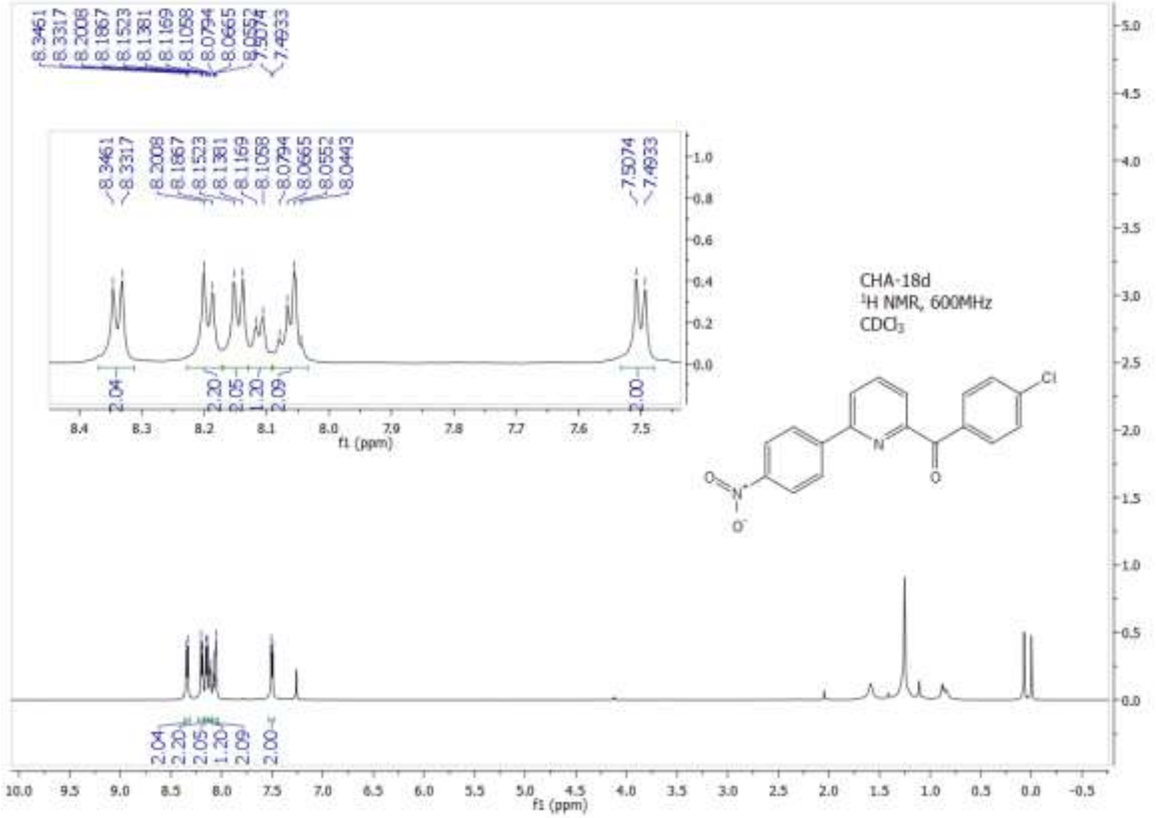

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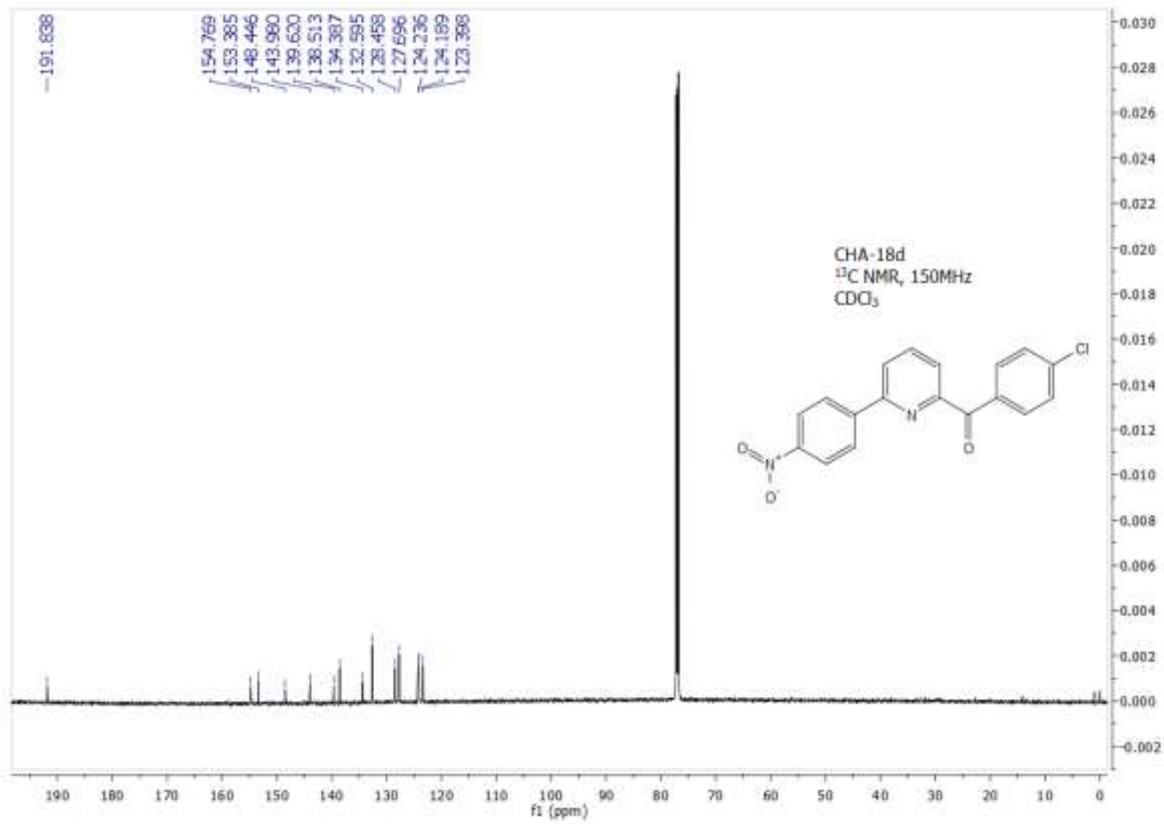

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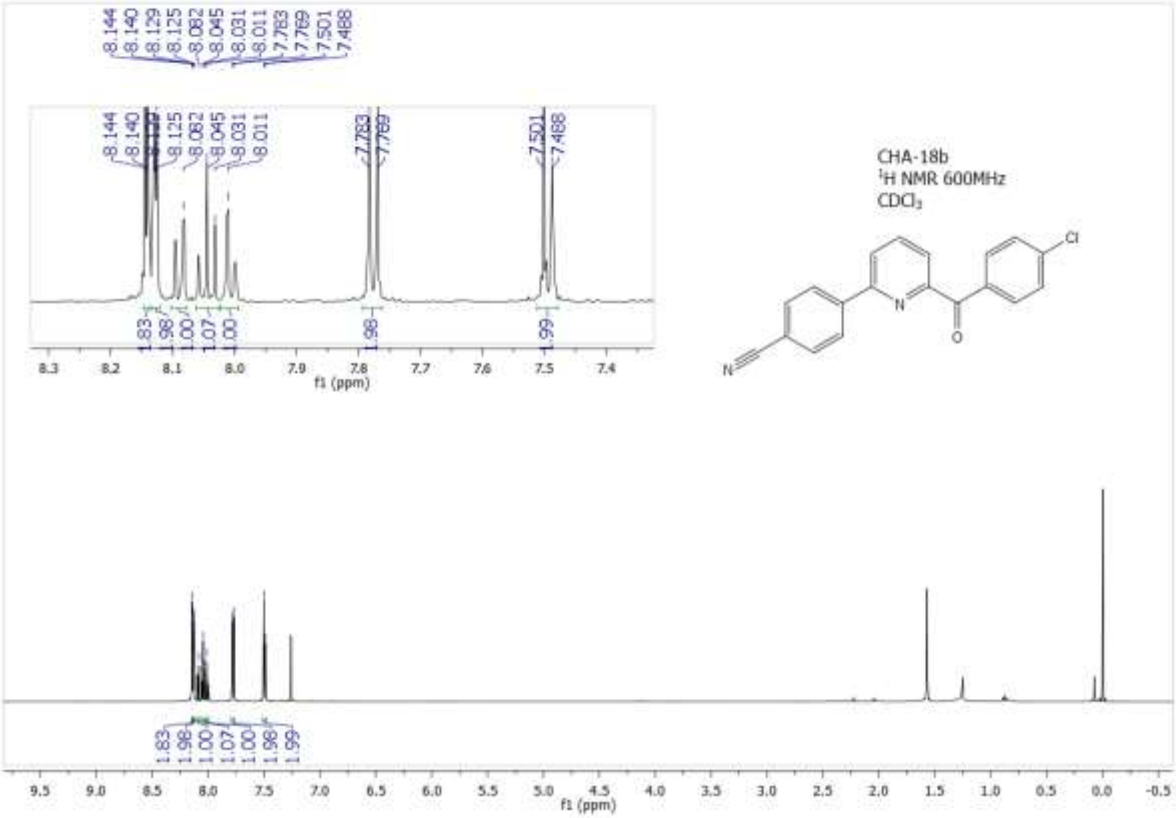

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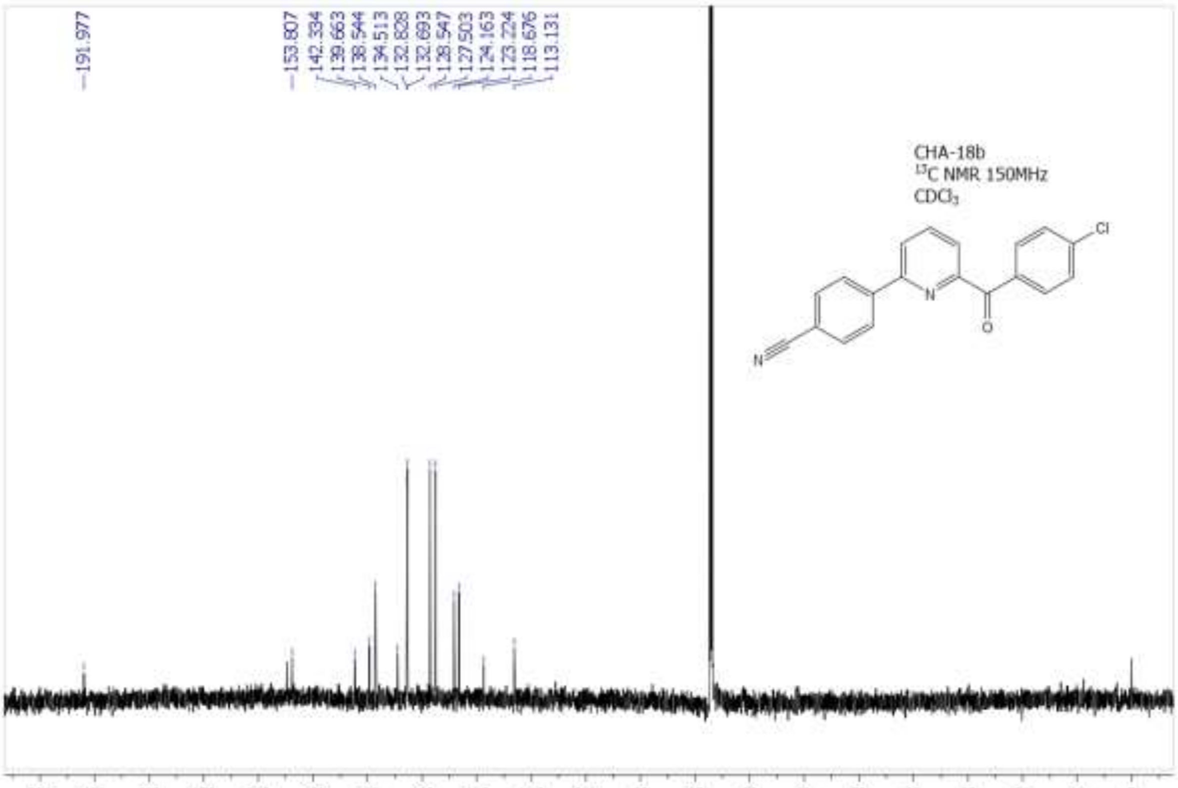

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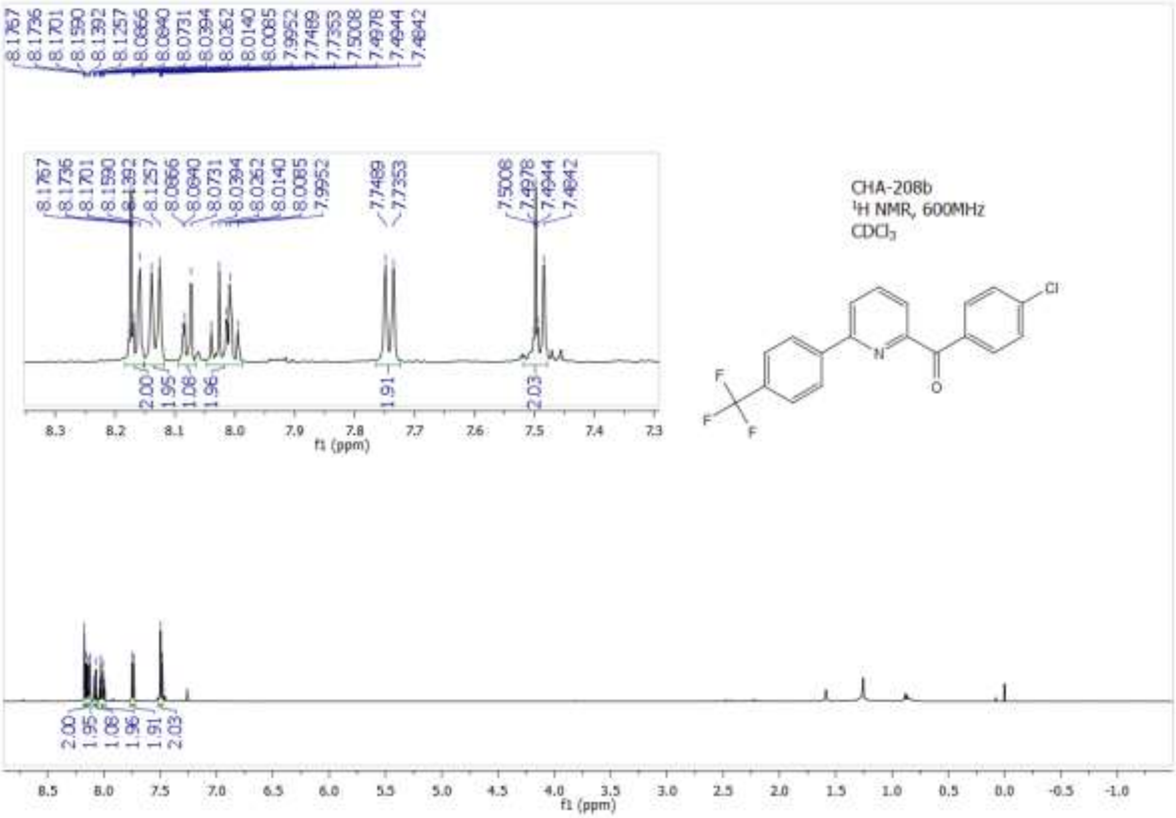

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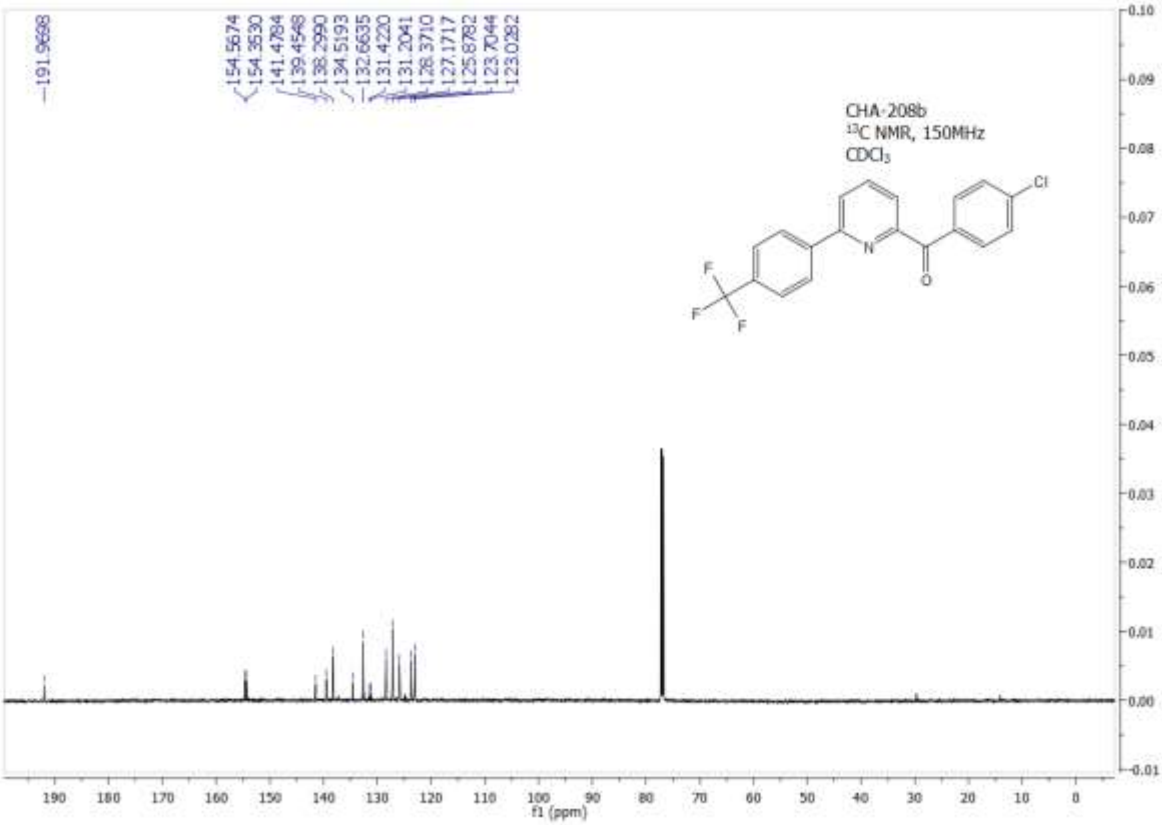

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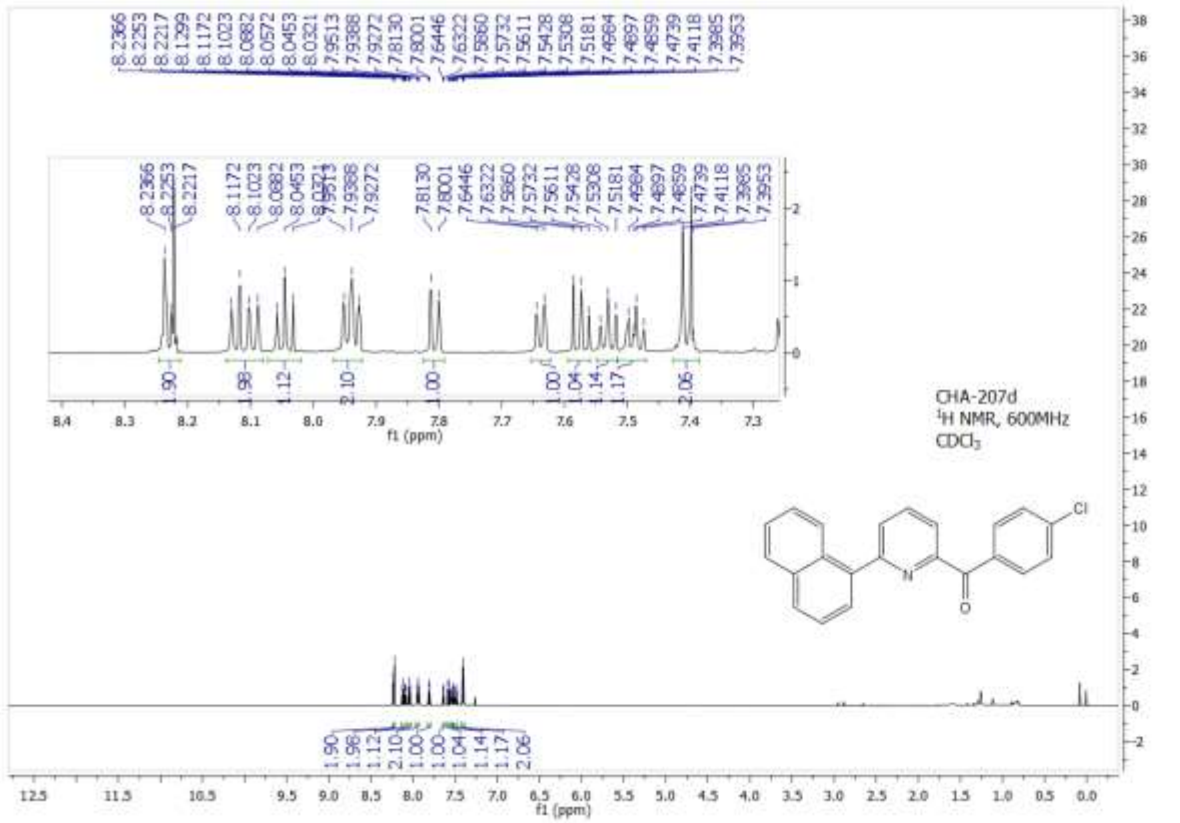

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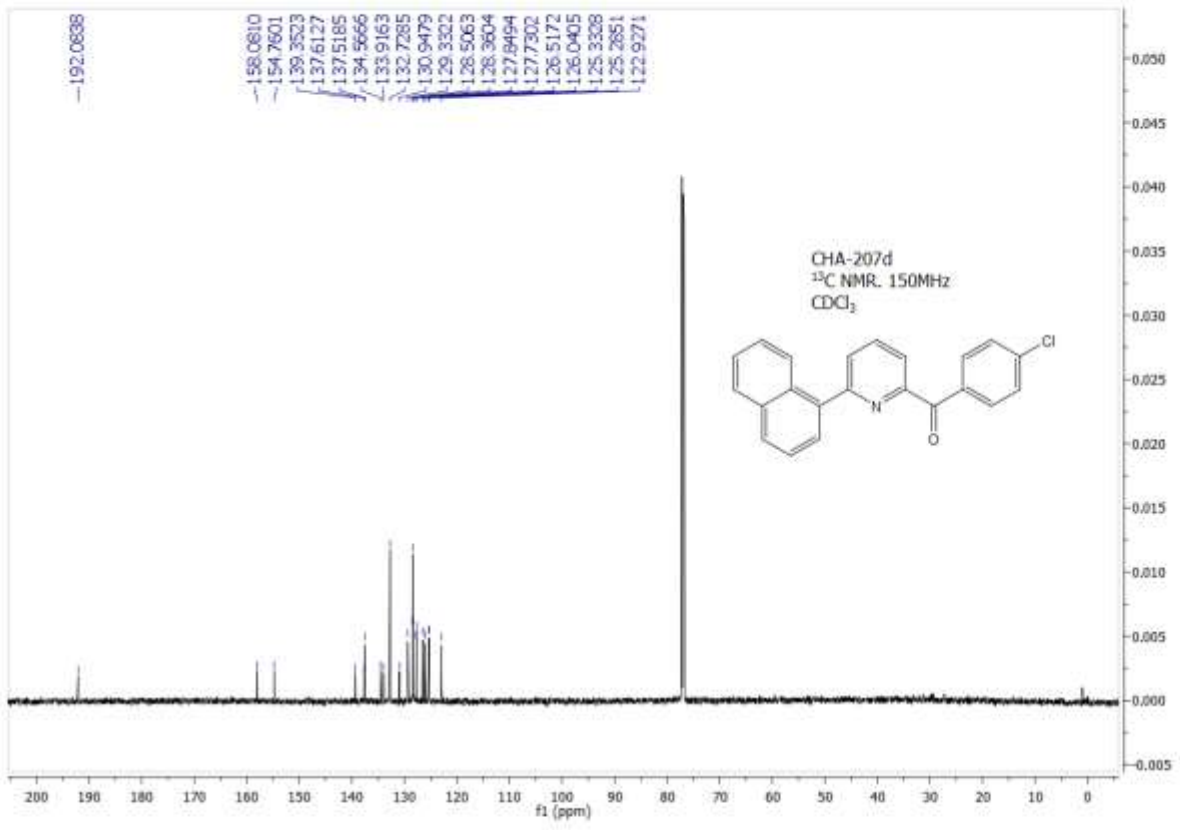

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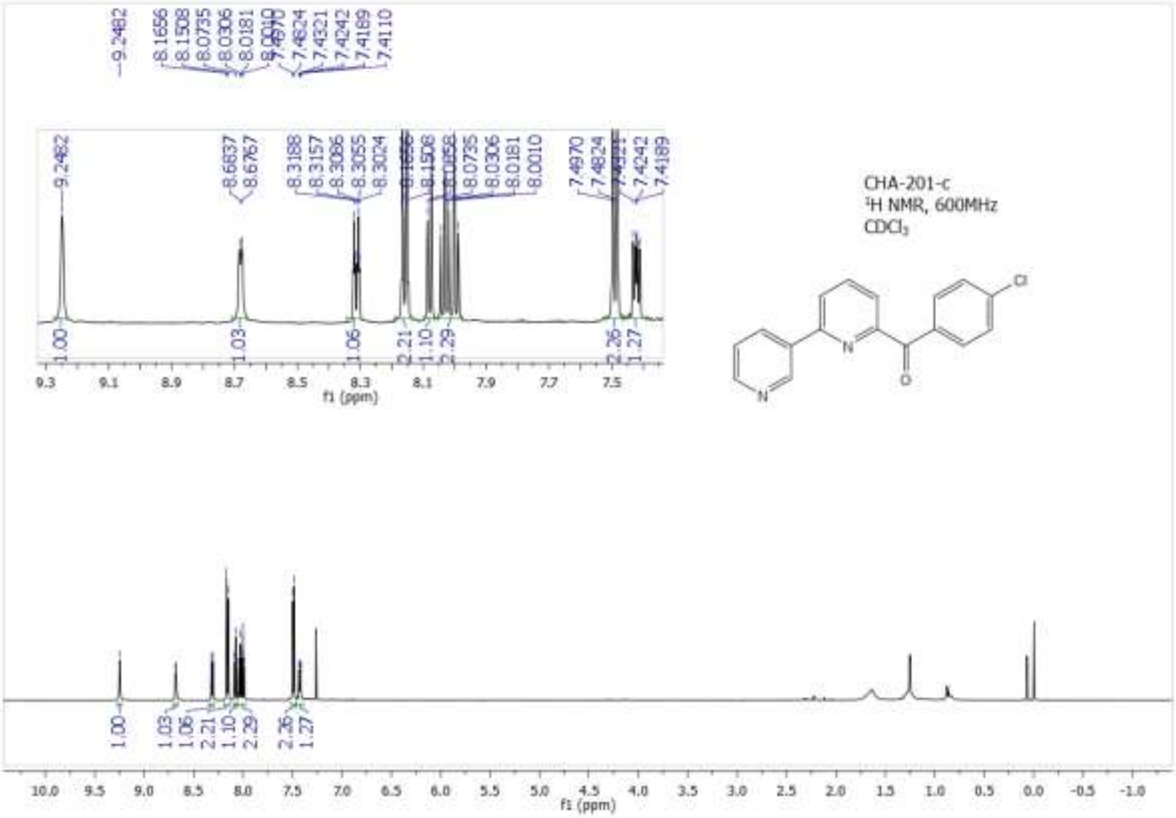

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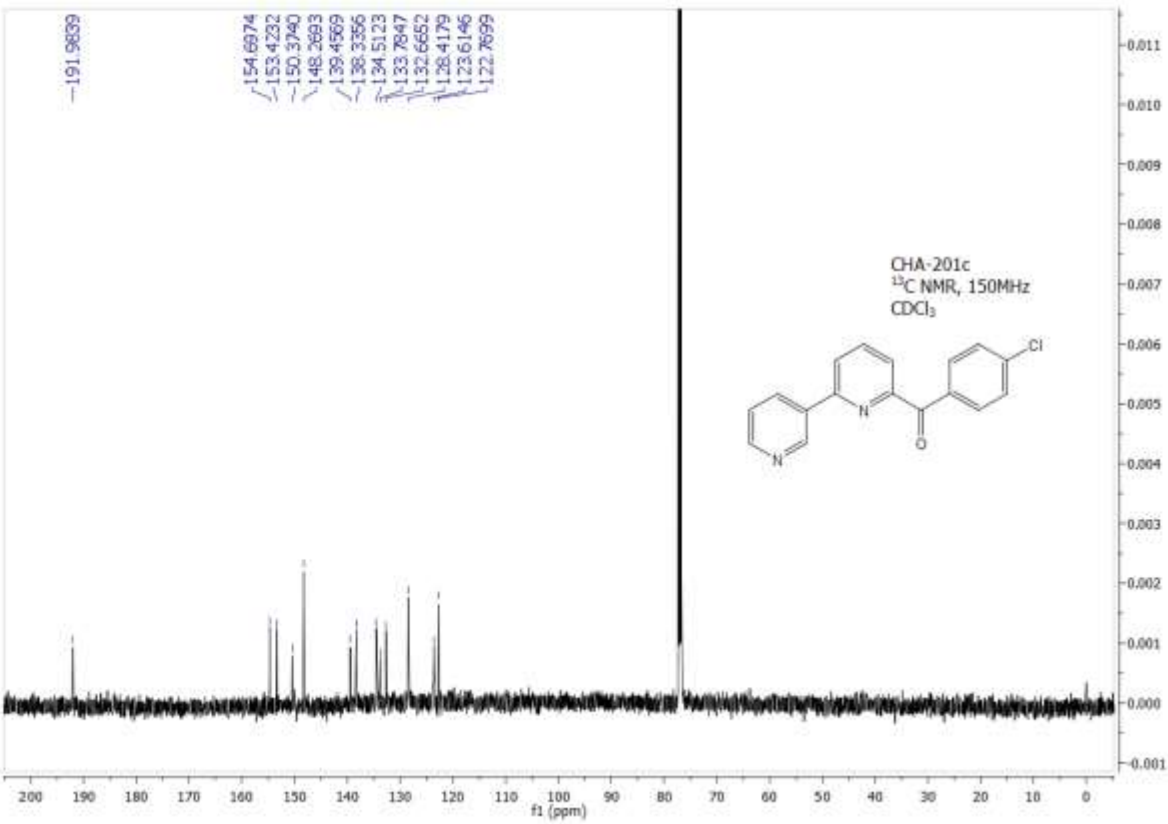

