Supporting Information

Rhenium-Catalyzed C-H Aminocarbonylation of Azobenzenes with Isocyanates

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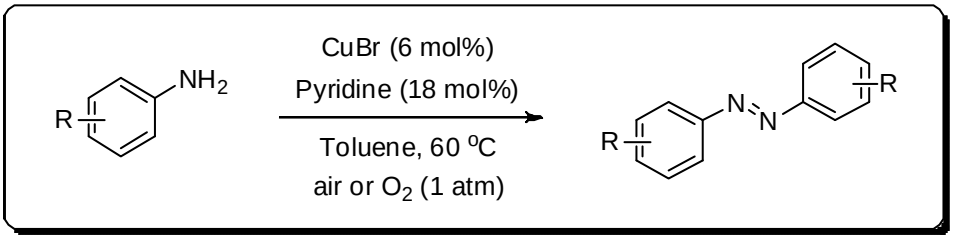
1. General Information

Unless otherwise noted, all Re-catalyzed reactions were carried out in oven-dried vessels with Teflon screw caps under a nitrogen atmosphere by using standard Schlenk techniques. Reaction temperatures are recorded on the temperature of the oil bath. Anhydrous solvents were purified and dried following standard procedures. Air-sensitive liquids and solutions were transferred via syringes. Anilines were purchased from J&K Chemicals, Inc. and sodium acetate and bromobenzene-d5 were purchased from Alfa Aesar. The catalysts, $Re_2(CO)_{10}$, $Re(CO)_5Br$, $Re(CO)_5Cl$ were obtained from Strem Chemicals, Inc., USA. All purchased chemicals were used as received without further purification. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh).

^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer and calibrated using TMS (0 ppm ^1H) or $CDCl_3$ (77.16 ppm ^{13}C). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, Hz). Melting points acquired by an electrothermal melting point apparatus, were uncorrected. The infrared spectra (IR) were recorded on FT-IR spectrometer Thermo Fisher Nicolet 6700. The mass spectra (MS) were recorded on a SHIMADZU QP-2010SE GC-MS spectrometer. The high resolution mass spectra were measured on a Bruker APEX IV FTMS mass spectrometer (ESI) in positive-ion mode and a Bruker BIFLEX III mass spectrometer (MALDI-TOF).

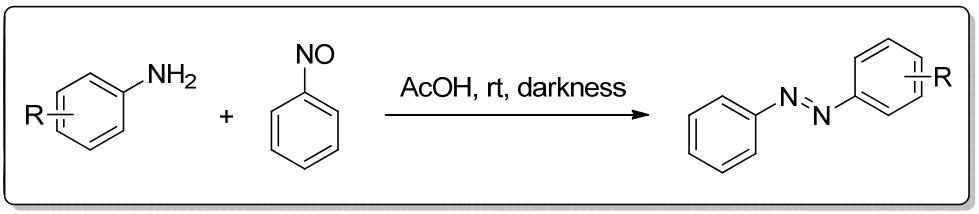
2. General procedure for the preparation of azobenzenes

General procedure A for the synthesis of azobenzenes



CuBr (0.6 mmol), pyridine (1.8 mmol), and aniline (20 mmol) were mixed in toluene (80 mL) under air (1 atm) or O_2 (1 atm). The mixture was stirred vigorously at 60 ^{o}C for 24 h. After cooling down to room temperature and concentrating under vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate) to afford azobenzenes.

General procedure B for the synthesis of azobenzenes



To a round bottom flask equipped with a stir bar was combined aniline (12 mmol, 1.2 equiv) and nitrosobenzene (10 mmol, 1.0 equiv) in acetic acid (100 mL) as solvent. The flask was covered with aluminum foil and the mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with hexane and washed with water (250 mL). The organic layer was dried over Na_2SO_4, concentrated. The residue was subjected to flash column chromatography to afford the azobenzenes (PE/EA=20:1).

The following azobenzenes displayed spectroscopic properties fully in accord with those published.

(*E*)-1,2-Diphenyldiazene (1a)[1a] from aniline according to general procedure A.

(*E*)-1,2-Di-*p*-tolyldiazene (1b)[1a] from *p*-toluidine according to general procedure A.

(*E*)-1,2-Di-*p*-tert-butyldiazene (1c)[1b] From 4-tert-butylaniline following general procedure A.

(*E*)-1,2-Bis(4-methoxyphenyl)diazene (1d)[1a] from *p*-anisidine according to general procedure A.

(*E*)-1,2-Bis(4-(trifluoromethoxy)phenyl)diazene (1e)[1a] from 4-trifluoromethoxy-aniline according to general procedure A.

(*E*)-1,2-Di-*p*-trifluoromethyldiazene (1f)[1b] from 4-trifluoromethylaniline following general procedure A.

(*E*)-1,2-Di-*o*-tolyldiazene (1g)[1a] from *o*-toluidine according to general procedure A.

(*E*)-1,2-Di-*o*-methoxydiazene (1h)[1b] from *o*-anisidine following general procedure A using O_2 as oxidant.

(*E*)-1,2-Bis(2,4-dimethylphenyl)diazene (1i)[1a] from 2,4-dimethylaniline according to general procedure A.

(*E*)-1,2-Bis(3,5-dimethylphenyl)diazene (1j)[1a] from 2,4-dimethylaniline according to general procedure A.

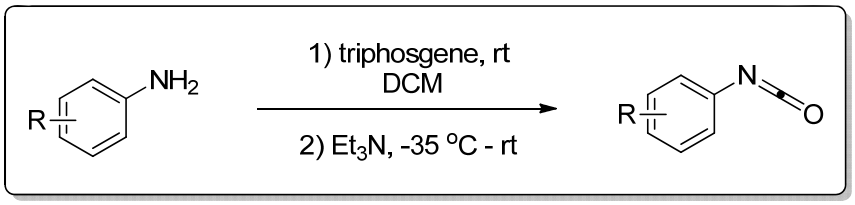
(*E*)-1,2-Di-*m*-tolyldiazene (1k)[1a] from *m*-toluidine according to general procedure A.

(*E*)-1-(2,4,6-trimethylphenyl)-2-phenyldiazene (1l)[2] from nitrosobenzene and 2,4,6-trimethylaniline according to general procedure B.

(*E*)-1-(3,5-dimethylphenyl)-2-phenyldiazene (1m)[2] from nitrosobenzene and 3,5-dimethylaniline according to general procedure B.

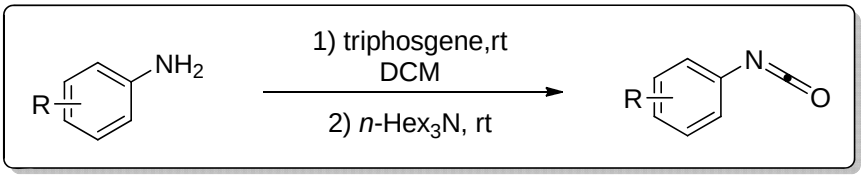
3. General procedure for the preparation of isocyanates.

General procedure A for the synthesis of isocyanates.



To a stirred DCM (50 mL) solution of triphosgene (22 mmol) was added a DCM (10 mL) solution of aniline (20 mmol) dropwise. After 30 min the mixture was cooled to -35^{o}C and Et_3N (6 mL) was added dropwise. The mixture was warmed to room temperature slowly and stirred for 2 hours. After removal of solvent under vacuum, the slurry residue was partially distilled or sublimed to give isocyanates.

General procedure B for the synthesis of isocyanates.

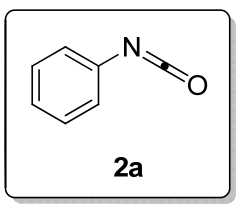


To a stirred DCM (50 mL) solution of triphosgene (22 mmol) was added a DCM (10 mL) solution of aniline (20 mmol) dropwise, after 30 min, *n*-Hex_3N (22 mmol) was added dropwise. The mixture was stirred for 3 hours. After concentrating under vacuum, the oily mixture was partially distilled to give isocyanates.

The following isocyanates, which are commercially available from Alfa Aesar, were used as received: **4-Biphenyl isocyanate (2c), 2-Nathphyl isocyanate (2o), *n*-Butyl isocyanate (2p), Cyclopentyl isocyanate (2q), Benzyl isocyanate (2r).**

Characterization data for isocyanates.

Phenyl isocyanate (2a)[3a]



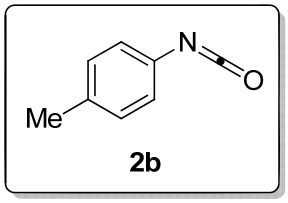
According to method B: aniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at room temperature. After workup, partial distillation afforded the title compound as

colorless liquid in 60 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 - 7.28 (m, 2H), 7.20 - 7.16 (m, 1H), 7.09 - 7.06 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 133.6, 129.6, 125.8, 124.8.

p-Tolyl isocyanate (2b)[3b]



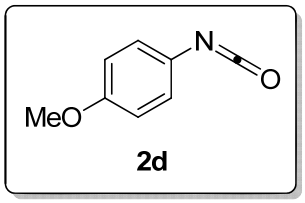
2b

According to method A: *p*-toluidine (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 61 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.6, 130.8, 130.2, 124.6, 21.0.

p-Methoxyphenyl isocyanate (2d)[3c]



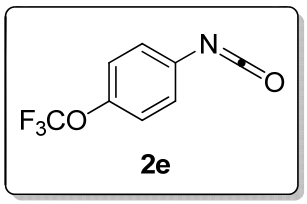
2d

According to method A: *p*-anisidine (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 57 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.02 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 157.5, 126.1, 125.7, 114.9, 55.6.

p-Trifluoromethoxyphenyl isocyanate (2e)



2e

According to method A: *p*-trifluoromethoxyaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 56 % yield.

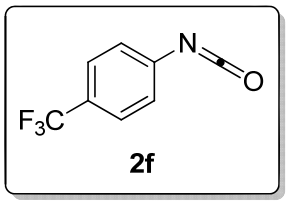
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 - 7.16 (m, 2H), 7.13 - 7.10 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 146.8, 132.4, 126.1, 122.4, 120.5 (q, $^{1}J_{C\text{-}F}$ = 257.6 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -58.1.

HRMS (ESI-MS): calculated for $C_8H_5O_2NF_3$ ($[M+H]^+$): 204.02667, found: 204.02651.

***p*-Trifluoromethylphenyl isocyanate (2f)**



2f

According to method A: *p*-trifluoromethylaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 60 % yield.

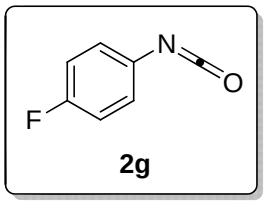
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.2, 128.1 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 126.9 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.1, 124.0 (q, $^{1}J_{C\text{-}F}$ = 273.8 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -62.1.

HRMS (ESI-MS): calculated for $C_8H_5ONF_3$ ($[M+H]^+$): 188.03178, found: 188.03189.

***p*-Fluorophenyl isocyanate (2g)**[3d]



2g

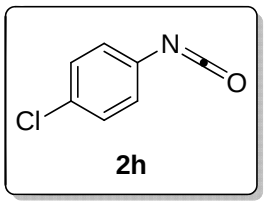
According to method B: *p*-fluoroaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 50 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.07 - 6.98 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.5 (d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 129.6, 126.2 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz),116.5 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -118.2.

_p_-Chlorophenyl isocyanate (2h)[3c]



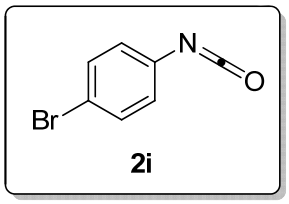
2h

According to method A: *p*-chloroaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 50 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 132.1, 131.3, 129.7, 125.9.

_p_-Bromophenyl isocyanate (2i)[3d]



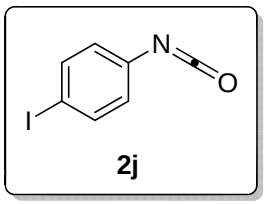
2i

According to method A: *p*-bromoaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 63 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 132.7, 132.7, 126.4, 119.1.

_p_-Iodophenyl isocyanate (2j)[3e]



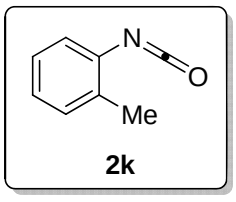
2j

According to method A: *p*-iodoaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, sublimation afforded the title compound as colorless solid in 60 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 138.7, 133.4, 126.7, 89.9.

***o*-Tolyl isocyanate (2k)**[3f]



2k

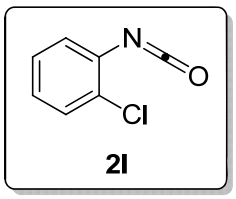
According to method A: *o*- toluidine (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid

in 50 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 - 7.17 (m, 1H), 7.16 - 7.12 (m, 1H), 7.11 - 7.07 (m, 1H), 7.06 - 7.04 (m, 1H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 133.0, 132.5, 130.8, 127.1, 125.9, 125.1, 18.4.

o-Chlorophenyl isocyanate (2l)[3d]

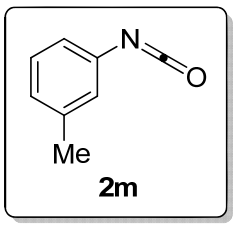


According to method A: *o*-chloroaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 50 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.23 - 7.17 (m, 1H), 7.15 - 7.10 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 131.9, 130.9, 129.9, 127.9, 126.7, 125.4.

m-Tolyl isocyanate (2m)[3f]



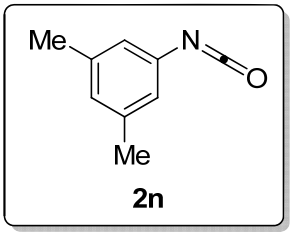
According to method A: *o*- toluidine (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 50 % yield. The obtained product is identical to a commercially available sample.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (t, J = 8.4 Hz, 1H), 7.00 - 6.98 (m, 1H), 6.90 - 6.87 (m, 2H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 139.8, 133.4, 129.4, 126.7, 125.5, 121.8, 21.3.

3,5-Dimethylphenyl isocyanate (2n)[3d]

According to method A: 3,5-dimethylaniline (20 mmol), triphosgene (22 mmol) in DCM (10 mL) were stirred at -35 ^{o}C. After workup, partial distillation afforded the title compound as colorless liquid in 62 % yield.



2n

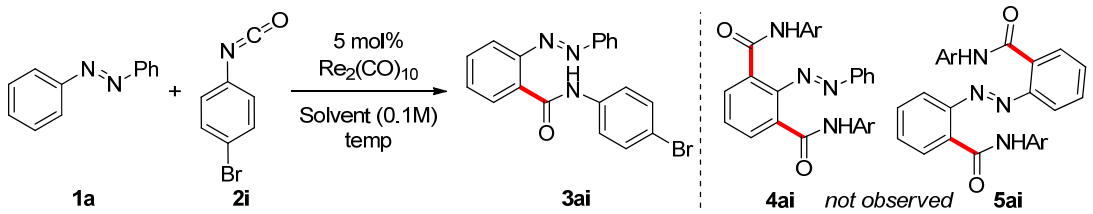
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.81 (s, 1H), 6.70 (s, 2H), 2.27 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 139.5, 133.2, 127.6, 122.5, 21.2.

4. Re-catalyzed C-H aminocarbonylation of azobenzenes

4.1 Optimization of reaction conditions

Table S1. Survey of the reaction parameters[a]



Entry	Cat.	**1a** (eq)/**2i** (eq)	Temp (^{o}C)	Solvent	Yield (%)[b]
1	---	1/2.5	150	Toluene	0
2	$Re_2(CO)_{10}$	1/2.5	150	Toluene	60
3	$Re_2(CO)_{10}$	1/2.5	150	DCE	46
4	$Re_2(CO)_{10}$	1/2.5	150	Xylene	58
5	$Re_2(CO)_{10}$	1/2.5	150	CCl_4	0
6	$Re_2(CO)_{10}$	1/2.5	150	CH_3CN	0
7	$Re_2(CO)_{10}$	1/2.5	150	THF	60
8	$Re_2(CO)_{10}$	1/2.5	150	Dioxane	55
9	$Re_2(CO)_{10}$	1/2.5	150	Cyclohexane	55
10	$Re_2(CO)_{10}$	1/2	150	Toluene	54
11	$Re_2(CO)_{10}$	1/1.5	150	Toluene	39
12	$Re_2(CO)_{10}$	1/1	150	Toluene	32
13	$Re_2(CO)_{10}$	1.5/1	150	Toluene	39
14	$Re_2(CO)_{10}$	2/1	150	Toluene	47
15	$Re_2(CO)_{10}$	2.5/1	150	Toluene	54
16	$Re_2(CO)_{10}$	2.5/1	140	Toluene	69
17	$Re_2(CO)_{10}$	2.5/1	130	Toluene	72
18	$Re_2(CO)_{10}$	1/2.5	130	Toluene	64
19	$Re_2(CO)_{10}$	2.5/1	120	Toluene	0
20[c]	$Re_2(CO)_{10}$	2.5/1	130	Toluene	74
21[c,d]	*$Re_2(CO)_{10}$*	*2.5/1*	*130*	*Toluene*	*77 (75)*[h]
22[e]	$Re_2(CO)_{10}$	2.5/1	130	Toluene	72
23[f]	$Re_2(CO)_{10}$	2.5/1	130	Toluene	47
24[g]	$Re_2(CO)_{10}$	2.5/1	130	Toluene	48
25	$Re(CO)_5Cl$	2.5/1	130	Toluene	0
26	$Re(CO)_5Br$	2.5/1	130	Toluene	0
27	$MnCO)_5Br$	2.5/1	130	Toluene	0
28	$Mn_2(CO)_{10}$	2.5/1	130	Toluene	0
29	$Co(acac)_2$	2.5/1	130	Toluene	0
30	$Pd(OAc)_2$	2.5/1	130	Toluene	0
31	$Rh(PPh_3)_3Cl$	2.5/1	130	Toluene	0
32	$Cu(OAc)_2$	2.5/1	130	Toluene	0

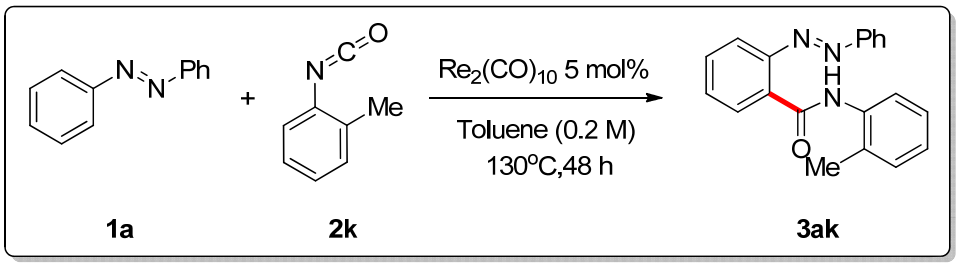
33	$Fe_2(CO)_9$	2.5/1	130	Toluene	0
34	$Ru_3(CO)_{12}$	2.5/1	130	Toluene	7

[a] Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2i** (0.5 mmol), catalyst (0.01 mmol), solvent (2 mL), 150 °C, 24 h under N_2 atmosphere. [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard. [c] 0.2 M. [d] 48 h. [e] NaOAc (20 mol%). [f] Et_3N (20 mol%). [g] Na_2CO_3 (20 mol%). [h] Isolated yield on 0.5 mmol scale, **1a** was recovered in 70% isolated yield. DCE = 1,2-dichloroethane, THF = tetrahydrofuran.

Of note, no bis-C-H functionalized products such as **4ai** and **5ai** were detected during the entire screening process, which showcased the excellent chemoselectivity in this reaction. As shown in Scheme S1, the reaction intermediate Re-complex **A** adopts an octahedron configuration, which is more sensitive to steric effect than those containing a tetrahedron configuration (such as Pd^{II} systems). We propose that the selectivity origins from the bulky hindrance of the benzamide group in mono-aminocarbonylation products, which renders the second C-H aminocarbonylation rather difficult for $Re_2(CO)_{10}$ catalyst.

The reaction of azobenzene with *ortho*-substituted isocyanate gave benzamide **3ak** in low yield under standard condition (Table S2, entry 1). A higher concentration provided **3ak** in 64% yield (entry 2). Introduction of a catalytic amount of NaOAc as a base to the reaction gave **3ak** in 71% isolated yield and the reaction almost completed in 24 h (entry 3).

Table S2. Optimization of reaction with *o*-tolyl isocyanate[a]

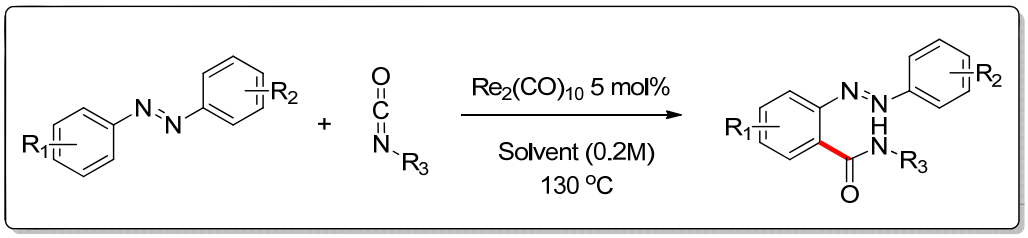


Entry	Base (eq.)	*c* (M)	Yield (**3ak**,%)[b]
1	---	0.2	25
2	---	0.4	64
3[c]	*NaOAc (0.2)*	*0.2*	*73 (71)*

[a] Reaction conditions unless otherwise noted: **1a** (1.25 mmol), **2k** (0.5 mmol), catalyst

(0.01 mmol), solvent (2.5 mL), 130 °C, 48 h under N_2 atmosphere. [b] Yields determined by ^1H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard. [c] 24 h.

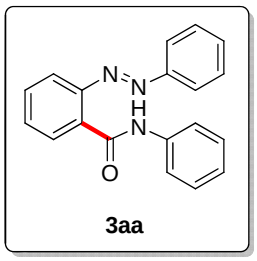
4.2. Typical procedure for C-H aminocarbonylation



To an oven-dried Teflon-screw-capped tube equipped with a magnetic stir bar were added $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), azobenzene (1.25 mmol), isocyanate (0.5 mmol), NaOAc (0.1 mmol, for substrates of low activity) and toluene (2.5 mL) sequentially under nitrogen. The closed tube was put into a pre-heated oil bath at 130 °C and stirred for 48 h or 24 h. After completion of the reaction, the resulting mixture was cooled down to room temperature, dilute with ethyl acetate (5 mL), filtered through a short pad of silica gel and washed with ethyl acetate (30 mL). The filtrate was pre-absorbed on silica gel and concentrated under vacuum. Flash chromatographic purification of residue provided the pure *o*-azobenzamides (petroleum ether:ethyl acetate=10:1).

4.3. Characterization of *o*-azobenzamides

(*E*)-*N*-phenyl-2-(phenyldiazenyl)benzamide (3aa)



3aa

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), phenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred at 130 ^oC for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 66 % yield.

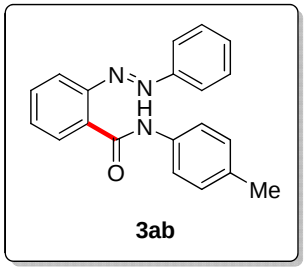
m.p.: 121-122 ^oC

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.71 (s, 1H), 8.43 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.87 – 7.85 (m, 2H), 7.79 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.60 – 7.51 (m, 5H), 7.32 (t, J = 7.6 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.6, 152.6, 149.2, 138.5, 132.3, 132.1, 131.9, 131.5, 129.5, 129.1, 124.1, 123.1, 120.2, 115.9.

HRMS (ESI-MS): calculated for $C_{19}H_{15}ON_3Na$ ($[M+Na]^+$): 324.11073, found: 324.11078.

(*E*)-2-(phenyldiazenyl)-*N*-(p-tolyl)benzamide (3ab)



3ab

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-methylphenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred at 130 ^oC for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 63 % yield.

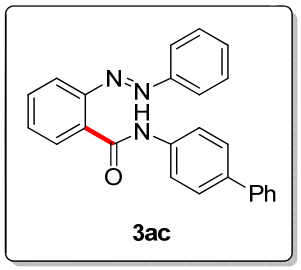
m.p.: 144-145 ^oC

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.63 (s, 1H), 8.42 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.86 – 7.84 (m, 2H), 7.77 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.59 – 7.50 (m, 7H), 7.12 (d, J = 8.4 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.5, 152.7, 149.2, 136.0, 133.9, 132.4. 132.0, 131.9, 131.7, 129.6, 129.6, 123.2, 120.2, 115.9, 21.0.

HRMS (ESI-MS): calculated for $C_{20}H_{17}ON_3Na$ ($[M+Na]^+$): 338.12611, found: 338.12619.

(*E*)-2-(phenyldiazenyl)-*N*-(4-biphenyl)benzamide (3ac)



3ac

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-biphenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 66 % yield.

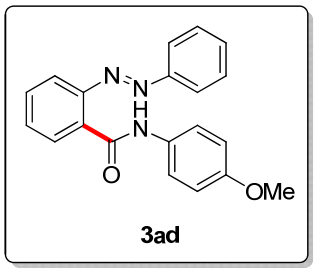
m.p.: 184-185 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.80 (s, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.52 (m, 9H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, 7.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.6, 152.7, 149.3, 140.6, 137.9, 137.1, 132.5, 132.2, 131.9, 131.6, 129.7, 128.8, 127.7, 127.1, 126.9, 123.2, 120.5, 116.0.

HRMS (ESI-MS): calculated for $C_{25}H_{19}ON_3Na$ ($[M+Na]^+$): 400.14203, found: 400.14186.

(*E*)-2-(phenyldiazenyl)-*N*-(4-methoxyphenyl)benzamide (3ad)



3ad

According to method B: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-methoxyphenyl isocyanate (0.5 mmol) NaOAc (0.1 mmol), in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 42 % yield.

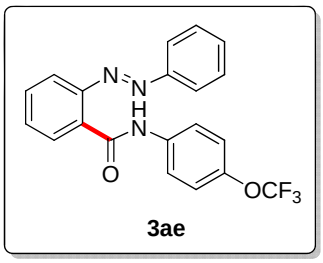
m.p.: 182-183 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.63 (s, 1H), 8.46 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.90 - 7.87 (m, 2H), 7.82 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.61 - 7.55 (m, 7H), 6.88 (d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.4, 156.5, 152.7, 149.3, 132.4, 132.0, 132.0, 131.9, 131.8, 131.7, 129.7, 123.2, 121.8, 116.0, 114.3, 55.6.

HRMS (ESI-MS): calculated for $C_{20}H_{17}O_2N_3Na$ ($[M+Na]^+$): 354.12130, found: 354.12128.

(*E*)-2-(phenyldiazenyl)-*N*-(4-trifluoromethoxyphenyl)benzamide (3ae)



3ae

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-trifluoromethoxyphenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 63 % yield.

m.p.: 159-160 °C

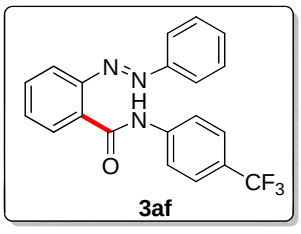
^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.86 (s, 1H), 8.43 (d, J = 7.2 Hz, 1H), 7.87 - 7.80 (m, 3H), 7.68 (d, J = 8.8 Hz, 2H), 7.62 - 7.55 (m, 5H), 7.17 (d, J = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.8, 152.7, 149.3, 145.3, 137.3, 132.6, 132.4, 132.0, 132.0, 131.2, 129.7, 123.1, 121.9, 121.3, 120.6 ($^1J_{C\text{-}F}$ = 252.5 Hz), 116.1.

^{19}F NMR ($CDCl_3$, 565 MHz) δ -58.0.

HRMS (ESI-MS): calculated for $C_{20}H_{17}O_2N_3F_3Na$ ($[M+Na]^+$): 408.09303, found: 408.09317.

(*E*)-2-(phenyldiazenyl)-*N*-(4-trifluoromethylphenyl)benzamide (3af)



3af

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-trifluoromethylphenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 74 % yield.

m.p.: 155-156 °C

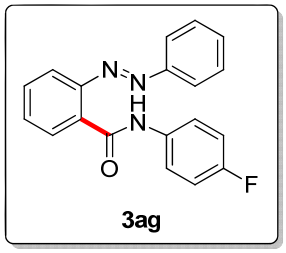
^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.00 (s, 1H), 8.40 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.86 – 7.84 (m, 3H), 7.76 (d, J = 8.4 Hz, 2H), 7.61 – 7.55 (m, 7H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.0, 152.8, 149.3, 141.6, 132.7, 132.6, 132.0, 132.0, 131.0, 129.7, 126.4 (q, $^3J_{C\text{-}F}$ = 4.1 Hz), 125.9 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 124.5 (q, $^1J_{C\text{-}F}$ = 271.6 Hz), 123.1, 119.8, 116.1.

^{19}F NMR ($CDCl_3$, 565 MHz) δ -62.0.

HRMS (ESI-MS): calculated for $C_{20}H_{15}ON_3F_3$ ($[M+H]^+$): 370.11617, found: 370.11614.

(*E*)-2-(phenyldiazenyl)-N-(4-fluorophenyl)benzamide (3ag)



According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-fluorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^oC for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 70 % yield.

m.p.: 167-169 ^oC

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.78 (s, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.87 - 7.80 (m, 3H), 7.64 - 7.56 (m, 7H), 7.02 (t, J = 8.8 Hz, 2H).

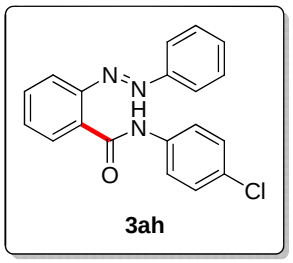
^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.6, 159.1 (d, $^1J_{C\text{-}F}$ = 245.5 Hz), 152.6, 149.2, 134.6 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 132.5, 132.2, 132.0, 131.9, 131.3, 129.7, 123.1, 121.8, (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 116.0, 115.7 (d, $^2J_{C\text{-}F}$ = 22.5 Hz).

^{19}F NMR (CDCl3, 565 MHz) δ -118.0.

HRMS (ESI-MS): calculated for $C_{19}H_{14}ON_3FNa$ ($[M+Na]^+$) 342.10131, found 342.10126.

(*E*)-2-(phenyldiazenyl)-*N*-(4-chlorophenyl)benzamide (3ah)

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred



3ah

at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 86 % yield.

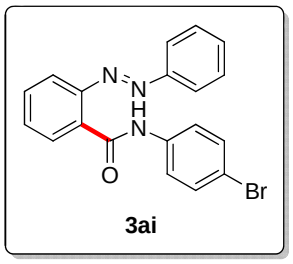
m.p.: 164-165 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.83 (s, 1H), 8.43 (d, *J* = 7.2 Hz, 1H), 7.86 – 7.82 (m, 3H), 7.63 – 7.58 (m, 7H), 7.45 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.6, 152.7, 149.2, 137.2, 132.5, 132.3, 132.0, 131.9, 131.2, 129.7, 129.2, 129.1, 123.1, 121.4, 116.0.

HRMS (ESI-MS): calculated for $C_{19}H_{14}ON_3ClNa$ ($[M+Na]^+$): 358.07176, found: 358.07178.

(*E*)-2-(phenyldiazenyl)-*N*-(4-bromophenyl)benzamide (3ai)



3ai

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-bromophenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 75 % yield.

m.p.: 168-169 °C

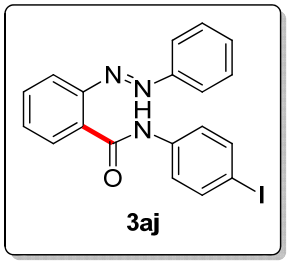
^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.82 (s, 1H), 8.42 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.61 – 7.55 (m, 7H), 7.42 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.7, 152.7, 149.2, 137.7, 132.6, 132.4, 132.1, 132.0, 132.0, 131.2, 129.7, 123.1, 121.7, 116.8, 116.0.

HRMS (ESI-MS): calculated for $C_{19}H_{14}ON_3BrNa$ ($[M+Na]^+$): 402.02125, found: 402.02136.

(*E*)-2-(phenyldiazenyl)-*N*-(4-iodophenyl)benzamide (3aj)

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 4-iodophenyl isocyanate (0.5 mmol) in toluene (2.5 mL) were stirred at



3aj

130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 62 % yield.

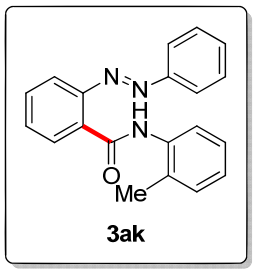
m.p.: 177-178 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.83 (s, 1H), 8.43 (d, *J* = 7.6 Hz, 1H), 7.87 – 7.84 (m, 3H), 7.63 – 7.58 (m, 7H), 7.45 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.7, 152.7, 149.2, 138.3, 138.0, 132.6, 132.4, 132.0, 131.9, 131.2, 129.7, 123.1, 122.0, 116.0, 87.4.

HRMS (ESI-MS): calculated for $C_{19}H_{14}ON_3INa$ ($[M+Na]^+$): 450.00738, found: 450.00735.

(*E*)-2-(phenyldiazenyl)-*N*-(2-methylphenyl)benzamide (3ak)



3ak

According to method B: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 2-methylphenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 71 % yield.

m.p.: 122-123 °C

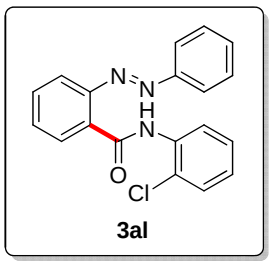
^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.03 (s, 1H), 8.46 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.78 (m, 3H), 7.64 – 7.56 (m, 2H), 7.52 – 7.48 (m, 3H), 7.26 – 7.07 (m, 3H) 2.08 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.0, 152.7, 149.8, 136.2, 132.2, 132.1, 131.9, 131.7, 131.7, 130.5, 130.3, 129.5, 126.6, 125.4, 124.3, 123.1, 116.3, 18.1.

HRMS (ESI-MS): calculated for $C_{20}H_{17}ON_3Na$ ($[M+Na]^+$): 338.12638, found: 338.12640.

(*E*)-2-(phenyldiazenyl)-*N*-(2-chlorophenyl)benzamide (3al)

According to method B: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene



3al

(1.25 mmol), 2-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 80 % yield.

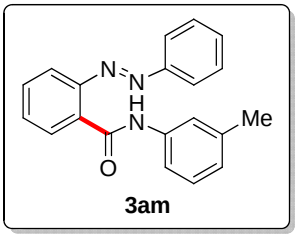
m.p.: 128-129 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.39 (s, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 7.2 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.77 – 7.52 (m, 1H), 7.59 – 7.57 (m, 2H), 7.48 – 4.46 (m, 3H), 7.34 – 7.28 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.2, 152.4, 149.8, 135.3, 132.3, 132.2, 131.8, 131.5, 129.2, 129.1, 127.5, 125.0, 124.2, 123.6, 123.5, 116.5.

HRMS (ESI-MS): calculated for $C_{19}H_{14}ON_3ClNa$ ($[M+Na]^+$): 358.07176, found: 358.07157.

(*E*)-2-(phenyldiazenyl)-*N*-(*m*-tolylphenyl)benzamide (3am)



3am

According to method B: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-Diphenyldiazene (1.25 mmol), *m*-tolyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 63 % yield.

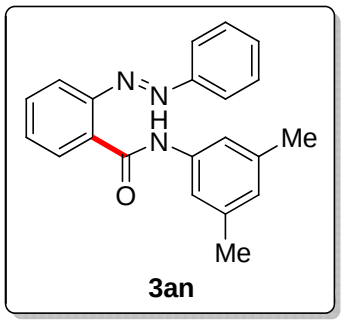
m.p.: 88-89 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.6 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.54 (m, 6H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.5, 152.7, 149.2, 138.9, 138.5, 132.4, 132.1, 131.9, 131.7, 129.6, 129.0, 125.1, 123.2, 120.9, 117.3, 115.9, 21.6.

HRMS (ESI-MS): calculated for $C_{20}H_{17}ON_3Na$ ($[M+Na]^+$): 338.12638, found: 338.12625.

(*E*)-2-(phenyldiazenyl)-*N*-(3,5-dimethylphenyl)benzamide (3an)



According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), 3,5-dimethylphenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 70 % yield.

m.p.: 159-160 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.69 (s, 1H), 8.45 (d, (d, *J* = 8.0 Hz, 1H), 7.90 - 7.88 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.62 - 7.53 (m, 5H), 7.33 (s, 2H), 6.75 (s, 1H), 2.29 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.4, 152.7, 149.2, 138.8, 138.4, 132.4, 132.0, 132.0, 131.9, 131.7, 129.5, 126.0, 123.3, 118.0, 115.8, 21.5.

HRMS (ESI-MS): calculated for $C_{21}H_{19}ON_3Na$ ($[M+Na]^+$): 352.14203, found: 352.14194.

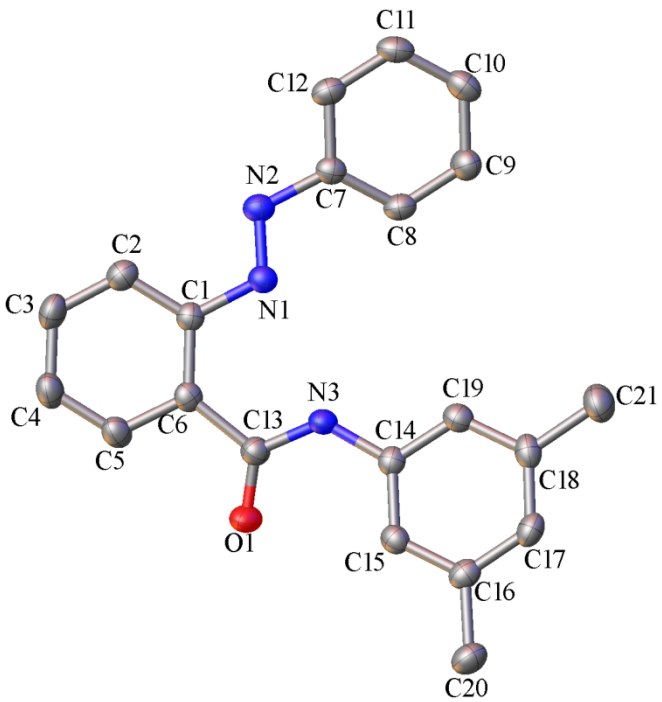
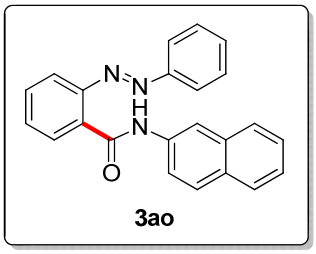


Figure S1. Molecular structures of **3an**, showing 30% probability ellipsoids and the partial atom-numbering scheme

(*E*)-*N*-(naphthalen-2-yl)-2-(phenyldiazenyl)benzamide (3ao)



3ao

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), naphthalen-2-yl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 67 % yield.

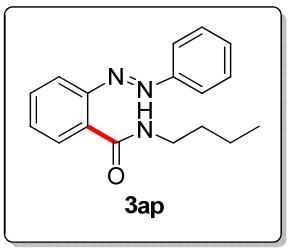
m.p.: 159-160 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.97 (s, 1H), 8.55 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 8.27 (d, J = 7.6 Hz, 1H), 7.83 - 7.78 (m, 4H), 7.71 - 7.58 (m, 4H), 7.53 - 7.44 (m, 2H), 7.41 - 7.36 (m, 3H), 7.08 (t, J = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.3, 152.5, 149.9, 134.2, 133.3, 132.3, 132.3, 132.2, 131.9, 131.4, 129.5, 128.7, 127.1, 126.0, 125.9, 125.4, 123.5, 121.6, 120.6, 116.4.

HRMS (ESI-MS): calculated for $C_{23}H_{17}ON_3Na$ ($[M+Na]^+$) 374.12638, found 374.12616.

(*E*)-*N*-butyl-2-(phenyldiazenyl)benzamide (3ap)



3ap

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), *n*-butyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 55 % yield.

m.p.: 105-106 °C

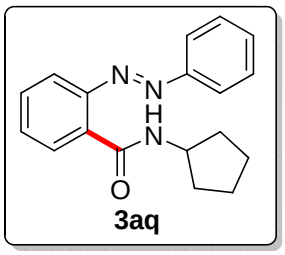
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (s, 1H), 8.34 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.84 - 7.81 (m, 2H), 7.75 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.58 - 7.49 (m, 5H), 3.52 (q, J = 6.8 Hz, 2H), 1.64 - 1.57 (m, 2H), 1.43 - 1.34 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.8, 152.6, 149.6, 132.1, 131.8, 131.6, 131.6,

129.5, 123.2, 115.8, 40.0, 31.8, 20.4, 13.8.

HRMS (ESI-MS): calculated for $C_{17}H_{19}ON_3Na$ ($[M+Na]^+$) 304.14203, found 304.14195.

(*E*)-2-(phenyldiazenyl)-*N*-cyclopentylbenzamide (3aq)



3aq

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), cyclopentayl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^oC for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as sticky oil in 55 % yield.

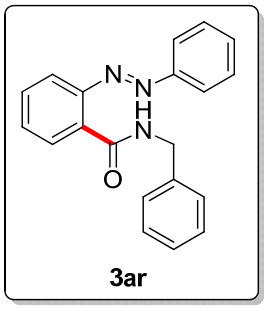
m.p.: 114-115 ^oC

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.50 (d, J = 4.8 Hz, 1H), 8.37 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.85 - 7.82 (m, 2H), 7.75 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.60 - 7.50 (m, 5H), 4.52 - 4.43 (m, 1H), 2.13 - 2.05 (m, 2H), 1.70 - 1.61 (m, 4H), 1.56 - 1.50 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.3, 152.7, 149.6, 132.2, 131.8, 131.6, 131.6, 131.5, 129.5, 123.1, 115.8, 51.9, 33.4, 24.0.

HRMS (MALDI-MS): calculated for $C_{18}H_{19}N_3NaO$ ($[M+Na]^+$) 316.14203, found 316.14228.

(*E*)-2-(phenyldiazenyl)-*N*-benzylbenzamide (3ar)



3ar

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-diphenyldiazene (1.25 mmol), benzyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^oC for 48 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as sticky oil in 57 % yield.

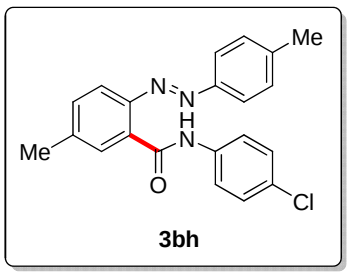
m.p.: 116-117 ^oC

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.92 (s, 1H), 8.39 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.56 - 7.27 (m, 12 H), 4.67 (d, *J* = 5.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.6, 152.2, 149.5, 138.2, 132.0, 131.8, 131.7, 131.6, 131.3, 129.4, 128.9, 128.5, 127.7, 123.2, 115.8, 44.8.

HRMS (ESI-MS): calculated for $C_{20}H_{17}ON_3Na$ ($[M+Na]^+$) 338.12638, found 338.12631.

(*E*)-5-methyl-2-(*p*-tolyldiazenyl)-*N*-(4-chlorophenyl)benzamide (3bh)



3bh

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-di-*p*-tolylphenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 78 % yield.

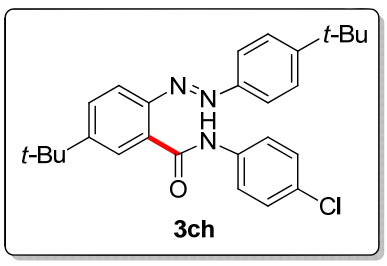
m.p.: 175-176 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.02, (s, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 7.76 - 7.74 (m, 3H), 7.65 - 7.62 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 3H), 7.31 - 7.29 (m, 2H), 2.47 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.9, 150.9, 147.5, 143.3, 142.6, 137.3, 133.1, 132.3, 130.6, 130.4, 129.2, 129.1, 123.1, 121.4, 116.0, 21.8, 21.7.

HRMS (MALDI-MS): calculated for $C_{21}H_{18}ClN_3NaO$ ($[M+Na]^+$) 386.10306, found 386.10323.

(*E*)-5-(tert-butyl)-2-((4-(tert-butyl)phenyl)diazenyl)-*N*-(4-chlorophenyl) benzamide (3ch)



3ch

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(tert-butyl) phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 24 h. After

workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 85 % yield.

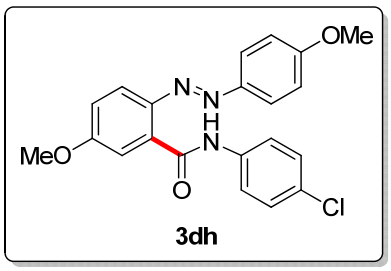
m.p.: 181-182 ^{o}C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.03, (s, 1H), 8.50 (d, *J* = 1.2 Hz, 1H), 7.81 - 7.76 (m, 3H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.60 - 7.57 (m, 3H), 7.30 (d, *J* = 8.8 Hz, 2H), 1.39 (s, 18H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 164.1, 156.3, 155.4, 150.6, 147.4, 137.3, 130.4, 129.5, 129.1, 129.0, 128.7, 126.6, 122.9, 121.4, 115.9, 35.3, 35.3, 31.3, 31.2.

HRMS (MALDI-MS): calculated for $C_{27}H_{30}ClN_3NaO$ ($[M+Na]^+$) 470.19696, found 470.19708.

(*E*)-*N*-(4-chlorophenyl)-5-(methoxy)-2-((4-methoxyphenyl)diazenyl)benzamide (3dh)



3dh

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(4-methoxy)phenyl diazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^{o}C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 76 % yield.

m.p.: 172-173 ^{o}C

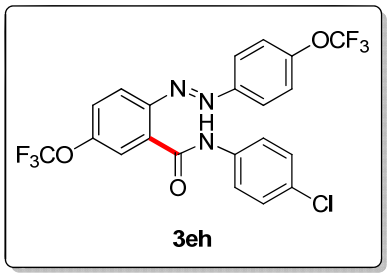
^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.32 (s, 1H), 7.90 (s, 1H), 7.83 - 7.75 (m, 3H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H). 7.02 (s, 3H), 3.91 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.5, 162.8, 162.1, 146.9, 143.8, 137.3, 132.3, 129.1, 124.9, 121.4, 119.4, 118.0, 114.8, 114.5, 55.9, 55.8.

HRMS (MALDI-MS): calculated for $C_{21}H_{18}ClN_3NaO_3$ ($[M+Na]^+$) 418.09289, found 418.09292.

(*E*)-*N*-(4-chlorophenyl)-5-(trifluoromethoxy)-2-((4-(trifluoromethoxy)phenyl)diaz

enyl)benzamide (3eh)



3eh

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(4-trilfuoromethoxy) phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^{o}C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 52 % yield.

m.p.: 140-141 ^{o}C

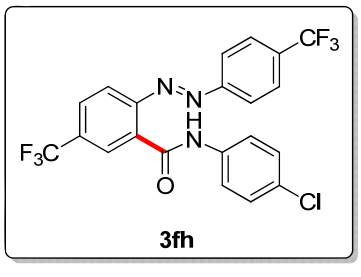
^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.53 (s, 1H), 8.21 (s, 1H), 7.91 - 7.86 (m, 3H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 162.1, 152.3 (q, $^{3}J_{C\text{-}F}$ = 2.1 Hz), 152.0 (q, $^{3}J_{C\text{-}F}$ = 2.1 Hz), 147.0, 136.6, 133.6, 129.8, 129.3, 124.9, 124.6, 124.1, 123.4, 121.7, 121.4, 120.5 (q, $^{1}J_{C\text{-}F}$ = 257.6 Hz), 120.4 (q, $^{1}J_{C\text{-}F}$ = 257.6 Hz), 118.4.

^{19}F NMR ($CDCl_3$, 565 MHz) δ -57.6, -57.6.

HRMS (MALDI-MS): calculated for $C_{21}H_{12}ClF_6N_3NaO_3$ ($[M+Na]^+$) 526.03636, found 526.03634.

(*E*)-*N*-(4-chlorophenyl)-5-(trifluoromethyl)-2-((4-(trifluoromethyl)phenyl)diazen yl)benzamide (3fh)



3fh

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(4-trifluoromethyl)phenyl diazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^{o}C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 46 % yield.

m.p.: 175-176 ^{o}C

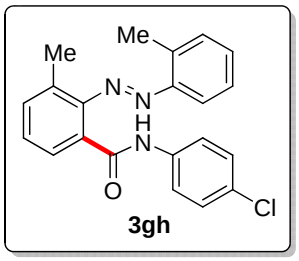
^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.30 (s, 1H), 8.68 (s, 1H), 8.01 - 7.83 (m, 7H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 162.2, 1542, 150.5, 136.5, 134.5 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 134.1 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 132.6, 129.4, 129.1 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 127.1 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.6 (q, $^1J_{C\text{-}F}$ = 273.5 Hz), 123.6, 123.4, (q, $^1J_{C\text{-}F}$ = 274.1 Hz), 121.4, 117.2.

