Supporting Information

for

Synergistic photocatalysis enables aerobic oxo-hydrazination of α-diazoacetates with azobenzenes

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1. General Information

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Varian Mercury-400 Plus or Agilent Technologies DD2 (600 MHz) spectrometers in $CDCl_3$ or DMSO-d_6. Chemical shifts (δ) for NMR were quoted in ppm relative to the solvent peak (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C in $CDCl_3$; 2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C in DMSO-d_6) or TMS (0.00 ppm for ^{1}H in $CDCl_3$). Coupling constants *J* are recorded in Hz. High-resolution mass spectra (HRMS) were reported from the Thermo Q Exactrive-Vanquish Core HPLC instrument (quadrupole; commom ion trap; spray voltage = 3800 V; capillary temperature = 270 °C; sheath gas flow rate = 5) with an ESI source. UV-visible absorption spectra were recorded on a SHIMADZU UV-2450 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA FluoroMax-4 spectrofluorometer. Cyclic voltammetry (CV) measurements were carried out on a CHI 660E electrochemical workstation by a standard three-electrode system. Melting points (m.p.) were measured on an XT4A apparatus (uncorrected). Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates (GF254). Flash column chromatography was performed on silica gel 60 (particle size 200–400 mesh ASTM, purchased from Liangchen, China) and eluted with petroleum ether/ethylacetate. α-Diazoacetates,[1] azobenzenes,[2] other diazo compounds (**S5**,[3] **S6**,[4] **S7**,[5] **S8**–**S9**,[6] **S11**[7] and **S12**[8]), and azocyclohexane (**S25**)[9] were prepared according to literature reported procedure. The other materials and solvents obtained from commercial suppliers were used directly without further purification.

The setup of the photochemical reaction is illustrated as Figure S1. The 16 W blue LED (440–450 nm) employed in this work were bought from Wuhan Jiushang Technology Co. LTD. The reaction vessels are 10 mL borosilicate glass tubes and are irradiated from side. The distance from the light source to the reaction tube is about 0.9 cm. The temperature is controlled by a fan.

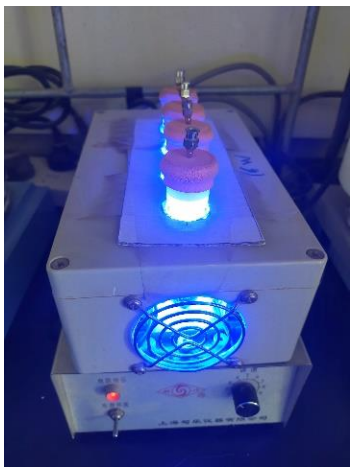
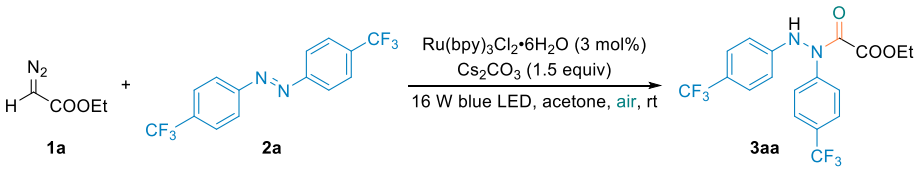


Figure S1. The reaction setup

2. Optimization of Reaction Conditions

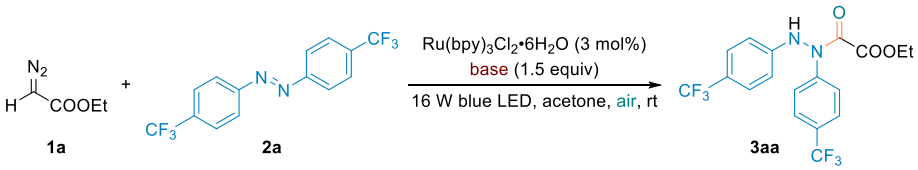
Table S1. Screening of amount ratio of **1a** to **2a**[a]



Entry	Mole ratio of **1a**:**2a**	Yield (%)[b]
1	2:1	12
2	3:1	53
3	4:1	69

[a]Reaction conditions: **1a** (x equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mol%), Cs_2CO_3 (1.5 equiv), acetone (3.0 mL), 16 W blue LED, air, rt, 24 h; [b]Isolated yield.

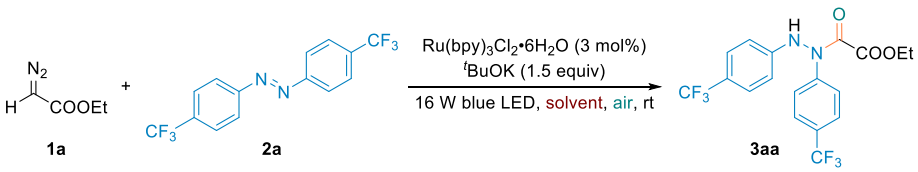
Table S2. Screening of base[a]



Entry	Base	Yield (%)[b]
1	Cs_2CO_3	69
2	$K_3PO_4{\cdot}3H_2O$	77
3	^tBuOK	84
4	NaOH	68
5	$NaHCO_3$	N.R.
6	DABCO	trace
7	Et_3N	trace

[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mol%), base (1.5 equiv), acetone (3.0 mL), 16 W blue LED, air, rt, 24 h; [b]Isolated yield. N.R. = No reaction occurred.

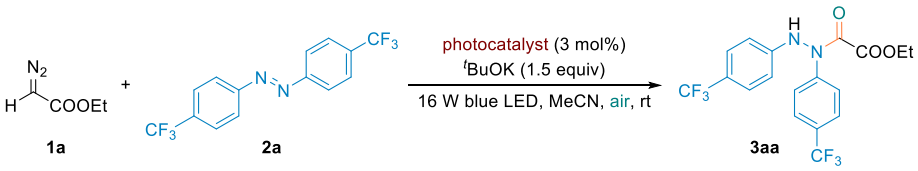
Table S3. Screening of solvent[a]



Entry	Solvent	Yield (%)[b]
1	acetone	84
2	EtOH	48
3	DCM	23
4	THF	trace
5	MeCN	86
6	DMSO	49
7	DMF	67
8	EtOAc	32
9	hexane	trace

[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mol%), ^{t}BuOK (1.5 equiv), solvent (3.0 mL), 16 W blue LED, air, rt, 24 h; [b]Isolated yield.

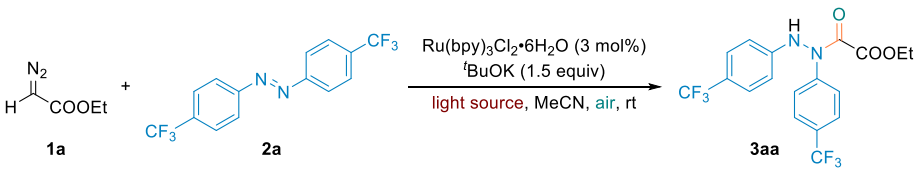
Table S4. Screening of photocatalyst[a]



Entry	Photocatalyst	Light source	Yield (%)[b]
1	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	16 W blue LED	86
2	Eosin Y	15 W green LED	trace
3	Methylene Blue	15 W green LED	trace
4	Rose Bengal	15 W green LED	19
5	$Ir(ppy)_2(dtbbpy)PF_6$	16 W blue LED	42
6	Mes-Acr$^+$ClO$_4^-$	16 W blue LED	trace
7	4CzIPN	16 W blue LED	21

[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), photocatalyst (3 mol%), ^{t}BuOK (1.5 equiv), MeCN (3.0 mL), air, rt, 24 h; [b]Isolated yield.

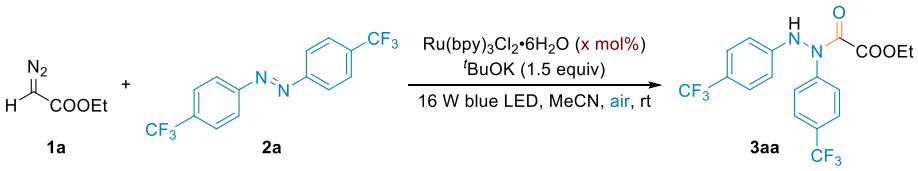
Table S5. Screening of light source[a]



Entry	Light source	Yield (%)[b]
1	16 W blue LED	86
2	30 W blue LED	87
3	6 W blue LED	78
4	6 W white LED	85
5	15 W green LED	11
6	20 W violet LED	50

[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mol%), ^{t}BuOK (1.5 equiv), MeCN (3.0 mL), light source, air, rt, 24 h; [b]Isolated yield.

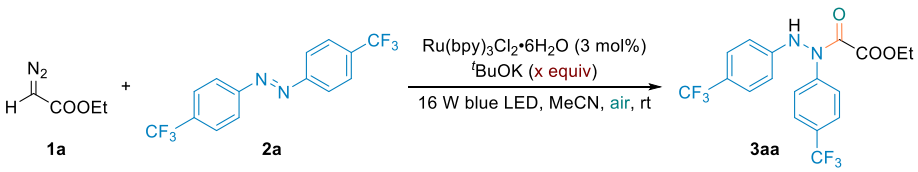
Table S6. Screening of the amount of photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$[a]



Entry	$Ru(bpy)_3Cl_2{\cdot}6H_2O$ (relative to **2a**)	Yield (%)[b]
1	3 mol%	86
2	2 mol%	69
3	4 mol%	84

[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (x mol%), ^{t}BuOK (1.5 equiv), MeCN (3.0 mL), 16 W blue LED, air, rt, 24 h; [b]Isolated yield.

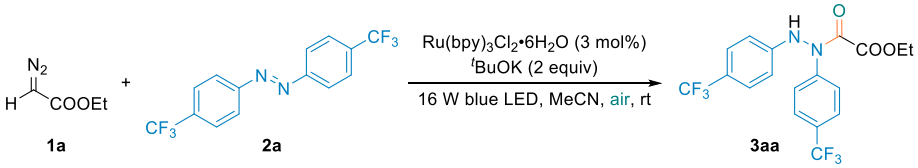
Table S7. Screening the amount of base ^{t}BuOK[a]



Entry	^{t}BuOK (x equiv relative to **2a**)	Yield (%)[b]
1	1.5	86
2	1.0	67
3	2.0	91

[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mol%), ^{t}BuOK (x equiv), MeCN (3.0 mL), 16 W blue LED, air, rt, 24 h; [b]Isolated yield.

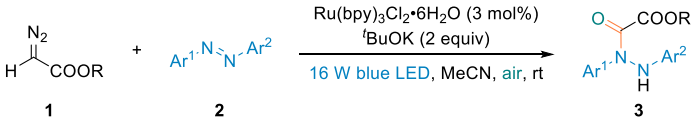
Table S8. Control experiments[a]



Entry	Deviation from the standard condition	Yield (%)[b]
1	none	91
2	no photocatalyst	trace
3	no ^{t}BuOK	trace
4	in the dark	N.R.
5	under Ar	N.D.
6	O_2 instead of air	63
7	in dry MeCN, O_2	64

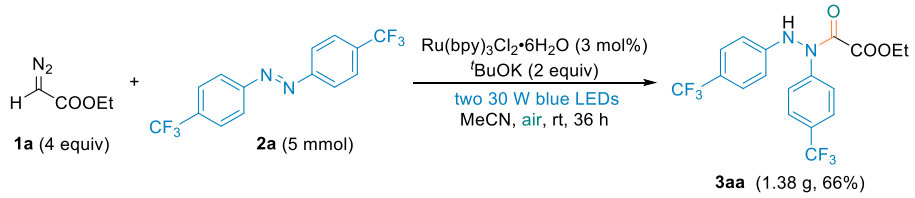
[a]Reaction conditions: **1a** (0.4 mmol, 4 equiv), **2a** (0.1 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mol%), ^{t}BuOK (2 equiv), MeCN (3.0 mL), 16 W blue LED, air, rt, 24 h; [b]Isolated yield. N.R. = No reaction occurred. N.D. = No product detected.

3. General Procedure for Synthesis of 3



α-Diazoacetates **1** (0.4 mmol, 4.0 equiv), azobnezenes **2** (0.1 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 0.003 mmol, 3 mol%), ^{t}BuOK (22.4 mg, 0.2 mmol, 2.0 equiv), and MeCN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue LED irradiation and air atmosphere at room temperature. After the completion of reaction (monitored by TLC), the reaction mixture was extracted with saturated NaCl aqueous and ethyl acetate. The organic phase was combined and concentrated under vacuum. The residue was purified by column chromatography (gradient elution with petrol ether/EtOAc = 30:1 to 5:1) to afford the pure product **3**.

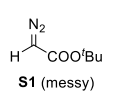
4. Procedure for Gram-Scale Synthesis of 3aa



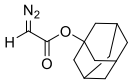
Ethyl α-diazoacetate **1a** (2.28 g, 20 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (1.59 g, 5 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (112.3 mg, 0.15 mmol, 3 mol%), ^{t}BuOK (1.12 g, 10 mmol, 2.0 equiv), and MeCN (50 mL) were added into a 100 mL Schlenk reaction flask. The reaction mixture was continually stirred under two 30 W blue LED bulbs irradiation and air atmosphere at room temperature. After the completion of reaction (36 h, monitored by TLC), the reaction mixture was extracted with saturated NaCl aqueous and ethyl acetate. The organic phase was combined and concentrated under vacuum. The residue was purified by column chromatography (gradient elution with petrol ether/EtOAc = 30:1 to 5:1) to afford the pure product **3aa** (1.378 g, 66%).

5. Unsuccessful Substrates

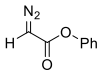
α-Diazoacetate:



S1 (messy)



S2 (messy)



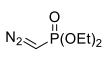
S3 (N.D.)

Other diazo compounds:

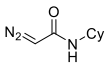
S4 (trace)

S5 (N.R.)

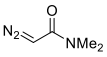
S6 (messy)



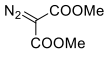
S7 (trace)



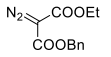
S8 (trace)



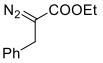
S9 (trace)



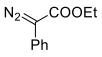
S10 (N.R.)



S11 (trace)

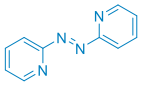


S12 (messy)



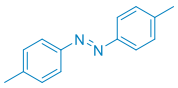
S13 (messy)

Heterocycle azoarene:

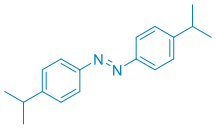


S14 (messy)

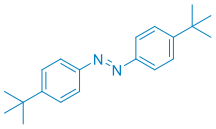
Symmetrical azobenzenes:



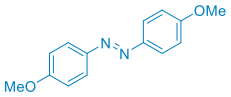
S15 (trace)



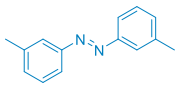
S16 (N.D.)



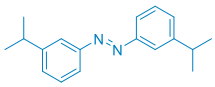
S17 (N.D.)



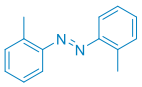
S18 (trace)



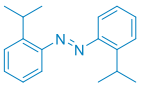
S19 (trace)



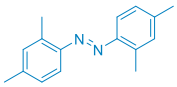
S20 (N.D.)



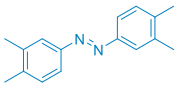
S21 (trace)



S22 (N.D.)

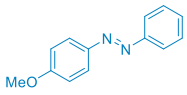


S23 (N.D.)



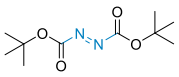
S24 (N.D.)

Unsymmetrical azobenzenes:

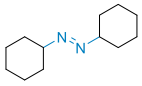


S25 (trace)

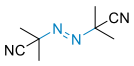
Non-aromatic azo compounds:



S26 (N.D.)



S27 (N.R.)



S28 (N.R.)

Note: N.D. = Not detected (with trace amounts of hydroazo byproducts); N.R. = No reaction occurred.

6. Mechanistic Studies

6.1 UV-Visible Absorption Spectra

The UV-visible absorption spectra of the ethyl α-diazoacetate **1a**, bis(*p*-trifluoromethyl) azobenzene **2a**, photocatalyst $Ru(bpy)_3Cl_2·6H_2O$, and their mixtures with different components in MeCN were determined respectively (Figure S2–S3). The results showed that the photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ and azobenzene **2a** have strong absorption and relatively weak absorption in the visible region, respectively, while the absorption of α-diazoacetate **1a** is very weak and can only be observed at high concentration. In addition, mixing them did not induce obvious changing of the absorption.

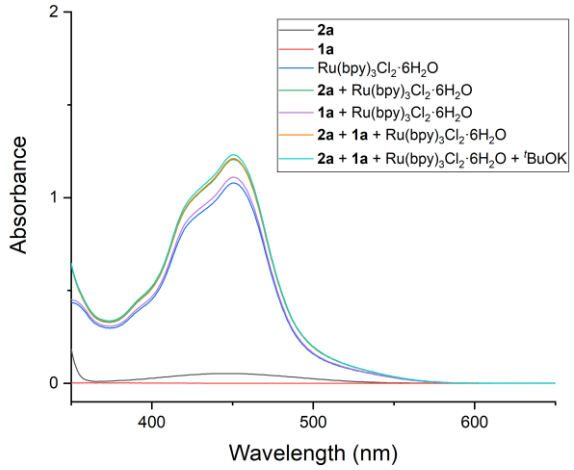


Figure S2. The UV-vis absorption spectra in MeCN (0.1 mM)

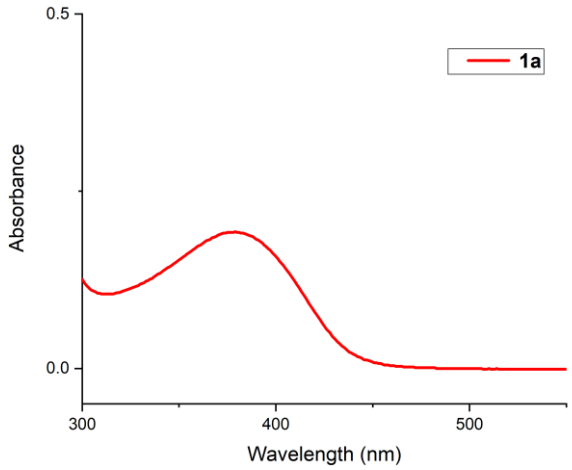


Figure S3. The UV-vis absorption spectrum of **1a** in MeCN (10 mM)

6.2 Fluorescence Quenching Experiments

The fluorescence quenching experiments were run with freshly prepared solutions of 1.0 $\times 10^{-5}$ M $Ru(bpy)_3Cl_2 \cdot 6H_2O$ and the appropriate amount of quencher in MeCN at room temperature. The solutions were irradiated at 453 nm. Then, appropriate amount of ethyl α-diazoacetate **1a**, ^{t}BuOK, or bis(*p*-trifluoromethyl) azobenzene **2a** was added to the solution of photocatalyst [Ru], the emission spectra of the samples were collected and analyzed (Figures S4–S9). The results showed that the excited state photocatalyst can be quenched by **1a**, **2a** or molecular oxygen respectively, but with different quenching effect.

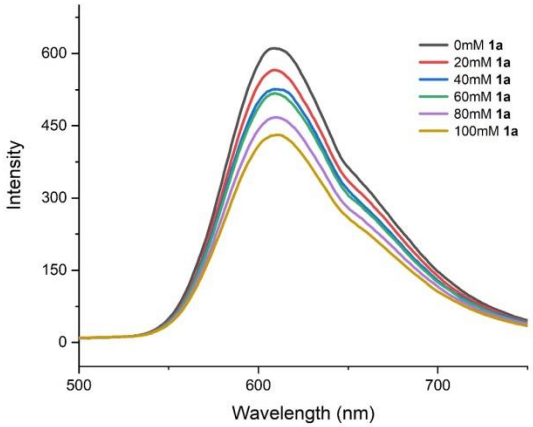


Figure S4. Fluorescence quenching of photocatalyst [Ru]* with **1a** (λ_{ex} = 453 nm)

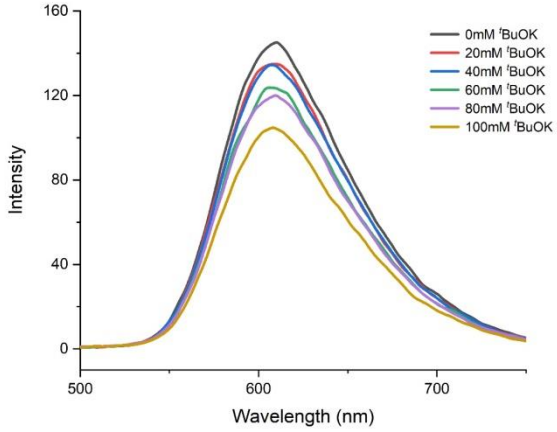


Figure S5. Fluorescence quenching of photocatalyst [Ru]* with ^{t}BuOK (λ_{ex} = 453 nm)

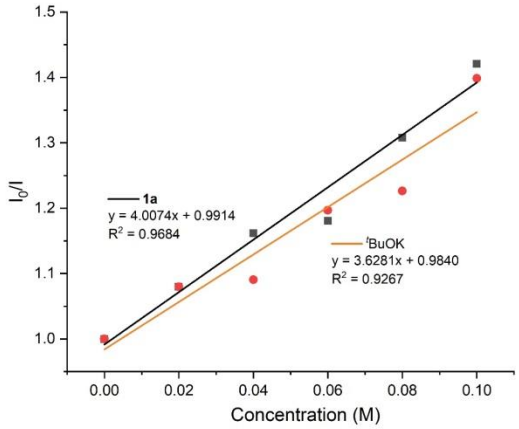


Figure S6. Stern-Volmer analysis (quenching Ru* with **1a** or ^{t}BuOK)

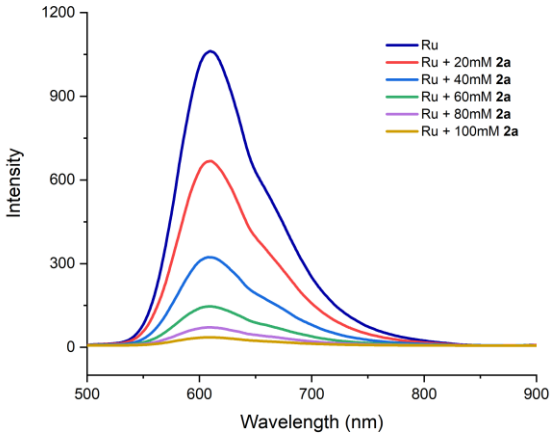


Figure S7. Fluorescence quenching of photocatalyst [Ru]* with **2a** (λ_{ex} = 453 nm)

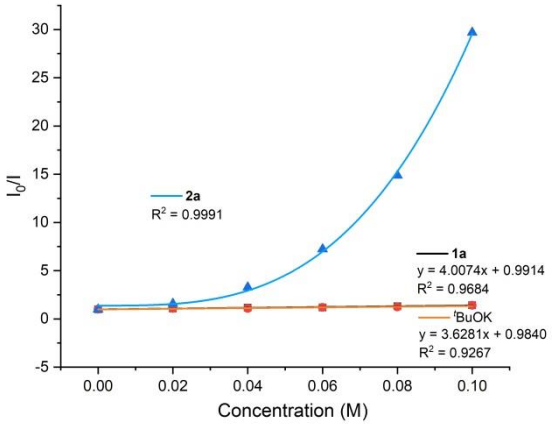


Figure S8. Stern-Volmer analysis (quenching Ru* with **1a**, ^{t}BuOK, or **2a**)

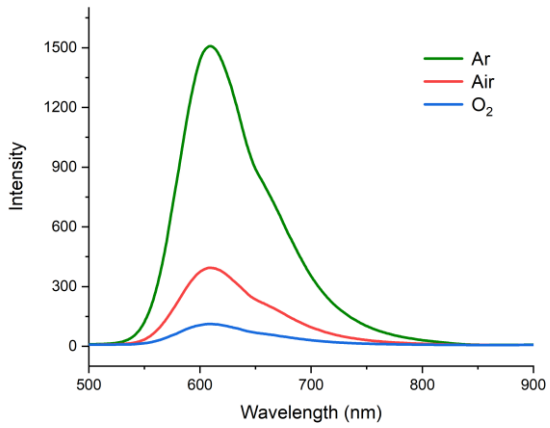


Figure S9. Fluorescence quenching of photocatalyst [Ru]* with molecular oxygen (λ_{ex} = 453 nm)

6.3 Cyclic Voltammetry (CV) Measurements

The cyclic voltammograms (Figure S10) were recorded in an electrolyte of $^{n}Bu_4NPF_6$ (0.1 M) in MeCN at room temperature under argon [scan rate: 50 mV/s; working electrode: glassy carbon (diameter, 5 mm); counter electrode: Pt wire; reference electrode: Ag/AgCl (saturated aq. KCl solution)]. The glassy carbon electrode was polished with figure-eight motions on a cloth polishing pad in a water-alumina slurry. The solvent and solutions were deoxygenated by sparging with argon.

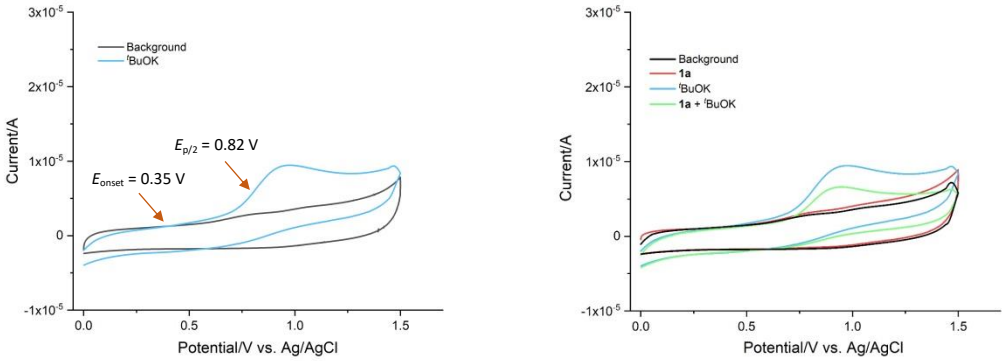
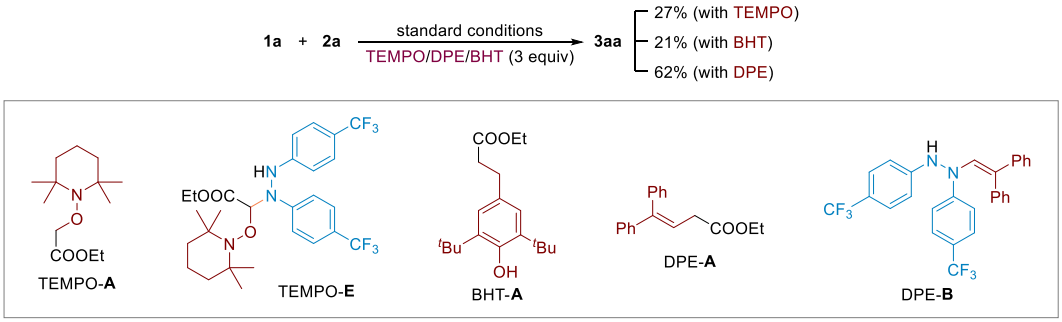


Figure S10. CV (IUPAC) for measurement of oxidant potentials of ^{t}BuOK and **1a** (1 mM in MeCN)

6.4 Control Experiments

1) Radical-inhibiting experiments



α-Diazoacetate **1a** (45.6 mg, 0.4 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (31.8 mg, 0.1 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 3 mol%), ^tBuOK (22.4 mg, 0.2 mmol, 2.0 equiv), TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv) or BHT (66.1 mg, 0.3 mmol, 3.0 equiv) or DPE (54.1 mg, 0.3 mmol, 3.0 equiv), and MeCN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue LED irradiation and air atmosphere at room temperature for 24 h. The reaction mixture was extracted with saturated NaCl aqueous and ethyl acetate. The organic phase was combined and concentrated under vacuum. A small portion of the sample was dipped by capillary tube for HRMS analysis, and the TEMPO-, BHT- or DPE-trapped radical species were detected (Figures S11–S13, data of $[M+H]^+$ are shown). The residue was purified by column chromatography (gradient elution with petrol ether/EtOAc = 30:1 to 5:1) to calculate the yield of **3aa**.

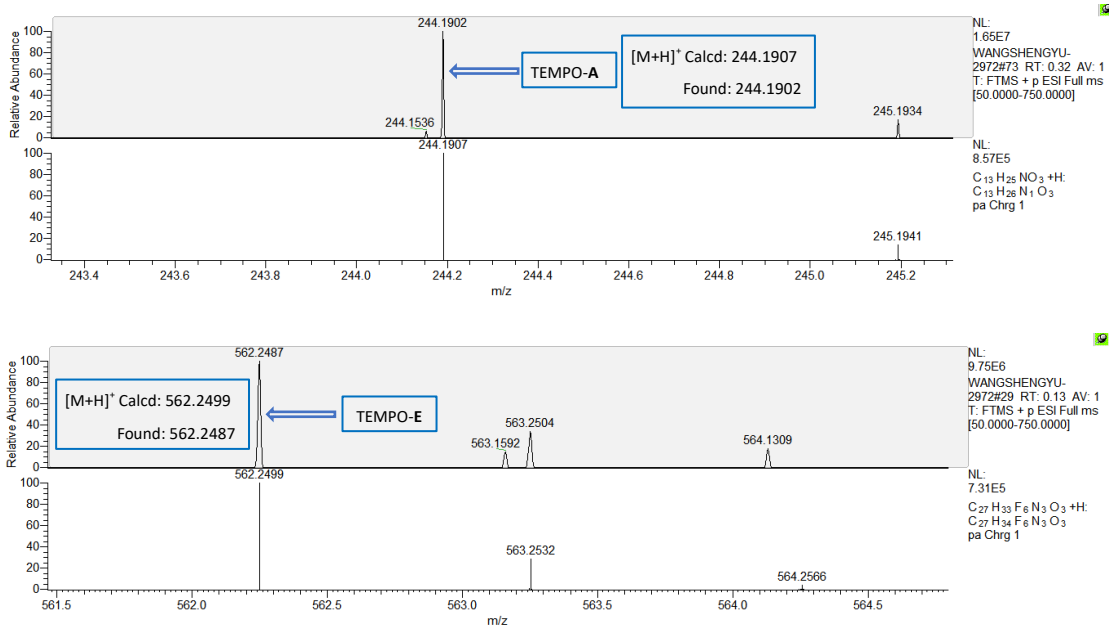


Figure S11. TEMPO-trapped radical species detected by HRMS

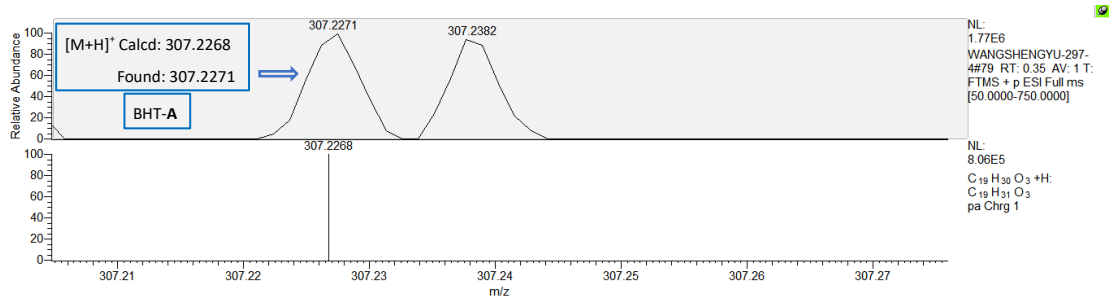


Figure S12. BHT-trapped radical species detected by HRMS

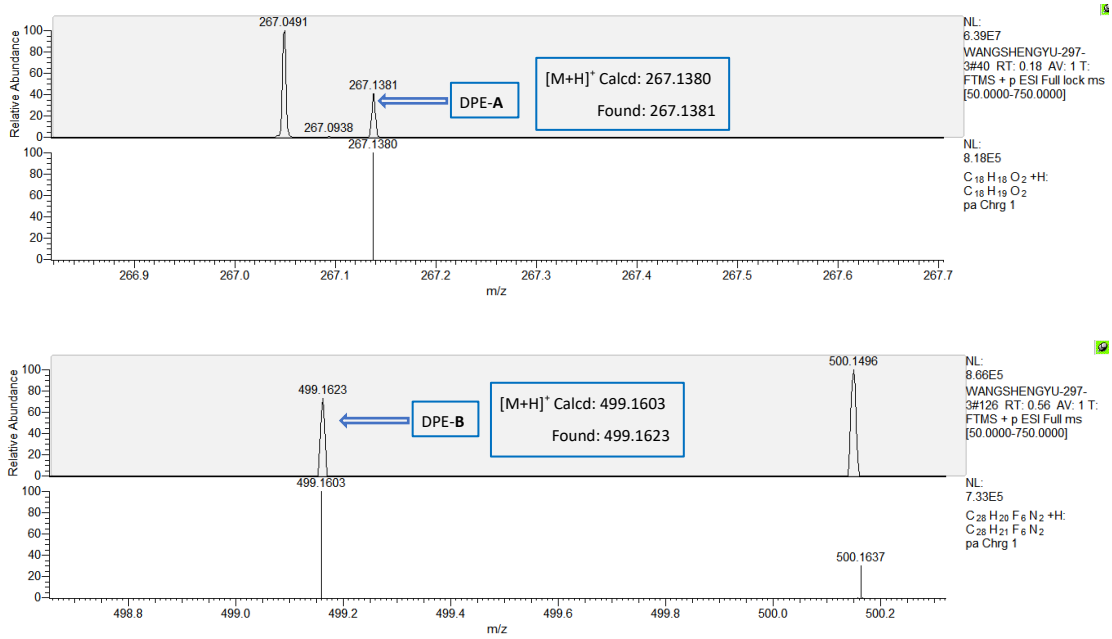
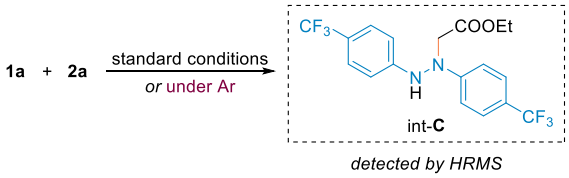


Figure S13. DPE-trapped radical species detected by HRMS

2) Detection of intermediate C by HRMS



α-Diazoacetate **1a** (45.6 mg, 0.4 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (31.8 mg, 0.1 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 3 mol%), ^tBuOK (22.4 mg, 0.2 mmol, 2.0 equiv), and MeCN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue LED irradiation and air/argon atmosphere at room temperature for 10 h. Intermediate **C** was detected by HRMS analysis in the reaction mixture without any treatment (Figure S14, data of $[M+H]^+$ is shown).

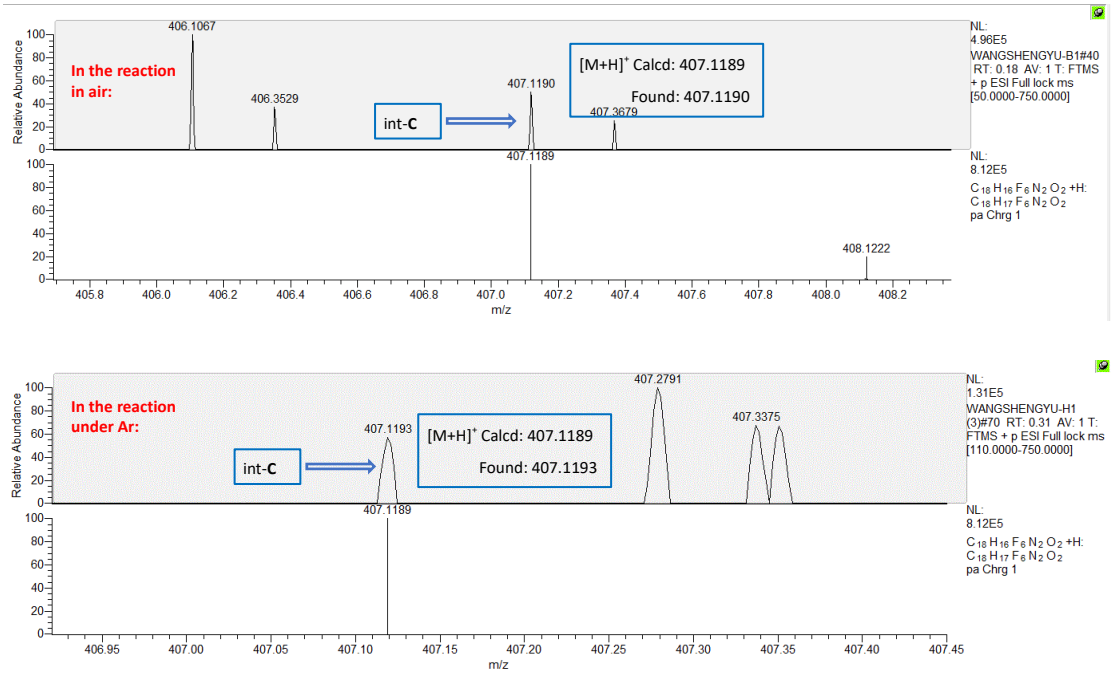
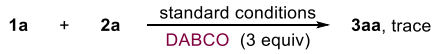


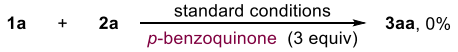
Figure S14. Intermediate **C** detected by HRMS

3) Singlet oxygen inhibiting with DABCO



α-Diazoacetate **1a** (45.6 mg, 0.4 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (31.8 mg, 0.1 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 3 mol%), ^tBuOK (22.4 mg, 0.2 mmol, 2.0 equiv), DABCO (33.7 mg, 0.3 mmol, 3.0 equiv), and MeCN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue LED irradiation and air atmosphere at room temperature for 24 h. The reaction was completely inhibited and only trace amount of **3aa** was observed (detected by TLC).

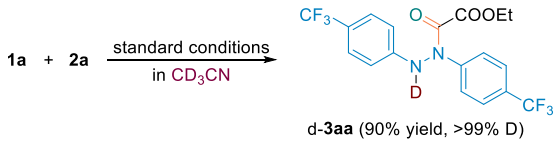
4) Superoxide radical anion inhibiting with *p*-benzoquinone



α-Diazoacetate **1a** (45.6 mg, 0.4 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (31.8 mg, 0.1 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 3 mol%), ^tBuOK (22.4 mg, 0.2 mmol, 2.0 equiv), *p*-benzoquinone (32.4 mg, 0.3 mmol, 3.0 equiv), and MeCN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue

LED irradiation and air atmosphere at room temperature for 24 h. The reaction was completely inhibited and no **3aa** was detected by TLC.

5) Deuteration experiment



d-**3aa** (90% yield, >99% D)

α-Diazoacetate **1a** (45.6 mg, 0.4 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (31.8 mg, 0.1 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 3 mol%), ^tBuOK (22.4 mg, 0.2 mmol, 2.0 equiv), and CD_3CN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue LED irradiation and air atmosphere at room temperature. After the completion of reaction (monitored by TLC), the reaction mixture was directly concentrated under vacuum to remove solvent. The residue was dissolved by $CDCl_3$ and the liquid was collected after filtration for ^1H NMR analysis. The crude product was recovered, concentrated under vacuum, and purified by column chromatography (gradient elution with petrol ether/EtOAc = 30:1 to 5:1) to obtain the pure d-**3aa** (90% yield). The deuterium incorporation ratio was calculated by comparing ^1H NMR spectra of **3aa** and crude d-**3aa** (Figure S15 vs Figure S16).