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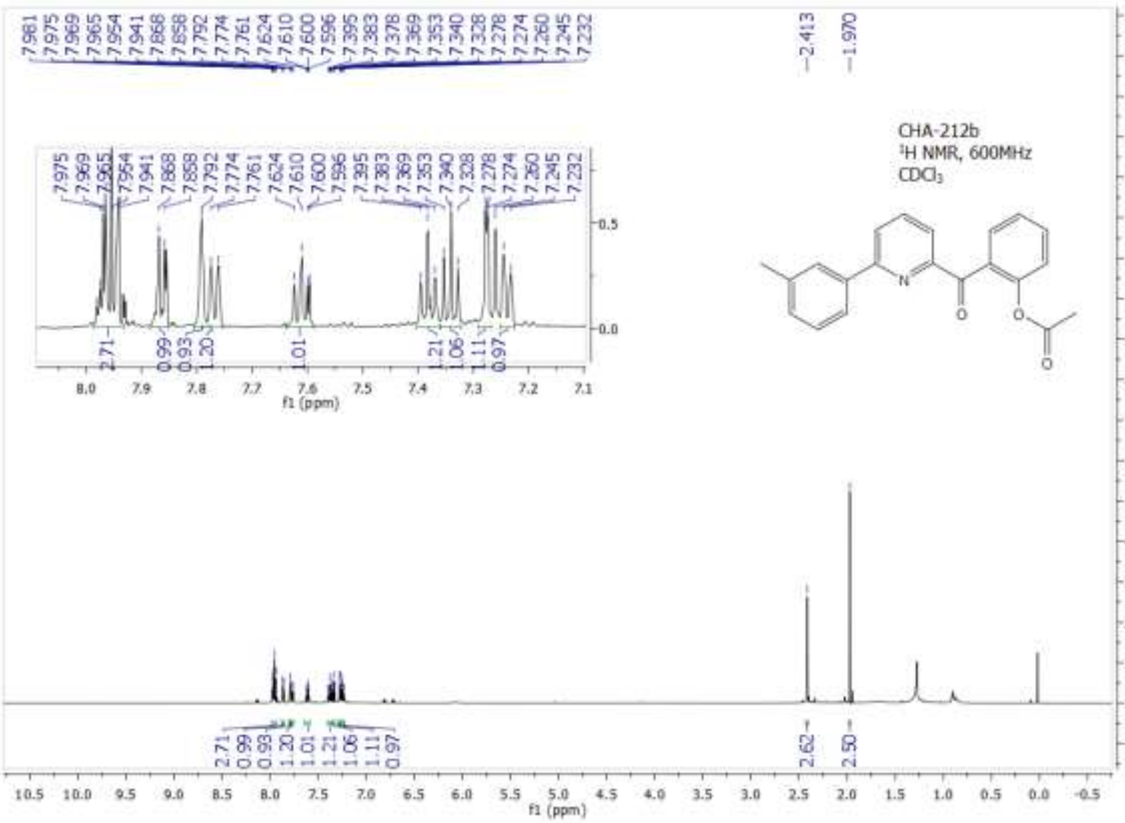

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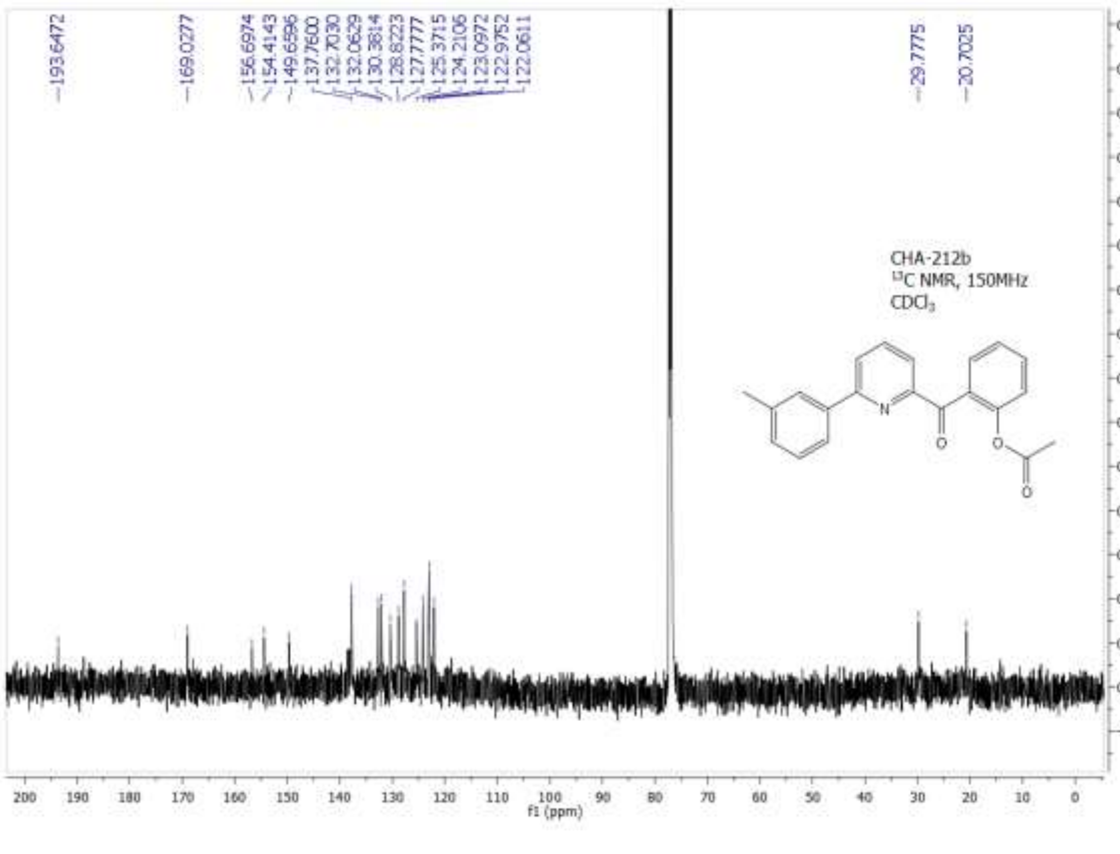

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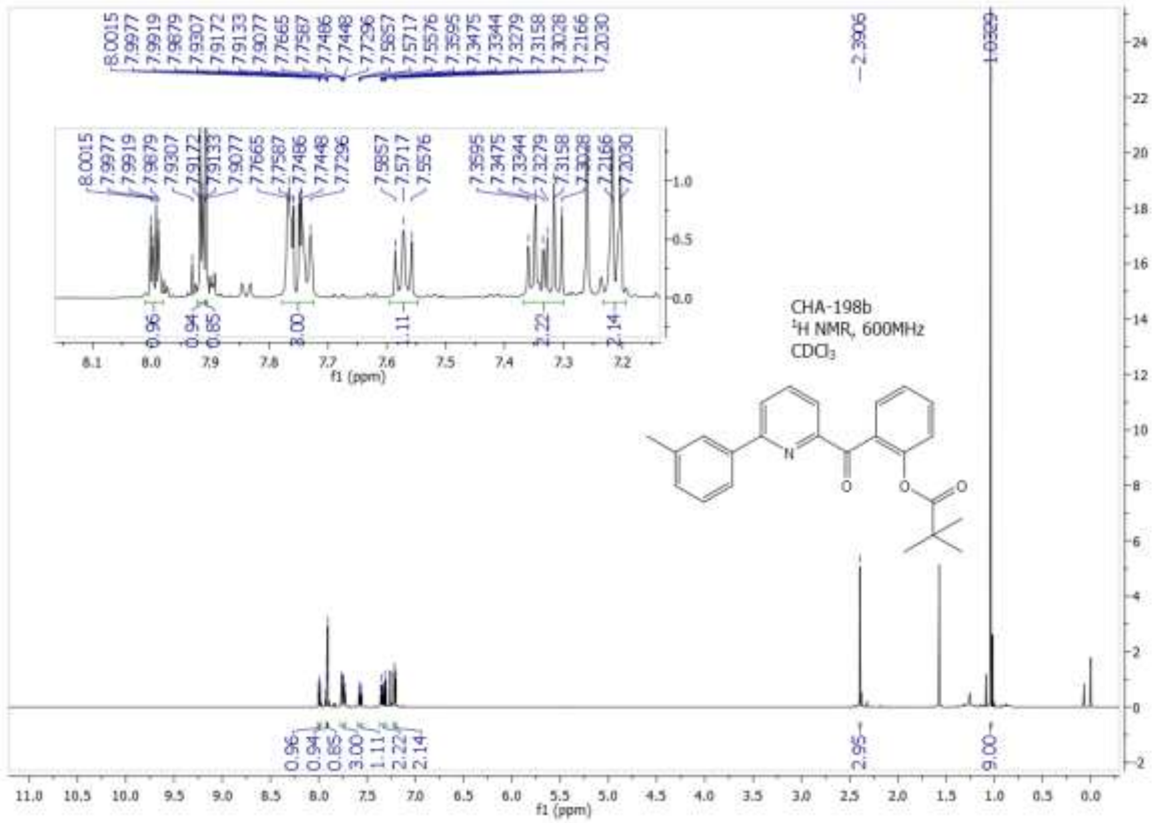

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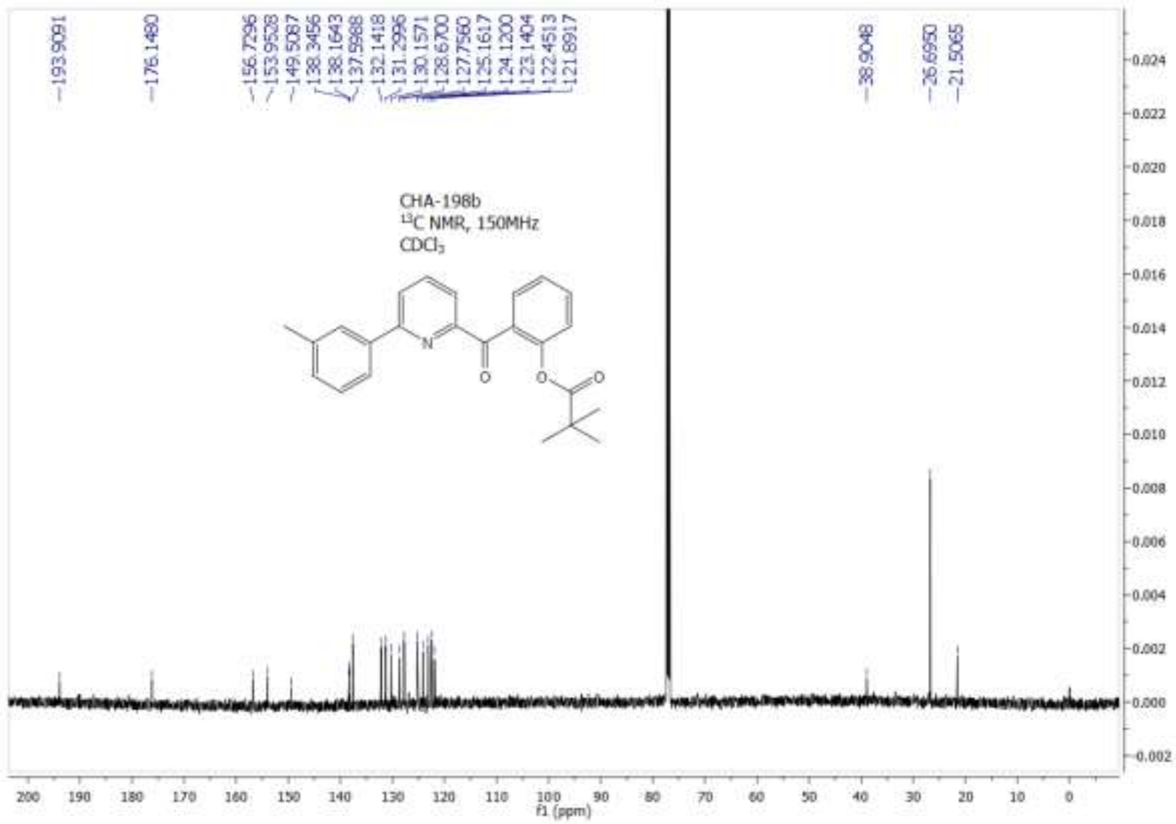

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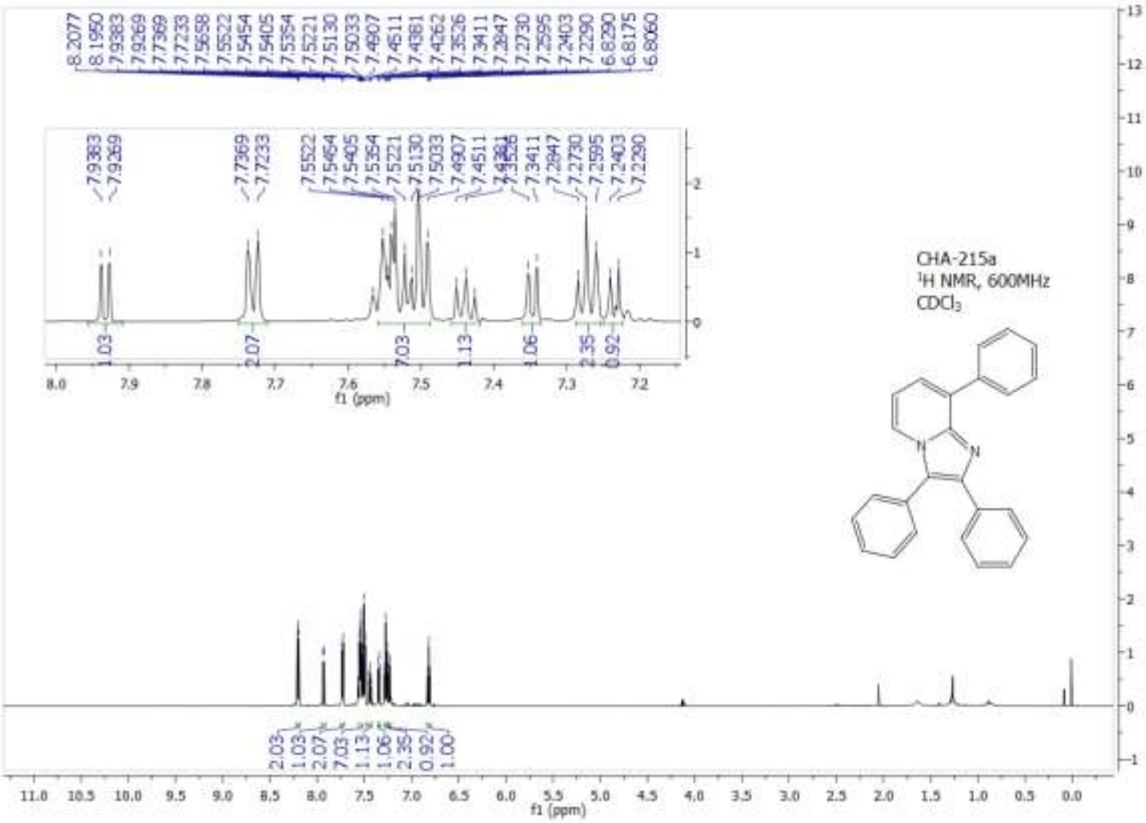

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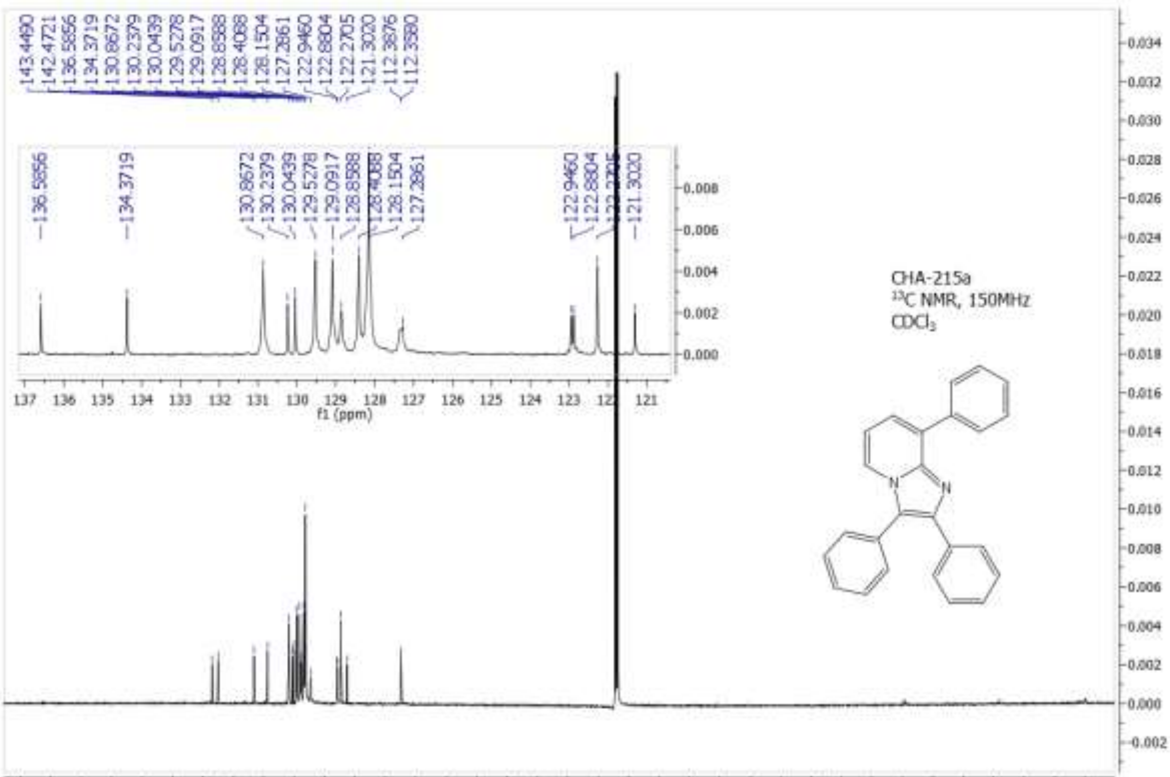

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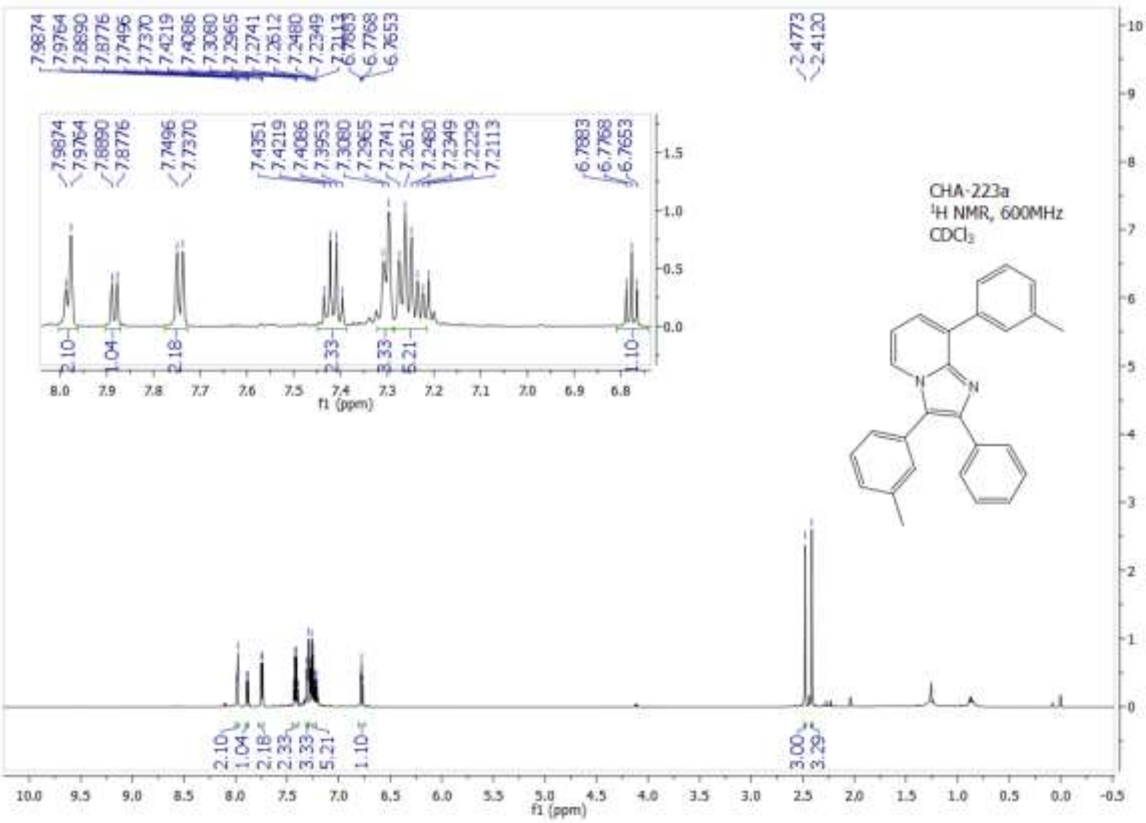

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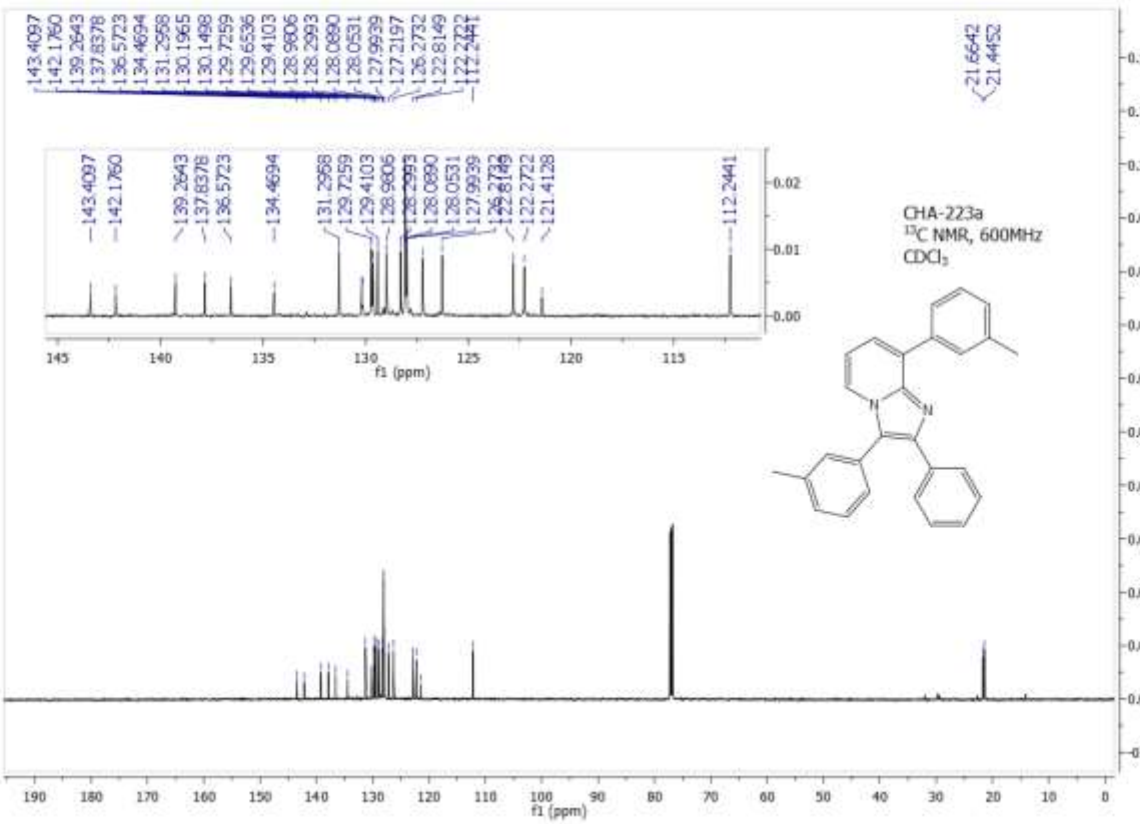

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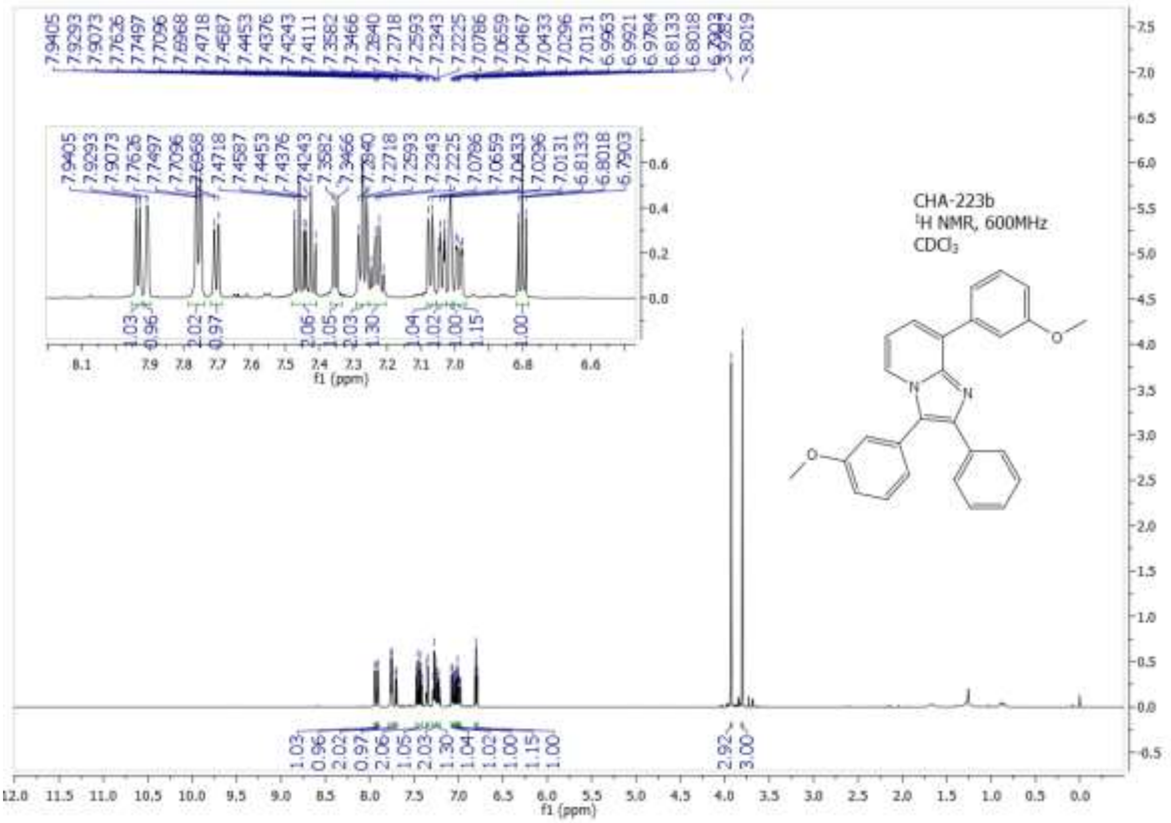

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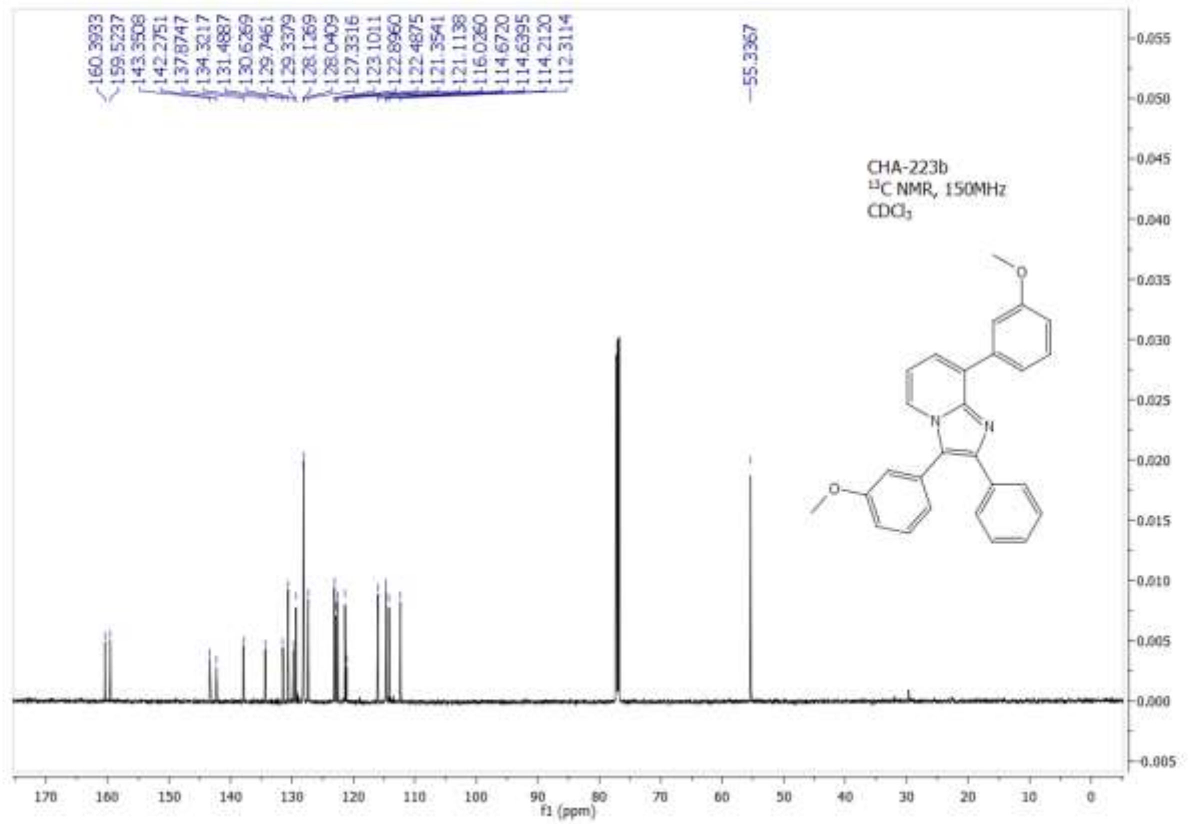

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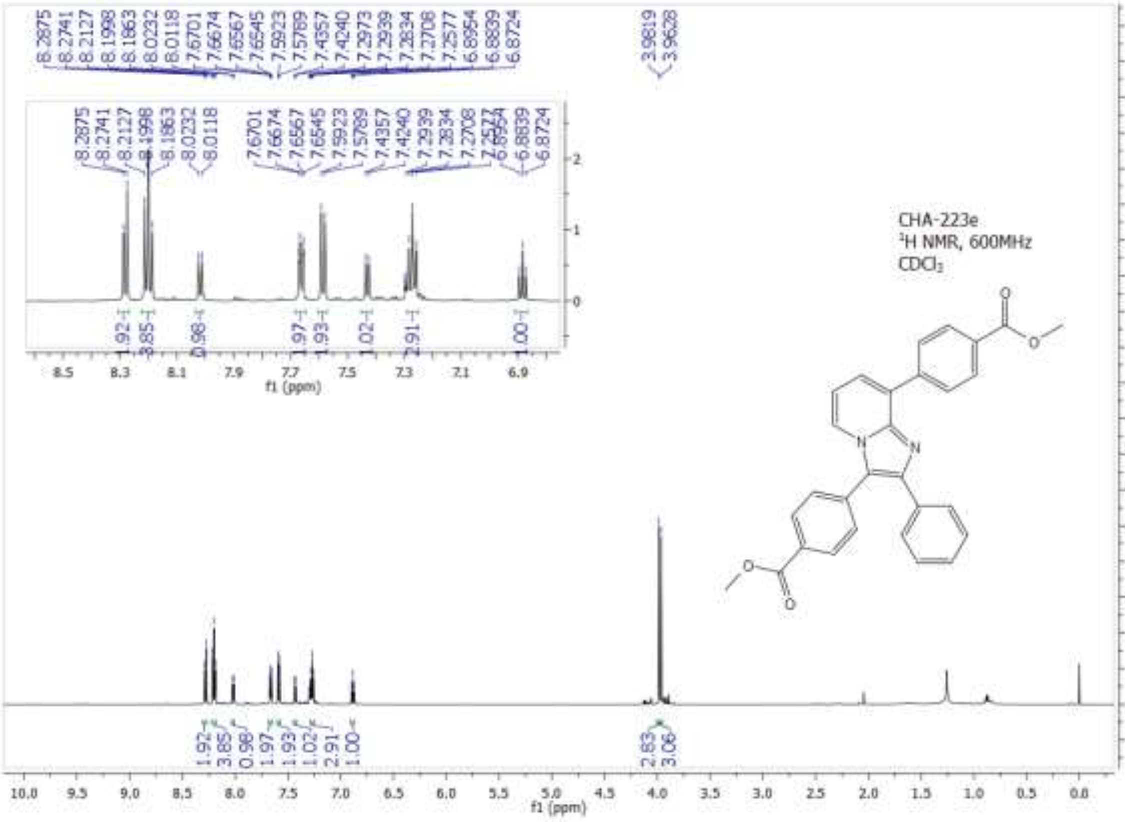