^{19}F NMR ($CDCl_3$, 565 MHz) δ -62.8, -63.0.

HRMS (MALDI-MS): calculated for $C_{21}H_{12}ClF_6N_3NaO$ ($[M+Na]^+$) 494.04653, found 494.04667.

(*E*)-*N*-(4-chlorophenyl)-3-methyl-2-(*o*-tolyldiazenyl)benzamide (3gh)



According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(2-methyl)phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^oC for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 57 % yield.

m.p.: 145-146 ^oC

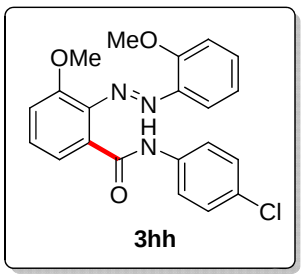
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.90 (s, 1H), 7.53 - 7.49 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.36 - 7.32 (m, 1H), 7.29 - 7.17 (m, 4H), 7.12 (d, *J* = 8.8 Hz, 2H), 2.47 (s, 3H), 2.44 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 166.7, 150.7, 149.2, 139.3, 137.1, 133.8, 133.6, 132.0, 131.7, 129.2, 128.8, 127.6, 126.4, 121.0, 115.1, 19.4, 17.7.

HRMS (MALDI-MS): calculated for $C_{21}H_{18}ClN_3NaO$ ($[M+Na]^+$) 386.10306, found 386.10325.

(*E*)-*N*-(4-chlorophenyl)-3-methoxy-2-(2-methoxyphenyl)diazenyl)benzamide (3hh)

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(2-methoxy)phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5



3hh

mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 60 % yield.

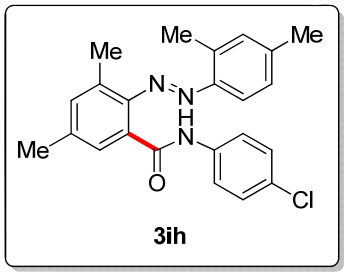
m.p.: 162-163 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.72 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 5.2 Hz, 2H), 7.33 (s, 1H), 7.27 - 7.24 (m, 3H), 7.10 - 7.08 (m, 2H), 3.87 (s, 3H), 3.83 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.4, 162.5, 160.7, 153.7, 150.3, 137.3, 133.6, 130.4, 129.0, 128.8, 124.2, 121.3, 118.9, 118.5, 116.7, 107.0, 99.5, 55.8, 55.6.

HRMS (MALDI-MS): calculated for $C_{21}H_{18}ClN_3NaO_3$ ($[M+Na]^+$) 418.09289, found 418.09299.

(*E*)-*N*-(4-chlorophenyl)-2-((2,4-dimethylphenyl)diazenyl)-3,5-dimethylbenzamide (3ih)



3ih

According to procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(2,4-dimethyl)phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 53 % yield.

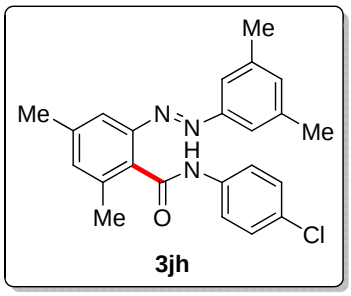
m.p.: 208-209 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.13 (s, 1H), 7.54 - 7.46 (m, 4H), 7.19 - 7.02 (m, 5H), 2.47 (s, 6H), 2.36 (s, 3H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 166.4, 149.0, 147.2, 142.5, 139.6, 139.3, 137.2, 135.0, 132.6, 132.3, 129.6, 128.9, 128.8, 127.3, 121.0, 114.8, 21.5, 21.2, 20.1, 17.7.

HRMS (MALDI-MS): calculated for $C_{23}H_{22}ClN_3NaO$ ($[M+Na]^+$) 414.13436, found 414.13445.

(*E*)-*N*-(4-chlorophenyl)-2-((3,5-dimethylphenyl)diazenyl)-2,6-dimethylbenzamide (3jh)



3jh

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(2,4-dimethyl)phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^{o}C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 73 % yield.

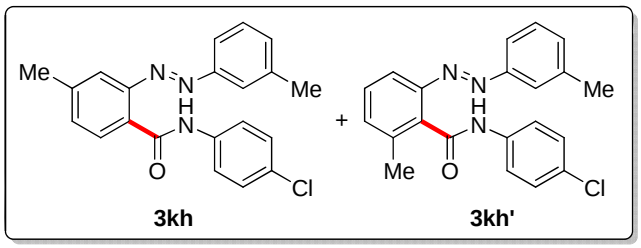
m.p.: 201-202 ^{o}C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (s, 1H), 7.56 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H), 7.40 (s, 1H), 7.37 (s, 2H), 7.29 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.12 (s, 1H), 7.07 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 2.29 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 167.2, 152.7, 149.2, 140.2, 138.9, 137.1, 136.8, 134.0, 133.7, 133.3, 129.5, 129.1, 121.5, 121.1, 114.0, 21.5, 21.3, 19.3.

HRMS (MALDI-MS): calculated for $C_{23}H_{22}ClN_3NaO$ ($[M+Na]^+$) 414.13436, found 414.13441.

(*E*)-*N*-(4-chlorophenyl)-4-methyl-2-(m-tolyldiazenyl)benzamide (3kh) and (*E*)-*N*-(4-chlorophenyl)-6-methyl-2-(m-tolyldiazenyl)benzamide (3kh')



3kh **3kh'**

According to general procedure: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1,2-bis(2-methyl)phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 ^{o}C for 24 h. The ratio of **3kh** and **3kh'** was determined by GC-MS to be 50:1. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 93 % yield..

Data for major product 3kh

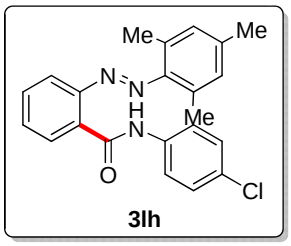
m.p.: 155-156 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.89 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.64 - 7.54 (m, 5H), 7.41 (t, *J* = 7.6 Hz, 1H),7.33 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.5, 152.6, 148.8, 143.0, 139.6, 137.3, 133.2, 132.7, 131.9, 129.4, 128.9, 128.7, 128.4, 122.5, 121.4, 121.1, 115.9, 21.5, 21.4.

HRMS (MALDI-MS): calculated for $C_{21}H_{18}ClN_3NaO$ ($[M+Na]^+$) 386.10306, found 386.10307

(*E*)-*N*-(4-chlorophenyl)-2-(mesityldiazenyl)benzamide (3lh)



3lh

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1-(2,4,6-trimethylphenyl)-2-phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 24 h. After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 84 % yield.

m.p.: 126-127 °C

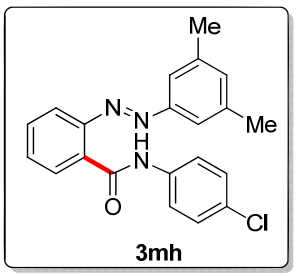
^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.70 (s, 1H), 8.33 - 8.31 (m, 1H), 7.75 - 7.74 (m, 1H), 7.53 - 7.47 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 2H), 2.35 (s, 6H), 2.33 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.9, 149.3, 149.1, 140.3, 137.1, 132.0, 131.6, 131.4, 131.3, 130.3, 128.9, 128.9, 121.3, 115.4, 21.2, 19.1.

HRMS (MALDI-MS): calculated for $C_{22}H_{20}ClN_3NaO$ ($[M+Na]^+$) 400.11871, found 400.11878.

(E)-N-(4-chlorophenyl)-2-((3,5-dimethylphenyl)diazenyl)benzamide (3mh)

According to method A: $Re_2(CO)_{10}$ (0.025 mmol, 5 mol %), (*E*)-1-(3,5-dimethylphenyl)-2-phenyldiazene (1.25 mmol), 4-chlorophenyl isocyanate (0.5 mmol), NaOAc (0.1 mmol) in toluene (2.5 mL) were stirred at 130 °C for 24 h.



3mh

After workup, column chromatography (PE:EA = 10:1) afford the title compound as orange solid in 70 % yield. **3md** was isolated as a single product.

m.p.: 116-117 ^{o}C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.04 (s, 1H), 8.41 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.77 (d, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.44 (s, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.17 (s, 1H), 2.39 (s, 3H).

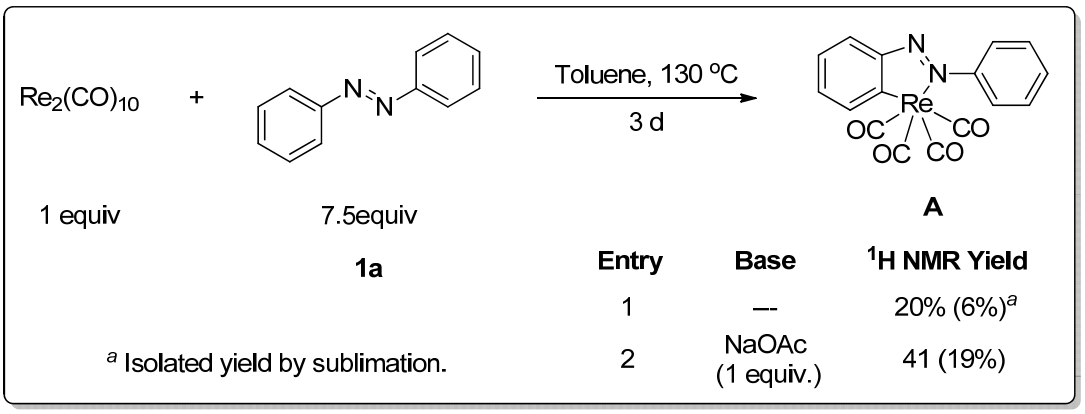
^{13}C NMR ($CDCl_3$, 101 MHz) δ 163.5, 152.8, 149.0, 139.4, 137.3, 134.3, 132.3, 131.9, 131.8, 130.9, 129.0, 129.0, 121.2, 121.0, 115.7, 21.3.

HRMS (MALDI-MS): calculated for $C_{21}H_{18}ClN_3NaO$ ($[M+Na]^+$) 386.10306, found 386.10304.

5. Mechanistic studies

5.1 Probe the possible reaction intermediate

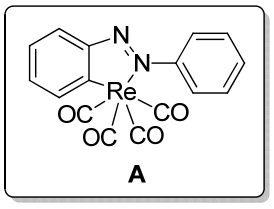
To probe the possible reaction intermediate, a series of reactions were carried out. First, we examined the stoichiometric reaction of $Re_2(CO)_{10}$ with azobenzene **1a**. It was shown that $Re_2(CO)_{10}$ reacted smoothly with azobenzene **1a** affording five-member rhenacycle **A** in 6% isolated yield (Scheme S1).



Scheme S1. Stoichiometric reaction of $Re_2(CO)_{10}$ with azobenzene **1a**

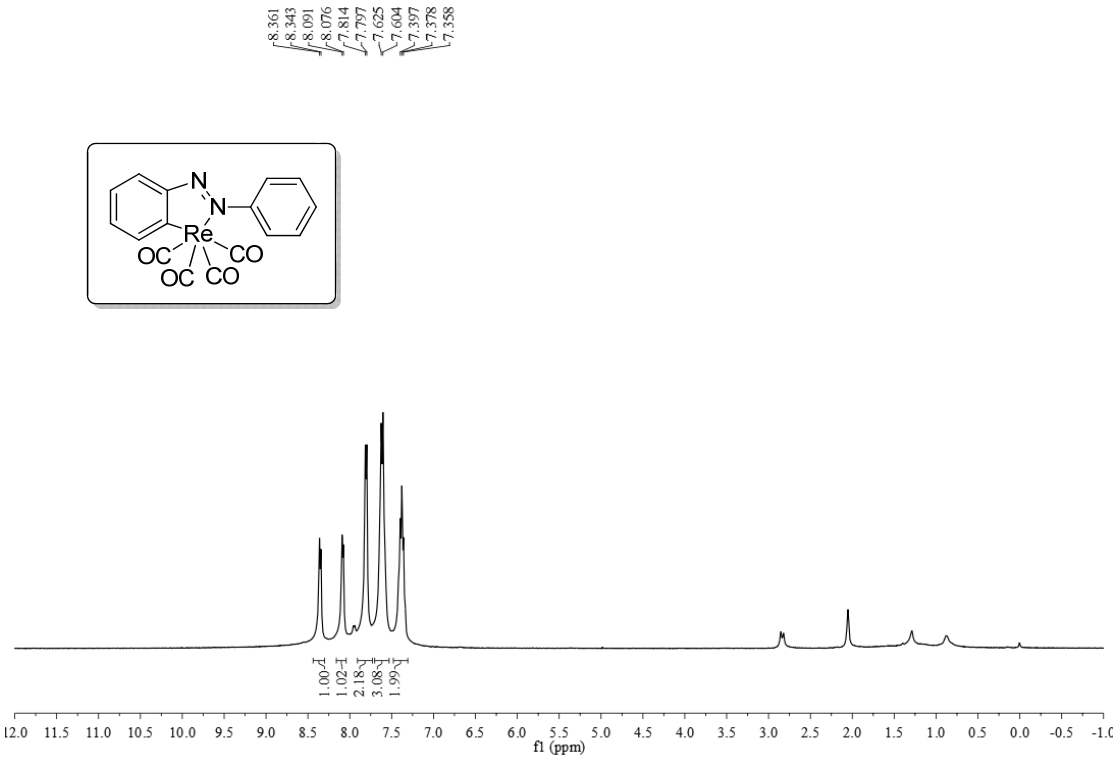
Experimental procedure:

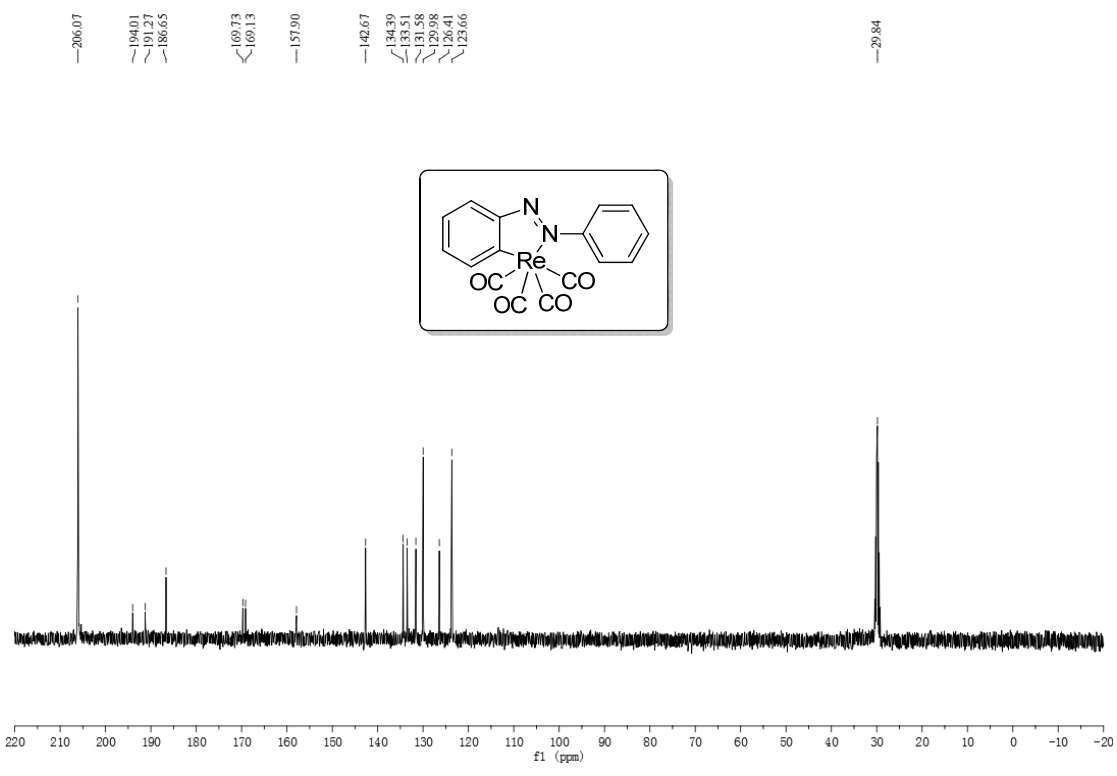
$Re_2(CO)_{10}$ (0.38 mmol, 248 mg), azobenzene **1a** (2.8 mmol, 510 mg) were added into an oven-dried reaction vessel with Teflon screw cap under a nitrogen atmosphere. Toluene (20 mL) was then added into the reaction tube. The reaction mixture was stirred at 130 °C for 3 days. After the completion, the solvent was removed by rotary evaporation and the residue was sublimed at 65 °C to remove azobenzene in vacuum. After azobenzene was completely removed, the mixture was further sublimed at 75 °C in vacuum for 2 hours affording the pure product **A** in 6% yield.[1b]



^{1}H NMR (400 MHz, Acetone-d_6): 8.35 (dd, J_1 = 7.6 Hz), 8.08 (d, J = 6.0 Hz, 1H), 7.81 - 7.80 (m, 2H), 7.63 - 7.61 (m, 3H), 7.40 - 7.36 (m, 2H).

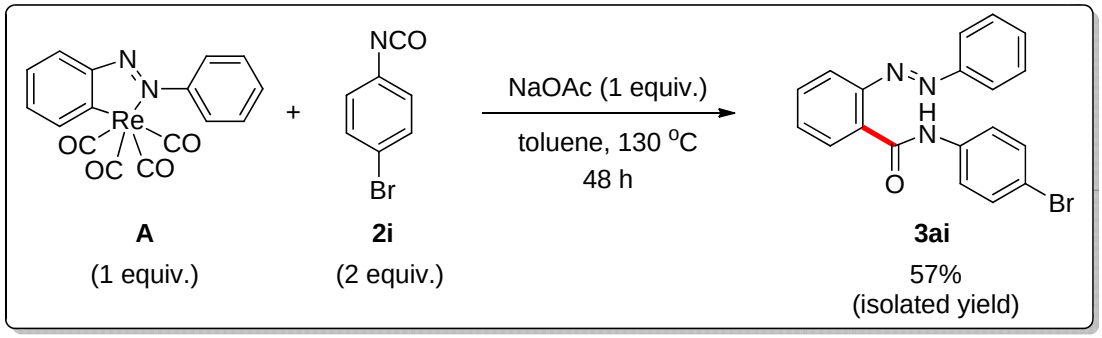
^{13}C NMR (101 MHz, Acetone-d_6): 194.0 (CO), 191.3 (CO), 186.7 (2CO), 169.7, 169.1, 158.0, 142.7, 134.4, 133.5, 131.6, 130.0, 126.4, 123.6.





Next, the stoichiometric reaction of **A** with **2i** was conducted and *o*-azobenzamide **3ai** was obtained in 57% isolated yield after column chromatography (Scheme S2). At last, we performed a catalytic reaction of azobenzene **1a** with isocyanate **2i** using

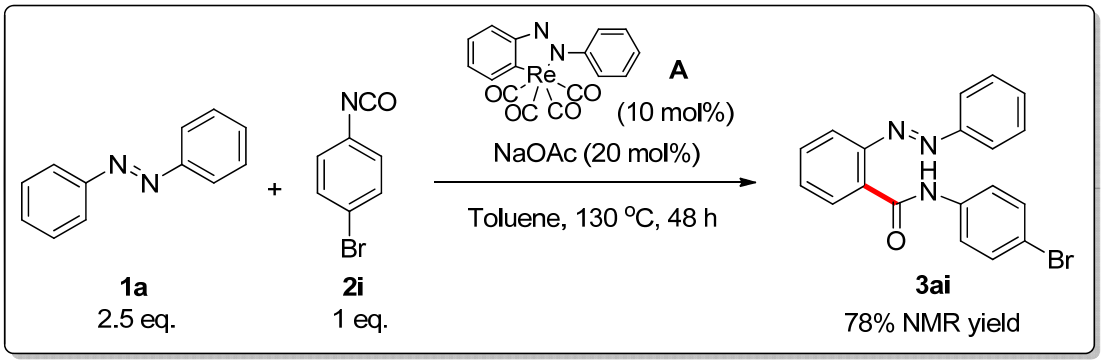
rhenacycle complex **A** as a catalyst under the standard conditions. The reaction proceeded successfully affording the product **3ai** in 78% NMR yield (Scheme S3). These results indicated that the five-member rhenacycle **A** might be a key reaction intermediate in the catalytic reaction.



Scheme S2. Stoichiometric reaction of rhenacycle **A** with **2i**

Experimental procedure:

To an oven-dried tube was added **A** (0.05 mmol 24 mg), *p*-bromophenyl isocyanate **2i** (0.1 mmol, 19.8 mg), NaOAc (0.05 mmol, 4.1 mg) and toluene (0.25 mL) under N_2 atmosphere. The vial was then placed in an oil bath preset to 130 °C. After stirring for 48 h, the vial was removed from the oil bath and was cooled to ambient temperature. After removal of the solvent under vacuum, the residue was subject to column chromatography affording product **3ai** in 57% yield.



Scheme S3. Rhenacycle **A** catalyzed reaction of **1a** and **2i**

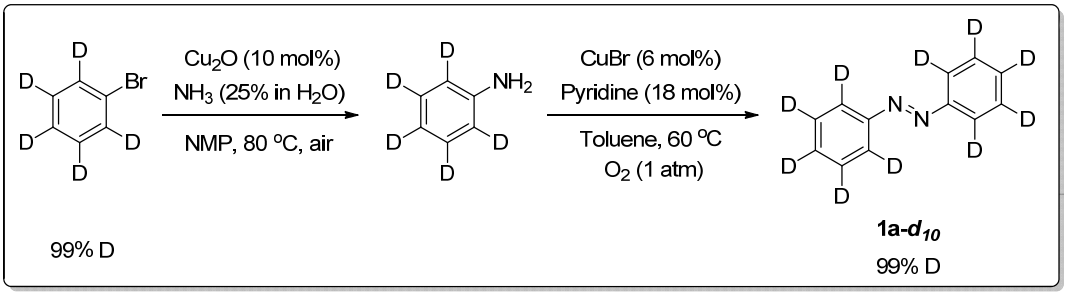
Experimental procedure:

To an oven-dried tube was added **A** (0.01 mmol 4.8 mg), azobenzene **1a** (0.25 mmol, 45.5 mg), *p*-bromophenyl isocyanate **2i** (0.1 mmol, 19.8 mg), NaOAc (0.02 mmol, 1.6 mg) and toluene (0.5 mL) under N_2 atmosphere. The vial was then placed

in an oil bath preset to 130 °C. After stirring for 48 h, the vial was removed from the oil bath and was cooled to ambient temperature. After removal of the solvent under vacuum, the yield of **3ai** was determined by ^{1}H NMR using equimolar amount of 1,3,5-trimethoxylbenzene as an internal standard.

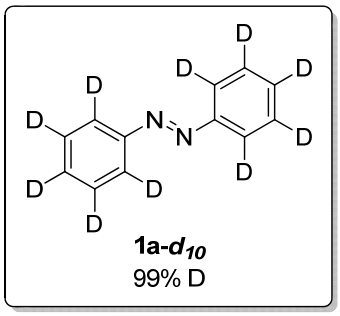
5.2 Probe the nature of the C-H activation step

Fully deuterated azobenzene **1a-*d*$_{10}$** was prepared from commercially available bromobenzene-*d*$_5$ (Alfa Aesar, >99% D) according to the procedure shown in Scheme S4.



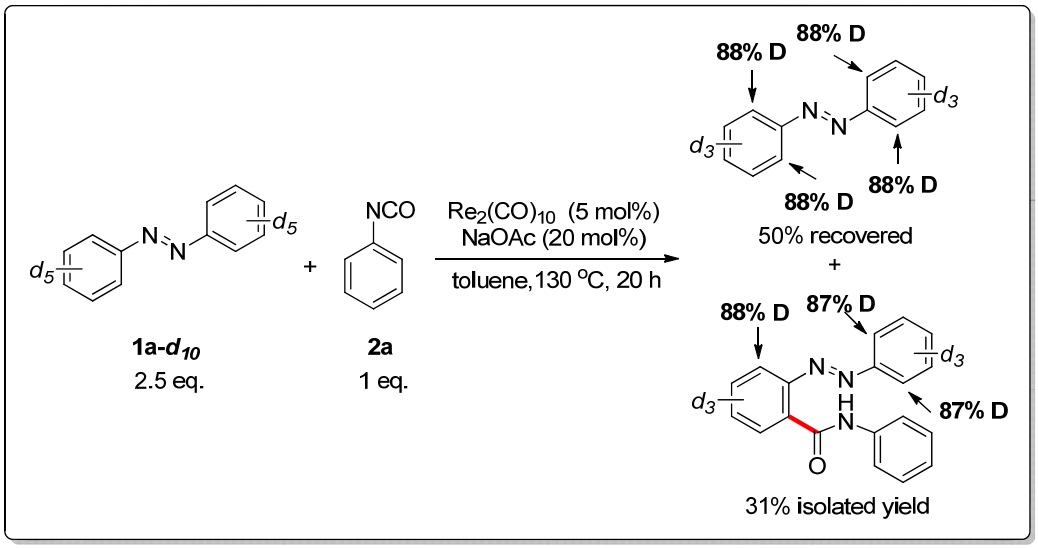
Scheme S4. Preparation of deuterated azobenzene **1a-*d*$_{10}$**

Dipentadeuteroazobenzene (1a-*d*$_{10}$)



Pentadeuteroaniline was prepared from bromobenzene-*d*$_5$ (10 mmol, 1.6 g) by a known procedure[4] and then treated with CuBr, pyridine following the previous described general procedure A using O_2 as oxidant for the synthesis of dipentadeuteroazobenzene **1a-*d*$_{10}$**. After workup, the title compound was isolated by column chromatography (PE/EA = 50:1) as reddish solid in 50% yield.[1b]

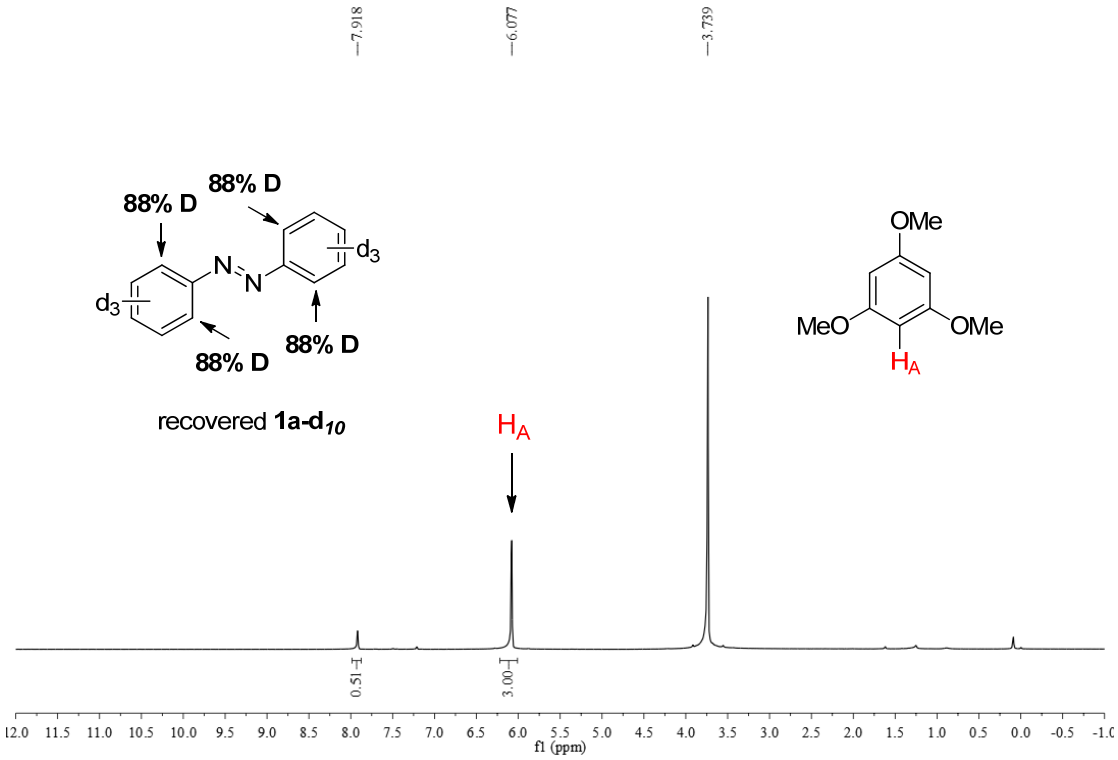
To determine whether the C-H activation step is a deprotonative cyclization process, deuterium-labeling experiments were next explored. The reaction of dipentadeuteroazobenzene **1a-*d*$_{10}$** with phenyl isocyanate **2a** resulted in the partial loss of deuterium at the *ortho*-positions of both the starting material and the product (Scheme S5). We proposed that the loss of deuterium arose from the exchange of deuterium with protons in the reaction solution.

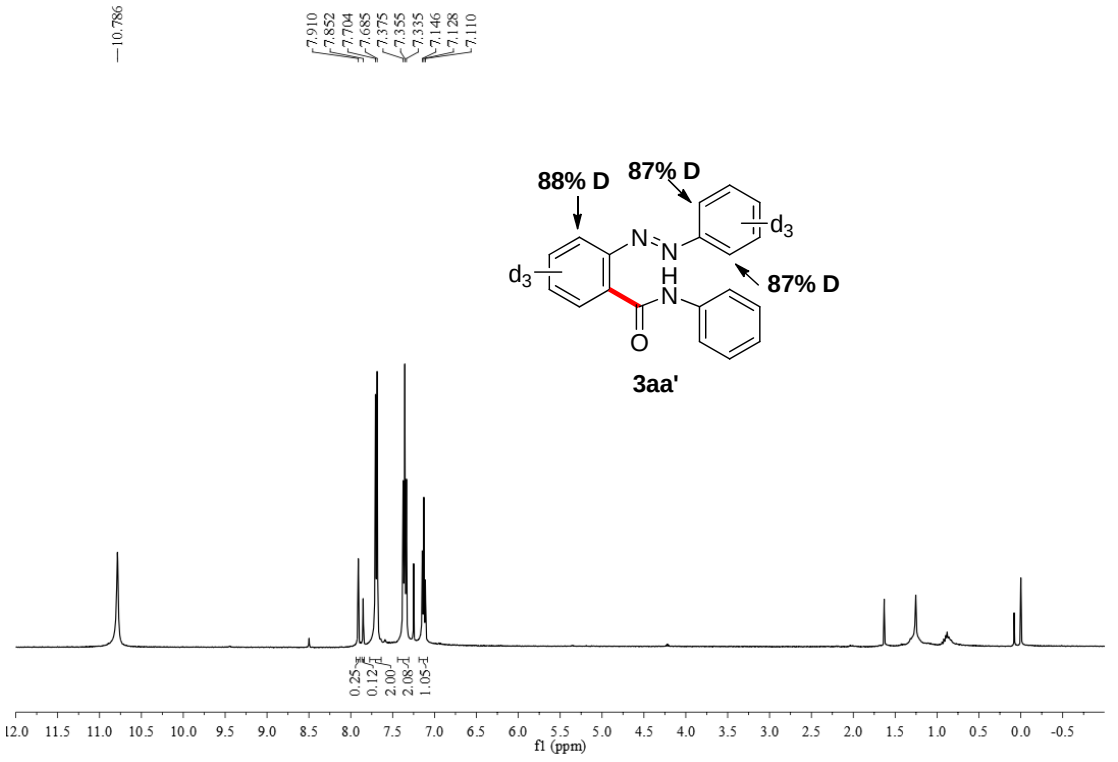


Scheme S5. Deuterium-labeling experiment with **1a-*d*$_{10}$**

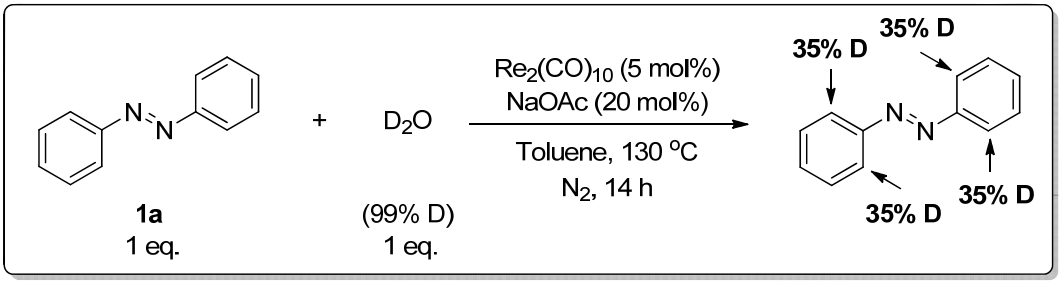
Experimental procedure:

$Re_2(CO)_{10}$ (0.01 mmol, 6.5 mg), NaOAc (0.04 mmol, 3.2 mg), phenyl isocyanate **2a** (0.2 mmol, 23.8 mg), dipentadeuteroazobenzene **1a-*d*$_{10}$** (0.5 mmol, 96.0 mg) and toluene (1 ml) were added into an owen-dried reaction vessel. The solution was stirred at 130 ^{o}C for 24 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography to afford the pure product in 31% yield and the recovered starting material in 50% yield (based on the loading of **1a-*d*$_{10}$**), which was analyzed by ^{1}H NMR in $CDCl_3$. The D-content in the recovered starting material was analyzed using an equimolar amount of 1,3,5-trimethoxylbenzene as the internal standard.





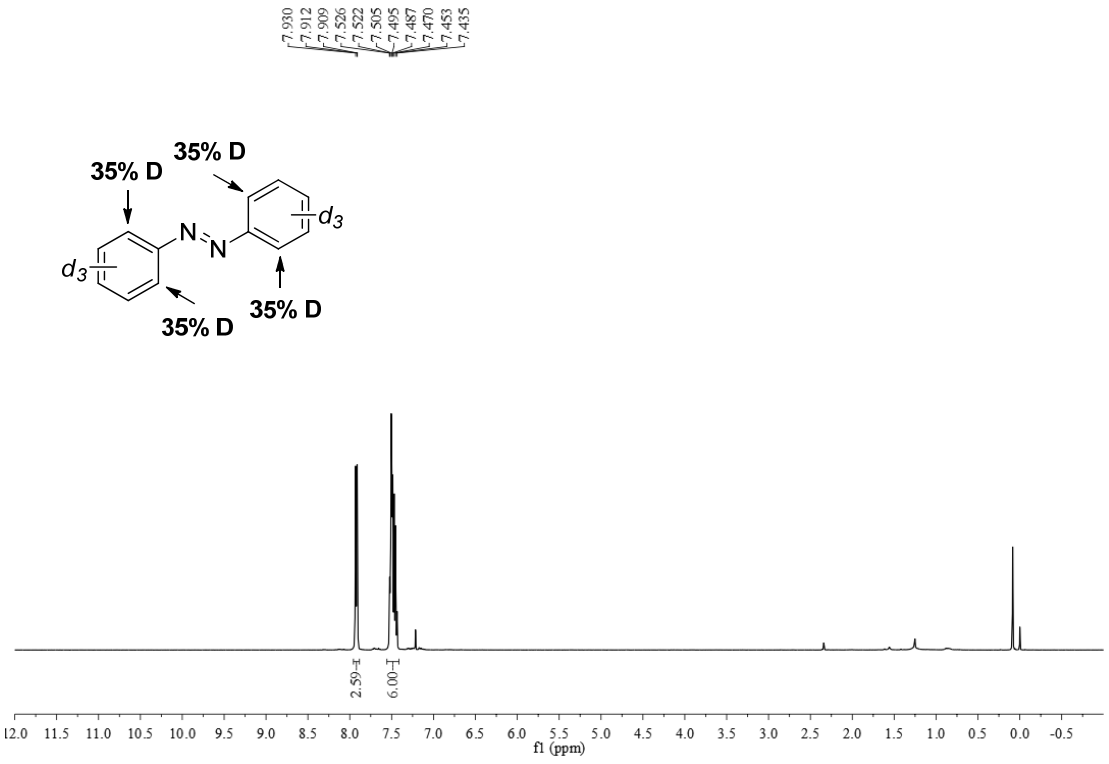
To further confirm the exchange of H/D, the reaction of azobenzene **1a** with D_2O was tested and the incorporation of deuterium at the *ortho*-positions of the recovered **1a** was detected, which confirmed our assumption (Scheme S6).



Scheme S6. H/D scrambling experiment of **1a** with D_2O

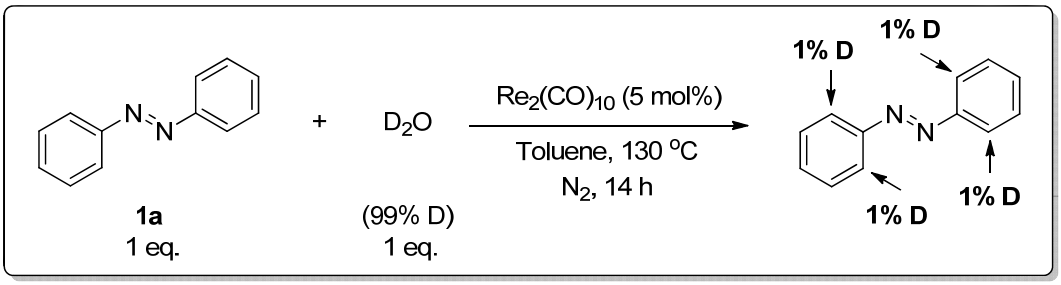
Experimental procedure:

$Re_2(CO)_{10}$ (0.025 mmol, 6.5 mg), azobenzene **1a** (0.2 mmol, 36.4 mg), NaOAc (0.04 mmol, 3.2 mg), D_2O (0.2 mmol, 3.6 mg) and toluene (1 mL) were added into an owen-dried reaction vessel. The solution was stirred at 130 °C for 14 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was analyzed by ^1H NMR in $CDCl_3$.



To investigate whether the C-H activation step is reversible without the addition of NaOAc, the combination of azobenzene **1a** with a catalytic mount of $Re_2(CO)_{10}$ in

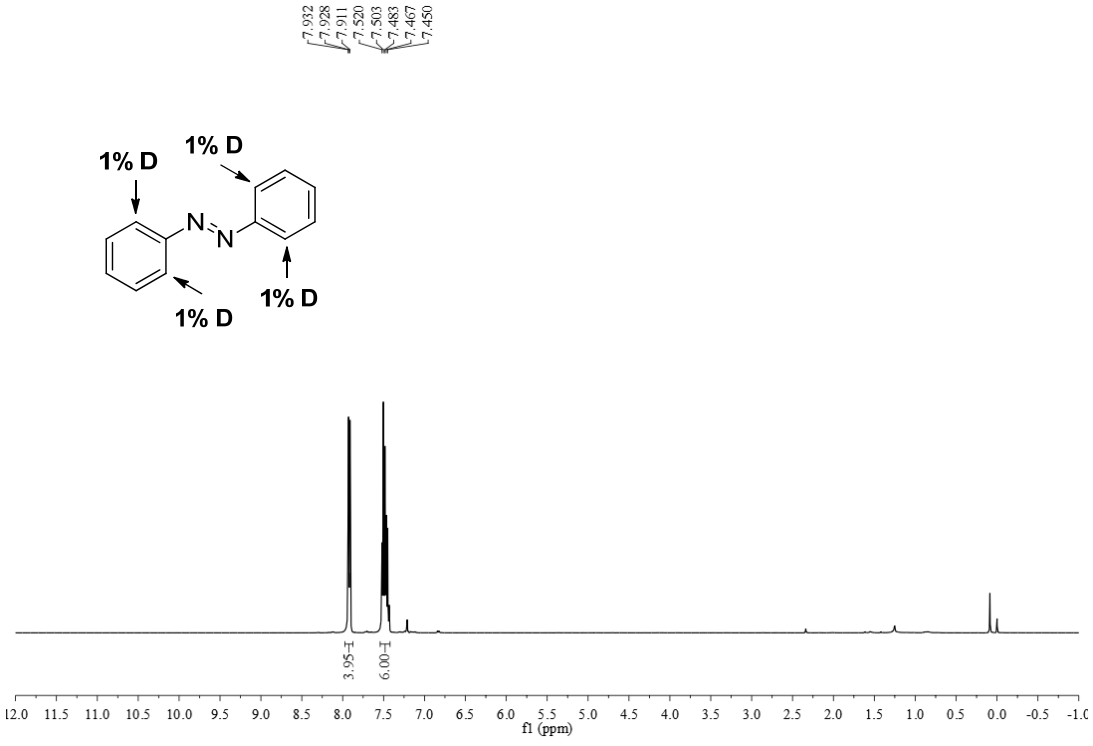
the present of D_2O was examined. It turned out that only negligible D-incorporation at the *ortho*-positions of recovered **1a** was observed (Scheme S7)**.** This result indicated that an irreversible C-H activation step occurred in the absent of NaOAc.



Scheme S7. H/D exchange experiment of **1a** and D_2O in the absence of NaOAc.

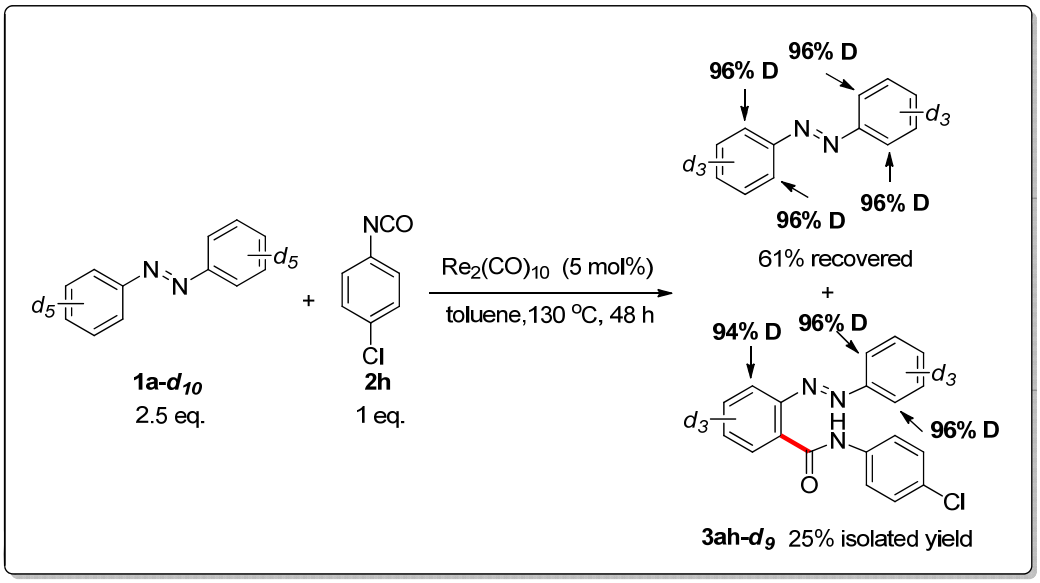
Experimental procedure:

$Re_2(CO)_{10}$ (0.025 mmol, 6.5 mg), azobenzene **1a** (0.2 mmol, 36.4 mg), D_2O (0.2 mmol, 3.6 mg) and toluene (1 mL) were added into an owen-dried reaction vessel. The solution was stirred at 130 °C for 14 h. After completion, the solvent was removed by rotary evaporation and the residue was analyzed by ^1H NMR in $CDCl_3$.



Similarly, the reaction of dipentadeuteroazobenzene **3a-*d*$_{10}$** with *p*-chlorophenyl isocyanate **2h** under the standard conditions resulted in only a very small amount of

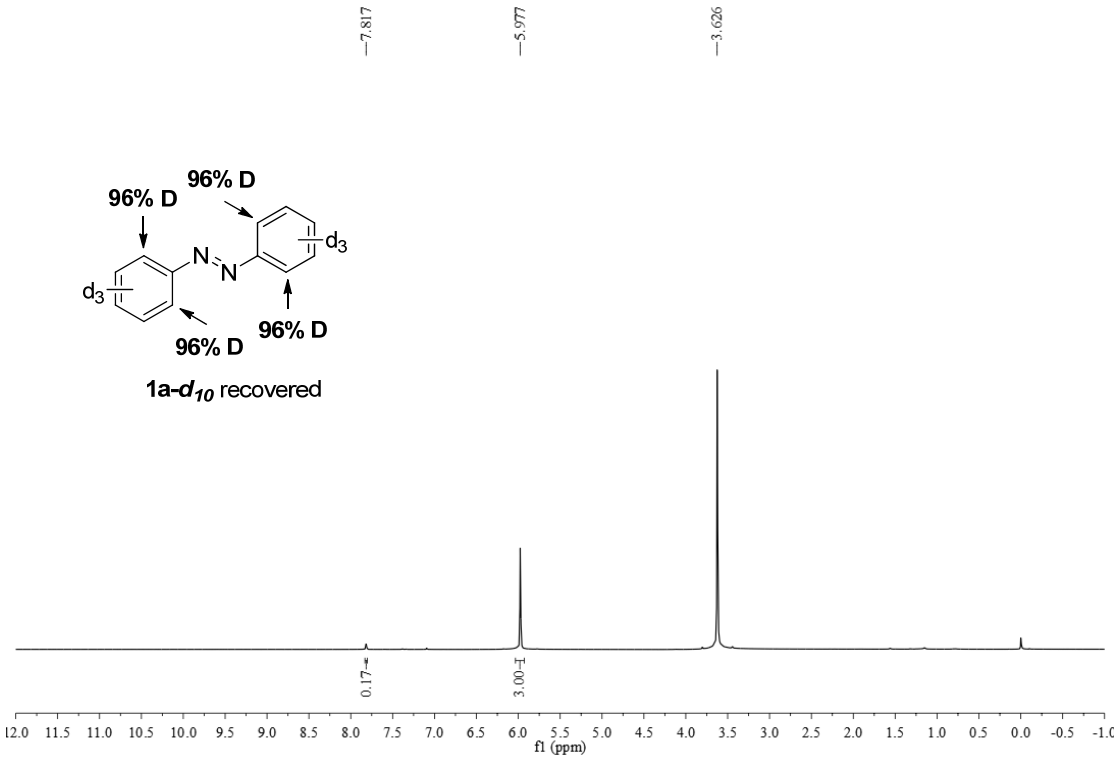
deuterium loss in the product **3ah-*d*$_9$** as well as the recovered azobenzene **1a-*d*$_{10}$** (Scheme S8).

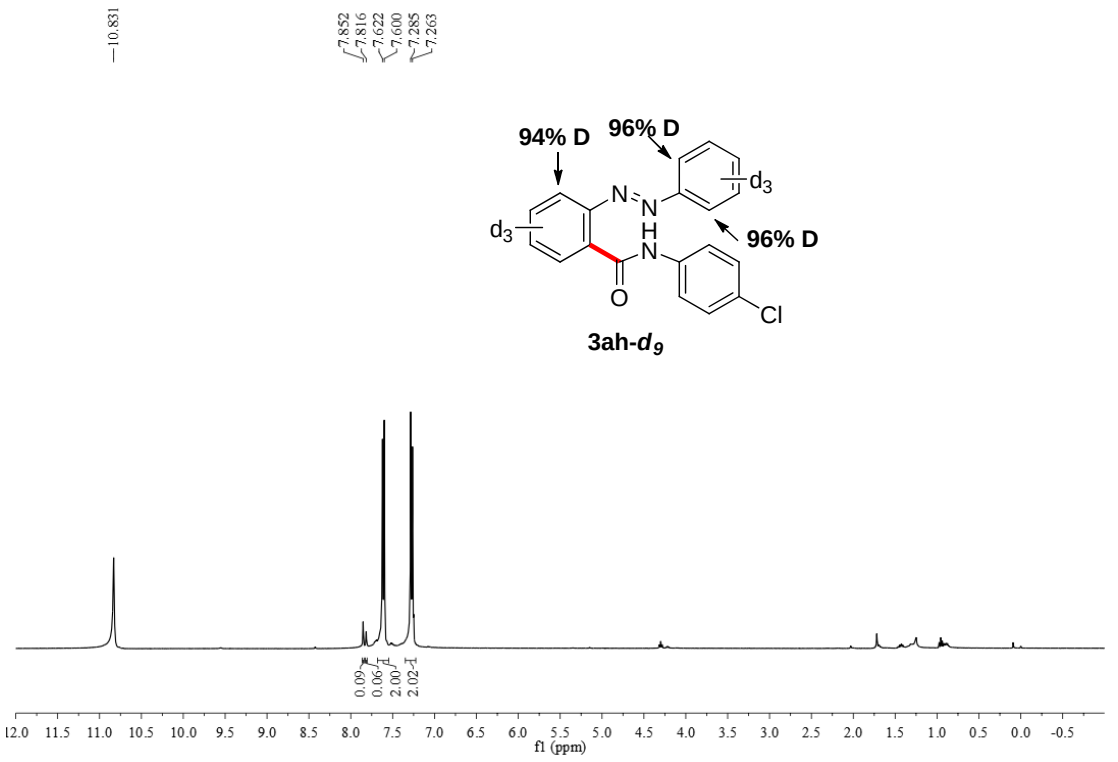


Scheme S8. H/D exchange experiment of **1a-*d*$_{10}$** with **2h** in the absence of NaOAc.