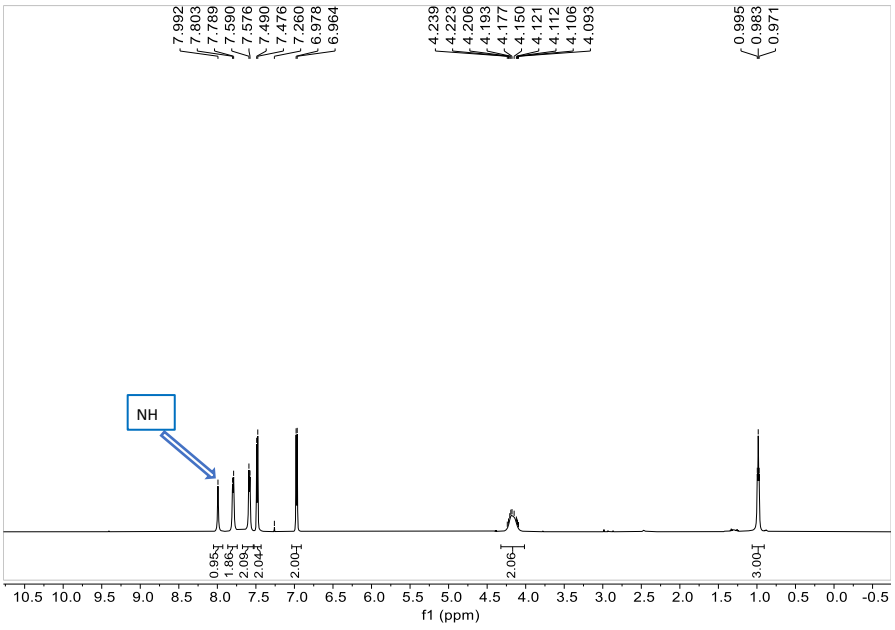


Figure S15. ^1H NMR spectra of **3aa**

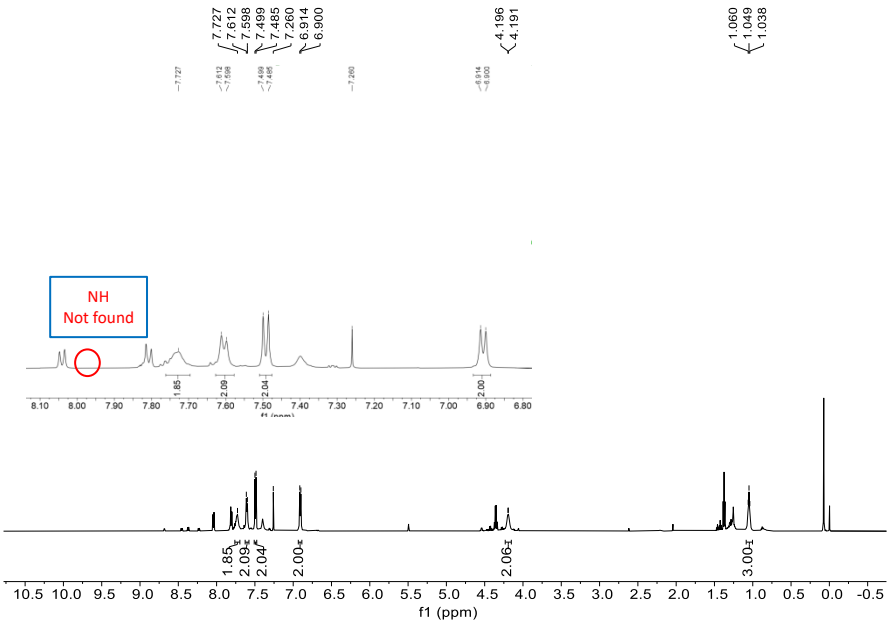


Figure S16. ^{1}H NMR spectra of crude d-**3aa**

6) Deuteration experiment

The photon flux was determined by standard ferrioxalate actinometry.[10] A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux, 2.0 mL of the ferrioxalate solution was placed in a reaction tube and irradiated and stirred for 90.0 seconds at λ = 436 nm blue LED. After irradiation, 0.35 mL of the phenanthroline solution was added to the tube. The solution was then stirred for 1 h in the dark to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A_{510\ nm}}{l \cdot \varepsilon} \qquad (1)$$

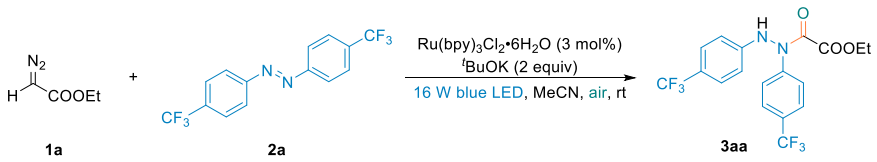
Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L·mol^{-1}·cm^{-1}). The mole of Fe^{2+} was 5.09 × 10^{-7} mol.

$$Photon\ flux = \frac{mol\ Fe^{2+}}{\Phi_{Fe^{2+}(436\ nm)} \cdot t \cdot f} \quad (2)$$

The photon flux can be calculated using eq 2. Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 436 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 436 nm (0.99833). The photon flux was calculated to be 5.70 × 10^{-9} einstein/s.

$$f = 1 - 10^{-A} \quad (3)$$

The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 436 nm. The absorbance of the above ferrioxalate solution at 436 nm was >3, indicating that f = 1.



α-Diazoacetate **1a** (45.6 mg, 0.4 mmol, 4.0 equiv), bis(*p*-trifluoromethyl) azobenzene **2a** (31.8 mg, 0.1 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2.2 mg, 3 mol%), ^{t}BuOK (22.4 mg, 0.2 mmol, 2.0 equiv) and MeCN (3.0 mL) were added into a 10 mL borosilicate glass reaction tube. The reaction mixture was continually stirred under 16 W blue LED irradiation and air atmosphere at room temperature for 1 h using the same setup as for the photon flux determination. The reaction was repeated three times. The final average isolated yield was 15%.

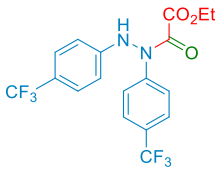
The quantum yield was determined using eq 4. Essentially all incident light ($f \approx 1$) is absorbed by the $Ru(bpy)_3Cl_2 \cdot 6H_2O$ at the reaction conditions described above.

$$\Phi = \frac{mol\ product}{photon\ flux \cdot t \cdot f} \quad (4)$$

$$\Phi = \frac{0.1 \times 15\% \times 10^{-3}}{5.70 \times 10^{-9} \times 3600 \times 1} = 0.73$$

7. Characterization Data of Products

1) Ethyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3aa）



Compound **3aa** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Yellow oil; yield: 38.2 mg (91%).

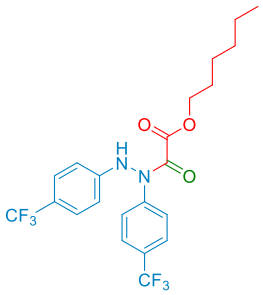
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.24–4.09 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.1, 163.2, 147.0, 141.8, 128.7 (q, *J* = 33.0 Hz), 126.9 (q, *J* = 3.0 Hz), 126.4 (d, *J* = 4.5 Hz), 124.3 (q, *J* = 270.0 Hz), 124.2 (q, *J* = 33.0 Hz), 123.7 (q, *J* = 270.0 Hz), 121.5, 113.6, 62.6, 13.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −61.902, −62.660.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}F_6N_2O_3^+$: 421.0981; found: 421.0982.

2) Hexyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ba）



Compound **3ba** was prepared according to the general procedure from hexyl 2-diazoacetate **1b** (68.1 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 43.4 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.4 Hz, 2H), 7.63–7.58 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H),

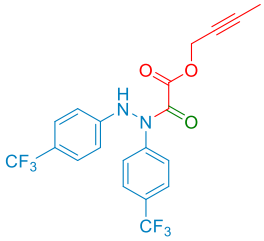
6.90 (d, *J* = 8.4 Hz, 2H), 4.09 (s, 2H), 1.33–1.06 (m, 8H), 0.81 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): *δ* = 163.8, 163.3, 146.9, 141.1, 128.9, 127.1 (d, *J* = 12.0 Hz), 126.6, 124.5 (q, *J* = 33.0 Hz), 124.2 (q, *J* = 270.0 Hz), 123.7 (q, *J* = 270.0 Hz), 121.2, 113.4, 66.8, 31.3, 28.2, 25.3, 22.4, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$): *δ* = −61.933, −62.669.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{23}F_6N_2O_3^+$: 477.1607; found: 477.1610.

3) But-2-yn-1-yl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ca）



Compound **3ca** was prepared according to the general procedure from but-2-yn-1-yl 2-diazoacetate **1c** (55.2 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 22.6 mg (51%).

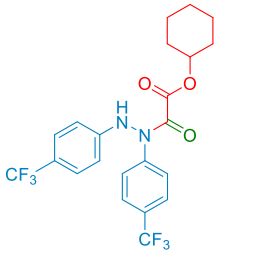
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.70 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 2H), 1.70 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): *δ* = 163.0 162.0, 146.7, 141.1, 127.1 (q, *J* = 4.5 Hz), 126.7, 125.0, 124.8, 124.2 (q, *J* = 270.0 Hz), 123.7 (q, *J* = 270.0 Hz), 121.1, 113.6, 84.9, 71.4, 54.4, 3.6.

^{19}F NMR (376 MHz, $CDCl_3$): *δ* = −61.915, −62.665.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{15}F_6N_2O_3^+$: 445.0981; found: 445.0985.

4) Cyclohexyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3da）



Compound **3da** was prepared according to the general procedure from cyclohexyl 2-diazoacetate **1d** (67.3 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg,

0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc =30:1 to 5:1).

White solid; yield: 33.6 mg (71%); m.p. 136–137 °C.

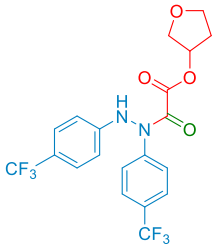
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.13 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 4.86–4.80 (m, 1H), 1.78–1.01 (m, 10H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 163.3, 161.7, 148.2, 141.3, 126.9 (d, J = 31.5 Hz), 126.6 (q, J = 4.5 Hz), 126.4 (q, J = 4.5 Hz), 124.5 (q, J = 270.0 Hz), 123.8 (q, J = 270.0 Hz), 121.9, 121.2 (q, J = 31.5 Hz), 113.2, 74.2, 30.6, 30.2, 24.6, 22.6, 22.4.

^{19}F NMR (376 MHz, DMSO-d_6): δ = −60.172, −61.094.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{21}F_6N_2O_3^+$: 475.1451; found: 475.1452.

5) Tetrahydrofuran-3-yl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ea）



Compound **3ea** was prepared according to the general procedure from tetrahydrofuran-3-yl 2-diazoacetate **1e** (62.4 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 41.2 mg (89%).

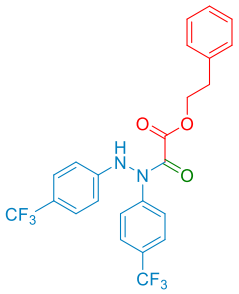
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.4 Hz, 2H), 7.62–7.58 (m, 3H), 7.49 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.38–5.34 (m, 1H), 3.83–3.47 (m, 4H), 2.21–1.59 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.3, 162.4, 146.7, 140.9, 128.9 (q, J = 33.0 Hz), 127.2 (q, J = 3.0 Hz), 126.6 (d, J = 3.0 Hz), 124.6 (q, J = 33.0 Hz), 124.1 (q, J = 270.0 Hz), 123.6 (q, J = 270.0 Hz), 121.0, 113.4, 72.4, 66.7, 32.4, 29.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −61.915, −62.651.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{17}F_6N_2O_4^+$: 463.1087; found: 463.1091.

6) Phenethyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3fa）



Compound **3fa** was prepared according to the general procedure from phenethyl 2-diazoacetate **1f** (76.1 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 39.7 mg (80%).

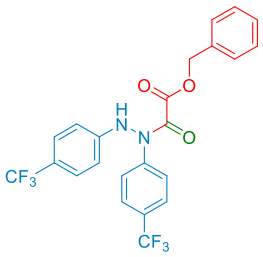
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.15 (s, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.26–7.11 (m, 5H), 6.99 (d, J = 8.4 Hz, 2H), 4.43–4.37 (m, 2H), 2.84–2.68 (m, 2H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 163.1, 162.2, 148.1, 141.2, 137.1, 128.6, 128.4, 126.8 (d, J = 31.5 Hz), 126.6 (q, J = 3.0 Hz), 126.5, 126.4 (d, J = 3.0 Hz), 124.5 (q, J = 270.0 Hz), 123.8 (q, J = 270.0 Hz), 122.1, 121.4 (q, J = 31.5 Hz), 113.5, 65.9, 33.9.

^{19}F NMR (376 MHz, DMSO-d_6): δ = −60.203, −61.153.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}F_6N_2O_3^+$: 497.1294; found: 497.1296.

7) Benzyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ga）



Compound **3ga** was prepared according to the general procedure from benzyl 2-diazoacetate **1g** (70.5 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

White solid; yield: 31.8 mg (66%); m.p. 139–141 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.15 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H),

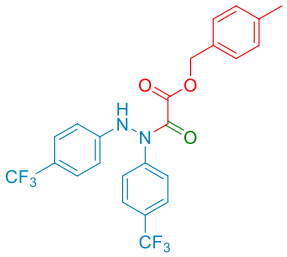
7.51 (d, *J* = 8.4 Hz, 2H), 7.31–7.21 (m, 3H), 7.12 (d, *J* = 6.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.26 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 163.0, 162.1, 148.0, 141.2, 134.5, 128.4, 128.3, 128.3, 126.8 (d, *J* = 31.5 Hz), 126.6 (q, *J* = 4.5 Hz), 126.5 (q, *J* = 4.5 Hz), 124.5 (q, *J* = 270.0 Hz), 123.8 (q, *J* = 270.0 Hz), 122.1, 121.3 (q, *J* = 31.5 Hz), 113.4, 67.1.

^{19}F NMR (376 MHz, DMSO-d_6): δ = −60.093, −61.074.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{17}F_6N_2O_3^+$: 483.1138; found: 483.1139.

8) 4-Methylbenzyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ha）



Compound **3ha** was prepared according to the general procedure from 4-methylbenzyl 2-diazoacetate **1h** (76.1 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

White solid; yield: 29.4 mg (59%); m.p. 177–178 °C.

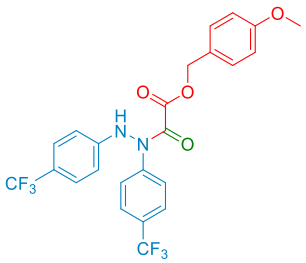
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.14 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.03–6.99 (m, 4H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 163.1, 162.2, 148.0, 141.2, 137.8, 131.4, 128.8, 128.6, 126.9 (d, *J* = 31.5 Hz), 126.5 (q, *J* = 3.0 Hz), 126.4 (q, *J* = 4.5 Hz), 124.6 (q, *J* = 270.0 Hz), 123.8 (q, *J* = 270.0 Hz), 122.1, 121.4 (q, *J* = 31.5 Hz), 113.4, 67.1, 20.6.

^{19}F NMR (376 MHz, DMSO-d_6): δ = −60.245, −61.220.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}F_6N_2O_3^+$: 497.1294; found: 497.1295.

9) 4-Methoxybenzyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ia）



Compound **3ia** was prepared according to the general procedure from 4-methoxybenzyl 2-diazoacetate **1i** (82.5 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 34.1 mg (67%).

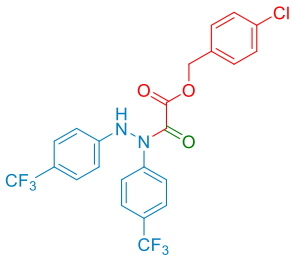
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.23–7.14 (m, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.75–6.67 (m, 4H), 5.12–5.10 (m, 2H), 3.77 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.5, 161.7, 159.2, 145.6, 140.1, 129.8, 127.8 (d, *J* = 33.0 Hz), 126.0 (d, *J* = 4.5 Hz), 125.6 (d, *J* = 1.5 Hz), 124.8, 123.3 (q, *J* = 270.0 Hz), 122.7 (q, *J* = 270.0 Hz), 123.4 (q, *J* = 34.5 Hz), 120.0, 113.0, 112.3, 67.1, 54.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −61.723, −62.616.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}F_6N_2O_4^+$: 513.1244; found: 513.1248.

10) 4-Chlorobenzyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ja）



Compound **3ja** was prepared according to the general procedure from 4-chlorobenzyl 2-diazoacetate **1j** (84.2 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

White solid; yield: 28.5 mg (55%); m.p. 186–187 °C.

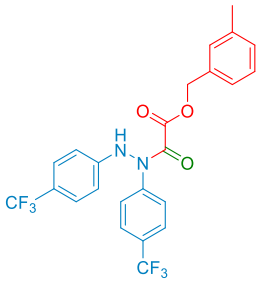
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.13 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.31 (d, *J* = 12.4 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 162.9, 162.0, 147.9, 141.1, 133.4, 133.2, 130.3, 128.2, 126.9 (d, J = 31.5 Hz), 126.5 (q, J = 4.5 Hz), 126.4 (q, J = 3.0 Hz), 124.5 (q, J = 270.0 Hz), 123.8 (q, J = 270.0 Hz), 122.1, 121.4 (q, J = 31.5 Hz), 113.4, 66.2.

^{19}F NMR (376 MHz, DMSO-d_6): δ = −60.204, −61.180.

HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{23}H_{16}ClF_6N_2O_3^+$: 517.0748; found: 517.0750.

11) 3-Methylbenzyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3ka）



Compound **3ka** was prepared according to the general procedure from 3-methylbenzyl 2-diazoacetate **1k** (76.1 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 40.6 mg (82%).

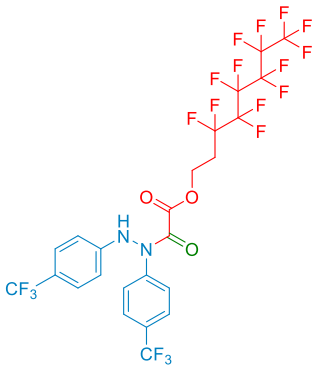
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 6.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.20 (s, 1H), 7.09 (d, J = 4.8 Hz, 2H), 6.90 (s, 1H), 6.82–6.77 (m, 3H), 5.11 (s, 2H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.2, 169.5, 151.7, 144.9 (d, J = 217.5 Hz), 139.4, 138.6, 133.0, 131.0 (d, J = 37.5 Hz), 130.5 (d, J = 36.0 Hz), 130.1 (d, J = 55.5 Hz), 130.0 (d, J = 27.0 Hz), 128.5 (d, J = 289.5 Hz), 126.7 (d, J = 33.0 Hz), 126.1 (d, J = 193.5 Hz), 123.1, 117.7 (d, J = 184.5 Hz), 112.0, 100.5, 68.2 (d, J = 151.1 Hz), 21.9 (d, J = 4.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = −61.832, −62.629.

HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{24}H_{19}F_6N_2O_3^+$: 497.1294; found: 497.1299.

12) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-(1,2-bis(4-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3la）



Compound **3la** was prepared according to the general procedure from 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-diazoacetate **1l** (172.8 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene **2a** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 67.6 mg (92%).

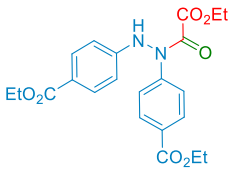
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.41 (s, 2H), 2.22–2.12 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2, 162.5, 146.5, 140.8, 129.2 (q, *J* = 33.0 Hz), 127.2 (q, *J* = 4.5 Hz), 126.7 (d, *J* = 1.5 Hz), 125.0 (q, *J* = 31.5 Hz), 124.1 (q, *J* = 270.0 Hz), 123.6 (q, *J* = 270.0 Hz), 121.2, 118.9 (t, *J* = 31.5 Hz), 118.3 (t, *J* = 33.0 Hz), 117.2 (t, *J* = 31.5 Hz), 116.4 (t, *J* = 33.8 Hz), 115.5 (t, *J* = 31.5 Hz), 114.5, 113.5, 58.0, 30.1 (t, *J* = 21.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.531, −63.056, −81.189 to −81.243, −114.119 to −114.297, −122.109 to −122.258, −123.116 to −123.221, −123.873 to −114.981, −126.431 to −126.529.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{14}F_{19}N_2O_3^+$: 739.0696; found: 739.0699.

13) Diethyl 4,4'-(1-(2-ethoxy-2-oxoacetyl)hydrazine-1,2-diyl)dibenzoate（3ab）



Compound **3ab** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and diethyl 4,4'-(diazene-1,2-diyl)(*E*)-dibenzoate **2b** (32.6 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Yellow oil; yield: 25.2 mg (59%).

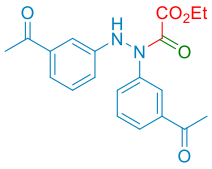
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04–7.93 (m, 3H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H),

6.84 (d, *J* = 8.4 Hz, 2H), 4.31–4.25 (m, 4H), 4.17–4.13 (m, 2H), 1.31 (q, *J* = 7.2 Hz, 6H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.3, 165.7, 163.7, 162.6, 148.3, 142.1, 131.3, 130.6, 128.2, 123.9, 120.6, 113.0, 62.2, 61.2, 60.8, 14.3, 14.2, 13.6.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_7^+$: 429.1656; found: 429.1657.

14) Ethyl 2-(2-(3-acetylphenyl)-1-(4-acetylphenyl)hydrazineyl)-2-oxoacetate（3ac）



Compound **3ac** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,1'-(diazene-1,2-diylbis(3,1-phenylene))bis(ethan-1-one) **2c** (26.6 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc =30:1 to 5:1).

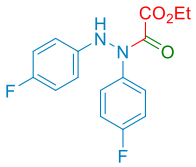
Yellow oil; yield: 12.3 mg (33%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.93 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.54 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.45–7.42 (m, 1H), 7.33–7.29 (m, 1H), 7.13–7.12 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.541 (s, 3H), 2.535 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.1, 197.6, 163.9, 163.0, 144.8, 138.6, 138.1, 138.0, 129.8, 129.5, 127.0, 126.8, 122.5, 121.5, 118.9, 113.7, 62.1, 26.74, 26.70, 13.8.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{21}N_2O_5^+$: 369.1445; found: 369.1444.

15) Ethyl 2-(1,2-bis(4-fluorophenyl)hydrazineyl)-2-oxoacetate（3ad）



Compound **3ad** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-fluorophenyl)diazene **2d** (21.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Yellow oil; yield: 10.4 mg (32%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.38 (m, 2H), 7.10–6.98 (m, 2H), 6.94–6.90 (m, 2H), 6.87 (s,

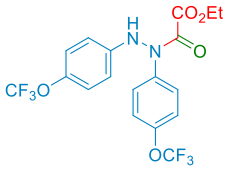
1H), 6.84–6.80 (m, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 163.5, 161.0 (d, *J* = 246.0 Hz), 158.6 (d, *J* = 238.5 Hz), 140.2, 134.0 (d, *J* = 3.0 Hz), 134.0 (d, *J* = 3.0 Hz), 116.23 (d, *J* = 19.5 Hz), 116.21 (d, *J* = 18.0 Hz), 116.17 (d, *J* = 16.5 Hz), 62.2, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −113.773 to −113.841, −121.197 to −121.265.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}F_2N_2O_3^+$: 321.1045; found: 321.1048.

16) Ethyl 2-(1,2-bis(4-(trifluoromethoxy)phenyl)hydrazineyl)-2-oxoacetate（3ae）



Compound **3ae** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(4-(trifluoromethoxy)phenyl)diazene **2e** (35.0 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 26.0 mg (58%).

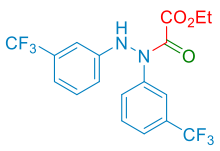
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.9, 163.4, 147.4, 144.1, 142.8, 136.5, 123.2, 122.5, 121.7, 120.6 (q, *J* = 255.0 Hz), 120.5 (q, *J* = 256.5 Hz), 115.0, 60.3, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −58.229, −58.548.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}F_6N_2O_5^+$: 453.0880; found: 453.0882.

17) Ethyl 2-(1,2-bis(3-(trifluoromethyl)phenyl)hydrazineyl)-2-oxoacetate（3af）



Compound **3af** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(3-(trifluoromethyl)phenyl)diazene **2f** (31.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Yellow oil; yield: 30.5 mg (73%).

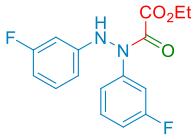
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.76 (s, 1H), 7.69–7.66 (m, 1H), 7.48–7.45 (m, 2H), 7.35–7.32 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.0, 163.2, 144.5, 138.6, 132.0 (q, *J* = 33.0 Hz), 131.9 (q, *J* = 33.0 Hz), 130.2, 130.0, 125.1, 123.9 (q, *J* = 271.5 Hz), 123.8, 123.6 (q, *J* = 271.5 Hz), 119.0 (d, *J* = 3.0 Hz), 118.9, 117.2, 110.9 (d, *J* = 4.5 Hz), 62.6, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.985, −63.085.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}F_6N_2O_3^+$: 421.0981; found: 421.0982.

18) Ethyl 2-(1,2-bis(3-fluorophenyl)hydrazineyl)-2-oxoacetate（3ag）



Compound **3ag** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(3-fluorophenyl)diazene **2g** (21.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 13.0 mg (41%).

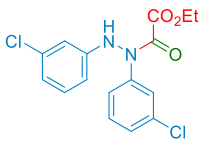
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 3H), 7.19–7.14 (m, 2H), 6.90–6.88 (m, 1H), 6.63–6.60 (m, 2H), 6.58–6.55 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.6, 163.4 (d, *J* = 150.0 Hz), 162.9, 162.88 (d, *J* = 246.0 Hz), 146.0 (d, *J* = 9.0 Hz), 139.7 (d, *J* = 9.0 Hz), 130.9 (d, *J* = 10.5 Hz), 130.5 (d, *J* = 9.0 Hz), 116.8, 113.8 (d, *J* = 21.0 Hz), 109.6 (d, *J* = 3.0 Hz), 109.2 (d, *J* = 27.0 Hz), 109.1 (d, *J* = 21.0 Hz), 101.6 (d, *J* = 25.5 Hz), 62.3, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −110.357 to −110.424, −111.342 to −111.409.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}F_2N_2O_3^+$: 321.1045; found: 321.1046.

19) Ethyl 2-(1,2-bis(3-chlorophenyl)hydrazineyl)-2-oxoacetate（3ah）



Compound **3ah** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(3-chlorophenyl)diazene **2h** (25.1 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

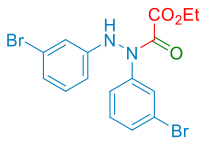
Colorless oil; yield: 25.3 mg (72%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.36–7.27 (m, 1H), 7.25–7.22 (m, 1H), 7.15–7.10 (m, 2H), 6.89–6.87 (m, 1H), 6.84 (s, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 163.1, 145.3, 139.1, 135.2, 134.9, 130.6, 130.2, 127.1, 122.3, 121.9, 119.7, 114.2, 112.3, 62.4, 13.7.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}Cl_2N_2O_3^+$: 353.0454; found: 353.0455.

20) Ethyl 2-(1,2-bis(3-chlorophenyl)hydrazineyl)-2-oxoacetate（3ai）



Compound **3ai** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(3-bromophenyl)diazene **2i** (34.0 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

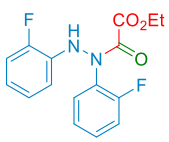
Colorless oil; yield: 22.8 mg (52%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.31–7.15 (m, 3H), 7.08–7.02 (m, 2H), 7.00 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.7, 163.0, 145.4, 139.2, 130.8, 130.5, 130.0, 125.3, 124.8, 123.2, 122.8, 120.2, 117.1, 112.7, 62.4, 13.7.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}Br_2N_2O_3^+$: 442.9423; found: 442.9424.

21) Ethyl 2-(1,2-bis(2-fluorophenyl)hydrazineyl)-2-oxoacetate（3aj）



Compound **3aj** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(2-fluorophenyl)diazene **2j** (21.8 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

Colorless oil; yield: 17.8 mg (56%).

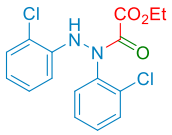
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (t, *J* = 7.8 Hz, 1H), 7.27–7.23 (m, 2H), 7.13–7.10 (m, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.96–6.93 (m, 1H), 6.88–6.84 (m, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 162.9, 157.3 (d, *J* = 250.5 Hz), 151.8 (d, *J* = 240.0 Hz), 131.9 (d, *J* = 10.5 Hz), 130.4 (d, *J* = 7.5 Hz), 128.0, 124.7 (d, *J* = 3.0 Hz), 123.1 (d, *J* = 7.5 Hz), 117.4, 116.9 (d, *J* = 19.5 Hz), 115.3 (d, *J* = 19.5 Hz), 62.1, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −119.282 to −119.347, −134.667 to −134.729.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}F_2N_2O_3^+$: 321.1045; found: 321.1046.

22) Ethyl 2-(1,2-bis(2-chlorophenyl)hydrazineyl)-2-oxoacetatel（3ak）



Compound **3ak** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(2-chlorophenyl)diazene **2k** (25.1 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

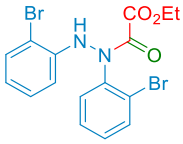
Colorless oil; yield: 22.6 mg (64%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51–7.50 (m, 1H), 7.44–7.38 (m, 3H), 7.26–7.18 (m, 4H), 6.88–6.84 (m, 1H), 4.34–4.30 (m, 2H), 1.23–1.21 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.1, 162.8, 140.0, 134.5, 131.2, 130.8, 130.5, 129.8, 129.5, 127.8, 127.6, 123.2, 120.6, 117.1, 62.1, 13.8.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}Cl_2N_2O_3^+$: 353.0454; found: 353.0455.

23) Ethyl 2-(1,2-bis(2-bromophenyl)hydrazineyl)-2-oxoacetate（3al）



Compound **3al** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-bis(2-bromophenyl)diazene **2l** (34.0 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

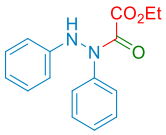
Colorless oil; yield: 22.9 mg (52%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62–7.60 (m, 1H), 7.54 (s, 1H), 7.40–7.34 (m, 3H), 7.29–7.24 (m, 2H), 7.18–7.15 (m, 1H), 6.82–6.79 (m, 1H), 4.32 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.1, 162.8, 141.0, 136.1, 134.0, 132.7, 130.9, 130.4, 128.4, 128.2, 123.7, 121.1, 117.4, 110.2, 62.1, 13.9.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}Br_2N_2O_3^+$: 442.9423; found: 442.9424.

24) Ethyl 2-(1,2-diphenylhydrazineyl)-2-oxoacetate（3am）



Compound **3am** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1,2-diphenyldiazene **2m** (18.2 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

White solid; yield: 5.5 mg (19%); m.p. 136–137 °C.

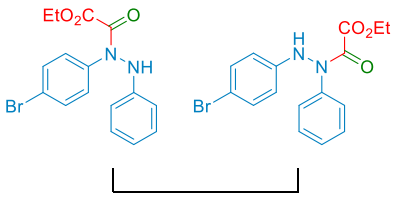
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.47 (s, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.41–7.37 (m, 2H), 7.23–7.15 (m, 3H), 6.82–6.79 (m, 3H), 4.27–4.11 (m, 2H), 1.05 (t, J = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 163.3, 163.0, 144.9, 137.8, 129.0, 128.9, 126.6, 122.5, 120.9, 113.9, 61.2, 14.2.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{17}N_2O_3^+$: 285.1234; found: 285.1233.

25) Ethyl 2-(1-(4-bromophenyl)-2-phenylhydrazineyl)-2-oxoacetate &

Ethyl 2-(2-(4-bromophenyl)-1-phenylhydrazineyl)-2-oxoacetate（3an）



Compound **3an** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1-(4-bromophenyl)-2-phenyldiazene **2n** (26.1 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

3an-1:

Colorless oil; yield: 7.7 mg (21%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.23–7.20 (m, 2H), 6.99 (s, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.9, 163.2, 144.0, 137.4, 132.2, 129.5, 123.3, 122.4, 120.0, 114.3, 62.1, 13.7.

And

3an-2:

Colorless oil; yield: 4.2 mg (12%).

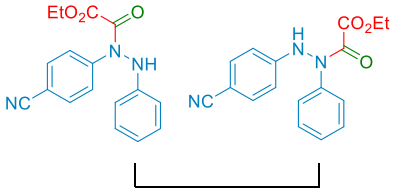
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.4 Hz, 2H), 7.41–7.29 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 163.4, 143.5, 138.0, 132.3, 129.3, 127.1, 122.0, 116.1, 114.5, 62.1, 13.9.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{16}BrN_2O_3^+$: 363.0339; found: 363.0338.

26) Ethyl 2-(1-(4-cyanophenyl)-2-phenylhydrazineyl)-2-oxoacetate &

Ethyl 2-(2-(4-cyanophenyl)-1-phenylhydrazineyl)-2-oxoacetate（3ao）



Compound **3ao** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-4-(phenyldiazenyl)benzonitrile **2o** (20.7 mg, 0.1 mmol) and

purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

3ao-1:

Yellow oil; yield: 15.5 mg (50%).

1H NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.23–7.20 (m, 3H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.0, 162.6, 143.7, 142.5, 133.2, 129.6, 122.5, 121.3, 118.3, 113.8, 109.5, 62.3, 13.6.

And

3ao-2:

Yellow oil; yield: 4.6 mg (15%).

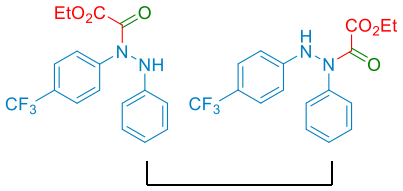
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82–7.77 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.21–4.11 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.5, 163.0, 148.4, 137.8, 133.7, 129.3, 127.2, 121.7, 119.2, 113.9, 104.4, 62.2, 13.7.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}N_3O_3^+$: 310.1186; found: 310.1172

27) Ethyl 2-oxo-2-(1-phenyl-2-(4-(trifluoromethyl)phenyl)hydrazineyl)acetate &

Ethyl 2-oxo-2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)hydrazineyl)acetate （3ap）



Compound **3ap** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene **2p** (25.0 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

3ap-1:

Yellow oil; yield: 11.2 mg (32%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 6.3 (m, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.03 (t, *J* =

7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.2, 163.1, 143.9, 141.4, 129.5, 128.2 (q, J = 31.5 Hz), 126.3 (d, J = 4.5 Hz), 123.7 (q, J = 271.5 Hz), 122.4, 121.3, 114.0, 62.2, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.560.

And

3ap-2:

Yellow oil; yield: 9.5 mg (27%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.42 (s, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 4.20–4.15 (m, 2H), 1.03 (t, J = 7.2 Hz, 3H).

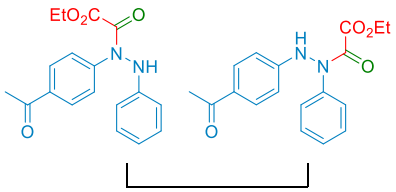
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.7, 163.3, 147.4, 138.0, 129.4, 127.1, 126.8 (q, J = 4.5 Hz), 124.7 (d, J = 166.5 Hz), 123.7 (d, J = 70.5 Hz), 121.8, 113.7, 62.3, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.771.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}F_3N_2O_3^+$: 353.1108; found: 353.1107.

28) Ethyl 2-(1-(4-acetylphenyl)-2-phenylhydrazineyl)-2-oxoacetate &

Ethyl 2-(2-(4-acetylphenyl)-1-phenylhydrazineyl)-2-oxoacetate（3aq）



Compound **3aq** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and (*E*)-1-(4-(phenyldiazenyl)phenyl)ethan-1-one **2q** (22.4 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

3aq-1:

Yellow oil; yield: 11.7 mg (36%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.41–7.30 (m, 1H), 7.18 (t, J = 7.8 Hz, 2H), 6.88 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.1, 164.0, 162.8, 144.0, 142.5, 134.5, 129.4, 122.2, 120.8, 114.0, 62.0, 26.5, 13.6.

And

3aq-2:

Yellow oil; yield: 5.3 mg (16%).

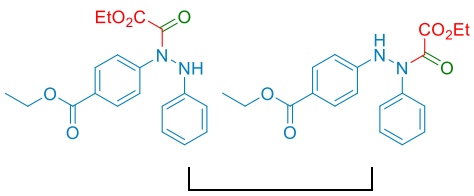
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86–7.82 (m, 3H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 4.17–4.13 (m, 2H), 2.48 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.0, 163.5, 163.0, 148.9, 138.0, 131.0, 130.3, 129.2, 126.9, 121.6, 113.2, 62.0, 26.3, 13.7.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}N_2O_4^+$: 327.1339; found: 327.1340.

29) Ethyl 4-(1-(2-ethoxy-2-oxoacetyl)-2-phenylhydrazineyl)benzoate &

Ethyl 4-(2-(2-ethoxy-2-oxoacetyl)-2-phenylhydrazineyl)benzoate（3ar）



Compound **3ar** was prepared according to the general procedure from ethyl diazoacetate **1a** (45.6 mg, 0.4 mmol, 4 equiv) and ethyl (*E*)-4-(phenyldiazenyl)benzoate **2r** (25.4 mg, 0.1 mmol) and purified by column chromatography on silica gel (gradient elution with petrol ether/EtOAc = 30:1 to 5:1).

3ar-1:

Yellow oil; yield: 11.1 mg (31%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.7, 164.0, 162.9, 144.0, 142.2, 130.5, 129.3, 127.9, 122.1, 120.7, 114.0, 62.0, 61.1, 14.2, 13.6.

And

3ar-2:

Yellow oil; yield: 8.6 mg (24%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.18–4.16

(m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.4, 163.6, 163.2, 148.6, 138.2, 131.4, 129.3, 127.0, 124.0, 121.7, 113.3, 62.1, 60.8, 14.4, 13.8.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_5^+$: 357.1445; found: 357.1446.