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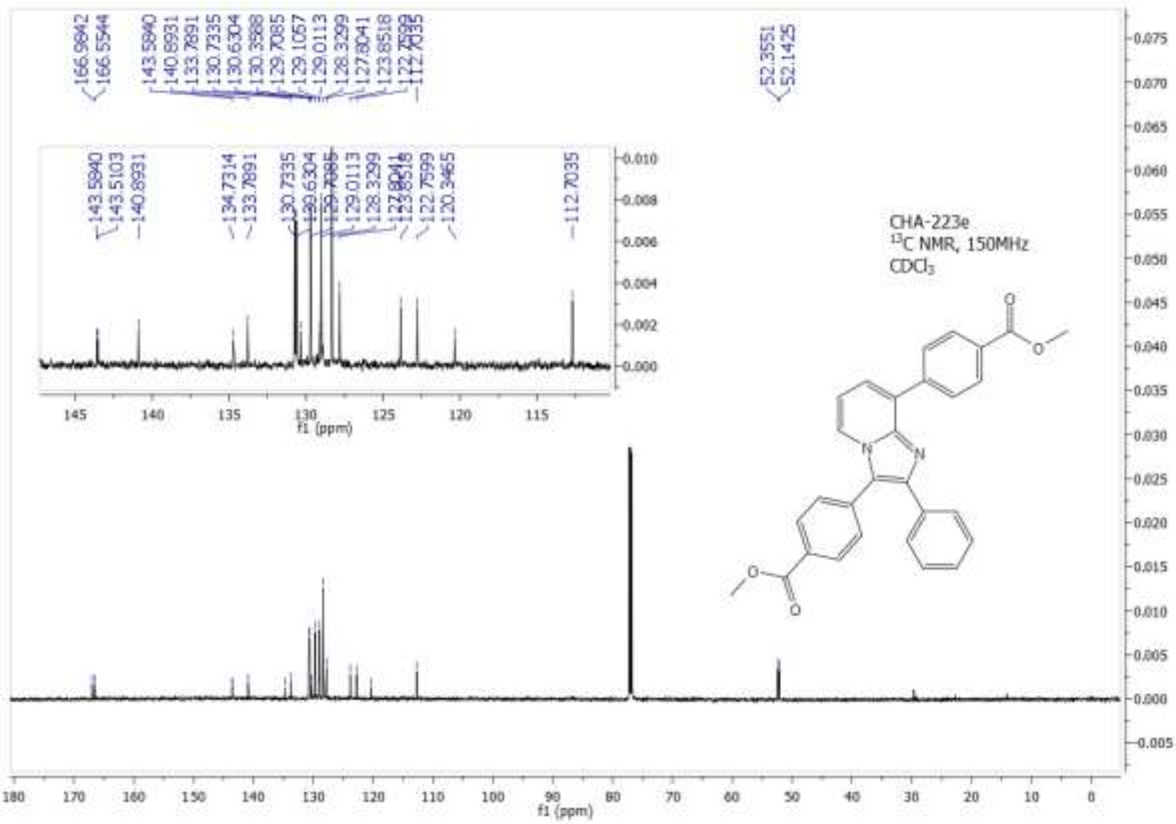

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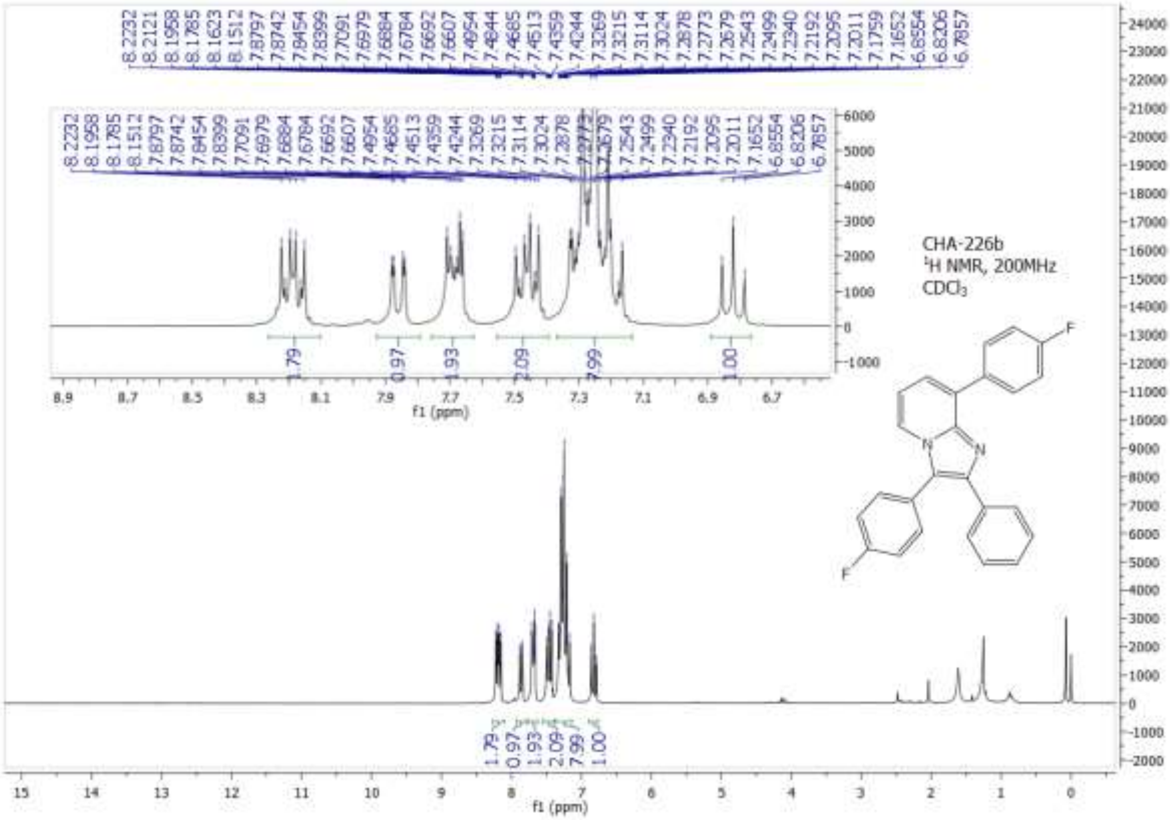

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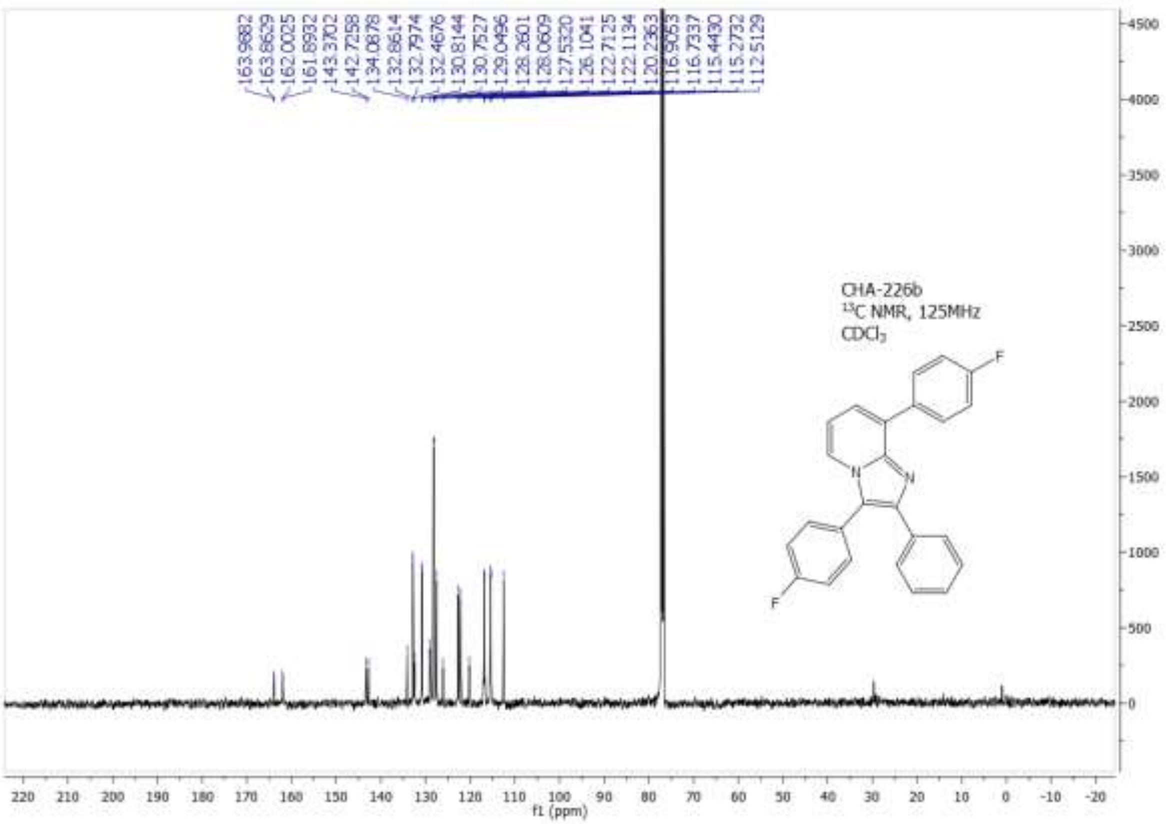

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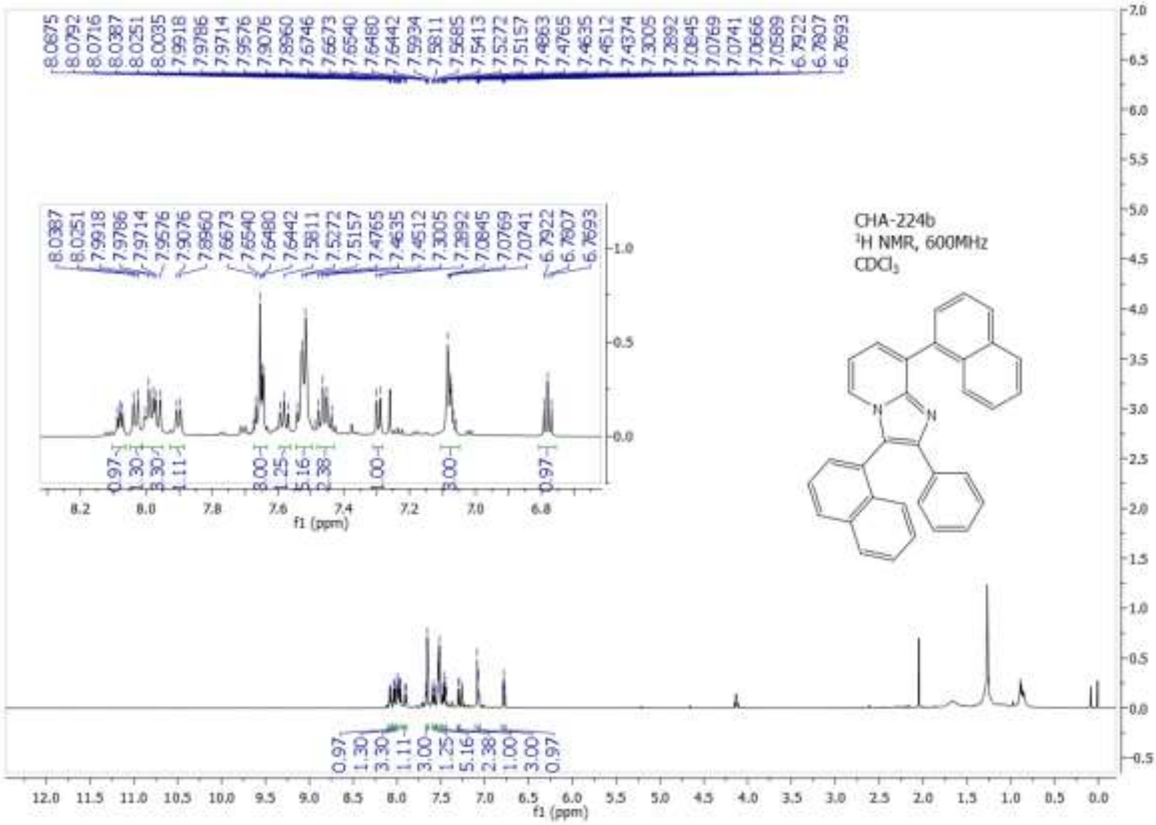

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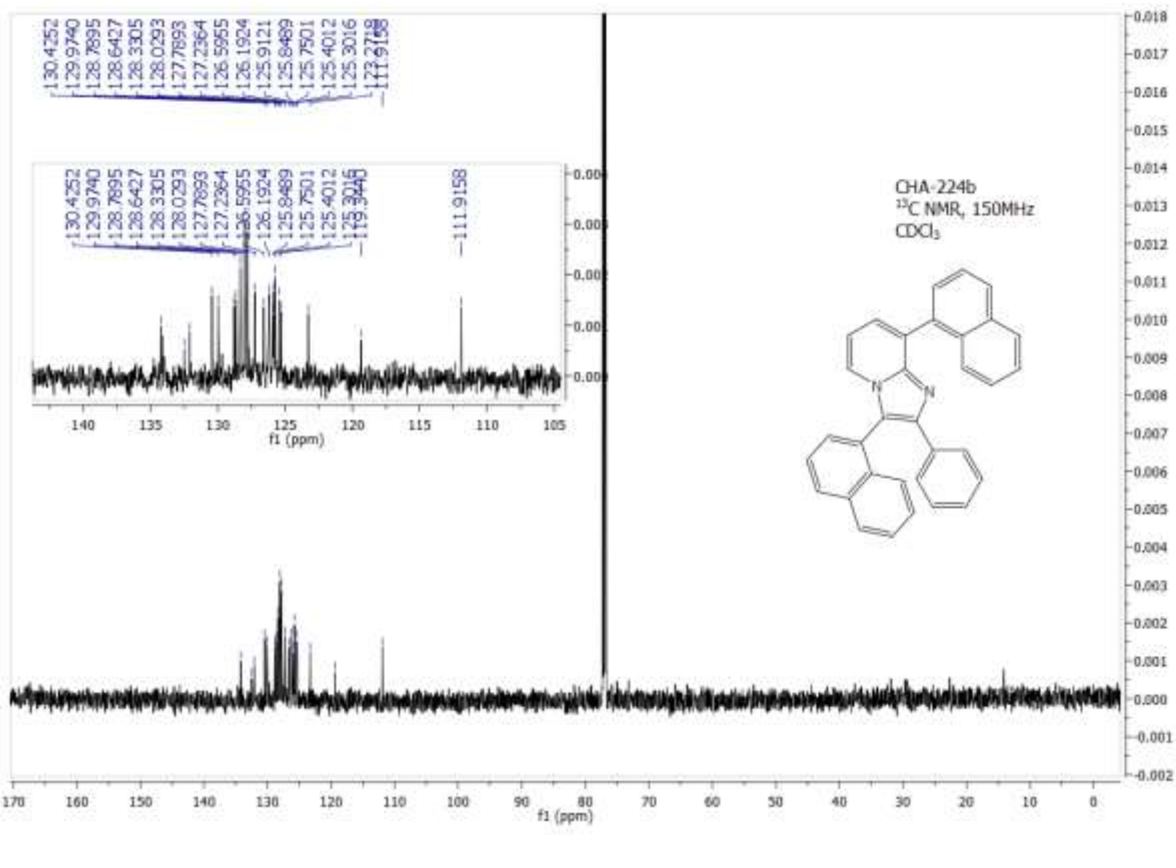
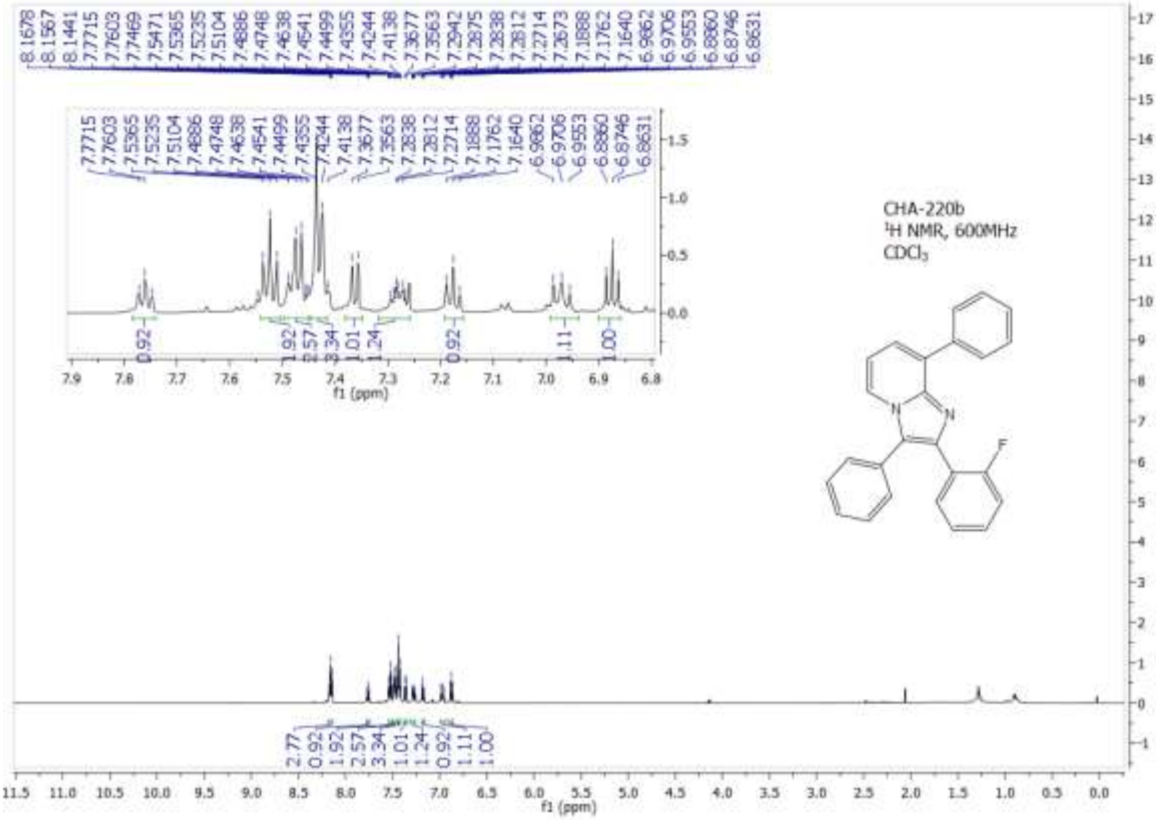
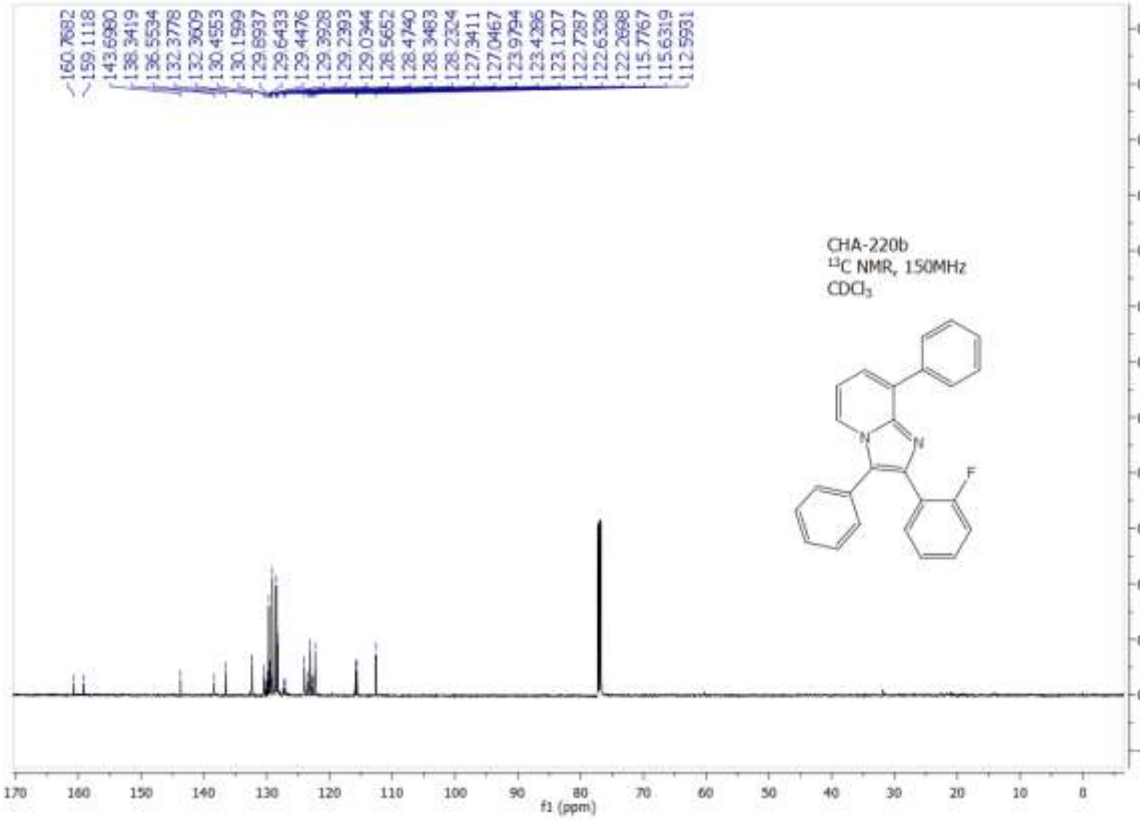


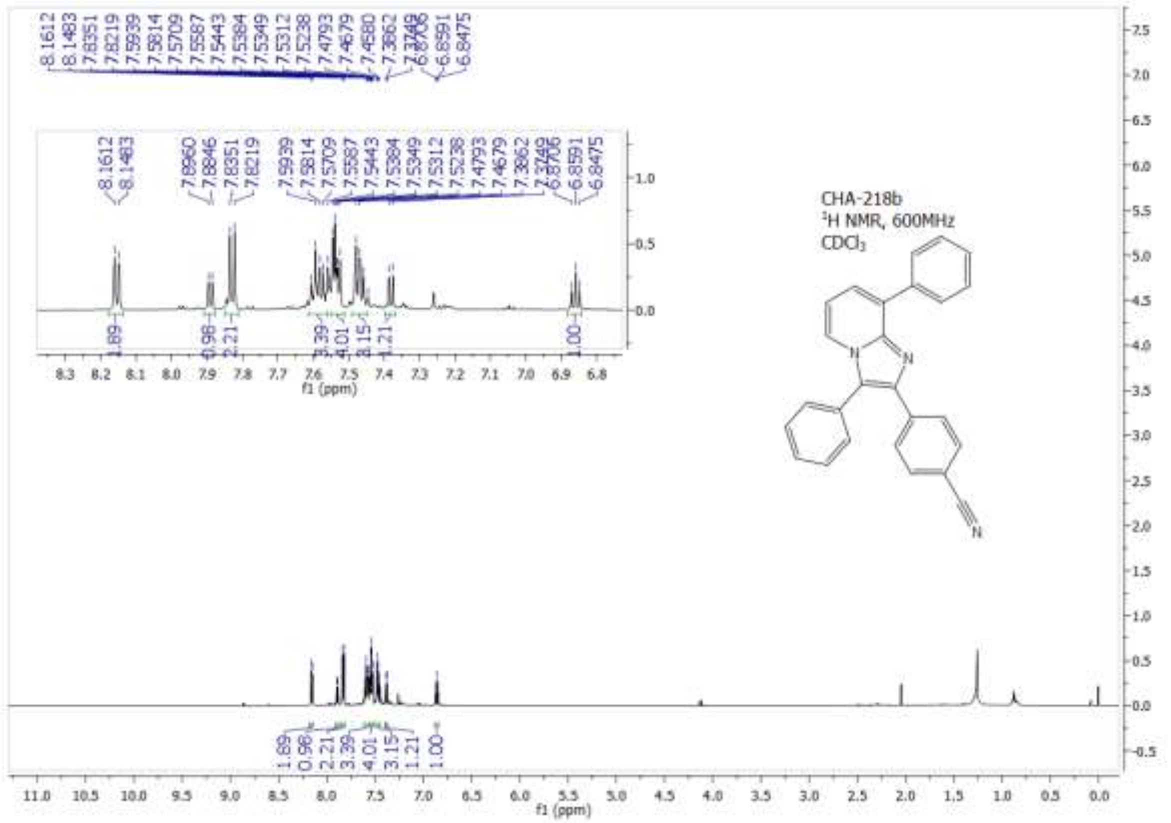
^{13}C NMR of **6f**



^{1}H NMR of **6g**



^{13}C NMR of **6g**



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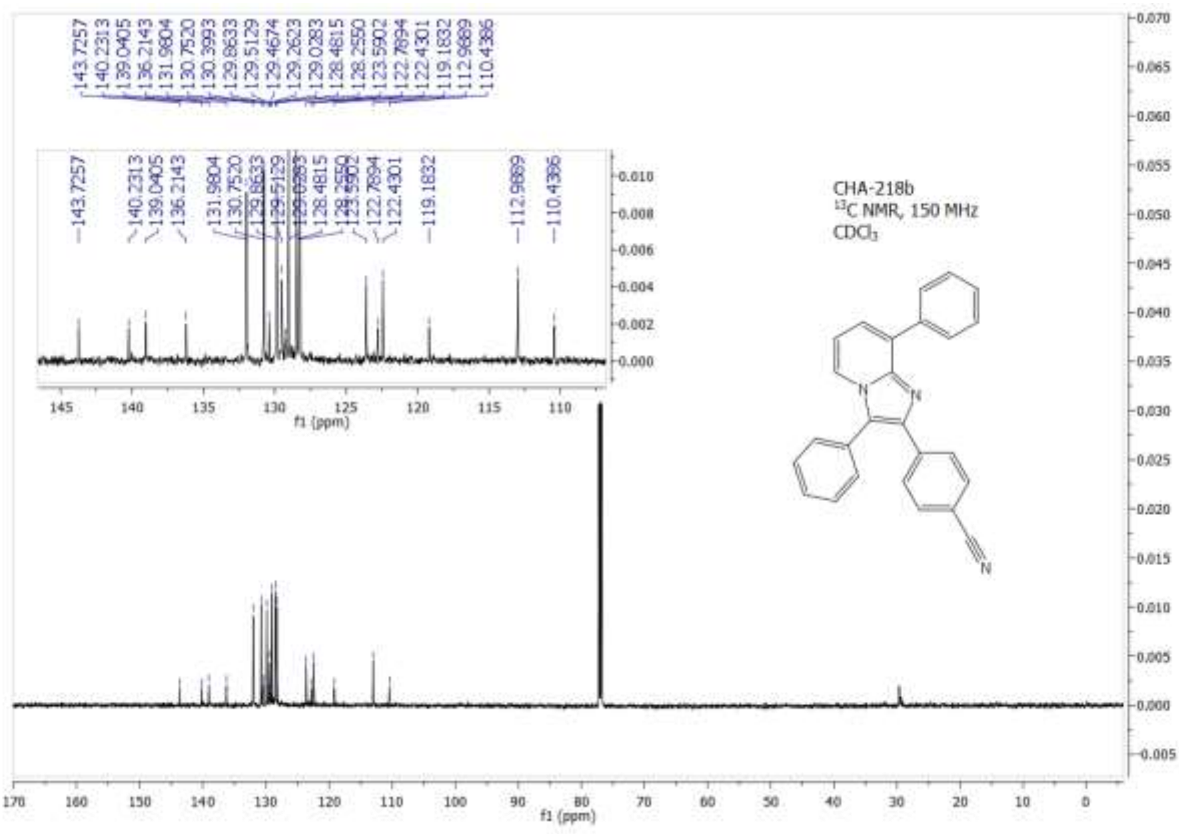