Experimental procedure:

$Re_2(CO)_{10}$ (0.025 mmol, 6.5 mg), azobenzene **1a-*d*$_{10}$** (0.5 mmol, 96.0 mg), *p*-cholrophenyl isocyanate **2h** (0.2 mmol, 30.7 mg) and toluene (1 mL) were added into an owen-dried reaction vessel. The solution was stirred at 130 °C for 48 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography to afford the pure product **3ah-*d*$_9$** in 25% yield and the recovered starting material in 61% yield (based on the loading of **1a-*d*$_{10}$**), which was analyzed by ^{1}H NMR in $CDCl_3$. The D-content in the recovered starting material was analyzed using an equimolar amount of 1,3,5-trimethoxylbenzene as the internal standard.





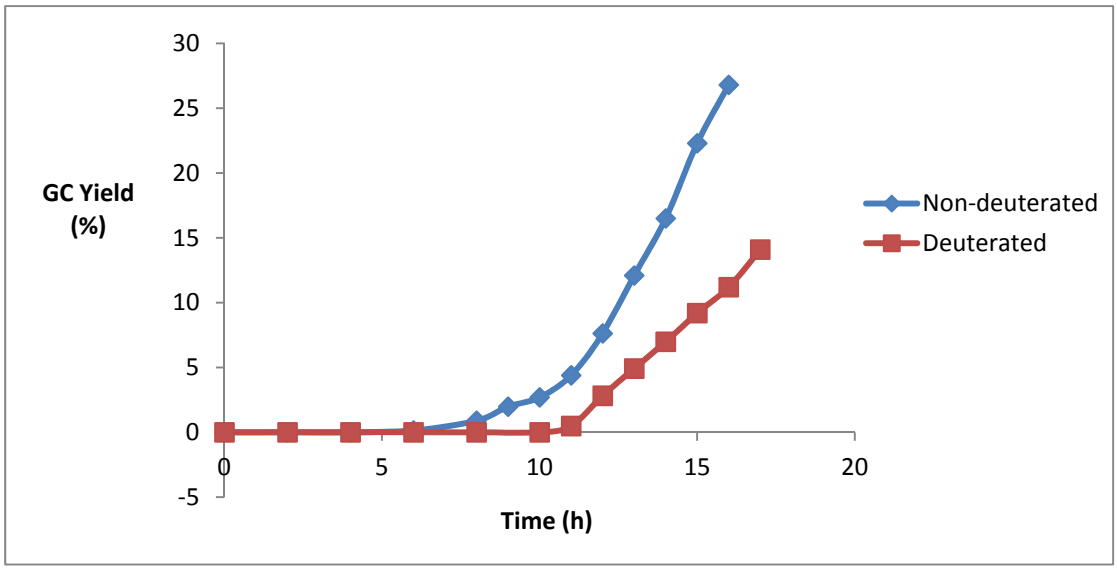
5.3 KIE experiments

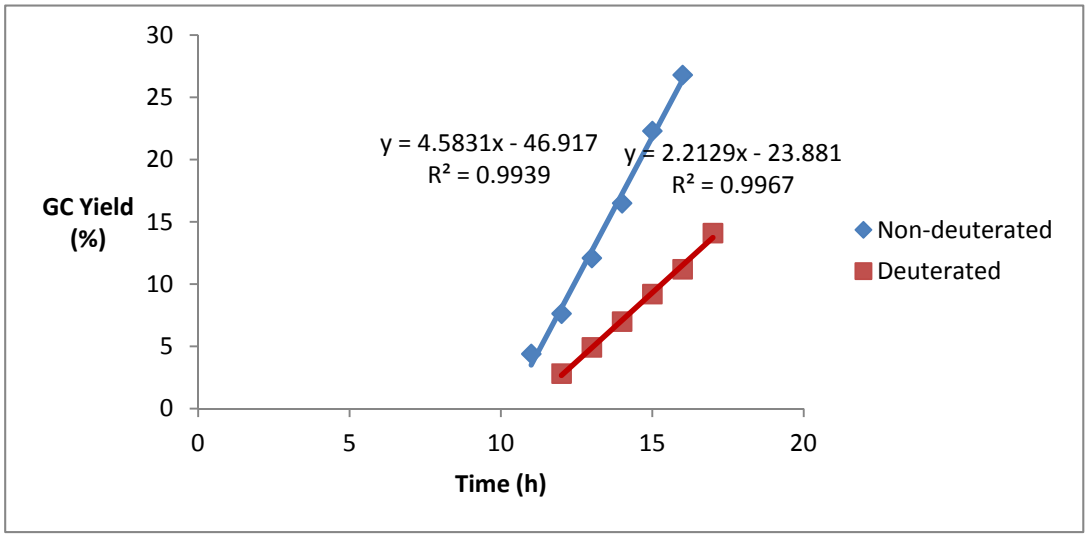
Two parallel reactions of **2a** with **1a** and **1a-*d*$_{10}$** respectively were performed to determine the corresponding KIE value. **1a** (0.25 mmol, 45.5 mg) and **1a-*d*$_{10}$** (0.25

mmol, 48.0 mg) were placed in an oven-dried Schlenk tube respectively, and then treated with the same mixture of **2a** (0.1 mmol, 11.9 mg), $Re_2(CO)_{10}$ (0.005 mmol, 3.2 mg), 1,3,5-trimethoxybenzene (internal standard, 0.1 mmol, 16.8 mg) in anhydrous toluene (0.5 mL) at 130 °C under N_2 atmosphere. Each reaction was sampled at the following indicated points and analyzed by GC-MS. The GC yields were calculated after calibrating the response of GC.

Time (h)	0	2	4	6	8	9	10	11
GC Yield of **3aa** (%)	0	0	0	0.150	0.899	1.98	2.70	4.40
Time (h)	12	13	14	15	16			
GC Yield of **3aa** (%)	7.63	12.1	16.5	22.3	26.8			

Time (h)	0	2	4	6	8	9	10	11
GC Yield of **3aa'** (%)	0	0	0	0	0	0	0	0.487
Time (h)	12	13	14	15	16	17		
GC Yield of **3aa'** (%)	2.82	4.92	6.99	9.20	11.2	14.1		



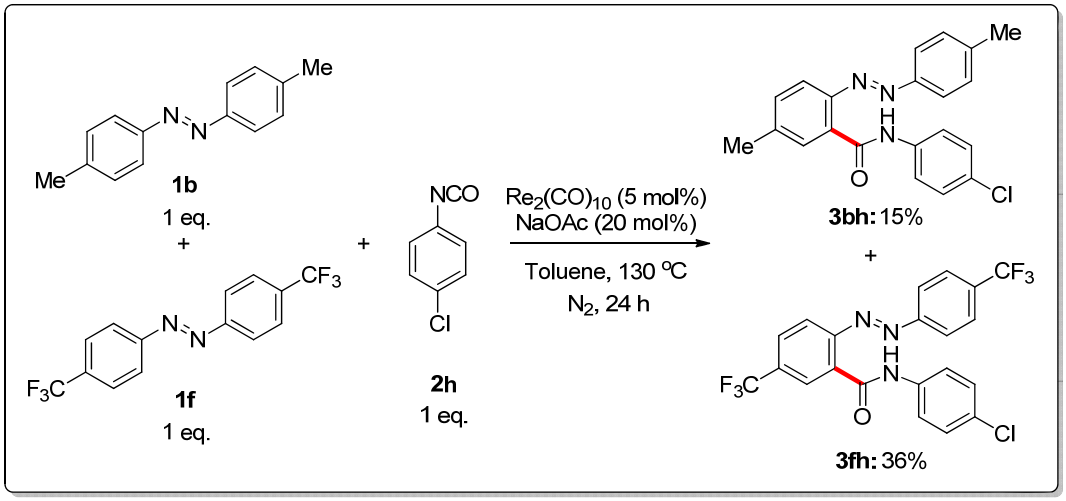


KIE = 4.583/2.212 = 2.07

KIE value from the two parallel reactions was determined to be 2.07. The primary KIE measured by the above experiments indicated that the cleavage of the C–H bond might be involved in the rate-determining step of the reaction.

5.4 Competition Experiments.

In order to gain more insight into the reaction mechanism, competition experiments were studied. Equalmolar amounts of azobenzene **1b** and **1f** bearing Me and CF_3 groups respectively at the *para*-positions were treated with equalmolar amount of *p*-chlorophenyl isocyanate **2h** in the presence of $Re_2(CO)_{10}$ and NaOAc (Scheme S9). The *o*-azobenzamide **3fh** derived from **1f** turned out to be the major product.

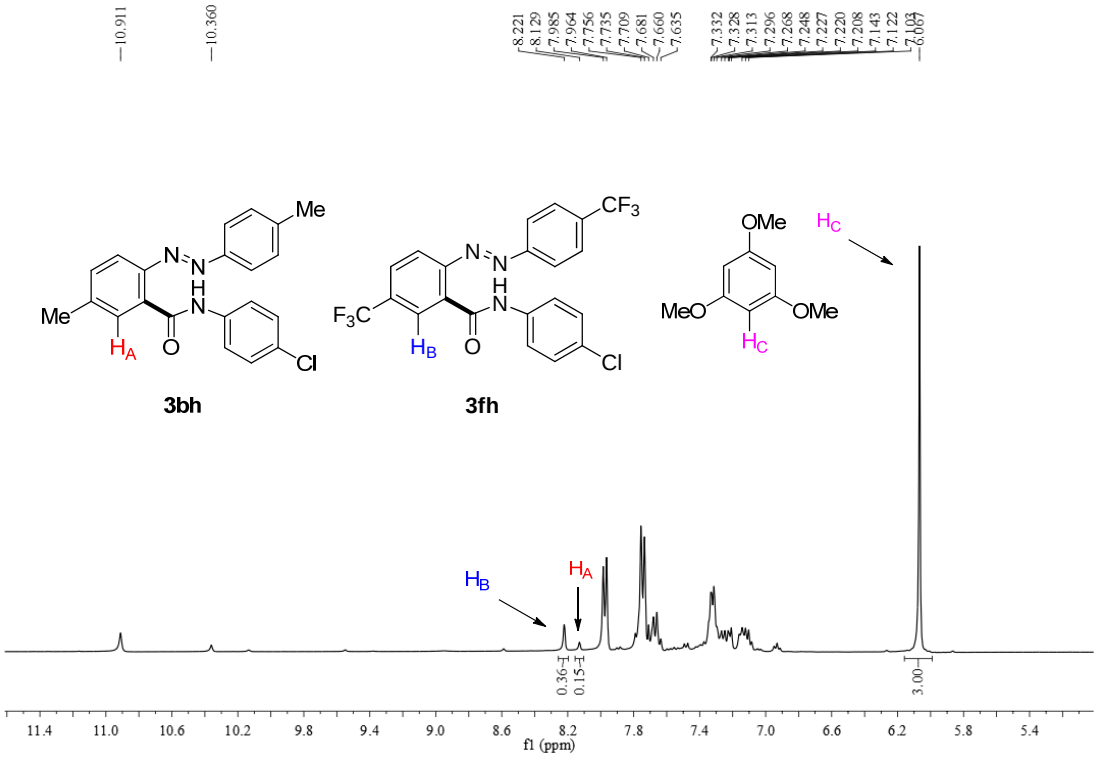


Scheme S9. Competition experiment of substituted azobenzenes

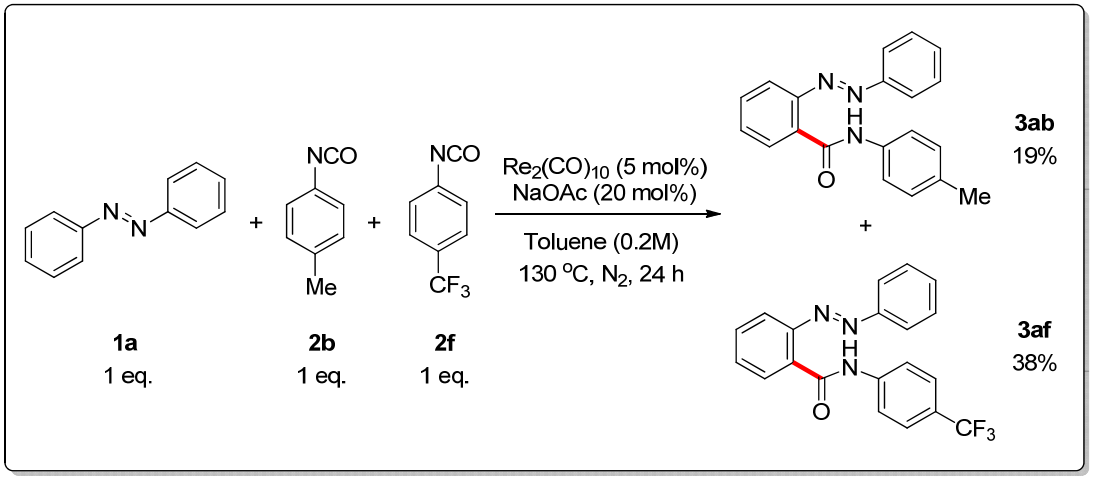
A deprotonation pathway is proposed to be involved in the C-H activation step. Therefore, azobenzenes bearing electron-withdrawing group such as CF_3 undergo easier deprotonative C-H activation to give kinetically more favored product as shown in Scheme 6. However, azoarenes bearing electron-donating groups such as Me group might form the thermodynamically more favored product in higher yield, albeit with lower reaction rate in comparison with electron-poor azobenzenes.

Experimental procedure:

$Re_2(CO)_{10}$ (0.025 mmol, 6.5 mg), azobenzene **1b** (0.2 mmol, 42.0 mg), **1f** (0.2 mmol, 63.6 mg), NaOAc (0.04 mmol, 3.2 mg) and toluene (1 mL) were added into an owen-dried reaction vessel. The solution was stirred at 130 ^{o}C for 24 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was analyzed by ^{1}H NMR using equalmolar amount of 1,3,5-trimethoxybenzene as internal in $CDCl_3$.



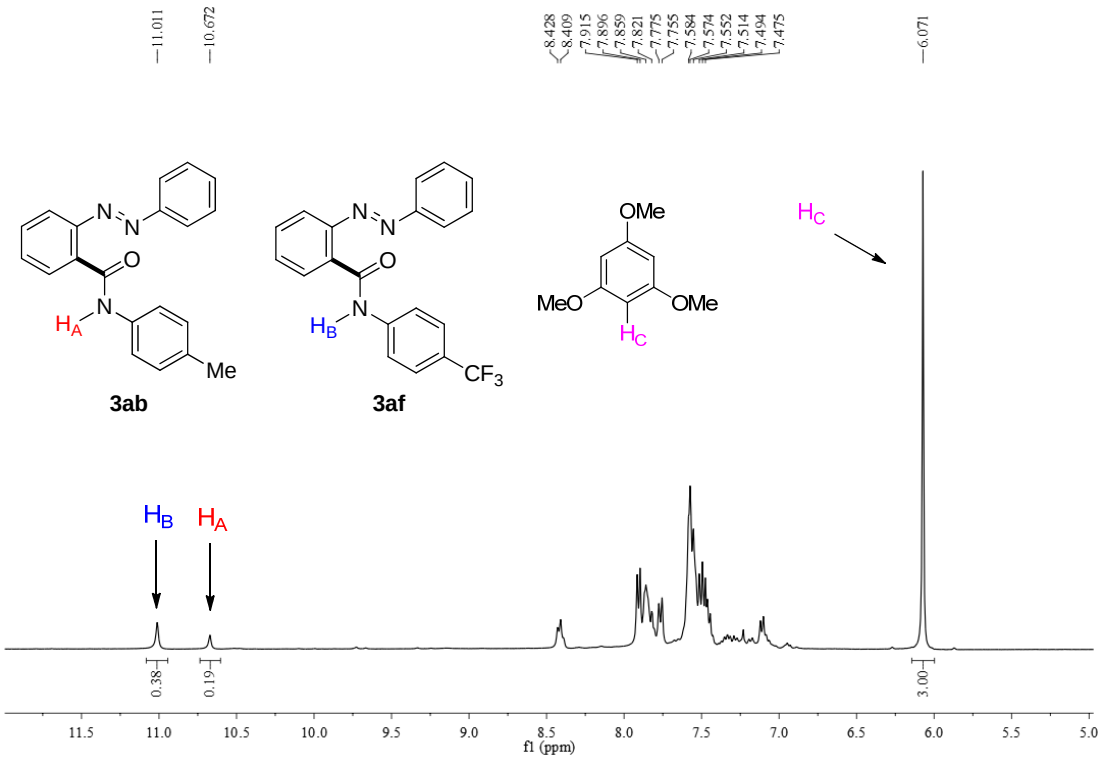
Moreover, the competition reaction between phenyl isocyanate **2b** and **2f** was carried out in order to probe the following steps after C–H bond activation (Scheme S10). It was shown that **1a** reacted preferentially with the electron-deficient phenyl isocyanate **2f** affording **3af** in 38% yield as the major product.



Scheme S10. Competition Experiment of substituted phenyl isocyanates

Experimental procedure:

$Re_2(CO)_{10}$ (0.025 mmol, 6.5 mg), azobenzene **1a** (0.2 mmol, 36.4 mg), **2b** (0.2 mmol, 26.6 mg), **2f** (0.2 mmol, 37.4 mg), NaOAc (0.04 mmol, 3.2 mg) and toluene (1 mL) were added into an owen-dried reaction vessel. The solution was stirred at 130 °C for 24 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was analyzed by ^{1}H NMR using equalmolar amount of 1,3,5-trimethoxybenzene as internal standard in $CDCl_3$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8.409
7.915
7.896
7.859
7.821
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7.755
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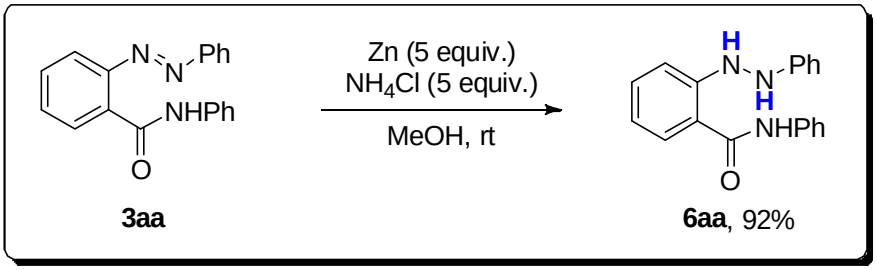
7.574
7.552
7.514
7.494
7.475
6.071
3ab
3af
OMe
MeO
OMe
HA
HB
HC
Me
CF3
0.38
0.19
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)

6. Synthetic transformations of *o*-azobenzamides

With the obtained *o*-azobenzamides in hand, we performed application experiments to shown their synthetic utilities. As an example, *o*-azobenzamide **3aa** was treated with Zn/NH_4Cl to afford the reduced product, diphenylhydrazine **6aa**, in 92% yield (Scheme S11).

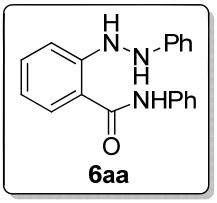


Scheme S11. Reduction of *o*-azobenzamide **3aa**

Experimental procedure:

o-Azobenzamide **3aa** (0.1 mmol, 30.1 mg), Zn (0.5 mmol, 32.5 mg), NH_4Cl (0.5 mmol, 56.5 mg), and absolute methanol (1 mL) were added into a round-bottom flask. The solution was stirred at room temperature for 5 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was subjected to column chromatography to afford the pure product **6aa** in 92% yield.

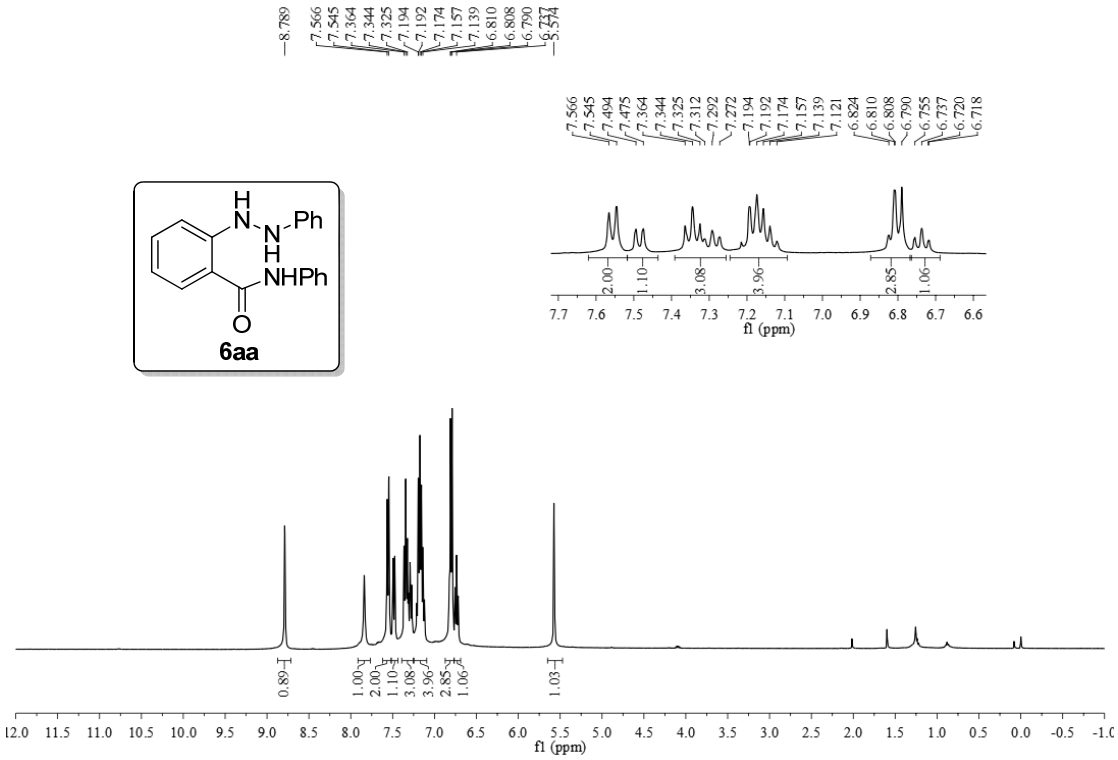
***N*-phenyl-2-(2-phenylhydrazinyl)benzamide (6aa)**

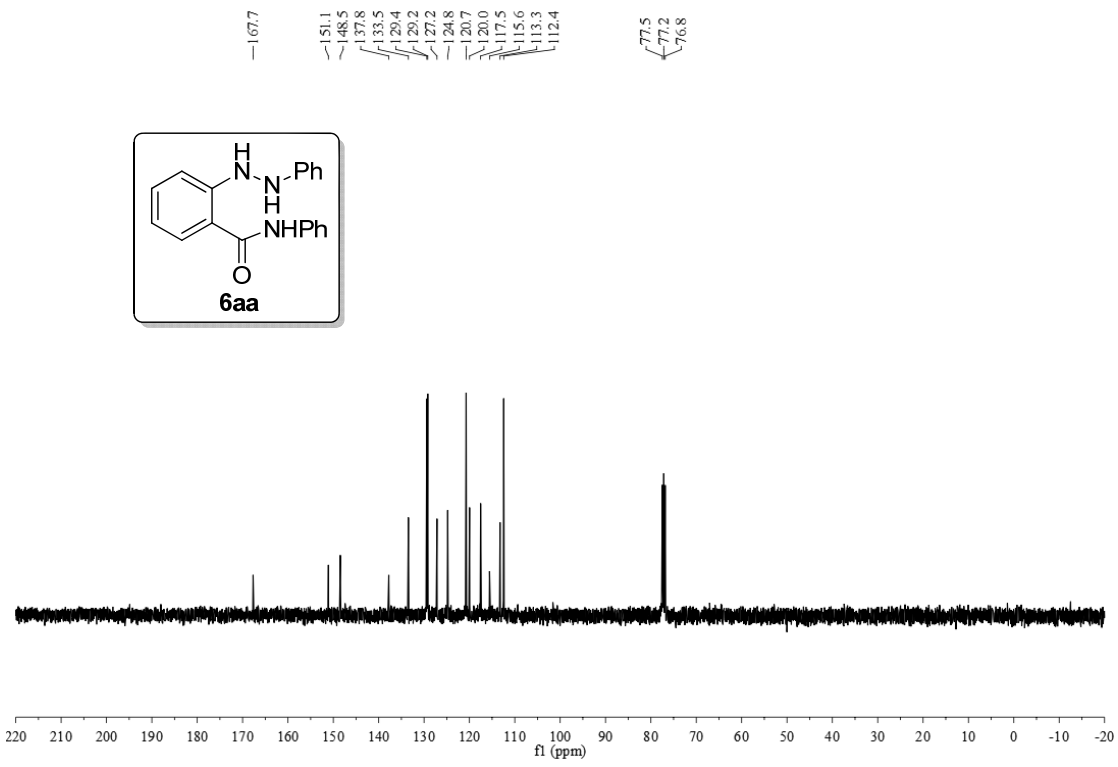


^{1}H NMR (400 MHz, $CDCl_3$): 8.79 (s, 1H), 7.84 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.22 – 7.12 (m, 4H), 6.82 – 6.79 (m, 3H), 7.67 (t, *J* = 7.2 Hz, 1H), 5.57 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): 167.7, 151.1, 148.5, 137.8, 133.5, 129.4, 129.2, 127.2, 124.8, 120.7, 120.0, 117.5, 115.6, 113.3, 112.4.

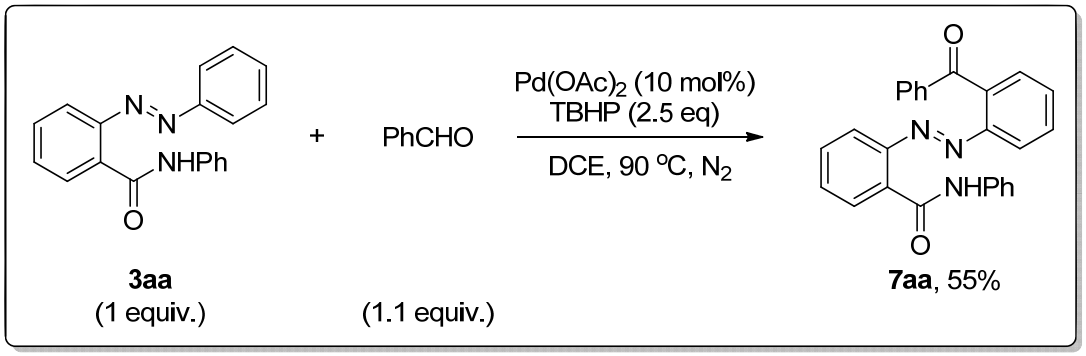
HRMS (**MALDI-MS**): calculated for $C_{19}H_{17}N_3NaO$ ($[M+Na]^+$) 326.12638, found 326.12644.





By combination of Re-catalyzed mono-C-H aminocarbonylation with other transition metal catalyzed C-H activation, sequential C-H bond transformations could be achieved. For instance, *o*-azobenzamide **3aa** underwent the second C-H acylation

reaction under the catalysis of palladium giving unsymmertrical azobenzene derivative **7aa** smoothly (Scheme S12).

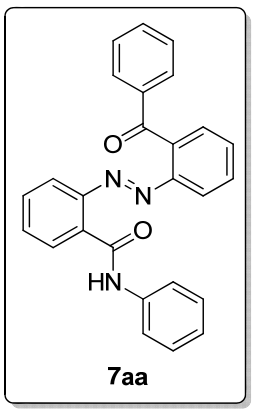


Scheme S12. Pd-catalyzed C-H acylation of *o*-azobenzamide **3aa**

Experimental procedure[5]:

$Pd(OAc)_2$ (0.01 mmol, 2.3 mg), *o*-azobenzamide **3aa** (0.1 mmol, 30.1 mg), TBHP (0.25 mmol) benzaldehyde (0.11 mmol, 11.2 mg) and 1,2-dichloroethane (0.5 mL) were added into an owen-dried reaction vessel under N_2 atmosphere. The solution was stirred at 90 ^oC for 24 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was subjected to column chromatography to afford the pure product **7aa** in 55% yield.

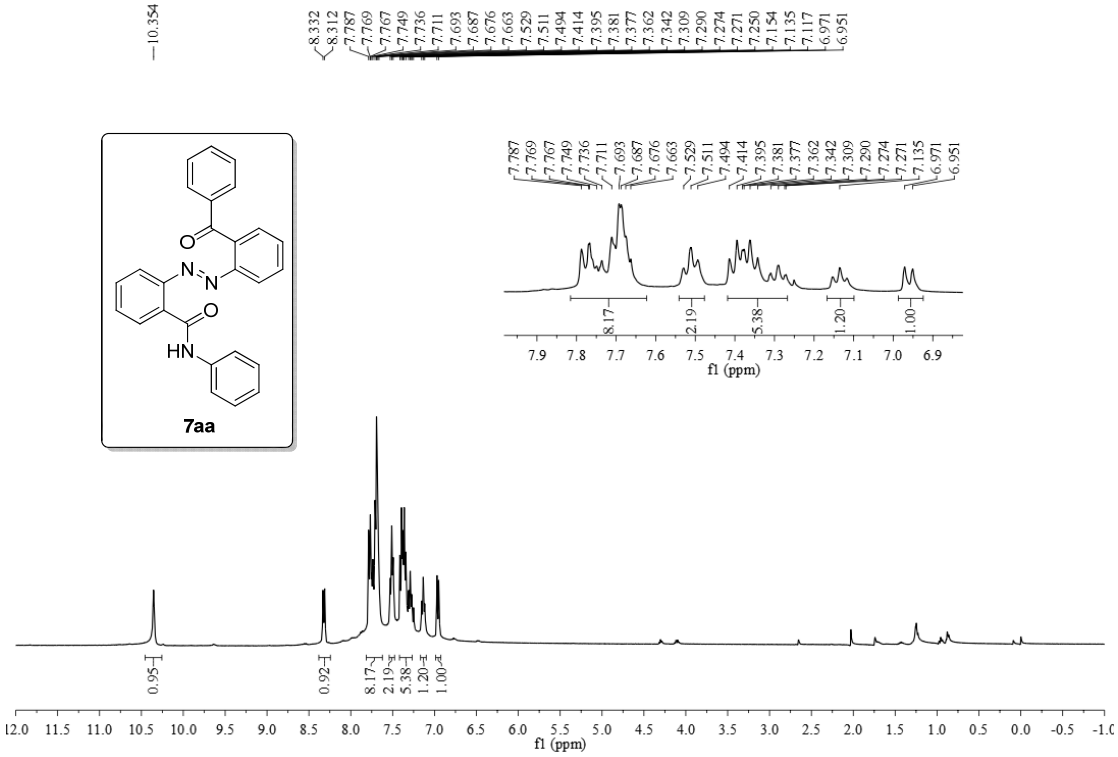
(*E*)-2-((2-benzoylphenyl)diazenyl)-*N*-phenylbenzamide (7aa)



^{1}H NMR (400 MHz, $CDCl_3$): 10.35 (s, 1H), 8.32 (d, *J* = 8.0 Hz), 7.79 – 7.66 (m, 8H), 7.51 – 7.49 (m, 2H), 7.41 – 7.25 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): 196.5, 163.6, 150.6, 149.0, 138.9, 138.5, 138.3, 133.3, 132.2, 132.1, 131.9, 131.7, 131.4, 129.8, 129.6, 129.2, 128.6, 124.5, 120.4, 117.2, 116.1.

HRMS (MALDI-MS): calculated for $C_{26}H_{19}N_3NaO_2$ ($[M+Na]^+$) 428.13695, found 428.13696.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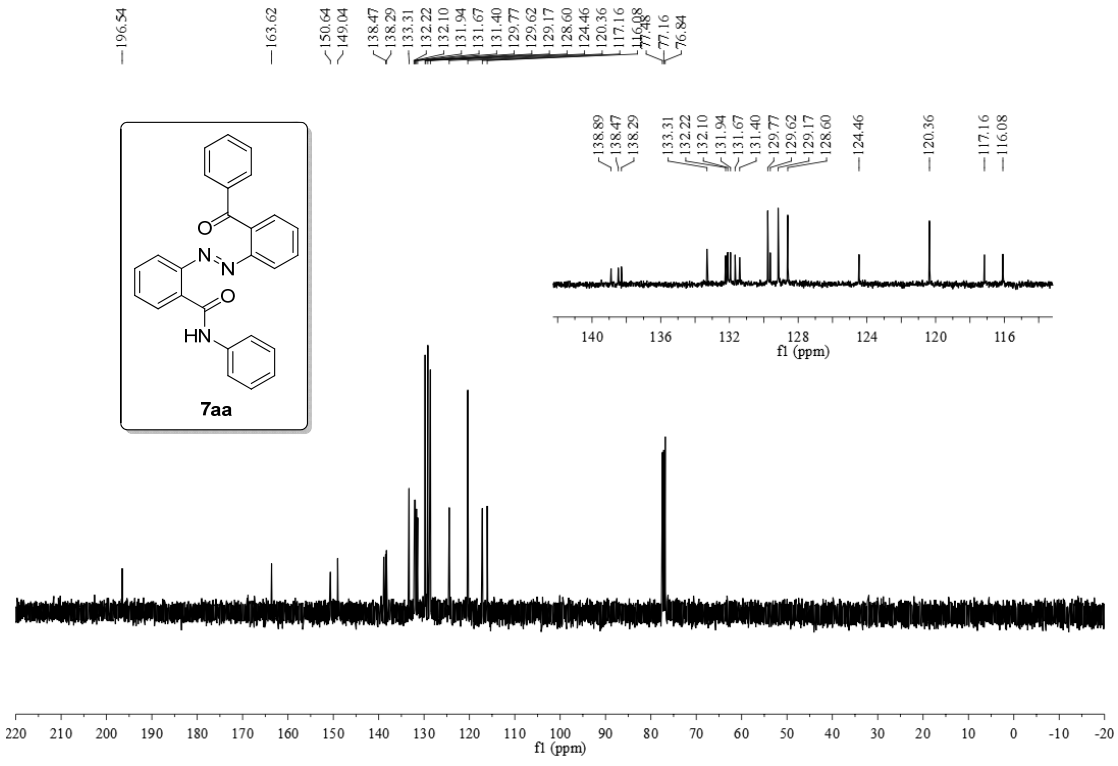
7.676
7.663
7.529
7.511
7.494
7.414
7.395
7.381
7.377
7.362
7.342
7.309
7.290
7.274
7.271
7.250
7.154
7.135
7.117
6.971
6.951
7aa
8.17
2.19
5.38
1.20
1.00
f1 (ppm)
0.95
0.92
8.17
2.19
5.38
1.20
1.00
f1 (ppm)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149.04
138.47
138.29
133.31
132.22
132.10
131.94
131.67
131.40
129.77
129.62
129.17
128.60
124.46
120.36
117.16
116.08
77.48
77.16
76.84
7aa
f1 (ppm)
f1 (ppm)

6. References

1 (a) C. Zhang and N. Jiao, *Angew. Chem. Int. Ed.* 2010, **49**, 6174-6177. (b) Geng, X.; Wang, C. *Org. Lett.* **2015**, DOI: 10.1021/acs.orglett.5b00938.

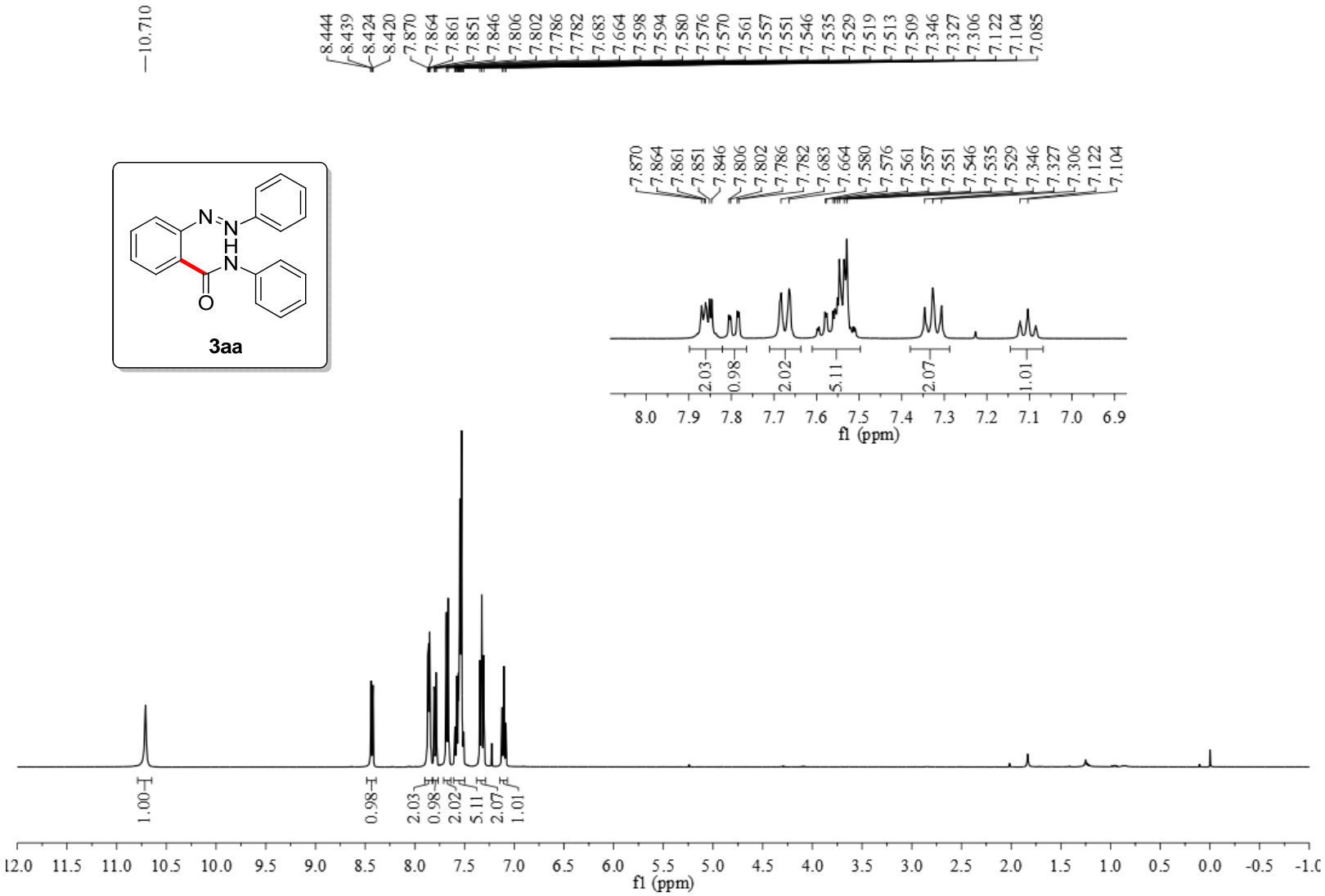
2 Badger, G. M.; Drewer, R. J.; Lewis, G. E. *Aust. J. Chem*. 1964, **17**, 1036-1049.

3 (a) K. Thalluri, S. R. Manne, D. Dev and B. Mandal, *J. Org. Chem.*, 2014, **79**, 3765-3775; (b) A. Yoshimura, M. Luedtke, V. Zhadankin, *J. Org. Chem.* 2012, **77**, 2087-2091; (c) S. Lesniak, A. Chrostowska, D. Kuc, M. Maciejczyk, S. Khayar, R. Nazarski and L. Urbaniak, *Tetrahedron*, 2009, **65**, 10581-10589; (d) V.; Usharani, R. Bhujanga, M. Reddy and P. Dubey, *Asian J. Chem.,* 2011, **23**, 1802-1806. (e) Y. Charalambides and S.Moratti, *Synthetic. Comm.,* 2007, **37**, 1037-1044; (f) E. P. Trub, E. N., Boitsov, B. M. Tsigin, *J. Appl. Spectrosc.,* 1984, **41**, 1232-1236.