8. References

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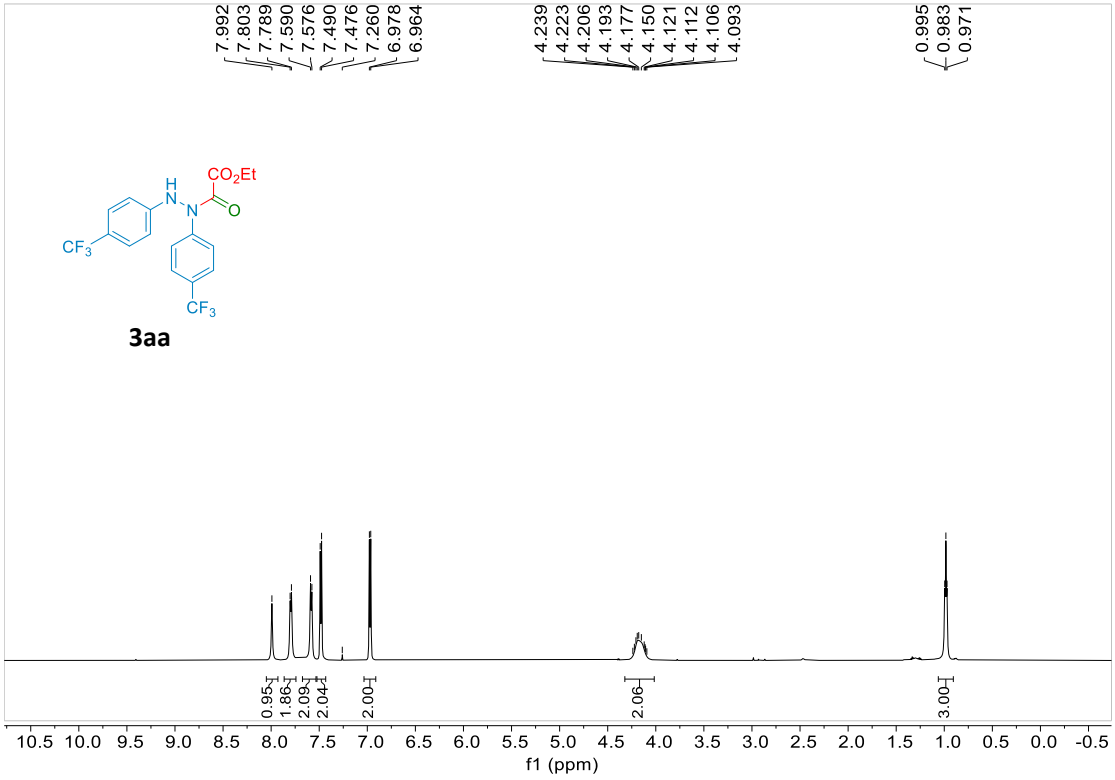
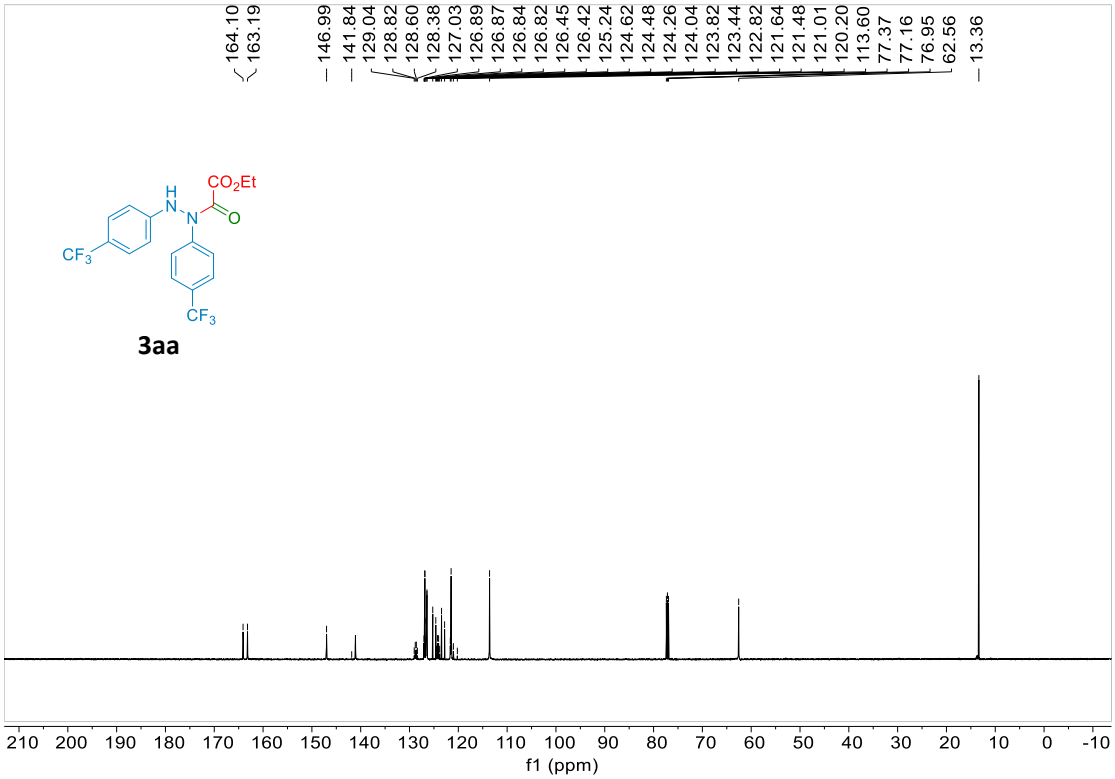
9. Copies of NMR Spectra

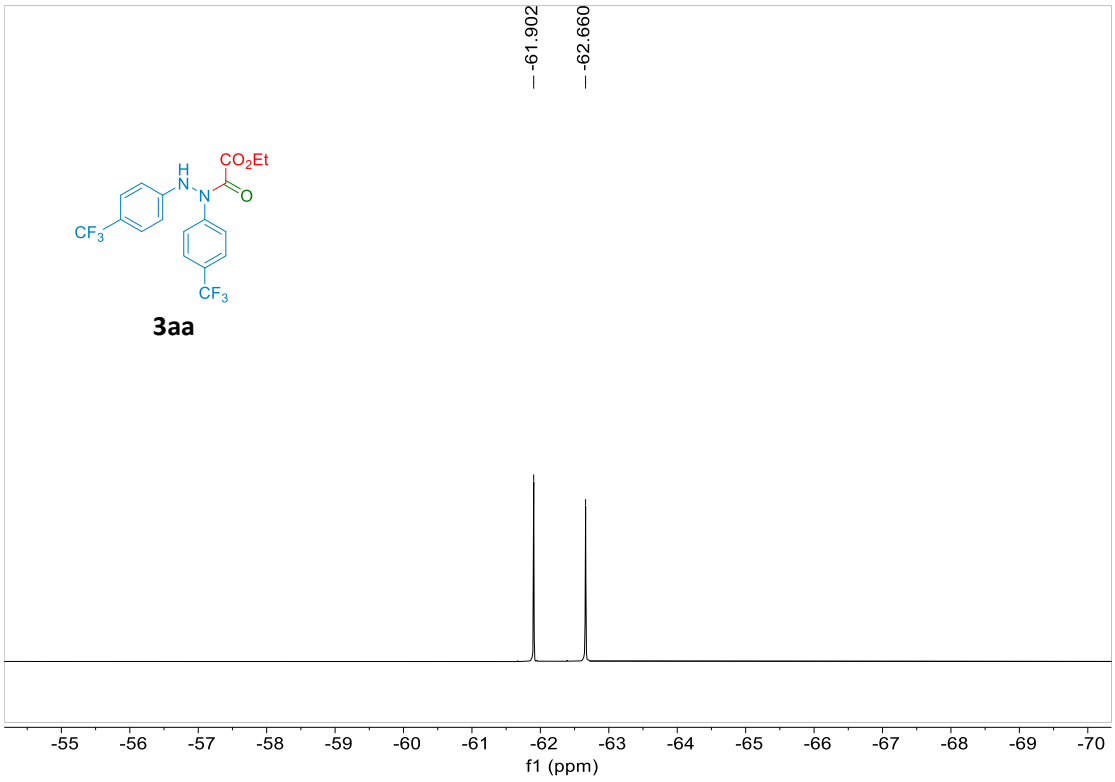
^{1}H NMR spectrum of **3aa** (600 MHz, $CDCl_3$):



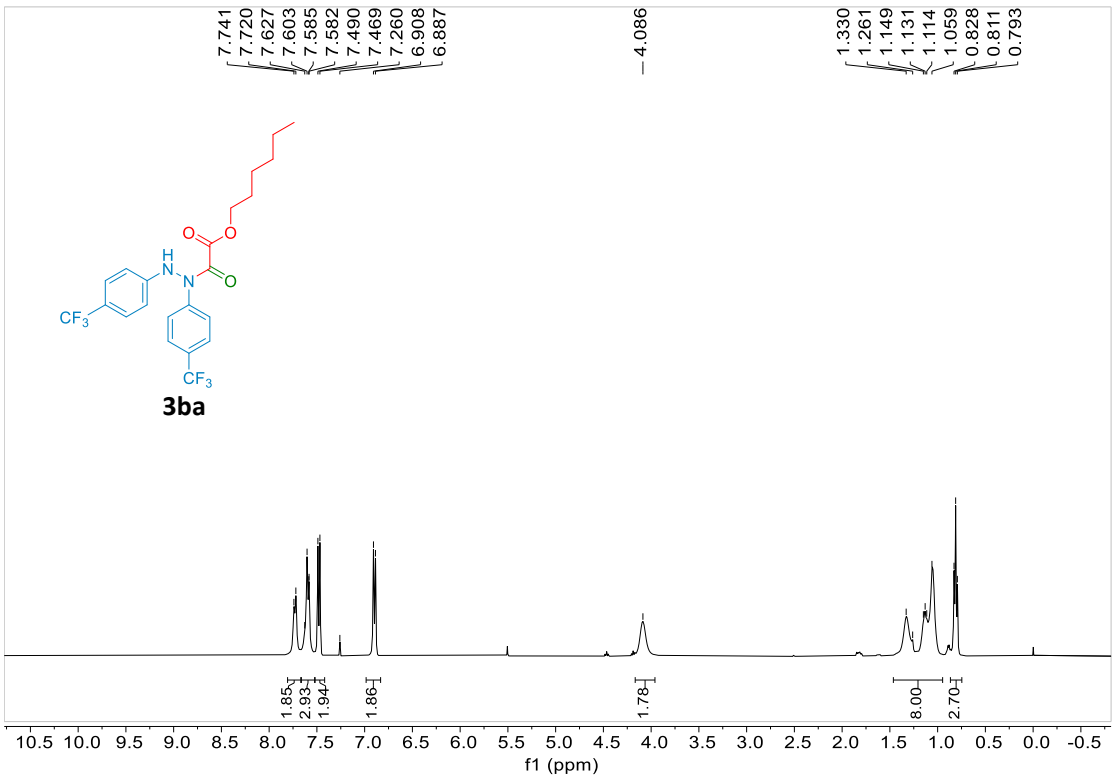
^{13}C NMR spectrum of **3aa** (150 MHz, $CDCl_3$):



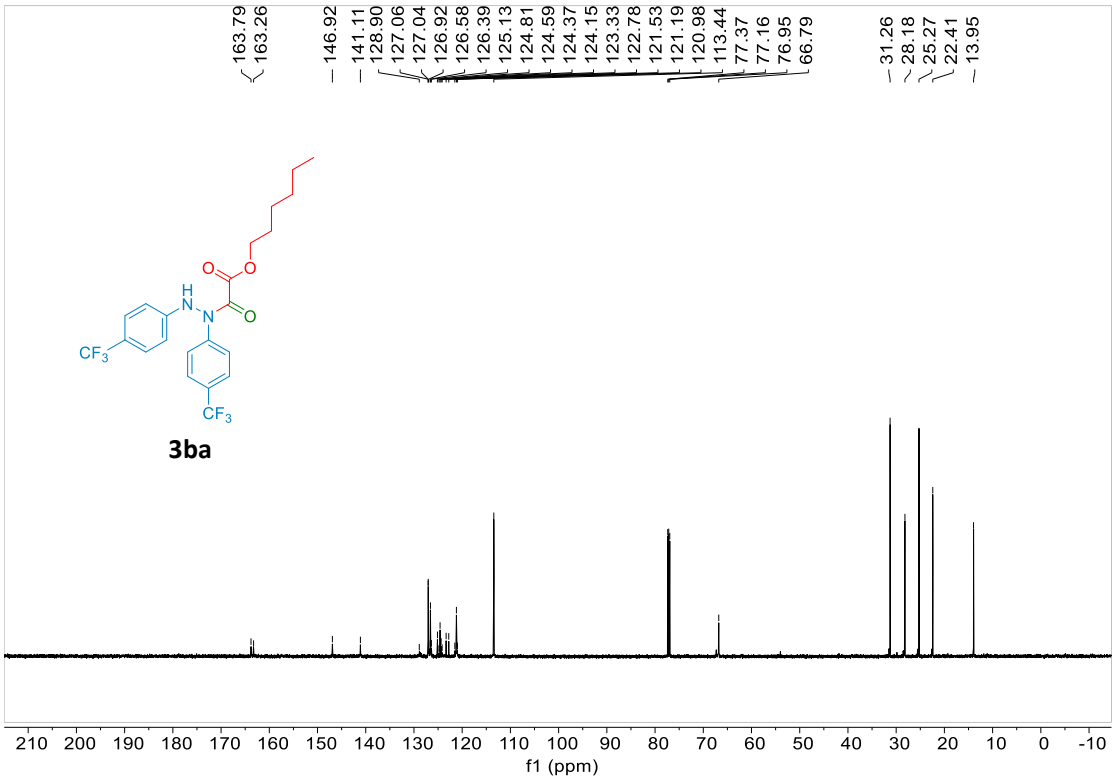
^{19}F NMR spectrum of **3aa** (376 MHz, $CDCl_3$):



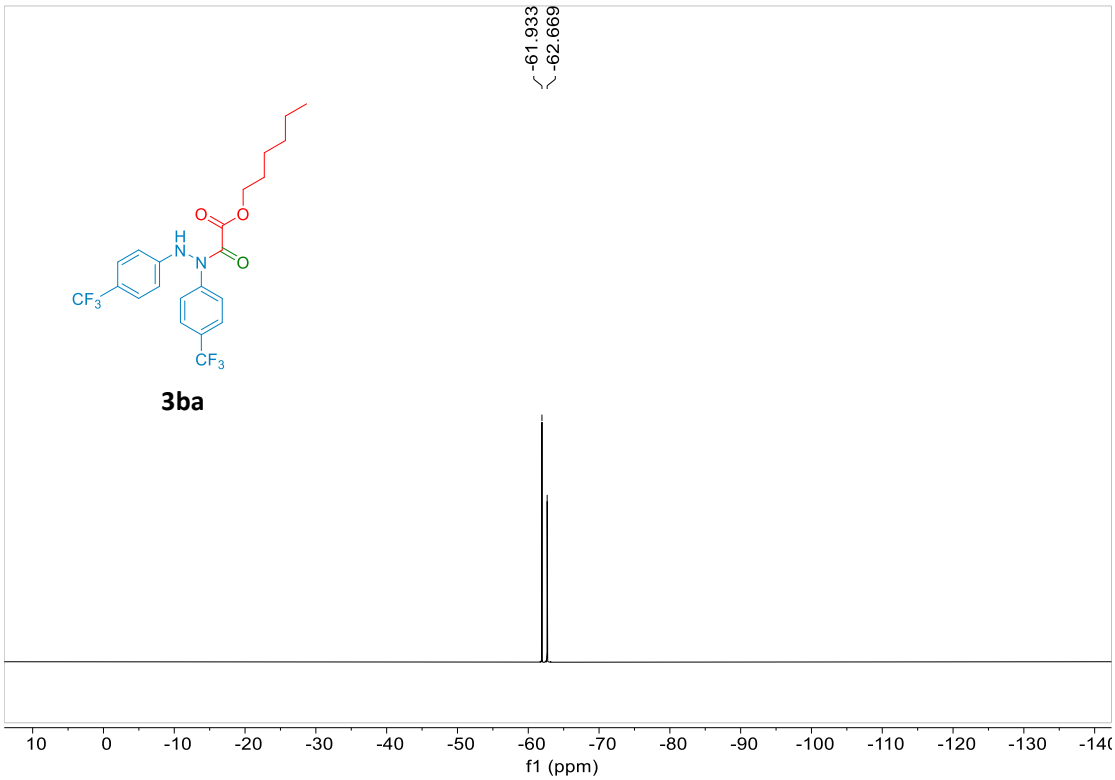
^{1}H NMR spectrum of **3ba** (400 MHz, $CDCl_3$):



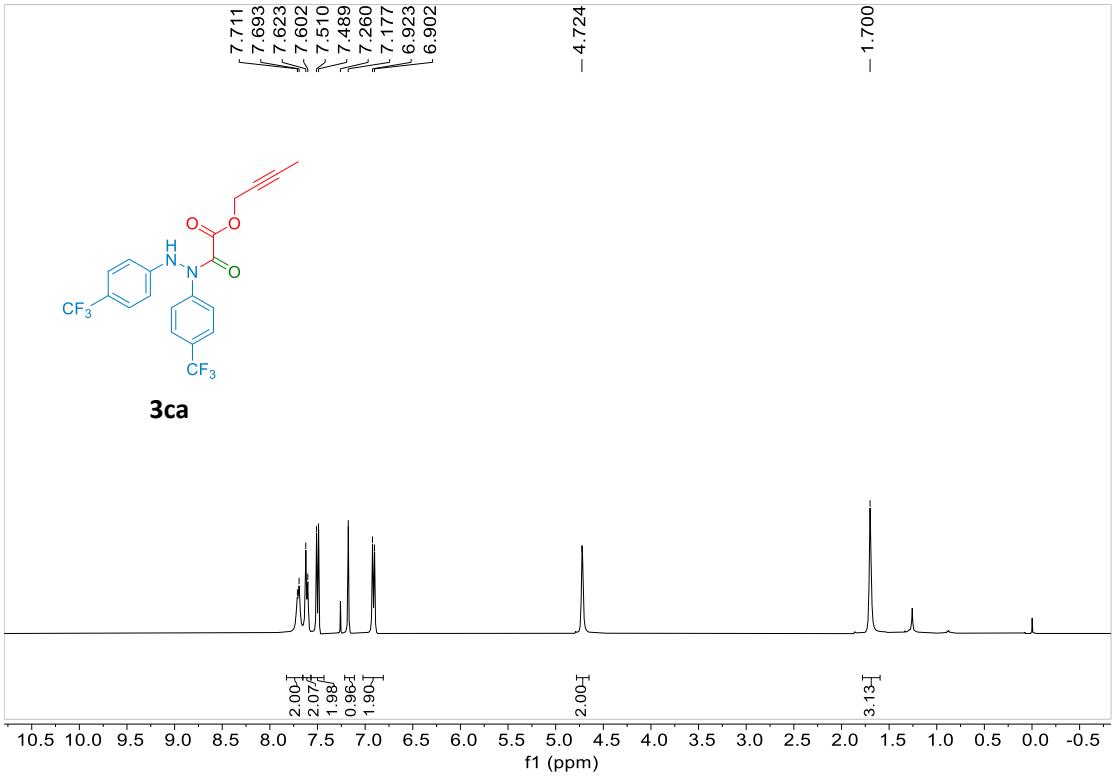
^{13}C NMR spectrum of **3ba** (150 MHz, $CDCl_3$):



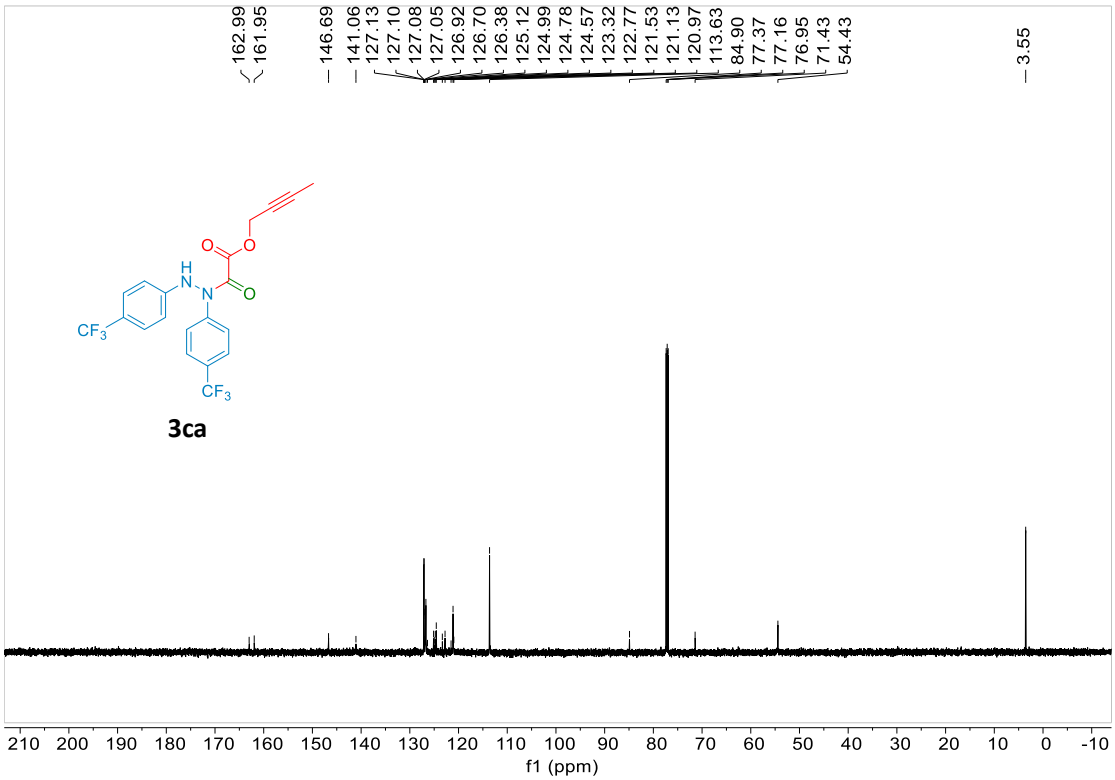
^{19}F NMR spectrum of **3ba** (376 MHz, $CDCl_3$):



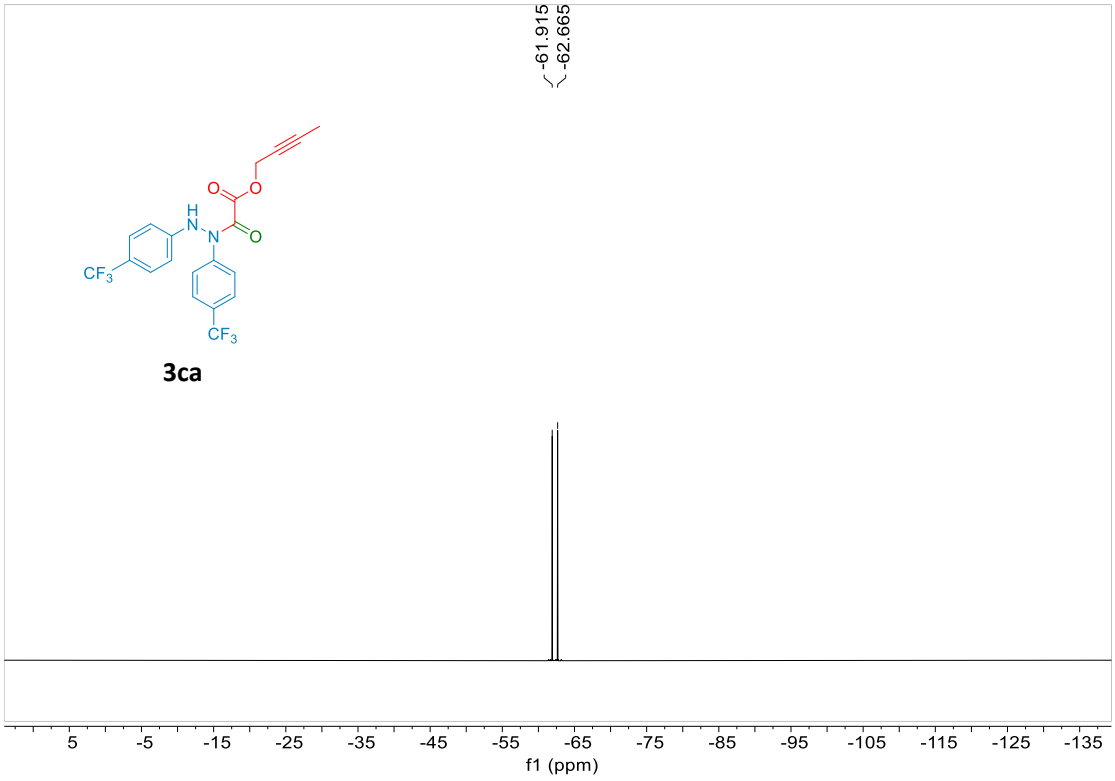
^{1}H NMR spectrum of **3ca** (400 MHz, $CDCl_3$):



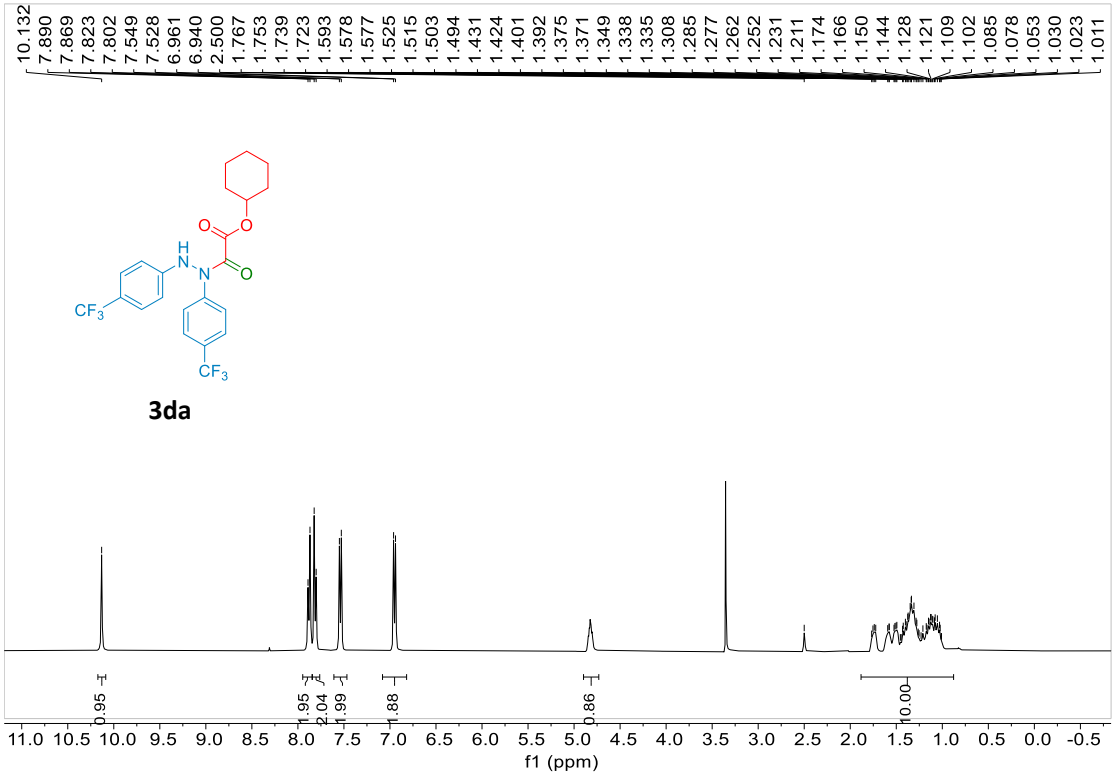
^{13}C NMR spectrum of **3ca** (150 MHz, $CDCl_3$):



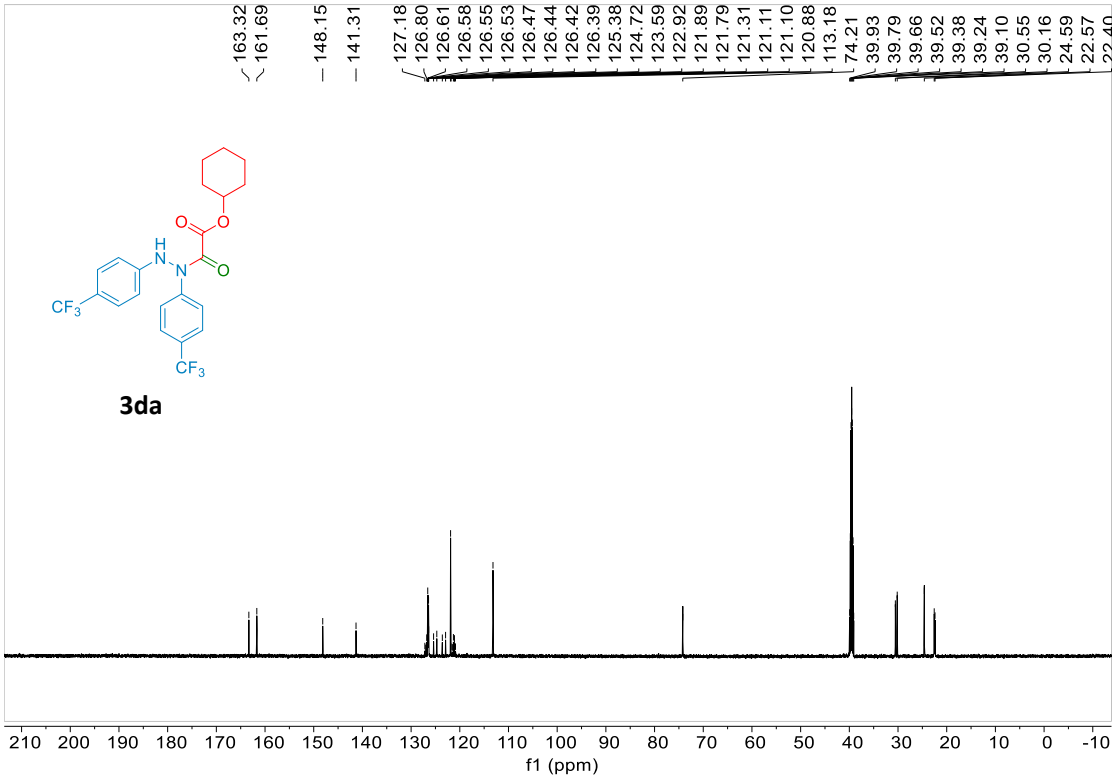
^{19}F NMR spectrum of **3ca** (376 MHz, $CDCl_3$):



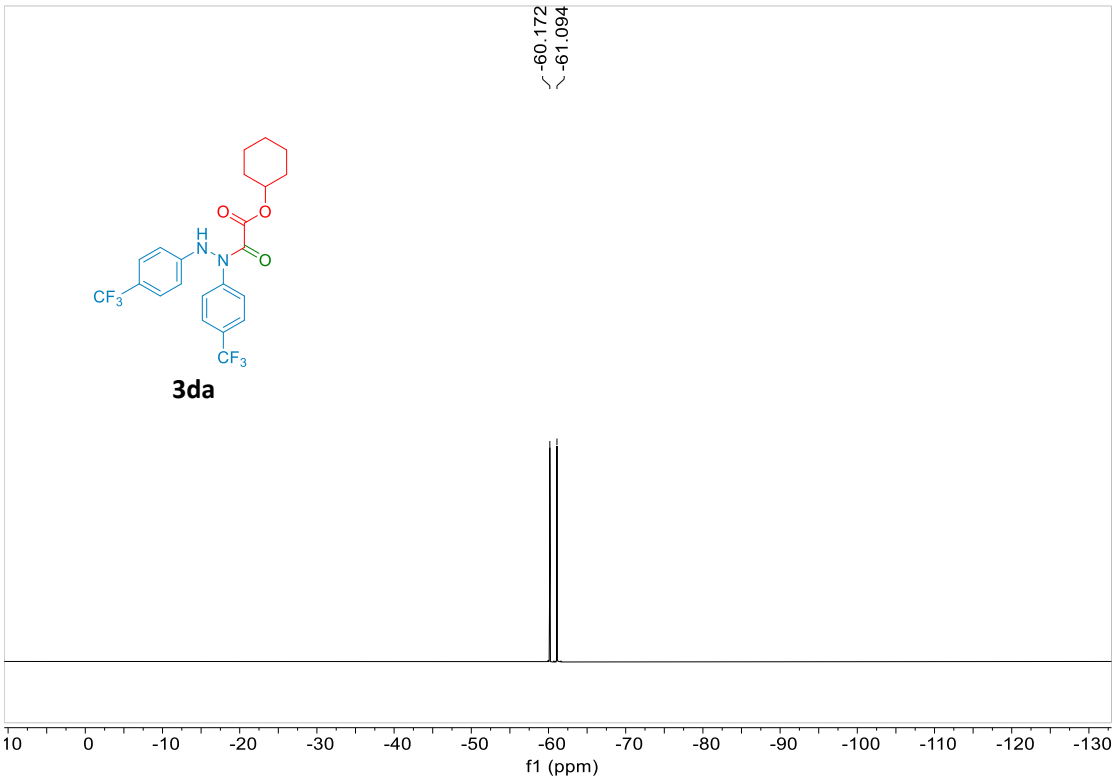
^{1}H NMR spectrum of **3da** (400 MHz, DMSO-d_6):



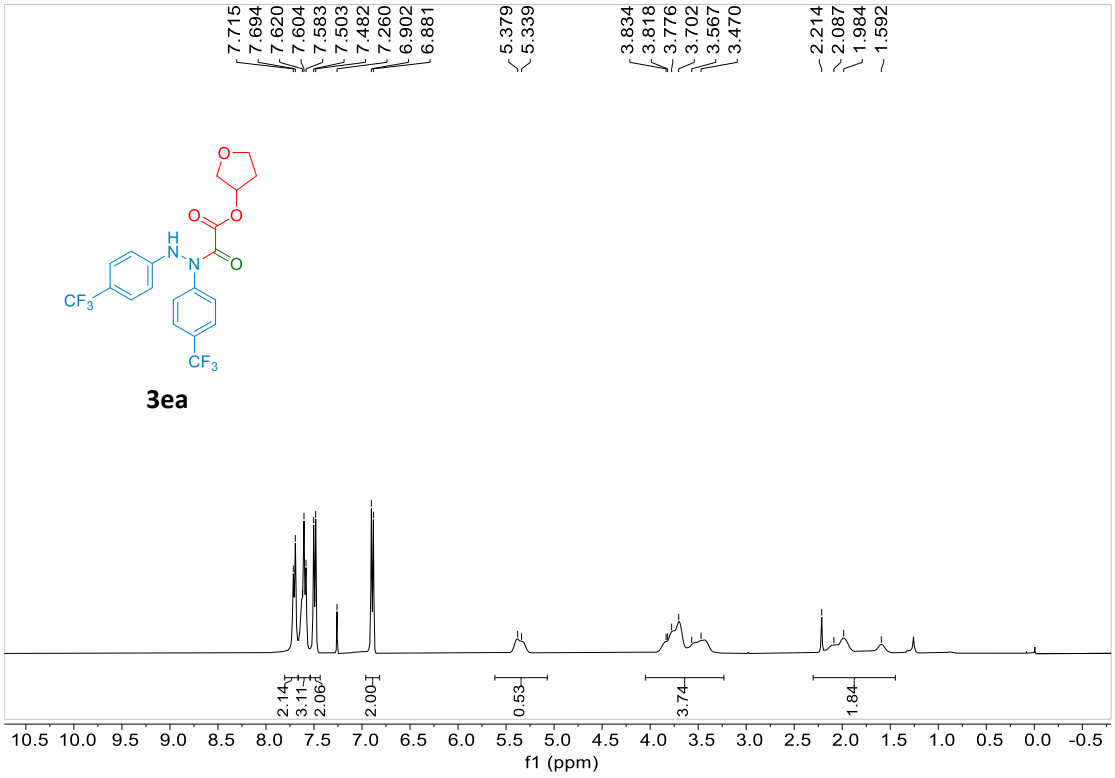
^{13}C NMR spectrum of **3da** (150 MHz, DMSO-d_6):



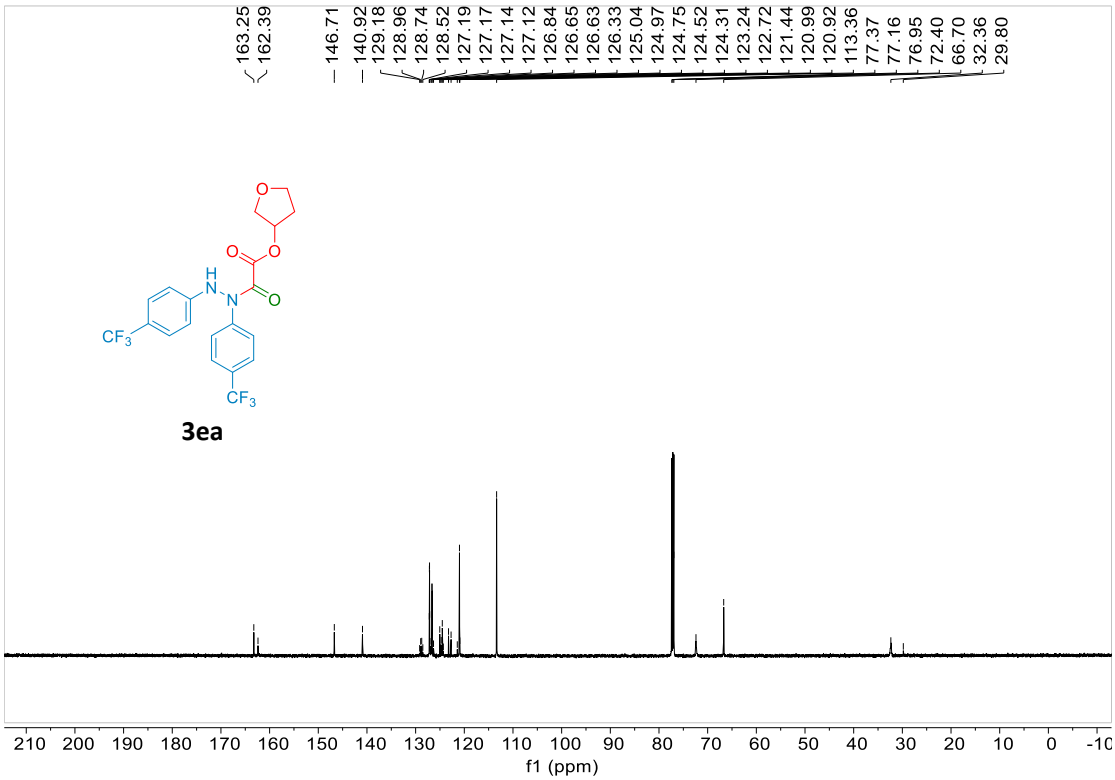
^{19}F NMR spectrum of **3da** (376 MHz, DMSO-d_6):



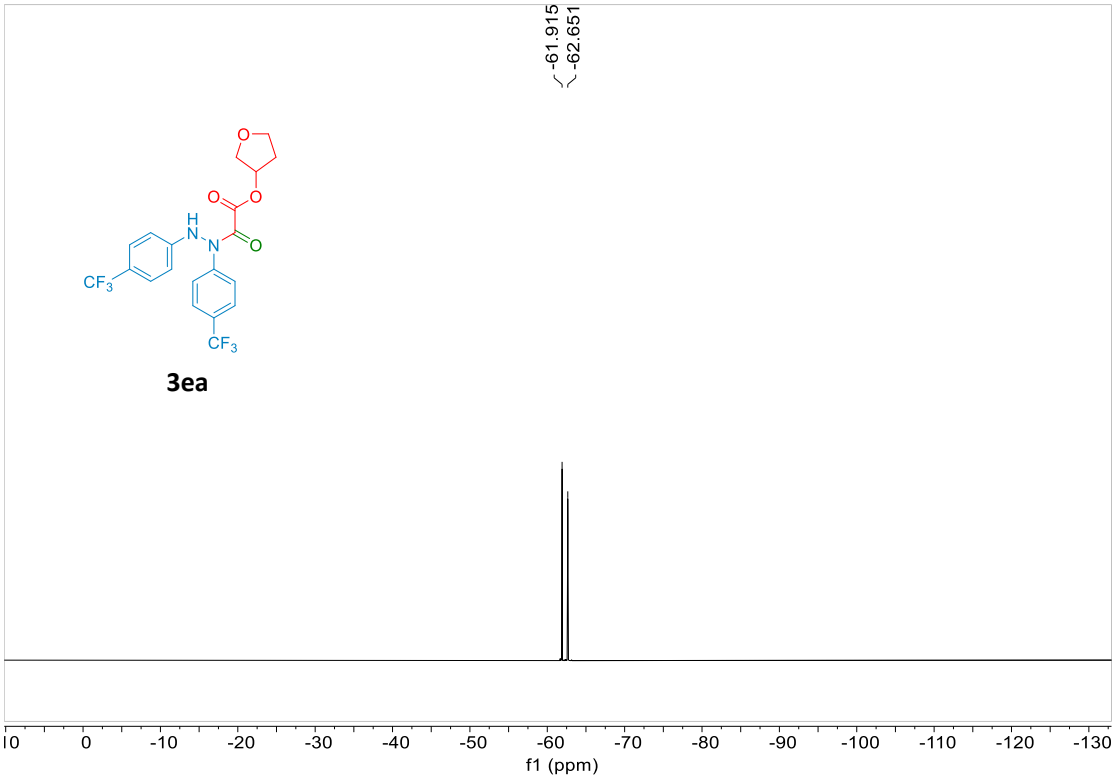
^{1}H NMR spectrum of **3ea** (400 MHz, $CDCl_3$):