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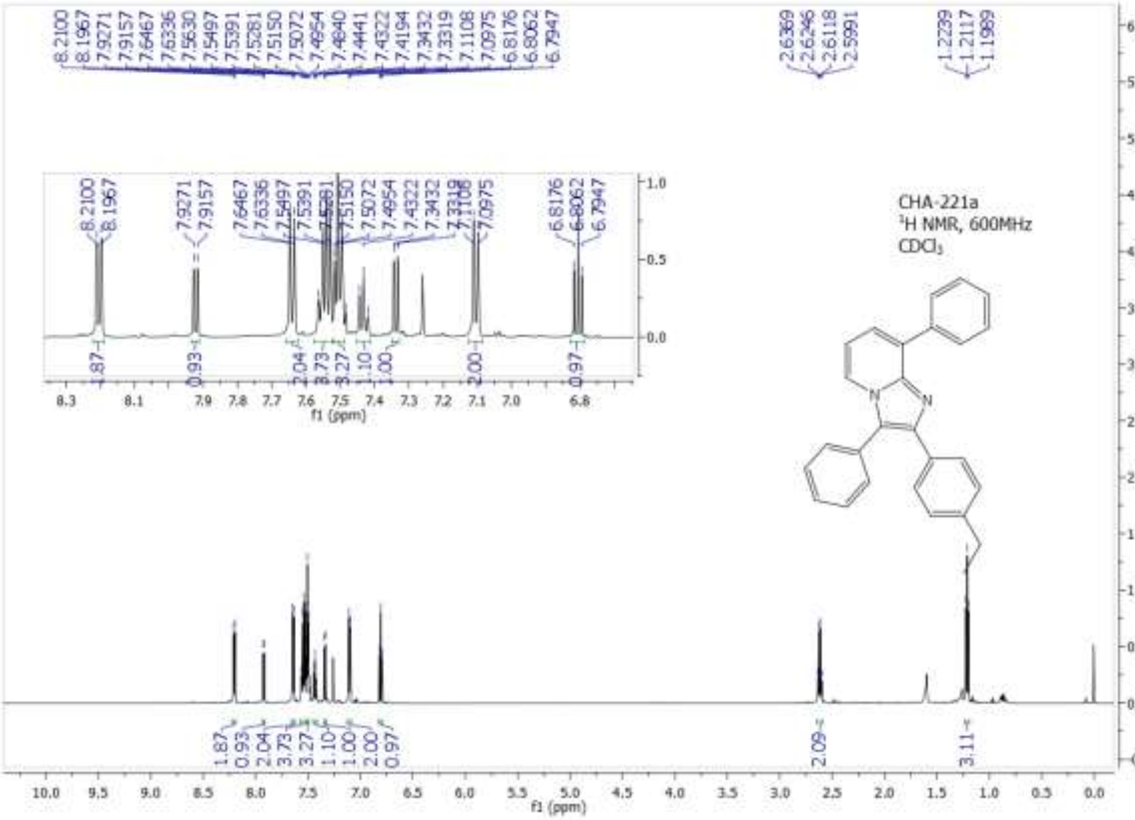
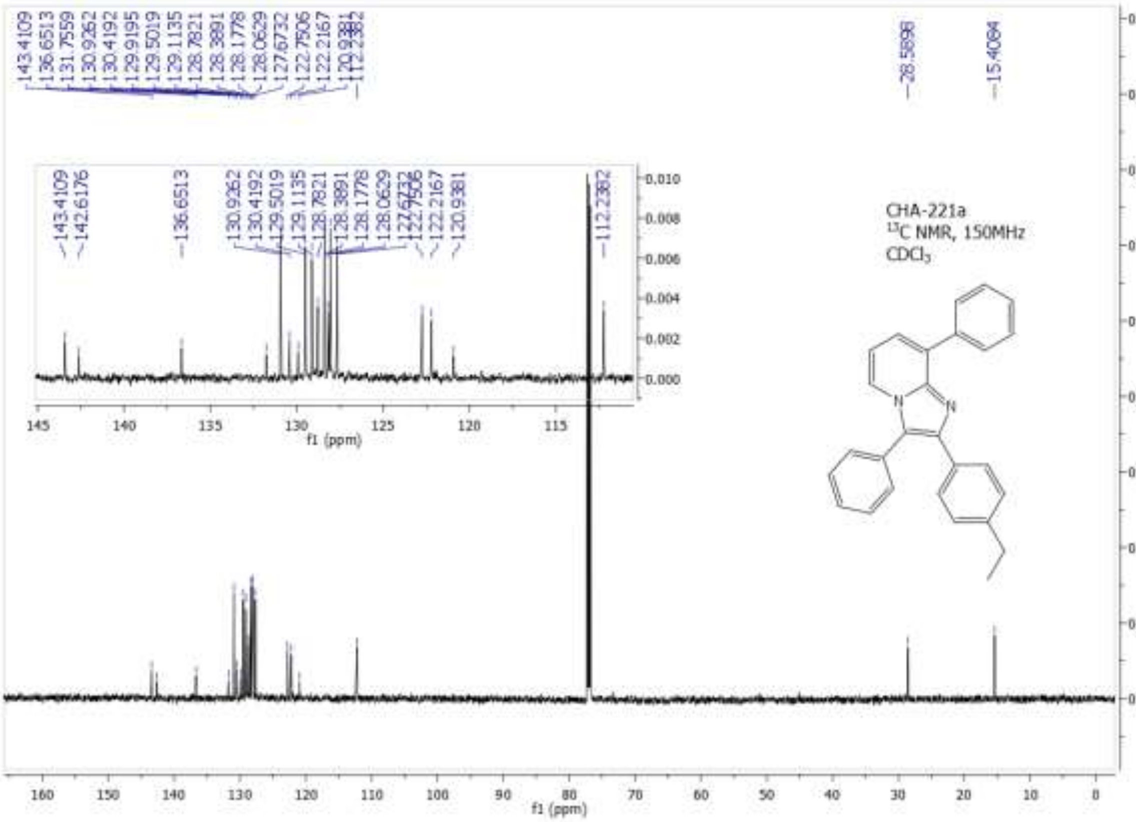


[1]H NMR of **6i**



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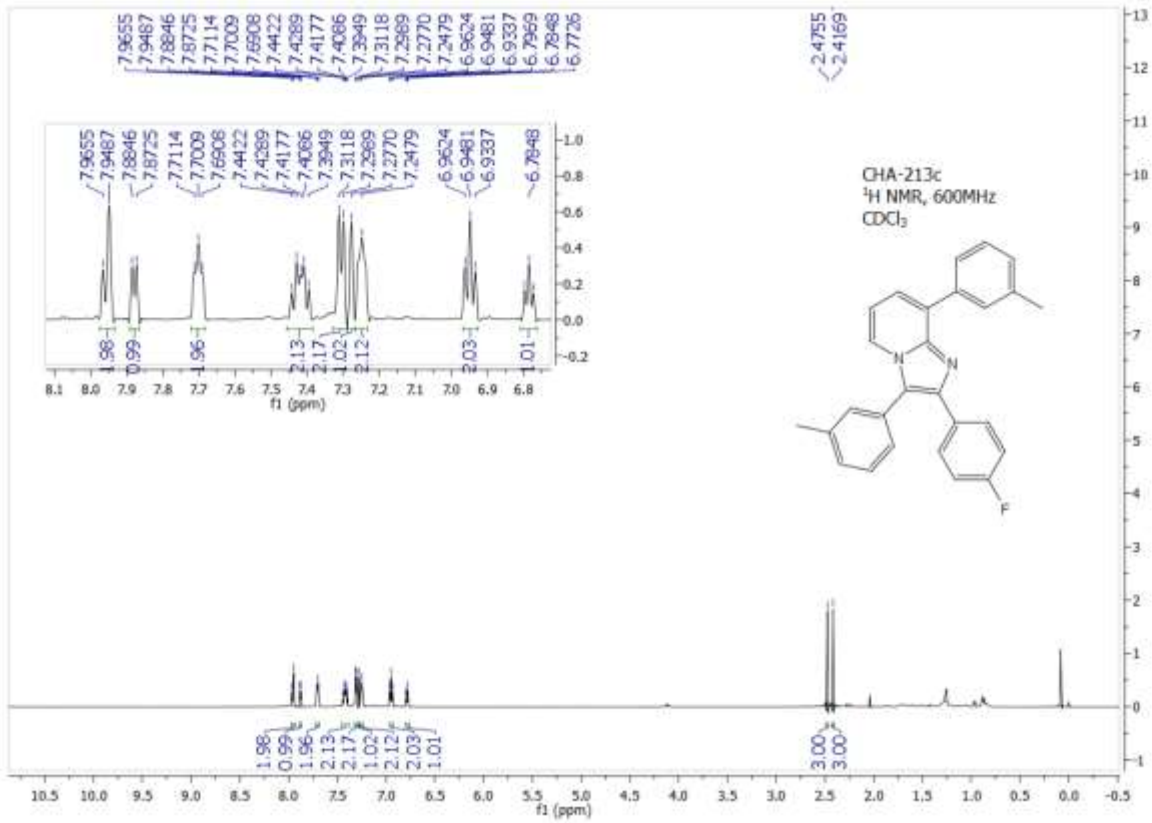

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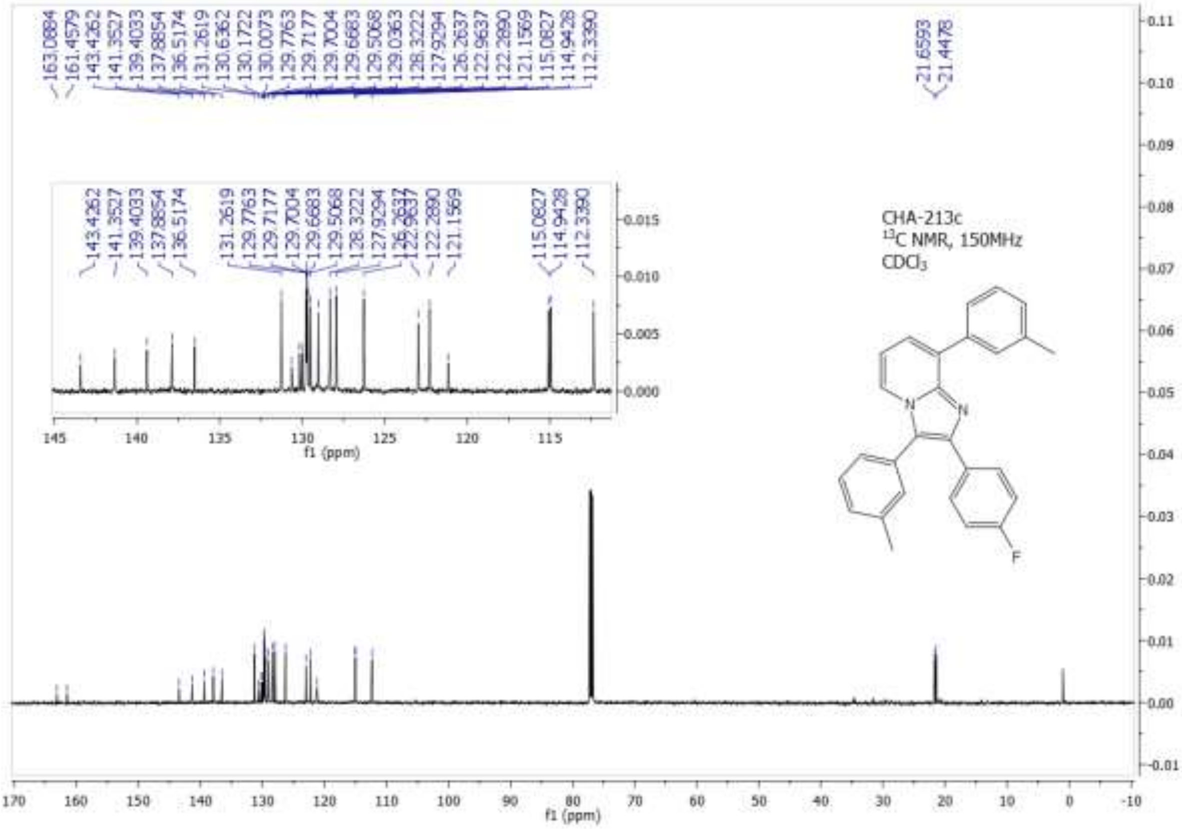

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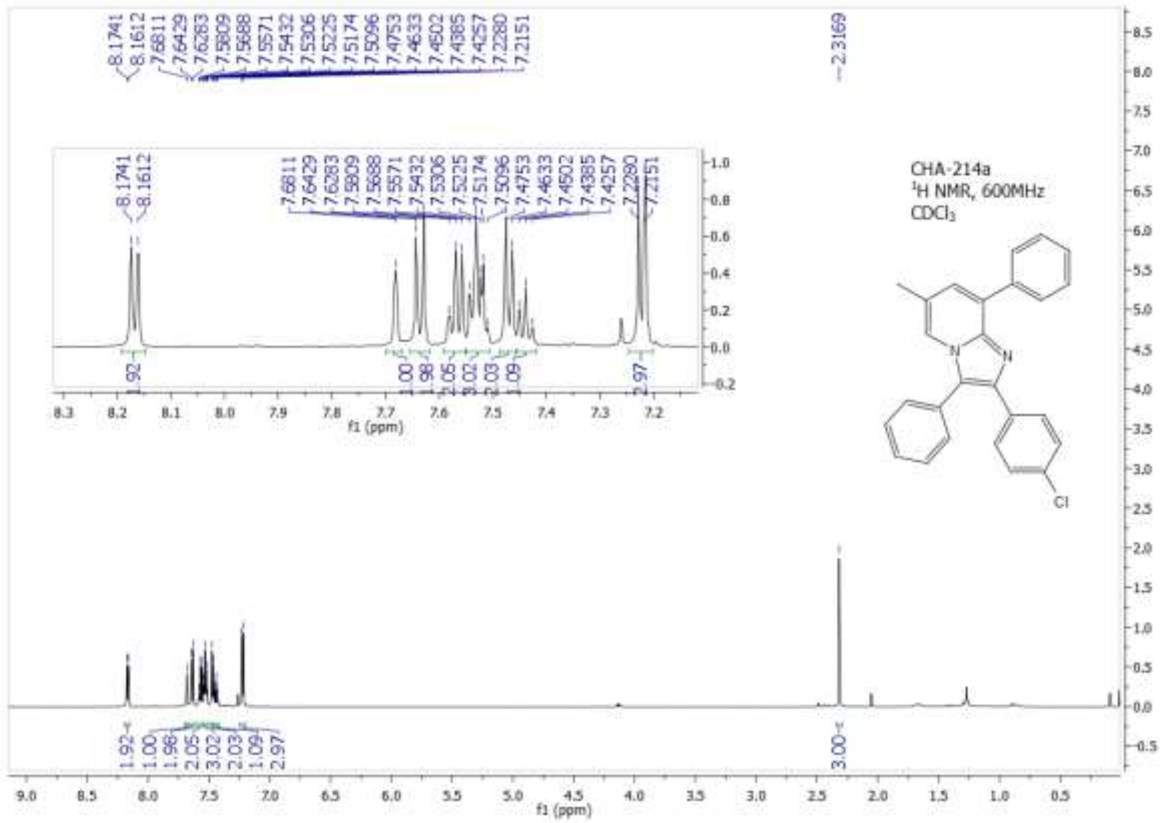

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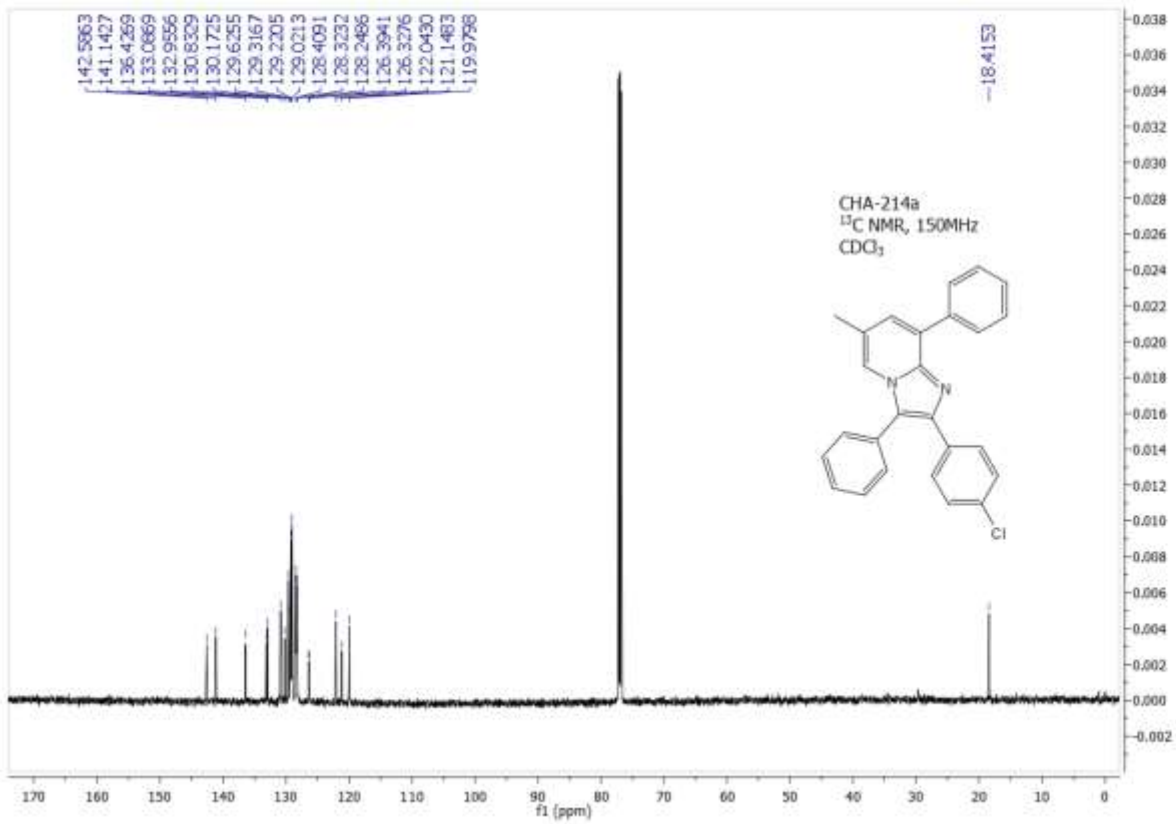

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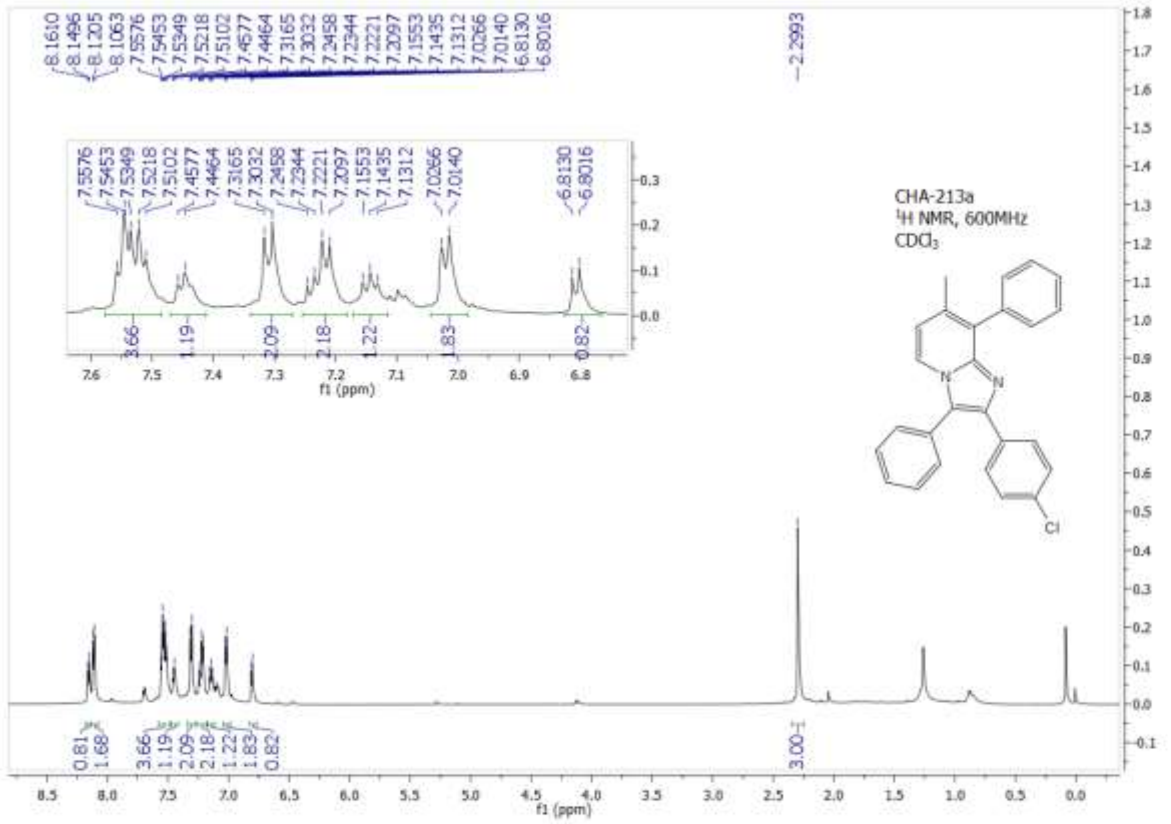

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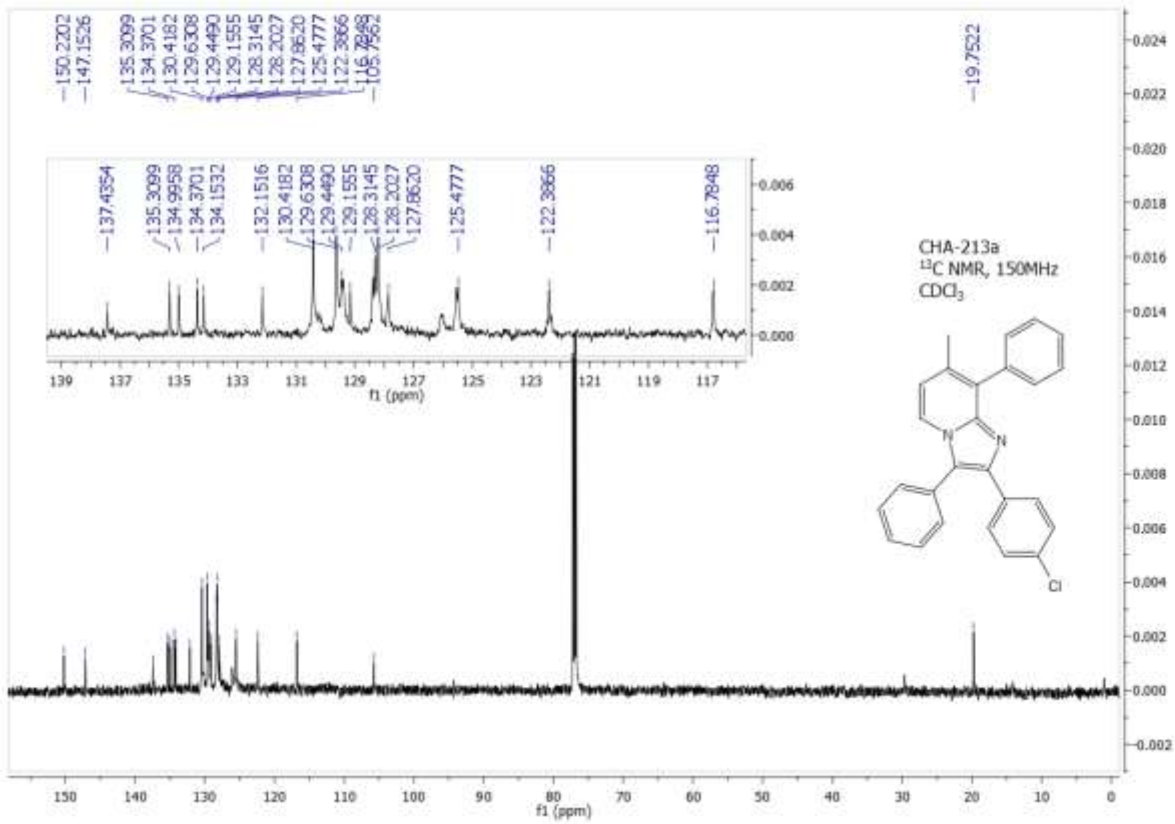

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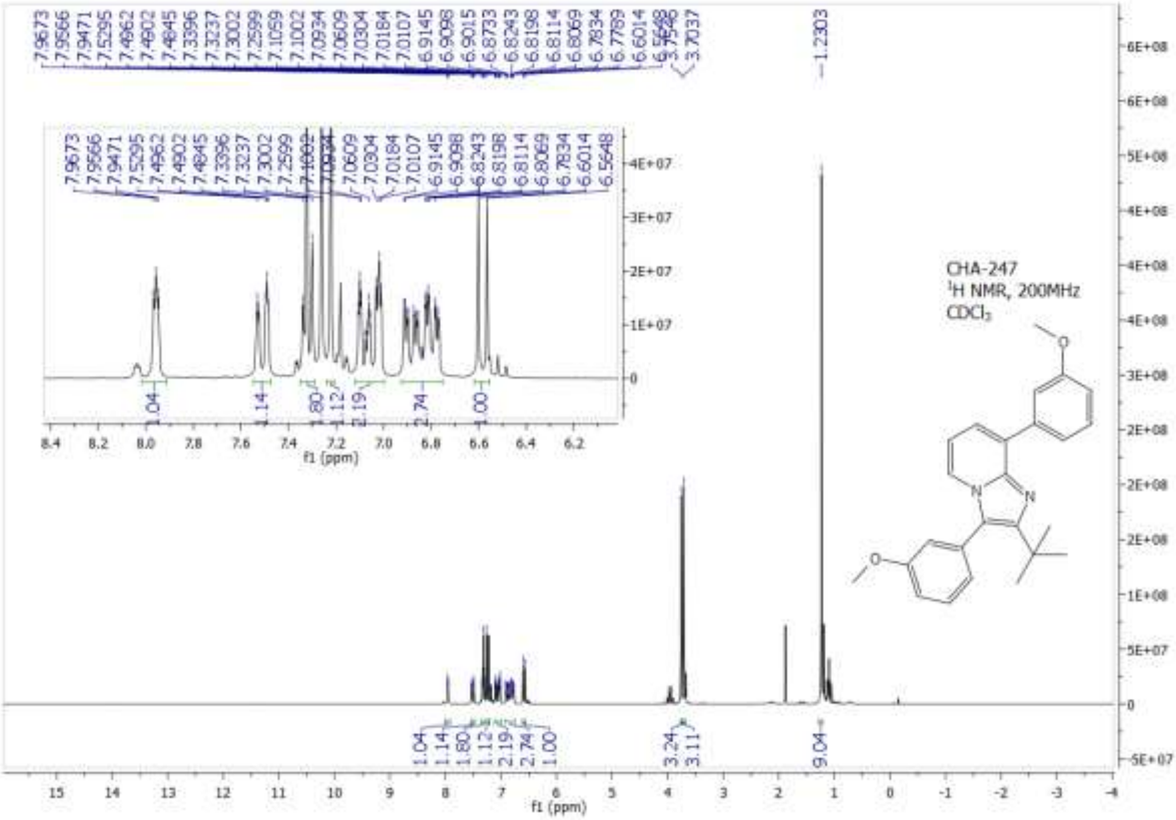

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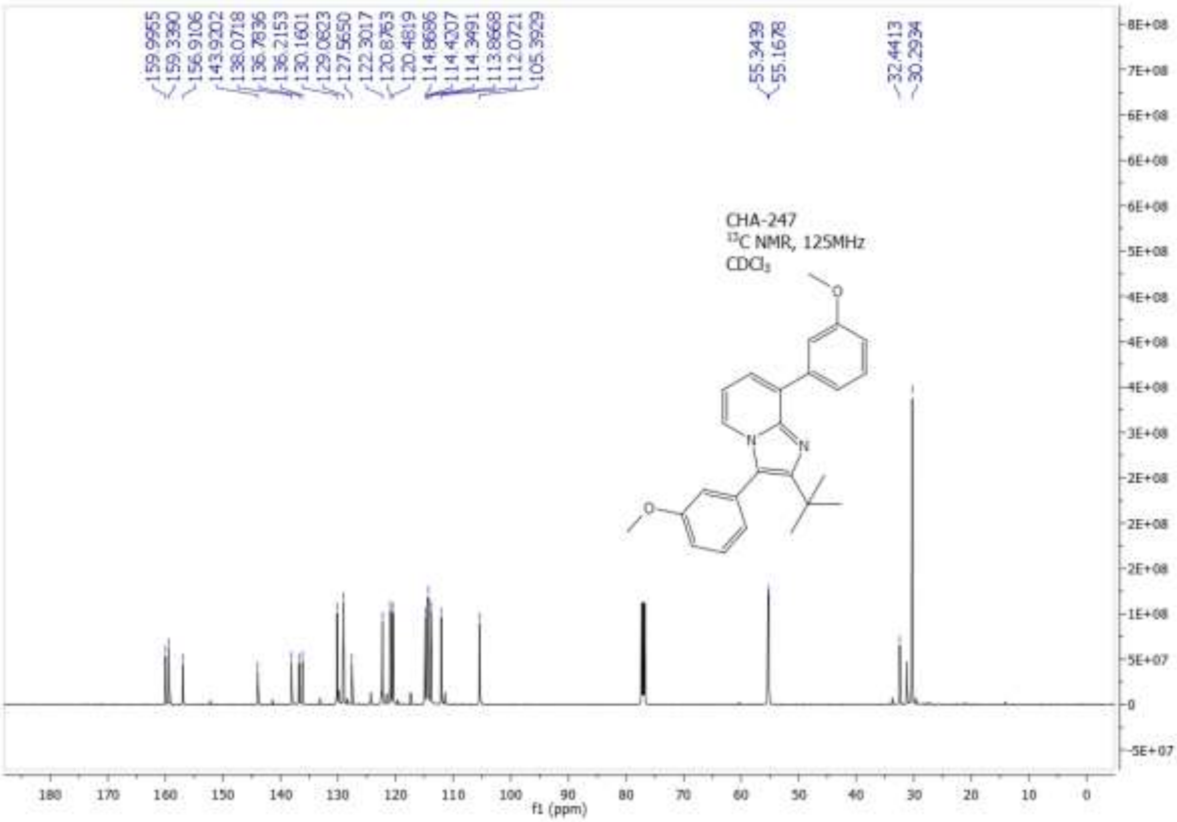
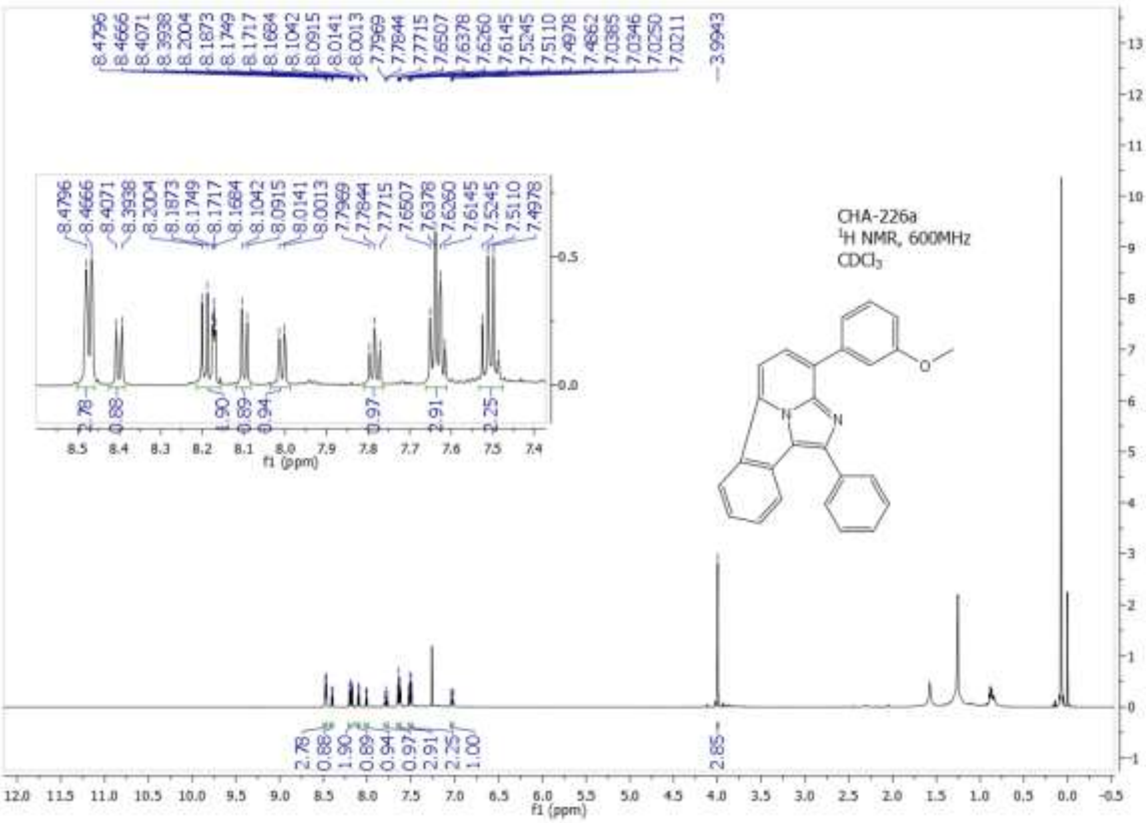