4 L. Zhang, K. Chen, G. Chen, B. Li, S. Luo, Q. Guo, J. Wei and Z.-J. Shi, *Org. Lett.* 2013, **15**, 10-13.

5 H. Li, P. Li and L. Wang, *Org. Lett.* 2013, **15**, 620-623.

7. Spectra of Products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7.782
7.683
7.664
7.598
7.594
7.580
7.576
7.570
7.561
7.557
7.551
7.546
7.535
7.529
7.519
7.513
7.509
7.346
7.327
7.306
7.122
7.104
7.085
3aa
2.03
0.98
2.02
5.11
2.07
1.01
fl (ppm)
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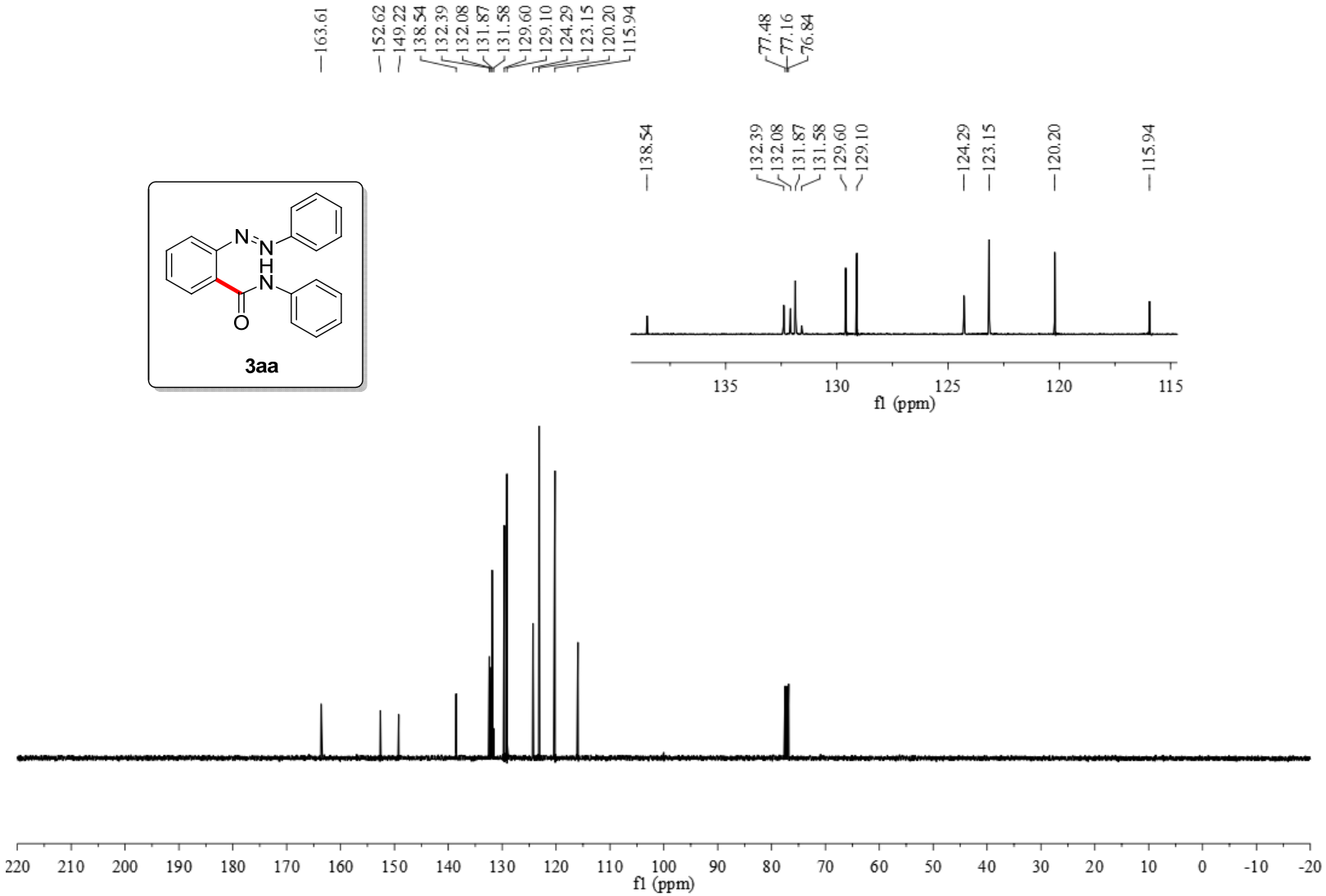
0.98
2.03
0.98
2.02
5.11
2.07
1.01
fl (ppm)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132.39
132.08
131.87
131.58
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124.29
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120.20
115.94
77.48
77.16
76.84
3aa
135
130
125
120
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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70
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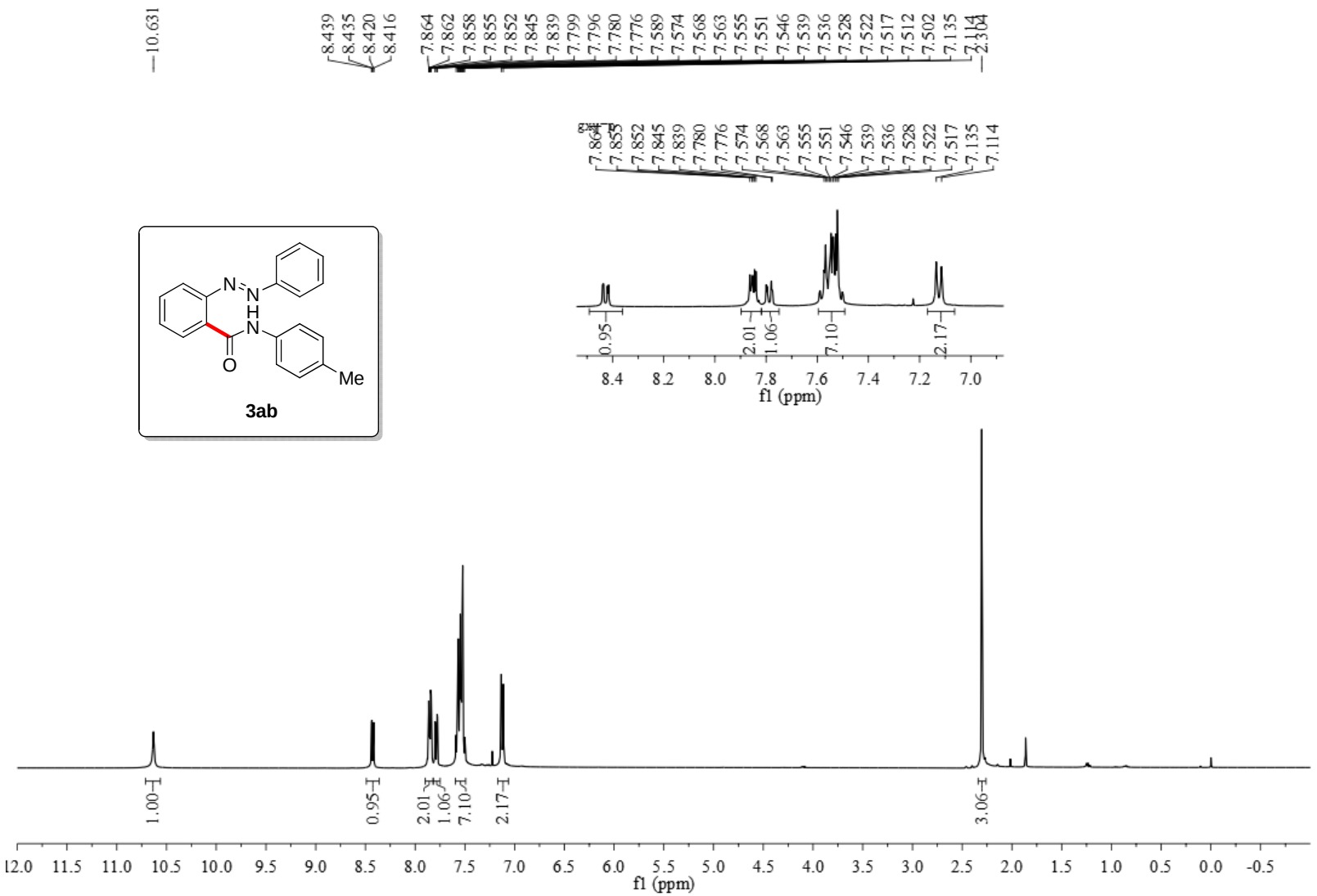
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.799
7.796
7.780
7.776
7.589
7.574
7.568
7.563
7.555
7.551
7.546
7.539
7.536
7.528
7.522
7.517
7.512
7.502
7.135
7.114
2.304
0.95
2.01
1.06
7.10
2.17
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
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N
H
N
O
Me
3ab
1.00
0.95
2.01
1.06
7.10
2.17
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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6.5
6.0
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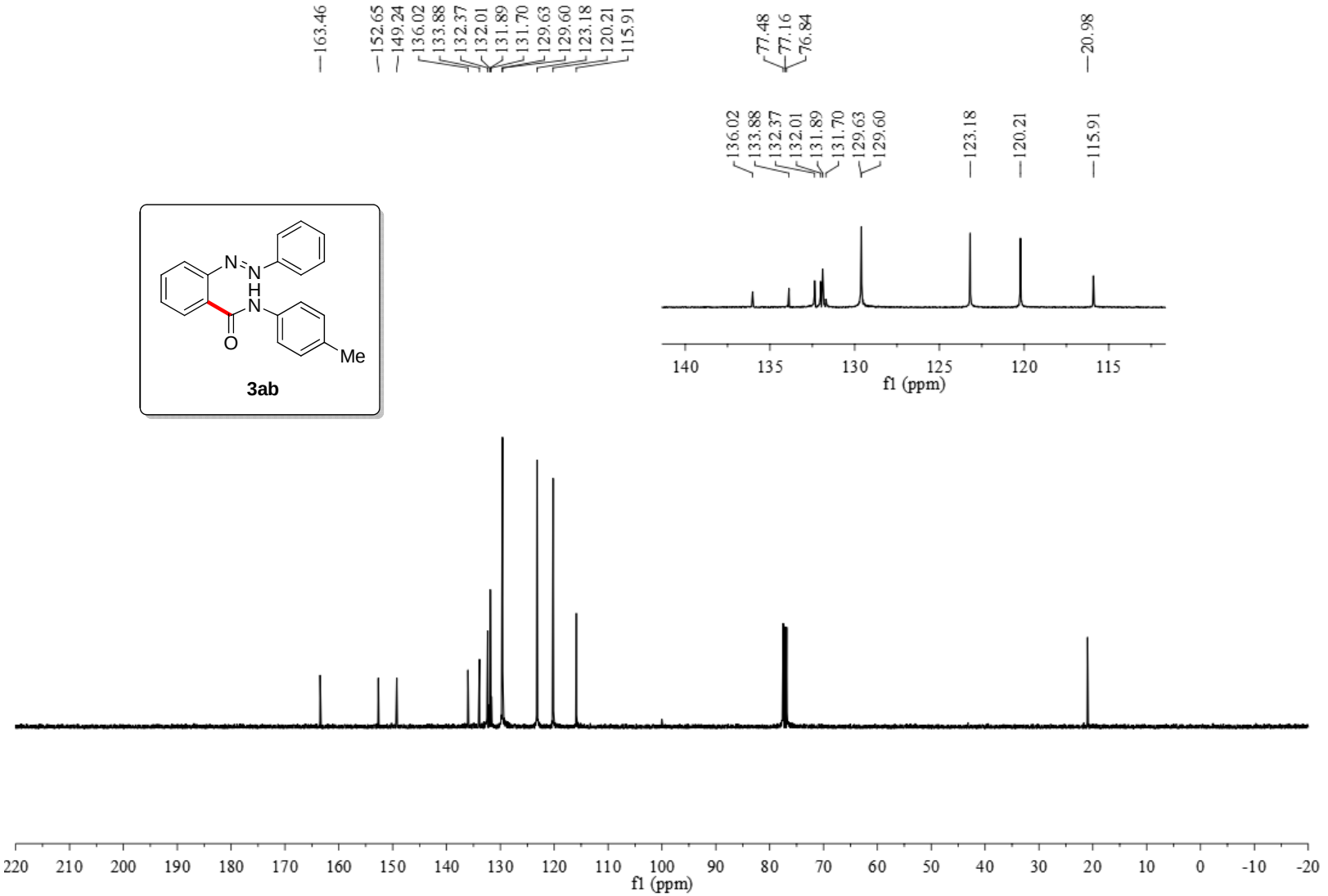
f1 (ppm)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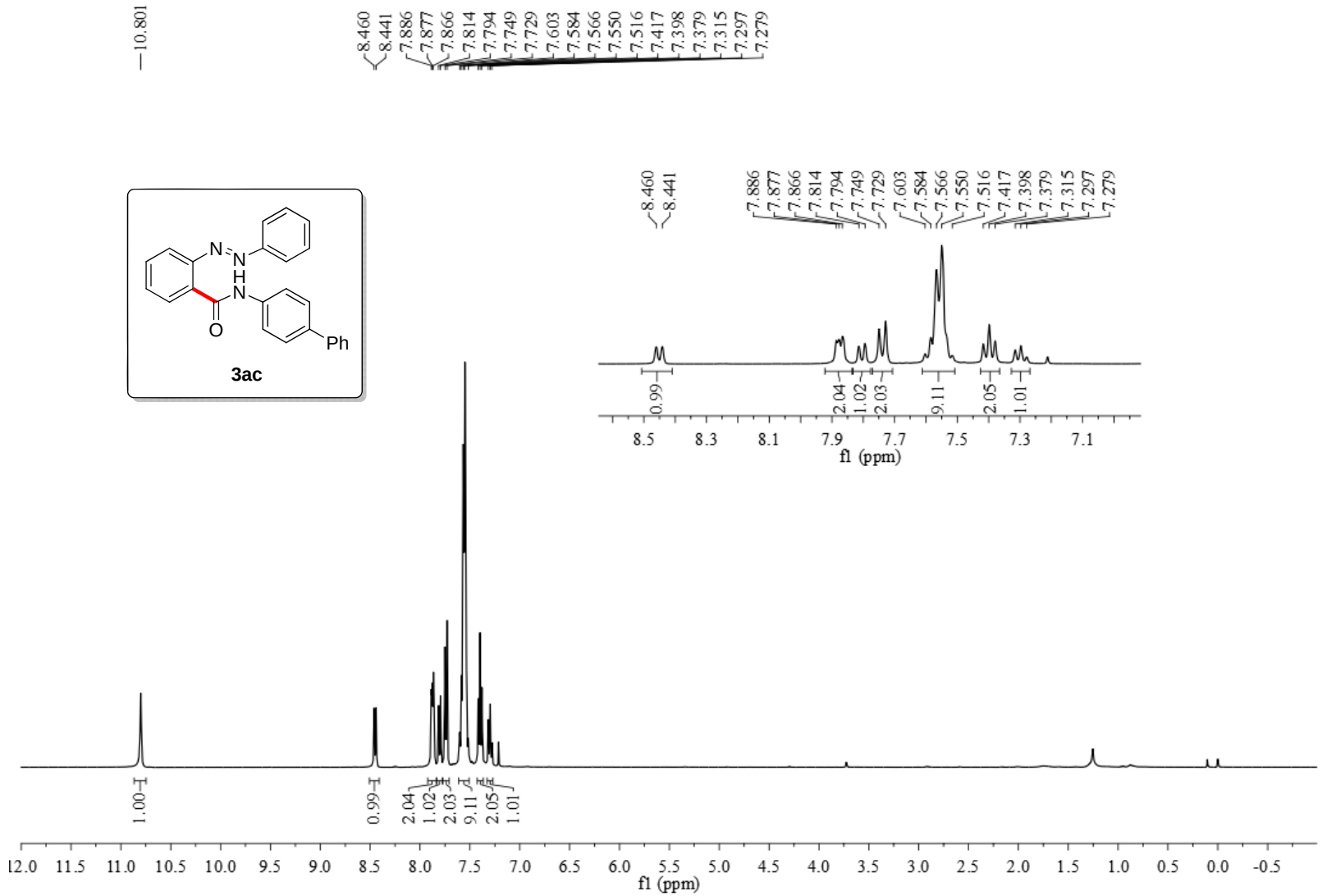
20.98
3ab
Me
fl (ppm)
fl (ppm)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7.550
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7.315
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7.279
N
N
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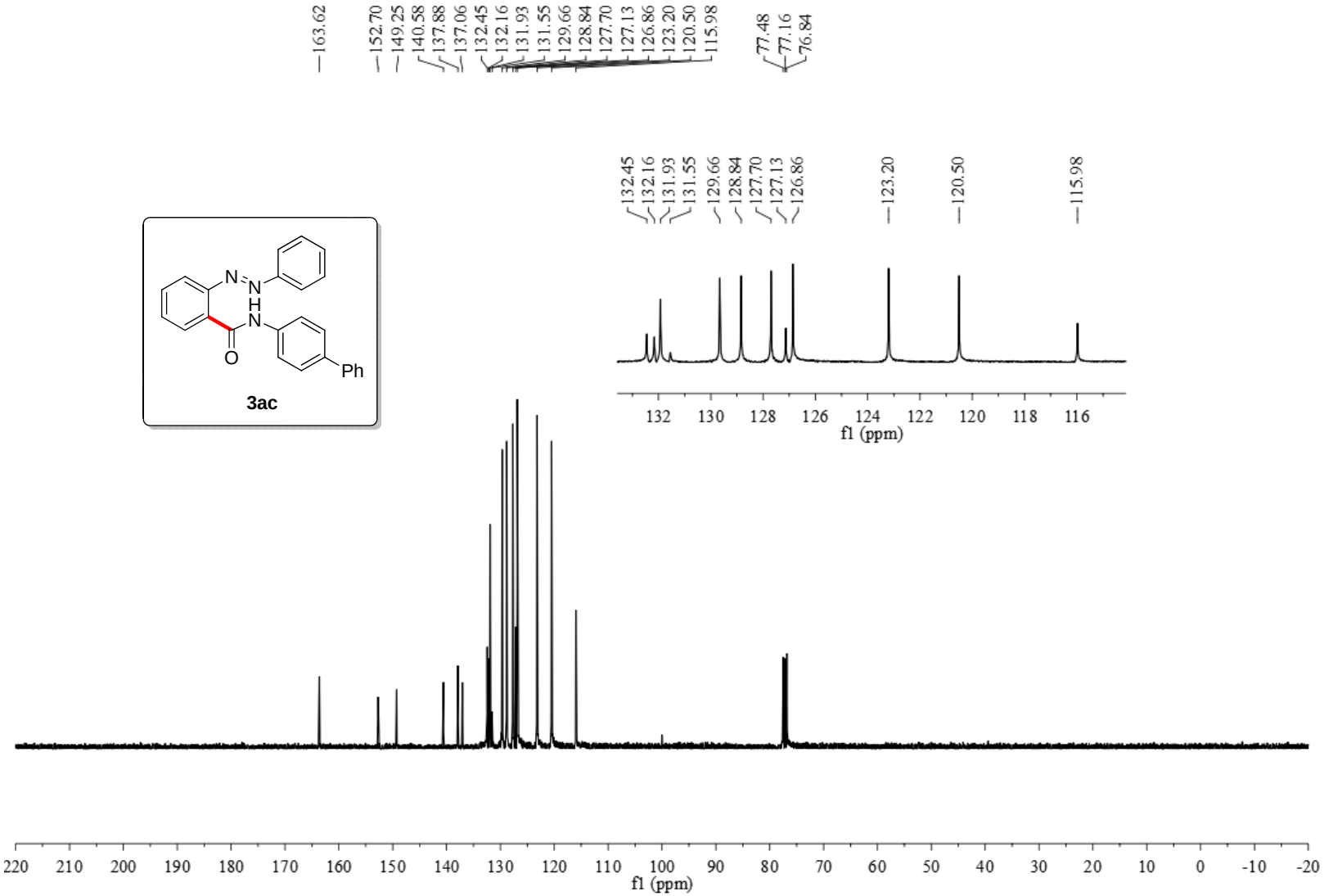
1.00
fl (ppm)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123.20
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77.48
77.16
76.84
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N
H
N
O
Ph
3ac
132.45
132.16
131.93
131.55
129.66
128.84
127.70
127.13
126.86
123.20
120.50
115.98
132
130
128
126
124
122
120
118
116
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
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100
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20
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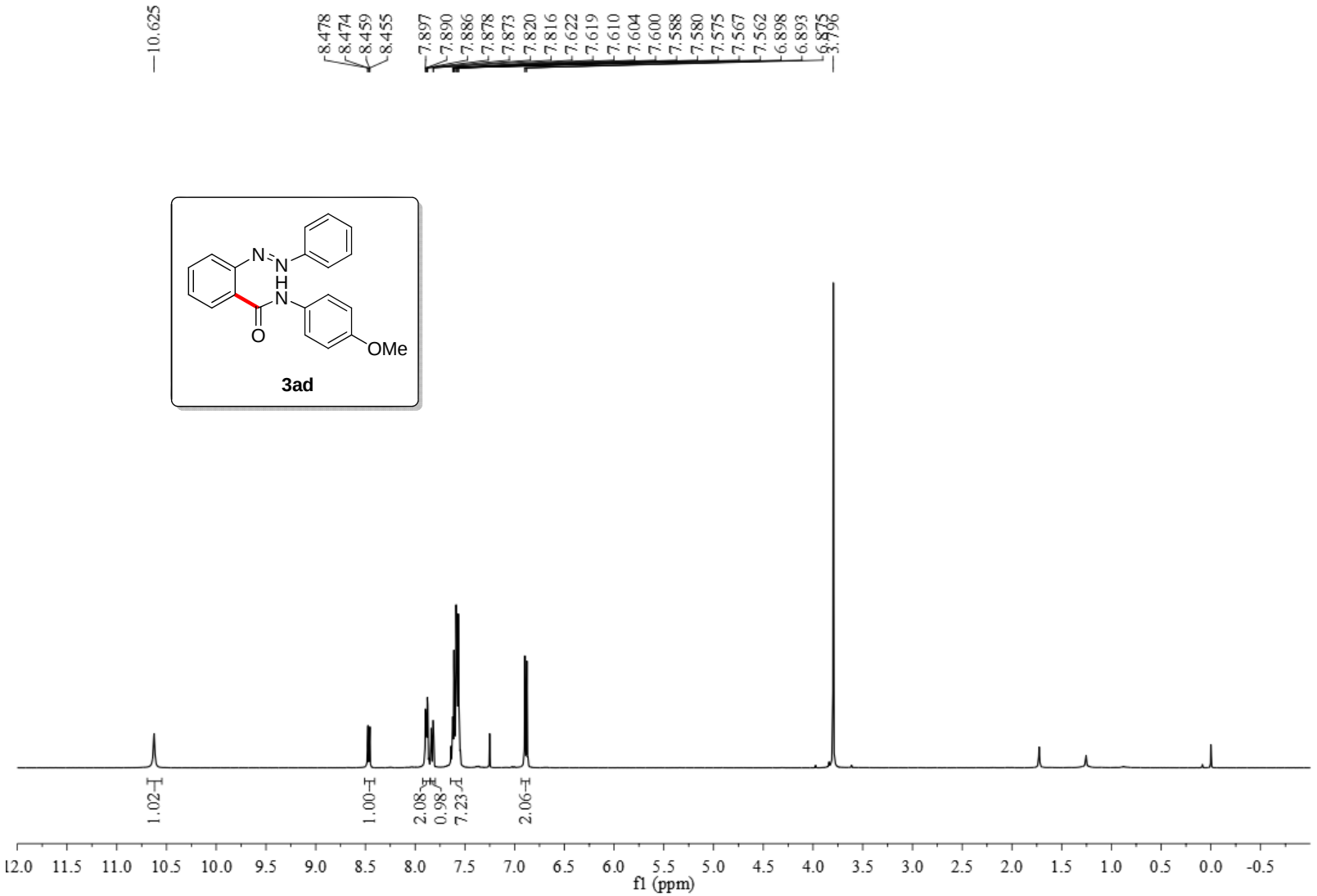
f1 (ppm)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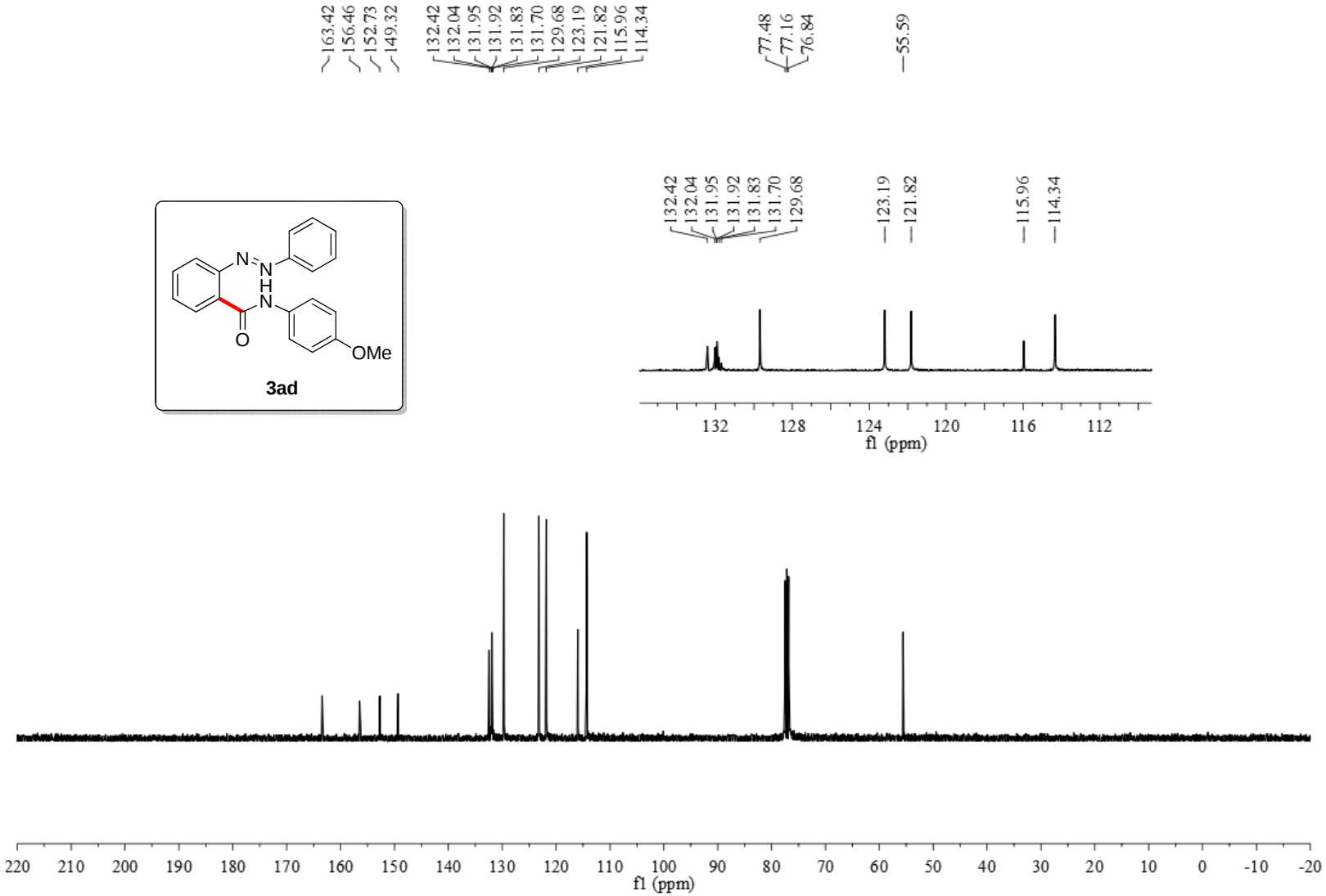
2.06
f1 (ppm)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132
128
124
120
116
112
f1 (ppm)
220
210
200
190
180
170
160
150
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100
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20
10
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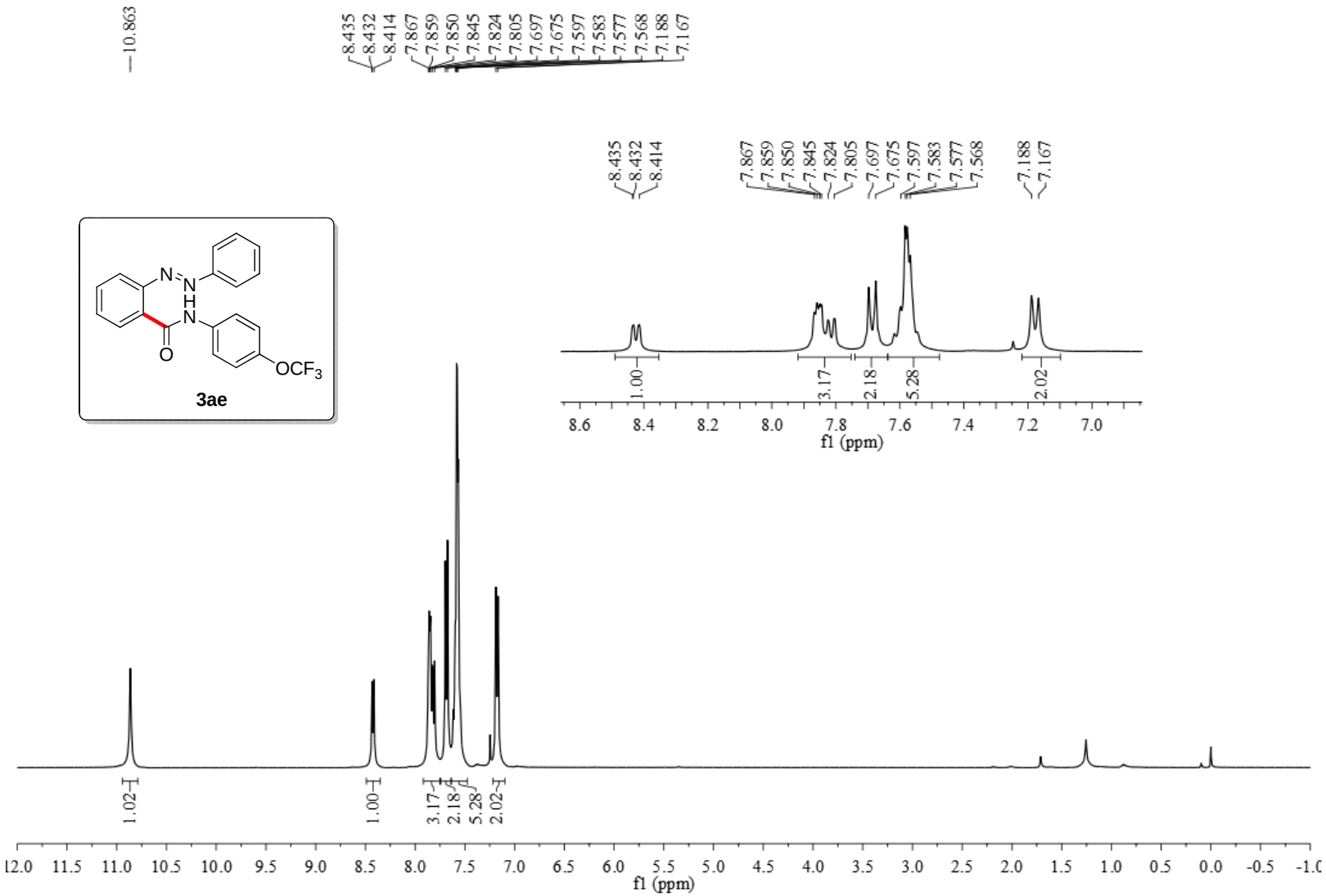
-20
f1 (ppm)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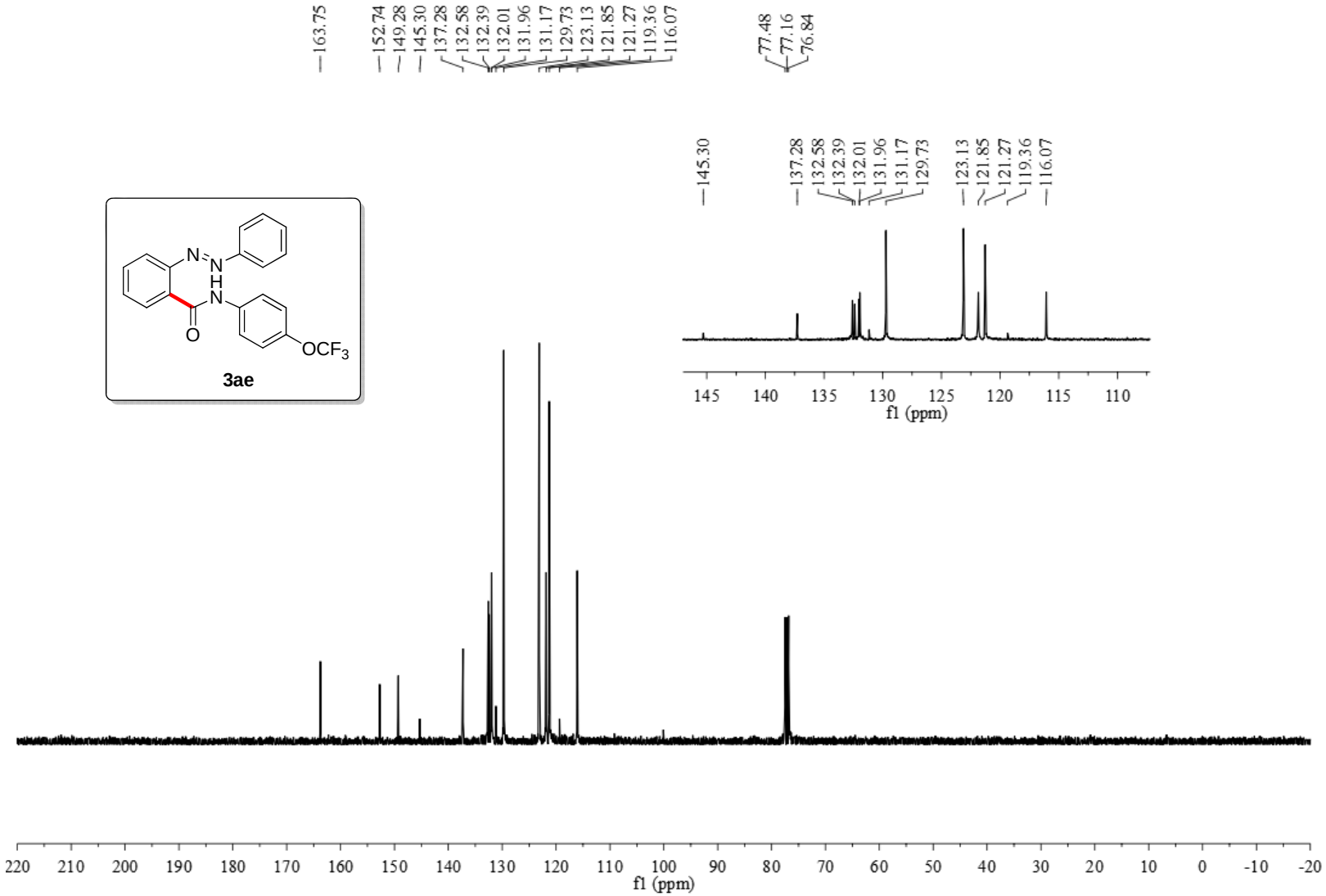
1.00
3.17
2.18
5.28
2.02
f1 (ppm)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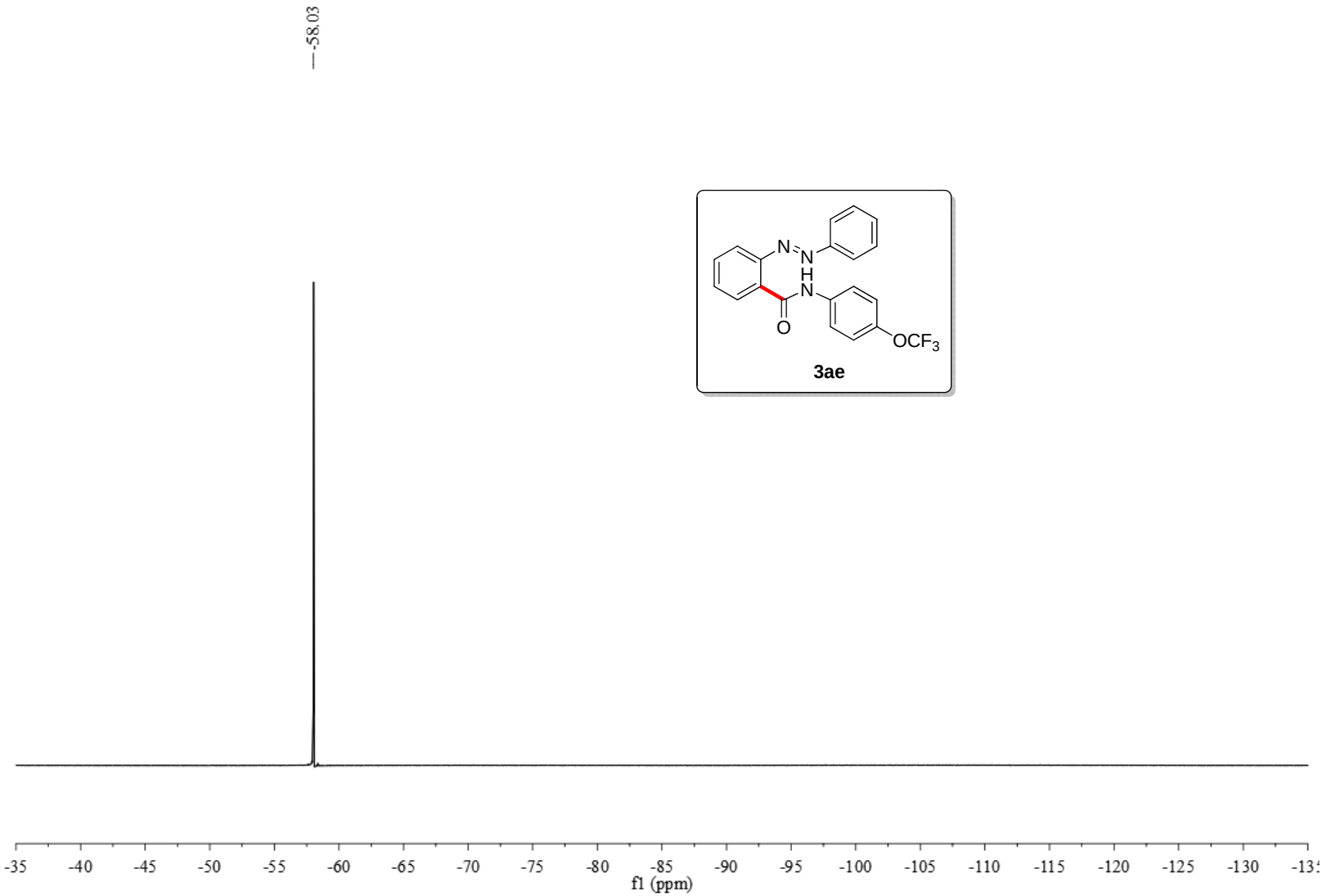
76.84
3ae
fl (ppm)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H
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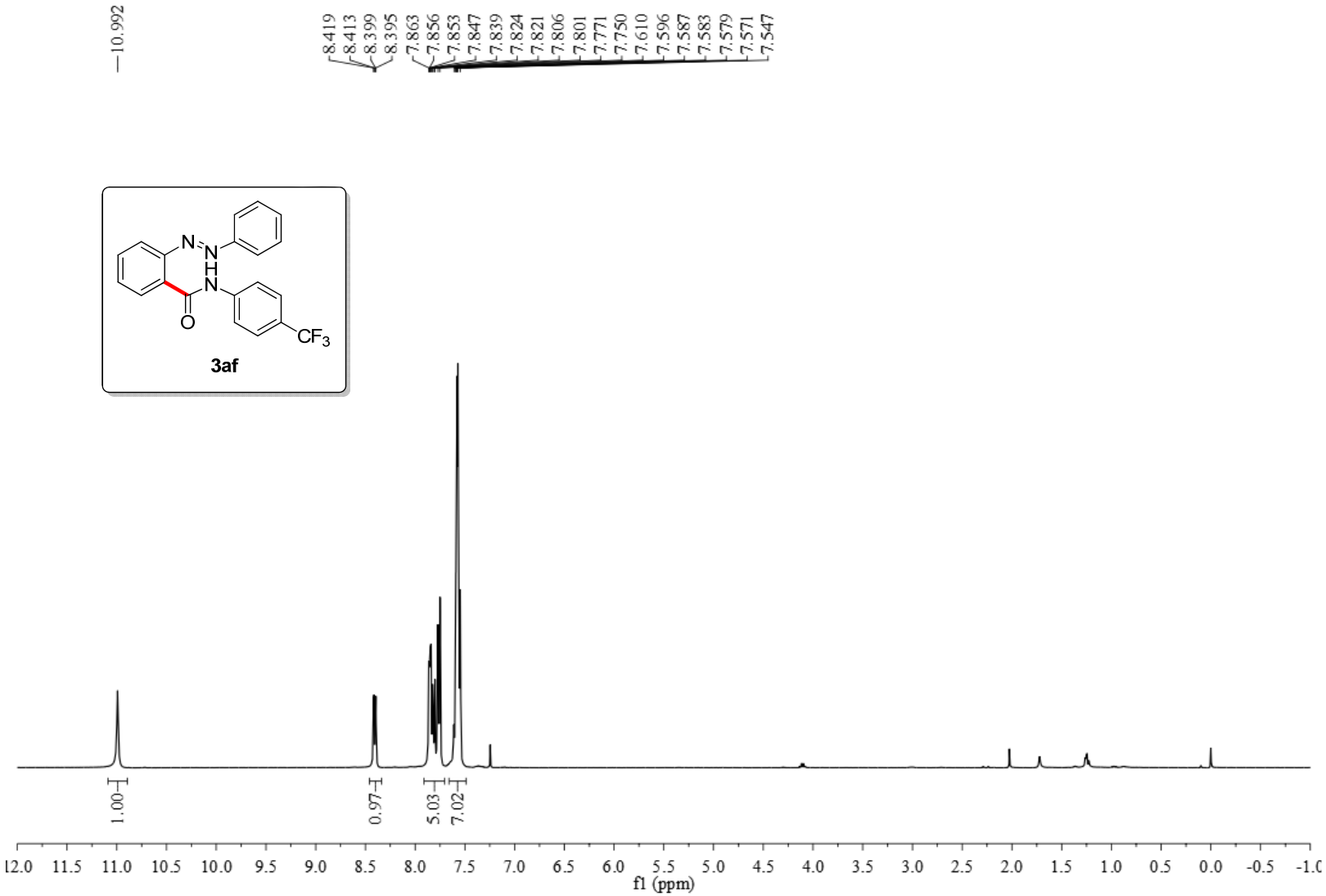
f1 (ppm)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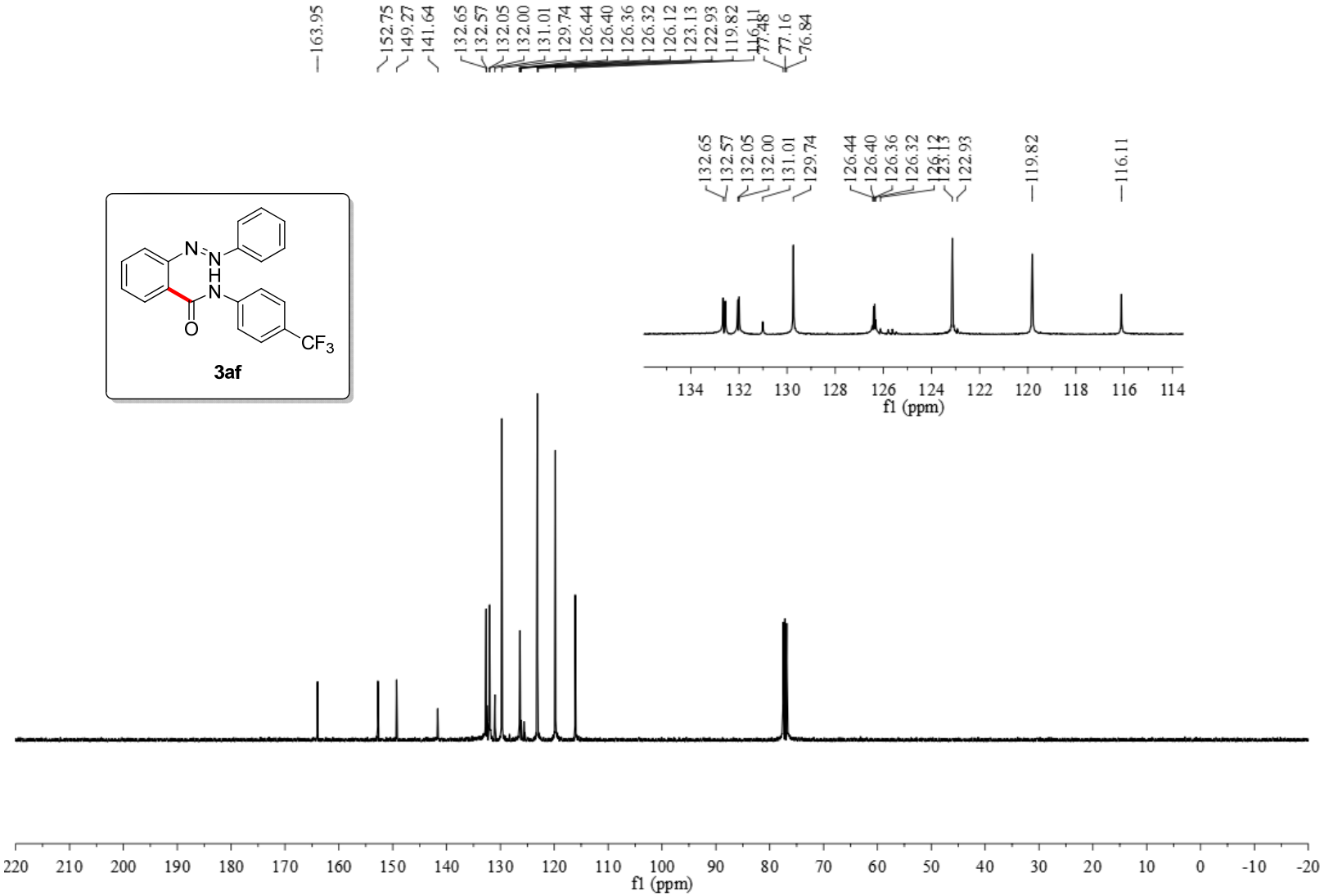
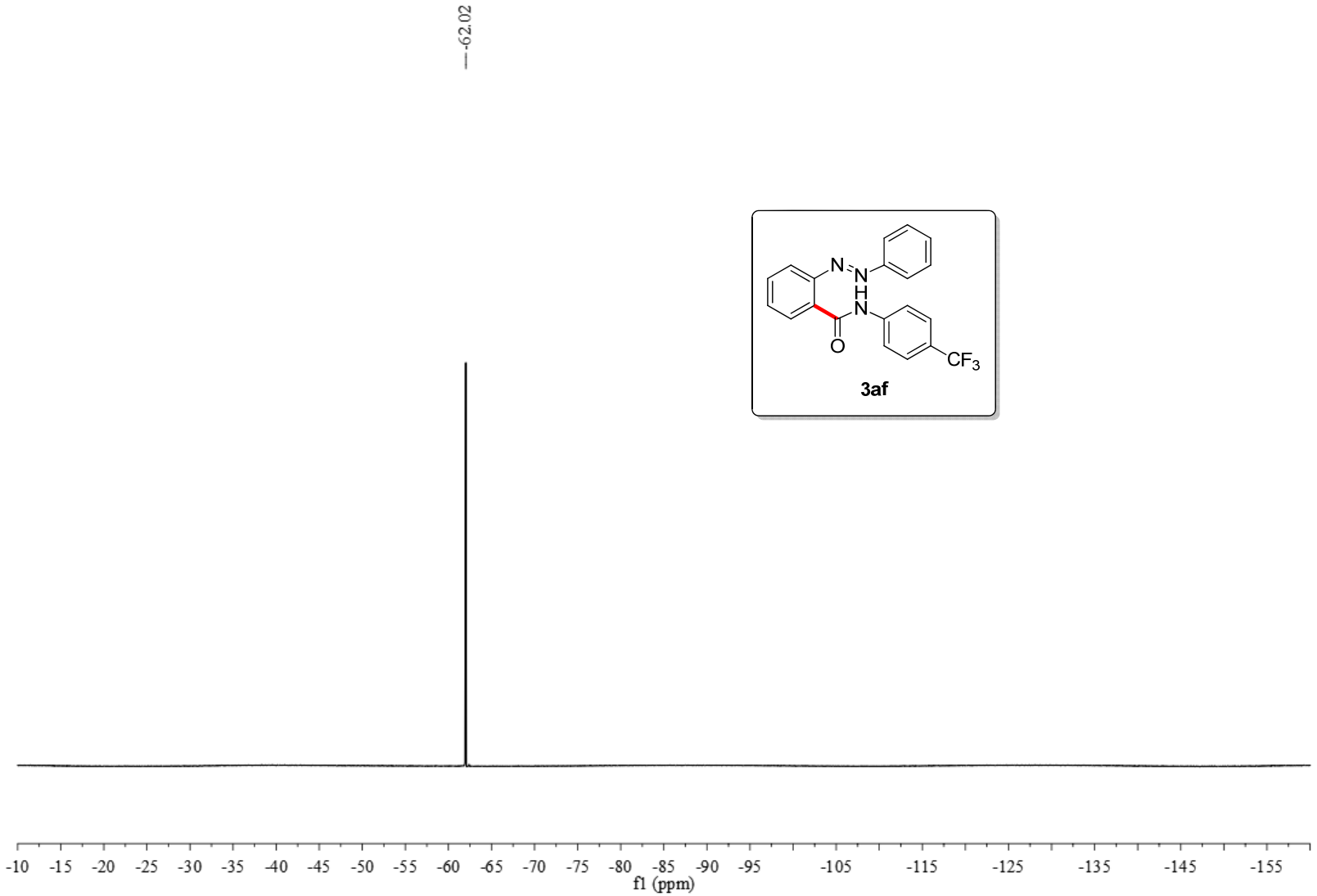
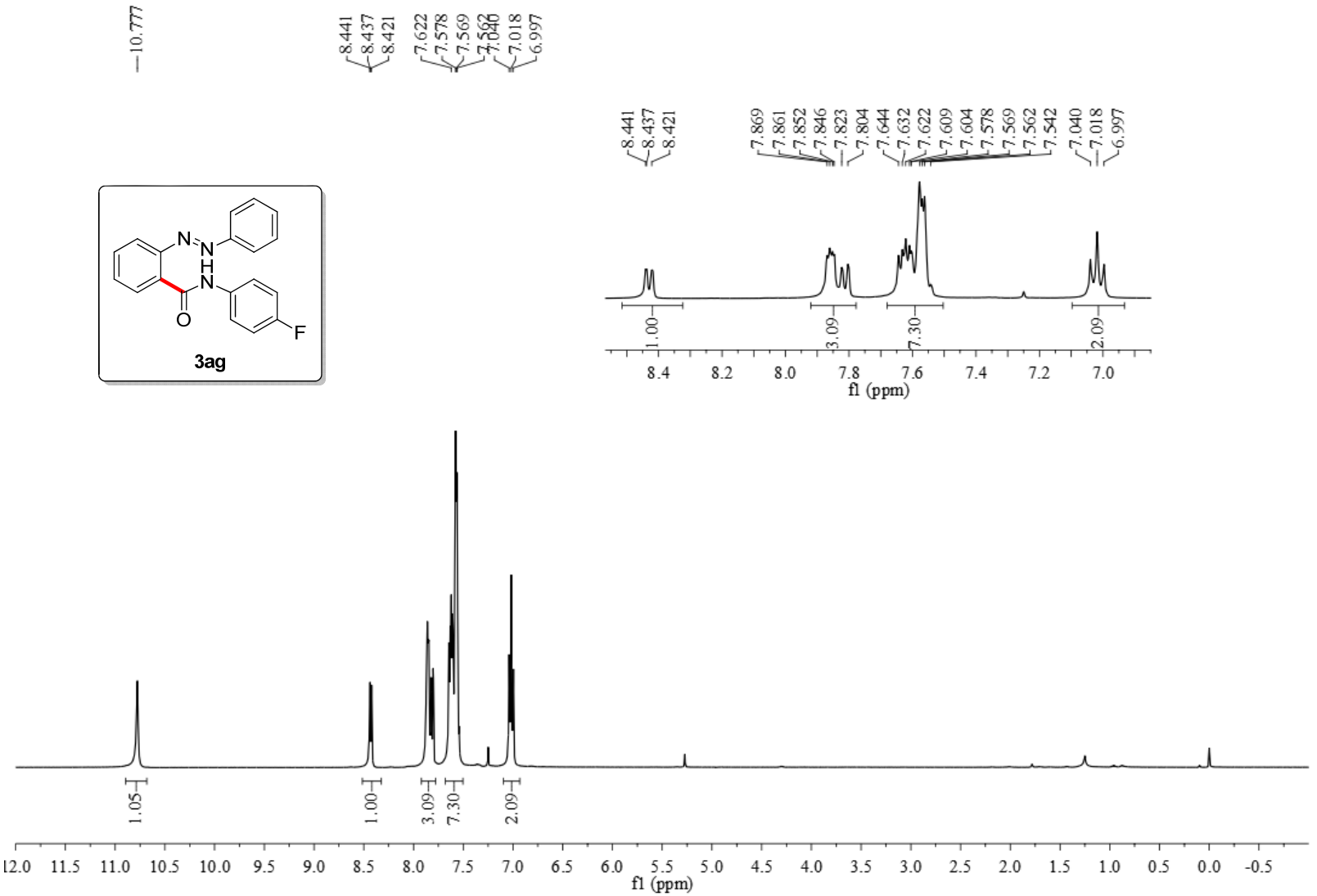
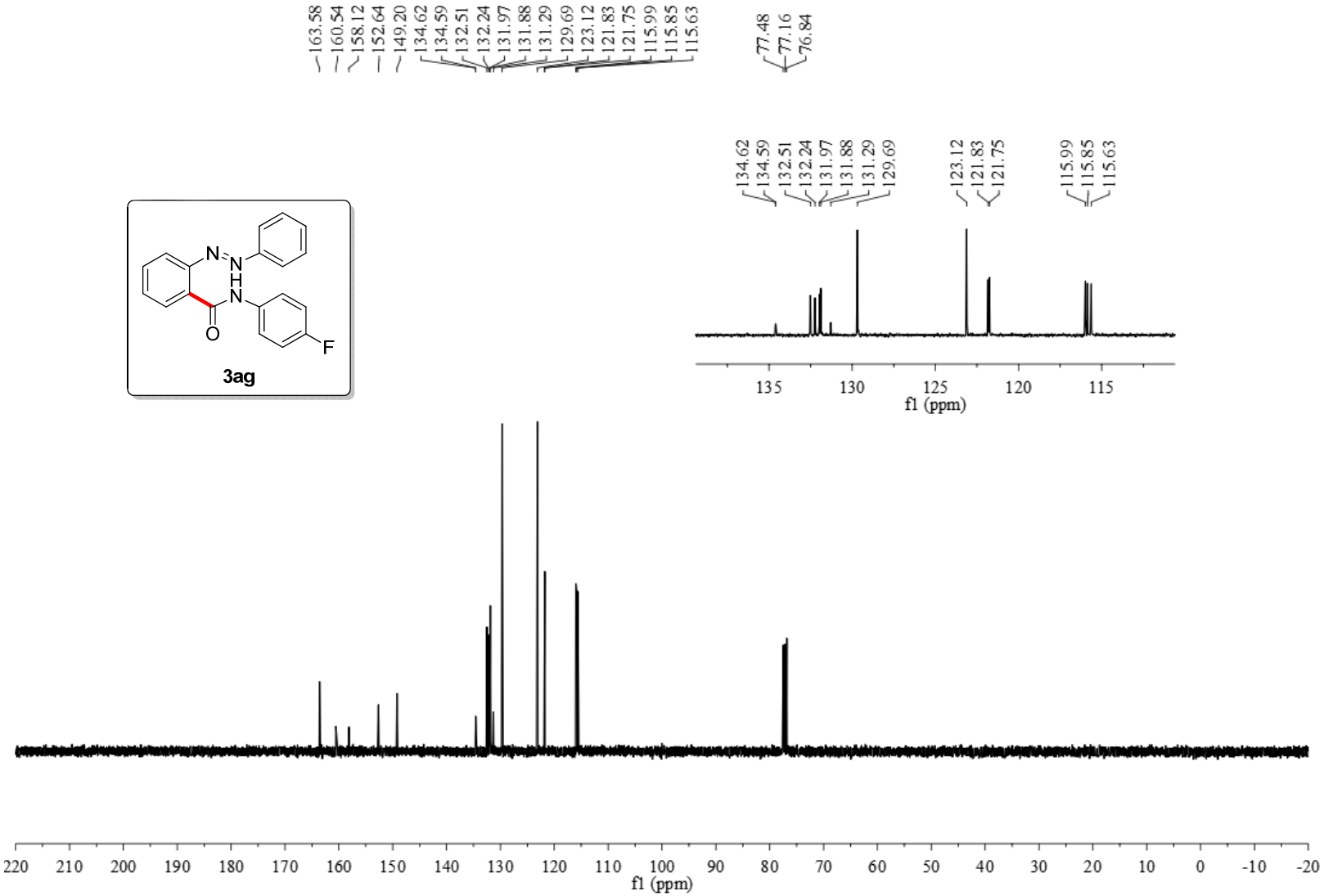
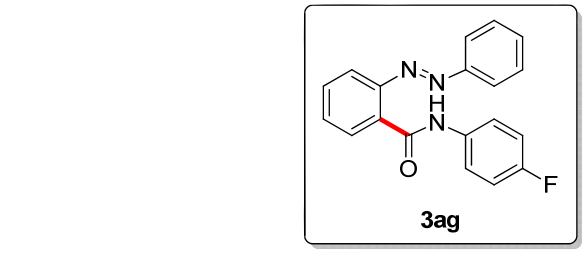
7.771
7.750
7.610
7.596
7.587
7.583
7.579
7.571
7.547
3af
1.00
0.97
5.03
7.02
f1 (ppm)