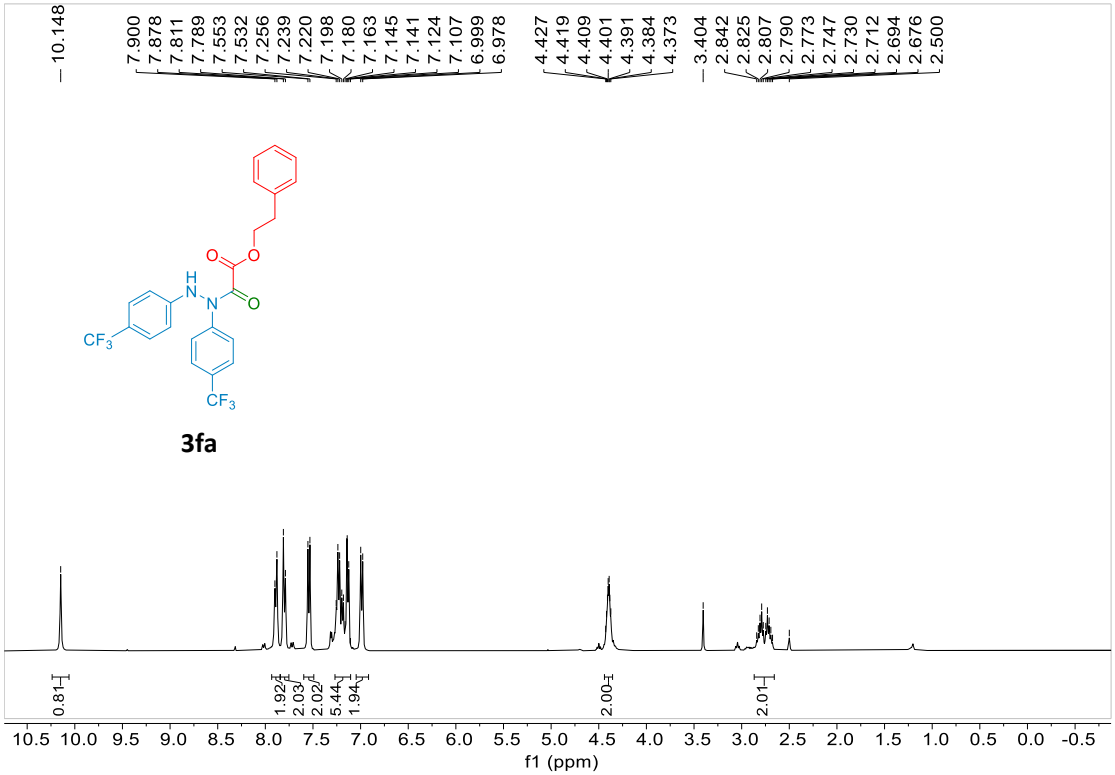
^{13}C NMR spectrum of **3ea** (150 MHz, $CDCl_3$):



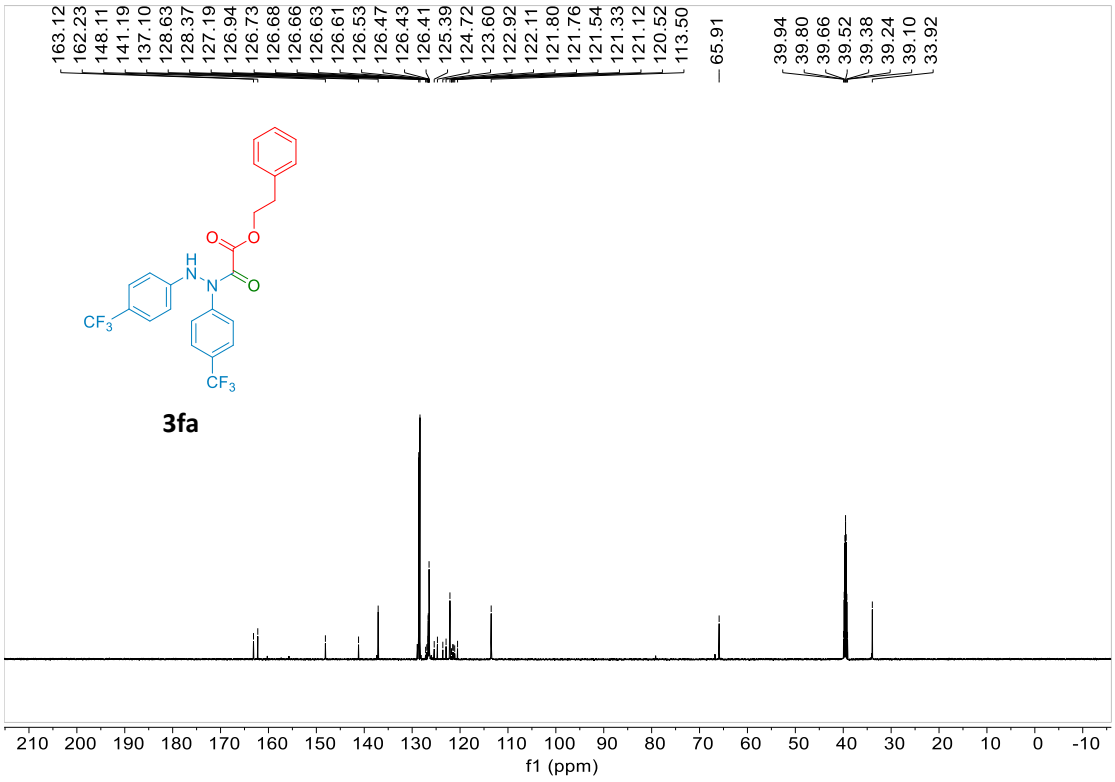
^{19}F NMR spectrum of **3ea** (376 MHz, $CDCl_3$):



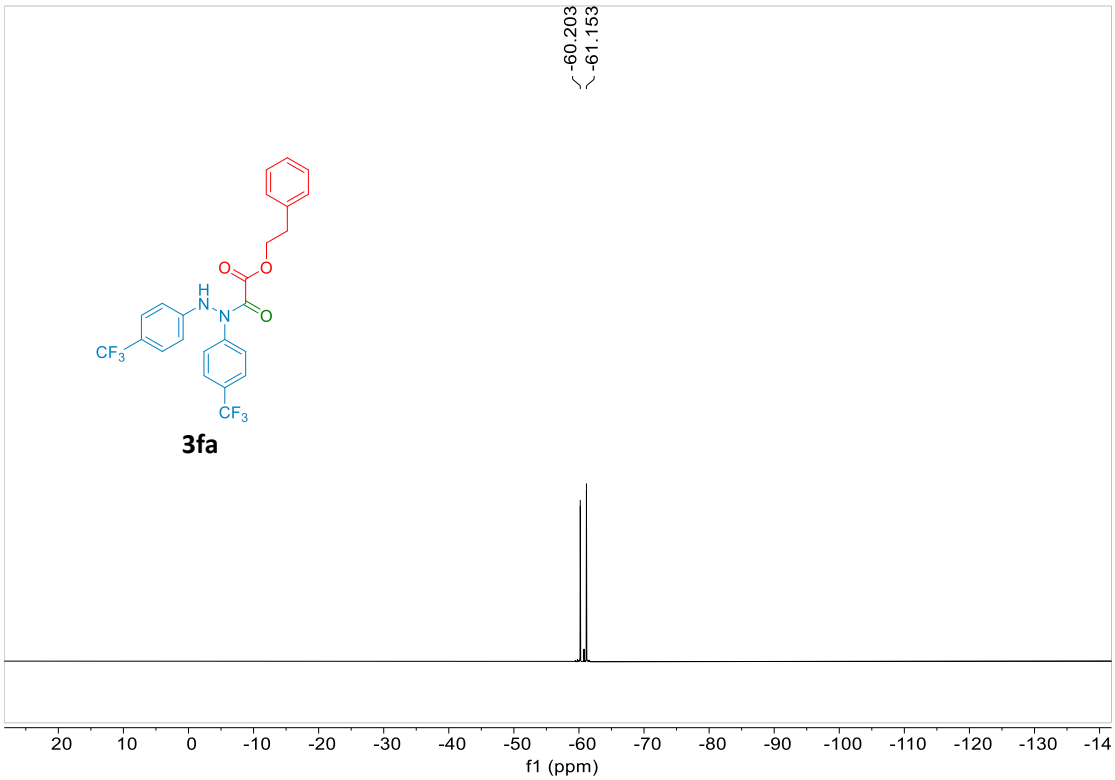
^{1}H NMR spectrum of **3fa** (400 MHz, DMSO-d_6):



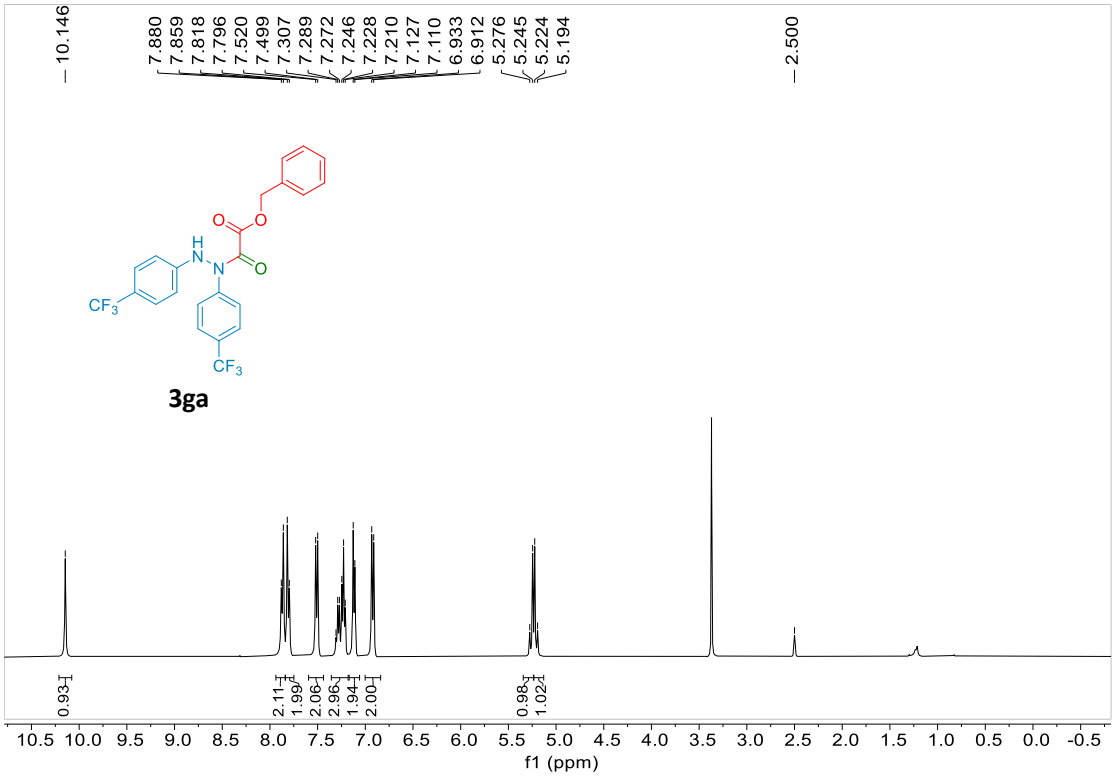
^{13}C NMR spectrum of **3fa** (150 MHz, DMSO-d_6):



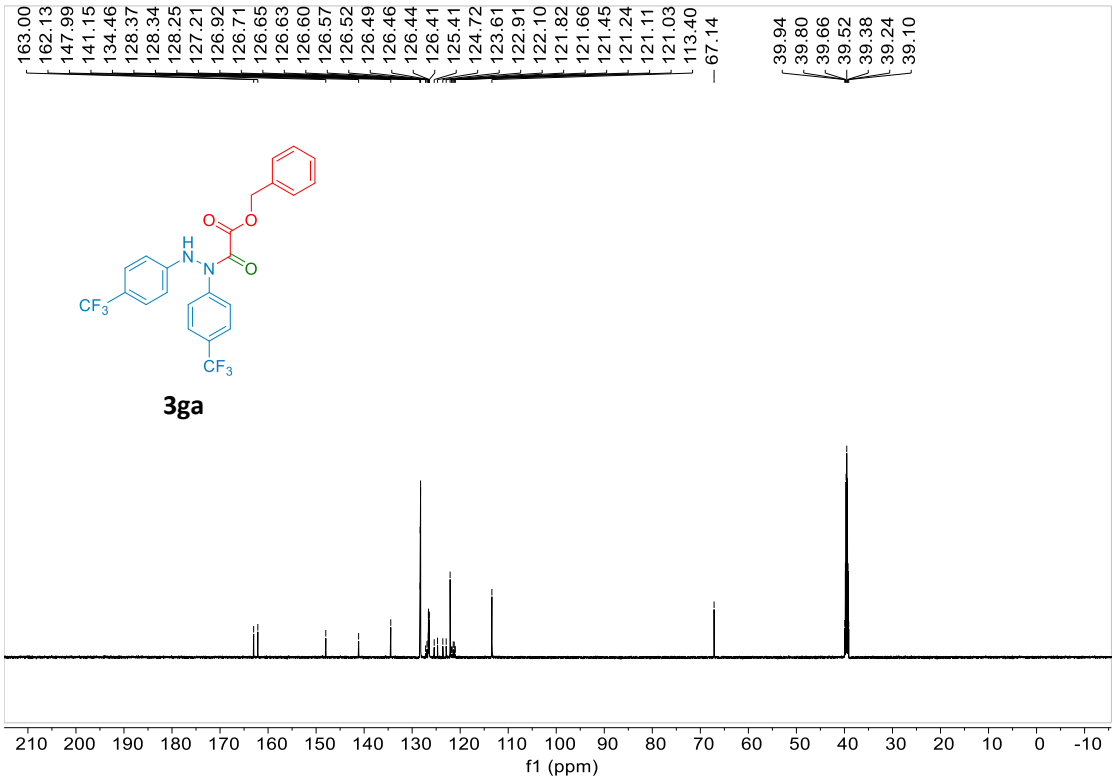
^{19}F NMR spectrum of **3fa** (376 MHz, DMSO-d_6):



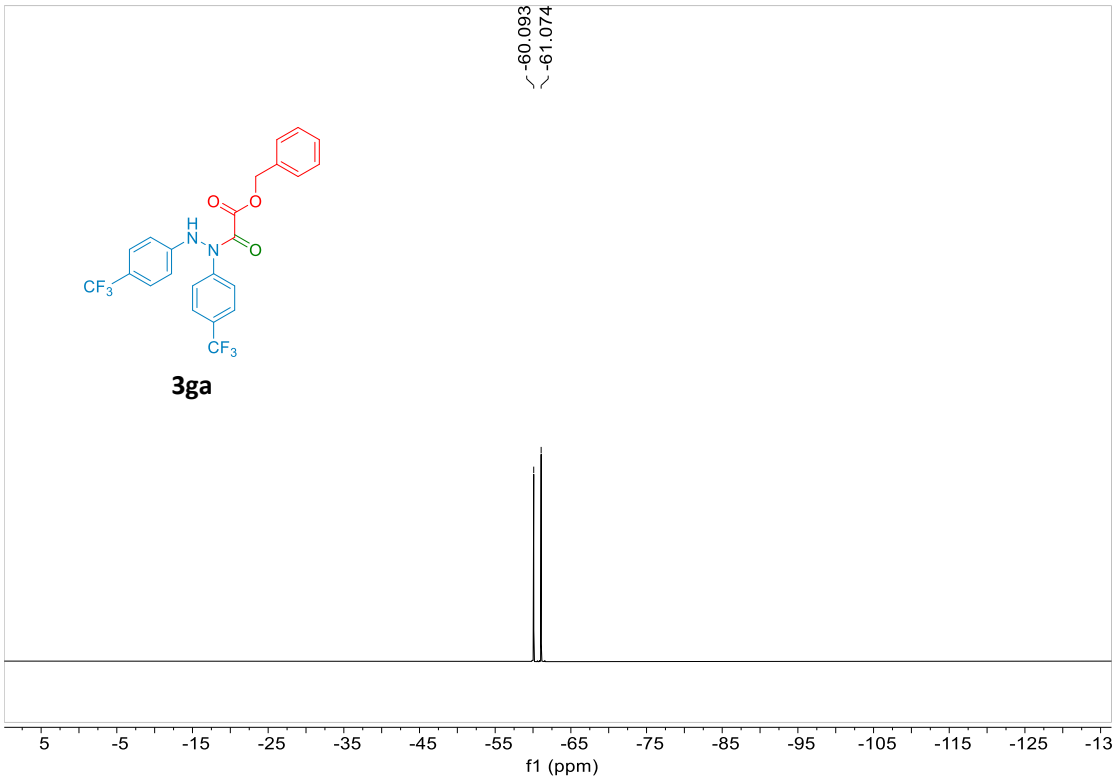
^{1}H NMR spectrum of **3ga** (400 MHz, DMSO-d_6):



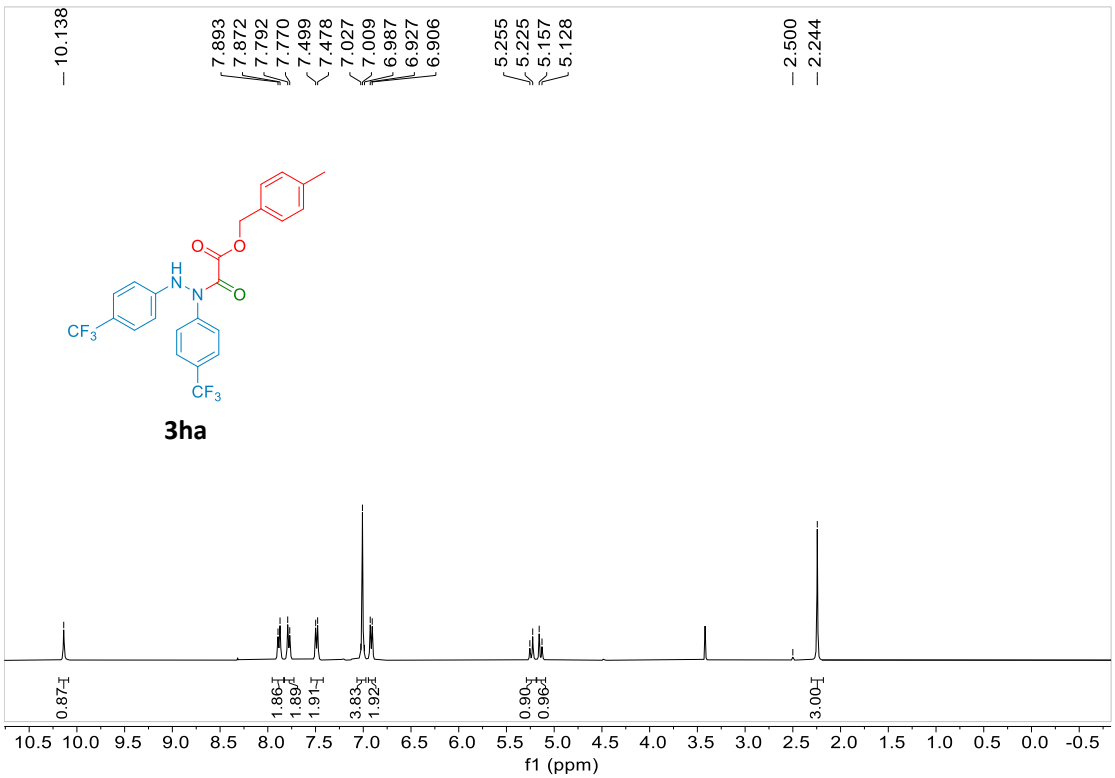
^{13}C NMR spectrum of **3ga** (150 MHz, DMSO-d_6):



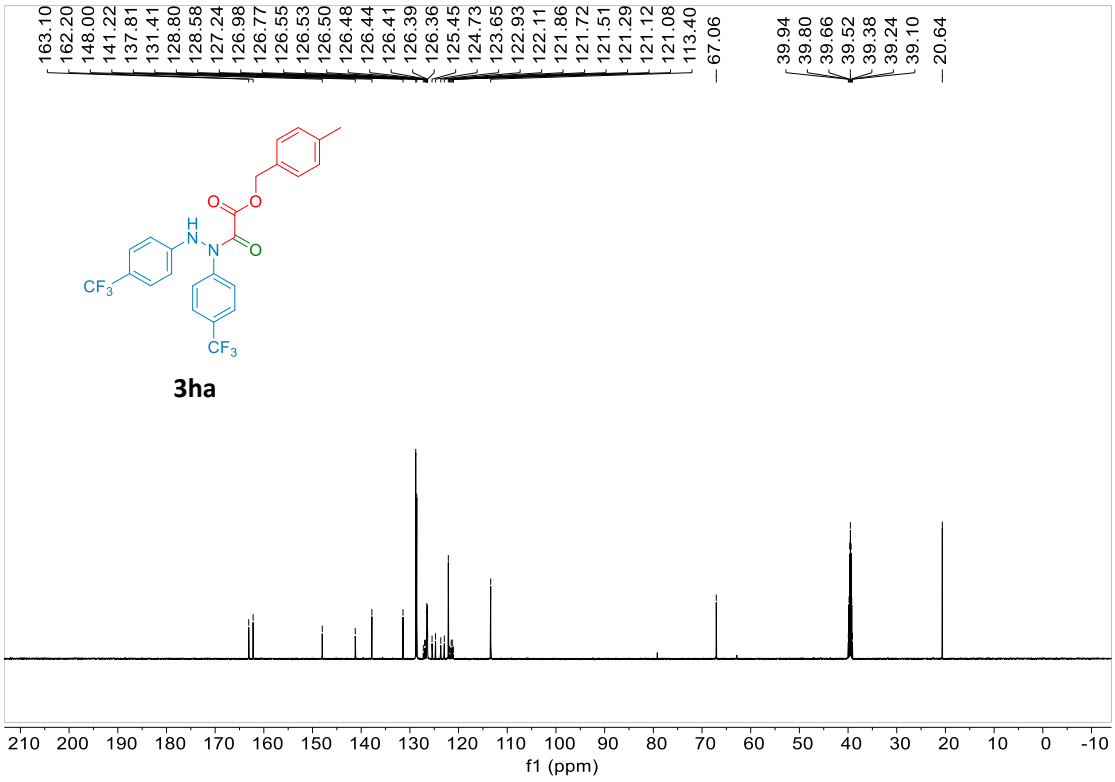
^{19}F NMR spectrum of **3ga** (376 MHz, DMSO-d_6):



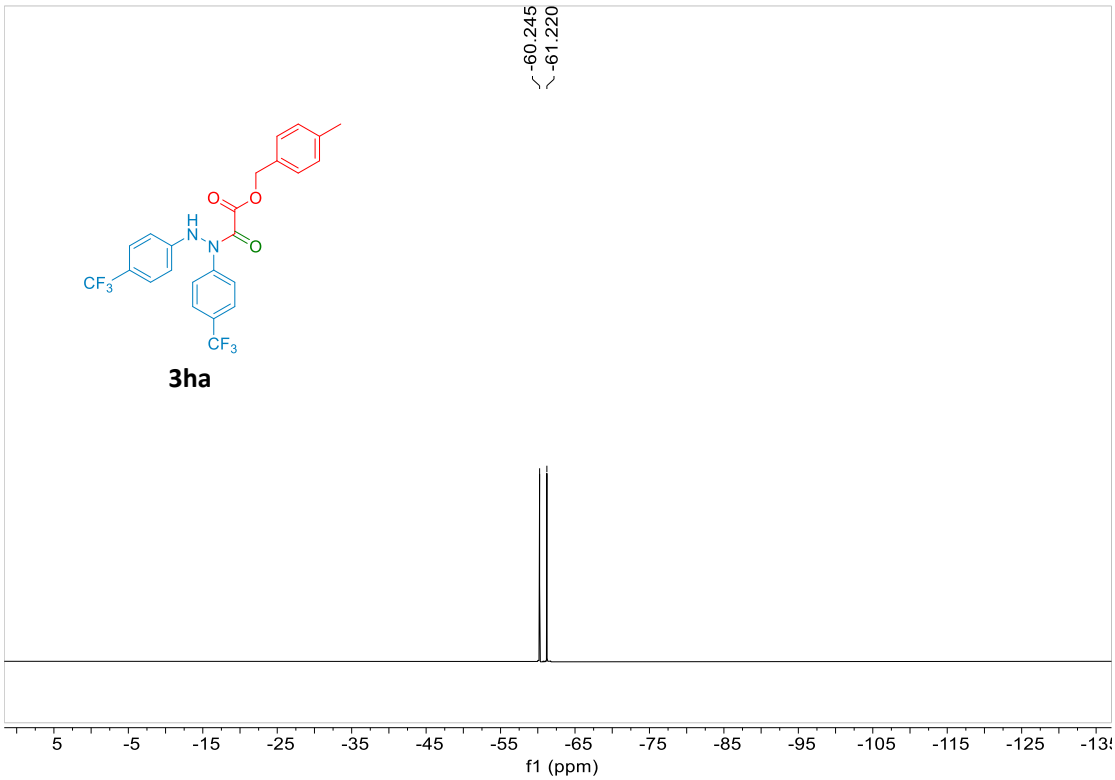
^{1}H NMR spectrum of **3ha** (400 MHz, DMSO-d_6):



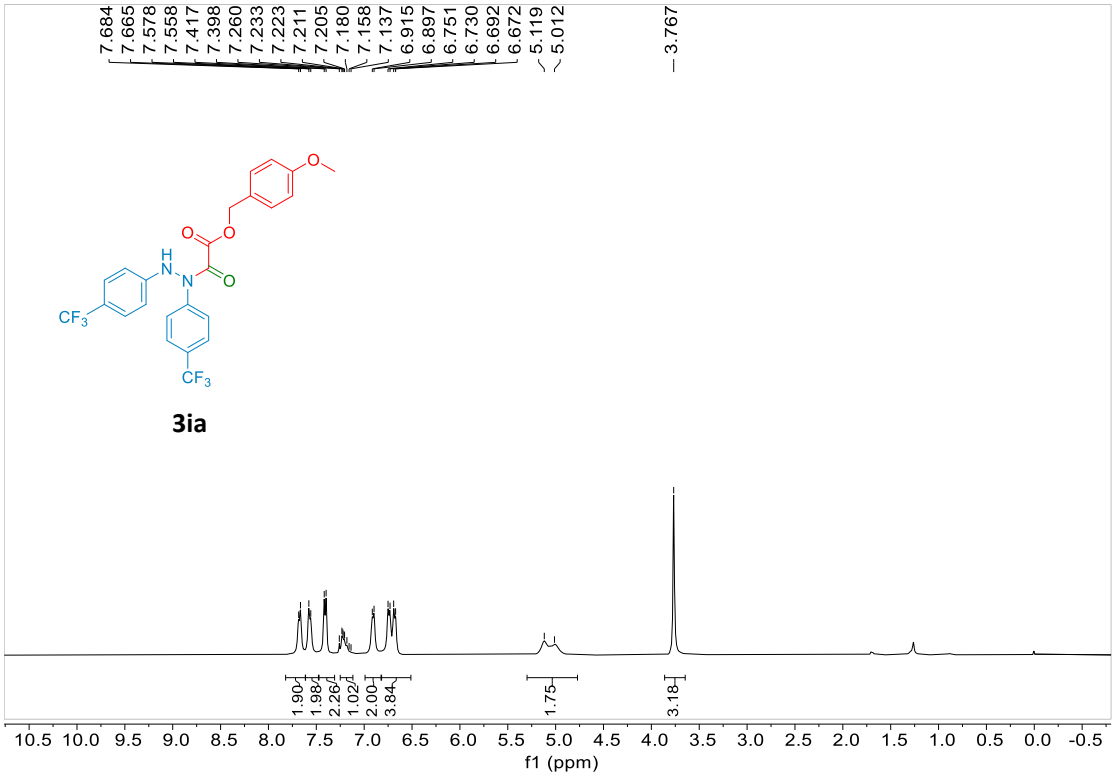
^{13}C NMR spectrum of **3ha** (150 MHz, DMSO-d_6):



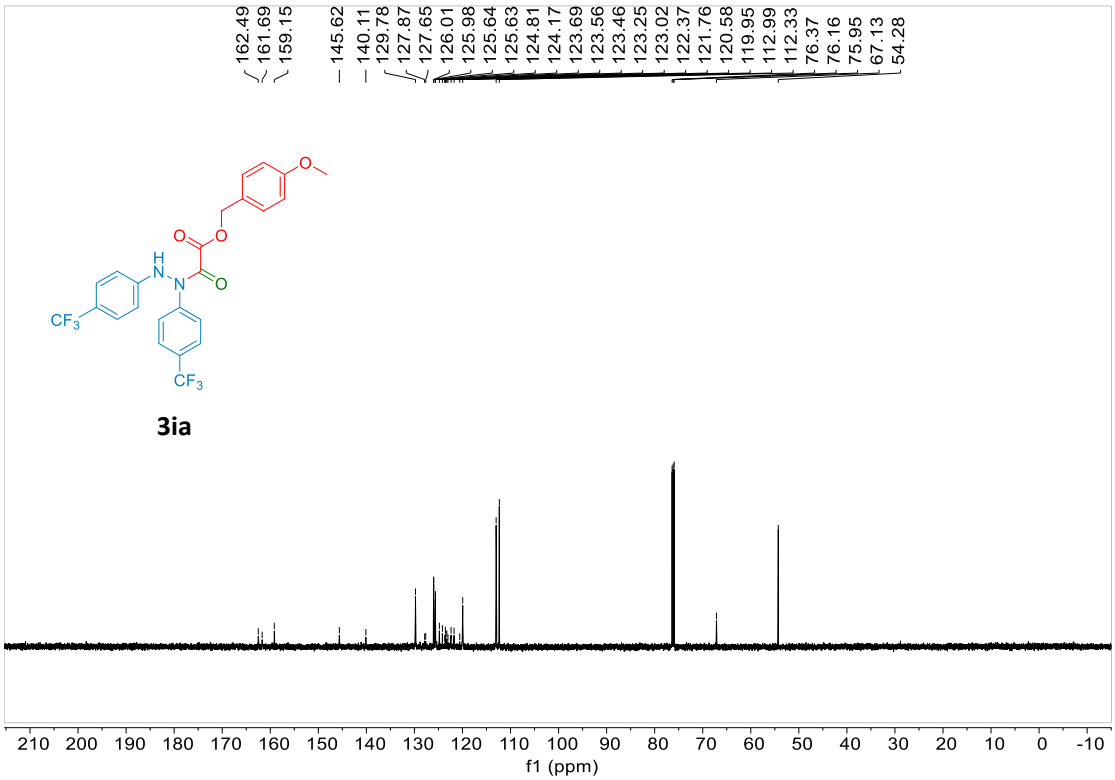
^{19}F NMR spectrum of **3ha** (376 MHz, DMSO-d_6):



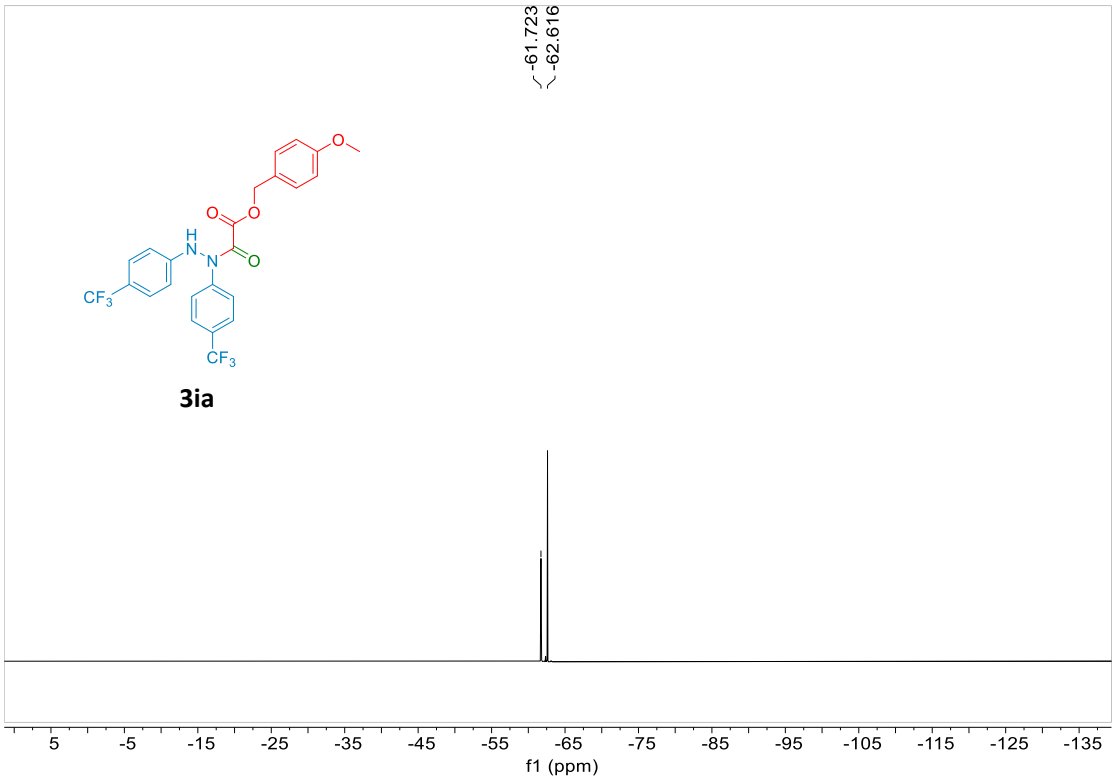
^{1}H NMR spectrum of **3ia** (400 MHz, $CDCl_3$):



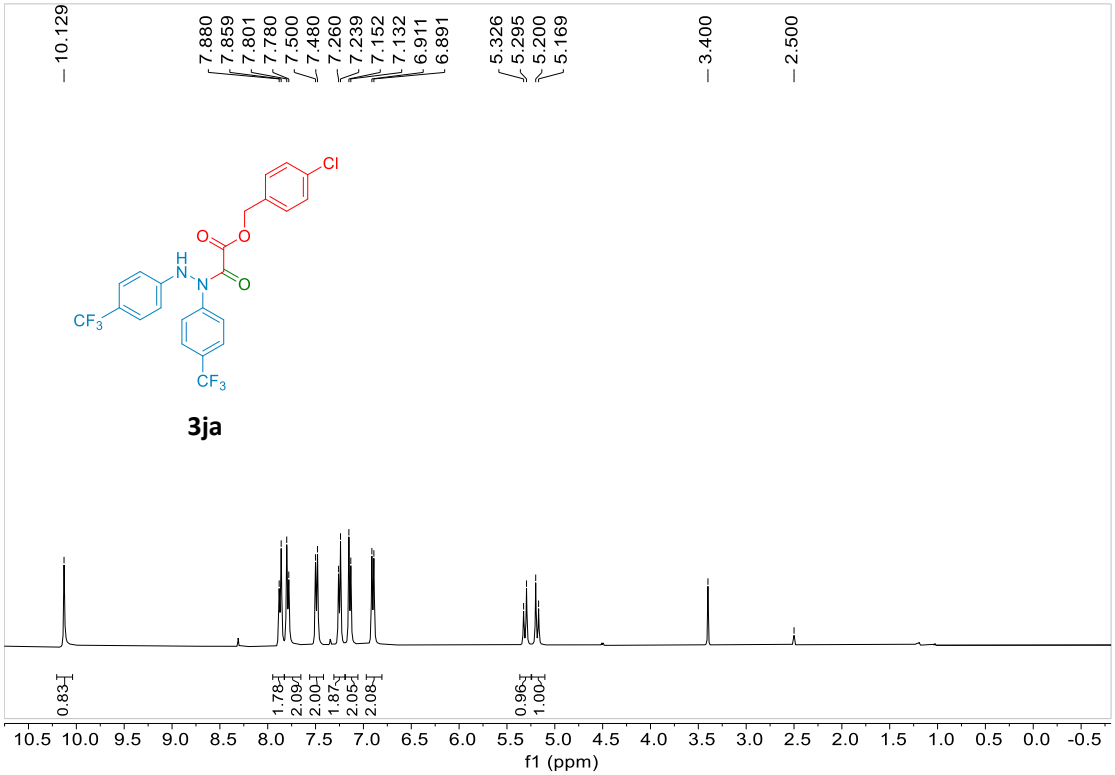
^{13}C NMR spectrum of **3ia** (150 MHz, $CDCl_3$):



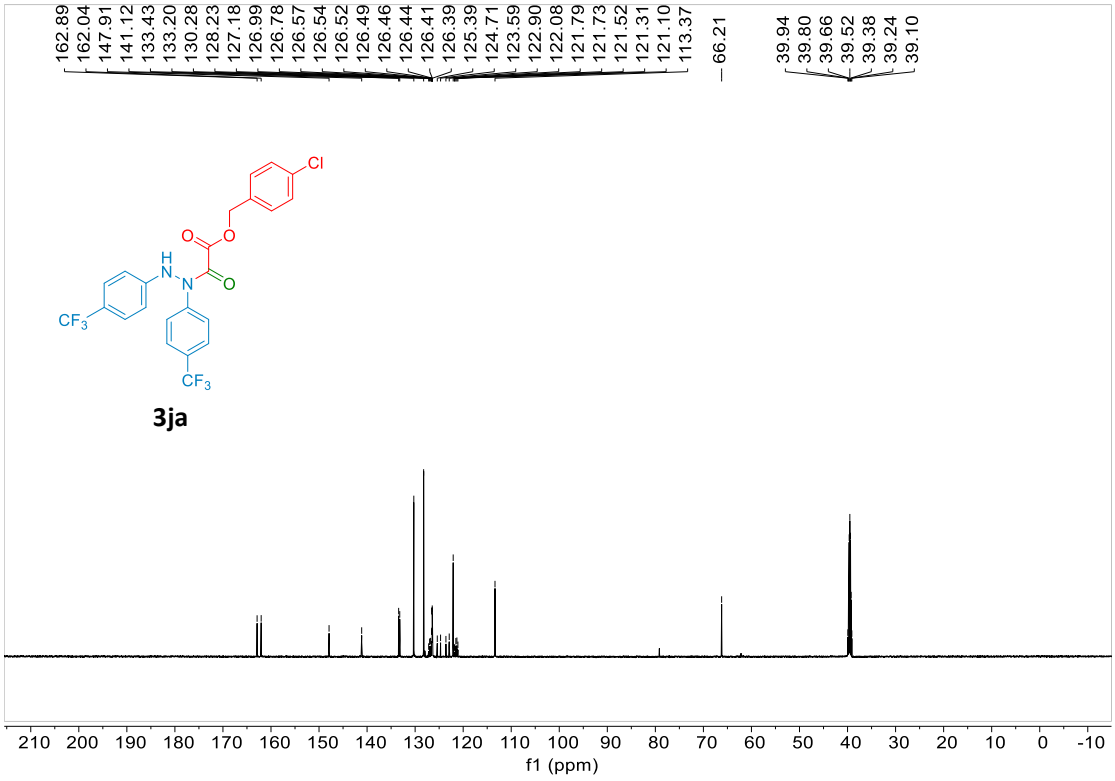
^{19}F NMR spectrum of **3ia** (376 MHz, $CDCl_3$):