^{13}C NMR of **6m**



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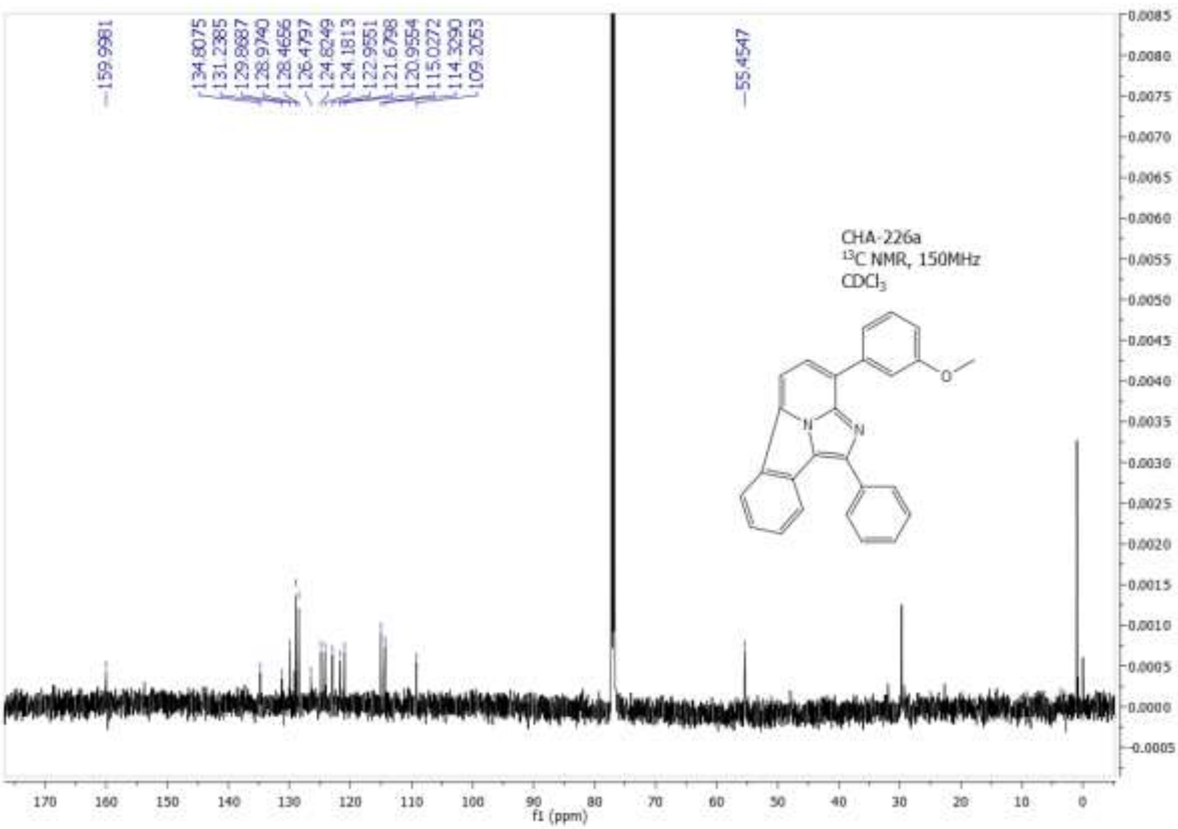

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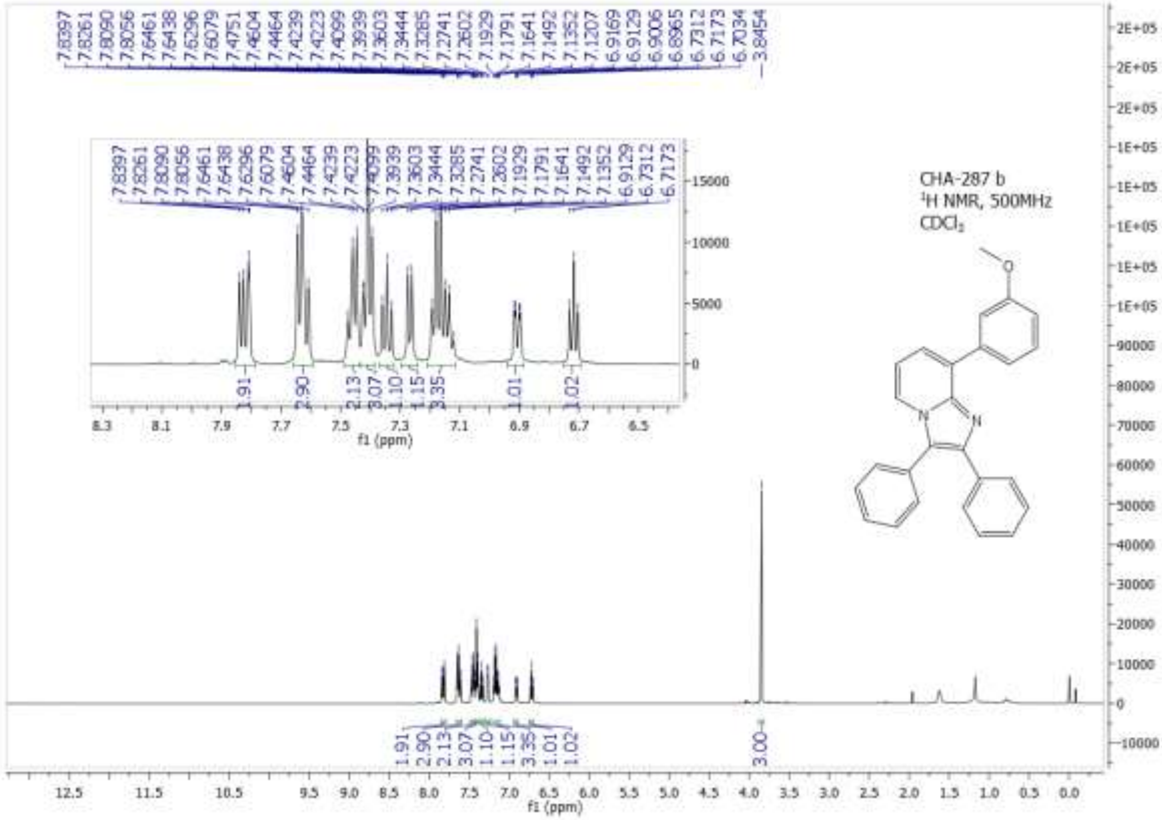
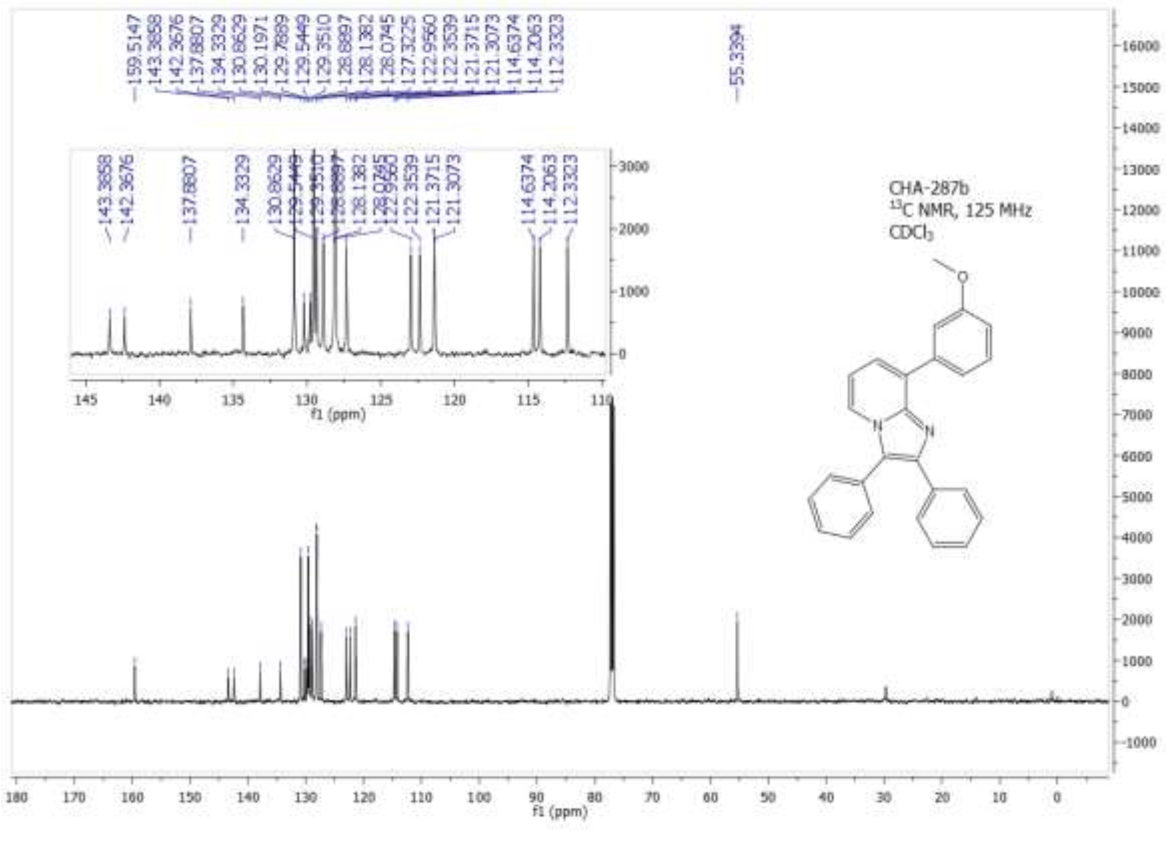


[1]H NMR of **6p**



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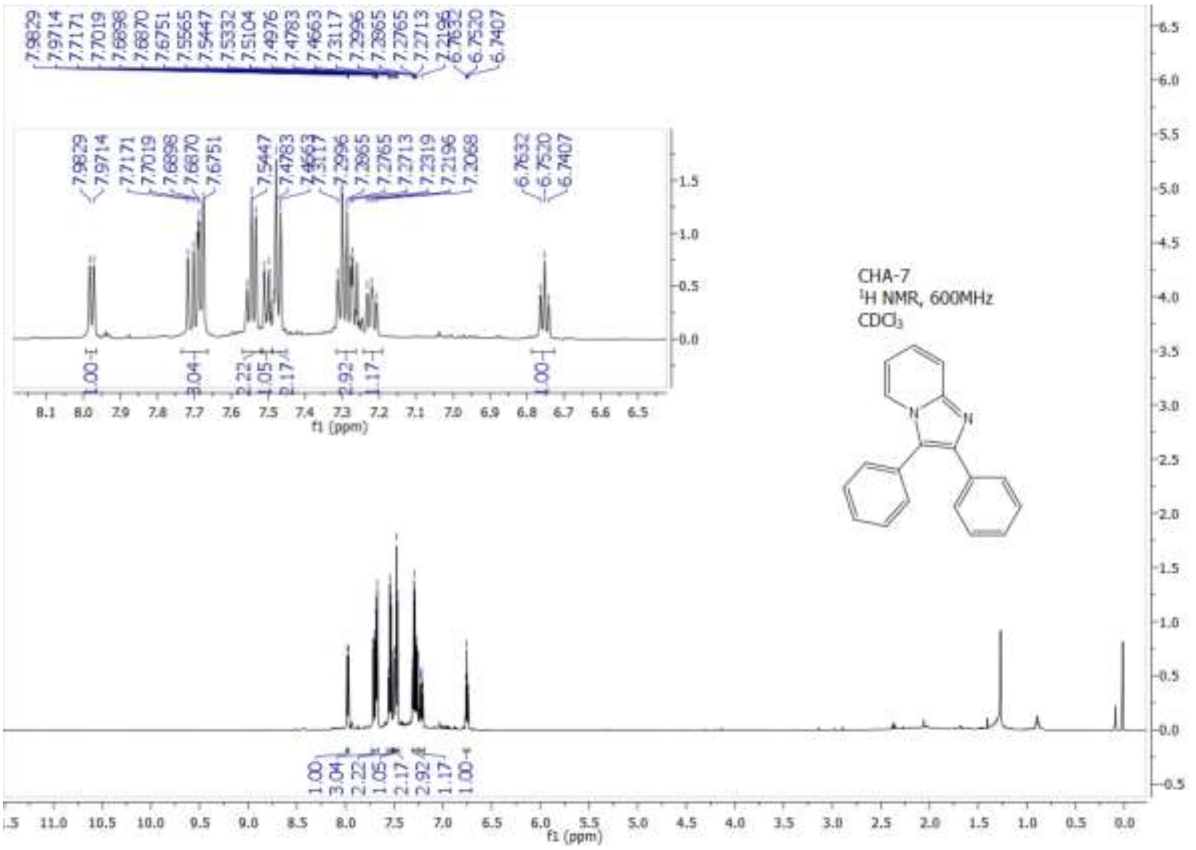
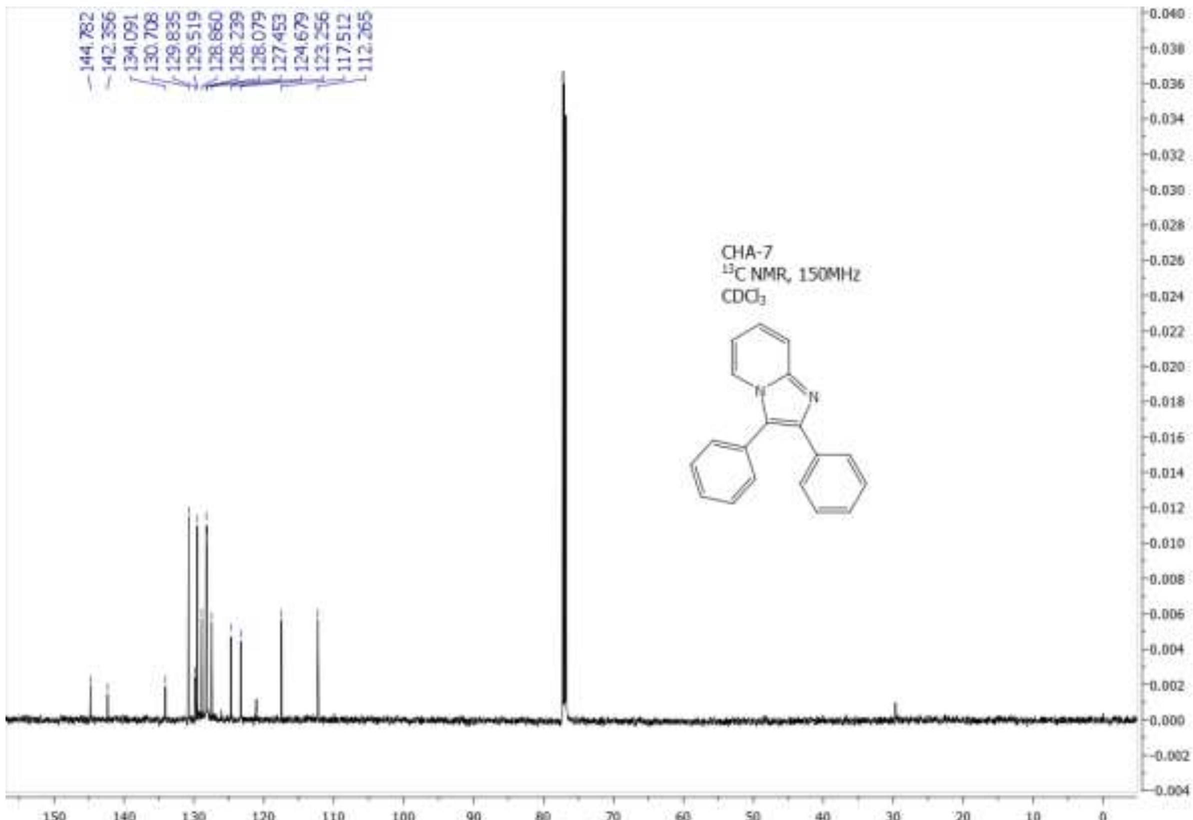


^{1}H NMR of **7**



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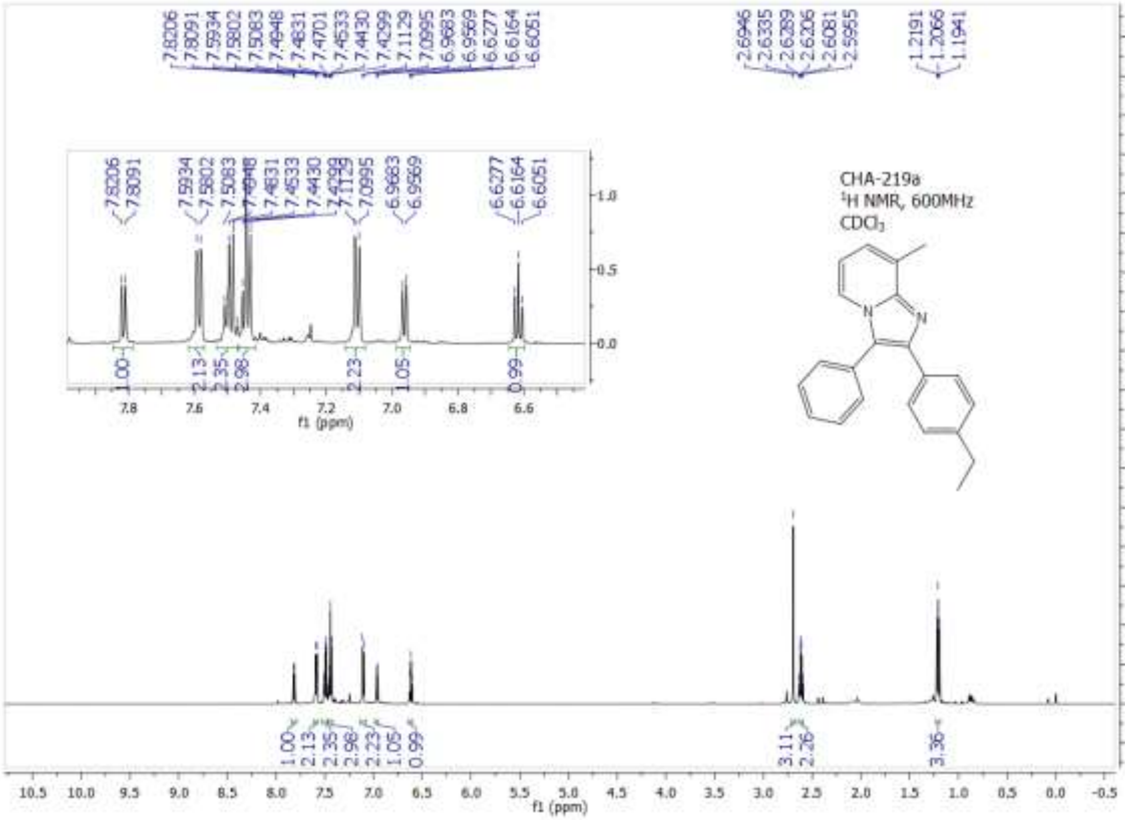
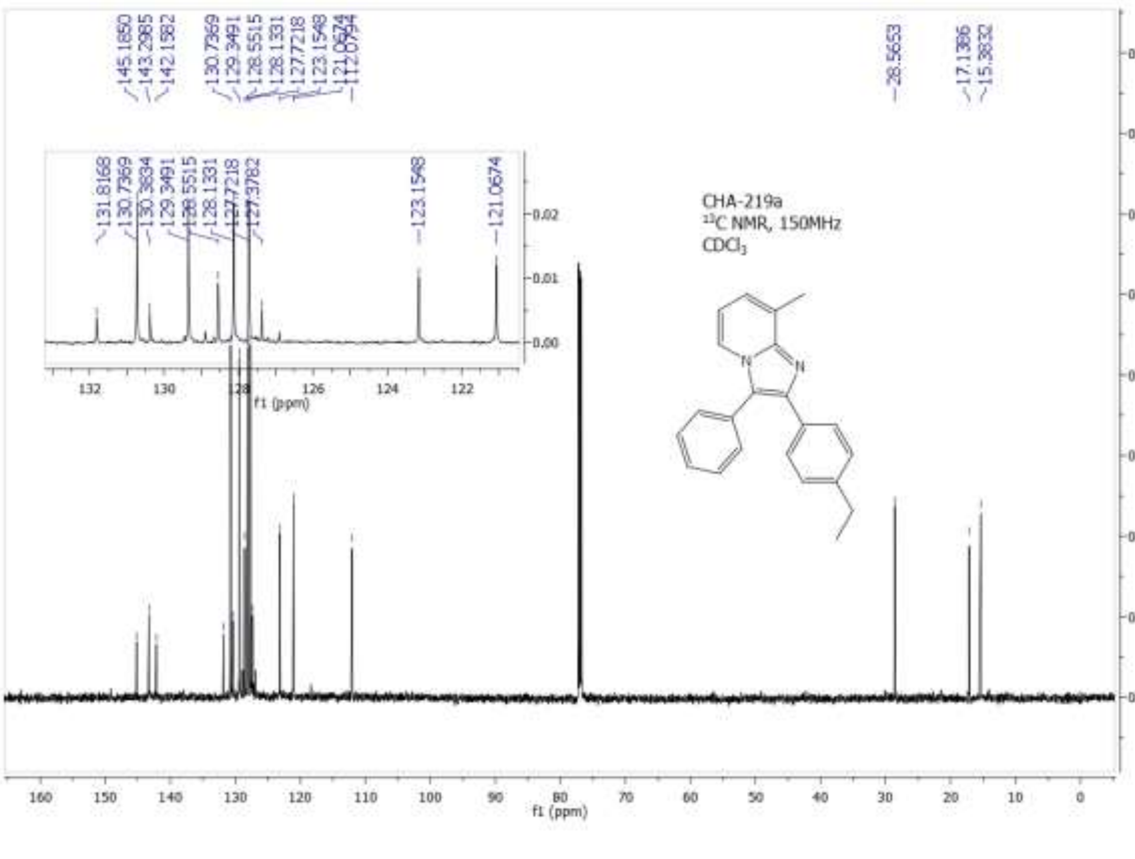


^{1}H NMR of **9**



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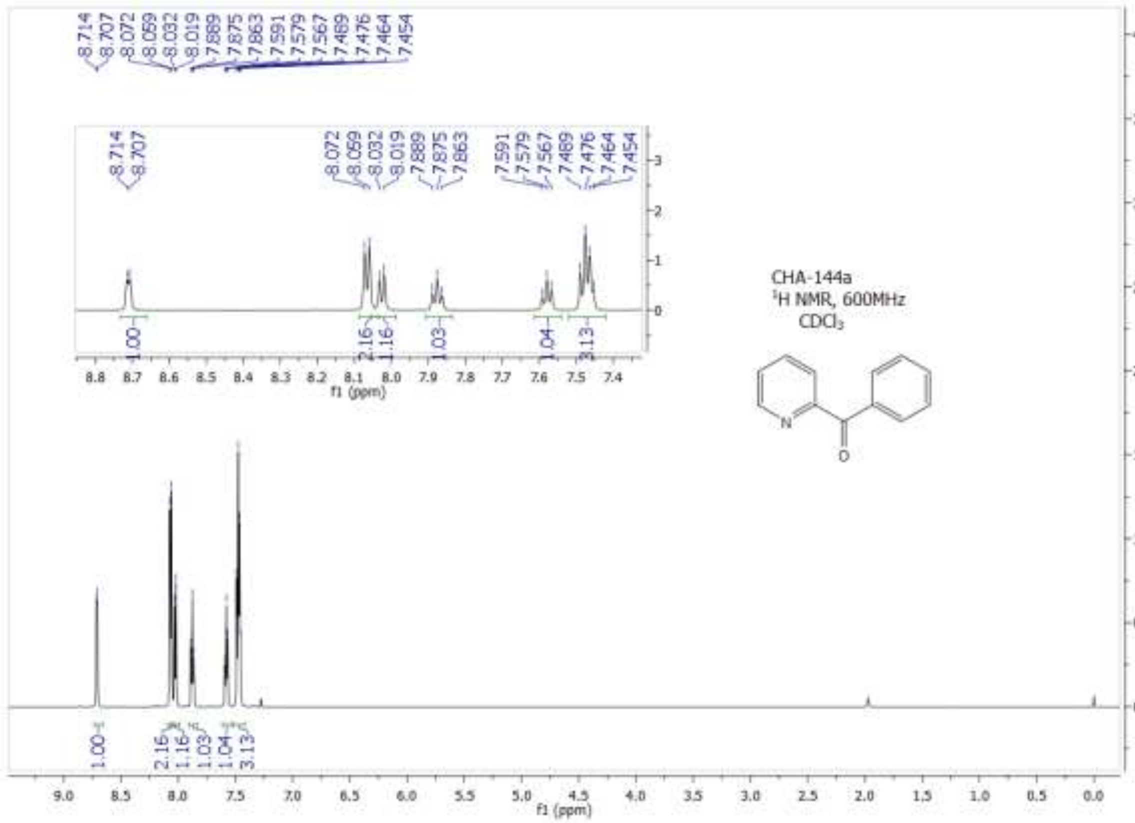
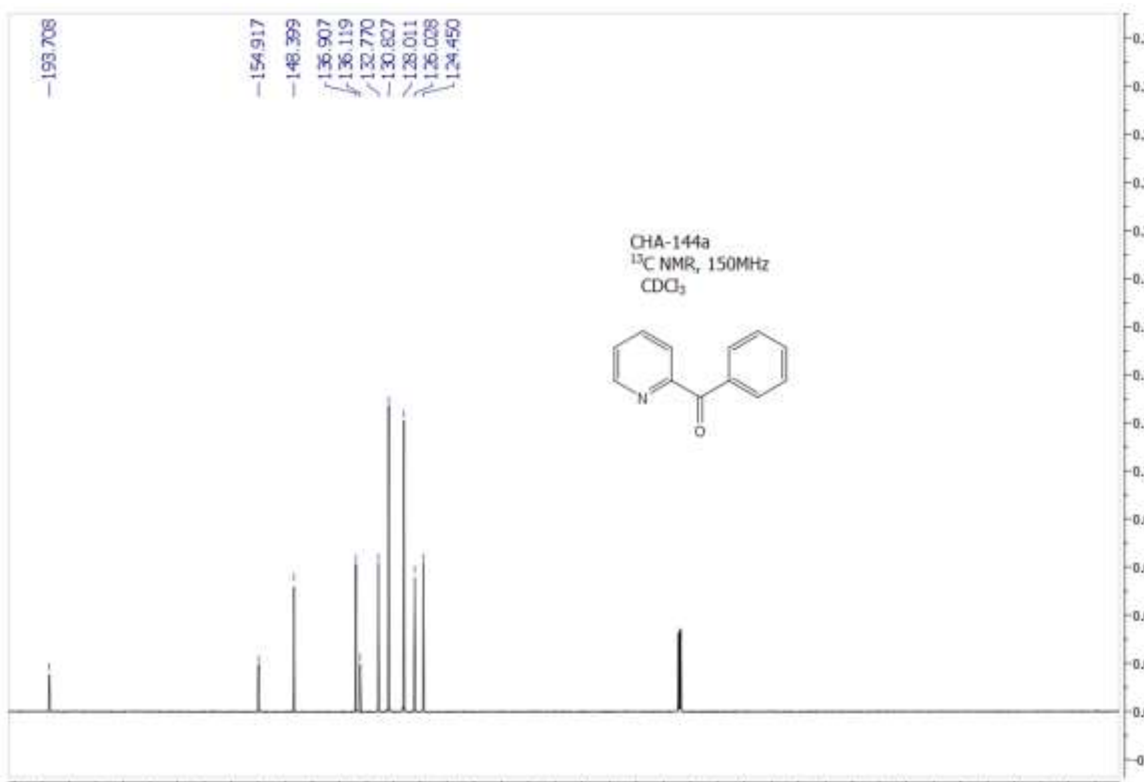
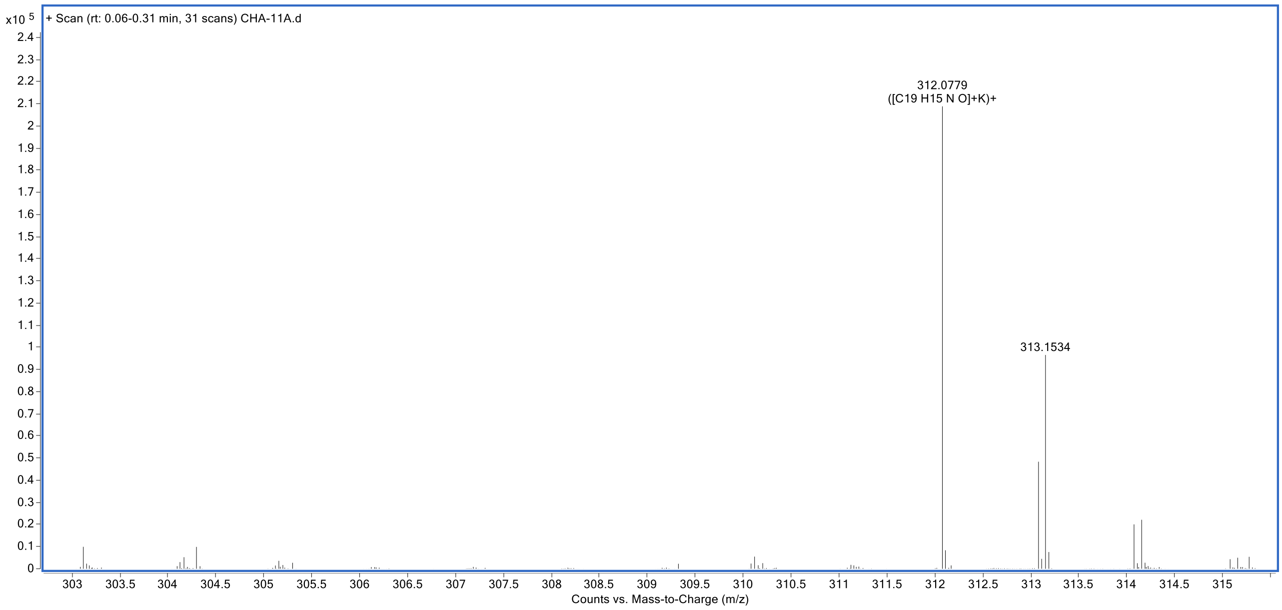