163.95
152.75
149.27
141.64
132.65
132.57
132.05
132.00
131.01
129.74
126.44
126.40
126.36
126.32
126.12
123.13
122.93
119.82
116.11
77.48
77.16
76.84
3af
134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-62.02
3af
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155
f1 (ppm)

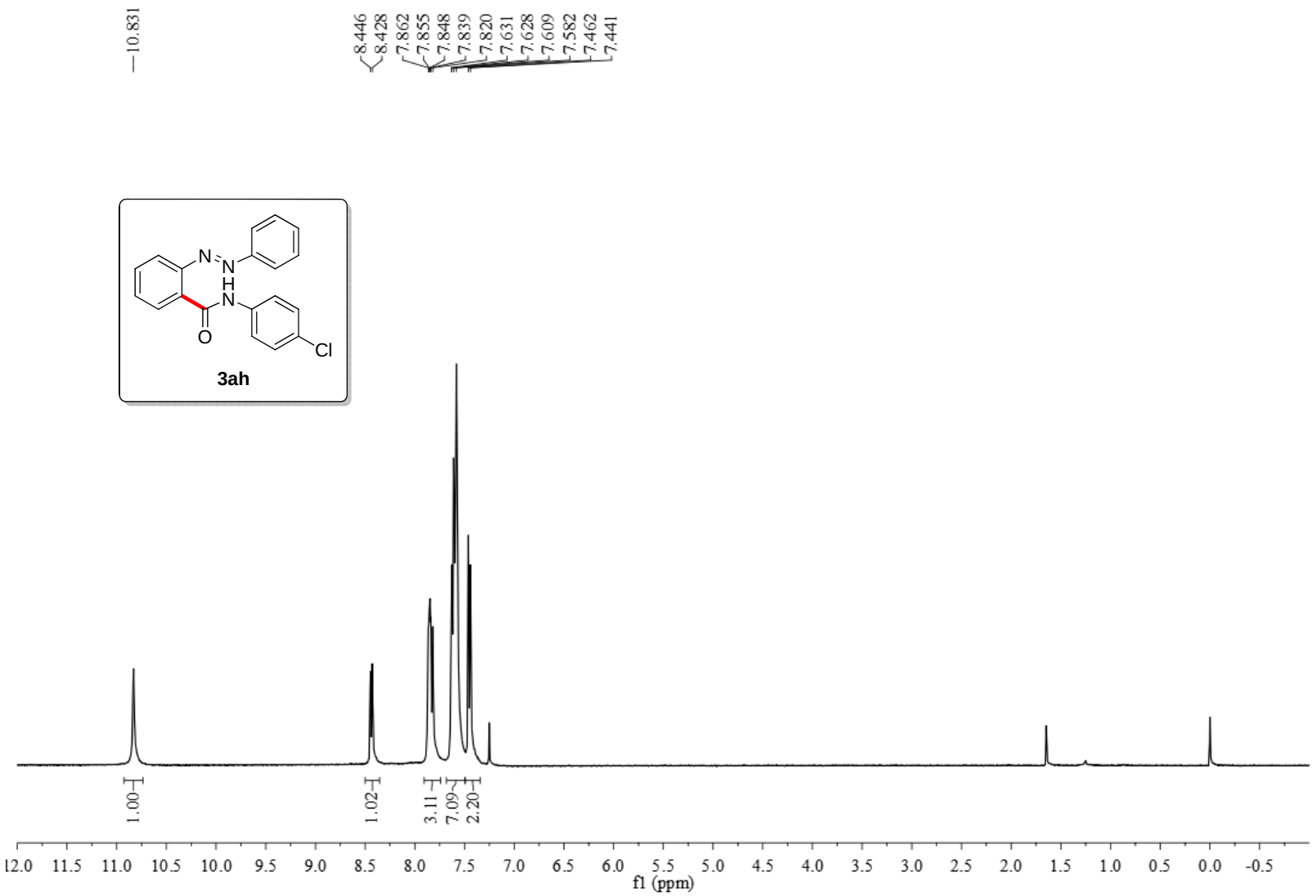

10.777
8.441
8.437
8.421
7.622
7.578
7.569
7.562
7.040
7.018
6.997
3ag
7.869
7.861
7.852
7.846
7.823
7.804
7.644
7.632
7.622
7.609
7.604
7.578
7.569
7.562
7.542
1.00
3.09
7.30
2.09
fl (ppm)
1.05
1.00
3.09
7.30
2.09
fl (ppm)

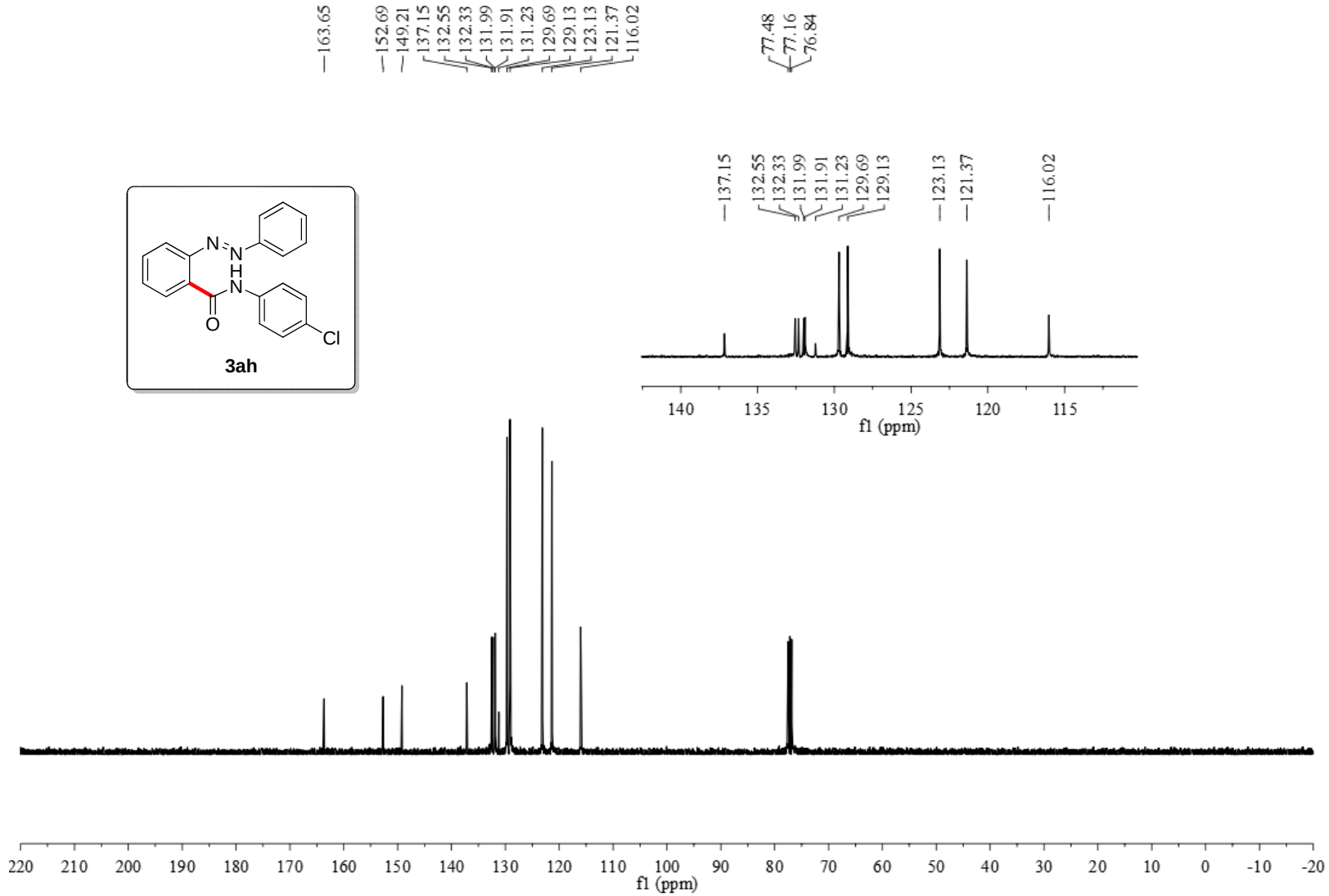

163.58
160.54
158.12
152.64
149.20
134.62
134.59
132.51
132.24
131.97
131.88
131.29
129.69
123.12
121.83
121.75
115.99
115.85
115.63
77.48
77.16
76.84
3ag
f1 (ppm)
f1 (ppm)

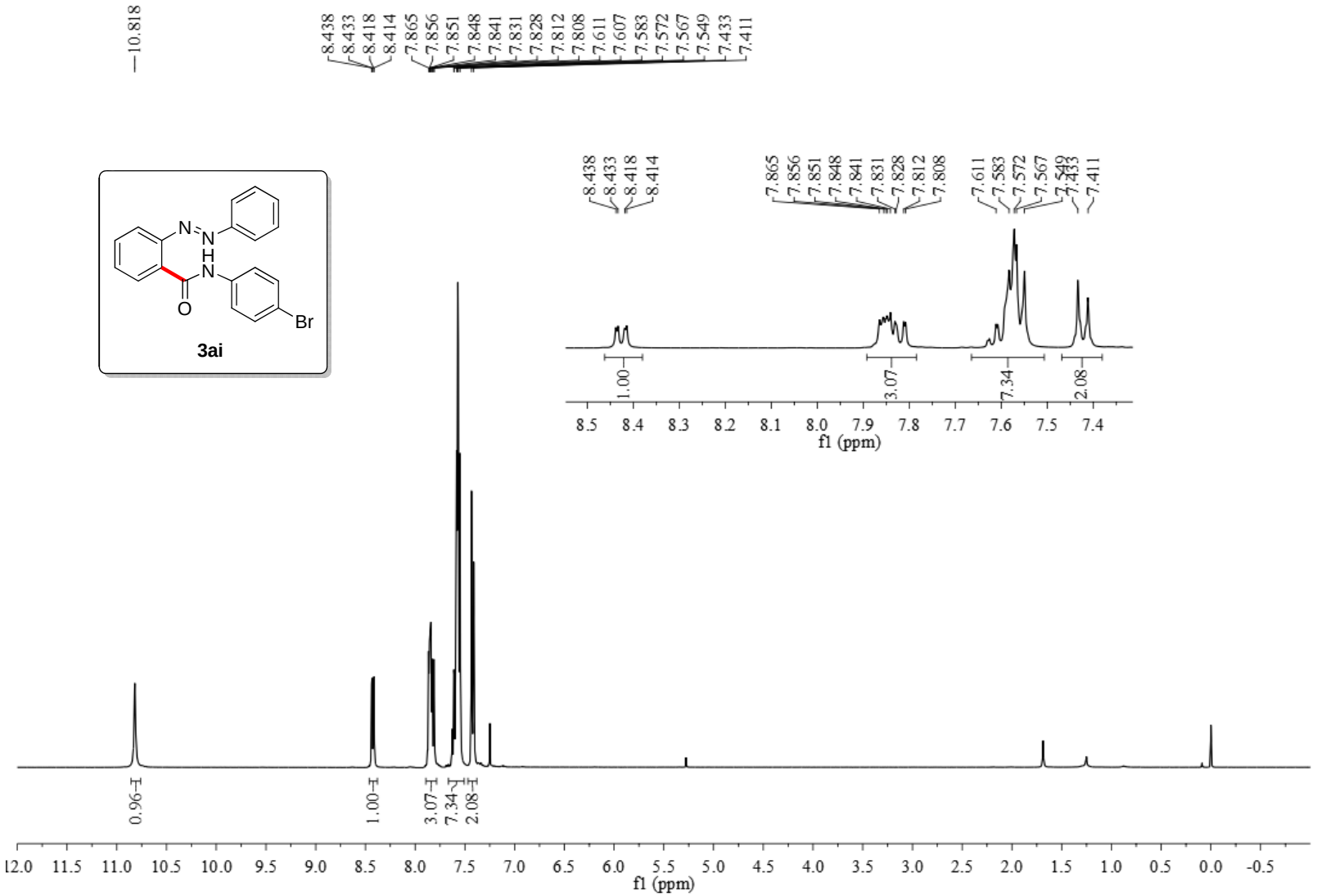

N
N
H
N
O
F

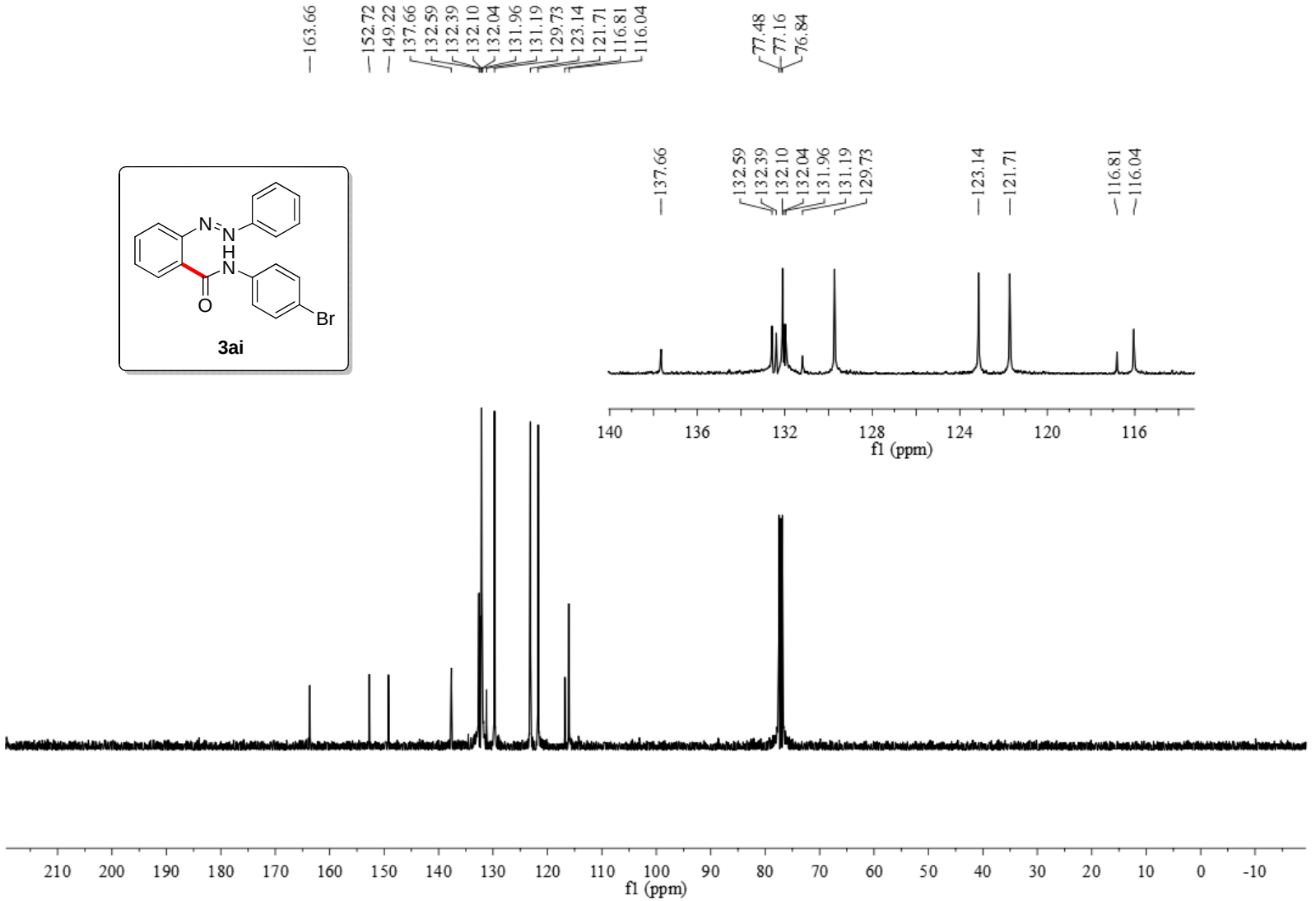
3ag

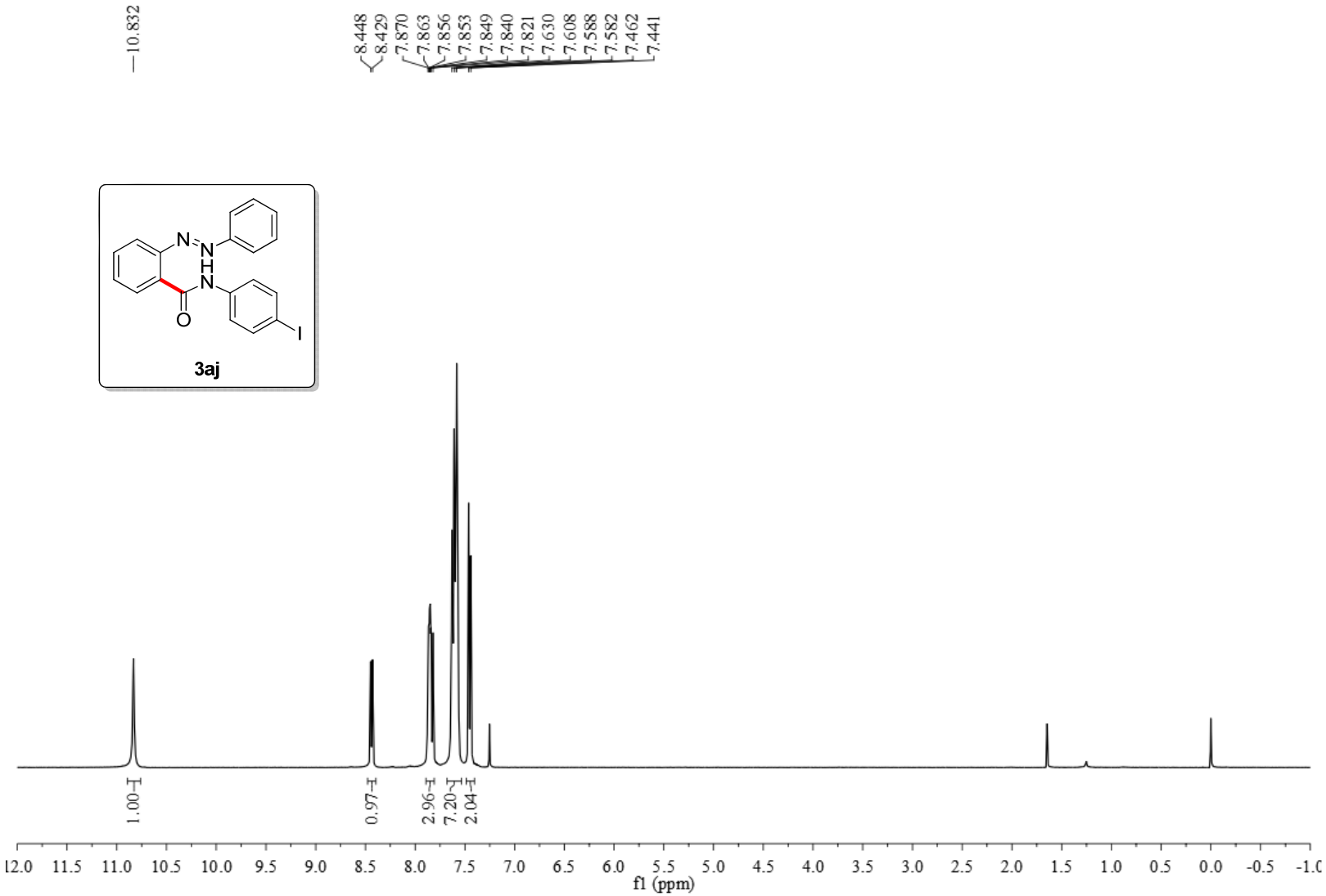
-118.02
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155
f1 (ppm)

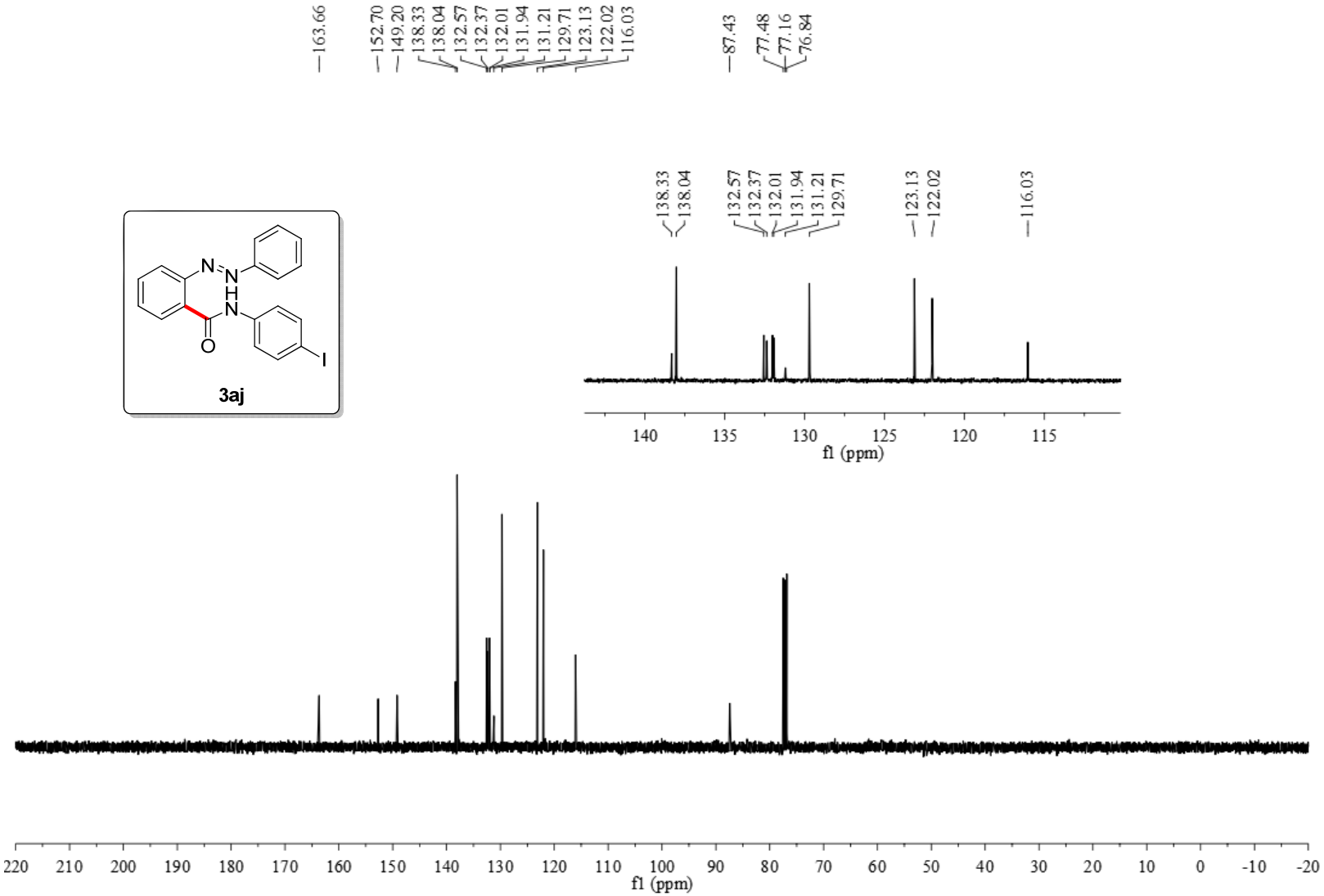

10.831
8.446
8.428
7.862
7.855
7.848
7.839
7.820
7.631
7.628
7.609
7.582
7.462
7.441
3ah
1.00
1.02
3.11
7.09
2.20
f1 (ppm)

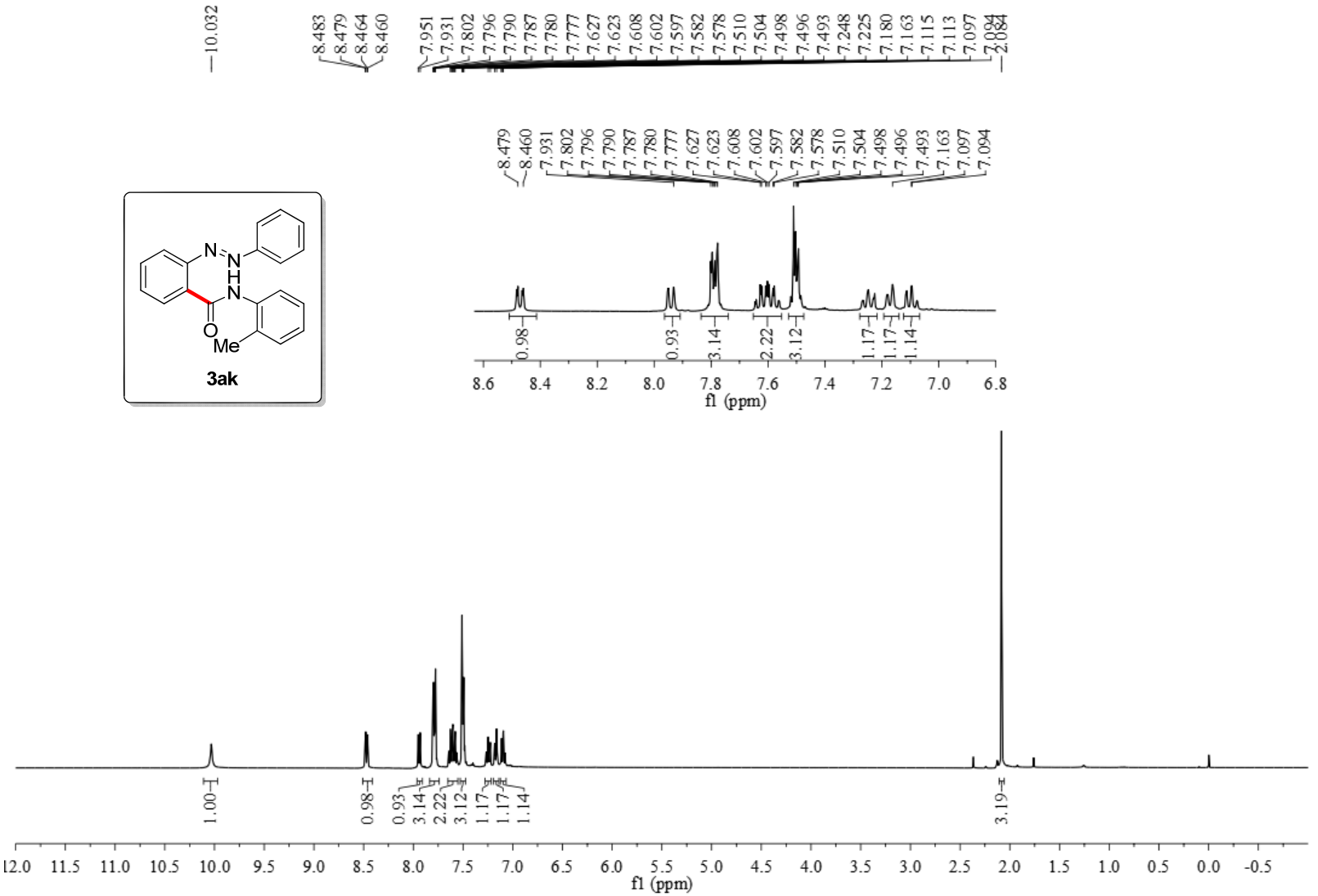

163.65
152.69
149.21
137.15
132.55
132.33
131.99
131.91
131.23
129.69
129.13
123.13
121.37
116.02
77.48
77.16
76.84
3ah
f1 (ppm)
f1 (ppm)

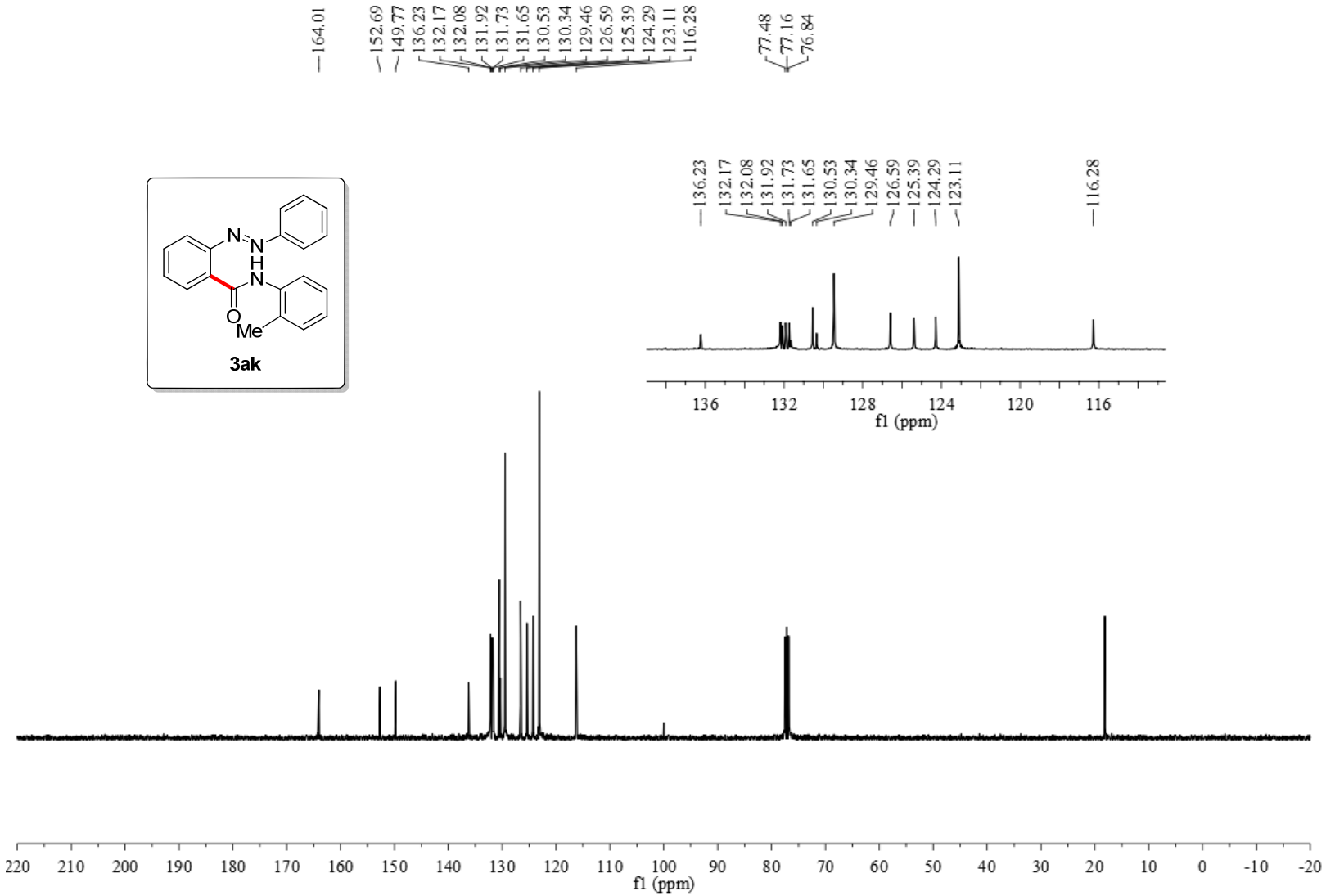

10.818
8.438
8.433
8.418
8.414
7.865
7.856
7.851
7.848
7.841
7.831
7.828
7.812
7.808
7.611
7.607
7.583
7.572
7.567
7.549
7.433
7.411
3ai
1.00
3.07
7.34
2.08
f1 (ppm)
0.96
1.00
3.07
7.34
2.08
f1 (ppm)

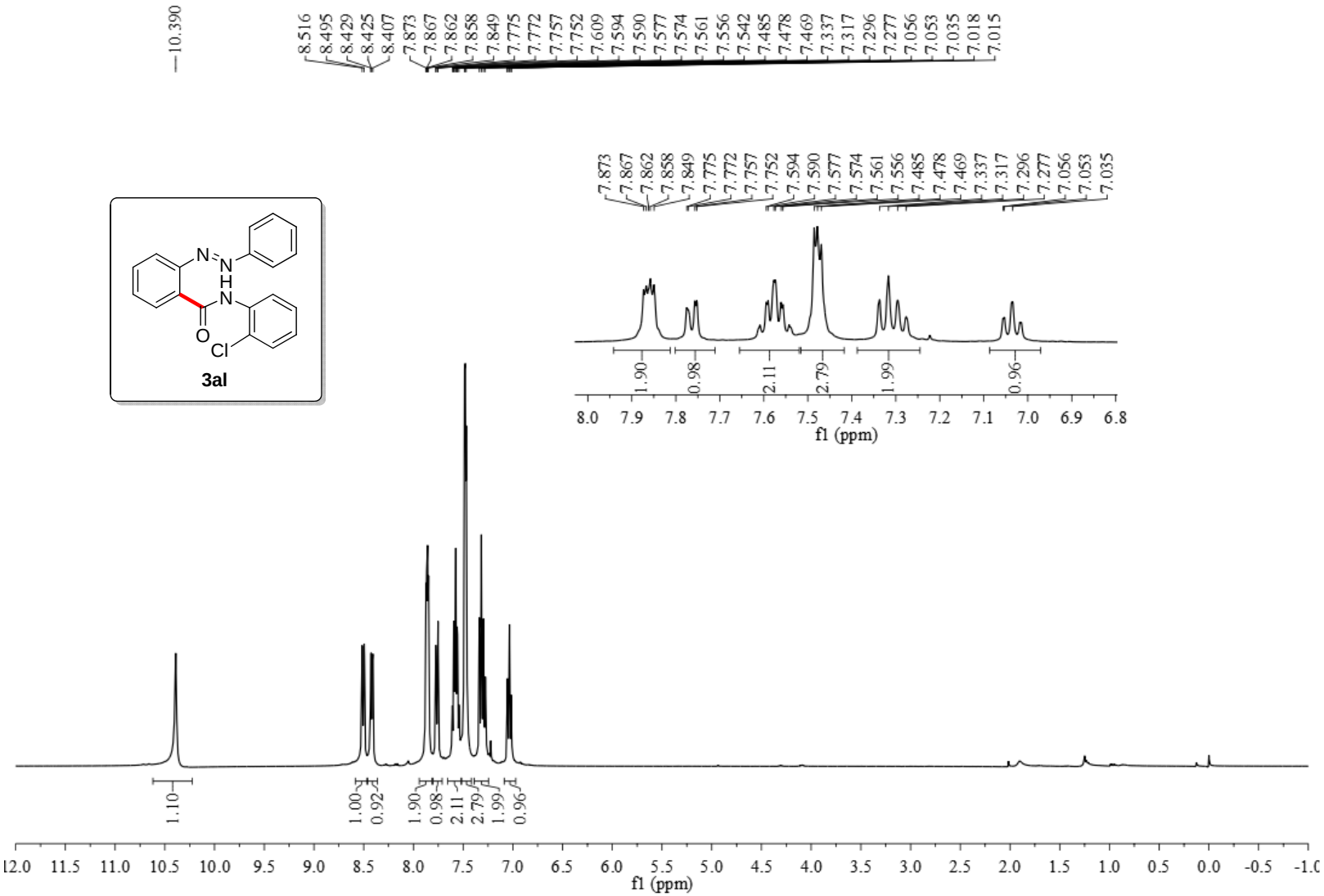

163.66
152.72
149.22
137.66
132.59
132.39
132.10
132.04
131.96
131.19
129.73
123.14
121.71
116.81
116.04
77.48
77.16
76.84
3ai
Br
O
N
H
fl (ppm)

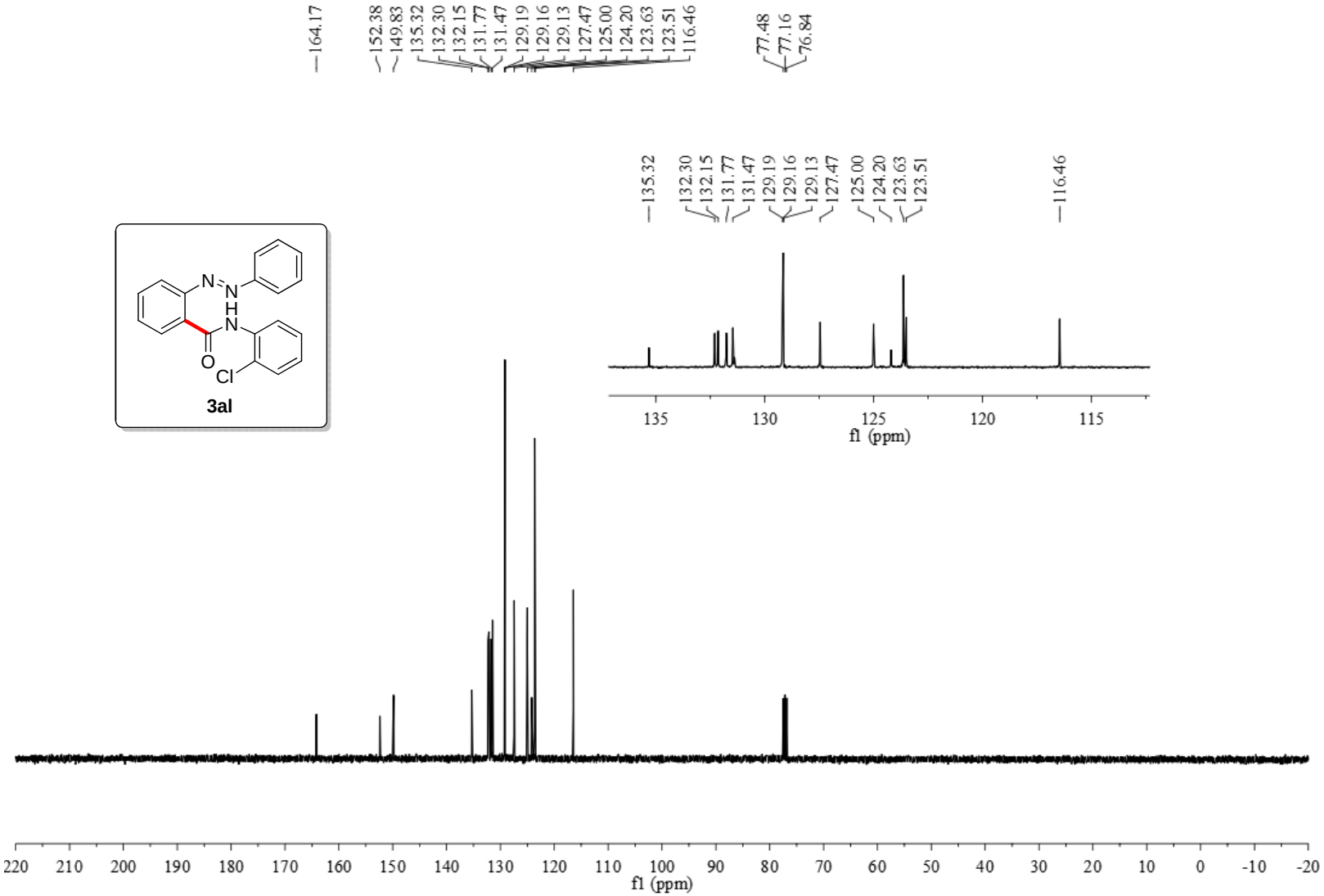

10.832
8.448
8.429
7.870
7.863
7.856
7.853
7.849
7.840
7.821
7.630
7.608
7.588
7.582
7.462
7.441
3aj
1.00
0.97
2.96
7.20
2.04
f1 (ppm)

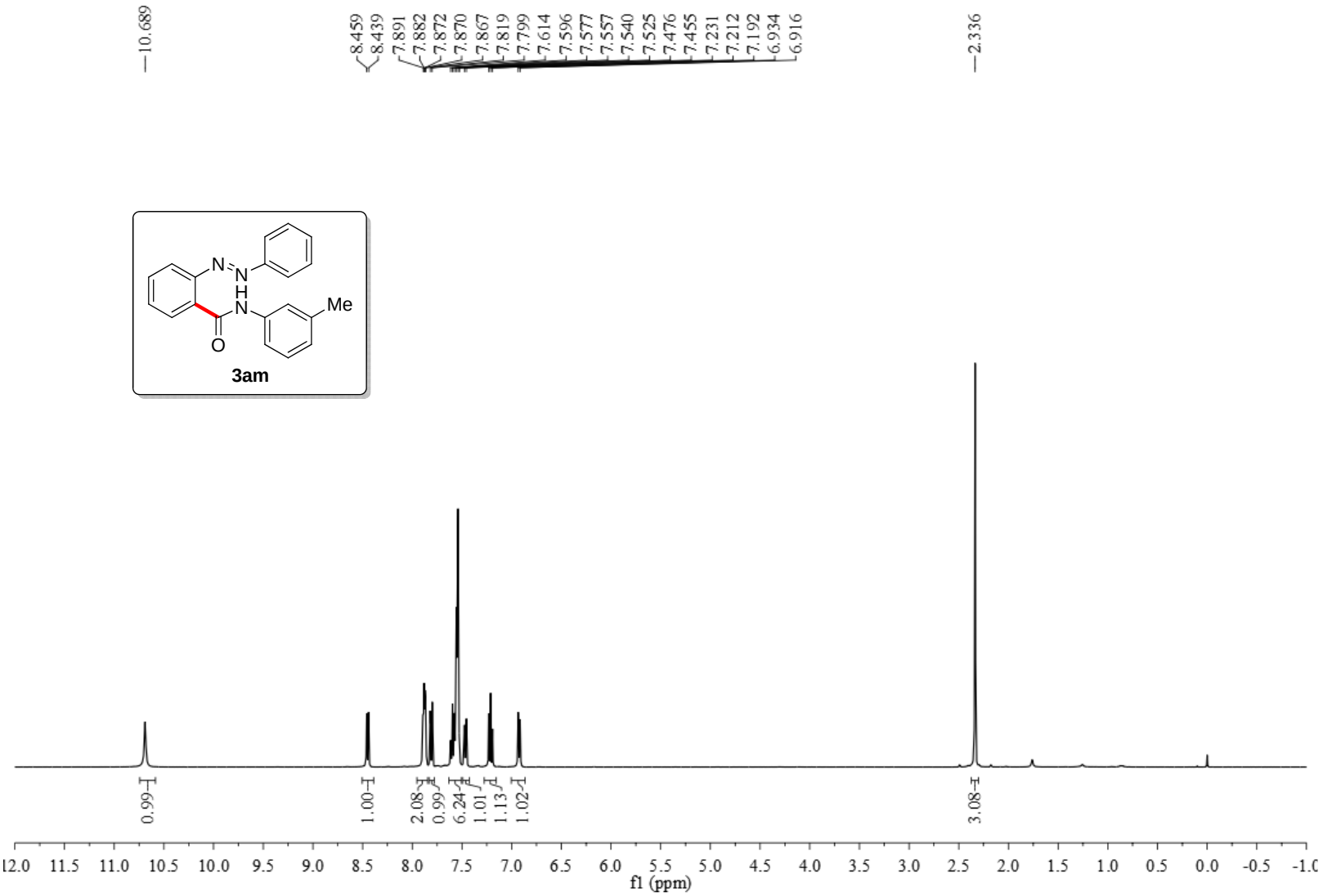

163.66
152.70
149.20
138.33
138.04
132.57
132.37
132.01
131.94
131.21
129.71
123.13
122.02
116.03
87.43
77.48
77.16
76.84
3aj
f1 (ppm)
f1 (ppm)

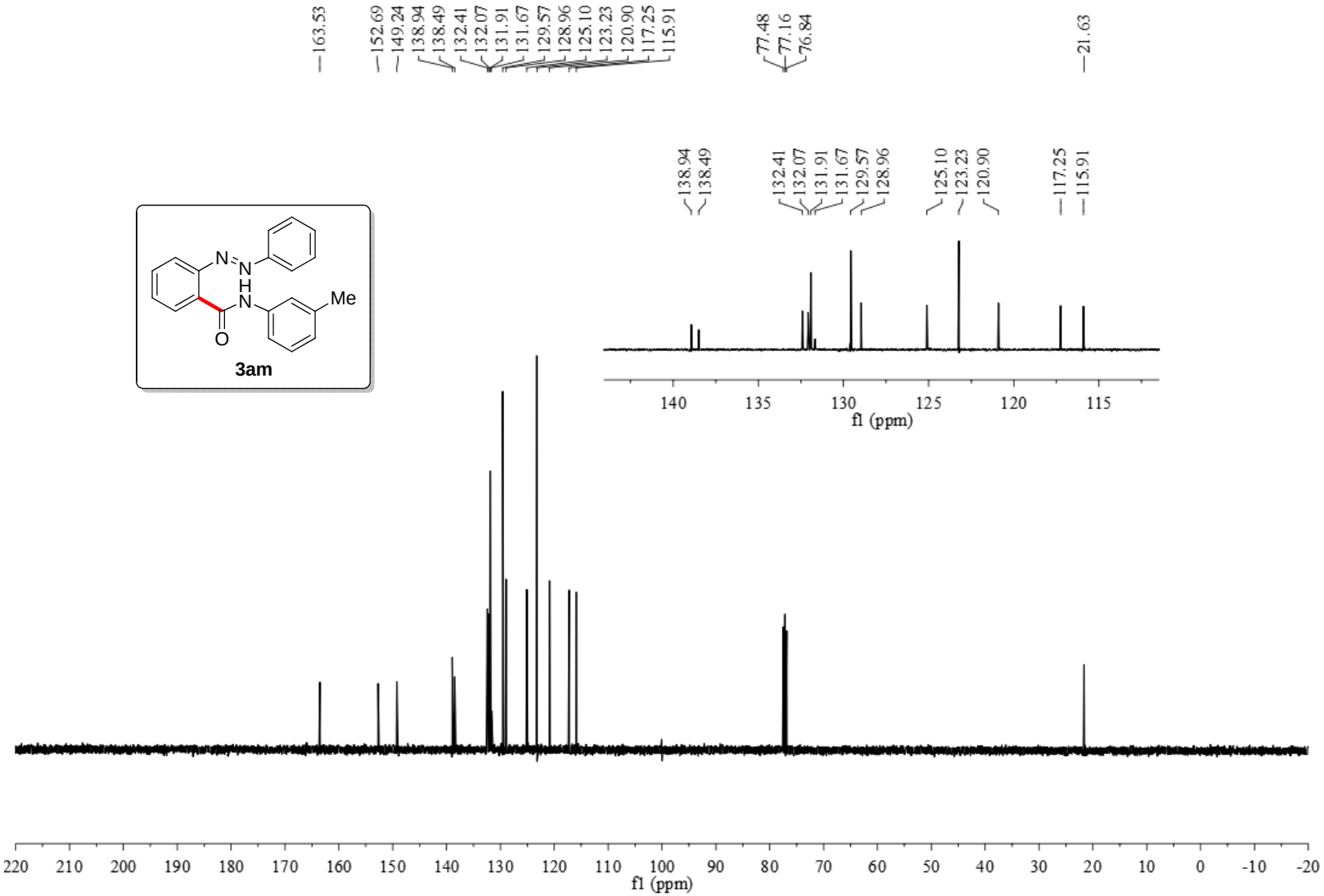

10.032
8.483
8.479
8.464
8.460
7.951
7.931
7.802
7.796
7.790
7.787
7.780
7.777
7.627
7.623
7.608
7.602
7.597
7.582
7.578
7.510
7.504
7.498
7.496
7.493
7.248
7.225
7.180
7.163
7.115
7.113
7.097
7.094
2.084
3ak
0.98
0.93
3.14
2.22
3.12
1.17
1.17
1.14
fl (ppm)
1.00
0.98
0.93
3.14
2.22
3.12
1.17
1.17
1.14
3.19
fl (ppm)