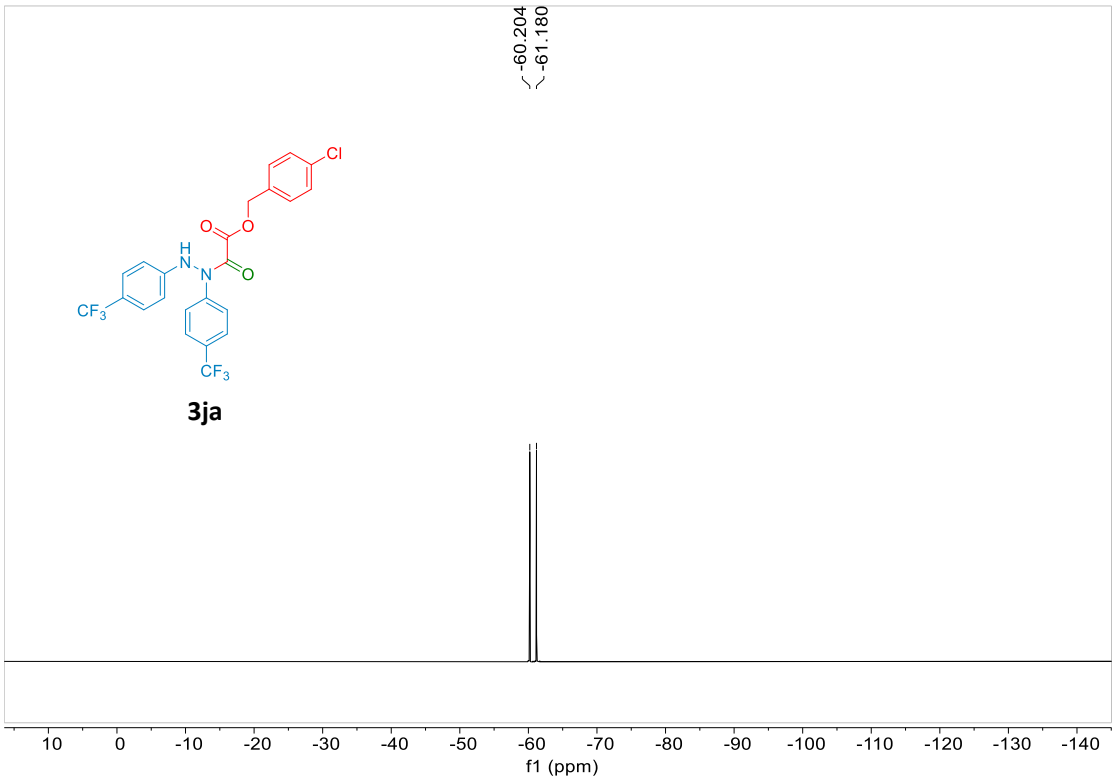
^{1}H NMR spectrum of **3ja** (400 MHz, DMSO-d_6):



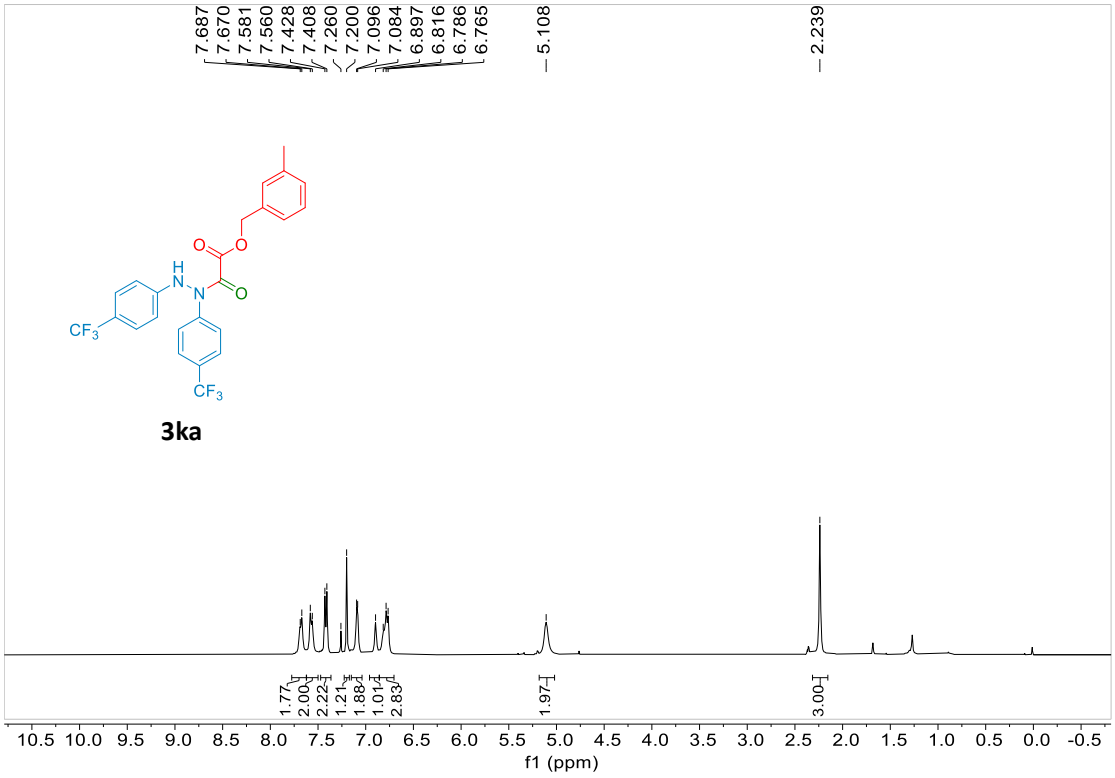
^{13}C NMR spectrum of **3ja** (150 MHz, DMSO-d_6):



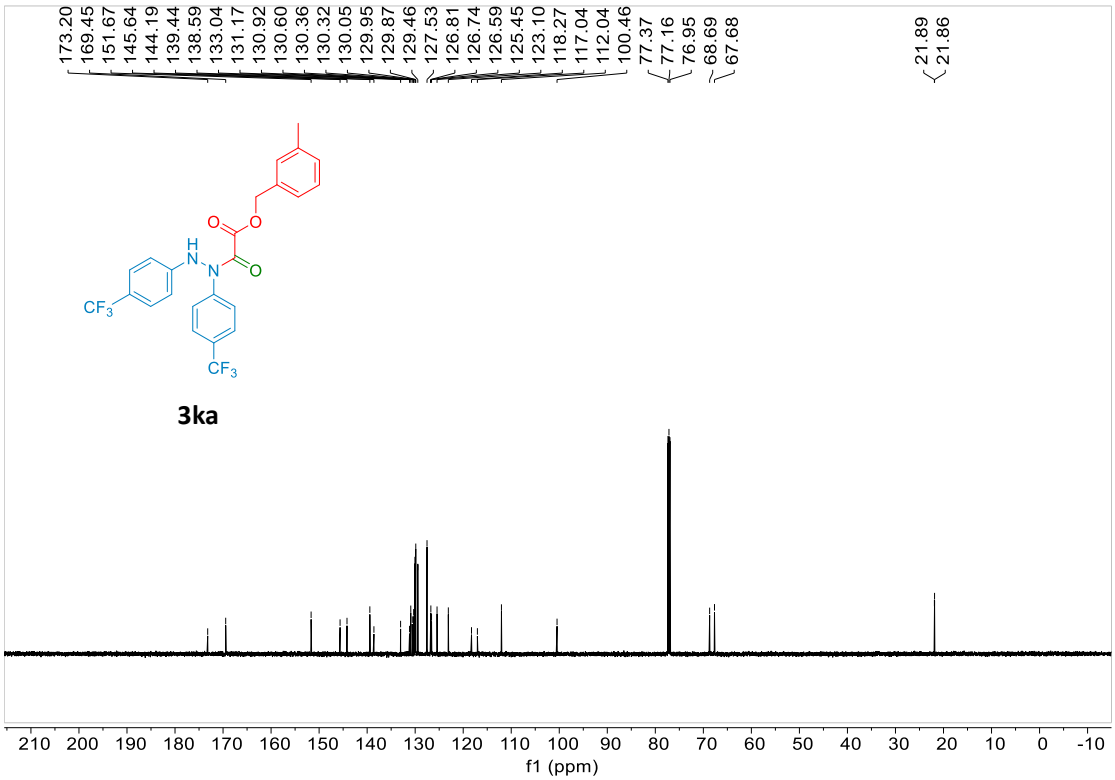
^{19}F NMR spectrum of **3ja** (376 MHz, DMSO-d_6):



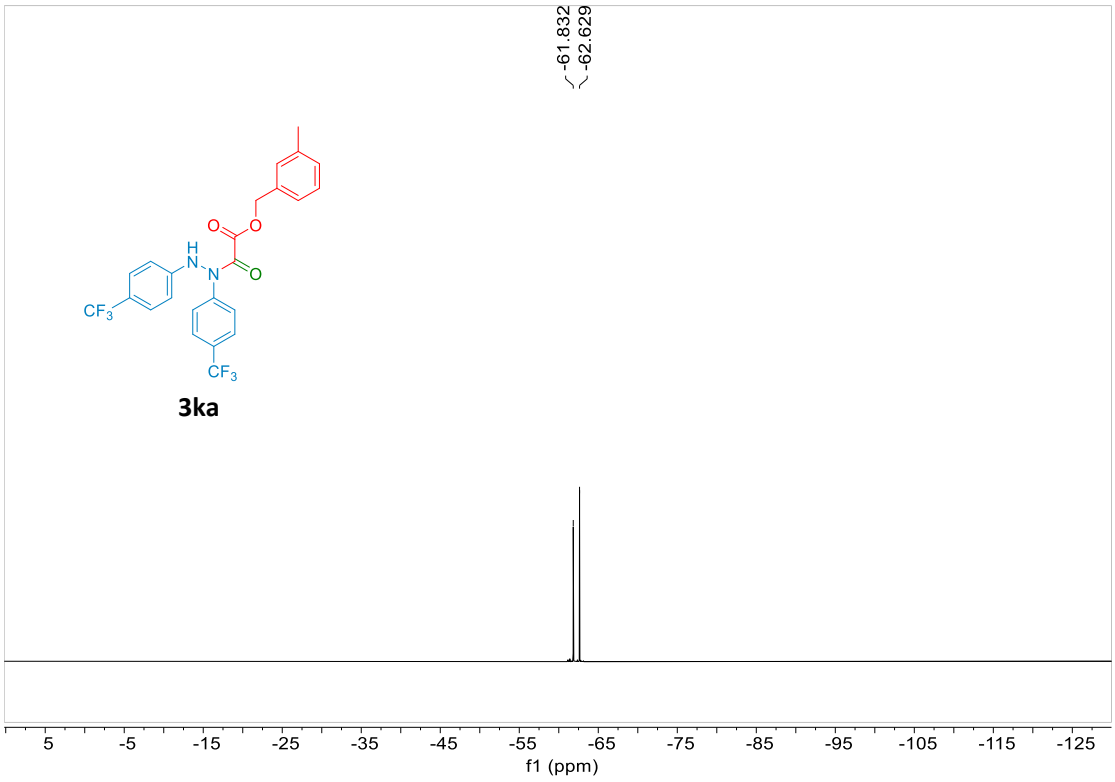
^{1}H NMR spectrum of **3ka** (400 MHz, $CDCl_3$):



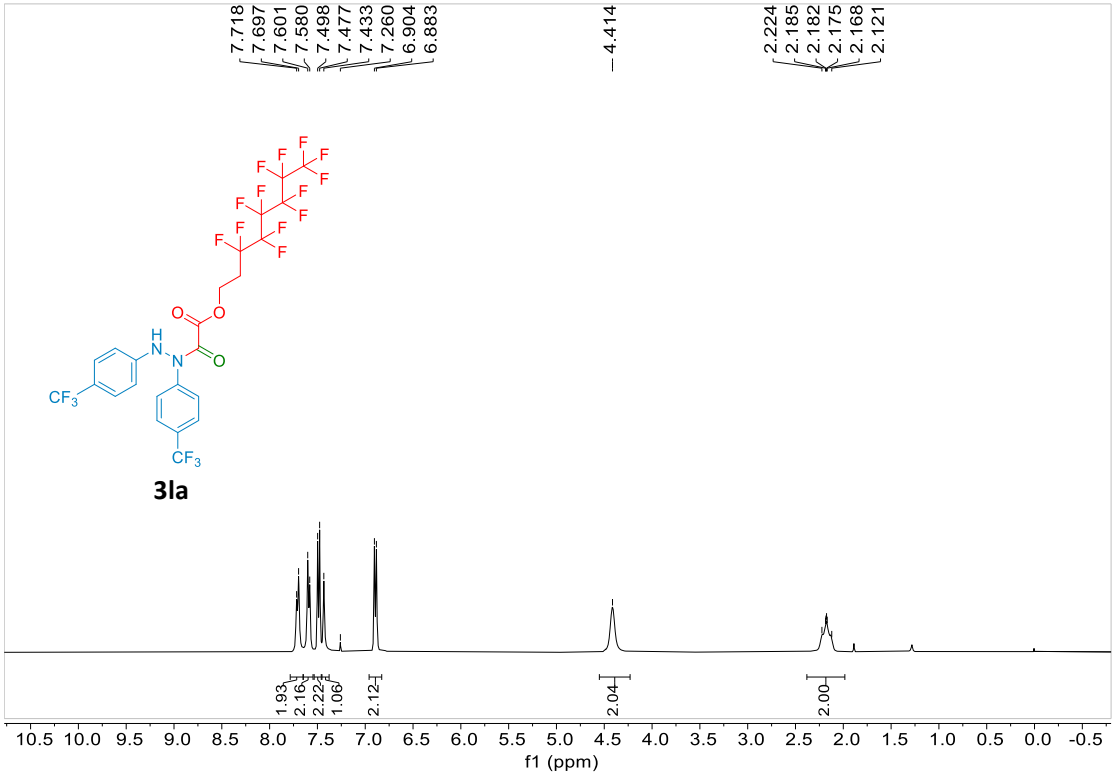
^{13}C NMR spectrum of **3ka** (150 MHz, $CDCl_3$):



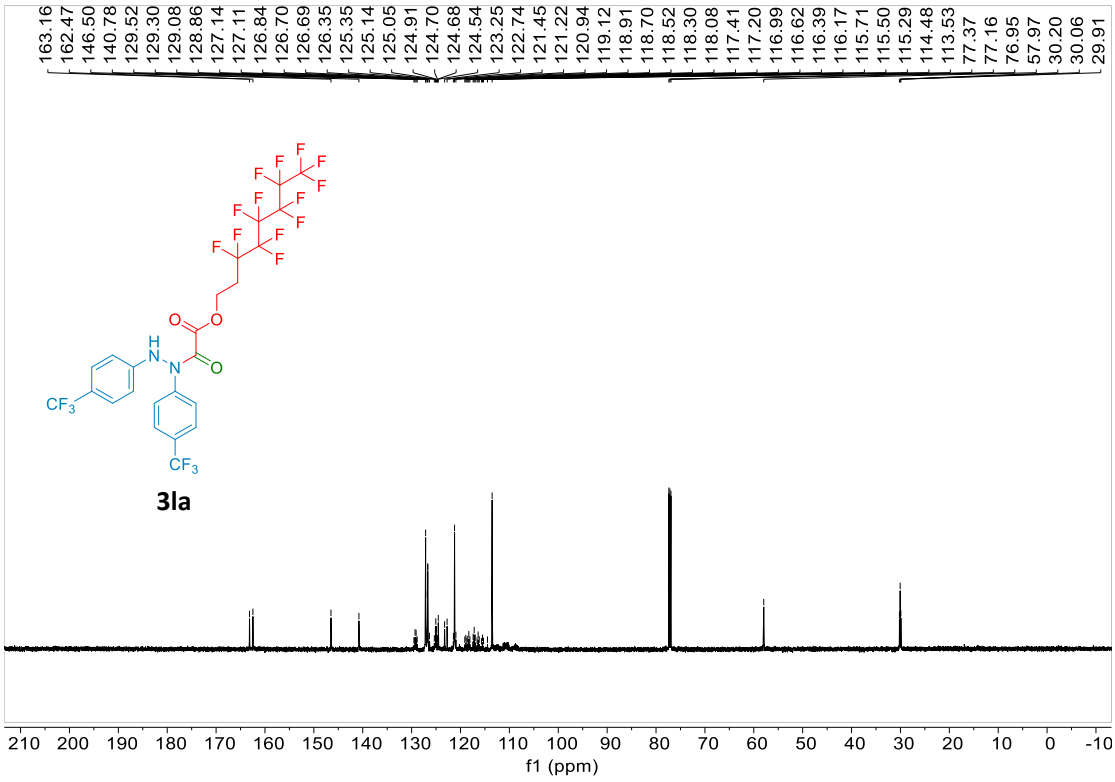
^{19}F NMR spectrum of **3ka** (376 MHz, $CDCl_3$):



^{1}H NMR spectrum of **3la** (400 MHz, $CDCl_3$):



^{13}C NMR spectrum of **3la** (150 MHz, $CDCl_3$):



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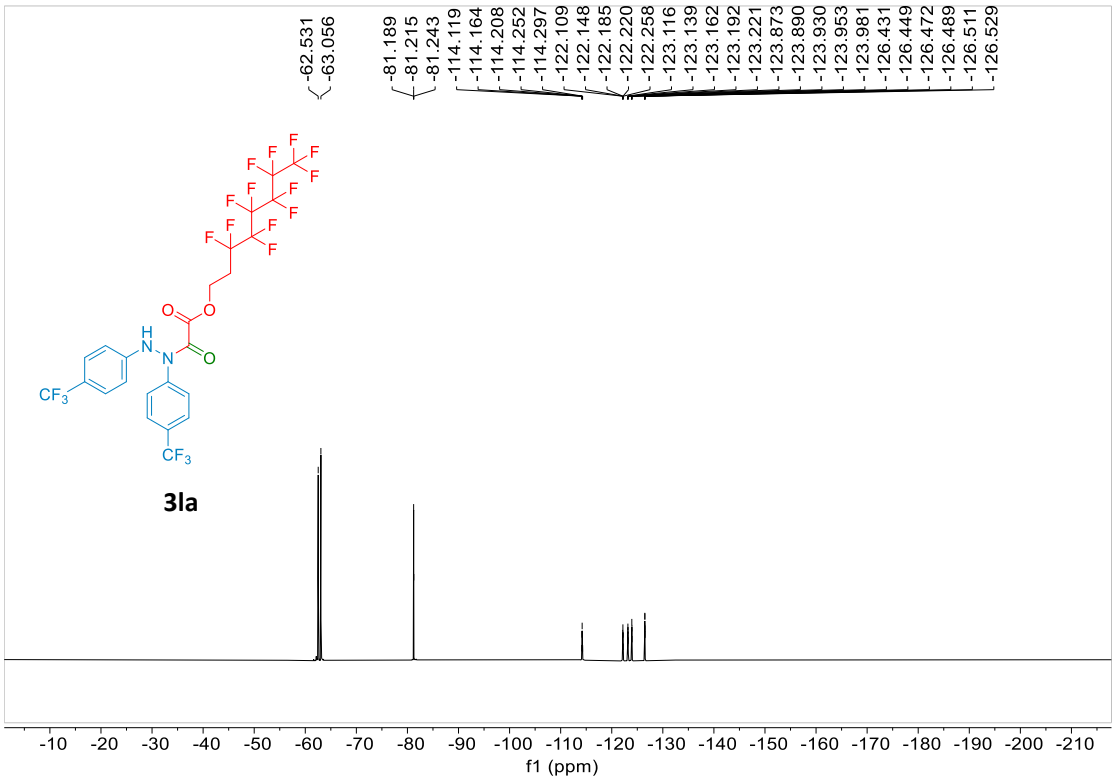
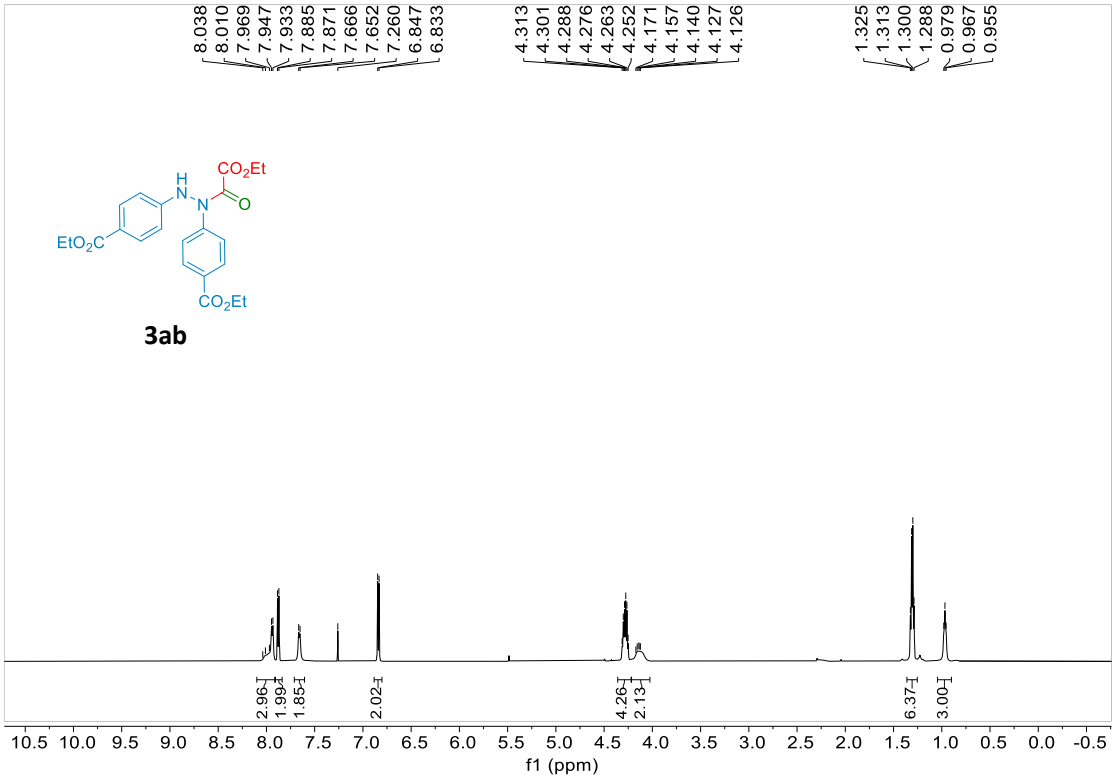
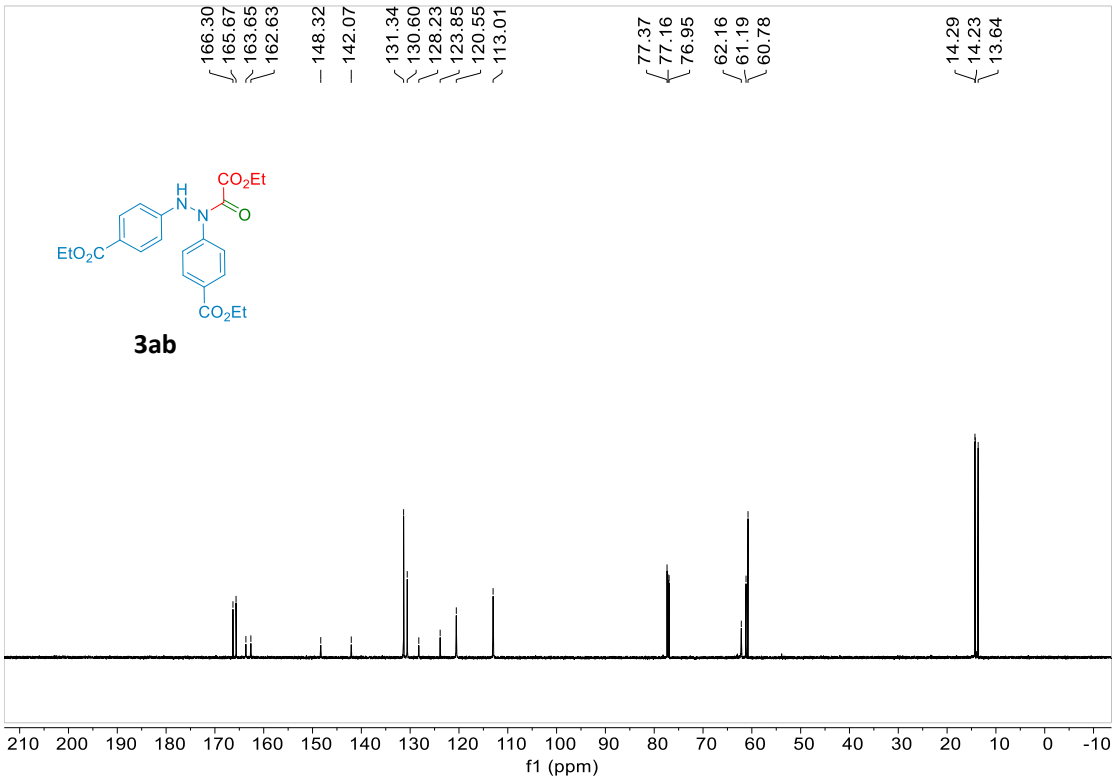


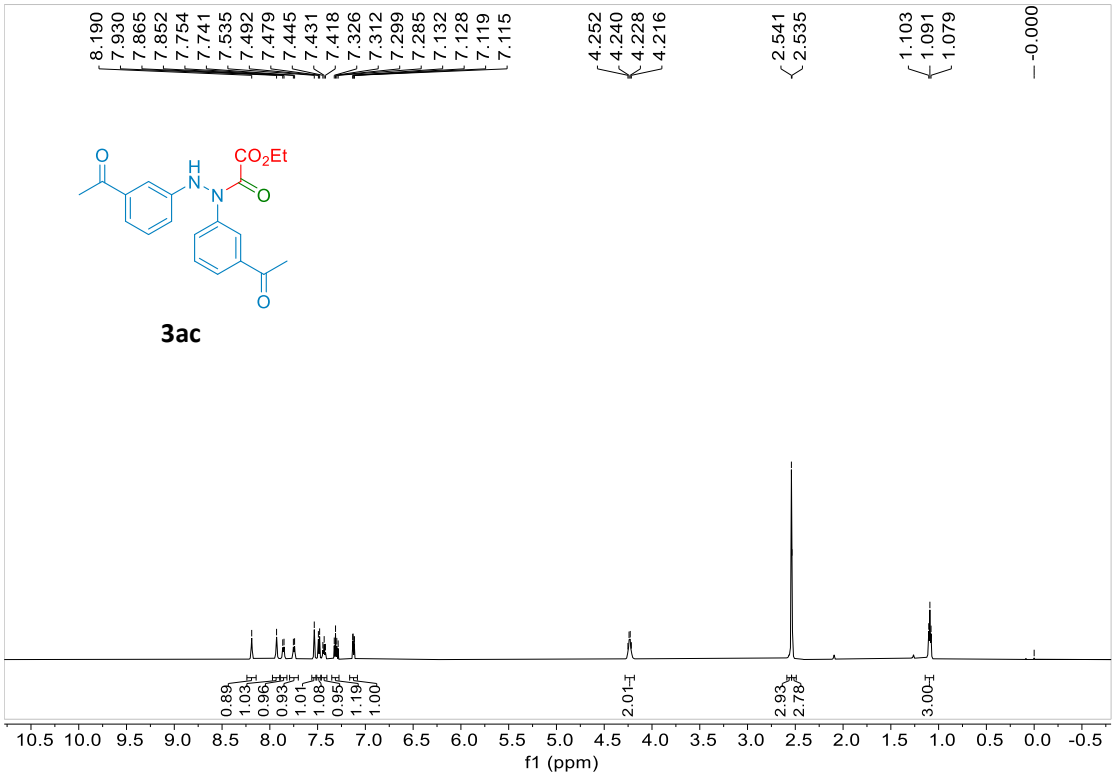
^{1}H NMR spectrum of **3ab** (600 MHz, $CDCl_3$):



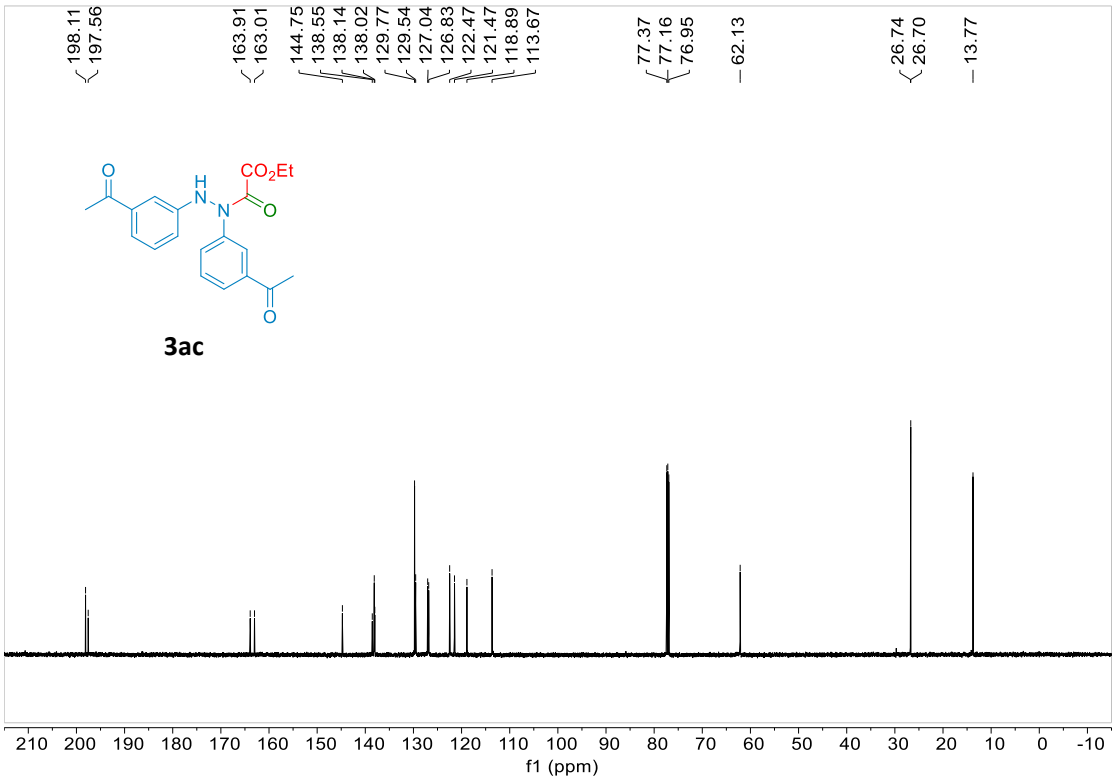
^{13}C NMR spectrum of **3ab** (150 MHz, $CDCl_3$):



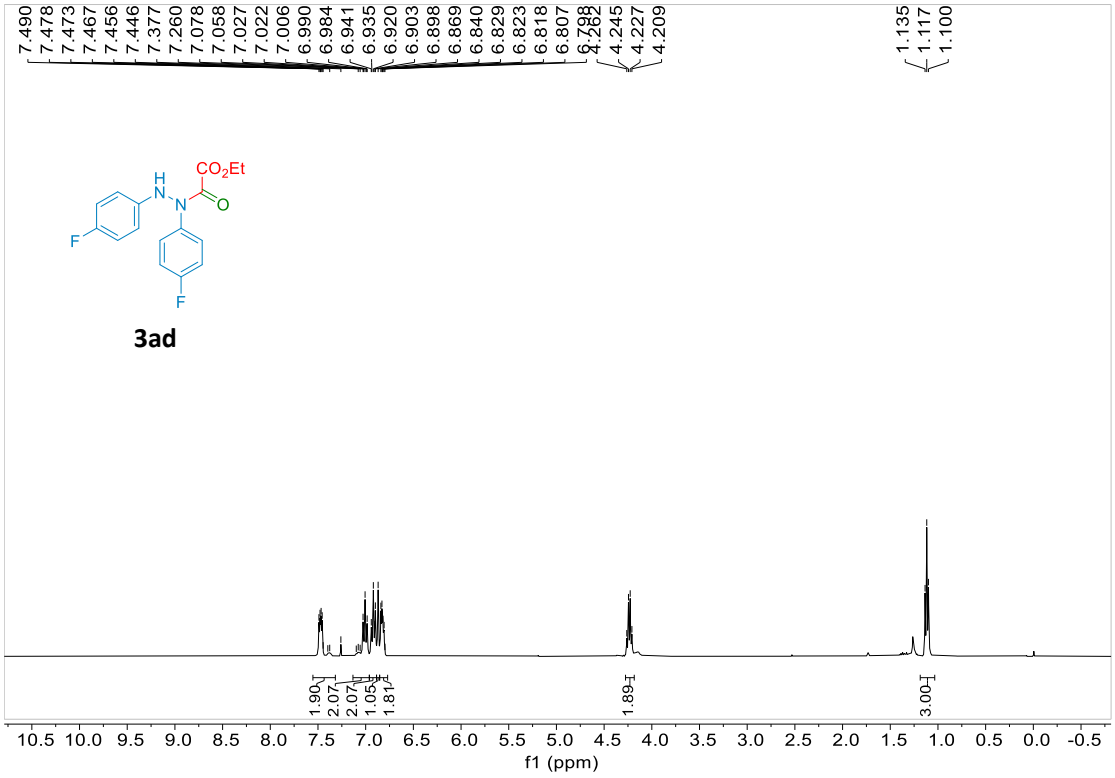
^{1}H NMR spectrum of **3ac** (600 MHz, $CDCl_3$):



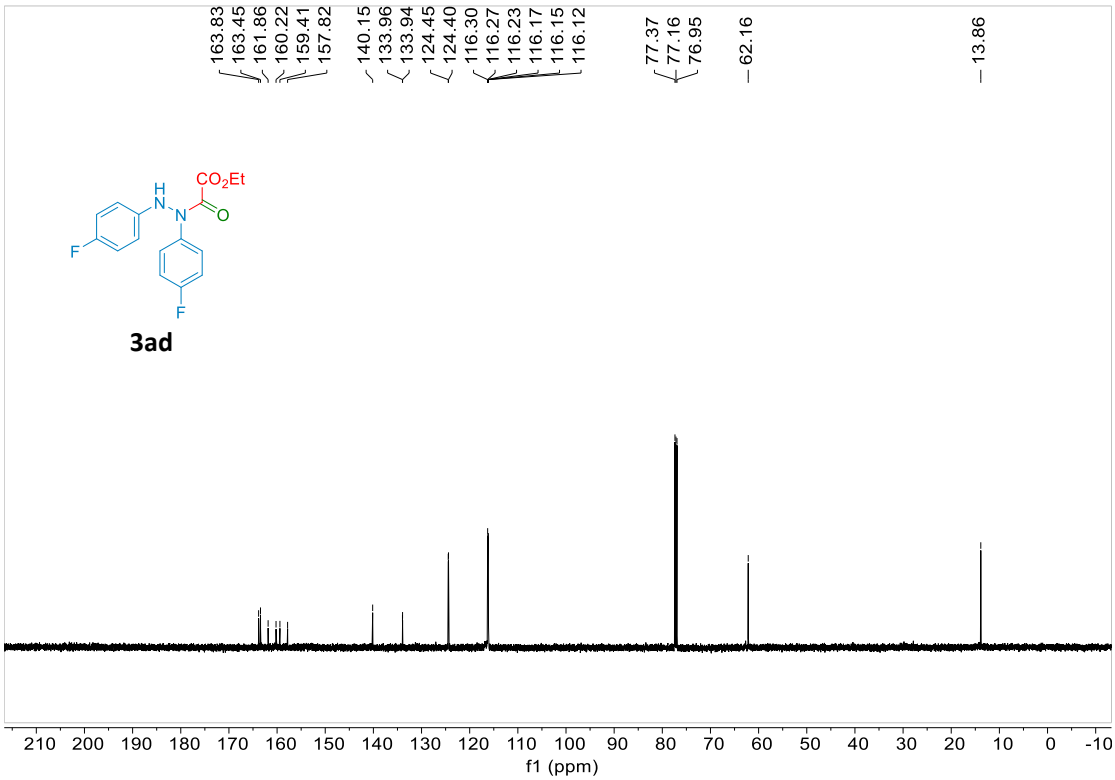
^{13}C NMR spectrum of **3ac** (150 MHz, $CDCl_3$):



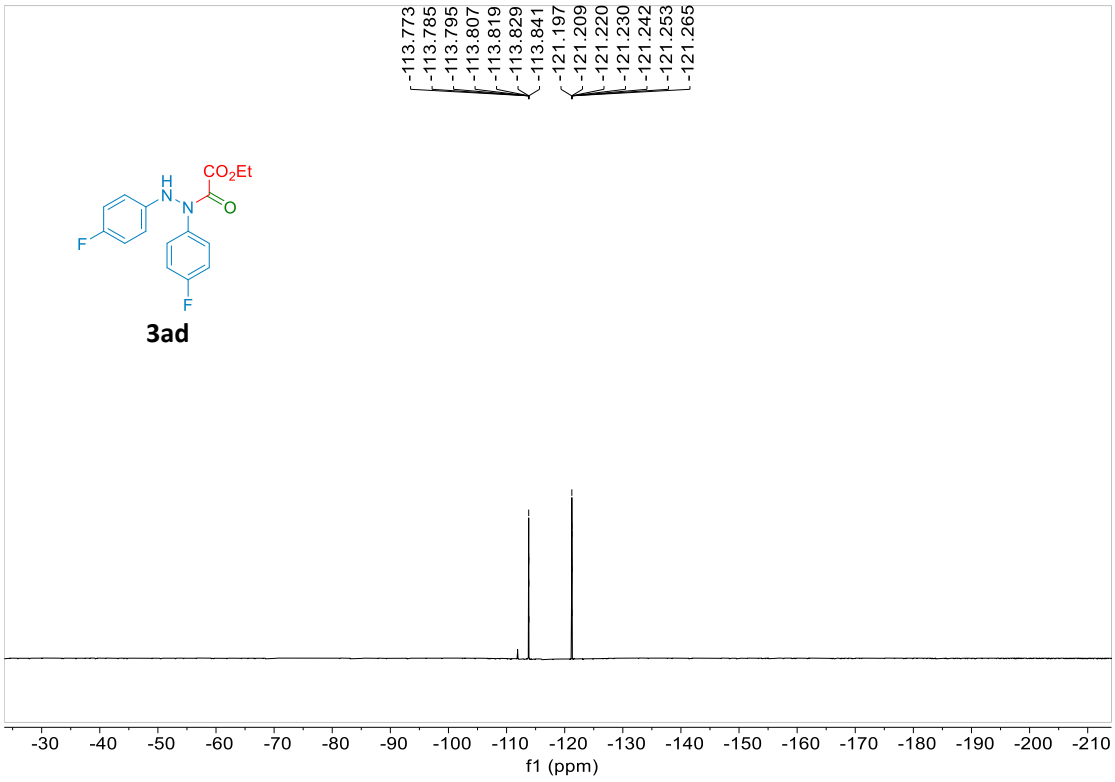
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$):



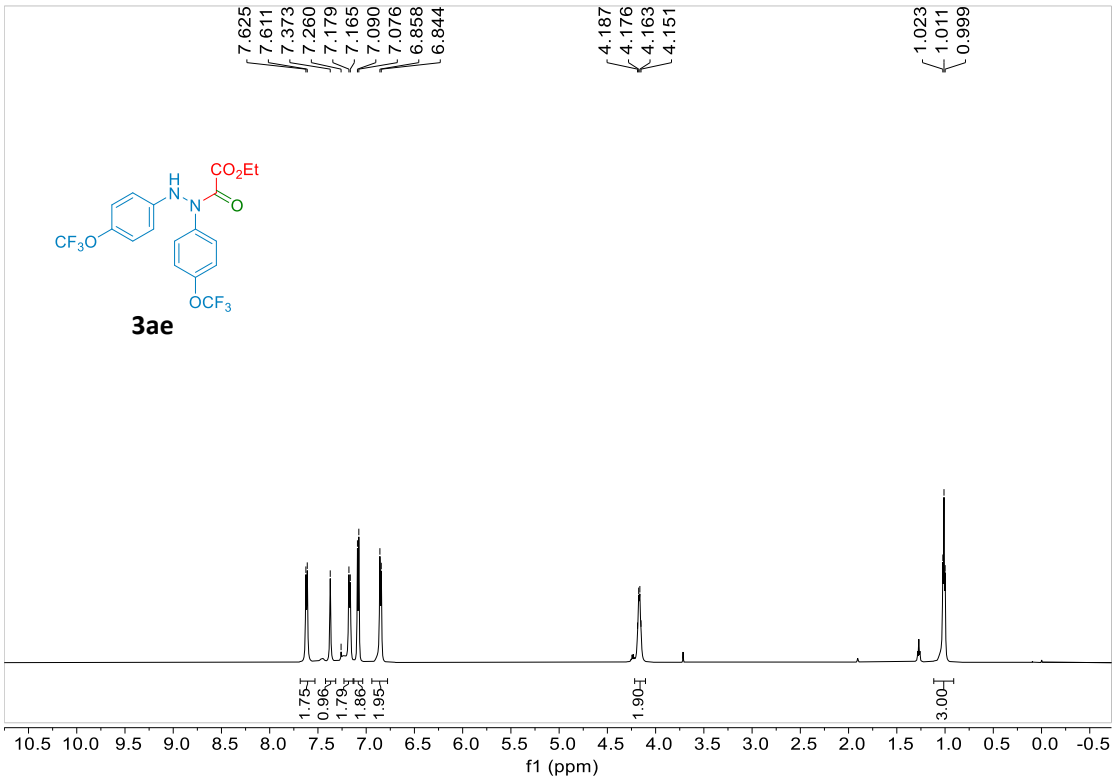
^{13}C NMR spectrum of **3ad** (150 MHz, $CDCl_3$):