[1]H NMR of **11**

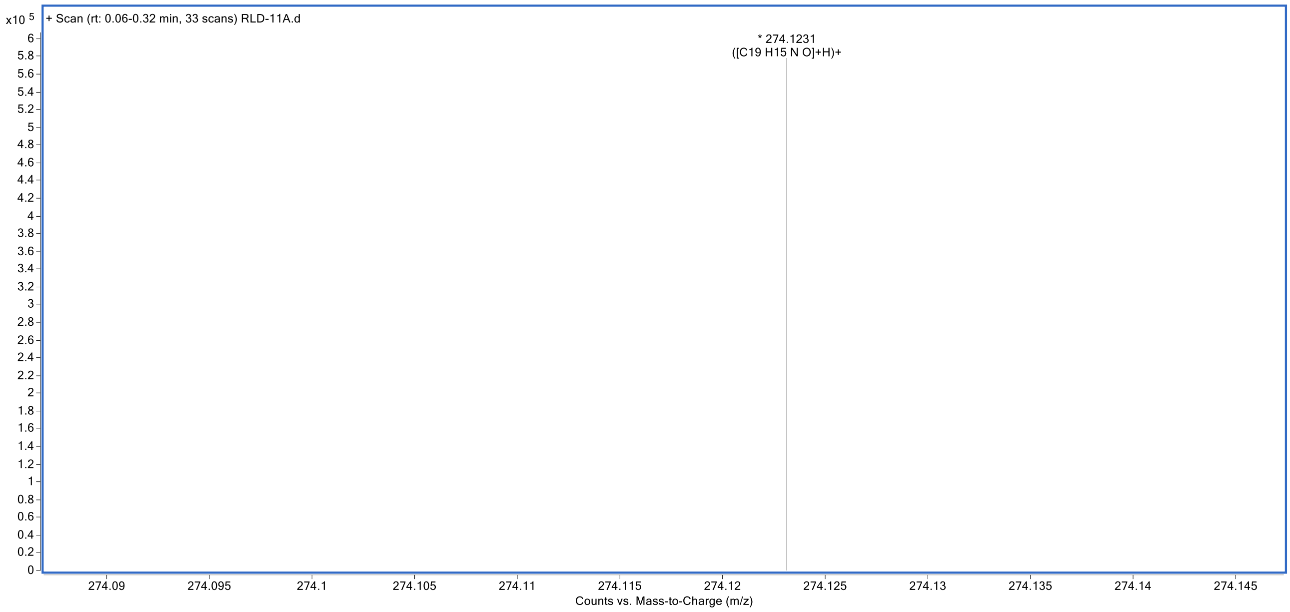


[13]C NMR of **11**

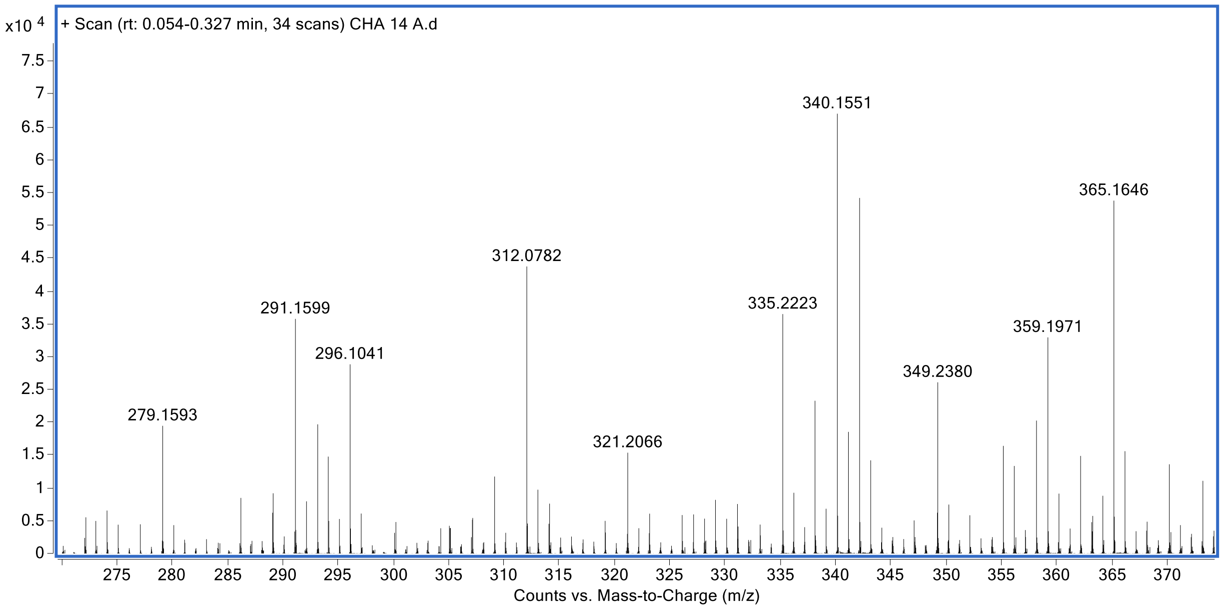
Copies of HRMS Spectra for New Compounds



HRMS of **3b**



HRMS of **3c**



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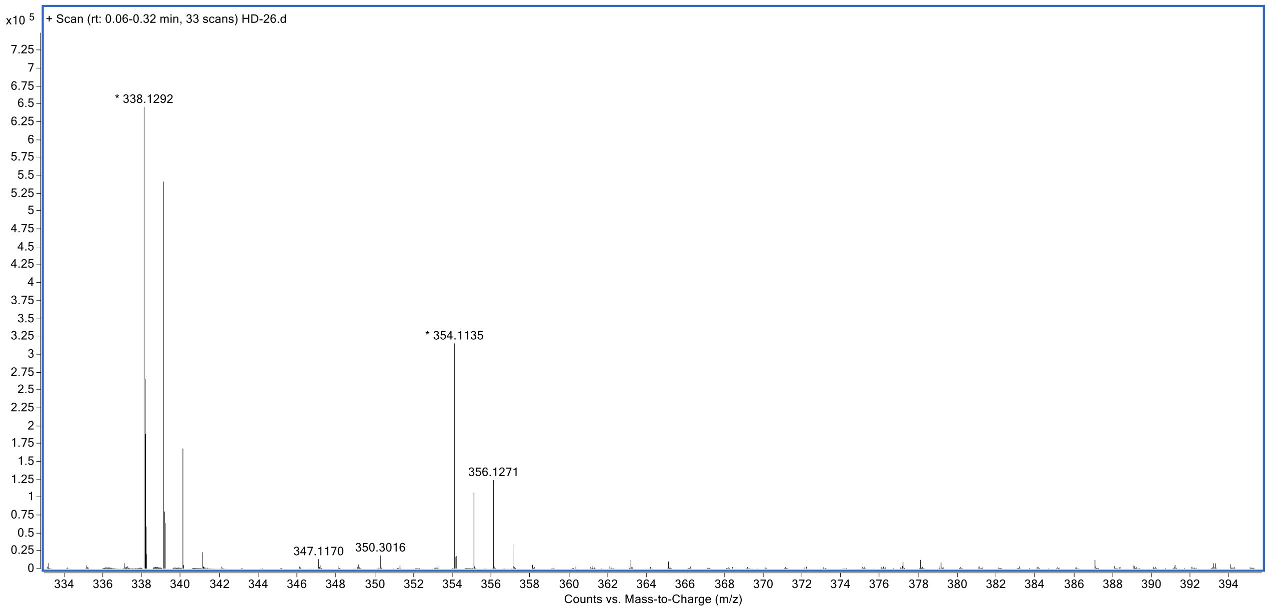

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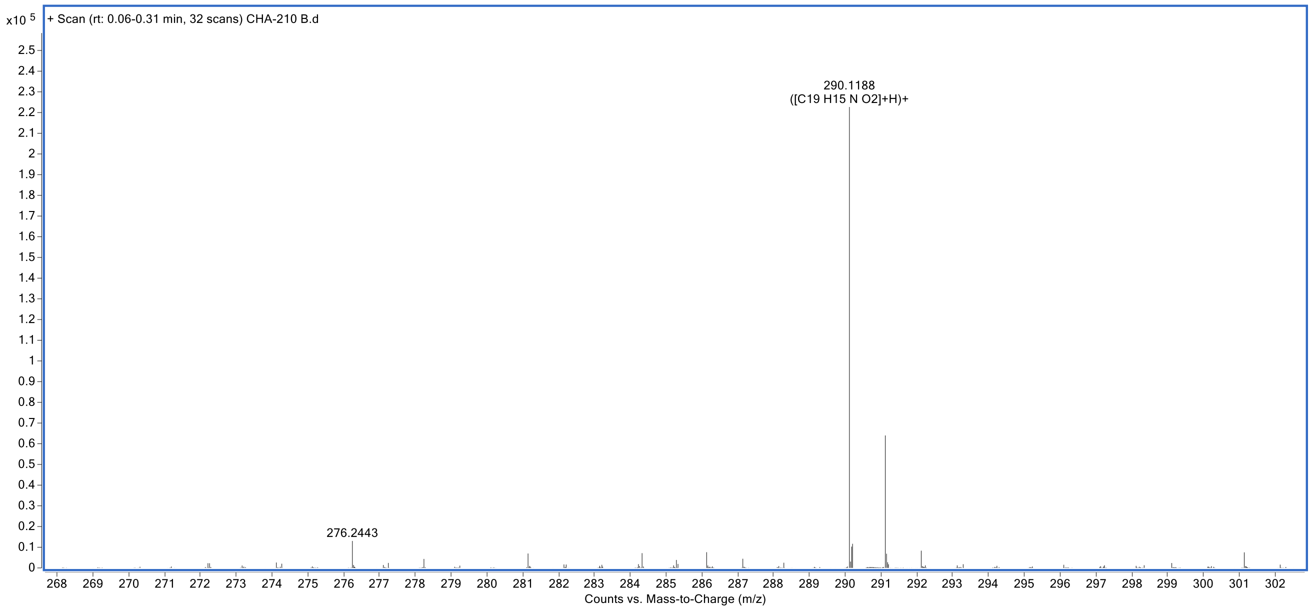

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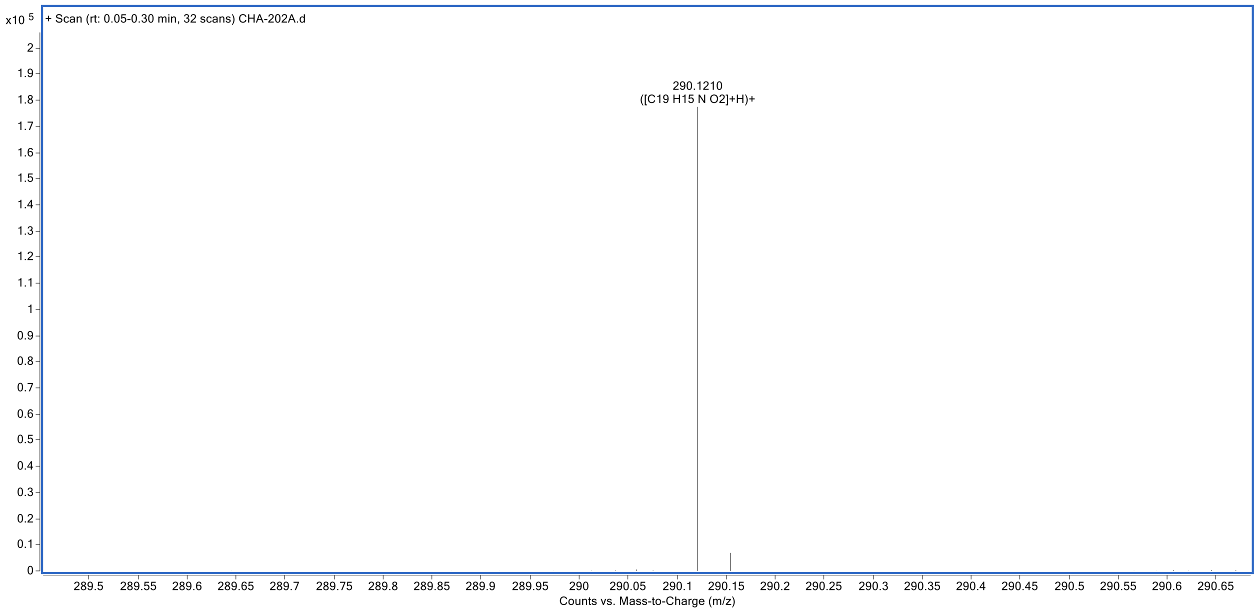

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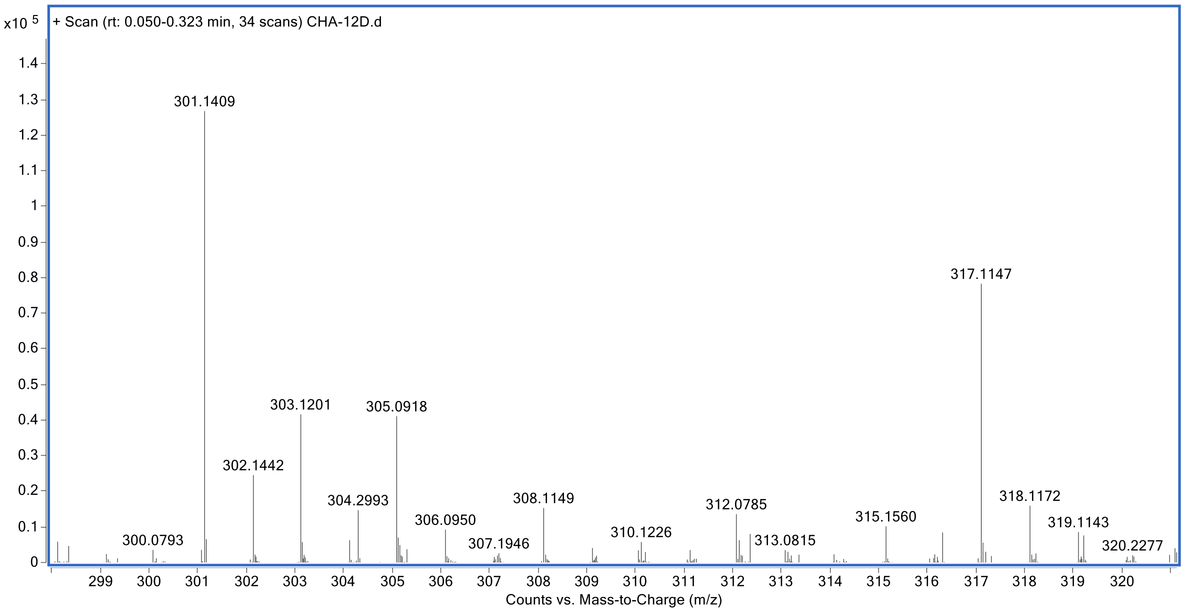

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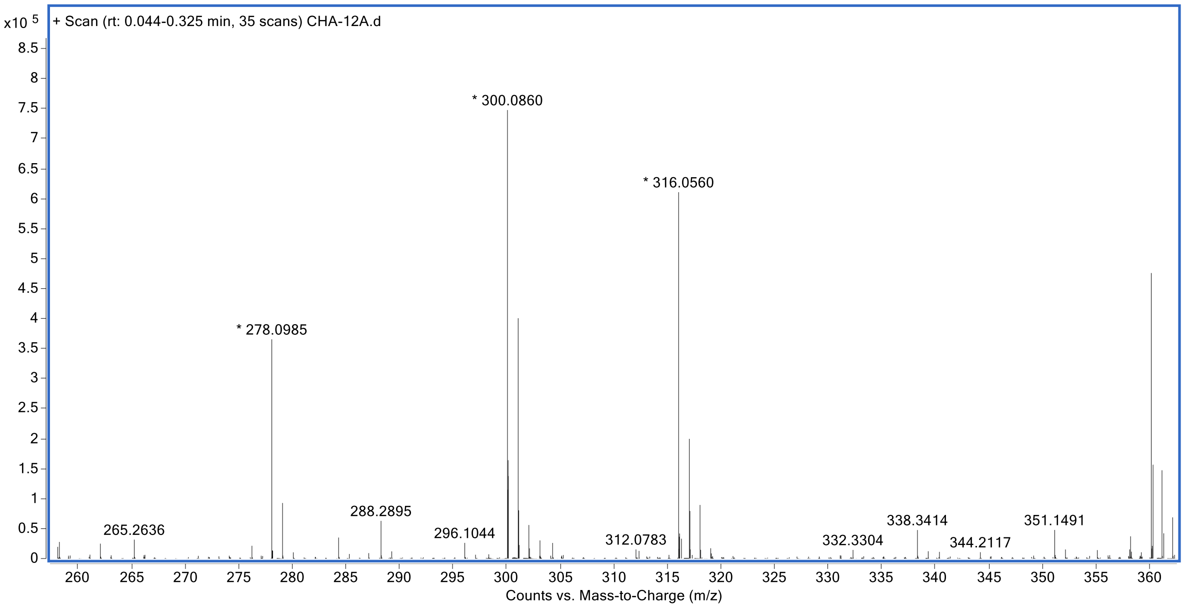

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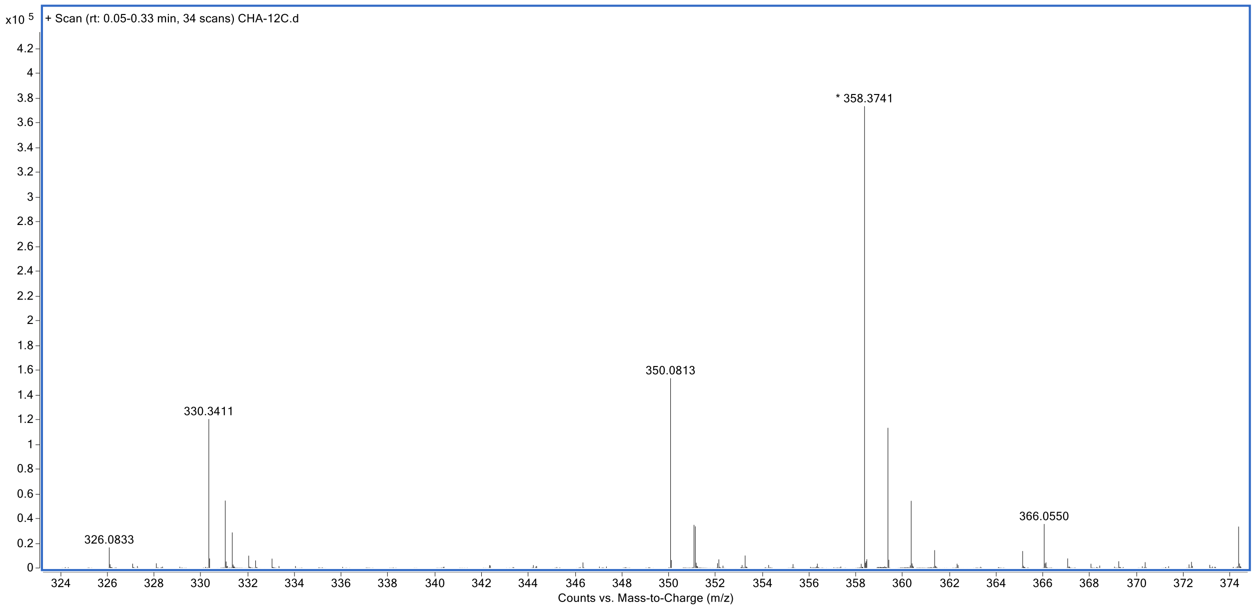

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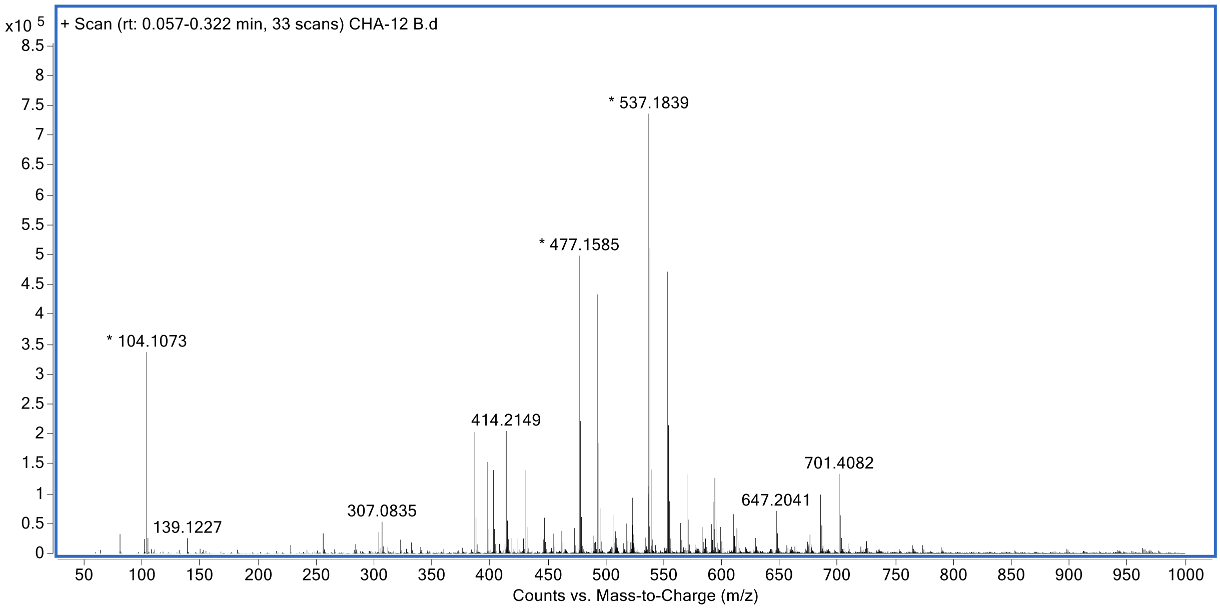

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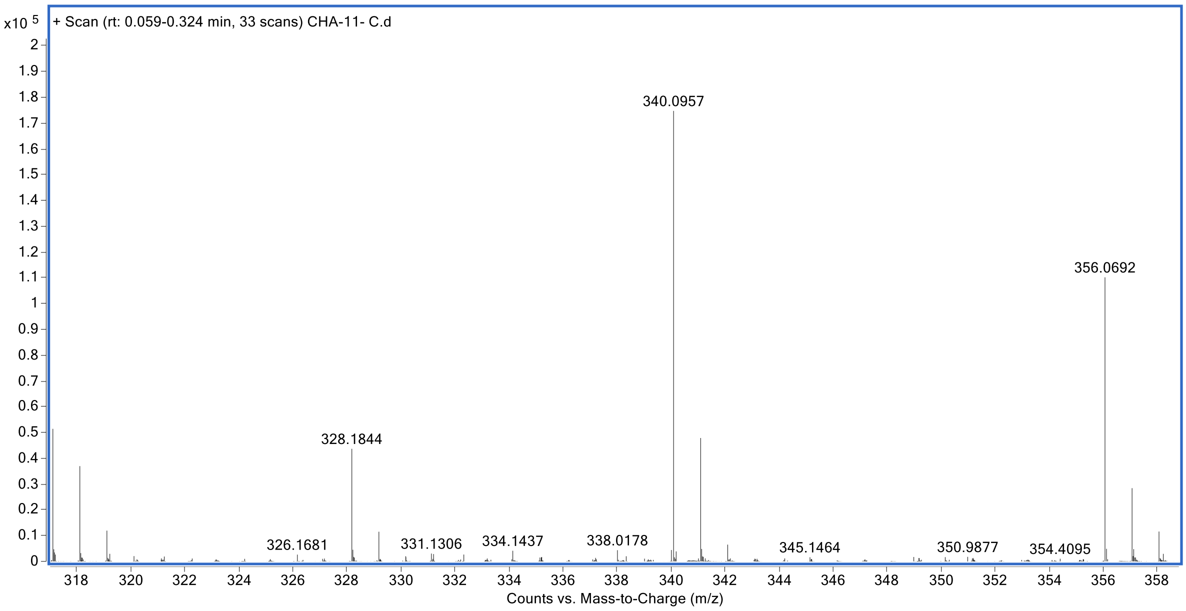

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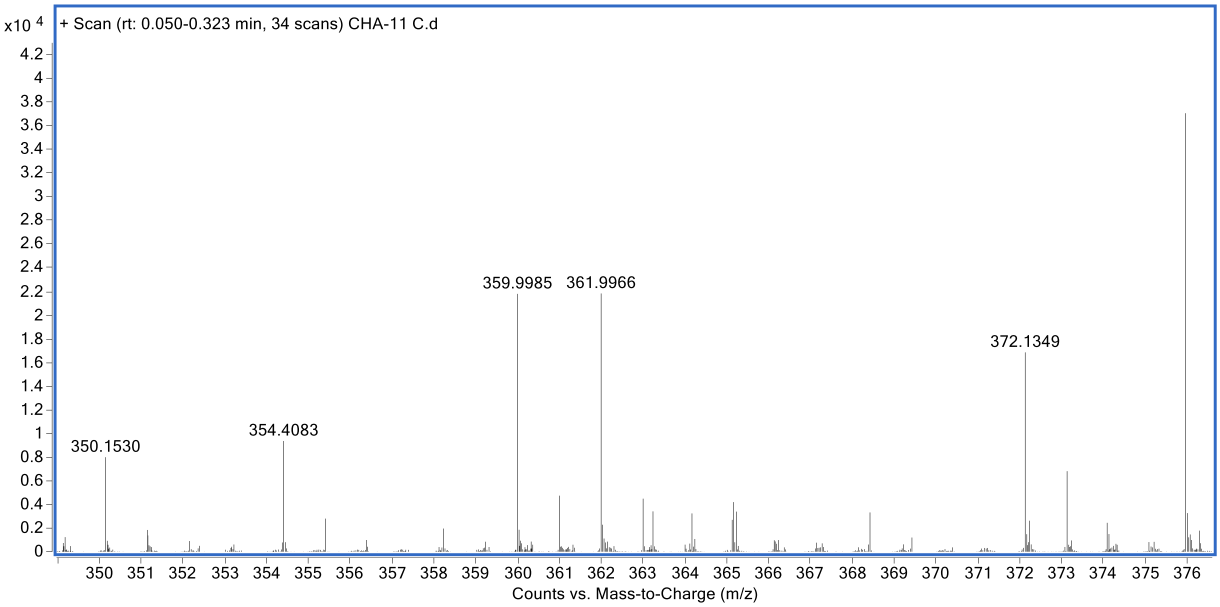

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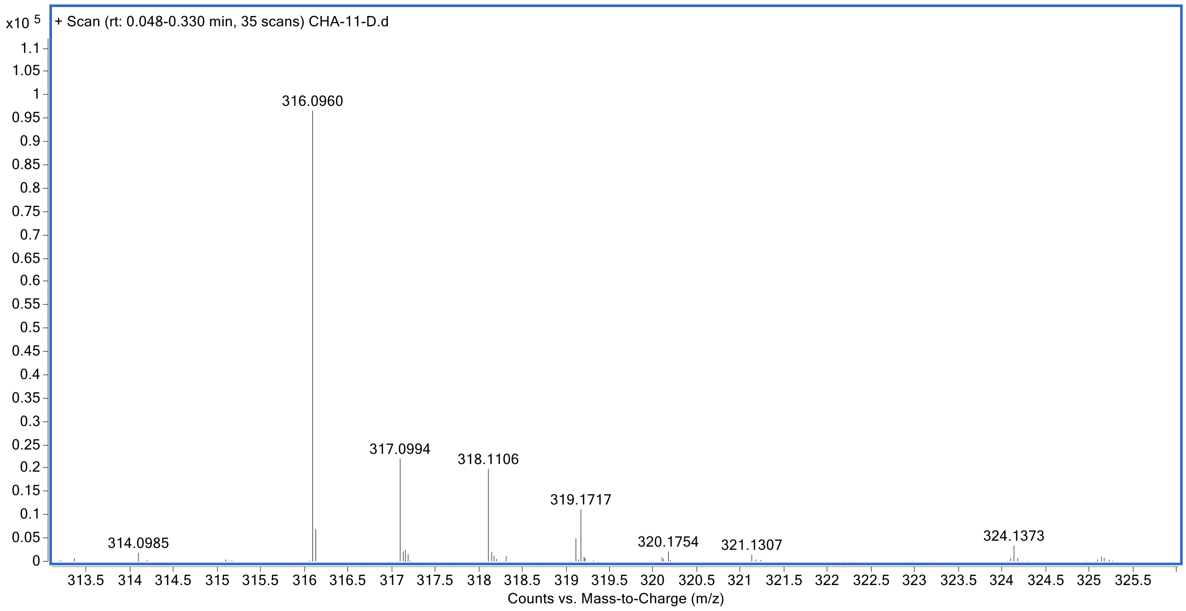

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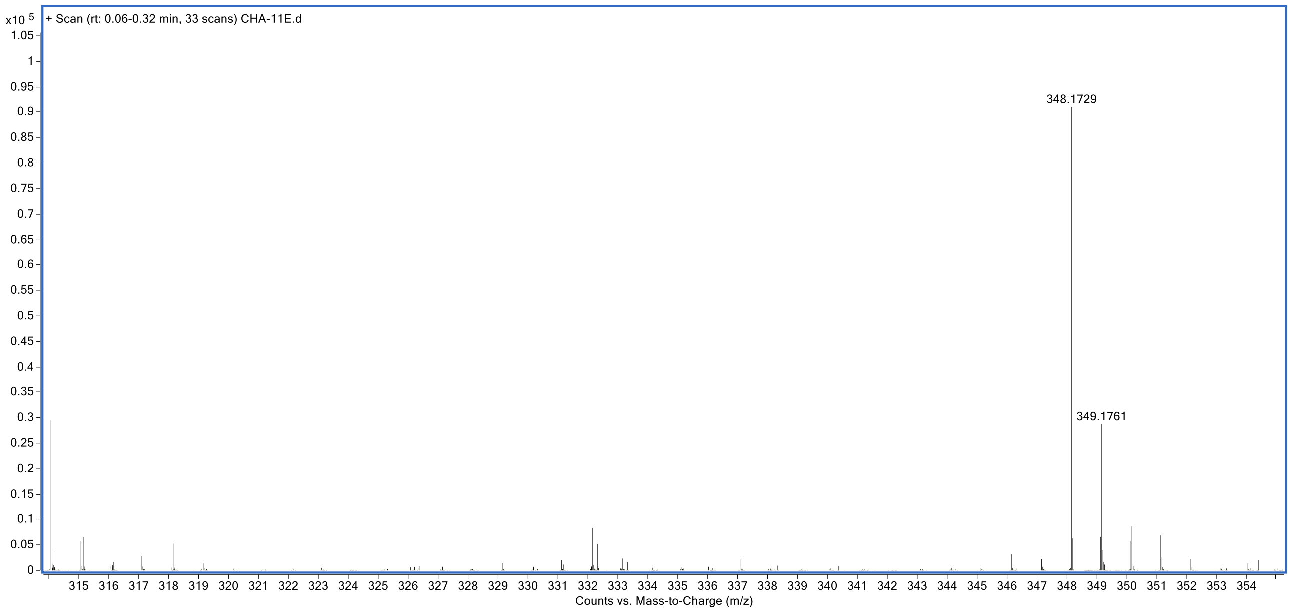