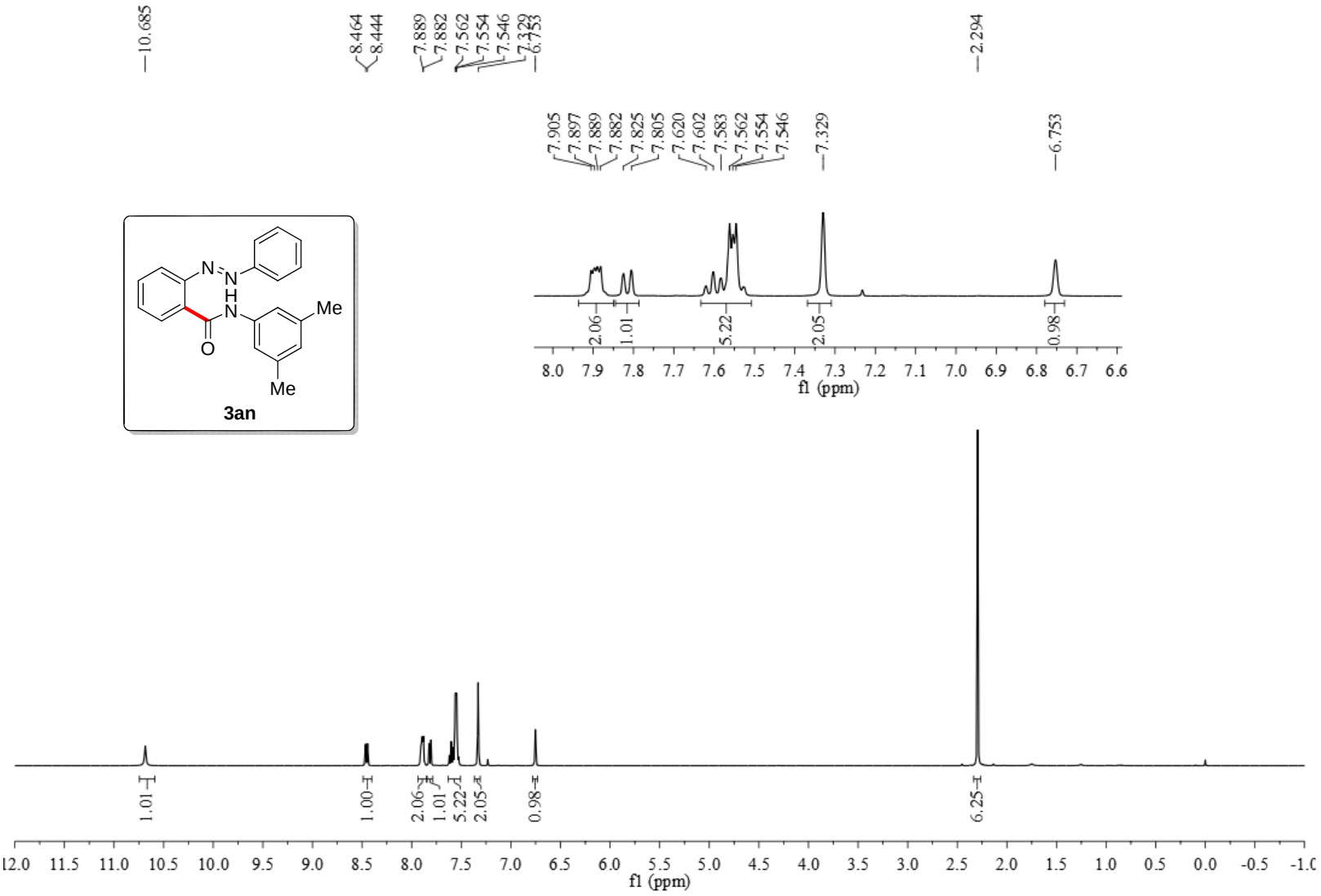

164.01
152.69
149.77
136.23
132.17
132.08
131.92
131.73
131.65
130.53
130.34
129.46
126.59
125.39
124.29
123.11
116.28
77.48
77.16
76.84
3ak
fl (ppm)
fl (ppm)

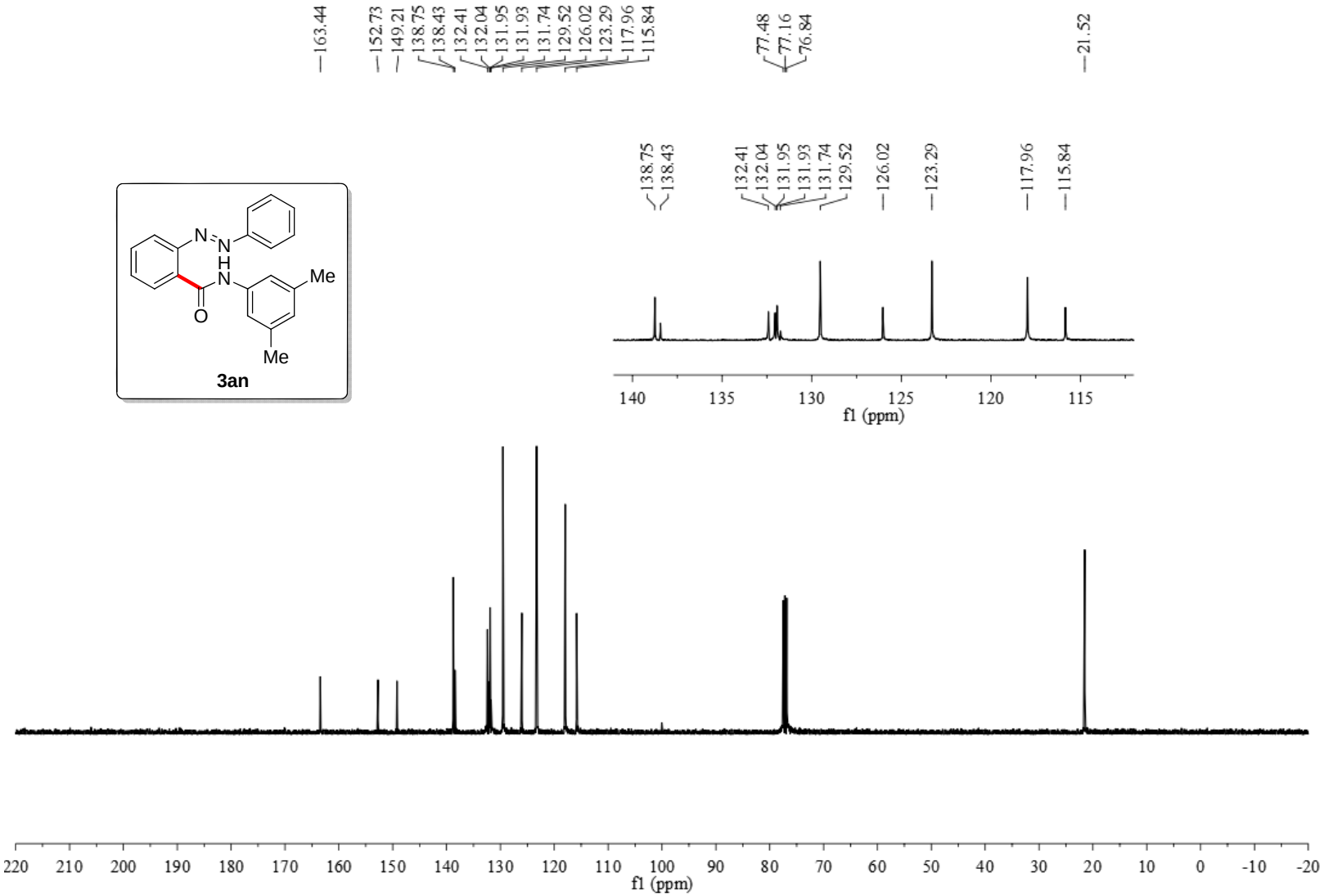

10.390
8.516
8.495
8.429
8.425
8.407
7.873
7.867
7.862
7.858
7.849
7.775
7.772
7.757
7.752
7.609
7.594
7.590
7.577
7.574
7.561
7.556
7.542
7.485
7.478
7.469
7.337
7.317
7.296
7.277
7.056
7.053
7.035
7.018
7.015
3al
1.90
0.98
2.11
2.79
1.99
0.96
f1 (ppm)
1.10
1.00
0.92
f1 (ppm)

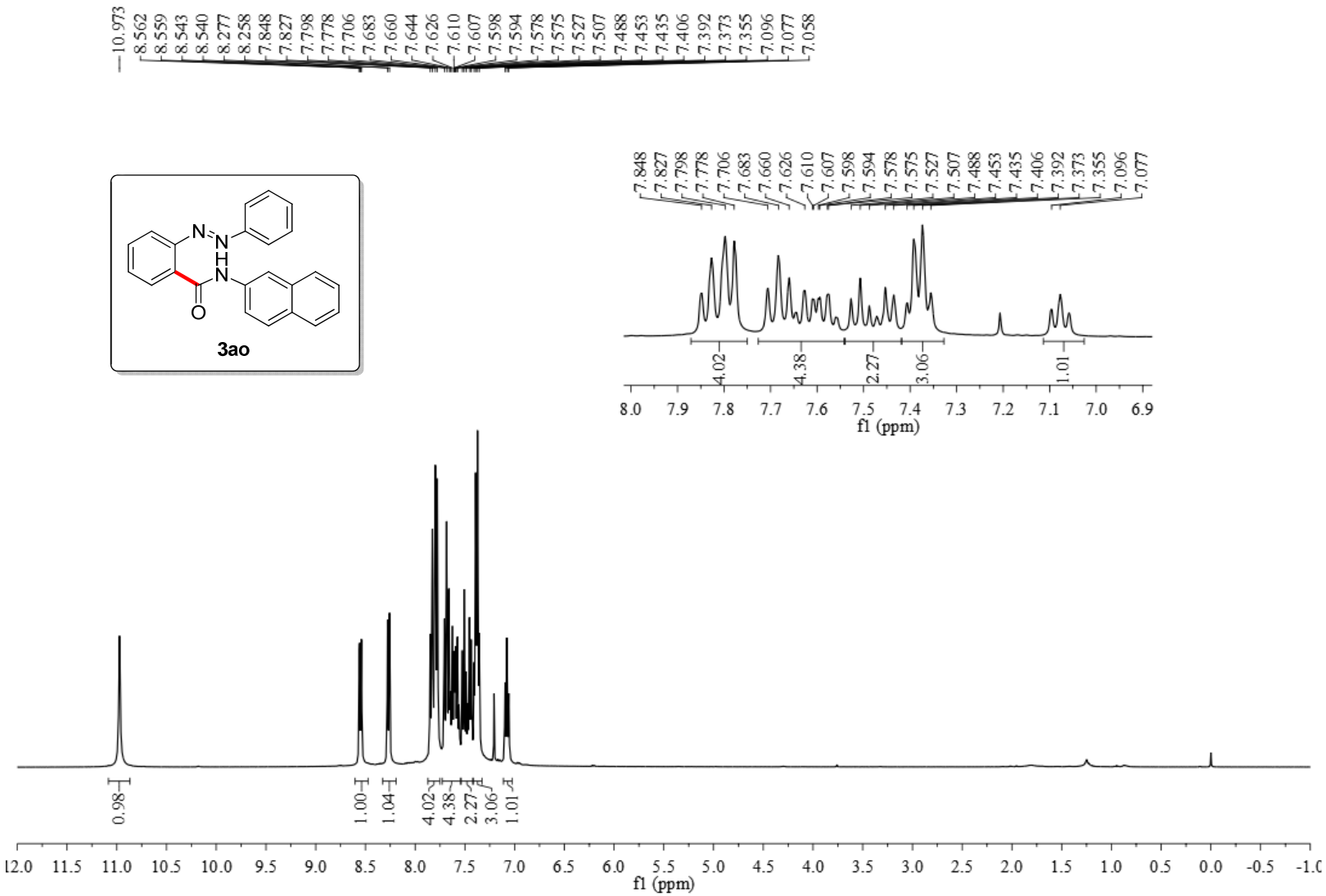

164.17
152.38
149.83
135.32
132.30
132.15
131.77
131.47
129.19
129.16
129.13
127.47
125.00
124.20
123.63
123.51
116.46
77.48
77.16
76.84
3al
135.32
132.30
132.15
131.77
131.47
129.19
129.16
129.13
127.47
125.00
124.20
123.63
123.51
116.46
135
130
125
120
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

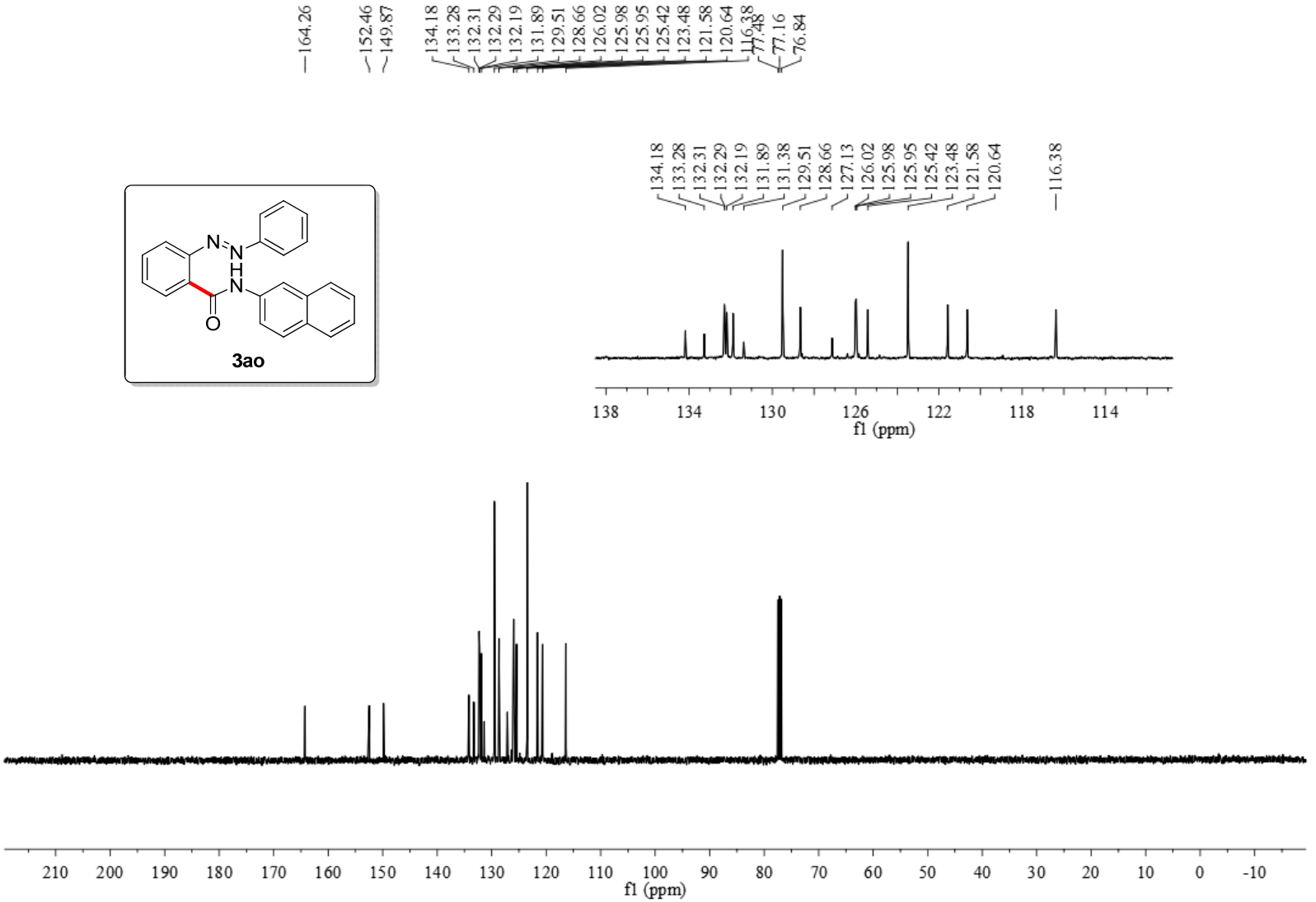

10.689
8.459
8.439
7.891
7.882
7.872
7.870
7.867
7.819
7.799
7.614
7.596
7.577
7.557
7.540
7.525
7.476
7.455
7.231
7.212
7.192
6.934
6.916
2.336
N
N
H
N
Me
O
3am
0.99
1.00
2.08
0.99
6.24
1.01
1.13
1.02
3.08
f1 (ppm)

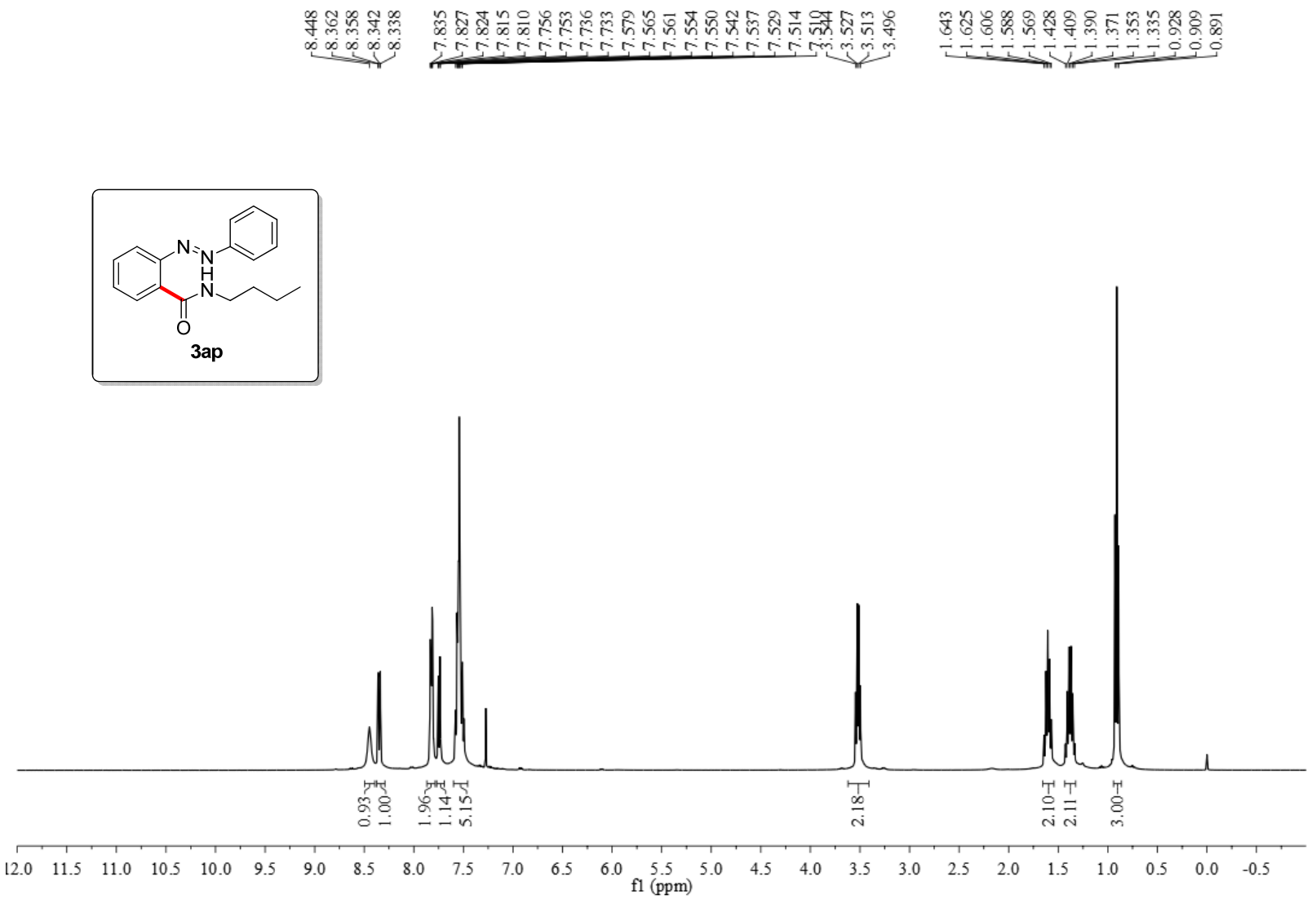

163.53
152.69
149.24
138.94
138.49
132.41
132.07
131.91
131.67
129.57
128.96
125.10
123.23
120.90
117.25
115.91
77.48
77.16
76.84
21.63
N
N
H
N
Me
O
3am
fl (ppm)
fl (ppm)


10.685
8.464
8.444
7.889
7.882
7.562
7.554
7.546
7.329
6.753
2.294
7.905
7.897
7.889
7.882
7.825
7.805
7.620
7.602
7.583
7.562
7.554
7.546
7.329
6.753
2.06
1.01
5.22
2.05
0.98
fl (ppm)
Me
Me
3an
1.01
1.00
2.06
1.01
5.22
2.05
0.98
6.25
fl (ppm)


163.44
152.73
149.21
138.75
138.43
132.41
132.04
131.95
131.93
131.74
129.52
126.02
123.29
117.96
115.84
77.48
77.16
76.84
21.52
N
N
H
N
O
Me
Me
3an
fl (ppm)
fl (ppm)


10.973
8.562
8.559
8.543
8.540
8.277
8.258
7.848
7.827
7.798
7.778
7.706
7.683
7.660
7.644
7.626
7.610
7.607
7.598
7.594
7.578
7.575
7.527
7.507
7.488
7.453
7.435
7.406
7.392
7.373
7.355
7.096
7.077
7.058
3ao
4.02
4.38
2.27
3.06
1.01
fl (ppm)
0.98
1.00
1.04
fl (ppm)


164.26
152.46
149.87
134.18
133.28
132.31
132.29
132.19
131.89
129.51
128.66
126.02
125.98
125.95
125.42
123.48
121.58
120.64
116.38
77.48
77.16
76.84
3ao
134.18
133.28
132.31
132.29
132.19
131.89
131.38
129.51
128.66
127.13
126.02
125.98
125.95
125.42
123.48
121.58
120.64
116.38
138
134
130
126
122
118
114
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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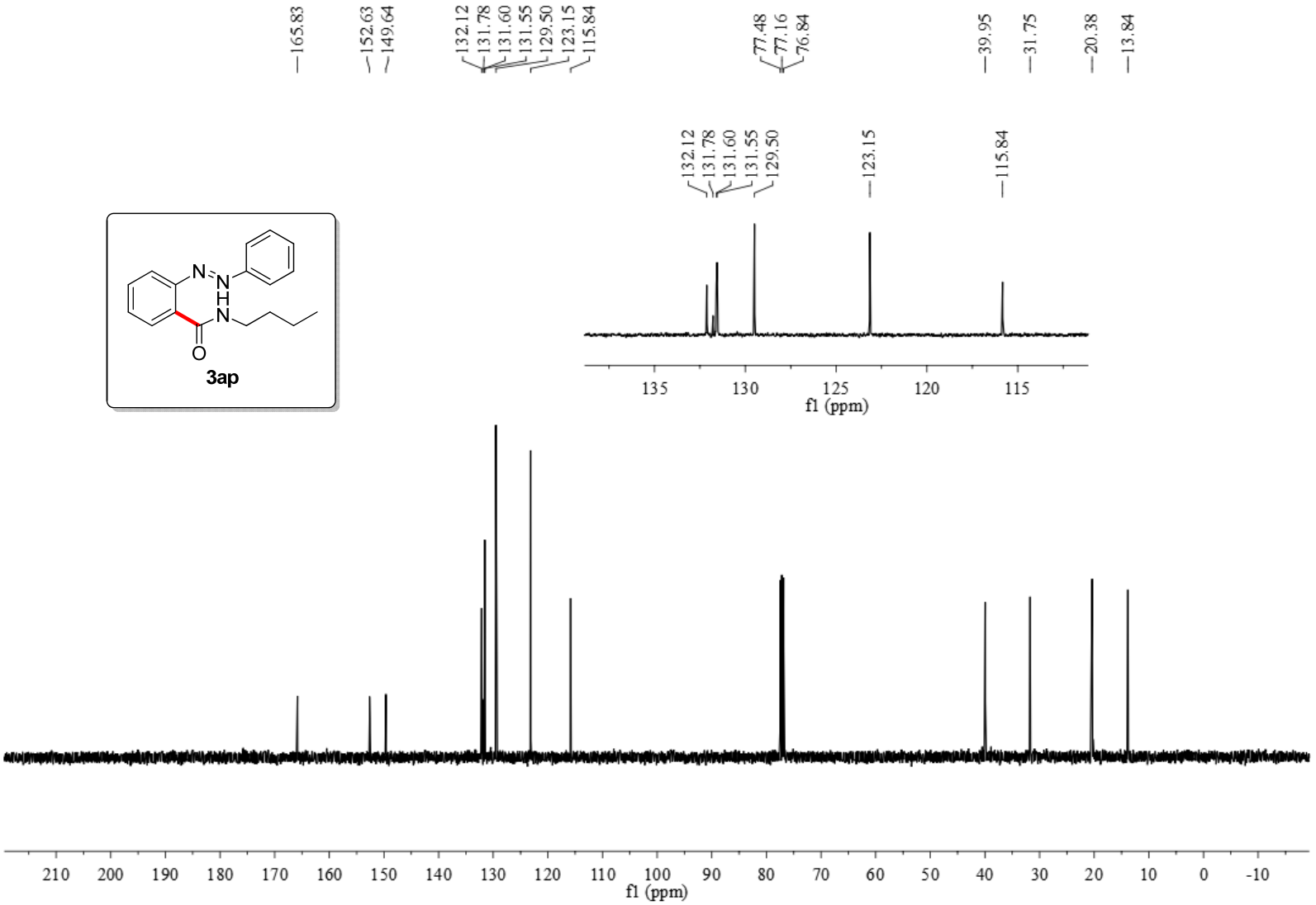
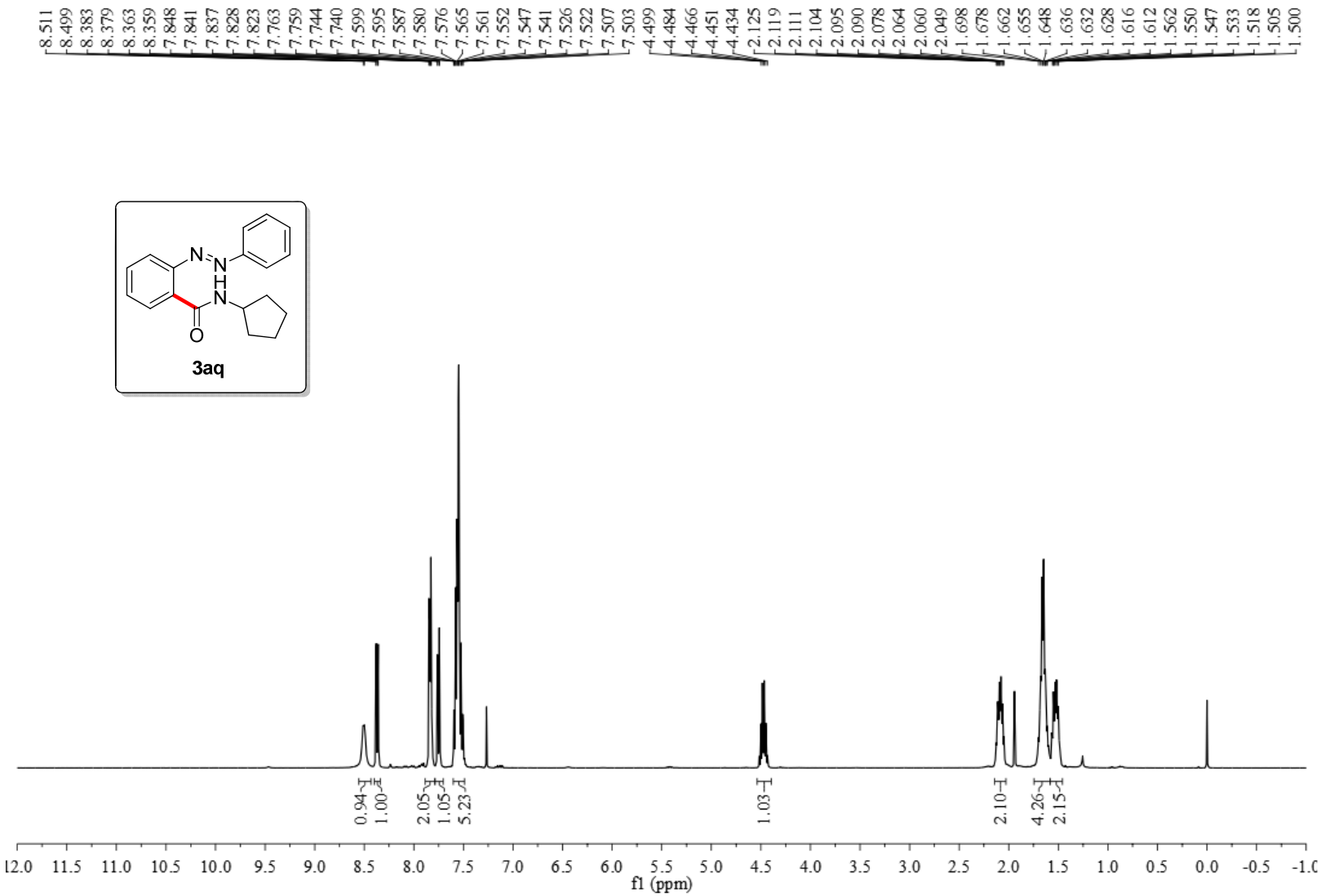
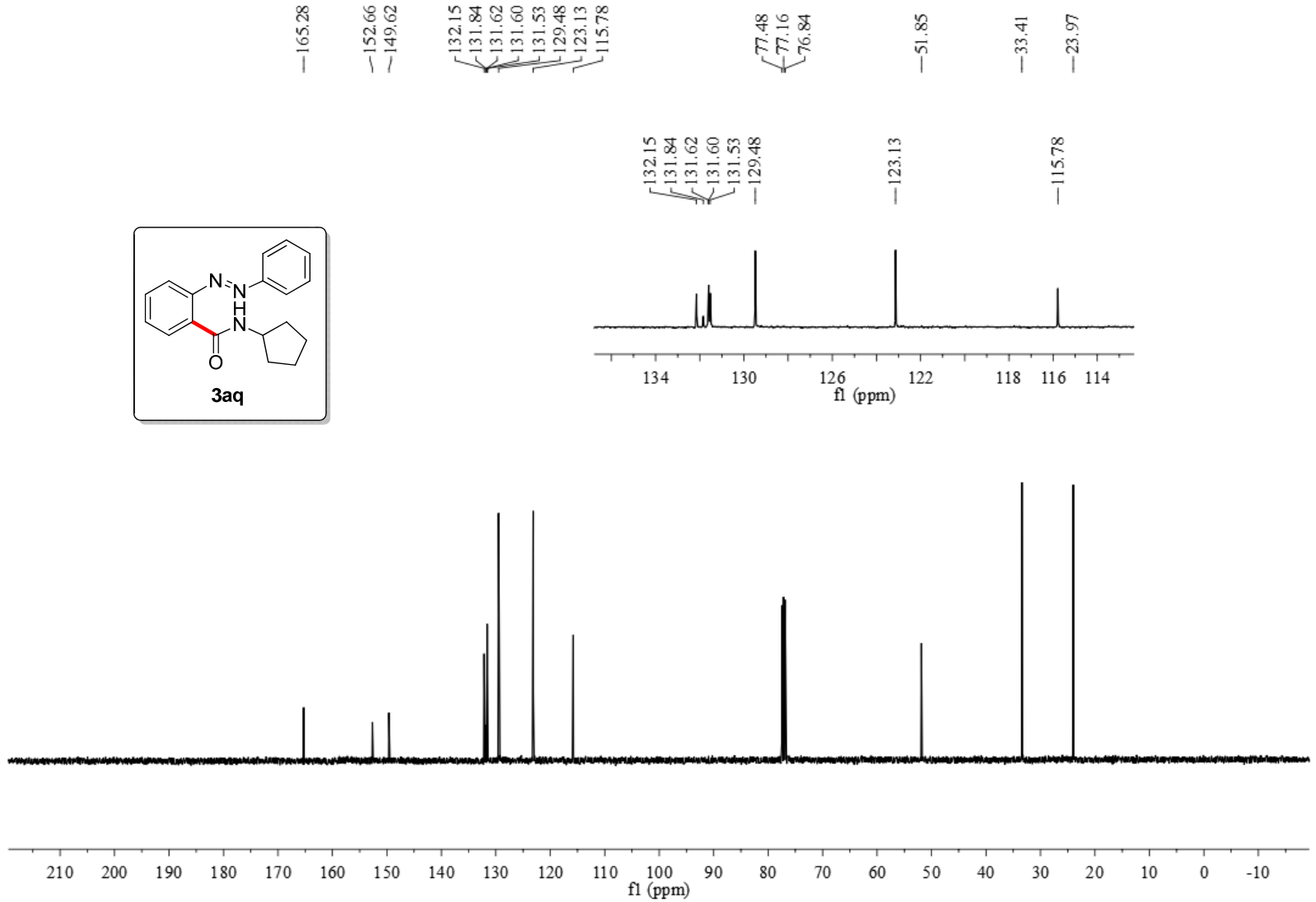
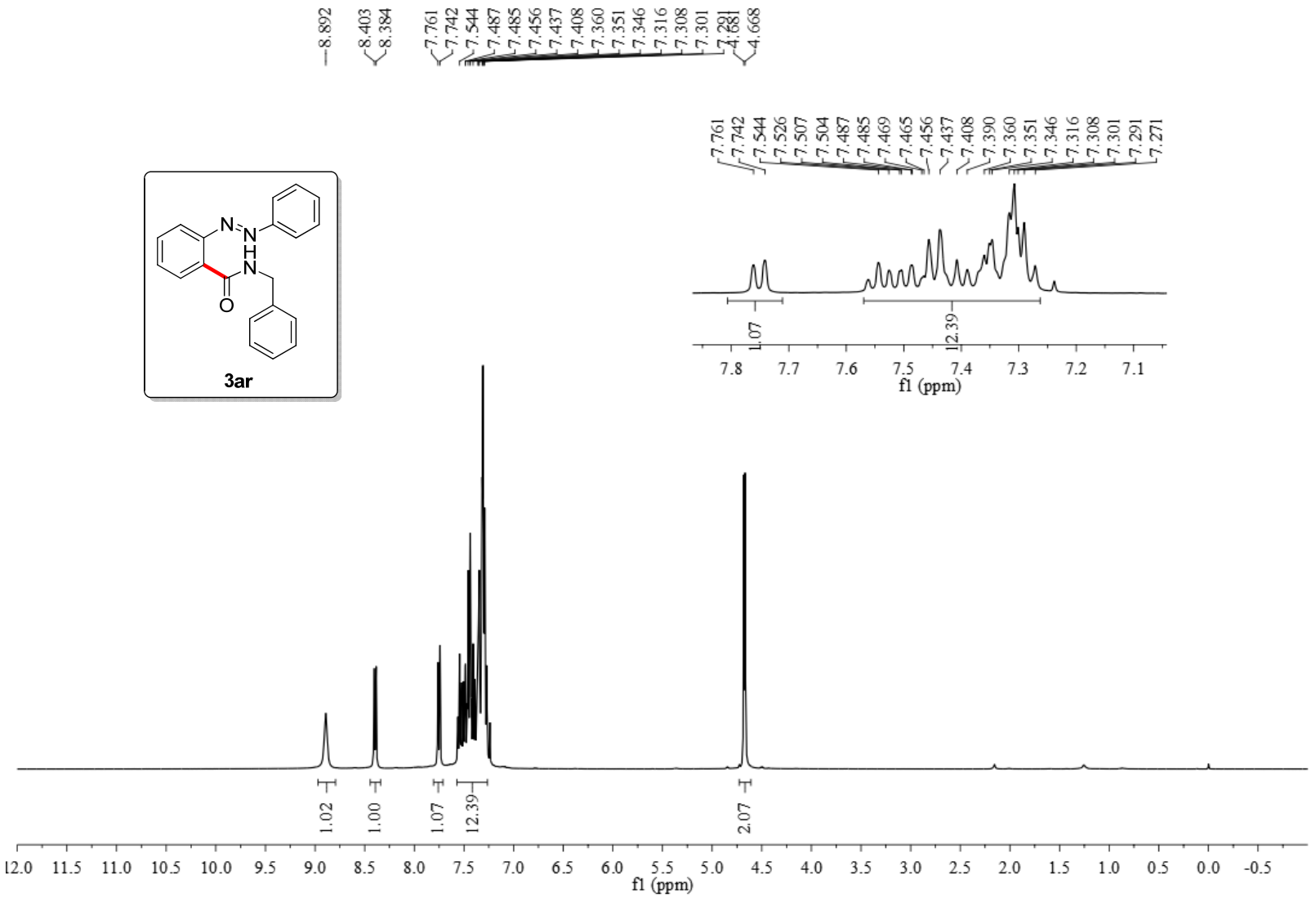
8.362
8.358
8.342
8.338
7.835
7.827
7.824
7.815
7.810
7.756
7.753
7.736
7.733
7.579
7.565
7.561
7.554
7.550
7.542
7.537
7.529
7.514
3.527
3.513
3.496
1.643
1.625
1.606
1.588
1.569
1.428
1.409
1.390
1.371
1.353
1.335
0.928
0.909
0.891
3ap
0.93
1.00
1.96
1.14
5.15
2.18
2.10
2.11
3.00
f1 (ppm)


165.83
152.63
149.64
132.12
131.78
131.60
131.55
129.50
123.15
115.84
77.48
77.16
76.84
39.95
31.75
20.38
13.84
3ap
f1 (ppm)
f1 (ppm)


8.511
8.499
8.383
8.379
8.363
8.359
7.848
7.841
7.837
7.828
7.823
7.763
7.759
7.744
7.740
7.599
7.595
7.587
7.580
7.576
7.565
7.561
7.552
7.547
7.541
7.526
7.522
7.507
7.503
4.499
4.484
4.466
4.451
4.434
2.125
2.119
2.111
2.104
2.095
2.090
2.078
2.064
2.060
2.049
1.698
1.678
1.662
1.655
1.648
1.636
1.632
1.628
1.616
1.612
1.562
1.550
1.547
1.533
1.518
1.505
1.500
N
N
H
N
O
3aq
0.94
1.00
2.05
1.05
5.23
1.03
2.10
4.26
2.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