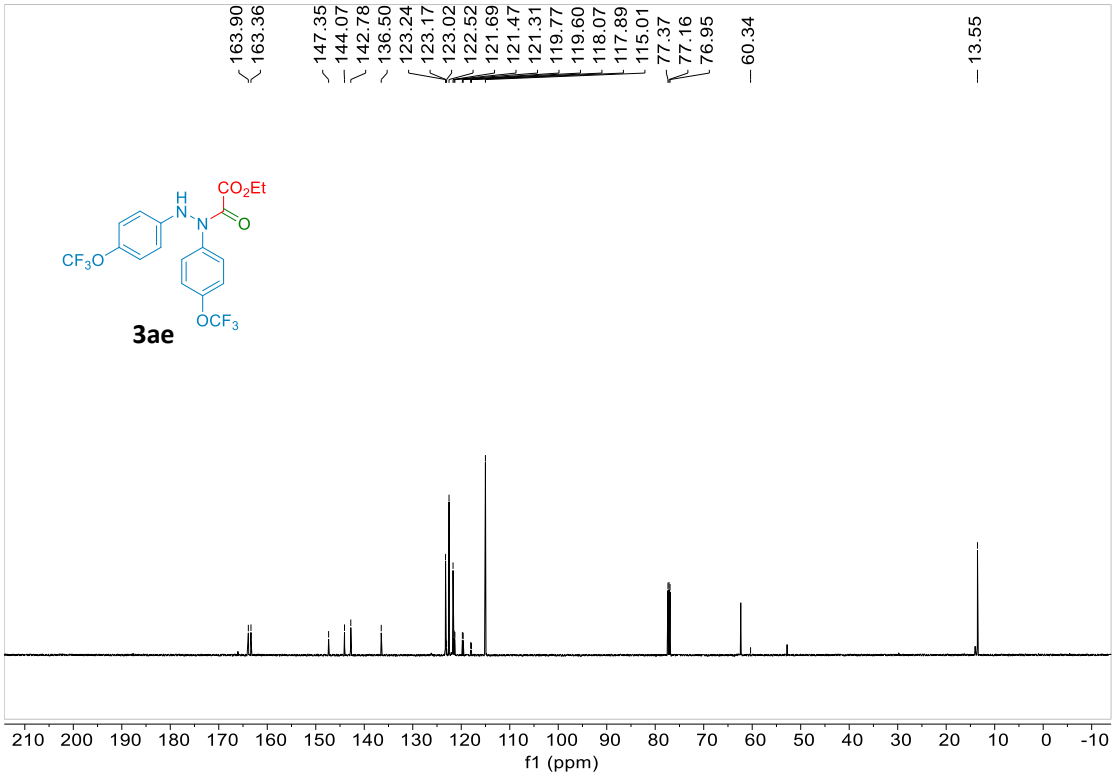
^{19}F NMR spectrum of **3ad** (376 MHz, $CDCl_3$):



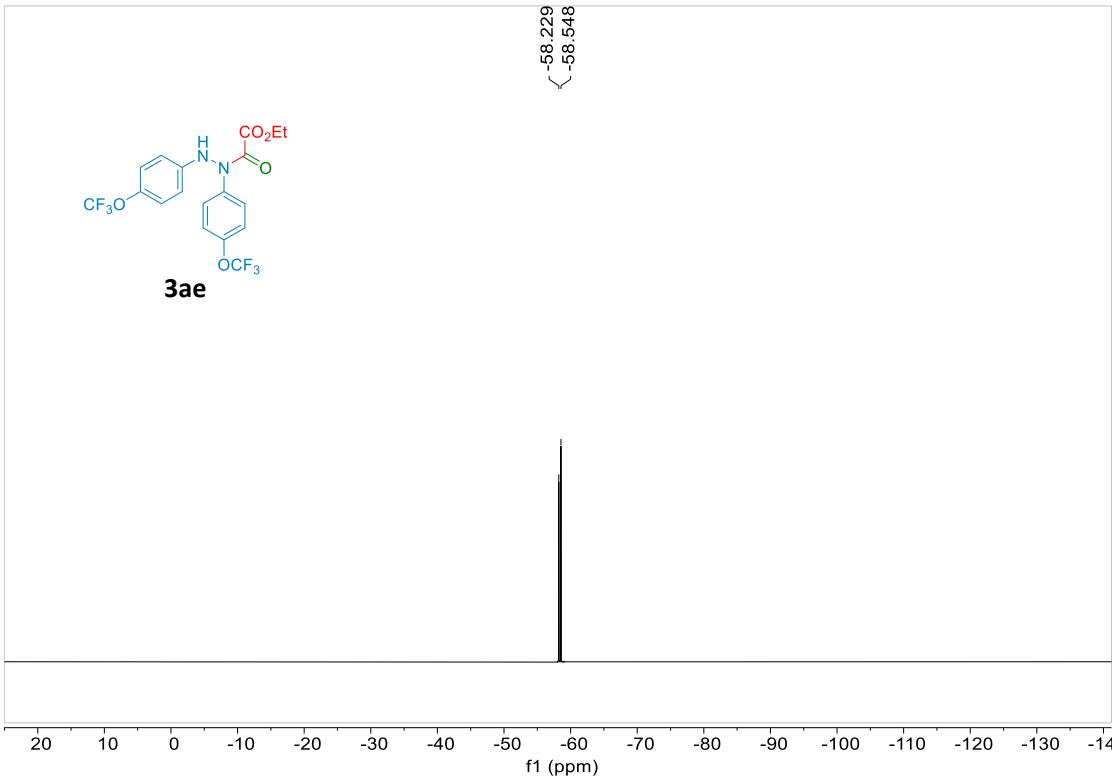
^{1}H NMR spectrum of **3ae** (600 MHz, $CDCl_3$):



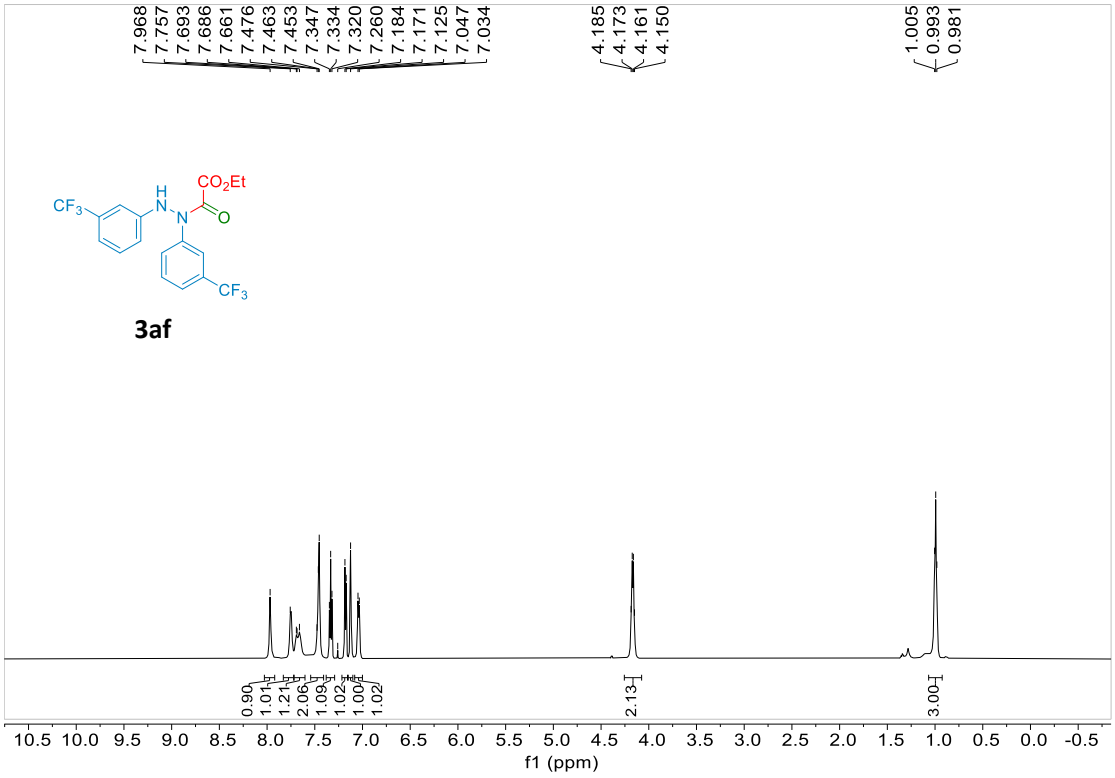
^{13}C NMR spectrum of **3ae** (150 MHz, $CDCl_3$):



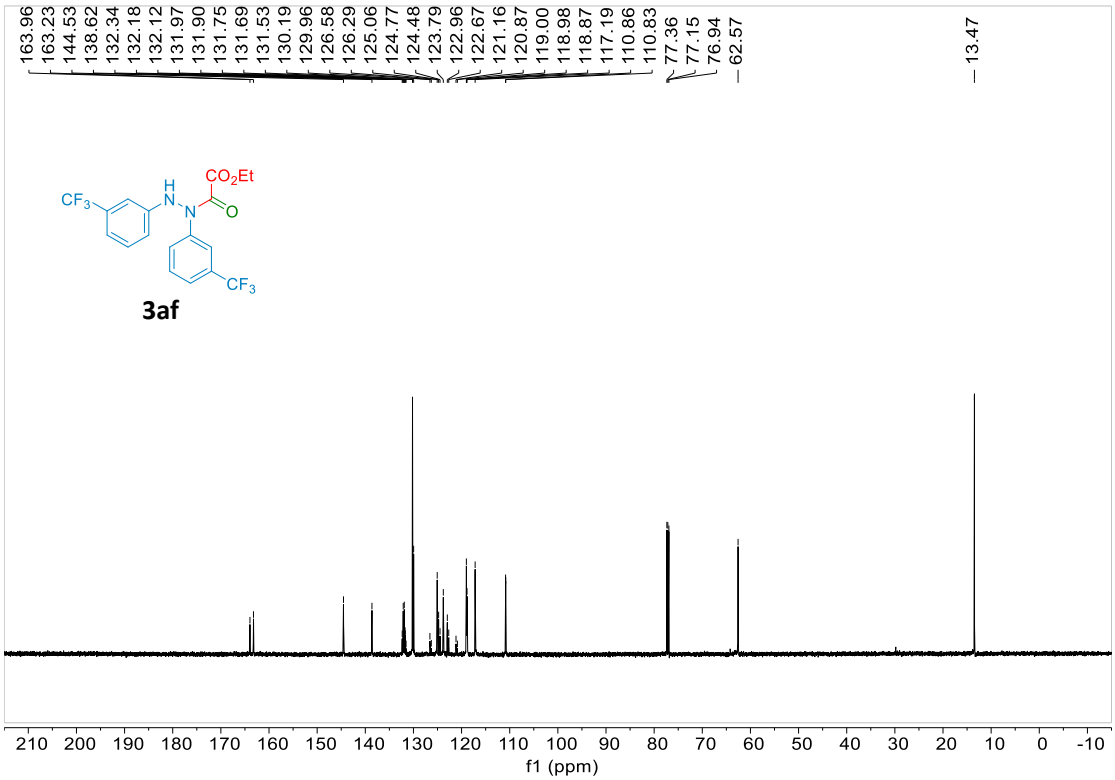
^{19}F NMR spectrum of **3ae** (376 MHz, $CDCl_3$):



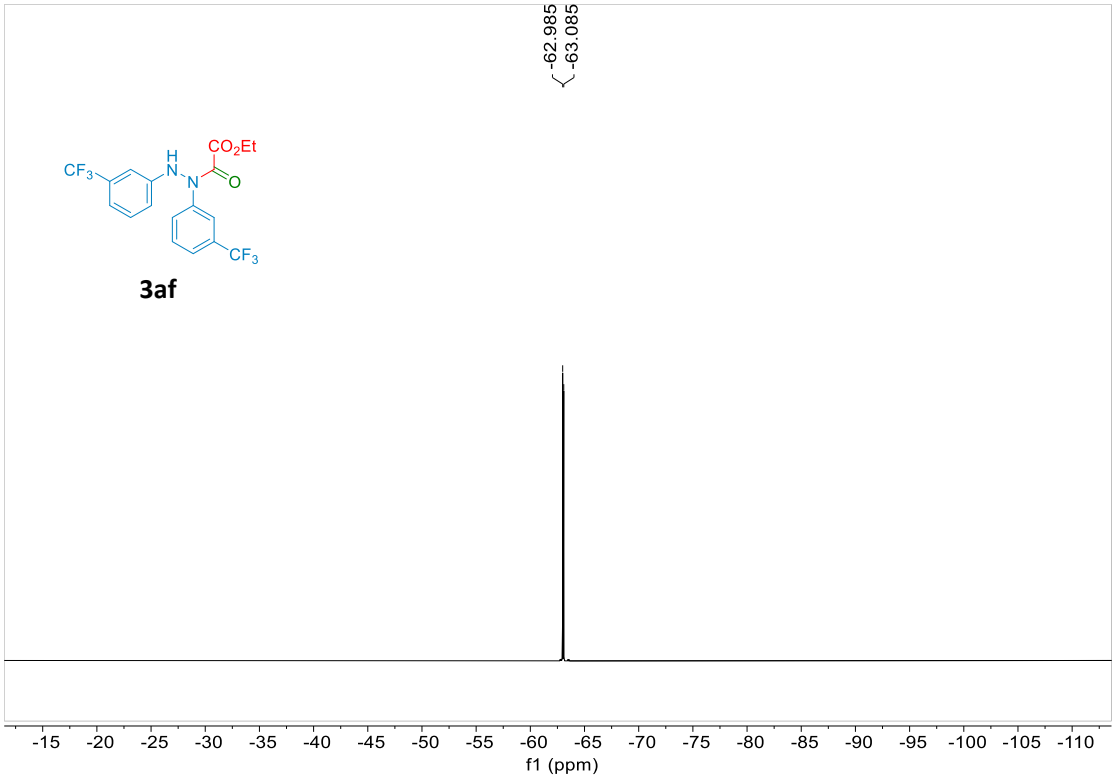
^{1}H NMR spectrum of **3af** (600 MHz, $CDCl_3$):



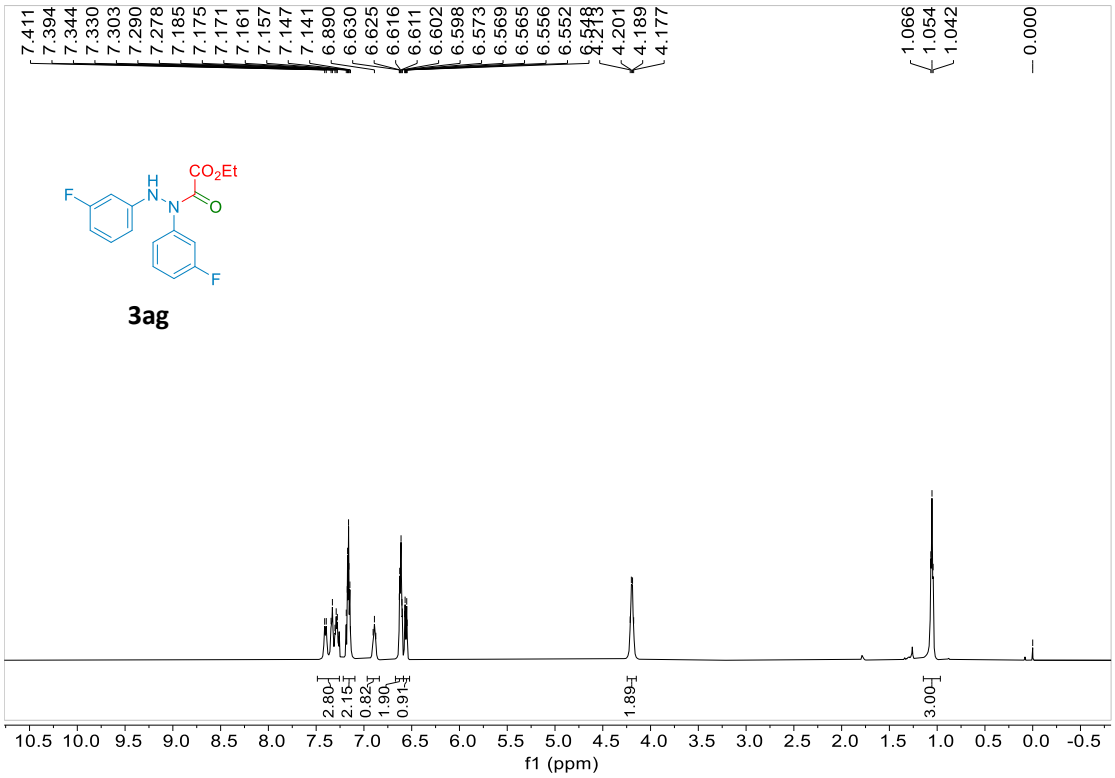
^{13}C NMR spectrum of **3af** (150 MHz, $CDCl_3$):



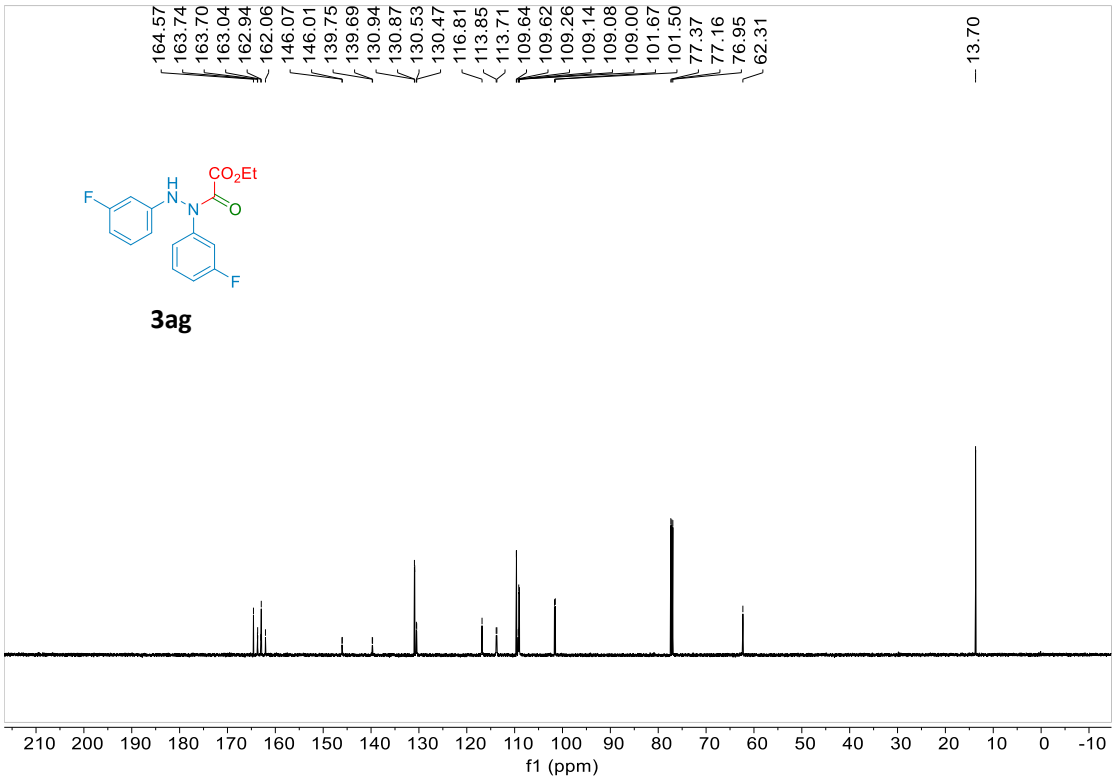
^{19}F NMR spectrum of **3af** (376 MHz, $CDCl_3$):



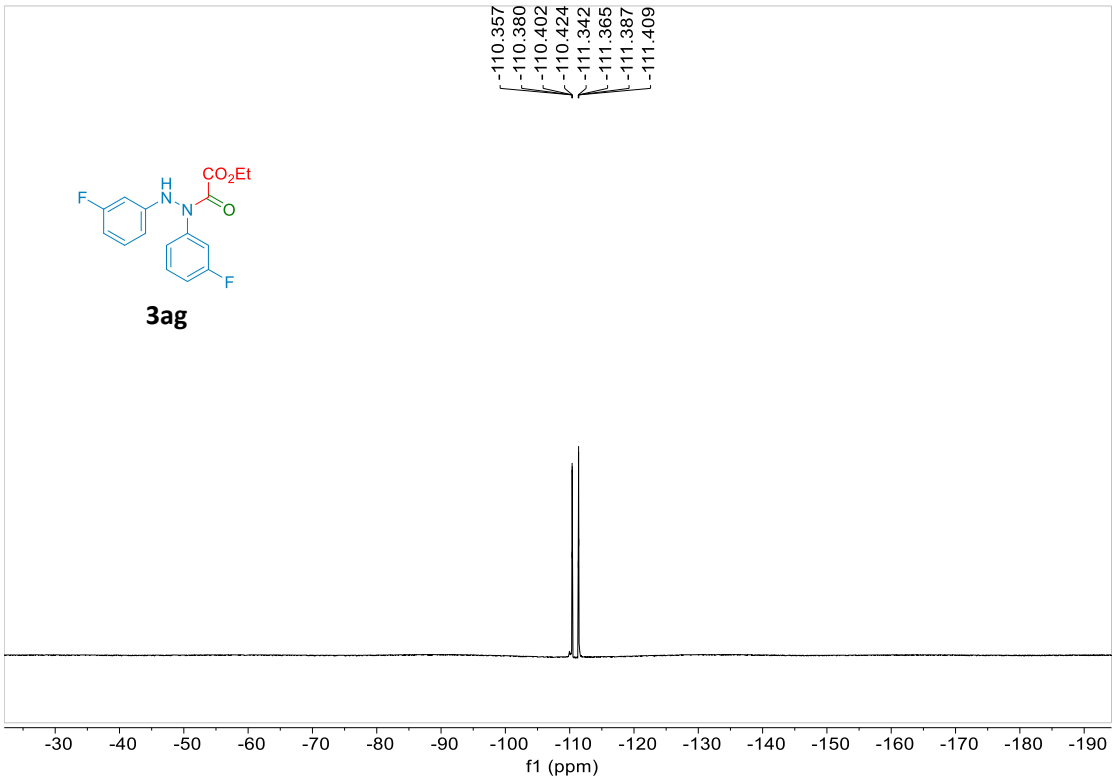
^{1}H NMR spectrum of **3ag** (600 MHz, $CDCl_3$):



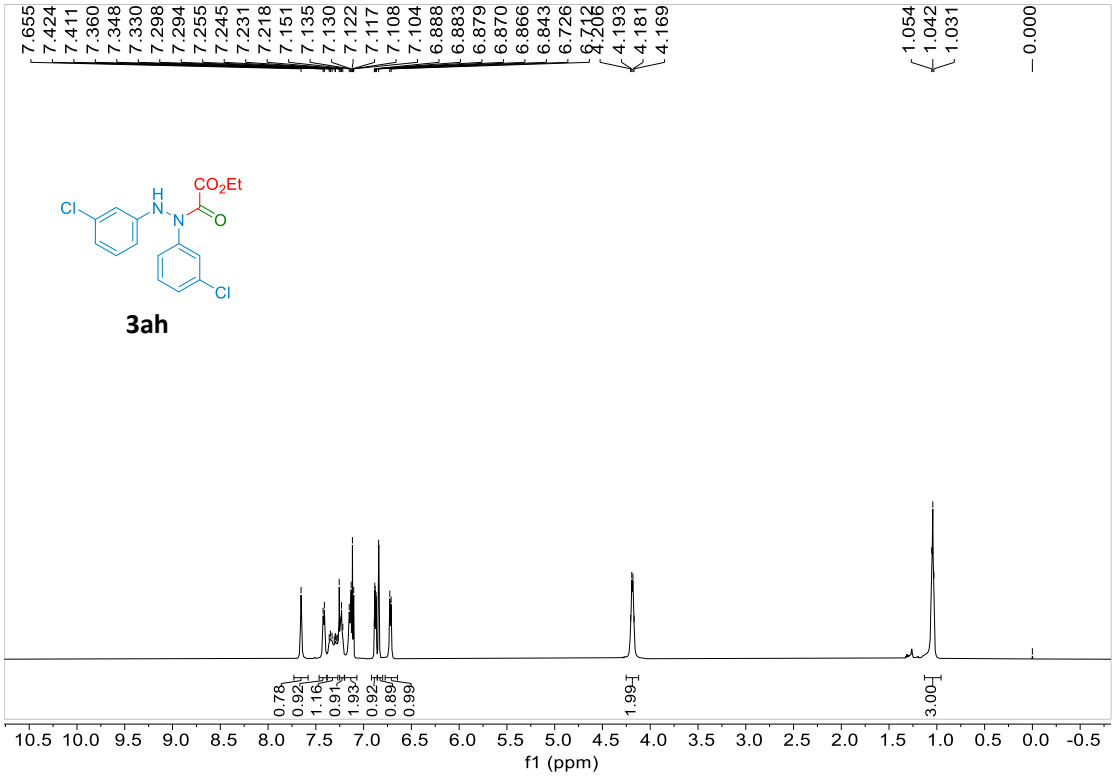
^{13}C NMR spectrum of **3ag** (150 MHz, $CDCl_3$):



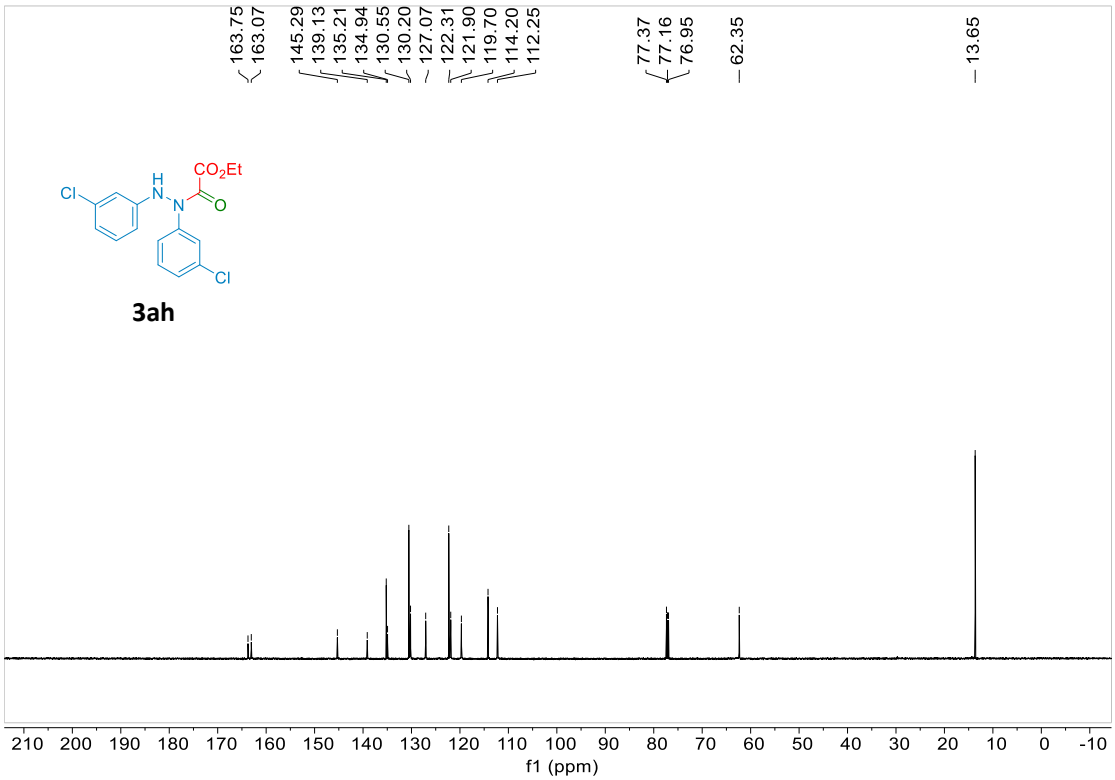
^{19}F NMR spectrum of **3ag** (376 MHz, $CDCl_3$):



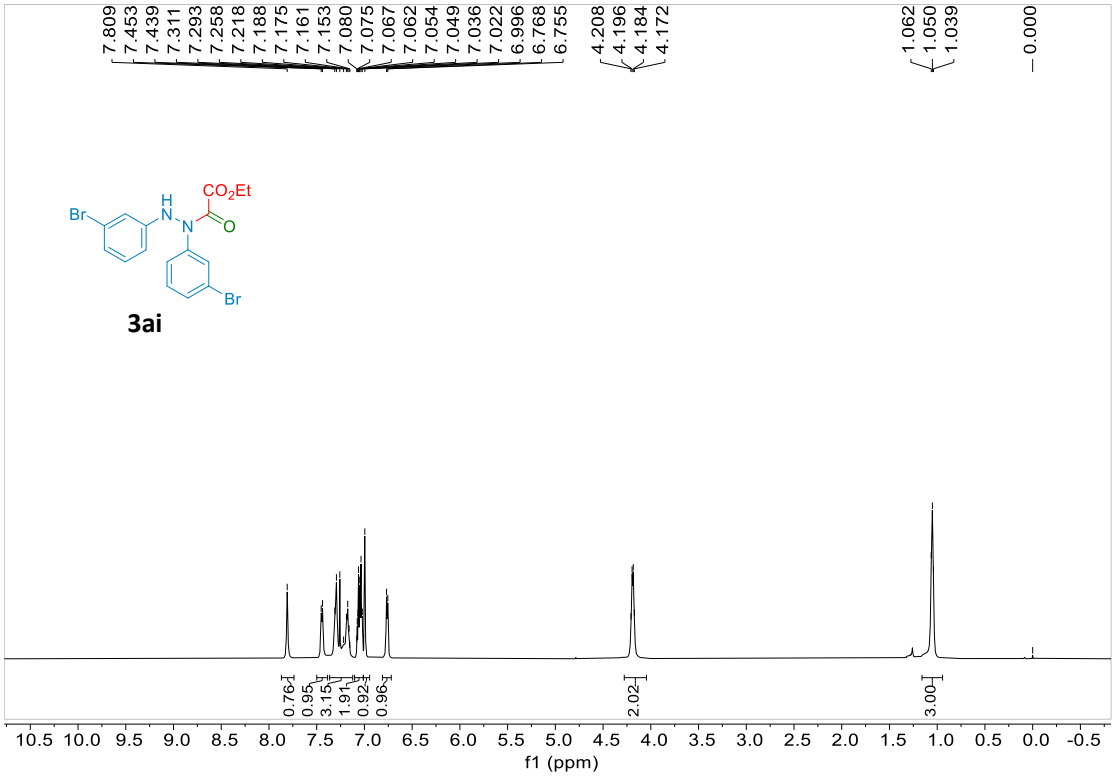
^{1}H NMR spectrum of **3ah** (600 MHz, $CDCl_3$):



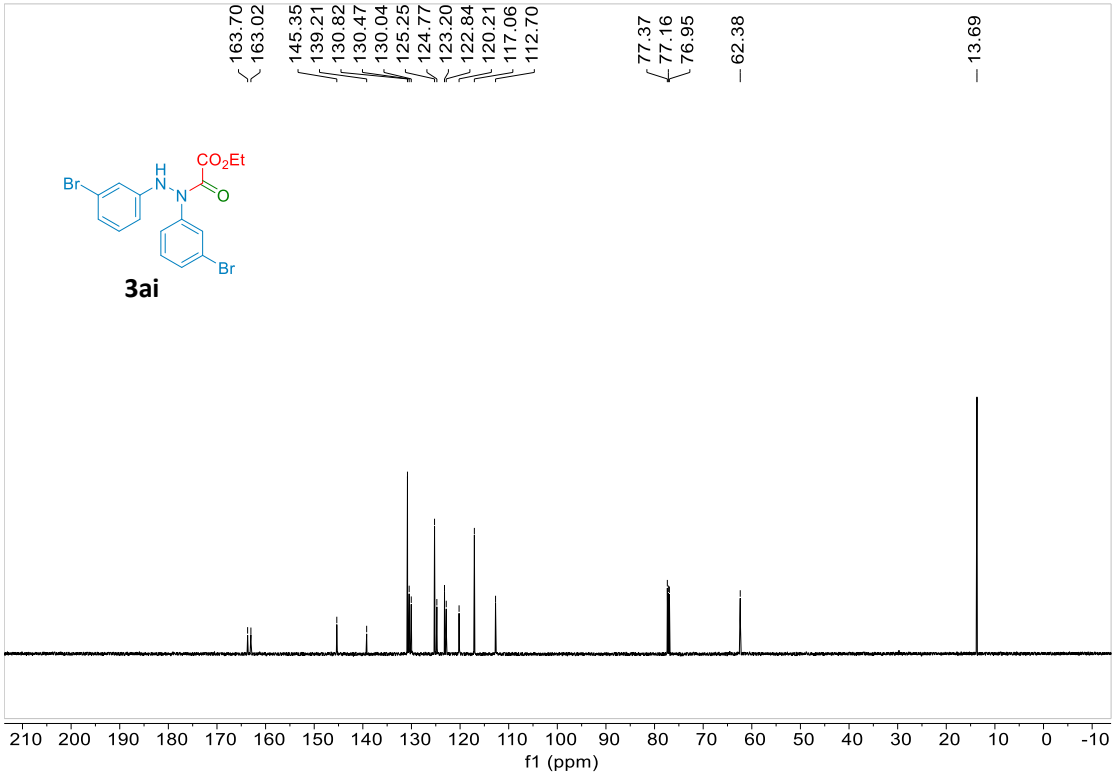
^{13}C NMR spectrum of **3ah** (150 MHz, $CDCl_3$):



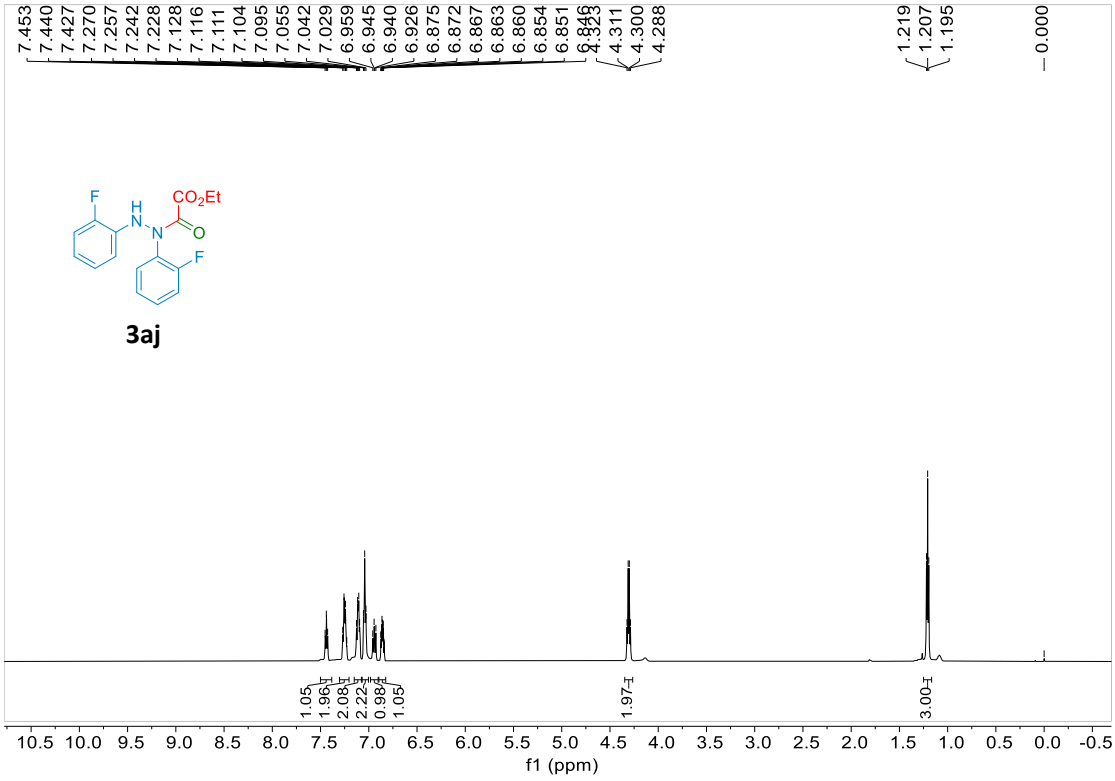
^{1}H NMR spectrum of **3ai** (600 MHz, $CDCl_3$):



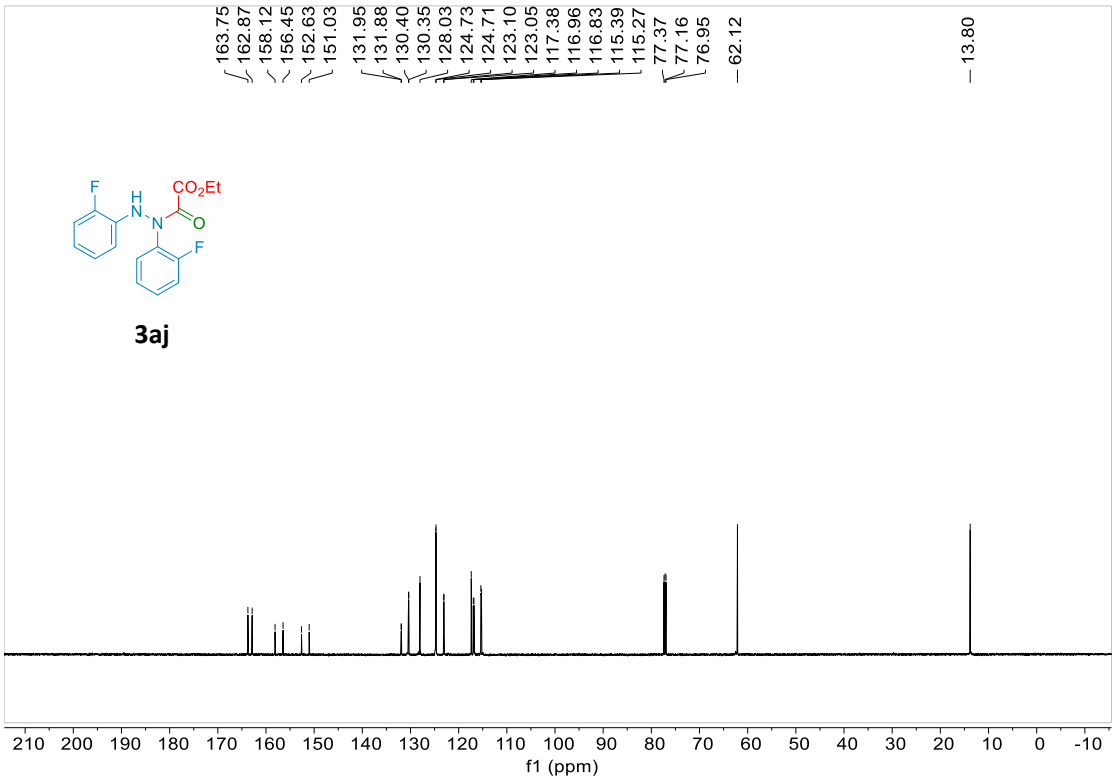
^{13}C NMR spectrum of **3ai** (150 MHz, $CDCl_3$):