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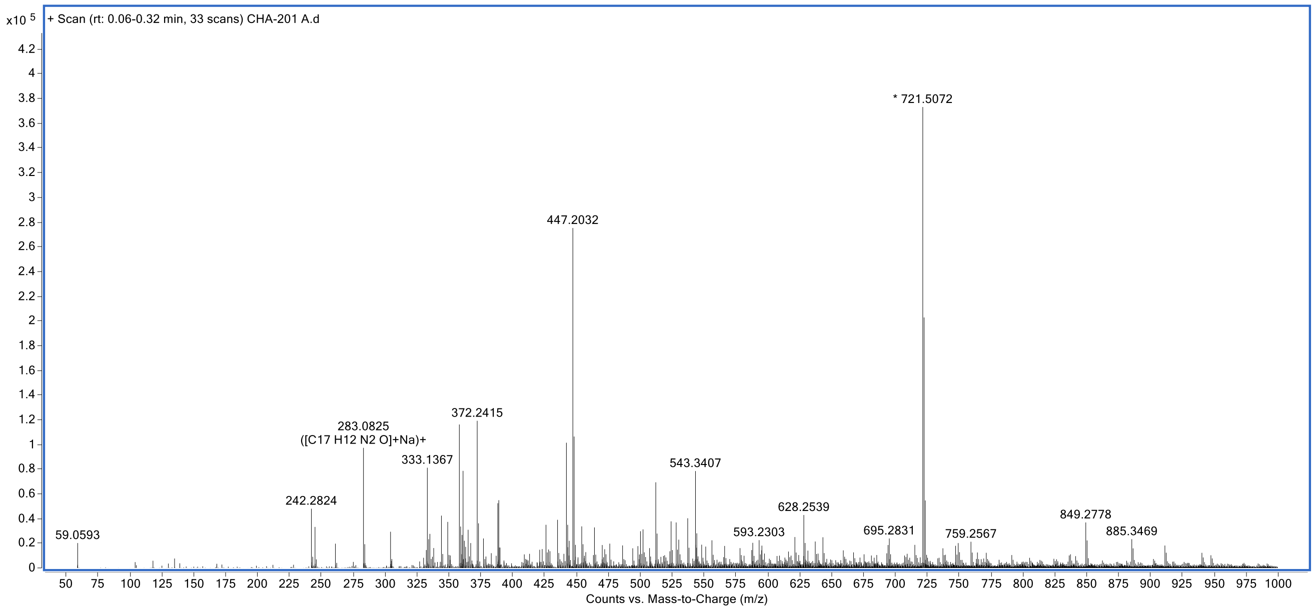

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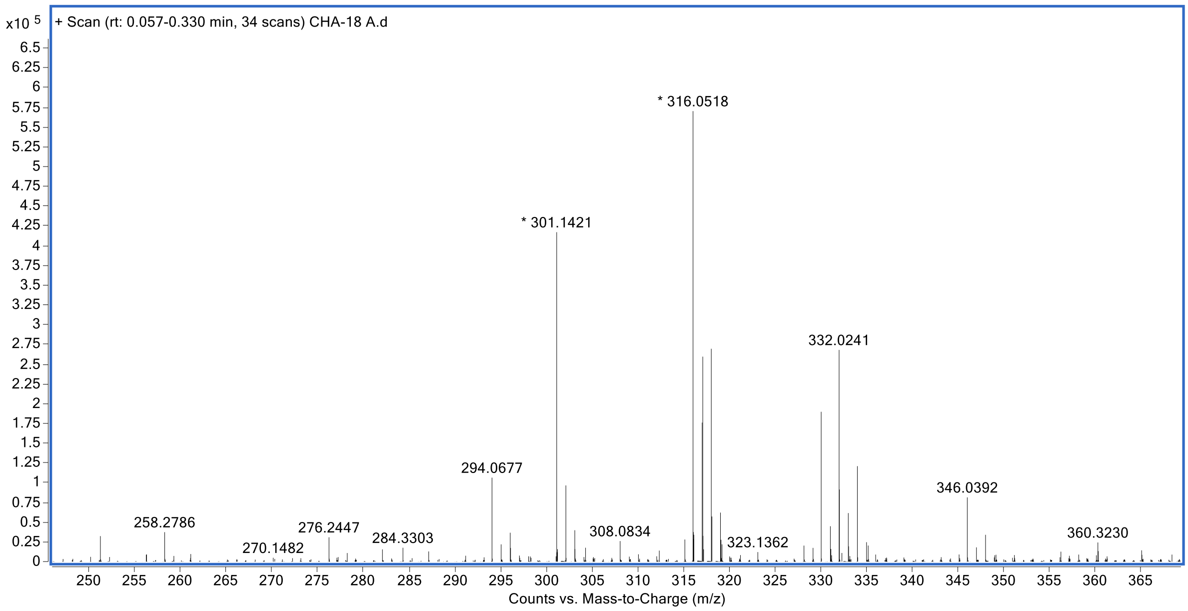

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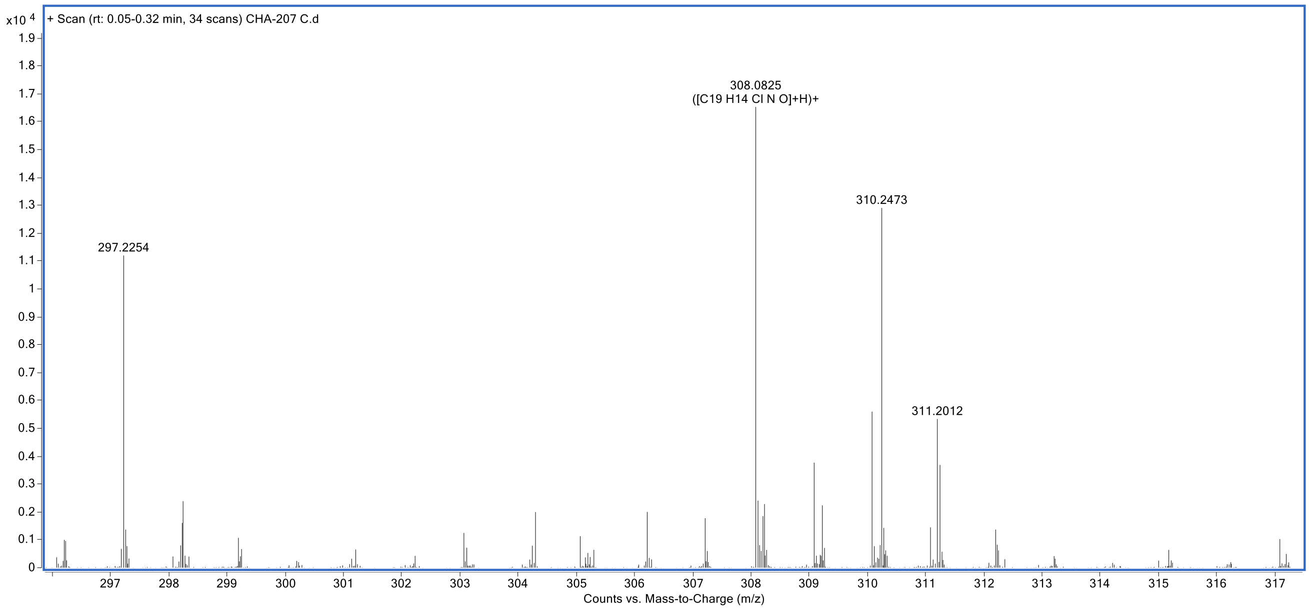

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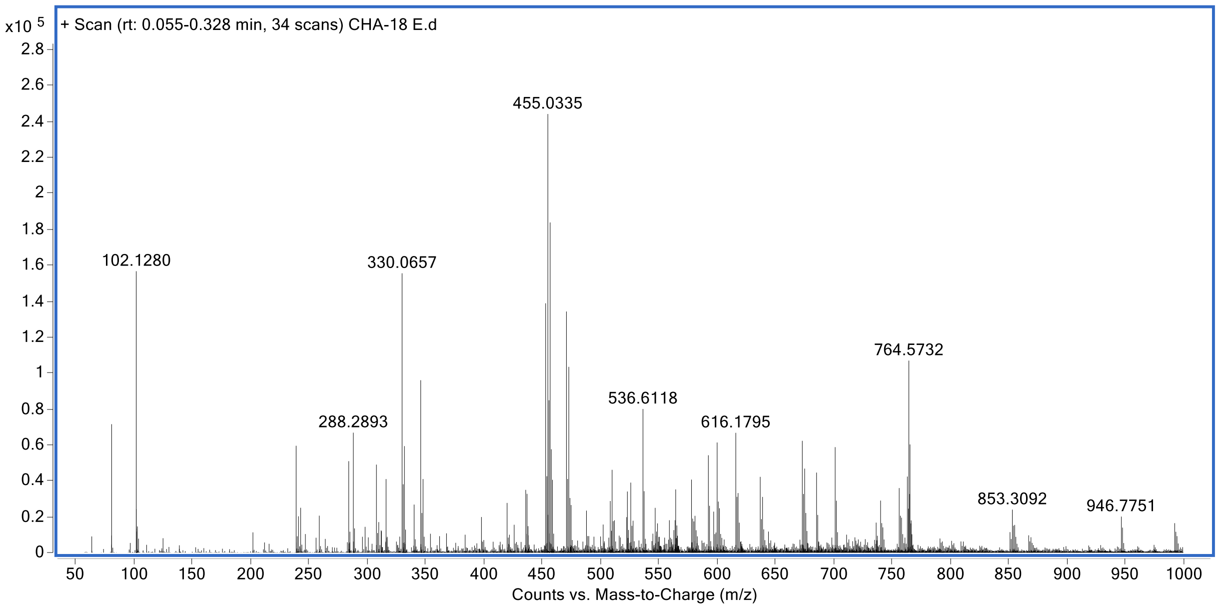

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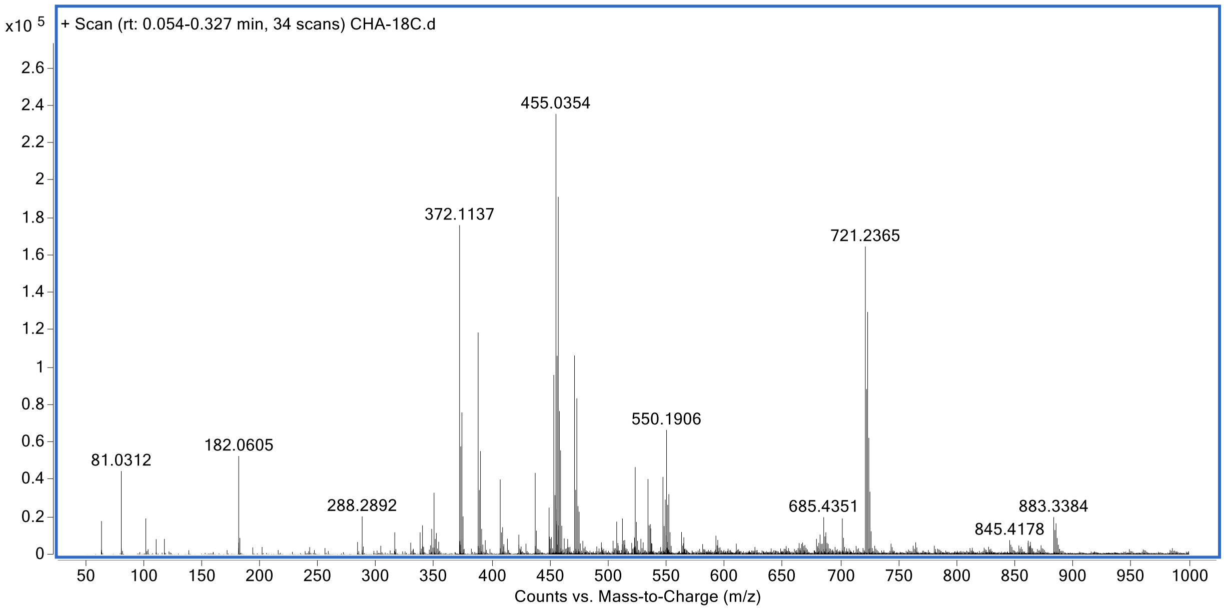

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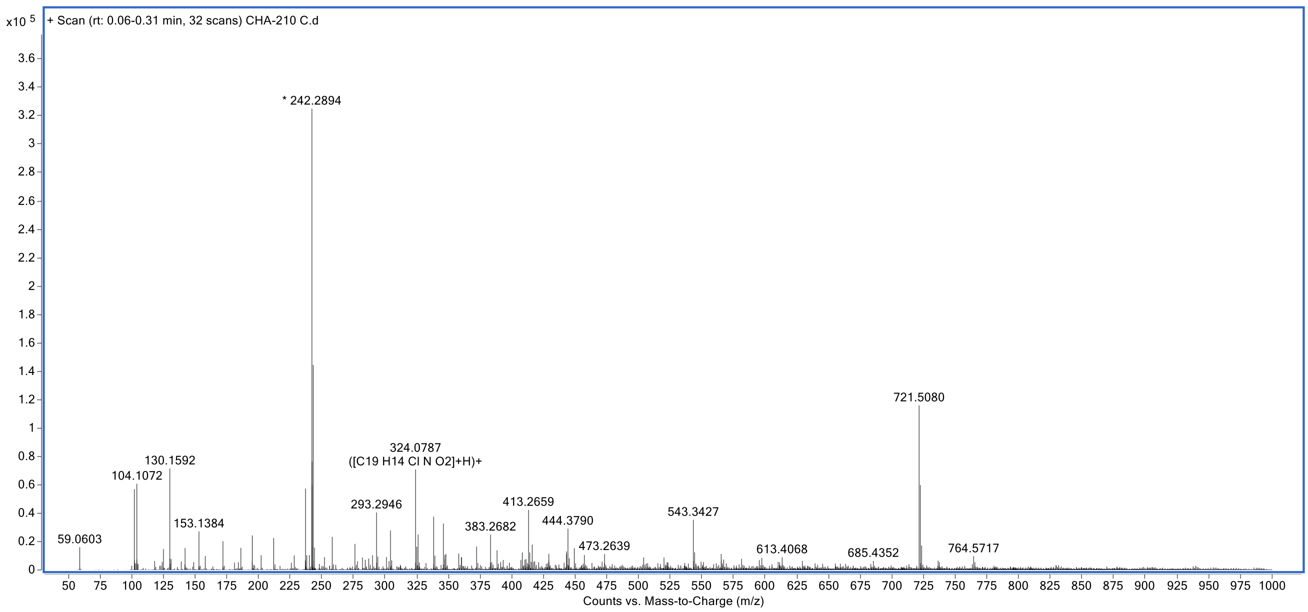

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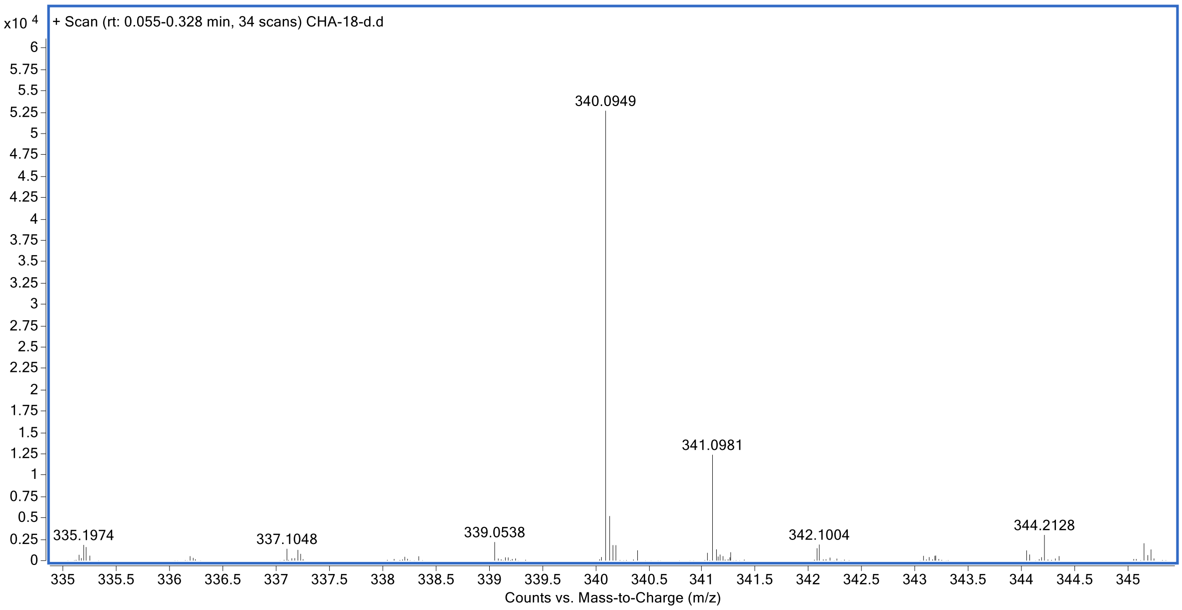

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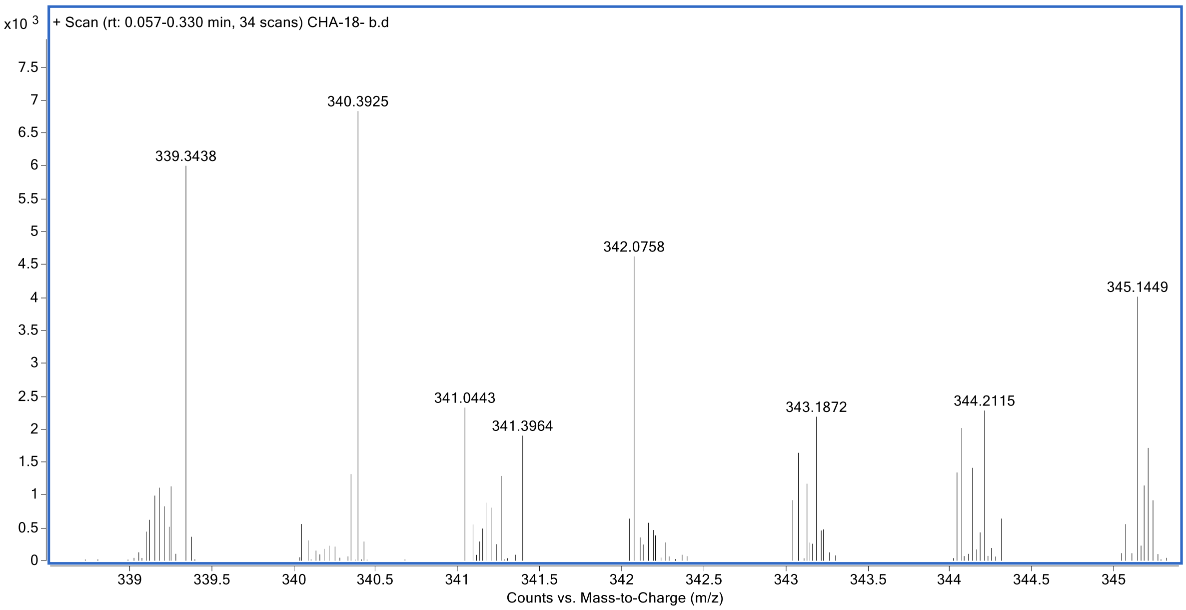

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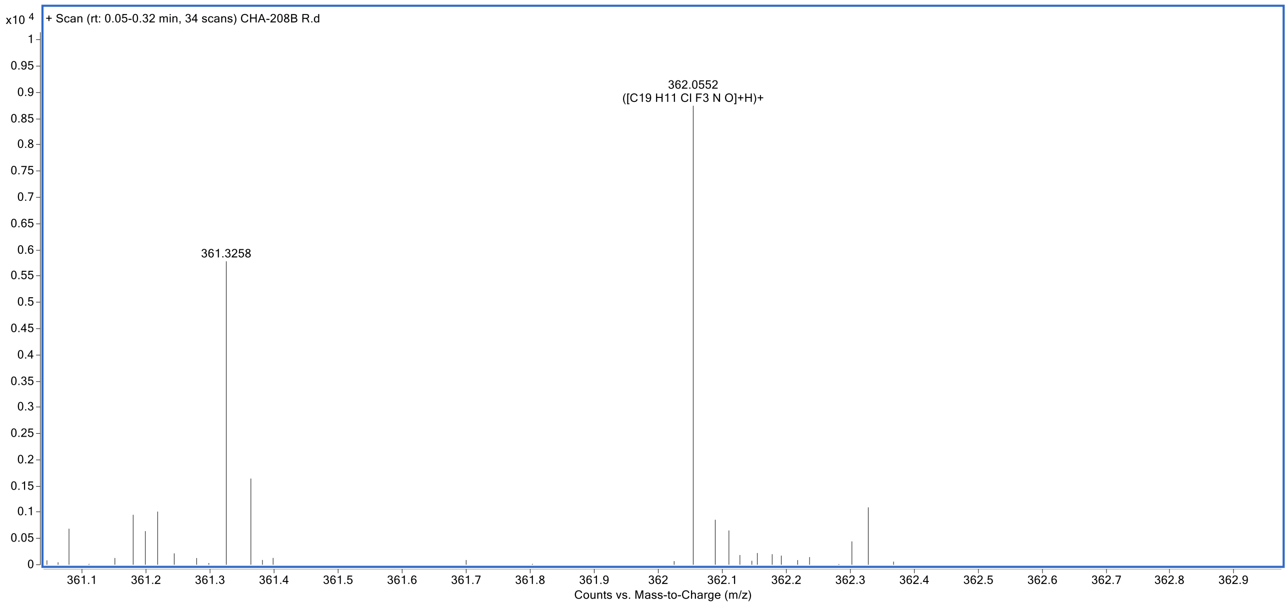

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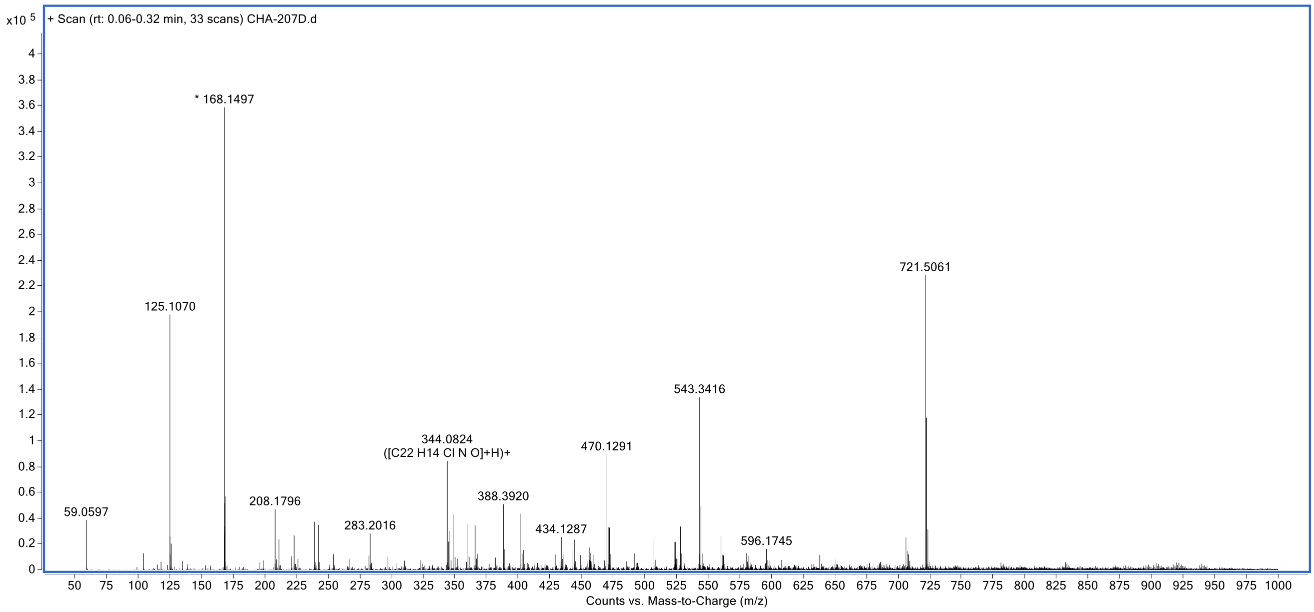

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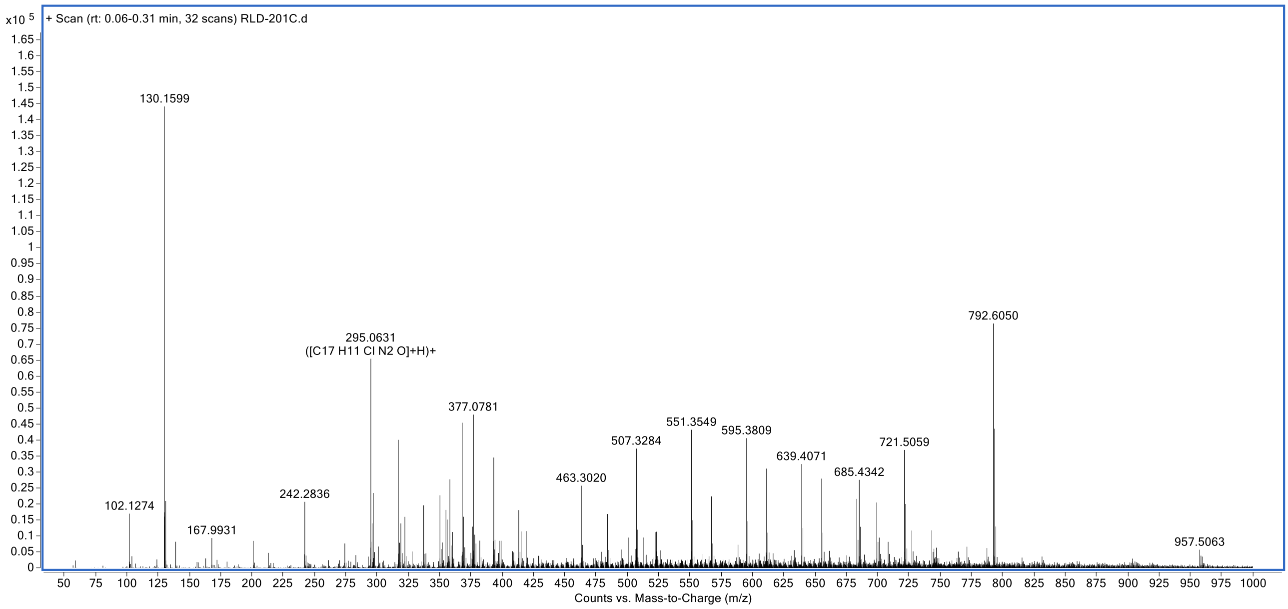

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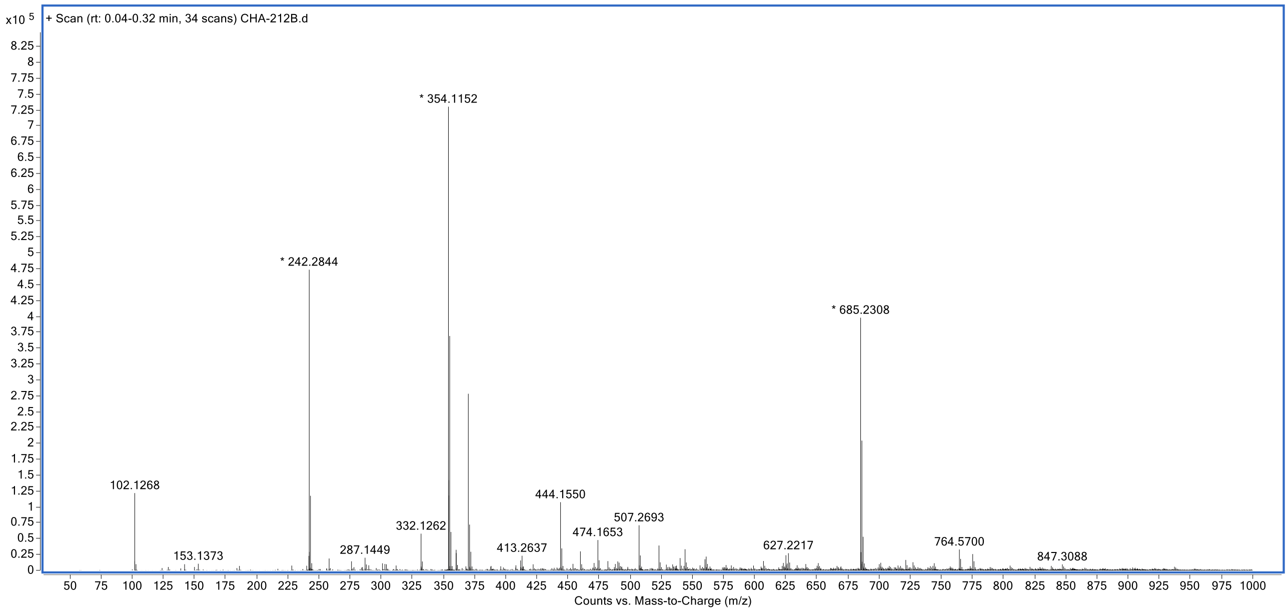

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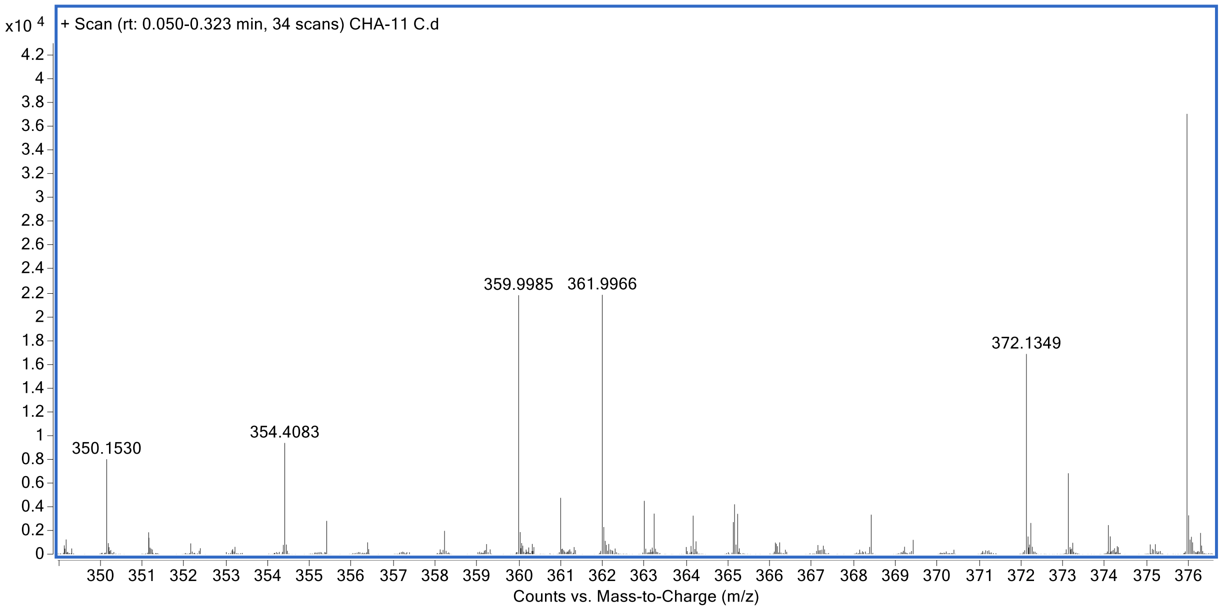