165.28
152.66
149.62
132.15
131.84
131.62
131.60
131.53
129.48
123.13
115.78
77.48
77.16
76.84
51.85
33.41
23.97
3aq
fl (ppm)
fl (ppm)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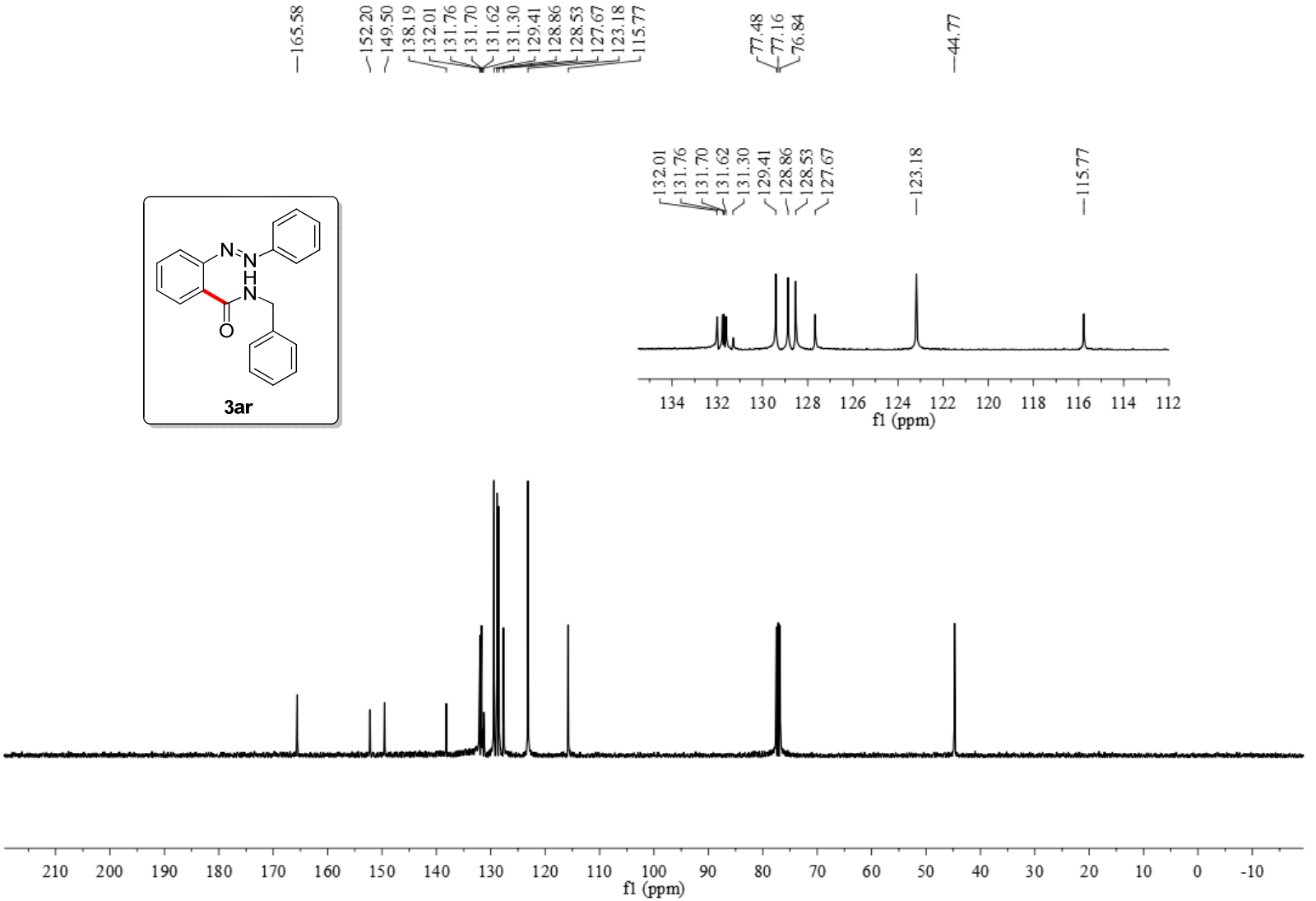
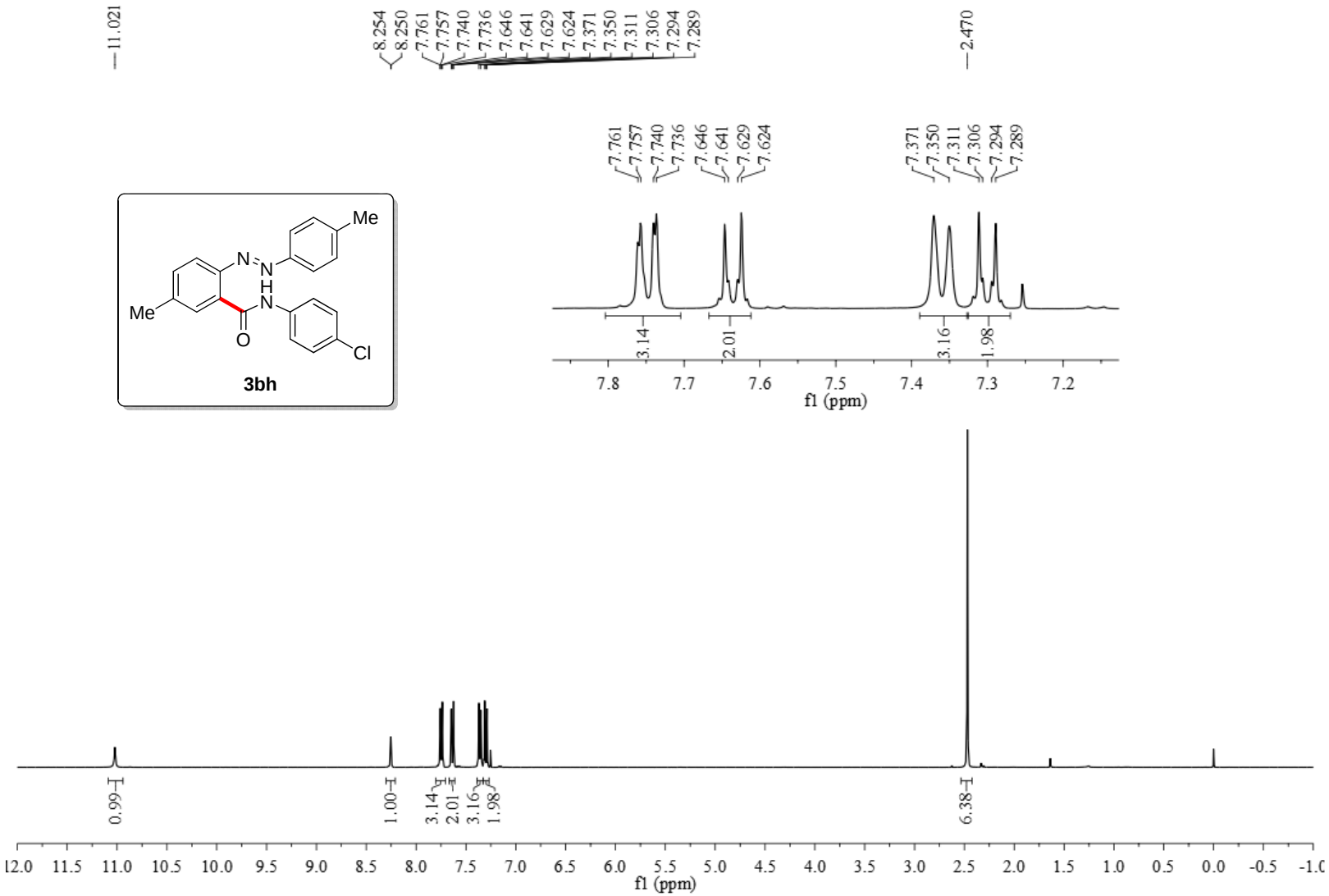
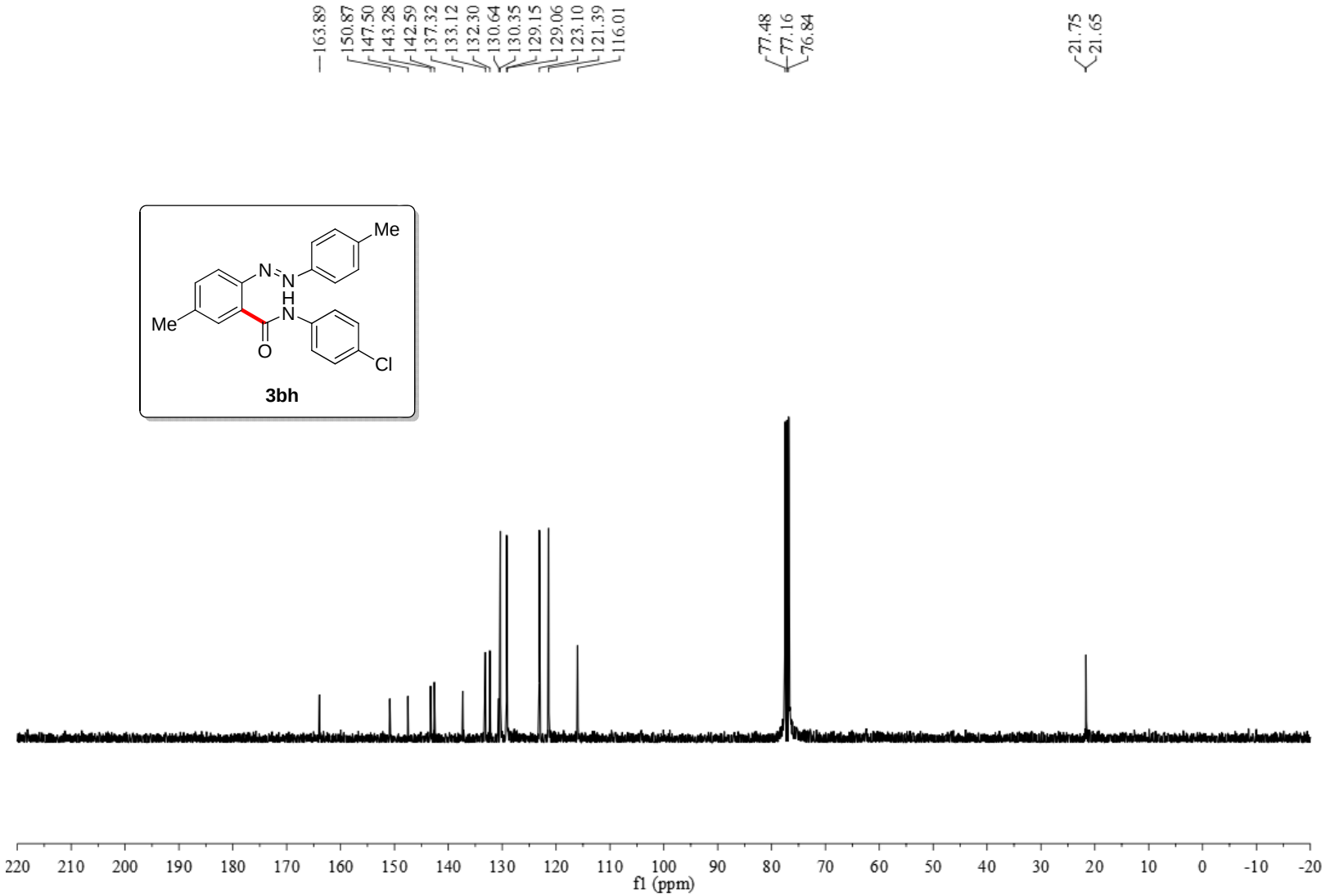
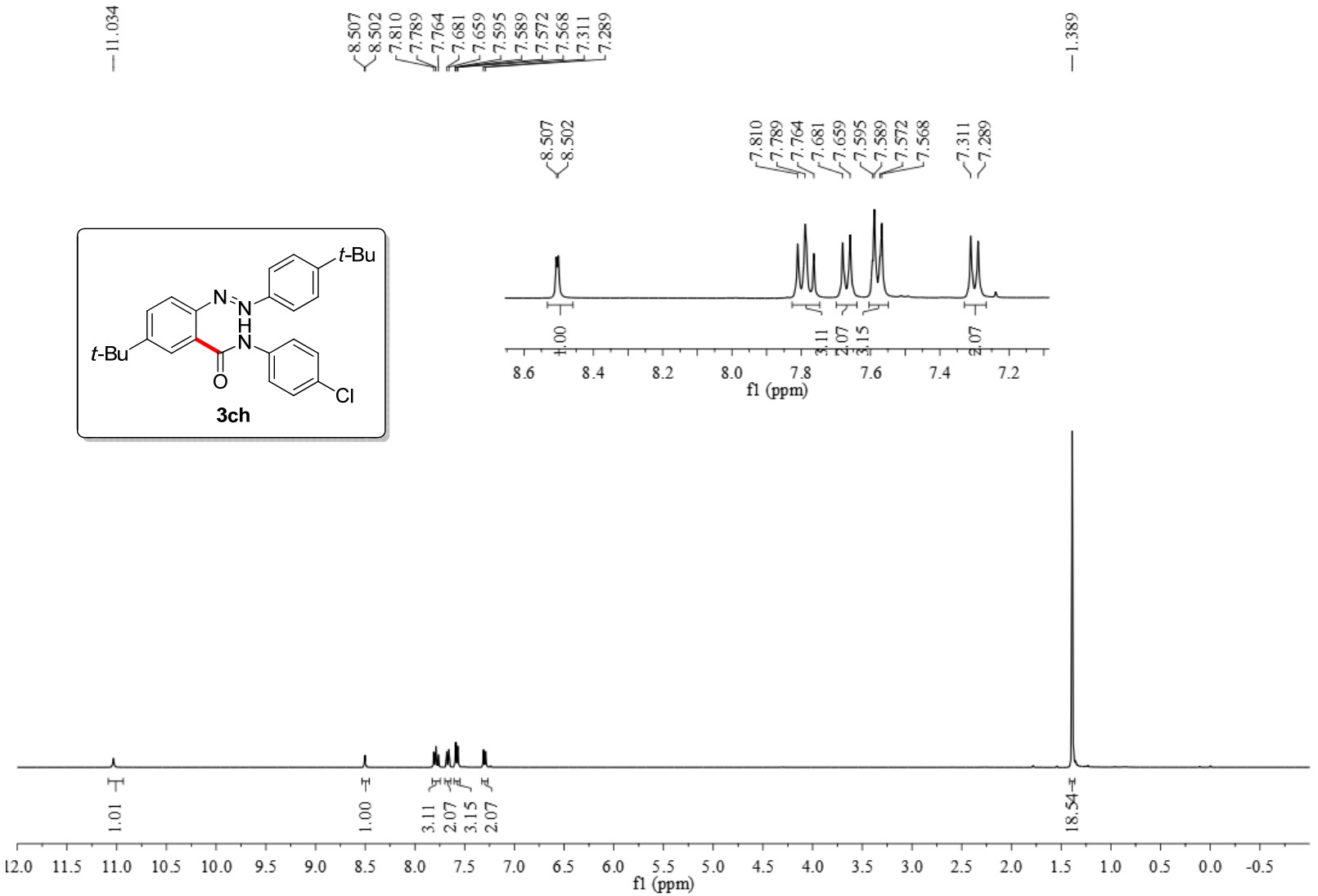
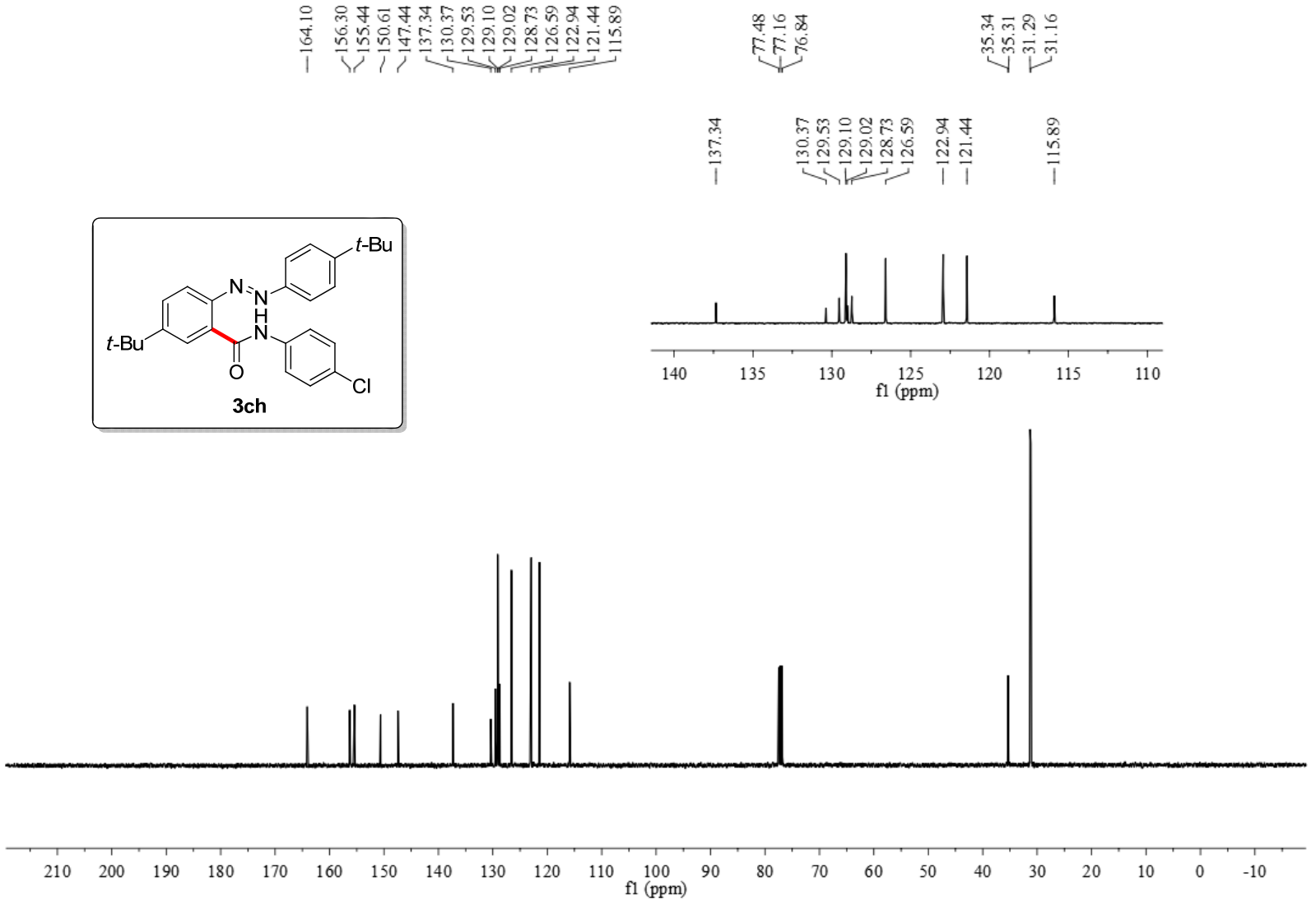
8.384
7.761
7.742
7.544
7.487
7.485
7.456
7.437
7.408
7.360
7.351
7.346
7.316
7.308
7.301
7.281
4.681
4.668
3ar
1.02
1.00
1.07
12.39
2.07
f1 (ppm)
7.761
7.742
7.544
7.526
7.507
7.504
7.487
7.485
7.469
7.465
7.456
7.437
7.408
7.390
7.360
7.351
7.346
7.316
7.308
7.301
7.291
7.271
1.07
12.39
f1 (ppm)

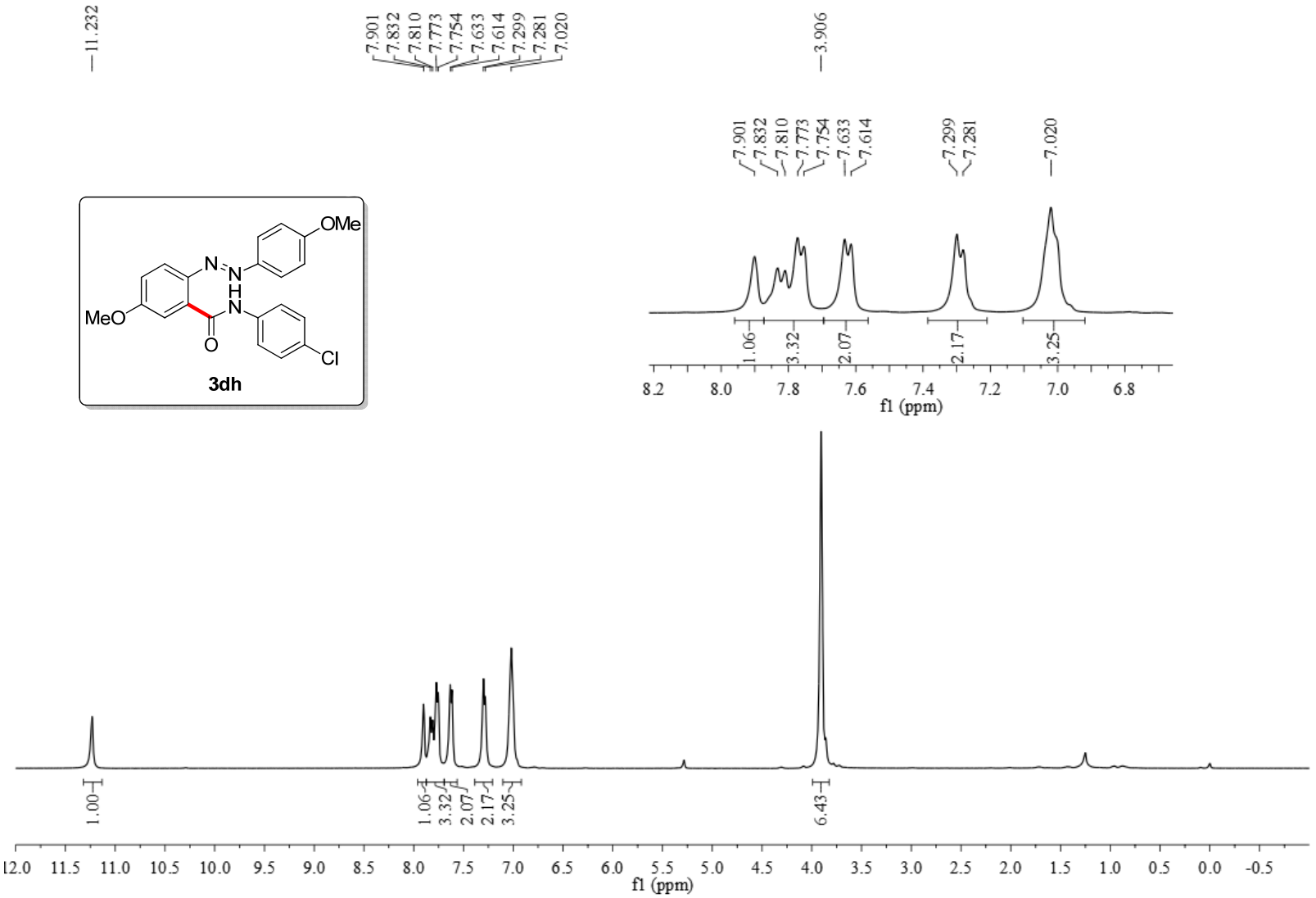

165.58
152.20
149.50
138.19
132.01
131.76
131.70
131.62
131.30
129.41
128.86
128.53
127.67
123.18
115.77
77.48
77.16
76.84
44.77
3ar
fl (ppm)
fl (ppm)

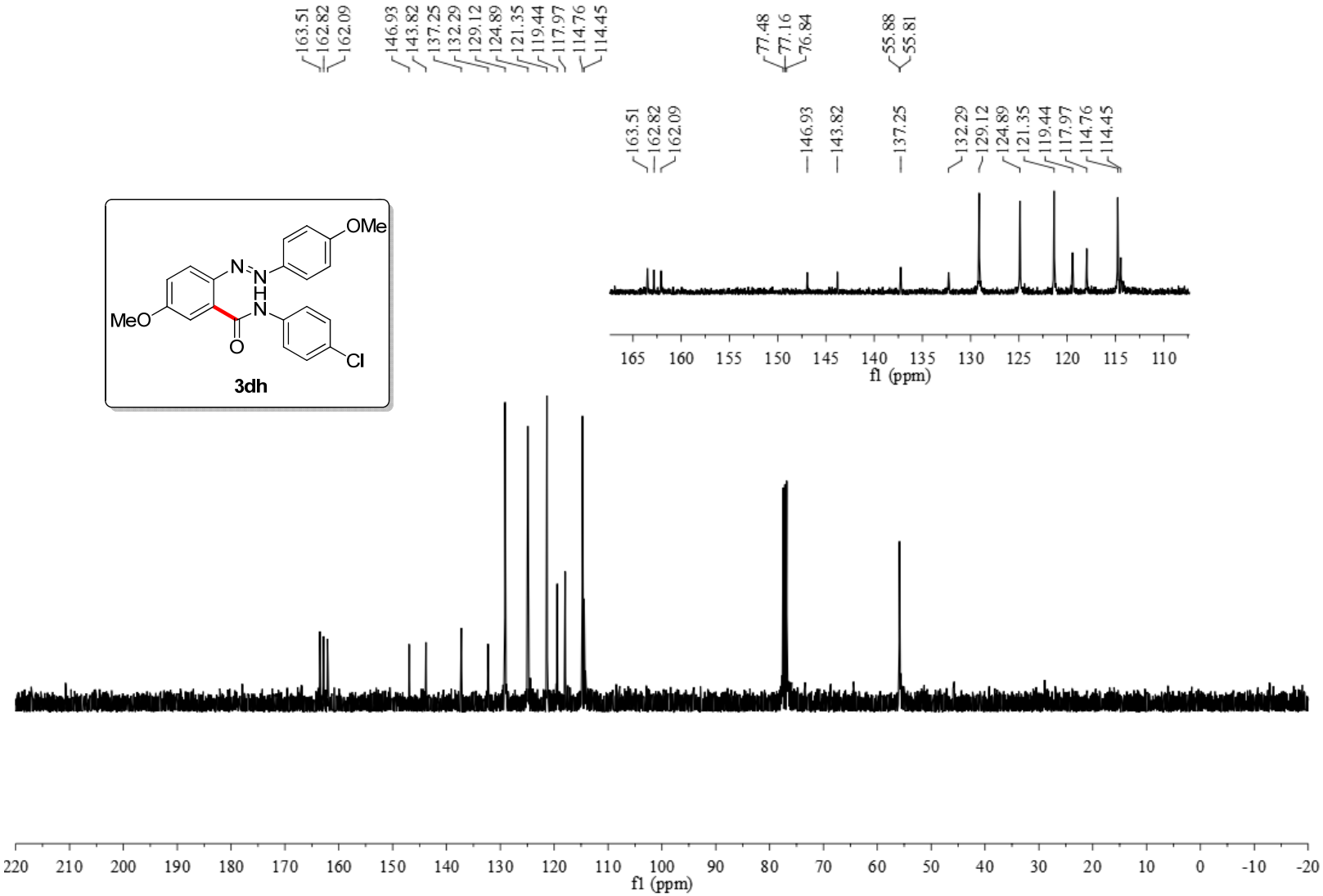

11.021
8.254
8.250
7.761
7.757
7.740
7.736
7.646
7.641
7.629
7.624
7.371
7.350
7.311
7.306
7.294
7.289
2.470
Me
Me
N
N
H
N
O
Cl
3bh
3.14
2.01
3.16
1.98
f1 (ppm)
0.99
1.00
6.38
f1 (ppm)

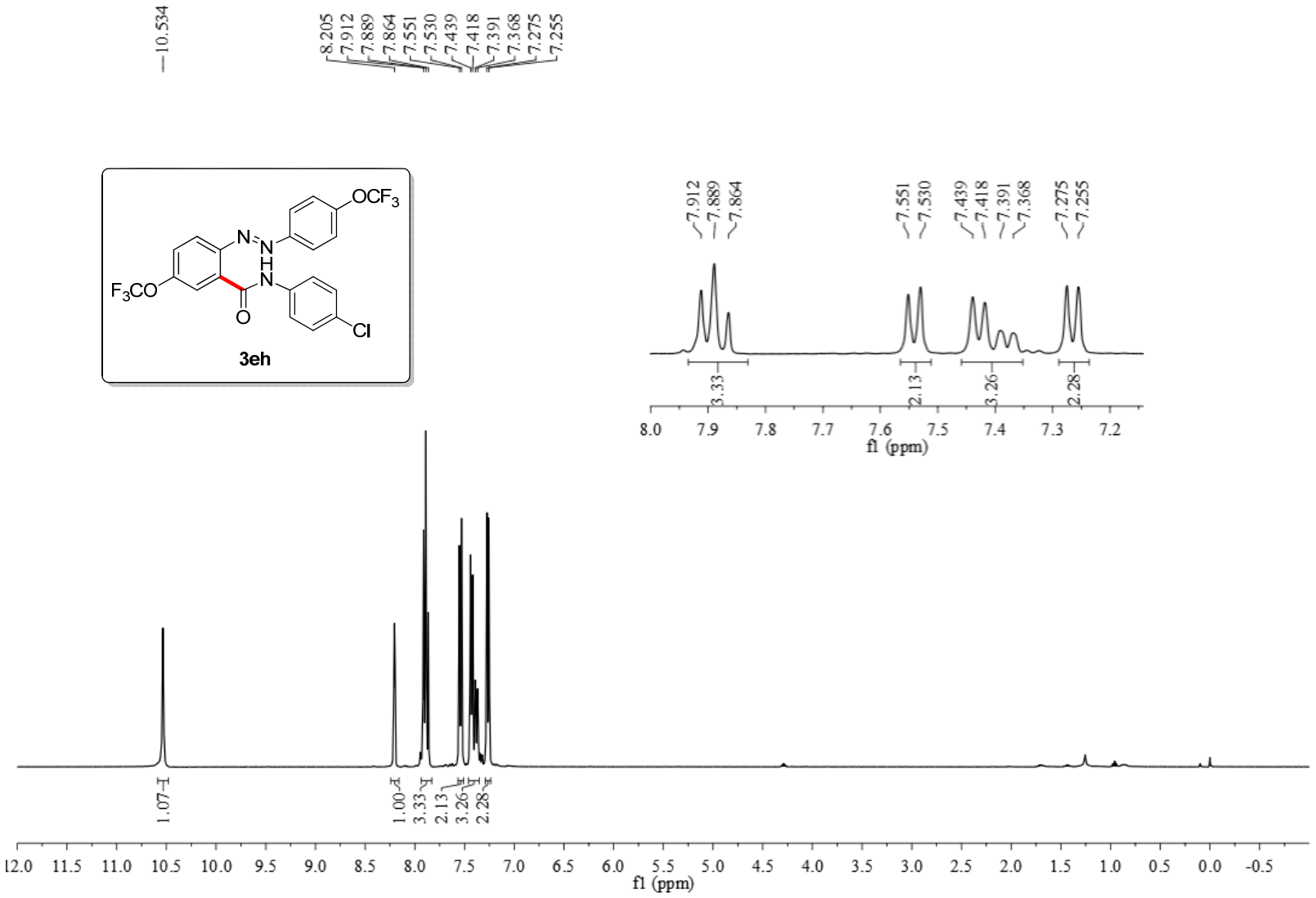

163.89
150.87
147.50
143.28
142.59
137.32
133.12
132.30
130.64
130.35
129.15
129.06
123.10
121.39
116.01
77.48
77.16
76.84
21.75
21.65
Me
N
N
H
N
Me
O
Cl
3bh
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

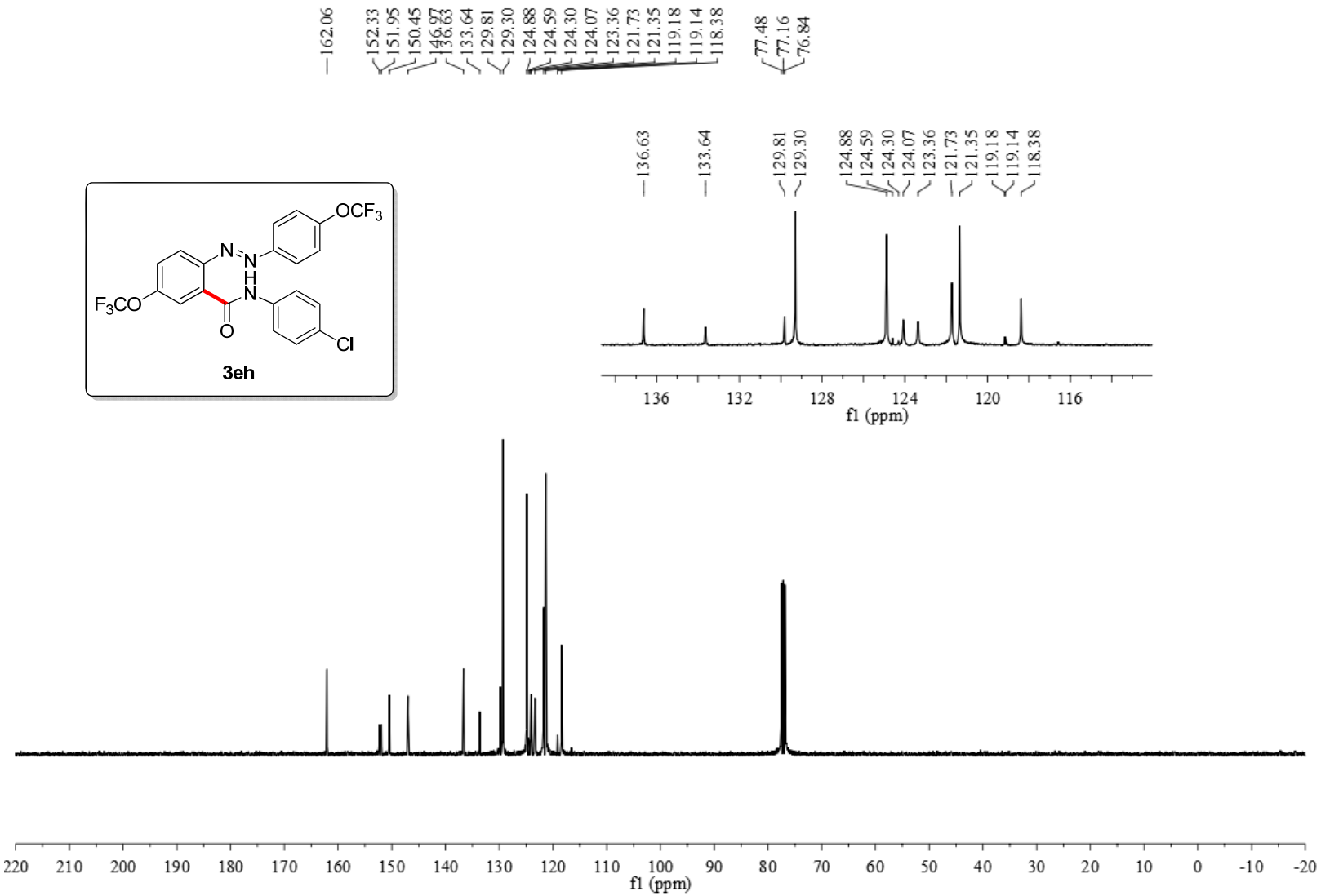

11.034
8.507
8.502
7.810
7.789
7.764
7.681
7.659
7.595
7.589
7.572
7.568
7.311
7.289
1.389
t-Bu
t-Bu
N
N
H
N
O
Cl
3ch
1.00
3.11
2.07
3.15
2.07
f1 (ppm)
1.01
1.00
3.11
2.07
3.15
2.07
18.54
f1 (ppm)


164.10
156.30
155.44
150.61
147.44
137.34
130.37
129.53
129.10
129.02
128.73
126.59
122.94
121.44
115.89
77.48
77.16
76.84
35.34
35.31
31.29
31.16
t-Bu
t-Bu
N
N
H
N
O
Cl
3ch
f1 (ppm)
f1 (ppm)


11.232
7.901
7.832
7.810
7.773
7.754
7.633
7.614
7.299
7.281
7.020
3.906
OMe
MeO
N
H
N
O
Cl
3dh
1.06
3.32
2.07
2.17
3.25
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.00
6.43
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.51
162.82
162.09
146.93
143.82
137.25
132.29
129.12
124.89
121.35
119.44
117.97
114.76
114.45
77.48
77.16
76.84
55.88
55.81
OMe
MeO
N
N
H
N
O
Cl
3dh
165 160 155 150 145 140 135 130 125 120 115 110
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


10.534
8.205
7.912
7.889
7.864
7.551
7.530
7.439
7.418
7.391
7.368
7.275
7.255
OCF3
F3CO
N
N
H
N
O
Cl
3eh
3.33
2.13
3.26
2.28
fl (ppm)
1.07
1.00
fl (ppm)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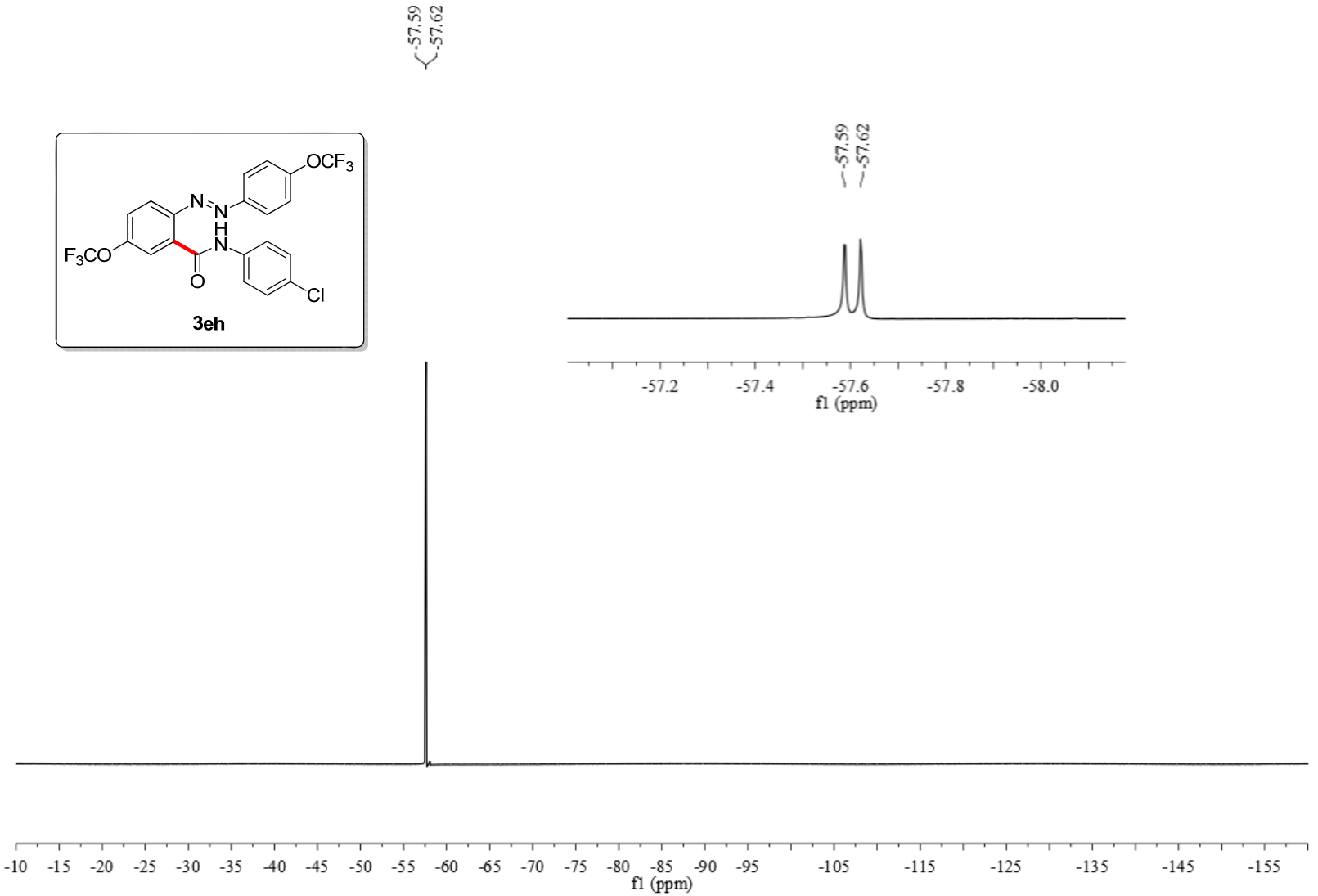
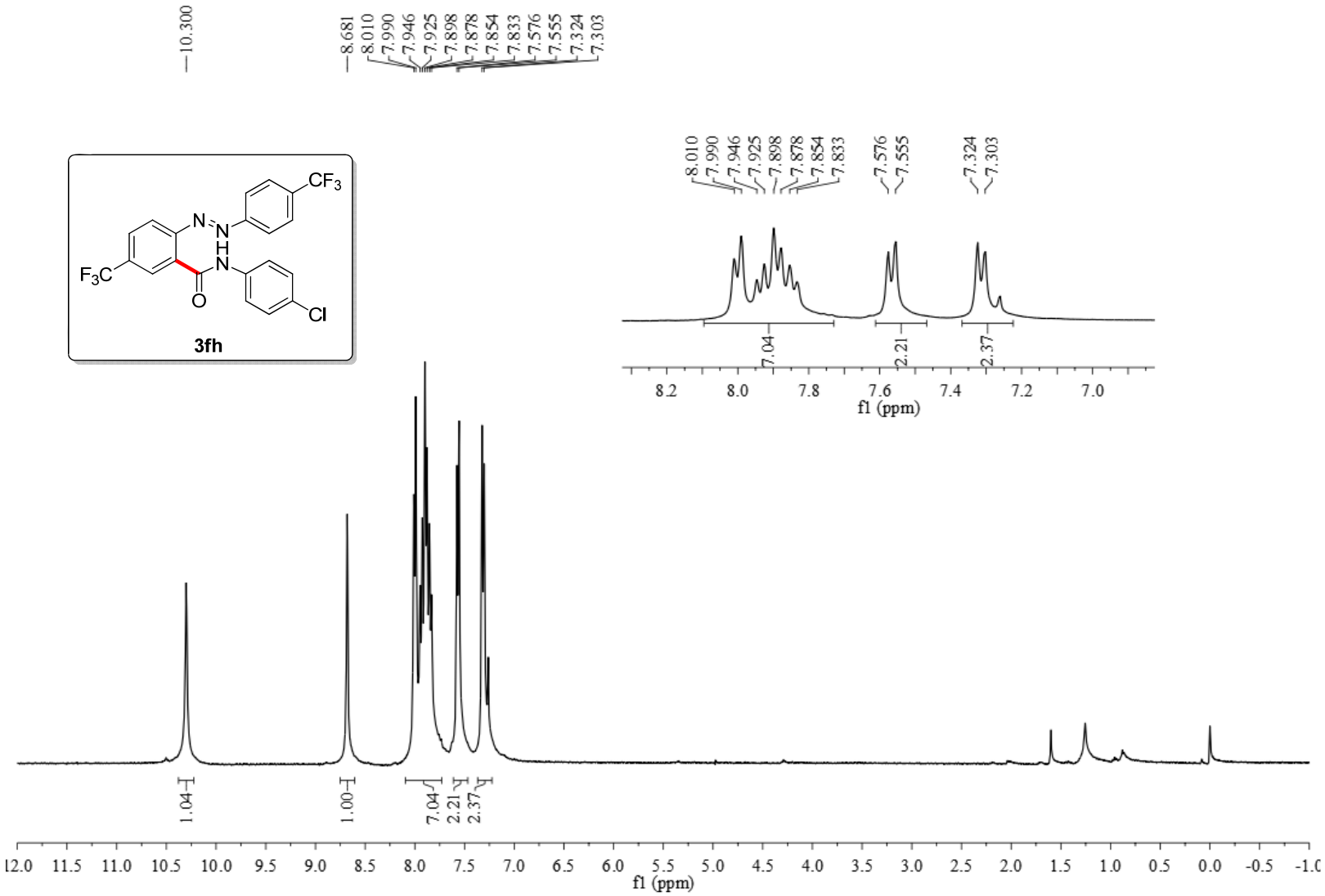
152.33
151.95
150.45
146.97
136.63
133.64
129.81
129.30
124.88
124.59
124.30
124.07
123.36
121.73
121.35
119.18
119.14
118.38
77.48
77.16
76.84
OCF3
F3CO
N
N
H
N
O
Cl
3eh
136.63
133.64
129.81
129.30
124.88
124.59
124.30
124.07
123.36
121.73
121.35
119.18
119.14
118.38
136
132
128
124
120
116
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


-57.59
-57.62
OCF3
N
N
H
N
F3CO
O
Cl
3eh
-57.59
-57.62
-57.2
-57.4
-57.6
-57.8
-58.0
f1 (ppm)
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
f1 (ppm)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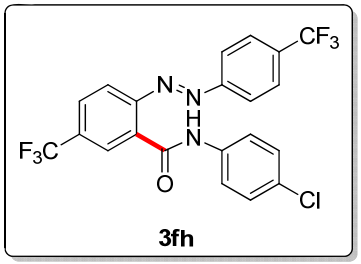
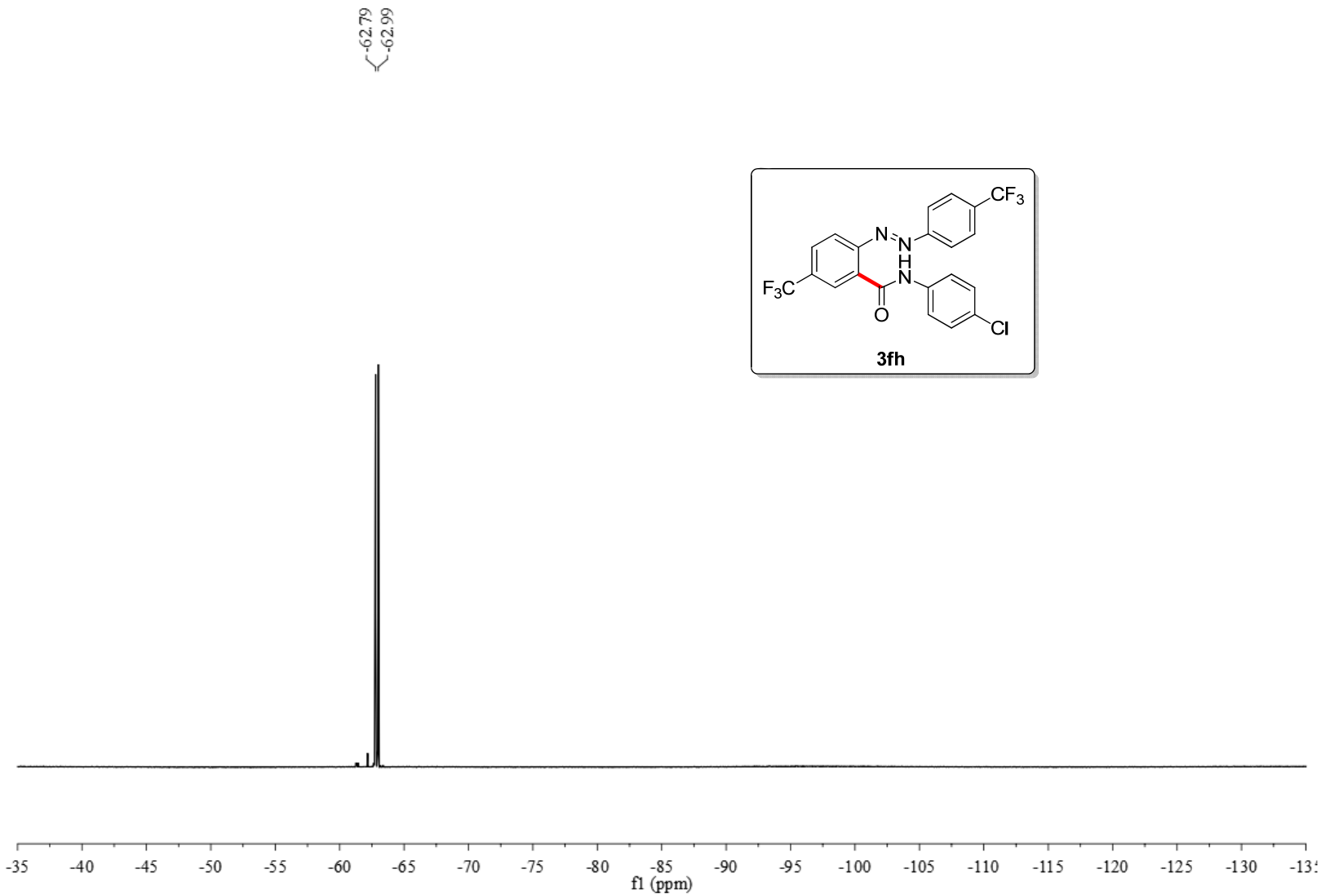
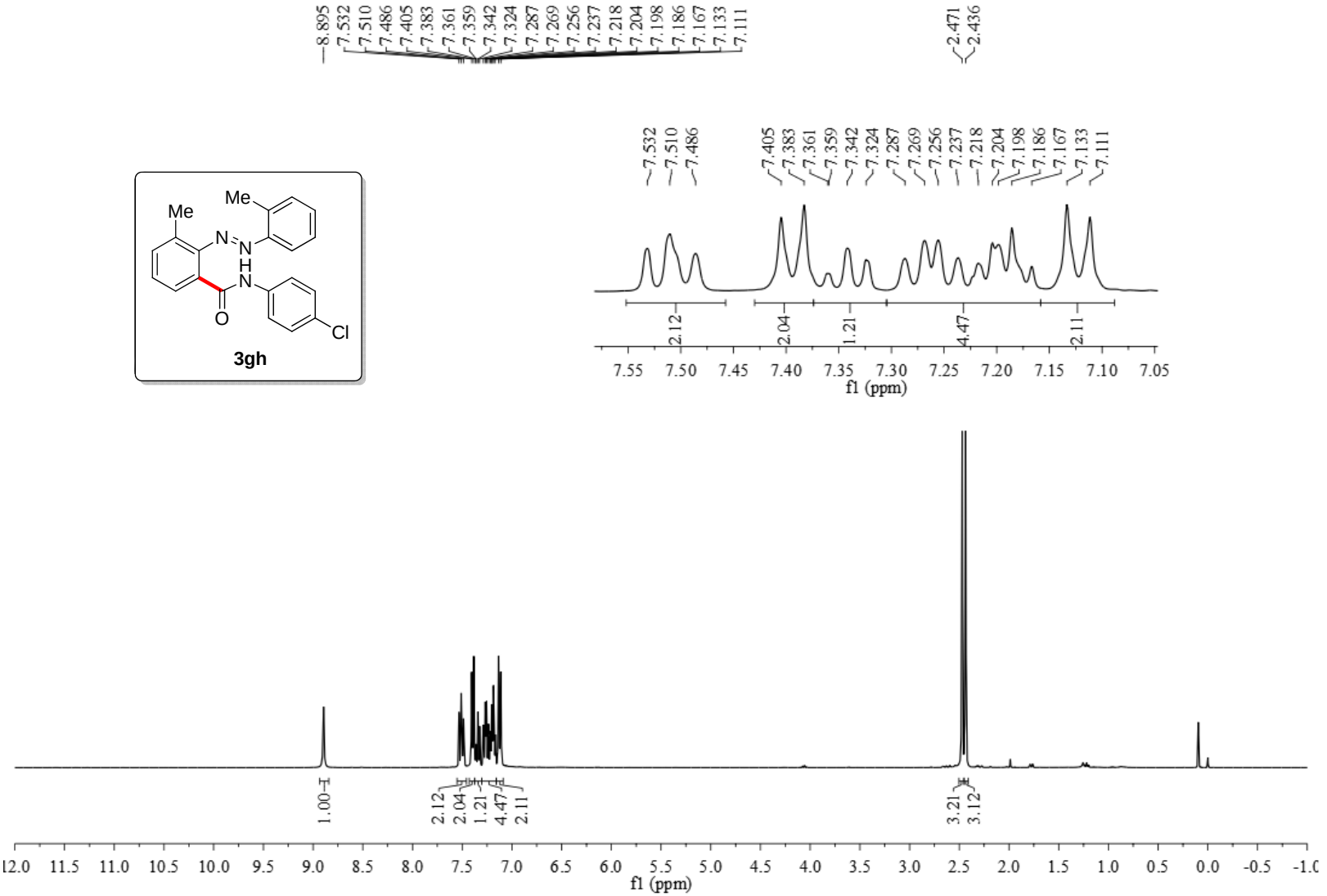
8.681
8.010
7.990
7.946
7.925
7.898
7.878
7.854
7.833
7.576
7.555
7.324
7.303
3fh
7.04
2.21
2.37
f1 (ppm)
1.04
1.00
7.04
2.21
2.37
f1 (ppm)

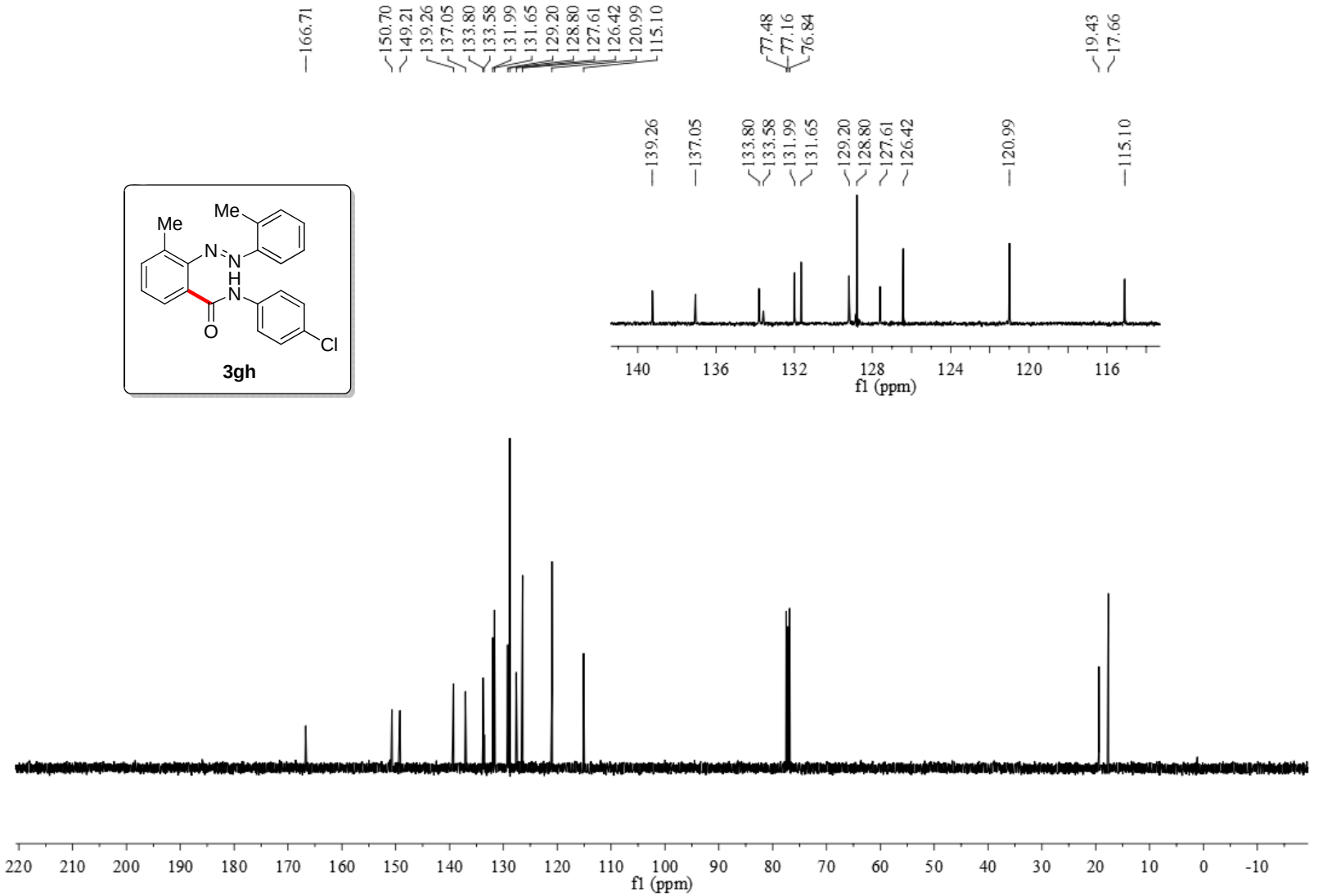

CF3
N
N
H
N
F3C
O
Cl

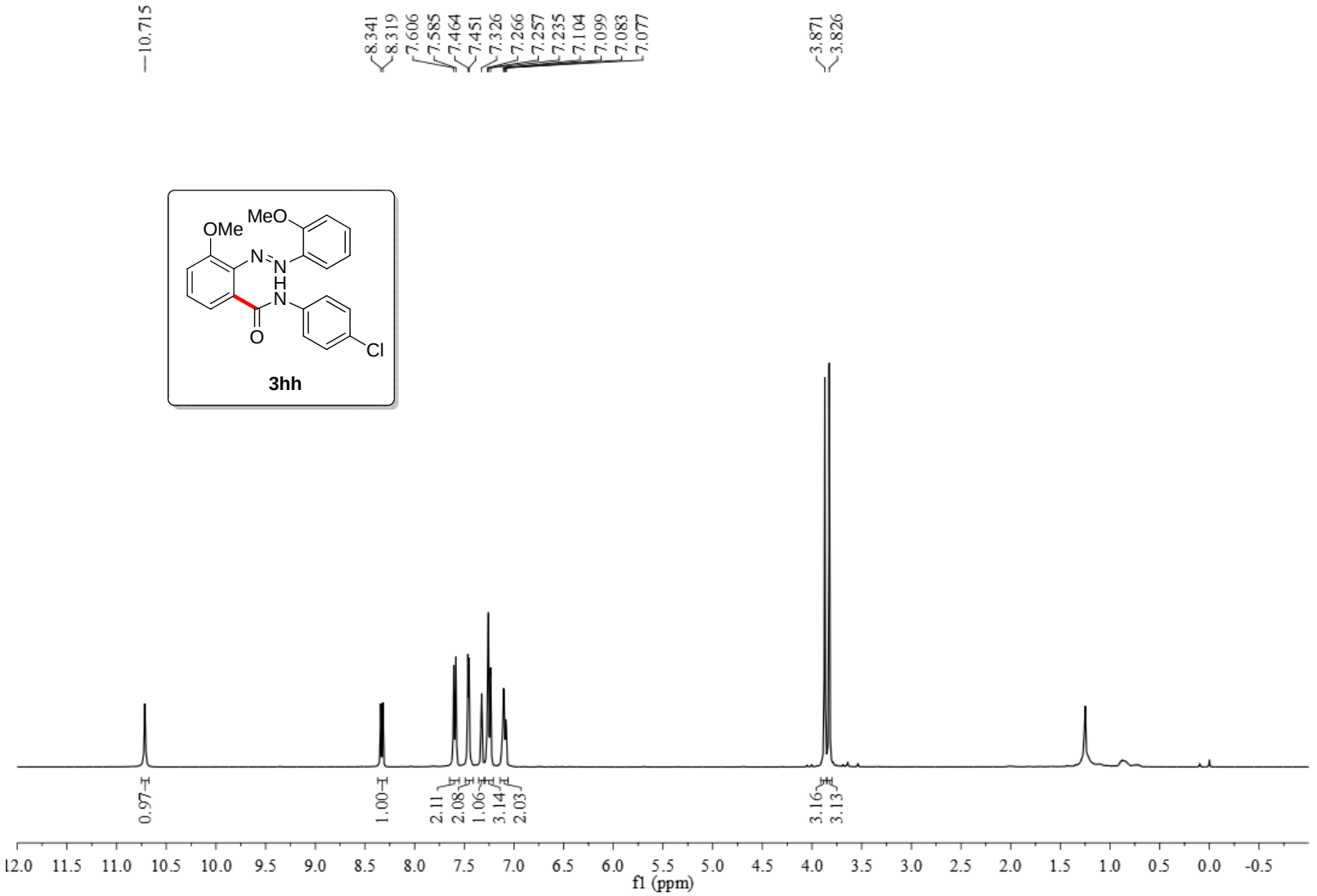
3fh

162.21
154.18
150.53
136.50
134.61
134.29
133.96
132.62
130.01
129.41
129.09
129.05
127.15
127.11
124.94
124.76
123.58
121.40
117.19
77.48
77.16
76.84
136.50
134.61
134.29
133.96
132.62
130.01
129.41
129.09
127.15
124.76
123.58
122.23
122.04
121.40
117.19
140
136
132
128
124
120
116
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-62.79
-62.99
CF3
N
N
H
N
F3C
O
Cl
3fh
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
f1 (ppm)