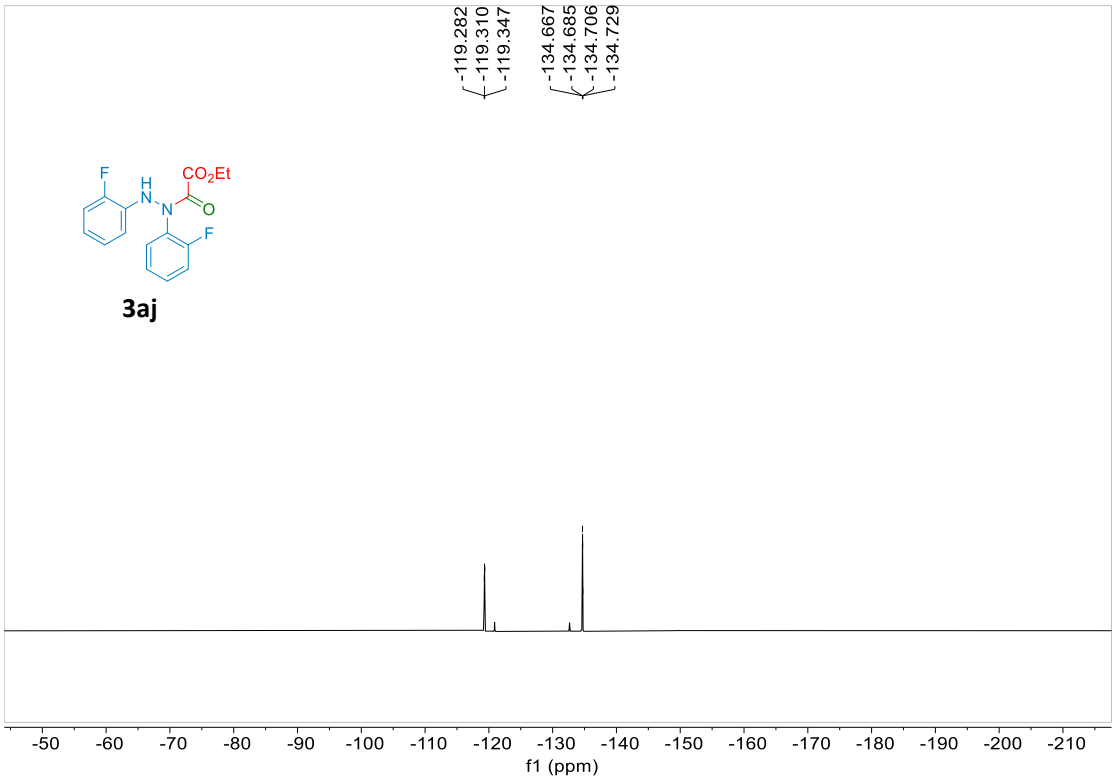
^{1}H NMR spectrum of **3aj** (600 MHz, $CDCl_3$):



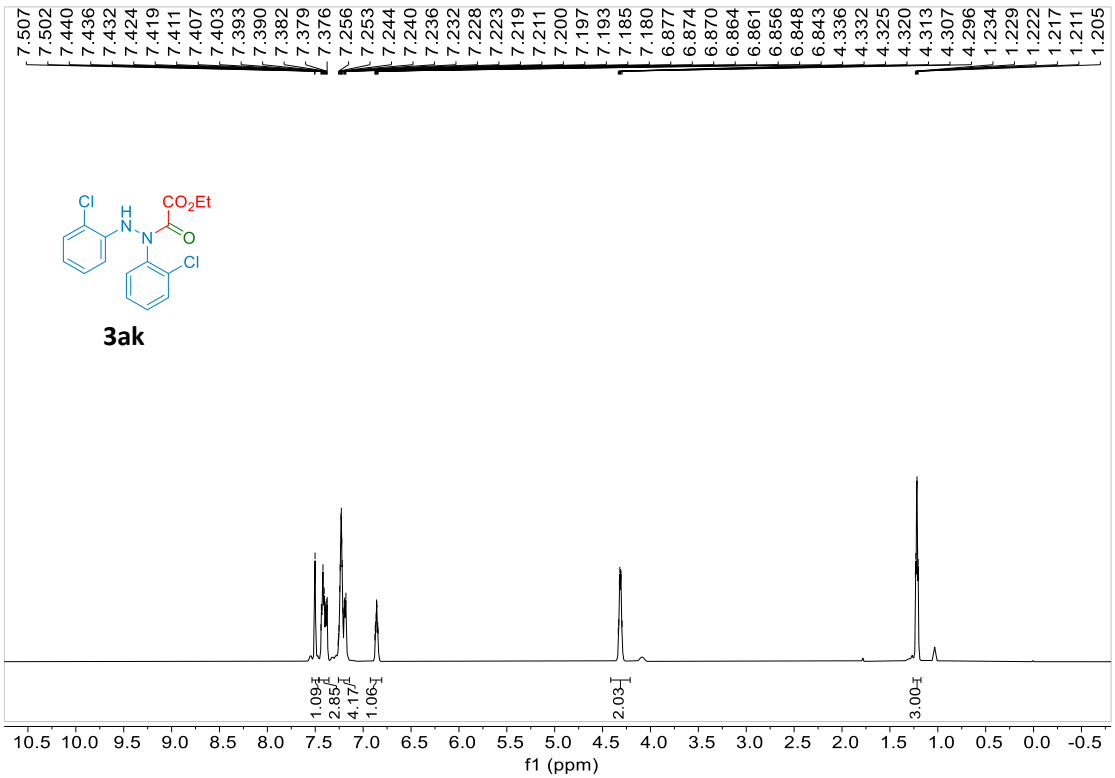
^{13}C NMR spectrum of **3aj** (150 MHz, $CDCl_3$):



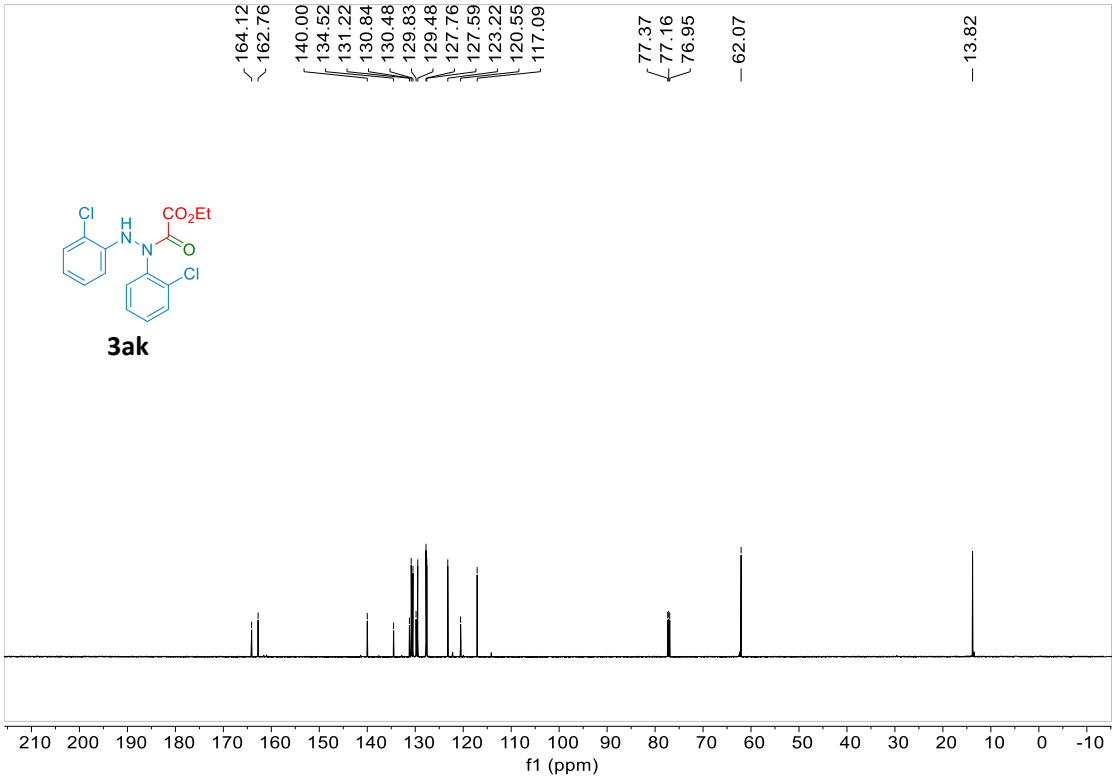
^{19}F NMR spectrum of **3aj** (376 MHz, $CDCl_3$):



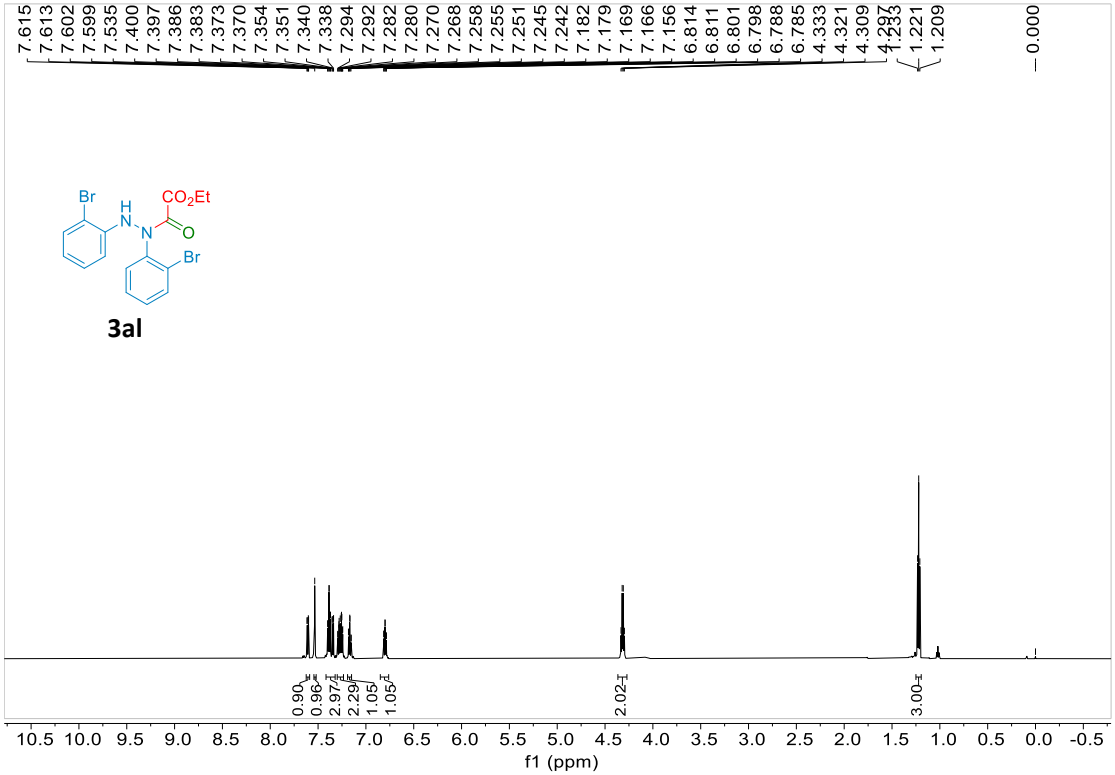
^{1}H NMR spectrum of **3ak** (600 MHz, $CDCl_3$):



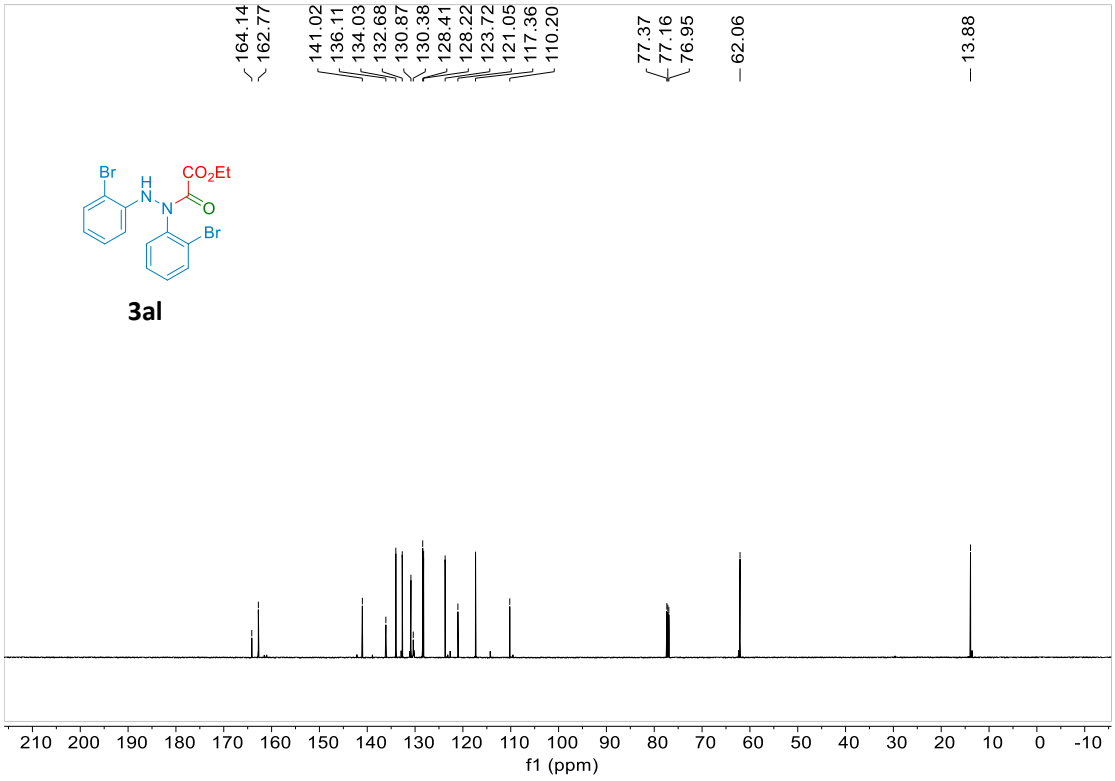
^{13}C NMR spectrum of **3ak** (150 MHz, $CDCl_3$):



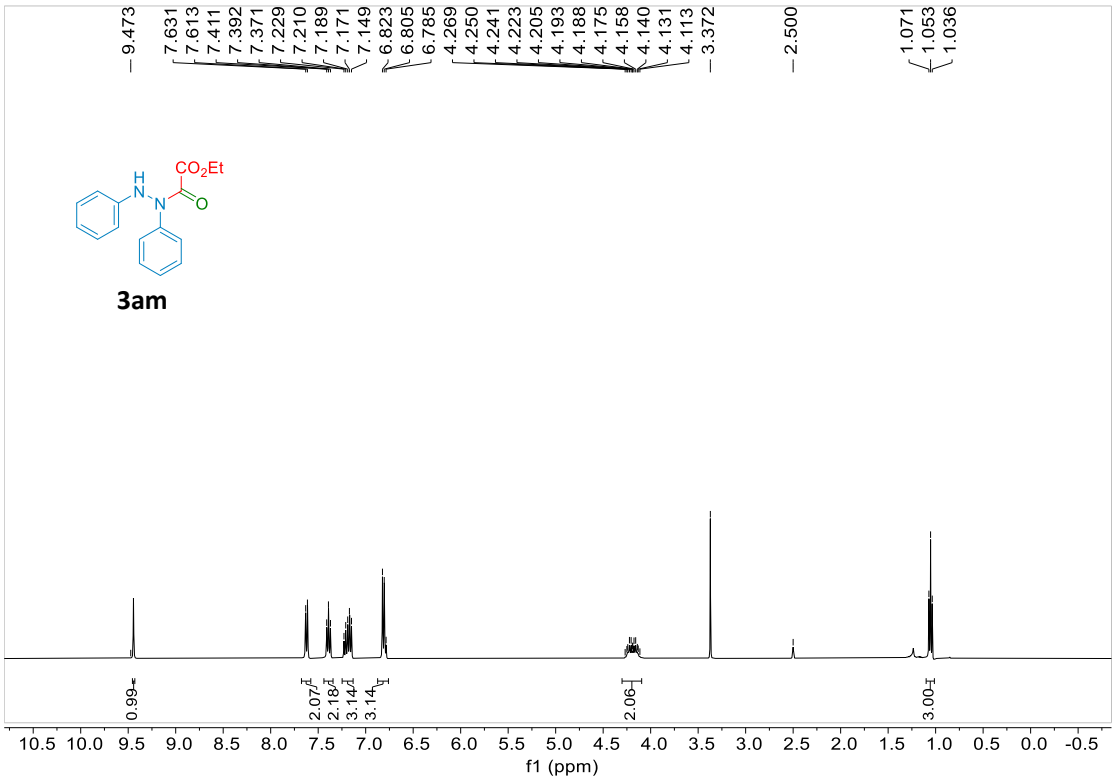
^{1}H NMR spectrum of **3al** (600 MHz, $CDCl_3$):



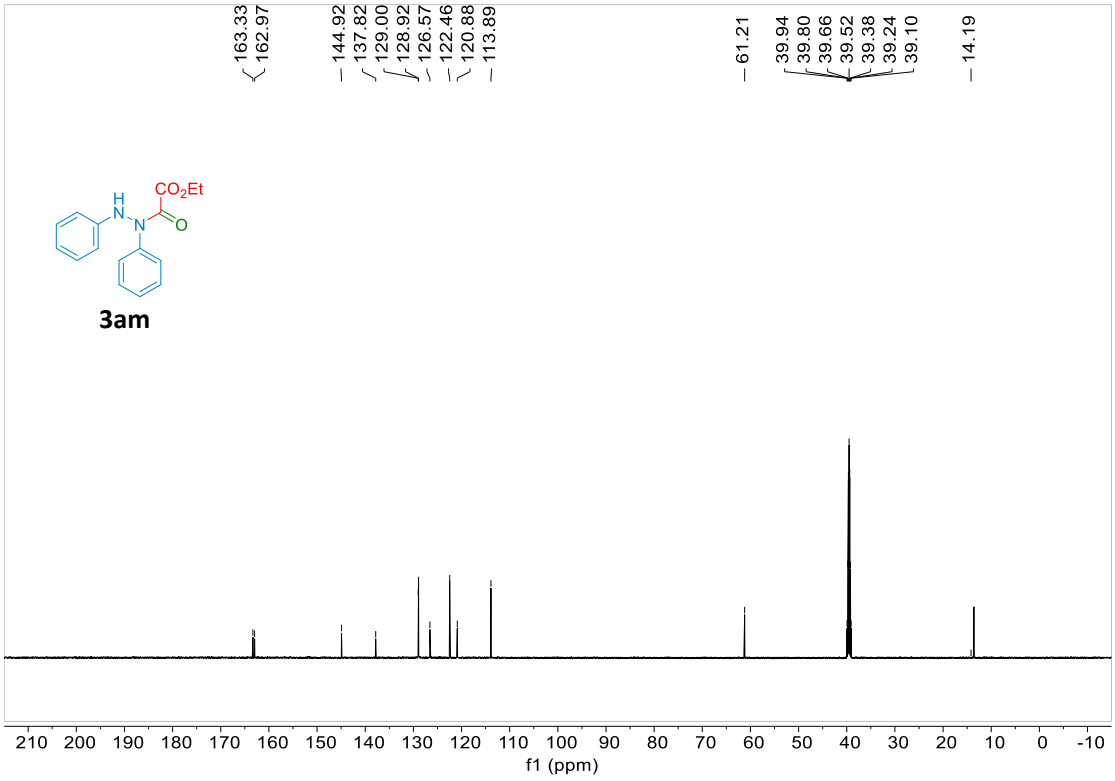
^{13}C NMR spectrum of **3al** (150 MHz, $CDCl_3$):



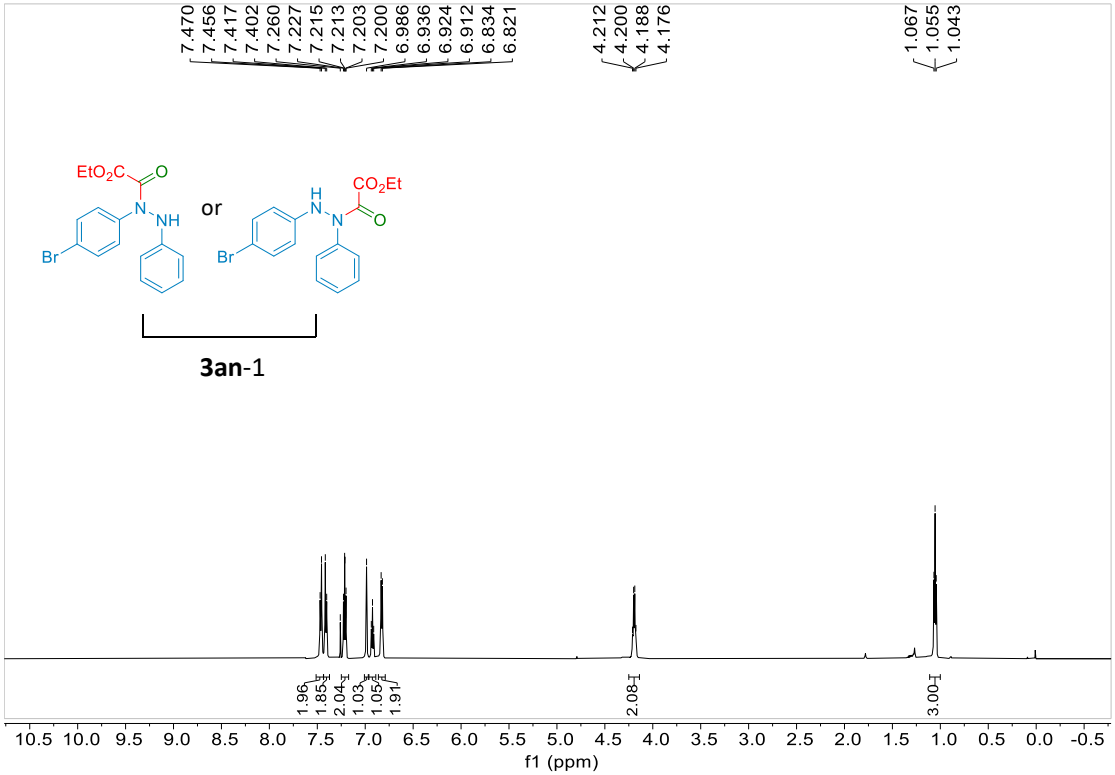
^{1}H NMR spectrum of **3am** (400 MHz, DMSO-d_6):



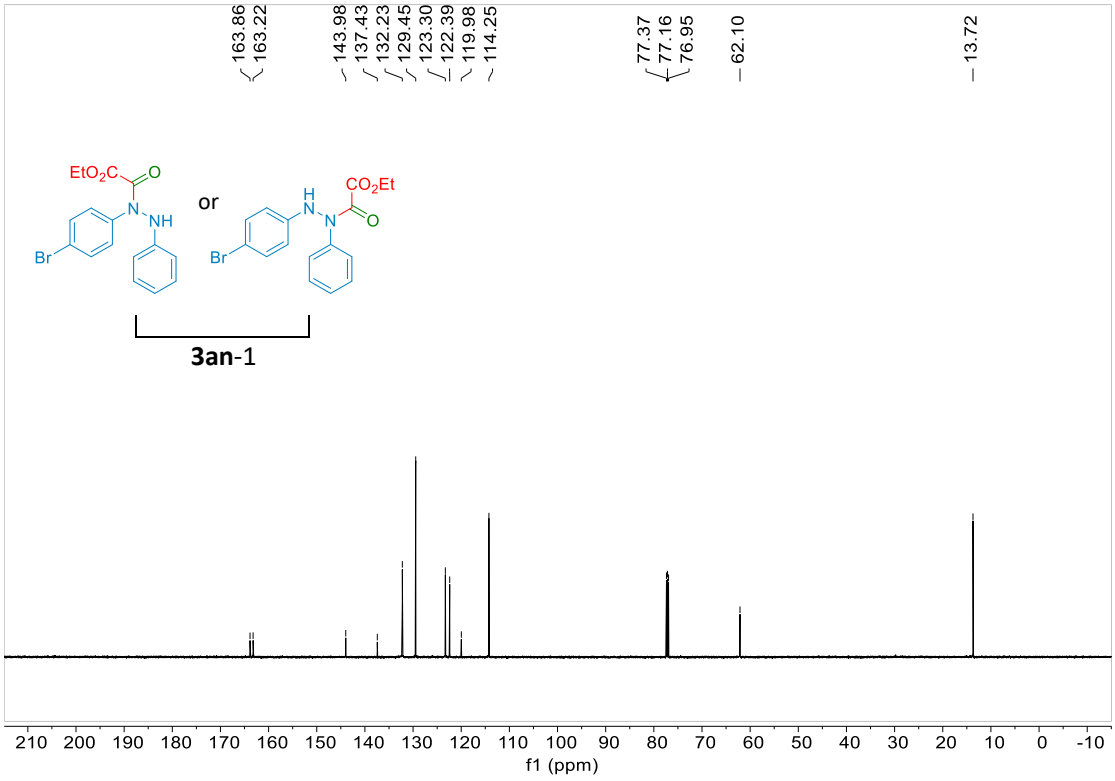
^{13}C NMR spectrum of **3am** (150 MHz, DMSO-d_6):



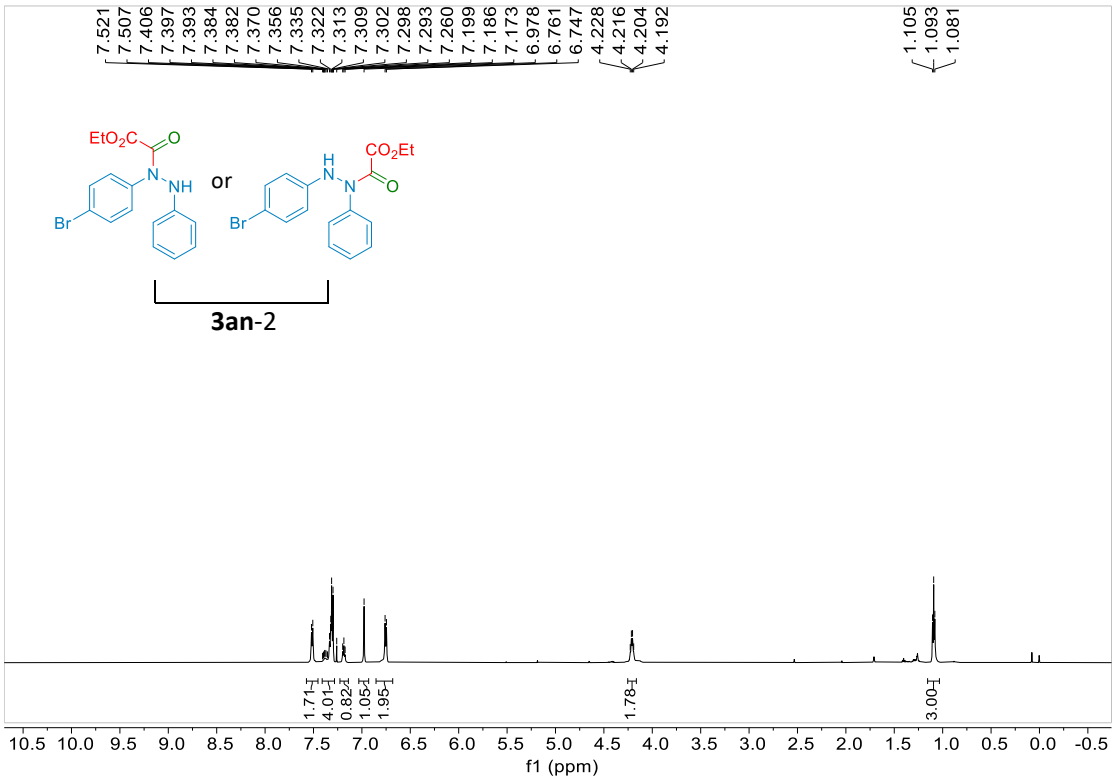
^{1}H NMR spectrum of **3an**-1 (600 MHz, $CDCl_3$):



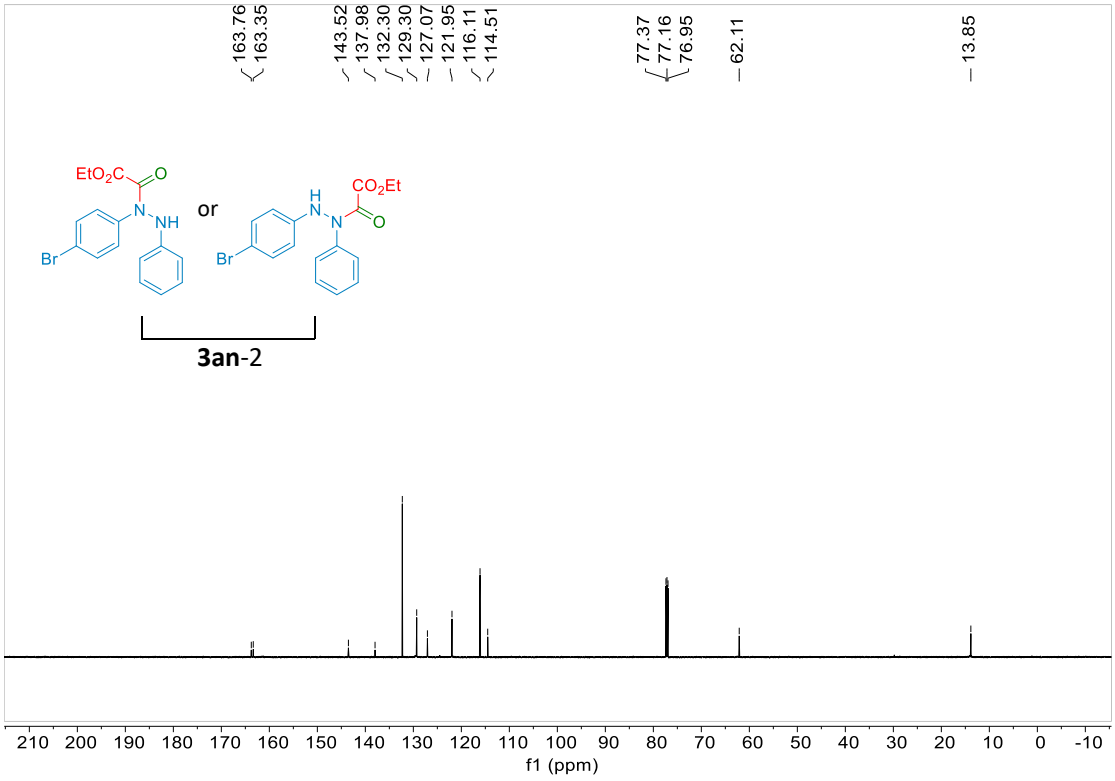
^{13}C NMR spectrum of **3an**-1 (150 MHz, $CDCl_3$):



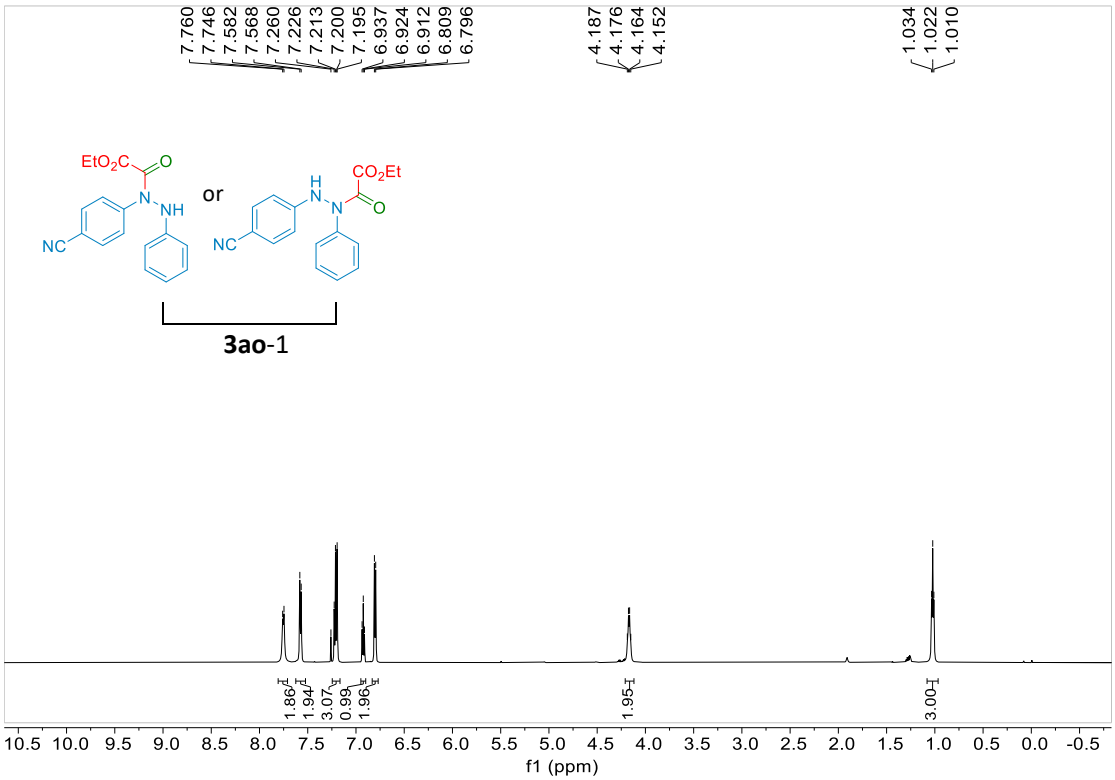
^{1}H NMR spectrum of **3an**-2 (600 MHz, $CDCl_3$):



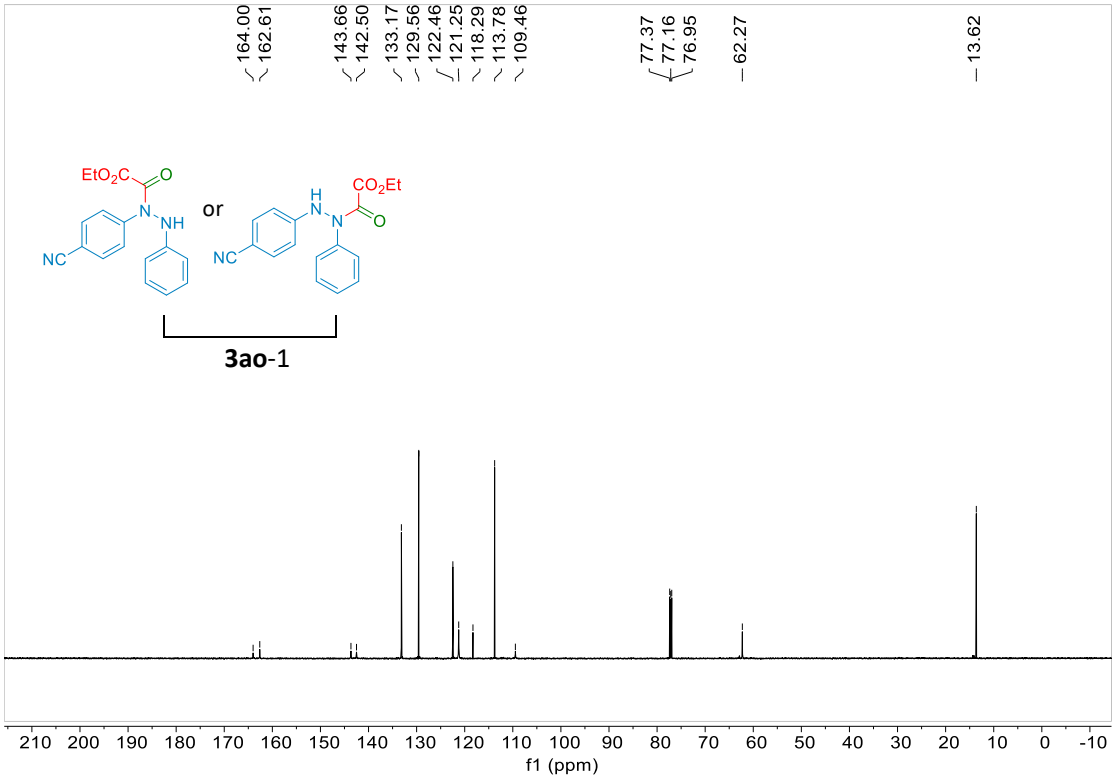
^{13}C NMR spectrum of **3an**-2 (150 MHz, $CDCl_3$):



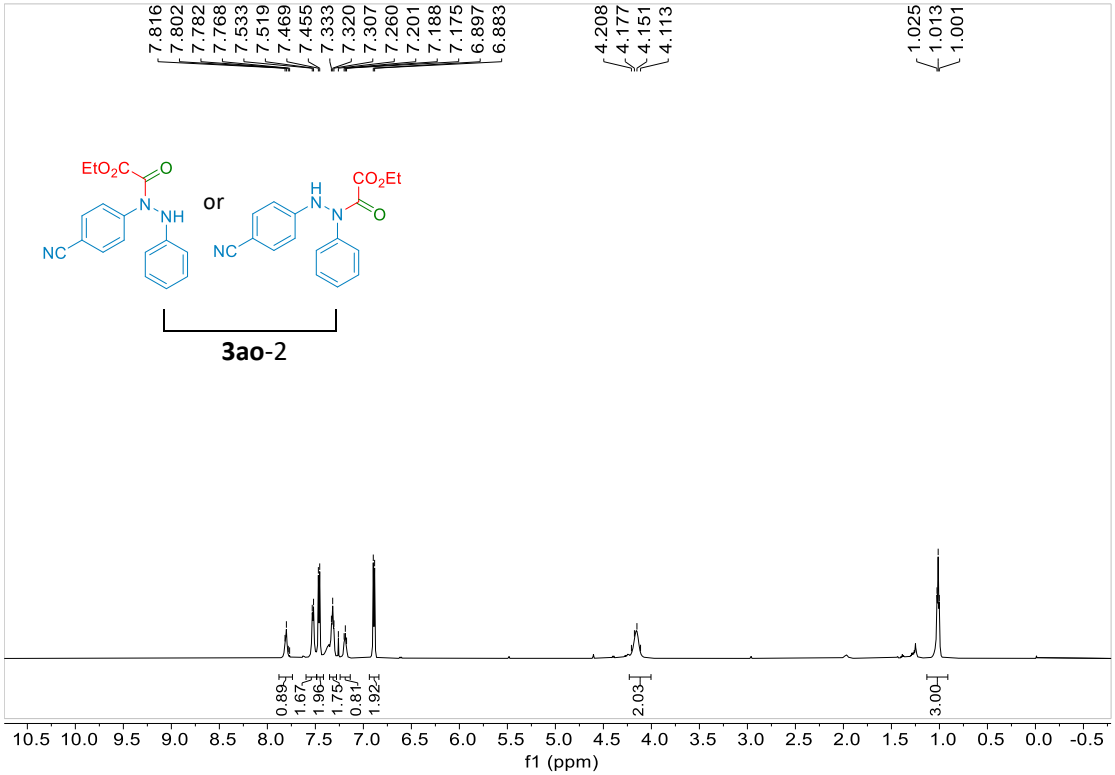
^{1}H NMR spectrum of **3ao**-1 (600 MHz, $CDCl_3$):