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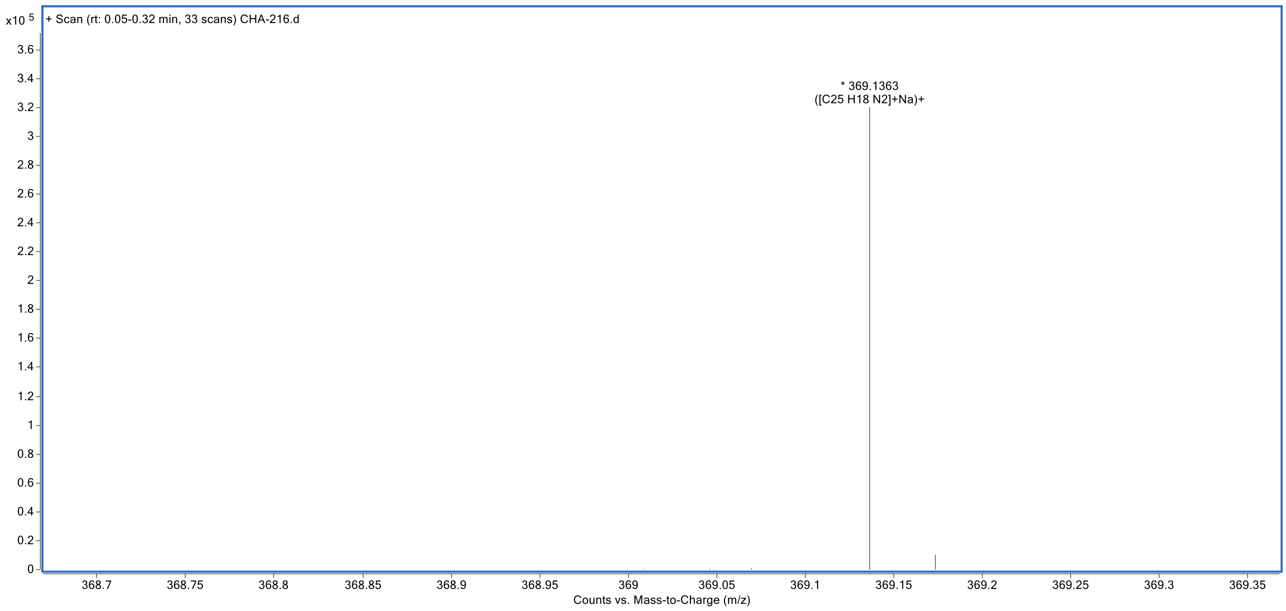

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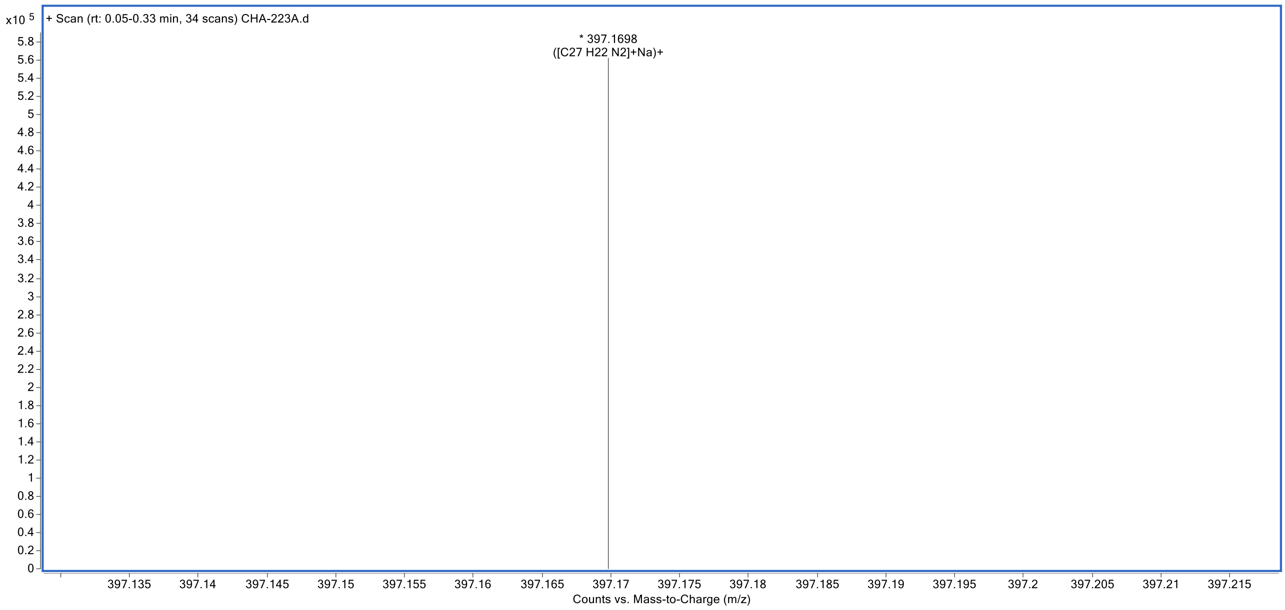

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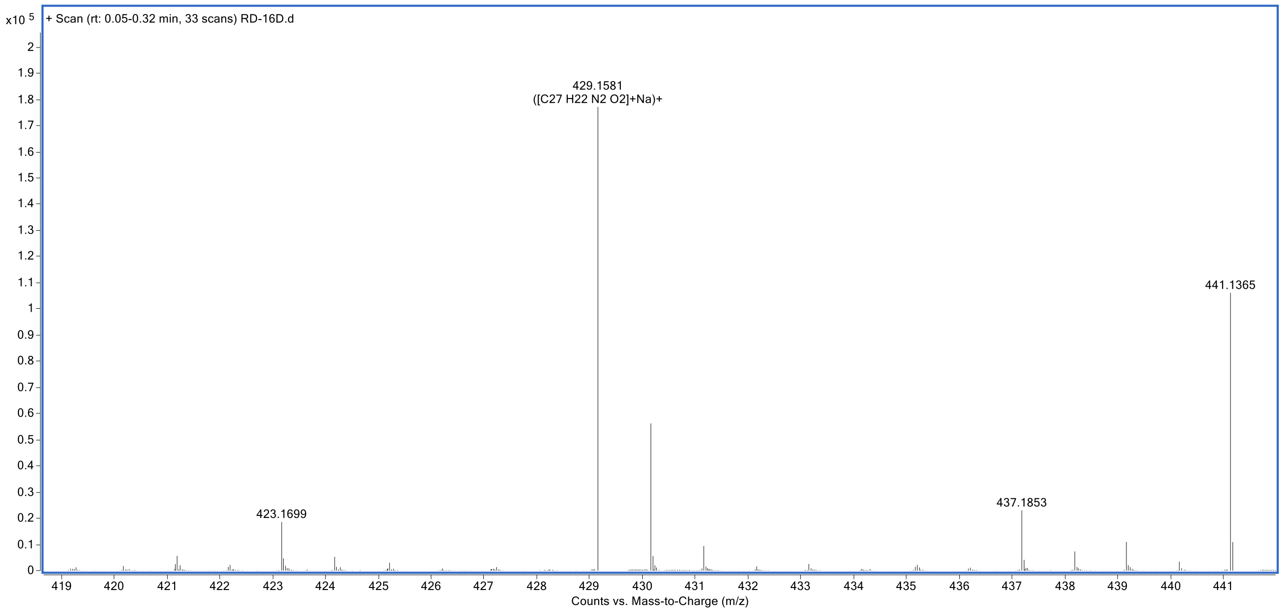

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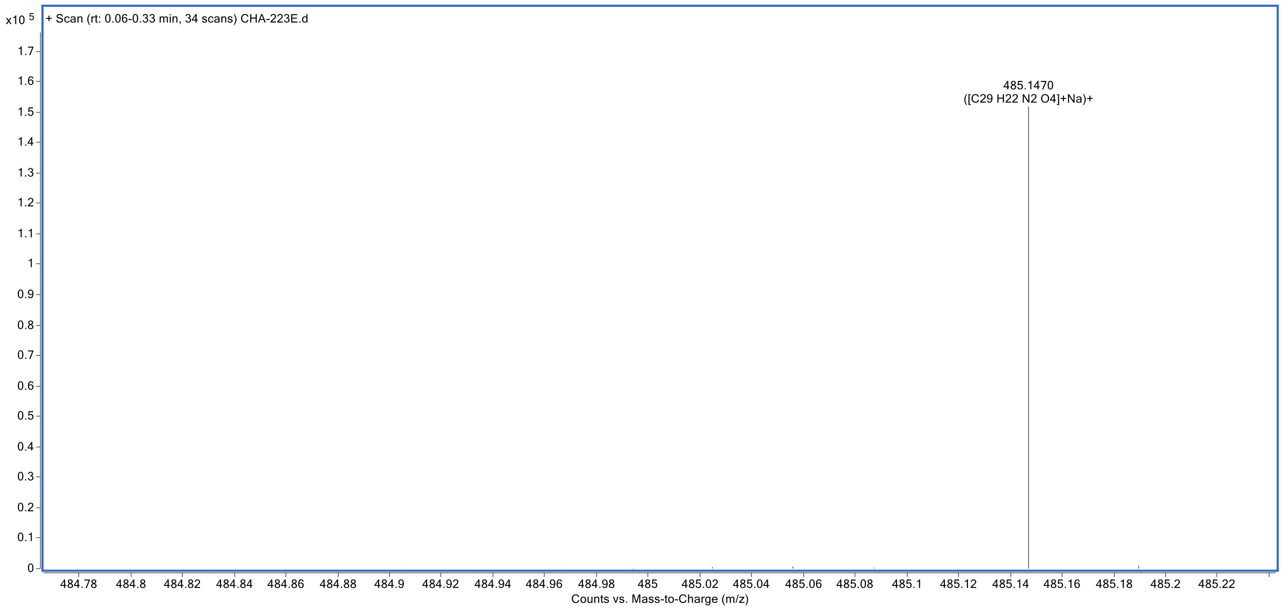

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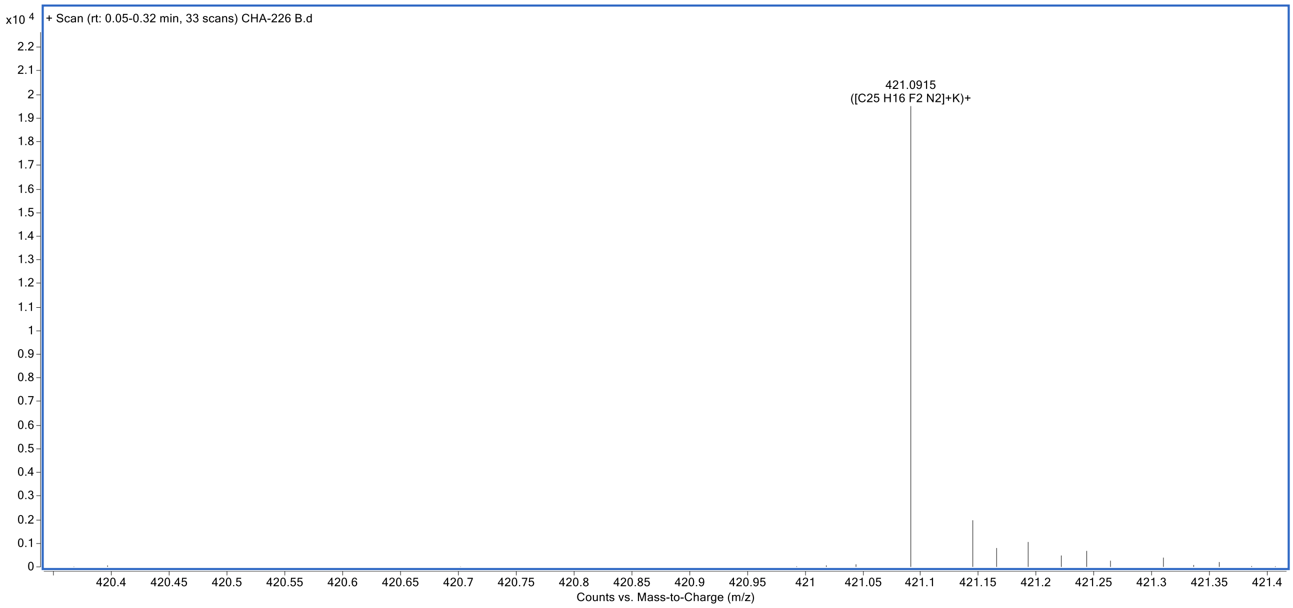

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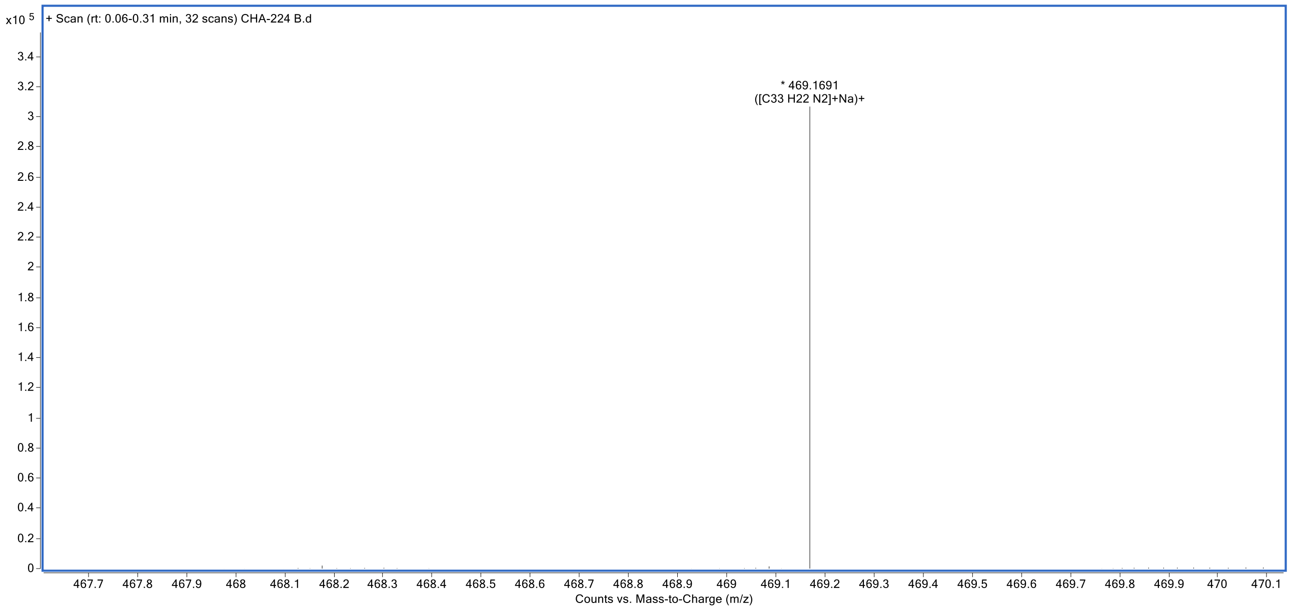

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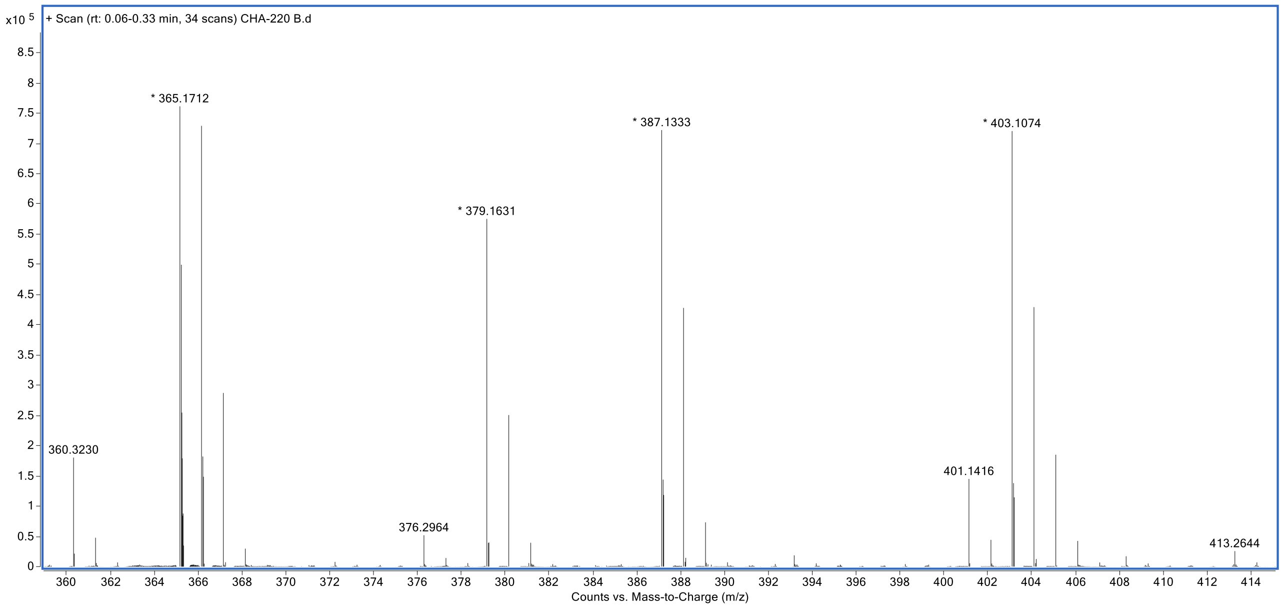

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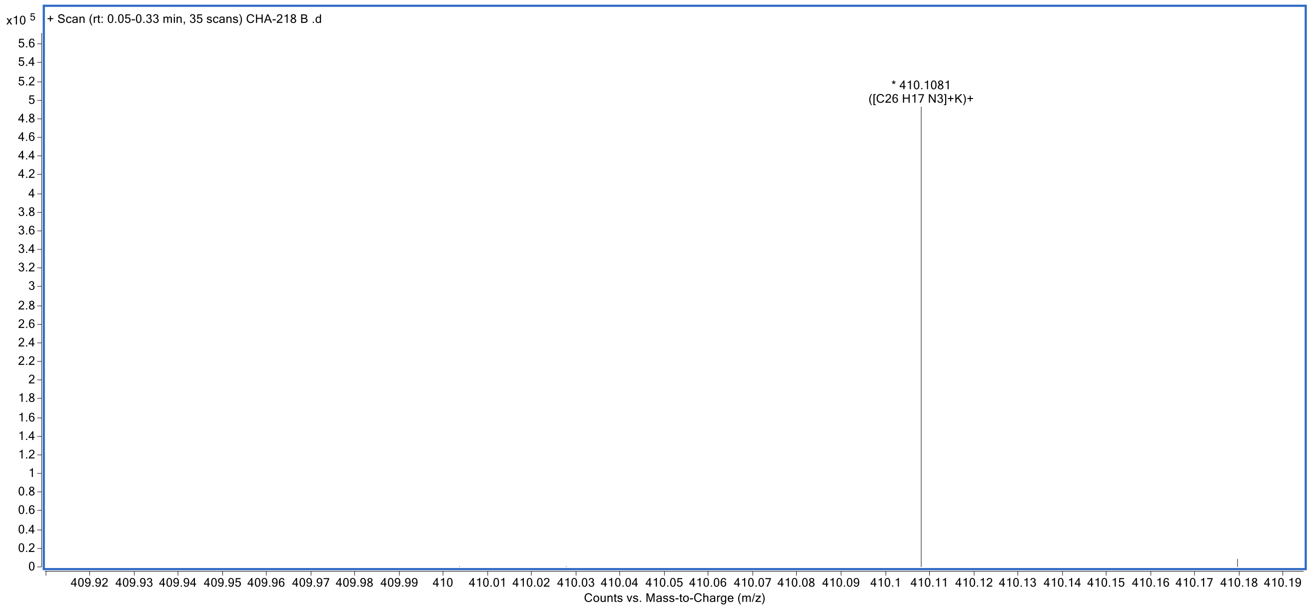

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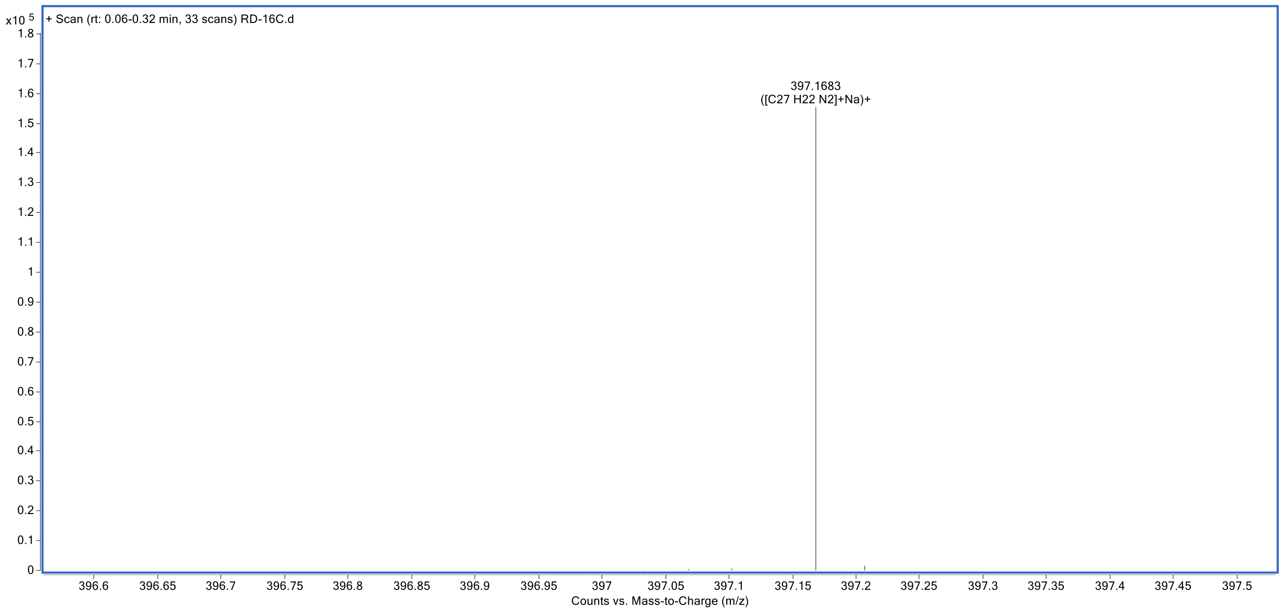

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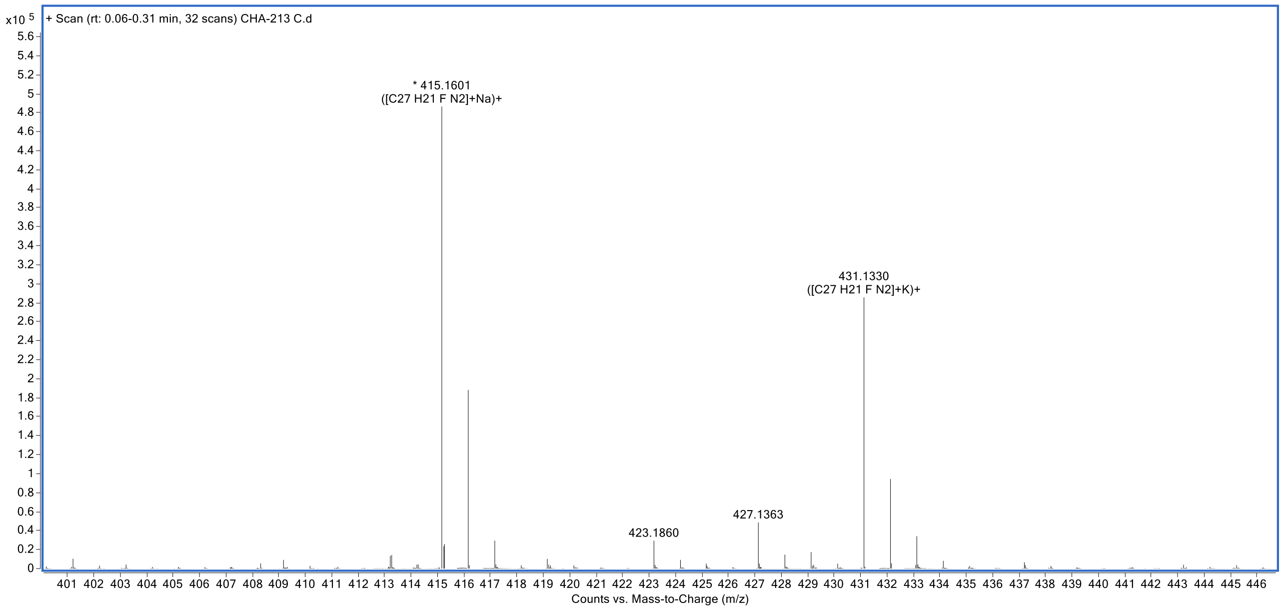

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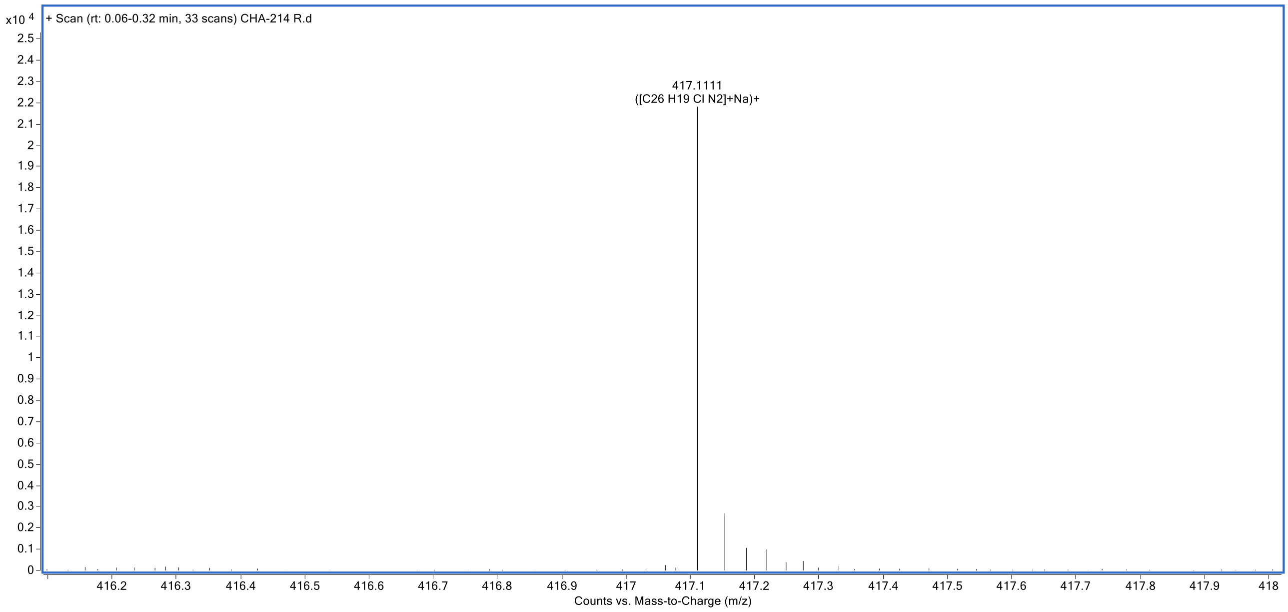
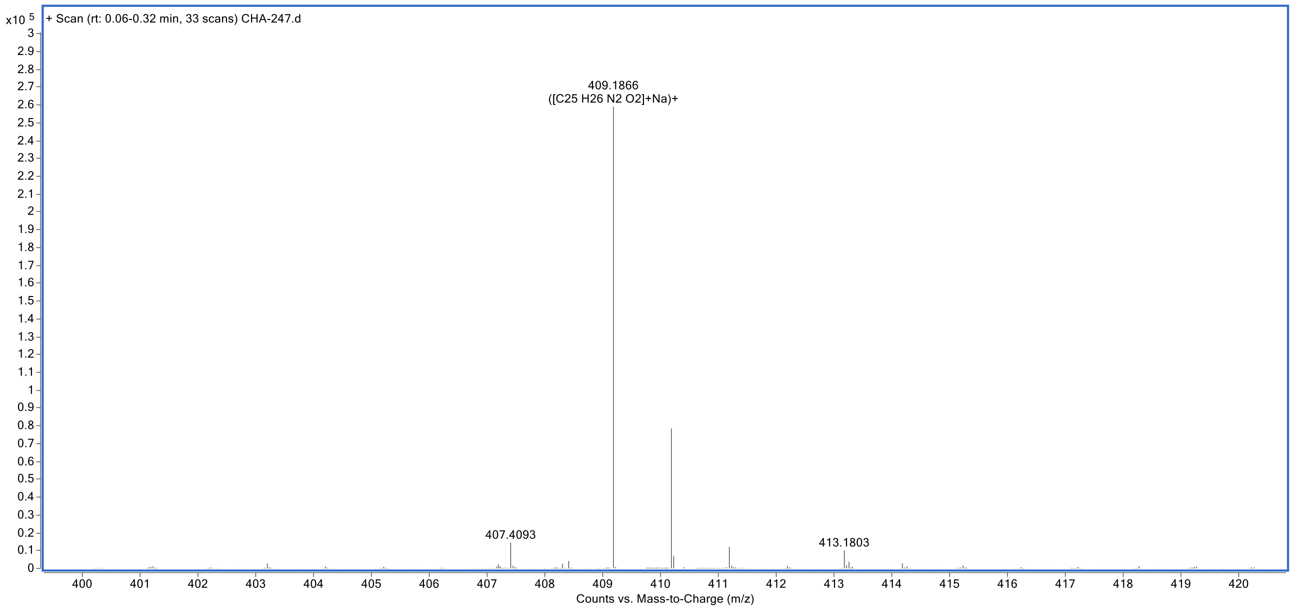
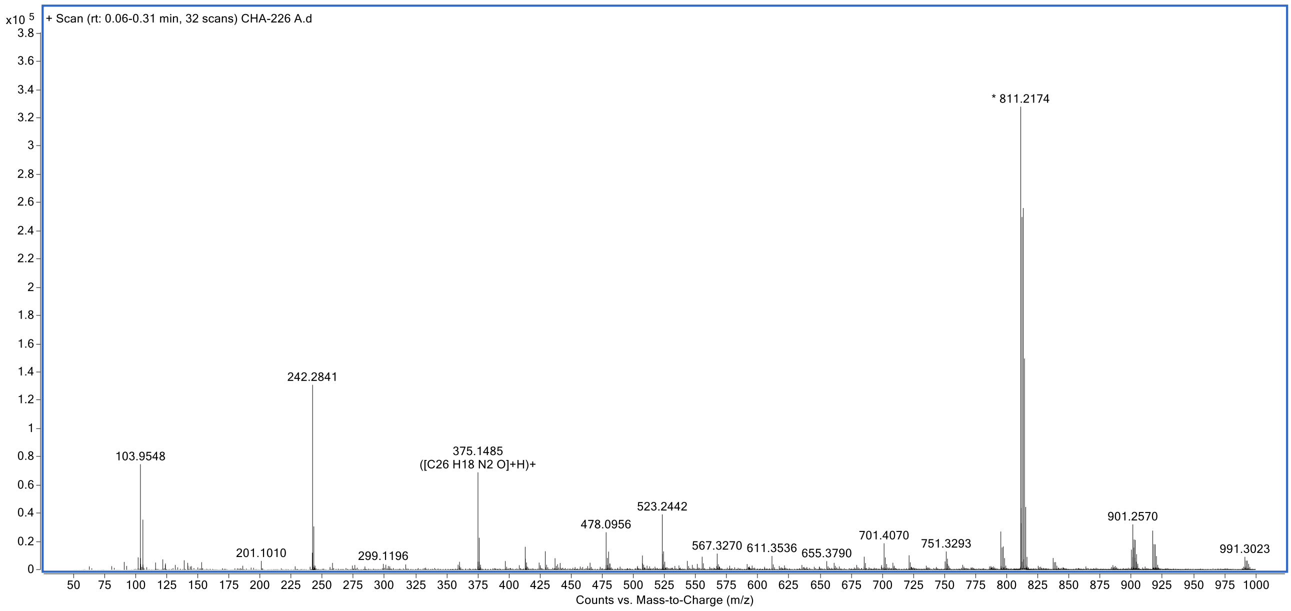


HRMS of **6k**



HRMS of **6m**



HRMS of **6n**