8.895
7.532
7.510
7.486
7.405
7.383
7.361
7.359
7.342
7.324
7.287
7.269
7.256
7.237
7.218
7.204
7.198
7.186
7.167
7.133
7.111
2.471
2.436
Me
Me
N
N
H
N
O
Cl
3gh
2.12
2.04
1.21
4.47
2.11
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
1.00
2.12
2.04
1.21
4.47
2.11
3.21
3.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


166.71
150.70
149.21
139.26
137.05
133.80
133.58
131.99
131.65
129.20
128.80
127.61
126.42
120.99
115.10
77.48
77.16
76.84
19.43
17.66
Me
Me
N
N
H
N
O
Cl
3gh
f1 (ppm)
f1 (ppm)


10.715
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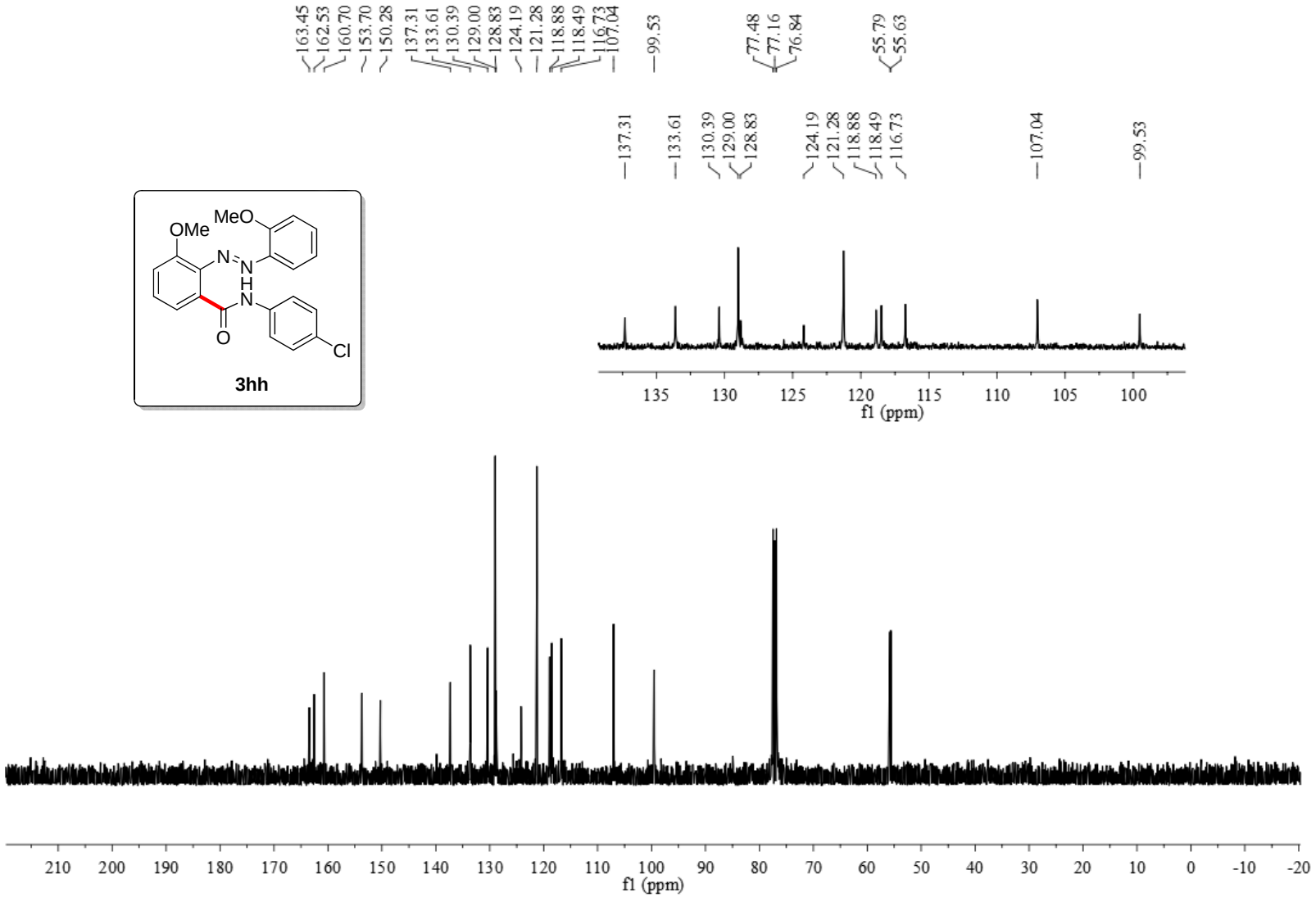
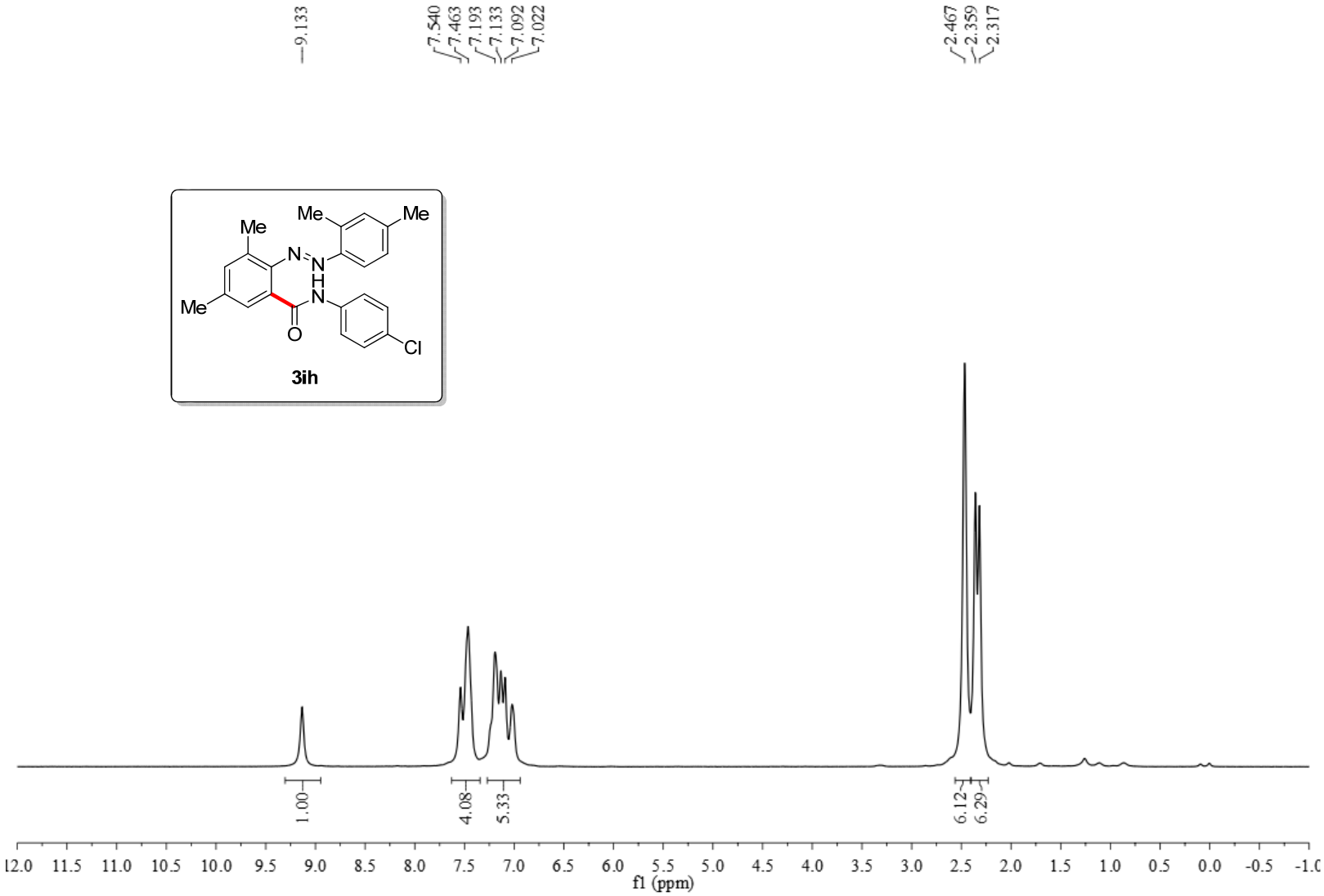
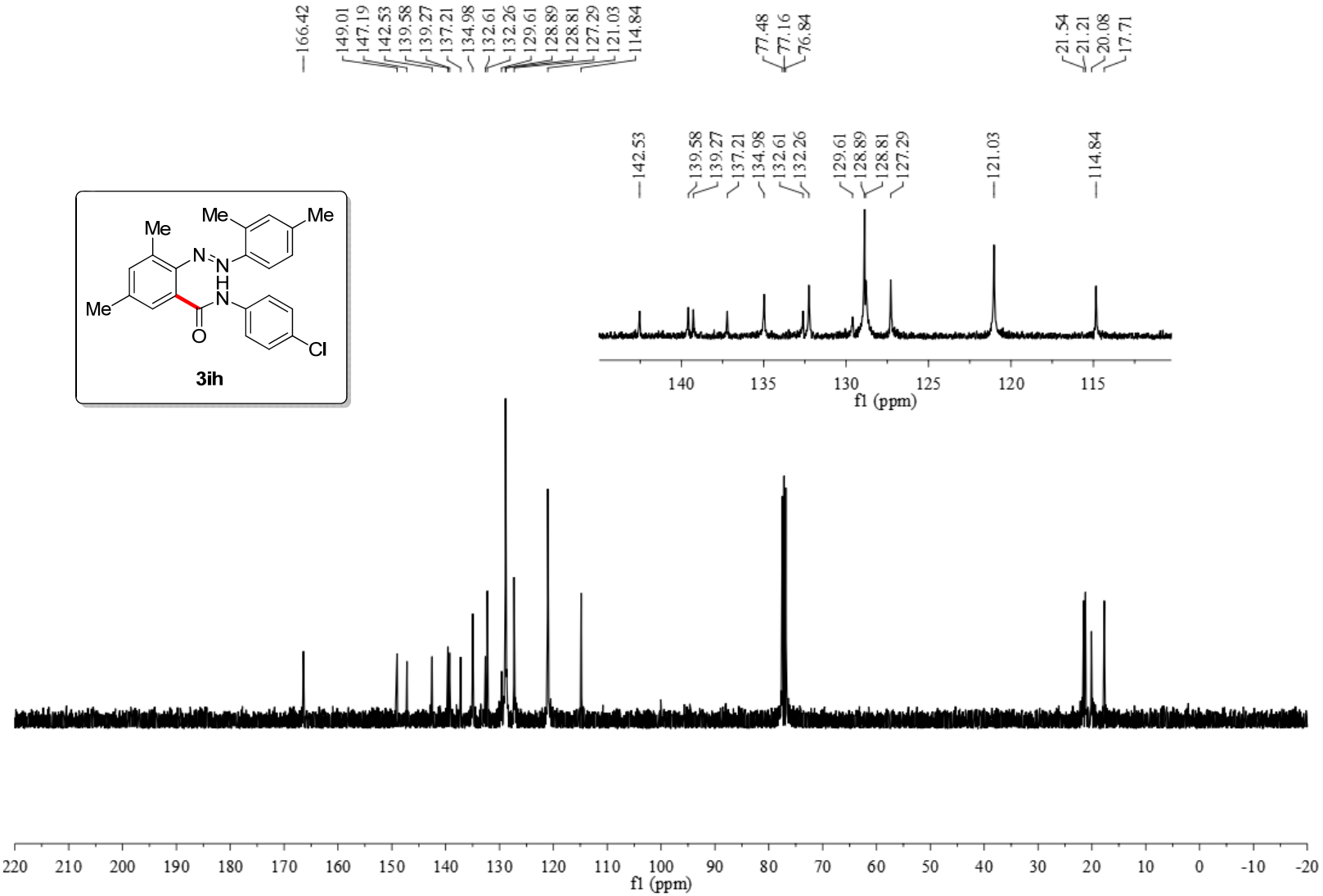
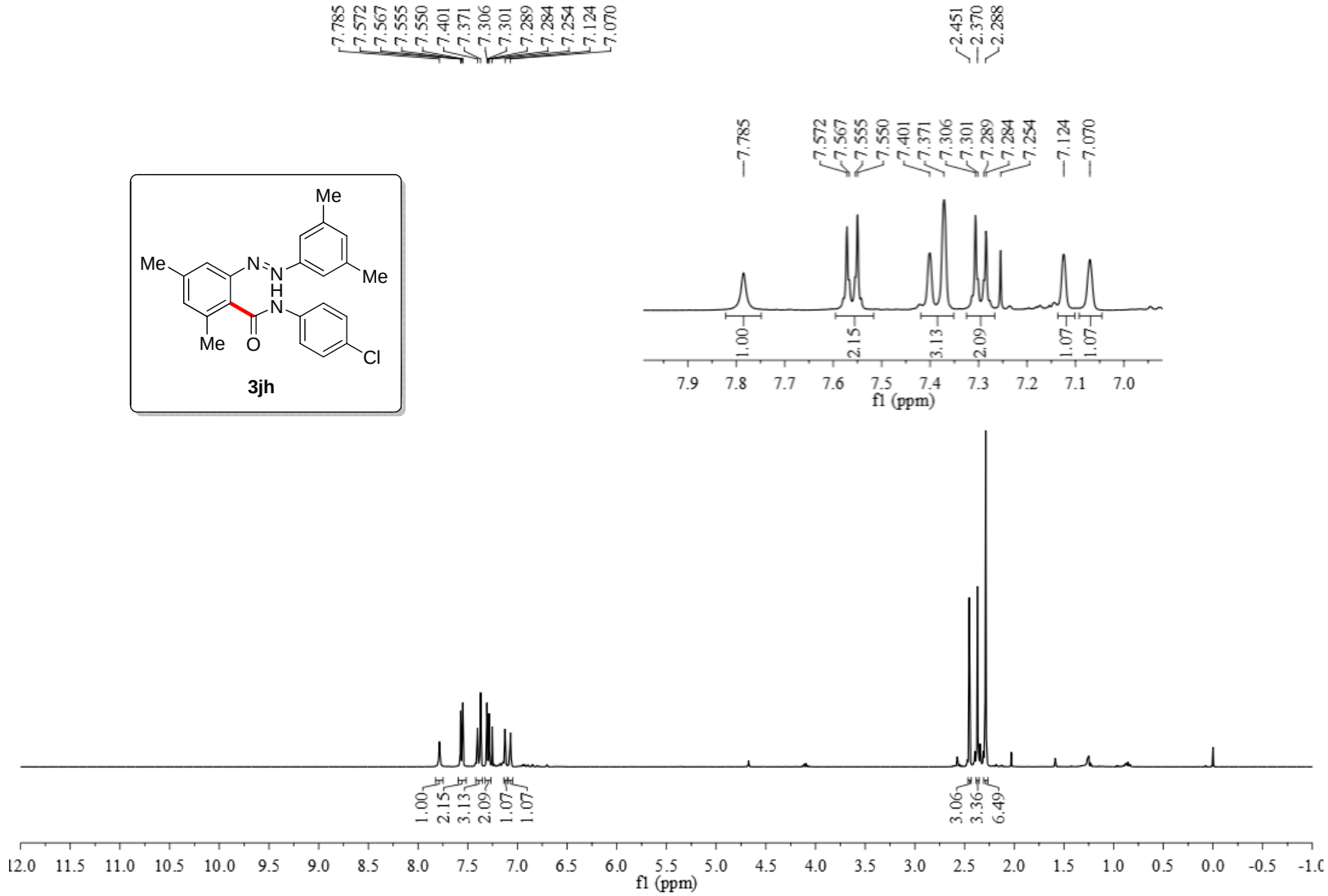
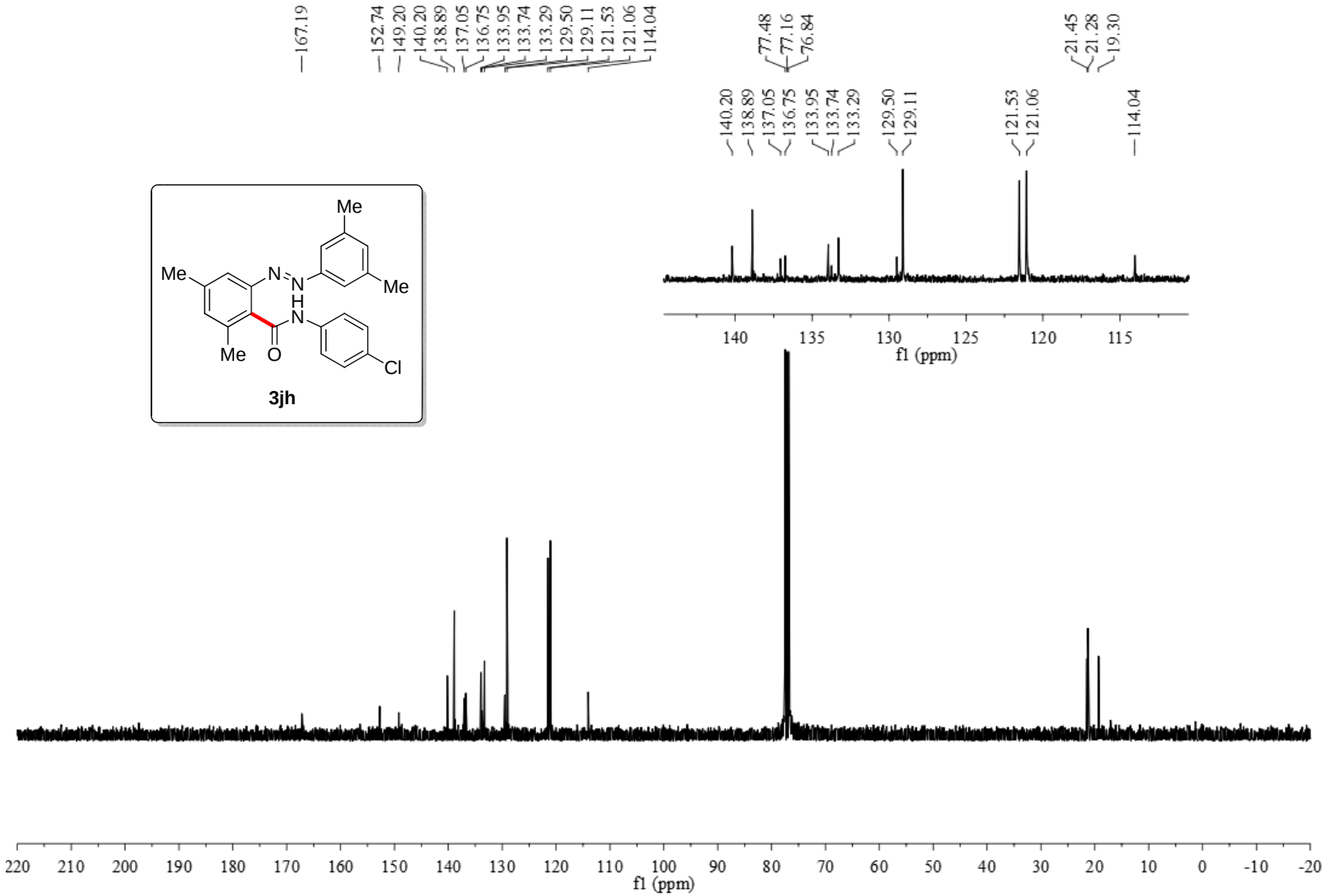
8.319
7.606
7.585
7.464
7.451
7.326
7.266
7.257
7.235
7.104
7.099
7.083
7.077
3.871
3.826
MeO
OMe
N
N
H
N
O
Cl
3hh
0.97
1.00
2.11
2.08
1.06
3.14
2.03
3.16
3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

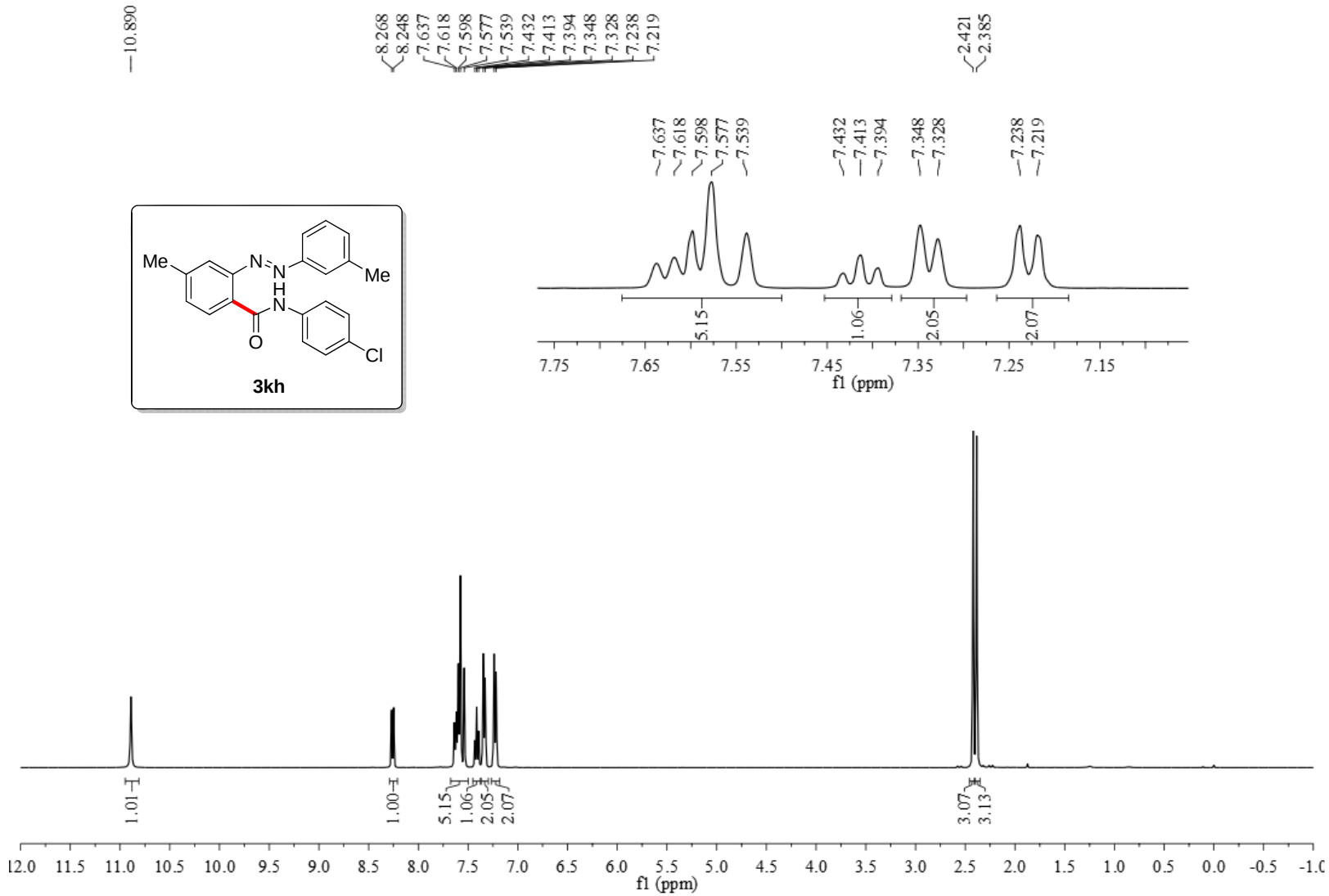

163.45
162.53
160.70
153.70
150.28
137.31
133.61
130.39
129.00
128.83
124.19
121.28
118.88
118.49
116.73
107.04
99.53
77.48
77.16
76.84
55.79
55.63
OMe
MeO
N
N
H
N
O
Cl
3hh
137.31
133.61
130.39
129.00
128.83
124.19
121.28
118.88
118.49
116.73
107.04
99.53
135
130
125
120
115
110
105
100
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

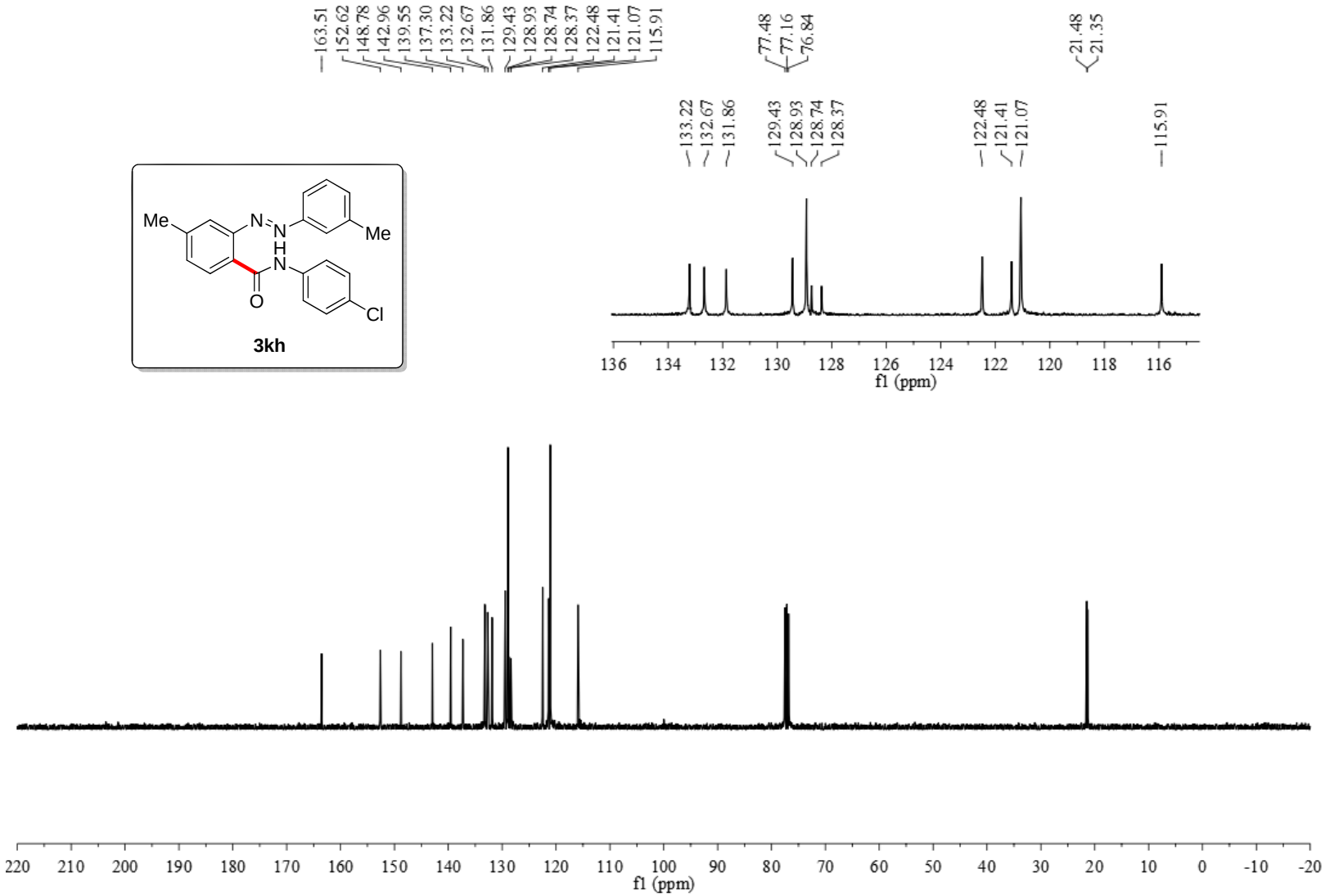

9.133
7.540
7.463
7.193
7.133
7.092
7.022
2.467
2.359
2.317
Me
Me
Me
Me
N
N
H
N
O
Cl
3ih
1.00
4.08
5.33
6.12
6.29
f1 (ppm)


166.42
149.01
147.19
142.53
139.58
139.27
137.21
134.98
132.61
132.26
129.61
128.89
128.81
127.29
121.03
114.84
77.48
77.16
76.84
21.54
21.21
20.08
17.71
Me
Me
Me
Me
N
N
H
N
O
Cl
3ih
fl (ppm)
fl (ppm)


7.785
7.572
7.567
7.555
7.550
7.401
7.371
7.306
7.301
7.289
7.284
7.254
7.124
7.070
2.451
2.370
2.288
Me
Me
Me
Me
N
N
H
N
O
Cl
3jh
1.00
2.15
3.13
2.09
1.07
1.07
3.06
3.36
6.49
f1 (ppm)


167.19
152.74
149.20
140.20
138.89
137.05
136.75
133.95
133.74
133.29
129.50
129.11
121.53
121.06
114.04
77.48
77.16
76.84
21.45
21.28
19.30
Me
Me
Me
Me
N
N
H
N
O
Cl
3jh
fl (ppm)
fl (ppm)


10.890
8.268
8.248
7.637
7.618
7.598
7.577
7.539
7.432
7.413
7.394
7.348
7.328
7.238
7.219
2.421
2.385
Me
N
N
H
N
Me
O
Cl
3kh
5.15
1.06
2.05
2.07
7.75
7.65
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
1.01
1.00
5.15
1.06
2.05
2.07
3.07
3.13
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


163.51
152.62
148.78
142.96
139.55
137.30
133.22
132.67
131.86
129.43
128.93
128.74
128.37
122.48
121.41
121.07
115.91
77.48
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21.35
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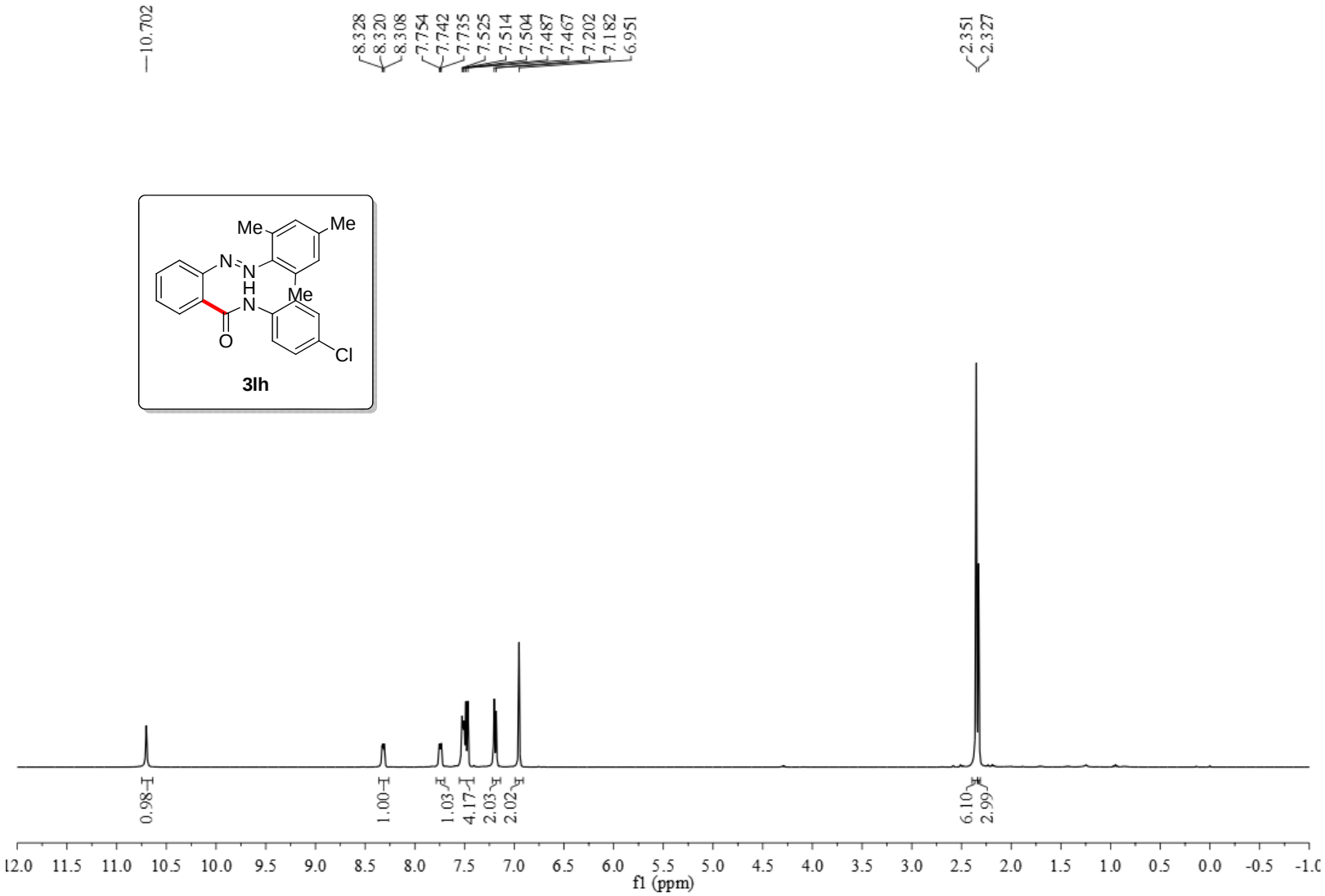
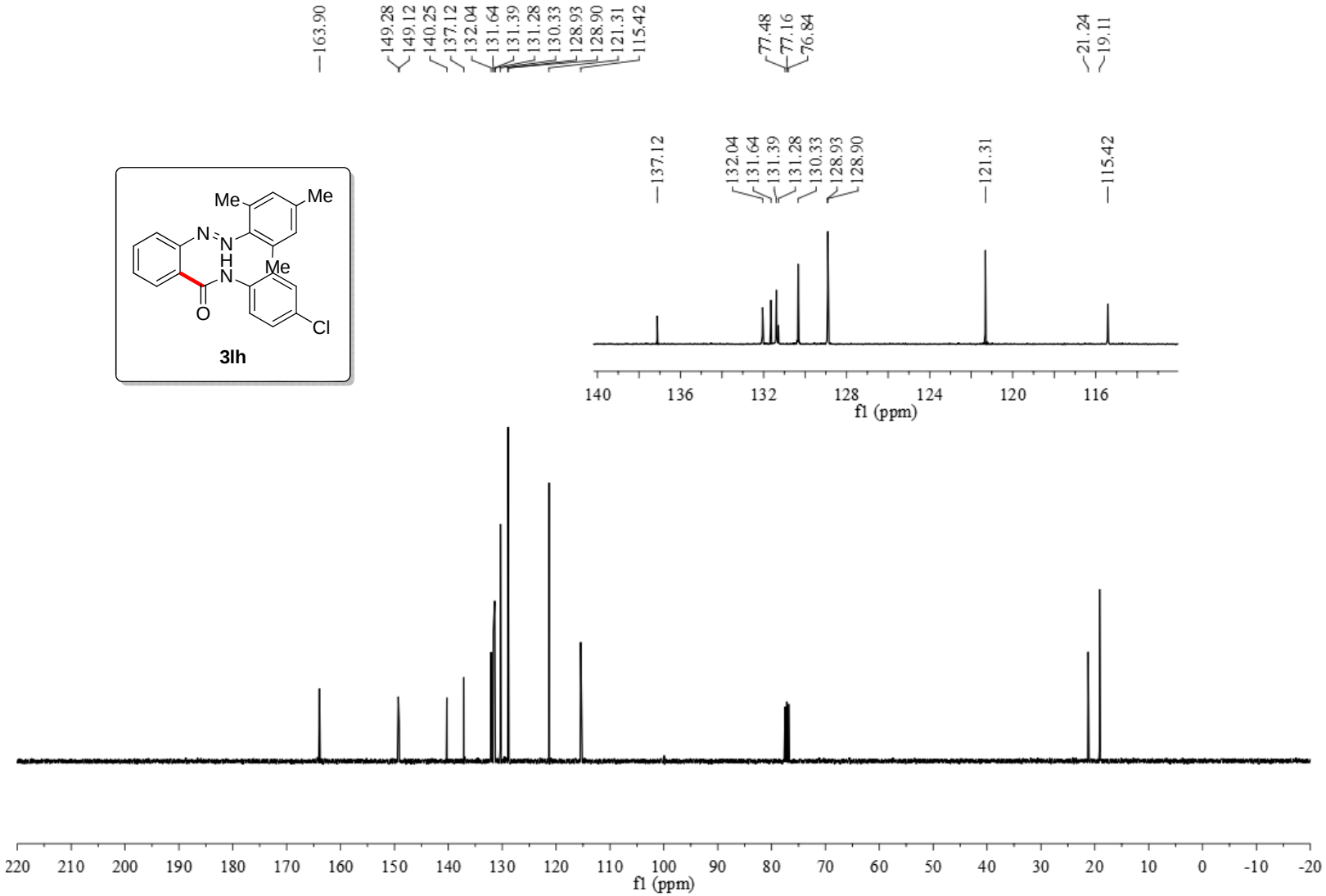
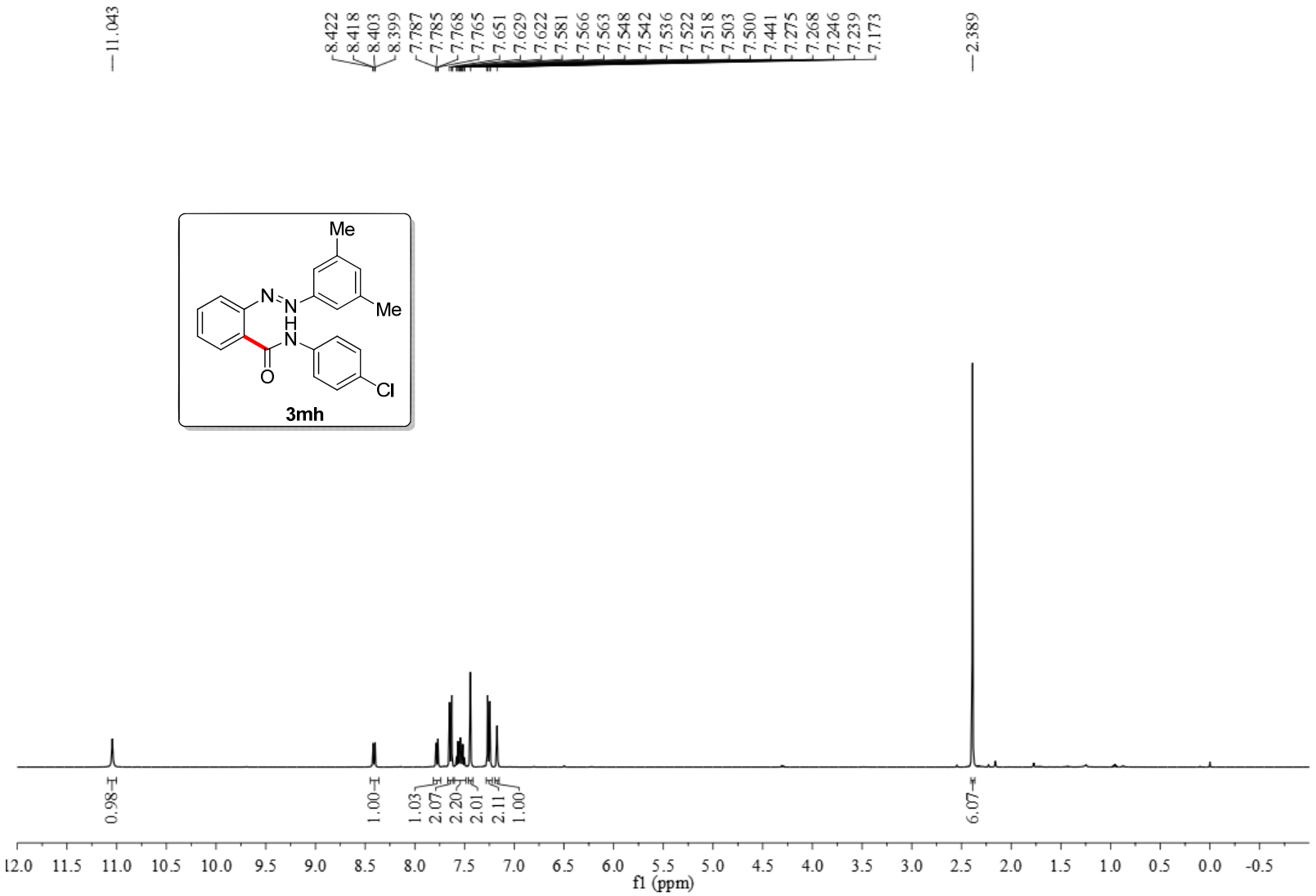
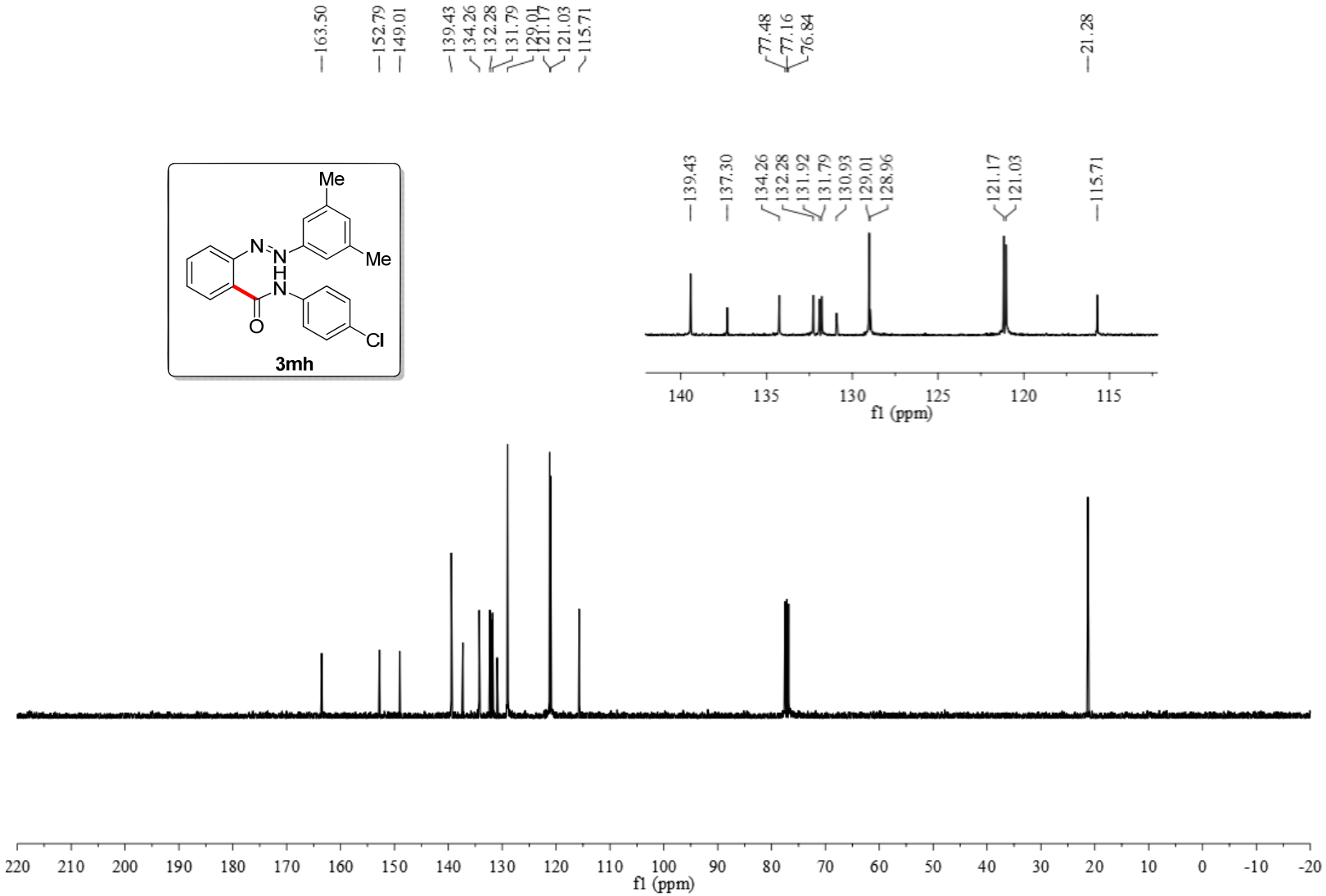
H
N
Me
O
Cl
3kh
fl (ppm)
fl (ppm)


10.702
8.328
8.320
8.308
7.754
7.742
7.735
7.525
7.514
7.504
7.487
7.467
7.202
7.182
6.951
2.351
2.327
Me
Me
Me
N
N
H
N
O
Cl
3lh
0.98
1.00
1.03
4.17
2.03
2.02
6.10
2.99
f1 (ppm)


163.90
149.28
149.12
140.25
137.12
132.04
131.64
131.39
131.28
130.33
128.93
128.90
121.31
115.42
77.48
77.16
76.84
21.24
19.11
Me
Me
Me
N
N
H
N
O
Cl
3lh
137.12
132.04
131.64
131.39
131.28
130.33
128.93
128.90
121.31
115.42
140
136
132
128
124
120
116
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


11.043
8.422
8.418
8.403
8.399
7.787
7.785
7.768
7.765
7.651
7.629
7.622
7.581
7.566
7.563
7.548
7.542
7.536
7.522
7.518
7.503
7.500
7.441
7.275
7.268
7.246
7.239
7.173
2.389
Me
Me
N
N
H
N
O
Cl
3mh
0.98
1.00
1.03
2.07
2.20
2.01
2.11
1.00
6.07
f1 (ppm)


163.50
152.79
149.01
139.43
134.26
132.28
131.79
129.01
121.17
121.03
115.71
77.48
77.16
76.84
21.28
Me
Me
N
N
H
N
O
Cl
3mh
139.43
137.30
134.26
132.28
131.92
131.79
130.93
129.01
128.96
121.17
121.03
115.71
140
135
130
125
120
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)