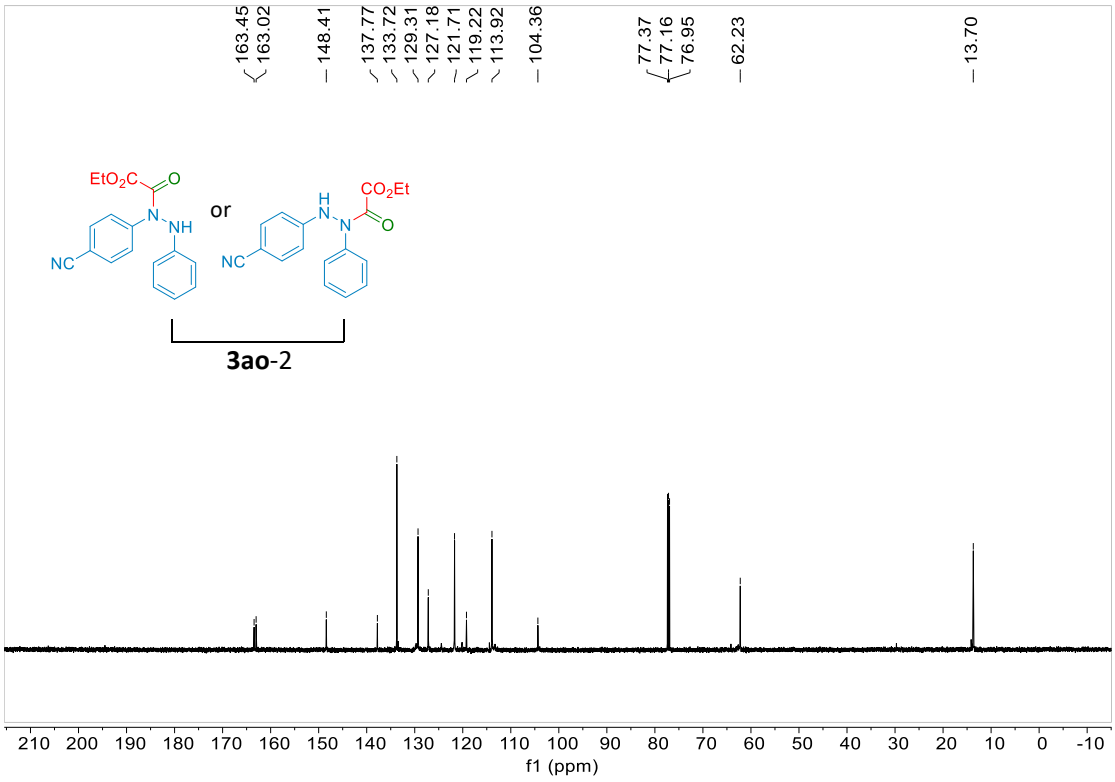
^{13}C NMR spectrum of **3ao**-1 (150 MHz, $CDCl_3$):



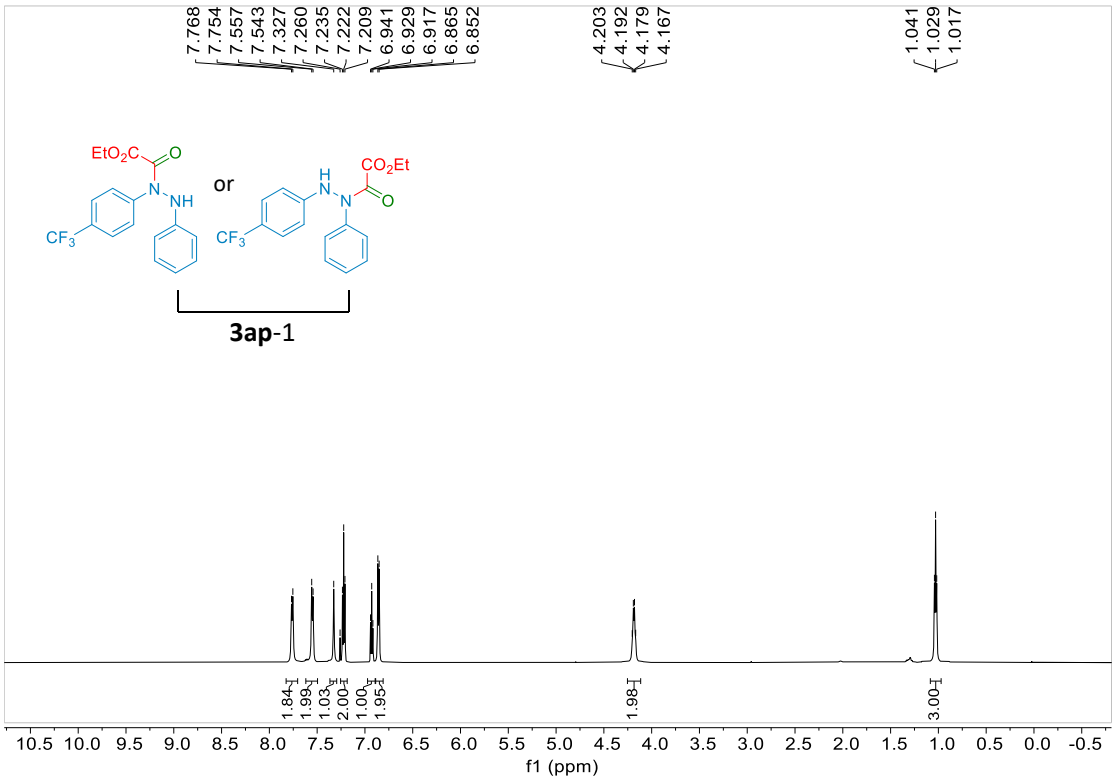
^{1}H NMR spectrum of **3ao**-2 (600 MHz, $CDCl_3$):



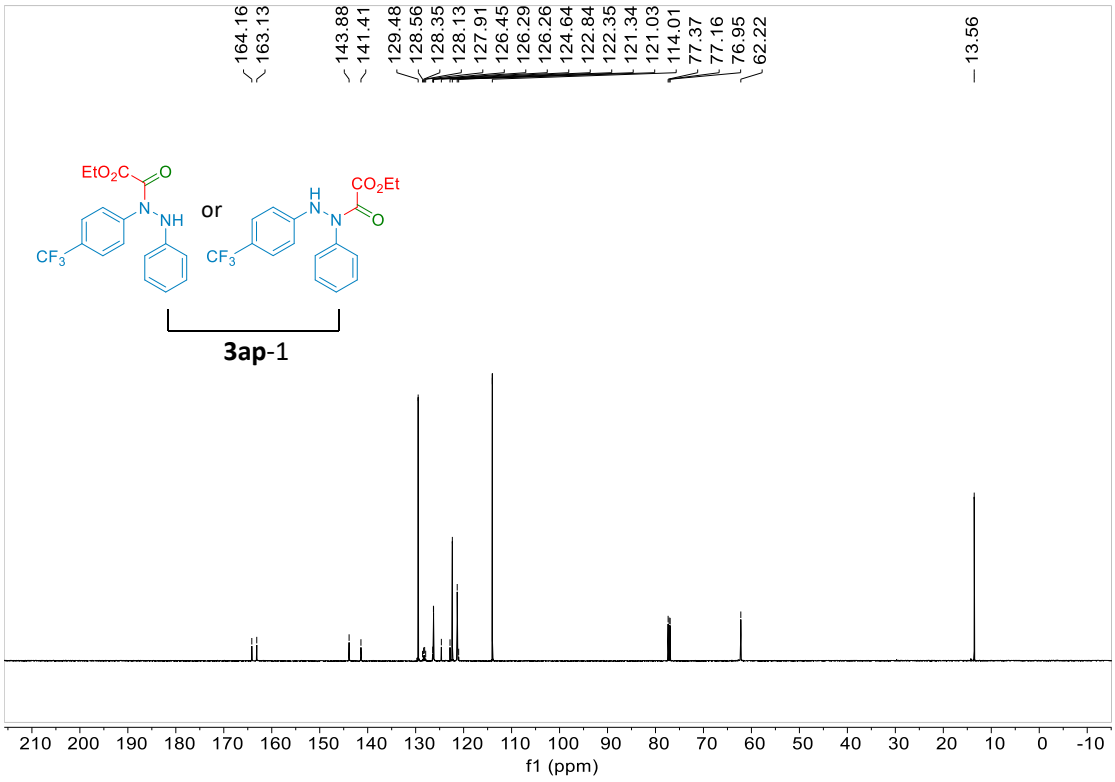
^{13}C NMR spectrum of **3ao**-2 (150 MHz, $CDCl_3$):



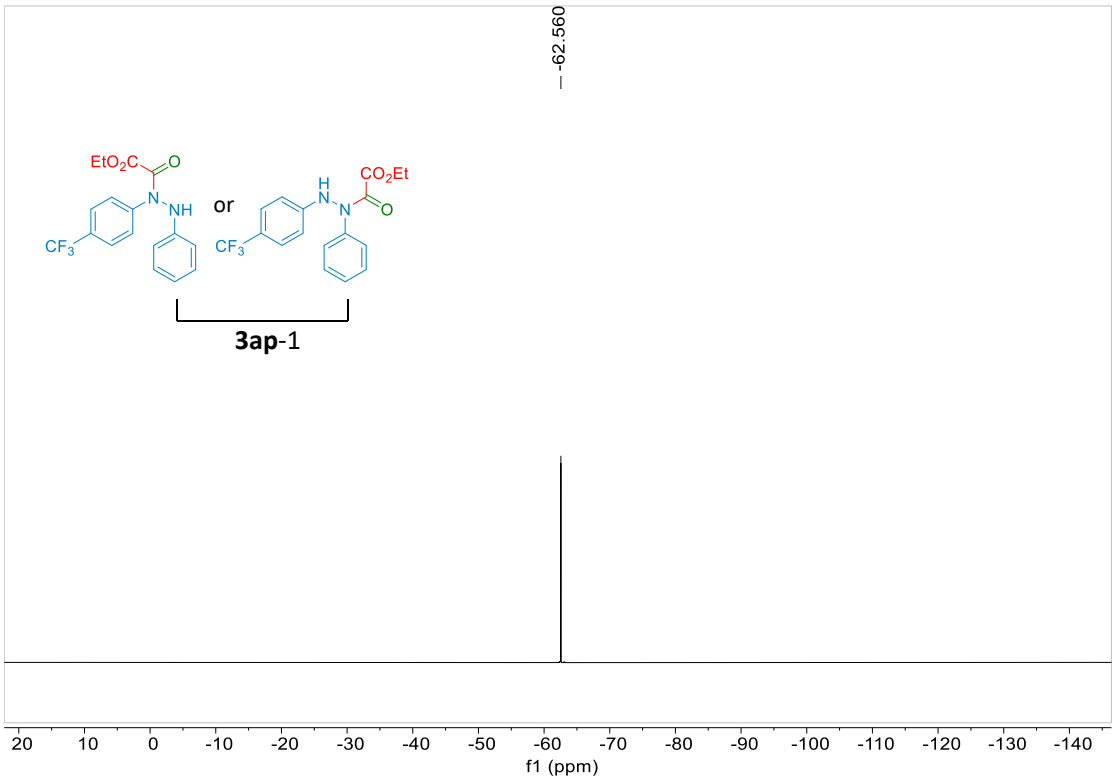
^{1}H NMR spectrum of **3ap**-1 (600 MHz, $CDCl_3$):



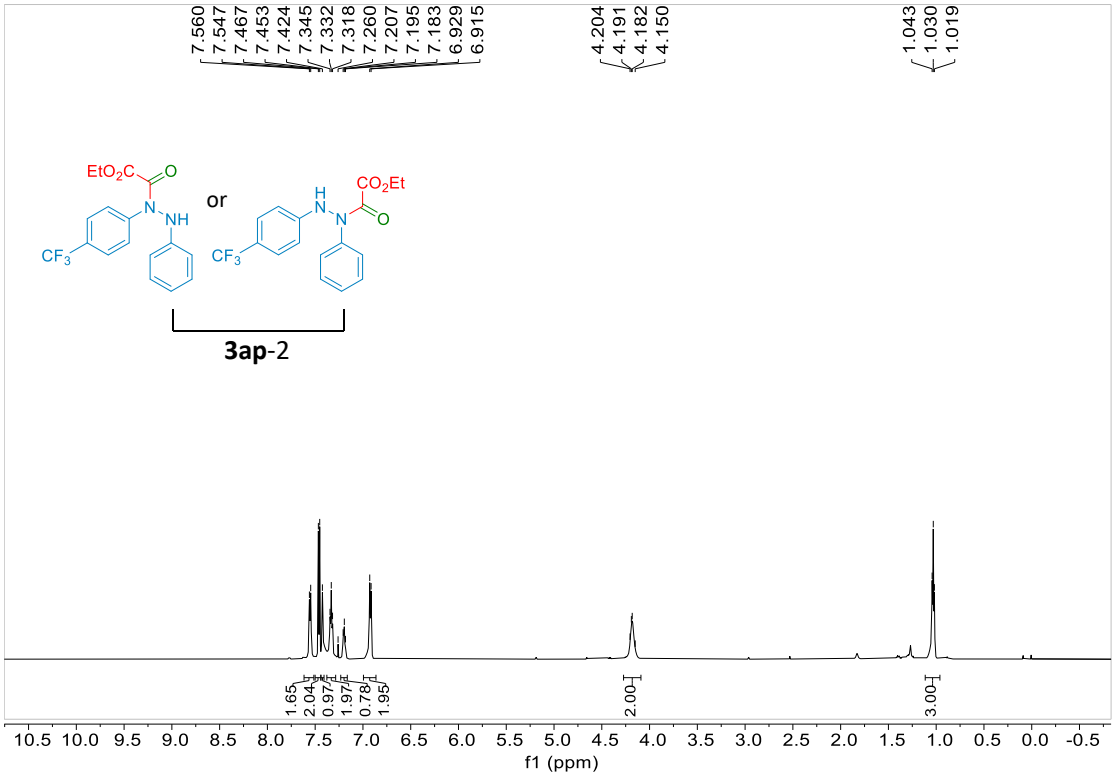
^{13}C NMR spectrum of **3ap**-1 (150 MHz, $CDCl_3$):



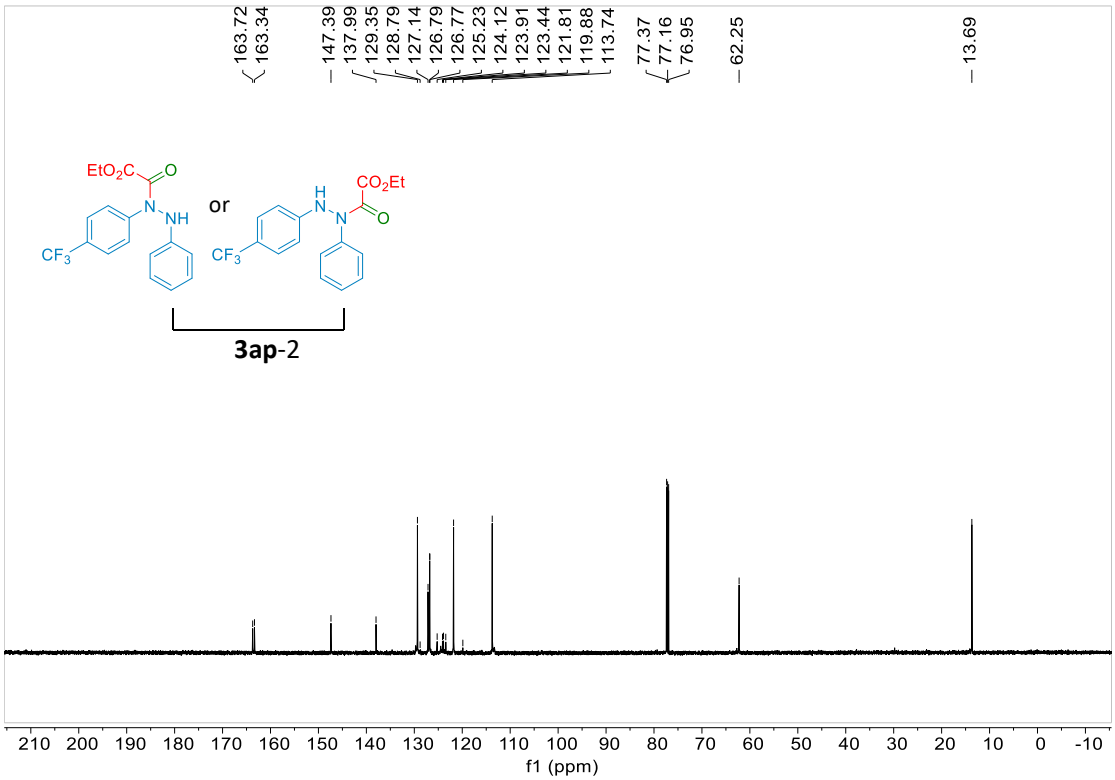
^{19}F NMR spectrum of **3ap**-1 (376 MHz, $CDCl_3$):



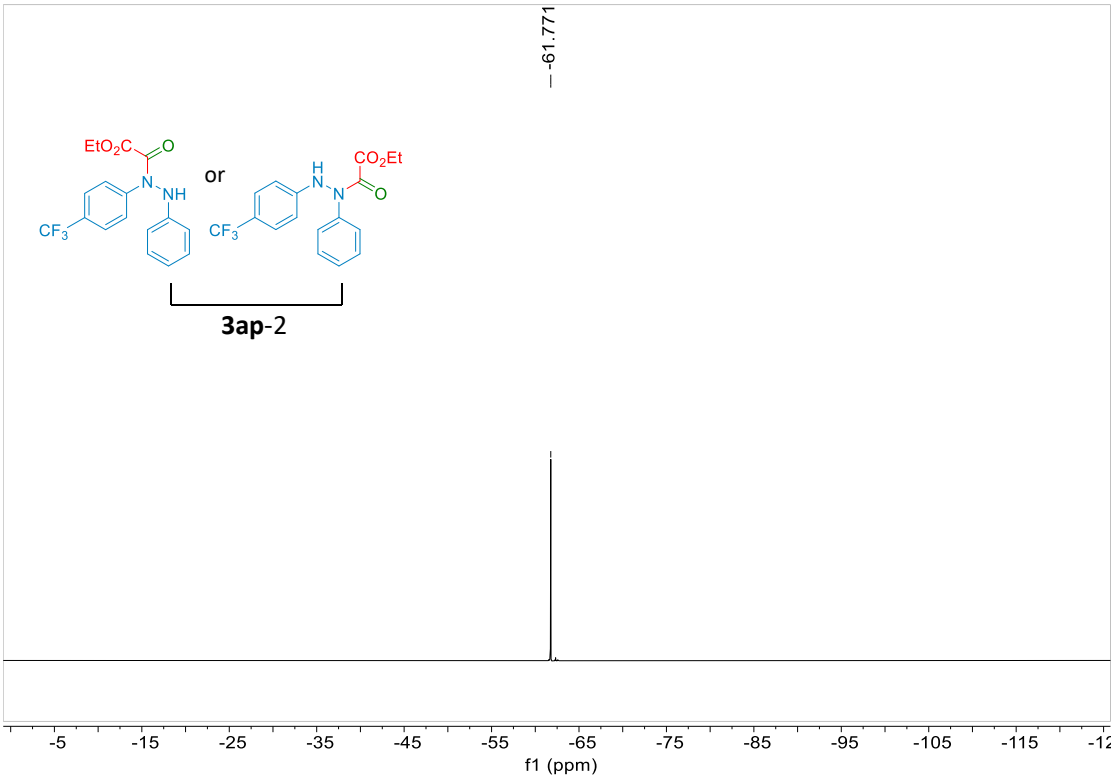
^{1}H NMR spectrum of **3ap**-2 (600 MHz, $CDCl_3$):



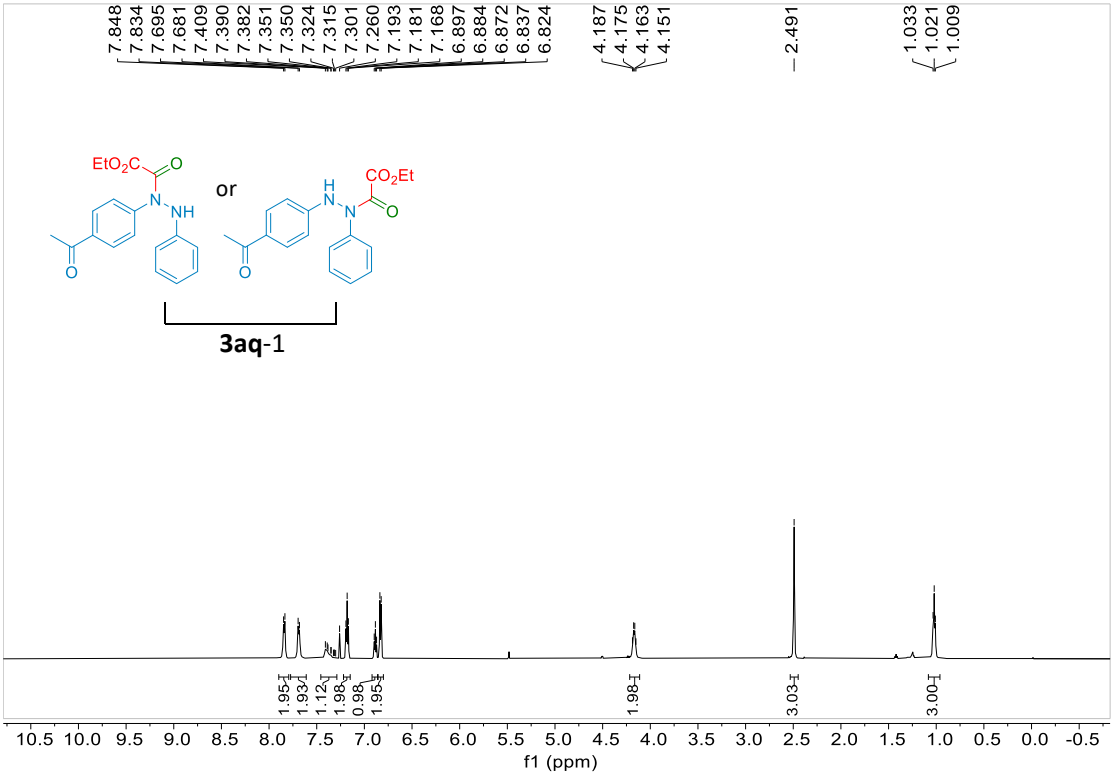
^{13}C NMR spectrum of **3ap**-2 (150 MHz, $CDCl_3$):



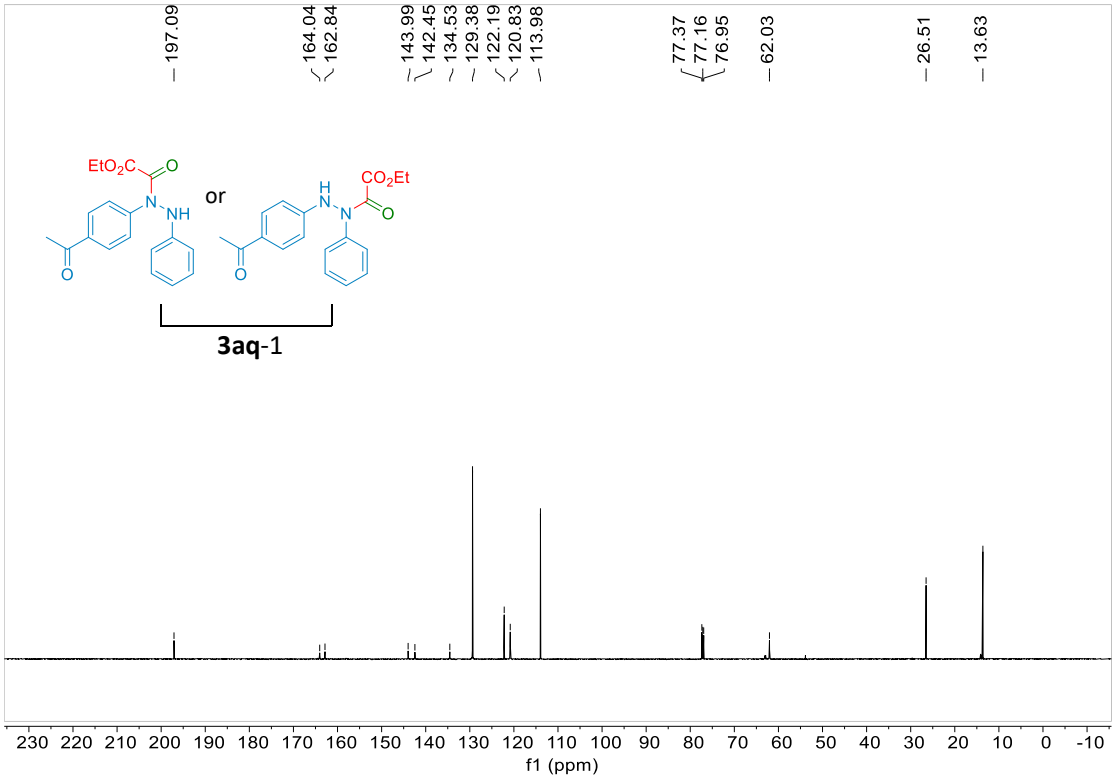
^{19}F NMR spectrum of **3ap**-2 (376 MHz, $CDCl_3$):



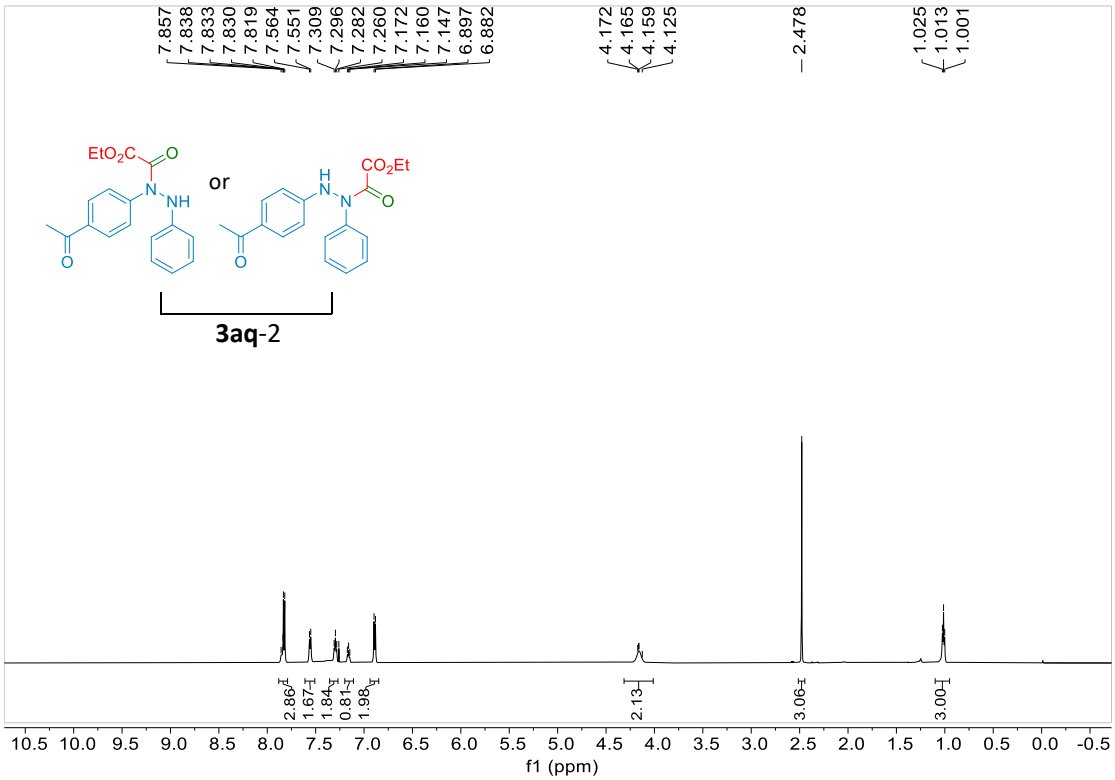
^{1}H NMR spectrum of **3aq**-1 (600 MHz, $CDCl_3$):



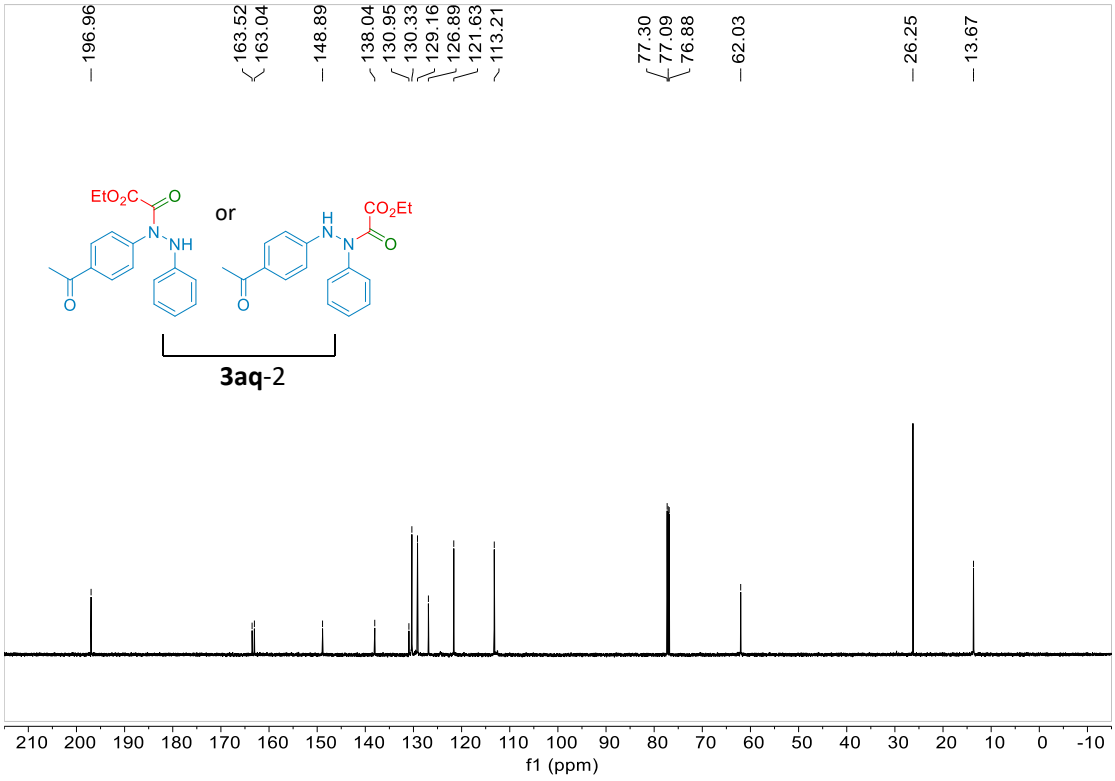
^{13}C NMR spectrum of **3aq**-1 (150 MHz, $CDCl_3$):



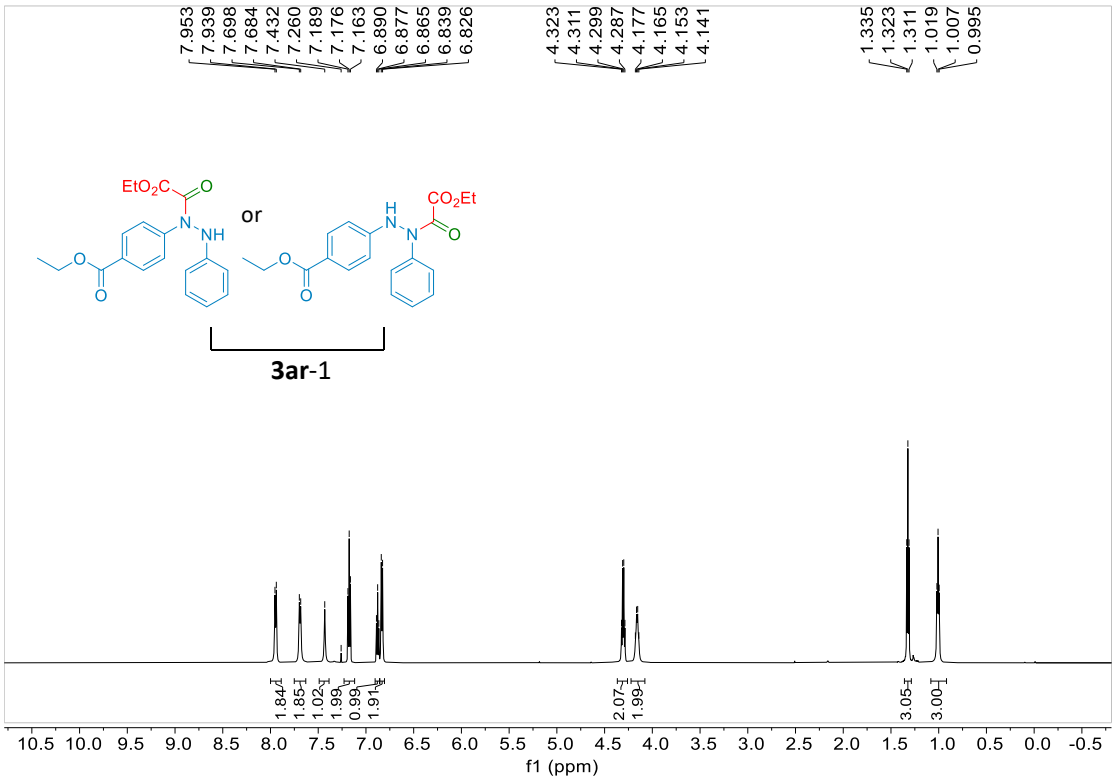
^{1}H NMR spectrum of **3aq**-2 (600 MHz, $CDCl_3$):



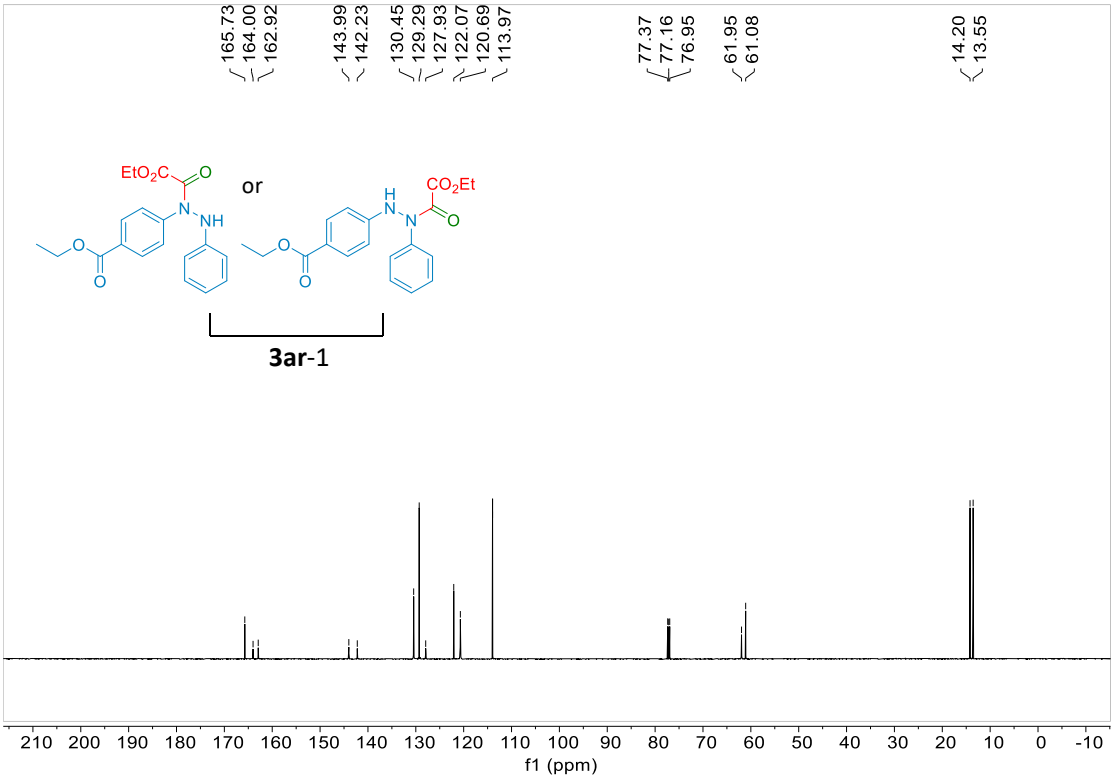
^{13}C NMR spectrum of **3aq**-2 (150 MHz, $CDCl_3$):



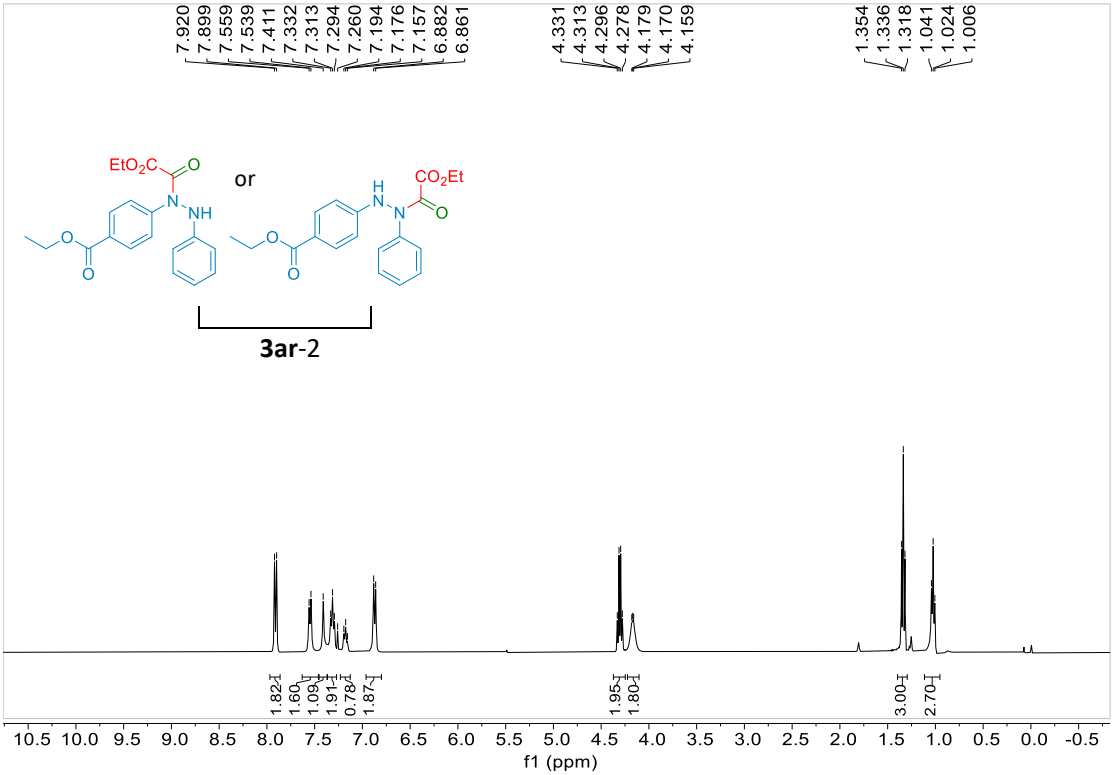
^{1}H NMR spectrum of **3ar**-1 (600 MHz, $CDCl_3$):



^{13}C NMR spectrum of **3ar**-1 (150 MHz, $CDCl_3$):



^{1}H NMR spectrum of **3ar**-2 (400 MHz, $CDCl_3$):



^{13}C NMR spectrum of **3ar**-2 (150 MHz, $CDCl_3$):